Catalytic Asymmetric Synthesis of N-Substituted Tetrahydroquinoxalines via Regioselective Heyns Rearrangement and Stereoselective Transfer Hydrogenation in One Pot

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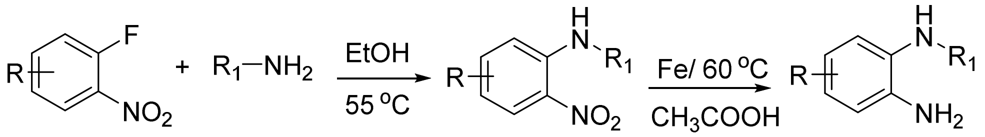
Content

General experimental procedures

All reactions that required anhydrous or airless conditions were carried by standard procedures under nitrogen atmosphere. Commercially available reagents from Tansoole and Adamas-beta were used as received. The solvents were dried by distillation over the appropriate drying reagents.

^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and, assignment. ^{13}C NMR spectra were collected on commercial instruments (101 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0). Mass spectra were recorded on ThermoQuest Finnigan LCQDECA system equipped with an ESI source. Enantiomeric excesses (*ee*) were determined by HPLC analysis using the corresponding commercial chiral column as stated in the experimental procedures at 30 °C with UV detector at 220 or 254 nm.

General procedure for the synthesis of *o*-PDAs[1]

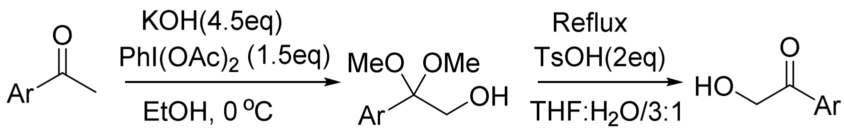


S1-1 **S1-2** **S1-3** **1**

Scheme S1 Method for preparation of the *o*-PDAs

To a solution of EtOH (5.0 ml) was added a suspension of o-nitrofluorobenzene **S1-1** (10.0 mmol) and primary amine **S1-2** (35 mmol) at 55 °C. After stirring for 3 h at 55 °C, remove the EtOH under the vacuum. The product was extracted with ethyl ether (50 mL x 3), and the combined organic extracts were washed with brine and dried over Na_2SO_4. After removal of the solvents under reduced pressure, crude **S1-3** was obtained without further purification. **S1-3** was dissolved in CH_3COOH (2 mL/mmol) with the addition of Fe (3.3 eq). The mixture was heated to 60 °C until the solution turns white. Quenched the reaction with sat. $NaHCO_3$ and extracted the product with EtOAc (50 mL x 3). The combined organic extracts were washed with brine and dried over Na_2SO_4. After removal of the solvents under reduced pressure, the residue was purified by flash column chromatography (hexane/EtOAc = 5/1 to 2/1) afforded substrate **1**.

General procedure for the synthesis of primary α-hydroxy ketones[2]

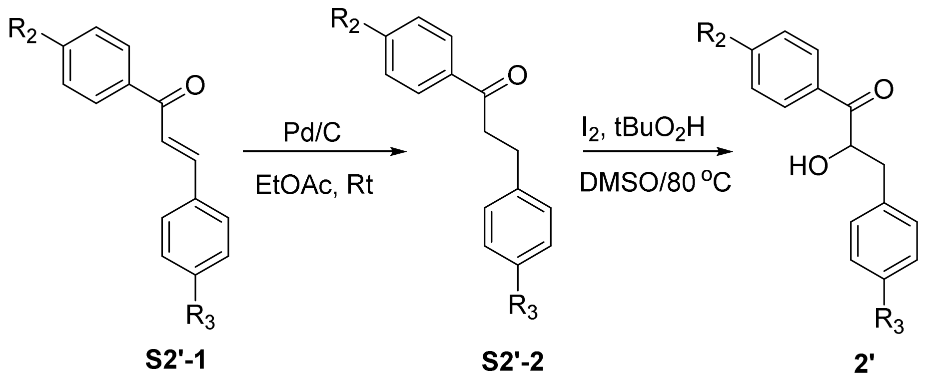


S2-1 **S2-2** **2**

Scheme S2 Method for preparation of the primary α-hydroxyl ketones

To a solution of KOH (112.5 mmol) in MeOH (150 mL) was added a suspension of ketone **S2-1** (25.0 mmol) in MeOH (50 mL) at 0 °C. Then $PhI(OAc)_2$ (37.5 mmol) was added portion wise. After stirring for 3 h at 0 °C, the reaction was quenched by the addition of water. Remove the MeOH under the vacuum. The product was extracted with EtOAc (50 mL x 3), and the combined organic extracts were washed with brine and dried over Na_2SO_4. After removal of the solvents under reduced pressure, crude **S2-2** was obtained as a white solid without further purification. **S2-2** was dissolved in THF: H_2O (37.5 mL: 12.5 mL) with the addition of p-TsOH (46.5 mmol). The mixture was heated to reflux for 4.5 h. monitored the reaction with TLC. Quenched the reaction with sat. $NaHCO_3$ and extracted the product with EtOAc (50 mL x 3). The combined organic extracts were washed with brine and dried over Na_2SO4. After removal of the solvents under reduced pressure, the residue was purified by flash column chromatography (hexane/EtOAc = 5/1 to 3/1) afforded substrate **2** as a white solid.

General procedure for the synthesis of the racemic α- hydroxyl ketones[3]

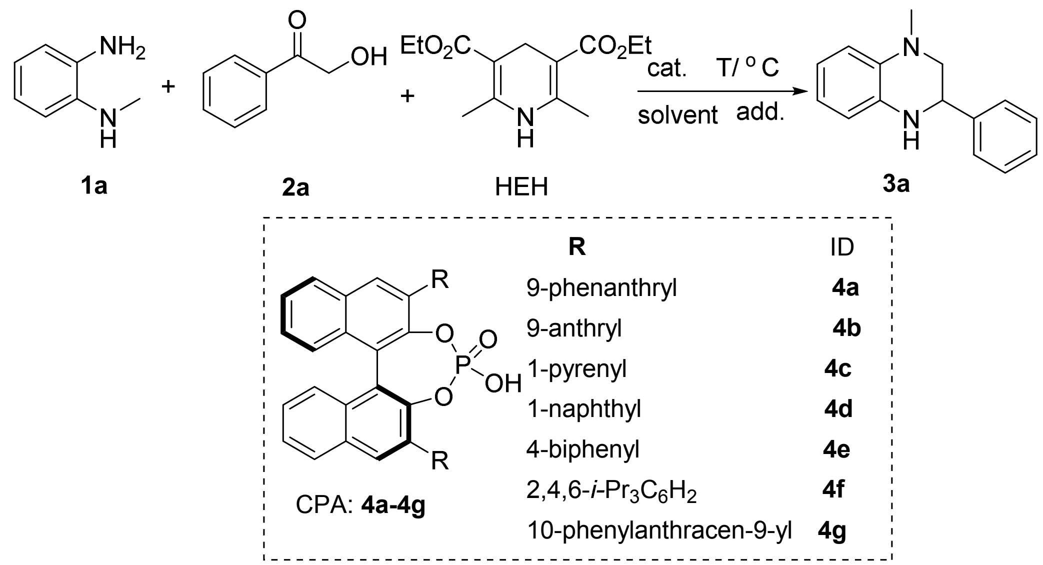


Scheme S3 Method for preparation of the racemic α-hydroxyl ketones

The chalcone **S2'-1**, 10% Pd/C (an amount equal to ¼ the quantity of the chalcone) and 30 mL of ethyl acetate were placed into the reactor. The reaction was conducted in room temperature for overnight and monitored by TLC using ethyl acetate as the solvent system. When the reaction was finished, the Pd/C was filtered, and the solvent was removed. In most cases, the crude product was purified by column chromatography using ethyl acetate/petroleum ether as the solvent system. All the compounds **S2'-2** without the spectrum data were obtained as pure products monitored by TLC, and the crude products **S2'-2** were directly used in the next step. Aryl ketones **S2'-2** (100 mg, 0.75 mmol), molecular iodine (0.5 equiv. 0.37 mmol) and TBHP (3 equiv. 2.23 mmol) in DMSO (1 mL) were stirred at 80 °C (6-12 h) in a 5 ml round bottomed flask. After the completion of the reaction (monitored by TLC), added water (25 mL) and extracted with ethyl acetate (3 x 20 mL). The combined organic layer was washed with dilute sodium thiosulphate solution (10 mL, 5% aqueous solution) and water. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified on a silica gel column using hexane/ EtOAc to get the pure product **2'**.

Optimizing the reaction conditions for the synthesis of THQ 3a

Table S1: Optimizing the reaction conditions for synthesis of 3a



Entry[a]	Sol.	T/ °C	Cat.	Yield[b] (%)	Ee[c](%)
1	PhMe	70	**4a**	70	68
2	PhMe	70	**4b**	65	69
3	PhMe	70	**4c**	55	44
4	PhMe	70	**4d**	68	10
5	PhMe	70	**4e**	58	10
6	PhMe	70	**4f**	62	67
7	PhMe	70	**4g**	56	58
8	m-xylene	70	**4a**	72	54
9	Benzene	70	**4a**	66	50
10	PhCl	70	**4a**	75	60
11	PhMe	70	**4a**	60	44
12	PhMe	60	**4a**	50	63
13	PhMe	80	**4a**	68	62
14[d]	PhMe	65	**4a**	92	80

[a] All the reactions were carried out using **1a** (0.05 mmol), **2a** (0.05 mmol) and HEH (1.5 eq.) under nitrogen atmosphere in solvent (1 mL) for 16 h. [b] The reaction yield was calculated based on purification via silica column. [c] The ee value was calculated via HPLC with chiral column. [d] The reaction adding sequence was changed as following: The mixture of **1a** and **2a** was run at 110 °C for 2 h, then the reaction temperature was decreased to 65 °C followed by the addition of HEH, and the reaction mixture was further reacted for 16 h.

In the initial stage, the reaction catalyst was screened (Entries 1-7, Table S1). According to the reaction results, CPA **4a** was chosen as the optimal catalyst considering the reaction yield and ee

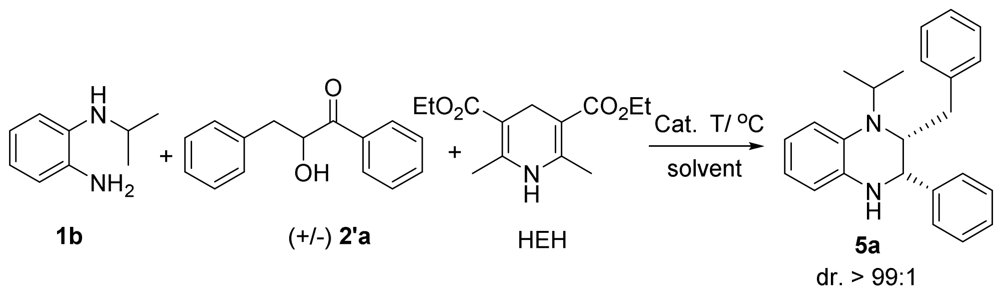
(Entry 1). Then the reaction solvent and the reaction temperature were screened, which demonstrated that better results could be obtained for the reaction proceeded in toluene at 65 °C. Then the reaction adding sequence was changed according to the reaction mechanism investigation result: the chirality of the reaction was formed via enantioselective transfer hydrogenation rather that enantioselective protonation. After the modification of the reaction adding sequence, both the reaction yield and the ee value were increased (Entry 14).

General procedure A for the synthesis of monosubstituted THQ 3

0.05 mmol of **1**, 0.05 mmol of **2**, 5 mmol% **4a** and 50 mg 4 Å MS were reacted in 1 mL of toluene at 110 °C for 2 h. Then the reaction temperature was decreased to 65 °C and HEH (1.5 eq.) was added, add the reaction mixture was further run at 65 °C for 16 h. After the finish of the reaction, 10 mL saturated sodium sulfite solution was added and the reaction product was extracted with CH_2Cl_2 (10 mL×2). Then the extractant was concentrated and purified with flash silica column eluted with CH_2Cl_2/petroleum ether (1:4-1:1).

Optimizing the reaction conditions for synthesis of disubstituted THQ 5a

Table S2. Optimizing the reaction conditions for synthesis of 5a



entry[a]	Sol.	T (°C)	Cat.	Add.	Yield (%)	Ee (%)
1	PhMe	85	**4a**	4 Å MS	30	62
2	PhCl	85	**4a**	4 Å MS	45	72
3	1,4-dioxane	85	**4a**	4 Å MS	35	44
4	MTBE	85	**4a**	4 Å MS	40	56
5	PhCl:n-hexane (1:1)	85	**4a**	4 Å MS	44	64
6	PhCl:$CHCl_3$ (1:1)	85	**4a**	4 Å MS	45	70
7	PhCl:DCE (1:1)	85	**4a**	4 Å MS	46	74
8	PhCl:DCE (1:1)	85	**4a**	--	40	64
9	PhCl:DCE (1:1)	85	**4a**	3 Å MS	38	74

10	PhCl:DCE (1:1)	85	**4a**	5 Å MS	40	64
11	PhCl:DCE (1:1)	85	**4a**	$MgSO_4$	35	62
12[b]	PhCl:DCE (1:1)	85	**4a**	4 Å MS	36	62
13[c]	PhCl:DCE (1:1)	85	**4a**	4 Å MS	45	78
14[d]	PhCl:DCE (1:1)	85	**4a**	4 Å MS	35	76
15[c]	PhCl:DCE (1:1)	85	**4b**	4 Å MS	40	80
16[c]	PhCl:DCE (1:1)	85	**4c**	4 Å MS	36	42
17[c]	PhCl:DCE (1:1)	85	**4g**	4 Å MS	42	80
18[c]	PhCl:DCE (1:1)	85	**4f**	4 Å MS	46	90
19[c]	PhCl:DCE (1:1)	95	**4f**	4 Å MS	40	88
20[c]	PhCl:DCE (1:1)	105	**4f**	4 Å MS	39	88

[a] All the reactions were carried out using **1b** (0.05 mmol), **2'a** (0.05 mmol) and HEH (1.5eq.) under nitrogen atmosphere in solvent (1 mL) for 16 h. [b] reaction proceeded in 0.5 mL solvent. [c] reaction proceeded in 1.5 mL solvent. [d] reaction proceeded in 2 mL solvent.

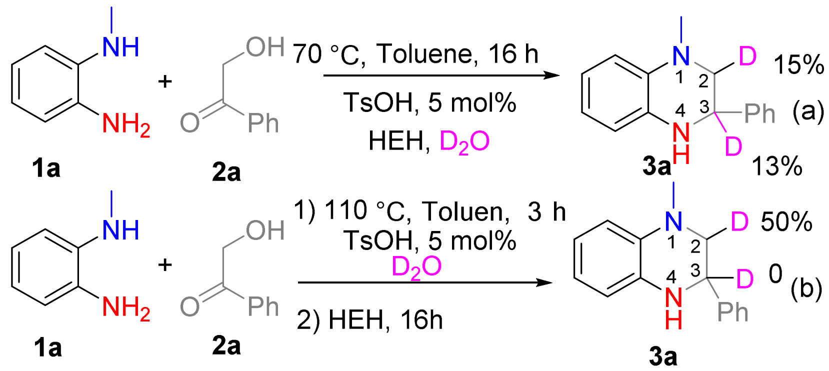
Considering the broad usage of THQ in pharmaceuticals, we optimized the reaction conditions for obtaining the disubstituted THQ. At the beginning, equal amount of *o*-PDA **1b** and racemic α-hydroxyl ketone **2’a**, and 1. 5 eq. of HEH were reacted in toluene at 85 °C. According to the result, the disubstituted THQ **5a** was obtained in excellent diastereoselectivity (99:1) with 30% yield and 62% ee (**Table S3,** Entry 1). Then we screened the reaction solvent (**Table S3,** Entries 2-4). The results demonstrated that PhCl was the optimal solvent (Entry 2). Then PhCl was chosen to mix with other solvent (Entries 5-7). The results demonstrated that the mixture of PhCl and DCE (1:1) was the optimal reaction solvent for higher ee (Entry 7). Next, different dehydration reagents were investigated (Entries 8-11). The results demonstrated that 4 Å molecular sieves was the optimal water drying reagent for both good yield and ee. Then, the effects of the concentration were studied (Entries 12-14), which indicated that 1.5 ml solvent was optimal for higher ee (Entry 13). Next, the reaction catalysts were screened (Entries 15-18), which demonstrated that TRIP **4f** was optimal for higher ee (Entry 18). Finally, the temperature was screened (Entries 19-20) which demonstrated that 85 °C was the optimal temperature. Based on the above results, the optimizing reaction conditions were summarized as following: equal amount of substrates and 1.5 eq. of HEH were reacted in 1.5 mL solvent (PhCl:DCE, 1:1) with 5 mol% of TRIP and 50 mg of 4 Å MS as additive at 85 °C under nitrogen atmosphere for 16 h. The disubstituted THQ **5a** was obtained in high diastereoselectivity (99:1) with high yield (46%) and good ee (90%).

General procedure B for synthesis of disubstituted THQ 5

0.05 mmol of **1**, 0.05 mmol of **2'**, 5 mmol% TRIP and 50 mg 4 Å MS were reacted in 1.5 mL of PhCl and DCE (1:1) at 85 °C for 16 h. Then, 10 mL saturated sodium sulfite solution was added and the reaction product was extracted with CH_2Cl_2 (10 mL×2). Then the extractant was concentrated and purified with flash silica column eluted with CH_2Cl_2/petroleum ether (1:4-1:1).

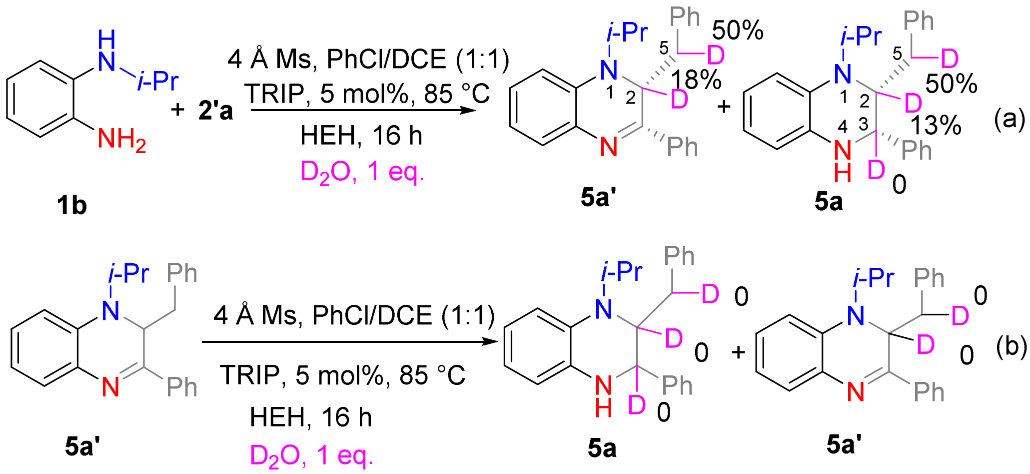
Investigation of the reaction mechanism by D_2O NMR experiment

For reactions with primary α-hydroxyl ketone, The following D_2O NMR experiments were done so as to ensure the reaction mechanism (Scheme S4). According to the results, the addition sequence of HEH was important for the reaction. When HEH was added at the beginning of the reaction, both of the hydrogens (C-2, C-3) were deuterated (Scheme S4a). However, when HEH was added after the formation of the dihydroquinoxaline ring, only the C2-H was deuterated (Scheme S4b). According to the above results, we modified the reaction conditions. The reductant HEH was added after mixing **1a** and **2a** at high temperature for 2 h. In this way, the ee value of **3a** could be improved because the chirality was formed by enantioselective transfer hydrogenation rather than protonation.



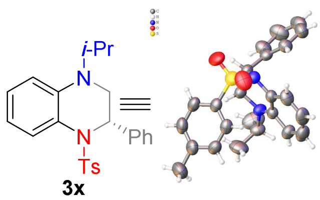
Scheme S4 D_2O NMR experiments for reactions with primary α-hydroxyl ketone as substrate

For reaction with racemic α-hydroxyl ketone, the reaction mechanism was investigated with the following D_2O NMR experiments (Scheme S5). According to the results, the C3-H was not deuterated for product **5a**, while both the C2-H and C5-H of product **5a** and **5a'** were deuterated (Scheme S5a). Therefore, we could concluded that the reaction proceeded by transfer hydrogenation of ketone imine rather than imnium ion. Meanwhile, ketone imine **5a'** was stable and could not isomerized into enamine under the reaction conditions according to the deuteration result (Scheme 5b).



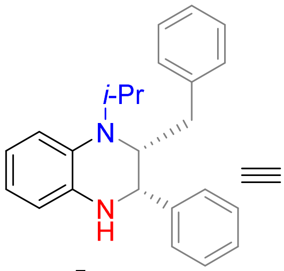
Scheme S5 D_2O NMR experiments for reactions with racemic α-hydroxyl ketone as substrate

X-ray results of the product

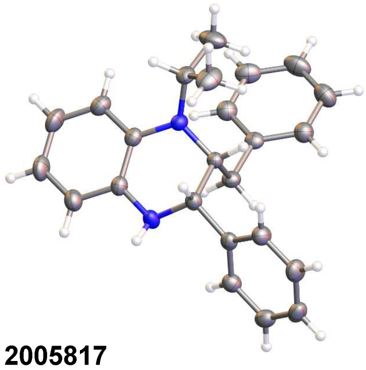


CCDC: 2005816

Chemical formula	C_{24} H_{26} N_2 O_2 S
Formula weight	406.53
Space group	P 21 21 21
Hall group	P 2ac 2ab
Z	4
a/Å	8.1129(5)
b/Å	8.6639(5)
c/Å	31.0808(15)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2184.6(2)
ρ_{calc}g/cm^3	1.236
Temperature/K	293 K
Flack parameter	-0.02(6)



5a



CCDC: 2005817

Chemical formula	$C_{24}\ H_{26}\ N_2$
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Hall group	P 2ac 2ab
Z	4
a/Å	7.63264(7)
b/Å	13.82175(12)
c/Å	18.09078(15)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1908.51(3)
ρ_{calc}g/cm^3	1.192
Temperature/K	180K
Flack parameter	-0.2(2)

References

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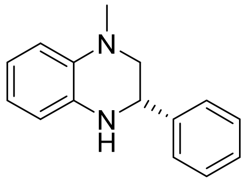
(2) Wang, H.-Y.; Yang, K.; Bennett, S. R.; Guo, S.-r.; Tang, W. Iridium-Catalyzed Dynamic Kinetic Isomerization: Expedient Synthesis of Carbohydrates from Achmatowicz Rearrangement Products. *Angew. Chem., Int. Ed.* **2015**, *54*, 8756-8759.

(3) Liang, Y.-F.; Wu, K.; Song, S.; Li, X.; Huang, X.; Jiao, N. I2- or NBS-Catalyzed Highly Efficient α-Hydroxylation of Ketones with Dimethyl Sulfoxide. *Org. Lett.* **2015**, *17*, 876-879.

Characteristic data for selected compounds

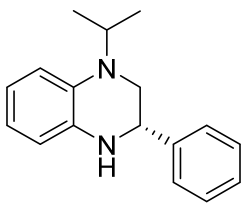


(S)-1-methyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline (3a): White oil (10.3 mg, yield 92%), with 80% ee (HPLC, Diacel Chiralcel AD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 9.888 min; $[\alpha]D^{25}$= +22° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.31 (m, 5H), 6.84 – 6.51 (m, 4H), 4.64 (dd, J = 8.2, 3.1 Hz, 1H), 3.98 (s, 1H), 3.38 – 3.18 (m, 2H), 2.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.76, 135.48, 134.64, 128.65, 127.95, 127.02, 118.89, 118.32, 113.43, 111.76, 57.63, 54.70, 39.10.

HRMS (ESI): $C_{15}H_{16}N_2$ Neutral mass: 224.1313, Observed ([M+H]) $^+$: 225.1384.

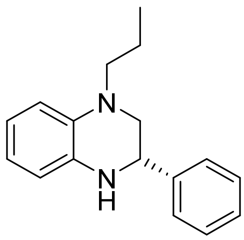


(S)-1-isopropyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline (3b): Yellow oil (11.8 mg, yield 95%), with 94% ee (HPLC, Diacel Chiralcel AD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 6.785 min; $[\alpha]D^{25}$= +33° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 4H), 7.37 – 7.32 (m, 1H), 6.75 (dd, J = 3.3, 1.6 Hz, 2H), 6.61 (q, J = 4.3 Hz, 2H), 4.47 (dd, J = 8.3, 3.1 Hz, 1H), 4.12 (dt, J = 13.2, 6.6 Hz, 1H), 3.97 (s, 1H), 3.40 (dd, J = 11.3, 3.2 Hz, 1H), 3.05 (dd, J = 11.3, 8.3 Hz, 1H), 1.24 (d, J = 6.6 Hz, 3H), 1.10 (d, J = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ142.26, 134.79, 134.23, 128.59, 127.86, 127.03, 118.94, 117.26, 113.98, 111.40, 55.00, 47.00, 46.75, 19.35, 17.94.

HRMS (ESI): $C_{17}H_{20}N_2$ Neutral mass: 252.1626, Observed ([M+H]) $^+$:253.1678.

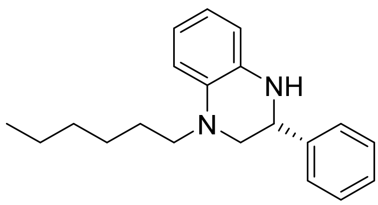


(S)-3-phenyl-1-propyl-1,2,3,4-tetrahydroquinoxaline (3c): Yellow oil (11.6 mg, yield 92%), with 90% ee (HPLC, Diacel Chiralcel AD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 6.372 min; $[\alpha]D^{25}$= +72° (c 0.02, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 4H), 7.40 – 7.33 (m, 1H), 6.77 (dd, *J* = 9.9, 4.1 Hz, 1H), 6.70 – 6.59 (m, 3H), 4.52 (t, *J* = 5.7 Hz, 1H), 3.96 (s, 1H), 3.38 (d, *J* = 5.7 Hz, 3H), 3.25 – 3.09 (m, 1H), 1.77 – 1.57 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.78, 134.32, 128.66, 127.94, 127.11, 119.21, 117.16, 114.02, 111.32, 55.86, 54.19, 53.36, 19.37, 11.66.

HRMS (ESI): $C_{17}H_{20}N_2$ Neutral mass: 252.1626, Observed ($[M+H]^+$): 253.1693.

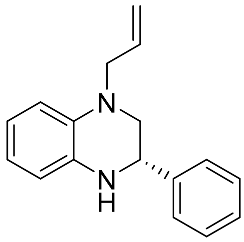


(S)-1-hexyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline (3d): Yellow oil (13.8 mg, yield 94%), with 90% ee (HPLC, Diacel Chiralcel AD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 5.997 min; $[\alpha]D^{25}$= +48° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.54 – 7.48 (m, 3H), 7.42 – 7.34 (m, 2H), 4.42 – 4.27 (m, 2H), 1.83 (dt, *J* = 15.6, 7.7 Hz, 2H), 1.52 (dd, *J* = 14.6, 7.1 Hz, 2H), 1.48 – 1.33 (m, 5H), 0.93 (t, *J* = 6.9 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.82, 134.33, 128.65, 127.93, 127.11, 119.21, 117.15, 114.00, 111.30, 55.77, 54.23, 51.56, 31.78, 26.99, 26.01, 22.71, 14.12.

HRMS (ESI): $C_{20}H_{26}N_2$ Neutral mass: 294.2096, Observed ($[M+H]^+$): 295.2140.

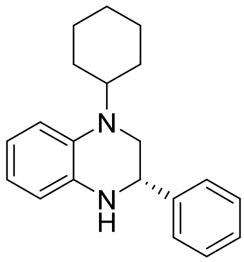


(S)-1-allyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline (3e): Yellow oil (11.9 mg, yield 95%), with 82% ee (HPLC, Diacel Chiralcel AD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 7.560 min; $[\alpha]D^{25}$= +21° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.32 (m, 5H), 6.82 – 6.57 (m, 4H), 5.91 (ddd, *J* = 22.5, 10.5, 5.4 Hz, 1H), 5.23 (ddd, *J* = 13.7, 11.7, 1.5 Hz, 2H), 4.54 (dd, *J* = 7.7, 4.0 Hz, 1H), 4.00 (dd, *J* = 16.5, 5.2 Hz, 2H), 3.83 (dd, *J* = 16.5, 5.5 Hz, 1H), 3.45 – 3.25 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ141.69, 134.49, 134.19, 133.52, 128.66, 127.96, 127.09, 119.09, 117.83, 116.86, 113.97, 112.01, 55.38, 54.36, 54.05

HRMS (ESI):$C_{17}H_{18}N_2$ Neutral mass: 250.1470, Observed ([M+H]) $^+$: 251.1491.

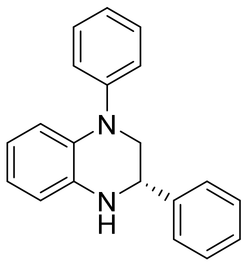


(S)-1-cyclohexyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline (3f): Yellow oil (14.1 mg, yield 97%), with 98% ee (HPLC, Diacel Chiralcel AD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 9.418 min; $[\alpha]D^{25}$= +78° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.2, 5.6 Hz, 4H), 7.40 – 7.33 (m, 1H), 6.76 (d, *J* = 6.6 Hz, 2H), 6.63 (s, 2H), 4.46 (d, *J* = 5.3 Hz, 1H), 3.97 (s, 1H), 3.64 (t, *J* = 9.6 Hz, 1H), 3.48 (d, *J* = 10.3 Hz, 1H), 3.19 – 3.07 (m, 1H), 1.89 (dd, *J* = 24.8, 11.8 Hz, 4H), 1.75 (d, *J* = 13.1 Hz, 1H), 1.60 – 1.26 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.26, 134.76, 134.23, 128.60, 127.86, 127.07, 119.00, 117.11, 114.12, 111.37, 56.17, 55.05, 48.62, 29.88, 28.86, 26.30, 26.16, 26.09.

HRMS (ESI): $C_{20}H_{24}N_2$ Neutral mass: 292.1939, Observed ([M+H]) $^+$: 293.2033.

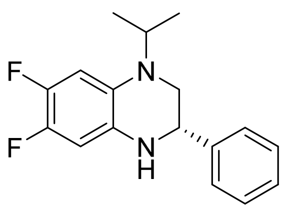


(S)-1,3-diphenyl-1,2,3,4-tetrahydroquinoxaline (3g): Yellow oil (13.7 mg, yield 96%), with 92% ee (HPLC, Diacel Chiralcel AD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 11.742 min; $[\alpha]D^{25}$= +53° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.53 – 7.32 (m, 7H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.15 – 6.92 (m, 2H), 6.75 (dd, *J* = 32.9, 26.2 Hz, 3H), 4.56 (s, 1H), 4.20 (s, 1H), 3.88 (s, 1H), 3.60 (s, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 147.98, 141.08, 135.78, 130.95, 129.29, 128.75, 128.07, 127.06, 122.91, 122.62, 120.80, 118.10, 117.47, 114.86, 55.99, 54.04.

HRMS (ESI): $C_{20}H_{18}N_2$ Neutral mass: 286.1470, Observed ([M+H]) $^+$: 287.1546.



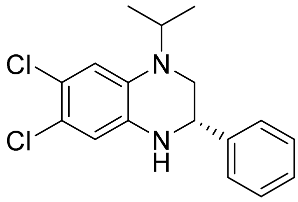
(S)-6,7-difluoro-1-isopropyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline (3h): Yellow oil (13.4 mg, yield 93%), with 84% ee (HPLC, Diacel Chiralcel AD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 8.617 min; $[\alpha]D^{25}$= +48° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.52 – 7.32 (m, 5H), 6.50 (dd, *J* = 13.5, 7.6 Hz, 1H), 6.38 (dd, *J* = 11.4, 7.9 Hz, 1H), 4.41 (dd, *J* = 8.2, 2.9 Hz, 1H), 3.93 (dt, *J* = 19.5, 6.4 Hz, 2H), 3.35 (dd, *J* = 11.4, 3.0 Hz, 1H), 2.99 (dd, *J* = 11.3, 8.4 Hz, 1H), 1.22 (d, *J* = 6.6 Hz, 3H), 1.08 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 141.59, 140.77, 140.64, 130.65 (dd, *J* = 8.08 Hz, 2.02 Hz), 130.42 (dd, *J* = 8.08 Hz, 2.02 Hz), 128.69, 128.08, 126.94, 101.43(d, *J* = 179.78 Hz), 101.22 130.65 (d, *J* = 180.79 Hz), 54.96, 47.53, 46.62, 19.24, 17.68.

^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$) δ -150.95 (d, *J* = 22.6)，-133.36 (d, *J* = 22.6).

HRMS (ESI): $C_{17}H_{18}F_2N_2$ Neutral mass: 288.1438, Observed ([M+H]) $^+$: 289.1456.

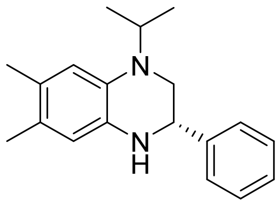


(S)-6,7-dichloro-1-isopropyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline (3i): Yellow oil (15.2 mg, yield 95%), with 94% ee (HPLC, Diacel Chiralcel AD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 9.572 min; $[\alpha]D^{25}$= +61° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.45 – 7.32 (m, 5H), 6.71 (s, 1H), 6.61 (s, 1H), 4.42 (dd, *J* = 7.7, 2.6 Hz, 1H), 3.98 (dt, *J* = 13.0, 6.5 Hz, 2H), 3.36 (dd, *J* = 11.3, 2.8 Hz, 1H), 3.01 (dd, *J* = 11.3, 8.1 Hz, 1H), 1.22 (d, *J* = 6.6 Hz, 3H), 1.07 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ141.40, 134.49, 133.99, 128.72, 128.15, 126.88, 120.84, 119.00, 114.06, 112.09, 54.69, 47.17, 46.30, 19.11, 17.89.

HRMS (ESI):$C_{17}H_{18}Cl_2N_2$ Neutral mass: 320.0847, Observed ([M+H]) $^+$: 321.0919.

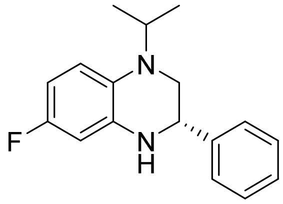


(S)-1-isopropyl-6,7-dimethyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline (3j): Yellow oil (12.7 mg, yield 91%), with 94% ee (HPLC, Diacel Chiralcel AD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 10.425 min; $[\alpha]D^{25}$= +43° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.51 – 7.32 (m, 5H), 6.56 (s, 1H), 6.43 (s, 1H), 4.43 (dd, *J* = 8.0, 2.4 Hz, 1H), 4.16 – 4.03 (m, 2H), 3.83 (s, 1H), 3.34 (d, *J* = 13.7 Hz, 1H), 3.00 (dd, *J* = 10.9, 8.5 Hz, 1H), 2.21 (s, 3H), 2.15 (s, 3H), 1.22 (d, *J* = 6.6 Hz, 3H), 1.09 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ142.56, 132.66, 132.11, 128.54, 127.76, 127.05, 126.28, 124.87, 115.83, 113.39, 55.25, 47.27, 46.86, 19.45, 18.74, 17.87.

HRMS (ESI): $C_{19}H_{24}N_2$ Neutral mass: 280.1939, Observed ([M+Na]) $^+$: 303.1851.



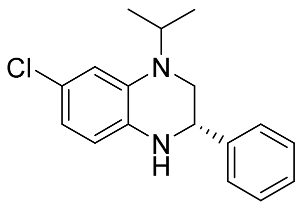
(S)-6-fluoro-1-isopropyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline (3k): Yellow oil (11.5 mg, yield 85%), with 86% ee (HPLC, Diacel Chiralcel AD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 8.768 min; [α]D^{25}= +44° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.48 – 7.31 (m, 5H), 6.62 (dd, *J* = 8.7, 5.3 Hz, 1H), 6.46 – 6.30 (m, 2H), 4.51 (d, *J* = 5.5 Hz, 1H), 4.03 (dt, *J* = 13.0, 6.1 Hz, 2H), 3.36 (d, *J* = 11.0 Hz, 1H), 2.97 (d, *J* = 19.4 Hz, 1H), 1.24 (d, *J* = 6.6 Hz, 3H), 1.07 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 156.02 (d, *J* =234.32 Hz), 141.92, 136.02 (d, *J* =10.10 Hz), 130.29 (d, *J* =3.03 Hz), 128.65, 127.98, 126.93, 112.06 (d, *J* =9.09 Hz), 103.75 (d, *J* =22.22 Hz), 100.76 (d, *J* =26.26 Hz), 55.29, 47.29, 46.73, 19.43, 17.57.

^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$) δ -127.28.

HRMS (ESI): $C_{17}H_{19}FN_2$ Neutral mass: 270.1532, Observed ([M+H]) $^+$: 271.1605.

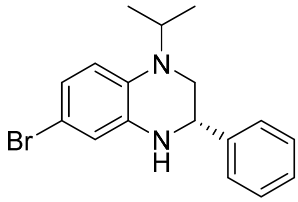


(S)-7-chloro-1-isopropyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline (3l): Yellow oil (13.1 mg, yield 92%), with 94% ee (HPLC, Diacel Chiralcel AD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 9.077 min; [α]D^{25}= +52° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.47 – 7.33 (m, 5H), 6.69 (s, 1H), 6.56 (d, *J* = 7.1 Hz, 1H), 6.49 (d, *J* = 8.1 Hz, 1H), 4.41 (d, *J* = 5.6 Hz, 1H), 4.05 (dt, *J* = 13.2, 6.5 Hz, 1H), 3.98 (s, 1H), 3.40 (d, *J* = 13.3 Hz, 1H), 3.13 – 2.98 (m, 1H), 1.24 (d, *J* = 6.5 Hz, 3H), 1.11 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ141.80, 135.27, 133.25, 128.68, 128.04, 127.01, 123.74, 116.37, 114.31, 111.03, 54.72, 46.97, 46.68, 19.18, 18.07.

HRMS (ESI):$C_{17}H_{19}ClN_2$ Neutral mass: 286.1237, Observed ([M+H]) $^+$: 287.1296.

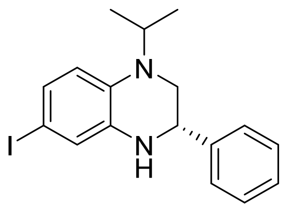


(S)-6-bromo-1-isopropyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline (3m): Yellow oil (14.3 mg, yield 87%), with 92% ee (HPLC, Diacel Chiralcel AD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 11.585 min; [α]D^{25}= +42° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.32 (m, 5H), 6.81 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.69 (d, *J* = 2.2 Hz, 1H), 6.58 (d, *J* = 8.7 Hz, 1H), 4.47 (dd, *J* = 7.9, 3.0 Hz, 1H), 4.04 (dt, *J* = 13.1, 6.5 Hz, 2H), 3.37 (dd, *J* = 11.4, 3.0 Hz, 1H), 3.01 (dd, *J* = 11.3, 8.1 Hz, 1H), 1.23 (d, *J* = 6.6 Hz, 3H), 1.08 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.79, 136.27, 133.33, 128.69, 128.04, 126.95, 121.03, 116.02, 112.61, 108.97, 54.90, 46.97, 46.59, 19.25, 17.8.

HRMS (ESI):$C_{17}H_{19}BrN_2$ Neutral mass: 330.0732, Observed ([M+H]) $^+$: 331.0791.

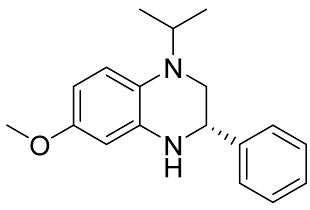


(S)-6-iodo-1-isopropyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline (3n): Yellow oil (17.0 mg, yield 90%), with 88% ee (HPLC, Diacel Chiralcel AD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 11.600 min; [α]D^{25}= +28° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 5H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.85 (s, 1H), 6.48 (d, *J* = 8.5 Hz, 1H), 4.45 (dd, *J* = 7.7, 2.3 Hz, 1H), 4.08 – 3.96 (m, 2H), 3.38 (dd, *J* = 11.4, 2.6 Hz, 1H), 3.01 (dd, *J* = 11.2, 8.2 Hz, 1H), 1.22 (d, *J* = 6.6 Hz, 3H), 1.07 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ141.74, 136.60, 134.05, 128.67, 128.05, 127.31, 126.95, 126.46, 121.64, 113.18, 54.77, 46.88, 46.59, 38.80, 19.23, 17.94.

HRMS (ESI):$C_{17}H_{19}IN_2$ Neutral mass: 378.0593, Observed ([M+H]) $^+$: 379.0656.

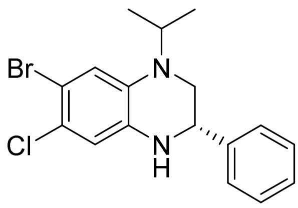


(S)-1-isopropyl-6-methoxy-3-phenyl-1,2,3,4-tetrahydroquinoxaline (3o): Yellow oil (11.8 mg, yield 85%), with 92% ee (HPLC, Diacel Chiralcel AD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 16.408 min; $[\alpha]D^{25}$= +46° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 8.7, 5.2 Hz, 4H), 7.37 – 7.31 (m, 1H), 6.66 (d, *J* = 8.7 Hz, 1H), 6.32 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.25 (d, *J* = 2.7 Hz, 1H), 4.51 (dd, *J* = 8.1, 2.7 Hz, 1H), 4.02 (dt, *J* = 13.0, 6.5 Hz, 2H), 3.77 (s, 3H), 3.34 (dd, *J* = 11.3, 2.7 Hz, 1H), 2.96 (dd, *J* = 11.1, 8.4 Hz, 1H), 1.23 (d, *J* = 6.6 Hz, 3H), 1.08 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.36, 142.30, 136.15, 128.51, 127.84, 126.98, 112.74, 102.90, 100.82, 55.53, 47.23, 19.55, 17.53.

HRMS (ESI):$C_{18}H_{22}N_2O$ Neutral mass: 282.1732, Observed ($[M+Na]^+$): 305.1650.

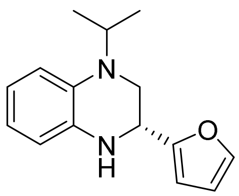


(S)-7-bromo-6-chloro-1-isopropyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline (3p): Yellow oil (17.3 mg, yield 95%), with 92% ee (HPLC, Diacel Chiralcel AD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 10.568 min; $[\alpha]D^{25}$= +56° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 5H), 6.85 (s, 1H), 6.63 (s, 1H), 4.43 (dd, *J* = 7.8, 3.0 Hz, 1H), 4.06 (s, 1H), 3.97 (dq, *J* = 13.2, 6.6 Hz, 1H), 3.36 (dd, *J* = 11.5, 3.1 Hz, 1H), 3.00 (dd, *J* = 11.4, 7.9 Hz, 1H), 1.22 (d, *J* = 6.6 Hz, 3H), 1.07 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ141.38, 135.12, 134.16, 128.72, 128.15, 126.87, 121.09, 115.02, 113.98, 109.65, 54.67, 47.15, 46.24, 19.10, 17.90.

HRMS (ESI):$C_{17}H_{18}BrClN_2$ Neutral mass: 364.0342, Observed ($[M+H]^+$): 365.0395.

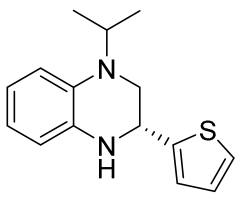


(S)-3-(furan-2-yl)-1-isopropyl-1,2,3,4-tetrahydroquinoxaline (3q): Yellow oil (11.8 mg, yield 98%), with 90% ee (HPLC, Diacel Chiralcel OD-H column 90:10 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 7.417 min; [α]D^{25}= +38° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 1.0 Hz, 1H), 6.79 – 6.69 (m, 2H), 6.66 – 6.57 (m, 2H), 6.38 (dd, *J* = 3.1, 1.8 Hz, 1H), 6.28 (d, *J* = 3.2 Hz, 1H), 4.64 (dd, *J* = 7.2, 3.0 Hz, 1H), 4.11 (dt, *J* = 13.2, 6.6 Hz, 1H), 4.02 (s, 1H), 3.49 (dd, *J* = 11.2, 3.1 Hz, 1H), 3.28 (dd, *J* = 11.2, 7.3 Hz, 1H), 1.24 (d, *J* = 6.6 Hz, 3H), 1.14 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ155.26, 141.70, 134.40, 133.57, 119.29, 117.39, 114.42, 111.47, 110.38, 105.91, 49.22, 46.72, 43.50, 19.07, 18.27.

HRMS (ESI): $C_{15}H_{18}N_2O$ Neutral mass: 242.1419, Observed ([M+H]) $^+$: 243.1428.

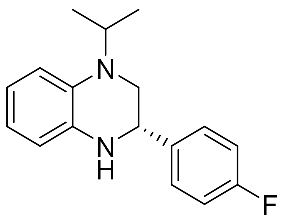


(S)-1-isopropyl-3-(thiophen-2-yl)-1,2,3,4-tetrahydroquinoxaline (3r): Yellow oil (12.3 mg, yield 96%), with 92% ee (HPLC, Diacel Chiralcel OD-H column 90:10 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 12.153 min; [α]D^{25}= +56° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 5.0, 0.9 Hz, 1H), 7.10 (d, *J* = 3.0 Hz, 1H), 7.04 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.80 – 6.73 (m, 2H), 6.66 – 6.56 (m, 2H), 4.85 (dd, *J* = 7.6, 3.1 Hz, 1H), 4.20 – 4.04 (m, 2H), 3.48 (dd, *J* = 11.3, 3.1 Hz, 1H), 3.19 (dd, *J* = 11.3, 7.6 Hz, 1H), 1.25 (d, *J* = 6.6 Hz, 3H), 1.17 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ146.18, 134.29, 133.83, 126.50, 125.00, 124.05, 119.39, 117.46, 114.35, 111.50, 50.91, 47.15, 46.70, 19.21, 18.14.

HRMS (ESI): $C_{15}H_{18}N_2S$ Neutral mass: 258.1191, Observed ([M+H]) $^+$: 259.1261.



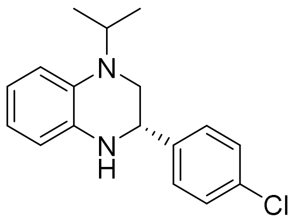
(S)-3-(4-fluorophenyl)-1-isopropyl-1,2,3,4-tetrahydroquinoxaline (3s): Yellow oil (12.0 mg, yield 89%), with 96% ee (HPLC, Diacel Chiralcel AD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 8.515 min; [α]D^{25}= +72° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.08 (t, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 2.7 Hz, 2H), 6.61 (s, 2H), 4.46 (d, *J* = 5.7 Hz, 1H), 4.11 (dt, *J* = 12.8, 6.4 Hz, 1H), 3.95 (s, 1H), 3.35 (d, *J* = 11.0 Hz, 1H), 3.07 – 2.93 (m, 1H), 1.23 (d, *J* = 6.6 Hz, 3H), 1.09 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.40 (d, *J* = 246.44 Hz), 138.12, 134.58, 134.18, 128.59 (d, *J* = 8.08 Hz), 119.06, 117.36, 115.41 (d, *J* = 21.21 Hz), 114.01, 111.43, 54.31, 46.91, 46.68, 19.27, 17.99.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -114.75.

HRMS (ESI): $C_{17}H_{19}FN_2$ Neutral mass: 270.1532, Observed ([M+H]) $^+$: 271.1601.

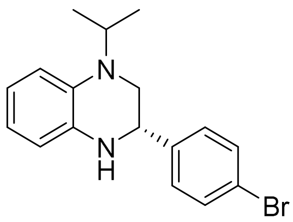


(S)-3-(4-chlorophenyl)-1-isopropyl-1,2,3,4-tetrahydroquinoxaline (3t): Yellow oil (13.3 mg, yield 93%), with 98% ee (HPLC, Diacel Chiralcel AD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 7.277 min; [α]D^{25}= +82° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 4H), 6.89 – 6.43 (m, 4H), 4.47 (d, *J* = 4.9 Hz, 1H), 4.19 – 3.82 (m, 2H), 3.35 (dd, *J* = 11.2, 2.5 Hz, 1H), 3.01 (dd, *J* = 11.1, 8.0 Hz, 1H), 1.29 (s, 1H), 1.22 (d, *J* = 6.6 Hz, 3H), 1.08 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.98, 134.44, 134.19, 133.48, 128.71, 128.37, 119.08, 117.44, 114.04, 111.50, 54.41, 46.69, 29.73, 19.18, 18.08.

HRMS (ESI): $C_{17}H_{19}ClN_2$ Neutral mass: 286.1237, Observed ([M+H]) $^+$: 287.1245.

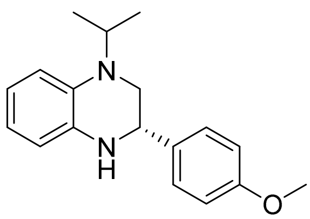


(S)-3-(4-bromophenyl)-1-isopropyl-1,2,3,4-tetrahydroquinoxaline (3u): Yellow oil (14.5 mg, yield 88%), with 99% ee (HPLC, Diacel Chiralcel AD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 9.283 min; $[\alpha]D^{25}$= +80° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 3.2 Hz, 2H), 6.75 (dd, *J* = 4.4, 2.0 Hz, 2H), 6.62 (qd, *J* = 7.3, 2.0 Hz, 2H), 4.45 (dd, *J* = 7.8, 3.0 Hz, 1H), 4.09 (dq, *J* = 13.2, 6.6 Hz, 1H), 3.95 (s, 1H), 3.34 (dd, *J* = 11.4, 3.1 Hz, 1H), 3.01 (dd, *J* = 11.3, 7.8 Hz, 1H), 1.22 (d, *J* = 6.6 Hz, 3H), 1.08 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 141.51, 134.41, 134.19, 131.66, 128.72, 121.59, 119.08, 117.44, 114.03, 111.50, 54.47, 46.66, 19.17, 18.09.

HRMS (ESI): $C_{17}H_{19}BrN_2$ Neutral mass: 330.0732, Observed ([M+H]) $^+$: 331.0795.

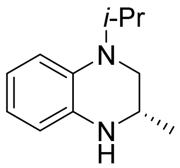


(S)-1-isopropyl-3-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoxaline (3v): Yellow oil (13.1 mg, yield 93%), with 98% ee (HPLC, Diacel Chiralcel AD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 10.752 min; $[\alpha]D^{25}$= +76° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.74 (d, *J* = 2.4 Hz, 2H), 6.67 – 6.54 (m, 2H), 4.40 (dd, *J* = 8.4, 3.0 Hz, 1H), 4.12 (dp, *J* = 13.4, 6.7 Hz, 1H), 3.93 (s, 1H), 3.85 (s, 3H), 3.36 (dd, *J* = 11.3, 3.1 Hz, 1H), 3.02 (dd, *J* = 11.2, 8.5 Hz, 1H), 1.23 (d, *J* = 6.6 Hz, 3H), 1.11 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 155.25, 141.70, 134.40, 133.56, 128.16, 119.29, 117.38, 114.42, 113.98, 111.47, 110.38, 105.91, 55.36, 49.21, 46.72, 43.49, 19.07, 18.26.

HRMS (ESI): $C_{18}H_{22}N_2O$ Neutral mass: 282.1732, Observed ([M+Na]) $^+$: 305.1744.

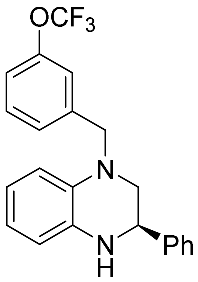


(S)-1-isopropyl-3-methyl-1,2,3,4-tetrahydroquinoxaline (3w) Yellow oil (7.6 mg, yield 80%), with 64% ee (HPLC, Diacel Chiralcel OD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 10.373 min; [α]D^{20}= +34° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.68 (d, *J* = 5.4 Hz, 2H), 6.60 – 6.49 (m, 2H), 4.16 – 4.04 (m, 1H), 3.50 (s, 1H), 3.29 – 3.20 (m, 1H), 2.84 – 2.72 (m, 1H), 1.22 (d, *J* = 1.9 Hz, 3H), 1.21 (d, *J* = 1.3 Hz, 3H), 1.18 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 134.49, 134.34, 118.86, 117.03, 113.99, 111.06, 46.38, 45.85, 20.32, 19.29, 17.88.

HRMS (ESI): $C_{12}H_{18}N_2$ Neutral mass: 190.1470, Observed ([M+H]) $^+$: 191.1479.



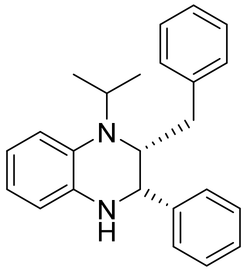
(R)-3-phenyl-1-(3-(trifluoromethoxy)benzyl)-1,2,3,4-tetrahydroquinoxaline (3y) Yellow oil (18.4 mg, yield 96%), with 94% ee (HPLC, Diacel Chiralcel AD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 10.990 min; [α]D^{20}= +54° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.41 (dd, *J* = 7.0, 4.7 Hz, 4H), 7.36 (dd, *J* = 5.1, 3.5 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.17 – 7.09 (m, 2H), 6.73 – 6.63 (m, 3H), 6.59 (dd, *J* = 7.6, 4.4 Hz, 1H), 4.58 (t, *J* = 5.6 Hz, 1H), 4.54 – 4.42 (m, 2H), 4.07 (s, 1H), 3.40 (d, *J* = 5.7 Hz, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 149.62 (d, *J* = 2.02), 141.40 (d, *J* = 15.15), 134.32 (d, *J* = 21.21), 129.93, 128.68, 128.02, 127.00, 125.22, 123.02 (t, *J* = 258.56) 121.74, 119.48, 119.32, 119.13, 118.37, 114.07, 112.04, 56.05, 55.15, 54.33.

HRMS (ESI): $C_{22}H_{19}F_3N_2O$ Neutral mass: 384.1449, Observed ([M+H]) $^+$: 385.1522

^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$) δ -57.66

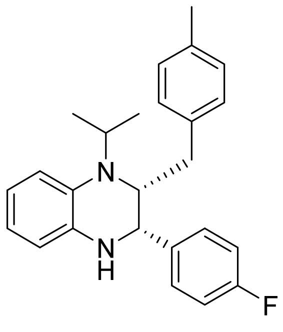


(2R,3S)-2-benzyl-1-isopropyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline (5a): White solid (7.9 mg, yield 46%), with 90% ee (HPLC, Diacel Chiralcel OD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 6.762 min; m.p. 122-125 °C; [α]D^{20}= -36° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38 (dt, *J* = 15.1, 7.5 Hz, 4H), 7.26 (t, *J* = 7.0 Hz, 1H), 7.03 (dq, *J* = 14.1, 6.9 Hz, 3H), 6.84 (d, *J* = 7.9 Hz, 1H), 6.73 (dd, *J* = 9.5, 5.7 Hz, 3H), 6.66 (d, *J* = 4.0 Hz, 2H), 4.22 (d, *J* = 2.5 Hz, 1H), 3.97 (s, 1H), 3.75 (dq, *J* = 13.5, 6.7 Hz, 1H), 3.44 (dt, *J* = 10.1, 3.0 Hz, 1H), 2.38 – 2.15 (m, 2H), 0.97 (d, *J* = 6.6 Hz, 3H), 0.33 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 141.50, 140.69, 134.93, 131.55, 130.59, 126.76, 125.56, 119.35, 118.68, 115.17, 58.33, 56.23, 53.57, 32.92, 20.83, 19.39.

HRMS (ESI): $C_{24}H_{26}N_2$ Neutral mass: 342.2096, Observed ([M+H]) $^+$: 343.2174.



(2R,3S)-3-(4-fluorophenyl)-1-isopropyl-2-(4-methylbenzyl)-1,2,3,4-tetrahydroquinoxaline (5b): White solid (7.5 mg, yield 40%), with 90% ee (HPLC, Diacel Chiralcel OD-H column 95:5

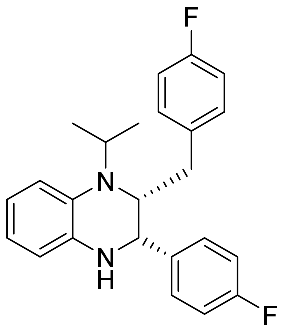
hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 4.117 min; m.p. 134-136 °C ; $[\alpha]D^{20}$= -49° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.91 – 6.73 (m, 7H), 4.29 (d, *J* = 2.1 Hz, 1H), 4.07 (s, 1H), 3.88 (dt, *J* = 13.3, 6.5 Hz, 1H), 3.46 (dt, *J* = 10.0, 3.0 Hz, 1H), 2.43 (d, *J* = 7.9 Hz, 3H), 2.37 (dt, *J* = 24.1, 12.0 Hz, 2H), 1.08 (d, *J* = 6.5 Hz, 3H), 0.46 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.34(d, *J* = 243.41 Hz), 138.36, 137.06, 136.34 (d, *J* = 3.03 Hz), 135.06, 132.85, 131.38(d, *J* = 8.08 Hz), 129.36, 126.60, 119.29, 118.83 (d, *J* =8.08 Hz), 115.14, 114.41, 114.20, 58.21, 55.81, 53.69, 31.96, 29.73, 21.16, 20.94, 19.36.

HRMS (ESI): $C_{25}H_{27}FN_2$ Neutral mass: 374.2158, Observed ($[M+Na]^+$): 397.2011.

$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -118.32.



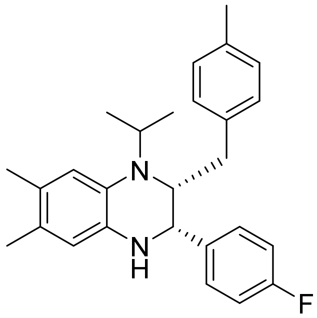
(2R,3S)-2-(4-fluorobenzyl)-3-(4-fluorophenyl)-1-isopropyl-1,2,3,4-tetrahydroquinoxaline (5c): White solid (5.7 mg, yield 30%), with 90% ee (HPLC, Diacel Chiralcel IC-H column 99:1 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 6.275 min; m.p. 122-125°C; $[\alpha]D^{20}$= -56° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 8.2, 5.5 Hz, 2H), 7.17 (t, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 7.9 Hz, 1H), 6.86 (dd, *J* = 11.9, 5.3 Hz, 3H), 6.78 (dt, *J* = 7.1, 5.4 Hz, 4H), 4.30 (s, 1H), 4.04 (s, 1H), 3.87 (dt, *J* = 13.4, 6.7 Hz, 1H), 3.43 (dd, *J* = 9.4, 4.2 Hz, 1H), 2.35 (d, *J* = 6.9 Hz, 2H), 1.07 (d, *J* = 6.6 Hz, 3H), 0.46 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.13 (d, *J* = 247.45 Hz), 161.38 (d, *J* = 244.42 Hz); 137.13 (d, *J* = 3.03 Hz), 136.02 (d, *J* = 3.03 Hz), 134.82, 132.81, 131.34 (d, *J* = 7.07 Hz), 128.26 (d, *J* = 8.08 Hz), 119.59, 118.96, 118.92, 115.59 (d, J = 21.21 Hz), 115.30, 114.40 (d, J = 21.21 Hz), 58.13, 55.47, 53.70, 31.82, 29.73, 20.91, 19.37.

$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -115.11, -118.08.

HRMS (ESI): $C_{24}H_{24}F_2N_2$ Neutral mass: 378.1908, Observed ($[M+H]^+$):379.1992.



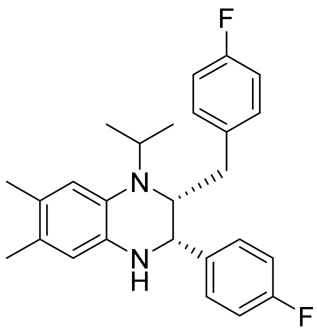
(2R,3S)-3-(4-fluorophenyl)-1-isopropyl-6,7-dimethyl-2-(4-methylbenzyl)-1,2,3,4-tetrahydroquinoxaline (5d): White solid (8.1 mg, yield 40%), with 94% ee (HPLC, Diacel Chiralcel IC-H column 99:1 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 4.603 min; m.p. 142-145°C; $[\alpha]D^{20}$= -48° (c 0.01, CH_2Cl_2).

^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 6.91 – 6.78 (m, 4H), 6.75 (s, 1H), 6.58 (s, 1H), 4.25 (s, 1H), 3.94 – 3.77 (m, 1H), 3.40 (d, J = 9.5 Hz, 1H), 2.44 (s, 3H), 2.39 – 2.30 (m, 2H), 2.25 (d, J = 6.9 Hz, 6H), 1.07 (d, J = 6.6 Hz, 3H), 0.47 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.31 (d, J = 243.41 Hz), 138.69, 136.90, 136.58 (d, J = 3.03), 132.94, 131.39 (d, J = 8.08 Hz), 130.64, 129.30, 127.08, 126.81, 126.58, 120.35, 116.70, 114.22 (d, J = 21.21), 58.54, 55.91, 53.71, 31.84, 21.13, 21.02, 19.42, 19.16, 19.03.

$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -118.49.

HRMS (ESI): $C_{27}H_{31}FN_2$ Neutral mass: 402.2471, Observed ($[M+H]^+$): 403.2482.



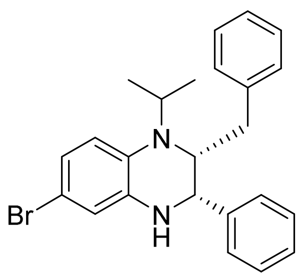
(2R,3S)-2-(4-fluorobenzyl)-3-(4-fluorophenyl)-1-isopropyl-6,7-dimethyl-1,2,3,4-tetrahydroquinoxaline (5e): White solid (6.1 mg, yield 30%), with 92% ee (HPLC, Diacel Chiralcel OD-H column 99:1 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 5.885 min; m.p. 140-143°C; [α]D^{20}= -36° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.46 (dd, *J* = 8.3, 5.5 Hz, 2H), 7.16 (t, *J* = 8.6 Hz, 2H), 6.93 – 6.78 (m, 4H), 6.75 (s, 1H), 6.58 (s, 1H), 4.27 (s, 1H), 3.80 (d, *J* = 48.6 Hz, 2H), 3.37 (s, 1H), 2.41 – 2.31 (m, 2H), 2.25 (d, *J* = 4.2 Hz, 6H), 1.07 (d, *J* = 6.5 Hz, 3H), 0.47 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 162.07 (d, *J* = 246.44 Hz), 161.34 (d, *J* = 243.41 Hz), 136,26, 136.24, 132.72 (d, *J* = 2.02 Hz), 131.34 (d, *J* = 8.08 Hz), 132.71, 130.58, 128.22 (d, *J* = 7.07 Hz), 126.98, 120.48, 116.81, 115.51 (d, *J* = 22.22 Hz), 114.31 (d, *J* = 21.21 Hz), 58.43, 55.55, 53.71, 31.70, 20.97, 19.45, 19.12.

^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$) δ -115.32, -118.26.

HRMS (ESI): $C_{26}H_{28}F2N_2$ Neutral mass: 406.2221, Observed ([M+H]) $^+$: 407.2230.

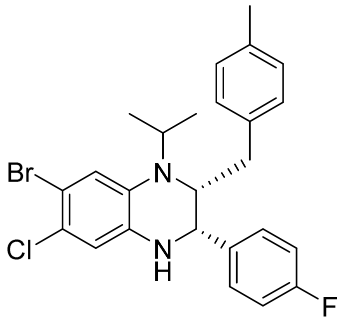


(2R,3S)-2-benzyl-6-bromo-1-isopropyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline (5f): White solid (6.3 mg, yield 30%), with 96% ee (HPLC, Diacel Chiralcel OD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 7.765 min; m.p. 133-135°C; [α]D^{20}= -68° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.47 (d, *J* = 4.4 Hz, 4H), 7.41 – 7.34 (m, 1H), 7.20 – 7.09 (m, 3H), 6.94 – 6.86 (m, 2H), 6.83 (d, *J* = 6.6 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 1H), 4.30 (d, *J* = 2.7 Hz, 1H), 4.14 (s, 1H), 3.78 (dt, *J* = 13.4, 6.7 Hz, 1H), 3.53 (dd, *J* = 13.4, 2.8 Hz, 1H), 2.44 – 2.25 (m, 2H), 1.06 (d, *J* = 6.6 Hz, 3H), 0.42 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 140.86, 140.28, 136.35, 131.98, 129.99, 128.76, 127.65, 126.68 (s), 125.69, 121.83, 119.98, 117.31, 110.46, 58.07, 56.15, 53.83, 32.82, 20.62, 19.41.

HRMS (ESI): $C_{24}H_{25}BrN_2$ Neutral mass: 420.1201, Observed ([M+H]) $^+$: 421.1274



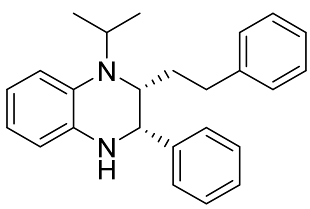
(2R,3S)-7-bromo-6-chloro-3-(4-fluorophenyl)-1-isopropyl-2-(4-methylbenzyl)-1,2,3,4-tetrahydroquinoxaline (5g): White solid (6.3 mg, yield 26%), with 90% ee (HPLC, Diacel Chiralcel IC-H column 99:1 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 5.563 min; m.p. 162-165°C; [α]D^{20}= -46° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 – 7.24 (m, 4H), 7.07 (s, 1H), 6.88 (t, *J* = 8.7 Hz, 2H), 6.84 – 6.74 (m, 3H), 4.23 (d, *J* = 2.4 Hz, 1H), 4.14 (s, 1H), 3.83 – 3.70 (m, 1H), 3.45 (d, *J* = 8.3 Hz, 1H), 2.43 (s, 3H), 2.41 – 2.34 (m, 1H), 2.32 – 2.22 (m, 1H), 1.07 (d, *J* = 6.5 Hz, 3H), 0.44 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 161.45 (d, *J* = 242.42 Hz), 137.49, 137.31, 135.66 (d, *J* = 3.03 Hz), 135.41, 132.91, 131.25 (d, *J* = 7.07 Hz), 129.52, 126.47, 122.92, 122.29, 115.45, 114.57 (d, *J* = 21.21 Hz), 110.11, 57.82, 55.92, 54.09, 32.04, 21.14, 20.60, 19.42.

^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$) δ -117.72.

HRMS (ESI): $C_{25}H_{25}BrClFN_2$ Neutral mass:486.0874, Observed ([M+H]) $^+$: 487.0892.



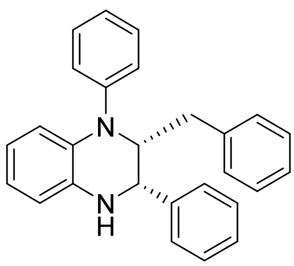
(2R,3S)-1-isopropyl-2-phenethyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline (5h): White solid (6.2 mg, yield 35%), with 82% ee (HPLC, Diacel Chiralcel OD-H column 95:5 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 6.288 min; m.p. 136-138°C; [α]D^{20}= -18° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.46 (q, *J* = 7.7 Hz, 4H), 7.36 (t, *J* = 6.6 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 2H), 6.82 (dd, *J* = 11.4, 4.8

Hz, 1H), 6.74 (q, J = 7.7 Hz, 2H), 4.33 (d, J = 2.4 Hz, 1H), 4.13 (dt, J = 13.3, 6.6 Hz, 1H), 4.03 (s, 1H), 3.53 – 3.43 (m, 1H), 2.69 (ddd, J = 14.4, 11.1, 5.2 Hz, 1H), 2.22 (ddd, J = 13.8, 11.4, 5.9 Hz, 1H), 1.72 – 1.59 (m, 1H), 1.56 – 1.44 (m, 1H), 1.35 (d, J = 6.8 Hz, 3H), 1.27 (d, J = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.61, 141.37, 135.05, 132.97, 128.60, 128.31, 128.09, 127.36, 126.85, 125.42, 119.05, 118.65, 118.23, 115.06, 55.99, 55.37, 53.48, 33.12, 29.07, 22.24, 19.68

HRMS (ESI): $C_{25}H_{28}N_2$ Neutral mass: 356.2252, Observed ([M+H]) $^+$: 357.2268.

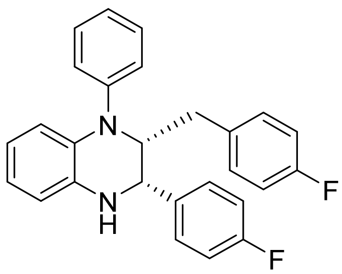


(2R,3S)-2-benzyl-1,3-diphenyl-1,2,3,4-tetrahydroquinoxaline (5i): White solid (6.0 mg, yield 32%), with 96% ee (HPLC, Diacel Chiralcel IC-H column 99:1 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 4.718 min; m.p. 139-141°C; [α]D^{20}= −92° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, J = 7.3, 6.0 Hz, 4H), 7.41 – 7.34 (m, 1H), 7.28 – 7.18 (m, 3H), 7.09 (t, J = 7.4 Hz, 3H), 7.02 (d, J = 7.0 Hz, 2H), 6.97 (t, J = 7.5 Hz, 1H), 6.87 (dd, J = 13.5, 7.0 Hz, 2H), 6.79 (t, J = 7.5 Hz, 1H), 6.54 (d, J = 8.1 Hz, 2H), 4.58 (d, J = 2.7 Hz, 1H), 4.28 (s, 1H), 3.98 – 3.87 (m, 1H), 2.70 – 2.59 (m, 1H), 2.54 (dd, J = 13.5, 2.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.42, 140.41, 140.08, 136.71, 129.81, 128.93, 128.71, 128.26, 127.91, 127.66, 126.92, 126.06, 123.37, 122.17, 121.63, 121.36, 118.79, 115.71, 67.32, 54.95, 31.99.

HRMS (ESI): $C_{27}H_{24}N_2$ Neutral mass: 376.1939, Observed ([M+H]) $^+$:377.2017.



