Supporting Information

tert-Butyl Nitrite (TBN) as the *N* atom source for the Synthesis of Substituted Cinnolines with 2-Vinylanilines and Relevant Mechanism was Studied

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General remark

^{1}H NMR and ^{13}C NMR spectra of materials and products were respectively recorded on 300MHz and 75MHz (VARIAN 300M), 400MHz and 100MHz (BRUKER 400M or JNM-ECS 400M) in $CDCl_3$. All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. All compounds were further characterized by HRMS; HRMS was performed on an FT-ICRMS mass instrument and measured with electrospray ionization (ESI). Copies of their ^{1}H NMR and ^{13}C NMR spectra are provided. Products were purified by flash chromatography on 200–300 mesh silica gels. All melting points were determined without correction. Unless otherwise noted, commercially available reagents and solvents were used without further purification.

Scheme 1. Control Experiments

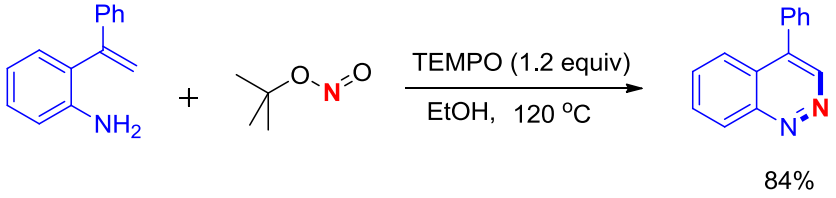


Figure 1. The data of EPR

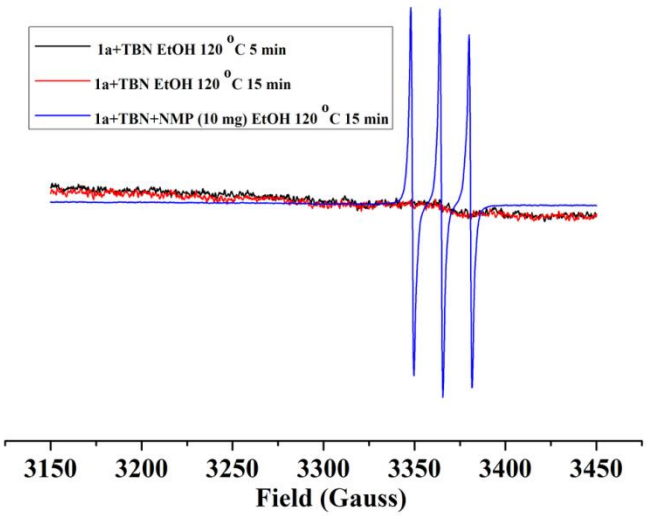
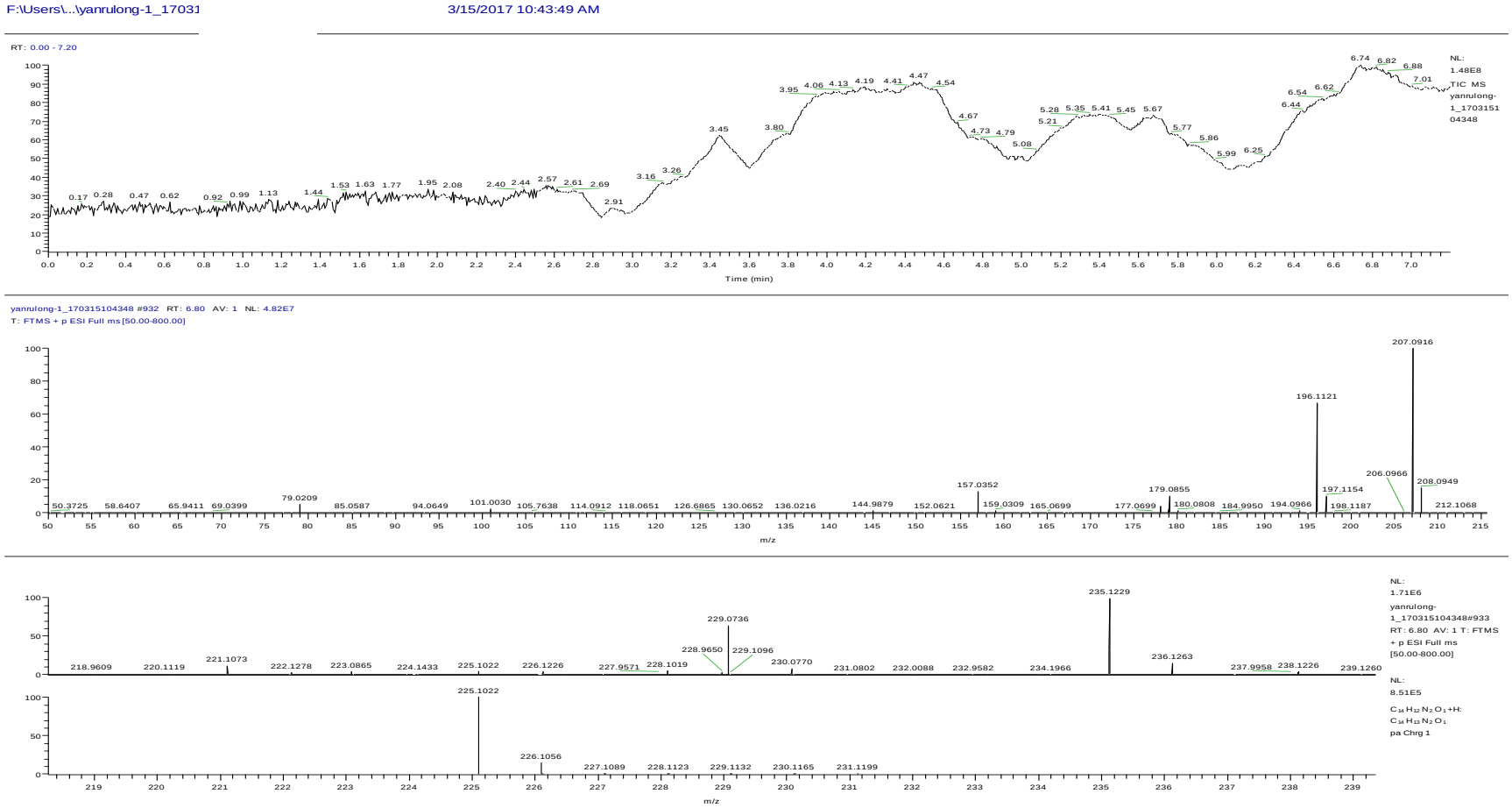
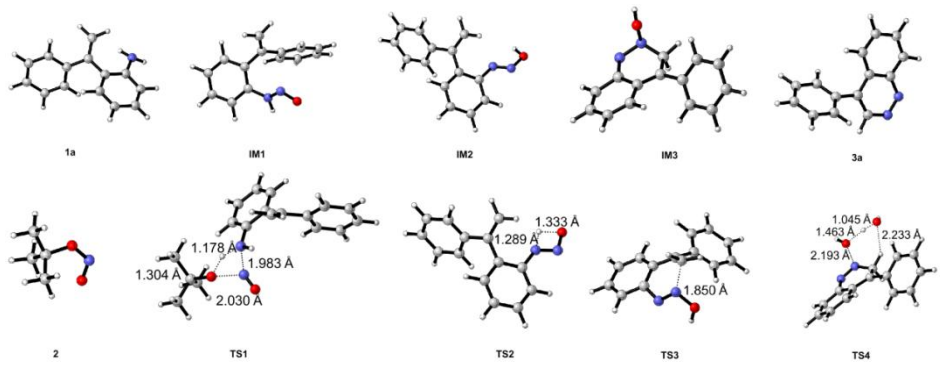


Figure 2. HRMS Analysis of the Reaction



Scheme 2. The Structures of Reactants, Intermediates, Transition states and Product in Path I from 1a and 2 to 3a.



Scheme 3. The Detailed Mechanisms of Path II from Reactants 1a and 2 to Product 3a.

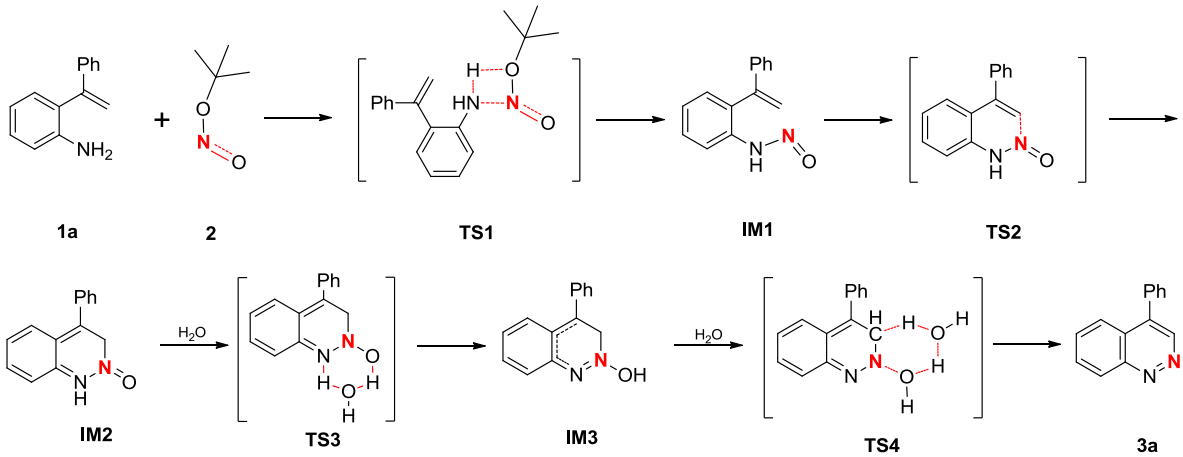
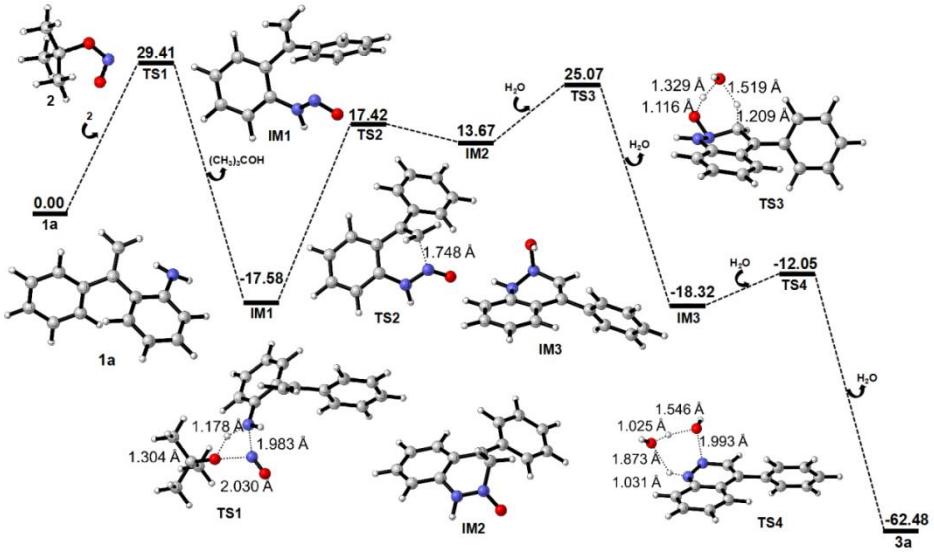


Figure 3. The Total Potential Energy Surface in the Path II for the Conversion from 1a and 2 to 3a.



This path II is different from path I. In this path II, the computational results in Figure 3. shows that the reactants **1a** and **2** would have an interaction to lose one *tert*-butanol molecule with energy barrier of 29.41 kcal/mol; and the next step is one ring-closing reaction to generate the intermediate **IM2** via transition state **TS2**; at third step, with the help of H_2O, **IM2** converts into **IM3** with the energy barrier of 11.40 kcal/mol; finally, the product **3a** can be obtained via transition state **TS4** with 6.27 kcal/mol energy. From the potential energy surface, it can be seen that the total reaction is one exothermal reaction and releases about 62.48 kcal/mol energy.

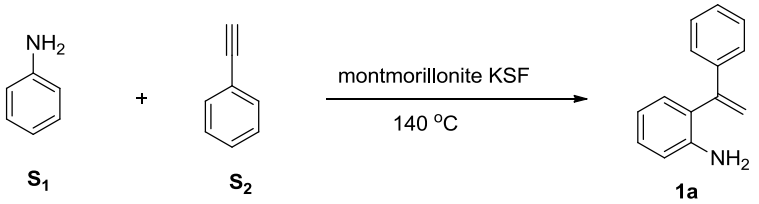
Table 1. The Charge and Fukui Function of Intermediates in Path I and II

	Atom	$q_{(NBO)}$	$f_{(NBO)}^{-}$	$f_{(NBO)}^{+}$	$f_{(NBO)}^{(2)}$
IM2	C1	-0.411	0.042	0.267	-0.225
(path I)	N2	0.172	0.245	0.004	0.241
IM1	C1	-0.409	0.224	0.264	-0.040
(path II)	N2	0.245	0.007	-0.005	0.012

The Fukui function can be used to predict the activity of atoms. The computational results shows that the value of C1 or N2 atom decrease from $f_{C1}^{(2)} = -0.225$ and $f_{N2}^{(2)} = 0.241$ to $f_{C1}^{(2)} = -0.040$ and $f_{N2}^{(2)} = 0.012$, indicating the electrocyclic reaction between C1 atom and N2 atom in IM2 of path I is much easier than in IM1 of path II. And the energy barrier can support this conclusion (31.66 kcal/mol in path I and 35.00 kcal/mol in path II).

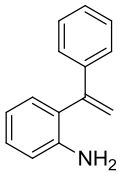
General procedure for the synthesis of 2-Vinylanilines[1-5]:

1) 1a-1q and 1u were prepared in the method.[1]



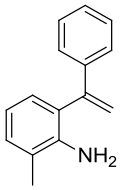
Aniline (10 mmol) **S_1**, phenylacetylene (1.0 g, 10 mmol) **S_2** and montraorillonite KSF

(1.0 g) are introduced in a round bottomed flask equipped with magnetic stirrer and a reflux condenser. The reaction mixture is heated at 140 ℃ for 5 hours and then cooled to room temperature. The products was dissolved with dichloromethane and filtered. Then the solvent were concentrated in vacuo and and the crude was purified by column chromatography (silica gel, appropriate mixture of petroleum ether /ethyl acetate) to give **1a-1q** and **1u**.



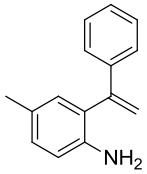
2-(1-phenylvinyl)aniline (1a) [1]

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.37-7.26 (m, 5 H), 7.19-7.09 (m, 2 H), 6.79-6.75 (m, 1 H), 6.67-6.65 (m, 1 H), 5.778-5.774 (d, *J* = 1.6 Hz, 1 H), 5.338-5.335 (d, *J* = 1.2 Hz, 1 H), 3.51 (br s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ =147.8, 144.6, 140.3, 131.5, 129.4, 129.2, 128.7, 127.9, 127.3, 118.9, 116.7, 116.2.



2-methyl-6-(1-phenylvinyl)aniline (1b) [1]

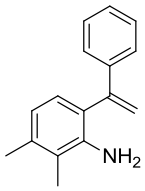
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.35-7.25 (m, 5 H), 7.04 (s, 1 H), 6.98 (s, 1 H), 6.71-6.69 (m, 1 H), 5.79-5.78 (m, 1 H), 5.33-5.32 (m, 1 H), 3.48 (br s, 2 H), 2.13 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ =148.0, 142.7, 140.4, 130.5, 129.2, 129.1, 128.7, 127.6, 127.2, 122.9, 118.4, 116.7, 18.3.



4-methyl-2-(1-phenylvinyl)aniline (1c) [1]

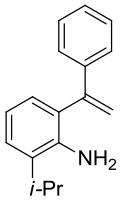
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.38-7.26 (m, 5 H), 6.97-6.92 (m, 2 H), 6.60-6.58 (d, *J* = 8.0 Hz, 1 H), 5.765-5.761 (d, *J* = 1.6 Hz, 1 H), 5.326-5.323 (d,

J = 1.2 Hz, 1 H), 3.31 (br s, 2 H), 2.25 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 148.0, 142.1, 140.4, 131.9, 130.0, 129.2, 128.7, 128.12, 128.08, 127.3, 116.6, 116.4, 21.1.



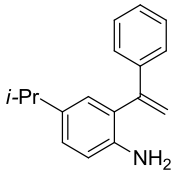
2,3-dimethyl-6-(1-phenylvinyl)aniline (1d)

Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.38-7.20 (m, 5 H), 6.90-6.87 (d, *J* = 9.0 Hz, 1 H), 6.66-6.63 (d, *J* = 9.0 Hz, 1 H), 5.79 (d, 1 H), 5.33 (d, 1 H), 3.46 (br s, 2 H), 2.30 (s, 3 H), 2.06 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 147.6, 141.9, 139.9, 136.4, 128.4, 127.9, 127.6, 126.6, 125.3, 120.7, 119.8, 115.9, 20.6,13.0. HRMS calcd for $C_{16}H_{18}N$ $[M+H]^+$ 224.1434; found: 224.1430.



2-isopropyl-6-(1-phenylvinyl)aniline (1e)

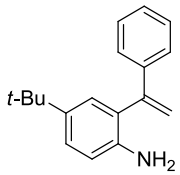
Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.36-7.26 (m, 5 H), 7.17-7.14 (m, 1 H), 6.99-6.96 (m, 1 H), 6.82-6.77 (m, 1 H), 5.83-5.81 (t, *J* = 3.0 Hz, 1 H), 5.35-5.34 (t, *J* = 3.0 Hz, 1 H), 3.52 (br s, 2 H), 2.93-2.79 (m, 1 H), 1.28-1.27 (d, *J* = 3.0 Hz, 3 H), 1.25-1.24 (d, *J* = 3.0 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 147.6, 140.8, 139.7, 132.6, 128.5, 128.0, 126.5, 124.7, 118.0, 116.1, 27.7, 22.3. HRMS calcd for $C_{17}H_{20}N$ $[M+H]^+$ 238.1590; found: 238.1593.



4-isopropyl-2-(1-phenylvinyl)aniline (1f) [2]

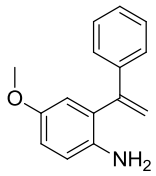
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.39-7.29 (m, 5 H), 7.04-7.02 (m, 1 H), 6.98-6.97 (d, *J* = 4.0 Hz, 1 H), 6.65-6.63 (d, *J* = 8.0 Hz, 1 H), 5.79 (d, 1 H), 5.35

(d, 1 H), 3.35 (br s, 2 H), 2.87-2.77 (m, 1 H), 1.23-1.21 (d, *J* = 8.0 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 147.6, 141.8, 139.8, 139.0, 128.9, 128.7, 128.2, 127.4, 126.8, 126.7, 116.1, 115.8, 33.3, 24.4.



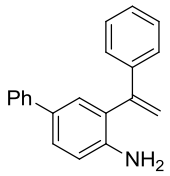
4-(tert-butyl)-2-(1-phenylvinyl)aniline (1g) [3]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.37-7.23 (m, 5 H), 7.18-7.12 (m, 2 H), 6.59-6.57 (d, *J* = 8.0 Hz, 1 H), 5.77 (s, 1 H), 5.33 (s, 1 H), 3.37 (br s, 2 H), 1.28 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 147.6, 141.3, 141.0, 139.6, 128.4, 127.9, 127.5, 126.8, 126.6, 125.5, 115.8, 115.2, 33.8, 31.5.



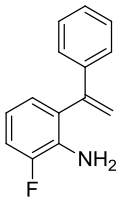
4-methoxy-2-(1-phenylvinyl)aniline (1h) [1]

Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.37-7.27 (m, 5 H), 6.77-6.71 (m, 2 H), 6.63-6.61 (d, *J* = 8.0 Hz, 1 H), 5.788-5.785 (d, *J* = 1.2 Hz, 1 H), 5.340-5.337 (d, *J* = 1.2 Hz, 1 H), 3.73 (s, 3 H), 3.23 (br s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 152.4, 147.1, 139.4, 137.6, 128.5, 128.0, 126.6, 116.8, 116.0, 114.6, 55.7.



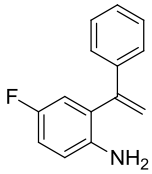
3-(1-phenylvinyl)-[1, 1'-biphenyl]-4-amine (1i) [3]

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.80-7.45 (m, 12 H), 6.93-6.90 (m, 1 H), 6.061-6.058 (d, *J* = 1.2 Hz, 1 H), 5647-5.643 (d, *J* = 1.6 Hz, 1 H), 3.78 (br s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ =147.4, 143.9, 141.2, 139.8, 129.6, 129.0, 128.9, 128.5, 127.7, 127.6, 127.0, 126.61, 126.55, 116.5, 116.3.



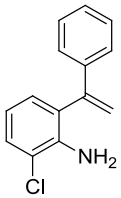
2-fluoro-6-(1-phenylvinyl)aniline (1j) [4]

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.50-7.41 (m, 5 H), 7.13-7.02 (m, 2 H), 6.83-6.78 (m, 1 H), 5.929-5.926 (d, *J* = 1.2 Hz, 1 H), 5.488-5.485 (d, *J* = 1.2 Hz, 1 H), 3.74 (br s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 152.9-150.6 (*J* = 230.0 Hz), 146.29-146.26 (*J* = 3.0 Hz), 139.4, 132.8-132.7 (*J* = 10.0 Hz), 129.33-129.30 (*J* = 3.0 Hz), 128.8, 128.4, 126.8, 126.1-126.0 (*J* = 10.0 Hz), 117.6-117.5 (*J* = 10.0Hz), 116.6, 114.5-114.3 (*J* = 20.0 Hz).



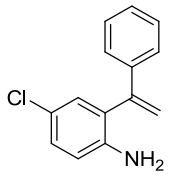
4-fluoro-2-(1-phenylvinyl)aniline (1k) [3]

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.41-7.33 (m, 5 H), 6.94-6.88 (m, 2 H), 6.67-6.64 (m, 1 H), 5.849-5.846 (d, *J* = 1.2 Hz, 1 H), 5.395-5.392 (d, *J* = 1.2 Hz, 1 H), 3.47 (br s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 157.3-154.9 (*J* = 240.0 Hz), 146.4, 140.09-140.07 (*J* = 2.0 Hz), 139.1, 128.7, 128.3,126.6, 117.2, 117.0, 116.6, 116.5-116.4 (*J* = 10.0 Hz), 115.3-115.1 (*J* = 20.0 Hz).



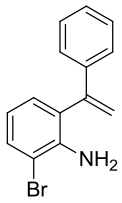
2-chloro-6-(1-phenylvinyl)aniline (1l) [5]

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.44-7.32 (m, 6 H), 7.11-7.09 (m, 1 H), 6.79-6.75 (m, 1 H), 5.90 (s, 1 H), 5.43 (s, 1 H), 4.06 (br s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 146.7, 140.8, 139.1, 129.3, 128.9, 128.8, 128.42, 128.37, 126.7, 119.5, 118.2, 116.7.



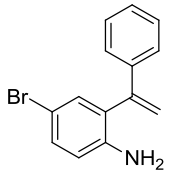
4-chloro-2-(1-phenylvinyl)aniline (1m) [1]

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.32-7.28 (m, 5 H), 7.10-7.07 (m, 2 H), 6.59-6.57 (d, *J* = 8.0 Hz, 1 H), 5.788-5.785 (d, *J* = 1.2 Hz, 1 H), 5.334-5.331 (d, *J* = 1.2 Hz, 1 H), 3.48 (br s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 146.8, 143.3, 139.6, 130.9, 129.3, 129.20, 129.15, 129.0, 127.2, 123.4, 117.4, 117.3.



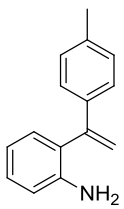
2-bromo-6-(1-phenylvinyl)aniline (1n) [6]

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.44-7.42 (m, 1 H), 7.36-7.32 (m, 5 H), 7.08-7.06 (m, 1 H), 6.68-6.64(m, 1 H), 5.84 (d, 1 H), 5.37 (d, 1 H), 4.05 (br s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 146.8, 141.8, 139.0, 132.1, 130.0, 128.8, 128.5, 128.4, 126.7, 118.8, 116.8, 109.8.



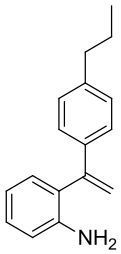
4-bromo-2-(1-phenylvinyl)aniline (1o) [1]

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.27-7.21 (m, 5 H), 7.17-7.13 (m, 2 H), 6.47-6.45 (d, *J* = 8.0 Hz, 1 H), 5.705-5.703 (d, *J* = 0.8 Hz, 1 H), 5.252-5.250 (d, *J* = 0.8 Hz, 1 H), 3.45 (br s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 146.7, 143.8, 139.6, 133.7, 132.1, 129.8, 129.4, 129.0, 127.3, 117.8, 117.5, 110.6.



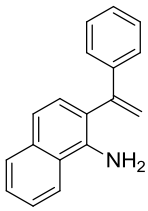
2-(1-(*p*-tolyl)vinyl)aniline (1p) [6]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.32-7.28 (m, 2 H), 7.21-7.14 (m, 4 H), 6.84-6.80 (m, 1 H), 6.72-6.70 (m, 1 H), 5.79-5.78 (t, 1 H), 5.34-5.33 (t, 1 H), 3.50 (br s, 2 H), 2.38 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ =147.1, 144.1, 138.1, 130.9, 129.44, 129.40, 128.8, 127.6, 126.9, 118.4, 115.7, 115.4, 21.3.



2-(1-(4-propylphenyl)vinyl)aniline (1q)

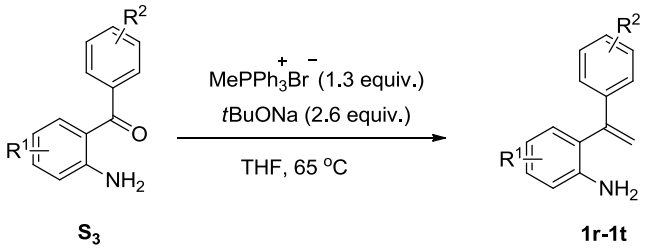
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.30-7.26 (m, 4 H), 7.14-7.11 (m, 2 H), 6.81-6.77 (m, 1 H), 6.71-6.69 (m, 1 H), 5.77 (d, 1 H), 5.31-5.30 (d, 1 H), 3.40 (br s, 2 H), 2.67-2.63 (t, *J* = 8.0 Hz, 2 H), 1.70-1.61 (m, 2 H), 0.97-0.93 (t, *J* = 8.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 148.7, 144.0, 142.9, 137.0, 135.0, 130.9, 128.8, 128.6, 126.6, 118.4, 115.7, 115.4, 38.1, 26.7, 14.0 . HRMS calcd for $C_{17}H_{20}N$ $[M+H]^+$ 238.1590; found: 238.1585.



2-(1-phenylvinyl)naphthalen-1-amine (1u) [7]

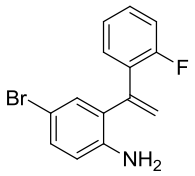
Brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.87-7.85 (d, *J* = 8.0 Hz, 2 H), 7.52-7.25 (m, 10 H), 6.02-5.98 (d, *J* = 14.0 Hz, 1 H), 5.51-5.48 (d, *J* = 14.0 Hz, 1 H), 4.08 (br s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 147.4, 140.0, 139.1, 134.0, 128.9, 128.6, 128.5, 128.2, 126.9, 125.8, 125.2, 123.7, 121.7, 121.2, 118.3, 116.7.

2) 1r-1t were prepared in the method.[8]



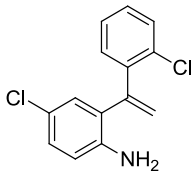
S$_3$ **1r-1t**

To a solution of methyltriphenylphosphonium bromide (4.64 g, 13 mmol), *t*BuONa (2.50 g, 26 mmol) in THF (100 mL) was added, then the resulting reaction mixture was stirred at room temperature for 5 min. Afterwards compounds **S$_3$** (10 mmol) was added and the reaction solution was stirred at 65 ^{o}C overnight. Then the solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether /ethyl acetate = 20 / 1) to afford the materials **1r-1t**.



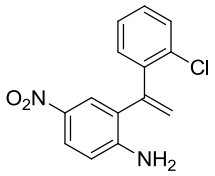
4-bromo-2-(1-(2-fluorophenyl)vinyl)aniline (1r)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.29-7.04 (m, 6 H), 6.56-6.54 (d, *J* = 8.0 Hz, 1 H), 5.85 (d, 1 H), 5.59 (d, 1 H), 3.66 (br s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 162.1-159.7 (*J* = 240.0 Hz), 143.4, 141.1, 133.1, 132.0, 130.94, 130.91, 130.3, 124.91-124.88 (*J* = 3.0 Hz), 122.2, 117.8, 117.0-116.7 (*J* = 30.0 Hz), 110.5 . HRMS calcd for $C_{14}H_{12}BrFN$ $[M+H]^+$ 292.0132; found: 292.0139.



4-chloro-2-(1-(2-chlorophenyl)vinyl)aniline (1s) [9]

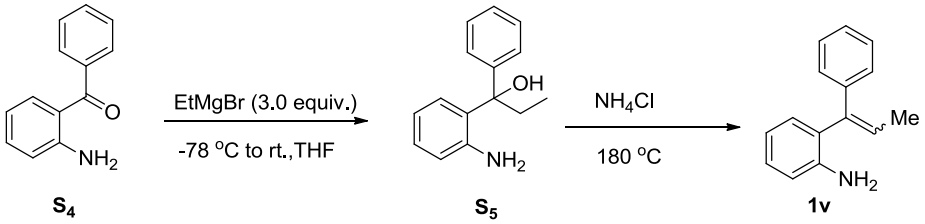
Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.38-7.25(m, 4 H), 7.04-7.01 (m, 1 H), 6.90-6.89 (d, *J* = 4.0 Hz, 1 H), 6.62-6.59 (d, *J* = 12.0 Hz, 1 H), 5.69 (d, 1 H), 5.62 (d, 1 H), 3.85 (br s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 144.4, 142.3, 140.3, 131.0, 130.2, 129.34, 129.25, 128.4, 128.2, 127.1, 122.8, 121.3, 117.1.



2-(1-(2-chlorophenyl)vinyl)-4-nitroaniline (1t)

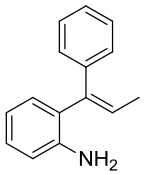
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.96-7.95 (m, 1 H), 7.85-7.84 (d, *J* = 4.0 Hz, 1 H), 7.38-7.34 (m, 2 H),7.31-7.25 (m, 2 H), 6.65-6.63 (d, *J* = 8.0 Hz, 1 H), 5.72 (d, 1 H), 5.69 (d, 1 H), 4.68 (br s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 150.3, 143.7, 139.6, 138.8, 132.6, 131.1, 130.3, 129.7, 127.3, 126.2, 125.5, 125.3, 122.2, 114.5. HRMS calcd for $C_{14}H_{12}ClN_2O_2$ $[M+H]^+$ 275.0582; found: 275.0589.

