Supporting Information

Convenient Synthesis of N-alkyl-3,1-Benzoxazin-2-ones from Carbamate Protected Anthranil Aldehydes and Ketones via One-step Alkylation/Alkoxy Rearrangement

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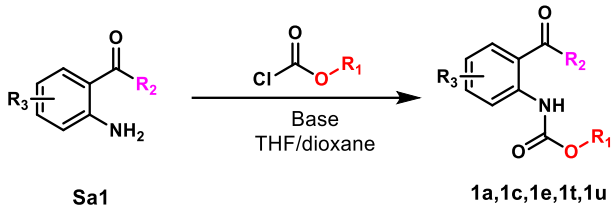
General information.

All moisture and oxygen sensitive reactions were performed in flame-dried glassware under a slight argon overpressure. All reactions were stirred magnetically. Sensitive solutions, solvents or reagents were transferred via cannula or syringe. Reactions were monitored by thin-layer chromatography (TLC) or NMR of the crude mixture. Evaporations were conducted under reduced pressure at temperatures less than 40 °C, unless otherwise noted. Further dryings of the residues were accomplished using a high vacuum pump. All solvents were purchased as the highest available grade from Sinopharm Chemical, Damas-beta, Macklin, General Reagent. All other reagents were used as received from Energy Chemical, Sinopharm Chemical, Accela, Bidepharm, Macklin, 3Achem, unless otherwise noted. Thin-layer chromatography was carried out on pre-coated Leyan HPTLC Silica Gel 60 GF254 to monitor all reactions. The detection of spots was first performed by using a UV (254 nm) lamp followed by visualization by an iodine based TLC stain. Preparative column chromatography was performed with silica gel from SiliaFlash (0.040-0.063 μm, 240-400 mesh). All NMR spectra were measured on Bruker Avance III 400, Avance III 500, Avance III 600 and Avance III 800. Chemical shifts are given in ppm and referenced to the solvent residual peaks (Chloroform-*d* ^{1}H, δ = 7.26 ppm, ^{13}C, δ = 77.16 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant *J*, integration. High-resolution mass spectra were measured on Agilent 1290/6545 UHPLC-QTOF/MS. Melting points were recorded on a SGWX-4A melting point apparatus (Shanghai instrument physical optics instrument Co., LTD.) and are uncorrected.

Synthesis of Carbamate Substrates

Method A

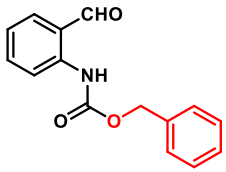


Sa1 **1a,1c,1e,1t,1u**

To a solution of the arylamine in THF or dioxane, base and chlorofomate was added at 0 ℃. The resulting mixture was stirred at room temperature overnight. The reaction was diluted with brine and extracted with EtOAc for three times. The combined organic layers were dried with anhydrous Na_2SO_4, evaporated under reduced pressure, and purified by flash column chromatography to afford the desired carbamate products **1a**, **1c**, **1e**, **1t**, **1u**.

Compound 1a

Benzyl (2-formylphenyl) carbamate



Following the Method A on 15.0 mmol scale with anthranilaldehyde, $NaHCO_3$ (16.5 mmol, 1.1 equiv) and benzyl chlorofomate (16.5 mmol, 1.1 equiv) in THF. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 2.59 g (68%) of the title compound **1a**.[1]

Physical State: white solid.

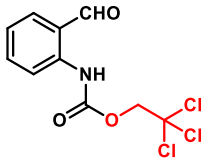
m.p.: 66 - 68 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 10.68 (s, 1H), 9.90 (s, 1H), 8.48 (d, *J* = 8.5 Hz, 1H), 7.64 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.46 – 7.42 (m, 2H), 7.41 – 7.32 (m, 3H), 7.21 – 7.15 (m, 1H), 5.24 (s, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 195.2, 153.6, 141.3, 136.2, 136.1, 128.7, 128.5, 128.4, 122.2, 121.5, 118.5, 67.2.

Compound 1c

2,2,2-Trichloroethyl (2-formylphenyl) carbamate



Following the Method A on 2.0 mmol scale with anthranilaldehyde, *N*-ethyldiisopropylamine (2.0 mmol, 1.0 equiv) and 2,2,2-richloroethylchloroformate (3.0 mmol, 1.5 equiv) in THF. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 480 mg (81%) of the title compound **1c**.

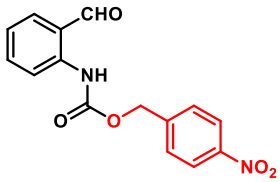
Physical State: white solid.

m.p.: 75 - 77 ℃.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 10.85 (s, 1H), 9.93 (s, 1H), 8.43 (d, *J* = 8.5 Hz, 1H), 7.69 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.26 – 7.21 (m, 1H), 4.85 (s, 2H).
^{13}C NMR (151 MHz, Chloroform-*d*): δ 195.3, 151.9, 140.5, 136.22, 136.18, 122.9, 121.8, 118.7, 95.2, 74.6.
HRMS (ESI-TOF): calculated for $C_{10}H_9Cl_3NO_3^+$ $[M+H]^+$: 295.9643; found: 295.9645.

Compound 1e

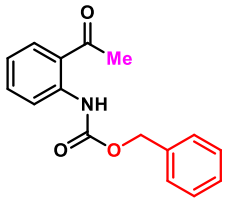
4-Nitrobenzyl (2-formylphenyl) carbamate



Following the Method A on 10.0 mmol scale with anthranilaldehyde, K_2CO_3 (20.0 mmol, 2.0 equiv) and *p*-nitrobenzyl chlorofomate (15.0 mmol, 1.5 equiv) in THF. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 2.10 g (70%) of the title compound **1e**.
Physical State: pale yellow solid.
m.p.: 138 - 140 °C.
^{1}H NMR (500 MHz, Chloroform-*d*): δ 10.79 (s, 1H), 9.92 (s, 1H), 8.43 (d, *J* = 8.5 Hz, 1H), 8.26 – 8.21 (m, 2H), 7.67 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.63 – 7.56 (m, 3H), 7.24 – 7.18 (m, 1H), 5.31 (s, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*): δ 195.4, 153.1, 147.9, 143.4, 140.9, 136.24, 136.22, 128.5, 124.0, 122.6, 121.6, 118.5, 65.6.
HRMS (ESI-TOF): calculated for $C_{15}H_{11}N_2O_5^-$ $[M-H]^-$: 299.0673; found: 299.0674.

Compound 1t

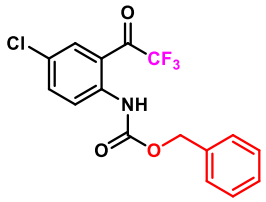
Benzyl (2-acetylphenyl) carbamate



Following the Method A on 10.0 mmol scale with *o*-acetylaniline, saturated $NaHCO_3$ (20 mL) and benzyl chloroformate (10.0 mmol, 1.0 equiv) in dioxane. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 1.84 g (68%) of the title compound **1t**.[2]
Physical State: pale yellow solid.
m.p.: 85 - 87 °C.
^{1}H NMR (500 MHz, Chloroform-*d*): δ 11.27 (s, 1H), 8.50 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.58 – 7.50 (m, 1H), 7.45 – 7.31 (m, 5H), 7.06 (t, *J* = 7.6 Hz, 1H), 5.22 (s, 2H), 2.64 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*): δ 202.4, 153.8, 141.4, 136.3, 135.1, 131.8, 128.7, 128.3, 121.65, 121.58, 119.4, 67.0, 28.6.
HRMS (ESI-TOF): calculated for $C_{16}H_{15}NNaO_3^+$ $[M+Na]^+$: 292.0944; found: 292.0945.

Compound 1u

Benzyl (4-chloro-2-(2,2,2-trifluoroacetyl)phenyl) carbamate



Following the Method A on 5.0 mmol scale with 4-chloro-2-(trifluoroacetyl)aniline•HCl, saturated $NaHCO_3$ (10 mL) and benzyl chloroformate (5.0 mmol, 1.0 equiv) in dioxane. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 1.10 g (62%) of the title compound **1u**.

Physical State: yellow solid.

m.p.: 91 - 93 ℃.

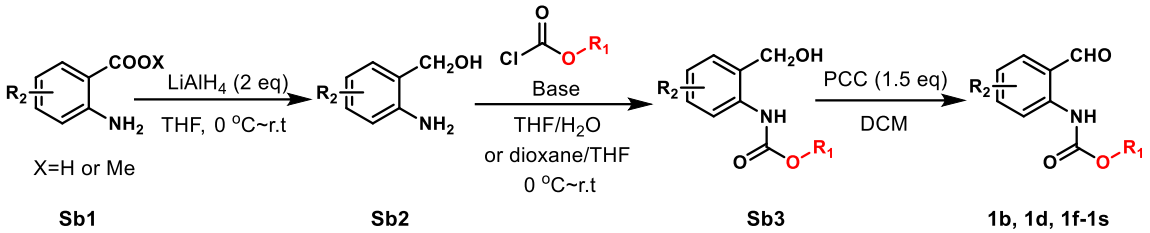
^{1}H NMR (500 MHz, Chloroform-*d*): δ 10.44 (s, 1H), 8.61 (d, *J* = 9.2 Hz, 1H), 7.91 – 7.86 (m, 1H), 7.63 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.46 – 7.33 (m, 5H), 5.24 (s, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 182.2 (q, *J* = 35.1 Hz), 153.2, 142.5, 137.5, 135.5, 131.0 (q, *J* = 4.4 Hz), 128.8, 128.7, 128.5, 127.3, 121.4, 116.4 (q, *J* = 291.8 Hz), 115.9, 67.75.

^{19}F NMR (753 MHz, Chloroform-*d*): δ -69.6.

HRMS (ESI-TOF): calculated for $C_{16}H_{10}ClF_3NO_3^-$ [M-H]$^-$: 356.0307; found: 356.0307.

Method B



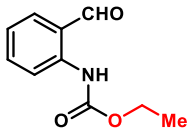
The following protocols were applied according to previously reported procedures. [3,4] To a solution of methyl 2-aminoarylate or 2-amino aromatic acid **Sb1** (5.0 mmol, 1.0 equiv) in dry THF (15 mL) was added $LiAlH_4$ (0.40 g, 10.0 mmol, 2.0 equiv) in portions while the temperature was maintained at 0 ℃. The obtained mixture was warmed to room temperature and stirred for 2 hours. After completion as indicated by TLC, the mixture was quenched by addition of brine (15 ml) and 5% aqueous NaOH (5.0 ml). The suspension was filtered and the precipitate washed with EtOAc. The filtrate was evaporated to afford **Sb2**, which was directly used in the next step without further purification.

To a solution of **Sb2** in dioxane/K_2CO_3-H_2O or THF/saturated $NaHCO_3$ (10 mL/10 mL), chloroformate was added dropwise at 0 ℃. The resulting mixture was stirred at room temperature overnight. The reaction was diluted with brine (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to afford **Sb3**, which was directly used in the next step without further purification.

To a solution of crude **Sb3** in CH_2Cl_2 (25 mL) was added PCC (1.61 g, 7.5 mmol, 1.5 equiv) and silica gel (10 g). The reaction mixture was stirred at room temperature for 4 hours. Solvent was evaporated under reduced pressure and the residue was purified by column chromatography to afford the desired products **1b, 1d, 1f-1s**.

Compound 1b

Ethyl (2-formylphenyl) carbamate



Following the Method B on 5.0 mmol scale with methyl anthranilate, K_2CO_3 (50.0 mmol, 10.0 equiv) in dioxane/H_2O and ethyl chloroformate (6.0 mmol, 1.2 equiv). Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 411 mg (43%) of the title compound **1b**.

Physical State: white solid.

m.p.: 72 - 74 ℃.

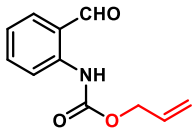
^{1}H NMR (500 MHz, Chloroform-*d*): δ 10.57 (s, 1H), 9.91 (s, 1H), 8.47 (d, *J* = 8.5 Hz, 1H), 7.64 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 195.2, 153.9, 141.5, 136.2, 122.0, 121.4, 118.4, 61.6, 14.6.

HRMS (ESI-TOF): calculated for $C_{10}H_{12}NO_3^+$ $[M+H]^+$: 194.0812; found: 194.0812.

Compound 1d

Allyl (2-formylphenyl) carbamate



Following the Method B on 2.0 mmol scale with methyl anthranilate, K_2CO_3 (20.0 mmol, 10.0 equiv) in dioxane/H_2O and allyl chloroformate (2.4 mmol, 1.2 equiv). Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 223 mg (47%) of the title compound **1d**.[5]

Physical State: white solid.

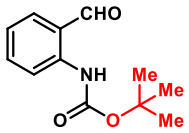
m.p.: 72 - 73 °C.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 10.65 (s, 1H), 9.91 (s, 1H), 8.46 (d, *J* = 8.5 Hz, 1H), 7.65 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.63 – 7.57 (m, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 6.04 – 5.95 (m, 1H), 5.43 – 5.35 (m, 1H), 5.31 – 5.25 (m, 1H), 4.69 (d, *J* = 5.7 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 195.2, 153.5, 141.3, 136.2, 132.4, 122.1, 121.5, 118.51, 118.47, 66.1.

Compound 1f

Tert-butyl (2-formylphenyl) carbamate



Following the Method B on 10.0 mmol scale with methyl anthranilate, K_2CO_3 (100.0 mmol, 10.0 equiv) in dioxane/H_2O and di-*tert*-butyl dicarbonate (12.0 mmol, 1.2 equiv). Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 1.07 g (48%) of the title compound **1f**.[6]

Physical State: white solid.

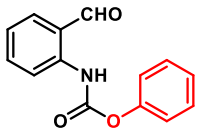
m.p.: 60 - 61 °C.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 10.39 (s, 1H), 9.90 (s, 1H), 8.46 (d, *J* = 8.5 Hz, 1H), 7.62 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 1.54 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 195.2, 153.0, 141.9, 136.2, 136.1, 121.6, 121.3, 118.4, 81.1, 28.4.

Compound 1g

Phenyl (2-formylphenyl)carbamate



Following the Method B on 10.0 mmol scale with methyl anthranilate, saturated $NaHCO_3$ (20 mL) and phenyl chloroformate (10.0 mmol, 1.0 equiv). Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 1.12 g (46%) of the title compound **1g**.[7]

Physical State: white solid.

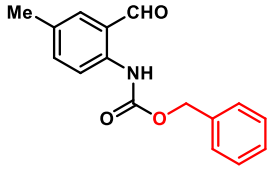
m.p.: 74 - 76 °C.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 10.93 (s, 1H), 9.90 (s, 1H), 8.43 (d, *J* = 8.5 Hz, 1H), 7.64 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.39 – 7.33 (m, 2H), 7.23 – 7.15 (m, 4H).

^{13}C NMR (151 MHz, Chloroform-*d*): δ 195.3, 152.0, 150.5, 140.8, 136.3, 136.2, 129.5, 125.9, 122.6, 121.7, 118.6.

Compound 1h

Benzyl (2-formyl-4-methylphenyl) carbamate



Following the Method B on 5.0 mmol scale with 2-amino-5-methylbenzoic, saturated $NaHCO_3$ (10 mL) and benzyl chloroformate (5.0 mmol, 1.0 equiv). Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 1.12 g (83%) of the title compound **1h**.

Physical State: white solid.

m.p.: 78 - 79 ℃.

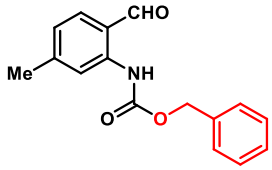
^{1}H NMR (800 MHz, Chloroform-*d*): δ 10.55 (s, 1H), 9.86 (s, 1H), 8.36 (d, *J* = 8.5 Hz, 1H), 7.45 – 7.37 (m, 6H), 7.36 – 7.32 (m, 1H), 5.22 (s, 2H), 2.37 (s, 3H).

^{13}C NMR (201 MHz, Chloroform-*d*): δ 195.2, 153.7, 138.9, 137.0, 136.2, 136.1, 131.7, 128.7, 128.4, 121.5, 118.5, 67.1, 20.5.

HRMS (ESI-TOF): calculated for $C_{16}H_{15}NNaO_3^+$ $[M+Na]^+$: 292.0944; found: 292.0944.

Compound 1i

Benzyl (2-formyl-5-methylphenyl)carbamate



Following the Method B on 5.0 mmol scale with 2-amino-4-methylbenzoic, saturated $NaHCO_3$ (10 mL) and benzyl chloroformate (5.0 mmol, 1.0 equiv). Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 1.03 g (77%) of the title compound **1i**.

Physical State: pale yellow solid.

m.p.: 61 - 63 ℃.

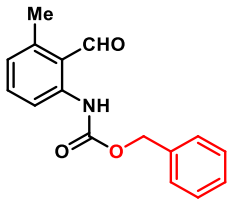
^{1}H NMR (600 MHz, Chloroform-*d*): δ 10.70 (s, 1H), 9.82 (s, 1H), 8.31 (s, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.45 – 7.32 (m, 5H), 6.99 – 6.95 (m, 1H), 5.23 (s, 2H), 2.42 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*): δ 194.5, 153.6, 147.8, 141.2, 136.2, 136.1, 128.7, 128.40, 128.36, 123.2, 119.5, 118.8, 67.1, 22.6.

HRMS (ESI-TOF): calculated for $C_{16}H_{15}NNaO_3^+$ $[M+Na]^+$: 292.0944; found: 292.0942.

Compound 1j

Benzyl (2-formyl-3-methylphenyl)carbamate



Following the Method B on 5.0 mmol scale with 2-amino-6-methylbenzoic, saturated $NaHCO_3$ (10 mL) and benzyl chloroformate (5.0 mmol, 1.0 equiv). Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 890 mg (66%) of the title compound **1j**.

Physical State: pale yellow solid.

m.p.: 58 - 60 ℃.

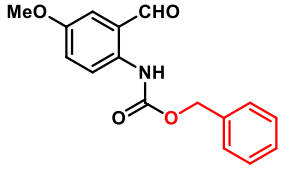
^{1}H NMR (500 MHz, Chloroform-*d*): δ 11.19 (s, 1H), 10.43 (s, 1H), 8.34 (d, *J* = 8.6 Hz, 1H), 7.48 – 7.31 (m, 6H), 6.88 (d, *J* = 7.5 Hz, 1H), 5.22 (s, 2H), 2.65 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 194.1, 153.8, 143.3, 142.2, 136.4, 136.2, 128.7, 128.4, 125.0, 119.1, 117.1, 67.1, 19.3.

HRMS (ESI-TOF): calculated for $C_{16}H_{15}NNaO_3^+$ $[M+Na]^+$: 292.0944; found: 292.0943.

Compound 1k

Benzyl (2-formyl-4-methoxyphenyl)carbamate



Following the Method B on 5.0 mmol scale with 2-amino-5-methoxybenzoic, saturated $NaHCO_3$ (10 mL) and benzyl chloroformate (5.0 mmol, 1.0 equiv). Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 1.06 g (74%) of the title compound **1k**.

Physical State: pale yellow solid.

m.p.: 65 - 67 ℃.

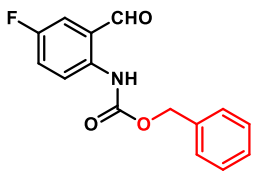
^{1}H NMR (800 MHz, Chloroform-*d*): δ 10.38 (s, 1H), 9.86 (s, 1H), 8.41 (d, *J* = 9.1 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.45 – 7.41 (m, 2H), 7.36 – 7.32 (m, 1H), 7.17 (dd, *J* = 9.2, 3.0 Hz, 1H), 7.12 (d, *J* = 3.1 Hz, 1H), 5.22 (s, 2H), 3.84 (s, 3H).

^{13}C NMR (201 MHz, Chloroform-*d*): δ 194.7, 154.5, 153.7, 136.1, 134.8, 128.6, 128.3, 128.3, 122.5, 122.1, 120.1, 119.3, 67.0, 55.8.

HRMS (ESI-TOF): calculated for $C_{16}H_{15}NNaO_4^+$ $[M+Na]^+$: 308.0893; found: 308.0894.

Compound 1l

Benzyl (4-fluoro-2-formylphenyl) carbamate



Following the Method B on 5.0 mmol scale with 2-amino-5-fluorobenzoic, saturated $NaHCO_3$ (10 mL) and benzyl chloroformate (5.0 mmol, 1.0 equiv). Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 974 mg (71%) of the title compound **1l**.

Physical State: pale yellow solid.

m.p.: 101 - 103 ℃.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 10.49 (s, 1H), 9.84 (s, 1H), 8.50 (dd, *J* = 9.0, 4.6 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.41 – 7.37 (m, 2H), 7.36 – 7.30 (m, 3H), 5.23 (s, 2H).

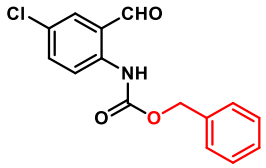
^{13}C NMR (151 MHz, Chloroform-*d*): δ 193.7, 157.3 (d, *J* = 243.9 Hz), 153.5, 137.5 (d, *J* = 2.1 Hz), 135.8, 128.6, 128.4, 128.3, 123.3 (d, *J* = 22.1 Hz), 122.0 (d, *J* = 5.3 Hz), 120.9 (d, *J* = 22.4 Hz), 120.5 (d, *J* = 6.7 Hz), 67.2.

^{19}F NMR (471 MHz, Chloroform-*d*): δ -120.4.

HRMS (ESI-TOF): calculated for $C_{15}H_{11}FNO_3^-$ $[M-H]^-$: 272.0728; found: 272.0725.

Compound 1m

Benzyl (4-chloro-2-formylphenyl) carbamate



Following the Method B on 5.0 mmol scale with 2-amino-5-chlorobenzoic, saturated $NaHCO_3$ (10 mL) and benzyl chloroformate (5.0 mmol, 1.0 equiv). Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 1.20 g (83%) of the title compound **1m**.

Physical State: yellow solid.

m.p.: 127 - 129 ℃.

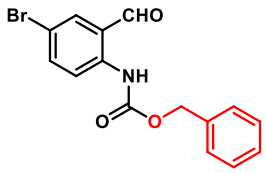
^{1}H NMR (600 MHz, Chloroform-*d*): δ 10.56 (s, 1H), 9.83 (s, 1H), 8.47 (d, *J* = 9.0 Hz, 1H), 7.60 (d, *J* = 2.5 Hz, 1H), 7.54 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.45 – 7.32 (m, 5H), 5.23 (s, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*): δ 193.9, 153.5, 139.8, 136.0, 135.8, 135.1, 128.8, 128.6, 128.5, 127.3, 122.4, 120.3, 67.4.

HRMS (ESI-TOF): calculated for $C_{15}H_{12}ClNO_3Na^+$ $[M+Na]^+$: 312.0398; found: 312.0399.

Compound 1n

Benzyl (4-bromo-2-formylphenyl) carbamate



Following the Method B on 5.0 mmol scale with 2-amino-5-bromobenzoic, saturated $NaHCO_3$ (10 mL) and benzyl chloroformate (5.0 mmol, 1.0 equiv). Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 1.04 g (62%) of the title compound **1n**.

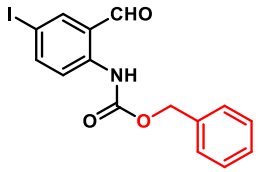
Physical State: yellow solid.

m.p.: 125 - 127 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 10.56 (s, 1H), 9.83 (s, 1H), 8.42 (d, *J* = 9.0 Hz, 1H), 7.75 (d, *J* = 2.4 Hz, 1H), 7.68 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.45 – 7.33 (m, 5H), 5.23 (s, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*): δ 193.9, 153.4, 140.3, 138.8, 138.1, 135.8, 128.8, 128.6, 128.5, 122.8, 120.5, 114.3, 67.5.
HRMS (ESI-TOF): calculated for $C_{15}H_{11}BrNO_3^-$ [M-H]$^-$: 331.9928; found: 331.9924.

Compound 1o

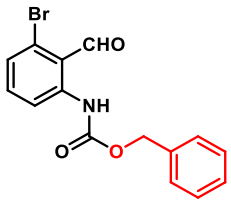
Benzyl (4-iodo-2-formylphenyl) carbamate



Following the Method B on 5.0 mmol scale with 2-amino-5-iodobenzoic, saturated $NaHCO_3$ (10 mL) and benzyl chloroformate (5.0 mmol, 1.0 equiv). Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 750 mg (39%) of the title compound **1o**.
Physical State: white solid.
m.p.: 124 - 125 ℃.
^{1}H NMR (500 MHz, Chloroform-*d*): δ 10.56 (s, 1H), 9.81 (s, 1H), 8.29 (d, *J* = 8.9 Hz, 1H), 7.92 (d, *J* = 2.1 Hz, 1H), 7.85 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.43 – 7.34 (m, 5H), 5.22 (s, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*): δ 193.9, 153.4, 144.5, 144.2, 140.9, 135.8, 128.8, 128.6, 128.5, 123.3, 120.7, 83.8, 67.5.
HRMS (ESI-TOF): calculated for $C_{15}H_{12}INO_3Na^+$ [M+Na]$^+$: 403.9754; found: 403.9755.

Compound 1p

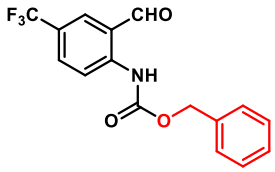
Benzyl (3-bromo-2-formylphenyl)carbamate



Following the Method B on 5.0 mmol scale with 2-amino-6-bromobenzoic, saturated $NaHCO_3$ (10 mL) and benzyl chloroformate (5.0 mmol, 1.0 equiv). Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 655 mg (39%) of the title compound **1p**.
Physical State: pale yellow solid.
m.p.: 82 - 83 ℃.
^{1}H NMR (500 MHz, Chloroform-*d*): δ 11.15 (s, 1H), 10.46 (s, 1H), 8.48 (d, *J* = 8.5 Hz, 1H), 7.45 – 7.29 (m, 7H), 5.23 (s, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*): δ 196.6, 153.4, 143.6, 136.7, 135.9, 129.9, 128.7, 128.54, 128.47, 127.4, 118.5, 117.9, 67.4.
HRMS (ESI-TOF): calculated for $C_{15}H_{11}BrNO_3^-$ [M-H]$^-$: 331.9928; found: 331.9927.

Compound 1q

Benzyl (2-formyl-4-(trifluoromethyl)phenyl)carbamate



Following the Method B on 2.0 mmol scale with 2-amino-5-(trifluoromethyl)benzoic, saturated $NaHCO_3$ (4 mL) and benzyl chloroformate (2.0 mmol, 1.0 equiv). Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 268 mg (41%) of the title compound **1q**.

Physical State: white solid.

m.p.: 135 - 137 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 10.80 (s, 1H), 9.95 (s, 1H), 8.65 (d, *J* = 8.9 Hz, 1H), 7.91 (s, 1H), 7.82 (dd, *J* = 8.9, 1.9 Hz, 1H), 7.46 – 7.34 (m, 5H), 5.25 (s, 2H).

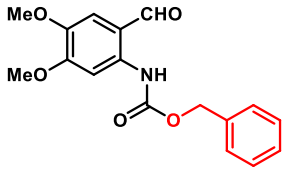
^{13}C NMR (126 MHz, Chloroform-*d*): δ 194.2, 153.4, 144.0, 135.6, 133.0 (q, *J* = 3.2 Hz), 132.6 (q, *J* = 2.8 Hz), 128.8, 128.7, 128.6, 124.4 (q, *J* = 33.9 Hz), 123.6 (q, *J* = 272.0 Hz), 120.8, 119.0, 67.7.

^{19}F NMR (753 MHz, Chloroform-*d*): δ -62.3.

HRMS (ESI-TOF): calculated for $C_{16}H_{11}F_3NO_3^-$ $[M-H]^-$: 322.0697; found: 322.0695.

Compound 1r

Benzyl (2-formyl-4,5-dimethoxyphenyl)carbamate



Following the Method B on 5.0 mmol scale with 2-amino-4,5-dimethoxybenzoic, saturated $NaHCO_3$ (10 mL) and benzyl chloroformate (5.0 mmol, 1.0 equiv). Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 546 mg (35%) of the title compound **1r**.

Physical State: dark yellow solid.

m.p.: 116 - 118 ℃.

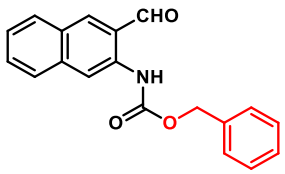
^{1}H NMR (500 MHz, Chloroform-*d*): δ 10.86 (s, 1H), 9.73 (s, 1H), 8.15 (s, 1H), 7.45 – 7.32 (m, 5H), 7.02 (s, 1H), 5.22 (s, 2H), 3.99 (s, 3H), 3.91 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 192.9, 155.7, 153.9, 144.1, 137.9, 136.0, 128.7, 128.5, 128.3, 116.5, 114.3, 101.7, 67.1, 56.5, 56.4.

HRMS (ESI-TOF): calculated for $C_{17}H_{17}NO_5Na^+$ $[M+Na]^+$: 338.0999; found: 338.0997.

Compound 1s

Benzyl (3-formylnaphthalen-2-yl)carbamate



Following the Method B on 5.0 mmol scale with 2-amino-3-naphthoic, saturated $NaHCO_3$ (10 mL) and benzyl chloroformate (5.0 mmol, 1.0 equiv). Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 930 mg (61%) of the title compound **1s**.

Physical State: yellow solid.

m.p.: 147 - 149 ℃.

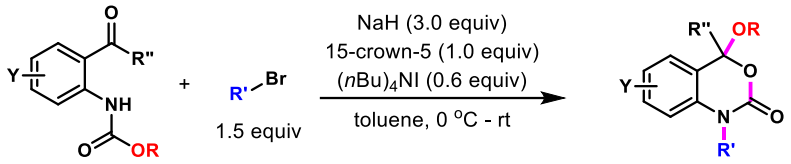
^{1}H NMR (500 MHz, Chloroform-*d*): δ 10.47 (s, 1H), 10.06 (s, 1H), 8.80 (s, 1H), 8.19 (s, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.48 – 7.32 (m, 6H), 5.27 (s, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 195.2, 153.9, 140.3, 137.3, 136.3, 135.9, 130.5, 129.1, 128.7, 128.4, 127.9, 125.7, 122.8, 115.5, 67.2.

HRMS (ESI-TOF): calculated for $C_{19}H_{15}NaNO_3^+$ $[M+Na]^+$: 328.0944; found: 328.0944.

Synthesis of and Characterization of *N*-alkyl-3,1-Benzoxazin-2-ones

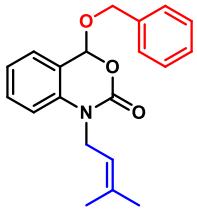
General Procedure



To a 30 mL flask equipped with a stir bar were added NaH (60% dispersion in mineral oil, 36 mg, 0.9 mmol, 3.0 equiv) and (nBu)$_4$NI (66 mg, 0.18 mmol, 0.6 equiv). The flask was evacuated and backfilled with argon for three times. A solution of (2-formylaryl) carbamate (0.3 mmol, 1.0 equiv) and 15-crown-5 (66 μL, 0.3 mmol, 1.0 equiv) in toluene (2 mL) was added at 0 ℃ followed by a solution of alkylation reagent (0.45 mmol, 1.5 equiv) in toluene (2 mL). The reaction was stirred at 0 ℃ for 1 hour and additional 2 hours at room temperature, before quenched with saturated NH_4Cl (5 ml) and saturated NaCl (5 ml). The mixture was extracted with EtOAc (10 mL × 3). The organic layers were then combined, dried over anhydrous Na_2SO_4, evaporated and purified by flash column chromatography to afford the desired product.

Compound 3a

4-(Benzyloxy)-1-(3-methylbut-2-en-1-yl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1a** and 0.45 mmol scale with 3,3-dimethylallyl bromide. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 78 mg (80%) of the title compound **3a**.

Physical State: pale yellow solid.

m.p.: 88 - 90 ℃.

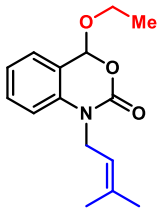
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.44 – 7.29 (m, 6H), 7.18 (dd, J = 7.5, 1.5 Hz, 1H), 7.15 – 7.06 (m, 1H), 6.95 (d, J = 8.3 Hz, 1H), 6.05 (s, 1H), 5.27 – 5.17 (m, 1H), 5.02 (d, J = 12.0 Hz, 1H), 4.86 (d, J = 12.0 Hz, 1H), 4.63 (dd, J = 16.1, 5.7 Hz, 1H), 4.50 (dd, J = 16.2, 6.4 Hz, 1H), 1.82 (s, 3H), 1.74 (d, J = 1.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 150.5, 136.8, 136.5, 136.0, 130.4, 128.7, 128.4, 128.3, 126.1, 122.9, 120.3, 119.3, 114.0, 97.7, 70.1, 43.1, 25.7, 18.3.

HRMS (ESI-TOF): calculated for $C_{20}H_{21}NO_3Na^+$ $[M+Na]^+$: 346.1414; found: 346.1412.

Compound 3b

4-Ethoxy-1-(3-methylbut-2-en-1-yl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1b** and 0.45 mmol scale with 3,3-dimethylallyl bromide. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 53 mg (68%) of the title compound **3b**.

Physical State: Colorless oil.

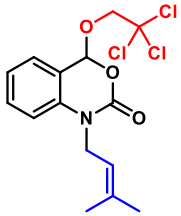
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.40 – 7.34 (m, 1H), 7.25 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.01 (s, 1H), 5.25 – 5.17 (m, 1H), 4.61 (dd, *J* = 16.2, 5.7 Hz, 1H), 4.48 (dd, *J* = 16.2, 6.3 Hz, 1H), 4.15 – 4.07 (m, 1H), 3.84 – 3.77 (m, 1H), 1.81 (s, 3H), 1.74 – 1.71 (d, *J* = 0.8 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 150.7, 136.7, 136.0, 130.4, 126.1, 123.0, 120.6, 119.4, 114.0, 99.3, 64.9, 43.1, 25.7, 18.3, 15.2.

HRMS (ESI-TOF): calculated for $C_{15}H_{20}NO_3^+$ $[M+H]^+$: 262.1438; found: 262.1441.

Compound 3c

1-(3-Methylbut-2-en-1-yl)-4-(2,2,2-trichloroethoxy)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1c** and 0.45 mmol scale with 3,3-dimethylallyl bromide. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 70 mg (64%) of the title compound **3c**.

Physical State: Colorless oil.

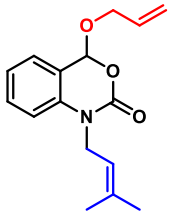
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.45 – 7.40 (m, 1H), 7.37 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.33 (s, 1H), 5.25 – 5.17 (m, 1H), 4.62 (dd, *J* = 16.2, 5.9 Hz, 1H), 4.55 – 4.43 (m, 3H), 1.81 (s, 3H), 1.73 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 149.7, 136.7, 136.5, 131.1, 126.7, 123.3, 119.0, 118.9, 114.2, 99.6, 96.3, 79.7, 43.3, 25.8, 18.4.

HRMS (ESI-TOF): calculated for $C_{15}H_{17}NCl_3O_3^+$ $[M+H]^+$: 364.0269; found: 364.0270.

Compound 3d

4-(Allyloxy)-1-(3-methylbut-2-en-1-yl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1d** and 0.45 mmol scale with 3,3-dimethylallyl bromide. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 54 mg (66%) of the title compound **3d**.

Physical State: Colorless oil.

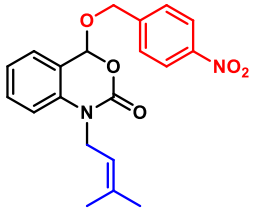
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.40 – 7.34 (m, 1H), 7.24 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.15 – 7.06 (m, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.04 (s, 1H), 6.02 – 5.87 (m, 1H), 5.36 (dd, *J* = 17.2, 1.5 Hz, 1H), 5.27 (dd, *J* = 10.4, 1.3 Hz, 1H), 5.24 – 5.17 (m, 1H), 4.61 (dd, *J* = 16.1, 5.7 Hz, 1H), 4.52 – 4.44 (m, 2H), 4.33 (dd, *J* = 12.8, 6.6 Hz, 1H), 1.80 (s, 3H), 1.73 (d, *J* = 1.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 150.6, 136.8, 136.1, 133.3, 130.5, 126.2, 123.0, 120.3, 119.4, 118.9, 114.0, 98.2, 69.5, 43.1, 25.7, 18.3.

HRMS (ESI-TOF): calculated for $C_{16}H_{20}NO_3^+$ $[M+H]^+$: 274.1438; found: 274.1437.

Compound 3e

1-(3-Methylbut-2-en-1-yl)-4-((4-nitrobenzyl)oxy)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1e** and 0.45 mmol scale with 3,3-dimethylallyl bromide. Purification by flash column chromatography (silica, 5:1 PE:EtOAc) afforded 63 mg (57%) of the title compound **3e**.

Physical State: yellow solid.

m.p.: 92 - 94 ℃.

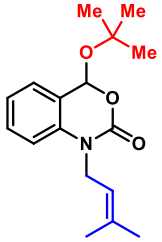
^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.45 – 7.38 (m, 1H), 7.24 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.13 (t, *J* = 7.3 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.08 (s, 1H), 5.24 – 5.18 (m, 1H), 5.13 (d, *J* = 12.9 Hz, 1H), 4.93 (d, *J* = 12.9 Hz, 1H), 4.61 (dd, *J* = 16.2, 5.8 Hz, 1H), 4.51 (dd, *J* = 16.2, 6.4 Hz, 1H), 1.81 (s, 3H), 1.73 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 150.2, 147.8, 144.2, 136.8, 136.4, 130.9, 128.4, 126.2, 123.9, 123.2, 119.7, 119.1, 114.2, 98.5, 68.9, 43.2, 25.8, 18.4.

HRMS (ESI-TOF): calculated for $C_{20}H_{21}N_2O_5^+$ $[M+H]^+$: 369.1445; found: 369.1443.

Compound 3f

4-(Tert-butoxy)-1-(3-methylbut-2-en-1-yl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1f** and 0.45 mmol scale with 3,3-dimethylallyl bromide. Without (nBu)$_4$NI and 15-Crown-5, the mixture was in toluene at 50 ℃ for 3 hours.

Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 42 mg (48%) of the title compound **3f**.

Physical State: Colorless oil.

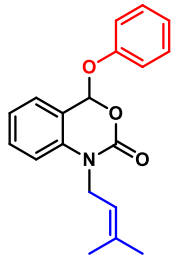
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.36 – 7.31 (m, 1H), 7.16 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.11 – 7.05 (m, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.25 (s, 1H), 5.25 – 5.17 (m, 1H), 4.59 (dd, *J* = 16.1, 5.9 Hz, 1H), 4.48 (dd, *J* = 16.1, 6.2 Hz, 1H), 1.80 (s, 3H), 1.73 (d, *J* = 1.2 Hz, 3H), 1.40 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 151.1, 136.9, 135.9, 129.9, 125.6, 122.8, 121.8, 119.6, 114.0, 94.4, 77.4, 43.0, 29.0, 25.7, 18.3.

HRMS (ESI-TOF): calculated for $C_{17}H_{23}NO_3Na^+$ $[M+Na]^+$: 312.1570; found: 312.1573.

Compound 3g

1-(3-Methylbut-2-en-1-yl)-4-phenoxy-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1g** and 0.45 mmol scale with 3,3-dimethylallyl bromide. Purification by flash column chromatography (silica, 20:1 PE:EtOAc) afforded 57 mg (61%) of the title compound **3g**.

Physical State: pale yellow solid.

m.p.: 108 - 110 °C.

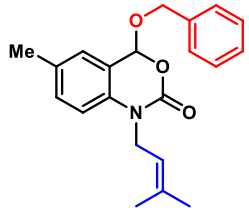
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.49 – 7.41 (m, 1H), 7.38 – 7.30 (m, 3H), 7.22 – 7.08 (m, 4H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.60 (s, 1H), 5.27 – 5.18 (m, 1H), 4.62 (dd, *J* = 16.1, 5.7 Hz, 1H), 4.53 (dd, *J* = 16.2, 6.4 Hz, 1H), 1.82 (s, 3H), 1.74 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 156.4, 149.9, 136.9, 136.4, 131.0, 129.9, 126.5, 123.7, 123.2, 119.4, 119.2, 117.9, 114.2, 97.8, 43.2, 25.7, 18.4.

HRMS (ESI-TOF): calculated for $C_{19}H_{20}NO_3^+$ $[M+H]^+$: 310.1438; found: 310.1437.

Compound 6a

4-(Benzyloxy)-6-methyl-1-(3-methylbut-2-en-1-yl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1h** and 0.45 mmol scale with 3,3-dimethylallyl bromide. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 80 mg (79%) of the title compound **6a**.

Physical State: pale yellow oil.

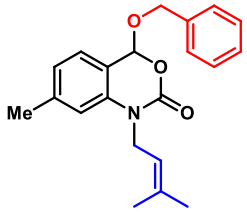
^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.41 – 7.29 (m, 5H), 7.19 – 7.12 (m, 1H), 6.96 (d, *J* = 1.5 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 5.99 (s, 1H), 5.19 (s, 1H), 5.00 (d, *J* = 11.9 Hz, 1H), 4.83 (d, *J* = 11.9 Hz, 1H), 4.58 (dd, *J* = 16.2, 5.7 Hz, 1H), 4.47 (dd, *J* = 16.1, 6.3 Hz, 1H), 2.30 (s, 3H), 1.79 (s, 3H), 1.71 (d, *J* = 1.1 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*): δ 150.6, 136.6, 135.9, 134.4, 132.7, 131.0, 128.7, 128.5, 128.3, 126.6, 120.1, 119.5, 113.9, 97.8, 70.0, 43.0, 25.7, 20.6, 18.3.

HRMS (ESI-TOF): calculated for $C_{21}H_{24}NO_3^+$ $[M+H]^+$: 338.1751; found: 338.1752.

Compound 6b

4-(Benzyloxy)-7-methyl-1-(3-methylbut-2-en-1-yl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1i** and 0.45 mmol scale with 3,3-dimethylallyl bromide. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 81 mg (80%) of the title compound **6b**.

Physical State: Colorless oil.

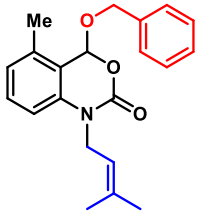
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.43 – 7.28 (m, 5H), 7.06 (d, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.75 (s, 1H), 6.02 (s, 1H), 5.22 (t, *J* = 6.1 Hz, 1H), 5.00 (d, *J* = 12.0 Hz, 1H), 4.84 (d, *J* = 12.0 Hz, 1H), 4.61 (dd, *J* = 16.1, 5.8 Hz, 1H), 4.48 (dd, *J* = 16.1, 6.4 Hz, 1H), 2.37 (s, 3H), 1.83 (s, 3H), 1.74 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 150.7, 140.7, 136.71, 136.67, 136.0, 128.7, 128.4, 128.2, 126.0, 123.7, 119.4, 117.5, 114.6, 97.8, 70.0, 43.0, 25.7, 22.0, 18.3.

HRMS (ESI-TOF): calculated for $C_{21}H_{24}NO_3^+$ $[M+H]^+$: 338.1751; found: 338.1750.

Compound 6c

4-(Benzyloxy)-5-methyl-1-(3-methylbut-2-en-1-yl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1j** and 0.45 mmol scale with 3,3-dimethylallyl bromide. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 91 mg (90%) of the title compound **6c**.

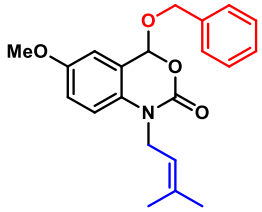
Physical State: Colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.44 – 7.30 (m, 5H), 7.24 (t, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 6.11 (s, 1H), 5.21 (t, *J* = 6.0 Hz, 1H), 4.99 (d, *J* = 11.6 Hz, 1H), 4.84 (d, *J* = 11.6 Hz, 1H), 4.62 (dd, *J* = 16.2, 5.5 Hz, 1H), 4.47 (dd, *J* = 16.2, 6.4 Hz, 1H), 2.11 (s, 3H), 1.80 (s, 3H), 1.72 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 150.6, 137.0, 136.2, 135.9, 135.5, 130.2, 129.1, 128.7, 128.5, 125.1, 119.6, 118.7, 112.0, 95.6, 70.1, 43.3, 25.7, 18.3, 17.5.
HRMS (ESI-TOF): calculated for $C_{21}H_{24}NO_3^+$ $[M+H]^+$: 338.1751; found: 338.1749.

Compound 6d

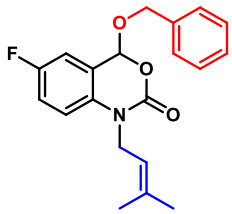
4-(Benzyloxy)-6-methoxy-1-(3-methylbut-2-en-1-yl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1k** and 0.45 mmol scale with 3,3-dimethylallyl bromide. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 74 mg (70%) of the title compound **6d**.
Physical State: pale yellow oil.
^{1}H NMR (800 MHz, Chloroform-*d*): δ 7.41 – 7.35 (m, 4H), 7.32 (t, *J* = 7.1 Hz, 1H), 6.91 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.71 (d, *J* = 2.6 Hz, 1H), 5.99 (s, 1H), 5.20 (s, 1H), 5.01 (d, *J* = 11.9 Hz, 1H), 4.84 (d, *J* = 11.9 Hz, 1H), 4.57 (dd, *J* = 16.2, 5.4 Hz, 1H), 4.48 (dd, *J* = 16.2, 6.2 Hz, 1H), 3.77 (s, 3H), 1.80 (s, 3H), 1.72 (s, 3H).
^{13}C NMR (201 MHz, Chloroform-*d*): δ 155.4, 150.4, 136.5, 135.9, 130.2, 128.6, 128.4, 128.3, 121.3, 119.4, 115.8, 115.1, 111.5, 97.5, 70.0, 55.7, 43.0, 25.6, 18.2.
HRMS (ESI-TOF): calculated for $C_{21}H_{24}NO_4^+$ $[M+H]^+$: 354.1700; found: 354.1698.

Compound 6e

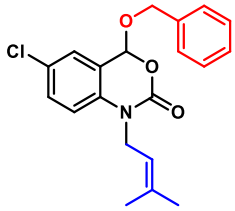
4-(Benzyloxy)-6-fluoro-1-(3-methylbut-2-en-1-yl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1l** and 0.45 mmol scale with 3,3-dimethylallyl bromide. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 70 mg (68%) of the title compound **6e**.
Physical State: Colorless oil.
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.45 – 7.31 (m, 5H), 7.11 – 7.03 (m, 1H), 6.92 – 6.87 (m, 2H), 5.98 (s, 1H), 5.19 (t, *J* = 6.0 Hz, 1H), 5.01 (d, *J* = 11.9 Hz, 1H), 4.84 (d, *J* = 11.9 Hz, 1H), 4.59 (dd, *J* = 16.2, 5.6 Hz, 1H), 4.48 (dd, *J* = 16.2, 6.3 Hz, 1H), 1.80 (s, 3H), 1.73 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*): δ 158.5 (d, *J* = 244.2 Hz), 150.2, 136.5, 136.2, 133.1 (d, *J* = 2.2 Hz), 128.8, 128.5 (d, *J* = 5.4 Hz), 121.8 (d, *J* = 7.4 Hz), 119.1, 117.3, 117.1, 115.5 (d, *J* = 7.8 Hz), 113.1(d, *J* = 24.1 Hz), 96.9, 70.3, 43.3, 25.7, 18.3.
^{19}F NMR (471 MHz, Chloroform-*d*): δ -119.8.
HRMS (ESI-TOF): calculated for $C_{20}H_{21}FNO_3^+$ $[M+H]^+$: 342.1500; found: 342.1502.

Compound 6f

4-(Benzyloxy)-6-chloro-1-(3-methylbut-2-en-1-yl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.1 mmol scale with **1m** and 0.15 mmol scale with 3,3-dimethylallyl bromide. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 22 mg (62%) of the title compound **6f**.

Physical State: yellow oil.

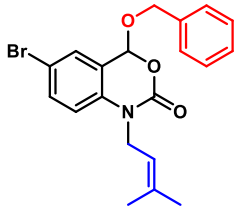
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.43 – 7.29 (m, 6H), 7.14 (d, *J* = 2.3 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 5.98 (s, 1H), 5.17 (t, *J* = 6.1 Hz, 1H), 5.01 (d, *J* = 11.8 Hz, 1H), 4.84 (d, *J* = 11.8 Hz, 1H), 4.59 (dd, *J* = 16.2, 5.7 Hz, 1H), 4.47 (dd, *J* = 16.2, 6.3 Hz, 1H), 1.80 (s, 3H), 1.73 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 150.2, 136.6, 136.2, 135.5, 130.4, 128.9, 128.62, 128.56, 128.3, 126.2, 121.9, 118.9, 115.5, 97.0, 70.4, 43.3, 25.7, 18.4.

HRMS (ESI-TOF): calculated for $C_{20}H_{21}ClNO_3^+$ $[M+H]^+$: 358.1204; found: 358.1202.

Compound 6g

4-(Benzyloxy)-6-bromo-1-(3-methylbut-2-en-1-yl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.1 mmol scale with **1n** and 0.15 mmol scale with 3,3-dimethylallyl bromide. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 25 mg (62%) of the title compound **6g**.

Physical State: yellow oil.

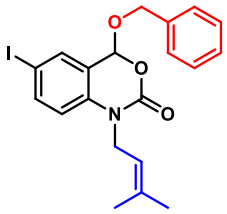
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.47 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.40 – 7.32 (m, 5H), 7.28 (d, *J* = 2.2 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 1H), 5.98 (s, 1H), 5.17 (t, *J* = 6.1 Hz, 1H), 5.01 (d, *J* = 11.8 Hz, 1H), 4.83 (d, *J* = 11.8 Hz, 1H), 4.58 (dd, *J* = 16.2, 5.7 Hz, 1H), 4.47 (dd, *J* = 16.2, 6.3 Hz, 1H), 1.79 (s, 3H), 1.72 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 150.1, 136.7, 136.2, 136.0, 133.4, 129.0, 128.8, 128.63, 128.56, 122.2, 118.9, 115.9, 115.6, 96.9, 70.4, 43.3, 25.7, 18.4.

HRMS (ESI-TOF): calculated for $C_{20}H_{21}BrNO_3^+$ $[M+H]^+$: 402.0699; found: 402.0692.

Compound 6h

4-(Benzyloxy)-6-iodo-1-(3-methylbut-2-en-1-yl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure D on 0.3 mmol scale with **1o** and 0.45 mmol scale with 3,3-dimethylallyl bromide. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 86 mg (64%) of the title compound **6h**.

Physical State: pale yellow oil.

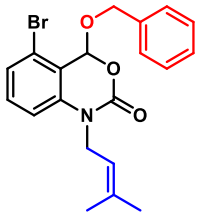
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.65 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.45 (d, *J* = 1.9 Hz, 1H), 7.41 – 7.32 (m, 5H), 6.70 (d, *J* = 8.7 Hz, 1H), 5.97 (s, 1H), 5.16 (t, *J* = 6.1 Hz, 1H), 5.01 (d, *J* = 11.8 Hz, 1H), 4.83 (d, *J* = 11.8 Hz, 1H), 4.57 (dd, *J* = 16.2, 5.7 Hz, 1H), 4.46 (dd, *J* = 16.2, 6.3 Hz, 1H), 1.79 (s, 3H), 1.72 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 150.1, 139.2, 136.7, 136.6, 136.1, 134.8, 128.8, 128.6, 128.5, 122.5, 118.8, 116.1, 96.7, 85.4, 70.3, 43.2, 25.7, 18.4.

HRMS (ESI-TOF): calculated for $C_{20}H_{21}INO_3^+$ $[M+H]^+$: 450.0561; found: 450.0563.

Compound 6i

4-(Benzyloxy)-5-bromo-1-(3-methylbut-2-en-1-yl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1p** and 0.45 mmol scale with 3,3-dimethylallyl bromide. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 88 mg (73%) of the title compound **6i**.

Physical State: white solid.

m.p.: 81 - 83 ℃.

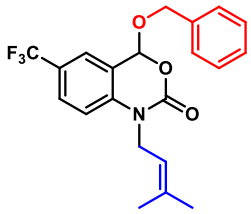
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.45 – 7.41 (m, 2H), 7.38 – 7.29 (m, 3H), 7.28 – 7.22 (m, 1H), 7.21 (t, *J* = 8.1 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.24 (s, 1H), 5.17 (t, *J* = 6.1 Hz, 1H), 5.04 (d, *J* = 11.2 Hz, 1H), 4.86 (d, *J* = 11.2 Hz, 1H), 4.61 (dd, *J* = 16.2, 5.6 Hz, 1H), 4.44 (dd, *J* = 16.2, 6.5 Hz, 1H), 1.79 (s, 3H), 1.73 – 1.70 (d, *J* = 1.0 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 150.3, 138.6, 136.5, 136.0, 131.4, 129.0, 128.6, 128.5, 127.0, 121.6, 120.1, 119.0, 113.4, 98.1, 71.2, 43.5, 25.7, 18.3.

HRMS (ESI-TOF): calculated for $C_{20}H_{21}BrNO_3^+$ $[M+H]^+$: 402.0699; found: 402.0700.

Compound 6j

4-(Benzyloxy)-1-(3-methylbut-2-en-1-yl)-6-(trifluoromethyl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1q** and 0.45 mmol scale with 3,3-dimethylallyl bromide. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 65 mg (55%) of the title compound **6j**.

Physical State: white solid.

m.p.: 78 - 80 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.63 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.42 (d, *J* = 1.6 Hz, 1H), 7.41 – 7.32 (m, 5H), 7.03 (d, *J* = 8.6 Hz, 1H), 6.08 (s, 1H), 5.18 (t, *J* = 6.2 Hz, 1H), 5.04 (d, *J* = 11.7 Hz, 1H), 4.86 (d, *J* = 11.7 Hz, 1H), 4.64 (dd, *J* = 16.2, 5.8 Hz, 1H), 4.52 (dd, *J* = 16.2, 6.4 Hz, 1H), 1.82 (s, 3H), 1.75 – 1.72 (d, *J* = 1.1 Hz, 3H).

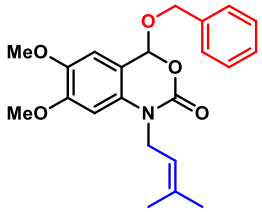
^{13}C NMR (126 MHz, Chloroform-*d*): δ 150.1, 139.8, 137.0, 136.0, 128.9, 128.65, 128.63, 127.8 (q, *J* = 3.6 Hz), 125.2 (q, *J* = 33.4 Hz), 123.9 (q, *J* = 272.1 Hz), 123.6 (q, *J* = 3.7 Hz), 120.7, 118.6, 114.3, 97.2, 70.5, 43.4, 25.7, 18.4.

^{19}F NMR (753 MHz, Chloroform-*d*): δ -62.0.

HRMS (ESI-TOF): calculated for $C_{21}H_{21}F_3NO_3^+$ $[M+H]^+$: 392.1468; found: 392.1467.

Compound 6k

4-(Benzyloxy)-6,7-dimethoxy-1-(3-methylbut-2-en-1-yl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1r** and 0.45 mmol scale with 3,3-dimethylallyl bromide. Purification by flash column chromatography (silica, 3:1 PE:EtOAc) afforded 52 mg (45%) of the title compound **6k**.

Physical State: yellow oil.

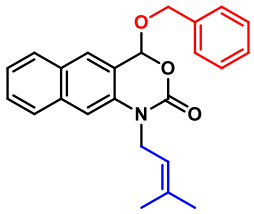
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.41 – 7.29 (m, 5H), 6.64 (s, 1H), 6.51 (s, 1H), 5.99 (s, 1H), 5.23 (t, *J* = 6.2 Hz, 1H), 5.00 (d, *J* = 11.8 Hz, 1H), 4.82 (d, *J* = 11.8 Hz, 1H), 4.60 (dd, *J* = 16.2, 5.7 Hz, 1H), 4.49 (dd, *J* = 16.2, 6.7 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 1.82 (s, 3H), 1.74 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 150.7, 150.6, 145.0, 136.7, 135.8, 130.9, 128.7, 128.5, 128.3, 119.8, 111.8, 109.2, 99.0, 97.9, 70.0, 56.5, 56.2, 43.3, 25.7, 18.3.

HRMS (ESI-TOF): calculated for $C_{22}H_{26}NO_5^+$ $[M+H]^+$: 384.1805; found: 384.1806.

Compound 6l

4-(Benzyloxy)-1-(3-methylbut-2-en-1-yl)-1,4-dihydro-2H-naphtho[2,3-d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1s** and 0.45 mmol scale with 3,3-dimethylallyl bromide. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 95 mg (85%) of the title compound **6l**.

Physical State: yellow oil.

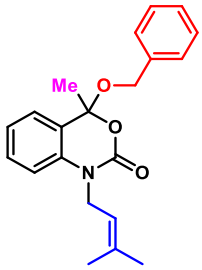
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.81 – 7.73 (m, 2H), 7.66 (s, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.45 – 7.32 (m, 6H), 7.26 (s, 1H), 6.19 (s, 1H), 5.31 (t, *J* = 5.8 Hz, 1H), 5.07 (d, *J* = 11.9 Hz, 1H), 4.91 (d, *J* = 11.9 Hz, 1H), 4.72 (dd, *J* = 16.1, 5.7 Hz, 1H), 4.62 (dd, *J* = 16.1, 6.3 Hz, 1H), 1.89 (s, 3H), 1.76 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 150.6, 136.5, 136.3, 134.31, 134.27, 129.3, 128.7, 128.5, 128.4, 128.0, 127.6, 127.5, 125.9, 125.3, 121.3, 119.2, 110.5, 97.8, 70.3, 43.5, 25.8, 18.4.

HRMS (ESI-TOF): calculated for $C_{24}H_{24}NO_3^+$ $[M+H]^+$: 374.1751; found: 374.1751.

Compound 6m

4-(Benzyloxy)-7-methyl-1-(3-methylbut-2-en-1-yl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1t** and 0.45 mmol scale with 3,3-dimethylallyl bromide. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 50 mg (49%) of the title compound **6m**.

Physical State: pale yellow oil.

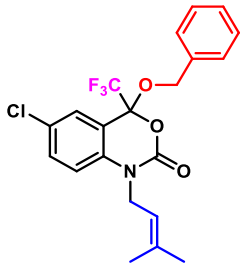
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.40 – 7.27 (m, 7H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 5.21 (t, *J* = 6.0 Hz, 1H), 4.67 (d, *J* = 11.0 Hz, 1H), 4.62 – 4.54 (m, 3H), 1.92 (s, 3H), 1.83 (s, 3H), 1.74 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 150.8, 137.4, 136.6, 136.2, 130.3, 128.5, 128.1, 127.9, 125.1, 123.8, 123.2, 119.4, 114.1, 104.2, 65.6, 42.9, 26.6, 25.8, 18.4.

HRMS (ESI-TOF): calculated for $C_{21}H_{24}NO_3^+$ $[M+H]^+$: 338.1751; found: 338.1754.

Compound 6n

4-(Benzyloxy)-7-methyl-1-(3-methylbut-2-en-1-yl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure D on 0.3 mmol scale with **1u** and 0.45 mmol scale with 3,3-dimethylallyl bromide. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 46 mg (36%) of the title compound **6n**.

Physical State: yellow oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.50 – 7.44 (m, 2H), 7.41 – 7.31 (m, 5H), 6.93 (d, *J* = 8.8 Hz, 1H), 5.16 – 5.09 (m, 1H), 4.79 (d, *J* = 11.0 Hz, 1H), 4.63 – 4.50 (m, 3H), 1.82 (s, 3H), 1.78 – 1.73 (d, *J* = 1.1 Hz, 3H).

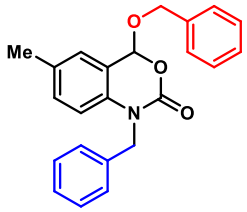
^{13}C NMR (126 MHz, Chloroform-*d*): δ 147.9, 137.7, 136.8, 135.5, 132.6, 129.2, 128.8, 128.5, 128.1, 127.5, 121.4 (q, *J* = 288.5 Hz), 117.9, 115.9, 115.7, 99.90 (q, *J* = 34.6 Hz), 67.00, 43.36, 25.78, 18.43.

^{19}F NMR (753 MHz, Chloroform-*d*): δ -83.9.

HRMS (ESI-TOF): calculated for $C_{21}H_{20}ClF_3NO_3^+$ $[M+H]^+$: 426.1078; found: 426.1081.

Compound 7a

1-Benzyl-4-(benzyloxy)-6-methyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1h** and 0.45 mmol scale with (bromomethyl)benzene. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 86 mg (80%) of the title compound **7a**.

Physical State: colorless oil.

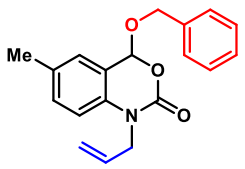
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.44 – 7.30 (m, 5H), 7.28 – 7.19 (m, 5H), 7.05 – 7.01 (m, 1H), 6.98 (s, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.07 (s, 1H), 5.25 – 5.14 (m, 2H), 5.07 (d, *J* = 11.7 Hz, 1H), 4.88 (d, *J* = 11.7 Hz, 1H), 2.26 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 151.1, 136.5, 136.2, 134.2, 133.0, 131.1, 128.9, 128.7, 128.6, 128.4, 127.4, 126.6, 126.4, 120.3, 114.4, 98.1, 70.2, 47.9, 20.6.

HRMS (ESI-TOF): calculated for $C_{23}H_{22}NO_3^+$ $[M+H]^+$: 360.1594; found: 360.1592.

Compound 7b

1-Allyl-4-(benzyloxy)-6-methyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1h** and 0.45 mmol scale with 3-Bromopropene. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 48 mg (52%) of the title compound **7a**.

Physical State: pale yellow oil.

