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Supplemental Information

Stereoselective Three-component Cascade Synthesis of α-Substituted 2,4-Dienamide from *gem*-Difluorochloro Ethanes

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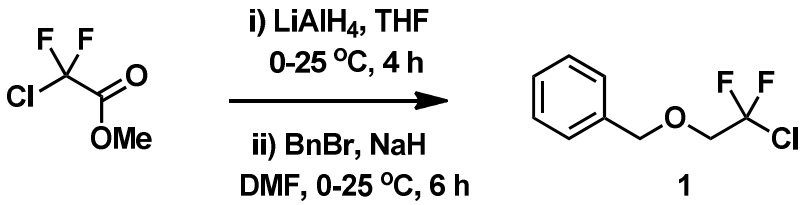
Contents

1. Experimental Section

All commercial reagents were used without further purification unless otherwise specified. Several solvents were distilled prior to use: dichloromethane and *N*, *N*-dimethylformamide (DMF) from CaH_2; tetrahydrofuran (THF) on Na/benzophenone. Air and/or moisture sensitive reactions were carried out in anhydrous solvents under an atmosphere of argon in oven-dried glassware. All reaction was monitored on pre-coated plate (Merck, silica gel $60F_{254}$). Flash Column chromatography was carried out by using silica gel (Merck, 70–230 and 230–400 mesh, ASTM) and automated Biotage Isolera™ System with Biotage® SNAP cartridges were used for purification. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Varian 400-MR (400 MHz) spectrometer at ambient temperature. TMS was used as an internal standard and the chemical shifts were reported in parts per million (ppm, δ units) relative to internal standard TMS (0.00 ppm) and for $CDCl_3$ (7.26 ppm). ^{19}F NMR was recorded at 376 MHz with Varian 400-MR spectrometer and relative internal standard $CFCl_3$ (0.00 ppm) and for $PhCF_3$ (-63.72 ppm). The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J* are reported in Hertz (Hz). Electrospray ionization (ESI) was obtained on a Varian 500-MS ion trap mass spectrometer (Varian, Palo Alto, CA, USA) and high-resolution mass spectrometry (HR-MS) were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump.

SI 1.1. General synthetic procedure for *gem*-difluoro ethane derivatives (1-7)

Synthesis of 1,1-difluoro-1-chloro-2-benzyloxy ethane (1)



To a solution of methyl chlorodifluoroacetate (MCDFA, 5 g, 34.6 mmol) in dry THF (50 mL) at 0 °C, $LiAlH_4$ (1.3 g, 34.6 mmol) was added in portion wise, the resulting suspension was allowing to warm to 25 °C and stirred for 4 h. The reaction was cooled to 0 °C and quenched with saturated solution of Na_2SO_4 in water (5 mL) very slowly (dropwise). The reaction mixture was filtered through Celite pad and washed with ethyl ether (50 mL × 3) and the combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure (P = 650 mbar, 32 °C). Without further purification, the resulting crude (3.5 g) was directly forward for the next step. To an ice-cooled solution (0 °C) of the obtained crude alcohol (3.5 g, 30.0 mmol) in DMF (10 mL) was added NaH (1.44 g, 36.05 mmol, 60% in mineral oil) portion wise and stirred for 30 min. Benzyl bromide (4.4 mL, 36.05 mmol) was added dropwise to the reaction mixture at 0 °C and stirred at 25 °C for additional 6 h. The reaction mixture was cooled to 0 °C and quenched with water, partitioned between ethyl acetate (EtOAc) and water. Organic layer was separated, washed with brine, dried over (Na_2SO_4), and concentrated under reduced pressure. Purification of the residue by column chromatography using 5% EtOAc/petroleum ether as eluant afforded **1** (6.7 g, 93%) as sweet-smelling colorless syrup. R_f =0.8 (2% EtOAc/hexane).

1,1-Difluoro-1-chloro-2-benzyloxy ethane (1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 (t, J = 11.2 Hz, 2H), 4.73 (s, 2H), 7.34–7.41 (m, 5H).

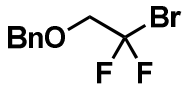
^{13}C NMR (100 MHz, $CDCl_3$) δ 72.8 (t, J = 27.6 Hz), 74.3, 127.3 (t, J = 293.3 Hz), 127.9, 128.3, 128.7, 136.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ 61.2 (dt, J = 2.6, 11.3 Hz, 2F).

HRMS (EI) m/z $[M]^+$ calcd for $C_9H_9ClF_2O$: 206.0310, found: 206.0309.

Synthesis of 1,1-difluoro-1-bromo-2-benzyloxy ethane[a]

Following the general procedure for *gem*-difluoro ethane derivatives, the reaction of ethyl bromodifluoroacetate (EBDFA, 3 g) with benzyl bromide (2 mL) gave 1,1-difluoro-1-bromo-2-benzyloxy ethane (2.75 g, 74 %) as colorless, sweet-smelling syrup. R_f=0.8 (2% EtOAc/petroleum ether).



1,1-Difluoro-1-bromo-2-benzyloxy ethane

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 (t, J = 12.0 Hz, 2H), 4.74 (s, 2H), 7.35–7.41 (m, 5H).

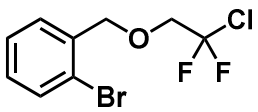
^{13}C NMR (100 MHz, $CDCl_3$) δ 74.2, 74.4 (t, J = 25.3 Hz), 120.8 (t, J = 306.6 Hz), 127.9, 128.3, 128.7, 136.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -55.5 (t, J = 12.0 Hz, 2F).

HRMS (EI) m/z $[M]^+$ calcd for $C_9H_9BrF_2O$: 249.9805, found: 249.9800.

Synthesis of 1-bromo-2-((2-chloro-2,2-difluoroethoxy)methyl)benzene (3)

Following the general procedure for *gem*-difluoro ethane derivatives, the reaction of MCDFA (3 g) with 2-bromo benzyl bromide (2.9 mL) gave 1-bromo-2-((2-chloro-2,2-difluoroethoxy)methyl)benzene **3** (5.4 g, 91%) as colorless syrup. R_f = 0.8 (3% EtOAc/petroleum ether).



1-Bromo-2-((2-chloro-2,2-difluoroethoxy)methyl)-benzene (3)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.03 (t, J = 11.2 Hz, 2H), 4.79 (s, 2H), 7.19 (td, J = 1.6, 7.2 Hz, 1H), 7.35 (td, J = 1.2, 7.6 Hz, 1H), 7.49 (dd, J = 1.2, 7.6 Hz, 1H), 7.56 (dd, J = 1.2, 8.0 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 73.6 (t, J = 28.3 Hz), 73.7, 122.8, 127.1 (t, J = 292.5 Hz), 127.7, 129.4, 129.6, 132.8, 136.3.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -61.32 (dt, J = 2.6, 11.3 Hz, 2F).

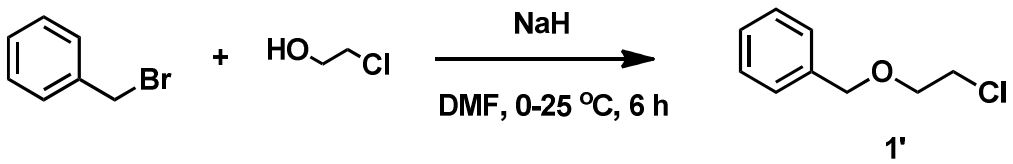
HRMS (EI) m/z $[M]^+$ calcd for $C_9H_8BrClF_2O$: 283.9415, found: 283.9419.

Synthesis of *para*-substituted *gem* difluorochloro ethanes (4-6)

Following the general procedure for *gem*-difluoro ethane synthesis, 1-chloro-4-((2-chloro-2,2-difluoroethoxy)methyl)benzene (**4**), 1-((2-chloro-2,2-difluoroethoxy)methyl)-4-(trifluoromethyl)benzene (**5**) and 4-((2-chloro-2,2-difluoroethoxy)methyl)benzonitrile (**6**) were also prepared and semi pure compounds (>80%) forward for next reaction without purification.

Other *gem*-difluoro ethane derivatives 1,1-difluoro-1-iodo-2-phenyl ethane (**2**) and 1,1-difluoro-1-iodo-2-(2-fluorophenyl) ethane (**7**) were prepared according to the reported procedure.[b,c]

Synthesis of ((2-chloroethoxy)methyl)benzene (1')



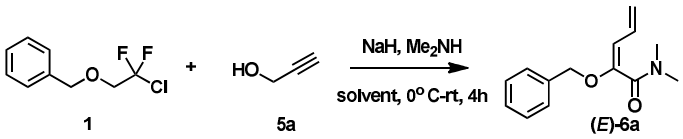
To an ice-cooled suspension (0 °C) of NaH (1.2 g, 29.8 mmol, 60% in mineral oil) in DMF (20 mL), benzyl bromide (3.64 mL, 29.8 mmol) was added, followed by 2-chloroethanol (1.7 ml , 24.84 mmol) was added dropwise (reverse addition) and stirred at 25 °C for additional 6 h. The reaction mixture was cooled to 0 °C and quenched with water, partitioned between ethyl acetate (EtOAc) and water. Organic layer was separated, washed with brine, dried over (Na_2SO_4), and concentrated under reduced pressure. Purification of the residue by column chromatography using 3% EtOAc/petroleum ether as eluant afforded **1'** (3.8 g, 90%) as colorless syrup. R_f =0.8 (2% EtOAc/hexane).

((2-Chloroethoxy)methyl)benzene (1')

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64–3.67 (m, 2H), 3.72–3.76 (m, 2H), 4.6 (s, 2H), 7.34–7.41 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 43.0, 70.2, 73.4, 127.8, 127.9, 128.6, 137.8.

SI 1.2. Reaction optimization by various solvents[a,b]



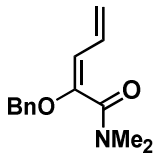
Entry	solvent	Yields of (*E*)-6a [%]
1	DMF	70
2	DCM	20
3	THF	25
4	DMSO	62
5	Dioxane	15
6	Et_2O	10
7[c]	THF-H_2O	trace

[a]Reaction conditions; propargly alcohol **5a** (0.57 mmol), **1** (0.48 mmol), NaH (0.96 mmol), Me_2NH (1.44 mmol in THF), solvent (3 mL), added base at 0 °C; [b]Isolated yields by using silica gel column chromatography; [c]2M NaOH used.

SI 1.3. General synthetic procedure for α-substituted 2,4-dienamides

Synthesis of (*Z*)-2-(benzyloxy)-*N*,*N*-dimethylpenta-2,4-dienamide ((*E*)-6a)

To a suspension of NaH (77.0 mg, 1.94 mmol) in DMF, propargyl alcohol **5a** (67 µL, 1.16 mmol) was added dropwise and stirred for at 0 °C 10 min. At the same temperature, Me_2NH (1.45 mL, 2.9 mmol, 2M in THF) and *gem*-difluoro ethane derivative **1** (200 mg, 0.97 mmol) were added to the reaction mixture, respectively, warmup to 25 °C and stirred for 4 h. The reaction mixture was cooled to 0 °C and quenched with water and extracted with EtOAc (20 mL × 3). Organic layer was separated, washed with brine, dried over (Na_2SO_4), and concentrated under reduced pressure. Purification of the residue by column chromatography using 30% EtOAc/hexane as eluant afforded (*E*)-**6a** (157 mg, 70%) as colorless syrup. R_f = 0.4 (40% EtOAc/petroleum ether).



(*Z*)-2-(Benzyloxy)-*N*,*N*-dimethylpenta-2,4-dienamide ((*E*)-6a)

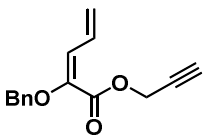
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.88 (s, 3H), 2.94 (s, 3H), 4.82 (s, 2H), 5.11 (ddd, *J* = 0.8, 2.0, 10.4 Hz, 1H), 5.23 (ddd, *J* = 0.8, 2.0, 17.2 Hz, 1H), 5.72 (dt, *J* = 0.8, 10.8 Hz, 1H), 6.72 (ddd, *J* = 10.4, 10.8, 21.2 Hz, 1H), 7.26–7.37 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 35.1, 38.2, 72.3, 116.9, 118.3, 128.2, 128.3, 128.6, 129.6, 136.9, 147.9, 166.5.

HRMS (CI) *m*/*z* $[M+H]^+$ calcd for $C_{14}H_{17}NO_2$: 232.1340, found: 232.1337.

Synthesis of (*E*)-prop-2-yn-1-yl 2-(benzyloxy)penta-2,4-dienoate (6a')

Following the general procedure for alkoxy dienamides without any amines, the reaction of propargyl alcohol **5a** (33 µL) with *gem*-difluoro ethane derivative **1** (100 mg) in DMSO gave **6a'** (26 mg, 22%) as colorless liquid. R_f = 0.7 (20% EtOAc/petroleum ether).



(*E*)-Prop-2-yn-1-yl 2-(benzyloxy)penta-2,4-dienoate (6a')

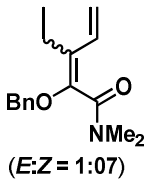
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51 (t, *J* = 2.4 Hz, 1H), 4.82 (d, *J* = 2.4 Hz, 2H), 4.94 (s, 2H), 5.31 (ddd, *J* = 0.8, 1.6, 10.0 Hz, 1H), 5.50 (ddd, *J* = 1.6, 2.4, 16.8 Hz, 1H), 6.68 (ddd, *J* = 10.0, 10.8, 20.8 Hz, 1H), 6.79 (d, *J* = 11.2 Hz, 1H), 7.34–7.42 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 52.6, 74.9, 75.3, 77.6, 123.6, 128.0, 128.4, 128.6, 128.7, 129.9, 136.7, 143.4, 163.4.

HRMS (ESI) *m*/*z* $[M]^+$ calcd for $C_{15}H_{14}O_3$: 242.0943, found: 242.0938.

Synthesis of 2-(benzyloxy)-3-ethyl-*N*,*N*-dimethylpenta-2,4-dienamide ((*E*/*Z*)-6b)

Following the general procedure for alkoxy dienamides, the reaction of pent-2-yn-1-ol **5b** (54 µL) with *gem*-difluoro ethane derivative **1** (100 mg) in the presence of Me_2NH gave the nonseparable mixture of (*E*/*Z*)-**6b** (88 mg, 70%) as colorless liquid. R_f = 0.5 (40% EtOAc/petroleum ether).



(*E*:*Z* = 1:07)

2-(Benzyloxy)-3-ethyl-*N*,*N*-dimethylpenta-2,4-dienamide ((*E*/*Z*)-6b)

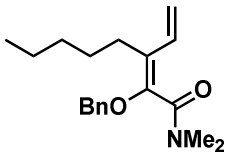
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 (t, *J* = 7.6 Hz, 3H, minor), 1.05 (t, *J* = 7.6 Hz, 3H, major), 2.17 (q, *J* = 7.2 Hz, 2H, major), 2.36 (q, *J* = 7.6 Hz, 2H, minor), 2.80 (s, 3H, minor), 2.93 (s, 3H, major), 2.97 (s, 3H, minor), 2.99 (s, 3H, major), 4.74 (s, 2H, major), 4.82 (s, 2H, minor), 5.03 (dd, *J* = 1.2, 10.8 Hz, 1H, minor), 5.12 (dd, *J* = 1.6, 11.2 Hz, 1H, major), 5.24 (td, *J* = 1.6, 18.0 Hz, 2H), 6.23 (dd, *J* = 10.8, 17.2 Hz, 1H, minor), 6.83 (dd, *J* = 11.2, 17.6 Hz, 1H, major), 7.30–7.37 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 13.1 (minor), 14.1 (major), 17.6 (minor), 20.0 (major), 34.3 (major), 34.4 (minor), 37.8 (minor), 37.9 (major), 71.7 (minor), 72.4 (major), 112.9 (minor), 114.1 (major), 124.2 (major), 124.3 (minor), 127.9 (major), 128.0 (minor), 128.1 (major), 128.2 (minor), 128.5 (major), 128.6 (minor), 130.3 (major), 132.1 (minor), 137.0 (major), 137.3 (minor), 145.1 (major), 146.5 (minor), 166.0 (minor), 166.5 (major).

HRMS (EI) *m*/*z* $[M]^+$ calcd for $C_{16}H_{21}NO_2$: 259.1572, found: 259.1570.

Synthesis of (*E*)-2-(benzyloxy)-*N*,*N*-dimethyl-3-vinyloct-2-enamide ((*E*)-6c) and (*Z*)-2-(benzyloxy)-*N*,*N*-dimethyl-3-vinyloct-2-enamide ((*Z*)-6c)

Following the general procedure for alkoxy dienamides, the reaction of oct-2-yn-1-ol **5c** (87 µL) with *gem*-difluoro ethane derivative **1** (105 mg) in the presence of Me_2NH gave the major product (*E*)-**6c** (95 mg, 62%) as colorless liquid. R_f = 0.48 (30% EtOAc/petroleum ether), along with the minor product (*Z*)-**6c** (18 mg, 12%). R_f = 0.5 (30% EtOAc/petroleum ether).

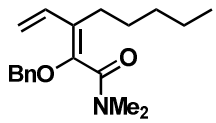


(*E*)-2-(benzyloxy)-*N*,*N*-dimethyl-3-vinyloct-2-enamide ((*E*)-6c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.8 Hz, 3H), 1.25–1.31 (m, 4H), 1.36–1.42 (m, 2H), 2.13 (m, 2H), 2.81 (s, 3H), 2.99 (s, 3H), 4.8 (s, 2H), 4.95 (dd, *J* = 1.2, 10.8 Hz, 1H), 5.20 (dd, *J* = 1.2, 17.2 Hz, 1H), 6.23 (dd, *J* = 11.2, 17.6 Hz, 1H), 7.30–7.39 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.6, 24.4, 28.1, 32.3, 34.3, 37.8, 71.6, 113.0, 123.0, 127.9, 128.1, 128.5, 132.5, 137.3, 146.9, 166.0.

HRMS (EI) *m*/*z* $[M]^+$ calcd for $C_{19}H_{27}NO_2$: 301.2042, found 301.2046.



(*Z*)-2-(Benzyloxy)-*N*,*N*-dimethyl-3-vinyloct-2-enamide ((*Z*)-6c)

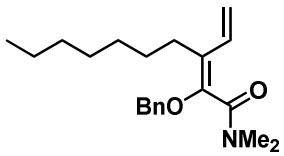
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.8 Hz, 3H), 1.23–1.33 (m, 4H), 1.39–1.47 (m, 2H), 2.13 (dt, *J* = 2.1, 7.6 Hz, 2H), 2.92 (s, 3H), 2.99 (s, 3H), 4.74 (s, 2H), 5.12 (dd, *J* = 1.6, 11.2 Hz, 1H), 5.25 (dd, *J* = 1.2, 18.0 Hz, 1H), 6.86 (dd, *J* = 11.2, 18.0 Hz, 1H), 7.29–7.37 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.6, 26.8, 29.0, 32.2, 34.3, 37.8, 72.4, 114.1, 123.2, 128.1, 128.2, 128.5, 130.7, 137.1, 145.3, 166.4.

