Enantioselective Synthesis of Tryptanthrin Derivatives Enabled by Asymmetric Aza-Friedel–Crafts Reaction

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Supporting Information

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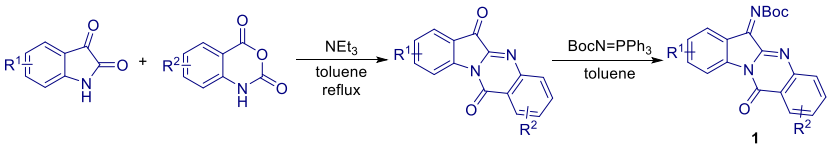
1. General Methods

Chemical reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by thin-layer chromatography (TLC). ^{1}H NMR (300, 400, and 600 MHz) and ^{13}C NMR (75, 101, and 151 MHz) spectra were recorded in DMSO-d_6 and $CDCl_3$. ^{1}H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS), with the solvent resonance employed as the internal standard (DMSO-d_6 at 2.50 ppm and $CDCl_3$ at 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard (DMSO-d_6 at 39.52 ppm and $CDCl_3$ at 77.16 ppm). The enantiomeric excesses were determined by chiral HPLC analysis. HPLC analysis was performed on Agilent 1260 II. Chiral AD-H and IC columns were manufactured by Daicel Chemical Industries. HRMS was recorded on the Agilent 6545 LC/Q-TOF mass spectrometer. Optical rotations were measured with a Rudolph Autopol-III polarimeter. Melting points were recorded on a OptiMelt MPA 1000.

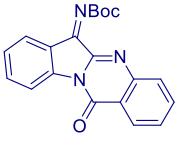
2. General procedure for the synthesis of tryptanthrin-derived ketimines 1



The tryptanthrin and substituted tryptanthrins were prepared according to the reported literature with modifications.[1] To a flame-dried flask was added substituted isatin (20 mmol), substituted isatoic anhydride (22 mmol, 1.1 equiv), toluene (25 mL), and triethyl amine (100 mmol, 5 equiv). The mixture was refluxed for 12 h. After completion (monitored by TLC), the mixture was cooled to room temperature and filtered. The filter cake was washed with EtOH (15 mL×2) and dried to give the substituted tryptanthrin, which was used for the next step without further purification.

To a flame-dried flask was added the substituted tryptanthrin (5 mmol), BocN=PPh_3 (10 mmol), and toluene (20 mL). The resulting mixture was refluxed to completion (monitored by TLC). After cooling to room temperature, the solvent was removed under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether /ethylacetate/ dichloromethane = 15:1:1–10:1:1) to give ketimine **1**.

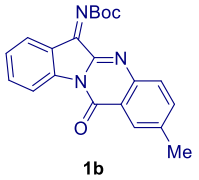
***tert*-butyl (12-oxoindolo[2,1-*b*]quinazolin-6(12*H*)-ylidene)carbamate (1a)**



The product was purified by flash column chromatography (petroleum ether : ethyl acetate : dichloromethane = 10:1:1 as the eluent). Yellow solid; 62% yield, 1.08 g; mp 231.6–233.2 °C.
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71 – 8.39 (m, 1H), 8.33 (d, *J* = 7.9 Hz, 1H), 8.02 – 7.67 (m, 3H), 7.67 – 7.41 (m, 2H), 7.33 (t, *J* = 7.7 Hz, 1H), 1.71 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 160.0, 158.3, 153.2, 146.7, 143.3, 142.1, 135.5, 134.8, 129.5, 127.4, 126.9, 124.1, 124.1, 123.0, 117.4, 83.8, 28.3.
HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{20}H_{17}N_3O_3Na$ 370.1162, found 370.1169.

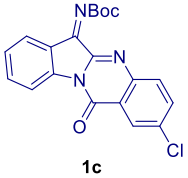
***tert*-butyl (2-methyl-12-oxoindolo[2,1-*b*]quinazolin-6(12*H*)-ylidene)carbamate (1b)**



1b

The product was purified by flash column chromatography (petroleum ether : ethyl acetate : dichloromethane = 15:1:1 as the eluent). Yellow solid; 57% yield, 1.03 g; mp 228.3–230.4 °C.
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (d, *J* = 7.9 Hz, 1H), 8.16 (s, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.80 – 7.47 (m, 3H), 7.35 (t, *J* = 7.6 Hz, 1H), 2.50 (s, 3H), 1.71 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2, 158.5, 153.3, 144.7, 143.4, 141.5, 140.4, 136.1, 135.5, 129.4, 127.2, 126.9, 124.1, 123.3, 122.8, 117.5, 83.8, 28.4, 21.7.
HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{21}H_{19}N_3O_3Na$ 384.1319, found 384.1327.

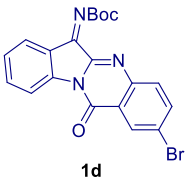
***tert*-butyl (2-chloro-12-oxoindolo[2,1-*b*]quinazolin-6(12*H*)-ylidene)carbamate (1c)**



1c

The product was purified by flash column chromatography (petroleum ether : ethyl acetate : dichloromethane = 15:1:1 as the eluent). Yellow solid; 68% yield, 1.30 g; mp 229.4–231.2 °C.
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71 – 8.41 (m, 1H), 8.35 (s, 1H), 8.08 – 7.56 (m, 4H), 7.39 (t, *J* = 7.6 Hz, 1H), 1.71 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 159.9, 157.2, 152.8, 145.1, 143.0, 142.2, 135.8, 135.6, 135.1, 130.8, 127.3, 127.0, 124.2, 124.1, 123.0, 117.5, 83.9, 28.3.
HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{20}H_{16}ClN_3O_3Na$ 404.0772, found 404.0776.

***tert*-butyl (2-bromo-12-oxoindolo[2,1-*b*]quinazolin-6(12*H*)-ylidene)carbamate (1d)**

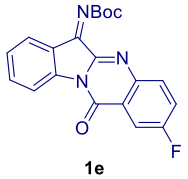


1d

The product was purified by flash column chromatography (petroleum ether : ethyl acetate : dichloromethane = 15:1:1 as the eluent). Yellow solid; 42% yield, 0.89 g; mp 229.5–231.9 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 – 8.18 (m, 2H), 7.88 (t, *J* = 10.0 Hz, 2H), 7.81 – 7.49 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 1.70 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 157.2, 152.9, 145.5, 143.1, 142.3, 138.1, 135.7, 131.0, 130.2, 127.3, 124.4, 124.3, 123.8, 123.1, 117.6, 84.0, 28.3.

HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd. for $C_{20}H_{17}BrN_3O_3$ 426.0448, found 426.0450.

***tert*-butyl (2-fluoro-12-oxoindolo[2,1-*b*]quinazolin-6(12*H*)-ylidene)carbamate (1e)**



1e

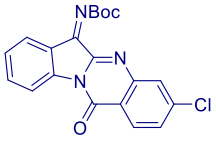
The product was purified by flash column chromatography (petroleum ether : ethyl acetate : dichloromethane = 15:1:1 as the eluent). Yellow solid; 39% yield, 0.71 g; mp 210.8–212.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 – 8.44 (m, 1H), 8.07 (dd, *J* = 8.3, 2.9 Hz, 1H), 7.93 (d, *J* = 7.4 Hz, 1H), 7.82 (s, 1H), 7.69 (t, *J* = 7.9 Hz, 1H), 7.52 (s, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 1.72 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7 (d, *J* = 254.5 Hz, 1C), 160.1, 157.6, 153.0, 143.3 (d, *J* = 22.2 Hz, 1C), 138.5, 135.7, 131.9, 127.3, 125.6, 124.9 (d, *J* = 9.1 Hz, 1C), 124.3, 123.1, 118.2, 117.6, 113.1 (d, *J* = 24.2 Hz, 1C), 83.99, 28.36.

HRMS (ESI-TOF) *m/z* $[M + K]^+$ calcd. for $C_{20}H_{16}FN_3O_3K$ 404.0807, found 404.0814.

***tert*-butyl (3-chloro-12-oxoindolo[2,1-*b*]quinazolin-6(12*H*)-ylidene)carbamate (1f)**



1f

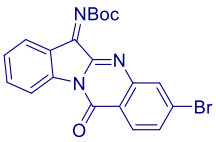
The product was purified by flash column chromatography (petroleum ether : ethyl acetate : dichloromethane = 15:1:1 as the eluent). Yellow solid; 45% yield, 0.86 g; mp 210.7–212.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 – 8.40 (m, 1H), 8.33 (d, *J* = 8.5 Hz, 1H), 7.99 – 7.85 (m, 1H), 7.74 (s, 1H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.56 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 1.72 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 157.8, 152.9, 147.7, 143.2, 141.2, 138.5, 135.7, 130.0, 128.9, 128.8, 127.3, 124.3, 123.0, 121.5, 117.5, 84.1, 28.4.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{20}H_{16}ClN_3O_3Na$ 404.0772, found 404.0779.

***tert*-butyl (3-bromo-12-oxoindolo[2,1-*b*]quinazolin-6(12*H*)-ylidene)carbamate (1g)**



1g

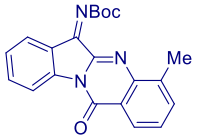
The product was purified by flash column chromatography (petroleum ether : ethyl acetate : dichloromethane = 15:1:1 as the eluent). Yellow solid; 65% yield, 1.38 g; mp 219.3–222.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 – 8.36 (m, 2H), 7.98 – 7.81 (m, 2H), 7.75 – 7.54 (m, 2H), 7.38 (t, *J* = 7.7 Hz, 1H), 1.70 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 157.2, 152.9, 145.5, 143.0, 138.1, 135.7, 132.8, 131.0, 130.2, 128.8, 127.3, 124.4, 124.3, 123.8, 117.5, 84.0, 28.3.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{20}H_{16}BrN_3O_3Na$ 448.0267, found 448.0272.

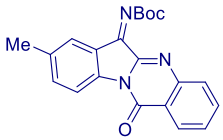
***tert*-butyl (4-methyl-12-oxoindolo[2,1-*b*]quinazolin-6(12*H*)-ylidene)carbamate (1h)**



1h

The product was purified by flash column chromatography (petroleum ether : ethyl acetate : dichloromethane = 15:1:1 as the eluent). Yellow solid; 36% yield, 0.65 g; mp 208.5–210.3 °C.
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.50 (s, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 7.85 (s, 1H), 7.72 – 7.50 (m, 2H), 7.49 – 7.27 (m, 2H), 2.65 (s, 3H), 1.68 (s, 9H).
^{13}C NMR (75 MHz, DMSO-d_6) δ 159.7, 158.6, 152.6, 145.1, 143.1, 141.0, 138.7, 135.8, 135.5, 129.1, 126.7, 125.0, 124.1, 123.0, 117.5, 83.3, 28.5, 18.0.
HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{21}H_{19}N_3O_3Na$ 384.1319, found 384.1326.

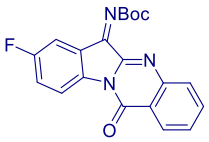
***tert*-butyl (8-methyl-12-oxoindolo[2,1-*b*]quinazolin-6(12*H*)-ylidene)carbamate (1i)**



1i

The product was purified by flash column chromatography (petroleum ether : ethyl acetate : dichloromethane = 15:1:1 as the eluent). Yellow solid; 61% yield, 1.10 g; mp 205.6–206.9 °C.
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.32 (d, *J* = 8.0 Hz, 2H), 8.09 – 7.69 (m, 2H), 7.69 – 7.49 (m, 2H), 7.39 (d, *J* = 8.3 Hz, 1H), 2.36 (s, 3H), 1.70 (s, 9H).
^{13}C NMR (75 MHz, DMSO-d_6) δ 160.1, 158.1, 153.2, 146.7, 142.3, 141.2, 137.0, 136.2, 134.6, 129.4, 127.3, 126.0, 124.3, 123.1, 117.1, 83.7, 28.3, 21.2.
HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{21}H_{19}N_3O_3Na$ 384.1319, found 384.1323.

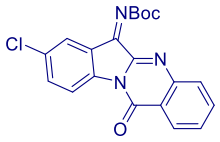
***tert*-butyl (8-fluoro-12-oxoindolo[2,1-*b*]quinazolin-6(12*H*)-ylidene)carbamate (1j)**



1j

The product was purified by flash column chromatography (petroleum ether : ethyl acetate : dichloromethane = 15:1:1 as the eluent). Yellow solid; 66% yield, 1.21 g; mp 193.1–194.8 °C.
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.77 – 8.46 (m, 1H), 8.42 (d, *J* = 7.9 Hz, 1H), 7.81 (d, *J* = 4.7 Hz, 2H), 7.70 – 7.53 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 1.72 (s, 9H).
^{13}C NMR (75 MHz, DMSO-d_6) δ 161.1 (d, *J* = 249.5 Hz, 1C), 159.6, 158.1, 152.5, 146.5, 142.0, 139.4, 134.9, 129.7, 129.6, 127.4, 125.0 (d, *J* = 9.1 Hz, 1C), 122.9, 122.1 (d, *J* = 23.2 Hz, 1C), 119.0 (d, *J* = 8.1 Hz, 1C), 111.0 (d, *J* = 25.2 Hz, 1C), 84.1, 28.3.
HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{20}H_{16}FN_3O_3Na$ 388.1068, found 388.1074.

***tert*-butyl (8-chloro-12-oxoindolo[2,1-*b*]quinazolin-6(12*H*)-ylidene)carbamate (1k)**



1k

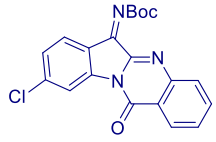
The product was purified by flash column chromatography (petroleum ether : ethyl acetate : dichloromethane = 15:1:1 as the eluent). Yellow solid; 58% yield, 1.11 g; mp 208.8–210.6 °C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.46 (d, *J* = 8.6 Hz, 1H), 8.37 (d, *J* = 7.9 Hz, 1H), 8.05 – 7.70 (m, 3H), 7.70 – 7.47 (m, 2H), 1.71 (s, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 159.7, 158.3, 152.2, 146.7, 141.6, 135.2, 135.0, 132.9, 129.8, 129.7, 127.6, 124.8, 124.2, 123.0, 118.7, 84.2, 28.4.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{20}H_{16}ClN_3O_3Na$ 404.0772, found 404.0778.

***tert*-butyl (9-chloro-12-oxoindolo[2,1-*b*]quinazolin-6(12*H*)-ylidene)carbamate (1l)**



1l

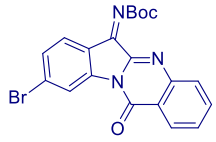
The product was purified by flash column chromatography (petroleum ether : ethyl acetate : dichloromethane = 15:1:1 as the eluent). Yellow solid; 40% yield, 0.76 g; mp 226.1–227.9 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.80 – 8.46 (m, 1H), 8.40 (d, *J* = 7.8 Hz, 1H), 8.07 – 7.68 (m, 3H), 7.67 – 7.58 (m, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 1.72 (s, 9H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 159.9, 158.3, 152.2, 146.6, 143.9, 142.0, 141.6, 135.1, 129.8, 129.7, 127.6, 127.5, 125.0, 122.8, 121.6, 118.1, 84.1, 28.4.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{20}H_{16}ClN_3O_3Na$ 404.0772, found 404.0774.

***tert*-butyl (9-bromo-12-oxoindolo[2,1-*b*]quinazolin-6(12*H*)-ylidene)carbamate (1m)**



1m

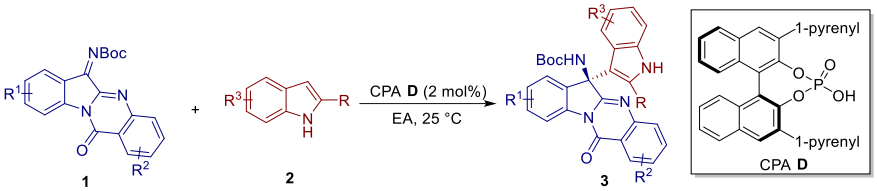
The product was purified by flash column chromatography (petroleum ether : ethyl acetate : dichloromethane = 15:1:1 as the eluent). Yellow solid; 49% yield, 1.04 g; mp 207.4–209.1 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.98 – 8.69 (m, 1H), 8.42 (d, *J* = 7.9 Hz, 1H), 8.13 – 7.71 (m, 3H), 7.67 – 7.62 (m, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 1.72 (s, 9H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 159.9, 158.2, 152.4, 146.6, 143.7, 141.8, 135.1, 130.4, 130.0, 129.8, 129.6, 127.6, 125.1, 122.8 122.0, 120.8, 84.1, 28.3.

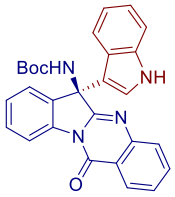
HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{20}H_{16}BrN_3O_3Na$ 448.0267, found 448.0270.

3. General procedure for the synthesis of chiral tryptanthrin derivatives 3



To a suspension of substitute ketimine **1** (0.1 mmol) and CPA **D** (0.002 mmol, 2 mol%) in ethyl acetate (1.0 ml) was added substituted indole **2** (0.1 mmol). The resulted reaction mixture was stirred at 25 ºC till reaction completion (monitored by TLC). The reaction mixture was concentrated under vacuum and the residue was purified by flash chromatography on silica gel (petroleum ether : ethylacetate = 3:1–2:1) to give the product **3**.

***tert*-butyl (*R*)-(6-(1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3aa)**



3aa

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 45.1 mg, 97% yield; mp 121.2–122.9 ºC; 98% ee; $[\alpha]_D^{20}$ = –197.46 (*c* 2.3, CH_2Cl_2).

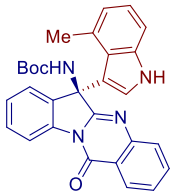
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 14.4 min (minor), 10.2 min (major).

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.19 (s, 1H), 8.64 – 8.50 (m, 1H), 8.29 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.82 (t, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.64 – 7.49 (m, 4H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.16 – 7.01 (m, 2H), 6.94 (t, *J* = 7.6 Hz, 1H), 1.05 (brs, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 160.9, 159.3, 154.2, 147.1, 138.9, 137.0, 134.9, 134.8, 129.2, 127.5, 127.1, 126.8, 126.4, 124.4, 123.8, 121.5, 120.8, 120.7, 118.9, 115.9, 112.4, 111.8, 78.9, 63.4, 27.6.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{28}H_{24}N_4O_3Na$ 487.1741, found 487.1744.

***tert*-butyl (*R*)-(6-(4-methyl-1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3ab)**



3ab

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 46.8 mg, 98% yield; mp 198.6–200.3 ºC; >99% ee; $[\alpha]_D^{20}$ = –463.0 (*c* 1.1, CH_2Cl_2).

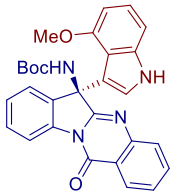
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 8.9 min (minor), 11.2 min (major).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.10 (s, 1H), 8.56 (d, *J* = 7.9 Hz, 1H), 8.25 (d, *J* = 9.0 Hz, 1H), 7.77 (t, *J* = 7.5 Hz, 1H), 7.68 – 7.46 (m, 6H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.08 – 7.03 (m, 1H), 6.96 (d, *J* = 7.2 Hz, 1H), 6.39 (s, 1H), 3.31 (s, 3H), 1.27 – 0.76 (m, 9H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 160.6, 159.4, 153.7, 146.9, 138.8, 138.5, 136.0, 134.7, 132.1, 129.4, 127.2, 127.0, 126.9, 126.2, 125.3, 124.5, 124.4, 122.4, 121.8, 120.5, 115.9, 113.5, 109.7, 78.6, 63.2, 27.8, 23.8.

HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd. for $C_{29}H_{26}N_4O_3Na$ 501.1897, found 501.1899.

***tert*-butyl (*R*)-(6-(4-methoxy-1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3ac)**



3ac

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 42.9 mg, 87% yield; mp 112.5–114.2 ºC; 72% ee; $[\alpha]_D^{20}$ = –104.1 (*c* 1.5, CH_2Cl_2).

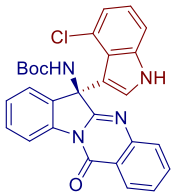
The ee was determined by HPLC (Chiralpak IC, *i*-propanol/*n*-hexane 20/80, flow rate = 0.5 mL/min, λ = 254 nm) t_R = 16.2 min (minor), 18.4 min (major).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.32 (s, 1H), 8.52 (d, *J* = 7.9 Hz, 1H), 8.37 (d, *J* = 9.2 Hz, 1H), 7.98 (s, 1H), 7.85 – 7.79 (m, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.57 (m, 1H), 7.52 – 7.33 (m, 3H), 7.28 – 7.22 (m, 1H), 6.97 (d, *J* = 6.2 Hz, 2H), 6.37 (d, *J* = 5.1 Hz, 1H), 3.53 (s, 3H), 1.08 (s, 9H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 162.0, 159.5, 154.2, 152.1, 147.2, 139.5, 138.7, 136.4, 134.5, 128.5, 127.5, 127.1, 126.4, 123.6, 123.5, 122.5, 121.4, 115.7, 114.2, 112.8, 105.4, 100.0, 79.0, 63.2, 54.8, 27.7.

HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd. for $C_{29}H_{26}N_4O_4Na$ 517.1846, found 517.1841.

***tert*-butyl (*R*)-(6-(4-chloro-1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3ad)**



3ad

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 24.4 mg, 49% yield; mp 120.5–121.5 ºC; 96% ee; $[\alpha]_D^{20}$ = –55.3.0 (*c* 0.6, CH_2Cl_2).

The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0

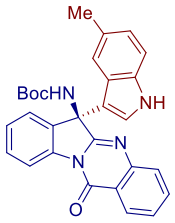
mL/min, λ = 254 nm) t_R = 13.7 min (minor), 7.1 min (major).

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.67 (s, 1H), 8.48 (d, *J* = 8.0 Hz, 1H), 8.32 (d, *J* = 7.7 Hz, 1H), 8.10 (s, 1H), 7.88 – 7.77 (m, 1H), 7.68 – 7.57 (m, 3H), 7.50 – 7.28 (m, 4H), 7.07 – 6.91 (m, 2H), 1.09 (s, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 161.2, 153.9, 147.2, 139.4, 139.2, 135.8, 134.6, 129.0, 127.5, 127.4, 127.3, 126.5, 126.4, 124.6, 124.0, 122.2, 121.8, 121.3, 121.2, 116.0, 112.1, 111.2, 78.8, 63.2, 27.8.

HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd. for $C_{28}H_{23}ClN_4O_3Na$ 521.1351, found 521.1353.

***tert*-butyl (*R*)-(6-(5-methyl-1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3ae)**



3ae

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 47.3 mg, 99% yield; mp 123.6–125.4 ºC; 97% ee; $[\alpha]_D^{20}$ = –246.5 (*c* 0.9, CH_2Cl_2).

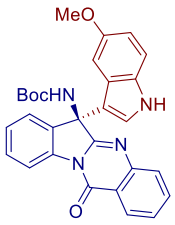
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 13.7 min (minor), 17.5 min (major).

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.06 (s, 1H), 8.56 (d, *J* = 7.9 Hz, 1H), 8.30 (d, *J* = 7.9 Hz, 2H), 7.87 – 7.78 (m, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.67 – 7.49 (m, 4H), 7.48 – 7.41 (m, 1H), 7.24 (d, *J* = 8.3 Hz, 1H), 7.02 – 6.84 (m, 2H), 2.33 (s, 3H), 1.01 (d, *J* = 102.0 Hz, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 160.9, 159.3, 154.1, 147.1, 138.9, 135.4, 135.0, 134.8, 129.1, 127.5, 127.2, 127.0, 126.7, 126.4, 124.8, 124.6, 123.8, 123.1, 120.8, 120.7, 116.0, 111.8, 111.5, 78.9, 63.4, 27.6, 21.5.

HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd. for $C_{29}H_{26}N_4O_3Na$ 501.1897, found 501.1901.

***tert*-butyl (*R*)-(6-(5-methoxy-1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3af)**



3af

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 48.9 mg, 99% yield; mp 134.9–136.5 ºC; 97% ee; $[\alpha]_D^{20}$ = –314.8 (*c* 1.0, CH_2Cl_2).

The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0

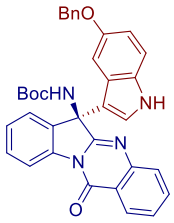
mL/min, λ = 254 nm) t_R = 6.9 min (minor), 11.4 min (major).

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.08 (s, 1H), 8.56 (d, *J* = 7.8 Hz, 1H), 8.29 (d, *J* = 7.7 Hz, 2H), 7.89 – 7.77 (m, 1H), 7.75 – 7.39 (m, 5H), 7.24 (d, *J* = 8.6 Hz, 1H), 7.04 (d, *J* = 37.0 Hz, 2H), 6.71 (d, *J* = 8.2 Hz, 1H), 3.65 (s, 3H), 1.02 (d, *J* = 105.9 Hz, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 160.9, 159.2, 152.9, 147.0, 138.9, 134.8, 132.0, 129.2, 127.4, 127.0, 126.8, 126.4, 125.2, 124.8, 123.8, 120.8, 115.9, 112.4, 111.7, 111.5, 102.7, 78.9, 63.3, 55.2, 27.6.

HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd. for $C_{29}H_{27}N_4O_4$ 495.2027, found 495.2032.

***tert*-butyl (*R*)-(6-(5-(benzyloxy)-1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3ag)**



3ag

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 55.9 mg, 98% yield; mp 110.9–112.6 ºC; 97% ee; $[\alpha]_D^{20}$ = –331.9 (*c* 1.0, CH_2Cl_2).

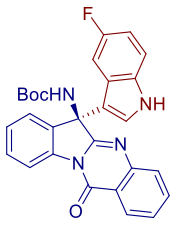
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 9.1 min (minor), 15.1 min (major).

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.08 (s, 1H), 8.55 (d, *J* = 8.3 Hz, 1H), 8.29 (d, *J* = 8.2 Hz, 2H), 7.96 – 7.50 (m, 6H), 7.50 – 7.19 (m, 7H), 7.14 – 6.72 (m, 2H), 4.95 (s, 2H), 1.00 (d, *J* = 49.1 Hz, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 160.9, 159.3, 154.2, 151.9, 147.1, 138.9, 137.5, 134.9, 132.3, 129.3, 128.4, 127.7, 127.6, 127.5, 127.1, 126.8, 126.4, 125.3, 124.8, 123.8, 120.8, 116.0, 112.5, 112.4, 111.8, 104.5, 78.9, 69.8, 63.3, 27.6.

HRMS (ESI-TOF) *m/z* [M + K]$^+$ calcd. for $C_{35}H_{30}N_4O_4K$ 609.1899, found 609.1934.

***tert*-butyl (*R*)-(6-(5-fluoro-1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3ah)**



3ah

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 47.7 mg, 99% yield; mp 137.1–139.0 ºC; 96% ee; $[\alpha]_D^{20}$ = –339.4 (*c* 1.0, CH_2Cl_2).

The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 10/90, flow rate = 1.0

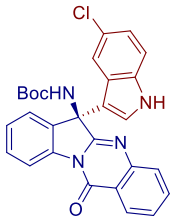
mL/min, λ = 254 nm) t_R = 21.3 min (minor), 30.2 min (major).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.29 (s, 1H), 8.73 – 8.05 (m, 3H), 7.81 (t, *J* = 7.3 Hz, 1H), 7.70 (s, 1H), 7.55 – 7.39 (m, 5H), 7.36 (dd, *J* = 8.8, 4.7 Hz, 1H), 7.03 (s, 1H), 6.95 (td, *J* = 9.1, 2.6 Hz, 1H), 1.31 – 0.63 (m, 9H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 160.7, 159.3, 156.6 (d, *J* = 232.5 Hz, 1C), 154.7, 147.0, 138.9, 134.9, 134.4, 133.8, 129.4, 127.5, 127.1, 126.9, 126.7, 126.4, 124.9 (d, *J* = 10.6 Hz, 1C), 123.9, 120.8, 116.0, 112.8 (d, *J* = 10.6 Hz, 1C), 112.5 (d, *J* = 4.5 Hz, 1C), 109.9 (d, *J* = 27.2 Hz, 1C), 106.2 (d, *J* = 27.2 Hz, 1C), 78.9, 63.2, 27.4.

HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd. for $C_{28}H_{23}FN_4O_3Na$ 505.1646, found 505.1650.

***tert*-butyl (*R*)-(6-(5-chloro-1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3ai)**



3ai

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 48.9 mg, 98% yield; mp 123.7–125.6 ºC; 98% ee; $[\alpha]_D^{20}$ = –324.7 (*c* 1.0, CH_2Cl_2).

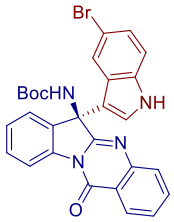
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 20/80, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 7.1 min (minor), 10.5 min (major).

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.33 (s, 1H), 8.75 – 8.10 (m, 3H), 8.09 – 7.77 (m, 2H), 7.72 – 7.53 (m, 4H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 8.6 Hz, 1H), 7.10 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.93 (s, 1H), 1.27 – 0.75 (m, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 160.6, 159.2, 154.1, 146.9, 138.8, 135.6, 134.8, 134.2, 129.4, 127.3, 127.1, 126.8, 126.4, 126.3, 125.7, 123.8, 123.4, 121.5, 120.9, 120.7, 116.0, 113.3, 112.1, 78.9, 63.1, 27.6.

HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd. for $C_{28}H_{23}ClN_4O_3Na$ 521.1351, found 521.1352.

***tert*-butyl (*R*)-(6-(5-bromo-1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3aj)**



3aj

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 53.7 mg, 99% yield; mp 141.0–142.9 ºC; 98% ee; $[\alpha]_D^{20}$ = –232.4 (*c* 0.8, CH_2Cl_2).

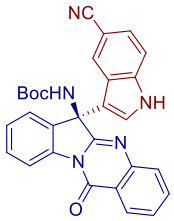
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 5.3 min (minor), 7.4 min (major).

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.35 (s, 1H), 8.53 (d, *J* = 7.4 Hz, 1H), 8.46 – 7.96 (m, 3H), 7.85 (t, *J* = 7.1 Hz, 1H), 7.66 – 7.47 (m, 5H), 7.34 – 7.26 (m, 1H), 7.20 (d, *J* = 8.7 Hz, 1H), 6.90 (s, 1H), 1.02 (d, *J* = 94.1 Hz, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 160.6, 159.2, 154.2, 146.9, 138.9, 135.8, 135.0, 134.2, 129.5, 127.3, 127.2, 126.9, 126.5, 126.4, 126.3, 124.1, 123.8, 120.8, 116.0, 113.8, 112.0, 111.5, 79.0, 63.1, 27.6.

HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd. for $C_{28}H_{23}BrN_4O_3Na$ 567.0830, found 567.0831.

***tert*-butyl (*R*)-(6-(5-cyano-1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3ak)**



3ak

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 45.5 mg, 93% yield; mp 148.9–150.7 ºC; 96% ee; $[\alpha]_D^{20}$ = –458.7 (*c* 1.0, CH_2Cl_2).

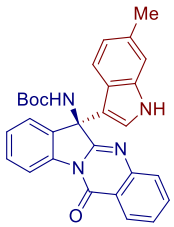
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 6.9 min (minor), 11.4 min (major).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.69 (s, 1H), 8.80 – 8.28 (m, 3H), 8.26 (d, *J* = 7.9 Hz, 1H), 7.85 (t, *J* = 7.3 Hz, 1H), 7.75 – 7.59 (m, 3H), 7.59 – 7.42 (m, 4H), 6.99 (s, 1H), 1.33 – 0.53 (m, 9H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 160.5, 159.2, 153.7, 146.9, 139.0, 138.9, 135.0, 133.9, 129.6, 127.8, 127.5, 127.4, 127.2, 127.0, 126.4, 124.6, 124.2, 123.9, 120.8, 116.1, 113.5, 113.3, 100.9, 79.1, 63.0, 27.7.

HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd. for $C_{29}H_{23}N_5O_3Na$ 512.1693, found 512.1696.

***tert*-butyl (*R*)-(6-(6-methyl-1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3al)**



3al

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 46.9 mg, 98% yield; mp 115.2–117.1 ºC; 98% ee; $[\alpha]_D^{20}$ = –208.1 (*c* 1.6, CH_2Cl_2).

The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0

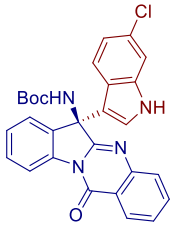
mL/min, λ = 254 nm) t_R = 25.9 min (minor), 13.1 min (major).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.18 (s, 1H), 8.58 – 8.52 (m, 1H), 8.44 – 7.72 (m, 2H), 7.71 – 7.46 (m, 5H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.16 – 7.01 (m, 2H), 6.93 (t, *J* = 7.6 Hz, 1H), 2.44 (s, 3H), 1.27 – 0.69 (m, 9H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 160.1, 159.3, 154.4, 145.1, 139.0, 137.0, 136.9, 136.0, 135.0, 129.2, 127.3, 126.7, 125.8, 124.5, 124.4, 123.8, 121.5, 120.7, 120.6, 118.9, 116.0, 112.6, 111.8, 78.9, 63.3, 27.7, 20.8.

HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd. for $C_{29}H_{26}N_4O_3Na$ 501.1897, found 501.1898.

***tert*-butyl (*R*)-(6-(6-chloro-1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3am)**



3am

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 48.4 mg, 97% yield; mp 131.9–133.0 ºC; 98% ee; $[\alpha]_D^{20}$ = –248.2 (*c* 1.5, CH_2Cl_2).

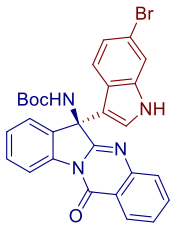
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 14.3 min (minor), 10.0 min (major).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.27 (d, *J* = 2.8 Hz, 1H), 8.74 – 8.06 (m, 3H), 7.82 (t, *J* = 7.6 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.63 – 7.51 (m, 3H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.40 (d, *J* = 1.9 Hz, 1H), 7.05 (d, *J* = 8.3 Hz, 1H), 6.98 (s, 1H), 1.43 – 0.50 (m, 9H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 160.6, 159.2, 154.3, 147.0, 138.9, 137.5, 134.8, 134.4, 129.4, 127.5, 127.1, 126.8, 126.4, 125.7, 123.8, 123.4, 122.9, 122.8, 120.8, 119.2, 116.0, 112.8, 111.3, 78.9, 63.1, 27.6.

HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd. for $C_{28}H_{23}ClN_4O_3Na$ 521.1351, found 521.1388.

***tert*-butyl (*R*)-(6-(6-bromo-1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3an)**



3an

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 37.5 mg, 69% yield; mp 145.2–146.1 ºC; 97% ee; $[\alpha]_D^{20}$ = –195.3 (*c* 1.1, CH_2Cl_2).

The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0

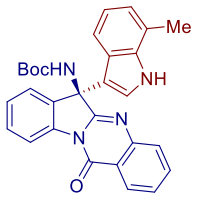
mL/min, λ = 254 nm) t_R = 14.6 min (minor), 10.2 min (major).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.27 (s, 1H), 8.78 – 8.06 (m, 3H), 8.02 – 7.65 (m, 3H), 7.64 – 7.51 (m, 4H), 7.46 (s, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 6.96 (s, 1H), 1.29 – 0.66 (m, 9H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 160.6, 159.2, 153.7, 147.0, 138.9, 138.0, 134.8, 134.4, 129.4, 127.5, 127.1, 126.8, 126.4, 125.6, 123.8, 123.7, 123.2, 121.8, 120.8, 116.0, 114.4, 114.3, 112.8, 78.9, 63.2, 27.6.

HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd. for $C_{28}H_{24}BrN_4O_3$ 543.1026, found 543.1029.

***tert*-butyl (*R*)-(6-(7-methyl-1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3ao)**



3ao

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 47.3 mg, 99% yield; mp 155.7–157.4 ºC; >99% ee; $[\alpha]_D^{20}$ = –176.9 (*c* 1.3, CH_2Cl_2).

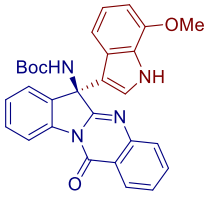
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 20/80, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 29.9 min (minor), 11.7 min (major).

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.19 (s, 1H), 8.55 (d, *J* = 7.8 Hz, 1H), 8.29 (d, *J* = 7.7 Hz, 2H), 7.84 – 7.76 (m, 1H), 7.69 – 7.52 (m, 4H), 7.48 – 7.36 (m, 1H), 7.20 (s, 2H), 6.90 – 6.74 (m, 2H), 2.38 (s, 3H), 1.24 – 0.67 (m, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 161.0, 159.4, 154.3, 147.1, 139.0, 136.4, 135.0, 134.9, 129.3, 127.5, 127.2, 126.9, 126.4, 124.1, 123.9, 121.9, 121.0, 120.8, 119.2, 117.9, 116.0, 112.8, 79.0, 63.4, 27.7, 16.7.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{29}H_{26}N_4O_3Na$ 501.1897, found 501.1902.

***tert*-butyl (*R*)-(6-(7-methoxy-1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3ap)**



3ap

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 48.4 mg, 98% yield; mp 205.6–207.2 ºC; 98% ee; $[\alpha]_D^{20}$ = –160.6 (*c* 1.6, CH_2Cl_2).

The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 34.6 min (minor), 16.2 min (major).

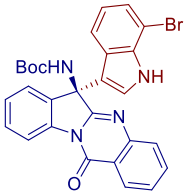
^{1}H NMR (300 MHz, DMSO-d_6) δ 11.32 (s, 1H), 8.54 (d, *J* = 7.1 Hz, 1H), 8.29 (d, *J* = 7.1 Hz, 2H), 7.95 – 7.76 (m, 1H), 7.68 (d, *J* = 6.0 Hz, 1H), 7.63 – 7.48 (m, 3H), 7.48 – 7.33 (m, 1H), 7.06 (brs,

2H), 6.83 (t, *J* = 6.7 Hz, 1H), 6.60 (d, *J* = 6.2 Hz, 1H), 3.84 (s, 3H), 1.12 (brs, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 161.0, 159.3, 154.2, 147.1, 146.3, 138.9, 135.0, 134.9, 129.3, 127.5, 127.2, 126.8, 126.4, 125.9, 123.9, 123.8, 120.8, 119.6, 116.0, 113.2, 113.0, 102.0, 79.0, 63.3, 55.2, 27.6.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{29}H_{26}N_4O_4Na$ 517.1846, found 517.1877.

***tert*-butyl (*R*)-(6-(7-bromo-1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3aq)**



3aq

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 44.5 mg, 82% yield; mp 195.6–197.4 ºC; 99% ee; $[\alpha]_D^{20}$ = –107.5 (*c* 1.6, CH_2Cl_2).

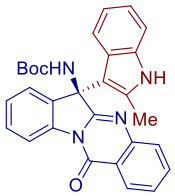
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 20/80, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 30.1 min (minor), 15.1 min (major).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.41 (s, 1H), 8.82 – 7.97 (m, 3H), 7.96 – 7.79 (m, 1H), 7.79 – 7.35 (m, 6H), 7.30 (d, *J* = 6.9 Hz, 1H), 7.05 (s, 1H), 6.93 (s, 1H), 1.54 – 0.40 (m, 9H).k

^{13}C NMR (151 MHz, DMSO-d_6) δ 160.9, 159.5, 154.9, 147.3, 139.2, 135.5, 135.2, 134.6, 129.8, 127.8, 127.5, 127.2, 126.7, 126.6, 125.9, 124.5, 124.1, 121.1, 120.7, 116.3, 114.2, 104.7, 79.3, 63.5, 27.8.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{28}H_{23}BrN_4O_3Na$ 565.0846, found 565.0848.

***tert*-butyl (*R*)-(6-(2-methyl-1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3ar)**



3ar

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 46.4 mg, 97% yield; mp 130.9–132.6 ºC; 93% ee; $[\alpha]_D^{20}$ = –41.6 (*c* 1.4, CH_2Cl_2).

The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 20.3 min (minor), 5.4 min (major).

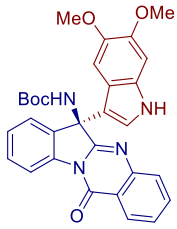
^{1}H NMR (300 MHz, DMSO-d_6) δ 11.17 (s, 1H), 8.57 (d, *J* = 7.9 Hz, 1H), 8.28 (d, *J* = 8.7 Hz, 2H), 7.79 (t, *J* = 7.0 Hz, 1H), 7.73 – 7.57 (m, 3H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 2.37 (s, 3H), 1.36 – 0.61 (m, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 161.4, 159.2, 154.3, 147.2, 139.1, 135.2, 134.8, 134.7, 129.3,

127.5, 127.0, 126.7, 126.3, 126.1, 124.4, 120.8, 120.2, 119.4, 118.6, 116.0, 110.6, 106.8, 78.8, 63.8, 27.6, 13.9.

HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd. for $C_{29}H_{27}N_4O_3$ 479.2078, found 479.2083.

***tert*-butyl (*R*)-(6-(5,6-dimethoxy-1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3as)**



3as

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 39.3 mg, 75% yield; mp 119.8–121.7 ºC; 96% ee; $[\alpha]_D^{20}$ = –242.3 (*c* 1.4, CH_2Cl_2).

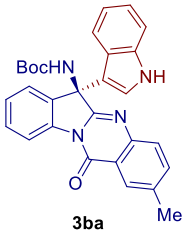
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 9.7 min (minor), 16.0 min (major).

^{1}H NMR (300 MHz, DMSO-d_6) δ 10.88 (s, 1H), 8.54 (d, *J* = 8.0 Hz, 1H), 8.47 – 7.93 (m, 2H), 7.84 (t, *J* = 7.6 Hz, 1H), 7.69 (s, 1H), 7.57 (d, *J* = 7.6 Hz, 3H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.32 – 6.68 (m, 3H), 3.70 (s, 3H), 3.65 (s, 3H), 1.36 – 0.61 (m, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 160.9, 159.3, 154.2, 147.0, 146.7, 144.0, 138.9, 134.9, 131.5, 129.2, 127.5, 127.1, 126.8, 126.4, 123.8, 122.9, 120.7, 117.4, 115.9, 111.8, 103.5, 95.2, 78.9, 63.4, 55.8, 55.7, 27.6.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{30}H_{28}N_4O_5Na$ 547.1952, found 547.1951.

***tert*-butyl (*R*)-(6-(1*H*-indol-3-yl)-2-methyl-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3ba)**



3ba

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 47.3 mg, 99% yield; mp 132.8–134.1 ºC; 98% ee; $[\alpha]_D^{20}$ = –200.1(*c* 2.1, CH_2Cl_2).

The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 15/85, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 39.8 min (minor), 30.1 min (major).

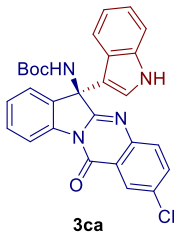
^{1}H NMR (600 MHz, DMSO-d_6) δ 11.18 (s, 1H), 8.54 (d, *J* = 7.8 Hz, 1H), 8.07 (s, 2H), 7.87 – 7.36 (m, 6H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.11 (s, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 2.44 (s, 3H), 1.40 – 0.55 (m, 9H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 160.1, 159.3, 154.4, 145.1, 139.0, 137.0, 136.8, 136.0, 135.0, 129.2, 127.3, 126.7, 125.8, 124.5, 124.4, 123.8, 121.5, 120.7, 120.6, 118.9, 116.0, 112.5, 111.8,

78.9, 63.2, 27.6, 20.8.

HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd. for $C_{29}H_{27}N_4O_3$ 479.2078, found 479.2086.

***tert*-butyl (*R*)-(2-chloro-6-(1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3ca)**



3ca

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 32.4 mg, 65% yield; mp 130.4–132.2 ºC; 99% ee; $[\alpha]_D^{20}$ = –216.4 (*c* 1.0, CH_2Cl_2).

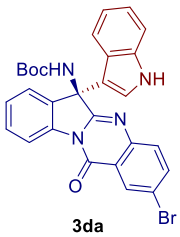
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 15/85, flow rate = 0.8 mL/min, λ = 254 nm) t_R = 30.0 min (minor), 20.4 min (major).

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.19 (d, *J* = 2.8 Hz, 1H), 8.74 – 7.91 (m, 3H), 7.83 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.77 – 7.49 (m, 4H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.06 (t, *J* = 7.2 Hz, 2H), 6.95 (t, *J* = 7.6 Hz, 1H), 1.25 – 0.74 (m, 9H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 161.4, 158.2, 154.0, 145.8, 138.6, 137.0, 134.9, 131.4, 129.7, 129.4, 127.1, 125.4, 124.6, 124.5, 123.9, 122.1, 121.5, 120.9, 119.0, 116.0, 112.0, 111.8, 79.0, 63.4, 27.6.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{28}H_{23}ClN_4O_3Na$ 521.1351, found 521.1358.

***tert*-butyl (*R*)-(2-bromo-6-(1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3da)**



3da

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 53.7 mg, 99% yield; mp 142.4–143.9 ºC; 99% ee; $[\alpha]_D^{20}$ = –214.8 (*c* 2.0, CH_2Cl_2).

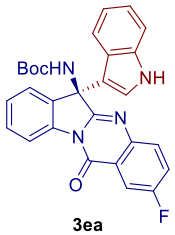
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 15/85, flow rate = 0.8 mL/min, λ = 254 nm) t_R = 30.6 min (minor), 21.3 min (major).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.19 (s, 1H), 8.52 (d, *J* = 8.0 Hz, 2H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.88 (s, 1H), 7.81 – 7.49 (m, 4H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.17 – 7.01 (m, 2H), 6.98 (t, *J* = 7.7 Hz, 1H), 1.38 – 0.57 (m, 9H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 162.4, 158.8, 154.1, 148.2, 138.7, 137.0, 134.8, 130.1, 129.7, 129.3, 128.4, 128.3, 127.0, 124.7, 124.5, 123.8, 121.5, 121.0, 119.9, 119.0, 116.0, 112.0, 111.8, 79.0, 63.5, 27.6.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{28}H_{23}BrN_4O_3Na$ 565.0846, found 565.0849.

***tert*-butyl (*R*)-(2-fluoro-6-(1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3ea)**



3ea

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 47.6 mg, 99% yield; mp 121.9–123.1 ºC; 98% ee; $[\alpha]_D^{20}$ = –220.0 (*c* 1.9, CH_2Cl_2).

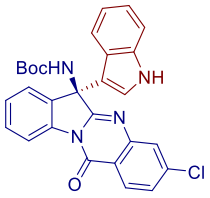
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 9.7 min (minor), 16.0 min (major).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.18 (s, 1H), 8.53 (d, *J* = 7.9 Hz, 1H), 8.50 – 8.00 (m, 1H), 7.97 (dd, *J* = 8.5, 3.0 Hz, 1H), 7.88 – 7.73 (m, 1H), 7.72 – 7.68 (m, 1H), 7.68 – 7.37 (m, 4H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.18 – 7.01 (m, 2H), 6.95 (t, *J* = 7.7 Hz, 1H), 1.41 – 0.53 (m, 9H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 160.5, 160.3 (d, *J* = 246.1 Hz, 1C), 158.5, 154.2, 143.9, 138.6, 137.0, 134.9, 130.2 (d, *J* = 7.6 Hz, 1C), 129.3, 127.0, 124.5, 124.4, 123.9, 123.2 (d, *J* = 22.6 Hz, 1C), 122.1 (d, *J* = 7.6 Hz, 1C), 121.5, 120.8, 119.0, 116.0, 112.2, 111.8, 111.2 (d, *J* = 24.2 Hz, 1C), 78.9, 63.3, 27.7.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{28}H_{23}FN_4O_3$ 505.1646, found 505.1654.

***tert*-butyl (*R*)-(3-chloro-6-(1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3fa)**



3fa

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 46.9 mg, 94% yield; mp 129.4–131.6 ºC; 89% ee; $[\alpha]_D^{20}$ = –202.28 (*c* 1.8, CH_2Cl_2).

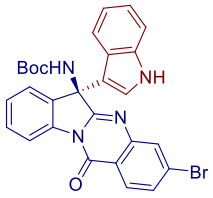
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 15.9 min (minor), 7.4 min (major).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.20 (s, 1H), 8.52 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 8.5 Hz, 2H), 7.98 – 7.39 (m, 6H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.21 – 7.01 (m, 2H), 6.98 (d, *J* = 7.8 Hz, 1H), 1.30 – 0.69 (m, 9H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 162.4, 158.6, 154.3, 148.2, 139.4, 138.7, 137.0, 134.7, 129.3, 128.4, 127.3, 127.0, 126.6, 124.7, 124.5, 123.8, 121.5, 121.0, 119.6, 119.0, 116.0, 112.0, 111.8, 79.0, 63.5, 27.7.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{28}H_{23}ClN_4O_3Na$ 521.1351, found 521.1354.

***tert*-butyl (*R*)-(3-bromo-6-(1H-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-b]quinazolin-6-yl)carbamate (3ga)**



3ga

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 53.8 mg, 99% yield; mp 142.2–143.9 ºC; 93% ee; $[\alpha]_D^{20}$ = –148.8 (*c* 0.3, CH_2Cl_2).

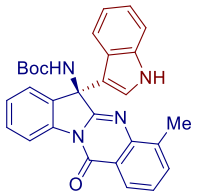
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 14.9 min (minor), 7.3 min (major).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.19 (s, 1H), 8.52 (d, *J* = 8.0 Hz, 1H), 8.33 (d, *J* = 2.4 Hz, 2H), 7.87 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.82 – 7.48 (m, 4H), 7.47 – 7.37 (m, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.17 – 7.00 (m, 2H), 6.97 (t, *J* = 7.7 Hz, 1H), 1.30 – 0.59 (m, 9H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 161.5, 158.1, 153.6, 146.1, 138.6, 137.6, 137.0, 134.8, 129.8, 129.4, 128.4, 127.1, 124.6, 124.5, 123.9, 122.4, 121.6, 120.9, 119.6, 119.0, 116.1, 112.0, 111.8, 79.0, 63.5, 27.6.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{28}H_{23}BrN_4O_3Na$ 565.0846, found 565.0852.

***tert*-butyl (*R*)-(6-(1*H*-indol-3-yl)-4-methyl-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3ha)**



3ha

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 45.3 mg, 95% yield; mp 143.7–145.3 ºC; 82% ee; $[\alpha]_D^{20}$ = –21.1 (*c* 0.1, CH_2Cl_2).

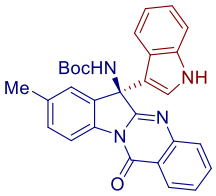
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 5.2 min (minor), 8.9 min (major).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.11 (s, 1H), 8.53 (d, *J* = 8.0 Hz, 1H), 8.51 – 8.25 (m, 1H), 8.25 – 8.09 (m, 1H), 8.09 – 8.04 (m, 1H), 7.77 – 7.55 (m, 3H), 7.50 (s, 1H), 7.42 – 7.27 (m, 2H), 7.19 – 7.02 (m, 2H), 6.74 – 6.63 (m, 1H), 2.55 (s, 3H), 1.30 – 0.62 (m, 9H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 159.6, 154.6, 145.7, 138.9, 137.2, 135.3, 135.1, 129.3, 126.7, 126.4, 124.7, 124.5, 124.0, 123.9, 122.6, 121.7, 120.6, 118.5, 116.0, 112.4, 111.8, 78.7, 63.2, 28.0, 17.2.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{29}H_{26}N_4O_3Na$ 501.1897, found 501.1904.

***tert*-butyl (*R*)-(6-(1*H*-indol-3-yl)-8-methyl-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3ia)**



3ia

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 46.2 mg, 97% yield; mp 128.2–129.5 ºC; 84% ee; $[\alpha]_D^{20}$ = –142.4 (*c* 1.8, CH_2Cl_2).

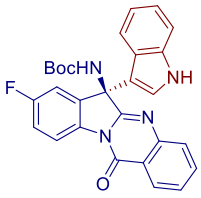
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 8.4 min (minor), 10.2 min (major).

^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ 11.18 (s, 1H), 8.41 (d, *J* = 7.9 Hz, 1H), 8.27 (d, *J* = 8.0 Hz, 2H), 7.80 (t, *J* = 7.4 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.44 (m, 2H), 7.37 (d, *J* = 8.5 Hz, 3H), 7.15 (s, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 2.38 (s, 3H), 1.03 (s, 9H).

^{13}C NMR (75 MHz, DMSO-*d*$_6$) δ 161.0, 159.0, 154.1, 147.0, 136.9, 136.6, 136.2, 134.9, 134.6, 129.5, 127.4, 126.9, 126.2, 124.4, 124.0, 121.4, 120.8, 120.5, 118.8, 115.7, 112.4, 111.8, 78.8, 63.3, 27.6, 21.0.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{29}H_{26}N_4O_3Na$ 501.1987, found 501.1900.

***tert*-butyl (*R*)-(8-fluoro-6-(1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3ja)**



3ja

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 45.4 mg, 94% yield; mp 130.1–132.3 ºC; 98% ee; $[\alpha]_D^{20}$ = –170.8 (*c* 1.8, CH_2Cl_2).

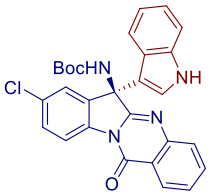
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 10.0 min (minor), 19.1 min (major).

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 11.24 (s, 1H), 8.61 – 8.53 (m, 1H), 8.29 (d, *J* = 7.9 Hz, 2H), 7.82 (t, *J* = 7.8 Hz, 1H), 7.77 – 7.49 (m, 3H), 7.49 – 7.29 (m, 3H), 7.17 (s, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 6.97 (t, *J* = 7.7 Hz, 1H), 1.34 – 0.67 (m, 9H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 160.8, 160.6 (d, *J* = 267.7 Hz, 1C), 159.1, 154.5, 147.0, 137.5, 137.0, 135.1, 134.9, 127.5, 127.2, 126.4, 124.6, 124.3, 121.6, 120.7, 120.6, 119.1, 117.6 (d, *J* = 8.1 Hz, 1C), 115.9 (d, *J* = 23.2 Hz, 1C), 111.9, 111.7, 111.2 (d, *J* = 25.2 Hz, 1C), 79.2, 63.3, 27.7.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{28}H_{23}FN_4O_3Na$ 505.1646, found 505.1653.

***tert*-butyl (*R*)-(8-chloro-6-(1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3ka)**



3ka

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 48.7 mg, 98% yield; mp 111.8–112.6 ºC; 99% ee; $[\alpha]_D^{20}$ = –184.4 (*c* 2.1, CH_2Cl_2).

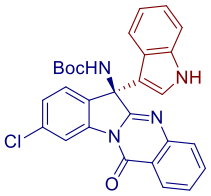
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 11.5 min (minor), 8.8 min (major).

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.25 (s, 1H), 8.54 (d, *J* = 8.5 Hz, 1H), 8.29 (d, *J* = 7.9 Hz, 2H), 7.82 (t, *J* = 7.6 Hz, 1H), 7.76 – 7.45 (m, 5H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.18 (s, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 1.10 (brs, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 160.3, 159.1, 154.2, 147.0, 137.6, 137.2, 137.0, 134.9, 130.8, 129.2, 127.5, 127.2, 126.4, 124.5, 124.3, 123.6, 121.6, 120.6, 120.5, 119.0, 117.5, 111.9, 111.7, 79.2, 63.2, 27.6.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{28}H_{23}ClN_4O_3Na$ 521.1351, found 521.1349.

***tert*-butyl (*R*)-(9-chloro-6-(1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3la)**



3la

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 49.6 mg, 99% yield; mp 139.4–142.1 ºC; 95% ee; $[\alpha]_D^{20}$ = –200.0 (*c* 2.0, CH_2Cl_2).

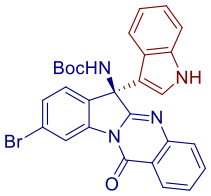
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 10.3 min (minor), 11.5 min (major).

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.22 (s, 1H), 8.55 (s, 1H), 8.52 – 7.95 (m, 2H), 7.95 – 7.63 (m, 3H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.54 (q, *J* = 8.6, 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.03 (m, 2H), 6.99 (t, *J* = 7.6 Hz, 1H), 1.41 – 0.66 (m, 9H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 160.5, 159.3, 154.5, 146.9, 139.7, 137.0, 135.1, 133.8, 133.1, 127.6, 127.3, 126.8, 126.5, 125.3, 124.6, 124.4, 121.6, 120.9, 120.6, 119.0, 115.8, 111.9, 111.8, 79.1, 63.1, 27.7.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{28}H_{23}ClN_4O_3Na$ 521.1351, found 521.1356.

***tert*-butyl (*R*)-(9-bromo-6-(1*H*-indol-3-yl)-12-oxo-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (3ma)**



3ma

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 53.8 mg, 99% yield; mp 135.3–137.8 ºC; 92% ee; $[\alpha]_D^{20}$ = –160.8 (*c* 2.3, CH_2Cl_2).

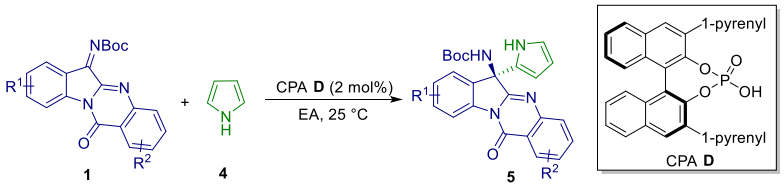
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 20/80, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 10.5 min (minor), 12.6 min (major).

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.22 (s, 1H), 8.70 (s, 1H), 8.48 (brs, 1H), 8.26 (d, *J* = 7.9 Hz, 1H), 7.82 (t, *J* = 7.8 Hz, 1H), 7.79 – 7.58 (m, 3H), 7.54 (t, *J* = 7.3 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.20 – 7.03 (m, 2H), 6.99 (t, *J* = 7.6 Hz, 1H), 1.38 – 0.64 (m, 9H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 160.4, 159.3, 153.9, 147.0, 139.9, 137.0, 135.1, 134.3, 129.6, 127.6, 127.3, 126.5, 125.6, 124.6, 124.4, 121.6, 121.4, 120.9, 120.6, 119.0, 118.6, 111.9, 111.7, 79.1, 63.2, 27.7.

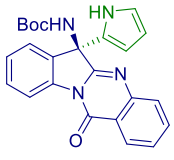
HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{28}H_{23}BrN_4O_3Na$ 565.0846, found 565.0851.

4. General procedure for the synthesis of chiral tryptanthrin derivatives 5



To a suspension of substitute ketimine **1** (0.1 mmol) and CPA **D** (0.002 mmol, 2 mol%) in ethyl acetate (1.0 ml) was added pyrrole **4** (0.1 mmol). The resulted reaction mixture was stirred at 25 ºC till reaction completion (monitored by TLC). The reaction mixture was concentrated under vacuum and the residue was purified by flash chromatography on silica gel (petroleum ether /ethylacetate = 3:1–2:1) to give the product **5**.

***tert*-butyl (*S*)-(12-oxo-6-(1*H*-pyrrol-2-yl)-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (5a)**



5a

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 40.6 mg, 98% yield; mp 104.6–106.5 ºC; 92% ee; $[\alpha]_D^{20}$ = –50.5 (*c* 1.2, CH_2Cl_2).

The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 20/80, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 26.1 min (minor), 11.2 min (major).

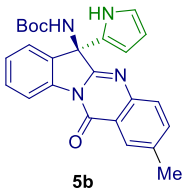
^{1}H NMR (600 MHz, DMSO-d_6) δ 11.04 (s, 1H), 8.46 (d, *J* = 8.0 Hz, 1H), 8.30 (dd, *J* = 8.0, 1.5 Hz,

2H), 7.88 (t, *J* = 7.4 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 6.75 (td, *J* = 2.8, 1.6 Hz, 1H), 5.86 (q, *J* = 2.7 Hz, 1H), 5.71 (s, 1H), 1.45 – 0.43 (m, 9H).

^{13}C NMR (151 MHz, DMSO-*d*$_6$) δ 160.0, 159.2, 154.1, 147.0, 138.6, 134.8, 134.0, 129.2, 127.4, 127.2, 126.8, 126.7, 126.4, 123.8, 121.0, 120.3, 116.0, 107.6, 106.9, 78.9, 62.6, 27.6.

HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd. for $C_{24}H_{22}N_4O_3Na$ 437.1584, found 437.1587.

***tert*-butyl (*S*)-(2-methyl-12-oxo-6-(1*H*-pyrrol-2-yl)-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (5b)**



5b

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 30.3 mg, 71% yield; mp 96.5–98.3 ºC; 90% ee; $[\alpha]_D^{20}$ = –82.0 (*c* 0.3, CH_2Cl_2).

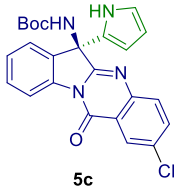
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 14.2 min (minor), 8.9 min (major).

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 11.02 (s, 1H), 8.45 (d, *J* = 8.0 Hz, 1H), 8.10 (s, 2H), 7.88 – 7.57 (m, 3H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 6.74 (q, *J* = 2.3 Hz, 1H), 5.85 (q, *J* = 2.8 Hz, 1H), 5.69 (s, 1H), 2.49 (s, 3H), 1.32 – 0.57 (m, 9H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 159.2, 159.1, 153.7, 145.0, 138.6, 137.0, 136.0, 134.1, 129.1, 127.2, 126.9, 126.5, 125.8, 123.7, 120.8, 120.2, 115.9, 107.5, 106.8, 78.8, 62.4, 27.6, 20.8.

HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd. for $C_{25}H_{24}N_4O_3Na$ 451.1741, found 451.1745.

***tert*-butyl (*S*)-(2-chloro-12-oxo-6-(1*H*-pyrrol-2-yl)-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (5c)**



5c

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 44.5 mg, 99% yield; mp 93.5–95.0 ºC; 96% ee; $[\alpha]_D^{20}$ = –69.3 (*c* 1.4, CH_2Cl_2).

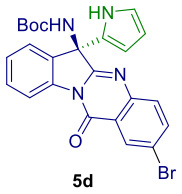
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 20.8 min (minor), 7.5 min (major).

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 11.04 (s, 1H), 8.76 – 7.96 (m, 3H), 7.89 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.65 (d, *J* = 7.3 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 6.75 (td, *J* = 2.7, 1.6 Hz, 1H), 5.86 (dt, *J* = 3.5, 2.5 Hz, 1H), 5.73 (s, 1H), 1.23 – 0.63 (m, 9H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 160.6, 158.1, 153.5, 145.8, 138.3, 134.9, 134.2, 131.6, 129.5, 129.2, 127.0, 126.5, 125.4, 123.8, 122.4, 120.3, 116.0, 107.7, 107.0, 79.0, 62.6, 27.6.

HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd. for $C_{24}H_{21}ClN_4O_3Na$ 471.1194, found 471.1200.

***tert*-butyl (*S*)-(2-bromo-12-oxo-6-(1*H*-pyrrol-2-yl)-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (5d)**



5d

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 47.8 mg, 97% yield; mp 113.8–115.7 ºC; 96% ee; $[\alpha]_D^{20}$ = –48.2 (*c* 1.7, CH_2Cl_2).

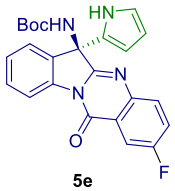
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 17.1 min (minor), 7.1 min (major).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.04 (s, 1H), 8.74 – 7.83 (m, 4H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.3 Hz, 1H), 6.75 (td, *J* = 2.7, 1.5 Hz, 1H), 5.86 (q, *J* = 2.6 Hz, 1H), 5.74 (d, *J* = 5.9 Hz, 1H), 1.37 – 0.54 (m, 9H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 160.7, 158.0, 154.0, 146.0, 138.3, 137.6, 134.2, 129.7, 129.2, 128.5, 127.0, 126.4, 123.8, 122.7, 120.3, 119.8, 116.0, 107.8, 107.0, 79.0, 62.7, 27.6.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{24}H_{21}BrN_4O_3Na$ 517.0672, found 517.0679.

***tert*-butyl (*S*)-(2-fluoro-12-oxo-6-(1*H*-pyrrol-2-yl)-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (5e)**



5e

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 42.7 mg, 99% yield; mp 86.5–88.1 ºC; 93% ee; $[\alpha]_D^{20}$ = –95.2 (*c* 0.4, CH_2Cl_2).

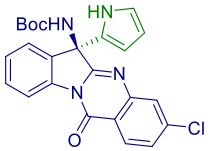
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 21.1 min (minor), 5.9 min (major).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.04 (s, 1H), 8.45 (d, *J* = 8.0 Hz, 1H), 7.98 (dd, *J* = 8.5, 3.0 Hz, 2H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.75 (t, *J* = 7.1 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 6.75 (td, *J* = 2.8, 1.6 Hz, 1H), 5.86 (q, *J* = 2.7 Hz, 1H), 5.74 (s, 1H), 1.34 – 0.41 (m, 9H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 160.4 (d, *J* = 246.1 Hz, 1C), 159.6, 158.4, 154.2, 143.8, 138.4, 134.2, 130.1 (d, *J* = 9.1 Hz, 1C), 129.2, 126.9, 126.7, 123.8, 123.1 (d, *J* = 24.2 Hz, 1C), 122.4 (d, *J* = 9.1 Hz, 1C), 120.3, 116.0, 111.3 (d, *J* = 24.2 Hz, 1C), 107.7, 106.9, 79.0, 62.6, 27.6.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{24}H_{21}FN_4O_3Na$ 455.1490, found 455.1498.

***tert*-butyl (*S*)-(3-chloro-12-oxo-6-(1*H*-pyrrol-2-yl)-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (5f)**



5f

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 44.5 mg, 99% yield; mp 103.9–104.9 ºC; 91% ee; $[\alpha]_D^{20}$ = –8.6 (*c* 1.7, CH_2Cl_2).

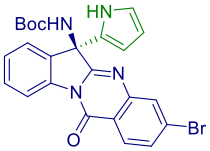
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 10.2 min (minor), 6.6 min (major).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.00 (s, 1H), 8.71 – 7.92 (m, 3H), 7.82 (s, 1H), 7.64 (dd, *J* = 15.3, 8.7 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 6.83 – 6.67 (m, 1H), 5.94 – 5.84 (m, 1H), 5.76 (s, 1H), 1.28 – 0.50 (m, 9H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 161.6, 158.6, 154.3, 148.1, 139.4, 138.4, 134.0, 129.2, 128.4, 127.5, 126.9, 126.5, 126.3, 123.8, 120.3, 119.9, 116.0, 107.8, 107.0, 79.0, 62.7, 27.7.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{24}H_{21}ClN_4O_3Na$ 471.1194, found 471.1201.

***tert*-butyl (*S*)-(3-bromo-12-oxo-6-(1*H*-pyrrol-2-yl)-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (5g)**



5g

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 48.7 mg, 99% yield; mp 96.3–98.1 ºC; 92% ee; $[\alpha]_D^{20}$ = +3.6 (*c* 0.3, CH_2Cl_2).

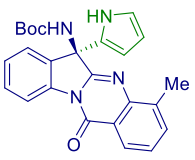
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 9.6 min (minor), 6.7 min (major).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.00 (s, 1H), 8.30 (dd, *J* = 151.5, 8.3 Hz, 3H), 7.96 (s, 1H), 7.69 (dd, *J* = 34.0, 8.1 Hz, 2H), 7.47 (dt, *J* = 56.4, 7.6 Hz, 2H), 6.75 (s, 1H), 5.97 – 5.80 (m, 1H), 5.74 (d, *J* = 12.2 Hz, 1H), 1.56 – 0.43 (m, 9H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 161.5, 158.7, 154.0, 148.1, 138.4, 134.0, 130.3, 129.6, 129.2, 128.4, 126.9, 126.3, 123.8, 120.4, 120.2, 116.0, 107.9, 107.0, 79.1, 62.7, 27.7.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{24}H_{21}BrN_4O_3Na$ 517.0672, found 517.0676.

***tert*-butyl (*S*)-(4-methyl-12-oxo-6-(1*H*-pyrrol-2-yl)-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (5h)**



5h

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–

2:1 as the eluent).

White solid; 42.3 mg, 99% yield; mp 75.6–77.5 ºC; 98% ee; $[\alpha]_D^{20}$ = –27.4 (*c* 1.6, CH_2Cl_2).

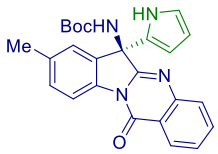
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 6.0 min (minor), 10.2 min (major).

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.98 (s, 1H), 8.62 – 7.98 (m, 3H), 7.72 (dt, *J* = 7.7, 2.3 Hz, 2H), 7.63 – 7.28 (m, 3H), 6.77 (q, *J* = 2.4 Hz, 1H), 5.86 (q, *J* = 2.7 Hz, 1H), 5.69 (d, *J* = 3.6 Hz, 1H), 2.61 (s, 3H), 1.35 – 0.57 (m, 9H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 159.4, 158.8, 153.9, 145.5, 138.5, 135.6, 135.2, 134.2, 129.0, 126.8, 126.6, 126.5, 124.0, 123.8, 121.0, 120.3, 115.9, 107.6, 106.8, 78.8, 62.5, 27.6, 17.3.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{25}H_{24}N_4O_3Na$ 451.1741, found 451.1744.

***tert*-butyl (*S*)-(8-methyl-12-oxo-6-(1*H*-pyrrol-2-yl)-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (5i)**



5i

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 41.0 mg, 96% yield; mp 105.8–107.1 ºC; 80% ee; $[\alpha]_D^{20}$ = –44.6 (*c* 1.0, CH_2Cl_2).

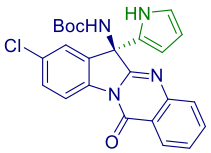
The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 14.2 min (minor), 6.7 min (major).

^{1}H NMR (300 MHz, DMSO-d_6) δ 10.99 (s, 1H), 8.47 – 8.03 (m, 3H), 7.86 (t, *J* = 7.4 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.45 (s, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 6.74 (q, *J* = 2.3 Hz, 1H), 5.86 (q, *J* = 2.8 Hz, 1H), 5.75 (s, 1H), 2.39 (s, 3H), 1.03 (brs, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 160.1, 158.9, 153.8, 147.0, 136.4, 136.0, 134.6, 134.1, 129.4, 127.2, 127.0, 126.8, 126.3, 124.1, 121.0, 120.1, 115.6, 107.6, 106.9, 78.9, 62.5, 27.5, 20.9.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{25}H_{24}N_4O_3Na$ 451.1741, found 451.1743.

***tert*-butyl (*S*)-(8-chloro-12-oxo-6-(1*H*-pyrrol-2-yl)-6,12-dihydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (5j)**



5j

The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 3:1–2:1 as the eluent).

White solid; 44.0 mg, 98% yield; mp 141.5–142.8 ºC; 92% ee; $[\alpha]_D^{20}$ = –56.7 (*c* 1.2, CH_2Cl_2).

The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 13.9 min (minor), 6.7 min (major).

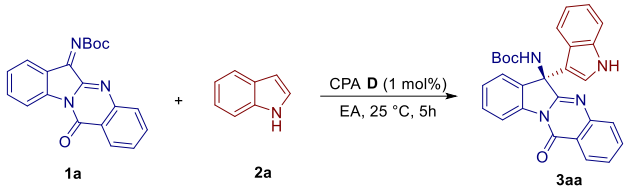
^{1}H NMR (300 MHz, DMSO-d_6) δ 11.12 (s, 1H), 8.60 – 8.05 (m, 3H), 7.89 (t, *J* = 7.5 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 2.2 Hz, 1H), 7.67 – 7.53 (m, 2H), 6.77 (q, *J* = 2.4 Hz, 1H), 5.88 (q,

J = 2.8 Hz, 1H), 5.78 (s, 1H), 1.11 (brs, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 159.6, 159.1, 154.2, 146.9, 137.2, 136.6, 135.0, 130.8, 129.1, 127.5, 127.4, 126.5, 126.2, 123.7, 120.9, 120.4, 117.5, 107.6, 107.1, 79.2, 62.5, 27.6.

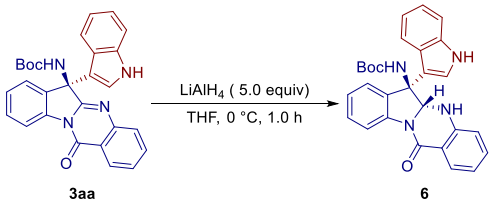
HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{24}H_{21}ClN_4O_3Na$ 471.1194, found 471.1193.

5. Gram-scale experiment



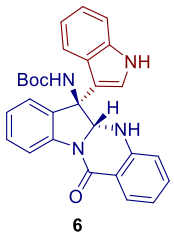
In a 50 mL dry round bottom flask equipped with a magnetic stirring bar, the ketimine **1a** (2.5 mmol, 1.0 equiv) were added to a solution of indoles **2** (3.0 mmol, 1.2 equiv) and CPA **D** (1 mol %) in ethyl acetate (25 mL) at 25 °C. And then, the mixture was stirred at the same temperature for 5 h. After completion of the reaction (monitored by TLC), the ethyl acetate was removed under vacuum and the residues were isolated by flash chromatography on silica gel (petroleum ether/ethyl acetate = 3:1–2:1) to give the product **3aa** as a white solid, 1.14 g, 98% yield, 98% ee.

6. Procedure for the synthesis of compound 6



To a suspension of compound **3** (0.3 mmol, 139 mg) in dry tetrahydrofuran (6.0 ml) was added $LiAlH_4$ (1.5 mmol, 57 mg, 5 equiv) at 0 °C. The resulted reaction mixture was stirred at 0 °C for 1.0 hour. After completion of the reaction (monitored by TLC), the mixture was quenched with ice water (5 mL) at 0 °C and extracted with ethyl acetate (15 mL×3). The combined organic layer was dried with anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether /ethylacetate = 5:1–3:1) to give the product **6**.

***tert*-butyl ((5a*R*,6*R*)-6-(1*H*-indol-3-yl)-12-oxo-5,5a,6,12-tetrahydroindolo[2,1-*b*]quinazolin-6-yl)carbamate (6)**



The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 5:1–3:1 as the eluent).

White solid; 130.0 mg, 93% yield; mp 140.6–141.5 °C; 90% ee; $[\alpha]_D^{20}$ = –75.2 (*c* 1.0, CH_2Cl_2).

The ee was determined by HPLC (Chiralpak AD-H, ethanol/*n*-hexane 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 6.8 min (minor), 8.3 min (major).

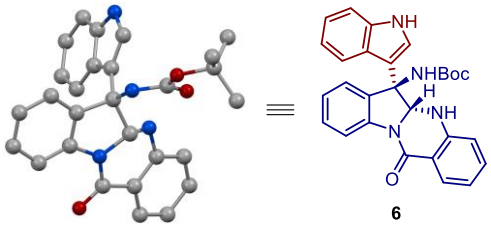
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.42 (d, *J* = 8.1 Hz, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.21 (q, *J* = 8.1 Hz, 2H), 7.07 (t, *J* = 8.4 Hz, 2H), 6.95 (dd, *J* = 16.4, 8.7 Hz, 3H), 6.86 (t, *J* = 7.6 Hz, 1H), 6.50 (d, *J* = 8.1 Hz, 1H), 5.93 (d, *J* = 6.5 Hz, 2H), 5.43 (s, 1H), 1.48 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 161.3, 155.6, 147.3, 139.9, 136.9, 133.7, 129.9, 128.4, 125.4, 124.8, 123.5, 123.2, 122.1, 120.4, 120.1, 119.6, 116.8, 116.4, 116.0, 114.6, 111.7, 81.2, 80.8, 66.6, 28.4.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd. for $C_{28}H_{26}N_4O_3Na$ 489.1897, found 489.1911.

7. X-ray Crystal Structure of Compounds 5f and 6

Single crystals of compound **6** were prepared from the mixture solvent of THF and pentane. Single crystals of compound **5f** were prepared from the mixture solvent of EtOH and CH_2Cl_2. For the X-ray analysis of both of compounds **5f** and **6**, a suitable crystal was selected for structure determination on a Xcalibur, Eos, Gemini diffractometer. Each crystal was kept at 293(2) K during data collection. Using Olex2[2], the structure was solved with the ShelXS[3] structure solution program using Direct Methods and refined with the ShelXL[3] refinement package using Least Squares minimisation.



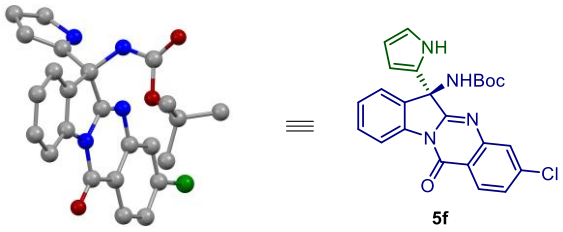
6

ORTEP of **6** (at 50% level)

Crystal data and structure refinement (after solvents removal) for **6 (**CCDC: 2267719**)**

Identification code	**6 • THF • H_2O**
Empirical formula	$C_{32}H_{36}N_4O_5$
Formula weight	556.65
Temperature/K	193.00
Crystal system	monoclinic
Space group	C2
a/Å	21.4211(19)
b/Å	10.3788(8)
c/Å	15.9818(14)
α/°	90
β/°	93.591(5)
γ/°	90
Volume/Å^3	3546.2(5)
Z	4
ρ_{calc}g/cm^3	1.043
μ/mm^{-1}	0.367
F(000)	1184.0

Crystal size/mm^3	0.12 × 0.11 × 0.1
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	7.194 to 120.4
Index ranges	-27 ≤ h ≤ 26, -13 ≤ k ≤ 13, -20 ≤ l ≤ 20
Reflections collected	21563
Independent reflections	7656 [R_{int} = 0.0604, R_{sigma} = 0.0575]
Data/restraints/parameters	7656/175/436
Goodness-of-fit on F^2	0.990
Final R indexes [I>=2σ (I)]	R_1 = 0.0923, wR_2 = 0.2367
Final R indexes [all data]	R_1 = 0.1273, wR_2 = 0.2736
Largest diff. peak/hole / e Å^{-3}	0.73/-0.38
Flack parameter	0.14(18)



ORTEP of **5f** (at 50% level)

Crystal data and structure refinement for **5f (**CCDC: 2267720**)**

Identification code	**5f**
Empirical formula	$C_{24}H_{21}ClN_4O_3$
Formula weight	448.90
Temperature/K	99.99(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	34.4794(6)
b/Å	9.4307(2)
c/Å	14.3293(2)
α/°	90
β/°	111.9310(10)
γ/°	90
Volume/Å^3	4322.20(14)
Z	8
ρ_{calc}g/cm^3	1.380
μ/mm^{-1}	1.854
F(000)	1872.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54178)

2Θ range for data collection/°	5.526 to 142.9
Index ranges	-42 ≤ h ≤ 28, -11 ≤ k ≤ 10, -14 ≤ l ≤ 17
Reflections collected	11801
Independent reflections	4086 [R_{int} = 0.0296, R_{sigma} = 0.0302]
Data/restraints/parameters	4086/0/296
Goodness-of-fit on F^2	1.094
Final R indexes [I>=2σ (I)]	R_1 = 0.0438, wR_2 = 0.0935
Final R indexes [all data]	R_1 = 0.0570, wR_2 = 0.0975
Largest diff. peak/hole / e $Å^{-3}$	0.24/-0.28

8. Biological activities evaluation

8.1 The results of biological activities evaluation with products 3 and 5

In the basis of preparation of diverse optically pure tryptanthrin derivatives **3** and **5**, we set out to identify the potential bioactivity of these compounds. Two human cancer cell lines, K562 leukemia and A549 lung cancer cells, were selected for an in vitro cytotoxicity assay to assess the anti-tumor activity of randomly chosen products.[5] The results indicated that most of tested compounds demonstrated good cytotoxicity against K562 and A549 cell lines, with IC_{50} values in the micromolar range (Figure S1, partial data). Generally, for the compounds obtained in this manuscript, the cytotoxicity against K562 cell lines was higher than that against A549 cell lines. Particularly, some compounds, such as **3aj**, **3ao**, **3ea**, and **3ha** showed impressive cytotoxicity against the K562 leukemia cells with promising IC_{50} values that are equivalent to or lower than that of cisplatin. Therefore, further structural modulation and biological investigations may render this class of tryptanthrin derivatives a promising candidate for medicinal applications.

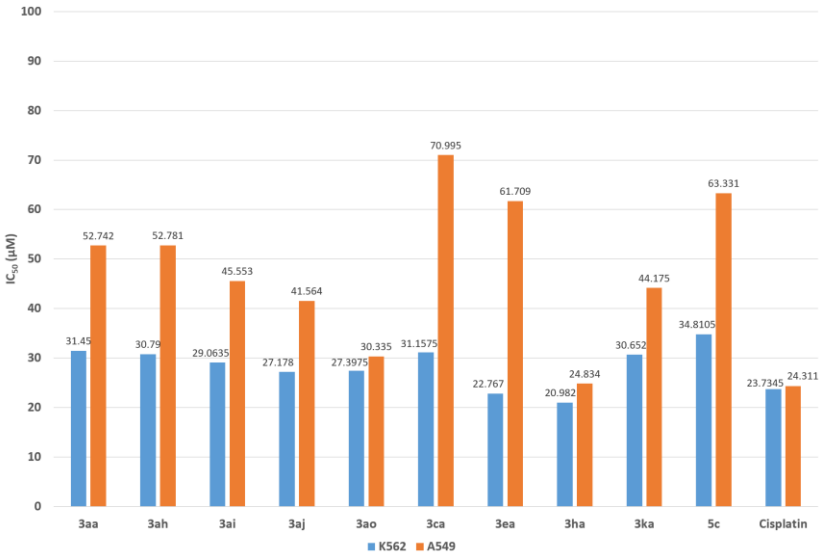


Fig. S1 Biological activities evaluation.

8.2 General experimental procedures for in vitro cytotoxicity assay

Two human cancer cell lines, human leukemia cells K562 and human lung cancer cells A549, were purchased from Chinese Academy of Sciences, Kunming Cell Bank and Chinese Academy of

Sciences, Shanghai Cell Bank respectively. All the cells were cultured in RPMI-1640 medium (GIBICO, USA), supplemented with 10% fetal bovine serum (Hyclone, USA) and Penicillin-Streptomycin (respectively 100 U/mL) in 5% CO_2 at 37 °C. The cytotoxicity assay was performed according to the MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide) method in 96-well microplates. Briefly, 5000 cells were seeded into each well of 96-well cell culture plates and allowed to grow for 24 h before the drug is added. K562 tumor cell line was exposed to compounds (**3aa**, **3ah**, **3ai**, **3aj**, **3ao**, **3ca**, **3ea**, **3ha**, **3ka**, **5c**, **5i** and **5j**) at the concentrations of 1, 2, 4, 8 and 20 μmol·L^{-1} and A549 tumor cell line was exposed to the test compounds (**3aa**, **3ah**, **3ai**, **3aj**, **3ao**, **3ca**, **3ea**, **3ha**, **3ka**, **5c**, **5i** and **5j**) at the concentrations of 5, 10, 20, 40 and 80 μmol·L^{-1} in triplicates for 48 h, comparable to cisplatin (Aladdin, China). Then the MTT reagent was added to reaction with the cancer cells for 4 hours. At least, measure the OD value at 490 wavelengths. The average 50% inhibitory concentration (IC_{50}) of all the compounds is calculated by IBM SPSS Statistics (version 19). Each concentration was analyzed in triplicate at least, and the whole experiment was repeated three times.

Table S1. Cell Inhibitory Assay of target products in K562 and A549 Cells

compound	IC_{50} (*u*M)[a]	
	K562	**A549**
3aa	31.450	52.742
3ah	30.790	52.781
3ai	29.064	45.553
3aj	27.178	41.564
3ao	27.398	30.335
3ca	31.158	70.995
3ea	22.767	61.709
3ha	20.982	24.834
3ka	30.652	44.175
5c	34.811	63.331
5i	32.469	>100
5j	25.514	>100
cisplatin[b]	23.734	24.311

[a]IC_{50} is the concentration of a compound that affords a 50% reduction in cell growth (after 48 h of incubation), expressed as the mean of triplicate experiments. [b]Commercially available broad-spectrum anticancer drug cisplatin as a positive control.

9. References

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2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst*. 2009, **42**, 339-341.