3) 1v were prepared in the method.[10]



S4 **S5** **1v**

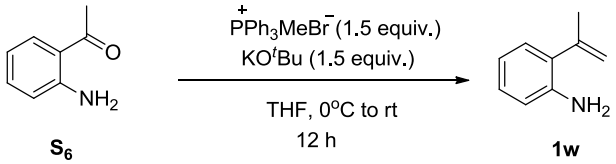
To a solution of 2-aminobenzophenone (1.97 g, 10 mmol) **S4** in THF (50 mL), EtMgBr (2.0 M in THF, 16 mL, 31 mmol) was added at -78 °C. After being stirred at room temperature for 30 min, the reaction mixture was quenched by saturated aqueous solution of NH_4Cl and filtered through Celite pad. After the filtrate was extracted with EtOAc (50 mL×3), the organic layer was washed with brine, dried over anhydrous Na_2SO_4, and evaporated. The residue was purified with silica gel column chromatography (eluent: petroleum ether /ethyl acetate = 10 / 1) to give 1-(2-aminophenyl)-1-phenyl-1-propanol **S5** as yellow crystals. Then the above **S5** (1.76 g, 7.8 mmol) was treated with solid NH_4Cl (1.24 g, 23.3 mmol) for 20 min at 180 °C. The reaction mixture was cooled to ambient temperature and purified with silica gel column chromatography (eluent: petroleum ether /ethyl acetate = 20 / 1) to give the E/Z mixture of 2-(1-phenyl-1-propenyl)aniline.



(*E*/*Z*)-2-(1-phenylprop-1-en-1-yl)aniline (1v) [10]

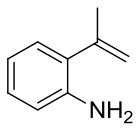
Yellow oil. (E/Z =1.5/1) ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.45-7.16 (m, 10 H), 7.10-7.08 (m, 1 H), 6.92-6.82 (m, 2 H), 6.70-6.68 (d, *J* = 8.0 Hz,1 H), 6.49-6.44 (m, 1 H), 3.63 (br s, 1 H), 2.02-2.00 (d, *J* = 8.0 Hz, 2 H), 1.81-1.79 (d, *J* = 8.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ =144.2, 144.1, 141.0, 140.2, 139.5, 139.1, 131.03, 130.97, 130.1, 129.3, 128.5, 128.43, 128.37, 128.3, 127.1, 126.3, 125.9, 125.0, 118.4, 118.3, 115.8, 115.4, 15.6, 15.5.

4) 1w were prepared in the method.[11]



S6 **1w**

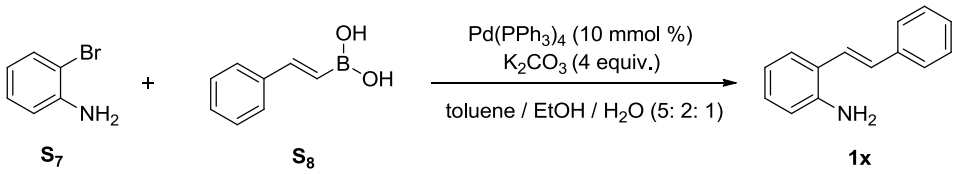
To a stirred solution of Ph_3PMeBr (1.5 equiv., 12.2 mmol) in Dry THF (15 mL) was added KO^{t}Bu (1.5equiv. 12.2 mmol) in portions under nitrogen. After the mixture was stirred at room temperature for 0.5 h, a solution of corresponding benzophenone (1 equiv. 8.14 mmol) **S6** in THF (15 mL) was added dropwise. The reaction mixture was then stirred at room temperature under nitrogen overnight. The reaction mixture was quenched with water and extracted with ethyl acetate (50 mL ×2). The combined organic layers was washed with saturated $NaHCO_3$ (50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4, and concentrated on rotary evaporator under vacuum and purified by column chromatography (silica gel, appropriate mixture of petroleum ether /ethyl acetate) to afford **1w**.



2-(prop-1-en-2-yl)aniline (1w) [11]

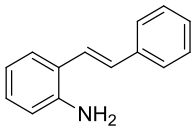
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.08-7.03 (m, 2 H), 6.75-6.69 (m, 2 H), 5.29 (d, 1 H), 5.06 (d, 1 H), 3.83 (br s, 2 H), 2.07 (d, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 144.1, 143.4, 129.9, 128.9, 128.5, 118.8, 116.2, 116.0, 24.6.

5) 1x were prepared in the method.[12]



S7 **S8** **1x**

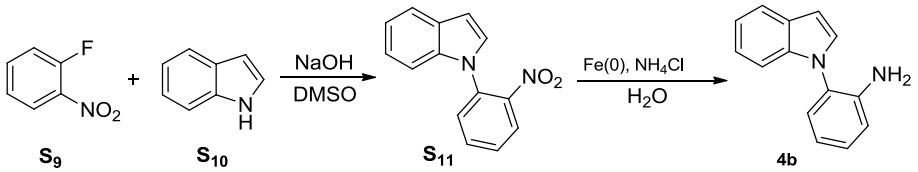
The general procedure was followed 2-bromoaniline **S7** (2.0 mmol, 1.0 equiv.), trans-2-phenyl-vinylboronic acid **S8** (3.0 mmol, 1.5 equiv.), 10 mmol % of $Pd(PPh_3)_4$ (0.2 mmol) and 4 equiv. of K_2CO_3 (8.0 mmol) were added to a mixed solvent of toluene, EtOH and H_2O (5/2/1, 4 mL). The reaction mixtrure was poured into water and extracted with diethyl ether for several times. The combined organic layers were dried over Na_2SO_4. Filtered and concentrated. The residue was purified by column chromatography (petroleum ether /ethyl acetate) to afford the products **1x**.



(*E*)-2-styrylaniline (1x) [12]

White solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.56-7.54 (m, 2 H), 7.46-7.44 (m, 1 H), 7.42-7.38 (m, 2 H), 7.32-7.28 (m, 1 H), 7.22-7.18 (d, *J* = 16.0 Hz, 1 H), 7.17-7.13 (m, 1 H), 7.05-7.01 (d, *J* = 16.0 Hz, 1 H), 6.88-6.84 (m, 1 H), 6.75-6.73 (m, 1 H), 3.77 (br s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ =143.8, 137.5, 130.2, 128.62 128.60, 127.5, 127.1, 126.4, 124.1, 123.8, 119.1, 116.2.

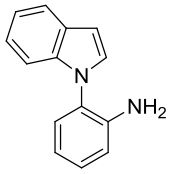
6) 4b was prepared in the method.[13]



S9 **S10** **S11** **4b**

2-(1*H*-indol-1-yl)aniline was prepared according to a modified literature procedure. A mixture of 2-nitroaniline (2 mmol) , indol (2 mmol) and NaOH (2 mmol) in DMSO (4 mL) was stirred vigorously for 2 h. After cooling, the reaction mixture was poured into water (30 mL) and extracted with EtOAc three times (3×30 mL). The combined

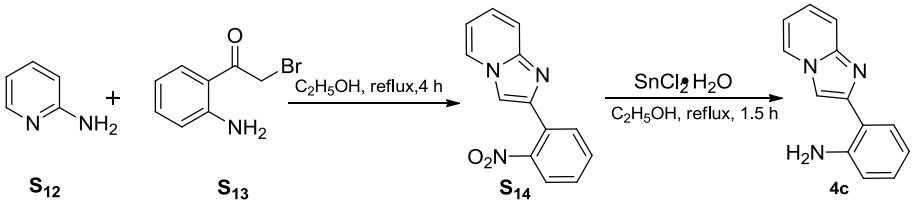
organic layers were dried with $MgSO_4$ and the solvent was removed in vacuo to afford a residue. The residue was added to iron powder (16 mmol) and NH_4Cl (1 mmol) in water (30 mL) and refluxed for 4 h. After cooling, the reaction mixture was poured into water (100 mL) and extracted with ethyl acetate twice (3×30 mL). The combined organic layers were dried with $MgSO_4$ and the solvent was removed in vacuo to afford a residue. The residue was purified by column chromatography on silica gel using petroleum ether / ethyl acetate as eluent to provide the desired product **4b**.



2-(1*H*-indol-1-yl)aniline (4b) [13]

White liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.69-7.67 (m, 1 H), 7.22-7.11 (m, 6 H), 6.82-6.78 (m, 2 H), 6.67-6.66 (d, *J* = 3.1 Hz, 1 H), 3.48 (br s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 143.2, 136.5, 129.3, 128.7, 128.6, 124.9, 122.3, 121.1, 120.3, 118.6, 116.3, 110.9, 103.3, 102.6.

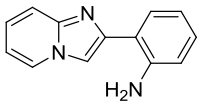
7) 4c was prepared in the method.[14]



S12 **S13** **S14** **4c**

A solution of 2-amino-pyridine **S12** (500 mg, 5.31 mmol) and 2-bromo-1-(2-nitro-phenyl)-ethanone **S13** (1.29 g, 5.31 mmol) in ethanol (20 mL) was refluxed for 4 h. After the solvent was removed, the residue was basified to pH 8 with $NaHCO_3$ solution and extracted with EtOAc (40 mL). The organic layer was washed with water (30 mL) and brine (30 mL) and dried over anhydrous Na2SO4. The organic layer was evaporated to dryness under reduced pressure. The residue was purified by silica gel chromatography using hexane-ethyl acetate (85/15, v/v) to afford 2-(2-nitro-phenyl)-imidazo[1,2-a]pyridine **S14**.

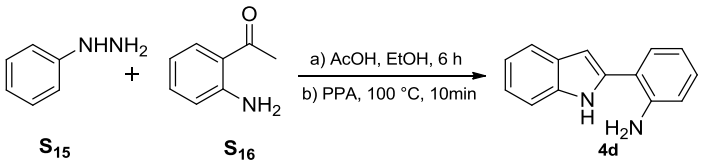
A solution of 2-(2-Nitro-phenyl)-imidazo[1,2-a]pyridine **S_{14}** (500 mg, 2.09 mmol) and $SnCl_2 \cdot 2H_2O$ (2.36 g, 10.45 mmol) in ethanol (40 mL) was refluxed under nitrogen for 1.5 h. The solution was allowed to cool down, and then it was poured into ice; the pH was made slighitly basic (pH = 8) by addition of 5% aqueous $NaHCO_3$. EtOAc (50 mL) was added to the mixture, and it was filtered through a bed of celite. The organic layer was finally washed with water (50 mL) and brine (50 mL) and dried over anhydrous Na_2SO_4. The organic layer was evaporated to dryness under reduced pressure. The residue was purified by silica gel chromatography using hexaneethyl acetate (75/25, v/v) to afford 2-imidazo[1,2-a]pyridin-2-yl-phenylamine **4c.**



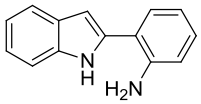
2-(imidazo[1,2-*a*]pyridin-2-yl)aniline (4c) **[14]**

White solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 8.12-8.08 (m, 1 H), 7.78 (s, 1 H), 6.82-6.78 (m, 2 H), 7.55-7.49 (m, 2 H), 7.14-7.11 (m, 2 H), 6.78-6.73 (m, 2 H), 5.77 (br, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 146.8, 146.1, 144.7, 129.1, 128.4, 125.4, 124.3, 117.5, 117.4, 116.9, 112.6, 109.9, 108.5.

8) 4c was prepared in the method.[15]



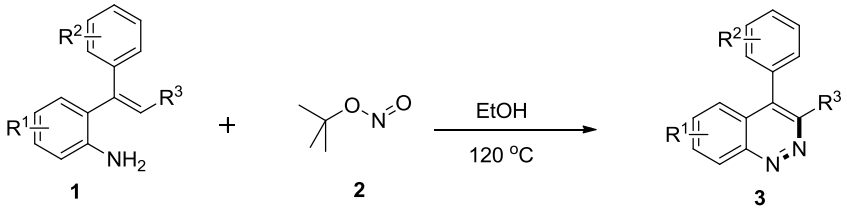
A mixture of phenylhydrazine (10 mmol) and 1-(2-aminophenyl)ethanone (10 mmol) in 20 mL of EtOH with AcOH (5 mmol %) was stirred at room temperature for 6 h, and then 20 mL of PPA (polyphosphoric acid) was added and the temperature raised to 100 ℃ for 2 h. Next, the reaction mixture was poured into water (100 mL), and Na_2CO_3 was added slowly until the pH = 7. The mixture was extracted with ethyl acetate three times (3 × 30 mL). The combined organic layers were dried with $MgSO_4$, and the solvent was removed in vacuo to afford a residue. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent = 1:2 to provide the desired product **4d**.



2-(1*H*-indol-2-yl)aniline (4d) [15]

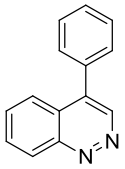
Brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.45 (s, 1 H), 7.65-7.63 (d, *J* = 7.6 Hz, 1 H), 7.40-7.37 (m, 2 H), 7.24-7.12 (m, 3 H), 6.88-6.72 (m, 2 H), 6.71 (s, 1 H), 4.09 (br, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 144.1, 136.2, 135.9, 129.3, 129.1, 128.9, 122.2, 120.4, 120.2, 119.1, 118.8, 116.6, 110.8, 101.6.

General procedure for synthesis of substituted cinnolines:



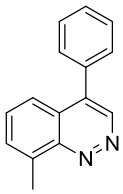
2-Vinylanilines **1** (0.3 mmol) and tert-butyl nitrite (TBN) **2** (0.6 mmol) were mixed in 2 mL of EtOH and this mixture was carried out under Ar at 120 °C. The reaction mixture was cooled to room temperature and evaporated in vacuo. Then the crude product was purified by column chromatography, eluting with petroleum ether/EtOAc (10:1) to afford the desired cinnolines **3**.

The data of products:



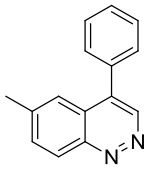
4-phenylcinnoline (3a)

Yellow oil (54 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.26 (s, 1 H), 8.61-8.59 (d, *J* = 8.0 Hz, 1 H), 8.01-7.99 (d, *J* = 8.0 Hz, 1 H), 7.88-7.84 (m, 1 H), 7.75-7.71 (m, 1 H), 7.59-7.53 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 150.6, 144.5, 135.2, 134.2, 131.3, 130.4, 130.2, 129.8, 129.3, 129.0, 124.7, 124.4; HRMS calcd for $C_{14}H_{11}N_2$ $[M+H]^+$ 207.0917; found: 207.0916.



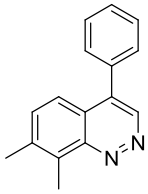
8-methyl-4-phenylcinnoline (3b)

Yellow oil (63 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.26 (s, 1 H), 7.82-7.80 (d, *J* = 8.0 Hz, 1 H), 7.66-7.51 (m, 7 H), 3.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ =149.6, 144.5, 138.6, 135.2, 134.6, 131.1, 130.3, 129.9, 129.1, 128.9, 124.5, 122.6, 18.2; HRMS calcd for $C_{15}H_{13}N_2$ $[M+H]^+$ 221.1073; found: 221.1070.



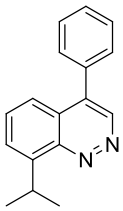
6-methyl-4-phenylcinnoline (3c)

Yellow oil (62 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.19 (s, 1 H), 8.49-8.47 (d, *J* = 8.0 Hz, 1 H), 7.72-7.67 (m, 2 H), 7.61-7.53 (m, 5 H), 2.53 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 149.6, 144.6, 142.1, 134.53, 134.49, 132.9, 129.84, 129.76, 129.1, 129.0, 124.6, 122.8, 22.3; HRMS calcd for $C_{15}H_{13}N_2$ $[M+H]^+$ 221.1073; found: 221.1076.



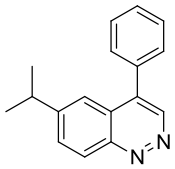
7,8-dimethyl-4-phenylcinnoline (3d)

Yellow oil (62 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.22 (s, 1 H), 7.75-7.72 (d, *J* = 8.8 Hz, 1 H), 7.60-7.51 (m, 6 H), 3.05 (s, 3 H), 2.58 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ =149.6, 143.8, 138.1, 135.5, 135.0, 134.8, 134.5, 129.9, 129.0, 128.9, 122.9, 121.5, 20.5, 13.4; HRMS calcd for $C_{16}H_{15}N_2$ $[M+H]^+$ 235.1230; found: 235.1234.



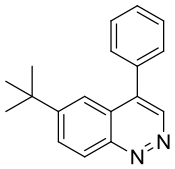
8-isopropyl-4-phenylcinnoline (3e)

Yellow solid (66 mg, 89%), melt point: 164-166 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.27 (s, 1 H), 7..84-7.81 (m, 1 H), 7.75-7.67 (m, 2 H), 7.61-7.53 (m, 5 H), 4.85-4.75 (m, 1 H), 1.52-1.51 (d, *J* = 4.0 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 148.8, 148.3, 144.4, 135.3, 134.8, 131.3, 129.9, 129.0, 128.9, 126.0, 124.6, 122.3, 27.4, 23.7; HRMS calcd for $C_{17}H_{17}N_2$ $[M+H]^+$ 249.1386; found: 249.1391.



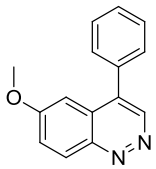
6-isopropyl-4-phenylcinnoline (3f)

Brown oil (68 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.21 (s, 1 H), 8.55-8.53 (d, *J* = 8.0 Hz, 1 H), 7.80-7.77 (m, 2 H), 7.63-7.55 (m, 5 H), 3.15-3.05 (m, 1 H), 1.32-1.31 (d, *J* = 4.0 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 152.5, 150.0, 144.6, 134.9, 134.6, 130.3, 130.1, 129.8, 129.1, 129.0, 124.7, 120.3, 34.7, 23.5; HRMS calcd for $C_{17}H_{17}N_2$ $[M+H]^+$ 249.1386; found: 249.1384.



6-(tert-butyl)-4-phenylcinnoline (3g)

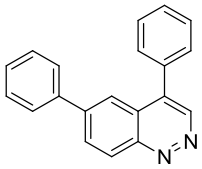
Brown oil (77 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.22 (s, 1 H), 8.55-8.53 (d, *J* = 8.0 Hz, 1 H), 7.98-7.95 (m, 1 H), 7.924-7.919 (d, *J* = 2.0 Hz, 1 H), 7.63-7.55 (m, 5 H), 1.38 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 154.6, 149.6, 144.7, 135.1, 134.6, 129.8, 129.6, 129.2, 129.0, 124.3, 118.9, 35.6, 30.8; HRMS calcd for $C_{18}H_{19}N_2$ $[M+H]^+$ 263.1543; found: 263.1538.



6-methoxy-4-phenylcinnoline (3h)

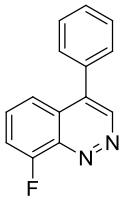
Brown solid (69 mg, 97%), melt point: 172-175 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.10 (s, 1 H), 8.46-8.44 (d, *J* = 8.0 Hz, 1 H), 7.60-7.52 (m, 5 H), 7.48-7.45

(m, 1 H), 7.14-7.13 (d, *J* = 4.0 Hz, 1 H), 3.85 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 161.3, 147.9, 144.6, 134.8, 134.0, 131.9, 129.5, 129.1, 126.5, 124.2, 100.5, 55.7; HRMS calcd for $C_{15}H_{13}N_2O$ $[M+H]^+$ 237.1023; found: 237.1020.



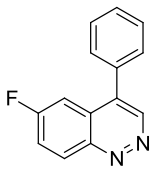
4,6-diphenylcinnoline (3i)

Brown oil (79 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.29 (s, 1 H), 8.70-8.68 (m, 1 H), 8.16-8.13 (m, 2 H), 7.67-7.56 (m, 7 H), 7.52-7.42 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ =149.9, 144.9, 143.9, 139.6, 135.2, 134.4, 130.7, 130.4, 129.8, 129.3, 129.1, 128.6, 127.7, 124.8, 121.9; HRMS calcd for $C_{20}H_{15}N_2$ $[M+H]^+$ 283.1230; found: 283.1236.



8-fluoro-4-phenylcinnoline (3j)

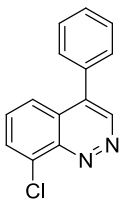
Brown solid (59 mg, 87%), melt point: 167-169 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.37 (s, 1 H), 7.82-7.80 (d, *J* = 8.0 Hz, 1 H), 7.73-7.68 (m, 1 H), 7.64-7.52 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 159.9-157.3 (*J* = 260.0 Hz), 145.4, 141.9-141.8 (*J* = 10.0 Hz), 134.80-134.77 (*J* = 3.0 Hz), 133.9, 131.3-131.2 (*J* = 8.0 Hz), 129.8, 129.5, 129.1, 126.0, 120.7-120.6 (*J* = 6.0 Hz), 114.2-114.0 (*J* = 20.0 Hz) ; HRMS calcd for $C_{14}H_{10}FN_2$ $[M+H]^+$ 225.0823; found: 225.0821.



6-fluoro-4-phenylcinnoline (3k)

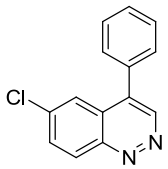
Yellow oil (55 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.25 (s, 1 H), 8.67-8.64 (m, 1 H), 7.67-7.55 (m, 7 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 164.5-162.0 (*J* = 250.0 Hz), 148.3, 144.5, 135.0-134.9 (*J* = 7.0 Hz), 133.9, 133.7, 133.6, 129.6-129.5 (*J* = 8.0 Hz), 129.2, 126.1-126.0 (*J* = 11.0 Hz), 121.7-121.4 (*J* =

27.0 Hz), 107.8-107.6 (J = 23.0 Hz); HRMS calcd for $C_{14}H_{10}FN_2$ $[M+H]^+$ 225.0823; found: 225.0825.



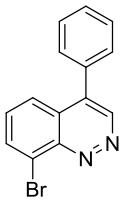
8-chloro-4-phenylcinnoline (3l)

Yellow oil (70 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.36 (s, 1 H), 7.95-7.91 (m, 2 H), 7.66-7.53 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 146.8, 145.4, 135.22, 135.16, 133.8, 131.0, 130.5, 129.8, 129.5, 129.1, 126.1, 124.0; HRMS calcd for $C_{14}H_{10}ClN_2$ $[M+H]^+$ 241.0527; found: 241.0523.



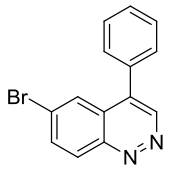
6-chloro-4-phenylcinnoline (3m)

Yellow solid (40 mg, 55%), melt point: 185-189 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.29 (s, 1 H), 8.58-8.56 (d, J = 8.0 Hz, 1 H), 7.982-7.977 (d, J = 2.0 Hz, 1 H), 7.82-7.80 (m, 1 H), 7.65-7.55 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ =148.9, 145.0, 137.8, 134.3, 133.6, 132.0, 131.7, 129.7, 129.6, 129.2, 125.2, 123.4; HRMS calcd for $C_{14}H_{10}ClN_2$ $[M+H]^+$ 241.0527; found: 241.0525.



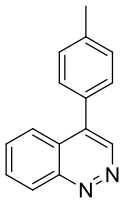
8-bromo-4-phenylcinnoline (3n)

Yellow oil (83 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.34 (s, 1 H), 8.17-8.15 (m, 1 H), 7.97-7.94 (m, 1 H), 7.61-7.52 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 147.3, 145.4, 135.2, 134.3, 133.7, 131.4, 129.9, 129.5, 129.1, 126.2, 126.0, 124.8; HRMS calcd for $C_{14}H_{10}BrN_2$ $[M+H]^+$ 285.0022; found: 285.0016.



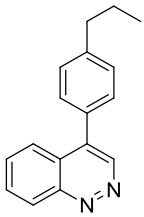
6-bromo-4-phenylcinnoline (3o)

Yellow solid (49 mg, 58%), melt point: 213-216 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.29 (s, 1 H), 8.50-8.48 (d, *J* = 8.0 Hz, 1 H), 8.17-8.16 (d, *J* = 4.0 Hz, 1 H), 7.96-7.93 (m, 1 H), 7.65-7.55 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 149.0, 145.0, 134.2, 134.1, 133.6, 131.9, 129.7, 129.6, 129.2, 126.8, 126.5, 125.5; HRMS calcd for $C_{14}H_{10}BrN_2$ $[M+H]^+$ 285.0022; found: 285.0025.



4-(p-tolyl)cinnoline (3p)

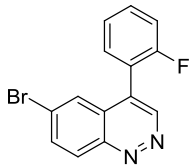
Yellow oil (50 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.23 (s, 1 H), 8.58-8.55 (d, *J* = 8.8 Hz, 1 H), 8.01-7.99 (d, *J* = 8.0 Hz, 1 H), 7.85-7.81 (m, 1 H), 7.72-7.67 (m, 1 H), 7.45-7.43 (d, *J* = 8.0 Hz, 2 H), 7.38-7.36 (d, *J* = 8.0 Hz, 2 H), 2.46 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 150.5, 144.6, 139.4, 135.2, 131.2, 131.1, 130.3, 130.1, 129.7, 124.7, 124.5, 21.3; HRMS calcd for $C_{15}H_{13}N_2$ $[M+H]^+$ 221.1073; found: 221.1070.



4-(4-propylphenyl)cinnoline (3q)

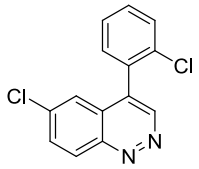
Yellow oil (39 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.28 (s, 1 H), 8.62-8.60 (d, *J* = 8.0 Hz, 1 H), 8.07-8.04 (d, *J* = 8.4 Hz, 1 H), 7.89-7.85 (m, 1 H), 7.56-7.72 (m, 1 H), 7.51-7.49 (d, *J* = 8.0 Hz, 2 H), 7.42-7.40 (d, *J* = 8.0 Hz, 2 H), 2.75-2.71 (t, *J* = 8.0 Hz, 2 H), 1.80-1.71 (m, 2 H), 1.05-1.02 (t, *J* = 8.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ =150.6, 144.6, 144.2, 135.3, 131.5, 131.1, 130.3, 130.1, 129.8, 129.1, 124.8, 124.5, 37.8, 24.5, 13.9; HRMS calcd for $C_{17}H_{17}N_2$

$[M+H]^+$ 249.1386; found: 249.1390.



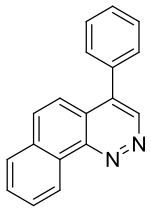
6-bromo-4-(2-fluorophenyl)cinnoline (3r)

Yellow solid (79 mg, 88%), melting point: 233-237 ^oC. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.29 (s, 1 H), 8.51-8.49 (d, *J* = 8.0 Hz, 1 H), 7.97-7.92 (m, 2 H), 7.63-7.57 (m, 1 H), 7.48-7.32 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 161.1-158.6 (*J* = 250.0 Hz), 149.0, 145.5, 134.4, 131.90-131.86 (*J* = 4.0 Hz), 131.8, 131.67-131.67 (*J* = 3.0 Hz), 128.8, 126.95-126.93 (*J* = 2.0 Hz), 126.7, 125.8, 125.0-124.9 (*J* = 10.0 Hz), 121.3-121.1 (*J* = 20.0 Hz), 116.66-116.45 (*J* = 21.0 Hz,); HRMS calcd for $C_{14}H_9BrFN_2$ $[M+H]^+$ 302.9928; found: 302.9922.



6-chloro-4-(2-chlorophenyl)cinnoline (3s)

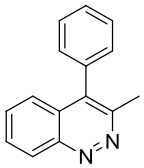
Brown oil (40 mg, 48%). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.25 (s, 1 H), 8.60-8.58 (d, *J* = 8.0 Hz, 1 H), 7.83-7.80 (m, 1 H), 7.66-7.63 (m, 1 H), 7.58-7.48 (m, 3 H), 7.39-7.37 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ =148.9, 145.4, 138.0, 133.6, 132.4, 132.1, 132.01, 131.96, 131.5, 130.9, 130.4, 127.3, 125.5, 123.5; HRMS calcd for $C_{14}H_9Cl_2N_2$ $[M+H]^+$ 275.0138; found:275.0134.



4-phenylbenzo[h]cinnoline (3u)

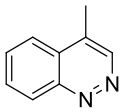
Yellow oil (59 mg, 77%). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.74-9.72 (d, *J* = 8.0 Hz, 1 H), 9.41 (s, 1 H), 7.98-7.81 (m, 5 H), 7.65-7.57 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 148.5, 147.1, 135.5, 134.6, 133.14, 133.06, 130.2, 130.0, 129.7, 129.1, 129.0, 128.7, 128.1, 124.8, 123.8, 121.0; HRMS calcd for $C_{18}H_{13}N_2$ $[M+H]^+$

257.1073; found: 257.1075.



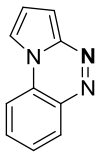
3-methyl-4-phenylcinnoline (3v)

Yellow solid, melt point: 171-173 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.54-8.52 (d, *J* = 8.0 Hz, 1 H), 7.76-7.72 (m, 1 H), 7.61-7.49 (m, 5 H), 7.32-7.30 (d, *J* = 8.0 Hz, 2 H), 2.76 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 151.5, 149.4, 134.5, 133.5, 130.8, 129.8, 129.3, 129.2, 128.8, 128.5, 125.4, 124.8, 21.0; HRMS calcd for $C_{15}H_{13}N_2$ $[M+H]^+$ 221.1073; found: 221.1074.



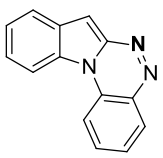
4-methylcinnoline (3w)

Yellow solid, melt point: 97-99 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.19 (s, 1 H), 8.56-8.54 (m, 1 H), 8.03-8.01 (m, 1 H), 7.89-7.78 (m, 2 H), 2.72 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 149.7, 146.0, 131.5, 130.8, 130.3, 130.2, 126.3, 123.0, 15.3; HRMS calcd for $C_9H_9N_2$ $[M+H]^+$ 145.0760; found: 145.0757.



benzo[e]pyrrolo[2,1-c][1,2,4]triazine (5a)[16]

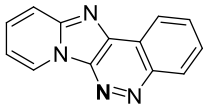
Yellow solid, melt point: 176-178 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 8.44-8.42 (d, *J* = 8.0 Hz, 1 H), 7.86-7.84 (m, 2 H), 7.75-7.70 (m, 1 H), 7.61-7.56 (m, 1 H), 7.44-7.43 (d, *J* = 4.0 Hz, 1 H), 7.12-7.10 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 141.2, 136.4, 132.1, 130.6, 125.7, 124.8, 116.2, 113.3, 110.9, 108.8; HRMS calcd for $C_{10}H_8N_3$ $[M+H]^+$ 170.0713; found: 170.0715.



benzo[5,6][1,2,4]triazino[4,3-a]indole (5b) [17]

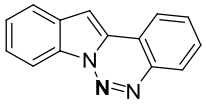
Red solid, melt point: 220-222 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 8.50-8.47

(d, *J* = 8.0 Hz, 1 H), 8.34-8.30 (m, 2 H), 8.07-8.05 (d, *J* = 8.0 Hz, 1 H), 7.83-7.77 (m, 1 H), 7.68 (s, 1 H), 7.64-7.48 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ =142.1, 136.6, 133.4, 131.6, 129.1, 128.6, 127.4, 125.8, 124.5, 123.43, 123.42, 114.8, 114.0, 102.2; HRMS calcd for $C_{14}H_{10}N_3$ $[M+H]^+$ 220.0869; found: 220.0873.



pyrido[2',1':2,3]imidazo[4,5-c]cinnoline (5c) [18]

White solid, melt point: 206-208 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 9.33-9.30 (m, 1 H), 8.73-8.68 (m, 2 H), 7.93-7.87 (m, 3 H), 7.77-7.73 (m, 1 H), 7.24-7.19 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 149.3, 148.7, 141.8, 134.1, 133.1, 130.6, 130.3, 129.2, 125.1, 122.0, 120.1, 118.0, 113.1; HRMS calcd for $C_{13}H_9N_4$ $[M+H]^+$ 221.0822; found: 221.0825.



benzo[4,5][1,2,3]triazino[1,6-a]indole (5d)

Yellow solid, melt point: 214-216 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 8.45-8.42 (m, 1 H), 8.24-8.21 (m, 1 H), 8.05-8.02 (m, 1 H), 7.87-7.82 (m, 1 H), 7.77-7.64 (m, 2 H), 7.55-7.48 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 136.0, 132.5, 131.8, 129.5, 129.2, 127.4, 124.8, 124.0, 123.2, 122.2, 120.6, 118.9, 111.6, 92.4; HRMS calcd for $C_{14}H_{10}N_3$ $[M+H]^+$ 220.0869; found: 220.0870.