HRMS (EI) *m*/*z* $[M]^+$ calcd for $C_{19}H_{27}NO_2$: 301.2042, found: 301.2047.

Synthesis of (*E*)-2-(benzyloxy)-*N*,*N*-dimethyl-3-vinyldec-2-enamide ((*E*)-6d)

Following the general procedure for alkoxy dienamides, the reaction of dec-2-yn-1-ol **5d** (107 µL) with *gem*-difluoro ethane derivative **1** (102 mg) in the presence of Me_2NH gave (*E*)-**6d** (134 mg, 82%) as colorless liquid. R_f = 0.4 (40% EtOAc/petroleum ether).



(*E*)-2-(Benzyloxy)-*N*,*N*-dimethyl-3-vinyldec-2-enamide ((*E*)-6d)

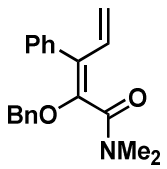
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.2 Hz, 3H), 1.26–1.31 (m, 8H), 1.38–1.42 (m, 2H), 2.32 (t, *J* = 7.6 Hz, 2H), 2.81 (s, 3H), 2.99 (s, 3H), 4.80 (s, 2H), 5.0 (dd, *J* = 1.2, 10.8 Hz, 1H), 5.20 (dd, *J* = 1.2, 17.2 Hz, 1H), 6.24 (dd, *J* = 10.8, 17.2 Hz, 1H), 7.29–7.36 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.8, 24.4, 28.5, 29.3, 30.1, 32.0, 34.4, 37.8, 71.6, 113.0, 123.1, 127.9, 128.1, 128.5, 132.5, 137.3, 146.9, 166.1.

HRMS (CI) *m*/*z* [*M*+H]$^+$ calcd for $C_{21}H_{31}NO_2$: 330.2436, found: 330.2433.

Synthesis of (*Z*)-2-(benzyloxy)-*N*,*N*-dimethyl-3-phenylpenta-2,4-dienamide ((*Z*)-6e)

Following the general procedure for alkoxy dienamides, the reaction of 3-phenylprop-2-yn-1-ol **5e** (72 µL) with *gem*-difluoro ethane derivative **1** (100 mg) in the presence of Me_2NH gave (*Z*)-**6e** (122 mg, 82%) as yellow solid; m.p. 82–84 °C; R_f = 0.6 (30% EtOAc/petroleum ether).



(*Z*)-2-(Benzyloxy)-*N*,*N*-dimethyl-3-phenylpenta-2,4-dienamide ((*Z*)-6e)

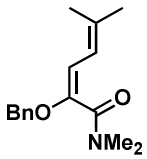
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.86 (s, 3H), 2.99 (s, 3H), 4.72 (s, 2H), 4.79 (dd, *J* = 1.6, 17.2 Hz, 1H), 5.02 (dd, *J* = 1.6, 10.8 Hz, 1H), 6.45 (dd, *J* = 10.8, 17.2 Hz, 1H), 7.07–7.09 (m, 2H), 7.14–7.16 (m, 2H), 7.2–7.24 (m, 3H), 7.27–7.34 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 34.4, 37.8, 72.2, 116.7, 124.9, 127.2, 128.0, 128.1, 128.2, 128.4, 130.1, 133.3, 134.8, 136.9, 146.7, 165.7.

HRMS (CI) *m*/*z* [*M*+H]$^+$ calcd for $C_{20}H_{21}NO_2$: 308.1653, found: 308.1650.

Synthesis of (*E*)-2-(benzyloxy)-*N*,*N*,5-trimethylhexa-2,4-dienamide ((*E*)-6f)

Following the general procedure for alkoxy dienamides, the reaction of 2-methylbut-3-yn-2-ol **5f** (57 µL) with *gem*-difluoro ethane derivative **1** (100 mg) in the presence of Me_2NH gave (*E*)-**6f** (55 mg, 44%) as colorless liquid. R_f = 0.5 (40% EtOAc/petroleum ether).



(*E*)-2-(Benzyloxy)-*N*,*N*,5-trimethylhexa-2,4-dienamide ((*E*)-6f)

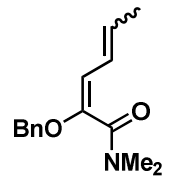
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74 (s, 3H), 1.82 (s, 3H), 2.94 (s, 6H), 4.78 (s, 2H), 6.07 (d, *J* = 11.6 Hz, 1H), 6.18–6.21 (m, 1H), 7.3–7.37 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 18.8, 26.6, 35.8, 38.3, 72.7, 115.0, 117.7, 128.2, 128.6, 137.2, 138.6, 138.7, 146.1, 167.5.

HRMS (EI) *m*/*z* $[M]^+$ calcd for $C_{16}H_{21}NO_2$: 259.1572, found: 259.1571.

Synthesis of (2*E*,4*Z*)-2-(benzyloxy)-*N*,*N*-dimethylhexa-2,4-dienamide and (2*E*,4*E*)-2-(benzyloxy)-*N*,*N*-dimethylhexa-2,4-dienamide ((*E,Z*)-6g and (*E,E*)-6g)

Following the general procedure, reaction of but-3-yn-2-ol **5g** (45 µL) with **1** (100 mg) in the presence of Me_2NH gave non-separable mixture of (*E,Z*)-**6g** and (*E,E*)-**6g** (74 mg, 62%) as colorless liquid. R_f = 0.5 (40% EtOAc/petroleum ether).



(***E*,*Z*:*E*,*E* = 2.6:1**)

The mixture of (*E,Z*)-6g and (*E,E*)-6g

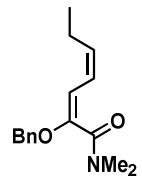
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.73 (dd, *J* = 2.0, 7.2 Hz, 3H, minor), 1.78 (dd, *J* = 2.0, 6.8 Hz, 3H, major), 2.93 (s, 9H), 4.79 (s, 2H, major), 4.80 (s, 2H, minor), 5.57–5.65 (m, 1H, minor), 5.73–5.82 (m, 2H, major), 6.08 (dd, *J* = 1.2, 11.6 Hz, 1H, minor), 6.34–6.46 (m, 1H), 7.28–7.37 (m, 7H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 13.78 (minor), 18.73 (major), 35.3, 38.3, 72.5, 112.5 (minor), 118.1 (major), 121.9 (minor), 124.2 (major), 128.1, 128.2, 128.3, 128.4, 128.6, 131.7, 137.0 (minor), 137.1 (major), 145.8 (major), 147.7 (minor), 167.0 (minor), 167.1 (major).

HRMS (CI) *m*/*z* [*M*+H]$^+$ calcd for $C_{15}H_{19}NO_2$: 246.1497, found: 246.1494.

Synthesis of (2*E*,4*Z*)-2-(benzyloxy)-*N*,*N*-dimethylhepta-2,4-dienamide ((*E*,*Z*)-6h) and (2*E*,4*E*)-2-(benzyloxy)-*N*,*N*-dimethylhepta-2,4-dienamide ((*E*,*E*)-6h)

Following the general procedure for alkoxy dienamides, the reaction of pent-1-yn-3-ol **5h** (51 µL) with *gem*-difluoro ethane derivative **1** (102 mg) in the presence of Me_2NH gave (*E*,*Z*)-**6h** (50 mg, 39%) as colorless liquid, along with (*E*,*E*)-**6h** (17 mg, 13%). R_f = 0.56 and 0.51 (40% EtOAc/petroleum ether).

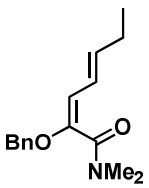


(2*E*,4*Z*)-2-(Benzyloxy)-*N*,*N*-dimethylhepta-2,4-dienamide ((*E*,*Z*)-6h)

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.6 Hz, 3H), 2.12–2.20 (m, 2H), 2.94 (s, 6H), 4.80 (s, 2H), 5.53 (ddd, *J* = 1.2, 7.2, 10.8 Hz, 1H), 6.06 (dd, *J* = 1.2, 11.6 Hz, 1H), 6.35 (tt, *J* = 1.6, 11.2 Hz, 1H), 7.28–7.35 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 21.4, 35.4, 38.3, 72.5, 112.7, 120.3, 128.2, 128.3, 128.6, 136.2, 137.0, 147.8, 167.1.

HRMS (CI) *m*/*z* [*M*-H]$^+$ calcd for $C_{16}H_{21}NO_2$: 258.1491, found: 258.1497.



(2*E*,4*E*)-2-(Benzyloxy)-*N*,*N*-dimethylhepta-2,4-dienamide ((*E*,*E*)-6h)

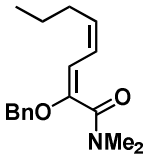
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, *J* = 7.6 Hz, 3H), 2.08–2.16 (m, 2H), 2.93 (s, 6H), 4.79 (s, 2H), 5.77–5.84 (m, 2H), 6.38 (ddt, *J* = 1.6, 10.8, 15.6 Hz, 1H), 7.29–7.37 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 26.2, 35.4, 38.3, 72.6, 118.4, 121.9, 128.2, 128.3, 128.6, 137.1, 138.7, 146.0, 167.1.

HRMS (CI) *m*/*z* [*M*-H]$^+$ calcd for $C_{16}H_{21}NO_2$: 258.1491, found: 258.1493.

Synthesis of (2*E*,4*Z*)-2-(benzyloxy)-*N*,*N*-dimethylocta-2,4-dienamide ((*E*,*Z*)-6i) and (2*E*,4*E*)-2-(benzyloxy)-*N*,*N*-dimethylocta-2,4-dienamide ((*E*,*E*)-6i)

Following the general procedure for alkoxy dienamides, the reaction of hex-1-yn-3-ol **5i** (66 µL) with *gem*-difluoro ethane derivative **1** (100 mg) in the presence of Me_2NH gave (*E*,*Z*)-**6i** (66 mg, 50%) as colorless liquid, along with (*E*,*E*)-**6i** (16 mg, 12%). R_f = 0.5 and 0.35 (30% EtOAc/petroleum ether).

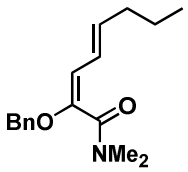


(2*E*,4*Z*)-2-(Benzyloxy)-*N*,*N*-dimethylocta-2,4-dienamide ((*E*,*Z*)-6i)

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.6 Hz, 3H), 1.33–1.43 (m, 2H), 2.12 (ddd, *J* = 1.6, 7.2, 14.8 Hz, 2H), 2.92 (s, 6H), 4.80 (s, 2H), 5.53 (ddd, *J* = 1.2, 7.6, 10.8 Hz, 1H), 6.05 (dd, *J* = 1.2, 7.6 Hz, 1H), 6.38 (tt, *J* = 1.2, 11.2 Hz, 1H), 7.28–7.35 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 22.8, 30.2, 35.3, 38.4, 72.5, 112.8, 121.0, 128.2, 128.3, 128.6, 134.5, 137.0, 147.7, 167.1.

HRMS (CI) *m*/*z* $[M+H]^+$ calcd for $C_{17}H_{23}NO_2$: 274.1810, found 274.1807.



(2*E*,4*E*)-2-(Benzyloxy)-*N*,*N*-dimethylocta-2,4-dienamide ((*E*,*E*)-6i)

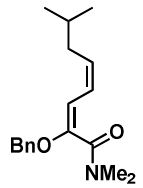
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.6 Hz, 3H), 1.33–1.43 (m, 2H), 2.12 (ddd, *J* = 1.6, 7.2, 14.8 Hz, 2H), 2.93 (s, 6H), 4.79 (s, 2H), 5.75 (dd, *J* = 6.8, 14.4 Hz, 1H), 6.05 (d, *J* = 11.2 Hz, 1H), 6.38 (ddt, *J* = 1.6, 10.8, 15.2 Hz, 1H), 7.28–7.35 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 18.6, 35.3, 35.4, 38.4, 72.6, 118.4, 123.0, 126.2, 128.2, 128.3, 128.6, 137.1, 145.9, 167.1.

HRMS (EI) *m*/*z* $[M]^+$ calcd for $C_{17}H_{23}NO_2$: 273.1729, found: 273.1725.

Synthesis of (2*E*,4*Z*)-2-(benzyloxy)-*N*,*N*,7-trimethylocta-2,4-dienamide ((*E*,*Z*)-6j) and (2*E*,4*E*)-2-(benzyloxy)-*N*,*N*,7-trimethylocta-2,4-dienamide ((*E*,*E*)-6j)

Following the general procedure for alkoxy dienamides, the reaction of 4-methylpent-1-yn-3-ol **5j** (52 µL) with *gem*-difluoro ethane derivative **1** (95 mg) in the presence of Me_2NH gave (*E*,*Z*)-**6j** (64 mg, 48%) as colorless liquid, along with (*E*,*E*)-**6j** (13 mg, 10%). R_f = 0.50 and 0.45 (30% EtOAc/petroleum ether).

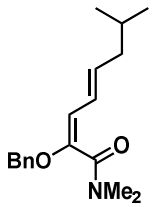


(2*E*,4*Z*)-2-(Benzyloxy)-*N*,*N*,7-trimethylocta-2,4-dienamide ((*E*,*Z*)-6j)

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (d, *J* = 6.8 Hz, 6H), 1.6–1.69 (m, 1H), 2.03 (ddd, *J* = 1.6, 7.2, 8.0 Hz, 2H), 2.96 (s, 6H), 4.81 (s, 2H), 5.56 (dddd, *J* = 1.2, 8.0, 15.6 Hz, 1H), 6.04 (dd, *J* = 1.2, 11.6 Hz, 1H), 6.42 (tt, *J* = 1.2, 11.2 Hz, 1H), 7.29–7.36 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 22.5 (2 C), 28.8, 35.3, 37.2, 38.3, 72.4, 112.9, 121.6, 128.2, 128.3, 128.6, 133.4, 137.0, 147.6, 167.1.

HRMS (EI) *m*/*z* $[M]^+$ calcd for $C_{18}H_{25}NO_2$: 287.1885, found: 287.1882.



(2*E*,4*E*)-2-(Benzyloxy)-*N*,*N*,7-trimethylocta-2,4-dienamide ((*E*,*E*)-6j)

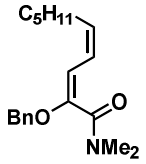
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (d, *J* = 6.8 Hz, 6H), 1.59–1.66 (m, 1H), 1.98 (dt, *J* = 1.2, 8.4 Hz, 2H), 2.93 (s, 6H), 4.79 (s, 2H), 5.74 (ddd, *J* = 6.8, 7.6, 14.8 Hz, 1H), 5.82 (d, *J* = 10.8 Hz, 1H), 6.37 (ddt, *J* = 1.2, 11.2, 15.6 Hz, 1H), 7.30–7.36 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 22.5 (2C), 28.6, 35.4, 38.4, 42.6, 72.6, 118.5, 123.9, 128.2, 128.3, 128.6, 136.1, 137.1, 146.0, 167.1

HRMS (EI) *m*/*z* $[M]^+$ calcd for $C_{18}H_{25}NO_2$: 287.1885, found: 287.1884.

Synthesis of (*2E*,*4Z*)-2-(benzyloxy)-*N*,*N*-dimethyldeca-2,4-dienamide ((*E*,*Z*)-6k) and (*2E*,*4E*)-2-(benzyloxy)-*N*,*N*-dimethyldeca-2,4-dienamide ((*E*,*E*)-6k)

Following the general procedure for alkoxy dienamides, the reaction of oct-1-yn-3-ol **5k** (58 µL) with *gem*-difluoro ethane derivative **1** (82 mg) in the presence of Me_2NH gave (*E*,*Z*)-**6k** (64 mg, 46%) as colorless liquid, along with (*E*,*E*)-**6k** (11 mg, 8%). R_f = 0.5 and 0.48 (40% EtOAc/petroleum ether).

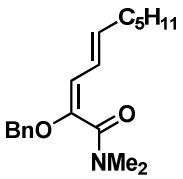


(2*E*,4*Z*)-2-(Benzyloxy)-*N*,*N*-dimethyldeca-2,4-dienamide ((*E*,*Z*)-6k)

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.2 Hz, 3H), 1.24–1.34 (m, 4H), 1.35–1.40 (m, 2H), 2.13 (ddd, *J* = 1.6, 7.2, 14.8 Hz, 2H), 2.94 (s, 6H), 4.80 (s, 2H), 5.54 (ddd, *J* = 0.8, 7.6, 10.8 Hz, 1H), 6.05 (dd, *J* = 0.8, 11.2 Hz, 1H), 6.37 (tt, *J* = 1.6, 11.2 Hz, 1H), 7.28–7.35 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.6, 28.1, 29.3, 31.6, 35.3, 38.3, 72.5, 112.7, 120.8, 128.2, 128.3, 128.6, 134.7, 137.0, 147.8, 167.1.

HRMS (EI) *m*/*z* $[M]^+$ calcd for $C_{19}H_{27}NO_2$: 301.2042, found: 301.2046.



(2*E*,4*E*)-2-(Benzyloxy)-*N*,*N*-dimethyldeca-2,4-dienamide ((*E*,*E*)-6k)

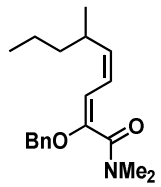
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.2 Hz, 3H), 1.23–1.34 (m, 4H), 1.35–1.41 (m, 2H), 2.09 (ddd, *J* = 1.2, 7.2, 14.4 Hz, 2H), 2.92 (s, 6H), 4.80 (s, 2H), 5.76 (dd, *J* = 6.8, 14.4 Hz, 1H), 5.8 (d, *J* = 11.2 Hz, 1H), 6.38 (ddt, *J* = 1.6, 10.8, 15.2 Hz, 1H), 7.29–7.37 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.6, 28.9, 31.5, 33.2, 35.4, 38.3, 72.6, 118.5, 122.9, 128.2, 128.3, 128.6, 137.1, 137.4, 146.0, 167.1.

HRMS (EI) *m*/*z* $[M]^+$ calcd for $C_{19}H_{27}NO_2$: 301.2042, found: 301.2047.

Synthesis of (*2E*,*4Z*)-2-(benzyloxy)-*N*,*N*,6-trimethylnona-2,4-dienamide ((*E*,*Z*)-6l)

Following the general procedure for alkoxy dienamides, the reaction of 4-methylhept-1-yn-3-ol **5l** (93 µL) with *gem*-difluoro ethane derivative **1** (100 mg) in the presence of Me_2NH gave (*E*,*Z*)-**6l** (77 mg, 50%) as colorless liquid. R_f = 0.4 (40% EtOAc/petroleum ether).