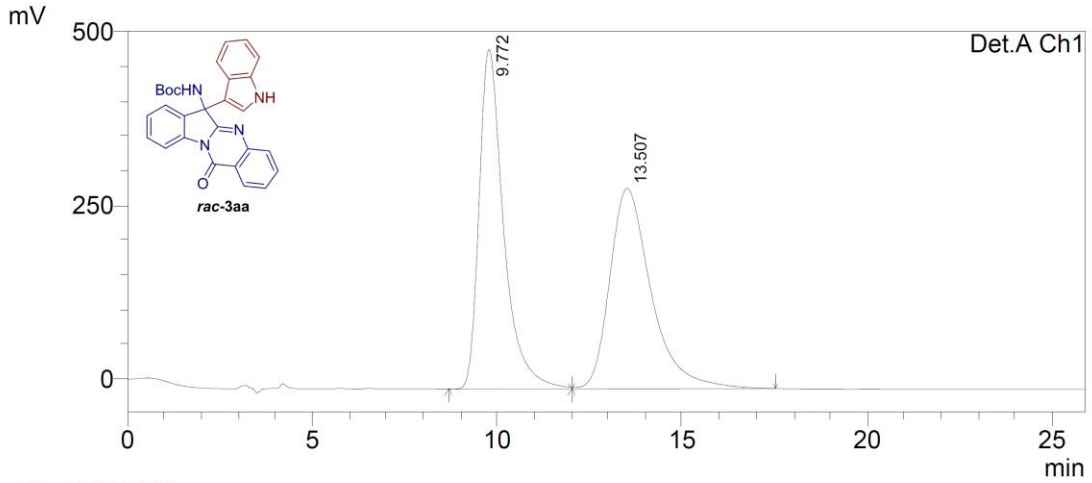
3. G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112-122.

4. G. M. Sheldrick, *Acta Cryst*. 2015, **C71**, 3-8.

5. (a) T. J. J. Mosmann, *Immunol. Methods*, 1983, **65**, 55−63; (b) M. C. Alley, D. A. Scudiero, A. Monks, M. L. Hursey, M. J. Czerwinski, D. L. Fine, B. J. Abbott, R. H. Shoemaker and M. R. Boyd, *Cancer Res.*, 1988, **48**, 589−601.

10. HPLC spectra of compounds 3, 5, and 6

HPLC spectra of 3aa

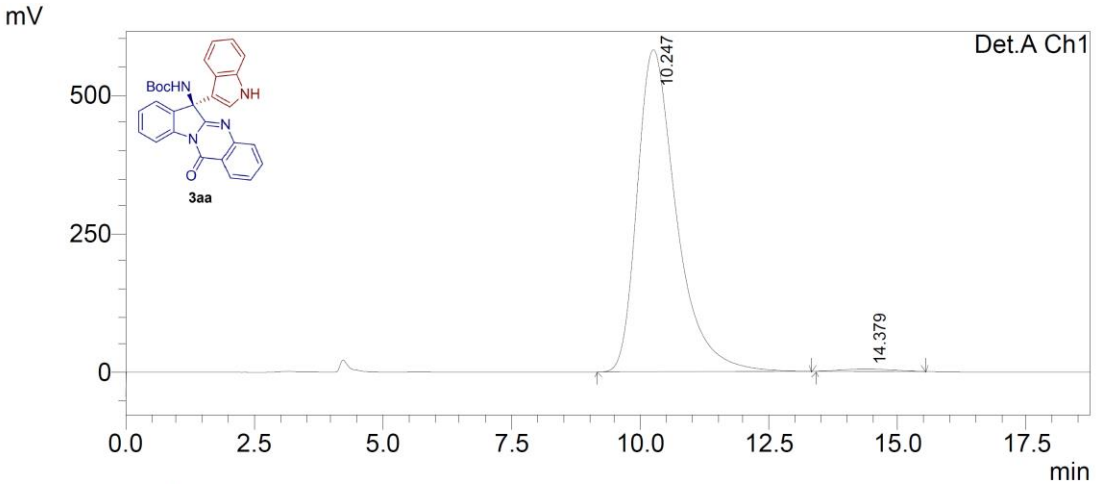


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	9.772	22523444	488792	50.098
2	13.507	22435142	288087	49.902
Total		44958586		100.000



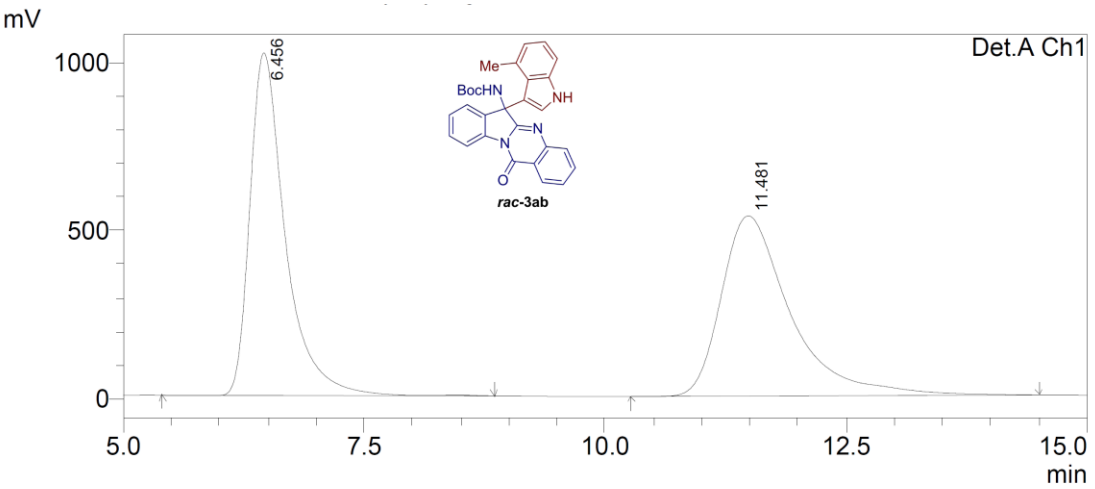
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.247	30775968	581031	99.083
2	14.379	284935	4222	0.917
Total		31060903		100.000

HPLC spectra of 3ab

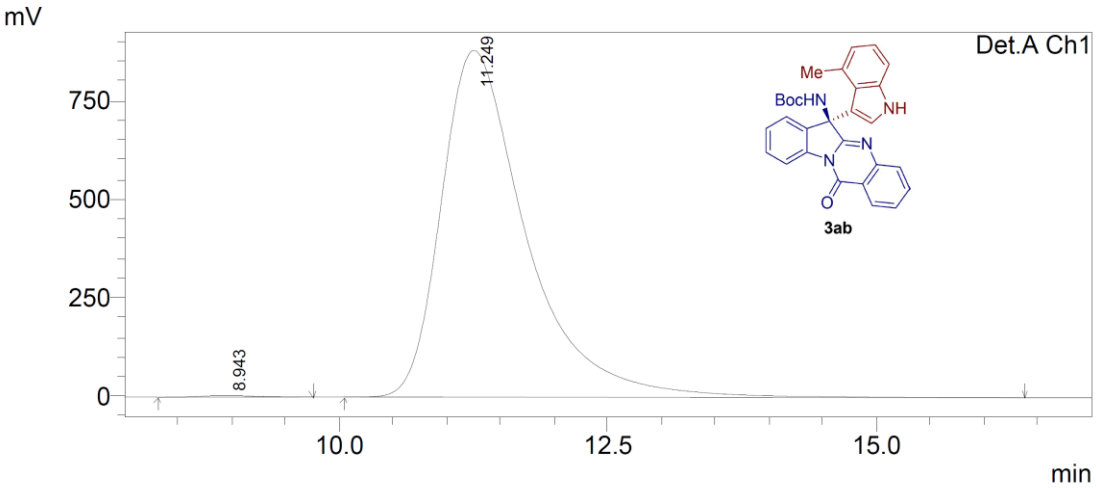


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	6.456	26052188	1019216	49.344
2	11.481	26744488	535806	50.656
Total		52796676		100.000



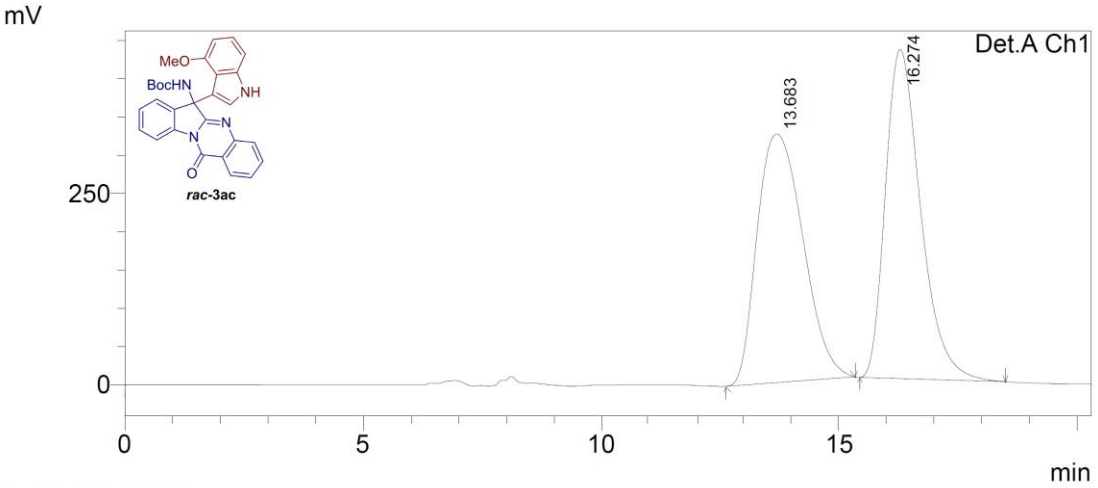
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.943	116795	3467	0.241
2	11.249	48340481	879014	99.759
Total		48457277		100.000

HPLC spectra of 3ac

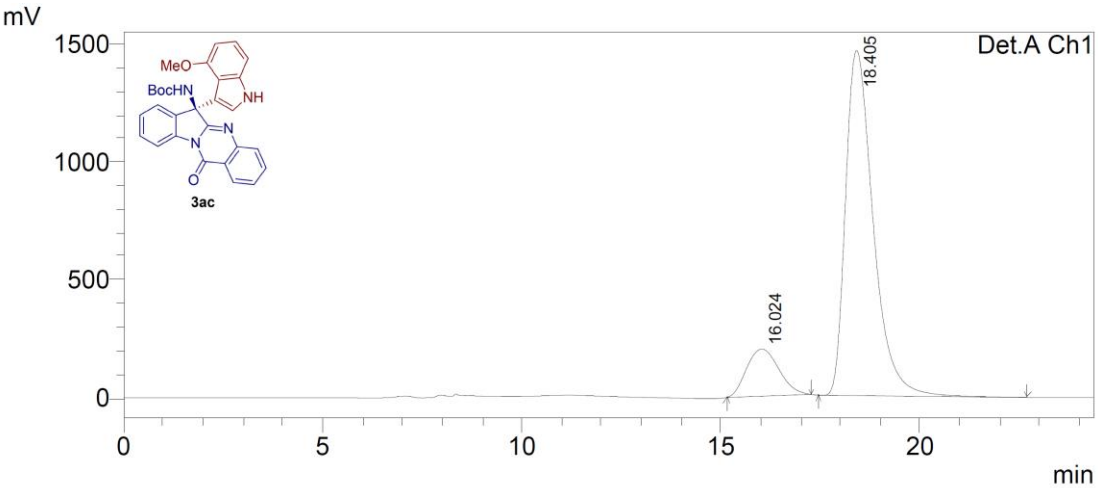


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	13.683	21790984	325516	49.599
2	16.274	22143558	431129	50.401
Total		43934542		100.000



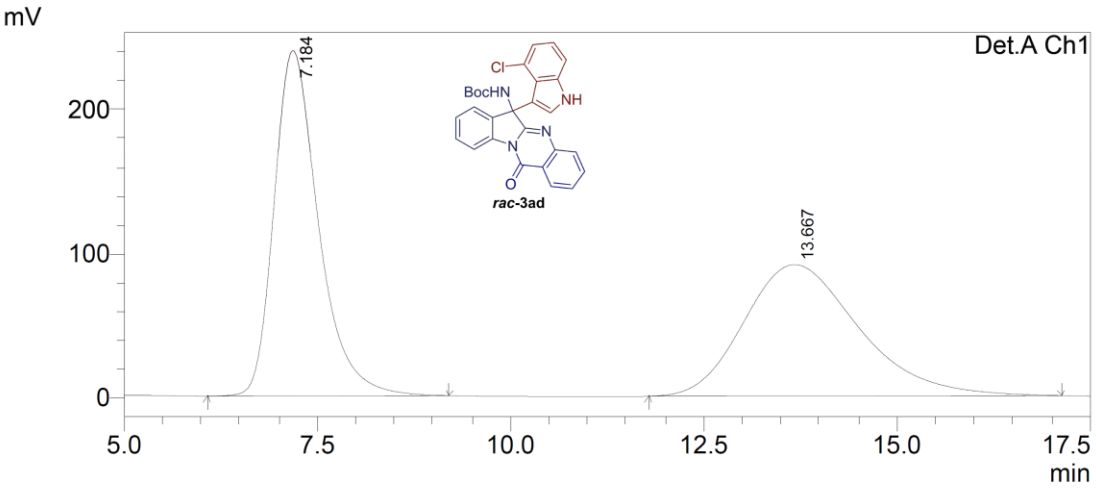
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	16.024	11267377	199736	13.726
2	18.405	70819377	1464166	86.274
Total		82086754		100.000

HPLC spectra of 3ad

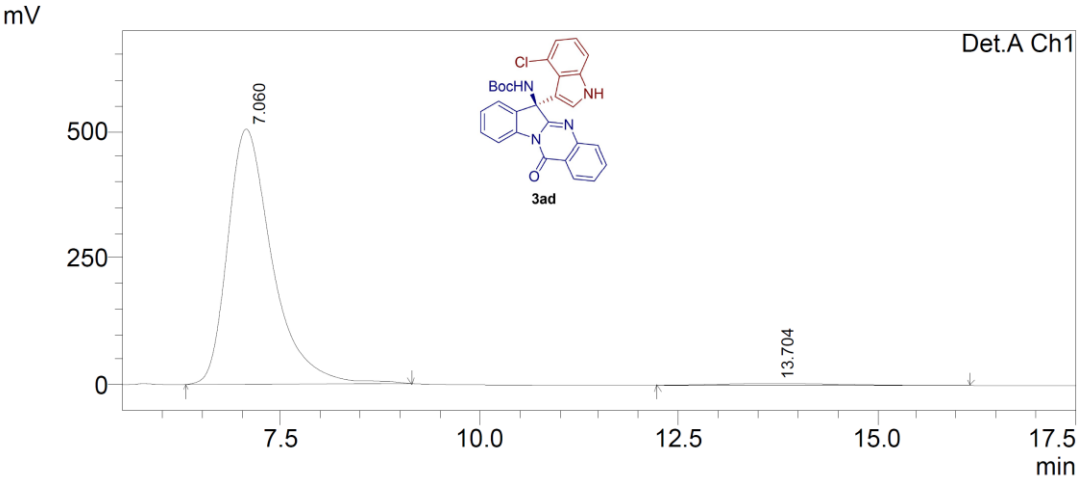


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.184	9627439	240063	50.453
2	13.667	9454554	91362	49.547
Total		19081992		100.000



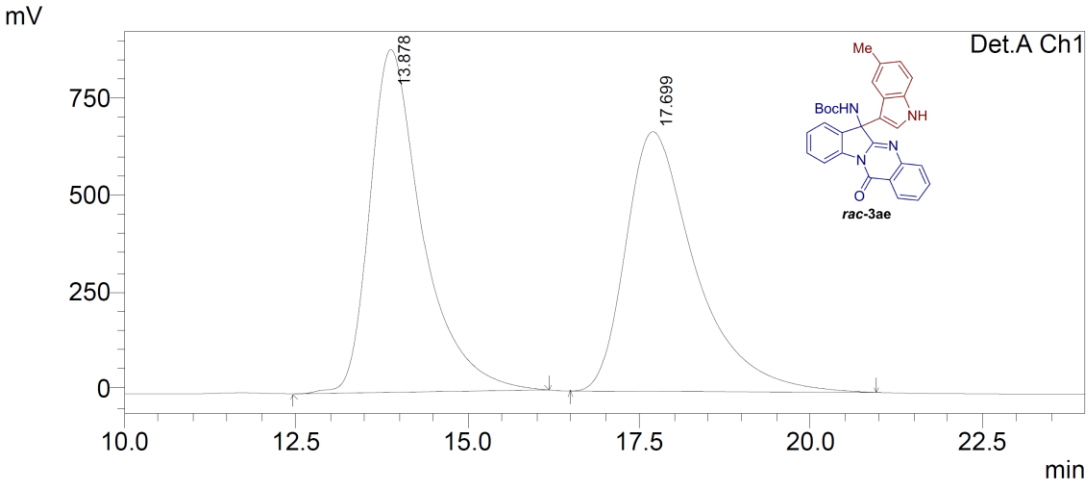
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.060	19624798	502285	98.185
2	13.704	362726	3542	1.815
Total		19987525		100.000

HPLC spectra of 3ae

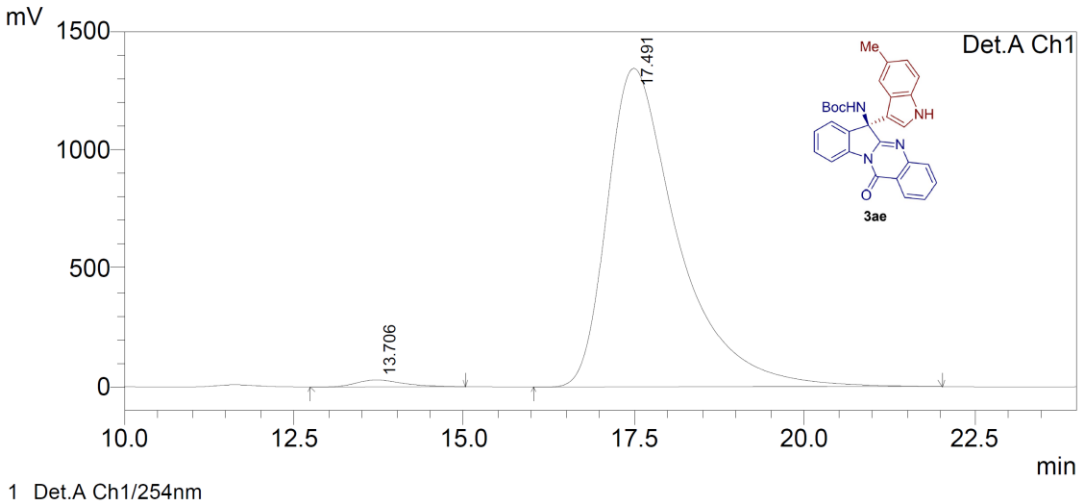


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	13.878	47302482	885176	49.904
2	17.699	47485161	670738	50.096
Total		94787643		100.000



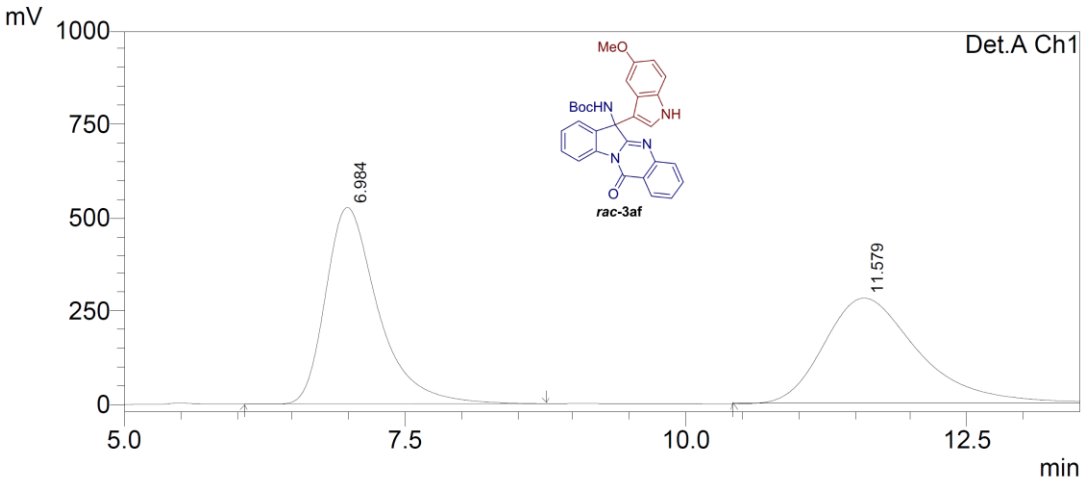
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	13.706	1388199	29294	1.403
2	17.491	97525480	1342495	98.597
Total		98913680		100.000

HPLC spectra of 3af

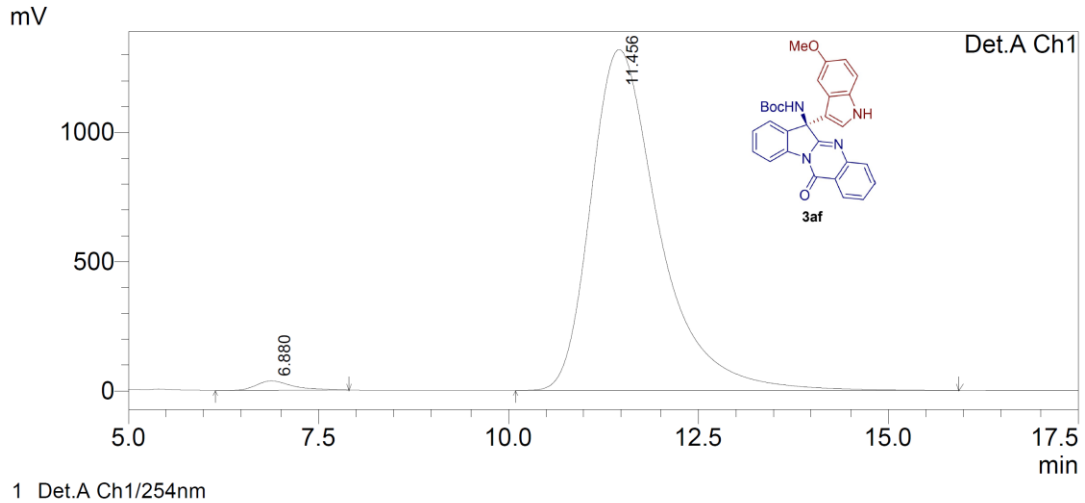


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	6.984	17031784	525459	50.760
2	11.579	16521916	281715	49.240
Total		33553701		100.000



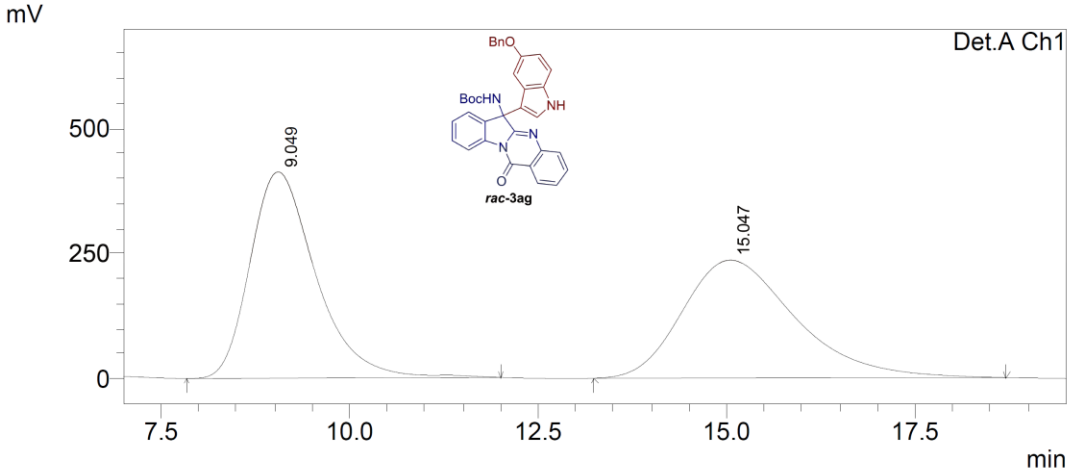
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	6.880	1158335	35759	1.388
2	11.456	82320279	1316675	98.612
Total		83478614		100.000

HPLC spectra of 3ag

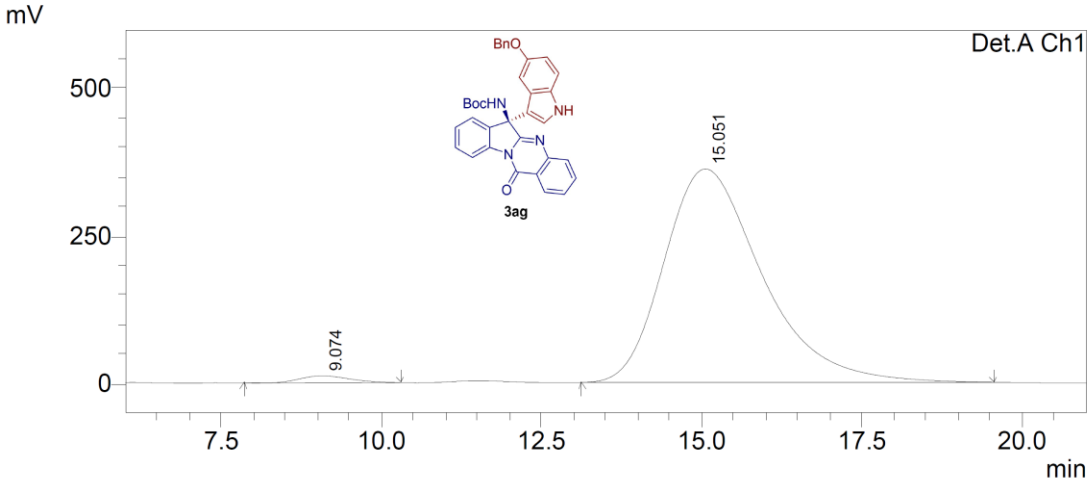


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	9.049	24978459	411697	50.460
2	15.047	24523160	235172	49.540
Total		49501618		100.000



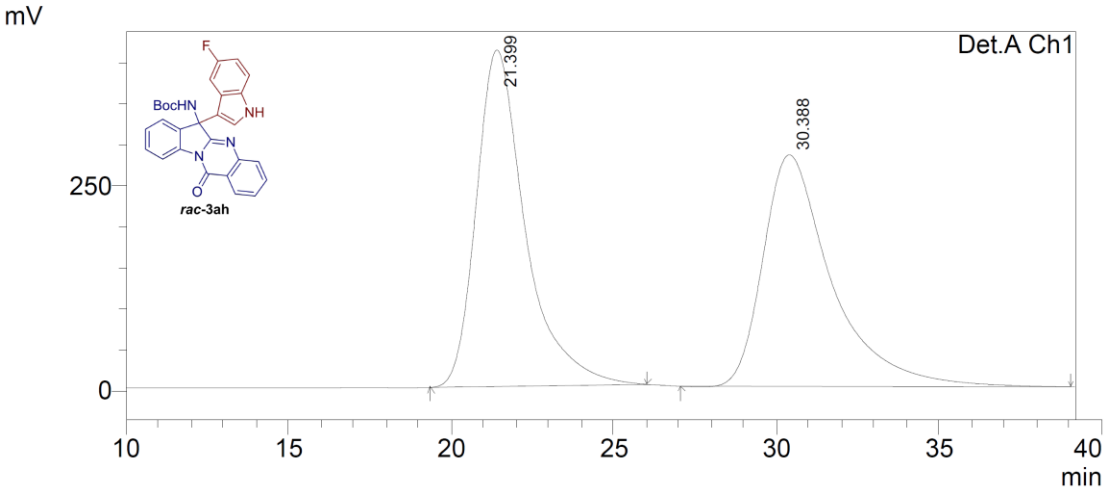
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	9.074	641859	11873	1.638
2	15.051	38544163	361913	98.362
Total		39186022		100.000

HPLC spectra of 3ah

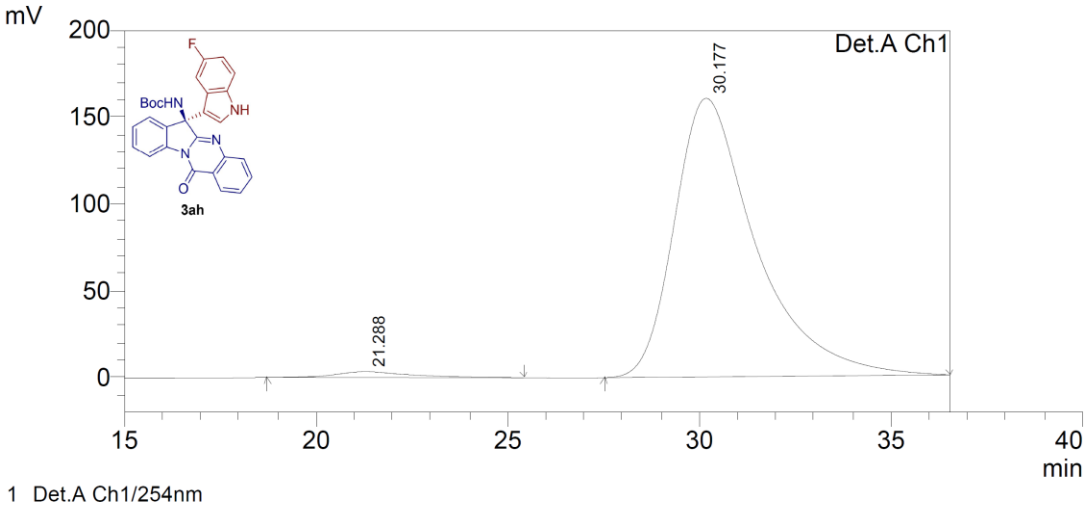


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	21.399	43179013	412042	50.941
2	30.388	41584512	283671	49.059
Total		84763525		100.000



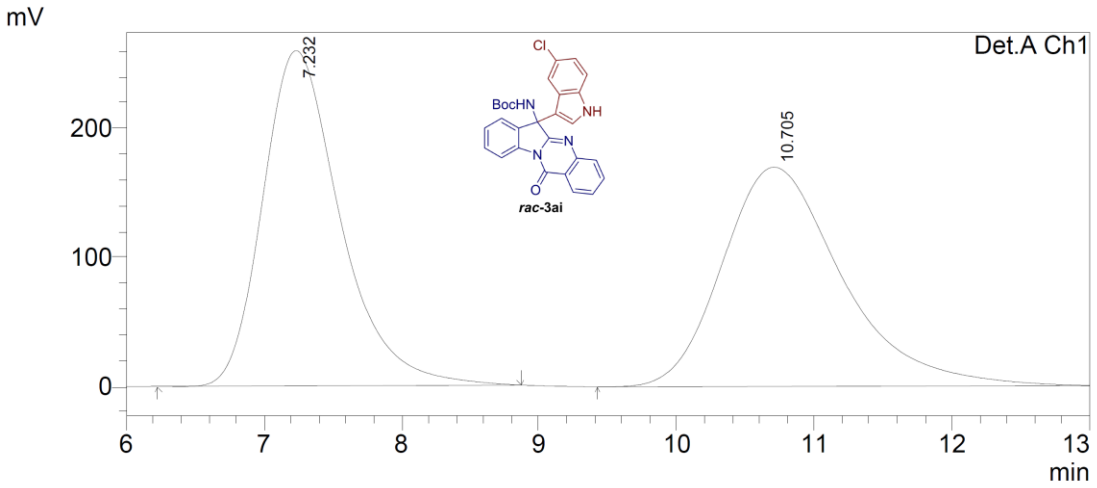
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	21.288	466295	3465	1.929
2	30.177	23702569	160291	98.071
Total		24168864		100.000

HPLC spectra of 3ai

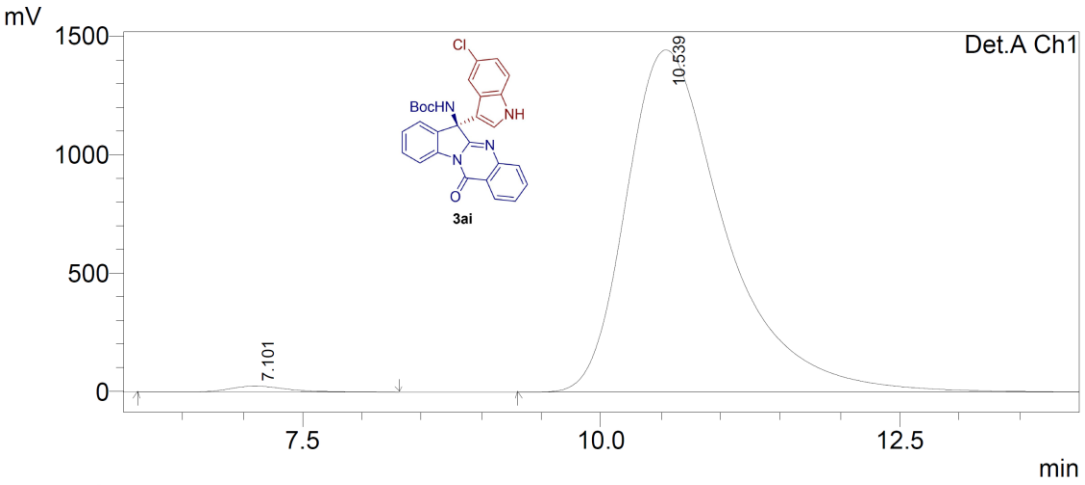


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.232	10163773	259859	49.663
2	10.705	10301600	170015	50.337
Total		20465374		100.000



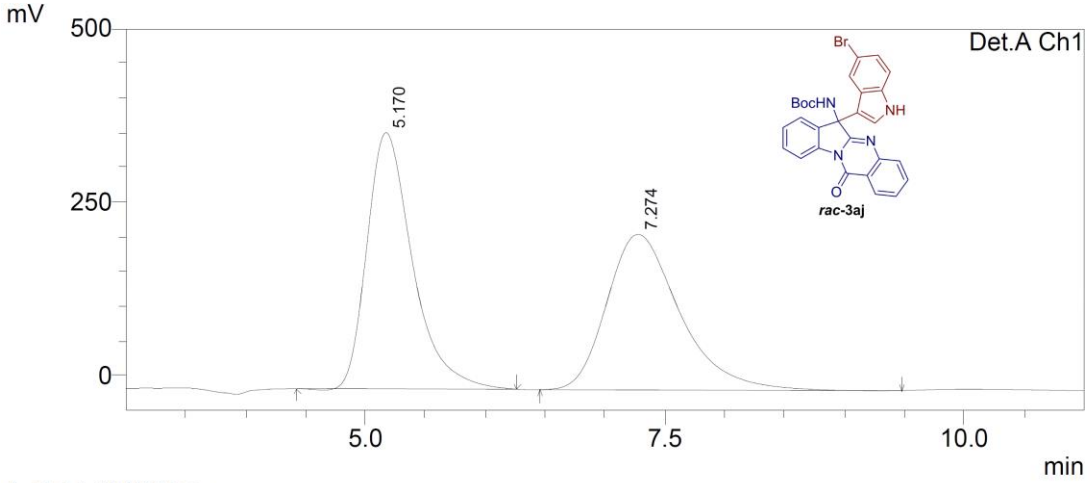
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.101	811600	24980	0.966
2	10.539	83183849	1441491	99.034
Total		83995449		100.000

HPLC spectra of 3aj

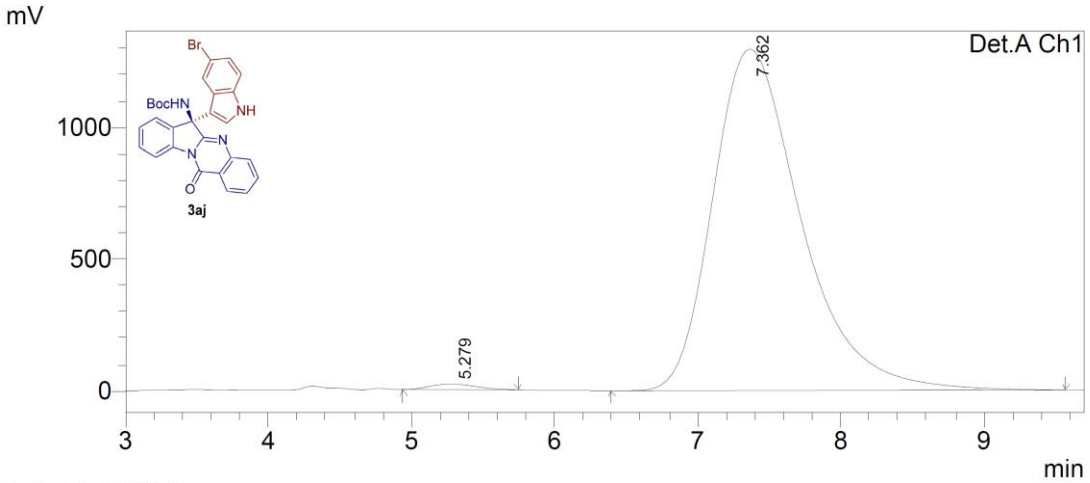


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	5.170	9726740	368815	50.666
2	7.274	9470890	223969	49.334
Total		19197630		100.000



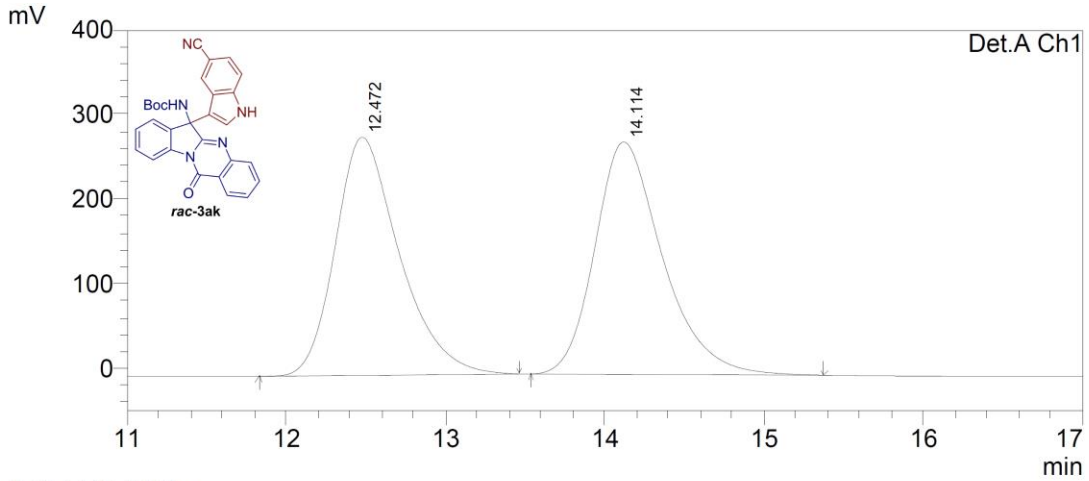
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	5.279	477873	21295	0.851
2	7.362	55647534	1295591	99.149
Total		56125407		100.000

HPLC spectra of 3ak

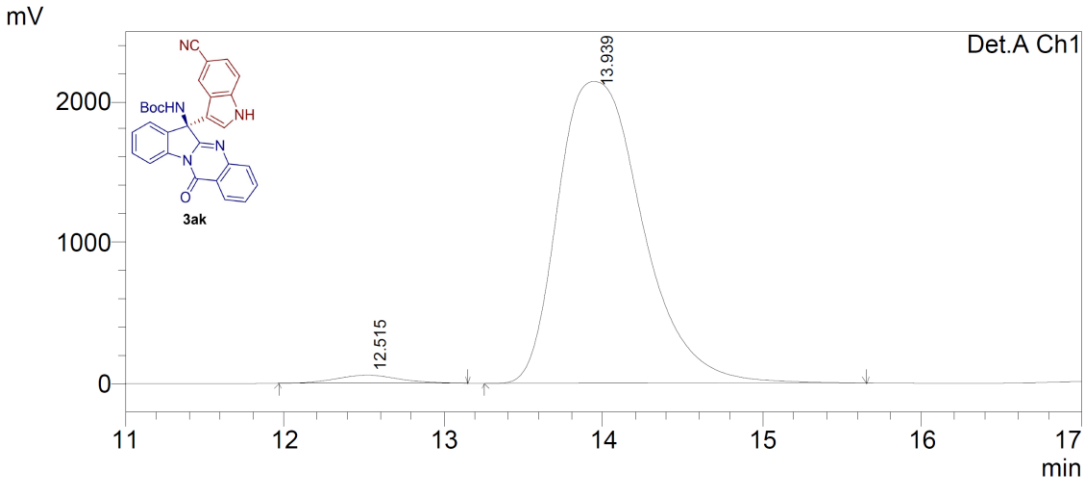


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.472	7865252	281241	49.245
2	14.114	8106449	274449	50.755
Total		15971701		100.000



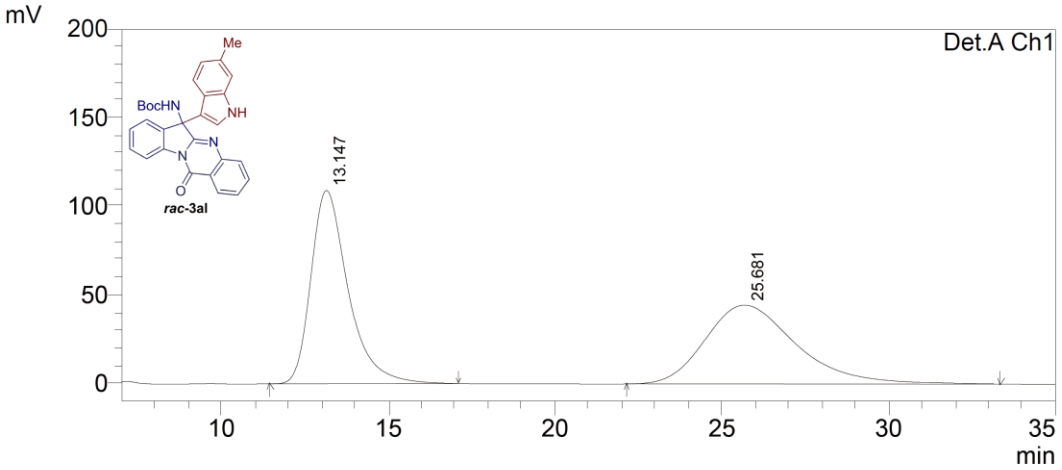
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.515	1599008	57915	1.987
2	13.939	78854513	2135858	98.013
Total		80453521		100.000

HPLC spectra of 3al

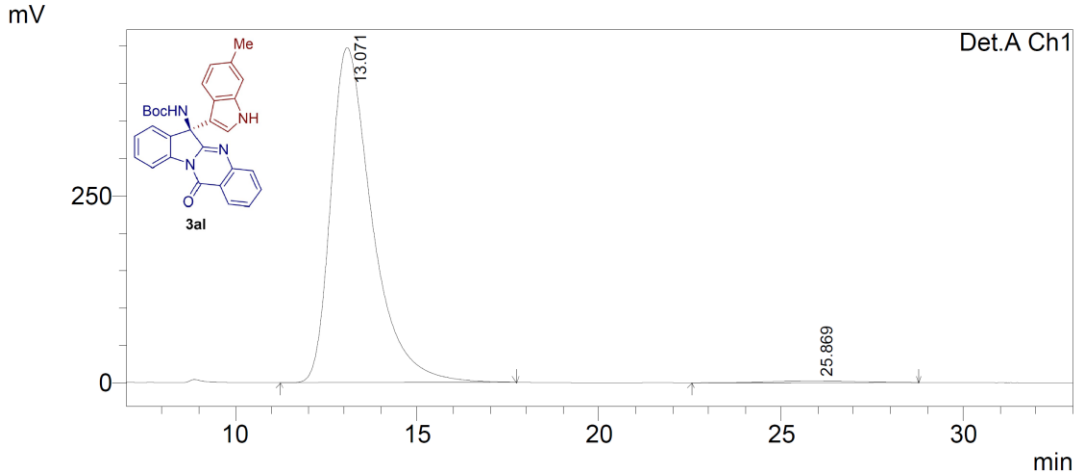


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	13.147	8460018	108981	50.002
2	25.681	8459320	44494	49.998
Total		16919339		100.000



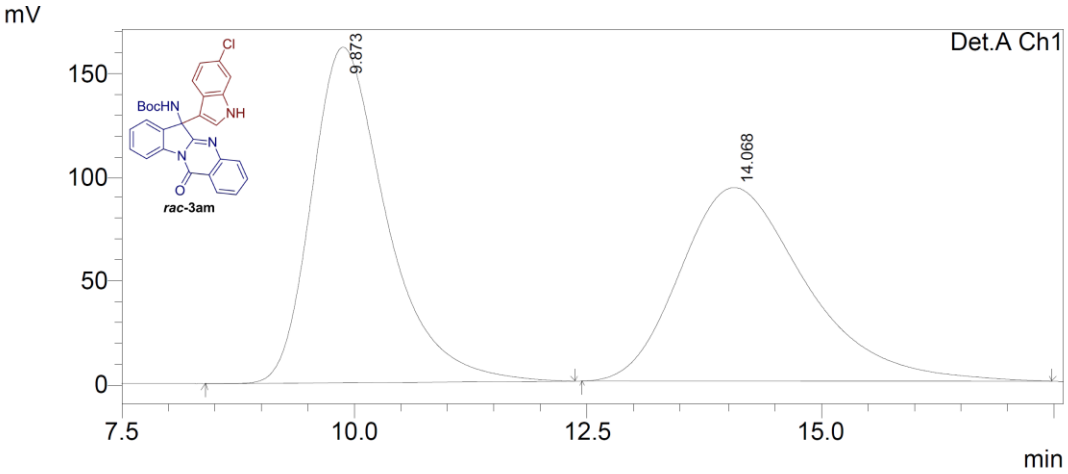
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	13.071	35424630	449089	98.974
2	25.869	367068	2198	1.026
Total		35791698		100.000

HPLC spectra of 3am

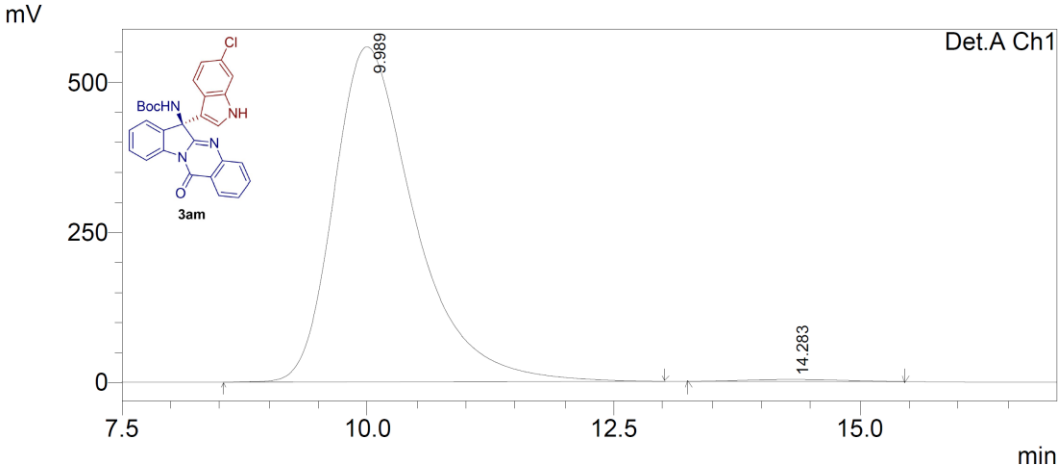


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	9.873	9092912	162144	50.834
2	14.068	8794664	93503	49.166
Total		17887577		100.000



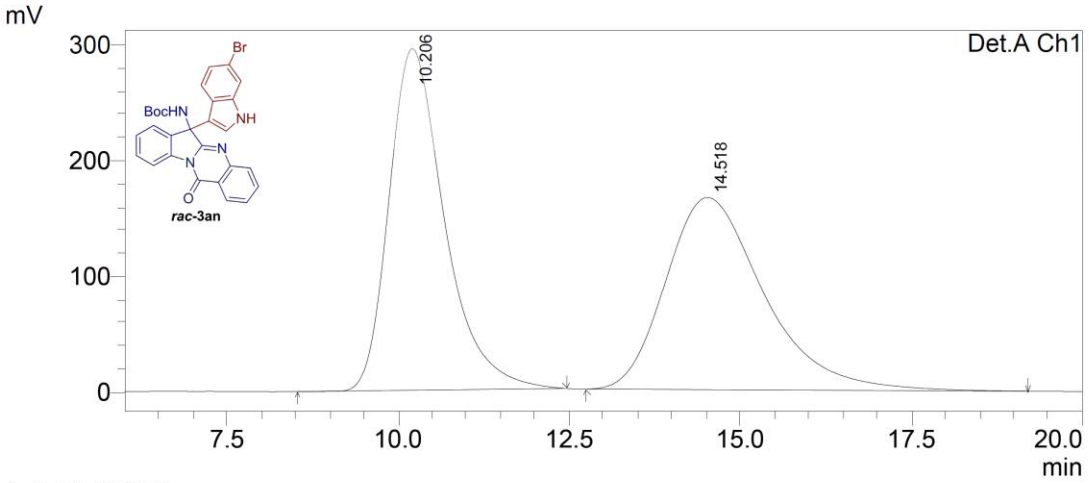
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	9.989	32076528	559432	99.277
2	14.283	233482	3271	0.723
Total		32310010		100.000

HPLC spectra of 3an

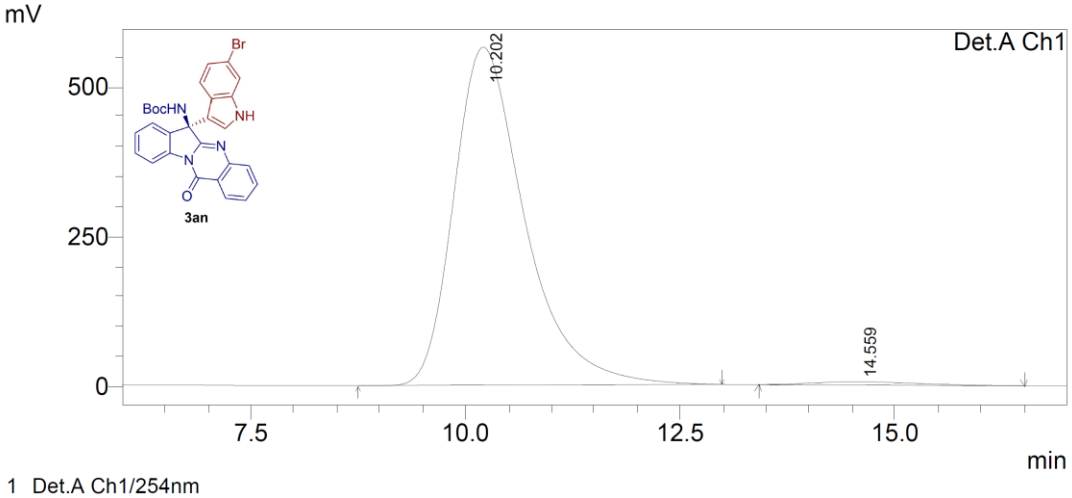


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.206	16613295	294815	50.094
2	14.518	16550634	165902	49.906
Total		33163929		100.000



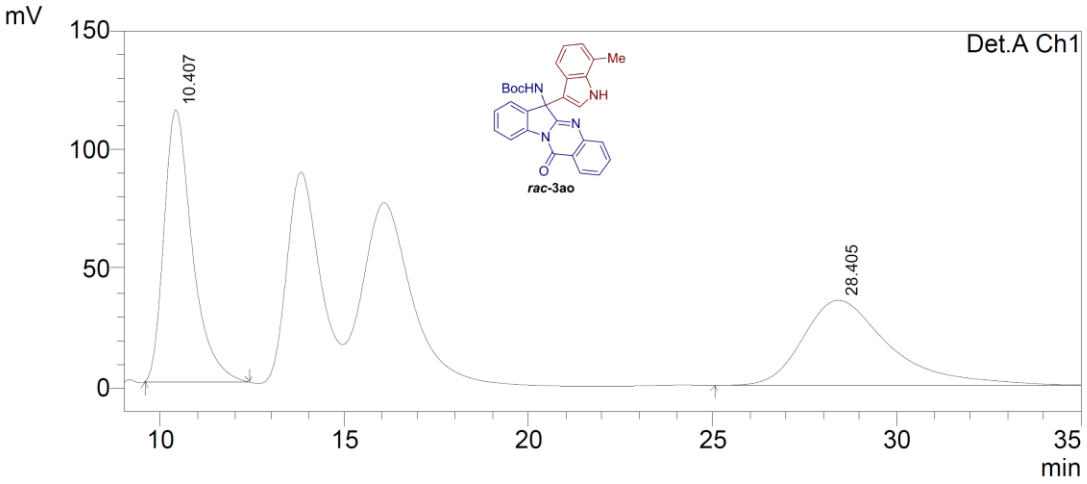
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.202	32461863	564243	98.613
2	14.559	456458	5395	1.387
Total		32918321		100.000

HPLC spectra of 3ao

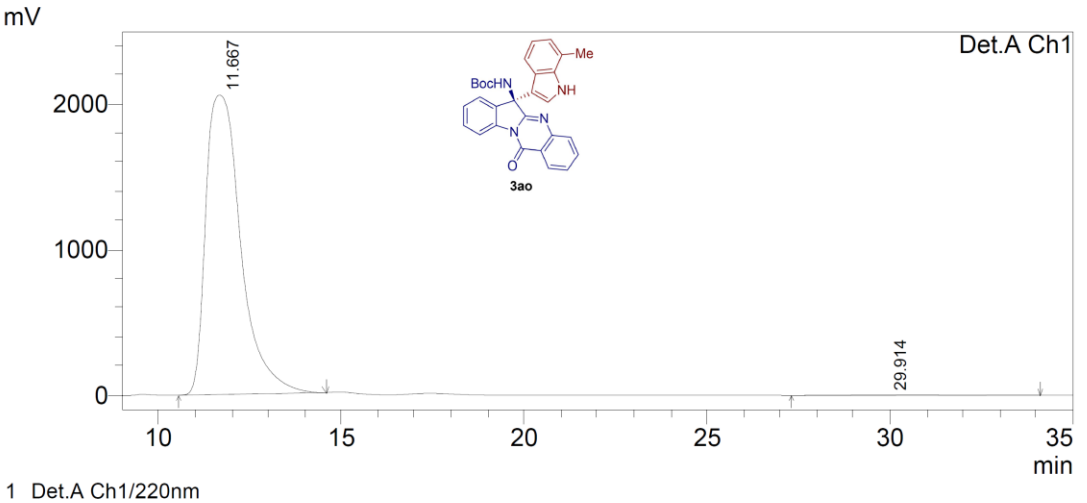


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	10.407	6093339	114053	50.987
2	28.405	5857445	35667	49.013
Total		11950785		100.000



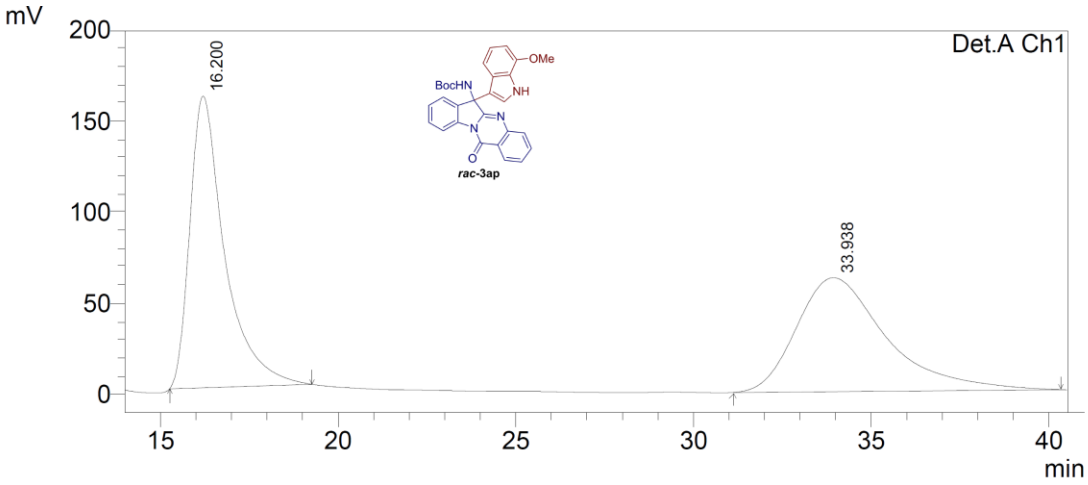
1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	11.667	137227939	2054139	99.636
2	29.914	502004	3015	0.364
Total		137729943		100.000

HPLC spectra of 3ap

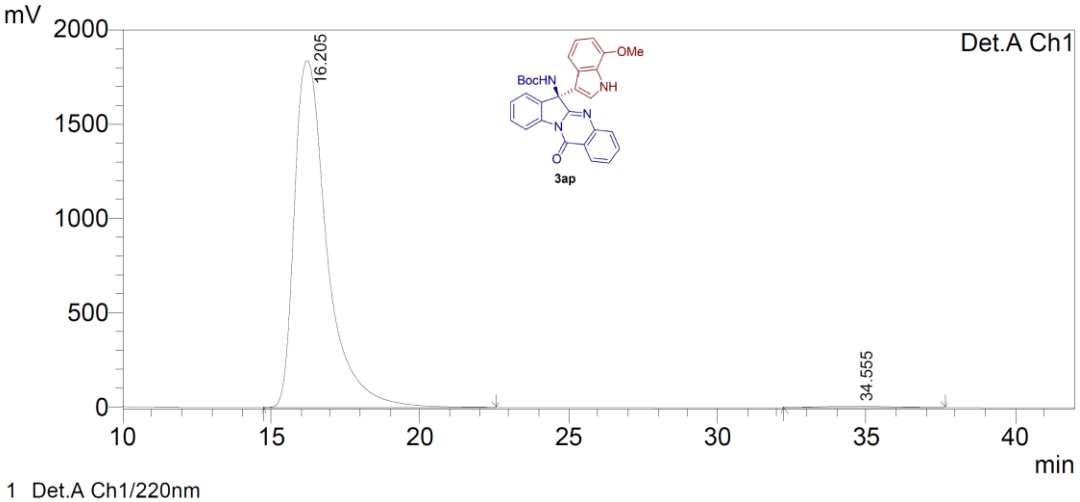


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	16.200	10908887	160019	49.851
2	33.938	10973955	62516	50.149
Total		21882843		100.000



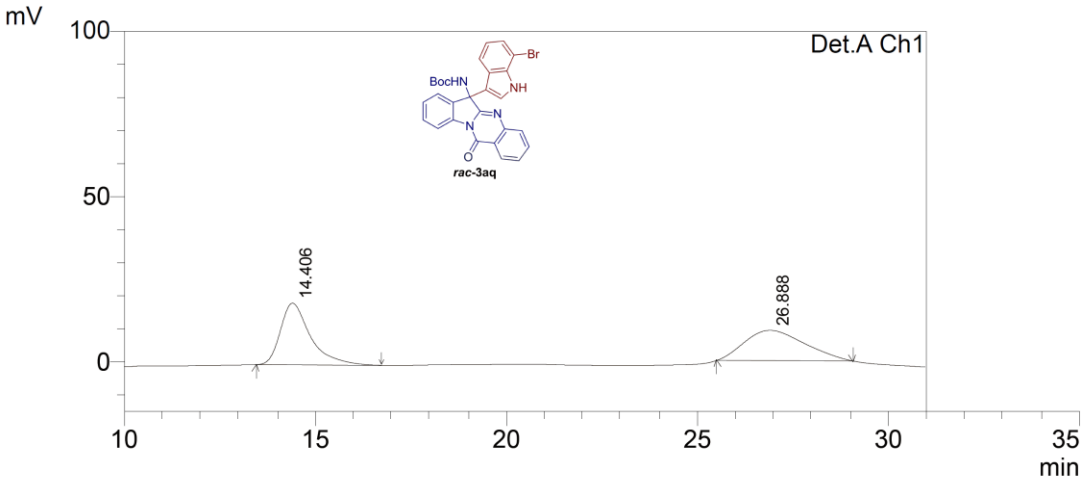
1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	16.205	140352453	1835379	99.125
2	34.555	1239469	8182	0.875
Total		141591922		100.000

HPLC spectra of 3aq

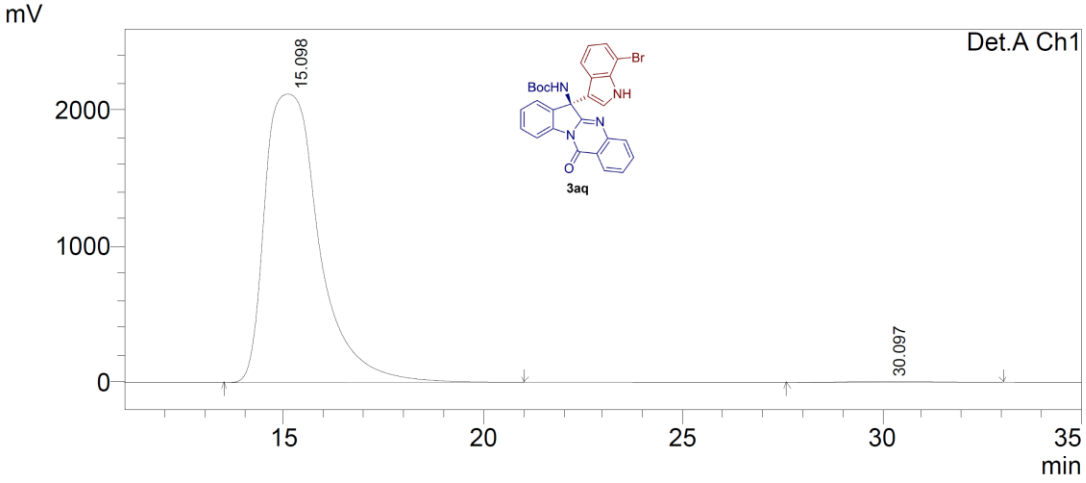


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	14.406	1021375	18624	50.704
2	26.888	993007	9084	49.296
Total		2014382		100.000



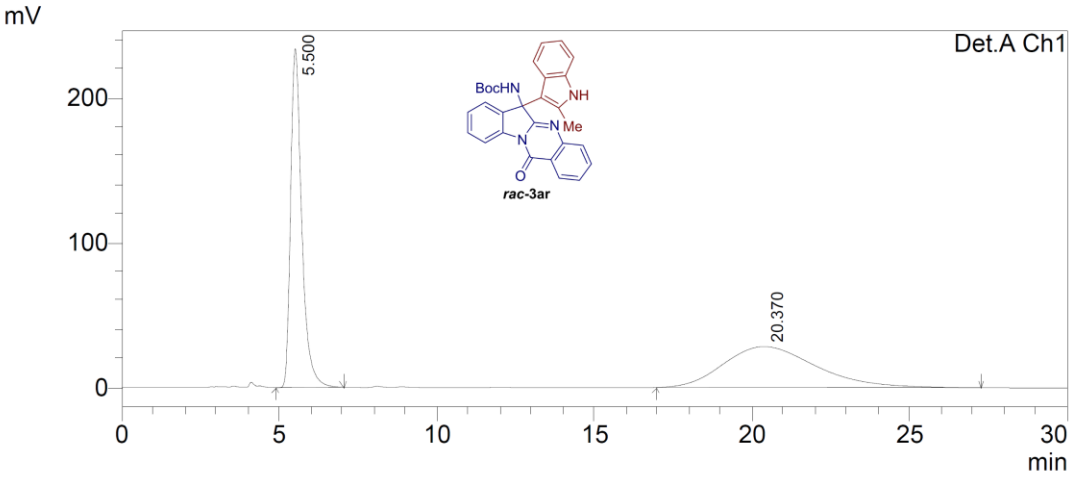
1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	15.098	201388027	2116193	99.423
2	30.097	1168020	8345	0.577
Total		202556047		100.000

HPLC spectra of 3ar

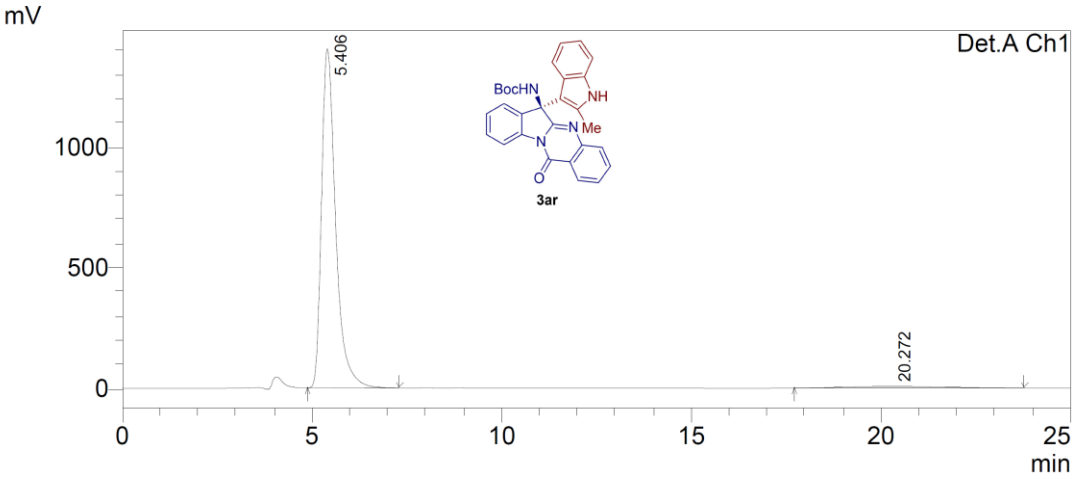


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	5.500	5714289	233644	49.702
2	20.370	5782824	28219	50.298
Total		11497112		100.000



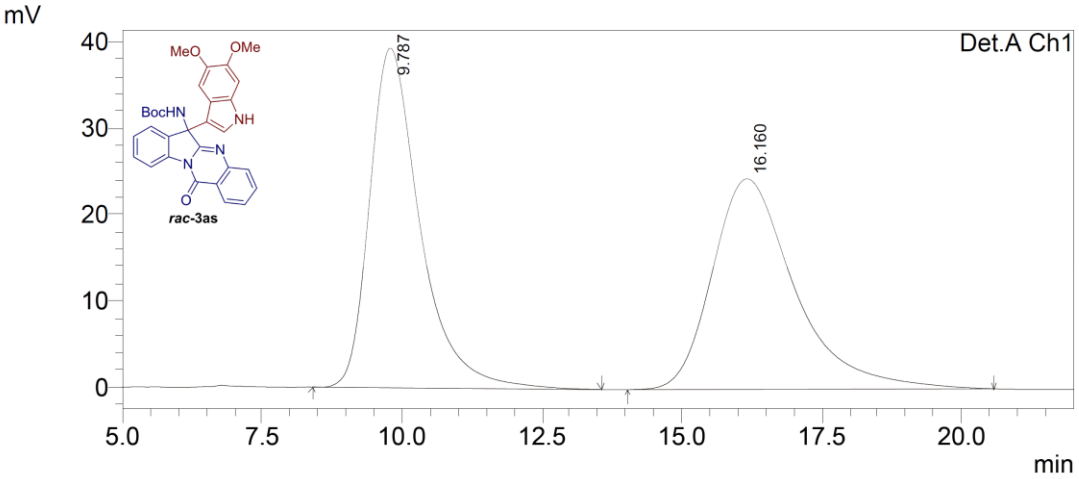
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	5.406	36329412	1405207	96.564
2	20.272	1292570	7008	3.436
Total		37621982		100.000

HPLC spectra of 3as

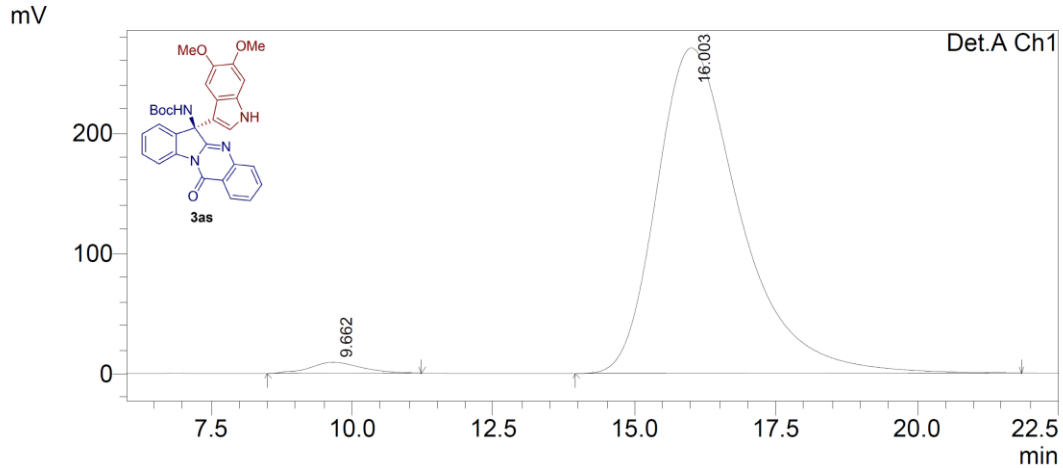


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	9.787	2464290	39312	49.655
2	16.160	2498542	24383	50.345
Total		4962833		100.000



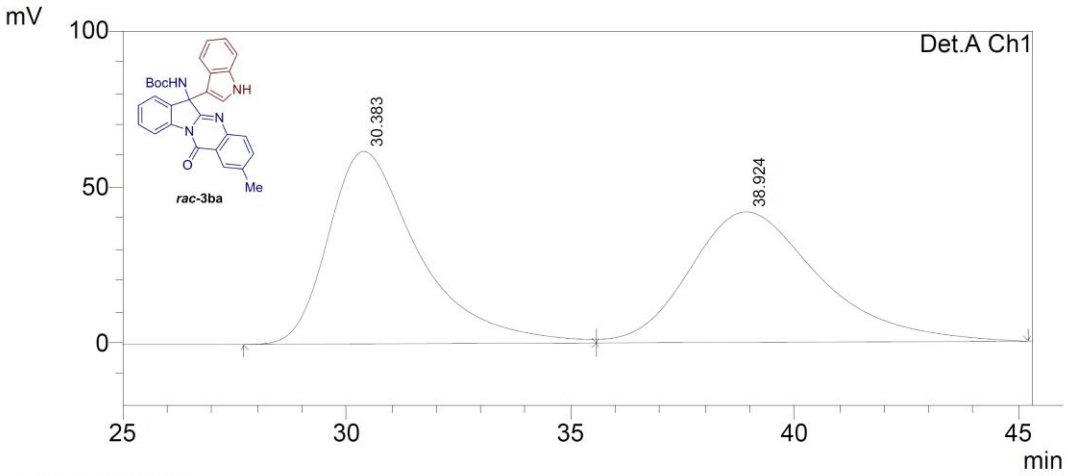
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	9.662	590629	9188	2.076
2	16.003	27853148	270024	97.924
Total		28443777		100.000

HPLC spectra of 3ba

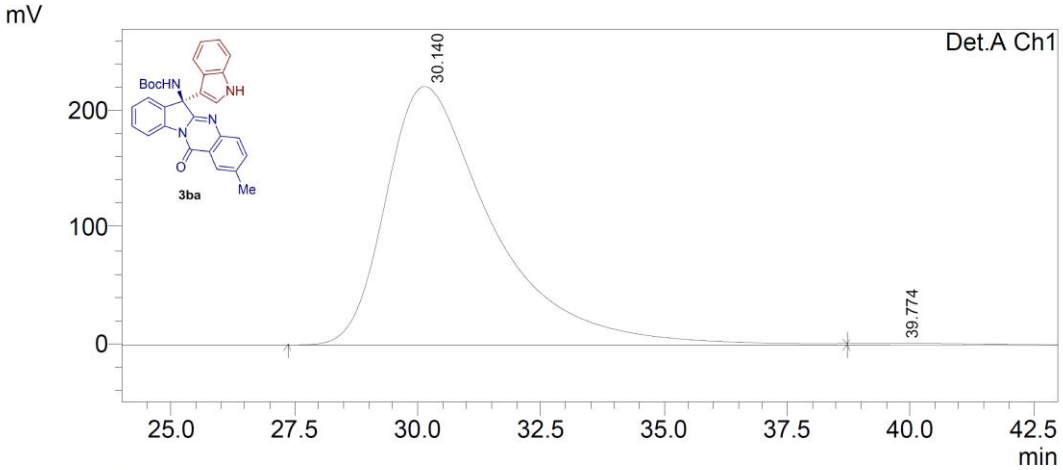


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	30.383	8692894	61573	50.750
2	38.924	8436104	41719	49.250
Total		17128998		100.000



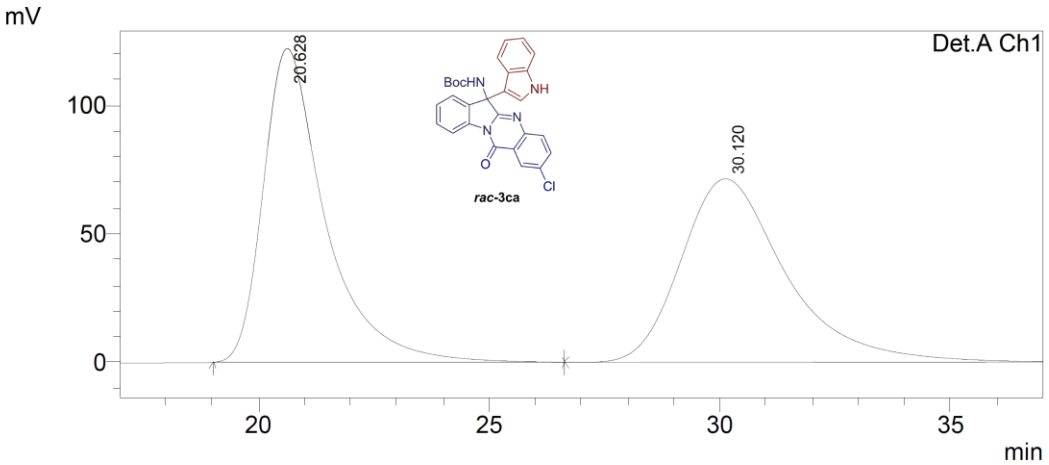
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	30.140	33541454	221618	99.050
2	39.774	321788	1662	0.950
Total		33863241		100.000

HPLC spectra of 3ca

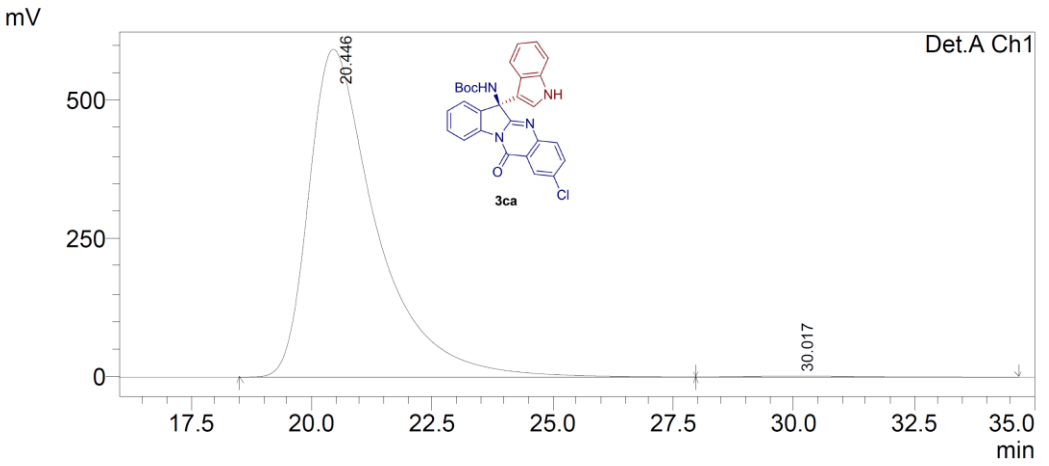


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	20.628	11433152	121844	50.397
2	30.120	11252870	71184	49.603
Total		22686022		100.000



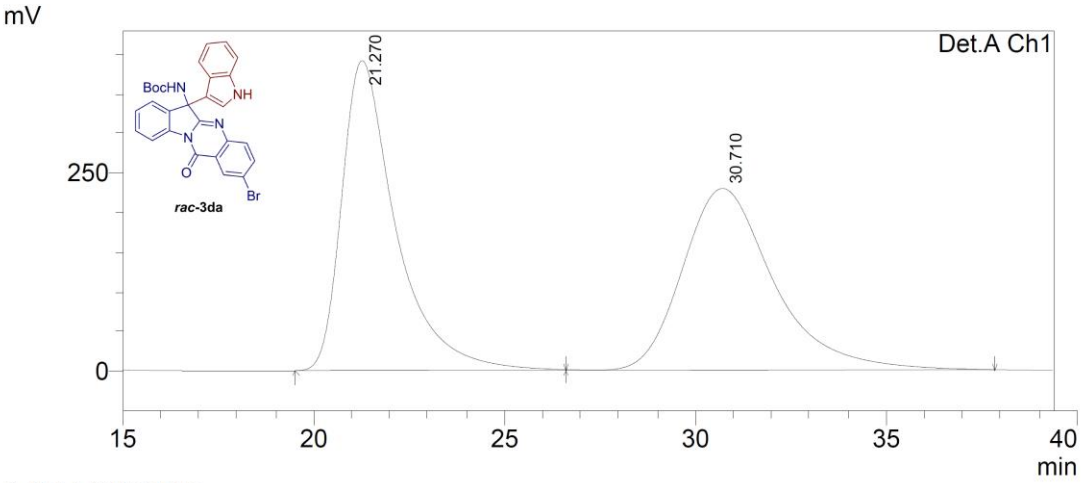
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	20.446	58202499	593098	99.434
2	30.017	331444	2062	0.566
Total		58533943		100.000

HPLC spectra of 3da

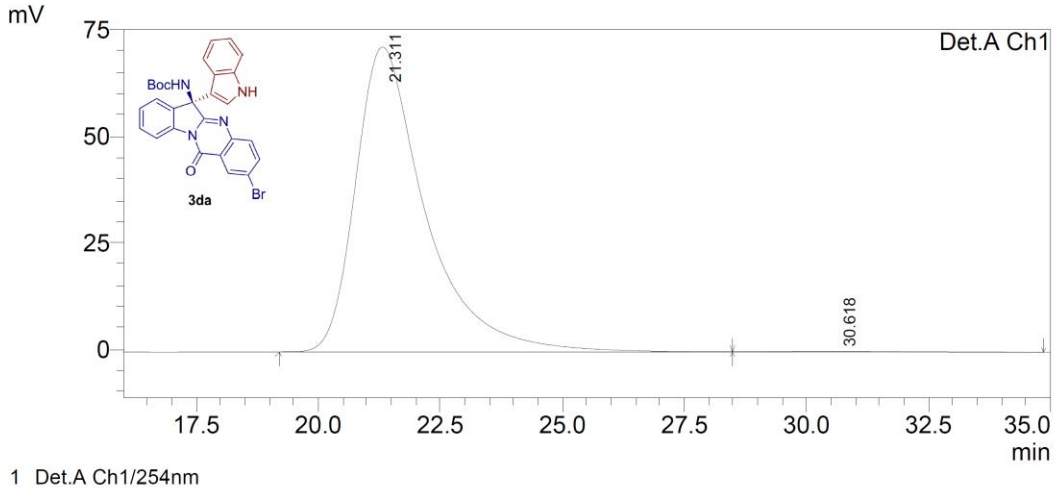


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	21.270	38521558	390591	50.302
2	30.710	38058734	228839	49.698
Total		76580292		100.000



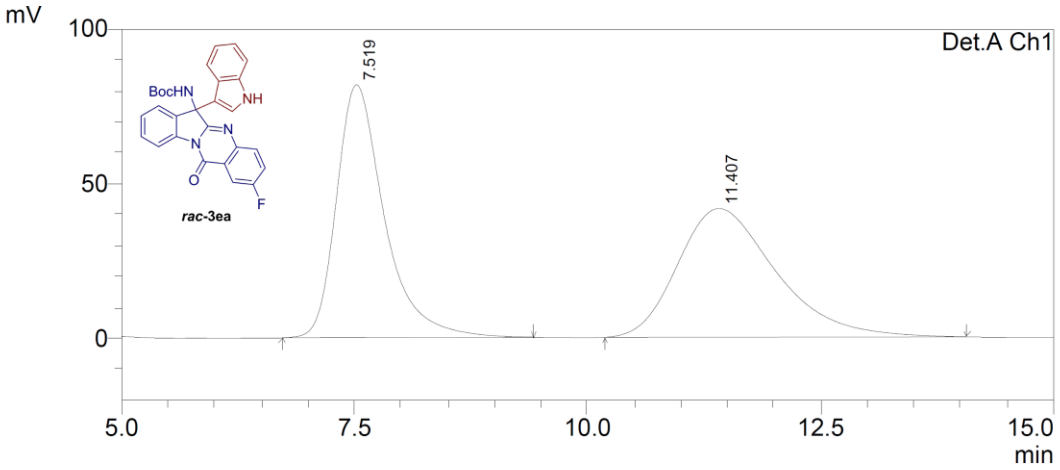
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	21.311	7139480	71520	99.397
2	30.618	43292	249	0.603
Total		7182772		100.000

HPLC spectra of 3ea

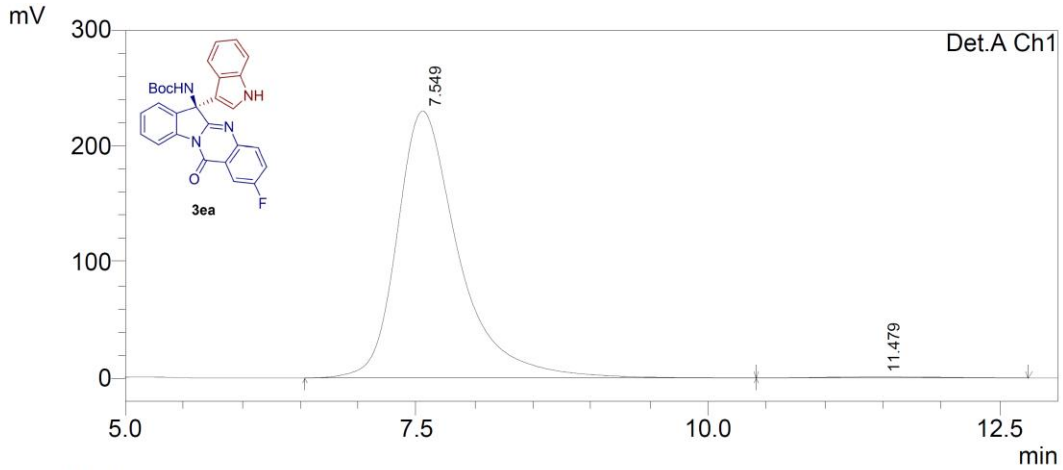


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.519	2916627	81609	48.994
2	11.407	3036384	41481	51.006
Total		5953011		100.000



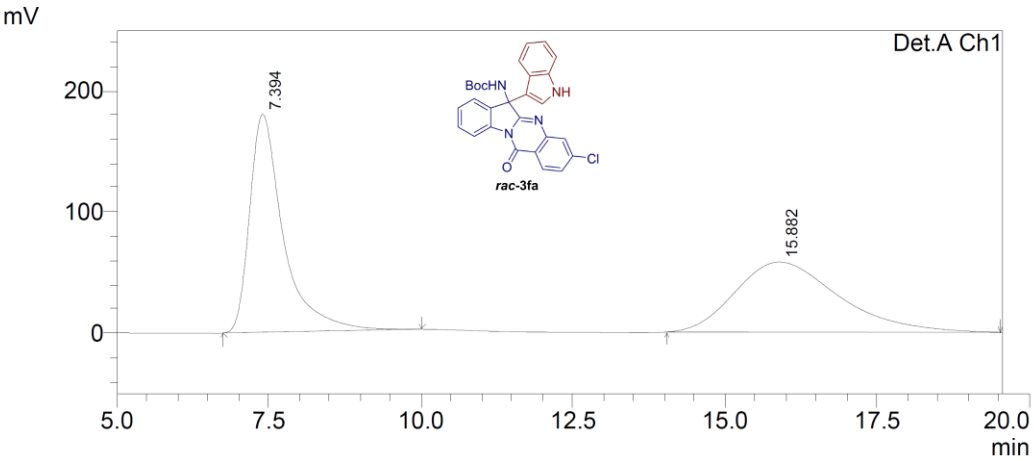
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.549	8451691	229713	99.127
2	11.479	74421	1167	0.873
Total		8526112		100.000

