

Supplementary Information

Synthesis of non-C₂ Symmetrical NOBIN-Type Biaryls Through a Cascade *N*-Arylation and [3,3]-Sigmatropic Rearrangement from *O*-Arylhydroxylamines and Diaryliodonium Salts

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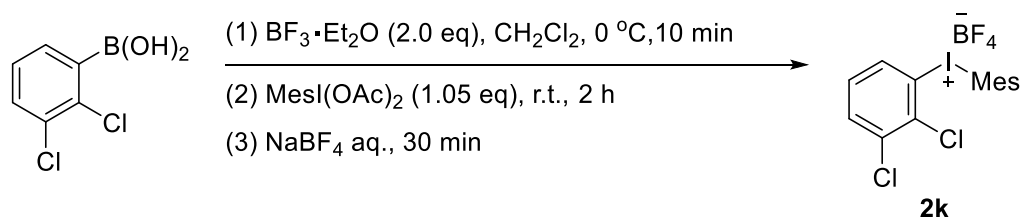
General remarks

All reactions were carried out under an atmosphere of nitrogen with magnetic stirring unless otherwise noted. Solvents were dried following standard procedures under argon. Syringe was used to transfer liquids and solutions. All reactions were monitored by thin-layer chromatography (TLC) with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Silica gel (particle size 200-300 mesh) purchased from SiliCycle was used for flash chromatography. For reactions that require heating, oil bath was used.

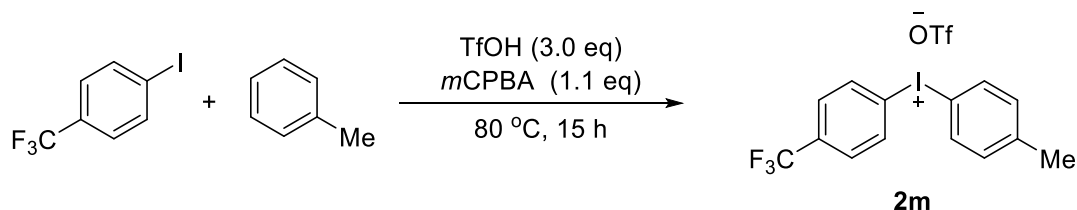
Proton (^1H) and carbon (^{13}C) NMR spectra were taken on a Bruker AV-500 spectrometer operating at 500 MHz or 400 MHz for proton and 126 MHz or 101 MHz for carbon nuclei using CDCl_3 or $\text{DMSO}-d_6$ as solvent, respectively. Chemical shifts are expressed as parts per million (δ , ppm) and are referenced to 7.26 (CDCl_3) for ^1H NMR and 77.00 (CDCl_3) for ^{13}C NMR. Proton signal data uses the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and J = coupling constant. High Resolution Mass Spectrometry was obtained with a Bruker Apex II mass instrument under the conditions of electrospray ionization (ESI) in both positive and negative mode.

Materials and Methods. Diaryliodonium substrates **2a-d**, **2h¹**; **2e**, **2i**, **2j²**; **2f**, **2l**, **2n³**; **2g⁴** and **2o⁵** were prepared according to literature procedures.

General procedure for the synthesis of Diaryliodonium Substrate

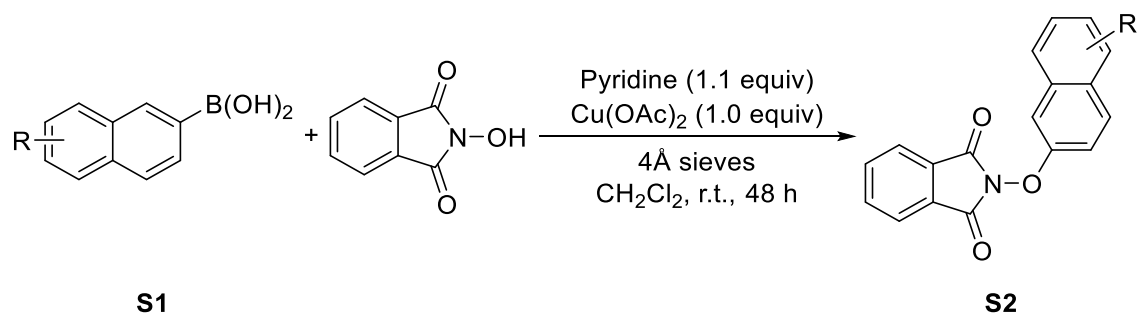


(2,3-dichlorophenyl)boronic acid (5 mmol, 1.0 equiv) and CH_2Cl_2 (50 mL) were combined in an oven-dried round-bottom flask equipped with a stir bar. The mixture was cooled to $0\text{ }^\circ\text{C}$, $\text{BF}_3 \cdot \text{OEt}_2$ (2.0 equiv) was added, and the mixture was stirred for 10 min. 2-(Diacetoxyiodo)mesitylene (5.25 mmol, 1.05 equiv) was then added as a solution in CH_2Cl_2 (15 mL), and the mixture was warmed to room temperature and stirred for 2 h. The reaction was quenched by the addition of saturated aqueous NaBF_4 . After 30 minutes of vigorous stirring, the aqueous layer was extracted with CH_2Cl_2 . The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated under vacuum. The crude residue was then recrystallized or stirred with Et_2O to obtain the desired compound.

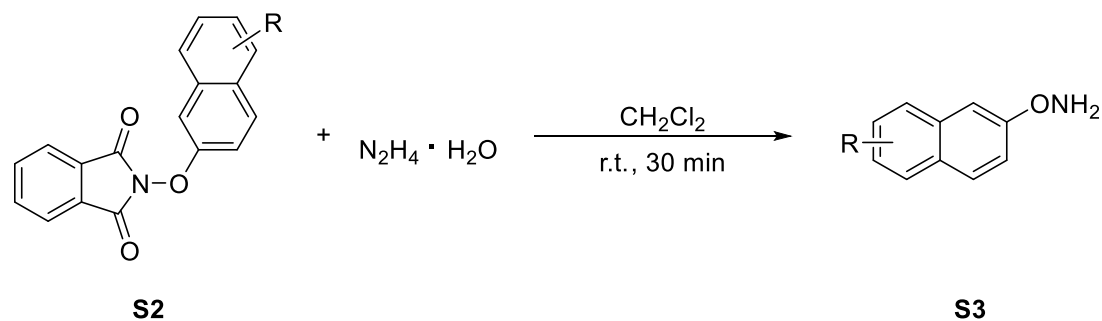


A suspension of (difluoro- λ^3 -methyl)(4-iodophenyl)- λ^2 -fluorane (5 mmol, 1.0 equiv) and *m*CPBA (1.1 equiv) in CH_2Cl_2 (25 mL) was stirred. Then, PhMe (1.1 equiv) was added, and TfOH (3.0 equiv) was added dropwise to the above mixture at room temperature. The reaction mixture was stirred in $80\text{ }^\circ\text{C}$ for 15 hours and subsequently concentrated under vacuum. Et_2O (20 mL) was added and the mixture was stirred at room temperature for 10 min to precipitate out a white solid.

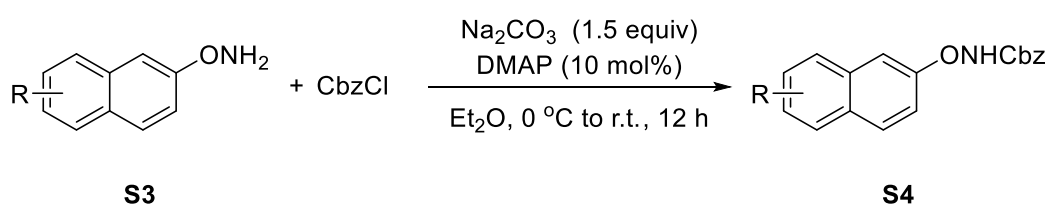
General procedure for the synthesis of protected *O*-Arylhydroxylamines^{7, 8}



A solution of naphthylboronic acid (1.0 equiv), *N*-hydroxyphthalimide (2.0 equiv), copper acetate (1.0 equiv) and freshly activated 4 Å molecular sieves (250 mg/mmol) in anhydrous CH₂Cl₂ (0.25 M). Then pyridine (1.1 equiv) was added to the suspension. The reaction mixture was stirred at room temperature under air atmosphere for 48 hours. The reaction mixture was filtered and concentrated. The residue was purified by column chromatography to give the desired product **S2**.



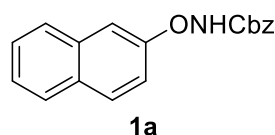
Hydrazine monohydrate (1.5 equiv) was added to the solution of *N*-aryloxyphthalimide (1.0 equiv) in CH₂Cl₂ (0.25 M). Then, the solution was stirred for 30 minutes at room temperature. The reaction mixture was filtered off and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography to obtain the product **S3**.



Under air atmosphere, a suspension of *N*-aryloxyamine (1.0 equiv), Na₂CO₃ (1.5 equiv) and DMAP (10 mol%) in Et₂O (15 mL) was stirred. Then, benzyl carbonochloridate (1.2 equiv) was added dropwise to the above mixture in 0 °C. The reaction mixture was stirred at room temperature for 12 hours. Upon completion, the solvent was removed in vacuo, the crude product was purified by flash chromatography to obtain **S4**.

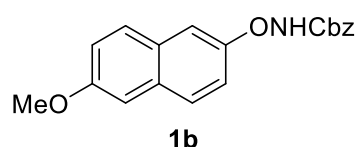
Analysis data of starting materials

1. benzyl (naphthalen-2-yloxy)carbamate (**1a**)



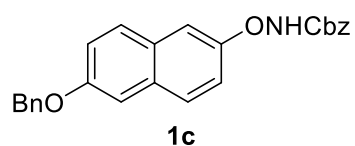
81% yield; Pink solid, m.p. = 156-158 °C; *R*_f = 0.3 (PE:EA = 5:1); ¹H NMR (500 MHz, CDCl₃) δ 7.76 (s, 1H), 7.73 – 7.69 (m, 2H), 7.67 – 7.64 (m, 1H), 7.42 – 7.36 (m, 2H), 7.33 – 7.26 (m, 6H), 7.18 (d, *J* = 2.8 Hz, 1H), 5.19 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 157.5, 157.3, 135.2, 134.1, 130.2, 129.6, 128.7, 128.6, 128.4, 127.7, 127.2, 126.6, 124.5, 115.4, 107.9, 68.2; HRMS (ESI) *m/z* calcd for [C₁₈H₁₆NO₃]⁺ [M+H]⁺: 294.1125, found 294.1130.

2. benzyl ((6-methoxynaphthalen-2-yl)oxy)carbamate (**1b**)



63% yield; White solid, m.p. = 151-153 °C; *R*_f = 0.3 (PE:EA = 5:1); ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.33 (s, 1H), 7.84 – 7.74 (m, 2H), 7.42 (dq, *J* = 17.5, 8.0, 6.0 Hz, 6H), 7.31 (t, *J* = 3.4 Hz, 1H), 7.25 (dd, *J* = 8.7, 2.9 Hz, 1H), 7.17 (dd, *J* = 8.6, 2.9 Hz, 1H), 5.22 (d, *J* = 4.6 Hz, 2H), 3.86 (d, *J* = 4.7 Hz, 3H); ¹³C NMR (101 MHz, DMSO- *d*₆) δ 157.3, 156.6, 156.5, 136.6, 131.0, 129.4, 128.93, 128.88, 128.8, 128.6, 128.4, 119.7, 116.2, 107.9, 106.6, 67.0, 55.6; HRMS (ESI) *m/z* calcd for [C₁₉H₁₈NO₄]⁺ [M+H]⁺: 324.1230, found 324.1234.

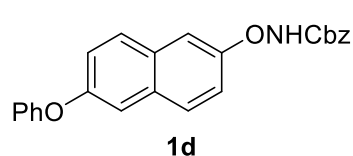
3. benzyl ((6-(benzyloxy)naphthalen-2-yl)oxy)carbamate (**1c**)



45% yield; Red solid, m.p. = 139-141 °C; *R*_f = 0.3 (PE:EA = 5:1); ¹H NMR (500 MHz, DMSO-*d*₆) δ 11.30

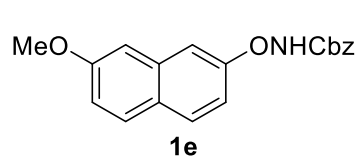
(s, 1H), 8.03 – 7.87 (m, 1H), 7.78 (d, $J = 9.0$ Hz, 1H), 7.69 – 7.58 (m, 1H), 7.53 – 7.32 (m, 11H), 7.27 – 7.17 (m, 2H), 5.19 (d, $J = 7.1$ Hz, 4H); ^{13}C NMR (126 MHz, DMSO- d_6) δ 157.3, 156.6, 155.7, 137.5, 136.6, 130.9, 129.5, 128.92, 128.89, 128.8, 128.6, 128.4, 128.31, 128.26, 128.2, 119.9, 116.3, 108.0, 107.9, 69.8, 67.0; HRMS (ESI) m/z calcd for $[\text{C}_{25}\text{H}_{22}\text{NO}_4]^+$ $[\text{M}+\text{H}]^+$: 400.1543, found 400.1535.

4. benzyl ((6-phenoxy)naphthalen-2-yl)oxy)carbamate (1d)



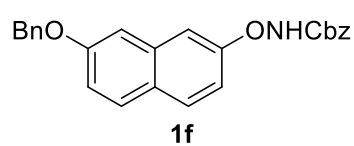
56% yield; White solid, m.p. = 143-145 °C; $R_f = 0.3$ (PE:EA = 5:1); ^1H NMR (500 MHz, DMSO- d_6) δ 11.34 (s, 1H), 7.90 (d, $J = 8.9$ Hz, 1H), 7.81 (d, $J = 9.0$ Hz, 1H), 7.50 (d, $J = 2.6$ Hz, 1H), 7.43 – 7.36 (m, 8H), 7.27 (ddd, $J = 9.1, 4.1, 2.5$ Hz, 2H), 7.18 – 7.13 (m, 1H), 7.07 – 7.04 (m, 2H), 5.20 (s, 2H); ^{13}C NMR (126 MHz, DMSO- d_6) δ 157.44, 157.37, 157.2, 153.6, 136.6, 130.9, 130.7, 130.5, 129.7, 129.3, 128.9, 128.6, 128.4, 123.9, 121.1, 119.0, 116.6, 114.7, 107.8, 67.0; HRMS (ESI) m/z calcd for $[\text{C}_{24}\text{H}_{20}\text{NO}_4]^+$ $[\text{M}+\text{H}]^+$: 386.1387, found 386.1392.

5. benzyl ((7-methoxynaphthalen-2-yl)oxy)carbamate (1e)



76% yield; Brown solid, m.p. = 118-120 °C; $R_f = 0.3$ (PE:EA = 5:1); ^1H NMR (400 MHz, CDCl_3) δ 7.81 (s, 1H), 7.71 (dd, $J = 9.2, 7.9$ Hz, 2H), 7.43 – 7.36 (m, 6H), 7.14 (dd, $J = 9.0, 2.5$ Hz, 1H), 7.08 – 7.05 (m, 2H), 5.29 (s, 2H), 3.93 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 163.4, 163.2, 162.0, 141.4, 140.5, 134.5, 134.3, 133.7, 133.4, 133.2, 130.0, 121.9, 117.9, 111.6, 110.8, 71.8, 60.4; HRMS (ESI) m/z calcd for $[\text{C}_{19}\text{H}_{18}\text{NO}_4]^+$ $[\text{M}+\text{H}]^+$: 324.1230, found 324.1237.

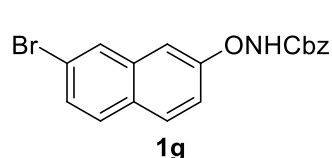
6. benzyl ((7-(benzyloxy)naphthalen-2-yl)oxy)carbamate (1f)



57% yield; Pink solid, m.p. = 154-156 °C; $R_f = 0.3$ (PE:EA = 5:1); ^1H NMR (400 MHz, DMSO- d_6) δ 11.34 (s, 1H), 7.80 (dd, $J = 9.0, 4.9$ Hz, 2H), 7.54 – 7.49 (m, 2H), 7.45 – 7.36 (m, 10H), 7.11 (ddd, $J = 9.0, 6.6, 2.5$ Hz, 2H), 5.21 (d, $J = 3.8$ Hz, 4H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 158.7, 157.5, 157.2, 137.4, 136.6, 135.7,

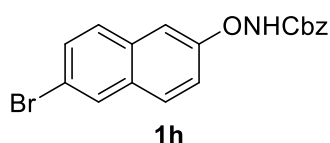
129.8, 129.7, 128.94, 128.92, 128.6, 128.4, 128.34, 128.26, 125.3, 117.4, 113.3, 107.4, 106.8, 69.7, 67.0; HRMS (ESI) m/z calcd for $[C_{25}H_{22}NO_4]^+ [M+H]^+$: 400.1543, found 400.1548.

7. benzyl ((7-bromonaphthalen-2-yl)oxy)carbamate (1g)



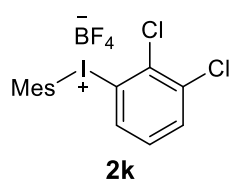
59% yield; Pink solid, m.p. = 175-177 °C; R_f = 0.3 (PE:EA = 5:1); 1H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 1.9 Hz, 1H), 7.80 – 7.75 (m, 2H), 7.67 (d, J = 8.7 Hz, 1H), 7.47 (dd, J = 8.7, 2.0 Hz, 1H), 7.39 (s, 4H), 7.30 – 7.27 (m, 3H), 5.29 (s, 2H); ^{13}C NMR (126 MHz, $DMSO-d_6$) δ 158.8, 157.2, 136.5, 135.6, 130.3, 130.2, 129.2, 128.9, 128.7, 128.5, 128.4, 127.7, 120.6, 116.5, 106.9, 67.1; HRMS (ESI) m/z calcd for $[C_{18}H_{15}BrNO_3]^+ [M+H]^+$: 372.0230, found 372.0234.

8. benzyl ((6-bromonaphthalen-2-yl)oxy)carbamate (1h)



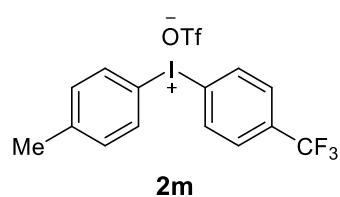
65% yield; Pink solid, m.p. = 158-160 °C; R_f = 0.3 (PE:EA = 5:1); 1H NMR (500 MHz, $DMSO-d_6$) δ 11.37 (s, 1H), 8.15 (d, J = 2.0 Hz, 1H), 7.88 (d, J = 9.0 Hz, 1H), 7.82 (d, J = 8.7 Hz, 1H), 7.58 (dd, J = 8.8, 2.1 Hz, 1H), 7.50 (d, J = 2.5 Hz, 1H), 7.39 – 7.30 (m, 6H), 5.18 (s, 2H); ^{13}C NMR (126 MHz, $DMSO-d_6$) δ 158.4, 157.2, 136.5, 132.8, 131.0, 130.0, 129.9, 129.7, 129.4, 128.9, 128.7, 128.4, 117.6, 117.1, 107.6, 67.1; HRMS (ESI) m/z calcd for $[C_{18}H_{15}BrNO_3]^+ [M+H]^+$: 372.0230, found 372.0214.

9. ((2,3-dichlorophenyl)(mesityl)- λ^3 -iodanyl)tetrafluoro- λ^5 -borane (2k)



82% yield; White solid, m.p. = 168-170 °C; R_f = 0.5 (DCM/MeOH = 10/1); 1H NMR (500 MHz, $DMSO-d_6$) δ 8.18 (dd, J = 8.1, 1.3 Hz, 1H), 7.93 (dd, J = 8.1, 1.3 Hz, 1H), 7.47 (t, J = 8.1 Hz, 1H), 7.22 (s, 2H), 2.61 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, $DMSO-d_6$) δ 143.8, 142.4, 137.9, 135.0, 134.3, 133.0, 131.8, 130.5, 123.7, 118.5, 26.7, 20.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -148.3; HRMS (ESI) m/z calcd for $[C_{15}H_{14}Cl_2I]^+ [M-BF_4]^-$: 390.9512, found 390.9519.

10. *p*-tolyl(4-(trifluoromethyl)phenyl)iodonium trifluoromethanesulfonate (2m)



26% yield; White solid, m.p. = 149-151 °C; R_f = 0.5

(DCM/MeOH = 10/1); ^1H NMR (500 MHz, DMSO- d_6) δ

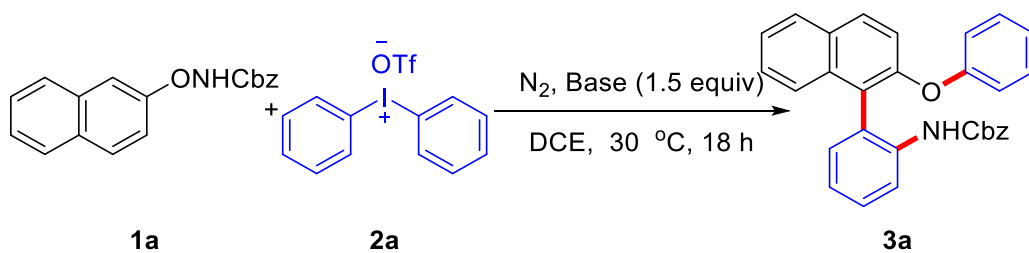
8.42 (d, J = 8.3 Hz, 2H), 8.18 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 2.35 (s, 3H);

^{13}C NMR (126 MHz, DMSO- d_6) δ 143.4, 136.2, 135.9, 133.0, 128.81, 128.78, 128.75,

128.7, 121.3, 113.5, 21.3; ^{19}F NMR (471 MHz, CDCl_3) δ -61.7, -77.8; HRMS (ESI)

m/z calcd for $[\text{C}_{14}\text{H}_{11}\text{F}_3\text{I}]^+ [\text{M}-\text{OTf}]^+$: 362.9852, found 362.9849.

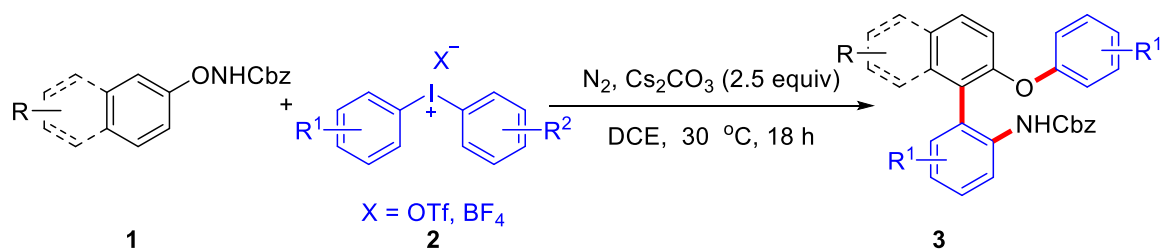
Optimization of reaction conditions^{a, b}

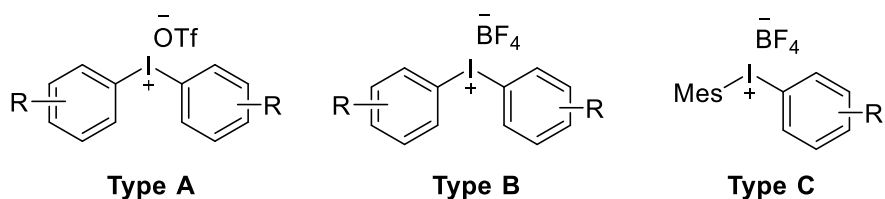


Entry	Base	Yield (%)
1	$t\text{BuOK}$	0
2	Et_3N	51
3	$t\text{BuONa}$	55
4	DBU	57
5	DABCO	0
6	pyridine	0
7	K_3PO_4	64
8	KOH	40
9	K_2CO_3	73
10	Cs_2CO_3	74
11	NaOH	13
12	Na_2CO_3	0
13	NaH	38

^aReaction conditions: **1a** (0.2 mmol), **2a** (2.0 equiv), Base (1.5 equiv), solvent (2 mL) at 30 °C for 18 h. ^bYields of the isolated products. Cbz = benzyloxycarbonyl; DCE = 1,2-dichloroethane; Tf = trifluoromethanesulfonyl.

General procedure for the synthesis of biaryls 3

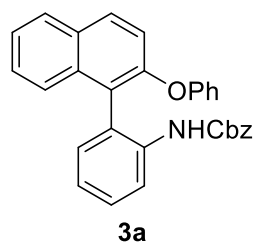




A solution of Cs_2CO_3 (0.75 mmol, 2.5 equiv), **1** (0.3 mmol, 1.0 equiv) and **2** (0.66 mmol, 2.2 equiv) in anhydrous DCE (3 mL) under N_2 atmosphere was stirred at 30 °C until the complete consumption of **1** detected by TLC analysis. Reagents **2** of **Type A** were used unless otherwise noted (**Type B**: **3e**, **3i**, **3j**; **Type C**: **3f**, **3g**, **3k**, **3l**). The reaction mixture was filtered and concentrated. The residue was purified by column chromatography to give the desired product **3**.

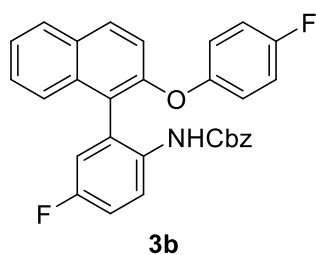
Analysis data of biaryl products 3

1. benzyl (2-(2-phenoxy-naphthalen-1-yl)phenyl)carbamate (**3a**)



88% yield; Viscous oily liquid; $R_f = 0.3$ (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (500 MHz, CDCl_3) δ 8.08 (s, 1H), 7.85 – 7.75 (m, 2H), 7.39 – 7.30 (m, 4H), 7.21 (td, $J = 5.1, 2.5$ Hz, 3H), 7.16 (dd, $J = 8.3, 3.1$ Hz, 3H), 7.13 – 7.06 (m, 3H), 7.03 (td, $J = 7.4, 1.2$ Hz, 1H), 6.94 – 6.88 (m, 1H), 6.77 – 6.71 (m, 2H), 6.36 (s, 1H), 5.02 – 4.91 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 157.5, 153.4, 151.7, 136.4, 136.1, 133.6, 131.4, 130.9, 130.5, 129.6, 129.1, 128.9, 128.7, 128.5, 128.3, 128.24, 128.23, 127.2, 125.4, 125.3, 123.9, 123.4, 123.0, 119.9, 118.2, 66.8; HRMS (ESI) m/z calcd for $[\text{C}_{30}\text{H}_{24}\text{NO}_3]^+ [\text{M}+\text{H}]^+$: 446.1751, found 446.1753.

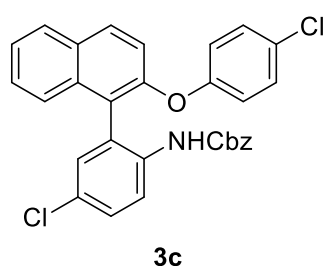
2. benzyl (4-fluoro-2-(2-(4-fluorophenoxy)naphthalen-1-yl)phenyl)carbamate (**3b**)



52% yield; Viscous oily liquid; $R_f = 0.3$ (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (500 MHz, CDCl_3) δ 8.02 (s, 1H), 7.88 – 7.76 (m, 2H), 7.40 (ddd, $J = 8.1, 5.3, 2.9$ Hz, 1H), 7.36 – 7.29 (m, 2H), 7.23 (dd, $J = 5.2, 1.9$ Hz, 3H), 7.18 – 7.14 (m, 2H), 7.11 (d, $J = 9.0$ Hz, 1H), 7.07 – 6.99 (m, 1H), 6.87 –

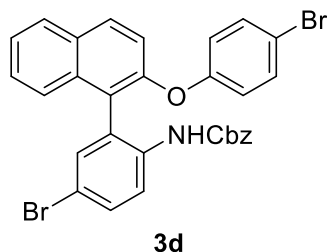
6.77 (m, 3H), 6.73 – 6.66 (m, 2H), 6.23 (s, 1H), 5.02 – 4.89 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 159.6, 153.1, 153.0, 151.9, 135.9, 133.2, 131.0, 130.7, 128.7, 128.6, 128.33, 128.27, 127.7, 127.6, 125.5, 124.9, 119.6, 119.5, 119.2, 118.0, 117.8, 116.3, 116.1, 115.7, 115.5, 67.0; ^{19}F NMR (471 MHz, CDCl_3) δ -120.1; HRMS (ESI) m/z calcd for $[\text{C}_{30}\text{H}_{22}\text{F}_2\text{NO}_3]^+ [\text{M}+\text{H}]^+$: 482.1562, found 482.1563.

3. benzyl (4-chloro-2-(2-(4-chlorophenoxy)naphthalen-1-yl)phenyl)carbamate (3c)



68% yield; Viscous oily liquid; R_f = 0.3 (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (500 MHz, CDCl_3) δ 8.05 (s, 1H), 7.84 – 7.78 (m, 2H), 7.41 – 7.32 (m, 3H), 7.28 (dd, J = 8.9, 2.5 Hz, 1H), 7.22 (dq, J = 4.7, 2.9, 2.2 Hz, 3H), 7.17 – 7.14 (m, 2H), 7.12 (d, J = 9.0 Hz, 1H), 7.07 – 7.03 (m, 3H), 6.67 – 6.63 (m, 2H), 6.25 (s, 1H), 5.00 – 4.89 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 155.9, 153.2, 151.5, 135.8, 135.2, 133.2, 131.2, 131.00, 130.95, 129.7, 129.6, 129.0, 128.7, 128.6, 128.44, 128.41, 128.38, 128.35, 128.3, 127.7, 125.7, 125.0, 122.5, 119.5, 119.4, 67.1; HRMS (ESI) m/z calcd for $[\text{C}_{30}\text{H}_{22}\text{Cl}_2\text{NO}_3]^+ [\text{M}+\text{H}]^+$: 514.0971, found 514.0972.

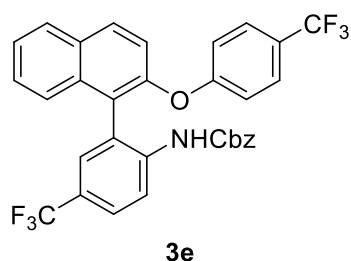
4. benzyl (4-bromo-2-(2-(4-bromophenoxy)naphthalen-1-yl)phenyl)carbamate (3d)



71% yield; Viscous oily liquid; R_f = 0.3 (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (500 MHz, CDCl_3) δ 8.00 (s, 1H), 7.87 – 7.74 (m, 2H), 7.45 – 7.31 (m, 4H), 7.26 – 7.11 (m, 9H), 6.65 – 6.54 (m, 2H), 6.24 (s, 1H), 5.02 – 4.89 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 156.4, 151.4, 135.74, 135.69, 133.8, 133.2, 132.60, 132.55, 131.9, 131.6, 131.2, 130.9, 128.6, 128.44, 128.42, 128.38, 128.3, 127.8, 127.7, 125.7, 125.0, 122.4, 119.8, 119.5, 115.7, 67.1; HRMS (ESI) m/z calcd for $[\text{C}_{30}\text{H}_{22}\text{Br}_2\text{NO}_3]^+ [\text{M}+\text{H}]^+$: 603.9940, found

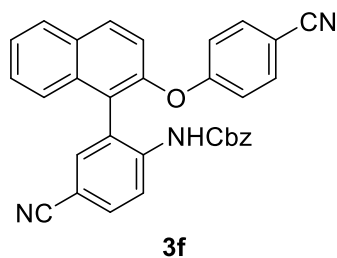
603.9953.

5. benzyl (4-(trifluoromethyl)-2-(2-(4-(trifluoromethyl)phenoxy)naphthalen-1-yl)phenyl)carbamate (3e)



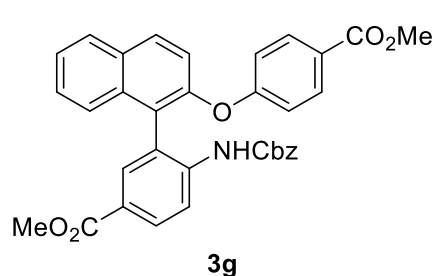
78% yield; Viscous oily liquid; $R_f = 0.3$ (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (500 MHz, CDCl_3) δ 8.26 (d, $J = 8.7$ Hz, 1H), 7.90 (d, $J = 8.9$ Hz, 1H), 7.84 (dd, $J = 8.2, 1.3$ Hz, 1H), 7.54 (dd, $J = 8.9, 2.1$ Hz, 1H), 7.43 (ddd, $J = 8.0, 6.8, 1.3$ Hz, 1H), 7.37 (ddd, $J = 8.3, 6.8, 1.4$ Hz, 1H), 7.33 – 7.26 (m, 4H), 7.25 – 7.19 (m, 4H), 7.17 (dd, $J = 7.1, 2.5$ Hz, 2H), 6.73 (d, $J = 8.5$ Hz, 2H), 6.40 (s, 1H), 5.02 – 4.91 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 160.0, 152.9, 150.9, 139.6, 135.5, 133.2, 131.7, 131.4, 128.7, 128.6, 128.47, 128.45, 128.4, 128.0, 127.09, 127.06, 127.03, 127.00, 126.28, 126.25, 126.1, 125.3, 125.0, 124.9, 123.1, 120.2, 117.4, 67.3; ^{19}F NMR (471 MHz, CDCl_3) δ -61.8, -62.0; HRMS (ESI) m/z calcd for $[\text{C}_{32}\text{H}_{22}\text{F}_6\text{NO}_3]^+ [\text{M}+\text{H}]^+$: 582.1498, found 582.1496.

6. benzyl (4-cyano-2-(2-(4-cyanophenoxy)naphthalen-1-yl)phenyl)carbamate (3f)



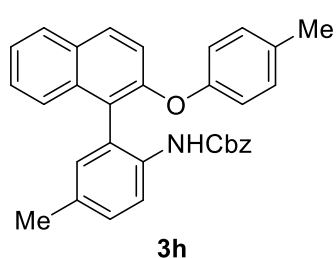
88% yield; Viscous oily liquid; $R_f = 0.3$ (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (500 MHz, CDCl_3) δ 8.44 (d, $J = 8.7$ Hz, 1H), 8.08 (d, $J = 8.9$ Hz, 1H), 8.00 (d, $J = 8.2$ Hz, 1H), 7.71 (d, $J = 8.7$ Hz, 1H), 7.60 (t, $J = 7.4$ Hz, 1H), 7.54 (t, $J = 7.4$ Hz, 1H), 7.45 (d, $J = 8.6$ Hz, 3H), 7.38 (dd, $J = 8.1, 5.0$ Hz, 4H), 7.35 – 7.28 (m, 3H), 6.87 (d, $J = 8.3$ Hz, 2H), 6.59 (s, 1H), 5.18 – 5.03 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 160.6, 152.6, 150.1, 140.7, 135.3, 135.0, 134.2, 133.3, 132.9, 132.2, 131.5, 128.8, 128.7, 128.6, 128.5, 128.3, 126.5, 124.7, 124.5, 122.4, 120.1, 119.6, 118.6, 118.5, 117.7, 106.54, 106.46, 67.6; HRMS (ESI) m/z calcd for $[\text{C}_{32}\text{H}_{22}\text{N}_3\text{O}_3]^+ [\text{M}+\text{H}]^+$: 496.1656, found 496.1658.

7. methyl 4-(((benzyloxy)carbonyl)amino)-3-(2-(4-(methoxycarbonyl)phenoxy)-naphthalen-1-yl)benzoate (3g)



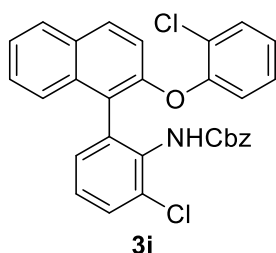
79% yield; Viscous oily liquid; R_f = 0.3 (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (500 MHz, CDCl_3) δ 8.36 (d, J = 8.8 Hz, 1H), 8.11 (dd, J = 8.7, 2.1 Hz, 1H), 8.01 (d, J = 8.9 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.93 – 7.88 (m, 3H), 7.55 (ddd, J = 8.1, 6.7, 1.4 Hz, 1H), 7.48 (ddd, J = 8.1, 6.7, 1.4 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.37 – 7.30 (m, 6H), 6.85 (d, J = 8.9 Hz, 2H), 6.61 (s, 1H), 5.13 – 5.06 (m, 2H), 3.90 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.44, 166.42, 161.3, 152.9, 150.7, 140.7, 135.5, 133.4, 132.9, 131.6, 131.4, 130.8, 128.6, 128.54, 128.50, 128.47, 128.4, 128.3, 127.77, 127.75, 126.0, 125.1, 124.68, 124.65, 123.6, 120.3, 117.0, 67.3, 52.02, 51.98; HRMS (ESI) m/z calcd for $[\text{C}_{34}\text{H}_{28}\text{NO}_7]^+$ $[\text{M}+\text{H}]^+$: 562.1860, found 562.1857.

8. benzyl (4-methyl-2-(2-(p-tolyloxy)naphthalen-1-yl)phenyl)carbamate (3h)



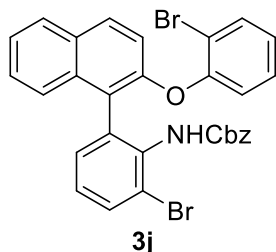
66% yield; Viscous oily liquid; R_f = 0.3 (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (500 MHz, CDCl_3) δ 7.94 (s, 1H), 7.78 – 7.73 (m, 2H), 7.38 – 7.27 (m, 4H), 7.19 (td, J = 7.0, 3.9 Hz, 3H), 7.17 – 7.13 (m, 2H), 7.12 – 7.10 (m, 1H), 6.93 – 6.89 (m, 3H), 6.68 – 6.65 (m, 2H), 6.30 (s, 1H), 4.99 – 4.90 (m, 2H), 2.21 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 155.1, 152.1, 136.2, 133.9, 133.7, 132.6, 131.9, 130.6, 130.3, 130.1, 129.4, 128.6, 128.5, 128.4, 128.21, 128.17, 128.16, 128.0, 127.1, 125.4, 125.1, 124.6, 119.4, 118.5, 115.3, 66.7, 20.8, 20.7; HRMS (ESI) m/z calcd for $[\text{C}_{32}\text{H}_{28}\text{NO}_3]^+$ $[\text{M}+\text{H}]^+$: 474.2064, found 474.2062.

9. benzyl (2-chloro-6-(2-(2-chlorophenoxy)naphthalen-1-yl)phenyl)carbamate (3i)



41% yield; Viscous oily liquid; $R_f = 0.3$ (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (400 MHz, CDCl_3) δ 7.77 (dd, $J = 8.8, 3.3$ Hz, 2H), 7.51 – 7.43 (m, 1H), 7.41 – 7.32 (m, 2H), 7.28 (d, $J = 6.6$ Hz, 1H), 7.23 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.17 – 7.08 (m, 5H), 7.04 – 6.95 (m, 2H), 6.88 (ddd, $J = 15.3, 7.6, 1.7$ Hz, 3H), 6.69 (dd, $J = 8.1, 1.5$ Hz, 1H), 6.50 (s, 1H), 4.85 – 4.66 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 154.0, 152.4, 150.2, 136.3, 135.7, 134.1, 133.7, 133.3, 130.8, 130.6, 130.4, 130.3, 129.8, 128.3, 128.1, 127.82, 127.75, 127.5, 127.2, 125.6, 125.2, 124.9, 124.3, 119.4, 118.1, 66.7; HRMS (ESI) m/z calcd for $[\text{C}_{30}\text{H}_{22}\text{Cl}_2\text{NO}_3]^+ [\text{M}+\text{H}]^+$: 514.0971, found 514.0973.

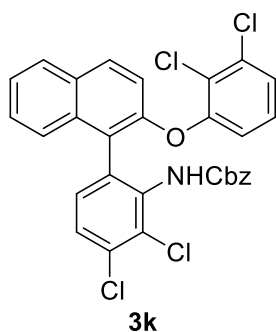
10. benzyl (2-bromo-6-(2-(2-bromophenoxy)naphthalen-1-yl)phenyl)carbamate (3j)



57% yield; Viscous oily liquid; $R_f = 0.3$ (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (400 MHz, CDCl_3) δ 7.77 (dd, $J = 9.0, 2.2$ Hz, 2H), 7.57 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.53 – 7.44 (m, 1H), 7.37 (ddd, $J = 17.3, 8.0, 1.4$ Hz, 2H), 7.32 – 7.23 (m, 1H), 7.16 – 7.04 (m, 6H), 7.04 – 7.00 (m, 1H), 6.90 – 6.85 (m, 2H), 6.79 (td, $J = 7.7, 1.5$ Hz, 1H), 6.63 (dd, $J = 8.2, 1.5$ Hz, 2H), 4.79 (d, $J = 12.1$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 153.9, 153.7, 149.9, 136.4, 136.1, 135.2, 133.6, 133.3, 132.9, 131.2, 130.9, 130.3, 128.5, 128.4, 128.24, 128.16, 128.0, 127.7, 127.4, 127.1, 125.7, 125.3, 124.9, 124.5, 118.7, 118.5, 113.7, 66.7; HRMS (ESI) m/z calcd for $[\text{C}_{30}\text{H}_{22}\text{Br}_2\text{NO}_3]^+ [\text{M}+\text{H}]^+$: 603.9940, found 603.9923.

11. benzyl (2,3-dichloro-6-(2-(2,3-dichlorophenoxy)naphthalen-1-yl)phenyl)-carbamate (3k)

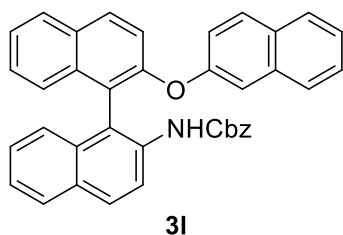
34% yield; Viscous oily liquid; $R_f = 0.3$ (PE:EA = 15:1); Purified directly by flash



chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (500 MHz, CDCl_3) δ 7.81 (d, $J = 8.7$ Hz, 2H), 7.45 (s, 1H), 7.42 – 7.37 (m, 2H), 7.33 (s, 1H), 7.19 (s, 1H), 7.15 – 7.12 (m, 2H), 7.09 (dd, $J = 8.2, 1.3$ Hz, 2H), 7.02 (d, $J = 9.0$ Hz, 1H), 6.96 (d, $J = 8.2$ Hz, 1H), 6.94 – 6.89 (m, 2H), 6.61 (dd, $J = 8.3, 1.4$ Hz, 1H), 6.46 (s, 1H), 4.87 – 4.68 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.8, 153.6, 149.9,

136.1, 135.3, 134.3, 133.8, 133.4, 133.0, 132.9, 130.9, 130.7, 130.2, 129.0, 128.6, 128.3, 128.2, 127.9, 127.5, 127.4, 125.5, 125.4, 125.1, 124.0, 123.9, 118.0, 117.1, 66.9; HRMS (ESI) m/z calcd for $[\text{C}_{30}\text{H}_{20}\text{Cl}_4\text{NO}_3]^+ [\text{M}+\text{H}]^+$: 584.0162, found 584.0166.

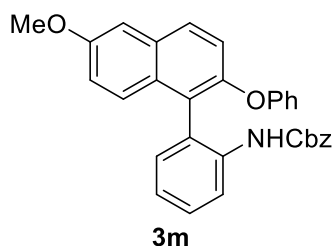
12. benzyl (2'-(naphthalen-2-yloxy)-[1,1'-binaphthalen]-2-yl)carbamate (3l)



44% yield; Viscous oily liquid; $R_f = 0.3$ (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (500 MHz, CDCl_3) δ 8.27 (s, 1H), 7.90 (d, $J = 8.9$ Hz, 1H), 7.84 (dd, $J = 14.4, 8.6$ Hz, 2H), 7.73 (d, $J = 8.1$ Hz, 1H),

7.61 (d, $J = 7.8$ Hz, 1H), 7.50 (d, $J = 8.9$ Hz, 1H), 7.43 (d, $J = 7.9$ Hz, 1H), 7.37 (ddd, $J = 8.0, 6.6, 1.1$ Hz, 1H), 7.31 – 7.26 (m, 2H), 7.24 – 7.18 (m, 6H), 7.17 – 7.13 (m, 3H), 7.10 – 7.05 (m, 3H), 6.87 (dd, $J = 8.9, 2.5$ Hz, 1H), 6.47 (s, 1H), 4.91 (s, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 154.8, 153.5, 153.0, 136.0, 134.4, 134.1, 133.9, 133.0, 130.92, 130.88, 130.6, 130.1, 129.7, 129.1, 128.6, 128.43, 128.36, 128.3, 128.1, 127.7, 127.5, 127.0, 126.4, 125.54, 125.45, 124.64, 124.60, 121.2, 119.8, 119.7, 114.0, 66.9; HRMS (ESI) m/z calcd for $[\text{C}_{38}\text{H}_{28}\text{NO}_3]^+ [\text{M}+\text{H}]^+$: 546.2064, found 546.2038.

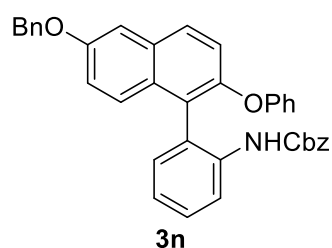
13. benzyl (2-(6-methoxy-2-phenoxy-naphthalen-1-yl)phenyl)carbamate (3m)



45% yield; Viscous oily liquid; $R_f = 0.3$ (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (500 MHz, CDCl_3) δ 8.05 (s, 1H), 7.69 (d, $J = 9.0$ Hz, 1H), 7.24 –

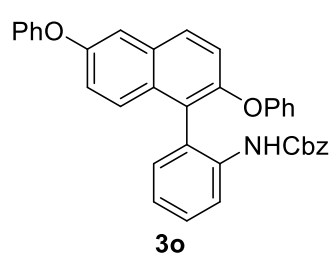
7.19 (m, 3H), 7.18 – 7.04 (m, 9H), 6.98 (ddd, $J = 9.1, 4.9, 2.0$ Hz, 2H), 6.87 (td, $J = 7.4, 1.3$ Hz, 1H), 6.73 – 6.69 (m, 2H), 6.36 (s, 1H), 4.95 (q, $J = 12.3$ Hz, 2H), 3.81 (d, $J = 3.9$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 157.9, 157.4, 149.9, 136.4, 136.1, 132.2, 131.3, 129.5, 129.2, 128.8, 128.7, 128.5, 128.3, 128.2, 127.7, 127.0, 124.4, 123.3, 122.7, 120.8, 120.6, 119.8, 118.2, 117.8, 106.5, 66.8, 55.4; HRMS (ESI) m/z calcd for $[\text{C}_{31}\text{H}_{26}\text{NO}_4]^+ [\text{M}+\text{H}]^+$: 476.1856, found 476.1857.

14. benzyl (2-(6-(benzyloxy)-2-phenoxy-naphthalen-1-yl)phenyl)carbamate (3n)



30% yield; Viscous oily liquid; $R_f = 0.3$ (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.39 (s, 1H), 7.88 (d, $J = 9.0$ Hz, 1H), 7.72 (d, $J = 8.2$ Hz, 1H), 7.55 – 7.50 (m, 3H), 7.40 (dt, $J = 12.6, 8.0$ Hz, 4H), 7.32 – 7.28 (m, 3H), 7.26 – 7.14 (m, 9H), 7.01 (t, $J = 7.3$ Hz, 1H), 6.95 – 6.86 (m, 2H), 5.24 (d, $J = 3.2$ Hz, 2H), 5.05 – 4.87 (m, 2H); ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 158.0, 156.0, 154.4, 149.8, 137.4, 137.3, 137.2, 132.0, 130.1, 129.2, 129.1, 128.9, 128.8, 128.73, 128.70, 128.6, 128.34, 128.26, 128.2, 127.9, 127.8, 127.2, 125.4, 124.5, 123.0, 120.7, 119.9, 118.3, 108.4, 69.8, 65.8; HRMS (ESI) m/z calcd for $[\text{C}_{37}\text{H}_{30}\text{NO}_4]^+ [\text{M}+\text{H}]^+$: 552.2169, found 552.2175.

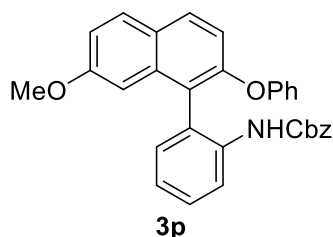
15. benzyl (2-(2,6-diphenoxynaphthalen-1-yl)phenyl)carbamate (3o)



69% yield; Viscous oily liquid; $R_f = 0.3$ (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (500 MHz, CDCl_3) δ 8.15 – 7.99 (m, 1H), 7.62 (d, $J = 8.9$ Hz, 1H), 7.34 – 7.23 (m, 7H), 7.22 – 7.16 (m, 5H), 7.08 (dt, $J = 8.7, 1.9$ Hz, 3H), 7.03 – 6.95 (m, 4H), 6.87 (t, $J = 7.4$ Hz, 1H), 6.74 – 6.69 (m, 2H), 6.37 (s, 1H), 5.00 – 4.93 (m, 2H); ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 157.7, 157.3, 154.5, 154.0, 150.8, 137.4, 137.2, 132.1, 131.8, 130.6, 130.3, 130.1, 129.6, 129.2, 128.9, 128.8, 128.73, 128.70, 128.6, 128.2, 128.0, 125.4, 124.0, 123.2, 120.9, 120.8, 119.0, 118.5, 115.0, 65.9; HRMS (ESI) m/z calcd for $[\text{C}_{36}\text{H}_{28}\text{NO}_4]^+ [\text{M}+\text{H}]^+$: 538.2013,

found 538.2001.

16. benzyl (2-(7-methoxy-2-phenoxy-naphthalen-1-yl)phenyl)carbamate (3p)



76% yield; Viscous oily liquid; $R_f = 0.3$ (PE:EA = 15:1);

Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, $J = 8.2$ Hz, 1H), 7.66 (dd, $J = 12.1, 8.9$

Hz, 2H), 7.28 (ddd, $J = 8.6, 7.4, 1.6$ Hz, 1H), 7.20 – 7.16

(m, 3H), 7.13 (d, $J = 2.5$ Hz, 1H), 7.12 (t, $J = 1.3$ Hz, 1H), 7.10 (d, $J = 1.4$ Hz, 1H),

7.07 – 7.04 (m, 2H), 7.02 – 6.96 (m, 3H), 6.87 (ddt, $J = 8.4, 7.1, 1.1$ Hz, 1H), 6.75 –

6.70 (m, 2H), 6.59 (d, $J = 2.5$ Hz, 1H), 6.36 (s, 1H), 4.95 (s, 2H), 3.52 (s, 3H); ^{13}C

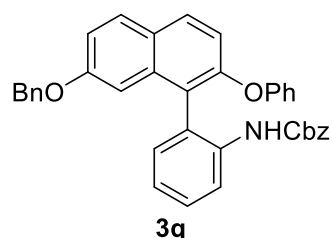
NMR (101 MHz, CDCl_3) δ 158.9, 157.5, 153.6, 152.5, 136.4, 136.2, 135.1, 131.3,

130.2, 129.8, 129.6, 128.9, 128.62, 128.57, 128.30, 128.25, 128.2, 126.3, 123.6, 123.0,

122.8, 118.2, 117.9, 117.3, 103.8, 66.8, 55.2; HRMS (ESI) m/z calcd for

$[\text{C}_{31}\text{H}_{26}\text{NO}_4]^+ [\text{M}+\text{H}]^+$: 476.1856, found 476.1859.

17. benzyl (2-(7-(benzyloxy)-2-phenoxy-naphthalen-1-yl)phenyl)carbamate (3q)



82% yield; Viscous oily liquid; $R_f = 0.3$ (PE:EA = 15:1);

Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 7.9$ Hz, 1H), 7.64 (dd, $J = 8.9, 4.9$

Hz, 2H), 7.15 (qd, $J = 7.5, 5.3$ Hz, 11H), 7.08 – 7.01 (m,

4H), 6.99 – 6.93 (m, 2H), 6.85 (t, $J = 7.4$ Hz, 1H), 6.71 – 6.68 (m, 2H), 6.66 (d, $J =$

2.5 Hz, 1H), 6.31 (s, 1H), 4.94 (d, $J = 2.4$ Hz, 2H), 4.78 (d, $J = 2.1$ Hz, 2H); ^{13}C NMR

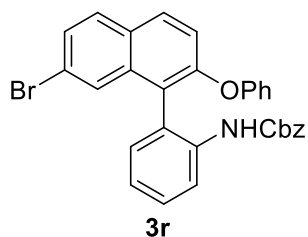
(101 MHz, CDCl_3) δ 157.8, 157.6, 153.5, 152.5, 136.6, 136.4, 136.2, 135.0, 131.3,

130.2, 129.9, 129.6, 128.9, 128.69, 128.65, 128.6, 128.33, 128.30, 128.2, 128.0, 127.8,

126.3, 123.6, 123.0, 122.8, 118.4, 118.3, 117.4, 105.4, 70.0, 66.8; HRMS (ESI) m/z

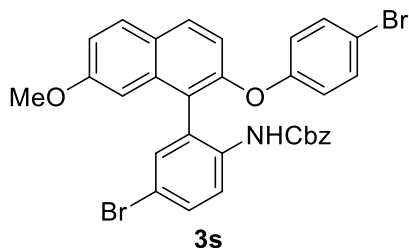
calcd for $[\text{C}_{37}\text{H}_{30}\text{NO}_4]^+ [\text{M}+\text{H}]^+$: 552.2169, found 552.2170.

18. benzyl (2-(7-bromo-2-phenoxy)naphthalen-1-yl)phenyl)carbamate (3r)



78% yield; Viscous oily liquid; $R_f = 0.3$ (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (400 MHz, CDCl_3) δ 8.12 – 8.01 (m, 1H), 7.69 (d, $J = 8.9$ Hz, 1H), 7.58 (d, $J = 8.7$ Hz, 1H), 7.49 (d, $J = 1.9$ Hz, 1H), 7.39 (dd, $J = 8.7, 2.0$ Hz, 1H), 7.22 – 7.13 (m, 6H), 7.11 – 7.03 (m, 5H), 6.93 – 6.87 (m, 1H), 6.74 – 6.68 (m, 2H), 6.33 (s, 1H), 5.00 – 4.91 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 157.0, 152.7, 136.5, 136.1, 135.0, 131.4, 130.5, 129.9, 129.7, 129.3, 129.1, 128.8, 128.71, 128.67, 128.6, 128.39, 128.35, 128.3, 127.5, 123.7, 123.4, 123.0, 122.0, 119.9, 118.5, 67.0; HRMS (ESI) m/z calcd for $[\text{C}_{30}\text{H}_{23}\text{BrNO}_3]^+ [\text{M}+\text{H}]^+$: 524.0856, found 524.0863.

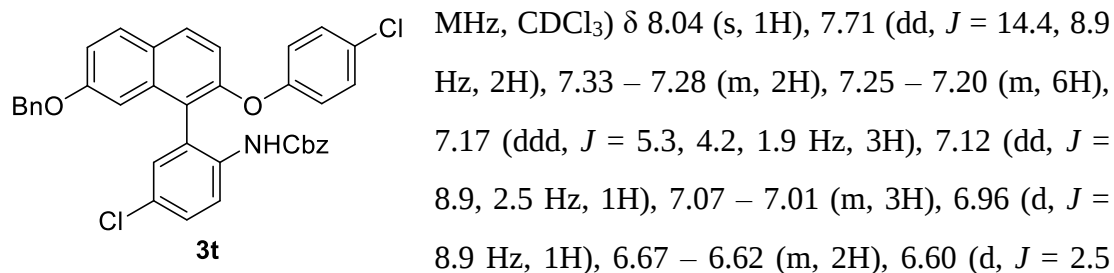
19. benzyl (4-bromo-2-(2-(4-bromophenoxy)-7-methoxynaphthalen-1-yl)phenyl)carbamate (3s)



74% yield; Viscous oily liquid; $R_f = 0.3$ (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.9$ Hz, 1H), 7.70 (dd, $J = 18.3, 9.0$ Hz, 2H), 7.41 (dd, $J = 8.9, 2.4$ Hz, 1H), 7.24 – 7.12 (m, 8H), 7.04 (dd, $J = 8.9, 2.5$ Hz, 1H), 6.95 (d, $J = 8.8$ Hz, 1H), 6.62 – 6.53 (m, 3H), 6.25 (s, 1H), 4.99 – 4.91 (m, 2H), 3.58 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 159.2, 156.4, 153.2, 152.2, 135.8, 135.6, 134.7, 133.8, 132.6, 131.9, 130.9, 130.0, 128.7, 128.6, 128.44, 128.37, 128.3, 126.3, 121.3, 119.9, 118.2, 116.9, 116.0, 115.7, 103.4, 67.1, 55.3; HRMS (ESI) m/z calcd for $[\text{C}_{31}\text{H}_{24}\text{Br}_2\text{NO}_4]^+ [\text{M}+\text{H}]^+$: 634.0046, found 634.0031.

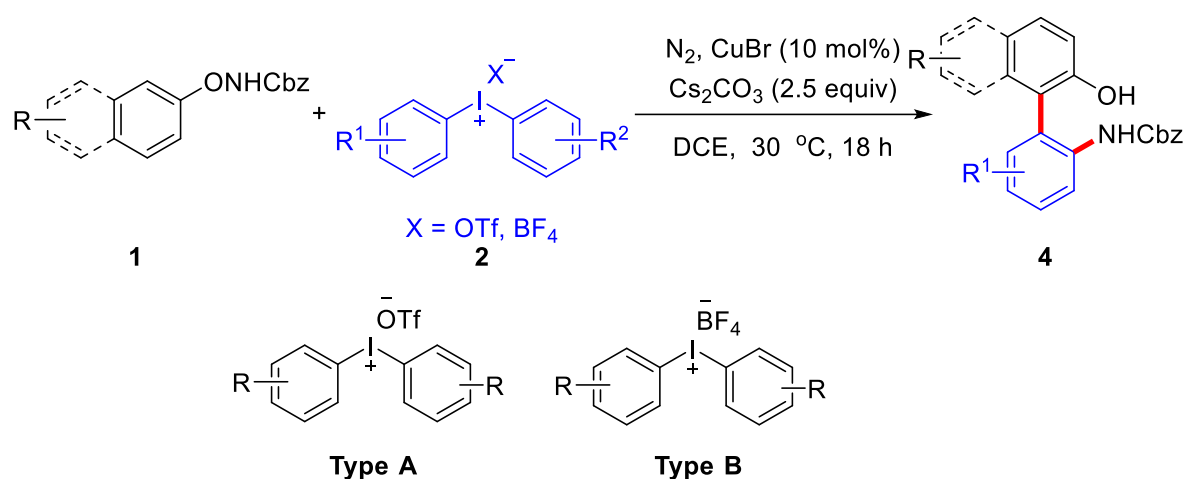
20. benzyl (2-(7-(benzyloxy)-2-(4-chlorophenoxy)naphthalen-1-yl)-4-chlorophenyl)carbamate (3t)

75% yield; Viscous oily liquid; $R_f = 0.3$ (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (500



Hz, 1H), 6.17 (s, 1H), 4.97 (q, J = 12.2 Hz, 2H), 4.87 (s, 2H); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 157.6, 156.4, 154.9, 152.3, 137.09, 137.05, 136.3, 134.3, 131.4, 130.6, 130.5, 130.4, 130.0, 129.1, 128.9, 128.8, 128.68, 128.65, 128.6, 128.3, 128.2, 127.7, 127.3, 126.2, 122.7, 120.7, 118.0, 117.1, 105.4, 69.5, 65.9; HRMS (ESI) m/z calcd for [C₃₇H₂₈Cl₂NO₄]⁺ [M+H]⁺: 620.1390, found 620.1401.

General procedure for the synthesis of NOBIN-type biaryls **4**

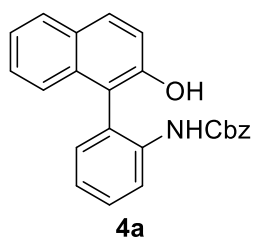


Under N₂ atmosphere, A dried flask was charged with **1** (0.3 mmol, 1.0 equiv), **2** (0.36 mmol, 1.2 equiv), Cs₂CO₃ (0.45 mmol, 1.5 equiv) and CuBr (0.03 mmol, 10 mol%), and the mixture was added anhydrous DCE (3 mL). Reagents **2** of **Type A** were used unless otherwise noted (**Type B**: **4f**). The mixture was stirred at 30 °C for 18 hours. The resulting solution was concentrated in vacuo and purified by flash chromatography on silica gel (PE/EtOAc = 10/1) to give **4**.

Analysis data of NOBIN-type biaryls **4**

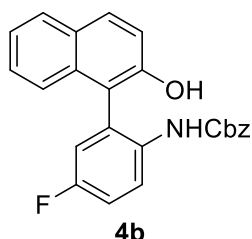
1. benzyl (2-(2-hydroxynaphthalen-1-yl)phenyl)carbamate (**4a**)

56% yield; White solid, m.p. = 125-127 °C; R_f = 0.2 (PE:EA = 5:1); ¹H NMR (500



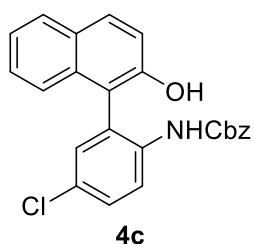
MHz, CDCl₃) δ 8.24 (d, J = 8.2 Hz, 1H), 7.82 – 7.69 (m, 2H), 7.44 (dt, J = 8.7, 4.5 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.22 – 7.11 (m, 9H), 6.28 (s, 1H), 5.19 (s, 1H), 4.95 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 153.5, 151.3, 137.4, 135.8, 132.9, 132.0, 130.8, 130.1, 129.2, 128.5, 128.33, 128.30, 128.26, 127.3, 124.3, 124.0, 123.8, 122.7, 120.5, 117.8, 115.3, 67.0; HRMS (ESI) m/z calcd for [C₂₄H₂₀NO₃]⁺ [M+H]⁺: 370.1438, found 370.1442.

2. benzyl (4-fluoro-2-(2-hydroxynaphthalen-1-yl)phenyl)carbamate (4b)



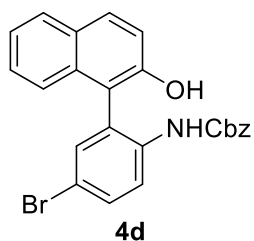
37% yield; Brown solid, m.p. = 135-137 °C; R_f = 0.2 (PE:EA = 5:1); ¹H NMR (500 MHz, CDCl₃) δ 8.15 (s, 1H), 7.80 – 7.73 (m, 2H), 7.29 (dd, J = 6.4, 3.2 Hz, 2H), 7.21 (qd, J = 4.7, 1.6 Hz, 3H), 7.18 (s, 1H), 7.16 – 7.12 (m, 4H), 6.93 (dd, J = 8.4, 3.0 Hz, 1H), 6.21 (s, 1H), 5.25 – 5.18 (m, 1H), 4.95 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 153.7, 151.1, 135.7, 133.4, 132.7, 131.2, 129.2, 128.5, 128.4, 128.34, 128.26, 127.6, 127.5, 124.0, 123.8, 118.6, 118.4, 117.9, 116.8, 116.6, 114.6, 67.1; ¹⁹F NMR (471 MHz, CDCl₃) δ -117.9; HRMS (ESI) m/z calcd for [C₂₄H₁₉FNO₃]⁺ [M+H]⁺: 388.1343, found 388.1346.

3. benzyl (4-chloro-2-(2-hydroxynaphthalen-1-yl)phenyl)carbamate (4c)



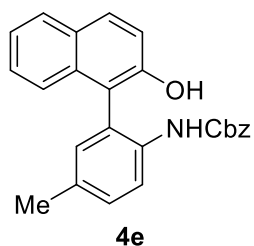
46% yield; Viscous oily liquid; R_f = 0.2 (PE:EA = 5:1); ¹H NMR (500 MHz, CDCl₃) δ 8.18 (d, J = 9.0 Hz, 1H), 7.78 – 7.73 (m, 2H), 7.39 (dd, J = 9.0, 2.5 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.20 (dd, J = 5.2, 1.8 Hz, 3H), 7.17 (dd, J = 4.4, 2.0 Hz, 2H), 7.15 – 7.12 (m, 3H), 6.27 (s, 1H), 5.27 (s, 1H), 4.94 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 153.4, 151.2, 136.1, 135.6, 132.7, 131.7, 131.3, 130.0, 129.2, 128.6, 128.5, 128.4, 128.3, 127.6, 127.5, 124.8, 124.0, 123.8, 121.6, 117.9, 114.2, 67.3; HRMS (ESI) m/z calcd for [C₂₄H₁₉ClNO₃]⁺ [M+H]⁺: 404.1048, found 404.1054.

4. benzyl (4-bromo-2-(2-hydroxynaphthalen-1-yl)phenyl)carbamate (4d)



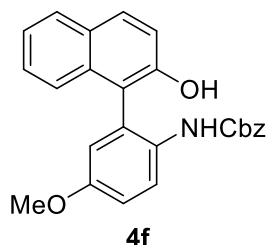
57% yield; Brown solid, m.p. = 128-130 °C; R_f = 0.2 (PE:EA = 5:1); ^1H NMR (500 MHz, CDCl_3) δ 8.14 (d, J = 9.0 Hz, 1H), 7.79 – 7.72 (m, 2H), 7.53 (dd, J = 9.0, 2.4 Hz, 1H), 7.32 (d, J = 2.4 Hz, 1H), 7.30 – 7.28 (m, 2H), 7.20 (dd, J = 5.2, 1.9 Hz, 3H), 7.16 (s, 1H), 7.15 – 7.12 (m, 3H), 6.28 (s, 1H), 5.22 (s, 1H), 4.94 (s, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.3, 151.2, 136.6, 135.5, 134.5, 132.9, 132.7, 131.3, 129.2, 128.6, 128.5, 128.42, 128.36, 127.6, 125.1, 124.1, 123.8, 121.8, 117.8, 116.6, 114.1, 67.3; HRMS (ESI) m/z calcd for $[\text{C}_{24}\text{H}_{19}\text{BrNO}_3]^+$ $[\text{M}+\text{H}]^+$: 448.0543, found 448.0540.

5. benzyl (2-(2-hydroxynaphthalen-1-yl)-4-methylphenyl)carbamate (4e)



60% yield; White solid, m.p. = 165-166 °C; R_f = 0.2 (PE:EA = 5:1); ^1H NMR (500 MHz, CDCl_3) δ 8.10 – 8.03 (m, 1H), 7.75 – 7.71 (m, 2H), 7.26 – 7.23 (m, 3H), 7.18 (ddd, J = 5.2, 3.8, 2.3 Hz, 4H), 7.15 (d, J = 1.9 Hz, 1H), 7.12 (dt, J = 7.0, 2.2 Hz, 2H), 6.97 (d, J = 2.1 Hz, 1H), 6.20 (s, 1H), 5.28 (s, 1H), 4.93 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.7, 151.2, 135.9, 134.8, 134.2, 133.0, 132.3, 130.70, 130.65, 129.1, 128.5, 128.4, 128.31, 128.26, 128.2, 127.2, 124.1, 123.8, 120.8, 117.8, 115.7, 67.0, 20.8; HRMS (ESI) m/z calcd for $[\text{C}_{25}\text{H}_{22}\text{NO}_3]^+$ $[\text{M}+\text{H}]^+$: 384.1594, found 384.1604.

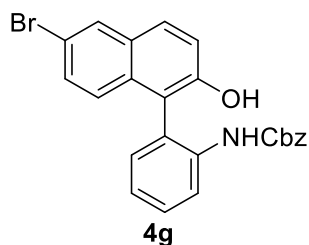
6. benzyl (2-(2-hydroxynaphthalen-1-yl)-4-methoxyphenyl)carbamate (4f)



51% yield; Brown solid, m.p. = 115-117 °C; R_f = 0.2 (PE:EA = 5:1); ^1H NMR (400 MHz, CDCl_3) δ 7.98 (s, 1H), 7.74 – 7.70 (m, 2H), 7.25 (dd, J = 6.2, 3.5 Hz, 3H), 7.17 (dt, J = 5.4, 2.4 Hz, 5H), 7.09 (dd, J = 7.0, 2.8 Hz, 2H), 6.96 (dd, J = 9.1, 3.0 Hz, 1H), 6.71 (d, J = 3.0 Hz, 1H), 6.13 (s, 1H), 4.91 (s, 2H), 3.67 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 151.2, 135.9, 132.9, 130.7, 130.3, 129.1, 128.7, 128.6, 128.5, 128.4, 128.32, 128.30, 128.22, 128.16, 127.24, 127.22, 124.1, 123.8, 118.0, 116.6, 115.6, 67.0, 55.6; HRMS (ESI) m/z calcd for $[\text{C}_{25}\text{H}_{22}\text{NO}_4]^+$

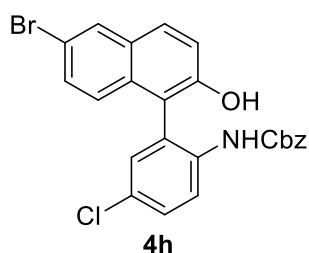
[M+H]⁺: 400.1543, found 400.1548.

7. benzyl (2-(6-bromo-2-hydroxynaphthalen-1-yl)phenyl)carbamate (4g)



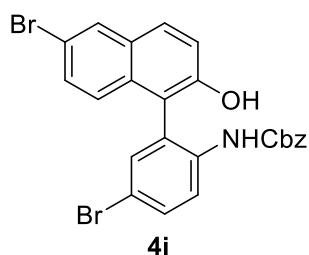
43% yield; Viscous oily liquid; R_f = 0.2 (PE:EA = 5:1); ¹H NMR (500 MHz, CDCl₃) δ 8.22 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 2.0 Hz, 1H), 7.67 (d, J = 8.9 Hz, 1H), 7.45 (ddd, J = 8.7, 7.2, 1.9 Hz, 1H), 7.31 (dd, J = 9.0, 2.1 Hz, 1H), 7.24 – 7.19 (m, 4H), 7.18 – 7.13 (m, 4H), 6.99 (d, J = 8.9 Hz, 1H), 6.20 (s, 1H), 5.17 (d, J = 12.7 Hz, 1H), 4.96 (d, J = 1.3 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 153.2, 152.1, 136.6, 135.4, 134.4, 134.0, 133.4, 131.3, 130.0, 128.6, 128.5, 128.4, 127.60, 127.58, 125.8, 124.1, 122.2, 122.1, 118.3, 116.9, 113.5, 67.4; HRMS (ESI) m/z calcd for [C₂₄H₁₉BrNO₃]⁺ [M+H]⁺: 448.0543, found 448.0539.

8. benzyl(2-(6-bromo-2-hydroxynaphthalen-1-yl)-4-chlorophenyl)carbamate (4h)



49% yield; Viscous oily liquid; R_f = 0.2 (PE:EA = 5:1); ¹H NMR (500 MHz, CDCl₃) δ 8.18 (d, J = 9.0 Hz, 1H), 7.90 (d, J = 2.0 Hz, 1H), 7.68 (d, J = 8.9 Hz, 1H), 7.41 (dd, J = 9.0, 2.5 Hz, 1H), 7.35 (dd, J = 8.9, 2.1 Hz, 1H), 7.22 (p, J = 2.9, 2.4 Hz, 3H), 7.20 – 7.13 (m, 4H), 6.99 (d, J = 8.9 Hz, 1H), 6.18 (s, 1H), 5.22 (d, J = 4.5 Hz, 1H), 4.96 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 153.3, 151.5, 136.0, 135.4, 131.5, 131.2, 130.8, 130.4, 130.31, 130.27, 130.2, 129.4, 128.6, 128.5, 128.4, 125.6, 124.1, 121.9, 119.0, 117.9, 114.5, 67.3; HRMS (ESI) m/z calcd for [C₂₄H₁₈BrClNO₃]⁺ [M+H]⁺: 482.0153, found 482.0117.

9. benzyl (4-bromo-2-(6-bromo-2-hydroxynaphthalen-1-yl)phenyl)carbamate (4i)

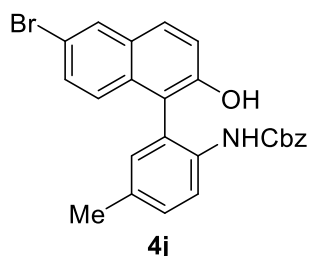


42% yield; Viscous oily liquid; R_f = 0.2 (PE:EA = 5:1); ¹H NMR (500 MHz, CDCl₃) δ 8.17 (d, J = 8.9 Hz, 1H), 7.92 (d, J = 2.0 Hz, 1H), 7.70 (d, J = 8.9 Hz, 1H), 7.57 (dd, J = 8.9, 2.4 Hz, 1H), 7.36 (dd, J = 8.9, 2.0 Hz, 1H), 7.31 (d, J =

2.4 Hz, 1H), 7.25 – 7.20 (m, 3H), 7.19 (d, $J = 2.0$ Hz, 1H), 7.16 (dd, $J = 7.3, 2.3$ Hz, 2H), 7.00 (d, $J = 9.0$ Hz, 1H), 6.18 (s, 1H), 5.09 (s, 1H), 4.97 (s, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.2, 151.5, 136.6, 135.4, 134.3, 133.2, 131.2, 130.8, 130.4, 130.3, 128.6, 128.5, 128.4, 125.6, 122.0, 119.0, 117.9, 116.8, 114.3, 67.3; HRMS (ESI) m/z calcd for $[\text{C}_{24}\text{H}_{18}\text{Br}_2\text{NO}_3]^+ [\text{M}+\text{H}]^+$: 527.9627, found 527.9605.

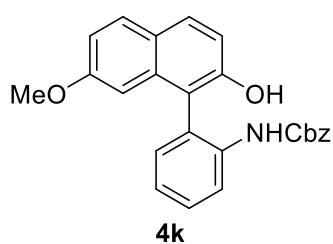
10. benzyl (2-(6-bromo-2-hydroxynaphthalen-1-yl)-4-methylphenyl)carbamate (4j)

56% yield; Viscous oily liquid; $R_f = 0.2$ (PE:EA = 5:1); ^1H NMR (500 MHz, CDCl_3) δ 8.16 (d, $J = 8.0$ Hz, 1H), 8.00 (d, $J = 2.0$ Hz, 1H), 7.76 (d, $J = 8.9$ Hz, 1H), 7.42 (dd, $J = 9.0, 2.1$ Hz, 1H), 7.40 – 7.30 (m, 5H), 7.27 – 7.23 (m, 2H), 7.14 (d, $J = 9.0$ Hz, 1H), 7.07 (d, $J = 2.1$ Hz, 1H), 6.25 (s, 1H), 5.44 (s, 1H), 5.06 (d, $J = 3.0$ Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.6, 151.5, 135.8, 134.7, 134.4, 132.1, 131.5, 130.9, 130.4, 130.2, 129.7, 128.7, 128.6, 128.4, 128.34, 128.25, 122.6, 121.2, 119.0, 117.6, 116.0, 67.1, 20.8; HRMS (ESI) m/z calcd for $[\text{C}_{25}\text{H}_{21}\text{BrNO}_3]^+ [\text{M}+\text{H}]^+$: 462.0699, found 462.0691.

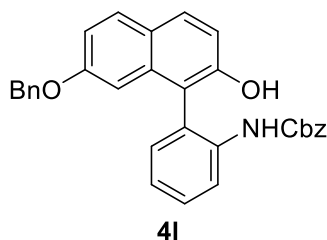


11. benzyl (2-(2-hydroxy-7-methoxynaphthalen-1-yl)phenyl)carbamate (4k)

63% yield; Gray solid, m.p. = 179-181 °C; $R_f = 0.2$ (PE:EA = 5:1); ^1H NMR (400 MHz, CDCl_3) δ 8.19 (d, $J = 8.3$ Hz, 1H), 7.63 (dd, $J = 13.9, 8.9$ Hz, 2H), 7.41 (ddd, $J = 8.7, 6.3, 2.7$ Hz, 1H), 7.22 – 7.09 (m, 7H), 7.01 (d, $J = 8.8$ Hz, 1H), 6.91 (dd, $J = 8.9, 2.5$ Hz, 1H), 6.42 – 6.27 (m, 2H), 5.24 (s, 1H), 4.99 – 4.89 (m, 2H), 3.52 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.9, 153.6, 151.9, 137.3, 135.8, 134.4, 131.9, 130.5, 130.1, 129.9, 128.6, 128.3, 128.2, 124.50, 124.46, 123.1, 120.7, 116.0, 115.2, 114.6, 102.9, 67.0, 55.2; HRMS (ESI) m/z calcd for $[\text{C}_{25}\text{H}_{22}\text{NO}_4]^+ [\text{M}+\text{H}]^+$: 400.1543, found 400.1535.

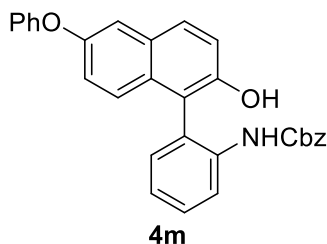


12. benzyl (2-(7-(benzyloxy)-2-hydroxynaphthalen-1-yl)phenyl)carbamate (4l)



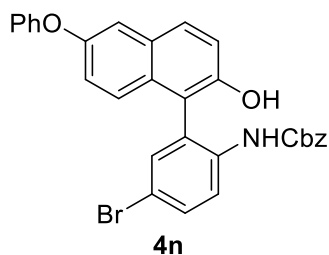
51% yield; Brown solid, m.p. = 148-150 °C; R_f = 0.2 (PE:EA = 5:1); ^1H NMR (400 MHz, CDCl_3) δ 8.20 (d, J = 8.3 Hz, 1H), 7.62 (dd, J = 8.8, 7.6 Hz, 2H), 7.43 (ddd, J = 8.6, 7.3, 1.8 Hz, 1H), 7.22 – 7.07 (m, 12H), 7.03 – 6.94 (m, 2H), 6.44 (d, J = 2.4 Hz, 1H), 6.23 (s, 1H), 5.22 (s, 1H), 4.93 (d, J = 3.8 Hz, 2H), 4.79 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 157.8, 153.6, 151.9, 137.4, 136.7, 135.8, 134.3, 131.9, 130.5, 130.0, 130.0, 128.57, 128.55, 128.33, 128.25, 127.9, 127.6, 124.54, 124.49, 123.1, 120.7, 116.5, 115.3, 114.6, 104.6, 69.9, 67.0; HRMS (ESI) m/z calcd for $[\text{C}_{31}\text{H}_{26}\text{NO}_4]^+$ $[\text{M}+\text{H}]^+$: 476.1856, found 476.1863.

13. benzyl (2-(2-hydroxy-6-phenoxy-naphthalen-1-yl)phenyl)carbamate (4m)



55% yield; Yellow solid, m.p. = 162-164 °C; R_f = 0.2 (PE:EA = 5:1); ^1H NMR (500 MHz, CDCl_3) δ 8.23 (d, J = 8.3 Hz, 1H), 7.61 (d, J = 8.9 Hz, 1H), 7.44 (ddd, J = 8.7, 5.3, 3.6 Hz, 1H), 7.26 – 7.23 (m, 3H), 7.21 (td, J = 6.4, 6.0, 2.9 Hz, 3H), 7.16 (dd, J = 9.0, 3.0 Hz, 5H), 7.12 (d, J = 9.1 Hz, 1H), 7.04 (ddd, J = 8.8, 6.5, 4.3 Hz, 2H), 6.98 – 6.94 (m, 2H), 6.30 (s, 1H), 5.11 (s, 1H), 5.01 – 4.93 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 157.3, 153.6, 153.5, 150.5, 137.4, 135.8, 131.9, 130.2, 130.0, 129.9, 129.8, 129.6, 128.58, 128.55, 128.4, 128.3, 126.1, 124.4, 123.3, 121.2, 120.5, 118.9, 118.5, 115.6, 115.1, 67.1; HRMS (ESI) m/z calcd for $[\text{C}_{30}\text{H}_{24}\text{NO}_4]^+$ $[\text{M}+\text{H}]^+$: 462.1700, found 462.1694.

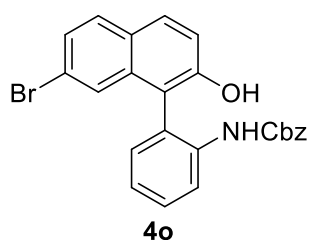
14. benzyl (4-bromo-2-(2-hydroxy-6-phenoxy-naphthalen-1-yl)phenyl)carbamate (4n)



44% yield; Viscous oily liquid; R_f = 0.2 (PE:EA = 5:1); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 9.82 (d, J = 6.4 Hz, 1H), 7.96 (s, 1H), 7.81 (dd, J = 21.6, 8.7 Hz, 2H), 7.61 (dd, J = 8.8, 2.4 Hz, 1H), 7.42 (d, J = 2.6 Hz, 1H), 7.39 – 7.34 (m, 3H), 7.32 – 7.26 (m, 4H), 7.23 – 7.18 (m,

3H), 7.14 – 7.10 (m, 2H), 7.03 – 6.99 (m, 2H), 5.05 – 4.96 (m, 2H); ^{13}C NMR (126 MHz, DMSO- d_6) δ 157.7, 154.0, 152.31, 152.27, 136.91, 136.85, 134.7, 131.1, 130.5, 130.4, 130.3, 129.6, 129.2, 128.8, 128.3, 128.1, 126.3, 123.6, 121.0, 119.6, 118.9, 118.6, 116.2, 116.1, 115.6, 66.2; HRMS (ESI) m/z calcd for $[\text{C}_{30}\text{H}_{23}\text{BrNO}_4]^+ [\text{M}+\text{H}]^+$: 540.0805, found 540.0814.