(2*E*,4*Z*)-2-(Benzyloxy)-*N*,*N*,6-trimethylnona-2,4-dienamide ((*E*,*Z*)-6l)

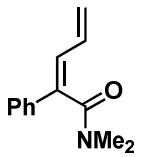
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, *J* = 7.2 Hz, 3H), 0.93 (d, *J* = 6.4 Hz, 3H), 1.17–1.28 (m, 4H), 2.49–2.57 (m, 1H), 2.91 (s, 3H), 2.94 (s, 3H), 4.81 (s, 2H), 5.3 (dt, *J* = 1.2, 11.2 Hz, 1H), 6.04 (dd, *J* = 0.8, 11.6 Hz, 1H), 6.32 (dt, *J* = 1.2, 11.6 Hz, 1H), 7.28–7.37 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 20.7, 21.2, 32.4, 35.3, 38.3, 39.7, 72.4, 113.1, 119.4, 128.2, 128.3, 128.6, 137.0, 141.1, 147.6, 167.1.

HRMS (EI) *m*/*z* $[M]^+$ calcd for $C_{19}H_{27}NO_2$: 301.2042, found: 301.2037.

Synthesis of (*Z*)-*N*,*N*-dimethyl-2-phenylpenta-2,4-dienamide ((*Z*)-7a)[d]

Following the general procedure for alkoxy dienamides, the reaction of propargyl alcohol **5a** (59 µL) with *gem*-difluoroiodo ethane derivative **2** (150 mg) in the presence of Me_2NH gave (*Z*)-**7a** (112 mg, 65%) as colorless liquid. R_f = 0.5 (40% EtOAc/petroleum ether).



(*Z*)-*N*,*N*-Dimethyl-2-phenylpenta-2,4-dienamide ((*Z*)-7a)

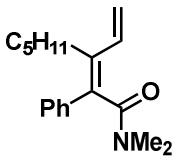
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.89 (s, 3H), 3.13 (s, 3H), 5.30 (dd, *J* = 0.8, 10.0 Hz, 1H), 5.46 (dd, *J* = 0.8, 16.8 Hz, 1H), 6.43 (ddd, *J* = 10.4, 11.2, 21.2 Hz, 1H), 6.65 (d, *J* = 11.2 Hz, 1H), 7.28–7.30 (m, 1H), 7.32–7.40 (m, 2H), 7.42–7.43 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 34.5, 38.0, 121.1, 125.7, 127.5, 128.4, 129.0, 133.3, 135.5, 138.3, 169.8.

HRMS (CI) *m*/*z* $[M+H]^+$ calcd for $C_{13}H_{15}NO$: 202.1235, found: 202.1232.

Synthesis of (Z)-*N*,*N*-dimethyl-2-phenyl-3-vinyloct-2-enamide ((*Z*)-7c)

Following the general procedure for alkoxy dienamides, the reaction of oct-2-yn-1-ol **5c** (150 µL) with *gem*-difluoro ethane derivative **2** (150 mg) gave (*Z*)-**7c** (130 mg, 56%) as colorless liquid. R_f = 0.6 (40% EtOAc/petroleum ether).



(*Z*)-*N*,*N*-Dimethyl-2-phenyl-3-vinyloct-2-enamide ((*Z*)-7c)

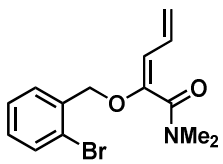
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (t, *J* = 6.8 Hz, 3H), 1.21–1.26 (m, 4H), 1.49–1.57 (m, 2H), 2.27 (t, *J* = 7.2 Hz, 2H), 2.97 (s, 3H), 2.99 (s, 3H), 5.26 (d, *J* = 10.8 Hz, 1H), 5.42 (d, *J* = 17.6 Hz, 1H), 6.40 (dd, *J* = 10.8, 15.6 Hz, 1H), 7.29–7.37 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.4, 27.6, 29.3, 32.1, 34.6, 37.9, 116.7, 127.7, 128.5, 128.7, 134.7, 136.4, 136.6, 137.4, 170.9.

HRMS (CI) *m*/*z* [*M*+H]$^+$ calcd for $C_{18}H_{25}NO$: 272.2017, found: 272.2014.

Synthesis of (*E*)-2-((2-bromobenzyl)oxy)-*N*,*N*-dimethylpenta-2,4-dienamide ((*E*)-8a)

Following the general procedure for alkoxy dienamides, the reaction of propargyl alcohol **5a** (60 µL) with *gem*-difluoro ethane derivative **3** (200 mg) in the presence of Me_2NH gave (*E*)-**8a** (156 mg, 72%) as colorless liquid. R_f = 0.4 (30% EtOAc/petroleum ether).



(*E*)-2-((2-Bromobenzyl)oxy)-*N*,*N*-dimethylpenta-2,4-dienamide ((*E*)-8a)

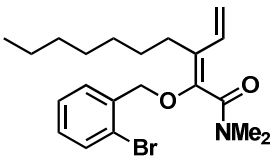
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.99 (s, 6H), 4.90 (s, 2H), 5.14 (ddd, *J* = 0.4, 1.6, 10.0 Hz, 1H), 5.27 (ddd, *J* = 0.8, 2.0, 17.2 Hz, 1H), 5.81 (d, *J* = 10.8 Hz, 1H), 6.76 (dt, *J* = 10.4, 17.6 Hz, 1H), 7.18 (td, *J* = 2.0, 7.6 Hz, 1H), 7.33 (td, *J* = 1.2, 7.2 Hz, 1H), 7.48 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.56 (dd, *J* = 1.2, 7.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 35.4, 38.4, 71.8, 117.8, 118.9, 123.4, 127.6, 129.6, 129.8, 130.2, 132.9, 136.2, 147.8, 166.5.

HRMS (EI) *m*/*z* [*M*]$^+$ calcd for $C_{14}H_{16}BrNO_2$: 309.0364, found: 309.0362.

Synthesis of (*E*)-2-((2-bromobenzyl)oxy)-*N*,*N*-dimethyl-3-vinyldec-2-enamide ((*E*)-8d)

Following the general procedure for alkoxy dienamides, the reaction of propargyl alcohol **5d** (74 µL) with *gem*-difluoro ethane derivative **3** (100 mg) in the presence of Me_2NH gave (*E*)-**8d** (110 mg, 77%) as colorless liquid. R_f = 0.5 (30% EtOAc/petroleum ether)



(*E*)-2-((2-Bromobenzyl)oxy)-*N*,*N*-dimethyl-3-vinyldec-2-enamide((*E*)-8d)

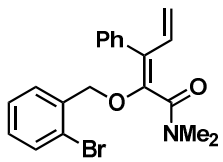
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, *J* = 7.2 Hz, 3H), 1.21–1.32 (m, 8H), 1.35–1.40 (m, 2H), 2.32 (t, *J* = 8.0 Hz, 2H), 2.99 (s, 3H), 3.04 (s, 3H), 4.85 (s, 2H), 5.02 (dd, *J* = 1.2, 10.8 Hz, 1H), 5.22 (dd, *J* = 1.2, 17.2 Hz, 1H), 6.26 (dd, *J* = 10.8, 17.2 Hz, 1H), 7.17 (td, *J* = 2.0, 9.6 Hz, 1H), 7.32 (td, *J* = 1.2, 8.8 Hz, 1H), 7.50 (dd, *J* = 1.6, 7.2 Hz, 1H), 7.55 (dd, *J* = 1.2, 8.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.8, 24.5, 28.5, 29.3, 30.1, 32.0, 34.5, 38.0, 71.1, 113.4, 123.3, 123.7, 127.6, 129.7, 130.1, 132.5, 132.8, 136.5, 146.7, 165.9.

HRMS (EI) *m*/*z* $[M]^+$ calcd for $C_{21}H_{30}BrNO_2$: 407.1460, found: 407.1461.

Synthesis of (*Z*)-2-((2-bromobenzyl)oxy)-*N*,*N*-dimethyl-3-phenylpenta-2,4-dienamide ((*Z*)-8e)

Following the general procedure for alkoxy dienamides, the reaction of propargyl alcohol **5e** (52 µL) with *gem*-difluoro ethane derivative **3** (100 mg) in the presence of Me_2NH gave (*E*)-**8e** (108 mg, 80%) as colorless liquid. R_f = 0.5 (30% EtOAc/petroleum ether).



(*Z*)-2-((2-Bromobenzyl)oxy)-N,N-dimethyl-3-phenylpenta-2,4-dienamide ((*Z*)-8e)

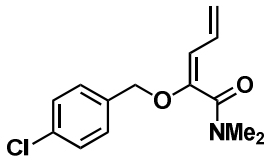
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.05 (s, 3H), 3.10 (s, 3H), 4.81 (s, 2H), 4.86 (dd, *J* = 1.6, 17.2 Hz, 1H), 5.08 (dd, *J* = 1.6, 10.8 Hz, 1H), 6.53 (dd, *J* = 10.4, 16.8 Hz, 1H), 7.07–7.15 (m, 2H), 7.17–7.21 (m, 3H), 7.27–7.37 (m, 3H), 7.46 (dd, *J* = 1.2, 8.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 34.6, 38.0, 71.4, 117.1, 122.8, 125.4, 127.3, 127.4, 128.1, 129.4, 129.9, 130.1, 132.5, 133.3. 134.7, 136.1, 146.5, 165.6.

HRMS (EI) *m/z* $[M]^+$ calcd for $C_{20}H_{20}BrNO_2$: 385.0677, found: 385.0674.

Synthesis of (*E*)-2-((4-chlorobenzyl)oxy)-*N*,*N*-dimethylpenta-2,4-dienamide ((*E*)-9a)

Following the general procedure for alkoxy dienamides, the reaction of propargyl alcohol **5a** (23 µL) with *gem*-difluoro ethane derivative **4** (100 mg) in the presence of Me_2NH gave (*E*)-**9a** (60 mg, 68%) as colorless liquid. R_f = 0.3 (30% EtOAc/petroleum ether).



(*E*)-2-((4-Chlorobenzyl)oxy)-*N*,*N*-dimethylpenta-2,4-dienamide ((*E*)-9a)

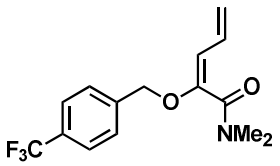
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.94 (s, 6H), 4.8 (s, 2H), 5.13 (dd, *J* = 1.6, 10.4 Hz, 1H), 5.25 (dd, *J* = 2.0, 17.2 Hz, 1H), 5.74 (d, *J* = 11.2 Hz, 1H), 6.68 (dt, *J* = 10.8, 17.2 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 35.2, 38.4, 71.5, 117.3, 118.8, 128.8, 129.4, 129.6, 134.2, 135.4 147.6, 166.5.

LCMS (EI) *m/z* $[M+H]^+$ calcd for $C_{14}H_{16}ClNO_2$: 266.0870, found: 266.2.

Synthesis of (*E*)-*N*,*N*-dimethyl-2-((4-(trifluoromethyl)benzyl)oxy)penta-2,4-dienamide ((*E*)-10a)

Following the general procedure for alkoxy dienamides, the reaction of propargyl alcohol **5a** (30 µL) with *gem*-difluoro ethane derivative **5** (150 mg) in the presence of Me_2NH gave (*E*)-**10a** (82 mg, 62%) as colorless liquid. R_f = 0.4 (30% EtOAc/petroleum ether).



(*E*)-*N*,*N*-dimethyl-2-((4-(trifluoromethyl)benzyl)oxy)penta-2,4-dienamide ((*E*)-10a)

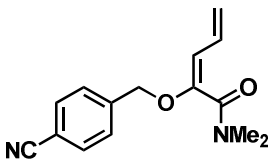
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.95 (s, 6H), 4.90 (s, 2H), 5.15 (dd, *J* = 1.2, 10.4 Hz, 1H), 5.28 (dd, *J* = 1.2, 17.2 Hz, 1H), 5.76 (d, *J* = 11.2 Hz, 1H), 6.71 (dt, *J* = 10.8, 17.2 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 38.5, 35.37, 71.5, 117.4, 119.1, 125.6, 125.6, 127.9, 128.1, 129.3, 140.9, 147.5, 166.3.

LCMS (EI) *m/z* $[M+H]^+$ calcd for $C_{15}H_{16}F_3NO_2$: 300.1133, found: 300.1.

Synthesis of (*E*)-2-((4-isocyanobenzyl)oxy)-*N*,*N*-dimethylpenta-2,4-dienamide ((*E*)-11a)

Following the general procedure for alkoxy dienamides, the reaction of propargyl alcohol **5a** (24 µL) with *gem*-difluoro ethane derivative **6** (100 mg) in the presence of Me_2NH gave (*E*)-**11a** (47 mg, 53%) as colorless liquid. R_f = 0.5 (30% EtOAc/petroleum ether).



(*E*)-2-((4-Isocyanobenzyl)oxy)-*N*,*N*-dimethylpenta-2,4-dienamide ((*E*)-11a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.98 (s, 6H), 4.98 (s, 2H), 5.16 (dd, *J* = 1.6, 10.4 Hz, 1H), 5.29 (dd, *J* = 1.6, 17.2 Hz, 1H), 5.77 (d, *J* = 11.2 Hz, 1H), 6.68 (dt, *J* = 10.4, 17.2 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H).

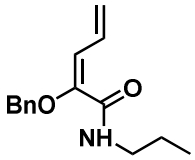
^{13}C NMR (100 MHz, $CDCl_3$) δ 35.3, 38.4, 71.3, 112.1, 117.5, 119.4, 128.3, 129.1, 132.4, 132.5, 142.2, 147.2, 166.2.

LCMS (EI) *m/z* $[M+H]^+$ calcd for $C_{15}H_{16}N_2O_2$: 257.1212, found: 257.2.

Synthesis of (*E*)-2-(benzyloxy)-*N*-propylpenta-2,4-dienamide ((*E*)-12)

In **Scheme 3**, DMSO was used as solvent for the synthesis of compounds (*E*)-**12**–**18**.

Following the general procedure for alkoxy dienamides, the reaction of propargyl alcohol **5a** (34 µL) and **^{n}PrNH$_2$** (119 µL) with *gem*-difluoro ethane derivative **1** (100 mg) in DMSO gave (*E*)-**12** (69 mg, 58%) as colorless liquid, along with cyclic **24** (6 mg, 5%). R_f = 0.5, 0.65, respectively (40% EtOAc/petroleum ether).

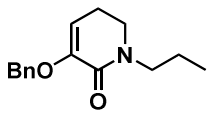


(*E*)-2-(Benzyloxy)-*N*-propylpenta-2,4-dienamide ((*E*)-12)

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, *J* = 7.2 Hz, 3H), 1.39–1.48 (m, 2H), 3.18–3.23 (m, 2H), 4.85 (s, 2H), 5.32 (ddd, *J* = 1.2, 2.0, 10.4 Hz, 1H), 5.51 (ddd, *J* = 0.4, 1.6, 16.8 Hz, 1H), 6.44 (brs, 1H), 6.65 (ddd, *J* = 10.0, 11.2, 21.2 Hz, 1H), 6.83 (d, *J* = 11.6 Hz, 1H), 7.38–7.41 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 11.4, 22.9, 41.1, 76.6, 121.7, 122.5, 128.3, 128.8, 128.9, 129.6, 136.5, 147.7, 163.7.

HRMS (CI) *m*/*z* [*M*+H]$^+$ calcd for $C_{15}H_{19}NO_2$: 246.1497, found: 246.1493.



3-(Benzyloxy)-1-propyl-5,6-dihydropyridin-2(1H)-one (24)

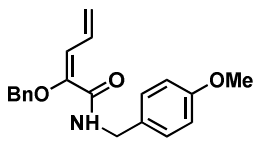
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.2 Hz, 3H), 1.56–1.58 (m, 1H), 160–1.64 (m, 1H), 2.30–2.35 (m, 2H), 3.34 (t, *J* = 7.2 Hz, 2H), 3.38–3.42 (m, 2H), 4.89 (s, 2H), 5.34 (t, *J* = 4.2 Hz, 1H), 7.28–7.41 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 11.5, 21.0, 22.3, 45.8, 48.8, 70.1, 105.9, 127.4, 127.8, 128.6, 136.8, 147.3, 161.6.

HRMS (ESI) *m*/*z* [*M*+H]$^+$ calcd for $C_{15}H_{19}NO_2$: 246.1497, found: 246.1492.

Synthesis of (*E*)-2-(benzyloxy)-*N*-(4-methoxybenzyl)penta-2,4-dienamide ((*E*)-13)

Following the general procedure for alkoxy dienamides, the reaction of propargyl alcohol **5a** (34 µL) and 4-methoxybenzylamine (190 µL) with *gem*-difluoro ethane derivative **1** (100 mg) in DMSO gave (*E*)-**13** (112 mg, 72%) as yellow syrup. R_f = 0.4 (40% EtOAc/petroleum ether).



(*E*)-2-(Benzyloxy)-*N*-(4-methoxybenzyl)penta-2,4-dienamide ((*E*)-13)

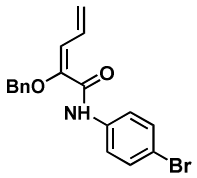
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 4.36 (d, *J* = 6.0 Hz, 2H), 4.83 (s, 2H), 5.34 (ddd, *J* = 0.8, 2.0, 10.4 Hz, 1H), 5.52 (ddd, *J* = 0.4, 2.4, 16.8 Hz, 1H), 6.60–6.70 (m, 2H), 6.83–6.85 (m, 2H), 6.87 (brs, 1H), 7.11–7.13 (m, 2H), 7.38–7.44 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 43.1, 55.5, 76.7, 114.2 (2C), 122.2, 122.8, 128.4, 128.8, 128.9, 129.2 (2C), 129.6, 130.2, 136.3, 147.5, 159.1, 163.6.

HRMS (CI) *m*/*z* [*M*+H]$^+$ calcd for $C_{20}H_{21}NO_3$: 324.1602, found: 324.1599.

Synthesis of (*E*)-2-(benzyloxy)-*N*-(4-bromophenyl)penta-2,4-dienamide ((*E*)-14)

Following the general procedure for alkoxy dienamides, the reaction of propargyl alcohol **5a** (34 µL) and 4-bromoaniline (250 mg) with *gem*-difluoro ethane derivative **1** (100 mg) in DMSO gave (*E*)-**14** (113 mg, 65%) as yellow liquid along with ester **6a'** (7 mg, 6%) R_f = 0.4 and 0.9, respectively (40% EtOAc/petroleum ether).



(*E*)-2-(Benzyloxy)-*N*-(4-bromophenyl)penta-2,4-dienamide ((*E*)-14)

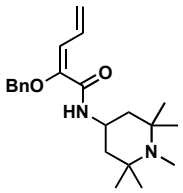
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.95 (s, 2H), 5.43 (ddd, *J* = 0.8, 1.6, 10.8 Hz, 1H), 5.61 (ddd, *J* = 0.4, 1.2, 17.6 Hz, 1H), 6.68–6.78 (m, 1H), 6.95 (d, *J* = 11.2 Hz, 1H), 7.27–7.30 (m, 2H), 7.37–7.40 (m, 2H), 7.38–7.44 (m, 5H), 8.13 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 76.6, 117.1, 121.2 (2C), 123.1 (2C), 123.8, 128.6, 129.2, 129.4, 132.1 (2C), 136.2, 136.6, 147.4, 161.7.