HPLC spectra of 3fa

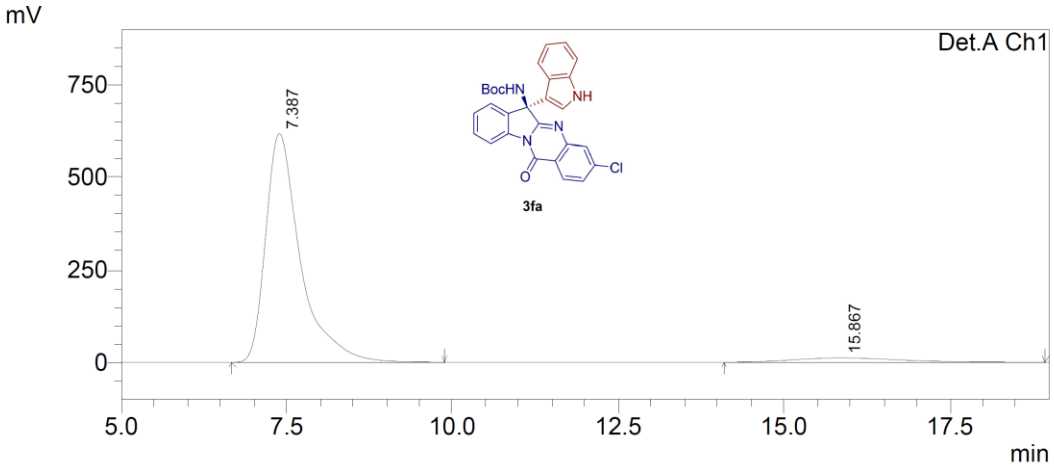


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.394	6931064	179617	50.324
2	15.882	6841915	57722	49.676
Total		13772979		100.000



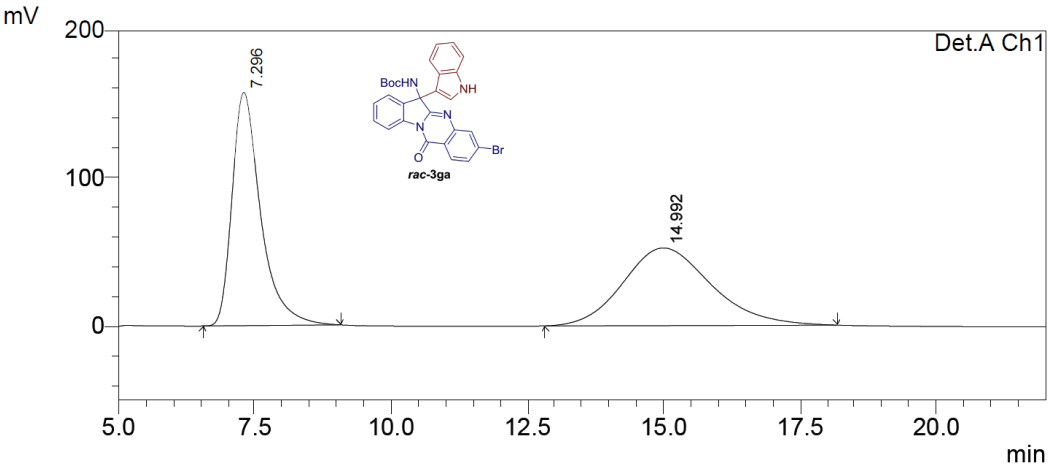
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.387	22477939	617301	94.486
2	15.867	1311768	11687	5.514
Total		23789706		100.000

HPLC spectra of 3ga

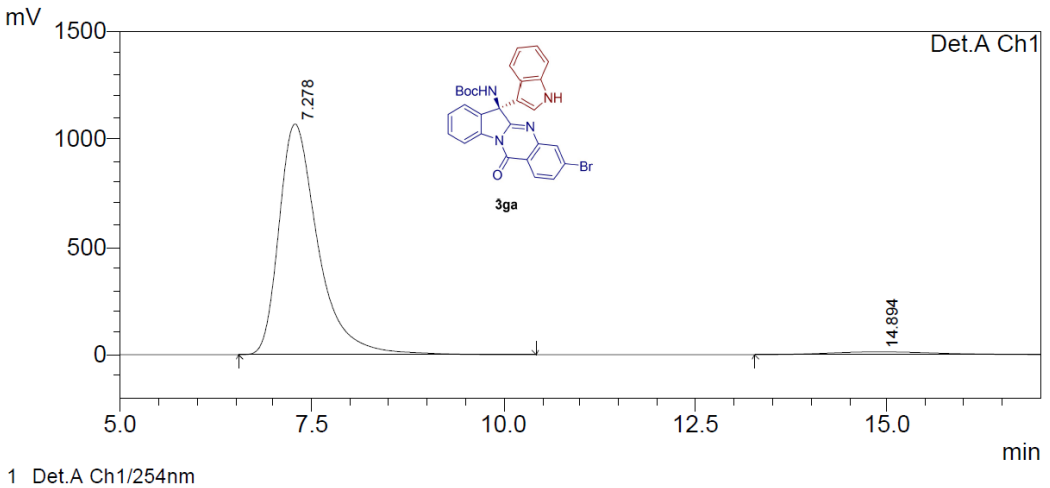


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.296	5756219	157619	49.352
2	14.992	5907426	52418	50.648
Total		11663645		100.000



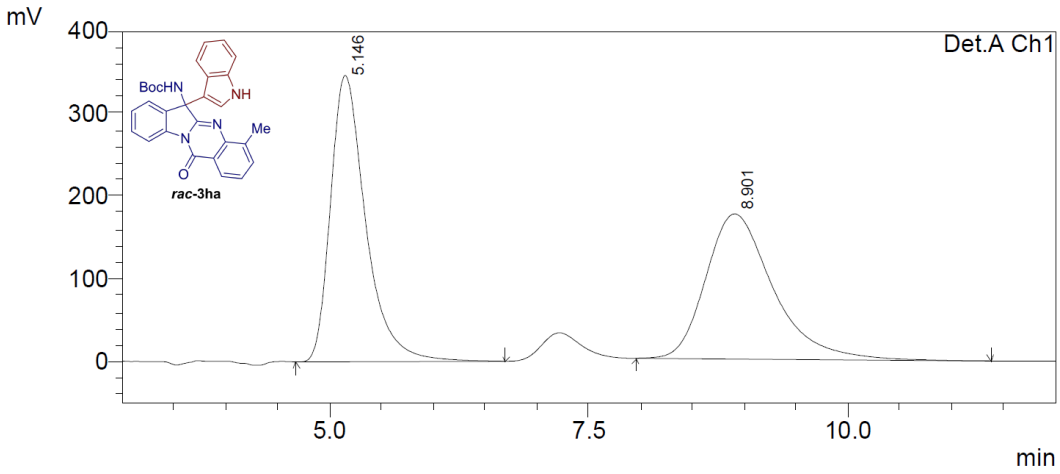
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.278	37885465	1068777	96.574
2	14.894	1343989	13039	3.426
Total		39229454		100.000

HPLC spectra of 3ha

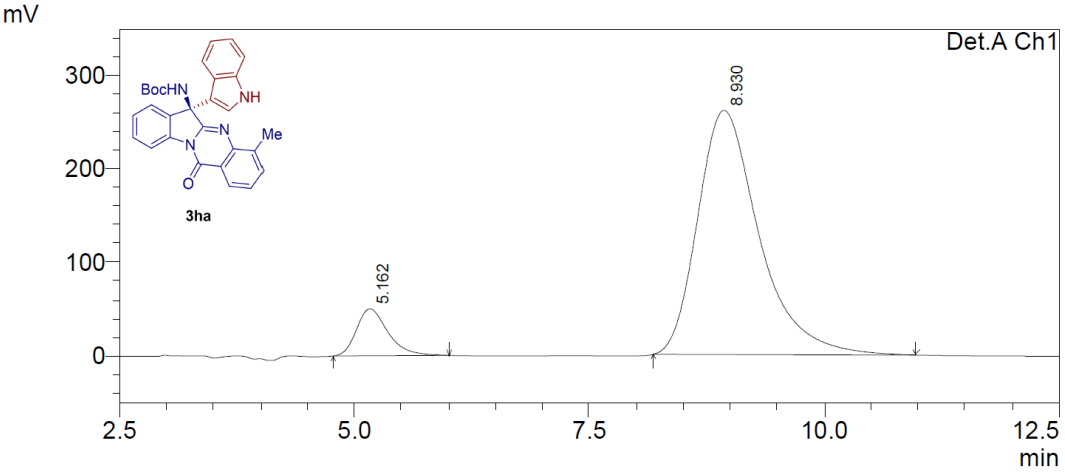


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	5.146	8182384	346154	50.784
2	8.901	7929853	175299	49.216
Total		16112238		100.000



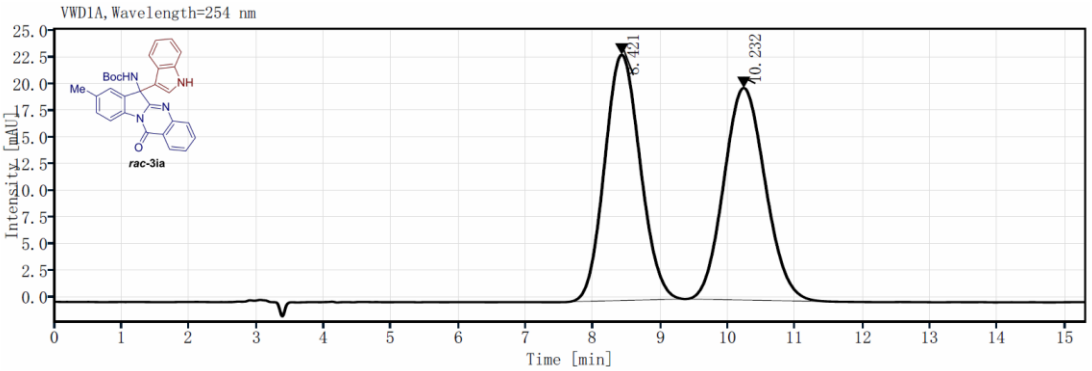
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

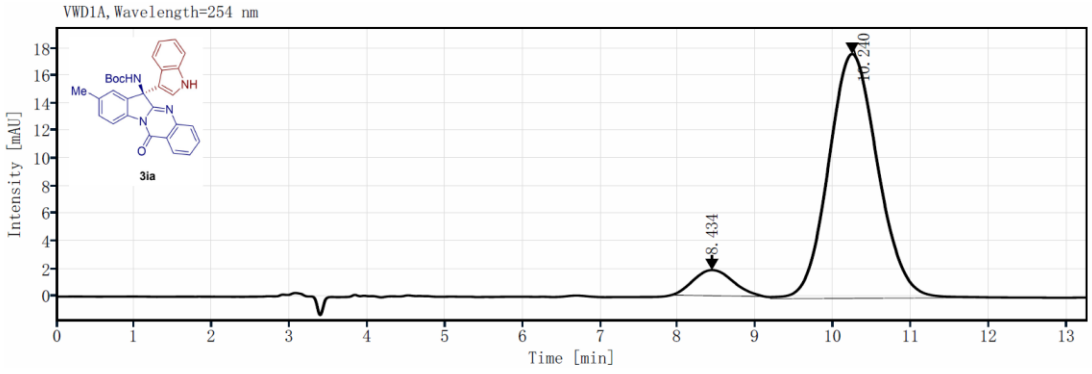
Peak#	Ret. Time	Area	Height	Area %
1	5.162	1169183	50152	8.988
2	8.930	11839355	260639	91.012
Total		13008538		100.000

HPLC spectra of 3ia



Signal: VWD1A, Wavelength=254 nm

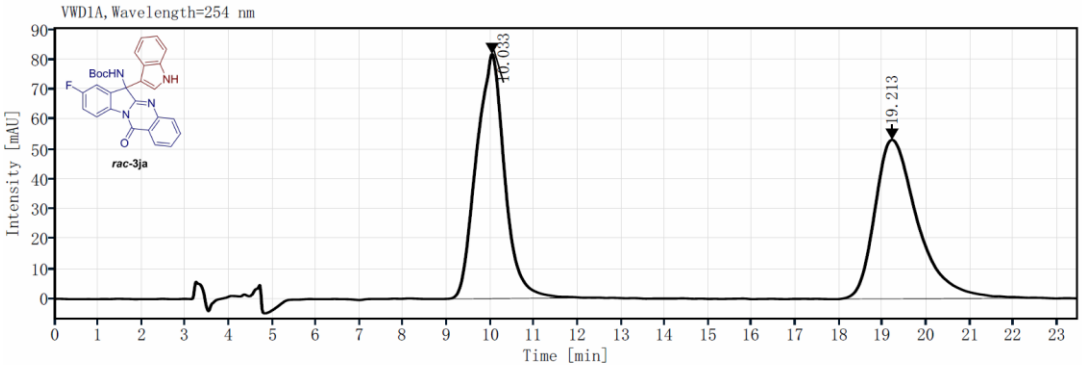
Retention Time [min]	Peak Width [min]	Peak Height [mAU]	Peak Height %	Peak Area [mAU*s]	Peak Area %
8.421	2.09	22.97	53.68	843.406	49.90
10.232	2.49	19.82	46.32	846.859	50.10
				Total	100.00



Signal: VWD1A, Wavelength=254 nm

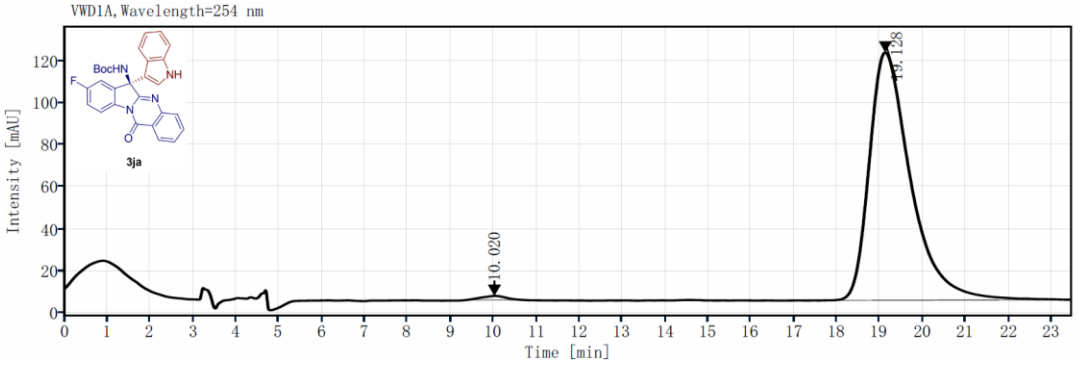
Retention Time [min]	Peak Width [min]	Peak Height [mAU]	Peak Height %	Peak Area [mAU*s]	Peak Area %
8.434	1.20	1.86	9.48	66.009	7.79
10.240	3.01	17.75	90.52	781.191	92.21
				Total	100.00

HPLC spectra of 3ja



Signal: VWD1A, Wavelength=254 nm

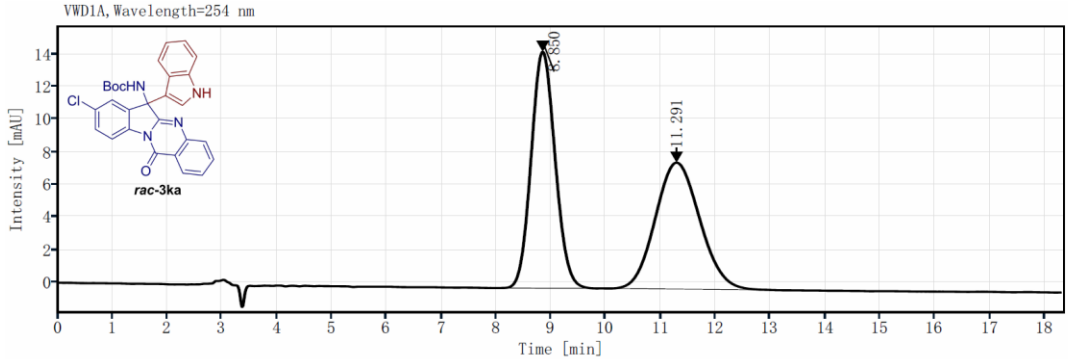
Retention Time [min]	Peak Width [min]	Peak Height [mAU]	Peak Height %	Peak Area [mAU*s]	Peak Area %
10.033	3.45	81.80	60.60	3687.293	50.41
19.213	5.11	53.17	39.40	3627.863	49.59
				Total	100.00



Signal: VWD1A, Wavelength=254 nm

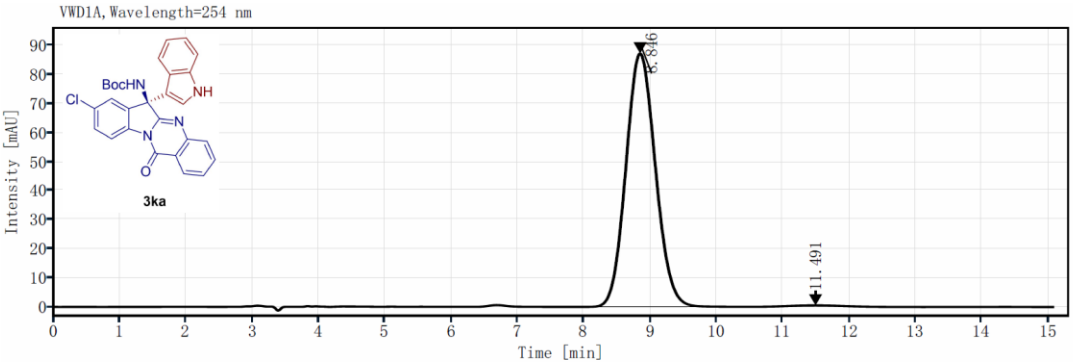
Retention Time [min]	Peak Width [min]	Peak Height [mAU]	Peak Height %	Peak Area [mAU*s]	Peak Area %
10.020	1.31	1.95	1.62	74.872	0.93
19.128	6.41	118.61	98.38	7938.759	99.07
				Total	100.00

HPLC spectra of 3ka



Signal: VWD1A, Wavelength=254 nm

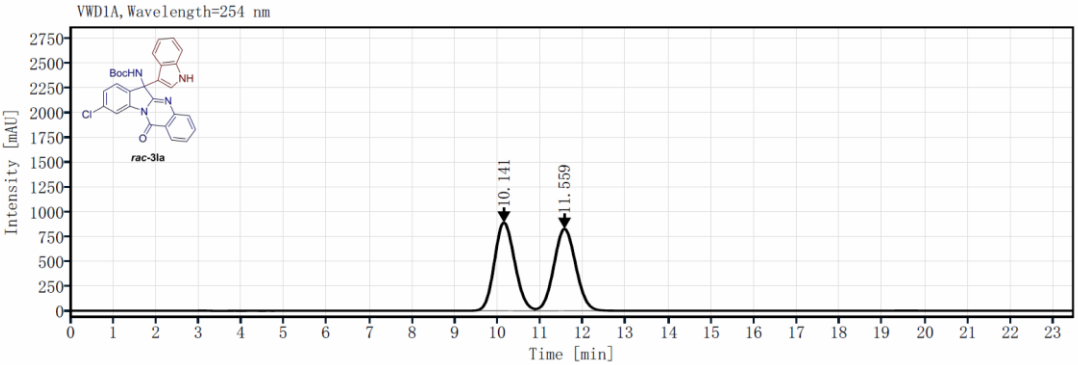
Retention Time [min]	Peak Width [min]	Peak Height [mAU]	Peak Height %	Peak Area [mAU*s]	Peak Area %
8.850	1.88	14.54	65.15	442.549	50.25
11.291	2.86	7.78	34.85	438.105	49.75
				Total	100.00



Signal: VWD1A, Wavelength=254 nm

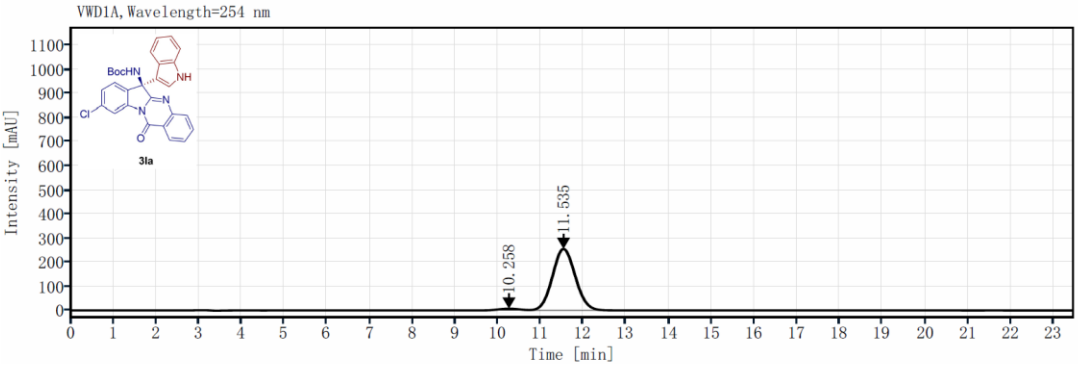
Retention Time [min]	Peak Width [min]	Peak Height [mAU]	Peak Height %	Peak Area [mAU*s]	Peak Area %
8.846	2.18	87.38	99.63	2701.298	99.53
11.491	1.07	0.32	0.37	12.660	0.47
				Total	100.00

HPLC spectra of 3la



Signal: VWD1A, Wavelength=254 nm

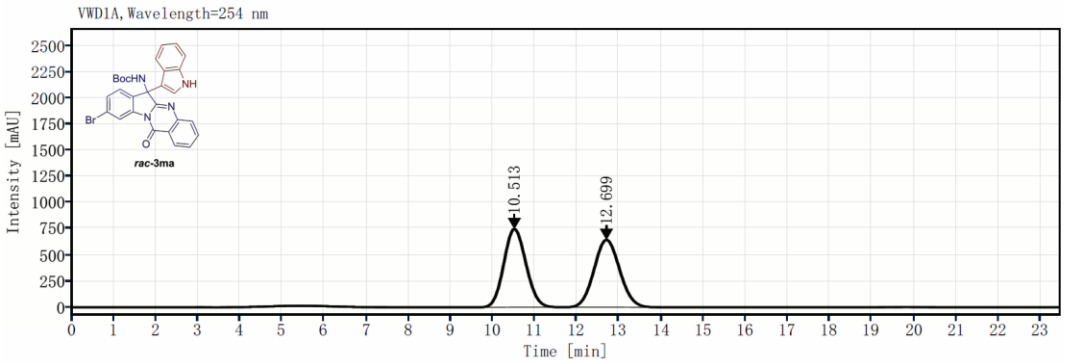
Retention Time [min]	Peak Width [min]	Peak Height [mAU]	Peak Height %	Peak Area [mAU*s]	Peak Area %
10.141	1.56	893.50	51.84	29476.824	49.91
11.559	1.90	830.20	48.16	29579.699	50.09
				Total	100.00



Signal: VWD1A, Wavelength=254 nm

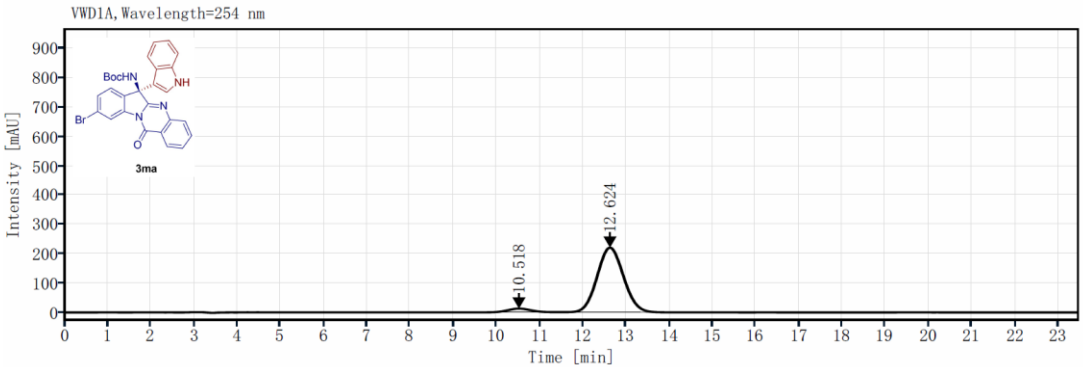
Retention Time [min]	Peak Width [min]	Peak Height [mAU]	Peak Height %	Peak Area [mAU*s]	Peak Area %
10.258	1.08	7.27	2.76	238.781	2.44
11.535	2.23	255.79	97.24	9535.015	97.56
				Total	100.00

HPLC spectra of 3ma



Signal: VWD1A, Wavelength=254 nm

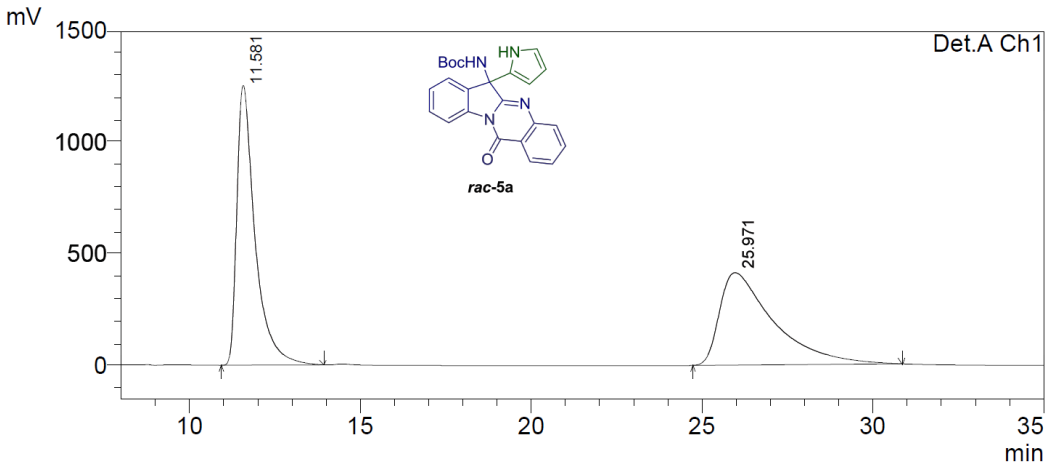
Retention Time [min]	Peak Width [min]	Peak Height [mAU]	Peak Height %	Peak Area [mAU*s]	Peak Area %
10.513	2.24	751.58	53.72	27533.950	50.06
12.699	2.37	647.50	46.28	27472.180	49.94
				Total	100.00



Signal: VWD1A, Wavelength=254 nm

Retention Time [min]	Peak Width [min]	Peak Height [mAU]	Peak Height %	Peak Area [mAU*s]	Peak Area %
10.518	1.14	11.63	5.01	391.809	4.03
12.624	3.12	220.48	94.99	9334.151	95.97
				Total	100.00

HPLC spectra of 5a

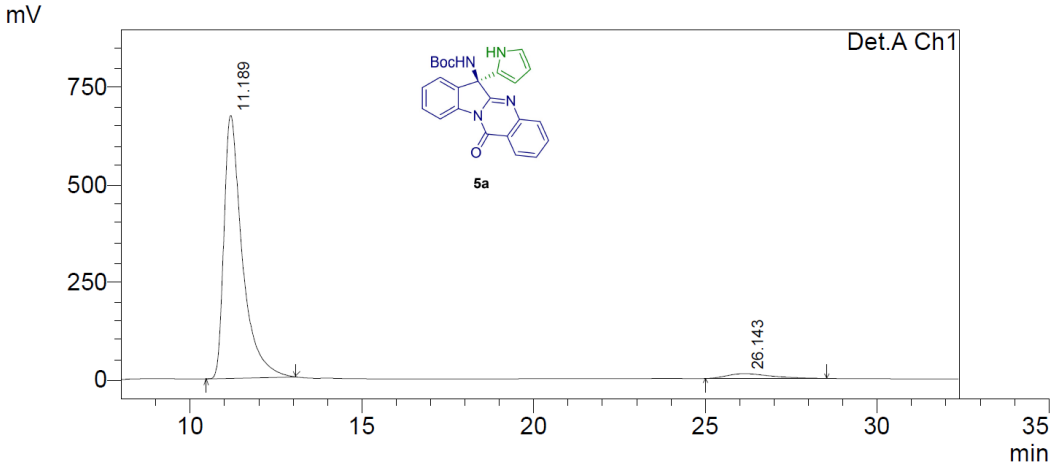


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	11.581	46392575	1252476	50.504
2	25.971	45466984	413888	49.496
Total		91859559		100.000



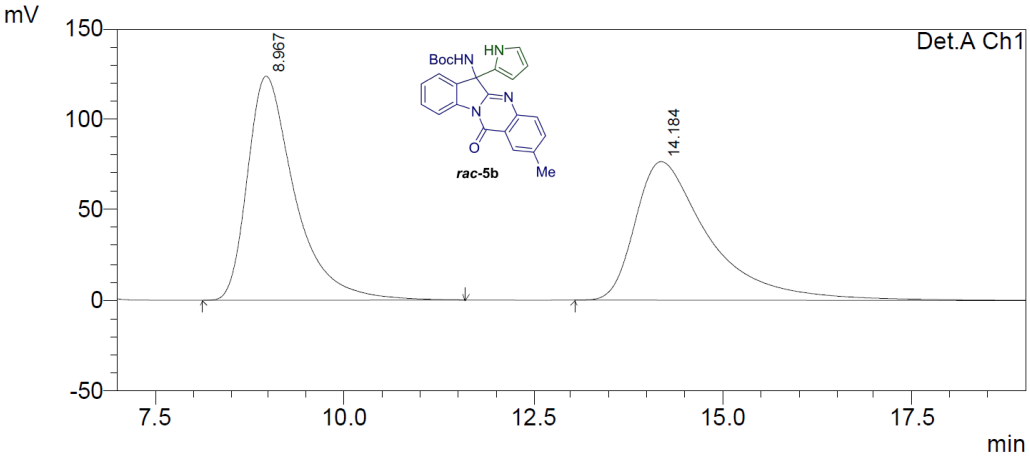
1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	11.189	25055729	674536	95.854
2	26.143	1083730	12329	4.146
Total		26139459		100.000

HPLC spectra of 5b

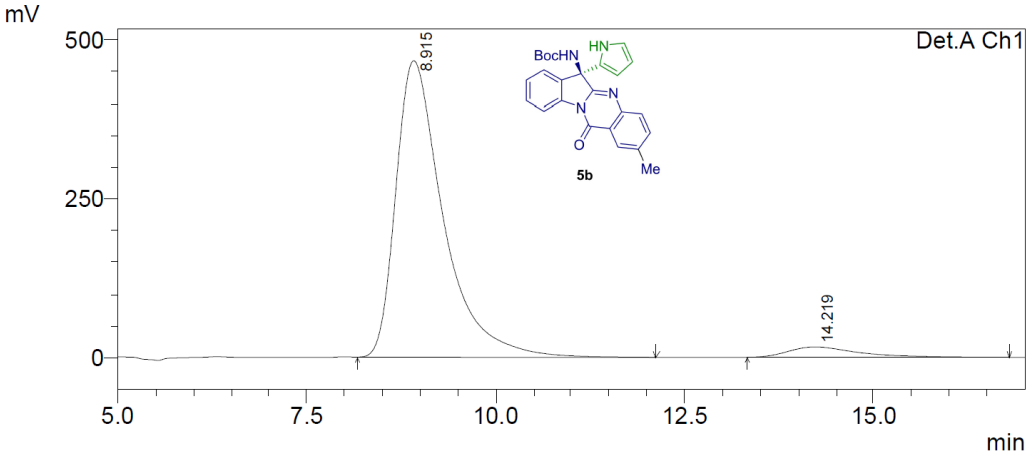


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.967	5371336	123587	50.732
2	14.184	5216347	76449	49.268
Total		10587683		100.000



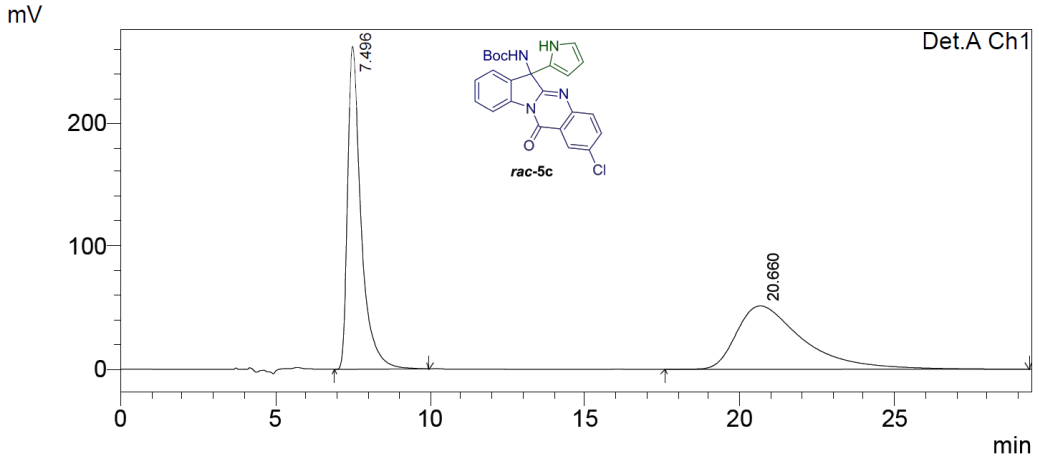
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.915	20416401	467255	95.079
2	14.219	1056773	16421	4.921
Total		21473175		100.000

HPLC spectra of 5c

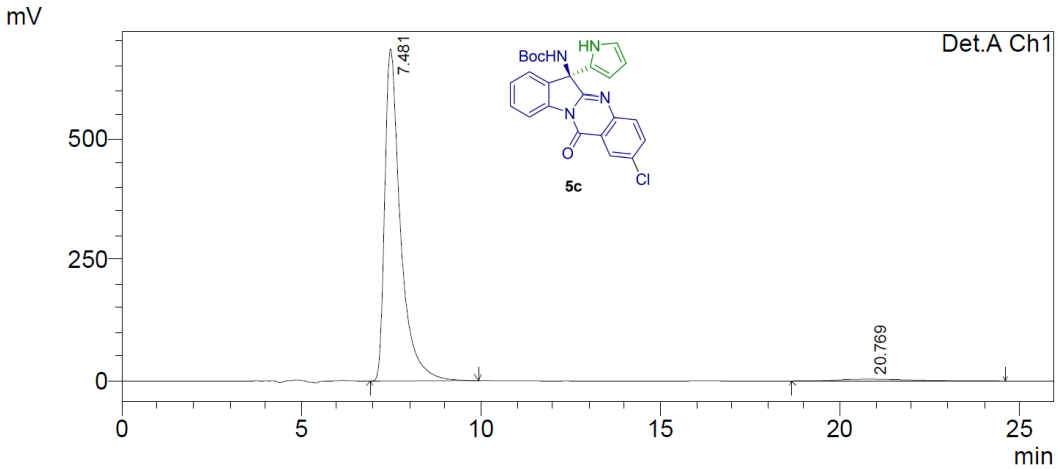


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.496	7924849	262142	50.645
2	20.660	7723118	51566	49.355
Total		15647966		100.000



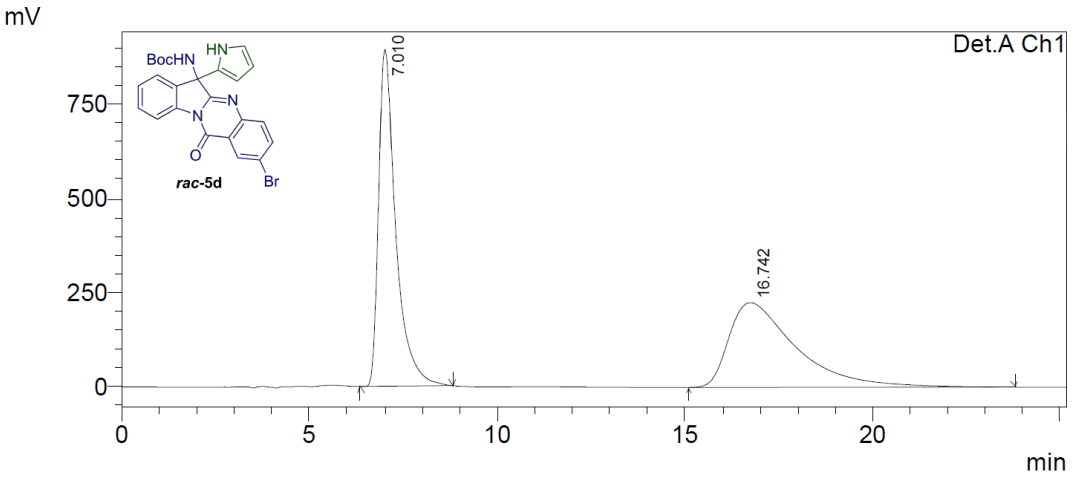
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.481	20878355	684611	97.769
2	20.769	476474	3562	2.231
Total		21354829		100.000

HPLC spectra of 5d

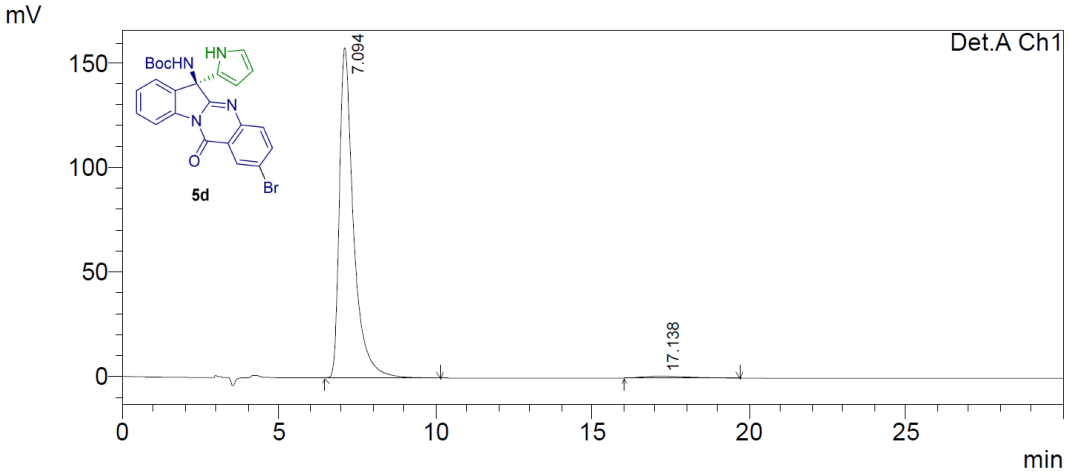


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.010	28470585	894412	50.417
2	16.742	27999606	225065	49.583
Total		56470191		100.000



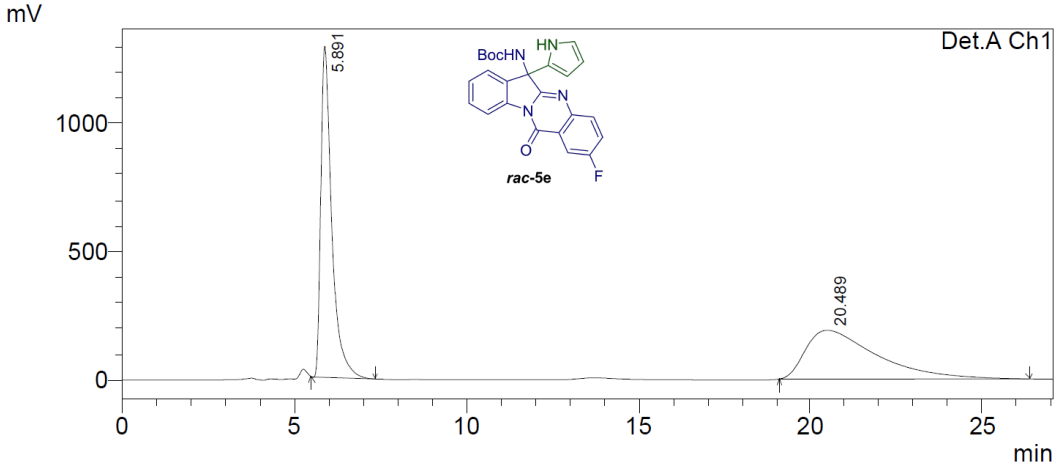
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.094	4949999	158293	98.172
2	17.138	92179	911	1.828
Total		5042178		100.000

HPLC spectra of 5e

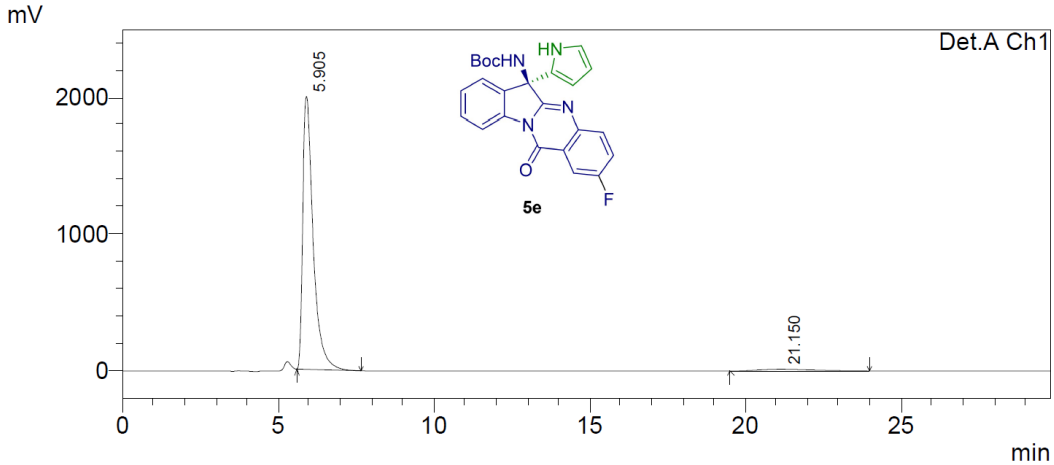


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	5.891	28501065	1289229	51.041
2	20.489	27338324	190123	48.959
Total		55839390		100.000



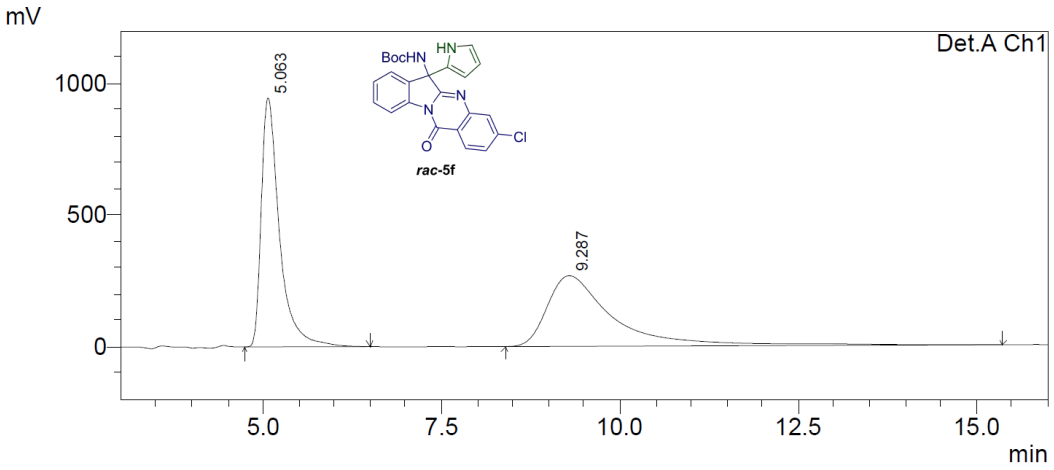
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	5.905	46222637	1993379	96.710
2	21.150	1572585	12989	3.290
Total		47795222		100.000

HPLC spectra of 5f

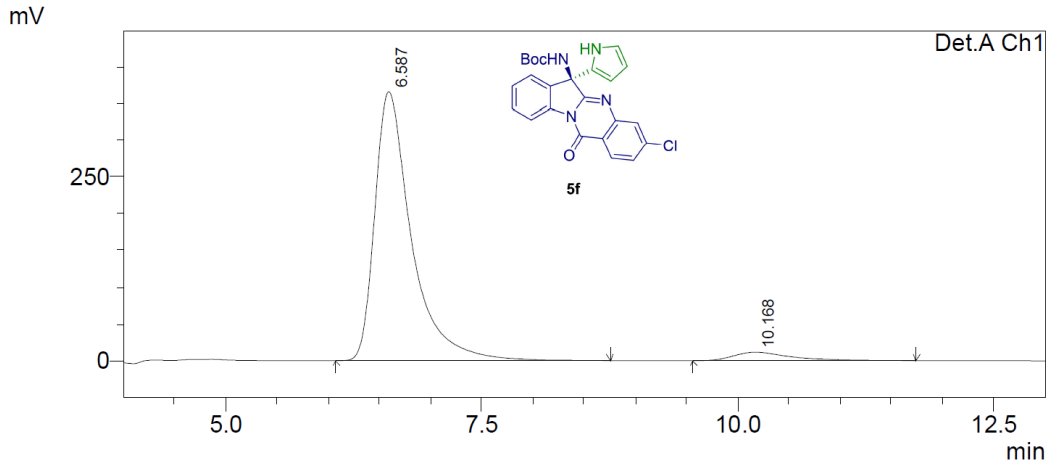


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	5.063	16737973	943328	49.117
2	9.287	17339730	267805	50.883
Total		34077703		100.000



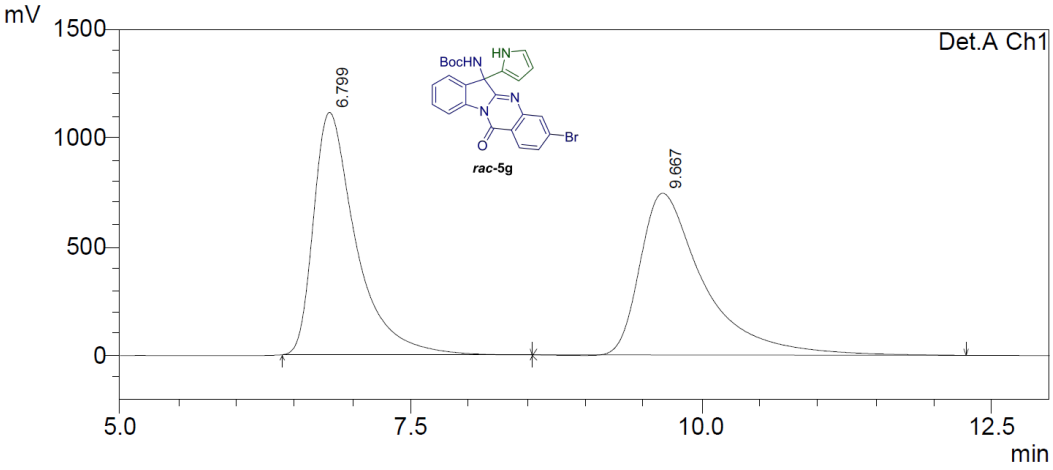
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	6.587	9115110	365826	95.280
2	10.168	451500	11588	4.720
Total		9566610		100.000

HPLC spectra of 5g

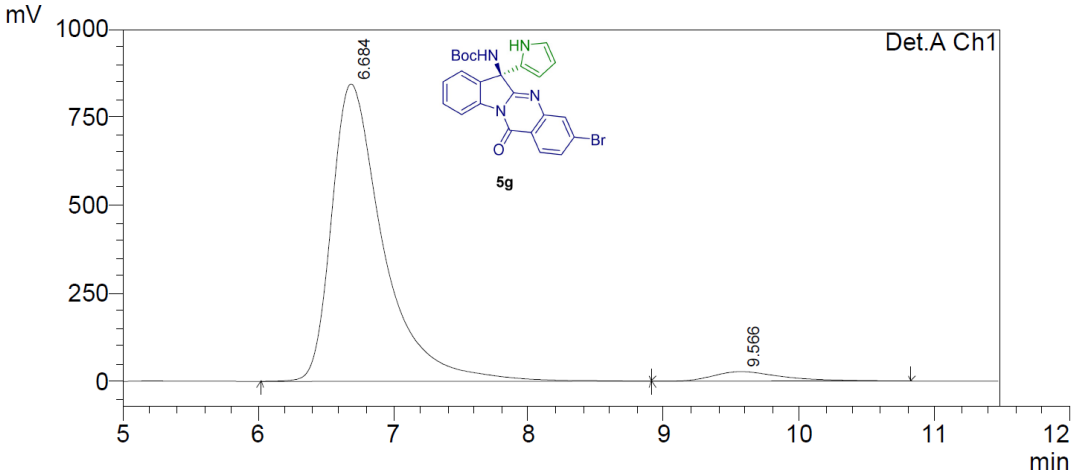


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	6.799	28212197	1110582	49.935
2	9.667	28286085	741321	50.065
Total		56498282		100.000



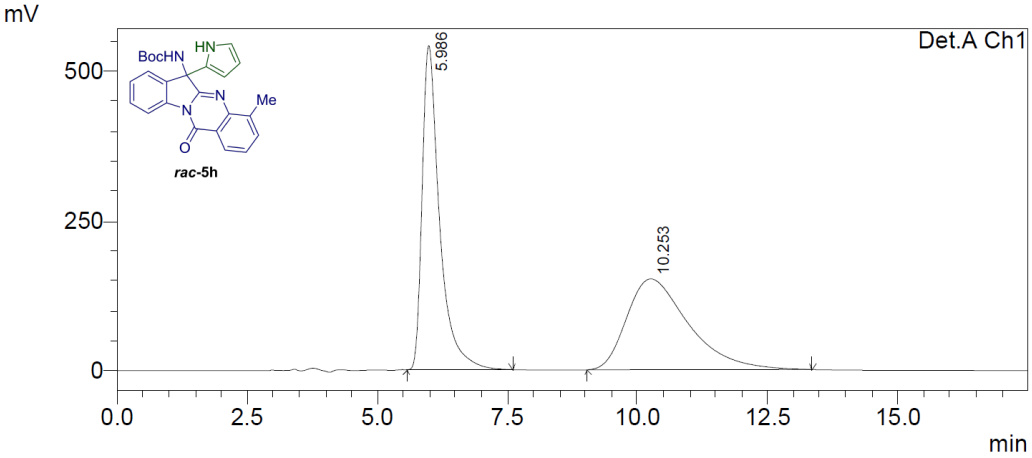
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	6.684	22452402	842406	95.901
2	9.566	959666	26998	4.099
Total		23412068		100.000

HPLC spectra of 5h

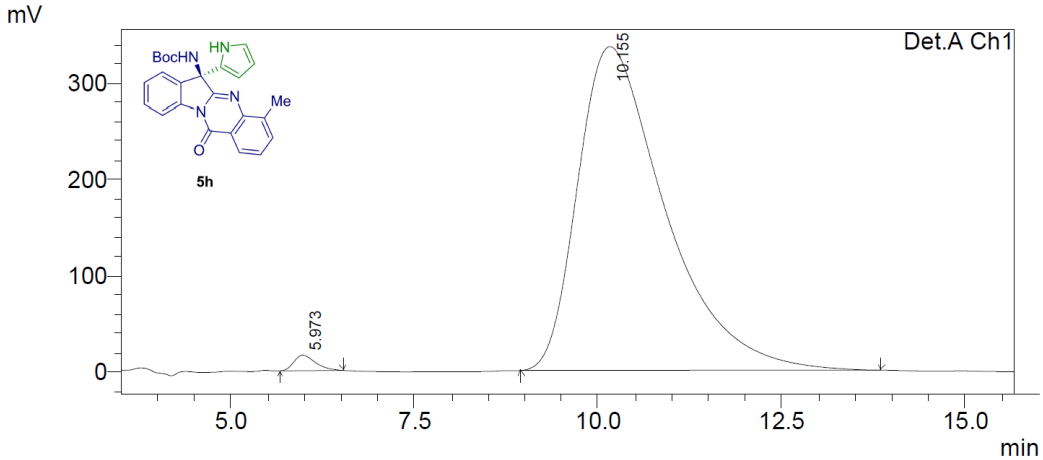


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	5.986	12615040	540844	50.175
2	10.253	12526813	151581	49.825
Total		25141853		100.000



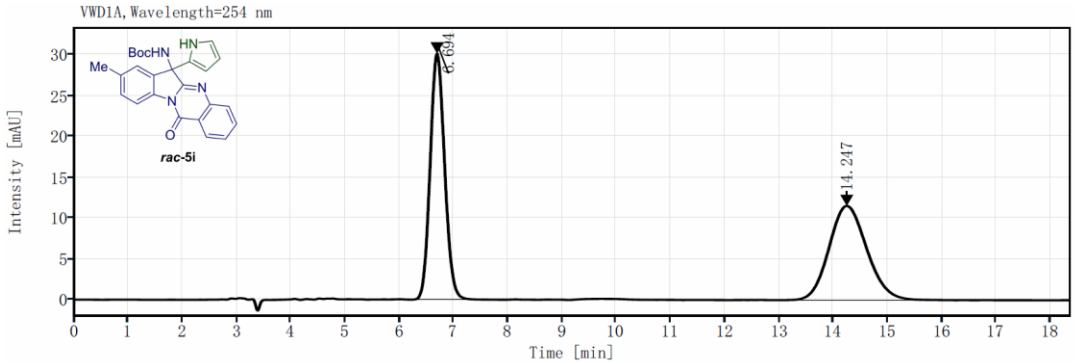
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

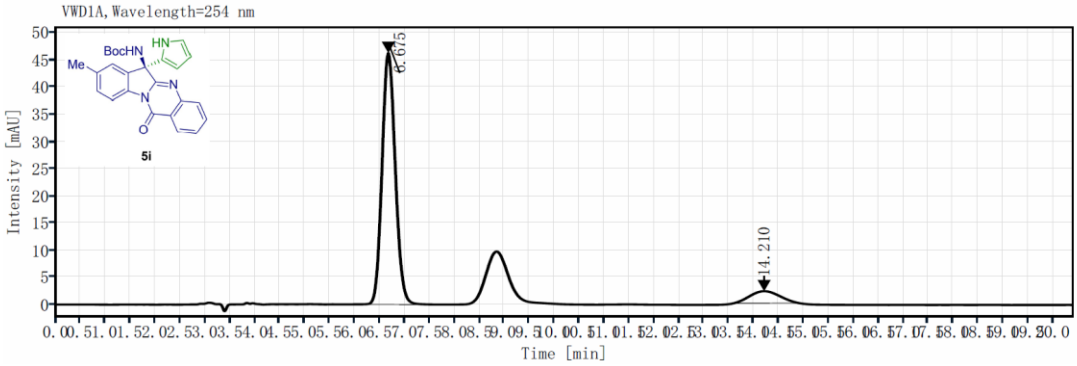
Peak#	Ret. Time	Area	Height	Area %
1	5.973	330562	16174	1.171
2	10.155	27906521	336355	98.829
Total		28237083		100.000

HPLC spectra of 5i



Signal: VWD1A, Wavelength=254 nm

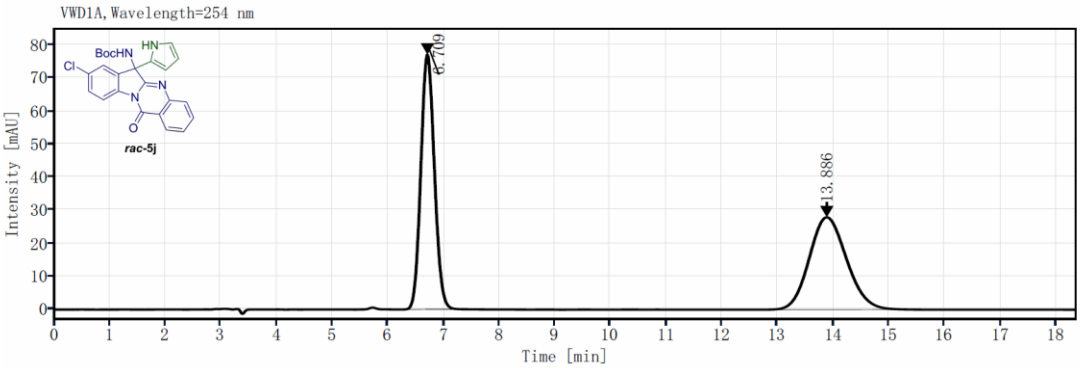
Retention Time [min]	Peak Width [min]	Peak Height [mAU]	Peak Height %	Peak Area [mAU*s]	Peak Area %
6.694	1.69	30.13	72.30	558.669	49.92
14.247	3.32	11.55	27.70	560.536	50.08
				Total	100.00



Signal: VWD1A, Wavelength=254 nm

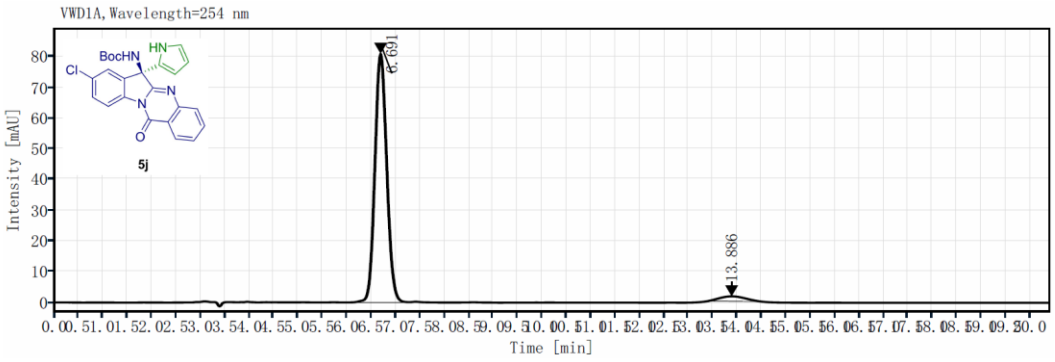
Retention Time [min]	Peak Width [min]	Peak Height [mAU]	Peak Height %	Peak Area [mAU*s]	Peak Area %
6.675	1.82	46.31	95.45	855.144	90.33
14.210	1.31	2.21	4.55	91.560	9.67
				Total	100.00

HPLC spectra of 5j



Signal: VWD1A, Wavelength=254 nm

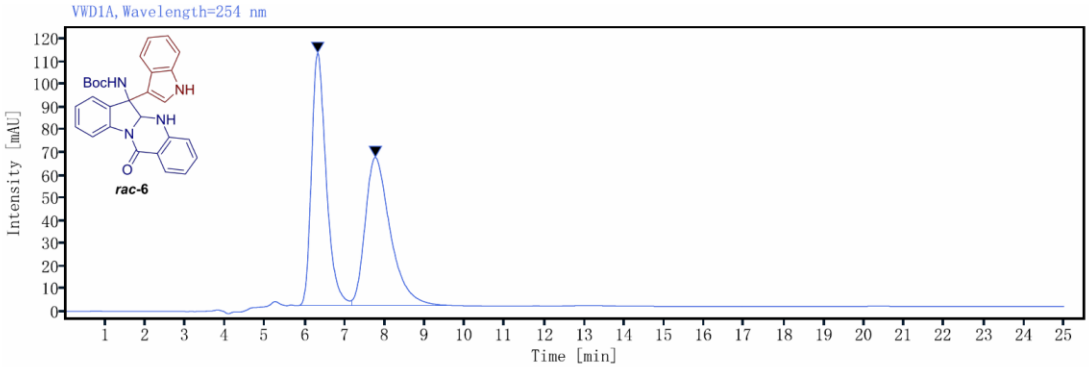
Retention Time [min]	Peak Width [min]	Peak Height [mAU]	Peak Height %	Peak Area [mAU*s]	Peak Area %
6.709	1.32	76.99	73.40	1304.281	50.04
13.886	2.79	27.90	26.60	1302.021	49.96
				Total	100.00



Signal: VWD1A, Wavelength=254 nm

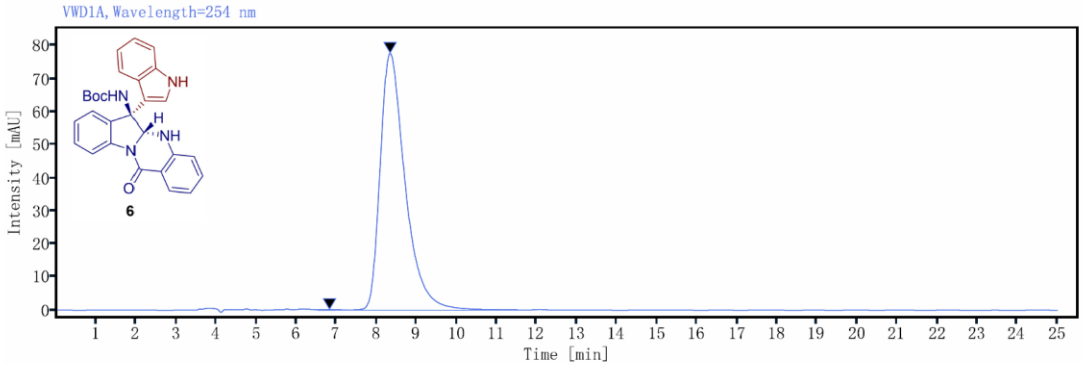
Retention Time [min]	Peak Width [min]	Peak Height [mAU]	Peak Height %	Peak Area [mAU*s]	Peak Area %
6.691	1.77	81.01	98.05	1373.405	95.86
13.886	1.10	1.61	1.95	59.269	4.14
				Total	100.00

HPLC spectra of 6



Signal: VWD1A, Wavelength=254 nm

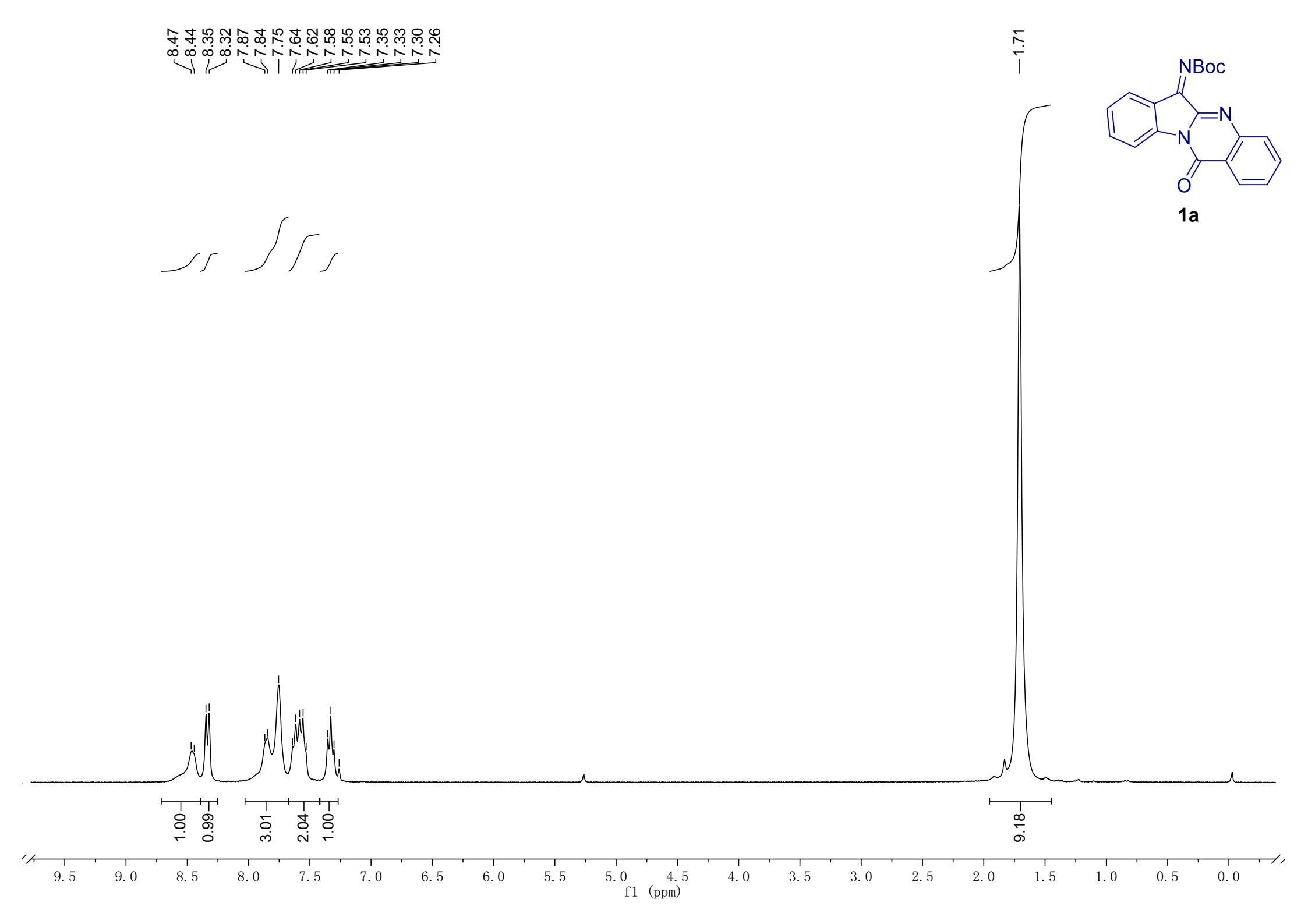
Retention Time [min]	Peak Width [min]	Peak Height [mAU]	Peak Height %	Peak Area [mAU*s]	Peak Area %
6.321	4.05	111.47	63.01	2855.115	49.88
7.762	2.65	65.43	36.99	2868.995	50.12
				Total	100.00

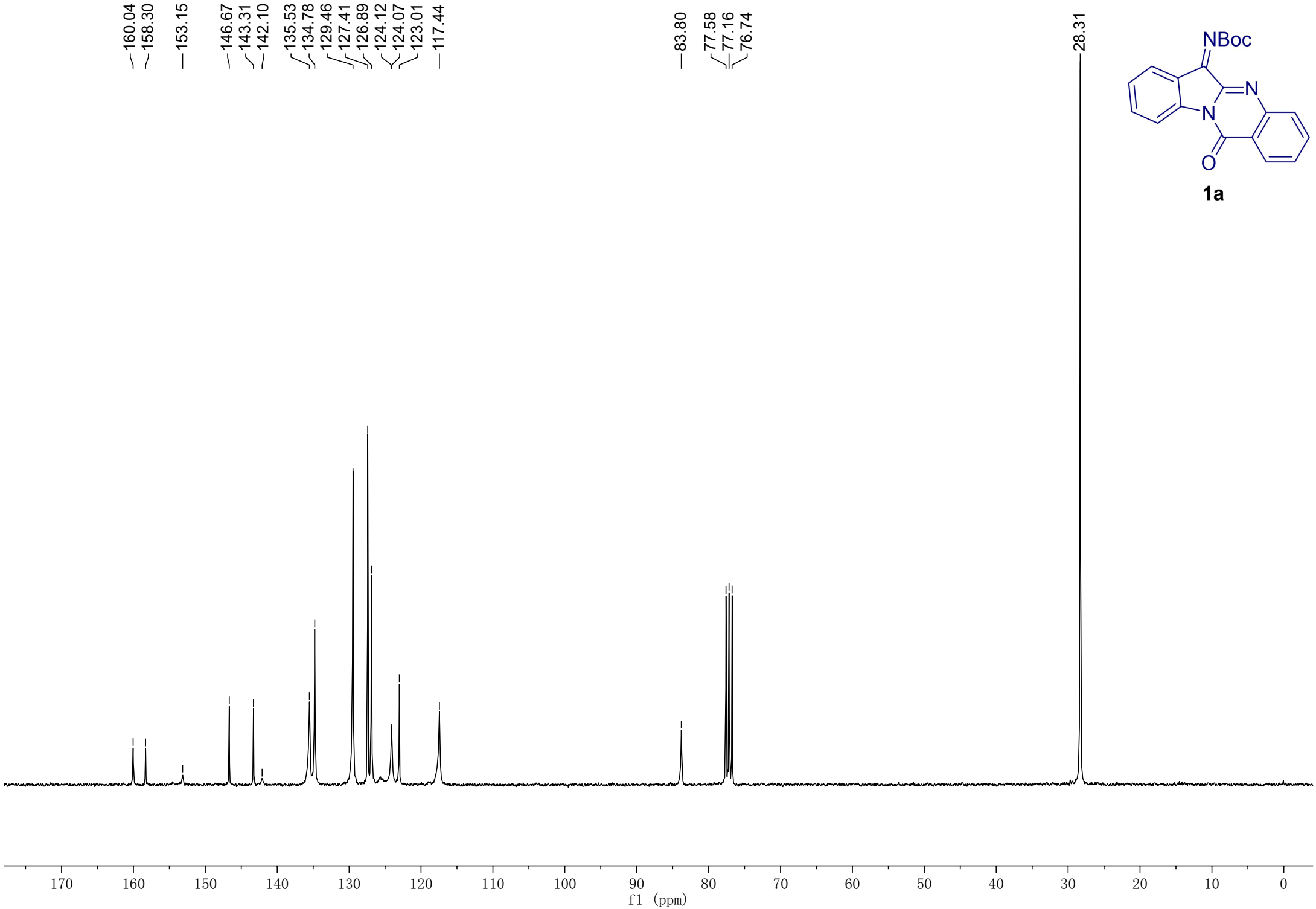


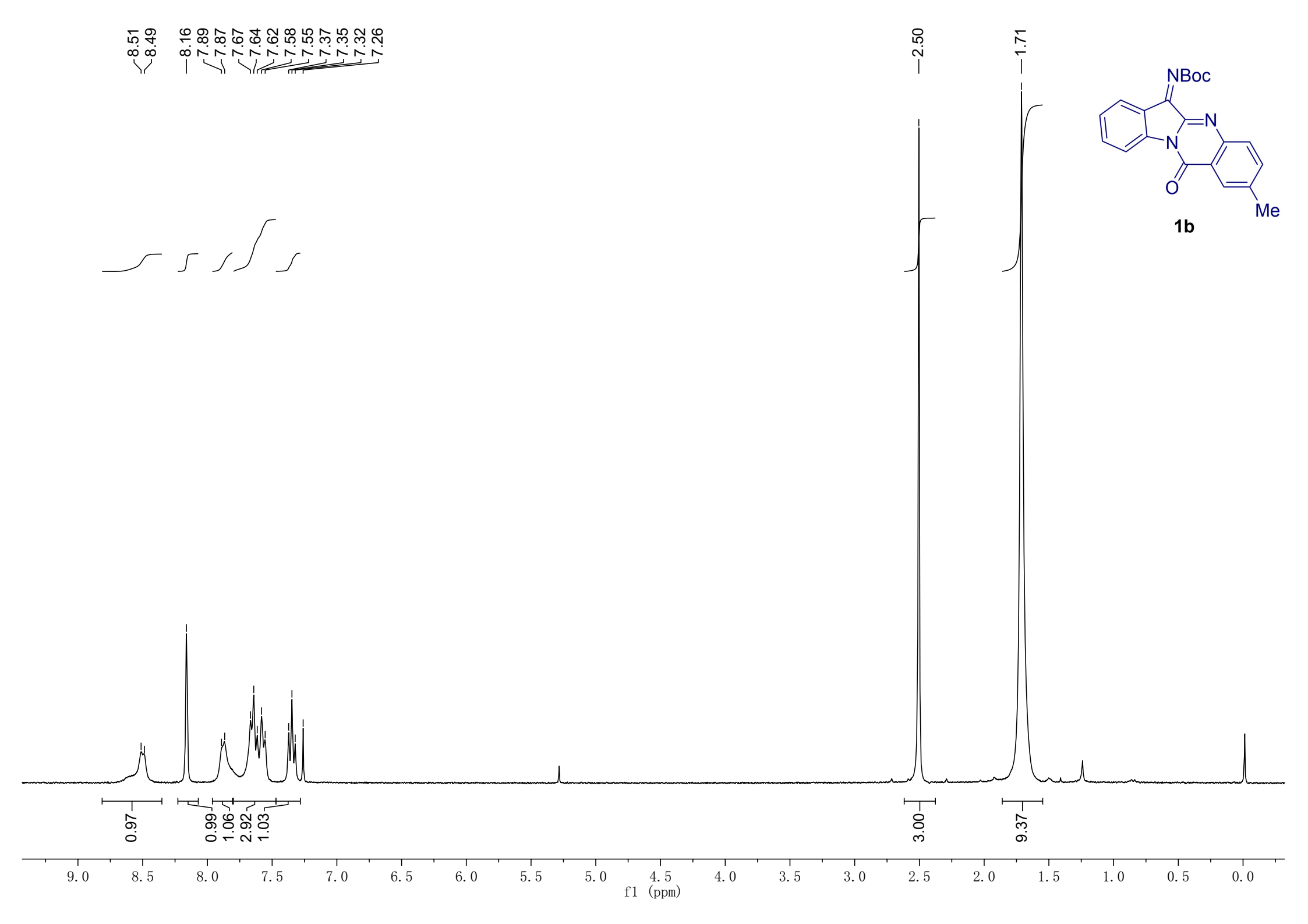
Signal: VWD1A, Wavelength=254 nm

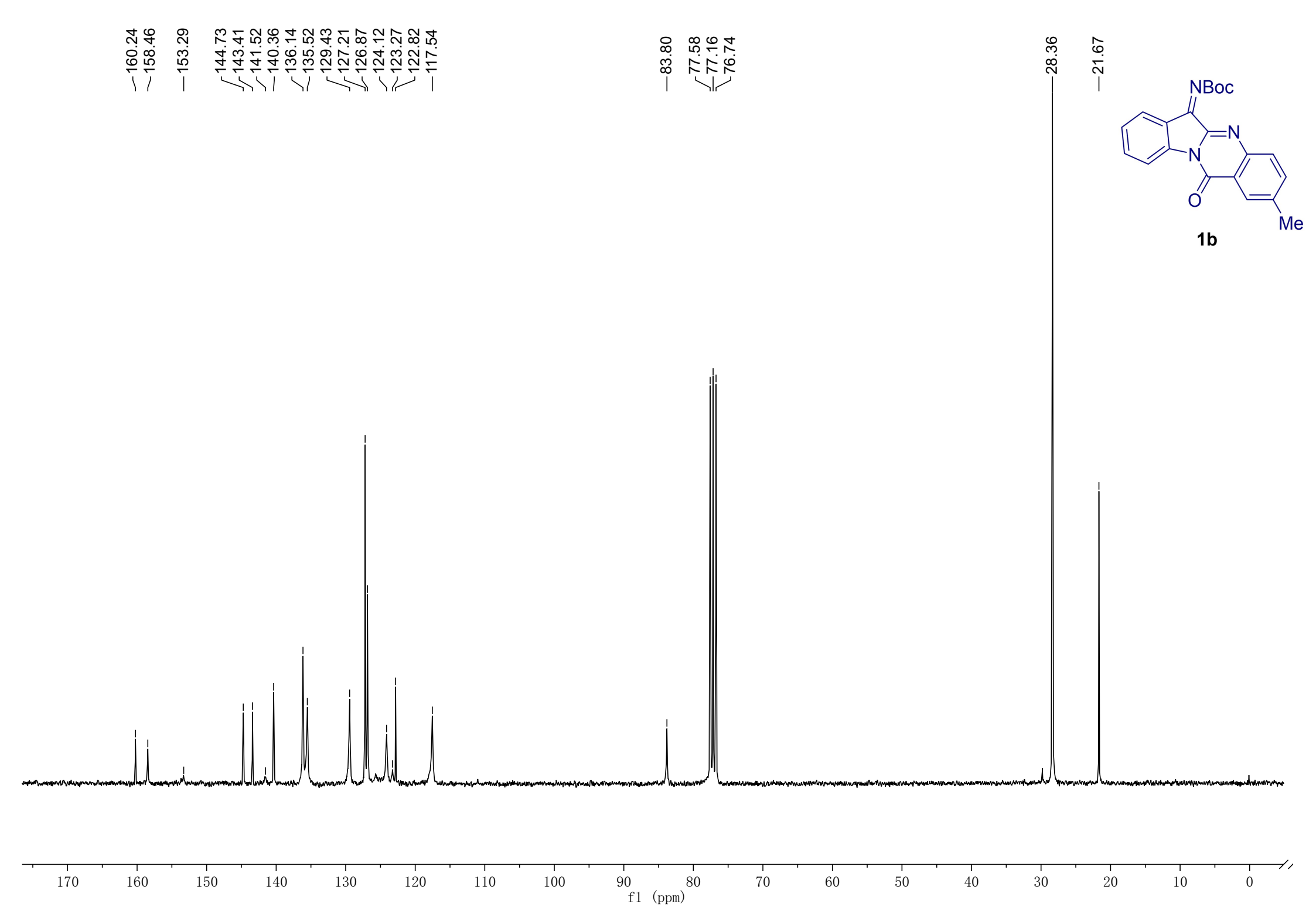
Retention Time [min]	Peak Width [min]	Peak Height [mAU]	Peak Height %	Peak Area [mAU*s]	Peak Area %
6.829	0.74	0.18	0.23	5.224	0.16
8.342	4.45	77.69	99.77	3363.413	99.84
				Total	100.00

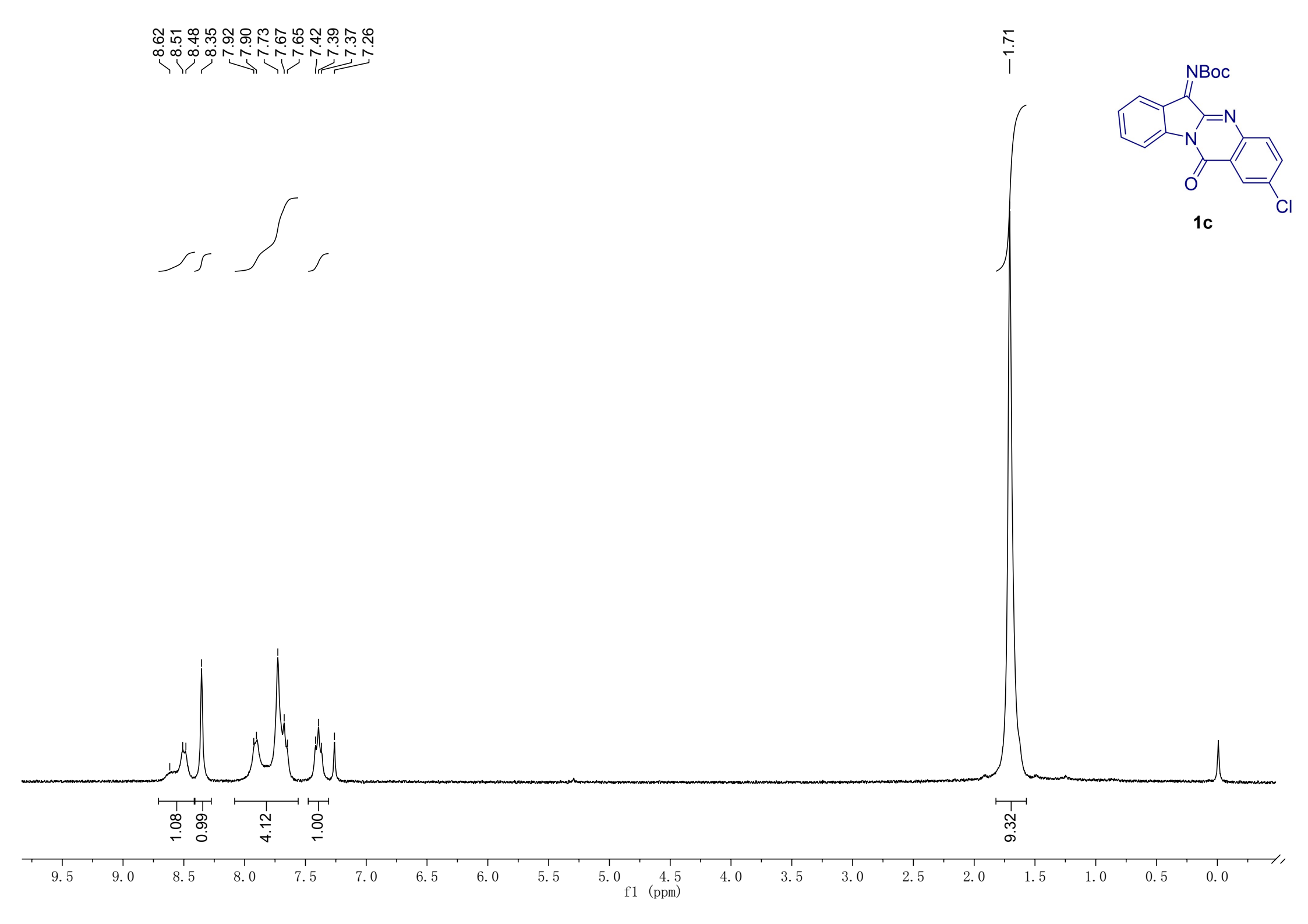
11. NMR spectra of compounds 1, 3, 5, and 6

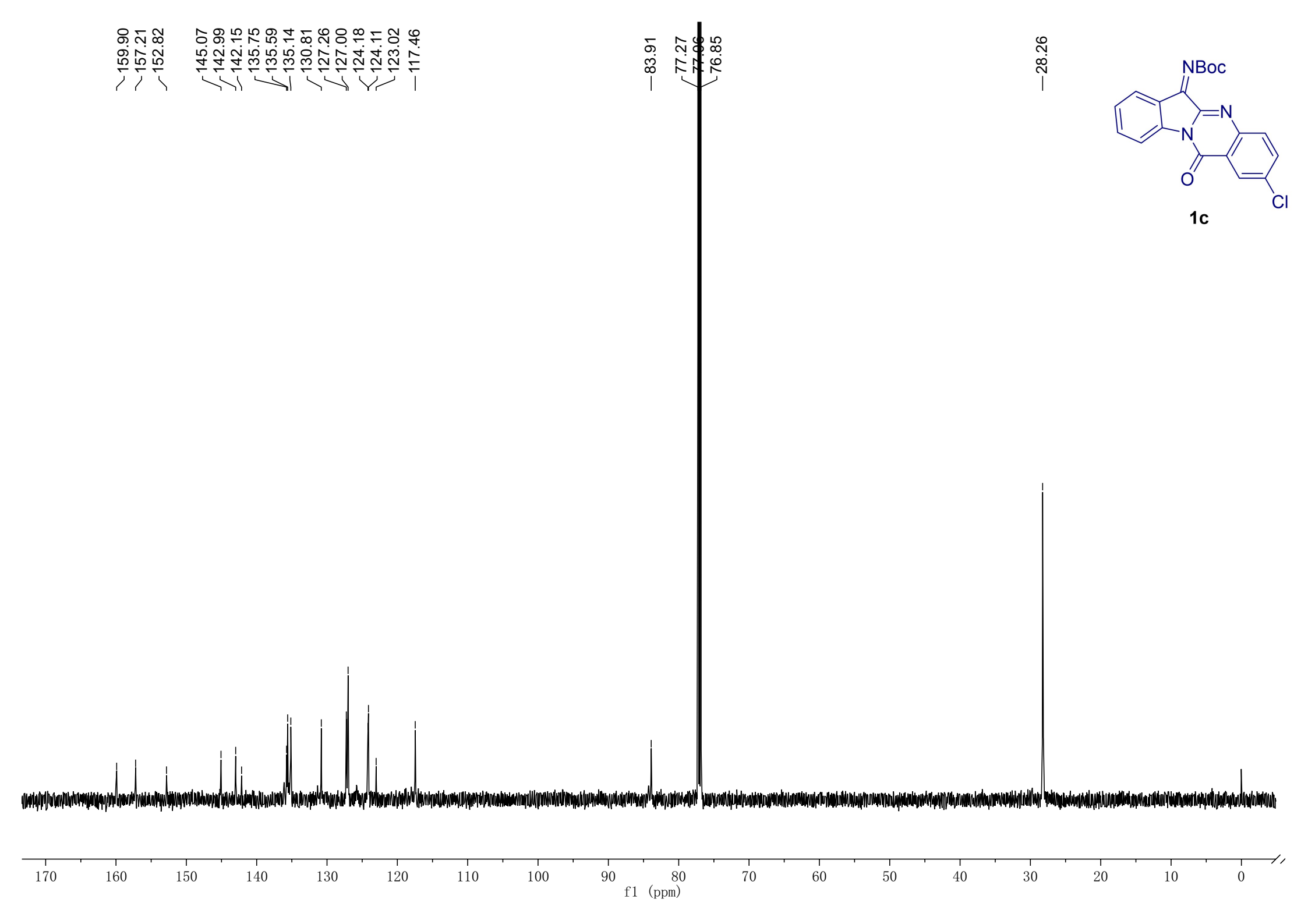

8.47
8.44
8.35
8.32
7.87
7.84
7.75
7.64
7.62
7.58
7.55
7.53
7.35
7.33
7.30
7.26
1.71
NBoc
N
N
O
1a
1.00
0.99
3.01
2.04
1.00
9.18
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