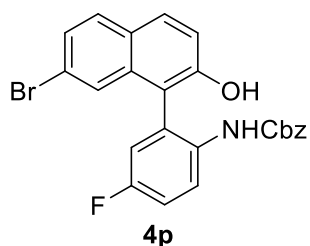
15. benzyl (2-(7-bromo-2-hydroxynaphthalen-1-yl)phenyl)carbamate (4o)



77% yield; Yellow solid, m.p. = 137-139 °C; R_f = 0.2 (PE:EA = 5:1); ^1H NMR (400 MHz, CDCl_3) δ 8.23 (d, J = 8.4 Hz, 1H), 7.72 (dd, J = 9.0, 0.7 Hz, 1H), 7.60 (d, J = 8.7 Hz, 1H), 7.47 (ddd, J = 8.7, 7.3, 1.8 Hz, 1H), 7.35 (dd, J = 8.6, 1.9 Hz, 1H), 7.27 (d, J = 1.9 Hz, 1H), 7.23 – 7.13 (m, 8H), 6.22 (s, 1H), 5.28 (s, 1H), 4.98 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 153.5, 152.1, 137.3, 135.7, 134.4, 132.0, 130.8, 130.5, 130.0, 128.6, 128.4, 128.3, 127.6, 127.3, 126.1, 124.6, 122.0, 121.9, 120.8, 118.2, 114.8, 67.2; HRMS (ESI) m/z calcd for $[\text{C}_{24}\text{H}_{19}\text{BrNO}_3]^+ [\text{M}+\text{H}]^+$: 448.0543, found 448.0555.

16. benzyl(2-(7-bromo-2-hydroxynaphthalen-1-yl)-4-fluorophenyl)carbamate

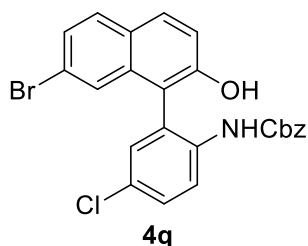
(4p)



36% yield; Viscous oily liquid; R_f = 0.2 (PE:EA = 5:1); ^1H NMR (500 MHz, CDCl_3) δ 8.17 (s, 1H), 7.75 (d, J = 8.9 Hz, 1H), 7.62 (d, J = 8.7 Hz, 1H), 7.38 (dd, J = 8.6, 1.9 Hz, 1H), 7.27 – 7.20 (m, 4H), 7.18 (dt, J = 7.7, 2.9 Hz, 4H), 6.91 (dd, J = 8.3, 3.0 Hz, 1H), 6.14 (s, 1H), 5.21 (d, J = 17.0 Hz, 1H), 4.99 (s, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 158.3, 153.7, 151.9, 135.6, 134.0, 133.4, 131.1, 130.0, 128.6, 128.4, 128.3, 127.6, 127.5, 125.9, 122.1, 118.6, 118.4, 118.3, 117.3, 117.1, 114.1, 67.3; ^{19}F NMR (471 MHz, CDCl_3) δ -117.3; HRMS (ESI) m/z calcd for $[\text{C}_{24}\text{H}_{18}\text{BrFNO}_3]^+ [\text{M}+\text{H}]^+$: 466.0449, found 466.0440.

17. benzyl(2-(7-bromo-2-hydroxynaphthalen-1-yl)-4-chlorophenyl)carbamate

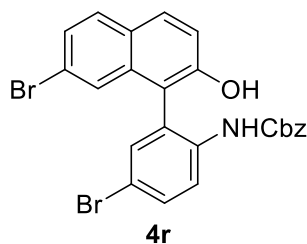
(4q)



45% yield; Viscous oily liquid; $R_f = 0.2$ (PE:EA = 5:1); ^1H NMR (500 MHz, CDCl_3) δ 8.19 (d, $J = 8.6$ Hz, 1H), 7.73 (d, $J = 8.9$ Hz, 1H), 7.61 (d, $J = 8.7$ Hz, 1H), 7.42 (dd, $J = 8.9$, 2.5 Hz, 1H), 7.37 (dd, $J = 8.7$, 2.0 Hz, 1H), 7.26 – 7.20 (m, 4H), 7.18 – 7.13 (m, 4H), 6.20 (s, 1H), 5.32 (s, 1H), 5.01 – 4.91 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.3, 152.1, 136.0, 135.4, 134.1, 131.6, 131.2, 130.4, 130.0, 129.5, 128.7, 128.6, 128.5, 128.43, 128.39, 127.6, 127.5, 125.9, 122.2, 118.3, 113.6, 67.4; HRMS (ESI) m/z calcd for $[\text{C}_{24}\text{H}_{18}\text{BrClNO}_3]^+ [\text{M}+\text{H}]^+$: 482.0153, found 482.0150.

18. benzyl(4-bromo-2-(7-bromo-2-hydroxynaphthalen-1-yl)phenyl)carbamate

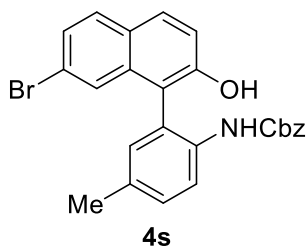
(4r)



30% yield; Viscous oily liquid; $R_f = 0.2$ (PE:EA = 5:1); ^1H NMR (500 MHz, CDCl_3) δ 10.04 (s, 1H), 8.26 (s, 1H), 7.87 (d, $J = 8.9$ Hz, 1H), 7.82 (d, $J = 8.7$ Hz, 1H), 7.73 (d, $J = 8.8$ Hz, 1H), 7.62 (dd, $J = 8.7$, 2.4 Hz, 1H), 7.41 (dd, $J = 8.6$, 2.0 Hz, 1H), 7.35 (d, $J = 2.4$ Hz, 1H), 7.32 – 7.26 (m, 4H), 7.24 (d, $J = 1.8$ Hz, 1H), 7.18 – 7.14 (m, 2H), 5.08 – 4.90 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.2, 152.1, 136.6, 135.4, 134.4, 134.0, 133.4, 131.3, 130.0, 128.6, 128.5, 128.4, 127.60, 127.58, 125.8, 122.2, 118.3, 116.9, 113.5, 67.4; HRMS (ESI) m/z calcd for $[\text{C}_{24}\text{H}_{18}\text{Br}_2\text{NO}_3]^+ [\text{M}+\text{H}]^+$: 527.9627, found 527.9615.

19. benzyl(2-(7-bromo-2-hydroxynaphthalen-1-yl)-4-methylphenyl)carbamate

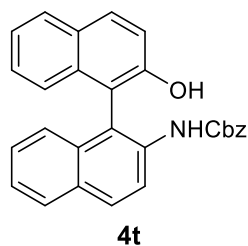
(4s)



45% yield; Viscous oily liquid; $R_f = 0.2$ (PE:EA = 5:1); ^1H NMR (500 MHz, CDCl_3) δ 8.15 – 8.01 (m, 1H), 7.71 (d, $J = 8.9$ Hz, 1H), 7.60 (d, $J = 8.6$ Hz, 1H), 7.35 (dd, $J = 8.6$, 2.0 Hz, 1H), 7.27 (dd, $J = 8.3$, 2.0 Hz, 2H), 7.25 – 7.14 (m, 6H), 6.95 (d, $J = 2.1$ Hz, 1H), 6.12 (s, 1H), 5.20 (d, $J = 7.4$

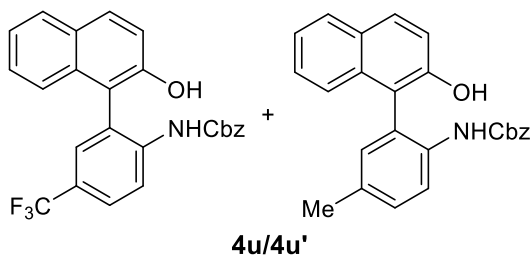
Hz, 1H), 4.97 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.6, 152.0, 135.8, 134.7, 134.5, 134.3, 132.2, 131.2, 130.6, 130.0, 128.6, 128.32, 128.27, 127.6, 127.2, 126.2, 121.8, 118.2, 115.1, 67.1, 20.8; HRMS (ESI) m/z calcd for $[\text{C}_{25}\text{H}_{21}\text{BrNO}_3]^+ [\text{M}+\text{H}]^+$: 462.0699, found 462.0672.

20. benzyl (2'-hydroxy-[1,1'-binaphthalen]-2-yl)carbamate (4t)



48% yield; Viscous oily liquid; R_f = 0.2 (PE:EA = 5:1); Purified directly by flash chromatography on silica gel (10:1, petroleum ether: ethyl acetate); ^1H NMR (500 MHz, CDCl_3) δ 8.51 (d, J = 9.1 Hz, 1H), 8.02 (d, J = 9.1 Hz, 1H), 7.94 (d, J = 8.9 Hz, 1H), 7.88 (t, J = 7.8 Hz, 2H), 7.40 (t, J = 7.5 Hz, 1H), 7.34 (dd, J = 8.4, 5.1 Hz, 2H), 7.32 – 7.20 (m, 7H), 7.09 (d, J = 8.5 Hz, 1H), 6.99 (d, J = 8.4 Hz, 1H), 6.47 (s, 1H), 5.09 (q, J = 4.6, 2.7 Hz, 1H), 5.02 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 153.6, 152.0, 135.9, 135.7, 133.2, 132.9, 131.3, 130.8, 130.4, 129.4, 128.6, 128.4, 128.34, 128.30, 128.27, 127.44, 127.38, 125.2, 125.1, 124.1, 124.0, 119.7, 117.9, 116.7, 112.7, 67.1; HRMS (ESI) m/z calcd for $[\text{C}_{28}\text{H}_{22}\text{NO}_3]^+ [\text{M}+\text{H}]^+$: 420.1594, found 420.1589.

21. benzyl (2-(2-hydroxynaphthalen-1-yl)-4-(trifluoromethyl)phenyl)carbamate (4u) and benzyl (2-(2-hydroxynaphthalen-1-yl)-4-methylphenyl)carbamate (4u')

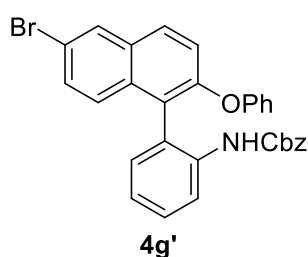


19% yield and 19% yield; Viscous oily liquid; R_f = 0.2 (PE:EA = 5:1); Purified directly by flash chromatography on silica gel (10:1, petroleum ether: ethyl acetate); ^1H

NMR (500 MHz, CDCl_3) δ 8.51 (d, J = 8.8 Hz, 1H), 8.14 (d, J = 8.0 Hz, 1H), 7.89 – 7.80 (m, 4H), 7.76 (dd, J = 8.9, 2.1 Hz, 1H), 7.53 (d, J = 2.1 Hz, 1H), 7.38 (dd, J = 6.3, 3.2 Hz, 2H), 7.36 – 7.32 (m, 3H), 7.30 – 7.26 (m, 6H), 7.26 – 7.19 (m, 7H), 7.16 (dd, J = 6.2, 3.4 Hz, 1H), 7.06 (d, J = 2.1 Hz, 1H), 6.55 (s, 1H), 6.27 (s, 1H), 5.32 (s, 1H), 5.26 (s, 1H), 5.04 (s, 2H), 5.02 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (126

MHz, CDCl₃) δ 153.7, 153.1, 151.3, 151.2, 140.6, 135.8, 135.4, 134.8, 134.2, 132.9, 132.8, 132.2, 131.5, 130.74, 130.66, 129.3, 129.14, 129.11, 128.6, 128.51, 128.48, 128.43, 128.36, 128.31, 128.26, 128.2, 127.7, 127.2, 127.11, 127.08, 126.0, 125.8, 124.14, 124.08, 123.8, 123.7, 123.0, 122.9, 119.6, 117.9, 117.7, 115.6, 113.9, 67.4, 67.0, 20.8; ¹⁹F NMR (471 MHz, CDCl₃) δ -61.9; HRMS (ESI) *m/z* calcd for [C₂₅H₂₂NO₃]⁺ [M+H]⁺: 384.1594 and [C₂₅H₁₉F₃NO₃]⁺ [M+H]⁺: 438.1312, found 384.1595 and 438.1309.

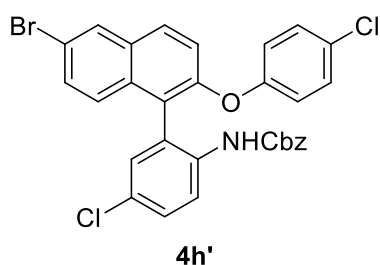
22. benzyl (2-(6-bromo-2-phenoxy)naphthalen-1-yl)phenyl)carbamate (4g')



27% yield; Viscous oily liquid; R_f = 0.3 (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 8.13 – 7.99 (m, 1H), 7.94 (d, *J* = 2.0 Hz, 1H), 7.69 (d, *J* = 8.9 Hz, 1H), 7.34 (qd, *J* = 8.8, 2.1 Hz, 2H), 7.24

– 7.20 (m, 3H), 7.19 – 7.08 (m, 6H), 7.08 – 7.01 (m, 2H), 6.96 – 6.90 (m, 1H), 6.77 – 6.71 (m, 2H), 6.29 (s, 1H), 5.02 – 4.92 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 157.1, 153.4, 152.1, 136.4, 136.0, 132.1, 131.9, 131.3, 130.5, 130.2, 129.7, 129.5, 129.1, 128.62, 128.57, 128.31, 128.28, 127.7, 127.2, 124.0, 123.6, 123.3, 120.8, 119.3, 118.3, 66.9; HRMS (ESI) *m/z* calcd for [C₃₀H₂₃BrNO₃]⁺ [M+H]⁺: 524.0856, found 524.0867.

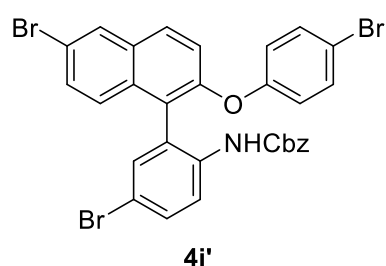
23. benzyl (2-(6-bromo-2-(4-chlorophenoxy)naphthalen-1-yl)-4-chlorophenyl)-carbamate (4h')



23% yield; Viscous oily liquid; R_f = 0.3 (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ¹H NMR (500 MHz, CDCl₃) δ 8.04 (s, 1H), 7.97 (d, *J* = 2.0 Hz, 1H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.42 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.31 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.25 (dd, *J* = 5.4, 1.9 Hz, 3H), 7.21 – 7.17 (m, 3H), 7.15 (d, *J* = 9.0 Hz, 1H), 7.10 – 7.06 (m, 2H), 7.06 (d, *J* = 2.6 Hz, 1H), 6.72 – 6.62 (m, 2H), 6.18 (s, 1H), 5.03 – 4.92 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ

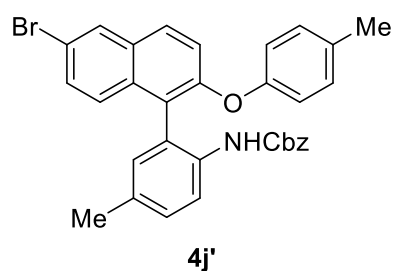
155.4, 153.1, 151.8, 135.7, 135.1, 131.9, 131.7, 131.0, 130.9, 130.3, 130.2, 129.8, 129.2, 128.63, 128.57, 128.5, 128.4, 126.8, 124.0, 122.6, 120.4, 119.7, 119.6, 67.2; HRMS (ESI) m/z calcd for $[C_{30}H_{21}BrCl_2NO_3]^+ [M+H]^+$: 592.0076, found 592.0069.

24. benzyl (4-bromo-2-(6-bromo-2-(4-bromophenoxy)naphthalen-1-yl)phenyl)-carbamate (4i')



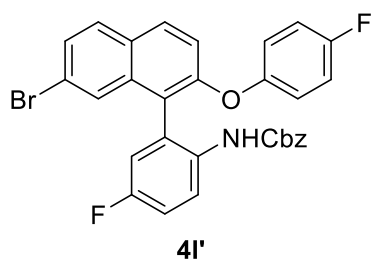
30% yield; Viscous oily liquid; R_f = 0.3 (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); 1H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 2.0 Hz, 2H), 7.73 (d, J = 9.0 Hz, 1H), 7.43 (ddd, J = 13.9, 9.0, 2.2 Hz, 2H), 7.27 – 7.22 (m, 4H), 7.22 – 7.16 (m, 5H), 7.14 (d, J = 9.0 Hz, 1H), 6.61 (d, J = 8.9 Hz, 2H), 6.17 (s, 1H), 5.02 – 4.90 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 153.0, 151.7, 135.7, 135.6, 133.7, 132.71, 132.66, 132.1, 131.9, 131.8, 131.7, 131.0, 130.3, 130.2, 128.6, 128.5, 128.4, 126.8, 122.6, 121.8, 120.4, 120.0, 119.8, 116.1, 67.2; HRMS (ESI) m/z calcd for $[C_{30}H_{21}Br_3NO_3]^+ [M+H]^+$: 681.9046, found 681.9051.

25. benzyl (2-(6-bromo-2-(*p*-tolylloxy)naphthalen-1-yl)-4-methylphenyl)carbamate (4j')



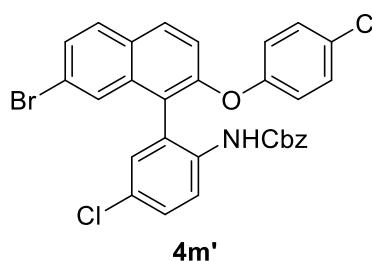
13% yield; Viscous oily liquid; R_f = 0.3 (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); 1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 2.0 Hz, 1H), 7.65 (d, J = 9.0 Hz, 1H), 7.35 (dd, J = 9.1, 2.1 Hz, 1H), 7.27 – 7.20 (m, 4H), 7.18 – 7.10 (m, 4H), 6.97 – 6.88 (m, 3H), 6.67 (d, J = 8.5 Hz, 2H), 6.23 (s, 1H), 5.04 – 4.88 (m, 2H), 2.22 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 153.5, 152.5, 136.1, 133.8, 132.9, 132.2, 131.8, 131.6, 130.4, 130.2, 130.1, 129.7, 129.2, 128.7, 128.5, 128.4, 128.23, 128.21, 127.7, 127.3, 123.7, 120.3, 119.0, 118.6, 66.8, 20.8, 20.7; HRMS (ESI) m/z calcd for $[C_{32}H_{27}BrNO_3]^+ [M+H]^+$: 552.1169, found 552.1161.

26. benzyl (2-(7-bromo-2-(4-fluorophenoxy)naphthalen-1-yl)-4-fluorophenyl)-carbamate (4l')



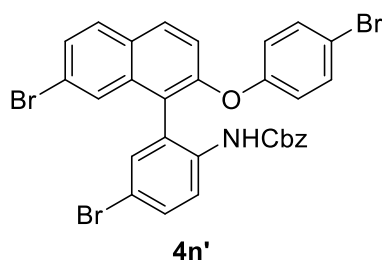
31% yield; Viscous oily liquid; $R_f = 0.3$ (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (400 MHz, CDCl_3) δ 8.03 (s, 1H), 7.77 (d, $J = 9.0$ Hz, 1H), 7.66 (d, $J = 8.5$ Hz, 1H), 7.47 (d, $J = 9.3$ Hz, 2H), 7.24 (dd, $J = 5.3, 1.8$ Hz, 3H), 7.21 – 7.16 (m, 2H), 7.07 (dd, $J = 14.5, 8.8$ Hz, 2H), 6.82 (t, $J = 8.8$ Hz, 3H), 6.70 (dd, $J = 9.1, 4.3$ Hz, 2H), 6.18 (s, 1H), 4.99 (q, $J = 12.2$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 160.1, 157.7, 153.5, 152.8, 135.8, 134.5, 132.6, 130.9, 129.9, 129.02, 128.94, 128.6, 128.4, 128.3, 127.0, 122.3, 120.00, 119.92, 119.1, 118.0, 117.7, 116.5, 116.2, 116.1, 115.9, 67.1; ^{19}F NMR (471 MHz, CDCl_3) δ -119.1, -119.5; HRMS (ESI) m/z calcd for $[\text{C}_{30}\text{H}_{21}\text{BrF}_2\text{NO}_3]^+ [\text{M}+\text{H}]^+$: 560.0667, found 560.0669.

27. benzyl (2-(7-bromo-2-(4-chlorophenoxy)naphthalen-1-yl)-4-chlorophenyl)-carbamate (4m')



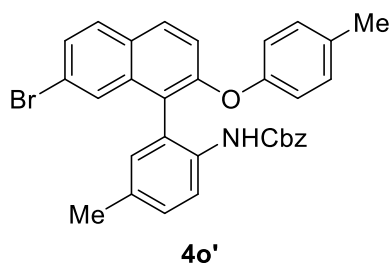
19% yield; Viscous oily liquid; $R_f = 0.3$ (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (400 MHz, CDCl_3) δ 8.06 (s, 1H), 7.78 (d, $J = 9.0$ Hz, 1H), 7.66 (d, $J = 8.6$ Hz, 1H), 7.52 – 7.43 (m, 2H), 7.31 (dd, $J = 8.8, 2.5$ Hz, 1H), 7.24 (dd, $J = 5.5, 1.8$ Hz, 3H), 7.21 – 7.16 (m, 2H), 7.11 (d, $J = 9.0$ Hz, 1H), 7.08 (s, 1H), 7.07 – 7.03 (m, 2H), 6.70 – 6.63 (m, 2H), 6.19 (s, 1H), 4.98 (q, $J = 12.1$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 155.4, 153.1, 152.5, 135.7, 135.2, 134.5, 131.1, 130.9, 130.0, 129.8, 129.3, 129.23, 129.18, 129.1, 128.71, 128.65, 128.5, 128.42, 128.37, 127.0, 125.7, 122.5, 121.5, 119.7, 119.5, 67.2; HRMS (ESI) m/z calcd for $[\text{C}_{30}\text{H}_{21}\text{BrCl}_2\text{NO}_3]^+ [\text{M}+\text{H}]^+$: 592.0076, found 592.0064.

28. benzyl (4-bromo-2-(7-bromo-2-(4-bromophenoxy)naphthalen-1-yl)phenyl)-carbamate, hydrogen salt (4n')



30% yield; Viscous oily liquid; $R_f = 0.3$ (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (500 MHz, CDCl_3) δ 8.02 (s, 1H), 7.79 (d, $J = 9.0$ Hz, 1H), 7.67 (d, $J = 8.7$ Hz, 1H), 7.51 – 7.43 (m, 3H), 7.25 (d, $J = 6.9$ Hz, 2H), 7.22 (d, $J = 2.1$ Hz, 1H), 7.22 – 7.17 (m, 4H), 7.12 (d, $J = 9.0$ Hz, 1H), 6.66 – 6.56 (m, 2H), 6.18 (s, 1H), 5.05 – 4.92 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 155.9, 153.0, 152.4, 135.67, 135.66, 134.54, 133.66, 132.71, 132.26, 131.12, 129.98, 129.24, 129.22, 128.7, 128.5, 128.4, 127.0, 122.5, 121.5, 120.1, 119.6, 116.2, 116.1, 67.2; HRMS (ESI) m/z calcd for $[\text{C}_{30}\text{H}_{21}\text{Br}_3\text{NO}_3]^+ [\text{M}+\text{H}]^+$: 681.9046, found 681.9054.

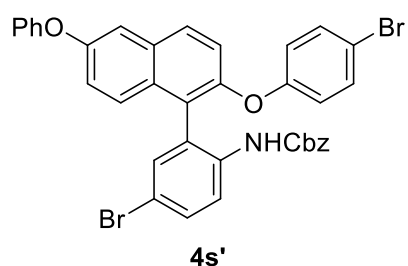
29. benzyl (2-(7-bromo-2-(p-tolyloxy)naphthalen-1-yl)-4-methylphenyl)carbamate (4o')



15% yield; Viscous oily liquid; $R_f = 0.3$ (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (400 MHz, CDCl_3) δ 7.94 (s, 1H), 7.71 (d, $J = 9.0$ Hz, 1H), 7.62 (d, $J = 8.7$ Hz, 1H), 7.51 (d, $J = 1.8$ Hz, 1H), 7.42 (dd, $J = 8.7, 1.9$ Hz, 1H), 7.25 – 7.13 (m, 6H), 7.10 (d, $J = 9.0$ Hz, 1H), 6.97 – 6.86 (m, 3H), 6.67 (d, $J = 8.5$ Hz, 2H), 6.25 (s, 1H), 5.03 – 4.93 (m, 2H), 2.24 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 154.7, 153.5, 153.1, 136.1, 135.0, 133.9, 133.0, 131.7, 130.2, 130.1, 129.79, 129.77, 129.6, 128.9, 128.6, 128.54, 128.49, 128.24, 128.22, 127.4, 122.6, 121.8, 119.4, 118.8, 66.9, 20.9, 20.7; HRMS (ESI) m/z calcd for $[\text{C}_{32}\text{H}_{27}\text{BrNO}_3]^+ [\text{M}+\text{H}]^+$: 552.1169, found 552.1156.

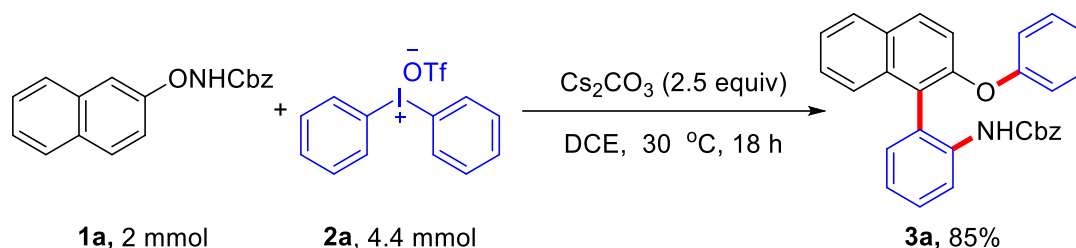
30. benzyl (4-bromo-2-(2-(4-bromophenoxy)-6-phenoxy)naphthalen-1-yl)phenyl)-carbamate (4s')

22% yield; Viscous oily liquid; $R_f = 0.3$ (PE:EA = 15:1); Purified directly by flash

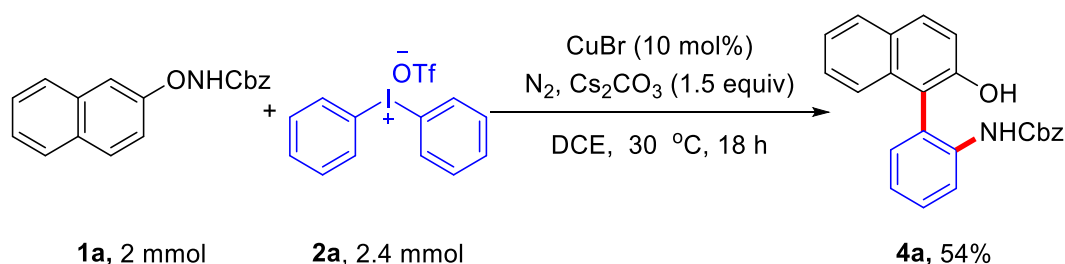


chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (400 MHz, CDCl_3) δ 8.07 (s, 1H), 7.76 (d, $J = 9.0$ Hz, 1H), 7.51 (dd, $J = 9.0, 2.4$ Hz, 1H), 7.41 – 7.37 (m, 2H), 7.37 (d, $J = 2.0$ Hz, 1H), 7.35 – 7.32 (m, 3H), 7.29 – 7.26 (m, 4H), 7.26 (s, 3H), 7.22 (d, $J = 4.3$ Hz, 1H), 7.18 (d, $J = 8.0$ Hz, 1H), 7.08 (dt, $J = 7.8, 1.1$ Hz, 2H), 6.73 – 6.62 (m, 2H), 6.32 (s, 1H), 5.11 – 5.01 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 157.6, 157.0, 154.9, 150.7, 136.4, 136.1, 131.9, 131.3, 130.1, 129.9, 129.6, 129.5, 129.1, 128.9, 128.7, 128.6, 128.29, 128.27, 127.5, 124.3, 123.7, 123.4, 122.9, 121.1, 120.8, 119.23, 119.21, 117.9, 114.3, 66.9; HRMS (ESI) m/z calcd for $[\text{C}_{36}\text{H}_{26}\text{Br}_2\text{NO}_4]^+ [\text{M}+\text{H}]^+$: 696.0203, found 696.0200.

Experimental procedure for large scale reaction

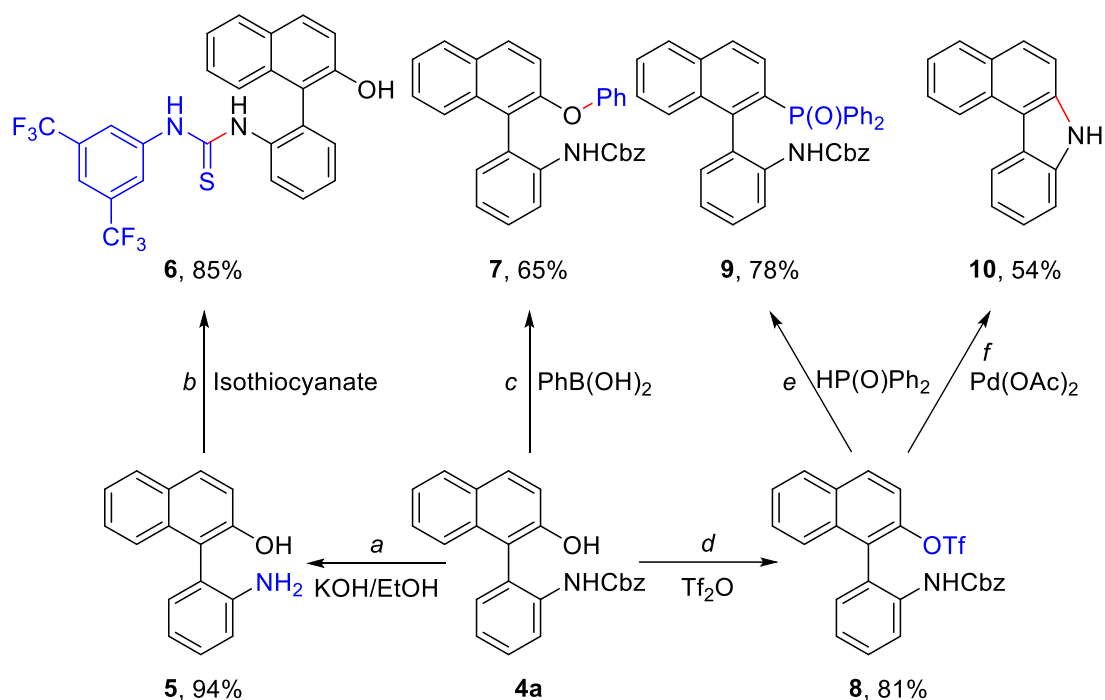


Benzyl(naphthalen-2-yloxy)carbamate (0.59 g, 2 mmol, 1.0 equiv) and diphenyl- λ^3 -iodanyl trifluoromethanesulfonate (4.4 mmol, 2.2 equiv) were dissolved in anhydrous DCE (20 mL) under air atmosphere and Cs_2CO_3 (5 mmol, 2.5 equiv) was added. The resulting mixture was stirred at 30 $^\circ\text{C}$ for 18 hours. After the solvent was removed in vacuum, the residue was purified by flash chromatography (PE/EtOAc = 20/1) to obtain **3a** (0.77 g, 85 %).



Under N_2 atmosphere, A dried flask was charged with Benzyl(naphthalen-2-yloxy)carbamate (0.59 g, 2 mmol, 1.0 equiv), diphenyl- λ^3 -iodanyl trifluoromethanesulfonate (2.4 mmol, 1.2 equiv), Cs_2CO_3 (3 mmol, 1.5 equiv) and CuBr (0.2 mmol, 10 mol%), and the mixture was added anhydrous DCE (20 mL). The mixture was stirred at 30 $^\circ\text{C}$ for 18 hours. The resulting solution was concentrated in vacuo and purified by flash chromatography on silica gel (PE/EtOAc = 10/1) to give **4a** (0.4 g, 54 %).

Synthetic applications of the biaryl products



General Procedure for the Synthesis of **5**⁸.

KOH (2 mmol, 0.132 g, 20 equiv) was added to a solution of **4a** (0.1 mmol, 1.0 equiv) in EtOH (2 mL) in a sealed-tube. The resulting mixture was stirred at 100 °C for 12 hours. After completion of the reaction, the mixture was cooled to room temperature. The solvent was removed in vacuum, and the resulting residue was purified on a silica gel column (PE/EtOAc = 5/1) to provide the desired products **5** (22 mg, 94%).

(a) General Procedure for the Synthesis of **6**⁹.

Compound **5** (0.2 mmol, 1.0 equiv), 3,5-bis(tri-fluoromethyl)phenyl isothiocyanate (1.0 equiv) was dissolved in dry THF (6.0 mL). The reaction mixture was stirred in 30 °C for 12 hours. After completion of the reaction, the solvent was removed in vacuum and was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain the desired product **6** (86 mg, 85%).

(b) General Procedure for the Synthesis of **7**¹⁰.

A solution of **4a** (0.2 mmol, 1.00 equiv), phenylboronic acid (50 mg, 0.4 mmol, 2.0

equiv), copper acetate (37.5 mg, 0.2 mmol, 1.0 equiv) and freshly activated 4 Å molecular sieves (250 mg/mmol) in ethyl acetate (2.0 mL). Then triethylamine (56 µL, 0.4 mmol, 2.0 equiv) was added to the suspension. The reaction mixture was stirred at 30 °C for 12 hours. The residue was purified by column chromatography to give the desired product **7**.

(c) General Procedure for the Synthesis of **8¹¹.**

To a solution of **4a** (0.2 mmol, 73.8 mg) in anhydrous CH₂Cl₂ (2.0 mL) was added triethylamine (34 µL, 0.24 mmol) at 0 °C under nitrogen atmosphere, and then triflic anhydride (0.24 mmol, 1.2 equiv) was slowly added to the mixture. After being stirred 0 °C for 5 minutes, the mixture was concentrated in vacuo. And purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain product **8** (162 mg, 81%).

(d) General Procedure for the Synthesis of **9¹².**

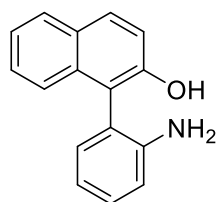
diphenylphosphine oxide (0.2 mmol, 2.0 equiv) was added to a solution of **4a** (0.1 mmol, 1.0 equiv), Pd(OAc)₂ (2.3 mg, 0.1 equiv), 1,3-bis(diphenylphosphino)propane (6.3 mg, 0.10 equiv), and *N,N*-diisopropylethylamine (86 µL, 0.15 equiv) in DMSO (1 mL). The mixture was stirred at 100 °C for 24 hours. After being cooled to room temperature, the mixture was diluted by ethyl acetate and washed with H₂O, the organic layer was washed with brine and dried over sodium sulfate. After the solvent was removed in vacuum, the crude product was purified by flash chromatography (PE/EtOAc = 5/1) to obtain desired product **9** (43 mg, 78%).

(e) General Procedure for the Synthesis of **10¹³.**

8 (0.22 g, 0.43 mmol), Pd(OAc)₂ (13 mg, 10 mol%) and Cs₂CO₃ (315 mg, 1.5 equiv) were combined in a toluene solution (6 mL) and stirred for 12 hours under a refluxing condition. After being cooled to room temperature, after the solvent was removed in vacuum, the crude product was purified by flash chromatography (PE/EtOAc = 10/1) to obtain desired product **10** (50 mg, 54%).

Analysis data of synthetic application products

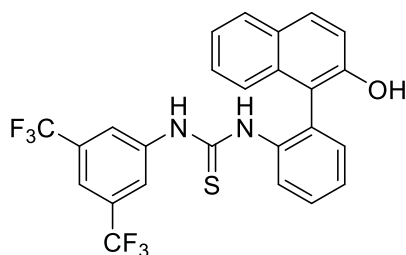
1. 1-(2-aminophenyl)naphthalen-2-ol (5)



5

94% yield; White solid, m.p. = 167-169 °C; R_f = 0.2 (PE:EA = 5:1); Purified directly by flash chromatography on silica gel (5:1, petroleum ether: ethyl acetate); ^1H NMR (500 MHz, CDCl_3) δ 7.76 – 7.73 (m, 2H), 7.38 – 7.34 (m, 1H), 7.31 – 7.20 (m, 4H), 7.10 (dd, J = 7.5, 1.6 Hz, 1H), 6.88 – 6.81 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 151.2, 145.1, 133.0, 132.5, 130.0, 129.9, 129.3, 128.2, 126.7, 124.6, 123.5, 119.5, 118.8, 118.1, 117.2, 116.2; HRMS (ESI) m/z calcd for $[\text{C}_{16}\text{H}_{14}\text{NO}]^+$ $[\text{M}+\text{H}]^+$: 236.1070, found 236.1060.

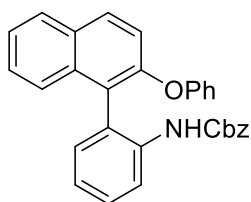
2. 1-(3,5-bis(trifluoromethyl)phenyl)-3-(2-(2-hydroxynaphthalen-1-yl)phenyl)thiourea (6)



6

85% yield; Viscous oily liquid; R_f = 0.2 (PE:EA = 5:1); Purified directly by flash chromatography on silica gel (5:1, petroleum ether: ethyl acetate); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 9.88 – 9.77 (m, 1H), 9.70 (s, 1H), 9.34 (s, 1H), 7.81 – 7.73 (m, 3H), 7.73 – 7.67 (m, 2H), 7.59 (s, 1H), 7.50 (td, J = 7.7, 1.6 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.30 – 7.24 (m, 2H), 7.14 (pd, J = 6.8, 1.6 Hz, 2H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ 179.9, 152.3, 142.0, 137.9, 133.7, 133.0, 132.9, 130.0, 129.8, 129.6, 128.4, 128.3, 128.2, 128.0, 126.7, 126.4, 124.8, 124.7, 123.44, 123.41, 122.8, 122.6, 118.6, 117.9, 116.6; ^{19}F NMR (471 MHz, CDCl_3) δ -62.9; HRMS (ESI) m/z calcd for $[\text{C}_{25}\text{H}_{17}\text{F}_6\text{N}_2\text{OS}]^+$ $[\text{M}+\text{H}]^+$: 507.0960, found 507.0957.

3. benzyl (2-(2-phenoxy-naphthalen-1-yl)phenyl)carbamate (7)

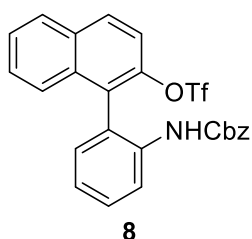


7

65% yield; Viscous oily liquid; R_f = 0.3 (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (500 MHz, CDCl_3) δ 8.08 (s, 1H), 7.85 – 7.75 (m, 2H), 7.39 – 7.30 (m, 4H), 7.21 (td,

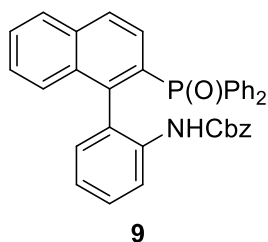
$J = 5.1, 2.5$ Hz, 3H), 7.16 (dd, $J = 8.3, 3.1$ Hz, 3H), 7.13 – 7.06 (m, 3H), 7.03 (td, $J = 7.4, 1.2$ Hz, 1H), 6.94 – 6.88 (m, 1H), 6.77 – 6.71 (m, 2H), 6.36 (s, 1H), 5.02 – 4.91 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 157.5, 153.4, 151.7, 136.4, 136.1, 133.6, 131.4, 130.9, 130.5, 129.6, 129.1, 128.9, 128.7, 128.5, 128.3, 128.24, 128.23, 127.2, 125.4, 125.3, 123.9, 123.4, 123.0, 119.9, 118.2, 66.8; HRMS (ESI) m/z calcd for $[\text{C}_{30}\text{H}_{24}\text{NO}_3]^+ [\text{M}+\text{H}]^+$: 446.1751, found 446.1753.

4. 1-(2-(((benzyloxy)carbonyl)amino)phenyl)naphthalen-2-yl trifluoromethanesulfonate (8)



81% yield; Viscous oily liquid; $R_f = 0.3$ (PE:EA = 15:1); Purified directly by flash chromatography on silica gel (20:1, petroleum ether: ethyl acetate); ^1H NMR (500 MHz, CDCl_3) δ 8.27 (s, 1H), 8.04 (dd, $J = 29.2, 8.6$ Hz, 2H), 7.63 (dd, $J = 9.7, 4.8$ Hz, 2H), 7.57 (dt, $J = 8.9, 3.1$ Hz, 2H), 7.52 (t, $J = 7.6$ Hz, 1H), 7.37 – 7.31 (m, 5H), 7.26 (dd, $J = 6.3, 2.9$ Hz, 2H), 6.27 (d, $J = 5.0$ Hz, 1H), 5.18 – 5.05 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.5, 144.9, 136.6, 136.0, 132.74, 132.68, 131.5, 131.4, 130.2, 128.52, 128.49, 128.4, 128.3, 128.2, 128.1, 127.5, 126.3, 124.2, 121.8, 119.7, 119.6, 117.2, 66.9; ^{19}F NMR (471 MHz, CDCl_3) δ -74.1; HRMS (ESI) m/z calcd for $[\text{C}_{25}\text{H}_{19}\text{F}_3\text{NO}_5\text{S}]^+ [\text{M}+\text{H}]^+$: 502.0931, found 502.0942.

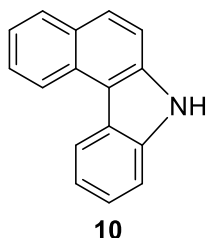
5. benzyl (2-(2-(diphenylphosphoryl)naphthalen-1-yl)phenyl)carbamate (9)



78% yield; Viscous oily liquid; $R_f = 0.3$ (PE:EA = 2:1); Purified directly by flash chromatography on silica gel (5:1, petroleum ether: ethyl acetate); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 8.44 (s, 1H), 8.05 (dd, $J = 13.0, 8.4$ Hz, 2H), 7.78 (dd, $J = 11.6, 7.6$ Hz, 2H), 7.64 (t, $J = 7.6$ Hz, 1H), 7.54 (dt, $J = 15.5, 7.7$ Hz, 3H), 7.44 (dq, $J = 18.6, 9.5, 8.5$ Hz, 5H), 7.33 (ddd, $J = 20.6, 11.0, 8.0$ Hz, 3H), 7.27 – 7.23 (m, 3H), 7.20 (t, $J = 7.8$ Hz, 1H), 7.14 – 7.07 (m, 3H), 6.75 (t, $J = 7.5$ Hz, 1H), 6.65 (d, $J = 7.7$ Hz, 1H), 4.93 (s, 2H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ 154.3, 142.7, 137.1, 137.0, 135.0, 133.0, 132.8, 132.7, 132.5, 132.1, 132.0, 131.9, 131.8, 131.3, 131.2, 130.1, 129.0, 128.9, 128.8, 128.72, 128.70, 128.6, 128.5, 128.4,

128.2, 127.8, 127.7, 126.5, 124.0, 65.8; ^{31}P NMR (202 MHz, CDCl_3): δ 27.1; HRMS (ESI) m/z calcd for $[\text{C}_{36}\text{H}_{29}\text{NO}_3\text{P}]^+ [\text{M}+\text{H}]^+$: 554.1880, found 554.1881.

6. 7*H*-benzo[*c*]carbazole (10)



54% yield; Brown solid, m.p. = 166-169 °C; R_f = 0.2 (PE:EA = 5:1); Purified directly by flash chromatography on silica gel (10:1, petroleum ether: ethyl acetate); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 9.43 (s, 1H), 7.80 (t, J = 8.8 Hz, 2H), 7.32 – 7.23 (m, 4H), 7.12 (td, J = 7.7, 1.7 Hz, 1H), 6.91 (dd, J = 7.5, 1.7 Hz, 1H), 6.85 – 6.77 (m, 1H), 6.69 (td, J = 7.3, 1.2 Hz, 1H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ 152.7, 146.7, 133.9, 132.0, 129.2, 128.7, 128.42, 128.36, 126.5, 124.7, 122.9, 121.3, 119.0, 118.4, 116.8, 115.3; HRMS (ESI) m/z calcd for $[\text{C}_{16}\text{H}_{12}\text{N}]^+ [\text{M}+\text{H}]^+$: 218.0964, found 218.0971.

References

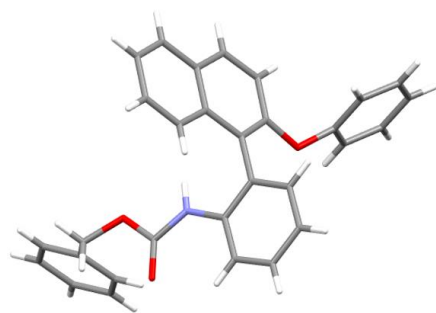
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X-ray crystal structure data for compound 3a and 4a

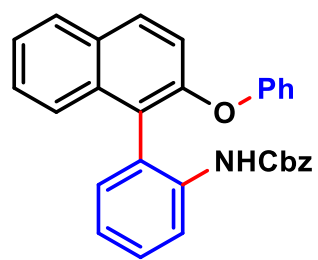
Single crystal was chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) to prevent decomposition. Intensity data and cell parameters were recorded at 173 K on a Bruker Apex II single crystal diffractometer, employing a Mo K α radiation (λ = 0.71073 Å) and a CCD area detector. The raw frame data were processed using SAINT and SADABS to yield the reflection data file.¹ The structure was solved using the charge-flipping algorithm, as implemented in the program *SUPERFLIP*² and refined by full-matrix least-squares techniques against F_o^2 using the SHELXL program³ through the OLEX2 interface.⁴ Hydrogen atoms at carbon were placed in calculated positions and refined isotropically by using a riding model. Appropriate restraints or constraints were applied to the geometry and the atomic displacement parameters of the atoms in the cluster. All structures were examined using the Addsym subroutine of PLATON⁵ to ensure that no additional symmetry could be applied to the models. CCDC **2049890** (**3a**) and CCDC **2049893** (**4a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

References

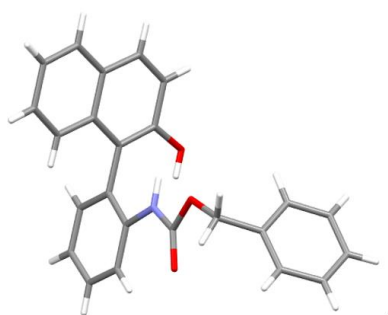
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5. A. L. Spek, *Acta. Crystallogr. Sect. D.*, 2009, **65**, 148-155.



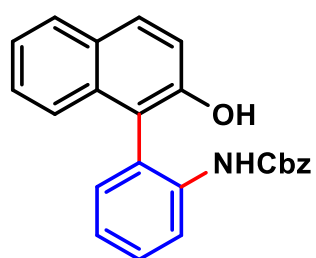
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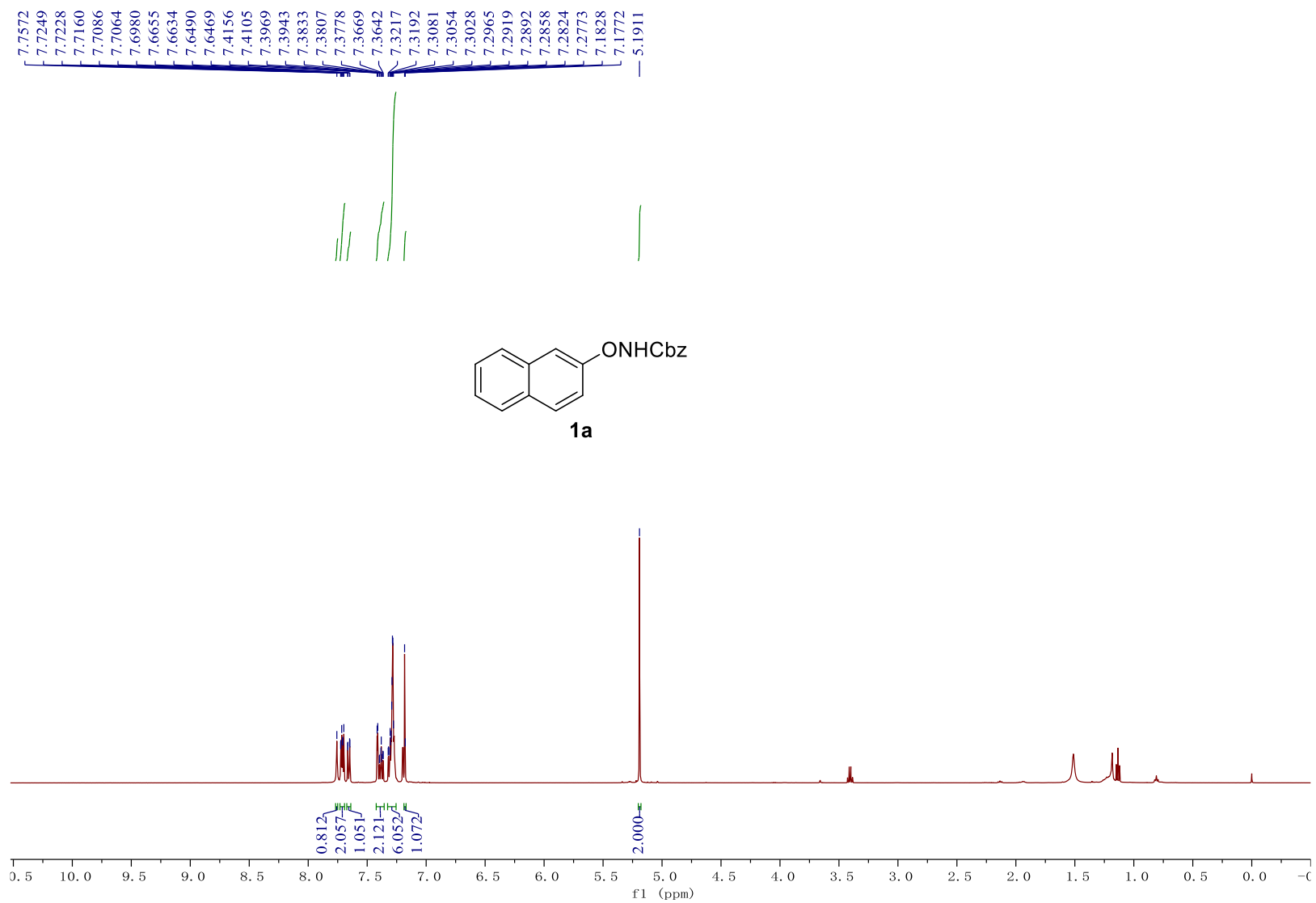
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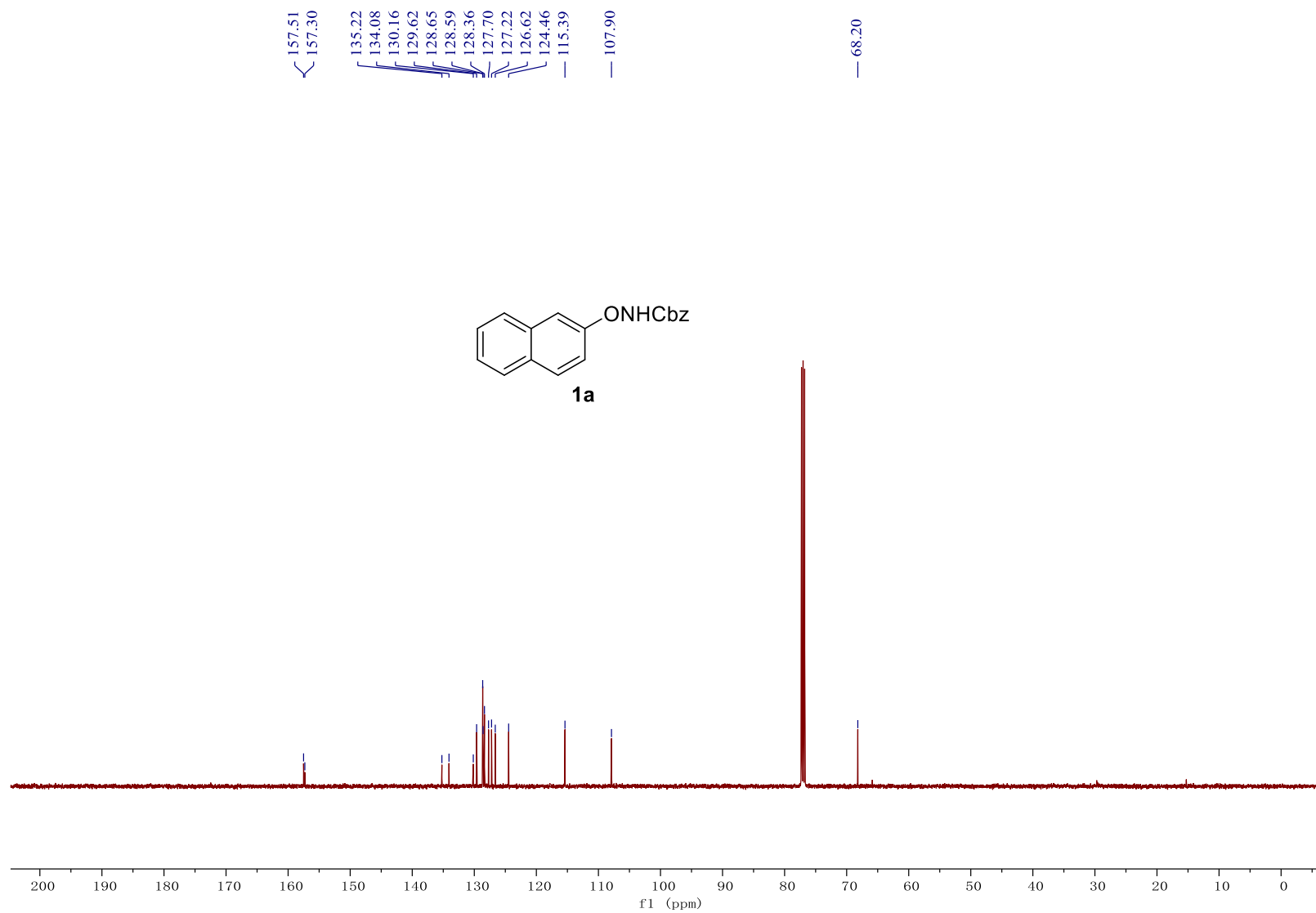
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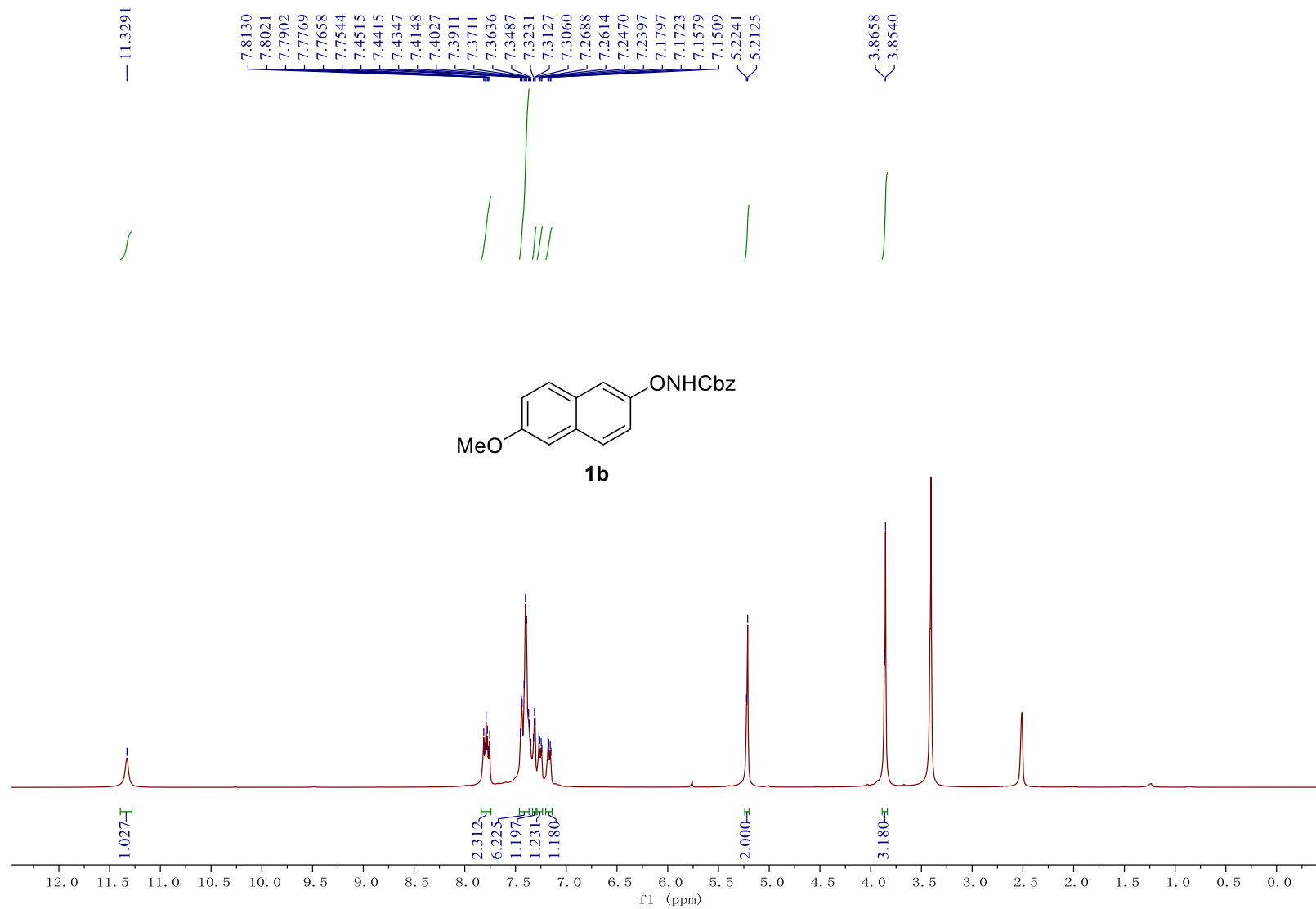
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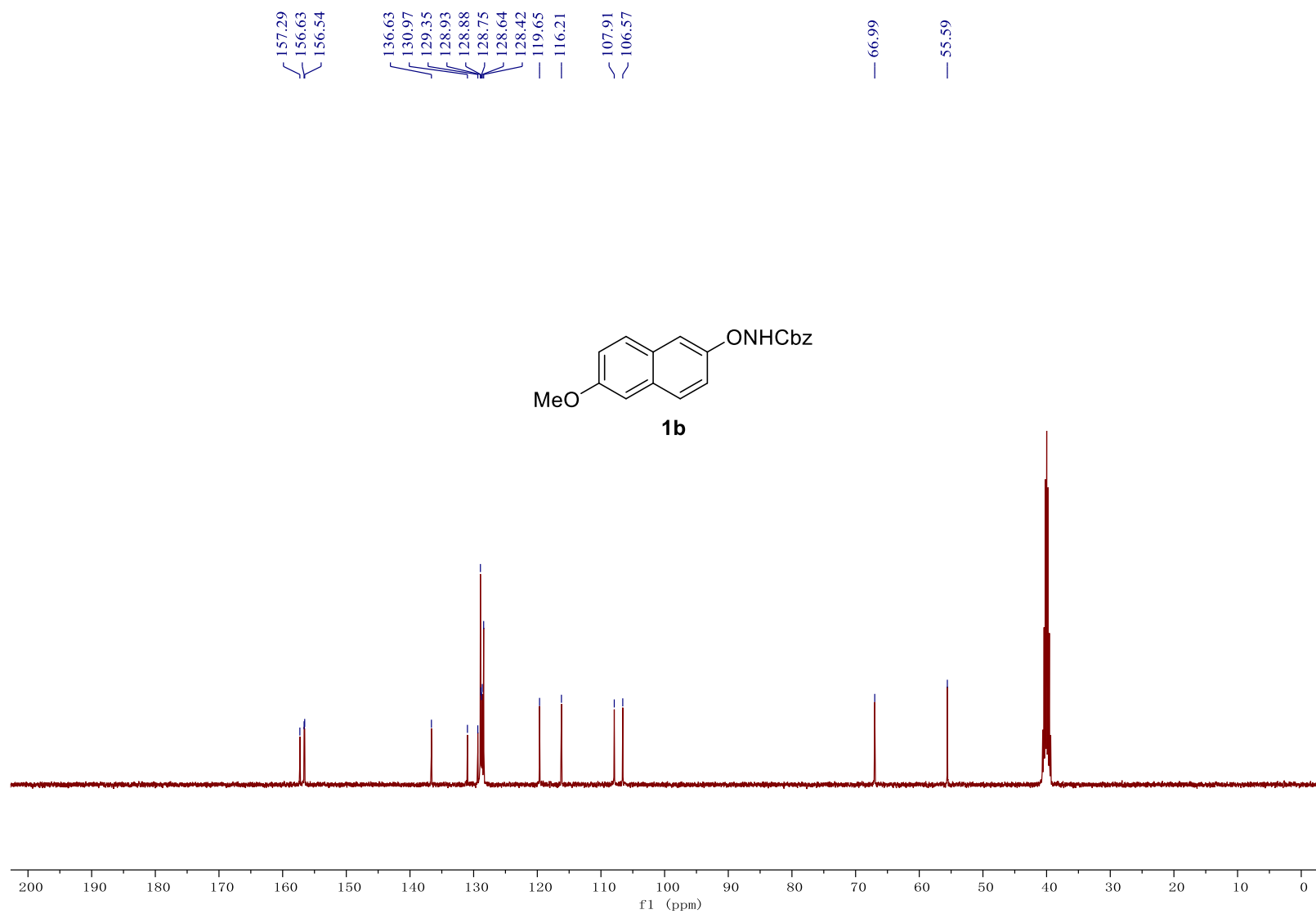


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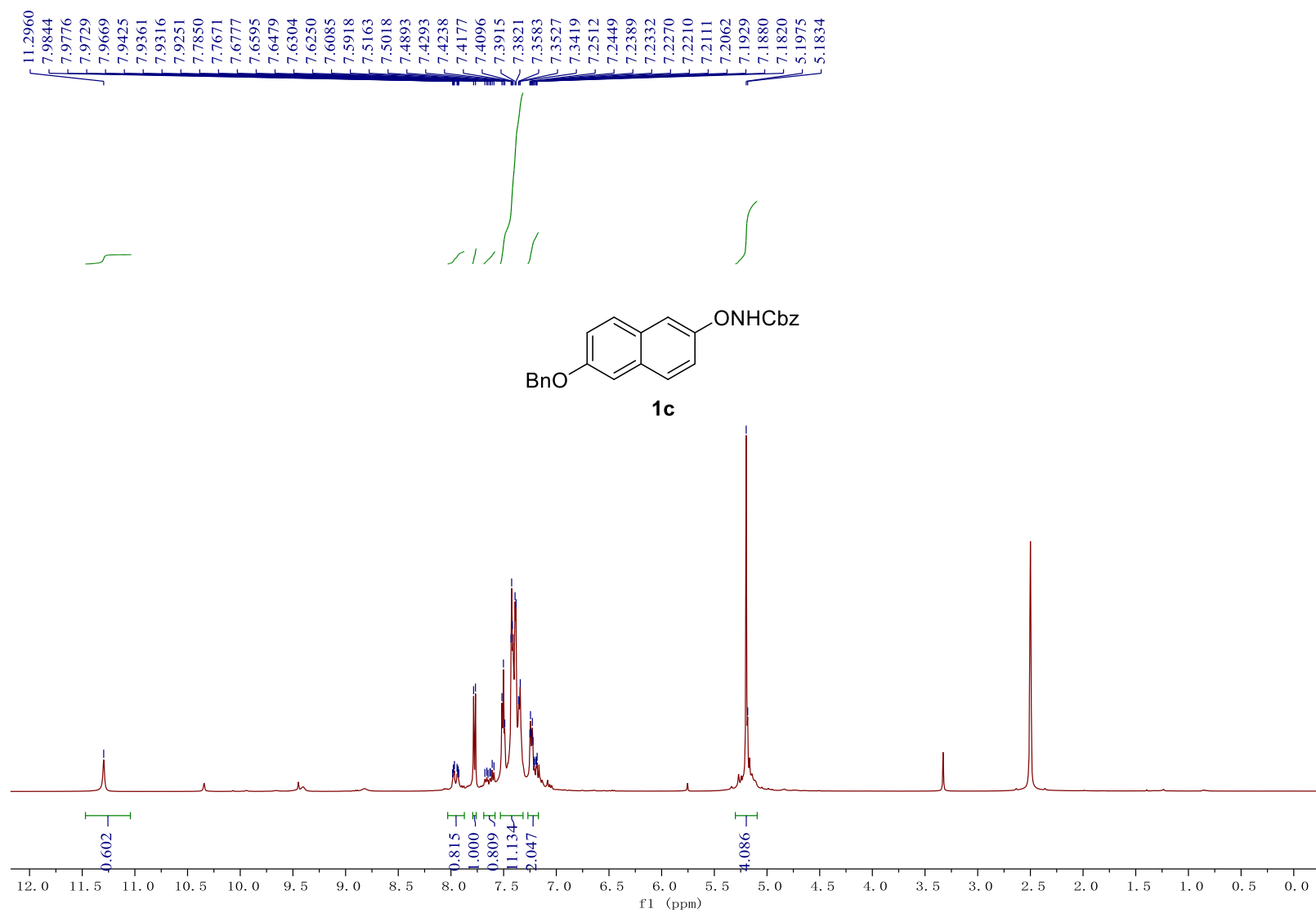


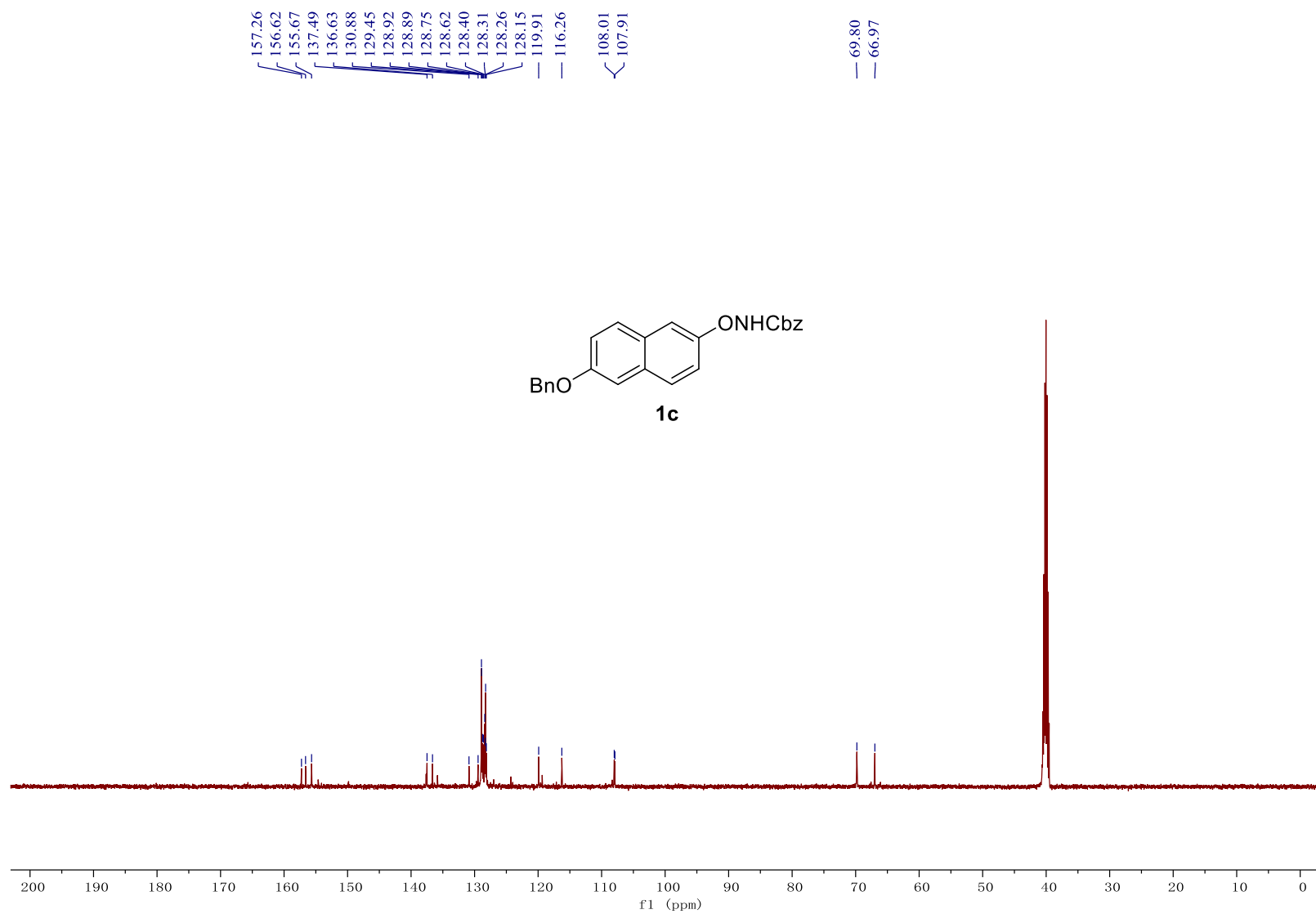
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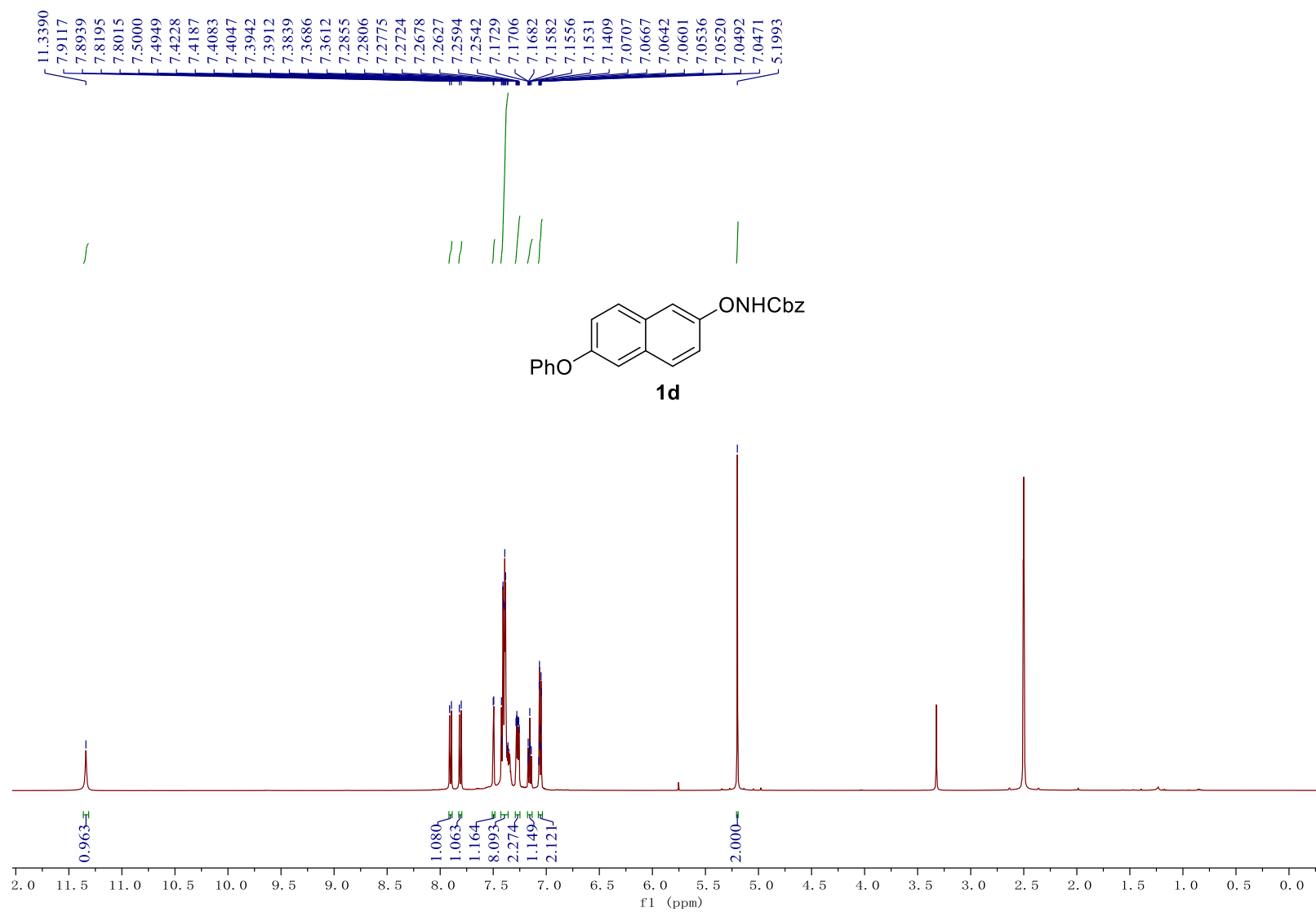


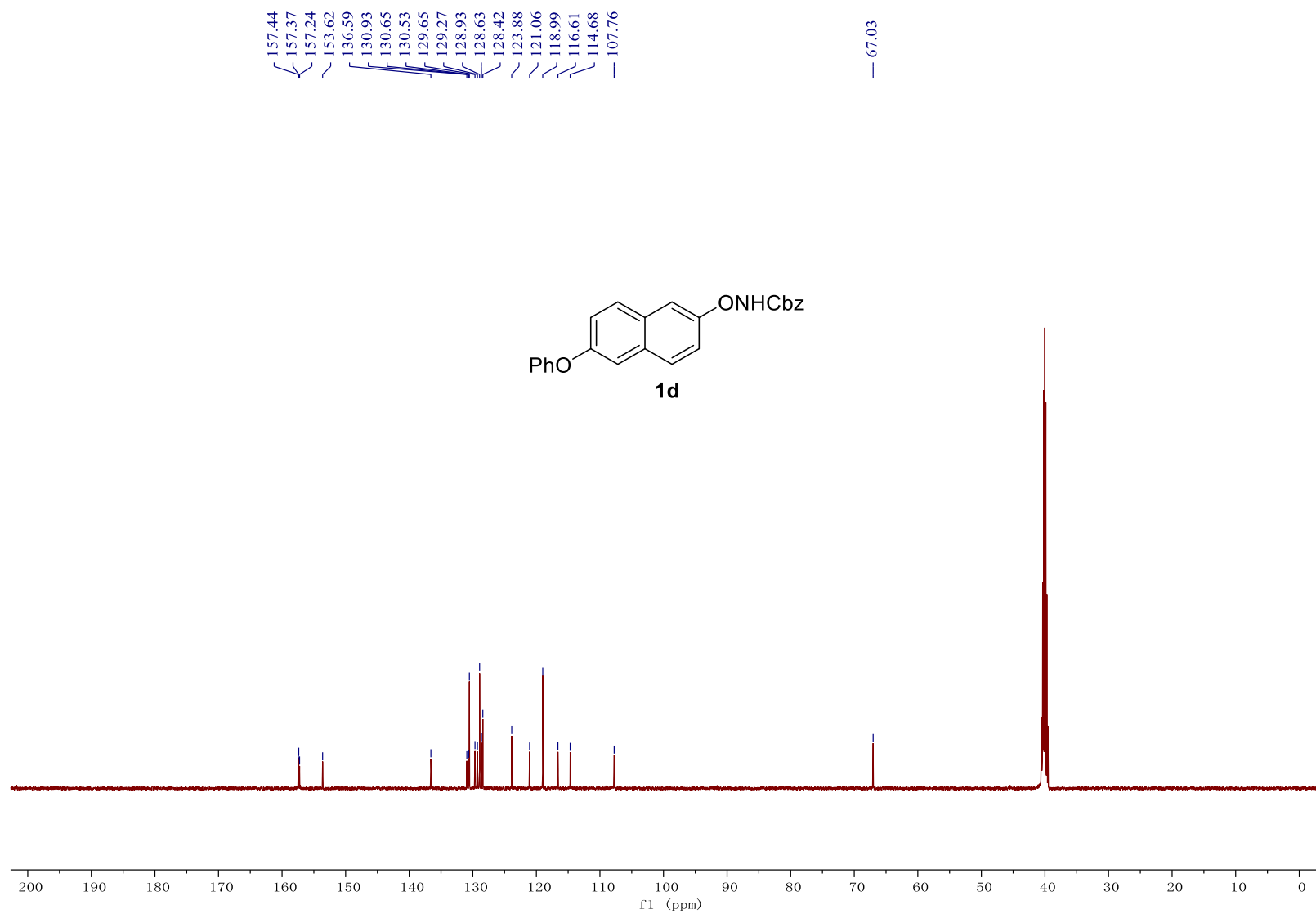


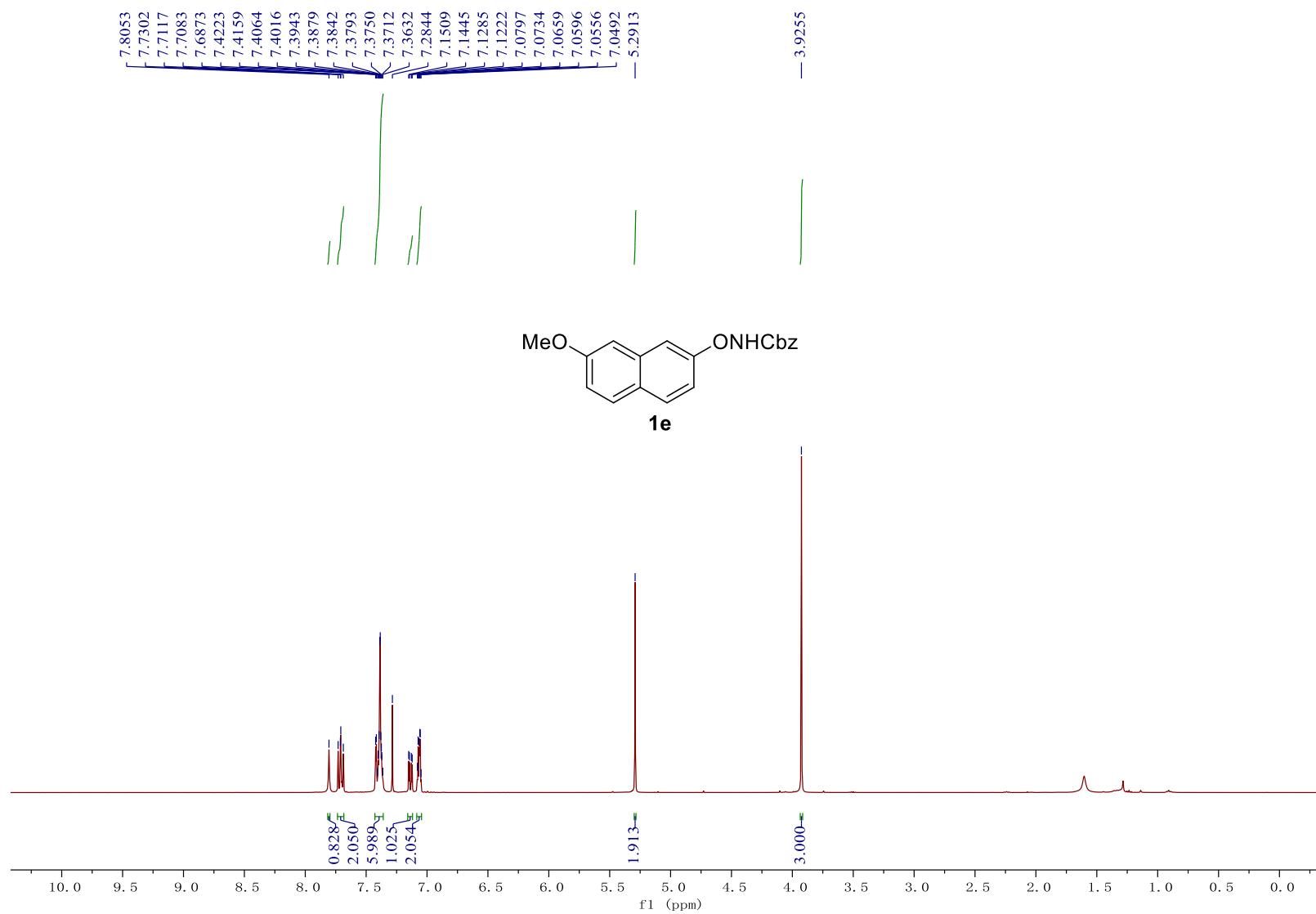
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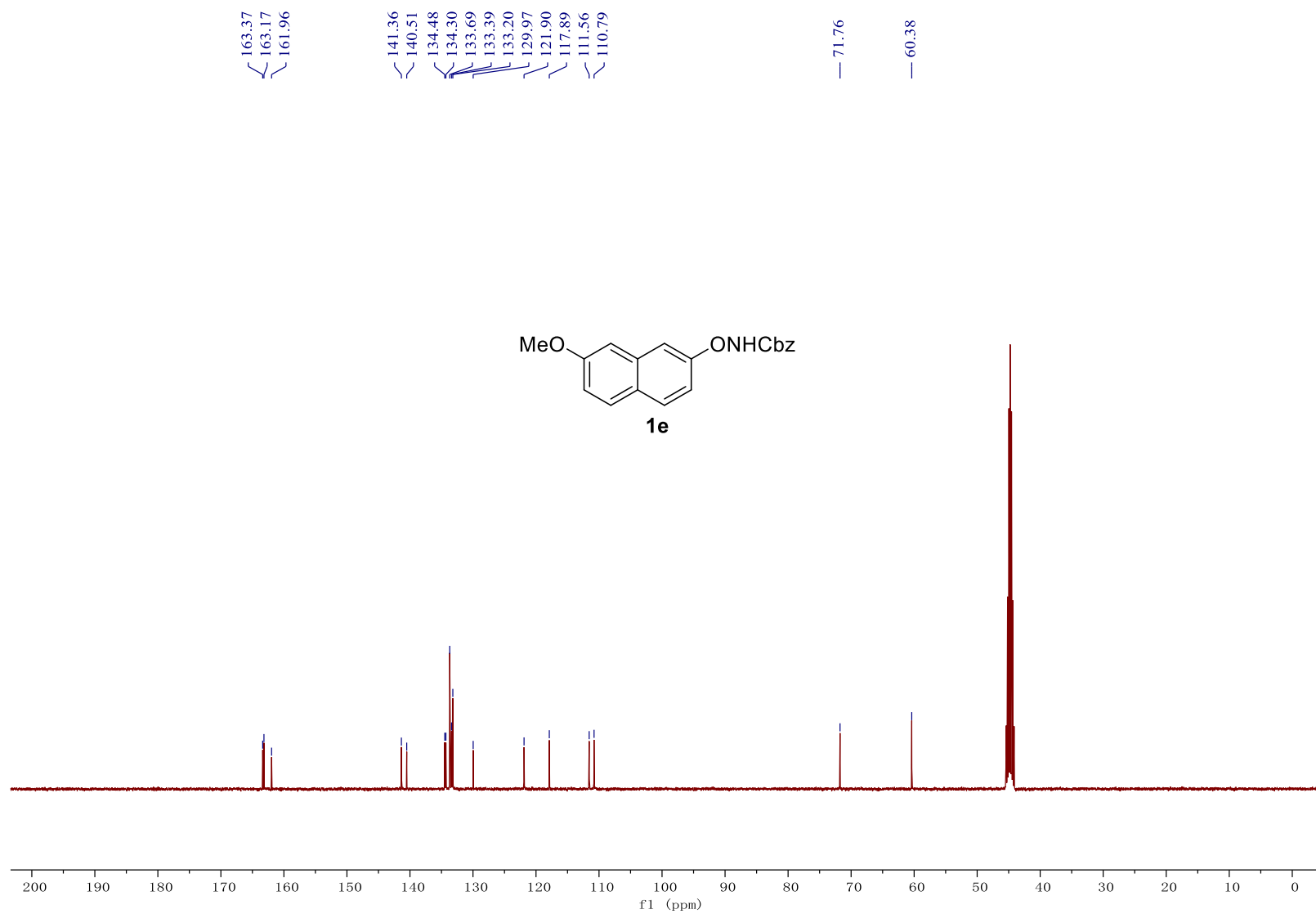