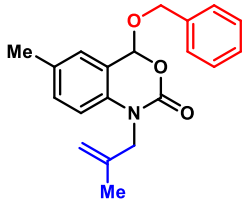
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.43 – 7.31 (m, 5H), 7.18 – 7.13 (m, 1H), 6.98 (s, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.02 (s, 1H), 5.98 – 5.86 (m, 1H), 5.27 – 5.19 (m, 2H), 5.02 (d, *J* = 11.9 Hz, 1H), 4.86 (d, *J* = 11.7 Hz, 1H), 4.70 – 4.63 (m, 1H), 4.52 – 4.44 (m, 1H), 2.31 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 150.5, 136.5, 134.3, 132.9, 131.8, 131.1, 128.7, 128.6, 128.4, 126.6, 120.1, 117.1, 114.2, 98.0, 70.2, 46.8, 20.7.

HRMS (ESI-TOF): calculated for $C_{19}H_{20}NO_3^+$ $[M+H]^+$: 310.1438; found: 310.1438.

Compound 7c

4-(Benzyloxy)-6-methyl-1-(2-methylallyl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1h** and 0.45 mmol scale with 3-bromo-2-methylpropene. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 52 mg (54%) of the title compound **7c**.

Physical State: yellow oil.

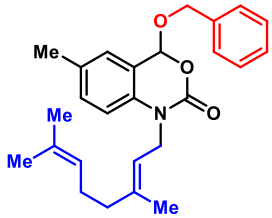
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.43 – 7.30 (m, 5H), 7.17 – 7.12 (m, 1H), 6.98 (s, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.03 (s, 1H), 5.03 (d, *J* = 11.8 Hz, 1H), 4.93 – 4.89 (m, 1H), 4.86 (d, *J* = 11.8 Hz, 1H), 4.81 (s, 1H), 4.55 – 4.44 (m, 2H), 2.31 (s, 3H), 1.78 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 150.7, 139.0, 136.5, 134.3, 132.9, 131.0, 128.7, 128.6, 128.3, 126.5, 120.1, 114.4, 111.6, 98.0, 70.2, 49.7, 20.7, 20.0.

HRMS (ESI-TOF): calculated for $C_{20}H_{21}NO_3Na^+$ $[M+Na]^+$: 346.1414; found: 346.1414.

Compound 7d

(E)-4-(benzyloxy)-1-(3,7-dimethylocta-2,6-dien-1-yl)-6-methyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1h** and 0.45 mmol scale with geranyl bromide. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 68 mg (56%) of the title compound **7d**.

Physical State: colorless oil..

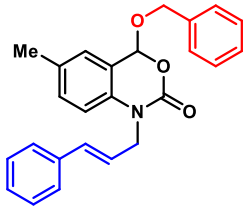
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.43 – 7.29 (m, 5H), 7.15 (d, *J* = 8.3 Hz, 1H), 6.97 (s, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 6.01 (s, 1H), 5.19 (t, *J* = 5.5 Hz, 1H), 5.07 – 4.98 (m, 2H), 4.85 (d, *J* = 11.9 Hz, 1H), 4.62 (dd, *J* = 16.2, 5.5 Hz, 1H), 4.49 (dd, *J* = 16.2, 6.3 Hz, 1H), 2.31 (s, 3H), 2.11 – 2.04 (m, 2H), 2.04 – 1.98 (m, 2H), 1.79 (s, 3H), 1.63 (s, 3H), 1.57 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 150.6, 139.3, 136.6, 134.4, 132.7, 131.8, 131.0, 128.7, 128.6, 128.3, 126.6, 123.9, 120.2, 119.5, 114.0, 97.8, 70.1, 43.1, 39.5, 26.4, 25.8, 20.7, 17.8, 16.7.

HRMS (ESI-TOF): calculated for $C_{26}H_{32}NO_3^+$ $[M+H]^+$: 406.2377; found: 406.2378.

Compound 7e

4-(Benzyloxy)-1-cinnamyl-6-methyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1h** and 0.45 mmol scale with Cinnamyl bromide. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 67 mg (58%) of the title compound **7e**.

Physical State: yellow oil.

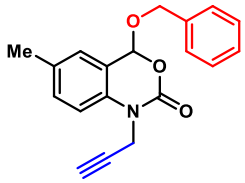
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.36 – 7.16 (m, 9H), 7.15 – 7.10 (m, 1H), 7.07 (d, *J* = 8.3 Hz, 1H), 6.93 – 6.89 (m, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.50 (d, *J* = 16.1 Hz, 1H), 6.24 – 6.15 (m, 1H), 5.97 (s, 1H), 4.97 (d, *J* = 11.8 Hz, 1H), 4.79 (d, *J* = 11.8 Hz, 1H), 4.77 – 4.70 (m, 1H), 4.60 – 4.52 (m, 1H), 2.23 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 150.6, 136.5, 136.4, 134.4, 133.0, 132.4, 131.2, 128.8, 128.6, 128.6, 128.4, 127.8, 126.63, 126.57, 123.4, 120.2, 114.1, 98.1, 70.2, 46.5, 20.7.

HRMS (ESI-TOF): calculated for $C_{25}H_{24}NO_3^+$ $[M+H]^+$: 386.1751; found: 386.1751.

Compound 7f

4-(Benzyloxy)-6-methyl-1-(prop-2-yn-1-yl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1h** and 0.45 mmol scale with propargyl bromide. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 51 mg (55%) of the title compound **7f**.

Physical State: pale yellow oil.

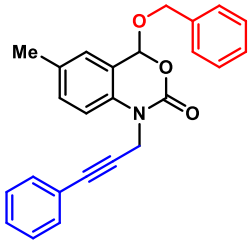
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.42 – 7.31 (m, 5H), 7.25 – 7.22 (m, 1H), 7.10 (d, *J* = 8.3 Hz, 1H), 7.00 (s, 1H), 6.03 (s, 1H), 5.01 (d, *J* = 11.9 Hz, 1H), 4.91 – 4.82 (m, 2H), 4.50 (dd, *J* = 17.8, 2.4 Hz, 1H), 2.33 (s, 3H), 2.29 (t, *J* = 2.4 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 150.2, 136.4, 133.5, 133.3, 131.2, 128.8, 128.6, 128.4, 126.6, 120.0, 113.9, 98.1, 77.8, 73.1, 70.3, 34.4, 20.7.

HRMS (ESI-TOF): calculated for $C_{19}H_{18}NO_3^+$ $[M+H]^+$: 308.1281; found: 308.1277.

Compound 7g

4-(Benzyloxy)-6-methyl-1-(3-phenylprop-2-yn-1-yl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1h** and 0.45 mmol scale with (3-bromoprop-1-yn-1-yl)benzene. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 53 mg (46%) of the title compound **7g**.

Physical State: yellow oil.

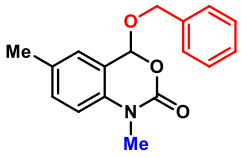
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.43 – 7.35 (m, 6H), 7.35 – 7.27 (m, 3H), 7.26 – 7.18 (m, 3H), 7.00 (s, 1H), 6.05 (s, 1H), 5.10 (d, *J* = 17.9 Hz, 1H), 5.02 (d, *J* = 11.9 Hz, 1H), 4.86 (d, *J* = 11.9 Hz, 1H), 4.71 (d, *J* = 17.9 Hz, 1H), 2.33 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 150.3, 136.4, 133.8, 133.2, 132.0, 131.2, 128.8, 128.64, 128.58, 128.4, 128.3, 126.6, 122.5, 120.0, 114.1, 98.1, 84.7, 83.2, 70.3, 35.3, 20.7.

HRMS (ESI-TOF): calculated for $C_{25}H_{21}NO_3Na^+$ $[M+Na]^+$: 406.1414; found: 406.1416.

Compound 7h

4-(Benzyloxy)-1,6-dimethyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one



Following the General Procedure on 0.3 mmol scale with **1h** and 0.45 mmol scale with methyl iodide and without $(n\text{Bu})_4\text{NI}$. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 62 mg (73%) of the title compound **7h**.

Physical State: white solid.

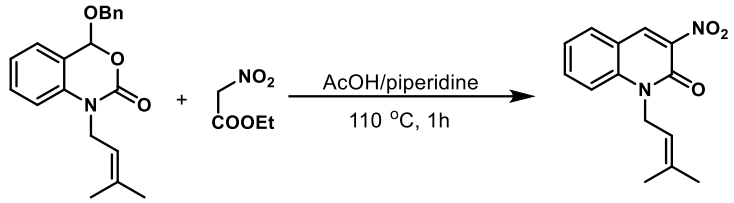
m.p.: 78 - 80 °C.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.42 – 7.30 (m, 5H), 7.22 – 7.18 (m, 1H), 6.98 (s, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.02 (s, 1H), 5.01 (d, *J* = 11.9 Hz, 1H), 4.85 (d, *J* = 11.9 Hz, 1H), 3.41 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 150.9, 136.5, 135.1, 132.9, 131.1, 128.7, 128.6, 128.4, 126.5, 119.9, 113.4, 97.9, 70.2, 31.5, 20.7.

HRMS (ESI-TOF): calculated for $C_{17}H_{17}NO_3Na^+$ $[M+Na]^+$: 306.1101; found: 306.1102.

Experimental Procedures for the Product Diversification

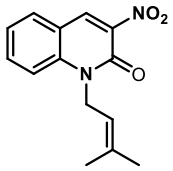


3a 9

To a 30 mL flask equipped with a stir bar were added compound **3a** (65 mg, 0.2 mmol, 1.0 equiv), ethyl nitroacetate (60 μL, 0.4 mmol, 2.0 equiv), acetic acid (2 mL) and piperidine (0.68 mL). The mixture was stirred at 110 ℃ for 1 hour. After cooling to room temperature, the crude mixture was directly purified by flash column chromatography (silica, 10:1 PE:EtOAc) to afford product **9** (45 mg, 87%).

Compound 9

1-(3-Methylbut-2-en-1-yl)-3-nitroquinolin-2(1H)-one

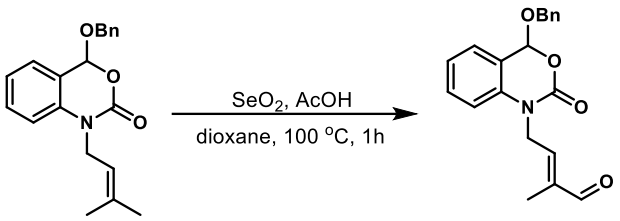


Physical State: yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.50 (s, 1H), 7.77 – 7.71 (m, 2H), 7.43 – 7.33 (m, 2H), 5.20 – 5.12 (m, 1H), 5.00 (d, *J* = 6.2 Hz, 2H), 1.92 (s, 3H), 1.74 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 154.1, 140.8, 139.9, 137.9, 136.8, 134.5, 131.5, 123.6, 117.9, 117.4, 115.3, 42.0, 25.8, 18.6.

HRMS (ESI-TOF): calculated for $C_{14}H_{14}N_2O_3Na^+$ $[M+Na]^+$: 281.0897; found: 281.0899.

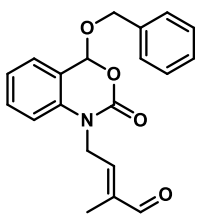


3a 10

To a 30 mL flask equipped with a stir bar were added compound **3a** (65 mg, 0.2 mmol, 1.0 equiv), SeO_2 (89 mg, 0.8 mmol, 4.0 equiv), acetic acid (46 μL, 0.8 mmol, 4.0 equiv) and dioxane (4 mL). The mixture was stirred at 100 ℃ for 1 hour. After cooling to room temperature, the crude mixture was directly purified by flash column chromatography (silica, 5:1 PE:EtOAc) to afford product **10** (40 mg, 59%), the alkene configuration of which was determined to be E by NOESY spectra analysis.

Compound 10

(E)-4-(4-(benzyloxy)-2-oxo-2H-benzo[d][1,3]oxazin-1(4H)-yl)-2-methylbut-2-enal



Physical State: pale yellow solid.

m.p.: 124 - 126 °C.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 9.41 (s, 1H), 7.41 – 7.36 (m, 5H), 7.37 – 7.31 (m, 1H), 7.22 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.16 – 7.12 (m, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 6.47 – 6.43 (m, 1H), 6.09 (s, 1H), 5.03 (d, *J* = 11.9 Hz, 1H), 4.94 (dd, *J* = 18.5, 5.9 Hz, 1H), 4.88 (d, *J* = 11.9 Hz, 1H), 4.83 (dd, *J* = 18.4, 6.3 Hz, 1H), 1.92 (d, *J* = 1.0 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*): δ 194.0, 150.6, 147.5, 141.0, 136.30, 136.27, 130.8, 128.8, 128.6, 128.5, 126.6, 123.7, 120.5, 113.3, 98.0, 70.5, 43.2, 9.7.

HRMS (ESI-TOF): calculated for $C_{20}H_{19}NNaO_4^+$ $[M+Na]^+$: 360.1206; found: 360.1204.

X-Ray Crystallographic Data for Compound 3a

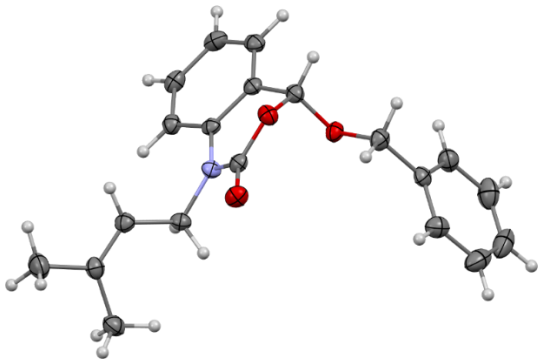


Table 1 Crystal data and structure refinement for **3a**

Identification code	CCDC 2258994
Empirical formula	$C_{20}H_{21}NO_3$
Formula weight	323.38
Temperature/K	100.0
Crystal system	orthorhombic
Space group	Pbca
a/Å	11.1141(4)
b/Å	14.4848(6)
c/Å	20.8204(8)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3351.8(2)
Z	8
ρ_{calc}g/cm^3	1.282
μ/mm^{-1}	0.086
F(000)	1376.0
Crystal size/mm^3	0.15 × 0.08 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.362 to 52.784
Index ranges	-13 ≤ h ≤ 13, -16 ≤ k ≤ 18, -26 ≤ l ≤ 26
Reflections collected	24220
Independent reflections	3416 [R_{int} = 0.0586, R_{sigma} = 0.0341]
Data/restraints/parameters	3416/0/219
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0401, wR_2 = 0.0880
Final R indexes [all data]	R_1 = 0.0631, wR_2 = 0.1033
Largest diff. peak/hole / e Å^{-3}	0.19/-0.22

Table 2 Fractional Atomic Coordinates (nem^4) and Equivalent Isotropic Displacement Parameters (Å^2× a^3) for 3a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O2	3725.6(9)	6775.4(7)	4546.4(5)	22.9(3)
O1	4031.7(9)	7391.7(7)	5565.0(5)	23.9(3)
O3	5997.5(10)	7404.4(8)	5760.1(5)	28.2(3)
N1	5037.0(11)	6014.4(9)	5754.7(6)	20.8(3)
C8	3204.3(14)	6897.4(11)	5152.1(7)	22.9(3)
C9	2959.7(13)	5970.6(11)	5431.7(7)	21.0(3)
C14	3933.7(13)	5529.0(11)	5724.9(7)	20.2(3)
C13	3796.6(14)	4640.5(11)	5969.1(7)	23.3(3)
C16	6176.3(14)	5524.2(11)	5874.2(7)	22.9(3)
C6	4371.2(14)	7417.9(11)	3547.7(8)	23.6(3)
C15	5091.1(14)	6950.6(11)	5692.3(7)	21.8(3)
C17	6575.2(14)	5569.8(11)	6564.3(7)	24.3(4)
C19	7678.5(14)	5381.9(11)	6769.9(7)	25.3(4)
C10	1854.2(14)	5529.7(11)	5388.3(7)	25.3(4)
C12	2688.1(15)	4208.3(11)	5913.0(7)	26.2(4)
C11	1713.8(15)	4642.3(12)	5628.4(8)	27.7(4)
C7	3932.4(15)	7636.4(11)	4212.1(8)	26.3(4)
C1	5482.8(15)	7725.4(12)	3335.1(9)	31.2(4)
C18	8682.6(15)	5090.3(12)	6330.8(8)	30.9(4)
C5	3652.6(16)	6910.0(12)	3133.8(8)	31.4(4)
C4	4039.9(19)	6718.2(14)	2516.2(9)	40.7(5)
C2	5864.2(18)	7542.1(13)	2715.1(10)	40.8(5)
C20	8010.2(17)	5421.7(14)	7470.5(9)	38.6(5)
C3	5142(2)	7042.0(13)	2306.2(9)	43.9(5)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	28.5(6)	20.0(6)	20.1(5)	1.3(4)	2.5(4)	2.8(5)
O1	26.5(6)	21.0(6)	24.2(6)	-2.6(5)	-2.9(5)	2.9(5)
O3	28.5(6)	25.7(6)	30.5(6)	-1.7(5)	0.9(5)	-5.4(5)
N1	20.5(7)	19.0(7)	22.8(6)	-1.0(5)	0.0(5)	1.2(5)
C8	22.9(8)	24.9(9)	20.7(7)	-2.0(6)	-1.3(6)	3.3(7)
C9	22.4(8)	22.9(9)	17.8(7)	-3.4(6)	2.5(6)	2.6(6)
C14	20.6(8)	22.2(8)	17.8(7)	-3.1(6)	2.7(6)	0.9(6)
C13	27.3(8)	22.2(9)	20.5(7)	0.0(6)	0.8(6)	2.2(7)
C16	20.4(8)	22.3(9)	25.9(8)	-2.1(6)	1.1(6)	2.4(6)
C6	26.8(8)	18.9(8)	25.2(8)	4.7(6)	-0.5(7)	4.5(7)
C15	24.2(8)	22.8(9)	18.3(7)	-1.9(6)	1.9(6)	-0.3(7)
C17	26.3(8)	23.7(9)	23.0(8)	-1.0(7)	2.3(7)	2.3(7)
C19	29.1(9)	20.9(8)	26.0(8)	2.8(7)	-1.8(7)	0.7(7)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C10	22.2(8)	30.7(10)	22.9(8)	-5.0(7)	0.6(6)	4.4(7)
C12	32.8(9)	23.0(9)	22.9(8)	-0.8(7)	4.3(7)	-3.7(7)
C11	24.9(8)	30.8(10)	27.4(8)	-5.6(7)	5.3(7)	-5.5(7)
C7	31.0(9)	20.1(9)	27.8(8)	3.4(7)	2.8(7)	0.2(7)
C1	28.2(9)	25.3(9)	40.1(10)	1.4(8)	3.4(8)	-0.4(7)
C18	26.8(9)	29.5(10)	36.5(9)	3.5(8)	-2.4(7)	5.0(7)
C5	31.7(9)	32.8(10)	29.9(9)	3.9(7)	-3.5(7)	-1.3(8)
C4	58.6(13)	35.9(11)	27.5(9)	-2.2(8)	-8.1(9)	1.2(9)
C2	43.9(11)	31.7(11)	46.8(11)	6.1(9)	20.1(9)	6.3(9)
C20	41.7(11)	44.5(11)	29.6(9)	2.5(8)	-8.3(8)	7.6(9)
C3	70.6(14)	32.5(11)	28.6(10)	5.8(8)	15.4(10)	13.9(10)

Table 4 Bond Lengths for 3a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O2	C8	1.3989(18)	C16	C17	1.505(2)
O2	C7	1.4467(19)	C6	C7	1.501(2)
O1	C8	1.4484(18)	C6	C1	1.386(2)
O1	C15	1.3656(18)	C6	C5	1.386(2)
O3	C15	1.2111(18)	C17	C19	1.327(2)
N1	C14	1.4148(19)	C19	C18	1.503(2)
N1	C16	1.4728(19)	C19	C20	1.506(2)
N1	C15	1.364(2)	C10	C11	1.388(2)
C8	C9	1.488(2)	C12	C11	1.385(2)
C9	C14	1.398(2)	C1	C2	1.384(3)
C9	C10	1.388(2)	C5	C4	1.384(3)
C14	C13	1.392(2)	C4	C3	1.382(3)
C13	C12	1.387(2)	C2	C3	1.376(3)

Table 5 Bond Angles for 3a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C8	O2	C7	112.99(11)	C5	C6	C7	119.85(15)
C15	O1	C8	115.55(12)	O3	C15	O1	119.06(14)
C14	N1	C16	120.86(12)	O3	C15	N1	124.43(14)
C15	N1	C14	121.89(13)	N1	C15	O1	116.48(13)
C15	N1	C16	117.23(12)	C19	C17	C16	124.83(14)

Table 5 Bond Angles for 3a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	C8	O1	109.55(12)	C17	C19	C18	123.19(15)
O2	C8	C9	108.32(12)	C17	C19	C20	122.07(15)
O1	C8	C9	109.24(12)	C18	C19	C20	114.72(14)
C14	C9	C8	116.24(13)	C9	C10	C11	120.15(15)
C10	C9	C8	123.46(14)	C11	C12	C13	121.71(15)
C10	C9	C14	120.24(15)	C12	C11	C10	119.11(15)
C9	C14	N1	117.58(14)	O2	C7	C6	108.26(12)
C13	C14	N1	122.56(14)	C2	C1	C6	120.61(17)
C13	C14	C9	119.85(14)	C4	C5	C6	120.32(17)
C12	C13	C14	118.93(15)	C3	C4	C5	120.08(18)
N1	C16	C17	113.16(12)	C3	C2	C1	119.93(18)
C1	C6	C7	121.09(15)	C2	C3	C4	119.99(18)
C1	C6	C5	119.05(16)				

Table 6 Torsion Angles for 3a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O2	C8	C9	C14	81.63(16)	C16	N1	C15	O3	-3.8(2)
O2	C8	C9	C10	-95.54(17)	C16	C17	C19	C18	-0.3(3)
O1	C8	C9	C14	-37.65(17)	C16	C17	C19	C20	-178.66(16)
O1	C8	C9	C10	145.18(14)	C6	C1	C2	C3	-0.7(3)
N1	C14	C13	C12	-179.17(14)	C6	C5	C4	C3	-0.8(3)
N1	C16	C17	C19	-163.37(15)	C15	O1	C8	O2	-63.03(16)
C8	O2	C7	C6	-174.28(12)	C15	O1	C8	C9	55.48(16)
C8	O1	C15	O3	146.31(14)	C15	N1	C14	C9	20.0(2)
C8	O1	C15	N1	-35.76(18)	C15	N1	C14	C13	-160.52(14)
C8	C9	C14	N1	2.77(19)	C15	N1	C16	C17	79.74(17)
C8	C9	C14	C13	-176.71(13)	C10	C9	C14	N1	-179.96(13)
C8	C9	C10	C11	176.22(14)	C10	C9	C14	C13	0.6(2)
C9	C14	C13	C12	0.3(2)	C7	O2	C8	O1	-64.60(15)
C9	C10	C11	C12	0.3(2)	C7	O2	C8	C9	176.33(12)
C14	N1	C16	C17	-98.55(16)	C7	C6	C1	C2	-178.16(15)
C14	N1	C15	O1	-3.4(2)	C7	C6	C5	C4	178.88(16)
C14	N1	C15	O3	174.42(14)	C1	C6	C7	O2	-120.33(15)
C14	C9	C10	C11	-0.8(2)	C1	C6	C5	C4	-0.3(3)
C14	C13	C12	C11	-0.9(2)	C1	C2	C3	C4	-0.4(3)
C13	C12	C11	C10	0.6(2)	C5	C6	C7	O2	60.47(19)
C16	N1	C14	C9	-161.78(13)	C5	C6	C1	C2	1.0(2)
C16	N1	C14	C13	17.7(2)	C5	C4	C3	C2	1.1(3)

Table 6 Torsion Angles for 3a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C16	N1	C15	O1	178.35(12)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3a.

Atom	*x*	*y*	*z*	U(eq)
H8	2435.74	7251.33	5110.41	27
H13	4451.79	4335.13	6171	28
H16A	6811.6	5794.77	5599.19	27
H16B	6079.71	4868.9	5749.36	27
H17	5994.24	5746.17	6875.74	29
H10	1191.95	5835.91	5193.82	30
H12	2594.6	3598.73	6073.87	31
H11	959.61	4336.66	5598.05	33
H7A	4540.37	8008.29	4444.12	32
H7B	3176.68	7996.74	4189.32	32
H1	5987.7	8065.06	3617.42	37
H18A	8750.45	4415.8	6333.89	46
H18B	9440.37	5362.86	6479.03	46
H18C	8511.42	5302.29	5893.25	46
H5	2890.61	6692.6	3274.75	38
H4	3547.91	6363.64	2236.26	49
H2	6623.96	7761.3	2572.03	49
H20A	8588.16	5922.67	7540.67	58
H20B	8372.58	4833.58	7599.71	58
H20C	7285.84	5534.9	7727.05	58
H3	5400.1	6919.35	1879.76	53

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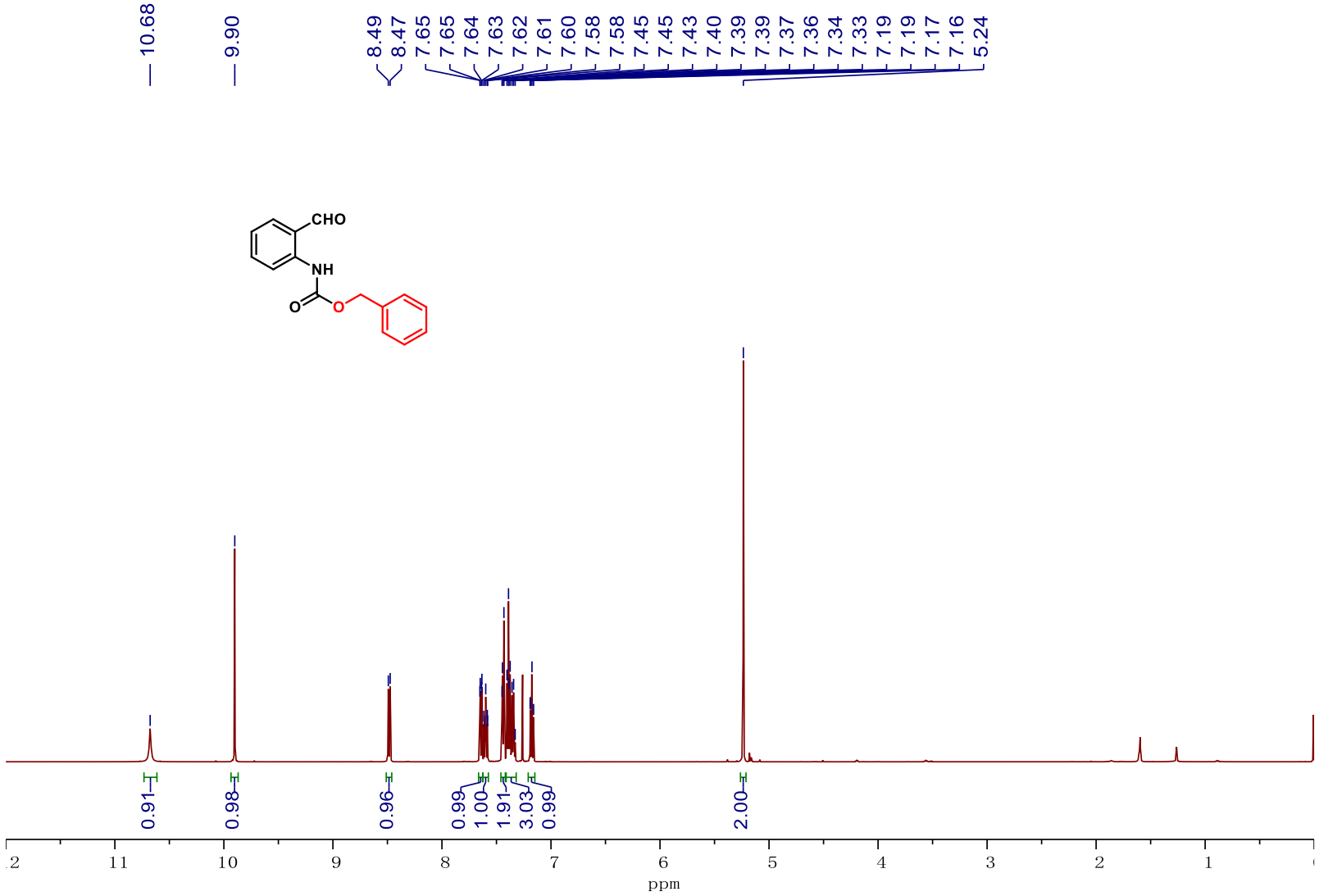
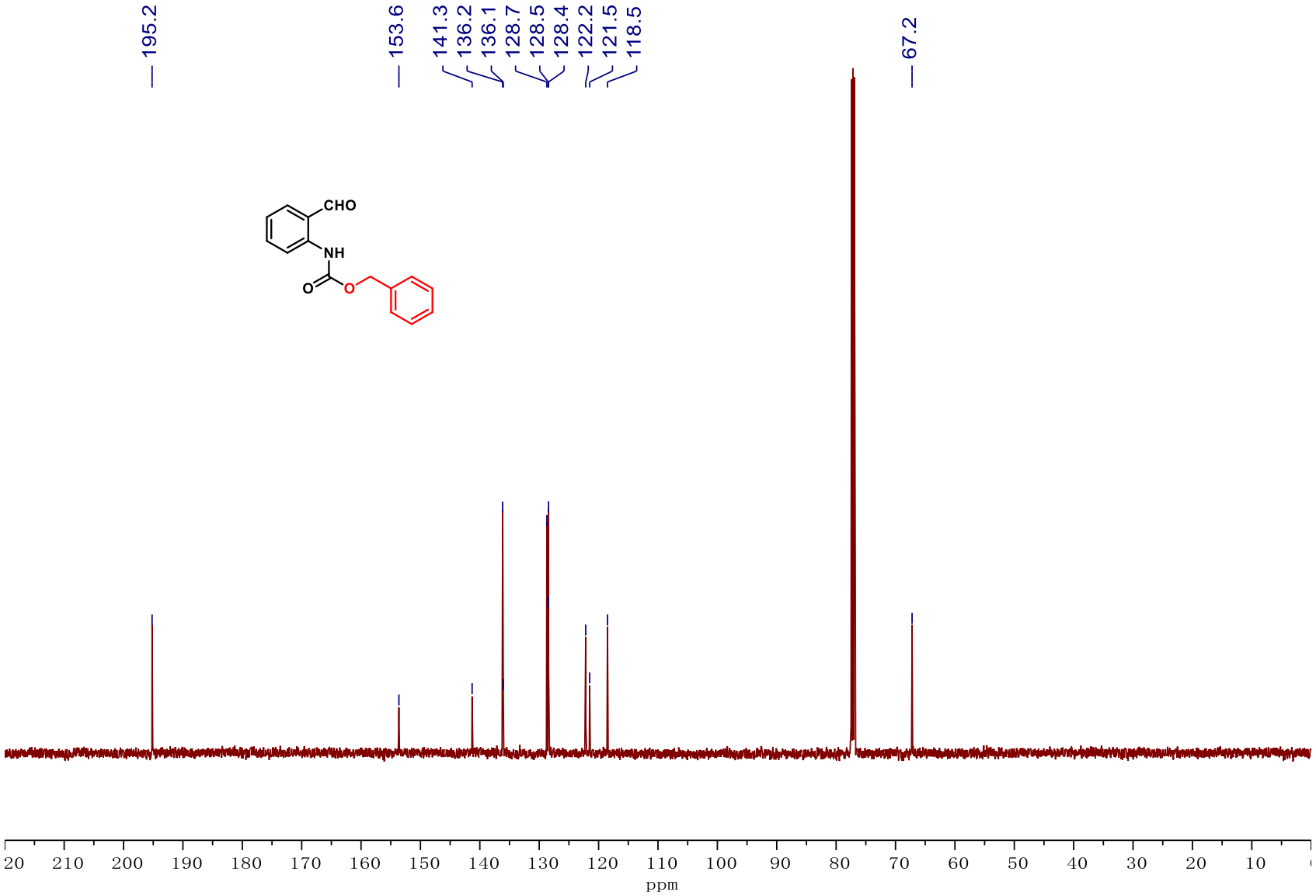
NMR Spectra

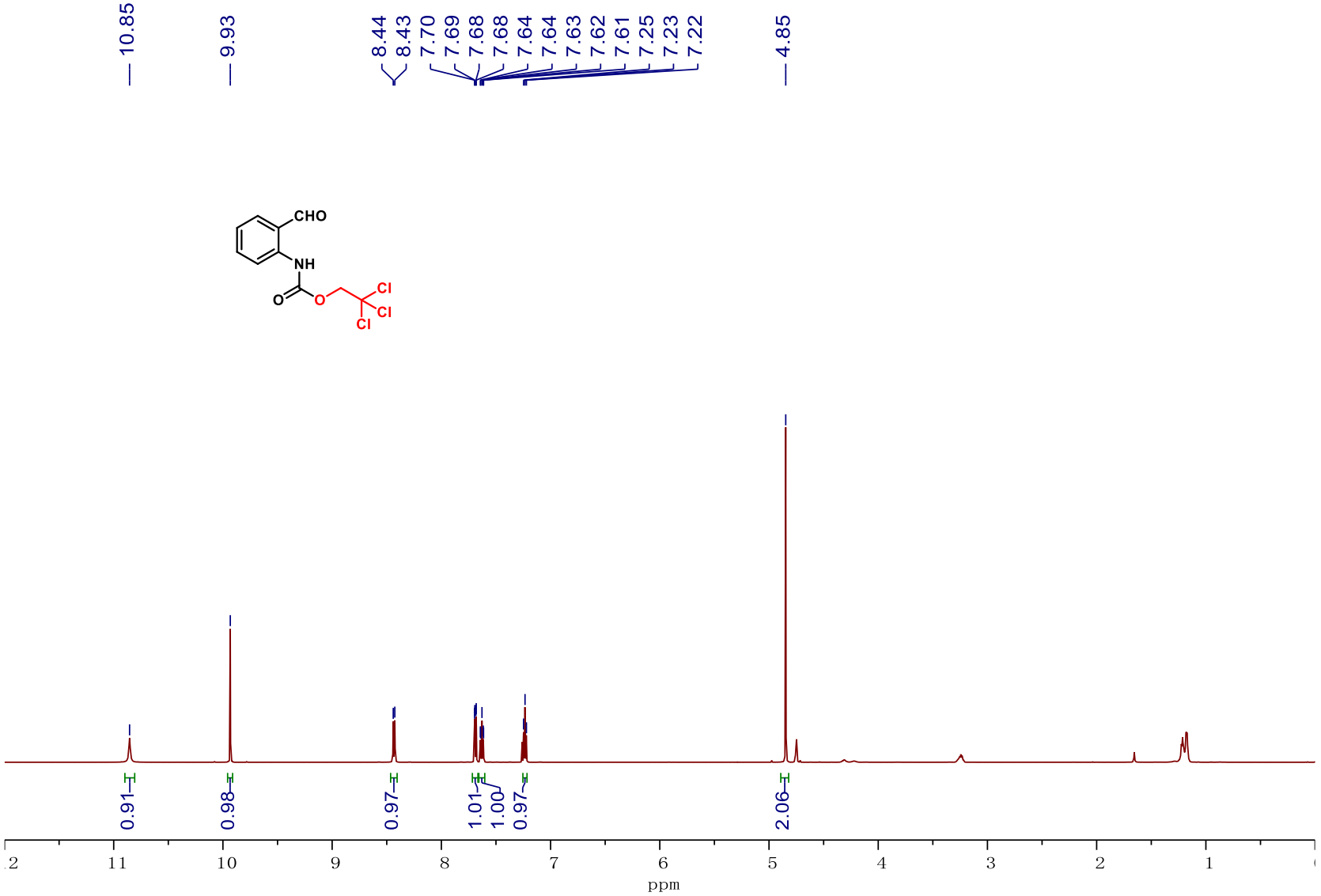
Compound 1a ^{1}H NMR



Compound 1a ^{13}C NMR



Compound 1c ^{1}H NMR



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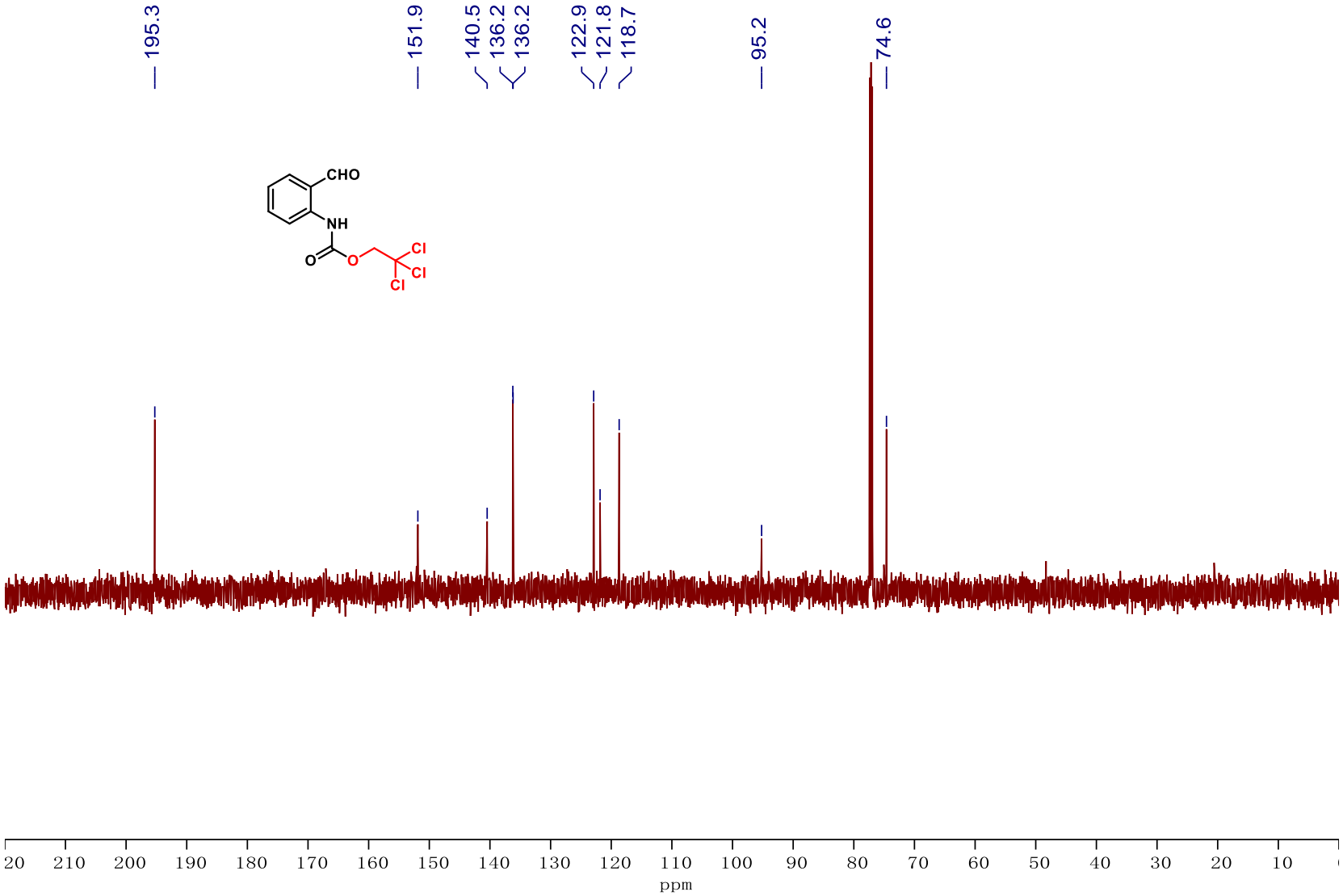

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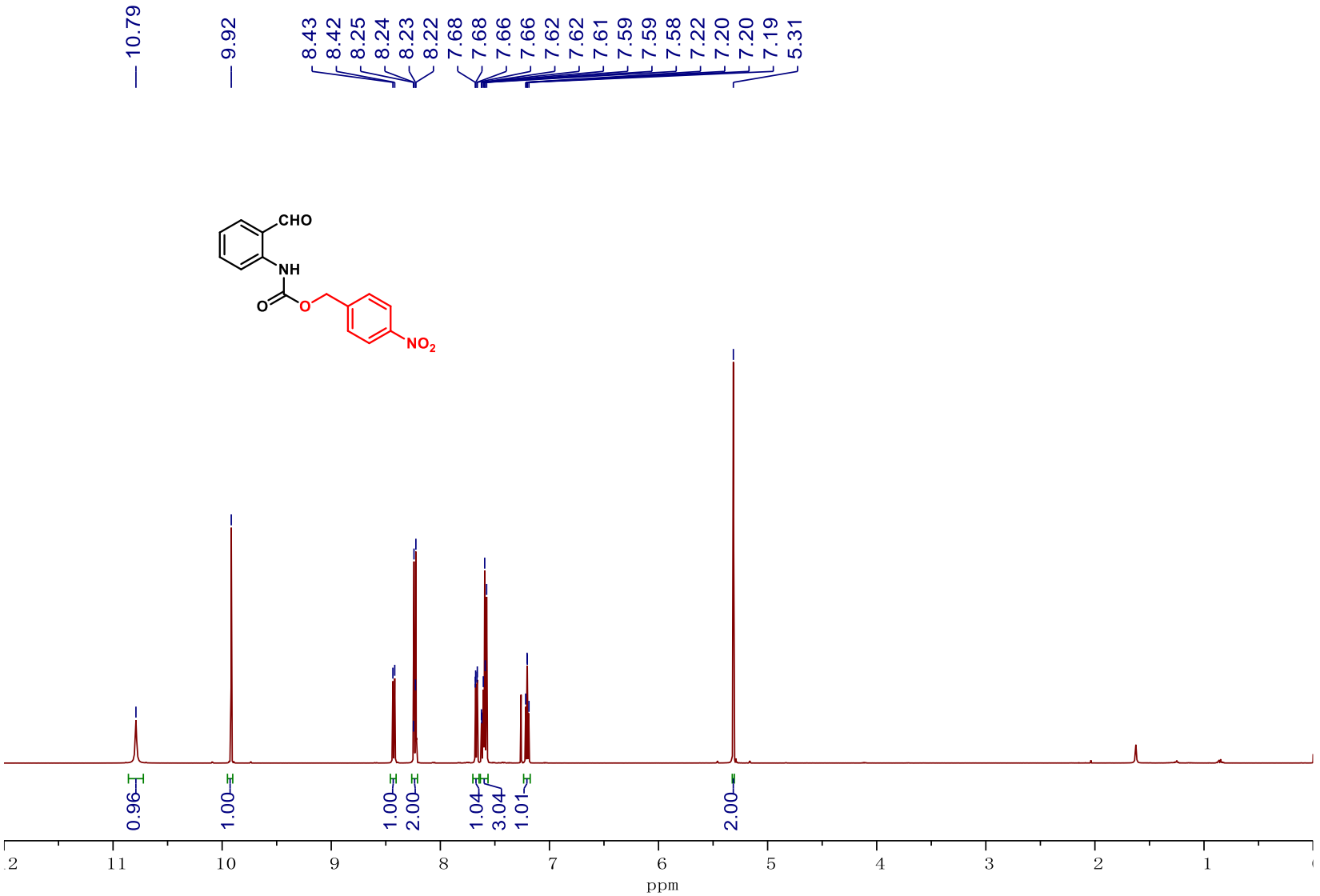

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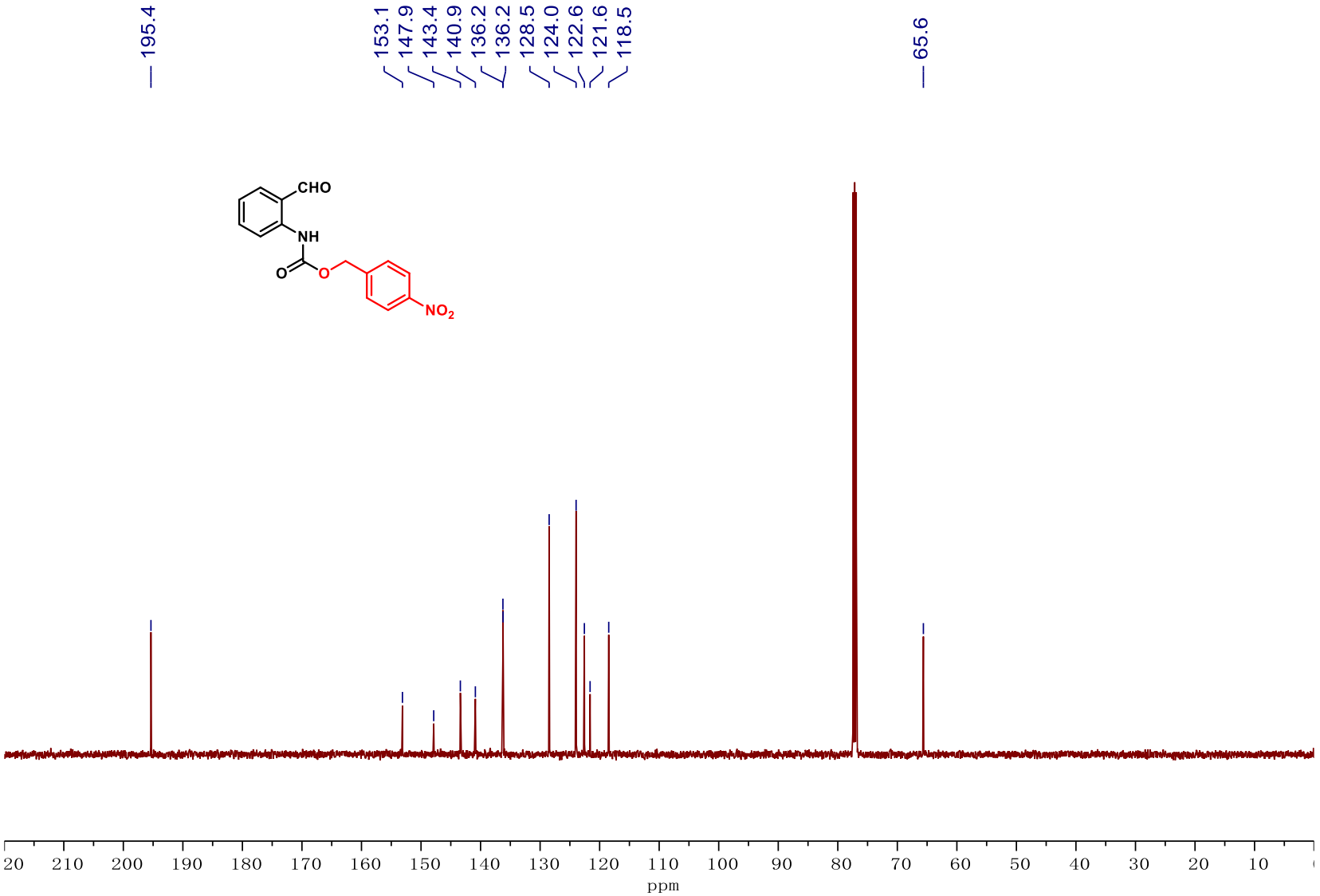

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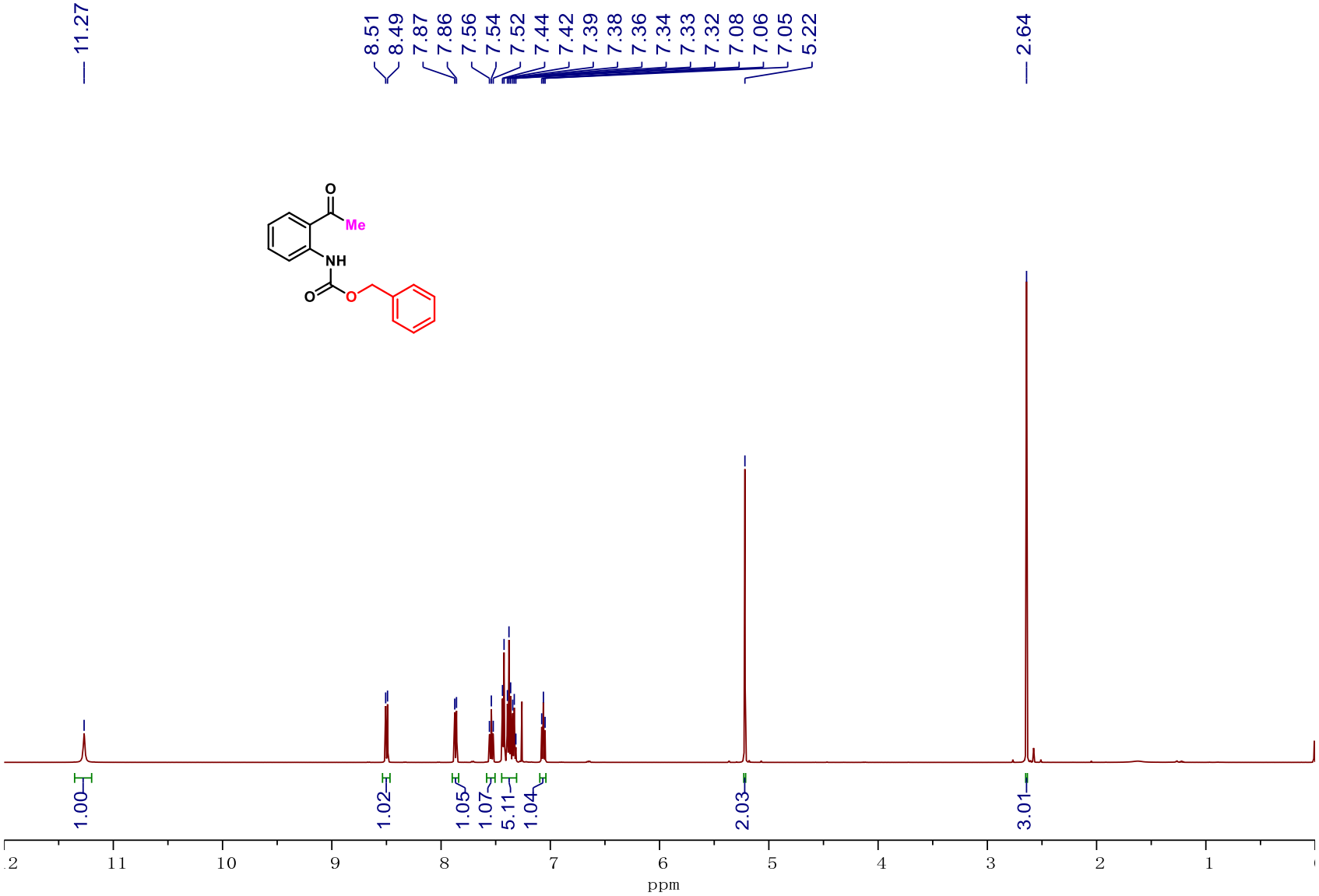

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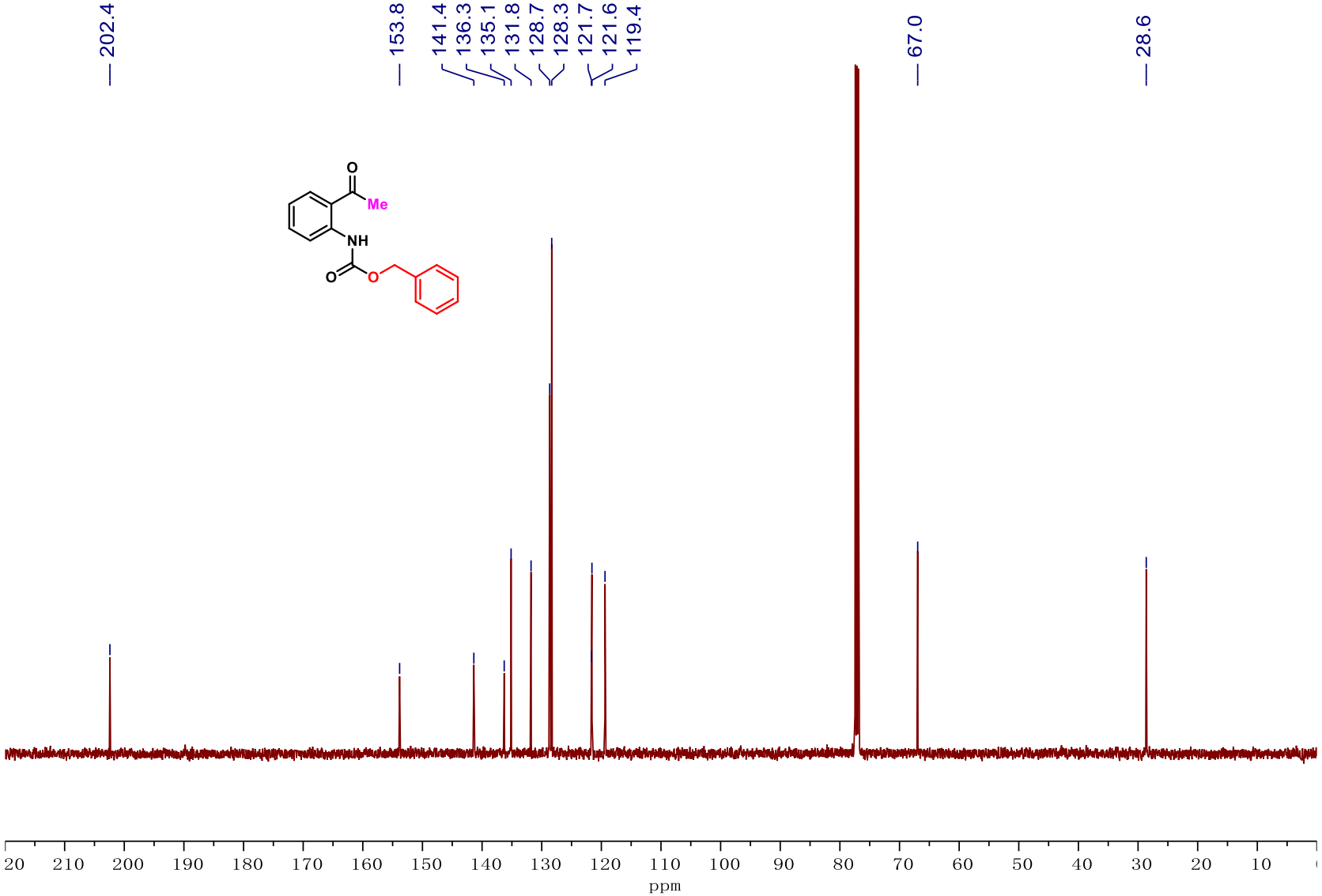
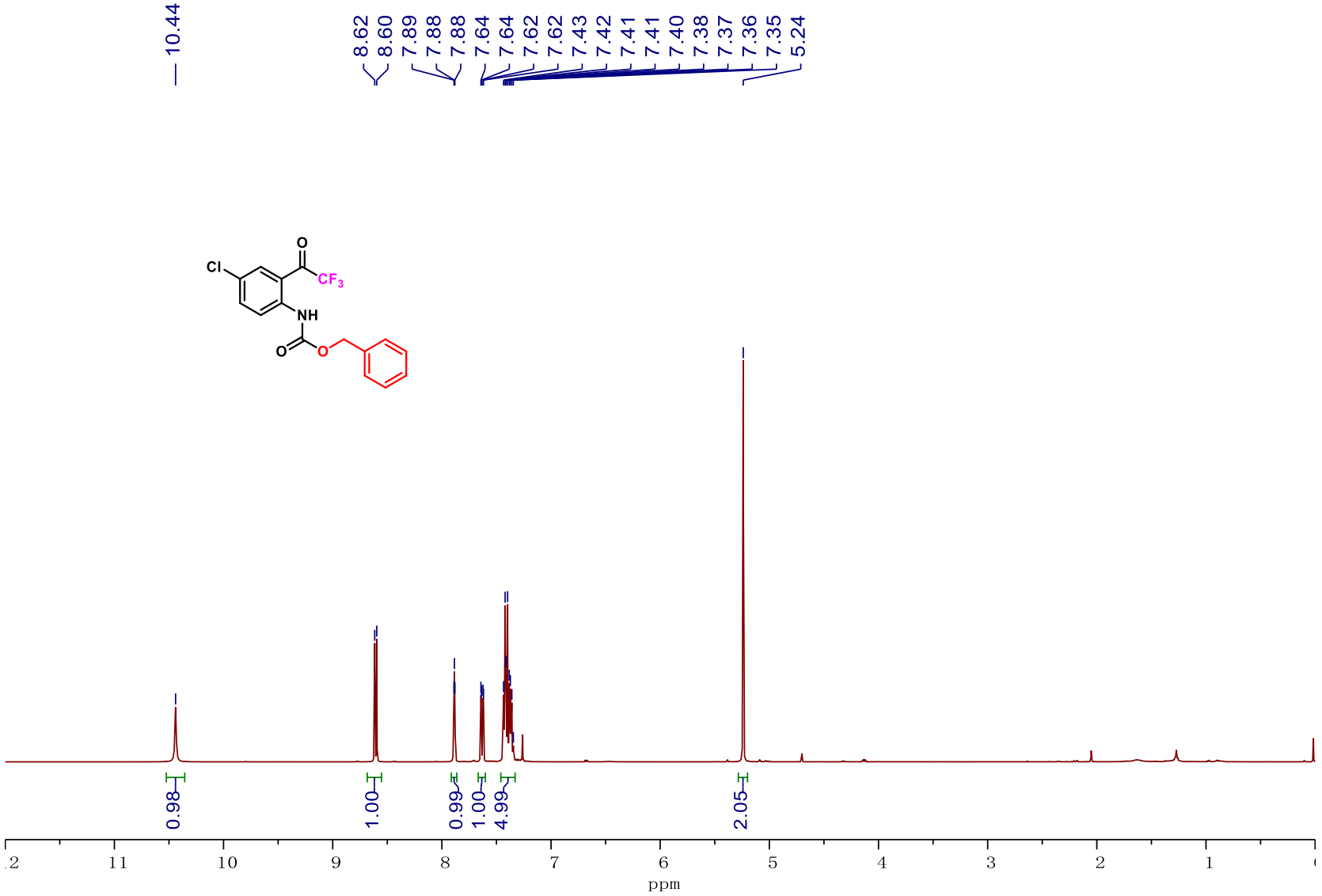
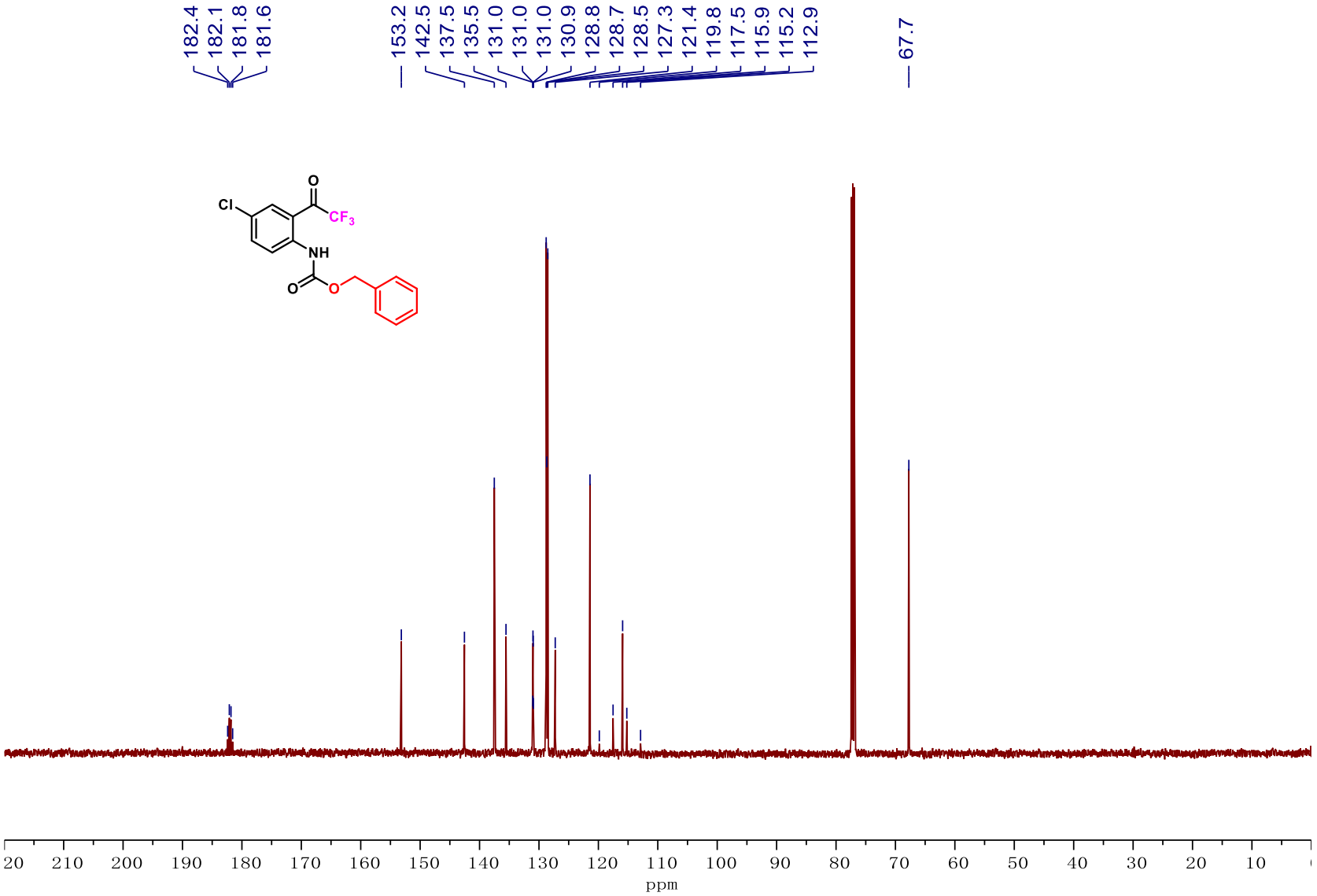