160.04
158.30
153.15
146.67
143.31
142.10
135.53
134.78
129.46
127.41
126.89
124.12
124.07
123.01
117.44
83.80
77.58
77.16
76.74
28.31
NBoc
N
N
O
1a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.51
8.49
8.16
7.89
7.87
7.67
7.64
7.62
7.58
7.55
7.37
7.35
7.32
7.26
2.50
1.71
NBoc
N
N
O
Me
1b
0.97
0.99
1.06
2.92
1.03
3.00
9.37
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


160.24
158.46
153.29
144.73
143.41
141.52
140.36
136.14
135.52
129.43
127.21
126.87
124.12
123.27
122.82
117.54
83.80
77.58
77.16
76.74
28.36
21.67
NBoc
N
N
O
Me
1b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.62
8.51
8.48
8.35
7.92
7.90
7.73
7.67
7.65
7.42
7.39
7.37
7.26
1.71
NBoc
N
N
O
Cl
1c
1.08
0.99
4.12
1.00
9.32
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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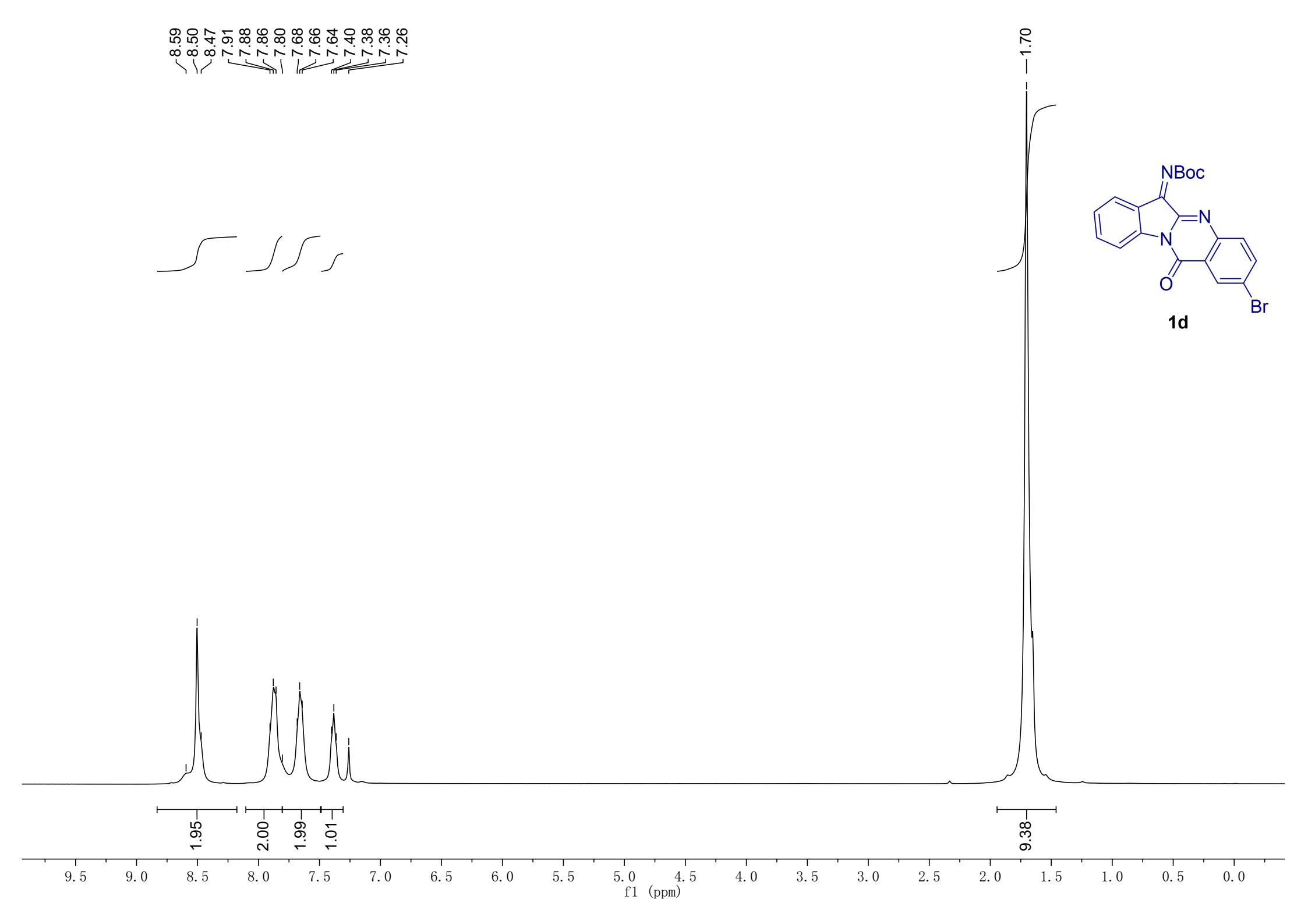
157.21
152.82
145.07
142.99
142.15
135.75
135.59
135.14
130.81
127.26
127.00
124.18
124.11
123.02
117.46
83.91
77.27
77.06
76.85
28.26
NBoc
N
N
O
Cl
1c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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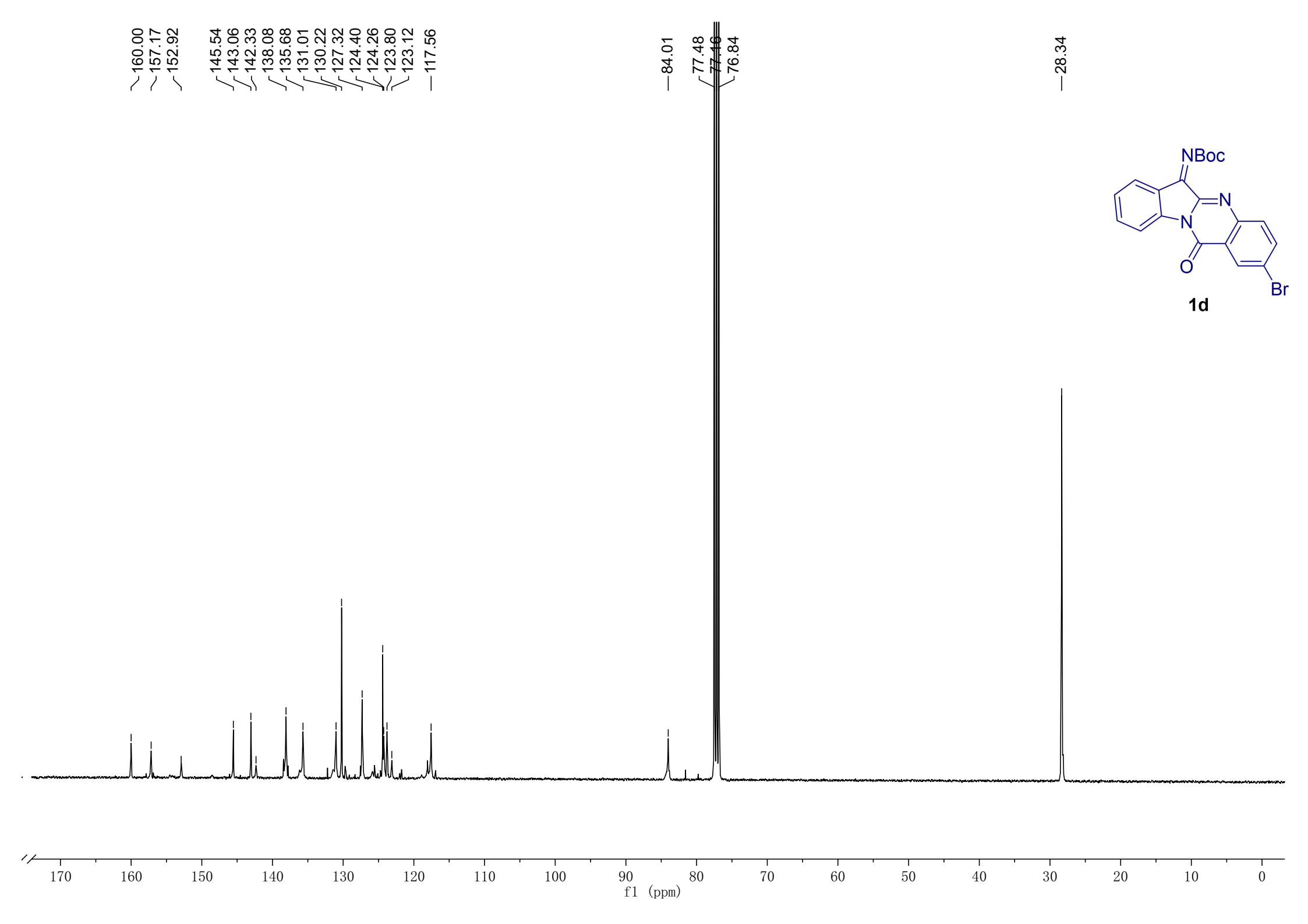
7.88
7.86
7.80
7.68
7.66
7.64
7.40
7.38
7.36
7.26
1.70
NBoc
N
N
O
Br
1d
1.95
2.00
1.99
1.01
9.38
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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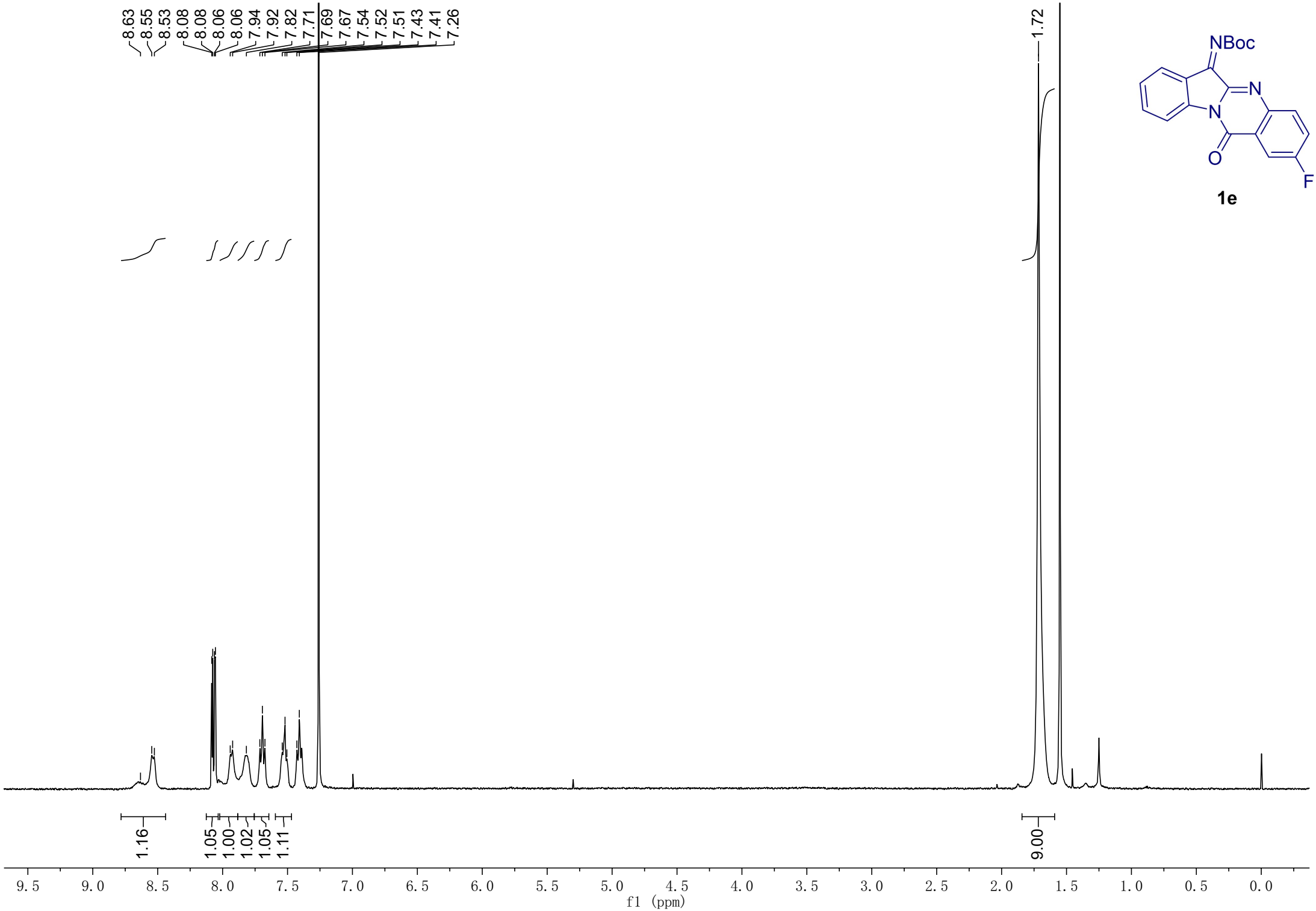
157.17
152.92
145.54
143.06
142.33
138.08
135.68
131.01
130.22
127.32
124.40
124.26
123.80
123.12
117.56
84.01
77.48
77.16
76.84
28.34
NBoc
N
N
O
Br
1d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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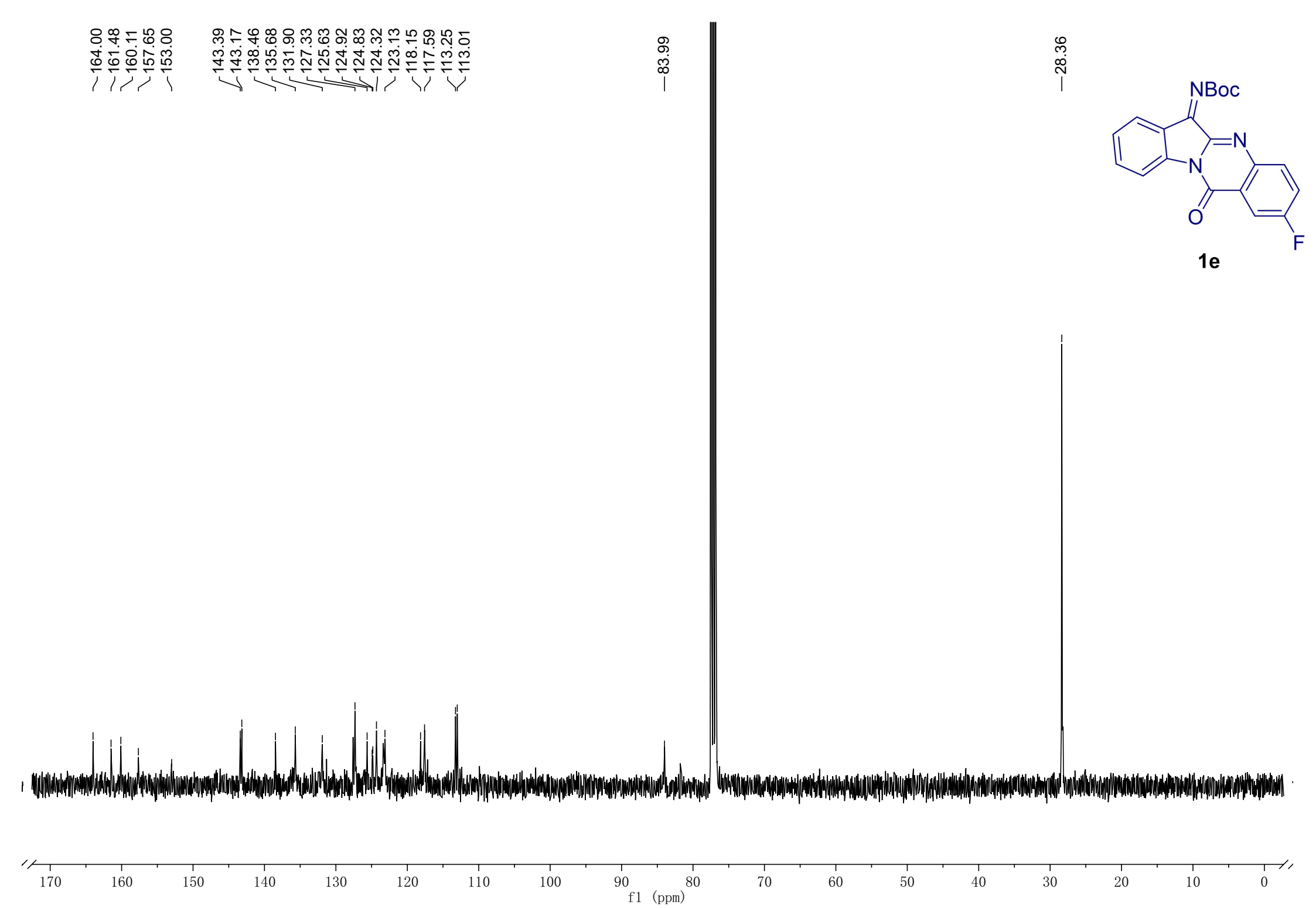
8.55
8.53
8.08
8.08
8.06
8.06
7.94
7.92
7.82
7.71
7.69
7.67
7.54
7.52
7.51
7.43
7.41
7.26
1.72
NBoc
N
N
O
F
1e
1.16
1.05
1.00
1.02
1.05
1.11
9.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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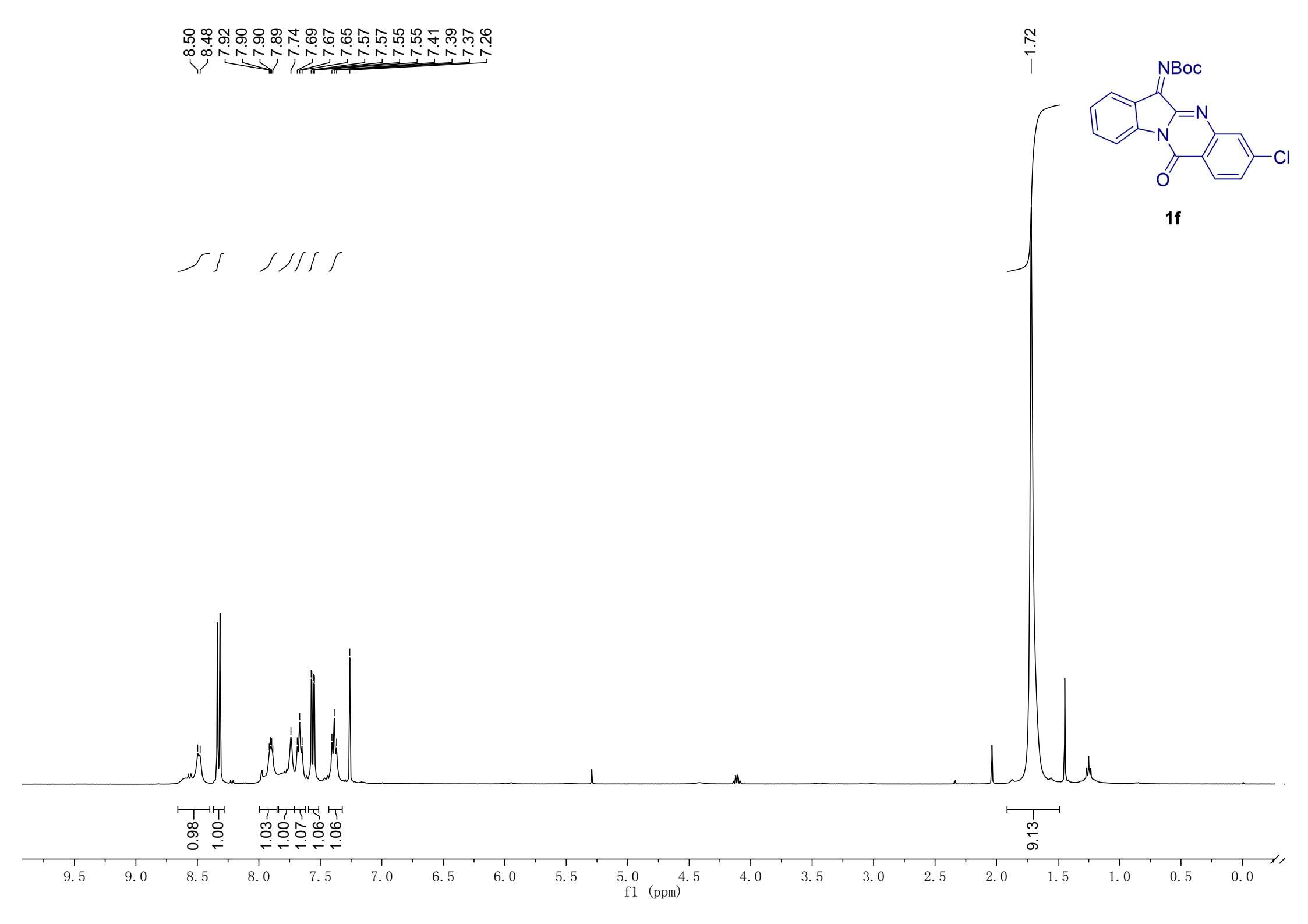
160.11
157.65
153.00
143.39
143.17
138.46
135.68
131.90
127.33
125.63
124.92
124.83
124.32
123.13
118.15
117.59
113.25
113.01
83.99
28.36
NBoc
N
N
O
F
1e
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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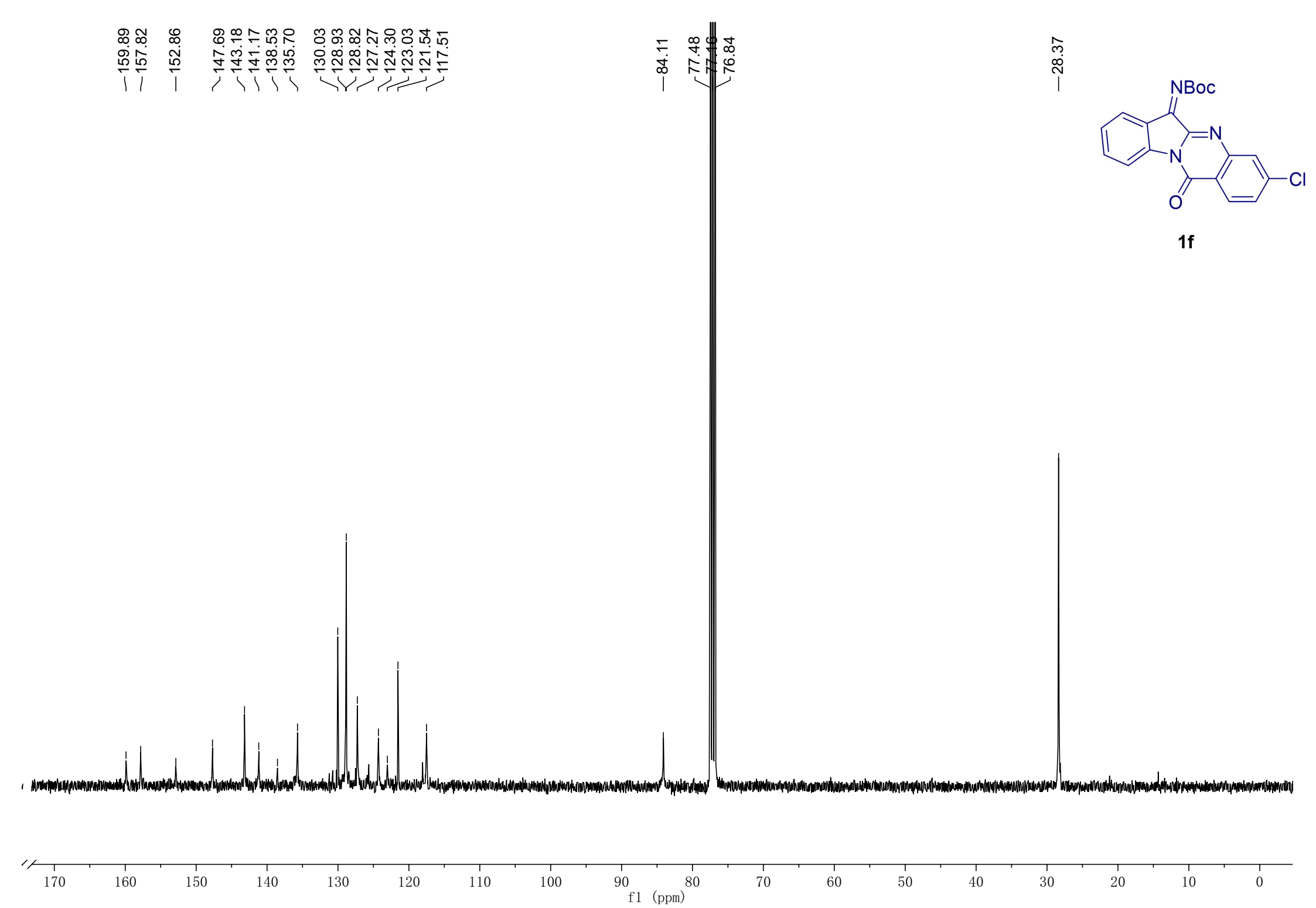
7.69
7.67
7.65
7.57
7.57
7.55
7.55
7.41
7.39
7.37
7.26
1.72
NBoc
N
N
O
Cl
1f
0.98
1.00
1.03
1.00
1.07
1.06
1.06
9.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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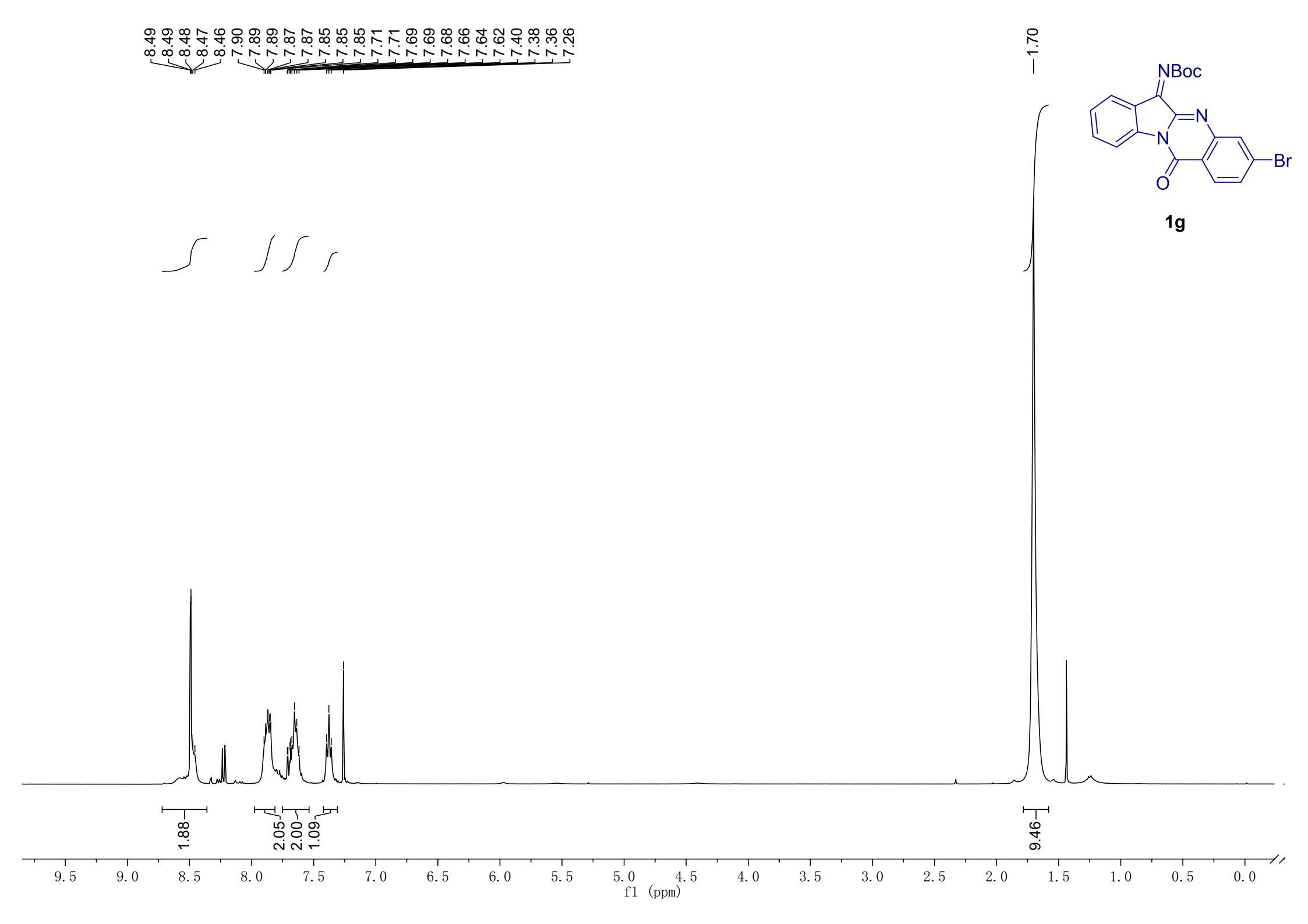
157.82
152.86
147.69
143.18
141.17
138.53
135.70
130.03
128.93
128.82
127.27
124.30
123.03
121.54
117.51
84.11
77.48
77.16
76.84
28.37
NBoc
N
N
O
Cl
1f
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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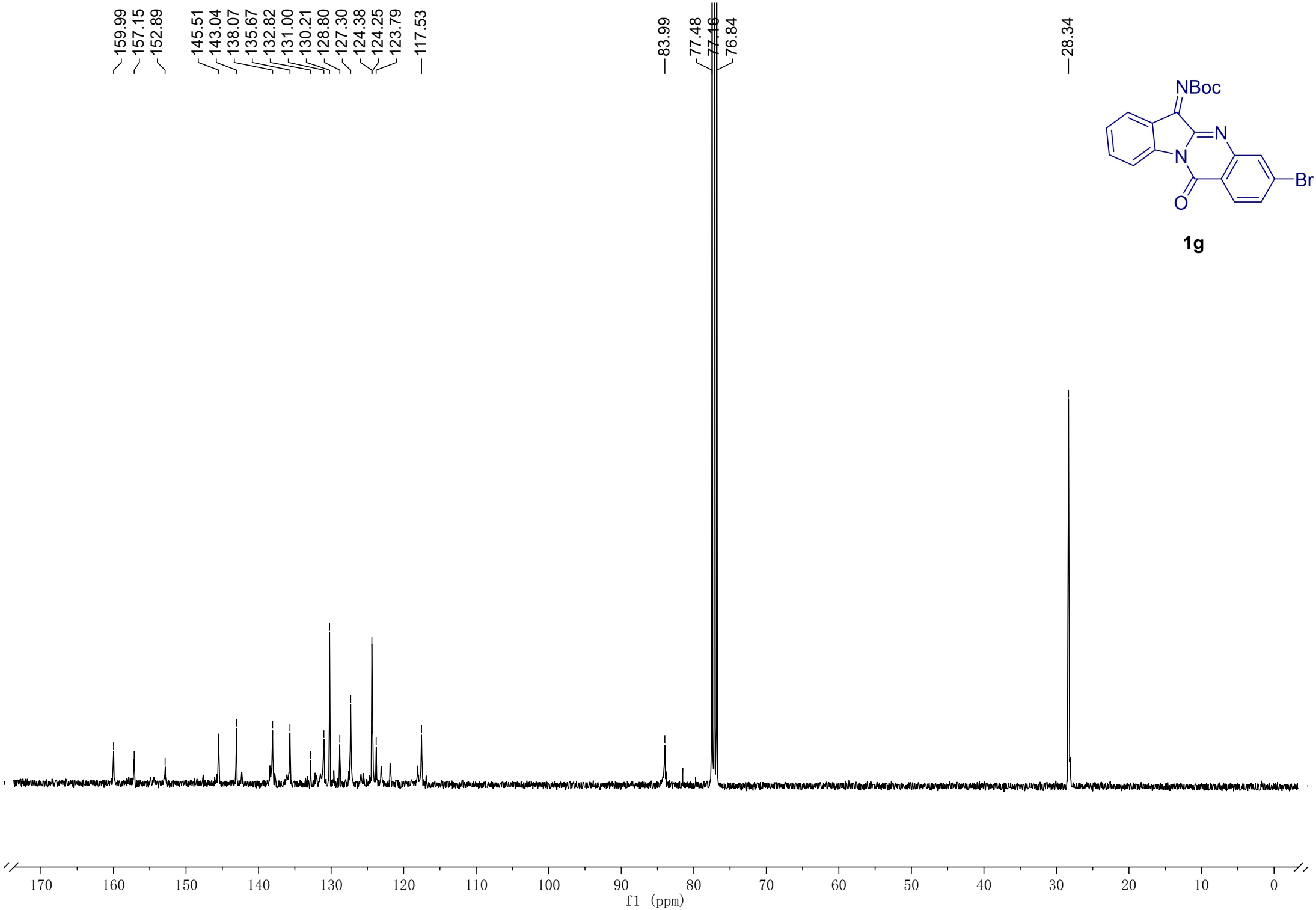
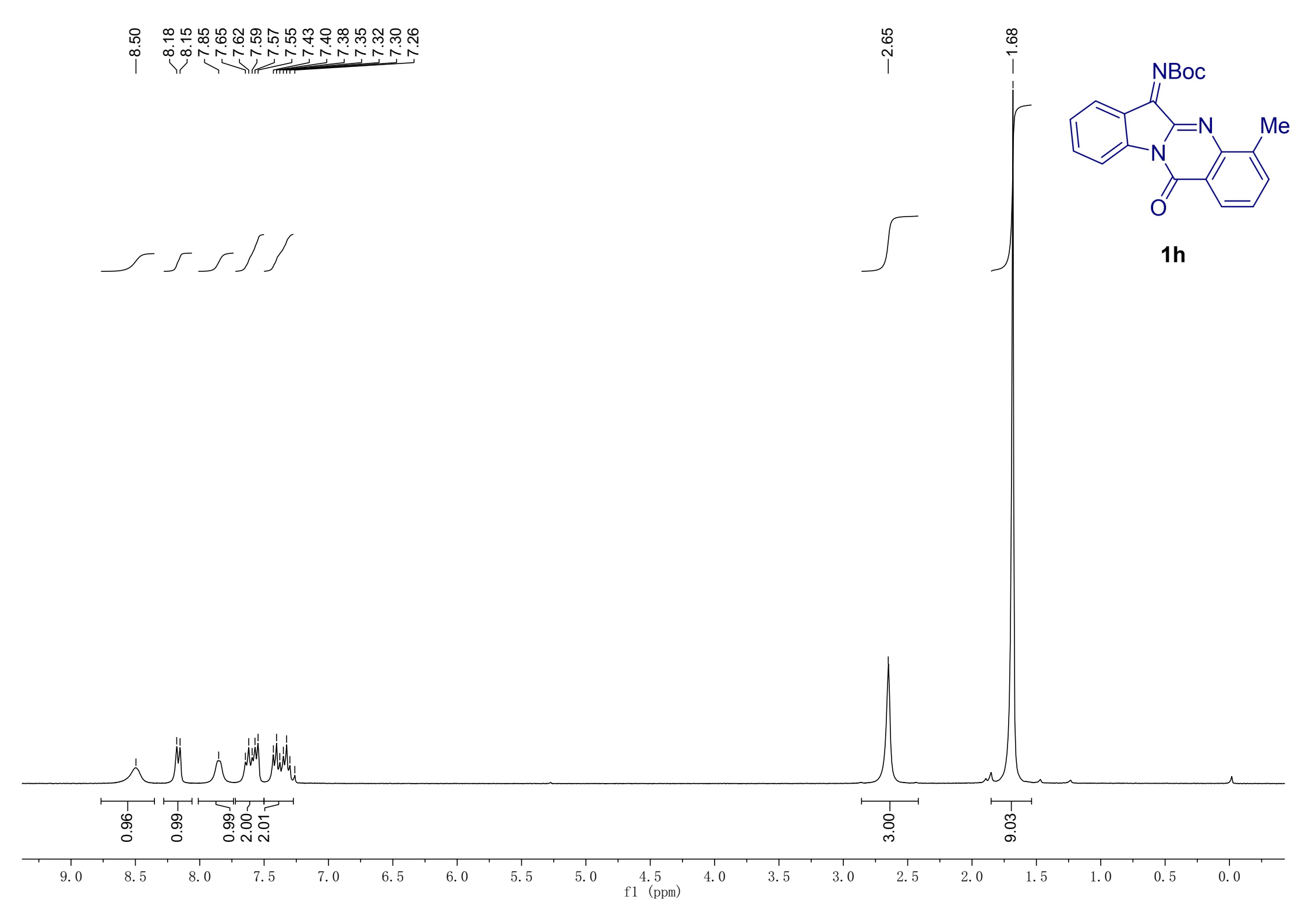
8.49
8.48
8.47
8.46
7.90
7.89
7.89
7.87
7.87
7.85
7.85
7.85
7.71
7.71
7.69
7.69
7.68
7.66
7.64
7.62
7.40
7.38
7.36
7.26
1.70
NBoc
N
N
O
Br
1g
1.88
2.05
2.00
1.09
9.46
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