(2R,3S)-2-(4-fluorobenzyl)-3-(4-fluorophenyl)-1-phenyl-1,2,3,4-tetrahydroquinoxaline (5j):

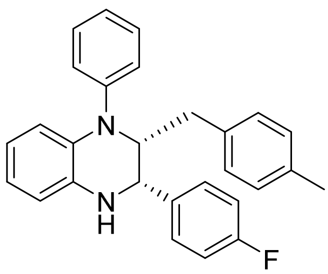
White solid (7.2 mg, yield 35%), with 92% ee (HPLC, Diacel Chiralcel IC-H column 99:1 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 6.275 min; m.p. 140-142°C; $[\alpha]D^{20}$= -58° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42 (dd, *J* = 8.4, 5.4 Hz, 2H), 7.11 (ddd, *J* = 20.9, 12.9, 8.7 Hz, 5H), 6.95 (dd, *J* = 10.0, 7.2 Hz, 5H), 6.88 (t, *J* = 7.3 Hz, 2H), 6.79 (t, *J* = 7.5 Hz, 1H), 6.54 (d, *J* = 7.8 Hz, 2H), 4.55 (d, *J* = 2.6 Hz, 1H), 4.22 (s, 1H), 3.89 – 3.72 (m, 1H), 2.67 – 2.55 (m, 1H), 2.51 – 2.40 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 162.22 (d, *J* = 250.48 Hz), 161.57 (d, *J* = 244.42 Hz), 150.35, 136.05 (d, *J* = 3.03 Hz), 136.45 (d, *J* = 3.03 Hz), 131.13 (d, *J* = 7.07Hz), 129.03, 128.47 (d, *J* = 7.07 Hz), 127.79, 123.39, 122.34, 121.57, 119.08, 115.86, 115.63 (d, *J* =21.21 Hz), 115.04 (d, *J* = 21.21 Hz), 114.94, 67.29, 54.19, 30.98.

^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$) δ -114.63, -117.26.

HRMS (ESI): $C_{27}H_{22}F_2N_2$ Neutral mass: 412.1751, Observed ([M+H]) $^+$:413.18258.



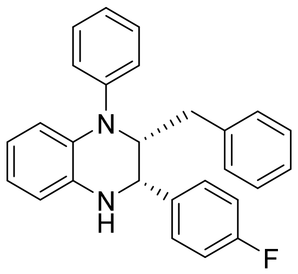
(2R,3S)-3-(4-fluorophenyl)-2-(4-methylbenzyl)-1-phenyl-1,2,3,4-tetrahydroquinoxaline (5k): White solid (7.1mg, yield 35%), with 96% ee (HPLC, Diacel Chiralcel IC-H column 99:1 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 11.297 min; m.p. 143-146°C; $[\alpha]D^{20}$= -49° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37 – 7.21 (m, 5H), 7.10 (dd, *J* = 15.9, 8.0 Hz, 3H), 6.96 (dd, *J* = 14.6, 6.6 Hz, 5H), 6.88 (t, *J* = 7.7 Hz, 2H), 6.79 (t, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 7.8 Hz, 2H), 4.54 (s, 1H), 4.24 (s, 1H), 3.86 (d, *J* = 11.1 Hz, 1H), 2.68 – 2.49 (m, 2H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 161.55 (d, *J* = 244.42 Hz), 150.46, 137.37, 137.27, 136.83, 135.76 (d, *J* = 3.03 Hz), 131.19 (d, *J* = 7.07 Hz), 129.41, 129.01, 127.71, 126.77, 123.39, 122.29, 121.54, 121.44, 118.75, 115.71, 114.99(d, *J* = 21.21 Hz), 67.28, 54.60, 31.11, 21.15.

^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$) δ -117.43.

HRMS (ESI): $C_{28}H_{25}FN_2$ Neutral mass: 408.2001, Observed ([M+H]) $^+$: 409.2076



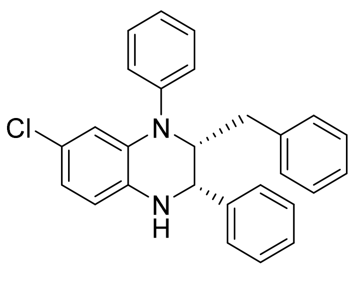
(2R,3S)-2-benzyl-3-(4-fluorophenyl)-1-phenyl-1,2,3,4-tetrahydroquinoxaline (5l): White solid (7.5 mg, yield 38%), with 88% ee (HPLC, Diacel Chiralcel IC-H column 99:1 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 12.630 min; m.p. 144-146°C; [α]D^{20}= -38° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.45 (d, *J* = 4.3 Hz, 4H), 7.38 (td, *J* = 8.3, 4.0 Hz, 1H), 7.10 (dd, *J* = 16.4, 8.4 Hz, 3H), 7.02 – 6.92 (m, 5H), 6.88 (t, *J* = 6.9 Hz, 2H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.56 (d, *J* = 7.9 Hz, 2H), 4.57 (s, 1H), 4.27 (s, 1H), 3.89 (d, *J* = 11.3 Hz, 1H), 2.69 – 2.56 (m, 1H), 2.51 (dd, *J* = 13.6, 2.4 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 161.54 (d, *J* = 244.42 Hz), 150.42, 140.28, 136.73, 135.64, 131.15 (d, *J* = 8.08 Hz), 129.01, 128.72, 127.71 (d, *J* =2.02 Hz), 126.88, 123.40, 122.32, 121.555, 121.49, 118.84, 115.76, 115.00 (d, *J* = 21.21Hz), 67.26, 54.80, 31.13.

^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$) δ -117.39

HRMS (ESI): $C_{27}H_{23}FN_2$ Neutral mass: 394.1845, Observed ([M+H]) $^+$: 395.1919.

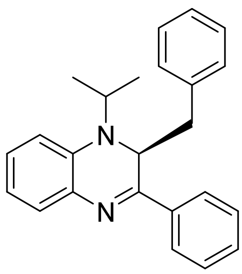


(2R,3S)-2-benzyl-7-chloro-1,3-diphenyl-1,2,3,4-tetrahydroquinoxaline (5m): White solid (5.1 mg, yield 30%), with 86% ee (HPLC, Diacel Chiralcel IC-H column 99:1 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 21.177 min; m.p. 146-148°C; $[\alpha]D^{20}$= -28° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.44 (d, *J* = 3.7 Hz, 4H), 7.40 – 7.34 (m, 1H), 7.28 – 7.19 (m, 3H), 7.10 (t, *J* = 7.9 Hz, 2H), 7.01 (dd, *J* = 12.4, 4.5 Hz, 3H), 6.89 (dd, *J* = 13.5, 4.9 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.49 (d, *J* = 7.9 Hz, 2H), 4.54 (d, *J* = 2.9 Hz, 1H), 4.28 (s, 1H), 3.87 (dt, *J* = 10.6, 3.0 Hz, 1H), 2.65 – 2.49 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 149.77, 139.96, 139.72, 135.08, 129.75, 129.22, 128.75, 128.36, 127.78, 126.85, 126.19, 123.27, 122.15, 121.75, 116.48, 67.32, 54.92, 32.15, 29.72.

HRMS (ESI): $C_{27}H_{23}ClN_2$ Neutral mass: 410.1549, Observed ([M+H]) $^+$: 411.1637.



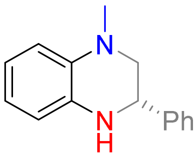
(S)-2-benzyl-1-isopropyl-3-phenyl-1,2-dihydroquinoxaline (5a'): Yellow solid (5.1 mg, yield 30%), with 94% ee (HPLC, Diacel Chiralcel IC-H column 99:1 hexanes/2-propanol, 1 mL/min, 254 nm; t_R = 8.968 min; m.p. 134-136°C; $[\alpha]D^{20}$= +28° (c 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.01 (dd, *J* = 7.3, 1.9 Hz, 2H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.51 – 7.42 (m, 3H), 7.27 (d, *J* = 7.4 Hz, 2H), 7.23 (d, *J* = 4.6 Hz, 1H), 7.20 (d, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 7.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 4.76 (dd, *J* = 9.6, 4.7 Hz, 1H), 3.82 (dt, *J* = 13.3, 6.7 Hz, 1H), 2.68 (dd, *J* = 13.4, 4.6 Hz, 1H), 2.52 (dd, *J* = 13.3, 9.6 Hz, 1H), 0.88 (d, *J* = 6.5 Hz, 3H), 0.80 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 156.69, 137.83, 137.02, 136.43, 130.08, 129.97, 128.68, 128.06, 127.58, 127.00, 126.37, 119.49, 118.44, 53.86, 50.91 – 50.58, 36.37, 29.72, 21.60, 21.17.

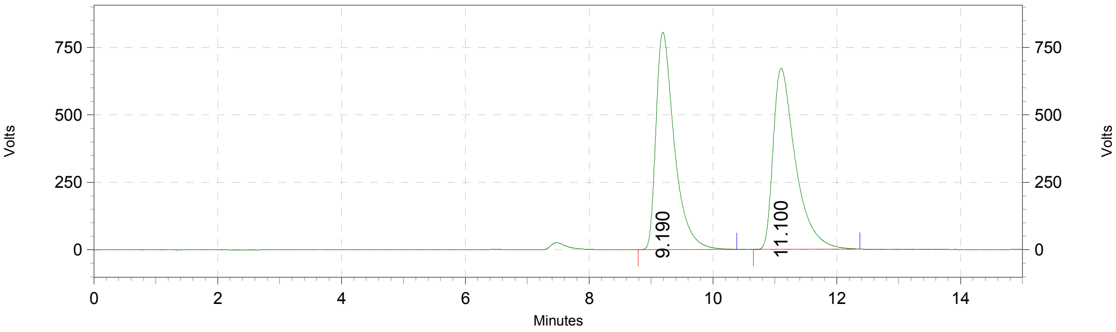
HRMS (ESI): $C_{24}H_{24}N_2$ Neutral mass: 340.1939, Observed ([M+H]) $^+$: 341.2013.

HPLC spectrum

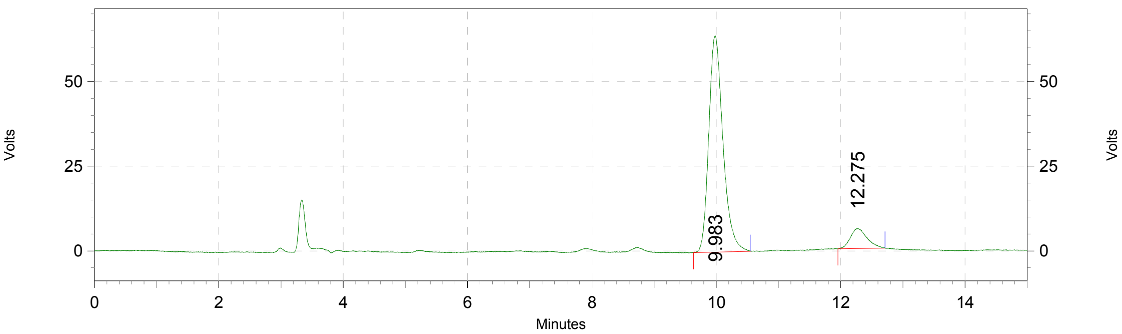


3a

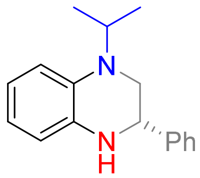
(***S***)-1-methyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	9.190	16577727	49.617
2	11.100	16833633	50.383

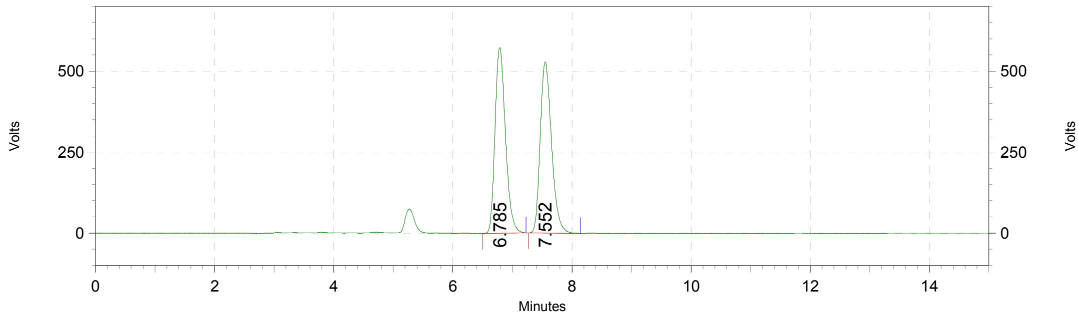


Peak#	t_R (min)	Area	Area (%)
1	9.983	1011626	90.185
2	12.275	110101	9.815

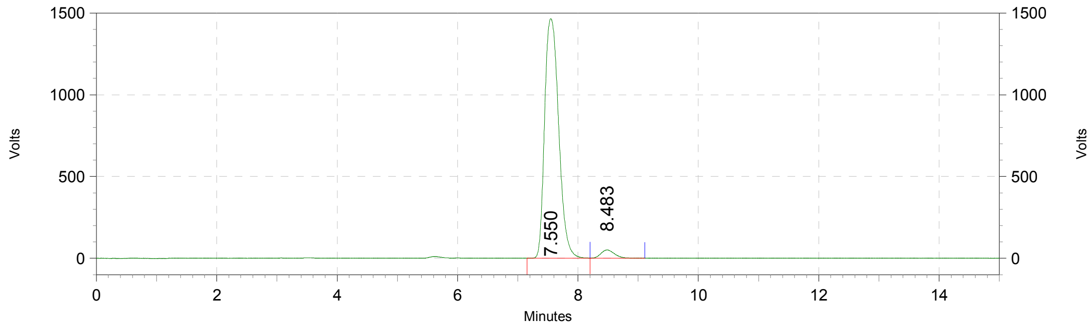


3b

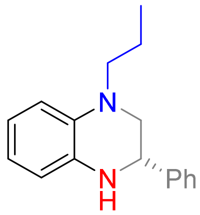
(***S***)-1-isopropyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	6.785	6995398	50.045
2	7.552	6982695	49.955

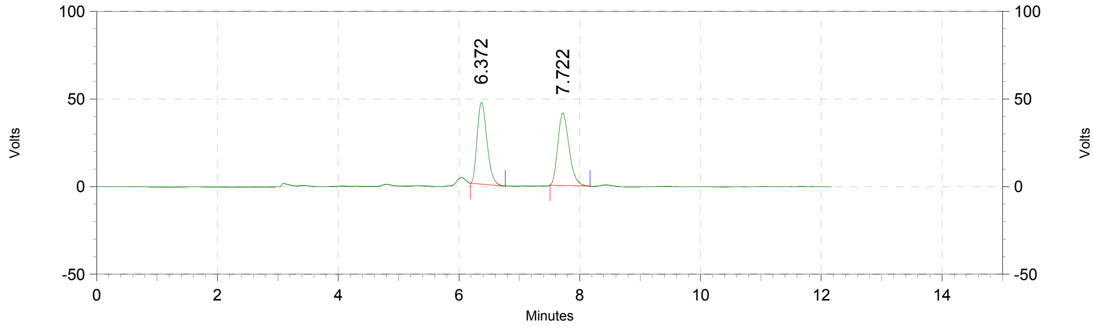


Peak#	t_R (min)	Area	Area (%)
1	7.550	23729277	96.859
2	8.483	769610	3.141

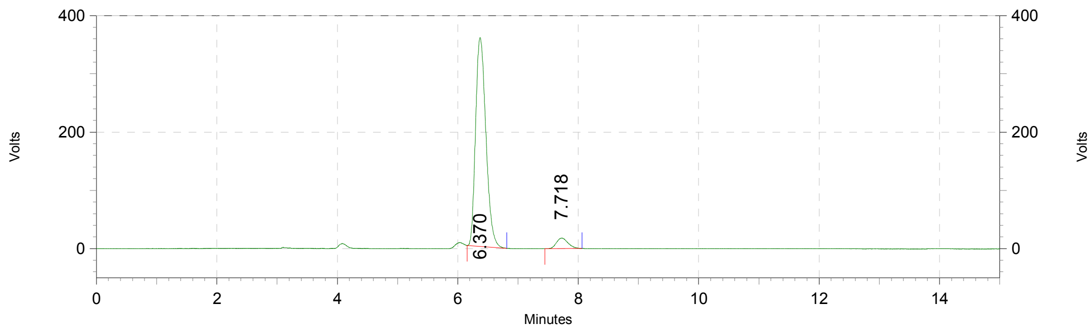


3c

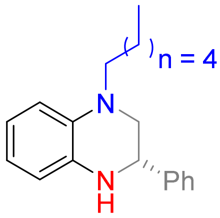
(S)-3-phenyl-1-propyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	6.372	527826	49.677
2	7.722	534685	50.323

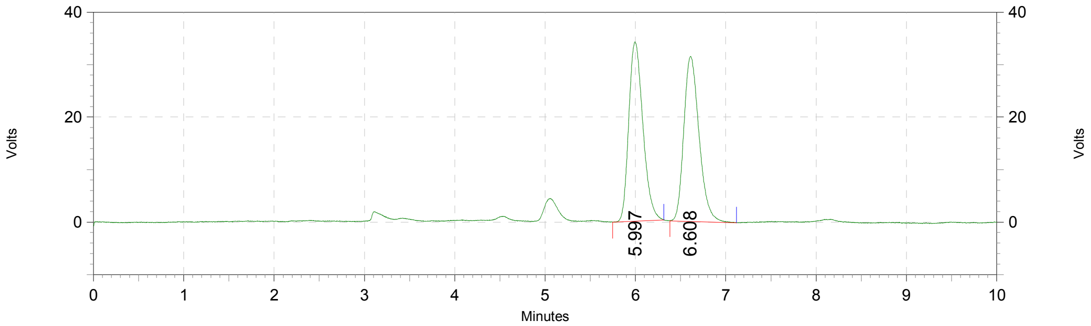


Peak#	t_R (min)	Area	Area (%)
1	6.370	4270769	94.649
2	7.718	241472	5.351

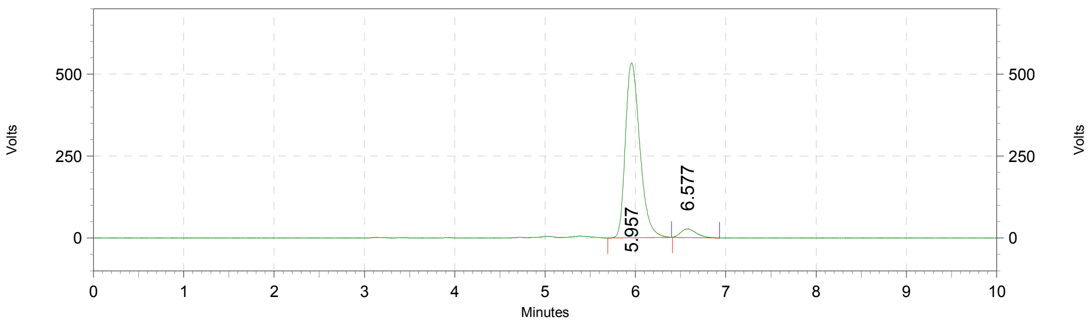


3d

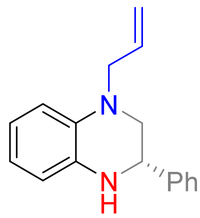
(S)-3-phenyl-1-propyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	5.997	372055	50.159
2	6.608	369694	49.841

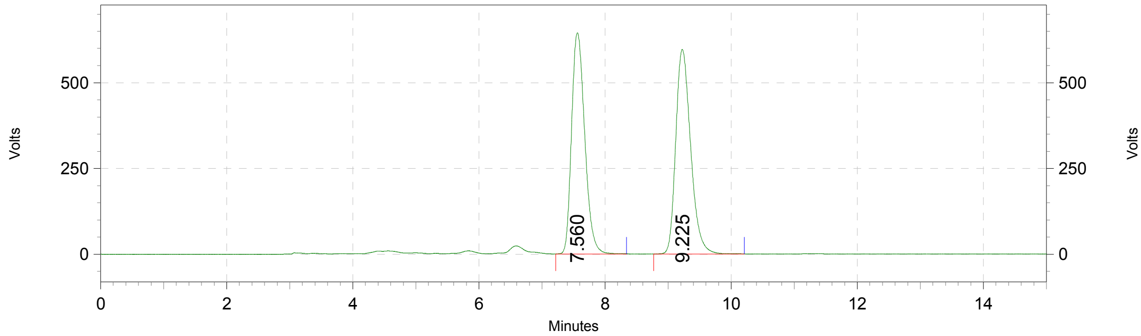


Peak#	t_R (min)	Area	Area (%)
1	5.957	5936868	95.130
2	6.577	303899	4.870

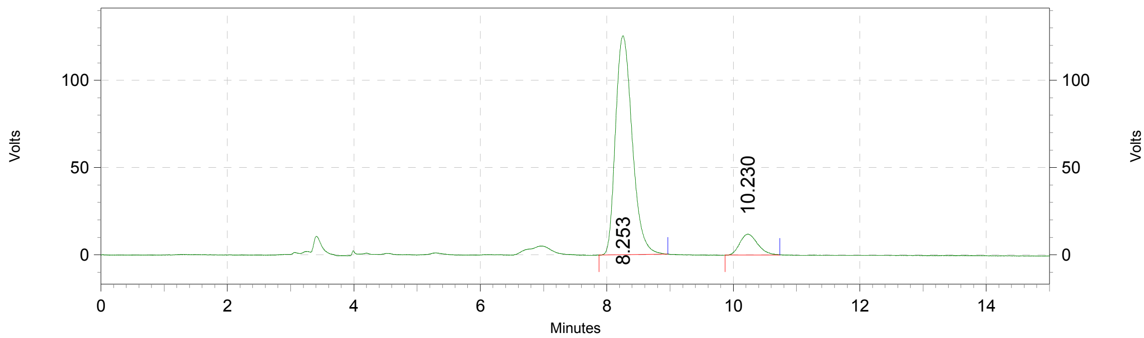


3e

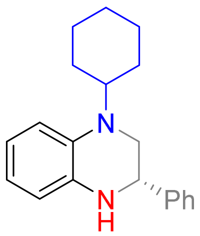
(***S***)-1-allyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	7.560	9350461	48.854
2	9.225	9789248	51.146

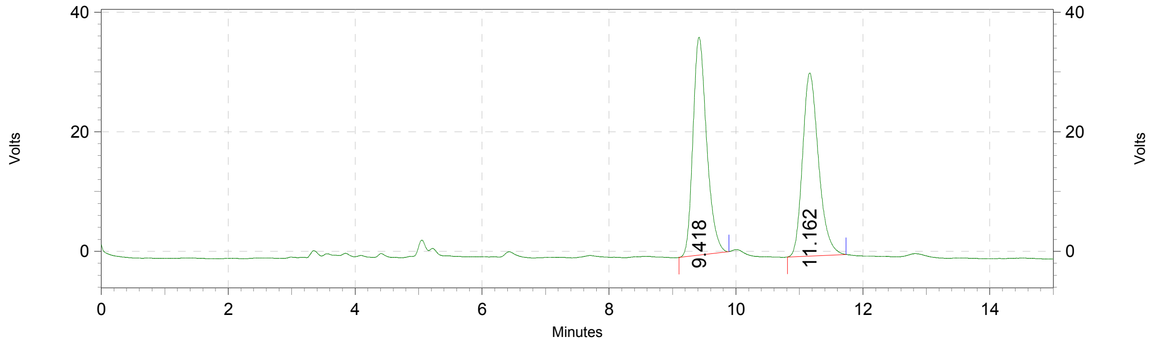


Peak#	t_R (min)	Area	Area (%)
1	8.253	2307581	90.770
2	10.230	234660	9.230

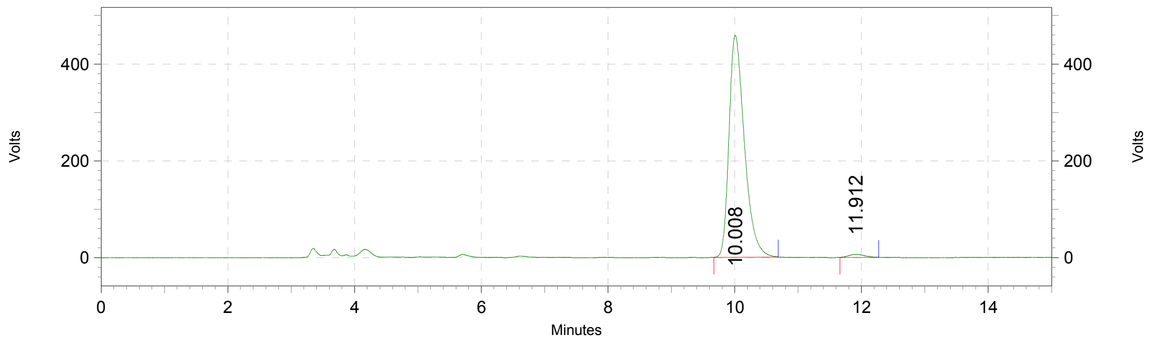


3f

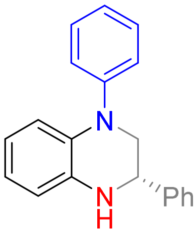
(***S***)-1-cyclohexyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	9.418	546231	50.538
2	11.162	534608	49.462

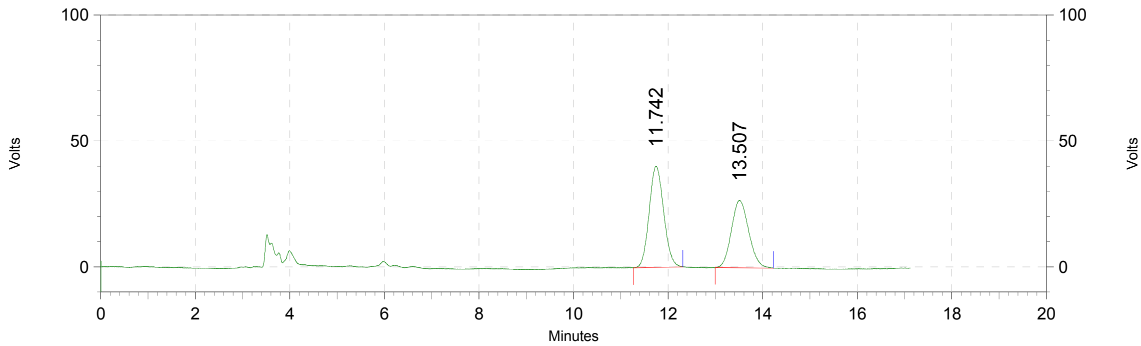


Peak#	t_R (min)	Area	Area (%)
1	10.008	7732100	98.682
2	11.912	103235	1.318

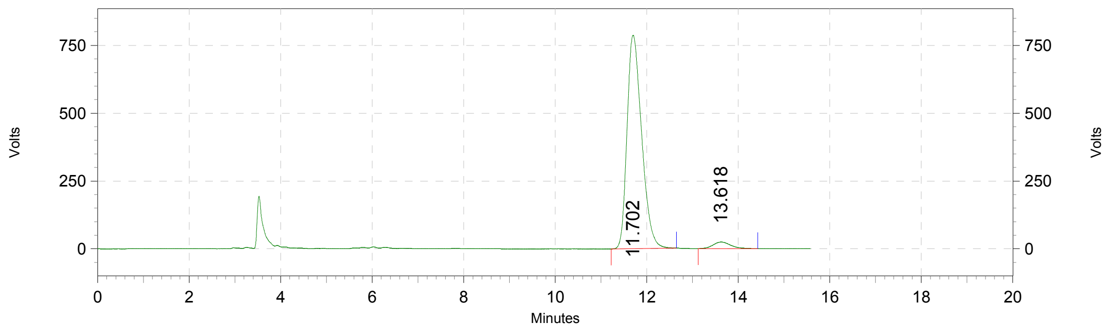


3g

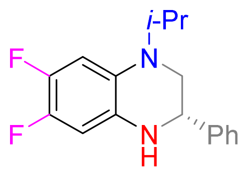
(***S***)-1,3-diphenyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	11.742	855448	55.590
2	13.507	683409	44.410

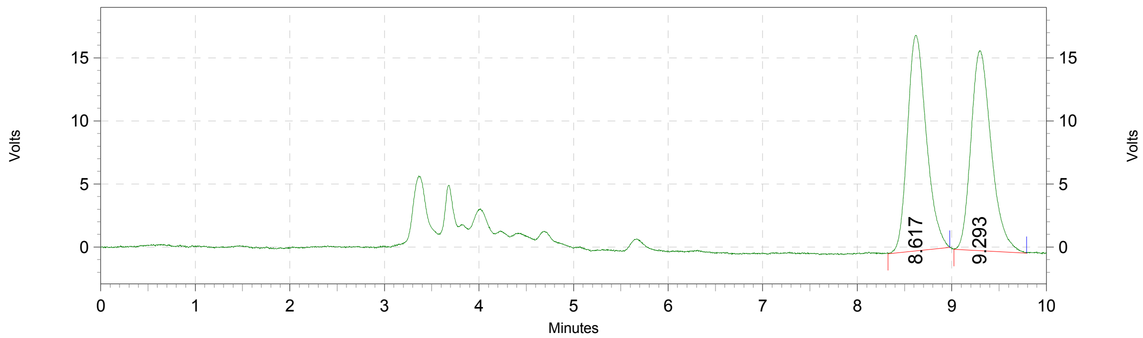


Peak#	t_R (min)	Area	Area (%)
1	11.702	17448937	96.468
2	13.618	638831	3.532

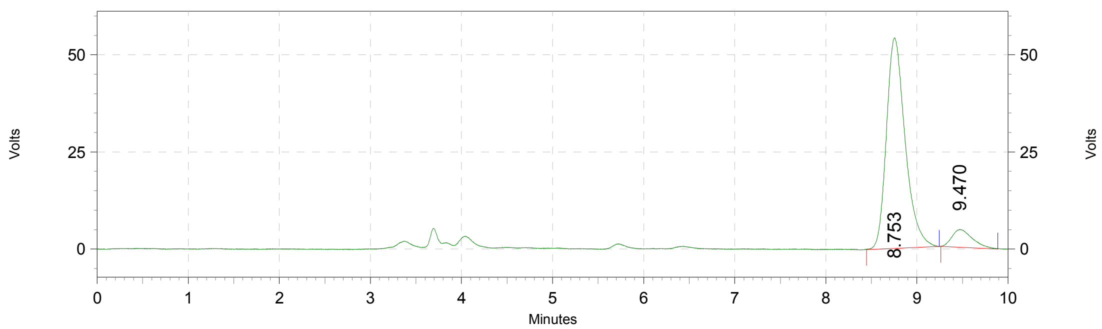


3h

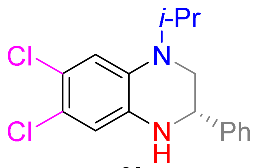
(***S***)-6,7-difluoro-1-isopropyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	8.617	237588	50.011
2	9.293	237485	49.989

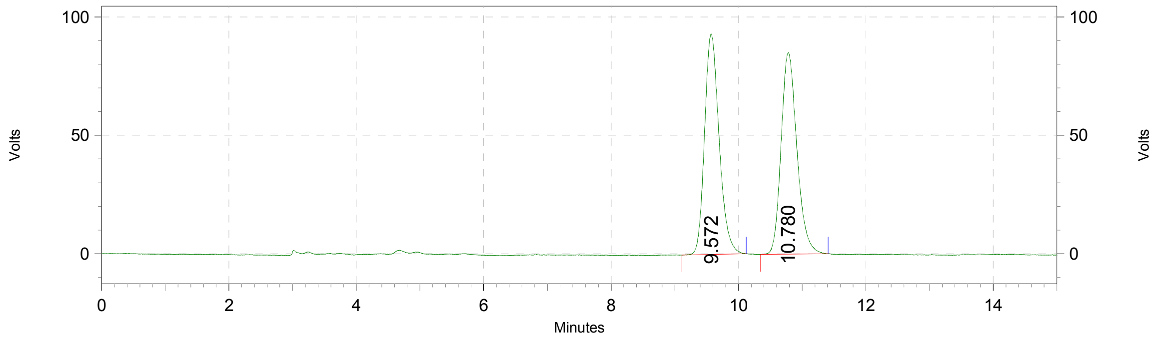


Peak#	t_R (min)	Area	Area (%)
1	8.753	775564	91.657
2	9.470	70593	8.343

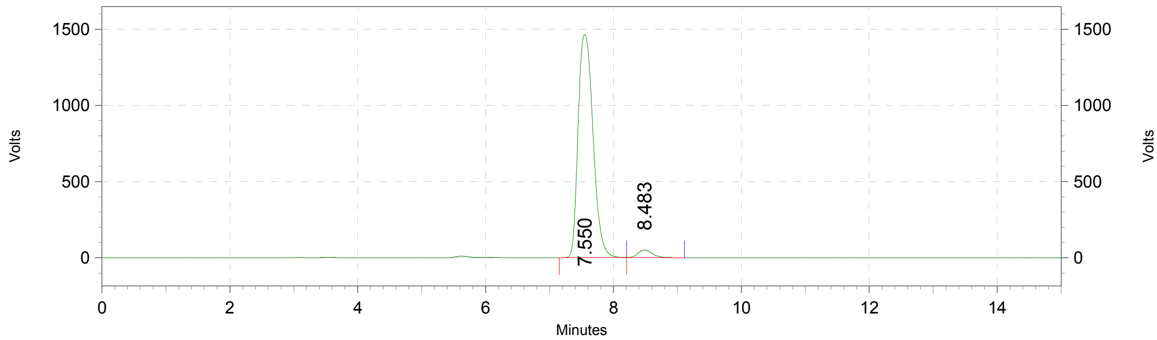


3i

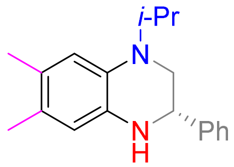
(***S***)-6,7-dichloro-1-isopropyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	9.572	1480019	50.147
2	10.780	1471326	49.853

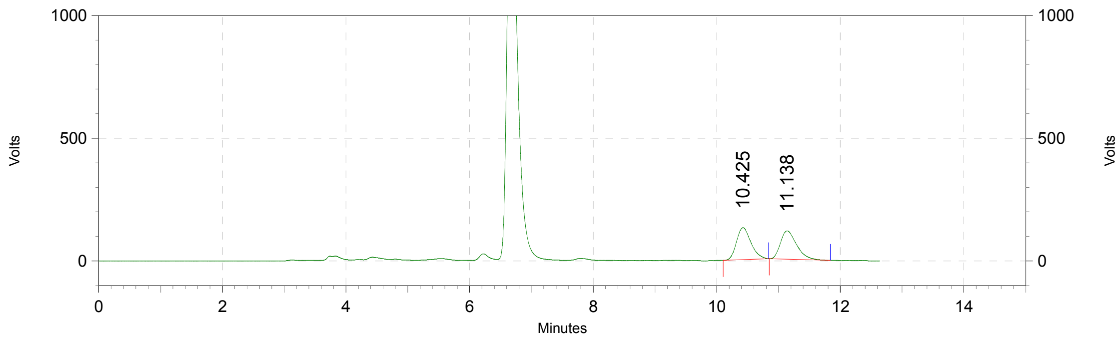


Peak#	t_R (min)	Area	Area (%)
1	7.550	23729277	96.859
2	8.483	769610	3.141

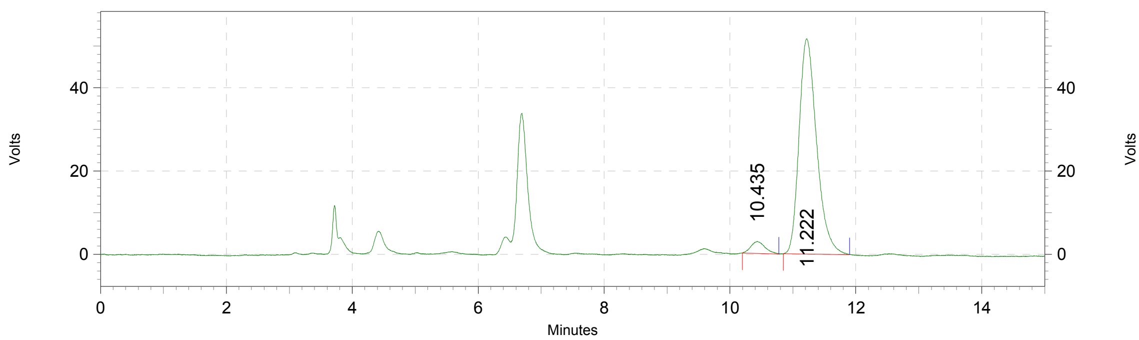


3j

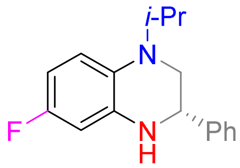
(***S***)-1-isopropyl-6,7-dimethyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	10.425	2122743	50.195
2	11.138	2106243	49.805

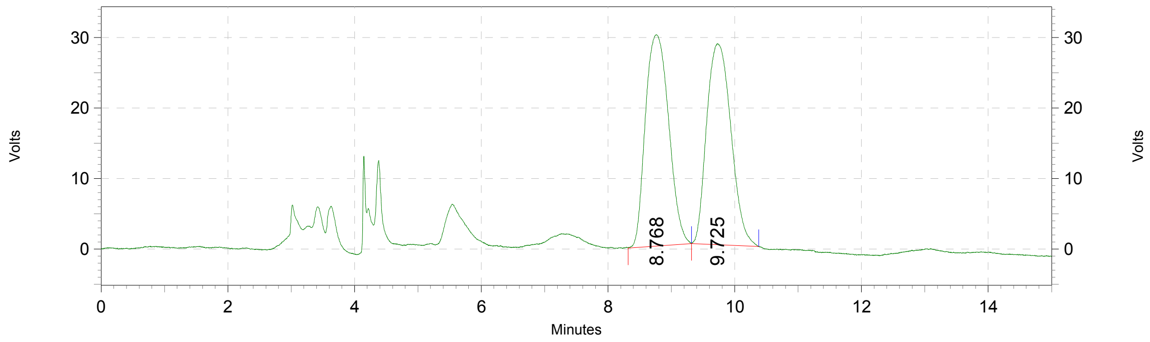


Peak#	t_R (min)	Area	Area (%)
1	10.435	44715	4.272
2	11.222	1001914	95.728

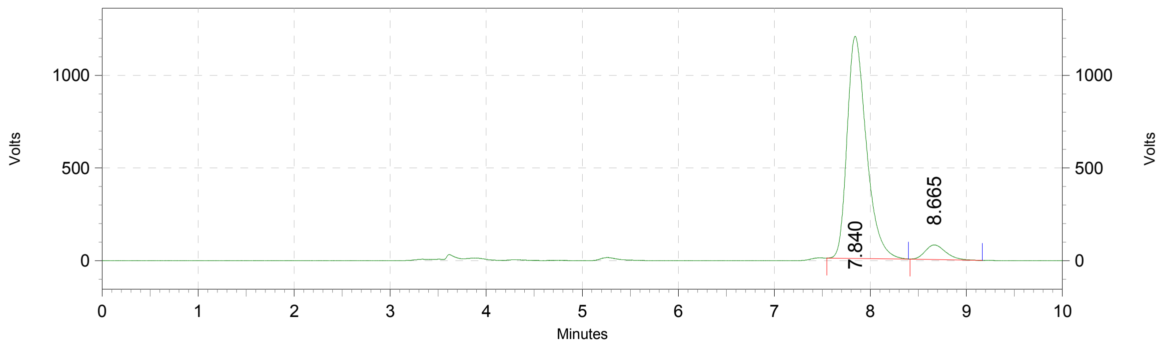


3k

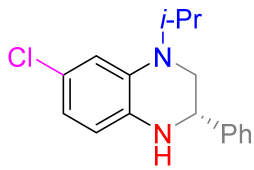
(*S*)-6-fluoro-1-isopropyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	8.768	767149	50.210
2	9.725	760723	49.790

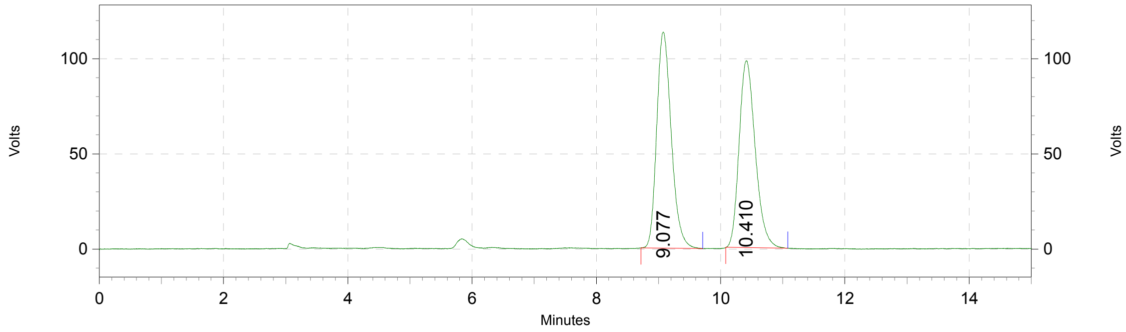


Peak#	t_R (min)	Area	Area (%)
1	7.840	16710902	93.474
2	8.665	1166660	6.526

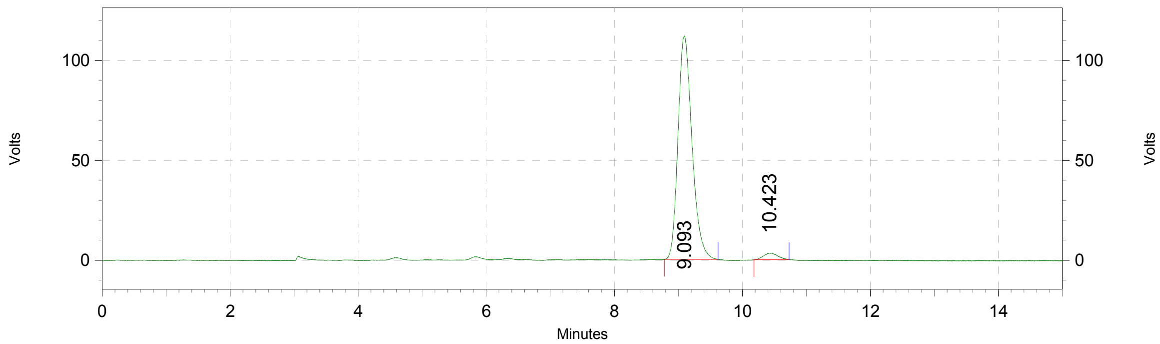


3l

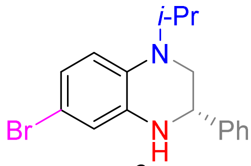
(***S***)-7-chloro-1-isopropyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	9.077	1846866	50.986
2	10.410	1775429	49.014

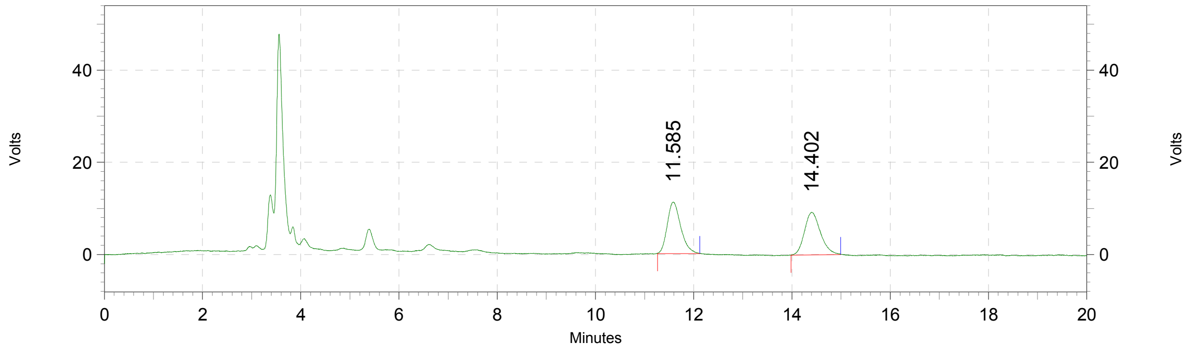


Peak#	t_R (min)	Area	Area (%)
1	9.093	1698256	96.971
2	10.423	53041	3.029

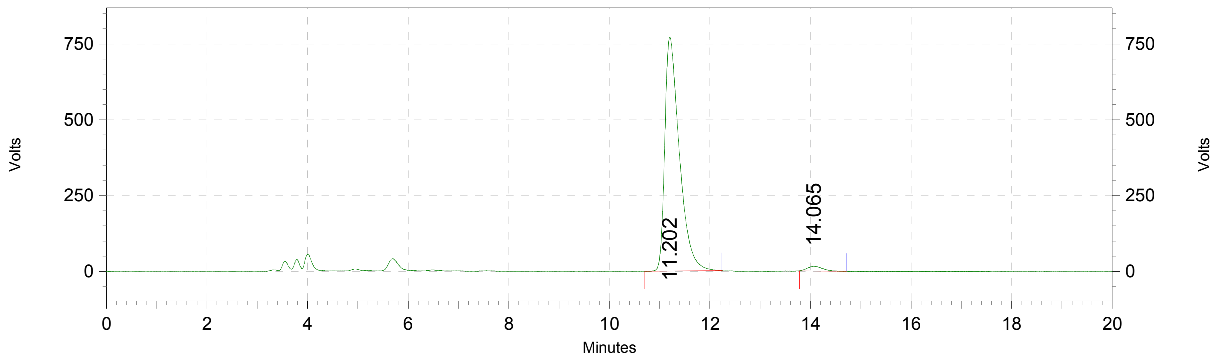


3m

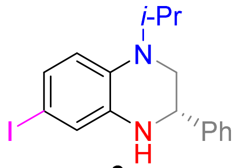
(***S***)-6-bromo-1-isopropyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	11.585	212874	50.465
2	14.402	208949	49.535

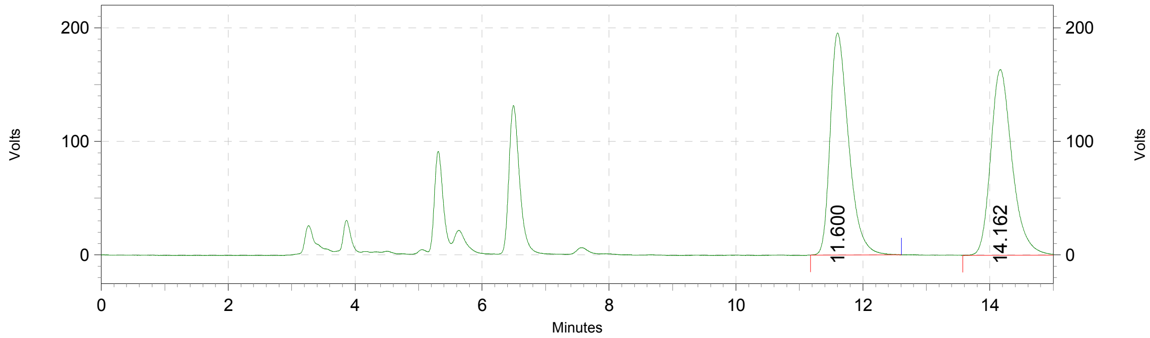


Peak#	t_R (min)	Area	Area (%)
1	11.202	15507407	97.978
2	14.065	319953	2.022

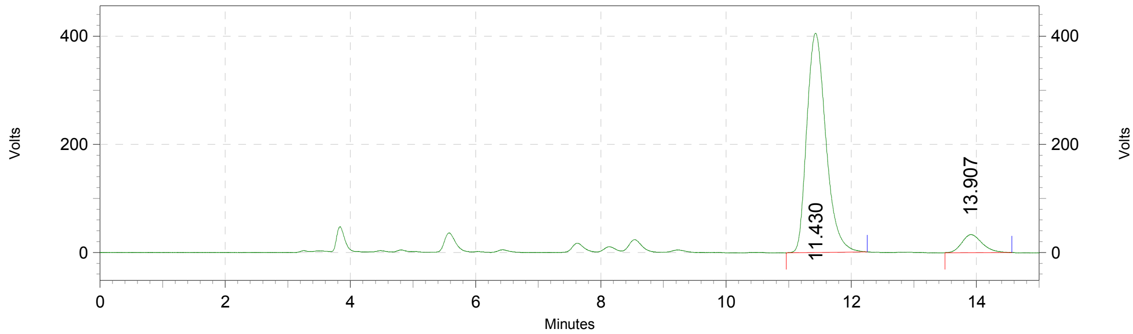


3n

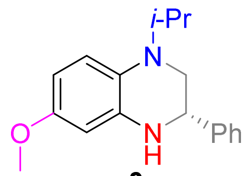
(***S***)-6-iodo-1-isopropyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	11.600	3948980	50.705
2	14.162	3839216	49.295

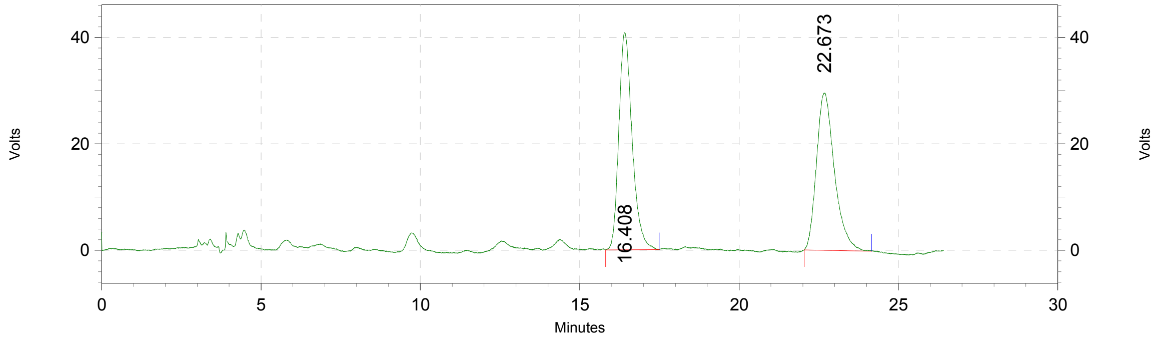


Peak#	t_R (min)	Area	Area (%)
1	11.430	8556139	91.909
2	13.907	753209	8.091

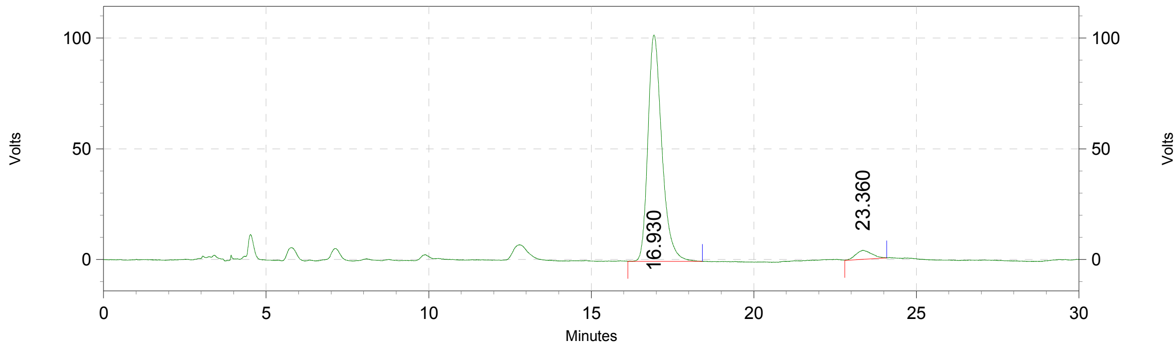


3o

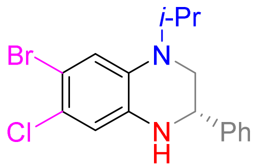
(*S*)-1-isopropyl-6-methoxy-3-phenyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	16.408	1184751	50.596
2	22.673	1156848	49.404

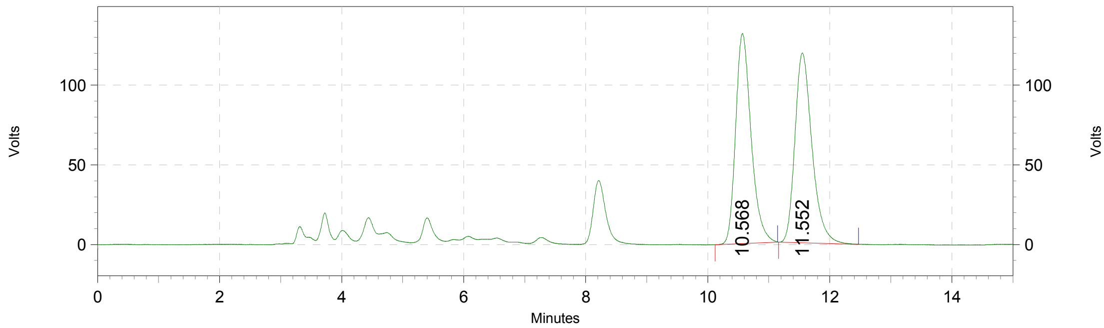


Peak#	t_R (min)	Area	Area (%)
1	16.930	3051360	95.676
2	23.360	137902	4.324

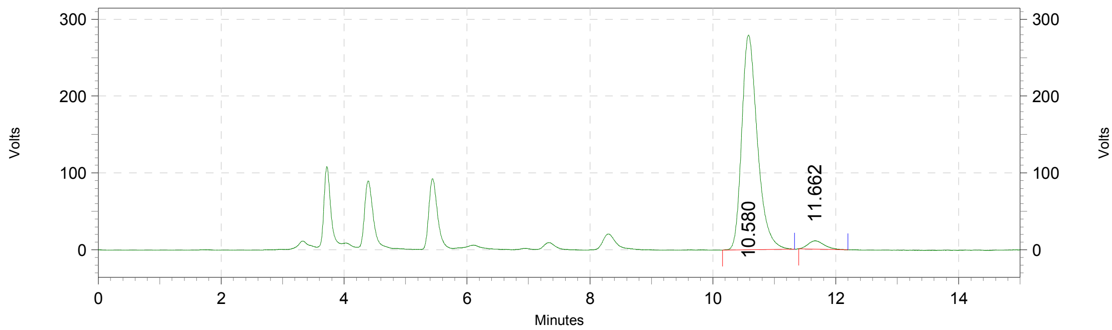


3p

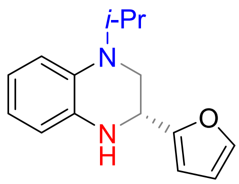
(*S*)-7-bromo-6-chloro-1-isopropyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	10.568	2315664	49.931
2	11.552	2322061	50.069

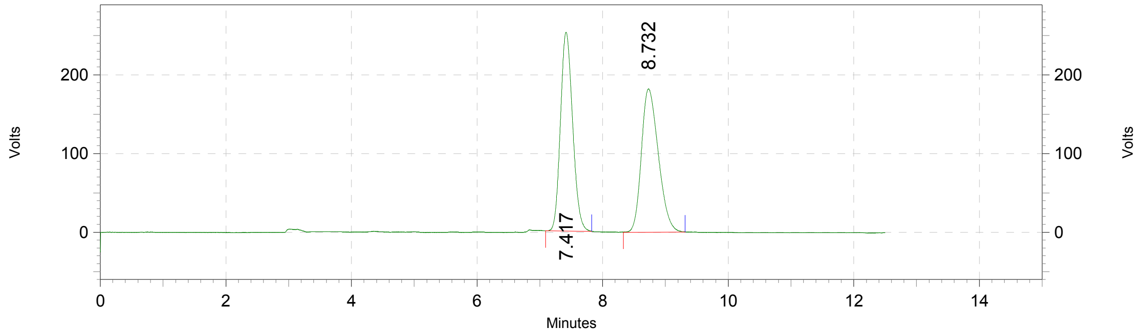


Peak#	t_R (min)	Area	Area (%)
1	10.580	4943535	96.110
2	11.662	200095	3.890

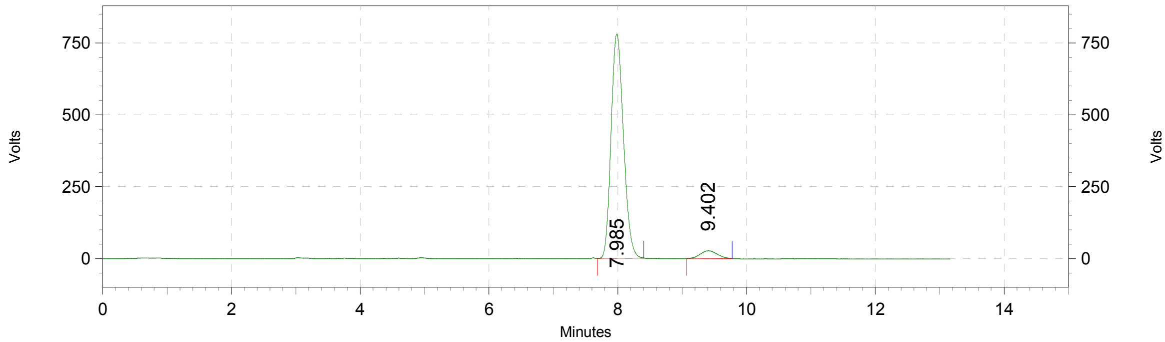


3q

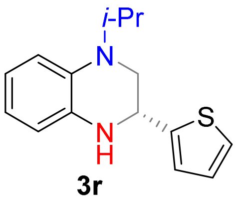
(***S***)-3-(furan-2-yl)-1-isopropyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	7.417	3392535	49.881
2	8.732	3408730	50.119

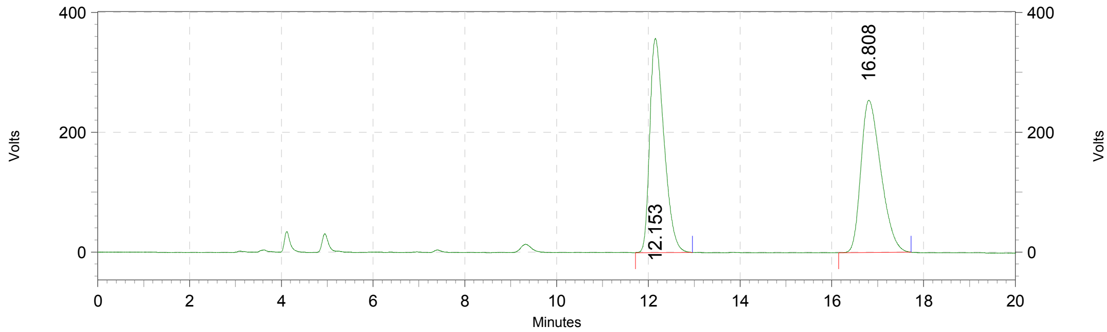


Peak#	t_R (min)	Area	Area (%)
1	7.985	10386163	95.441
2	9.402	496144	4.559

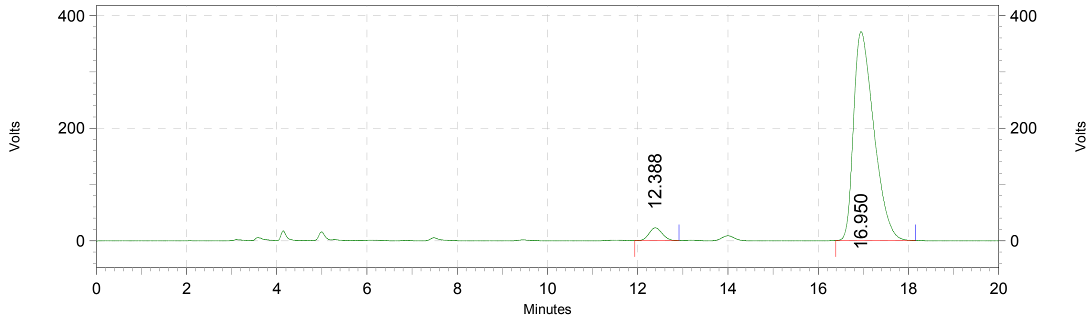


3r

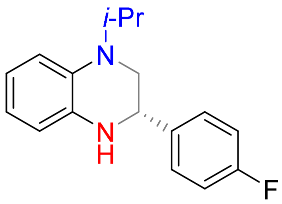
(***S***)-1-isopropyl-3-(thiophen-2-yl)-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	12.153	7700964	50.071
2	16.808	7679138	49.929

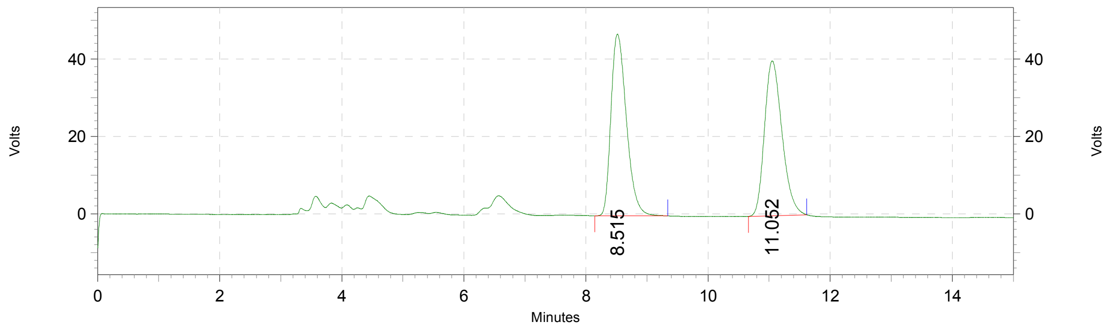


Peak#	t_R (min)	Area	Area (%)
1	12.388	466860	3.866
2	16.950	11607712	96.134

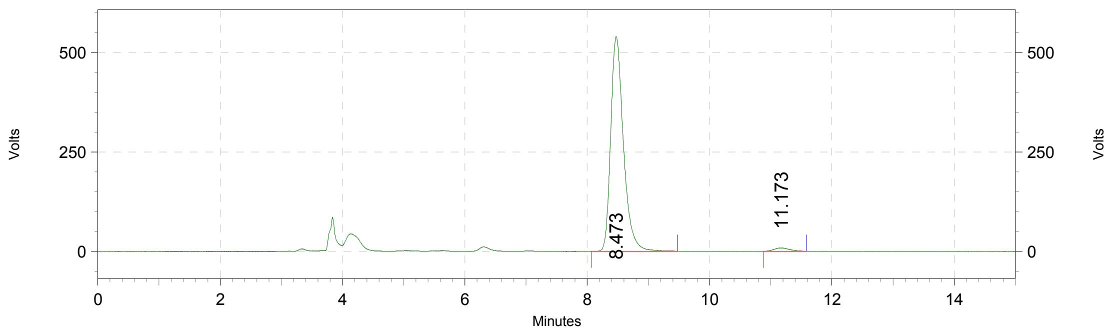


3s

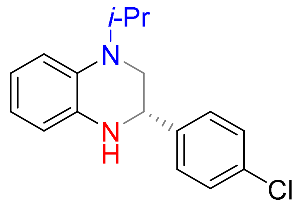
(S)-3-(4-fluorophenyl)-1-isopropyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	8.515	824710	50.826
2	11.052	797897	49.174

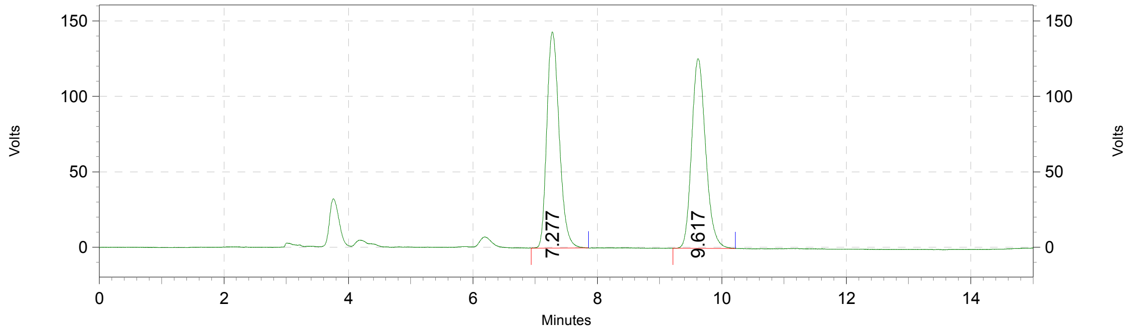


Peak#	t_R (min)	Area	Area (%)
1	8.473	7771545	98.177
2	11.173	144291	1.823

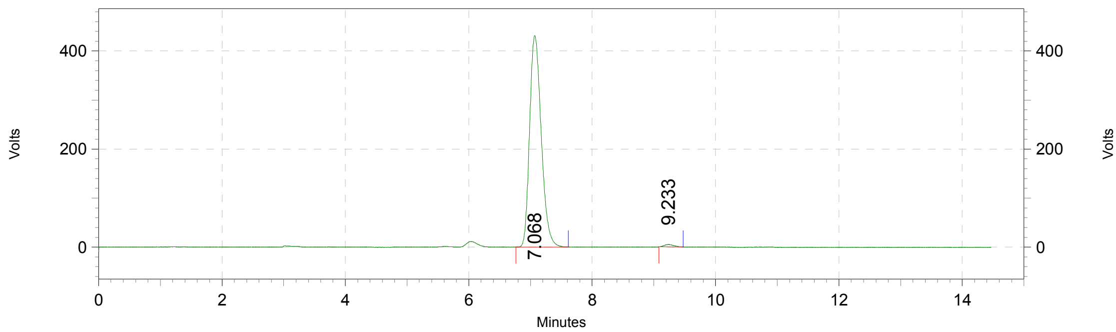


3t

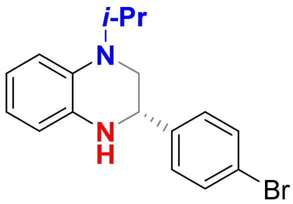
(S)-3-(4-chlorophenyl)-1-isopropyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	7.277	1980679	50.191
2	9.617	1965584	49.809

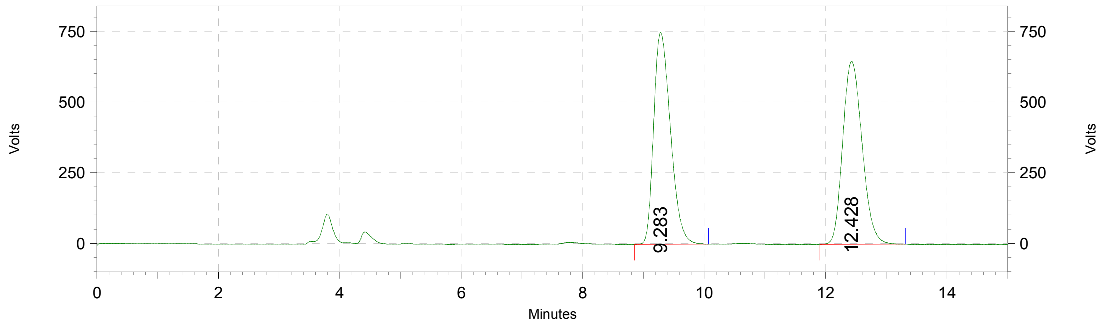


Peak#	t_R (min)	Area	Area (%)
1	7.068	5643367	99.107
2	9.233	50874	0.893

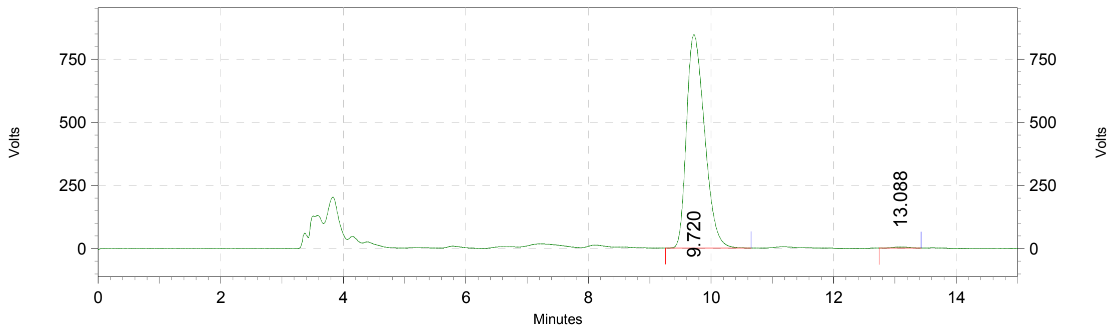


3u

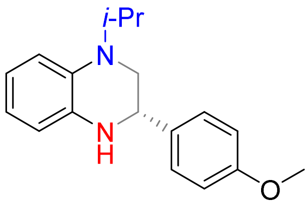
(S)-3-(4-bromophenyl)-1-isopropyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	9.283	14375099	50.055
2	12.428	14343717	49.945

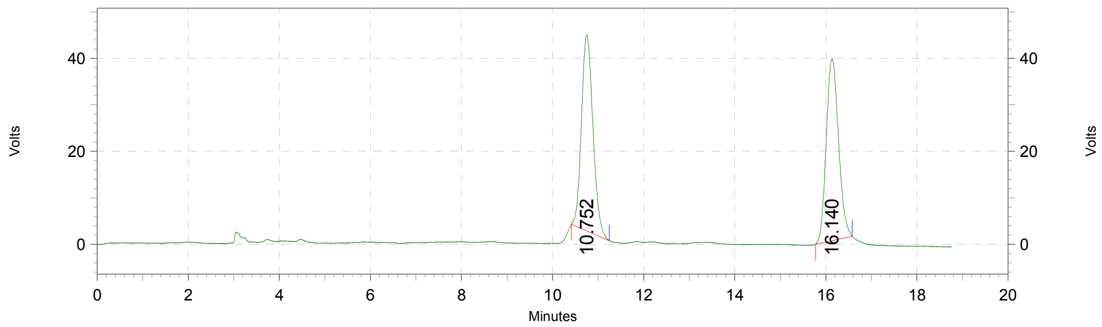


Peak#	t_R (min)	Area	Area (%)
1	9.720	17318158	99.553
2	13.088	77835	0.447

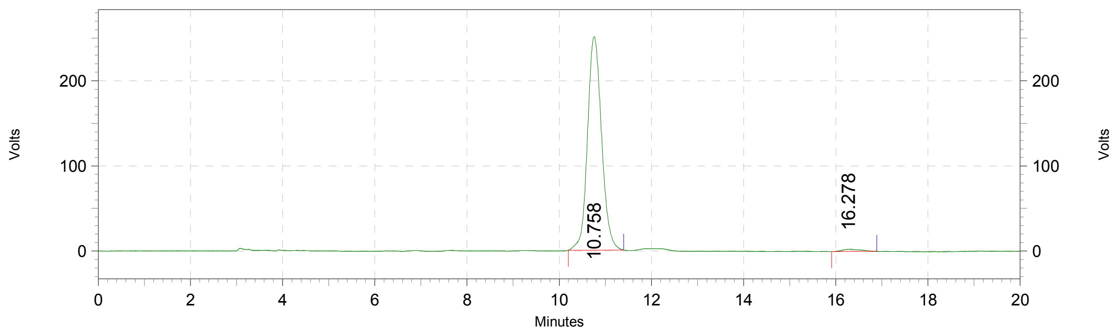


3v

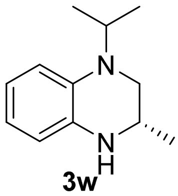
(S)-1-isopropyl-3-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	10.752	736772	50.218
2	16.140	730364	49.782