Refrence:

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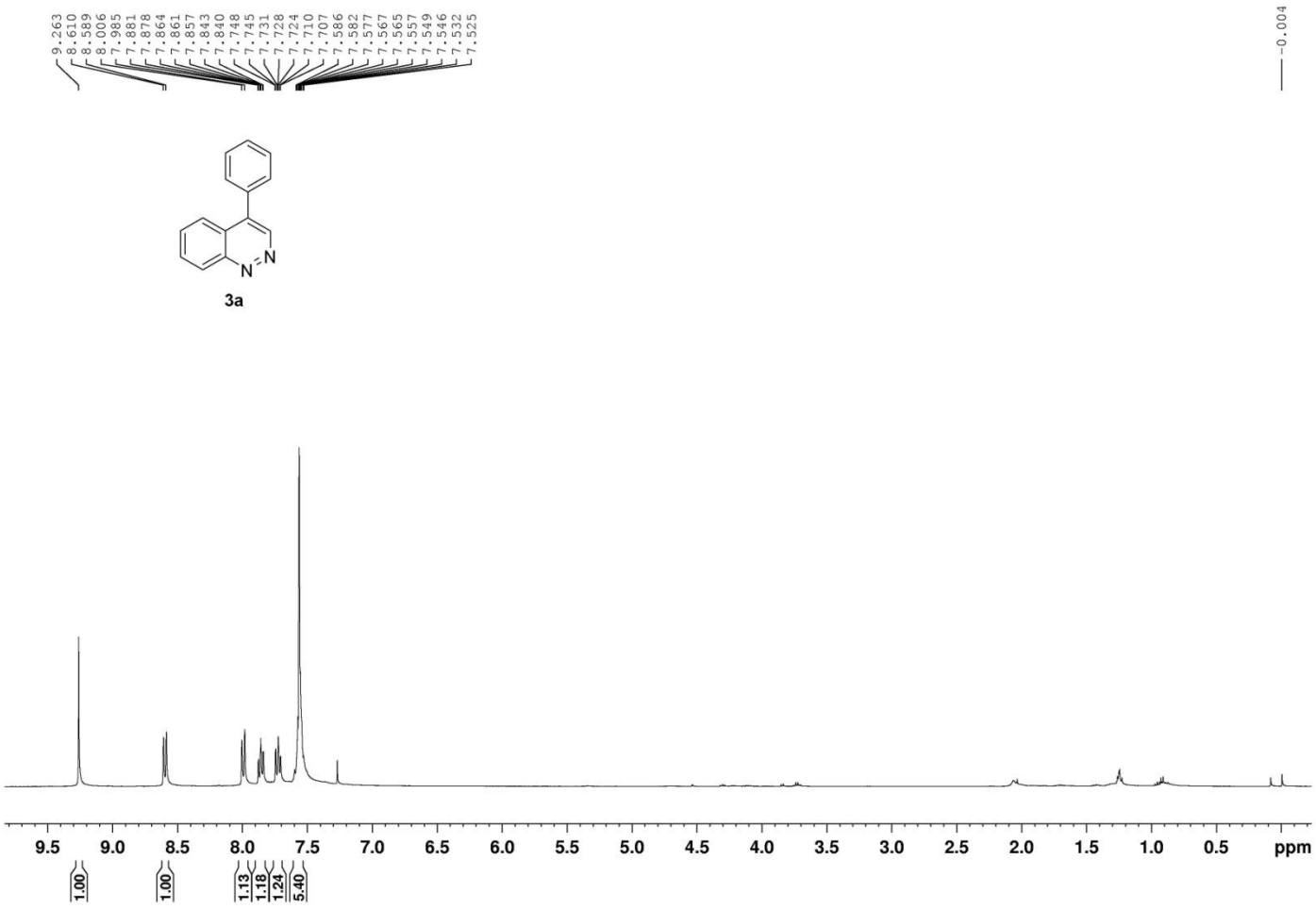
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7.586
7.582
7.577
7.567
7.565
7.557
7.549
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7.525
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N
3a
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9.0
8.5
8.0
7.5
7.0
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6.0
5.5
5.0
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4.0
3.5
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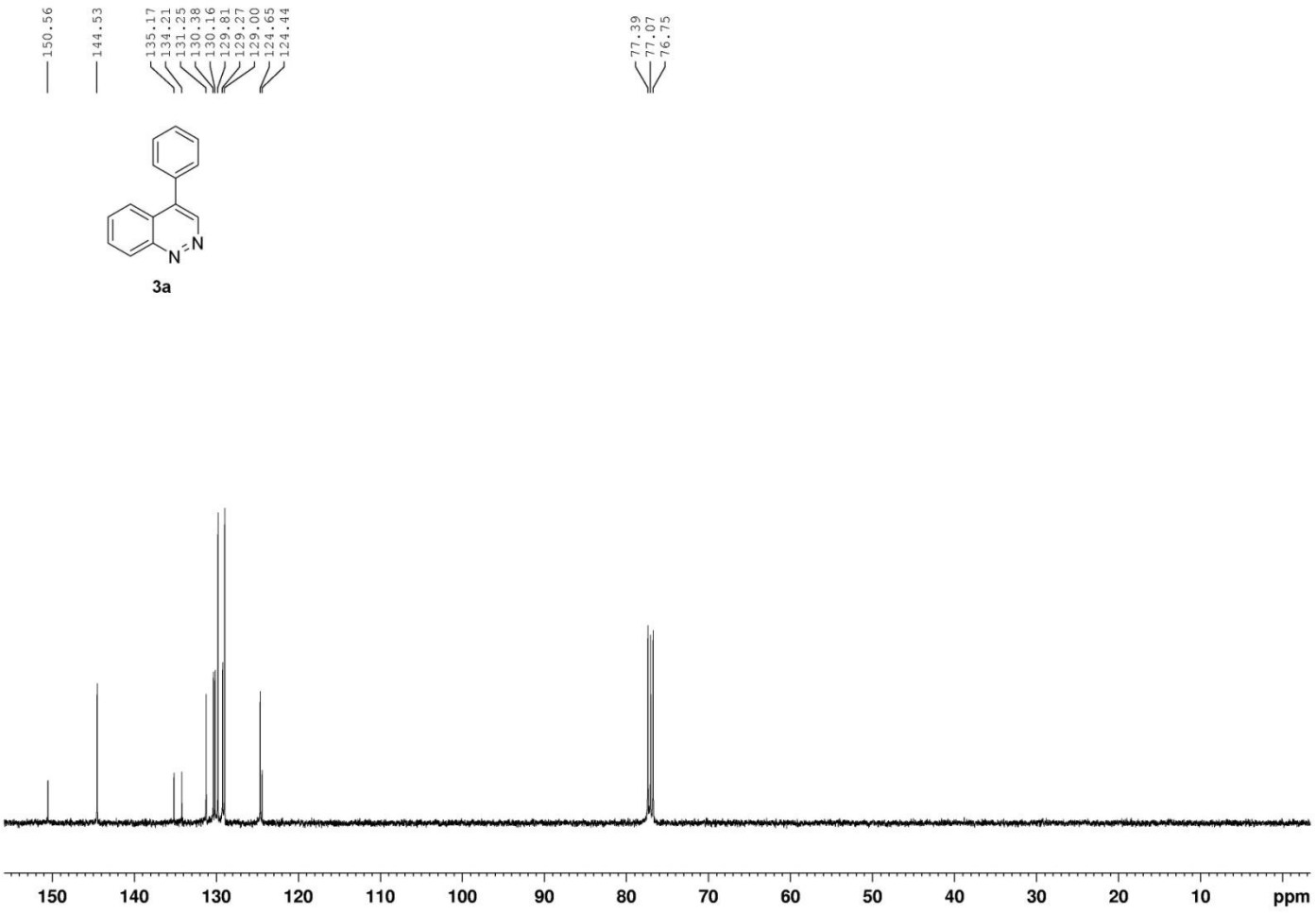
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77.07
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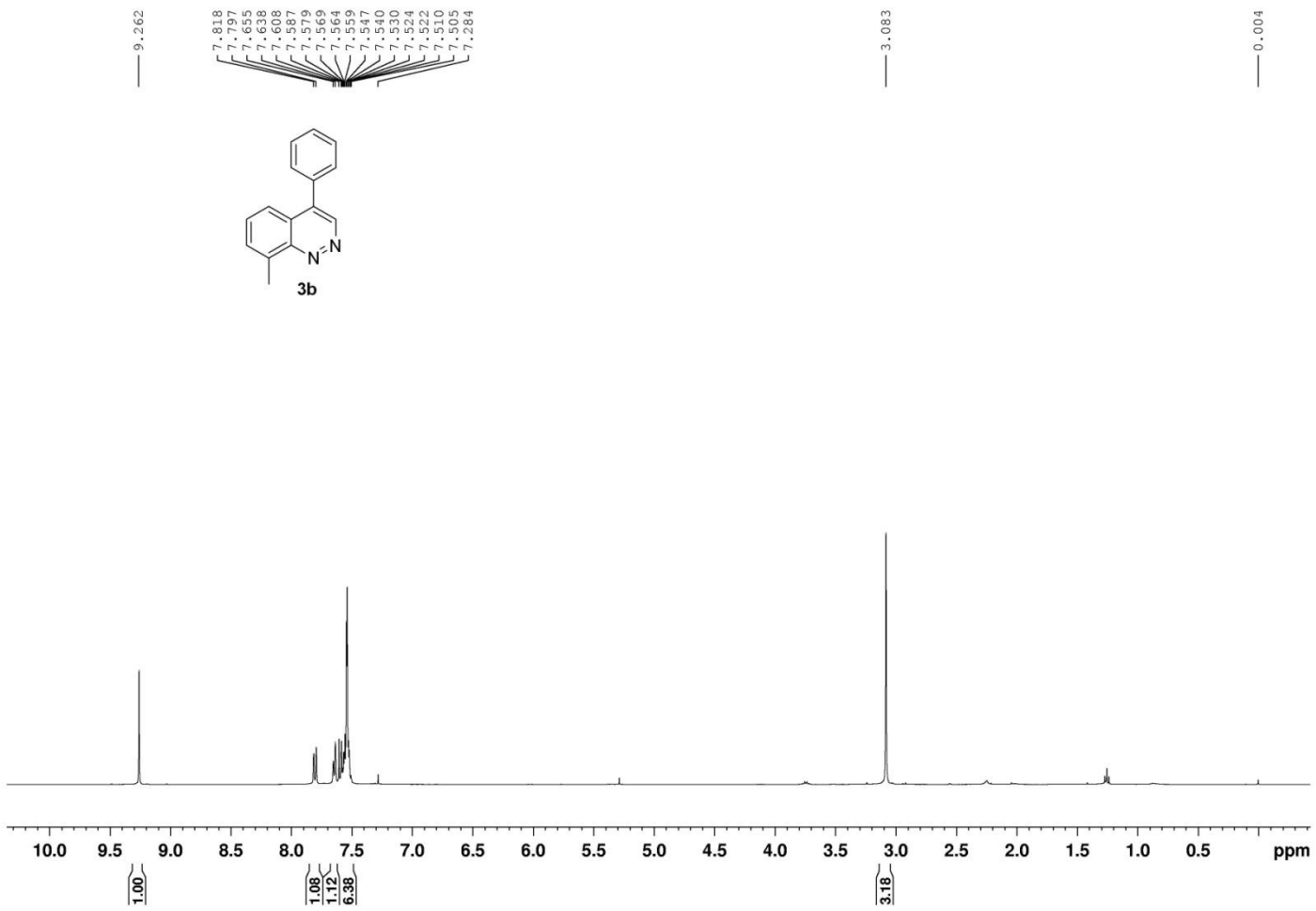
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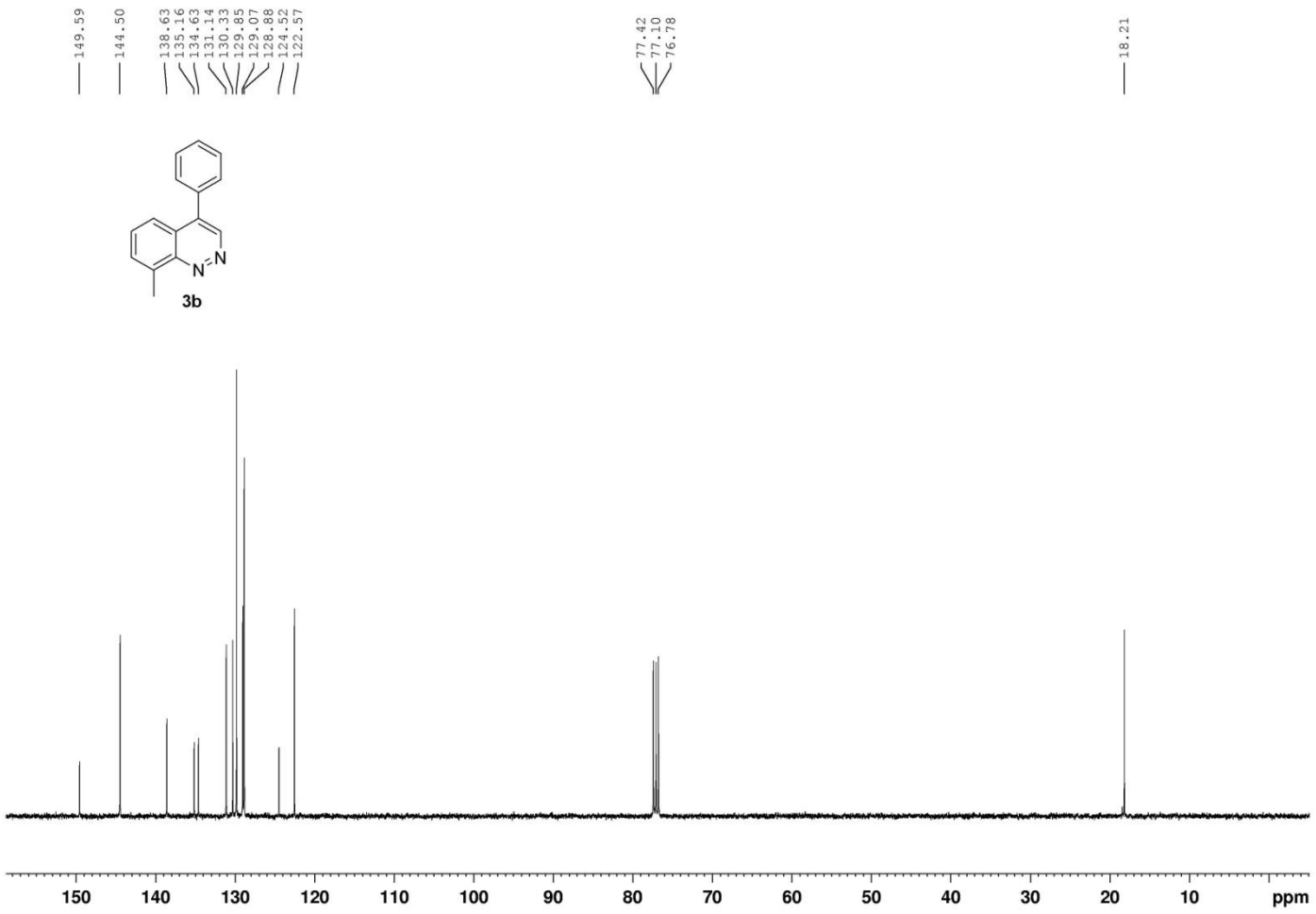
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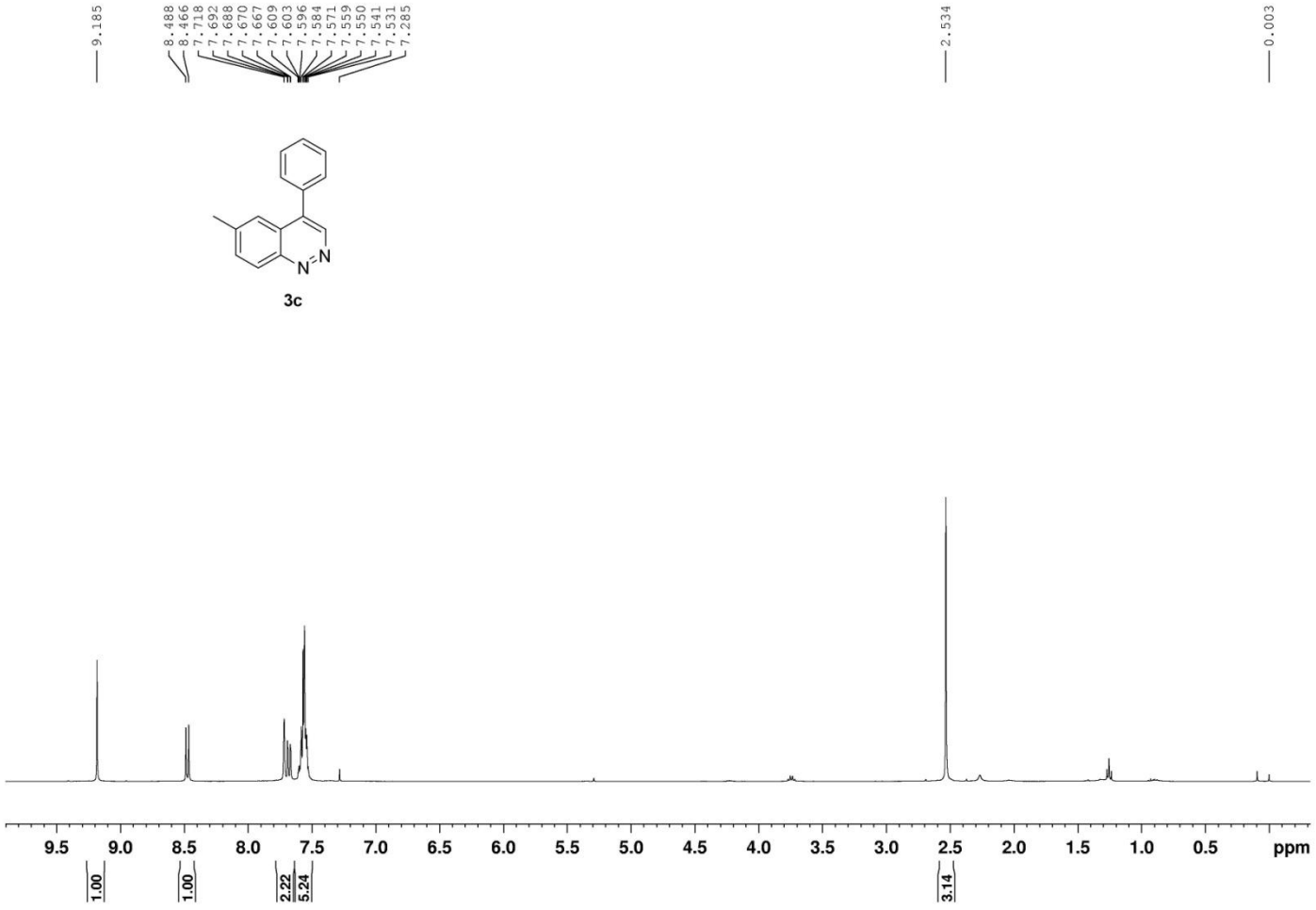
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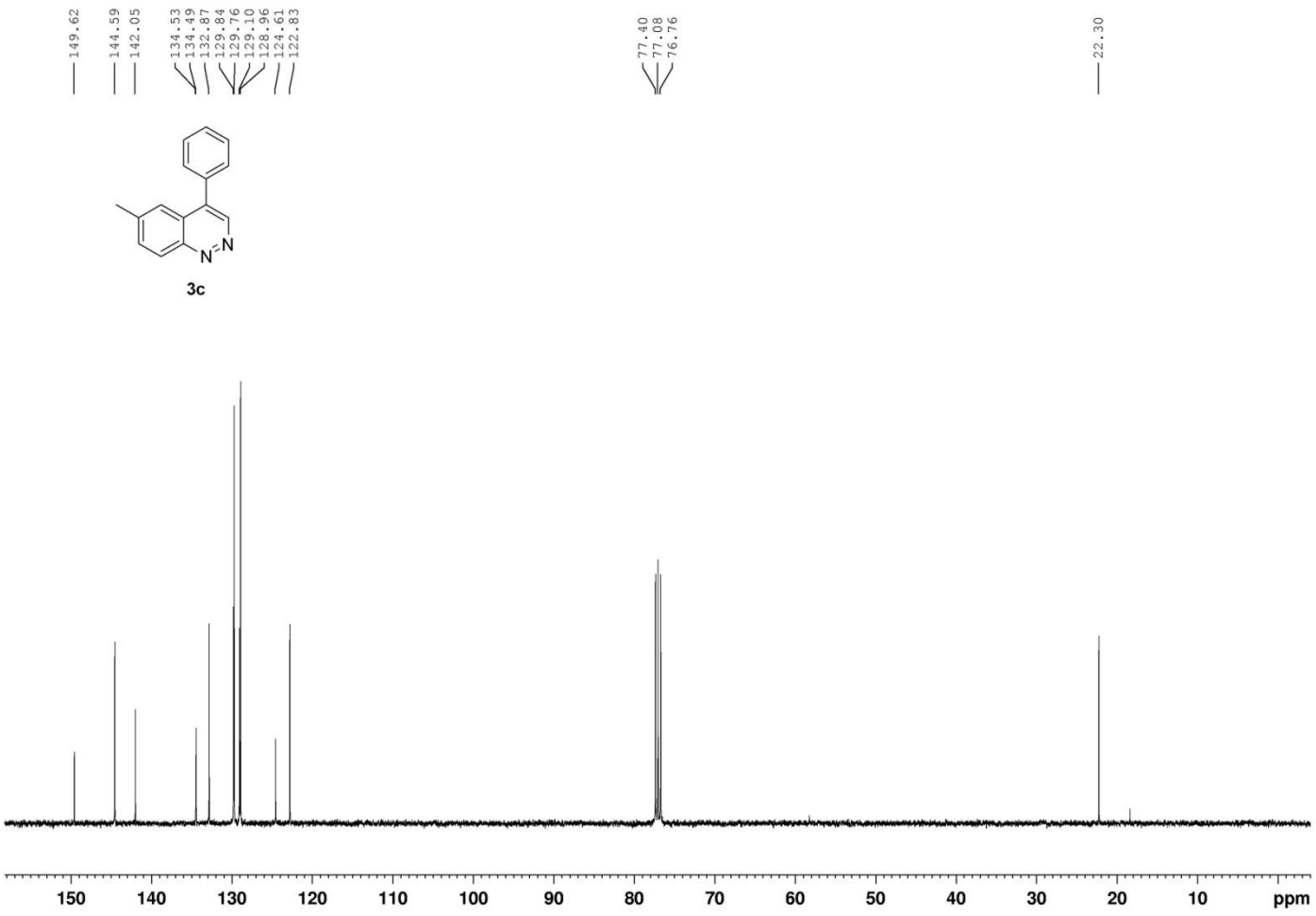
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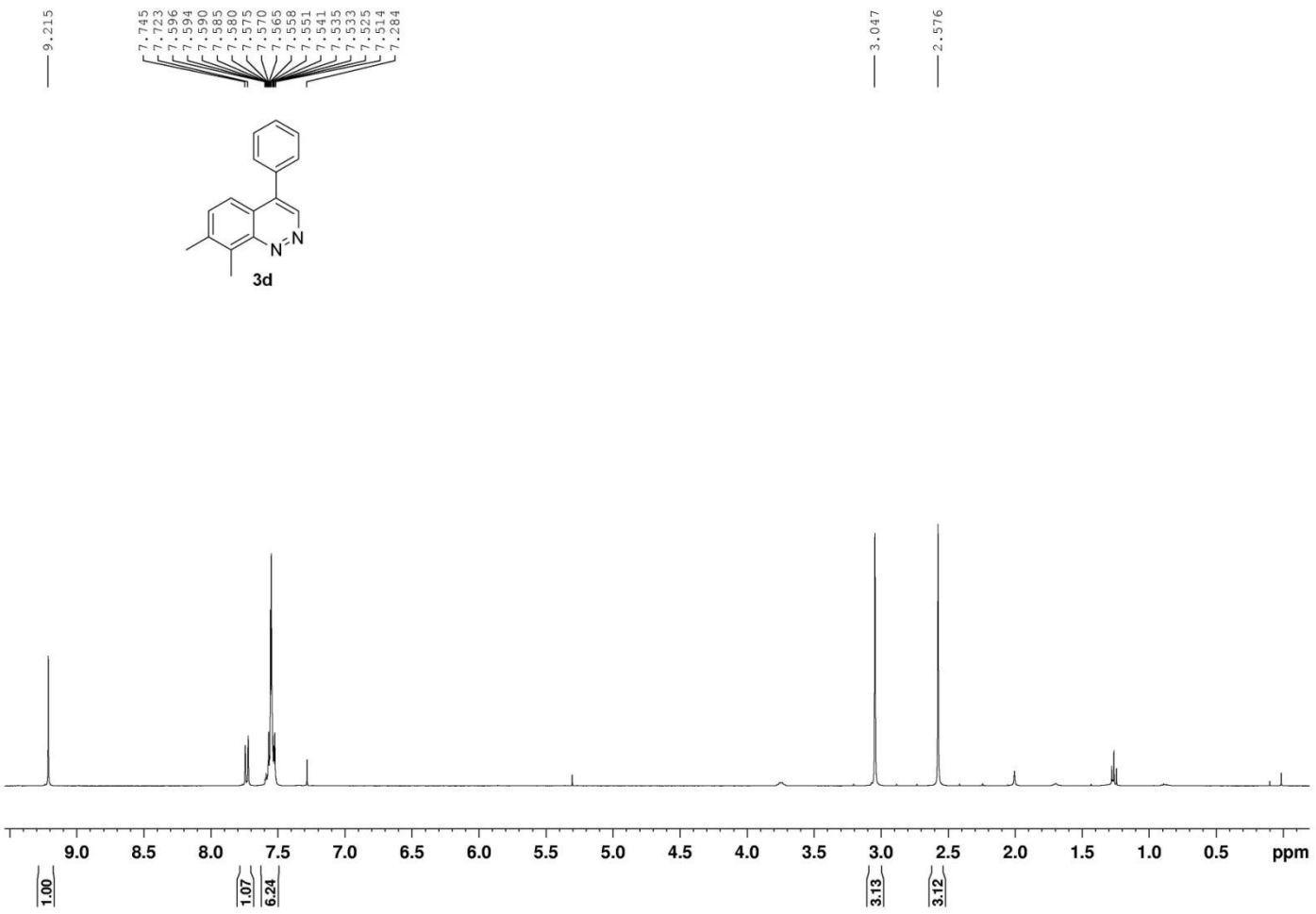
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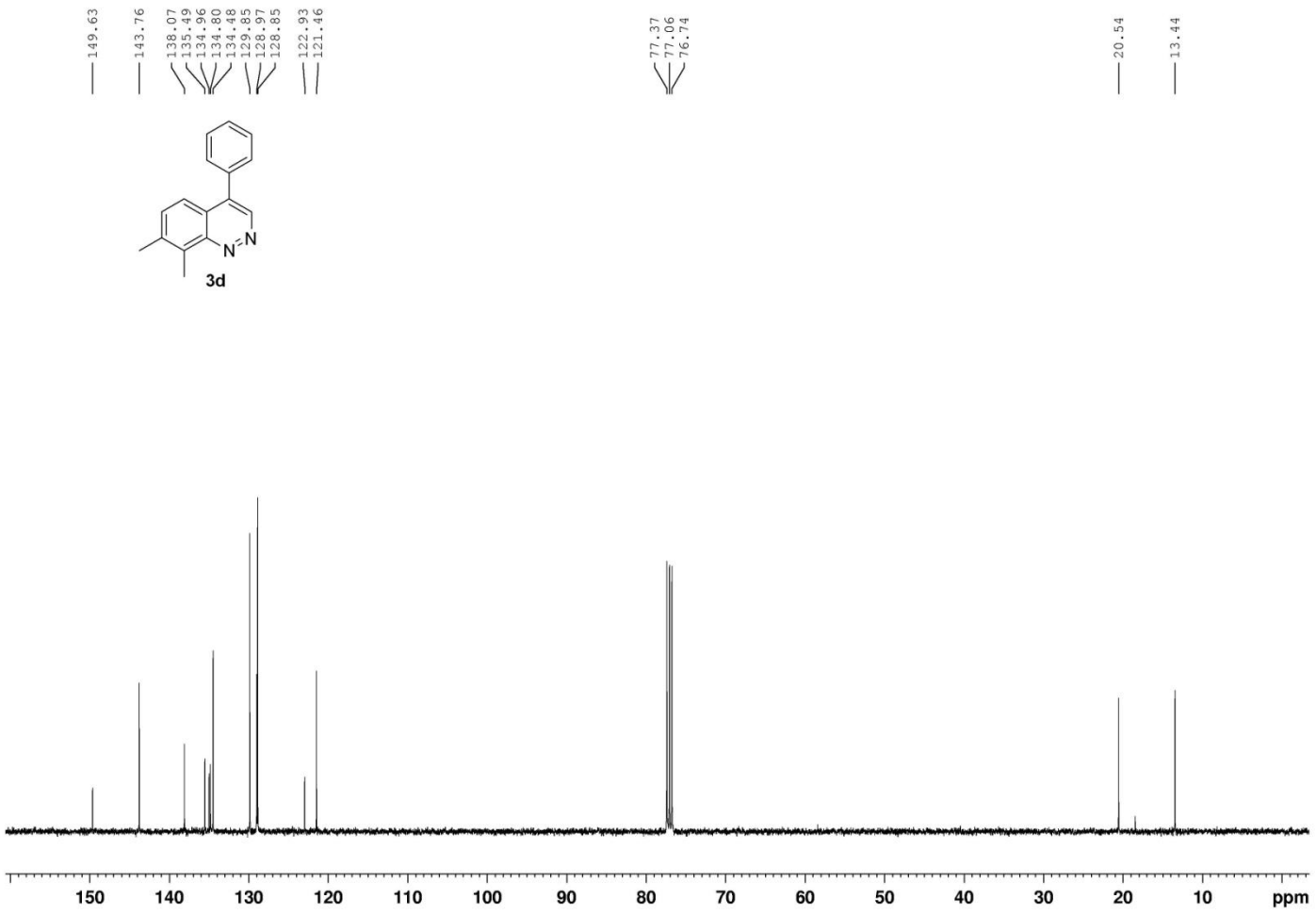
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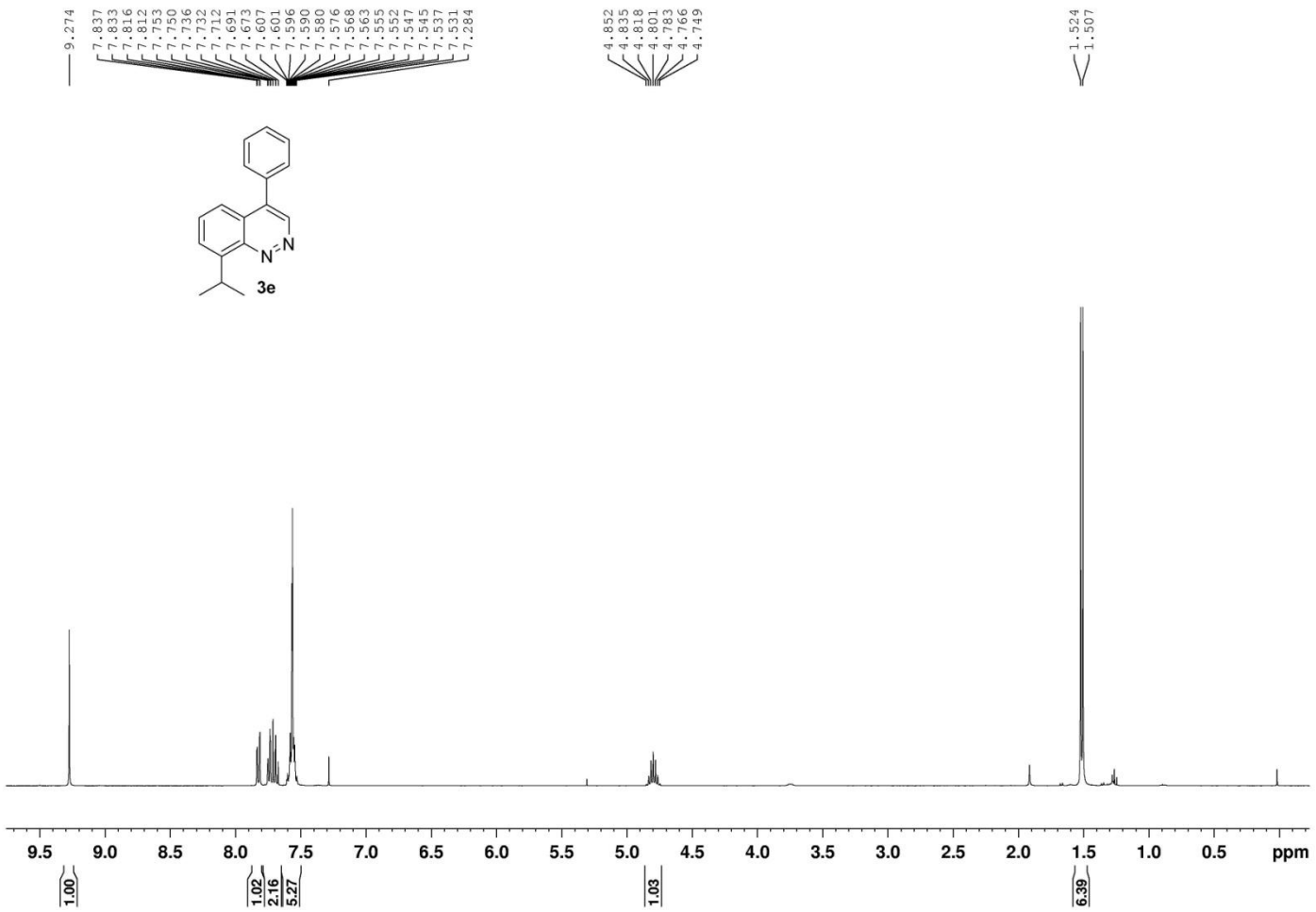
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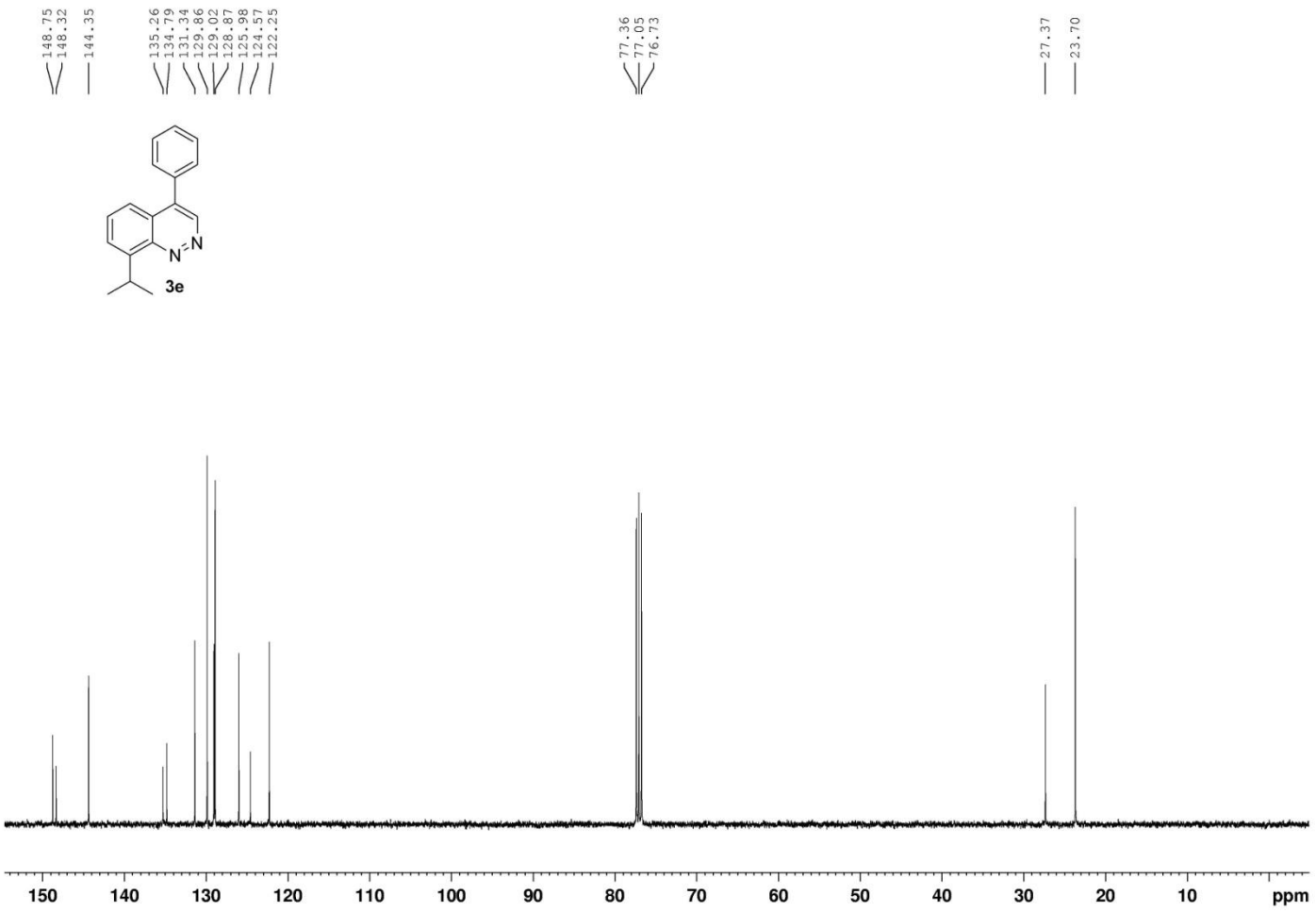
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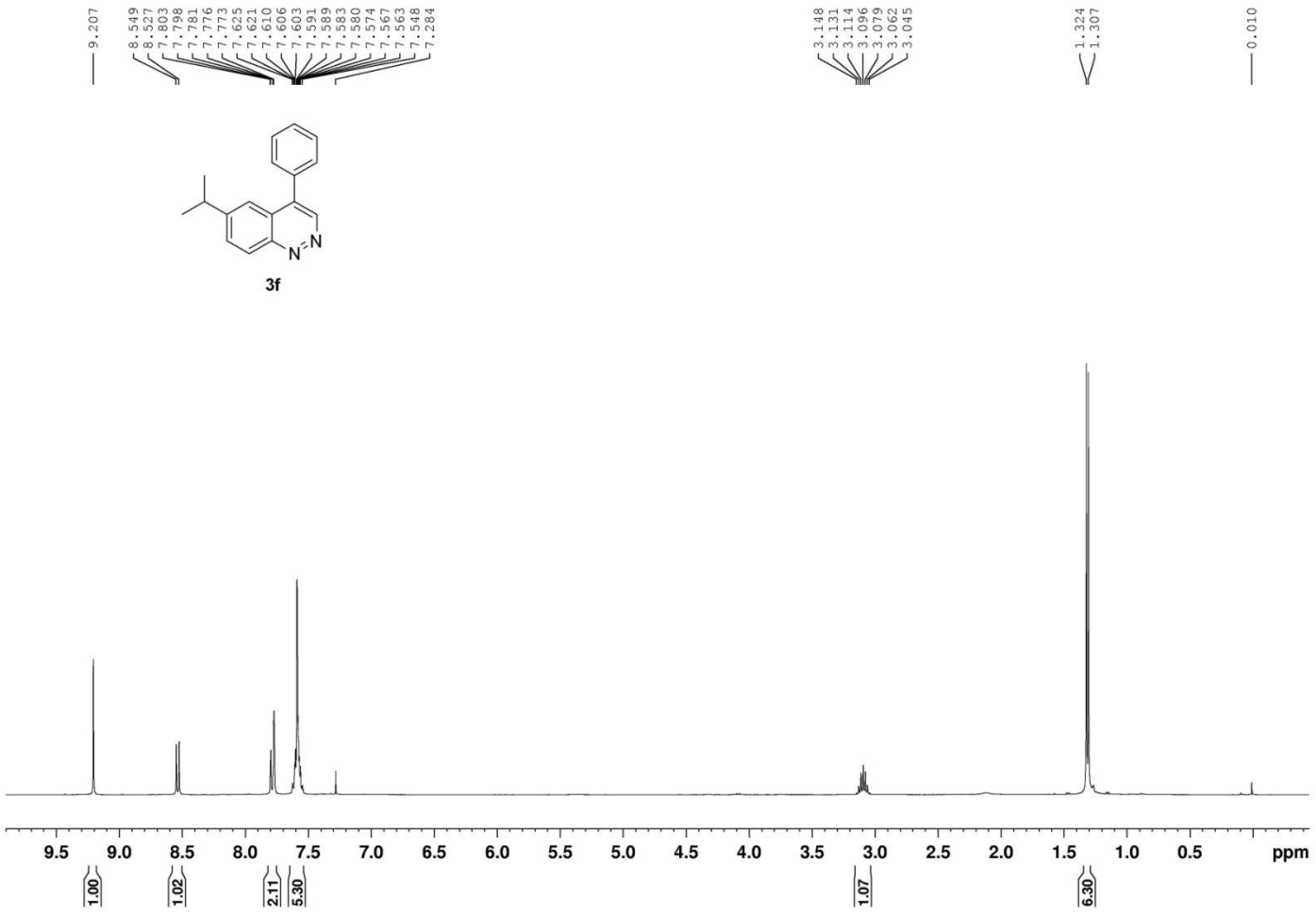
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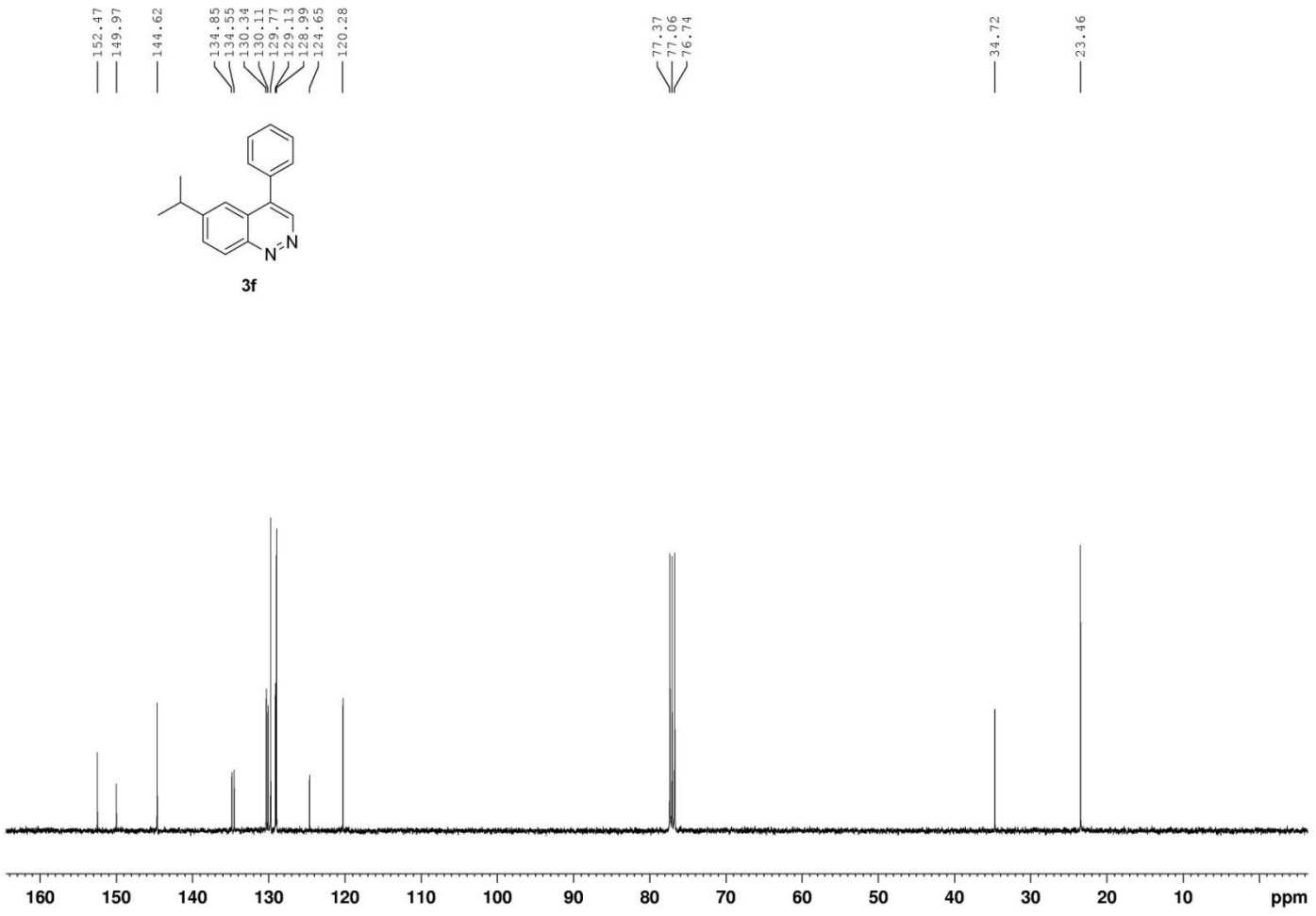