159.99
157.15
152.89
145.51
143.04
138.07
135.67
132.82
131.00
130.21
128.80
127.30
124.38
124.25
123.79
117.53
83.99
77.48
77.16
76.84
28.34
NBoc
N
N
O
Br
1g
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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Me
N
O
1h
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0.99
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2.01
3.00
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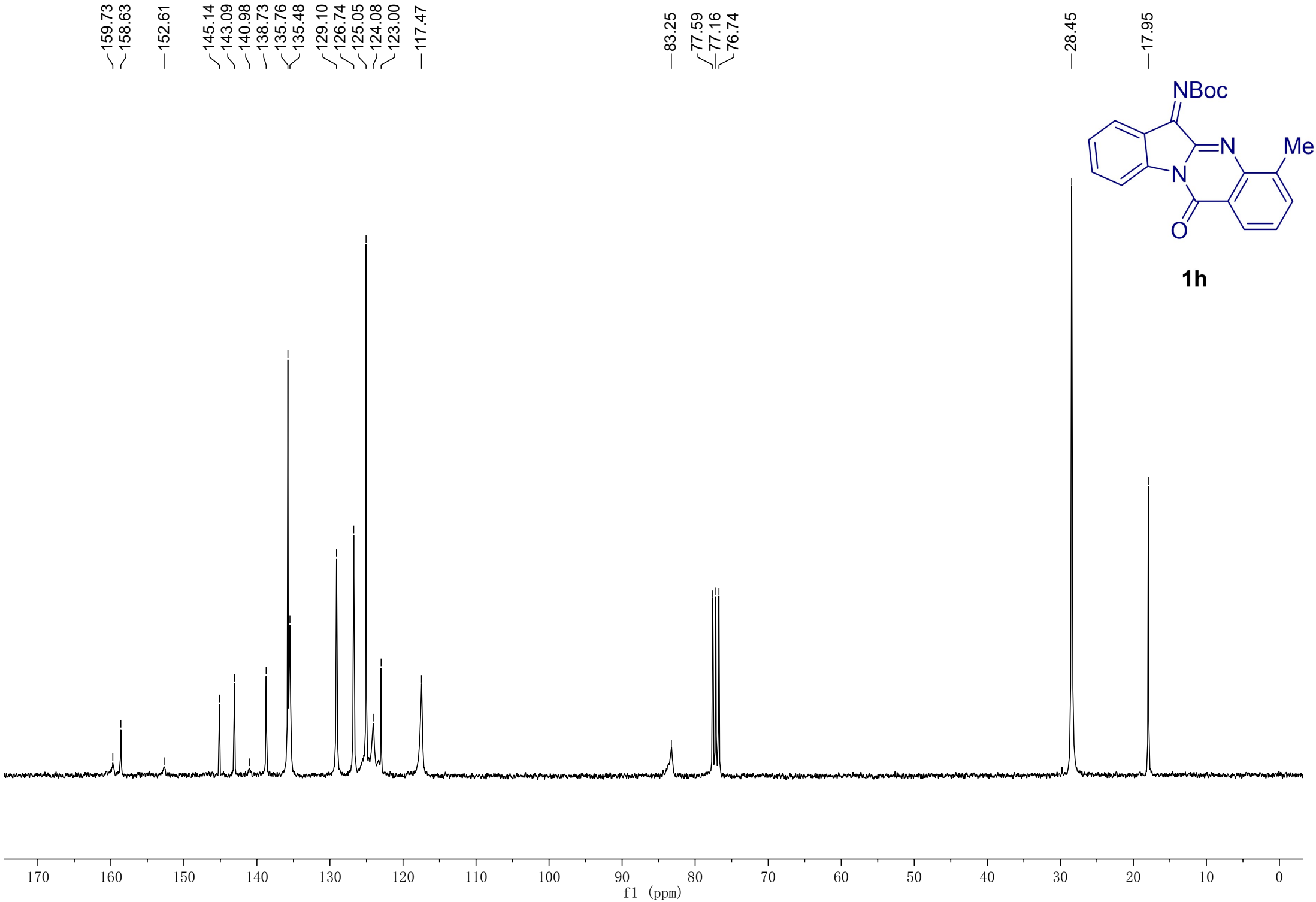
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124.08
123.00
117.47
83.25
77.59
77.16
76.74
28.45
17.95
NBoc
N
N
Me
O
1h
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10
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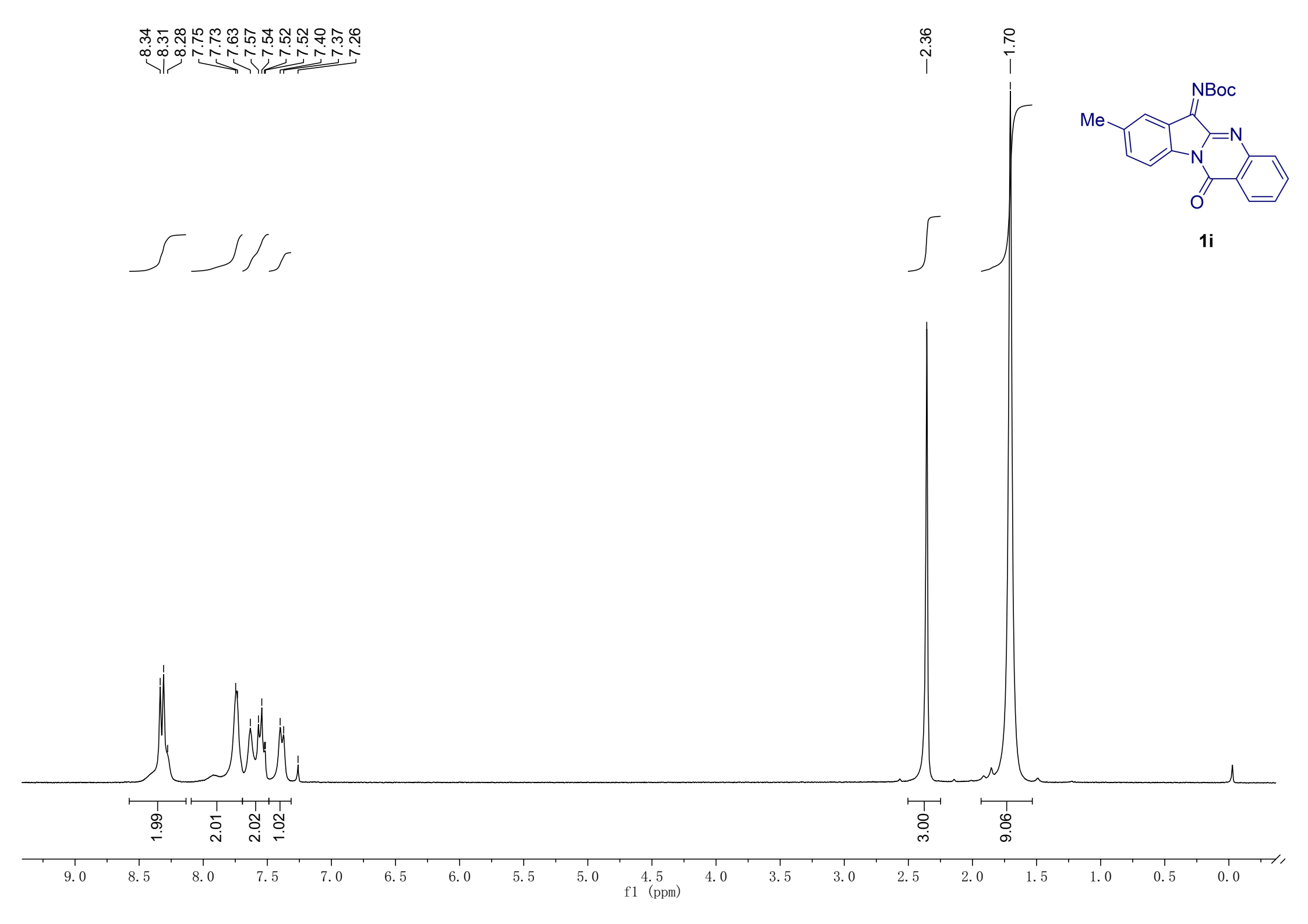
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2.02
1.02
3.00
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9.0
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8.0
7.5
7.0
6.5
6.0
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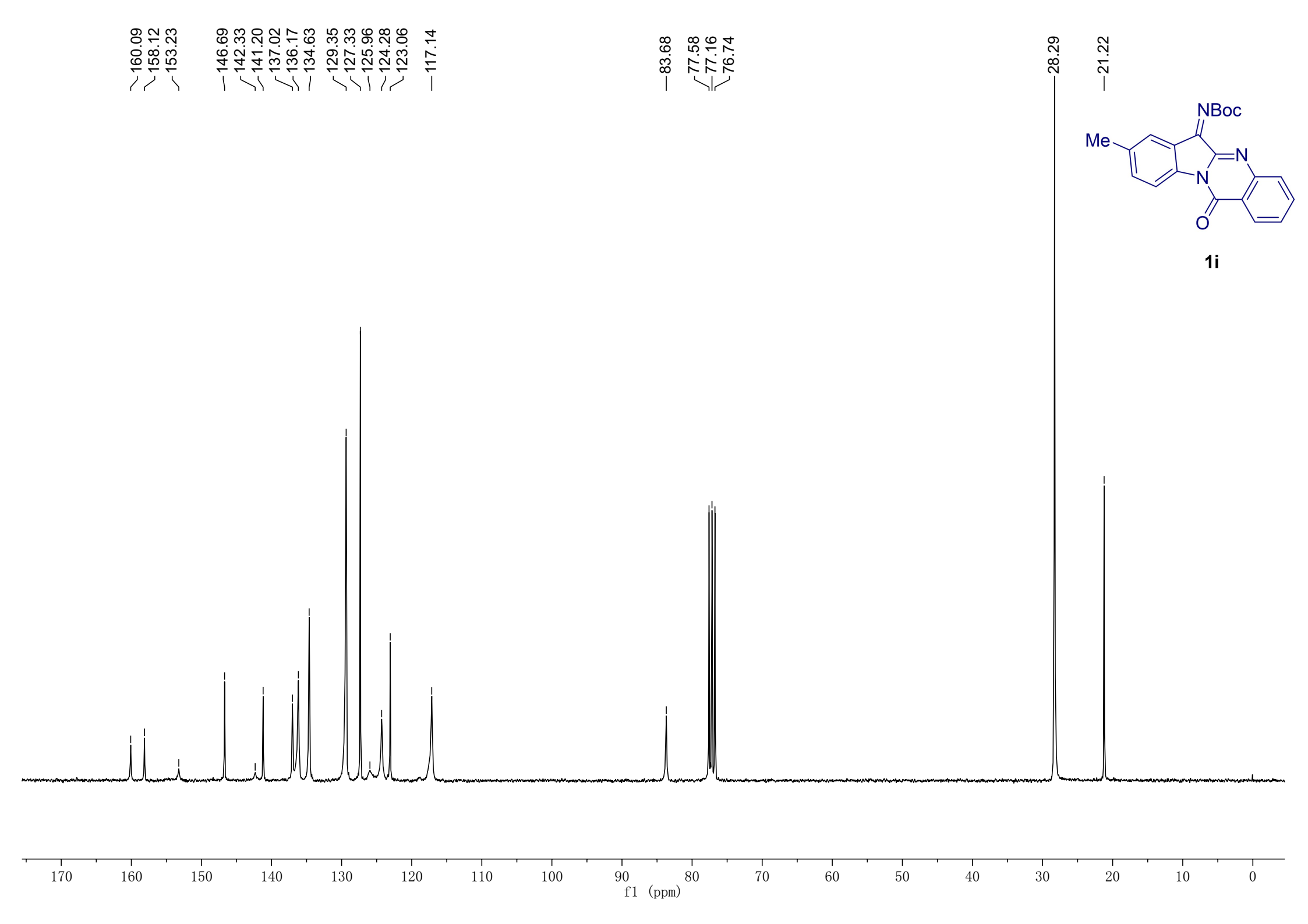
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83.68
77.58
77.16
76.74
28.29
21.22
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N
O
1i
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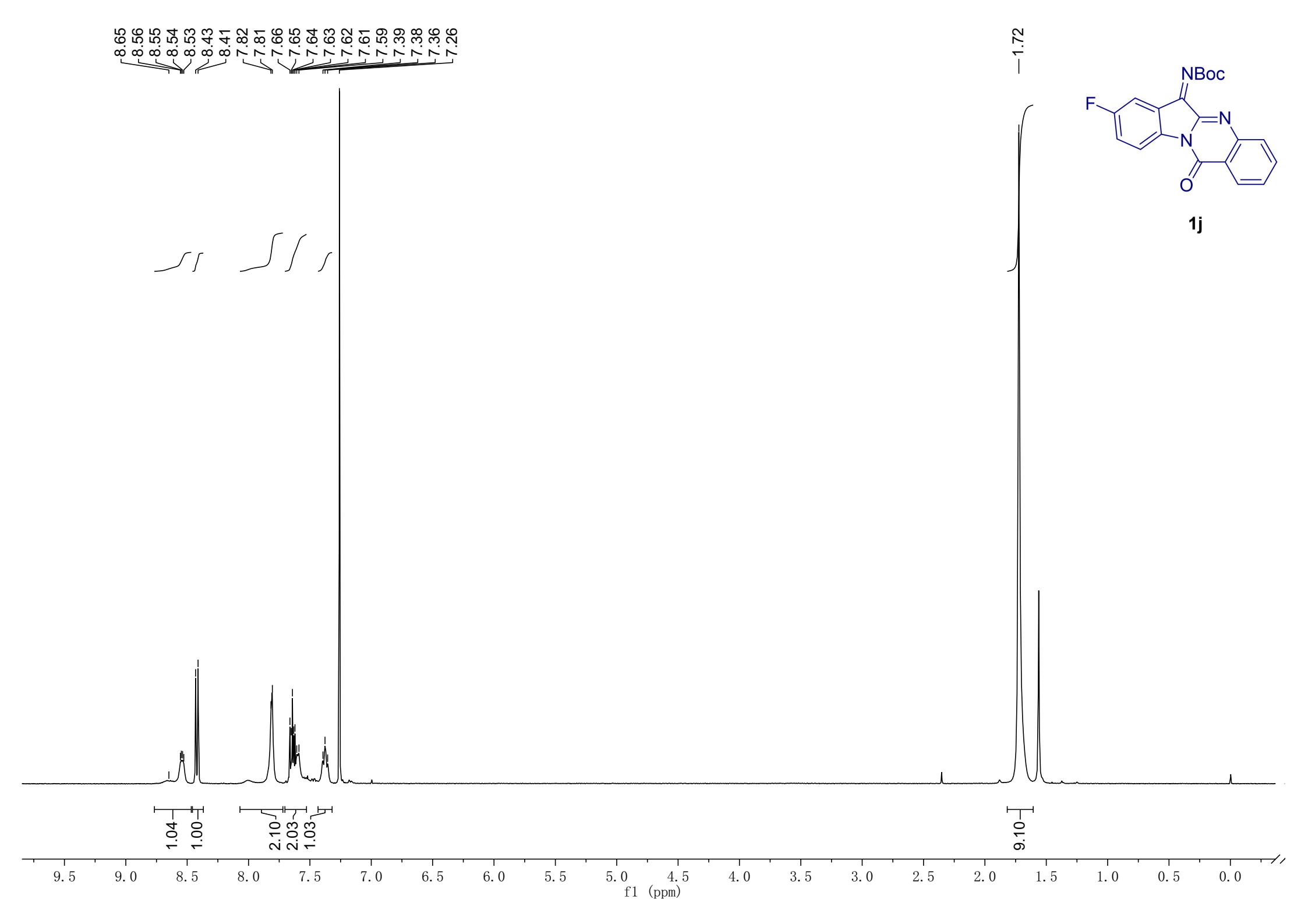
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7.38
7.36
7.26
1.72
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N
O
1j
1.04
1.00
2.10
2.03
1.03
9.10
9.5
9.0
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7.5
7.0
6.5
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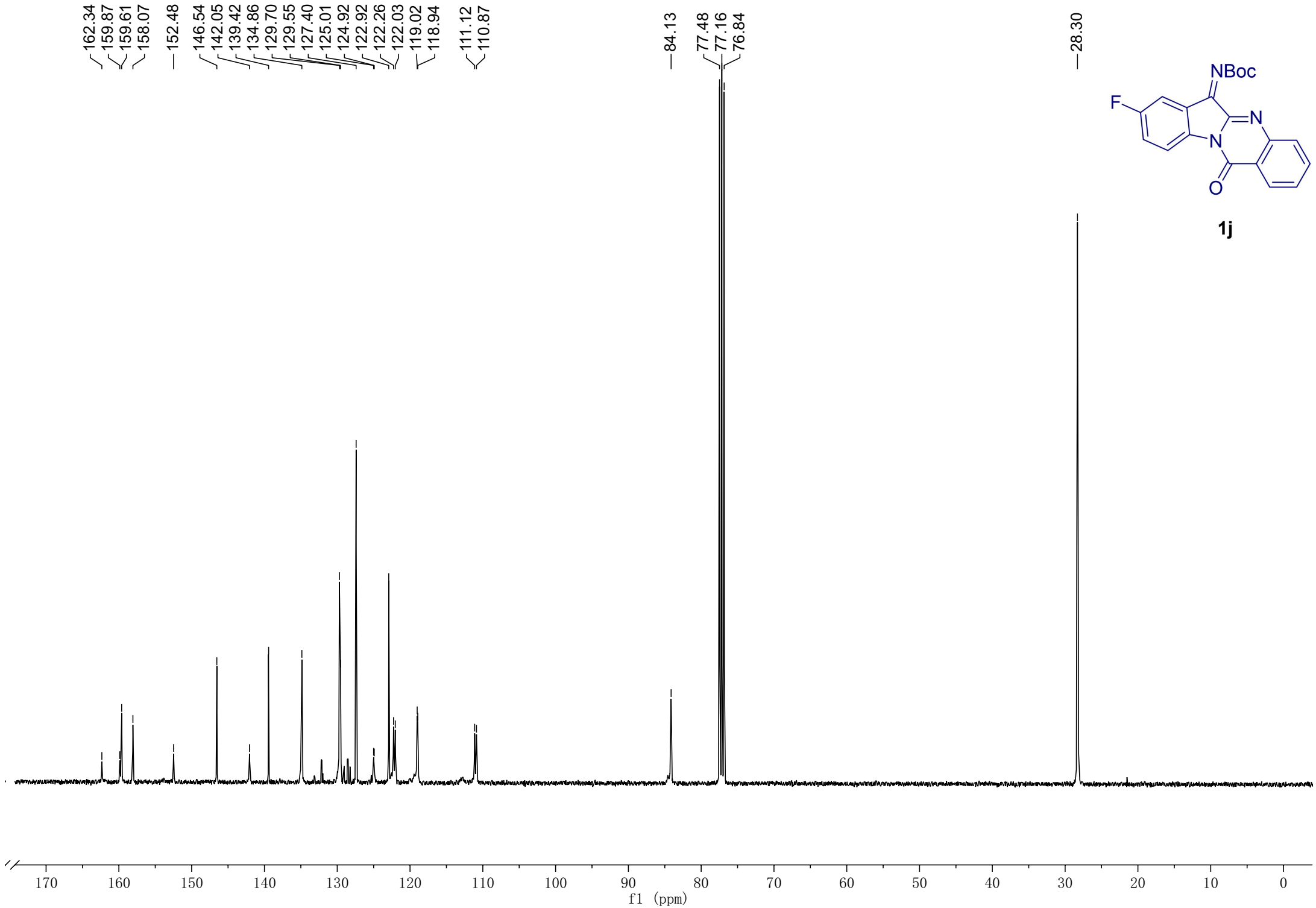
f1 (ppm)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76.84
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F
N
N
O
1j
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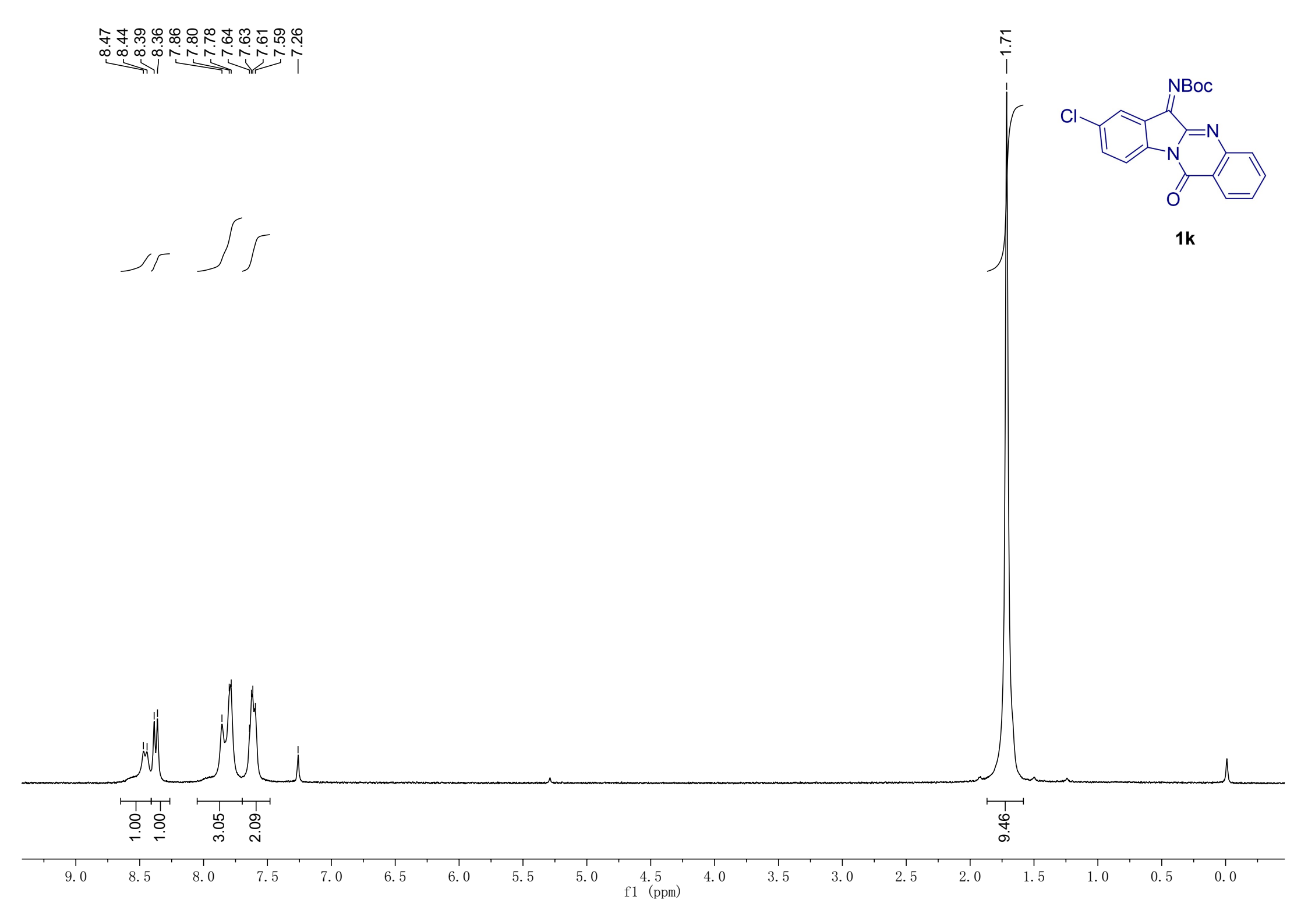
f1 (ppm)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7.61
7.59
7.26
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Cl
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N
O
1k
1.00
1.00
3.05
2.09
9.46
9.0
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8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
1.5
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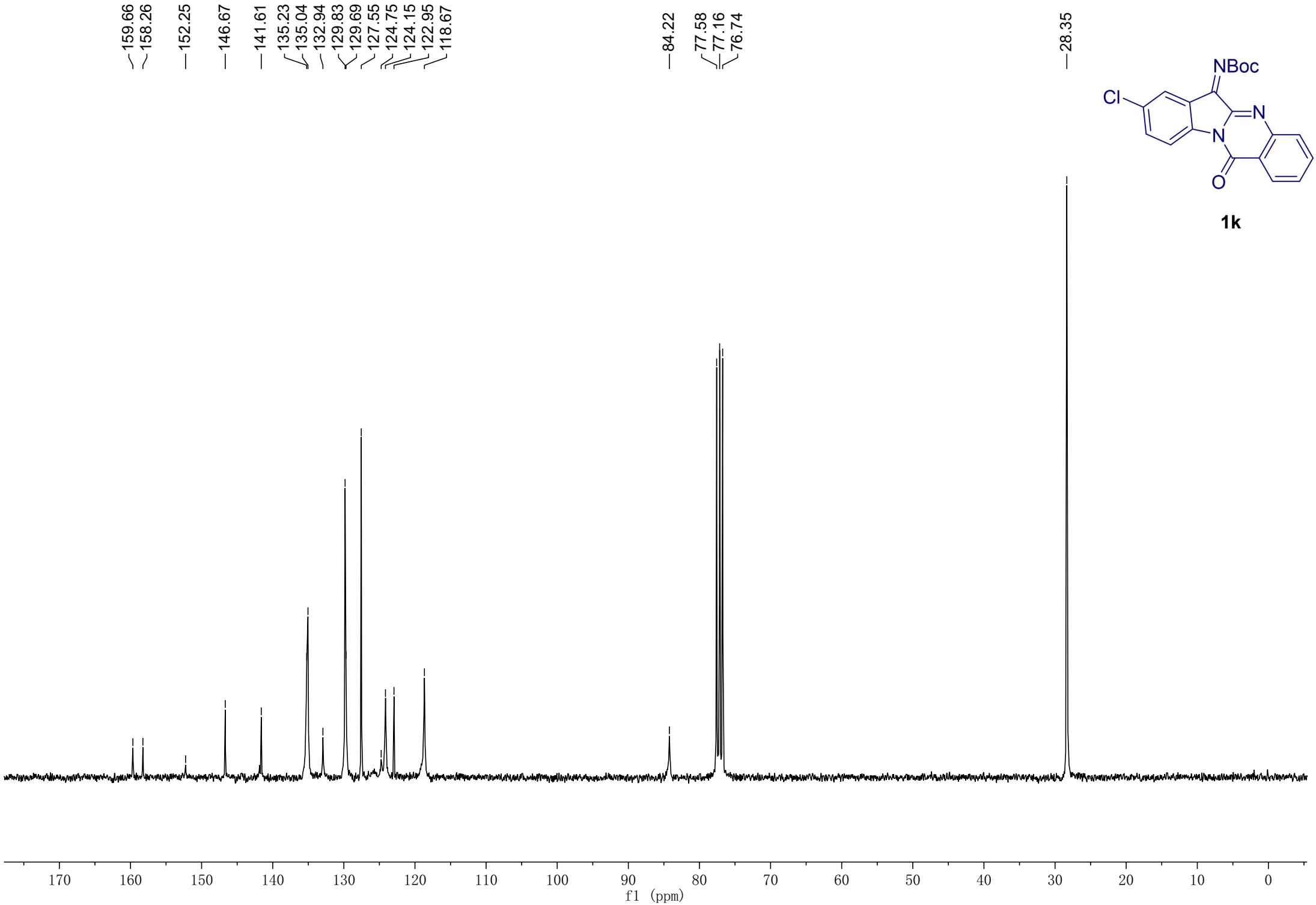
f1 (ppm)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124.15
122.95
118.67
84.22
77.58
77.16
76.74
28.35
NBoc
Cl
N
N
O
1k
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130
120
110
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30
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10
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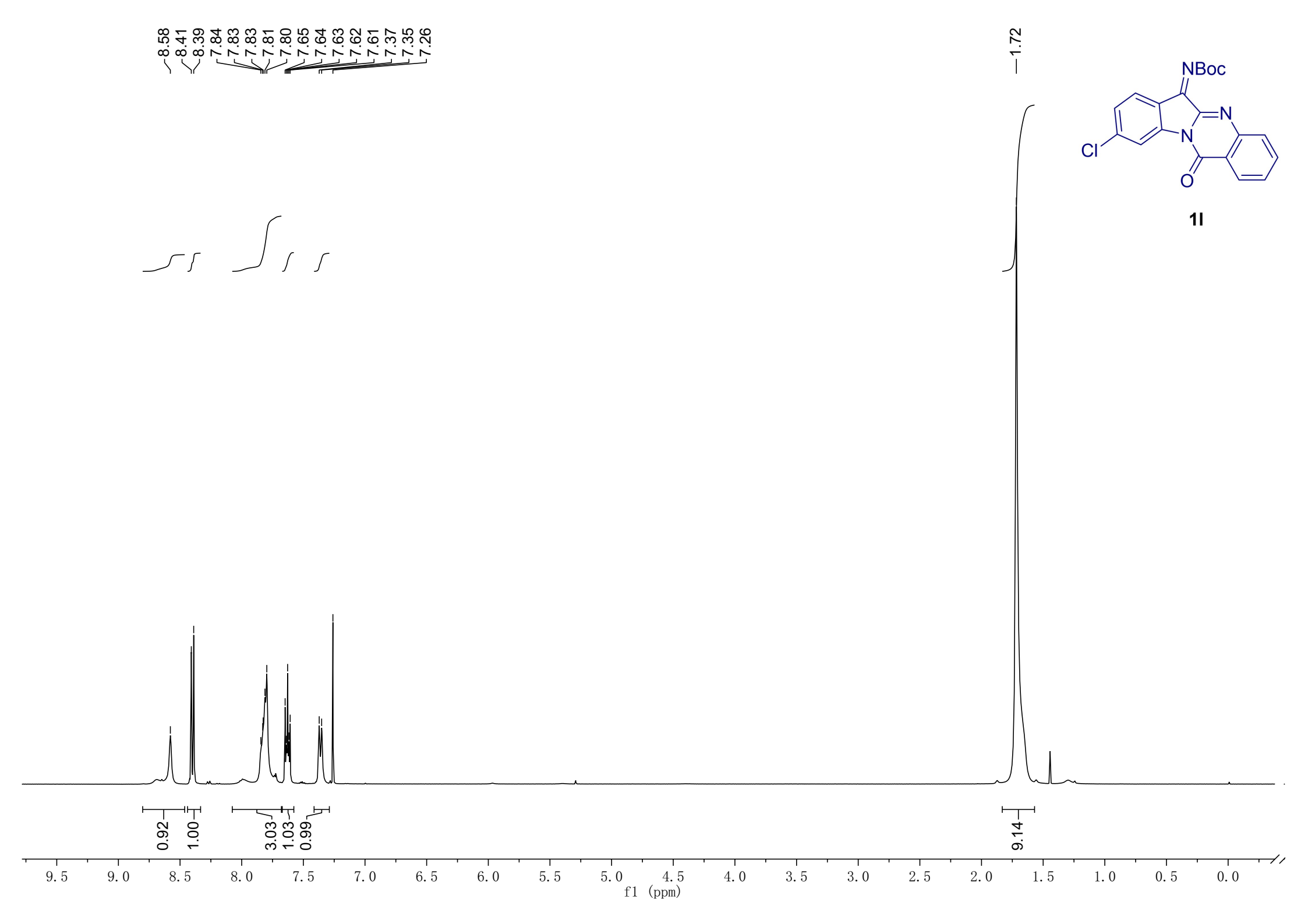
f1 (ppm)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7.37
7.35
7.26
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NBoc
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Cl
O
1I
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1.03
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9.5
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8.5
8.0
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7.0
6.5
6.0
5.5
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3.0
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2.0
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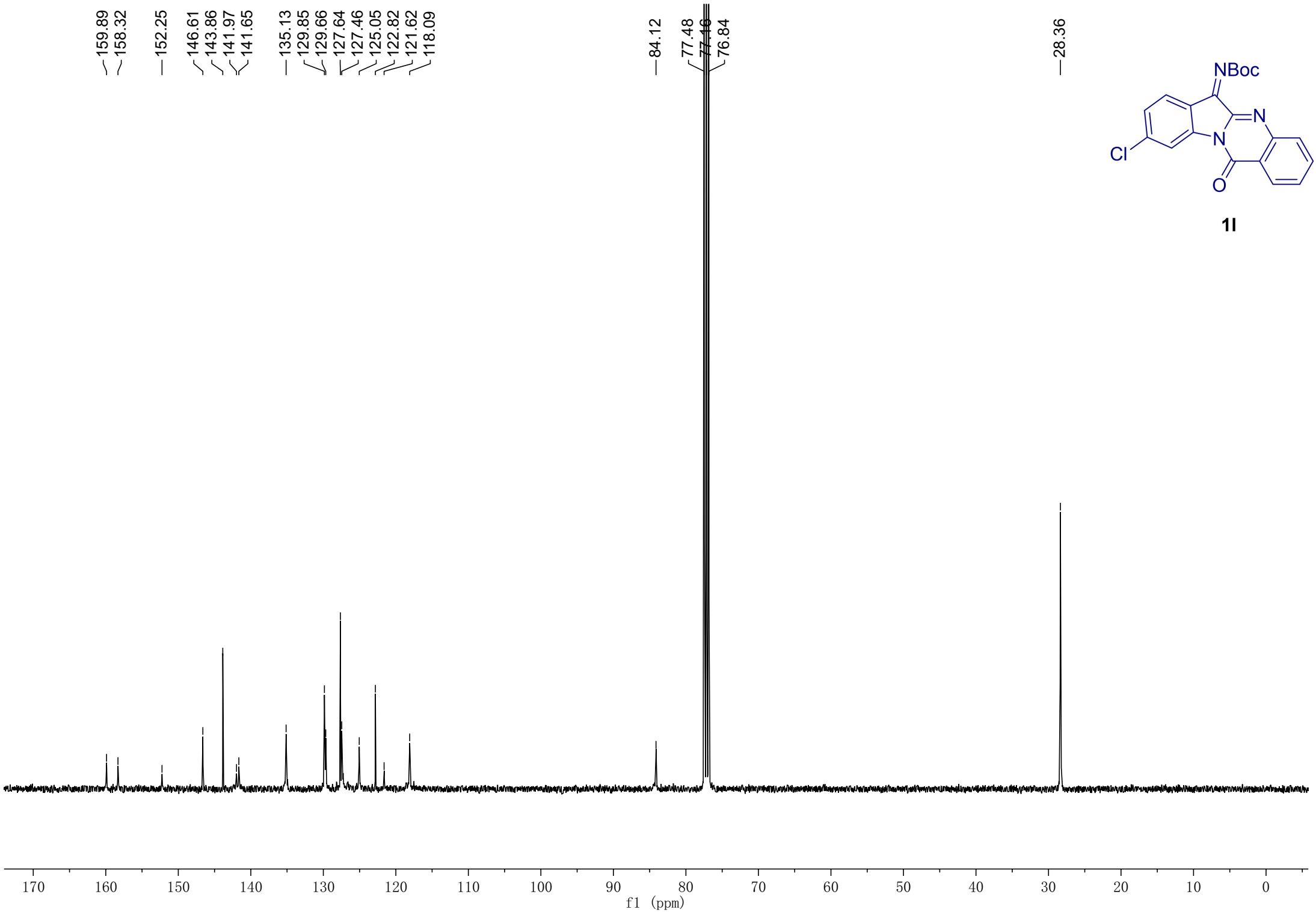
0.0
f1 (ppm)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28.36
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N
Cl
O
1l
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30
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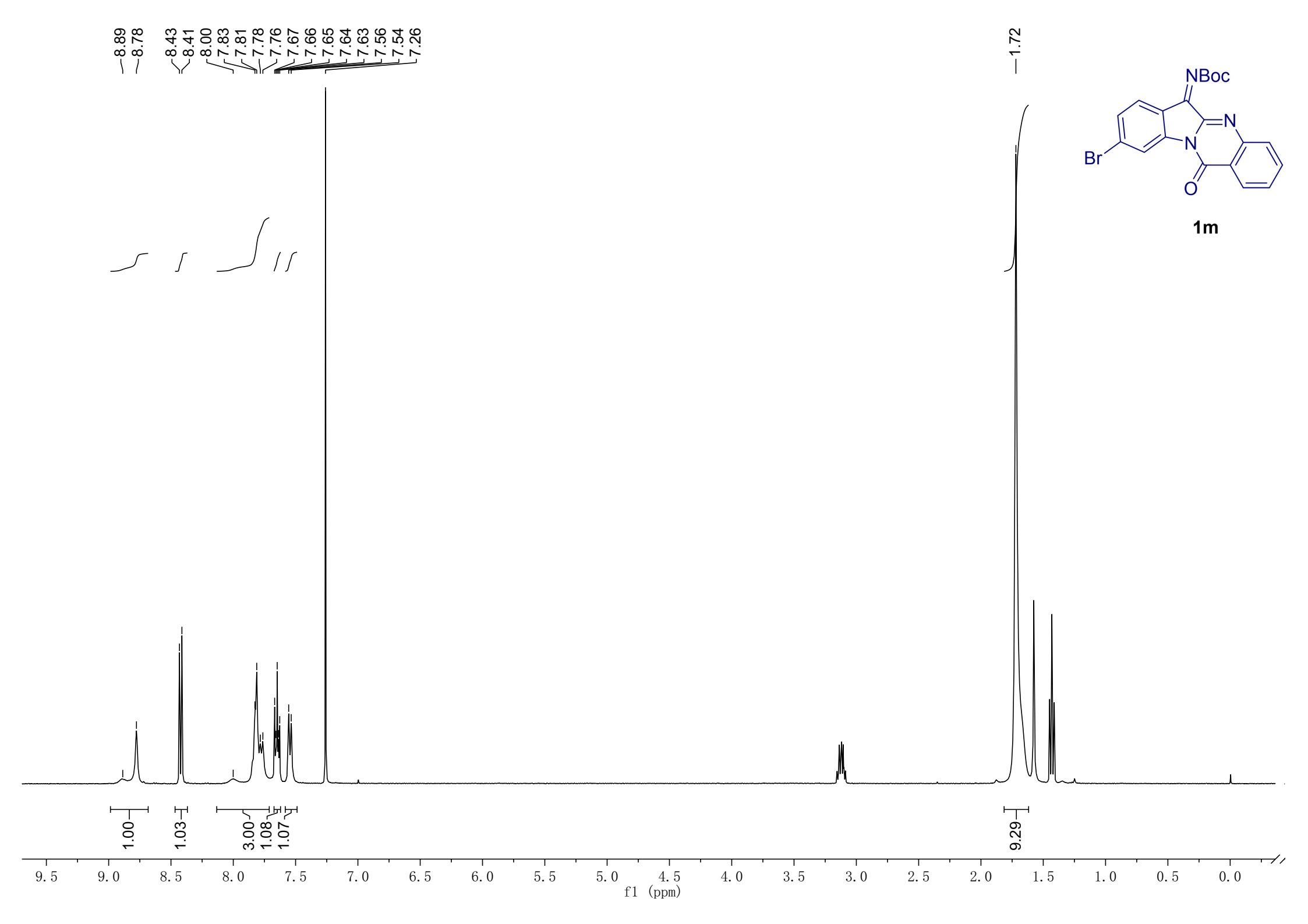
f1 (ppm)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7.54
7.26
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Br
O
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3.00
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9.5
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8.0
7.5
7.0
6.5
6.0
5.5
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2.0
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1.0
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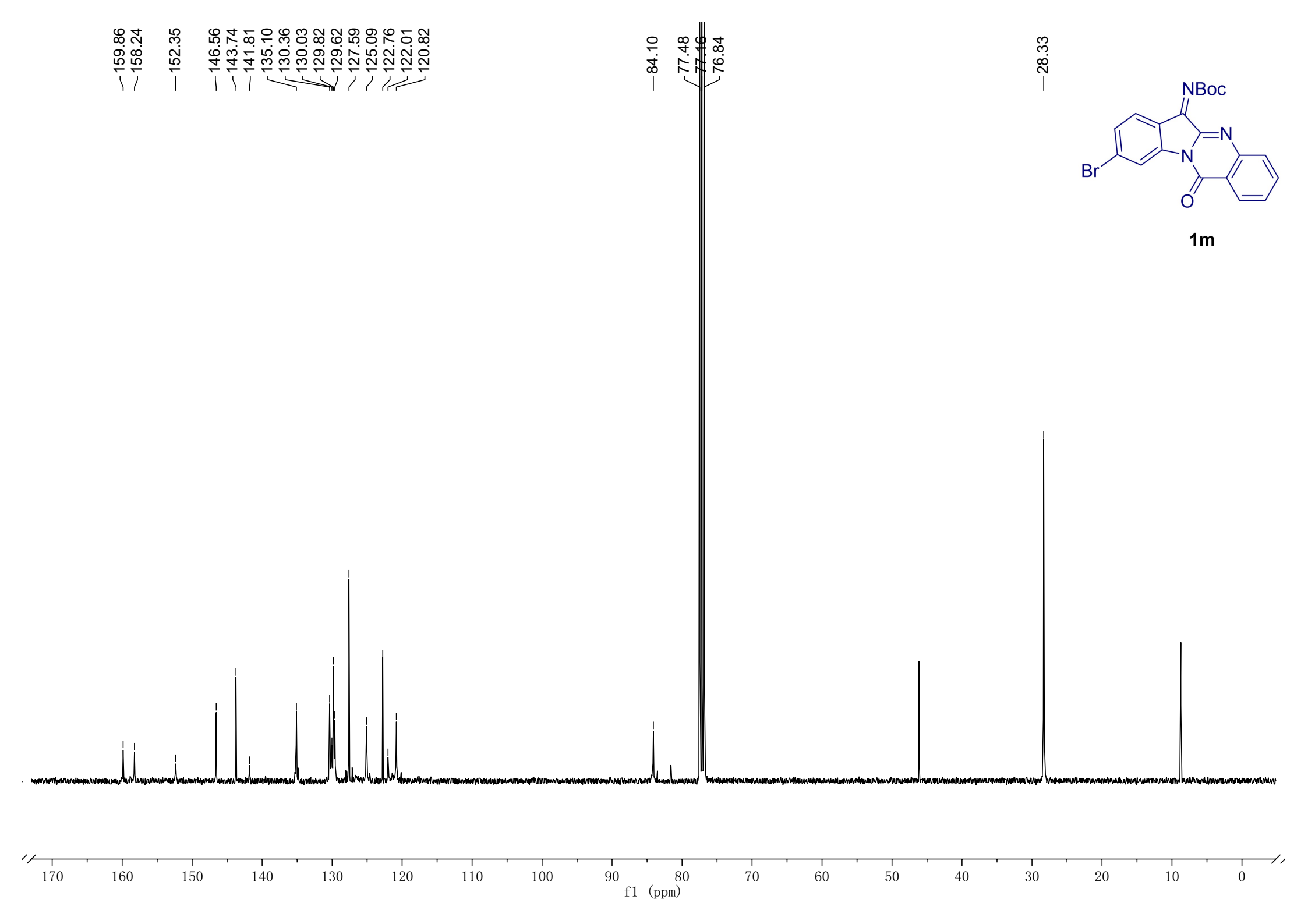
0.0
f1 (ppm)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122.01
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84.10
77.48
77.16
76.84
28.33
NBoc
N
N
Br
O
1m
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130
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110
100
90
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50
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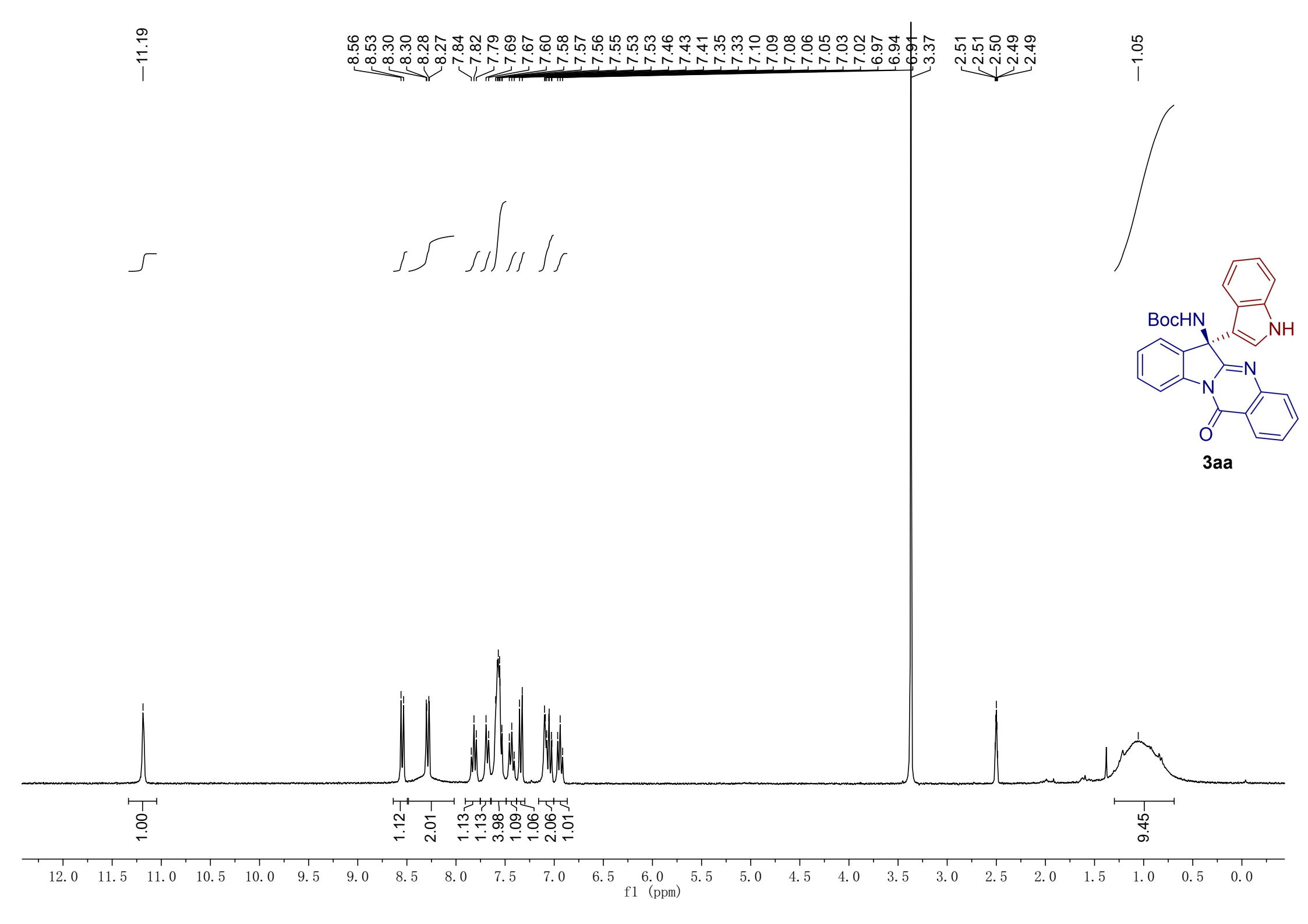
10
0
f1 (ppm)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7.10
7.09
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7.06
7.05
7.03
7.02
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6.94
6.91
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2.51
2.50
2.49
2.49
1.05
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N
O
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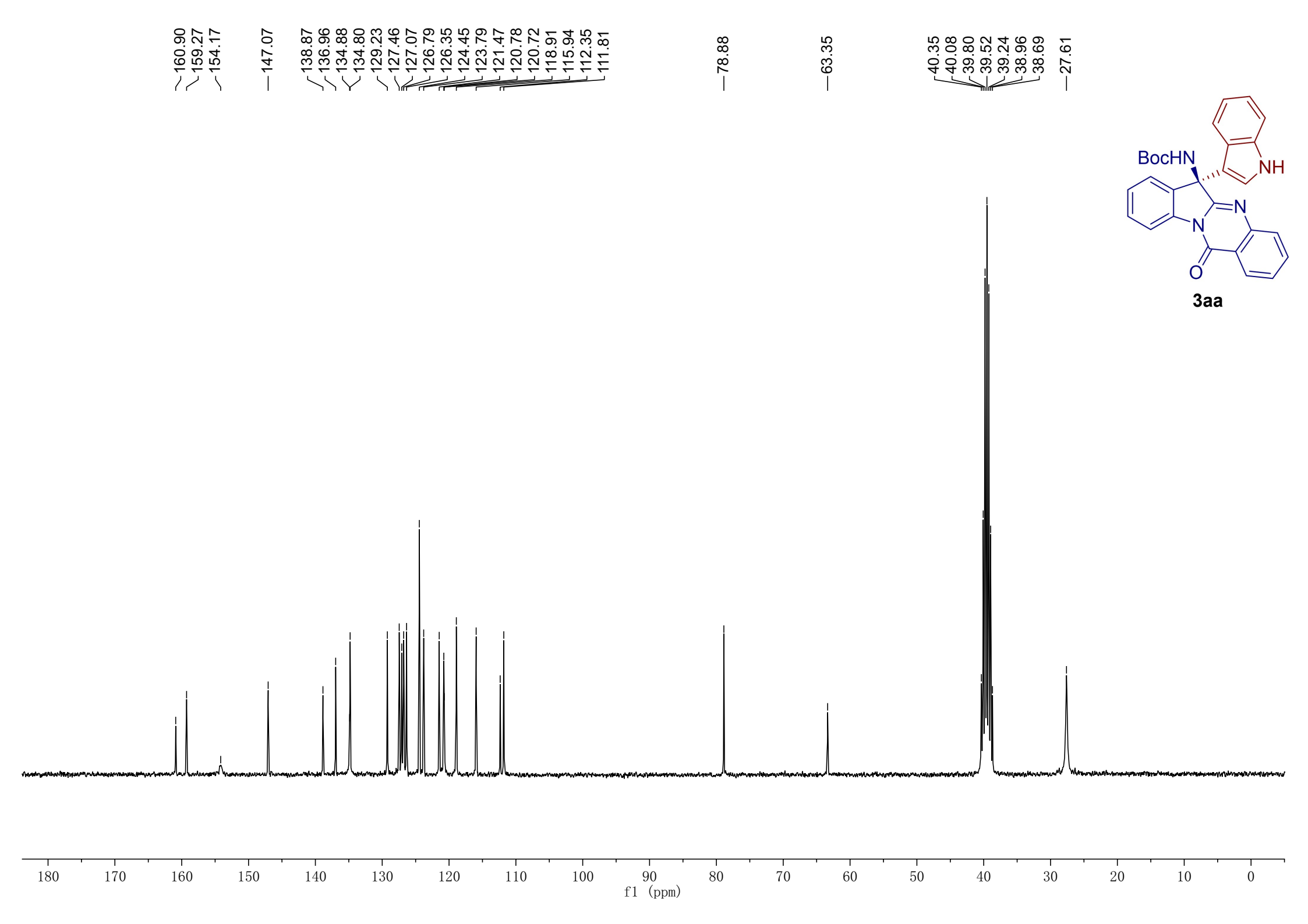
1.12
2.01
1.13
1.13
3.98
1.09
1.06
2.06
1.01
9.45
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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78.88
63.35
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40.08
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39.52
39.24
38.96
38.69
27.61
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N
N
O
3aa
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50
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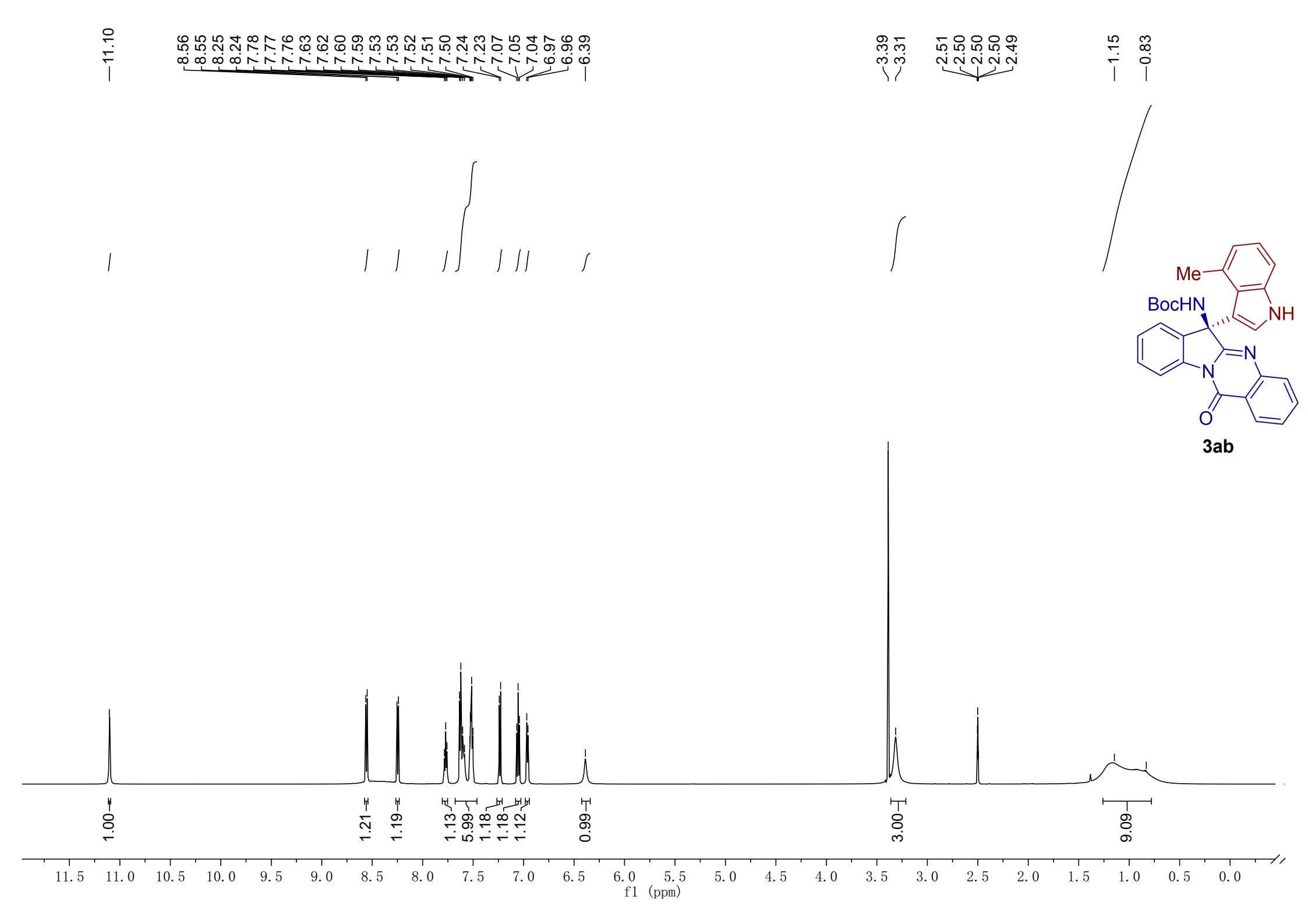
f1 (ppm)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7.53
7.52
7.51
7.50
7.24
7.23
7.07
7.05
7.04
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3.31
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1.15
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BocHN
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O
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9.5
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3.0
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2.0
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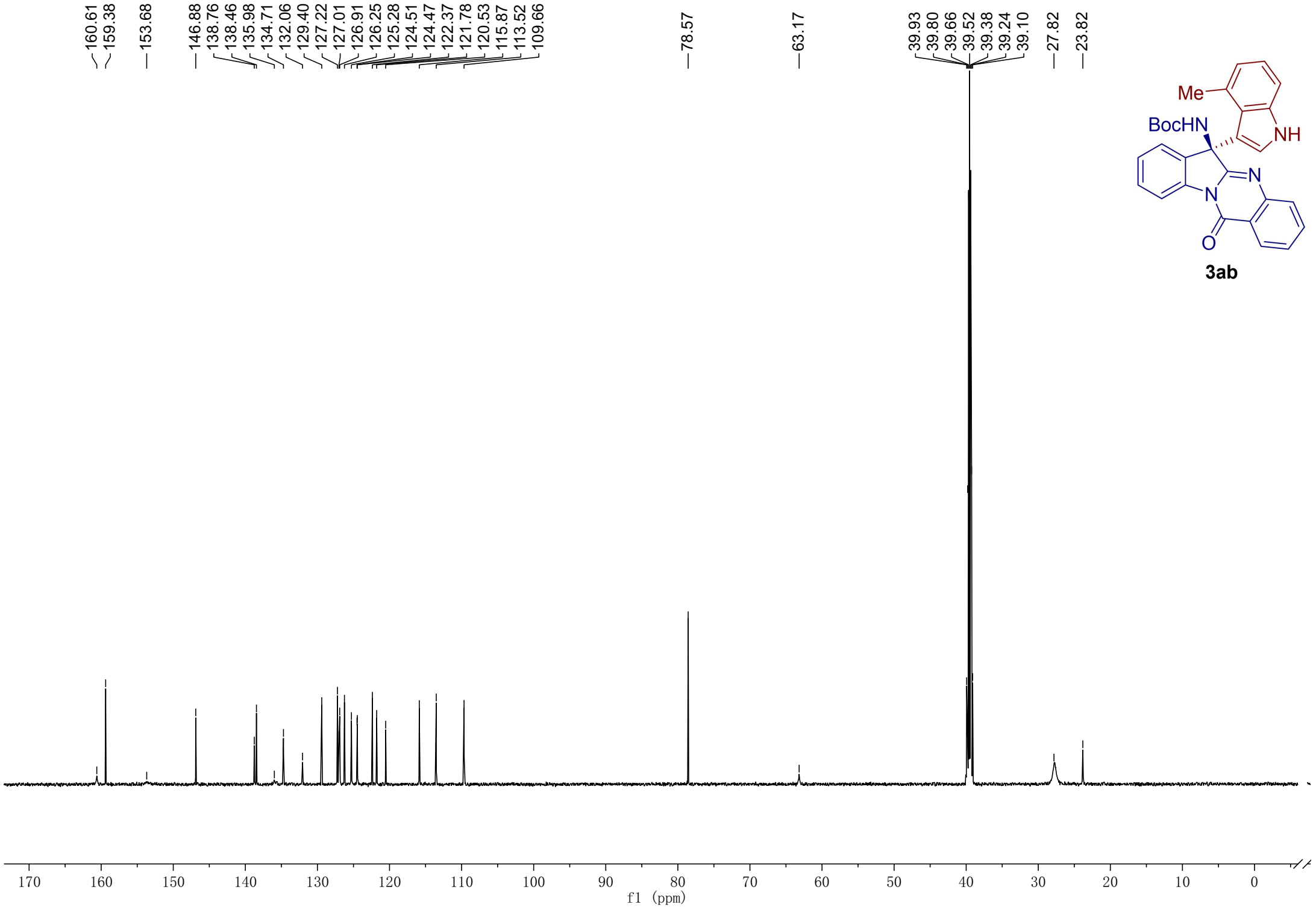
f1 (ppm)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39.10
27.82
23.82
Me
BocHN
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N
N
O
3ab
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130
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80
70
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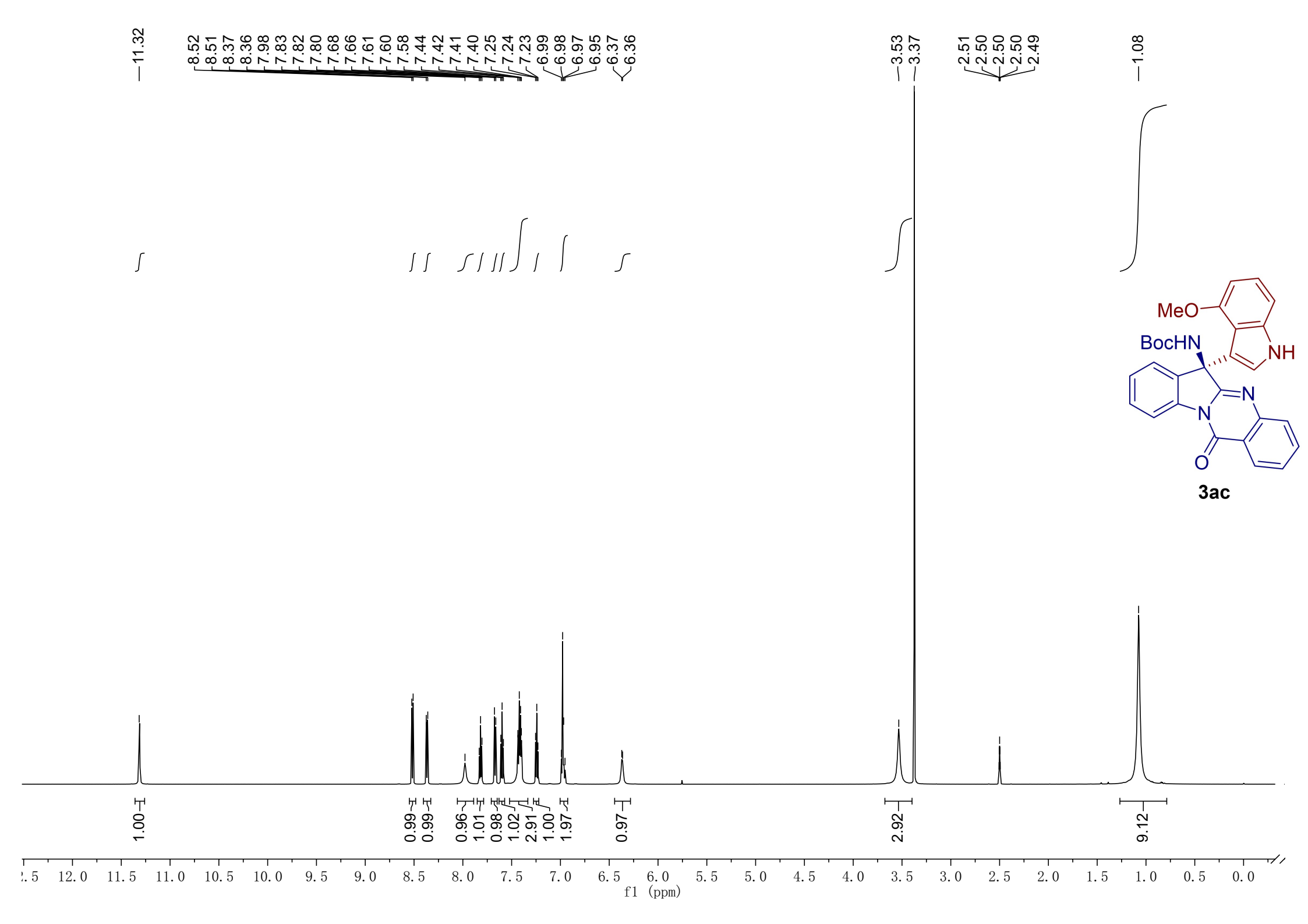
10
0
f1 (ppm)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7.40
7.25
7.24
7.23
6.99
6.98
6.97
6.95
6.37
6.36
3.53
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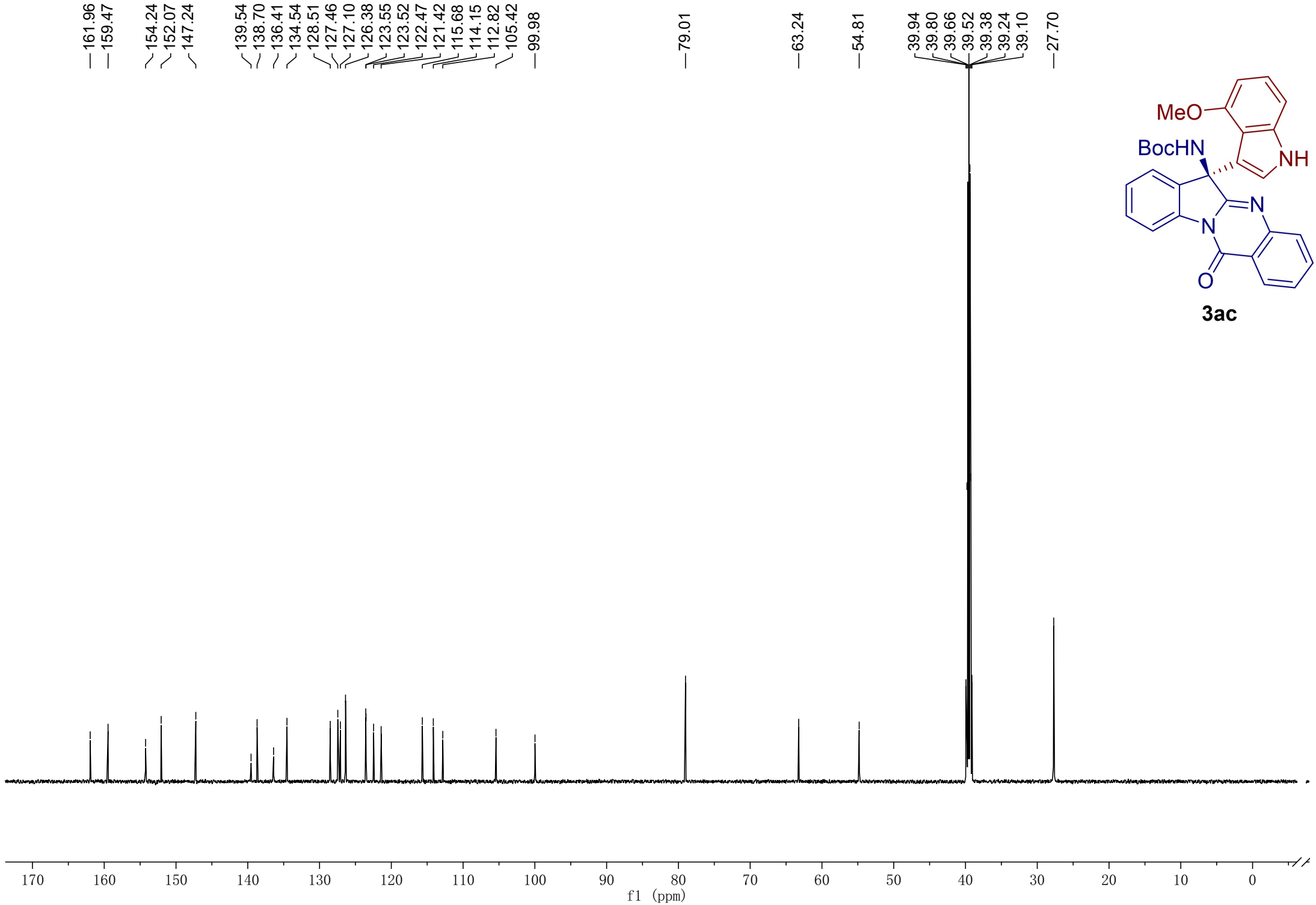
f1 (ppm)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39.52
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27.70
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BocHN
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N
O
3ac
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90
80
70
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50
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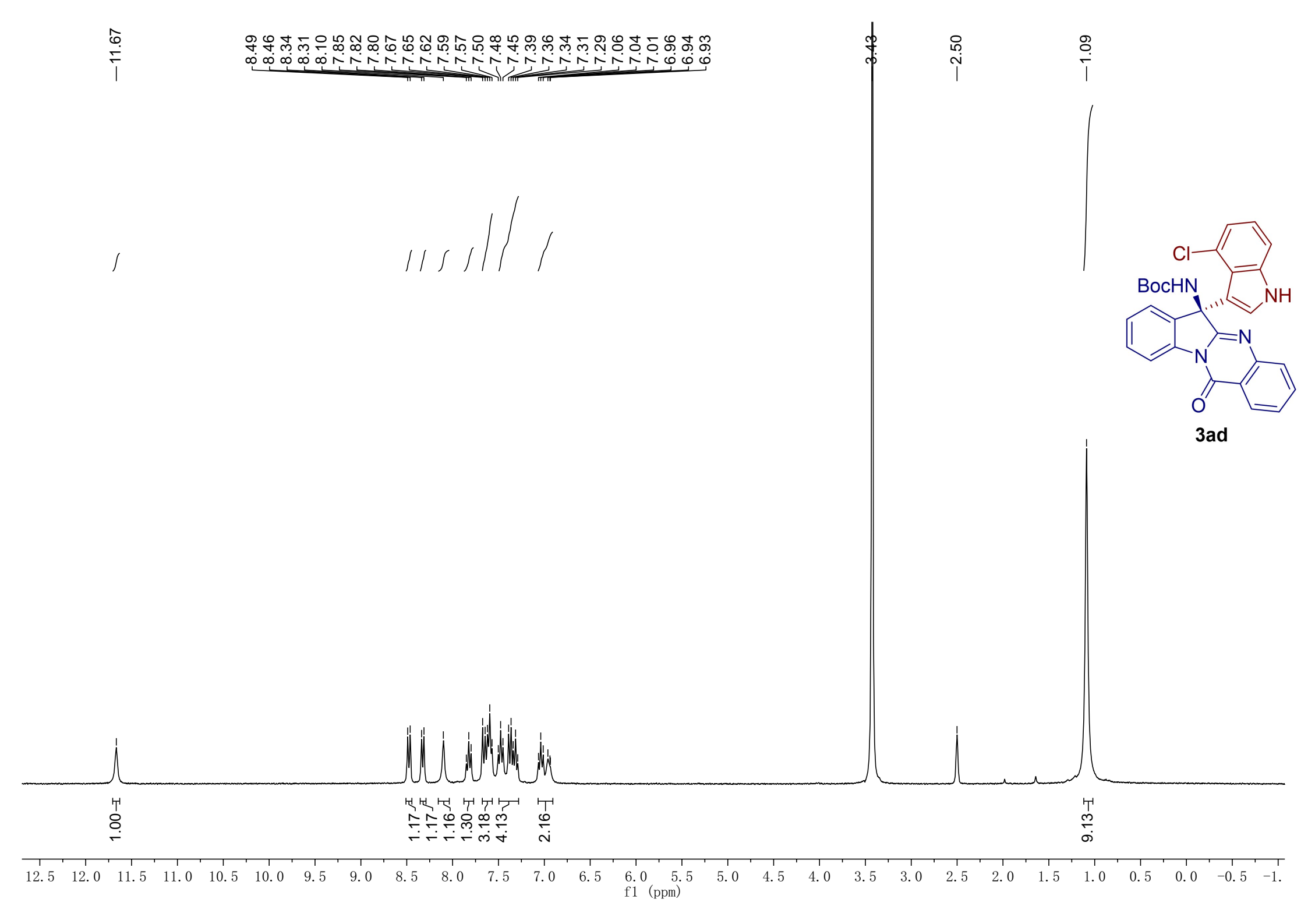
10
0
f1 (ppm)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7.45
7.39
7.36
7.34
7.31
7.29
7.06
7.04
7.01
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6.94
6.93
3.43
2.50
1.09
Cl
BocHN
NH
N
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1.17
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1.30
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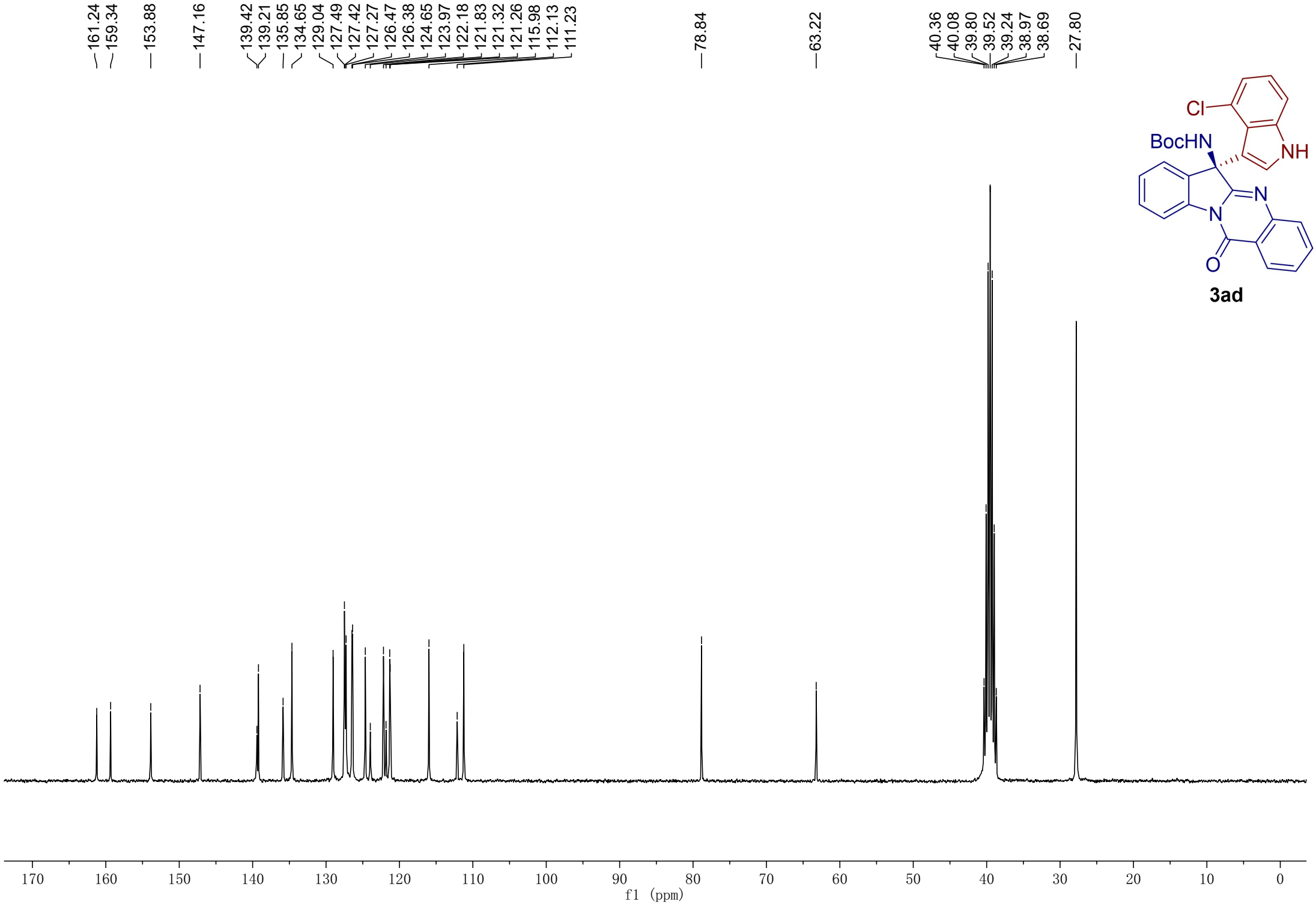
4.13
2.16
9.13
f1 (ppm)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126.38
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121.32
121.26
115.98
112.13
111.23
78.84
63.22
40.36
40.08
39.80
39.52
39.24
38.97
38.69
27.80
Cl
BocHN
NH
N
N
O
3ad
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130
120
110
100
90
80
70
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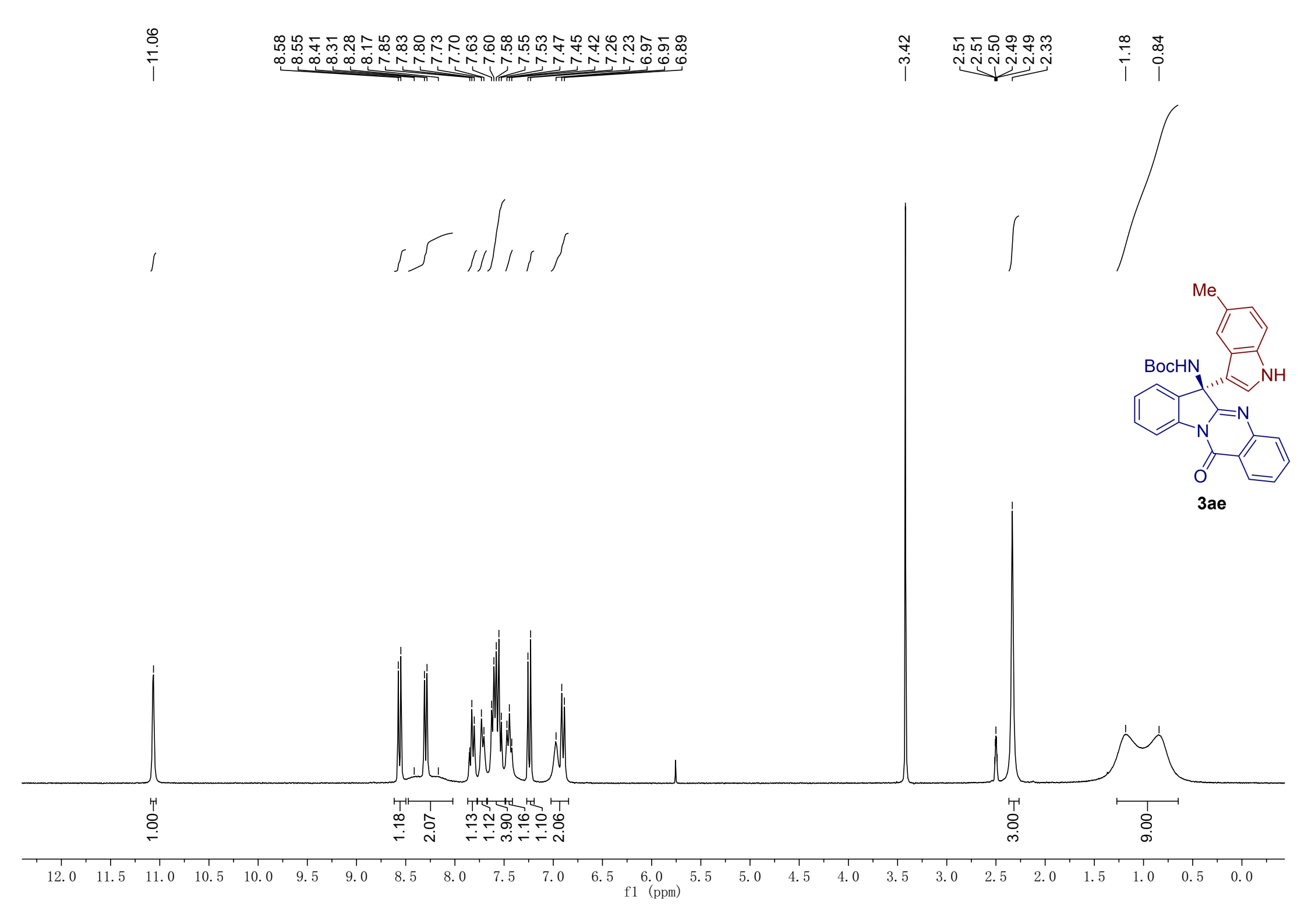
50
40
30
20
10
0
f1 (ppm)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7.55
7.53
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7.45
7.42
7.26
7.23
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6.91
6.89
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2.51
2.50
2.49
2.49
2.33
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O
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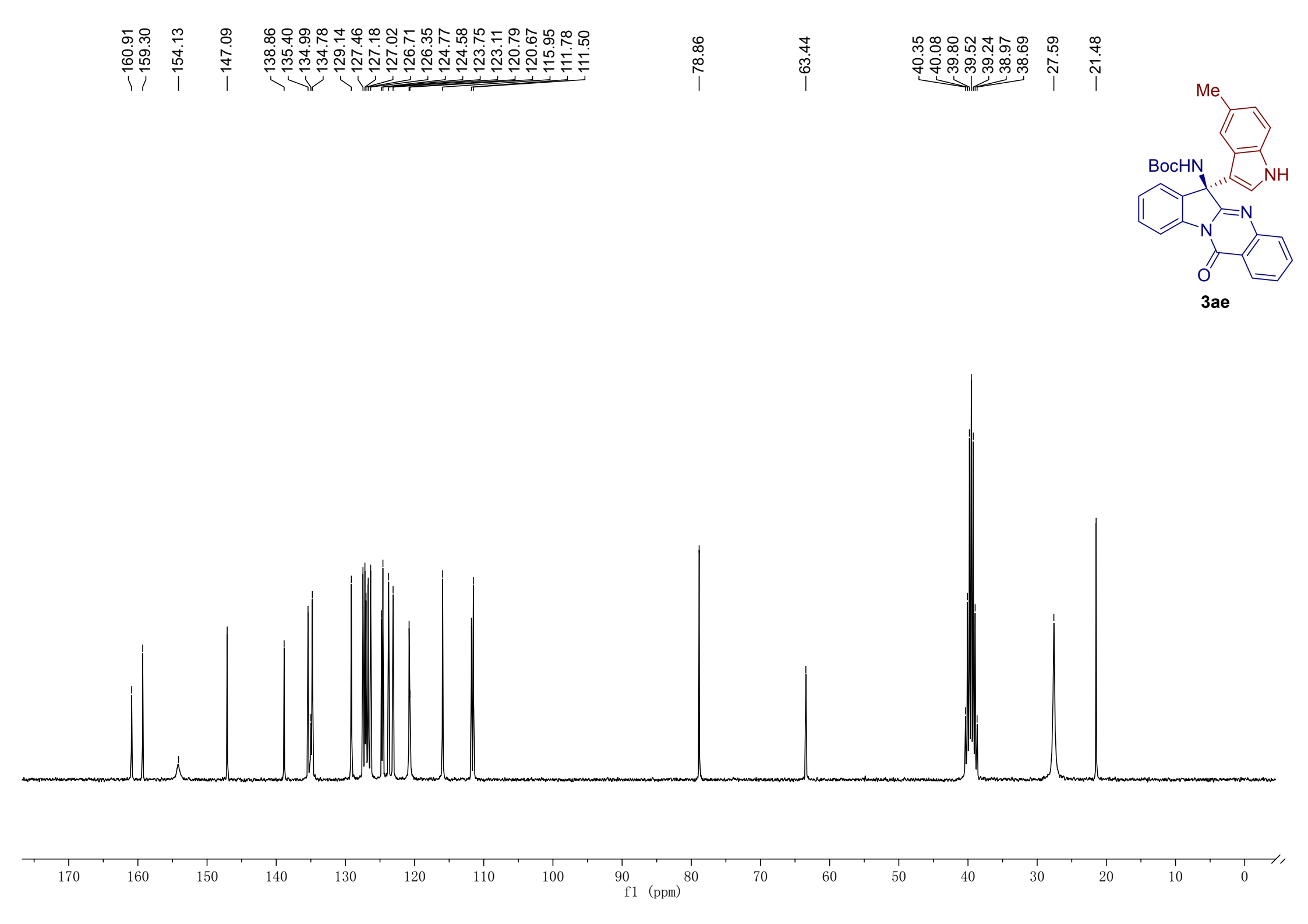
2.07
1.13
1.12
3.90
1.16
1.10
2.06
3.00
9.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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111.50
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27.59
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N
O
3ae
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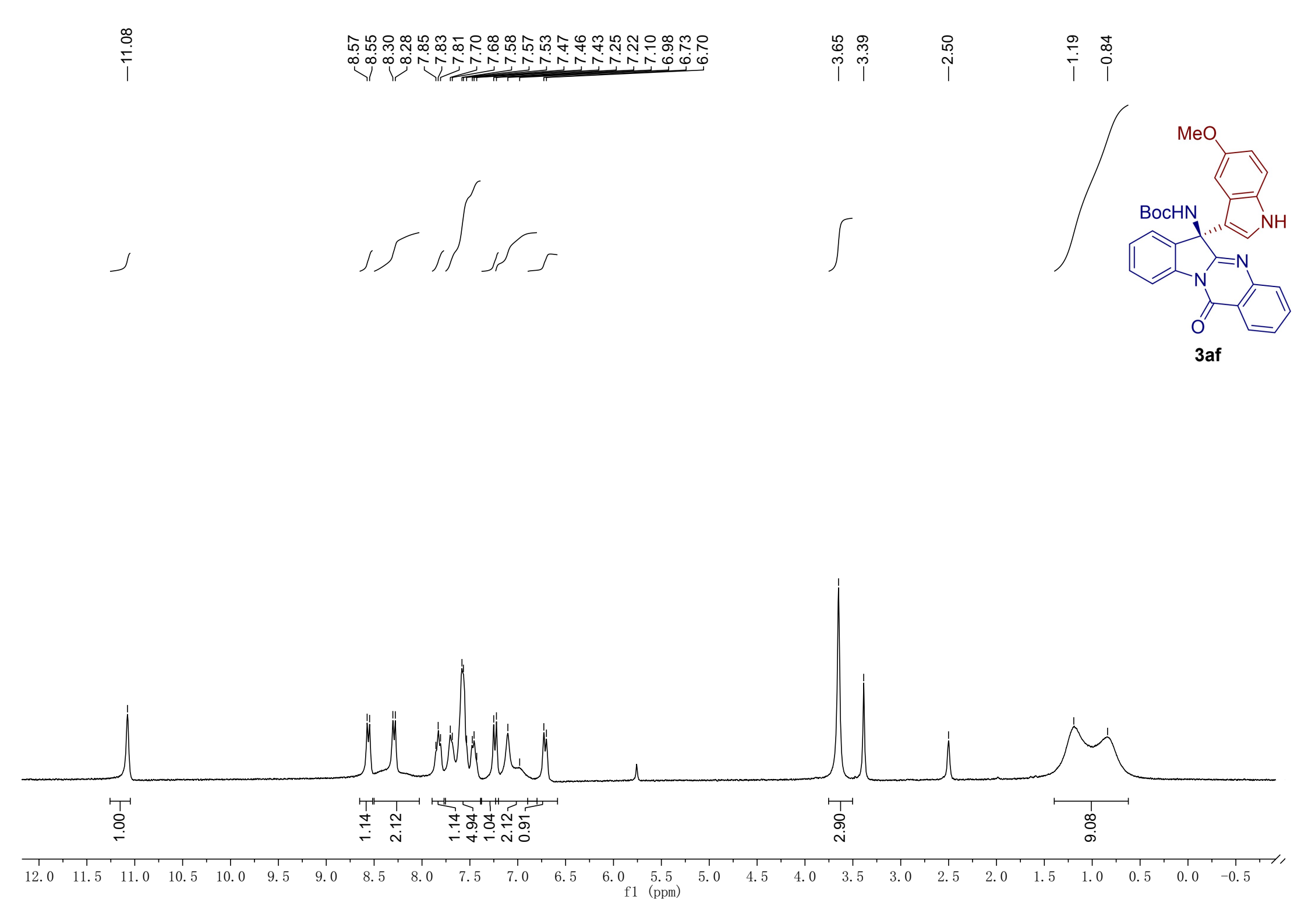
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6.70
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3.39
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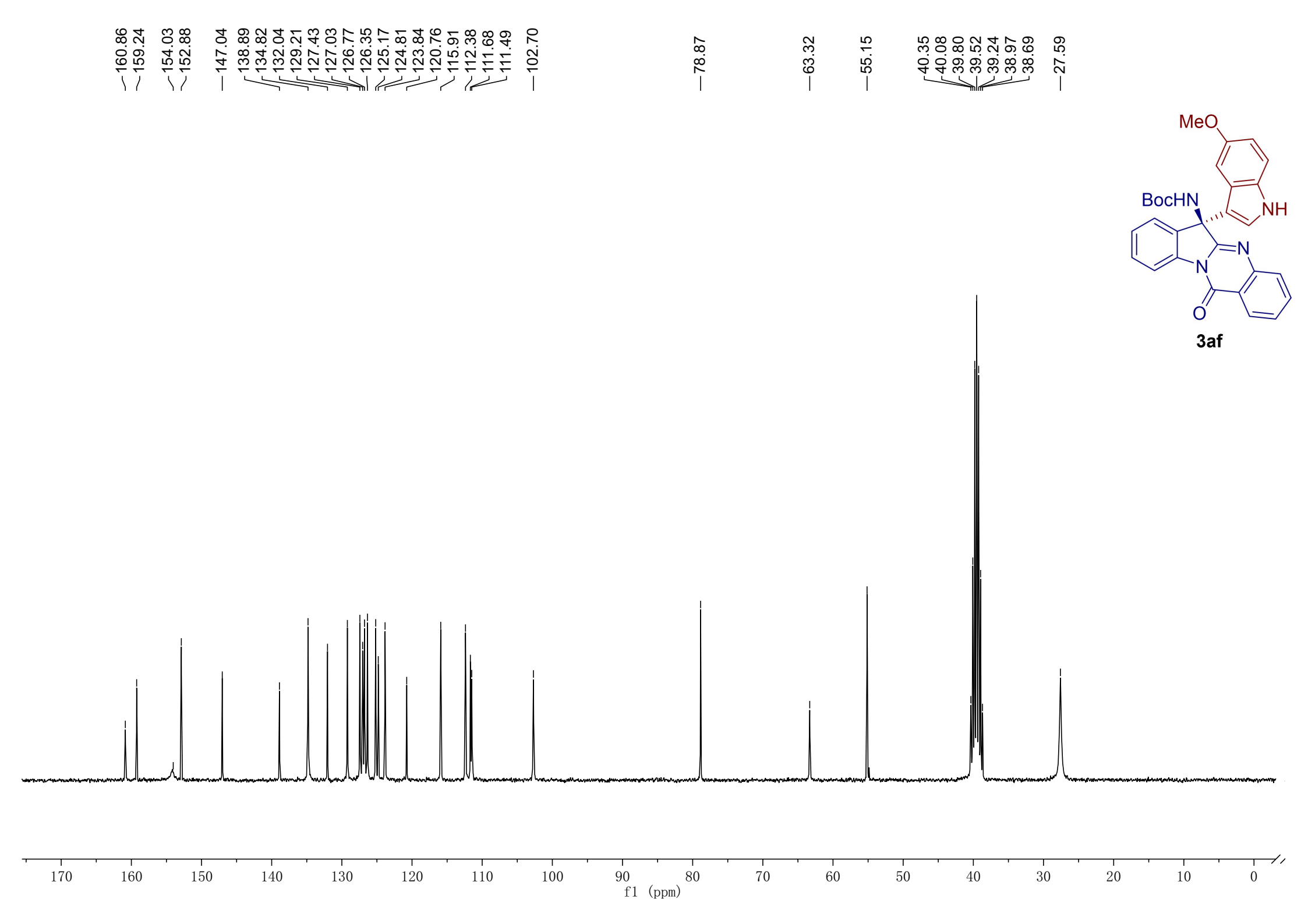
MeO
BocHN
NH
N
N
O
3af
1.00
1.14
2.12
1.14
4.94
1.04
2.12
0.91
2.90
9.08
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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38.69
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N
O
3af
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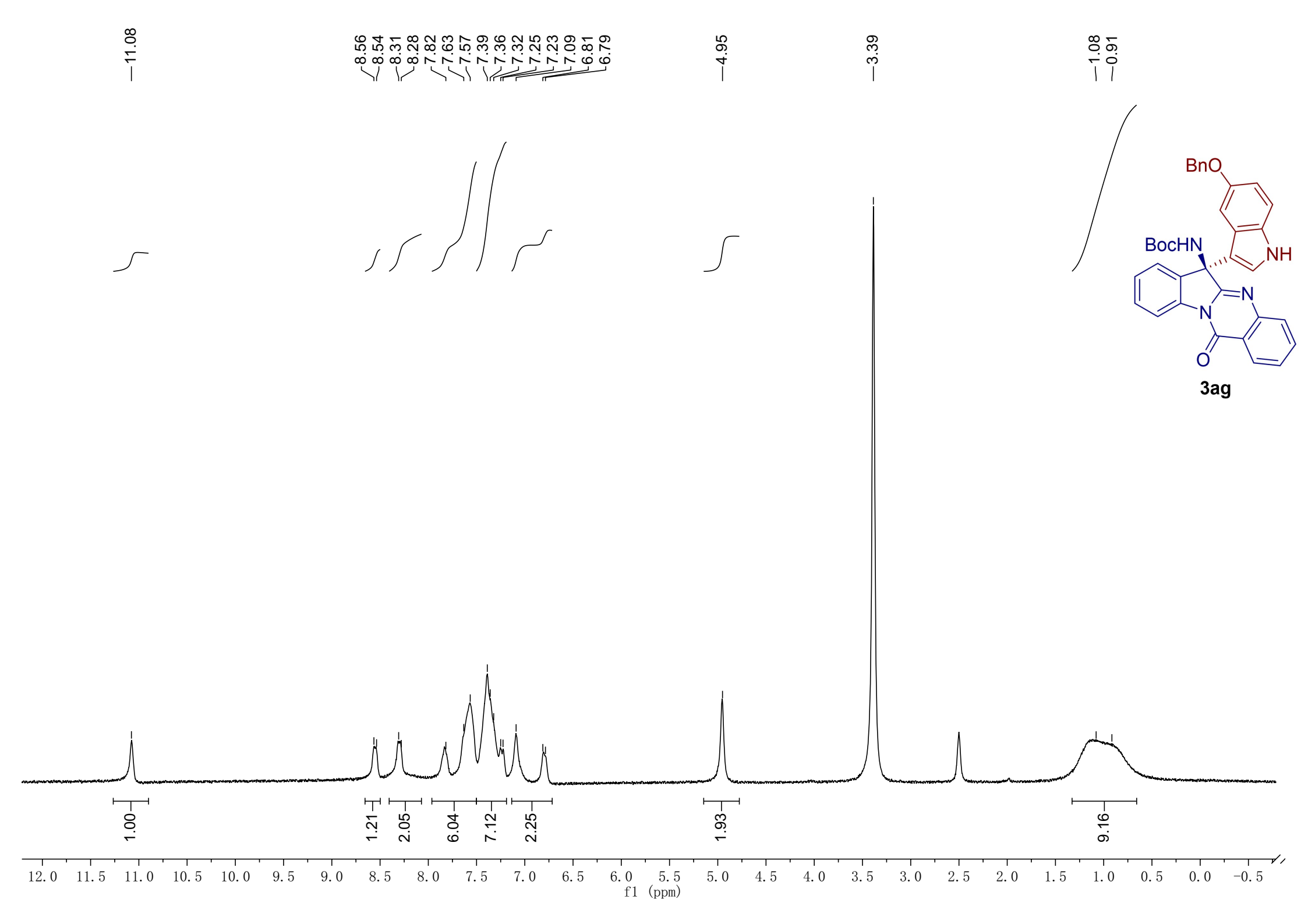
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6.79
4.95
3.39
1.08
0.91
BnO
BocHN
NH
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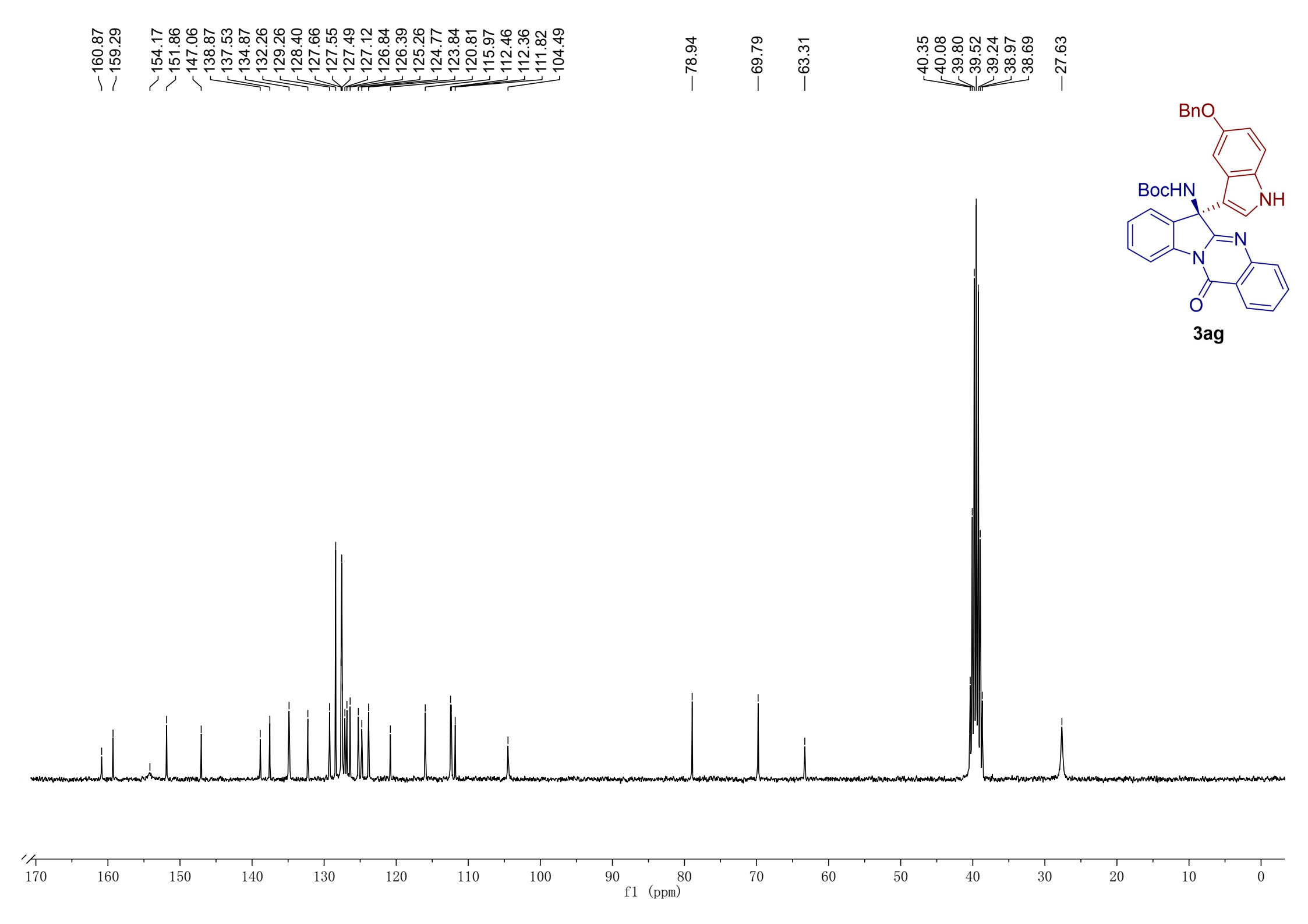
2.25
1.93
9.16
f1 (ppm)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38.69
27.63
BnO
BocHN
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N
N
O
3ag
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10
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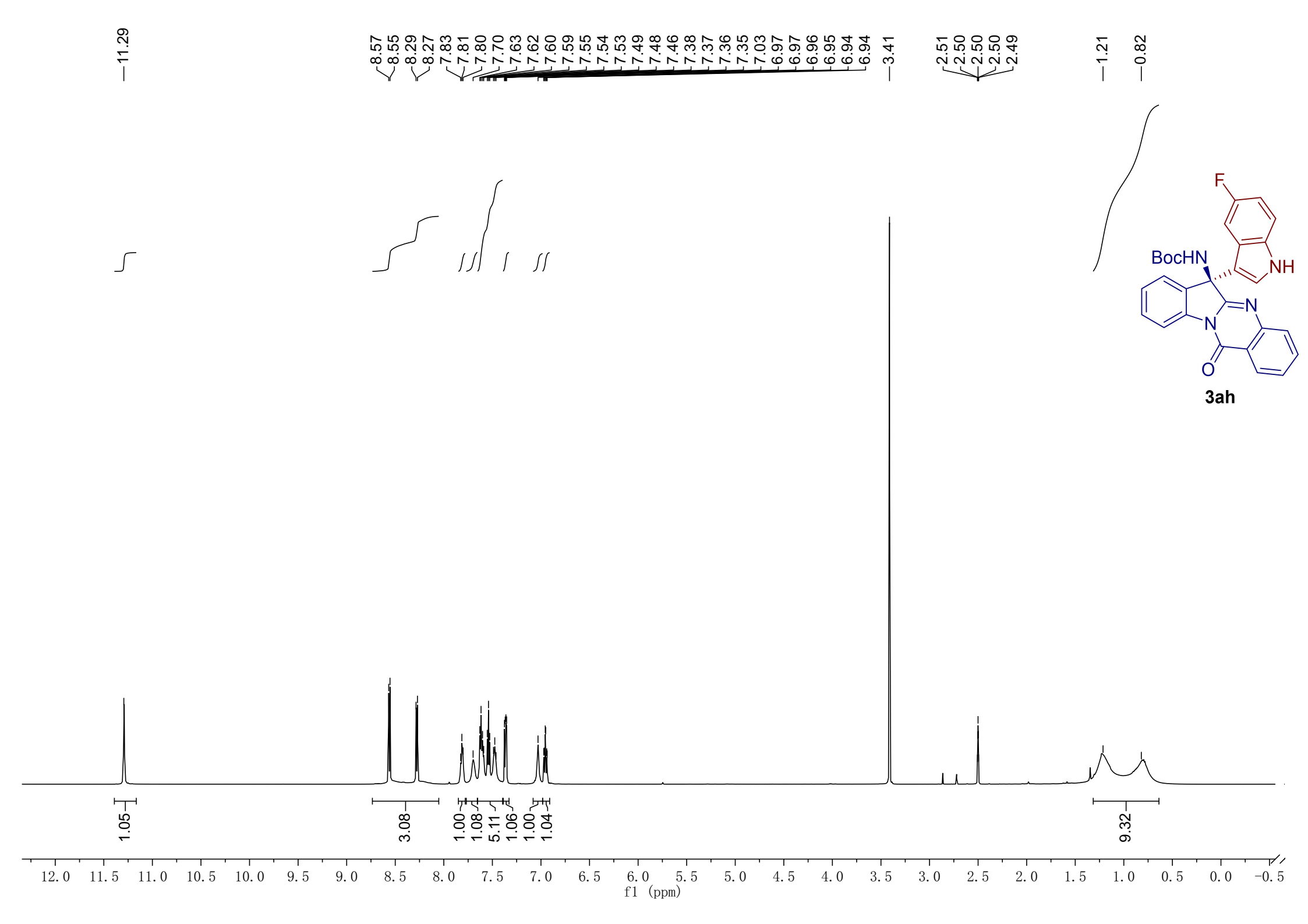
f1 (ppm)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7.53
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6.96
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6.94
6.94
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2.50
2.50
2.50
2.49