HRMS (CI) *m*/*z* [*M*+H]$^+$ calcd for $C_{18}H_{16}BrNO_2$: 358.0426, found: 358.0442.

Synthesis of (*E*)-2-(benzyloxy)-*N*-(1,2,2,6,6-pentamethylpiperidin-4-yl)penta-2,4-dienamide ((*E*)-15)

Following the general procedure for alkoxy dienamides, the reaction of propargyl alcohol **5a** (33 µL) and 4-amino-1,2,2,6,6-pentamethylpiperidine (247 mg) with *gem*-difluoro ethane derivative **1** (100 mg) in DMSO gave (*E*)-**15** (108 mg, 62%) as light yellow liquid R_f = 0.4 (20%MeOH/dichloromethane).



(*E*)-2-(Benzyloxy)-*N*-(1,2,2,6,6-pentamethylpiperidin-4-yl)penta-2,4-dienamide ((*E*)-15)

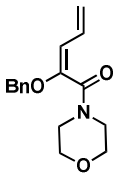
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13 (s, 6H), 1.38 (s, 6H) 1.54–1.72 (m, 4H), 2.47 (s, 3H) 4.12–4.24 (m, 1H), 4.84 (s, 2H), 5.34 (dd, *J* = 1.6, 10.0 Hz, 1H), 5.51 (dd, *J* = 2.0, 16.8 Hz, 1H), 6.40 (brs, 1H), 6.65 (ddd, J = 10.4, 11.6, 21.6 Hz, 1H), 6.78 (d, *J* = 11.6 Hz, 1H), 7.33–7.44 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0 (2C), 28.5 (2C), 31.1, 40.4, 44.8, 59.9, 76.9, 122.1, 122.8, 128.7, 129.0, 129.1, 129.6, 136.3, 147.4, 163.3.

HRMS (CI) *m*/*z* $[M+H]^+$ calcd for $C_{22}H_{32}N_2O_2$: 357.2544, found: 357.2549.

Synthesis of (*E*)-2-(benzyloxy)-1-morpholinopenta-2,4-dien-1-one ((*E*)-16)

Following the general procedure for alkoxy dienamides, the reaction of propargyl alcohol **5a** (33 μL) and Morpholine (126 mg) with *gem*-difluoro ethane derivative **1** (100 mg) in DMSO gave (*E*)-**16** (114 mg, 86%) as colorless liquid R_f = 0.4 (30% EtOAc/petroleum ether).



(*E*)-2-(Benzyloxy)-1-morpholinopenta-2,4-dien-1-one ((*E*)-16)

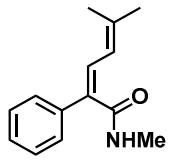
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.41–3.68 (m, 8H), 4.87 (s, 2H), 5.15 (ddd, *J* = 0.8, 2.0, 10.4 Hz, 1H), 5.27 (ddd, *J* = 0.8, 2.0, 17.2 Hz, 1H), 5.78 (dt, *J* = 0.8, 10.8 Hz, 1H), 6.72 (ddd, J = 10.0, 10.8, 21.2 Hz, 1H), 7.29–7.38 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 66.8(2C), 72.6, 118.1, 119.2, 128.2, 128.5, 128.7, 129.4, 136.7, 147.1, 165.3.

HRMS (CI) *m*/*z* $[M]^+$ calcd for $C_{16}H_{19}NO_3$: 273.1365, found: 273.1363.

Synthesis of (*Z*)-*N*,5-dimethyl-2-phenylhexa-2,4-dienamide ((*Z*)-17)

Following the general procedure for alkoxy dienamides, the reaction of 2-methylbut-3-yn-2-ol **5f** (100 µL) and methylamine (1.27 mL, 2M in THF) with *gem*-difluoro ethane derivative **2** (150 mg) gave (*Z*)-**17** (92 mg, 50%) as light yelow solid; m.p. 58–60 °C; R_f = 0.4 (40% EtOAc/petroleum ether).

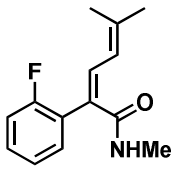


(*Z*)-*N*,5-Dimethyl-2-phenylhexa-2,4-dienamide ((*Z*)-17)

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.86 (s, 3H), 1.88 (s, 3H), 2.94 (d, *J* = 4.8 Hz, 3H), 5.58 (brs, 1H), 6.38–6.42 (m, 1H), 6.78 (d, *J* = 11.6 Hz, 1H), 7.24–7.29 (m, 1H), 7.31–7.35 (m, 2H), 7.38–7.41 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 18.6, 26.5, 26.8, 122.1, 126.9, 127.8, 128.2, 128.8, 134.7, 138.2, 142.1, 169.9.
HRMS (CI) *m*/*z* [*M*+H]$^+$ calcd for $C_{14}H_{17}NO$: 216.1391, found: 216.1390.

Synthesis of (*Z*)-2-(2-fluorophenyl)-*N*,5-dimethylhexa-2,4-dienamide ((*Z*)-18)

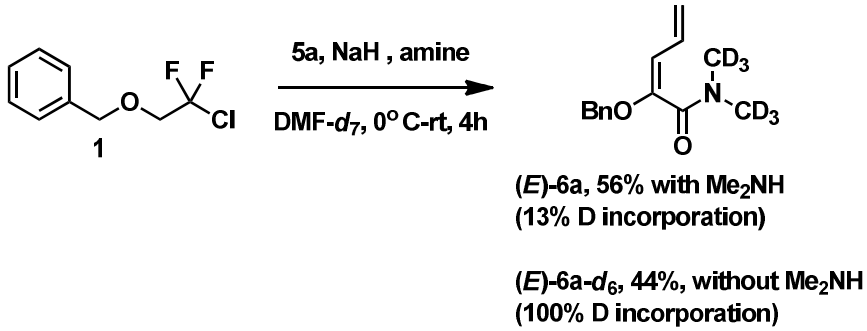
Following the general procedure for alkoxy dienamides, the reaction of 2-methylbut-3-yn-2-ol **5f** (80 µL) and methylamine (1.16 mL, 2M in THF) with *gem*-difluoro ethane derivative **7** (150 mg) gave (*Z*)-**18** (82 mg, 45%) as colorless liquid. R_f = 0.4 (40% EtOAc/petroleum ether).



(*Z*)-2-(2-Fluorophenyl)-*N*,5-dimethylhexa-2,4-dienamide ((*Z*)-18)

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.76 (s, 3H), 1.94 (s, 3H), 2.83 (d, *J* = 5.2 Hz, 3H), 5.31 (brs, 1H), 5.57 (dt, *J* = 11.6 Hz, 1H), 7.13–7.24 (m, 3H), 7.37–7.42 (m, 1H), 7.82 (d, *J* = 11.6 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 19.3, 27.0 (2C), 116.4 (d, *J* = 21.6 Hz), 121.5, 123.4 (d, *J* = 17.1 Hz), 124.67 (d, *J* = 3.7 Hz), 125.5, 130.5 (d, *J* = 7.4 Hz), 132.7, 135.3, 146.3, 160.2 (d, *J* = 246.4 Hz), 167.3.
^{19}F NMR (376 MHz, $CDCl_3$) δ -112.27 (ddd, 1F, *J* = 5.3, 9.0, 14.3 Hz).
HRMS (CI) *m*/*z* [*M*+H]$^+$ calcd for $C_{14}H_{16}FNO$: 234.1297, found: 234.1293.

Synthesis of (*E*)-2-(benzyloxy)-*N*,*N*-dimethyl(d_6) penta-2,4-dienamide ((*E*)-6a-d_6)



Following the general procedure for alkoxy dienamides, the reaction of propargyl alcohol **5a** (17 µL, 0.29 mmol) with *gem*-difluoro ethane derivative **1** (50 mg, 0.24 mmol) in DMF-d_7 (0.5 mL) in the presence of NaH (19 mg, 0.48 mmol) and Me_2NH (0.36 mL, 0.72 mmol, 2M in THF) gave deuterium labelled (*E*)-**6a** (32 mg, 56% and 13% of deuterium incorporation) as colorless syrup.R_f = 0.4 (40% EtOAc/hexane).

Spectral data of deuterium labelled of (*E*)-6a

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.91 (s, 5.2H (13% D), 4.82 (s, 2H), 5.11 (ddd, *J* = 0.8, 2.0, 10.4 Hz, 1H), 5.23 (ddd, *J* = 0.8, 2.0, 17.2 Hz, 1H), 5.72 (dt, *J* = 0.8, 10.8 Hz, 1H), 6.72 (ddd, *J* = 10.4, 10.8, 21.2 Hz, 1H), 7.28–7.36 (m, 5H).

HRMS (CI) *m/z* [*M*+H]$^+$ calcd for $C_{14}H_{17}NO_2$: 232.1336, found: 232.1334 and *m/z* [*M*+H]$^+$ calcd for $C_{14}H_{11}D_6NO_2$: 238.1717, found: 238.1712.

Following the general procedure for alkoxy dienamides without any amines, the reaction of propargyl alcohol **5a** (17 µL, 0.29 mmol) with *gem*-difluoro ethane derivative **1** (50 mg, 0.24mmol) and NaH (19 mg, 0.48 mmol) in DMF-d_7 (0.5 mL) gave (*E*)-**6a**-d_6 (25 mg, 44% and 100% of deuterium incorporation) as colorless syrup. R_f = 0.4 (40% EtOAc/hexane).

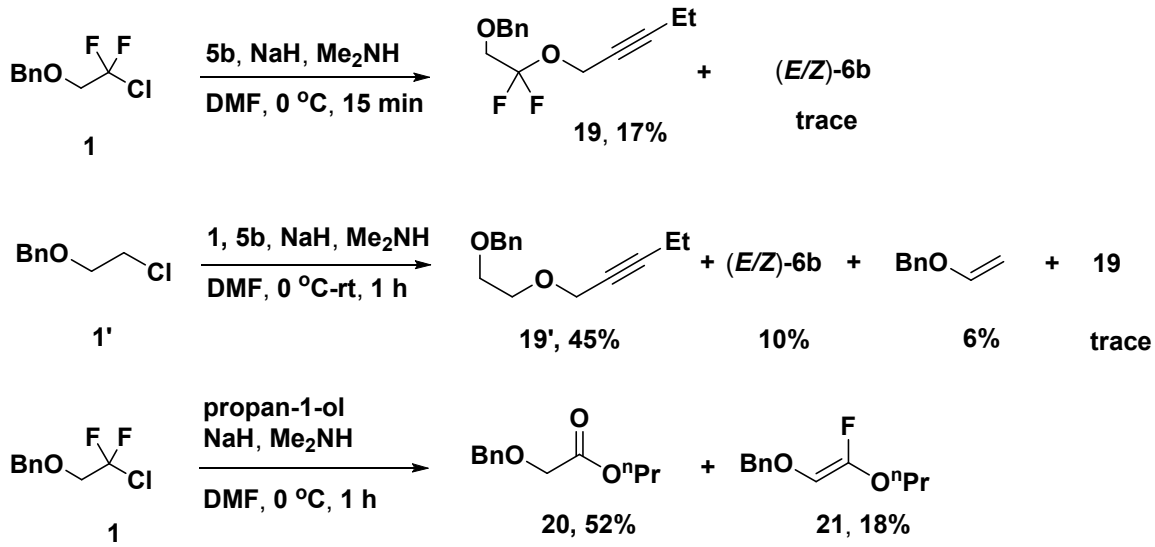
(*E*)-2-(benzyloxy)-*N*,*N*-dimethyl(d_6) penta-2,4-dienamide ((*E*)-6a-d_6)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.82 (s, 2H), 5.11 (ddd, *J* = 0.8, 2.0, 10.4 Hz, 1H), 5.23 (ddd, *J* = 0.8, 2.0, 17.2 Hz, 1H), 5.72 (dt, *J* = 0.8, 10.8 Hz, 1H), 6.72 (ddd, *J* = 10.4, 10.8, 21.2 Hz, 1H), 7.28–7.36 (m, 5H).

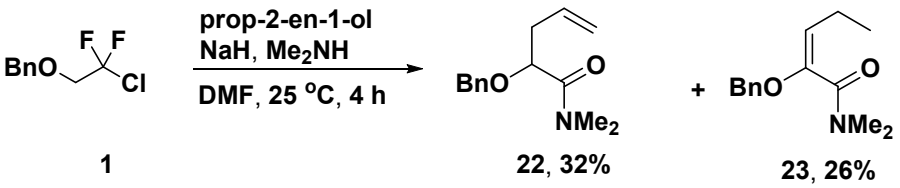
HRMS (CI) *m/z* [*M*+H]$^+$ calcd for $C_{14}H_{11}D_6NO_2$: 238.1717, found: 238.1712.

SI 1.4 Experiments to determine mechanism

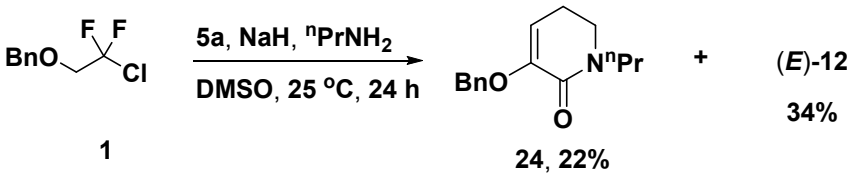
Eq. (i) Identification of intermediats propargyl ether 19, 19' and fluorovinyl ether 21



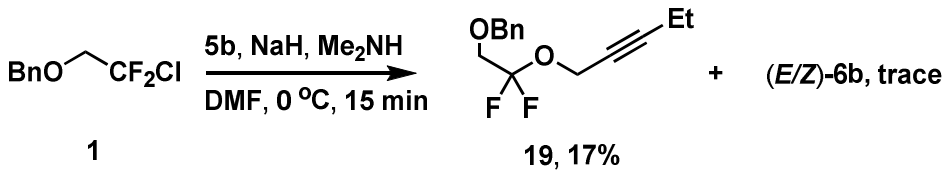
Eq. (ii) [3,3] sigmatropic rearrangement with propenol



Eq. (iii) Isolation of dihydro pyridinone 21



The detailed procedure for control experiments



Following the general procedure for alkoxy dienamides, the reaction of pent-2-yn-1-ol **5b** (54 µL, 0.58 mmol) with *gem*-difluoro ethane derivative **1** (100 mg, 0.48 mmol) in DMF in the presence of NaH (39 mg, 0.97 mmol) and Me_2NH (0.72 mL, 1.45 mmol, 2M in THF) for 15 min at 0 °C gave difluoro propargly ether **19** (21 mg, 17%) as colorless liquid. R_f = 0.6 (10% EtOAc/hexane) and trace of (*E/Z*)-**6b**.

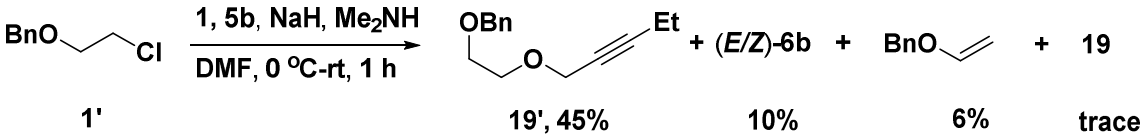
((2,2-Difluoro-2-(pent-2-yn-1-yloxy)ethoxy)methyl)benzene (19)

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (t, *J* = 7.2 Hz, 3H), 2.36 (tt, *J* = 2.4, 7.6 Hz, 2H), 3.76 (t, *J* = 9.2 Hz, 2H), 4.55 (t, *J* = 2.0 Hz, 2H), 4.68 (s, 2H), 7.3–7.36 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 12.6, 13.6, 52.3 (t, *J* = 9.0 Hz), 69.2 (t, *J* = 293.3 Hz), 73.3, 74.1, 89.4, 123.0 (t, *J* = 265.7 Hz), 128.0, 128.1, 128.6, 137.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -81.9 (t, *J* = 9.0 Hz, 2F).

HRMS (CI) *m/z* $[M\text{-H}]^+$ calcd for $C_{14}H_{16}F_2O_2$: 253.1040, found: 253.1047.

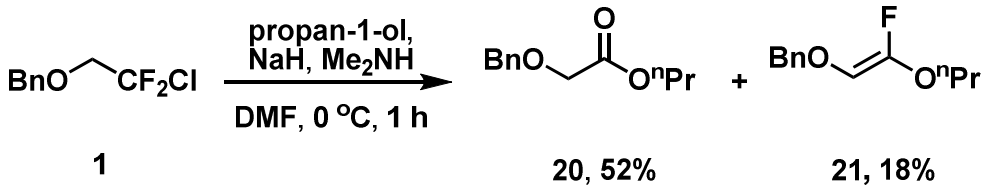


Following the general procedure for alkoxy dienamides, the reaction of pent-2-yn-1-ol **5b** (54 µL, 0.58 mmol) with *gem*-difluoro ethane derivative **1** (100 mg, 0.48 mmol) and **1'**(83 mg, 0.48 mmol) in DMF in the presence of NaH (39 mg, 0.97 mmol) and Me_2NH (0.72 mL, 1.45 mmol, 2M in THF) for 60 min at 0 °C-rt, gave propargly ether **19'** (48 mg, 45%) as colorless liquid. R_f = 0.7 (10% EtOAc/hexane), (*E/Z*)-**6b** (12 mg, 10%), benzyl vinyl ester (6%), and trace of **19**.

((2-(pent-2-yn-1-yloxy)ethoxy)methyl)benzene (19')

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (t, *J* = 7.2 Hz, 3H), 2.21–2.40 (m, 2H), 3.64–3.65 (m, 2H), 3.69–3.72 (m, 2H), 4.19 (t, *J* = 2.0 Hz, 2H), 4.58 (s, 2H), 7.27–7.36 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 12.6, 13.9, 59.1, 69.0, 69.4, 73.4, 75.3, 88.6, 127.7, 127.9, 128.5, 138.3.



Following the general procedure for alkoxy dienamides, the reaction of propan-1-ol (87 µL, 1.16 mmol) with *gem*-difluoro ethane derivative **1** (200 mg, 0.97 mmol) in DMF in the presence of NaH (77 mg, 1.94 mmol) and Me_2NH (1.45 mL, 2.9 mmol, 2M in THF) for 1 h at 0 °C gave **20** (105 mg, 52%) as colorless liquid, along with **21** (37 mg, 18%). R_f = 0.7 and 0.6 (20% EtOAc/hexane).

Propyl 2-(benzyloxy)acetate (20)

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J* = 7.2 Hz, 3H), 1.64–1.73 (m, 2H), 4.1 (s, 2H), 4.14 (t, *J* = 6.8 Hz, 2H), 4.65 (s, 2H), 7.33–7.37 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 10.4, 22.0, 66.5, 67.2, 73.4, 128.1, 128.2, 128.6, 137.2, 170.6.

HRMS (CI) *m/z* $[M+H]^+$ calcd for $C_{12}H_{16}O_3$: 209.1180, found: 209.1174.