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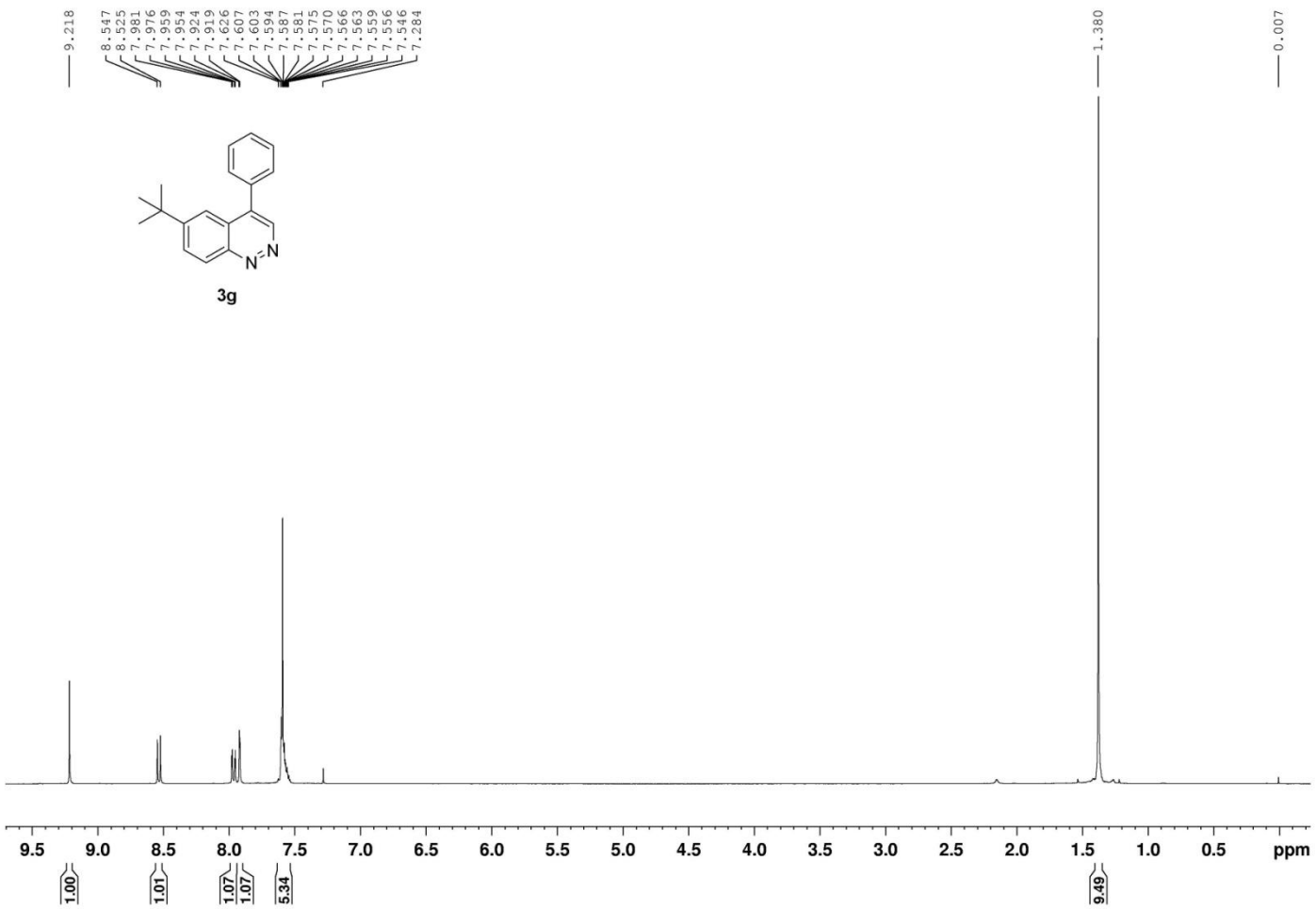
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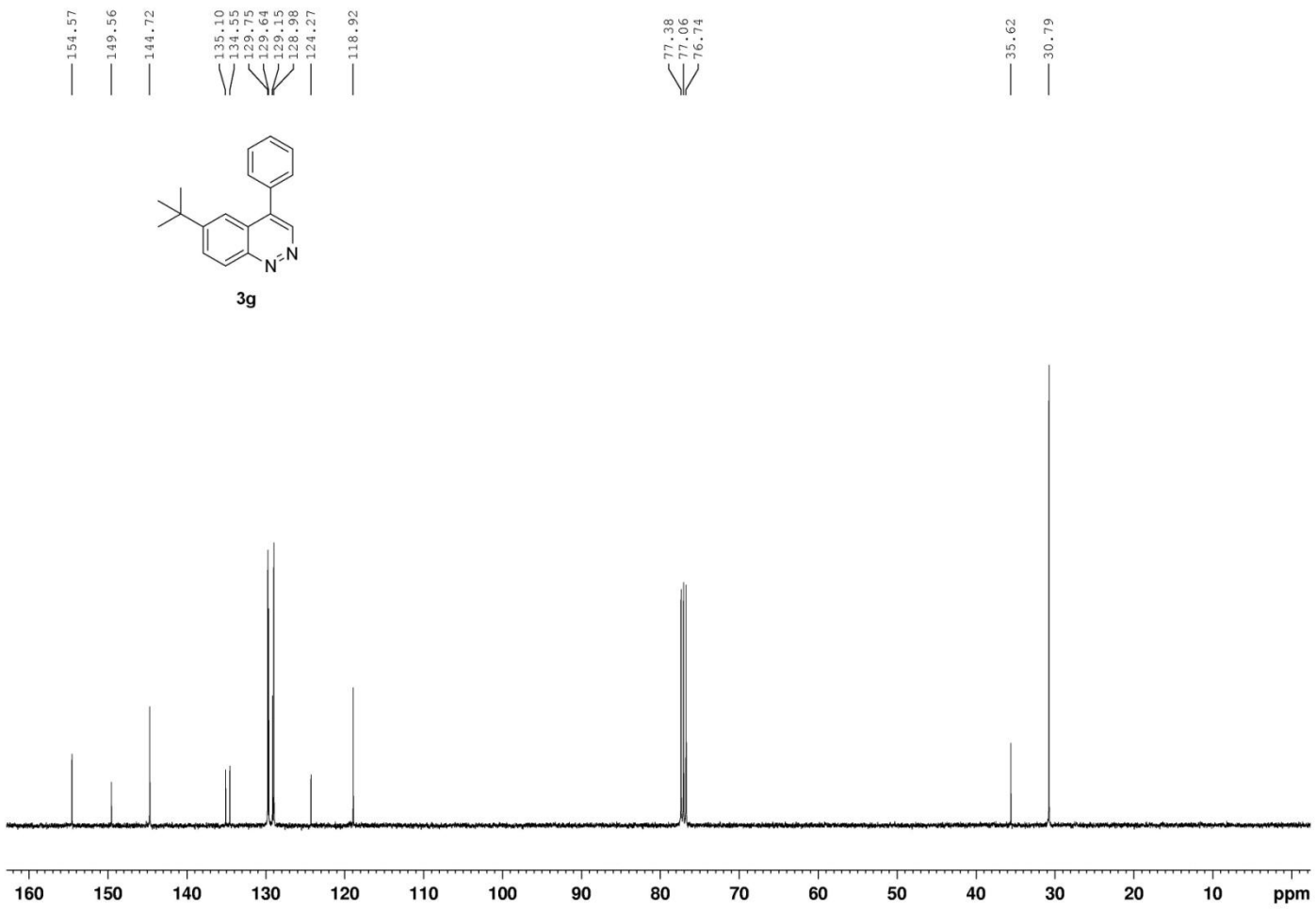
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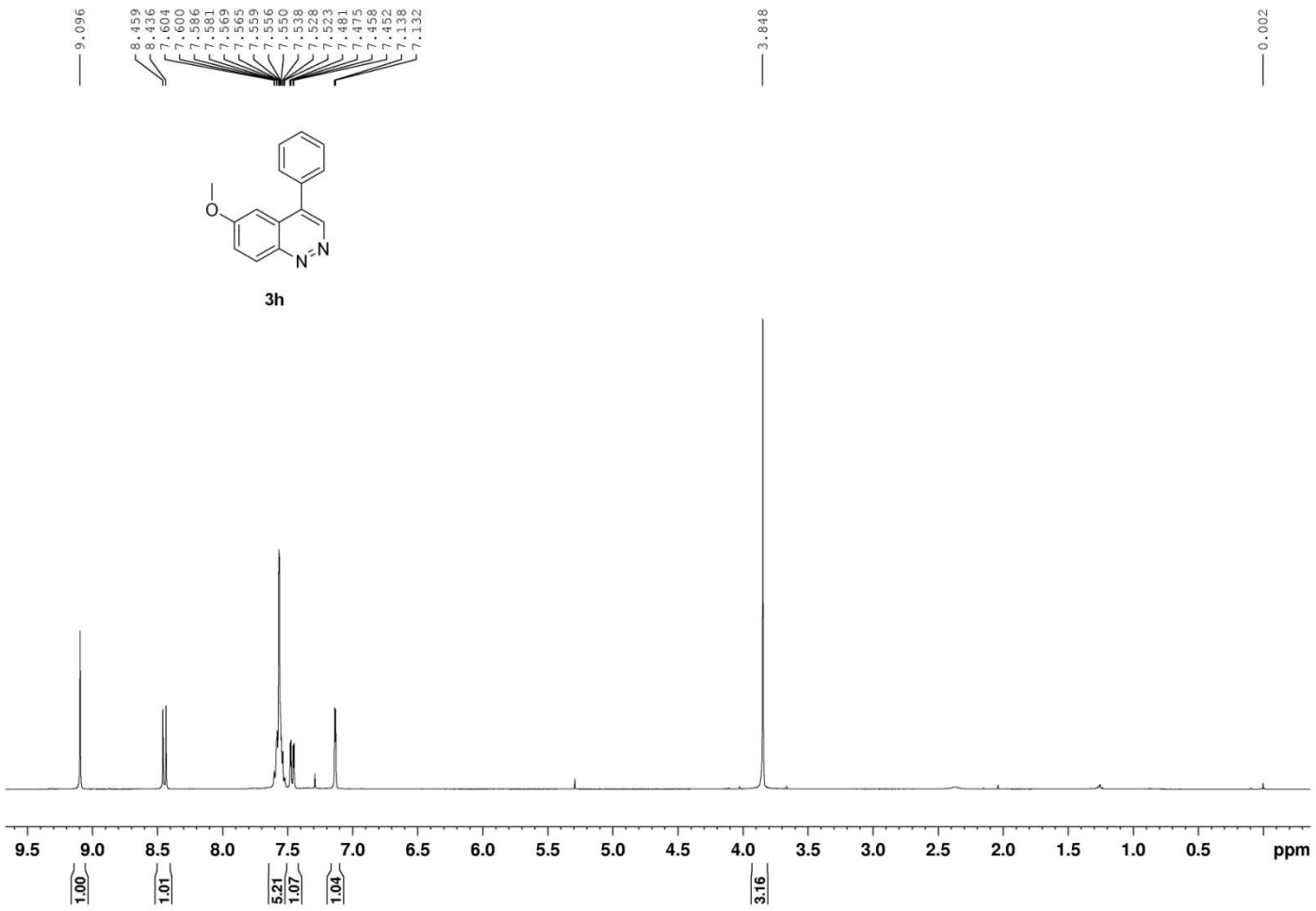
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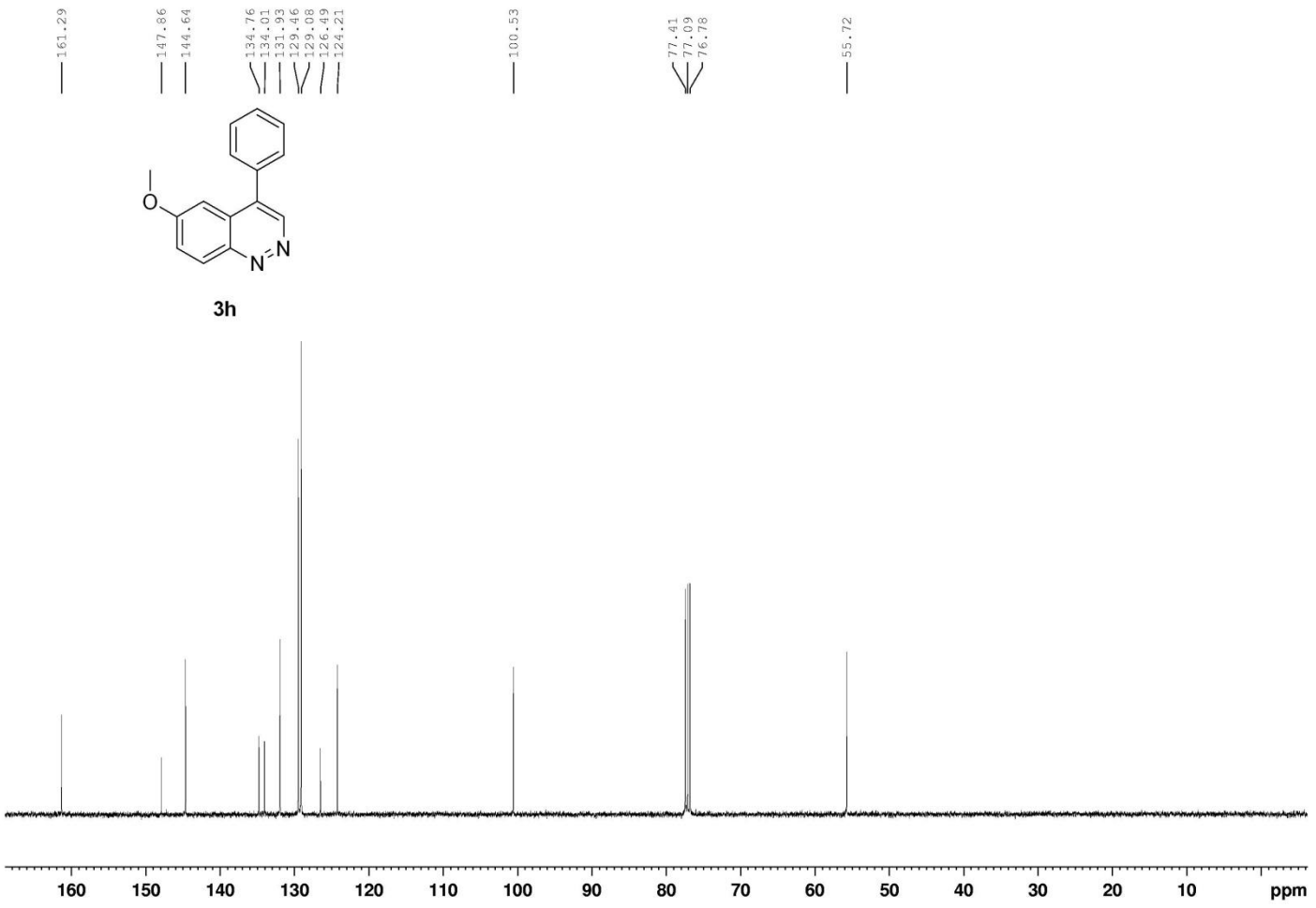
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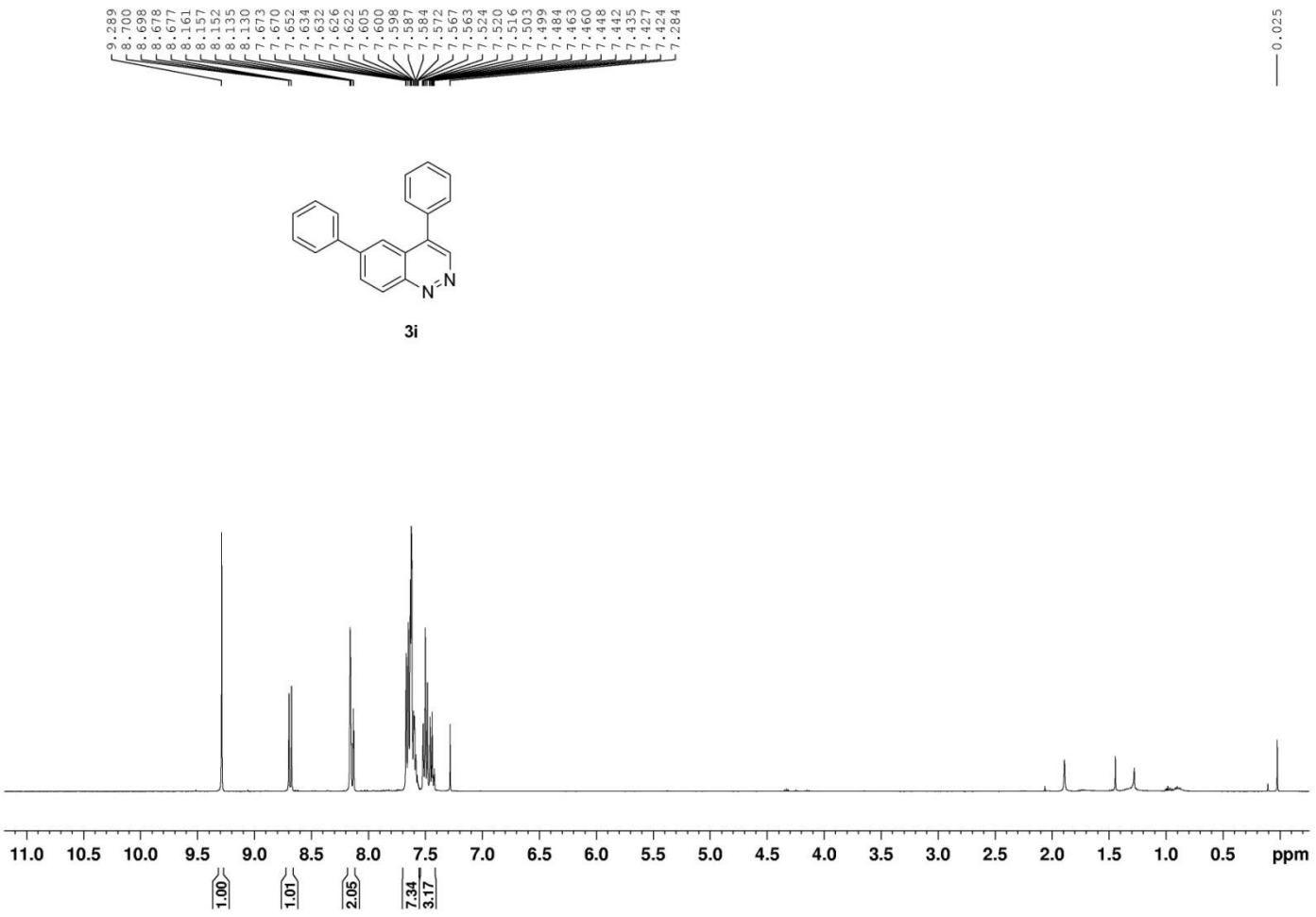
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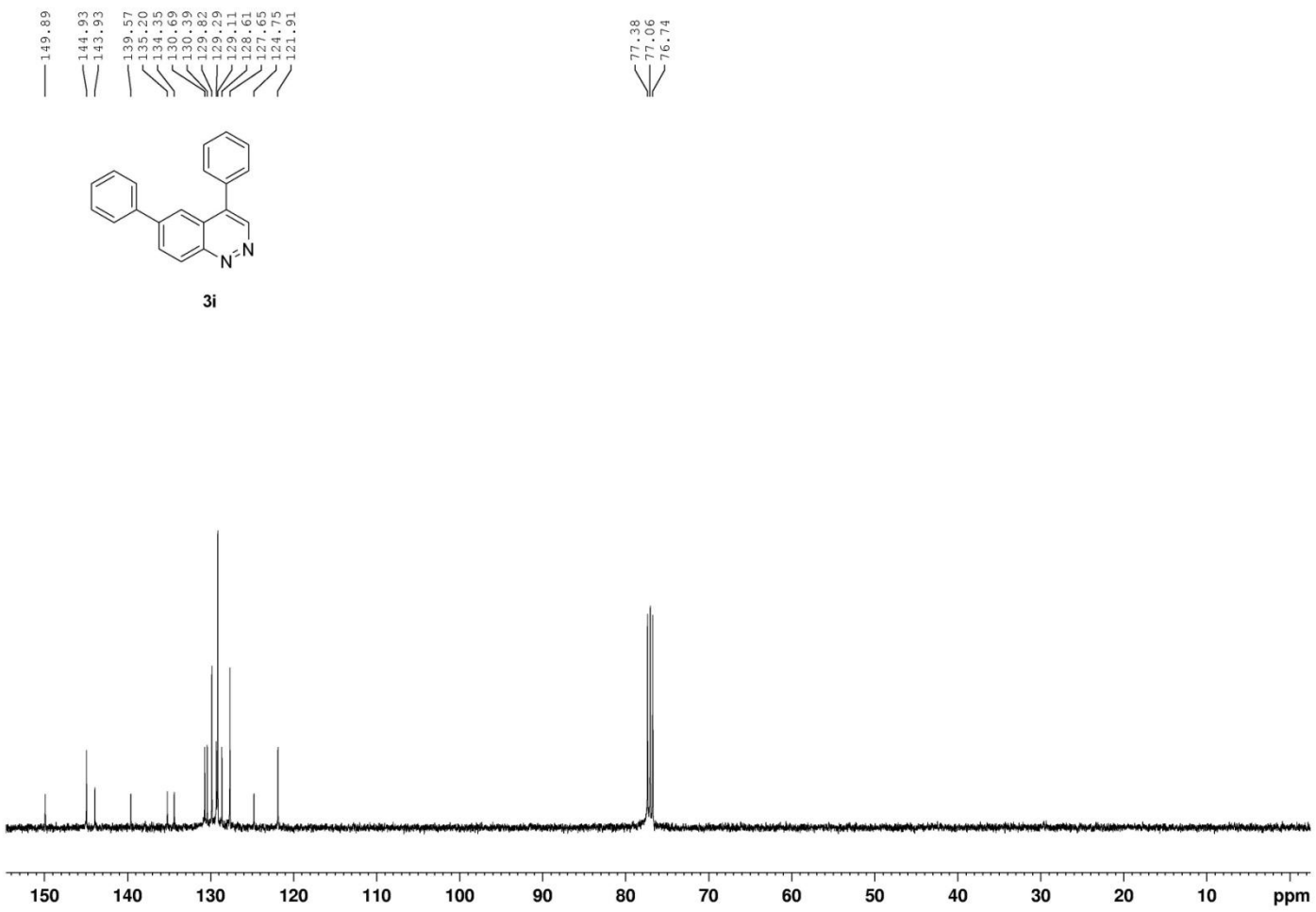
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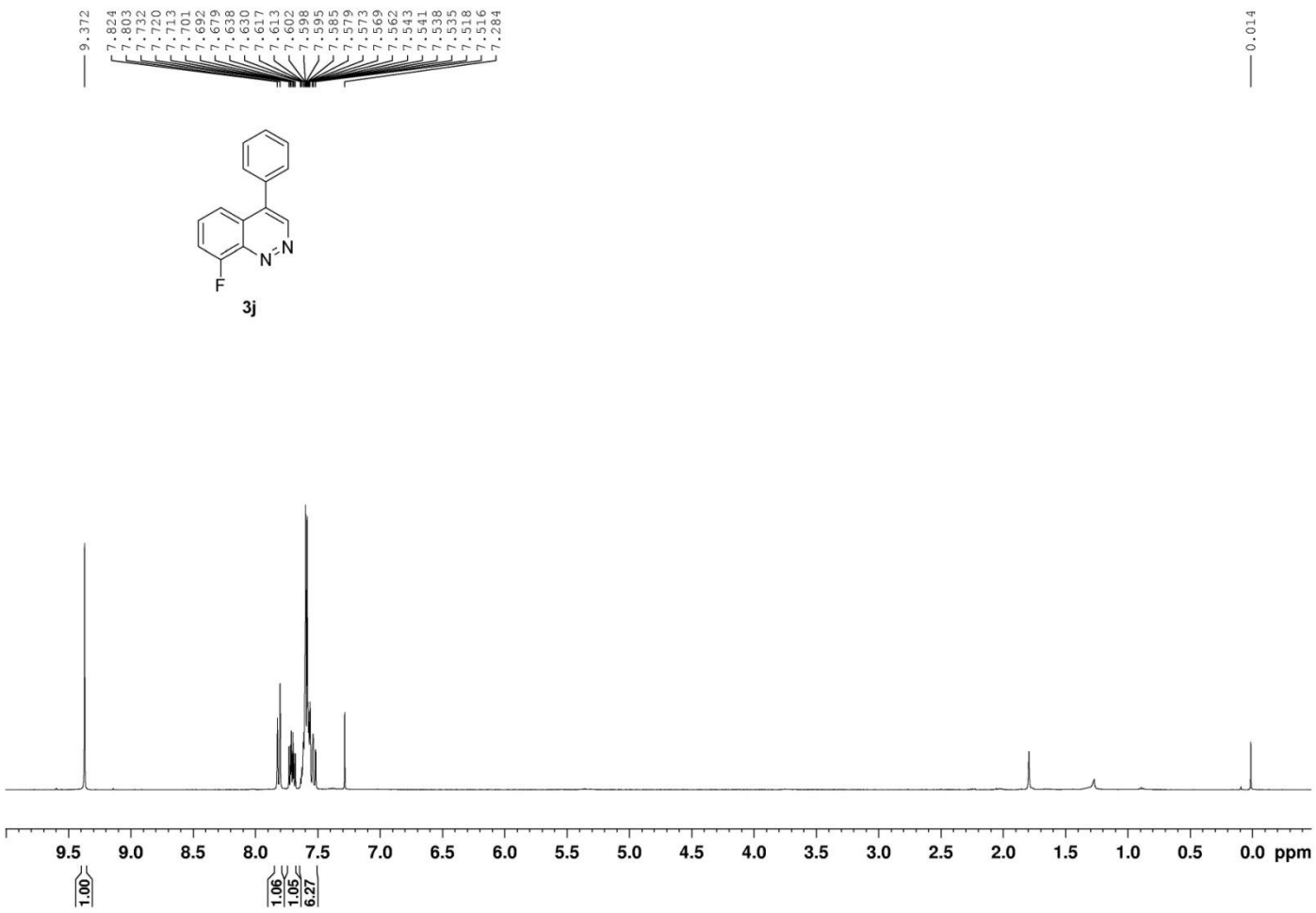
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7.538
7.535
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7.516
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N
F
3j
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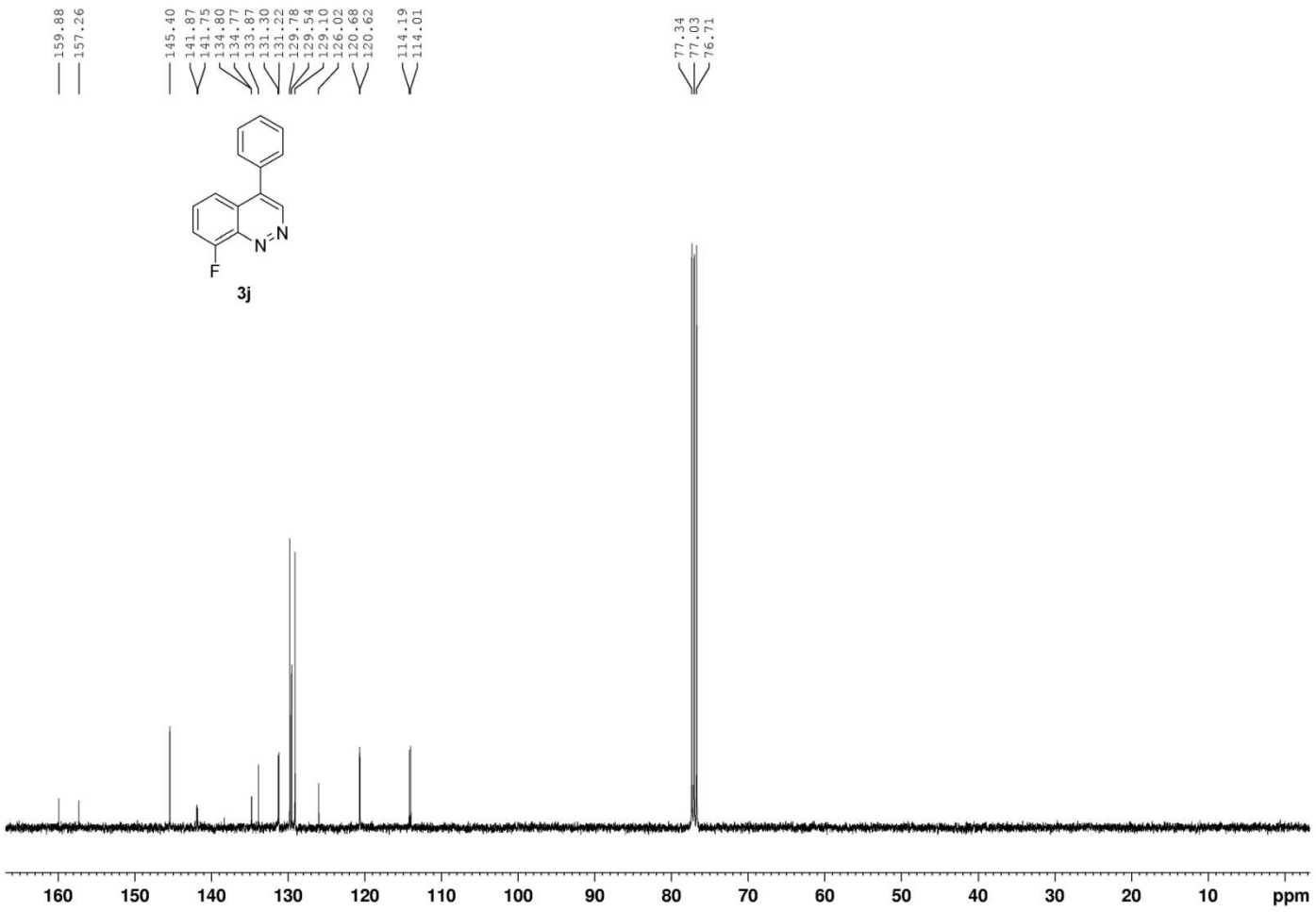
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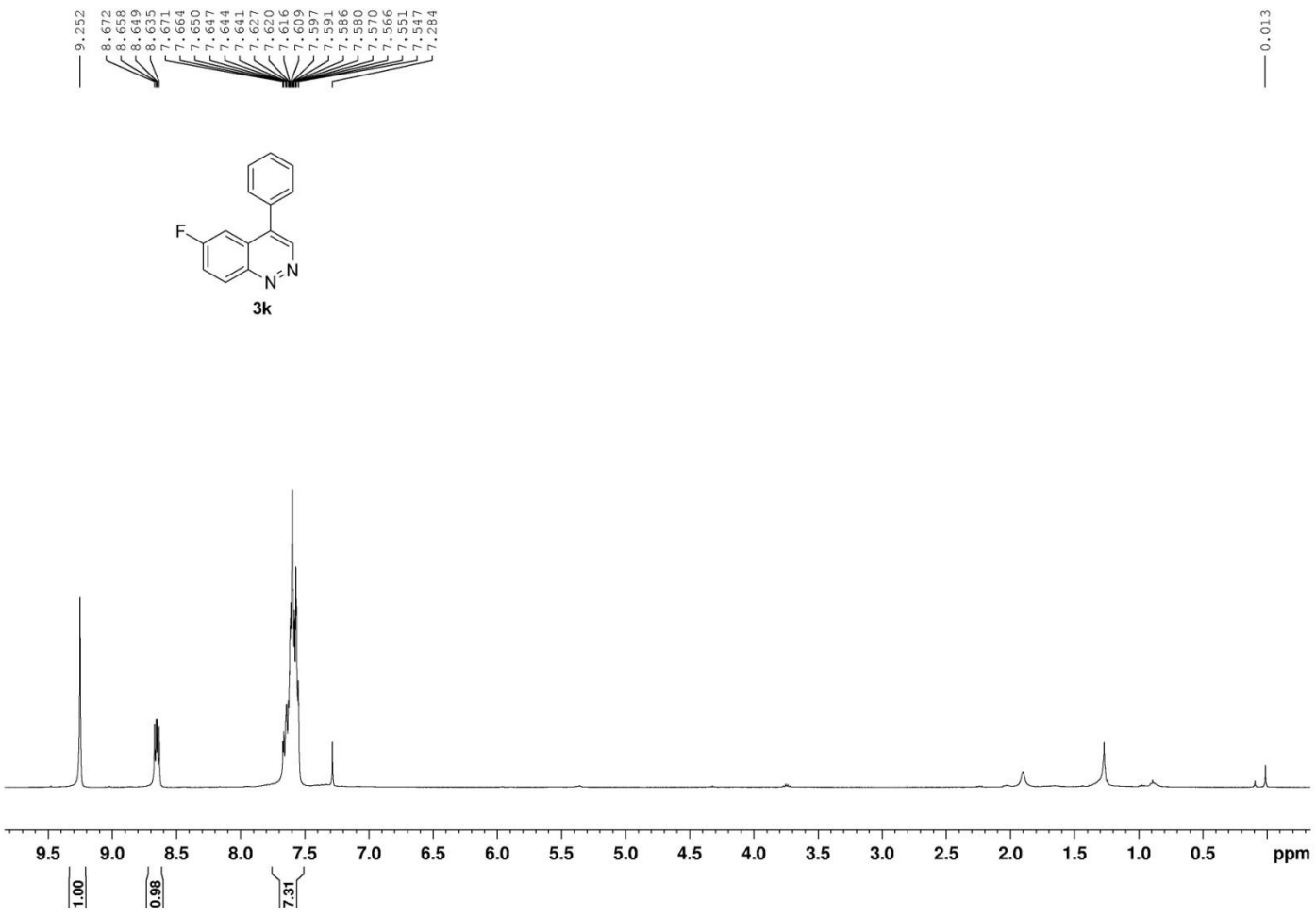
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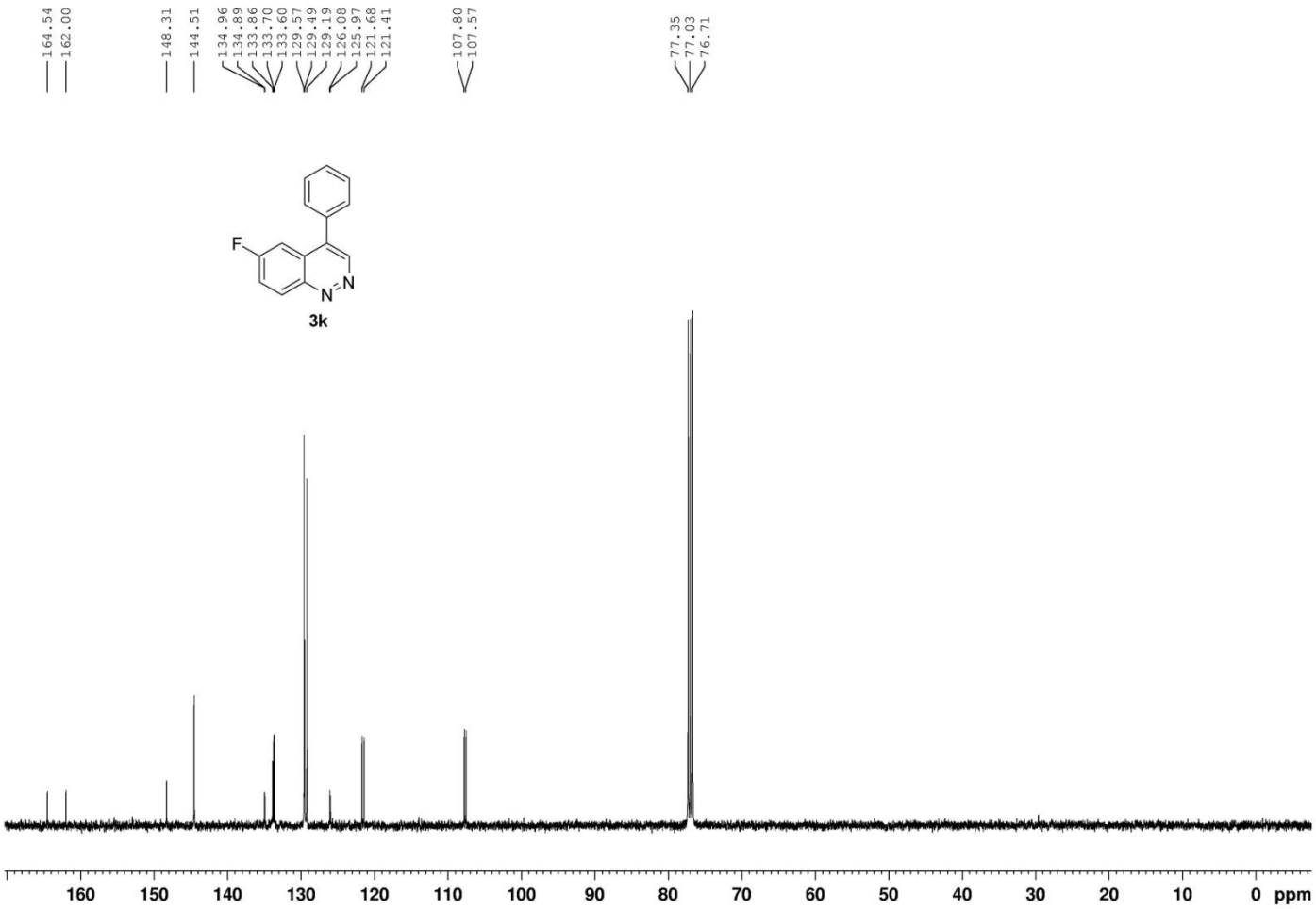
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76.71
F
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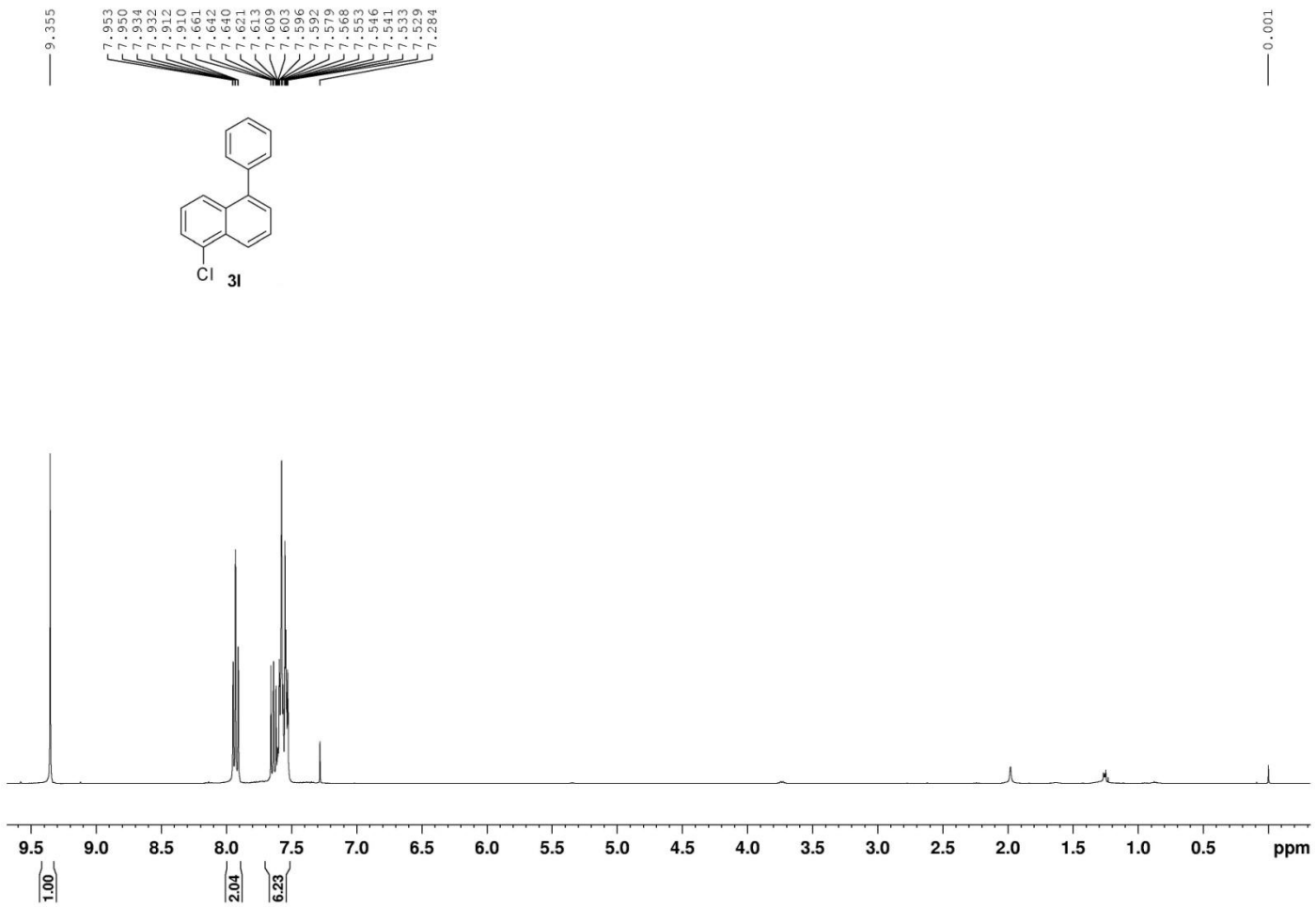
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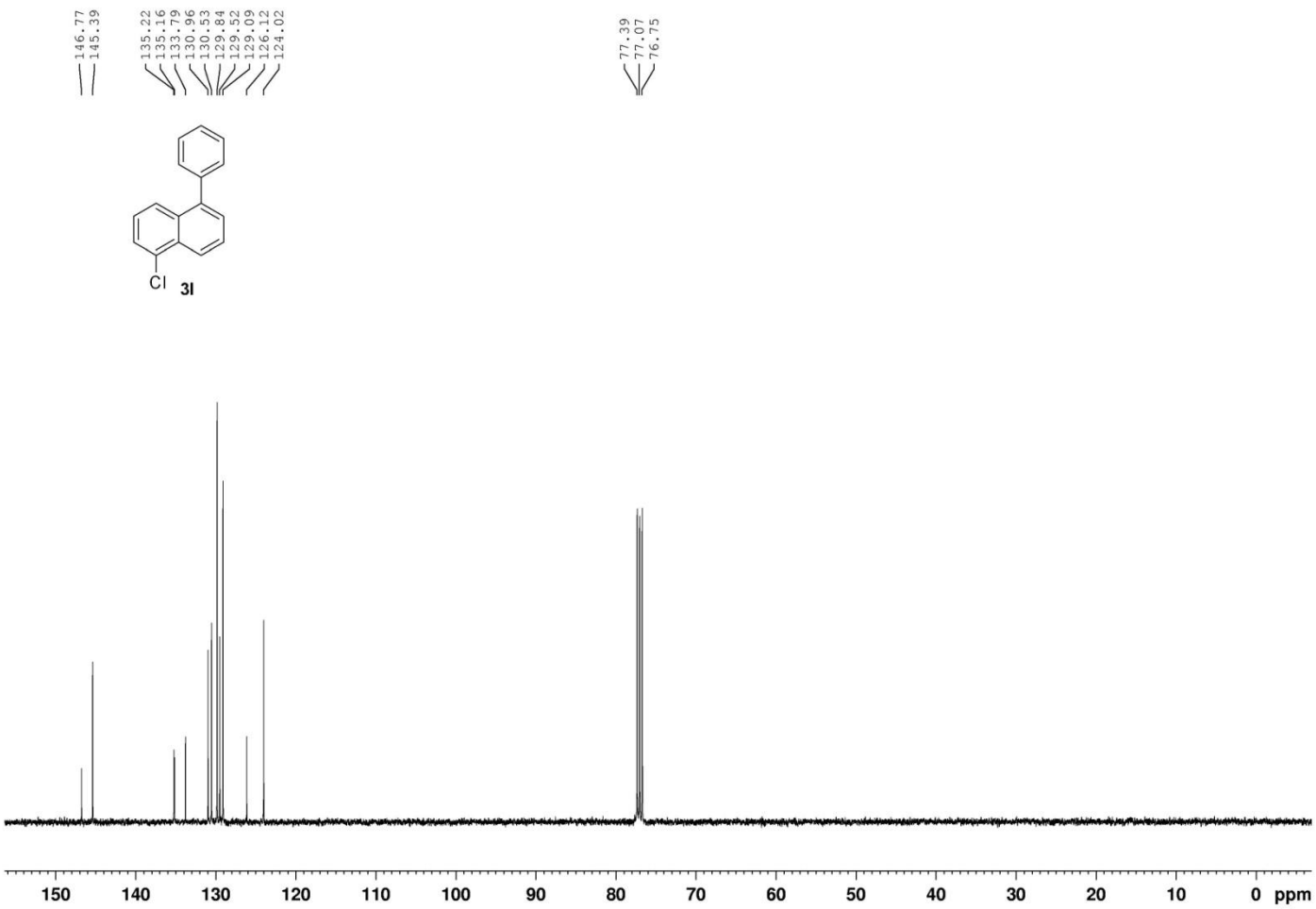
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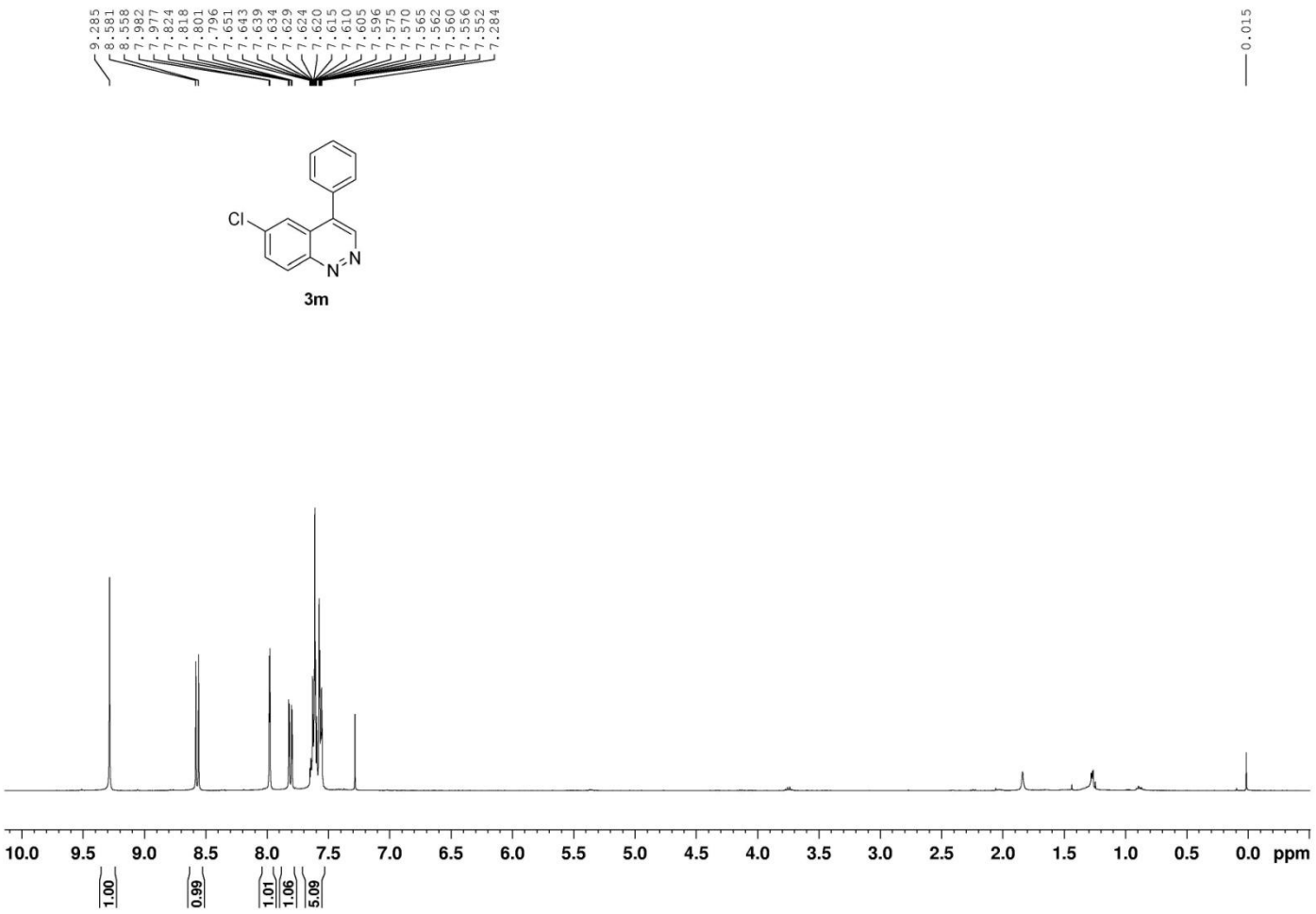
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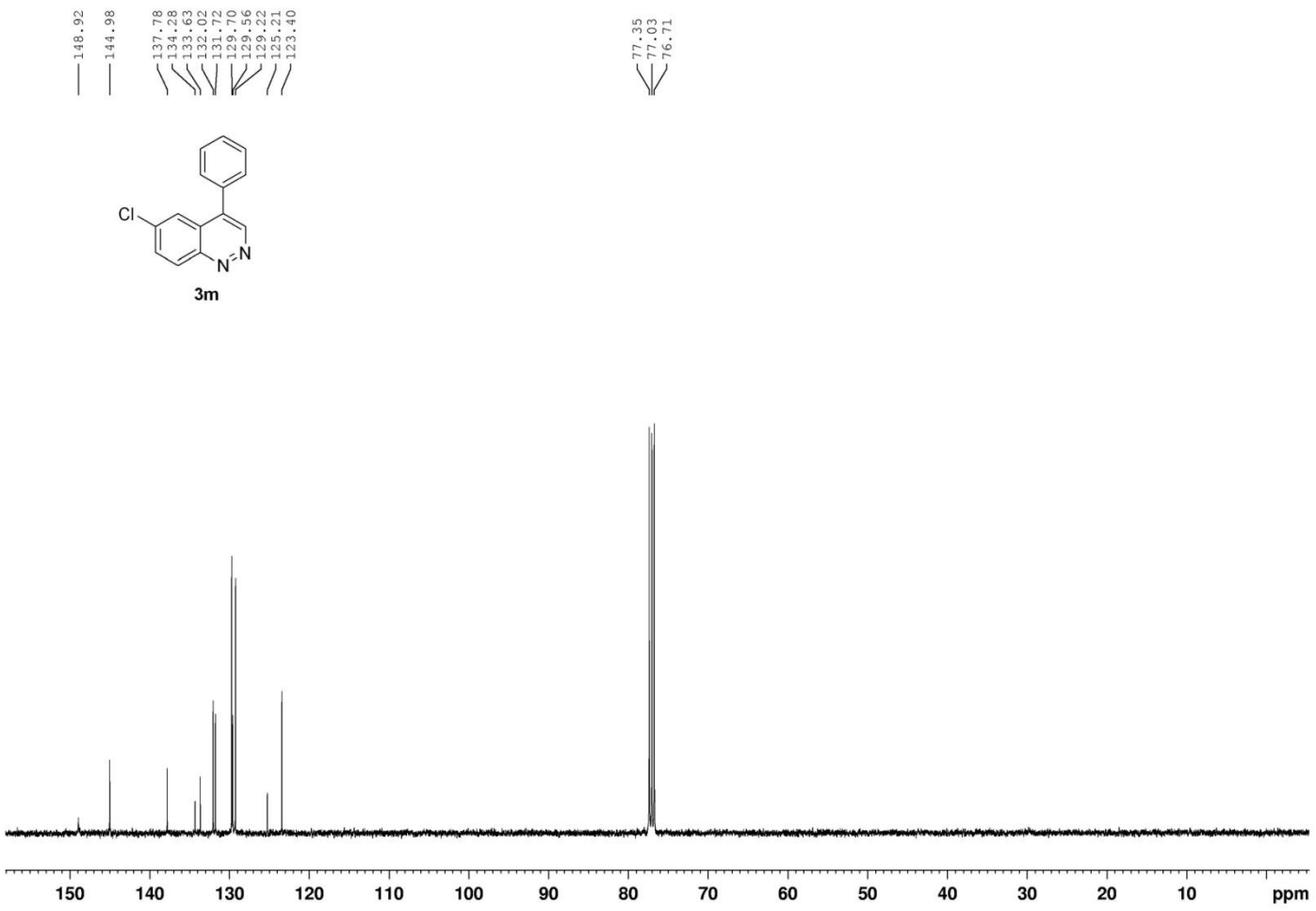
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77.03
76.71