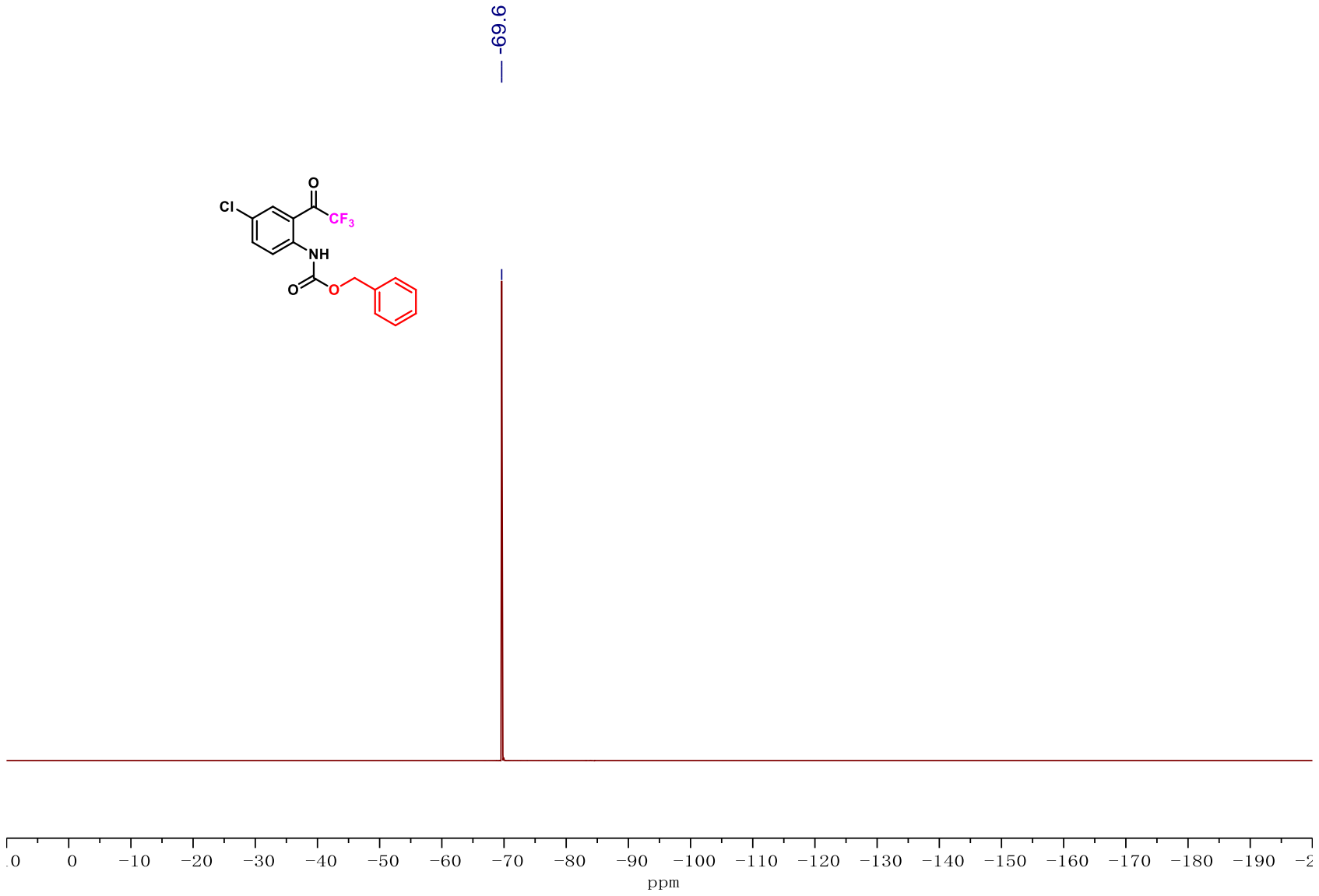
Compound 1u ^{1}H NMR



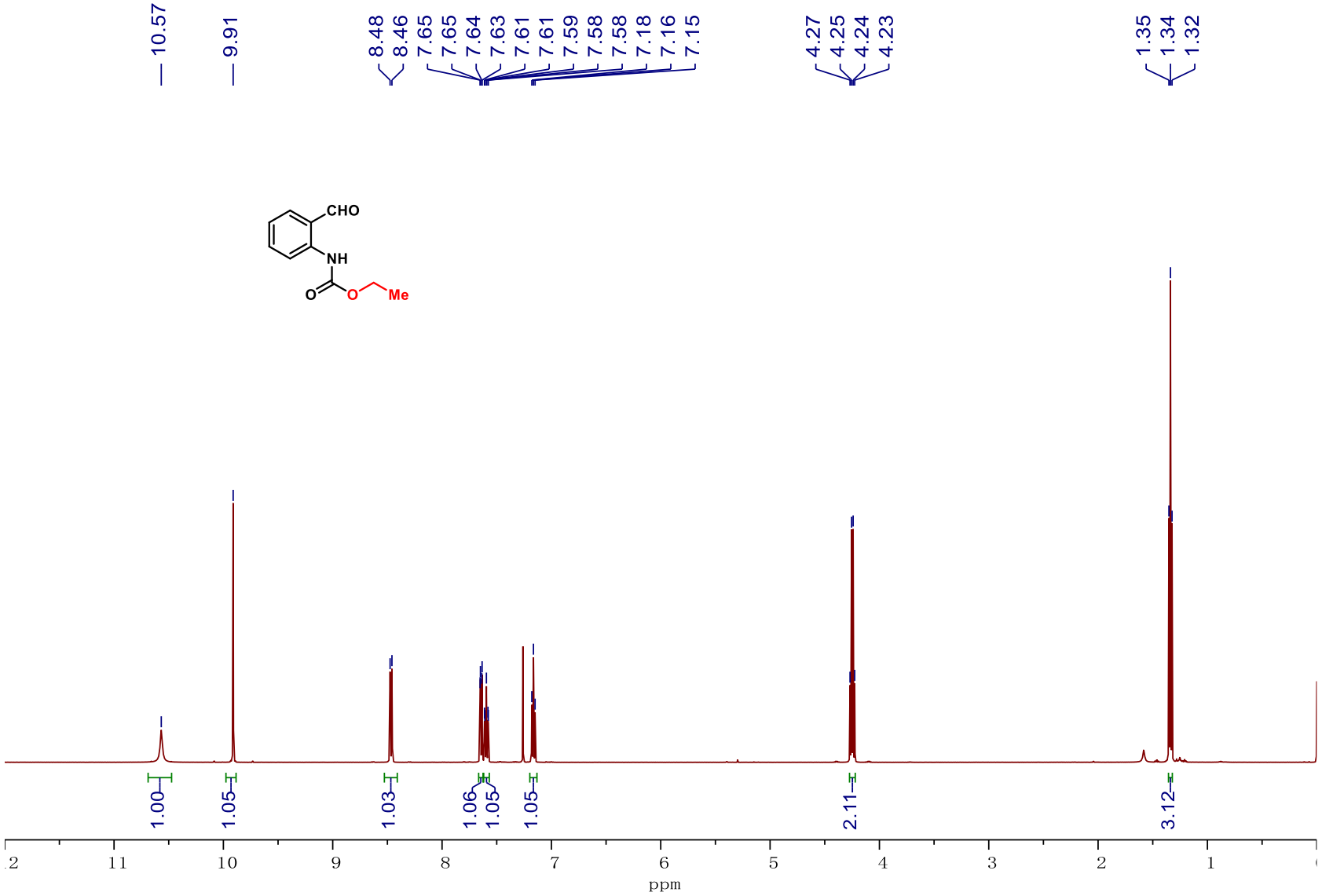
Compound 1u ^{13}C NMR



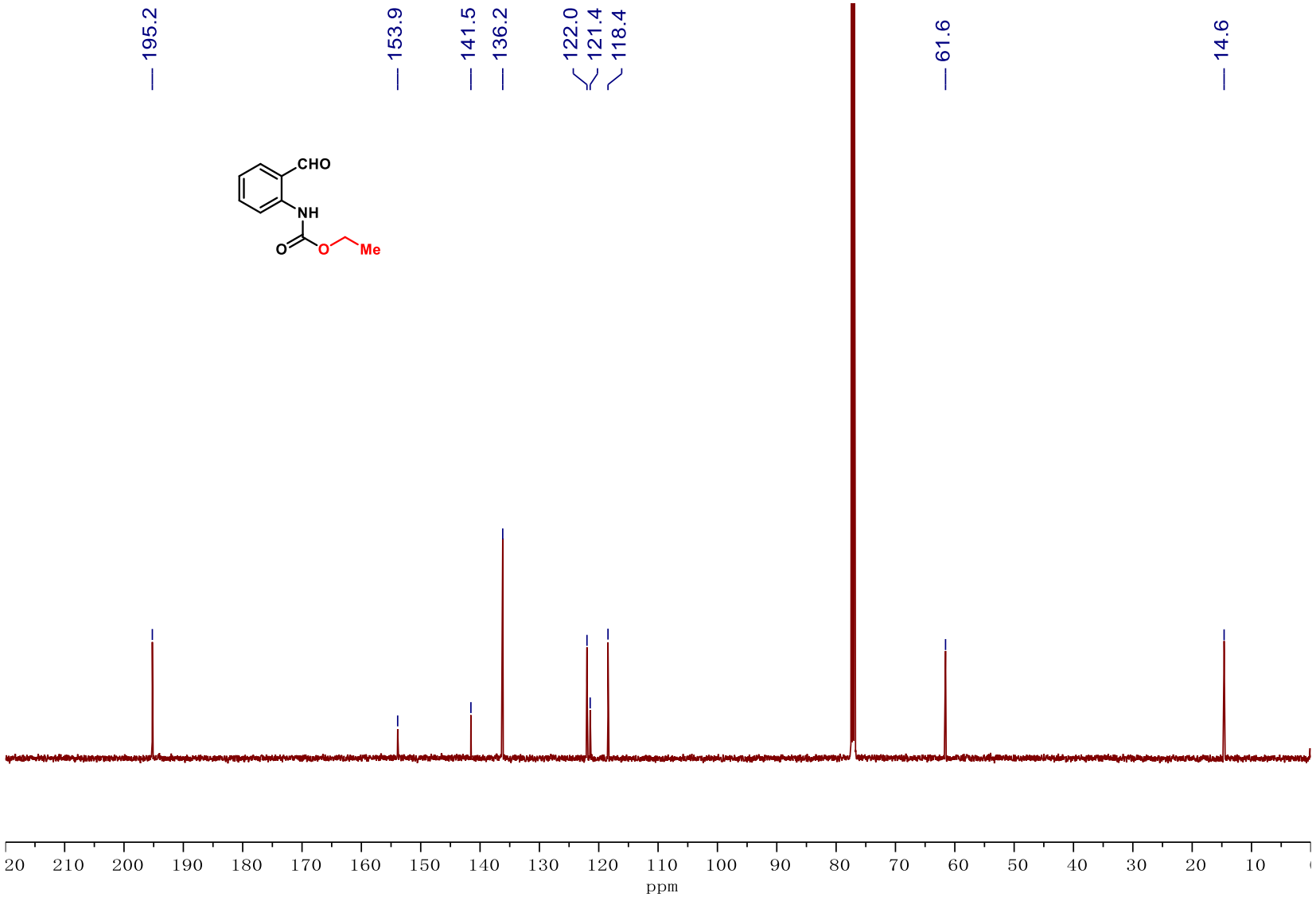
Compound 1u ^{13}F NMR



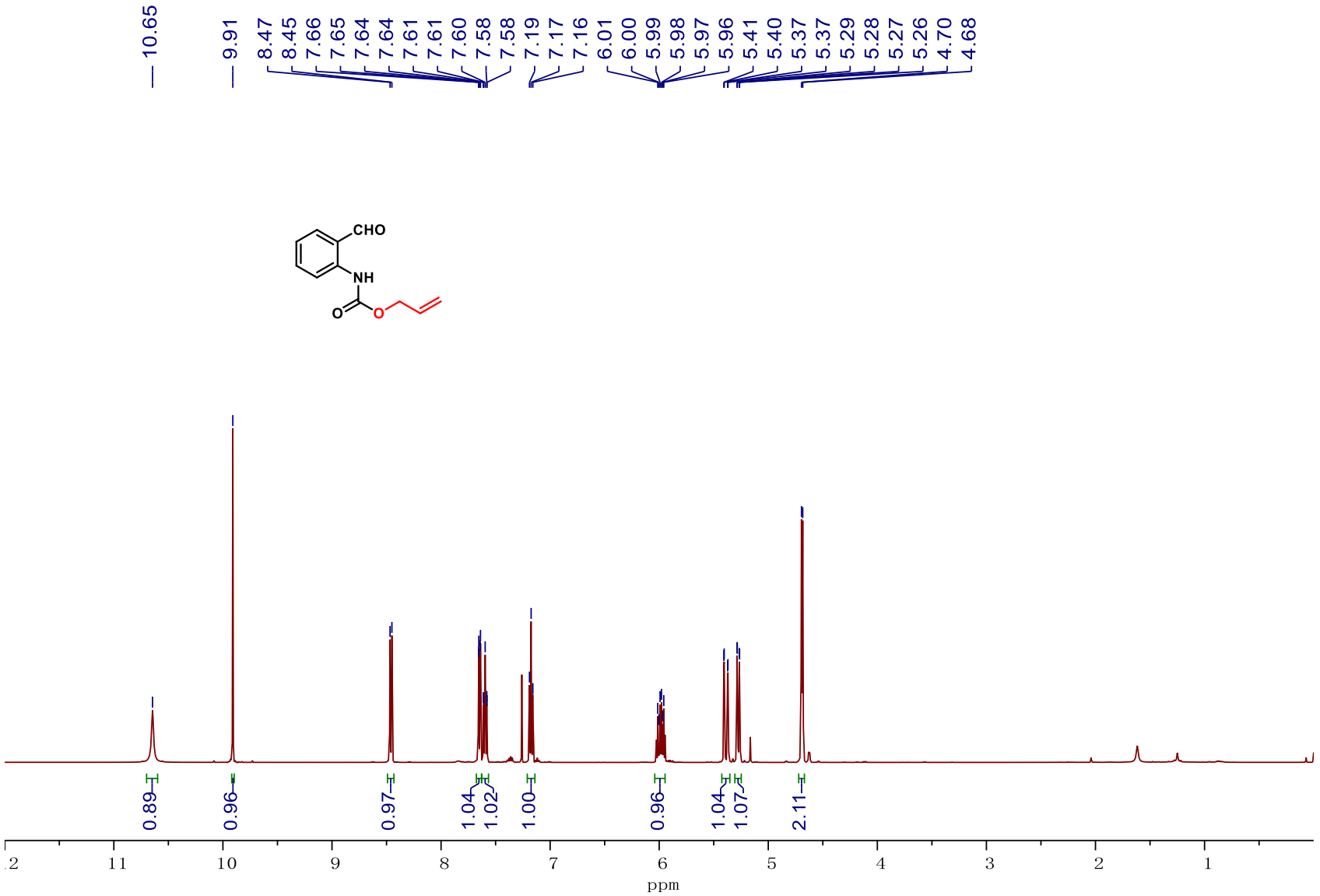
Compound 1b ^{1}H NMR



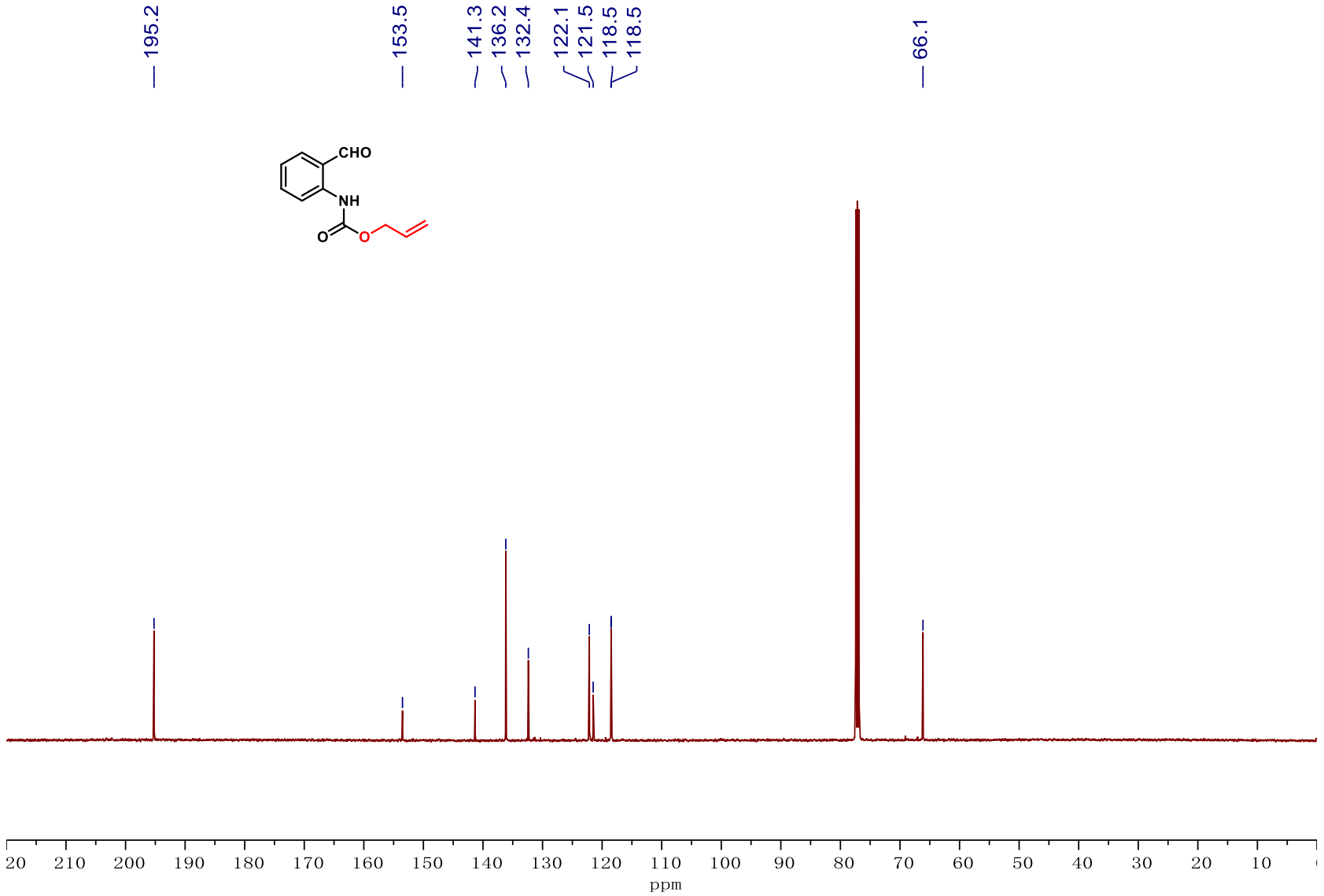
Compound 1b ^{13}C NMR



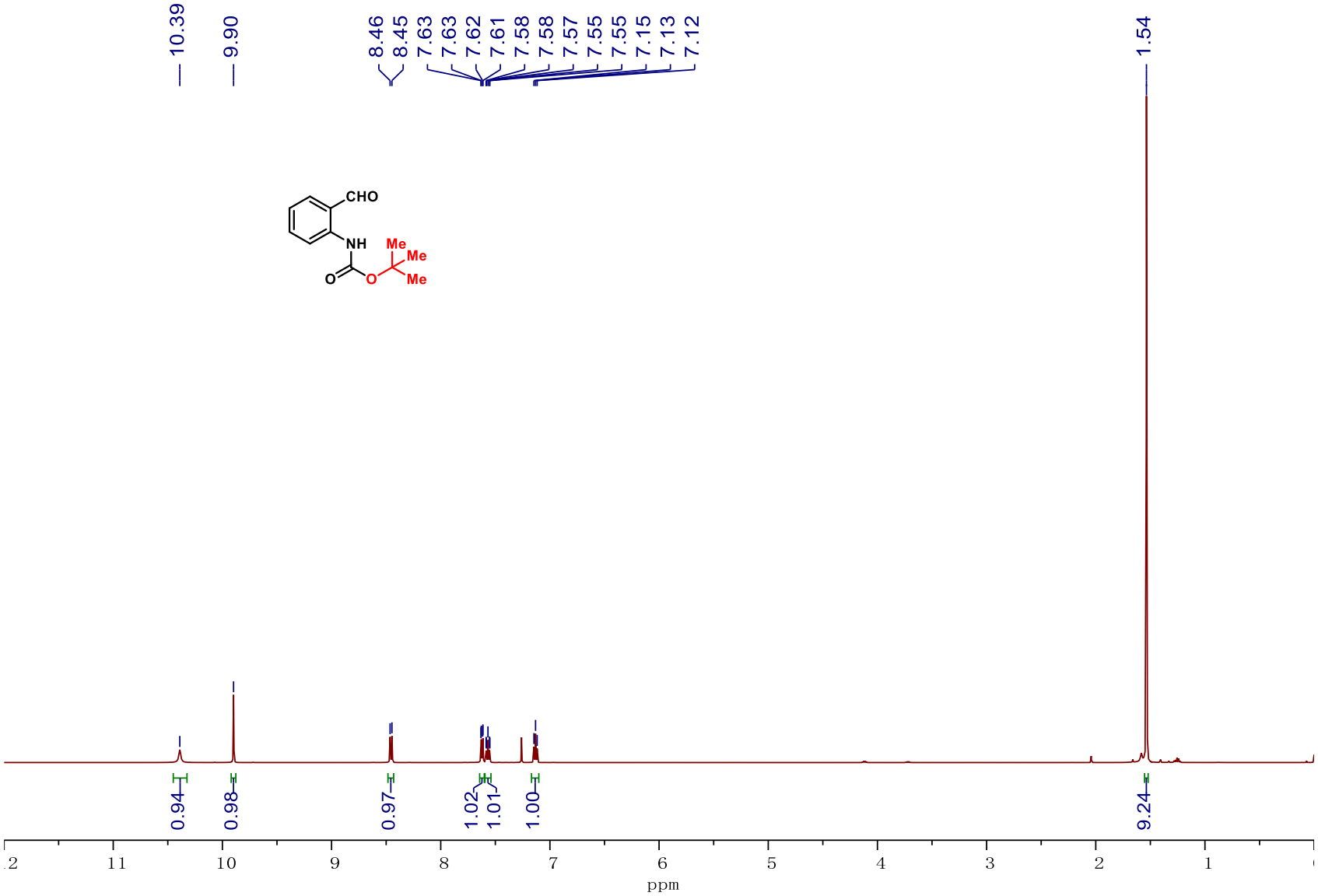
Compound 1d ^{1}H NMR



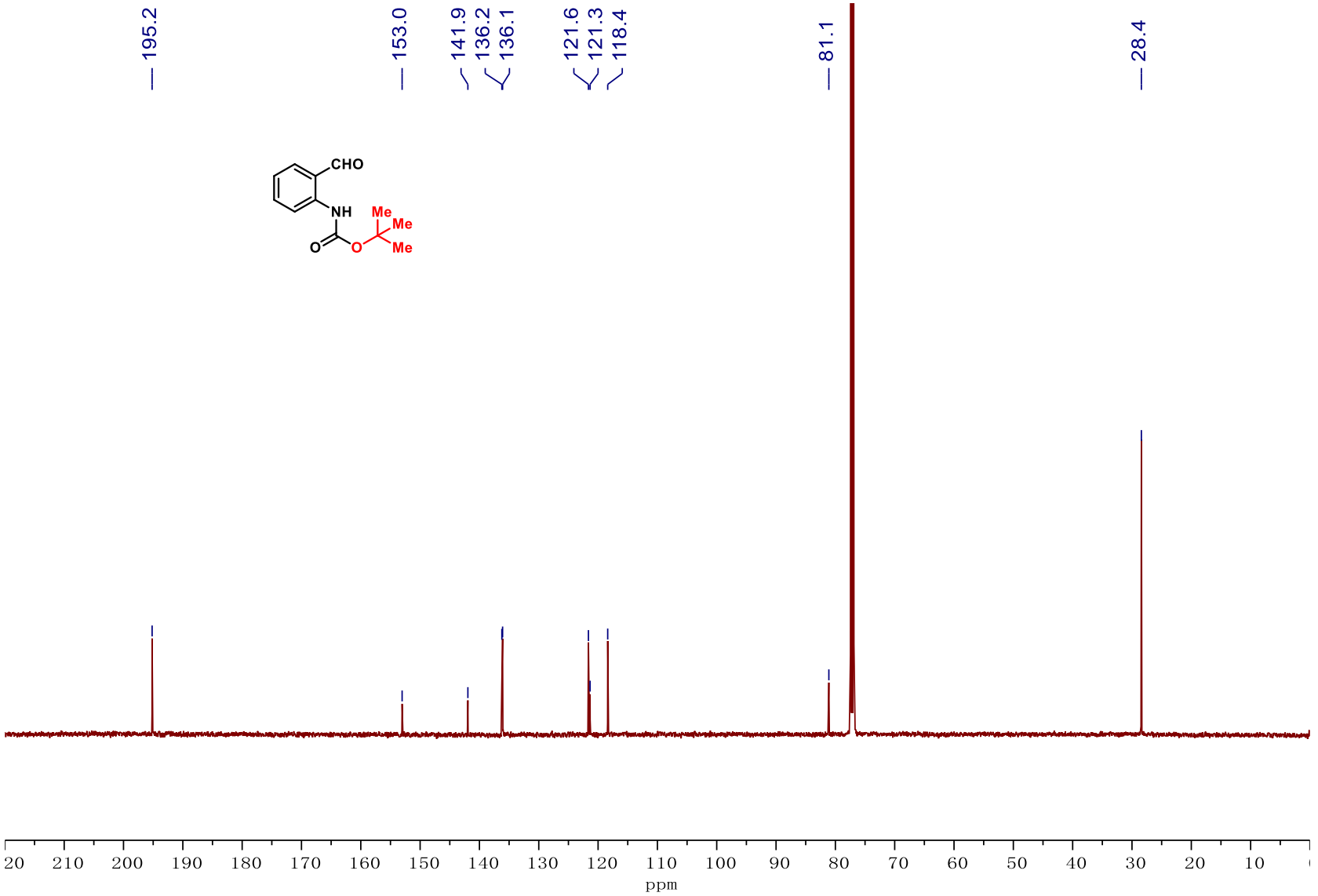
Compound 1d ^{13}C NMR



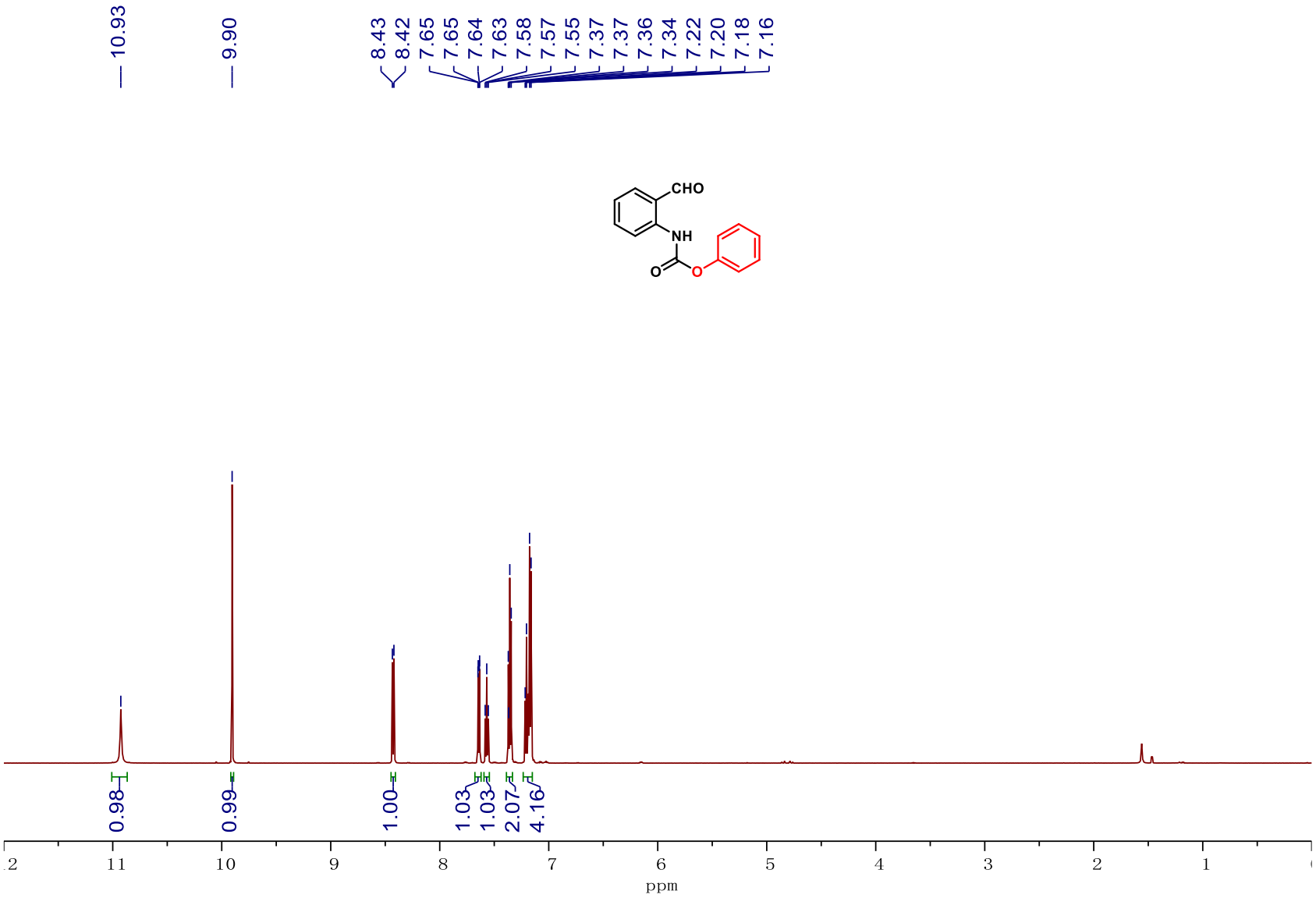
Compound 1f ^{1}H NMR



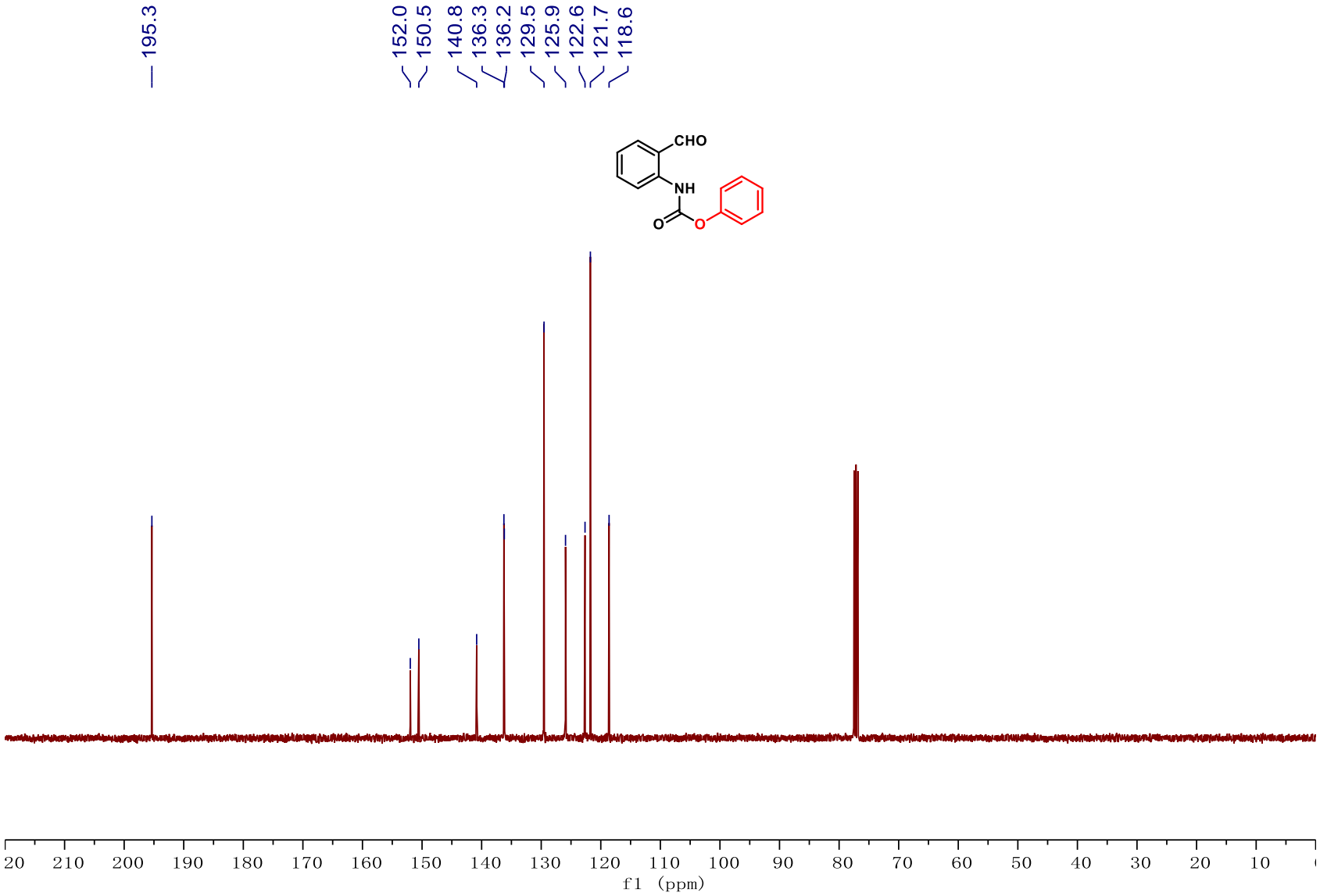
Compound 1f ^{13}C NMR



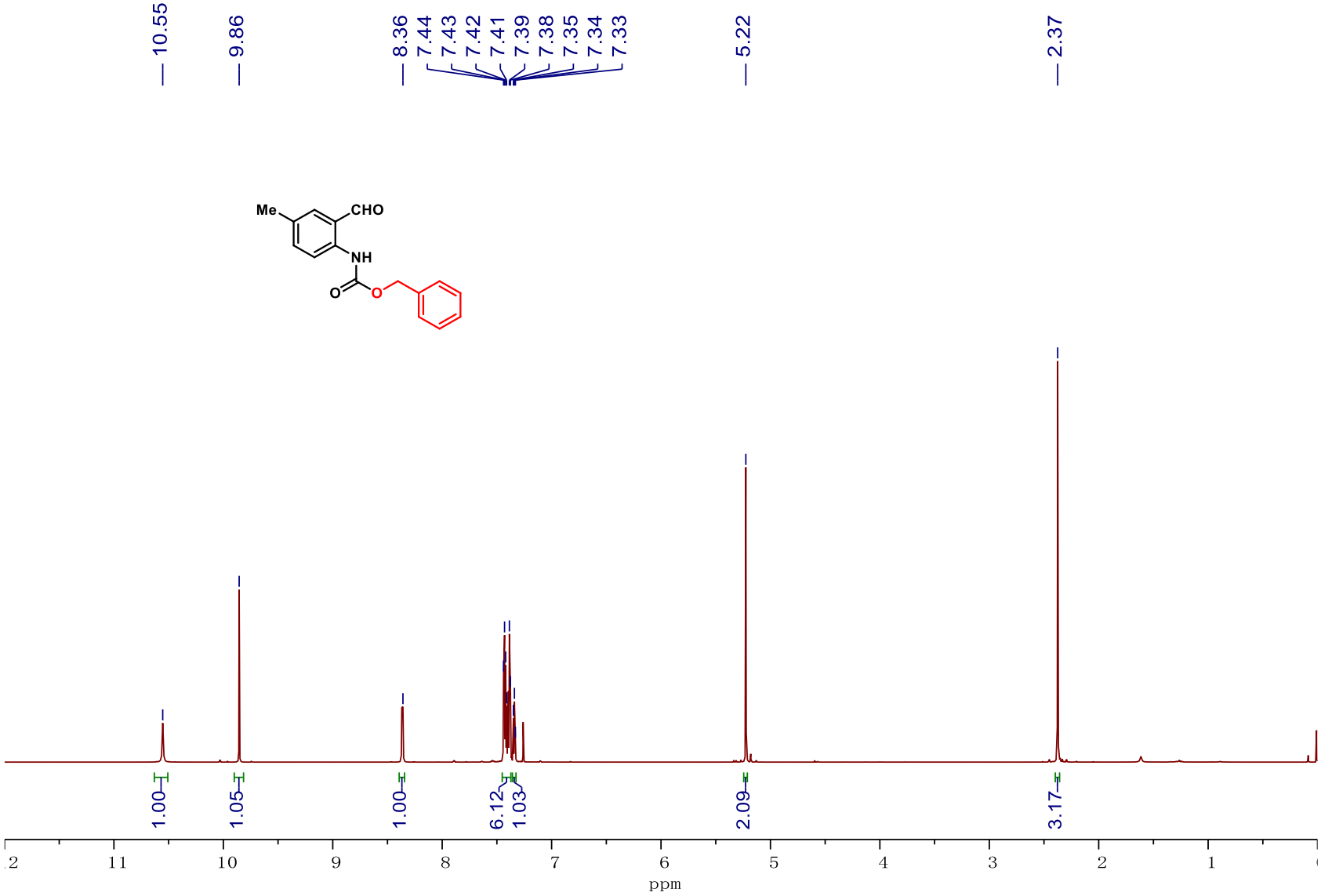
Compound 1g ^{1}H NMR



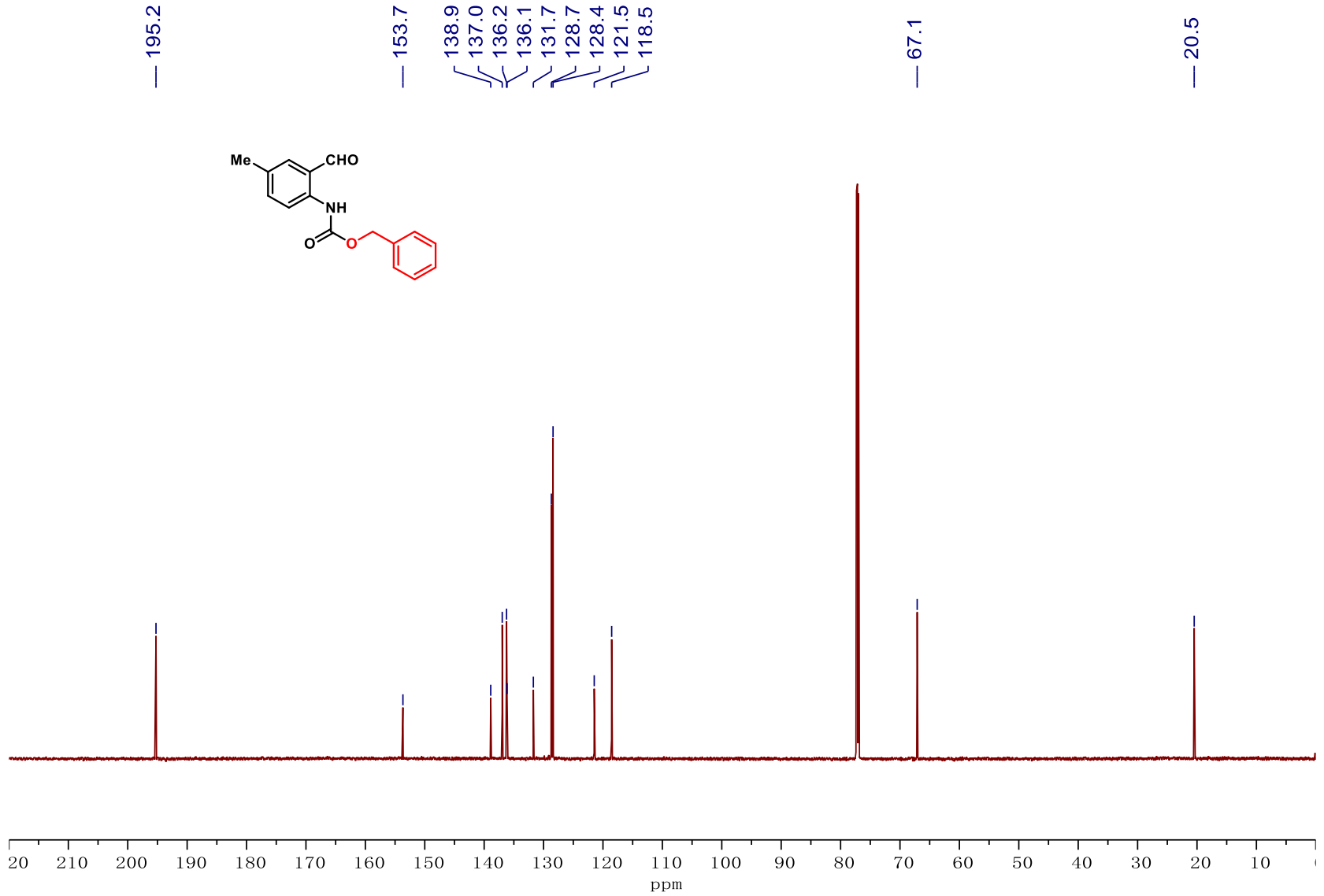
Compound 1g ^{13}C NMR



Compound 1h ^{1}H NMR



Compound 1h ^{13}C NMR



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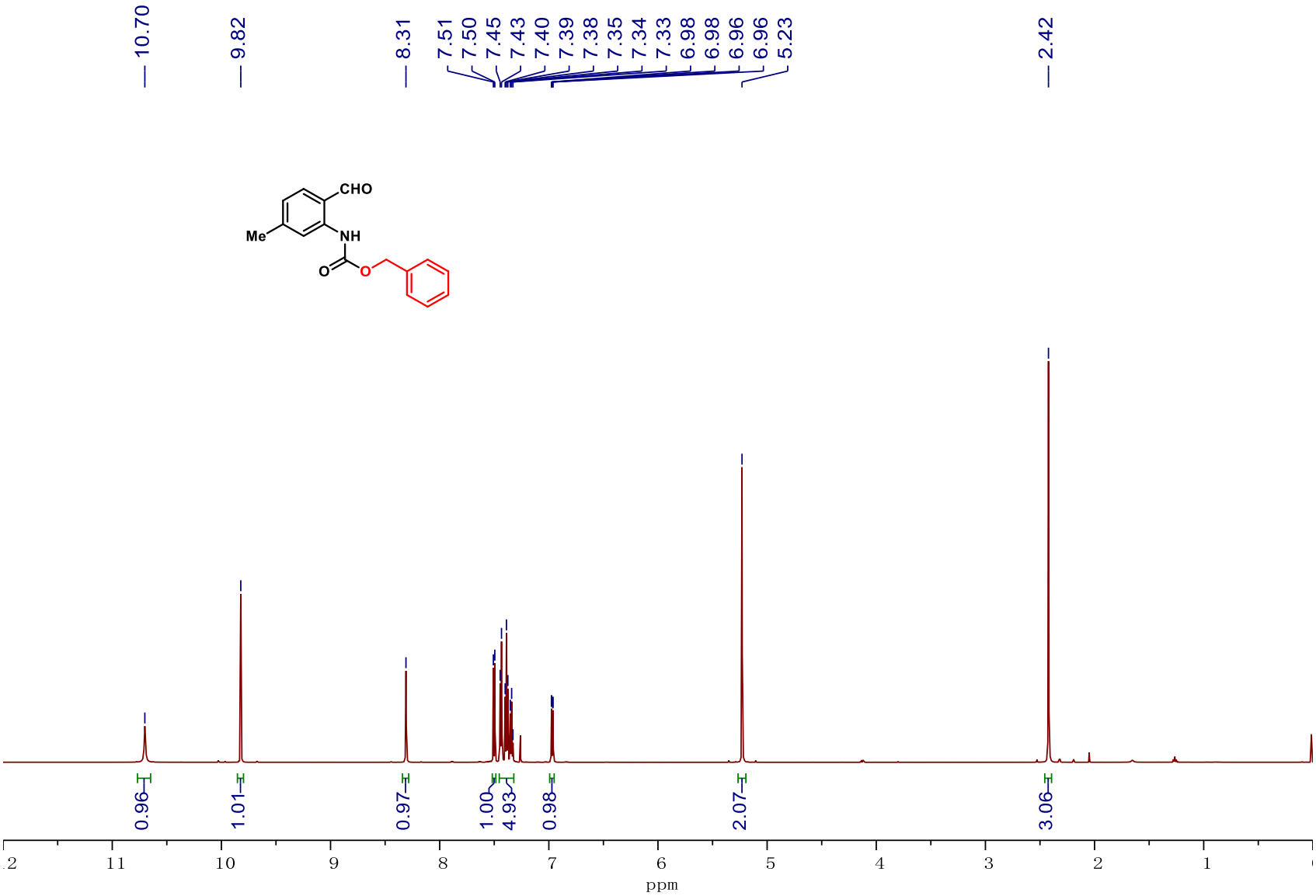

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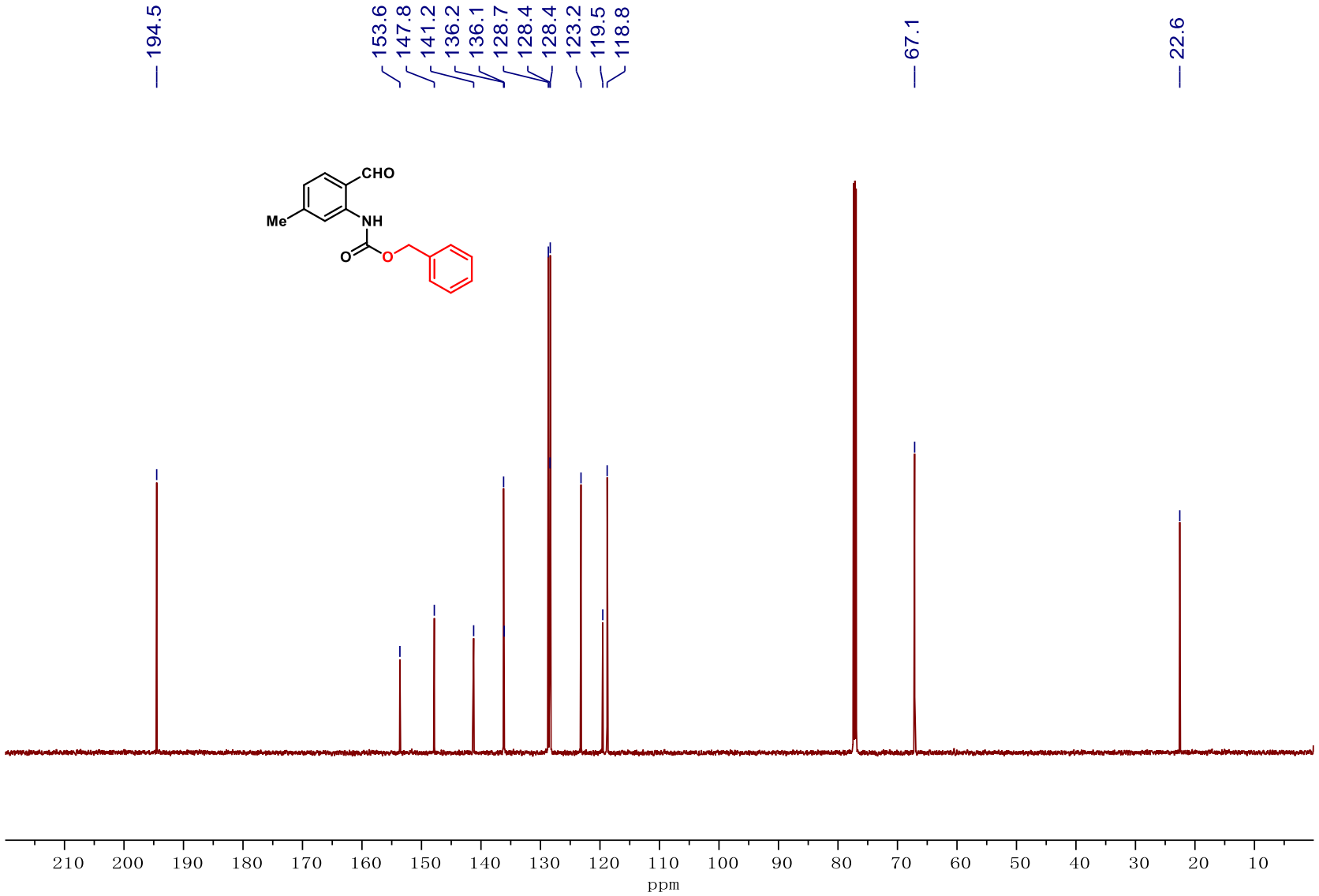

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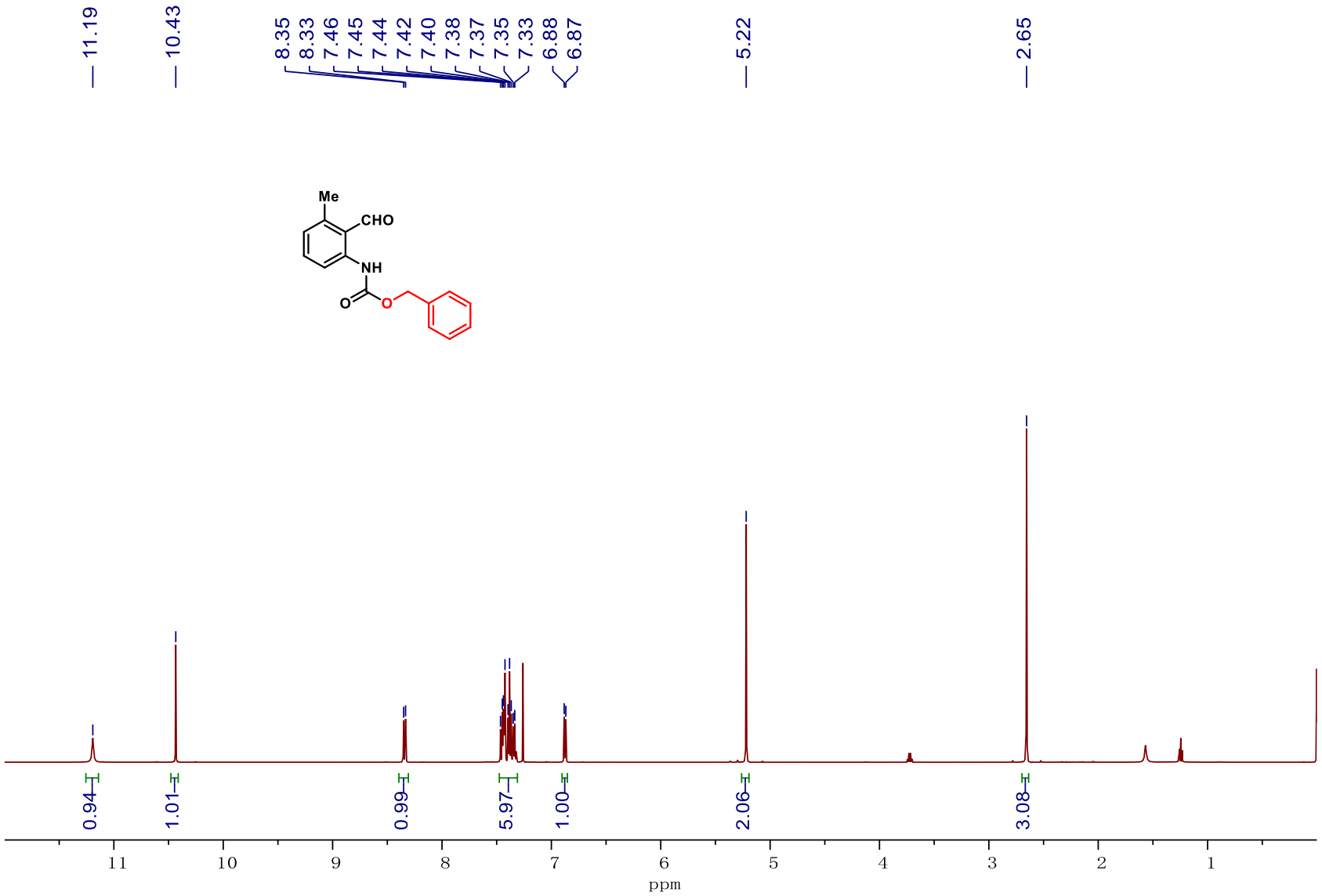

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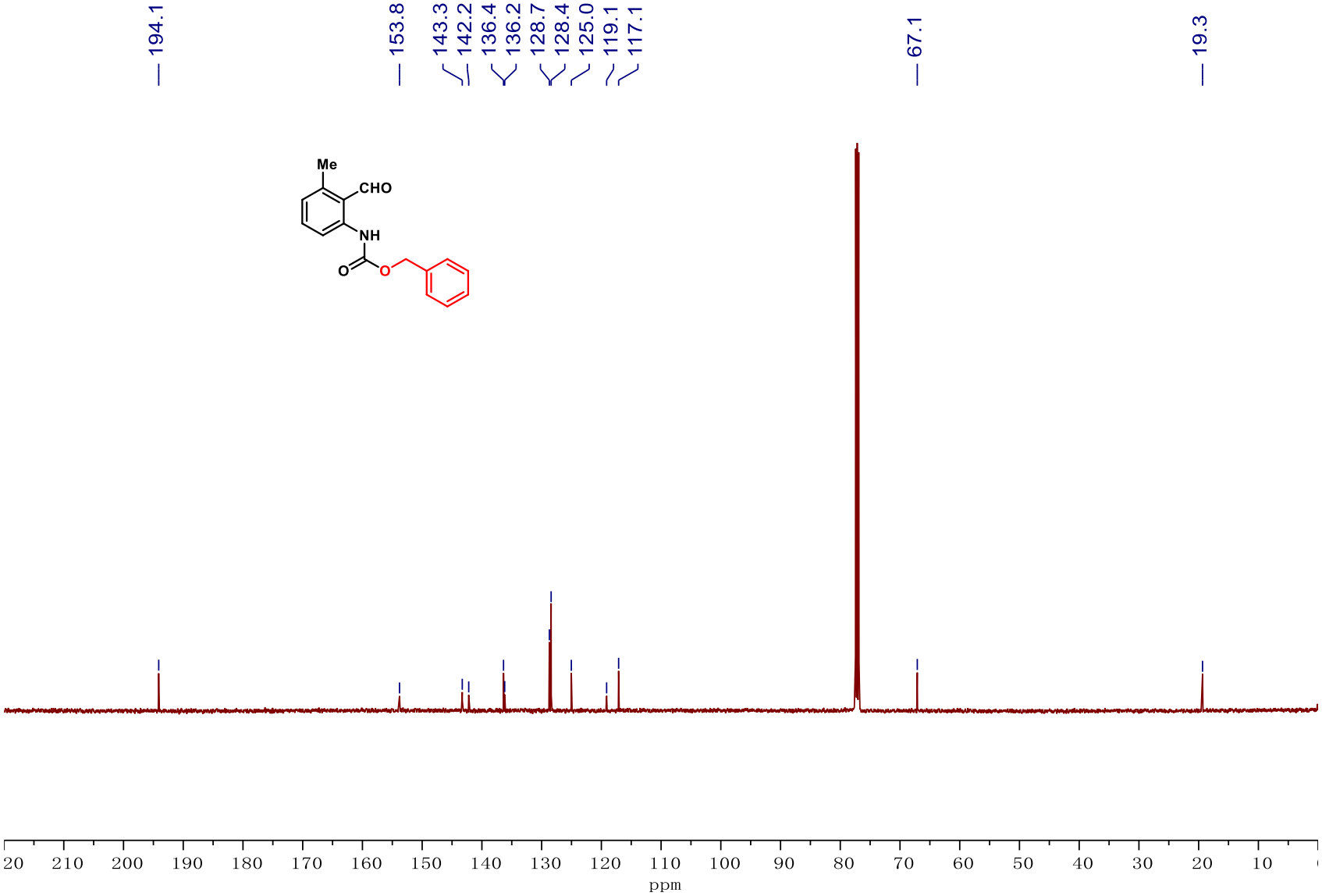

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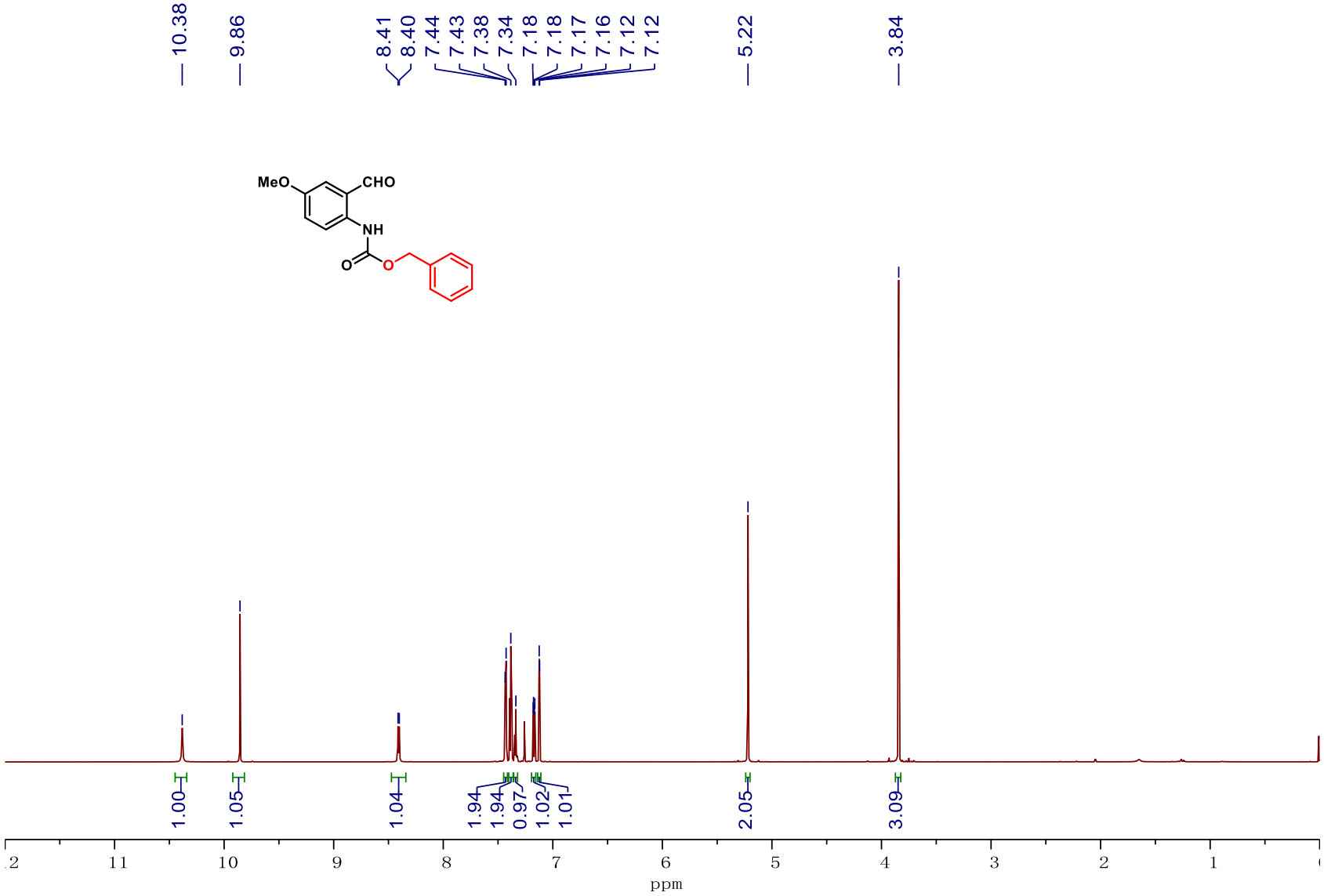

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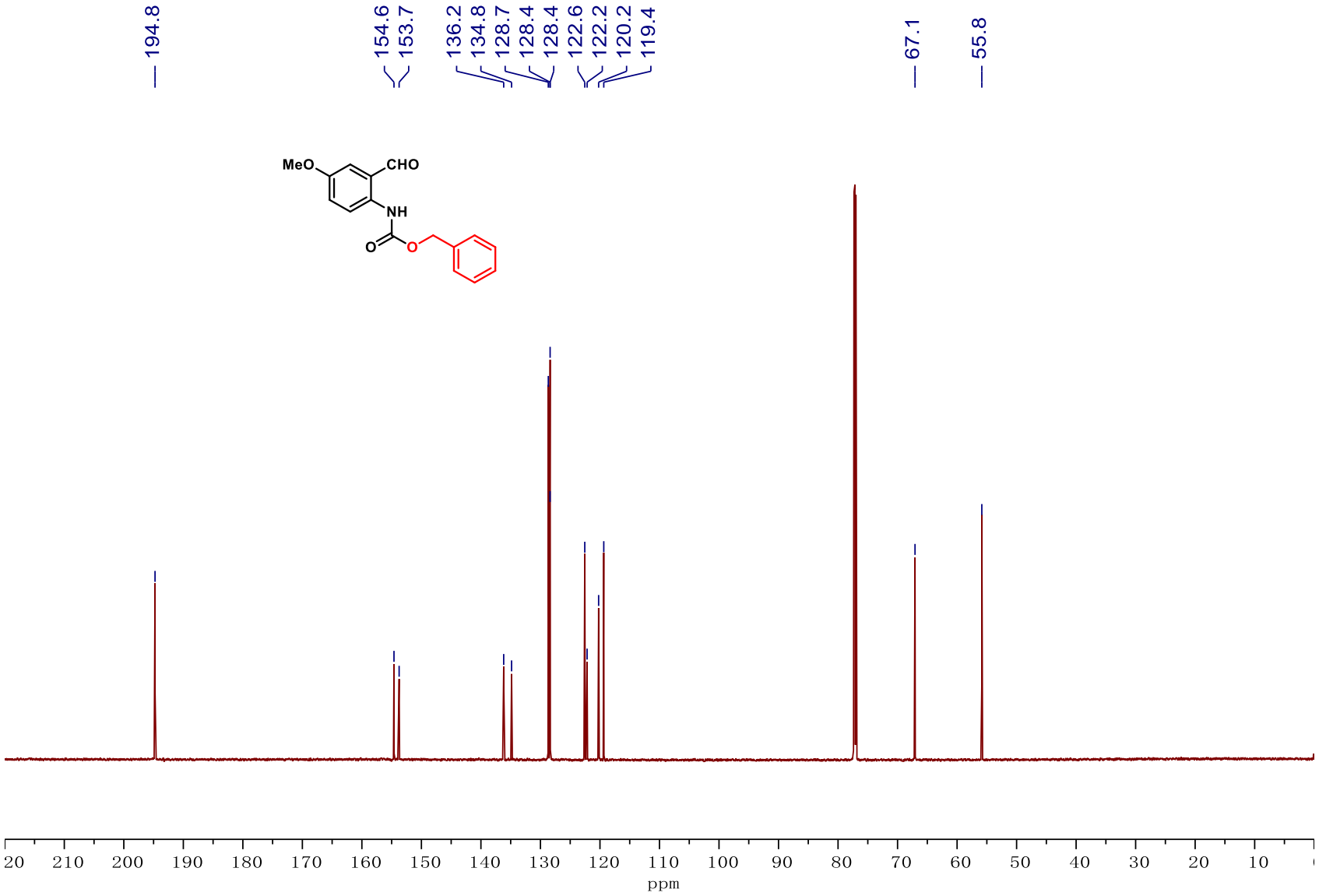