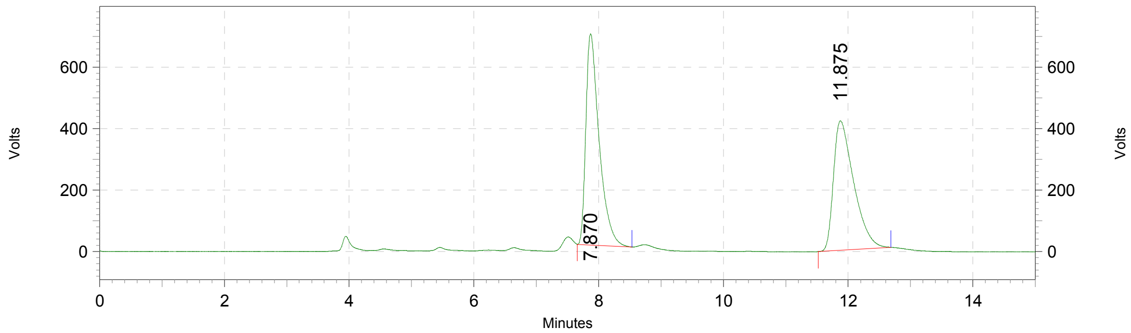


Peak#	t_R (min)	Area	Area (%)
1	10.758	5313205	98.577
2	16.278	76676	1.423

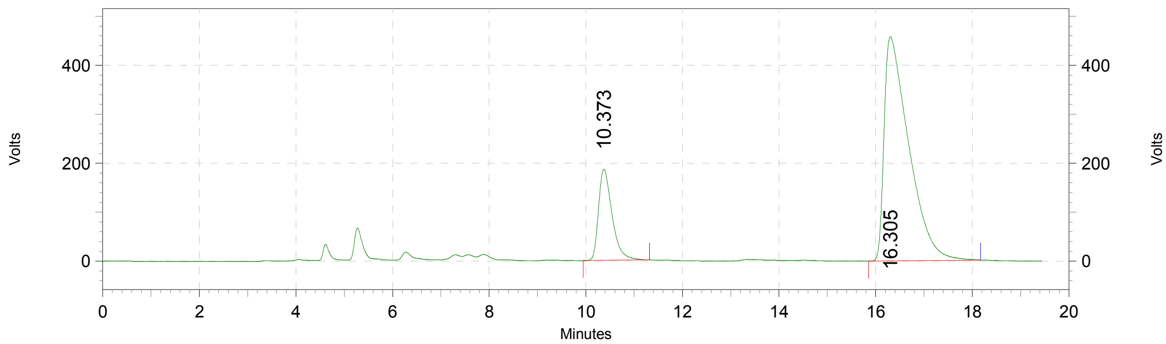


3w

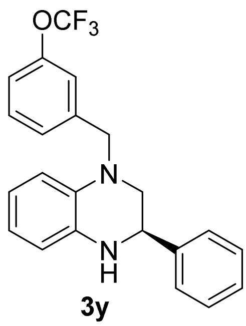
(***S***)-1-isopropyl-3-methyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	7.870	10170319	51.763
2	11.875	9477508	48.237

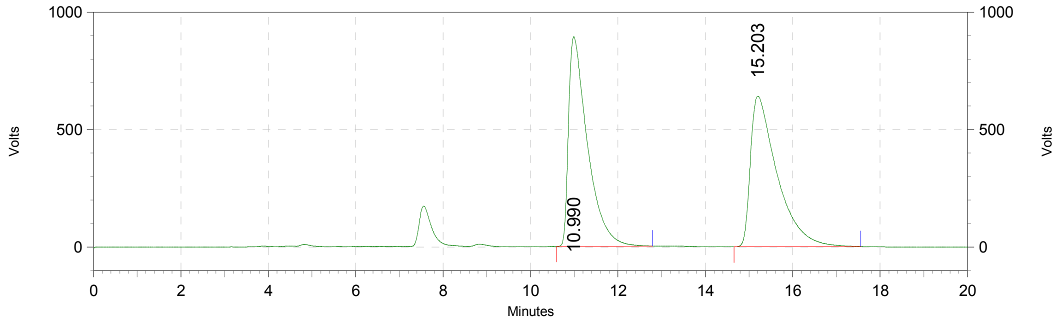


Peak#	t_R (min)	Area	Area (%)
1	10.373	3620967	18.252
2	16.305	16217791	81.748

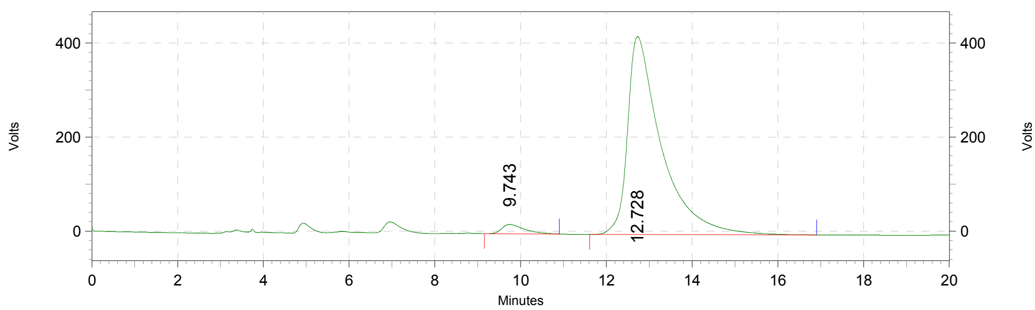


3y

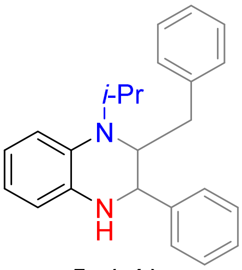
(R)-3-phenyl-1-(3-(trifluoromethoxy)benzyl)-1,2,3,4-tetrahydroquinoxaline



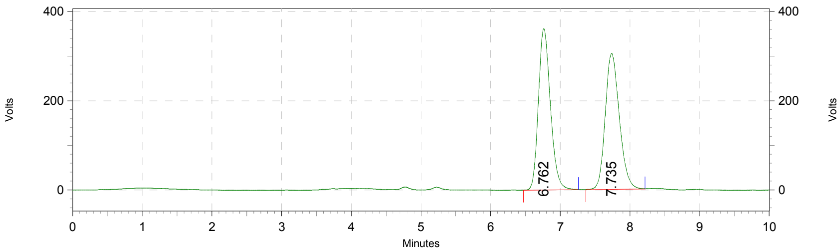
Peak#	t_R (min)	Area	Area (%)
1	10.990	26822883	49.788
2	15.203	27050988	50.212



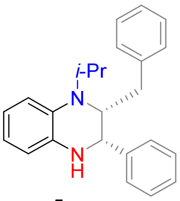
Peak#	t_R (min)	Area	Area (%)
1	9.743	721074	3.030
2	12.728	23073250	96.970



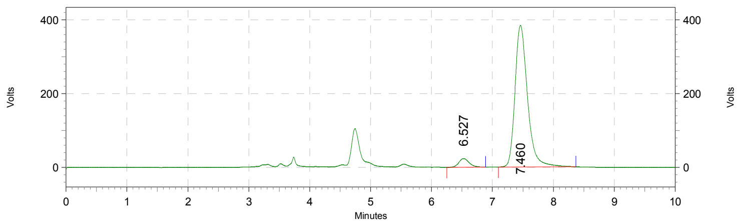
5a (+/-)



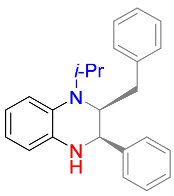
Peak#	t_R (min)	Area	Area (%)
1	6.762	4315264	50.267
2	7.735	4269416	49.733



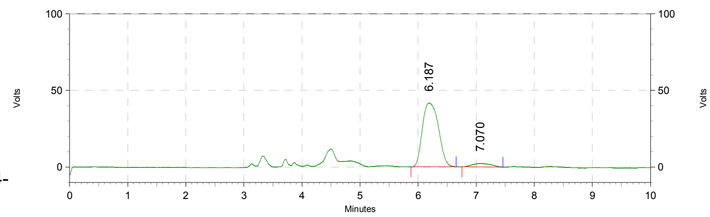
5a
(2*R*,3*S*)-2-benzyl-1-isopropyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline



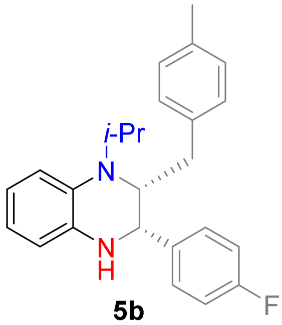
Peak#	t_R (min)	Area	Area (%)
1	6.527	275045	4.779
2	7.460	5480827	95.221



enantiomer of **5a**
(2*S*,3*R*)-2-benzyl-1-isopropyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline

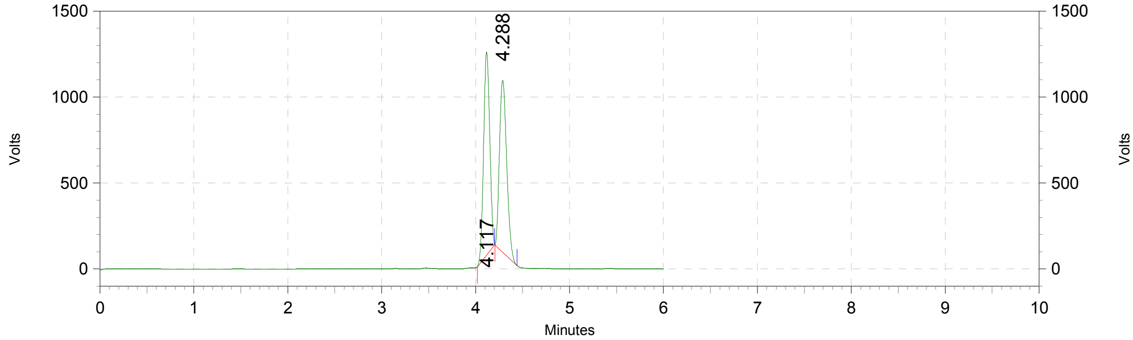


Peak#	t_R (min)	Area	Area (%)
1	6.187	800085	93.796
2	7.070	52922	6.204

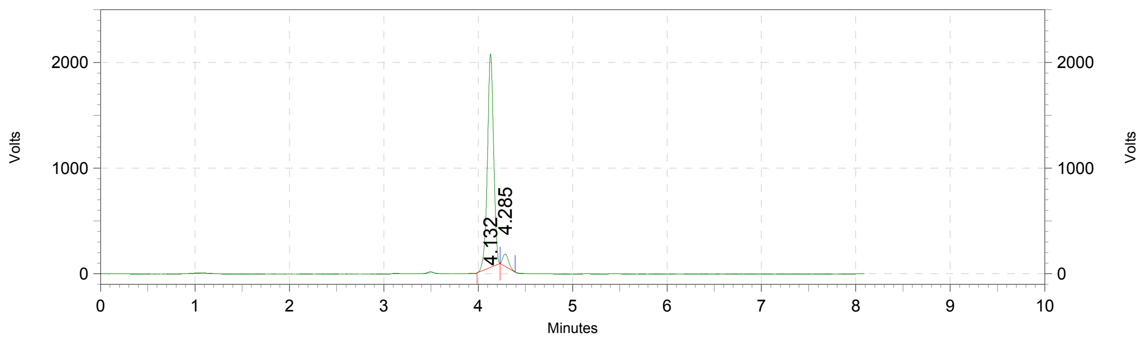


5b

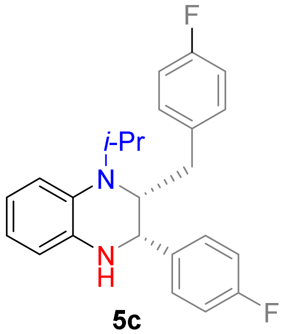
(2*R*,3*S*)-3-(4-fluorophenyl)-1-isopropyl-2-(4-methylbenzyl)-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	4.117	5331173	49.886
2	4.288	5355551	50.114

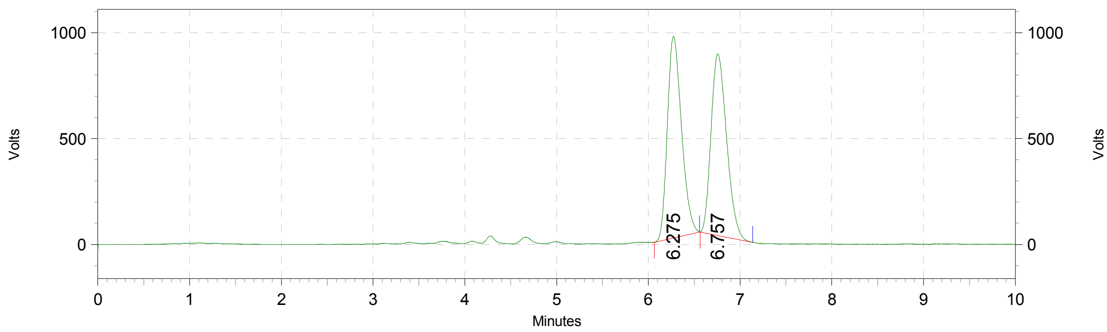


Peak#	t_R (min)	Area	Area (%)
1	4.132	9183271	94.781
2	4.285	505695	5.219

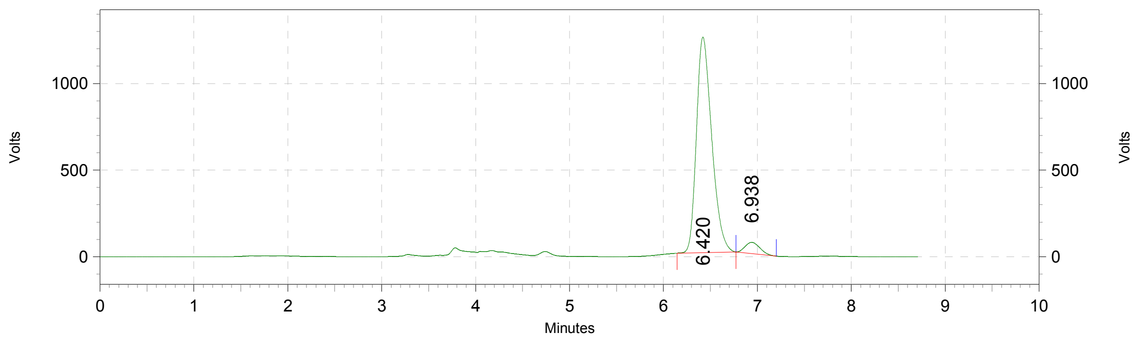


5c

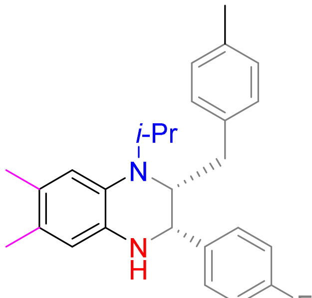
(2*R*,3*S*)-2-(4-fluorobenzyl)-3-(4-fluorophenyl)-1-isopropyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	6.275	10204949	50.217
2	6.757	10116907	49.783

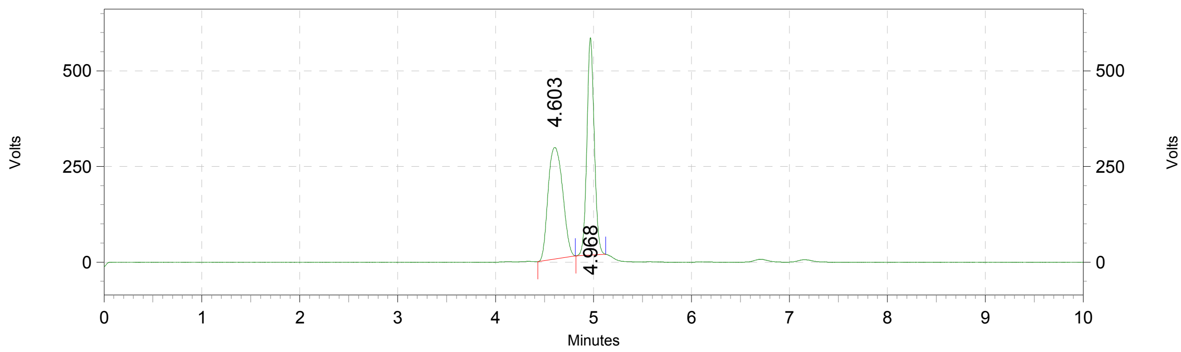


Peak#	t_R (min)	Area	Area (%)
1	6.420	14112330	95.213
2	6.938	709584	4.787

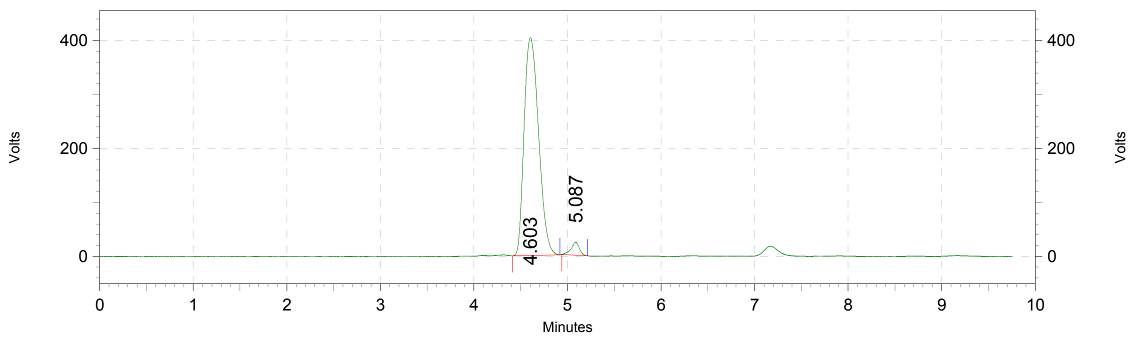


5d

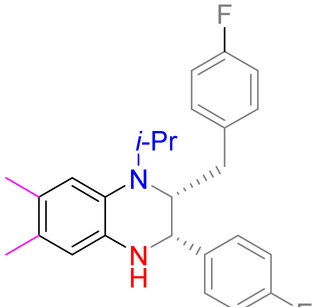
(2*R*,3*S*)-3-(4-fluorophenyl)-1-isopropyl-6,7-dimethyl-2-(4-methylbenzyl)-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	4.603	3014356	50.426
2	4.968	2963375	49.574

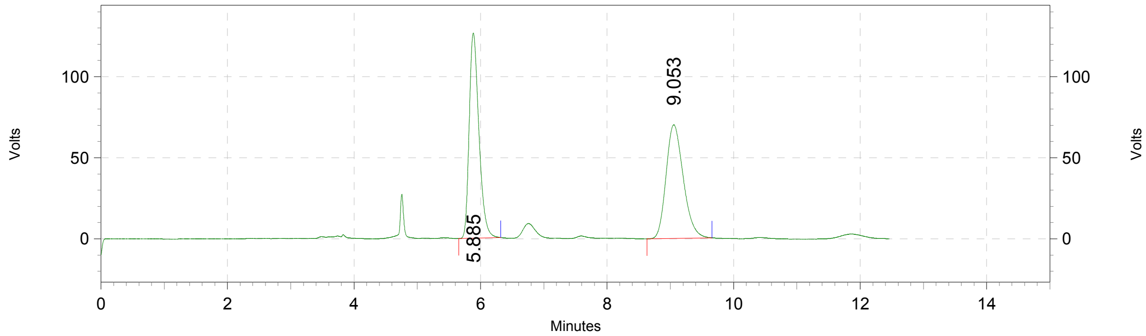


Peak#	t_R (min)	Area	Area (%)
1	4.603	4343730	96.702
2	5.087	148143	3.298

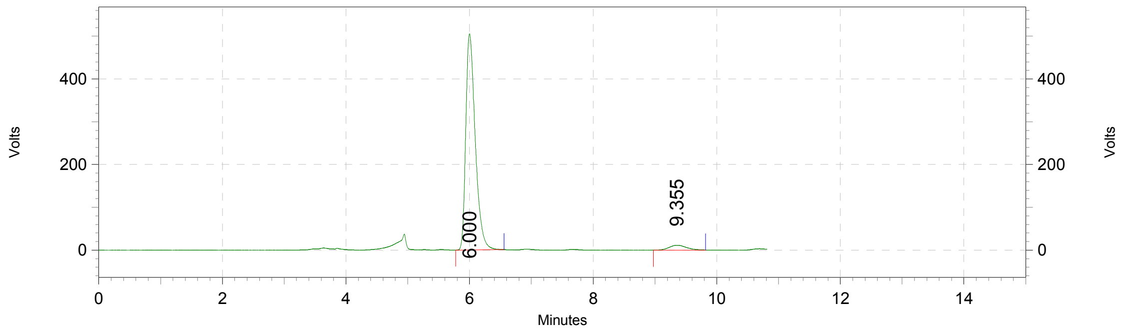


5e

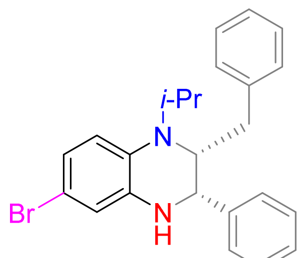
(2*R*,3*S*)-2-(4-fluorobenzyl)-3-(4-fluorophenyl)-1-isopropyl-6,7-dimethyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	5.885	1339845	50.270
2	9.053	1325474	49.730

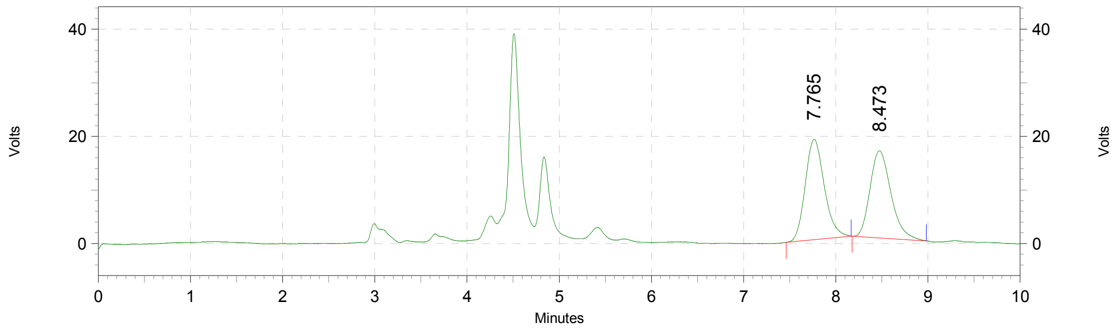


Peak#	t_R (min)	Area	Area (%)
1	6.000	5372685	96.087
2	9.355	218782	3.913

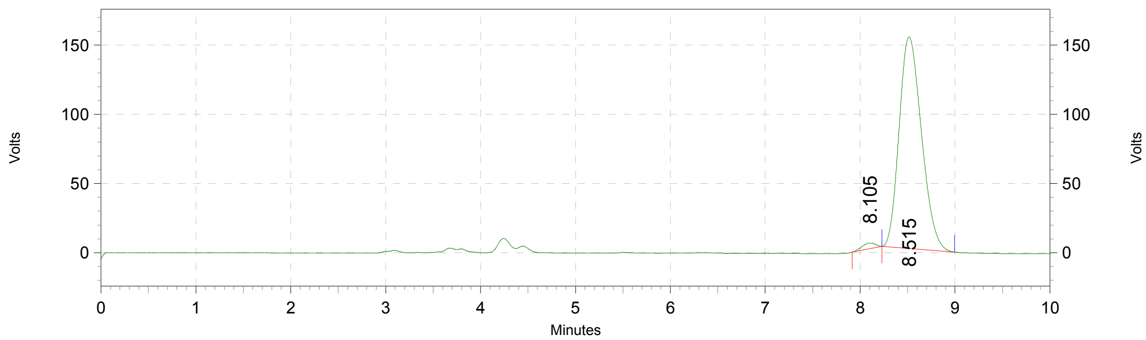


5f

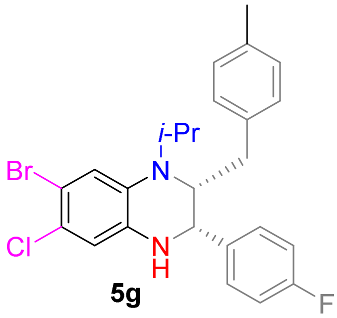
(2*R*,3*S*)-2-benzyl-6-bromo-1-isopropyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	7.765	269645	51.200
2	8.473	257006	48.800

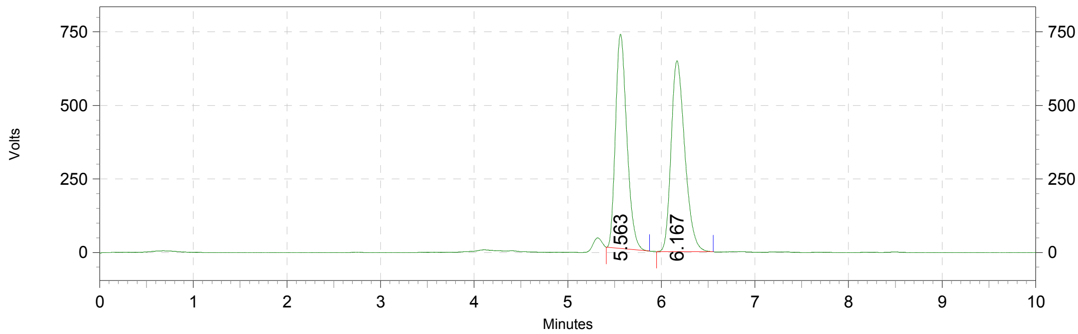


Peak#	t_R (min)	Area	Area (%)
1	8.105	41298	1.621
2	8.515	2506228	98.379

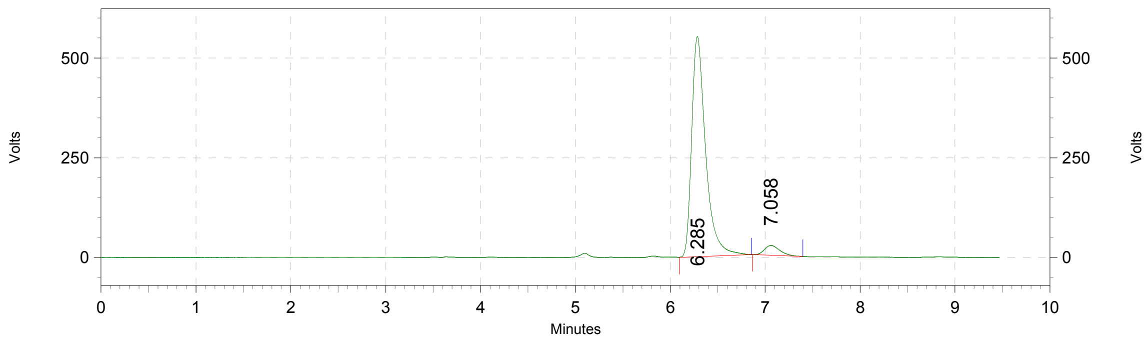


5g

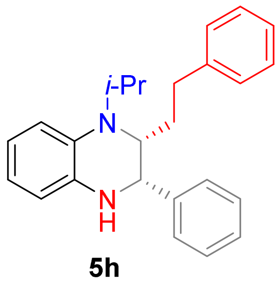
(2*R*,3*S*)-7-bromo-6-chloro-3-(4-fluorophenyl)-1-isopropyl-2-(4-methylbenzyl)-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	5.563	6132292	48.096
2	6.167	6617934	51.904

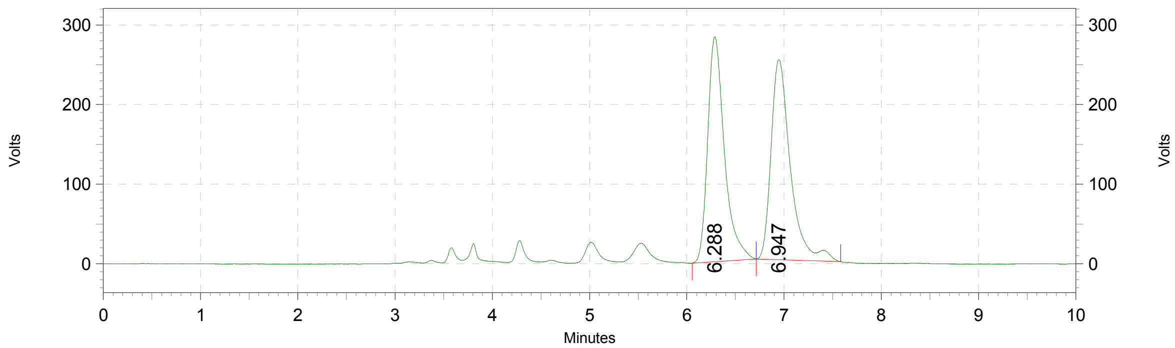


Peak#	t_R (min)	Area	Area (%)
1	6.285	5616480	95.240
2	7.058	280690	4.760

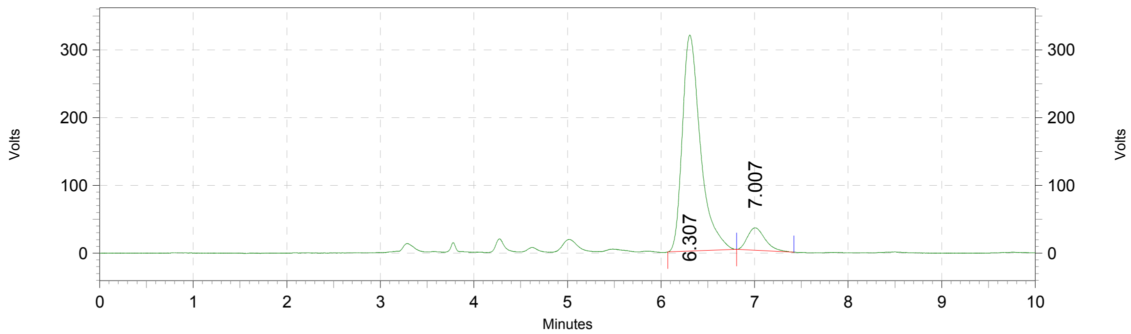


5h

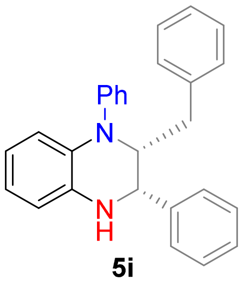
(2*R*,3*S*)-1-isopropyl-2-phenethyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	6.288	3369335	49.248
2	6.947	3472188	50.752

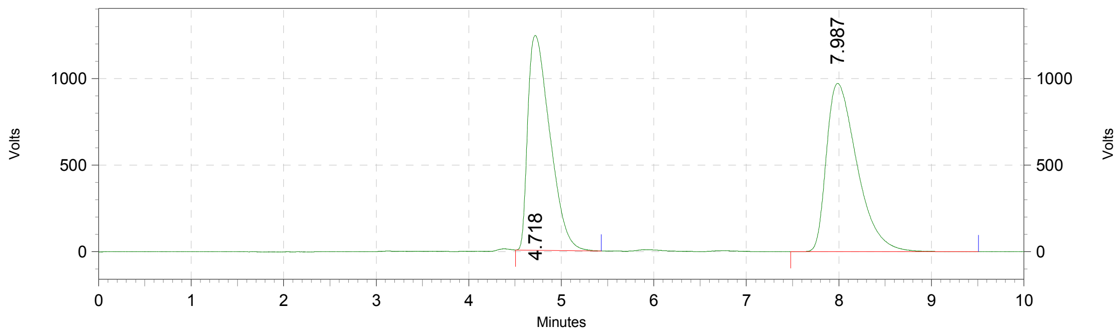


Peak#	t_R (min)	Area	Area (%)
1	6.307	4288656	90.742
2	7.007	437578	9.258

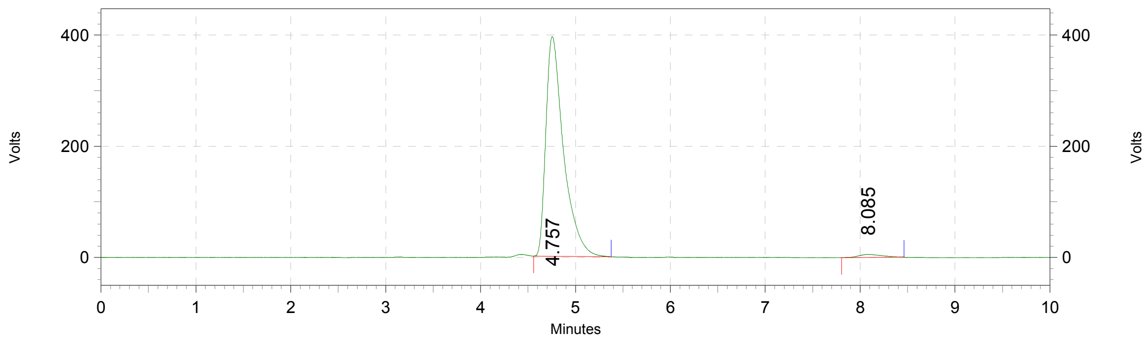


5i

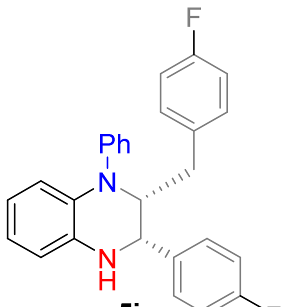
(2*R*,3*S*)-2-benzyl-1,3-diphenyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	4.718	20590253	47.977
2	7.987	22327021	52.023

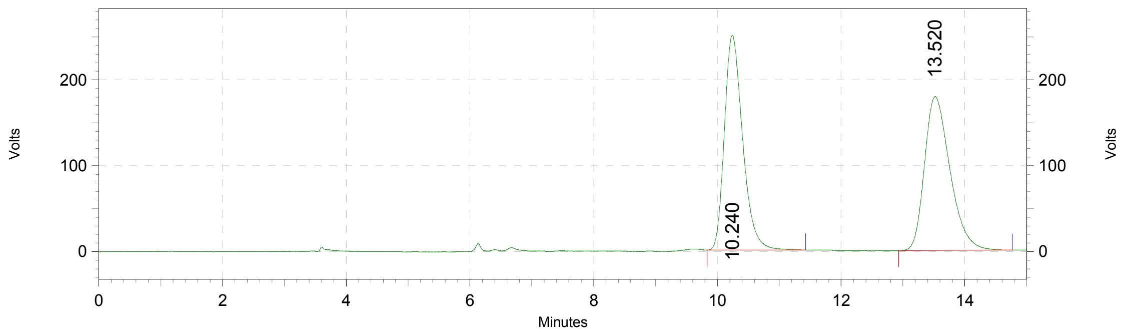


Peak#	t_R (min)	Area	Area (%)
1	4.757	5115169	98.218
2	8.085	92783	1.782

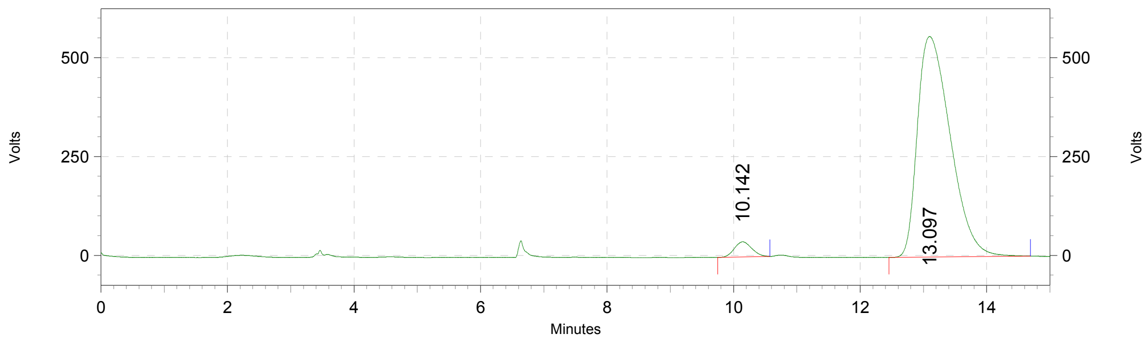


5j

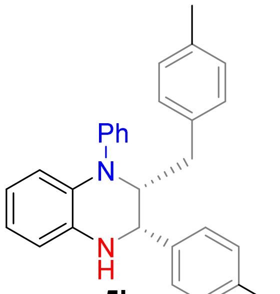
(2*R*,3*S*)-2-(4-fluorobenzyl)-3-(4-fluorophenyl)-1-phenyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	10.240	5146496	50.047
2	13.520	5136776	49.953

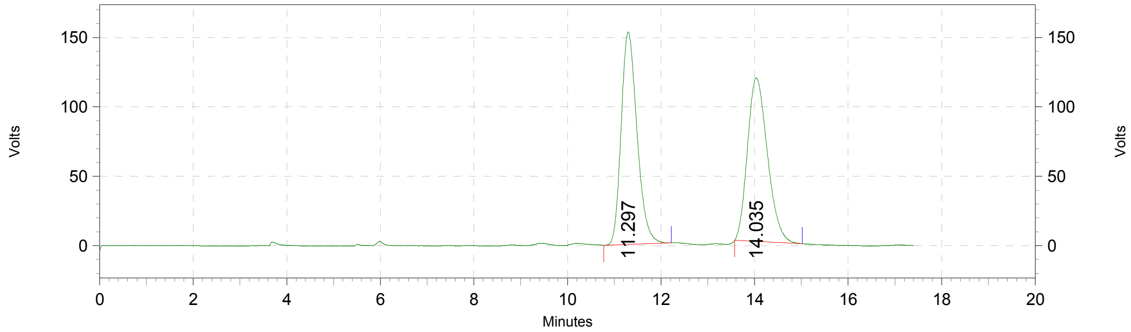


Peak#	t_R (min)	Area	Area (%)
1	10.142	736982	3.523
2	13.097	20181057	96.477

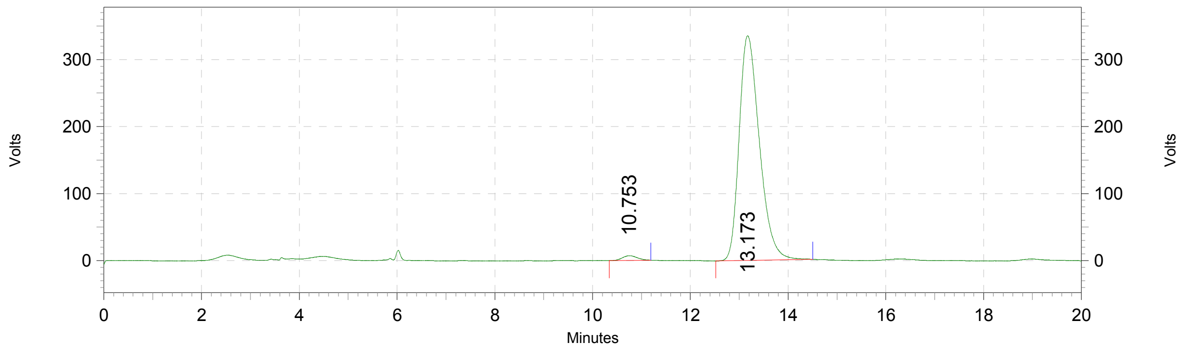


5k

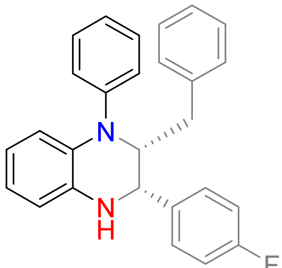
(2*R*,3*S*)-3-(4-fluorophenyl)-2-(4-methylbenzyl)-1-phenyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	11.297	3605898	50.795
2	14.035	3492960	49.205

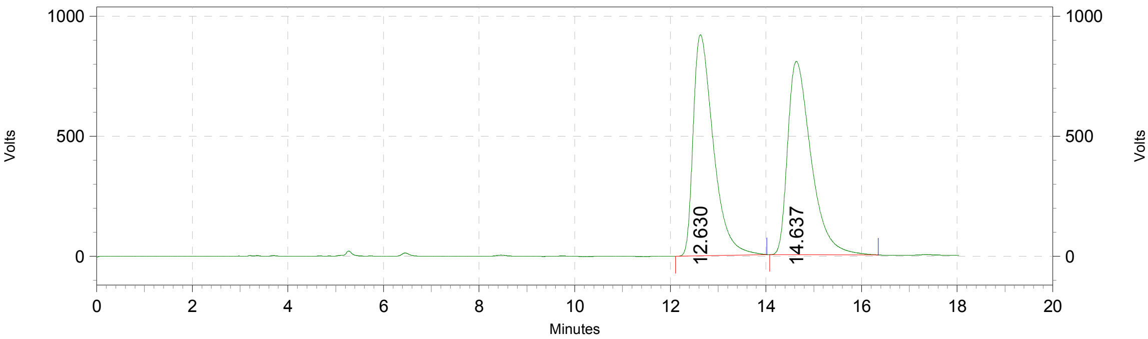


Peak#	t_R (min)	Area	Area (%)
1	10.753	149635	1.528
2	13.173	9643244	98.472

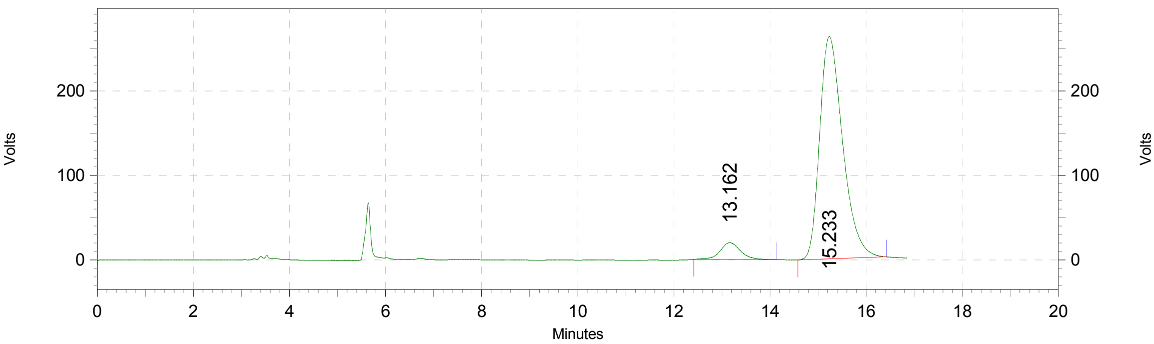


5l

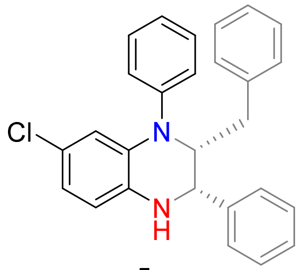
(2*R*,3*S*)-2-benzyl-3-(4-fluorophenyl)-1-phenyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	12.630	26892624	49.507
2	14.637	27427905	50.493

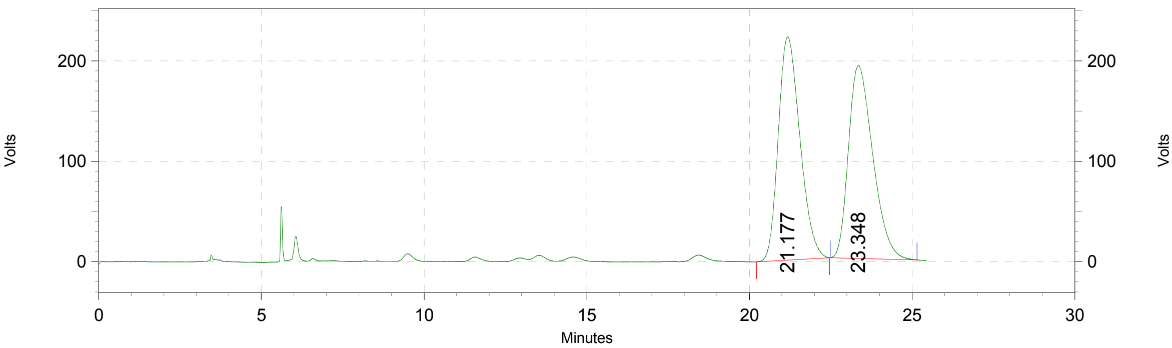


Peak#	t_R (min)	Area	Area (%)
1	13.162	589300	6.321
2	15.233	8734299	93.679

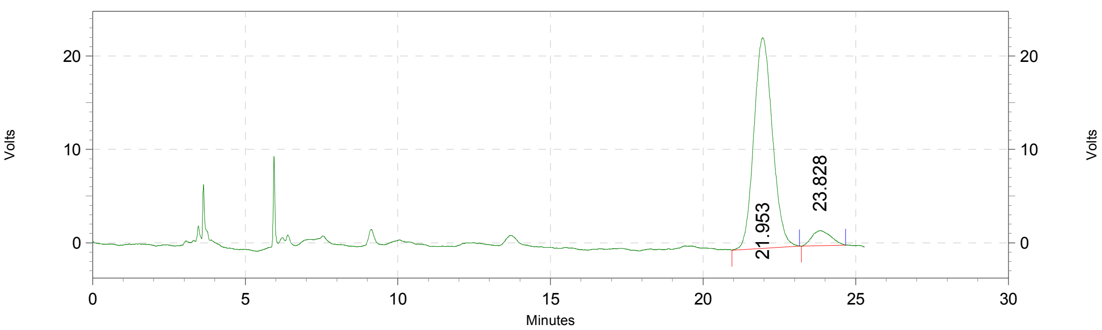


5m

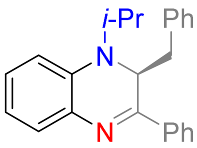
(2*R*,3*S*)-2-benzyl-7-chloro-1,3-diphenyl-1,2,3,4-tetrahydroquinoxaline



Peak#	t_R (min)	Area	Area (%)
1	21.177	10278456	50.701
2	23.348	9994242	49.299

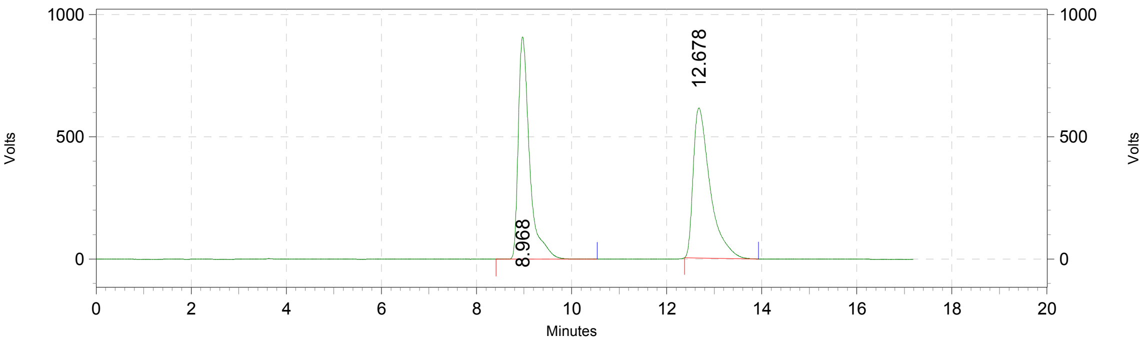


Peak#	t_R (min)	Area	Area (%)
1	21.953	953328	93.111
2	23.828	70534	6.889

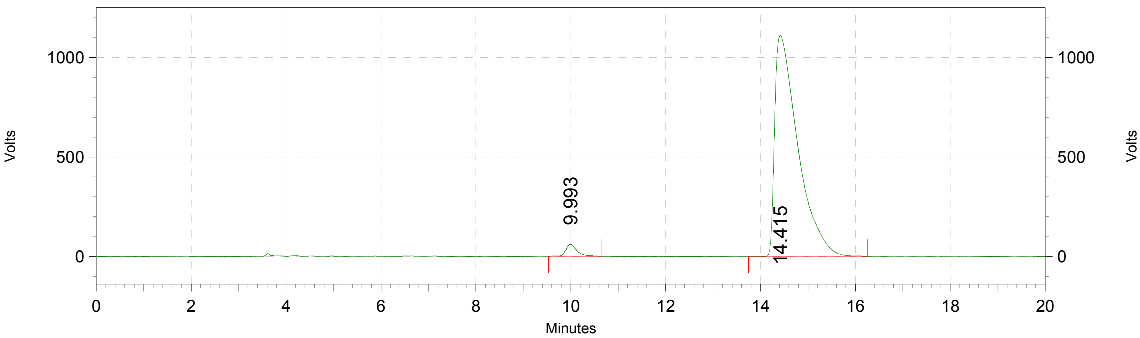


5a'

(***S***)-2-benzyl-1-isopropyl-3-phenyl-1,2-dihydroquinoxaline

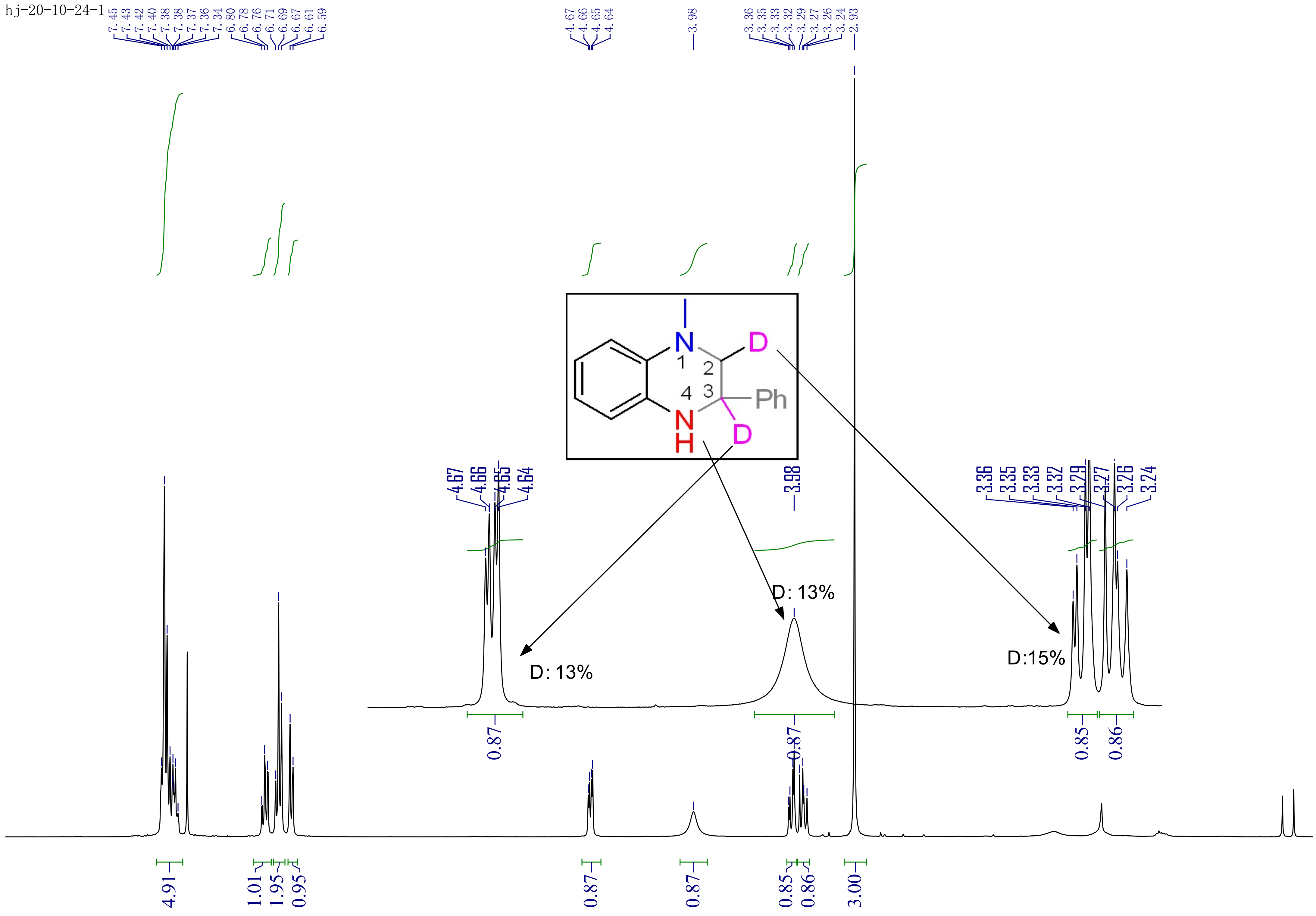


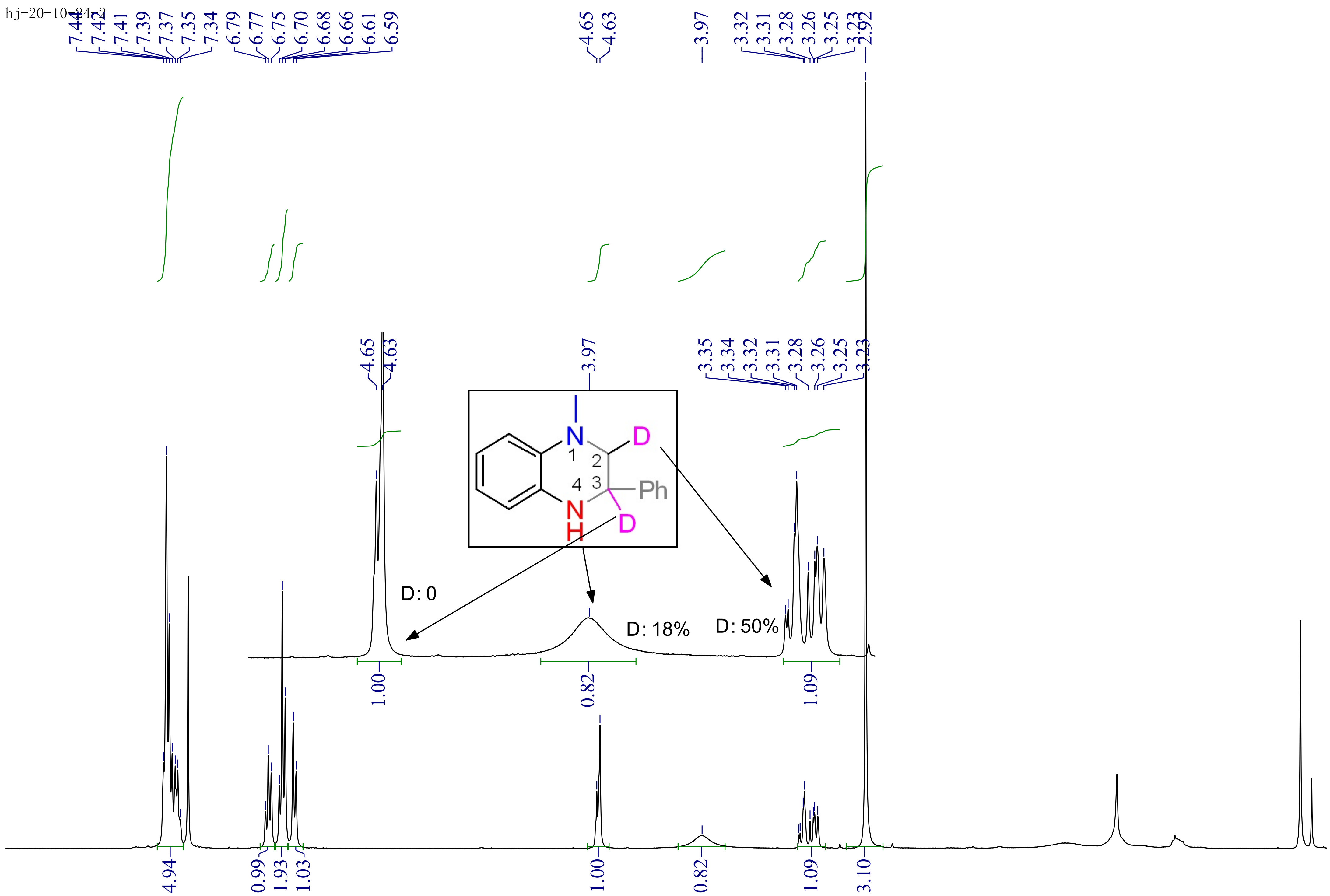
Peak#	t_R (min)	Area	Area (%)
1	8.968	15008150	49.869
2	12.678	15086908	50.131

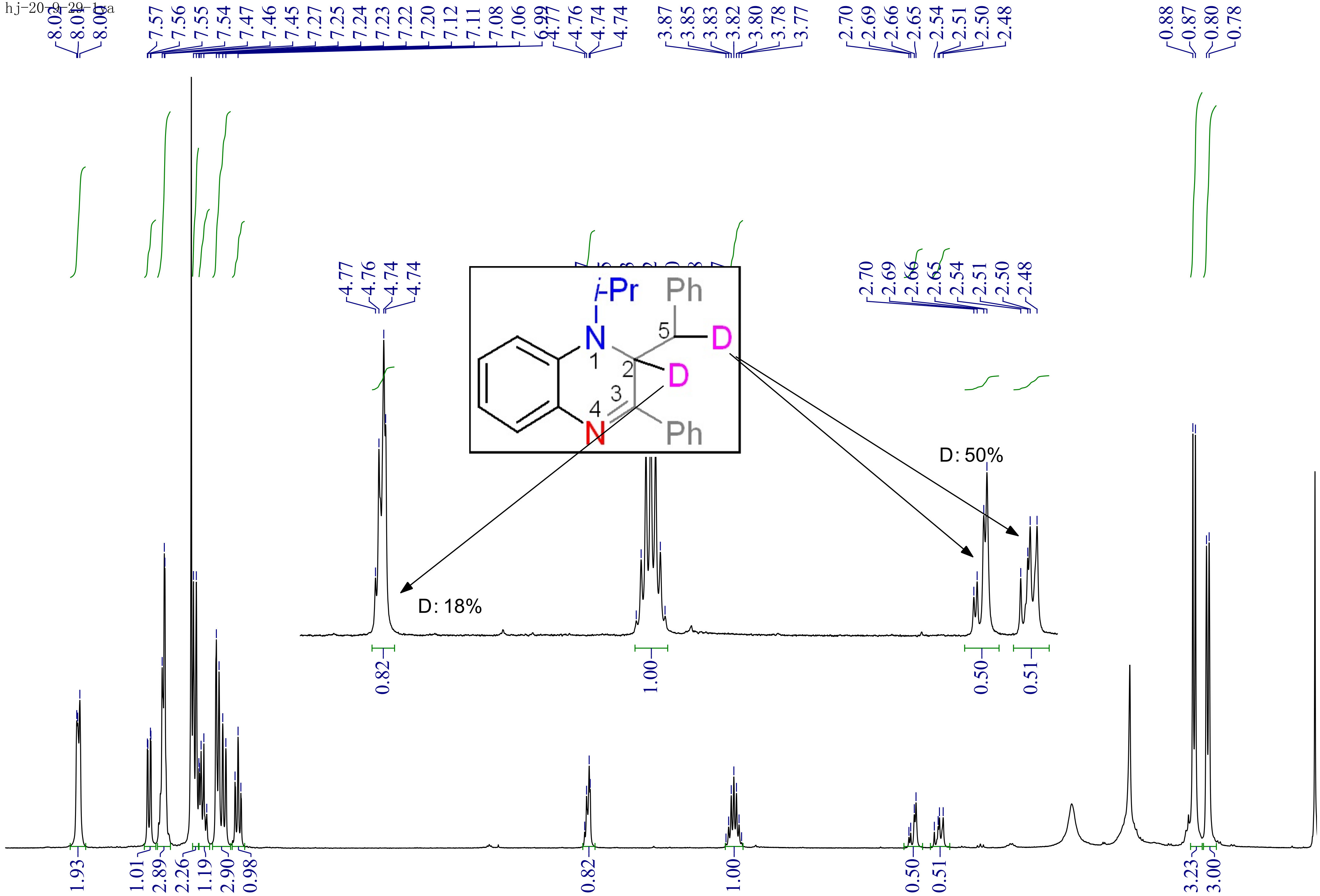


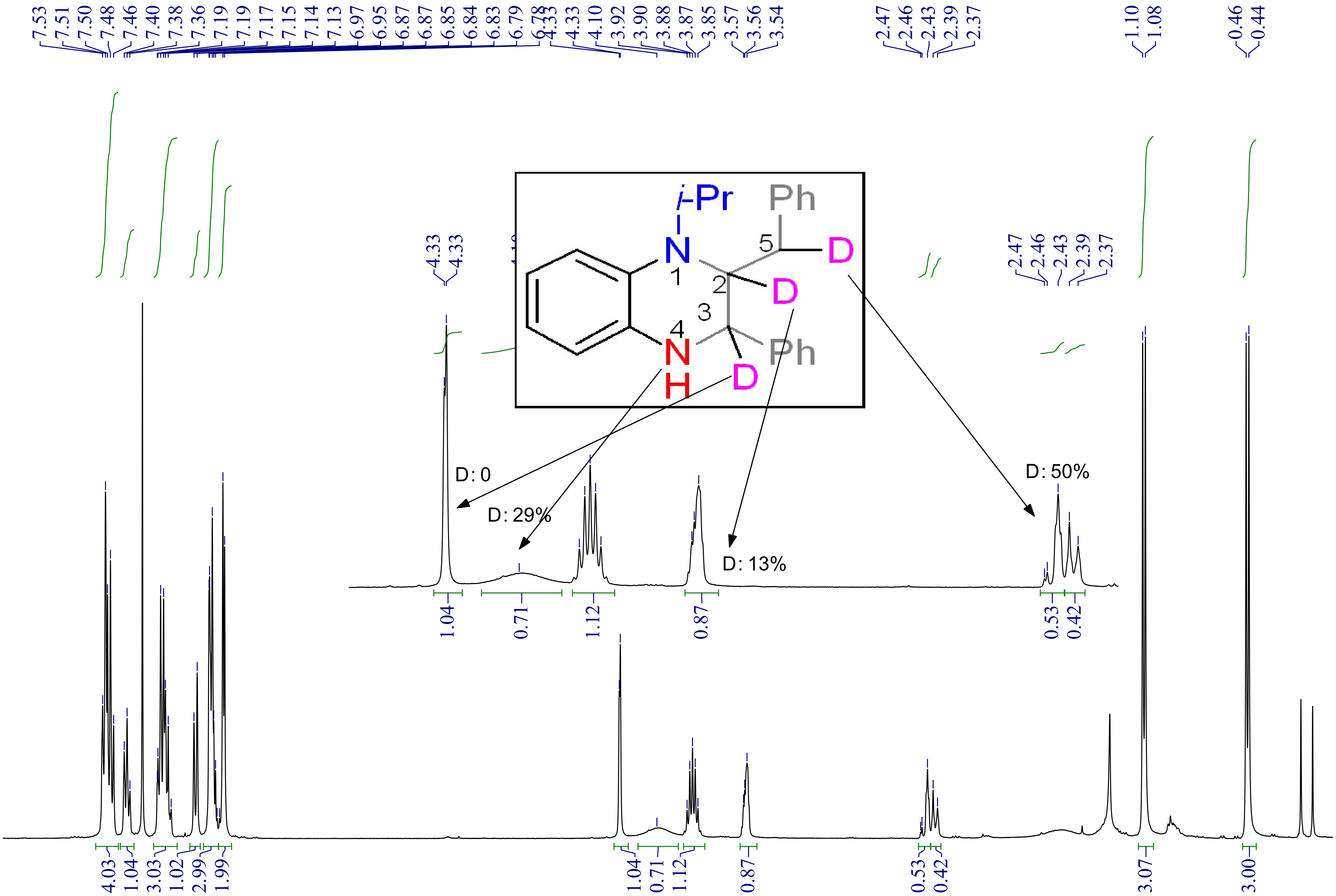
Peak#	t_R (min)	Area	Area (%)
1	9.993	987397	2.569
2	14.415	37441970	97.431

NMR spectrum

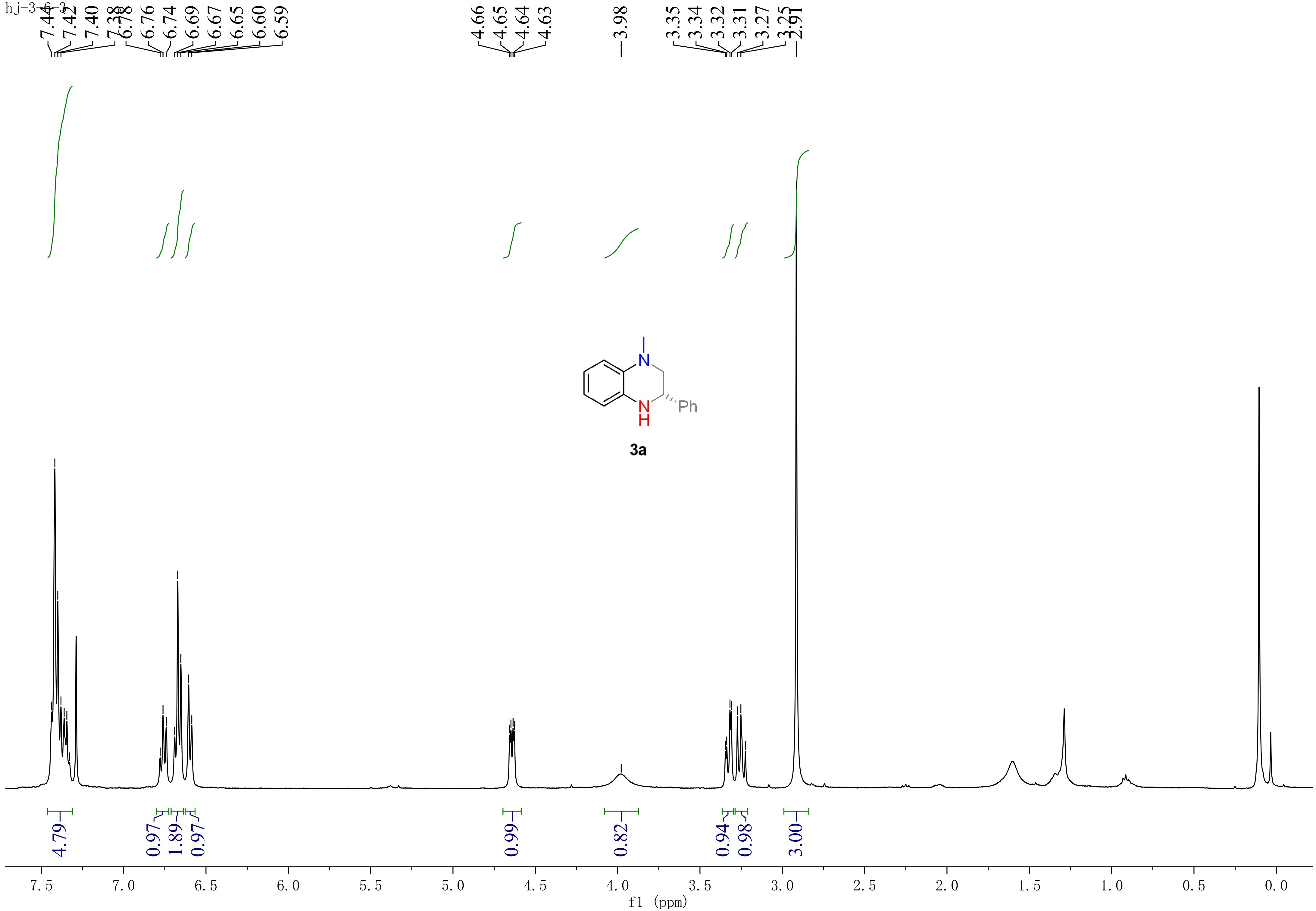

hj-20-10-24-1
7.45 7.43 7.42 7.40 7.38 7.38 7.37 7.36 7.34 6.80 6.78 6.76 6.71 6.69 6.67 6.61 6.59
4.67 4.66 4.65 4.64
3.98
3.36 3.35 3.33 3.32 3.29 3.27 3.26 3.24 2.93
N
D
1
2
4
3
Ph
N
H
D
D: 13%
D: 13%
D:15%
0.87
0.87
0.85
0.86
4.91
1.01
1.95
0.95
0.87
0.87
0.85
0.86
3.00