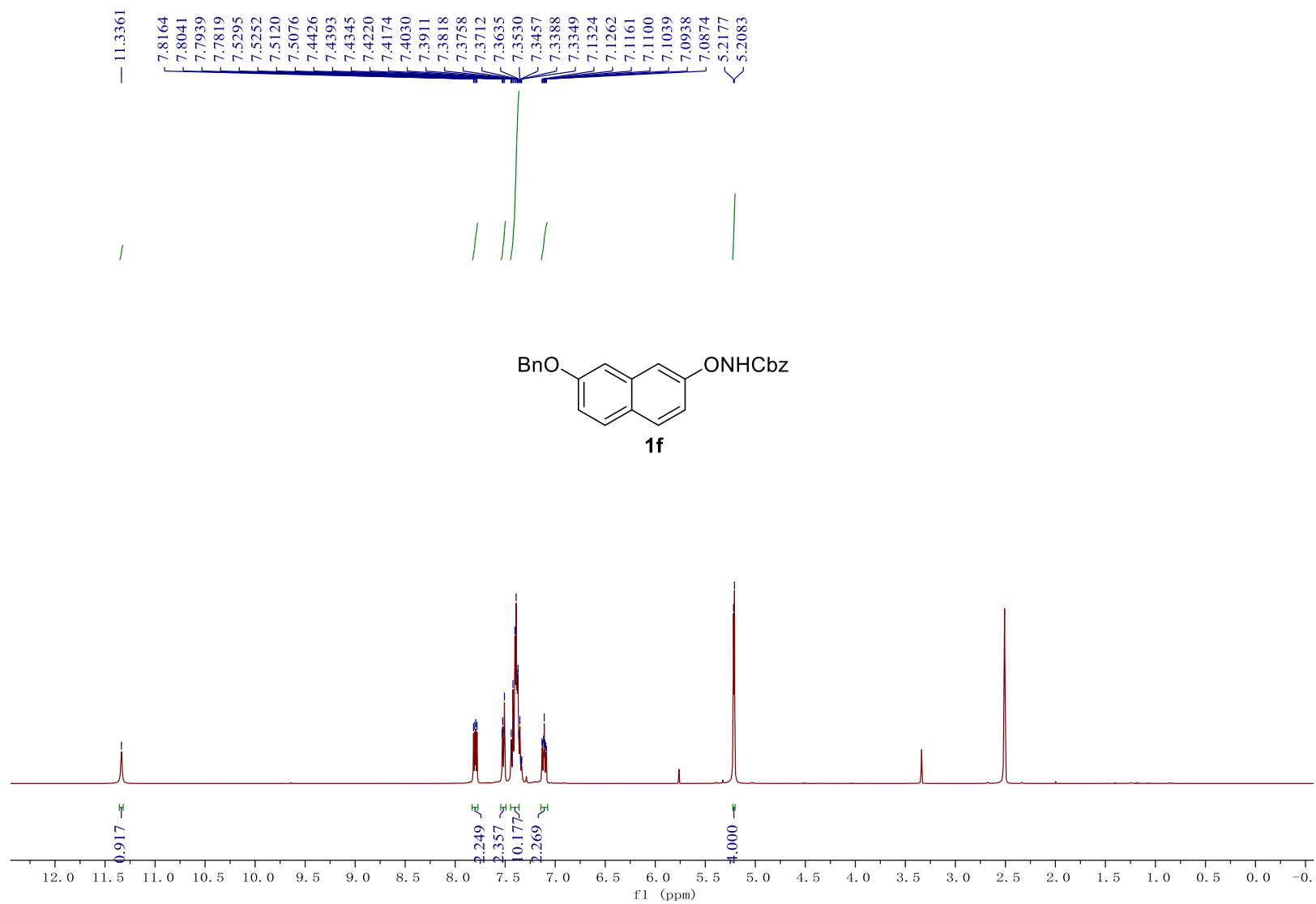




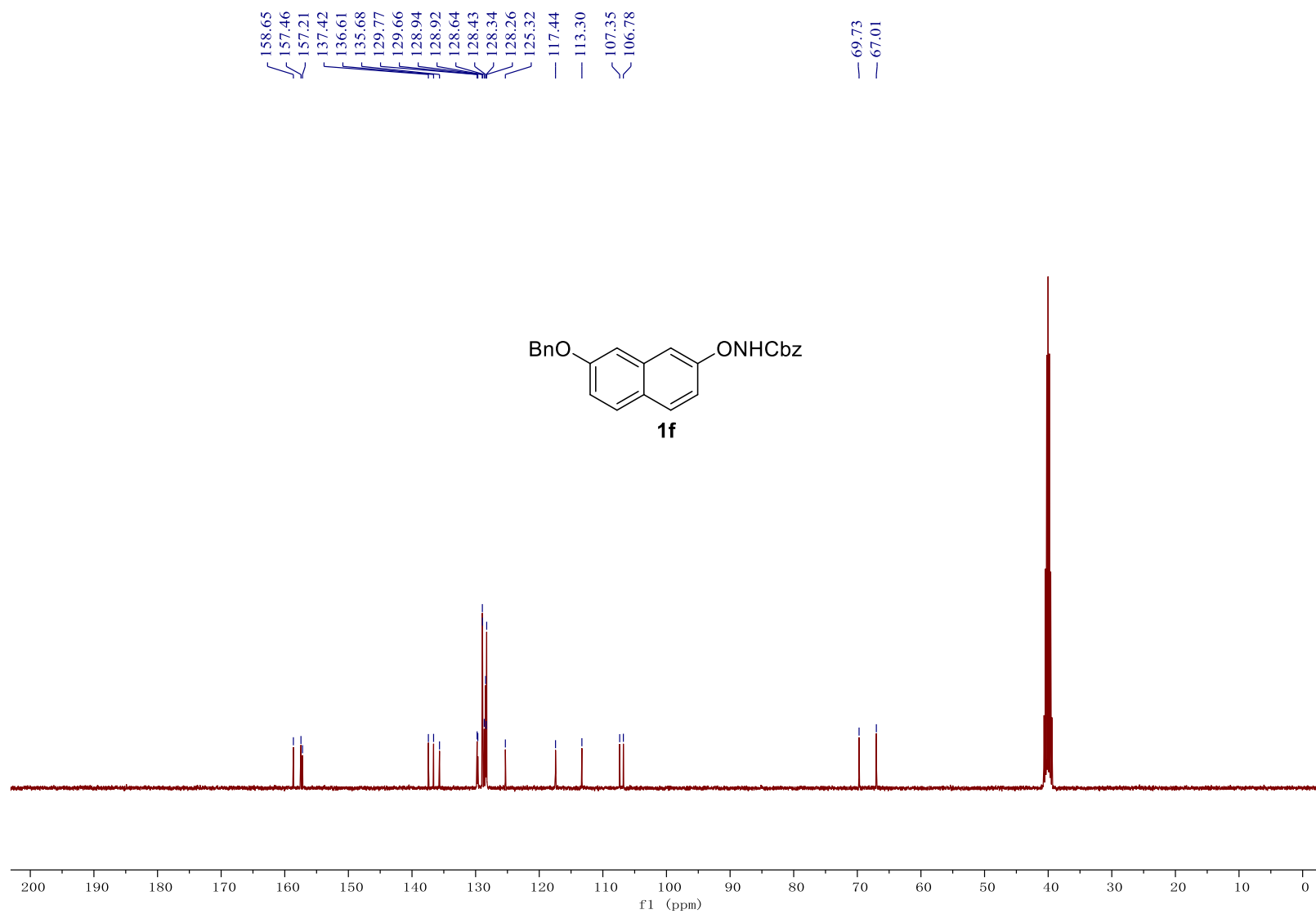
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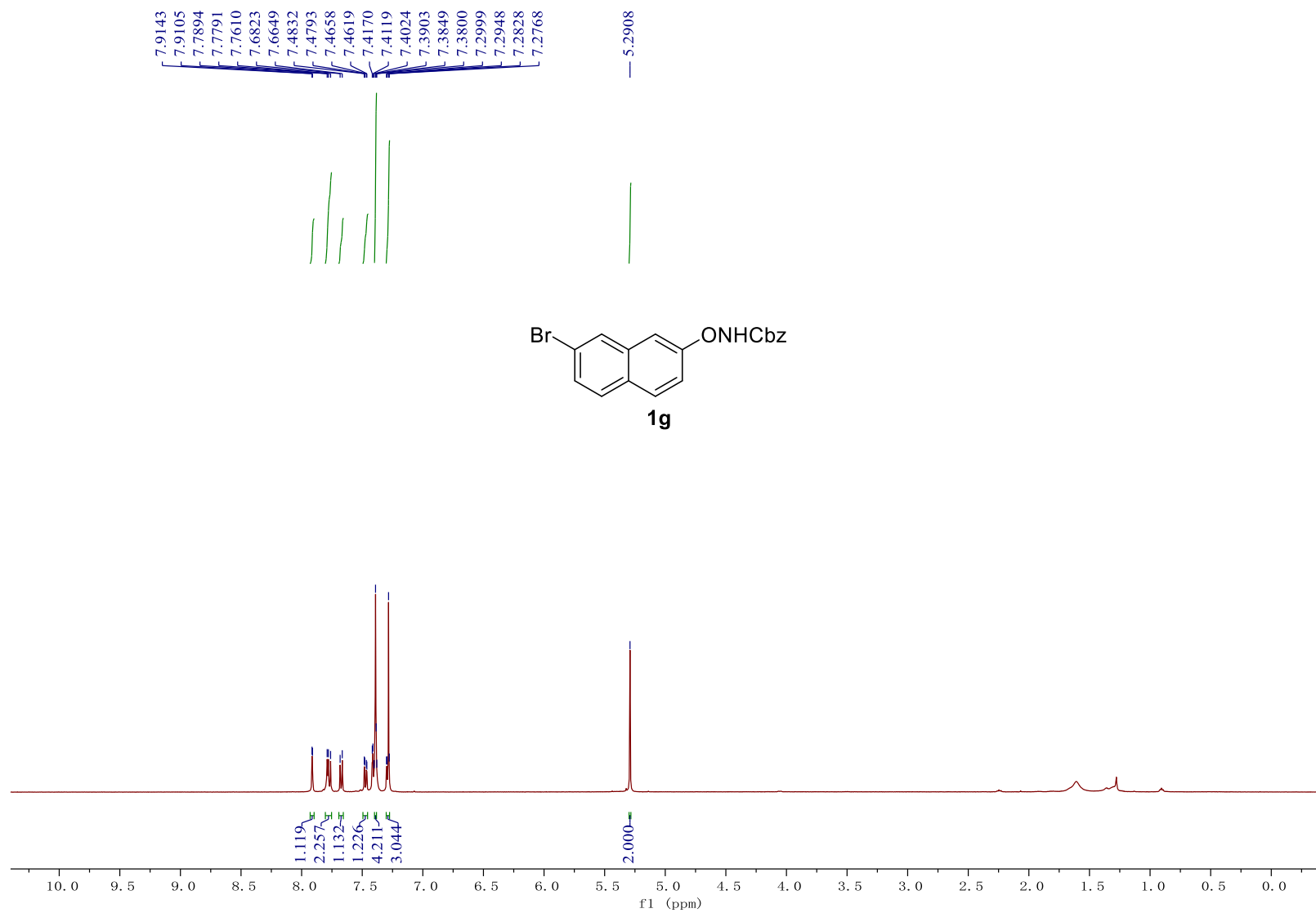
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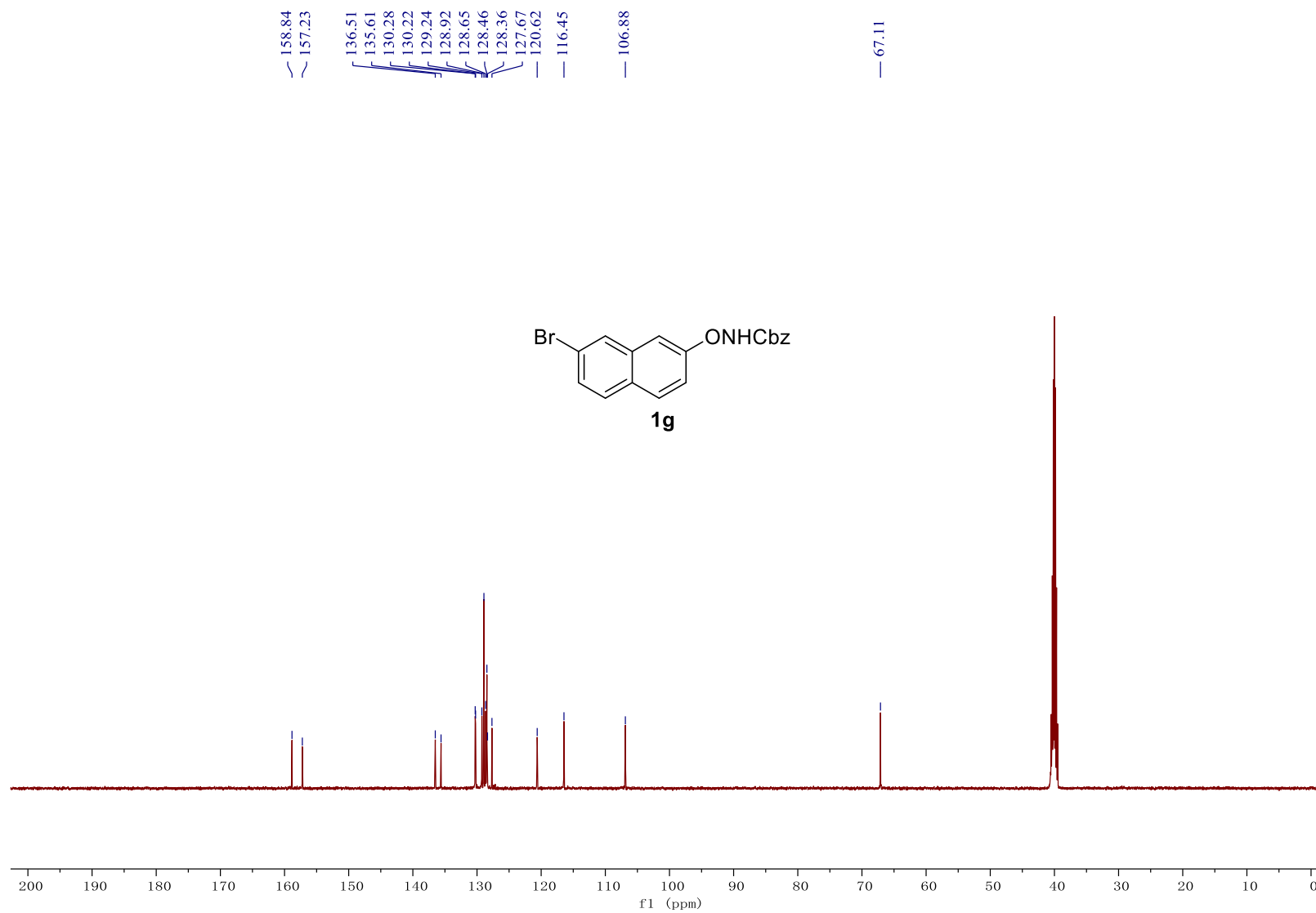
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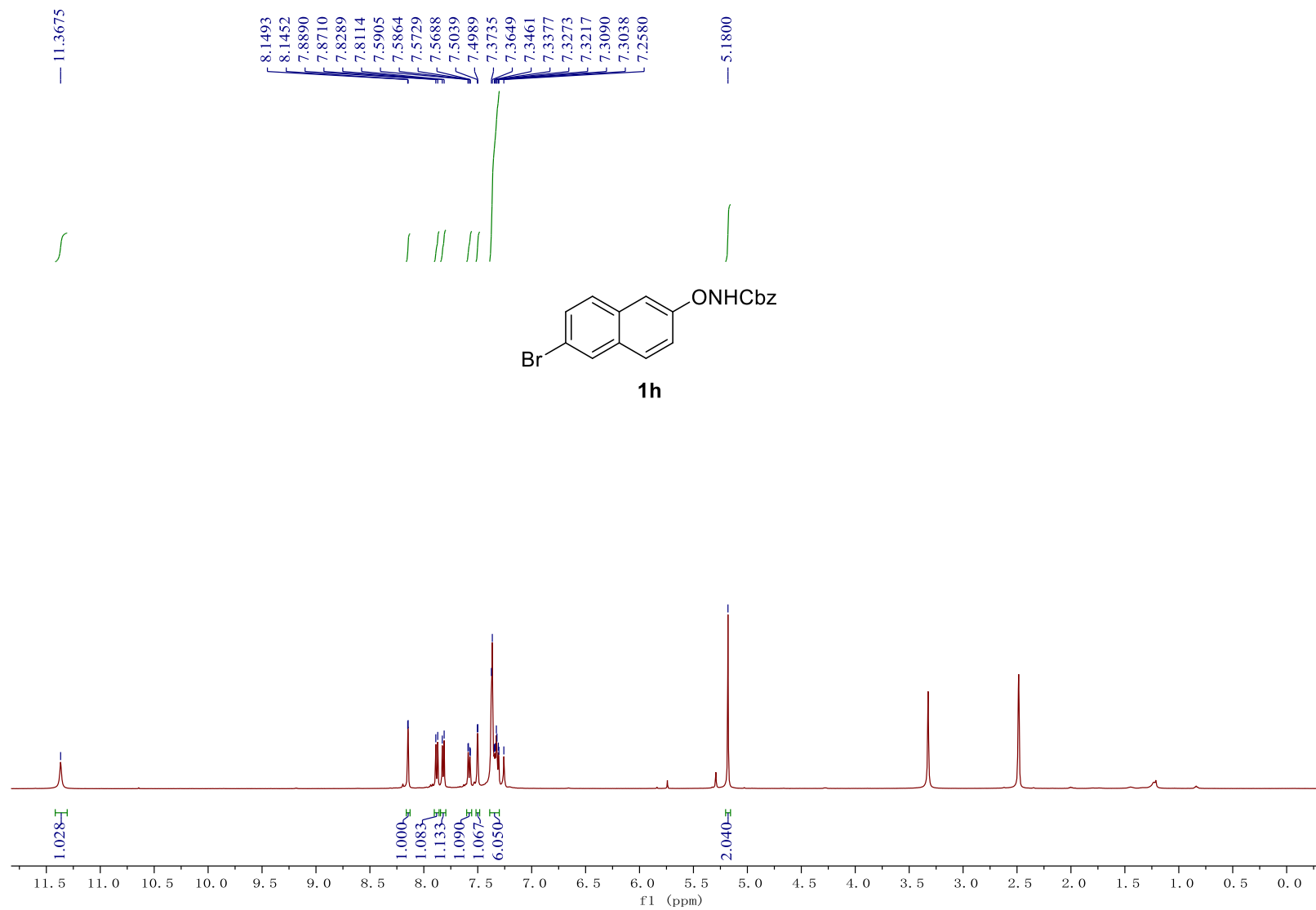
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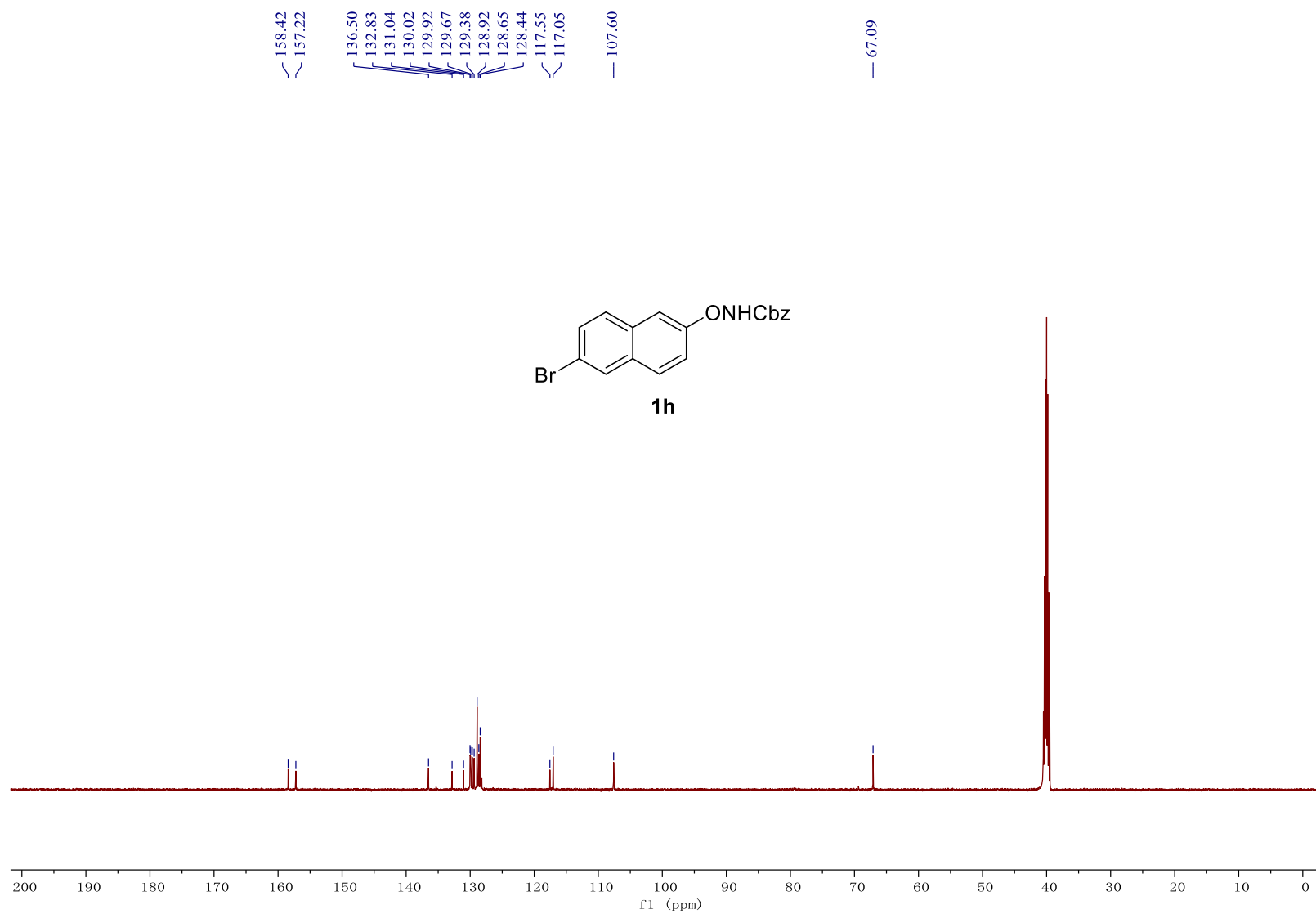


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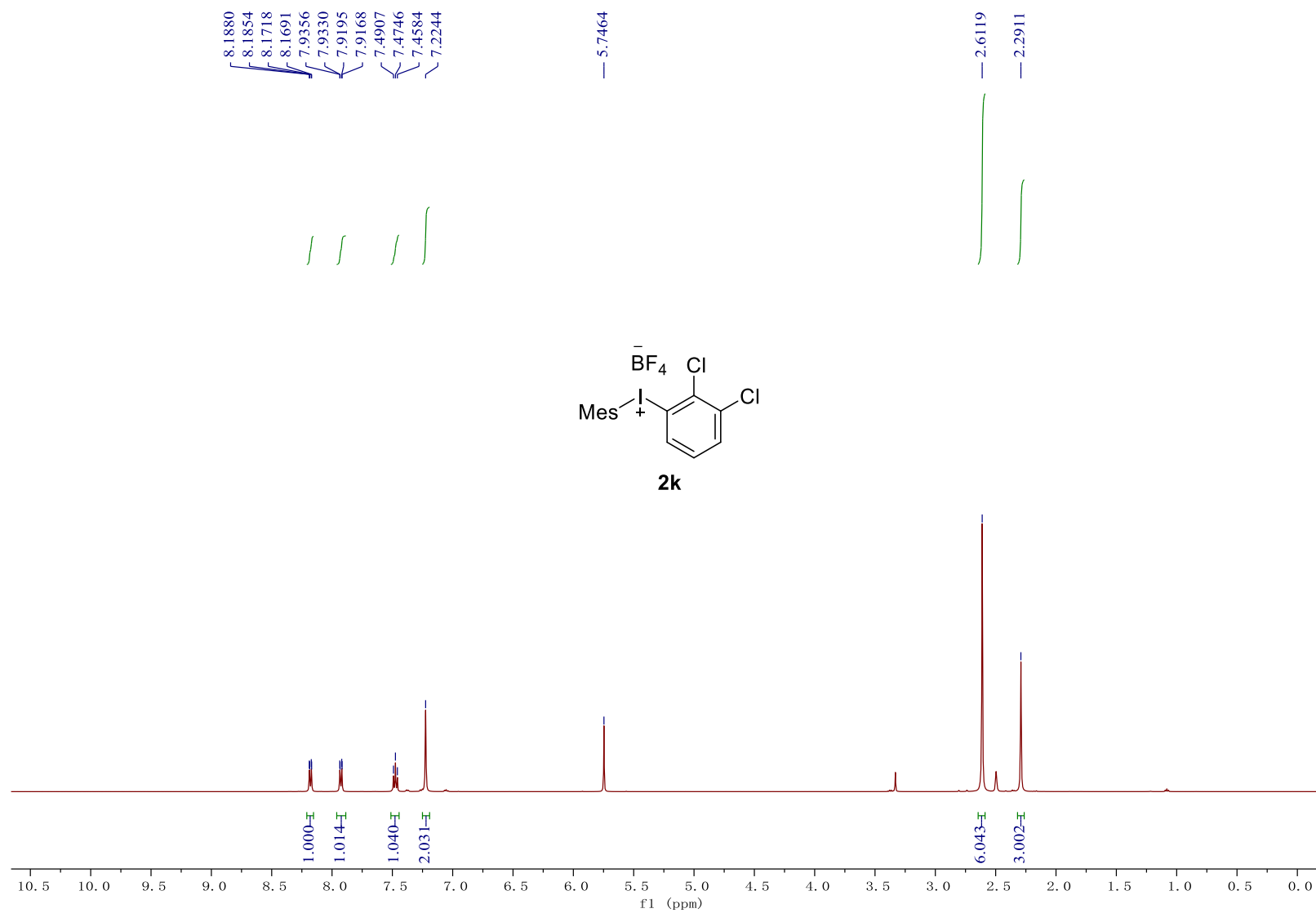


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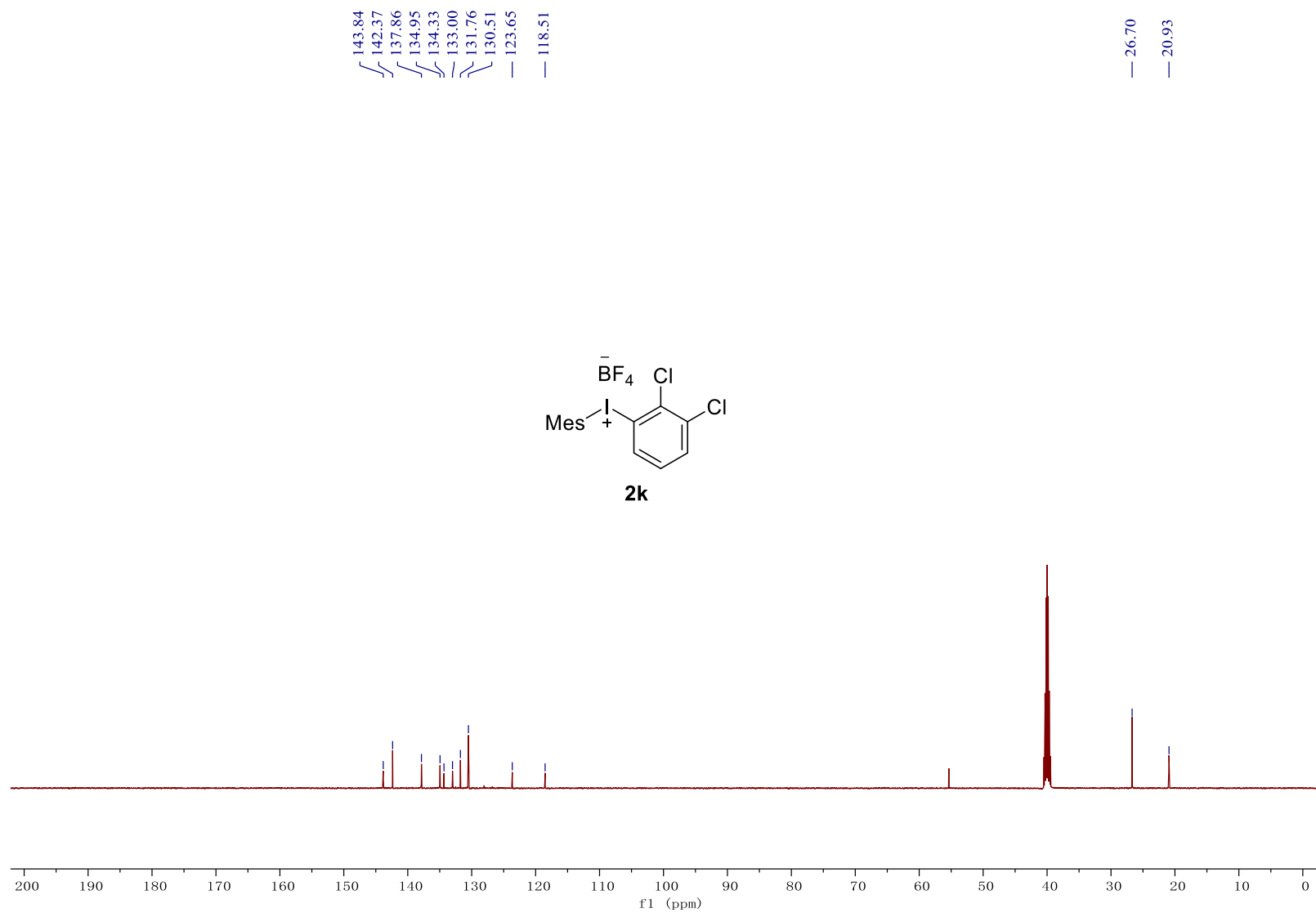




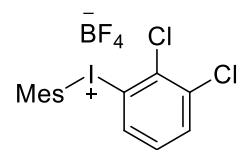
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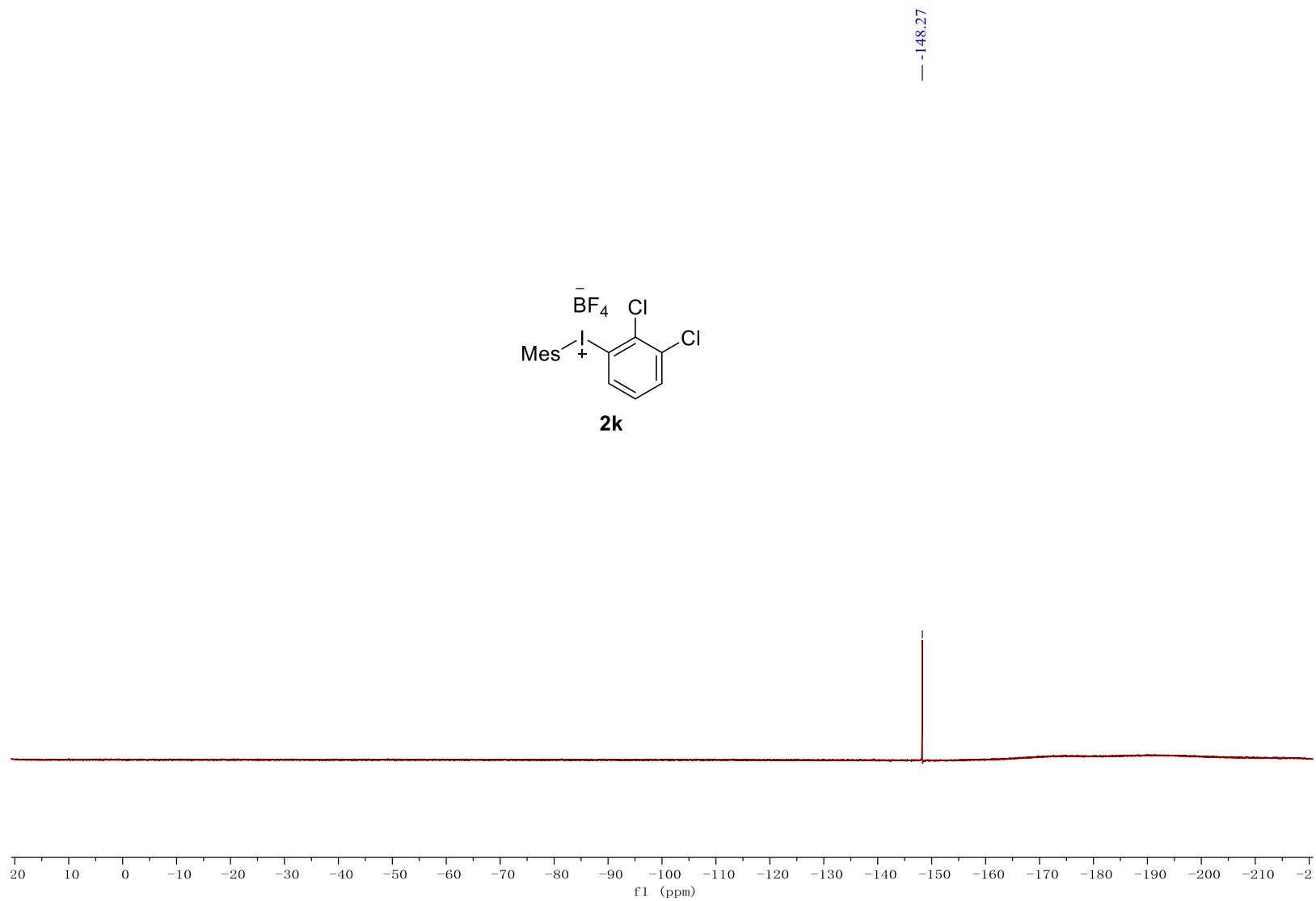
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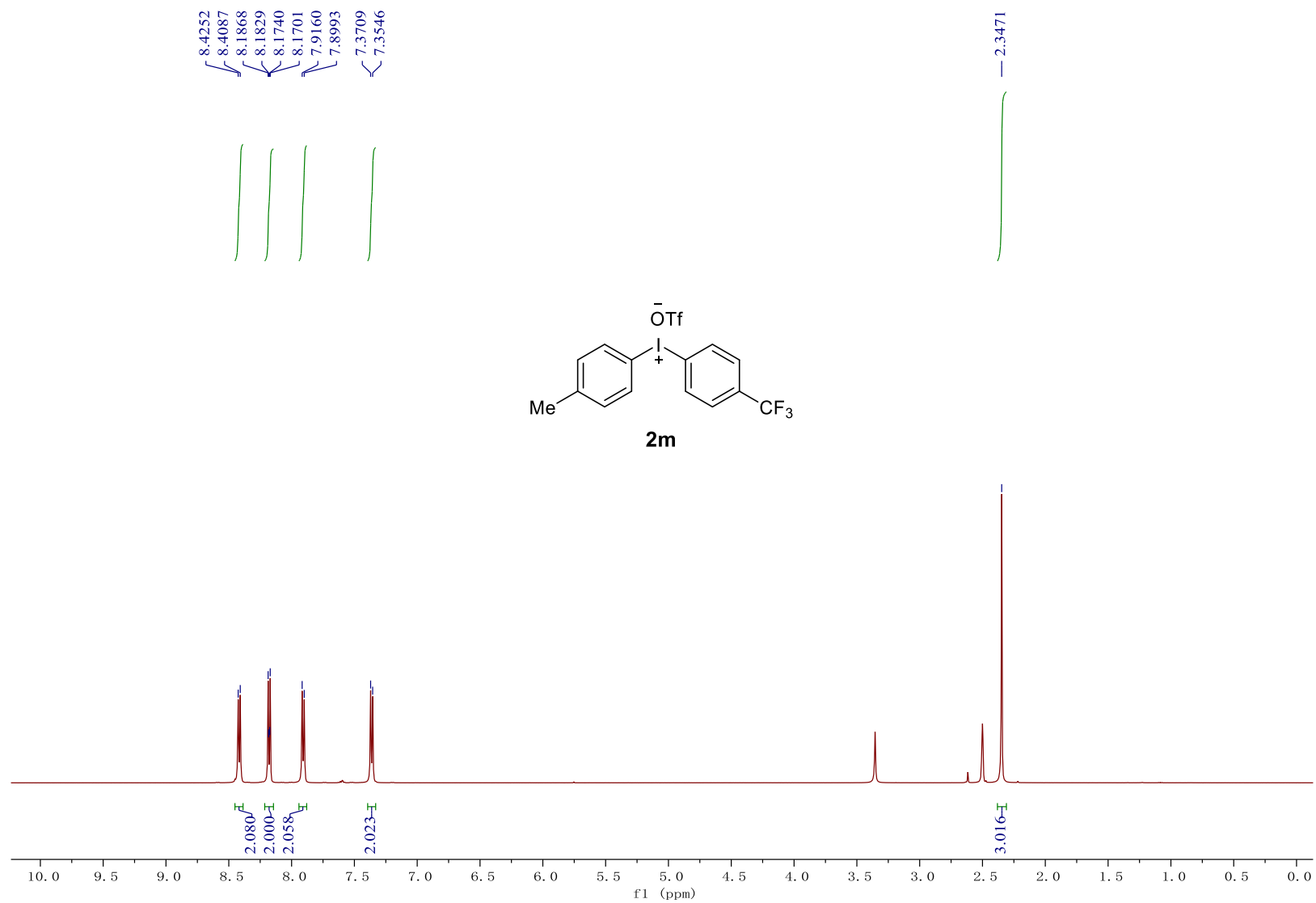


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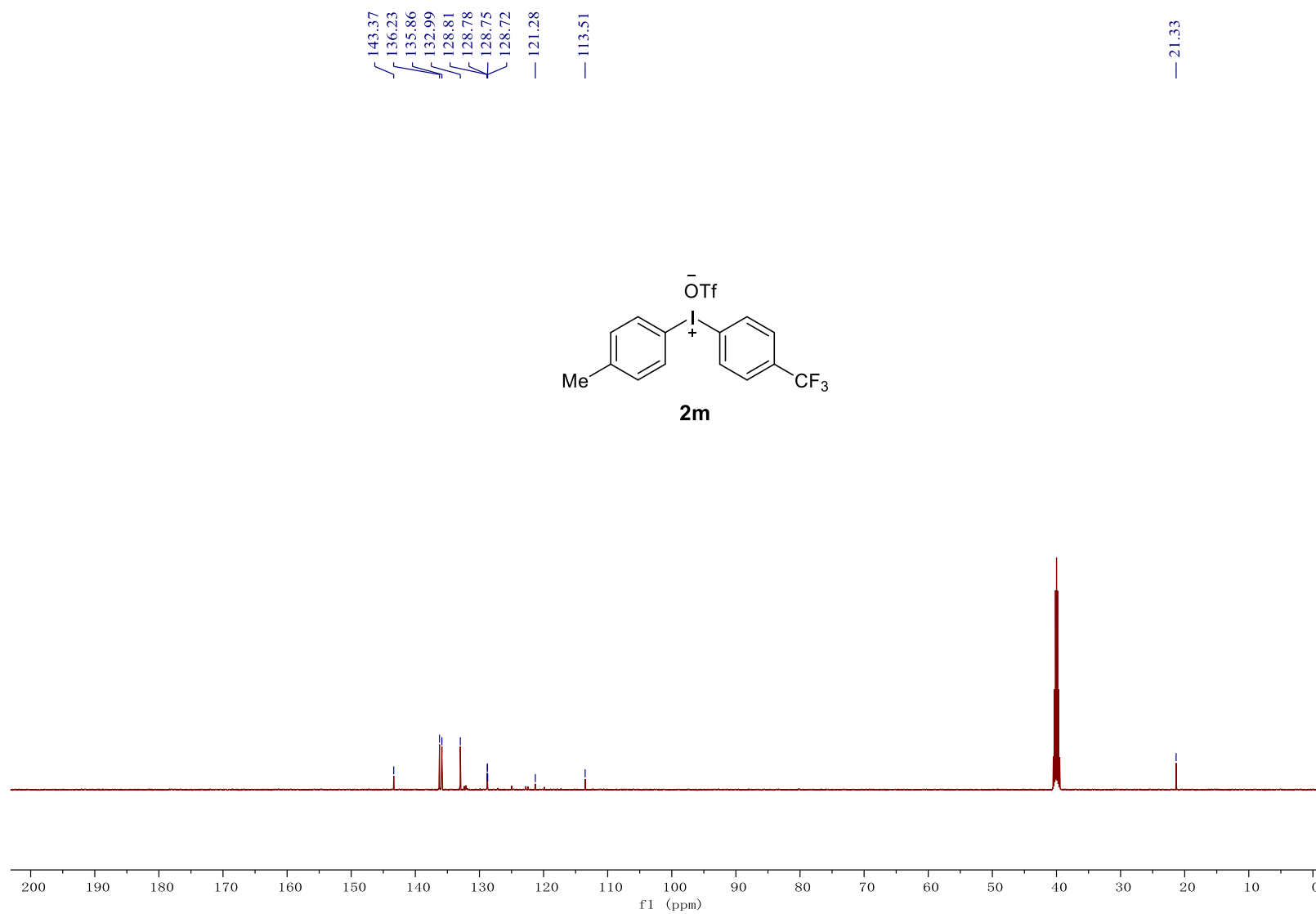


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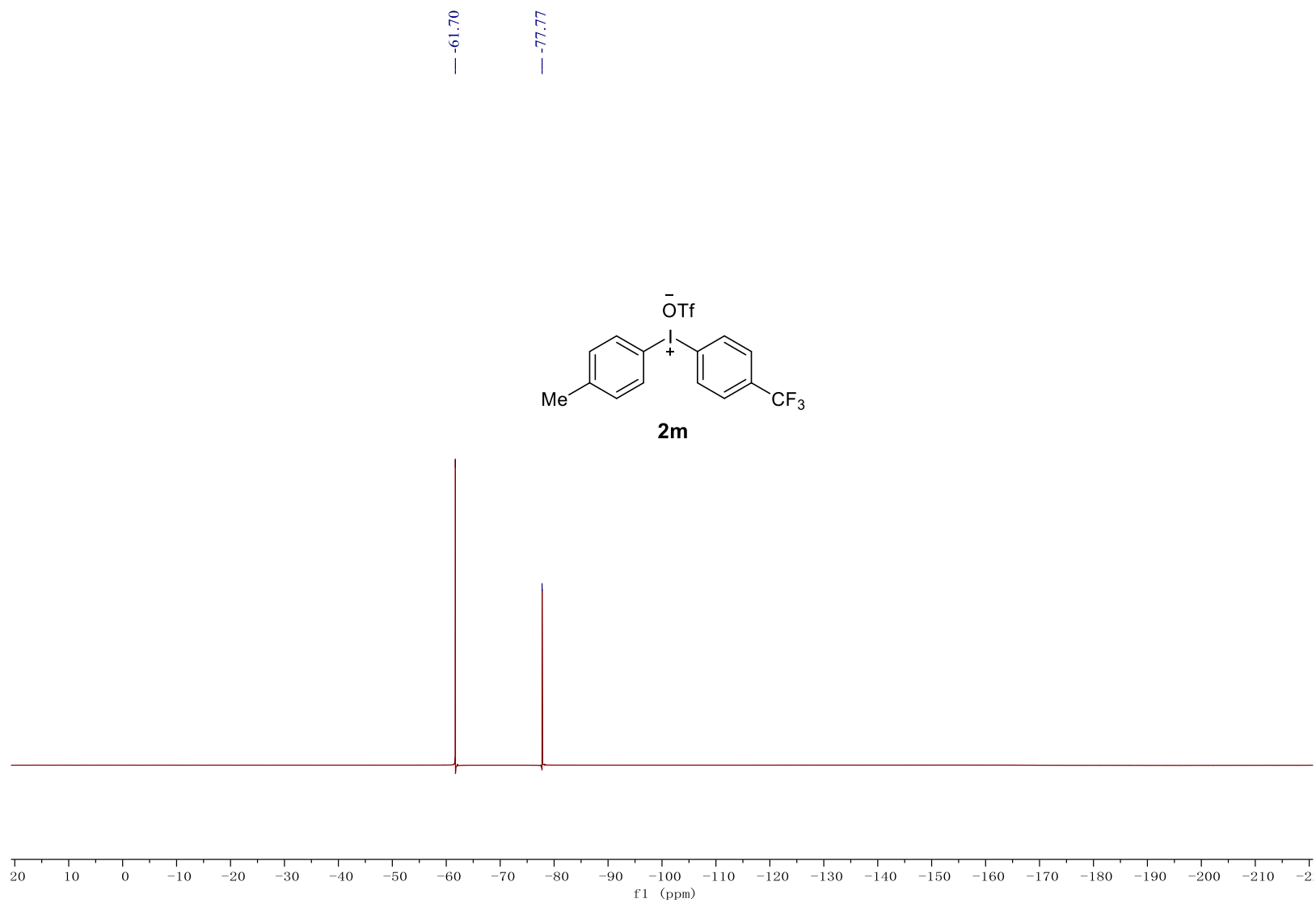




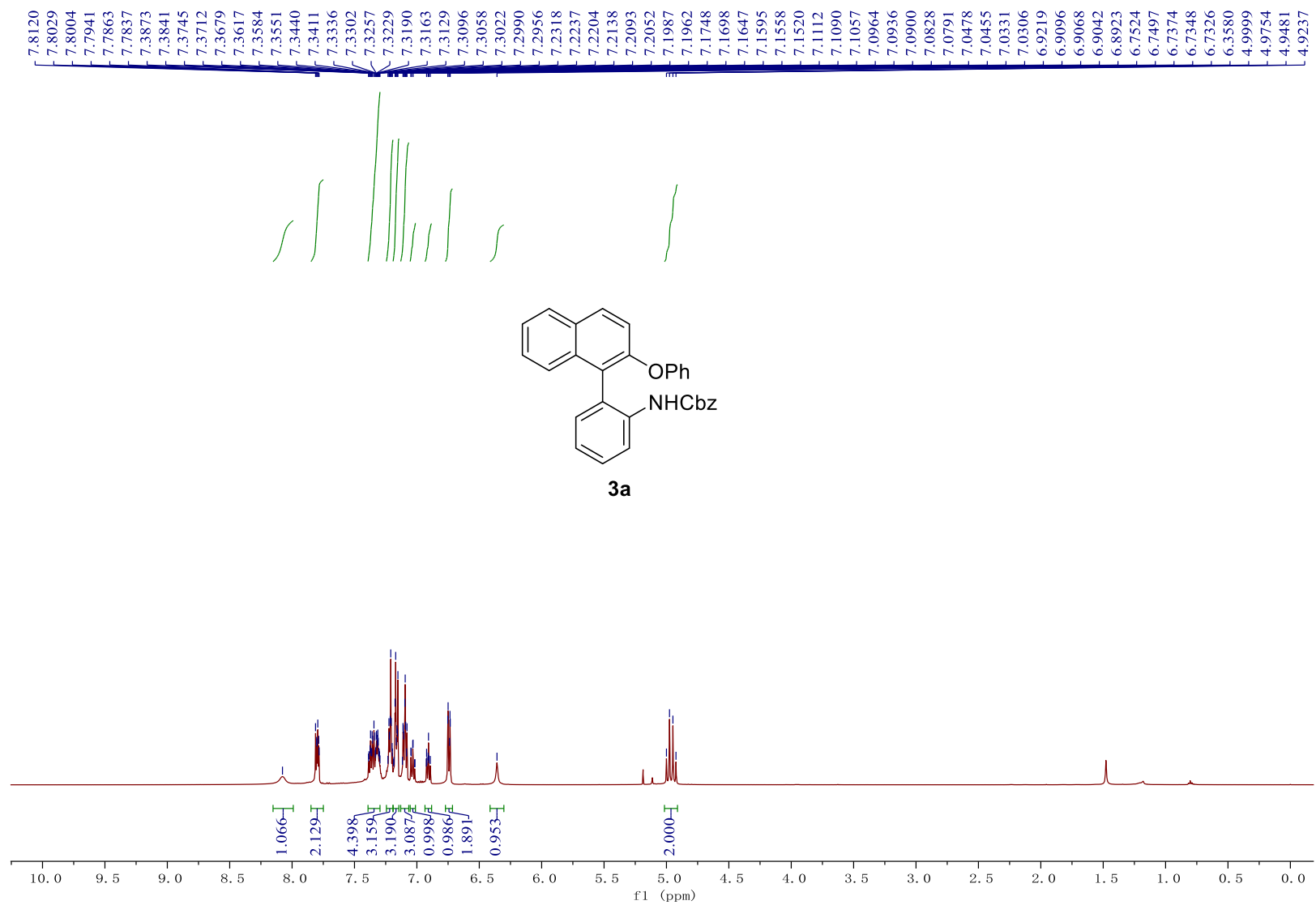
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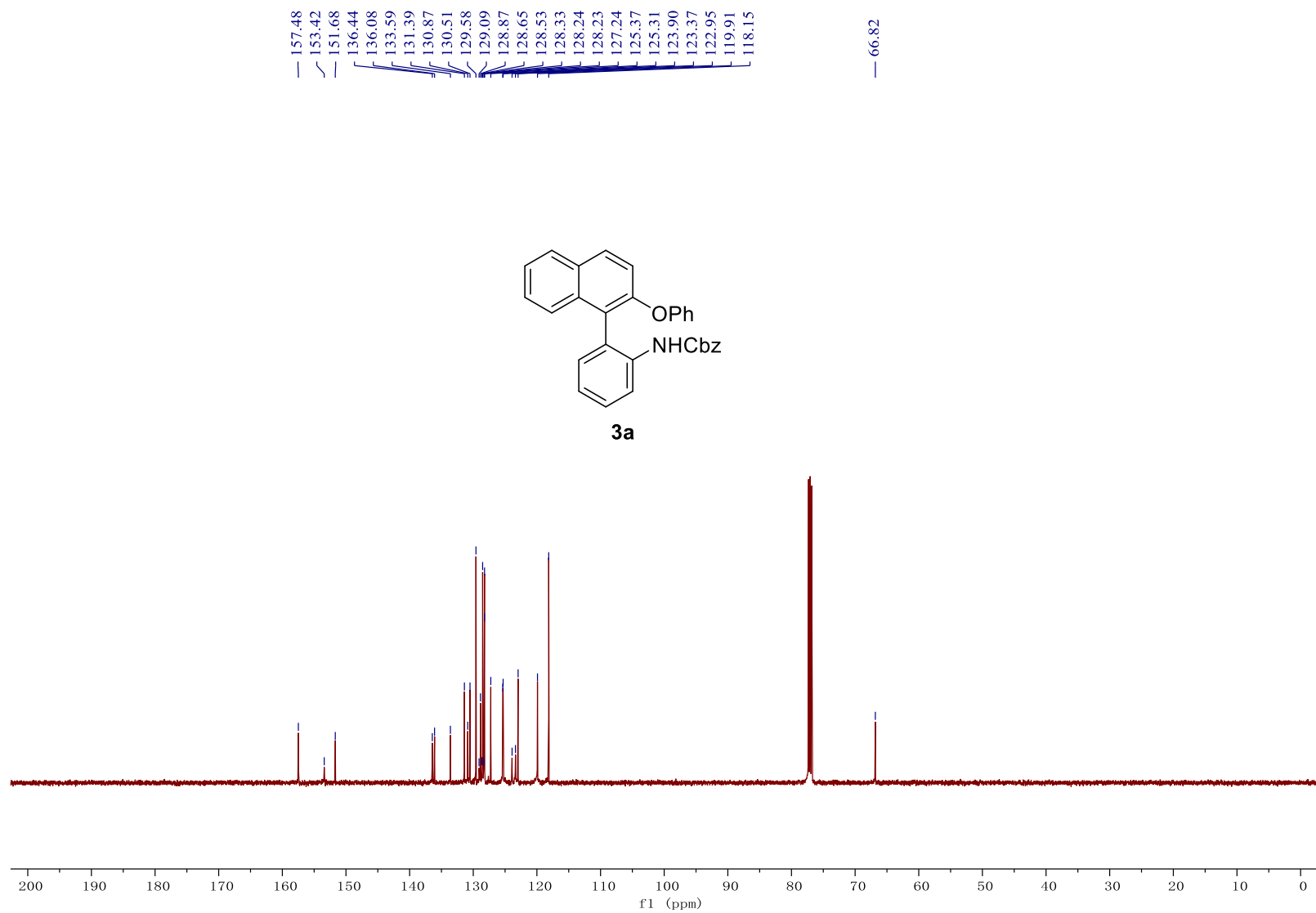


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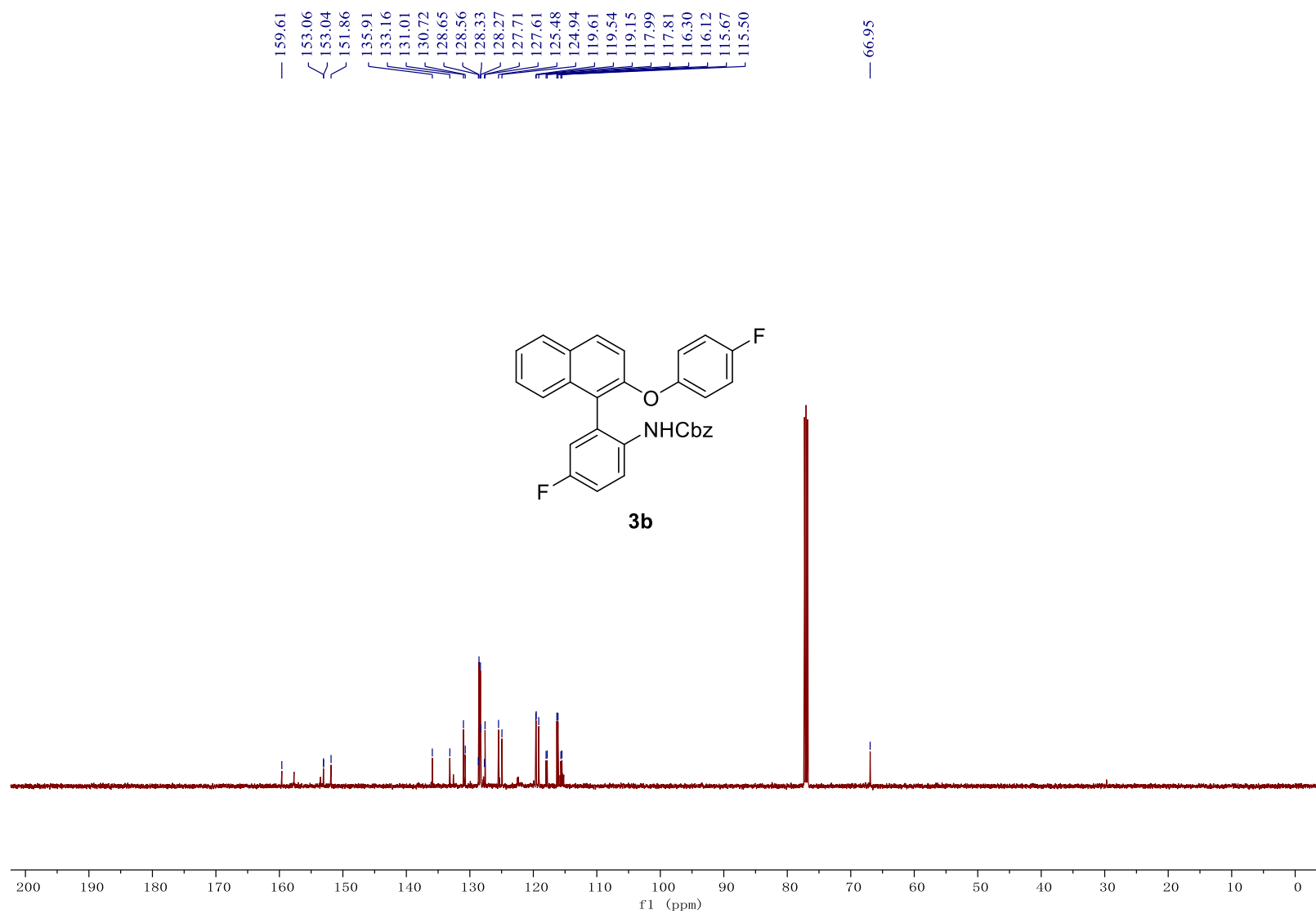


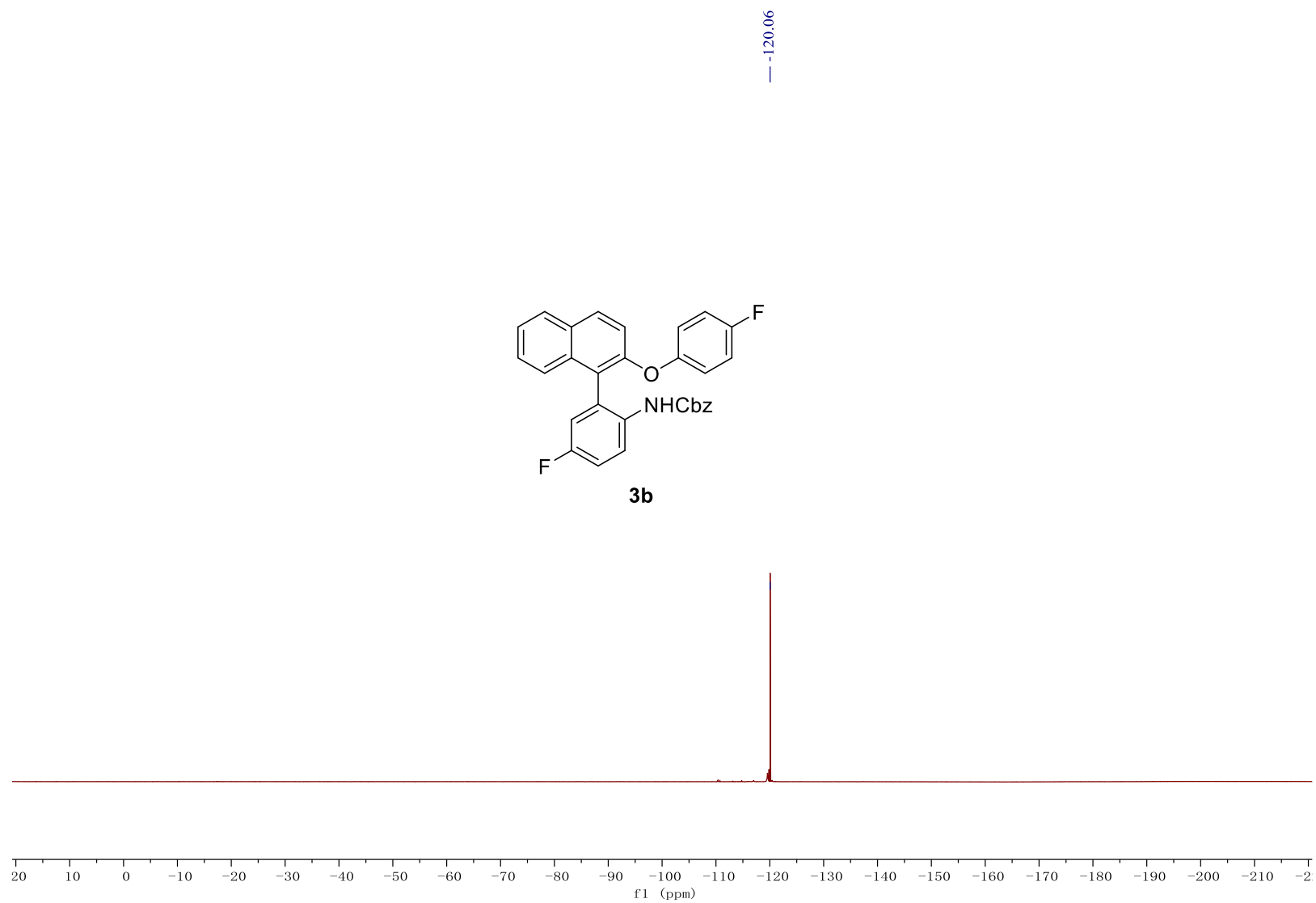
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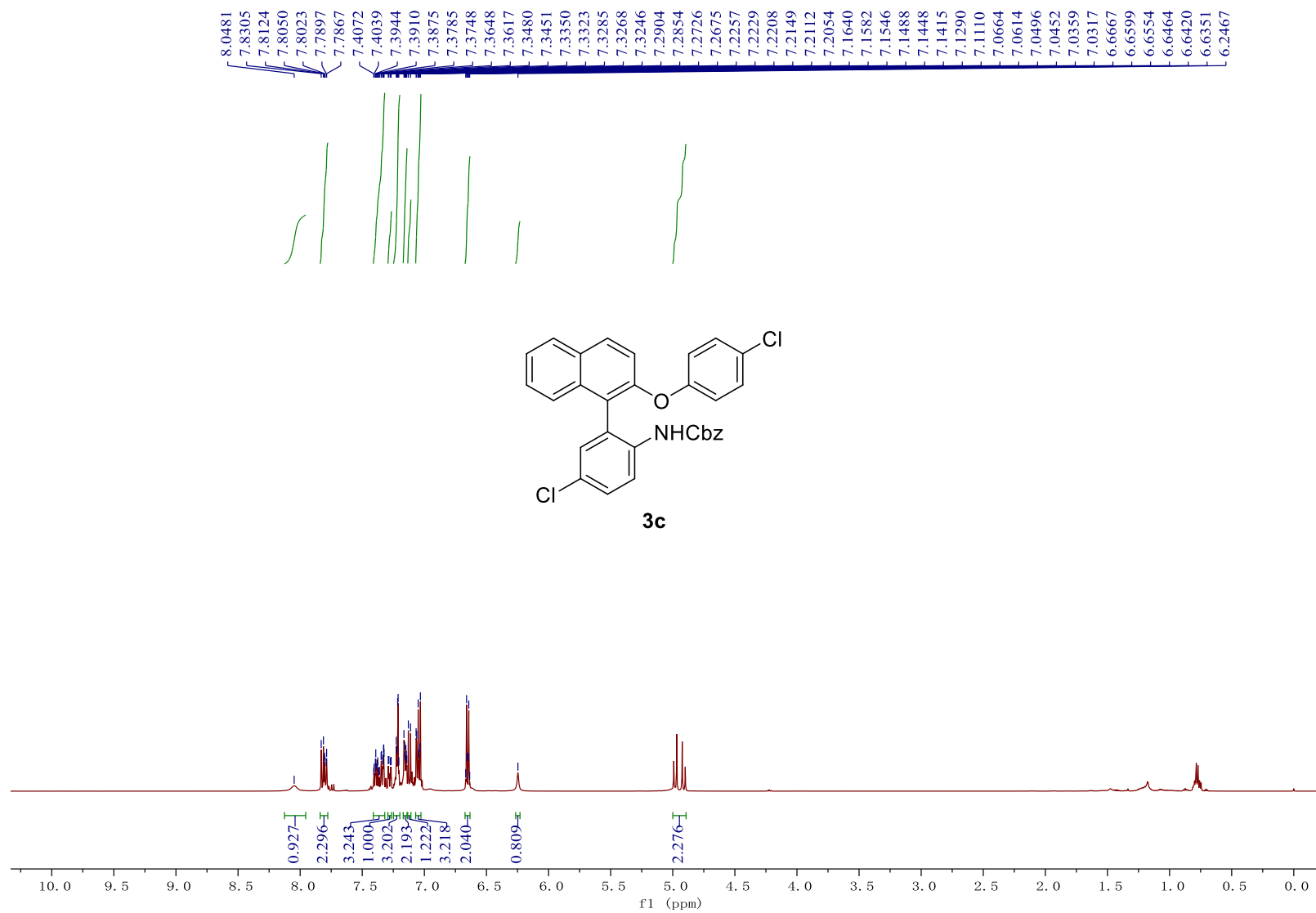


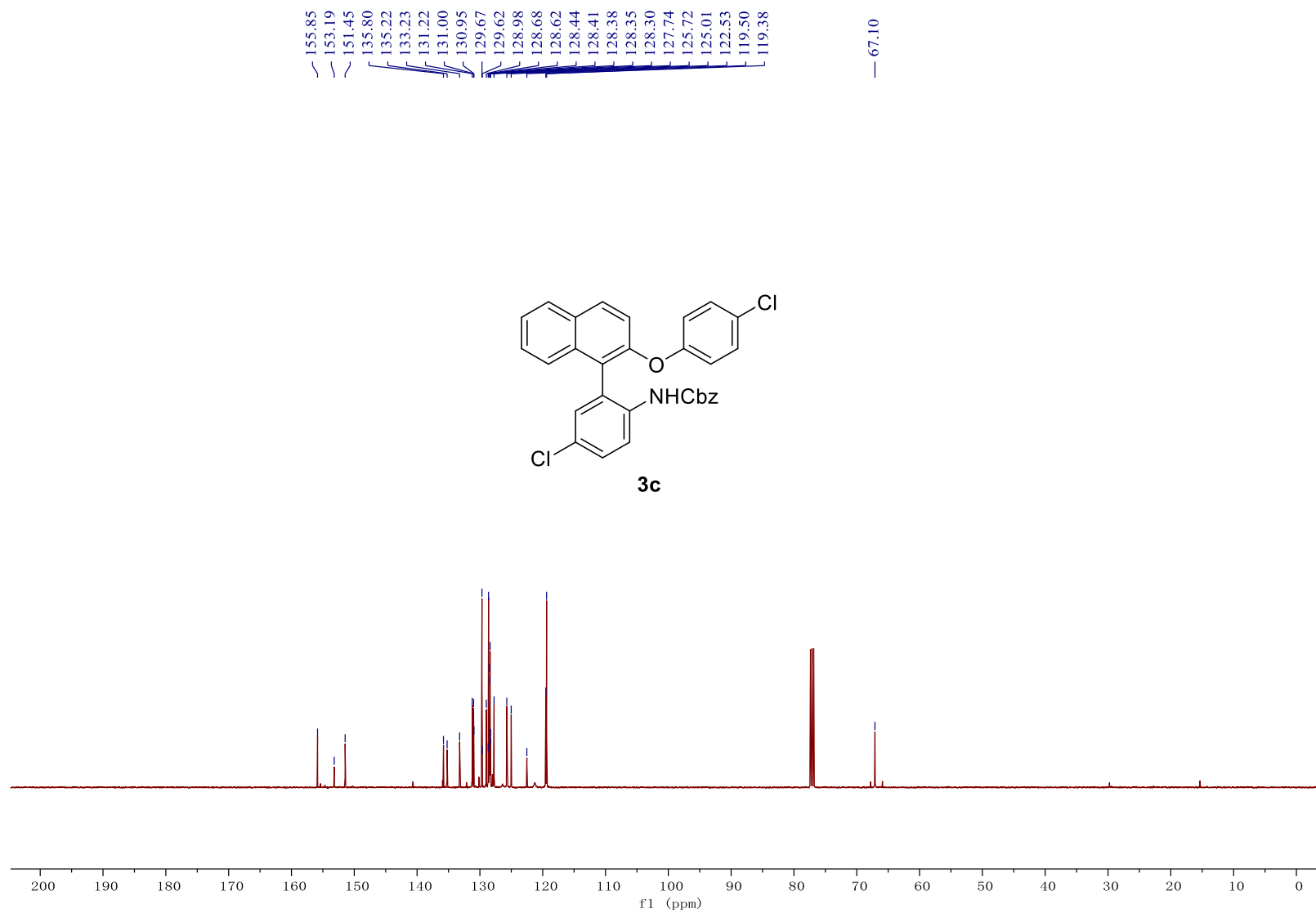
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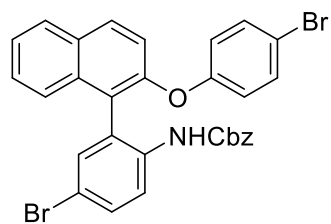


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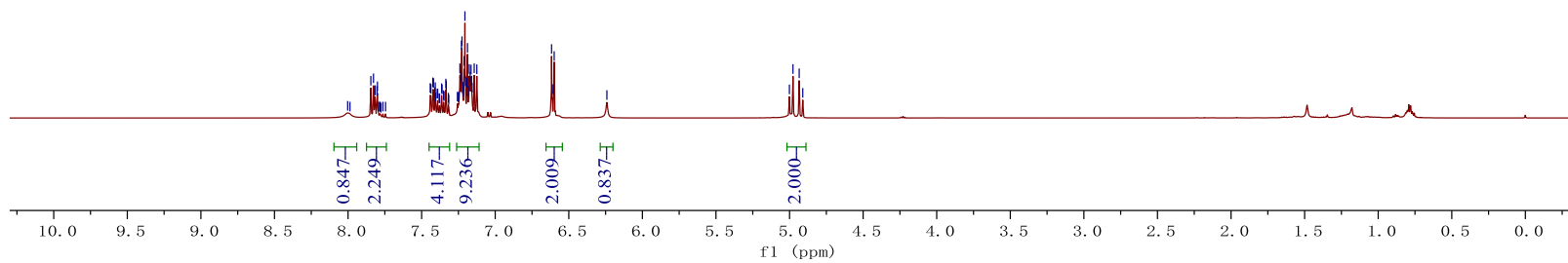


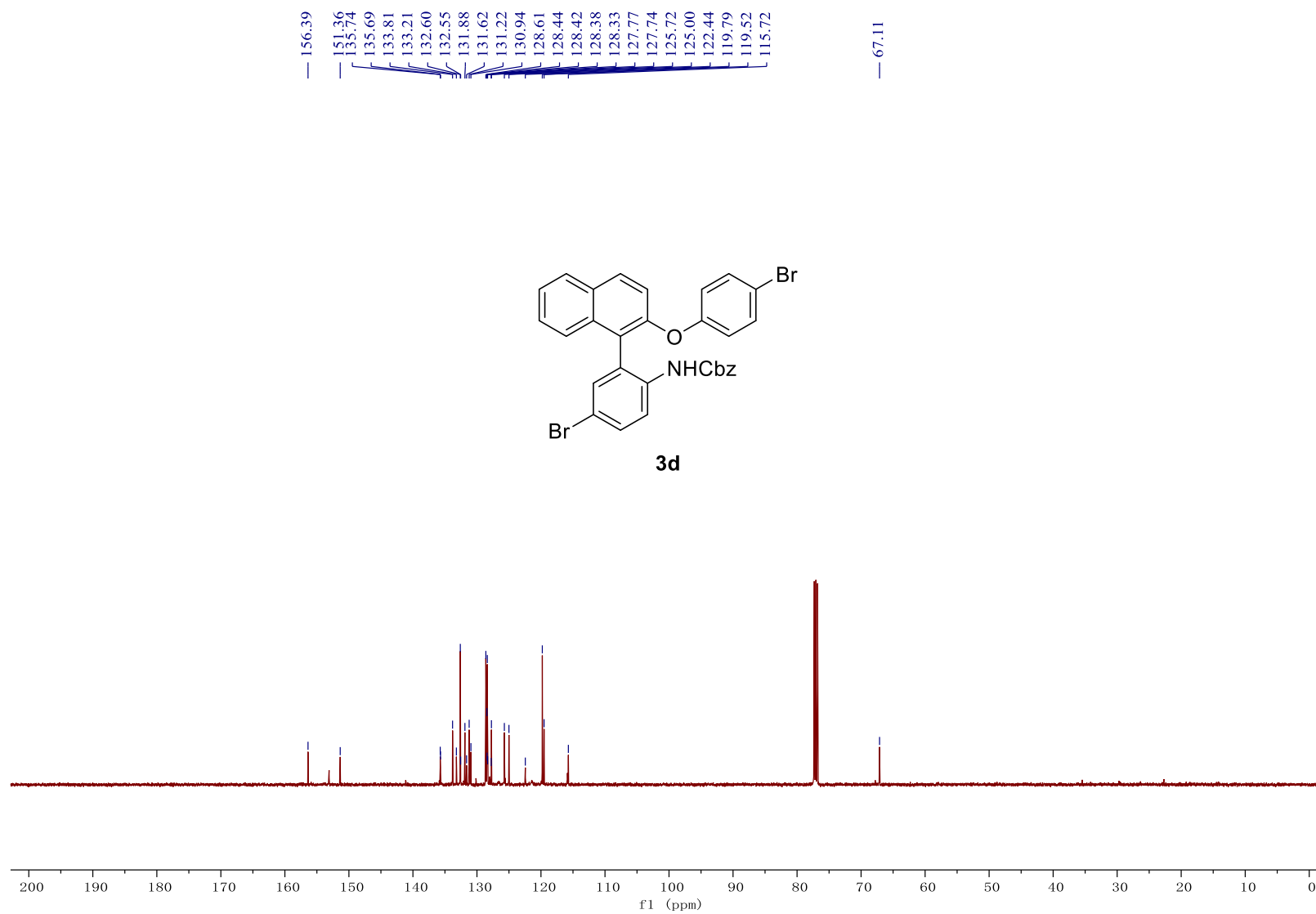


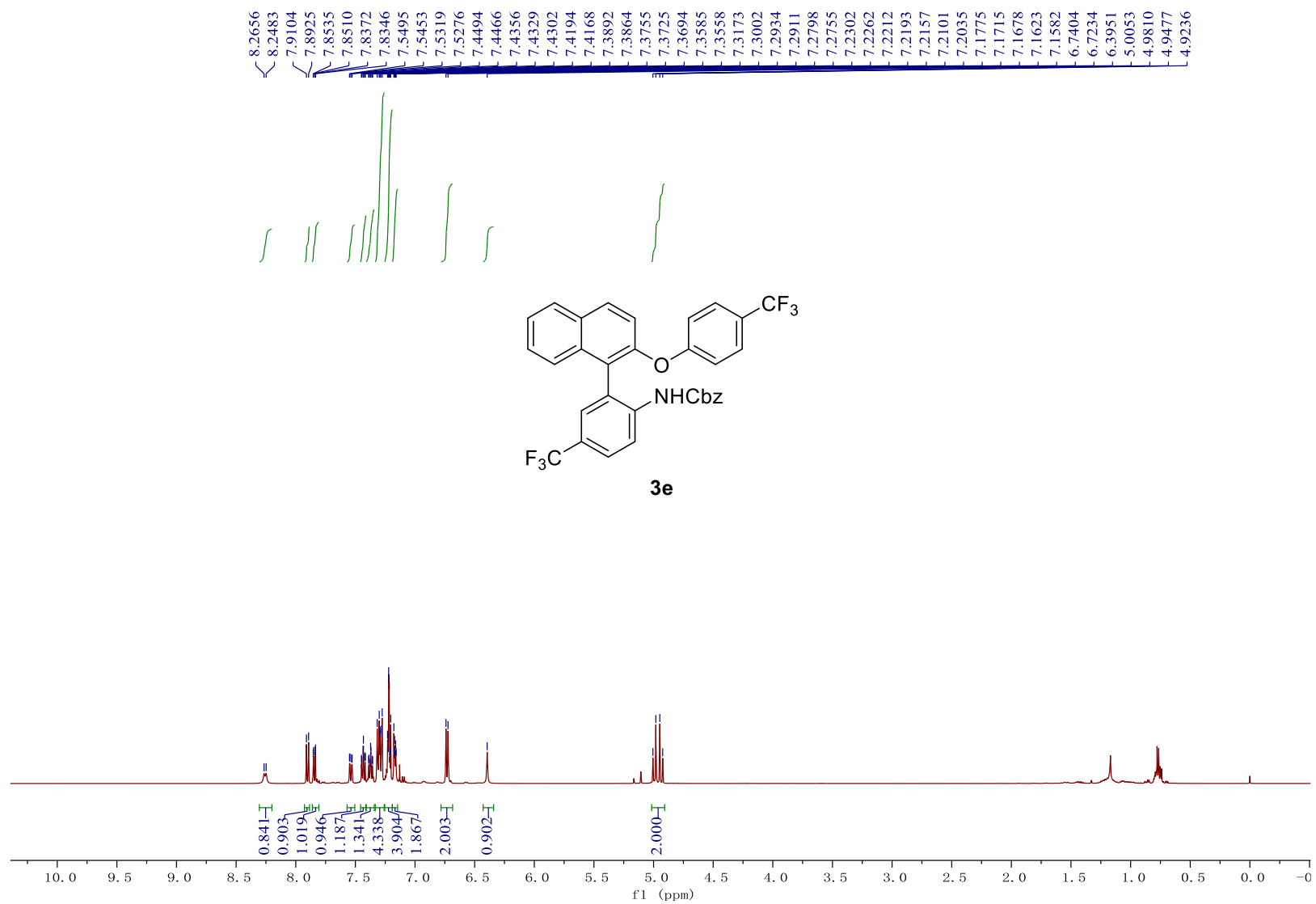
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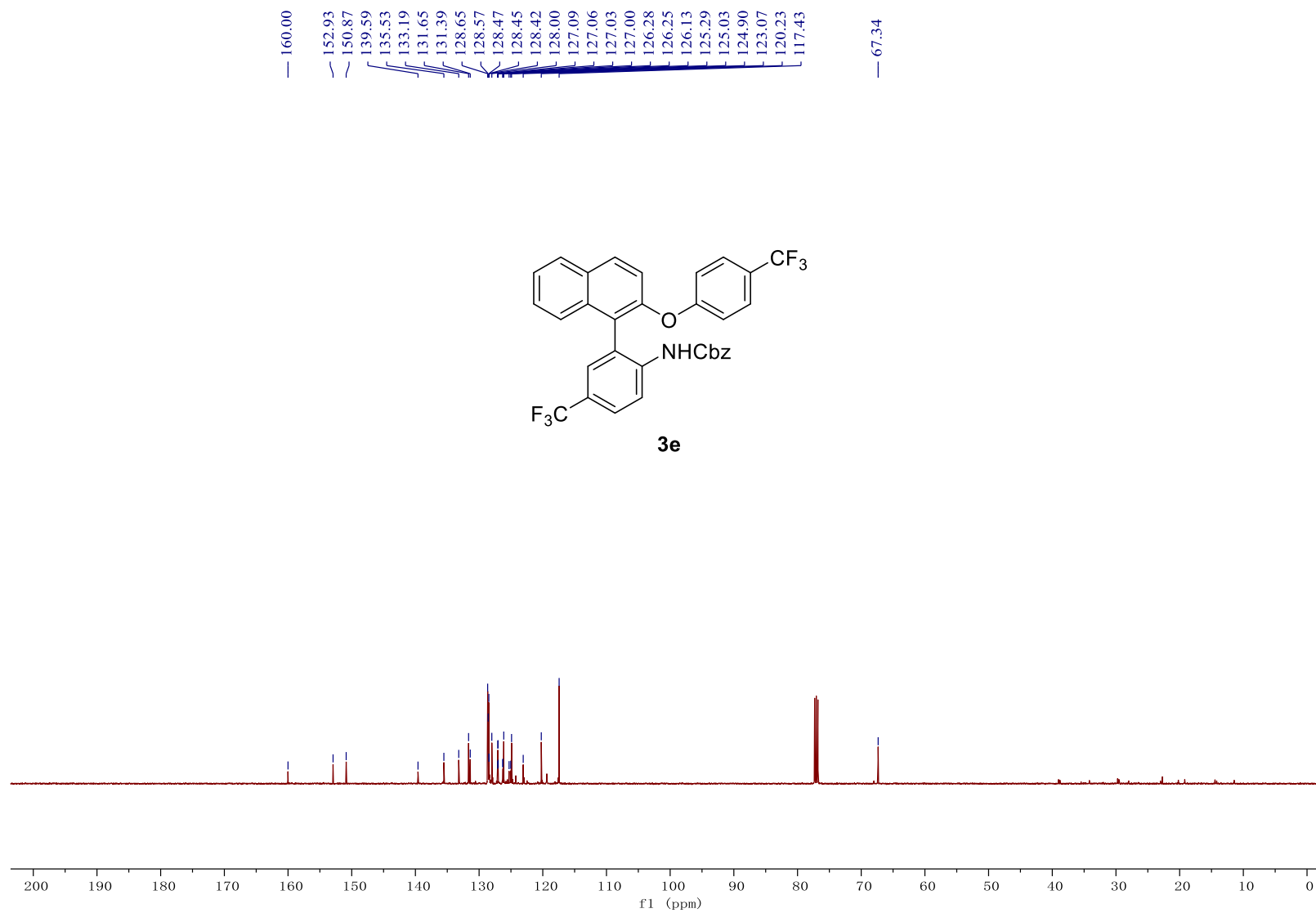
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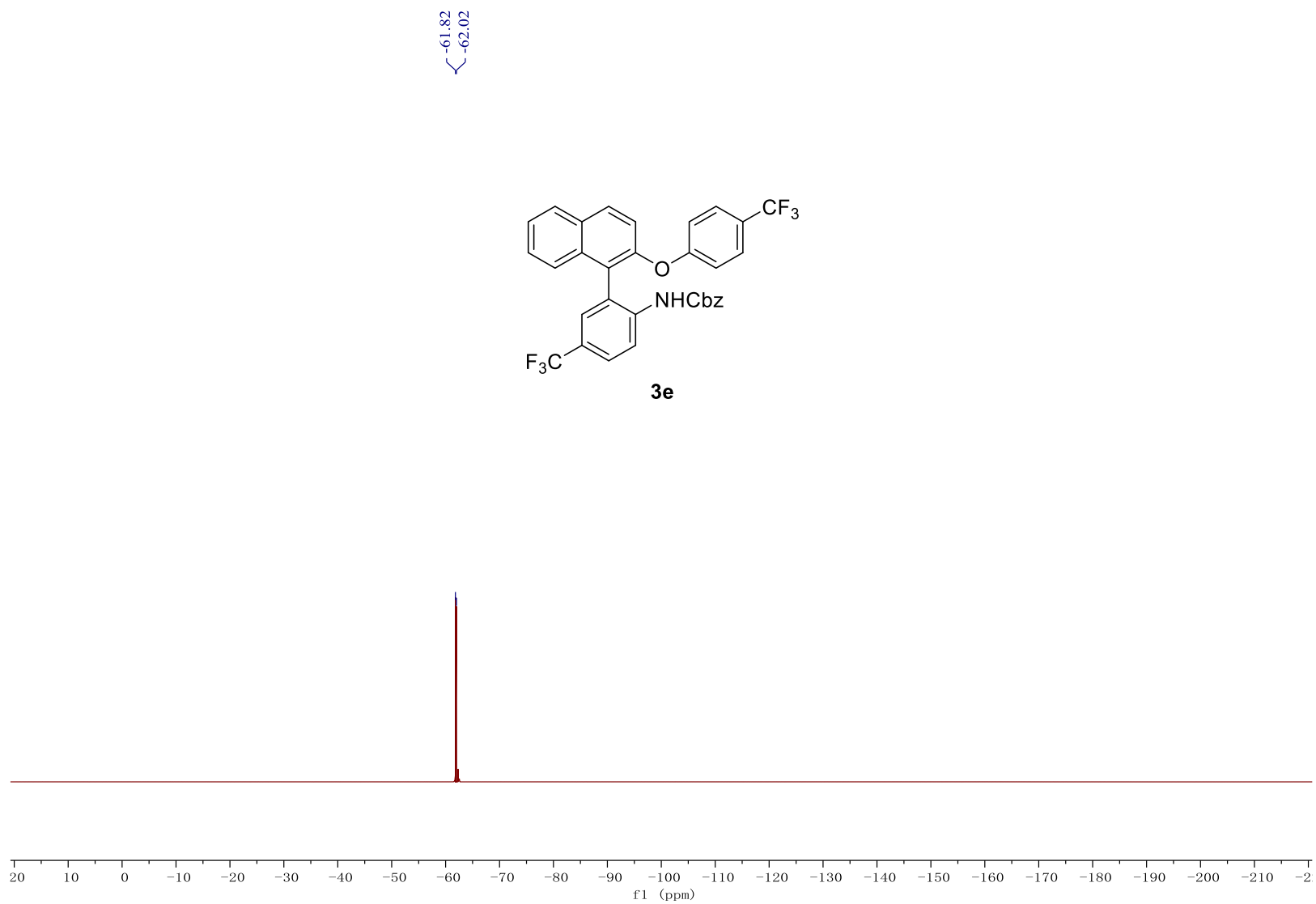
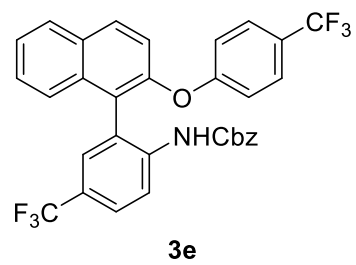