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0.82
F
BocHN
NH
N
N
O
3ah
1.05
3.08
1.00
1.08
5.11
1.06
1.00
1.04
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10.5
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7.0
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6.0
5.5
5.0
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0.5
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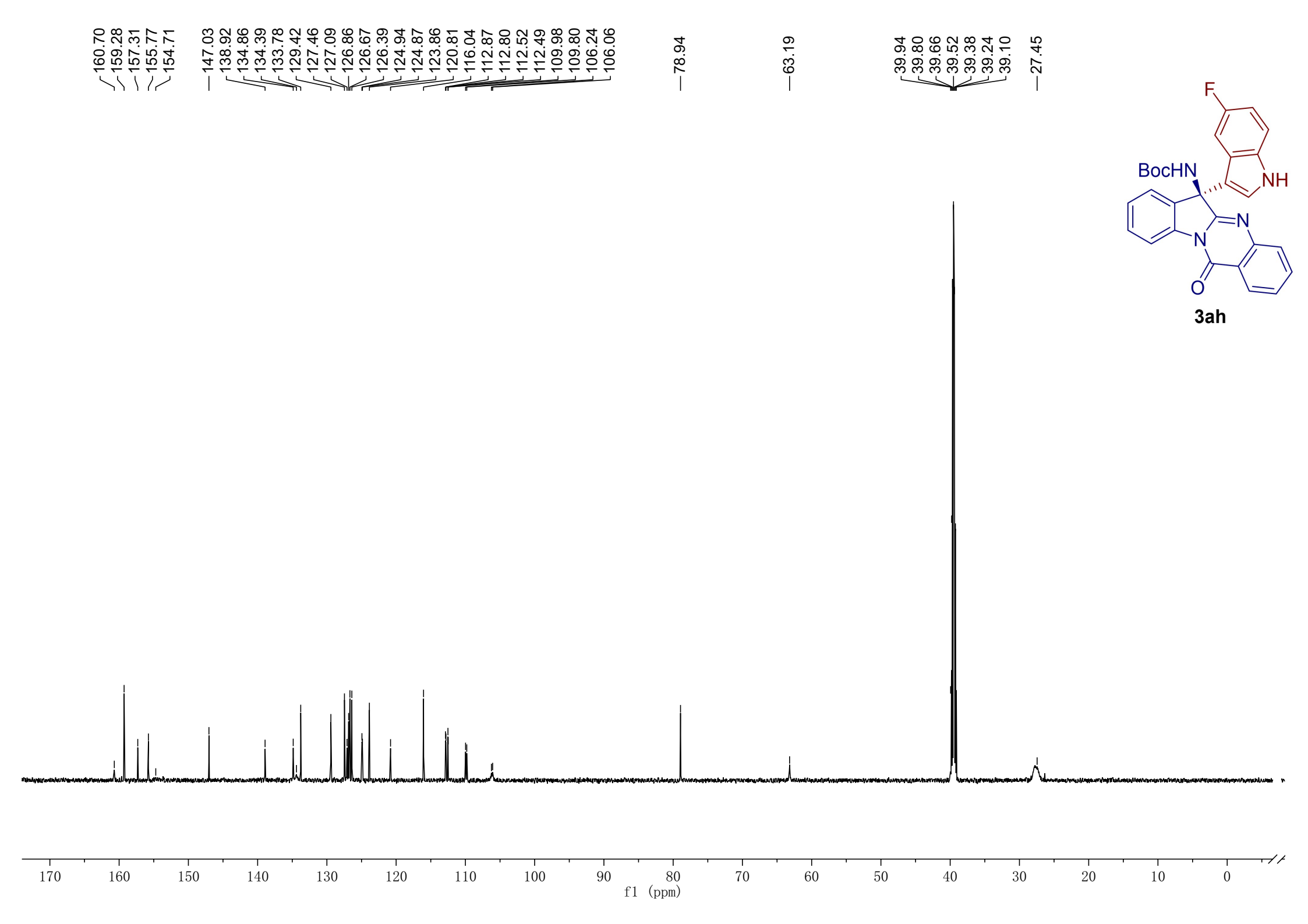
-0.5
f1 (ppm)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126.39
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63.19
39.94
39.80
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39.52
39.38
39.24
39.10
27.45
F
BocHN
NH
N
N
O
3ah
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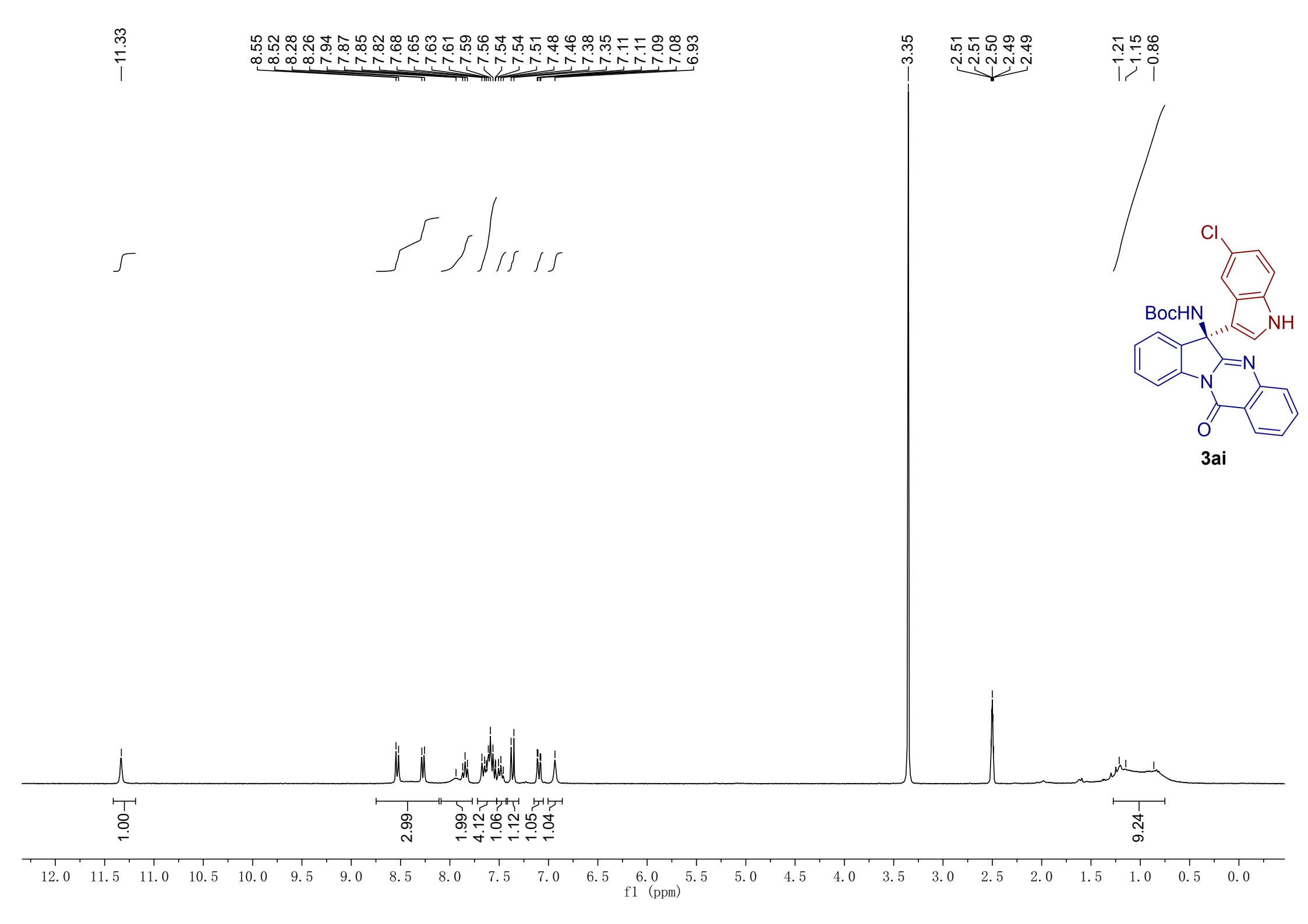
f1 (ppm)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7.61
7.59
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7.54
7.51
7.48
7.46
7.38
7.35
7.11
7.11
7.09
7.08
6.93
3.35
2.51
2.51
2.50
2.49
2.49
1.21
1.15
0.86
Cl
BocHN
NH
N
N
O
3ai
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2.99
1.99
4.12
1.06
1.12
1.05
1.04
9.24
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.0
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1.0
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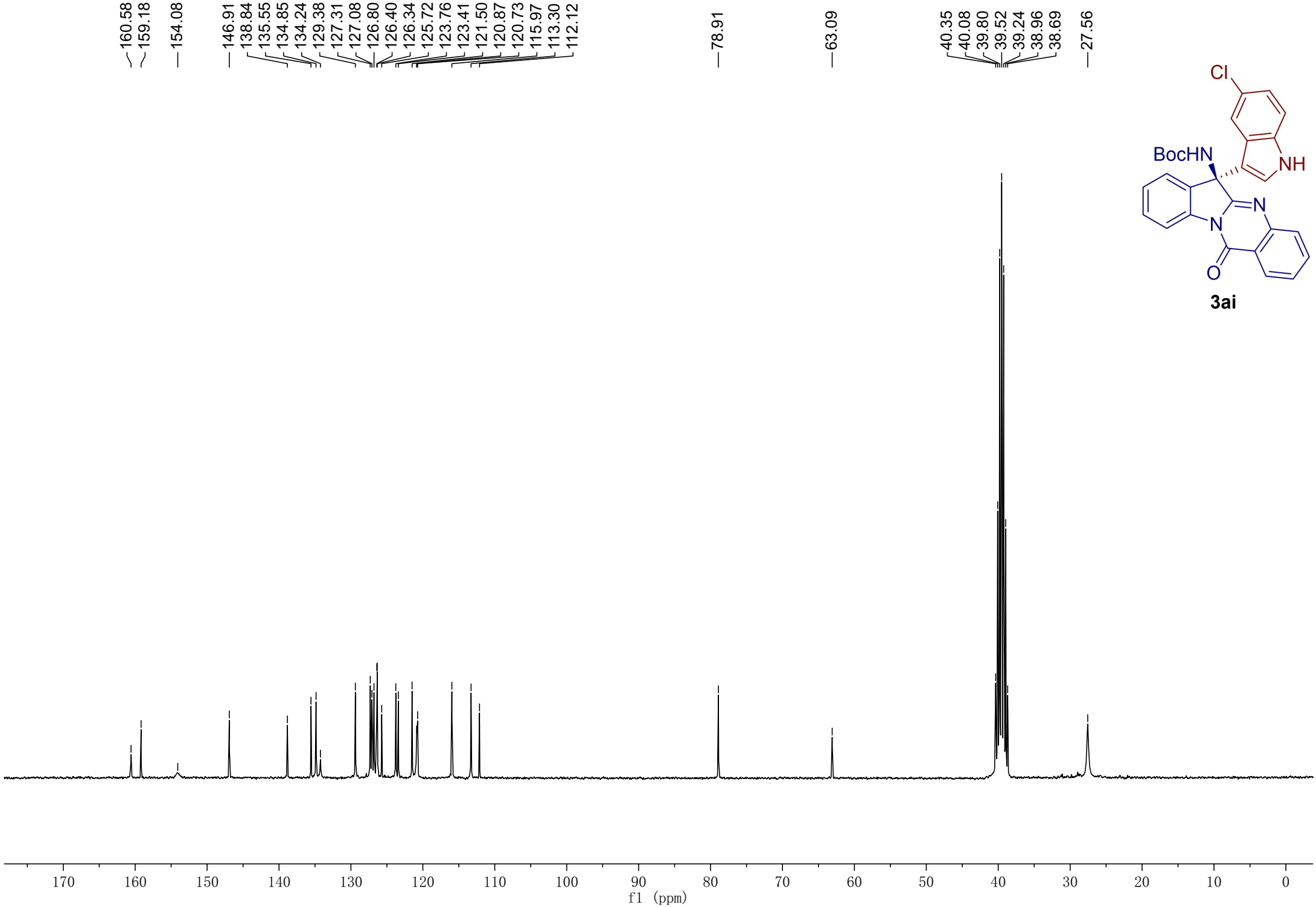
0.0
f1 (ppm)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123.41
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39.24
38.96
38.69
27.56
Cl
BocHN
NH
N
N
O
3ai
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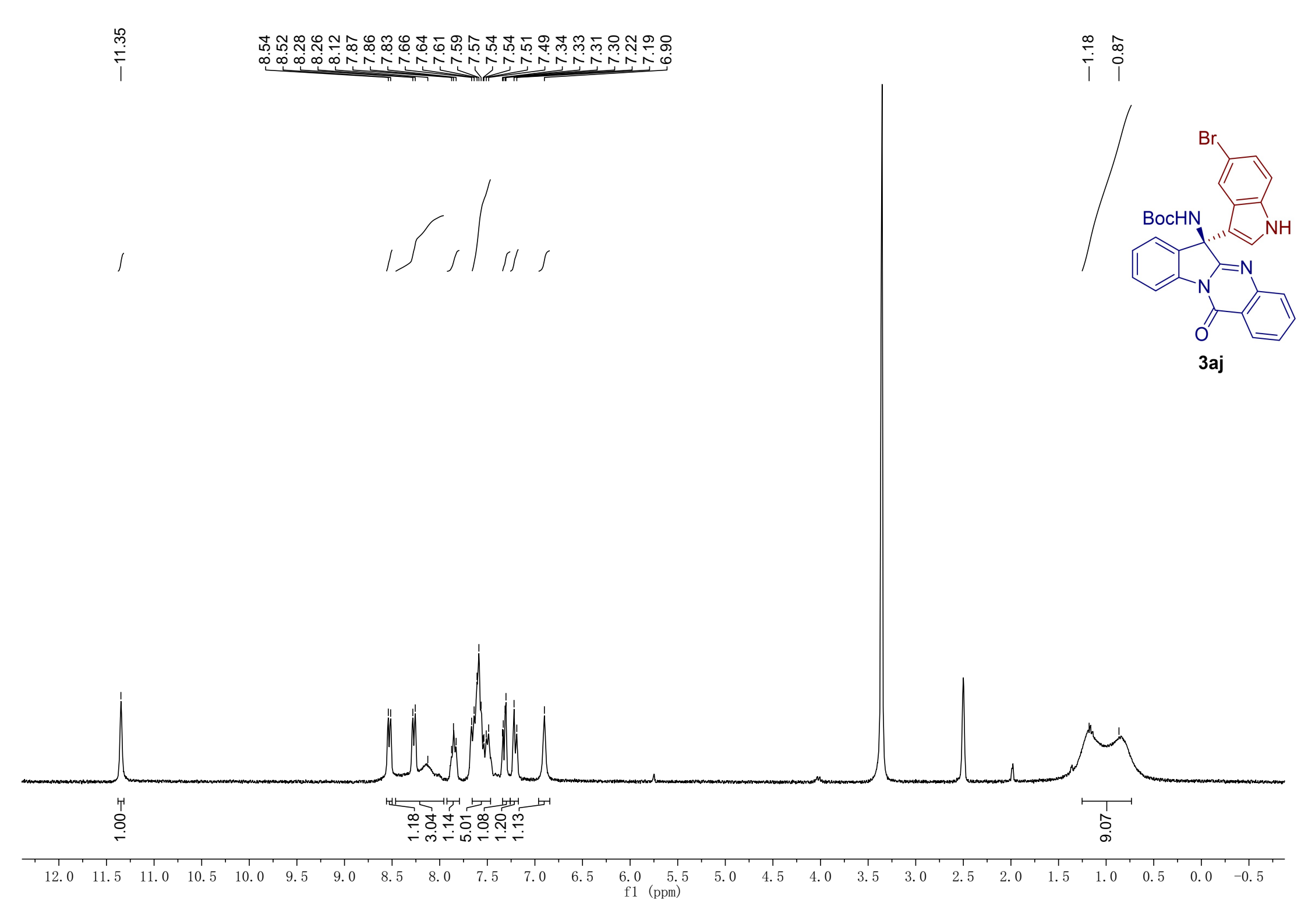
f1 (ppm)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7.57
7.54
7.54
7.51
7.49
7.34
7.33
7.31
7.30
7.22
7.19
6.90
1.18
0.87
Br
BocHN
NH
N
N
O
3aj
1.00
1.18
3.04
1.14
5.01
1.08
1.20
1.13
9.07
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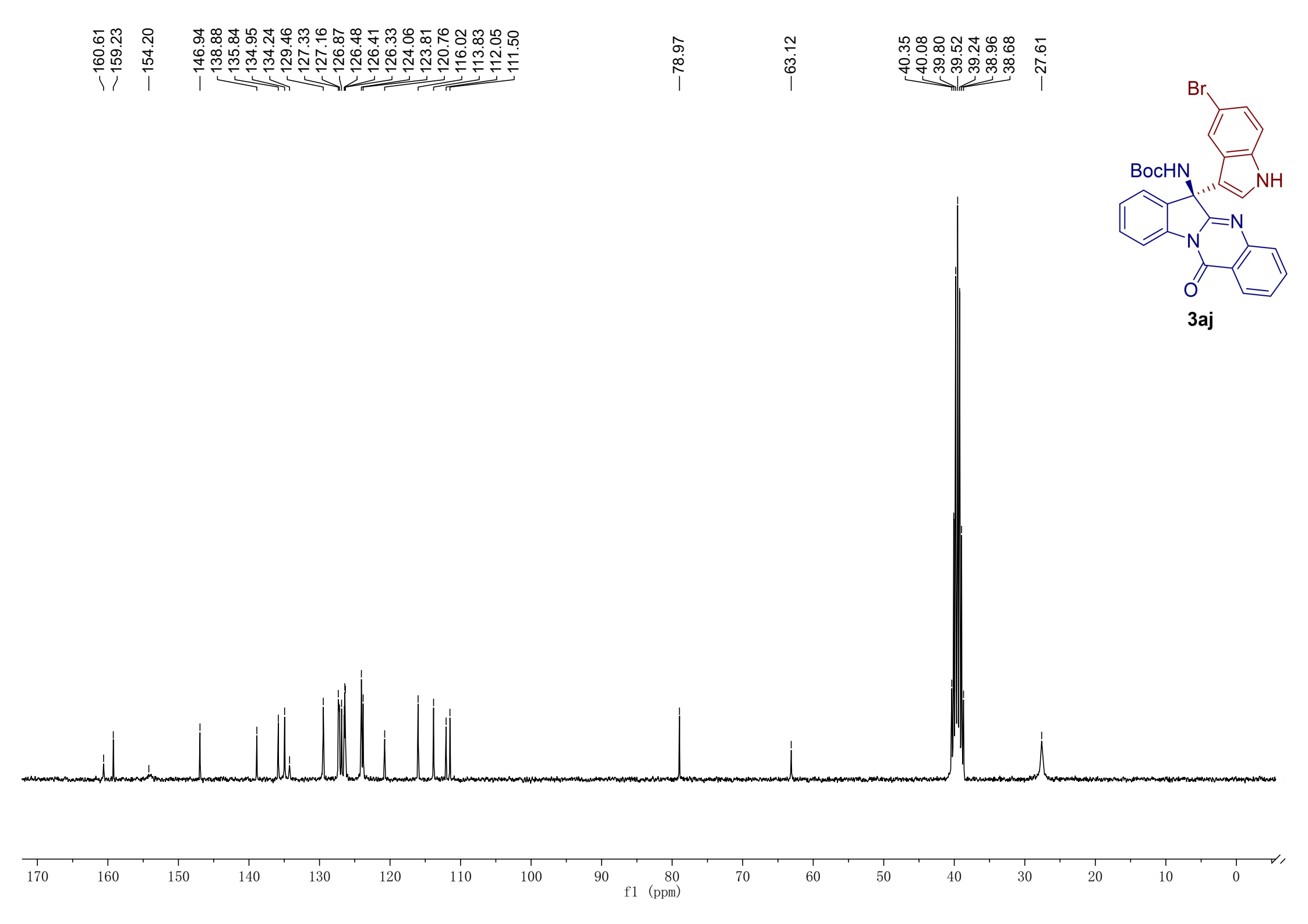
f1 (ppm)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123.81
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116.02
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112.05
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78.97
63.12
40.35
40.08
39.80
39.52
39.24
38.96
38.68
27.61
Br
BocHN
NH
N
N
O
3aj
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90
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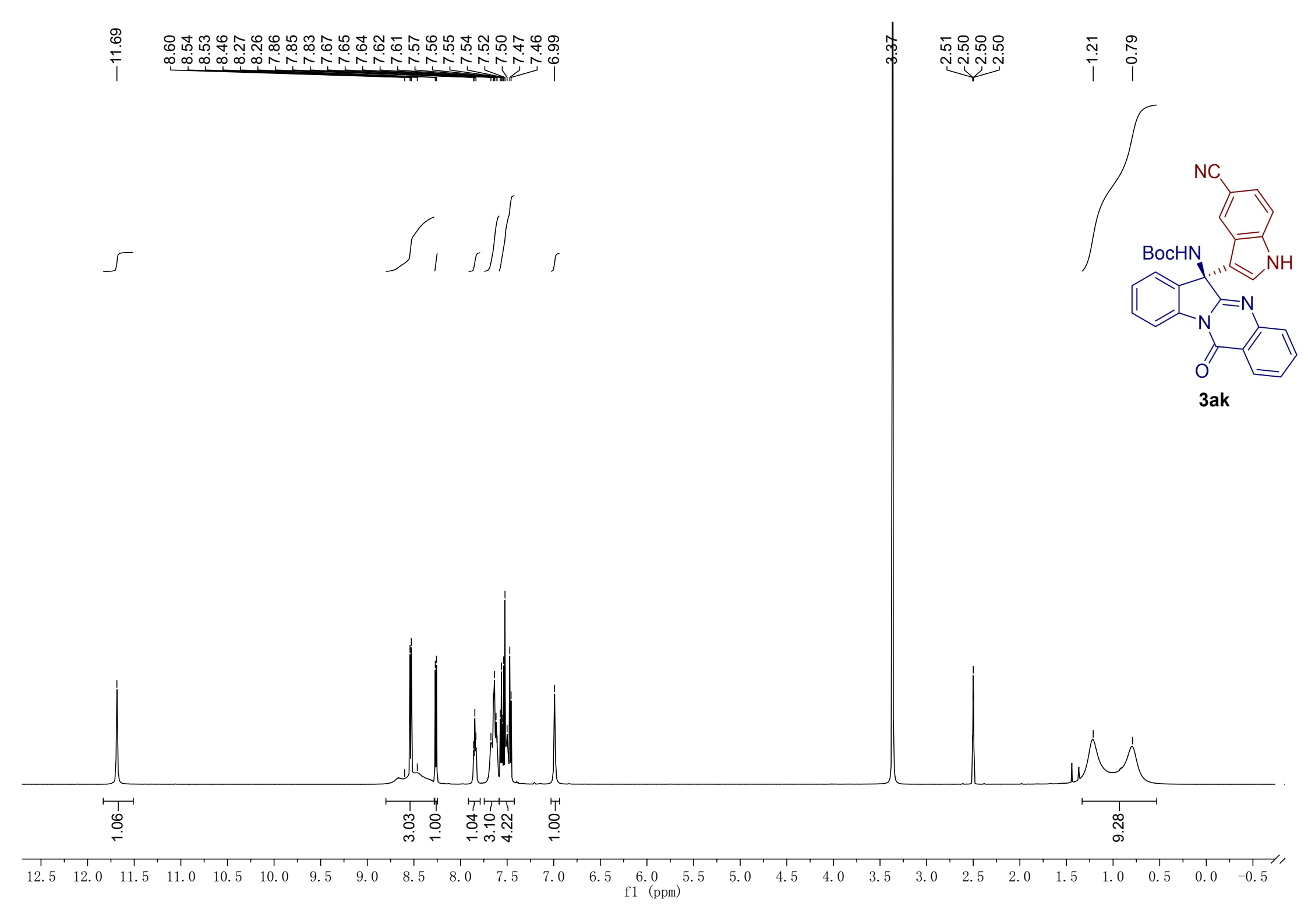
10
0
f1 (ppm)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7.62
7.61
7.57
7.56
7.55
7.54
7.52
7.50
7.47
7.46
6.99
3.37
2.51
2.50
2.50
2.50
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NC
BocHN
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N
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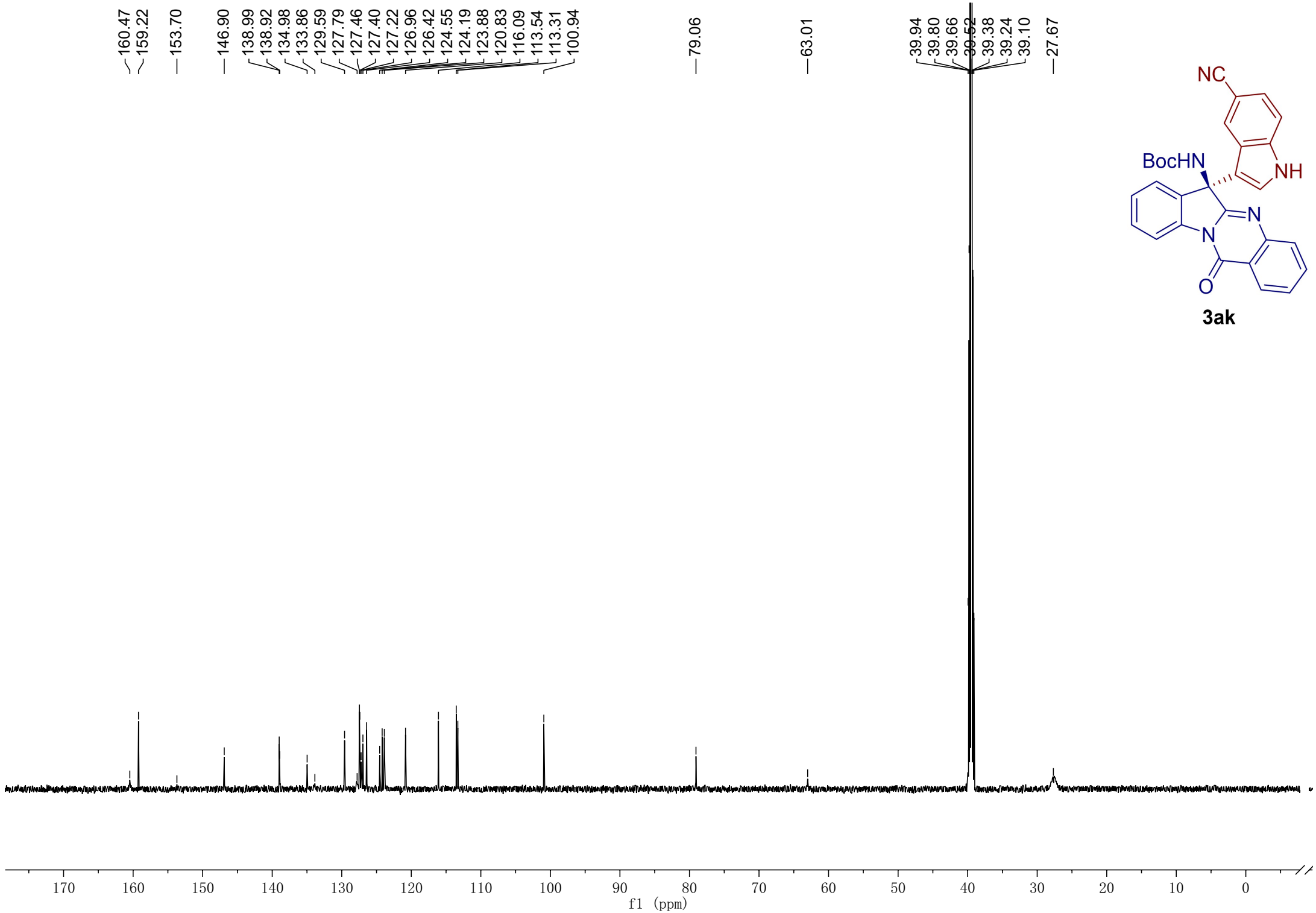
f1 (ppm)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116.09
113.54
113.31
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79.06
63.01
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39.80
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39.24
39.10
27.67
NC
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N
O
3ak
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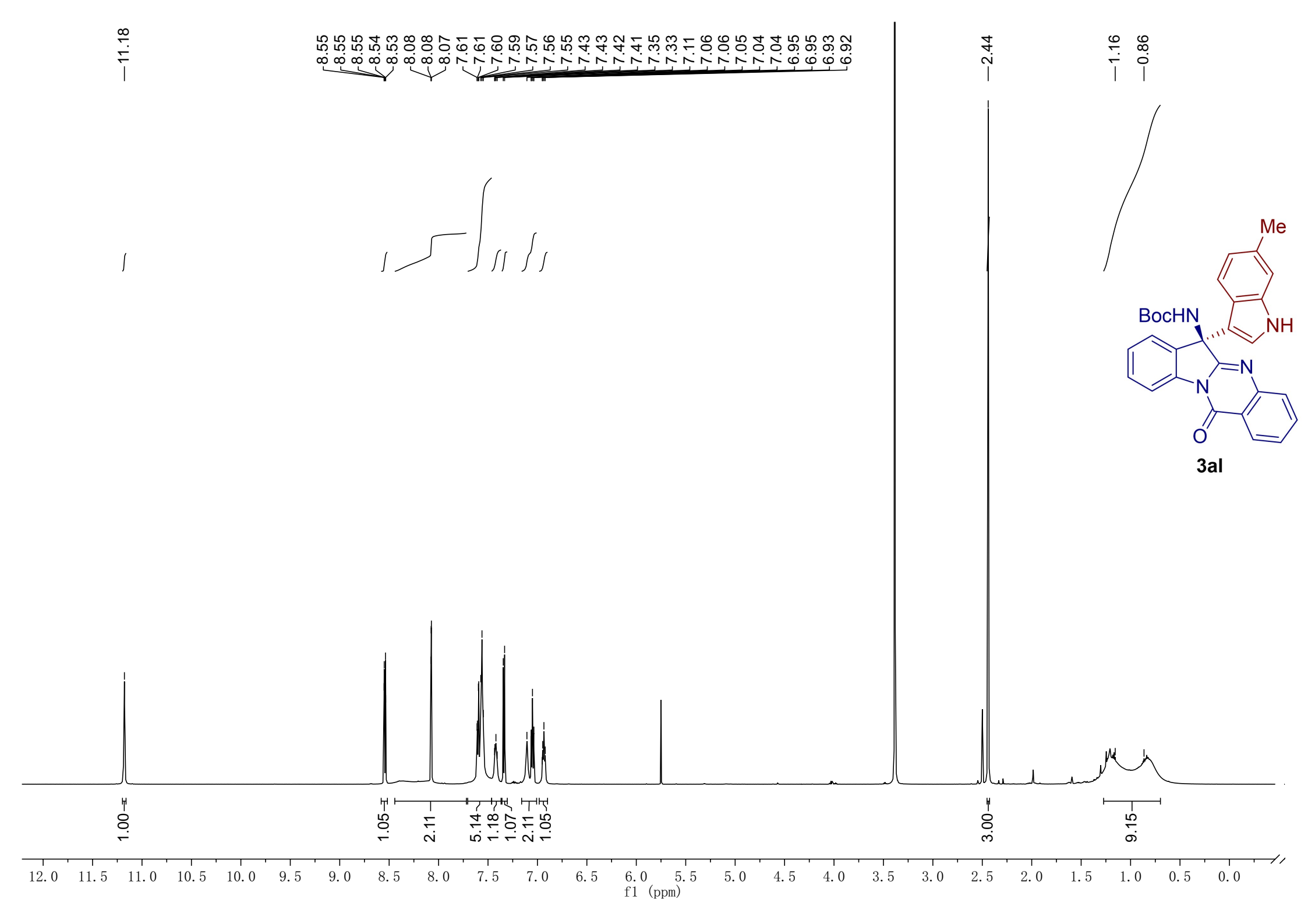
10
0
f1 (ppm)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7.55
7.43
7.43
7.42
7.41
7.35
7.33
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7.06
7.05
7.04
7.04
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6.95
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N
N
O
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1.07
2.11
1.05
3.00
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11.0
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10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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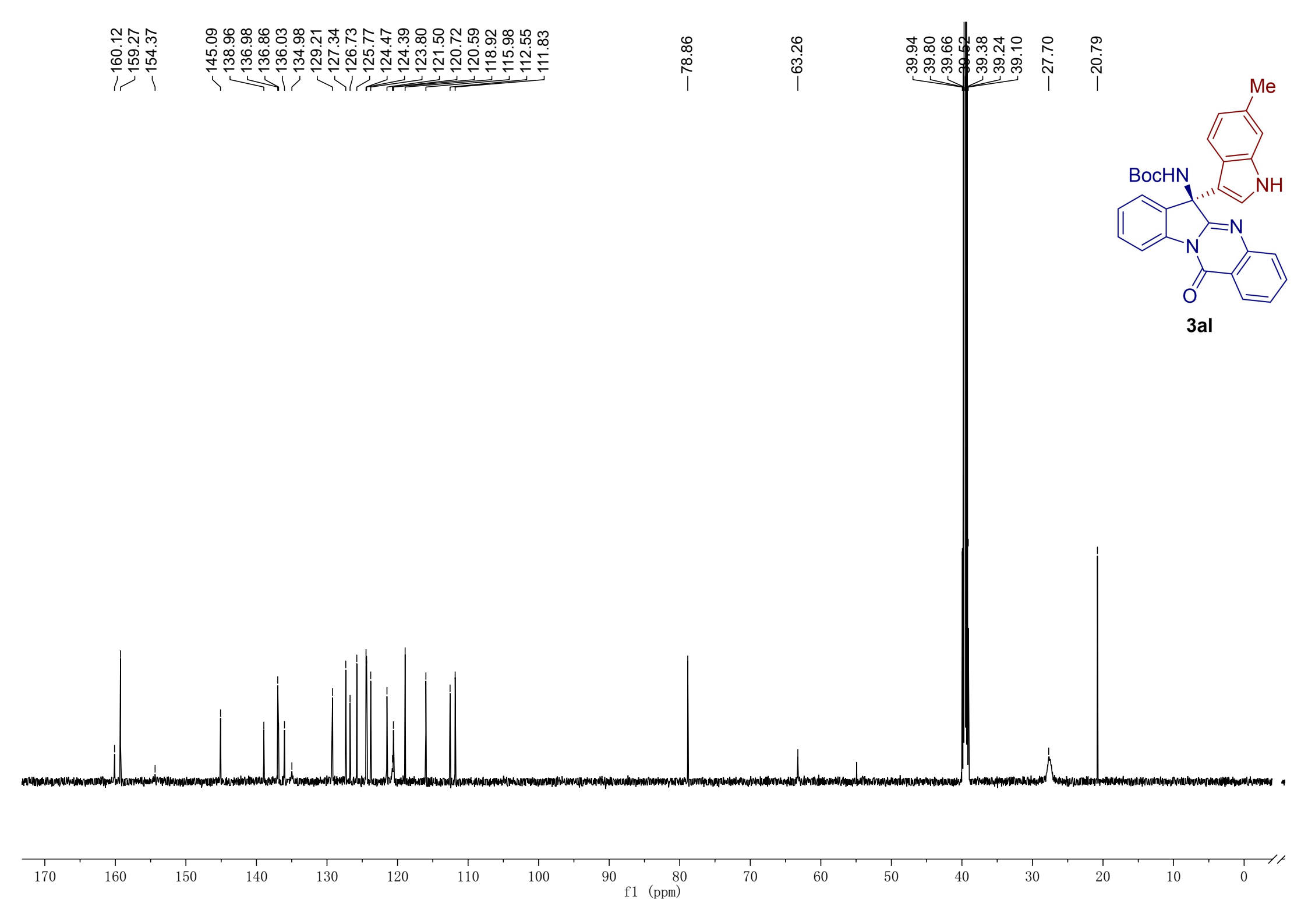
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3al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27.70
20.79
Me
BocHN
NH
N
N
O
3al
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100
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50
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30
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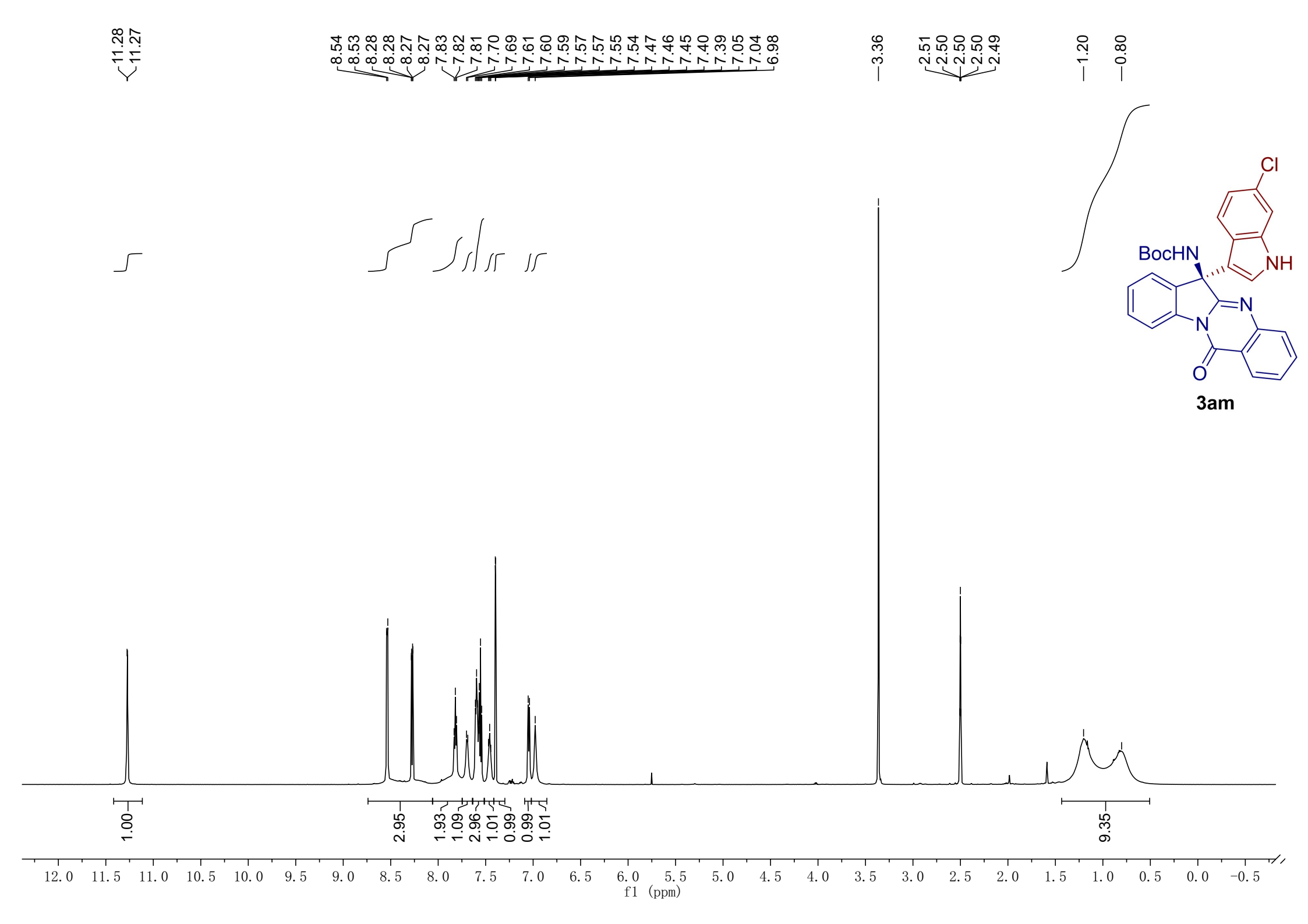
10
0
f1 (ppm)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7.69
7.61
7.60
7.59
7.57
7.57
7.55
7.54
7.47
7.46
7.45
7.40
7.39
7.05
7.04
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2.50
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2.49
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0.80
Cl
BocHN
NH
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N
O
3am
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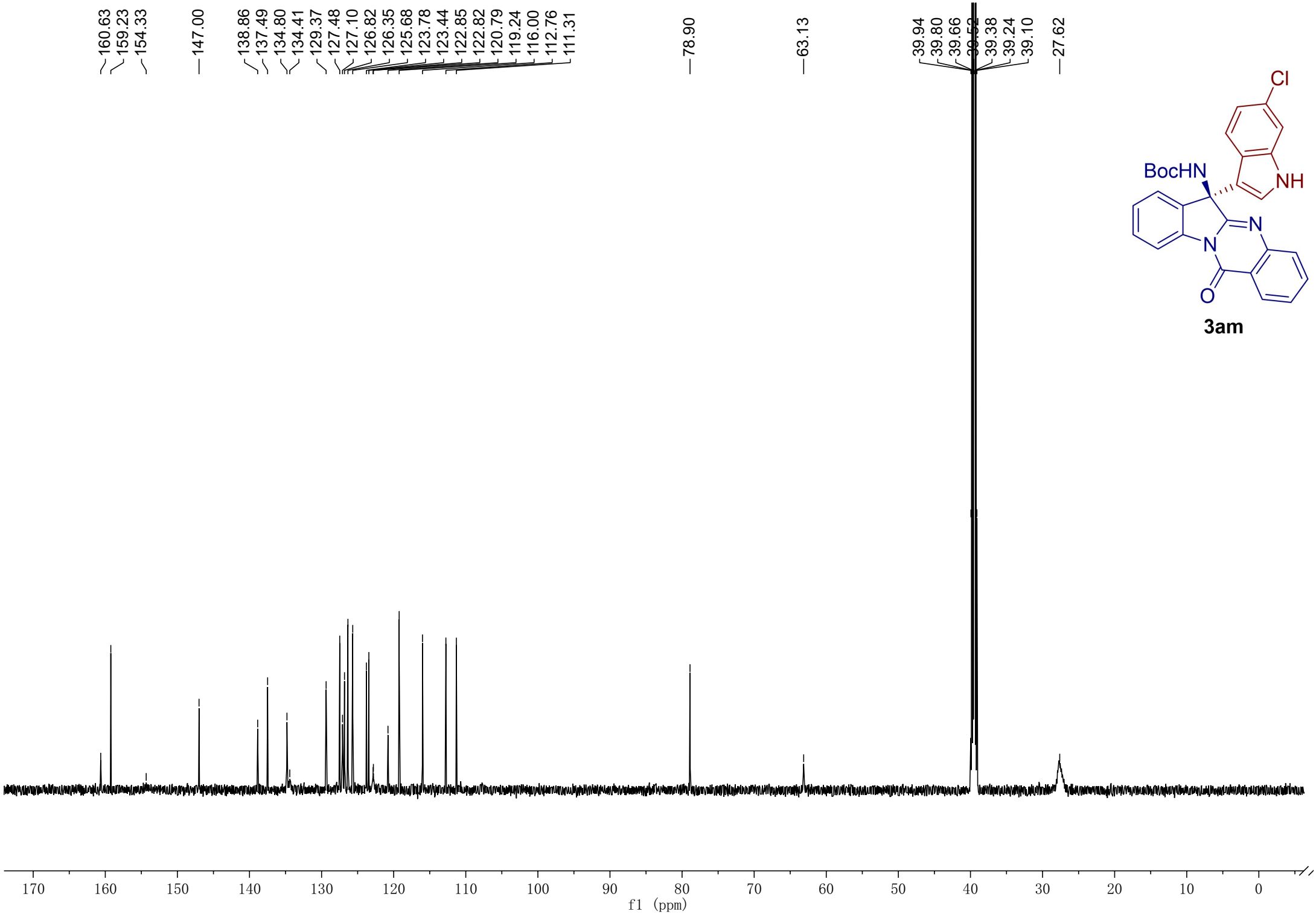
1.93
1.09
2.96
1.01
0.99
0.99
1.01
9.35
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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123.44
122.85
122.82
120.79
119.24
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112.76
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78.90
63.13
39.94
39.80
39.66
39.38
39.24
39.10
27.62
Cl
BocHN
NH
N
N
O
3am
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110
100
90
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50
40
30
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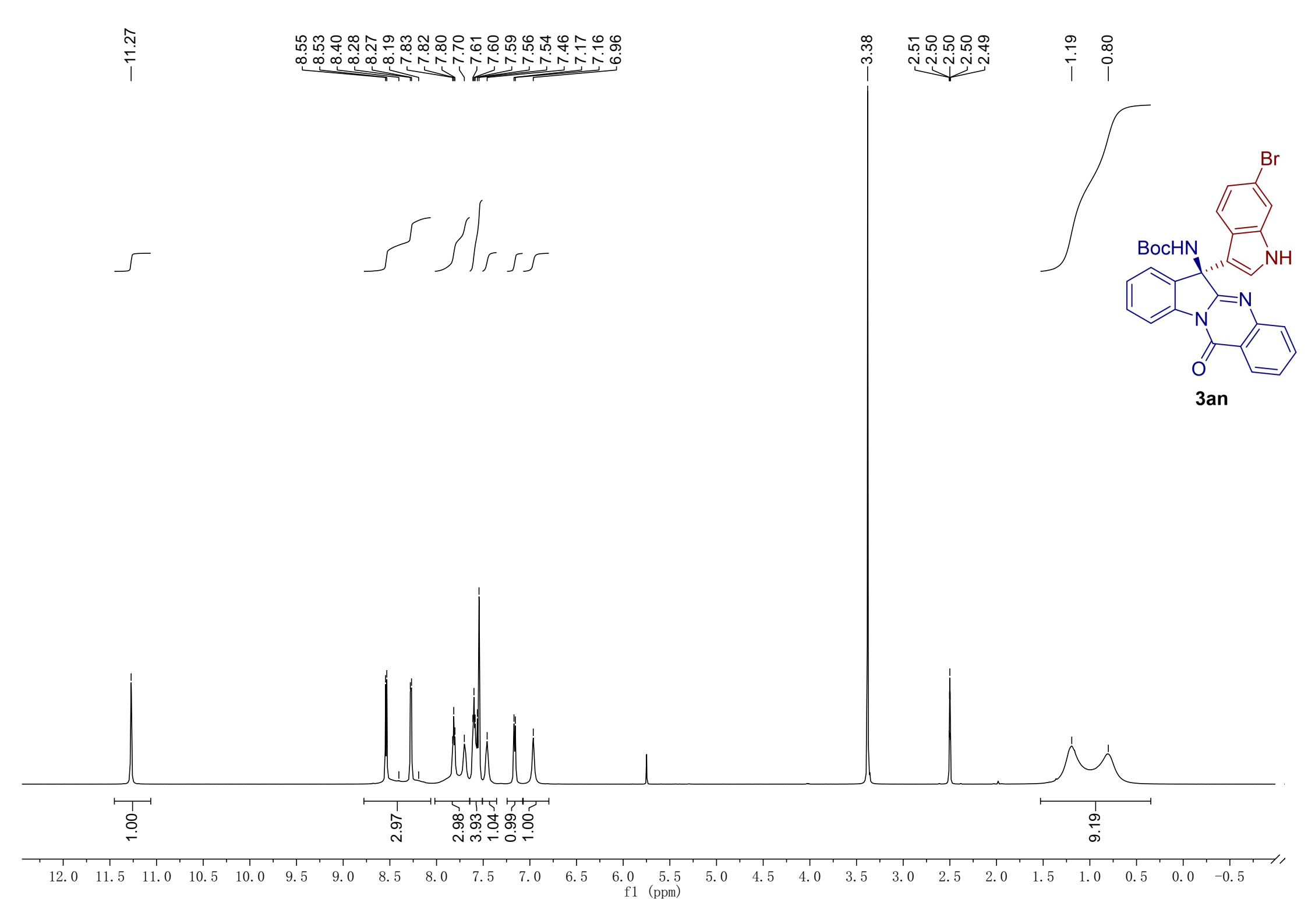
10
0
f1 (ppm)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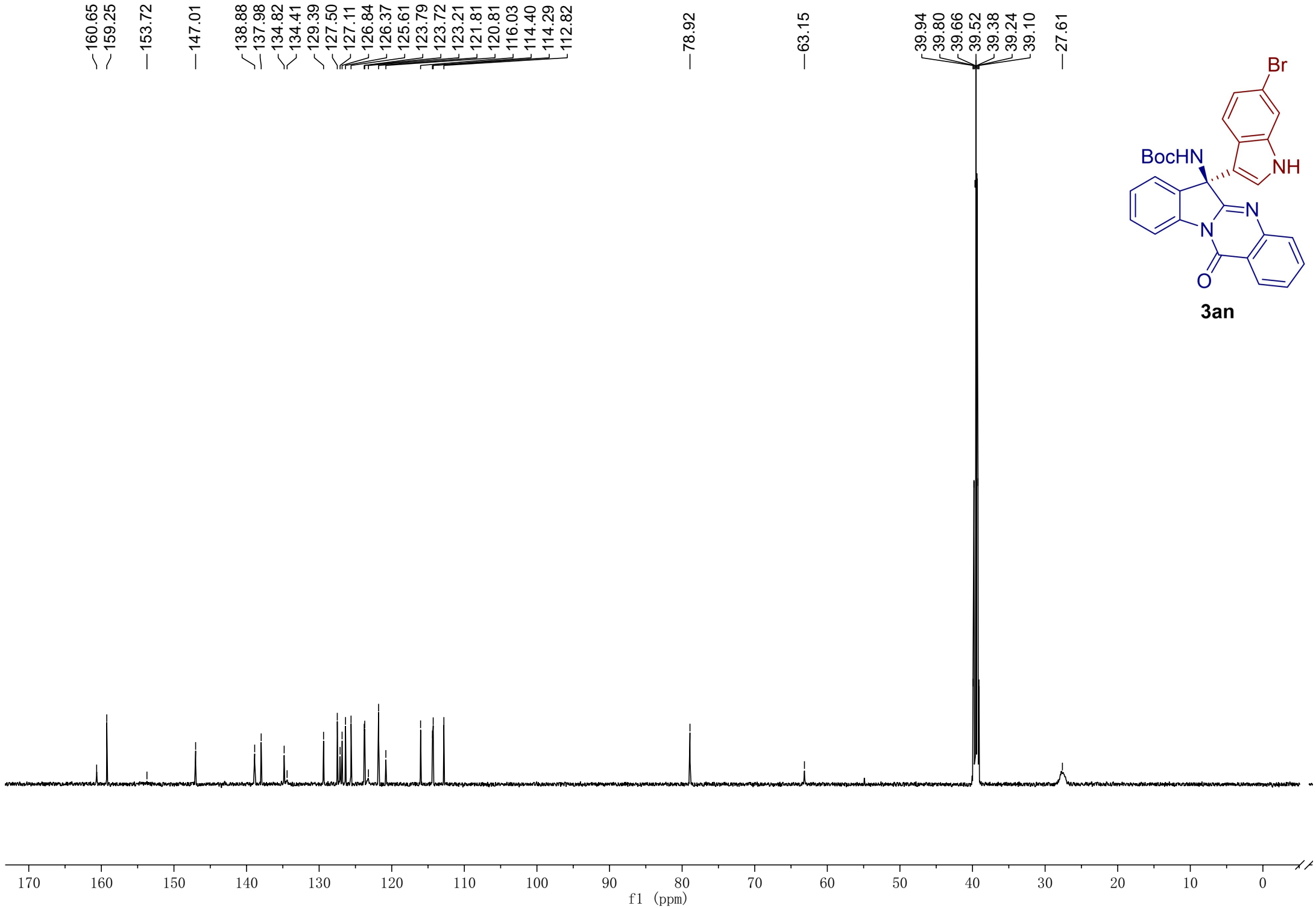
7.70
7.61
7.60
7.59
7.56
7.54
7.46
7.17
7.16
6.96
3.38
2.51
2.50
2.50
2.50
2.49
1.19
0.80
Br
BocHN
NH
N
N
O
3an
1.00
2.97
2.98
3.93
1.04
0.99
1.00
9.19
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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123.21
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116.03
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114.29
112.82
78.92
63.15
39.94
39.80
39.66
39.52
39.38
39.24
39.10
27.61
Br
BocHN
NH
N
N
O
3an
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130
120
110
100
90
80
70
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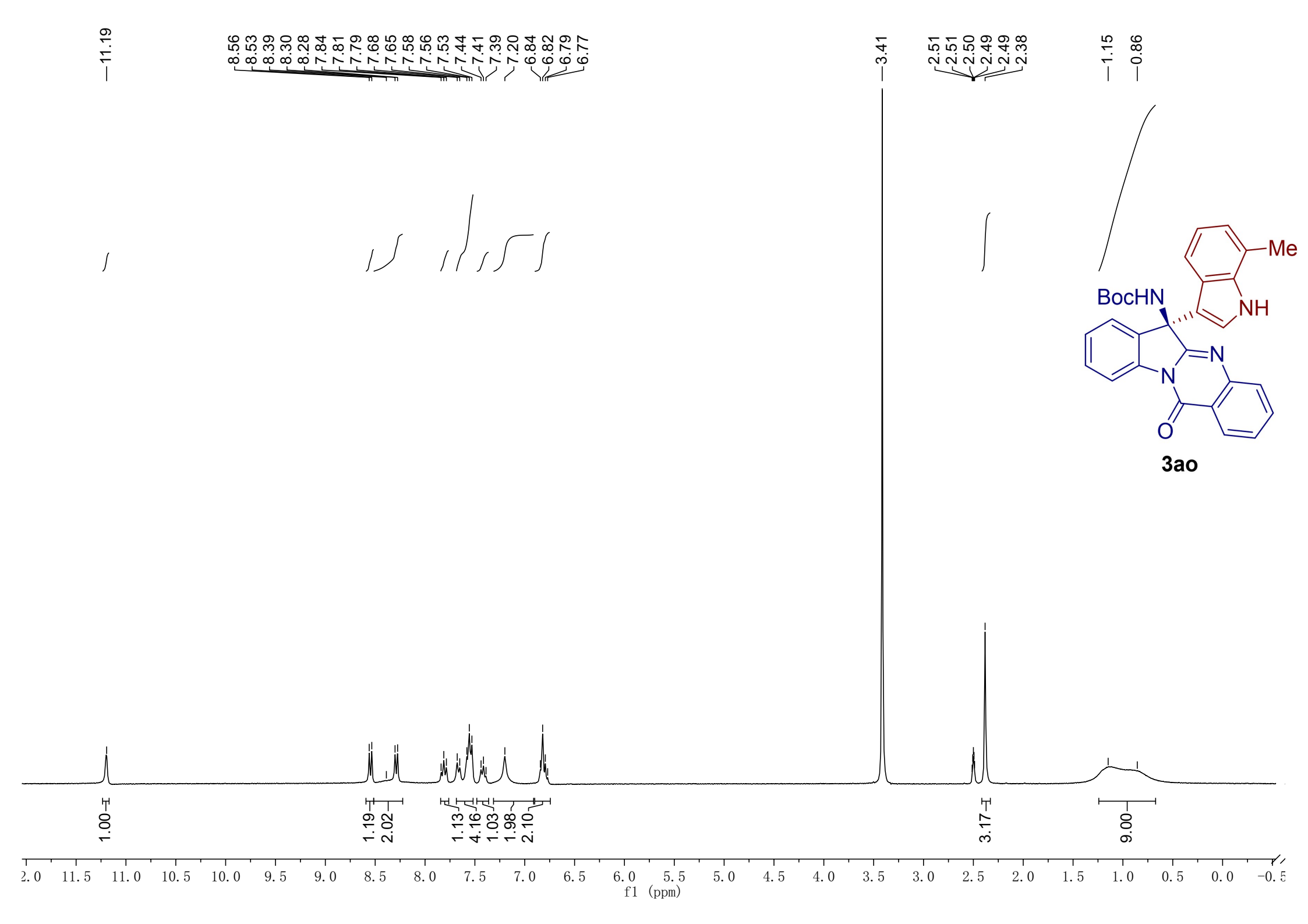
50
40
30
20
10
0
f1 (ppm)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7.56
7.53
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7.41
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7.20
6.84
6.82
6.79
6.77
3.41
2.51
2.51
2.50
2.49
2.49
2.38
1.15
0.86
Me
BocHN
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N
N
O
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4.16
1.03
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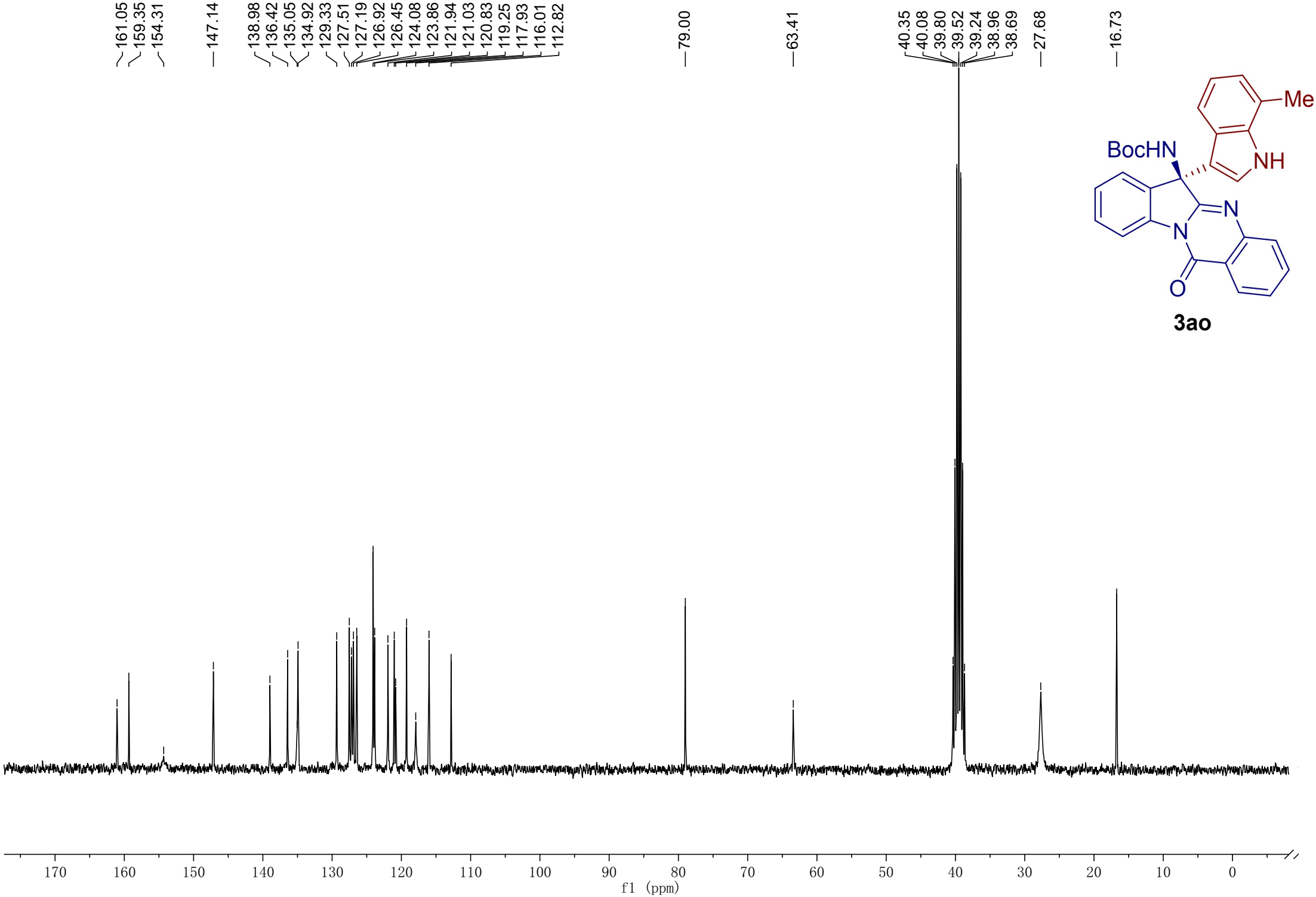
2.10
3.17
9.00
f1 (ppm)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117.93
116.01
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79.00
63.41
40.35
40.08
39.80
39.52
39.24
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27.68
16.73
Me
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O
3ao
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130
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100
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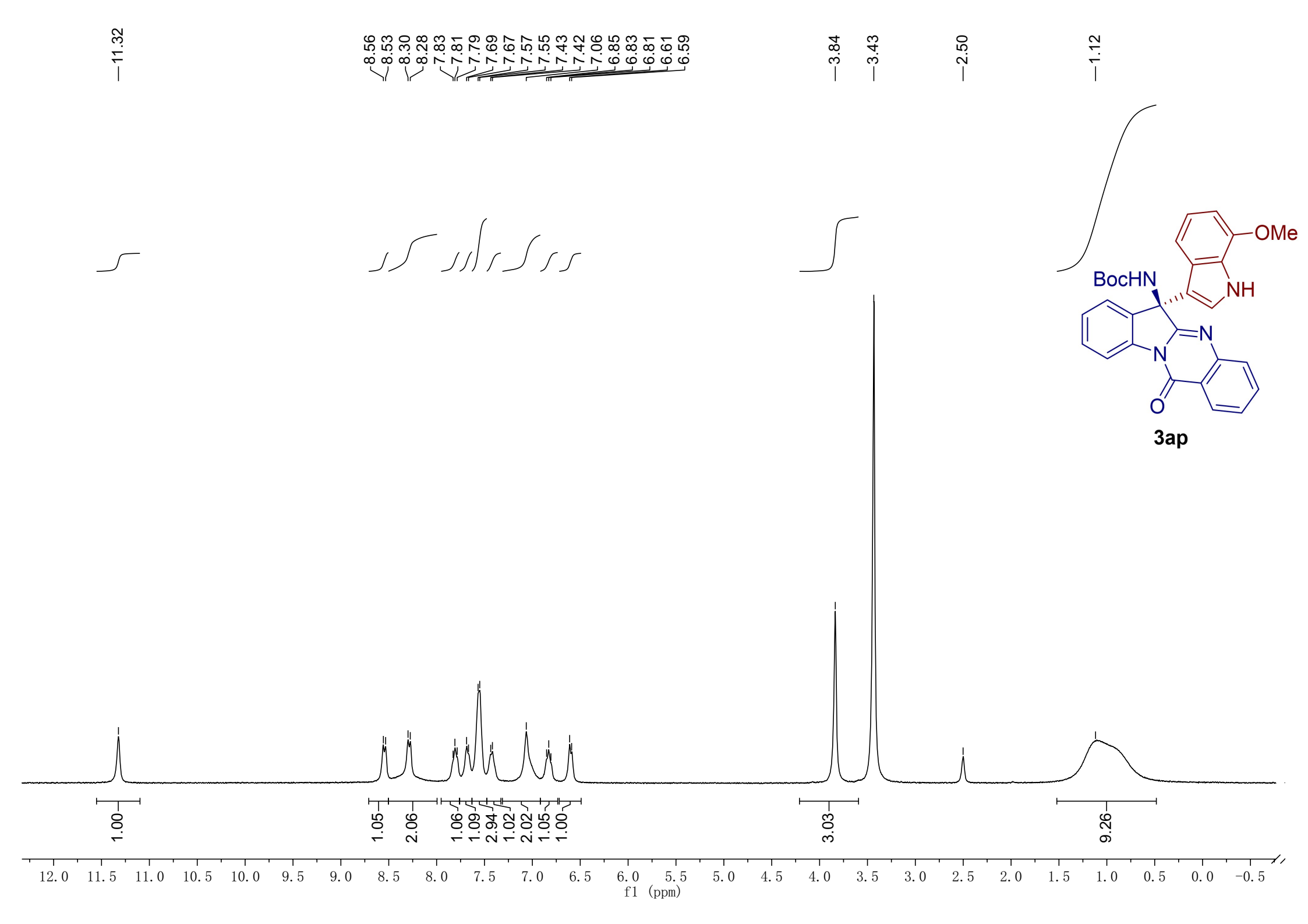
f1 (ppm)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7.57
7.55
7.43
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7.06
6.85
6.83
6.81
6.61
6.59
3.84
3.43
2.50
1.12
OMe
BocHN
NH
N
N
O
3ap
1.00
1.05
2.06
1.06
1.09
2.94
1.02
2.02
1.05
1.00
3.03
9.26
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 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
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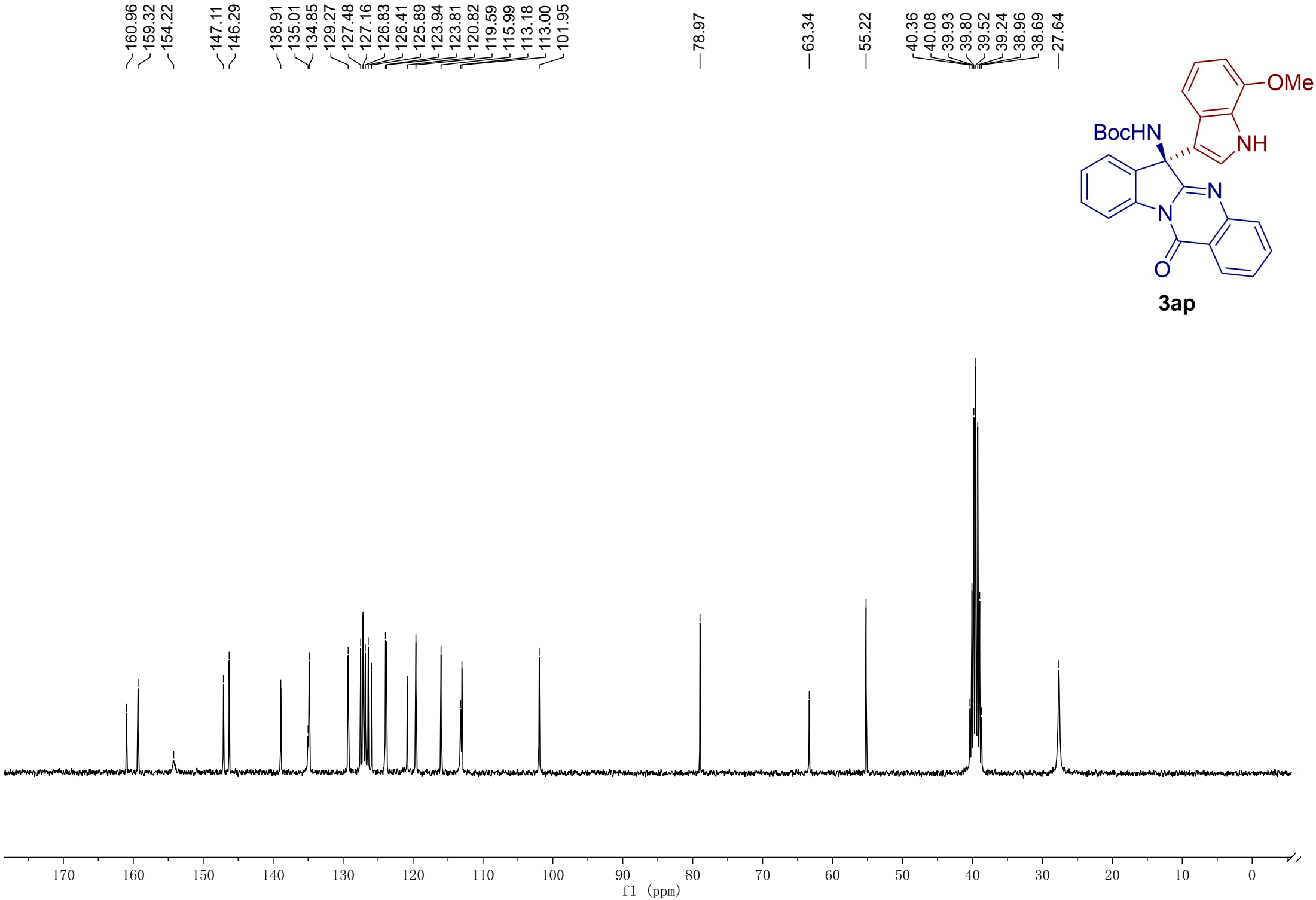
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123.81
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115.99
113.18
113.00
101.95
78.97
63.34
55.22
40.36
40.08
39.93
39.80
39.52
39.24
38.96
38.69
27.64
OMe
BocHN
NH
N
N
O
3ap
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110
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90
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70
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50
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10
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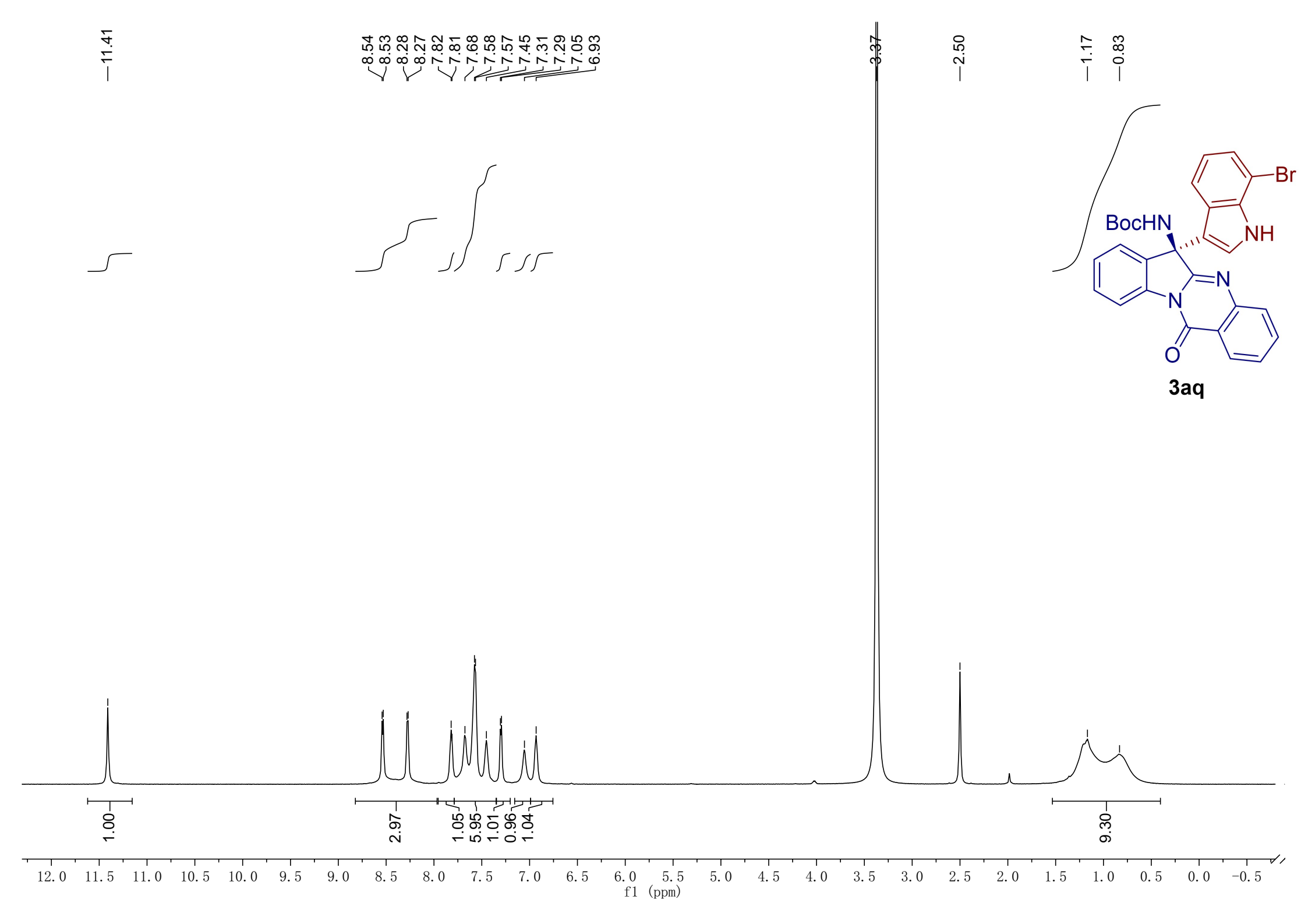
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7.31
7.29
7.05
6.93
3.37
2.50
1.17
0.83
Br
BocHN
NH
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N
O
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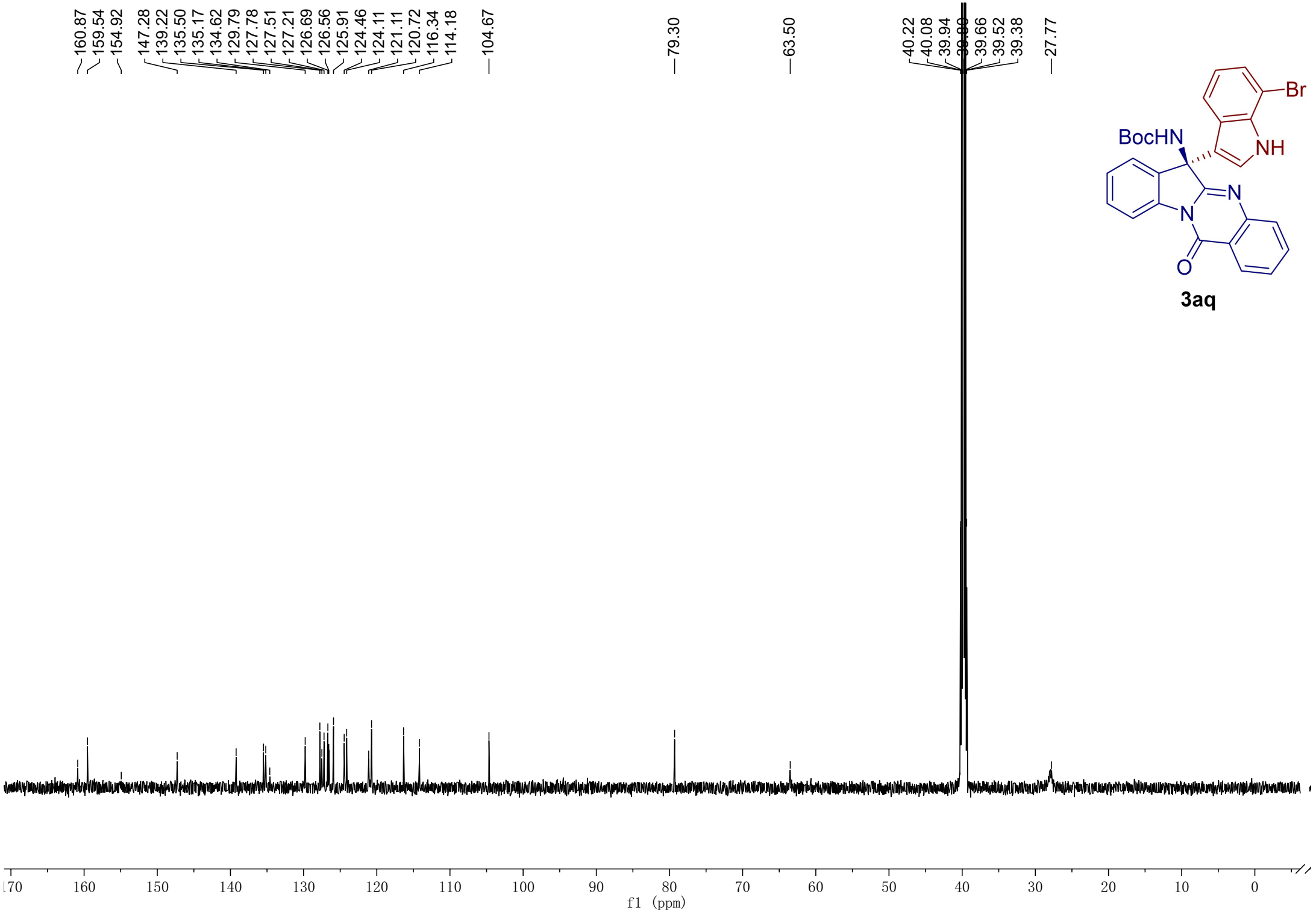
2.97
1.05
5.95
1.01
0.96
1.04
9.30
f1 (ppm)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124.46
124.11
121.11
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116.34
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79.30
63.50
40.22
40.08
39.94
39.80
39.66
39.52
39.38
27.77
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N
N
O
3aq
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100
90
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70
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50
40
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10
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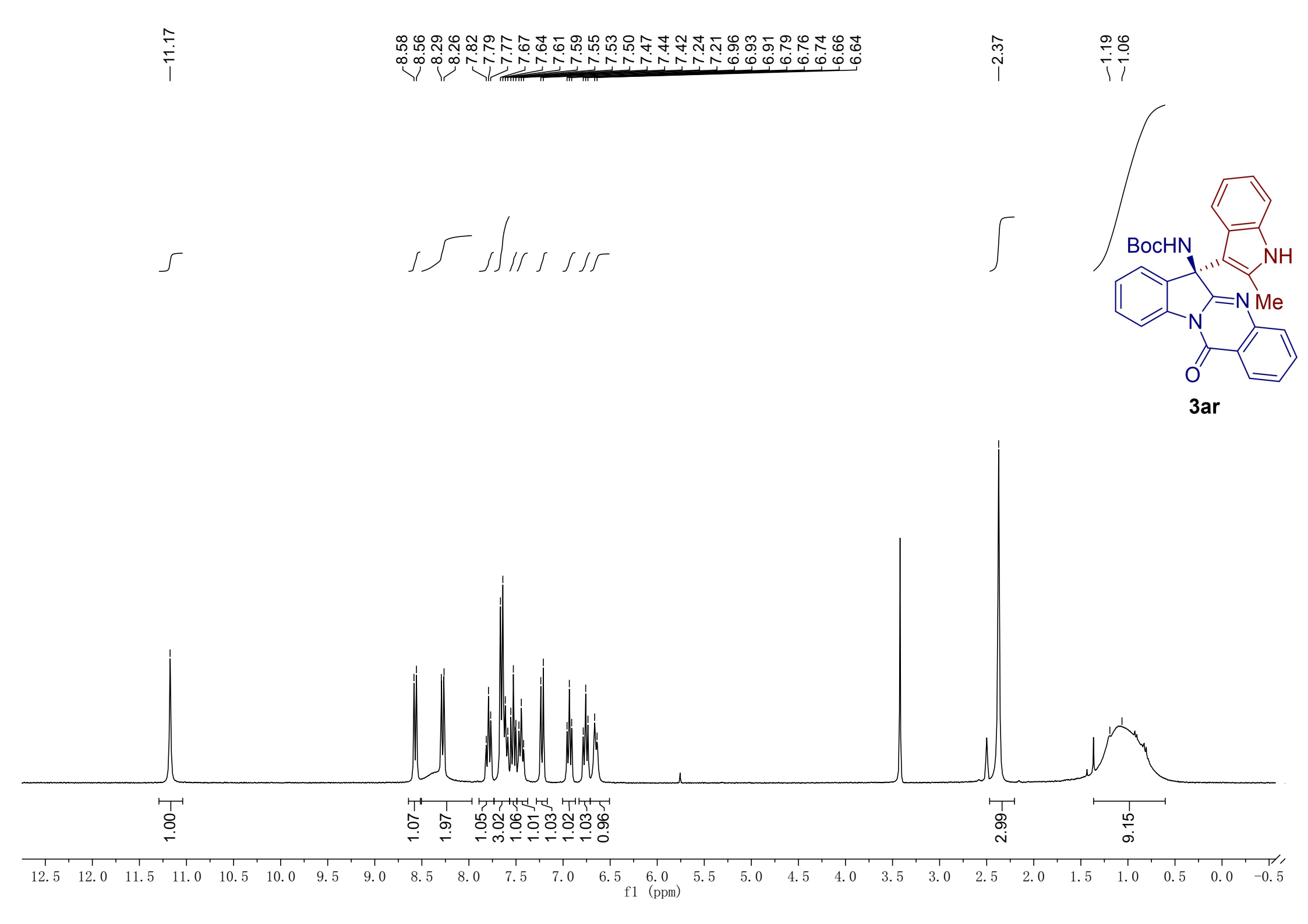
f1 (ppm)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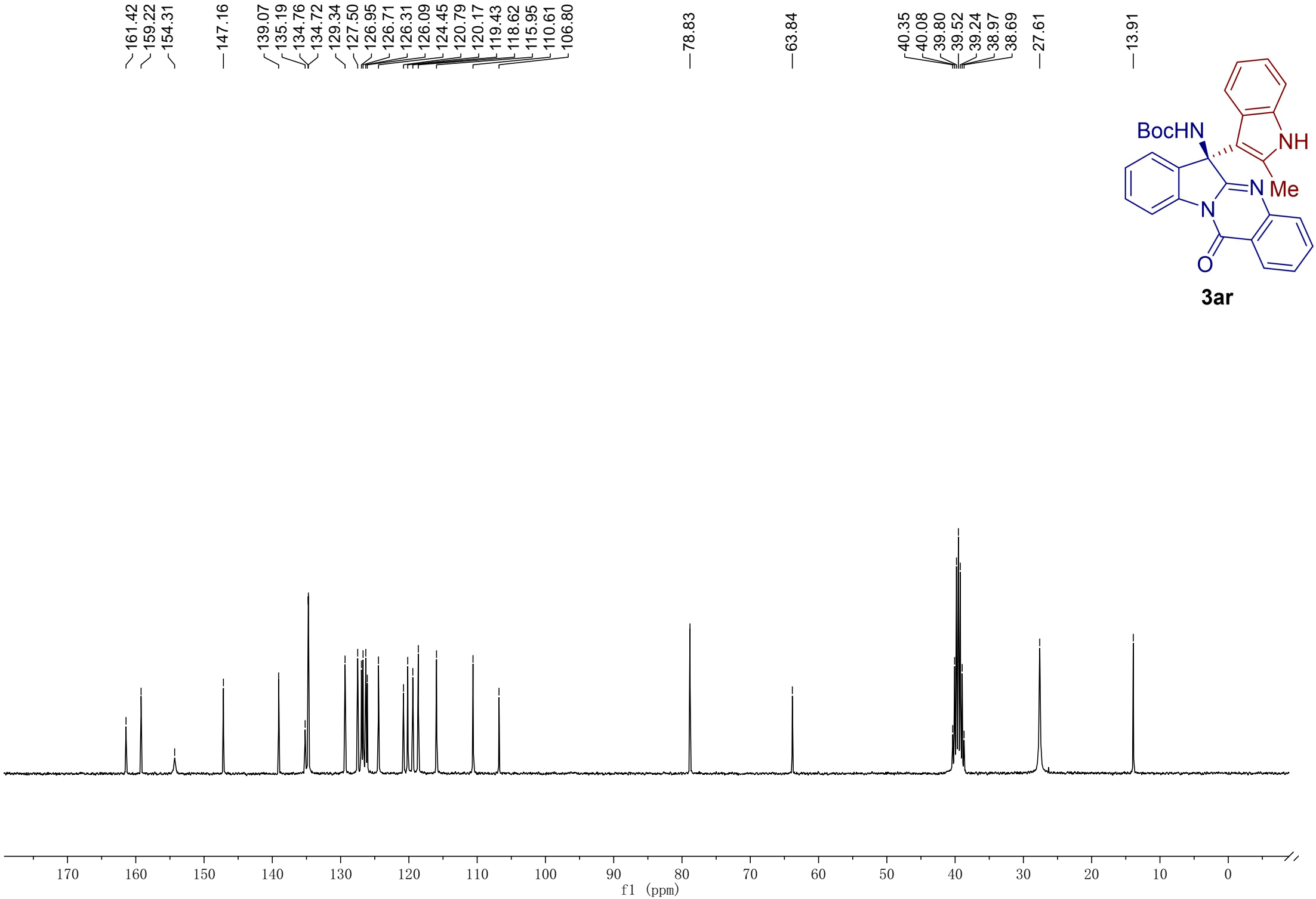
7.55
7.53
7.50
7.47
7.44
7.42
7.24
7.21
6.96
6.93
6.91
6.79
6.76
6.74
6.66
6.64
2.37
1.19
1.06
BocHN
NH
N
Me
N
O
3ar
1.00
1.07
1.97
1.05
3.02
1.06
1.01
1.03
1.02
1.03
0.96
2.99
9.15
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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126.31
126.09
124.45
120.79
120.17
119.43
118.62
115.95
110.61
106.80
78.83
63.84
40.35
40.08
39.80
39.52
39.24
38.97
38.69
27.61
13.91
BocHN
NH
N
Me
N
O
3ar
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130
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110
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90
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70
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50
40
30
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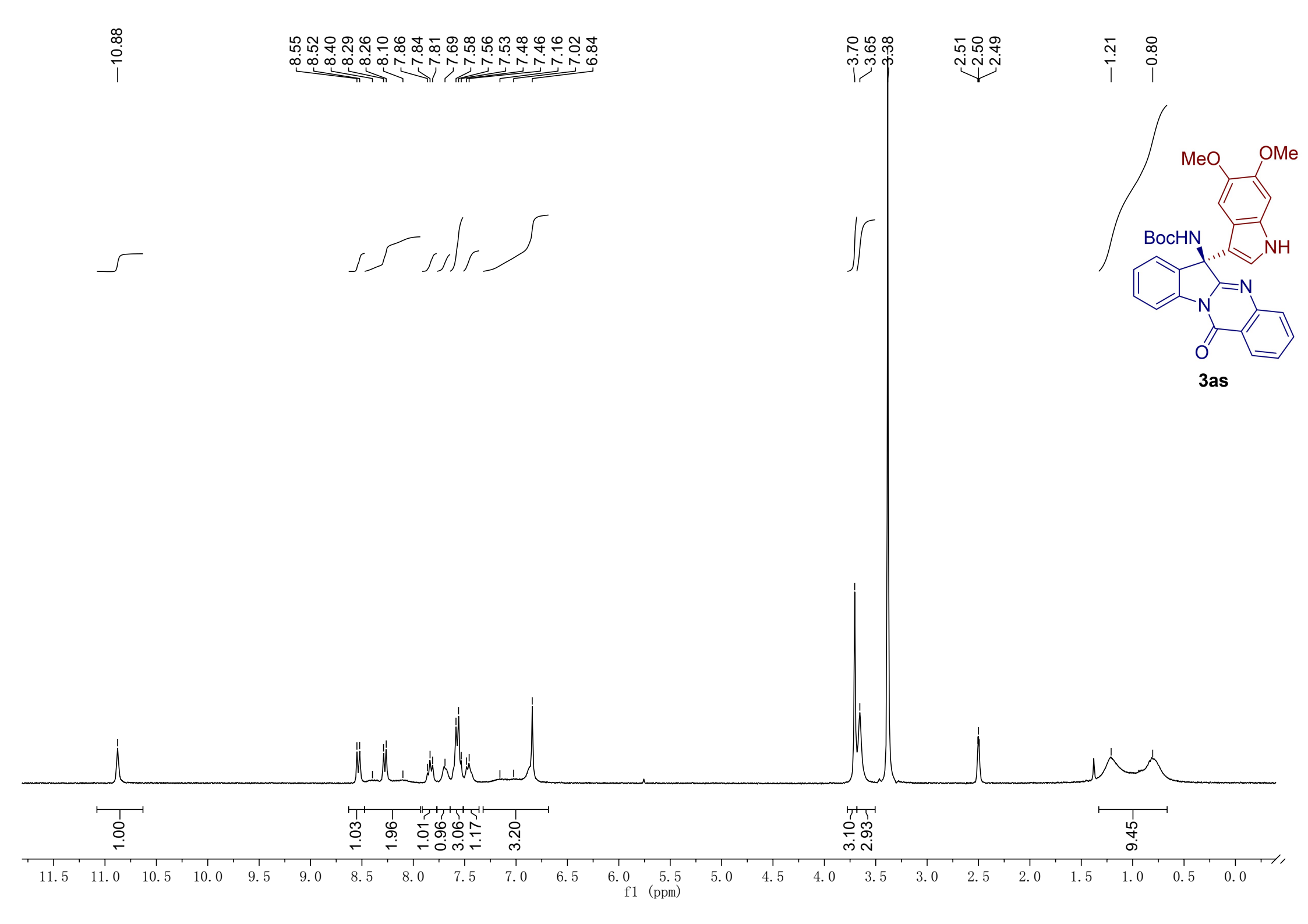
10
0
f1 (ppm)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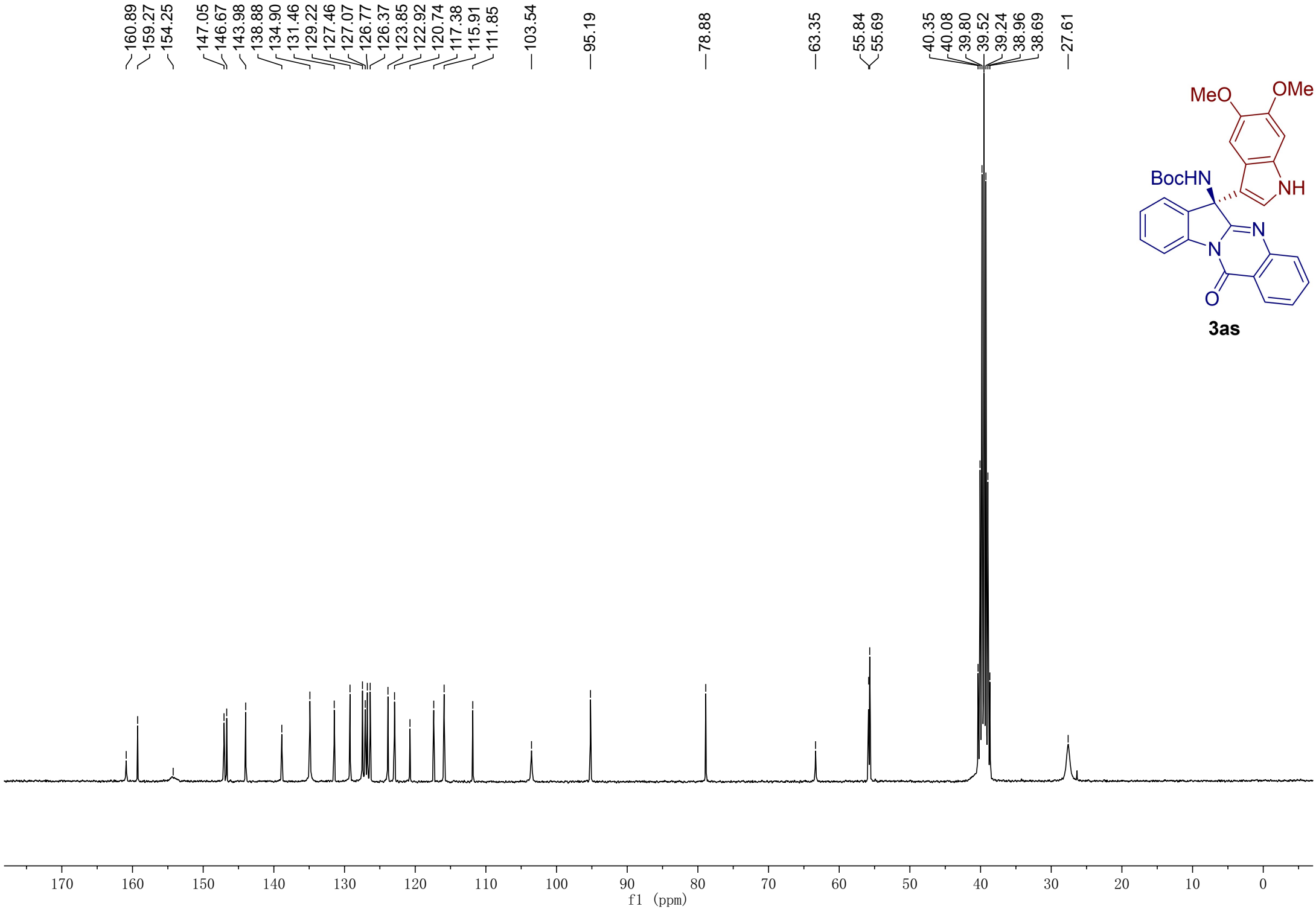
7.81
7.69
7.58
7.56
7.53
7.48
7.46
7.16
7.02
6.84
3.70
3.65
3.38
2.51
2.50
2.49
1.21
0.80
MeO
OMe
BocHN
NH
N
N
O
3as
1.00
1.03
1.96