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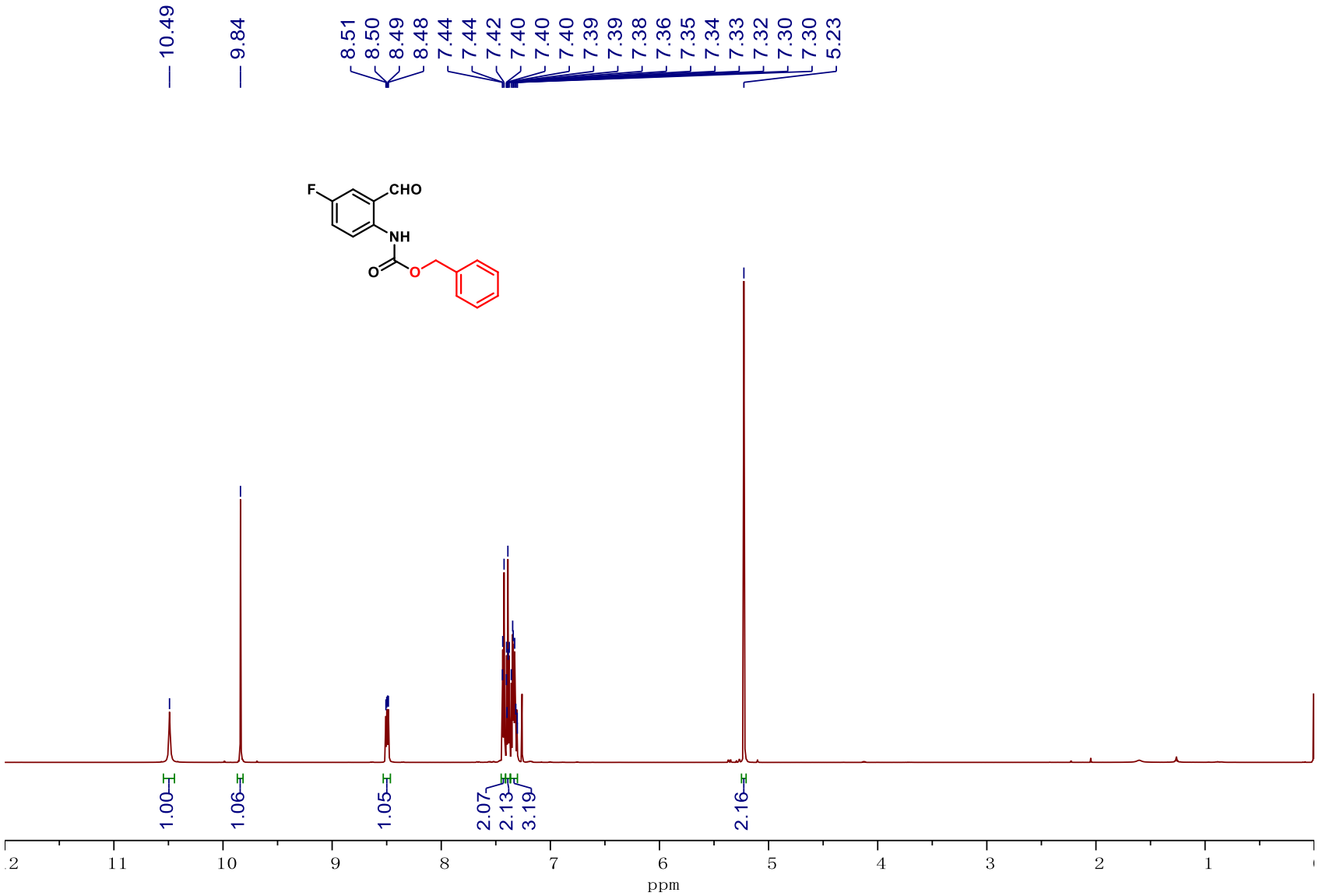

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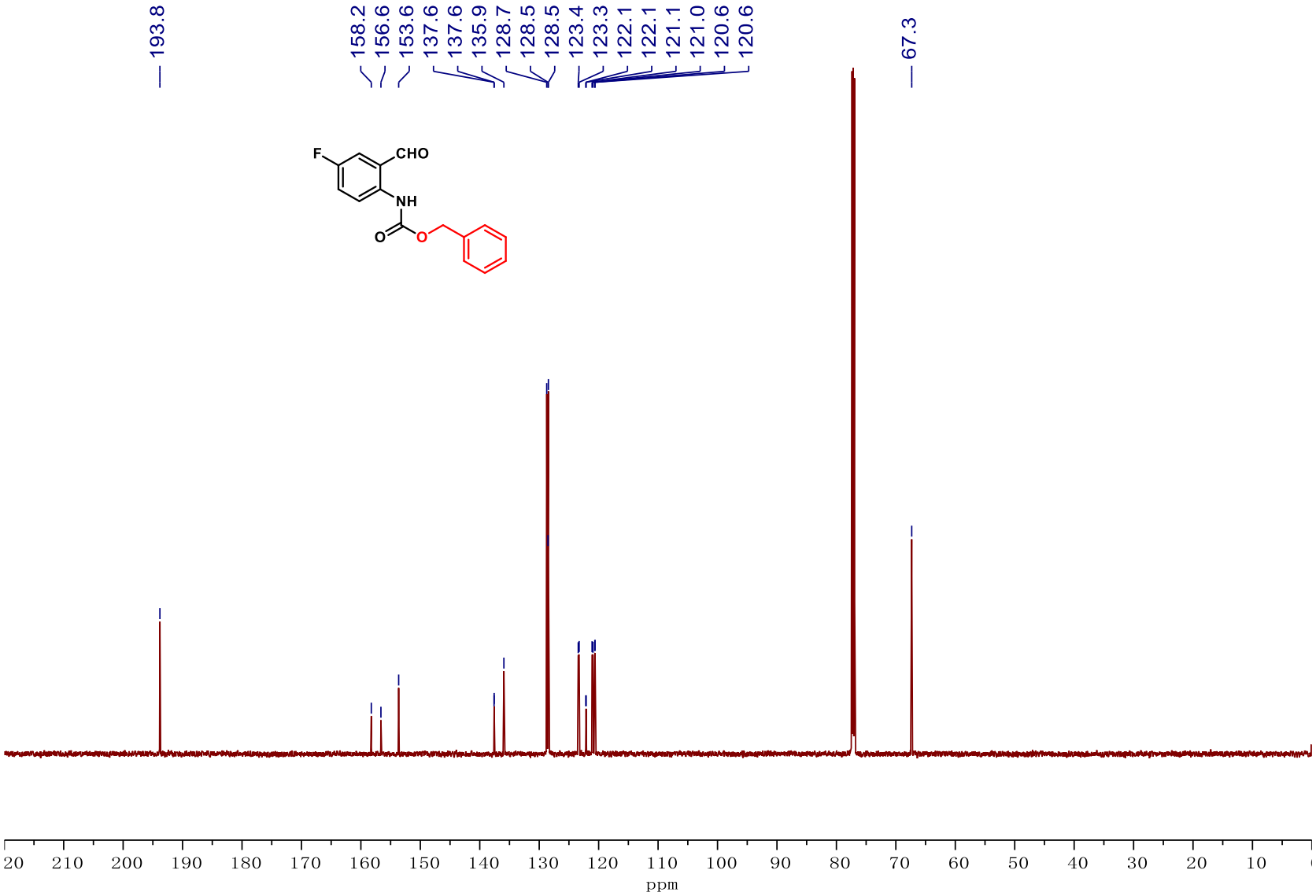
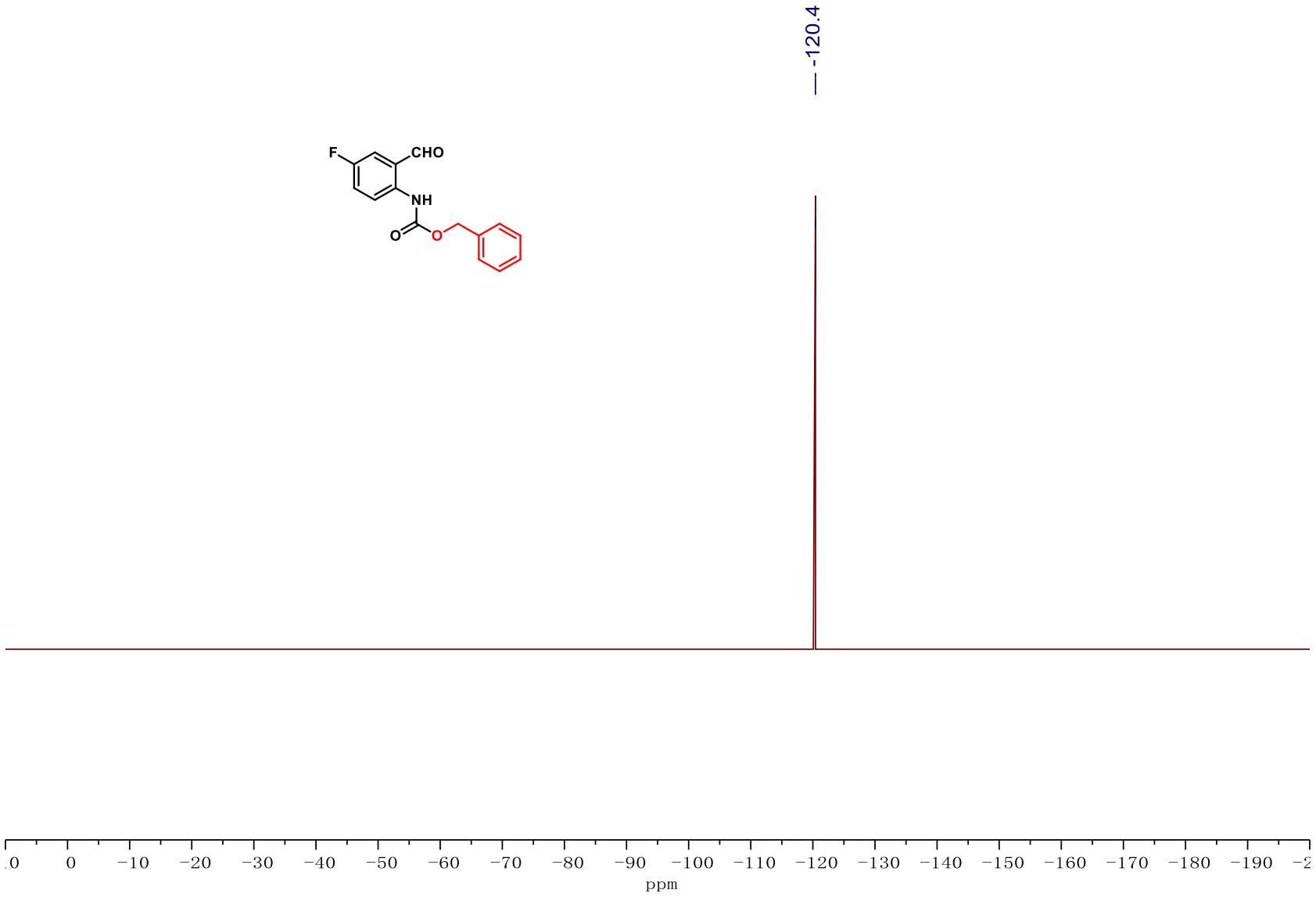


Compound 1l ^{19}F NMR



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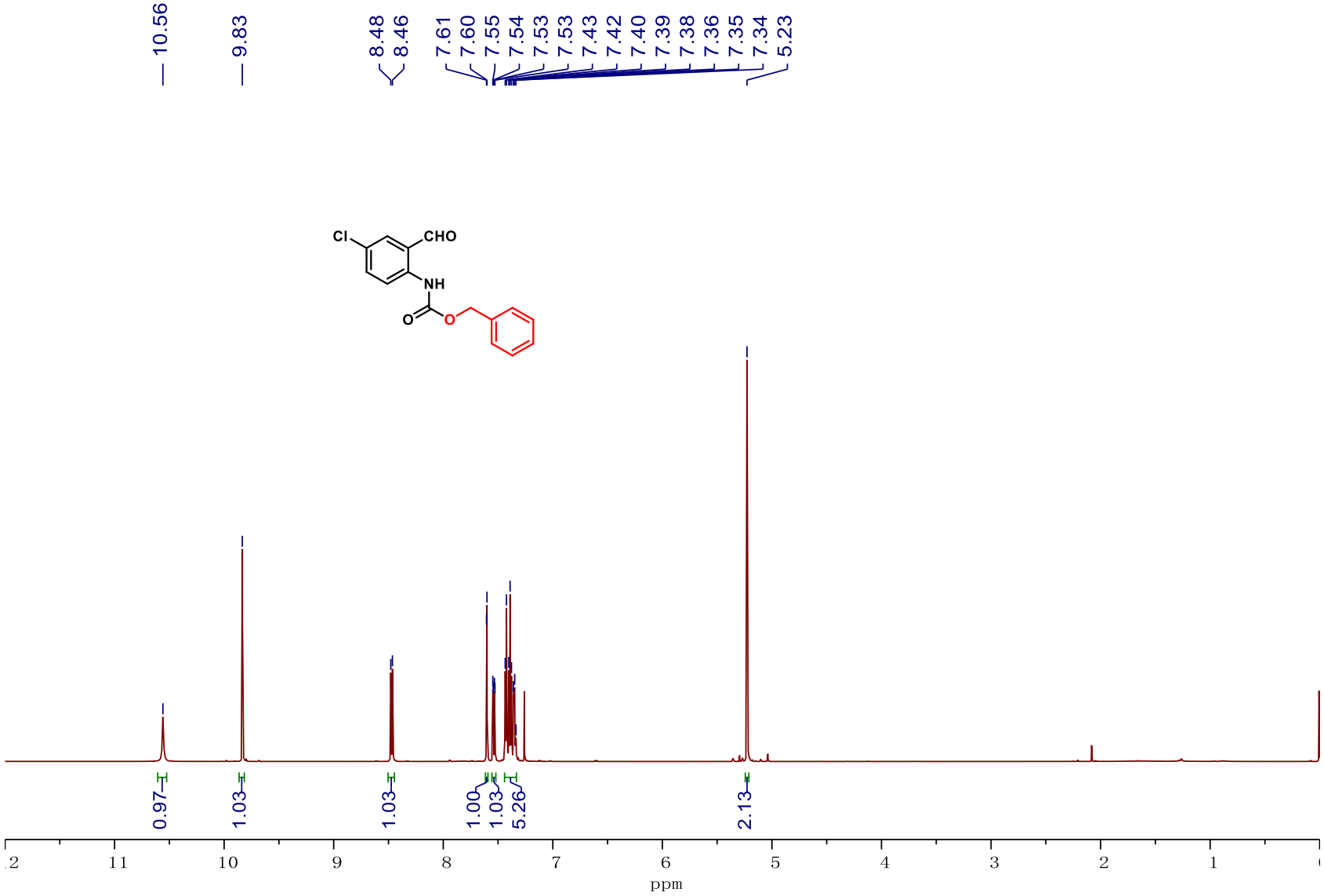

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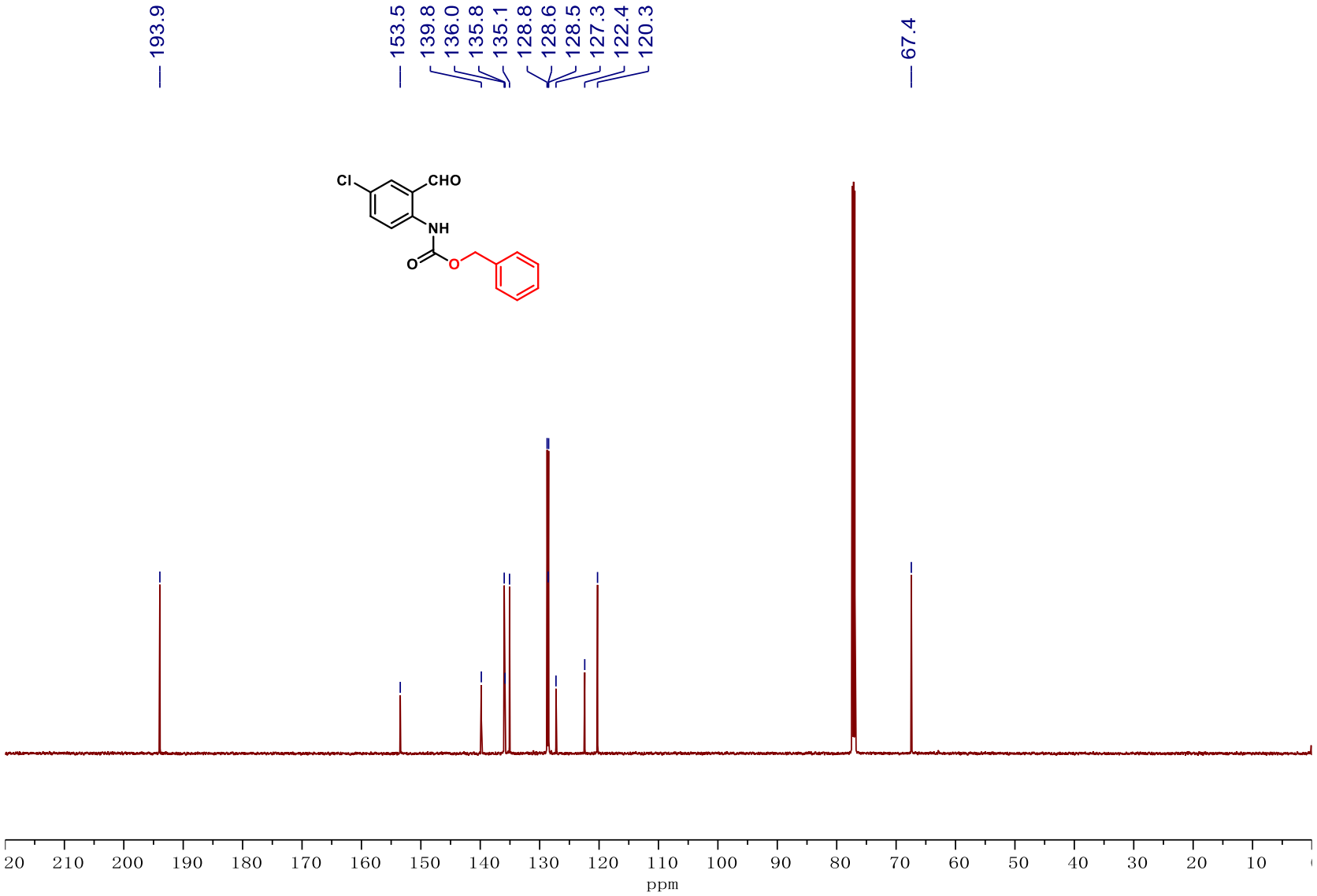

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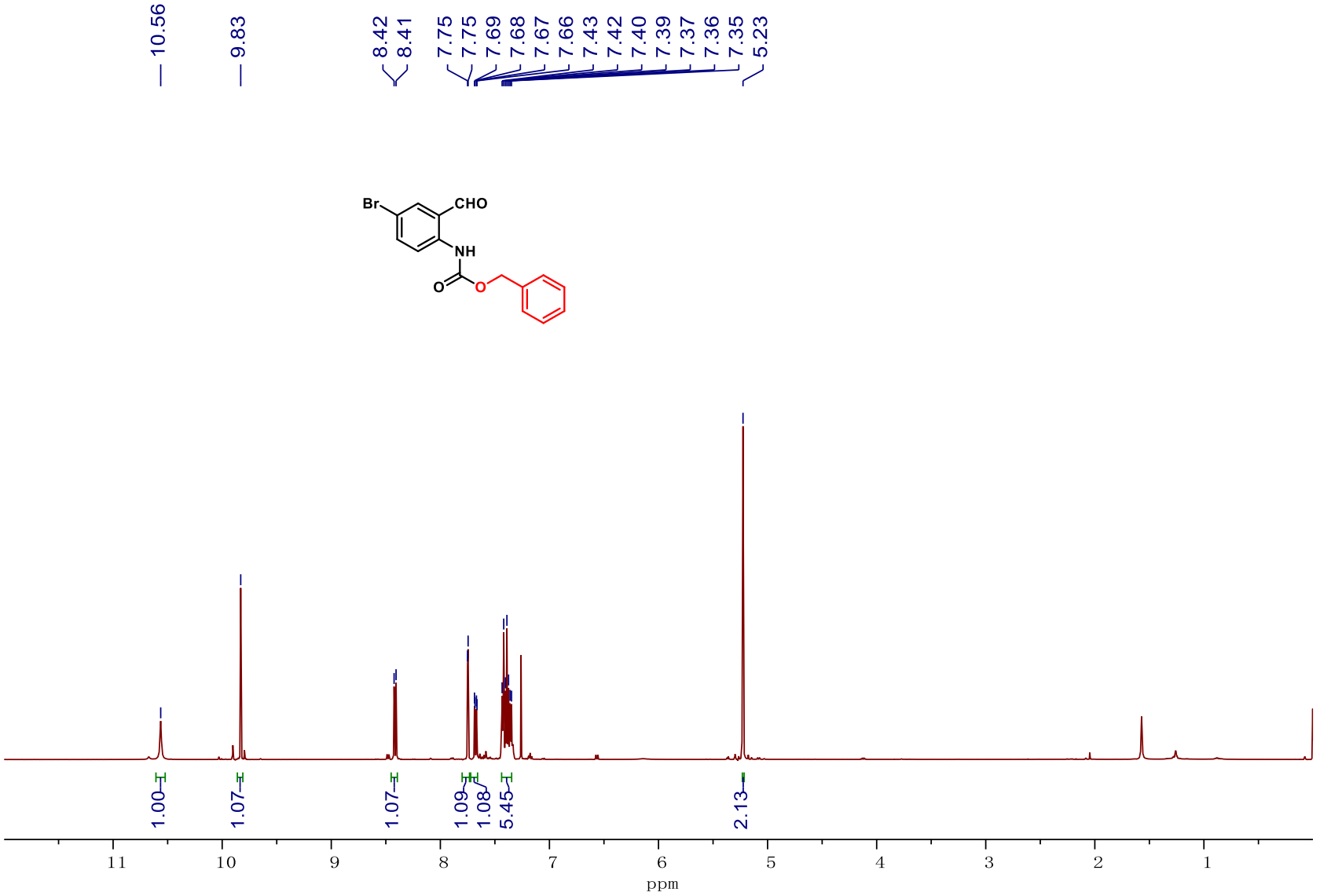

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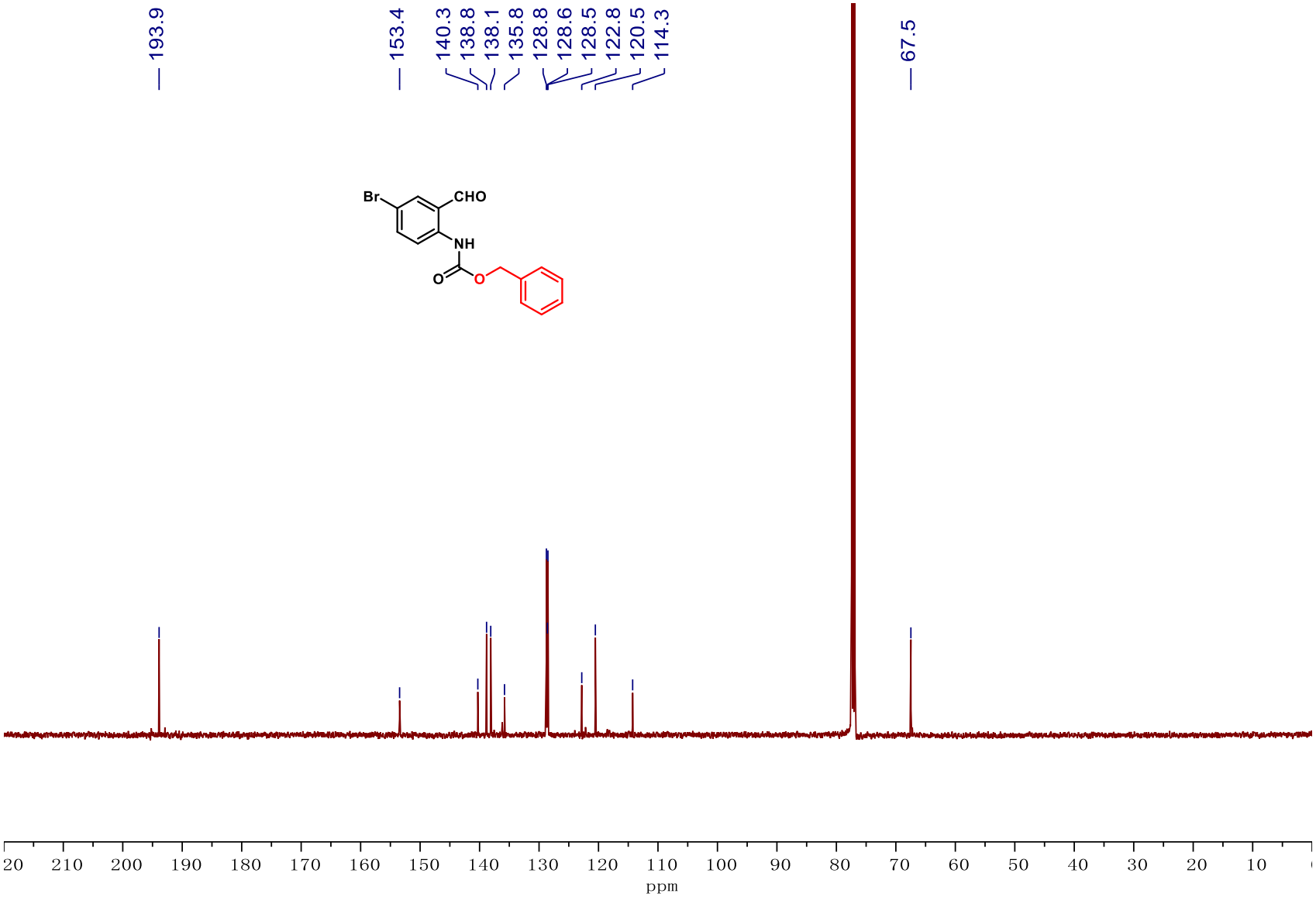

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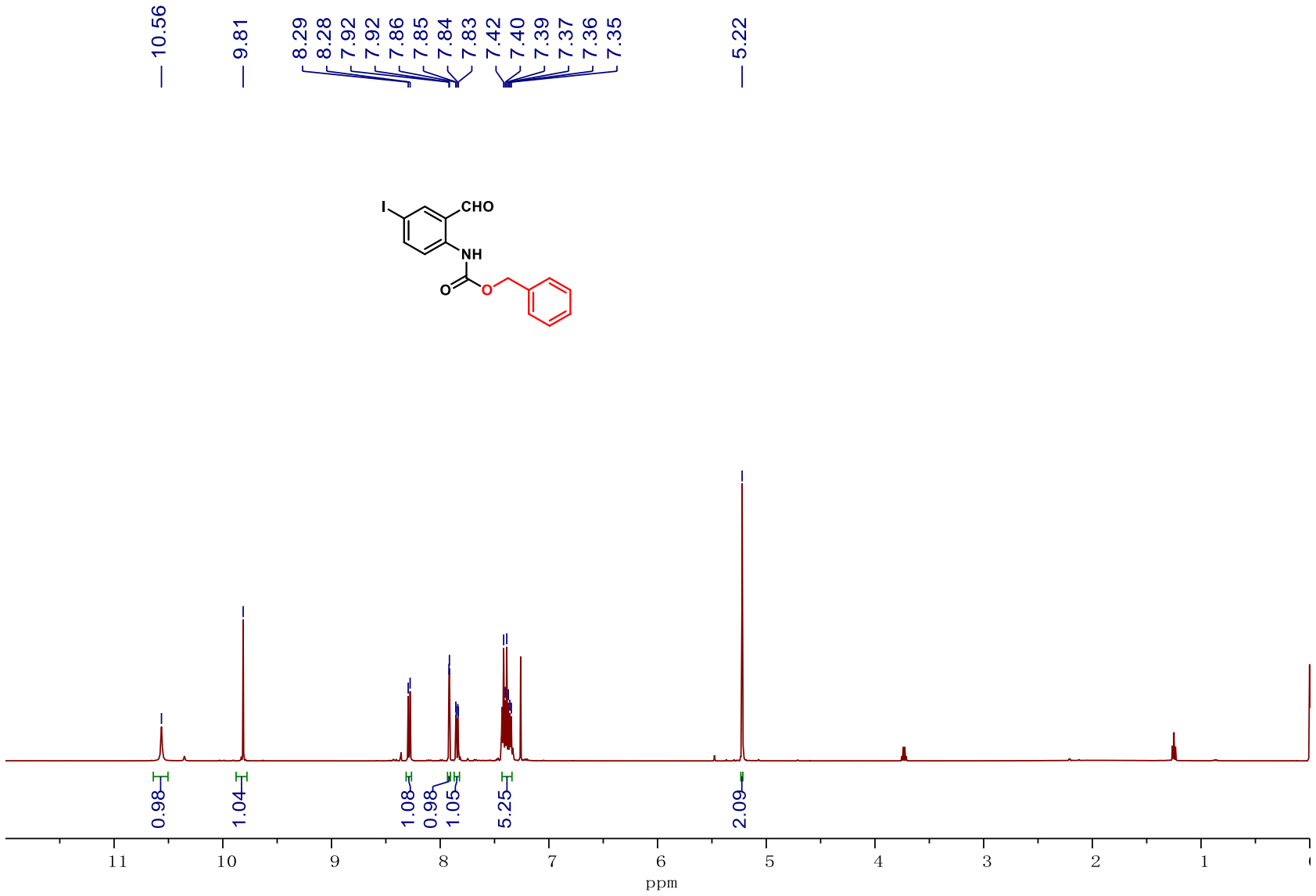

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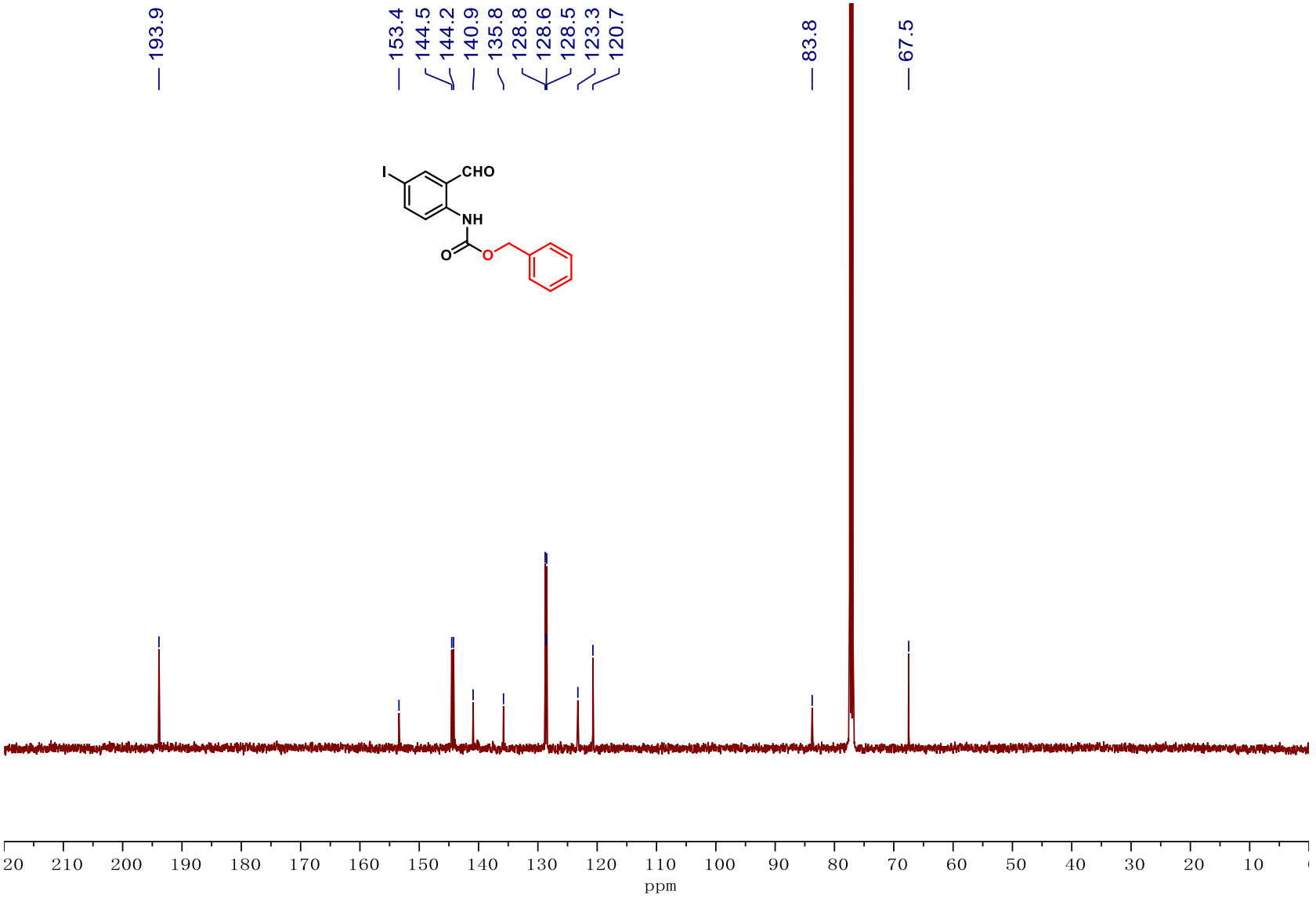
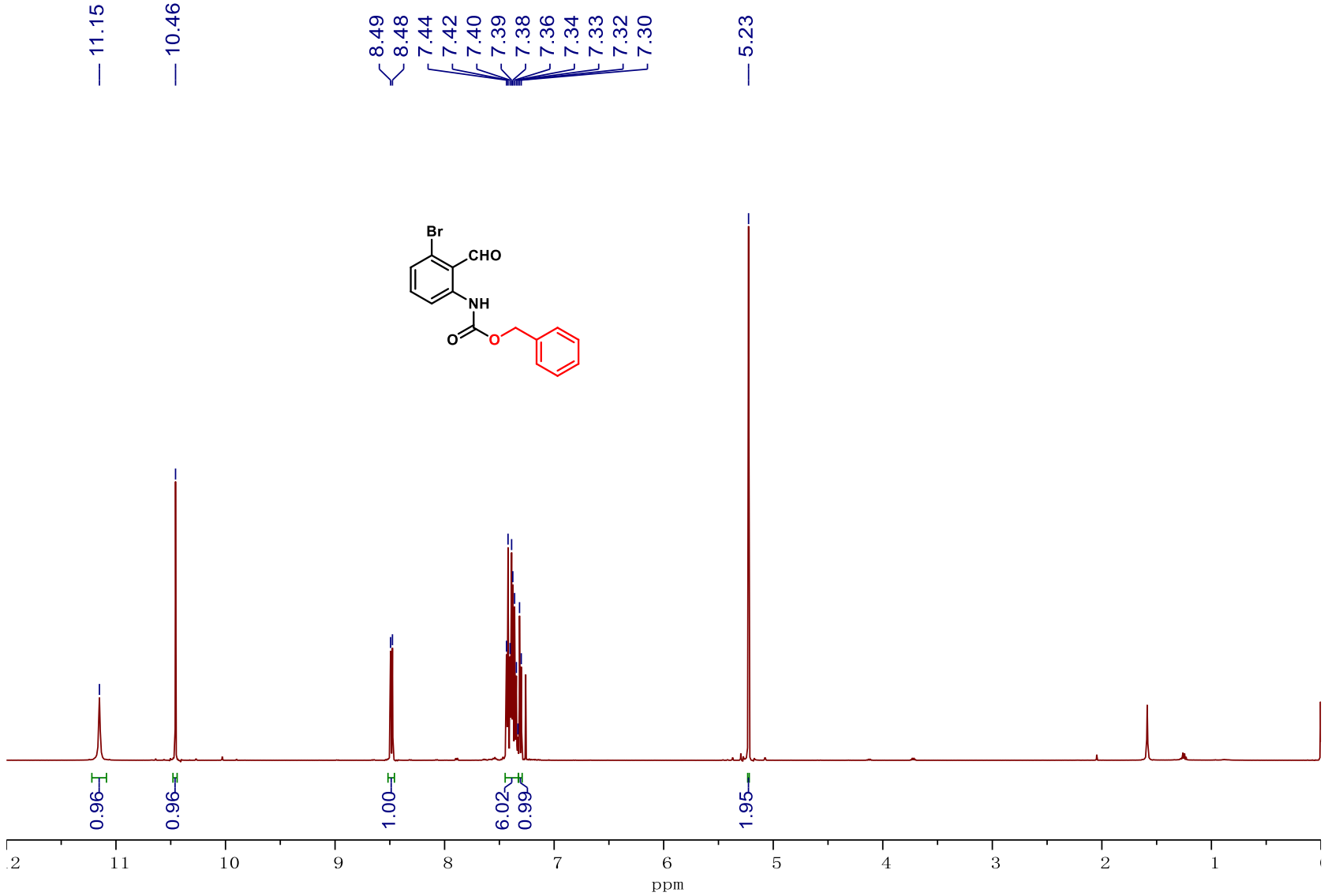


Compound 1p ^{1}H NMR



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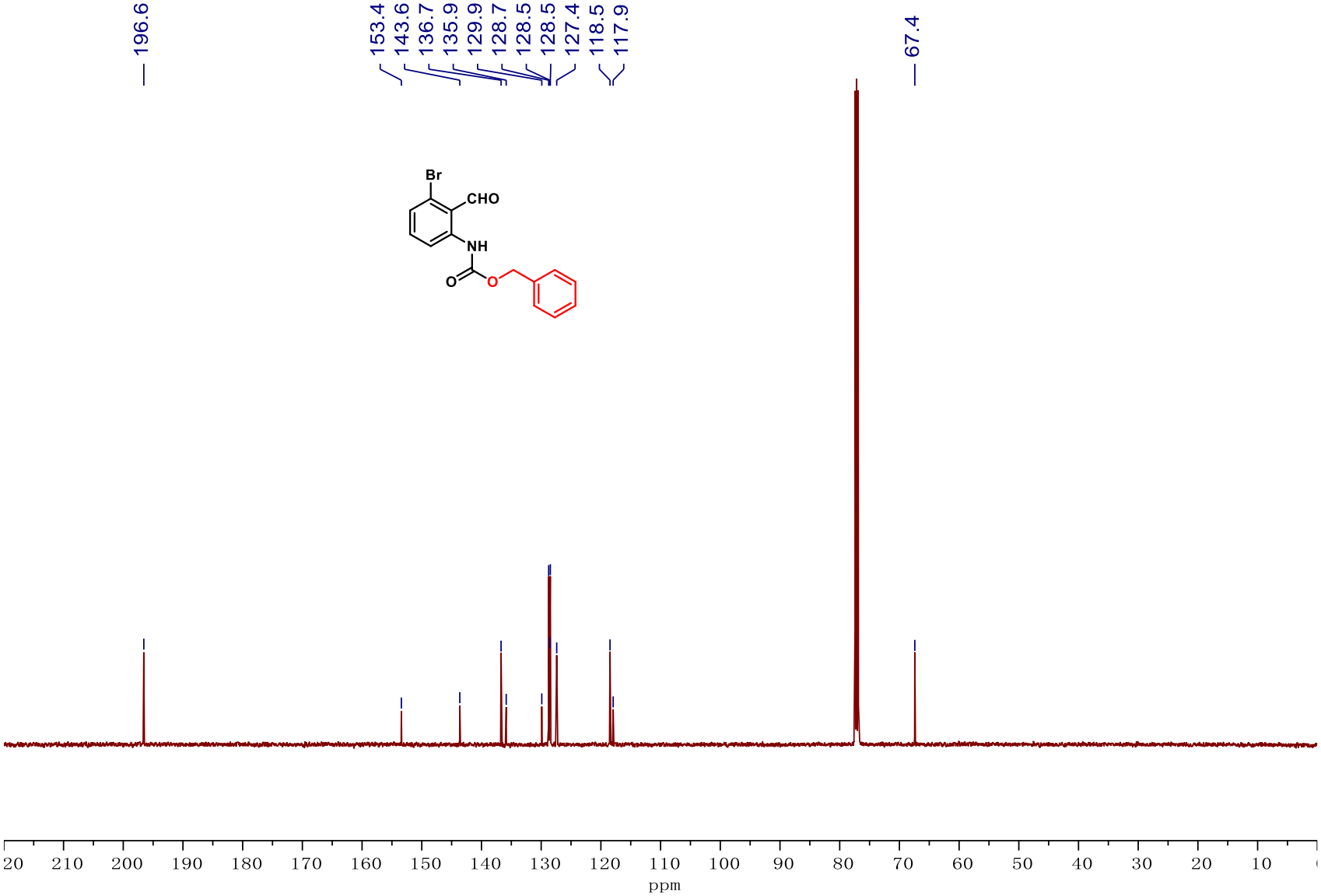

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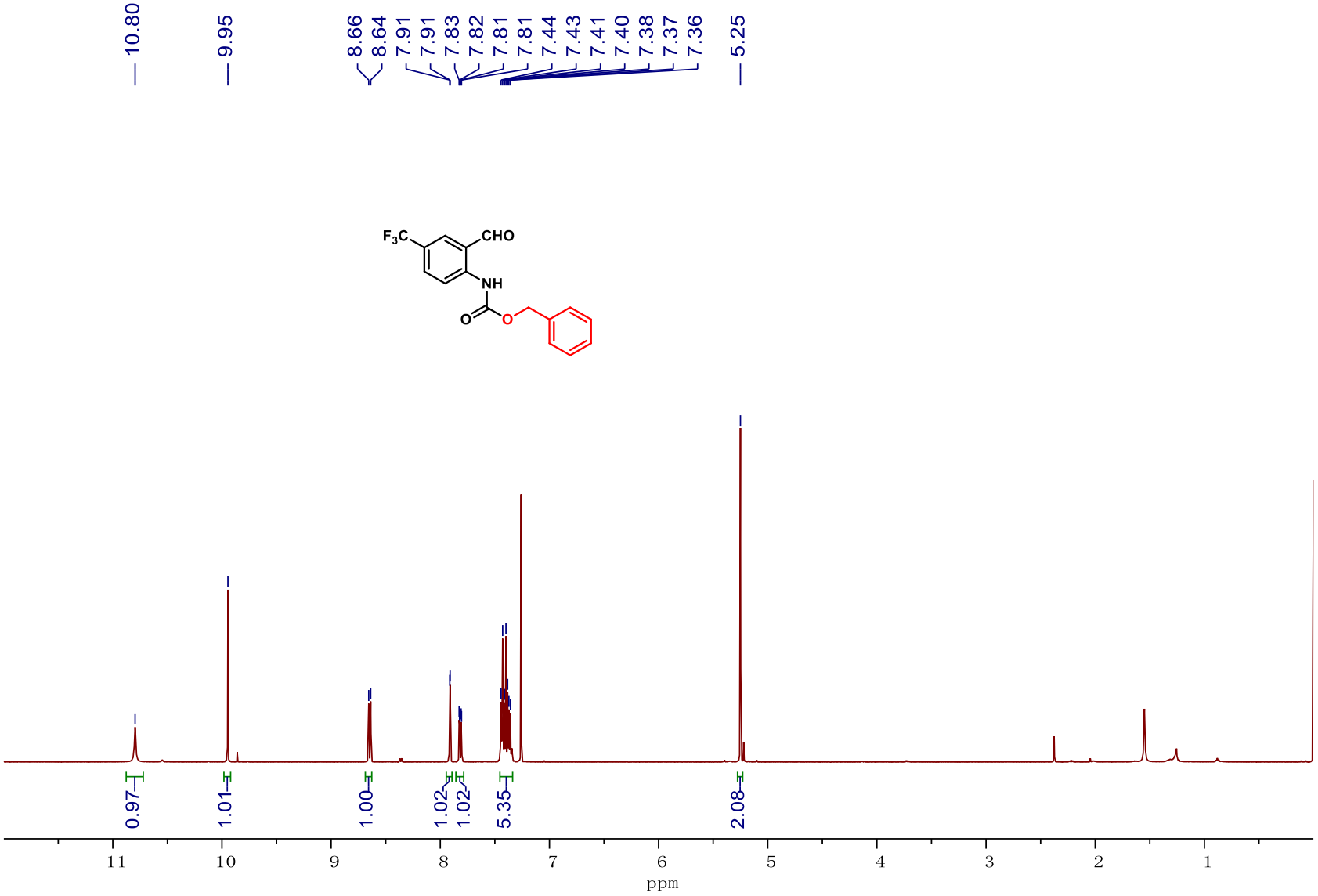

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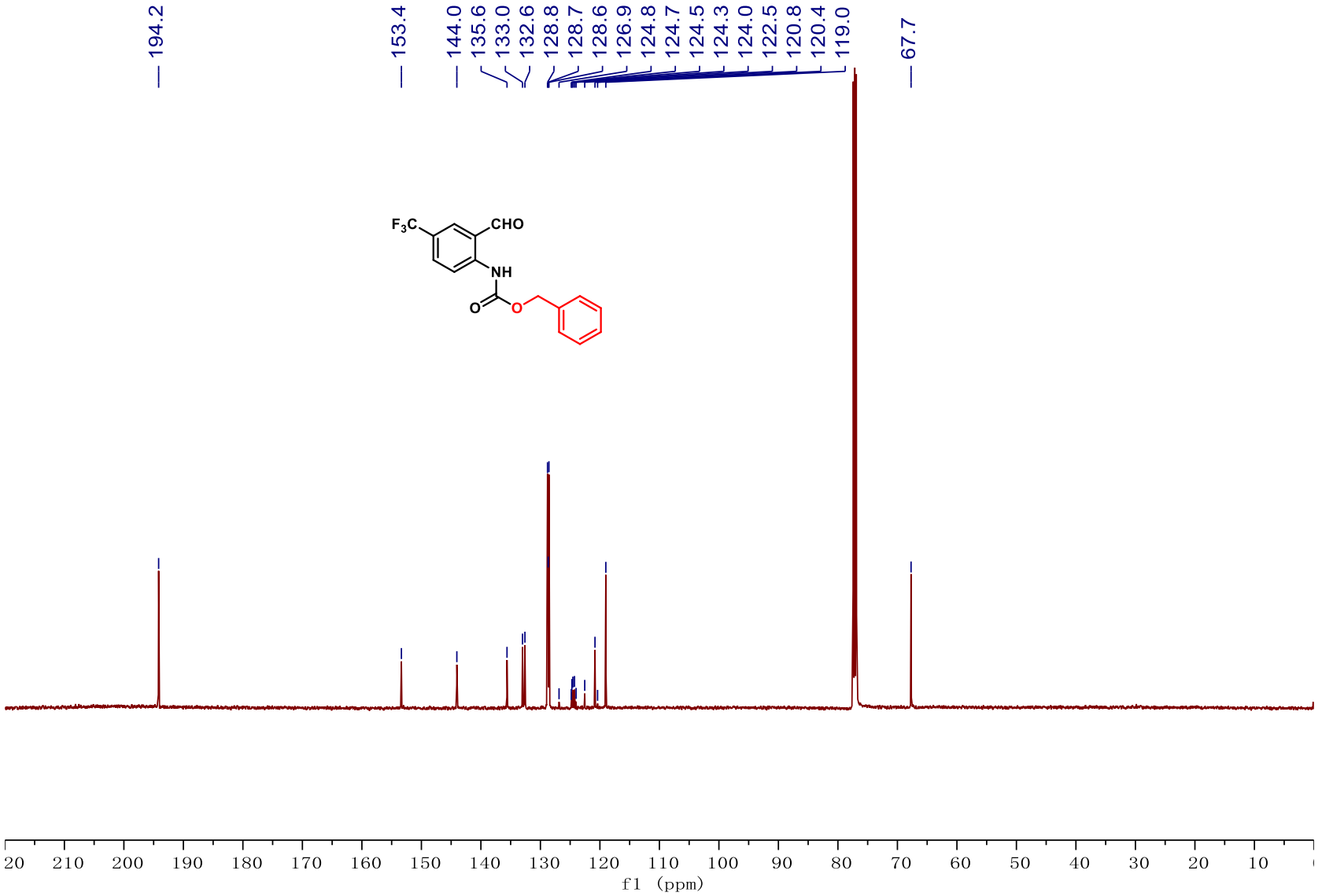
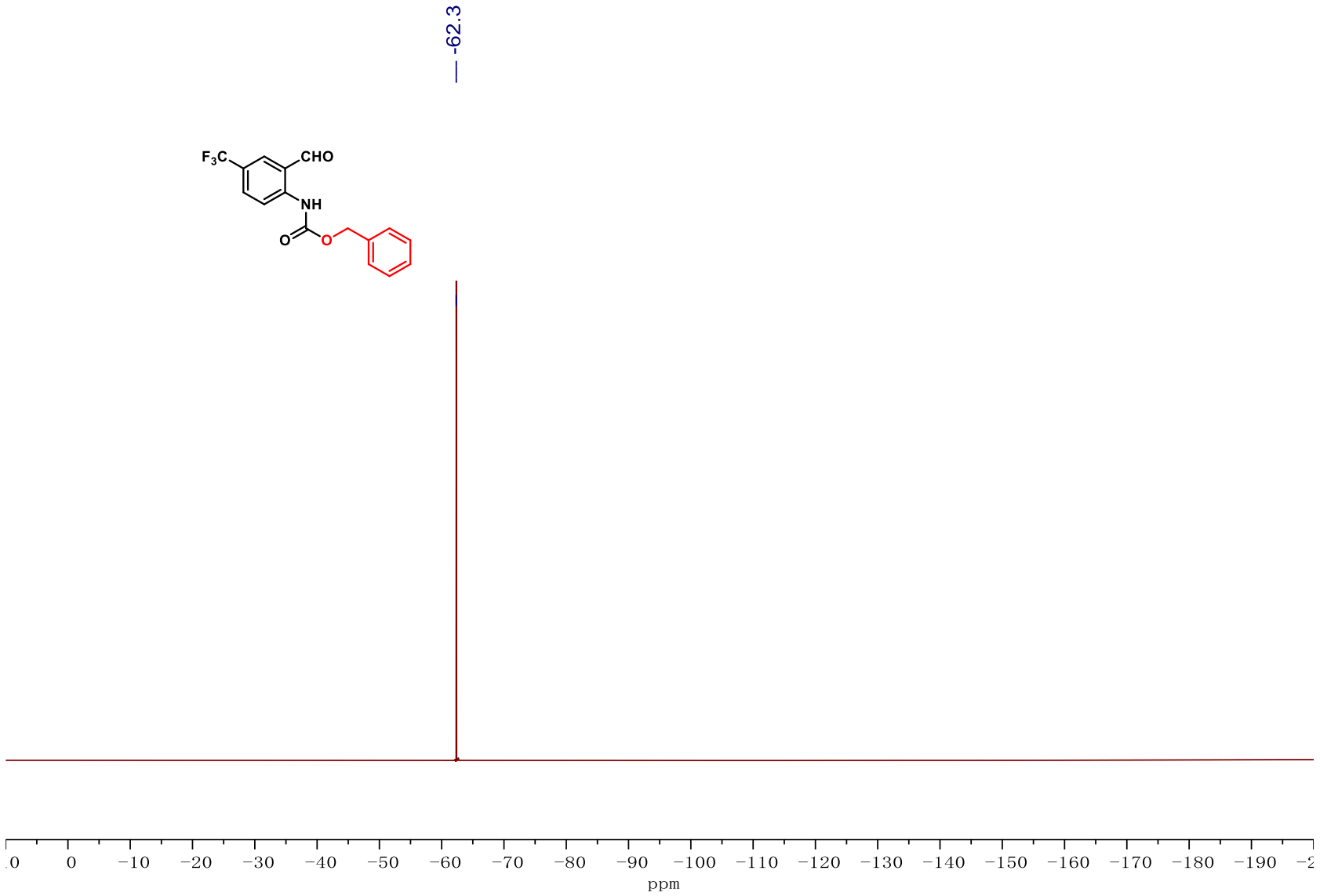


Compound 1q ^{19}F NMR



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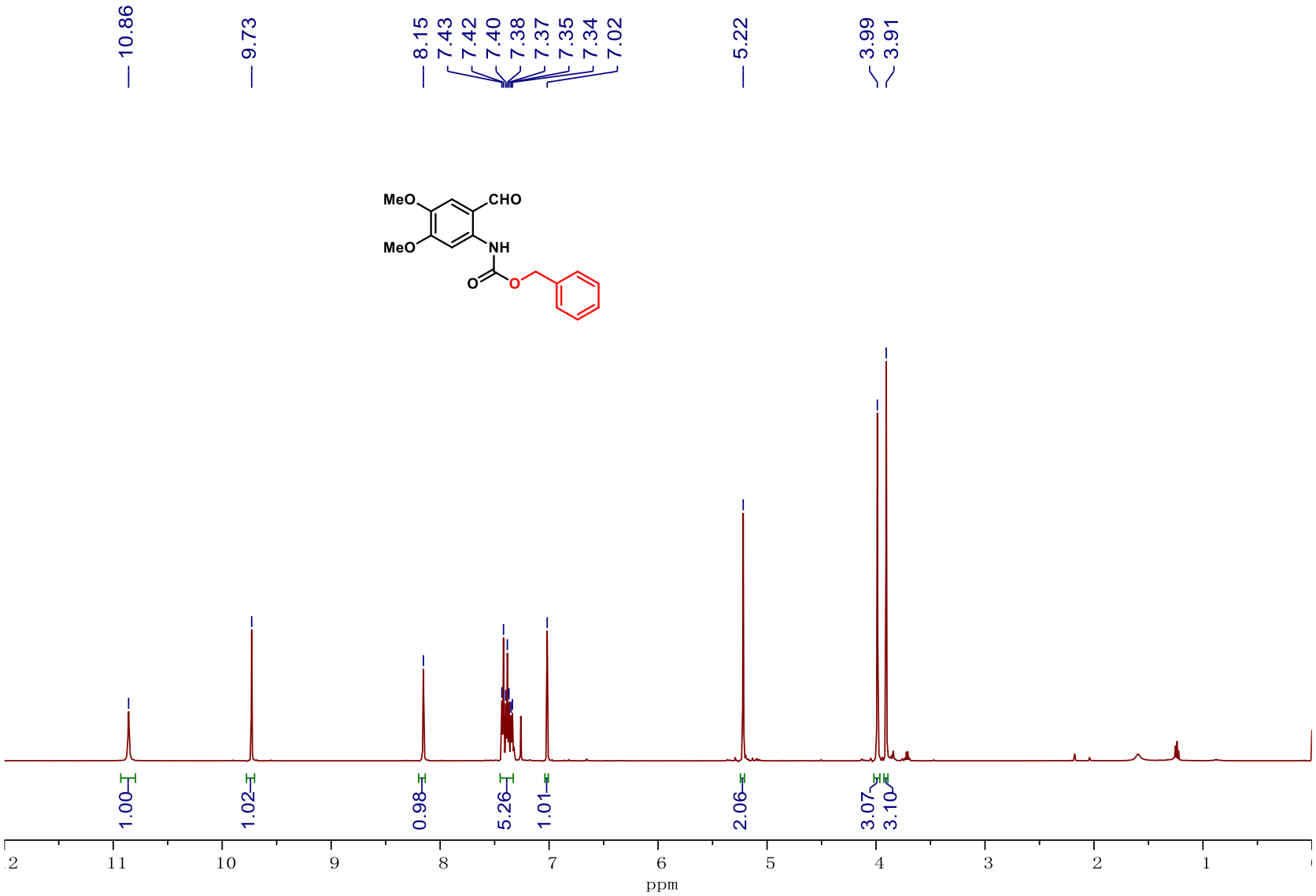