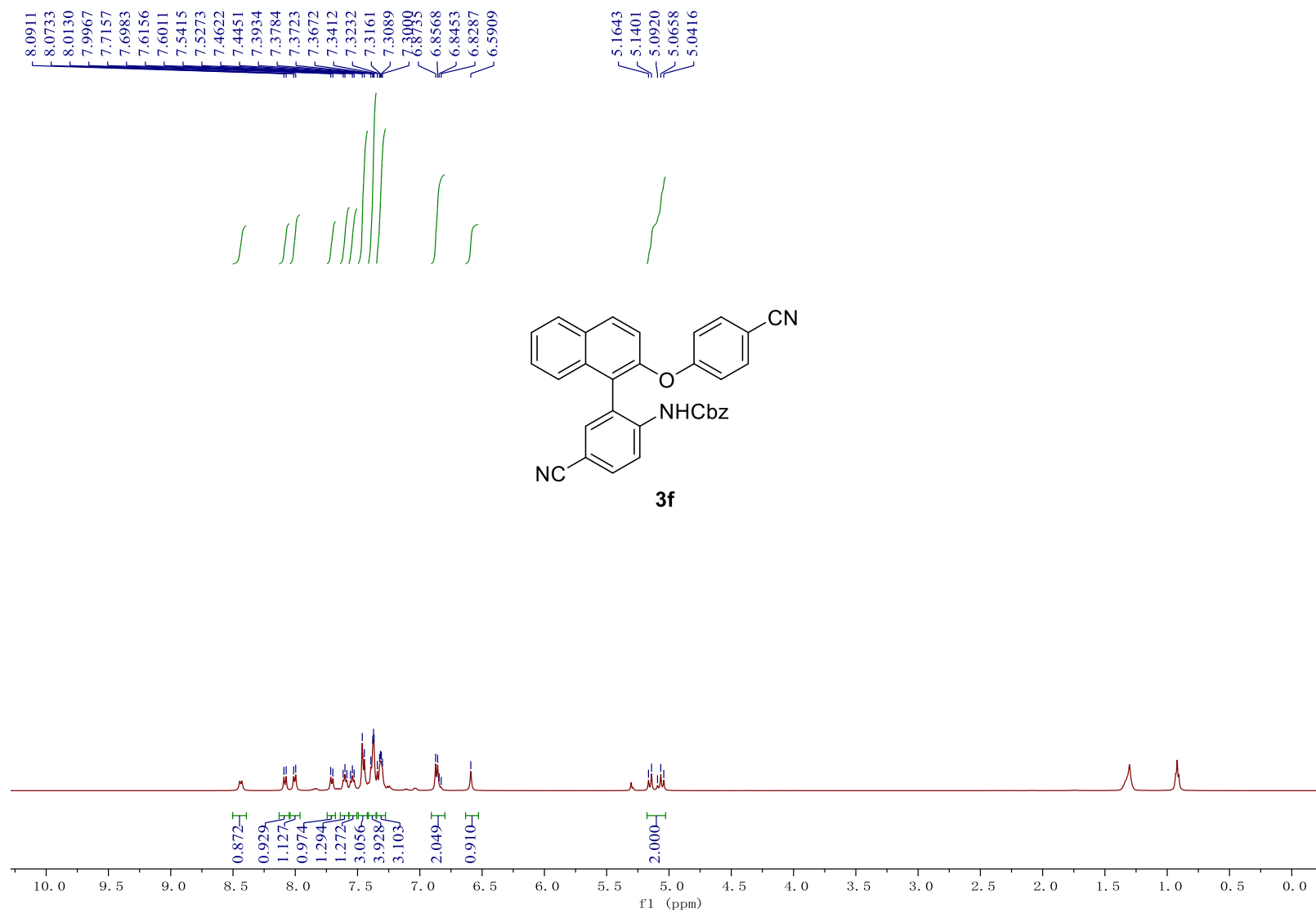


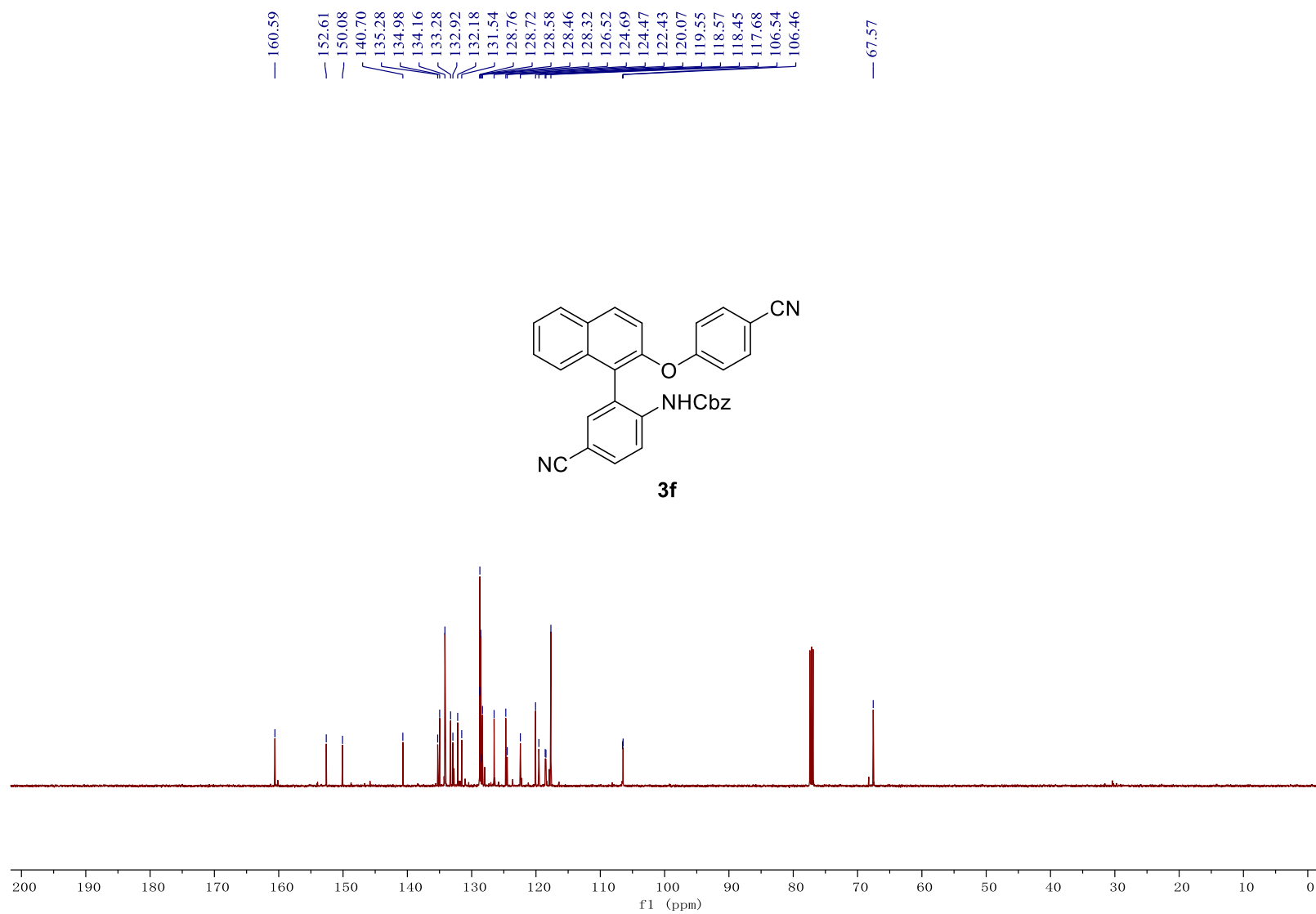


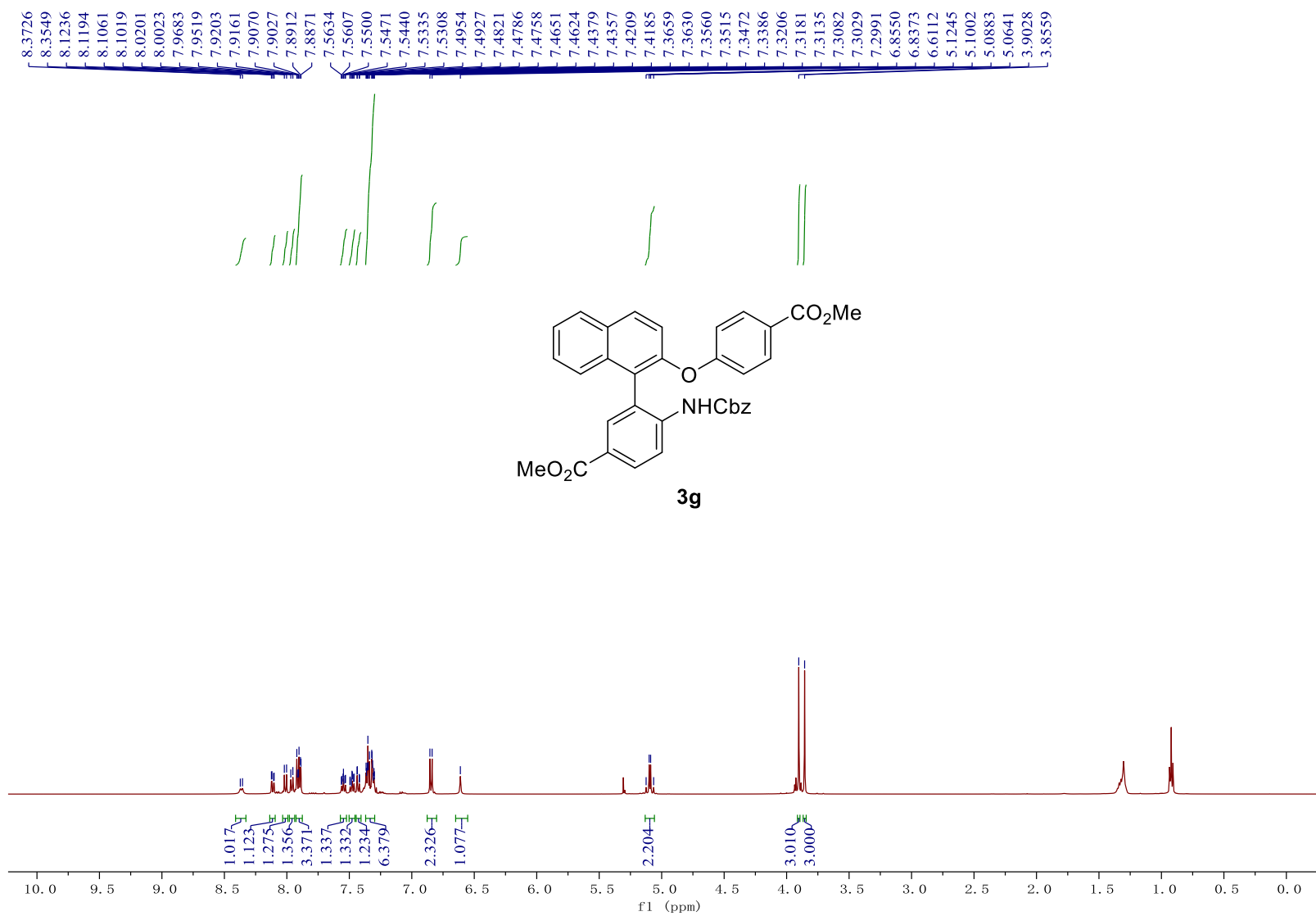
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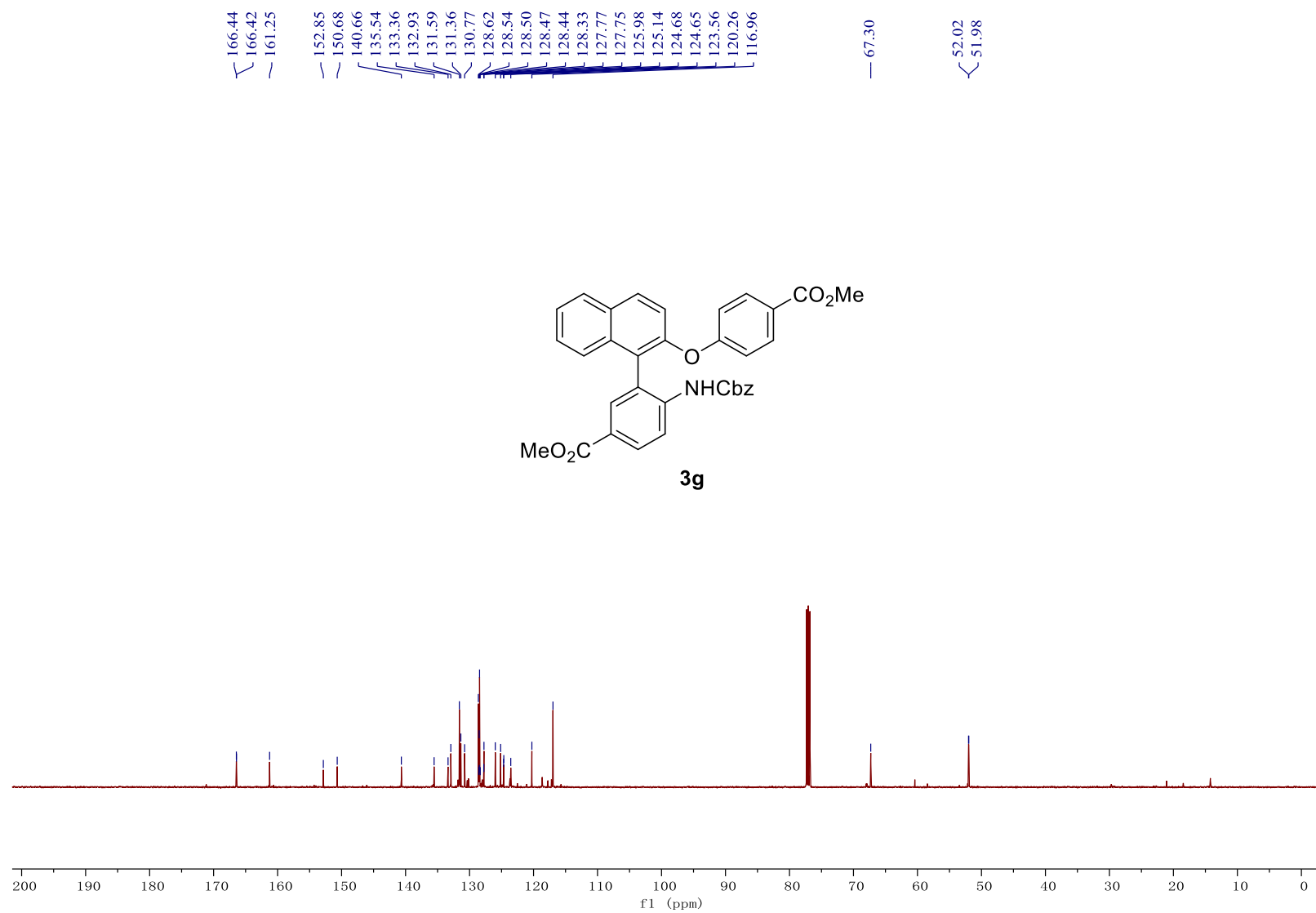


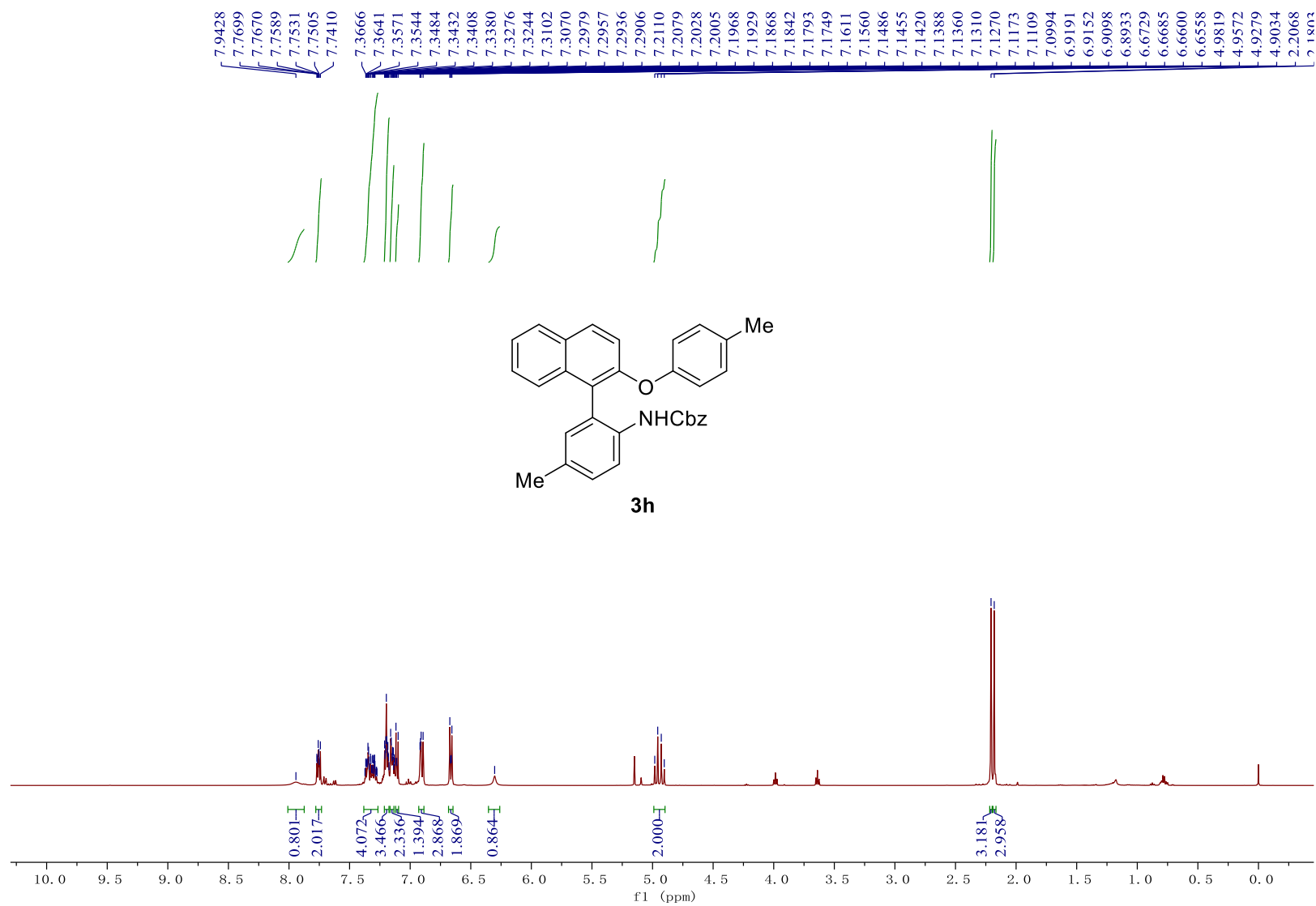




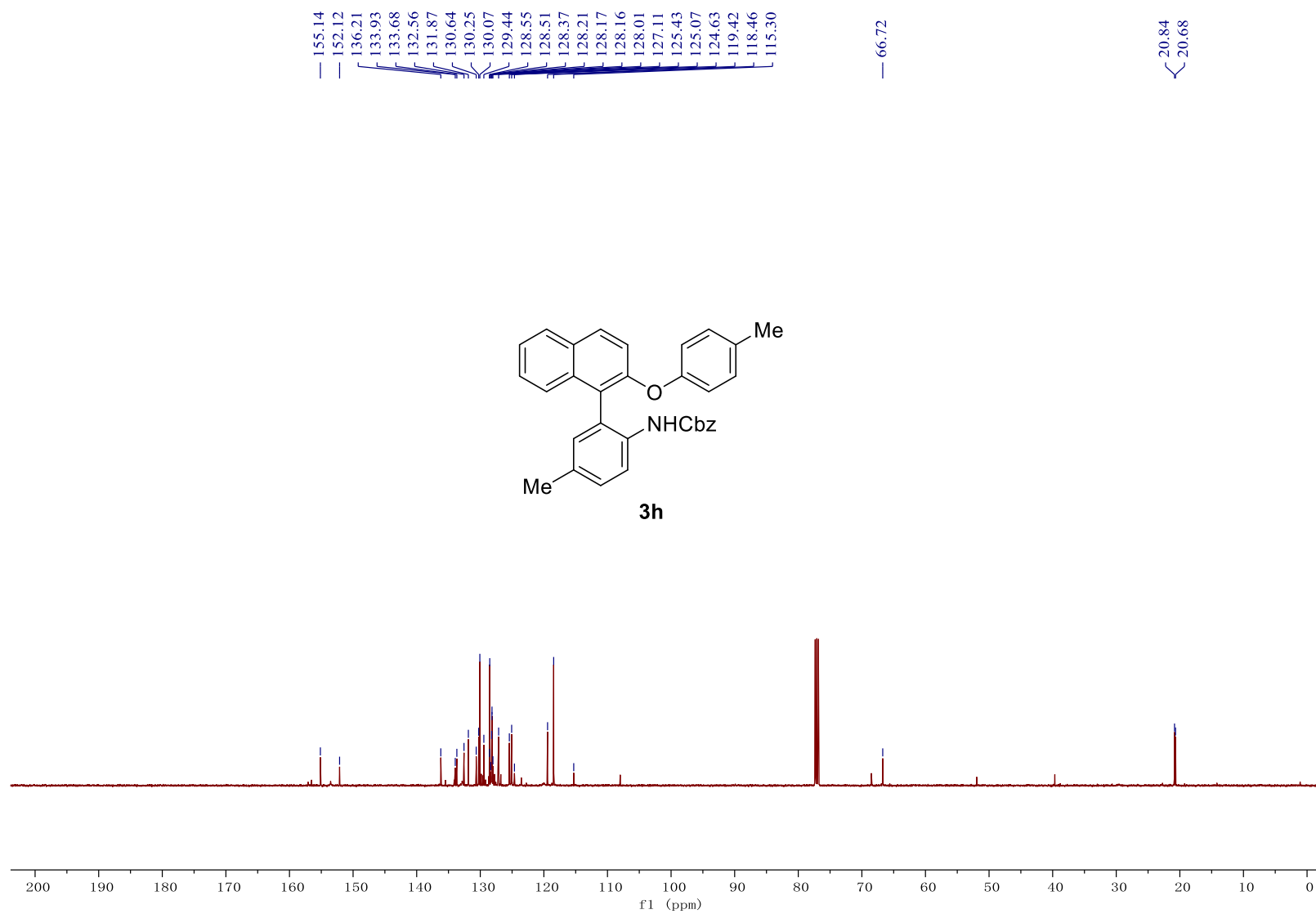




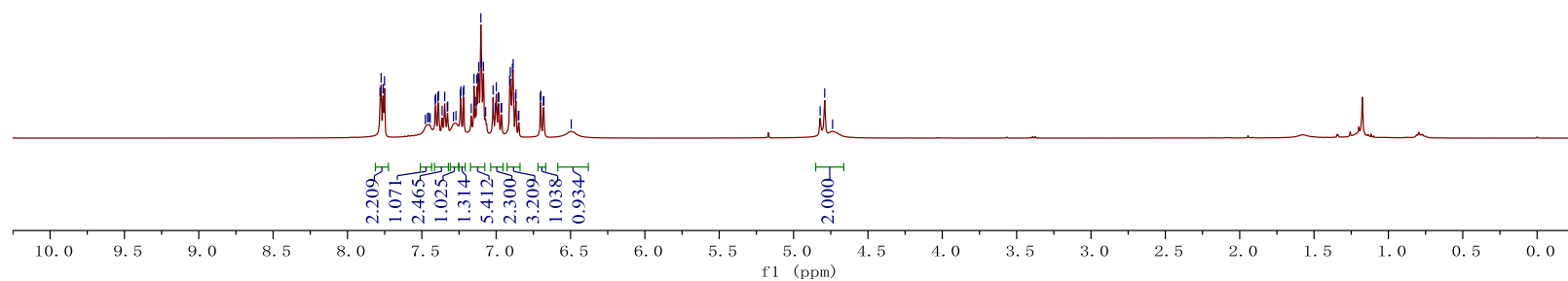
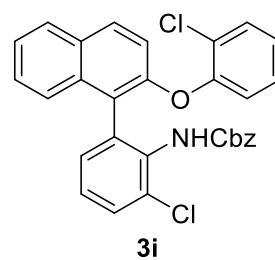
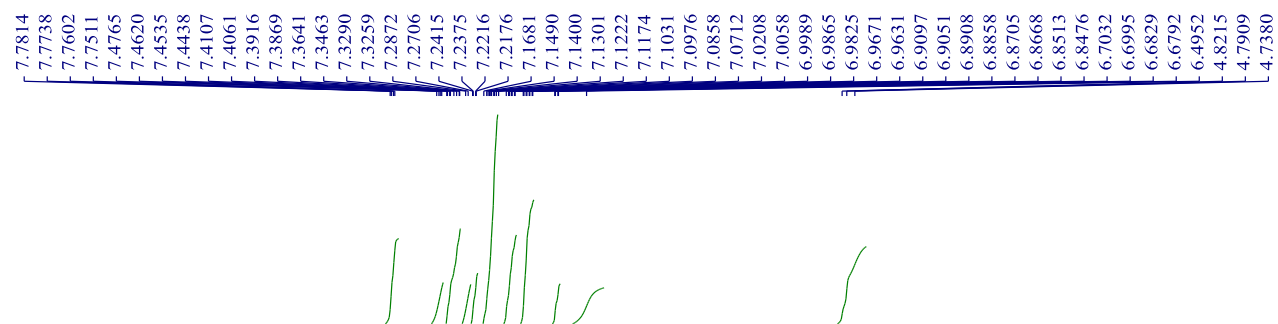




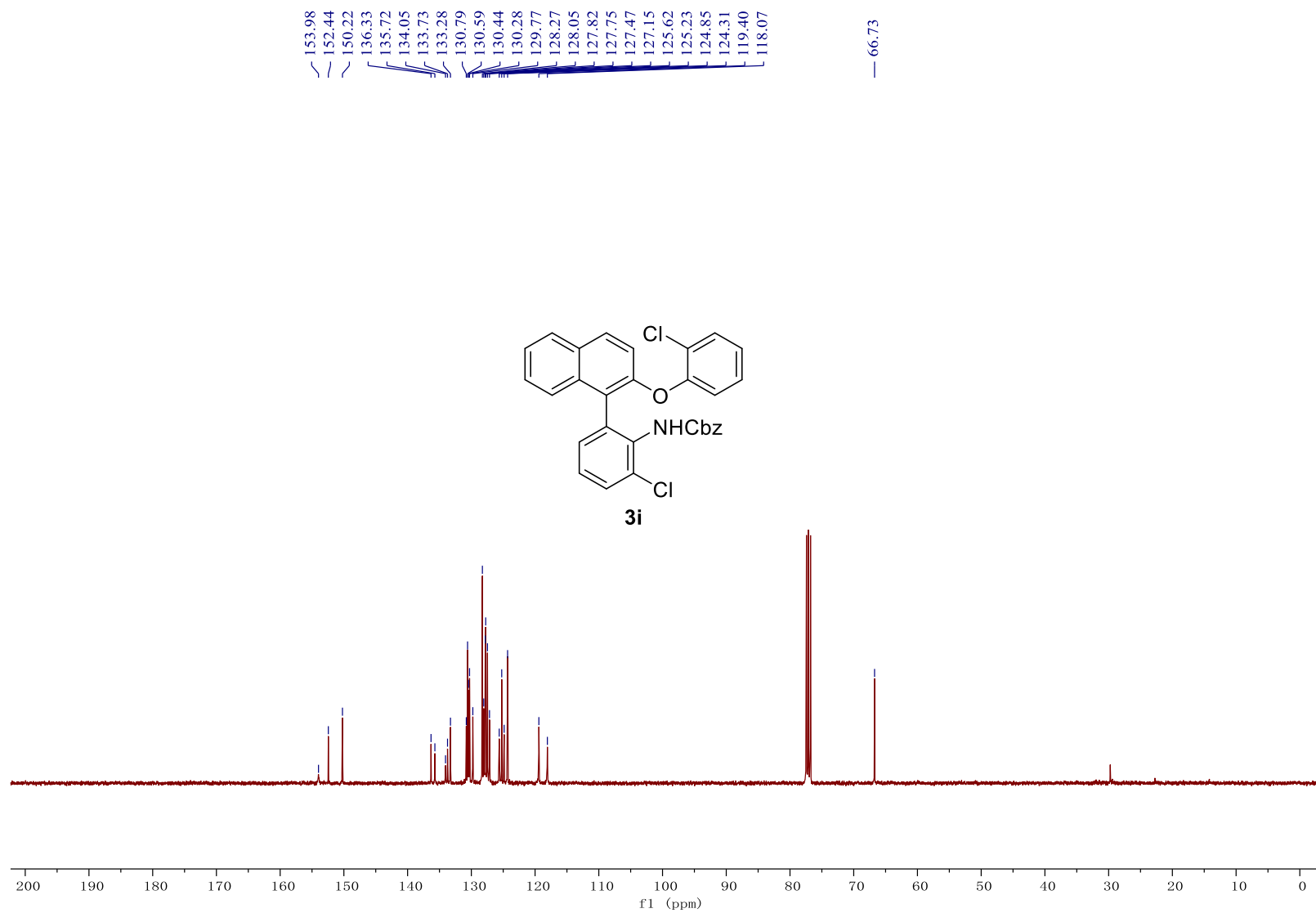
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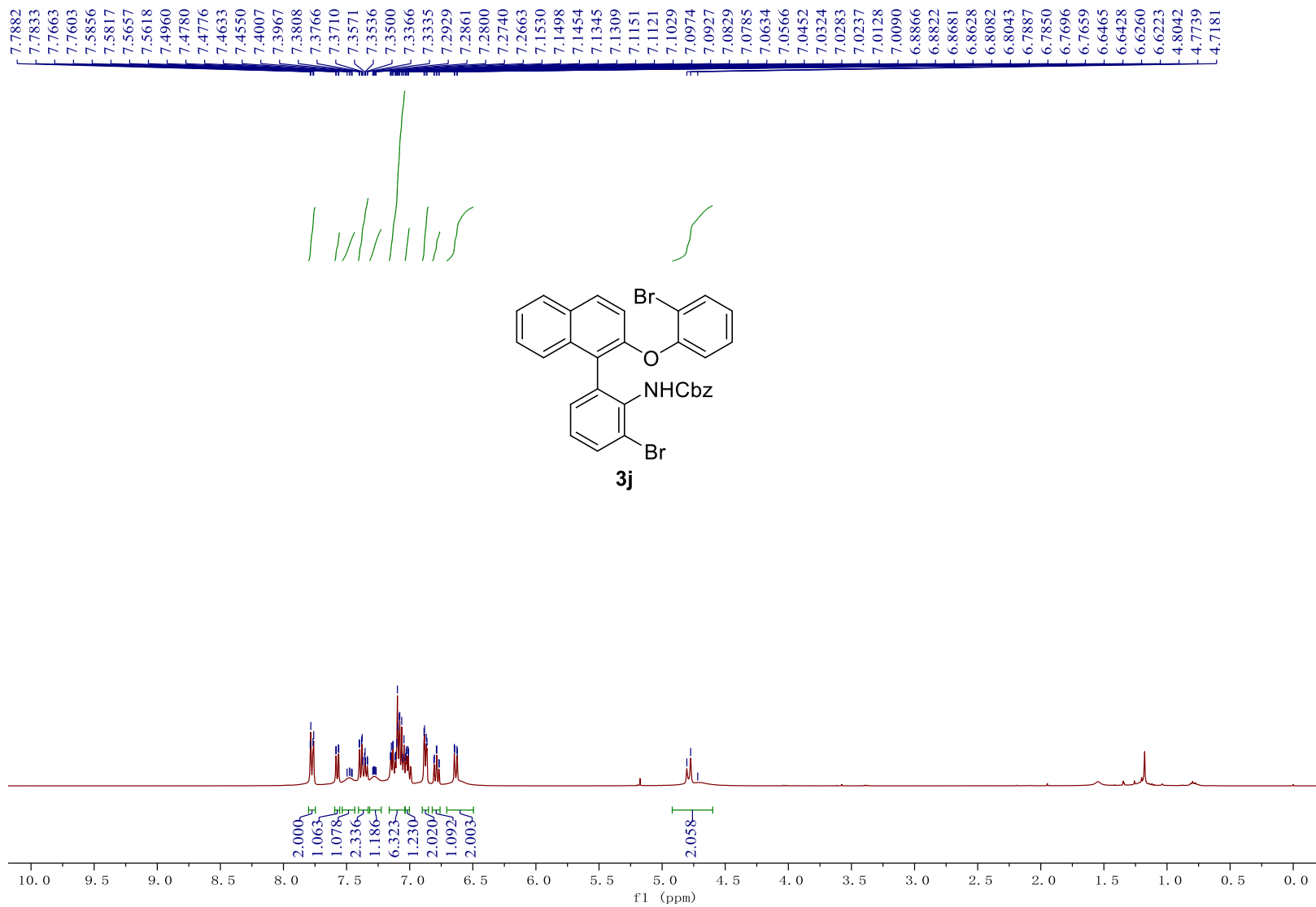
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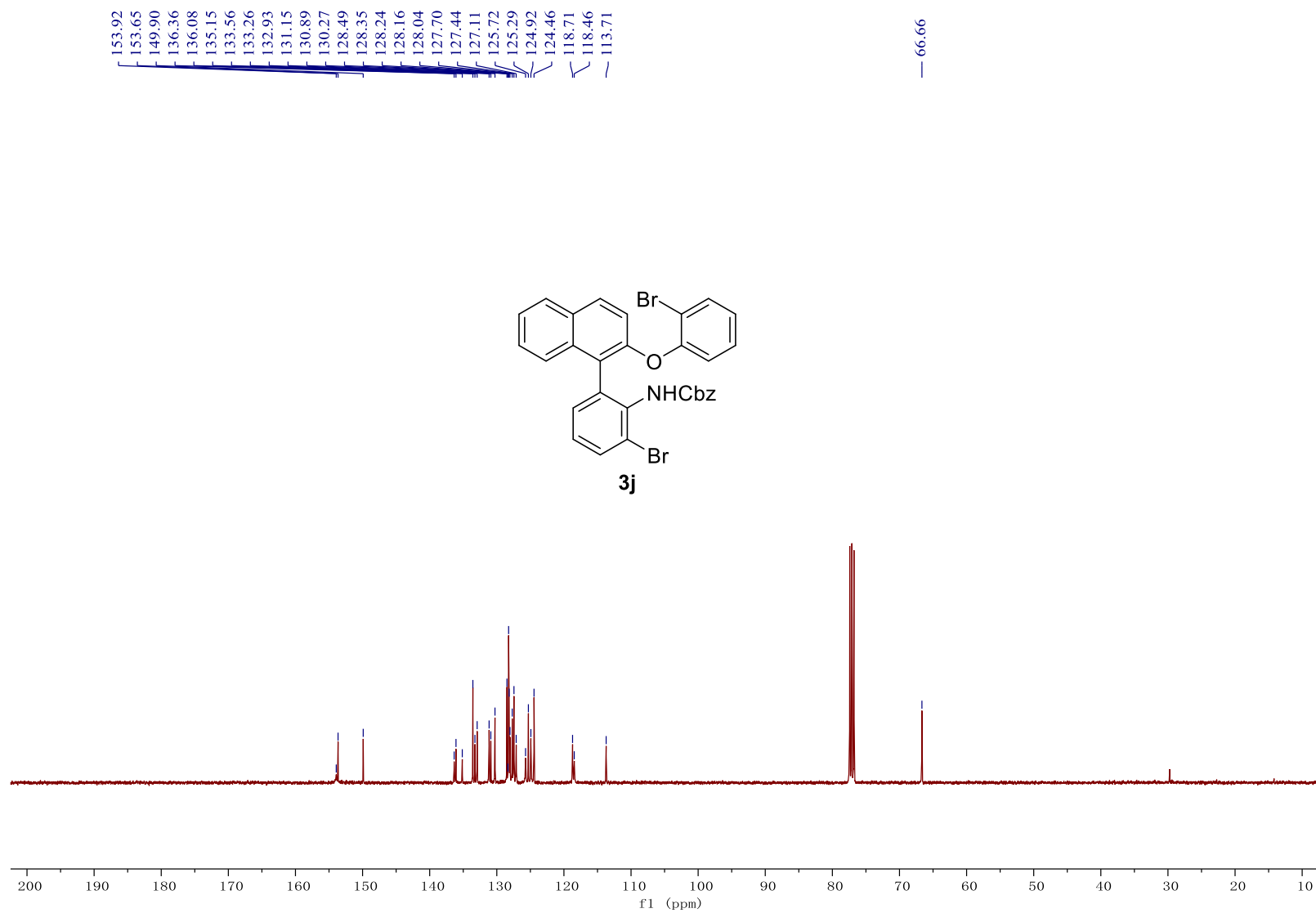
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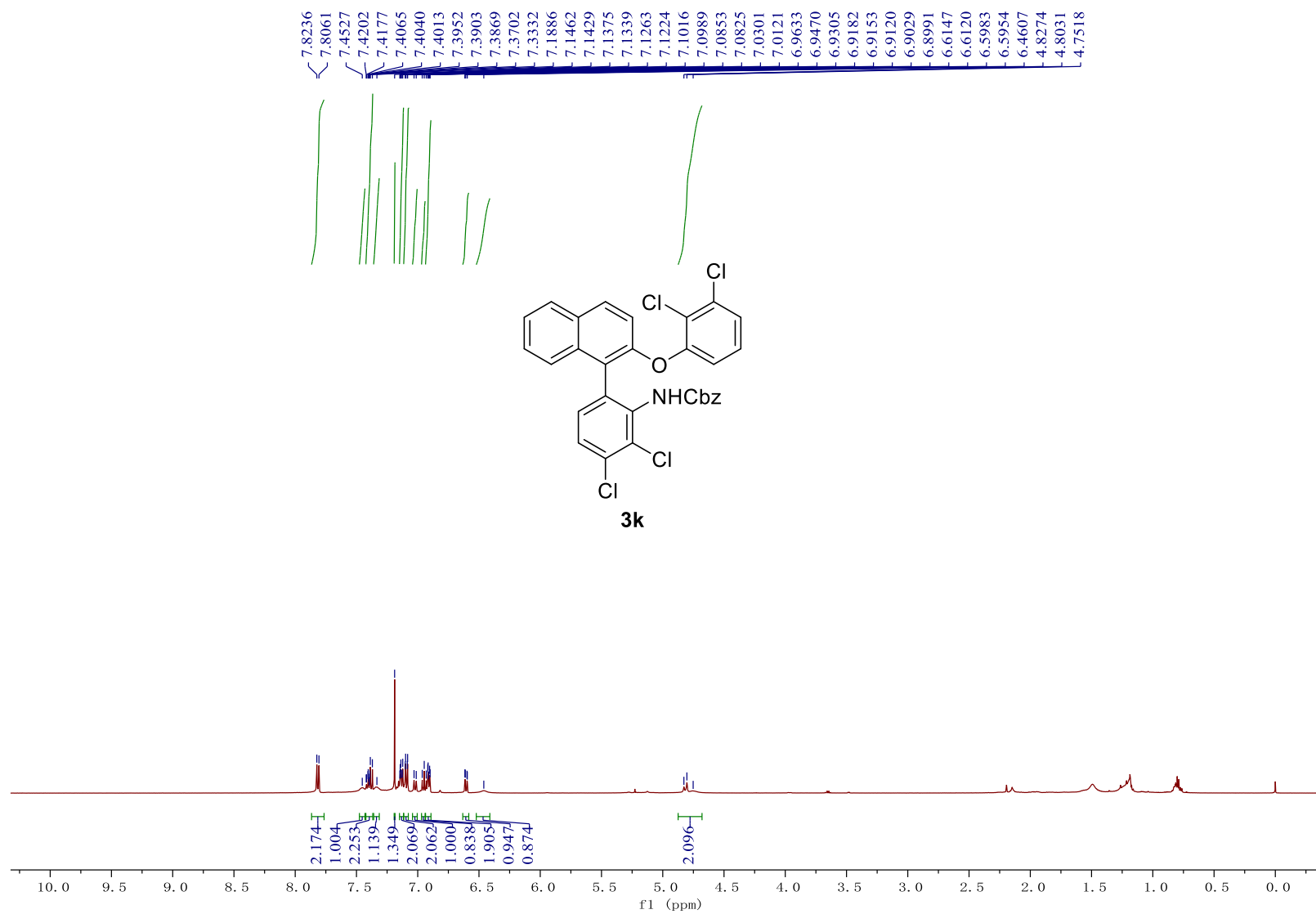
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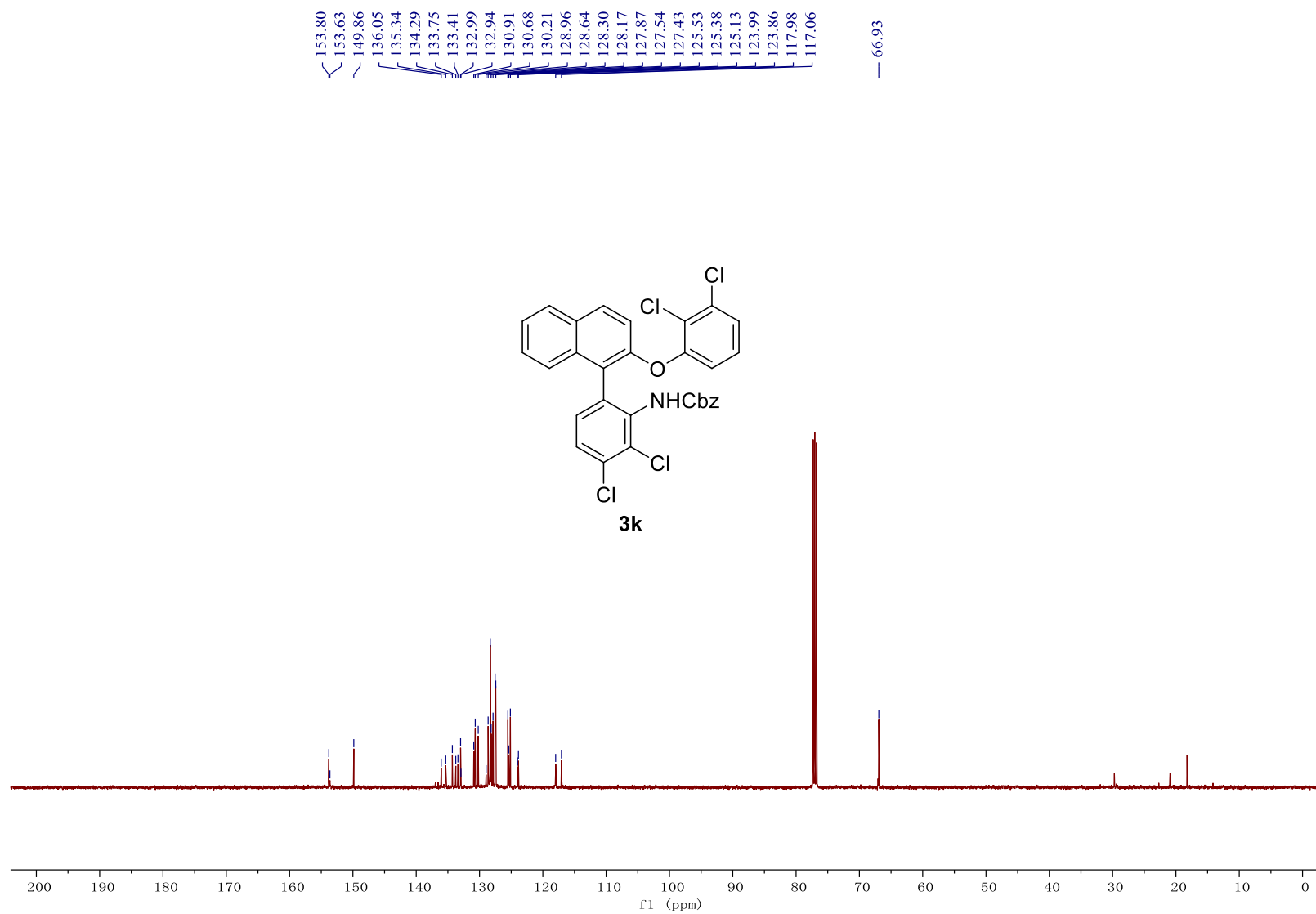


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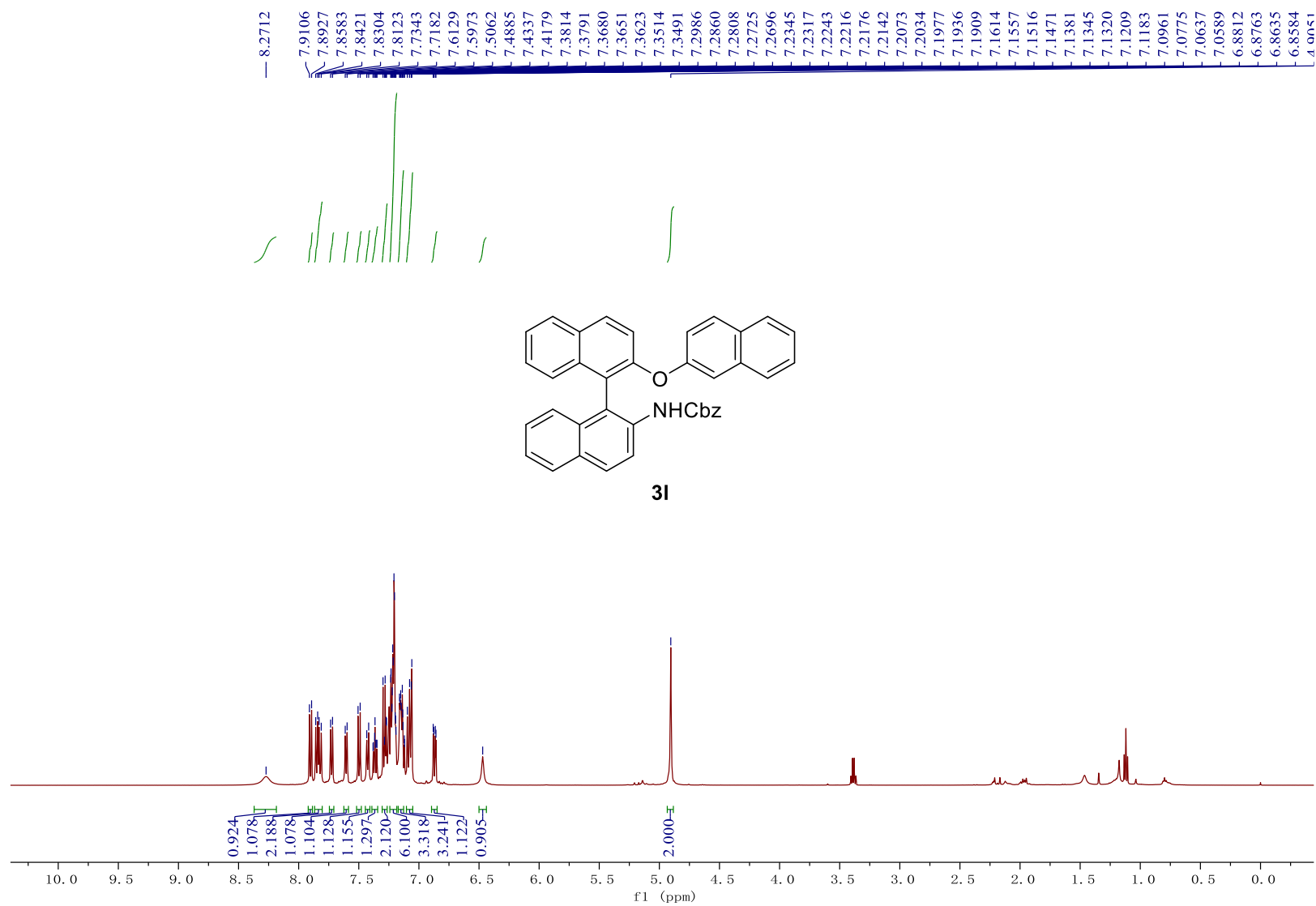


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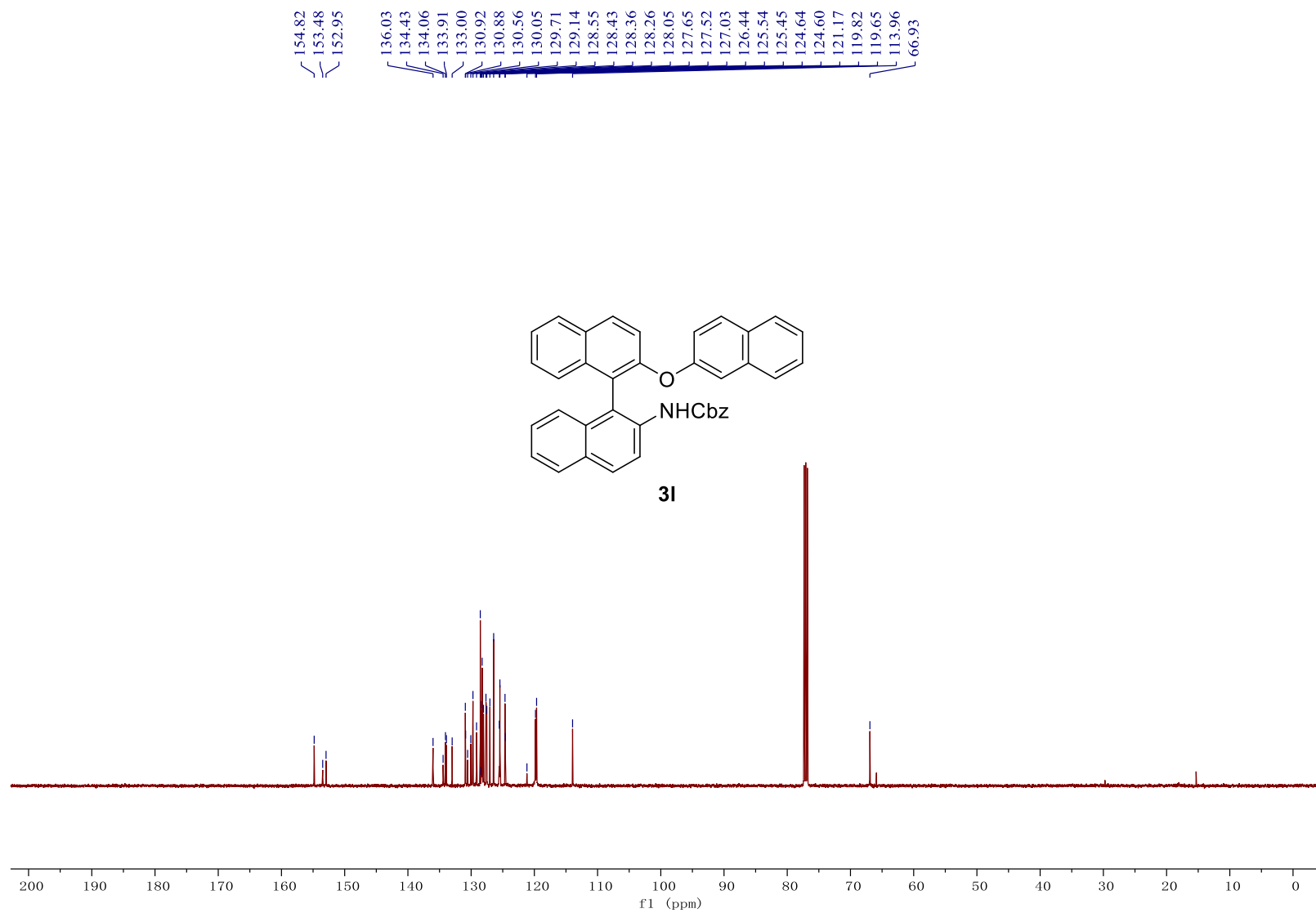




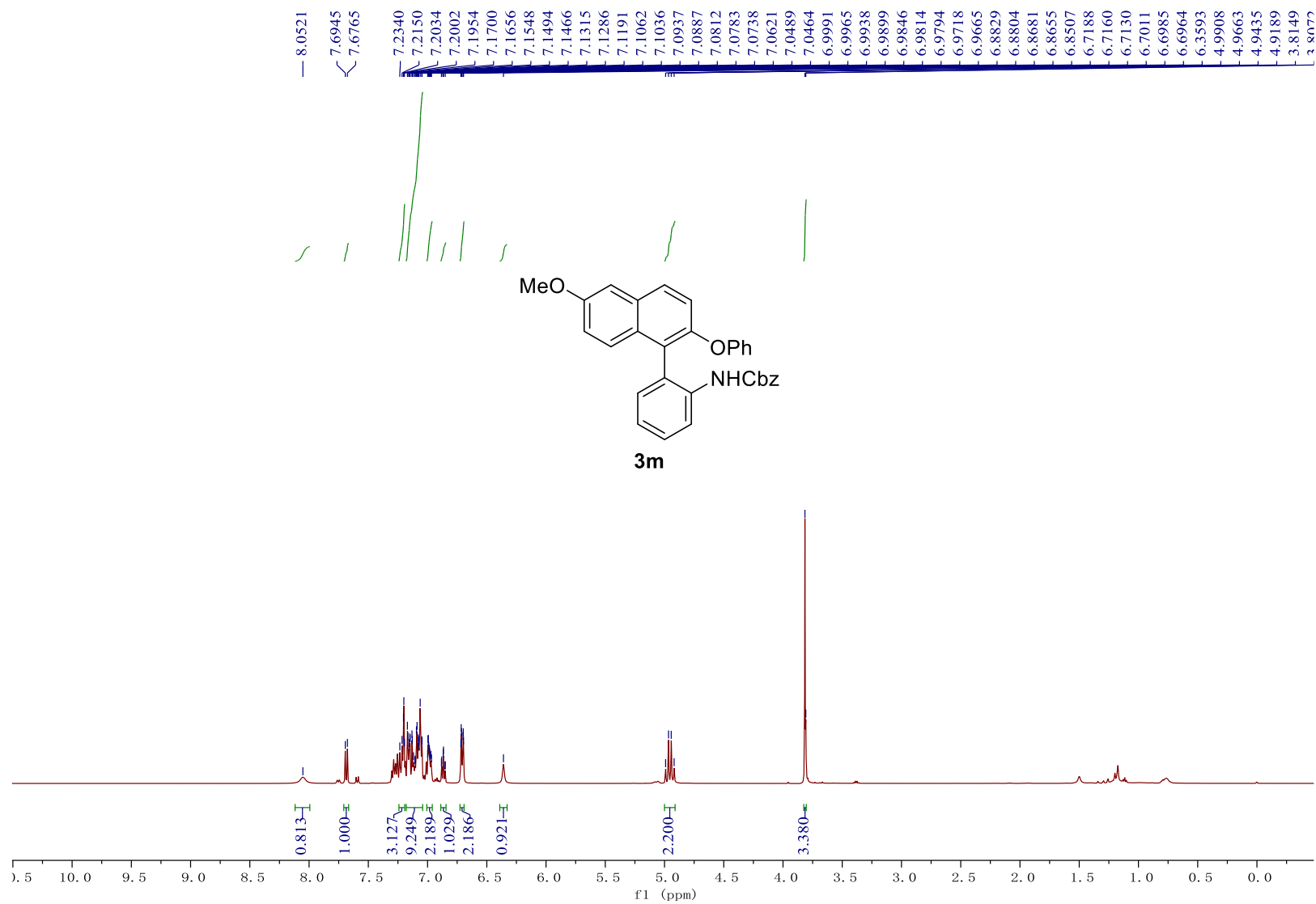
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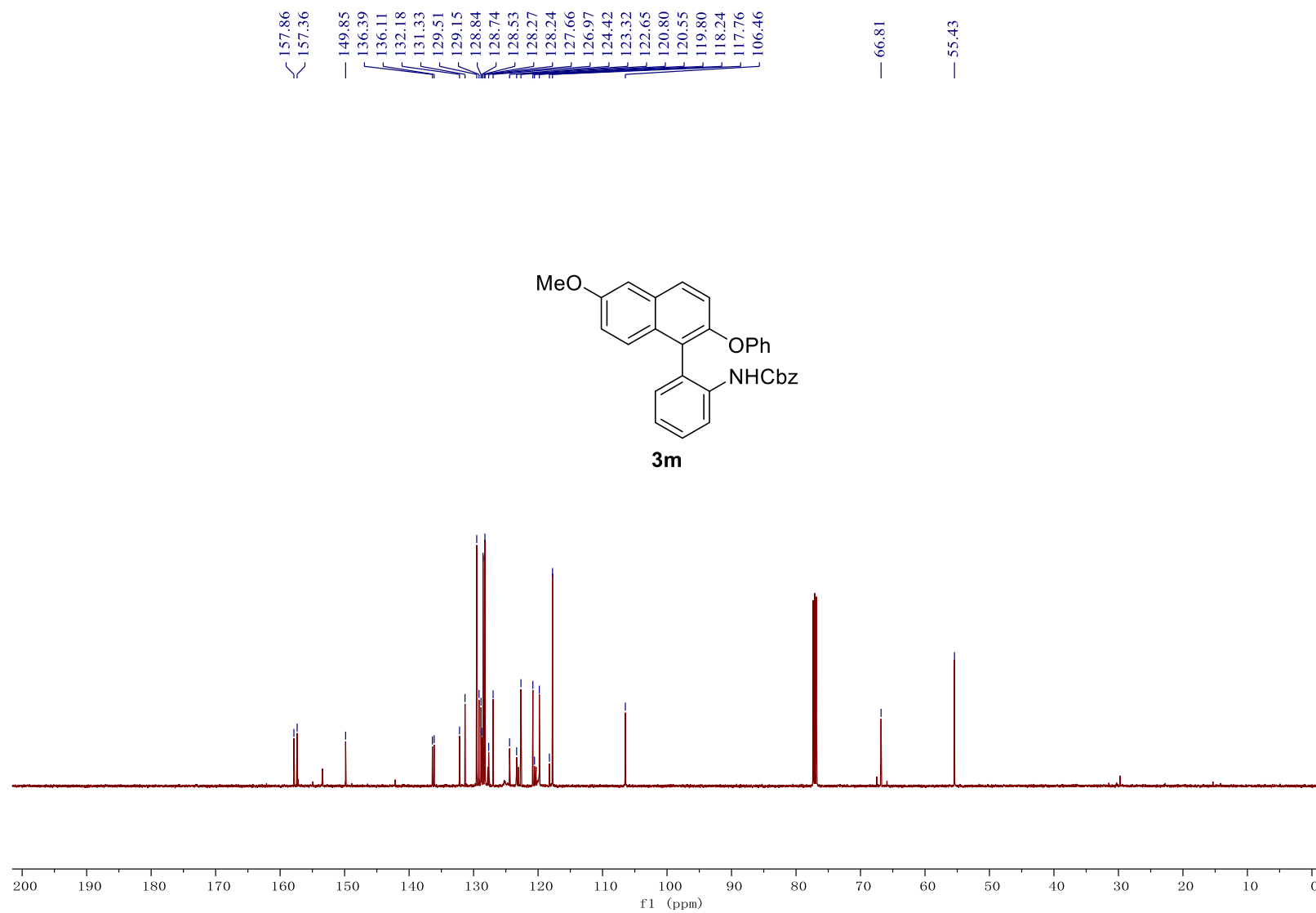
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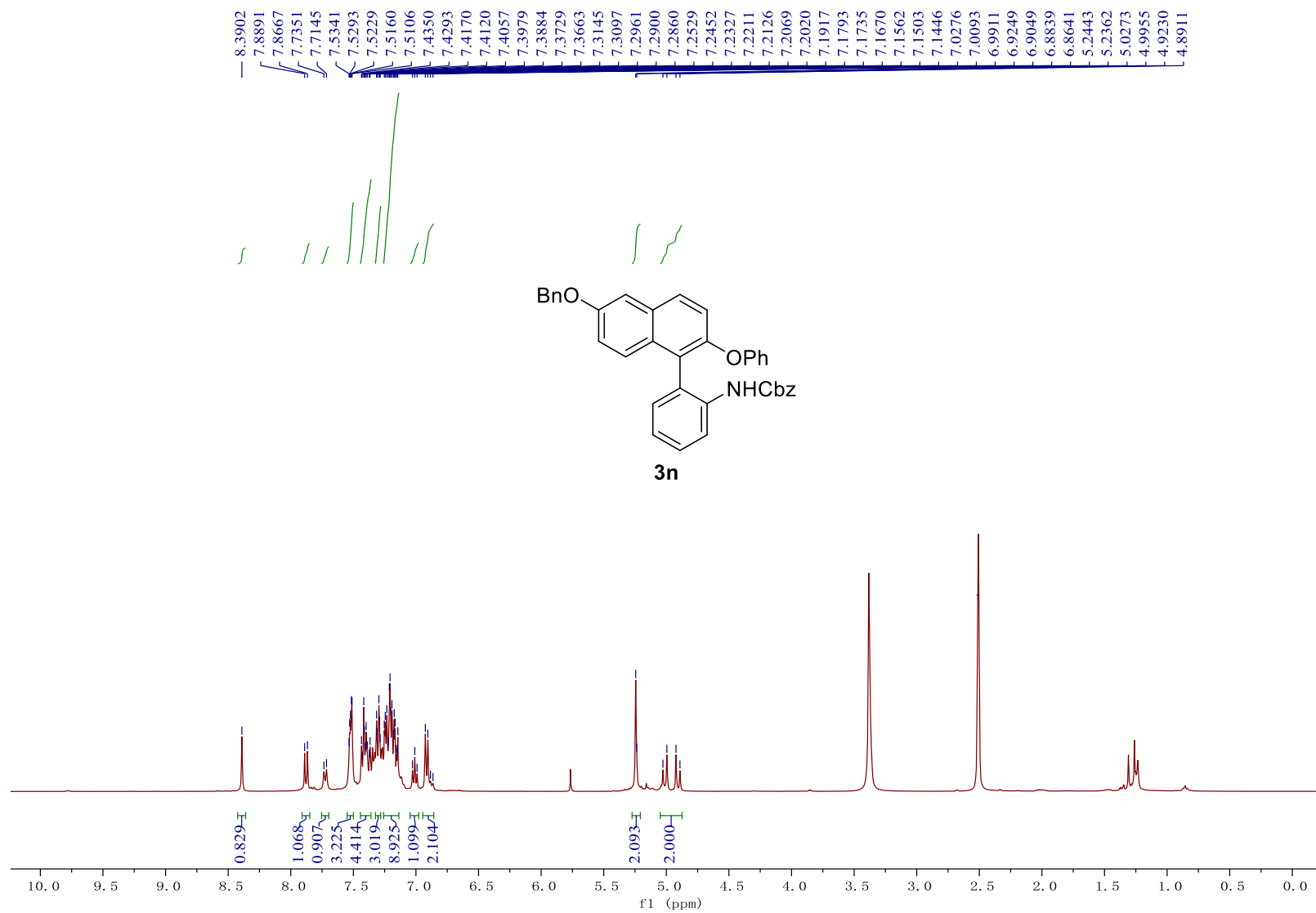
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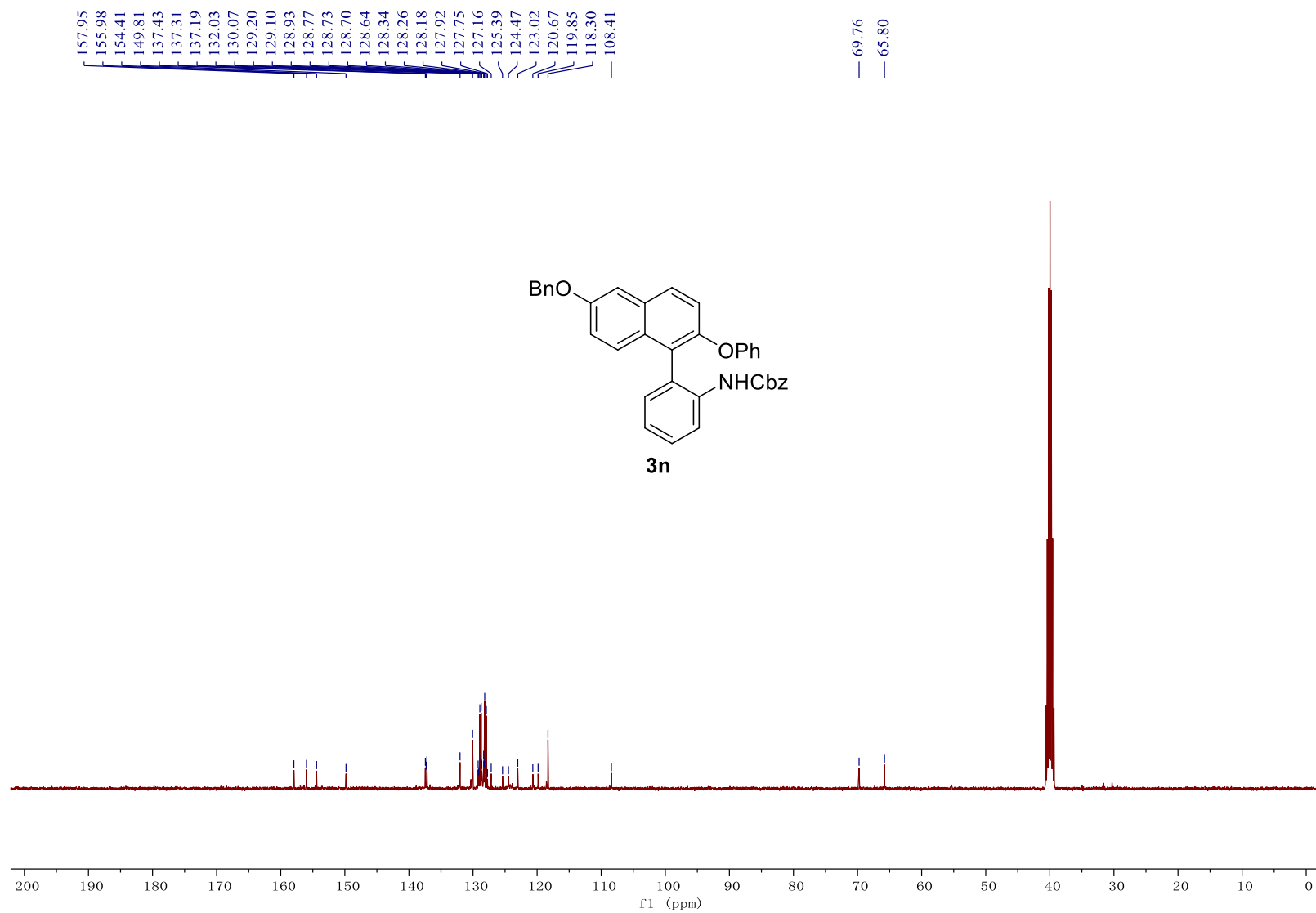
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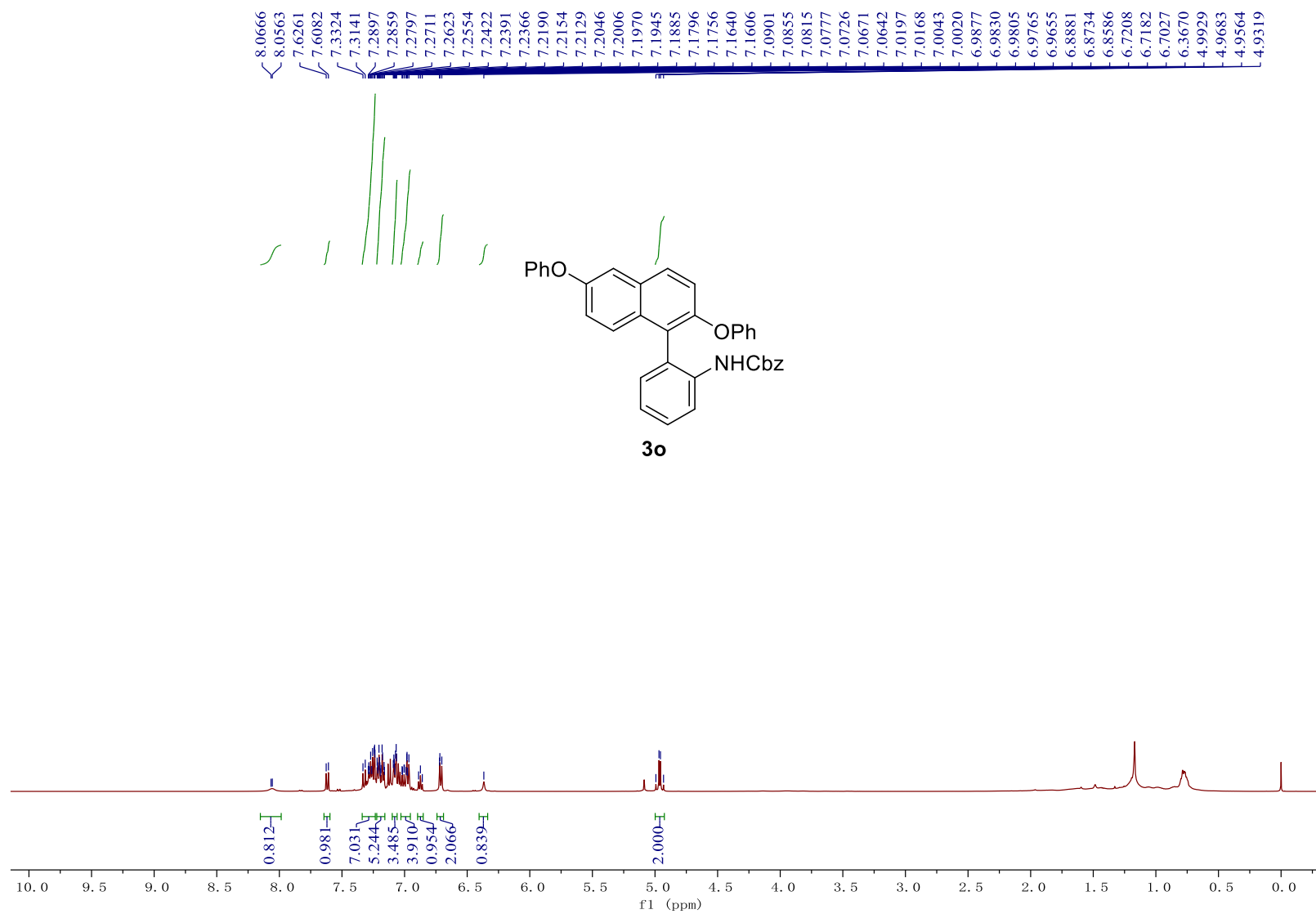
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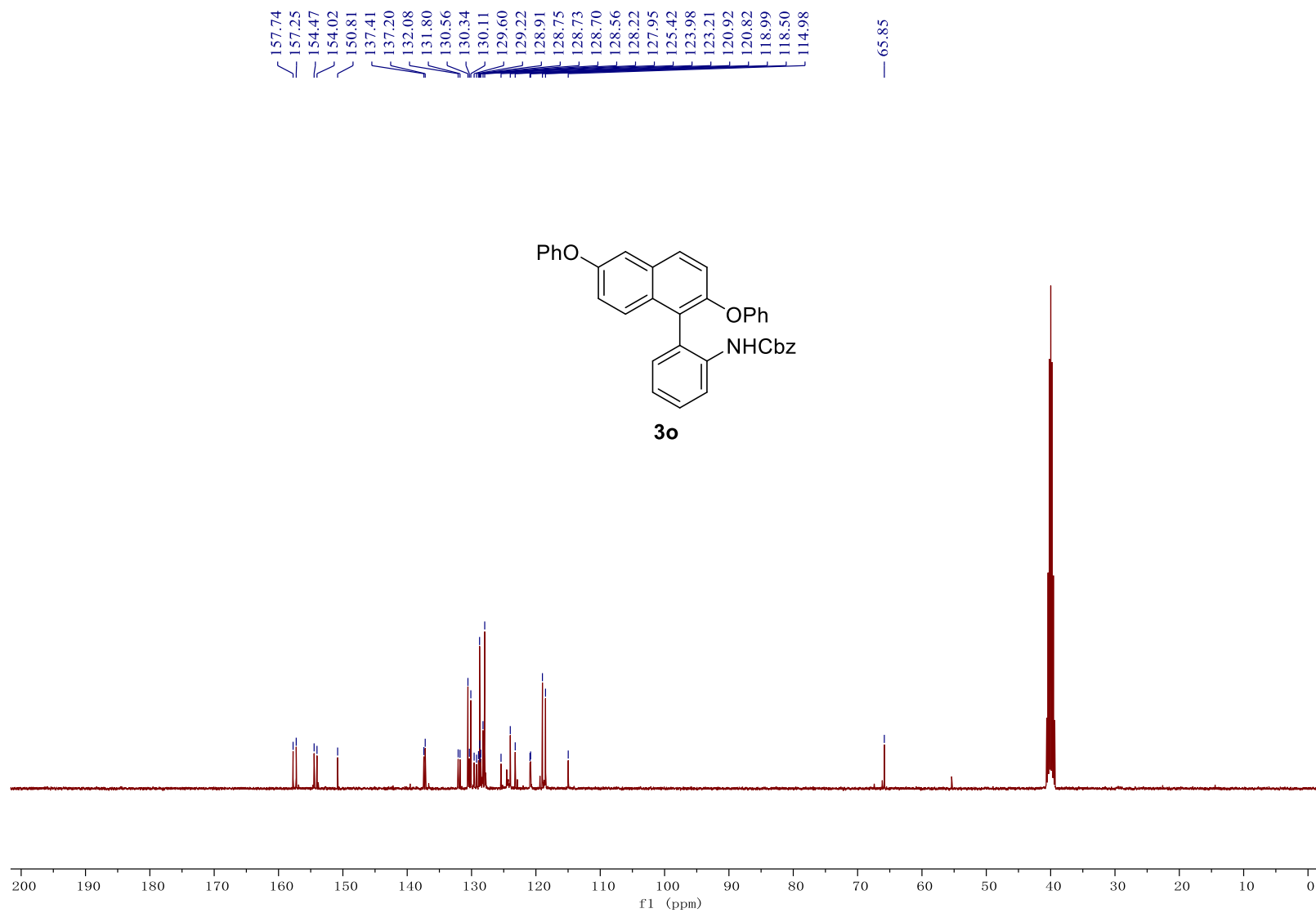
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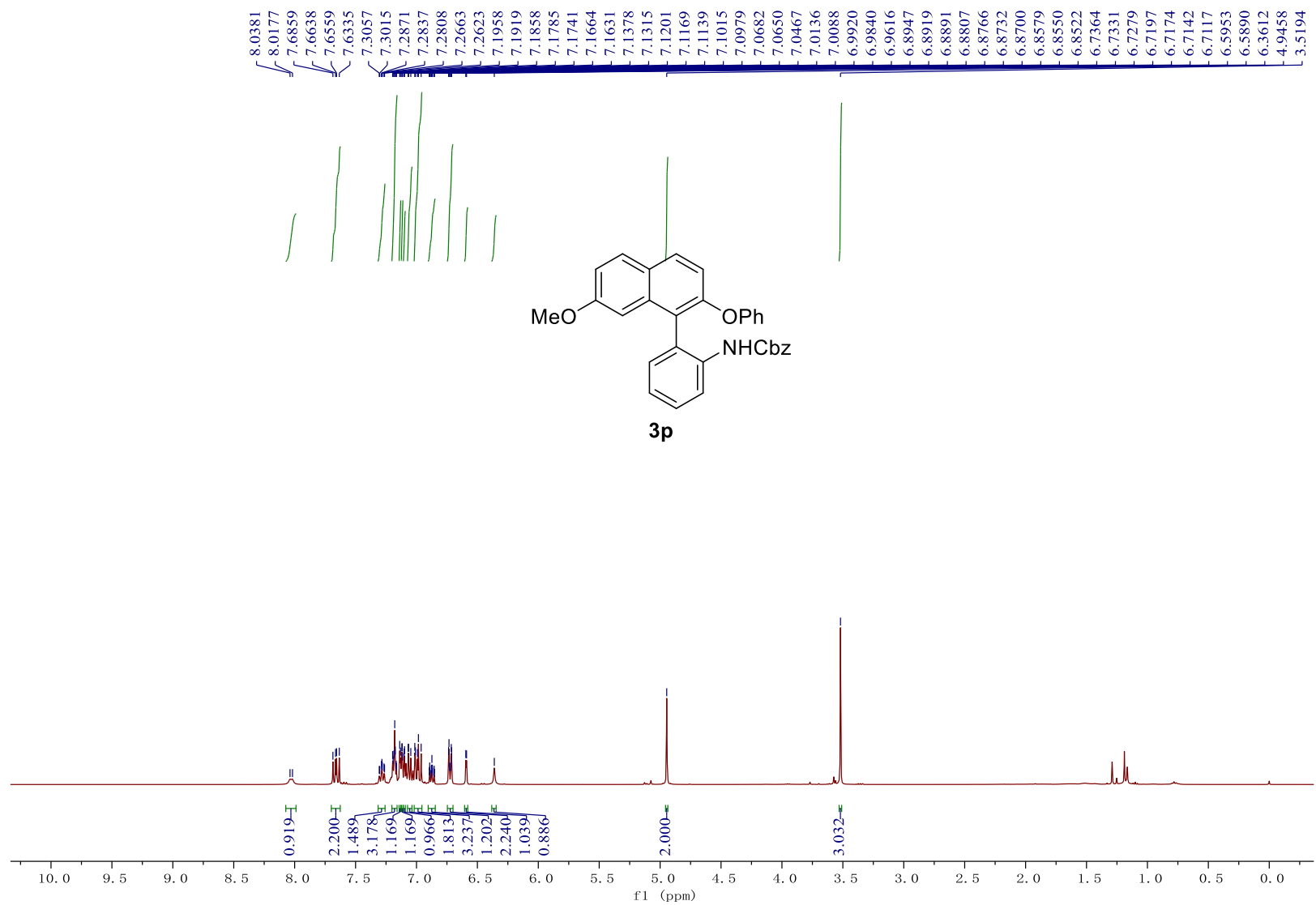
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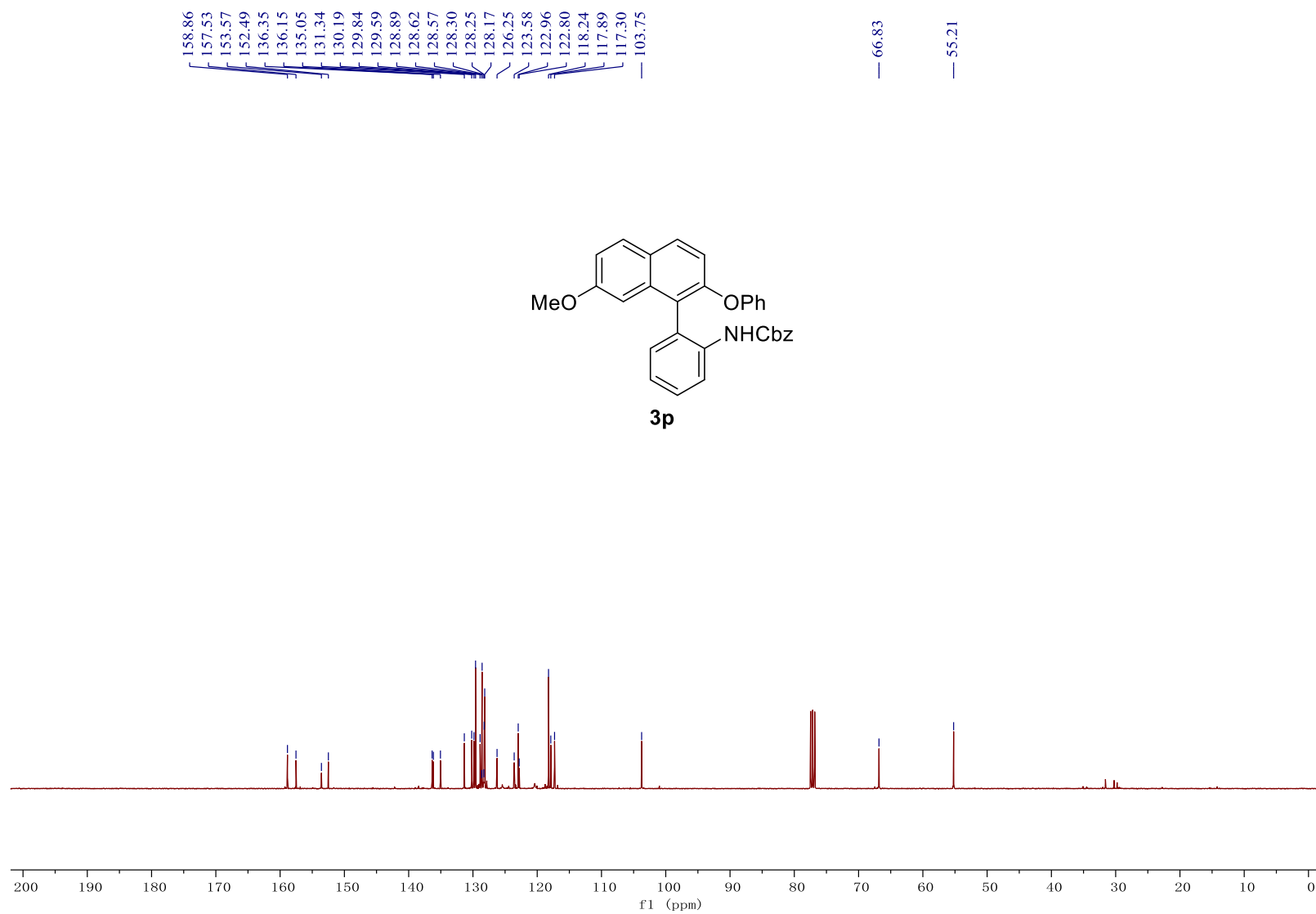
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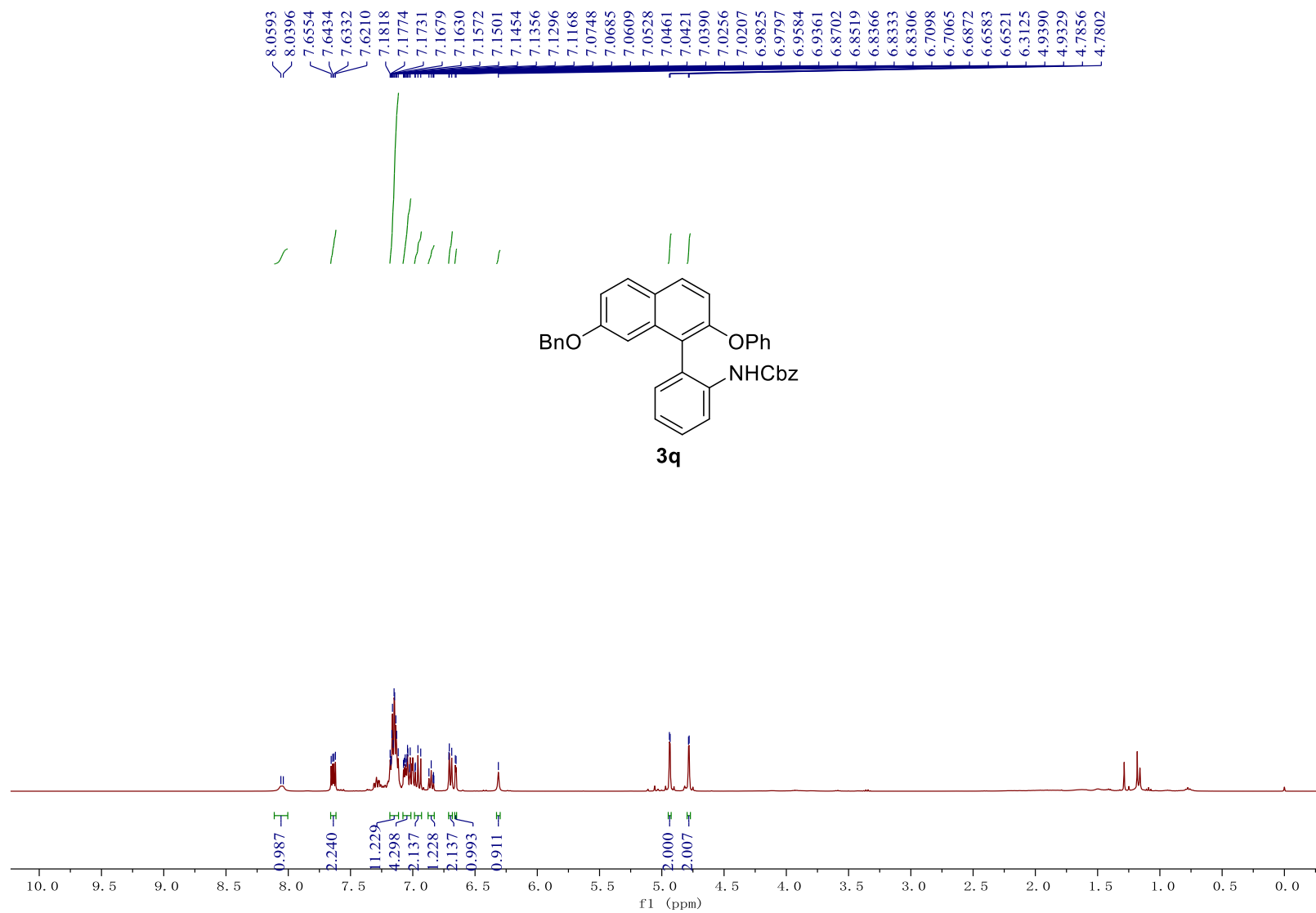