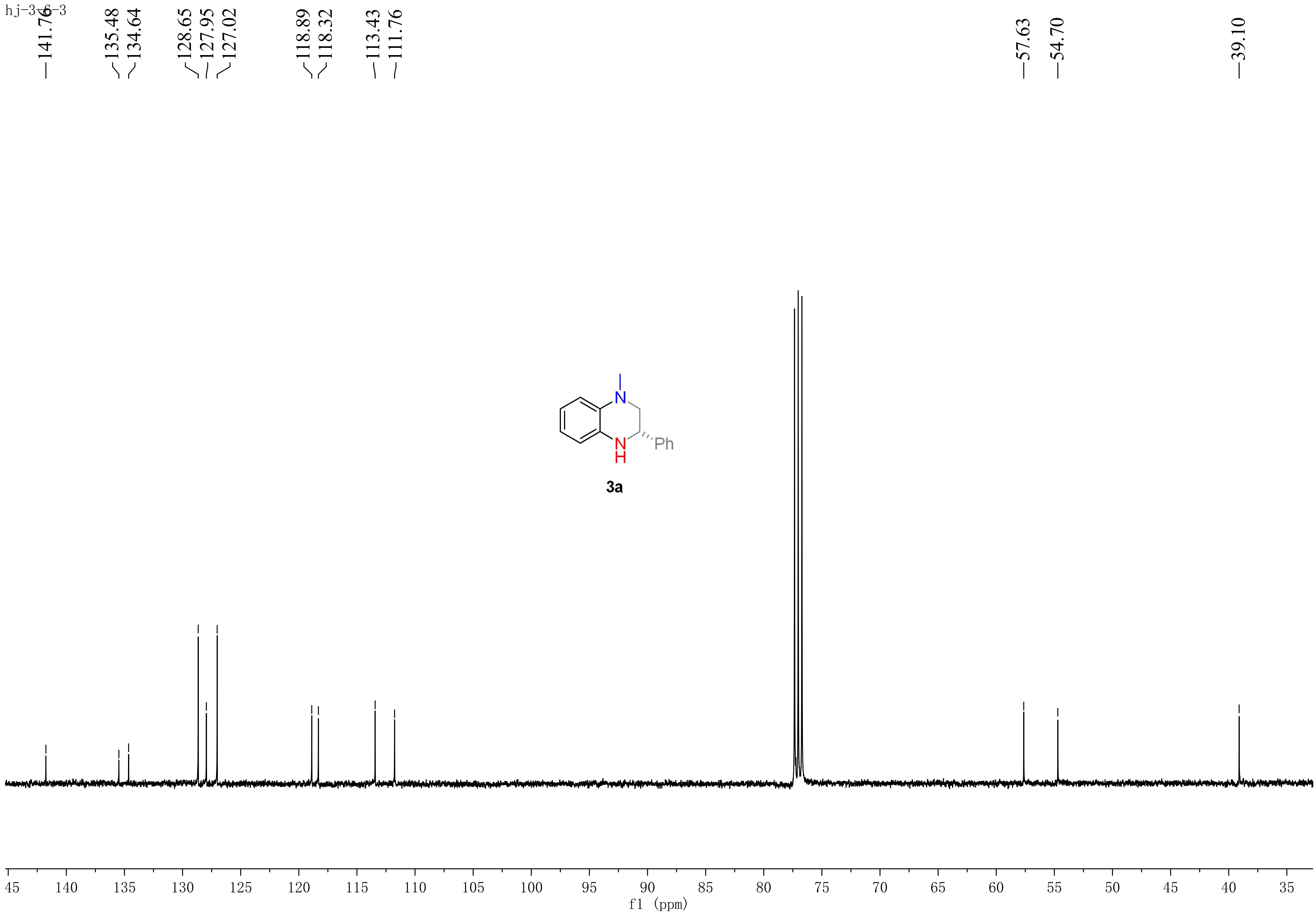

hj-20-10-24-2
D: 0
D: 18%
D: 50%
Ph

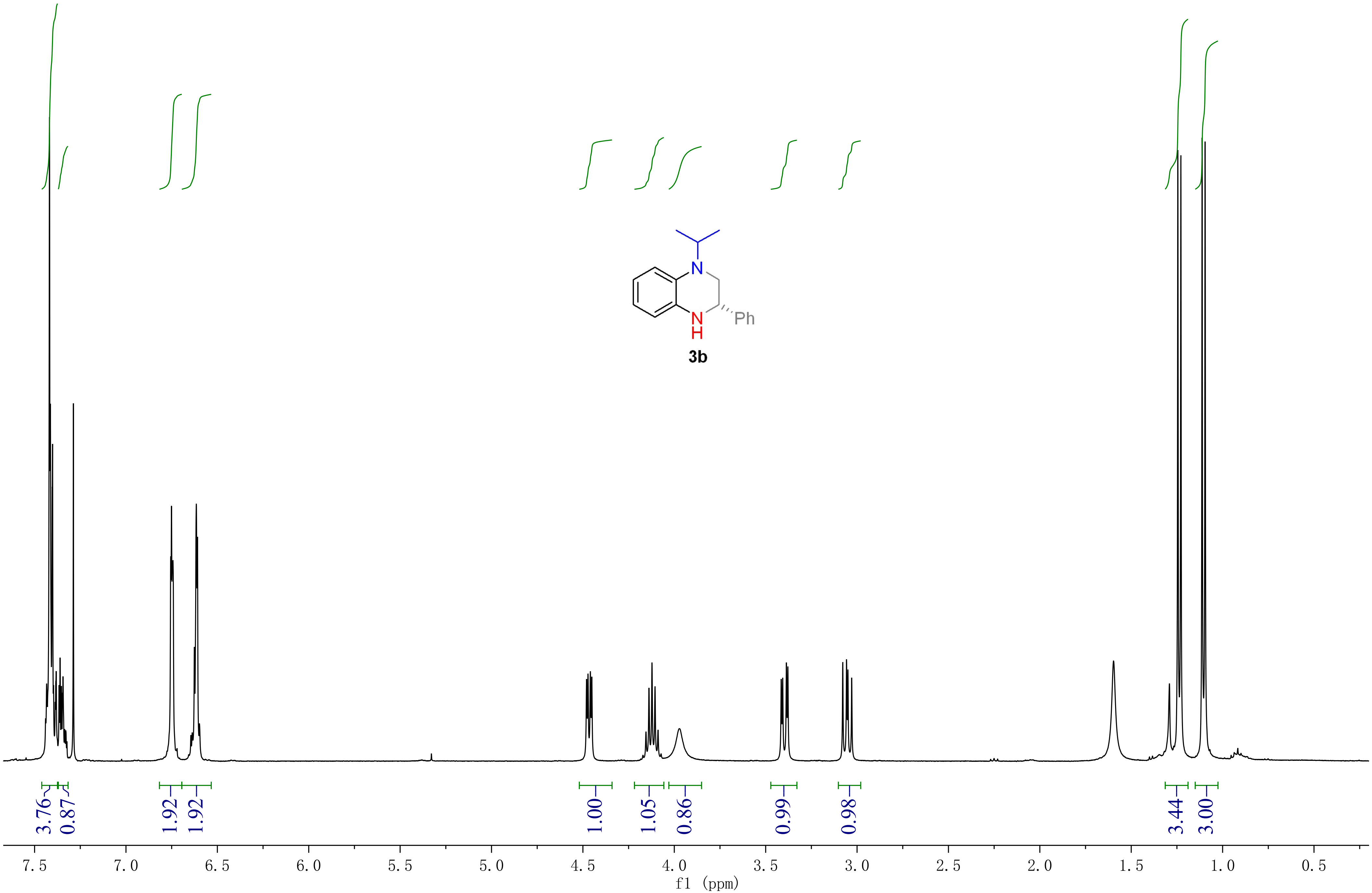

hj-20-9-29-1ya
8.03 8.01 8.01
7.57 7.56 7.55 7.54 7.47 7.46 7.45 7.27 7.25 7.24 7.23 7.22 7.20 7.12 7.11 7.08 7.06 6.99
4.77 4.76 4.74 4.74
3.87 3.85 3.83 3.82 3.80 3.78 3.77
2.70 2.69 2.66 2.65 2.54 2.51 2.50 2.48
0.88 0.87 0.80 0.78
i-Pr
Ph
N
D
1
2
3
4
5
Ph
D: 18%
D: 50%
0.82
1.00
0.50
0.51
1.93
1.01
2.89
2.26
1.19
2.90
0.98
3.23
3.00



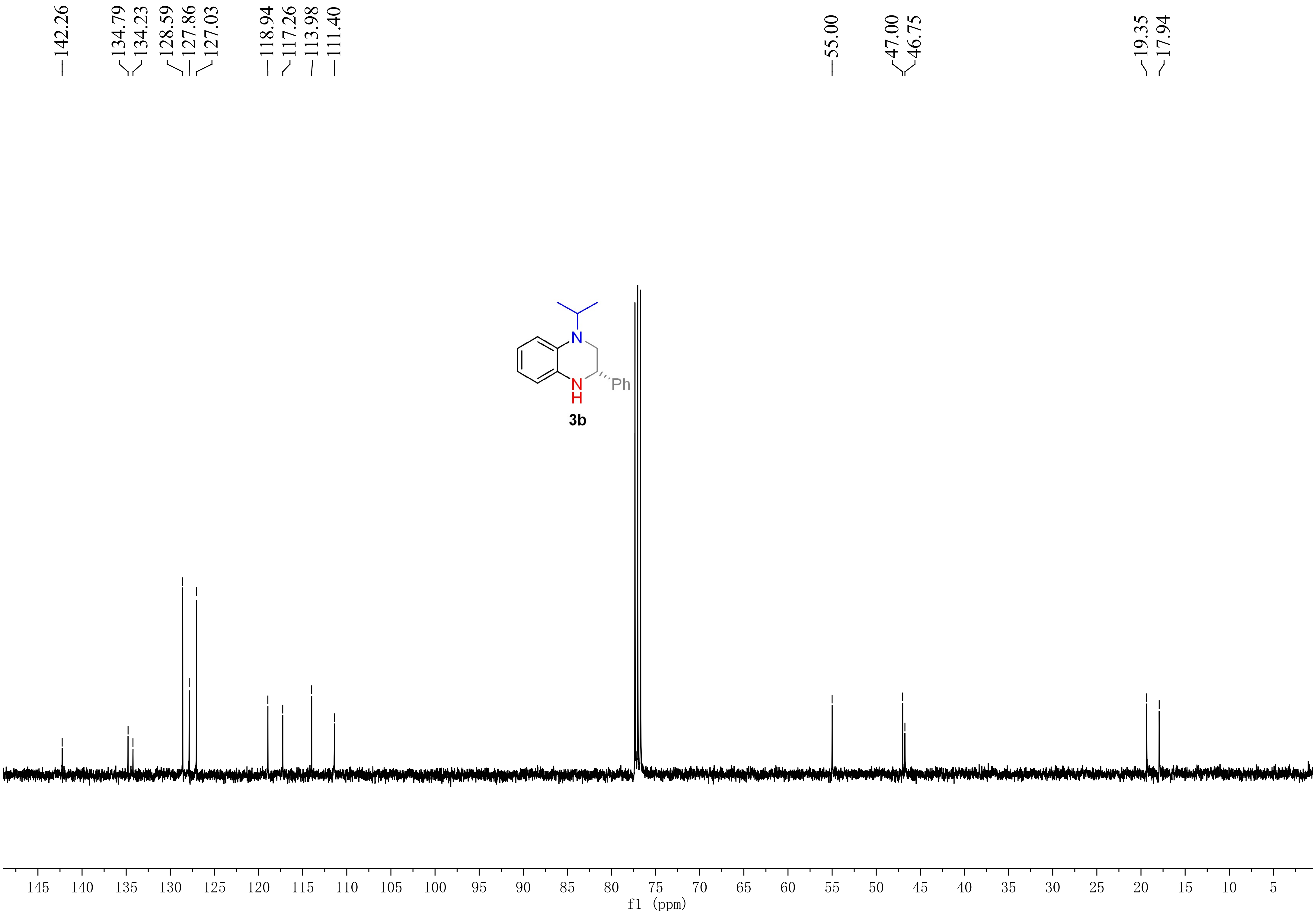
i-Pr
Ph
Ph
N
N
H
D
D
D
D: 0
D: 29%
D: 13%
D: 50%


hj-3-6-3
7.44
7.42
7.40
7.38
6.78
6.76
6.74
6.69
6.67
6.65
6.60
6.59
4.66
4.65
4.64
4.63
3.98
3.35
3.34
3.32
3.31
3.27
3.25
2.91
N
N
H
Ph
3a
4.79
0.97
1.89
0.97
0.99
0.82
0.94
0.98
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

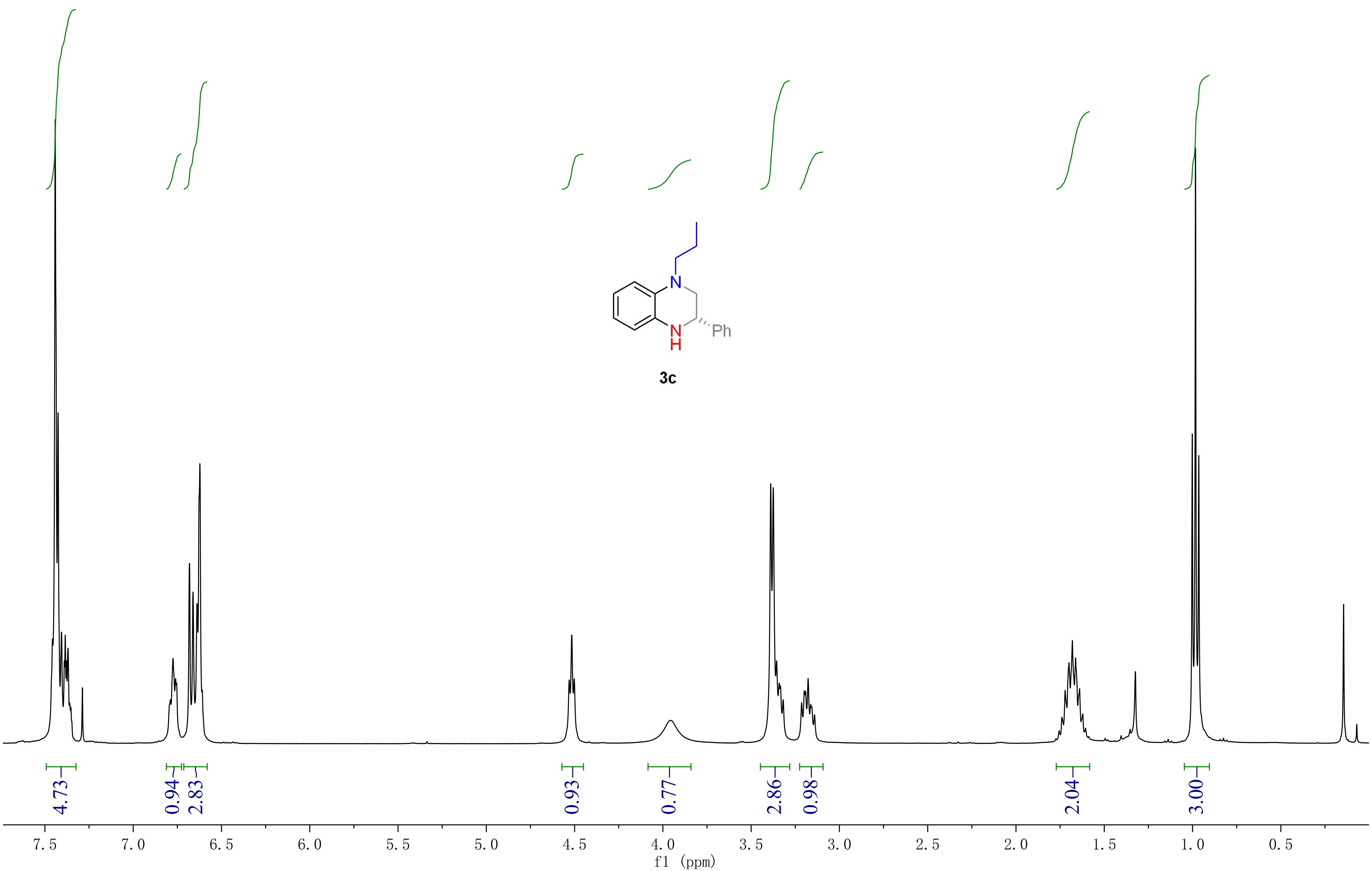

hj-3-6-3
141.76
135.48
134.64
128.65
127.95
127.02
118.89
118.32
113.43
111.76
57.63
54.70
39.10
N
N
H
Ph
3a
45 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35
f1 (ppm)

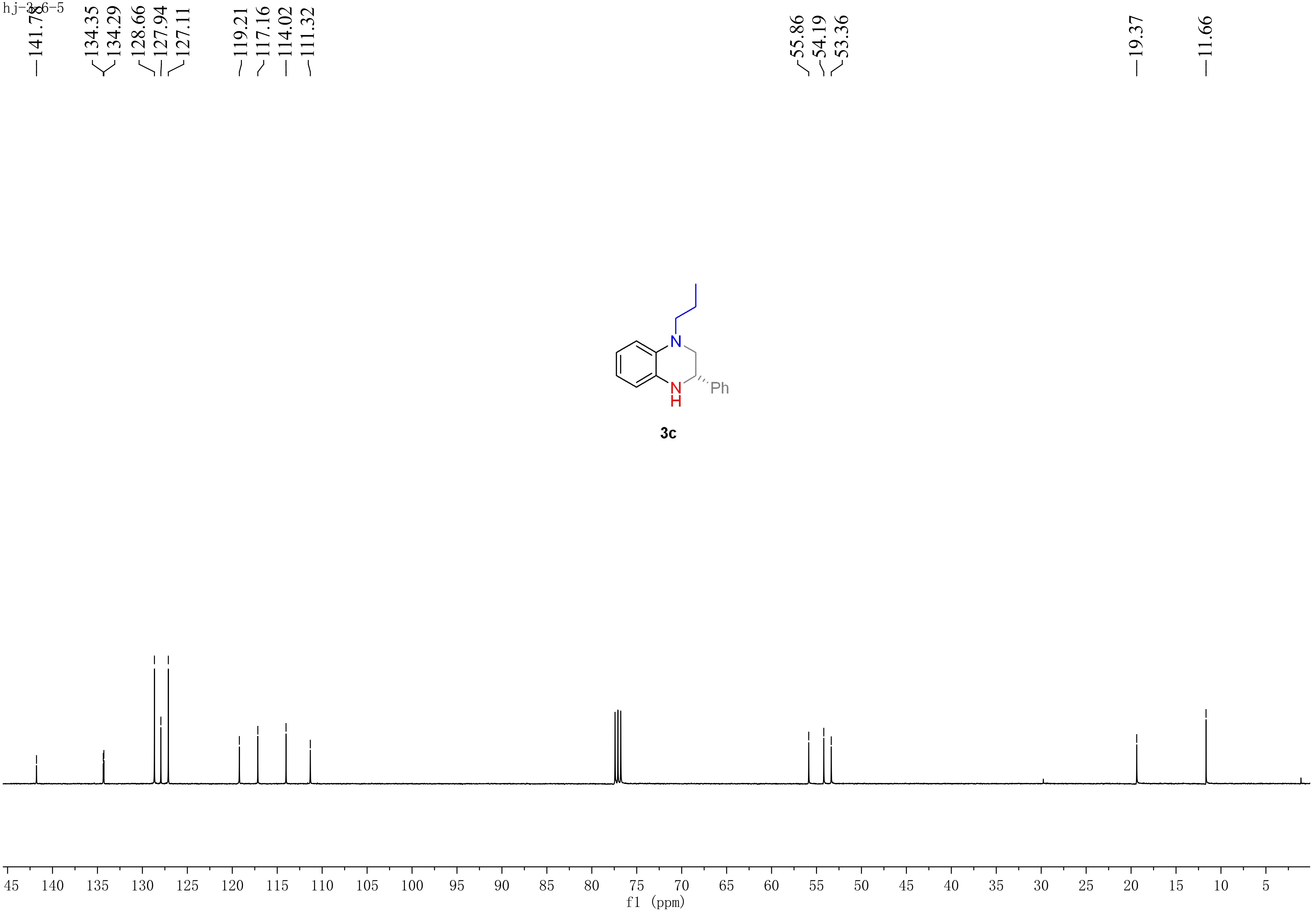


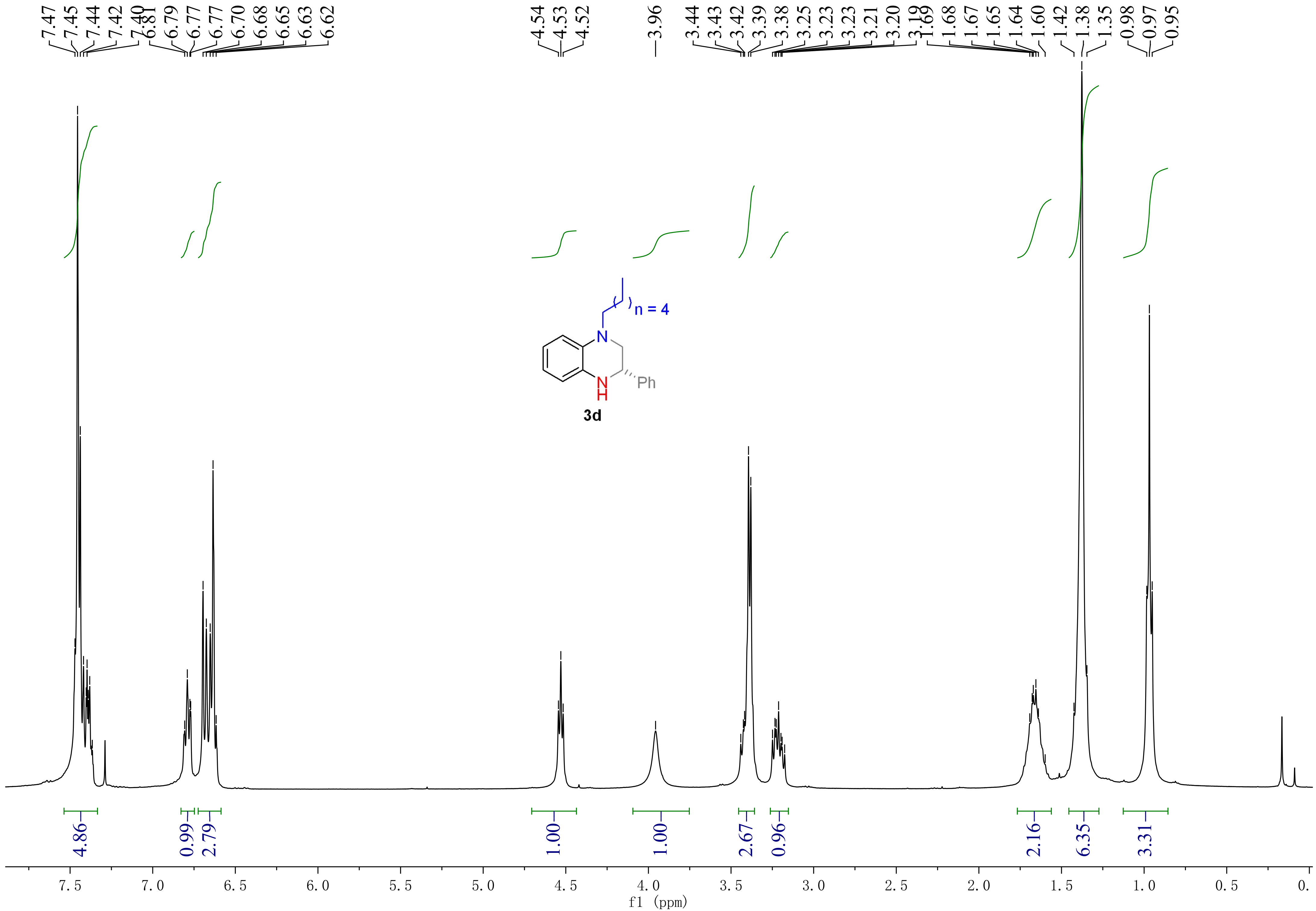
N
N
H
Ph
3b
3.76
0.87
1.92
1.92
1.00
1.05
0.86
0.99
0.98
3.44
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


142.26
134.79
134.23
128.59
127.86
127.03
118.94
117.26
113.98
111.40
55.00
47.00
46.75
19.35
17.94
N
N
H
Ph
3b
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

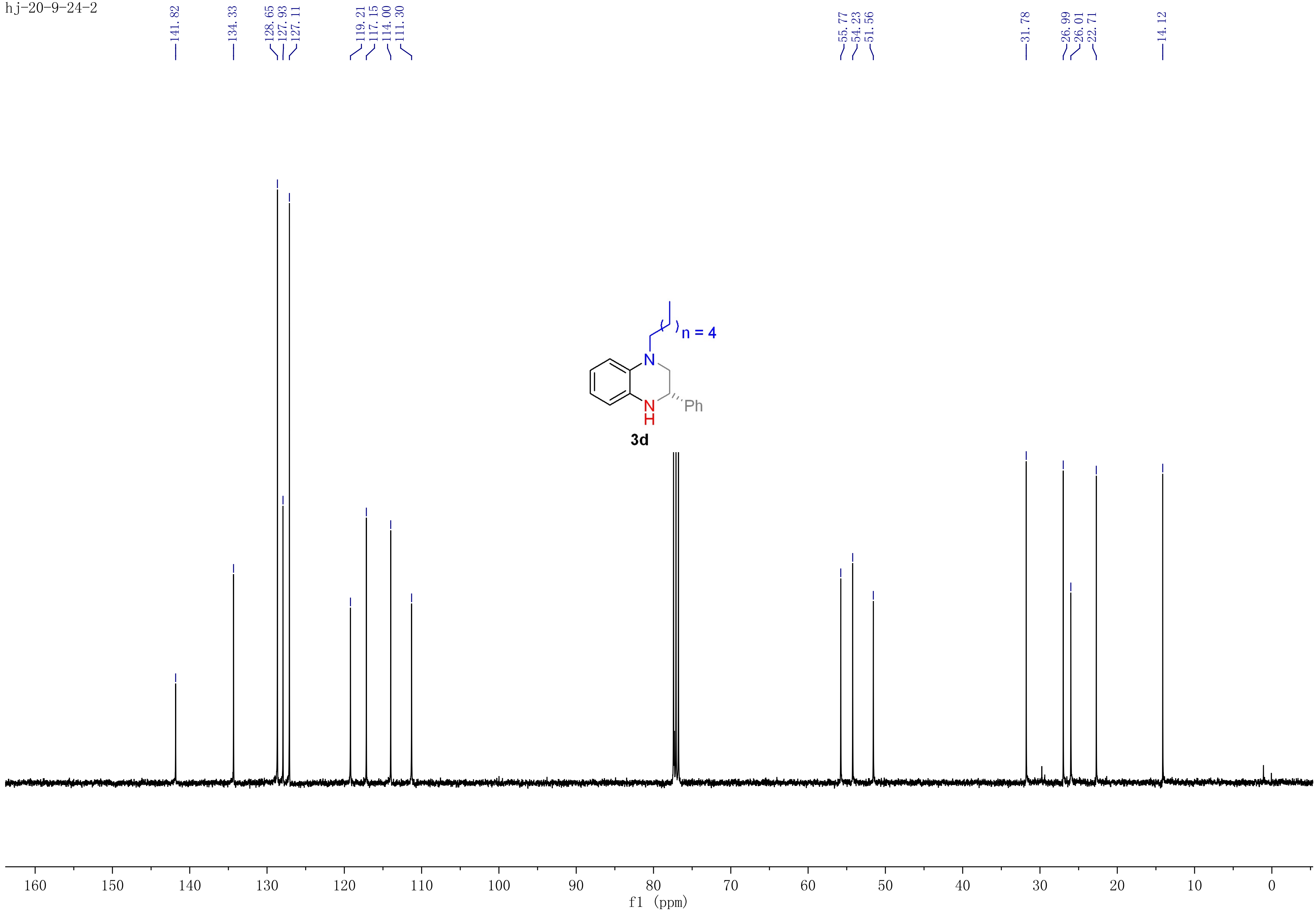
hj-3-6-5

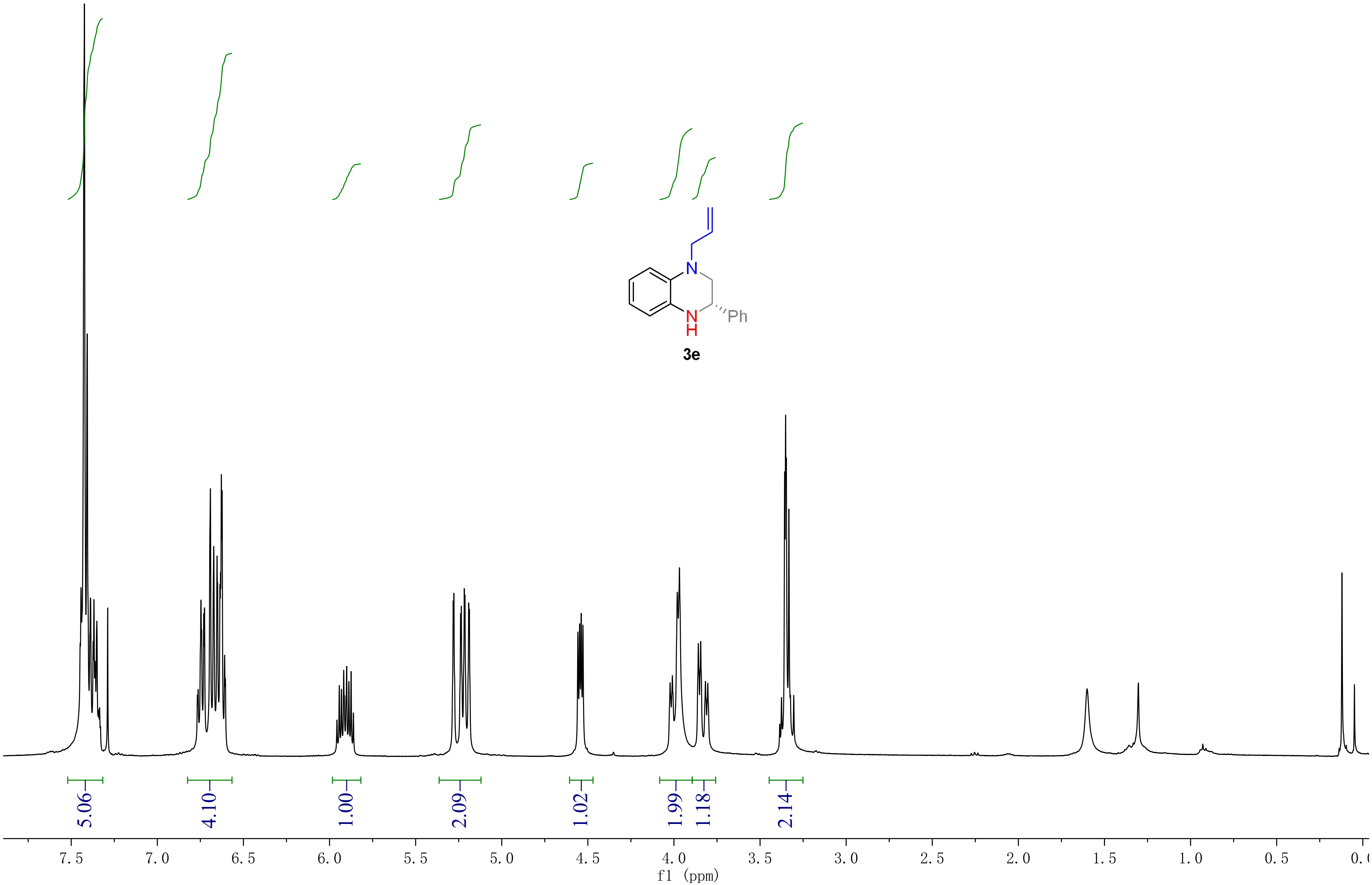

N
N
H
Ph
3c
4.73
0.94
2.83
0.93
0.77
2.86
0.98
2.04
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


hj-3-6-5
141.7
134.35
134.29
128.66
127.94
127.11
119.21
117.16
114.02
111.32
55.86
54.19
53.36
19.37
11.66
N
N
H
Ph
3c
45 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

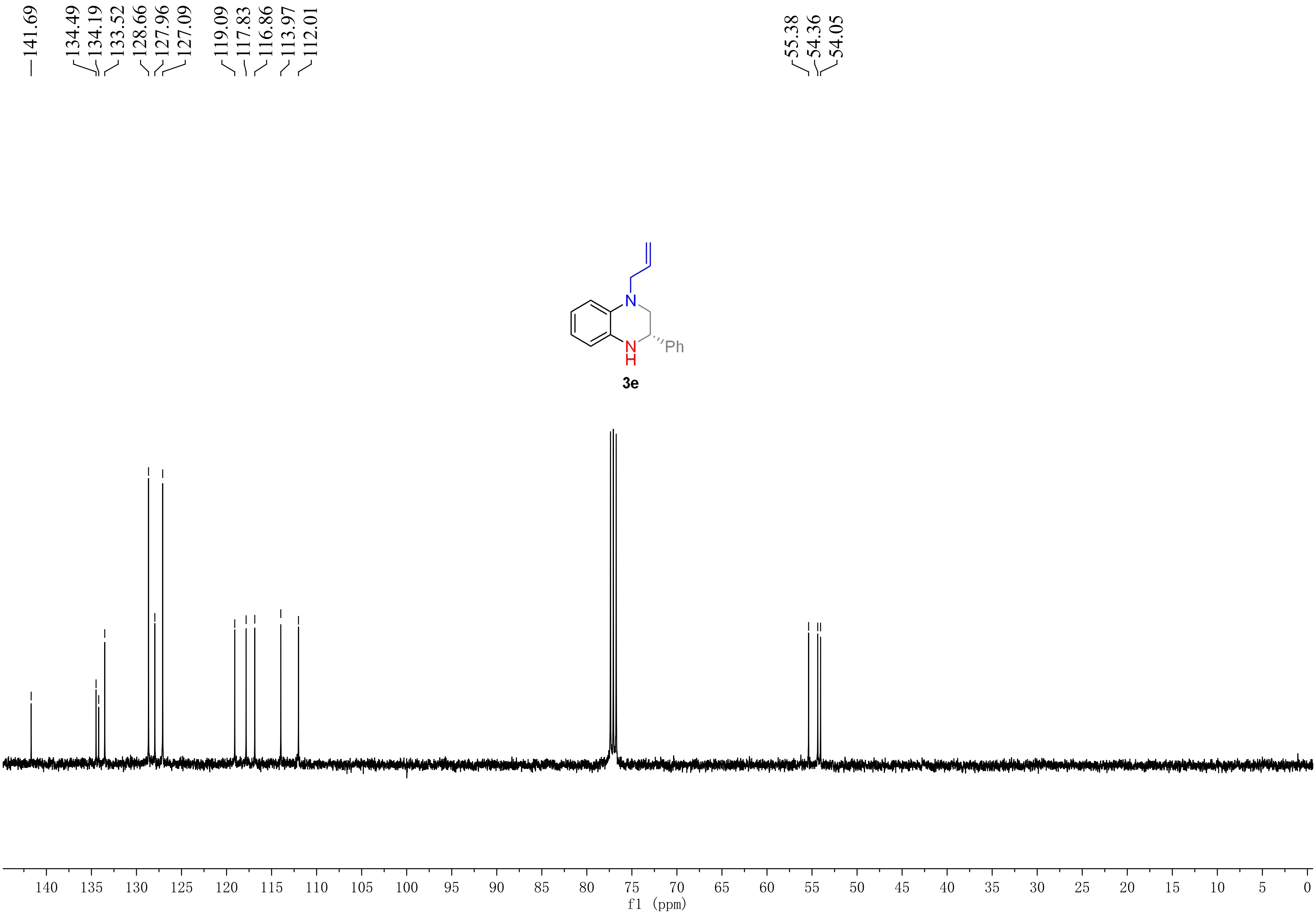


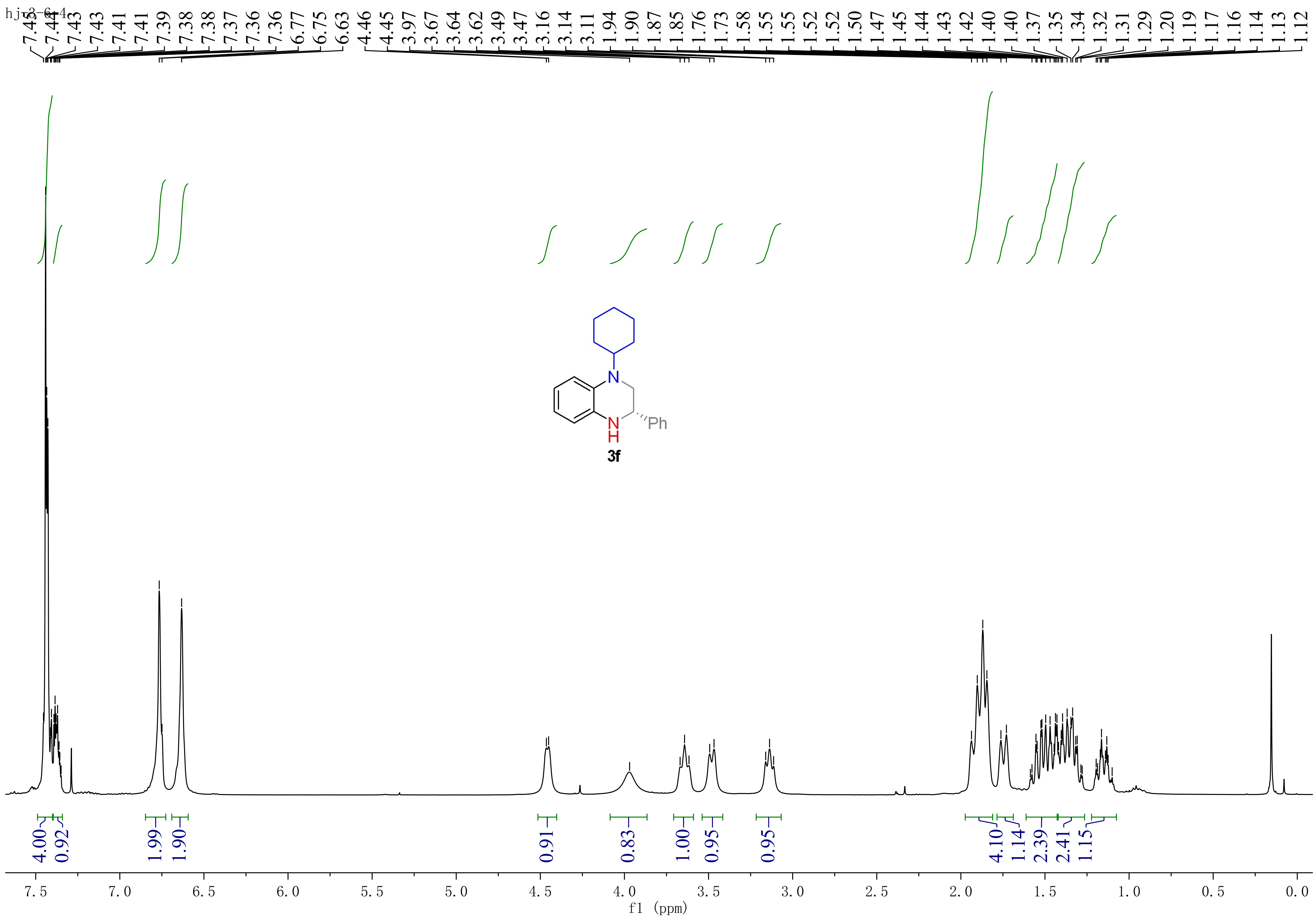
7.47
7.45
7.44
7.42
7.40
6.81
6.79
6.77
6.77
6.70
6.68
6.65
6.63
6.62
4.54
4.53
4.52
3.96
3.44
3.43
3.42
3.39
3.38
3.25
3.23
3.23
3.21
3.20
3.19
1.69
1.68
1.67
1.65
1.64
1.60
1.42
1.38
1.35
0.98
0.97
0.95
n = 4
N
N
H
Ph
3d
4.86
0.99
2.79
1.00
1.00
2.67
0.96
2.16
6.35
3.31
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


hj-20-9-24-2
141.82
134.33
128.65
127.93
127.11
119.21
117.15
114.00
111.30
55.77
54.23
51.56
31.78
26.99
26.01
22.71
14.12
n = 4
N
N
H
Ph
3d
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

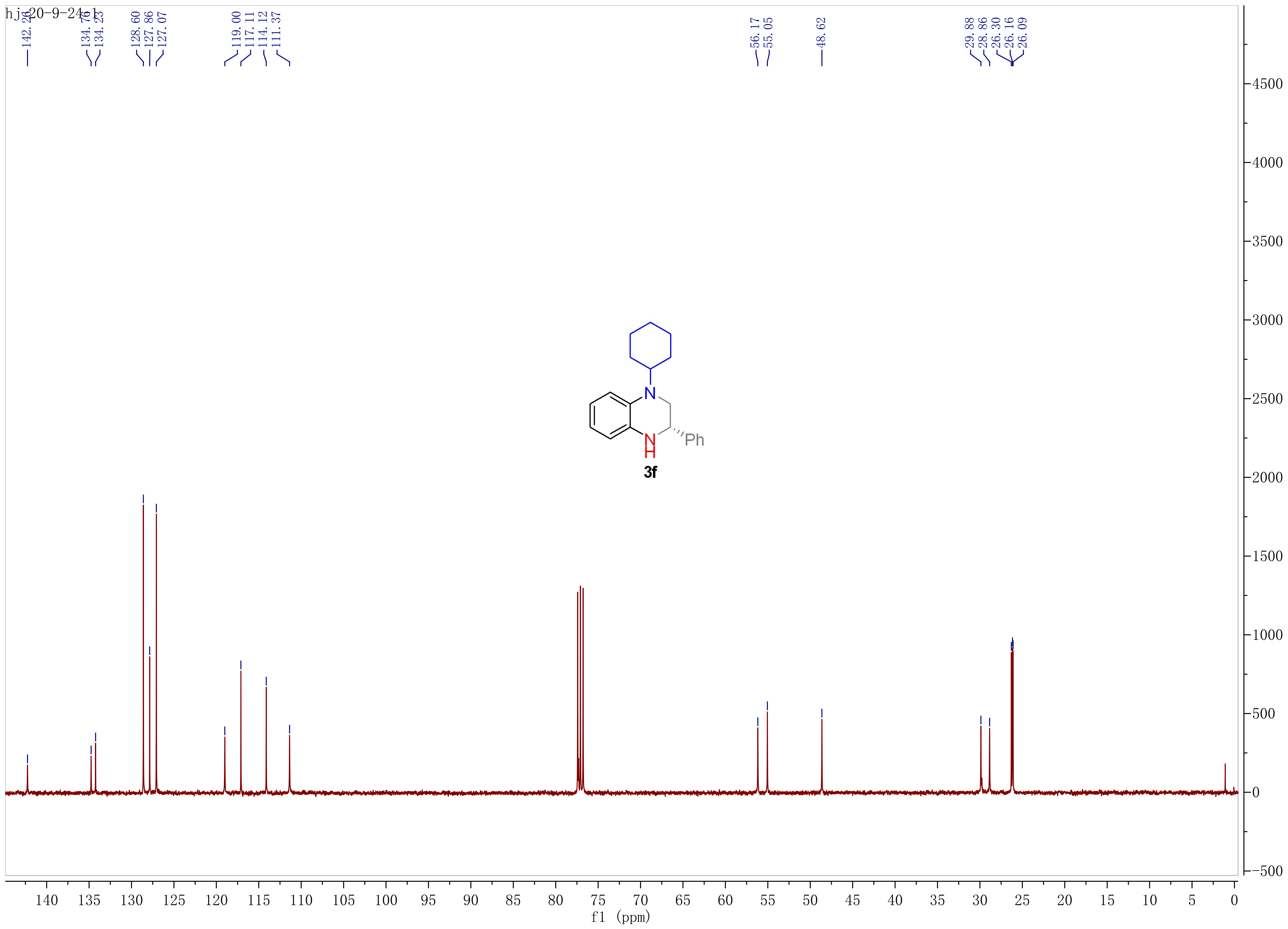


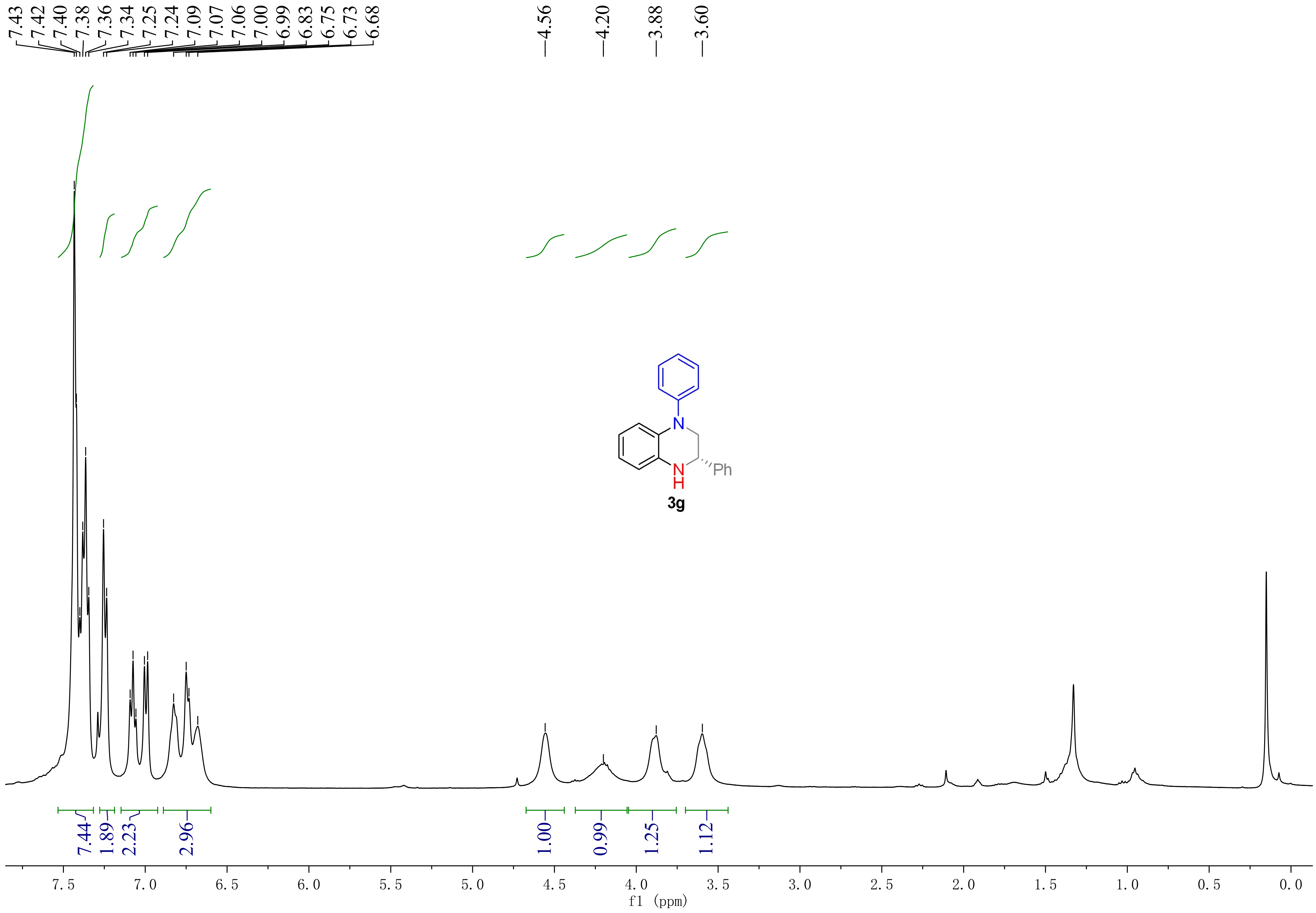
N
N
H
Ph
3e
5.06
4.10
1.00
2.09
1.02
1.99
1.18
2.14
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


141.69
134.49
134.19
133.52
128.66
127.96
127.09
119.09
117.83
116.86
113.97
112.01
55.38
54.36
54.05
N
N
H
Ph
3e
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

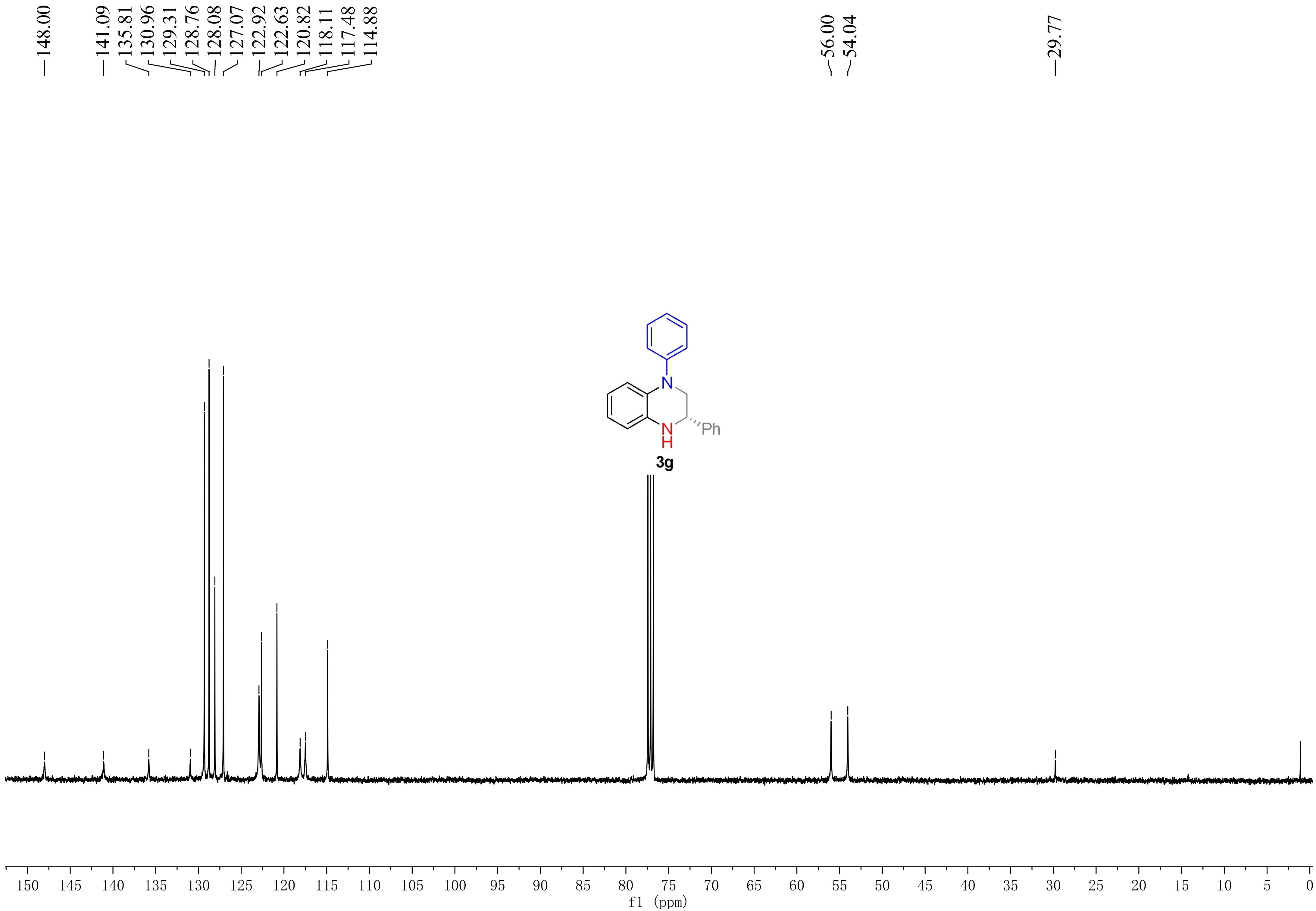


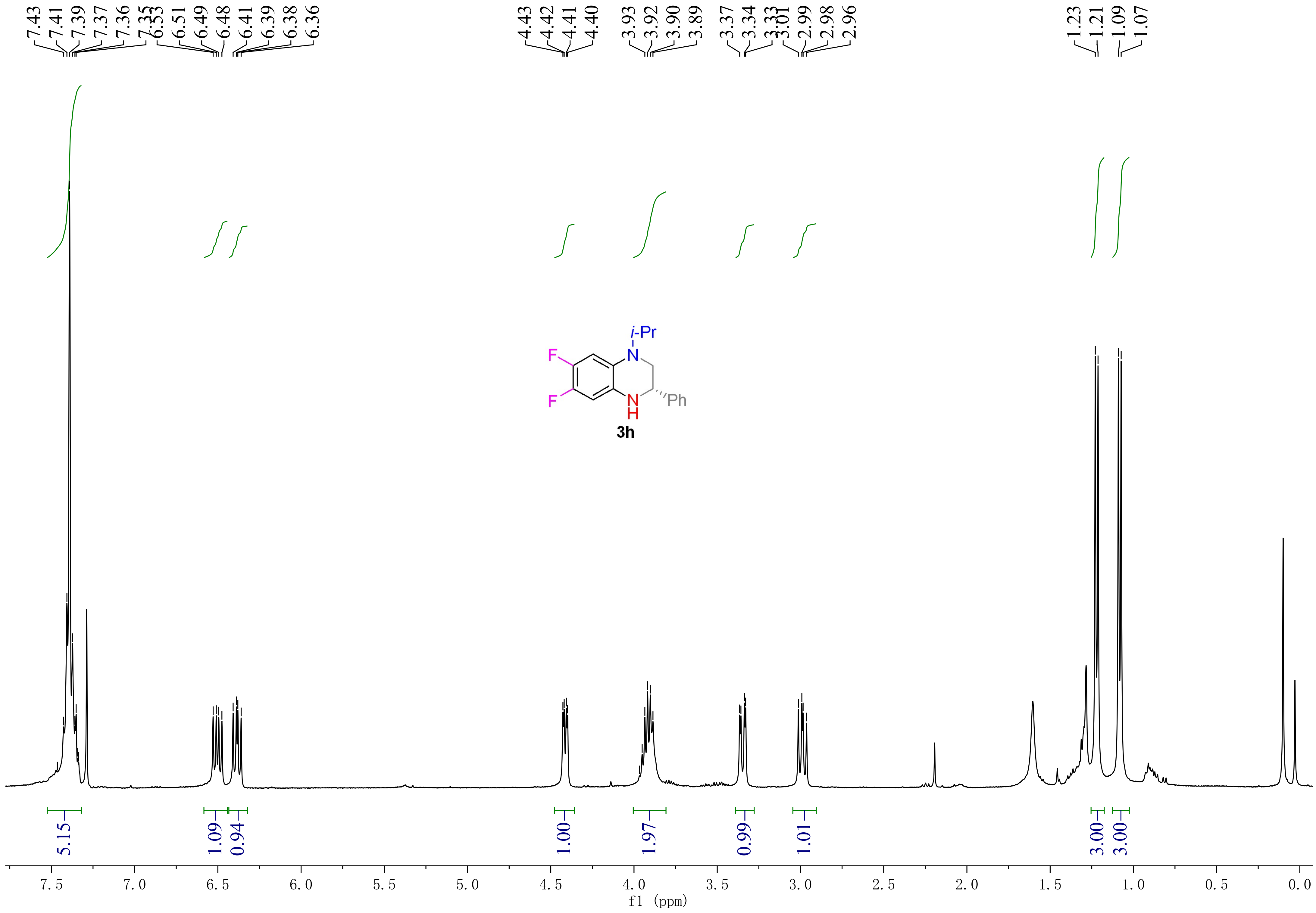
hjr3-6-4
7.45 7.44 7.43 7.43 7.41 7.41 7.39 7.38 7.38 7.37 7.36 7.36 6.77 6.75 6.63
4.46 4.45 3.97 3.67 3.64 3.62 3.49 3.47 3.16 3.14 3.11 1.94 1.90 1.87 1.85 1.76 1.73 1.58 1.55 1.55 1.52 1.52 1.50 1.47 1.45 1.44 1.43 1.42 1.40 1.40 1.37 1.35 1.34 1.32 1.31 1.29 1.20 1.19 1.17 1.16 1.14 1.13 1.12
N
N
H
Ph
3f
4.00 0.92 1.99 1.90 0.91 0.83 1.00 0.95 0.95 4.10 1.14 2.39 2.41 1.15
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

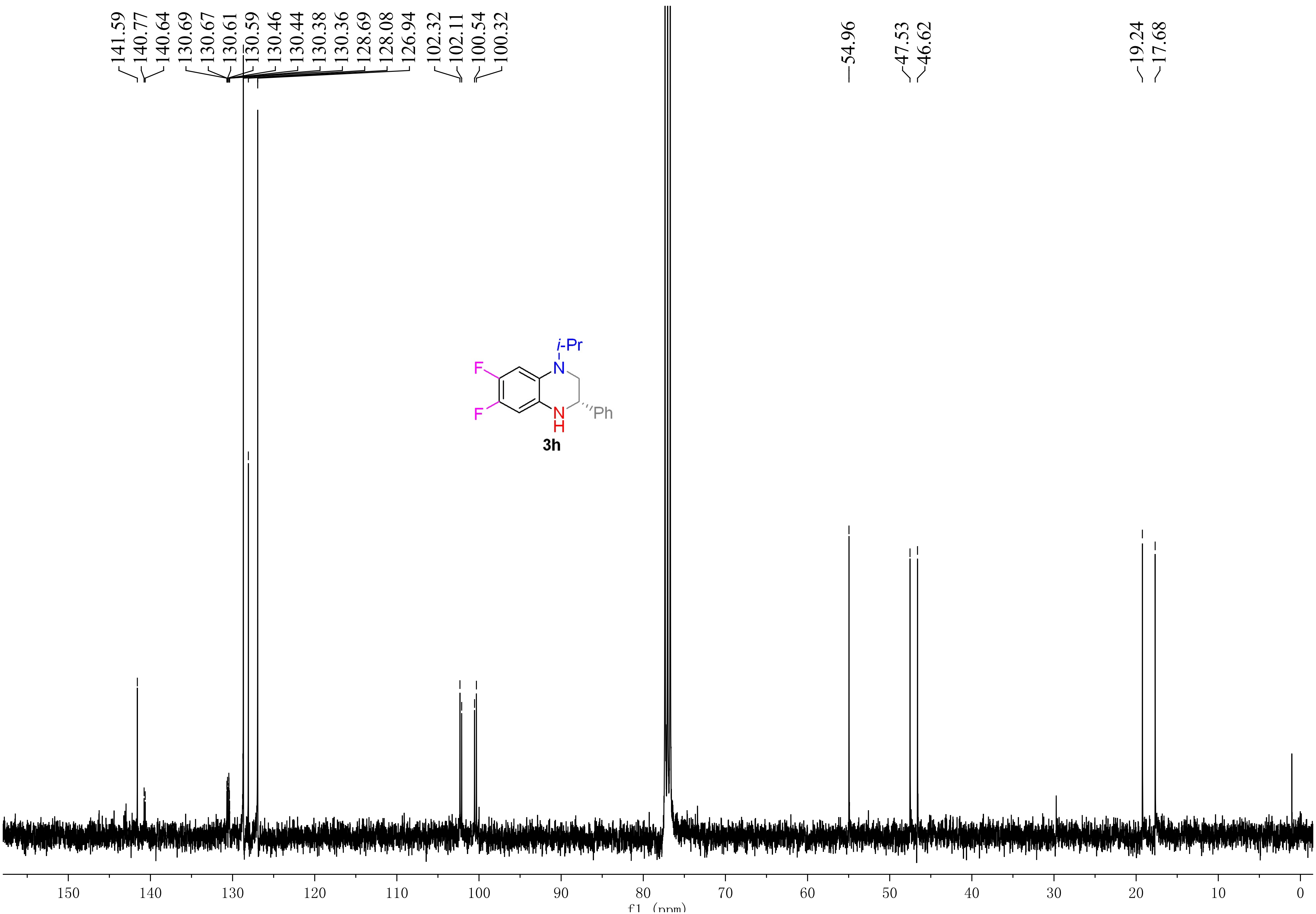

hj-20-9-24-1
142.26
134.76
134.23
128.60
127.86
127.07
119.00
117.11
114.12
111.37
56.17
55.05
48.62
29.88
28.86
26.30
26.16
26.09
N
N
H
Ph
3f
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

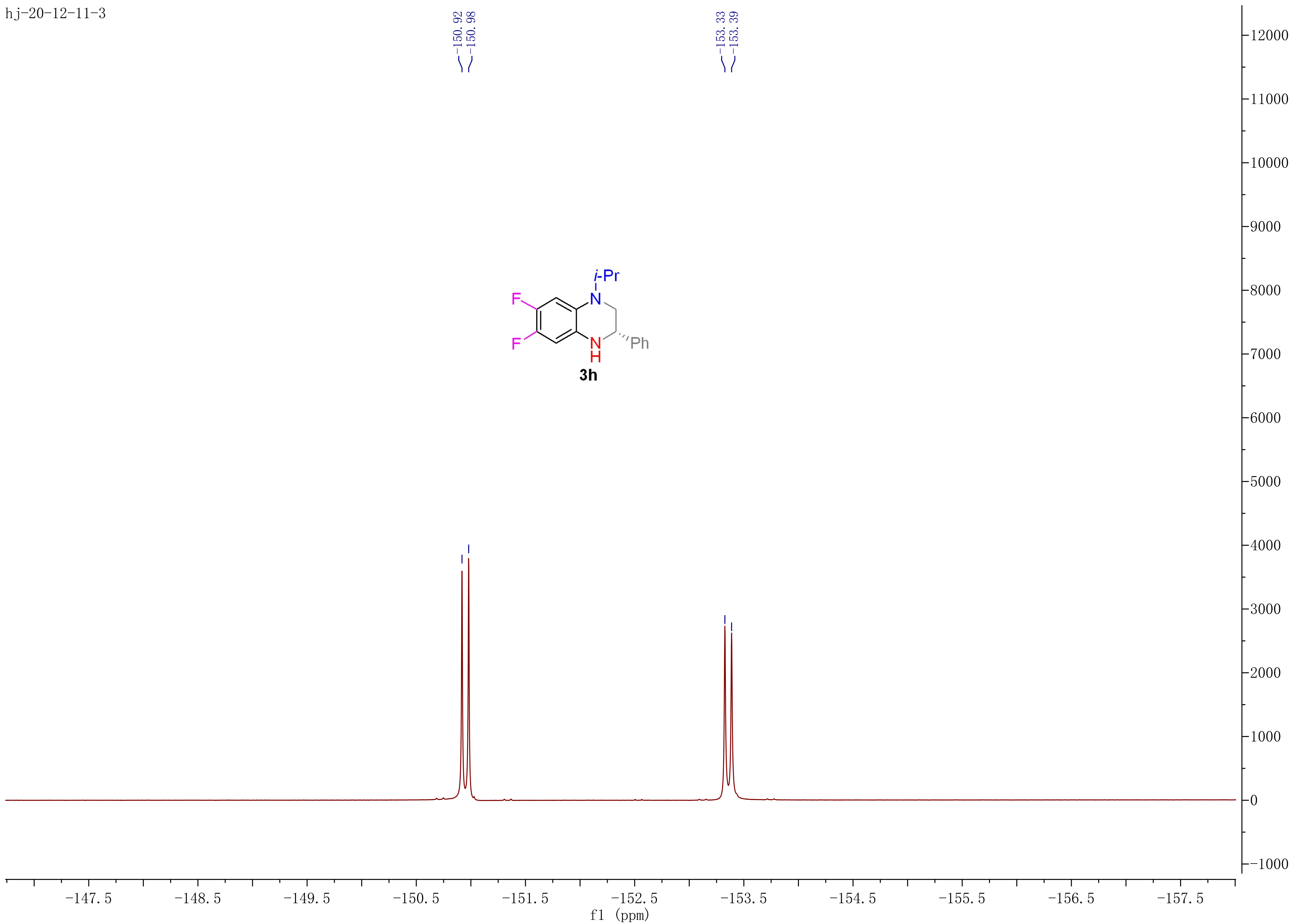


7.43
7.42
7.40
7.38
7.36
7.34
7.25
7.24
7.09
7.07
7.06
7.00
6.99
6.83
6.75
6.73
6.68
4.56
4.20
3.88
3.60
N
N
H
Ph
3g
7.44
1.89
2.23
2.96
1.00
0.99
1.25
1.12
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

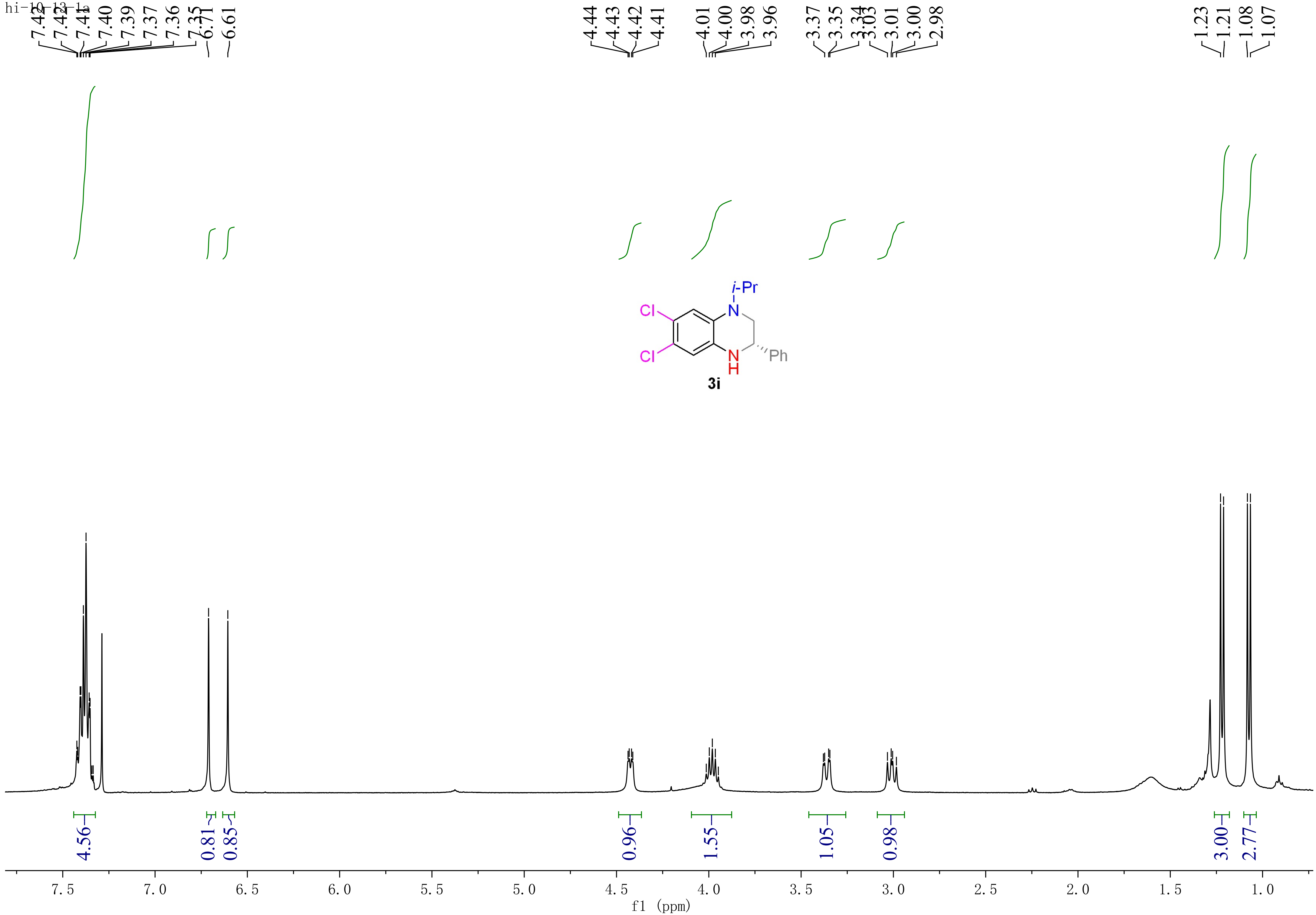

148.00
141.09
135.81
130.96
129.31
128.76
128.08
127.07
122.92
122.63
120.82
118.11
117.48
114.88
56.00
54.04
29.77
N
N
H
Ph
3g
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


7.43
7.41
7.39
7.37
7.36
7.35
6.53
6.51
6.49
6.48
6.41
6.39
6.38
6.36
4.43
4.42
4.41
4.40
3.93
3.92
3.90
3.89
3.37
3.34
3.33
3.01
2.99
2.98
2.96
1.23
1.21
1.09
1.07
i-Pr
F
F
N
N
H
Ph
3h
5.15
1.09
0.94
1.00
1.97
0.99
1.01
3.00
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

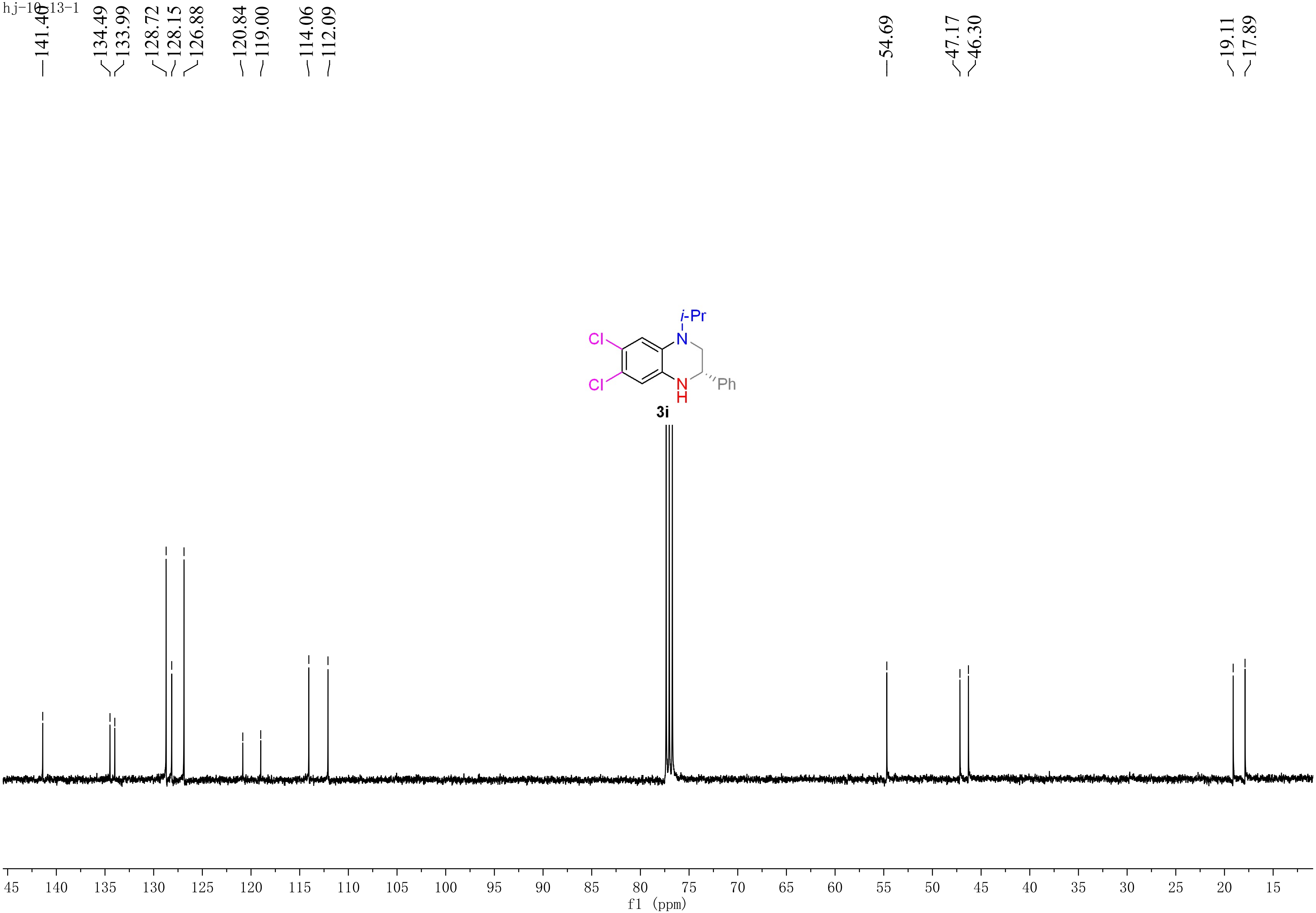

141.59
140.77
140.64
130.69
130.67
130.61
130.59
130.46
130.44
130.38
130.36
128.69
128.08
126.94
102.32
102.11
100.54
100.32
54.96
47.53
46.62
19.24
17.68
i-Pr
F
F
N
N
H
Ph
3h
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