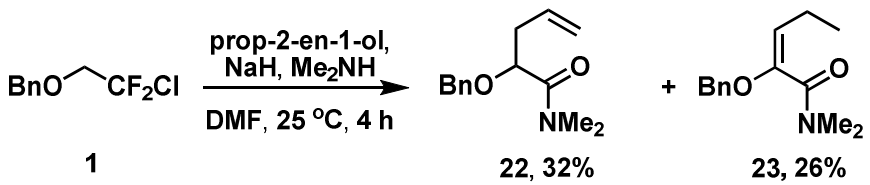
(*Z*)-(((2-Fluoro-2-propoxyvinyl)oxy)methyl)benzene (21)

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, *J* = 7.2 Hz, 3H), 1.58–1.73 (m, 2H), 3.94 (td, *J* = 1.2, 6.4 Hz, 2H), 4.7 (s, 2H), 5.75 (d, *J* = 2.4 Hz, 1H), 7.33–7.37 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 10.2, 22.7, 73.8, 74.9 (d, *J* = 23 Hz), 113.5 (d, *J* = 70 Hz), 128.1, 128.2, 128.6, 137.1, 155.1 (d, *J* = 263.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -122.8 (brs, 1F).

HRMS (CI) *m/z* $[M-H]^+$ calcd for $C_{12}H_{15}FO_2$: 209.0975, found: 209.0975.



Following the general procedure for alkoxy dienamides, the reaction of prop-2-en-1-ol (0.79 µL) with *gem*-difluoro ethane derivative **1** (200 mg) for 4 h at 25 °C gave **22** (72 mg, 32%) as a colorless liquids, along with **23** (60 mg, 26%). R_f = 0.4 and 0.35 (30% EtOAc/petroleum ether).

2-(Benzyloxy)-*N*,*N*-dimethylpent-4-enamide (22)

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46–2.53 (m, 1H), 2.55–2.63 (m, 1H), 2.96 (s, 3H), 3.04 (s, 3H), 4.27 (dd, *J* = 6.0, 8.4 Hz, 1H), 4.4 (d, *J* = 11.6 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 5.07–5.16 (m, 2H), 5.79–5.90 (m, 1H), 7.28–7.34 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 36.2, 36.7, 36.8, 71.2, 78.0, 117.8, 127.9, 128.1, 128.5, 133.8, 137.7, 171.1.

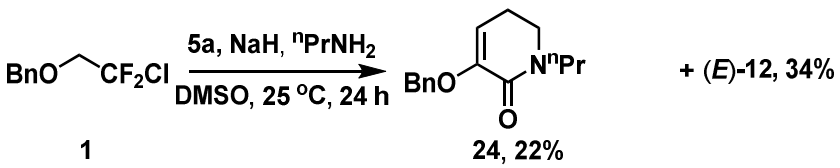
HRMS (CI) *m*/*z* $[M+H]^+$ calcd for $C_{14}H_{19}NO_2$: 234.1497, found: 234.1491.

(*E*)-2-(Benzyloxy)-*N*,*N*-dimethylpent-2-enamide (23)

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.2 Hz, 3H), 2.11–2.19 (m, 2H), 2.93 (s, 6H), 4.73 (s, 2H), 5.19 (t, *J* = 7.2 Hz, 1H), 7.28–7.35 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 18.3, 35.2, 38.4, 72.2, 120.5, 128.2, 128.3, 128.5, 137.2, 147.3, 167.3.

HRMS (CI) *m*/*z* $[M+H]^+$ calcd for $C_{14}H_{19}NO_2$: 234.1497, found: 234.1499.



Following the general procedure for alkoxy dienamides, reaction of propargyl alcohol **5a** (67 µL, 1.16 mmol) with *gem*-difluoro ethane derivative **1** (200 mg, 0.97 mmol) in DMF in the presence of NaH (77 mg, 1.94 mmol) and *n*-propyl amine (1.45 mL, 2.9 mmol, 2M in THF) for 24 h at 0 °C to 25 °C gave (*E*)-**12** (80 mg, 34%) as colorless liquid, along with cyclic **24** (53 mg, 22%). R_f = 0.5, 0.65, respectively (40% EtOAc/petroleum ether) and trace of (*Z*)-**12**.

2. References

a) M. Decostanzi, A. Van Der Lee, J. M. Campagne, E. Leclerc, *Adv. Synth. Catal.* **2015**, *357*, 3091–3097.

b) V. V. Levin, A. A. Zemtsov, M. I. Struchkova, A. D. Dilman, *Org. Lett*. **2013**, *15*, 917–919.

c) V. V. Levin, A. A. Zemtsov, M. I. Struchkova, A. D. Dilman, *J. Fluorine Chem*. **2015**, *171*, 97–101.

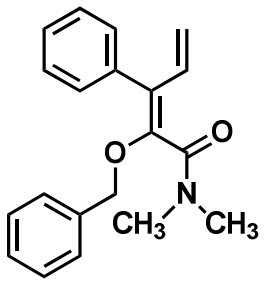
d) S. E. Steinhardt, J. S. Silverston, C. D. Vanderwal, *J. Am. Chem. Soc.* **2008**, *130*, 7560–7561.

X-Ray diffraction structural determination details

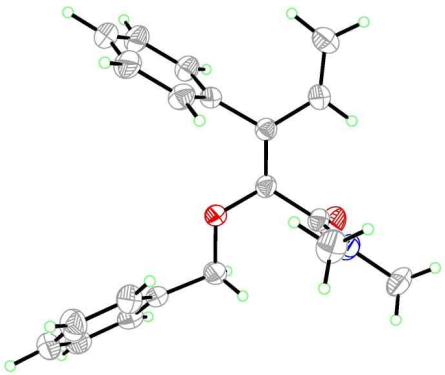
CCDC 1911472 and 1911473 contain the supplementary crystallographic data for **(*Z*)-6e** and **(*Z*)-17** respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

General information

A suitable crystal was coated with paratone-*N* oil and the diffraction data measured at 100 K either with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation on a Bruker Venture CMOS diffractometer. The structure was solved and refined by ShelXL using Least Squares minimization. All the non-hydrogen atoms were refined anisotropically. Due to highly poor crystallinity of **(*Z*)-17**, the quality of the X-ray data is bad. We attempted three times to utilize either a house X-ray machine or Pohang Accelerator Laboratory X-ray beamline, but we could not obtain better data due to highly thin property of crystals. Nevertheless, the connectivity of **(*Z*)-17** clearly confirms the geometry.



(*Z*)-6e



ORTEP structure of (*Z*)-6e

Table S1. Crystal data and structure refinement for **(*Z*)-6e**.

Identification code	**(*Z*)-6e**
Empirical formula	C20 H21 N O2
Formula weight	307.38
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 8.4728(7) Å = 90°.
	b = 33.754(3) = 95.686(4)°.
	c = 6.1208(6) Å = 90°.
Volume	1741.9(3) Å^3
Z	4

Density (calculated)	1.172 Mg/m^3
Absorption coefficient	0.075 mm^{-1}
F(000)	656
Crystal size	0.3 x 0.1 x 0.1 mm^3
Theta range for data collection	1.21 to 31.10°.
Index ranges	-12<=h<=12, -48<=k<=49, -8<=l<=8
Reflections collected	138284
Independent reflections	5592 [R(int) = 0.0414]
Completeness to theta = 31.10°	99.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5592 / 0 / 292
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0549, wR2 = 0.1443
R indices (all data)	R1 = 0.0714, wR2 = 0.1560
Largest diff. peak and hole	0.186 and -0.159 $e.Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **(*Z*)-6e**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-899(2)	492(1)	8646(2)	49(1)
C(2)	-1136(2)	697(1)	10529(3)	62(1)
C(3)	-2186(2)	558(1)	11921(3)	77(1)
C(4)	-3010(2)	215(1)	11444(3)	77(1)
C(5)	-2789(2)	8(1)	9586(3)	71(1)
C(6)	-1734(2)	147(1)	8177(3)	60(1)
C(7)	300(2)	632(1)	7192(3)	67(1)
C(8)	915(1)	1230(1)	5334(2)	45(1)
C(9)	2498(2)	1041(1)	5031(2)	50(1)
C(10)	3516(3)	1327(1)	8586(3)	79(1)
C(11)	5215(2)	915(1)	6433(4)	83(1)
C(12)	450(1)	1576(1)	4418(2)	45(1)
C(13)	-1147(1)	1740(1)	4745(2)	45(1)
C(14)	-2371(2)	1736(1)	3072(2)	58(1)
C(15)	-3845(2)	1894(1)	3392(3)	68(1)
C(16)	-4101(2)	2059(1)	5367(3)	68(1)
C(17)	-2901(2)	2065(1)	7034(3)	68(1)
C(18)	-1429(2)	1906(1)	6738(2)	57(1)
C(19)	1503(2)	1801(1)	3142(2)	57(1)
C(20)	1203(2)	2151(1)	2236(3)	74(1)
O(1)	-87(1)	1031(1)	6555(2)	59(1)
O(2)	2644(1)	846(1)	3379(2)	77(1)
N(1)	3675(1)	1099(1)	6623(2)	58(1)

Table S3. Bond lengths [Å] and angles [°] for **(*Z*)-6e**.

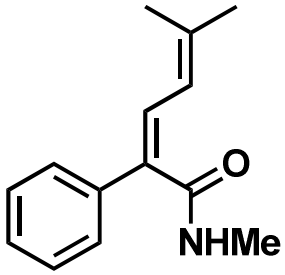
C(1)-C(2)	1.375(2)	C(3)-C(2)-C(1)	120.40(15)
C(1)-C(6)	1.378(2)	C(4)-C(3)-C(2)	120.29(17)
C(1)-C(7)	1.4913(19)	C(5)-C(4)-C(3)	120.08(16)
C(2)-C(3)	1.374(2)	C(4)-C(5)-C(6)	119.82(16)
C(3)-C(4)	1.369(3)	C(1)-C(6)-C(5)	120.45(15)
C(4)-C(5)	1.363(3)	O(1)-C(7)-C(1)	107.98(11)
C(5)-C(6)	1.384(2)	C(12)-C(8)-O(1)	119.15(10)
C(7)-O(1)	1.4320(16)	C(12)-C(8)-C(9)	122.95(11)
C(8)-C(12)	1.3377(17)	O(1)-C(8)-C(9)	117.88(10)
C(8)-O(1)	1.3624(15)	O(2)-C(9)-N(1)	123.42(12)
C(8)-C(9)	1.5126(16)	O(2)-C(9)-C(8)	119.44(12)
C(9)-O(2)	1.2240(16)	N(1)-C(9)-C(8)	117.15(11)
C(9)-N(1)	1.3377(17)	C(8)-C(12)-C(19)	120.61(11)
C(10)-N(1)	1.446(2)	C(8)-C(12)-C(13)	120.08(10)
C(11)-N(1)	1.460(2)	C(19)-C(12)-C(13)	119.30(11)
C(12)-C(19)	1.4563(18)	C(14)-C(13)-C(18)	118.33(12)
C(12)-C(13)	1.4942(16)	C(14)-C(13)-C(12)	121.29(11)
C(13)-C(14)	1.3833(18)	C(18)-C(13)-C(12)	120.38(11)
C(13)-C(18)	1.3840(17)	C(13)-C(14)-C(15)	120.67(14)
C(14)-C(15)	1.389(2)	C(16)-C(15)-C(14)	120.29(15)
C(15)-C(16)	1.368(2)	C(17)-C(16)-C(15)	119.63(14)
C(16)-C(17)	1.367(3)	C(16)-C(17)-C(18)	120.57(15)
C(17)-C(18)	1.386(2)	C(13)-C(18)-C(17)	120.52(14)
C(19)-C(20)	1.319(2)	C(20)-C(19)-C(12)	126.12(14)
		C(8)-O(1)-C(7)	118.41(10)
C(2)-C(1)-C(6)	118.95(13)	C(9)-N(1)-C(10)	123.92(13)
C(2)-C(1)-C(7)	120.40(14)	C(9)-N(1)-C(11)	119.25(15)
C(6)-C(1)-C(7)	120.58(14)	C(10)-N(1)-C(11)	116.81(16)

Symmetry transformations used to generate equivalent atoms:

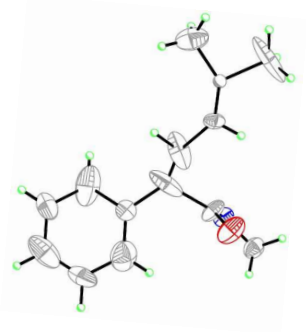
Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **(*Z*)-6e**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	46(1)	47(1)	56(1)	8(1)	6(1)	8(1)
C(2)	58(1)	66(1)	62(1)	-8(1)	5(1)	-5(1)
C(3)	75(1)	101(1)	58(1)	-5(1)	16(1)	3(1)
C(4)	58(1)	97(1)	79(1)	27(1)	16(1)	0(1)
C(5)	54(1)	59(1)	96(1)	18(1)	-5(1)	-6(1)
C(6)	63(1)	49(1)	66(1)	0(1)	-1(1)	9(1)
C(7)	66(1)	54(1)	87(1)	17(1)	32(1)	18(1)
C(8)	43(1)	51(1)	44(1)	0(1)	8(1)	5(1)
C(9)	47(1)	54(1)	51(1)	1(1)	11(1)	8(1)
C(10)	74(1)	108(2)	53(1)	-9(1)	-1(1)	2(1)
C(11)	49(1)	102(2)	99(2)	14(1)	8(1)	22(1)
C(12)	45(1)	48(1)	43(1)	-1(1)	6(1)	2(1)
C(13)	45(1)	41(1)	48(1)	2(1)	7(1)	2(1)
C(14)	53(1)	66(1)	56(1)	-4(1)	2(1)	5(1)
C(15)	48(1)	77(1)	78(1)	3(1)	-2(1)	5(1)
C(16)	55(1)	65(1)	86(1)	12(1)	19(1)	14(1)
C(17)	77(1)	66(1)	65(1)	-4(1)	22(1)	17(1)
C(18)	61(1)	59(1)	51(1)	-4(1)	5(1)	9(1)
C(19)	52(1)	60(1)	60(1)	4(1)	14(1)	0(1)
C(20)	79(1)	66(1)	81(1)	16(1)	21(1)	-4(1)
O(1)	54(1)	54(1)	72(1)	19(1)	23(1)	15(1)
O(2)	72(1)	92(1)	69(1)	-25(1)	14(1)	18(1)
N(1)	46(1)	72(1)	55(1)	3(1)	6(1)	10(1)

Table S5. Crystal data and structure refinement for **(*Z*)-17**.



(*Z*)-17



ORTEP of (*Z*)-17

Identification code	**(*Z*)-17**	
Empirical formula	C56 H68 N4 O4	
Formula weight	861.14	
Temperature	290(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.2925(9) Å	α= 89.994(3)°.
	b = 9.7764(10) Å	β= 89.985(3)°.
	c = 28.414(3) Å	γ = 90.048(3)°.
Volume	2581.3(4) Å^3	
Z	2	
Density (calculated)	1.108 Mg/m^3	
Absorption coefficient	0.069 mm^{-1}	
F(000)	928	
Crystal size	0.15 x 0.10 x 0.02 mm^3	
Theta range for data collection	0.72 to 24.74°.	
Index ranges	-10<=h<=10, -11<=k<=11, -33<=l<=33	
Reflections collected	47325	
Independent reflections	8792 [R(int) = 0.0925]	
Completeness to theta = 24.74°	99.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8792 / 0 / 541	
Goodness-of-fit on F^2	1.601	
Final R indices [I>2sigma(I)]	R1 = 0.1915, wR2 = 0.4975	
R indices (all data)	R1 = 0.3080, wR2 = 0.5484	
Largest diff. peak and hole	0.872 and -0.524 e.Å^{-3}	

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (*Z*)-**17**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	748(8)	1027(8)	2920(2)	71(2)
C(2)	-199(8)	1977(8)	2729(3)	156(5)
C(3)	-270(10)	2154(9)	2244(4)	130(4)
C(4)	606(12)	1382(12)	1950(2)	162(7)
C(5)	1553(11)	432(11)	2141(3)	133(4)
C(6)	1624(8)	254(8)	2626(3)	284(15)
C(7)	920(12)	737(14)	3407(5)	137(6)
C(8)	-11(9)	1742(10)	3786(3)	83(3)
O(1)	-1311(6)	1565(7)	3851(2)	103(2)
N(1)	716(7)	2802(7)	3921(2)	69(2)
C(9)	23(10)	3968(10)	4145(3)	98(3)
C(10)	1264(14)	8(17)	3664(4)	140(6)
C(11)	1523(8)	-542(8)	4130(3)	75(2)
C(12)	2184(14)	-1512(16)	4316(9)	221(11)
C(13)	3038(14)	-2651(13)	4184(5)	149(5)
C(14)	2055(17)	-1750(20)	4879(4)	223(11)
C(15)	743(8)	6022(8)	2079(2)	73(2)
C(16)	-220(8)	6951(8)	2273(3)	157(5)
C(17)	-297(10)	7109(10)	2759(4)	131(5)
C(18)	589(12)	6337(13)	3050(2)	157(6)
C(19)	1552(10)	5409(11)	2855(3)	137(5)
C(20)	1629(8)	5251(8)	2370(3)	370(20)
C(21)	909(11)	5693(14)	1608(5)	134(6)
C(22)	5(10)	6747(11)	1211(4)	86(3)
O(2)	-1306(6)	6561(7)	1142(3)	111(2)
N(2)	702(7)	7802(7)	1082(2)	71(2)
C(23)	18(10)	8954(10)	867(3)	95(3)
C(24)	1272(13)	5032(15)	1333(4)	128(5)
C(25)	1496(8)	4470(9)	872(3)	76(2)
C(26)	2232(16)	3421(19)	685(11)	277(15)
C(27)	2092(17)	3210(20)	125(4)	219(11)
C(28)	3011(15)	2343(13)	811(5)	150(5)
C(29)	5744(9)	3965(8)	2919(2)	73(2)
C(30)	4801(8)	3025(8)	2720(4)	157(5)
C(31)	4738(10)	2876(10)	2234(4)	132(5)
C(32)	5619(12)	3667(12)	1947(2)	186(8)
C(33)	6563(10)	4607(11)	2146(3)	131(5)
C(34)	6626(8)	4756(8)	2632(3)	213(9)
C(35)	5926(12)	4314(14)	3391(6)	147(7)
C(36)	4993(9)	3287(10)	3789(3)	80(3)
O(3)	3685(6)	3457(7)	3851(2)	108(2)
N(3)	5704(7)	2203(7)	3921(2)	72(2)
C(37)	5021(10)	1027(10)	4135(4)	100(3)