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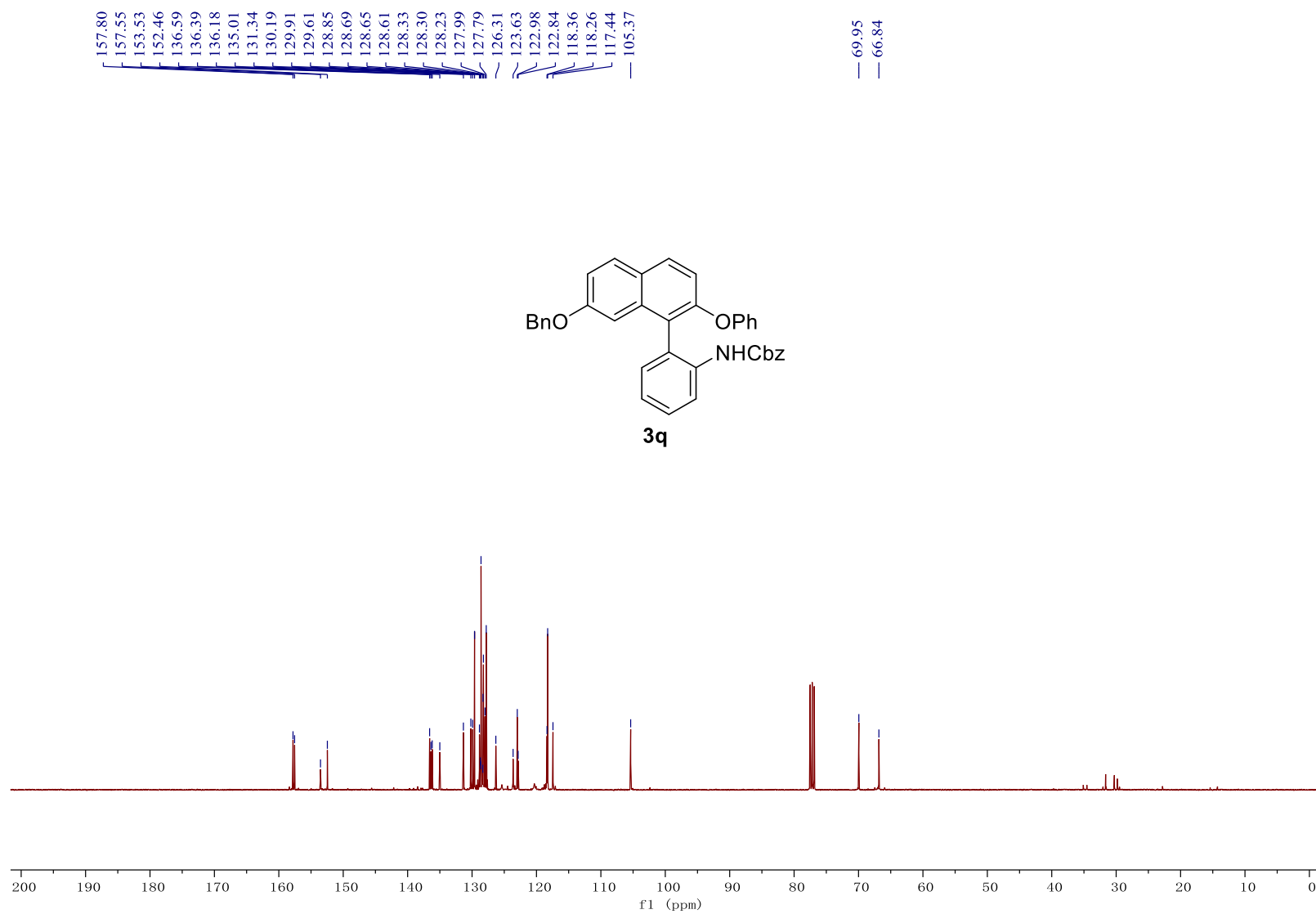


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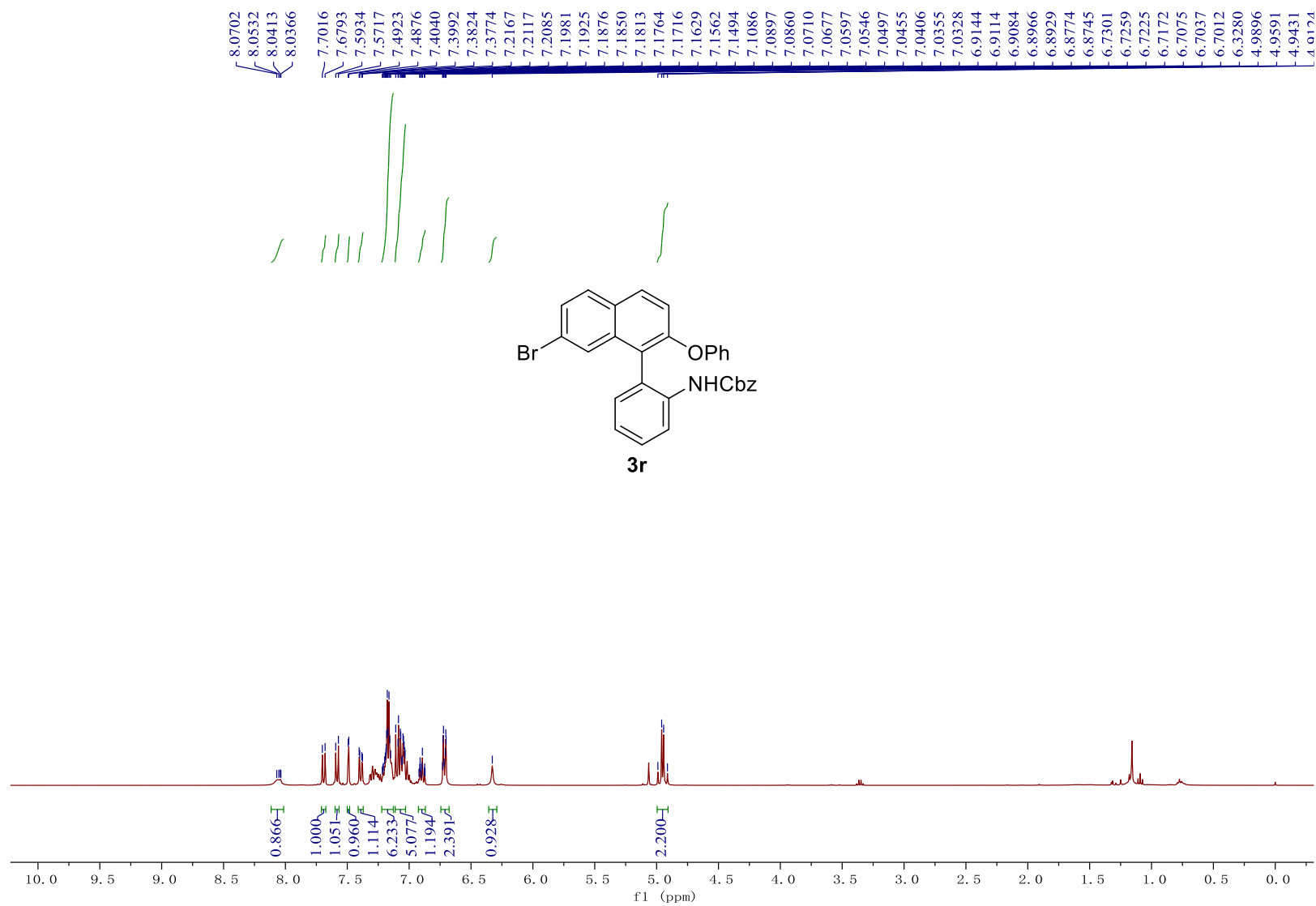




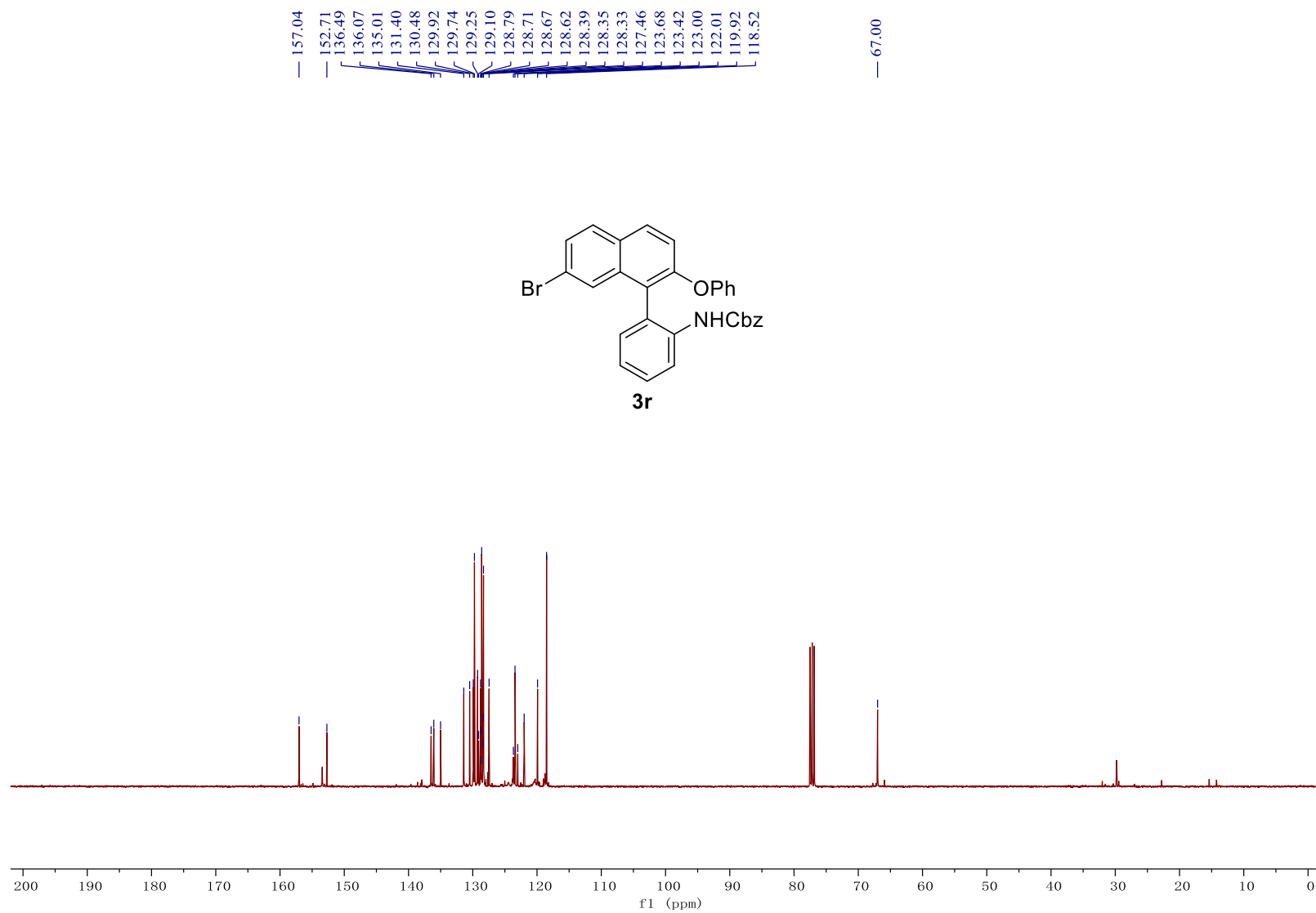
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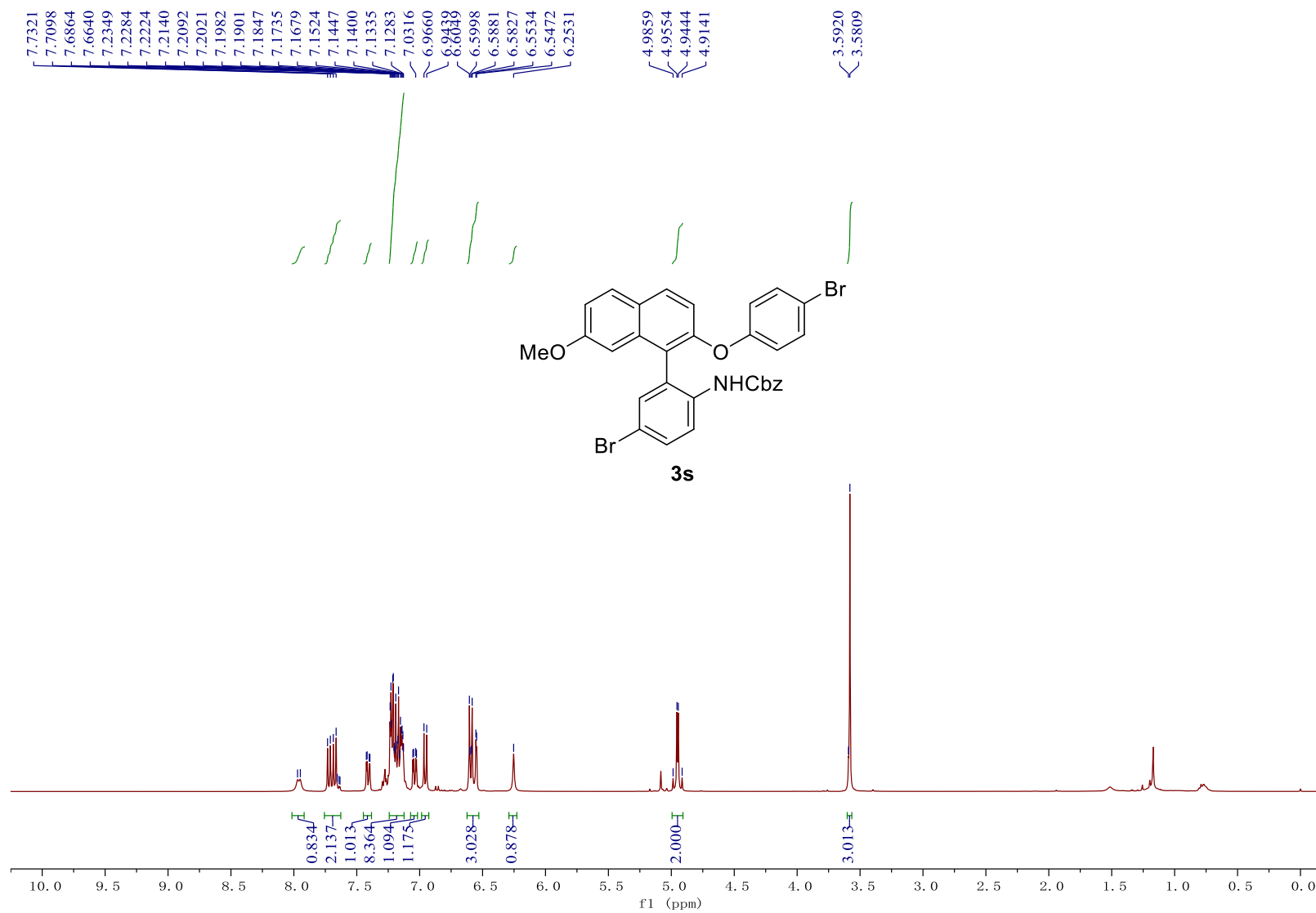
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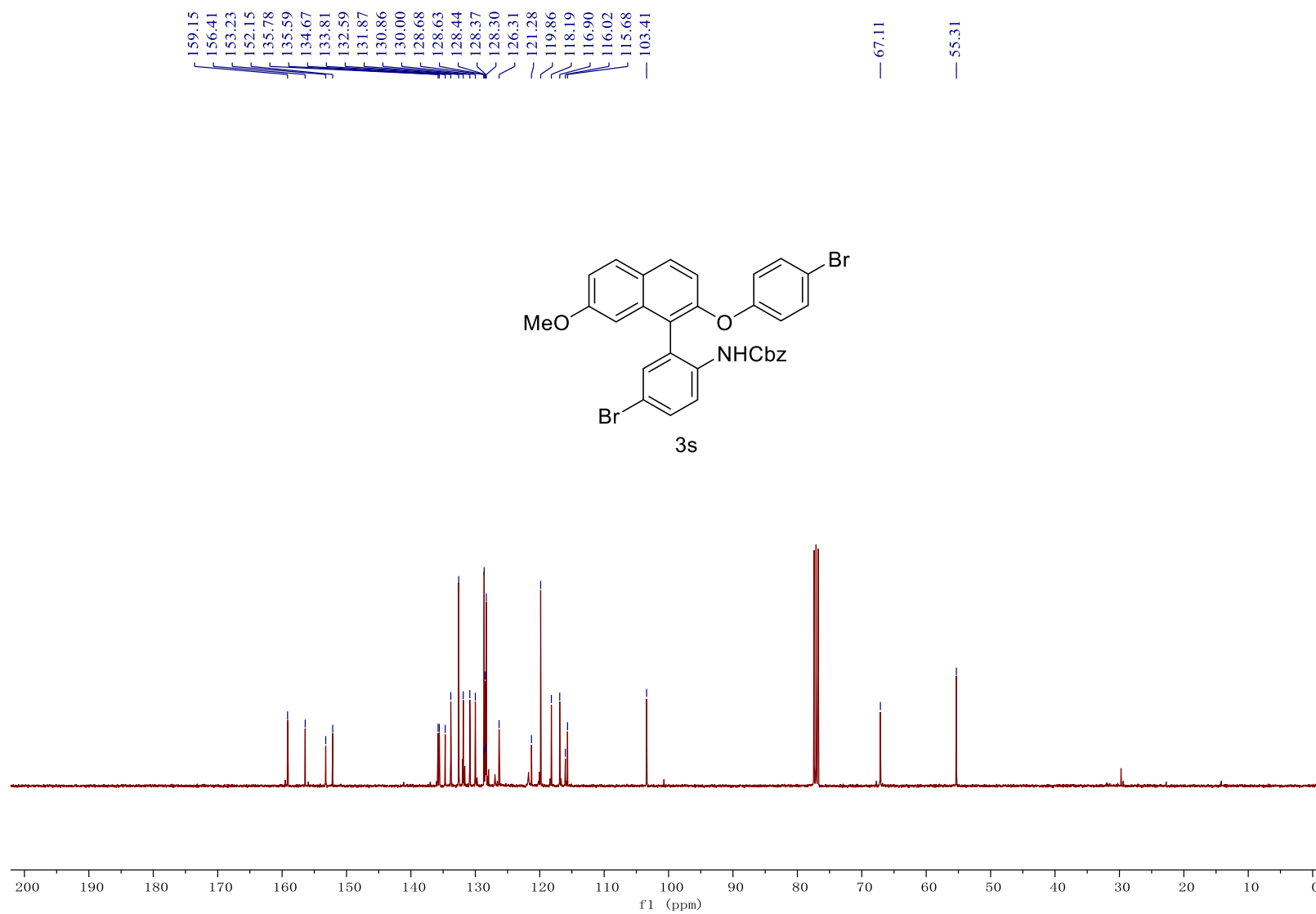
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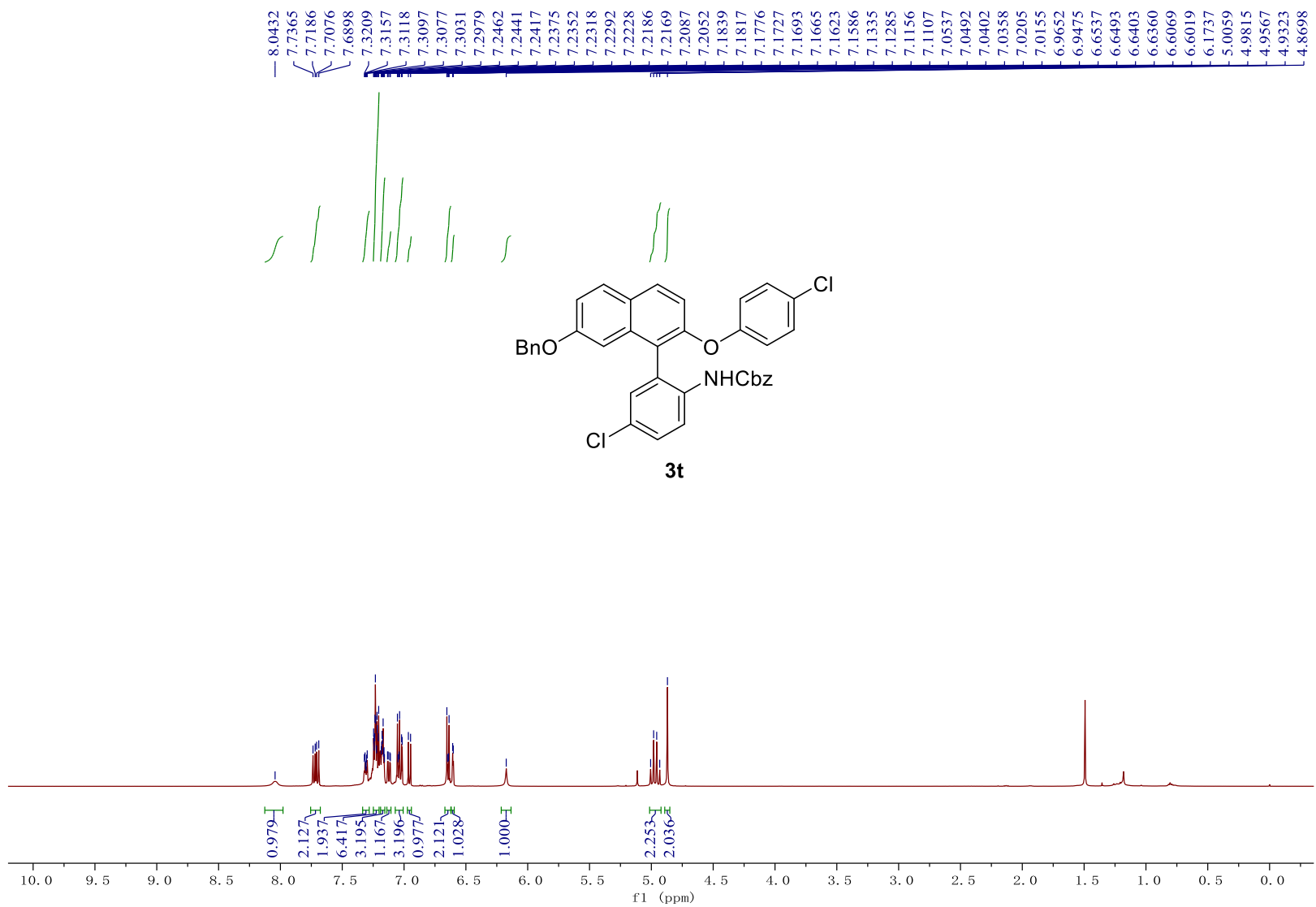
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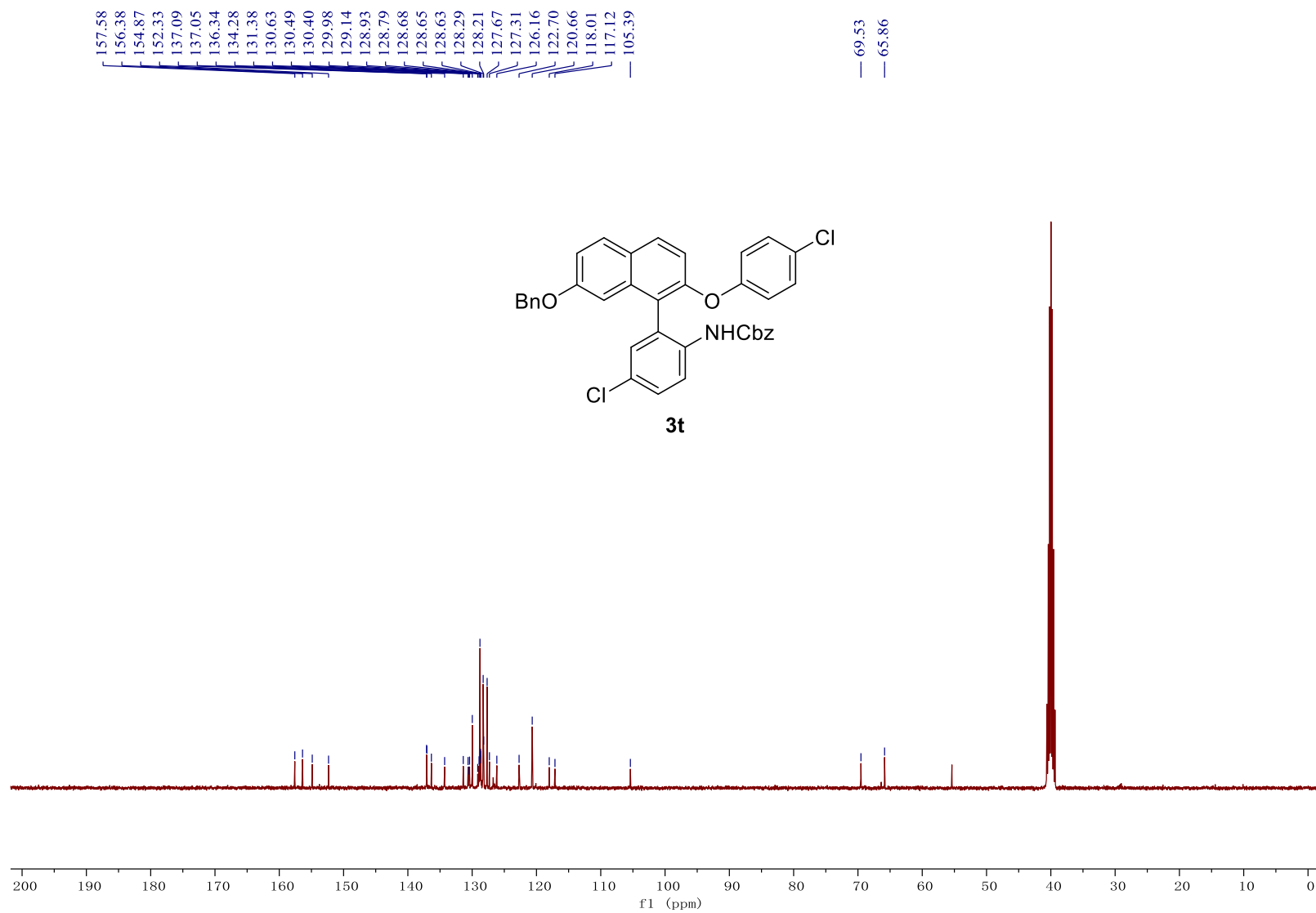
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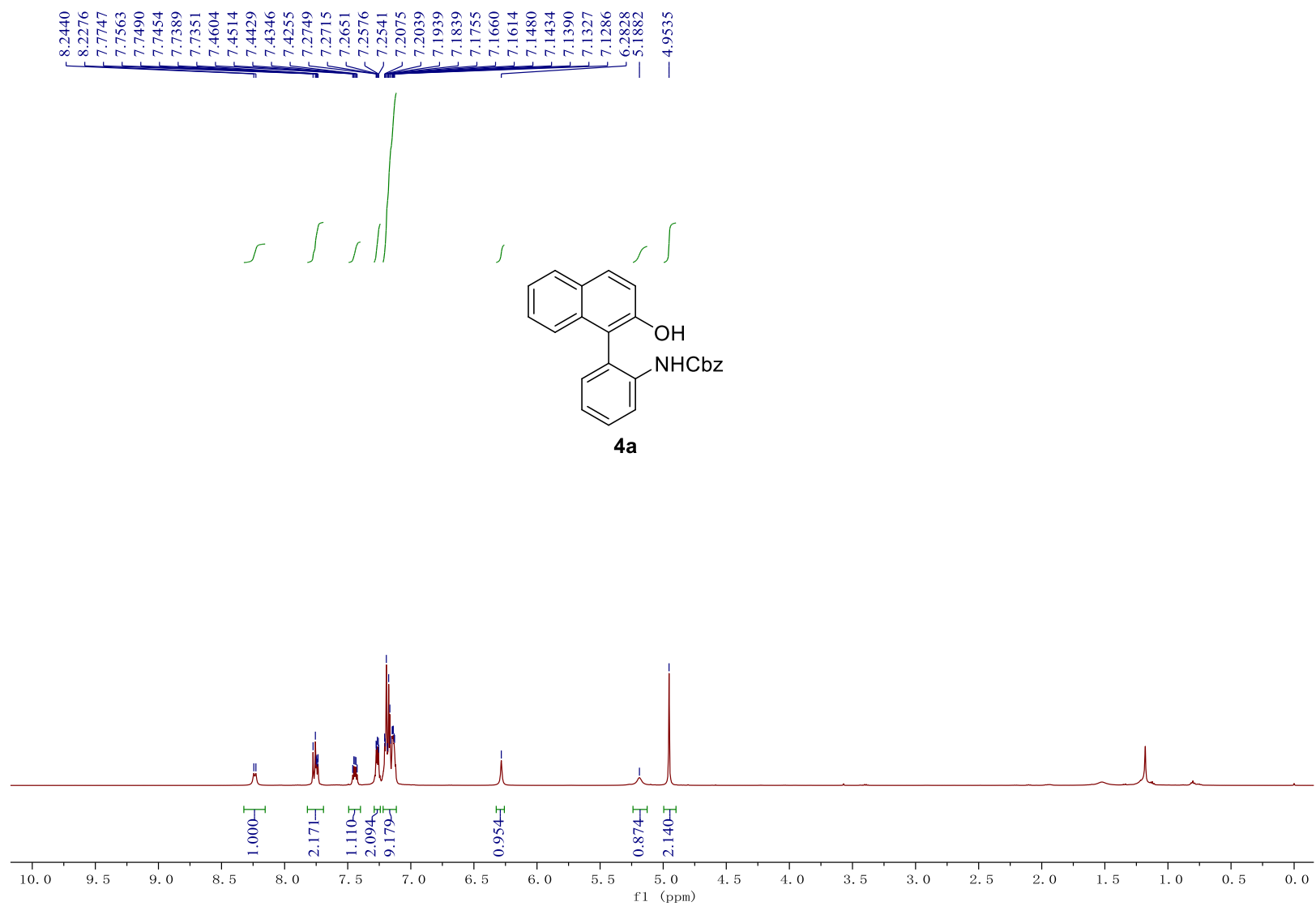
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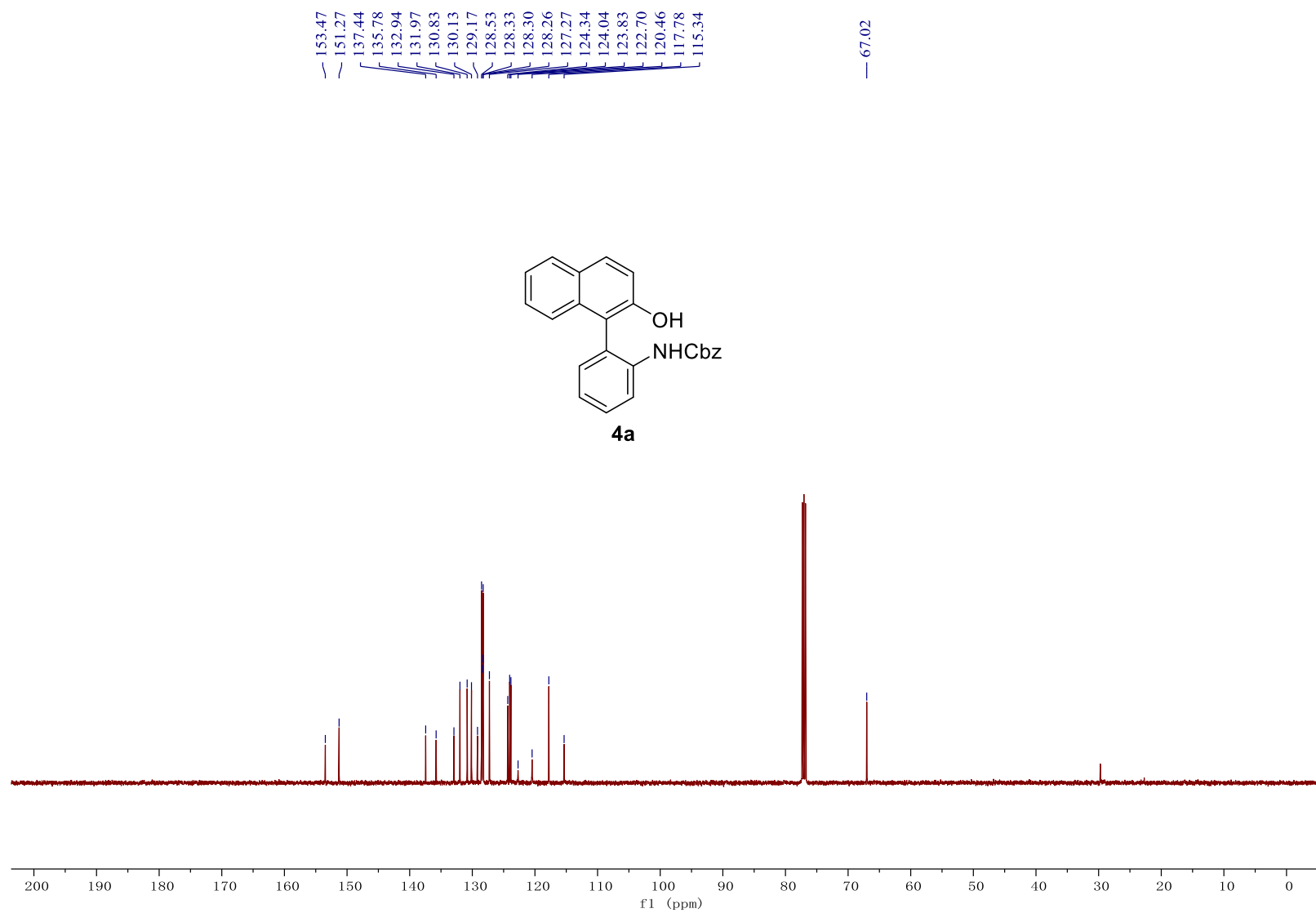
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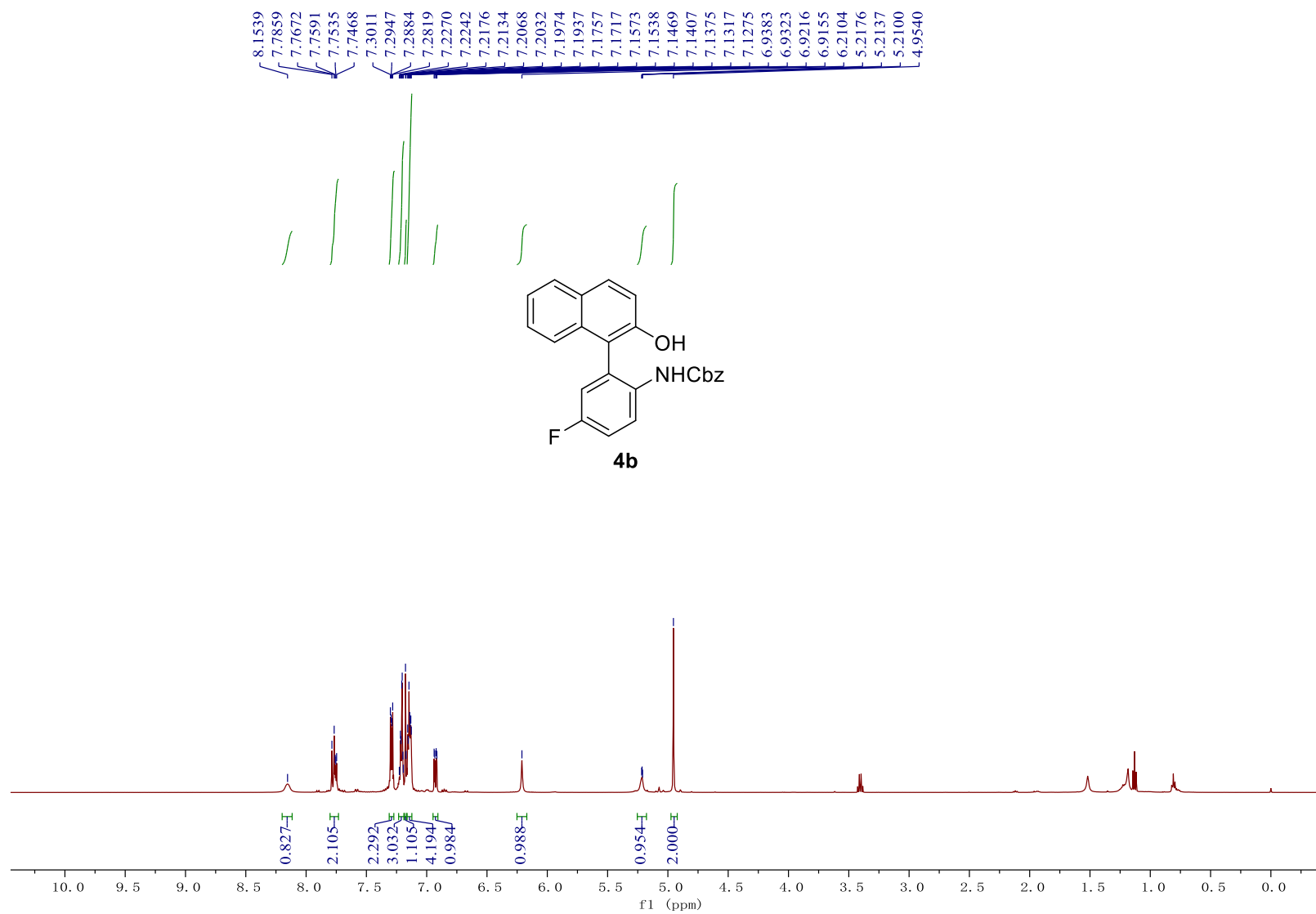
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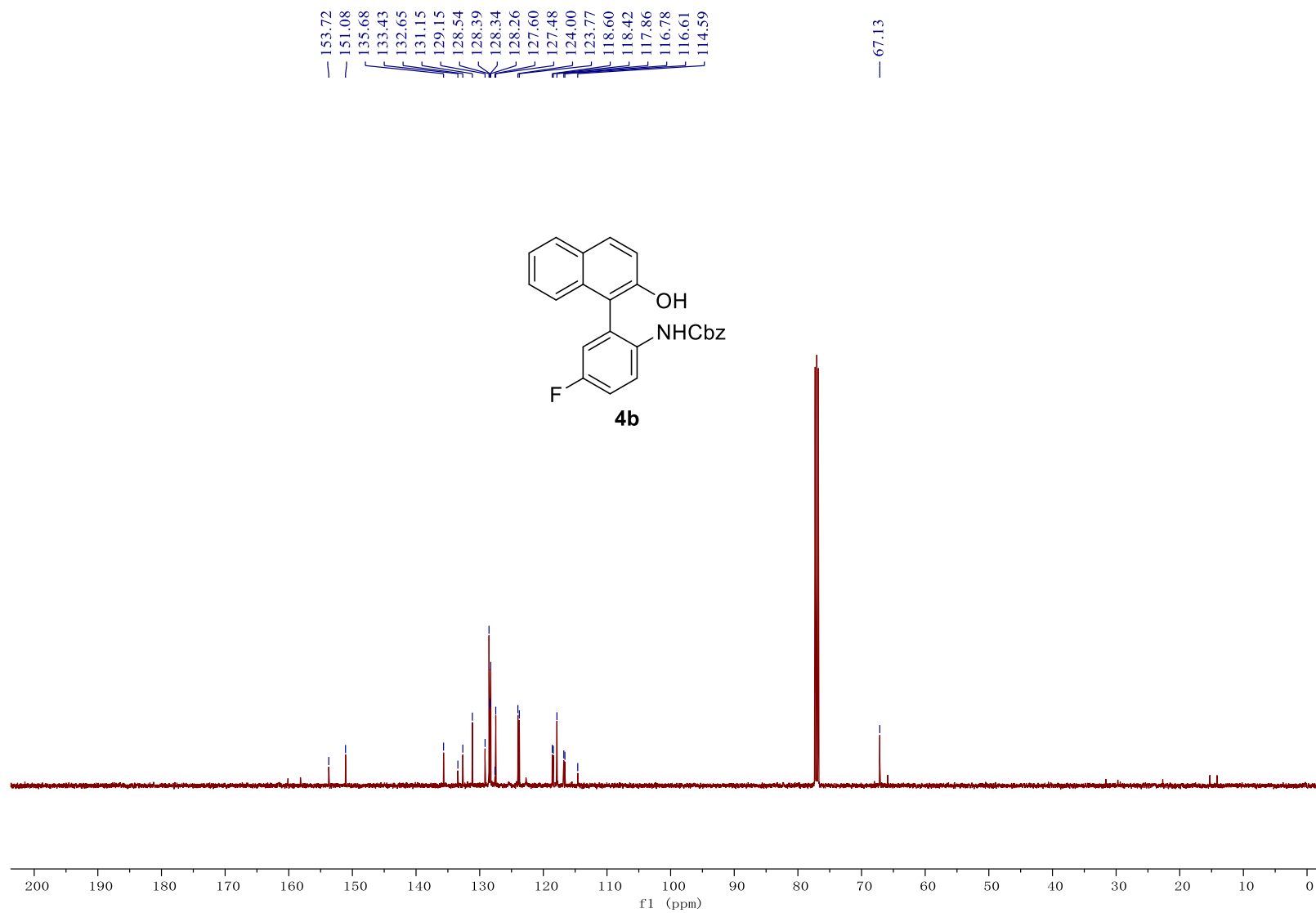
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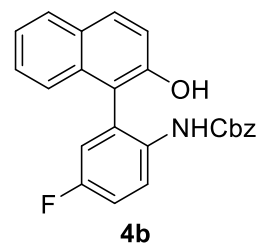
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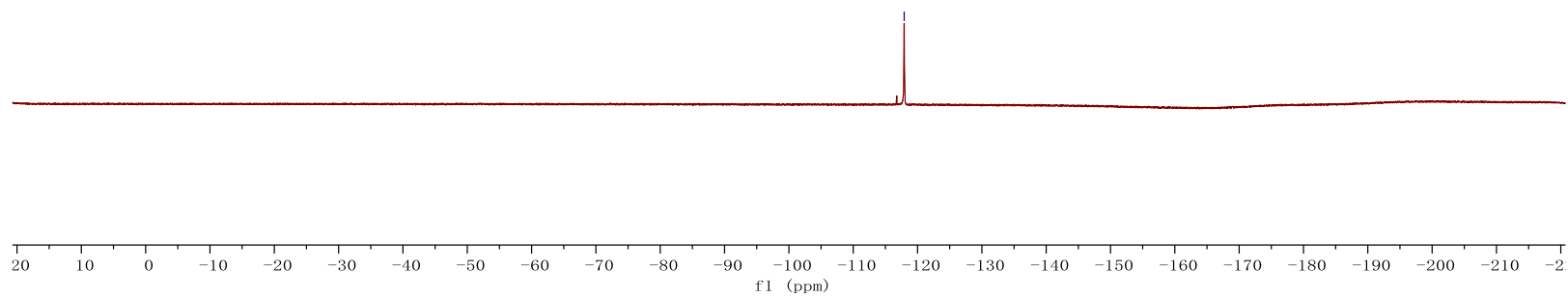
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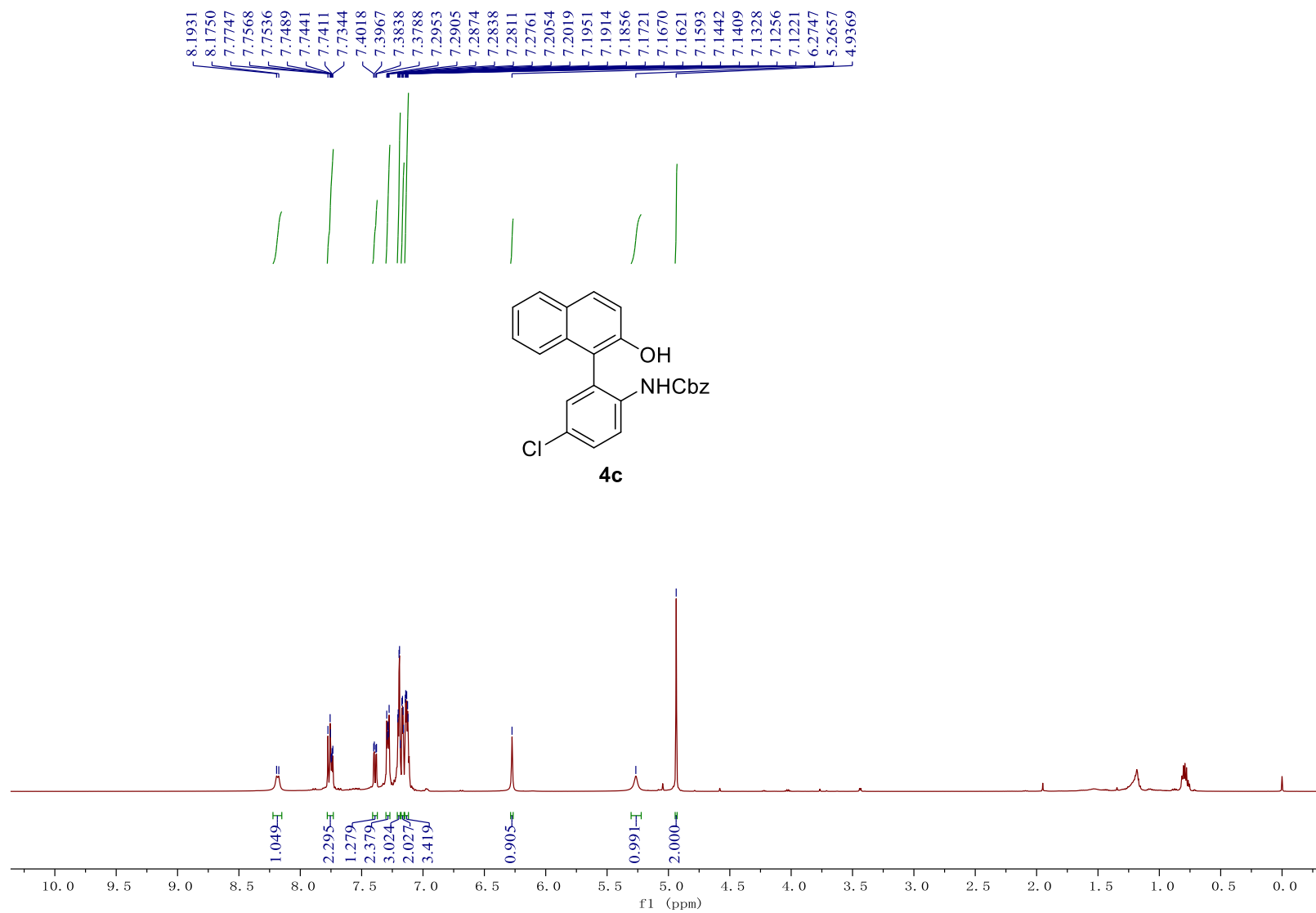
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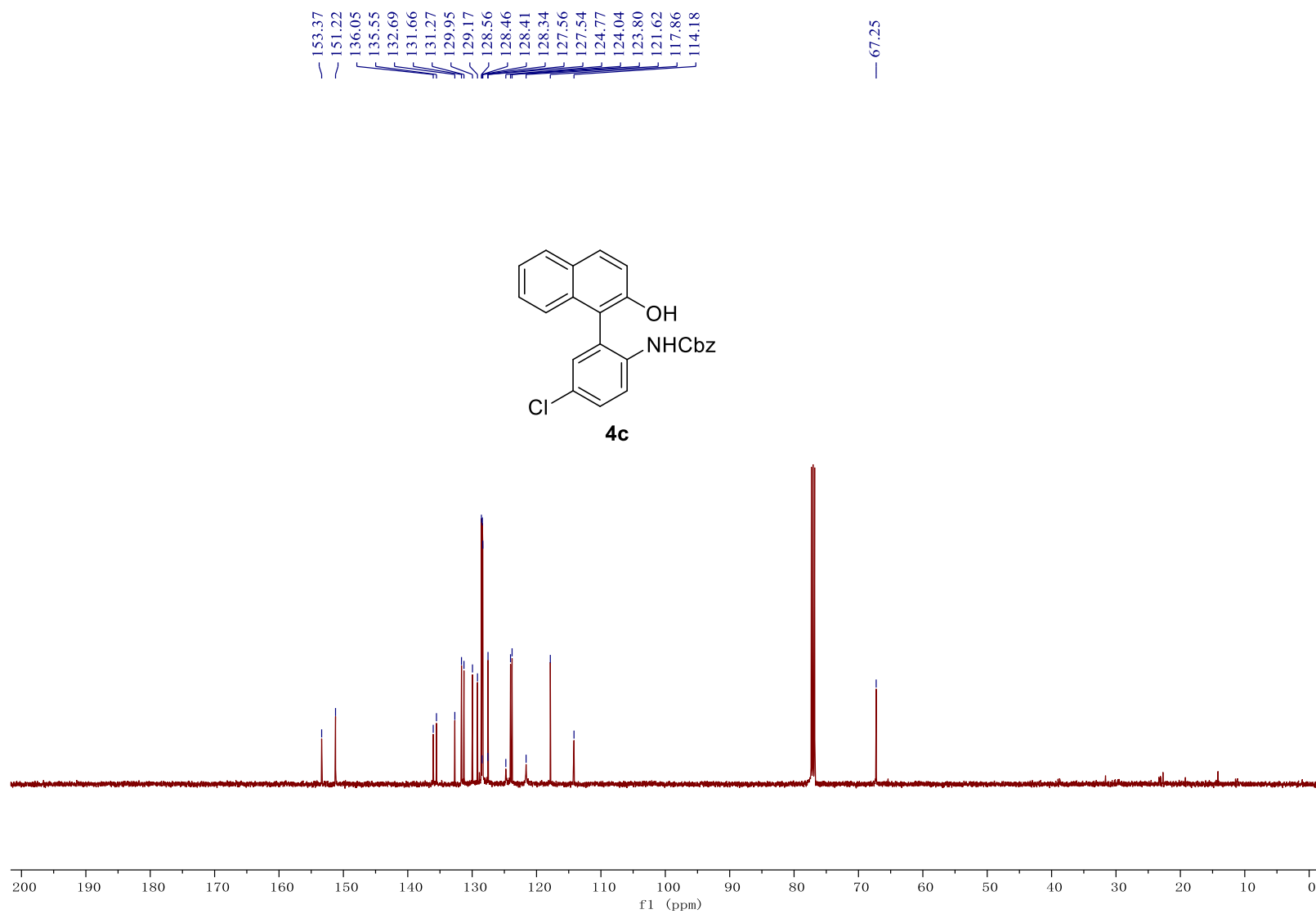
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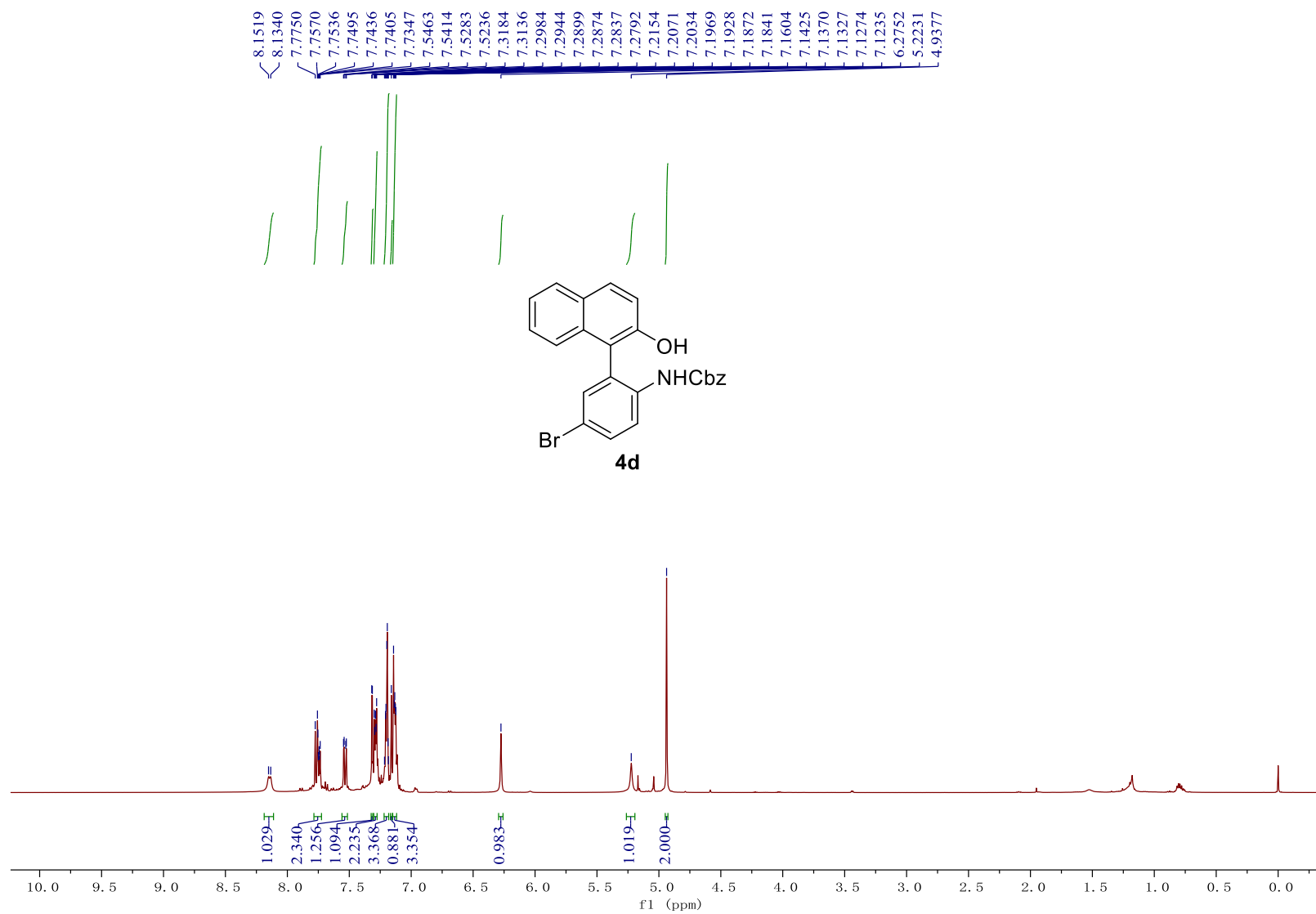
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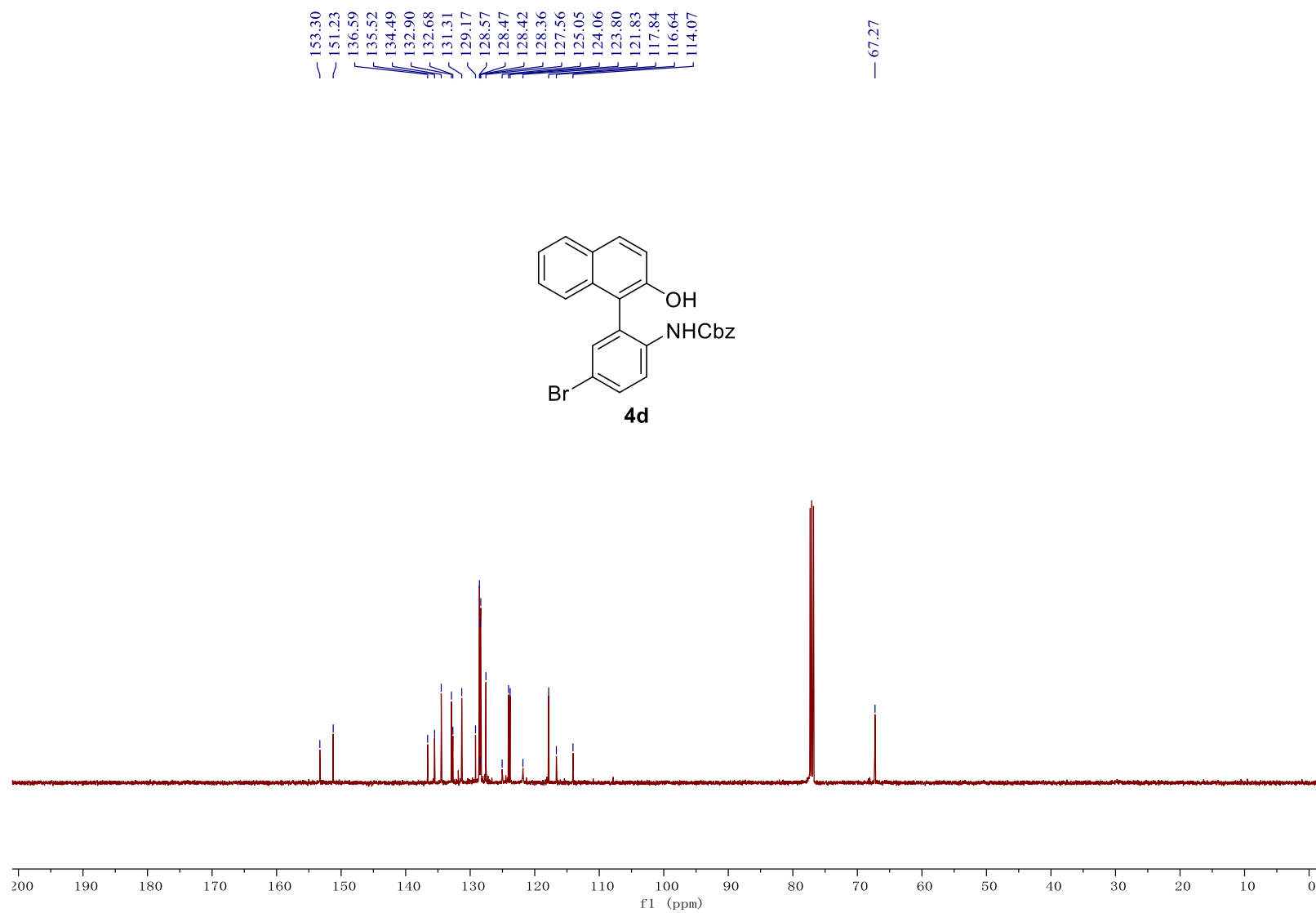
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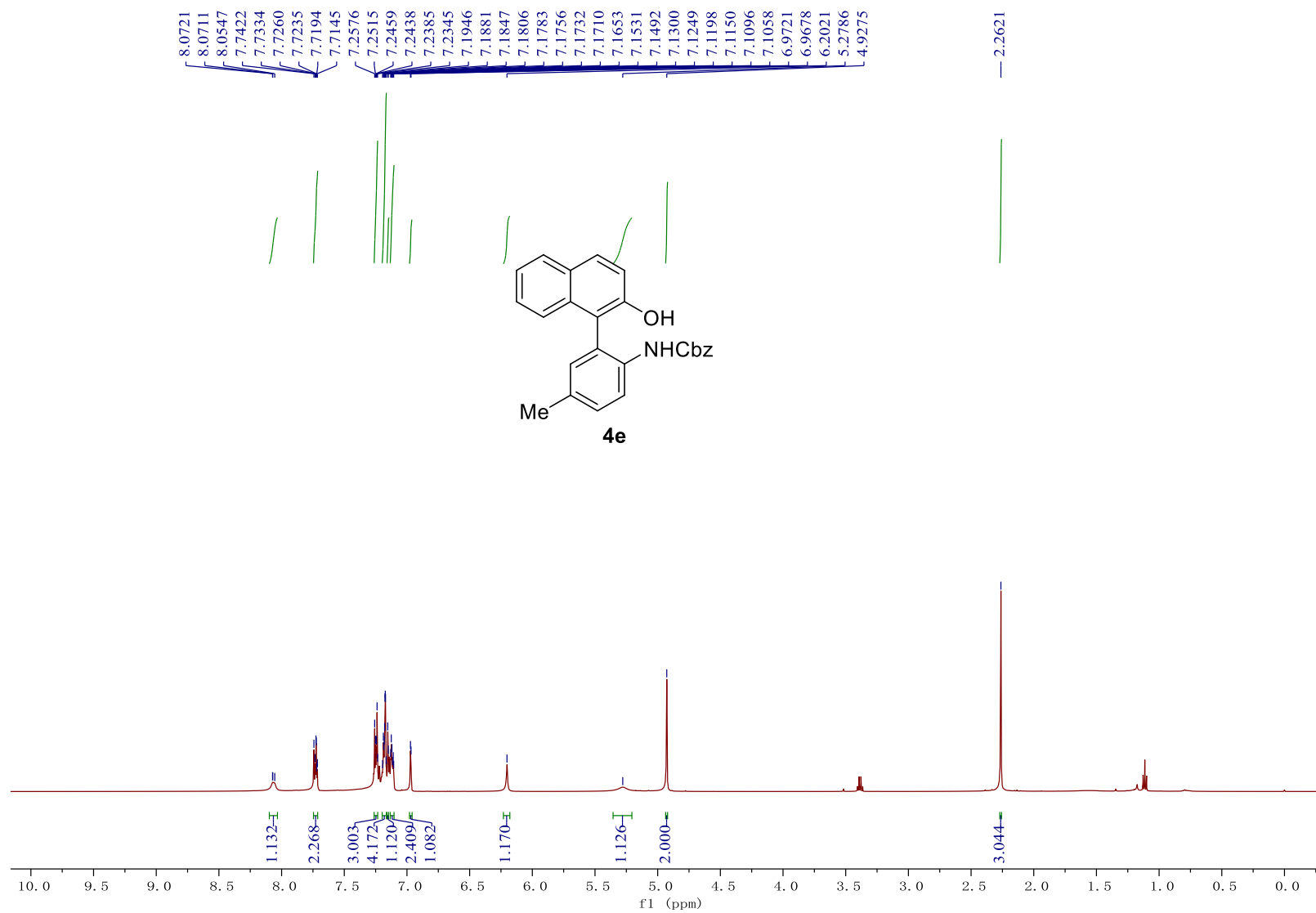
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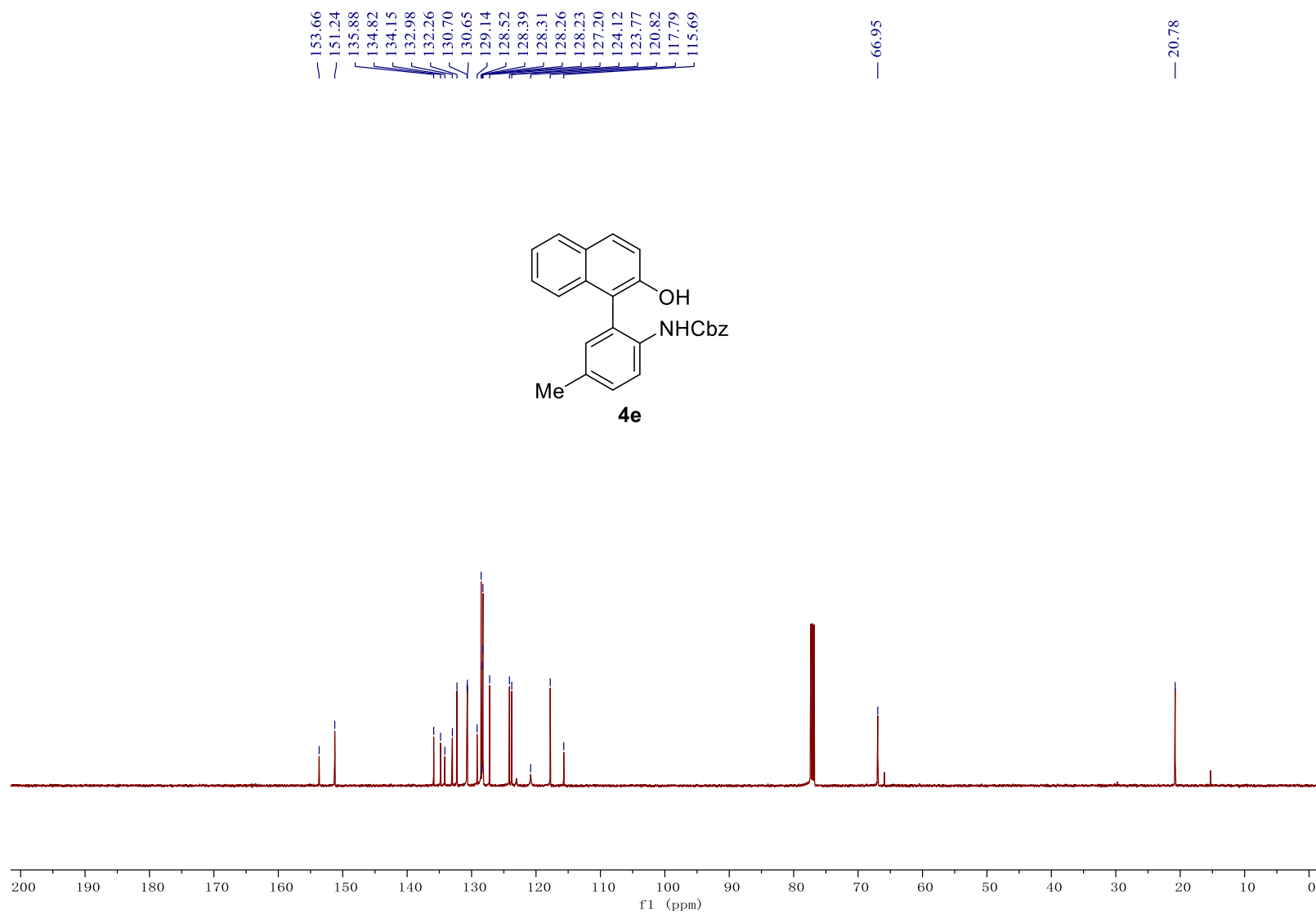
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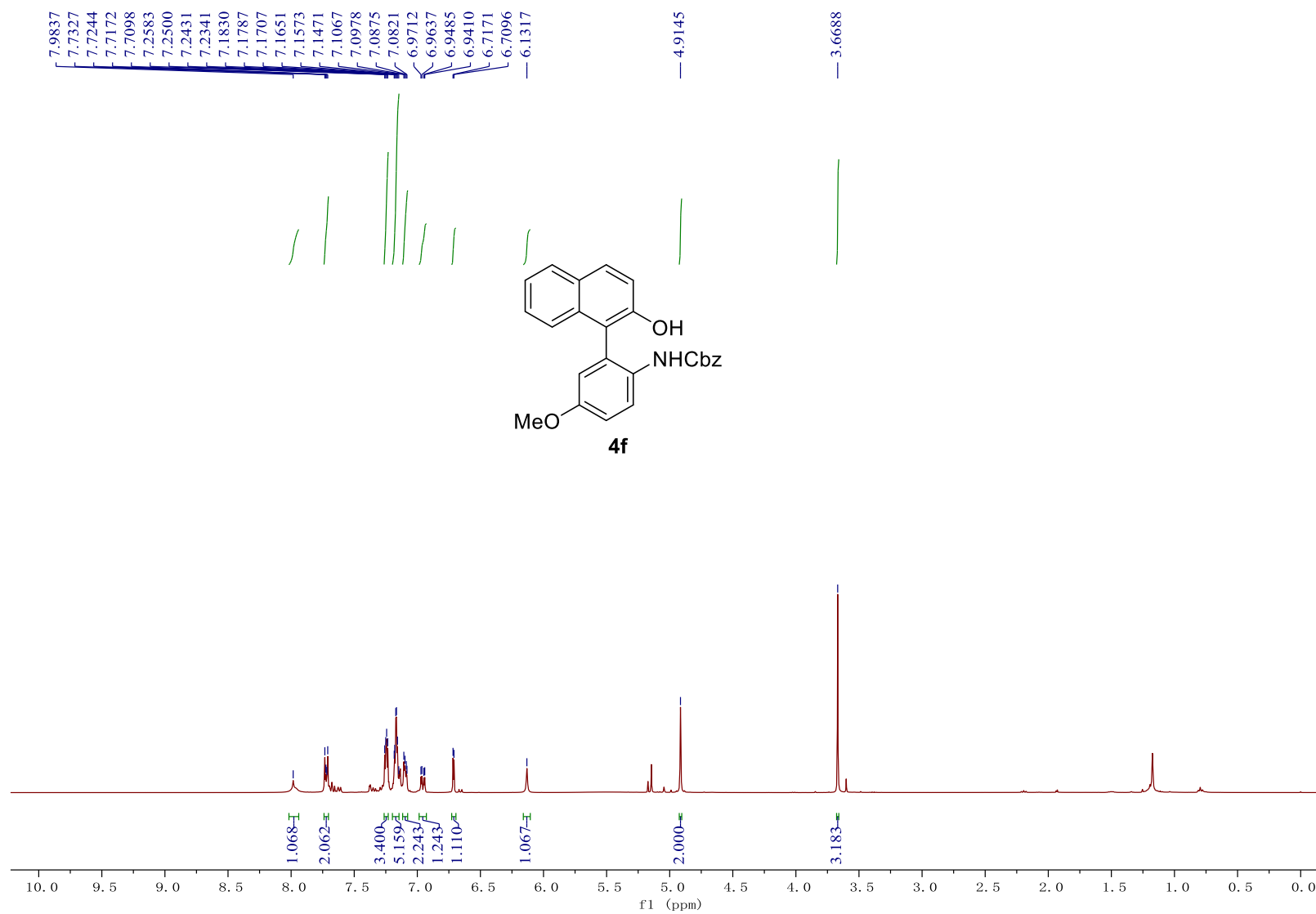
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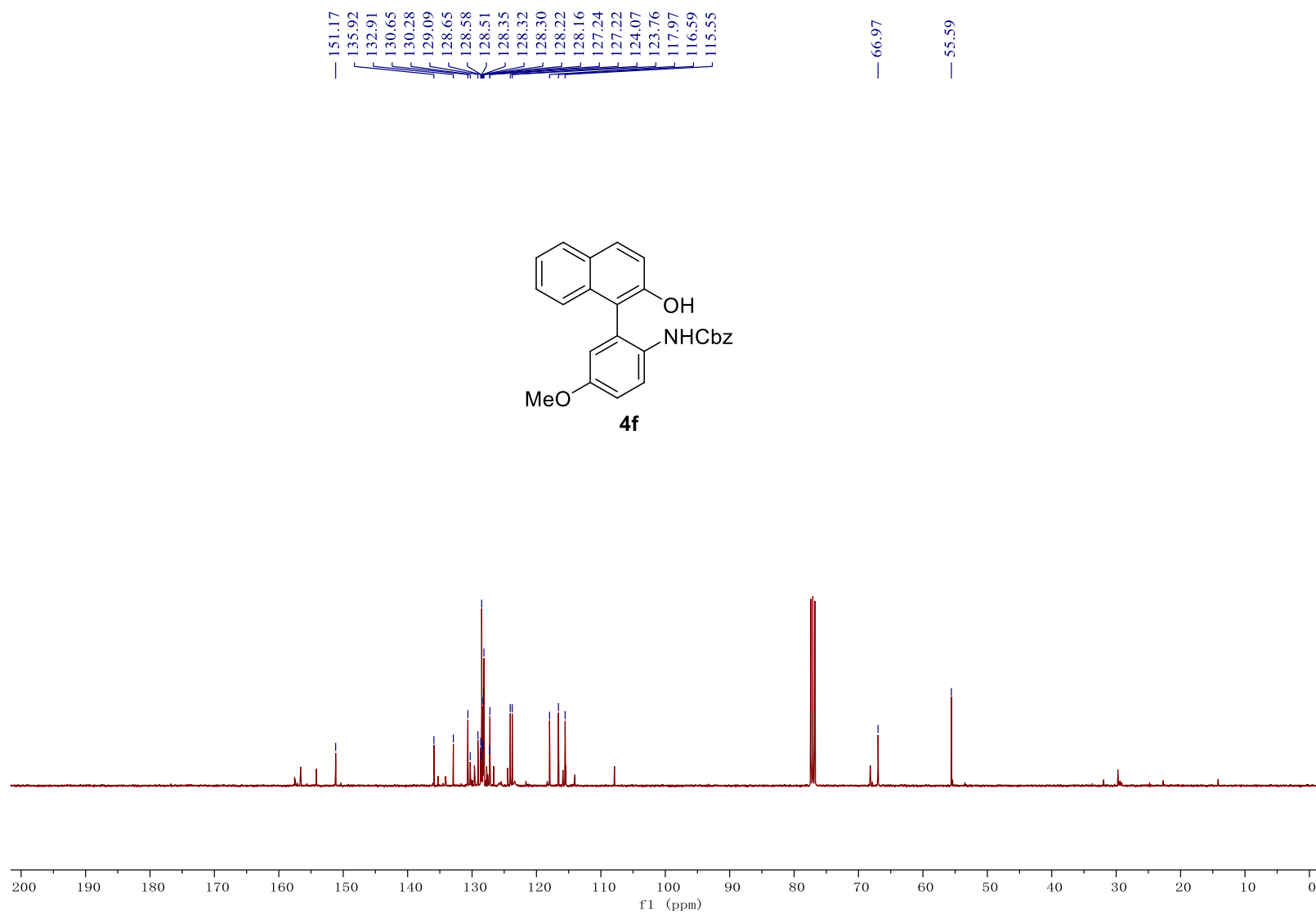
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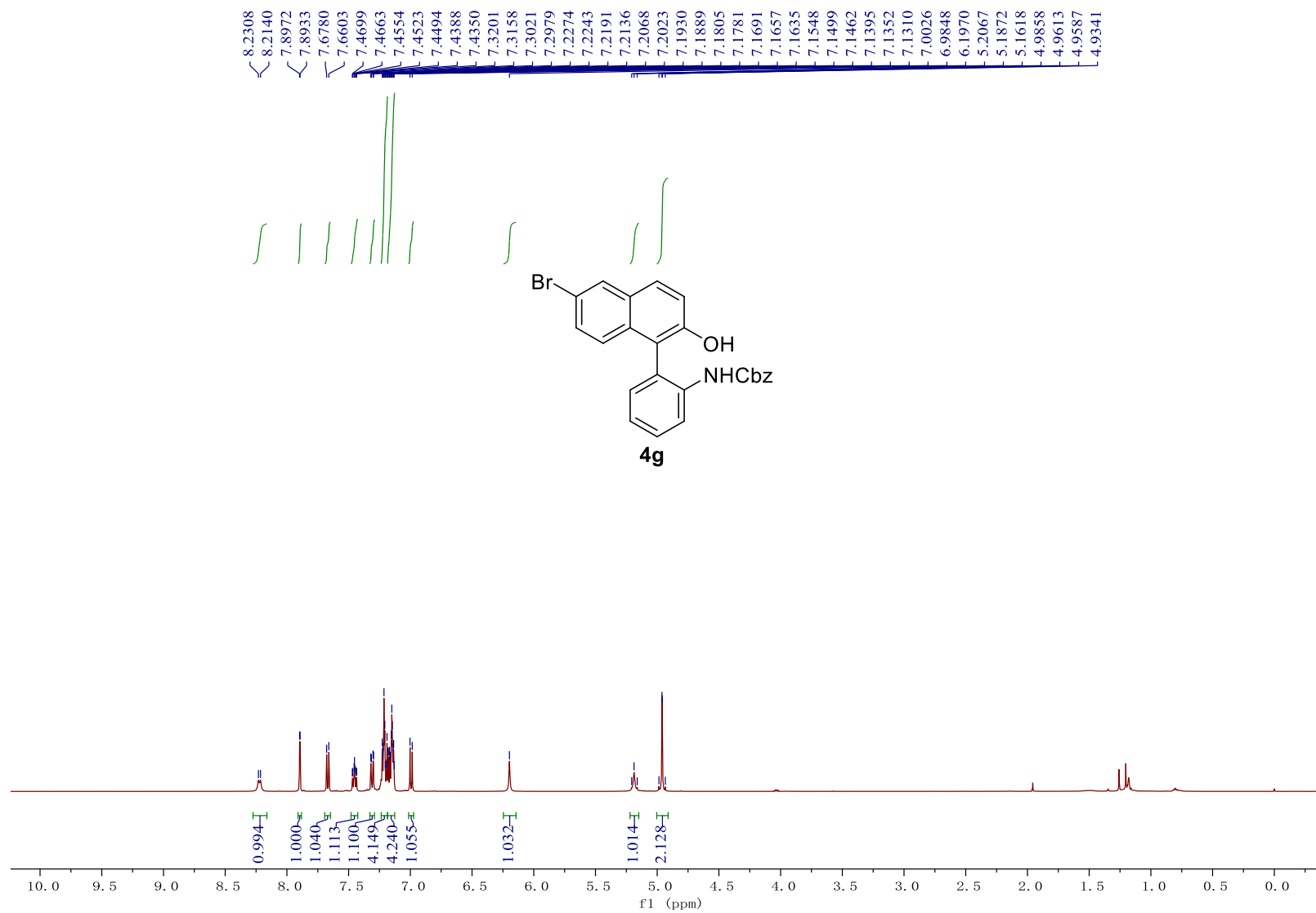
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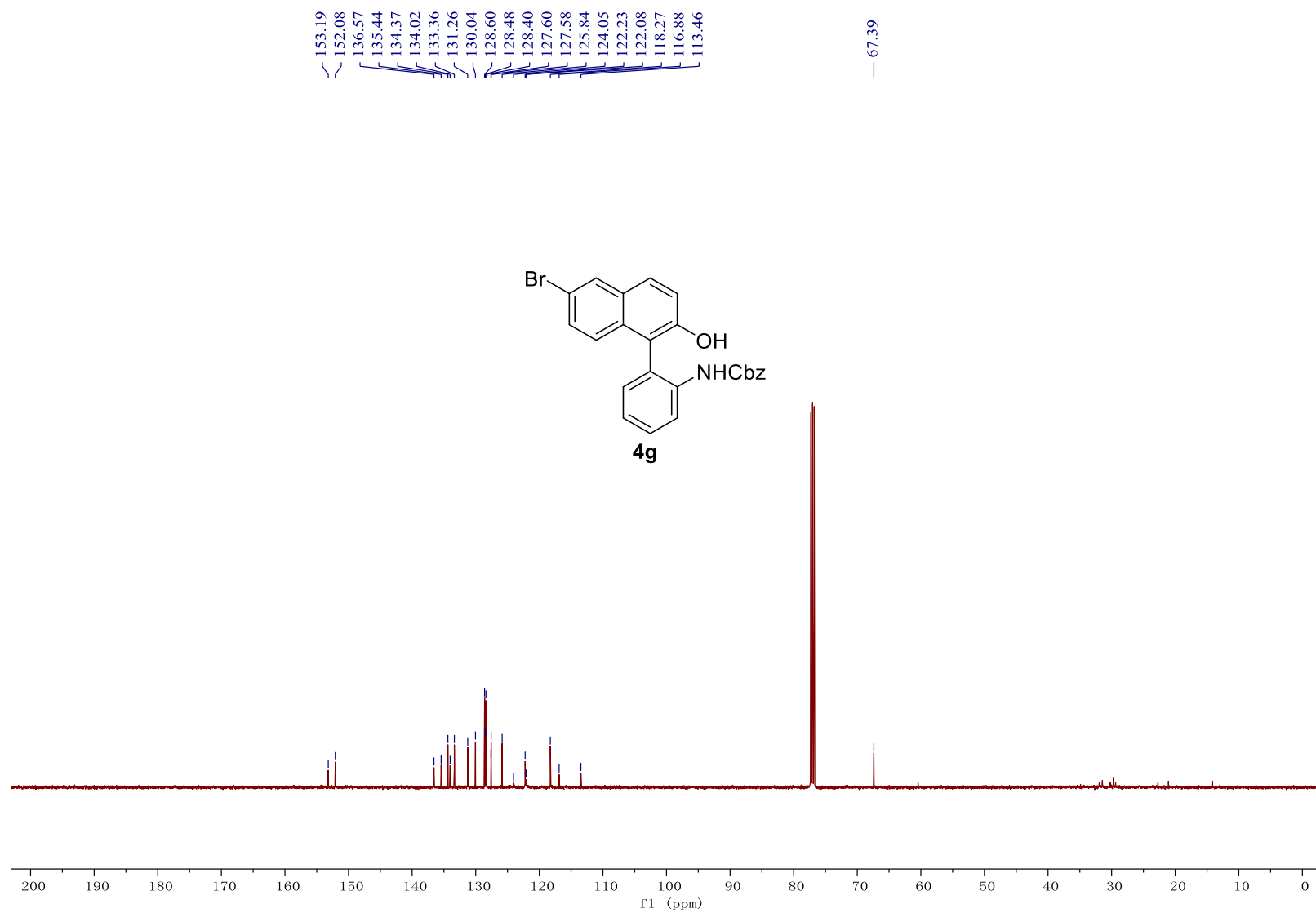
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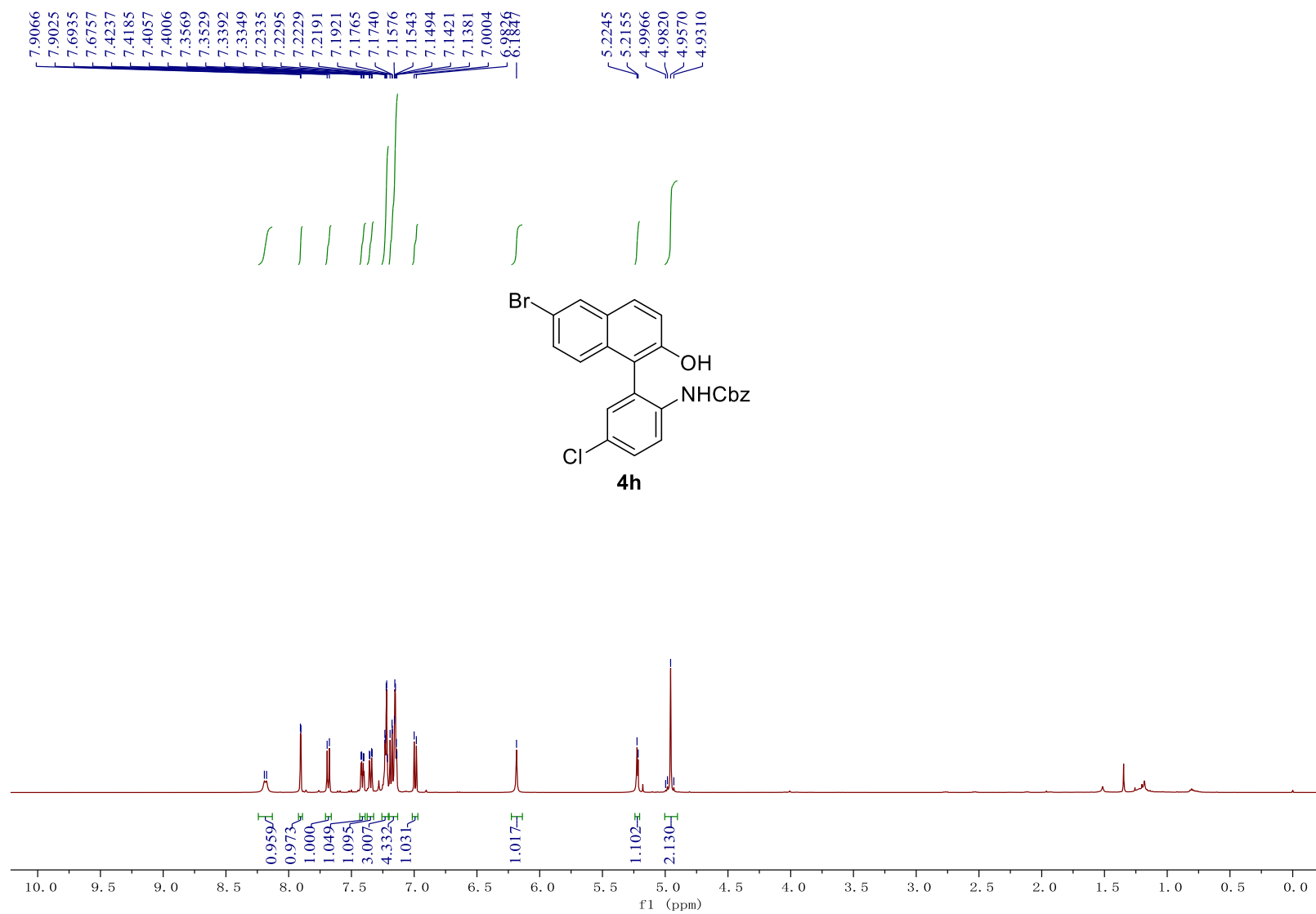
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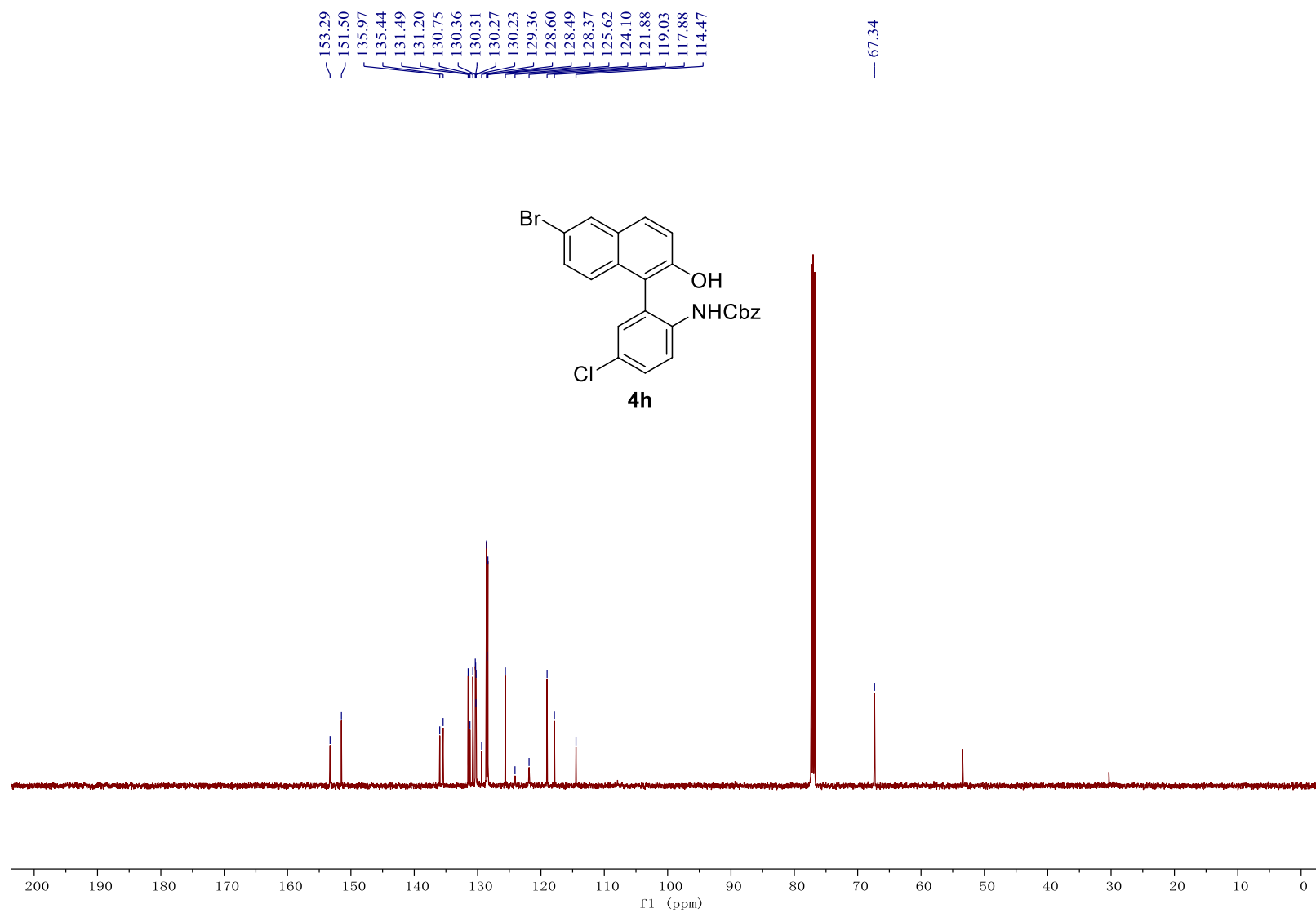
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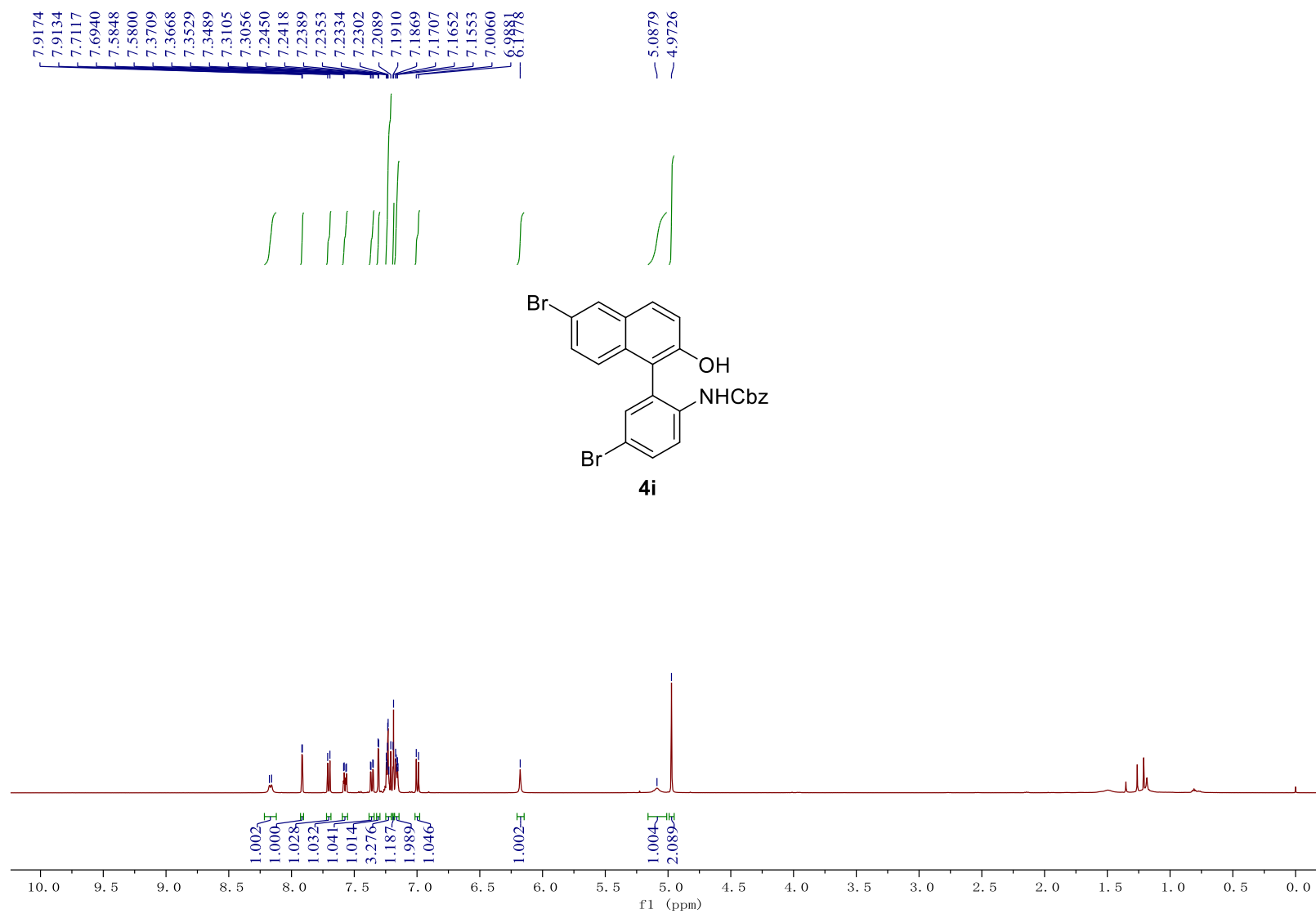
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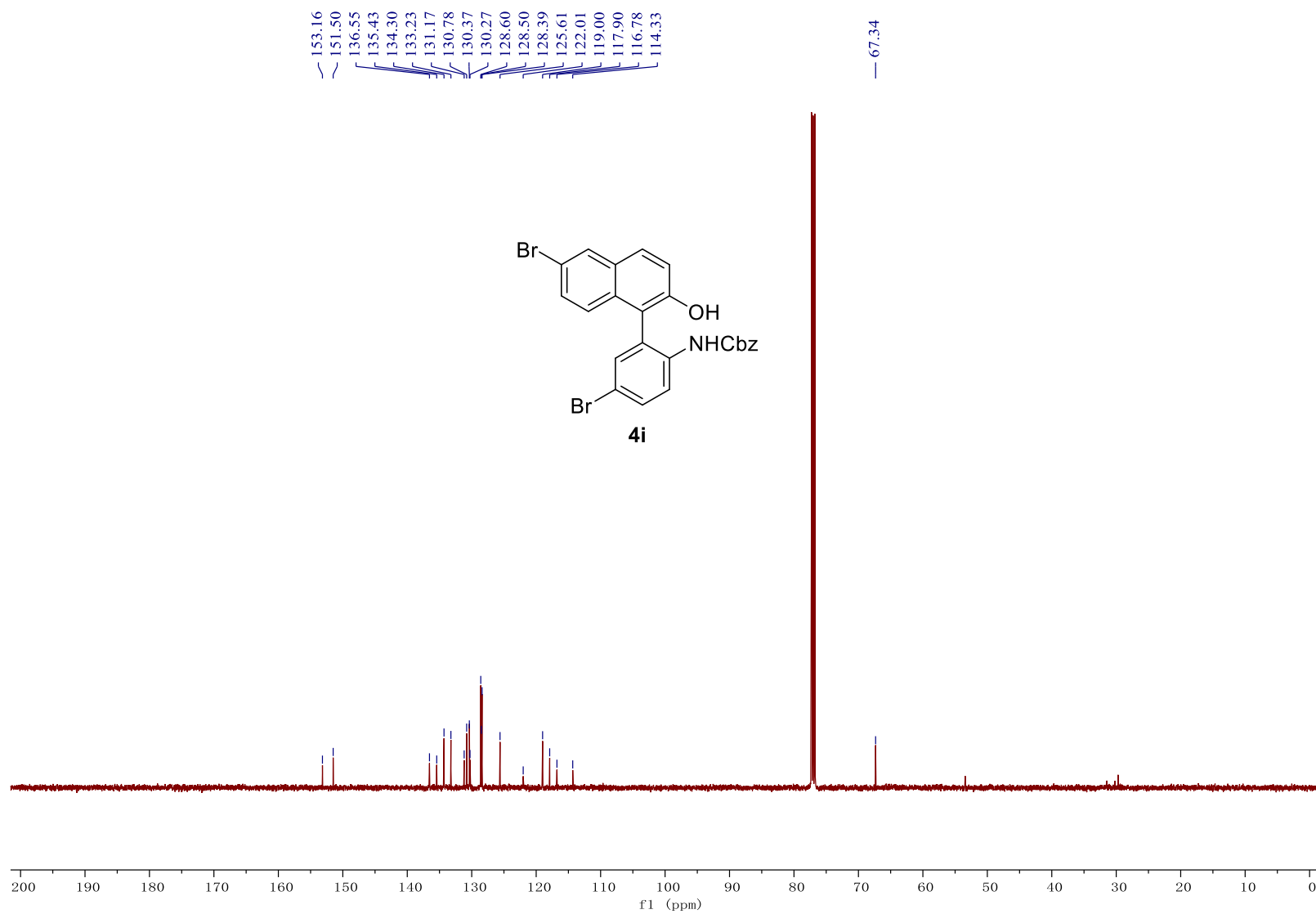
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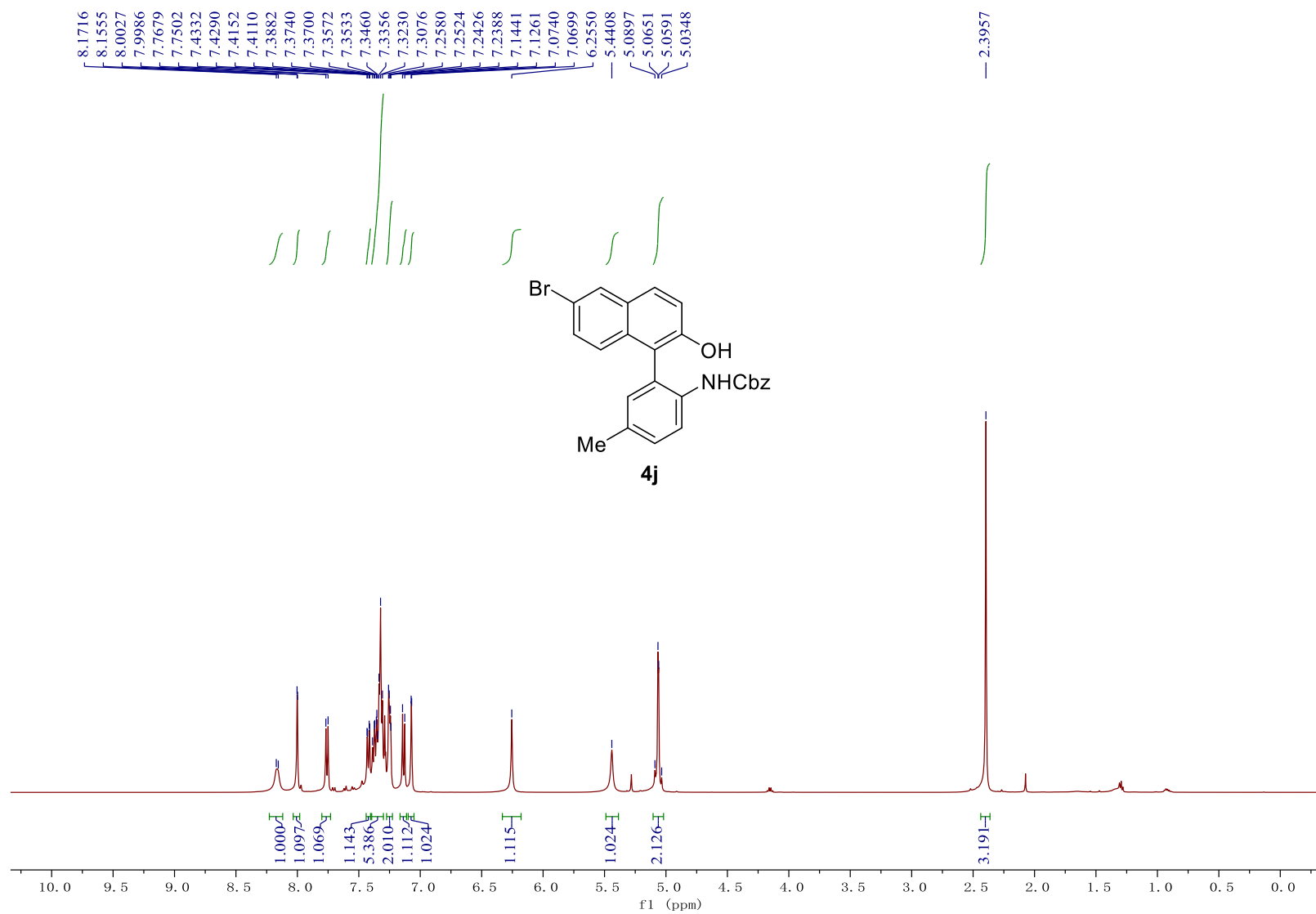
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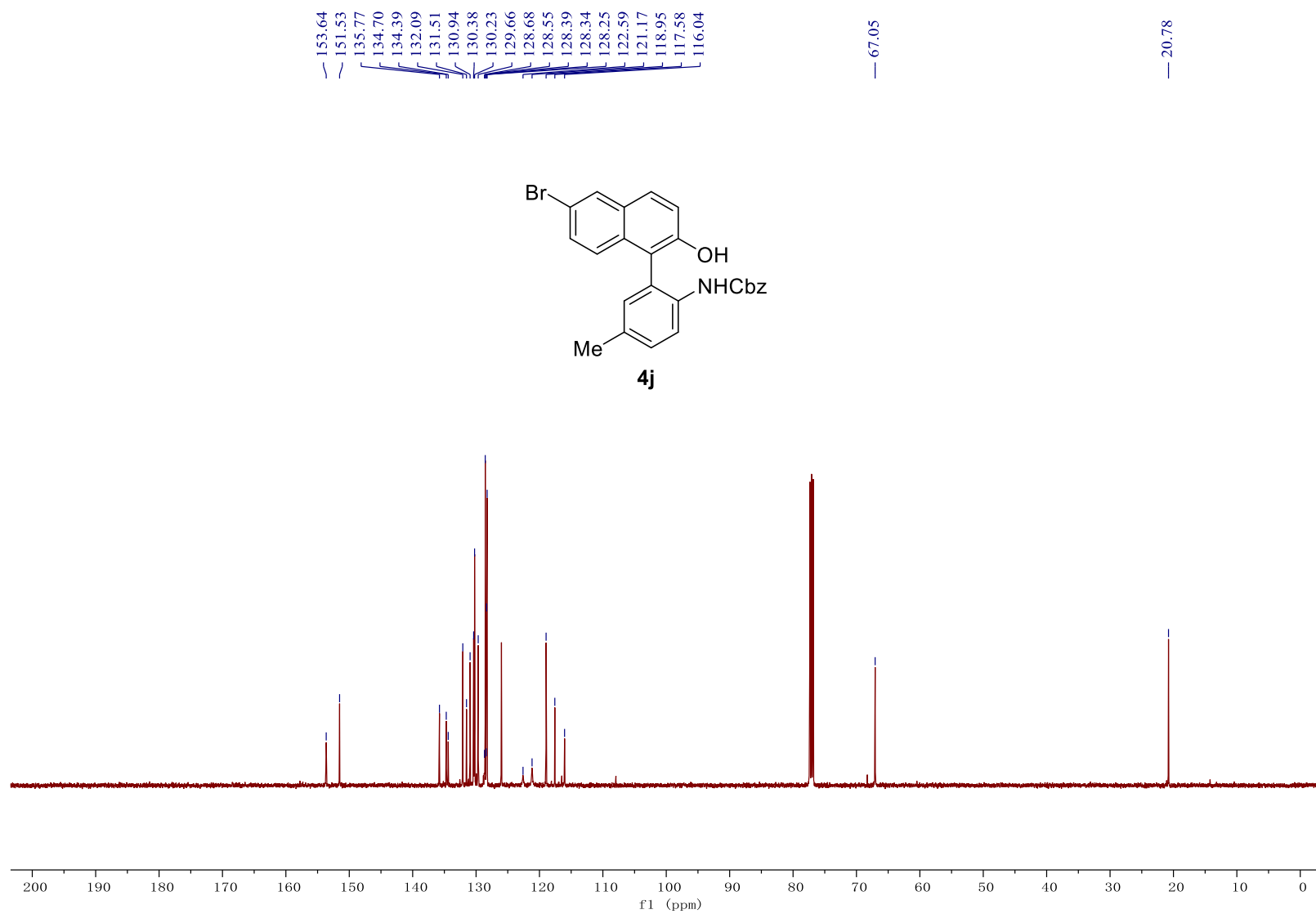
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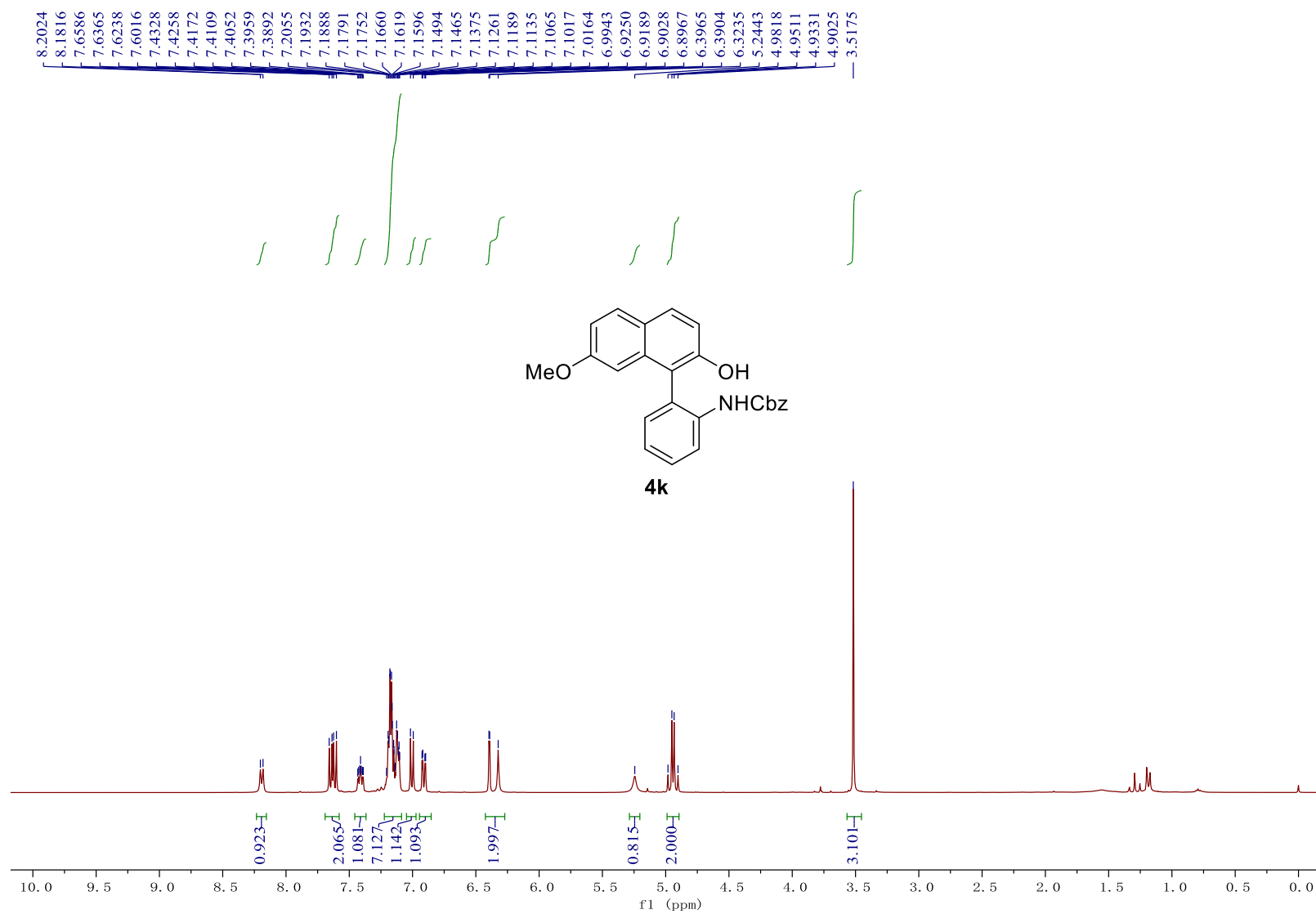
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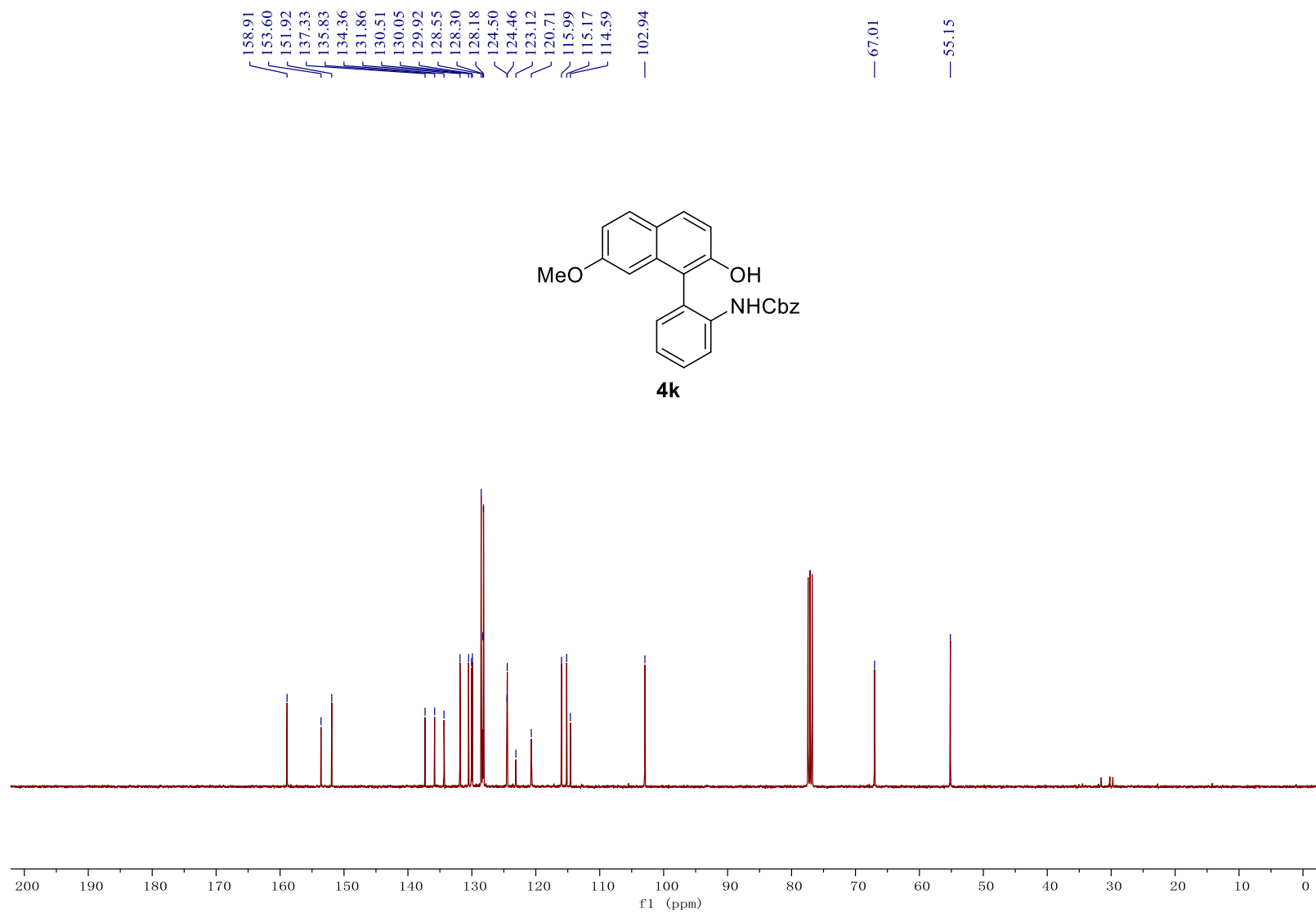
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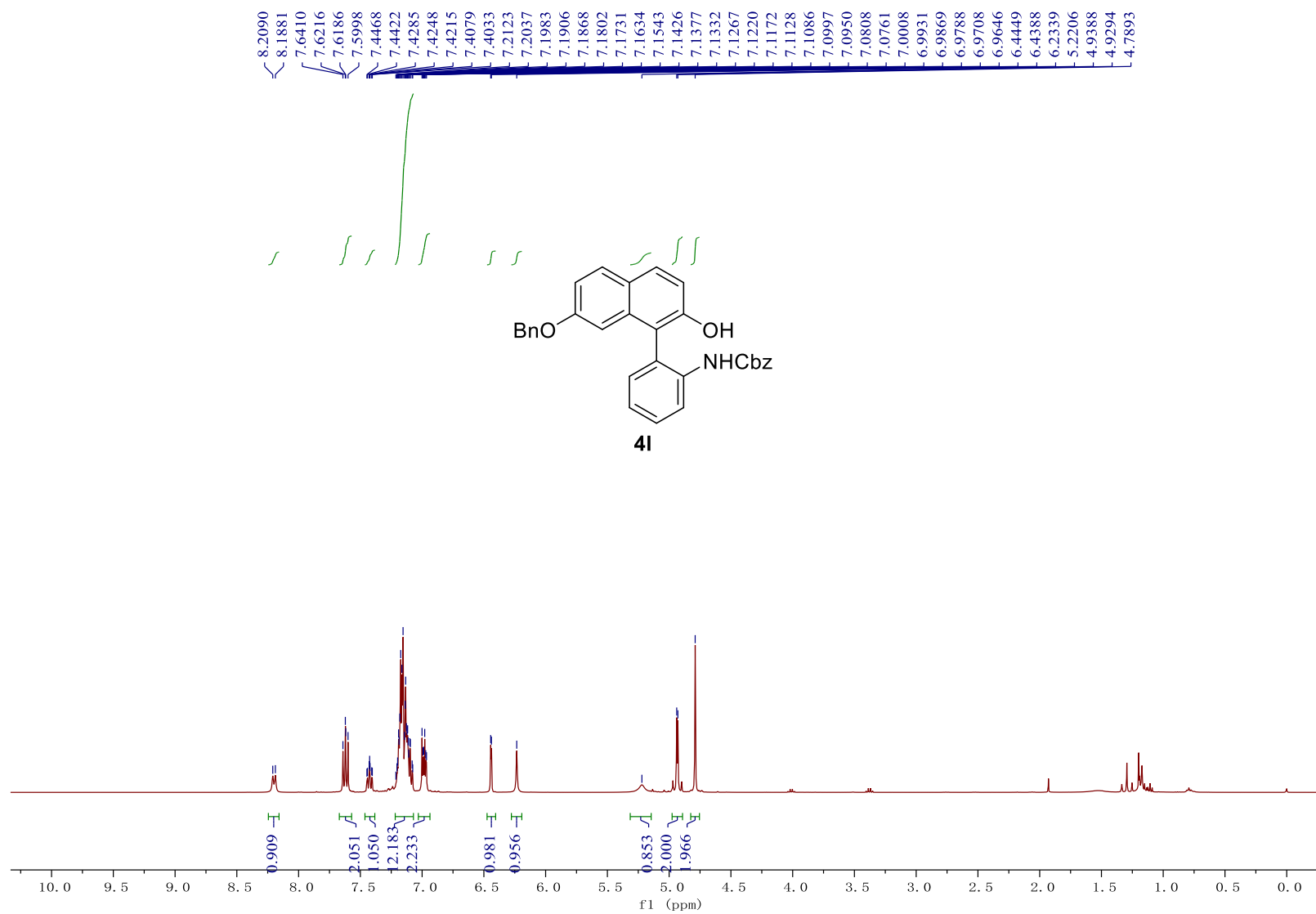
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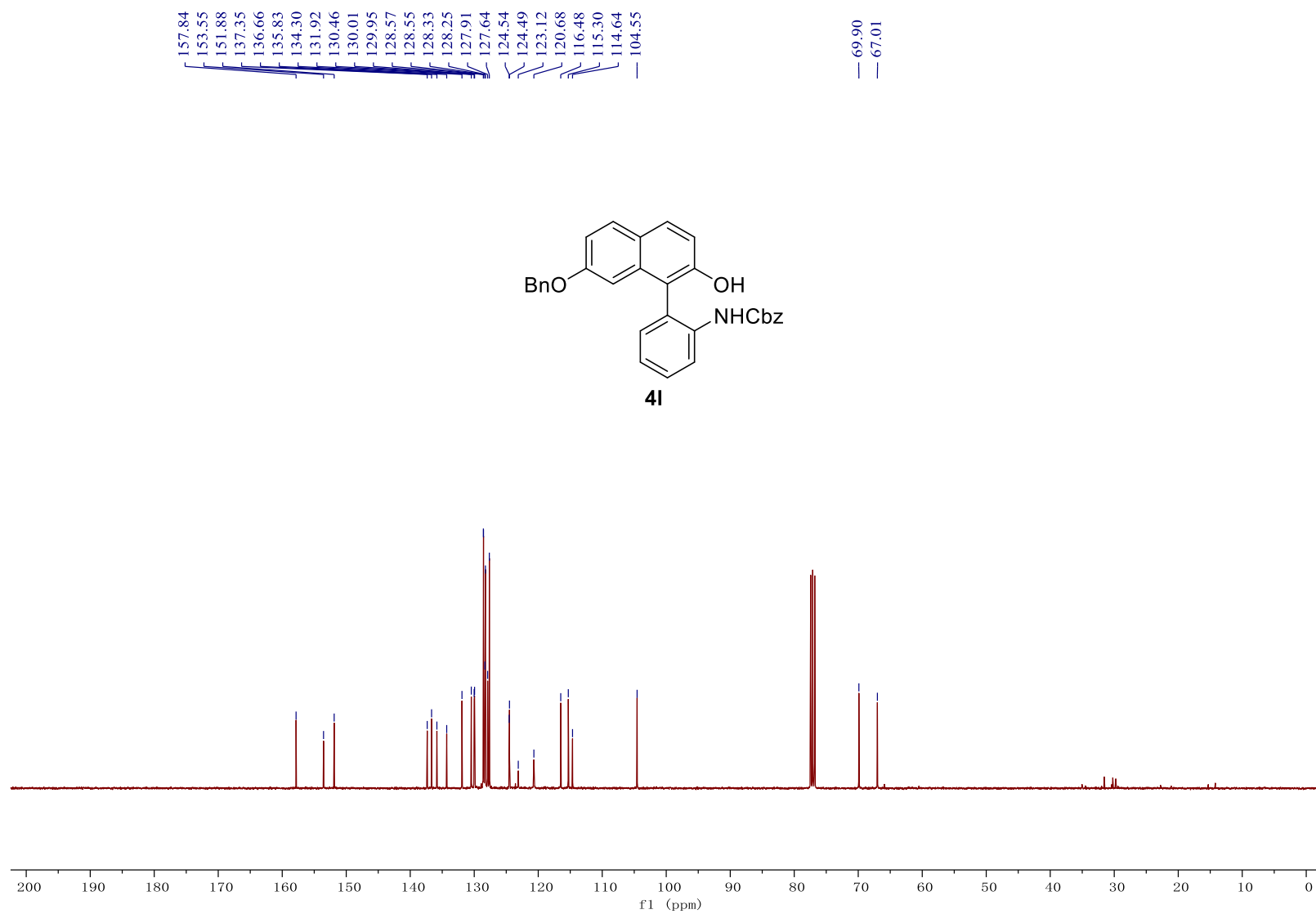
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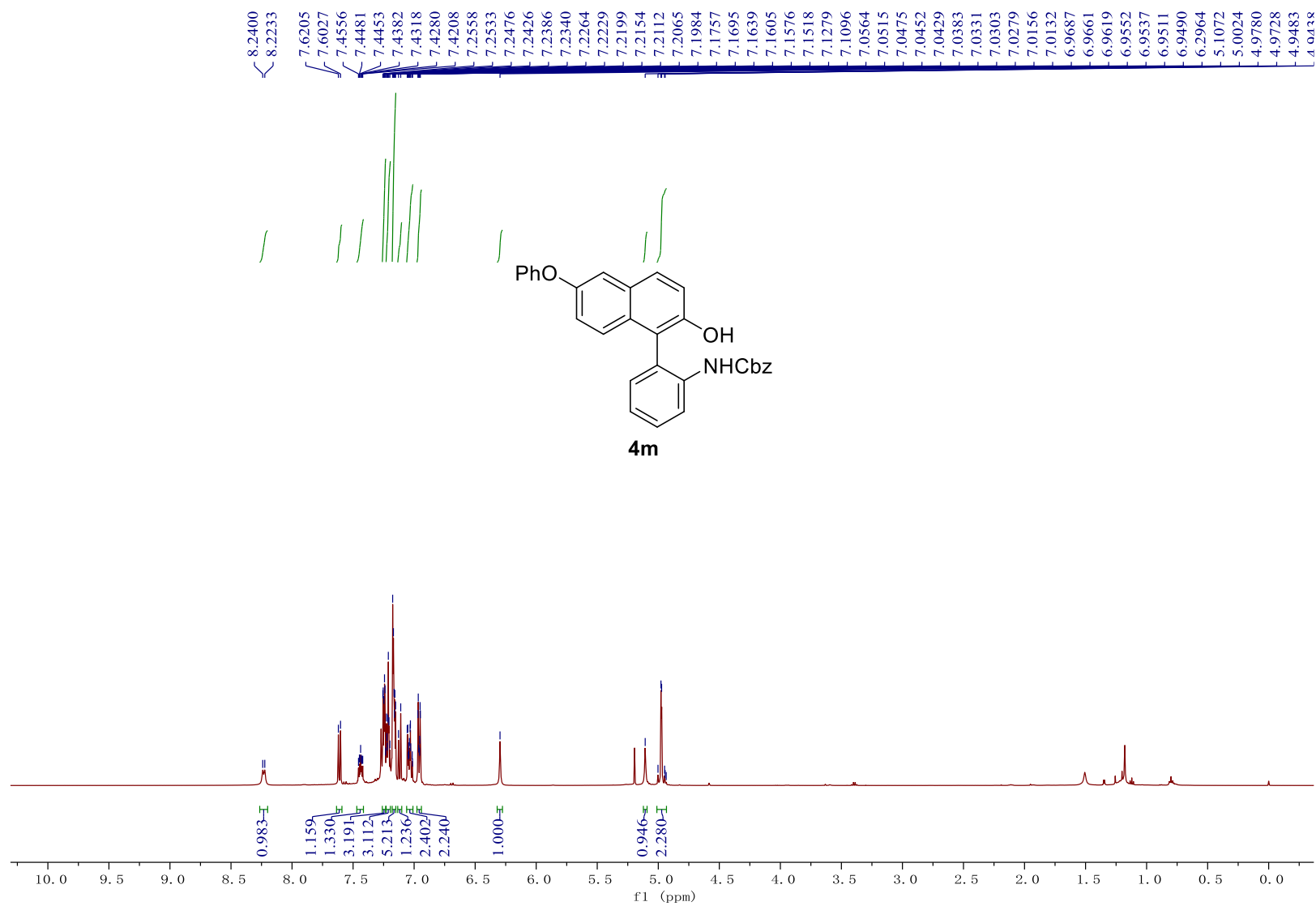
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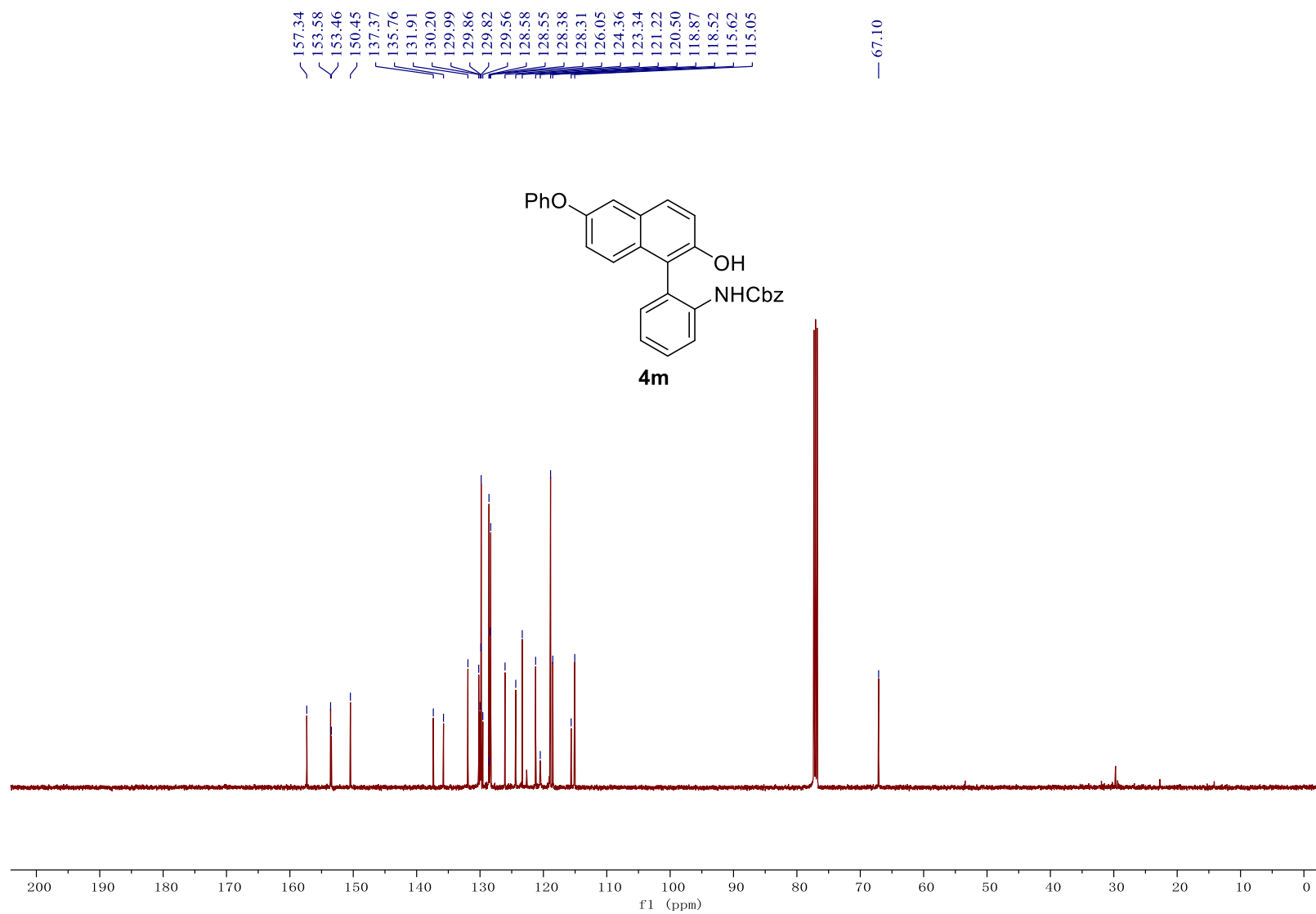