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30
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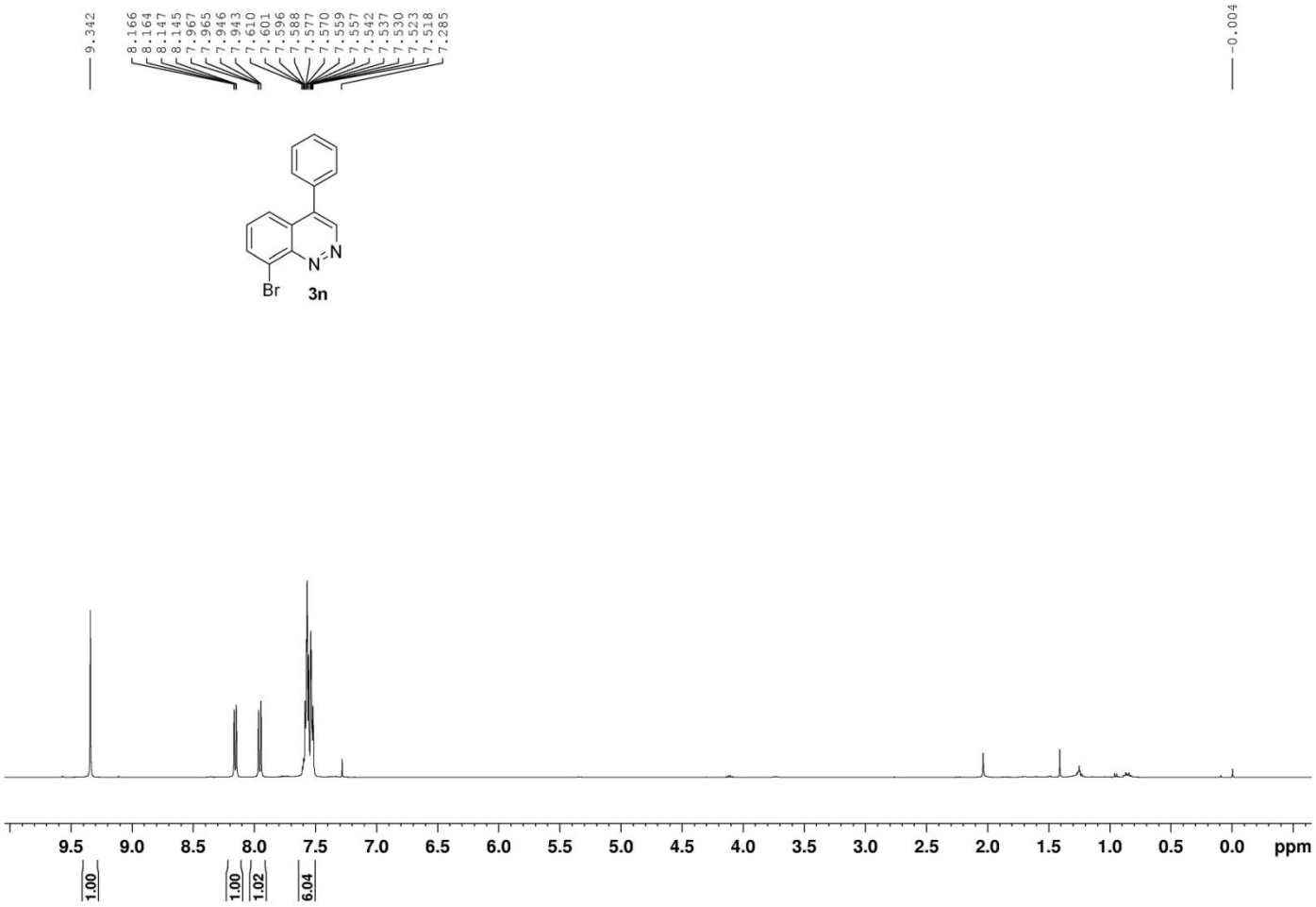
ppm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7.577
7.570
7.559
7.557
7.542
7.537
7.530
7.523
7.518
7.285
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N
Br
3n
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7.5
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6.5
6.0
5.5
5.0
4.5
4.0
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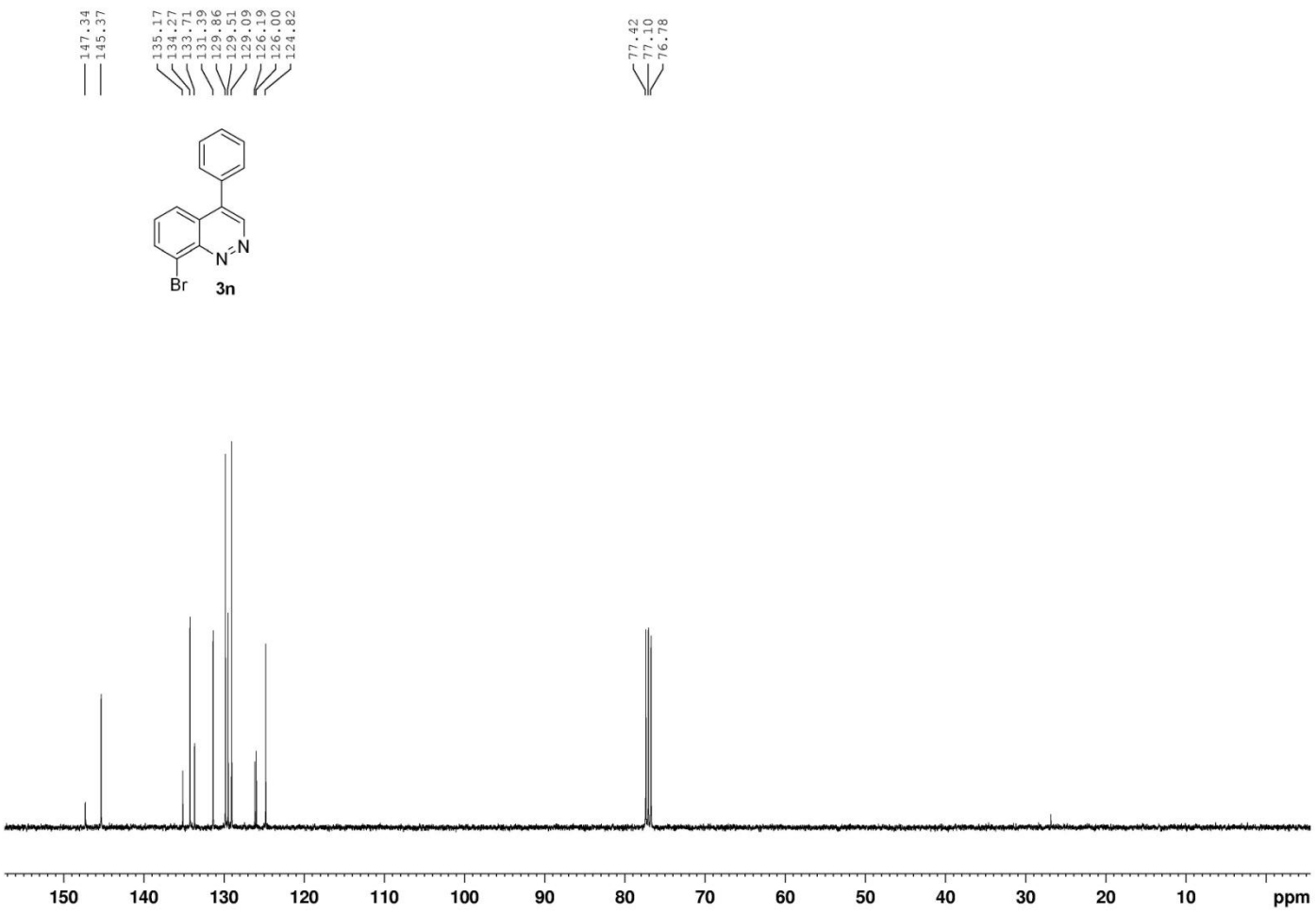
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77.10
76.78
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30
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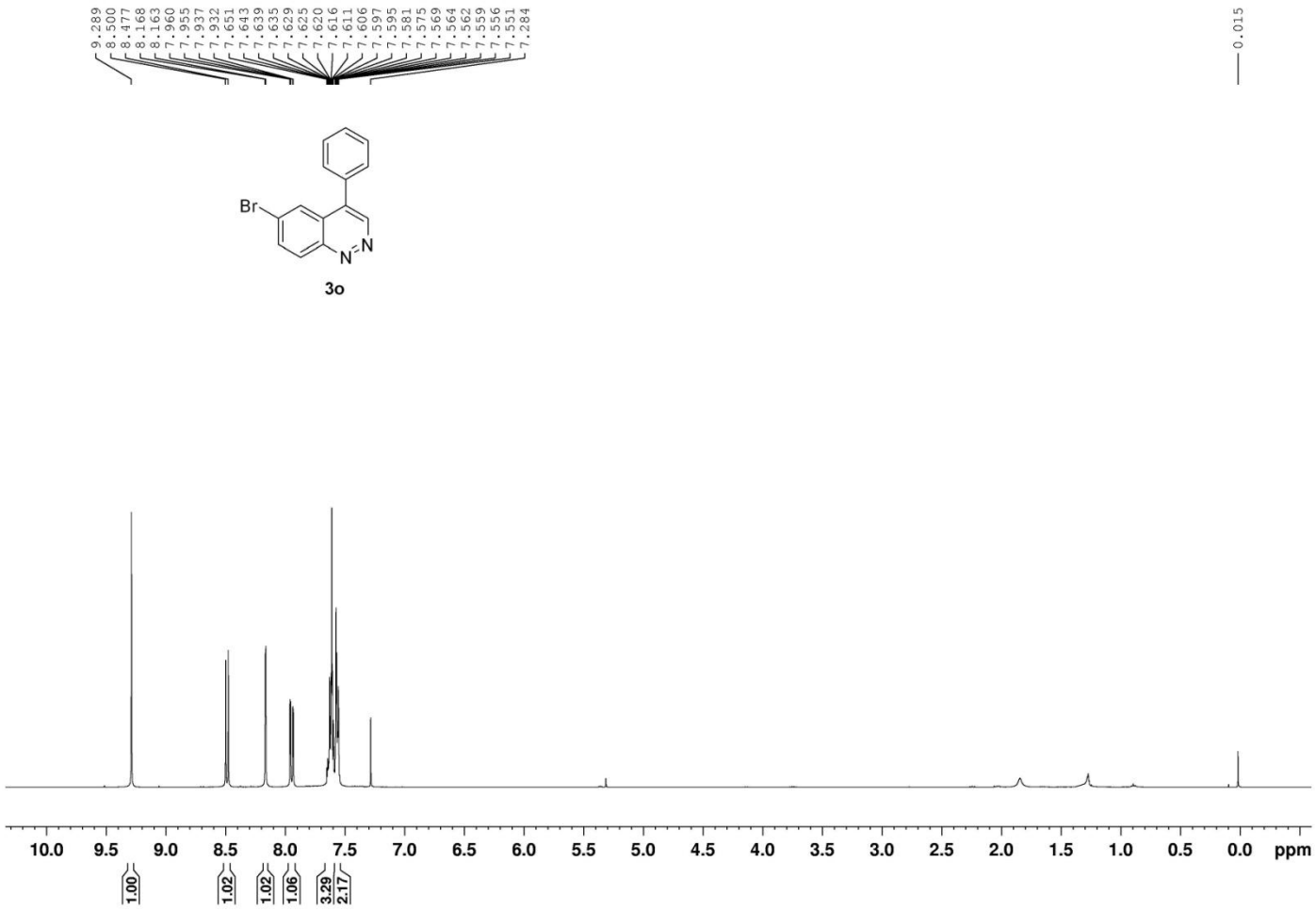
10
ppm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7.556
7.551
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N
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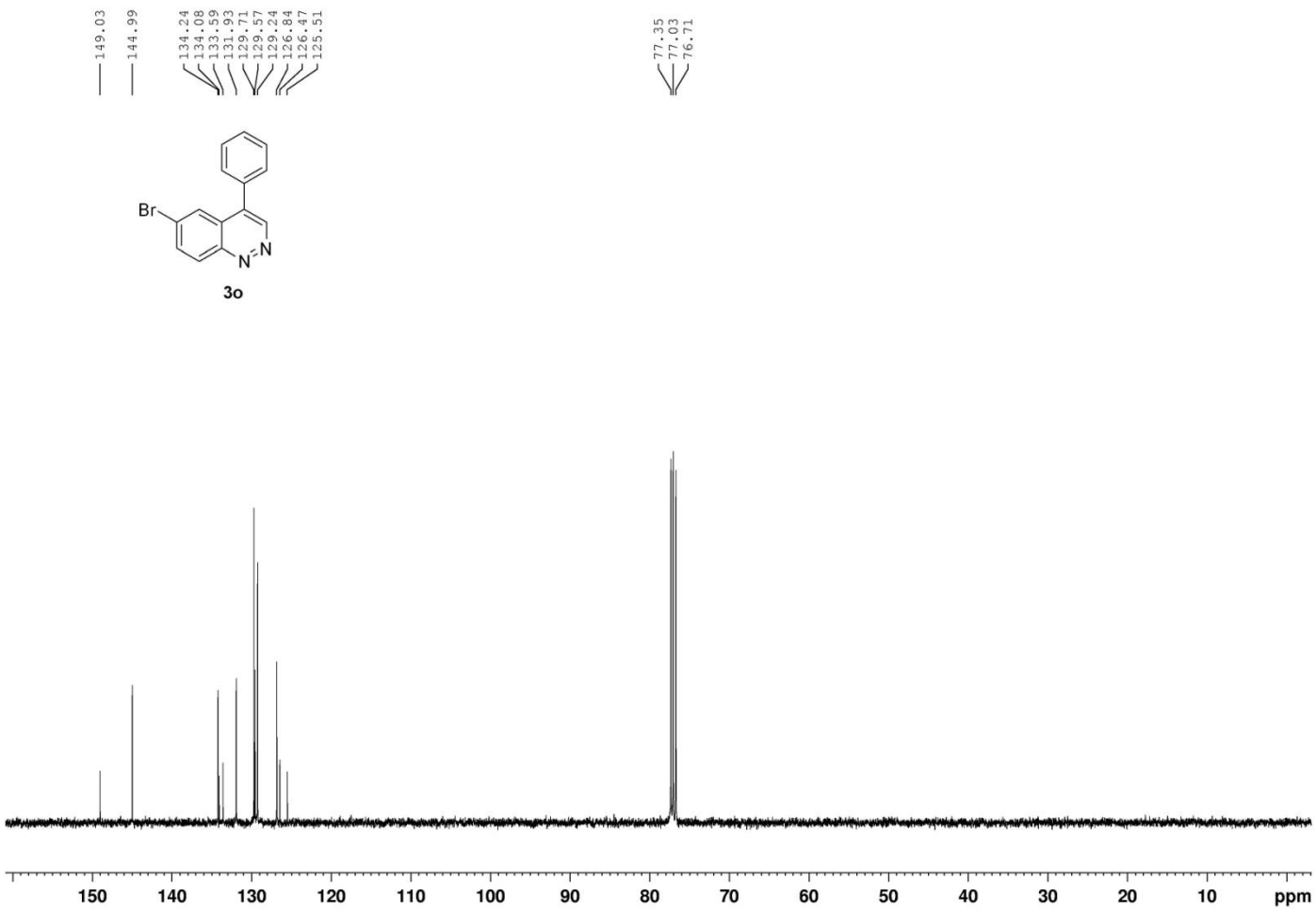
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77.03
76.71
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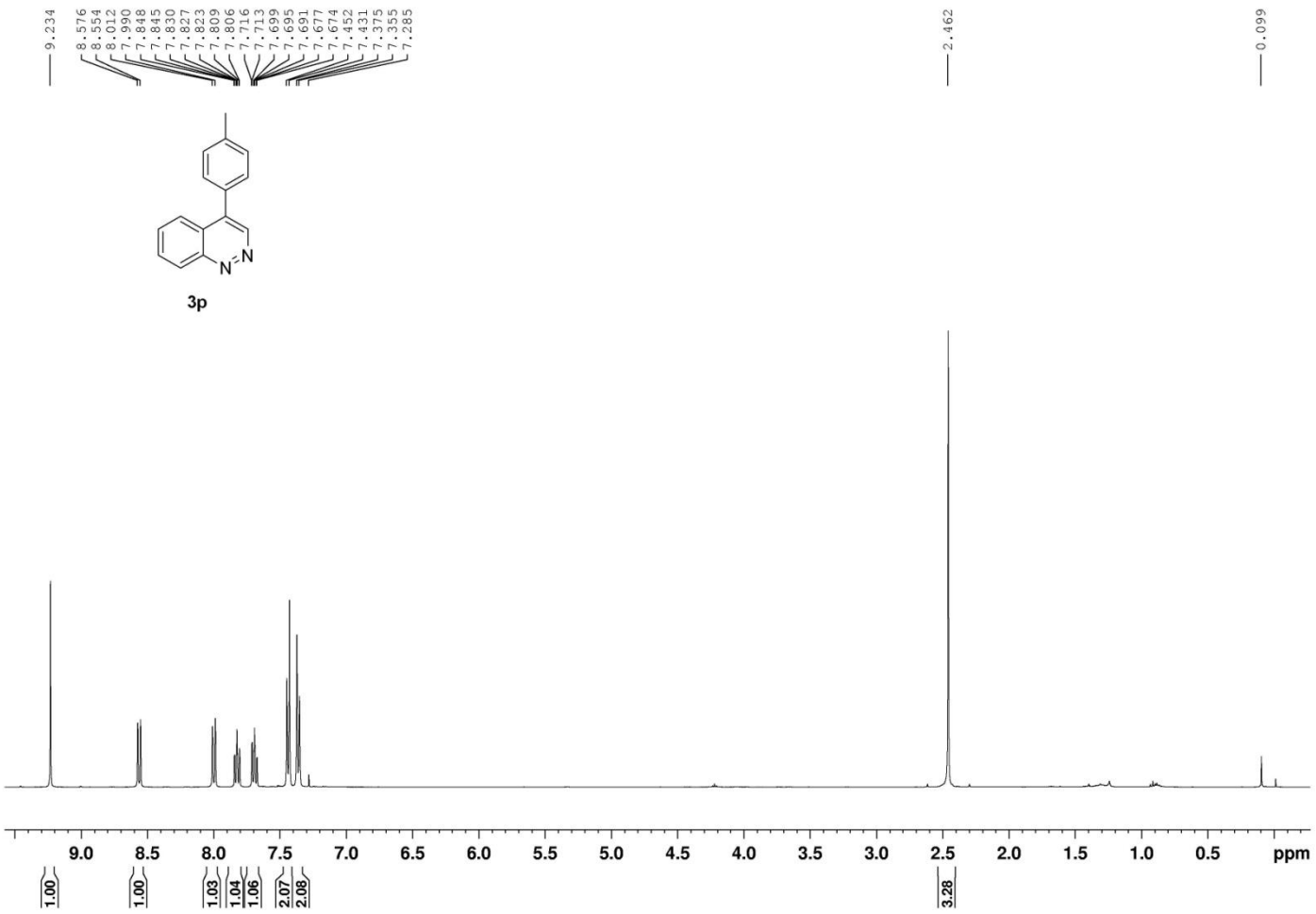
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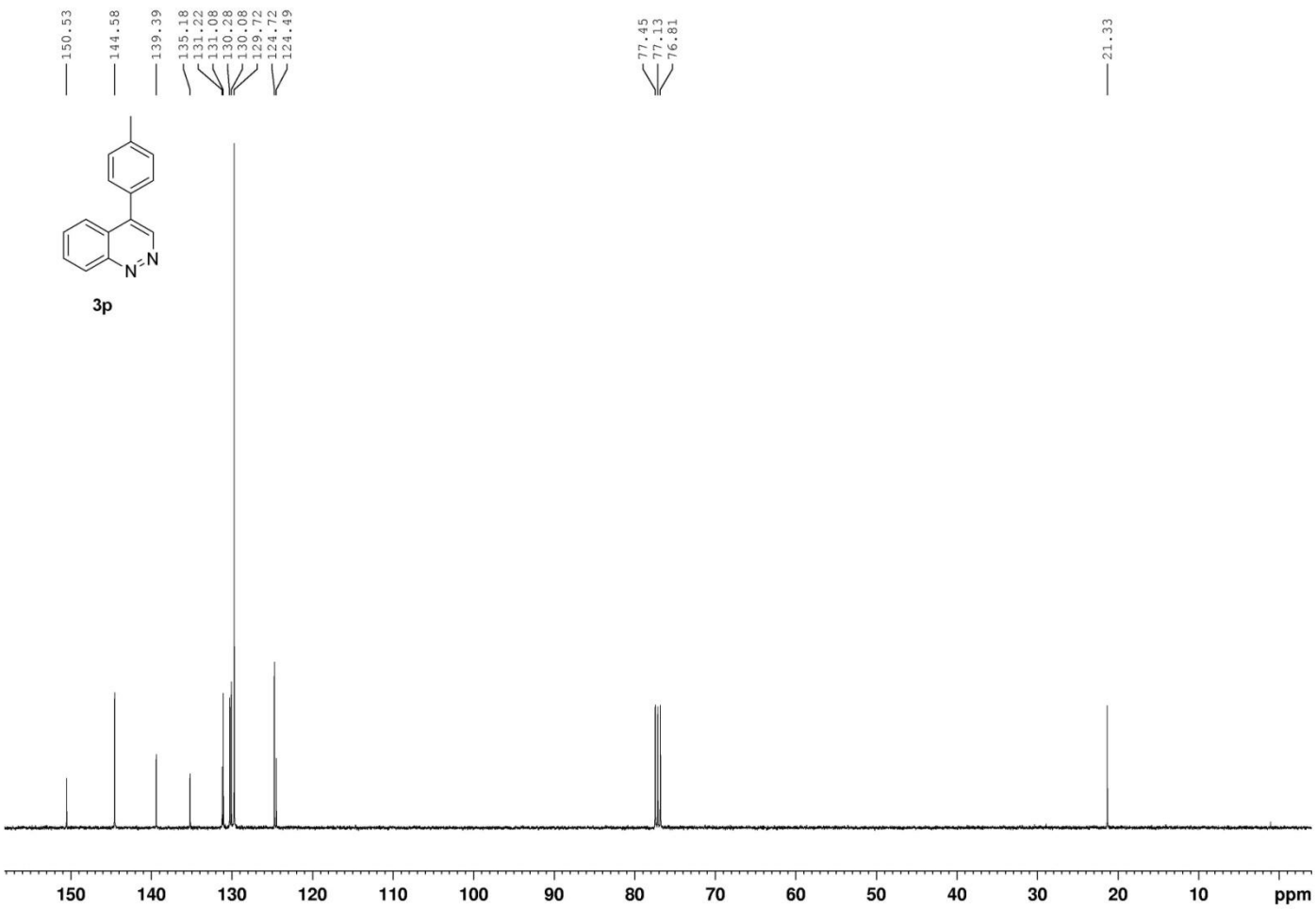
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76.81
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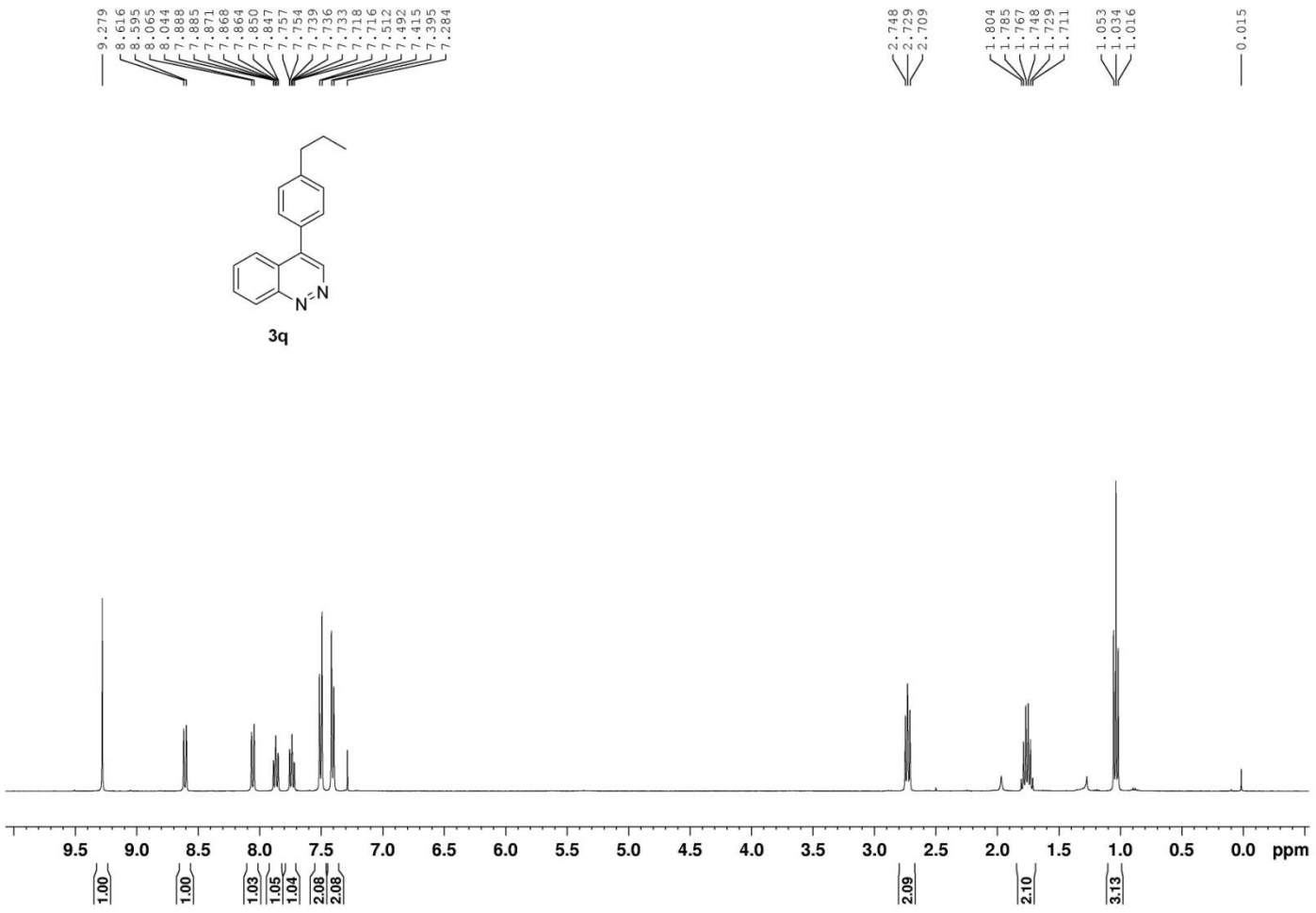
10
ppm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7.395
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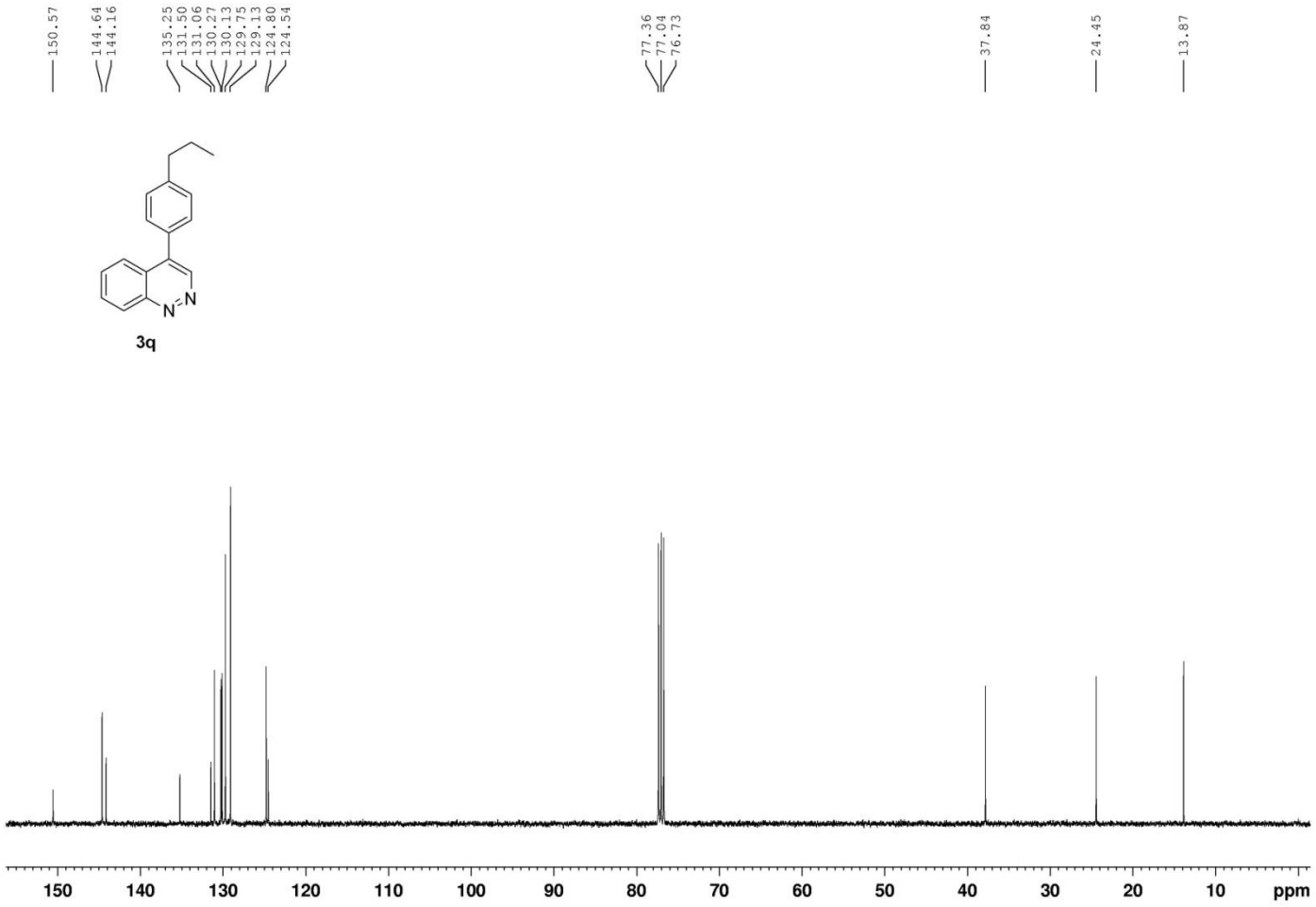
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40
30
20
10
ppm