C(38)	6304(12)	5005(16)	3661(4)	125(5)
C(39)	6513(8)	5536(9)	4128(4)	77(3)
C(40)	7189(15)	6541(18)	4308(9)	226(11)
C(41)	7996(15)	7681(14)	4191(5)	149(5)
C(42)	7039(17)	6722(19)	4882(4)	217(10)
C(43)	5737(8)	8970(8)	2084(2)	72(2)
C(44)	4778(8)	8040(8)	2280(4)	157(5)
C(45)	4713(10)	7880(10)	2766(4)	128(4)
C(46)	5607(12)	8651(13)	3055(2)	161(6)
C(47)	6566(11)	9581(12)	2858(3)	139(5)
C(48)	6631(8)	9741(8)	2373(3)	450(30)
C(49)	5918(11)	9306(13)	1611(5)	125(5)
C(50)	4988(10)	8254(11)	1209(3)	87(3)
C(51)	5008(10)	6046(9)	862(4)	97(3)
C(52)	6244(14)	9957(17)	1334(4)	138(6)
C(53)	6513(8)	10547(9)	878(3)	75(2)
C(54)	7257(15)	11550(18)	685(10)	245(13)
C(55)	7030(16)	11734(19)	125(4)	215(10)
C(56)	8003(15)	12658(13)	810(5)	151(5)
O(4)	3706(6)	8449(7)	1148(3)	107(2)
N(4)	5721(7)	7216(7)	1074(2)	71(2)

Table S7. Bond lengths [Å] and angles [°] for (*Z*)-**17**

C(1)-C(2)	1.3900	C(40)-C(41)	1.38(2)
C(1)-C(6)	1.3900	C(40)-C(42)	1.64(3)
C(1)-C(7)	1.422(13)	C(43)-C(44)	1.3900
C(2)-C(3)	1.3900	C(43)-C(48)	1.3900
C(3)-C(4)	1.3900	C(43)-C(49)	1.393(13)
C(4)-C(5)	1.3900	C(44)-C(45)	1.3900
C(5)-C(6)	1.3900	C(45)-C(46)	1.3900
C(7)-C(10)	1.070(14)	C(46)-C(47)	1.3900
C(7)-C(8)	1.696(18)	C(47)-C(48)	1.3900
C(8)-O(1)	1.234(9)	C(49)-C(52)	1.055(15)
C(8)-N(1)	1.295(10)	C(49)-C(50)	1.762(18)
N(1)-C(9)	1.456(10)	C(50)-O(4)	1.219(10)
C(10)-C(11)	1.450(14)	C(50)-N(4)	1.281(11)
C(11)-C(12)	1.248(16)	C(51)-N(4)	1.452(10)
C(12)-C(13)	1.42(2)	C(52)-C(53)	1.440(15)
C(12)-C(14)	1.62(3)	C(53)-C(54)	1.319(18)
C(15)-C(21)	1.384(13)	C(54)-C(56)	1.33(2)
C(15)-C(16)	1.3900	C(54)-C(55)	1.61(3)
C(15)-C(20)	1.3900		
C(16)-C(17)	1.3900	C(2)-C(1)-C(6)	120.0
C(17)-C(18)	1.3900	C(2)-C(1)-C(7)	125.7(9)
C(18)-C(19)	1.3900	C(6)-C(1)-C(7)	114.3(9)
C(19)-C(20)	1.3900	C(1)-C(2)-C(3)	120.0
C(21)-C(24)	1.070(14)	C(4)-C(3)-C(2)	120.0
C(21)-C(22)	1.744(18)	C(3)-C(4)-C(5)	120.0
C(22)-O(2)	1.247(10)	C(6)-C(5)-C(4)	120.0
C(22)-N(2)	1.272(11)	C(5)-C(6)-C(1)	120.0
N(2)-C(23)	1.431(10)	C(10)-C(7)-C(1)	146.3(19)
C(24)-C(25)	1.436(14)	C(10)-C(7)-C(8)	96.0(15)
C(25)-C(26)	1.342(18)	C(1)-C(7)-C(8)	116.5(9)
C(26)-C(28)	1.33(2)	O(1)-C(8)-N(1)	125.3(8)
C(26)-C(27)	1.61(3)	O(1)-C(8)-C(7)	120.9(8)
C(29)-C(30)	1.3900	N(1)-C(8)-C(7)	112.7(8)
C(29)-C(34)	1.3900	C(8)-N(1)-C(9)	121.7(7)
C(29)-C(35)	1.394(14)	C(7)-C(10)-C(11)	157.1(19)
C(30)-C(31)	1.3900	C(12)-C(11)-C(10)	138.6(16)
C(31)-C(32)	1.3900	C(11)-C(12)-C(13)	139(2)
C(32)-C(33)	1.3900	C(11)-C(12)-C(14)	119.2(19)
C(33)-C(34)	1.3900	C(13)-C(12)-C(14)	101.2(14)
C(35)-C(38)	1.081(14)	C(21)-C(15)-C(16)	127.4(9)
C(35)-C(36)	1.742(19)	C(21)-C(15)-C(20)	112.5(9)
C(36)-O(3)	1.239(9)	C(16)-C(15)-C(20)	120.0
C(36)-N(3)	1.304(10)	C(17)-C(16)-C(15)	120.0
N(3)-C(37)	1.446(10)	C(16)-C(17)-C(18)	120.0
C(38)-C(39)	1.437(14)	C(17)-C(18)-C(19)	120.0
C(39)-C(40)	1.274(18)	C(20)-C(19)-C(18)	120.0

C(19)-C(20)-C(15)	120.0
C(24)-C(21)-C(15)	152.0(19)
C(24)-C(21)-C(22)	92.0(14)
C(15)-C(21)-C(22)	115.7(9)
O(2)-C(22)-N(2)	124.7(9)
O(2)-C(22)-C(21)	119.1(9)
N(2)-C(22)-C(21)	114.9(8)
C(22)-N(2)-C(23)	122.4(7)
C(21)-C(24)-C(25)	160.9(19)
C(26)-C(25)-C(24)	136.6(17)
C(28)-C(26)-C(25)	141(3)
C(28)-C(26)-C(27)	101.9(15)
C(25)-C(26)-C(27)	117(2)
C(30)-C(29)-C(34)	120.0
C(30)-C(29)-C(35)	129.0(9)
C(34)-C(29)-C(35)	111.0(10)
C(29)-C(30)-C(31)	120.0
C(32)-C(31)-C(30)	120.0
C(33)-C(32)-C(31)	120.0
C(32)-C(33)-C(34)	120.0
C(33)-C(34)-C(29)	120.0
C(38)-C(35)-C(29)	151(2)
C(38)-C(35)-C(36)	93.5(15)
C(29)-C(35)-C(36)	115.0(10)
O(3)-C(36)-N(3)	124.4(8)
O(3)-C(36)-C(35)	120.1(8)
N(3)-C(36)-C(35)	113.8(7)
C(36)-N(3)-C(37)	123.0(7)
C(35)-C(38)-C(39)	157.6(19)
C(40)-C(39)-C(38)	135.8(16)
C(39)-C(40)-C(41)	142(2)
C(39)-C(40)-C(42)	116(2)
C(41)-C(40)-C(42)	101.4(15)
C(44)-C(43)-C(48)	120.0
C(44)-C(43)-C(49)	128.2(9)
C(48)-C(43)-C(49)	111.7(9)
C(43)-C(44)-C(45)	120.0
C(46)-C(45)-C(44)	120.0
C(47)-C(46)-C(45)	120.0
C(48)-C(47)-C(46)	120.0
C(47)-C(48)-C(43)	120.0
C(52)-C(49)-C(43)	153.4(19)
C(52)-C(49)-C(50)	90.6(15)
C(43)-C(49)-C(50)	115.3(9)
O(4)-C(50)-N(4)	126.9(9)
O(4)-C(50)-C(49)	118.8(9)
N(4)-C(50)-C(49)	113.3(8)
C(49)-C(52)-C(53)	164(2)
C(54)-C(53)-C(52)	139.7(16)
C(53)-C(54)-C(56)	140(3)
C(53)-C(54)-C(55)	115.1(19)
C(56)-C(54)-C(55)	103.9(15)
C(50)-N(4)-C(51)	120.4(7)

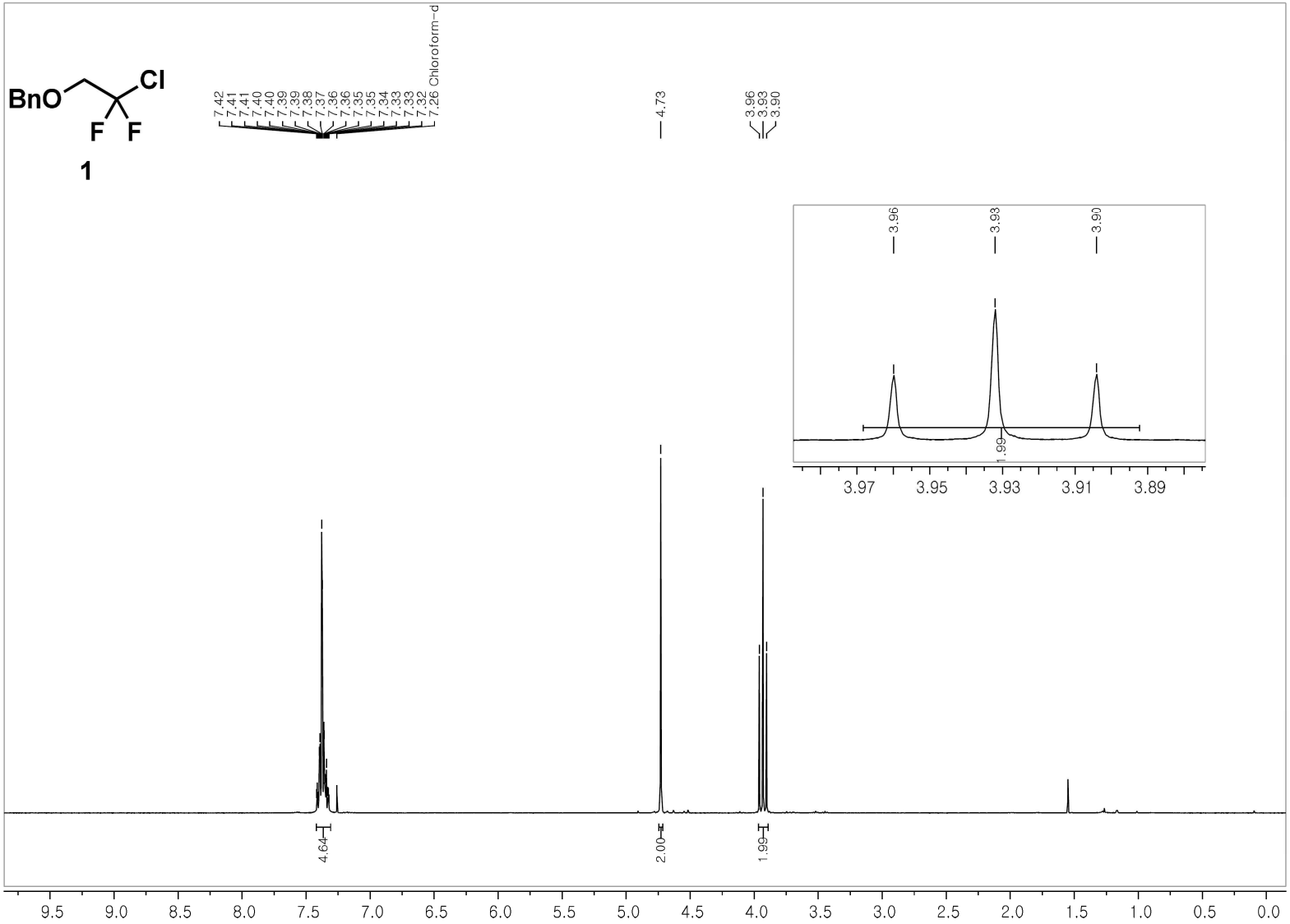
Symmetry transformations used to generate equivalent atoms:

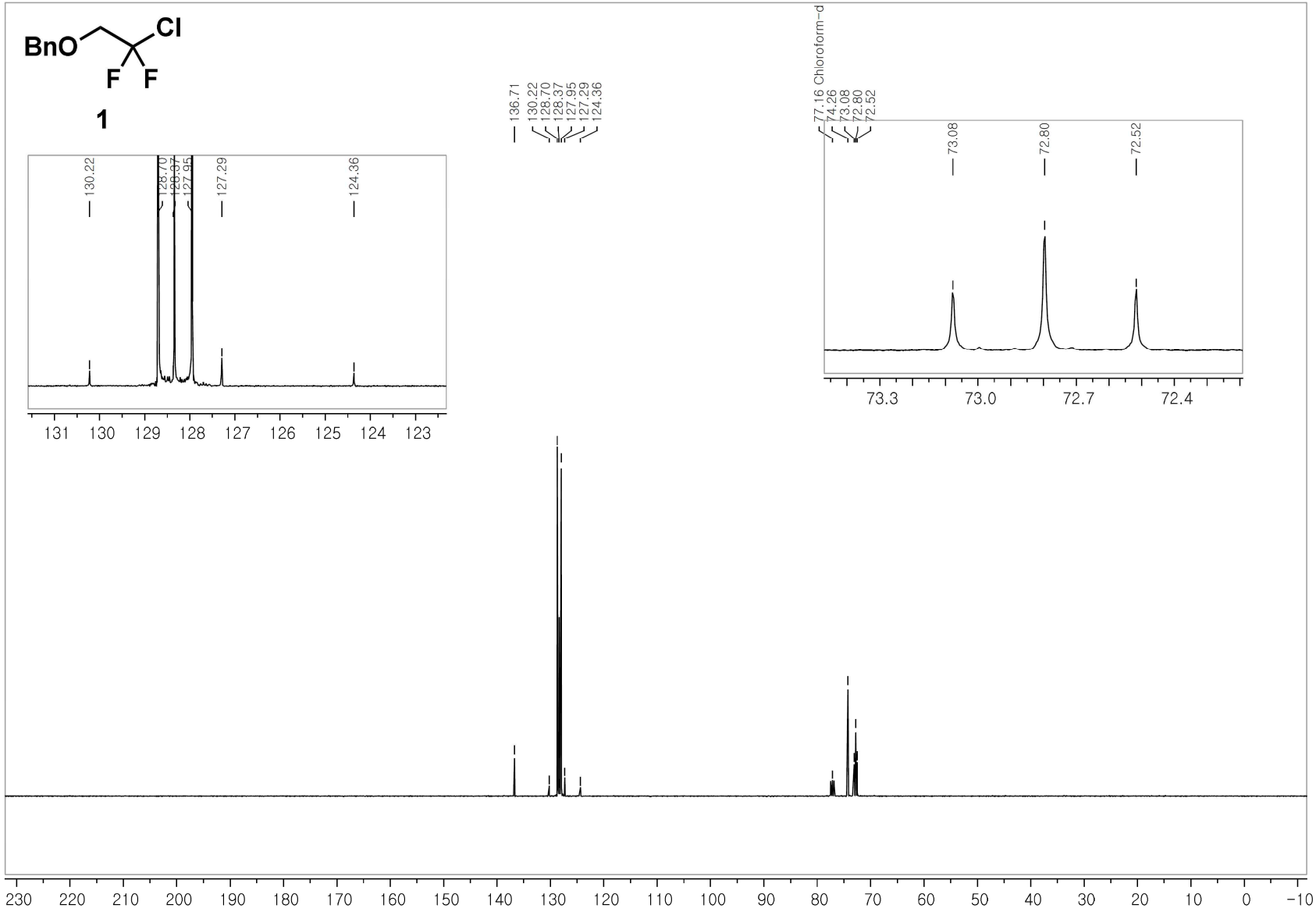
Table S8. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (*Z*)-**17**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	71(6)	81(6)	60(5)	9(4)	-13(4)	-7(4)
C(2)	112(10)	221(17)	135(12)	-8(11)	-9(8)	-7(11)
C(3)	139(11)	140(11)	111(10)	40(8)	-57(9)	-6(8)
C(4)	184(16)	227(18)	76(9)	33(11)	-29(10)	-86(13)
C(5)	135(11)	197(14)	68(7)	7(8)	-10(7)	-6(9)
C(6)	310(30)	310(30)	240(20)	-140(20)	180(20)	-170(20)
C(7)	93(8)	175(12)	142(11)	112(10)	-70(8)	-54(8)
C(8)	47(6)	88(7)	113(7)	-25(5)	3(5)	16(5)
O(1)	41(3)	114(5)	155(6)	-5(4)	25(3)	-2(3)
N(1)	45(4)	71(5)	91(5)	-2(4)	-3(3)	3(4)
C(9)	85(7)	93(7)	116(8)	-11(6)	14(5)	39(6)
C(10)	125(10)	219(15)	77(8)	27(9)	-19(7)	-116(10)
C(11)	51(5)	60(6)	116(8)	8(5)	-7(4)	12(4)
C(12)	71(8)	107(11)	480(40)	103(15)	-13(13)	-17(8)
C(13)	122(10)	114(10)	212(15)	44(9)	-49(9)	1(9)
C(14)	226(17)	360(20)	80(8)	126(12)	-82(10)	-171(17)
C(15)	75(6)	84(6)	61(6)	-1(5)	10(4)	-10(5)
C(16)	127(11)	202(16)	141(13)	-3(11)	16(9)	-1(11)
C(17)	126(10)	150(11)	117(10)	-43(9)	64(9)	-6(8)
C(18)	138(12)	246(19)	86(9)	-34(11)	16(9)	-47(12)
C(19)	117(10)	217(15)	75(8)	-7(8)	8(7)	-25(9)
C(20)	430(40)	350(30)	340(30)	250(30)	-300(30)	-290(30)
C(21)	82(7)	179(13)	140(11)	-110(10)	66(8)	-61(7)
C(22)	58(6)	91(7)	109(8)	11(6)	-2(5)	18(5)
O(2)	40(4)	144(6)	149(6)	15(4)	-25(4)	-7(3)
N(2)	44(4)	75(5)	95(5)	10(4)	2(3)	1(4)
C(23)	90(7)	87(7)	108(8)	6(5)	-20(5)	7(5)
C(24)	113(9)	186(13)	83(8)	-14(8)	19(7)	-107(9)
C(25)	45(5)	68(6)	115(8)	-15(5)	5(4)	11(4)
C(26)	80(9)	128(14)	620(50)	-140(20)	76(17)	-72(10)
C(27)	220(17)	350(20)	89(9)	-134(13)	85(10)	-155(16)
C(28)	145(12)	103(9)	202(14)	-22(9)	53(10)	32(9)
C(29)	70(6)	79(6)	70(6)	-1(5)	-4(5)	11(5)
C(30)	97(9)	213(16)	161(14)	15(11)	-14(9)	2(10)
C(31)	132(11)	156(12)	107(10)	-54(9)	-58(9)	16(9)
C(32)	205(18)	260(20)	88(10)	-23(12)	-31(11)	113(16)
C(33)	129(10)	197(13)	66(7)	-15(8)	-19(7)	12(9)
C(34)	216(18)	228(19)	194(18)	63(16)	92(16)	85(15)
C(35)	99(9)	171(13)	171(13)	-120(11)	-84(9)	74(8)
C(36)	40(5)	88(7)	113(7)	20(5)	4(5)	-10(5)
O(3)	41(4)	129(6)	153(6)	14(4)	14(3)	12(3)
N(3)	45(4)	75(5)	95(5)	2(4)	1(3)	-2(4)
C(37)	77(6)	101(8)	123(8)	7(6)	22(6)	-9(6)