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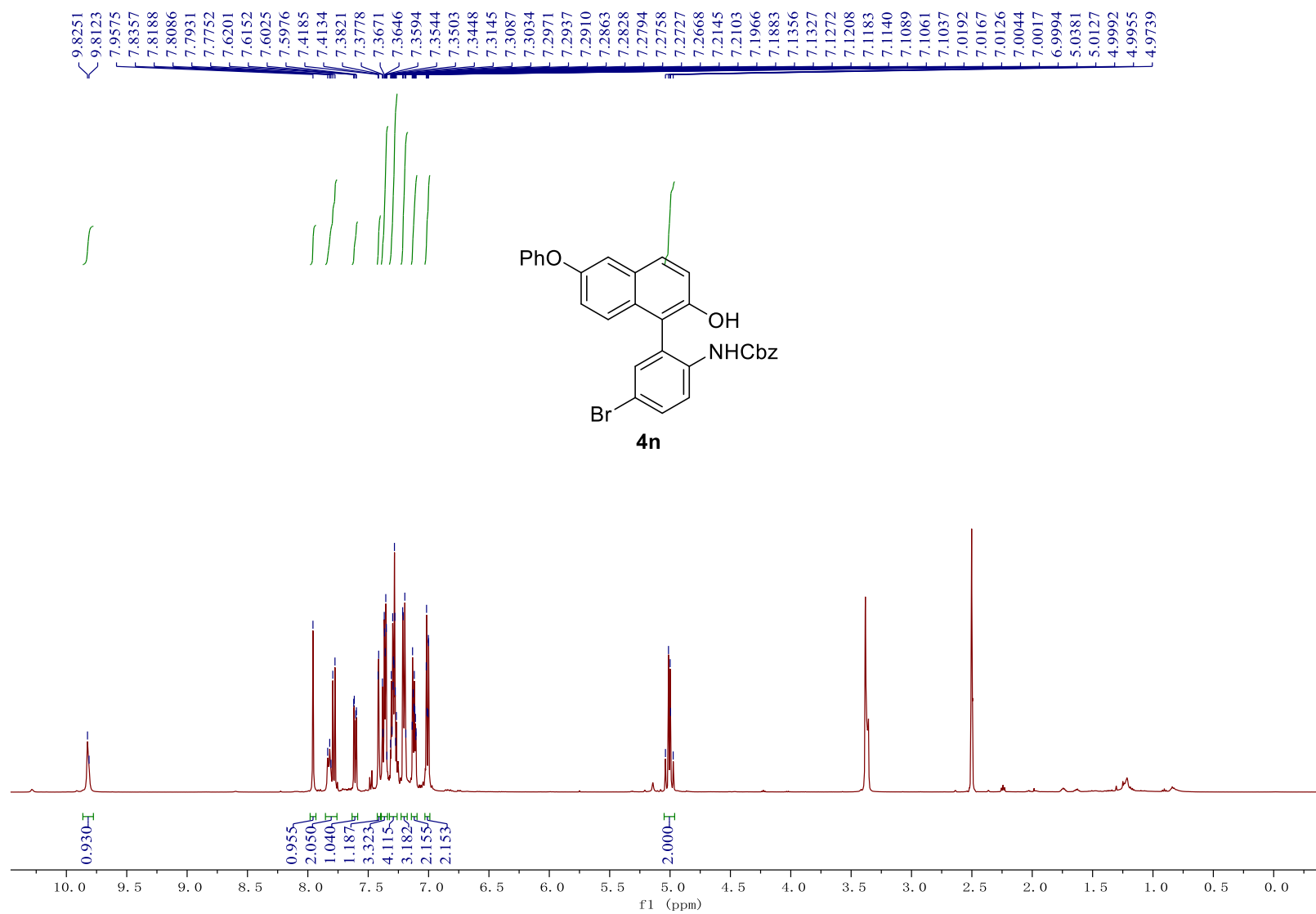


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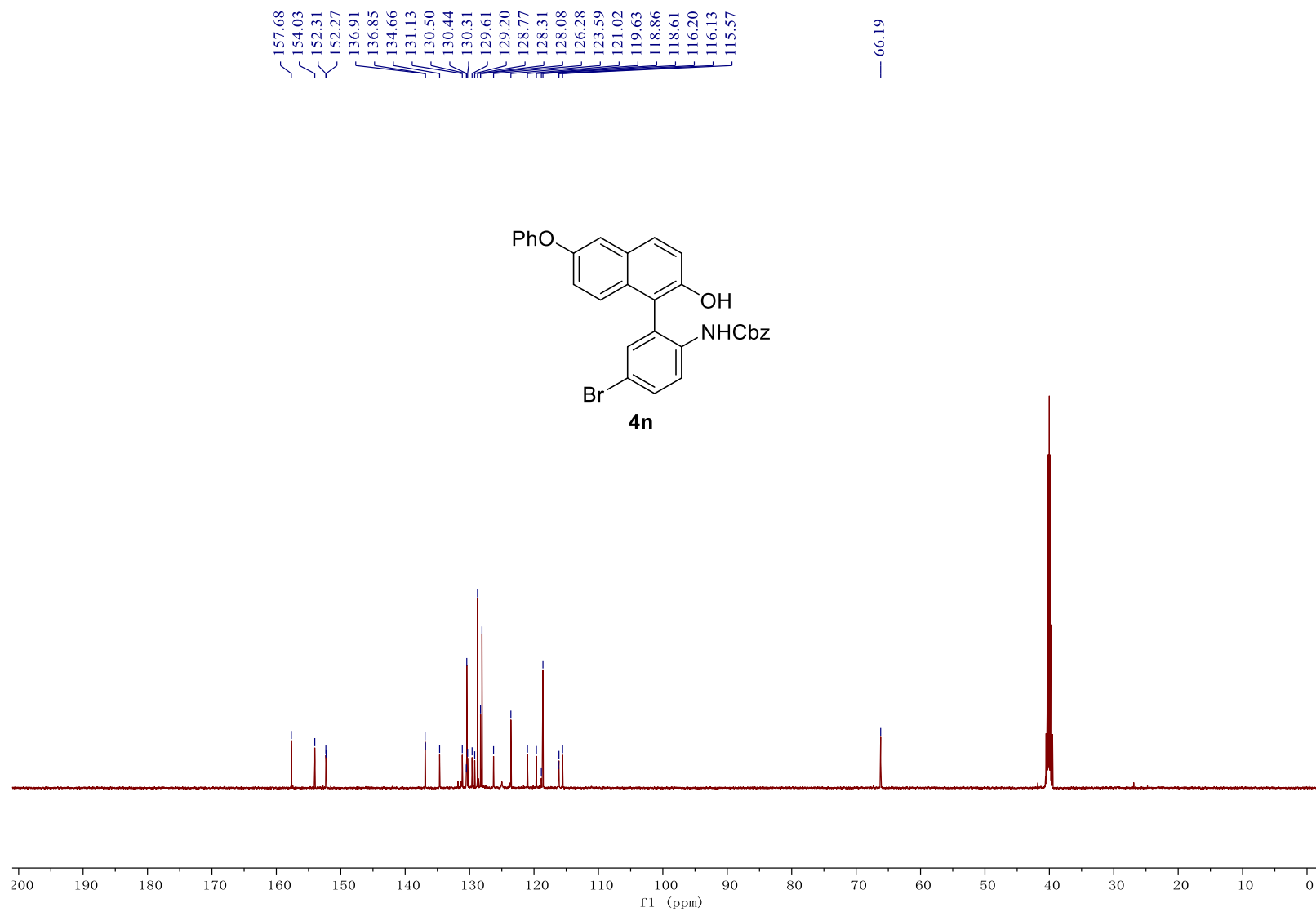