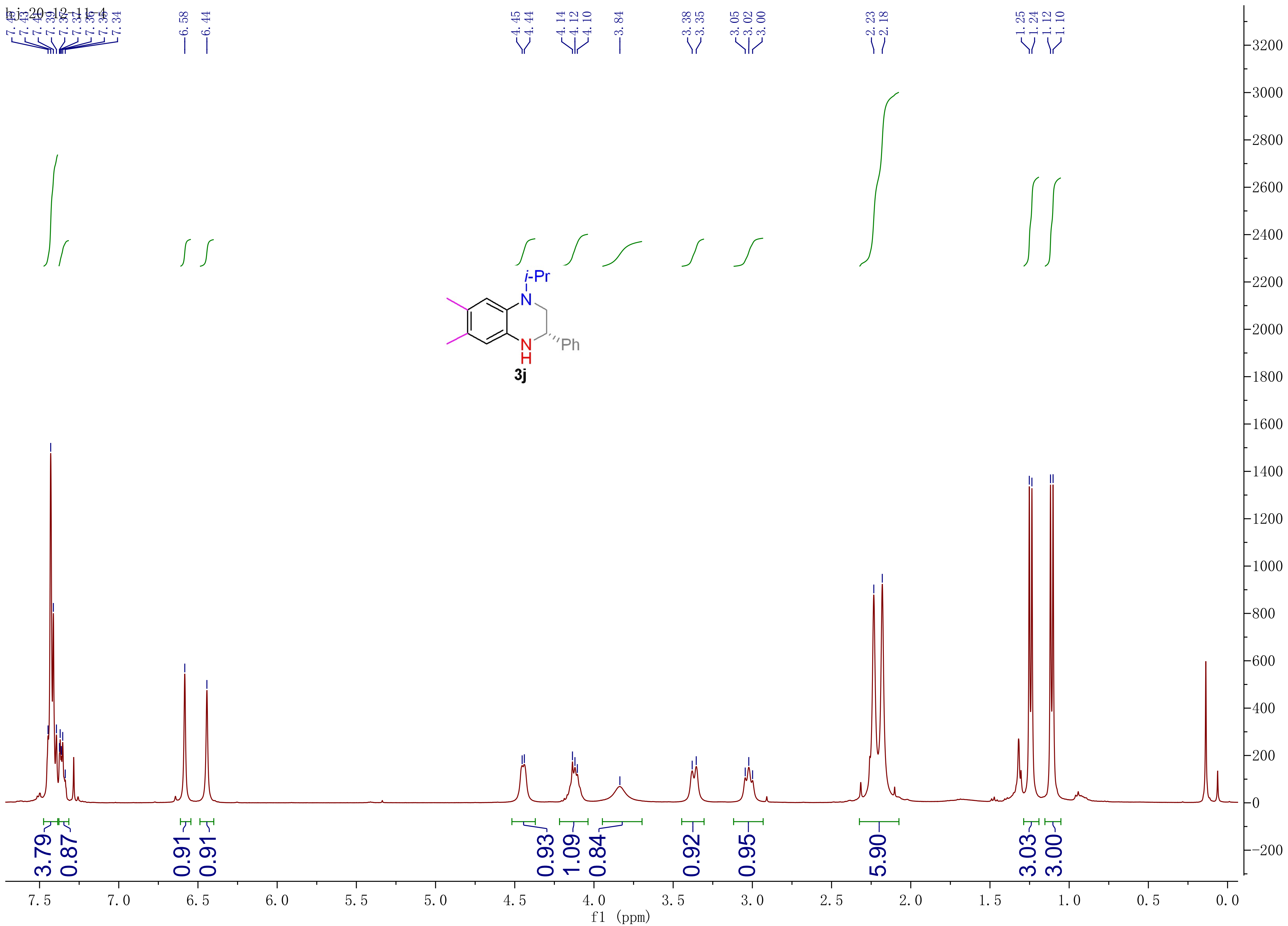
hj-20-12-11-3
-150.92
-150.98
-153.33
-153.39
i-Pr
F
F
N
N
H
Ph
3h
f1 (ppm)


hi-10-13-1a
7.42
7.42
7.41
7.40
7.39
7.37
7.36
7.35
6.71
6.61
4.44
4.43
4.42
4.41
4.01
4.00
3.98
3.96
3.37
3.35
3.34
3.03
3.01
3.00
2.98
1.23
1.21
1.08
1.07
i-Pr
Cl
Cl
N
N
H
Ph
3i
4.56
0.81
0.85
0.96
1.55
1.05
0.98
3.00
2.77
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

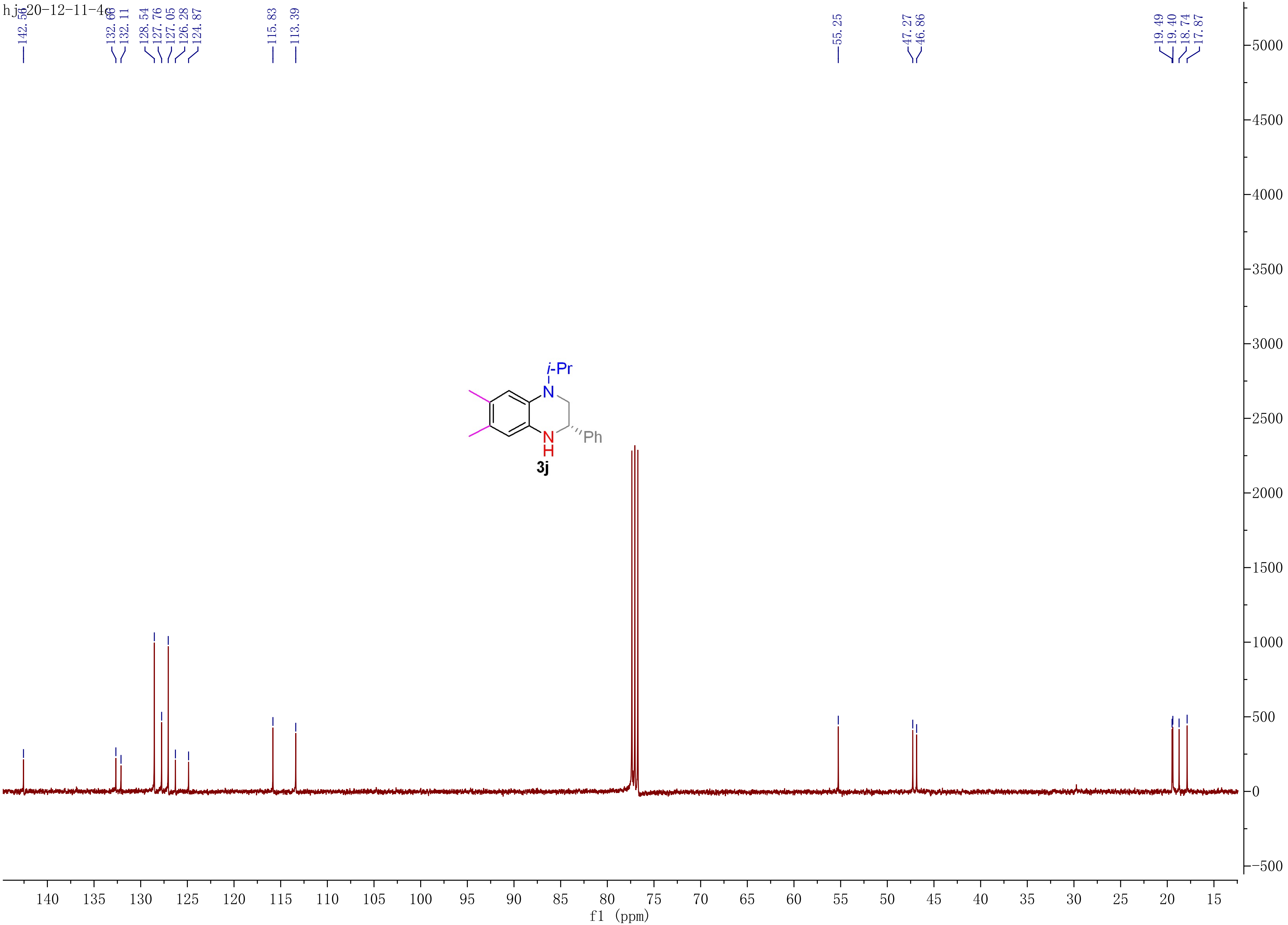
hj-10-13-1

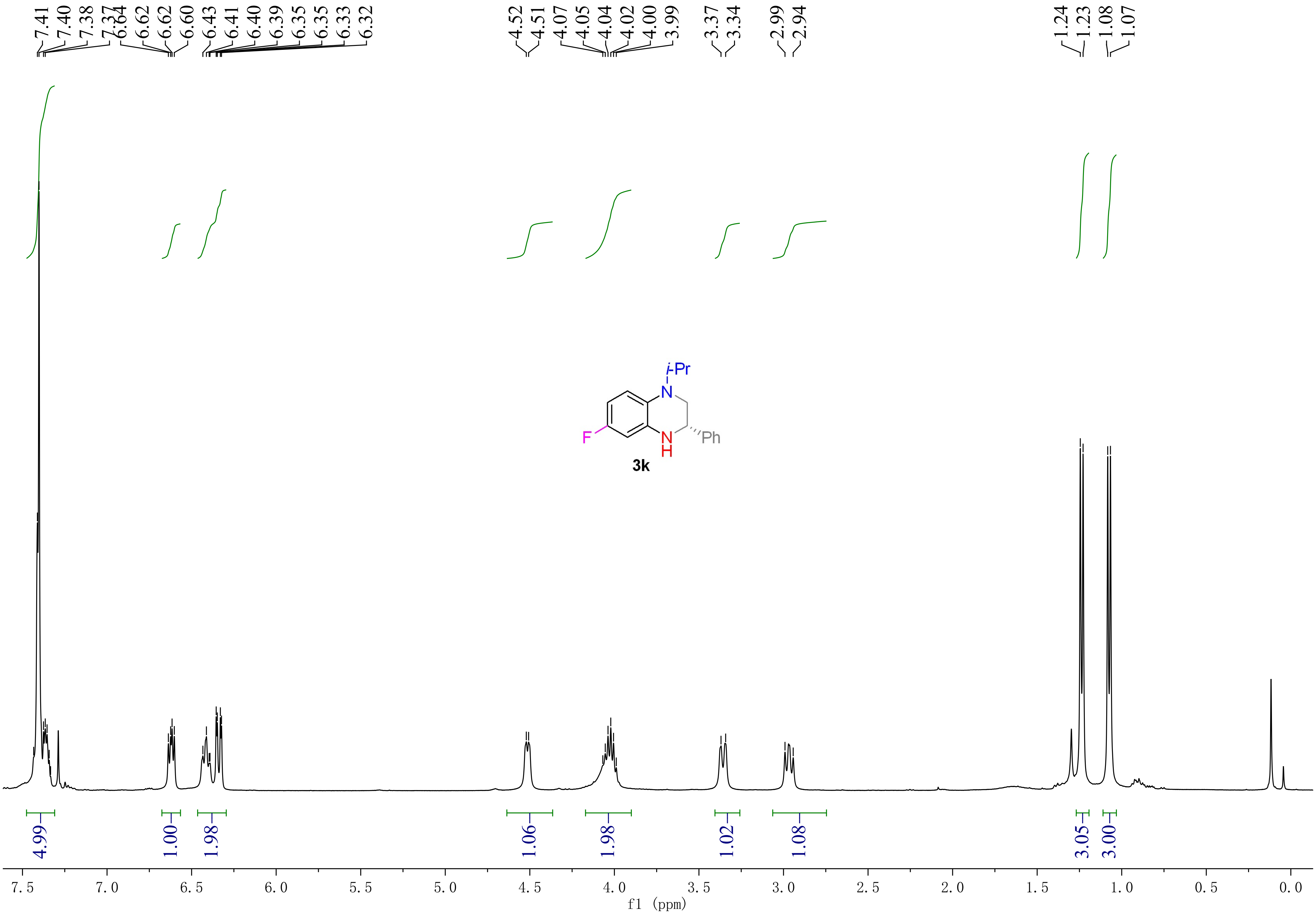


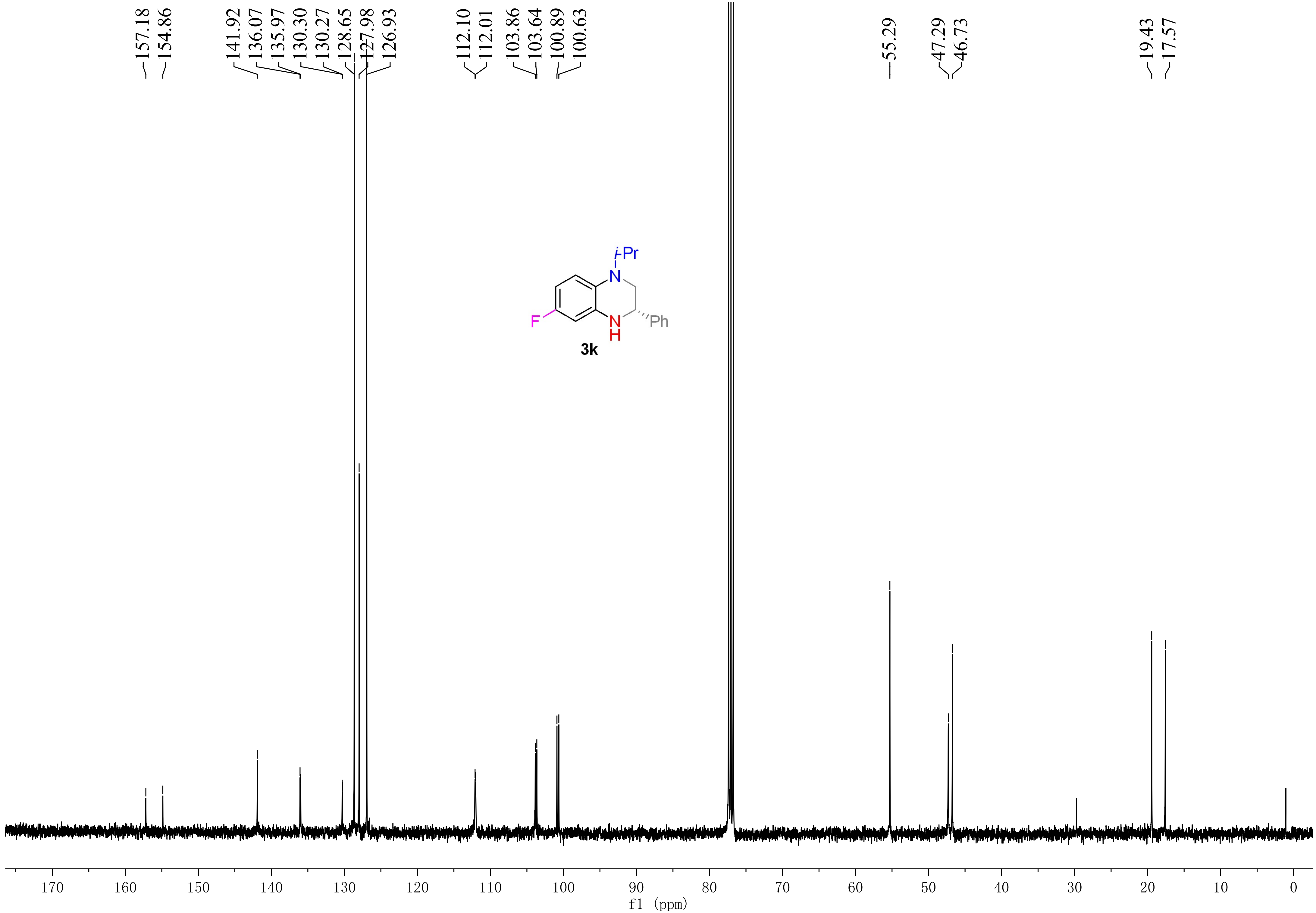
141.40
134.49
133.99
128.72
128.15
126.88
120.84
119.00
114.06
112.09
54.69
47.17
46.30
19.11
17.89
i-Pr
N
Cl
Cl
N
H
Ph
3i
f1 (ppm)



6.58
6.44
4.45
4.44
4.14
4.12
4.10
3.84
3.38
3.35
3.05
3.02
3.00
2.23
2.18
1.25
1.24
1.12
1.10
i-Pr
N
N
H
Ph
3j
3.79
0.87
0.91
0.91
0.93
1.09
0.84
0.92
0.95
5.90
3.03
3.00
f1 (ppm)

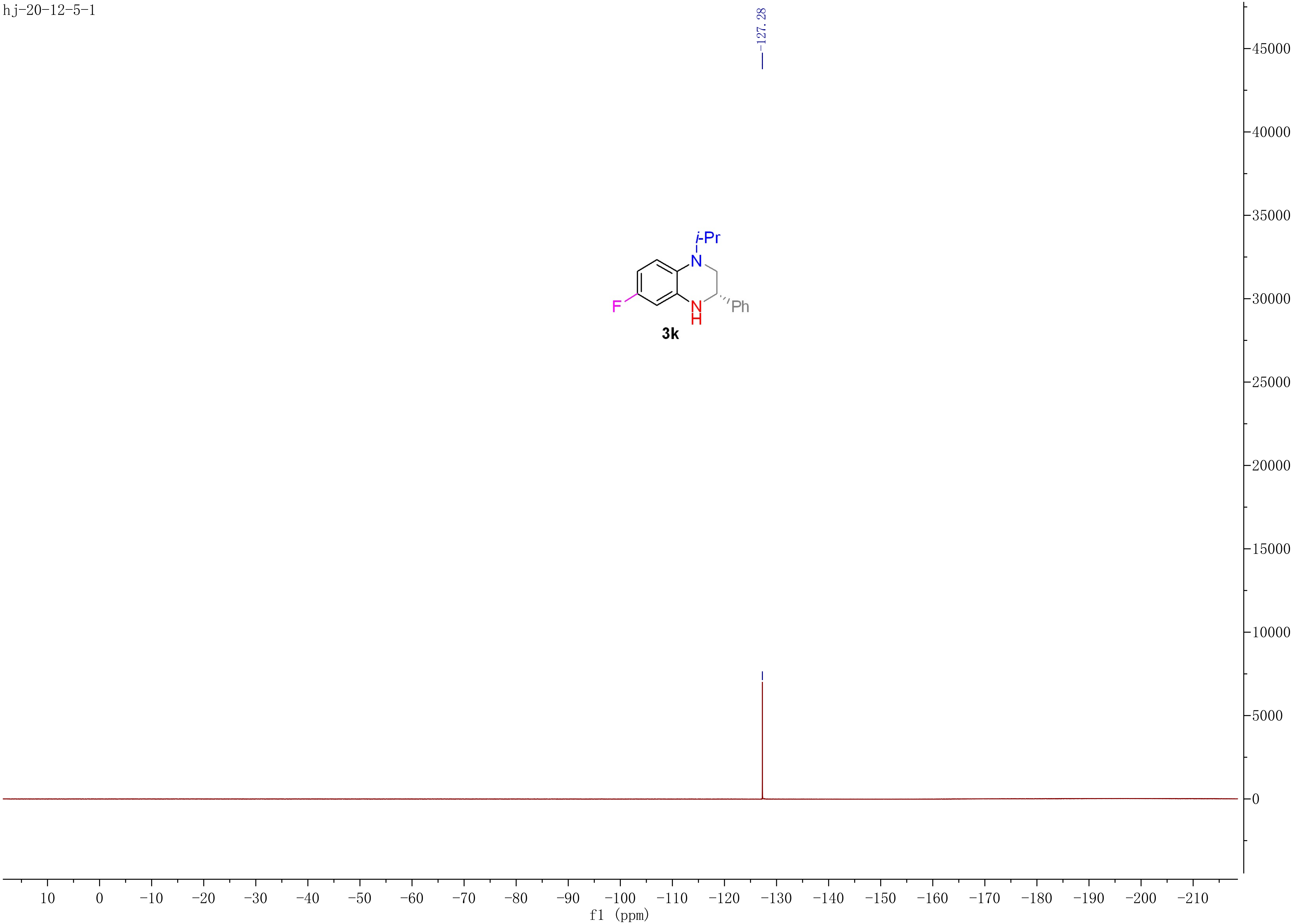

hj-20-12-11-4c
142.56
132.66
132.11
128.54
127.76
127.05
126.28
124.87
115.83
113.39
55.25
47.27
46.86
19.49
19.40
18.74
17.87
i-Pr
N
N
H
Ph
3j
f1 (ppm)


7.41
7.40
7.38
7.37
6.64
6.62
6.62
6.60
6.43
6.41
6.40
6.39
6.35
6.35
6.33
6.32
4.52
4.51
4.07
4.05
4.04
4.02
4.00
3.99
3.37
3.34
2.99
2.94
1.24
1.23
1.08
1.07
i-Pr
N
F
N
H
Ph
3k
4.99
1.00
1.98
1.06
1.98
1.02
1.08
3.05
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



157.18
154.86
141.92
136.07
135.97
130.30
130.27
128.65
127.98
126.93
112.10
112.01
103.86
103.64
100.89
100.63
55.29
47.29
46.73
19.43
17.57
i-Pr
N
N
H
F
Ph
3k
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

hj-20-12-5-1



-127.28
i-Pr
N
F
N
H
Ph
3k
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
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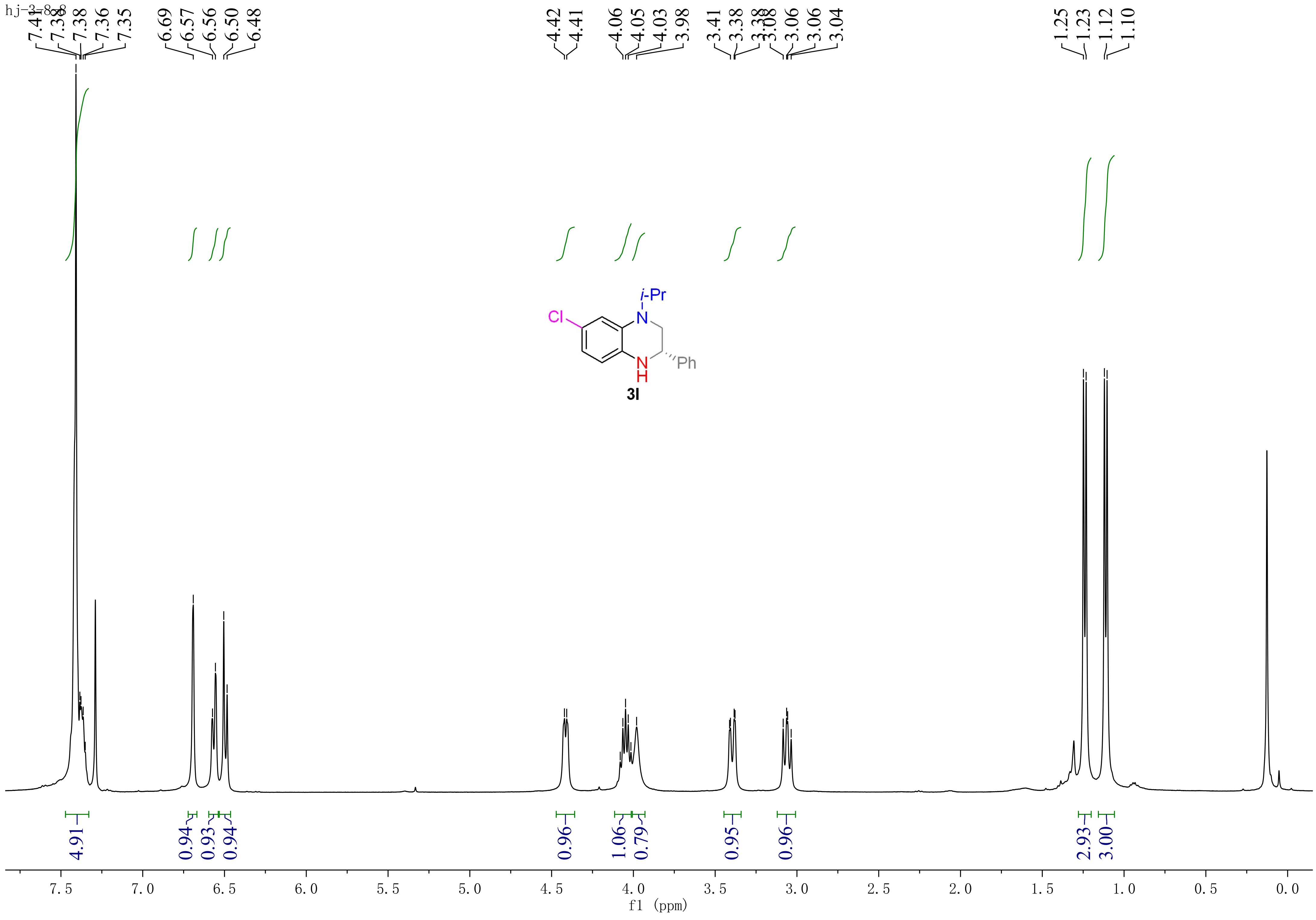
-200
-210
f1 (ppm)


hj-3-8-8
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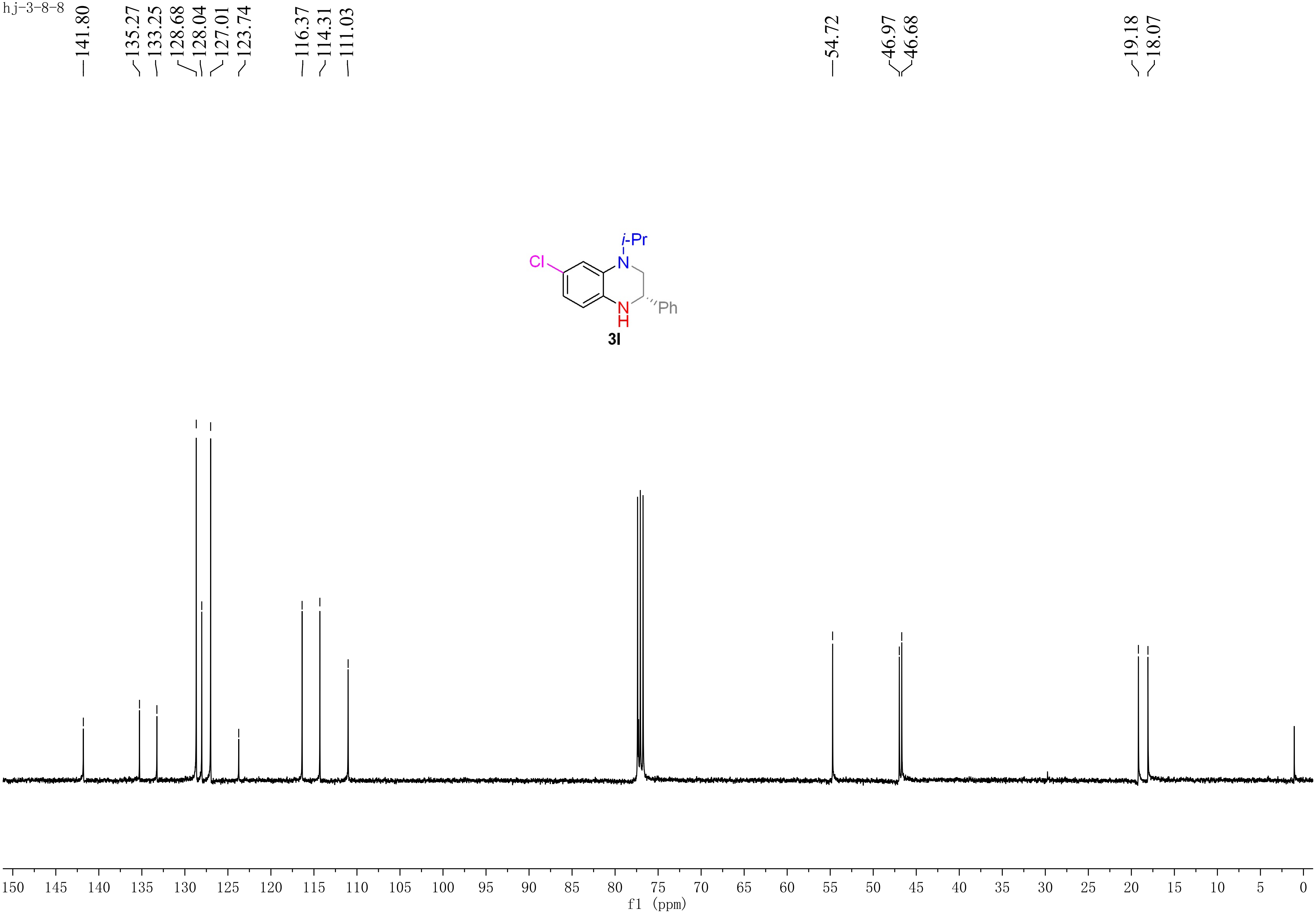
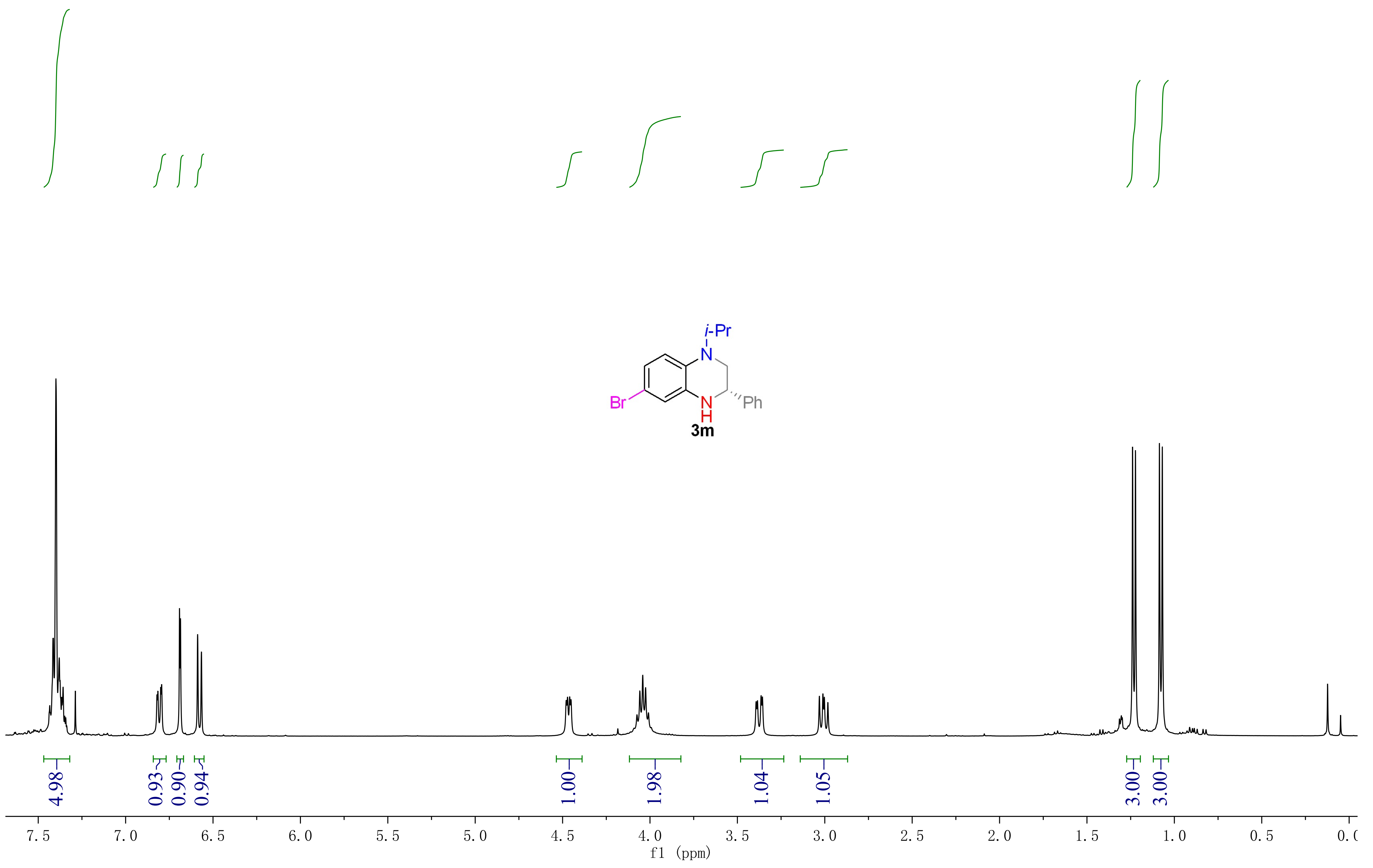
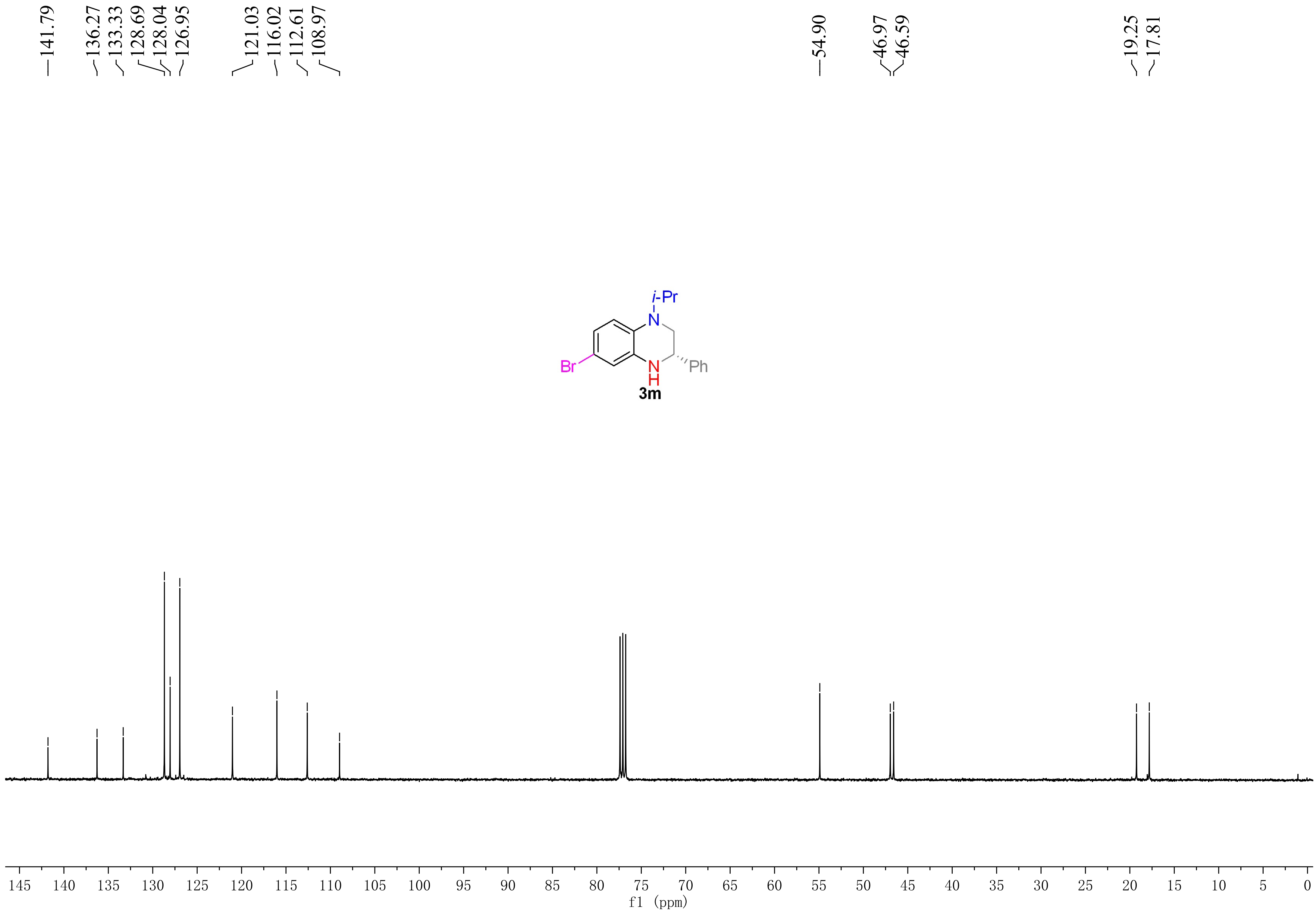
7.38
7.38
7.36
7.35
6.69
6.57
6.56
6.50
6.48
4.42
4.41
4.06
4.05
4.03
3.98
3.41
3.38
3.38
3.08
3.06
3.06
3.04
1.25
1.23
1.12
1.10
Cl
i-Pr
N
N
H
Ph
3l
4.91
0.94
0.93
0.94
0.96
1.06
0.79
0.95
0.96
2.93
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

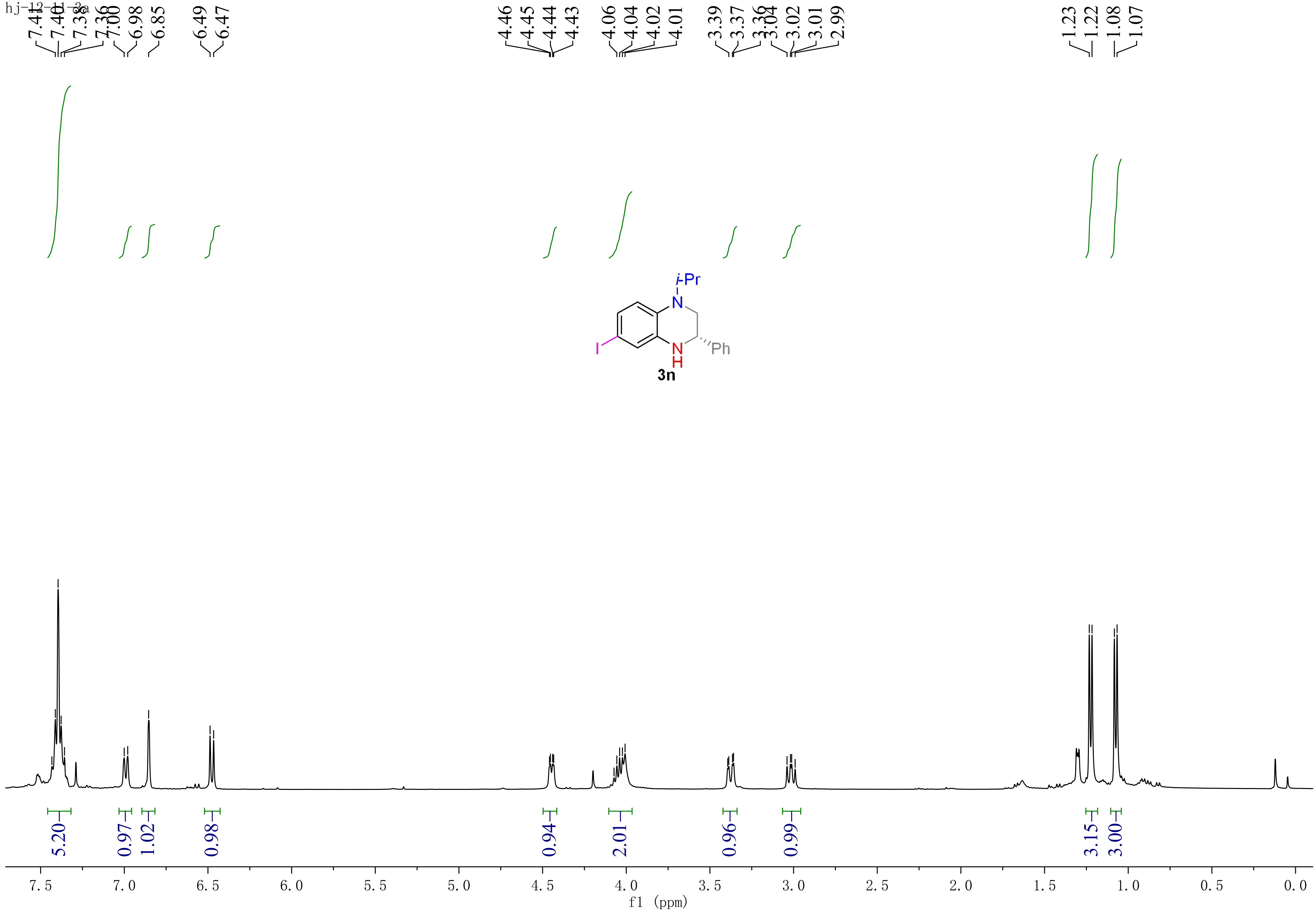

hj-3-8-8
141.80
135.27
133.25
128.68
128.04
127.01
123.74
116.37
114.31
111.03
54.72
46.97
46.68
19.18
18.07
Cl
i-Pr
N
N
H
Ph
3l
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

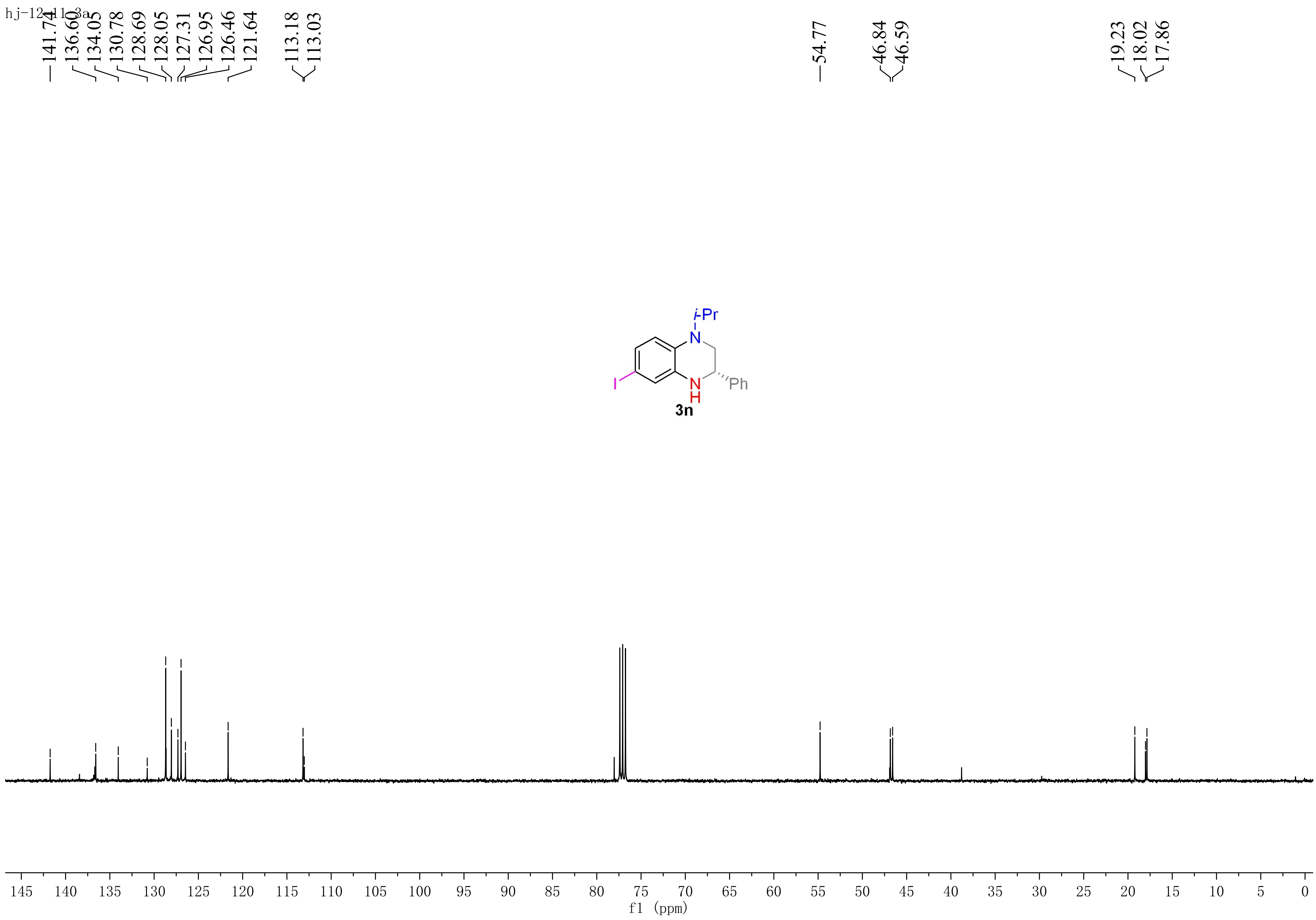


i-Pr
N
Br
N
H
Ph
3m
4.98
0.93
0.90
0.94
1.00
1.98
1.04
1.05
3.00
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



141.79
136.27
133.33
128.69
128.04
126.95
121.03
116.02
112.61
108.97
54.90
46.97
46.59
19.25
17.81
i-Pr
N
Br
N
H
Ph
3m
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


hj-12-11-3a
7.41 7.40 7.38 7.36 7.00 6.98 6.85 6.49 6.47
4.46 4.45 4.44 4.43 4.06 4.04 4.02 4.01 3.39 3.37 3.36 3.04 3.02 3.01 2.99
1.23 1.22 1.08 1.07
i-Pr
N
N
H
Ph
I
3n
5.20 0.97 1.02 0.98 0.94 2.01 0.96 0.99 3.15 3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


hj-12-11-3a
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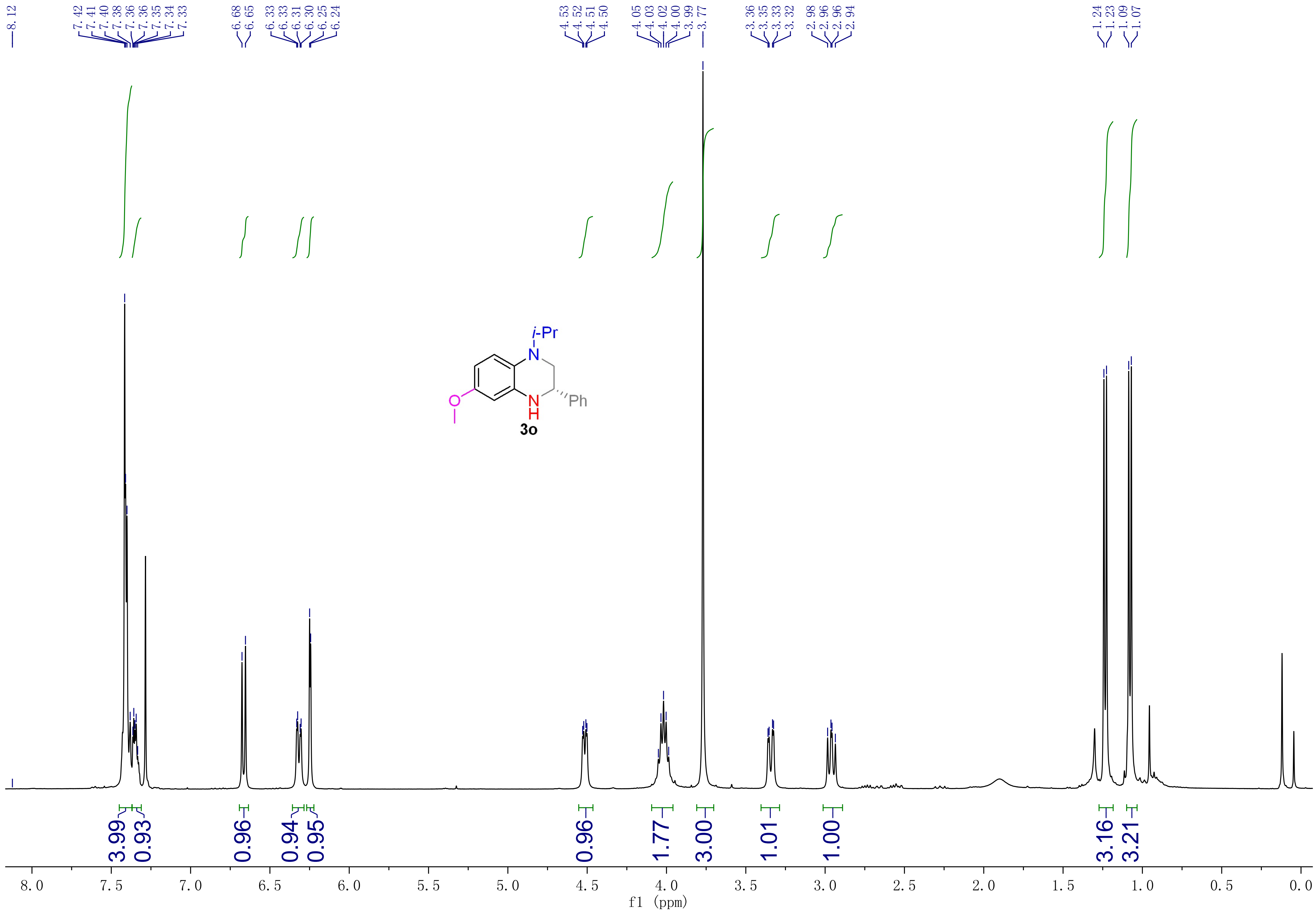
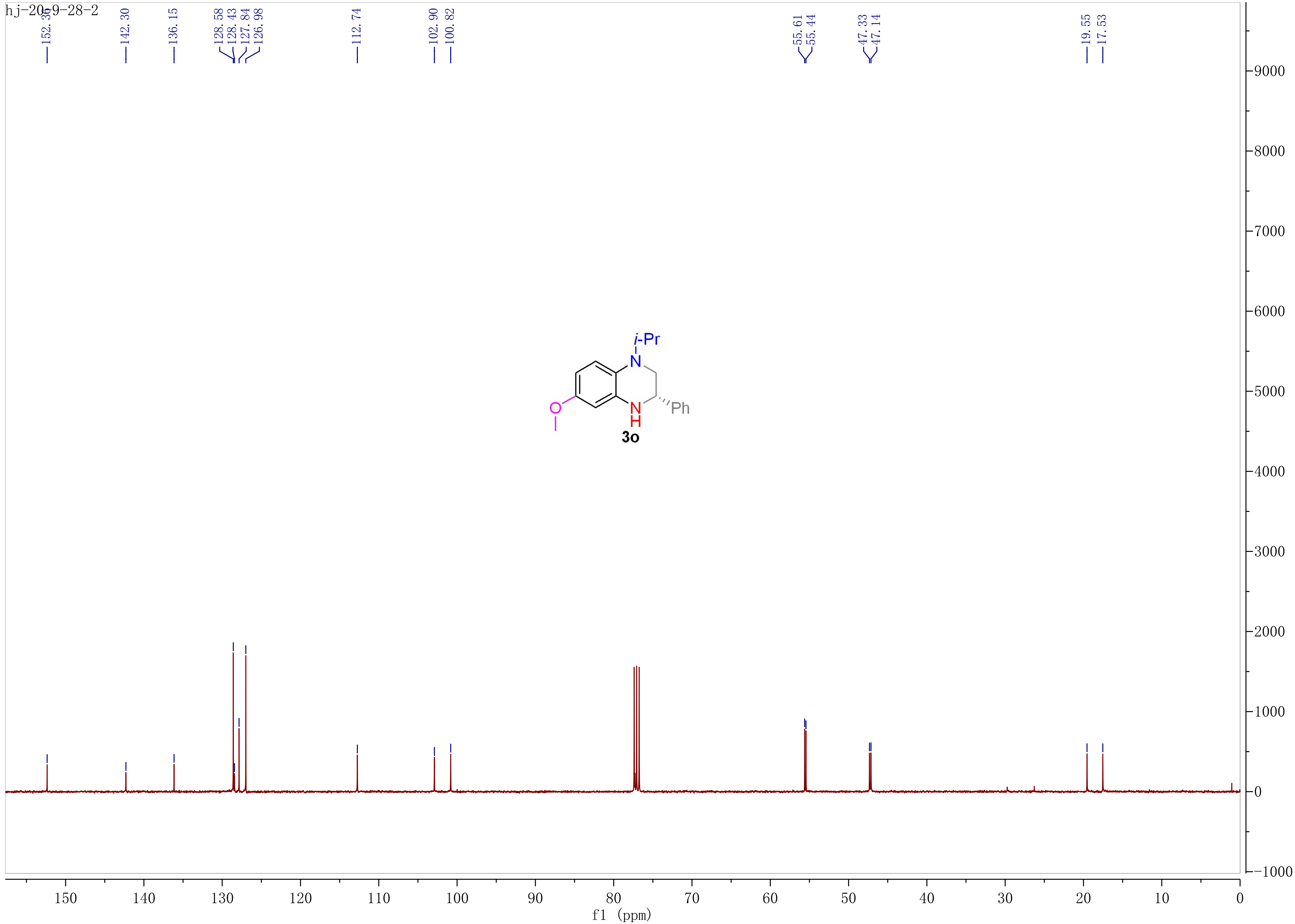
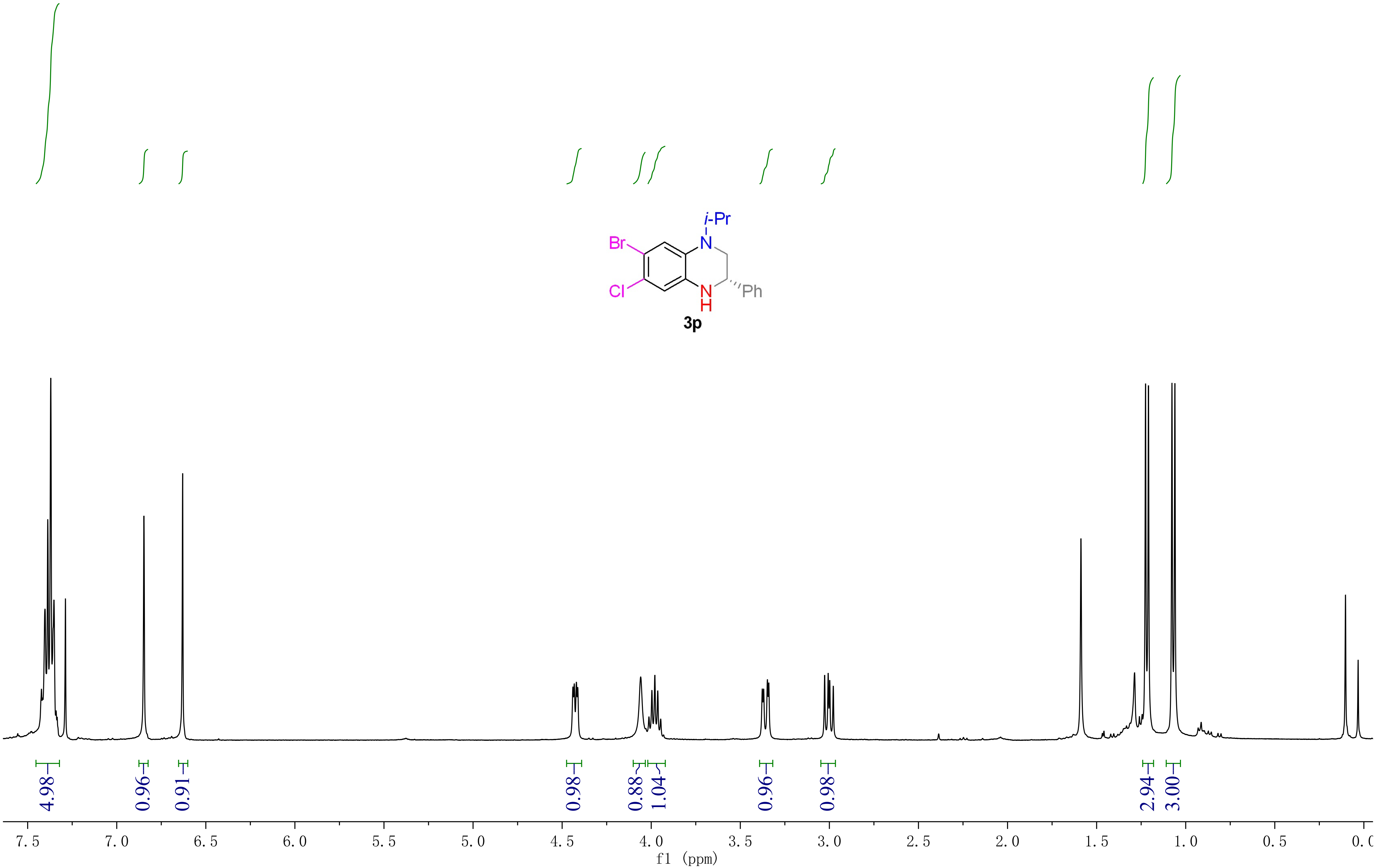
128.69
128.05
127.31
126.95
126.46
121.64
113.18
113.03
54.77
46.84
46.59
19.23
18.02
17.86
i-Pr
N
I
N
H
Ph
3n
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)



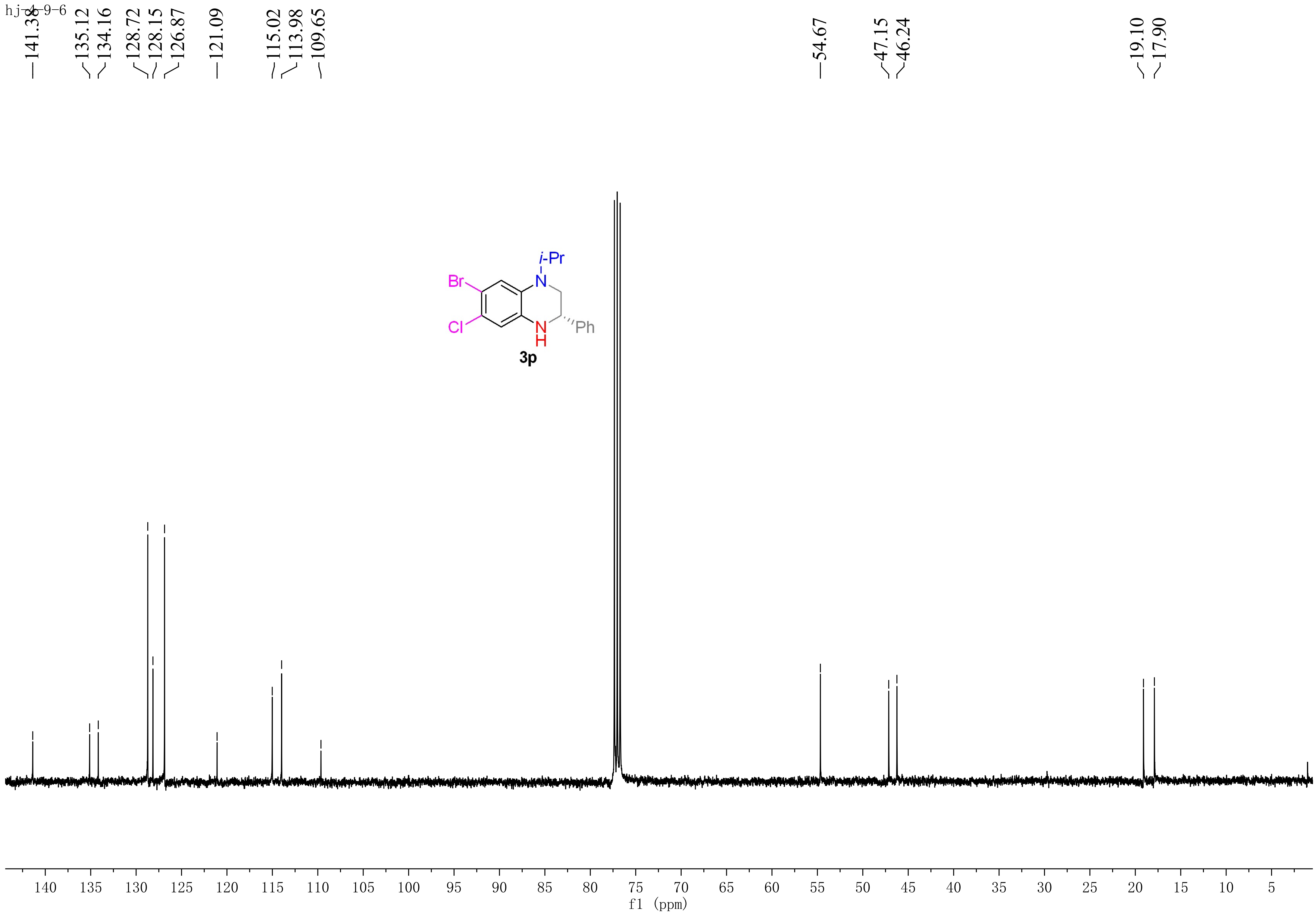
8.12
7.42 7.41 7.40 7.38 7.36 7.36 7.35 7.34 7.33
6.68 6.65
6.33 6.33 6.31 6.30 6.25 6.24
4.53 4.52 4.51 4.50
4.05 4.03 4.02 4.00 3.99 3.77
3.36 3.35 3.33 3.32
2.98 2.96 2.96 2.94
1.24 1.23 1.09 1.07
i-Pr
N
O
N
H
Ph
3o
3.99 0.93 0.96 0.94 0.95 0.96 1.77 3.00 1.01 1.00 3.16 3.21
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


hj-20-9-28-2
152.30
142.30
136.15
128.58
128.43
127.84
126.98
112.74
102.90
100.82
55.61
55.44
47.33
47.14
19.55
17.53
i-Pr
N
N
H
O
Ph
3o
f1 (ppm)

hj-4-9-6



Br
Cl
N
i-Pr
N
H
Ph
3p
4.98
0.96
0.91
0.98
0.88
1.04
0.96
0.98
2.94
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


hj-4-9-6
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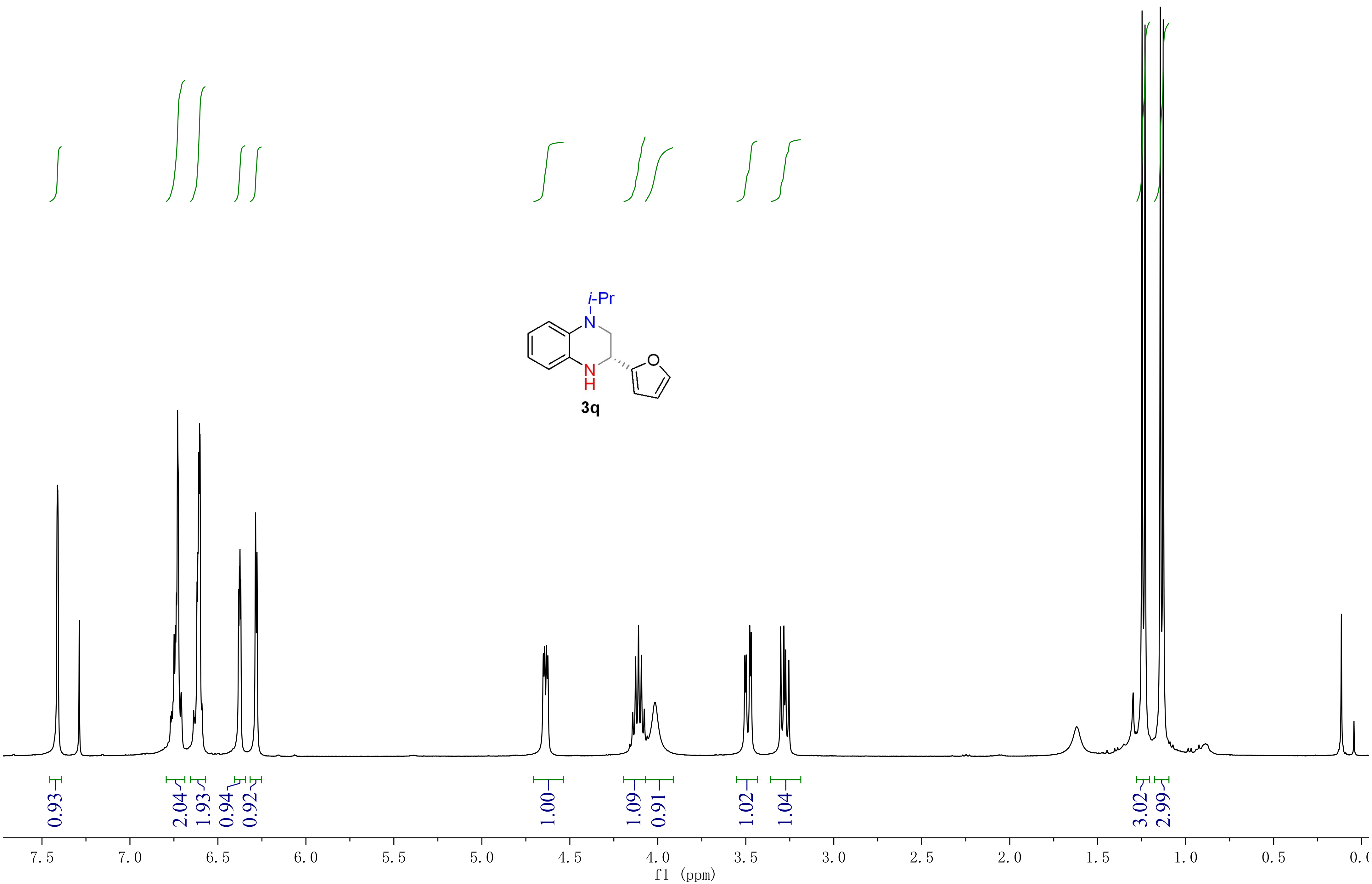
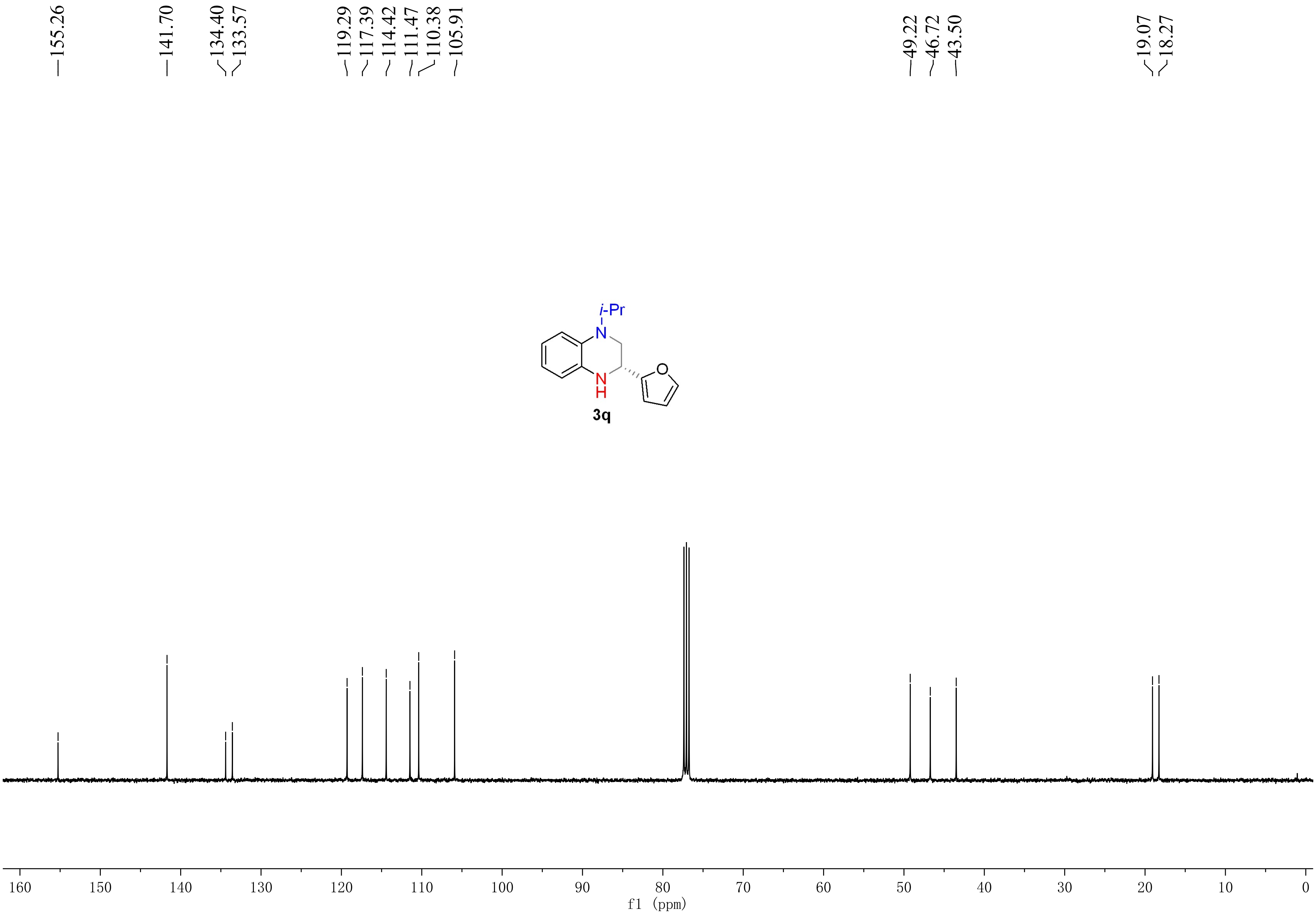
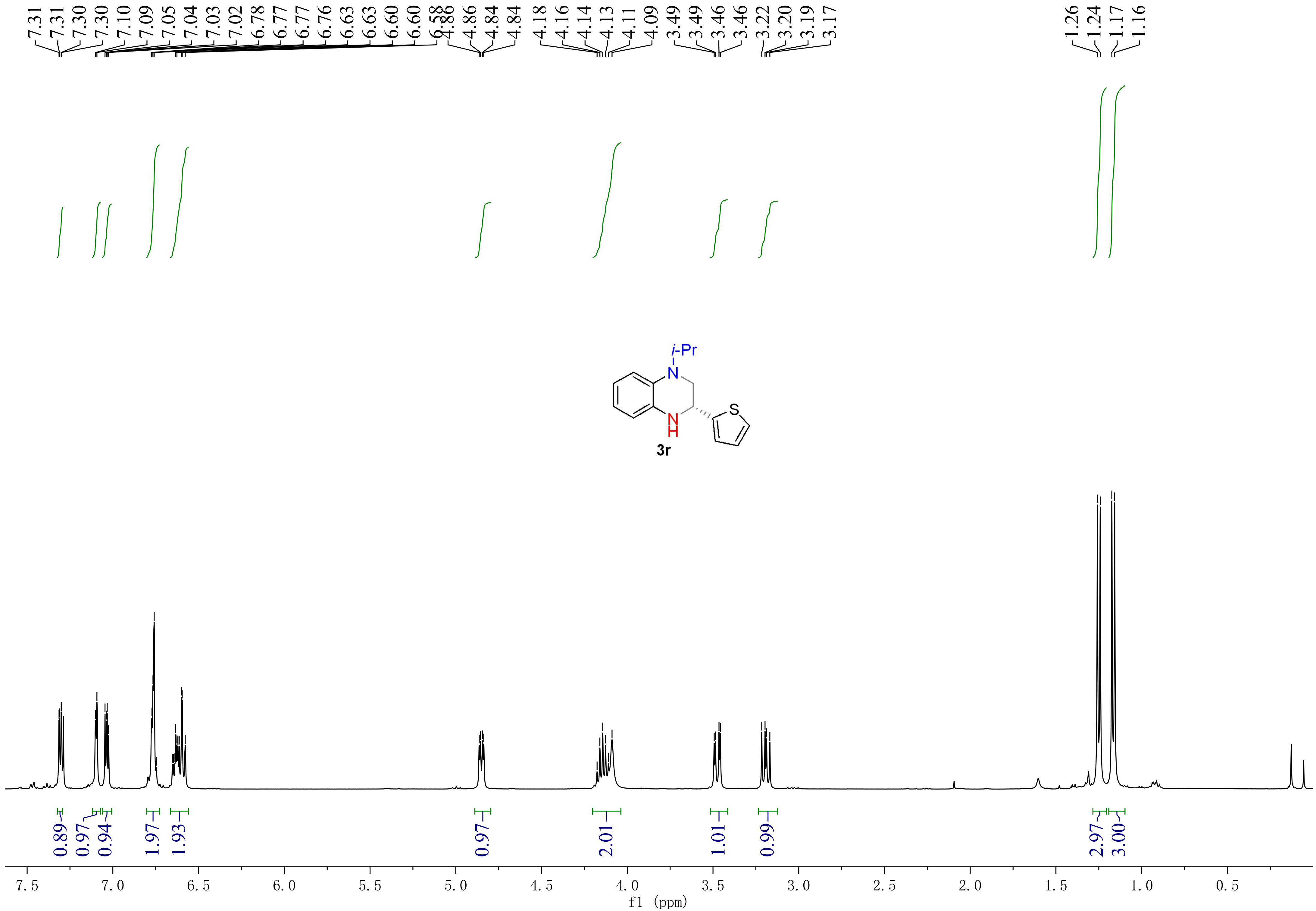
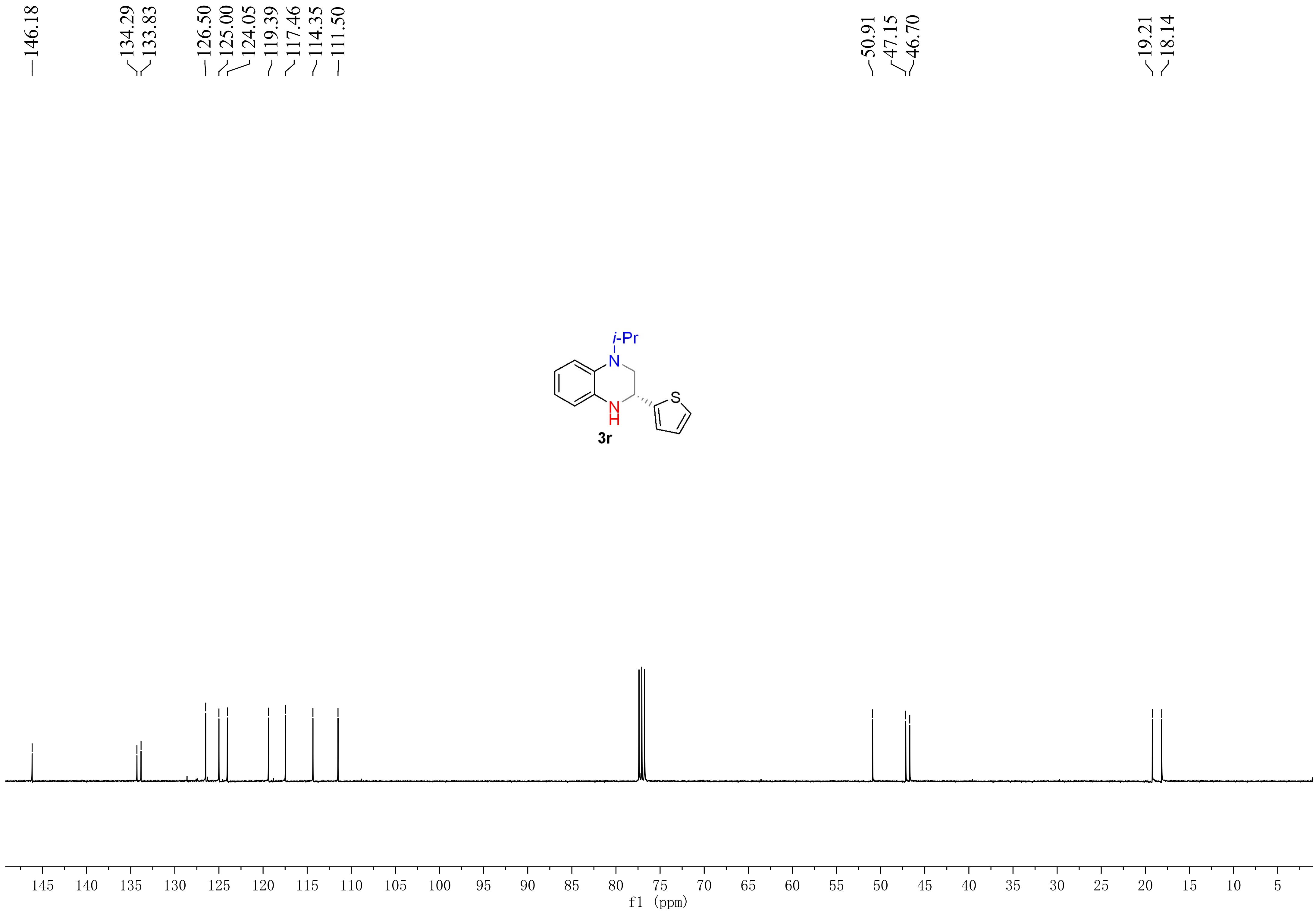
135.12
134.16
128.72
128.15
126.87
121.09
115.02
113.98
109.65
54.67
47.15
46.24
19.10
17.90
i-Pr
Br
N
Cl
N
H
Ph
3p
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