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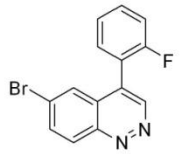
7.284

0.013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Br
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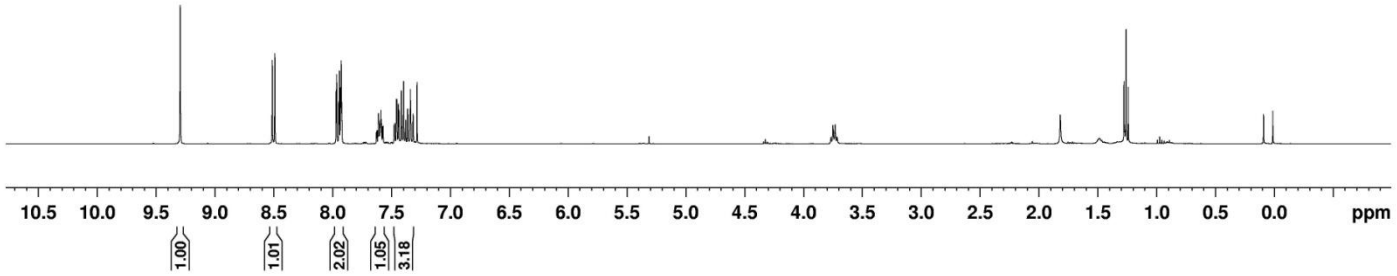
N