1.01
0.96
3.06
1.17
3.20
3.10
2.93
9.45
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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127.07
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126.37
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122.92
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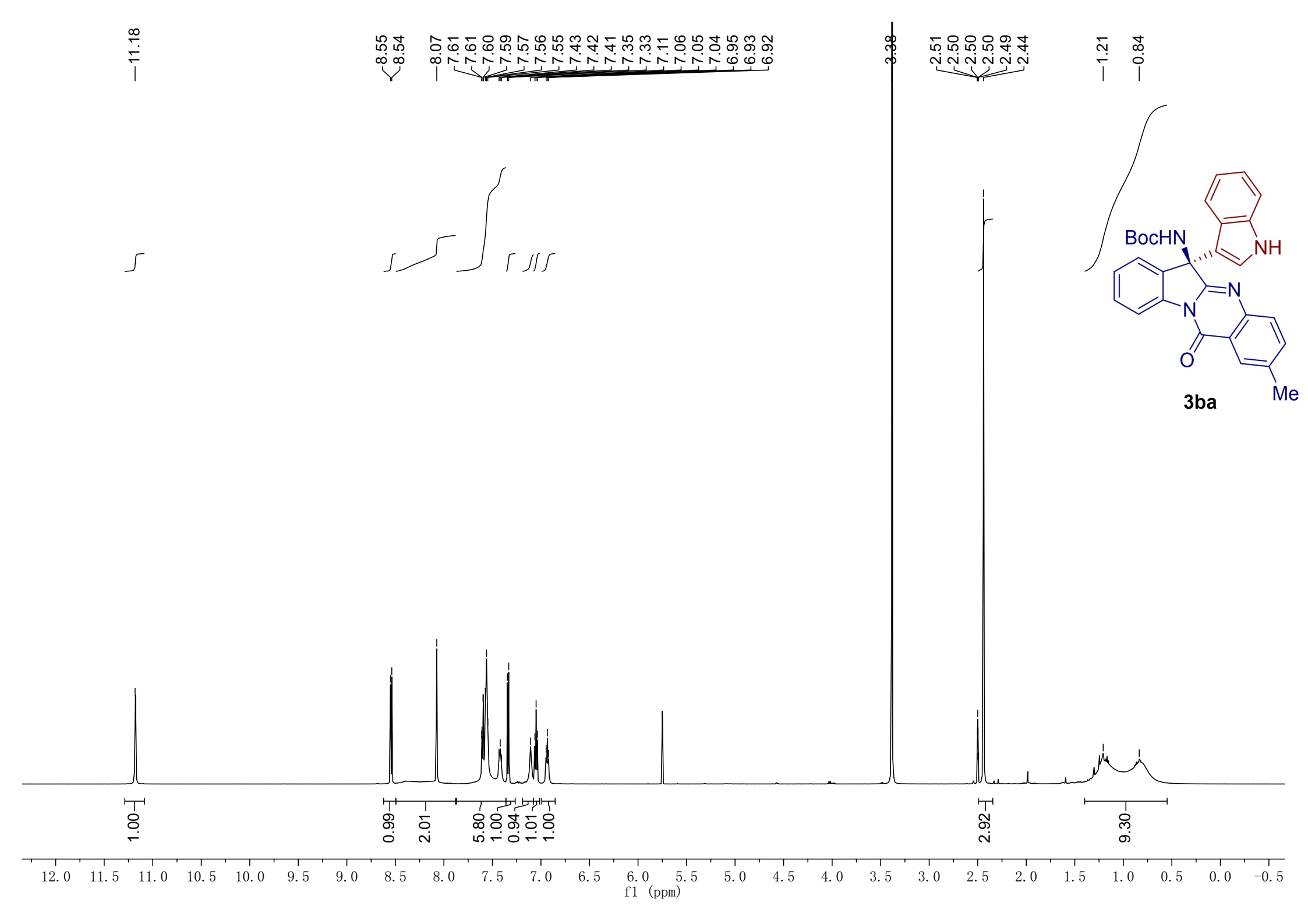
115.91
111.85
103.54
95.19
78.88
63.35
55.84
55.69
40.35
40.08
39.80
39.52
39.24
38.96
38.69
27.61
MeO
OMe
BocHN
NH
N
N
O
3as
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.57
7.56
7.55
7.43
7.42
7.41
7.35
7.33
7.11
7.06
7.05
7.04
6.95
6.93
6.92
3.38
2.51
2.50
2.50
2.50
2.49
2.44
1.21
0.84
BocHN
NH
N
N
O
Me
3ba
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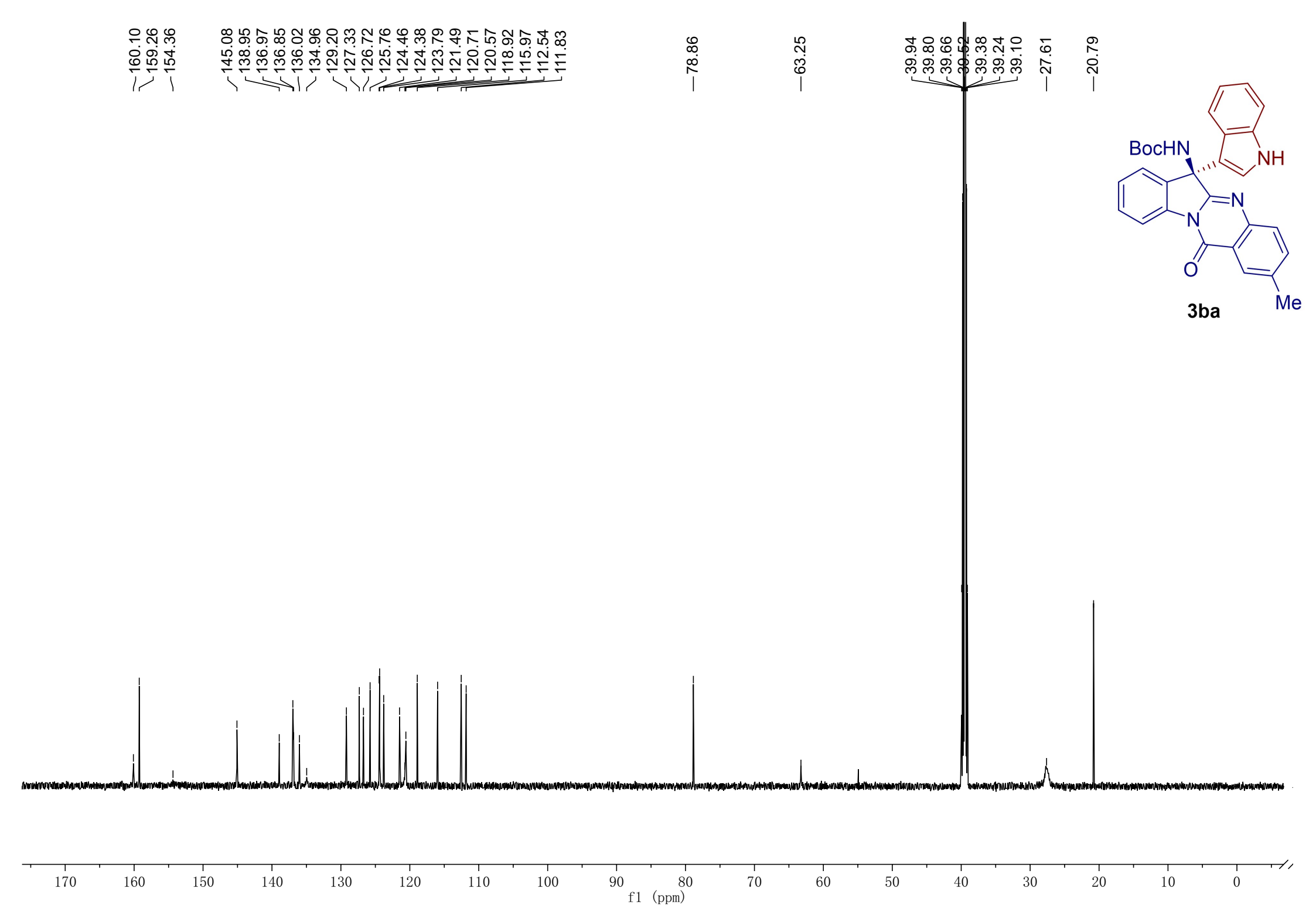
0.99
2.01
5.80
1.00
0.94
1.01
1.00
2.92
9.30
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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129.20
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126.72
125.76
124.46
124.38
123.79
121.49
120.71
120.57
118.92
115.97
112.54
111.83
78.86
63.25
39.94
39.80
39.66
39.52
39.38
39.24
39.10
27.61
20.79
BocHN
NH
N
N
O
Me
3ba
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130
120
110
100
90
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50
40
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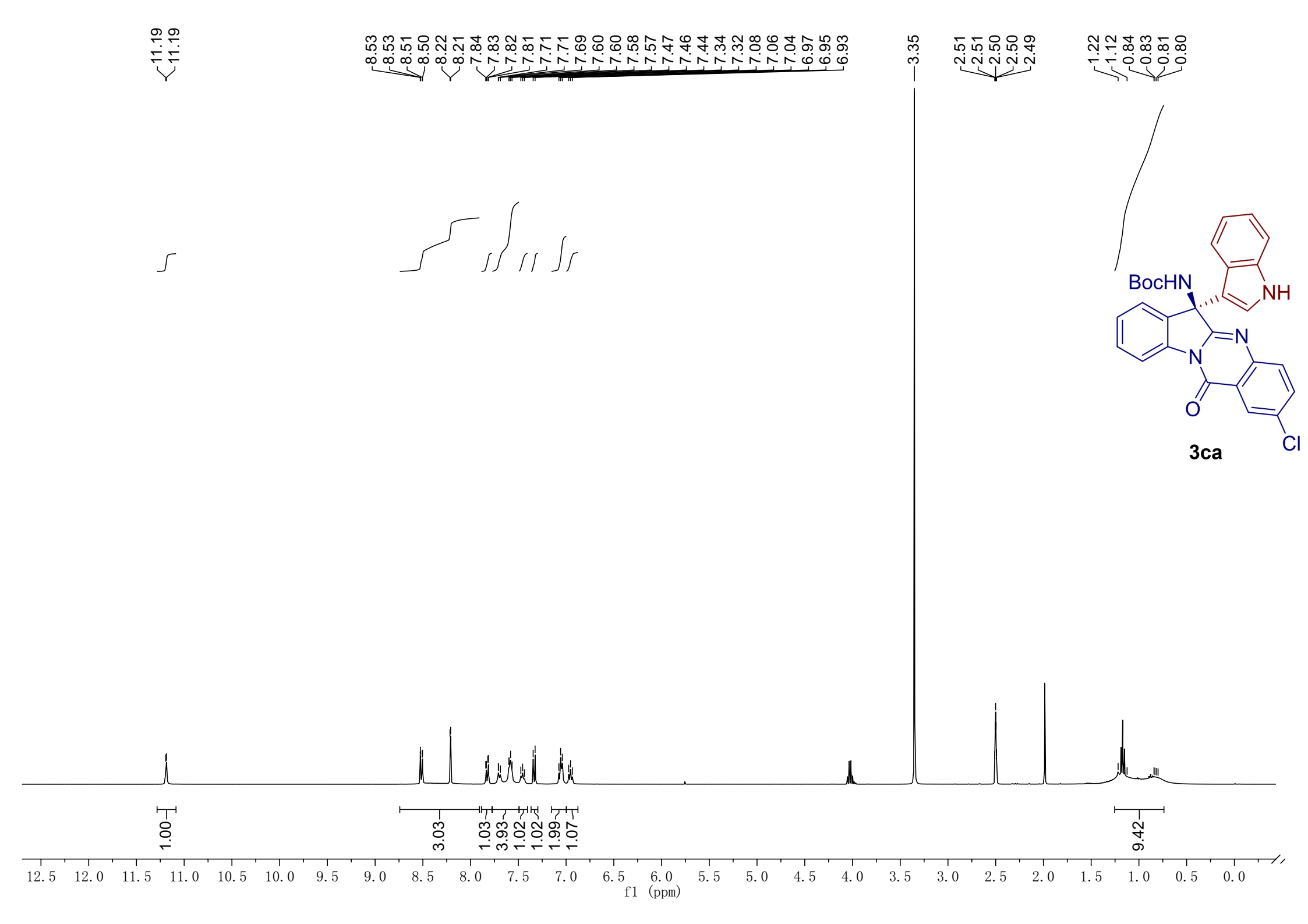
10
0
f1 (ppm)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7.71
7.71
7.69
7.60
7.60
7.58
7.57
7.47
7.46
7.44
7.34
7.32
7.08
7.06
7.04
6.97
6.95
6.93
3.35
2.51
2.51
2.50
2.50
2.49
1.22
1.12
0.84
0.83
0.81
0.80
BocHN
NH
N
N
O
Cl
3ca
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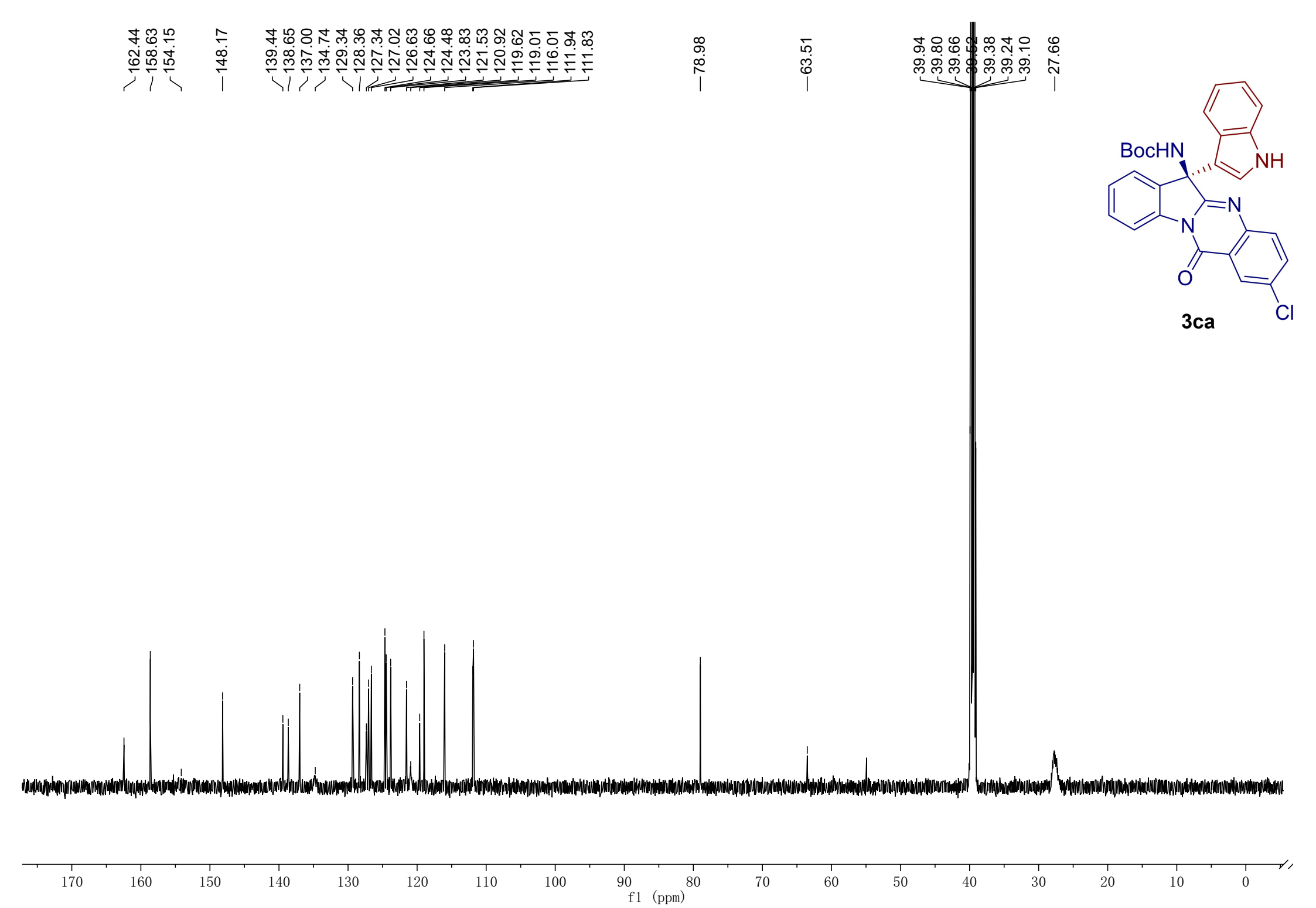
3.03
1.03
3.93
1.02
1.02
1.99
1.07
9.42
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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124.66
124.48
123.83
121.53
120.92
119.62
119.01
116.01
111.94
111.83
78.98
63.51
39.94
39.80
39.66
39.52
39.38
39.24
39.10
27.66
BocHN
NH
N
N
O
Cl
3ca
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130
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110
100
90
80
70
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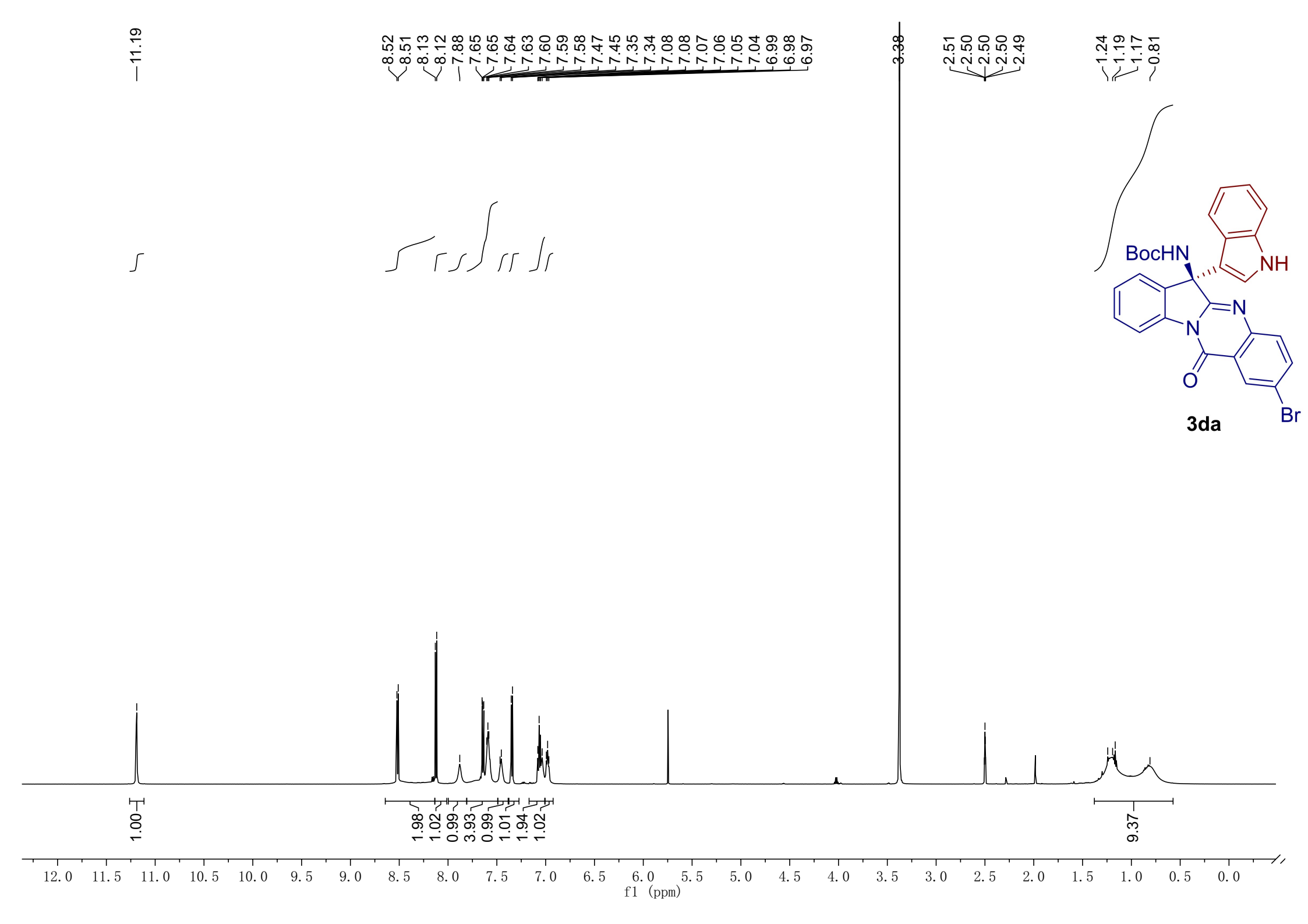
50
40
30
20
10
0
f1 (ppm)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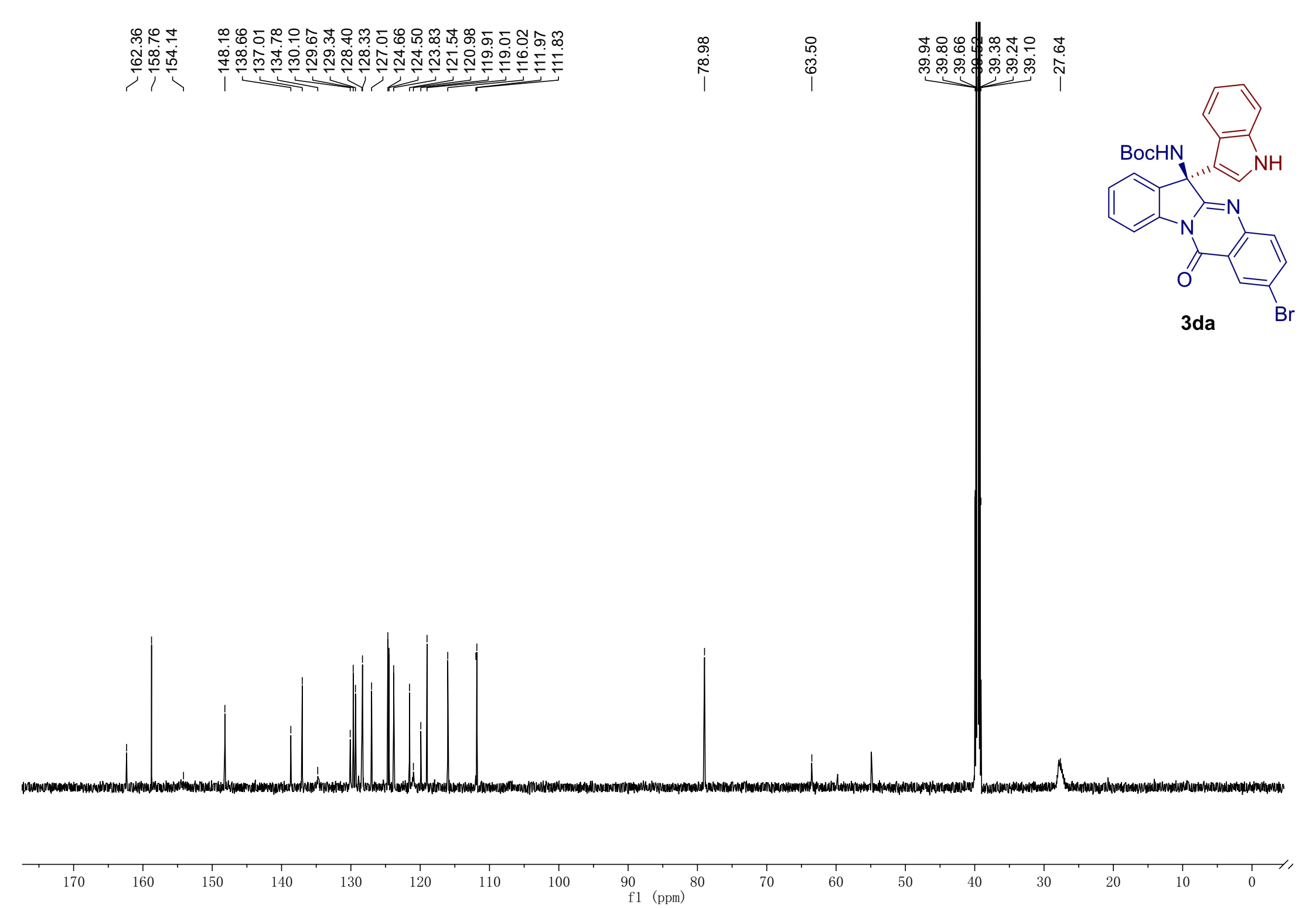
7.65
7.64
7.63
7.60
7.59
7.58
7.47
7.45
7.35
7.34
7.08
7.08
7.07
7.06
7.05
7.04
6.99
6.98
6.97
3.38
2.51
2.50
2.50
2.50
2.49
1.24
1.19
1.17
0.81
BocHN
NH
N
N
O
Br
3da
1.00
1.98
1.02
0.99
3.93
0.99
1.01
1.94
1.02
9.37
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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128.33
127.01
124.66
124.50
123.83
121.54
120.98
119.91
119.01
116.02
111.97
111.83
78.98
63.50
39.94
39.80
39.66
39.52
39.38
39.24
39.10
27.64
BocHN
NH
N
N
O
Br
3da
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110
100
90
80
70
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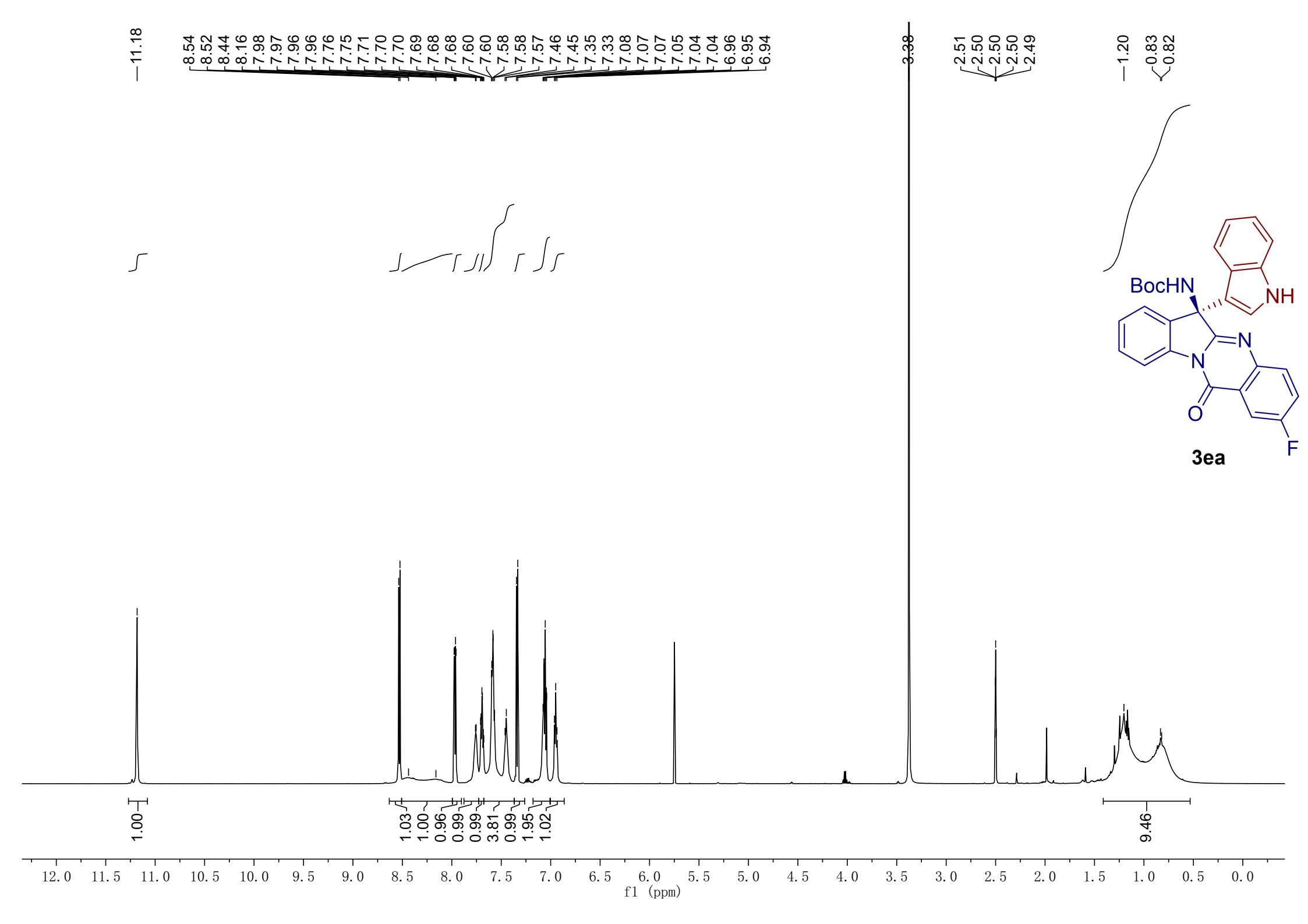
50
40
30
20
10
0
f1 (ppm)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7.71
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7.70
7.69
7.68
7.68
7.60
7.60
7.58
7.58
7.57
7.46
7.45
7.35
7.33
7.08
7.07
7.07
7.05
7.04
7.04
6.96
6.95
6.94
3.38
2.51
2.50
2.50
2.50
2.49
1.20
0.83
0.82
BocHN
NH
N
N
O
F
3ea
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1.03
1.00
0.96
0.99
0.99
3.81
0.99
1.95
1.02
9.46
12.0
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11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
5.5
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4.5
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3.0
2.5
2.0
1.5
1.0
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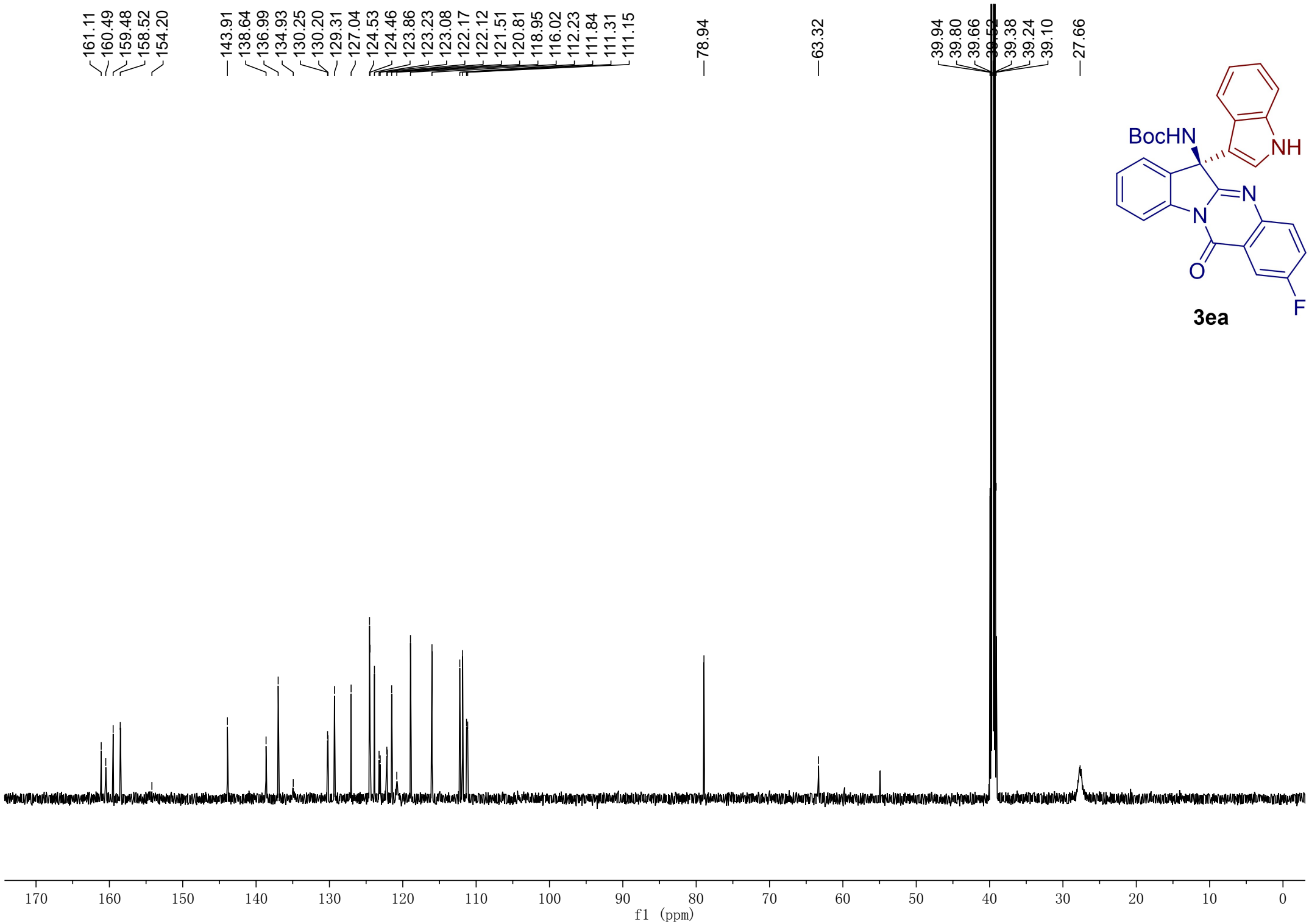
0.0
f1 (ppm)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124.46
123.86
123.23
123.08
122.17
122.12
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120.81
118.95
116.02
112.23
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111.15
78.94
63.32
39.94
39.80
39.66
39.52
39.38
39.24
39.10
27.66
BocHN
NH
N
N
O
F
3ea
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130
120
110
100
90
80
70
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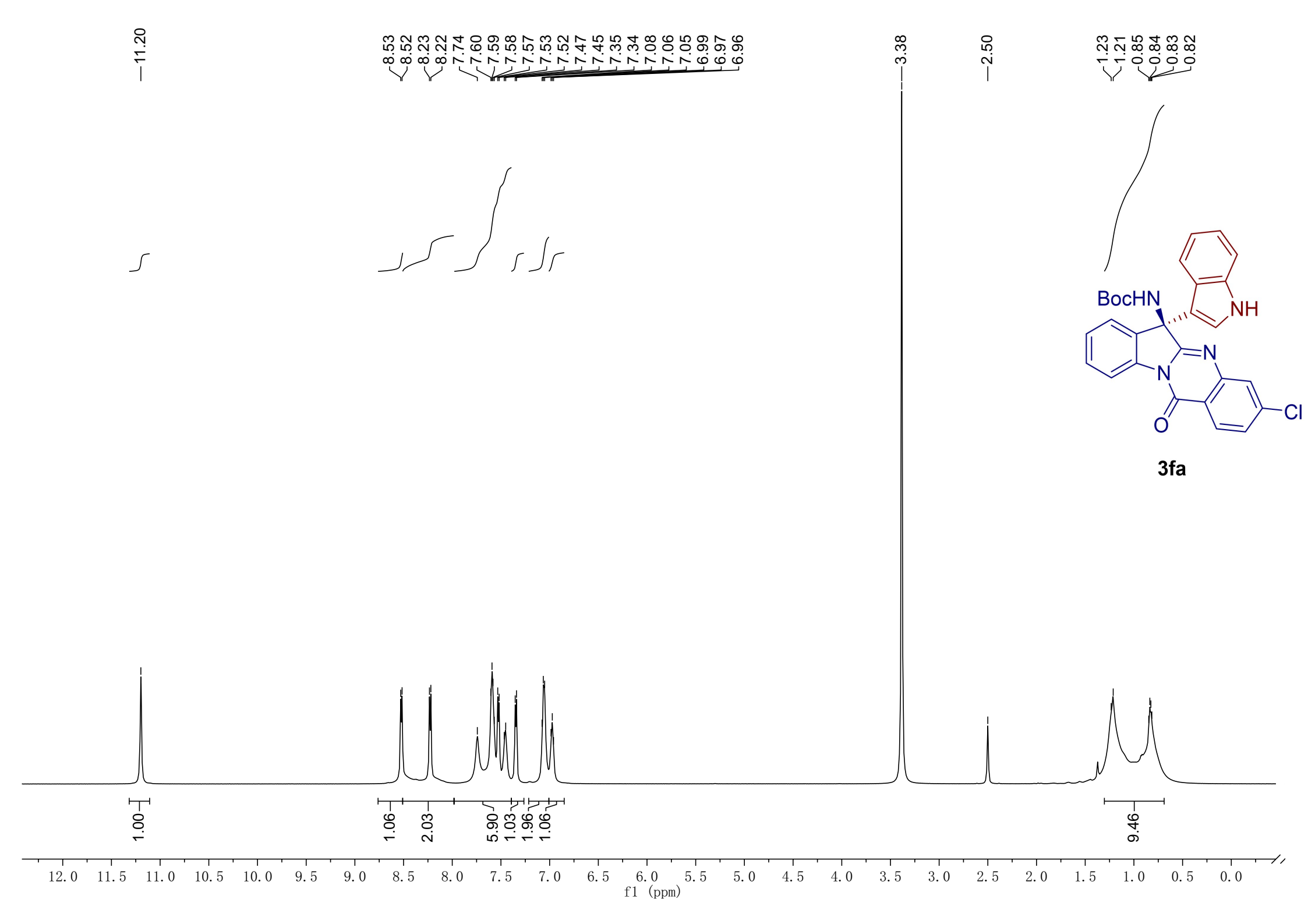
50
40
30
20
10
0
f1 (ppm)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7.59
7.58
7.57
7.53
7.52
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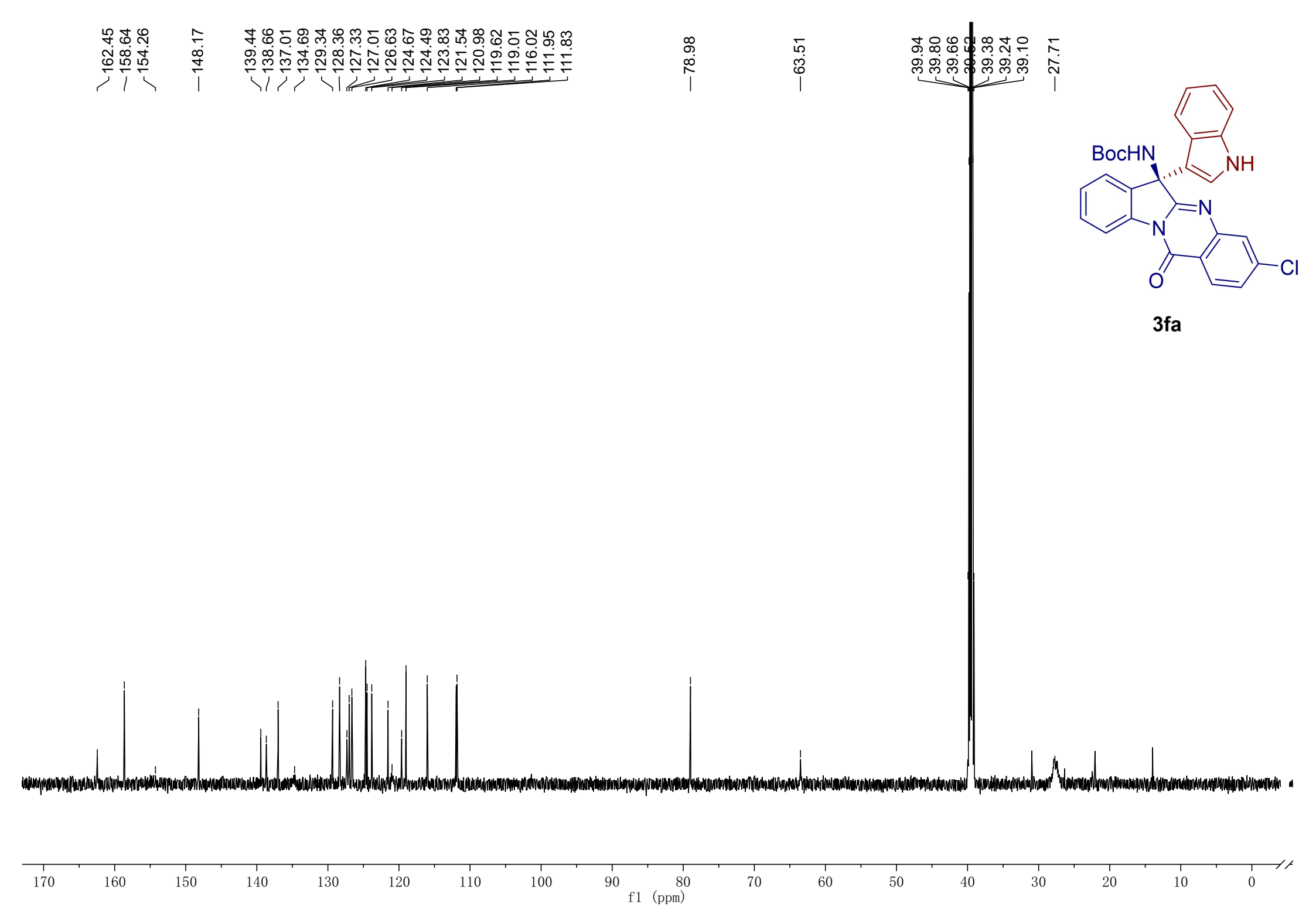
7.45
7.35
7.34
7.08
7.06
7.05
6.99
6.97
6.96
3.38
2.50
1.23
1.21
0.85
0.84
0.83
0.82
BocHN
NH
N
N
O
Cl
3fa
1.00
1.06
2.03
5.90
1.03
1.96
1.06
9.46
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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127.01
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124.49
123.83
121.54
120.98
119.62
119.01
116.02
111.95
111.83
78.98
63.51
39.94
39.80
39.66
39.52
39.38
39.24
39.10
27.71
BocHN
NH
N
N
O
Cl
3fa
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150
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130
120
110
100
90
80
70
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50
40
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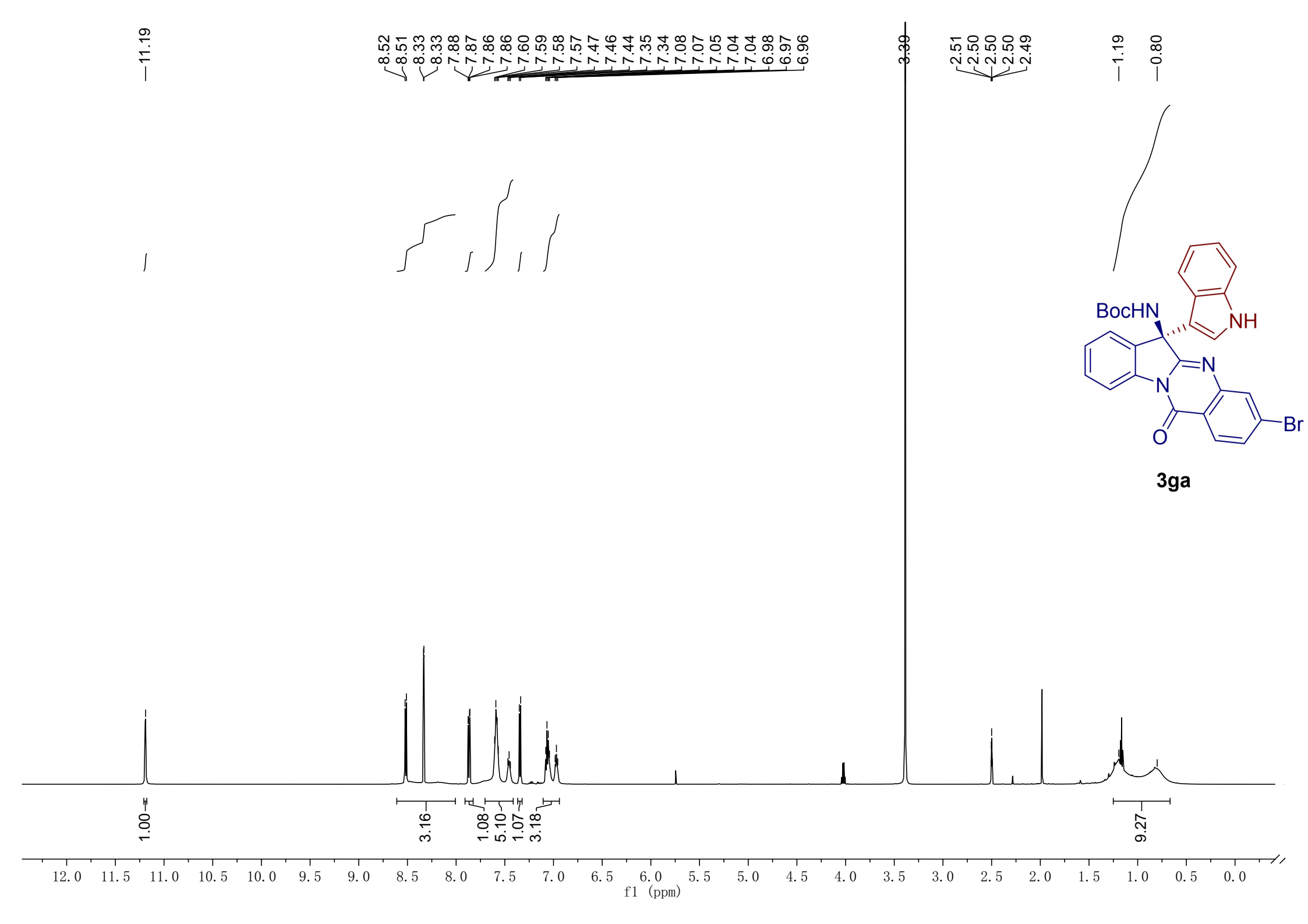
20
10
0
f1 (ppm)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7.86
7.86
7.60
7.59
7.58
7.57
7.47
7.46
7.44
7.35
7.34
7.08
7.07
7.05
7.04
7.04
6.98
6.97
6.96
3.39
2.51
2.50
2.50
2.50
2.49
1.19
0.80
BocHN
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N
N
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Br
3ga
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1.08
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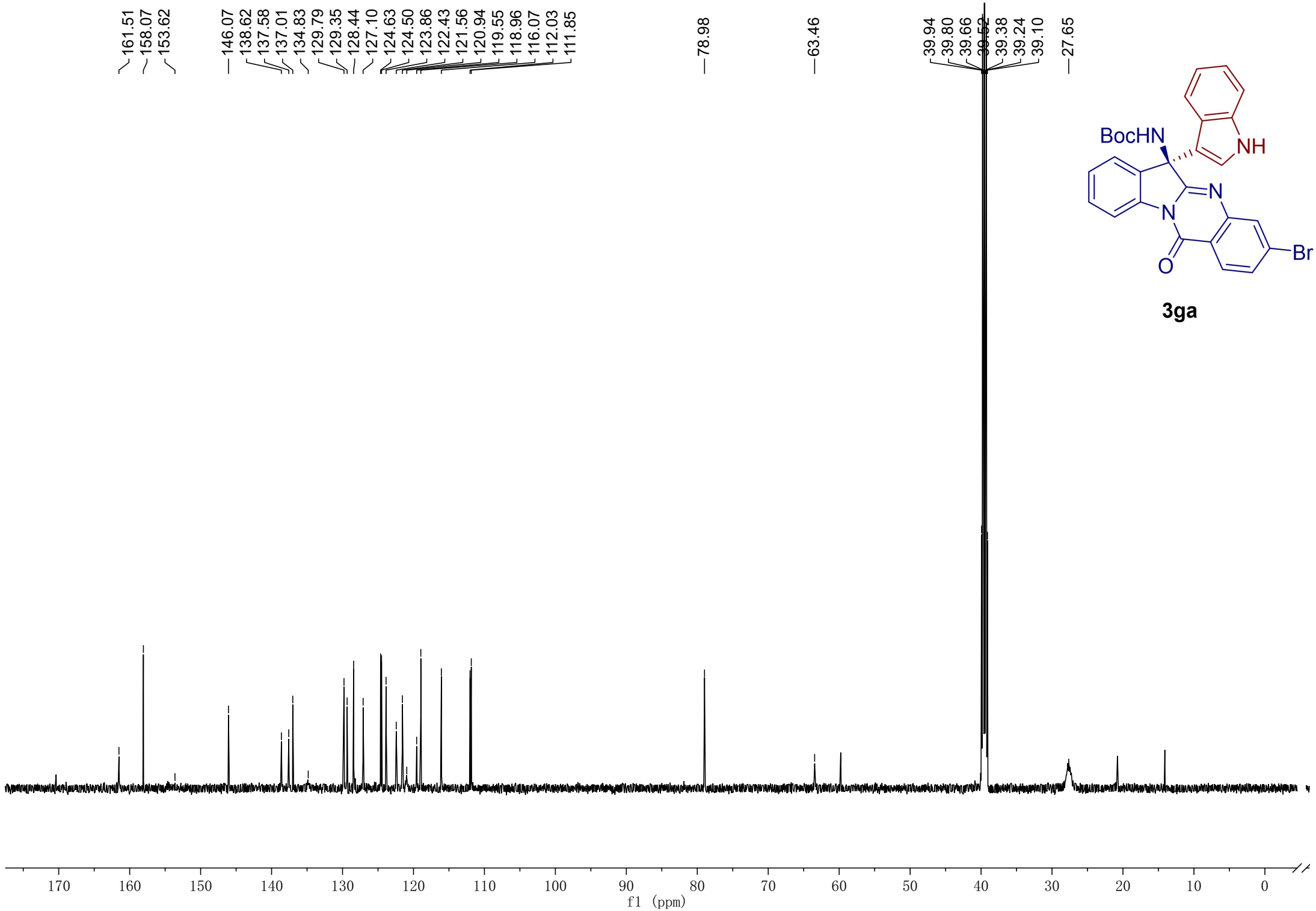
1.07
3.18
9.27
f1 (ppm)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124.63
124.50
123.86
122.43
121.56
120.94
119.55
118.96
116.07
112.03
111.85
78.98
63.46
39.94
39.80
39.66
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39.24
39.10
27.65
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NH
N
N
O
Br
3ga
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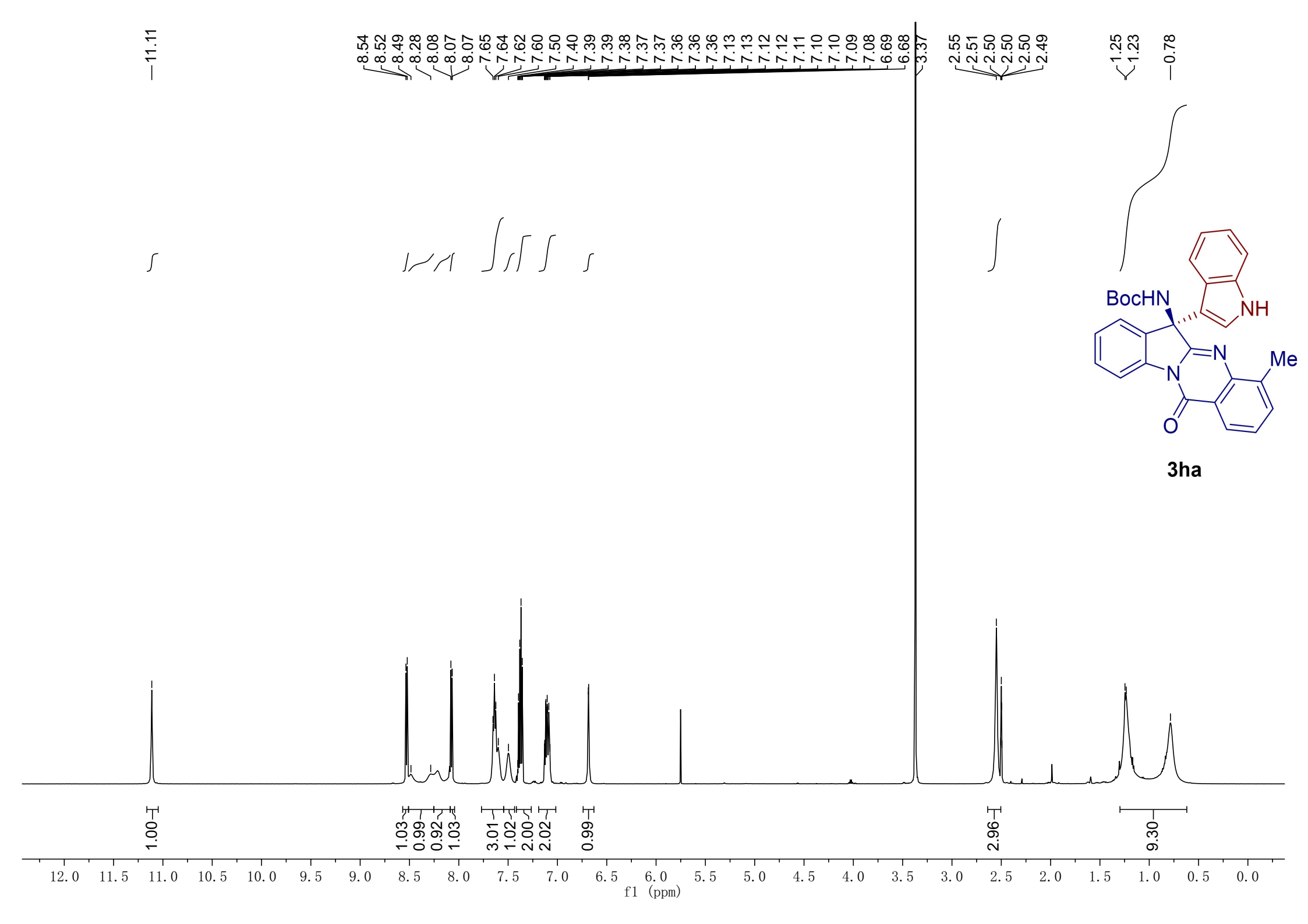
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7.50
7.40
7.39
7.39
7.38
7.37
7.37
7.36
7.36
7.36
7.13
7.13
7.12
7.12
7.11
7.10
7.10
7.09
7.08
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6.68
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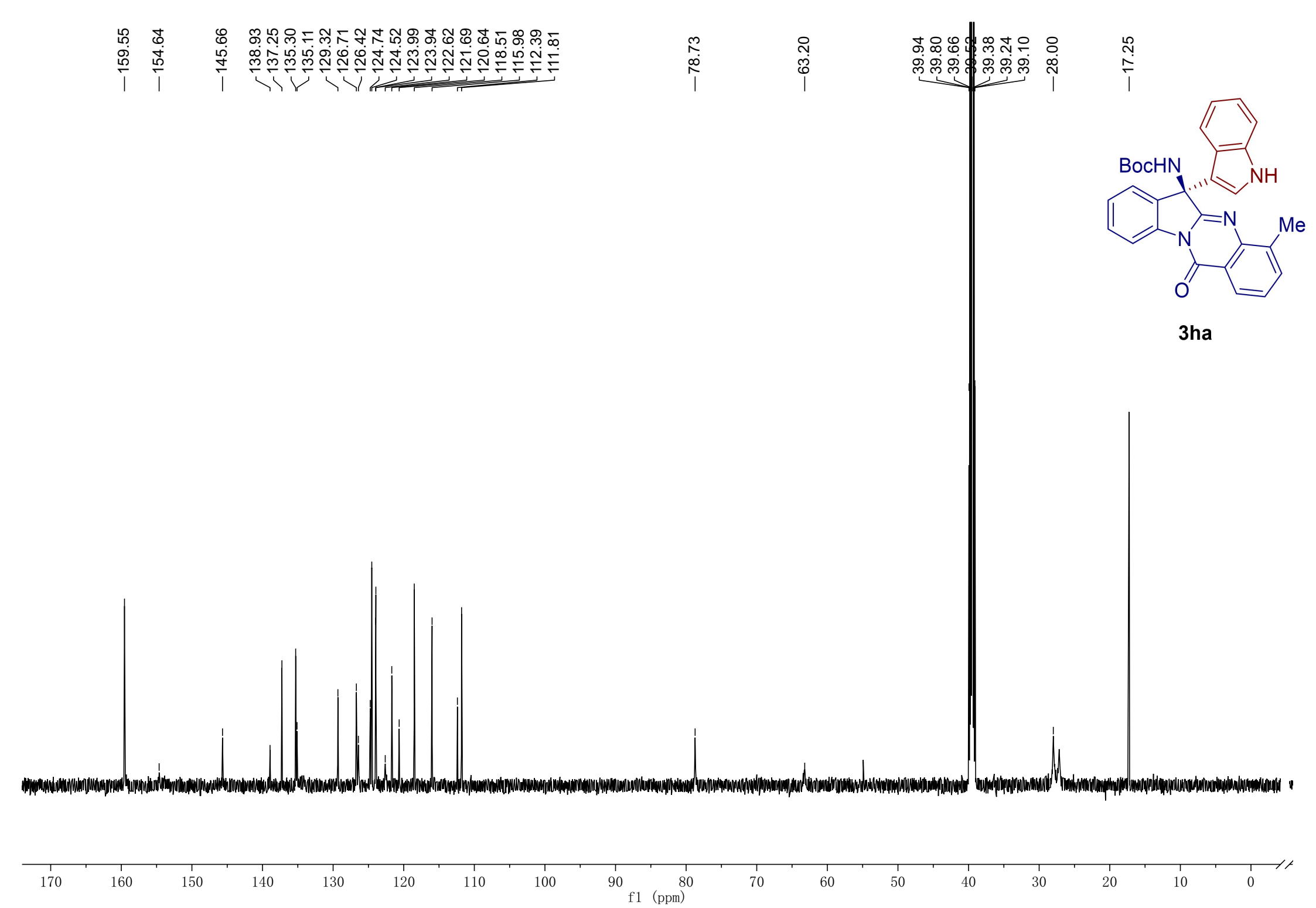
2.51
2.50
2.50
2.50
2.49
1.25
1.23
0.78
BocHN
NH
N
N
Me
O
3ha
1.00
1.03
0.99
0.92
1.03
3.01
1.02
2.00
2.02
0.99
2.96
9.30
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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124.52
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123.94
122.62
121.69
120.64
118.51
115.98
112.39
111.81
78.73
63.20
39.94
39.80
39.66
39.52
39.38
39.24
39.10
28.00
17.25
BocHN
NH
N
N
Me
O
3ha
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90
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50
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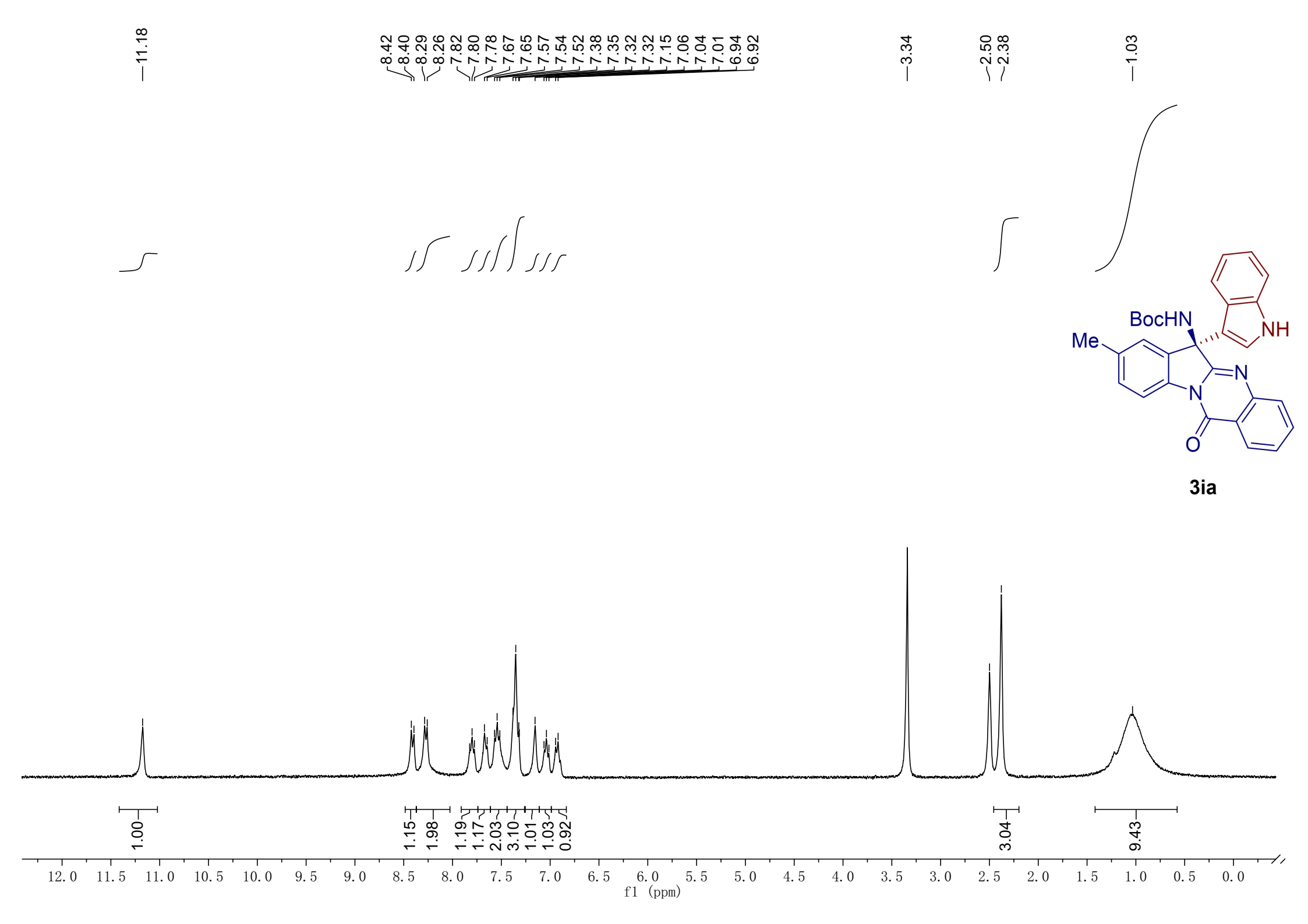
f1 (ppm)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7.54
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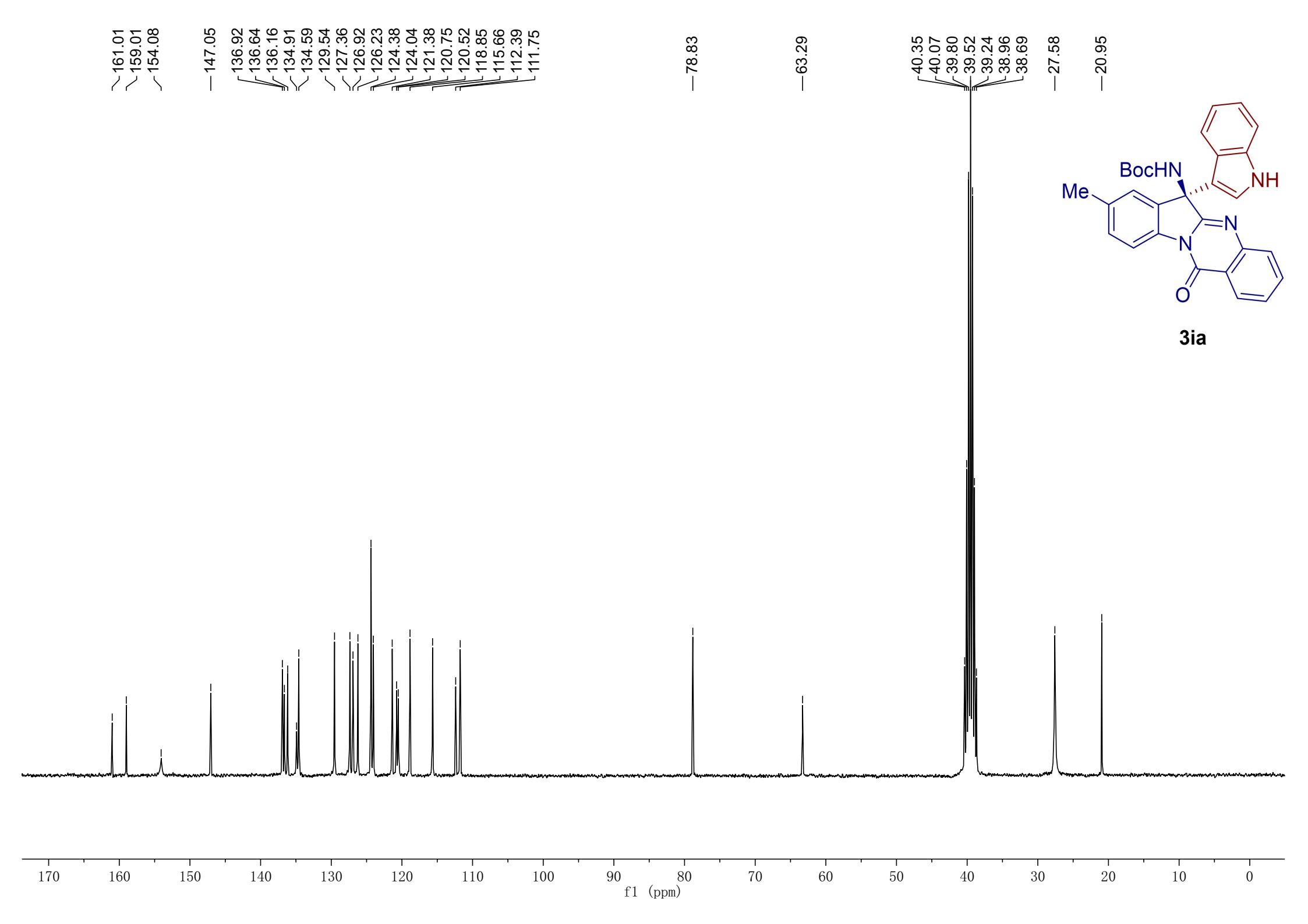
7.38
7.35
7.32
7.32
7.15
7.06
7.04
7.01
6.94
6.92
3.34
2.50
2.38
1.03
BocHN
NH
Me
N
N
O
3ia
1.00
1.15
1.98
1.19
1.17
2.03
3.10
1.01
1.03
0.92
3.04
9.43
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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159.01
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126.23
124.38
124.04
121.38
120.75
120.52
118.85
115.66
112.39
111.75
78.83
63.29
40.35
40.07
39.80
39.52
39.24
38.96
38.69
27.58
20.95
BocHN
NH
Me
N
N
O
3ia
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50
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30
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10
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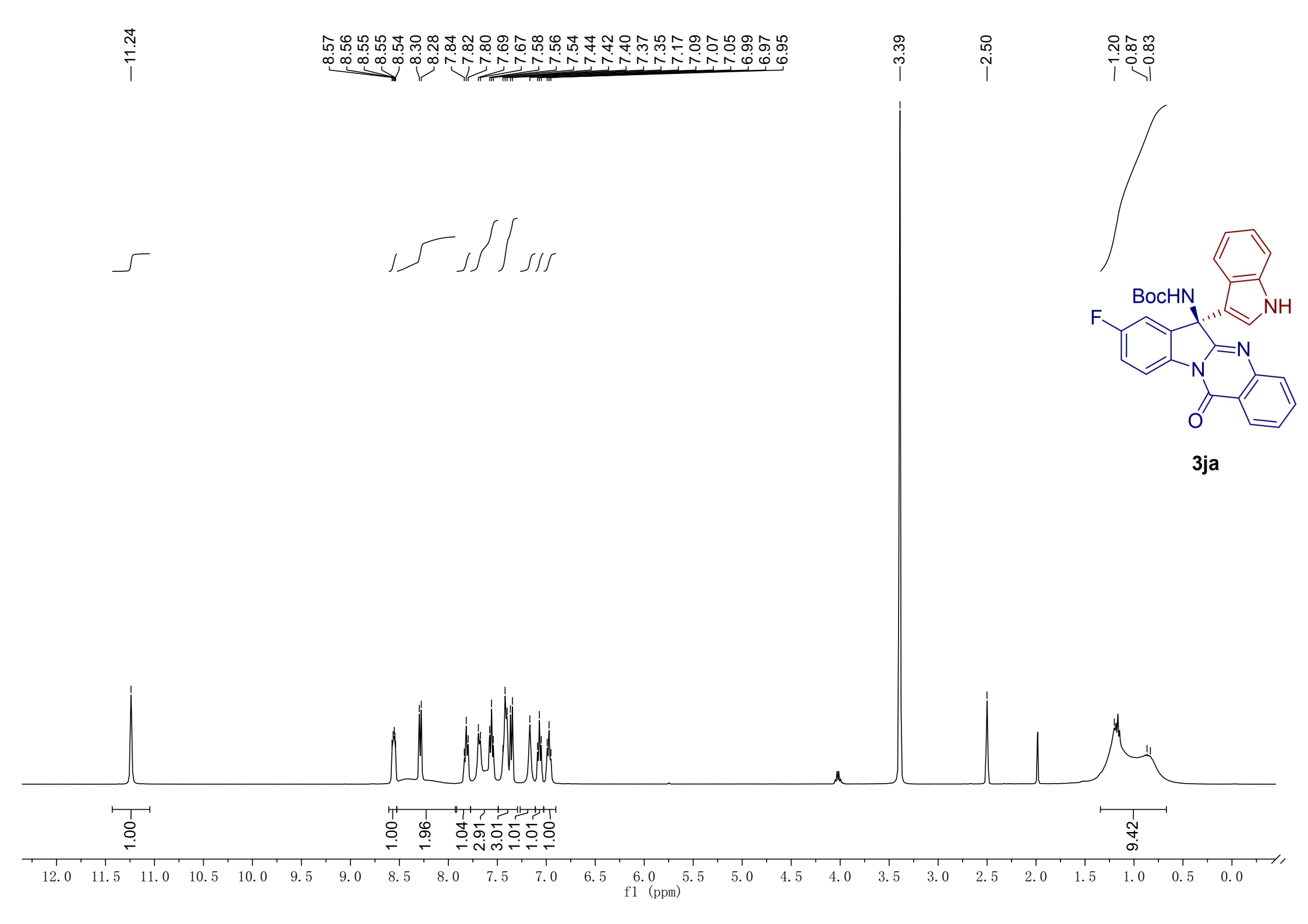
f1 (ppm)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7.80
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7.37
7.35
7.17
7.09
7.07
7.05
6.99
6.97
6.95
3.39
2.50
1.20
0.87
0.83
BocHN
NH
F
N
N
O
3ja
1.00
1.00
1.96
1.04
2.91
3.01
1.01
1.01
1.00
9.42
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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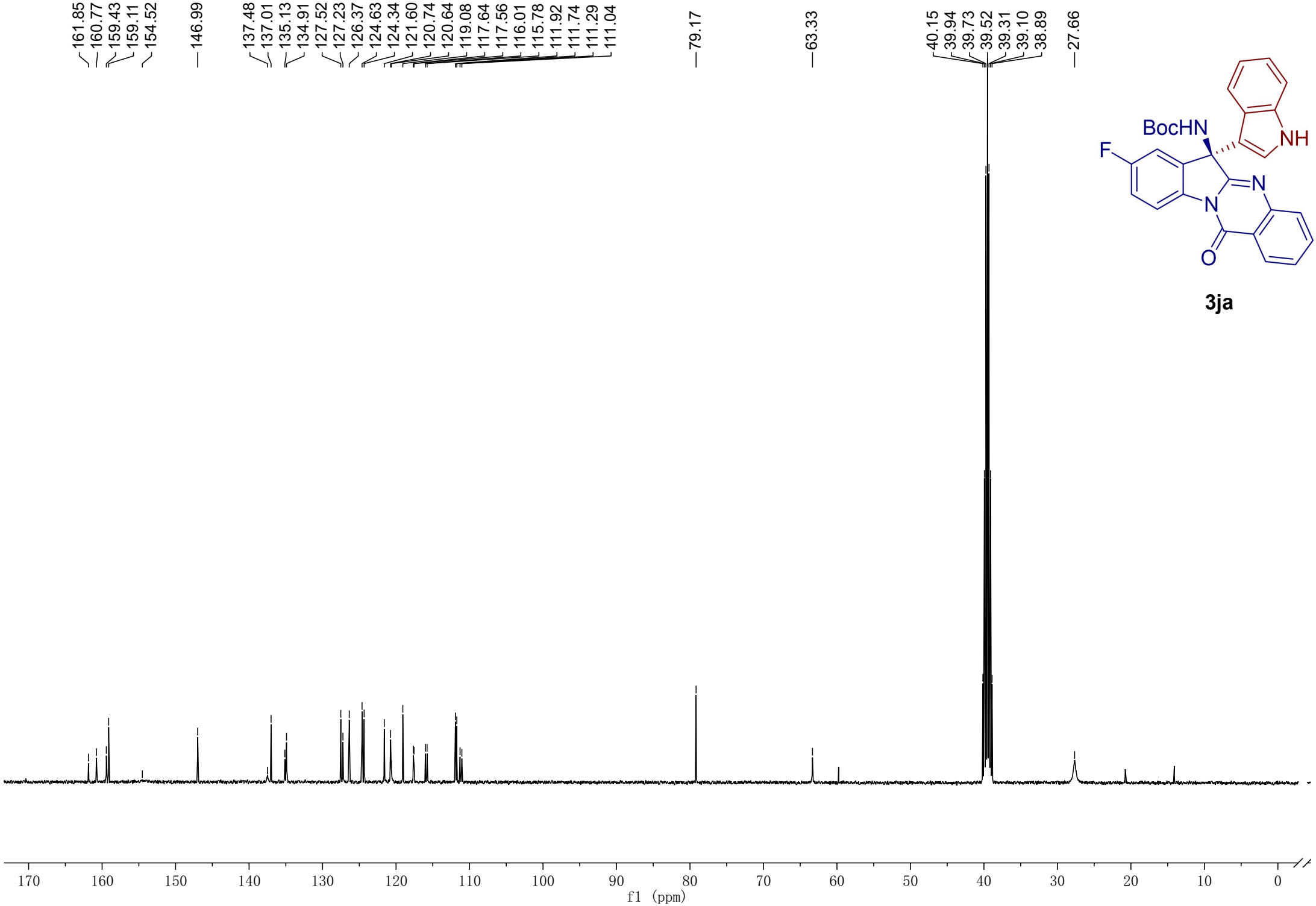
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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124.34
121.60
120.74
120.64
119.08
117.64
117.56
116.01
115.78
111.92
111.74
111.29
111.04
79.17
63.33
40.15
39.94
39.73
39.52
39.31
39.10
38.89
27.66
BocHN
NH
F
N
N
O
3ja
170
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150
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130
120
110
100
90
80
70
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50
40
30
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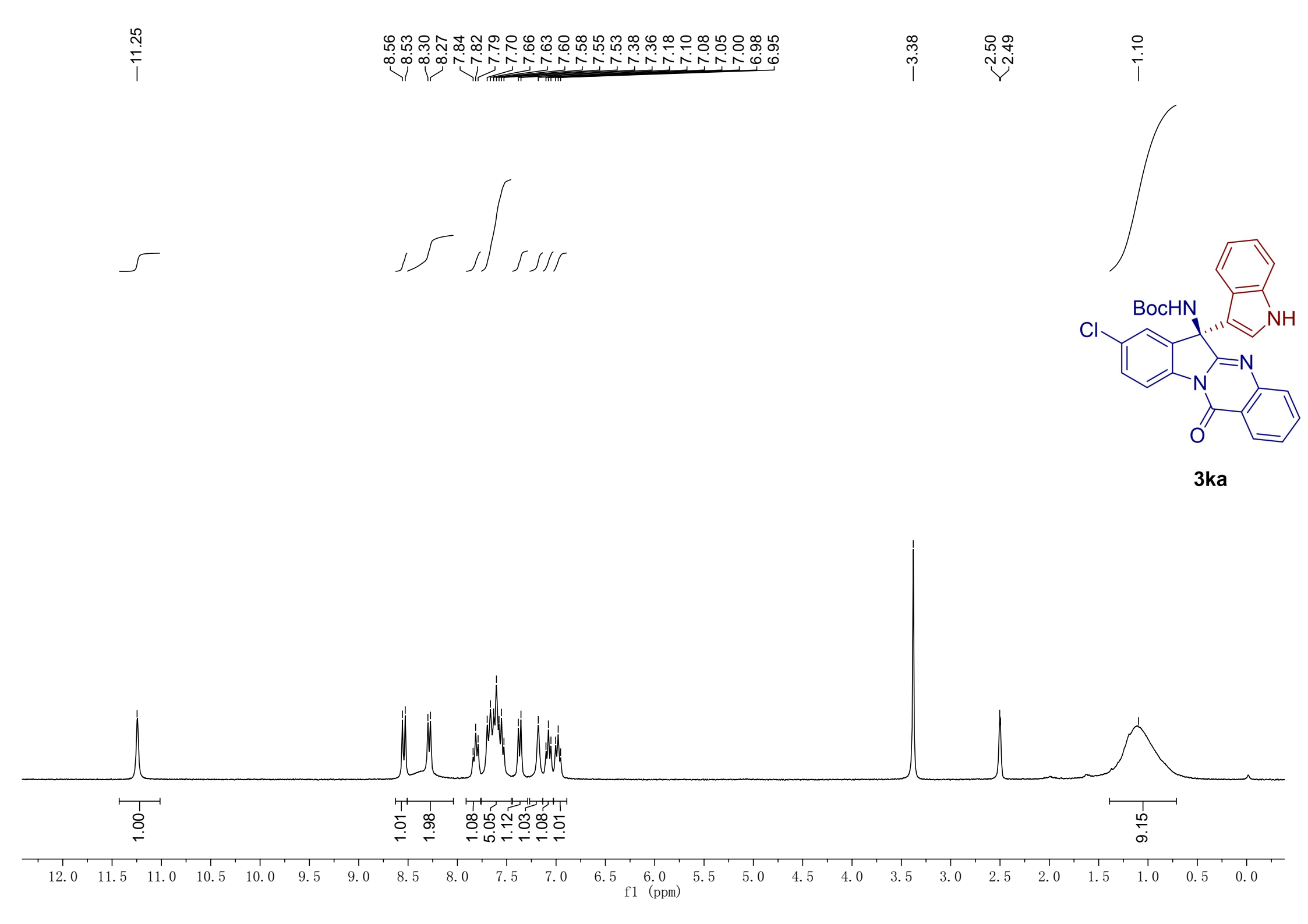
10
0
f1 (ppm)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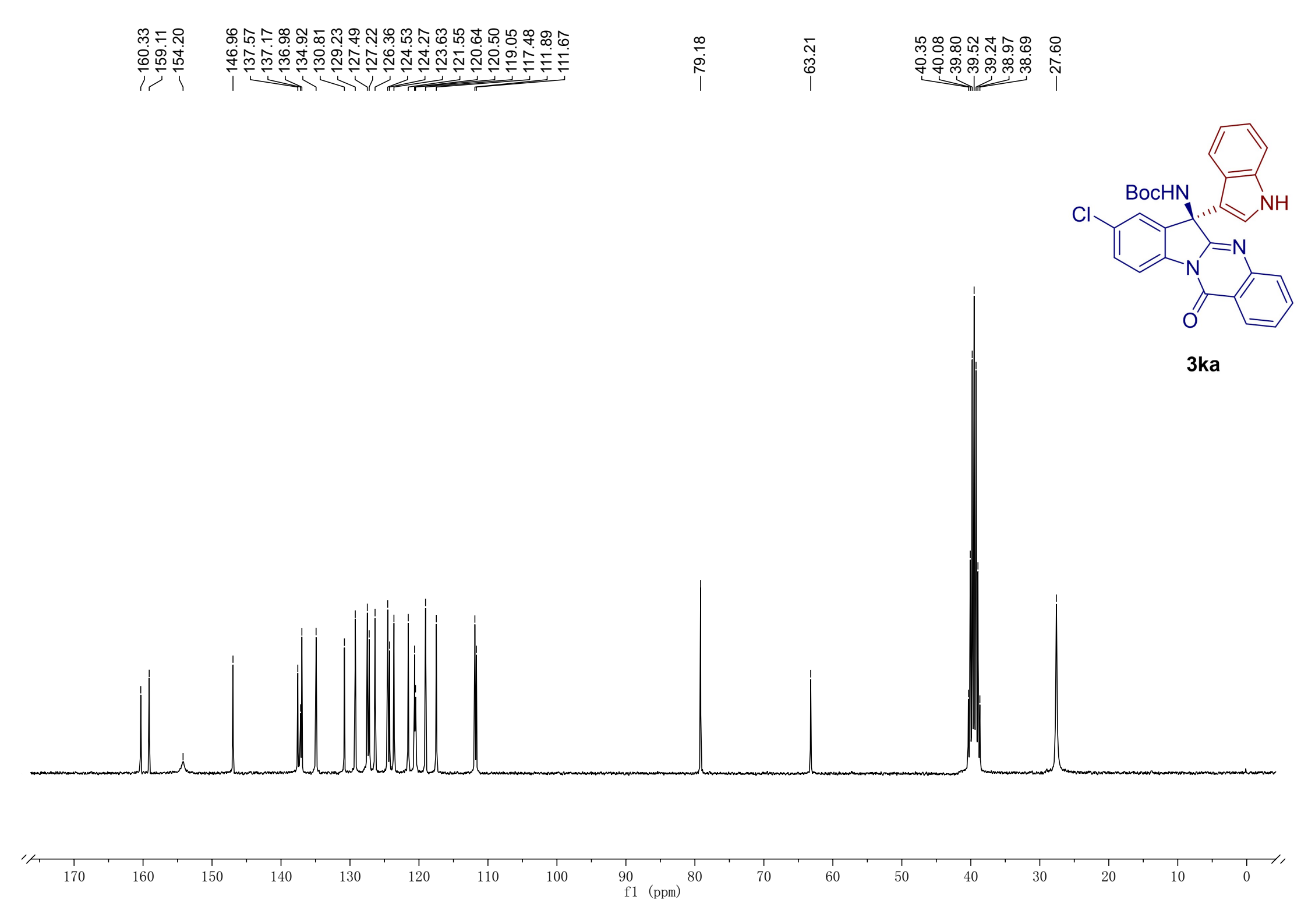
7.66
7.63
7.60
7.58
7.55
7.53
7.38
7.36
7.18
7.10
7.08
7.05
7.00
6.98
6.95
3.38
2.50
2.49
1.10
BocHN
NH
Cl
N
N
O
3ka
1.00
1.01
1.98
1.08
5.05
1.12
1.03
1.08
1.01
9.15
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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159.11
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137.57
137.17
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134.92
130.81
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127.22
126.36
124.53
124.27
123.63
121.55
120.64
120.50
119.05
117.48
111.89
111.67
79.18
63.21
40.35
40.08
39.80
39.52
39.24
38.97
38.69
27.60
BocHN
NH
Cl
N
N
O
3ka
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150
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130
120
110
100
90
80
70
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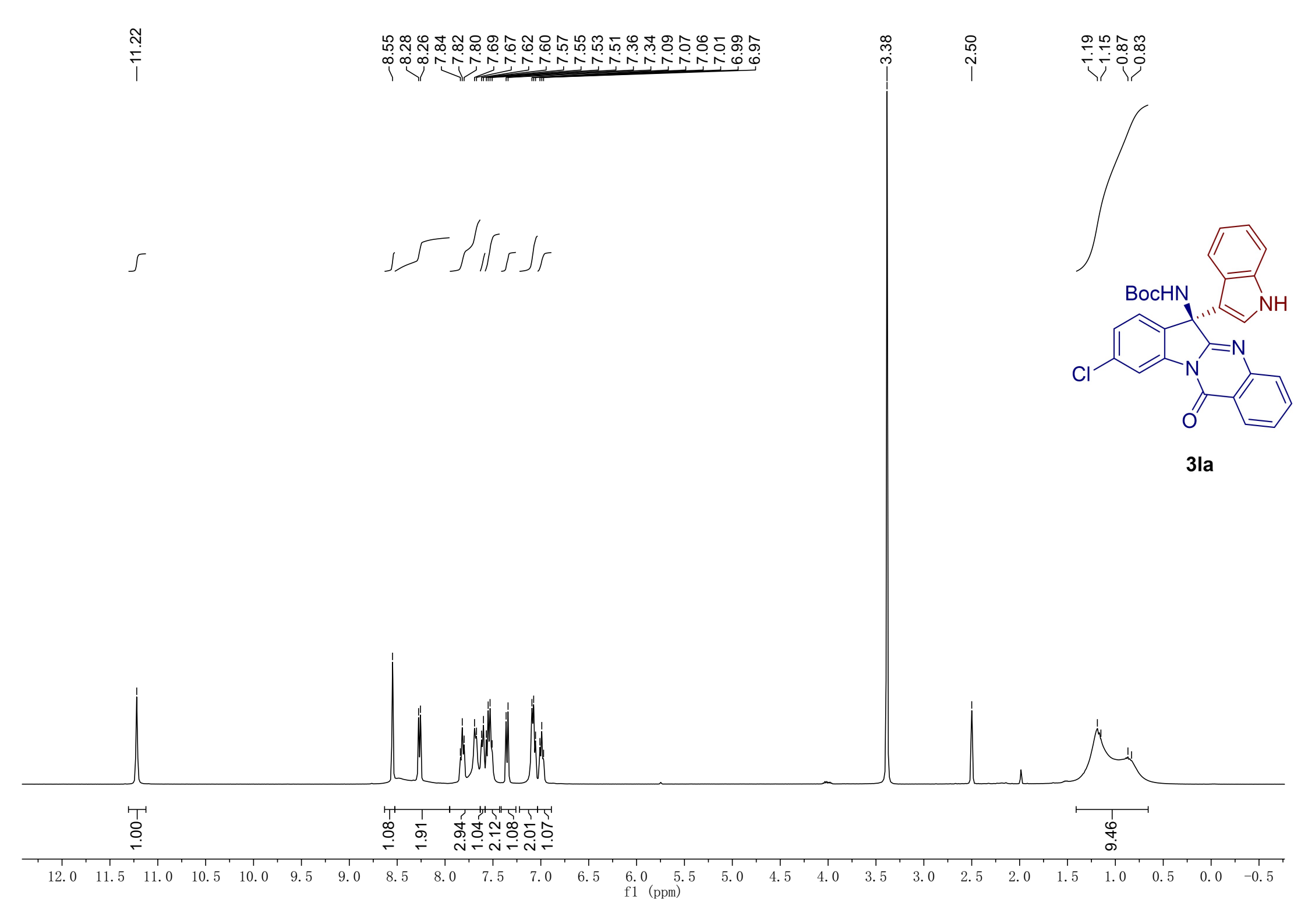
50
40
30
20
10
0
f1 (ppm)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7.60
7.57
7.55
7.53
7.51
7.36
7.34
7.09
7.07
7.06
7.01
6.99
6.97
3.38
2.50
1.19
1.15
0.87
0.83
BocHN
NH
N
N
Cl
O
3la
1.00
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1.91
2.94
1.04
2.12