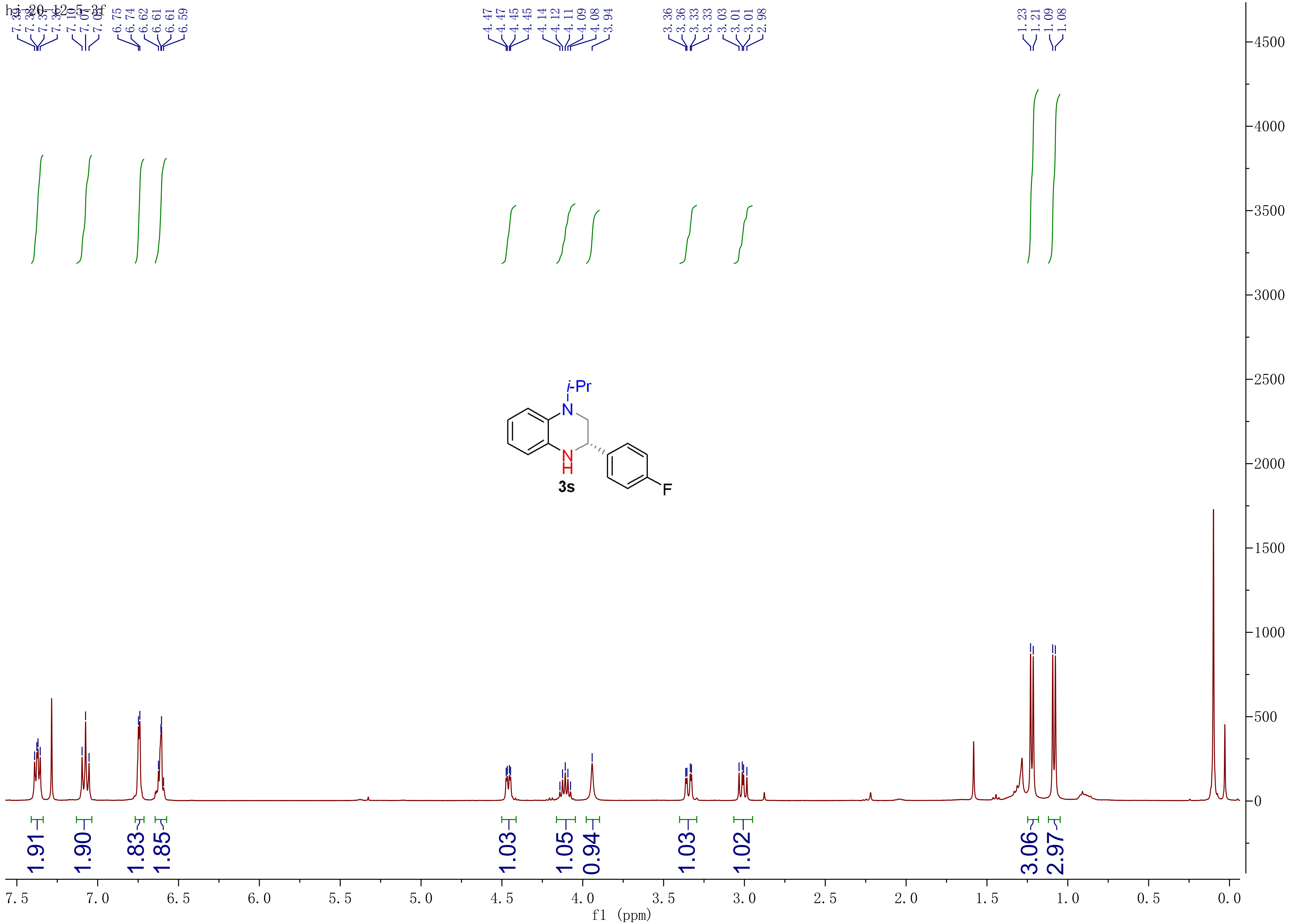


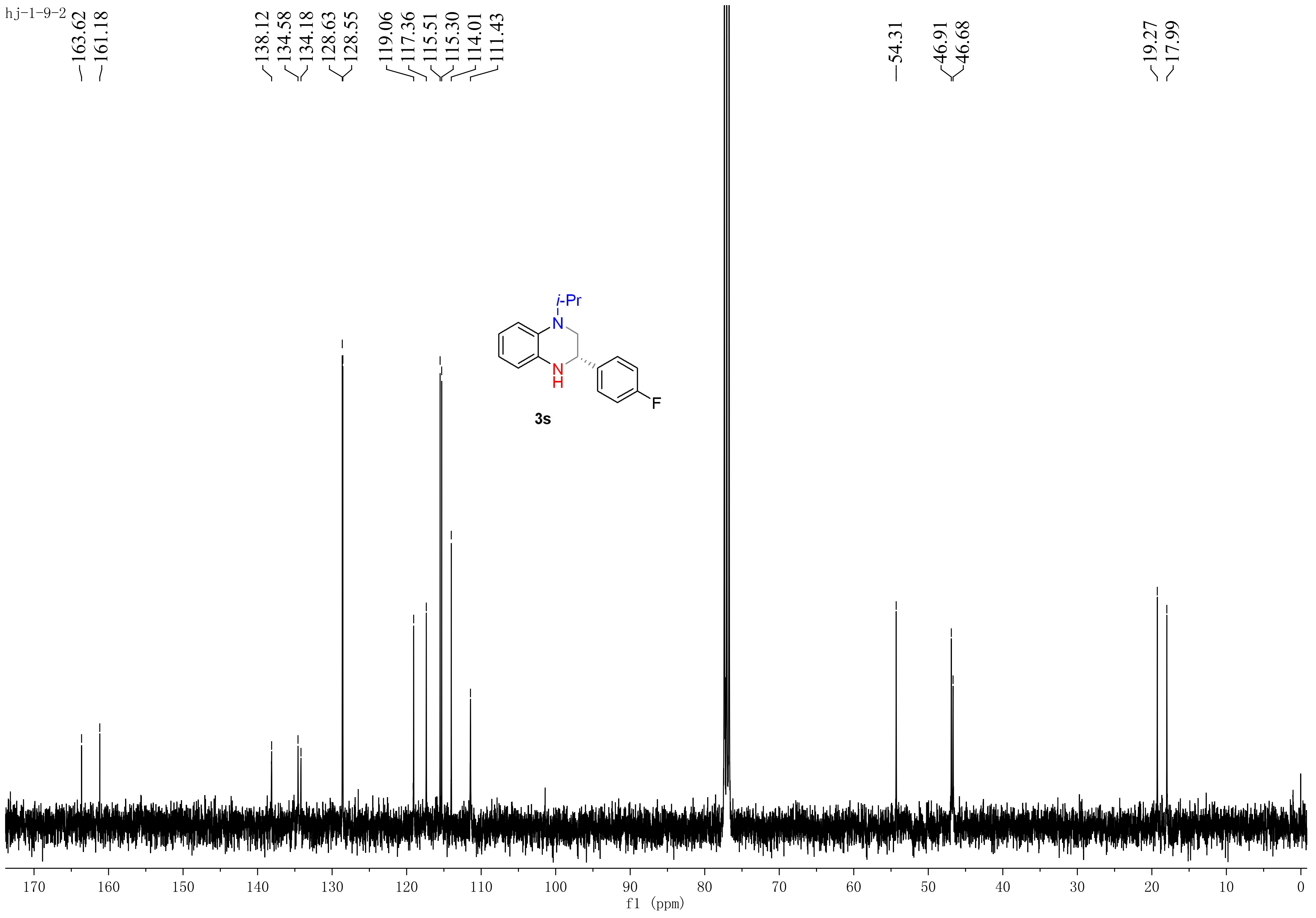
i-Pr
N
N
H
O
3q
0.93
2.04
1.93
0.94
0.92
1.00
1.09
0.91
1.02
1.04
3.02
2.99
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

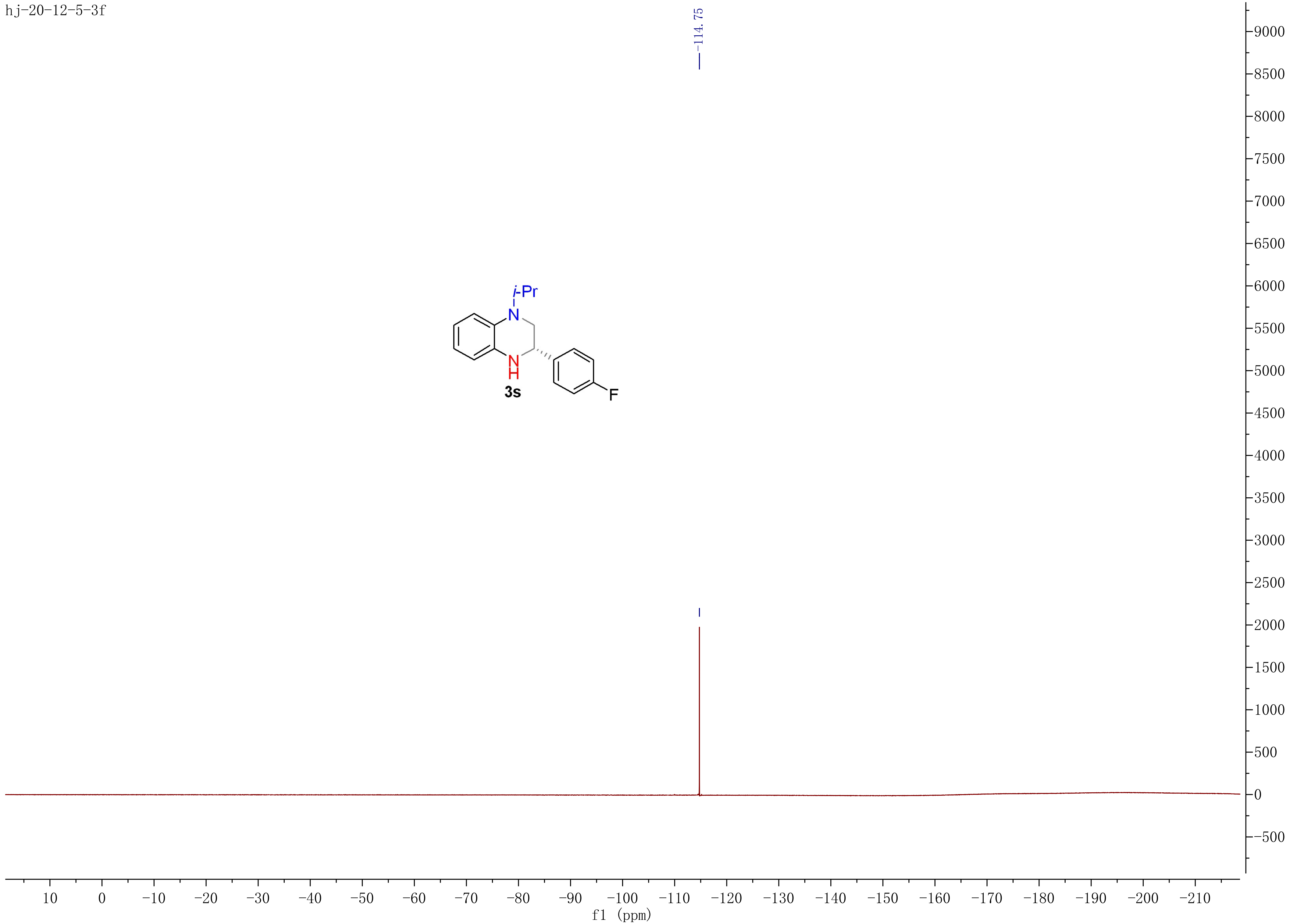

155.26
141.70
134.40
133.57
119.29
117.39
114.42
111.47
110.38
105.91
49.22
46.72
43.50
19.07
18.27
i-Pr
N
N
H
O
3q
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.31 7.31 7.30 7.30 7.10 7.09 7.05 7.04 7.03 7.02 6.78 6.77 6.77 6.76 6.63 6.63 6.60 6.60 6.58 4.86 4.86 4.84 4.84 4.18 4.16 4.14 4.13 4.11 4.09 3.49 3.49 3.46 3.46 3.22 3.20 3.19 3.17 1.26 1.24 1.17 1.16
i-Pr
N
N
H
S
3r
0.89 0.97 0.94 1.97 1.93 0.97 2.01 1.01 0.99 2.97 3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


146.18
134.29
133.83
126.50
125.00
124.05
119.39
117.46
114.35
111.50
50.91
47.15
46.70
19.21
18.14
i-Pr
N
N
H
S
3r
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)


hj-20-12-5-3f
i-Pr
N
N
H
F
3s
f1 (ppm)


hj-1-9-2
163.62
161.18
138.12
134.58
134.18
128.63
128.55
119.06
117.36
115.51
115.30
114.01
111.43
54.31
46.91
46.68
19.27
17.99
i-Pr
N
N
H
F
3s
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


hj-20-12-5-3f
-114.75
i-Pr
N
N
H
F
3s
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
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-180
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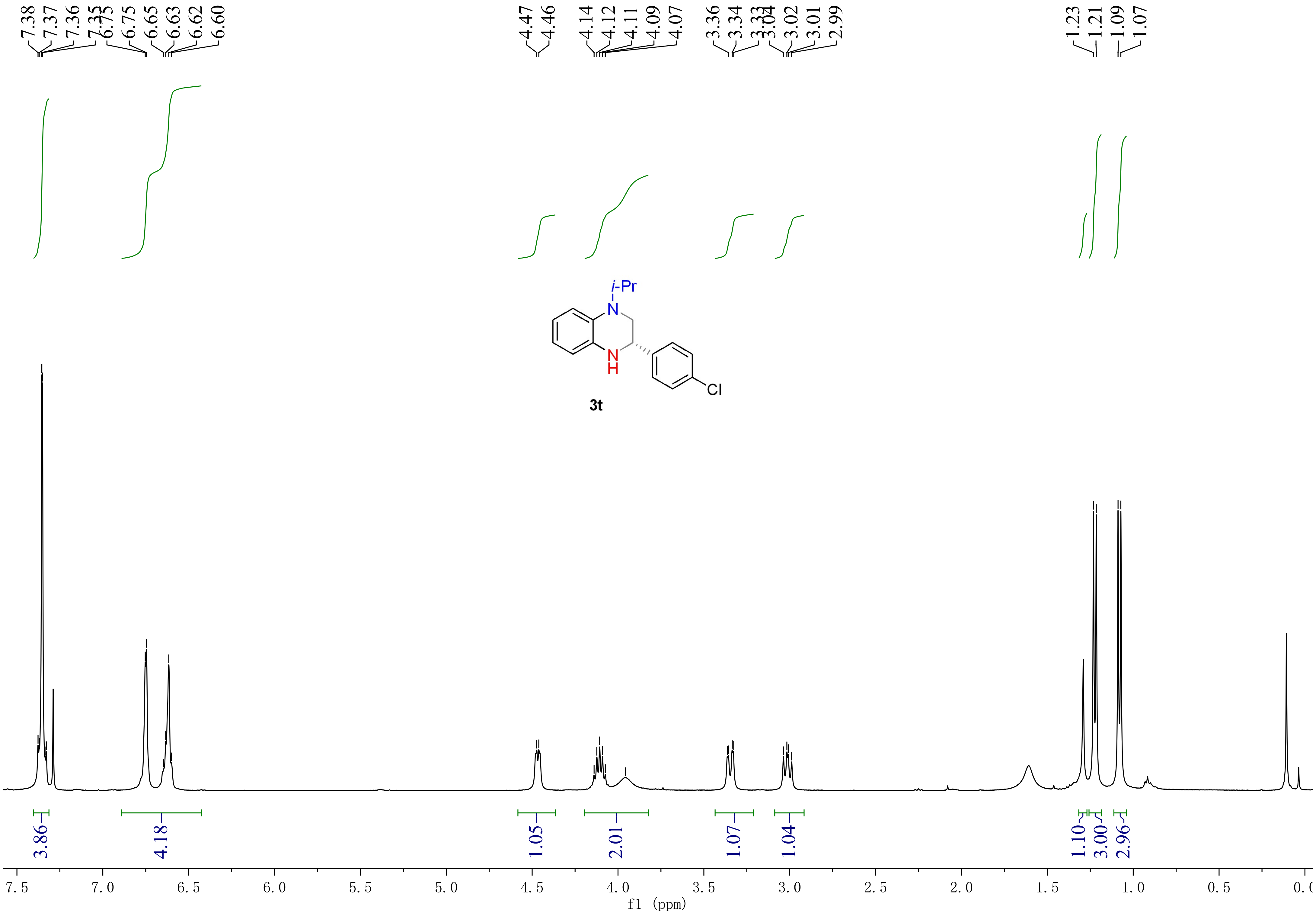
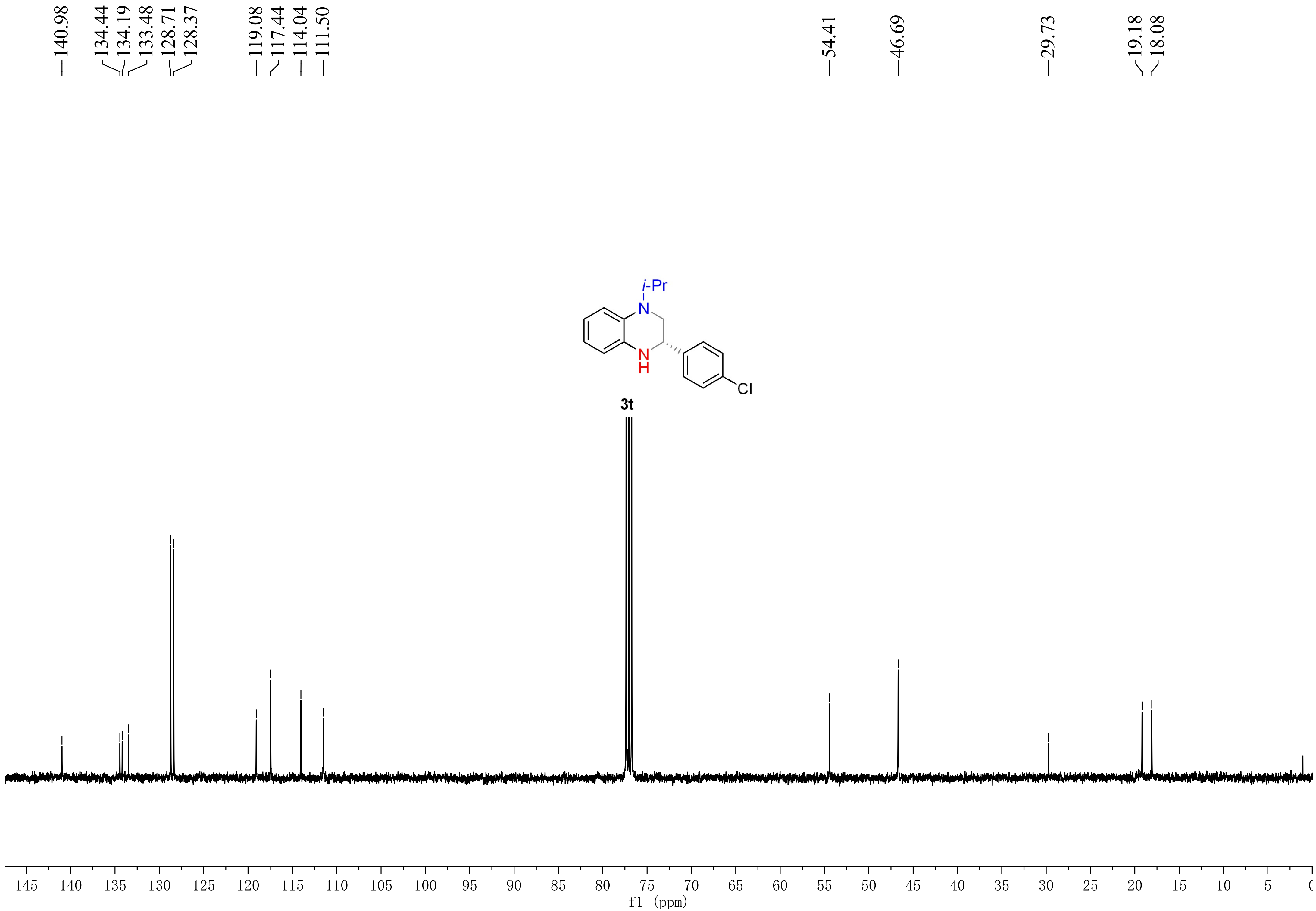
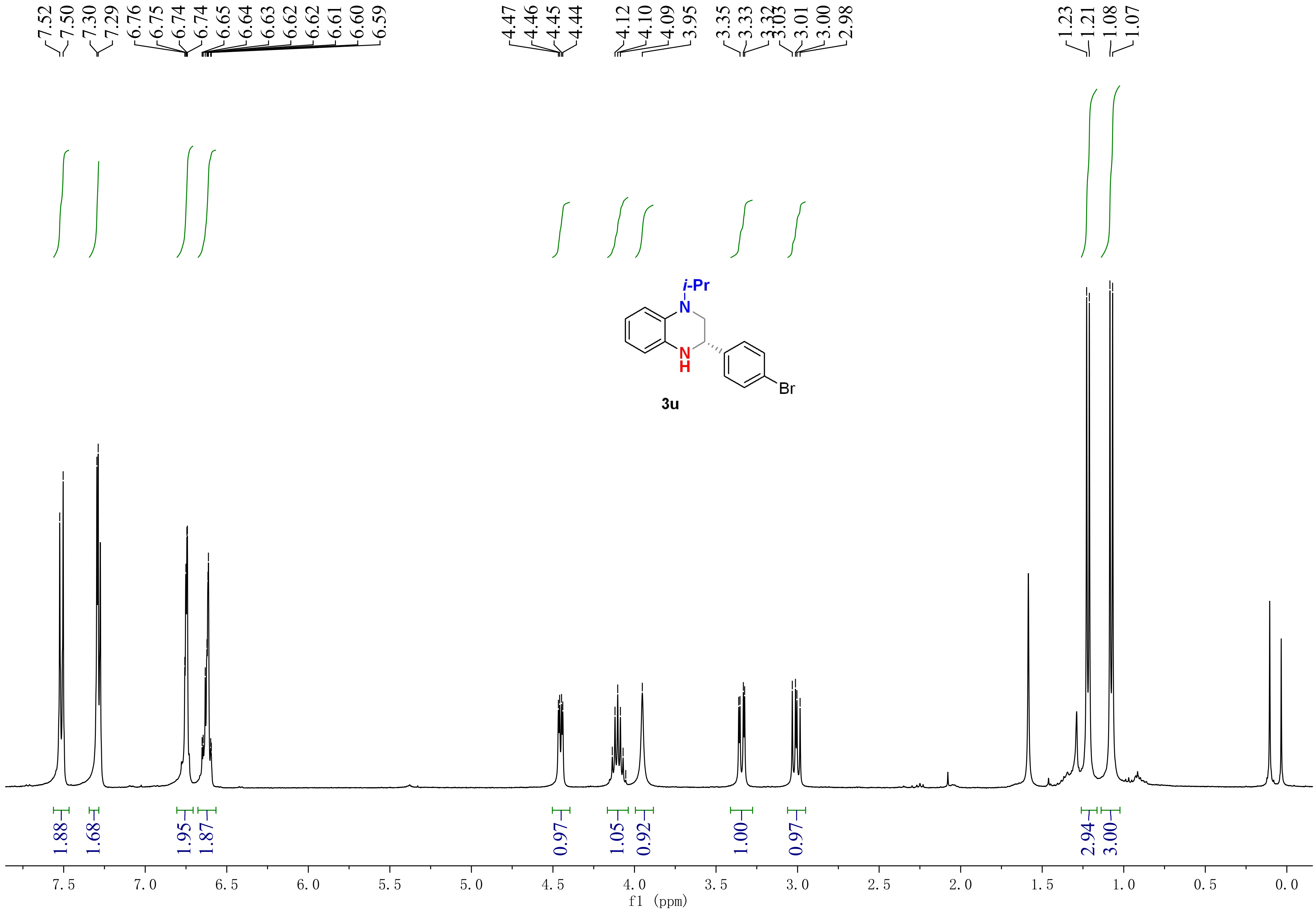
-200
-210
f1 (ppm)

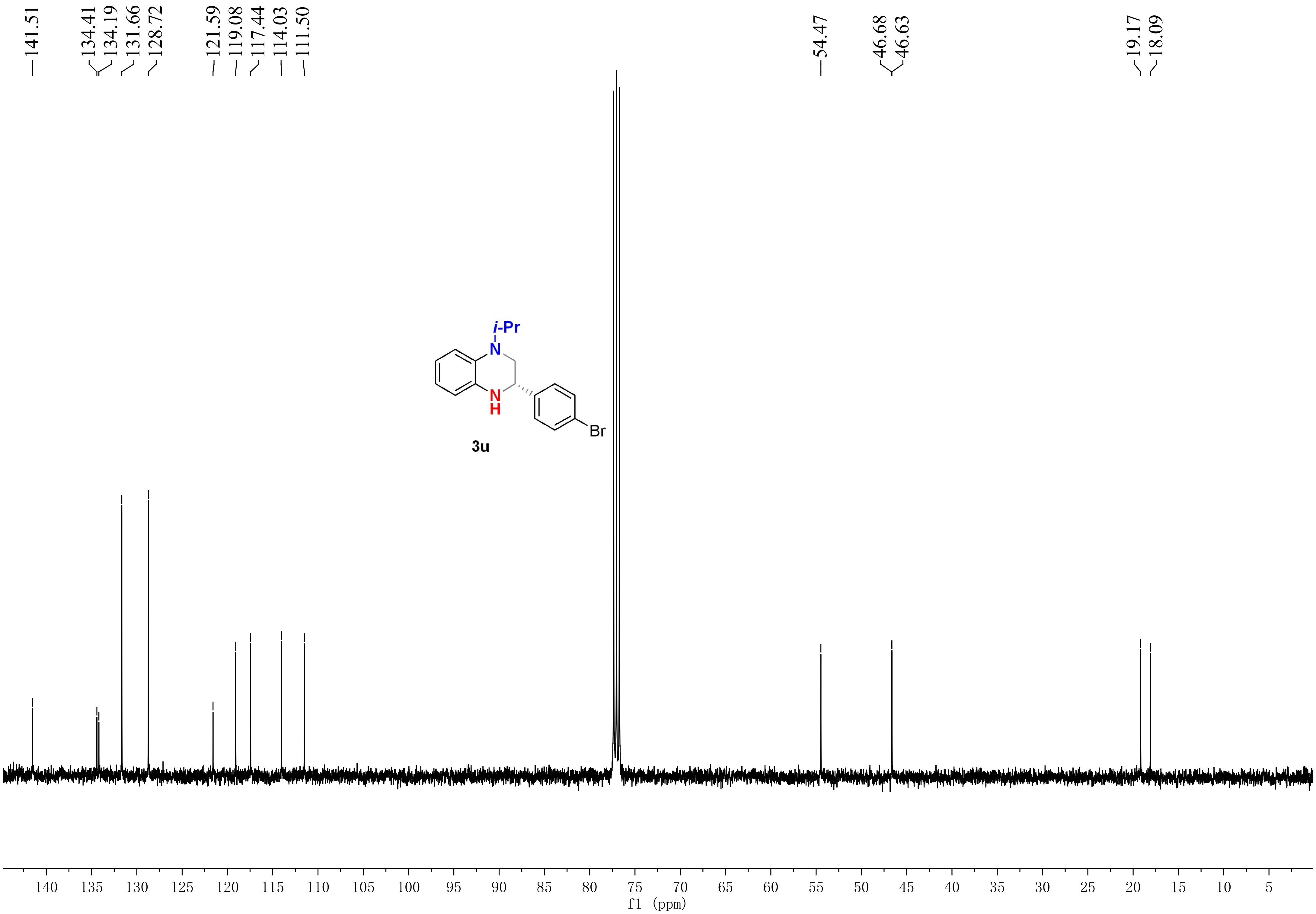


7.38
7.37
7.36
7.35
6.75
6.75
6.65
6.63
6.62
6.60
4.47
4.46
4.14
4.12
4.11
4.09
4.07
3.36
3.34
3.33
3.04
3.02
3.01
2.99
1.23
1.21
1.09
1.07
i-Pr
N
N
H
Cl
3.86
4.18
1.05
2.01
1.07
1.04
1.10
3.00
2.96
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

3t


140.98
134.44
134.19
133.48
128.71
128.37
119.08
117.44
114.04
111.50
54.41
46.69
29.73
19.18
18.08
i-Pr
N
N
H
Cl
3t
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)


7.52
7.50
7.30
7.29
6.76
6.75
6.74
6.74
6.65
6.64
6.63
6.62
6.62
6.61
6.60
6.59
4.47
4.46
4.45
4.44
4.12
4.10
4.09
3.95
3.35
3.33
3.32
3.03
3.01
3.00
2.98
1.23
1.21
1.08
1.07
i-Pr
N
N
H
Br
3u
1.88
1.68
1.95
1.87
0.97
1.05
0.92
1.00
0.97
2.94
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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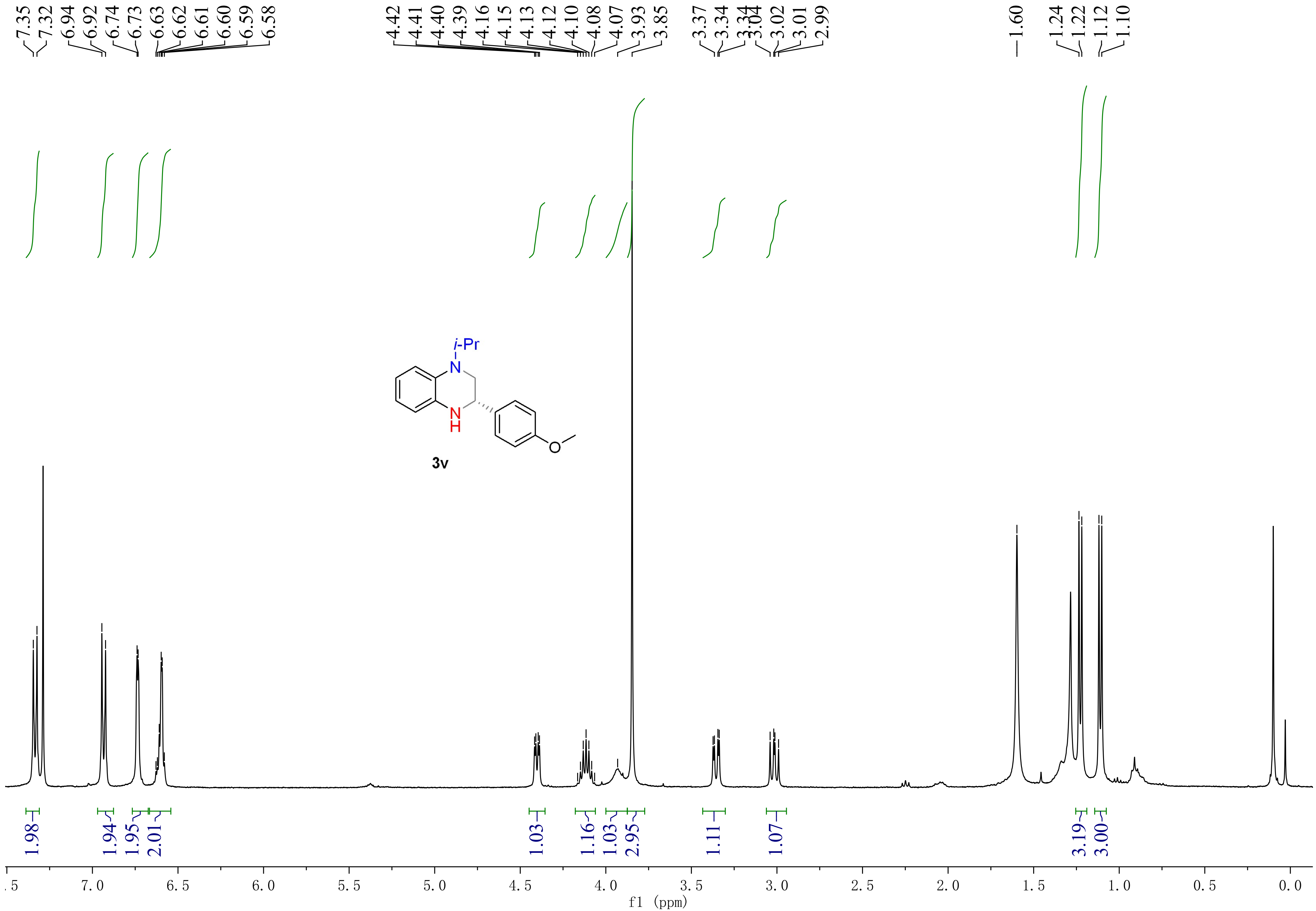
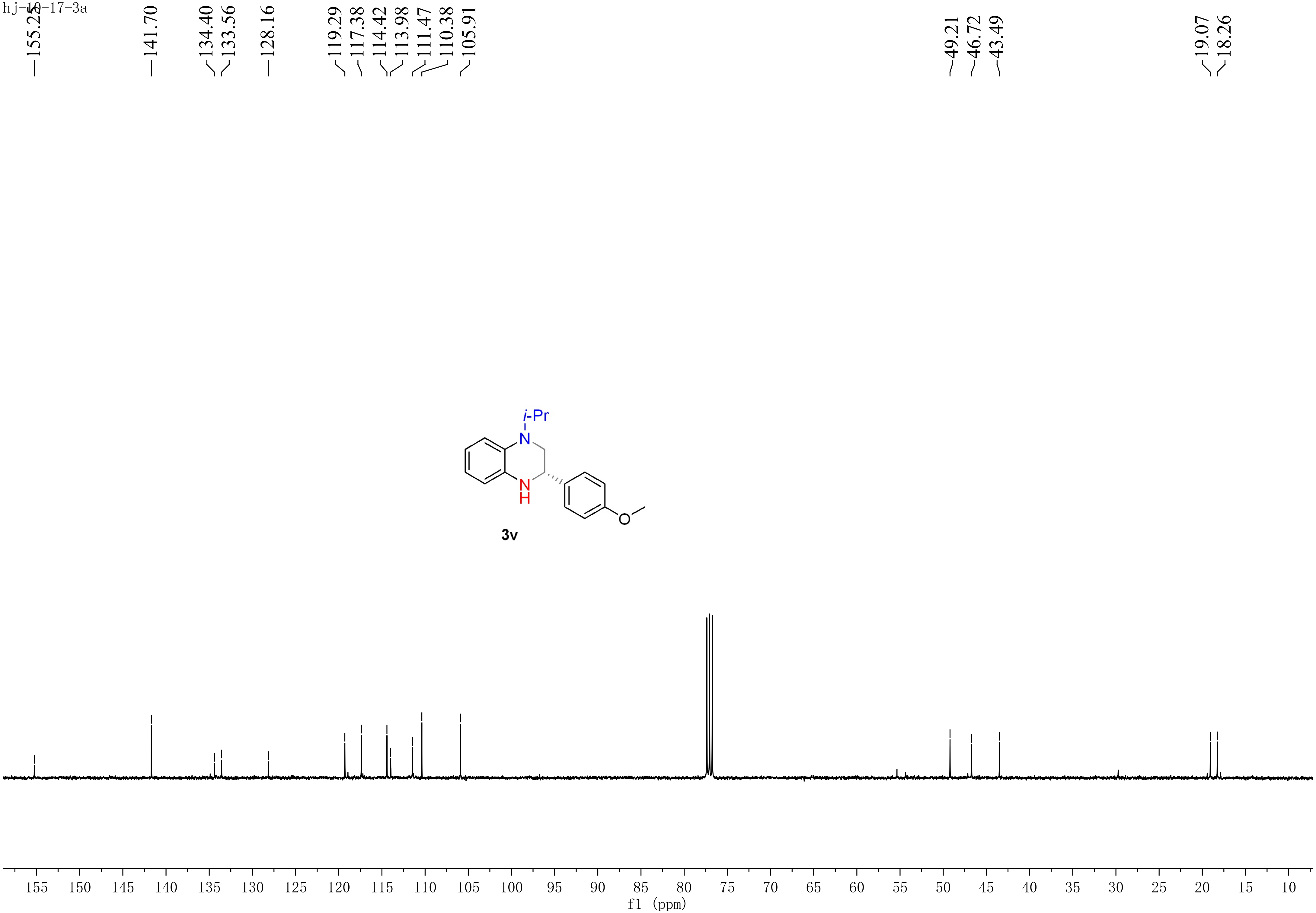
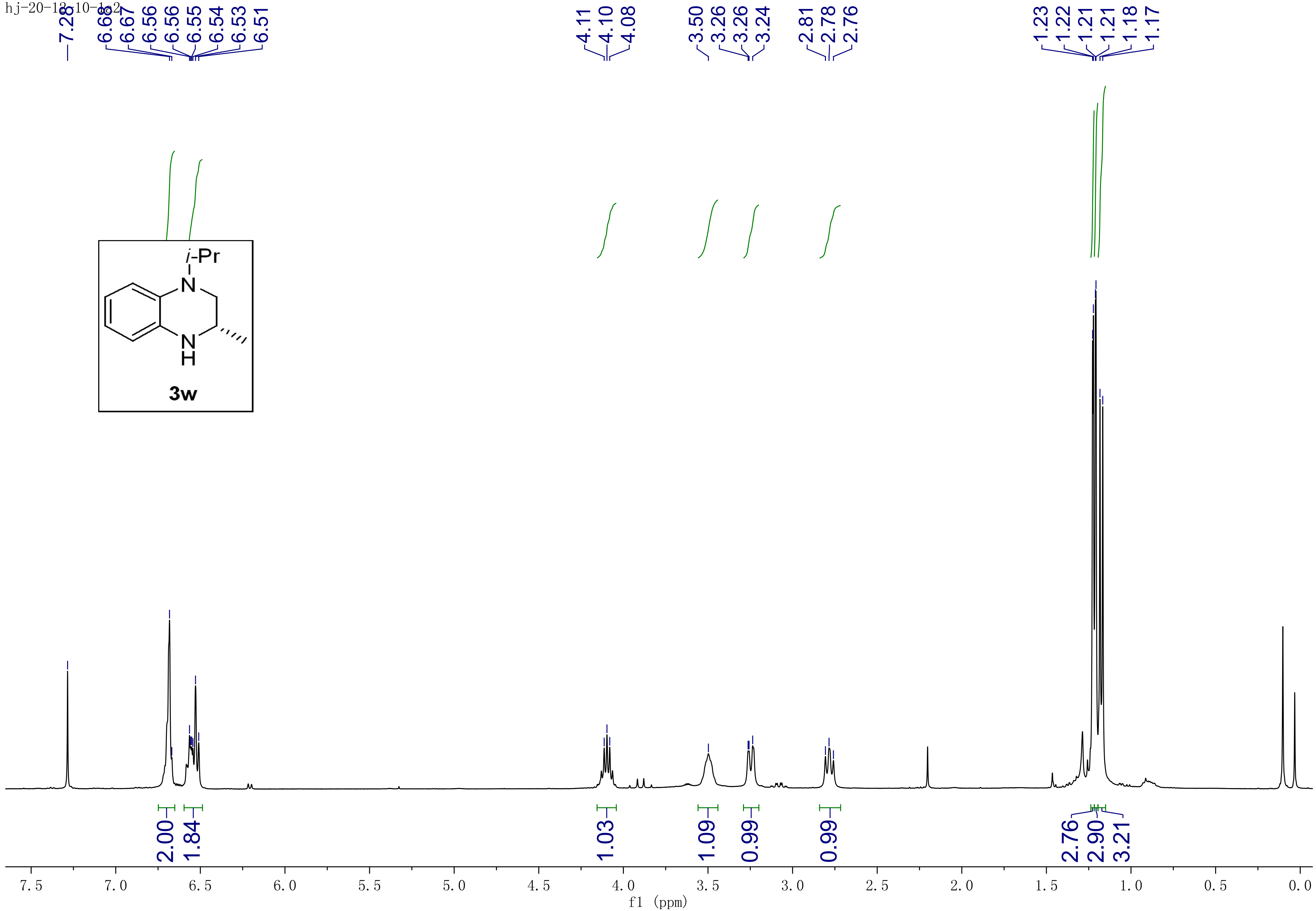
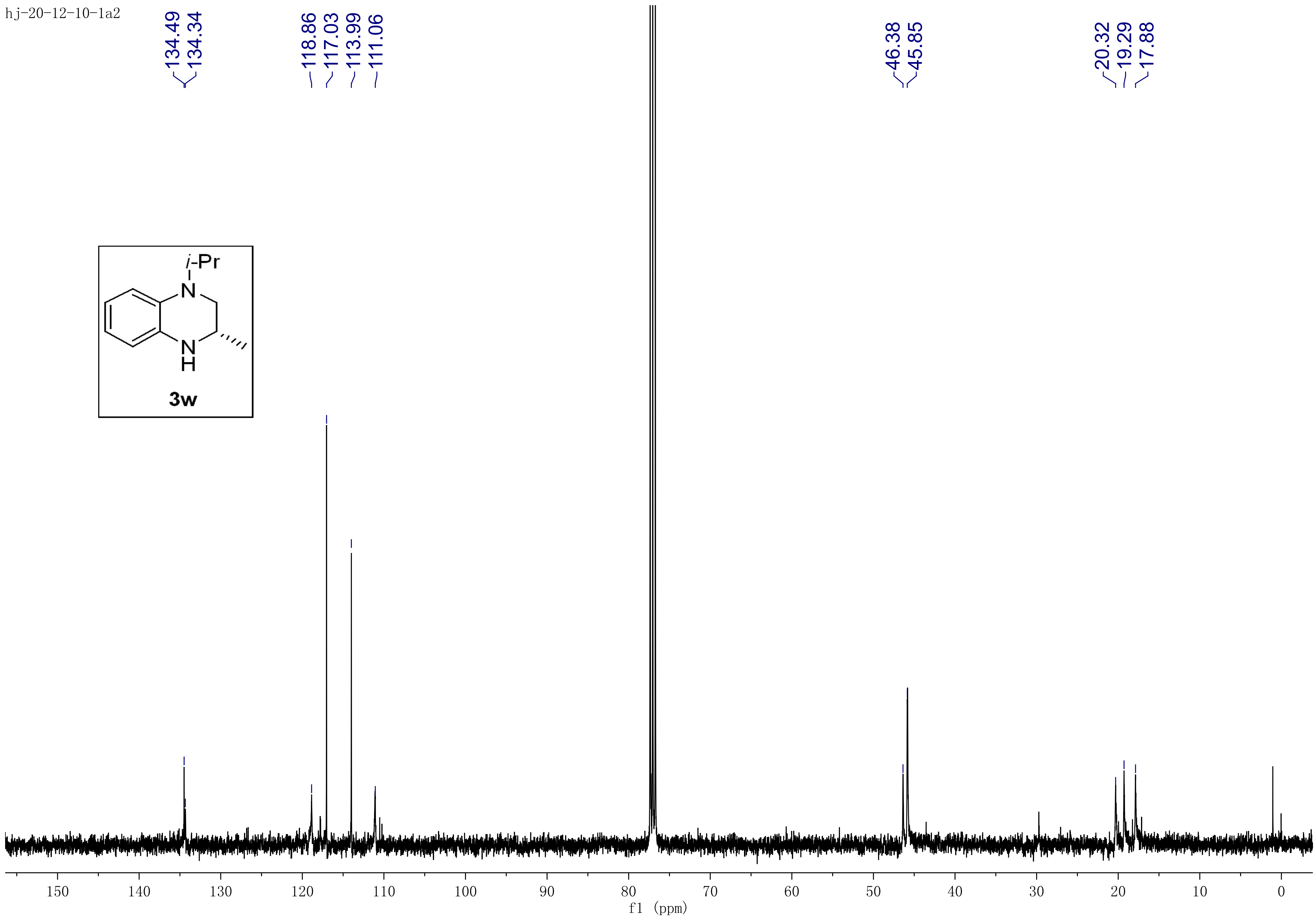
134.41
134.19
131.66
128.72
121.59
119.08
117.44
114.03
111.50
54.47
46.68
46.63
19.17
18.09
i-Pr
N
N
H
Br
3u
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

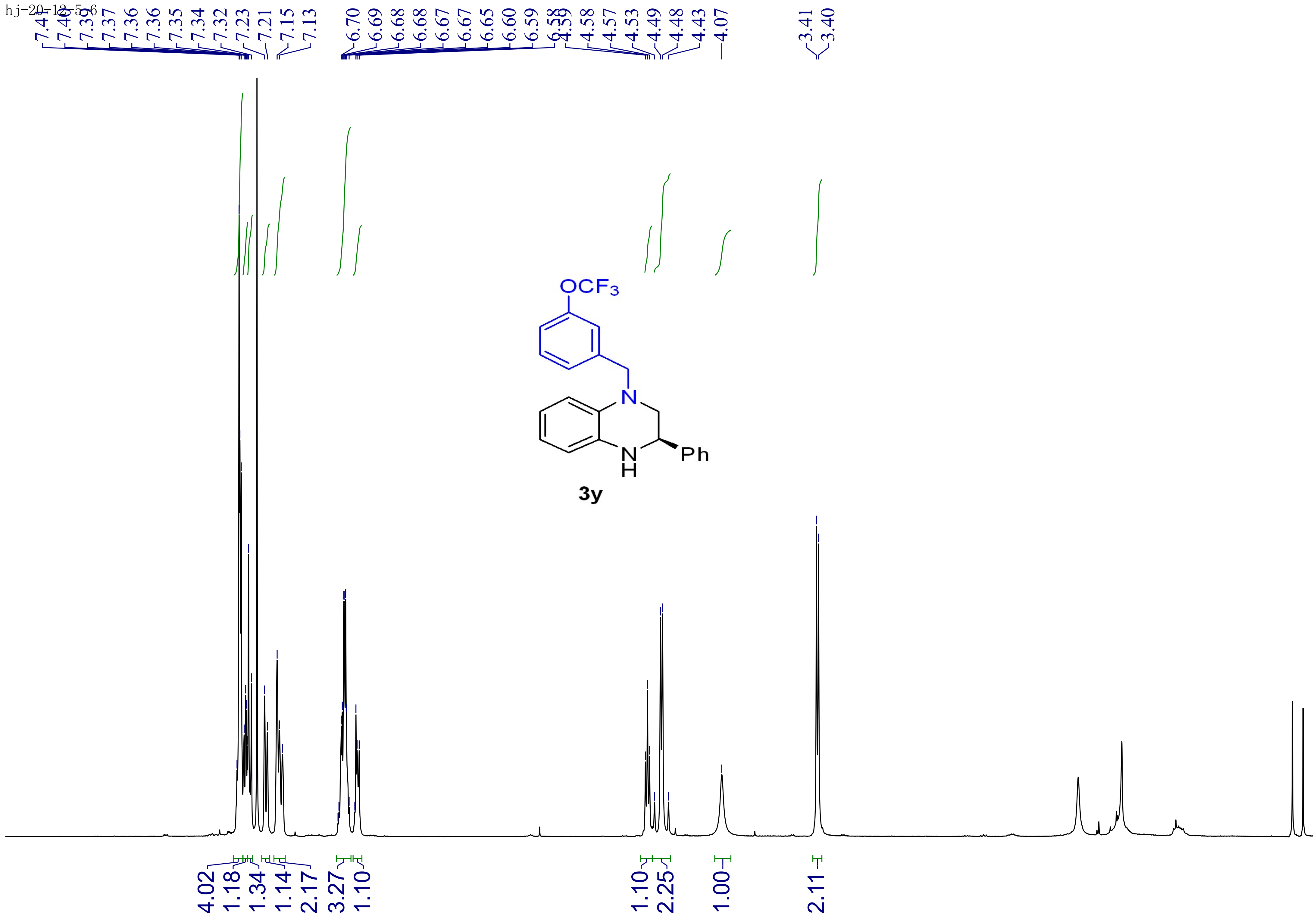

7.35
7.32
6.94
6.92
6.74
6.73
6.63
6.62
6.61
6.60
6.59
6.58
4.42
4.41
4.40
4.39
4.16
4.15
4.13
4.12
4.10
4.08
4.07
3.93
3.85
3.37
3.34
3.34
3.04
3.02
3.01
2.99
1.60
1.24
1.22
1.12
1.10
i-Pr
N
N
H
O
3v
1.98
1.94
1.95
2.01
1.03
1.16
1.03
2.95
1.11
1.07
3.19
3.00
.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

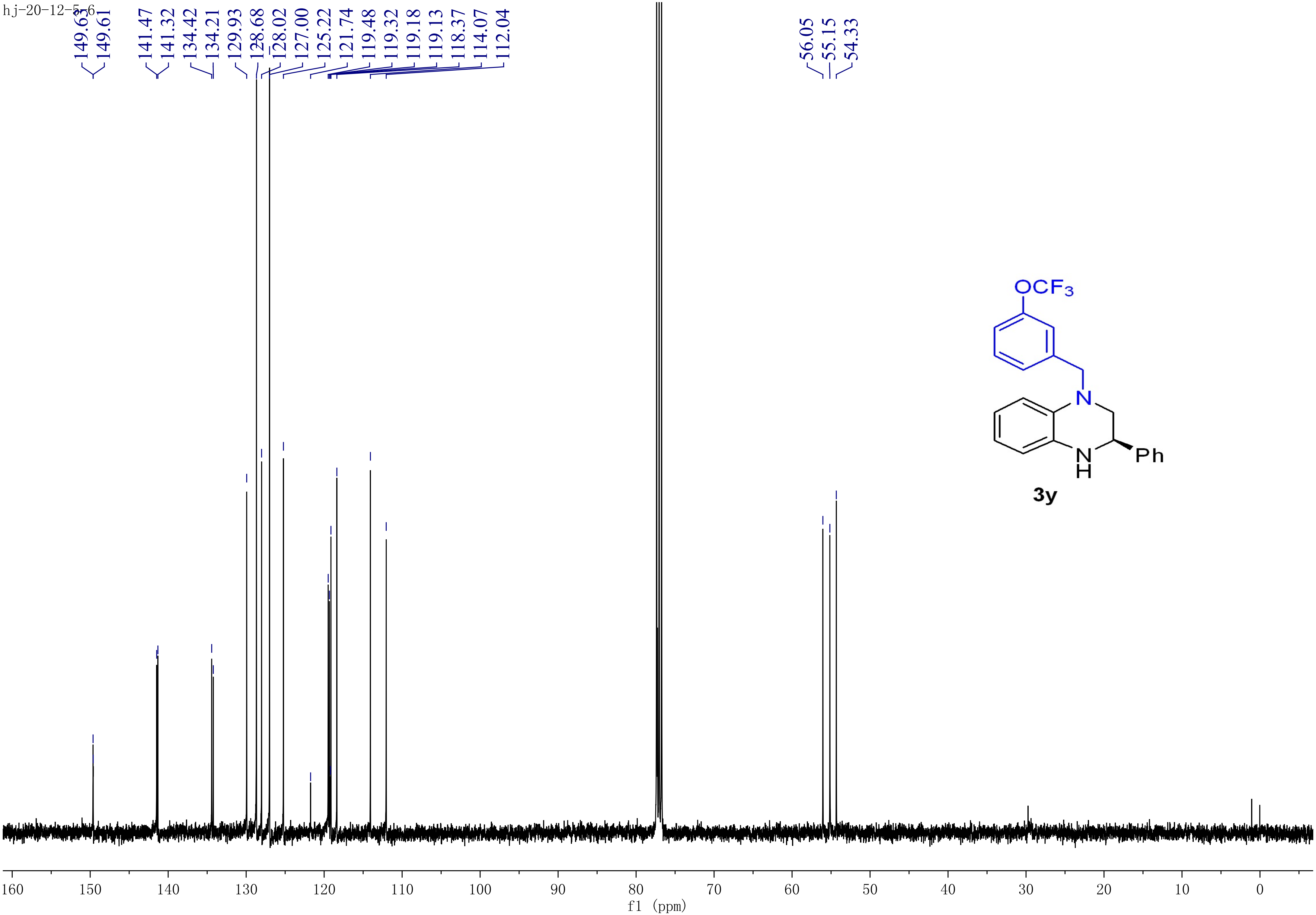


hj-10-17-3a
155.25
141.70
134.40
133.56
128.16
119.29
117.38
114.42
113.98
111.47
110.38
105.91
49.21
46.72
43.49
19.07
18.26
i-Pr
N
N
H
O
3v
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)


hj-20-12-10-1-2
7.28
6.68
6.67
6.56
6.56
6.55
6.54
6.53
6.51
4.11
4.10
4.08
3.50
3.26
3.26
3.24
2.81
2.78
2.76
1.23
1.22
1.21
1.21
1.18
1.17
i-Pr
N
N
H
3w
2.00
1.84
1.03
1.09
0.99
0.99
2.76
2.90
3.21
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


hj-20-12-10-1a2
134.49
134.34
118.86
117.03
113.99
111.06
46.38
45.85
20.32
19.29
17.88
i-Pr
N
N
H
3w
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


hj-20-12-5-6
7.41
7.40
7.39
7.37
7.36
7.36
7.35
7.34
7.32
7.23
7.21
7.15
7.13
6.70
6.69
6.68
6.68
6.67
6.67
6.65
6.60
6.59
6.58
4.59
4.58
4.57
4.53
4.49
4.48
4.43
4.07
3.41
3.40
OCF3
N
N
H
Ph
3y
4.02
1.18
1.34
1.14
2.17
3.27
1.10
1.10
2.25
1.00
2.11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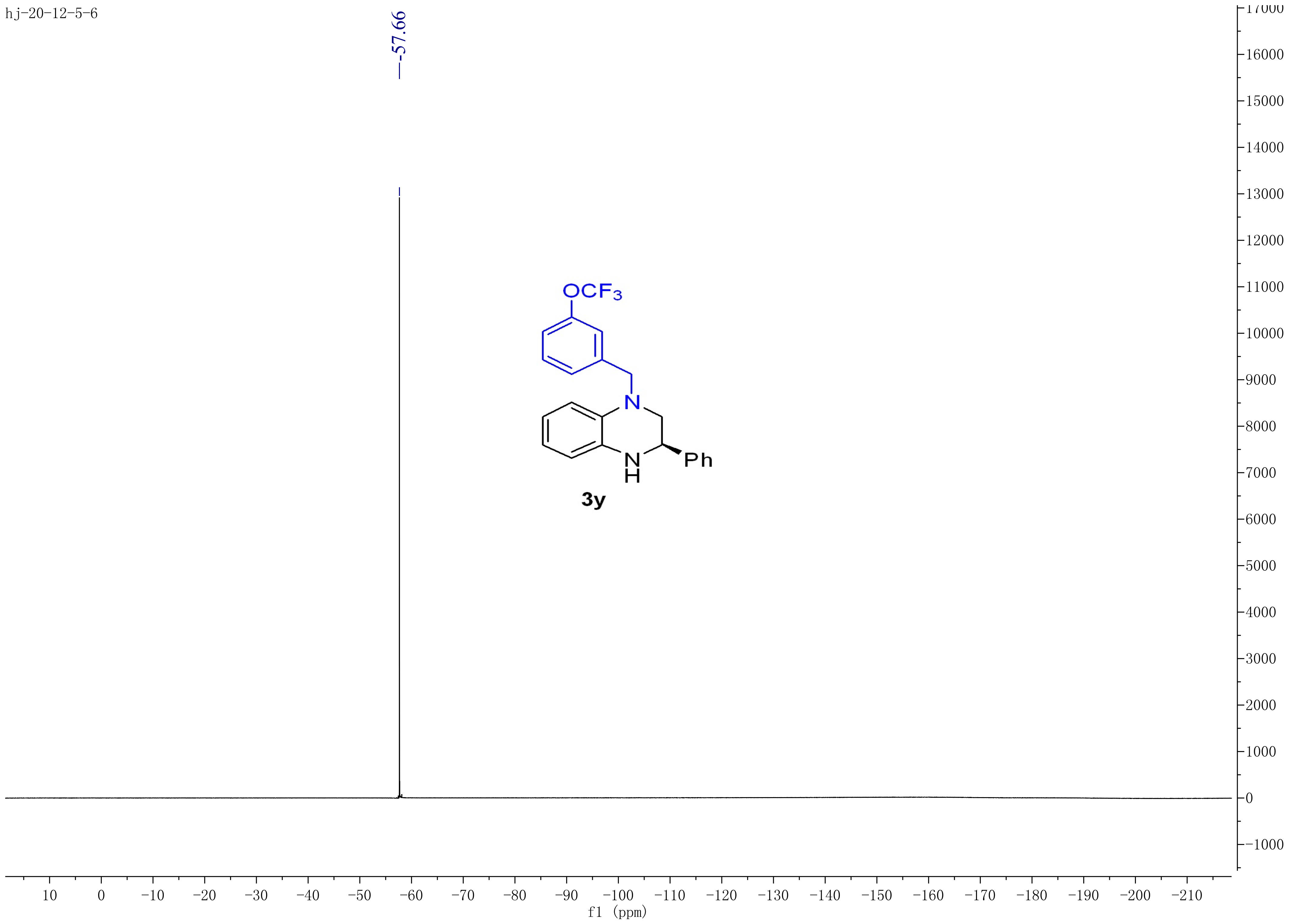
149.63
149.61
141.47
141.32
134.42
134.21
129.93
128.68
128.02
127.00
125.22
121.74
119.48
119.32
119.18
119.13
118.37
114.07
112.04
56.05
55.15
54.33
OCF3
N
N
H
Ph
3y
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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-57.66
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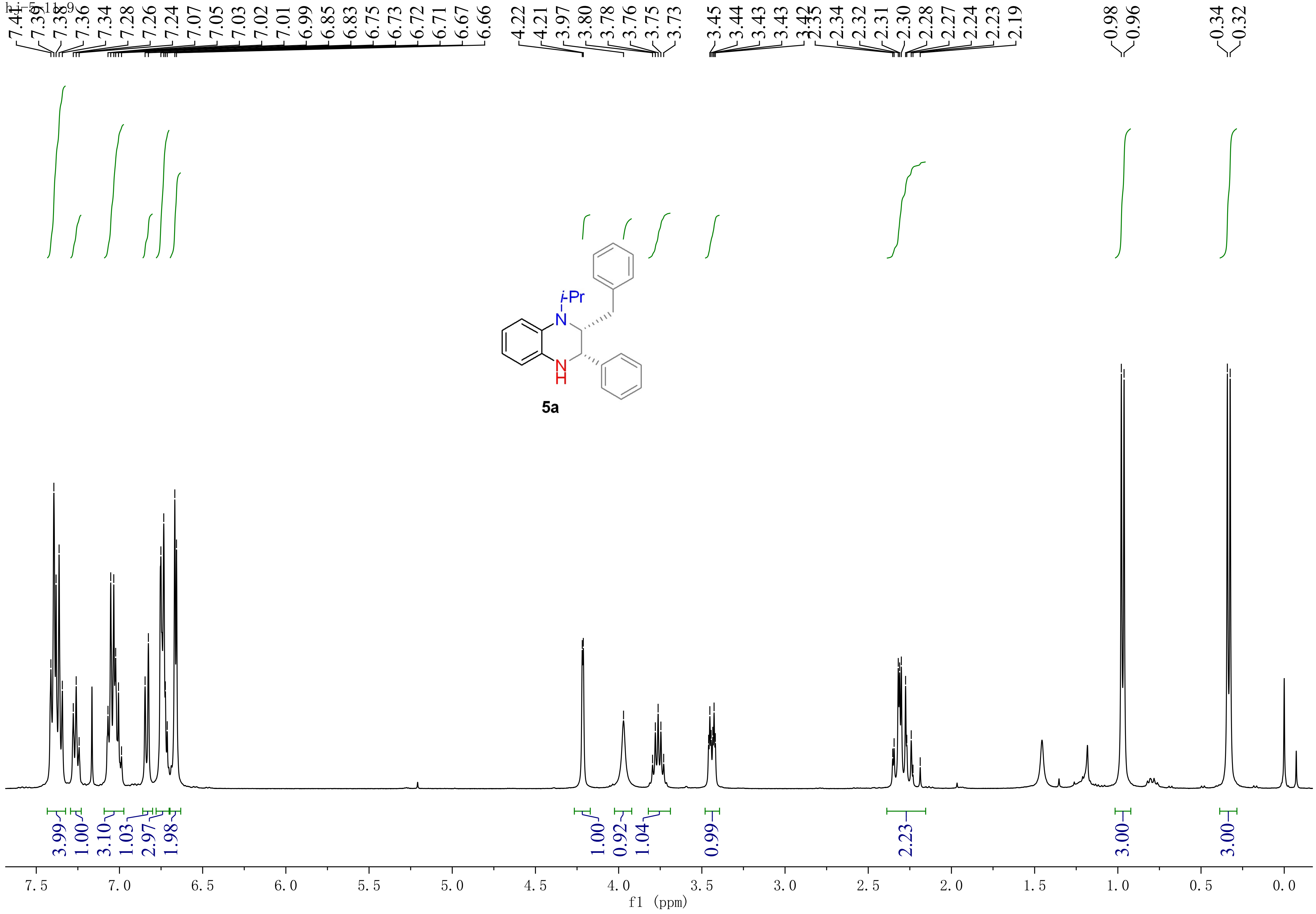
N
N
H
Ph
3y
f1 (ppm)