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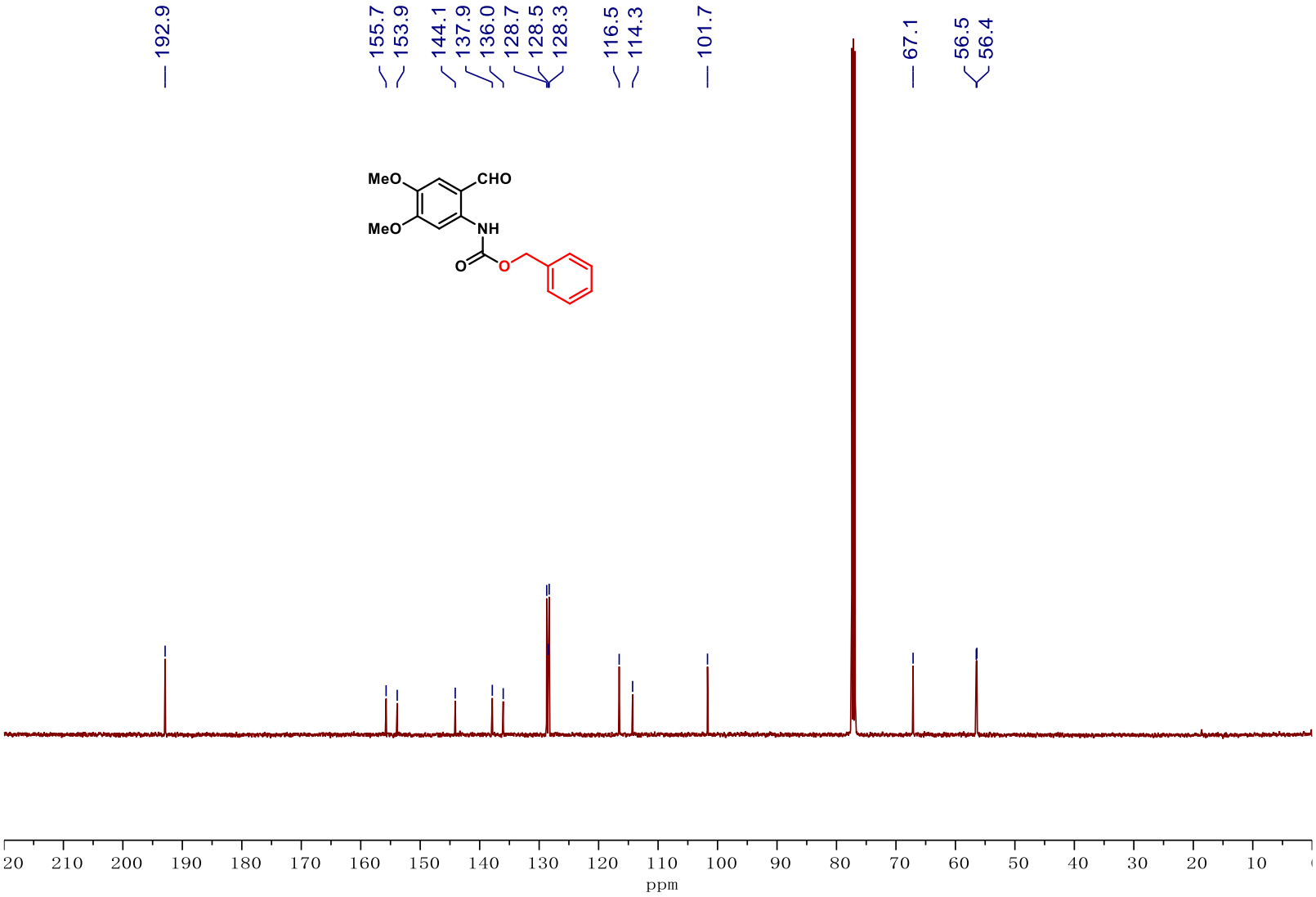
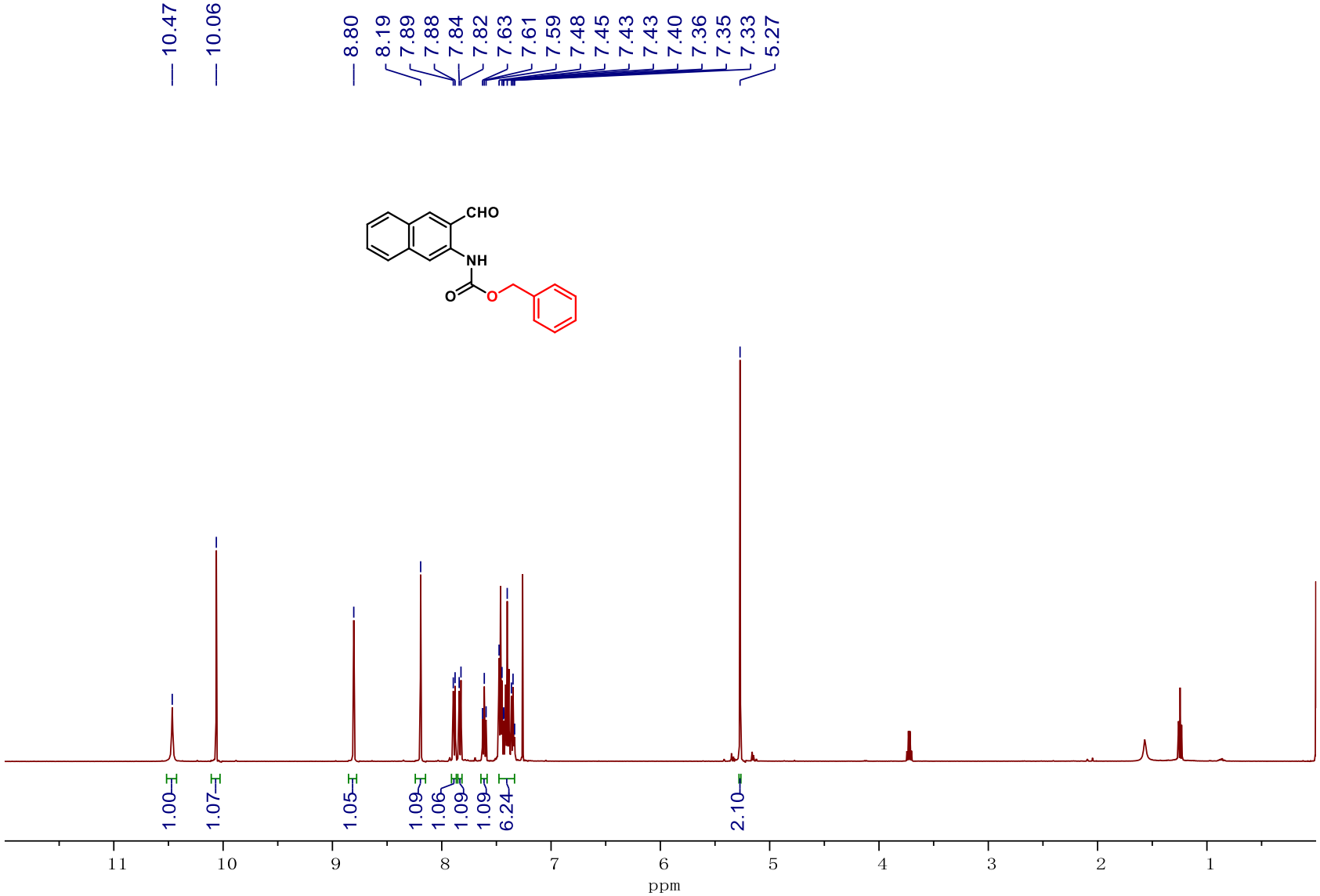
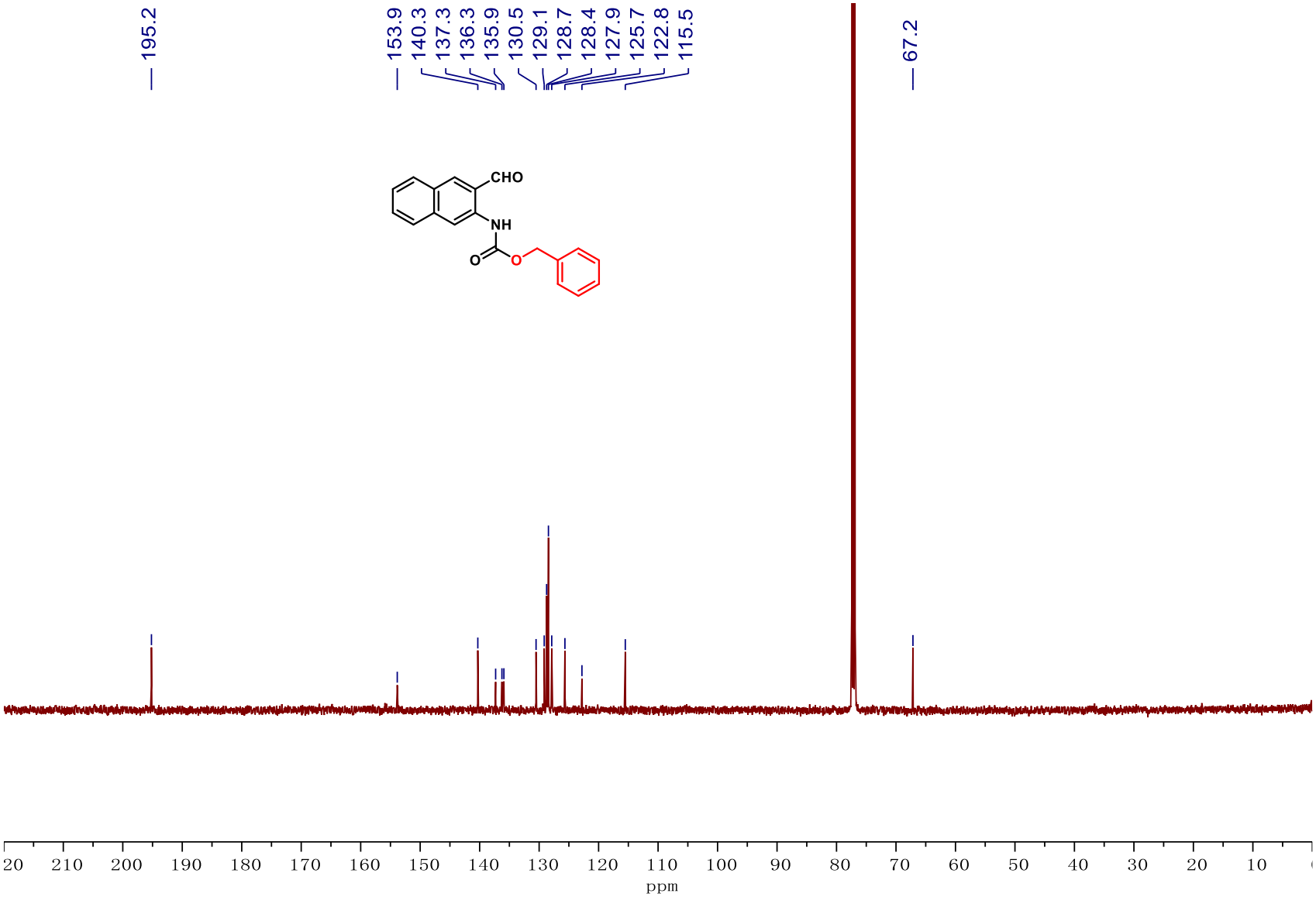


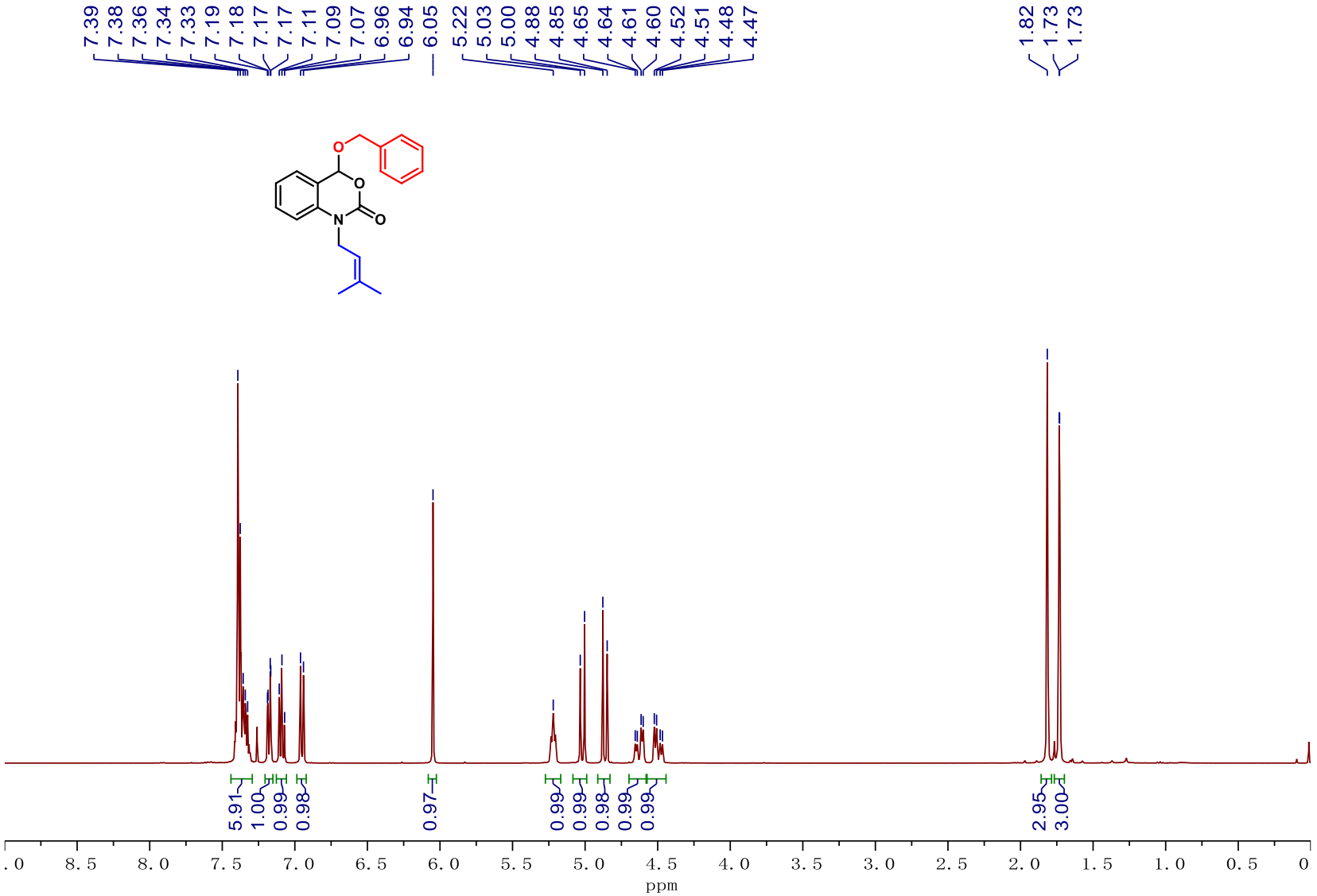
Compound 1s ^{1}H NMR



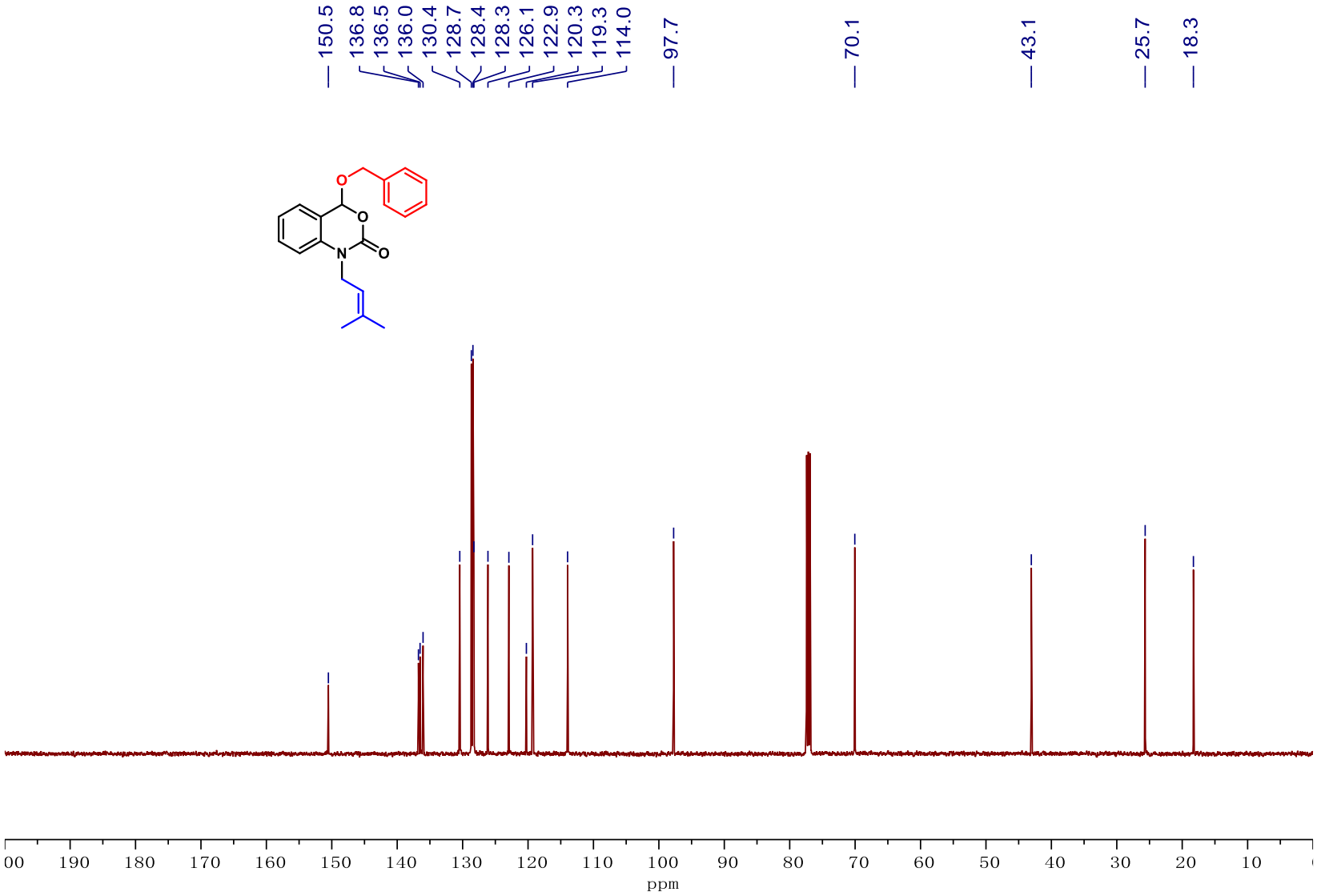
Compound 1s ^{13}C NMR



Compound 3a ^{1}H NMR



Compound 3a ^{13}C NMR



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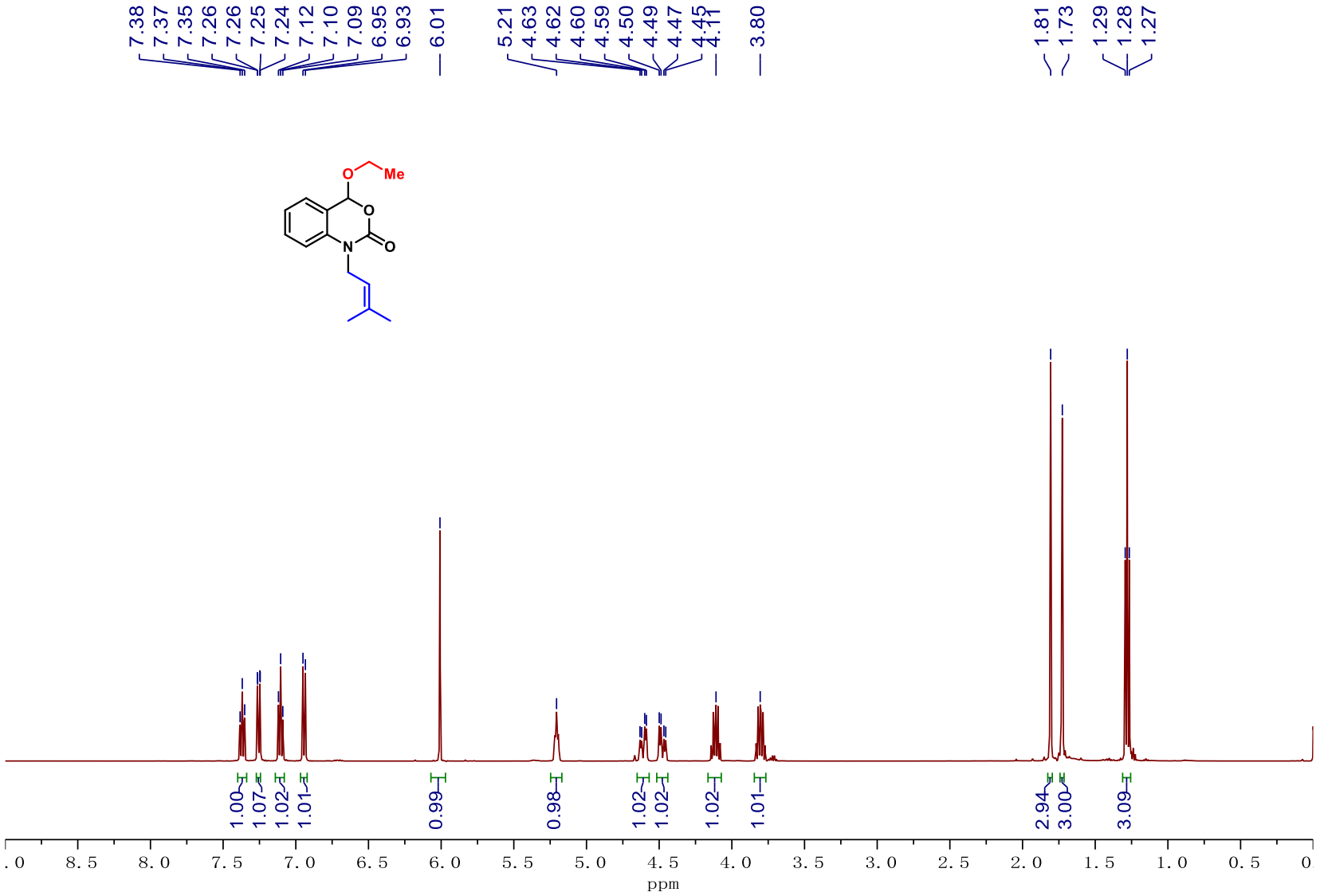

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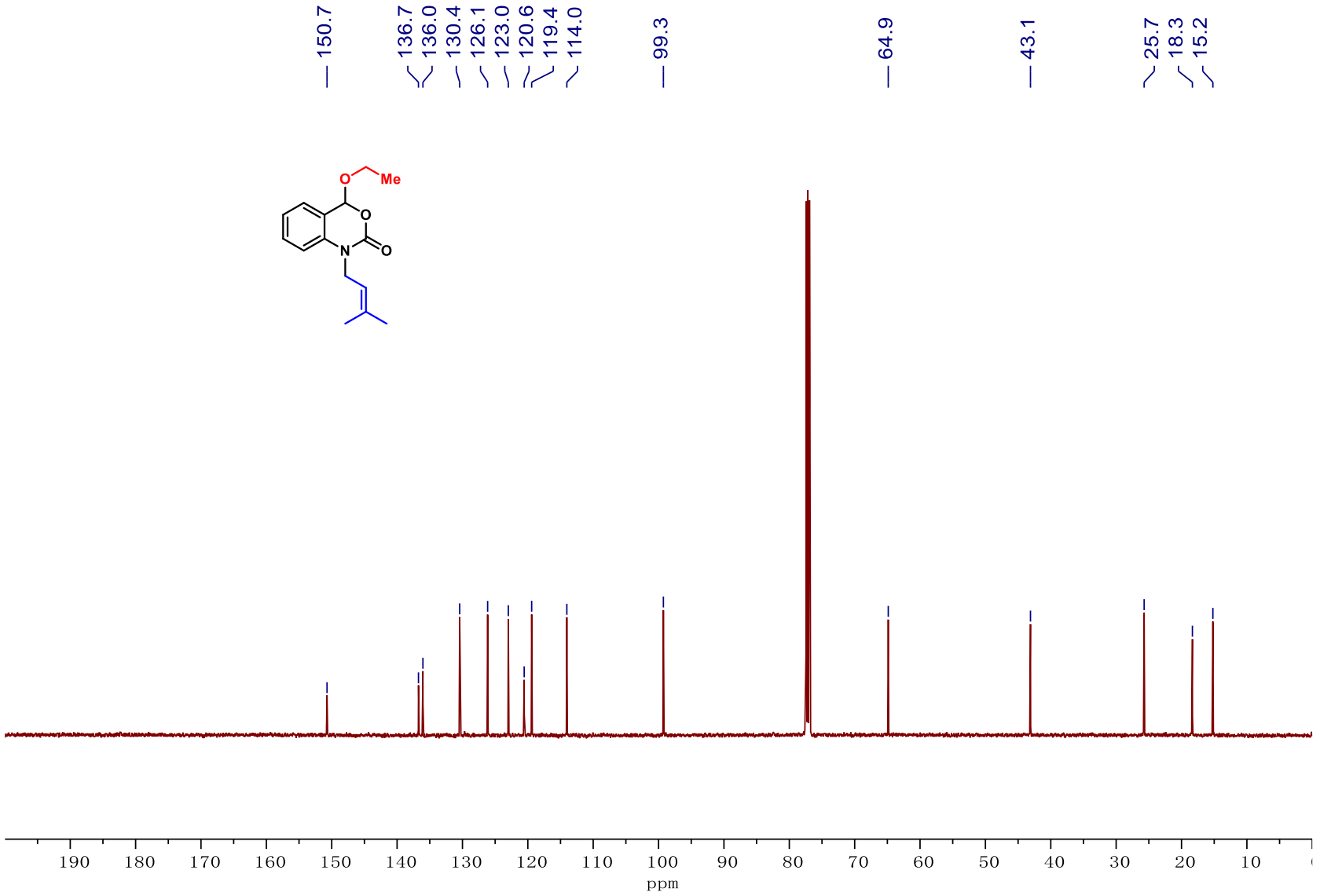

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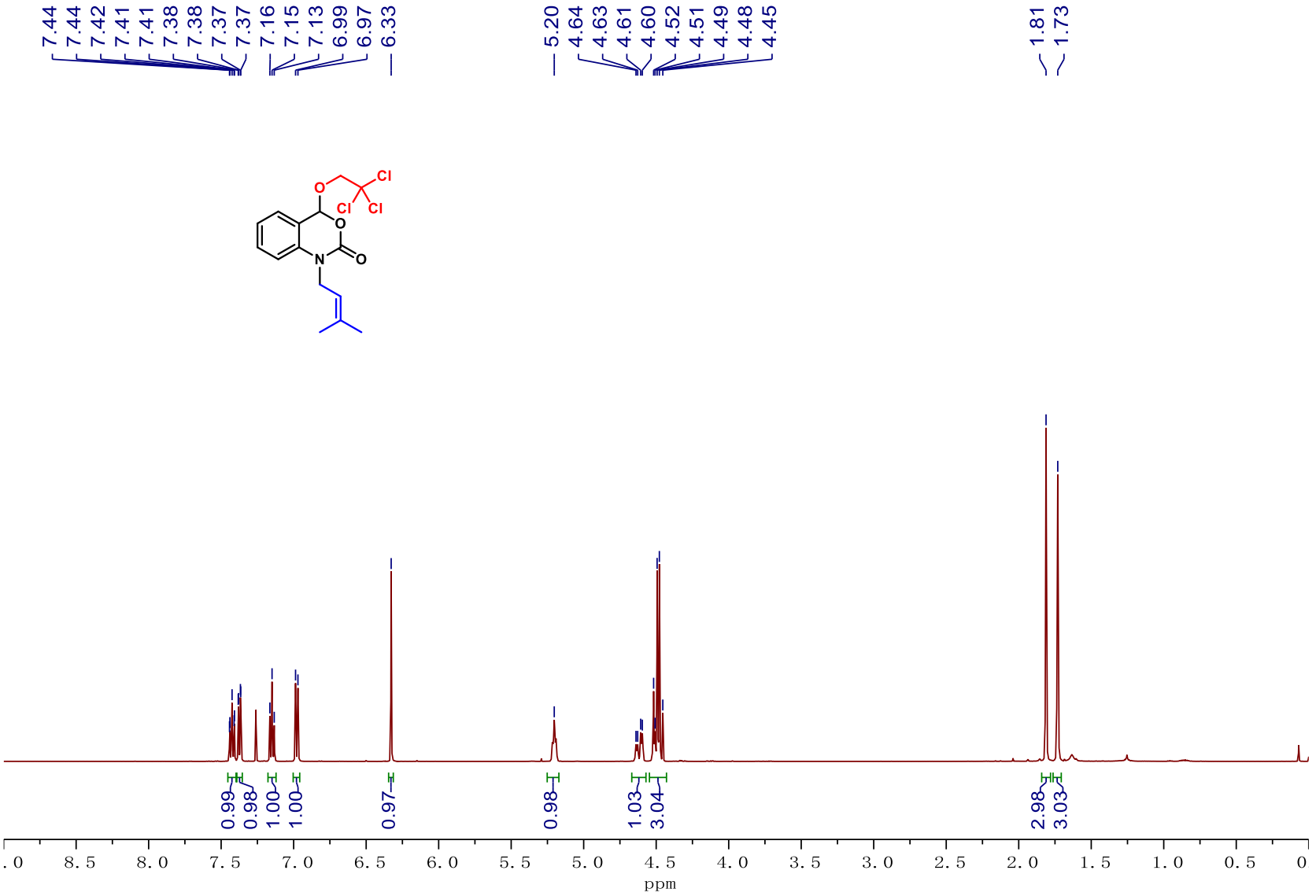

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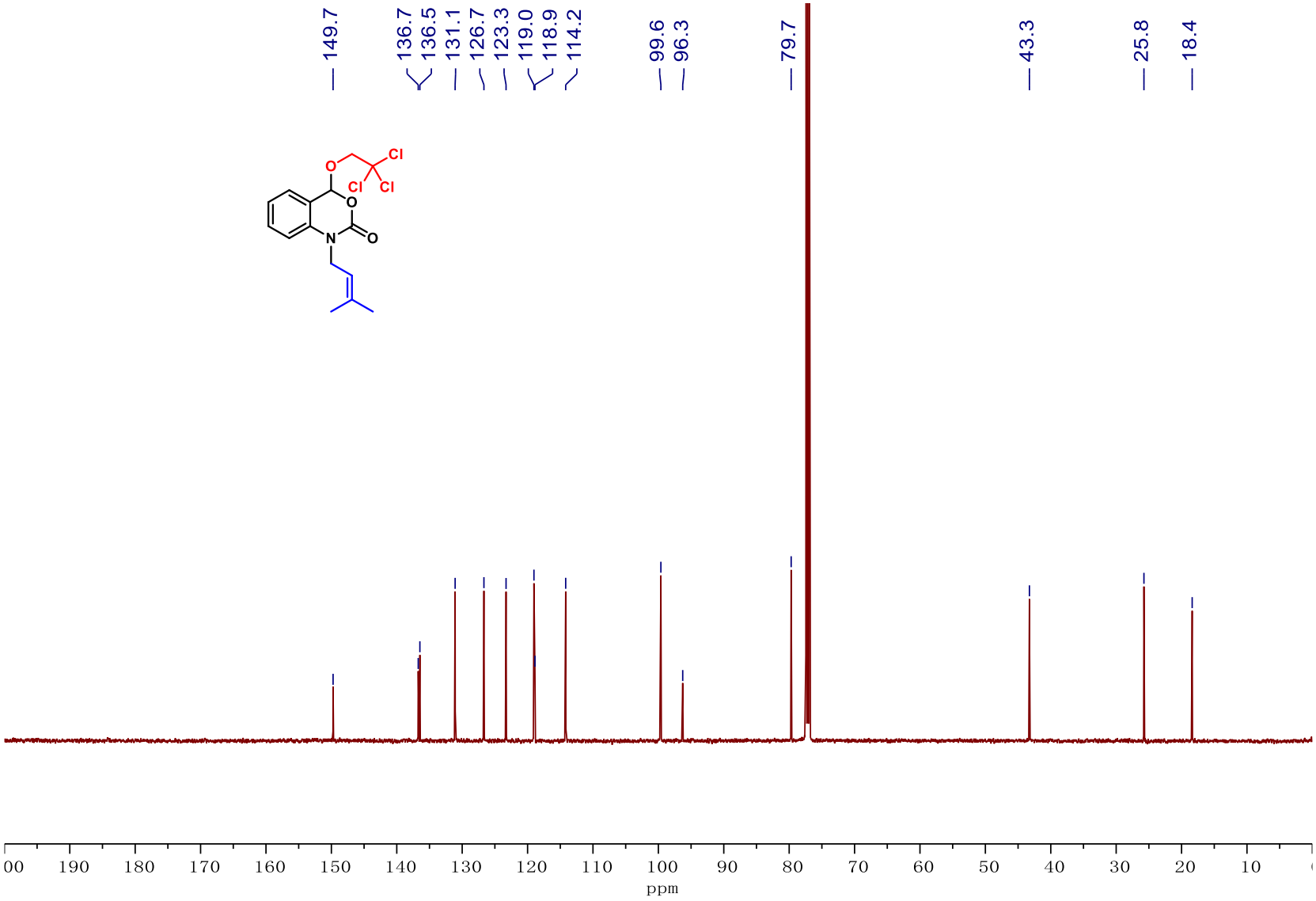

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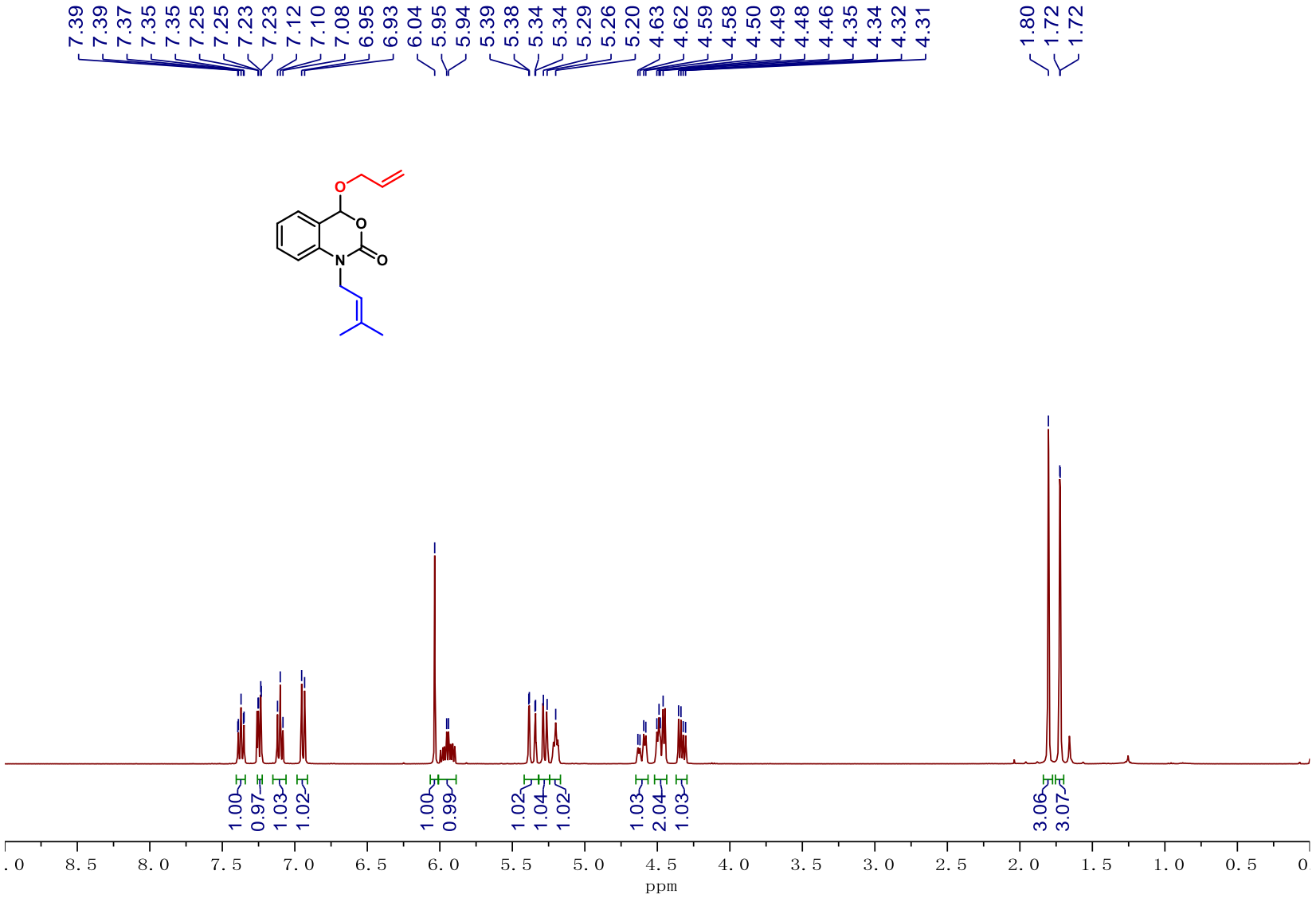

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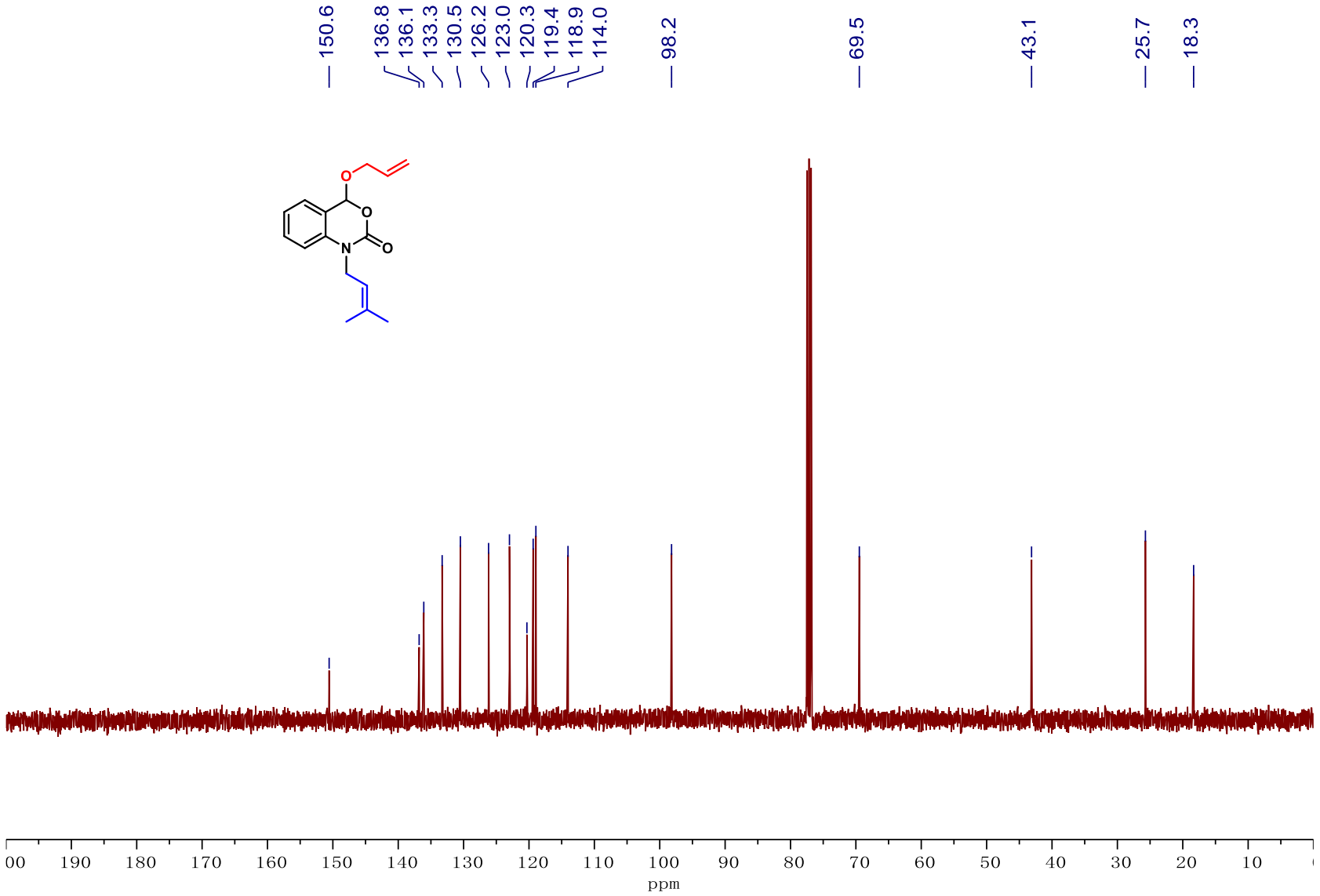

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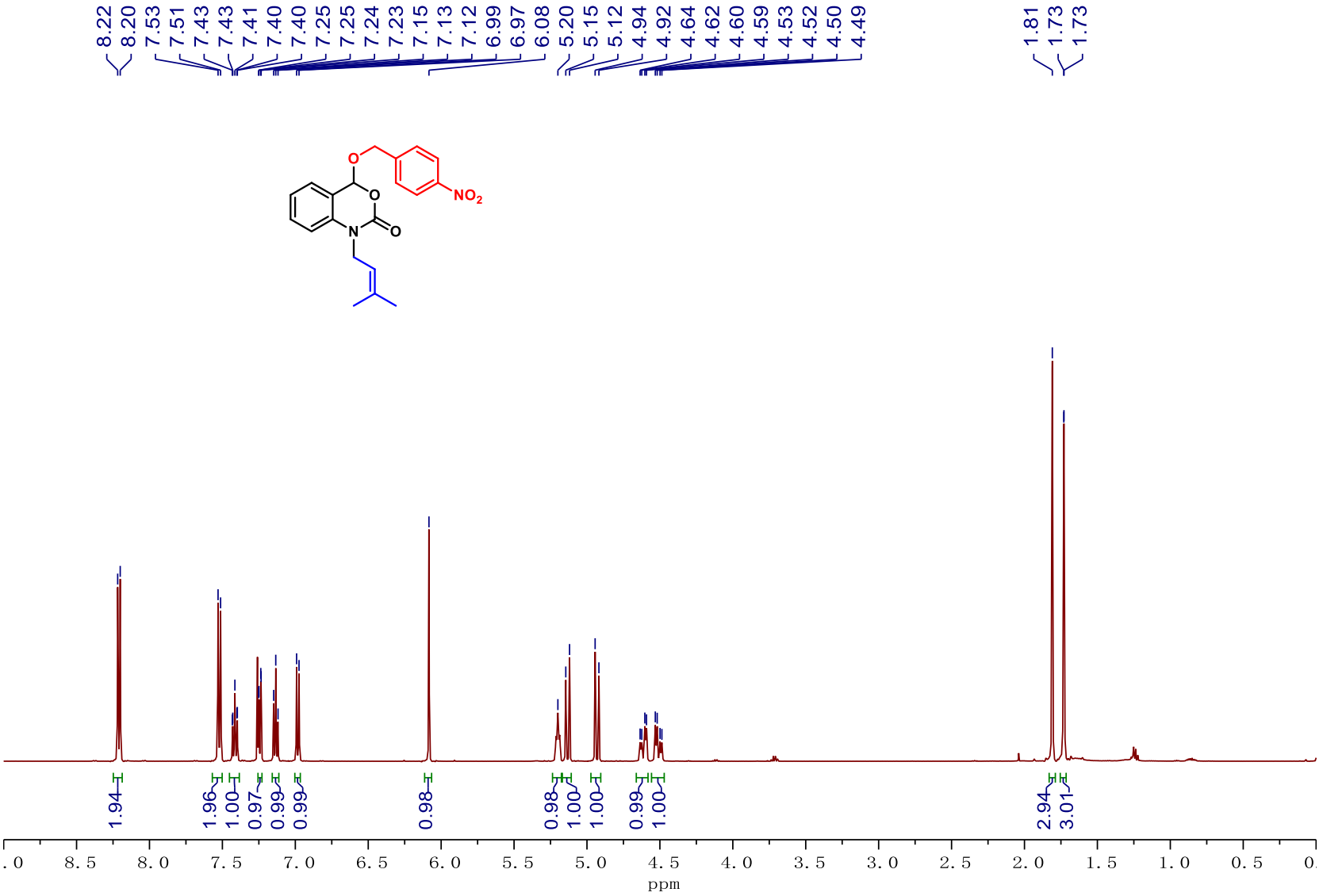

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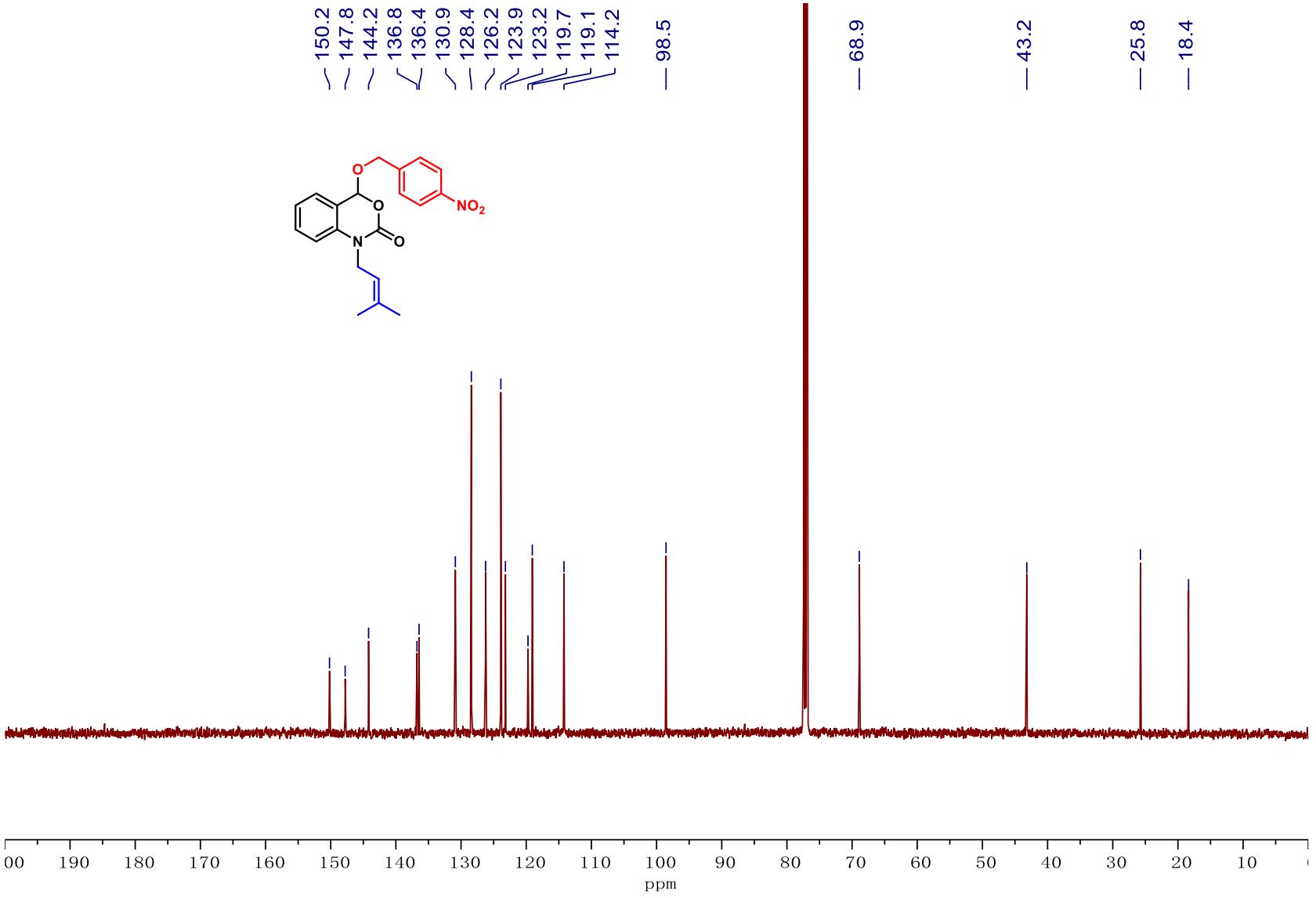
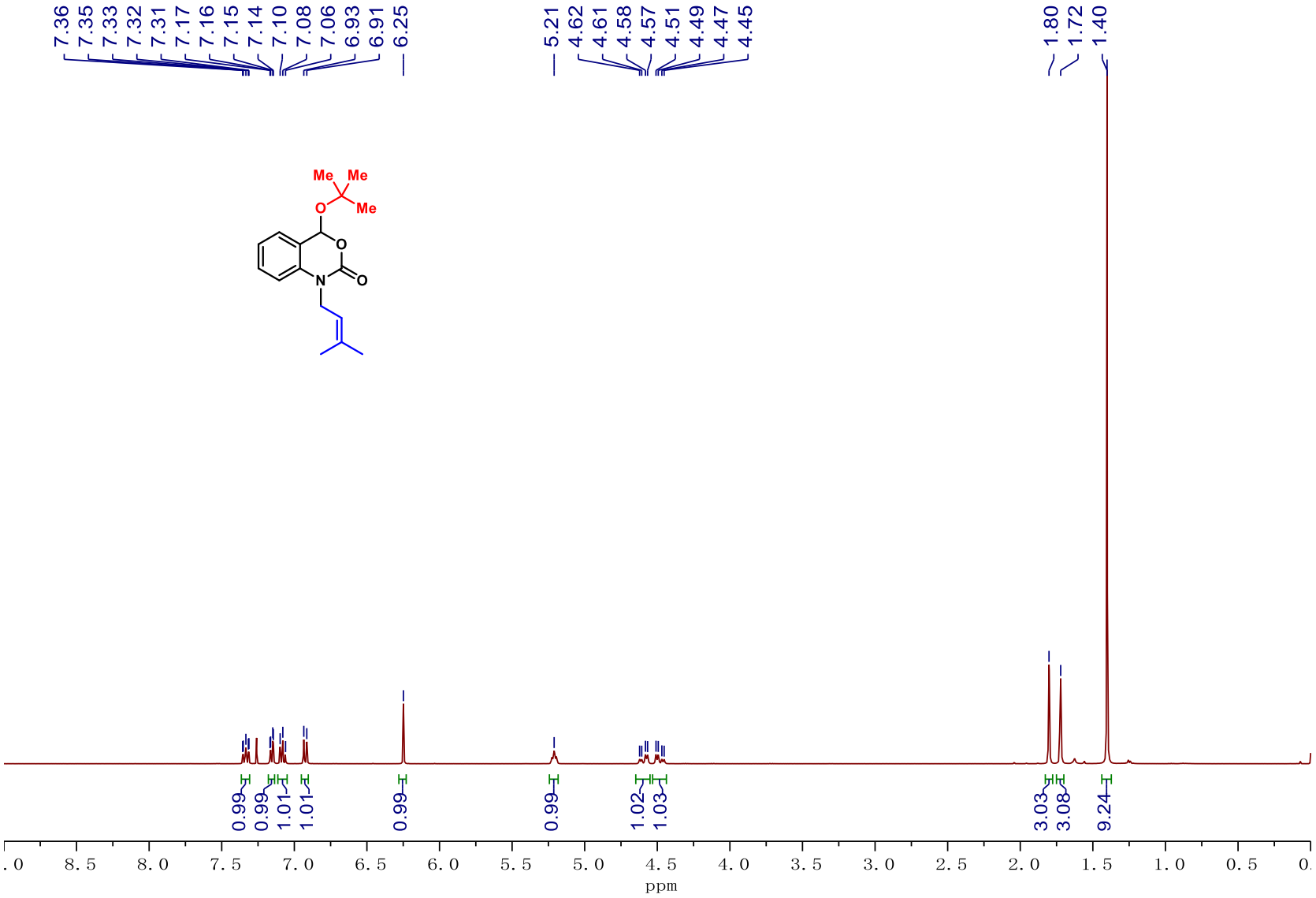


Compound 3f ^{1}H NMR



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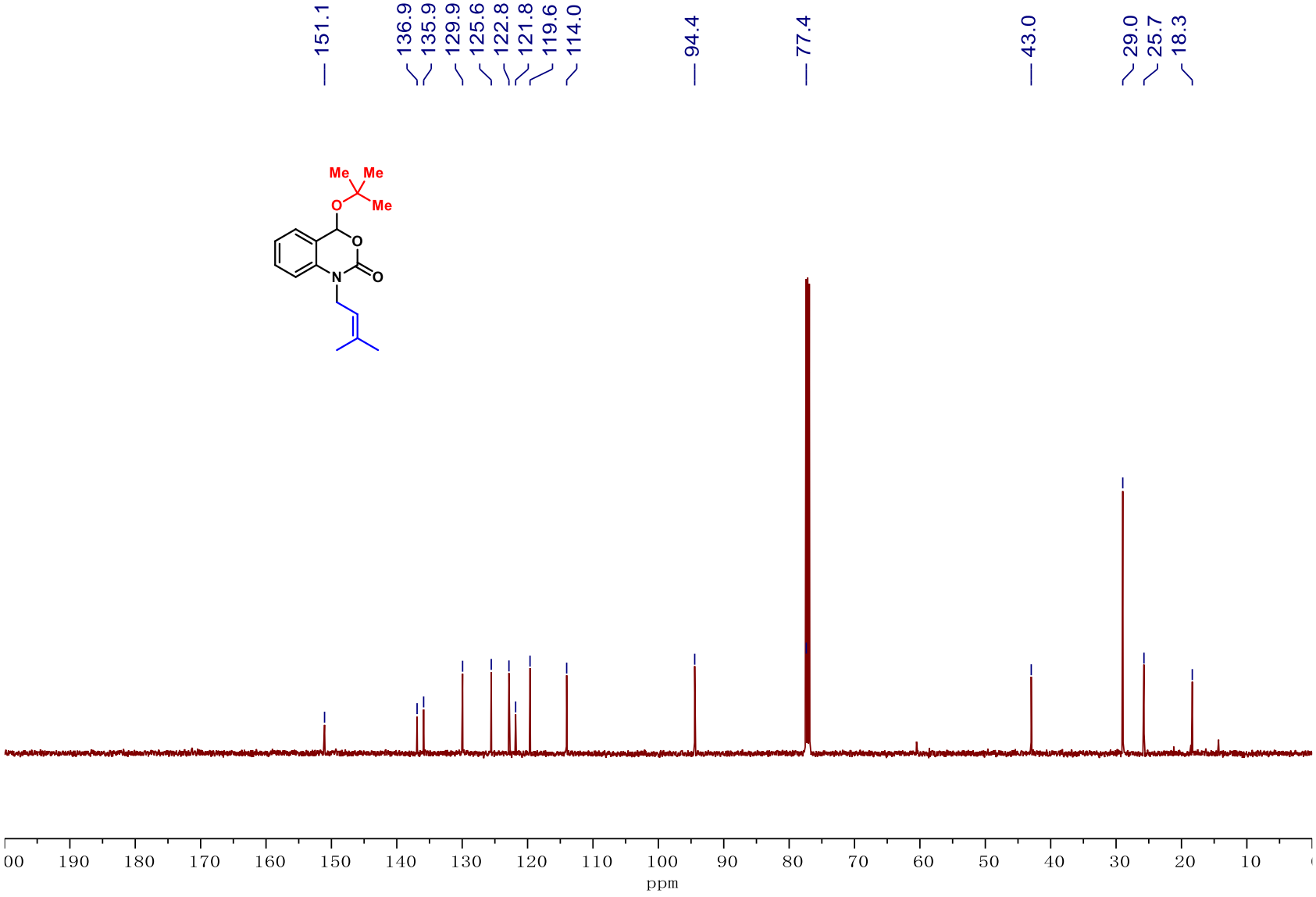

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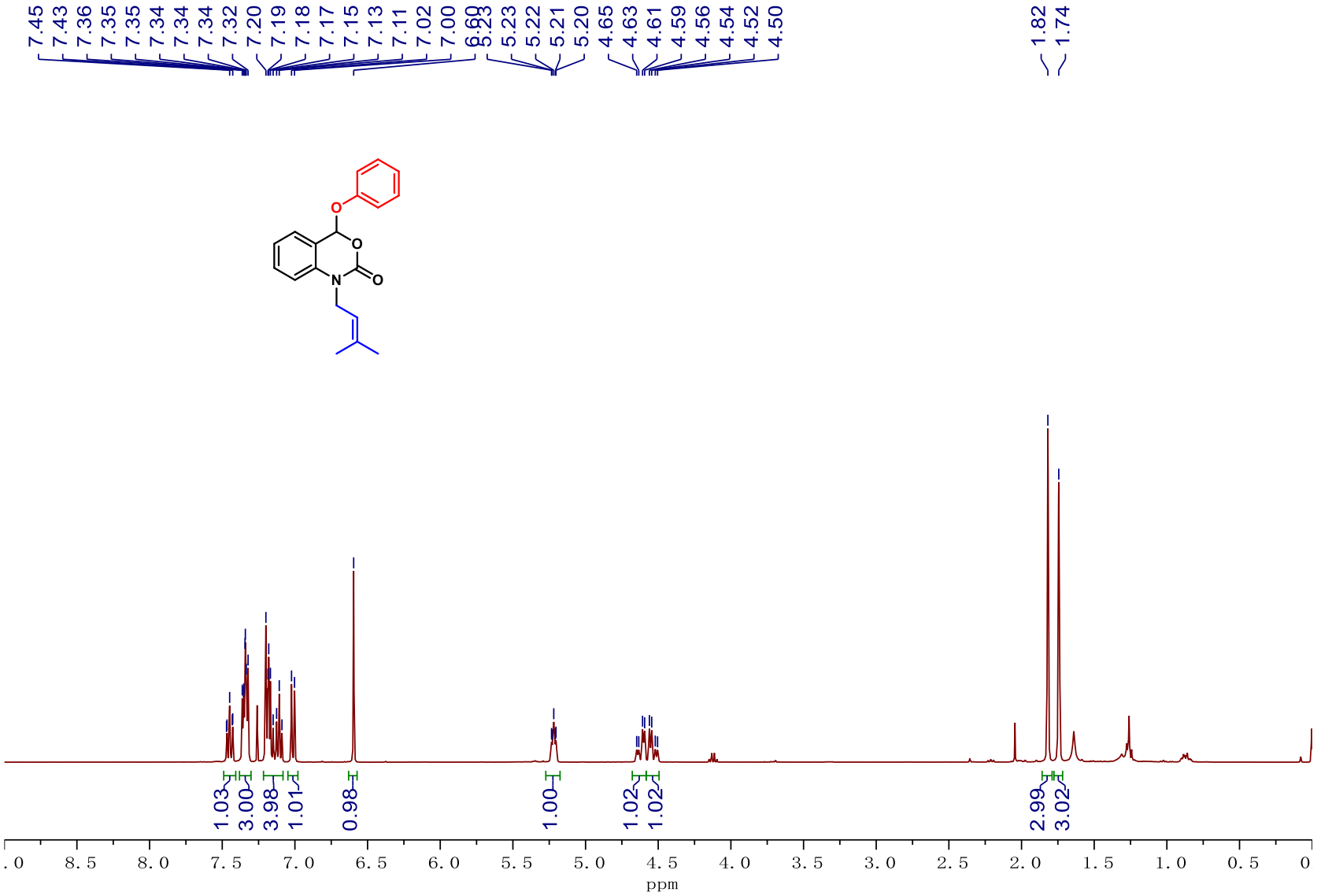

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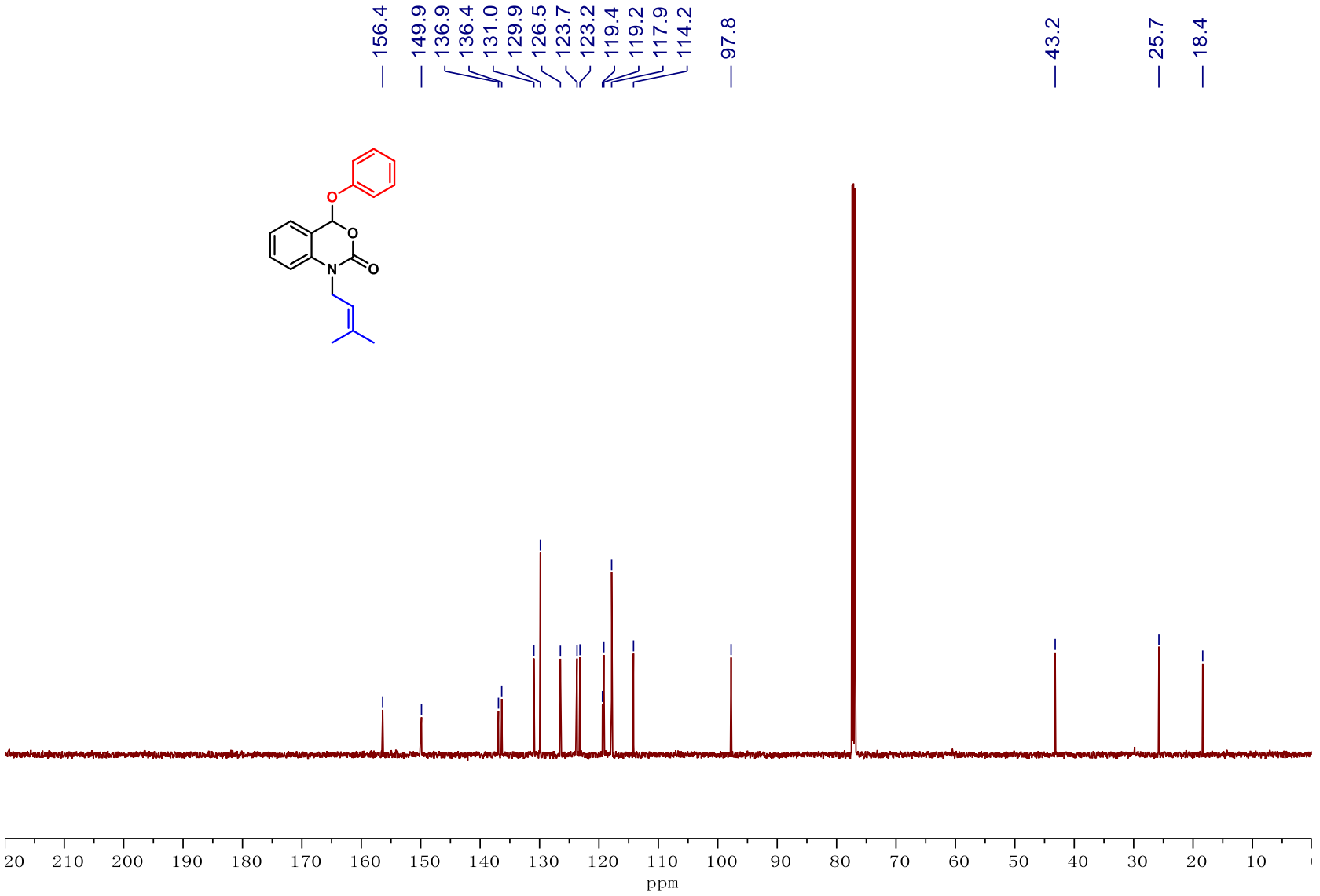
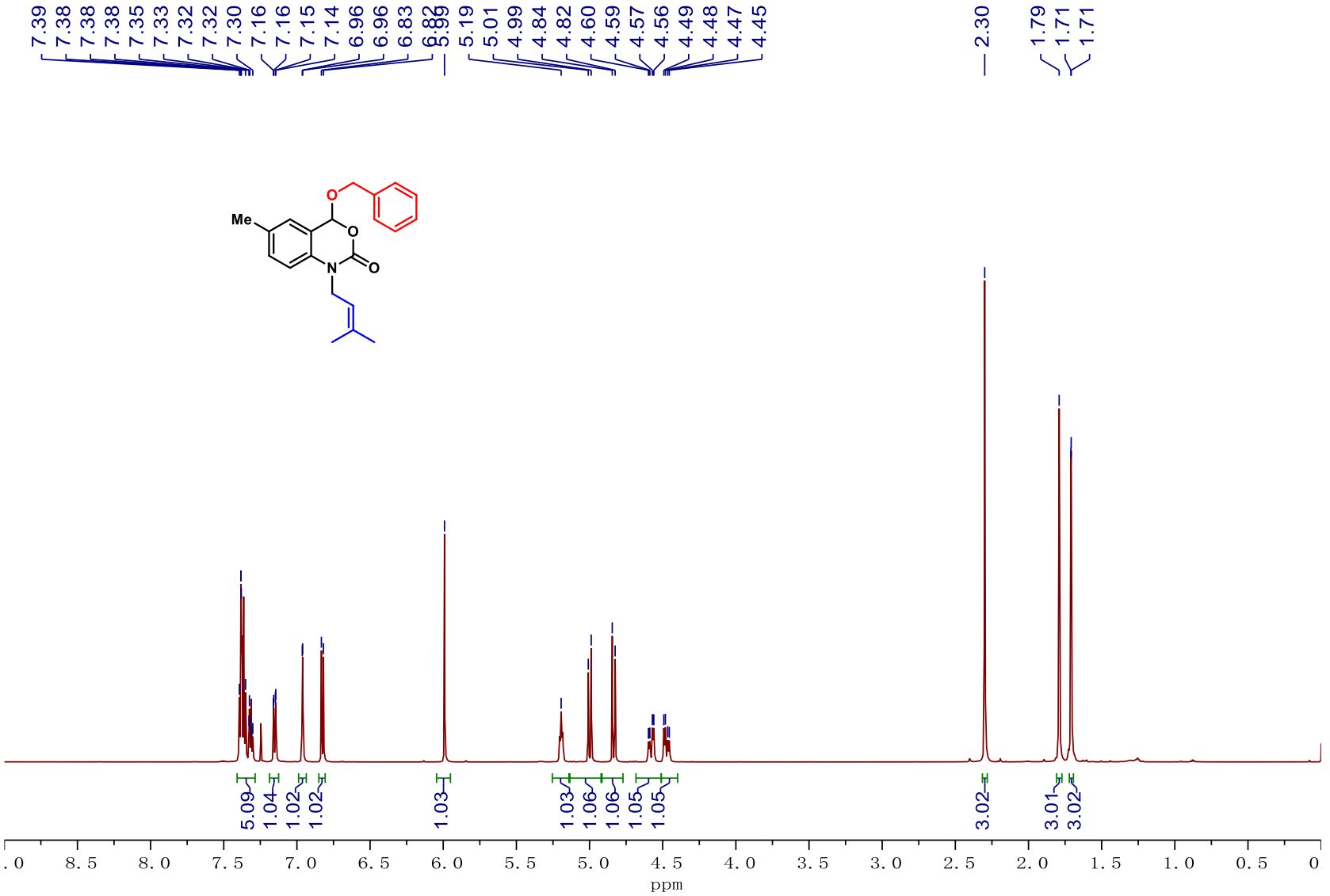
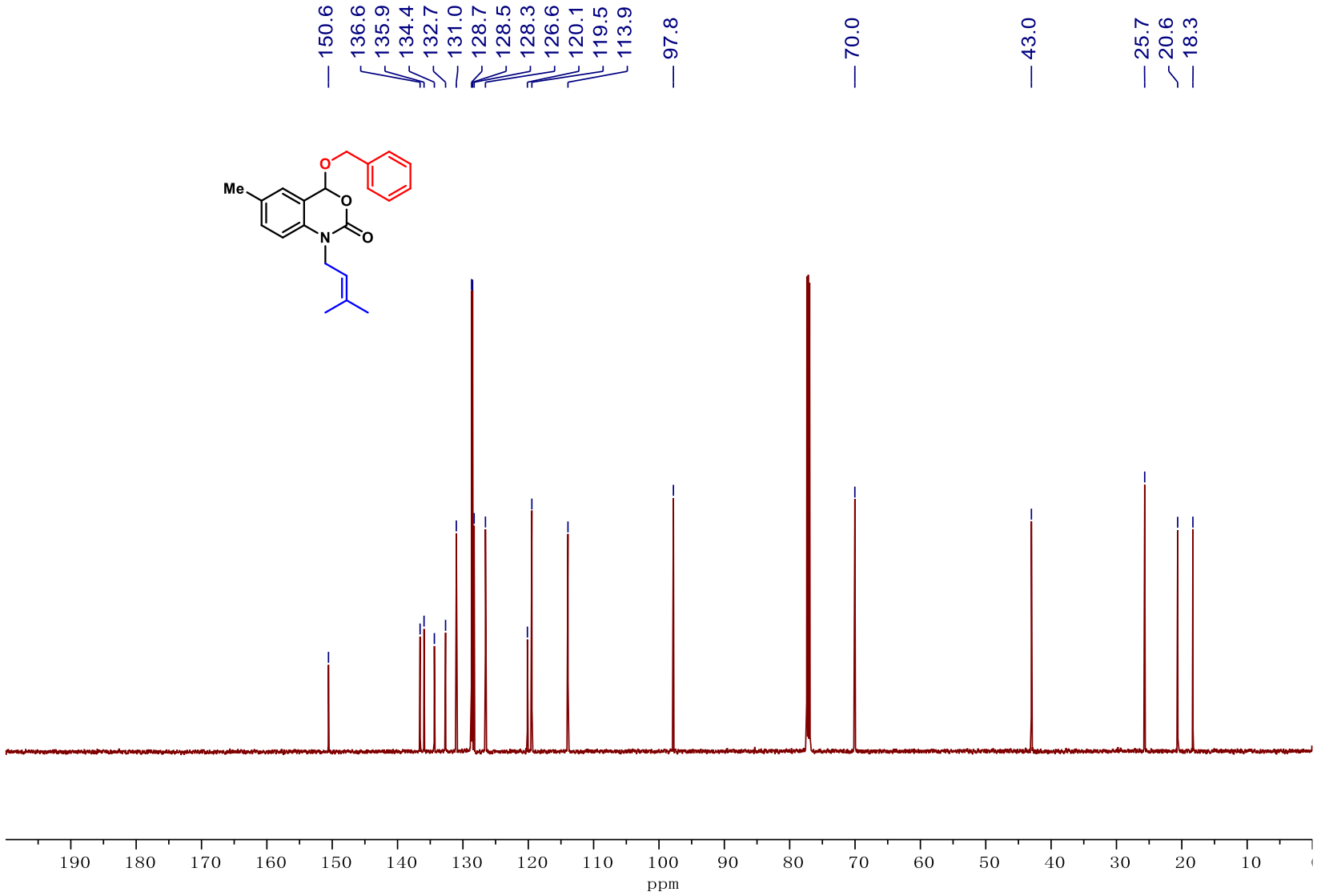