3r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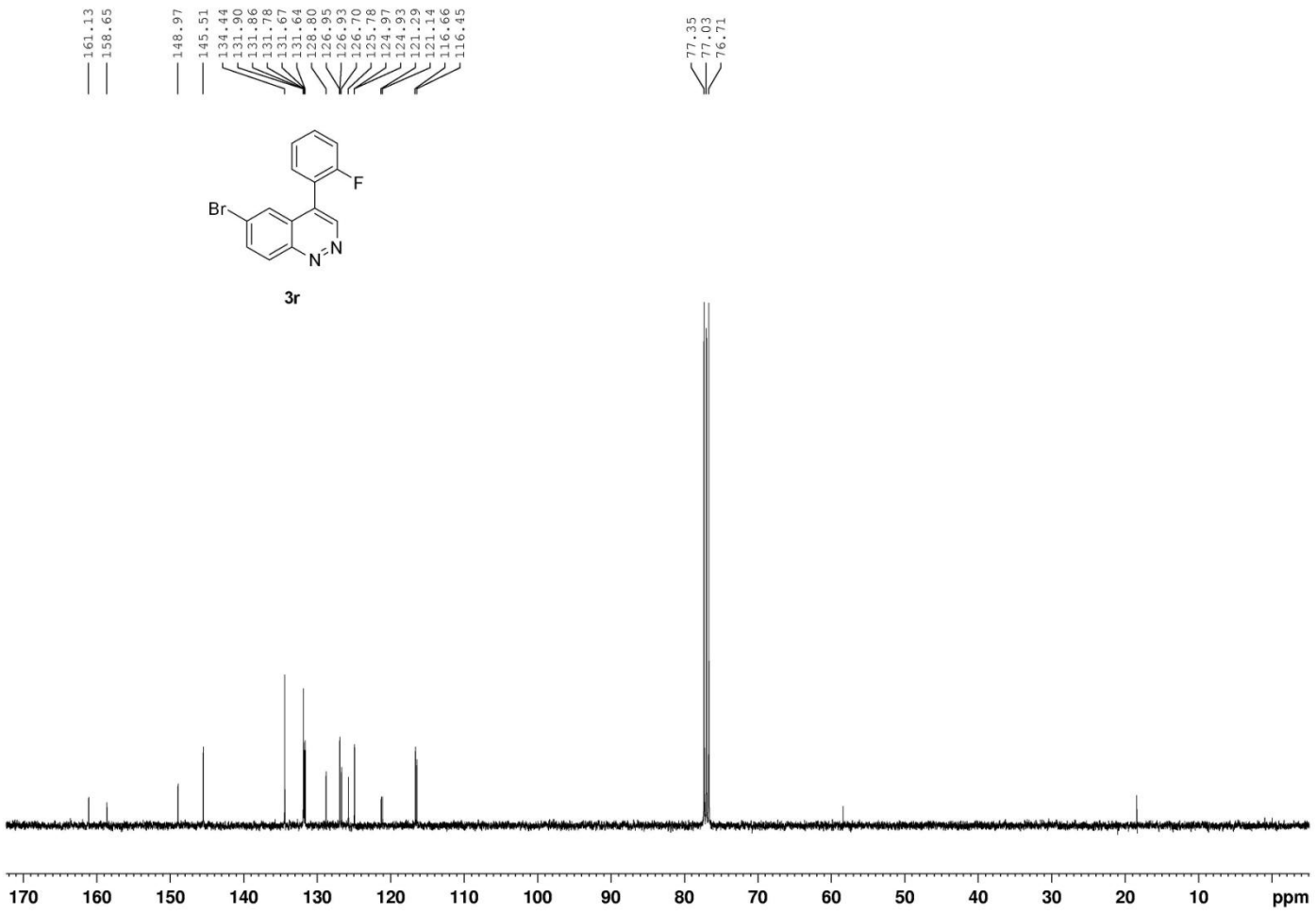
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124.93
121.29
121.14
116.66
116.45
77.35
77.03
76.71
F
Br
N
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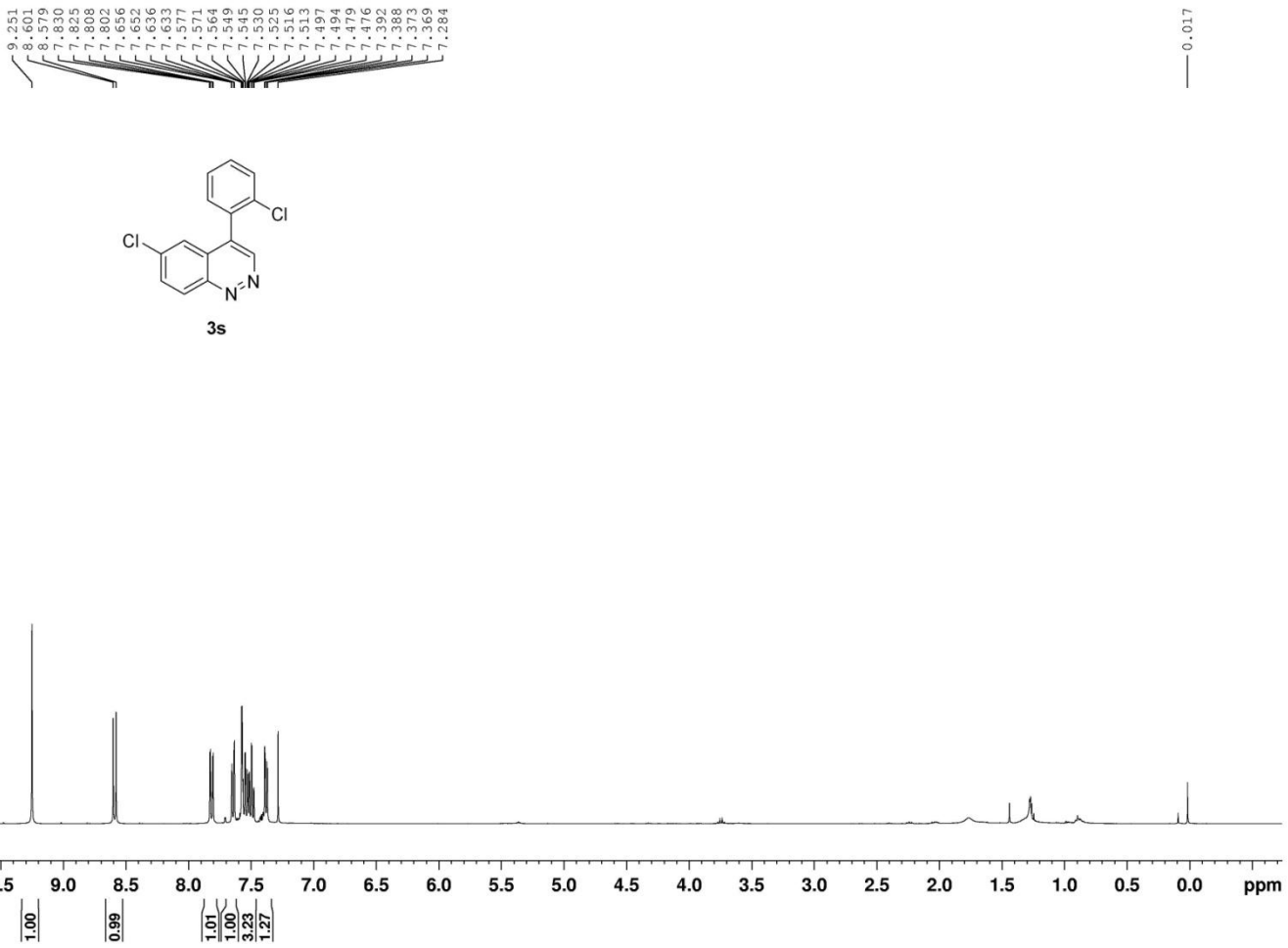
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7.530
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7.369
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5.5
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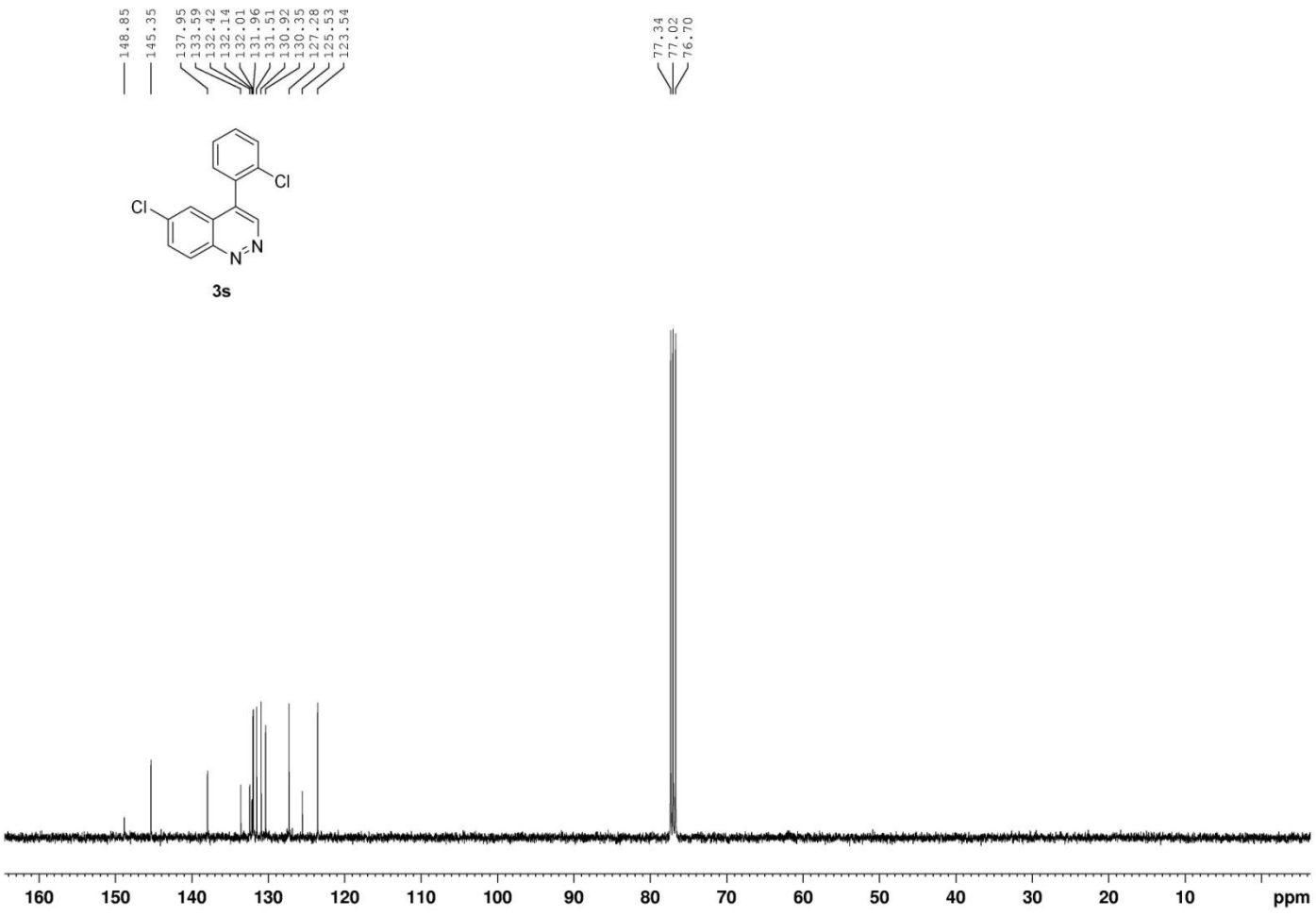
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77.34
77.02
76.70
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Cl
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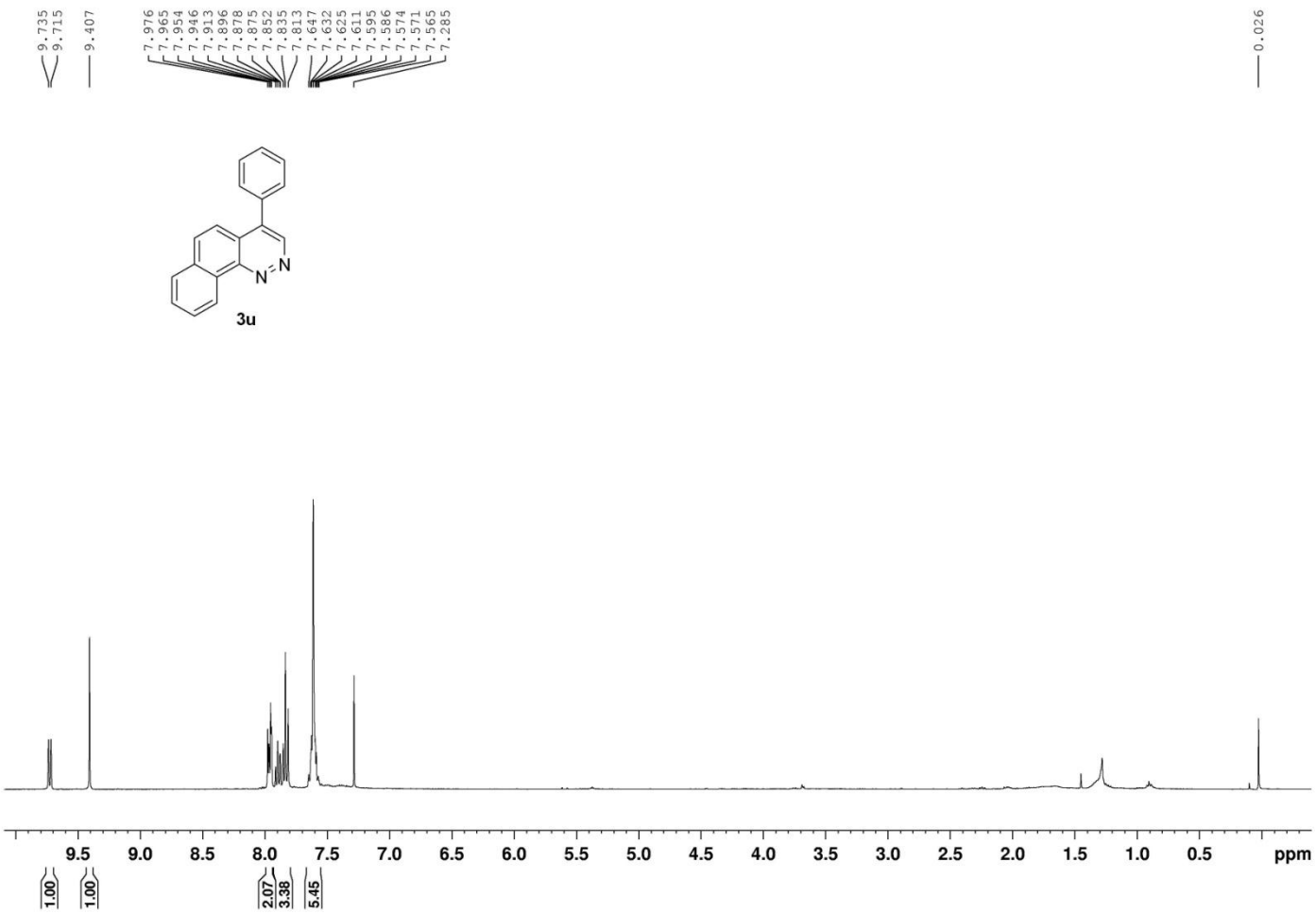
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7.595
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7.571
7.565
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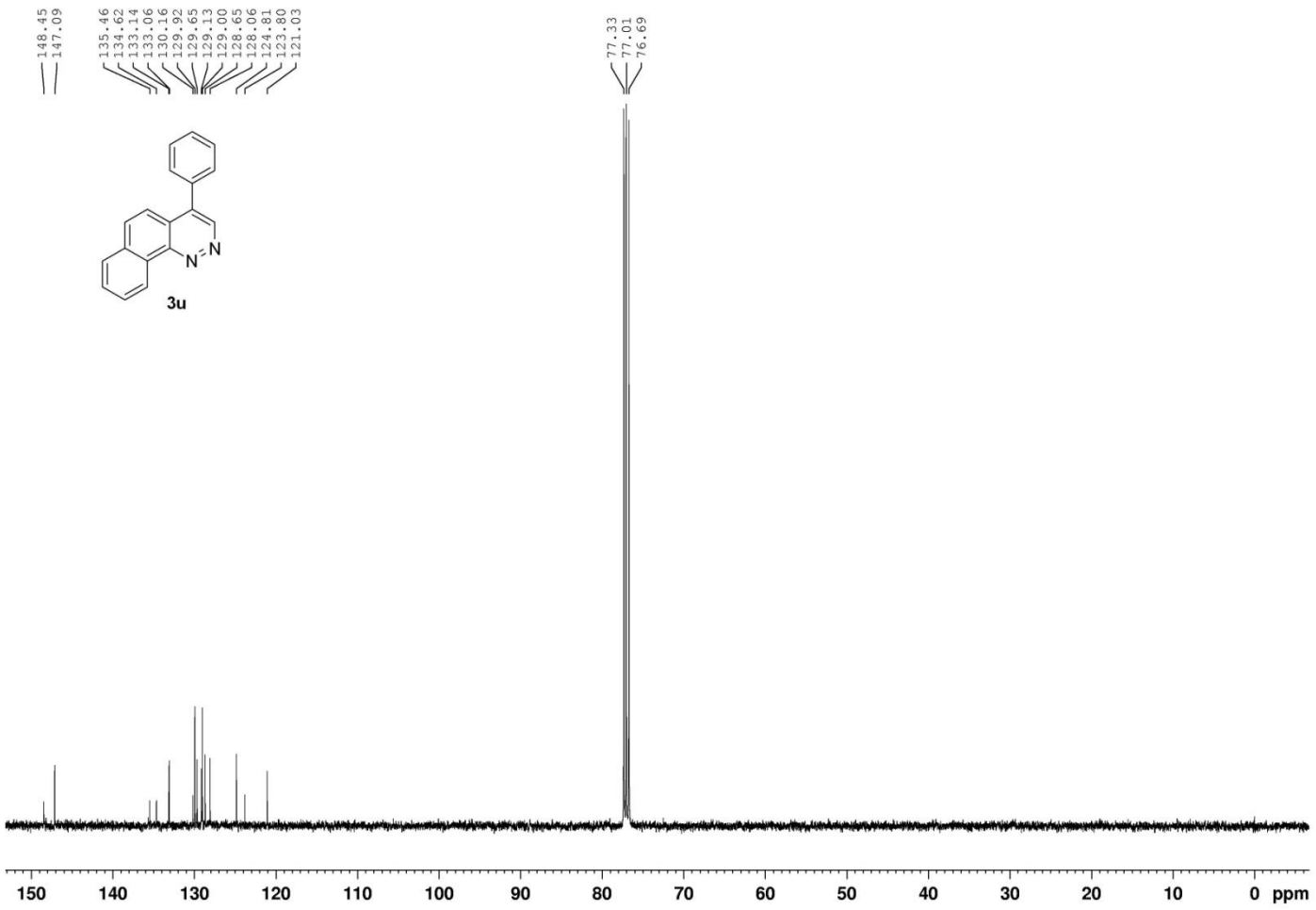
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77.01
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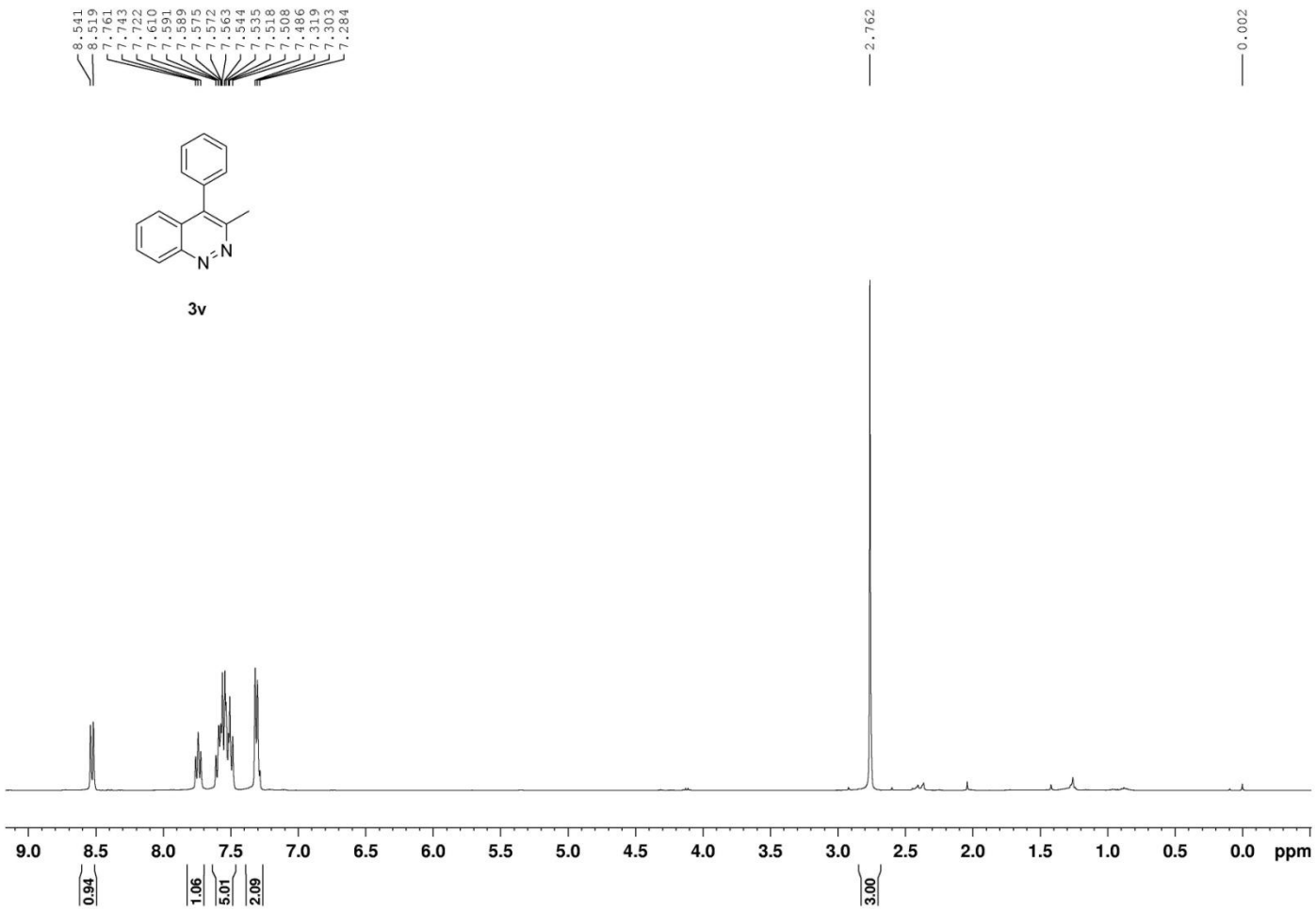
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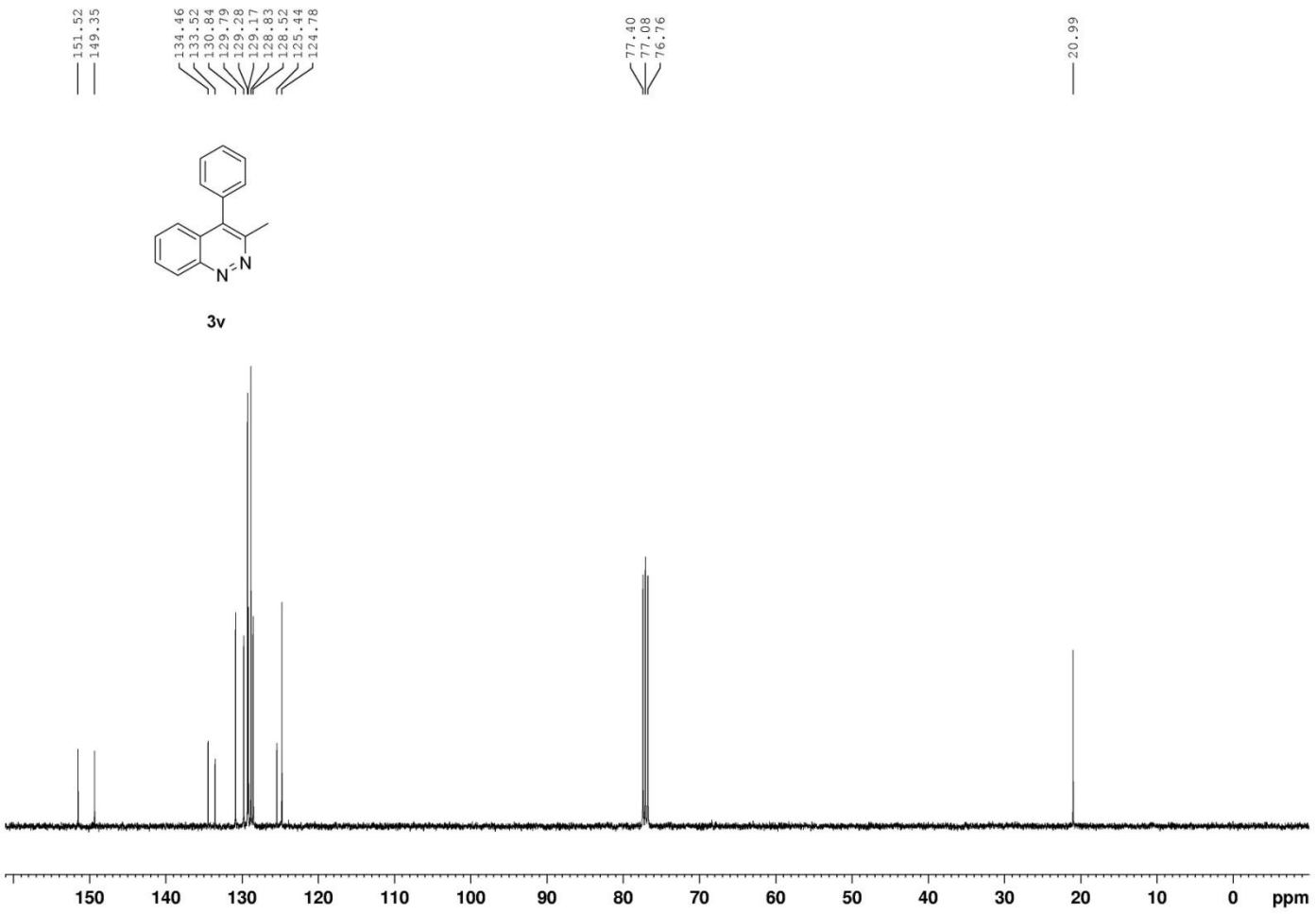
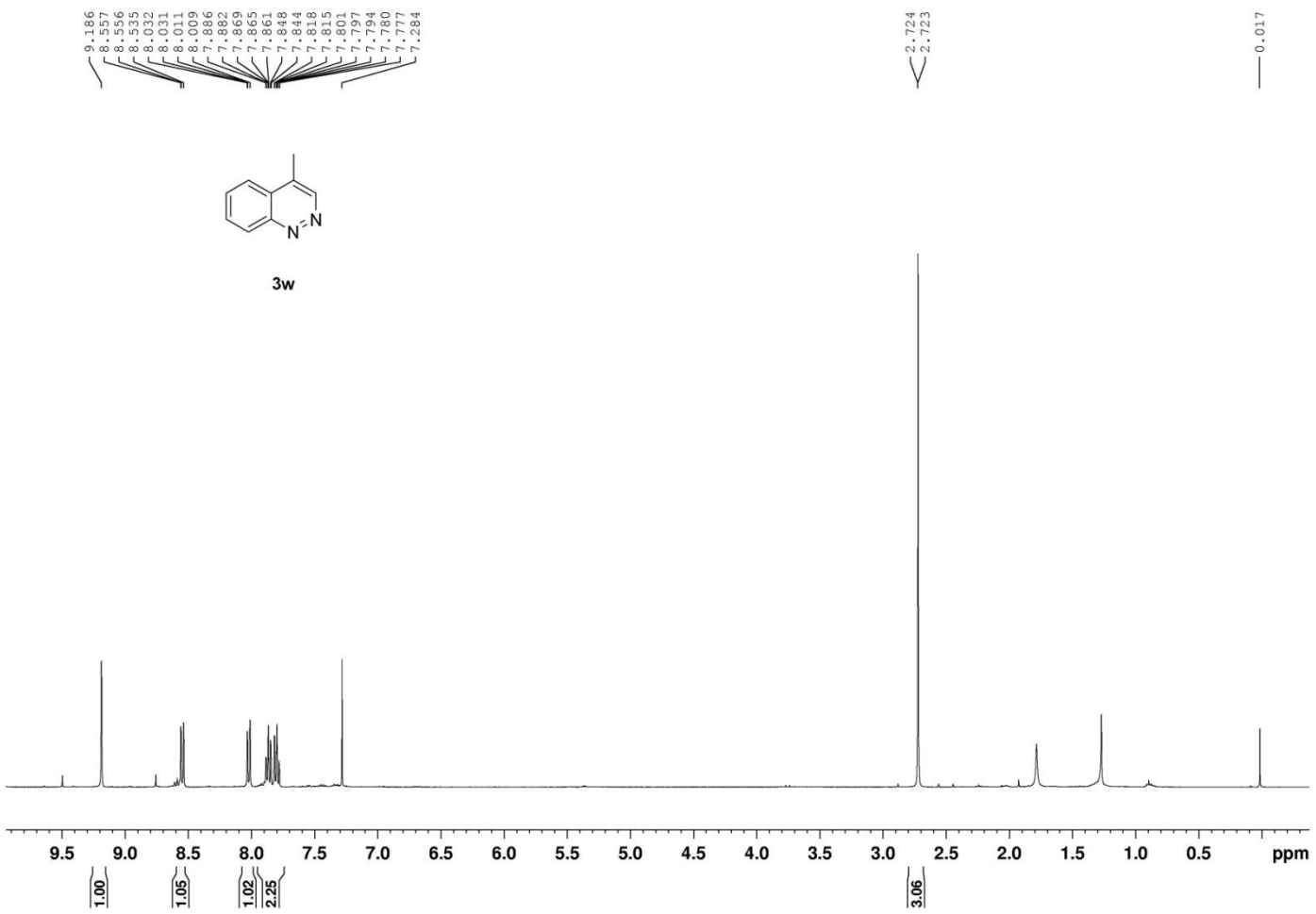
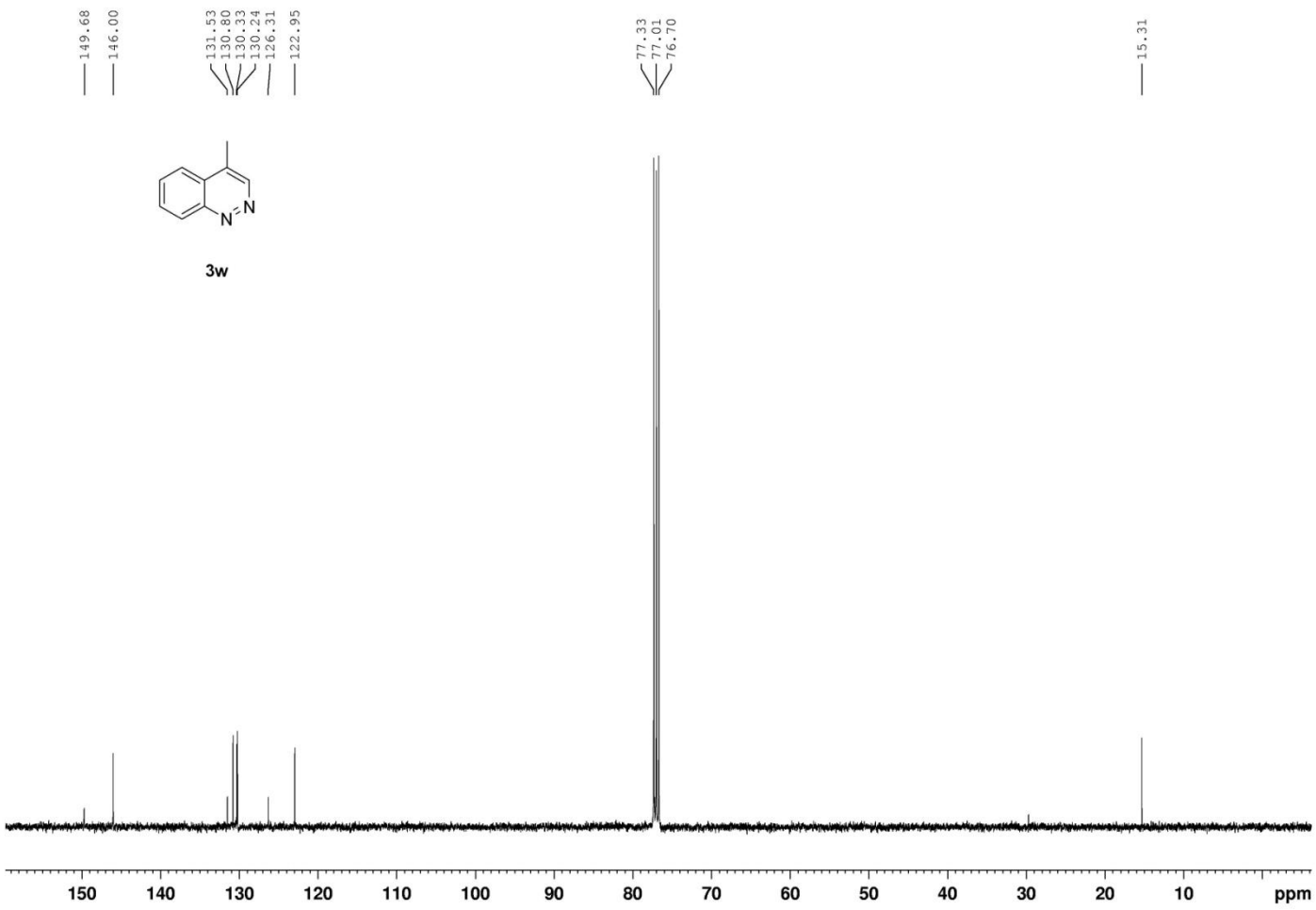
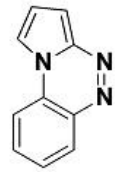