hj-5-11-9
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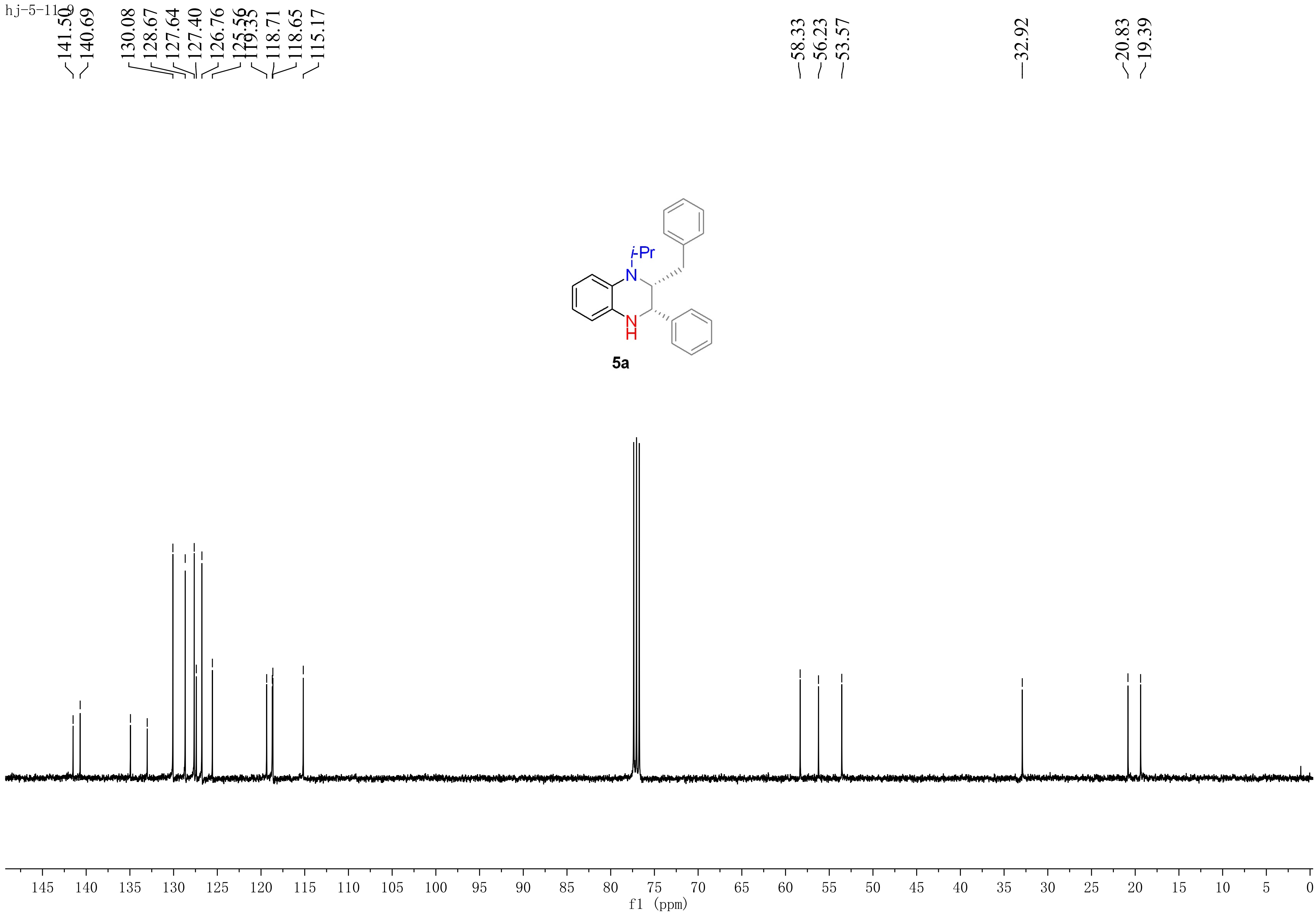
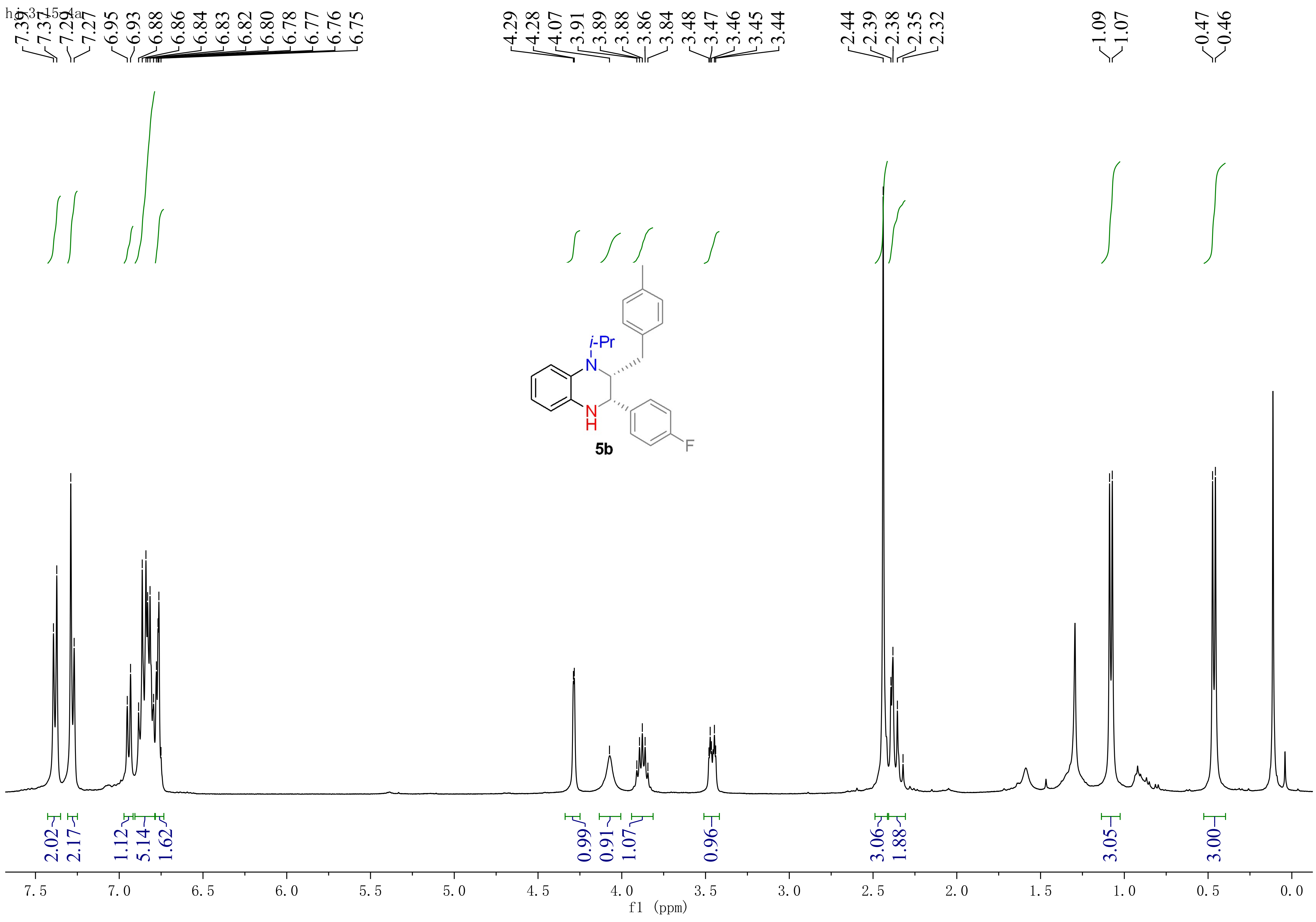
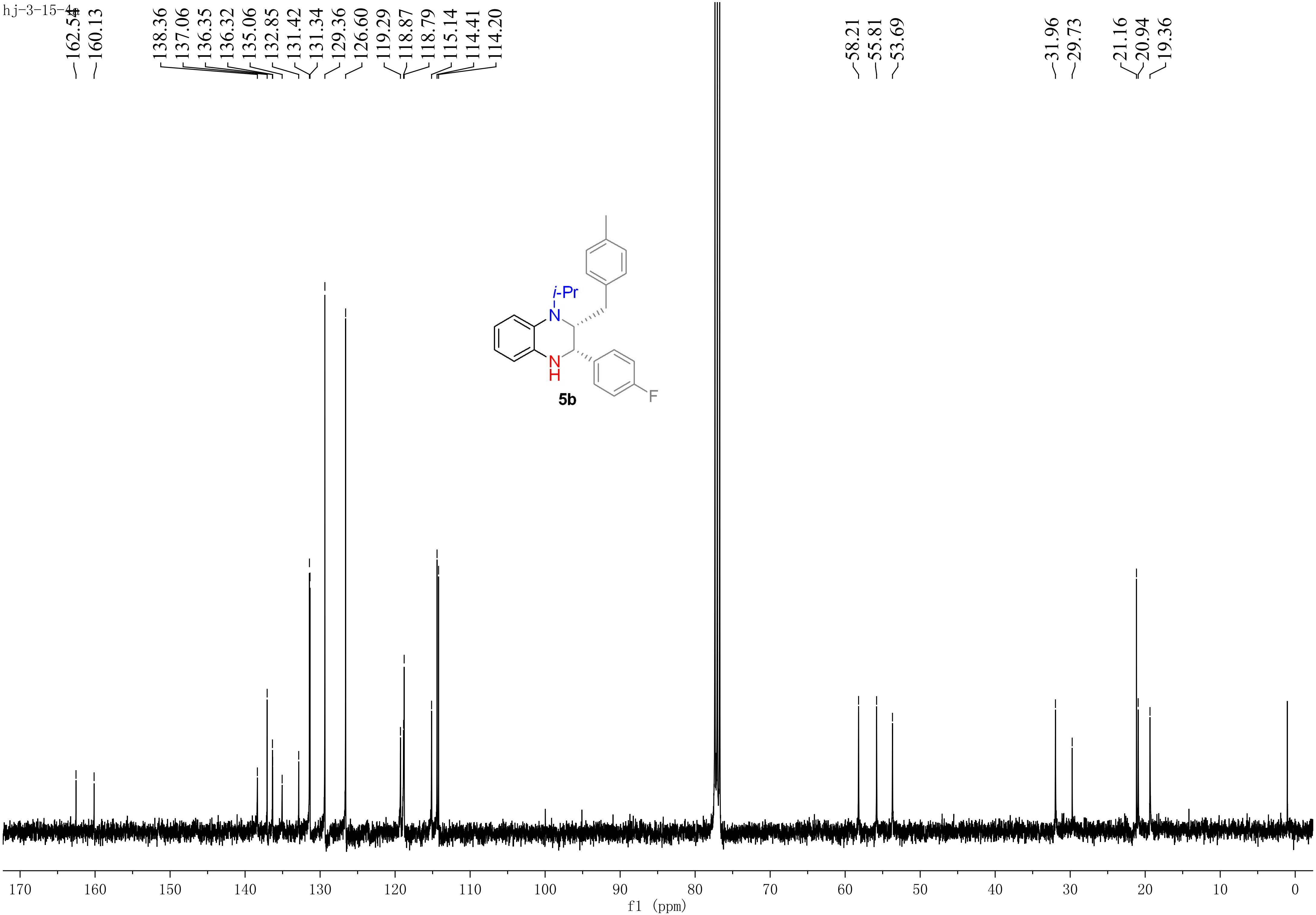
4.22 4.21 3.97 3.80 3.78 3.76 3.75 3.73
3.45 3.44 3.43 3.43 3.42 2.35 2.34 2.32 2.31 2.30 2.28 2.27 2.24 2.23 2.19
0.98 0.96
0.34 0.32
i-Pr
N
N
H
5a
3.99 1.00 3.10 1.03 2.97 1.98
1.00 0.92 1.04
0.99
2.23
3.00
3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



hj-5-11-9
141.50
140.69
130.08
128.67
127.64
127.40
126.76
125.56
119.35
118.71
118.65
115.17
58.33
56.23
53.57
32.92
20.83
19.39
i-Pr
N
N
H
5a
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


hj-3-15-4a
7.39
7.37
7.29
7.27
6.95
6.93
6.88
6.86
6.84
6.83
6.82
6.80
6.78
6.77
6.76
6.75
4.29
4.28
4.07
3.91
3.89
3.88
3.86
3.84
3.48
3.47
3.46
3.45
3.44
2.44
2.39
2.38
2.35
2.32
1.09
1.07
0.47
0.46
i-Pr
N
N
H
F
5b
2.02
2.17
1.12
5.14
1.62
0.99
0.91
1.07
0.96
3.06
1.88
3.05
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


hj-3-15-4
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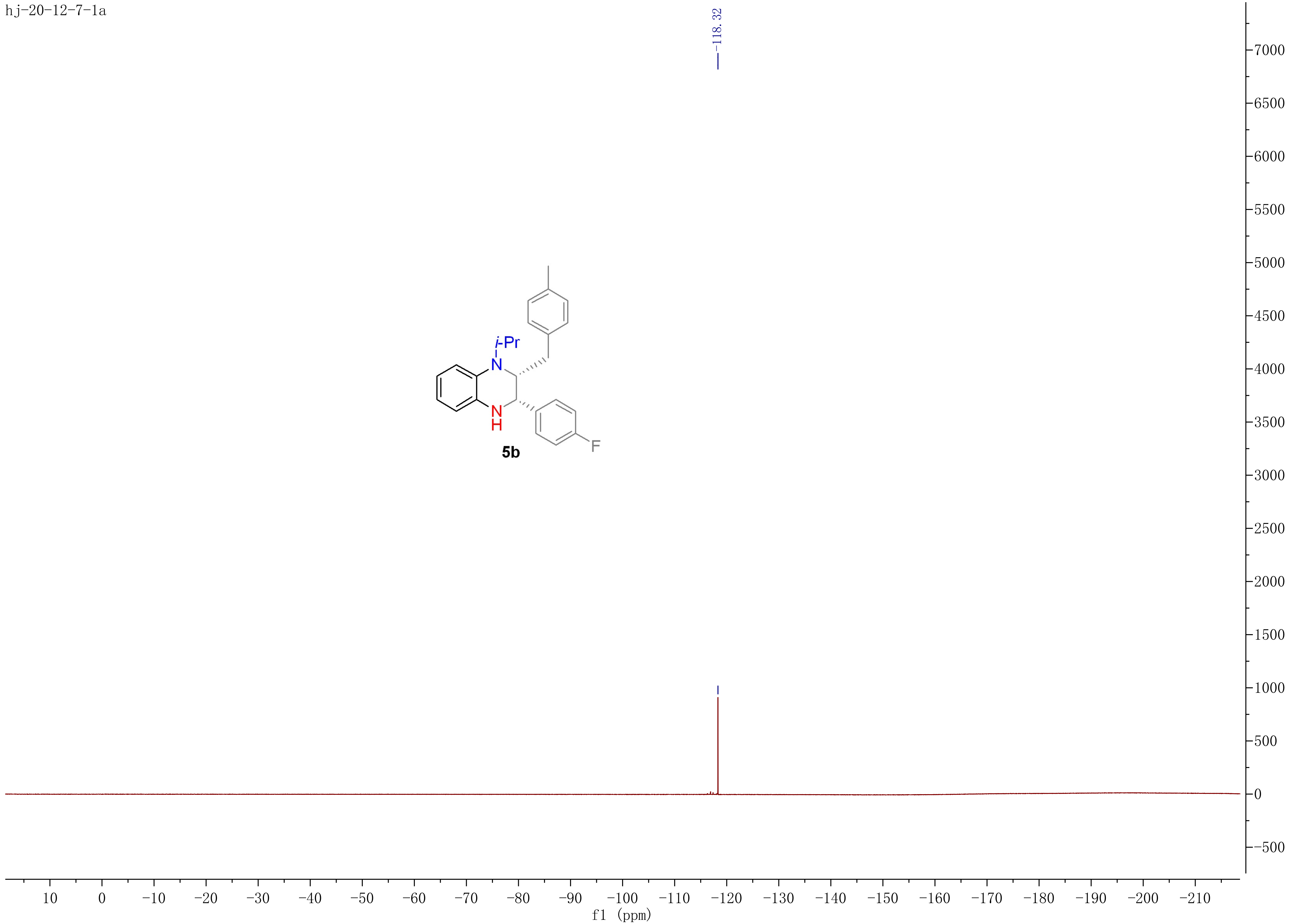
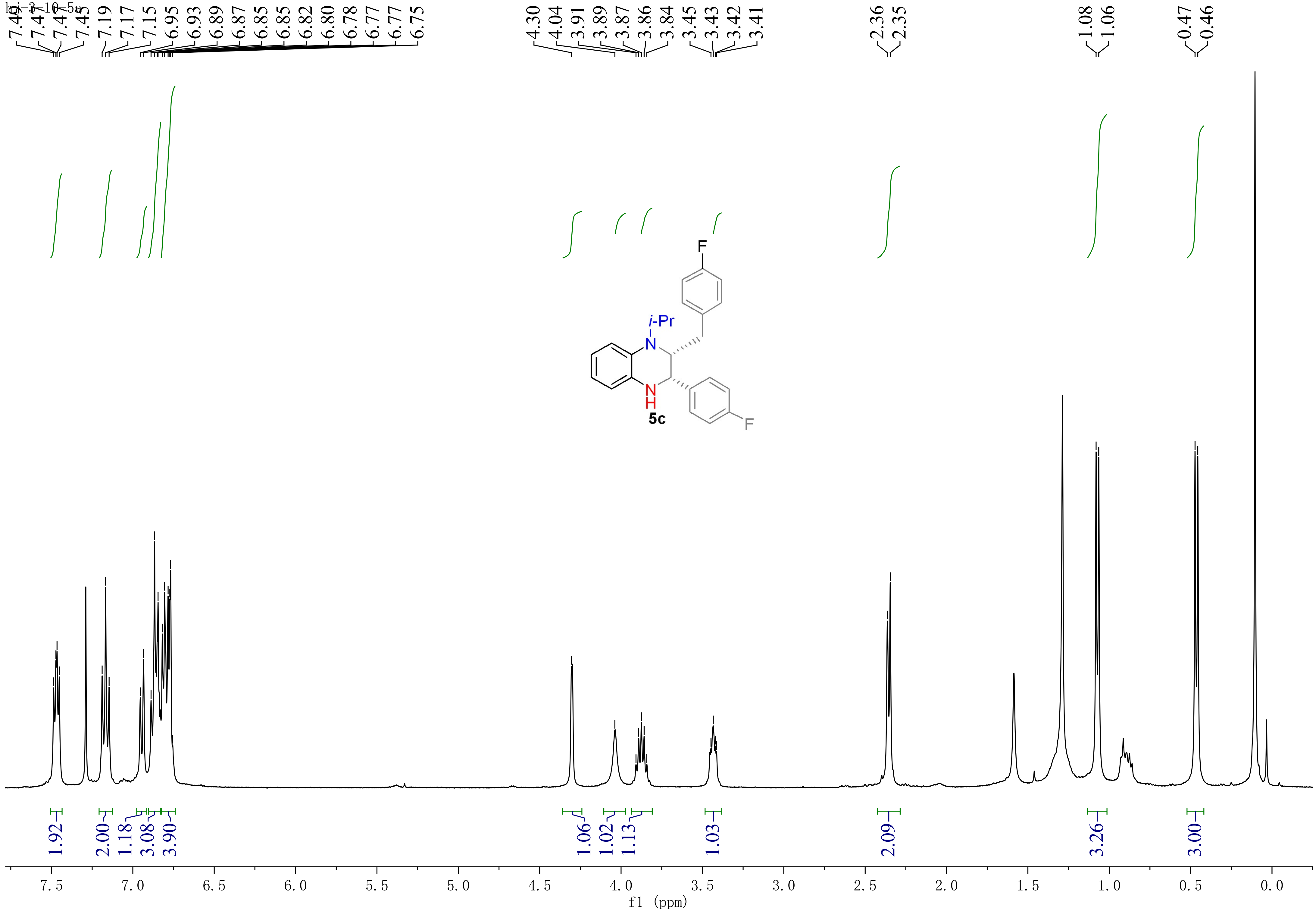
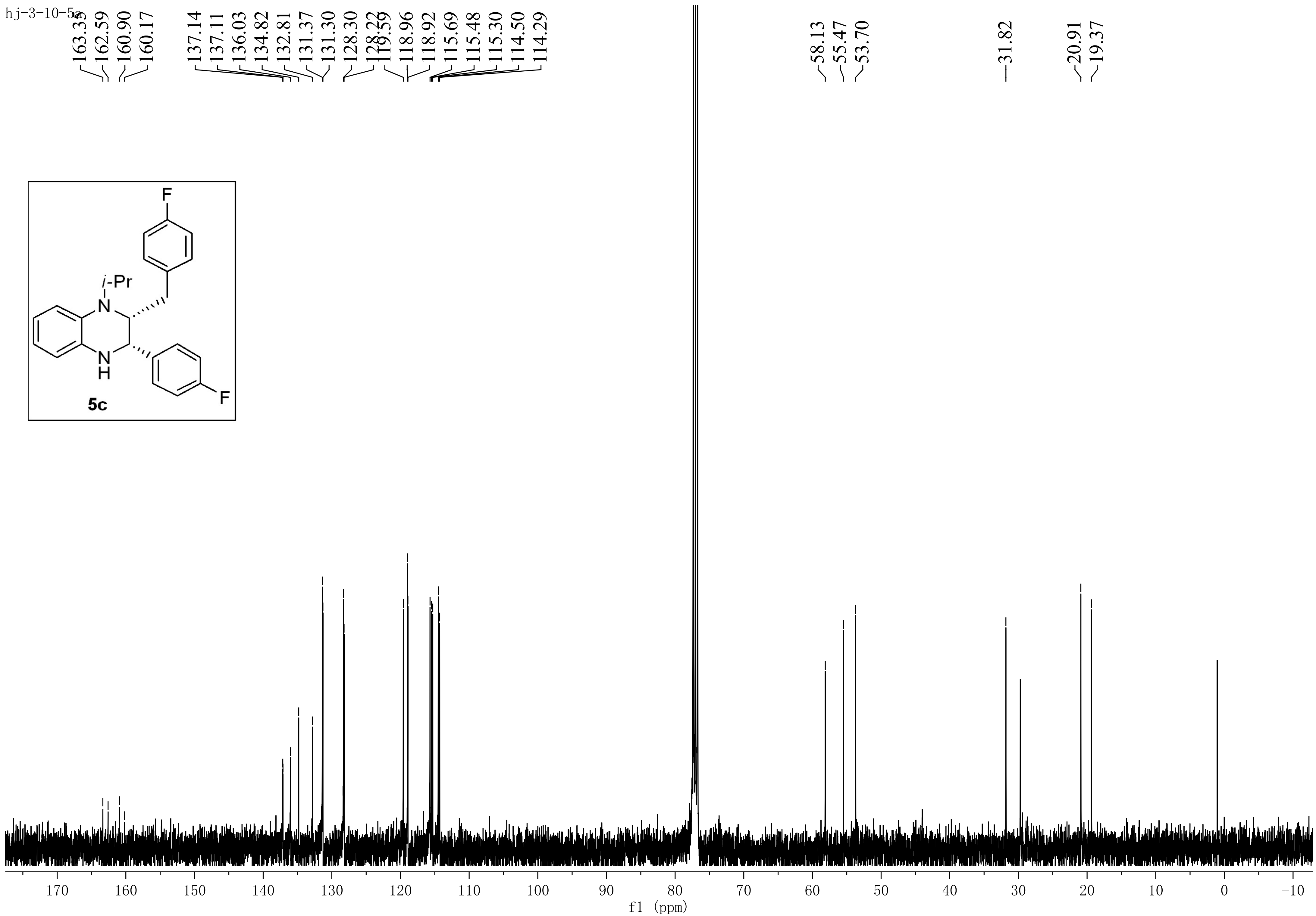
137.06
136.35
136.32
135.06
132.85
131.42
131.34
129.36
126.60
119.29
118.87
118.79
115.14
114.41
114.20
58.21
55.81
53.69
31.96
29.73
21.16
20.94
19.36
i-Pr
N
N
H
F
5b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


hj-20-12-7-1a
-118.32
i-Pr
N
N
H
F
5b
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



hcj-3-10-5a
7.49 7.47 7.47 7.45 7.19 7.17 7.15 6.95 6.93 6.89 6.87 6.85 6.85 6.82 6.80 6.78 6.77 6.77 6.75
4.30 4.04 3.91 3.89 3.87 3.86 3.84 3.45 3.43 3.42 3.41
2.36 2.35
1.08 1.06
0.47 0.46
F
i-Pr
N
N
H
5c
F
1.92 2.00 1.18 3.08 3.90 1.06 1.02 1.13 1.03 2.09 3.26 3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


hj-3-10-5a
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162.59
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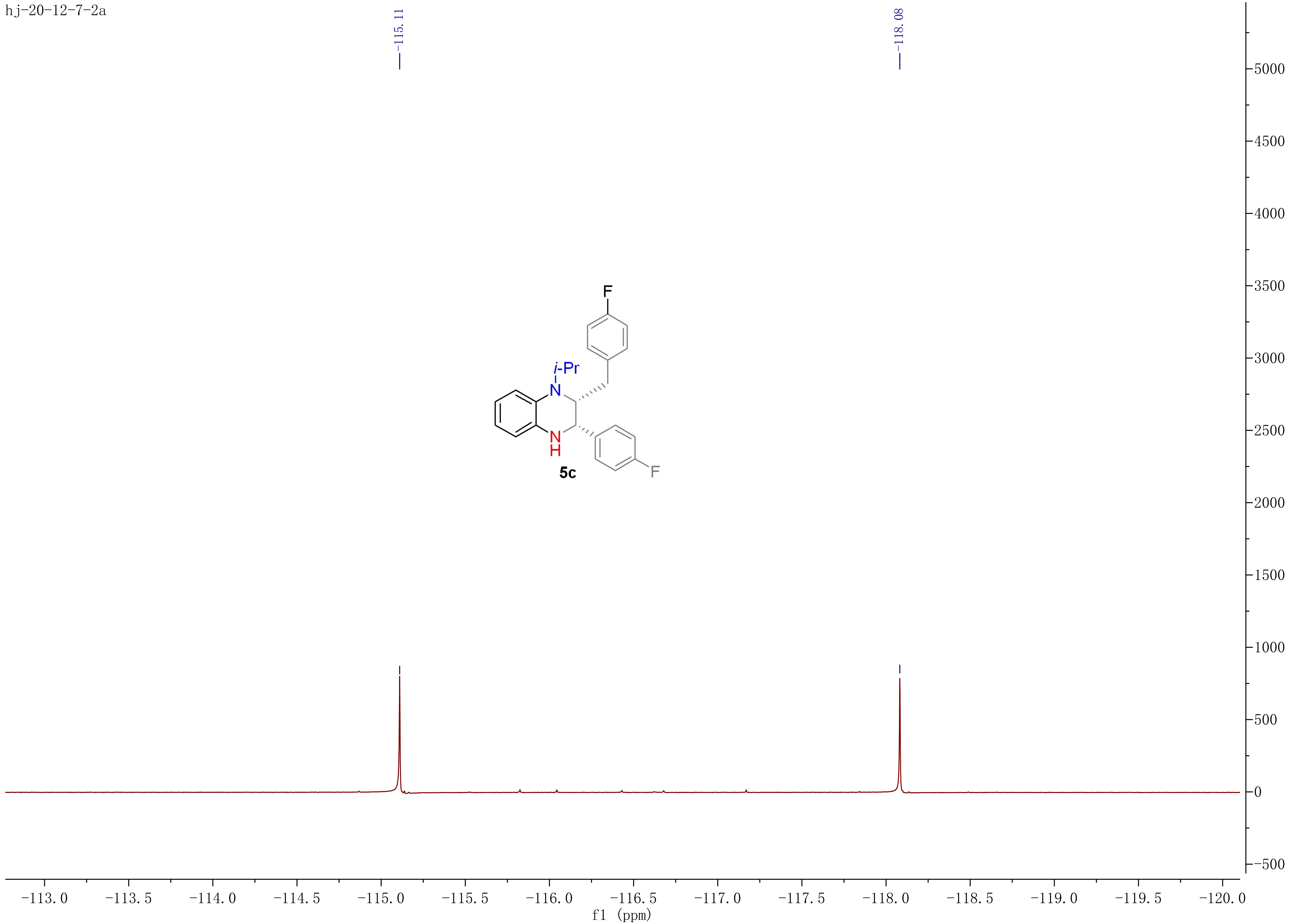
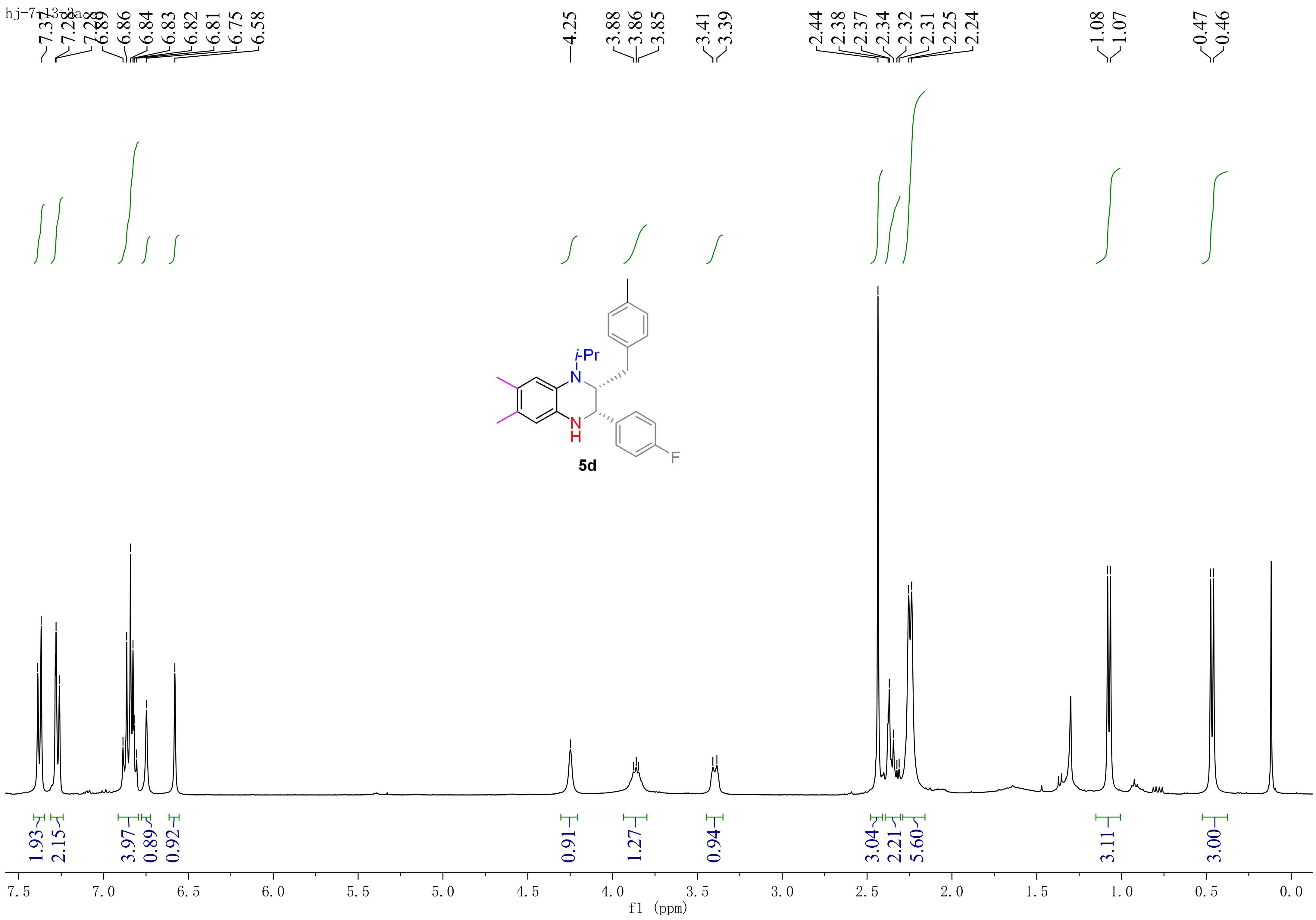
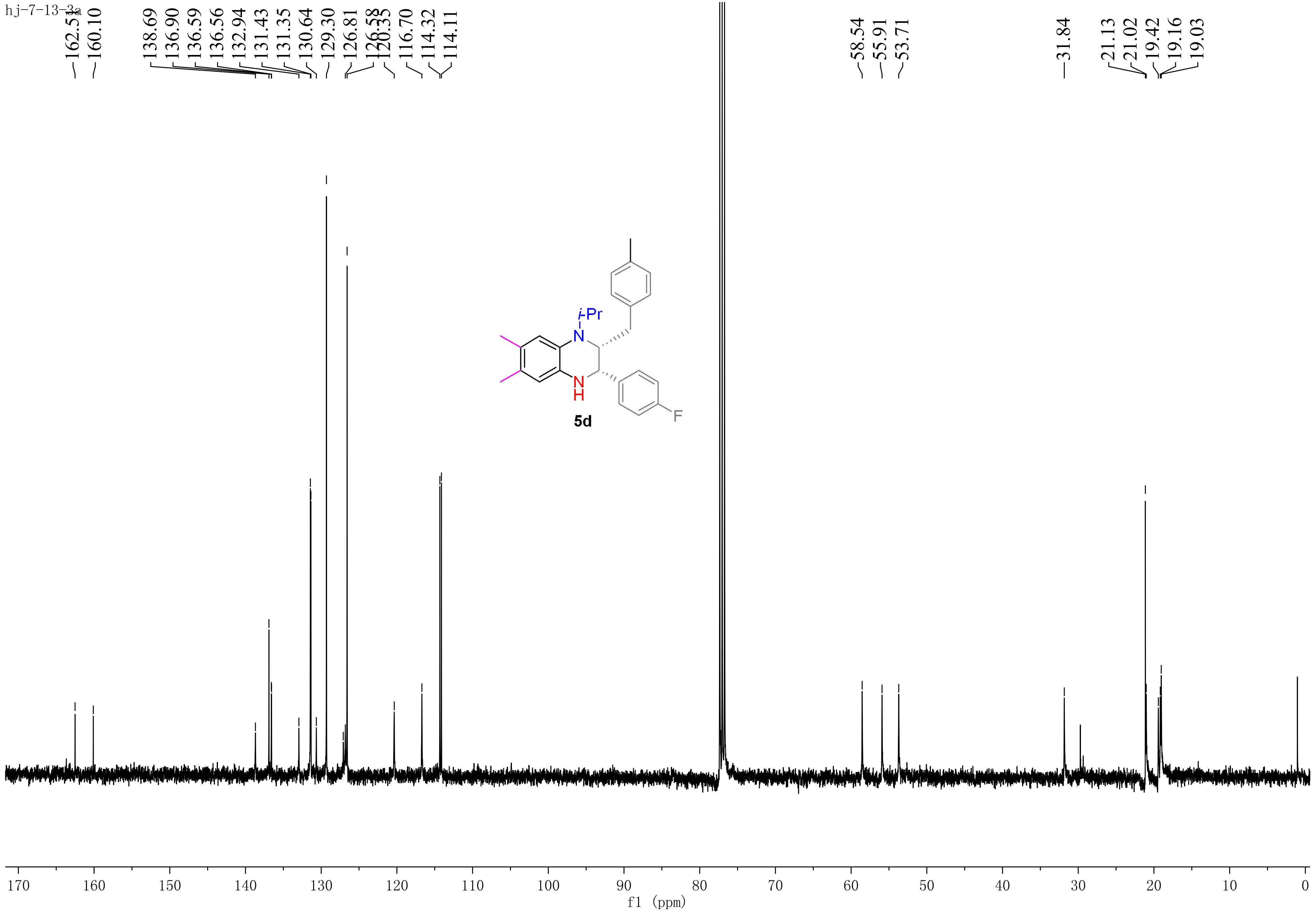
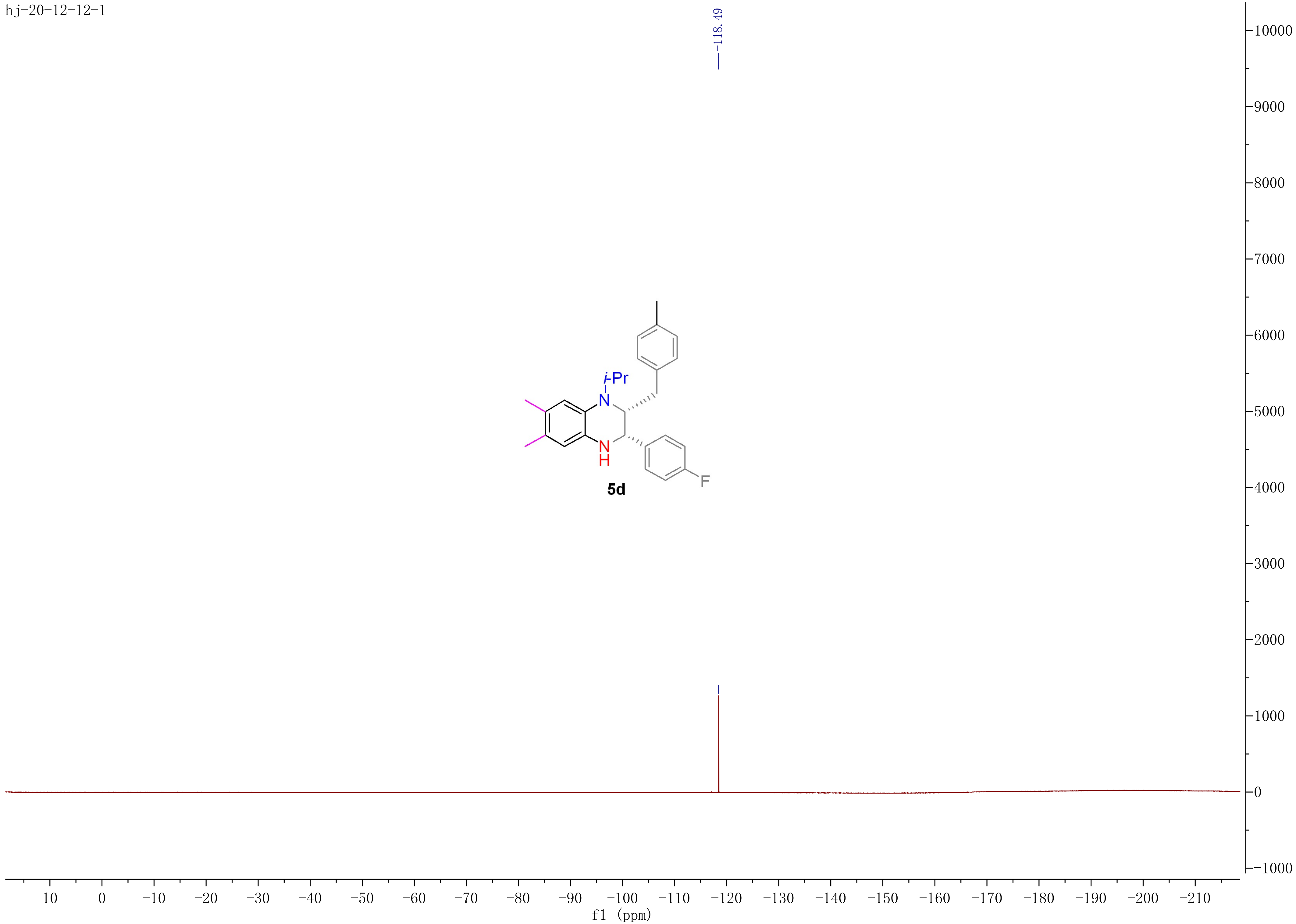
160.17
137.14
137.11
136.03
134.82
132.81
131.37
131.30
128.30
128.22
119.59
118.96
118.92
115.69
115.48
115.30
114.50
114.29
58.13
55.47
53.70
31.82
20.91
19.37
F
i-Pr
N
N
H
F
5c
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

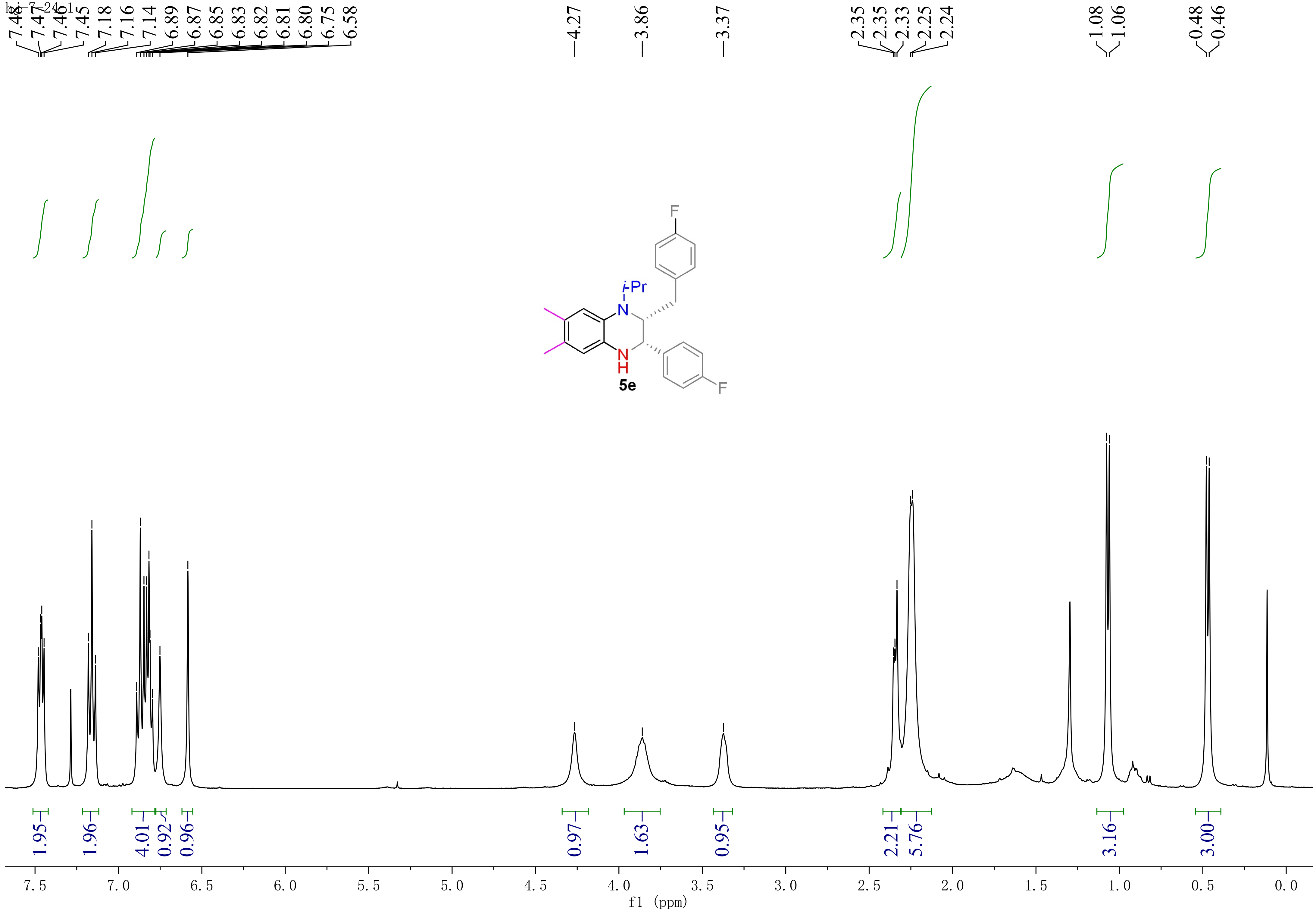

hj-20-12-7-2a
-115.11
-118.08
F
i-Pr
N
N
H
F
5c
-113.0
-113.5
-114.0
-114.5
-115.0
-115.5
-116.0
-116.5
-117.0
-117.5
-118.0
-118.5
-119.0
-119.5
-120.0
f1 (ppm)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500



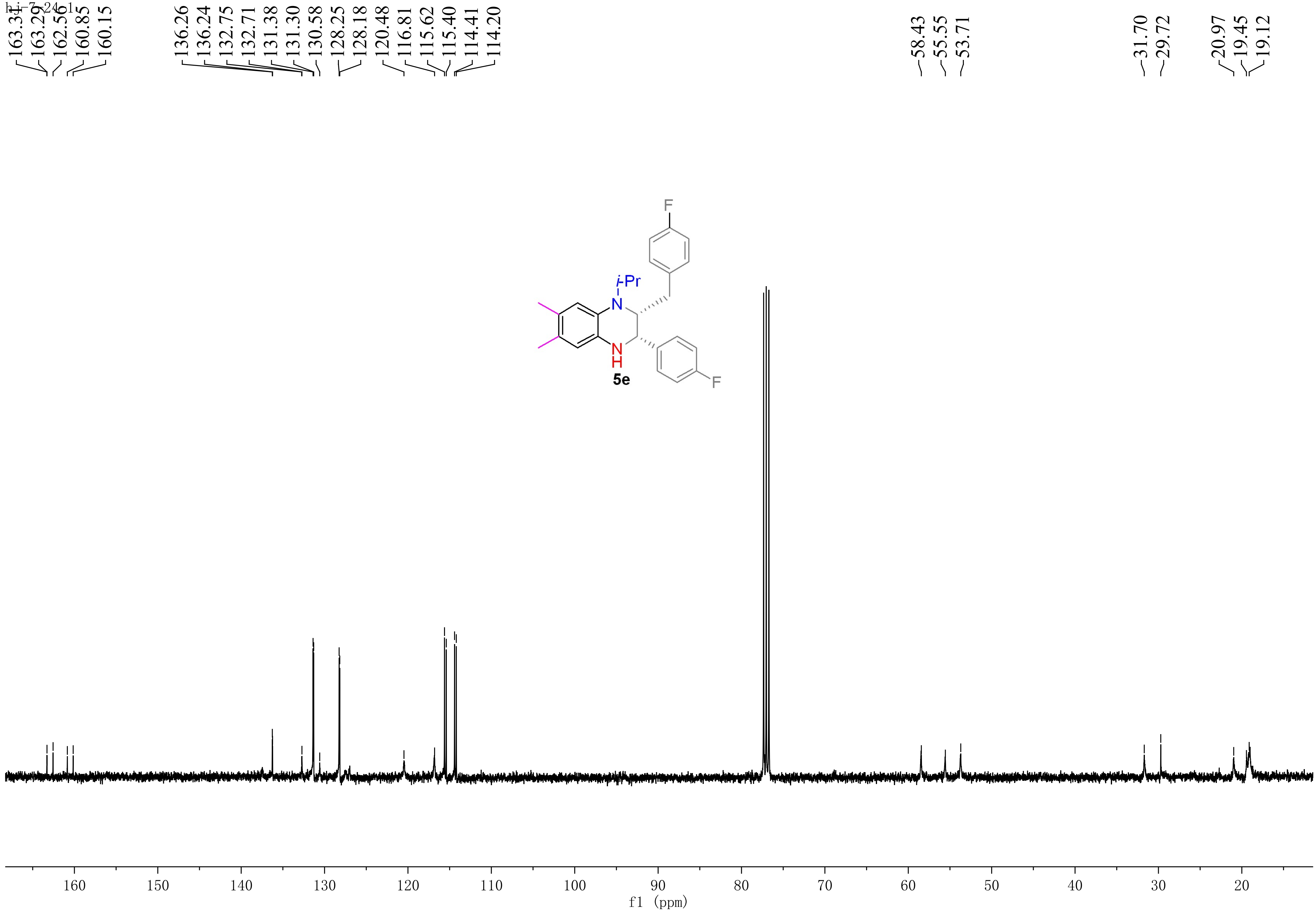
6.86
6.84
6.83
6.82
6.81
6.75
6.58
4.25
3.88
3.86
3.85
3.41
3.39
2.44
2.38
2.37
2.34
2.32
2.31
2.25
2.24
1.08
1.07
0.47
0.46
i-Pr
N
N
H
F
5d
1.93
2.15
3.97
0.89
0.92
0.91
1.27
0.94
3.04
2.21
5.60
3.11
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

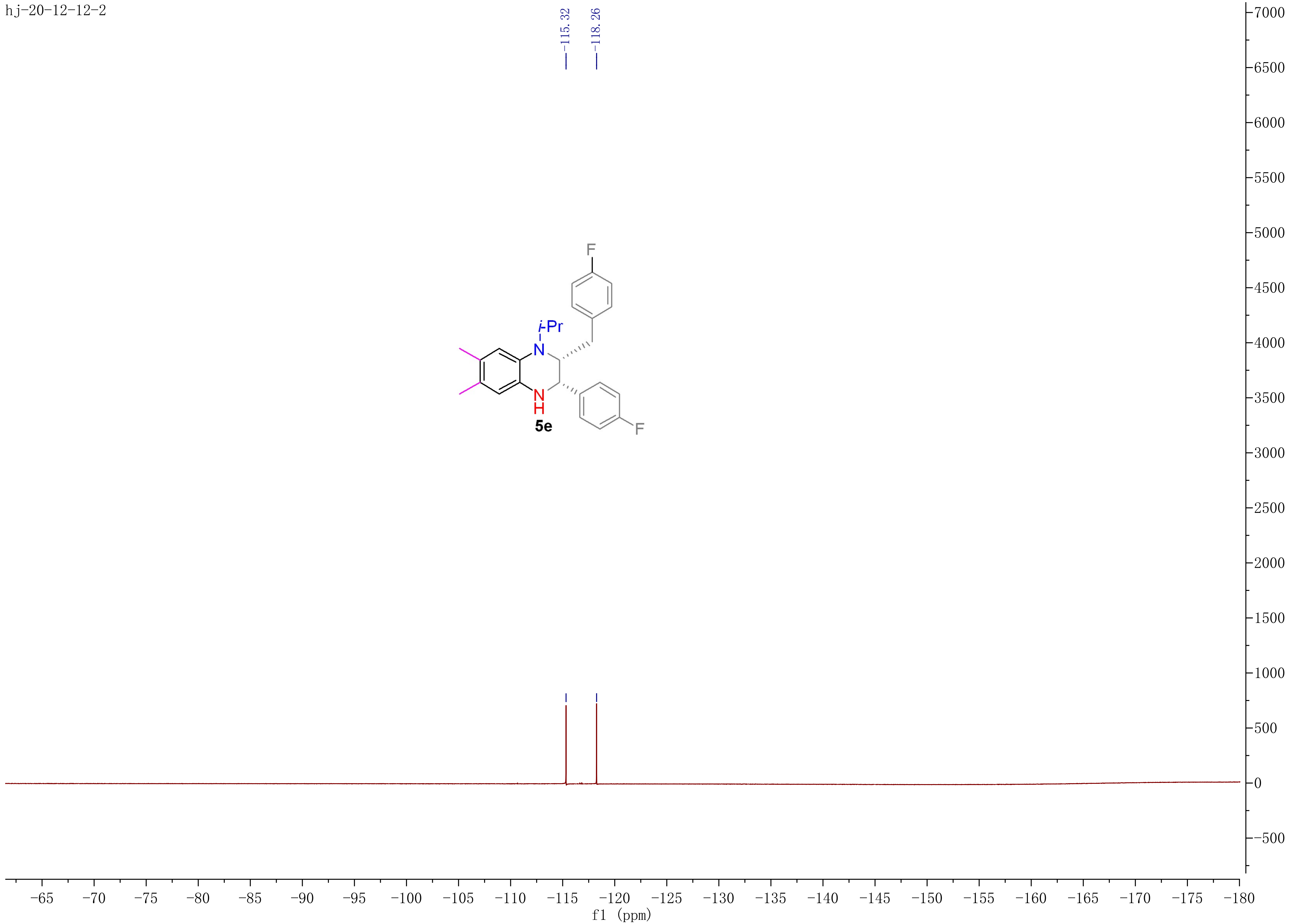

hj-7-13-3a
162.53
160.10
138.69
136.90
136.59
136.56
132.94
131.43
131.35
130.64
129.30
126.81
126.58
120.35
116.70
114.32
114.11
58.54
55.91
53.71
31.84
21.13
21.02
19.42
19.16
19.03
i-Pr
N
N
H
F
5d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

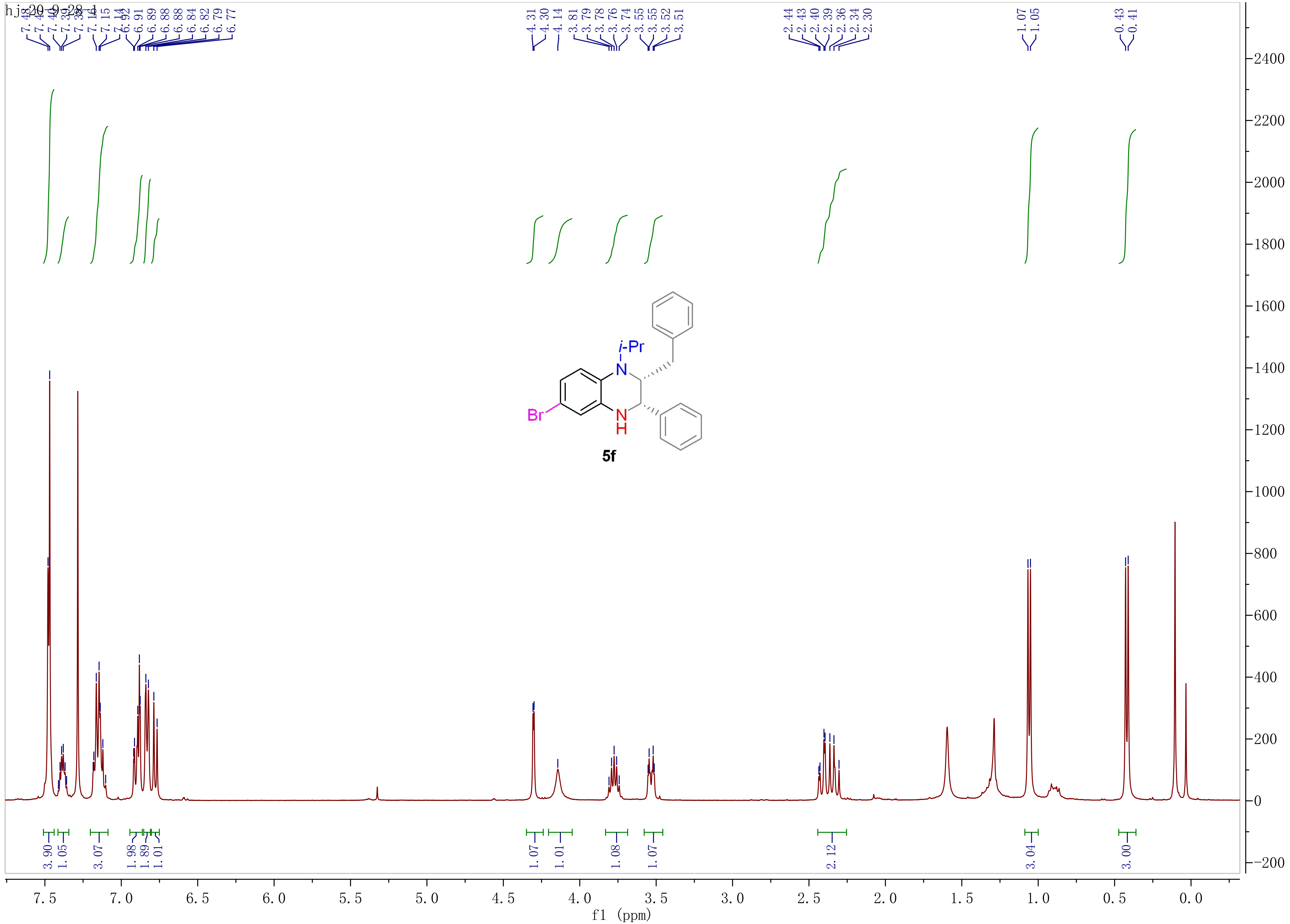

hj-20-12-12-1
-118.49
i-Pr
N
N
H
F
5d
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



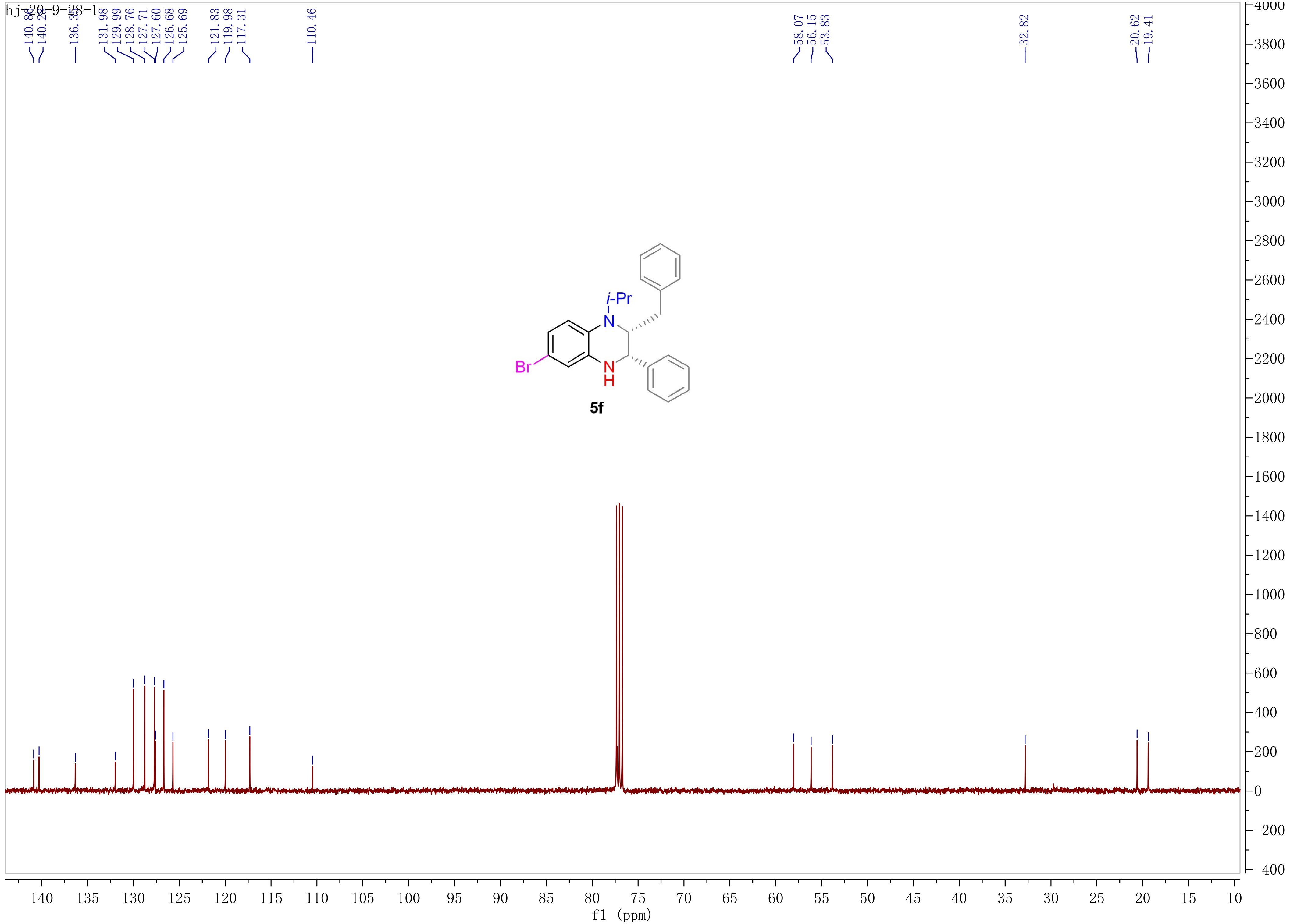
7.48 7.47 7.46 7.45 7.18 7.16 7.14 6.89 6.87 6.85 6.83 6.82 6.81 6.80 6.75 6.58
4.27
3.86
3.37
2.35 2.35 2.33 2.25 2.24
1.08 1.06
0.48 0.46
F
i-Pr
N
N
H
F
5e
1.95 1.96 4.01 0.92 0.96 0.97 1.63 0.95 2.21 5.76 3.16 3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

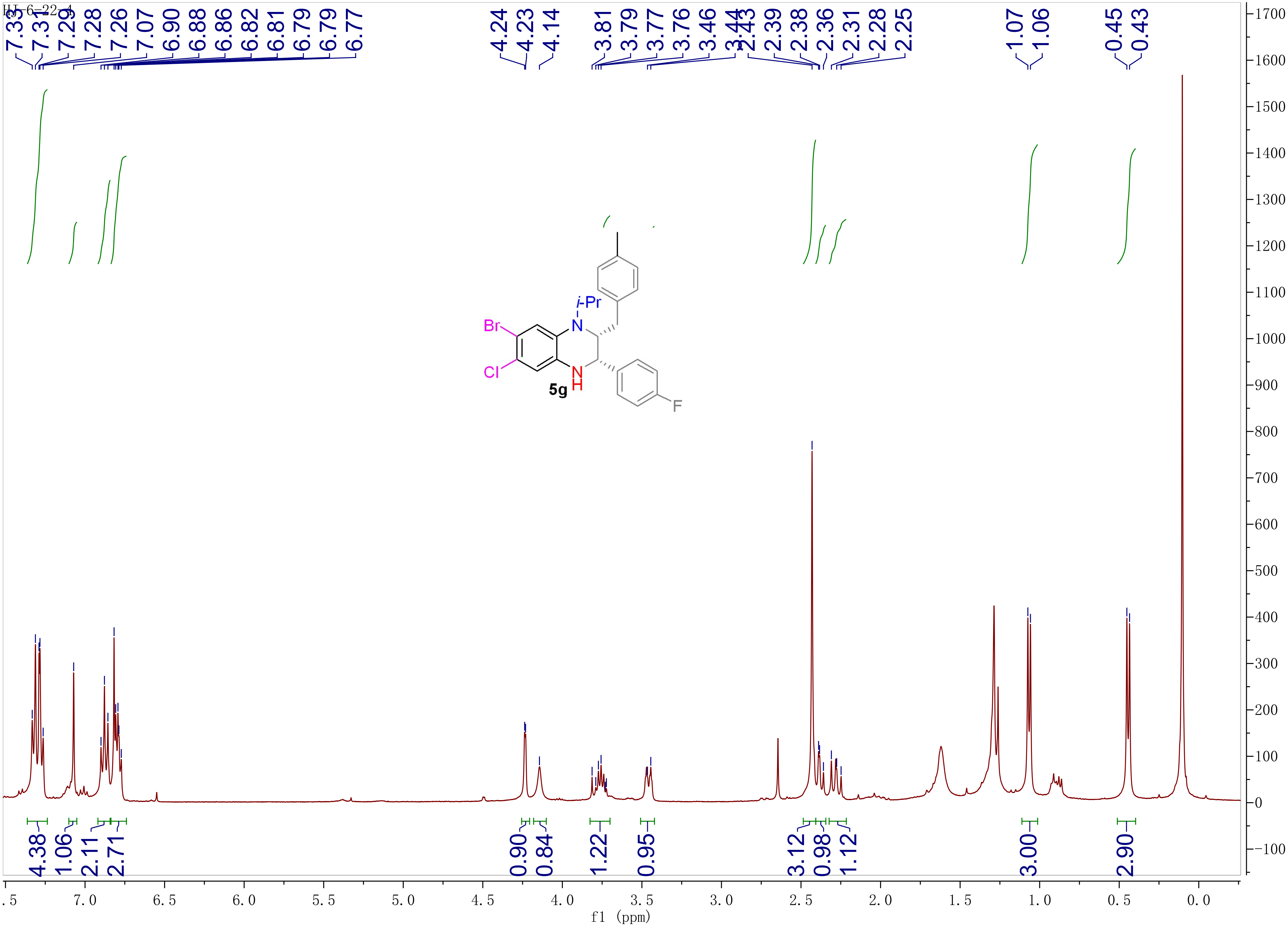

hj-7-24-1
163.31
163.29
162.56
160.85
160.15
136.26
136.24
132.75
132.71
131.38
131.30
130.58
128.25
128.18
120.48
116.81
115.62
115.40
114.41
114.20
58.43
55.55
53.71
31.70
29.72
20.97
19.45
19.12
F
i-Pr
N
N
H
F
5e
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


hj-20-12-12-2
-115.32
-118.26
F
i-Pr
N
N
H
F
5e
f1 (ppm)
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

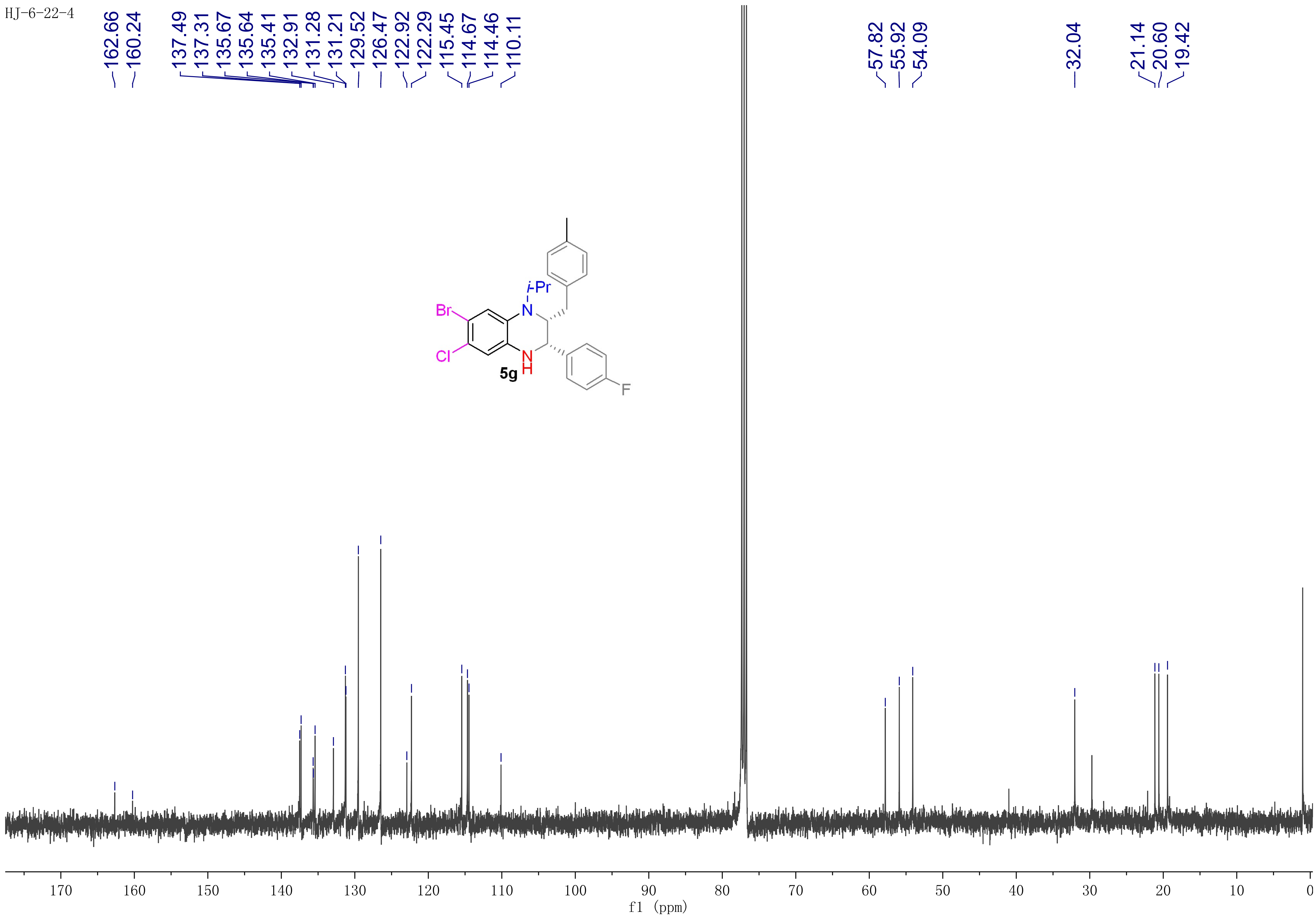


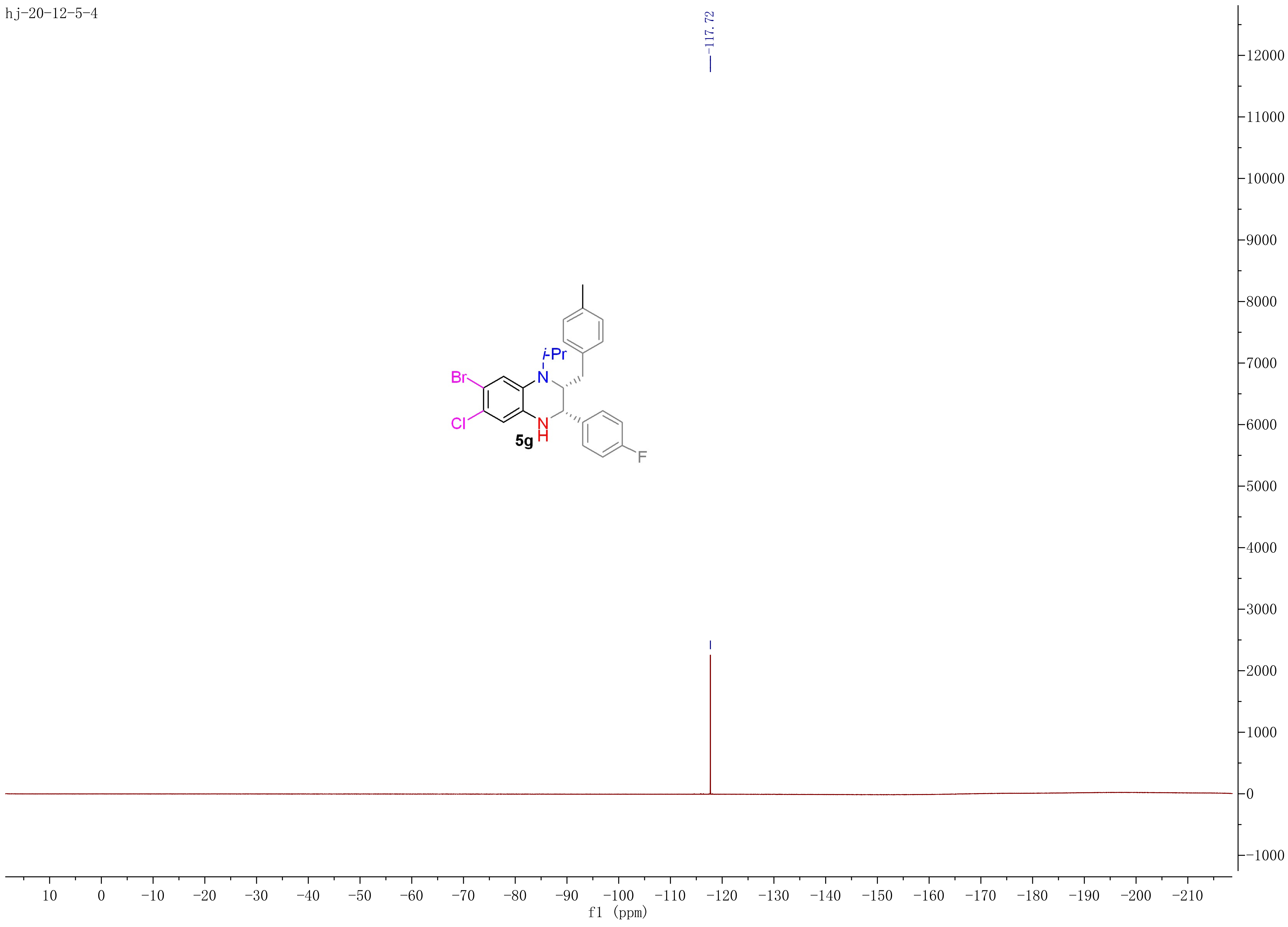
hjz-20-9-28-1
7.15
7.14
6.92
6.91
6.89
6.88
6.88
6.84
6.82
6.79
6.77
4.31
4.30
4.14
3.81
3.79
3.78
3.76
3.74
3.55
3.55
3.52
3.51
2.44
2.43
2.40
2.39
2.36
2.34
2.30
1.07
1.05
0.43
0.41
i-Pr
N
Br
N
H
5f
3.90
1.05
3.07
1.98
1.89
1.01
1.07
1.01
1.08
1.07
2.12
3.04
3.00
f1 (ppm)