Compound 6a ^{1}H NMR



Compound 6a ^{13}C NMR



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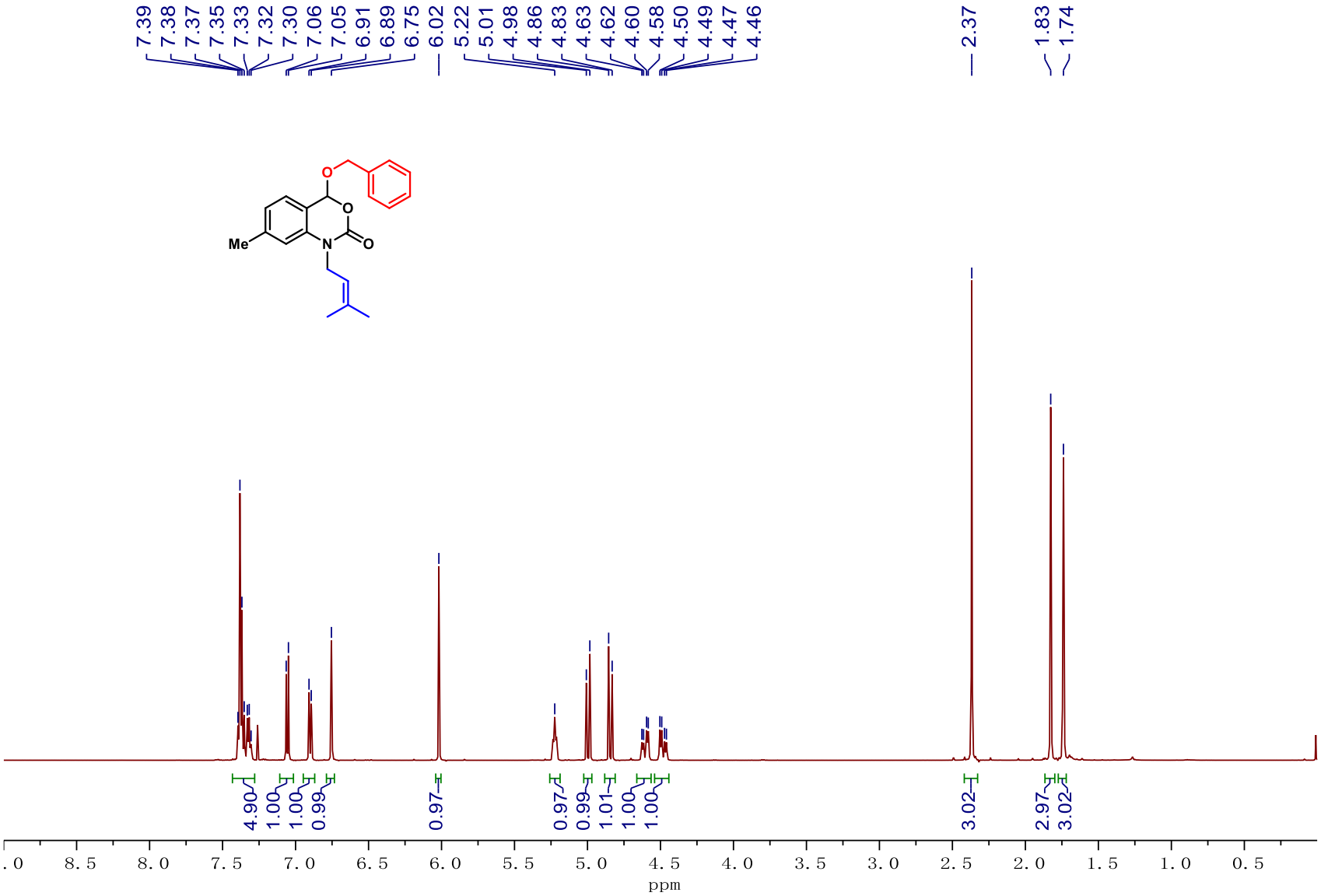
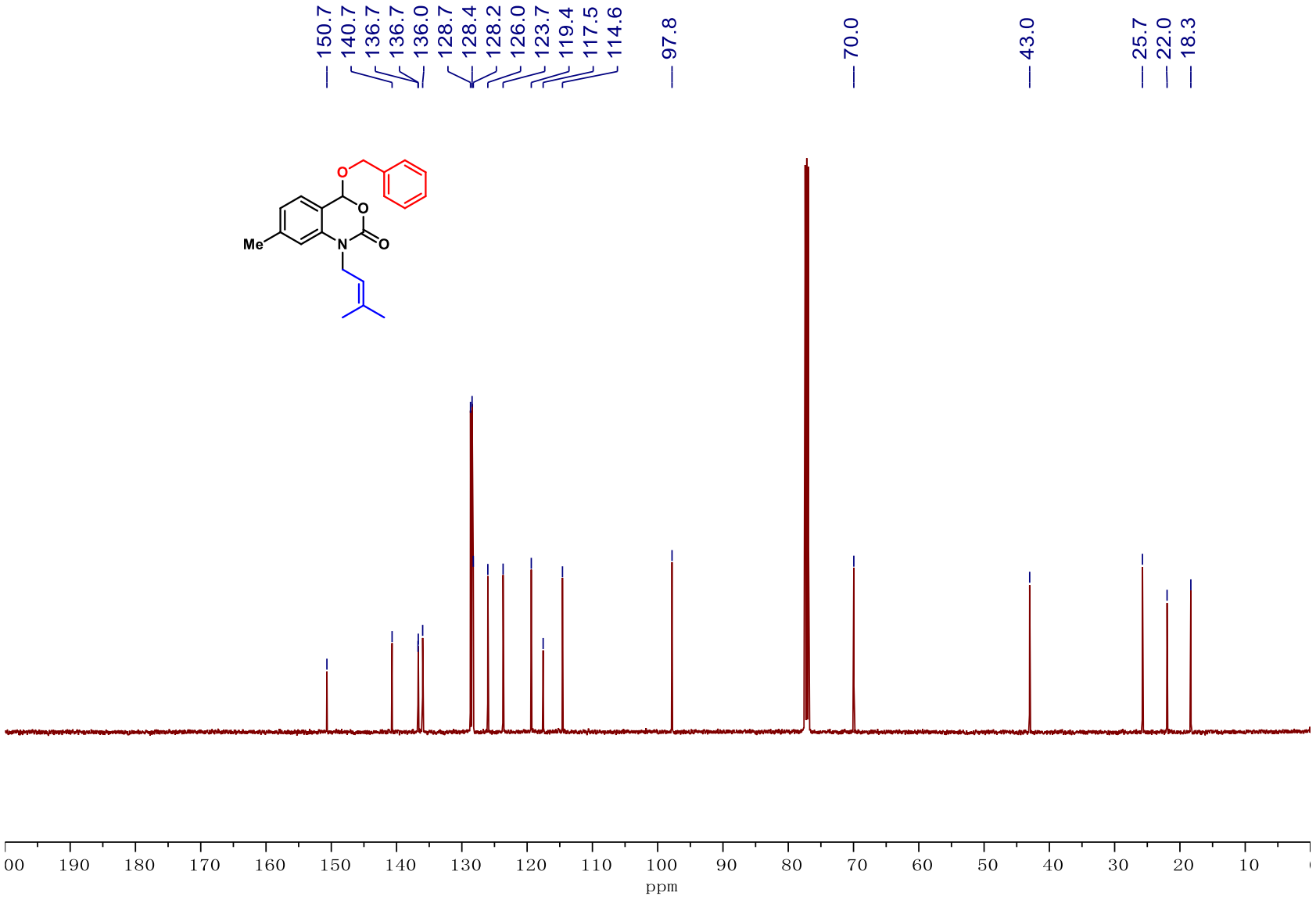
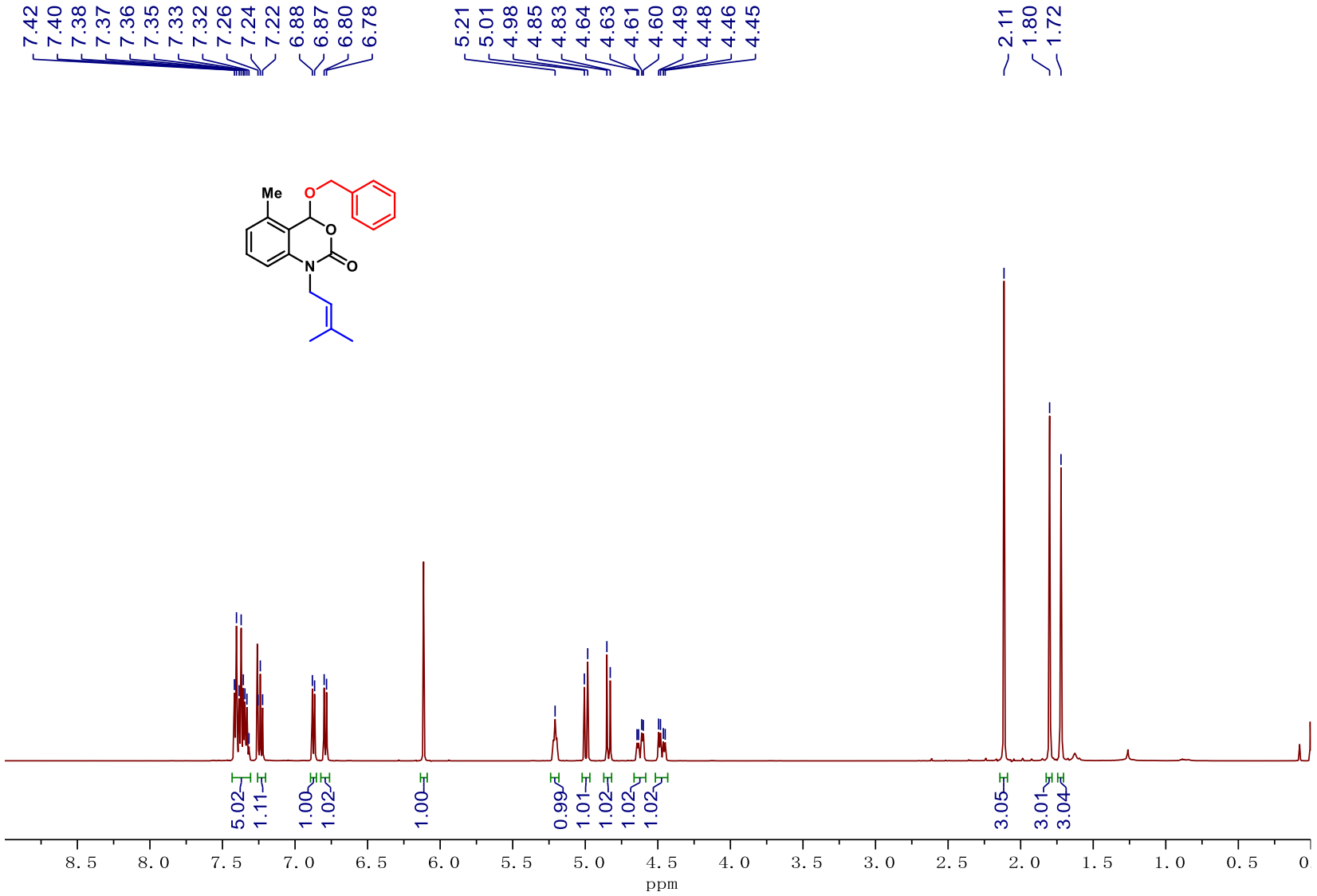


Compound 6b ^{13}C NMR



Compound 6c ^{1}H NMR



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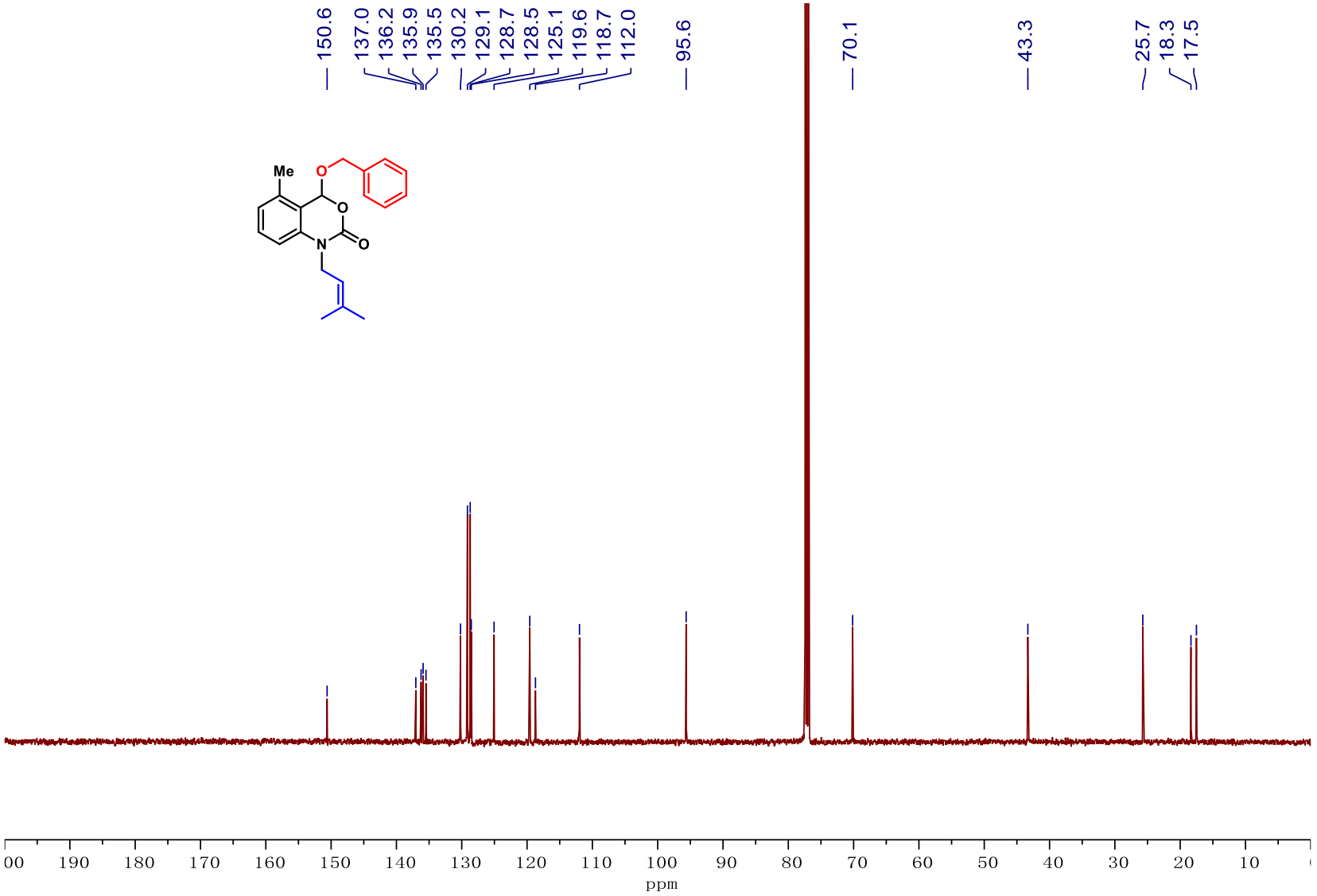
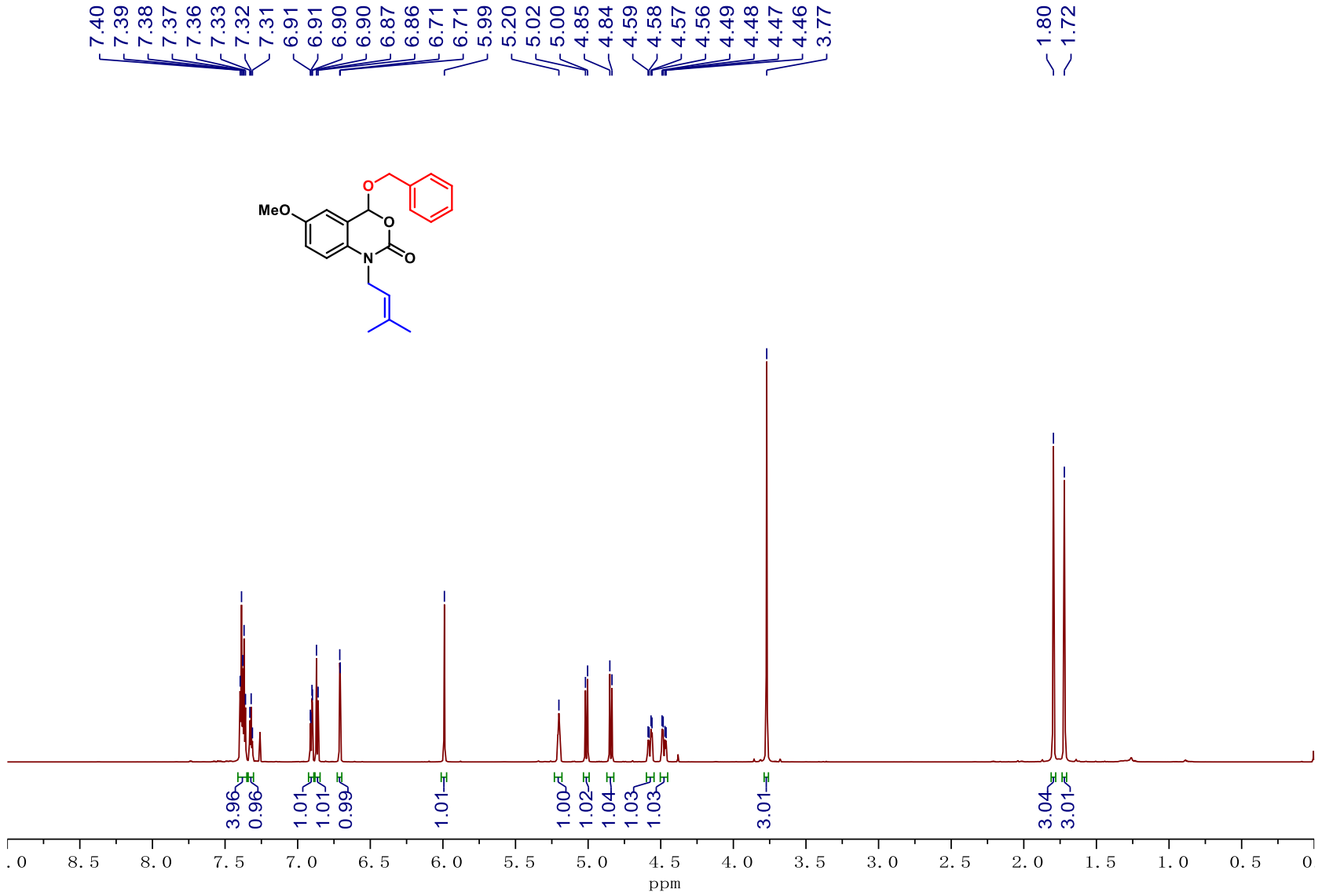


Compound 6d ^{1}H NMR



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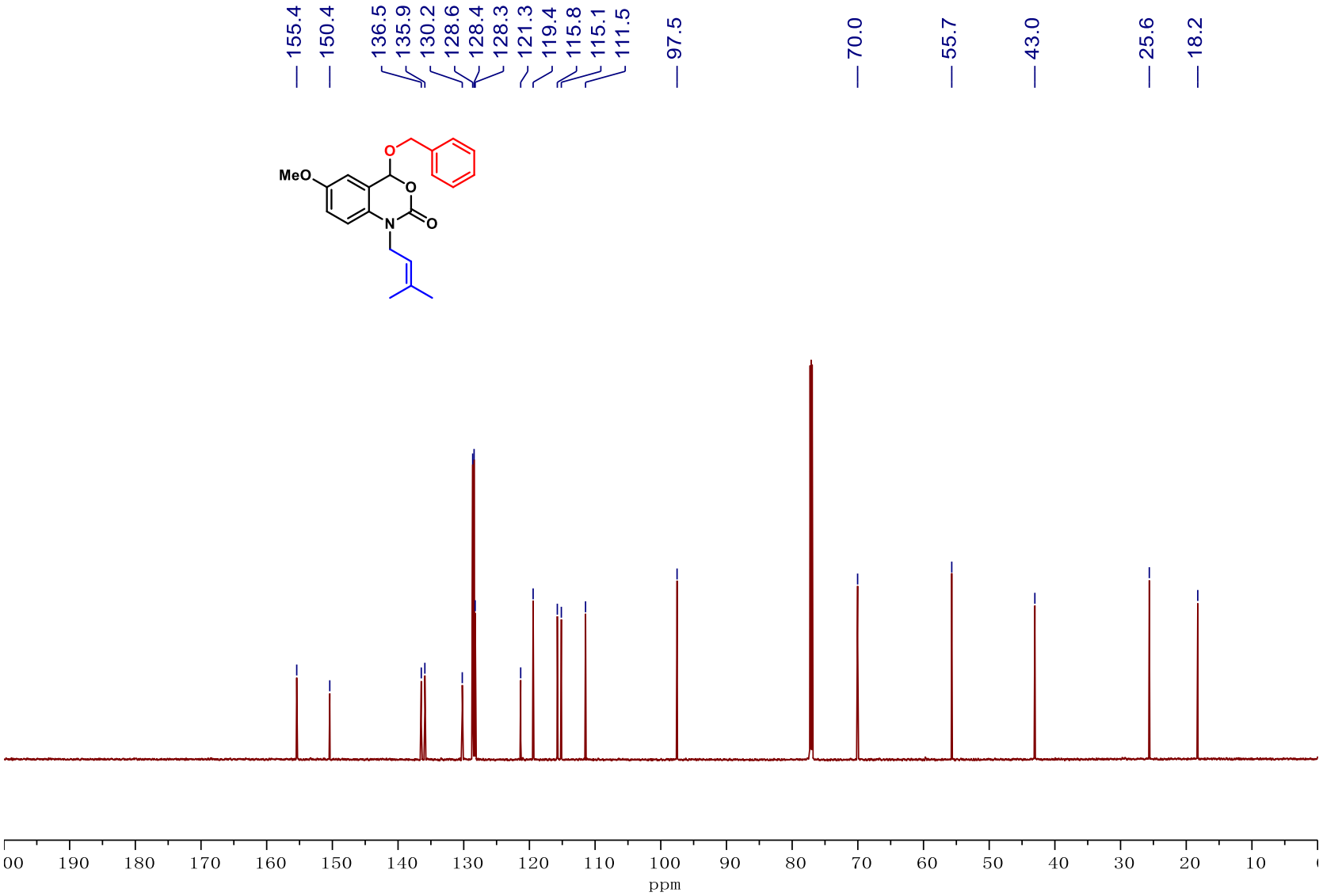

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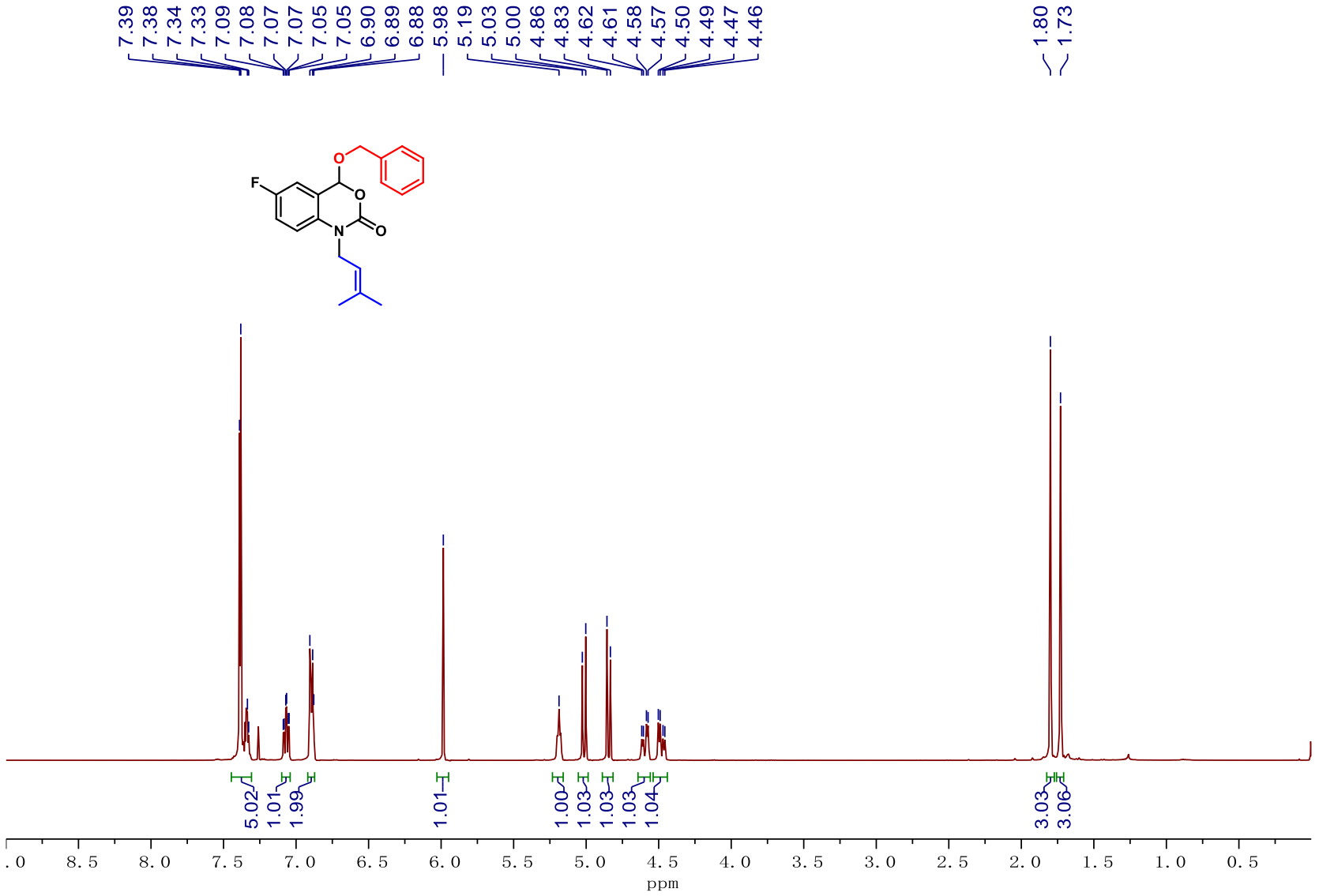
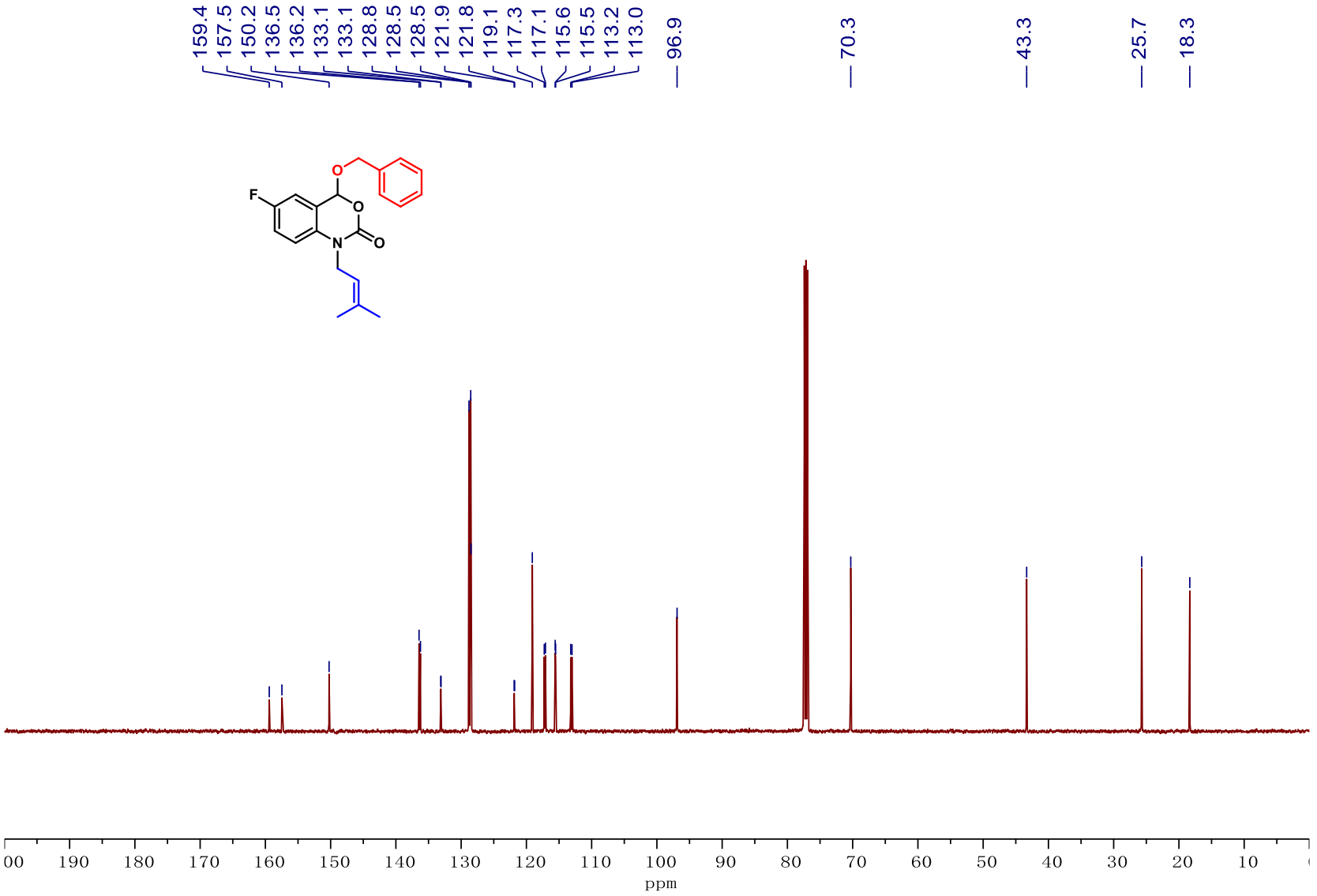
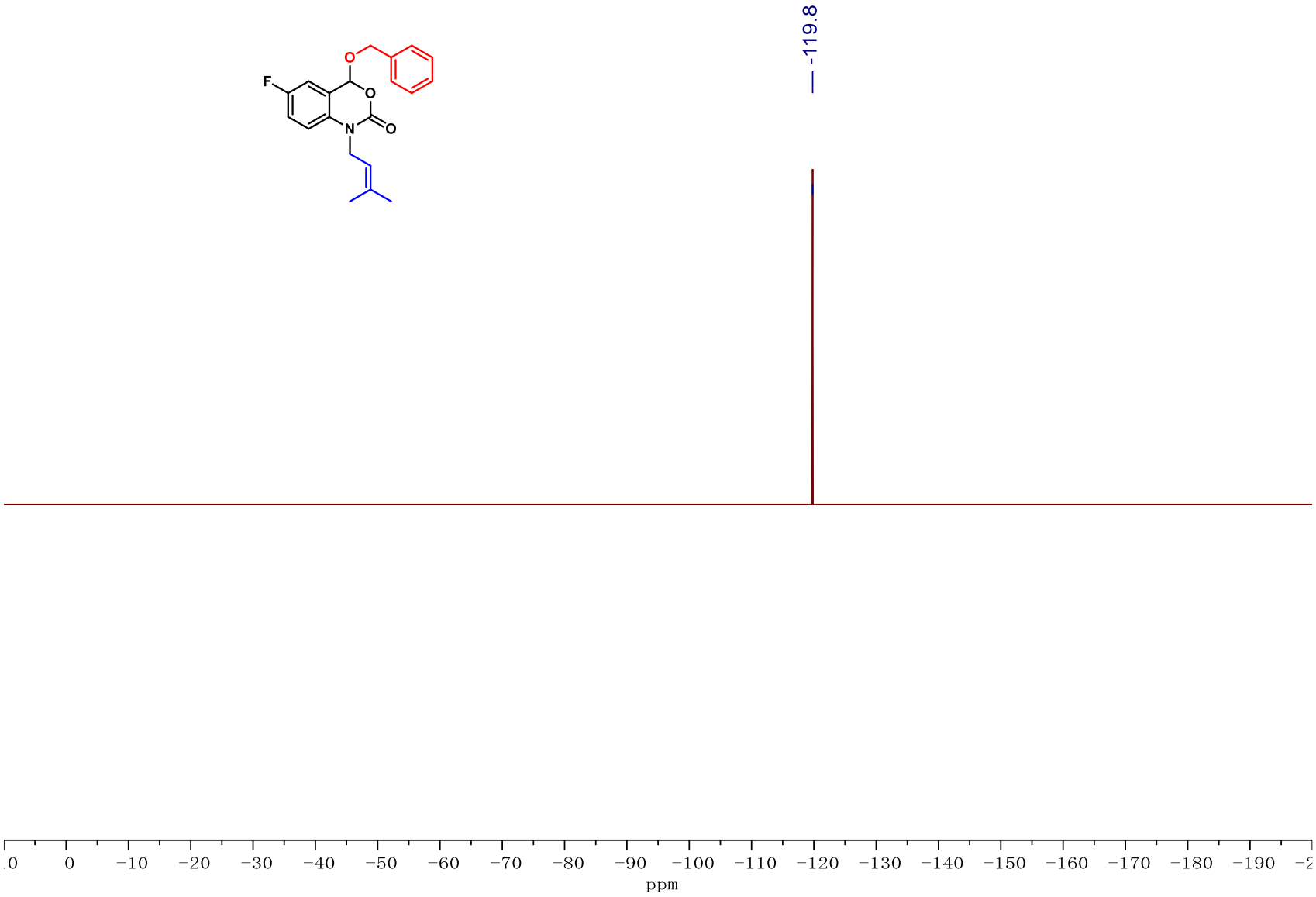


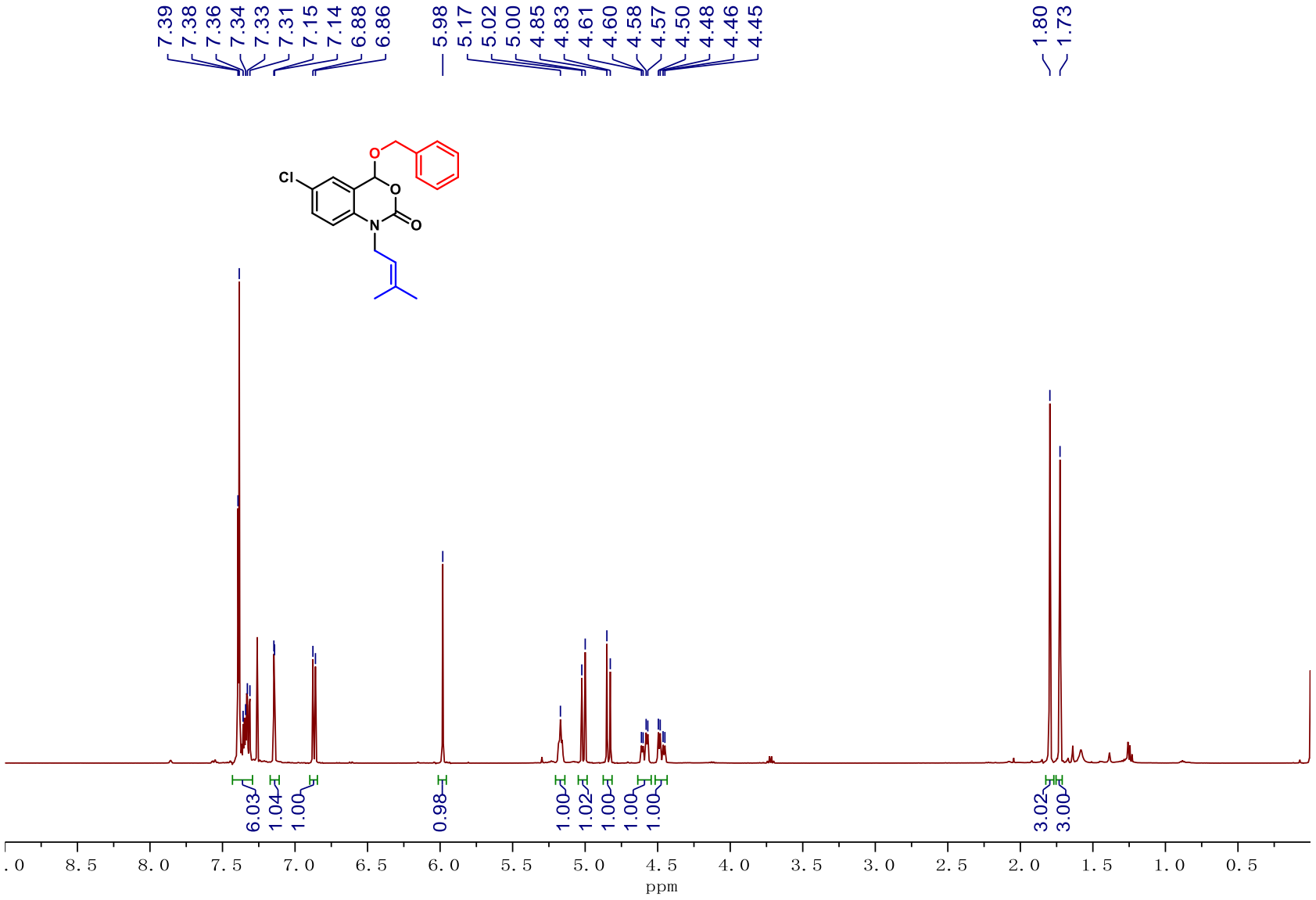
Compound 6e ^{13}C NMR



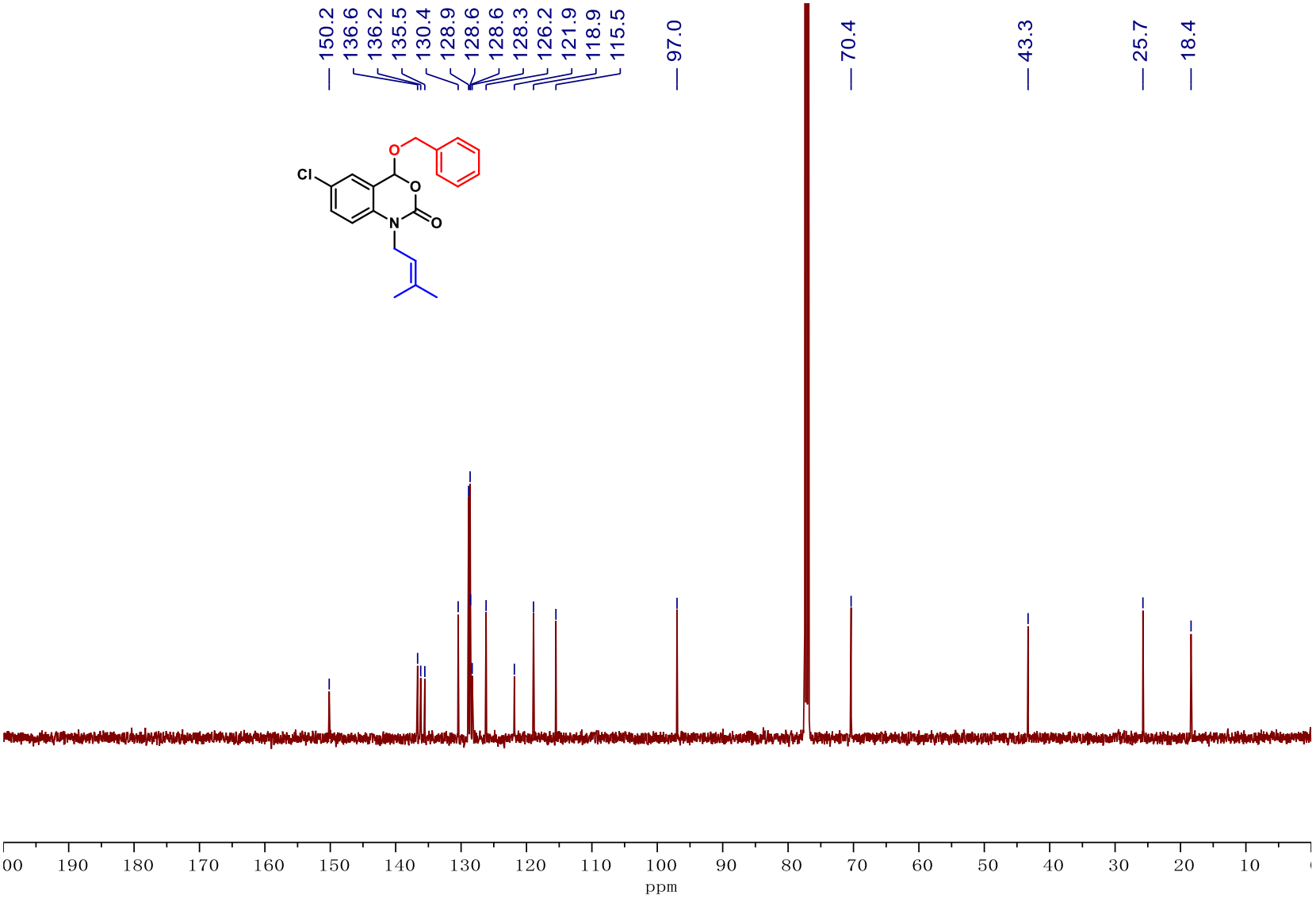
Compound 6e ^{19}F NMR



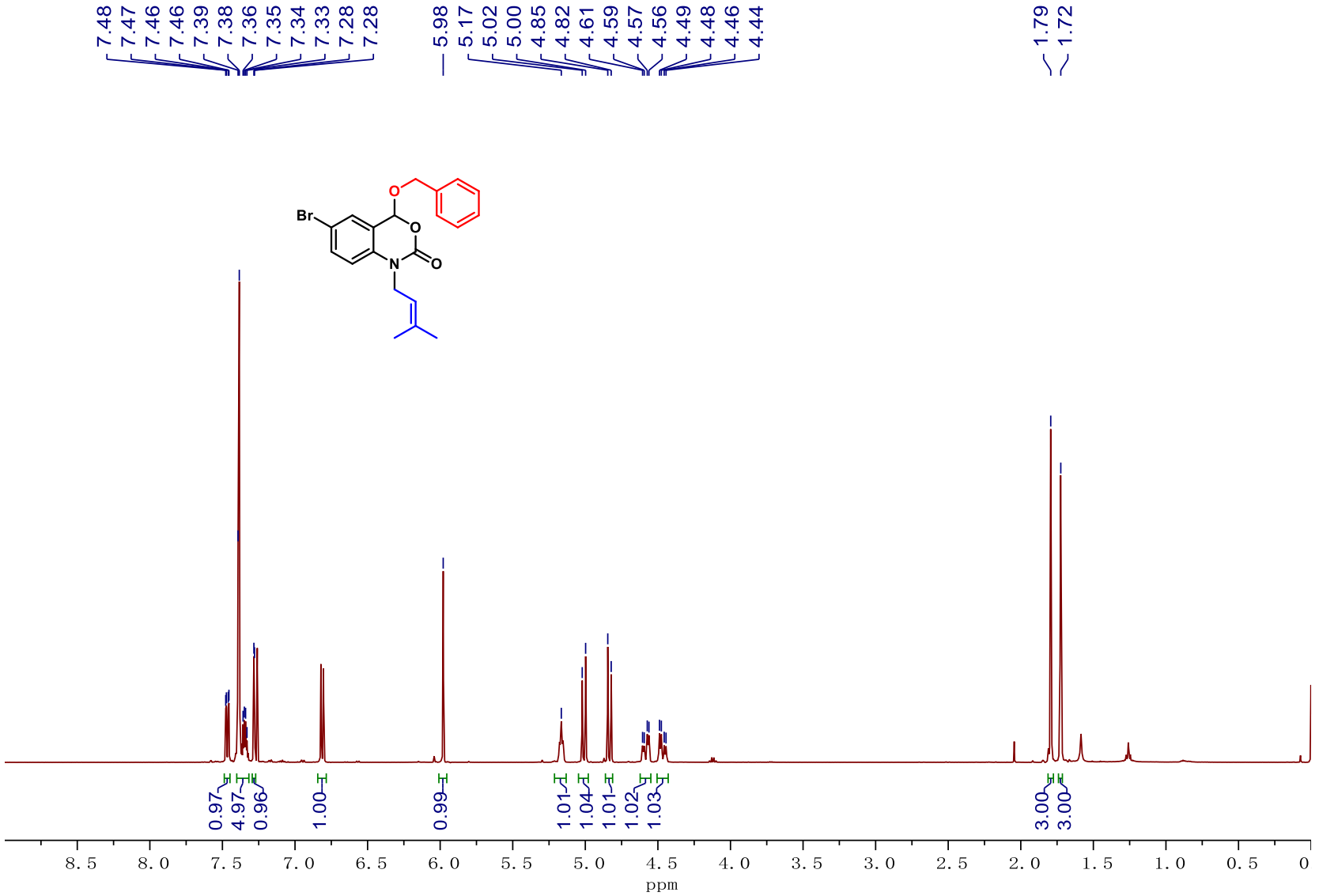
Compound 6f ^{1}H NMR



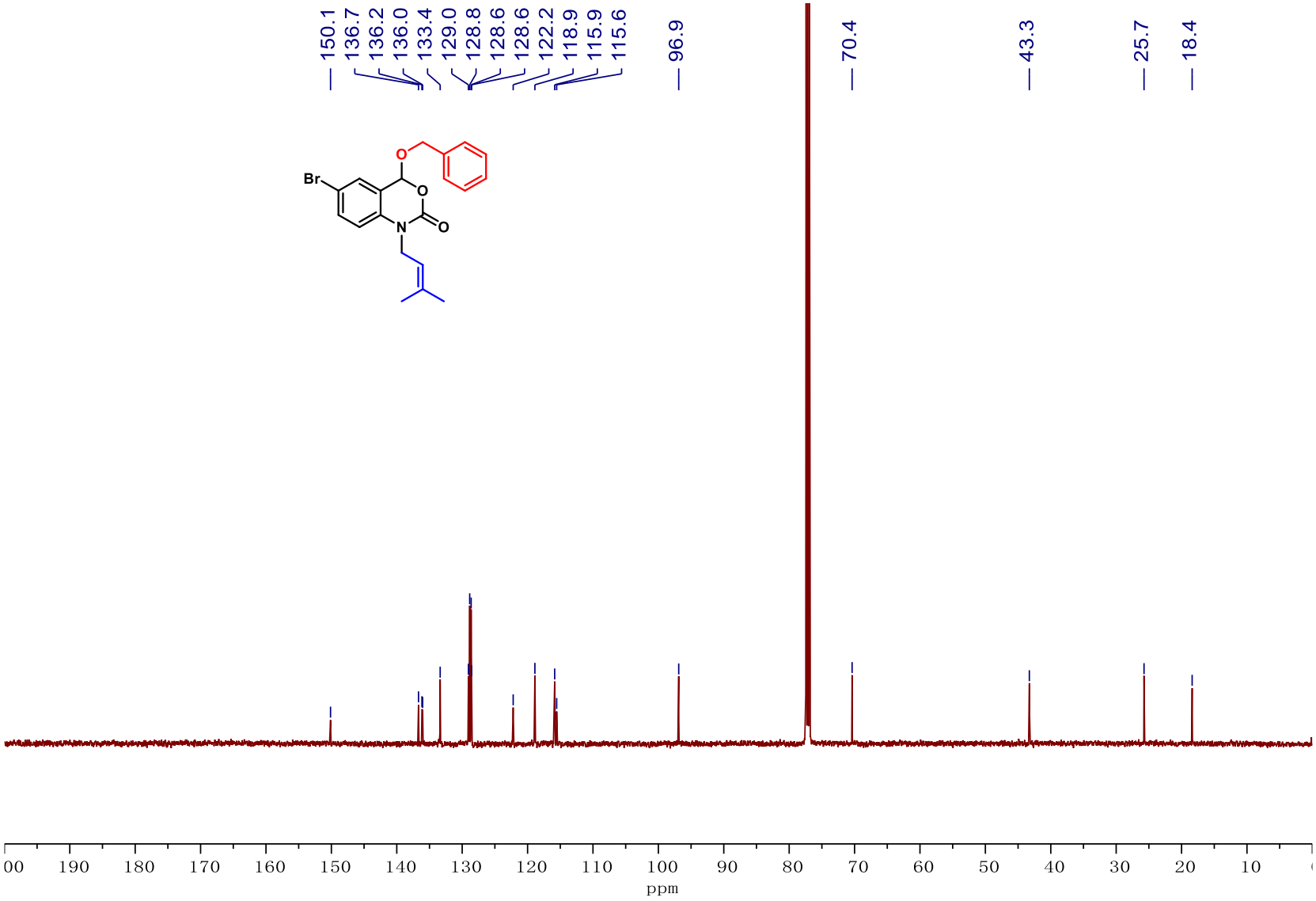
Compound 6f ^{13}C NMR



Compound 6g ^{1}H NMR



Compound 6g ^{13}C NMR



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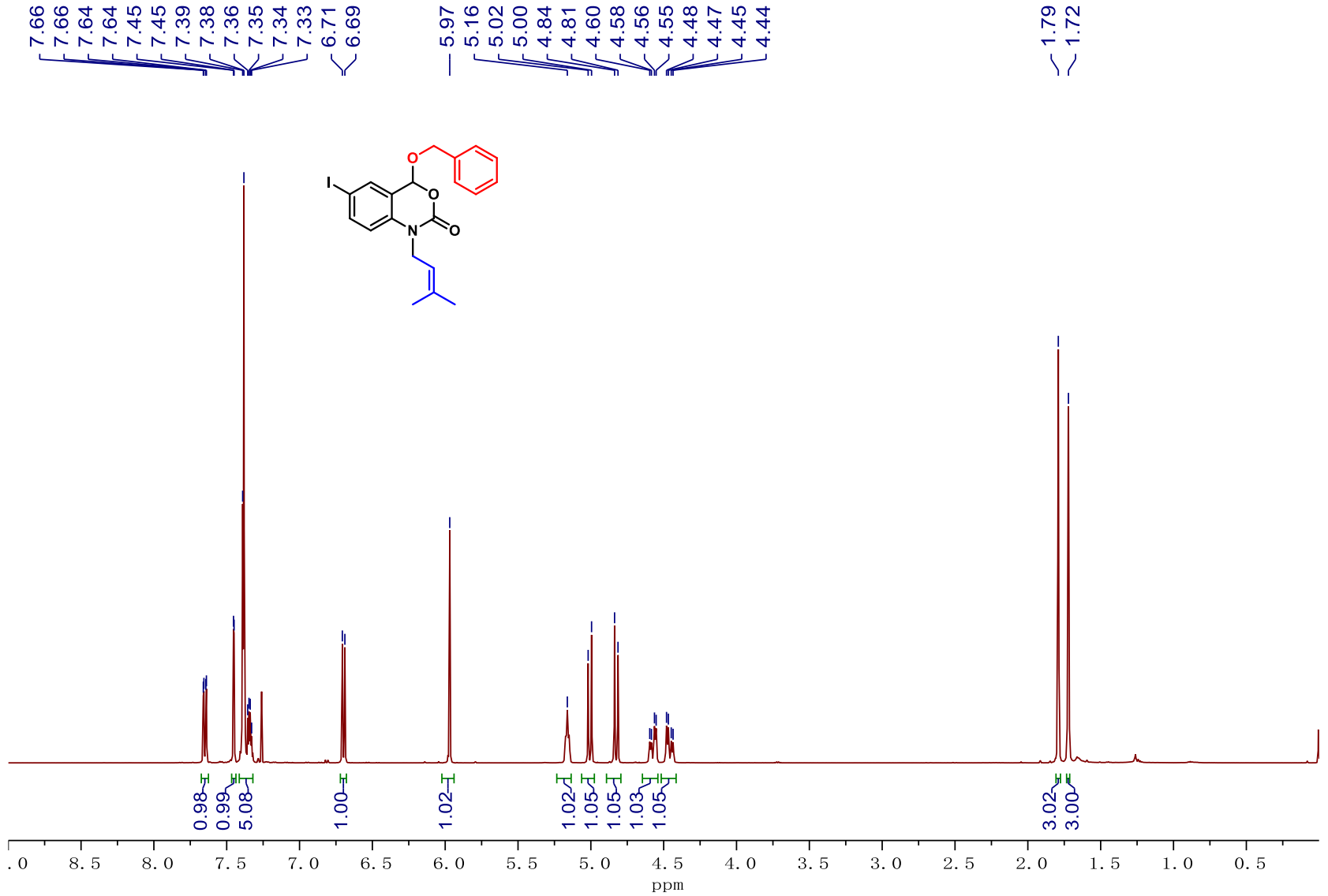
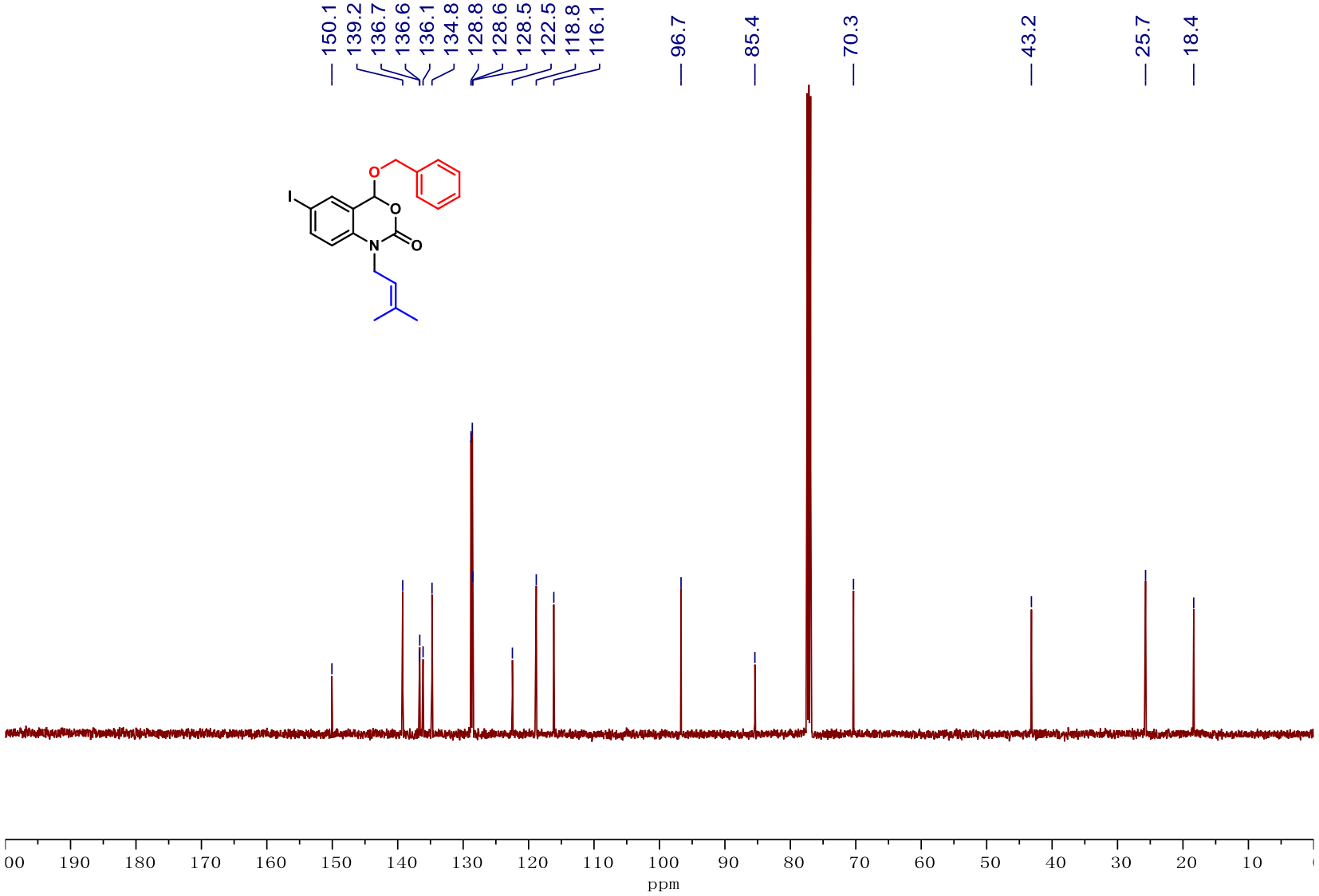
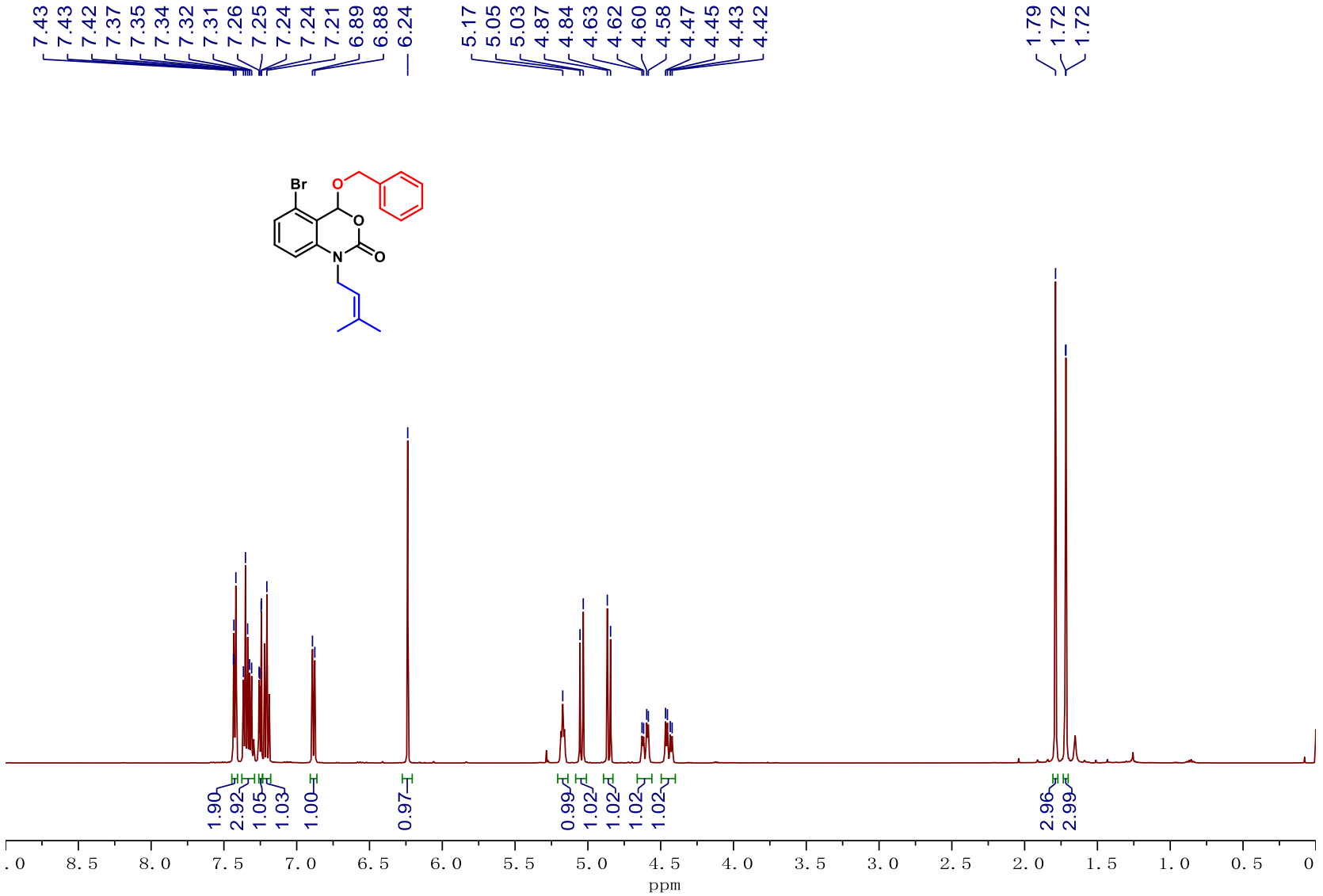