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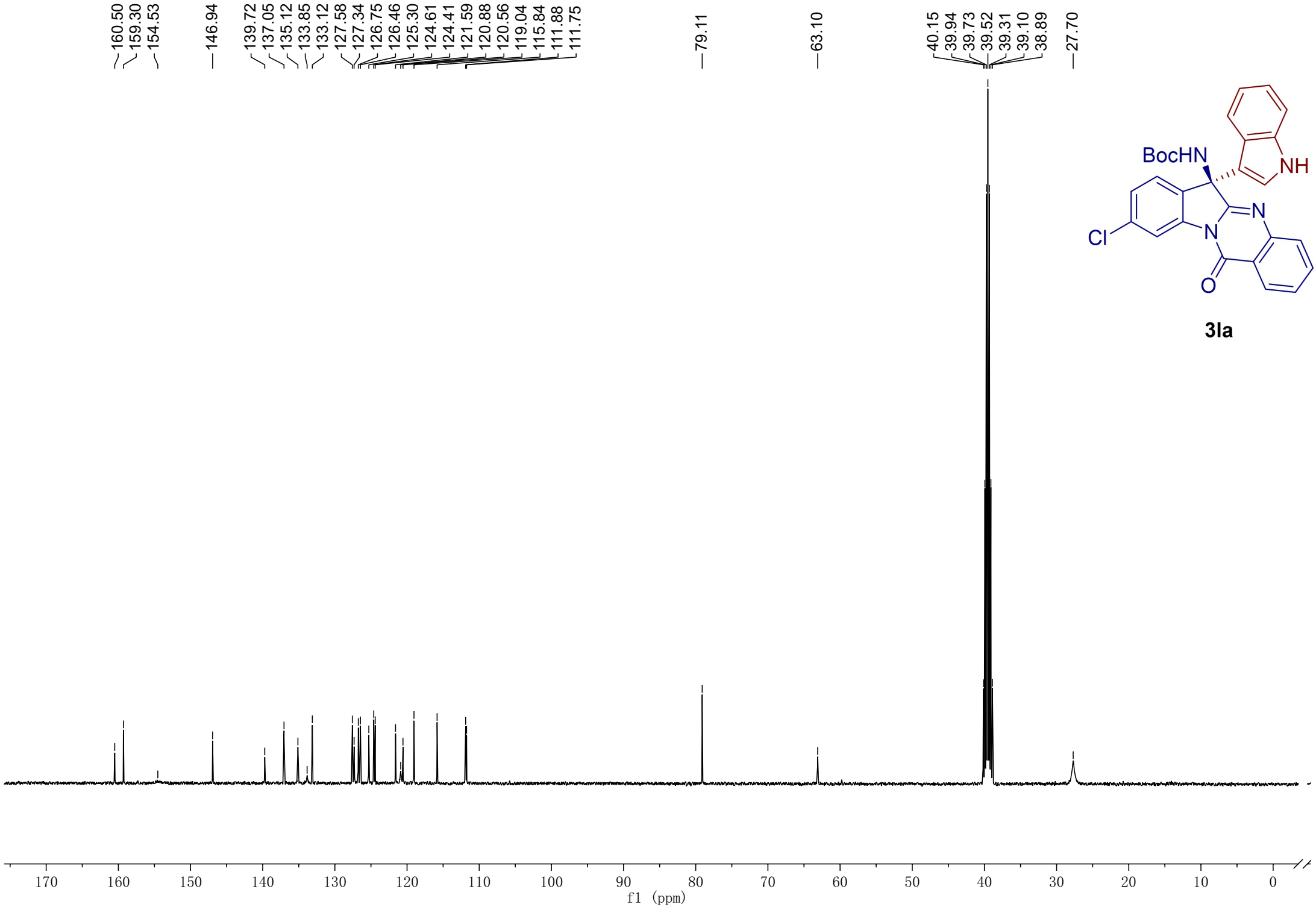
2.01
1.07
9.46
f1 (ppm)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127.34
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121.59
120.88
120.56
119.04
115.84
111.88
111.75
79.11
63.10
40.15
39.94
39.73
39.52
39.31
39.10
38.89
27.70
BocHN
NH
N
N
Cl
O
3la
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130
120
110
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90
80
70
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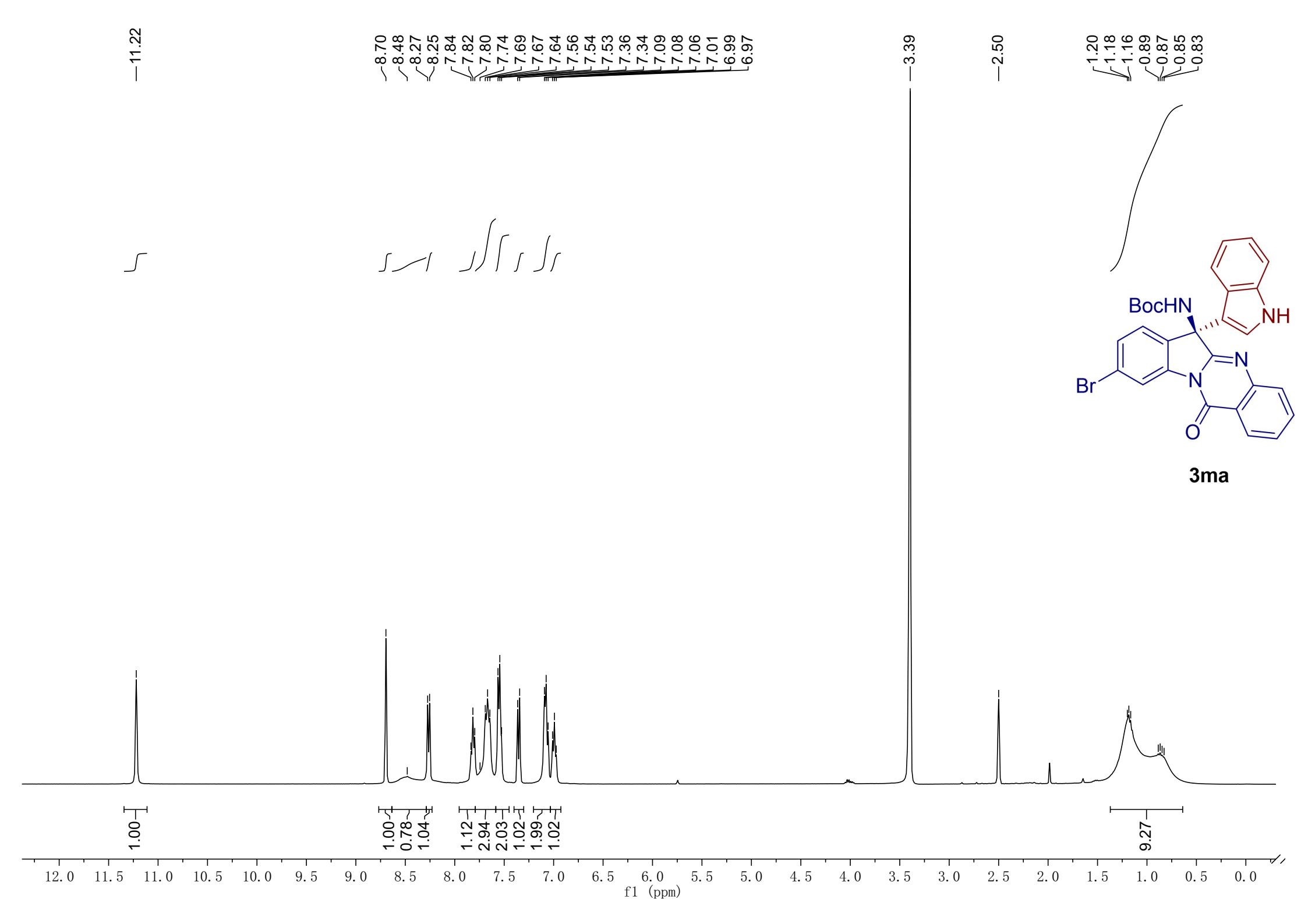
50
40
30
20
10
0
f1 (ppm)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7.69
7.67
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7.56
7.54
7.53
7.36
7.34
7.09
7.08
7.06
7.01
6.99
6.97
3.39
2.50
1.20
1.18
1.16
0.89
0.87
0.85
0.83
BocHN
NH
N
N
Br
O
3ma
1.00
1.00
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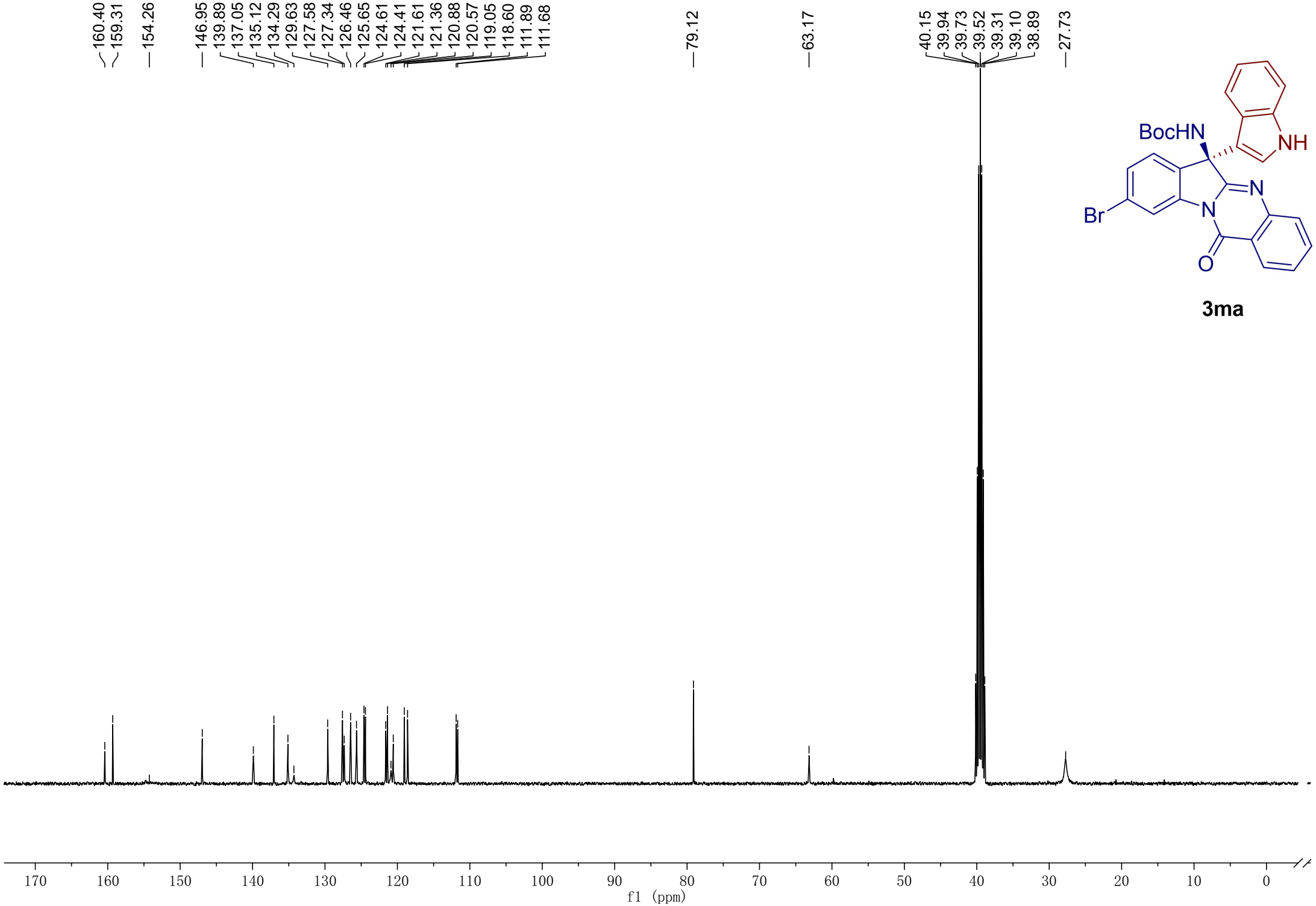
1.04
1.12
2.94
2.03
1.02
1.99
1.02
9.27
f1 (ppm)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124.41
121.61
121.36
120.88
120.57
119.05
118.60
111.89
111.68
79.12
63.17
40.15
39.94
39.73
39.52
39.31
39.10
38.89
27.73
BocHN
NH
N
N
Br
O
3ma
170
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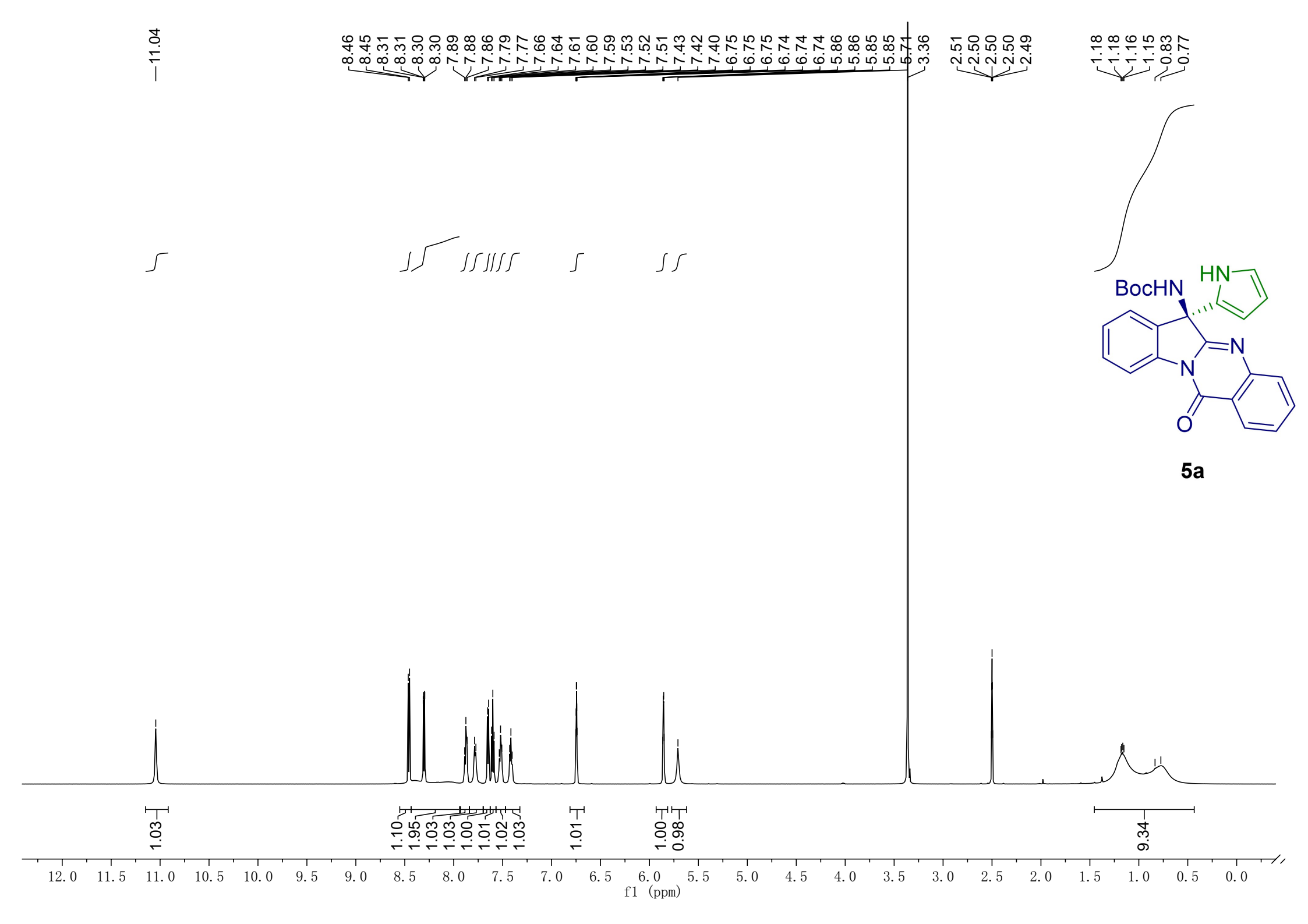
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.64
7.61
7.60
7.59
7.53
7.52
7.51
7.43
7.42
7.40
6.75
6.75
6.75
6.74
6.74
6.74
5.86
5.86
5.85
5.85
5.71
3.36
2.51
2.50
2.50
2.50
2.49
1.18
1.18
1.16
1.15
0.83
0.77
BocHN
HN
N
N
O
5a
1.03
1.10
1.95
1.03
1.03
1.00
1.01
1.02
1.03
1.01
1.00
0.98
9.34
12.0
11.5
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
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3.5
3.0
2.5
2.0
1.5
1.0
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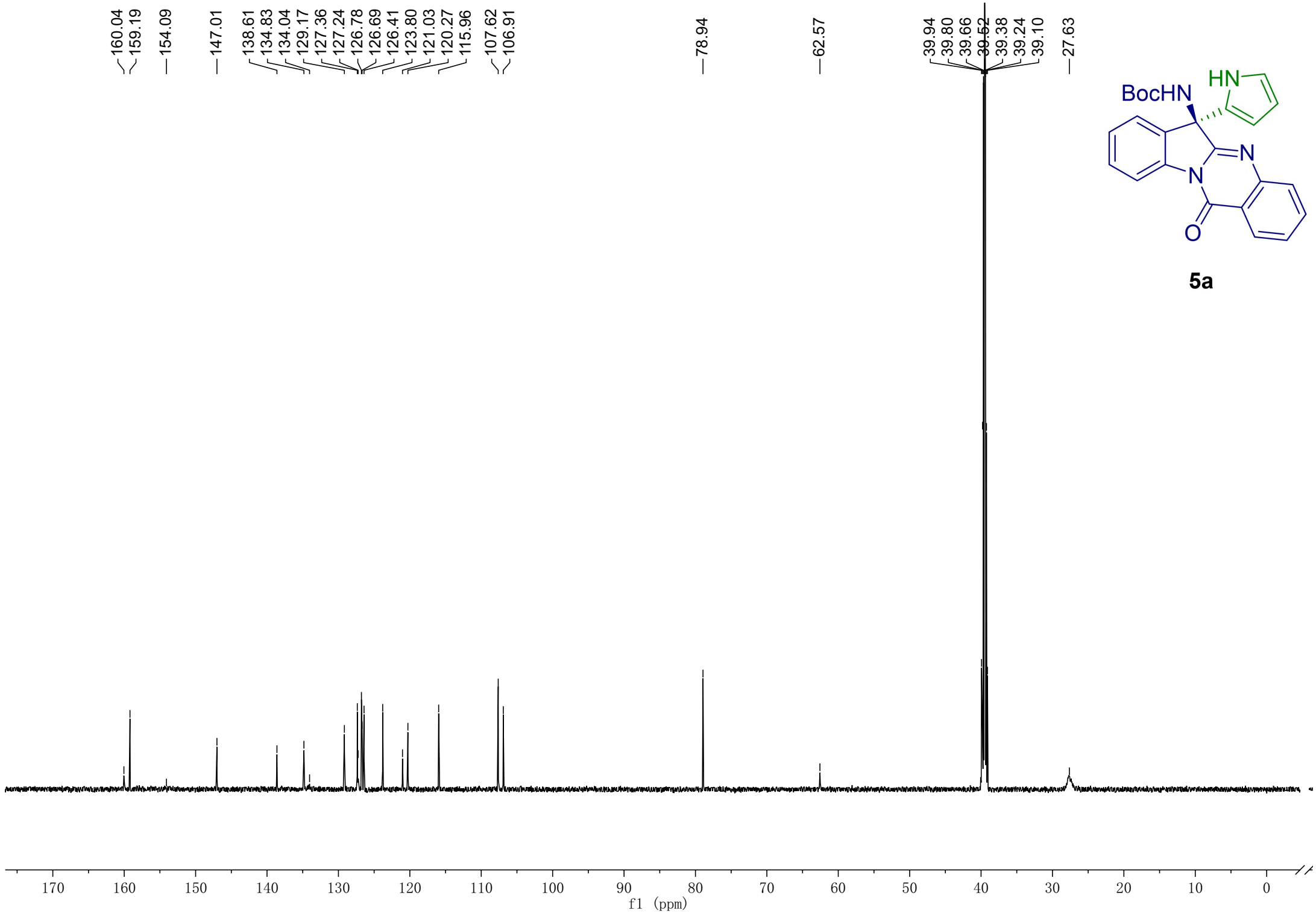
0.0
f1 (ppm)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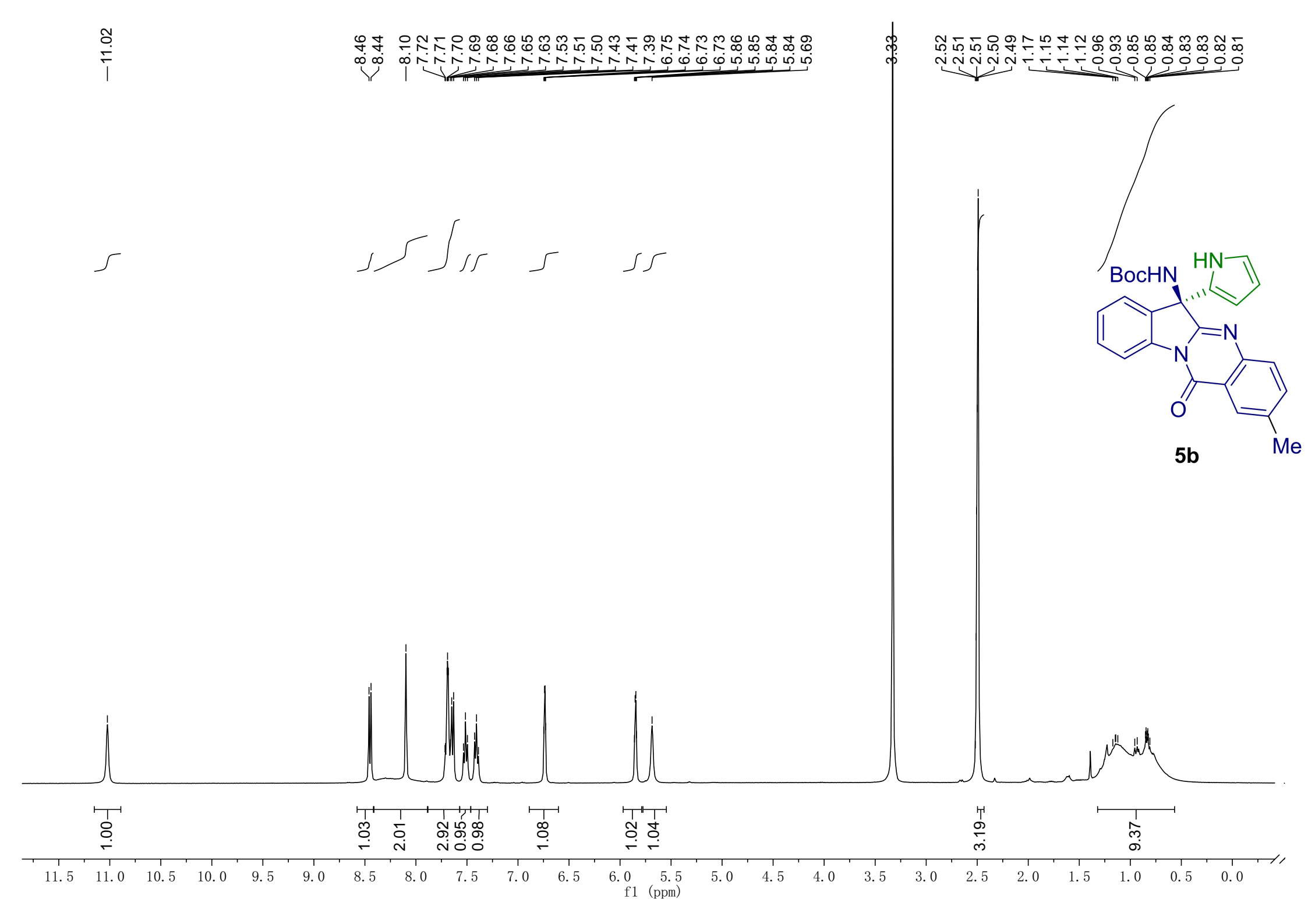
126.69
126.41
123.80
121.03
120.27
115.96
107.62
106.91
78.94
62.57
39.94
39.80
39.66
39.52
39.38
39.24
39.10
27.63
BocHN
HN
N
N
O
5a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.63
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7.51
7.50
7.43
7.41
7.39
6.75
6.74
6.73
6.73
5.86
5.85
5.84
5.84
5.69
3.33
2.52
2.51
2.51
2.50
2.49
1.17
1.15
1.14
1.12
0.96
0.93
0.85
0.85
0.84
0.83
0.83
0.82
0.81
BocHN
HN
N
N
O
Me
5b
1.00
1.03
2.01
2.92
0.95
0.98
1.08
1.02
1.04
3.19
9.37
11.5
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
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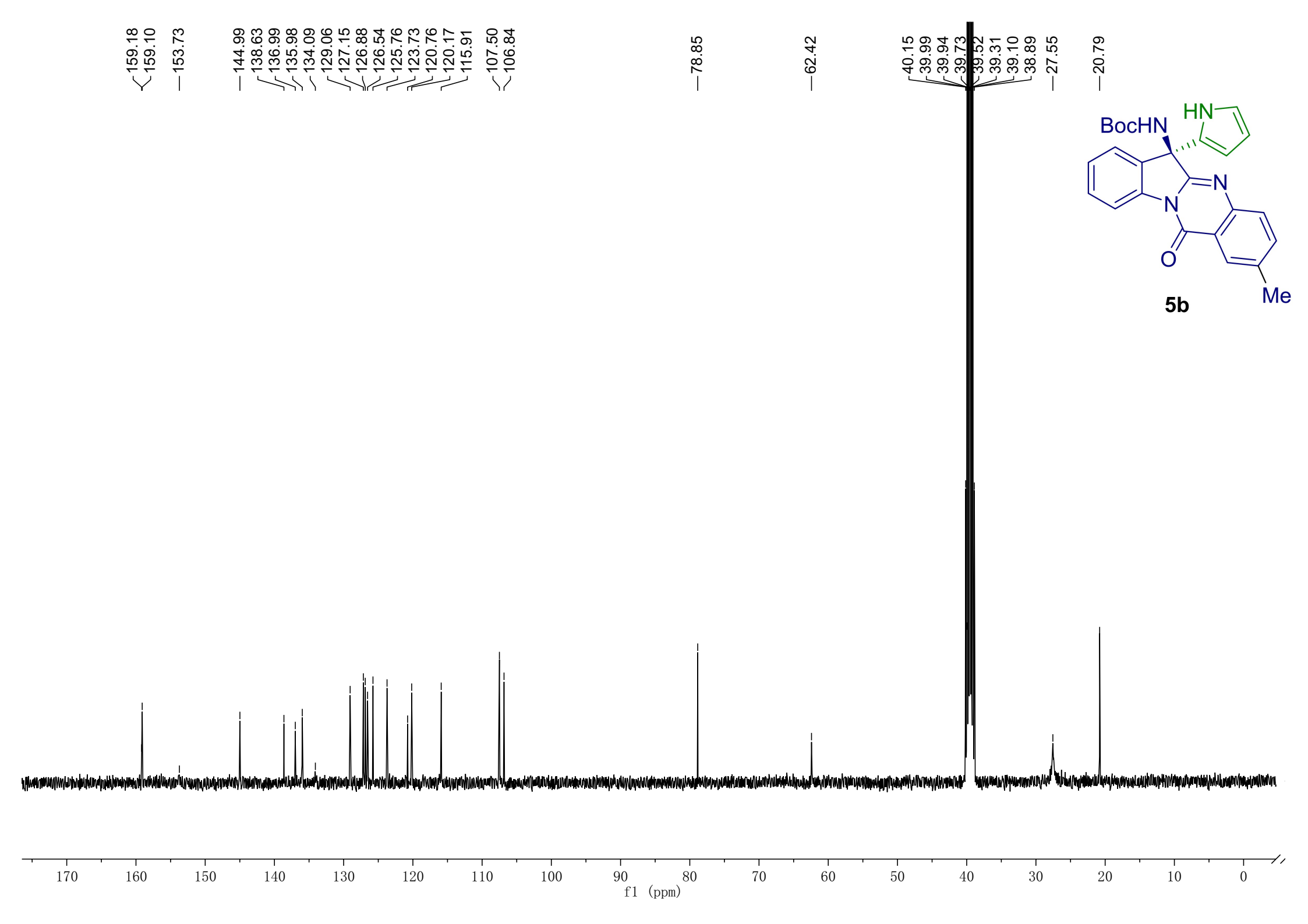
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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120.76
120.17
115.91
107.50
106.84
78.85
62.42
40.15
39.99
39.94
39.73
39.52
39.31
39.10
38.89
27.55
20.79
BocHN
HN
N
N
O
Me
5b
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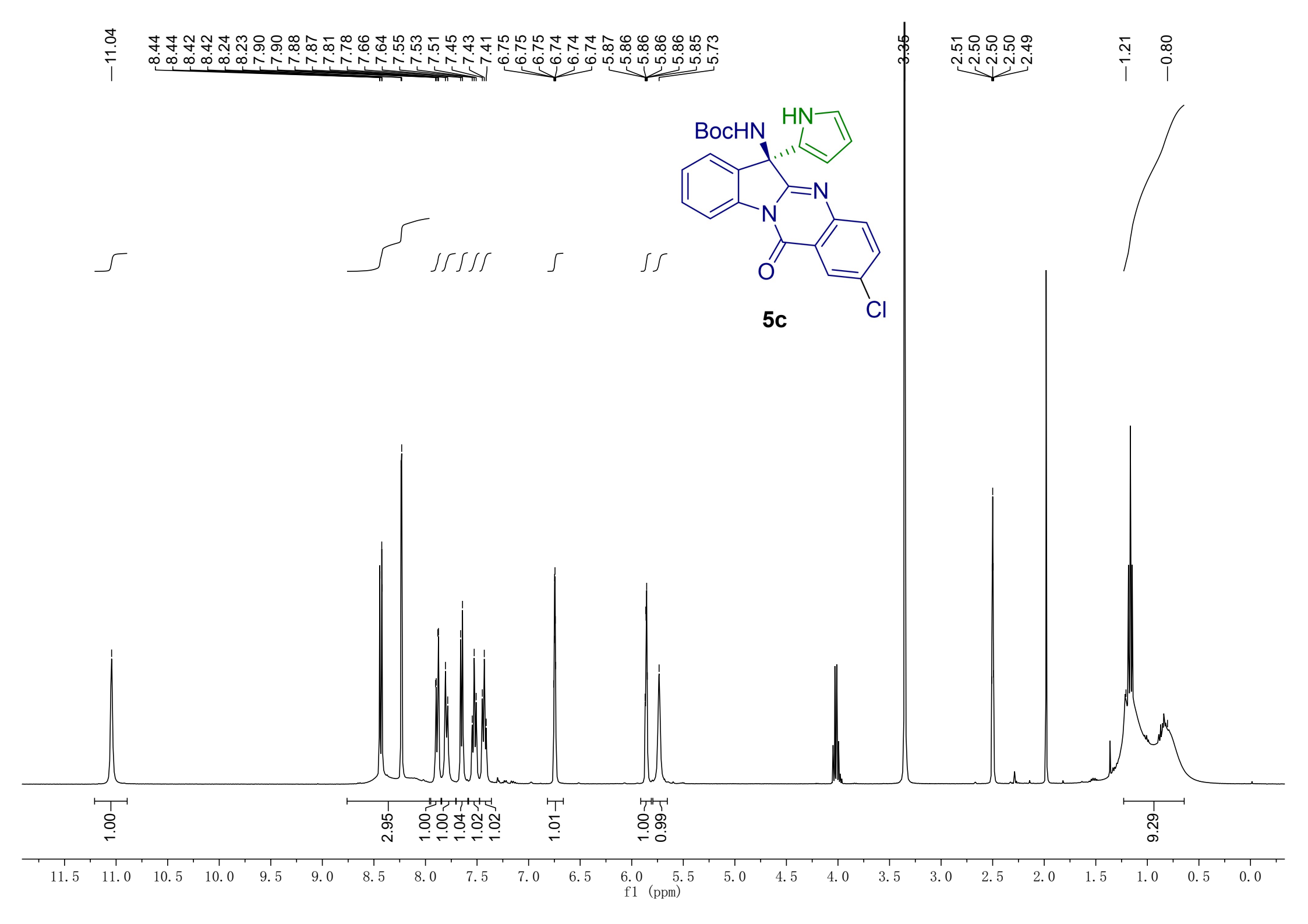
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.24
8.23
7.90
7.90
7.88
7.87
7.81
7.78
7.66
7.64
7.55
7.53
7.51
7.45
7.43
7.41
6.75
6.75
6.75
6.74
6.74
6.74
5.87
5.86
5.86
5.86
5.85
5.73
3.35
2.51
2.50
2.50
2.50
2.49
1.21
0.80
BocHN
HN
N
N
O
Cl
5c
1.00
2.95
1.00
1.00
1.04
1.02
1.02
1.01
1.00
0.99
9.29
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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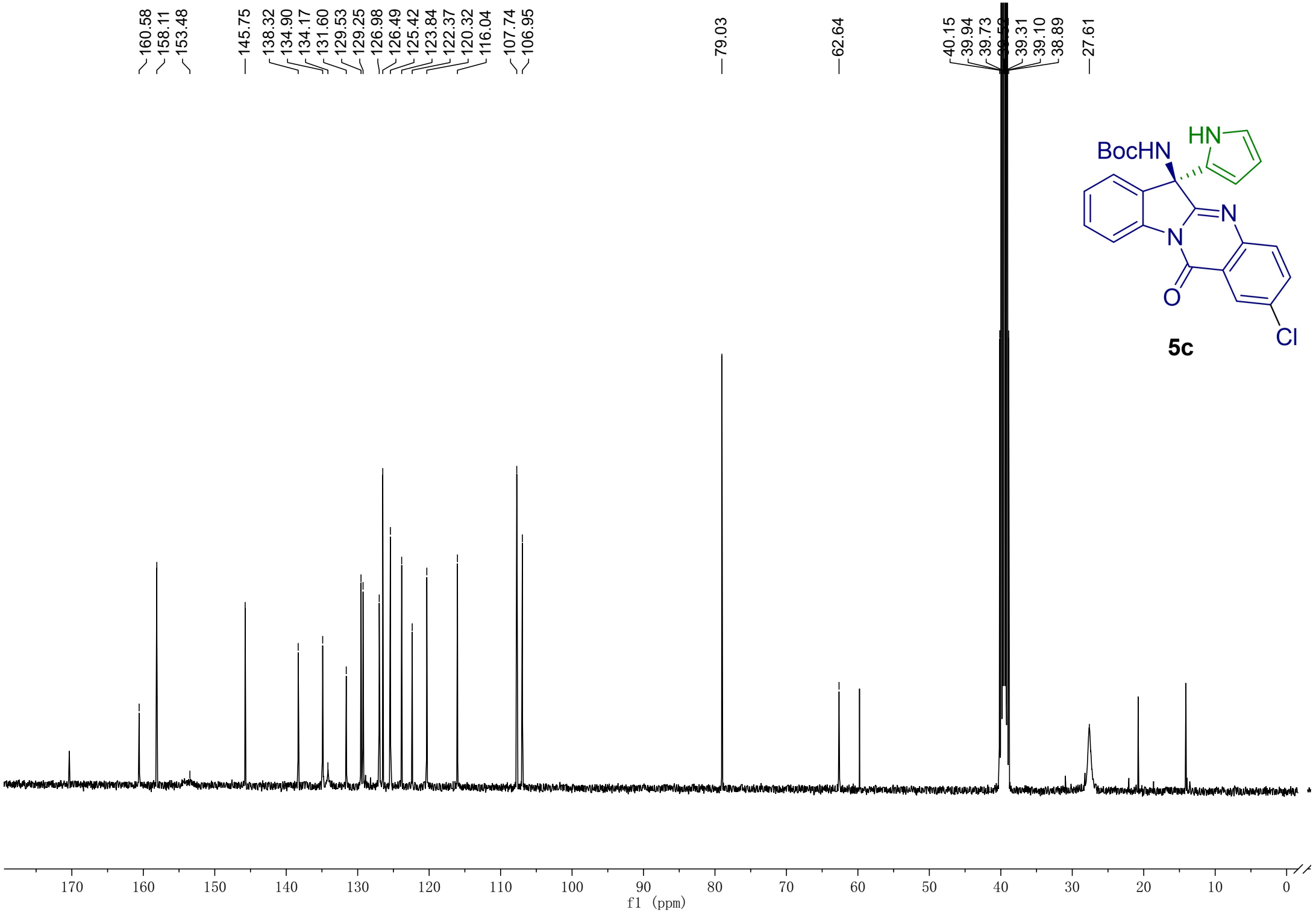
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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129.25
126.98
126.49
125.42
123.84
122.37
120.32
116.04
107.74
106.95
79.03
62.64
40.15
39.94
39.73
39.31
39.10
38.89
27.61
BocHN
HN
N
N
O
Cl
5c
170
160
150
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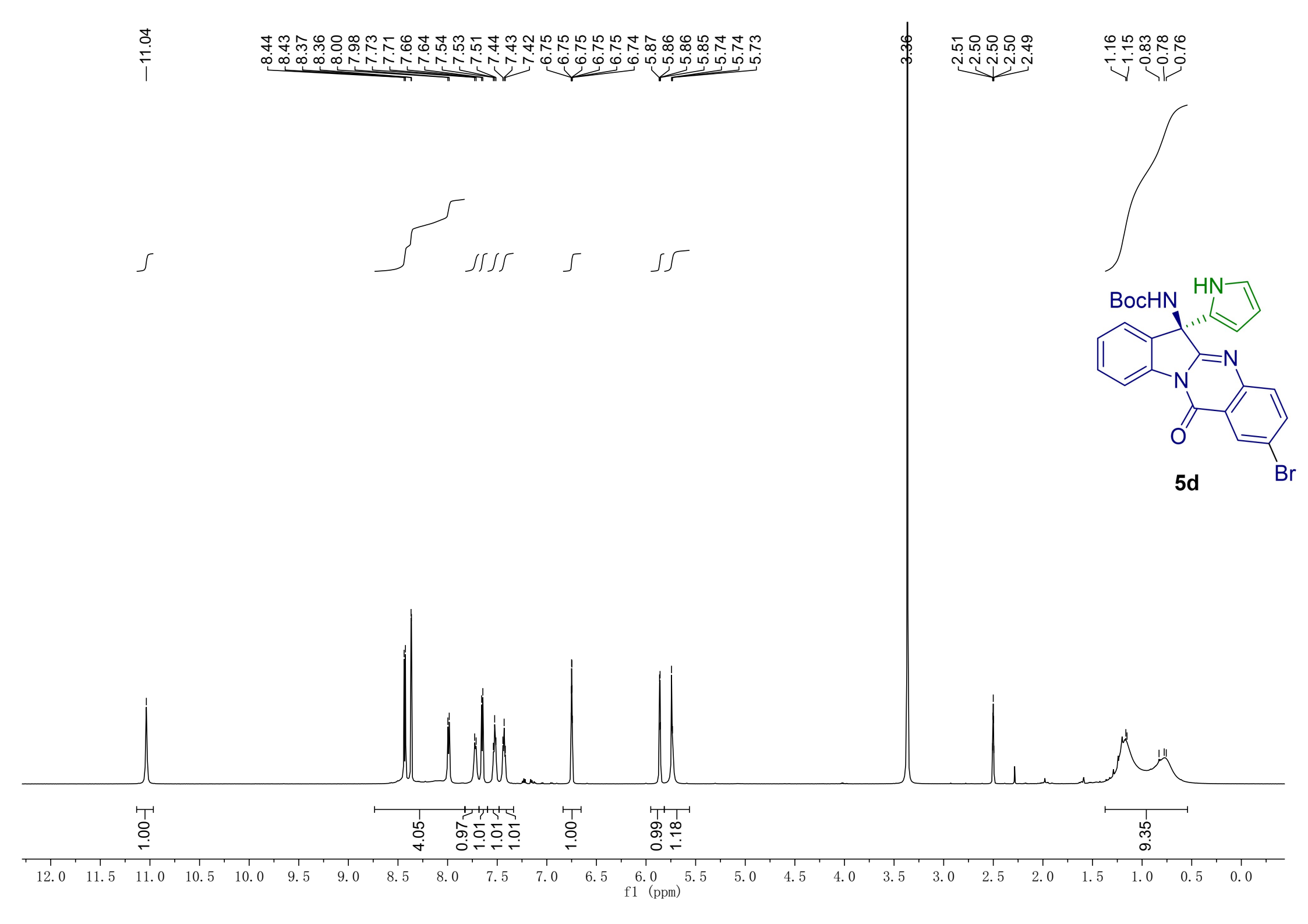
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.00
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7.73
7.71
7.66
7.64
7.54
7.53
7.51
7.44
7.43
7.42
6.75
6.75
6.75
6.75
6.74
5.87
5.86
5.86
5.85
5.74
5.74
5.73
3.36
2.51
2.50
2.50
2.50
2.49
1.16
1.15
0.83
0.78
0.76
HN
BocHN
N
N
O
Br
5d
1.00
4.05
0.97
1.01
1.01
1.01
1.00
0.99
1.18
9.35
12.0
11.5
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
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3.0
2.5
2.0
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1.0
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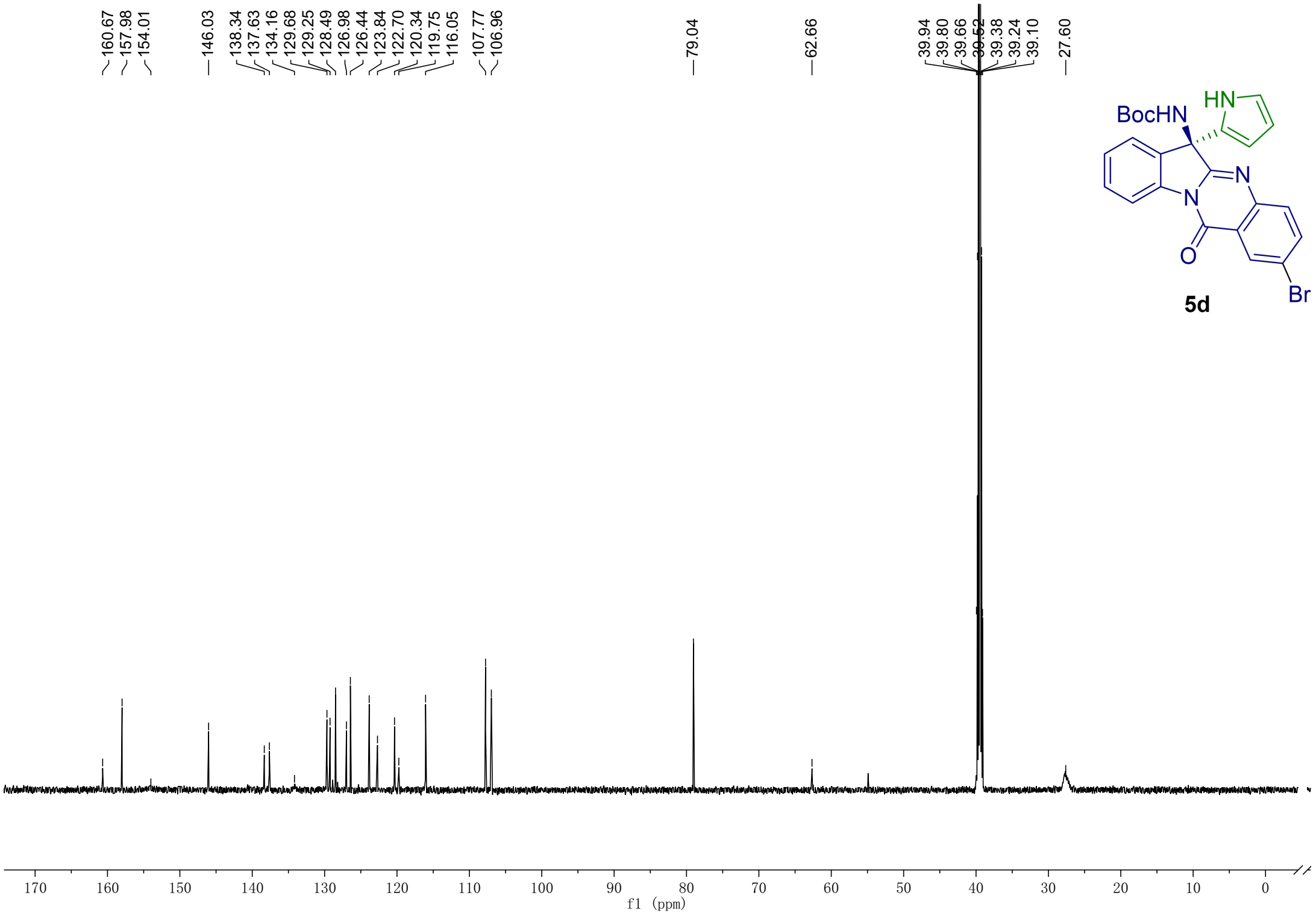
0.0
f1 (ppm)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154.01
146.03
138.34
137.63
134.16
129.68
129.25
128.49
126.98
126.44
123.84
122.70
120.34
119.75
116.05
107.77
106.96
79.04
62.66
39.94
39.80
39.66
39.52
39.38
39.24
39.10
27.60
BocHN
HN
N
N
O
Br
5d
170
160
150
140
130
120
110
100
90
80
70
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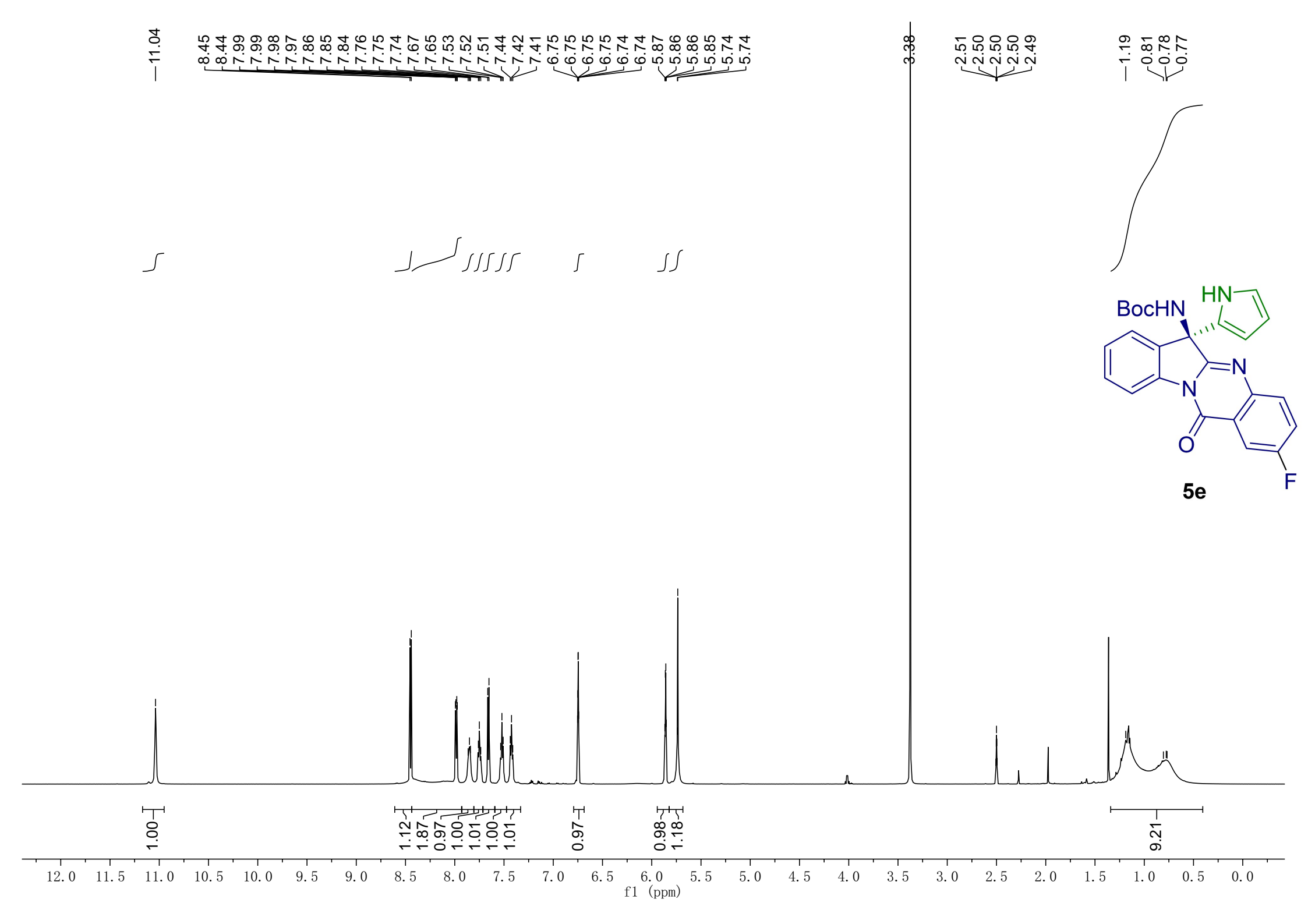
50
40
30
20
10
0
f1 (ppm)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8.44
7.99
7.99
7.98
7.97
7.86
7.85
7.84
7.76
7.75
7.74
7.67
7.65
7.53
7.52
7.51
7.44
7.42
7.41
6.75
6.75
6.75
6.75
6.74
6.74
5.87
5.86
5.86
5.85
5.74
5.74
3.38
2.51
2.50
2.50
2.50
2.49
1.19
0.81
0.78
0.77
BocHN
HN
N
N
O
F
5e
1.00
1.12
1.87
0.97
1.00
1.01
1.00
1.01
0.97
0.98
1.18
9.21
12.0
11.5
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
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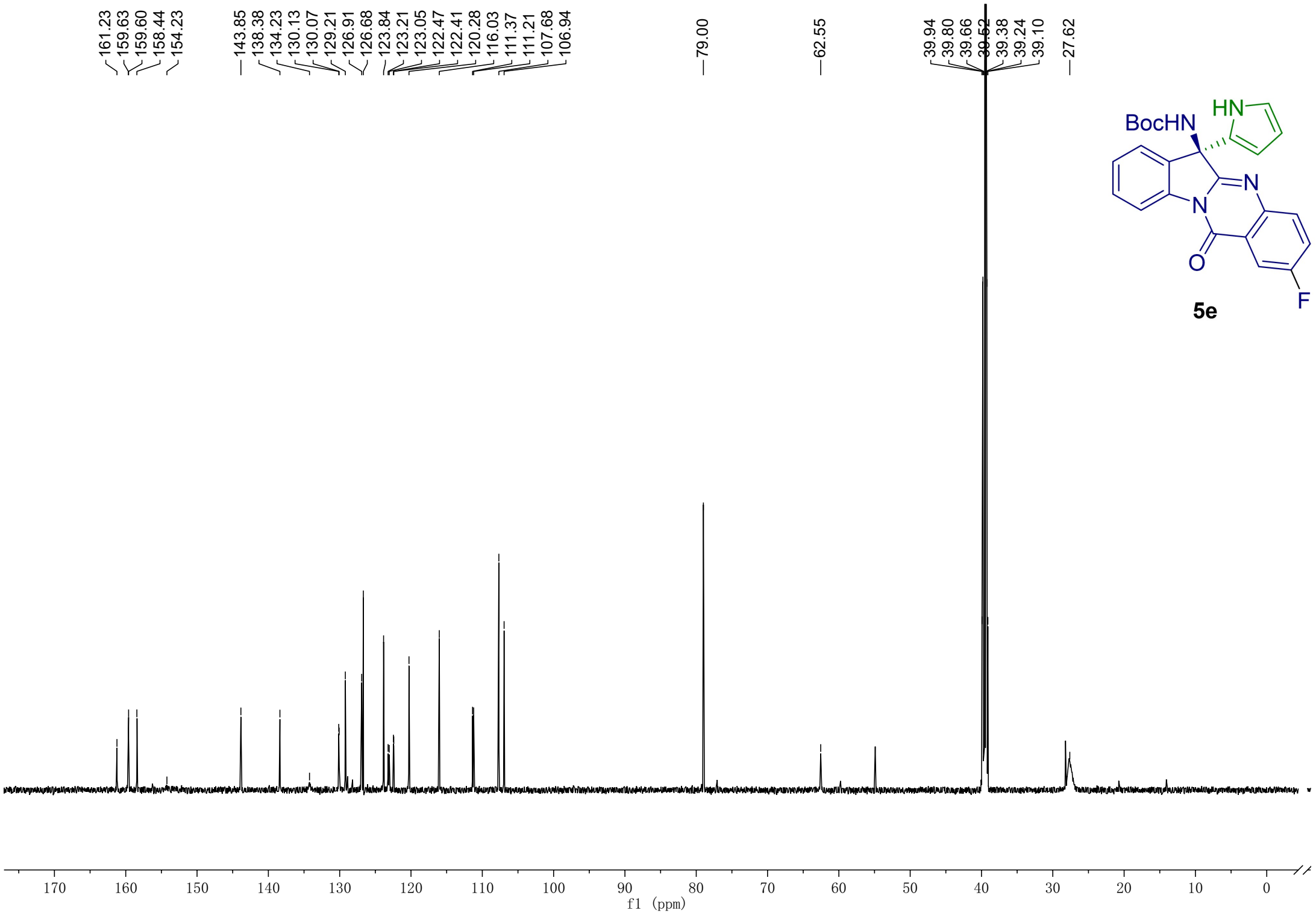
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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159.63
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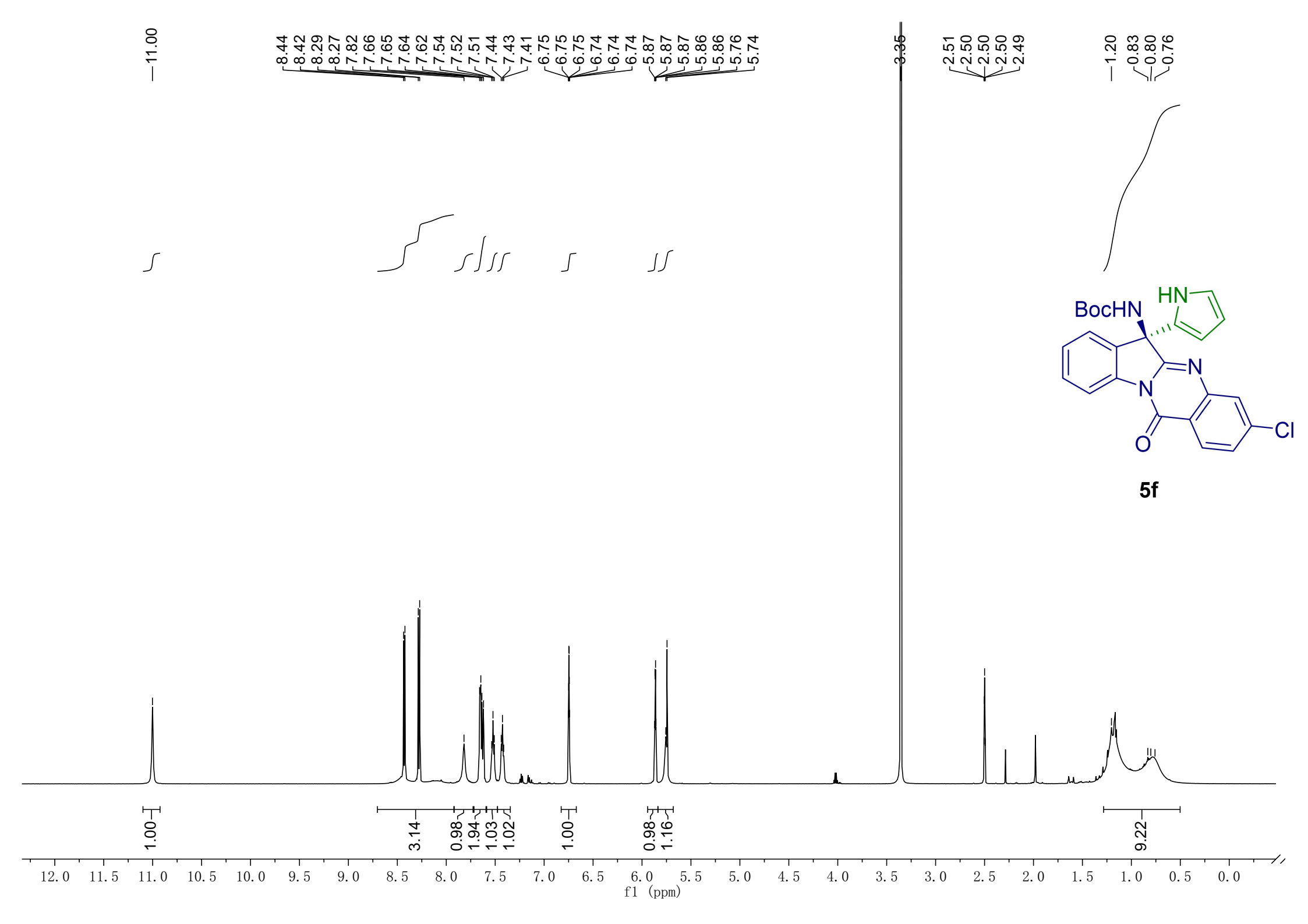
143.85
138.38
134.23
130.13
130.07
129.21
126.91
126.68
123.84
123.21
123.05
122.47
122.41
120.28
116.03
111.37
111.21
107.68
106.94
79.00
62.55
39.94
39.80
39.66
39.52
39.38
39.24
39.10
27.62
BocHN
HN
N
N
O
F
5e
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.44
8.42
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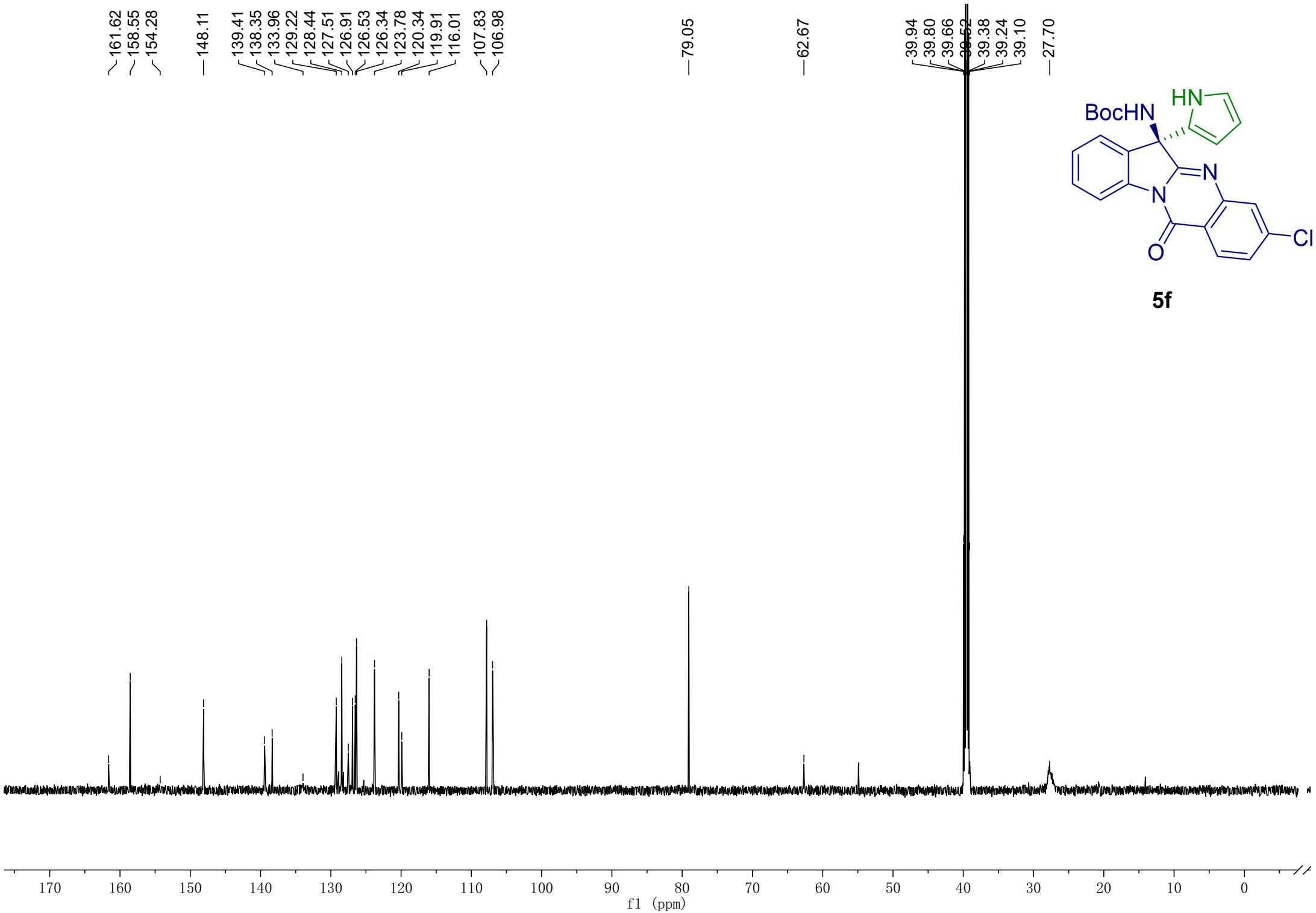
7.65
7.64
7.62
7.54
7.52
7.51
7.44
7.43
7.41
6.75
6.75
6.75
6.74
6.74
6.74
5.87
5.87
5.87
5.86
5.86
5.76
5.74
3.35
2.51
2.50
2.50
2.50
2.49
1.20
0.83
0.80
0.76
BocHN
HN
N
N
O
Cl
5f
1.00
3.14
0.98
1.94
1.03
1.02
1.00
0.98
1.16
9.22
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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139.41
138.35
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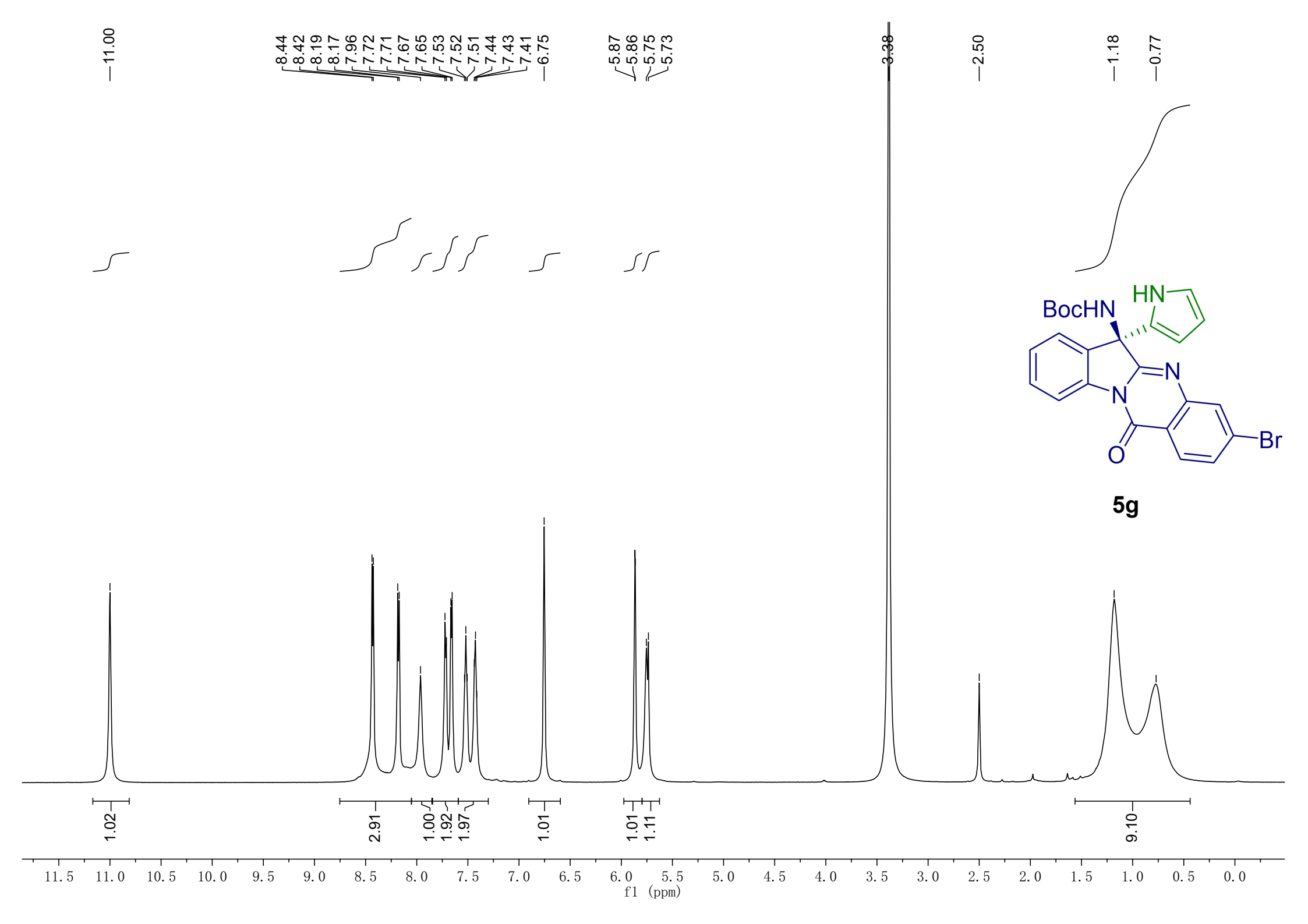
129.22
128.44
127.51
126.91
126.53
126.34
123.78
120.34
119.91
116.01
107.83
106.98
79.05
62.67
39.94
39.80
39.66
39.52
39.38
39.24
39.10
27.70
BocHN
HN
N
N
O
Cl
5f
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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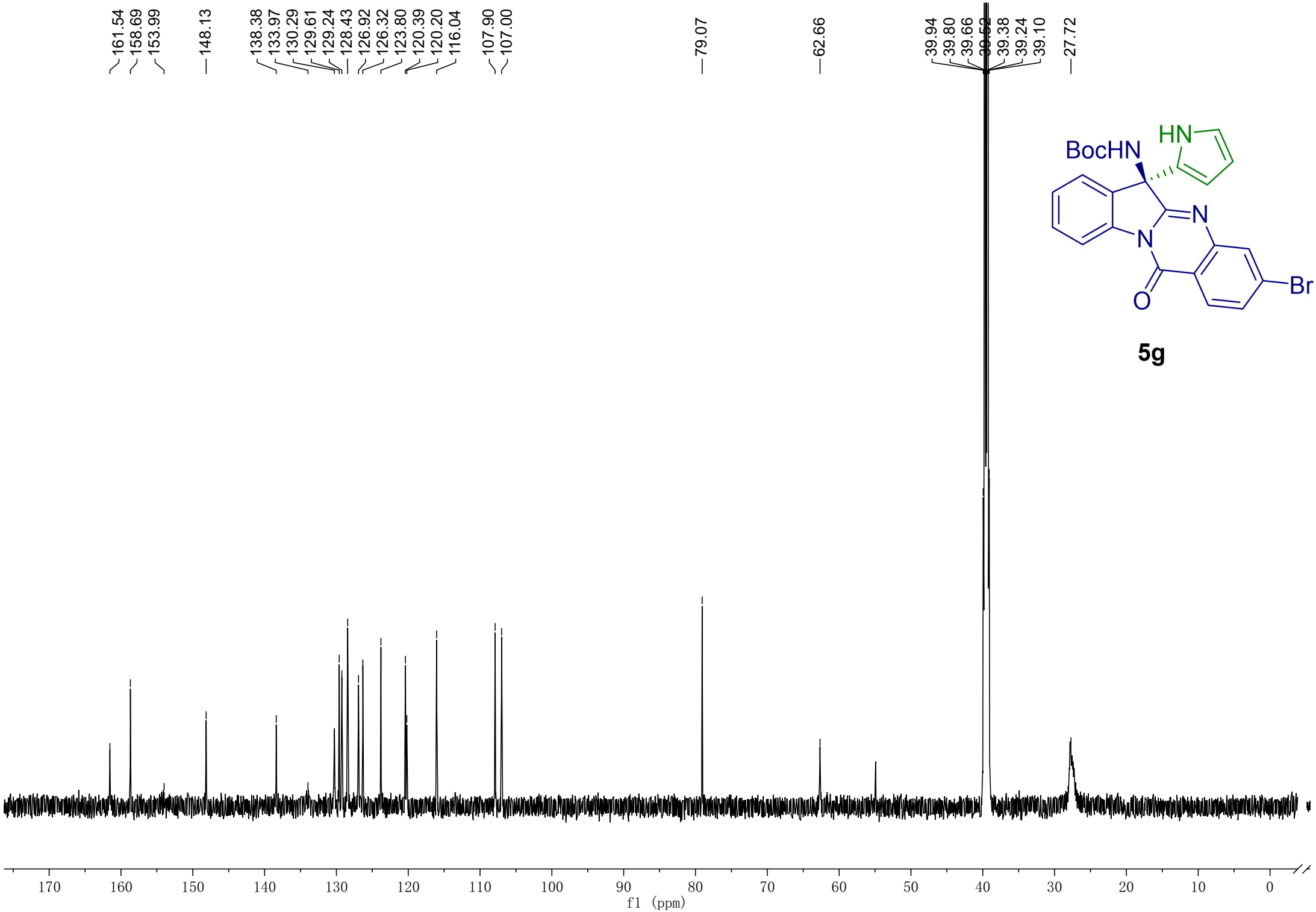
8.44
8.42
8.19
8.17
7.96
7.72
7.71
7.67
7.65
7.53
7.52
7.51
7.44
7.43
7.41
6.75
5.87
5.86
5.75
5.73
3.38
2.50
1.18
0.77
HN
BocHN
N
N
O
Br
5g
1.02
2.91
1.00
1.92
1.97
1.01
1.01
1.11
9.10
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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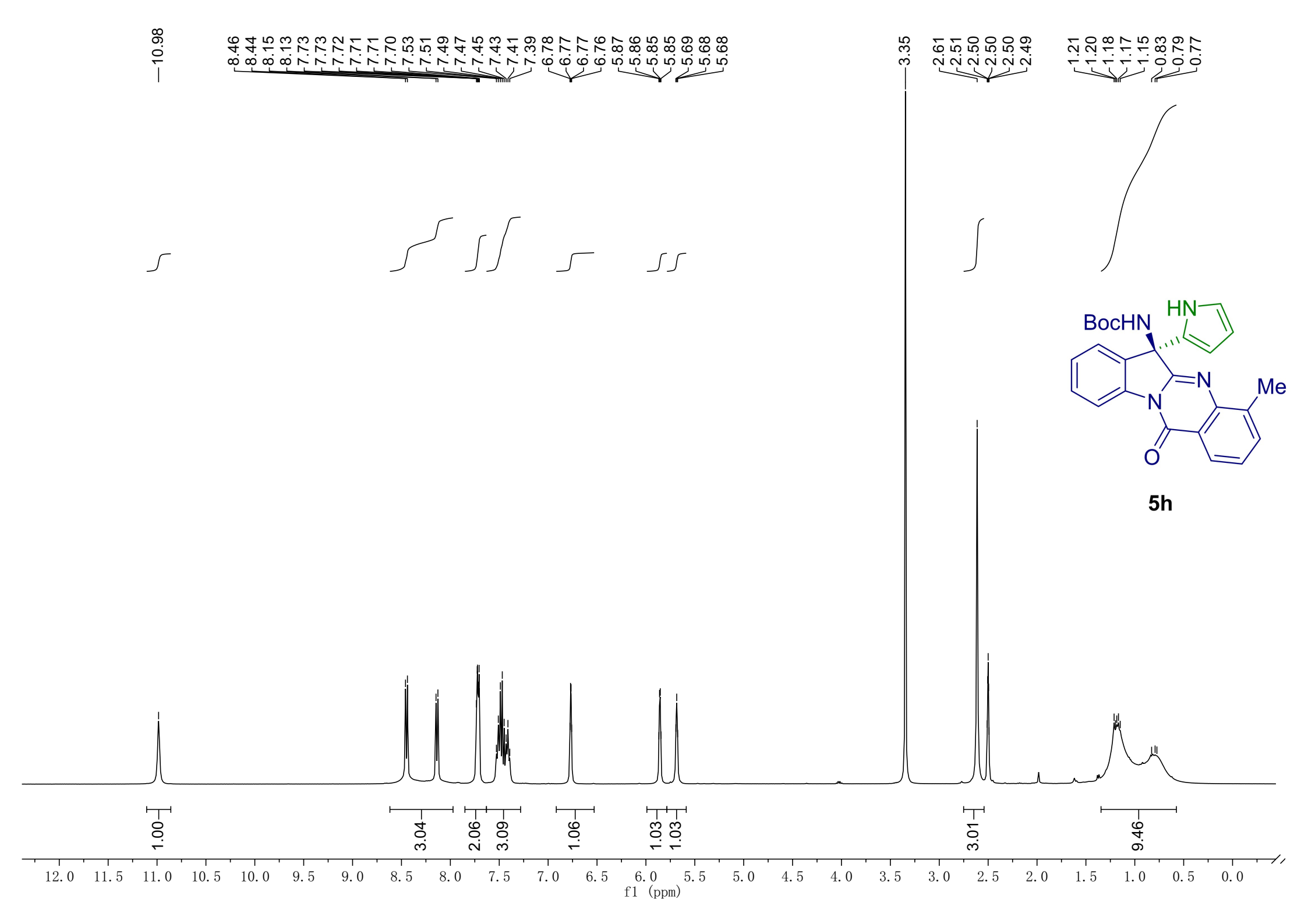
138.38
133.97
130.29
129.61
129.24
128.43
126.92
126.32
123.80
120.39
120.20
116.04
107.90
107.00
79.07
62.66
39.94
39.80
39.66
39.38
39.24
39.10
27.72
BocHN
HN
N
N
O
Br
5g
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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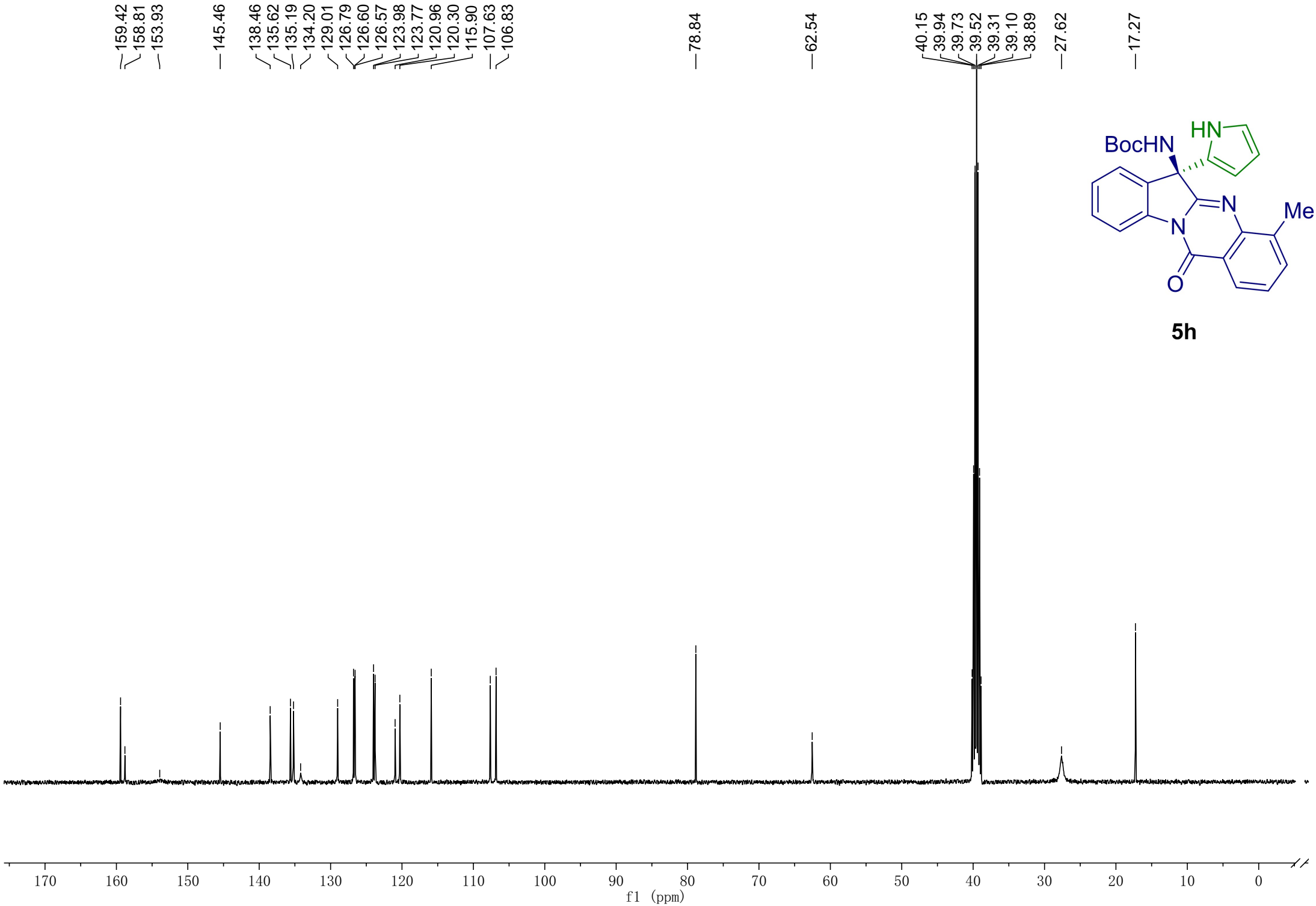
8.46
8.44
8.15
8.13
7.73
7.73
7.72
7.71
7.71
7.70
7.53
7.51
7.49
7.47
7.45
7.43
7.41
7.39
6.78
6.77
6.77
6.76
5.87
5.86
5.85
5.85
5.69
5.68
5.68
3.35
2.61
2.51
2.50
2.50
2.50
2.49
1.21
1.20
1.18
1.17
1.15
0.83
0.79
0.77
HN
BocHN
N
N
Me
O
5h
1.00
3.04
2.06
3.09
1.06
1.03
1.03
3.01
9.46
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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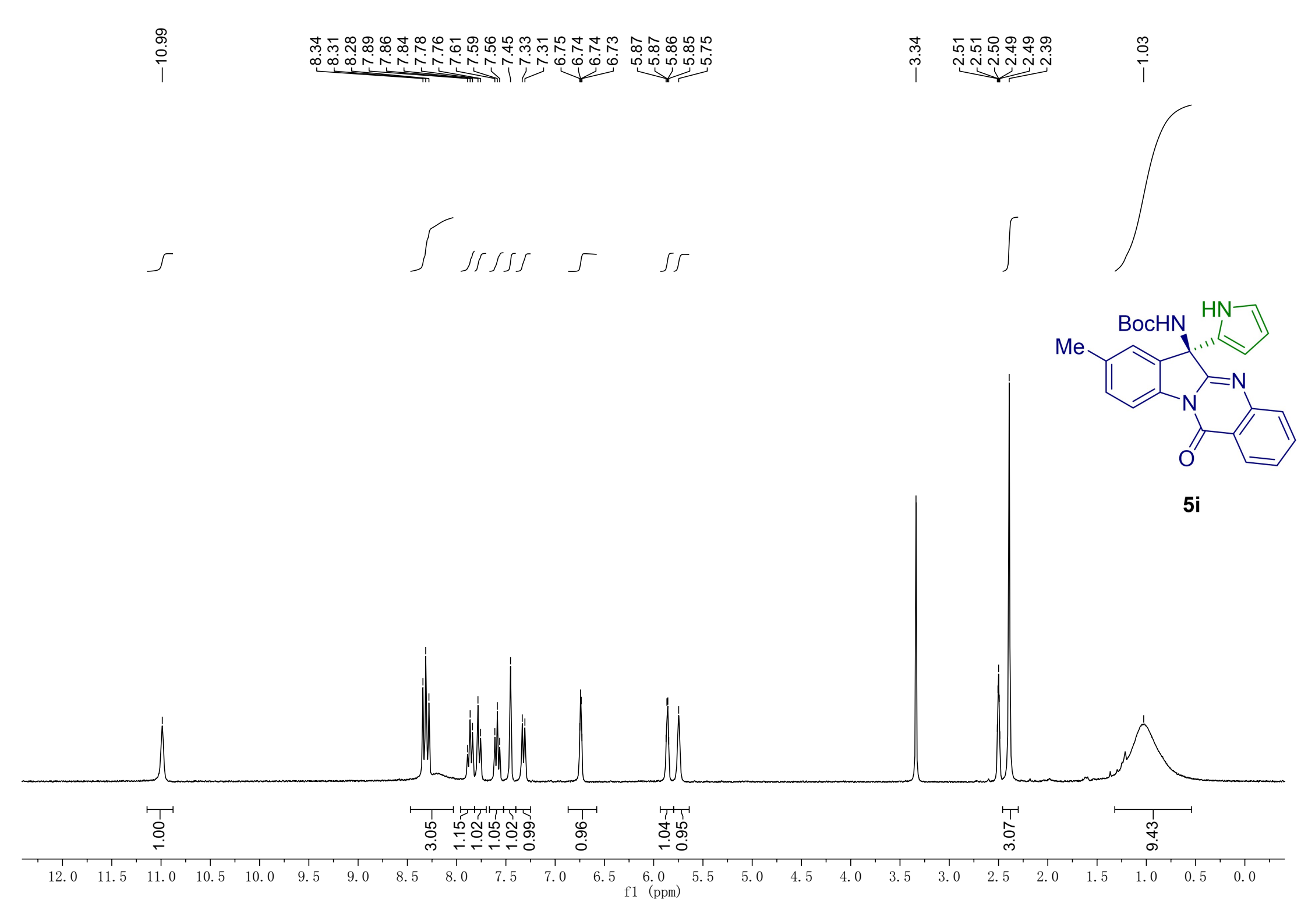
135.62
135.19
134.20
129.01
126.79
126.60
126.57
123.98
123.77
120.96
120.30
115.90
107.63
106.83
78.84
62.54
40.15
39.94
39.73
39.52
39.31
39.10
38.89
27.62
17.27
BocHN
HN
N
N
Me
O
5h
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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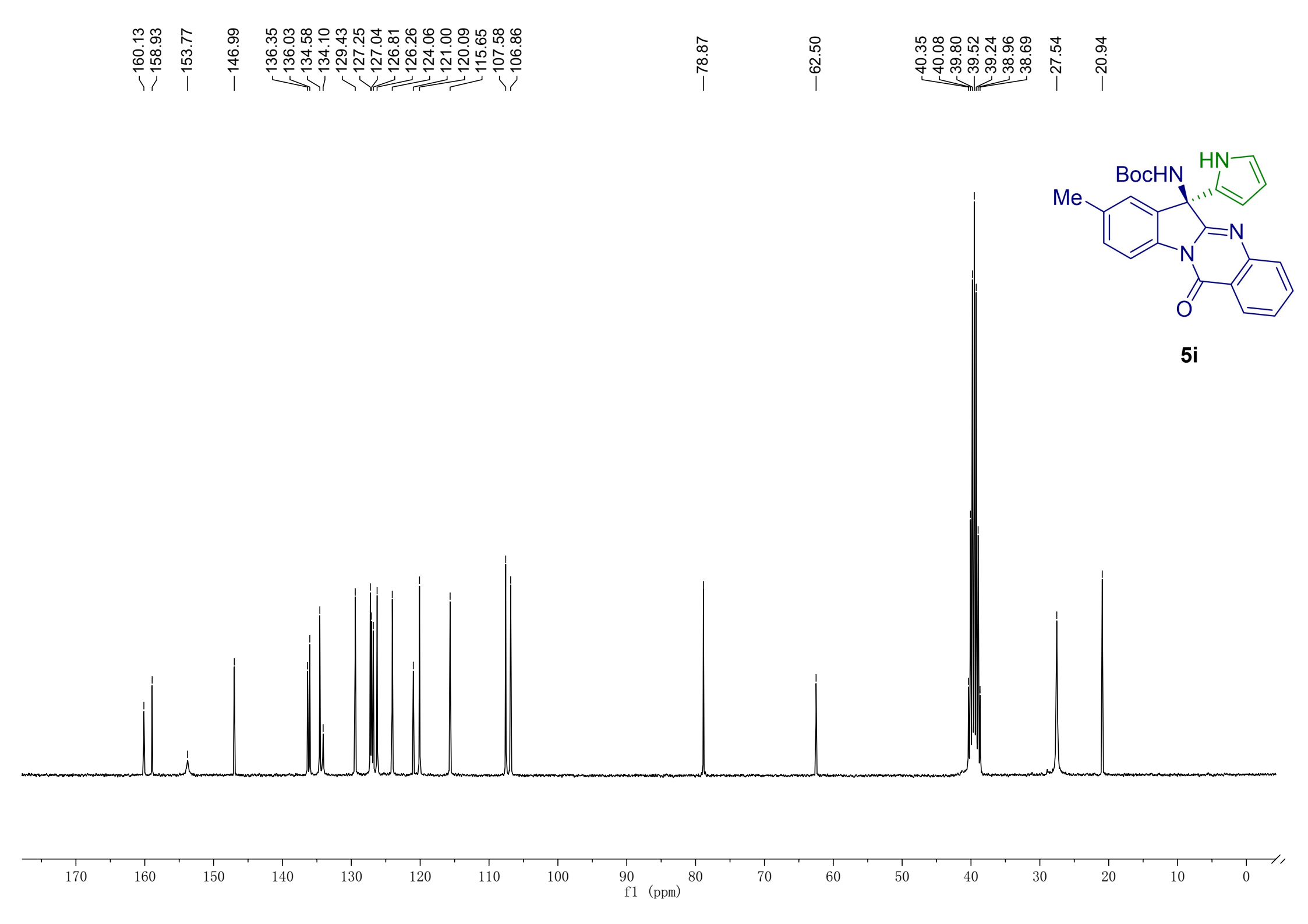
7.78
7.76
7.61
7.59
7.56
7.45
7.33
7.31
6.75
6.74
6.74
6.73
5.87
5.87
5.86
5.85
5.75
3.34
2.51
2.51
2.50
2.49
2.49
2.39
1.03
HN
BocHN
Me
N
N
O
5i
1.00
3.05
1.15
1.02
1.05
1.02
0.99
0.96
1.04
0.95
3.07
9.43
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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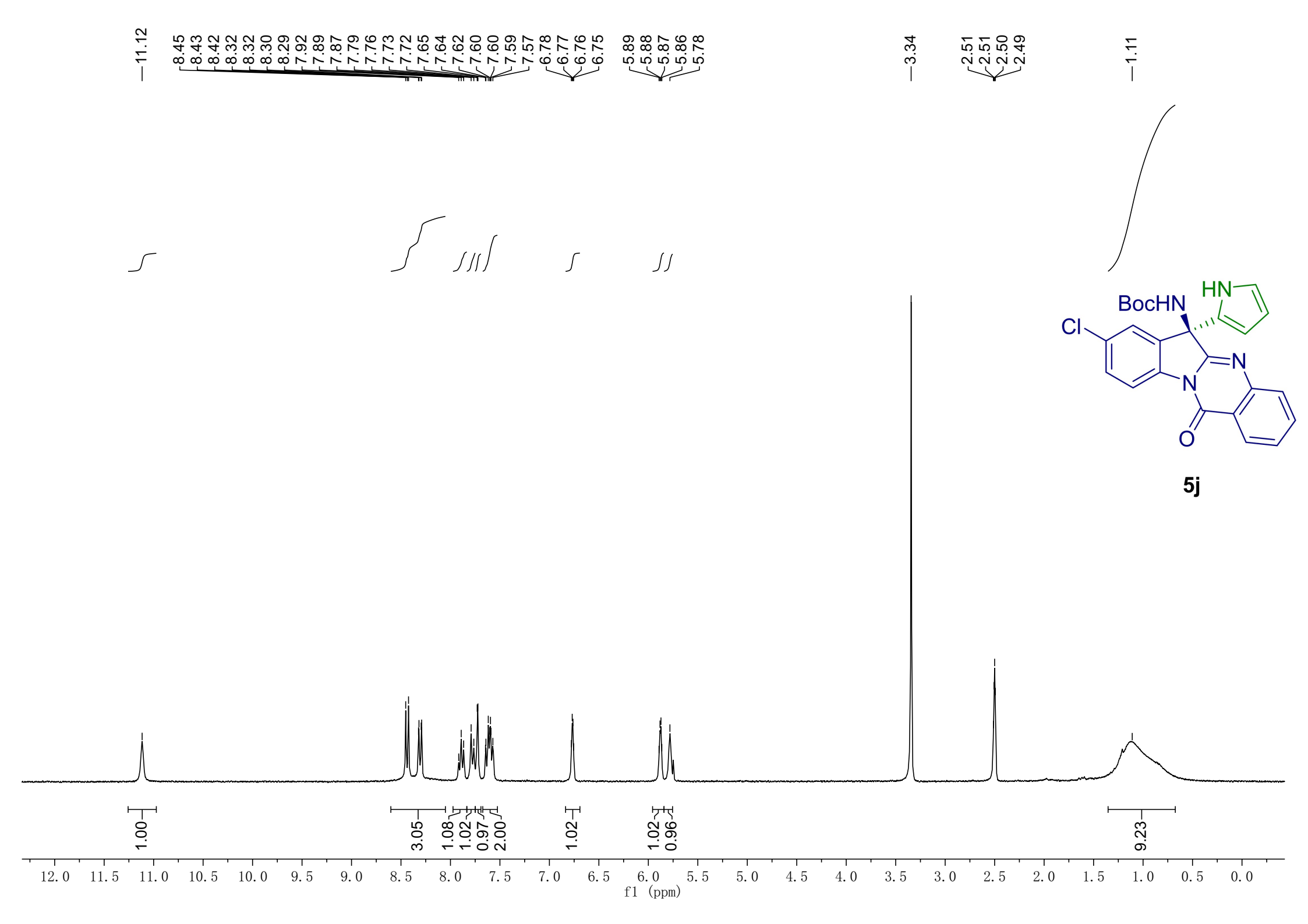
153.77
146.99
136.35
136.03
134.58
134.10
129.43
127.25
127.04
126.81
126.26
124.06
121.00
120.09
115.65
107.58
106.86
78.87
62.50
40.35
40.08
39.80
39.52
39.24
38.96
38.69
27.54
20.94
HN
BocHN
Me
N
N
O
5i
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.32
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8.29
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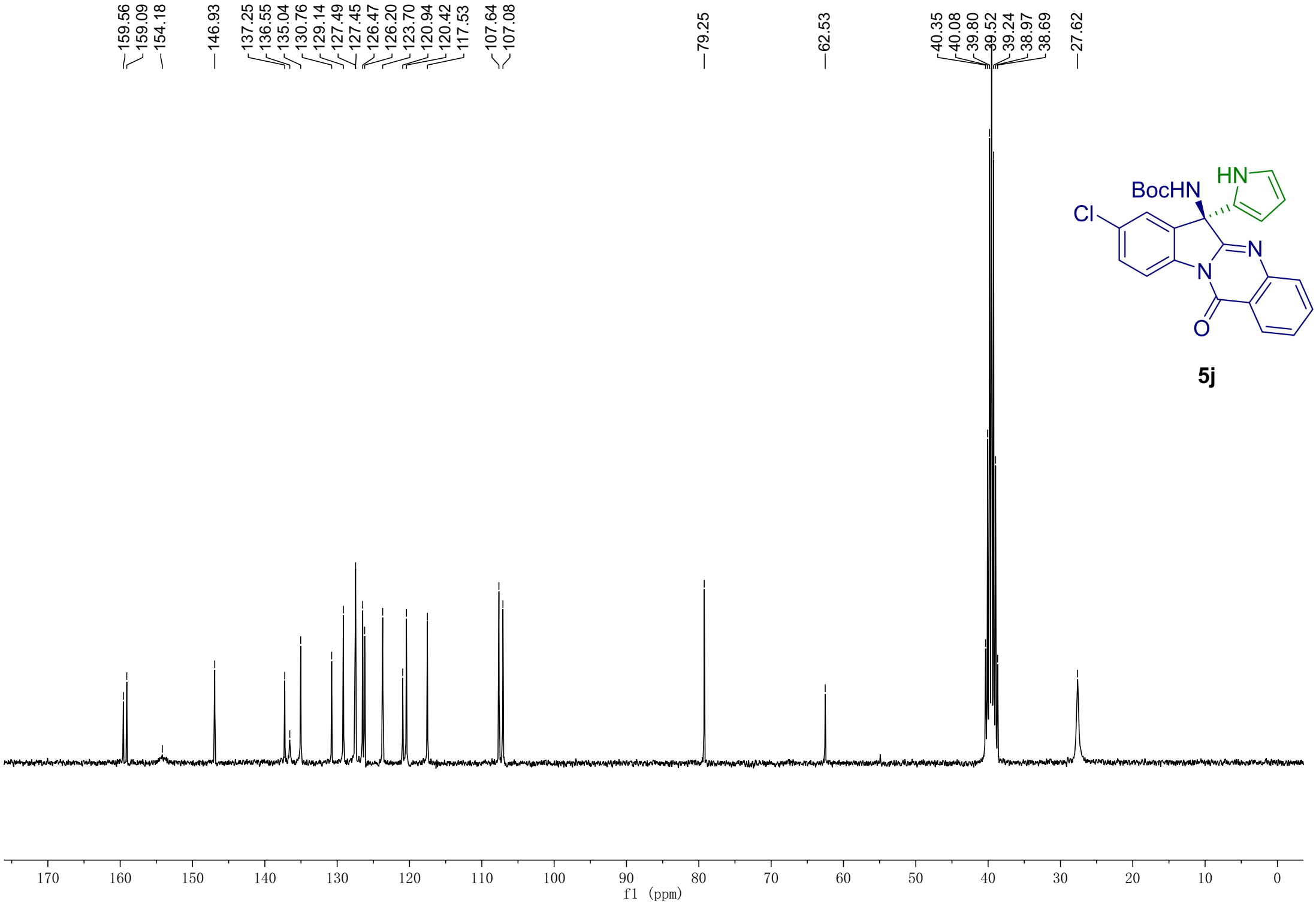
7.89
7.87
7.79
7.76
7.73
7.72
7.65
7.64
7.62
7.60
7.60
7.59
7.57
6.78
6.77
6.76
6.75
5.89
5.88
5.87
5.86
5.78
3.34
2.51
2.51
2.50
2.49
1.11
HN
BocHN
Cl
N
N
O
5j
1.00
3.05
1.08
1.02
0.97
2.00
1.02
1.02
0.96
9.23
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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136.55
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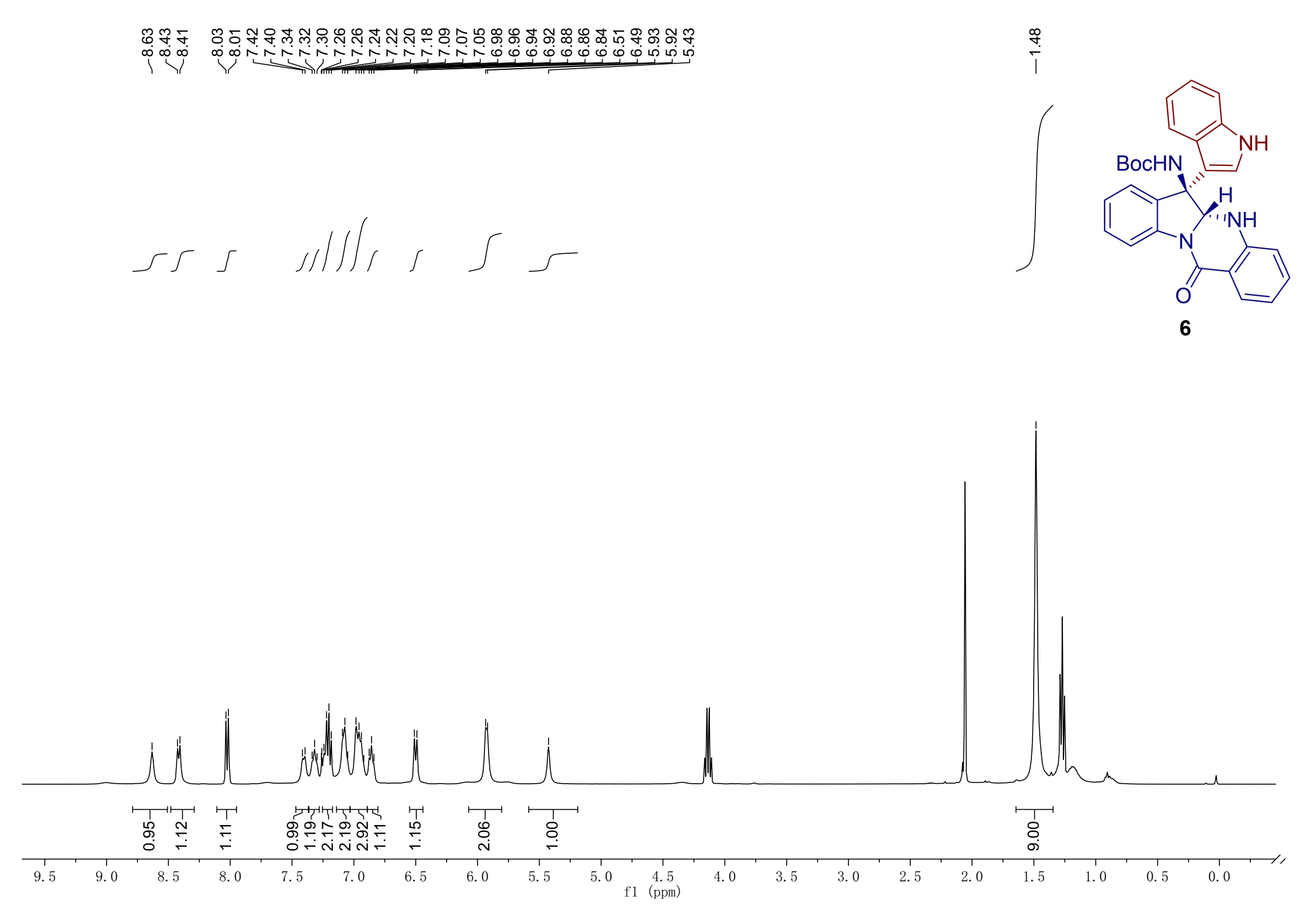
130.76
129.14
127.49
127.45
126.47
126.20
123.70
120.94
120.42
117.53
107.64
107.08
79.25
62.53
40.35
40.08
39.80
39.52
39.24
38.97
38.69
27.62
HN
BocHN
Cl
N
N
O
5j
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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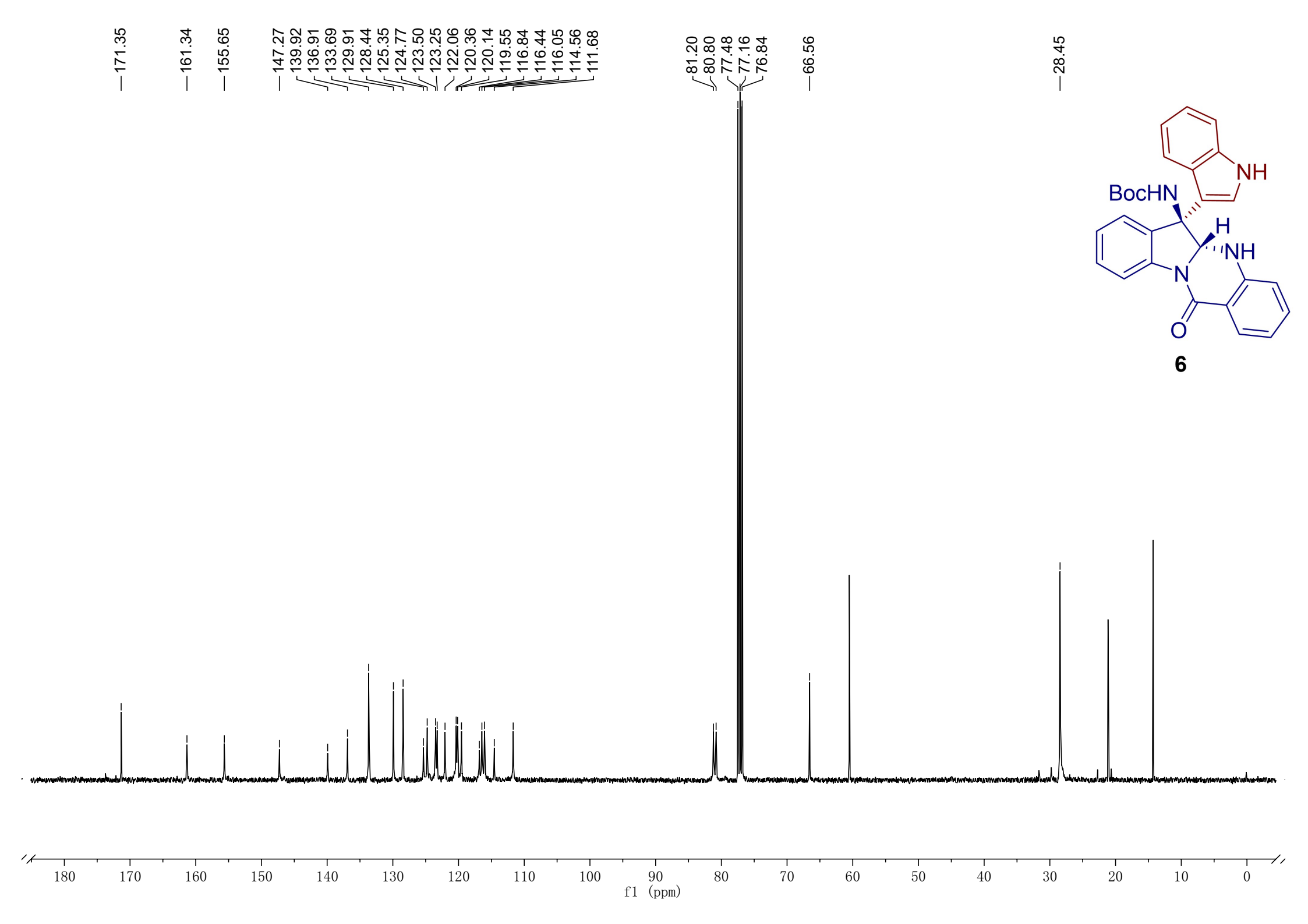
8.01
7.42
7.40
7.34
7.32
7.30
7.26
7.26
7.24
7.22
7.20
7.18
7.09
7.07
7.05
6.98
6.96
6.94
6.92
6.88
6.86
6.84
6.51
6.49
5.93
5.92
5.43
1.48
NH
BocHN
H
NH
N
O
6
0.95
1.12
1.11
0.99
1.19
2.17
2.19
2.92
1.11
1.15
2.06
1.00
9.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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161.34
155.65
147.27
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136.91
133.69
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128.44
125.35
124.77
123.50
123.25
122.06
120.36
120.14
119.55
116.84
116.44
116.05
114.56
111.68
81.20
80.80
77.48
77.16
76.84
66.56
28.45
NH
BocHN
H
NH
N
O
6
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)