C(38)	96(8)	192(14)	88(8)	-21(8)	-15(6)	92(9)
C(39)	43(5)	55(6)	132(9)	-15(5)	-3(5)	-11(4)
C(40)	75(9)	126(13)	480(40)	-84(17)	-40(14)	57(9)
C(41)	138(11)	122(10)	186(14)	-27(9)	-50(9)	-24(9)
C(42)	222(16)	350(20)	77(8)	-118(12)	-84(9)	165(16)
C(43)	71(6)	89(6)	57(5)	-1(5)	8(4)	6(5)
C(44)	126(11)	193(15)	153(14)	-9(11)	-5(9)	-9(11)
C(45)	141(11)	138(11)	105(10)	47(8)	51(9)	8(8)
C(46)	172(15)	234(18)	77(9)	27(11)	23(10)	64(13)
C(47)	120(10)	221(15)	76(8)	8(9)	11(7)	13(10)
C(48)	550(50)	480(40)	330(30)	-300(30)	-350(40)	420(40)
C(49)	69(7)	166(11)	140(11)	104(10)	51(7)	40(7)
C(50)	57(6)	102(8)	103(7)	-22(6)	1(5)	-15(5)
C(51)	94(7)	79(7)	120(8)	-5(5)	-20(6)	-28(5)
C(52)	120(10)	207(15)	88(9)	9(9)	8(7)	110(11)
C(53)	57(5)	69(6)	99(7)	10(5)	3(4)	-6(4)
C(54)	77(9)	121(13)	540(40)	121(18)	10(15)	30(9)
C(55)	228(16)	340(20)	76(8)	135(12)	73(9)	158(16)
C(56)	129(11)	112(10)	212(15)	43(9)	54(9)	-17(9)
O(4)	37(3)	123(6)	161(6)	-6(4)	-21(3)	-1(3)
N(4)	48(4)	73(5)	94(5)	-3(4)	5(3)	-1(4)

3. NMR spectra

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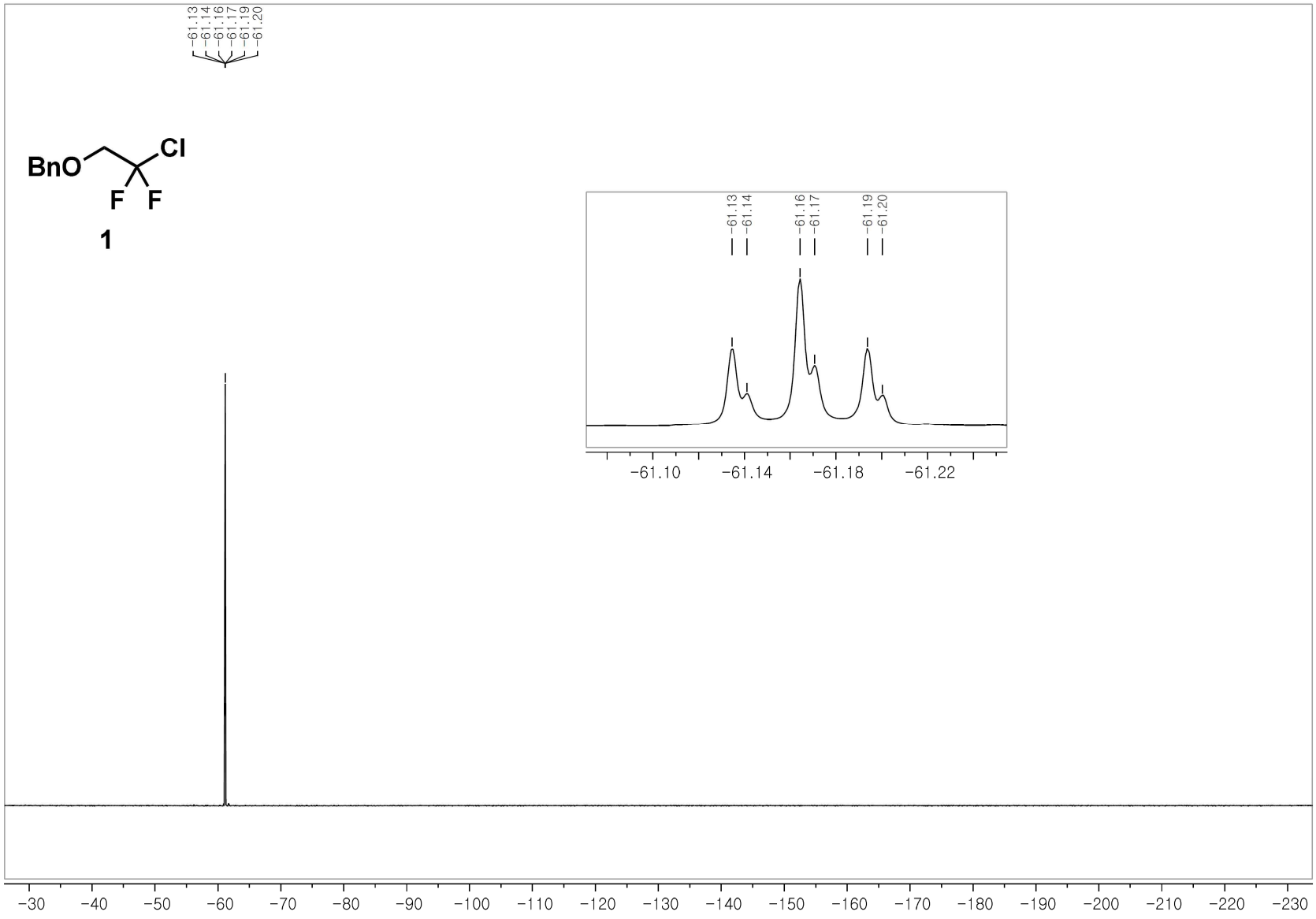
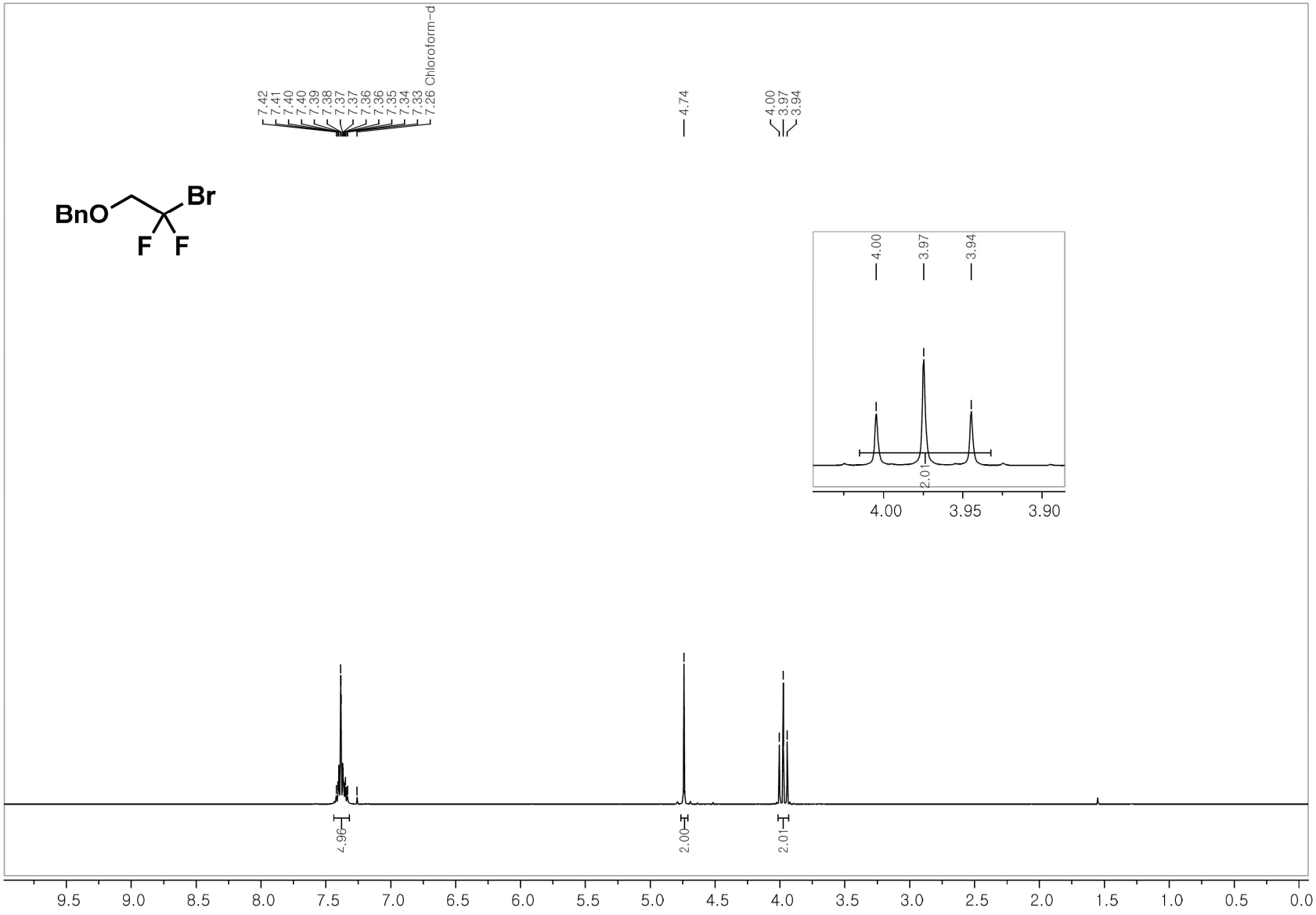
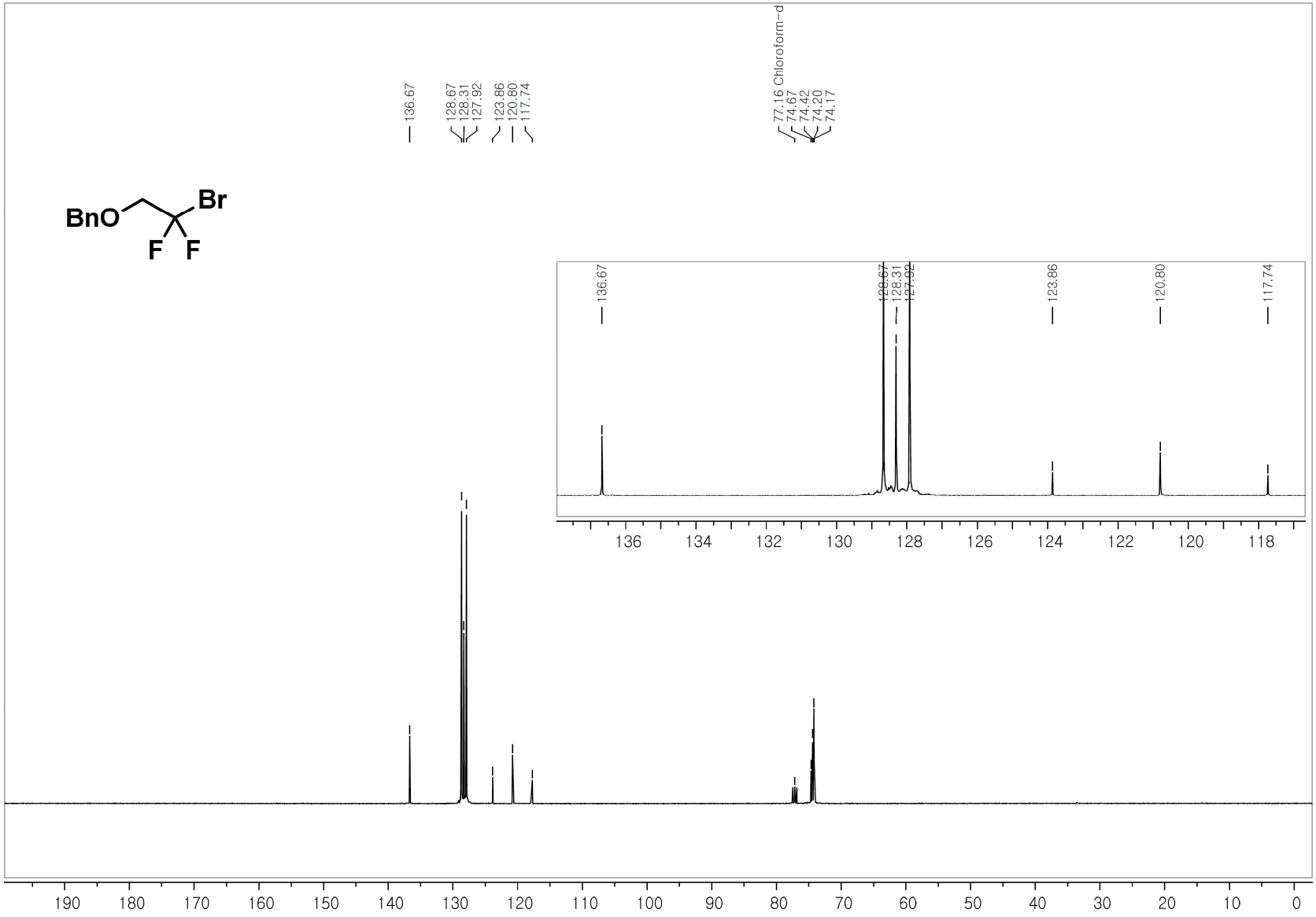
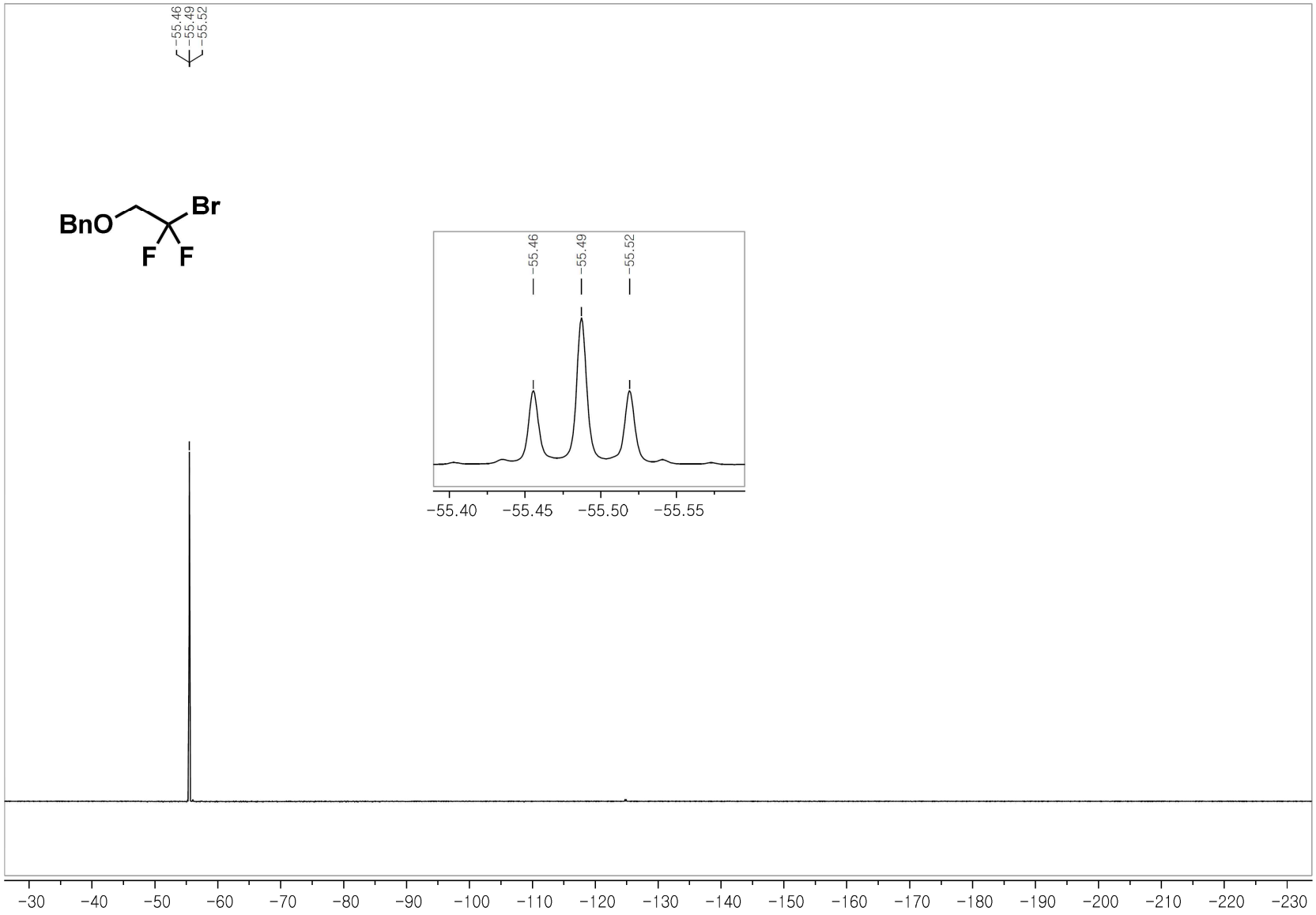
Cl
F F
1
136.71
130.22
128.70
128.37
127.95
127.29
124.36
77.16 Chloroform-d
74.26
73.08
72.80
72.52
130.22
128.70
128.37
127.95
127.29
124.36
131 130 129 128 127 126 125 124 123
73.08
72.80
72.52
73.3 73.0 72.7 72.4
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


-61.13
-61.14
-61.16
-61.17
-61.19
-61.20
BnO
Cl
F F
1
-61.10
-61.14
-61.18
-61.22
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230


7.42
7.41
7.40
7.40
7.39
7.38
7.37
7.37
7.36
7.36
7.35
7.34
7.33
7.26 Chloroform-d
4.74
4.00
3.97
3.94
BnO
Br
F
F
4.00
3.97
3.94
2.01
4.00
3.95
3.90
4.96
2.00
2.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