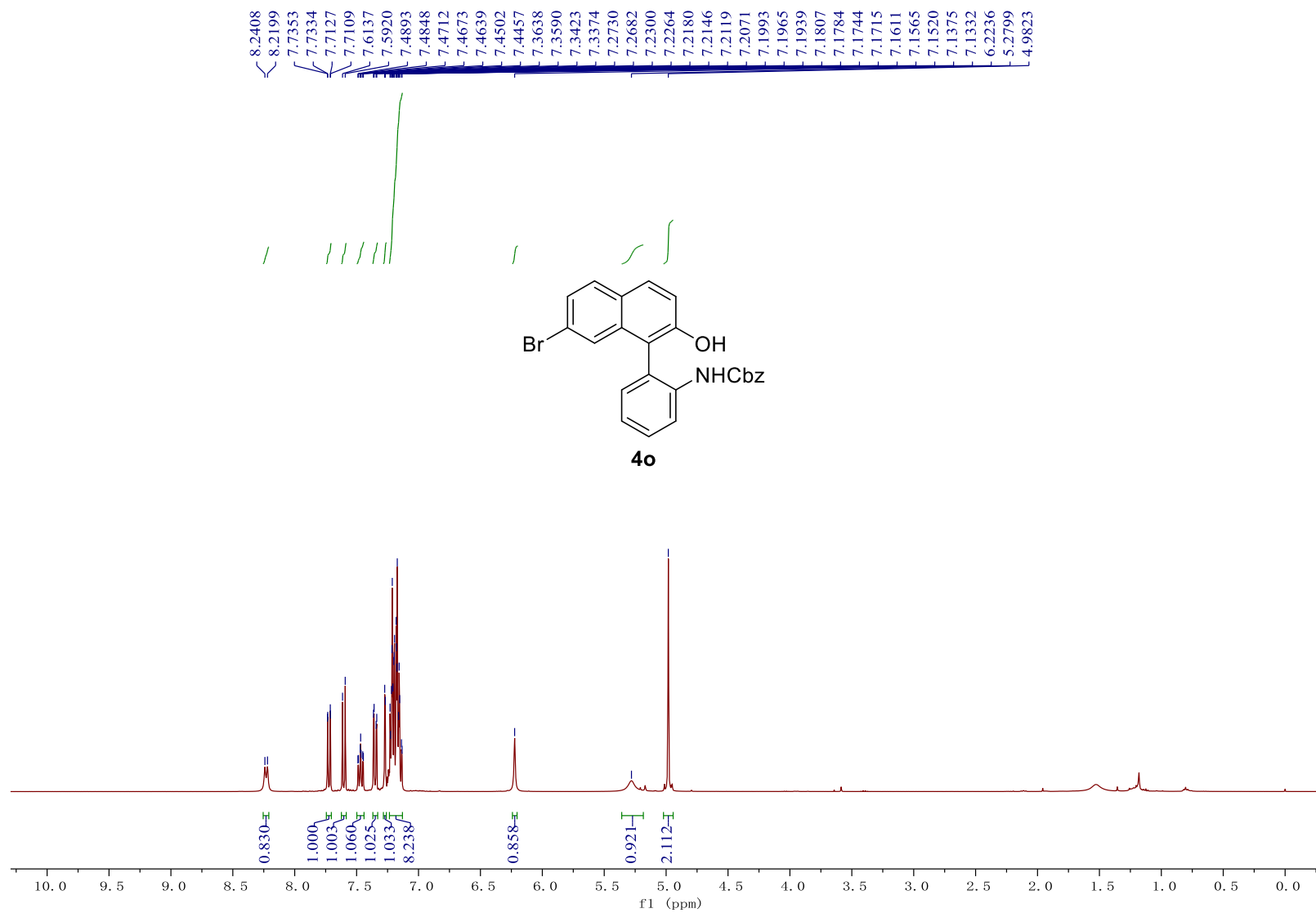
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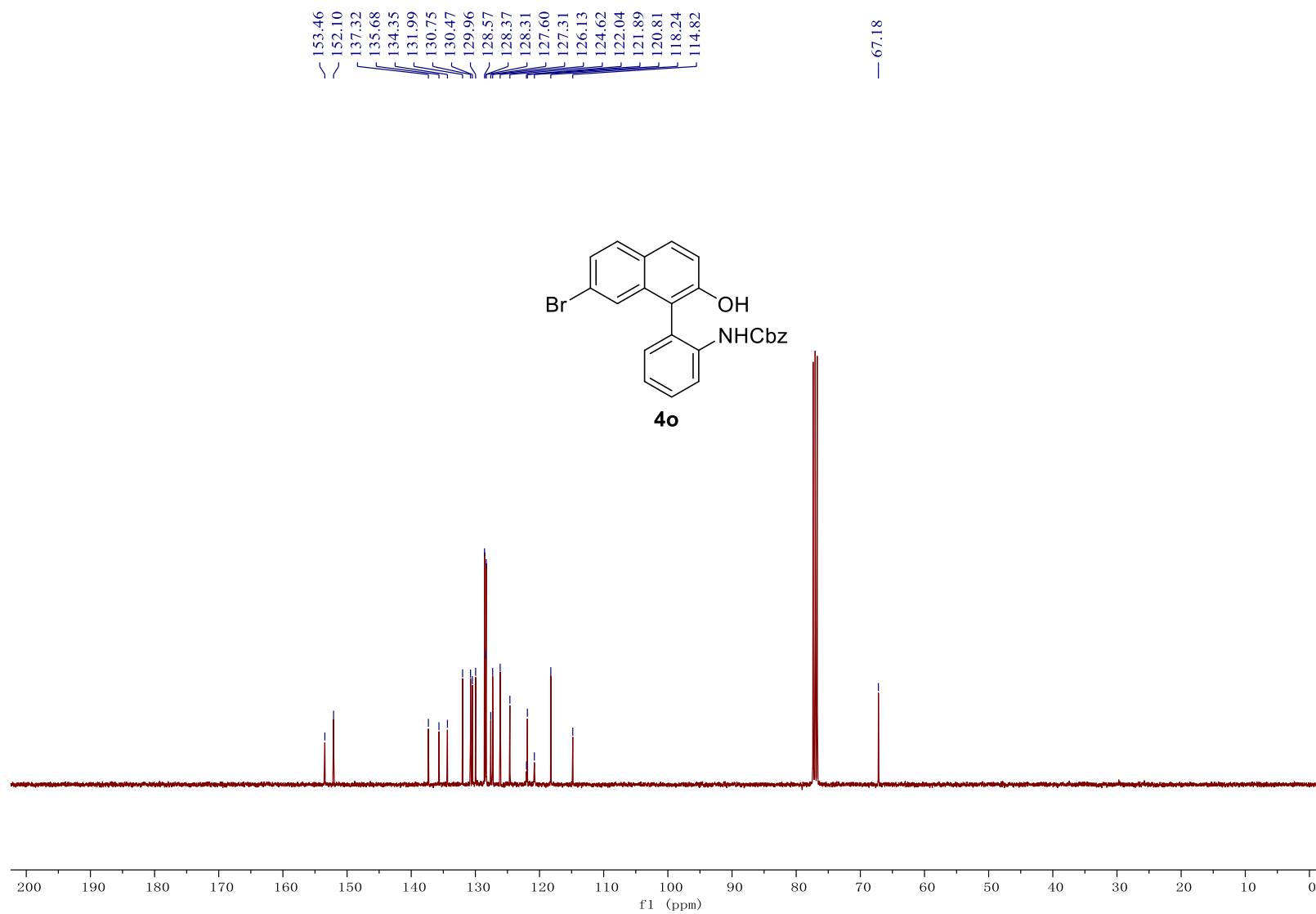
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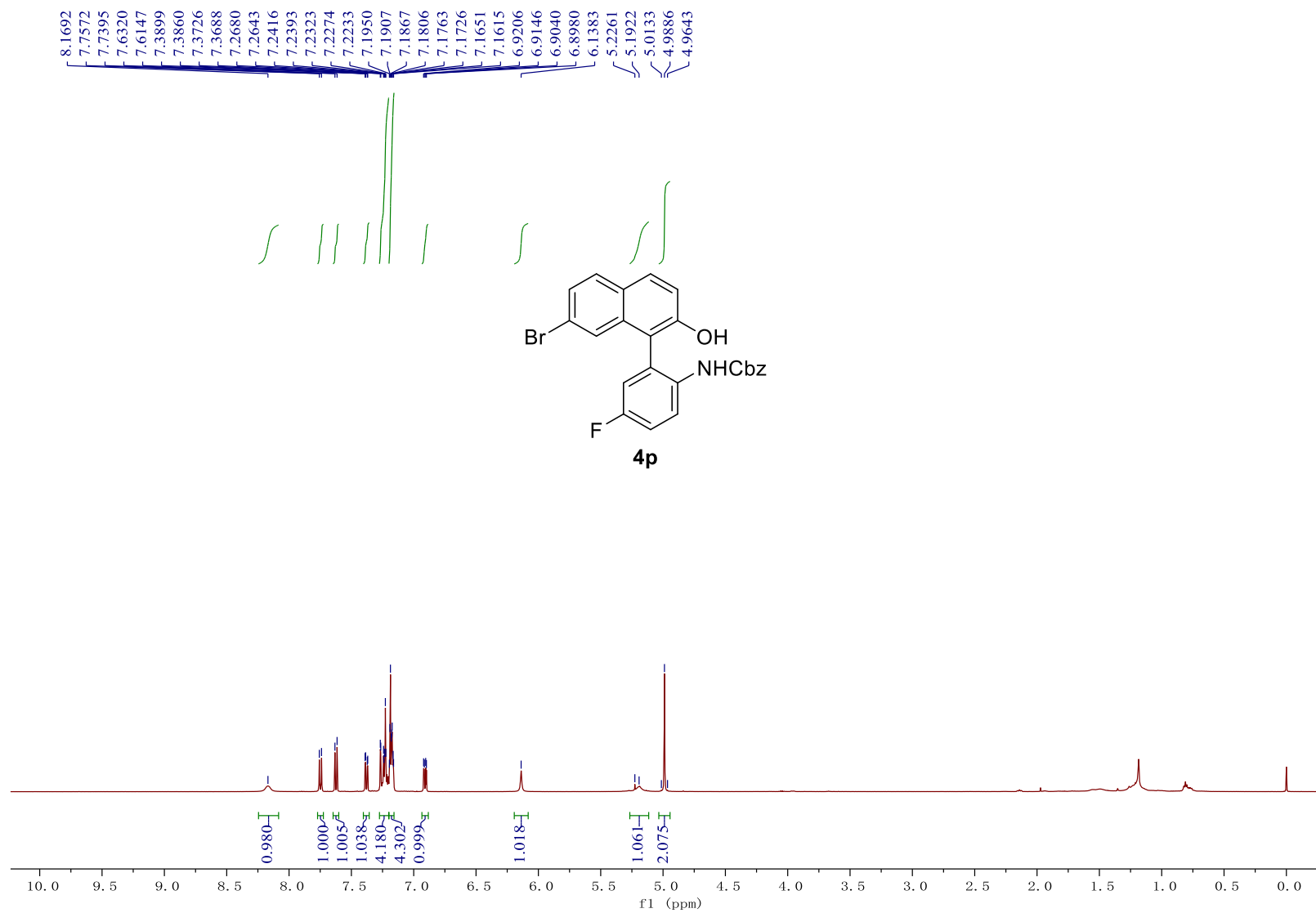
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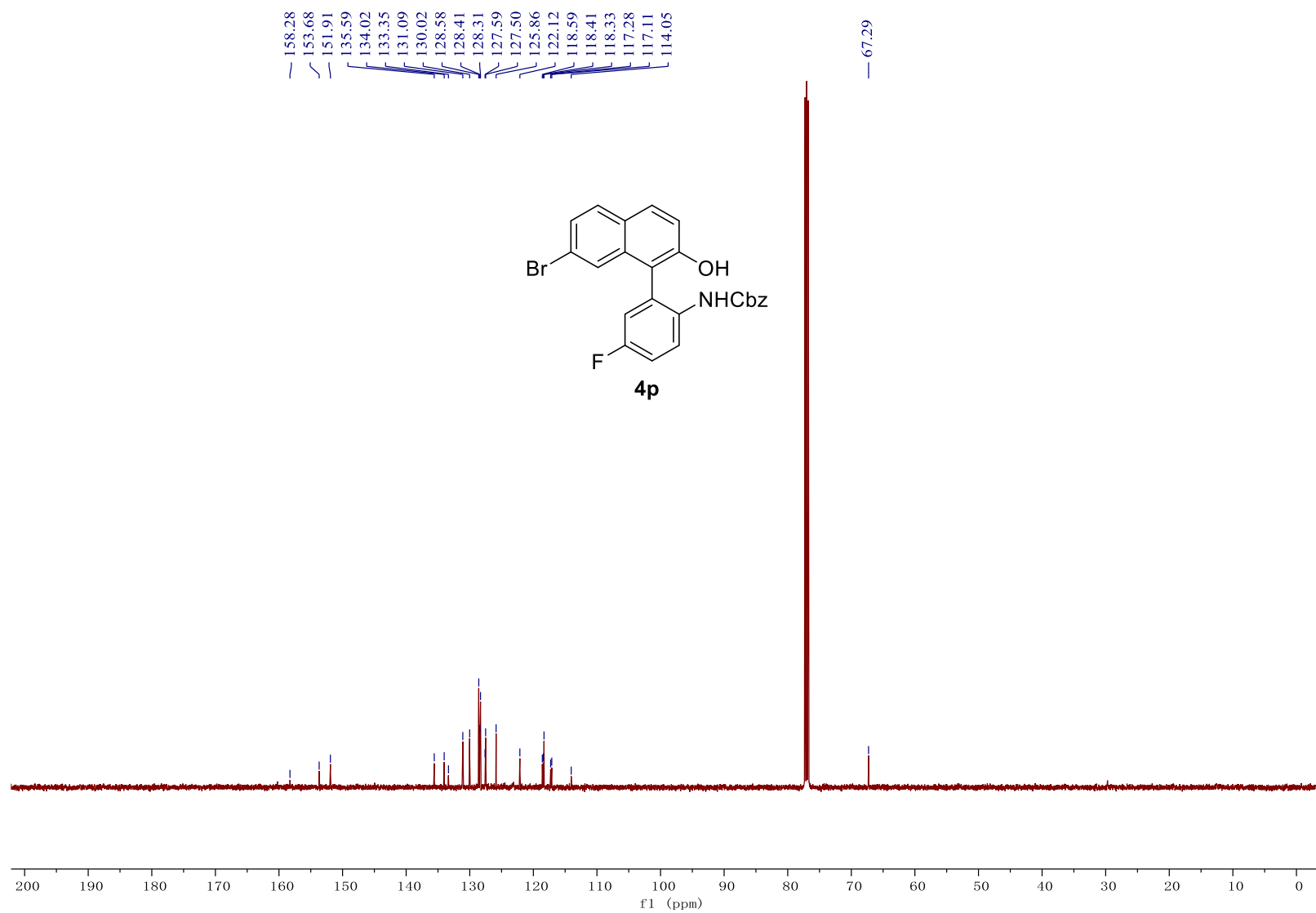
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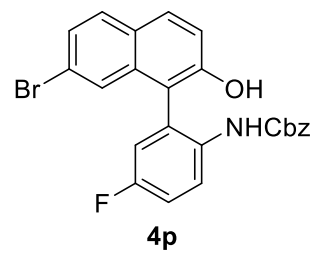
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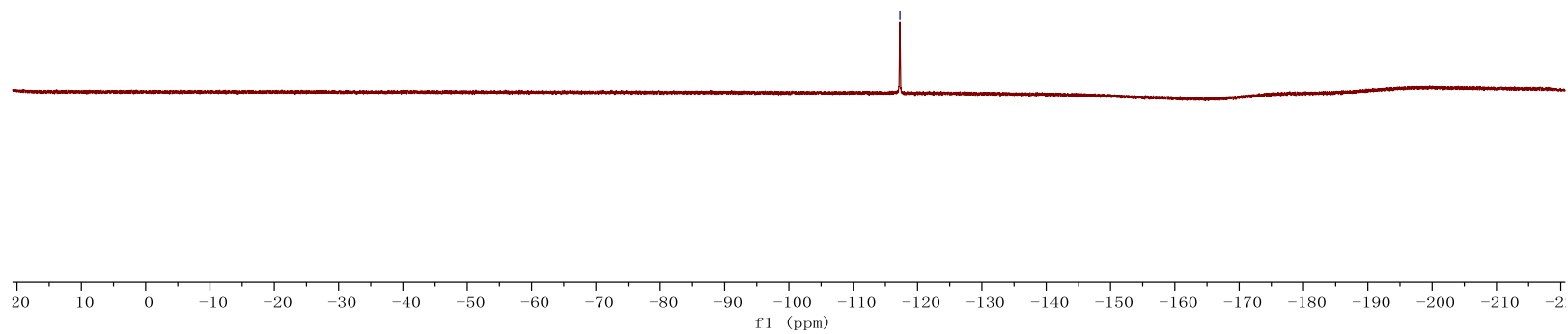
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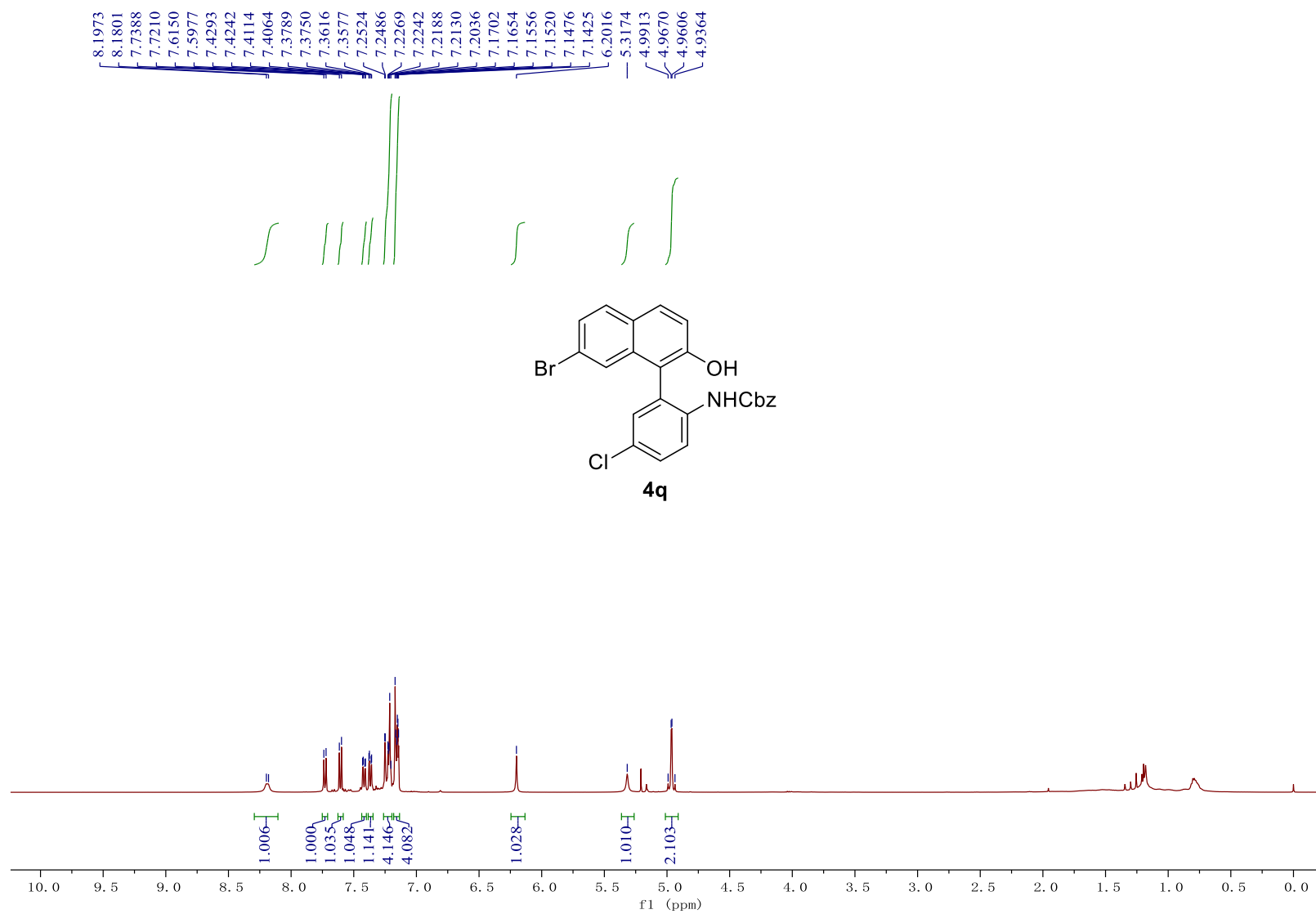
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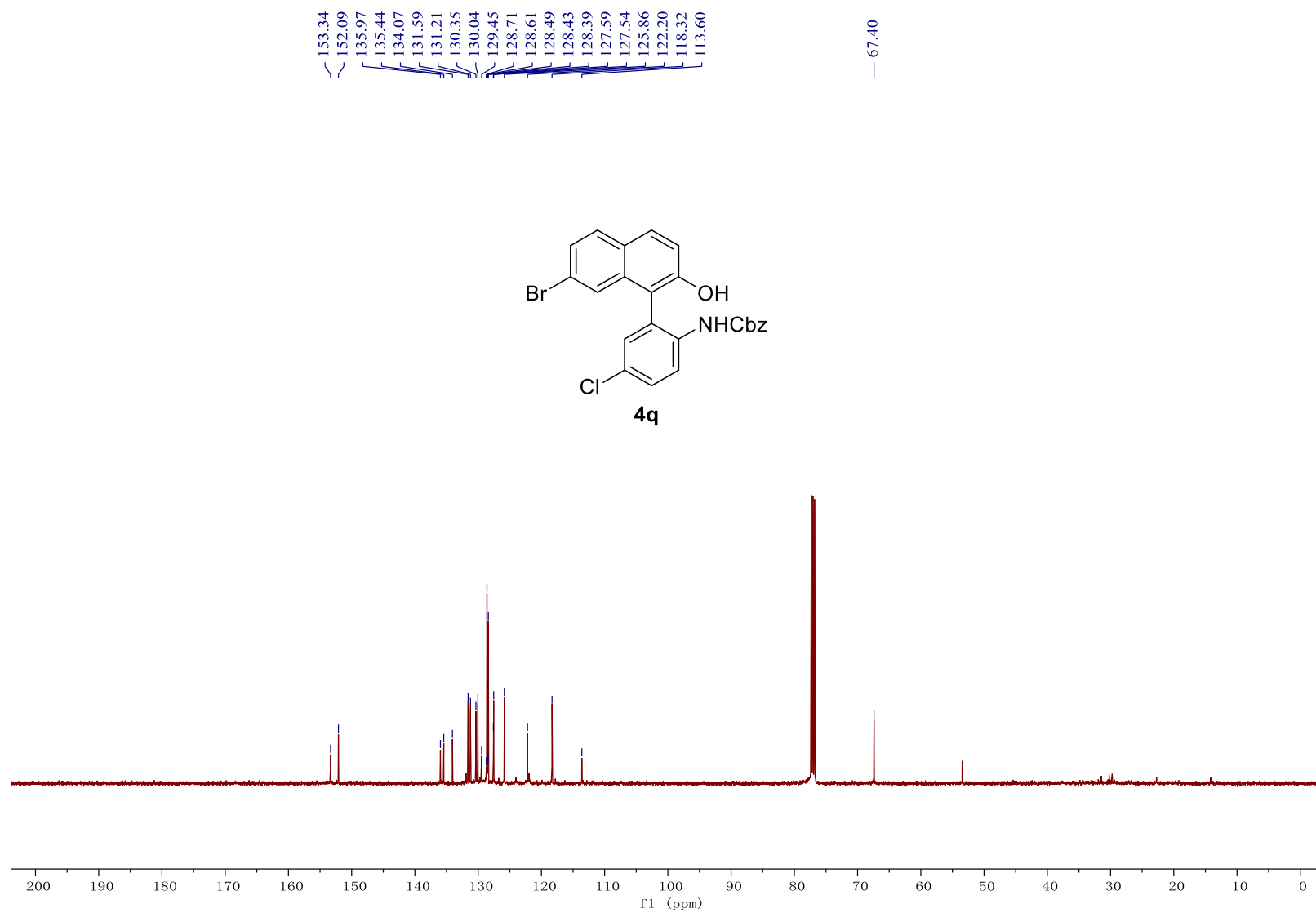
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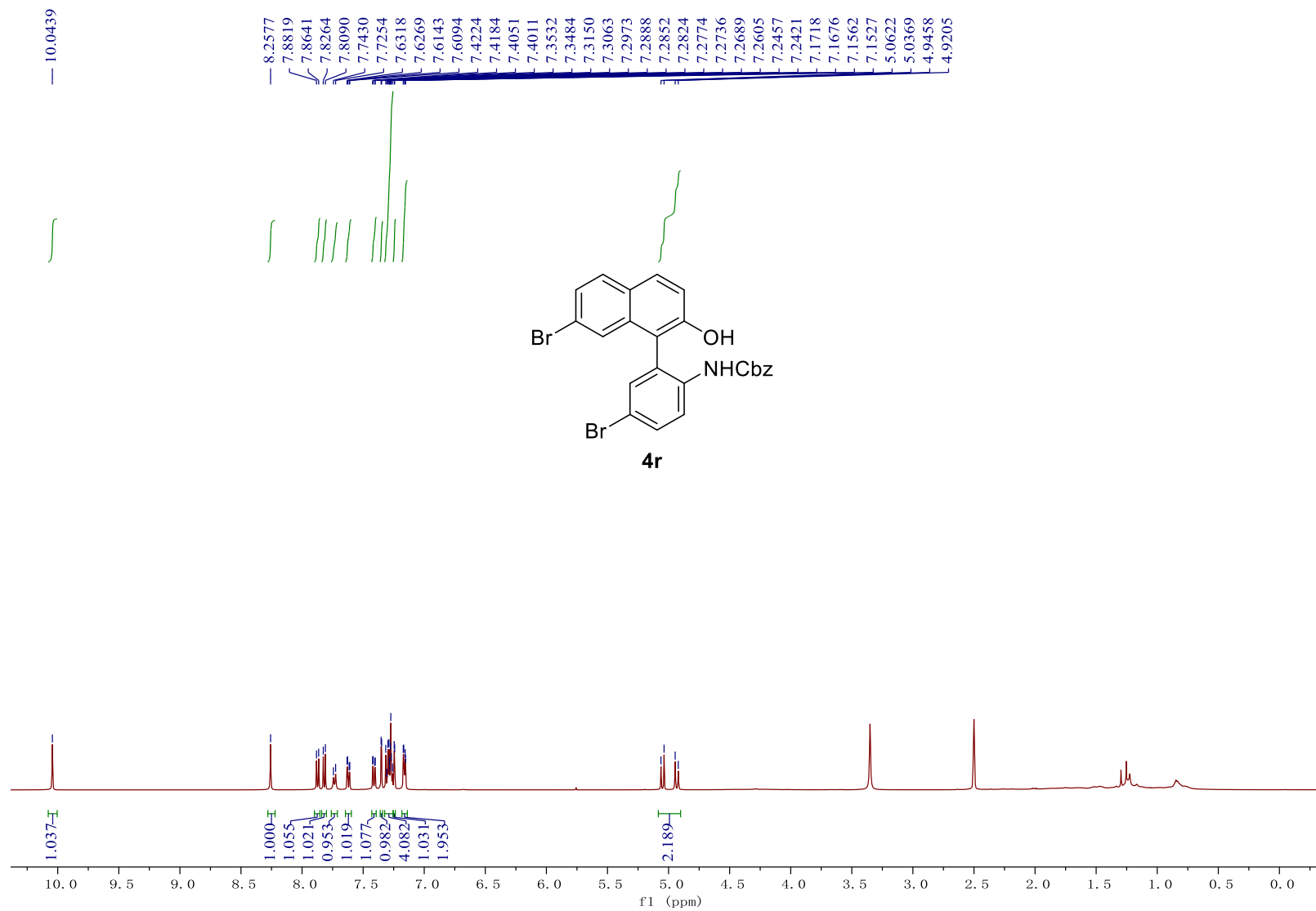
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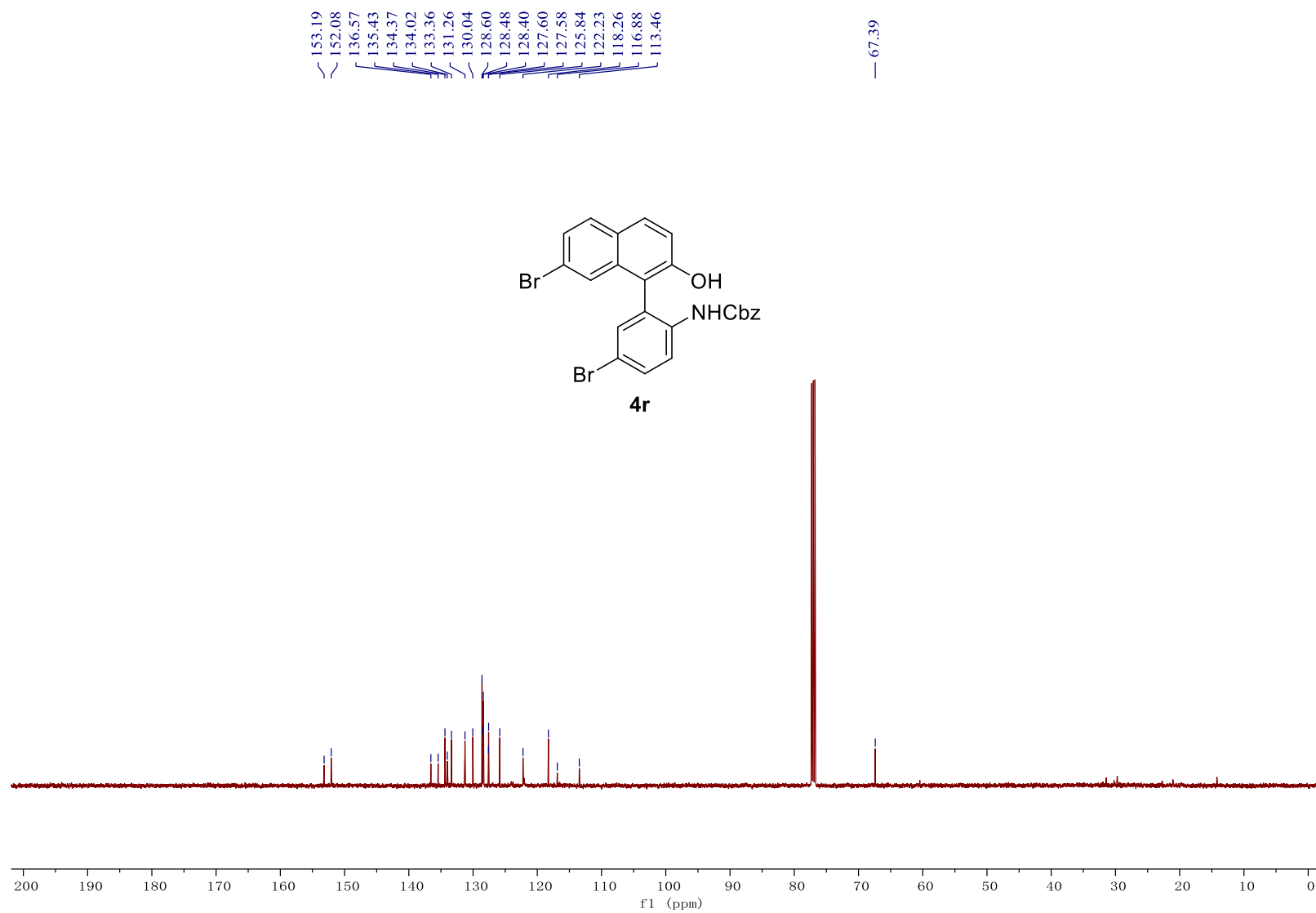
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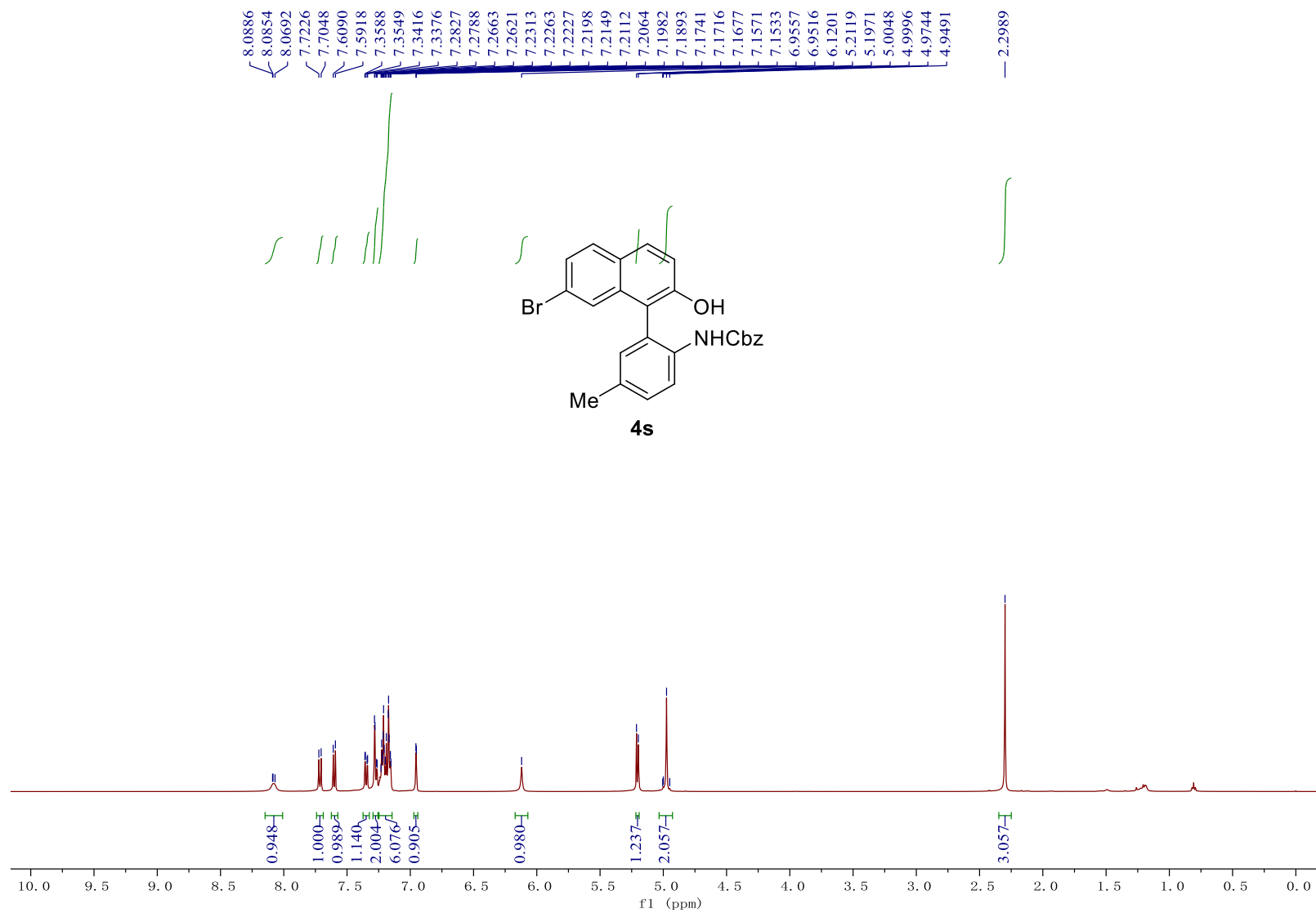
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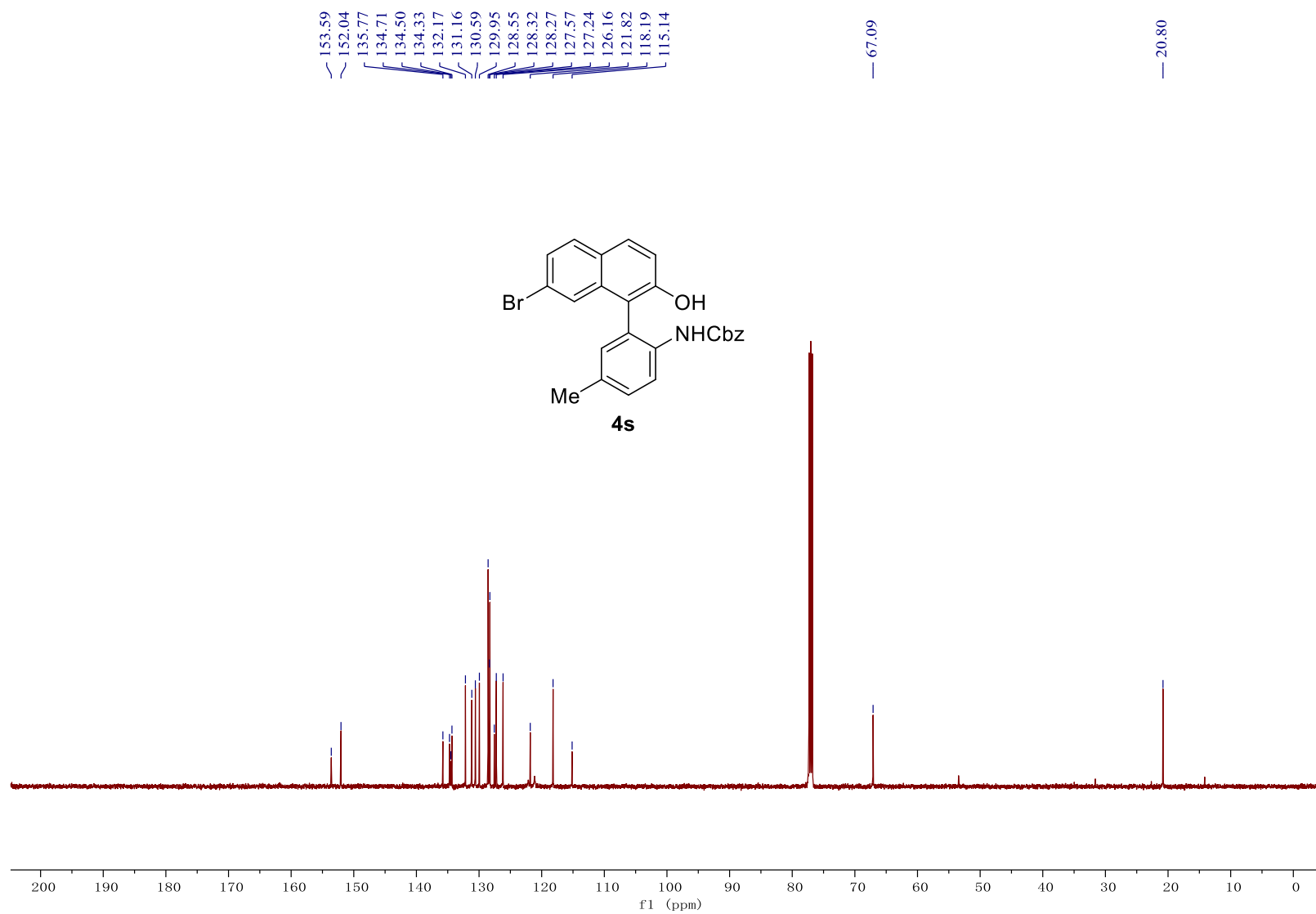
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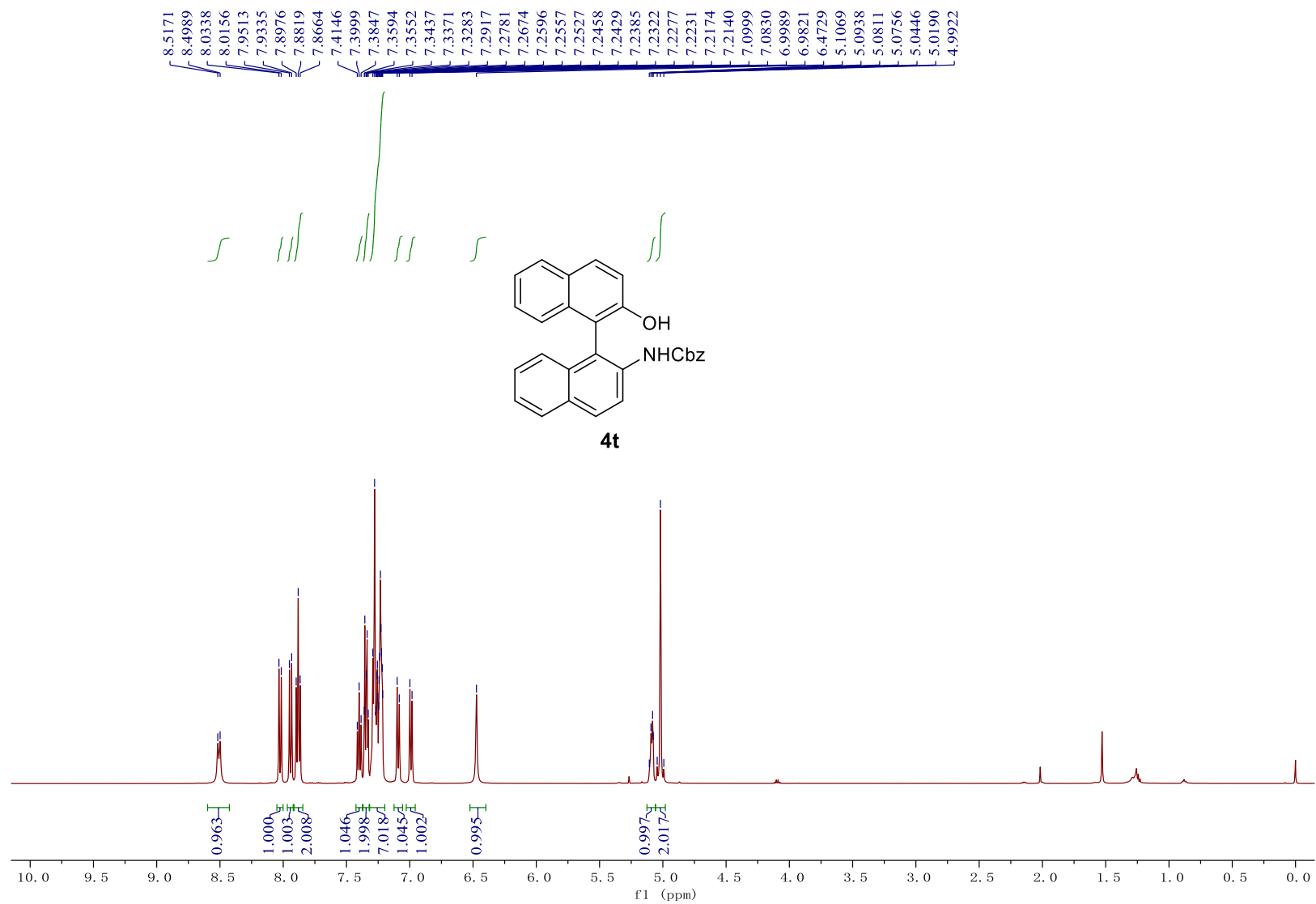
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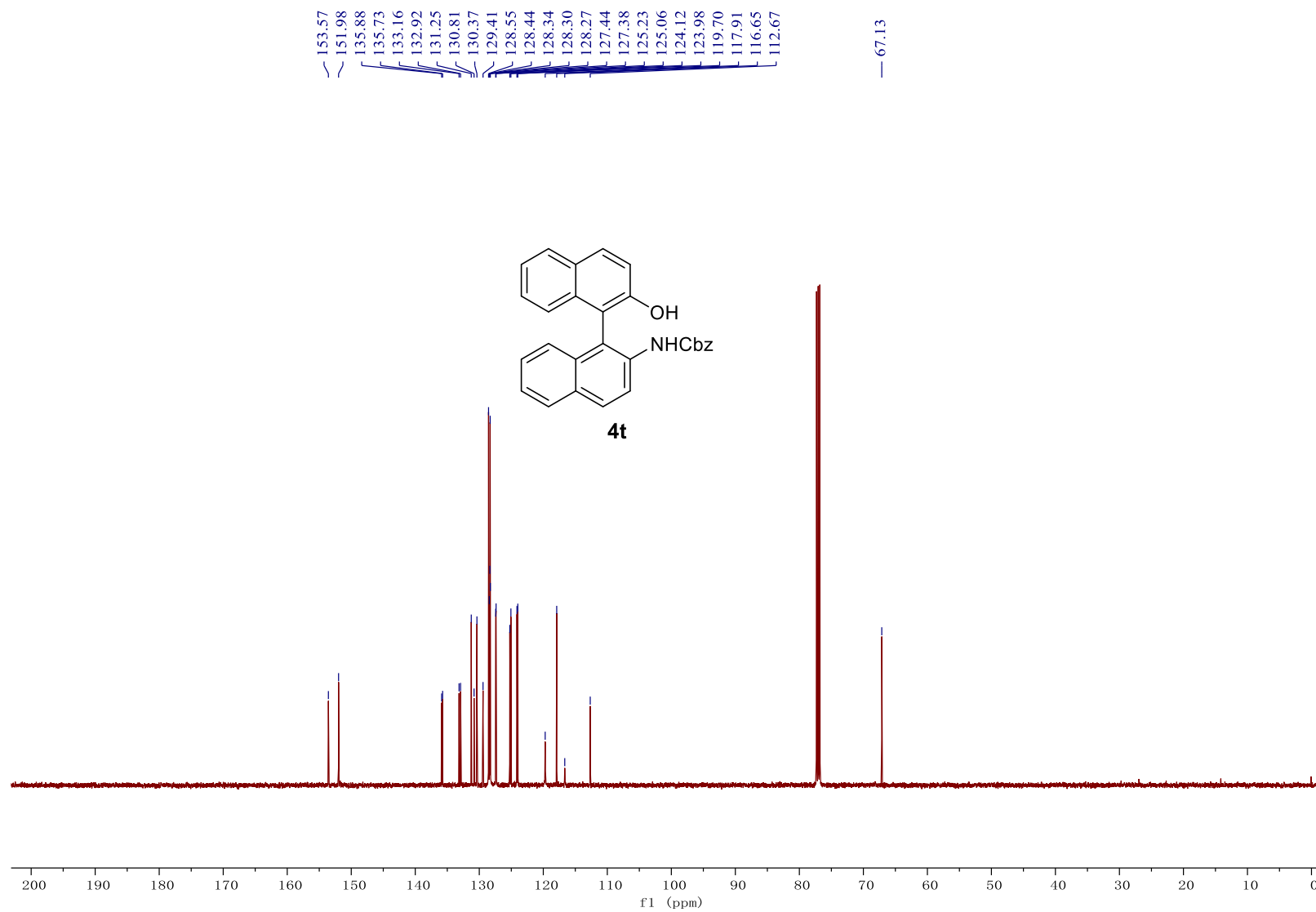
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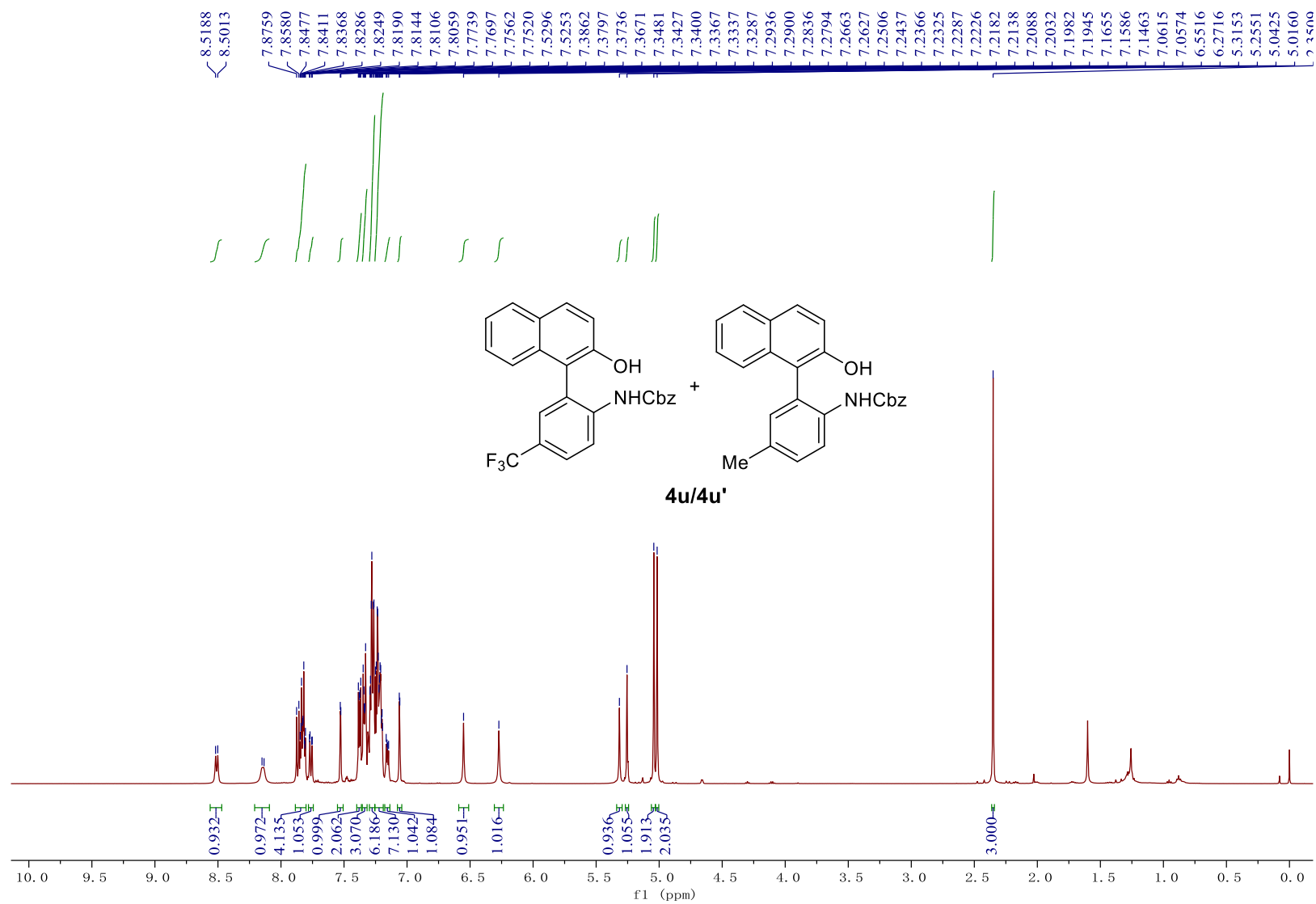
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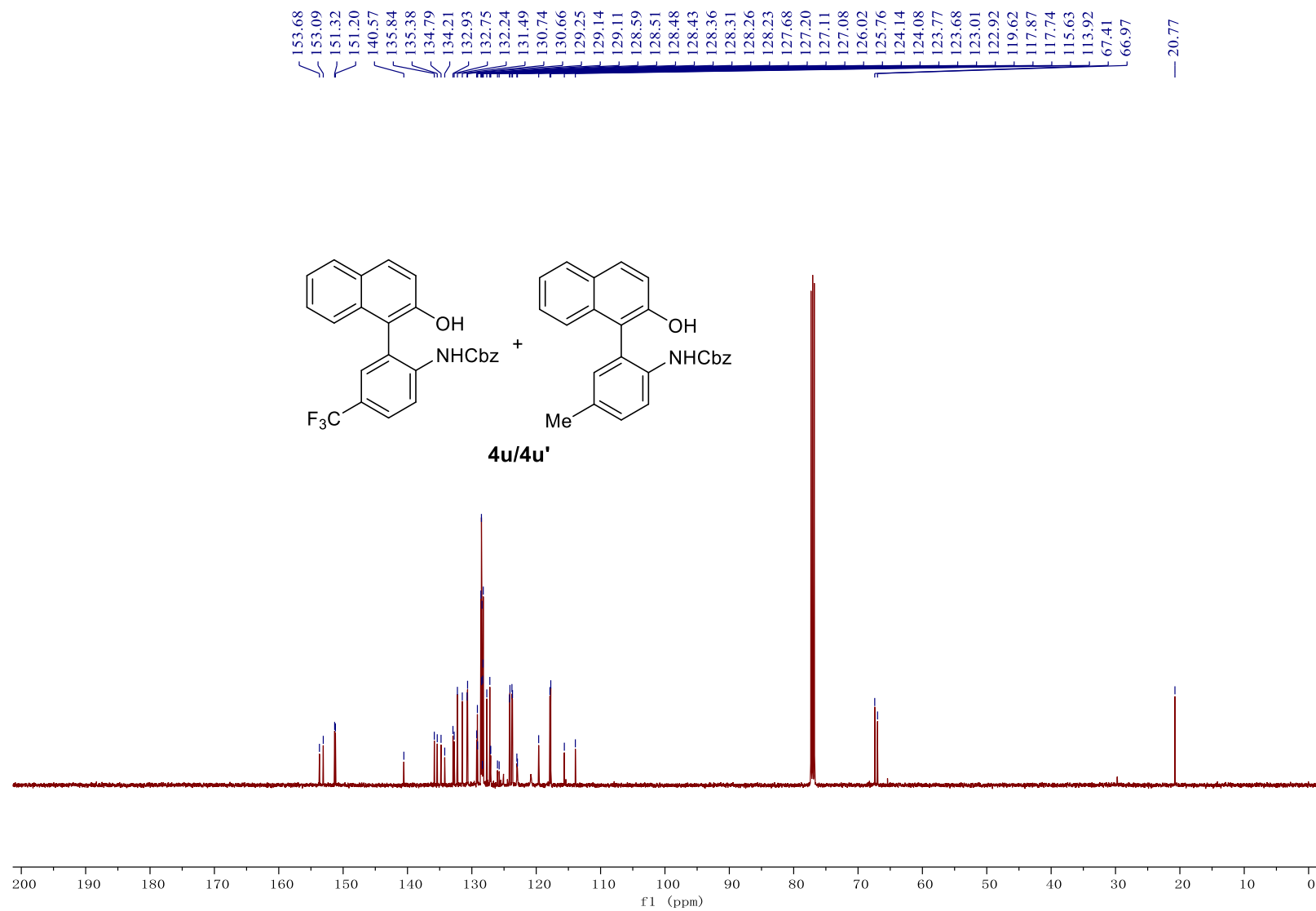
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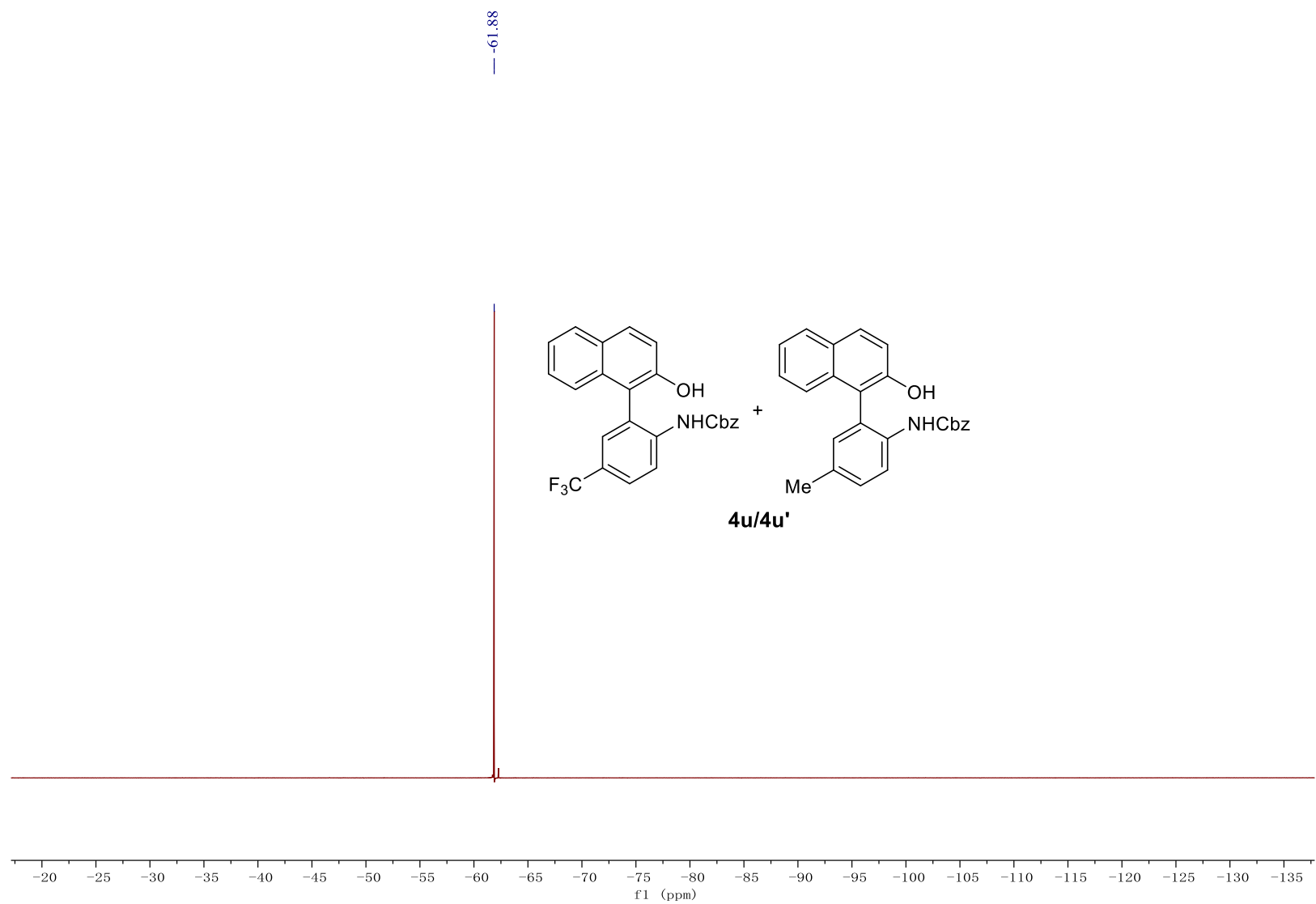
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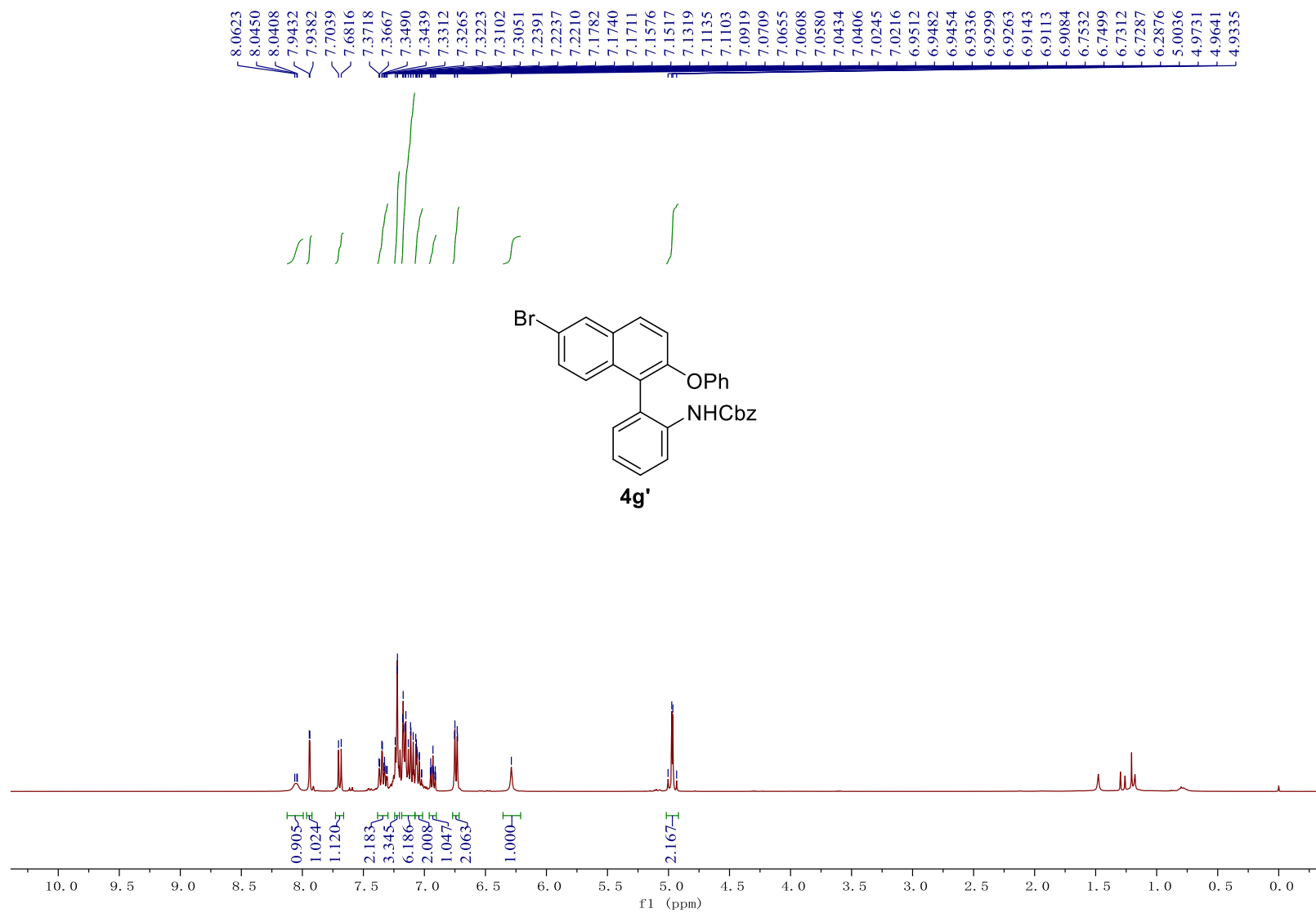
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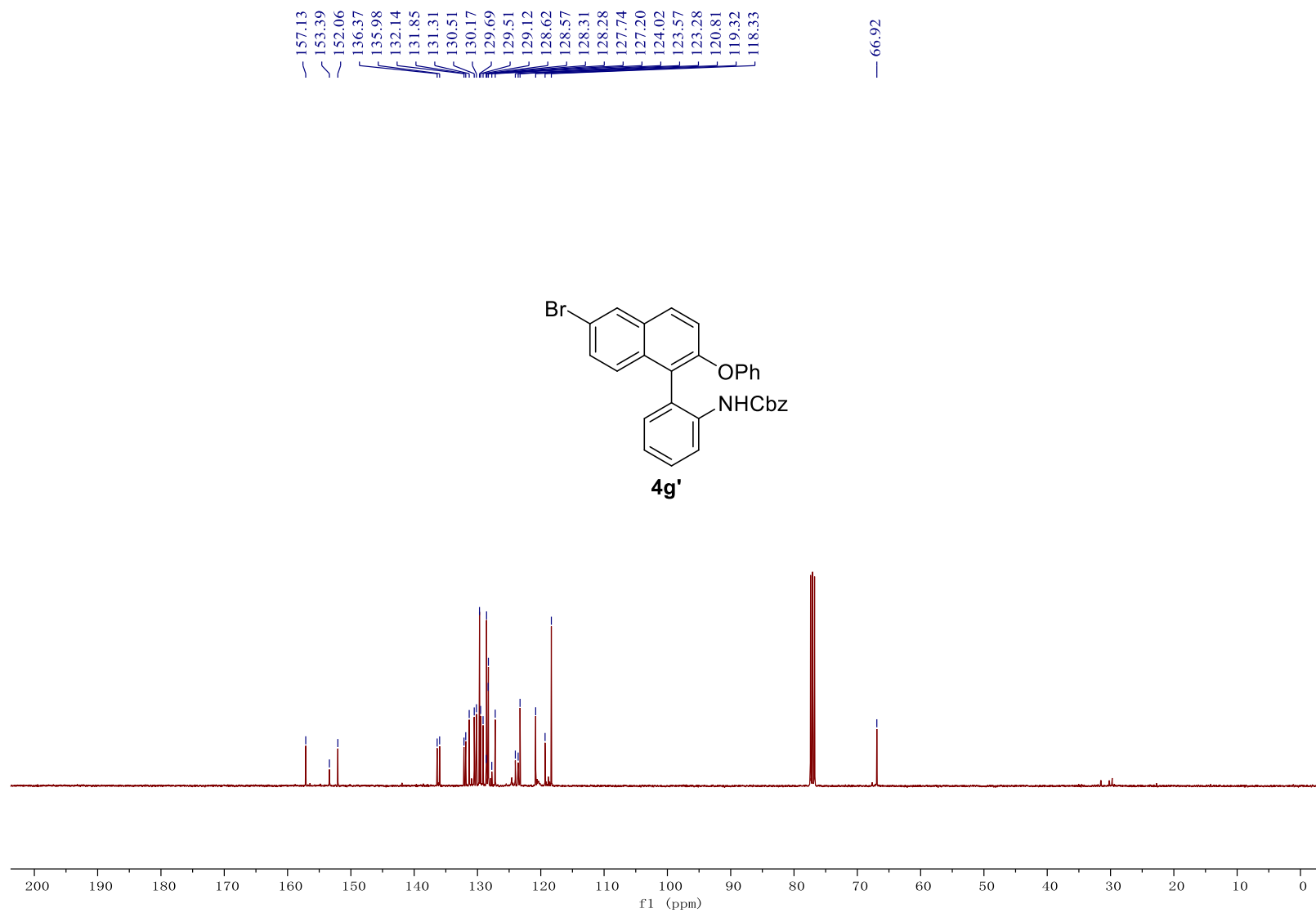
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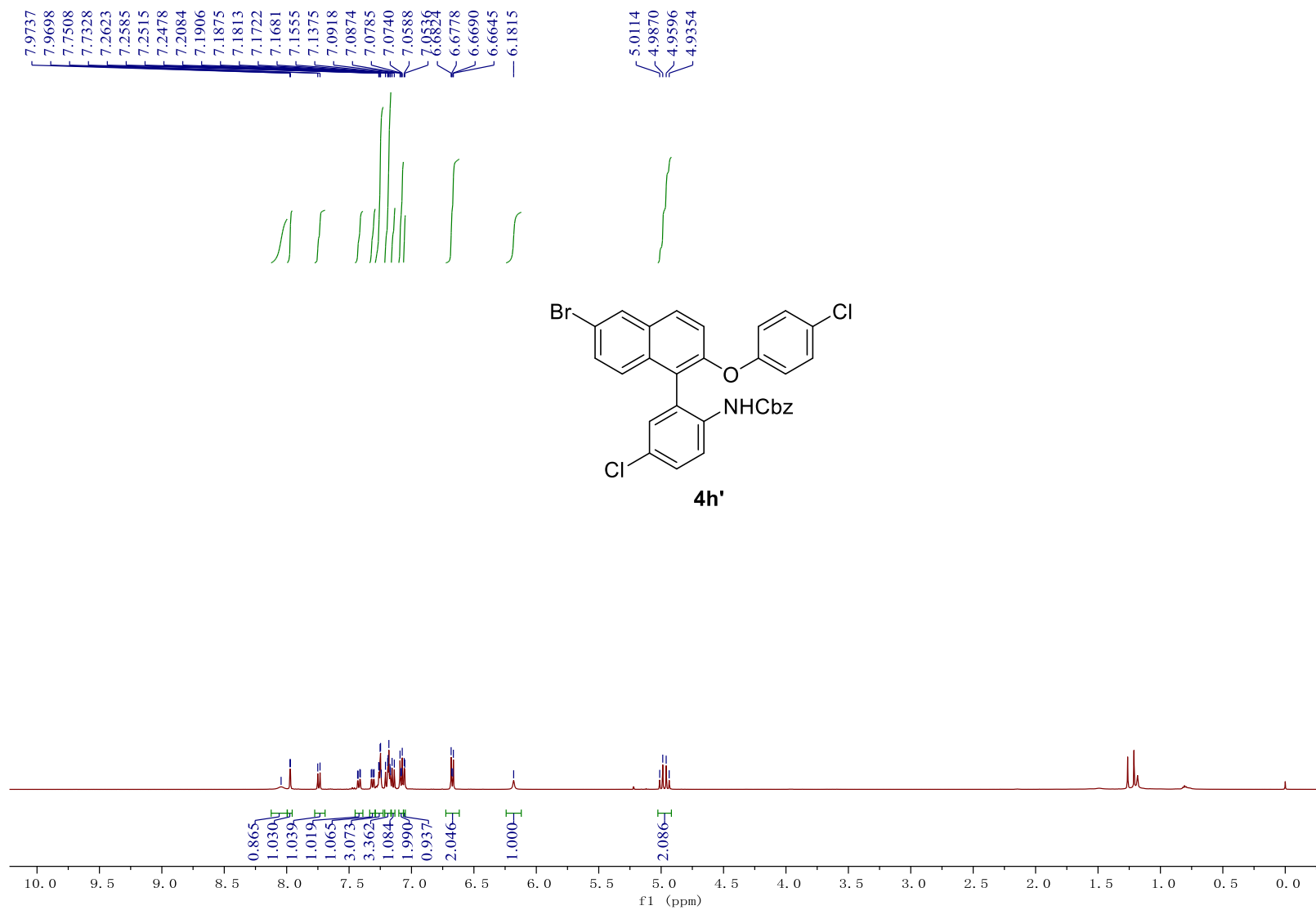
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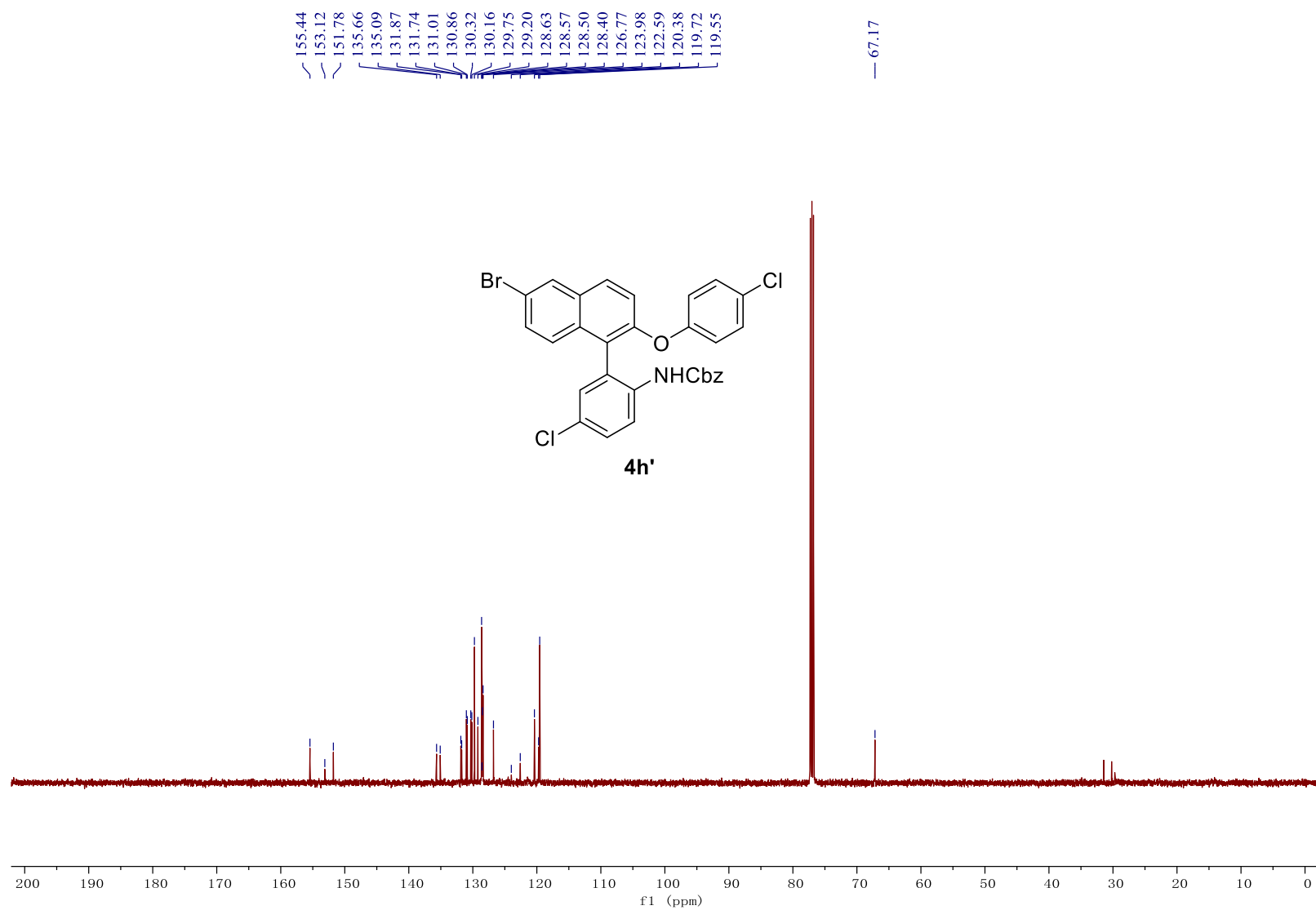
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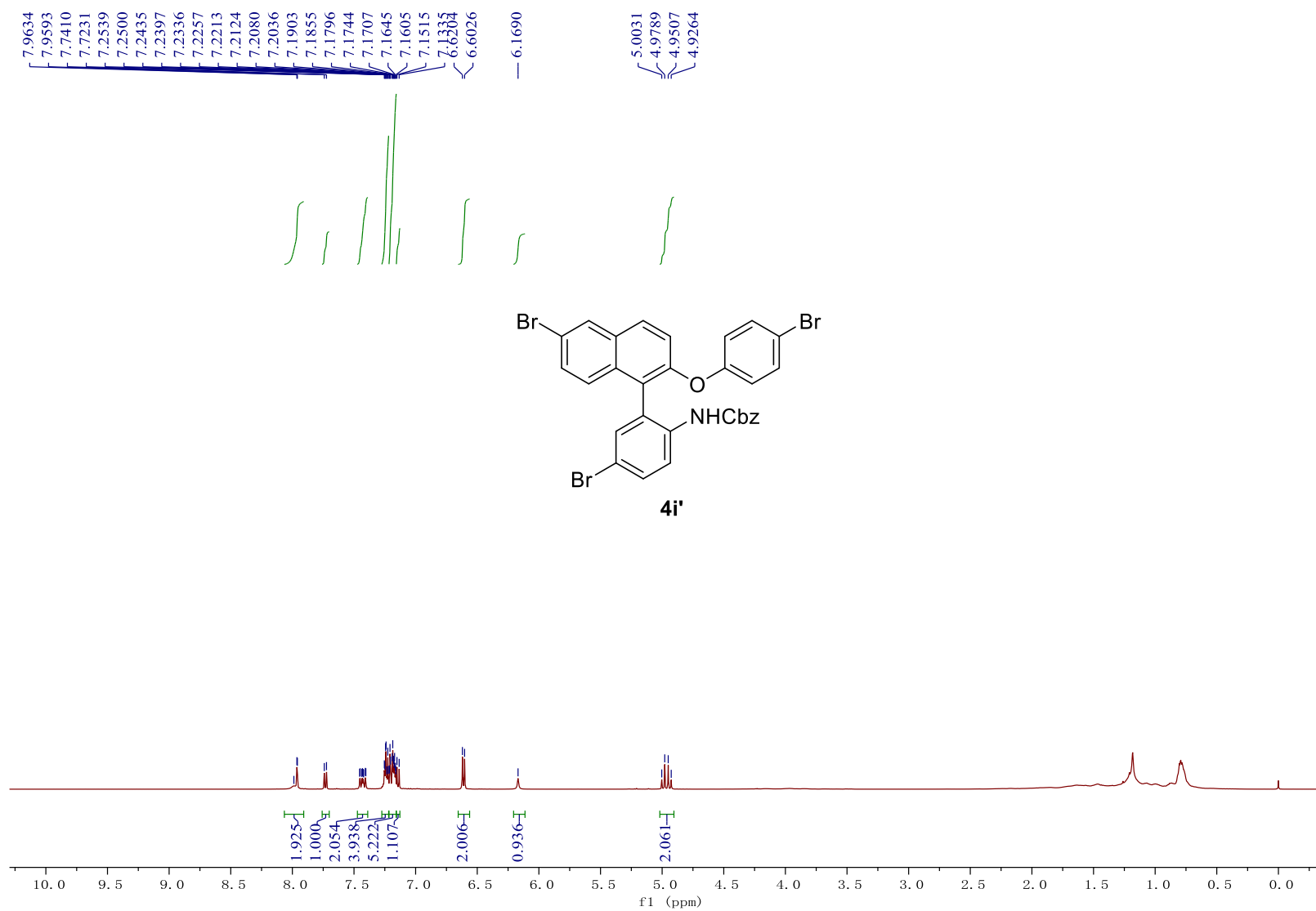
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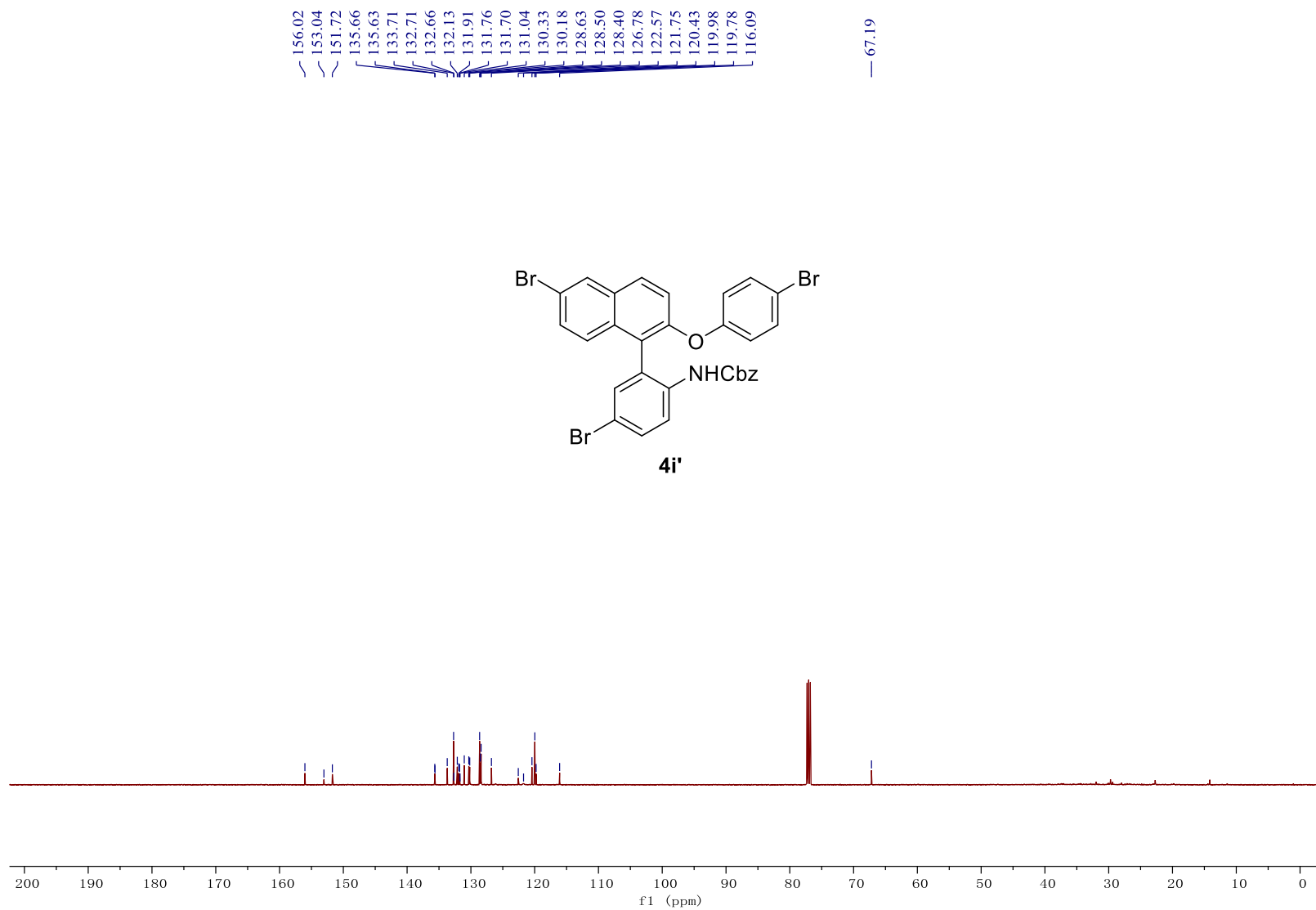
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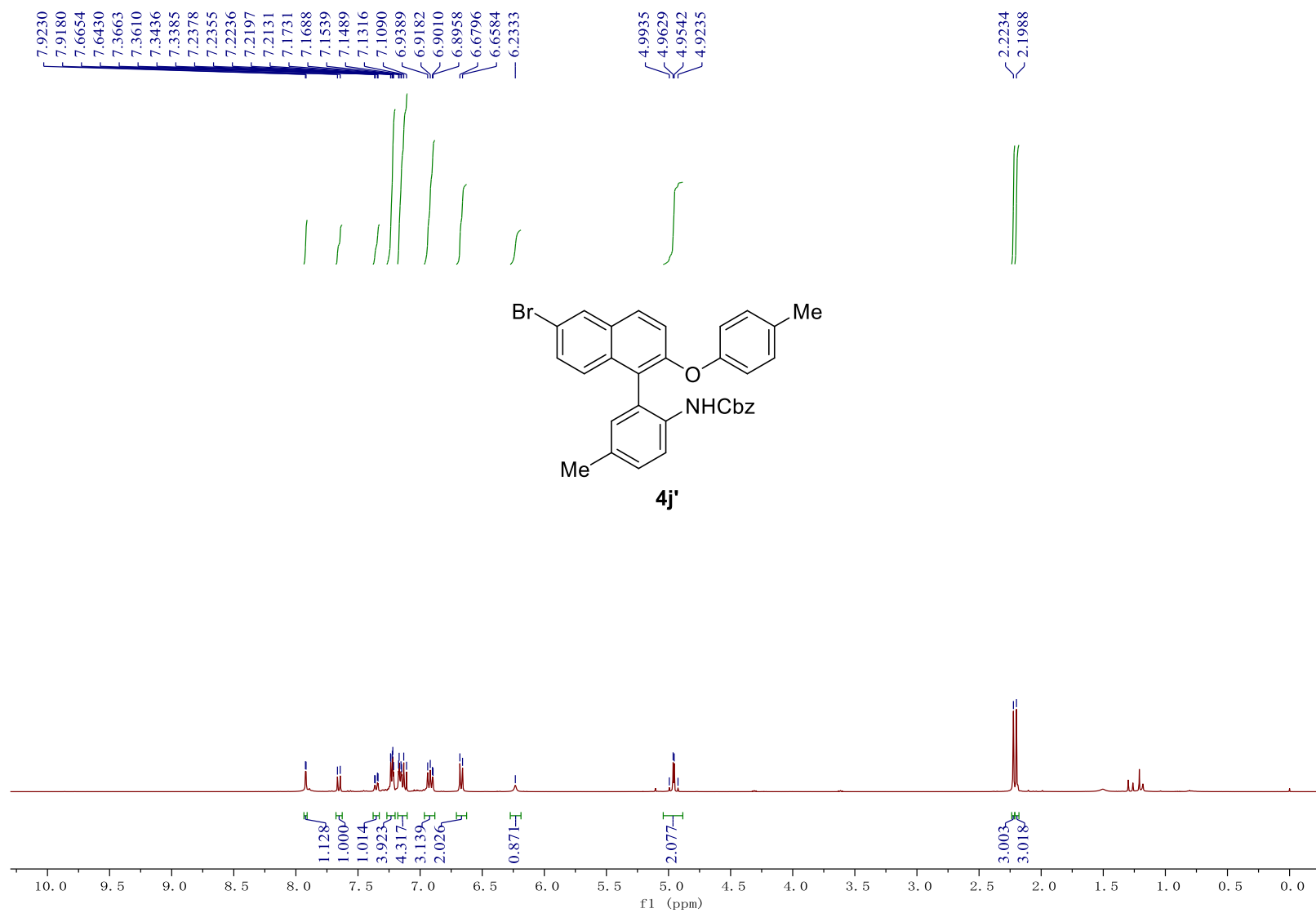
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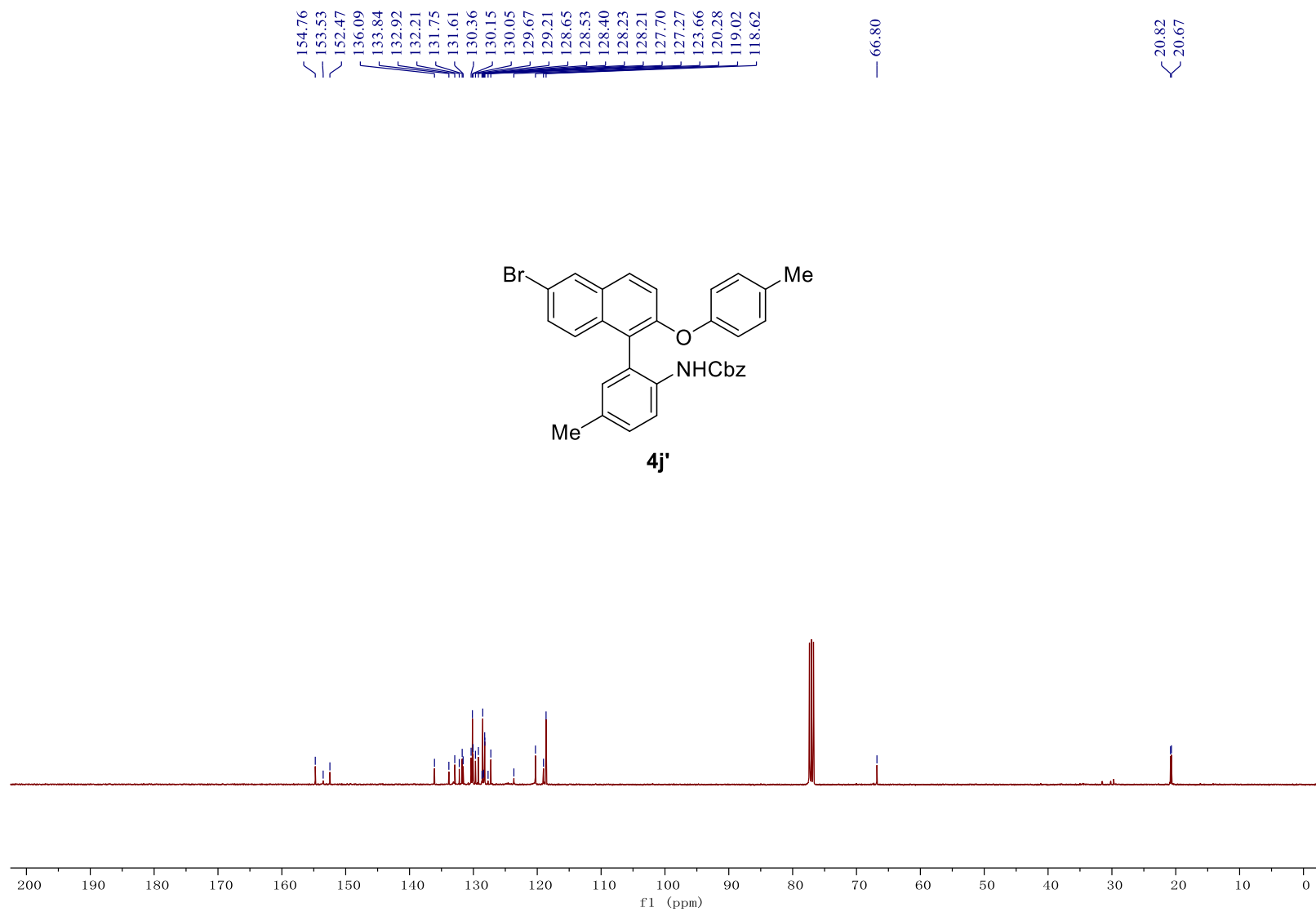
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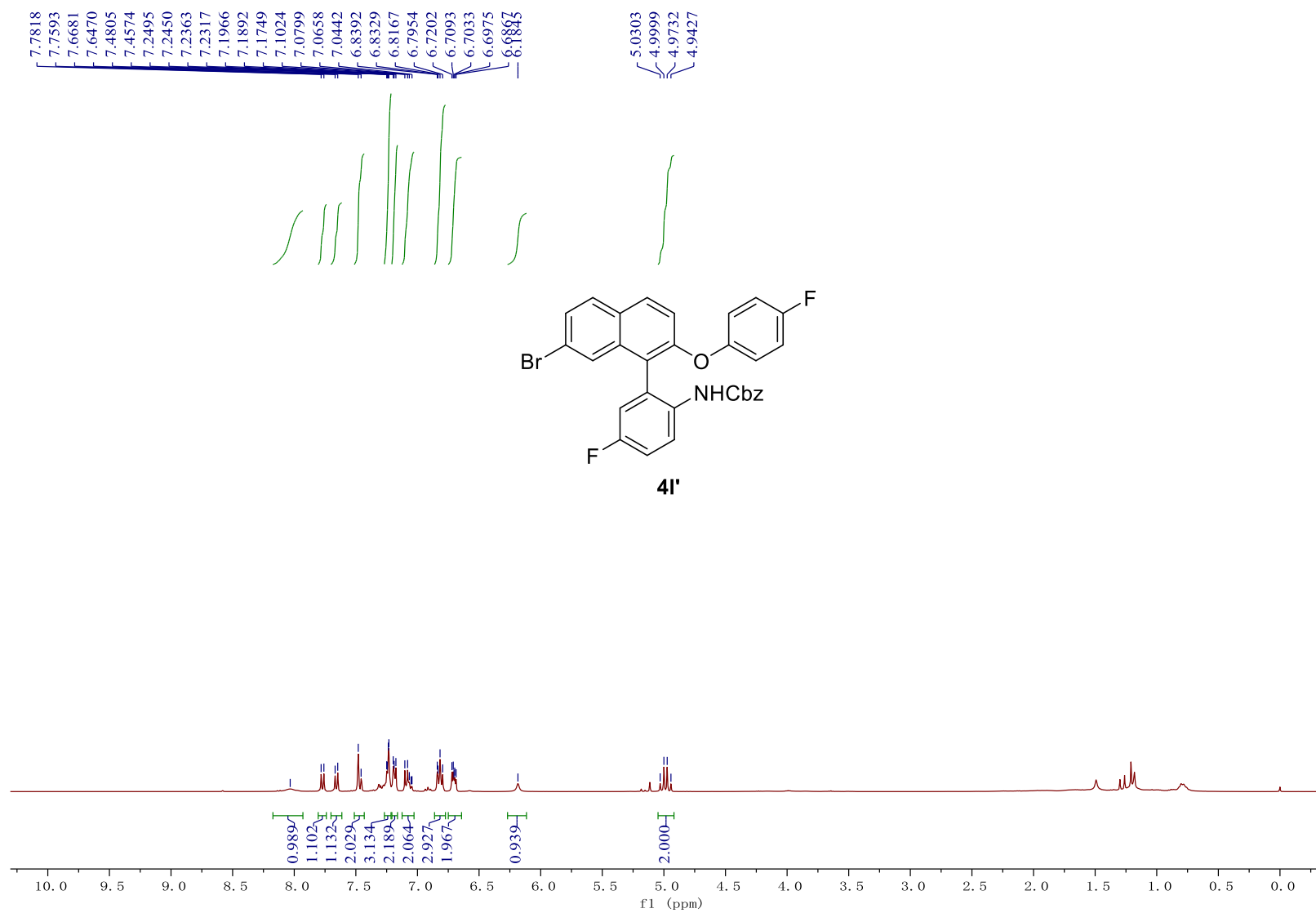
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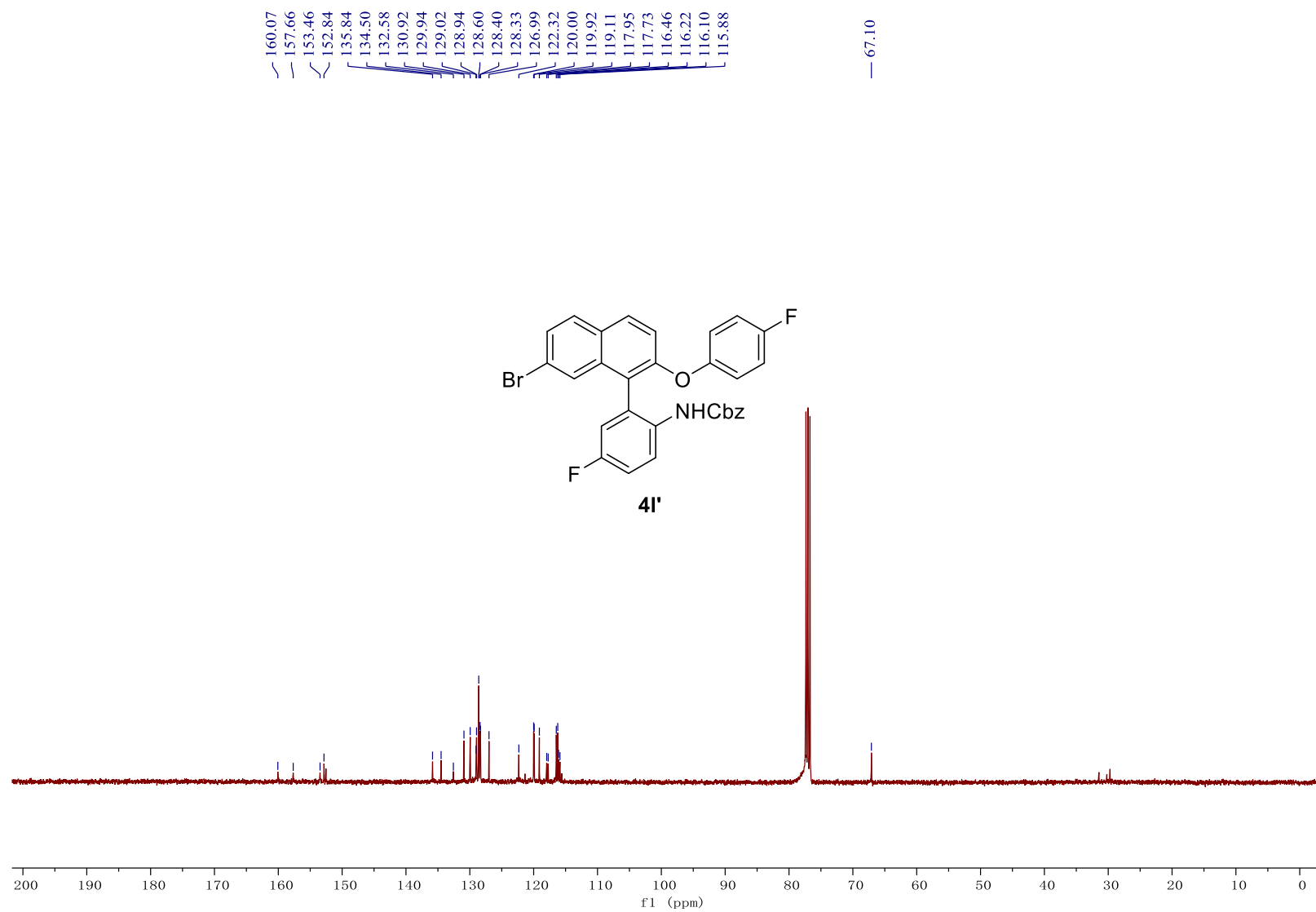
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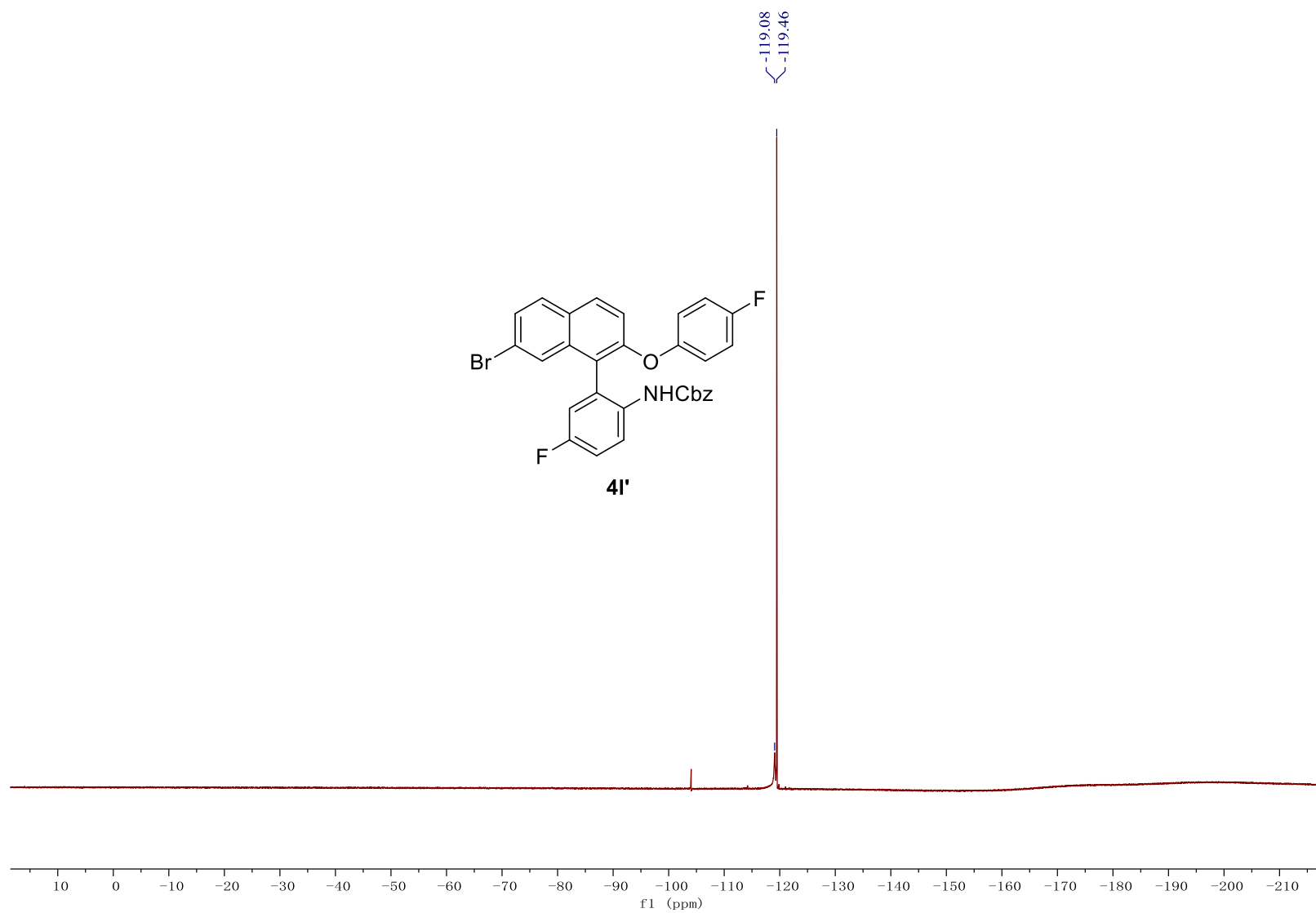
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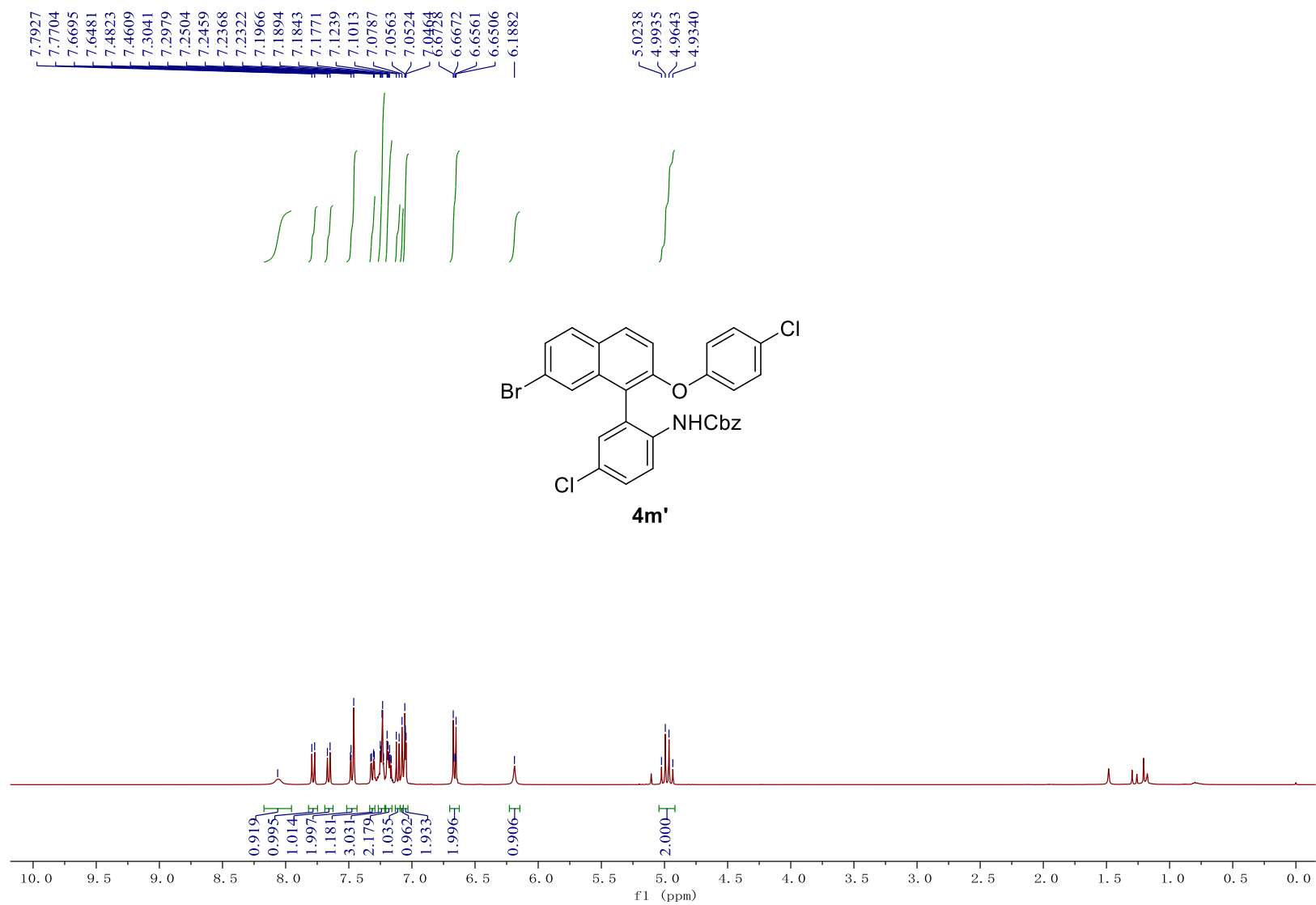
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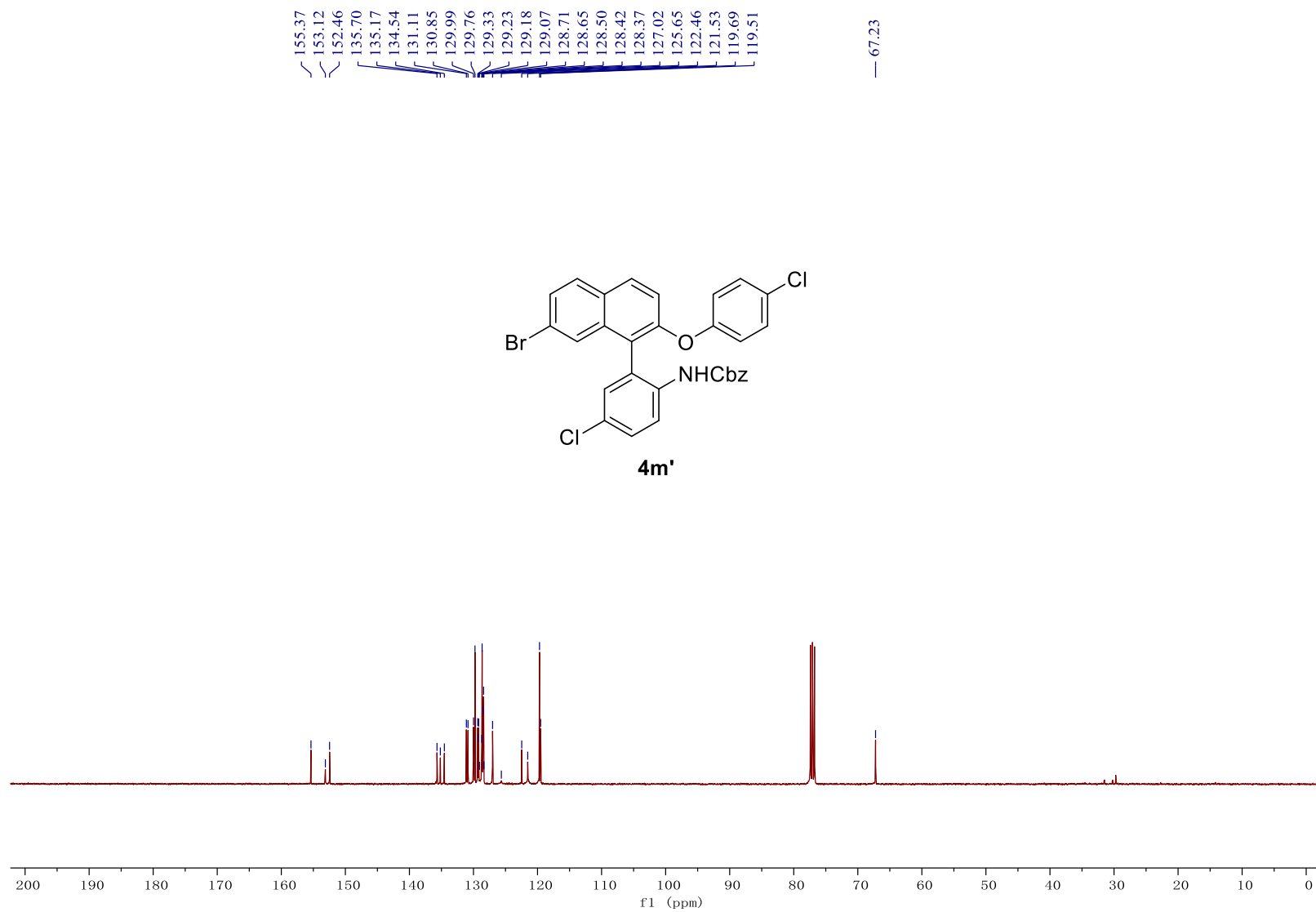
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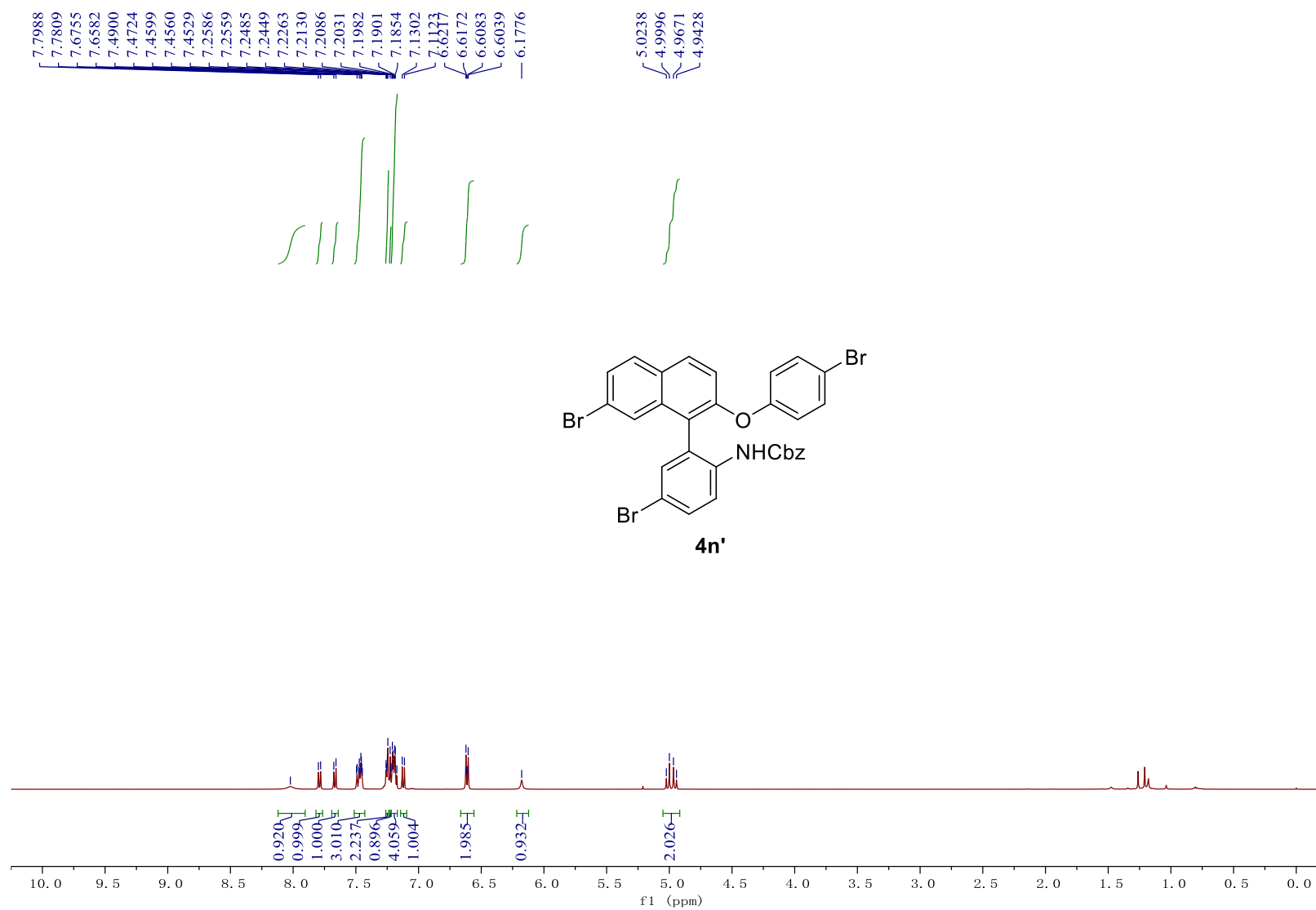
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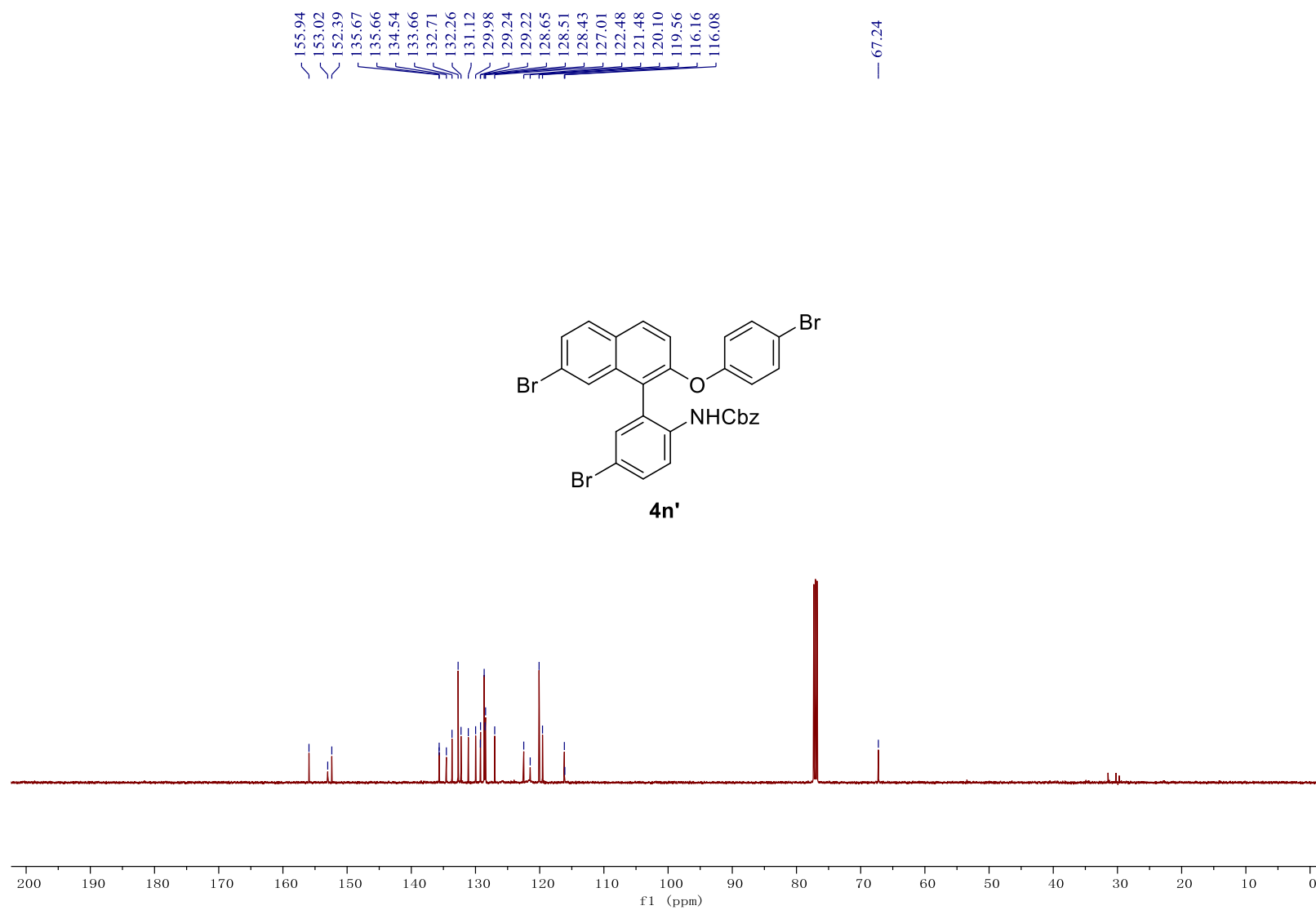
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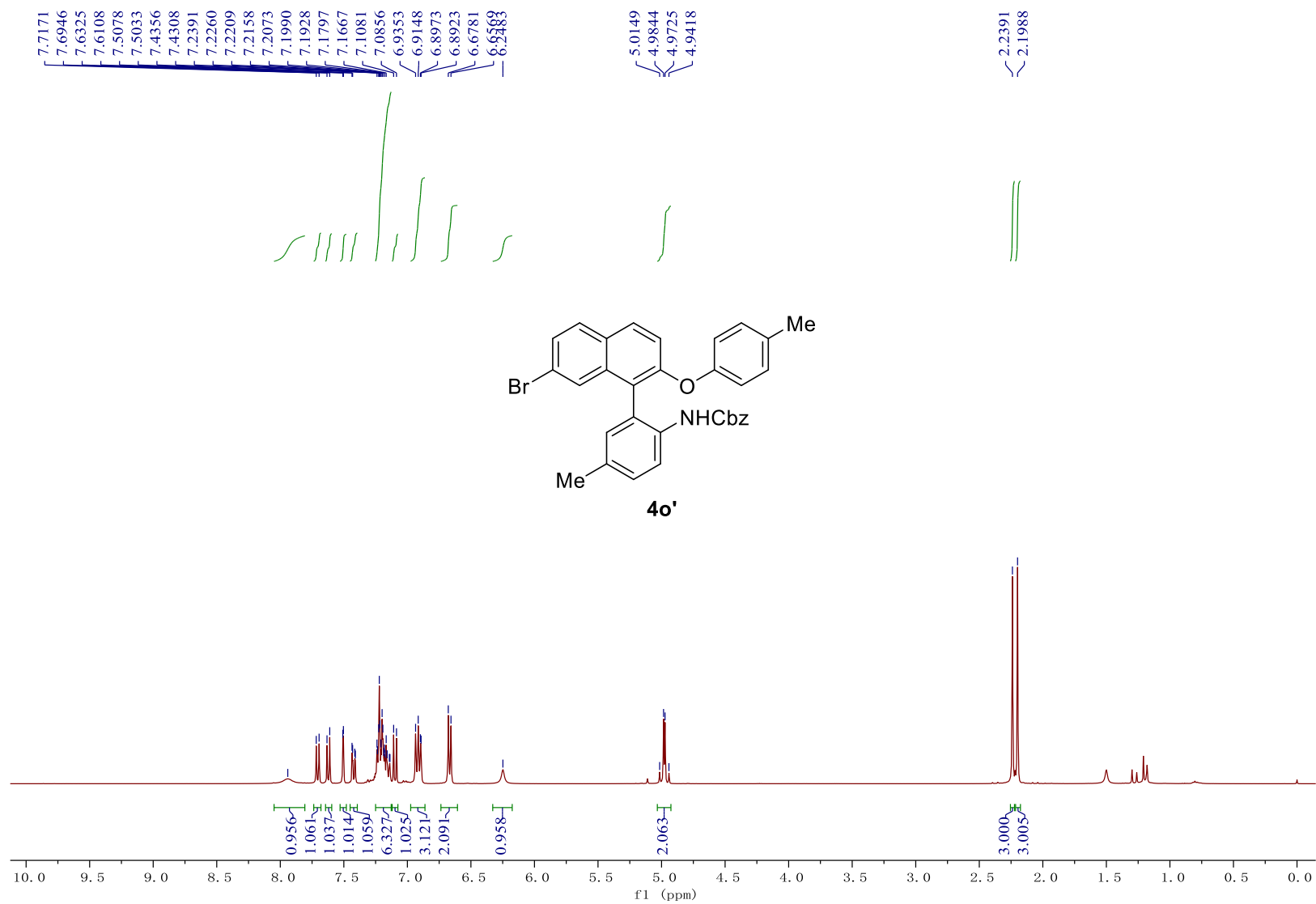
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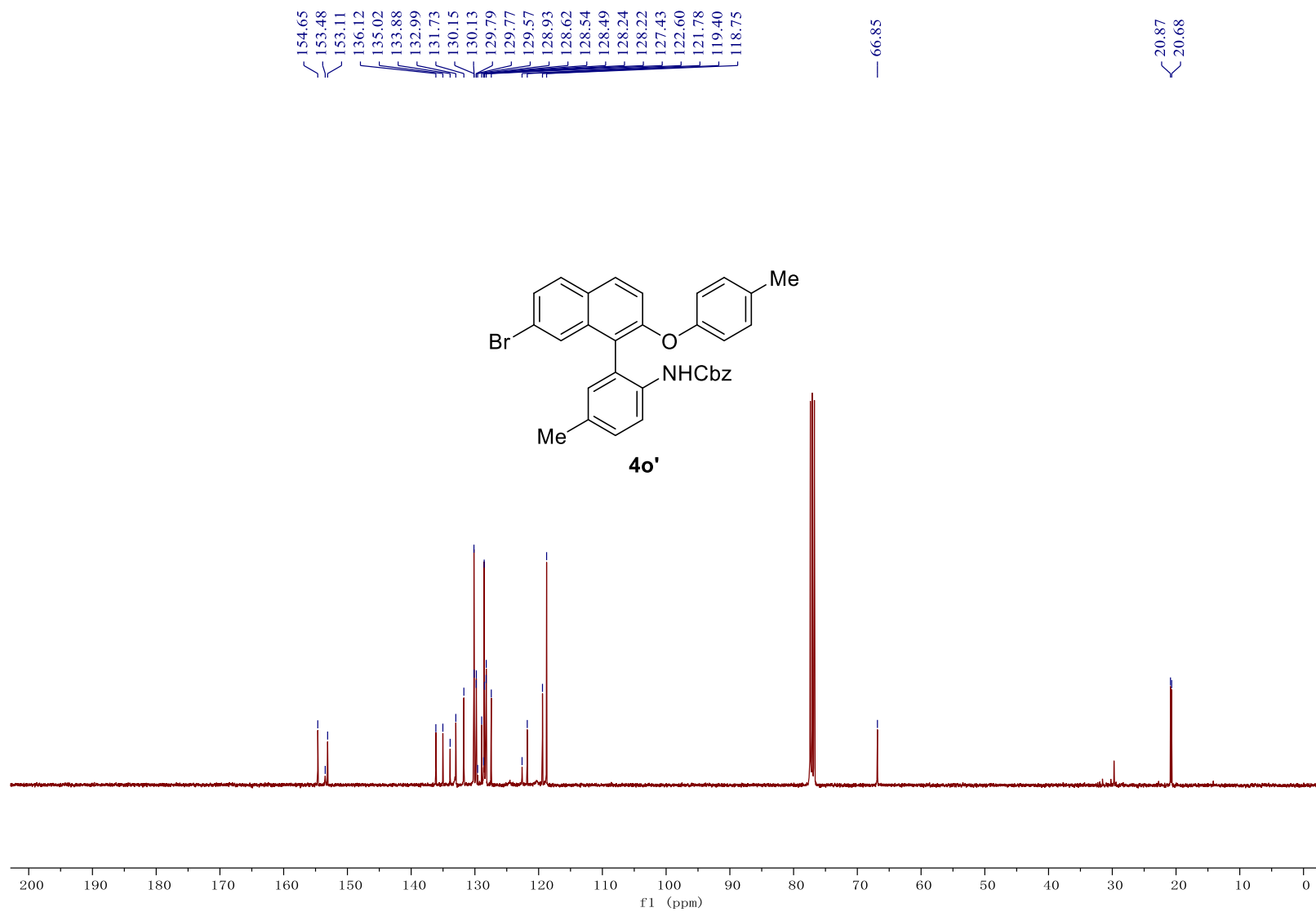
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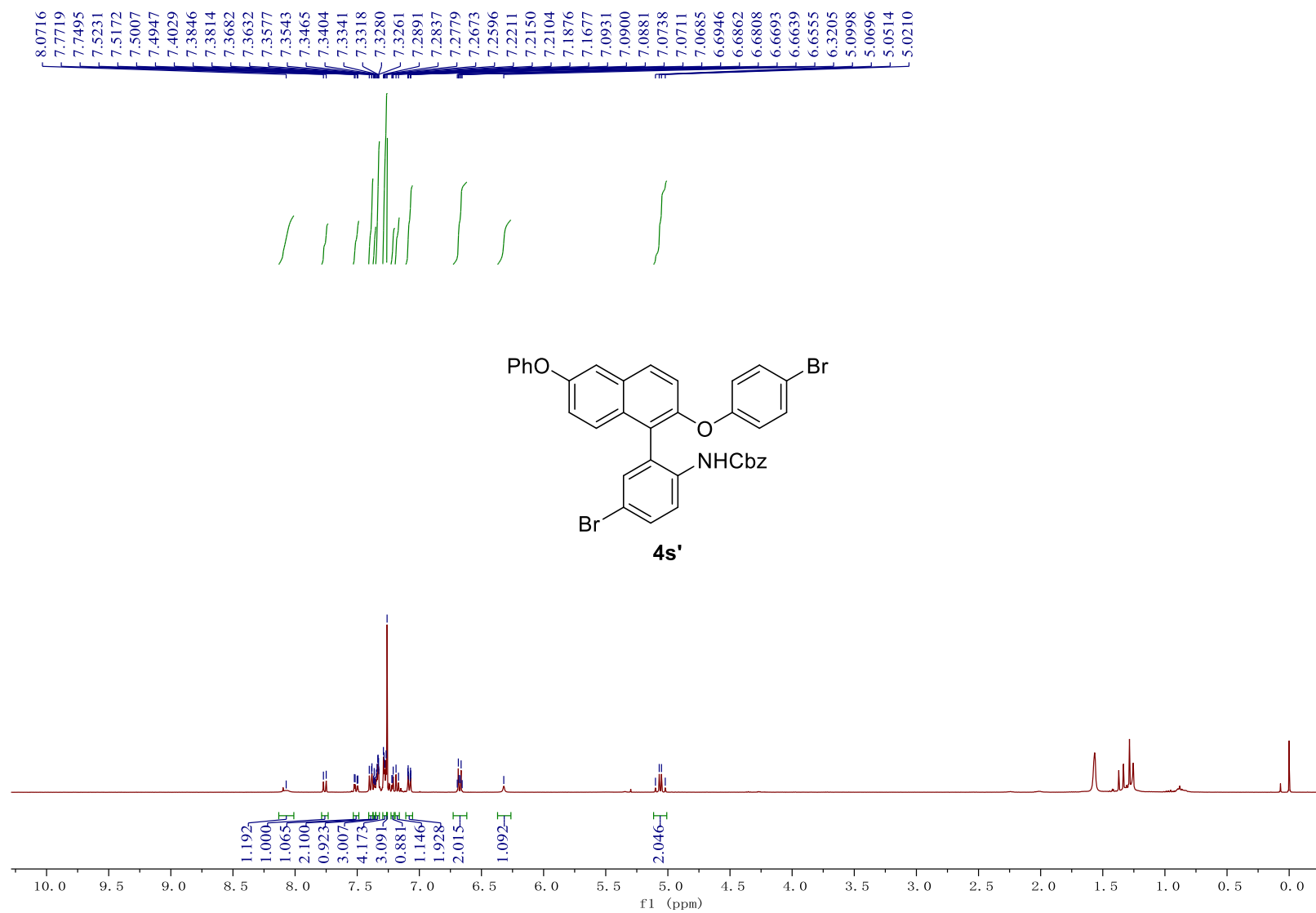
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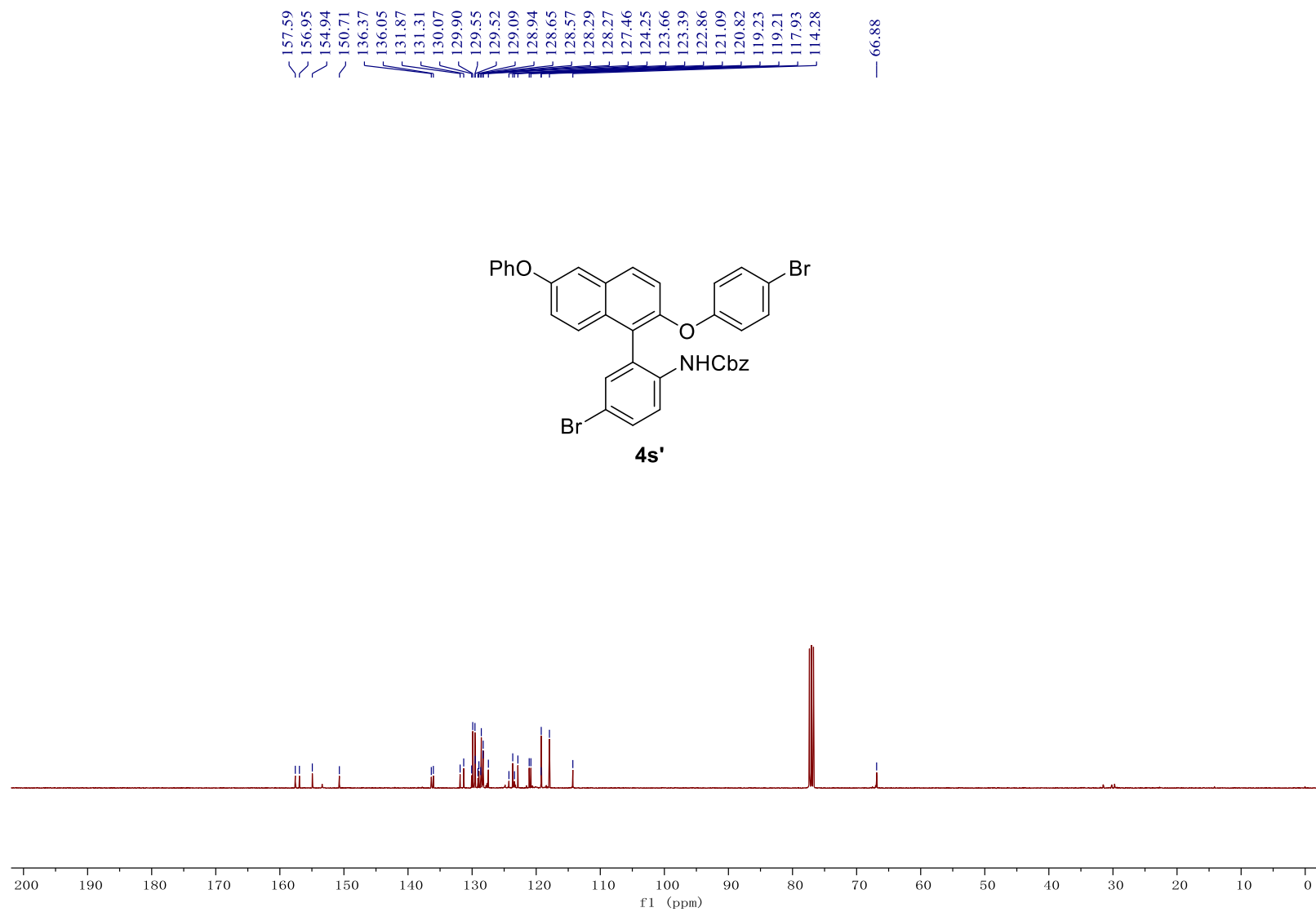
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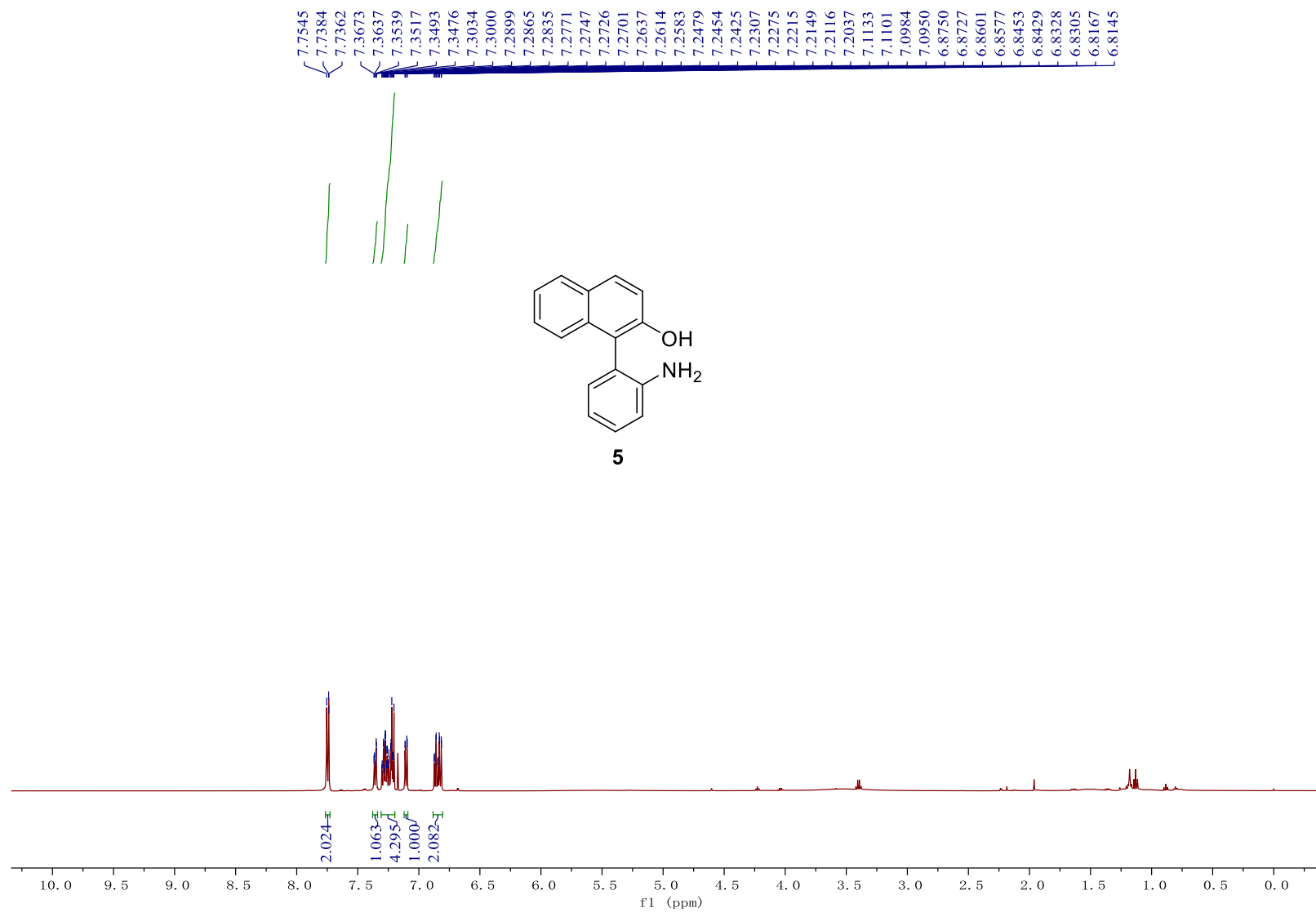
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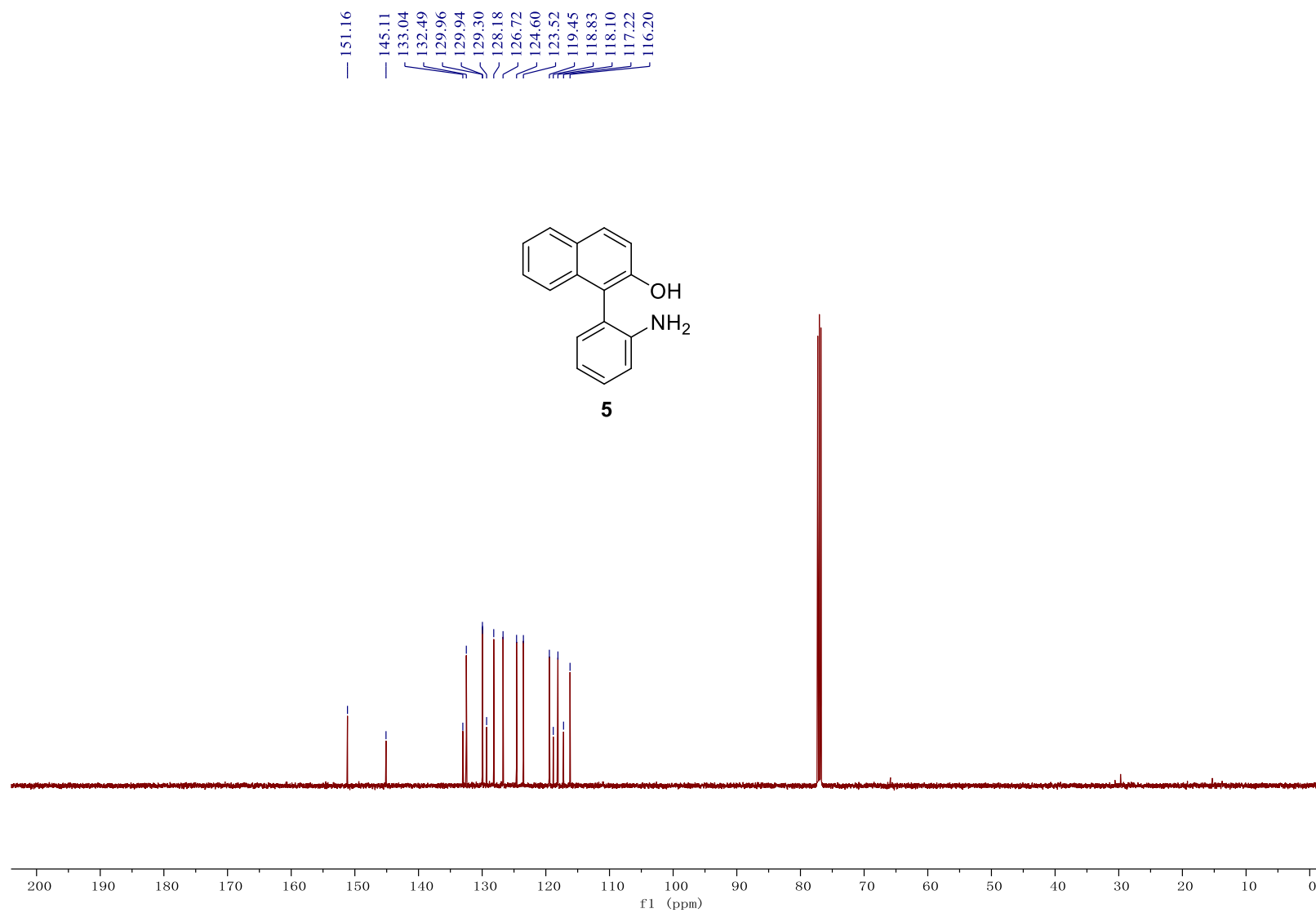
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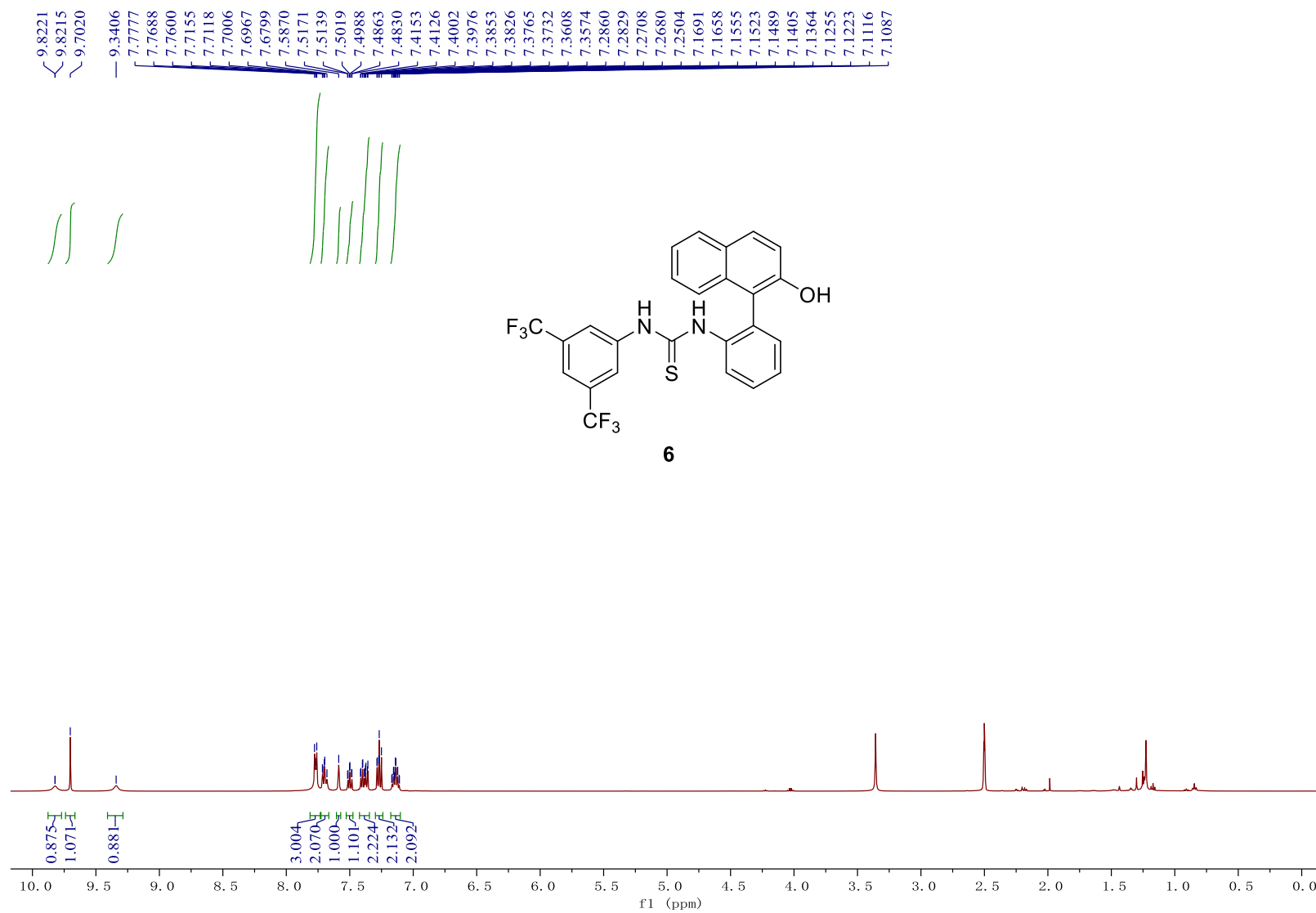
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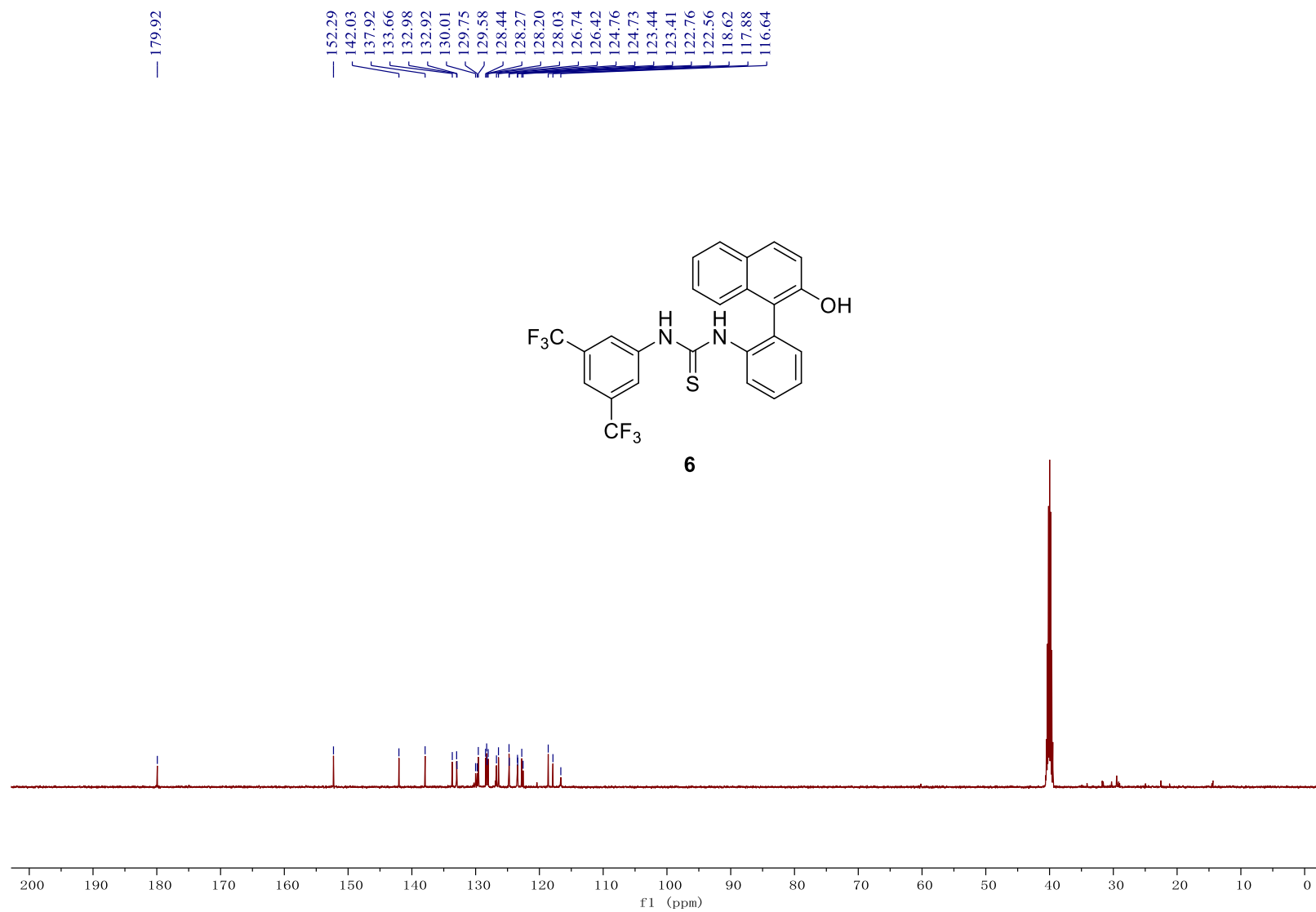
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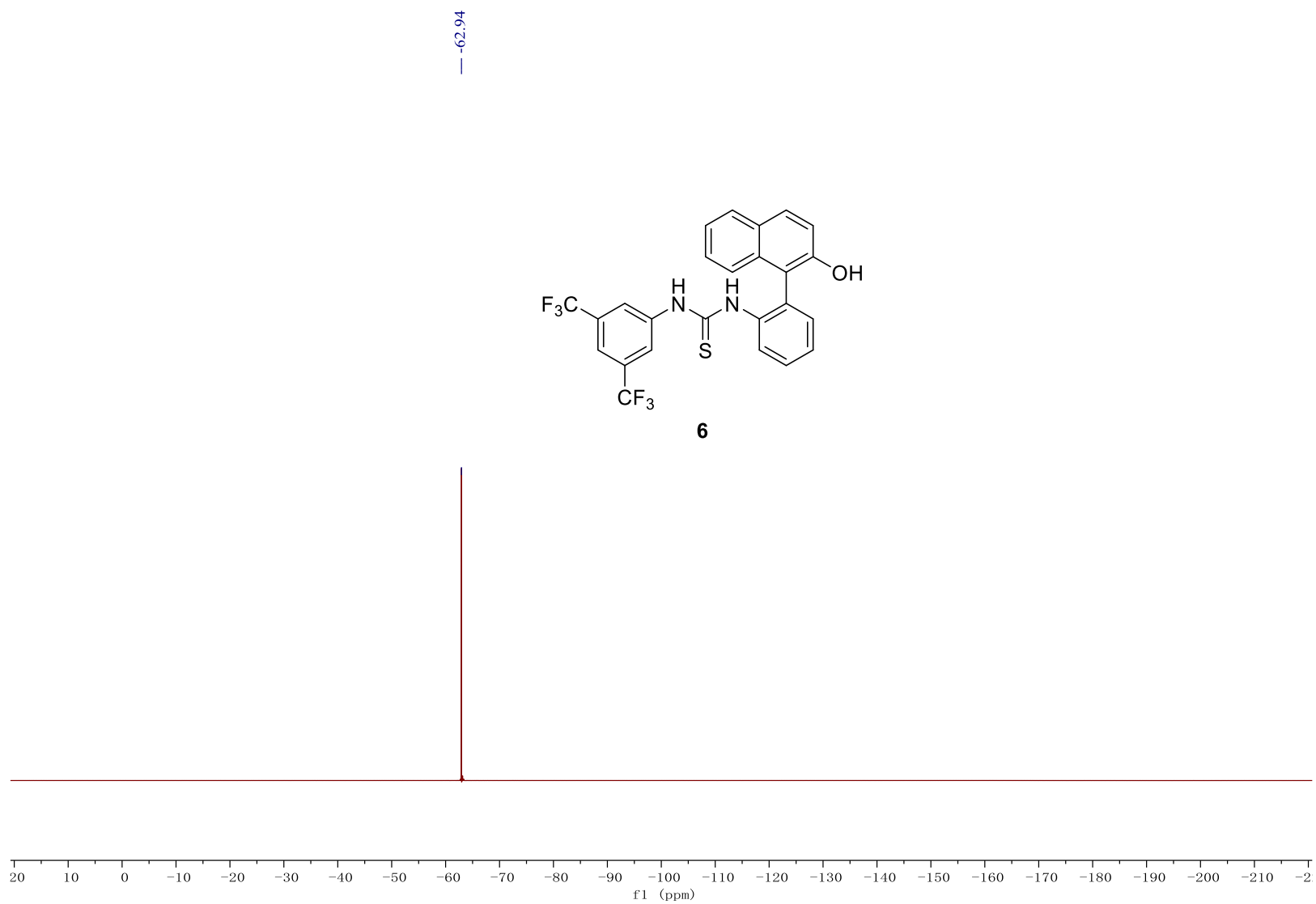
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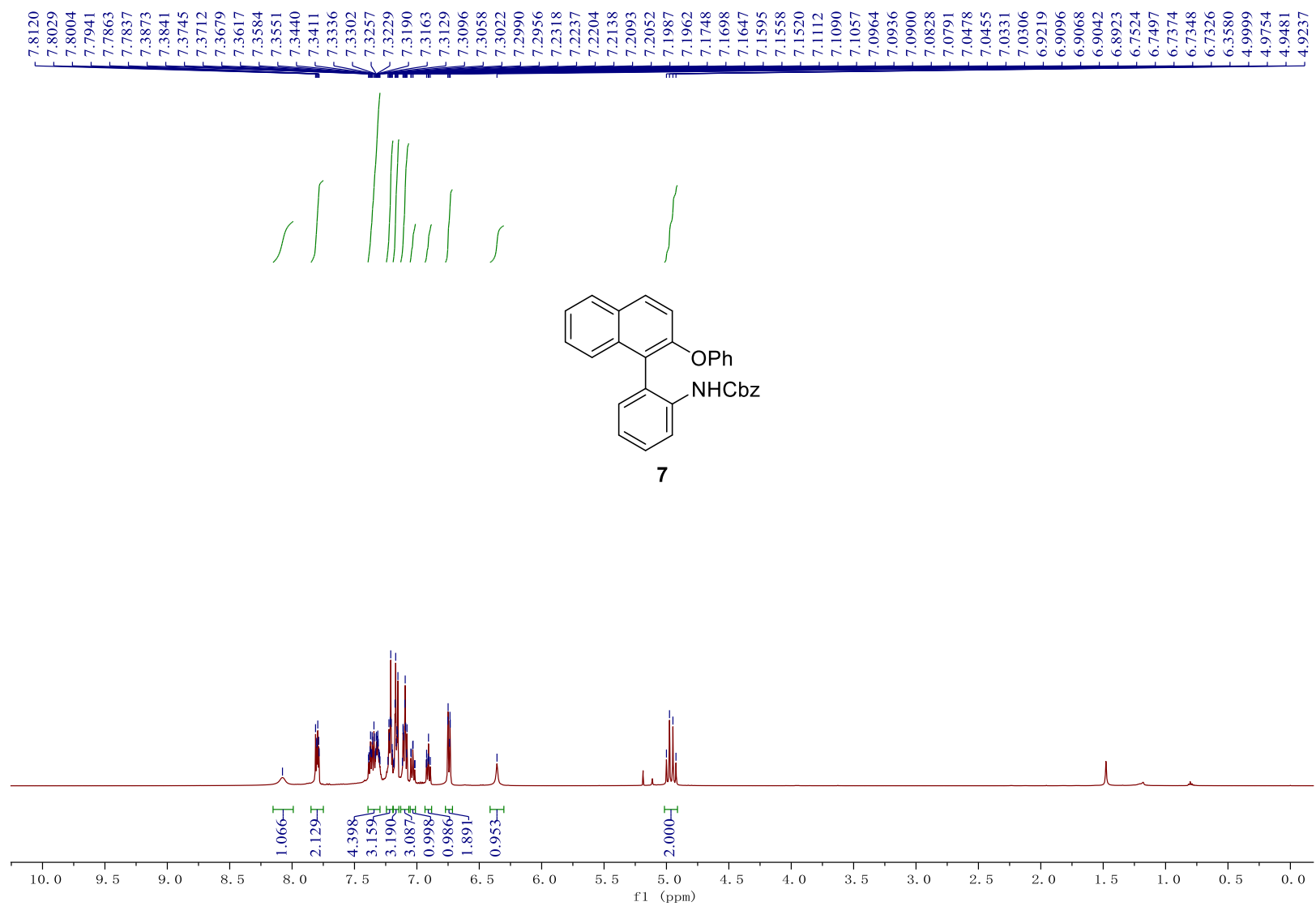
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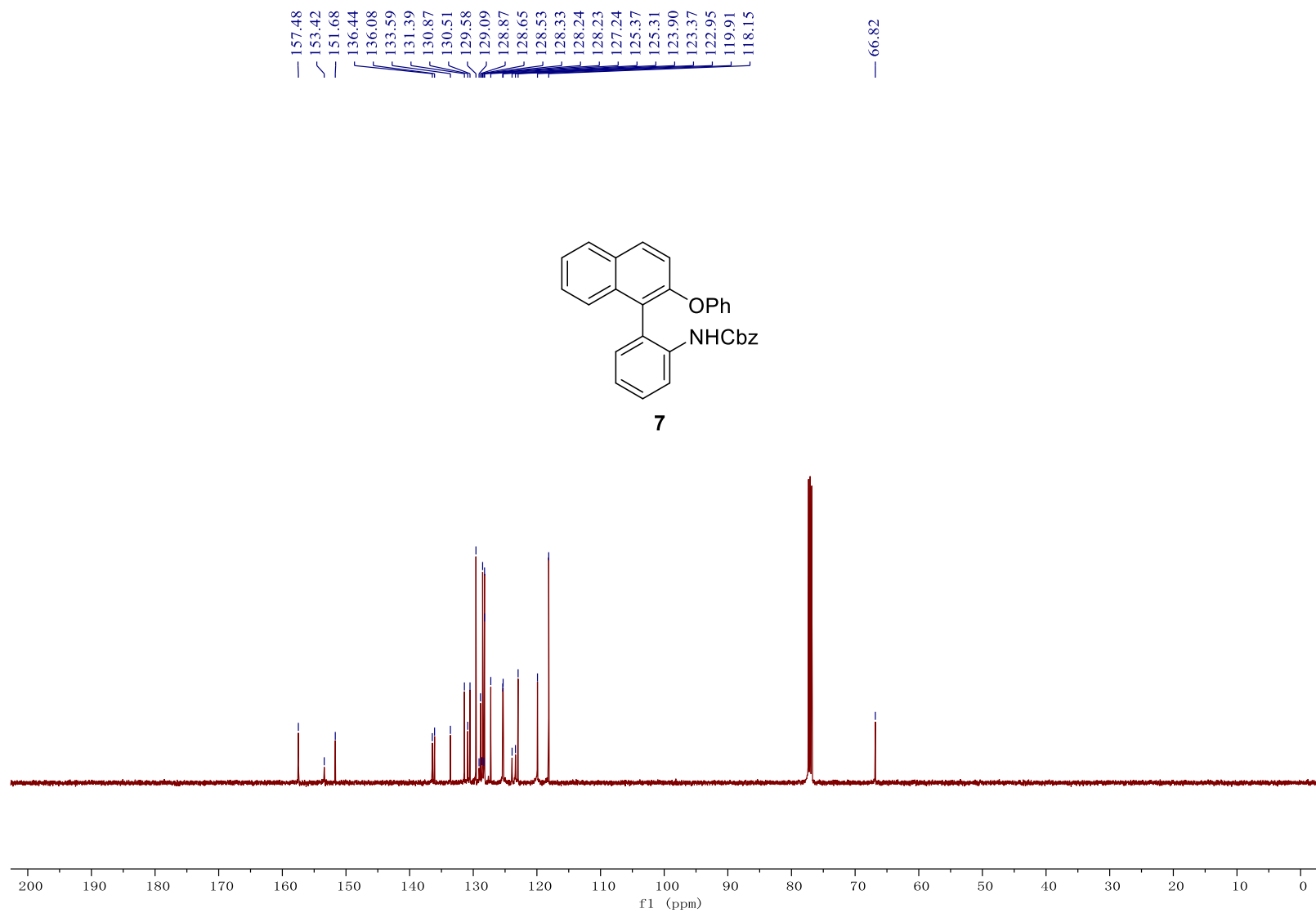
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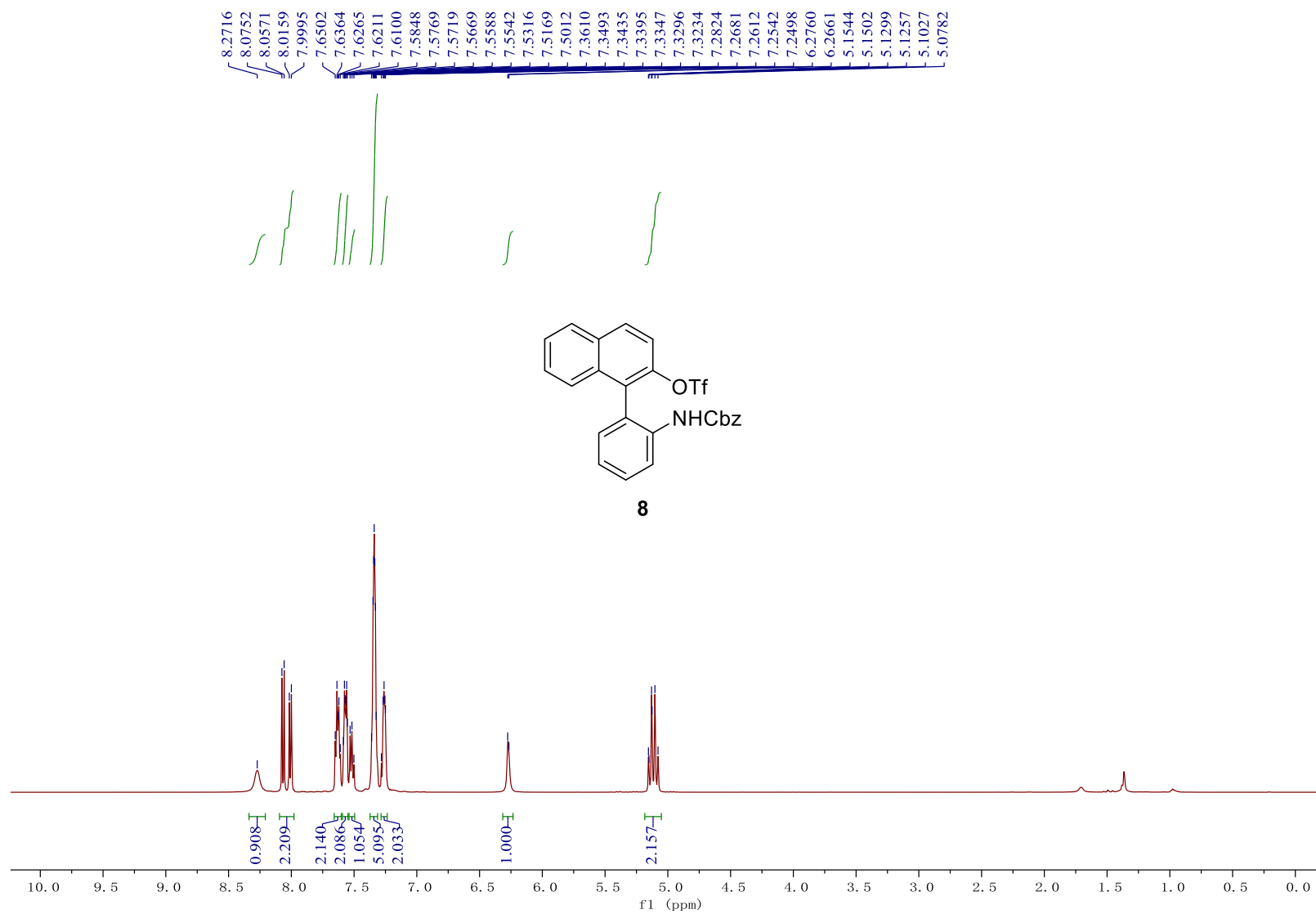
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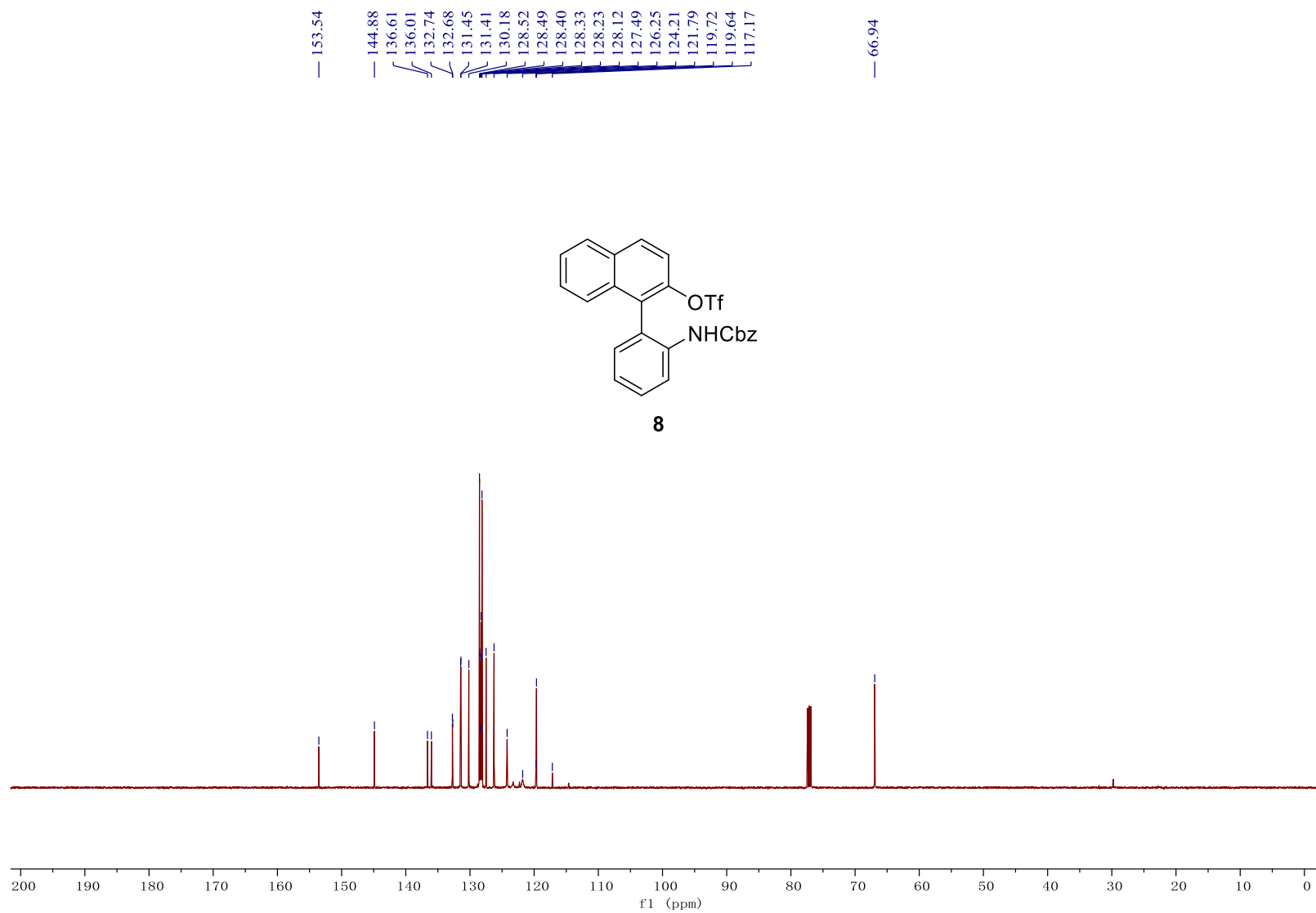
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S176