151.52
149.35
134.46
133.52
130.84
129.79
129.28
129.17
128.83
128.52
125.44
124.78
77.40
77.08
76.76
20.99
N
N
3v
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

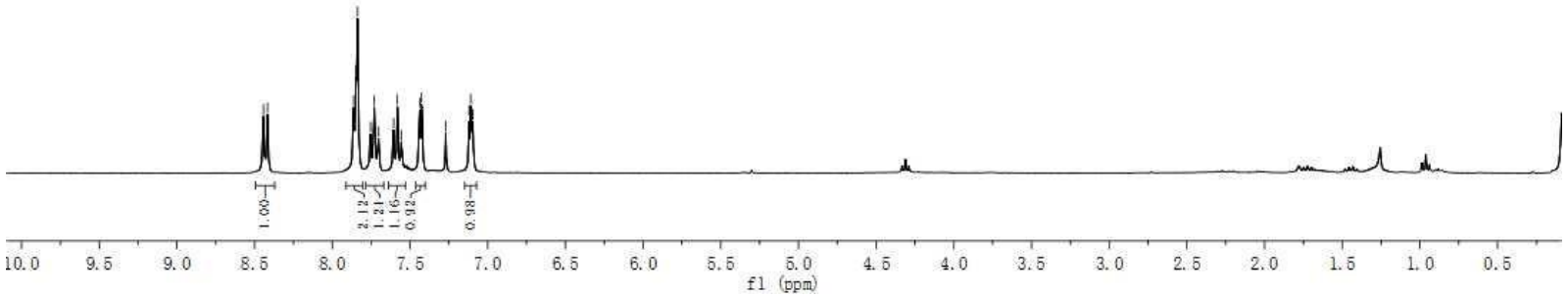

9.186
8.557
8.556
8.535
8.032
8.031
8.011
8.009
7.886
7.882
7.869
7.865
7.861
7.848
7.844
7.818
7.815
7.801
7.797
7.794
7.780
7.777
7.284
2.724
2.723
0.017
N
N
3w
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.05
1.02
2.25
3.06

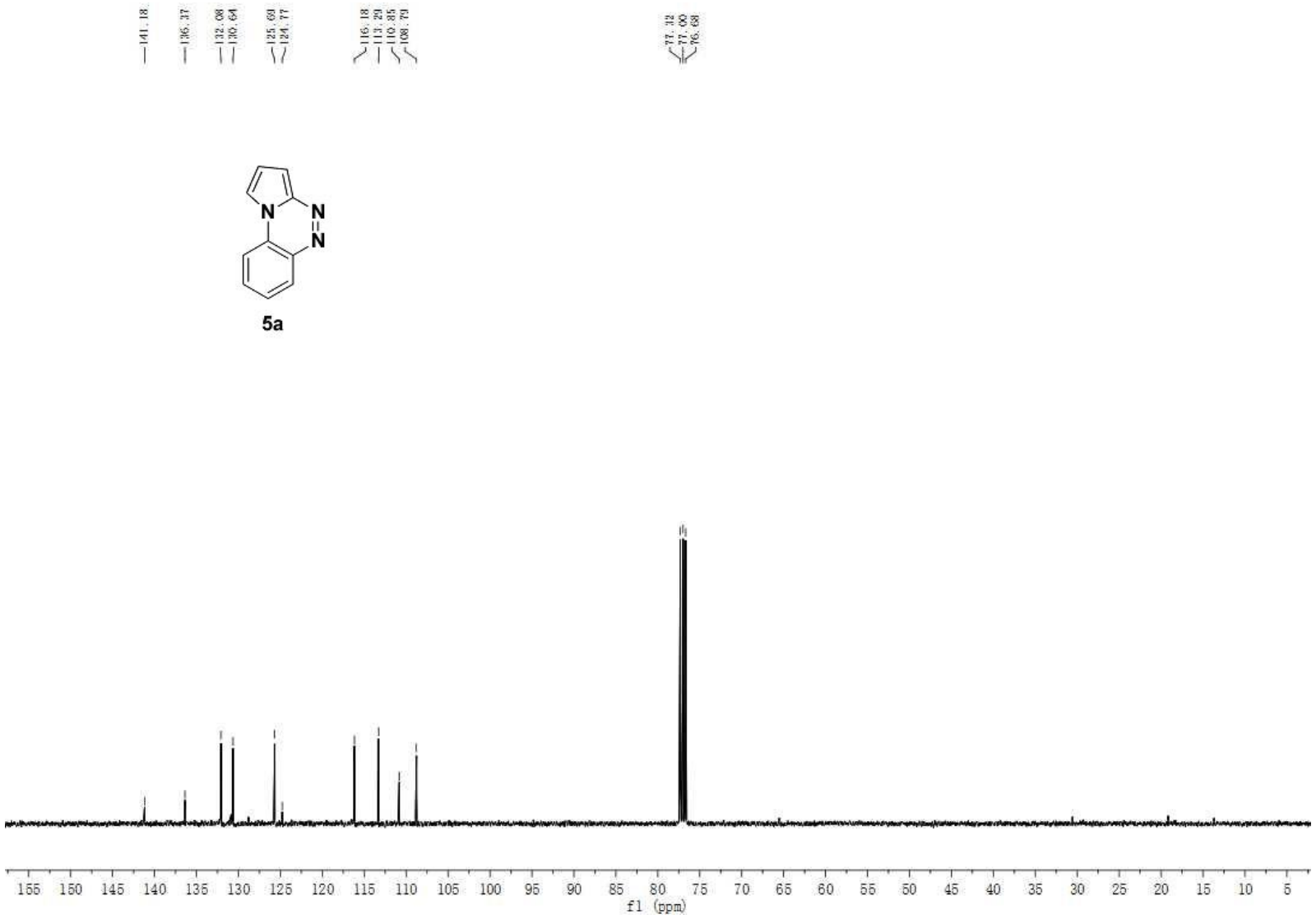

149.68
146.00
131.53
130.80
130.33
130.24
126.31
122.95
77.33
77.01
76.70
15.31
N
N
3w
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

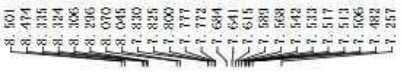

8.443
8.416
7.863
7.847
7.838
7.753
7.729
7.702
7.605
7.581
7.557
7.436
7.425
7.270
7.118
7.109
7.095


N
N
N

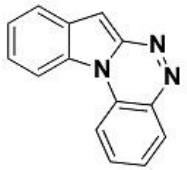
5a


1.00
2.12
1.21
1.16
0.92
0.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

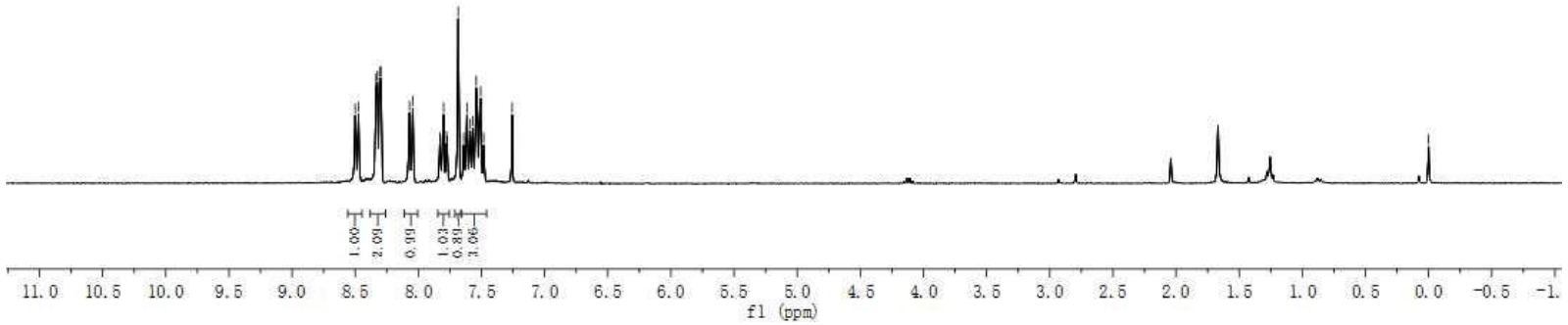

141.18
136.37
132.08
130.64
125.69
124.77
116.18
113.29
110.85
108.79
77.32
77.00
76.68
N
N
N
5a
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

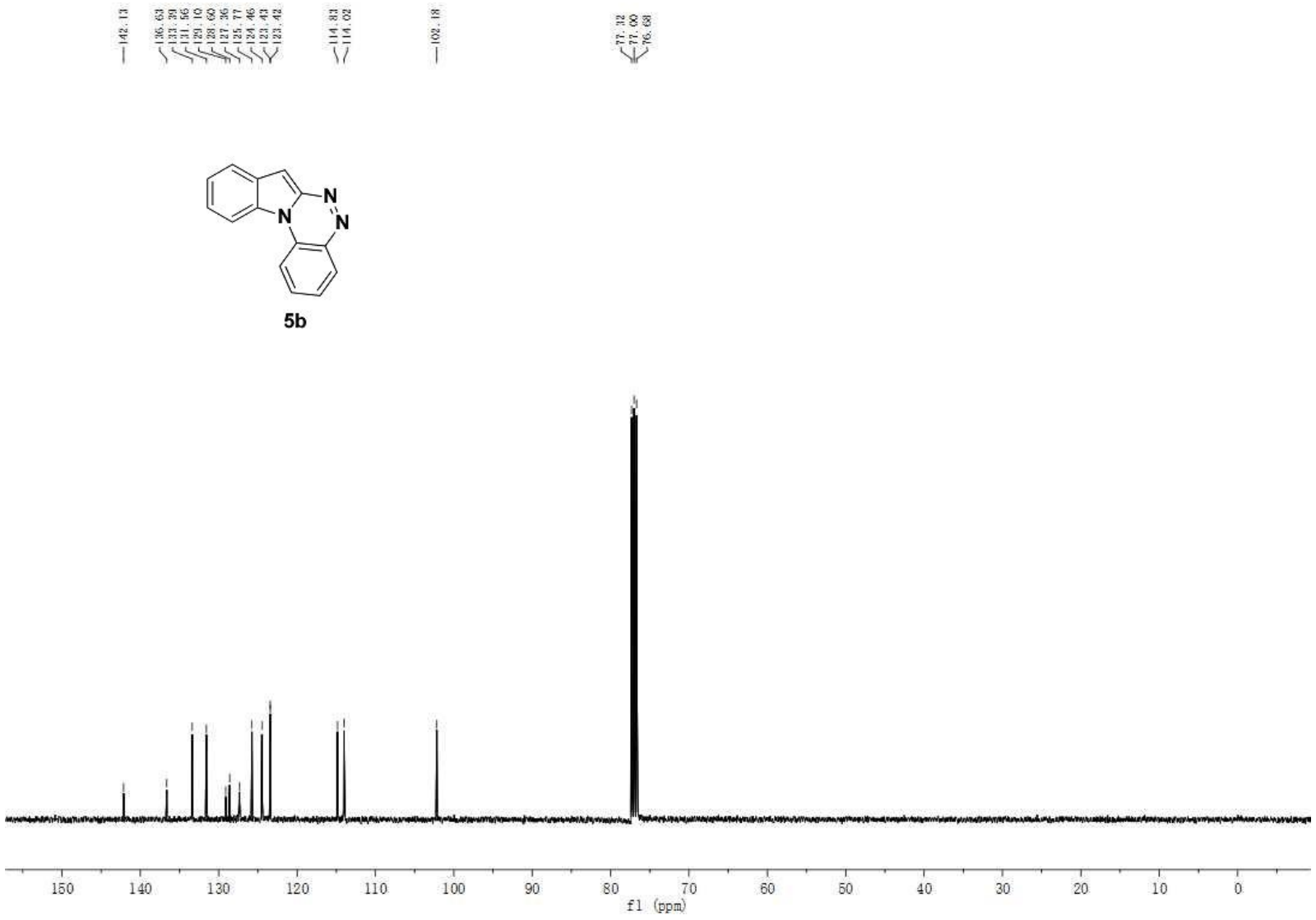

8.501
8.474
8.335
8.324
8.306
8.296
8.070
8.045
7.839
7.825
7.809
7.777
7.772
7.684
7.641
7.615
7.589
7.569
7.542
7.533
7.517
7.513
7.506
7.482
7.257

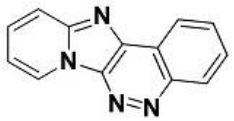
0.000


N
N
N

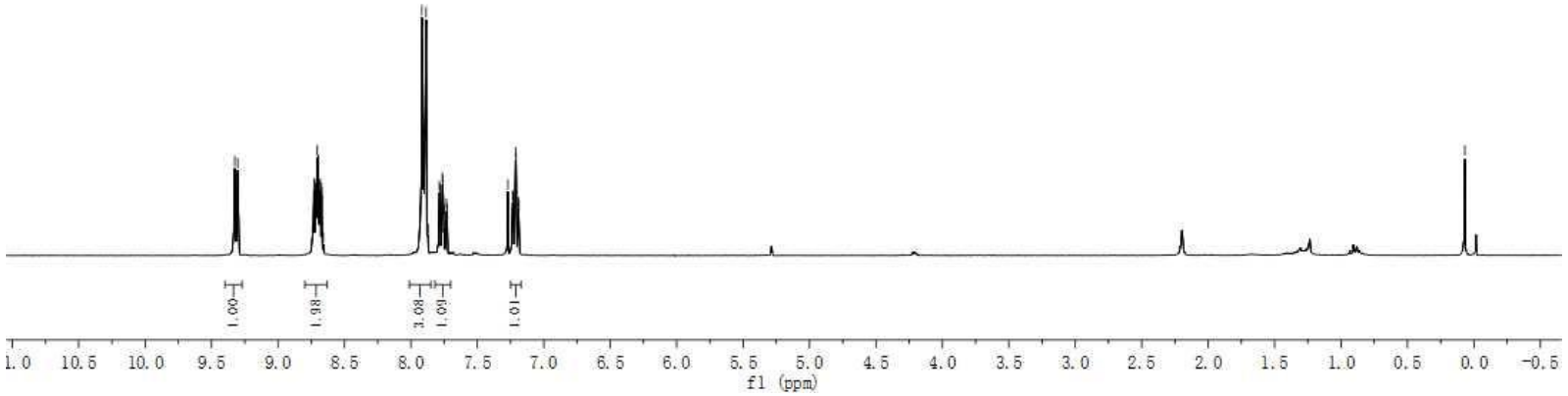
5b

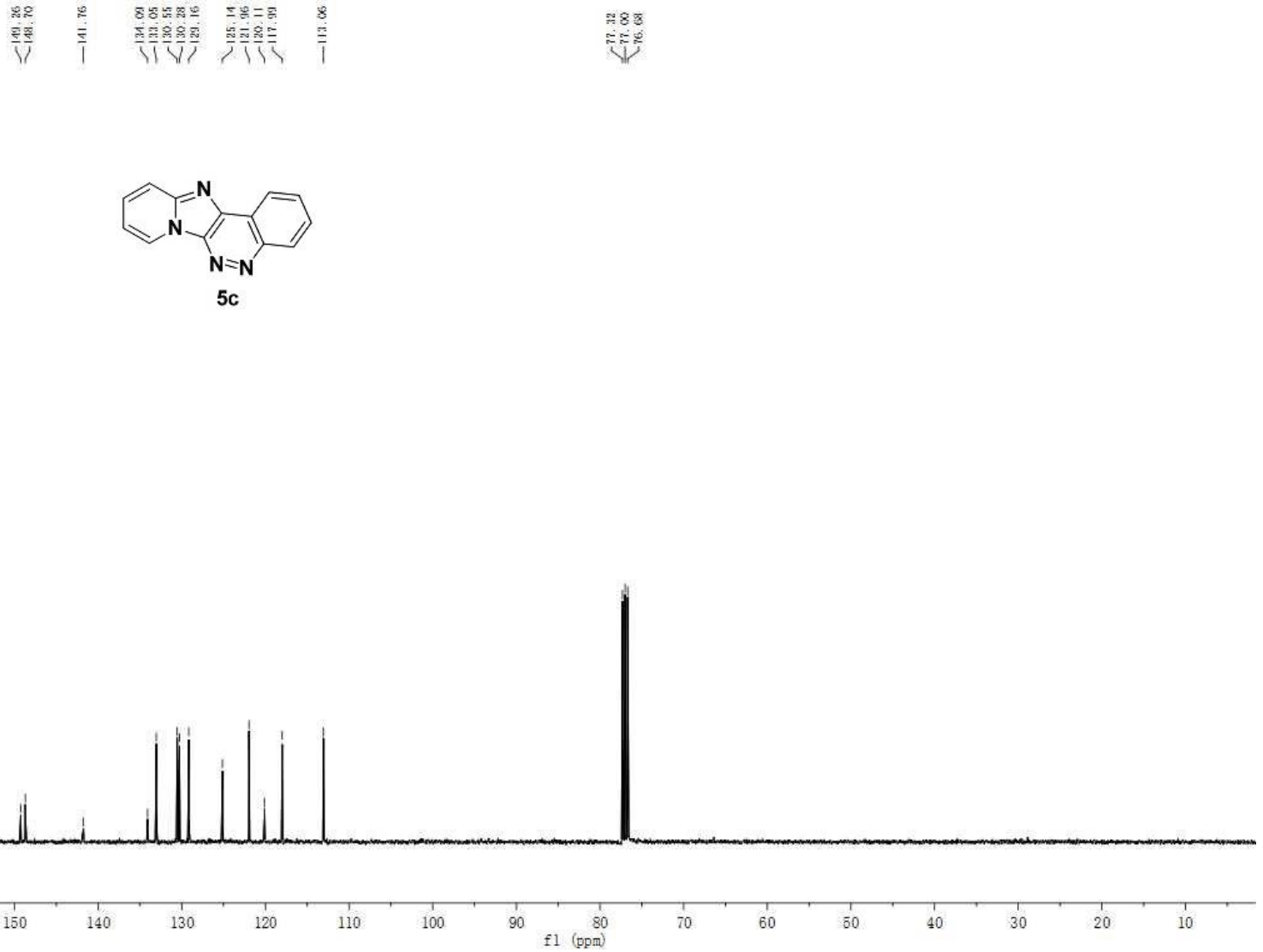

1.00
2.09
0.99
1.03
0.89
3.06
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)

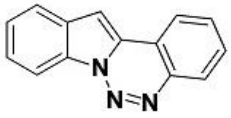

142.13
136.63
133.39
131.56
129.10
128.60
127.36
125.77
124.46
123.43
123.42
114.83
114.02
102.18
77.32
77.00
76.68
N
N
N
5b
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



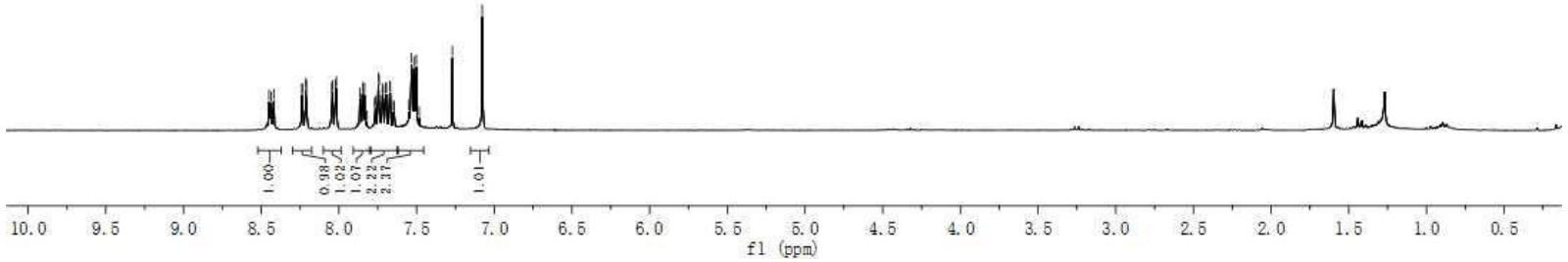
5c

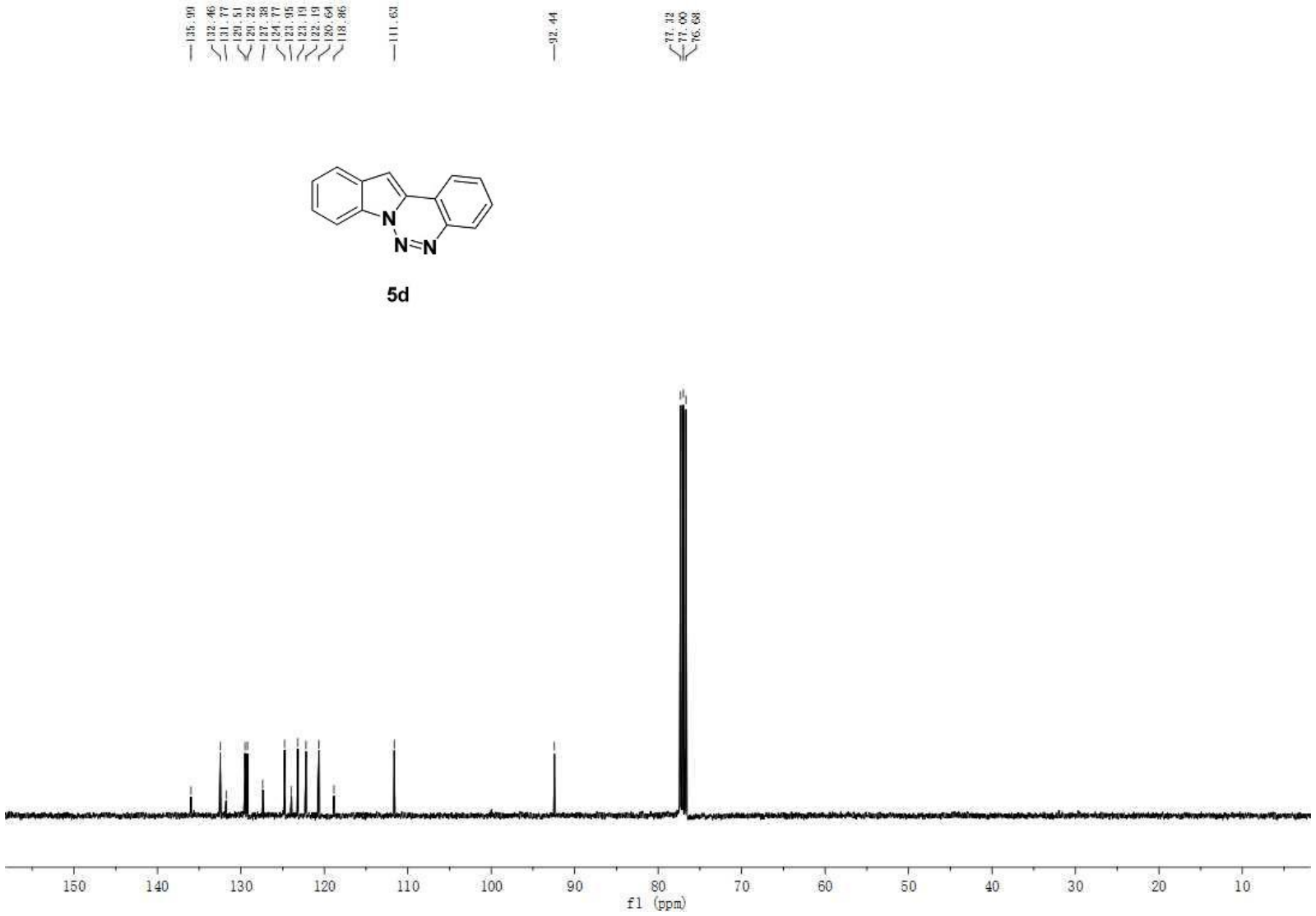

1.00
1.38
3.08
1.09
1.01
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


149.26
148.70
141.76
134.09
133.05
130.55
130.28
129.16
125.14
121.96
120.11
117.99
113.06
77.32
77.00
76.68
N
N
N=N
5c
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



5d


1.00
0.98
1.02
1.07
2.22
2.17
1.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


135.99
132.46
131.77
131.51
129.22
127.38
124.77
123.95
123.19
122.19
120.64
118.86
111.63
92.44
77.32
77.00
76.68
N
N=N
5d
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)