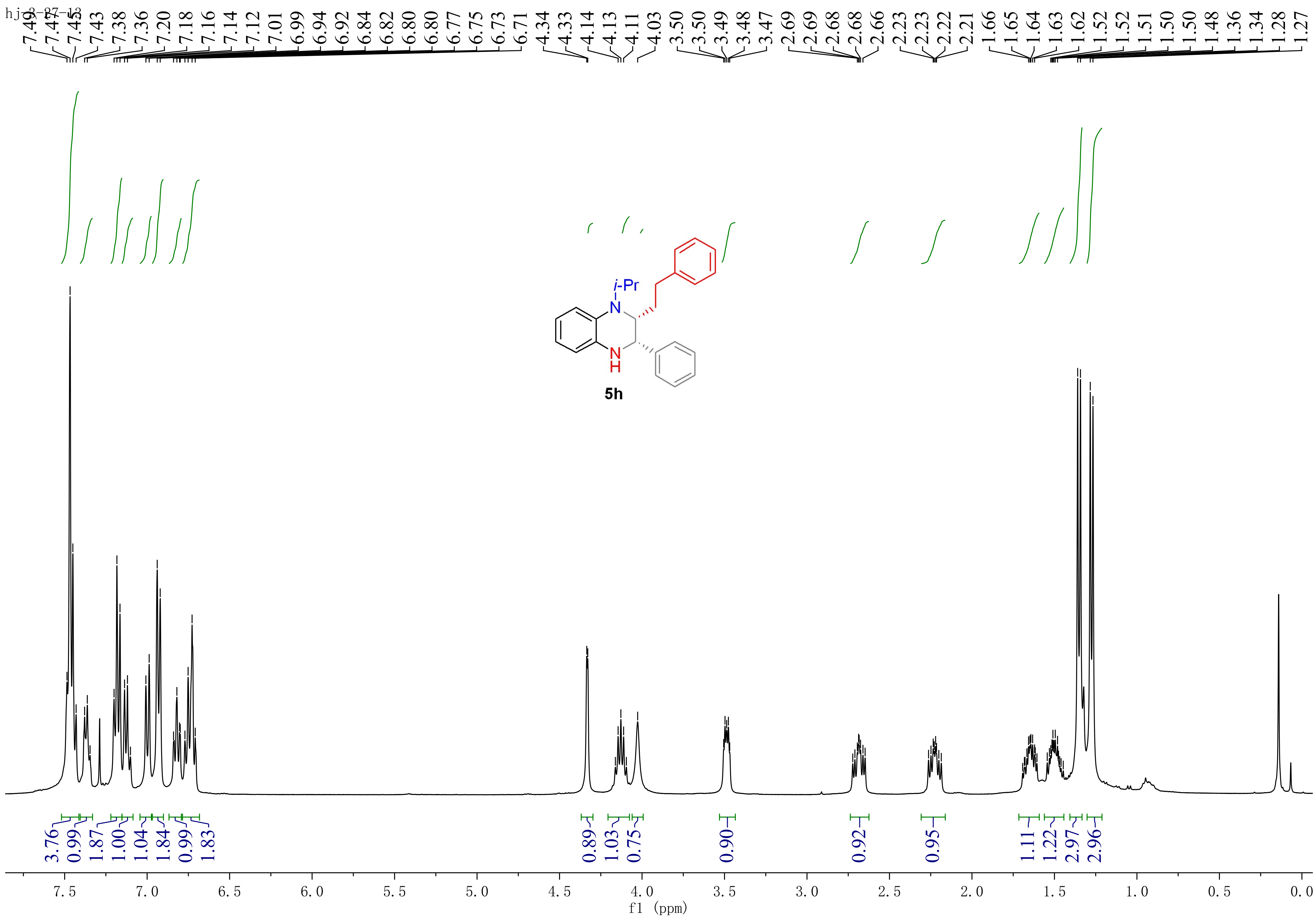

hj-20-9-28-1
140.86
140.28
136.35
131.98
129.99
128.76
127.71
127.60
126.68
125.69
121.83
119.98
117.31
110.46
58.07
56.15
53.83
32.82
20.62
19.41
i-Pr
N
N
H
Br
5f
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)
4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200 -400

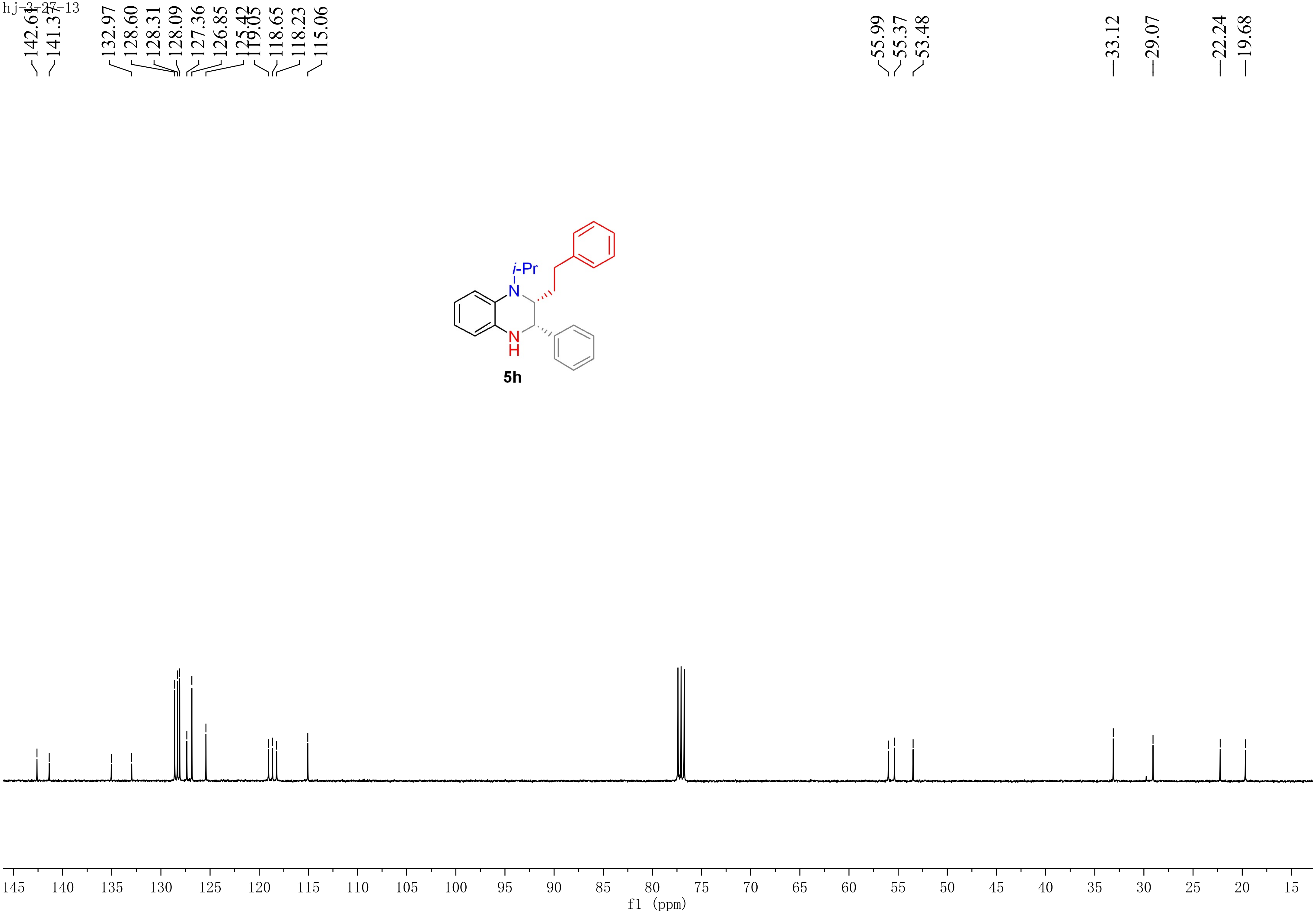


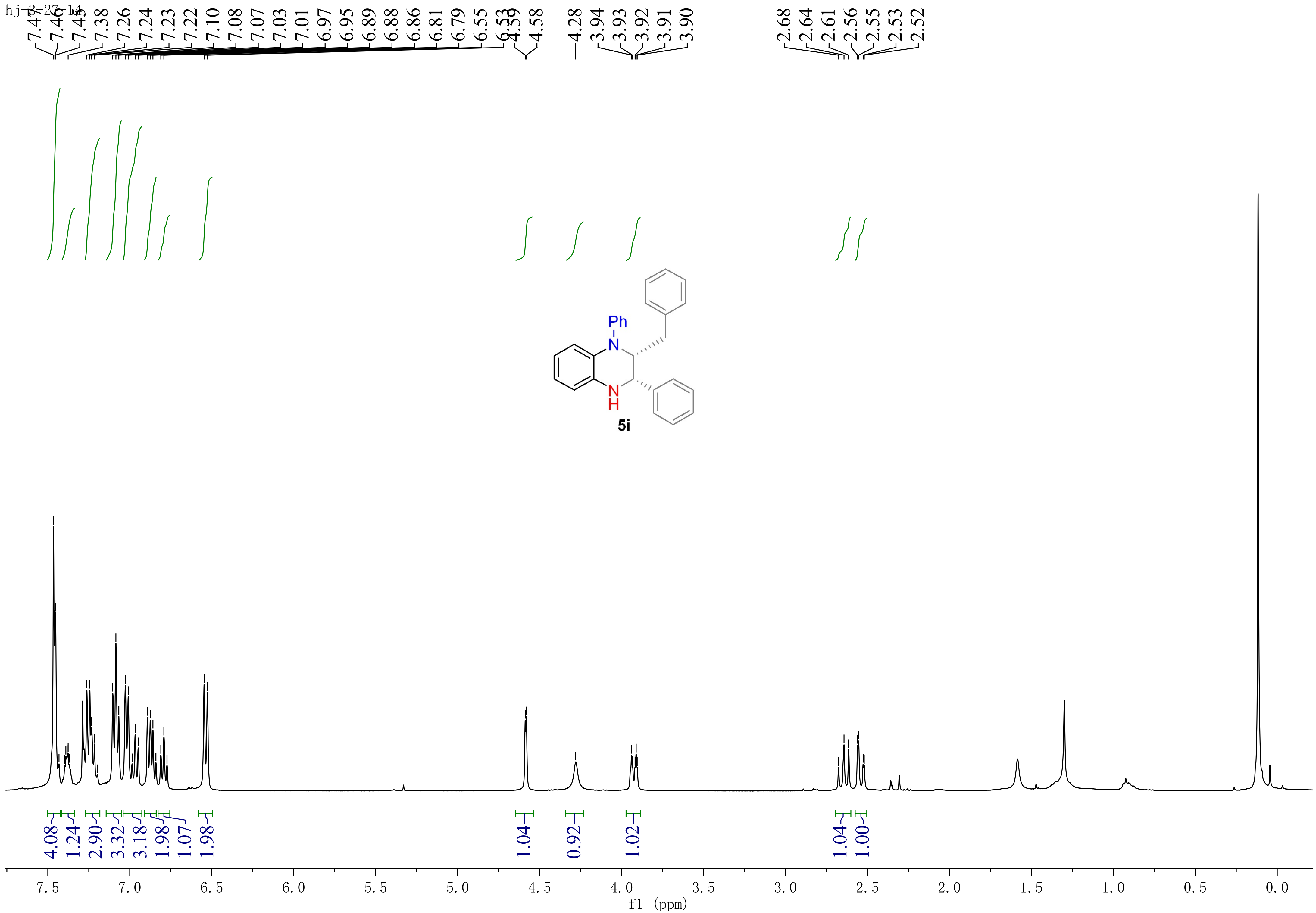
HJ-6-22-4
7.33
7.31
7.29
7.28
7.26
7.07
6.90
6.88
6.86
6.82
6.81
6.79
6.79
6.77
4.24
4.23
4.14
3.81
3.79
3.77
3.76
3.46
3.44
2.43
2.39
2.38
2.36
2.31
2.28
2.25
1.07
1.06
0.45
0.43
Br
Cl
N
i-Pr
N
H
F
5g
4.38
1.06
2.11
2.71
0.90
0.84
1.22
0.95
3.12
0.98
1.12
3.00
2.90
f1 (ppm)

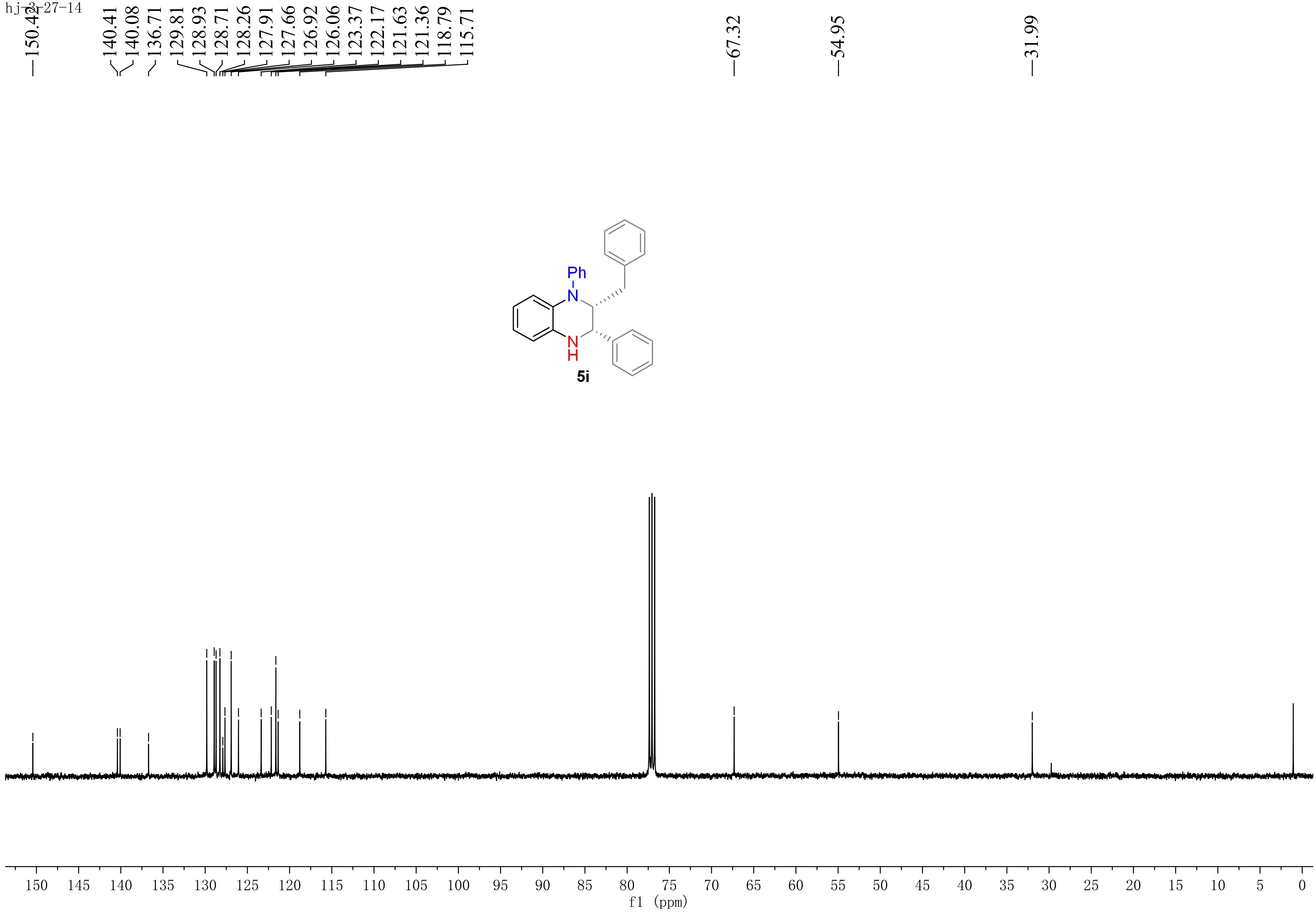

HJ-6-22-4
162.66
160.24
137.49
137.31
135.67
135.64
135.41
132.91
131.28
131.21
129.52
126.47
122.92
122.29
115.45
114.67
114.46
110.11
57.82
55.92
54.09
32.04
21.14
20.60
19.42
Br
Cl
N
i-Pr
N
H
5g
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

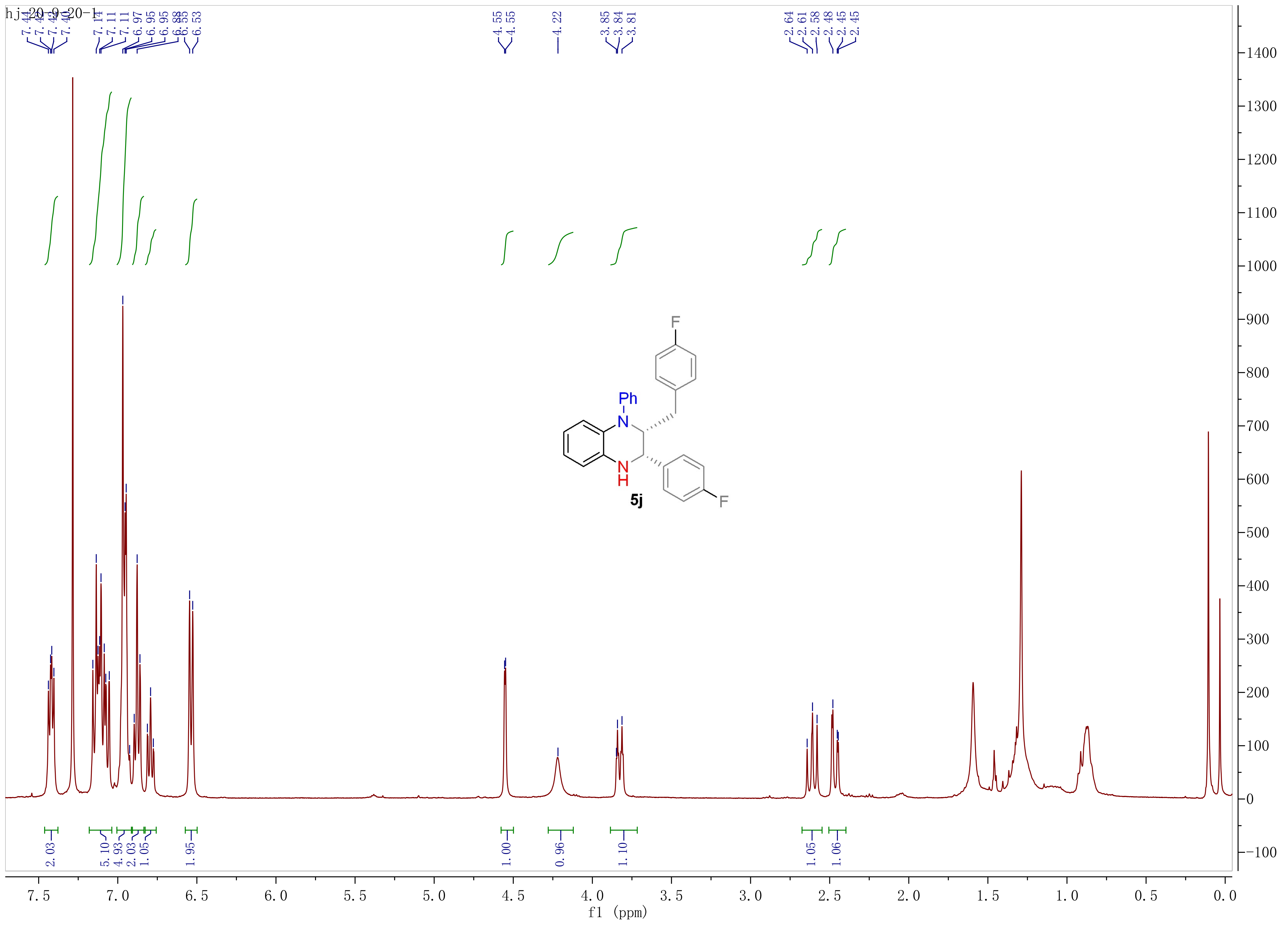

hj-20-12-5-4
−117.72
Br
Cl
N
i-Pr
N
H
5g
F
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

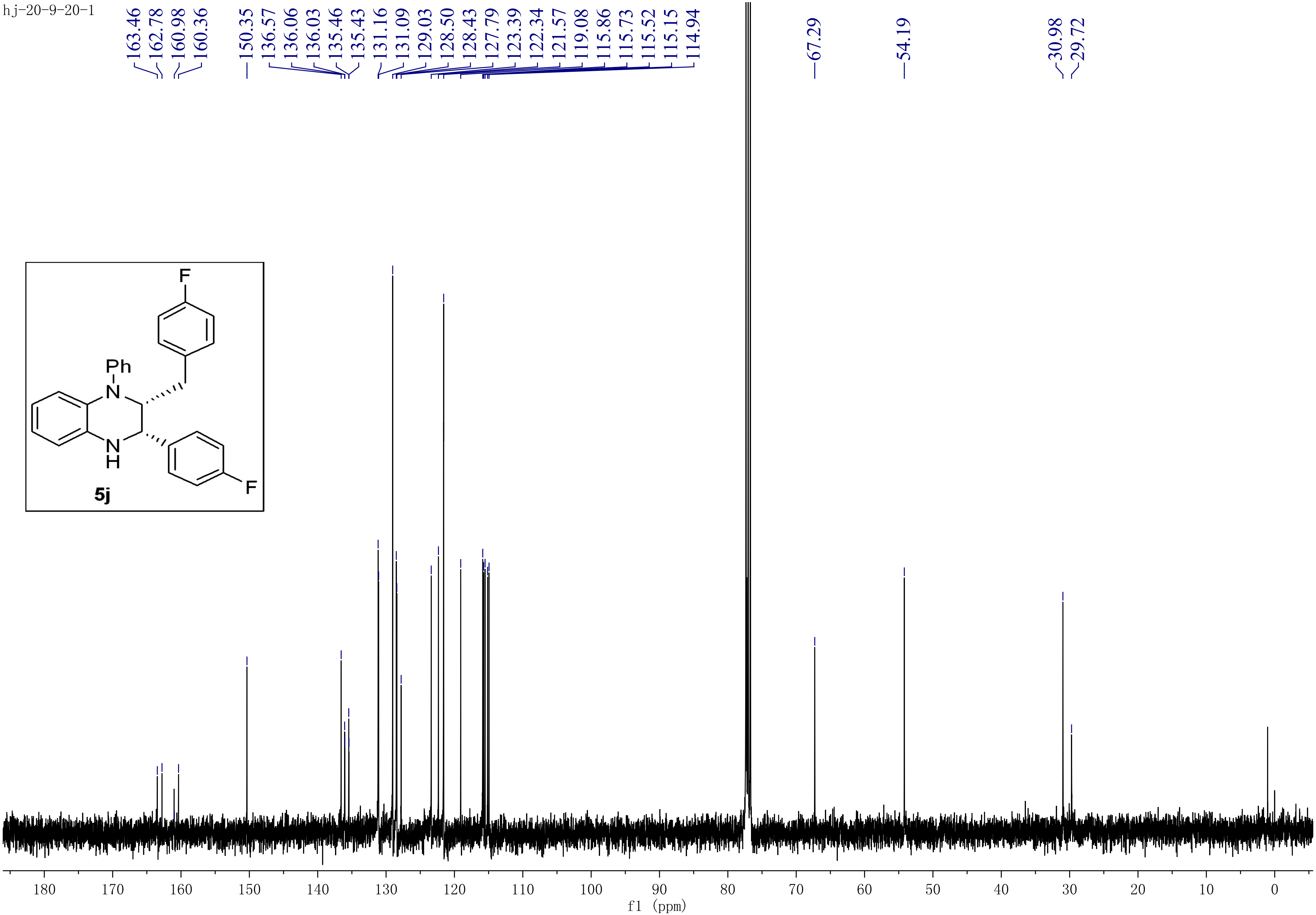

hj-3-27-13
7.49 7.47 7.45 7.43 7.38 7.36 7.20 7.18 7.16 7.14 7.12 7.01 6.99 6.94 6.92 6.84 6.82 6.80 6.80 6.77 6.75 6.73 6.71 4.34 4.33 4.14 4.13 4.11 4.03 3.50 3.50 3.49 3.48 3.47 2.69 2.69 2.68 2.68 2.66 2.23 2.23 2.22 2.21 1.66 1.65 1.64 1.63 1.62 1.52 1.52 1.51 1.50 1.50 1.48 1.36 1.34 1.28 1.27
i-Pr
N
N
H
5h
3.76 0.99 1.87 1.00 1.04 1.84 0.99 1.83 0.89 1.03 0.75 0.90 0.92 0.95 1.11 1.22 2.97 2.96
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


hj-3-27-13
142.61
141.37
132.97
128.60
128.31
128.09
127.36
126.85
125.42
119.05
118.65
118.23
115.06
55.99
55.37
53.48
33.12
29.07
22.24
19.68
i-Pr
N
N
H
5h
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)

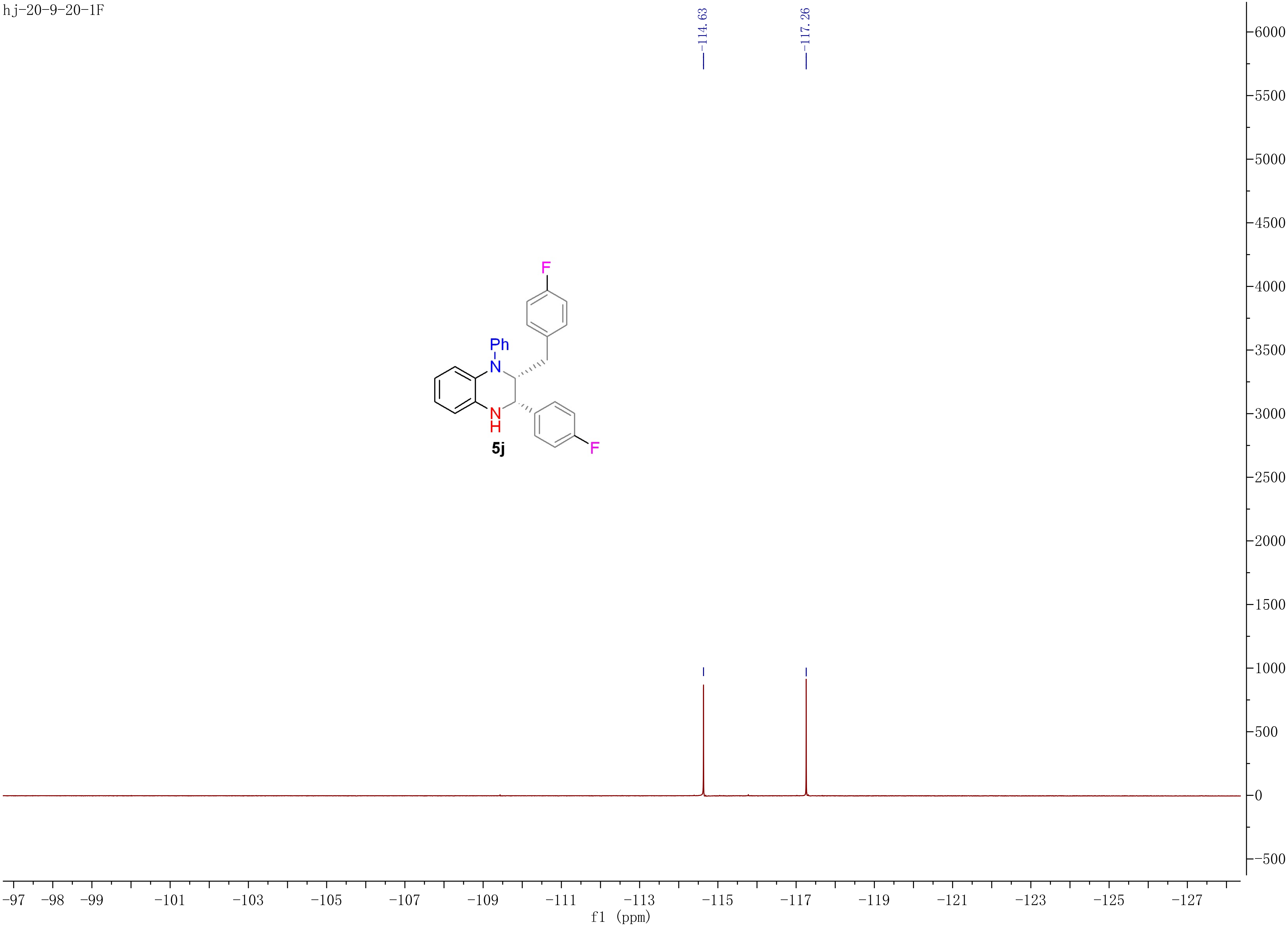

hj-3-27-14
7.47 7.46 7.45 7.38 7.26 7.24 7.23 7.22 7.10 7.08 7.07 7.03 7.01 6.97 6.95 6.89 6.88 6.86 6.81 6.79 6.55 6.53 4.59 4.58
4.28 3.94 3.93 3.92 3.91 3.90
2.68 2.64 2.61 2.56 2.55 2.53 2.52
Ph
N
N
H
5i
4.08 1.24 2.90 3.32 3.18 1.98 1.07 1.98
1.04 0.92 1.02
1.04 1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


hj-3-27-14
150.4
140.41
140.08
136.71
129.81
128.93
128.71
128.26
127.91
127.66
126.92
126.06
123.37
122.17
121.63
121.36
118.79
115.71
67.32
54.95
31.99
Ph
N
N
H
5i
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

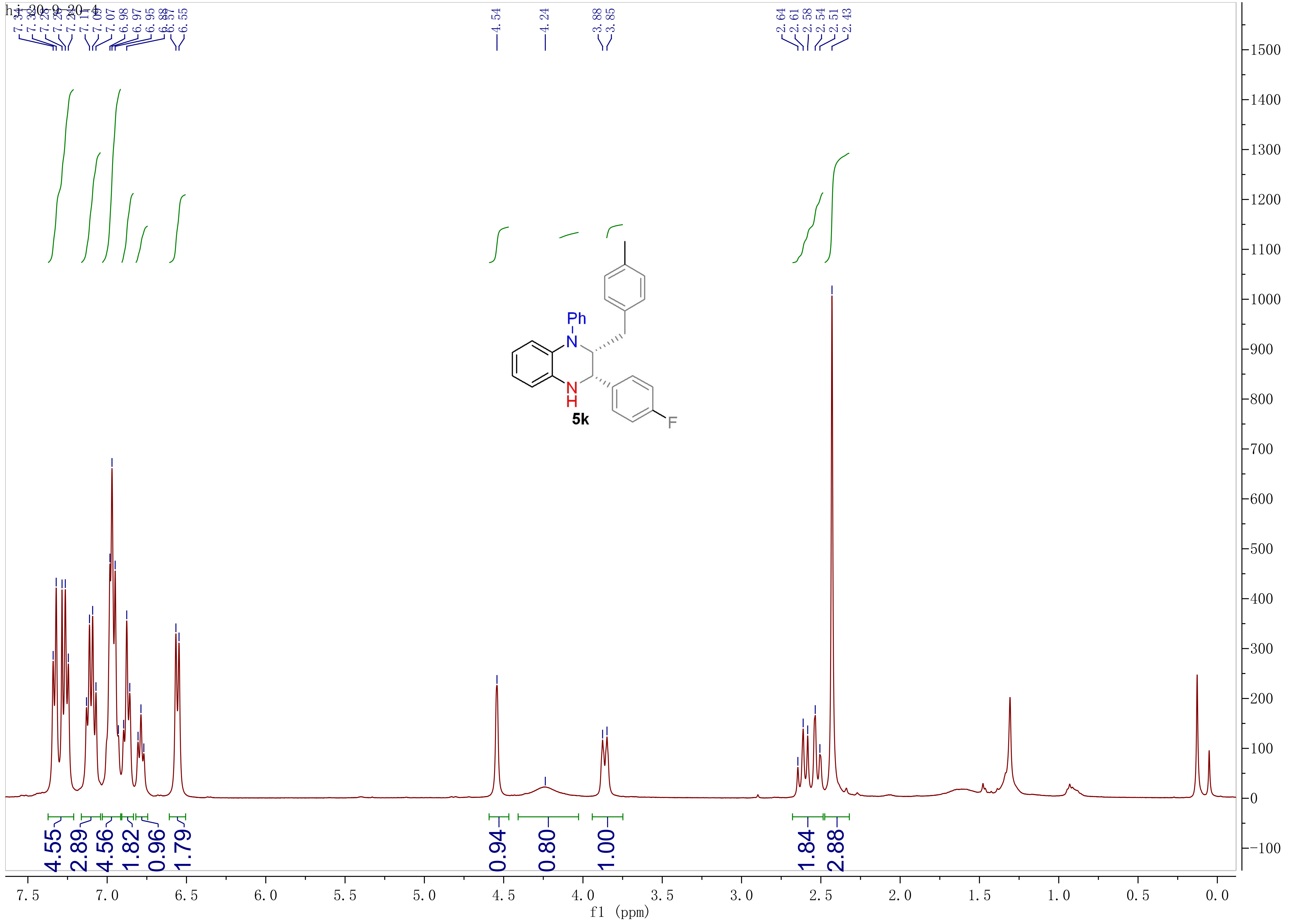

hj-20-9-20-1
7.44 7.43 7.42 7.40 7.14 7.11 7.11 6.97 6.95 6.95 6.88 6.55 6.53
4.55 4.55
4.22
3.85 3.84 3.81
2.64 2.61 2.58 2.48 2.45 2.45
2.03
5.10
4.93
2.03
1.05
1.95
1.00
0.96
1.10
1.05
1.06
F
Ph
N
N
H
F
5j
f1 (ppm)

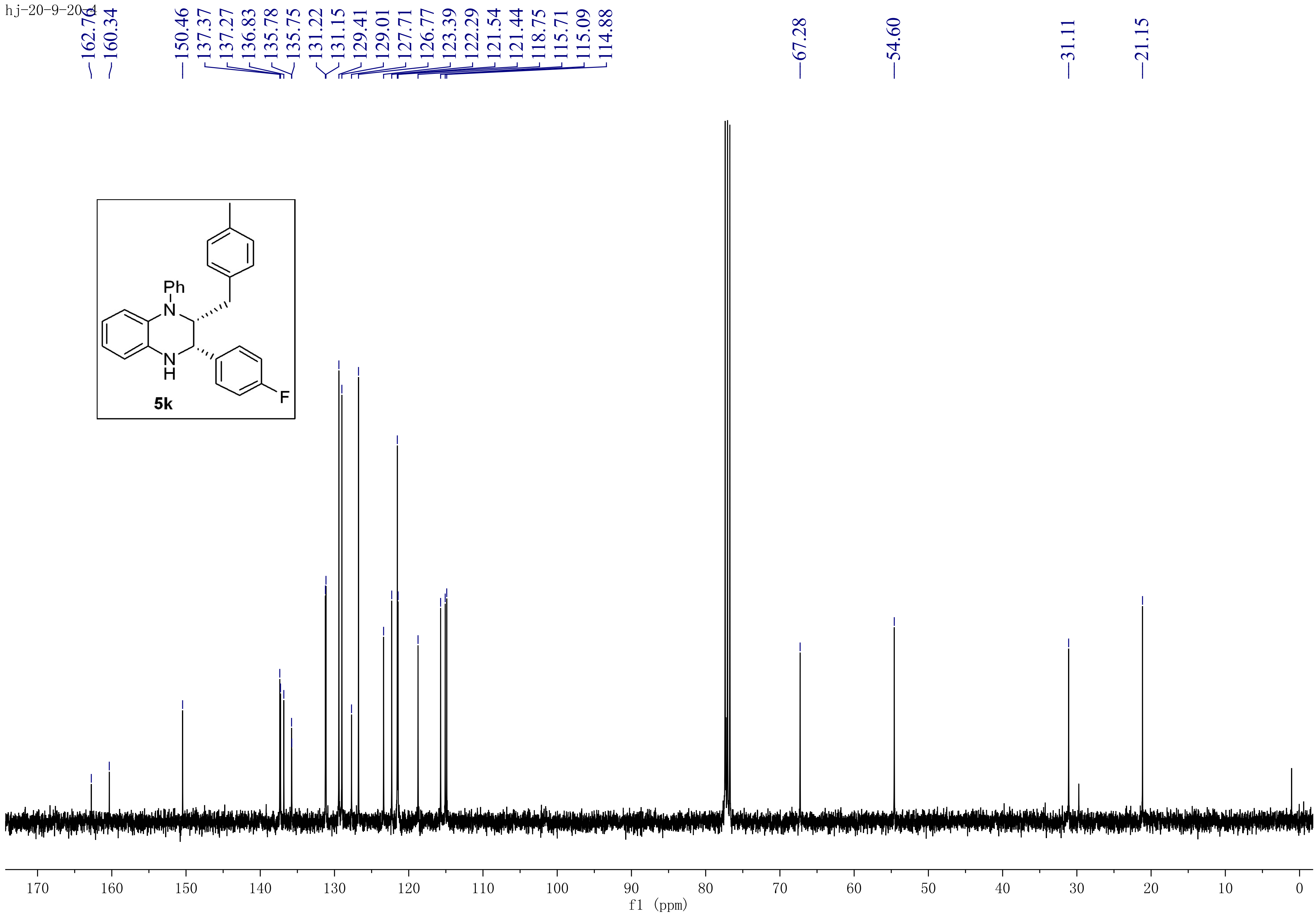

hj-20-9-20-1
163.46
162.78
160.98
160.36
150.35
136.57
136.06
136.03
135.46
135.43
131.16
131.09
129.03
128.50
128.43
127.79
123.39
122.34
121.57
119.08
115.86
115.73
115.52
115.15
114.94
67.29
54.19
30.98
29.72
F
Ph
N
N
H
F
5j
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

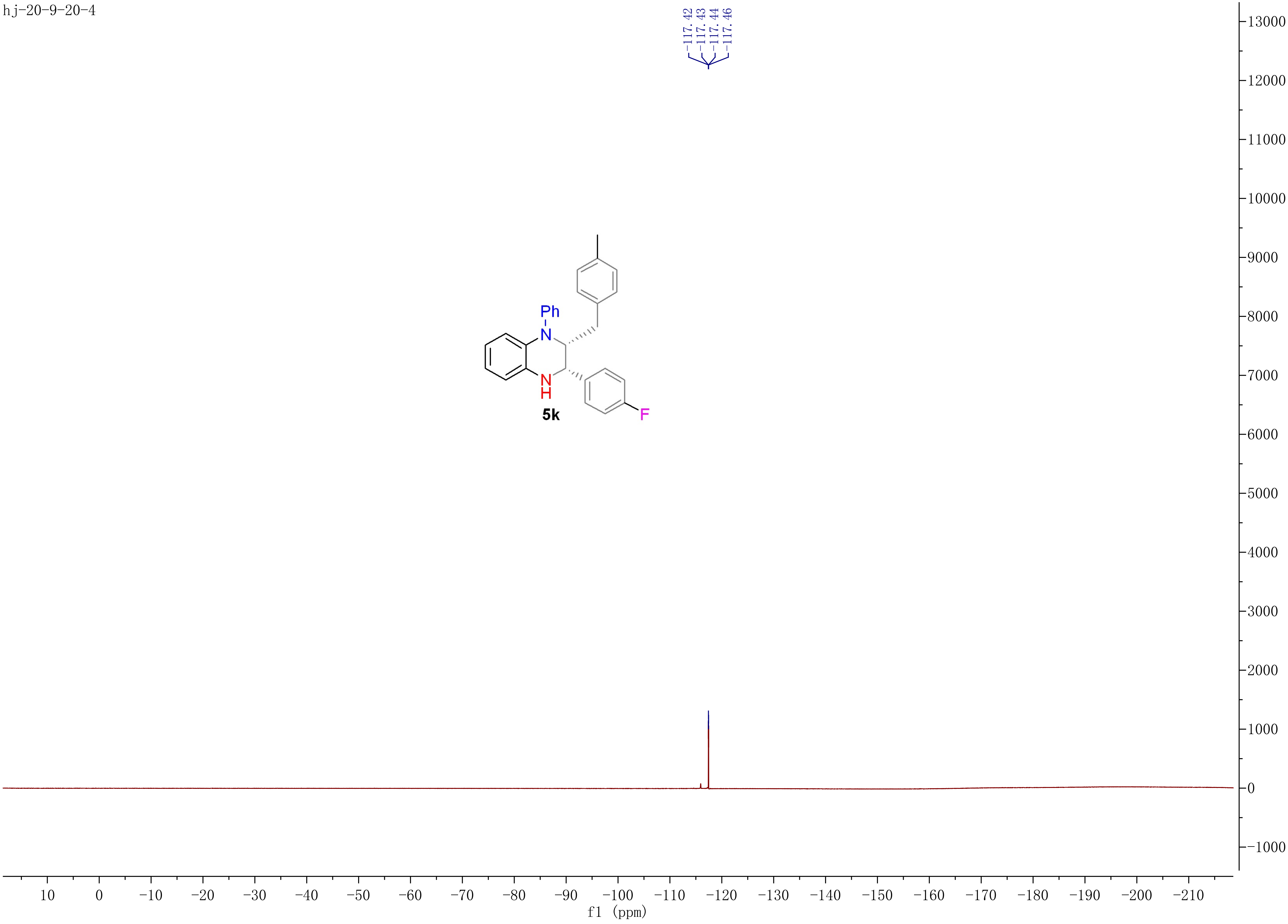
hj-20-9-20-1F

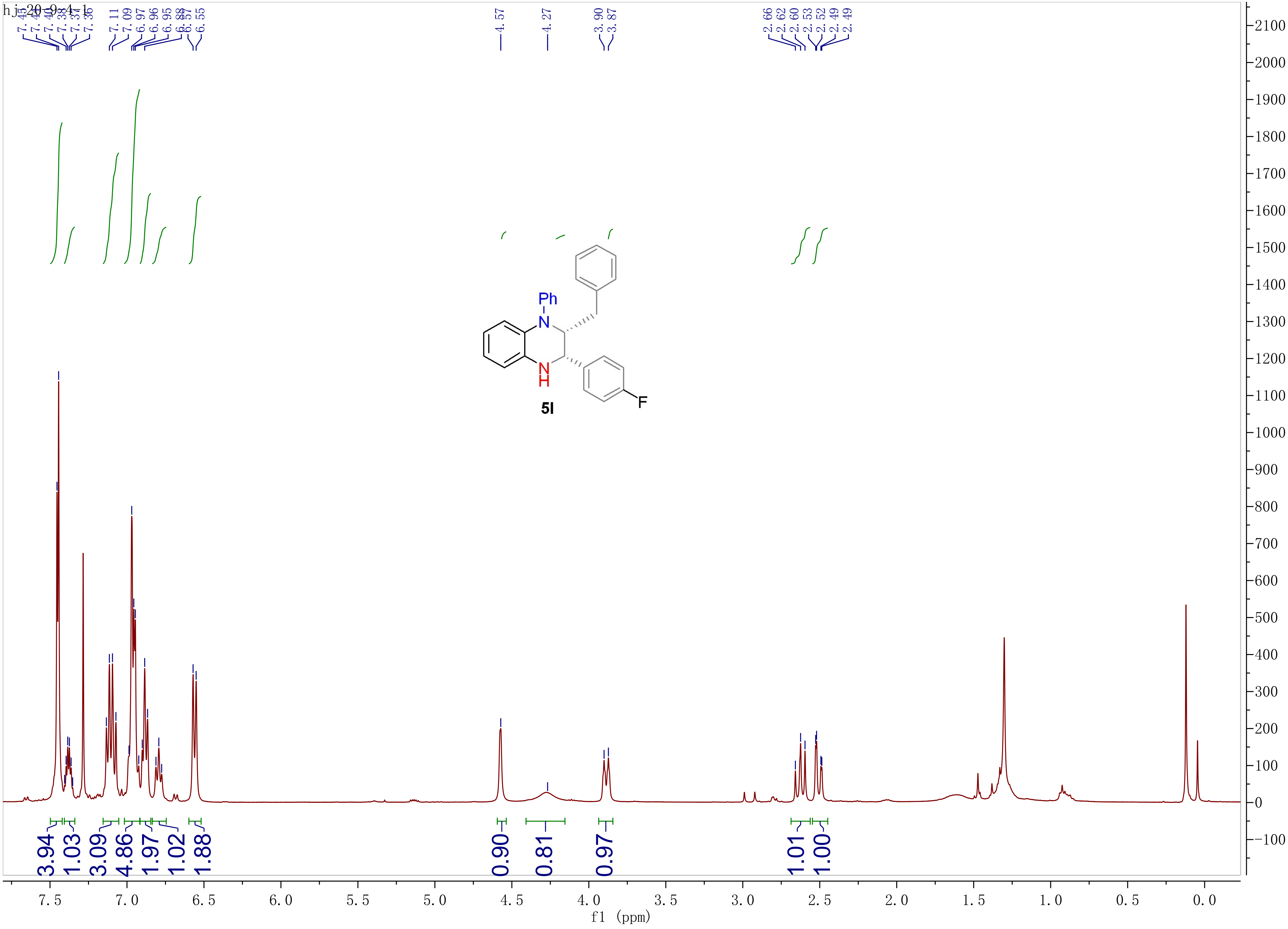


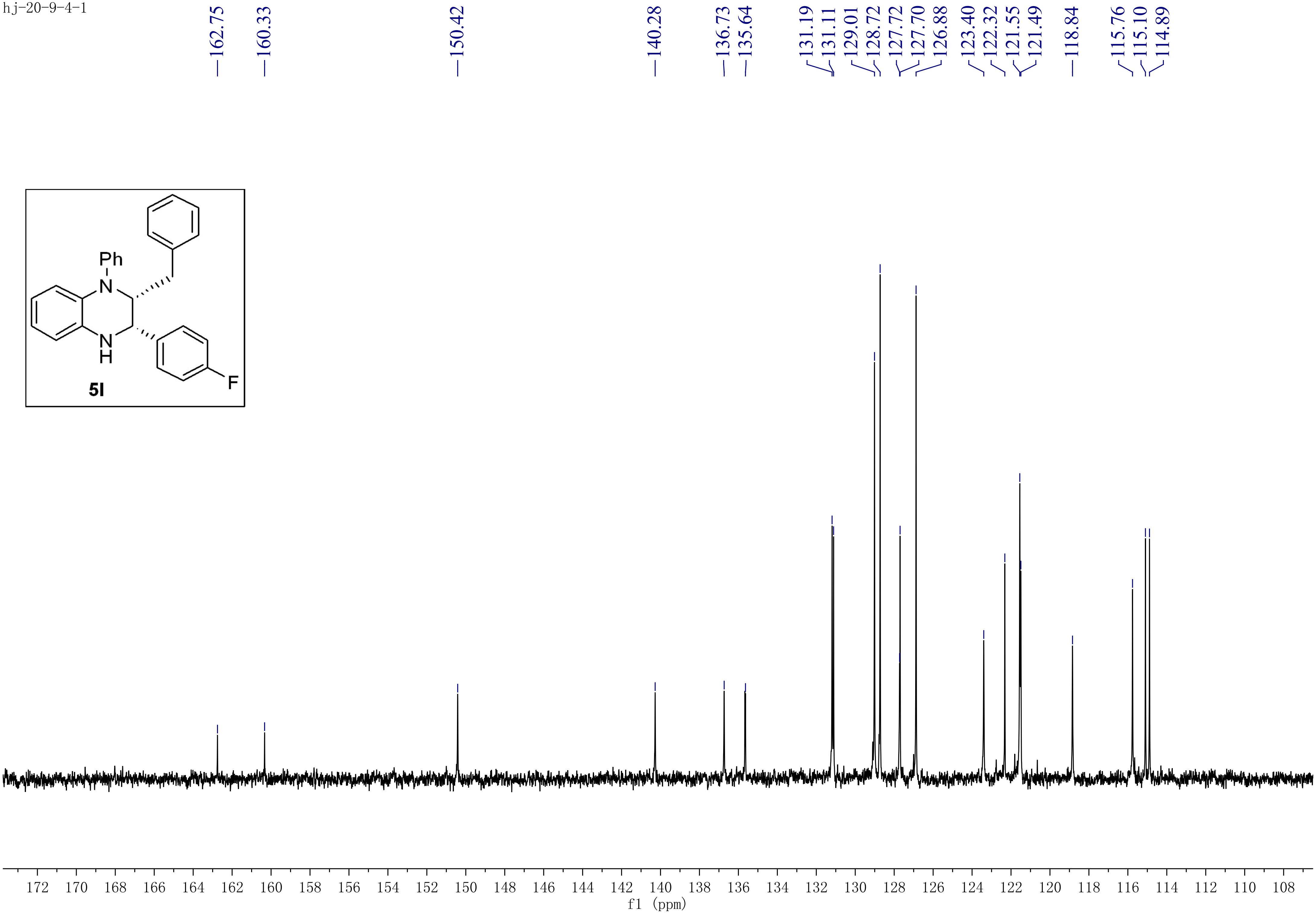
-114.63
-117.26
F
Ph
N
N
H
F
5j
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-97 -98 -99 -101 -103 -105 -107 -109 -111 -113 -115 -117 -119 -121 -123 -125 -127
f1 (ppm)


hj-20-9-20-4
7.34
7.32
7.29
7.28
7.26
7.11
7.09
7.07
6.98
6.97
6.95
6.88
6.57
6.55
4.54
4.24
3.88
3.85
2.64
2.61
2.58
2.54
2.51
2.43
Ph
N
N
H
F
5k
4.55
2.89
4.56
1.82
0.96
1.79
0.94
0.80
1.00
1.84
2.88
f1 (ppm)

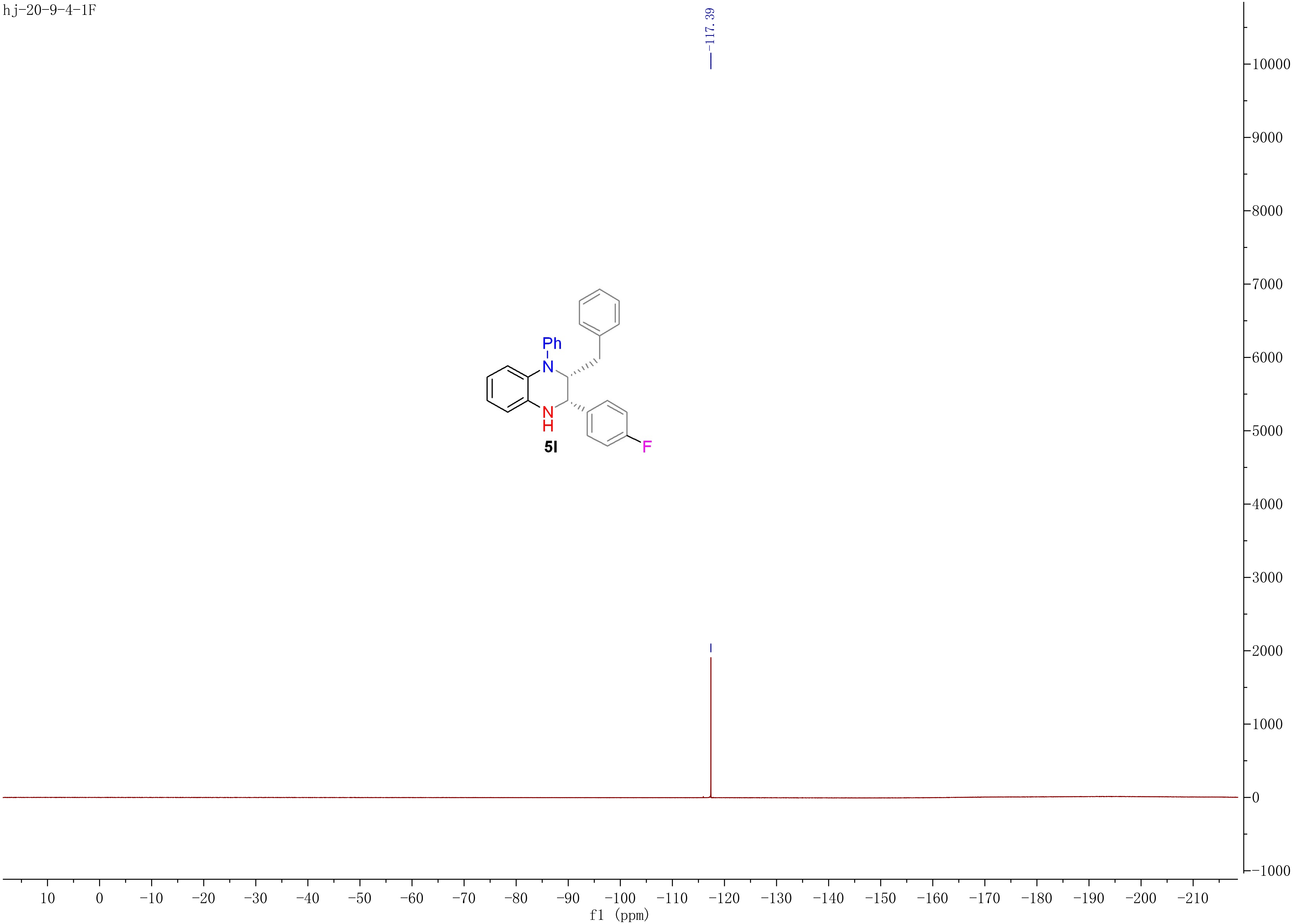

hj-20-9-20-4
162.76
160.34
150.46
137.37
137.27
136.83
135.78
135.75
131.22
131.15
129.41
129.01
127.71
126.77
123.39
122.29
121.54
121.44
118.75
115.71
115.09
114.88
67.28
54.60
31.11
21.15
Ph
N
N
H
F
5k
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


hj-20-9-20-4
-117.42
-117.43
-117.44
-117.46
Ph
N
N
H
5k
F
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

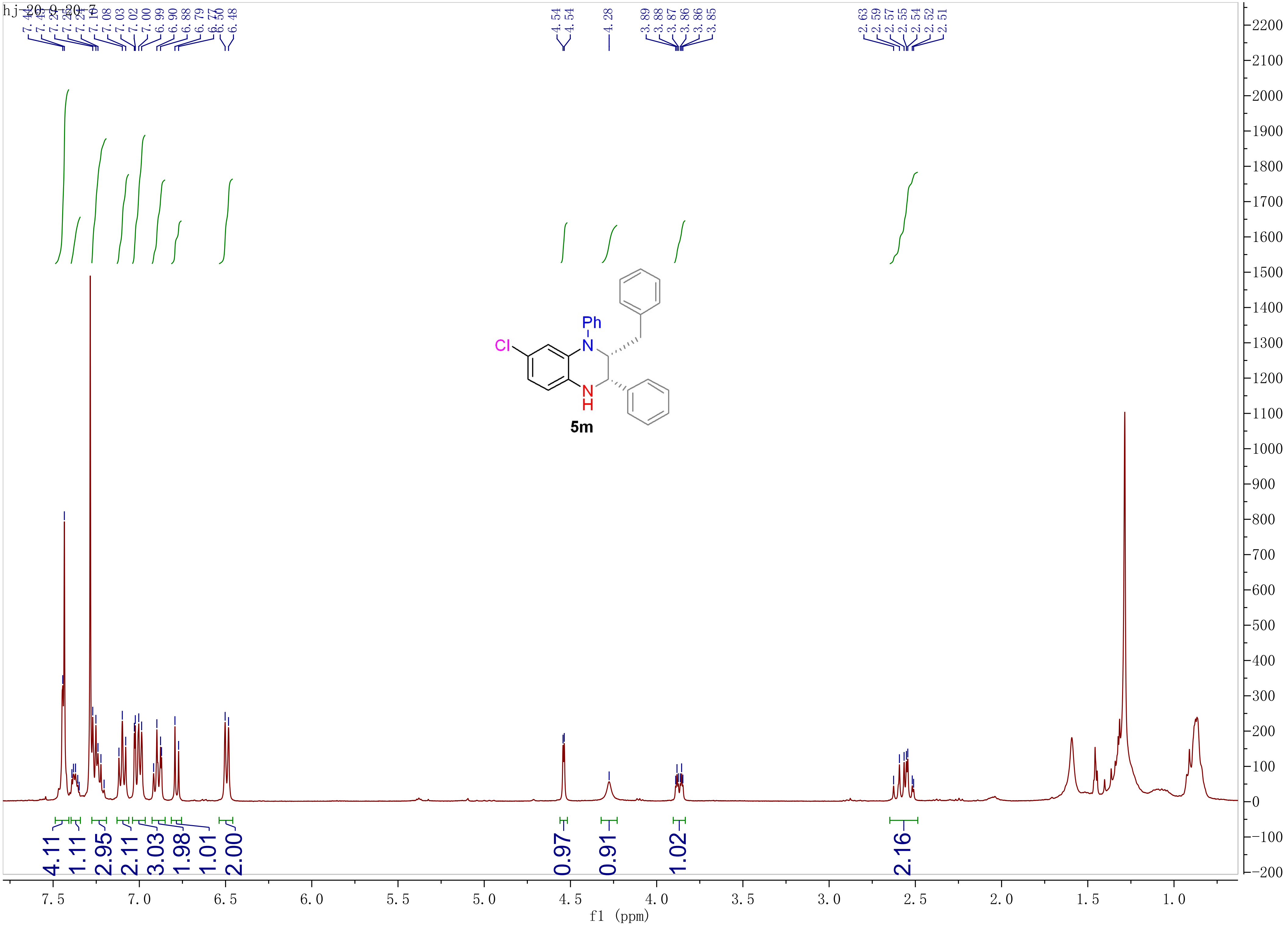

hj-20-9-4-1
7.11
7.09
6.97
6.96
6.95
6.88
6.57
6.55
4.57
4.27
3.90
3.87
2.66
2.62
2.60
2.53
2.52
2.49
2.49
Ph
N
N
H
F
5l
3.94
1.03
3.09
4.86
1.97
1.02
1.88
0.90
0.81
0.97
1.01
1.00
f1 (ppm)


hj-20-9-4-1
162.75
160.33
150.42
140.28
136.73
135.64
131.19
131.11
129.01
128.72
127.72
127.70
126.88
123.40
122.32
121.55
121.49
118.84
115.76
115.10
114.89
Ph
N
N
H
F
5l
172 170 168 166 164 162 160 158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108
f1 (ppm)

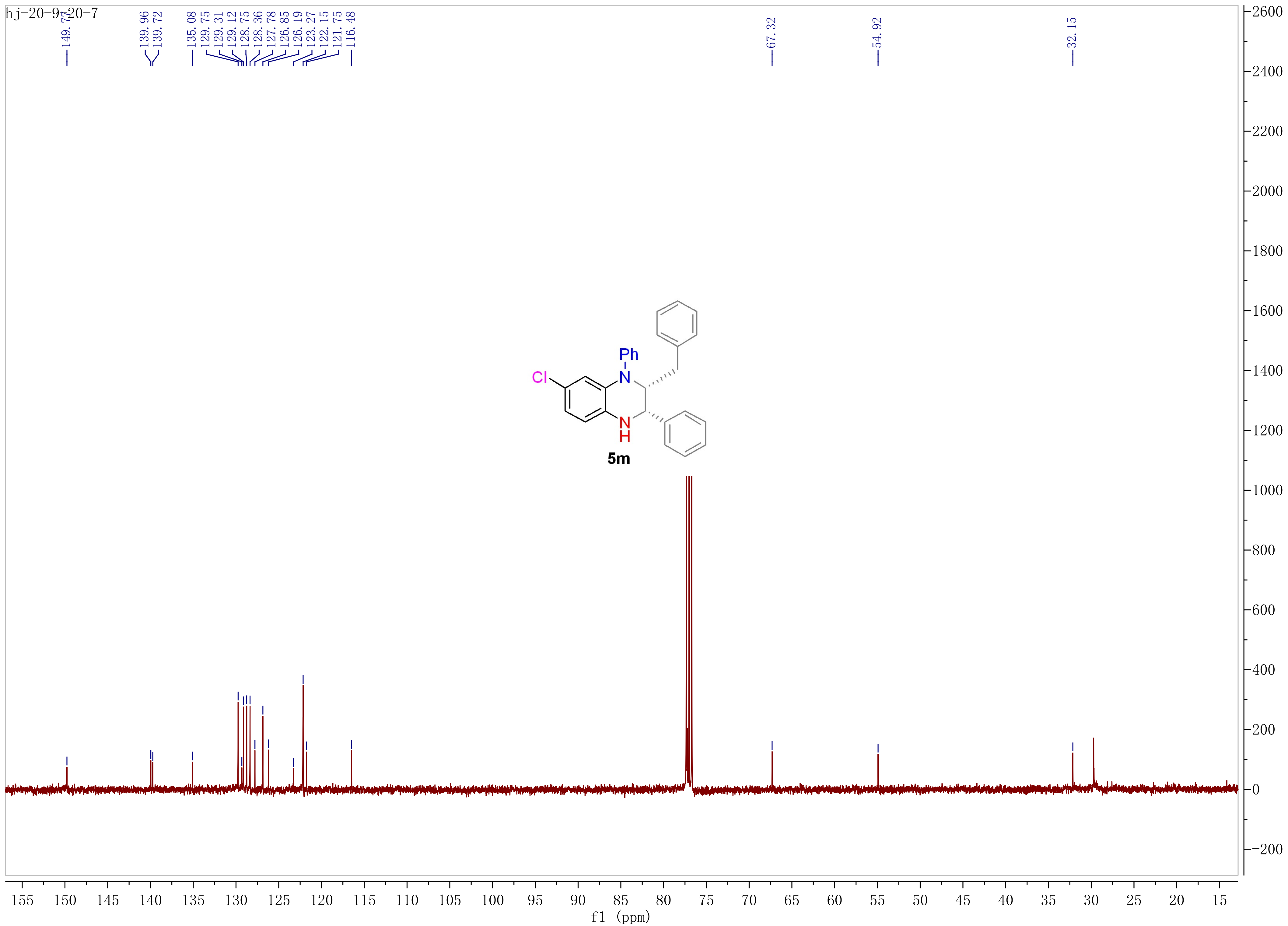
hj-20-9-4-1F



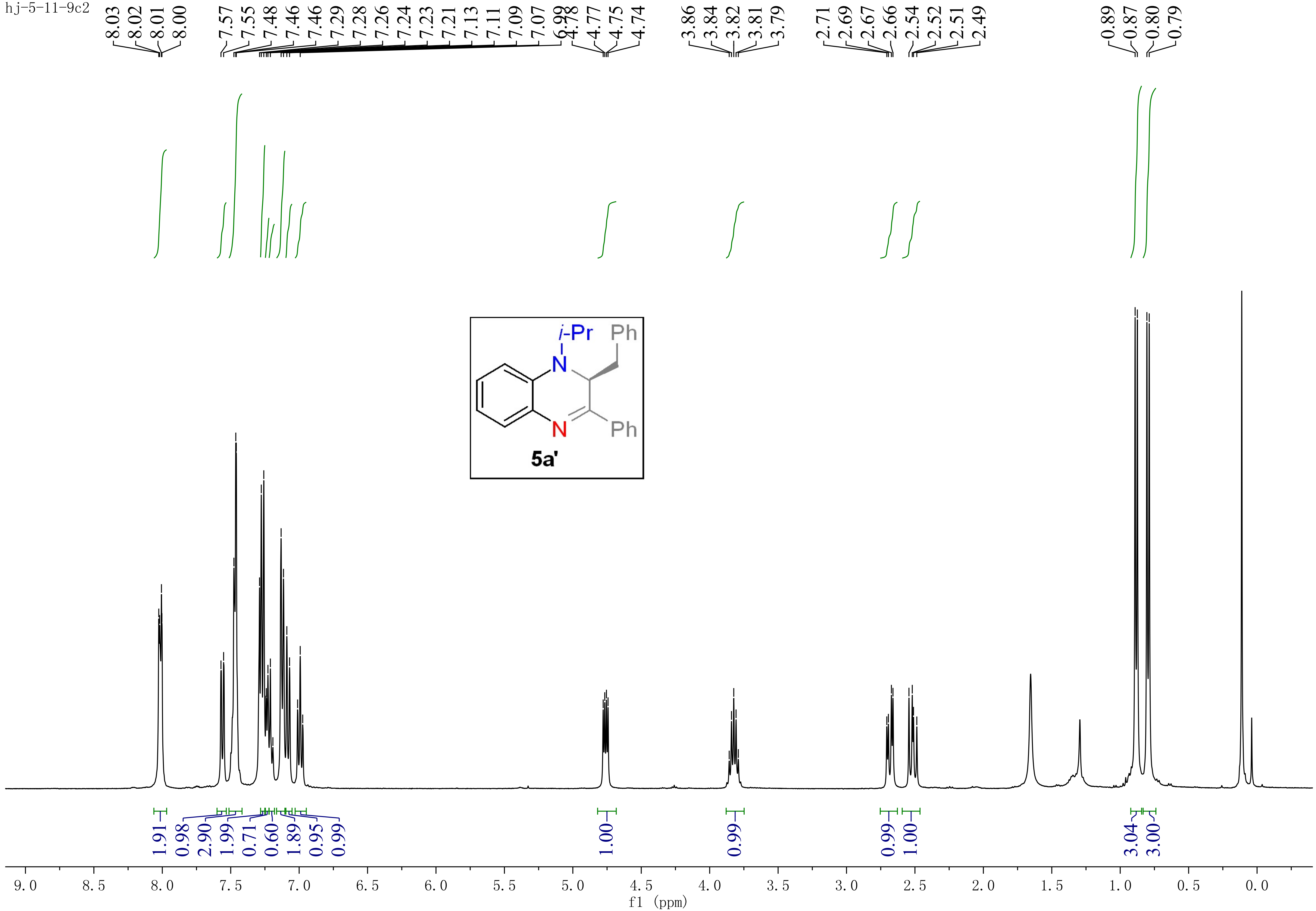
-117.39
Ph
N
N
H
F
5l
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

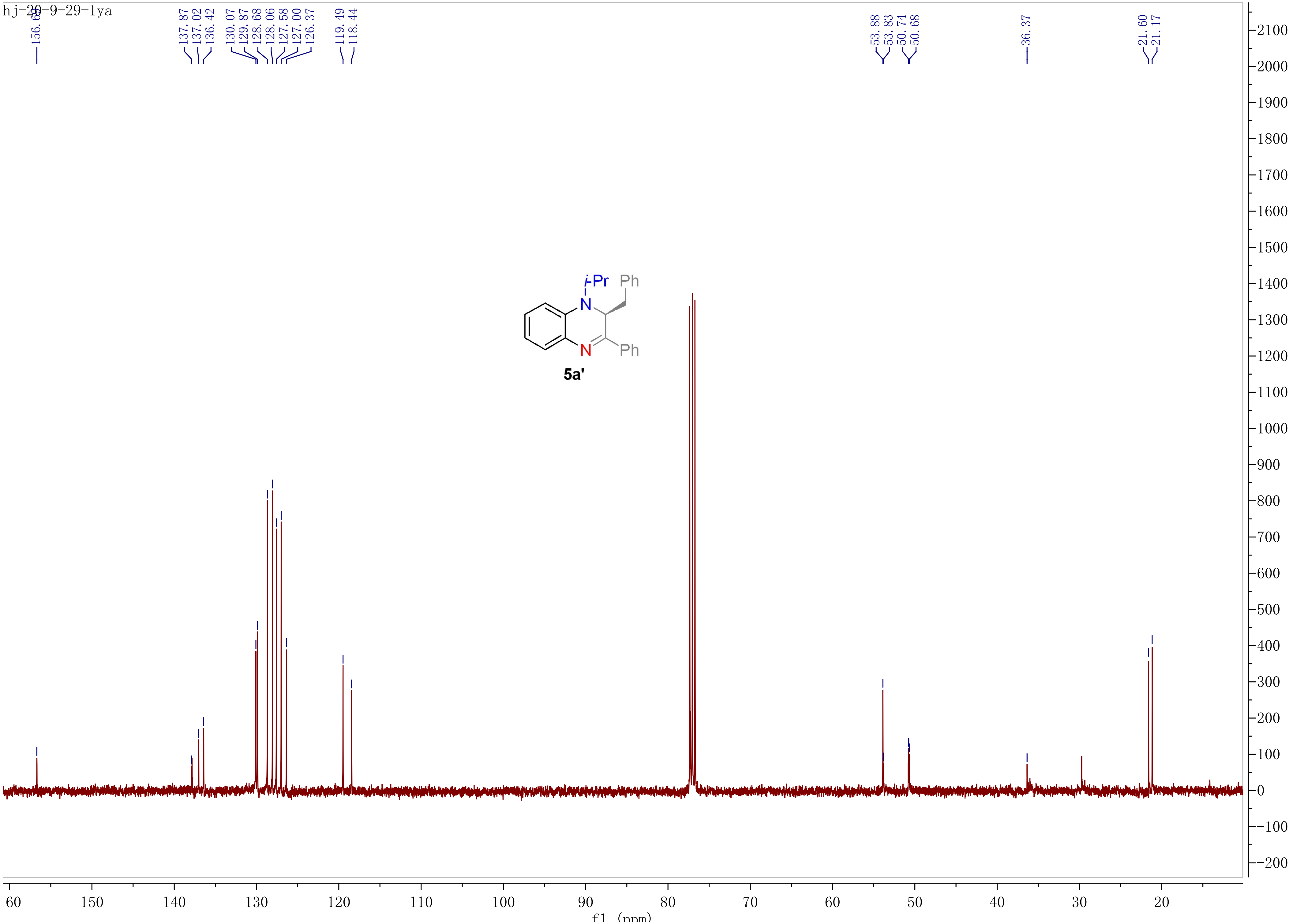


hj-20-9-20-7
7.08
7.03
7.02
7.00
6.99
6.90
6.88
6.79
6.48
4.54
4.54
4.28
3.89
3.88
3.87
3.86
3.86
3.85
2.63
2.59
2.57
2.55
2.54
2.52
2.51
Ph
N
Cl
N
H
5m
4.11
1.11
2.95
2.11
3.03
1.98
1.01
2.00
0.97
0.91
1.02
2.16
f1 (ppm)



hj-20-9-20-7
149.77
139.96
139.72
135.08
129.75
129.31
129.12
128.75
128.36
127.78
126.85
126.19
123.27
122.15
121.75
116.48
67.32
54.92
32.15
Cl
Ph
N
N
H
5m
f1 (ppm)


hj-5-11-9c2
8.03 8.02 8.01 8.00 7.57 7.55 7.48 7.46 7.46 7.29 7.28 7.26 7.24 7.23 7.21 7.13 7.11 7.09 7.07 6.99 4.78 4.77 4.75 4.74 3.86 3.84 3.82 3.81 3.79 2.71 2.69 2.67 2.66 2.54 2.52 2.51 2.49 0.89 0.87 0.80 0.79
i-Pr
Ph
N
N
Ph
5a'
1.91 0.98 2.90 1.99 0.71 0.60 1.89 0.95 0.99 1.00 0.99 0.99 1.00 3.04 3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


hj-20-9-29-1ya
156.60
137.87
137.02
136.42
130.07
129.87
128.68
128.06
127.58
127.00
126.37
119.49
118.44
53.88
53.83
50.74
50.68
36.37
21.60
21.17
i-Pr
Ph
N
N
Ph
5a'
f1 (ppm)