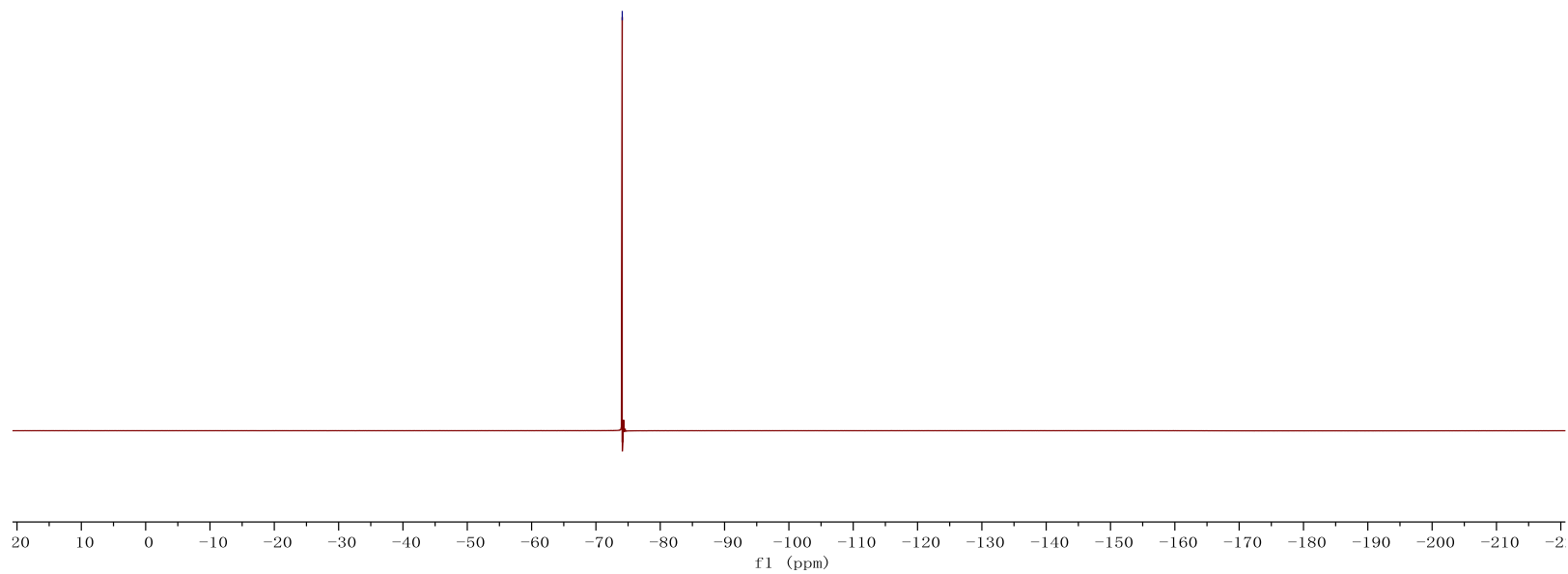
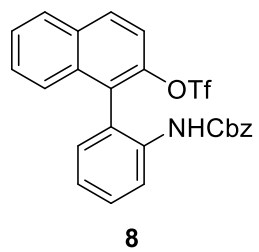


S177

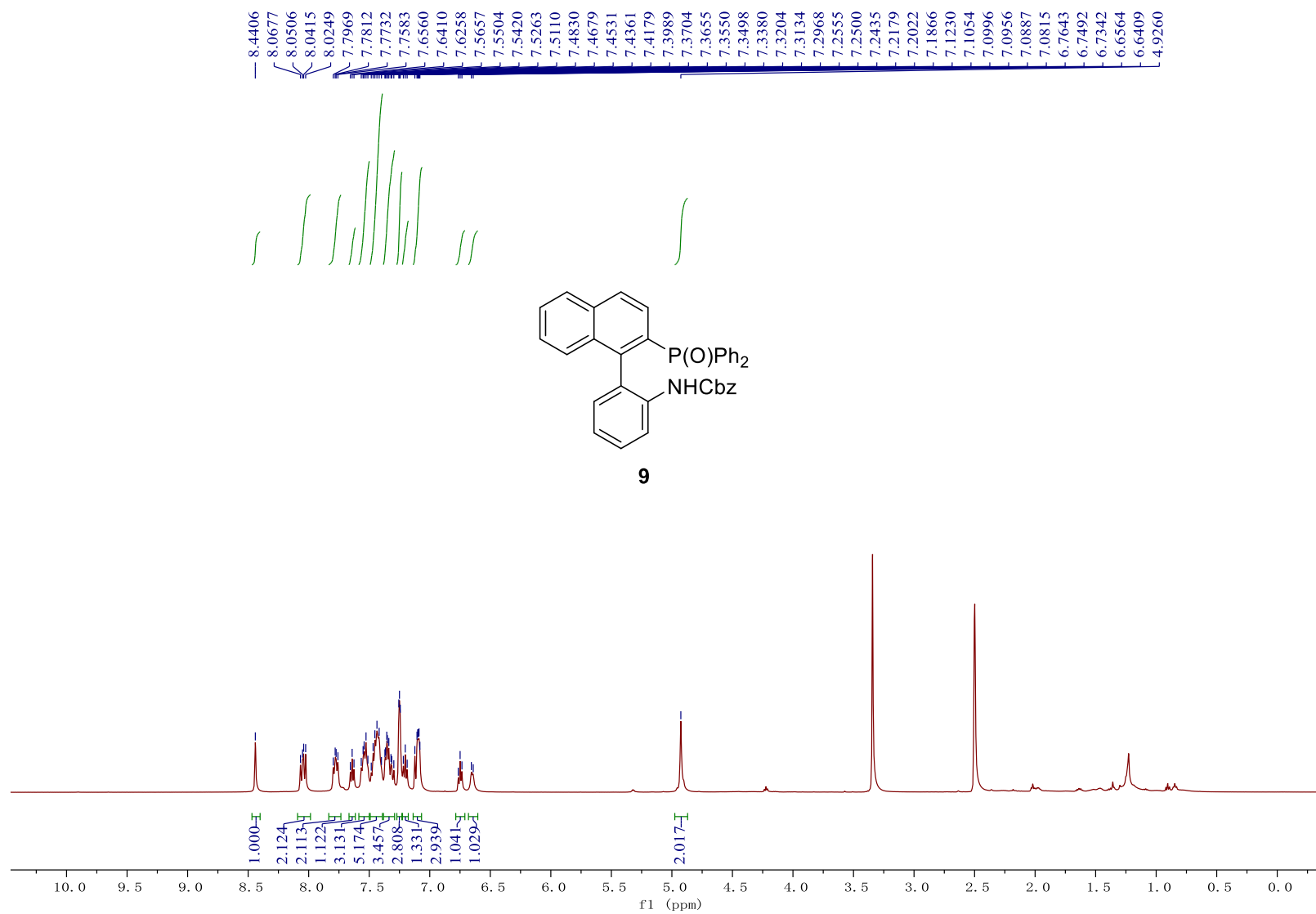


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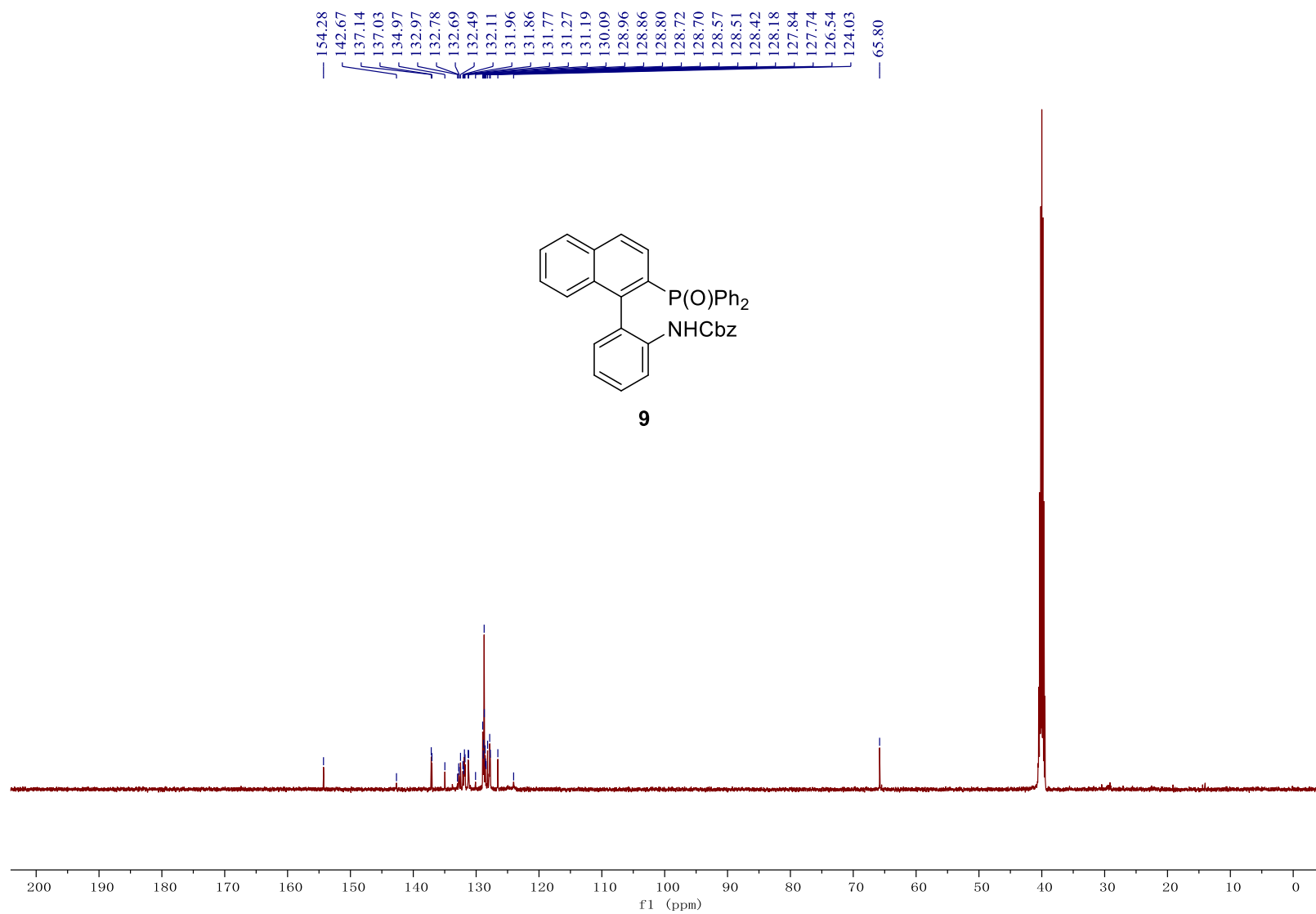
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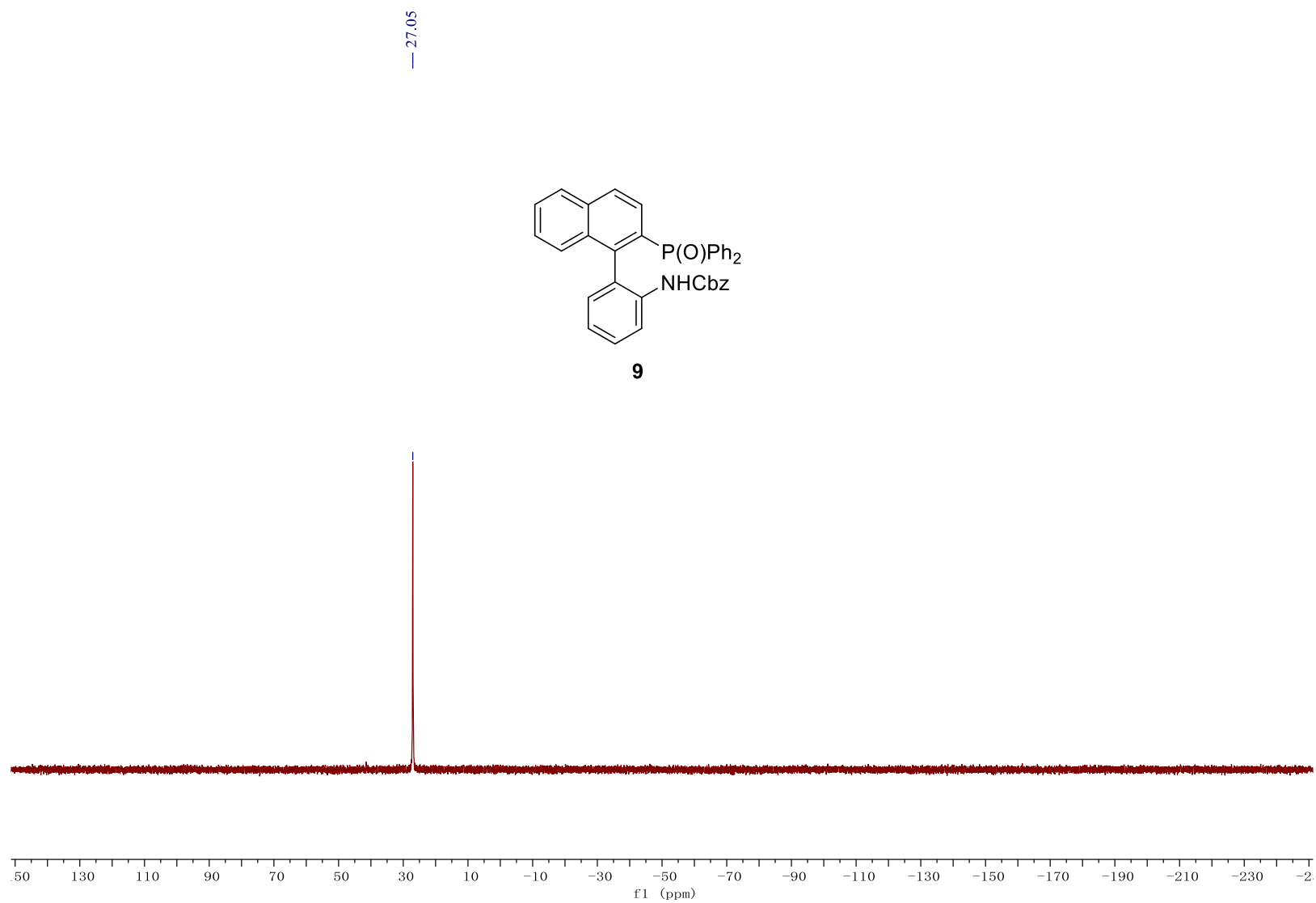
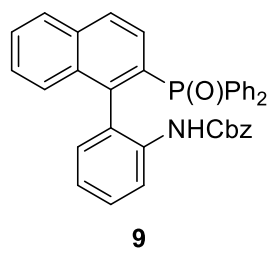
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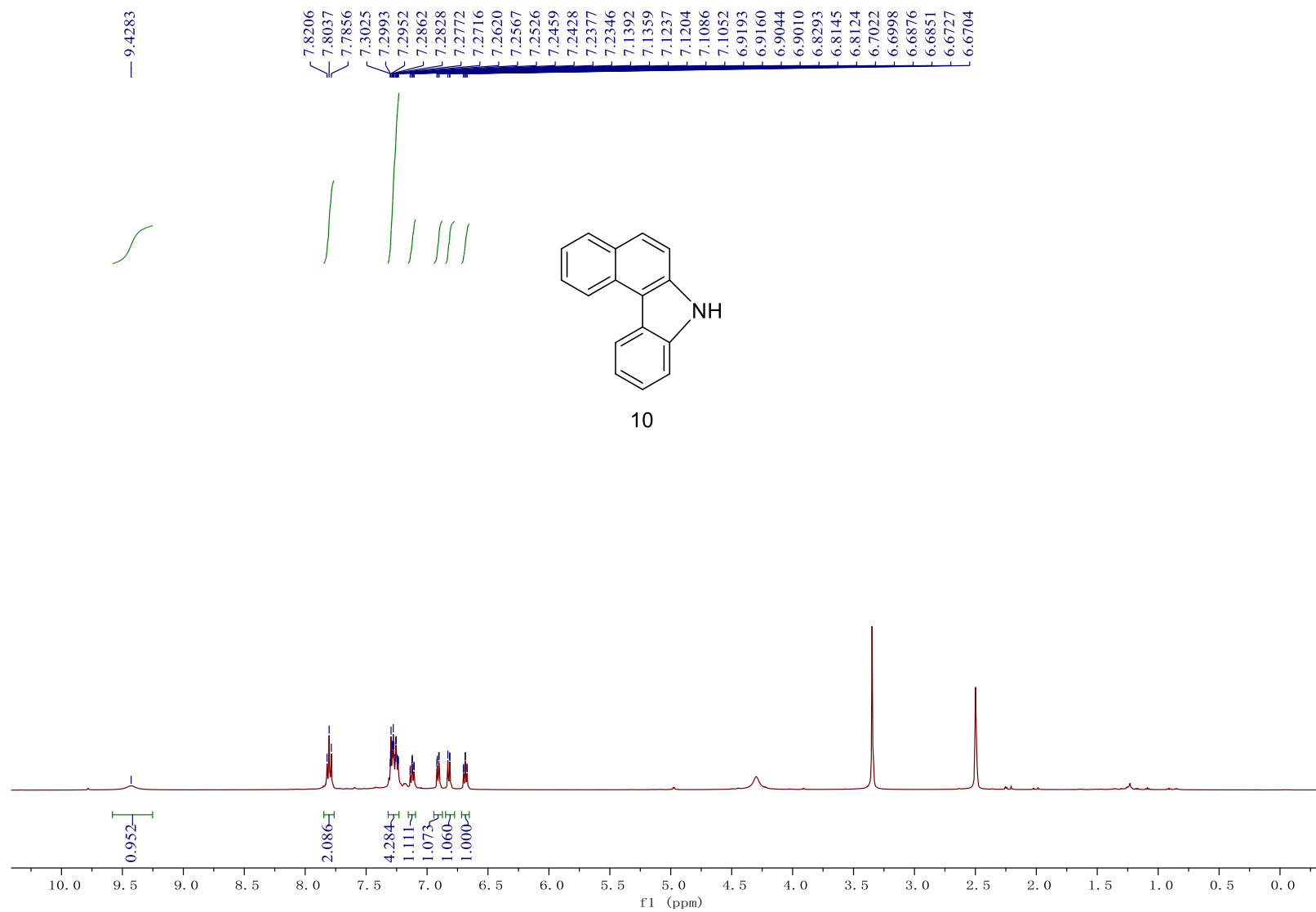
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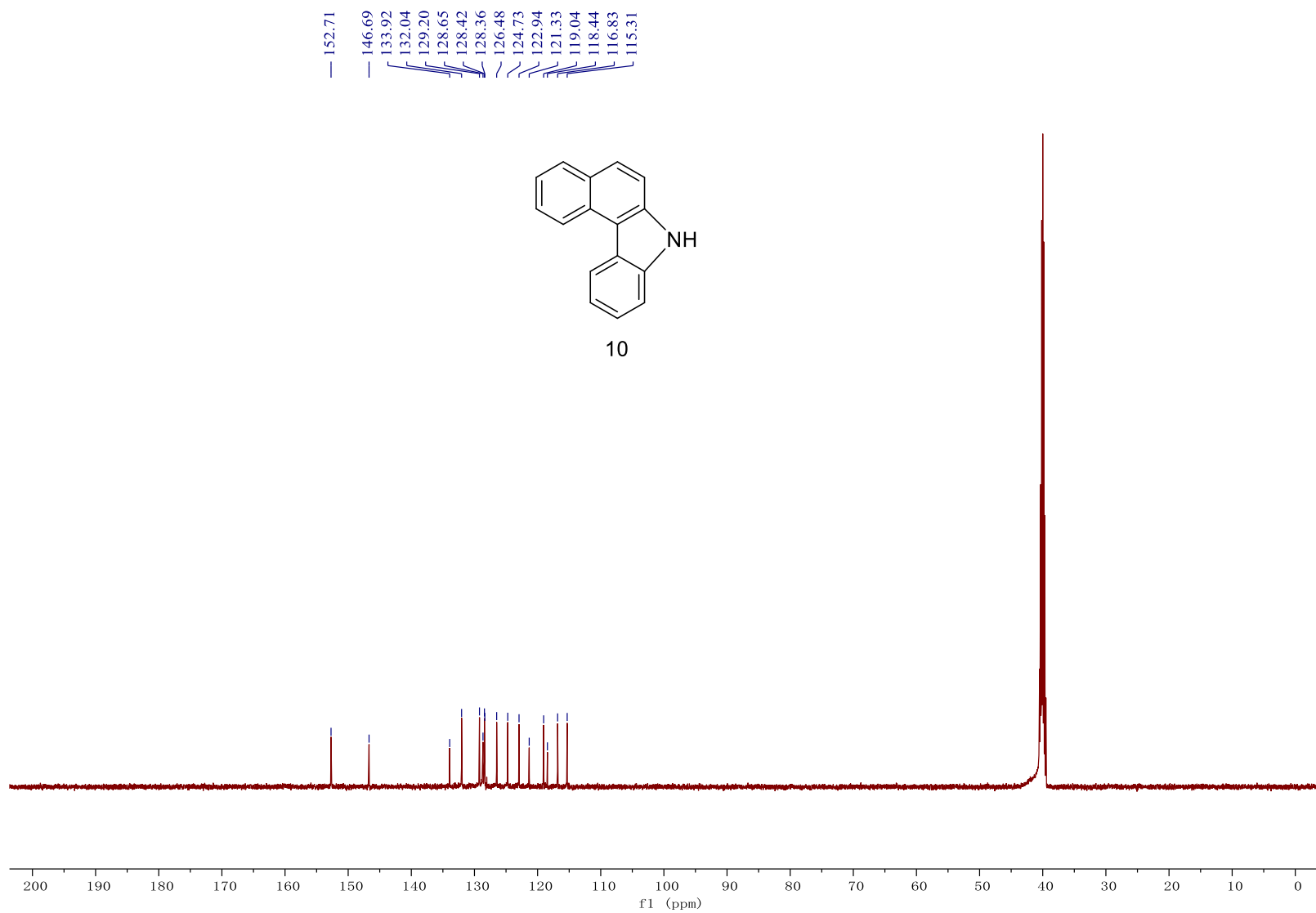
S181



S182



S183



S184