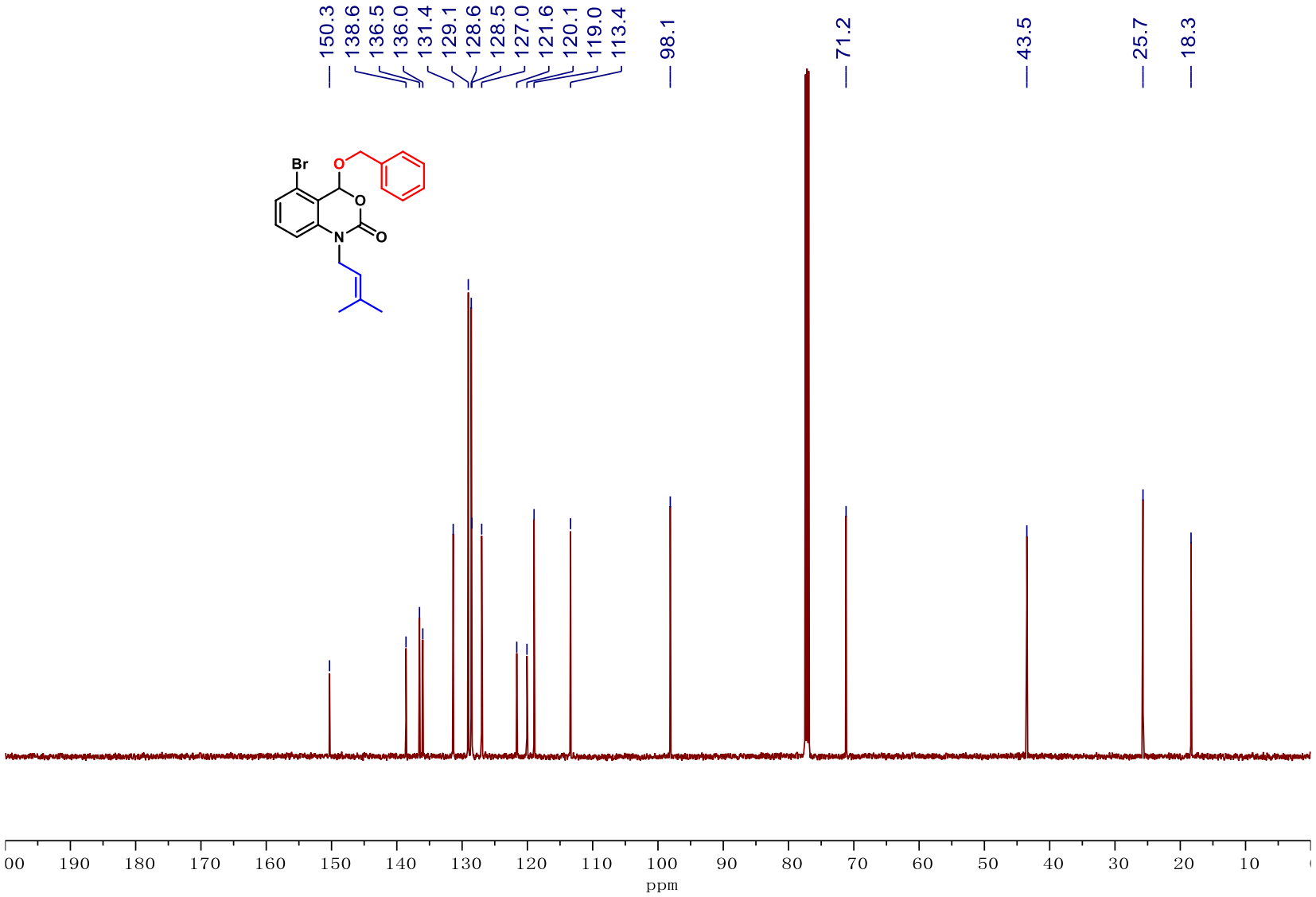
Compound 6h ^{13}C NMR



Compound 6i ^{1}H NMR



Compound 6i ^{13}C NMR



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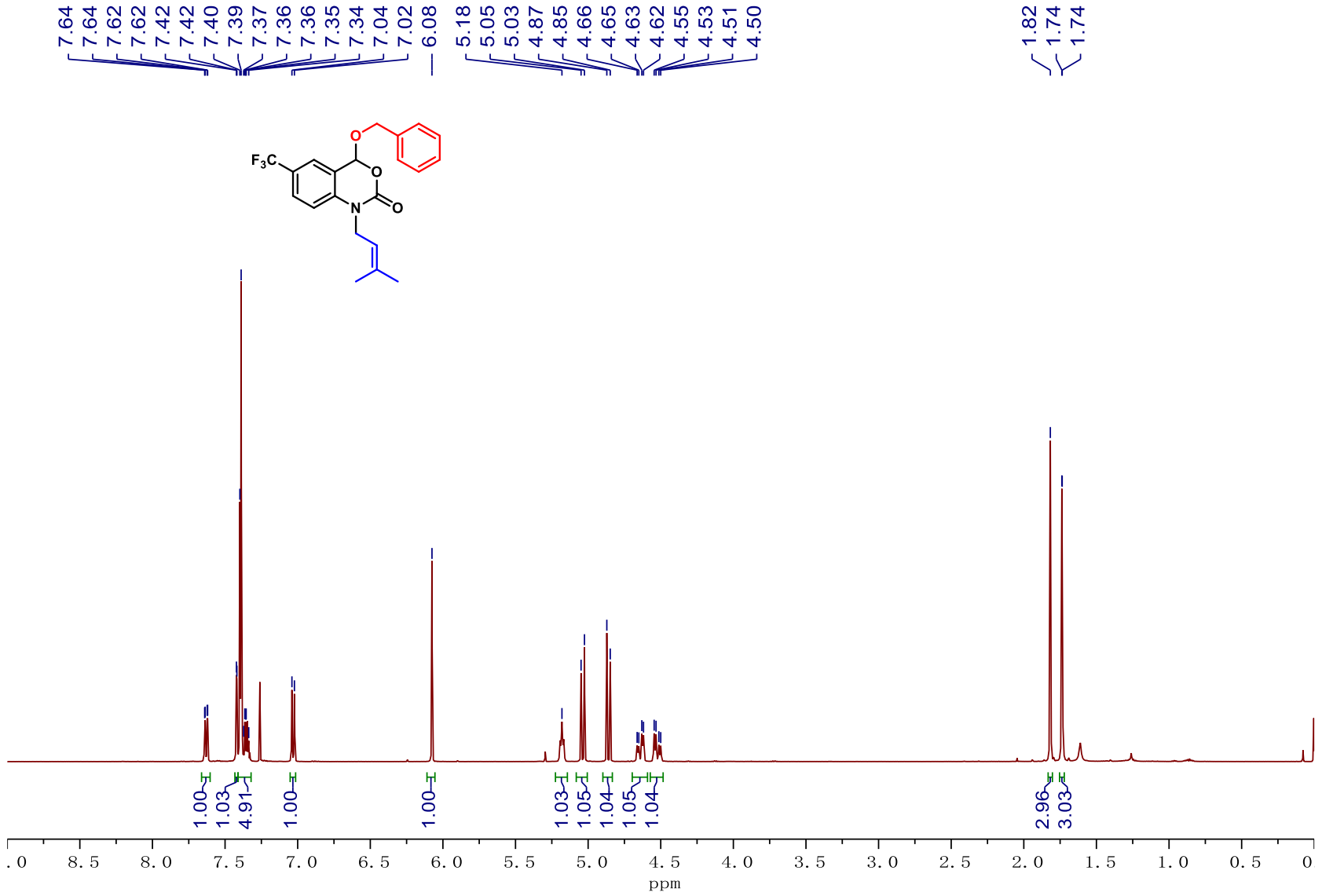

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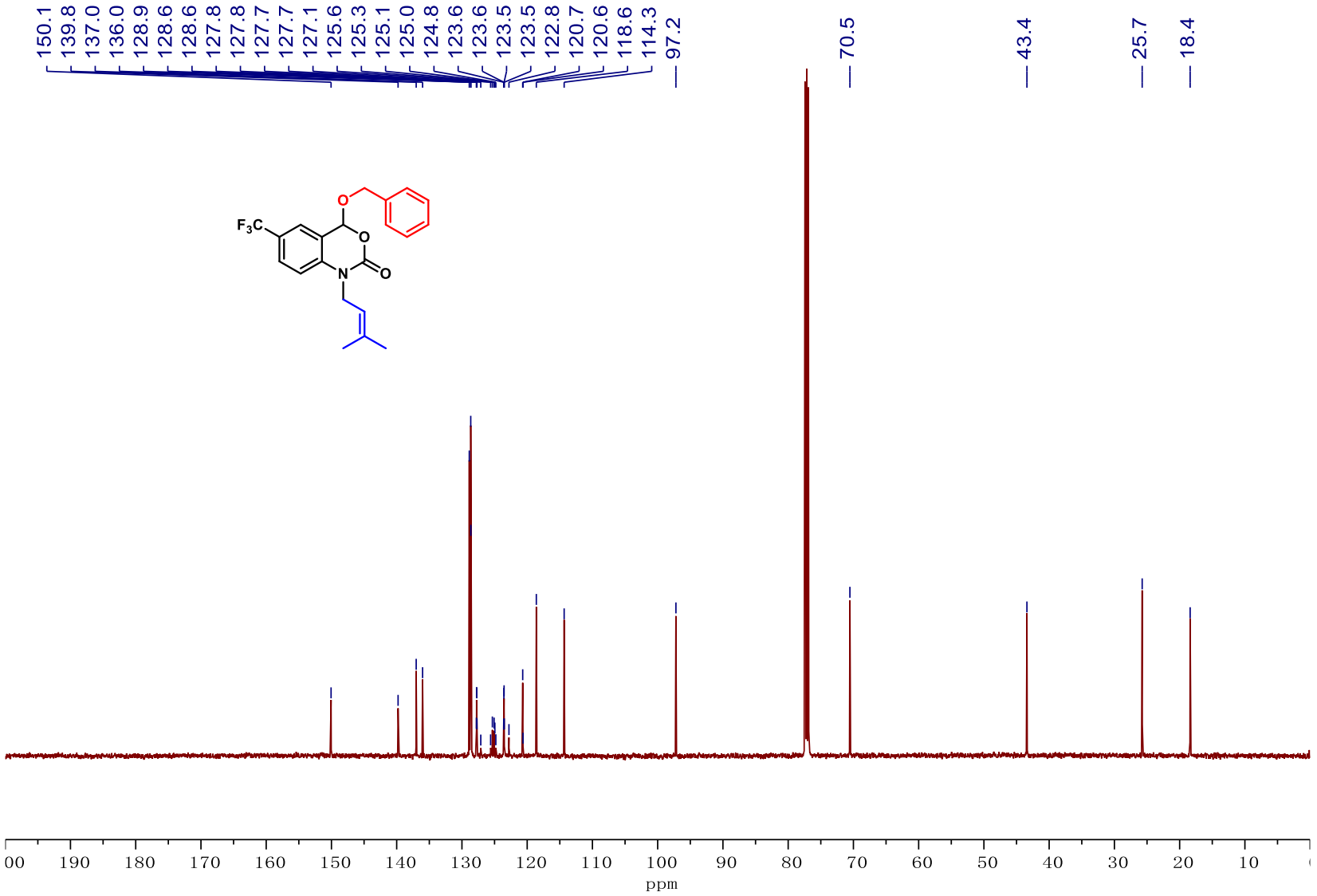
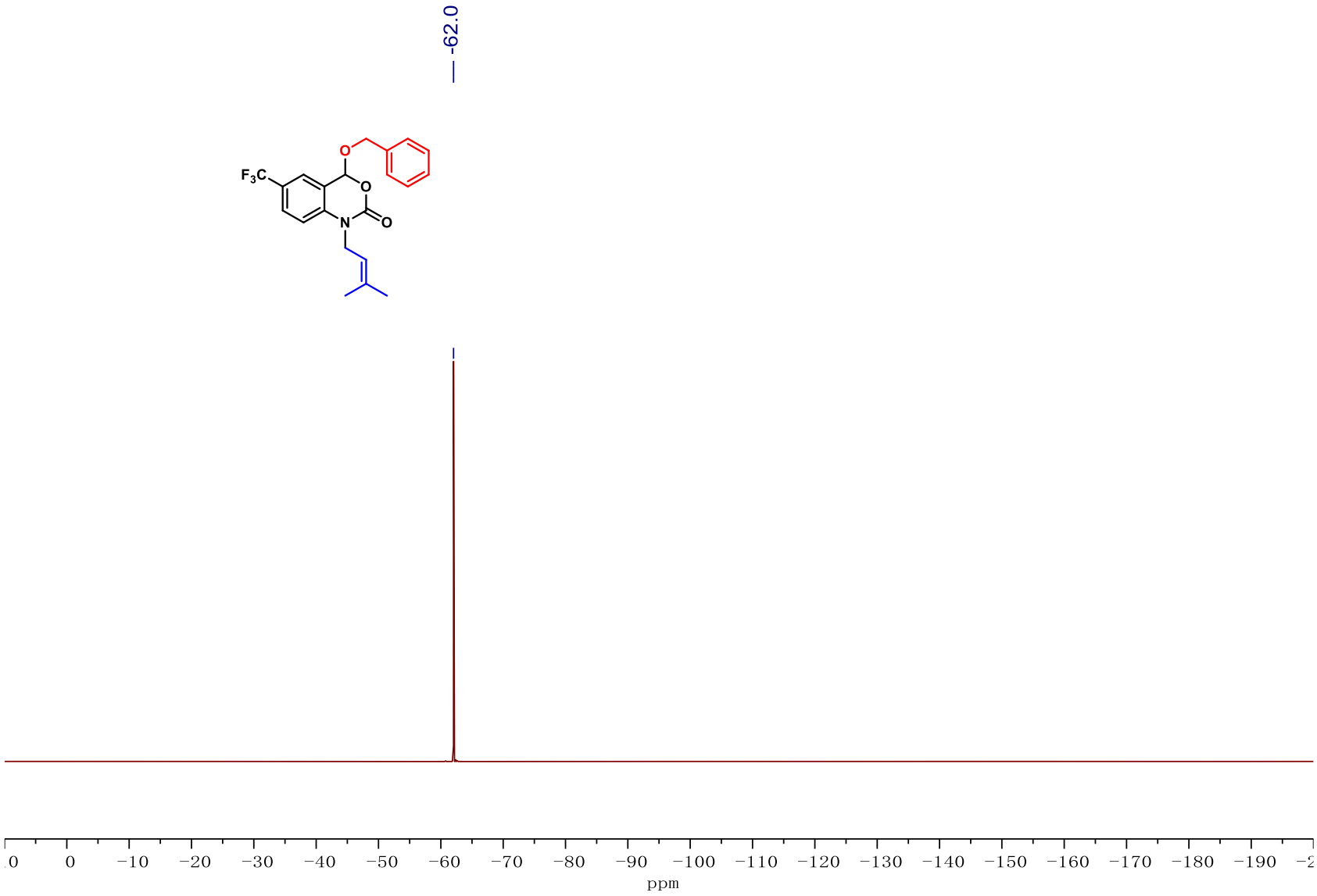


Compound 6j ^{19}F NMR



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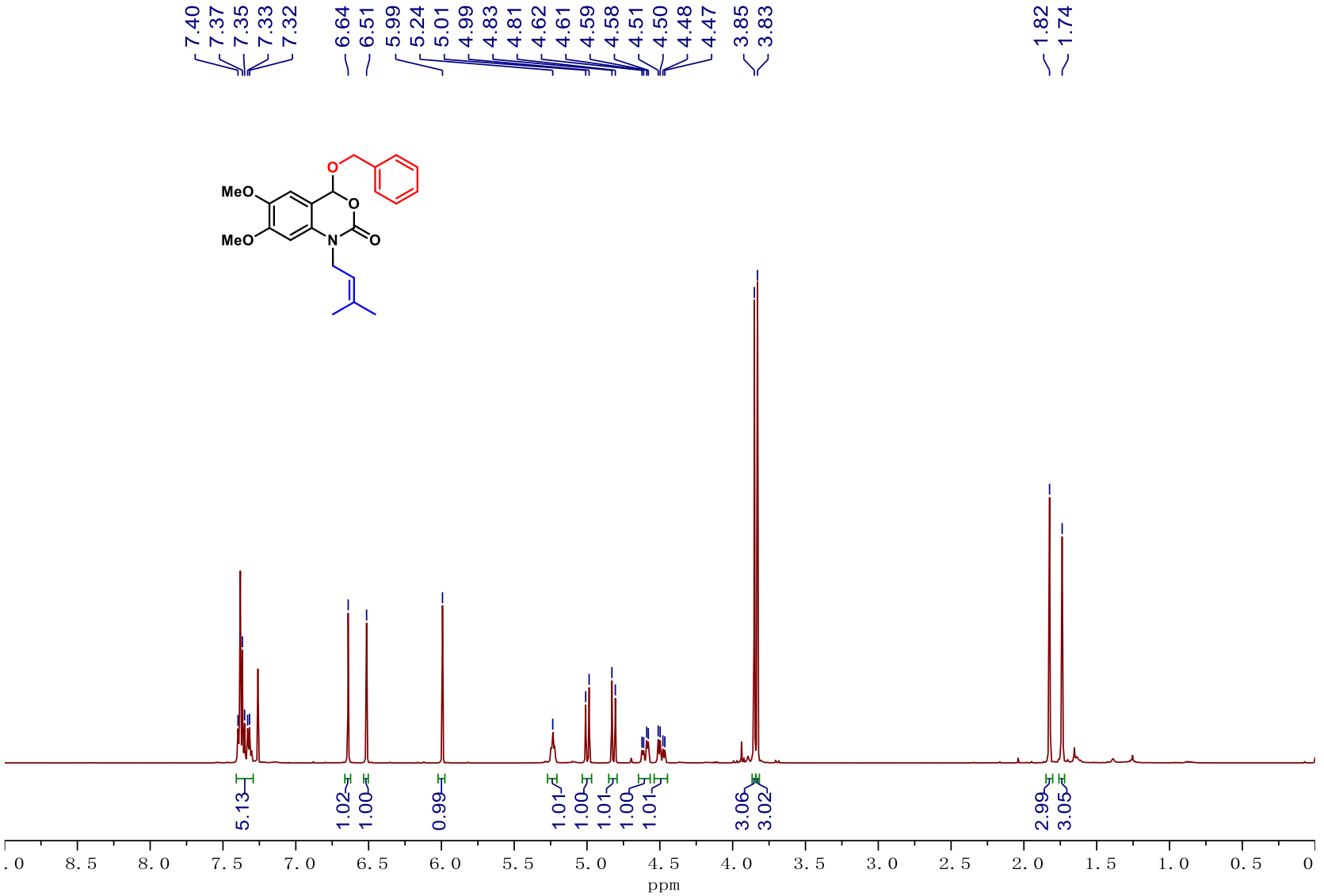

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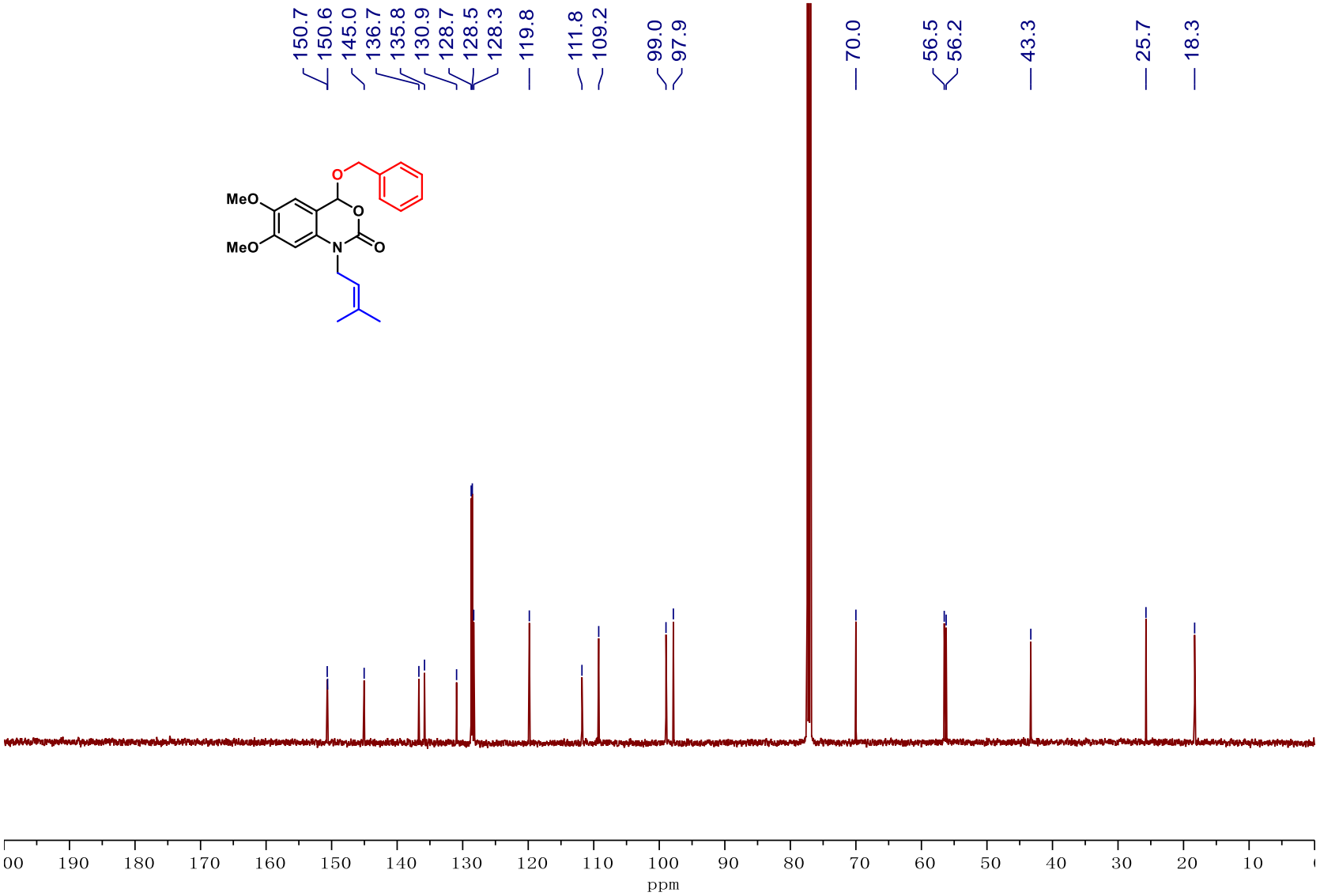

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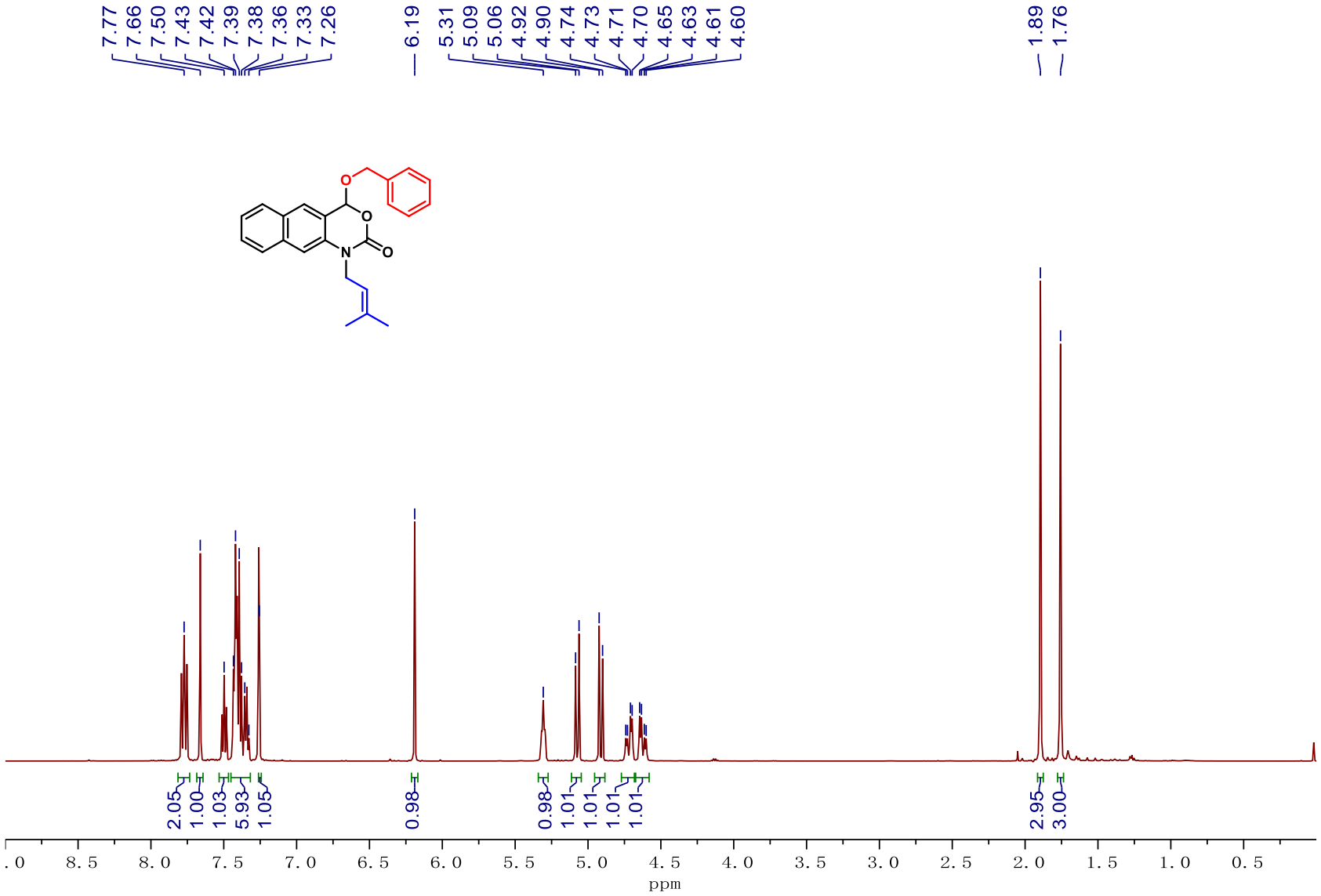

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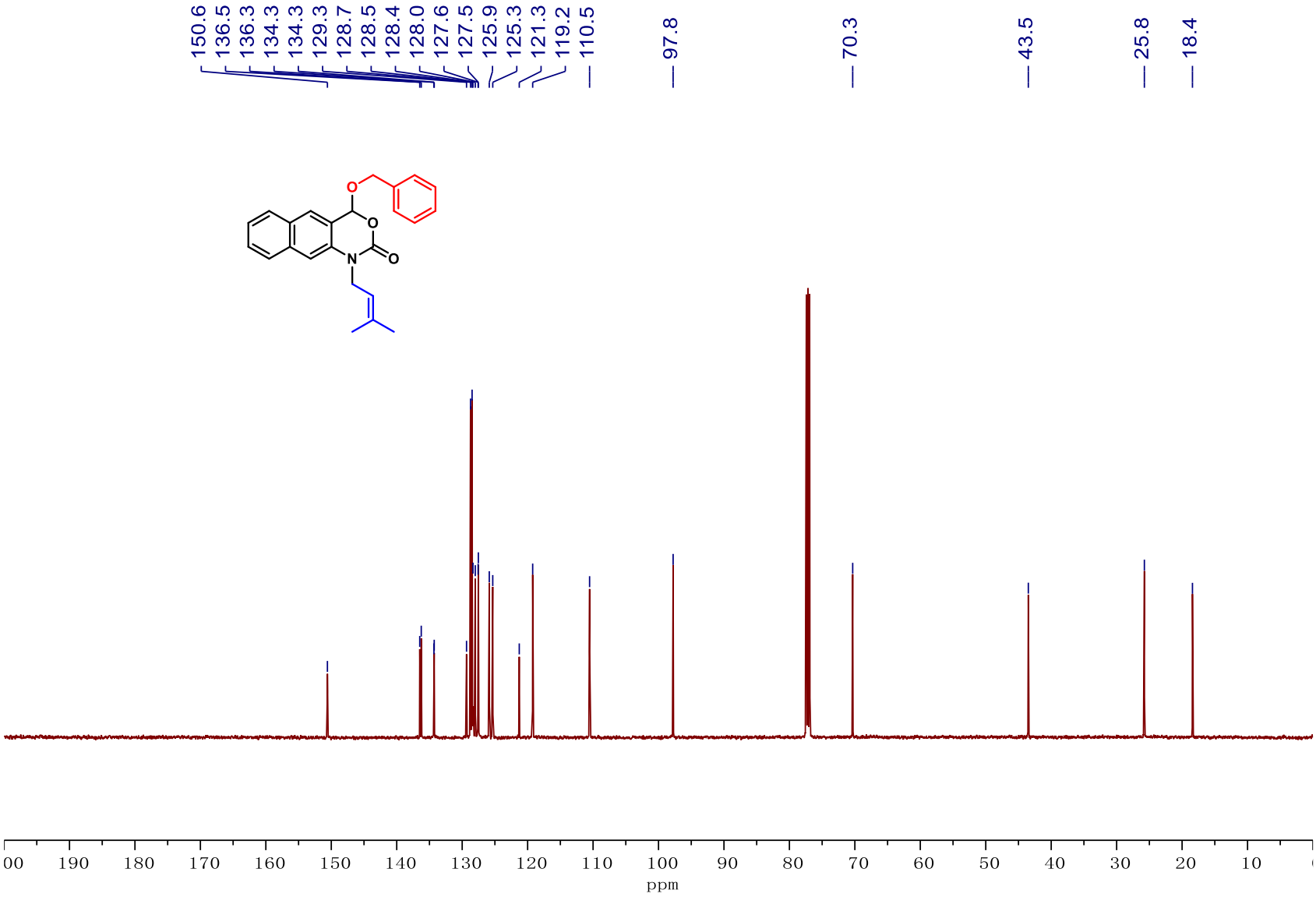

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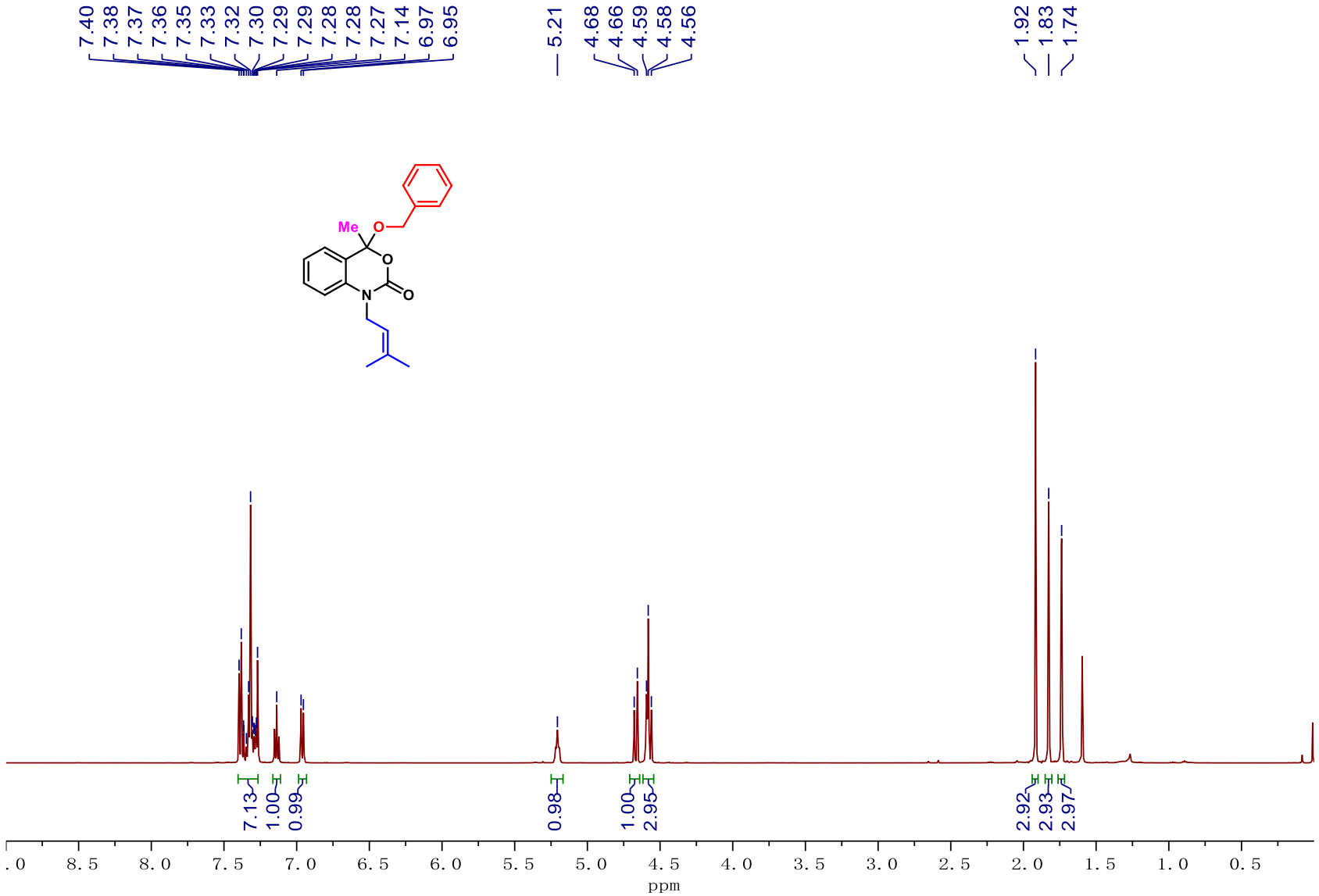

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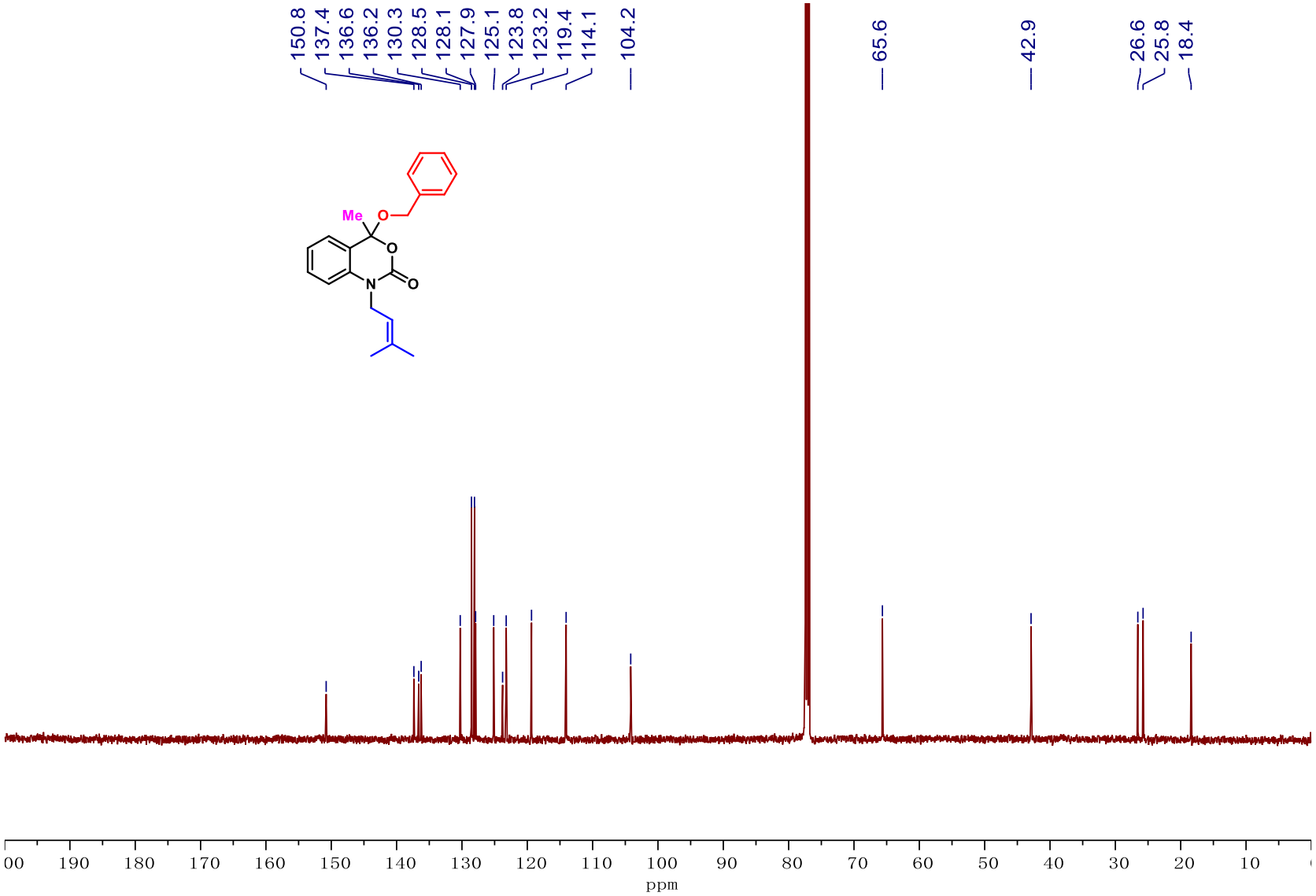

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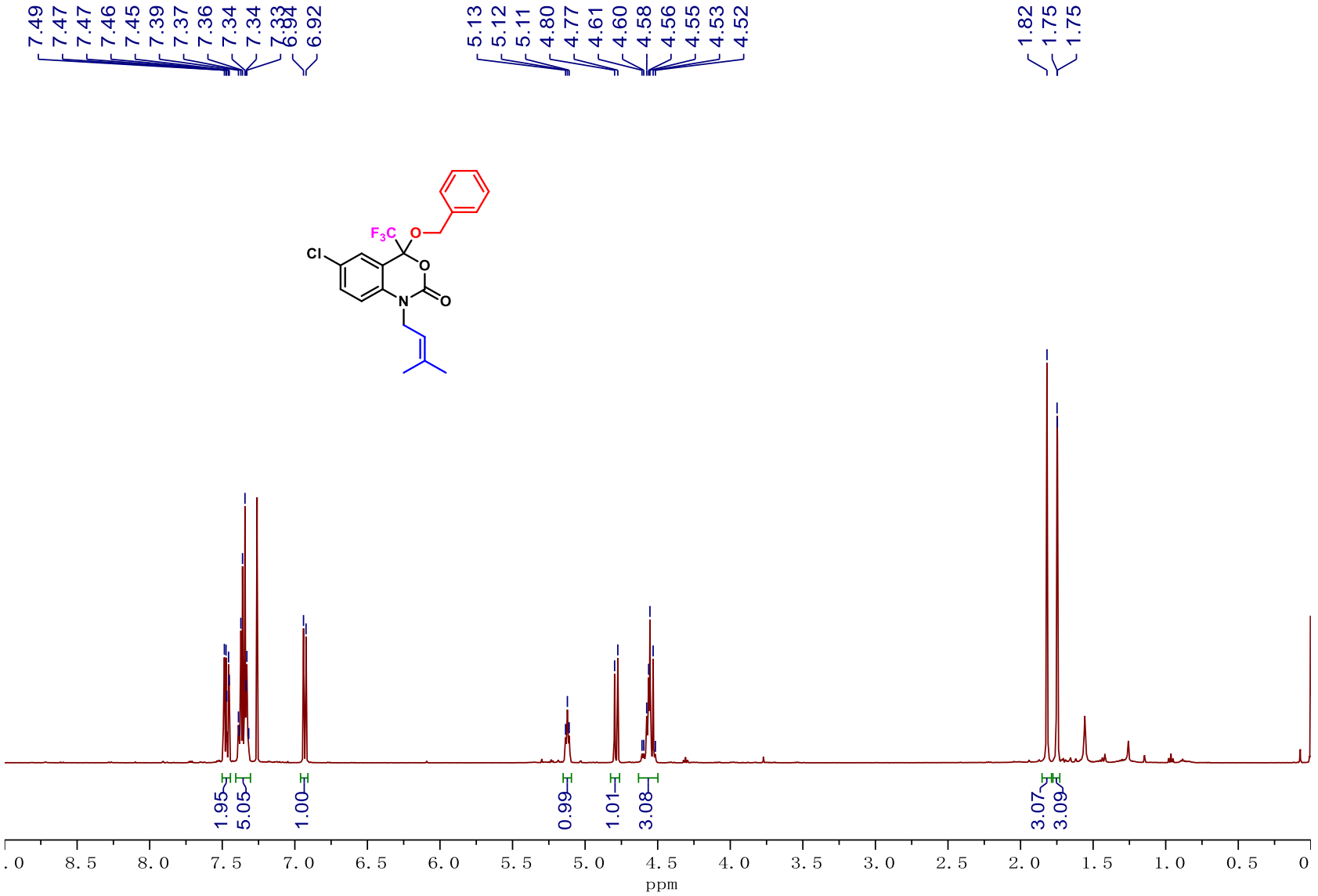

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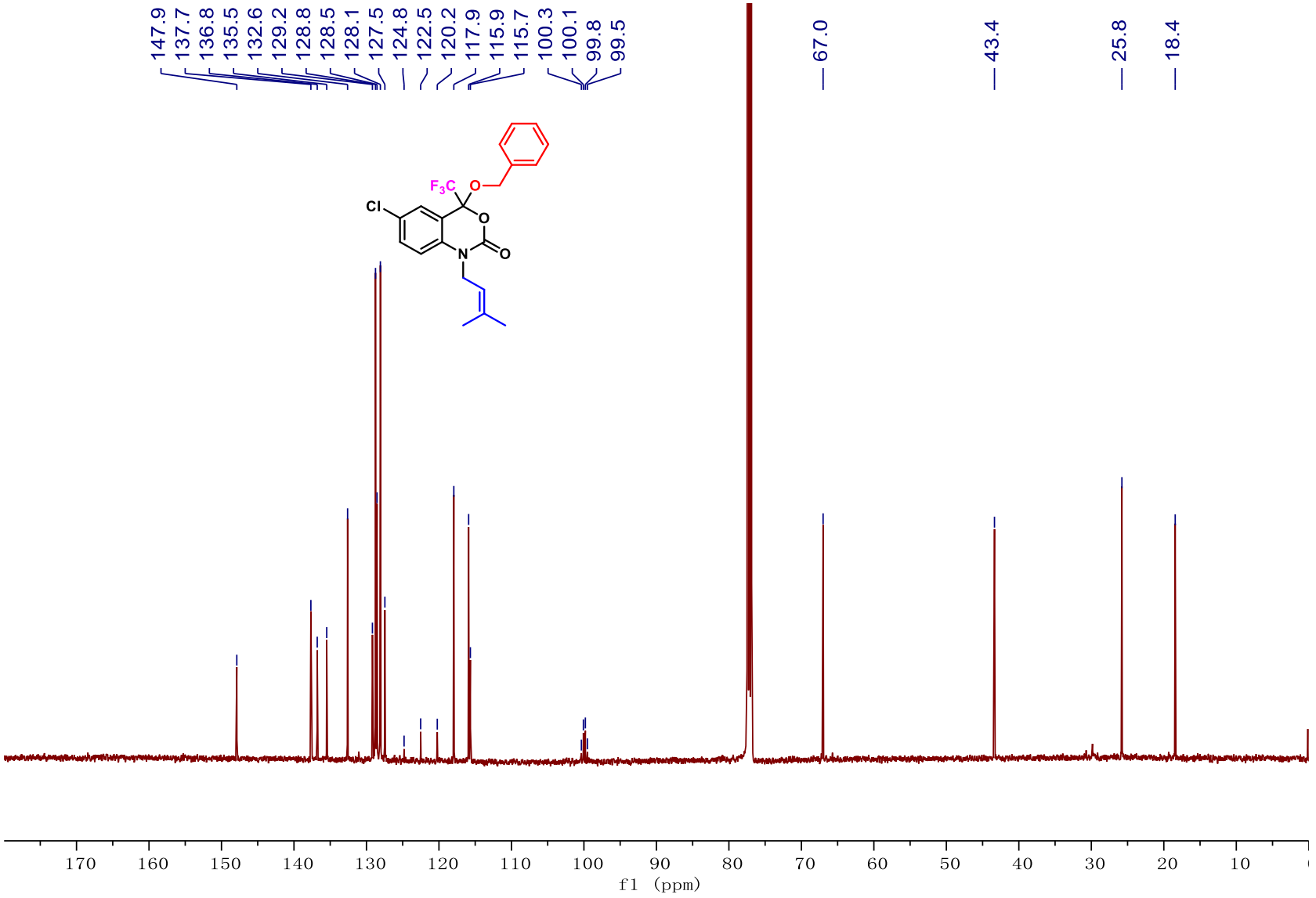
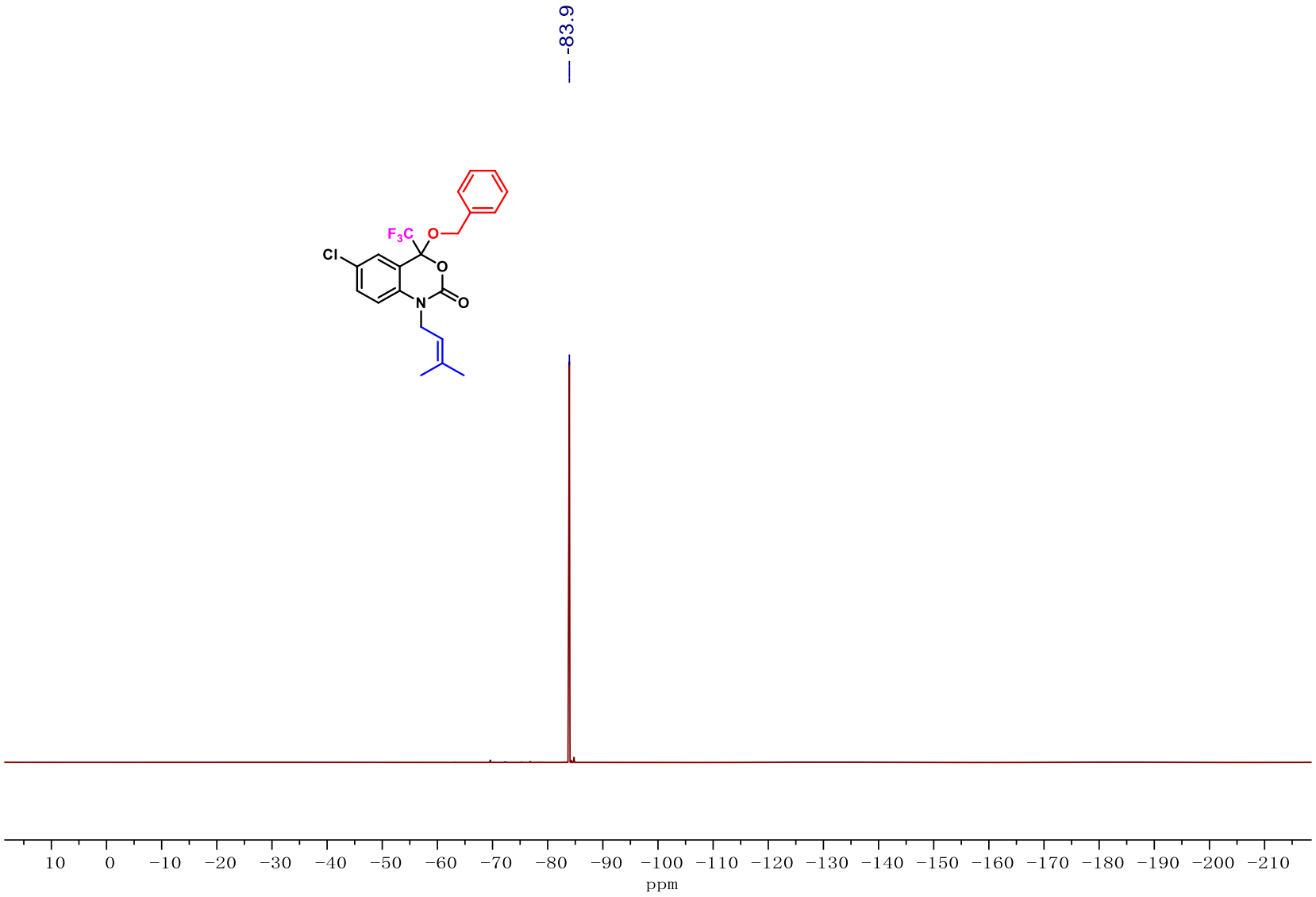
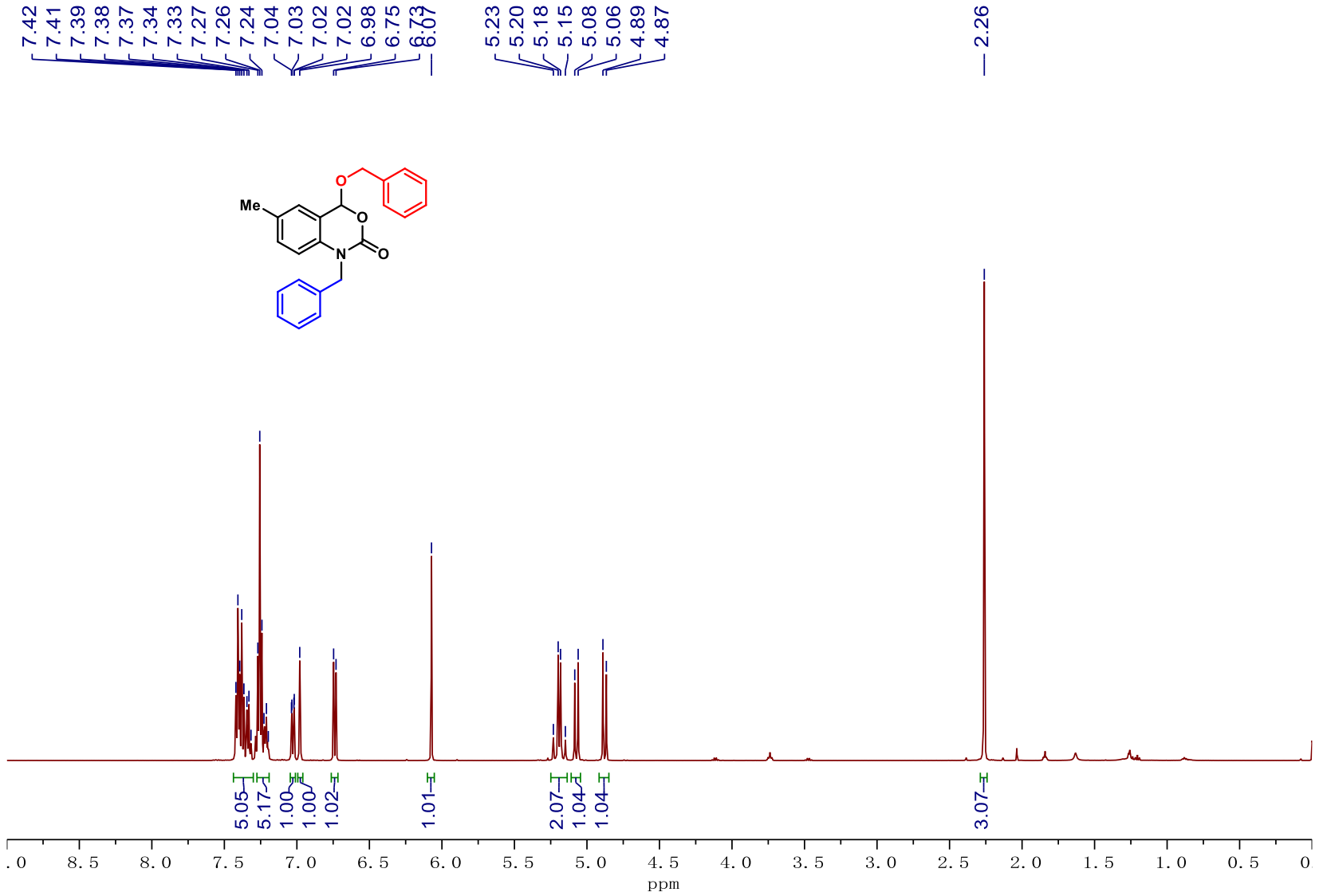


Compound 6n ^{19}F NMR



Compound 7a ^{1}H NMR



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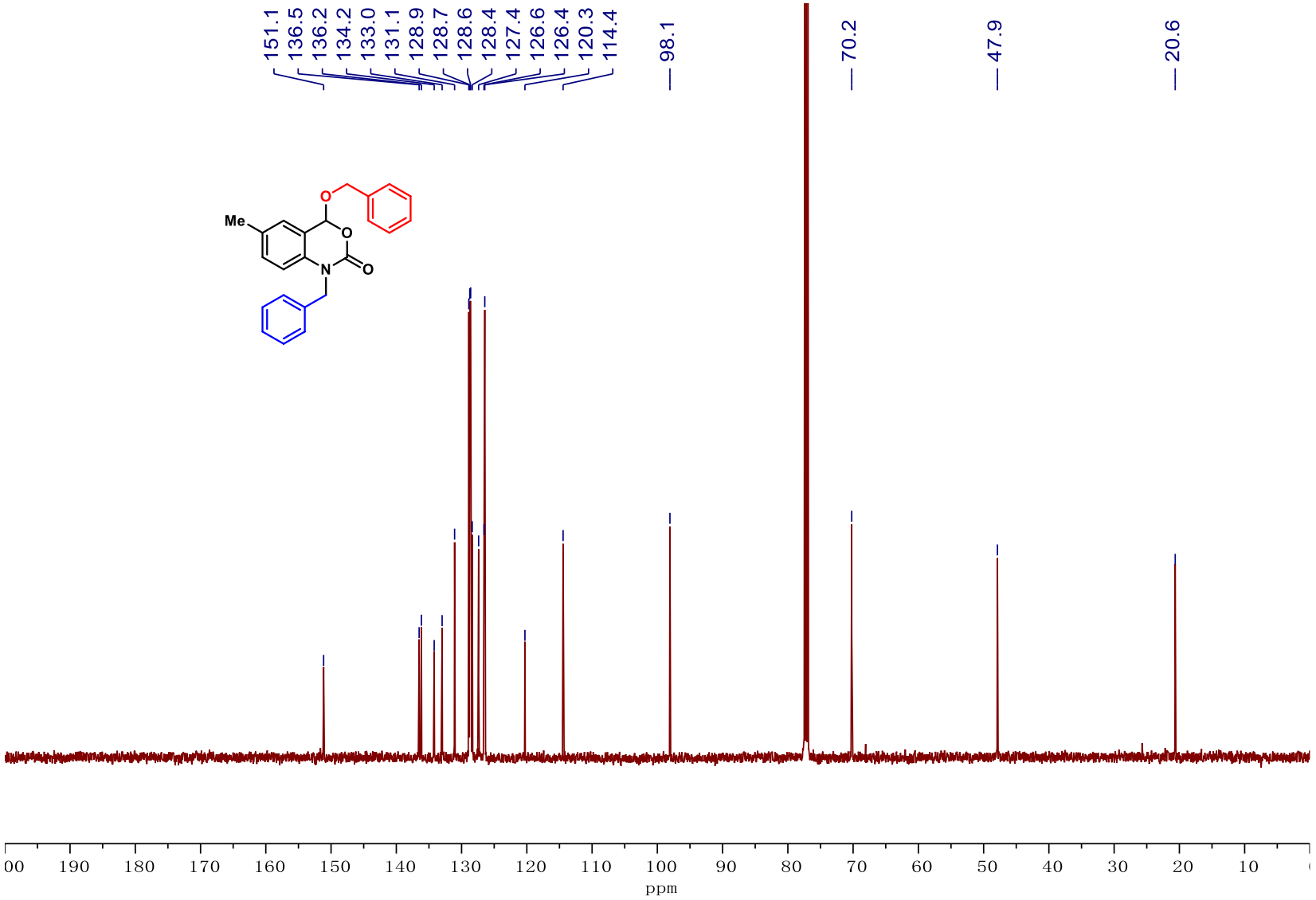

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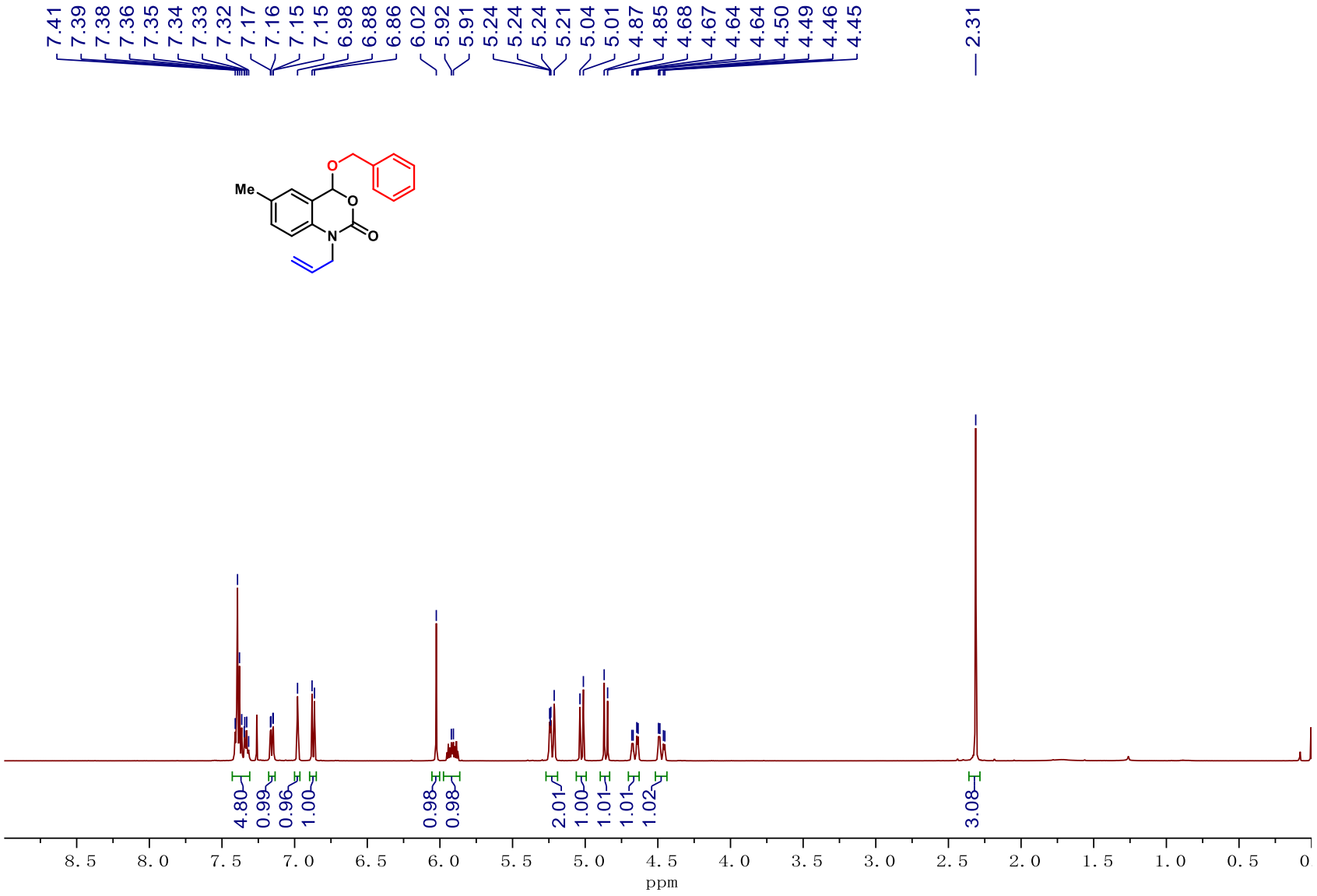

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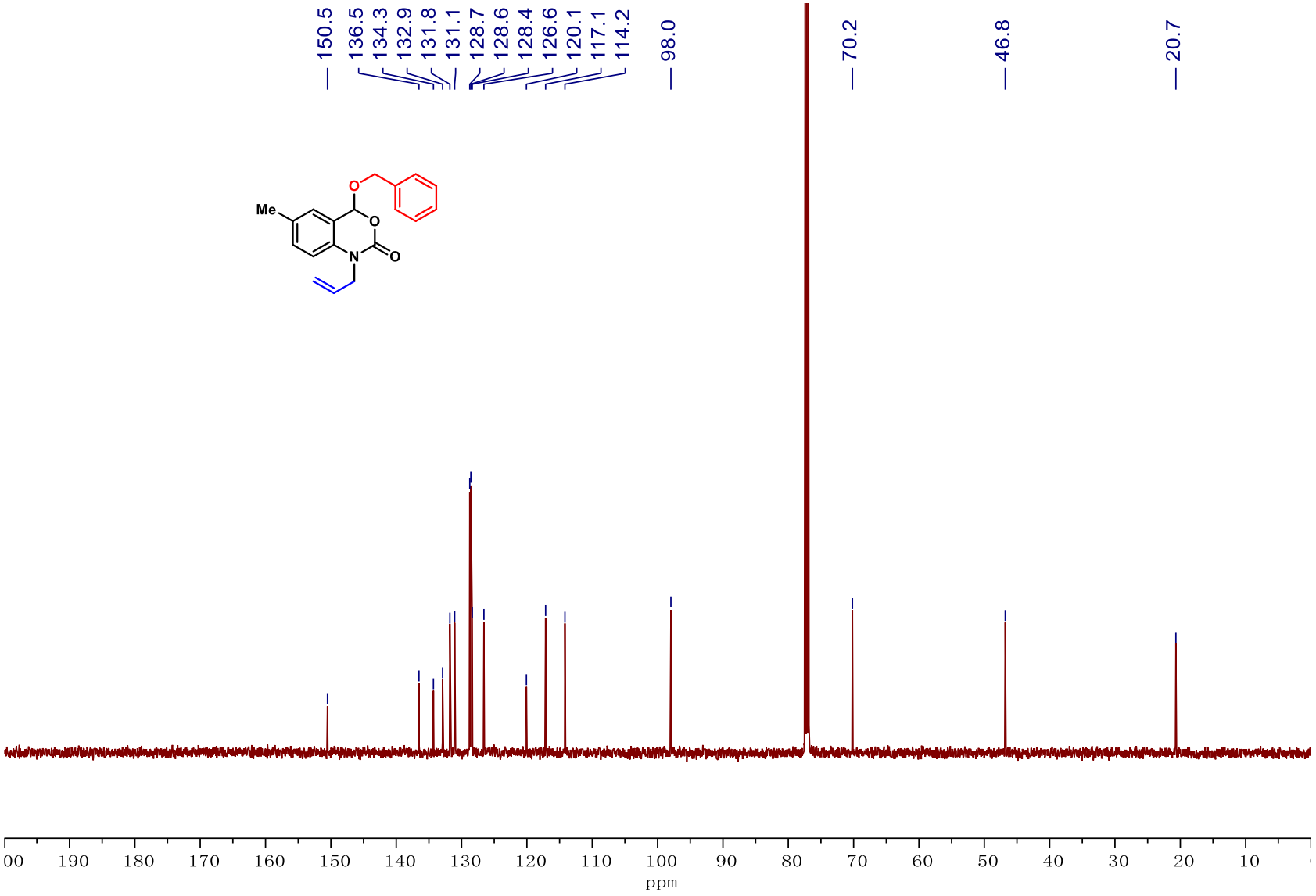

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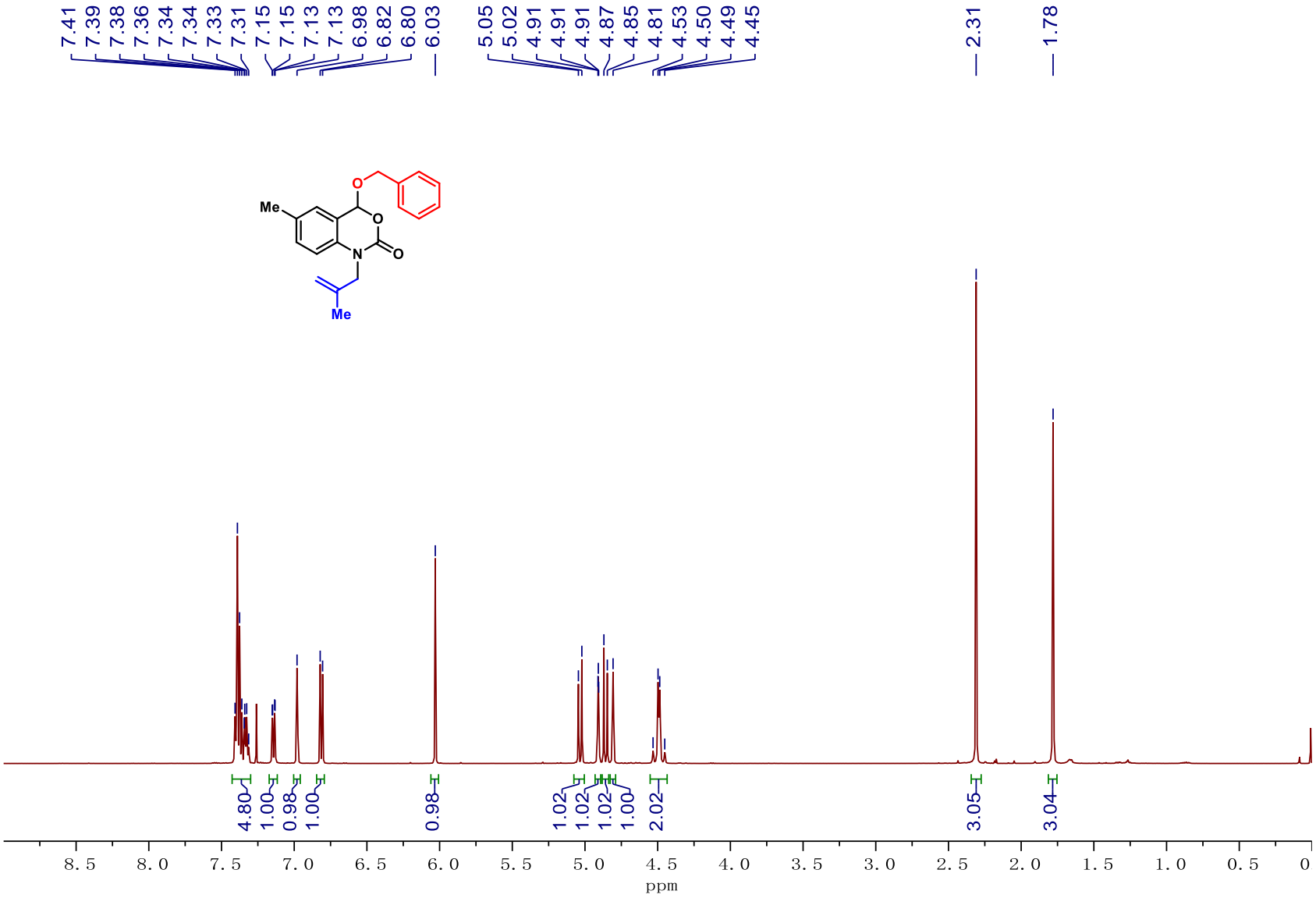

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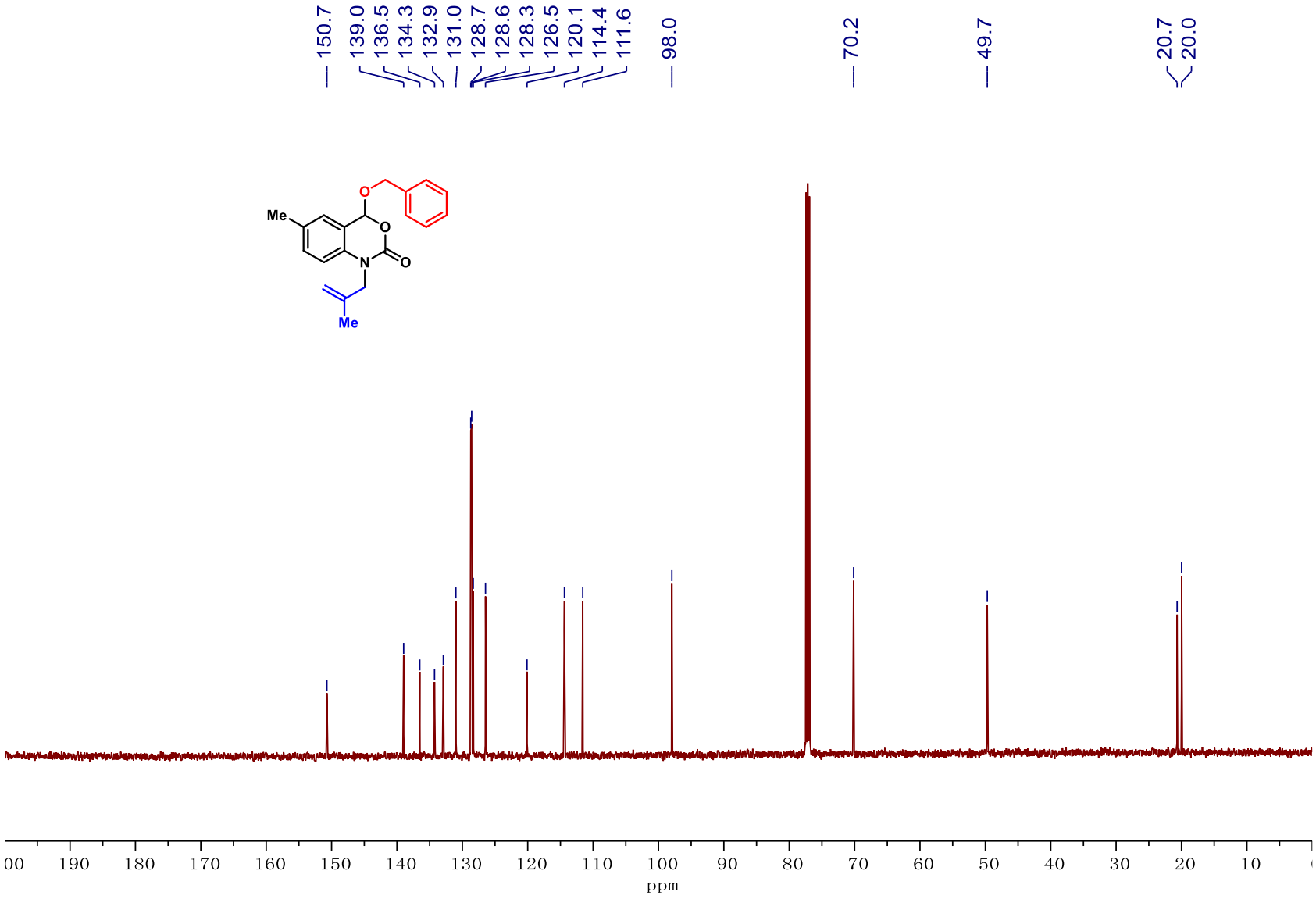

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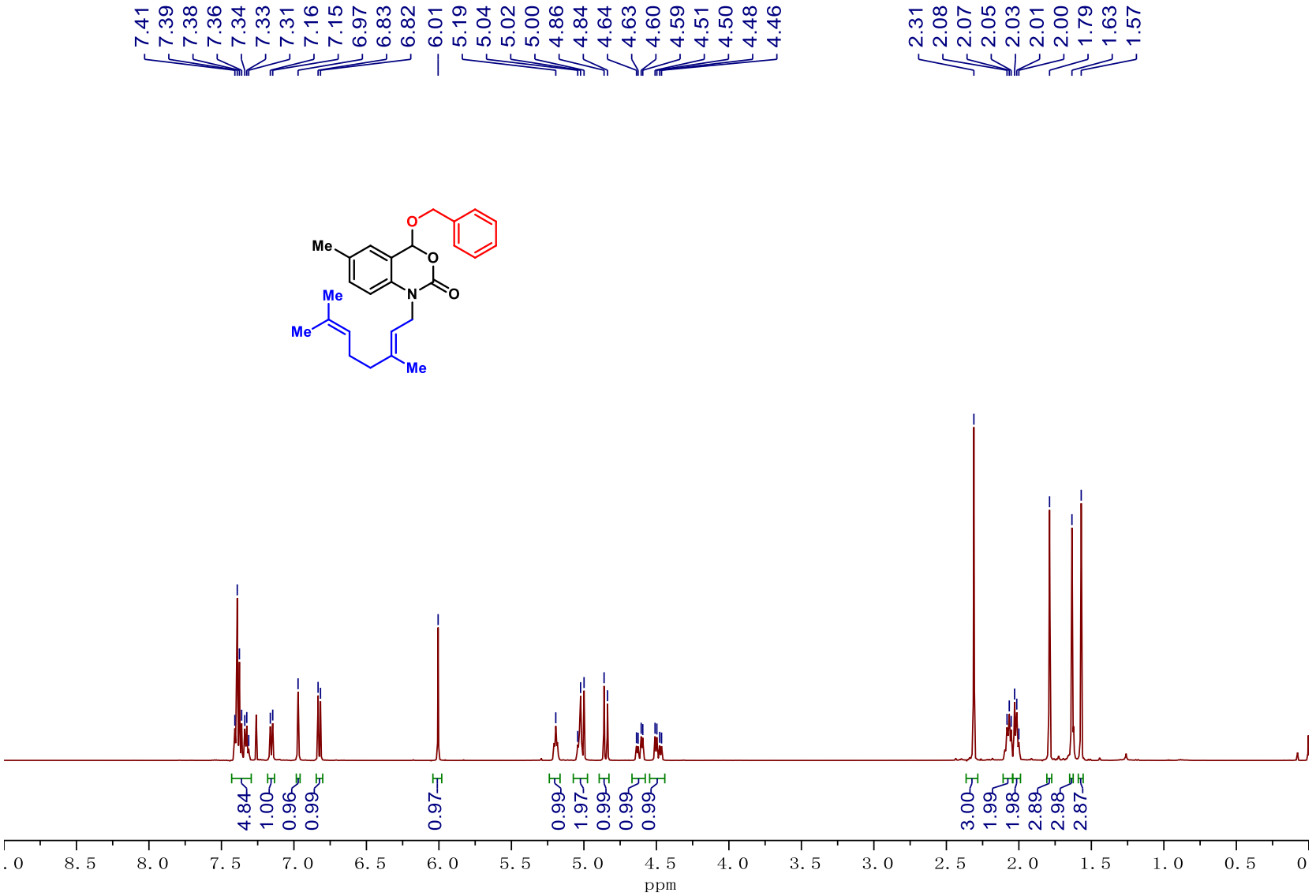

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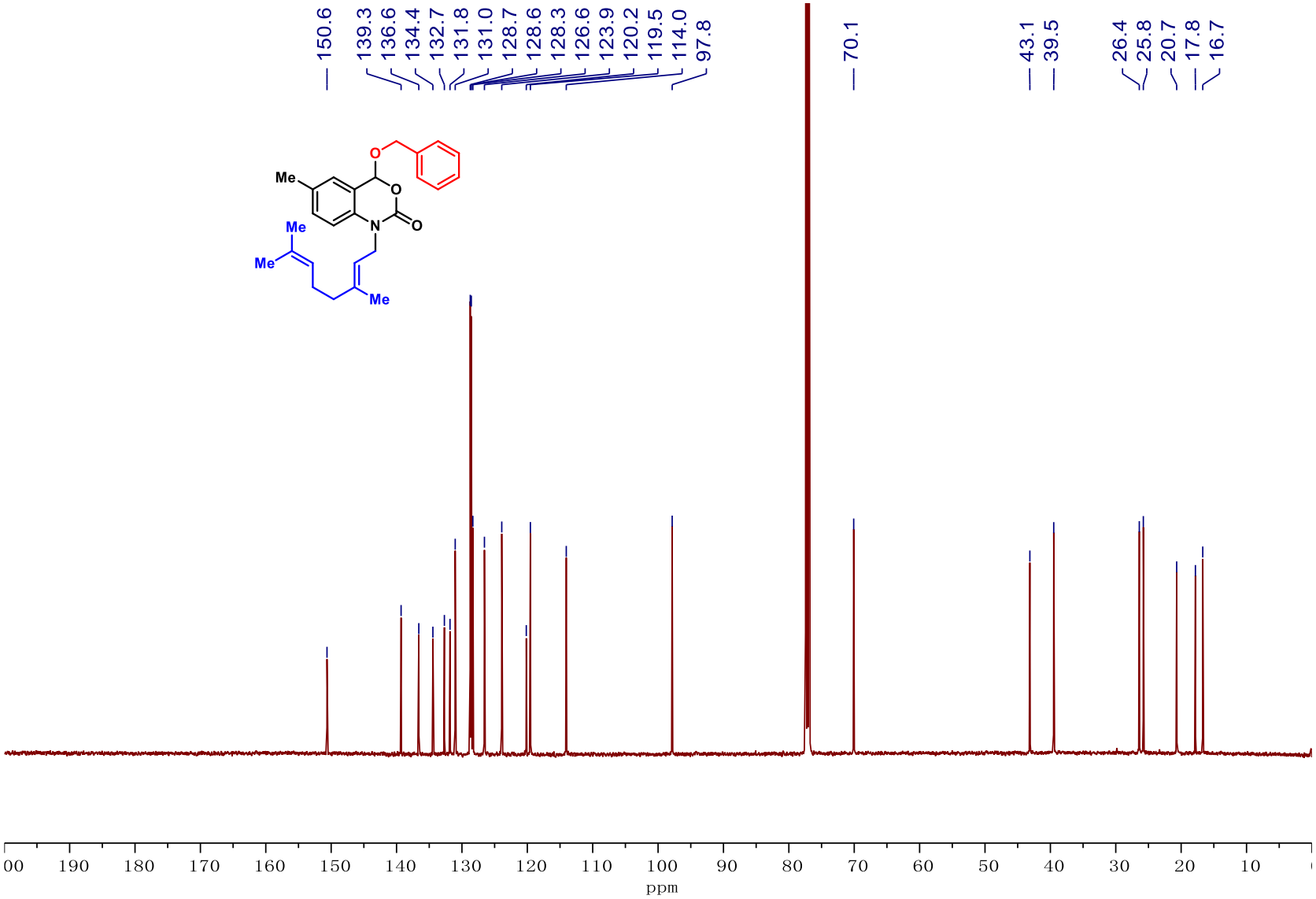

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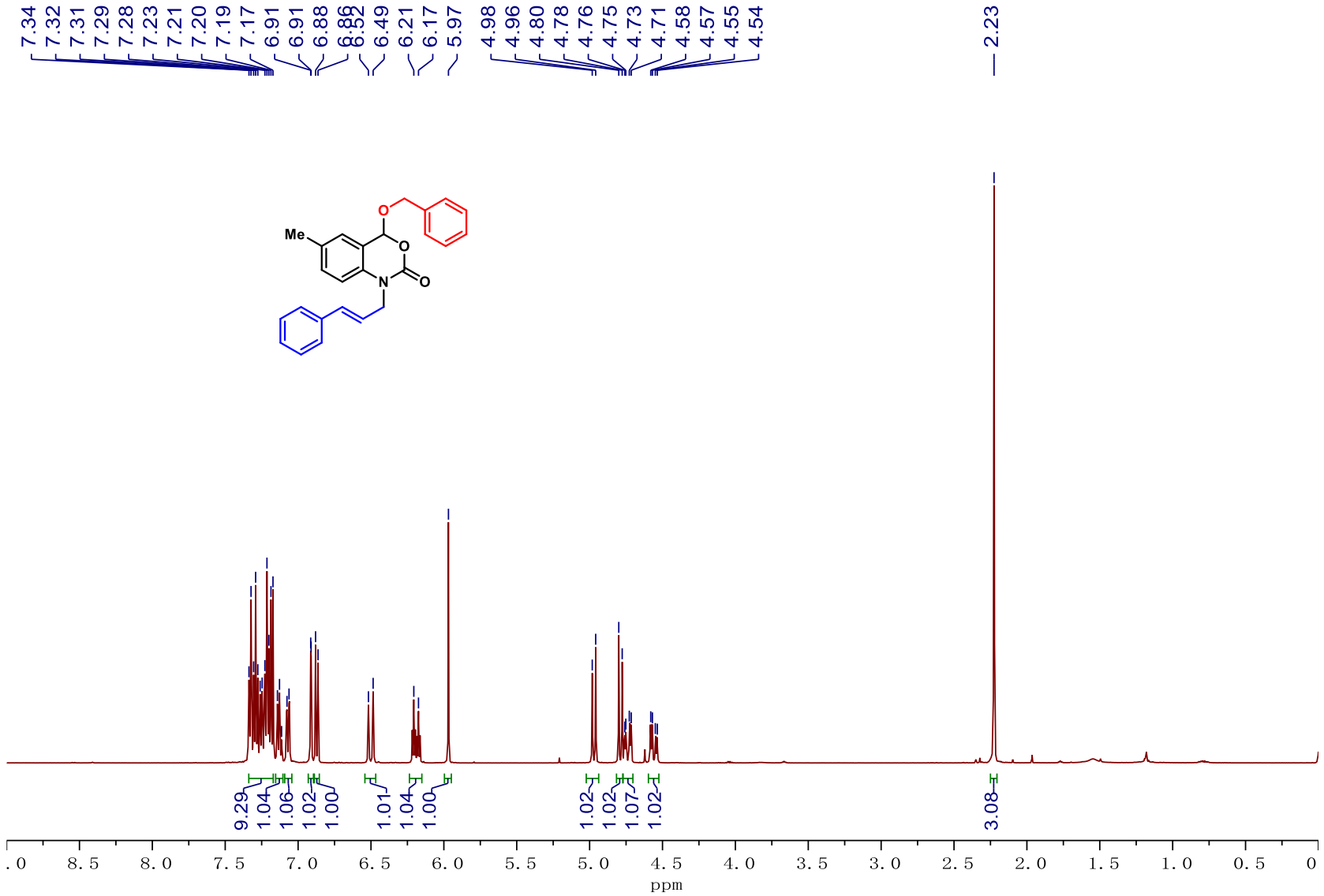

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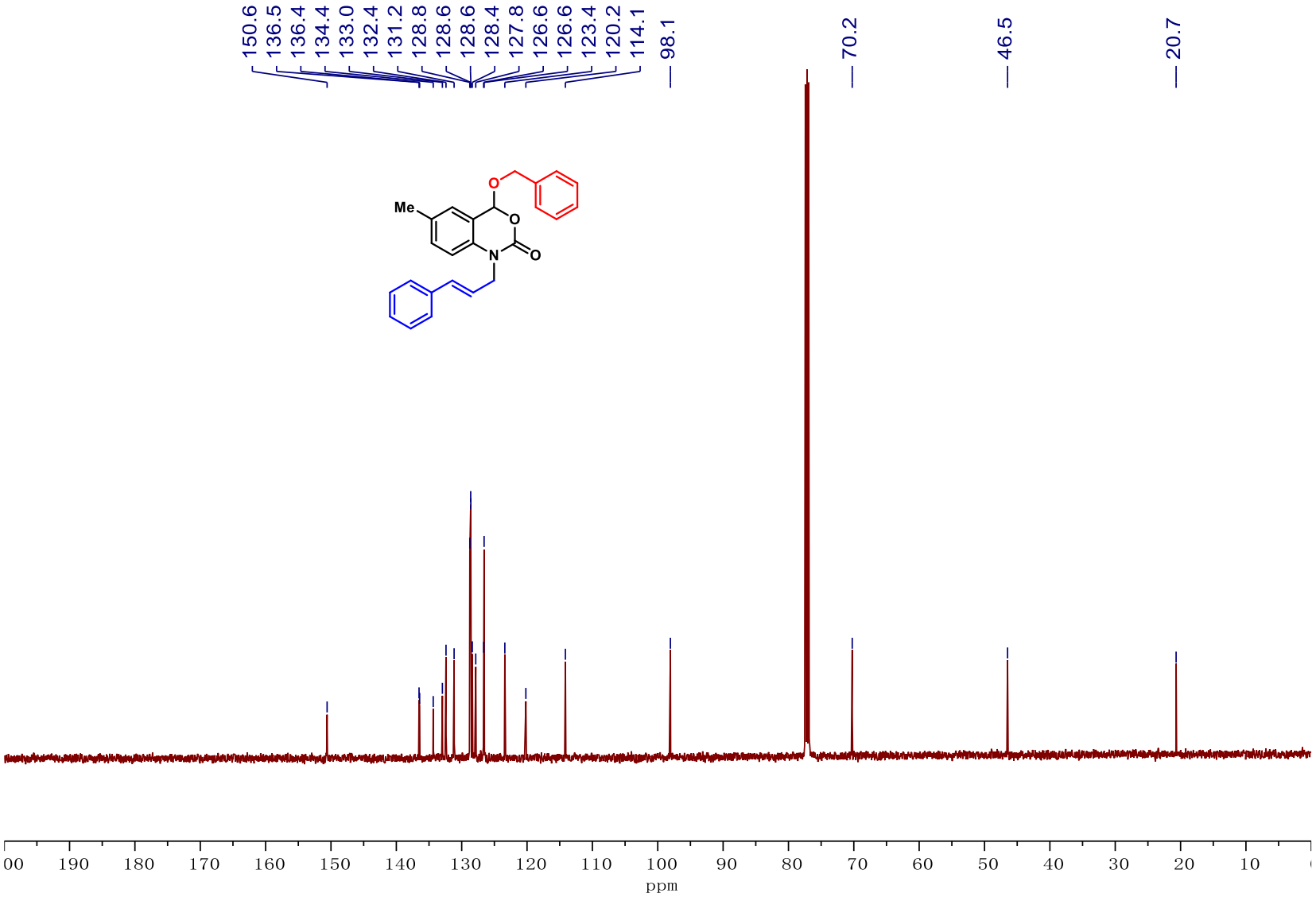

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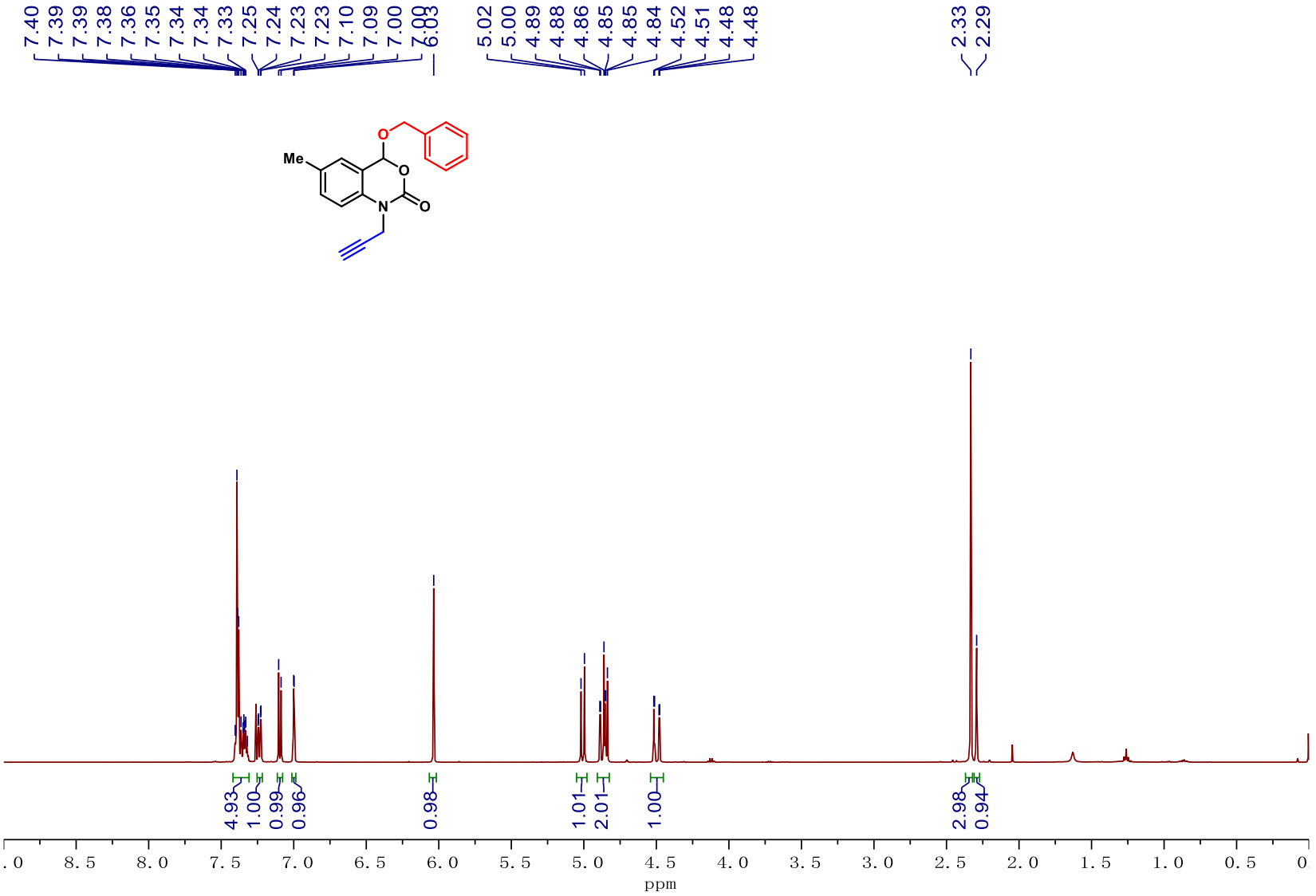

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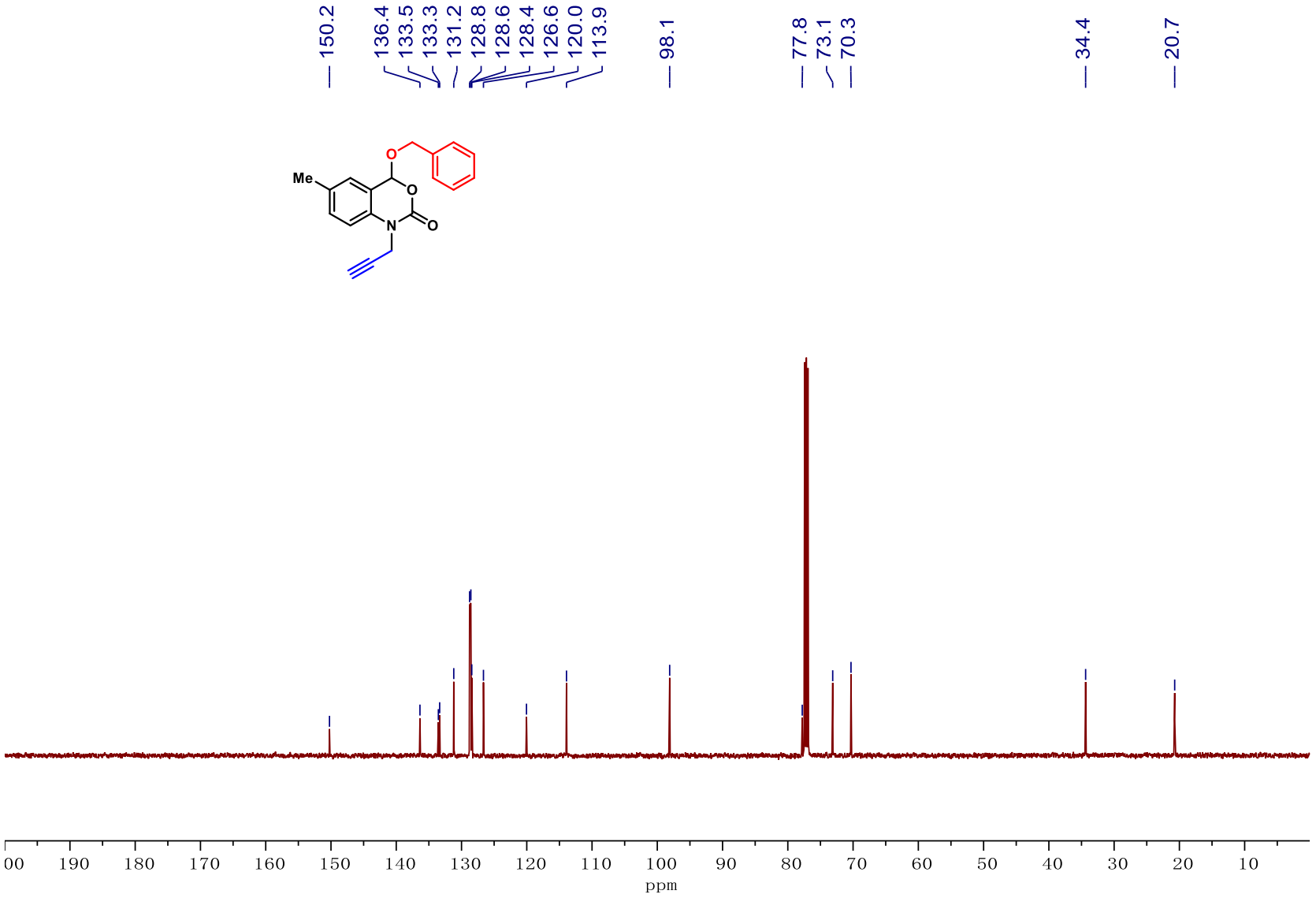
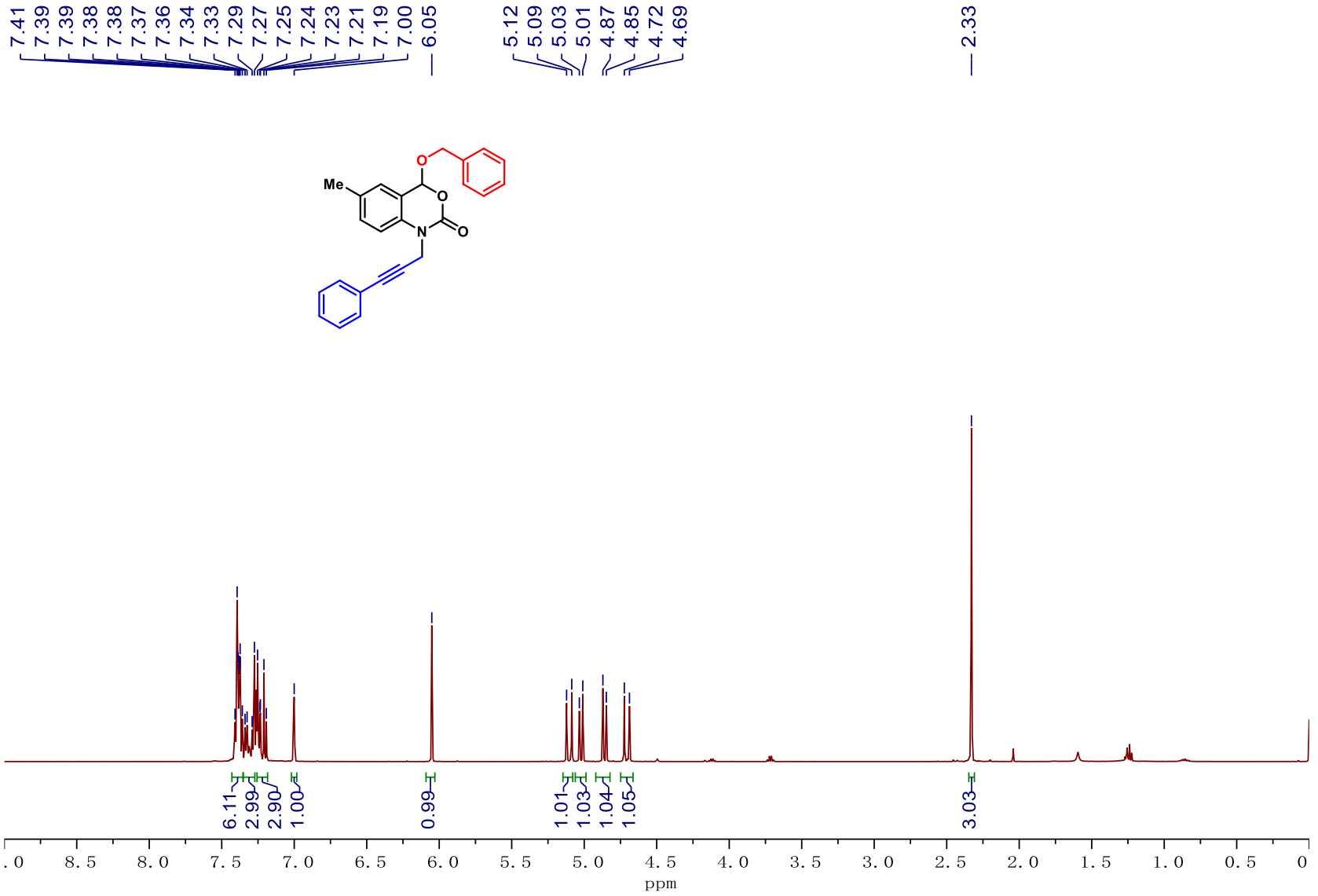


Compound 7g ^{1}H NMR



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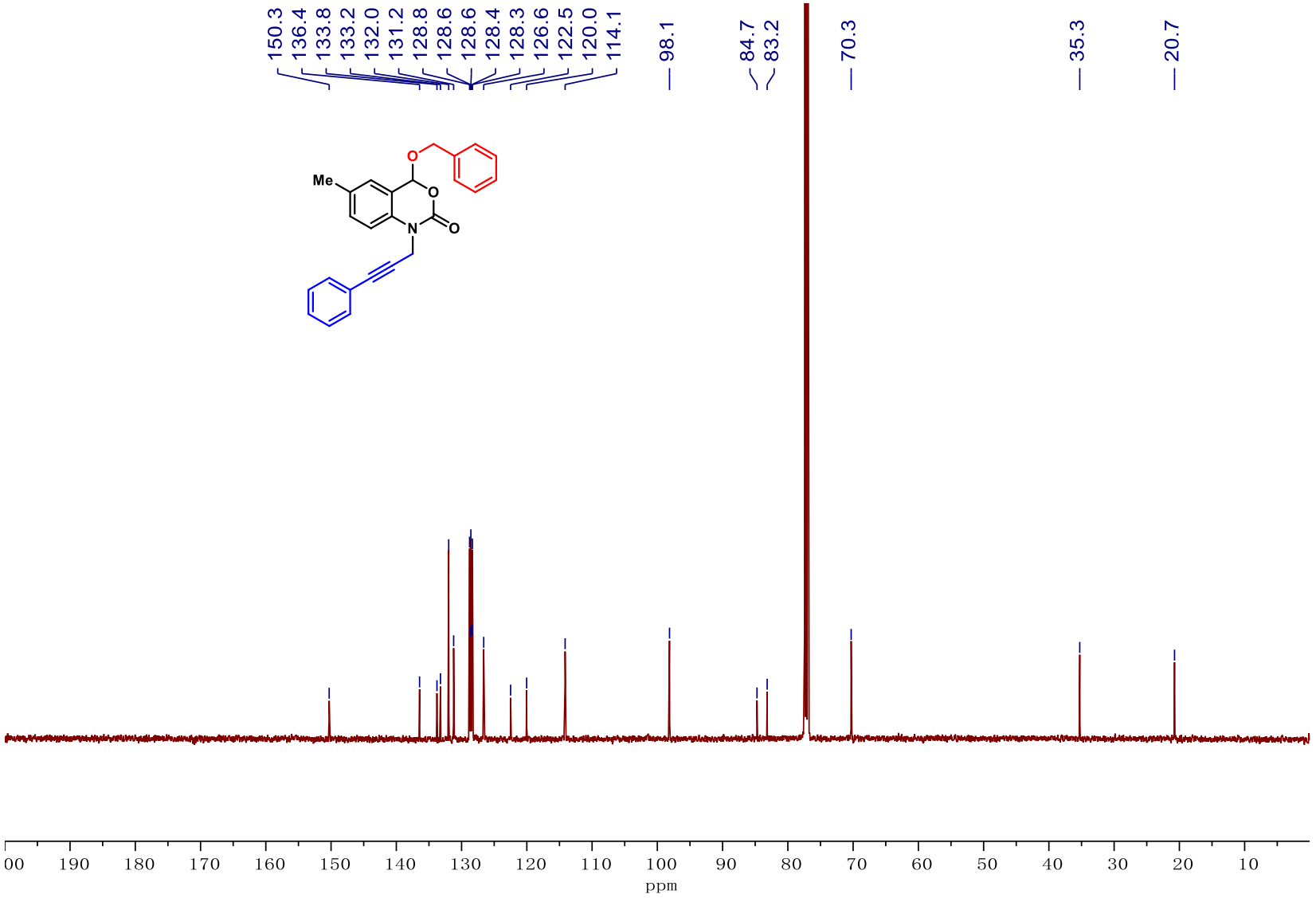

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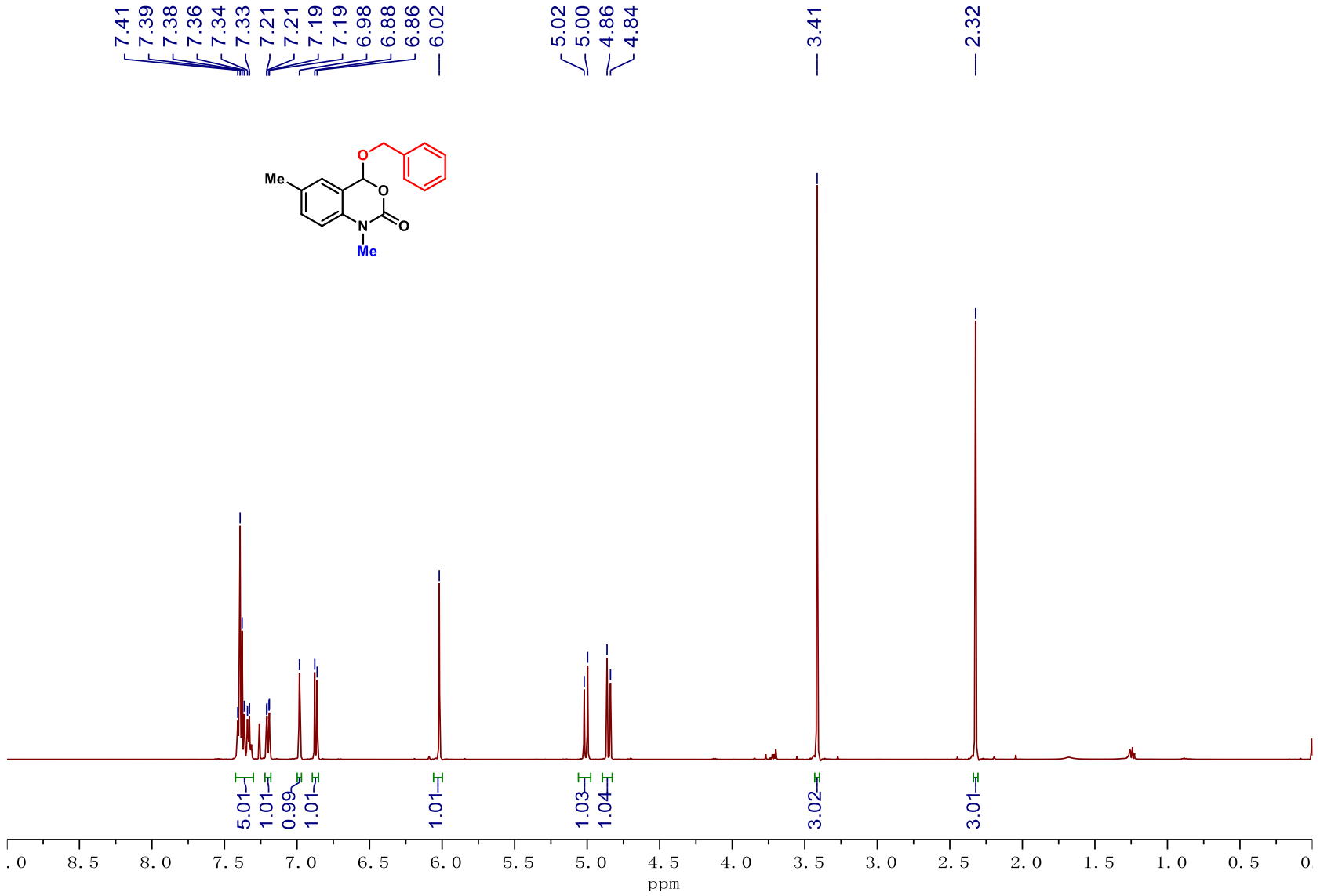

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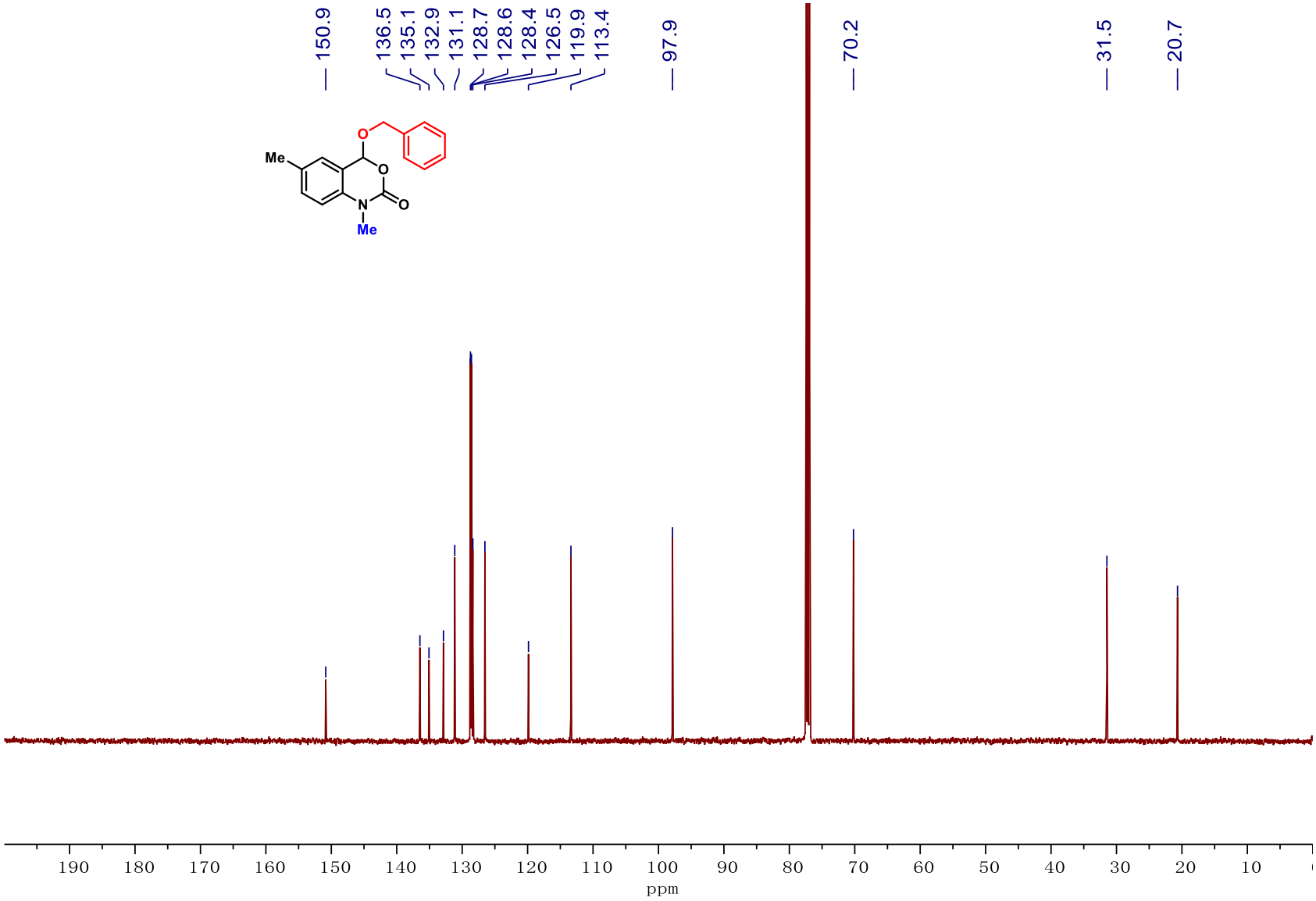
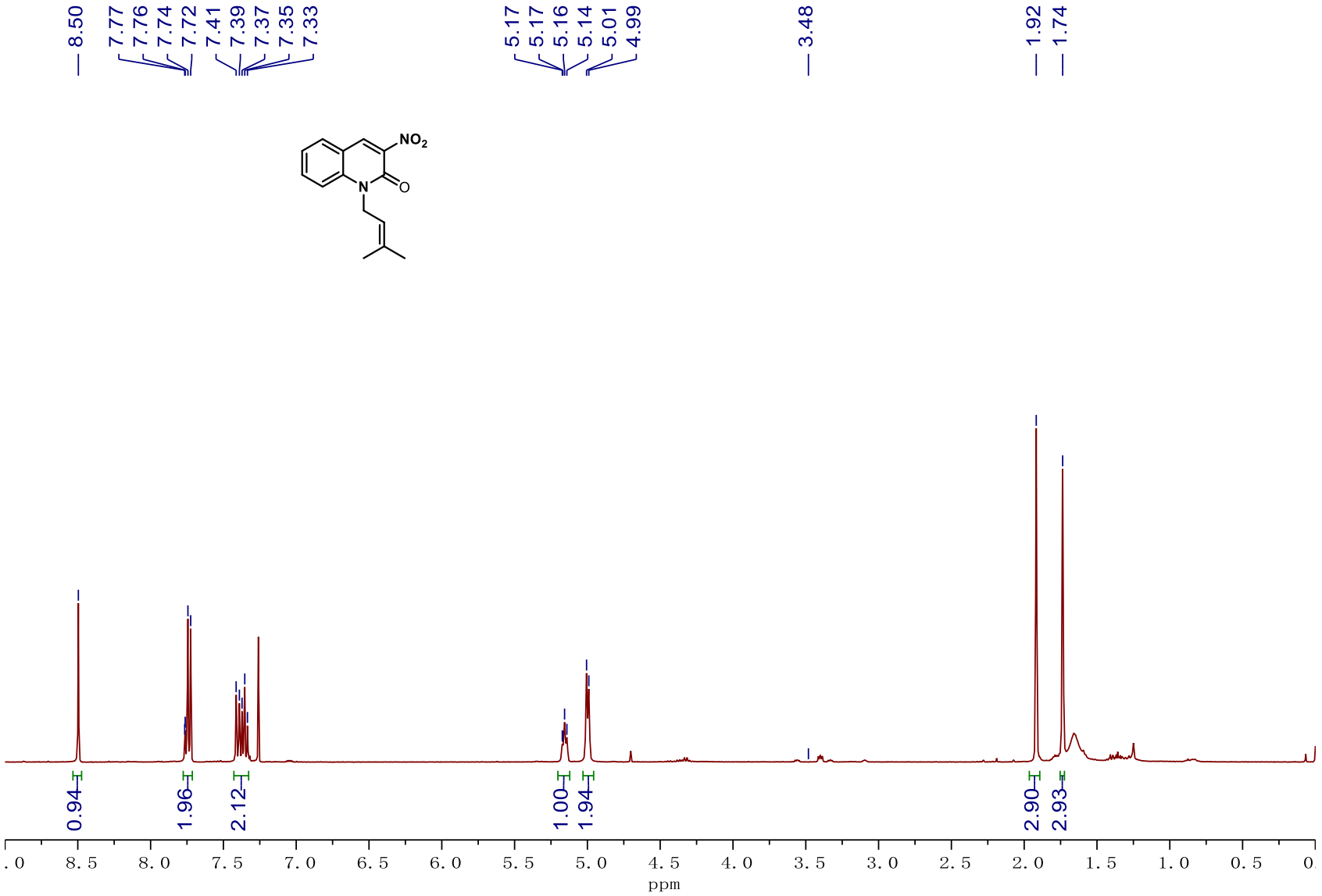
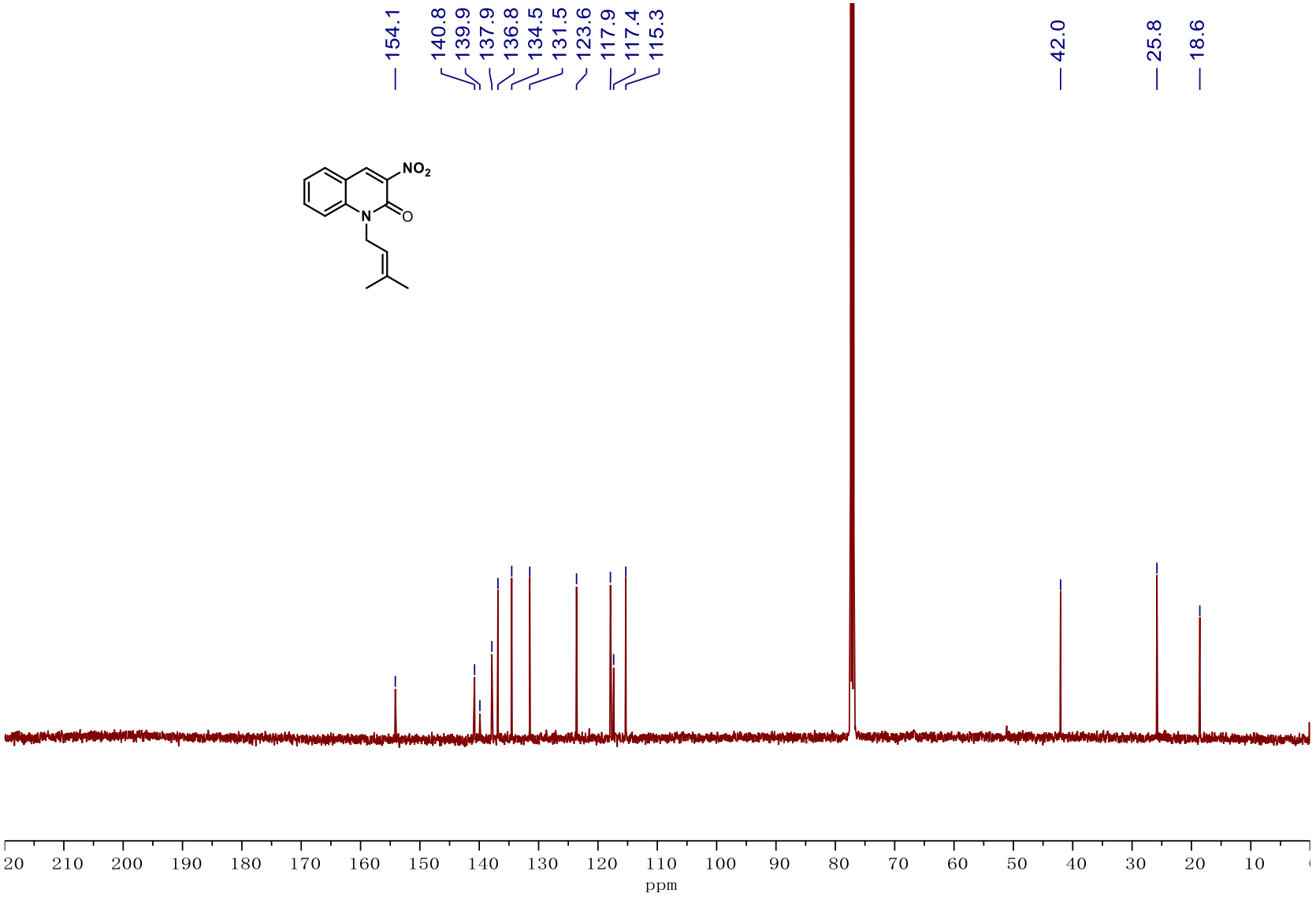


Compound 9 ^{1}H NMR



Compound 9 ^{13}C NMR



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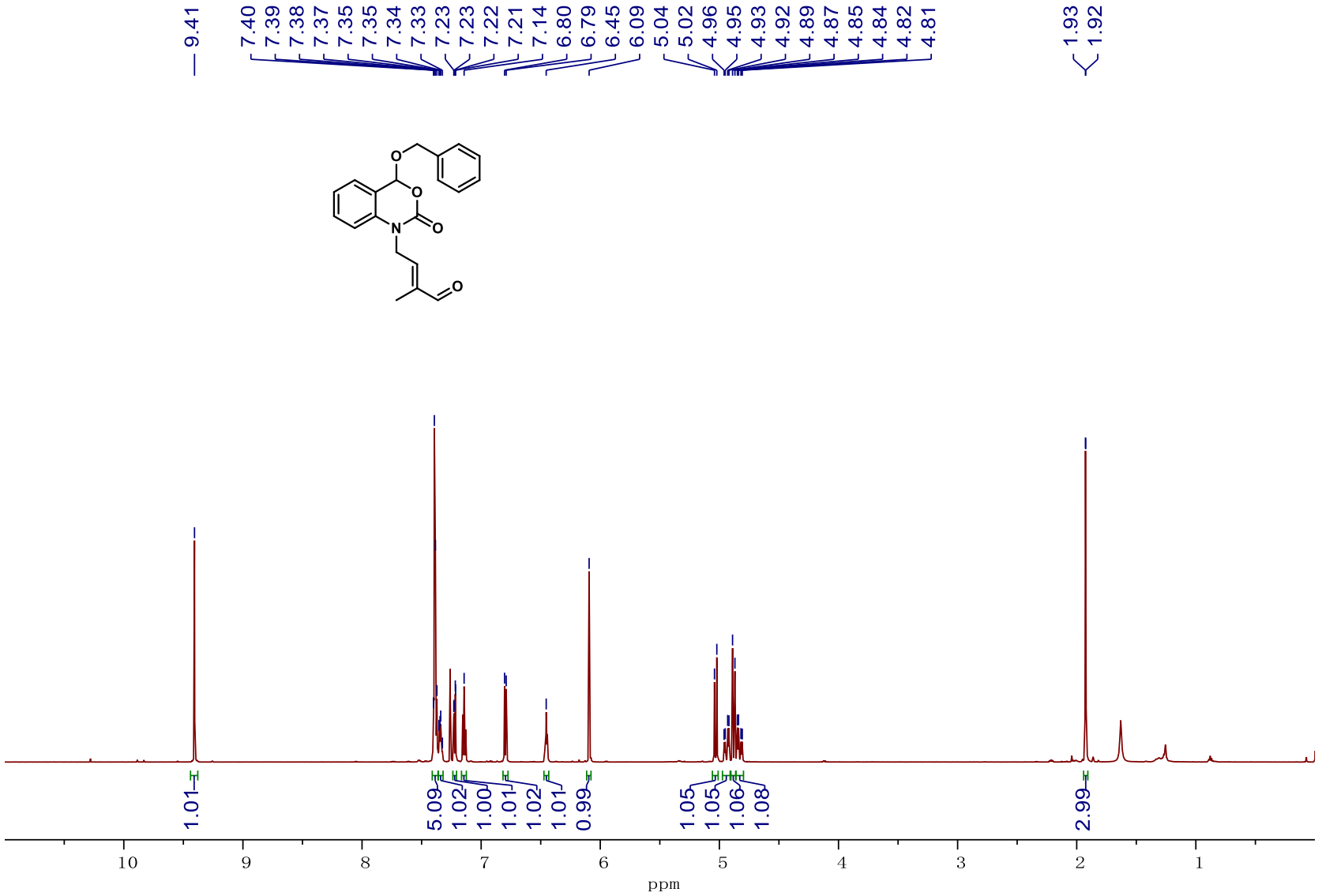

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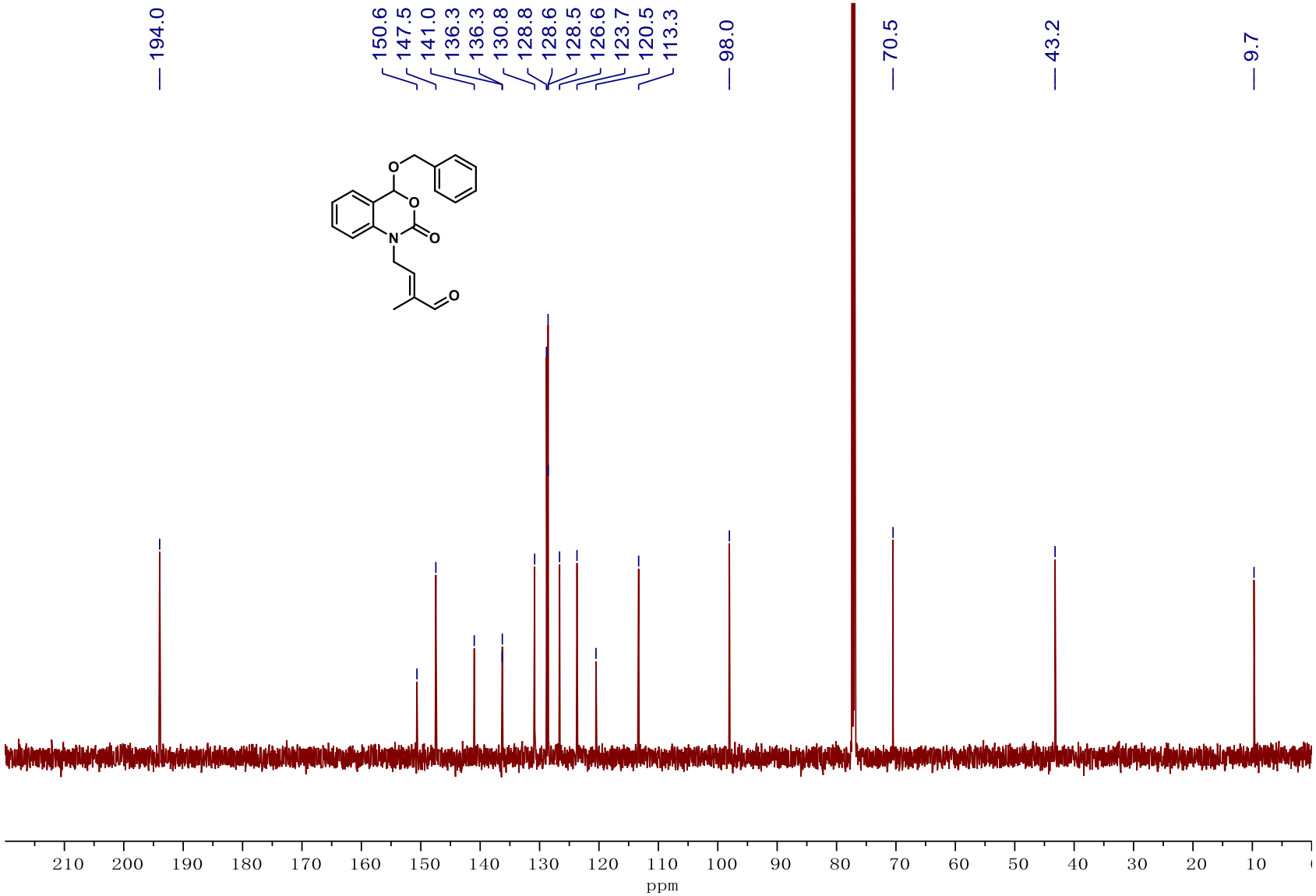

Compound 10 NOESY