136.67
128.67
128.31
127.92
123.86
120.80
117.74
77.16 Chloroform-d
74.67
74.42
74.20
74.17
BnO
Br
F
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
136
134
132
130
128
126
124
122
120
118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-55.49
-55.52
BnO
Br
F
F
-55.40
-55.45
-55.50
-55.55
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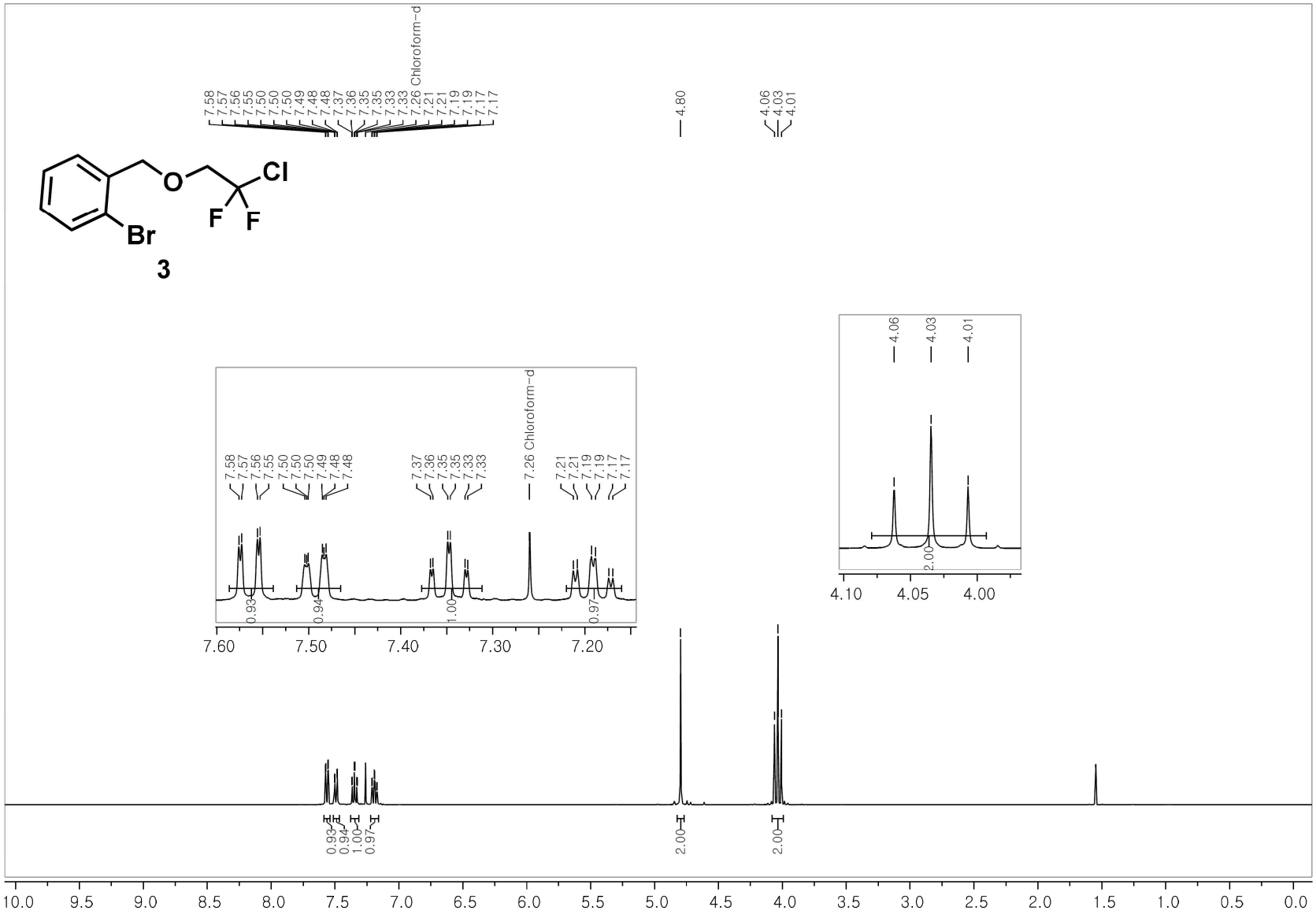
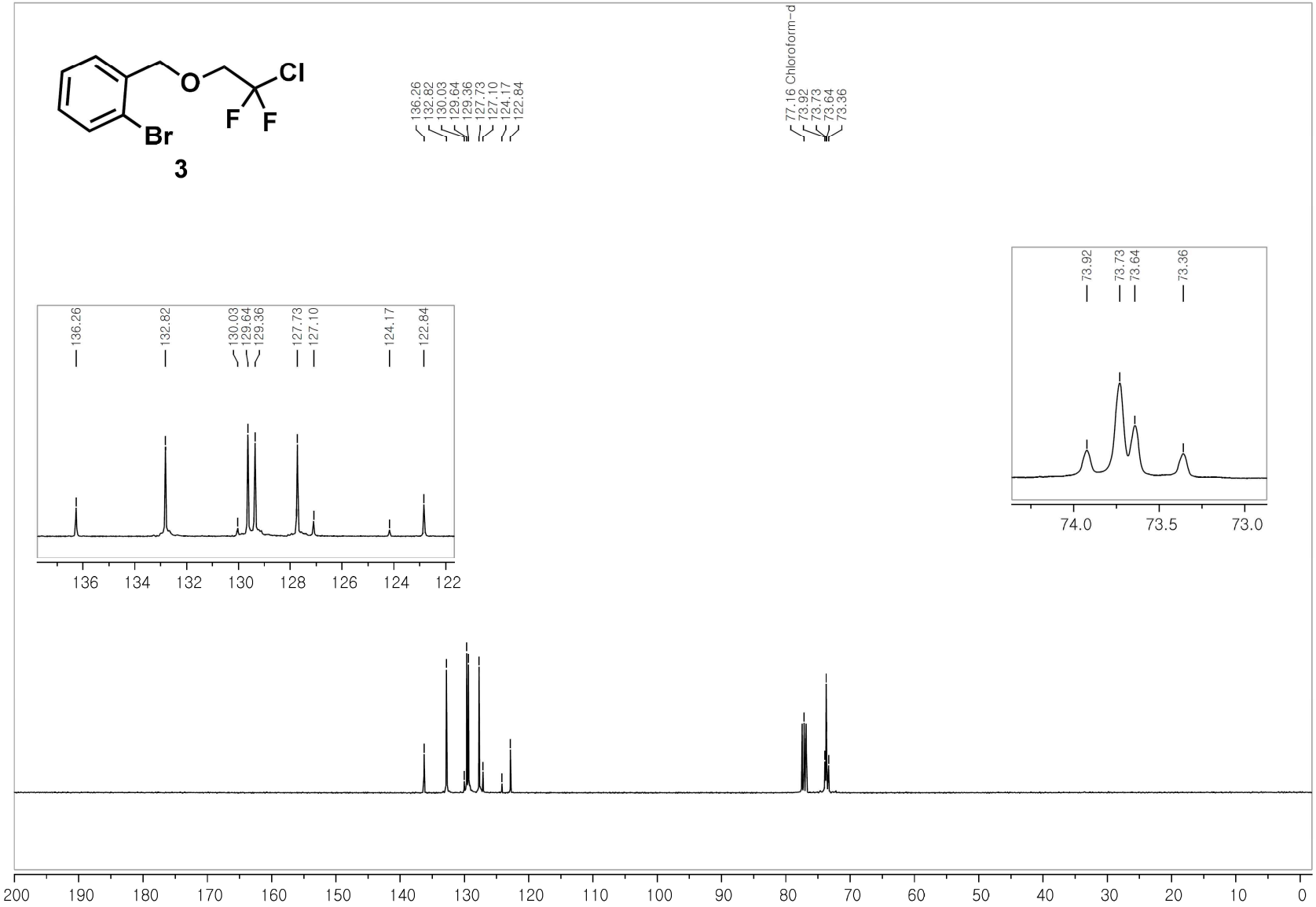
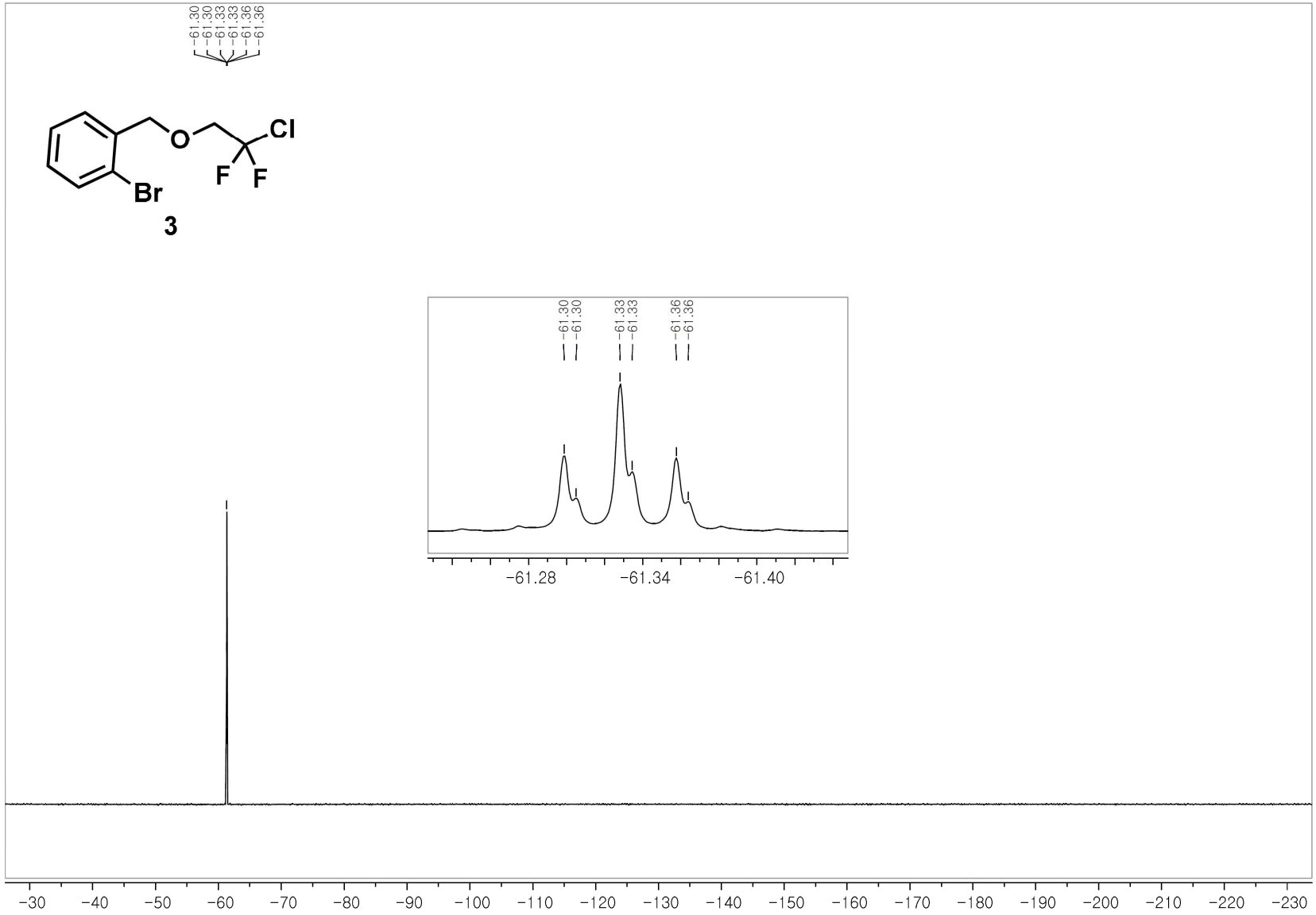
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230


7.58
7.57
7.56
7.55
7.50
7.50
7.49
7.48
7.48
7.37
7.36
7.35
7.35
7.33
7.33
7.26 Chloroform-d
7.21
7.21
7.19
7.19
7.17
7.17
4.80
4.06
4.03
4.01
Cl
O
F
F
Br
3
0.93
0.94
1.00
0.97
2.00
2.00
7.60
7.50
7.40
7.30
7.20
4.10
4.05
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


Br
O
Cl
F
F
3
136.26
132.82
130.03
129.64
129.36
127.73
127.10
124.17
122.84
77.16 Chloroform-d
73.92
73.73
73.64
73.36
136
134
132
130
128
126
124
122
74.0
73.5
73.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


-61.30
-61.30
-61.33
-61.33
-61.36
-61.36
O
Cl
F
F
Br
3
-61.28
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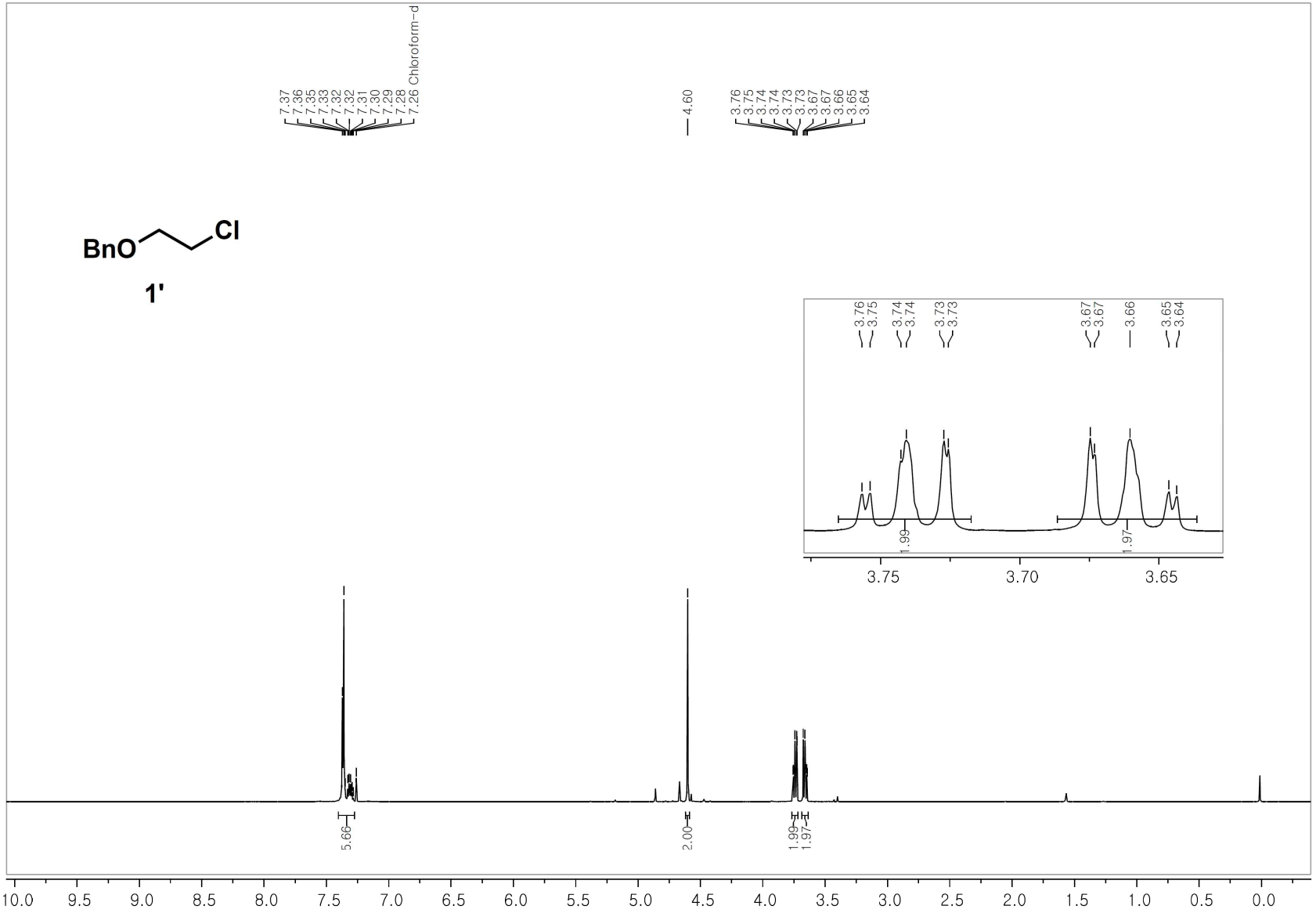
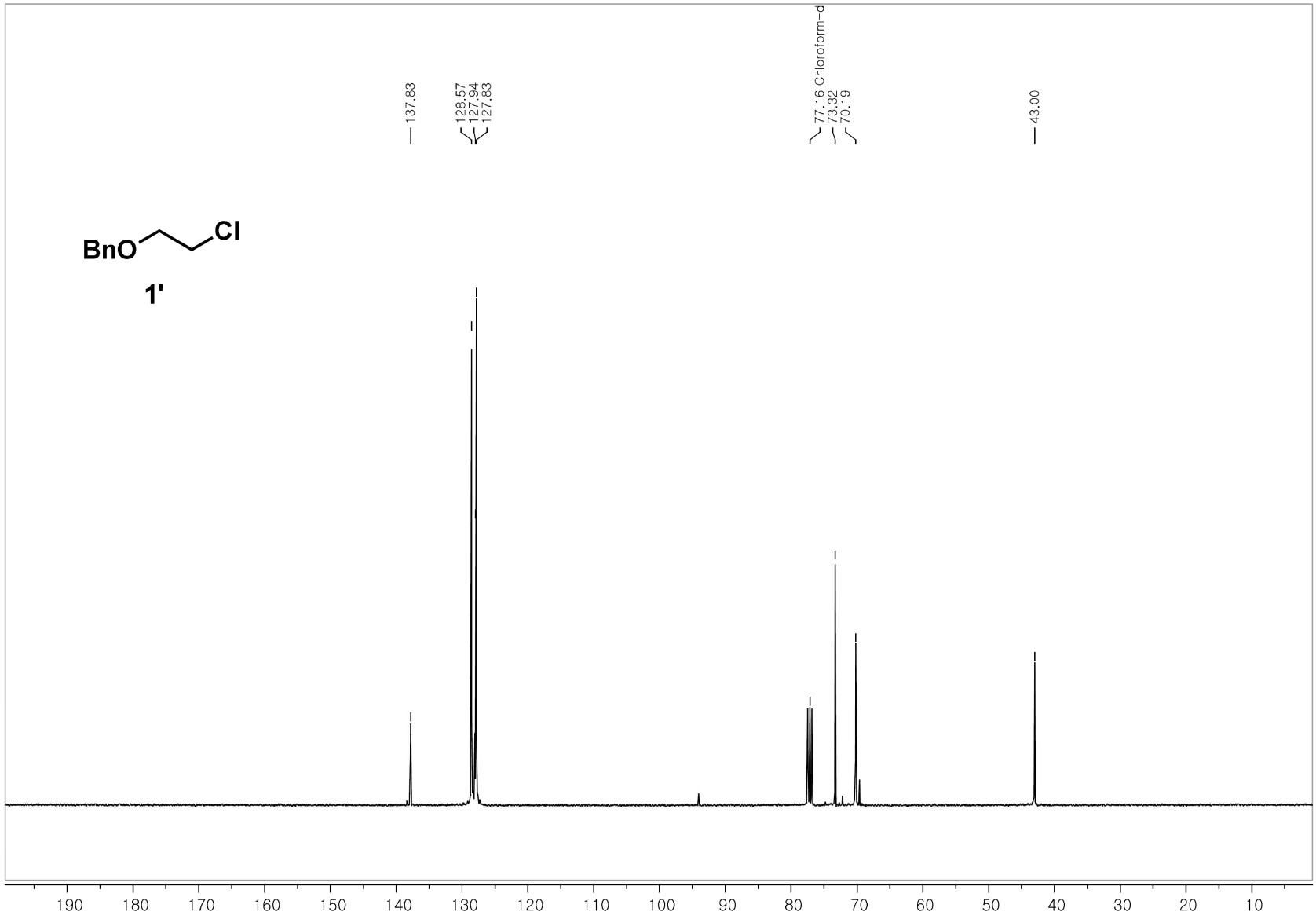
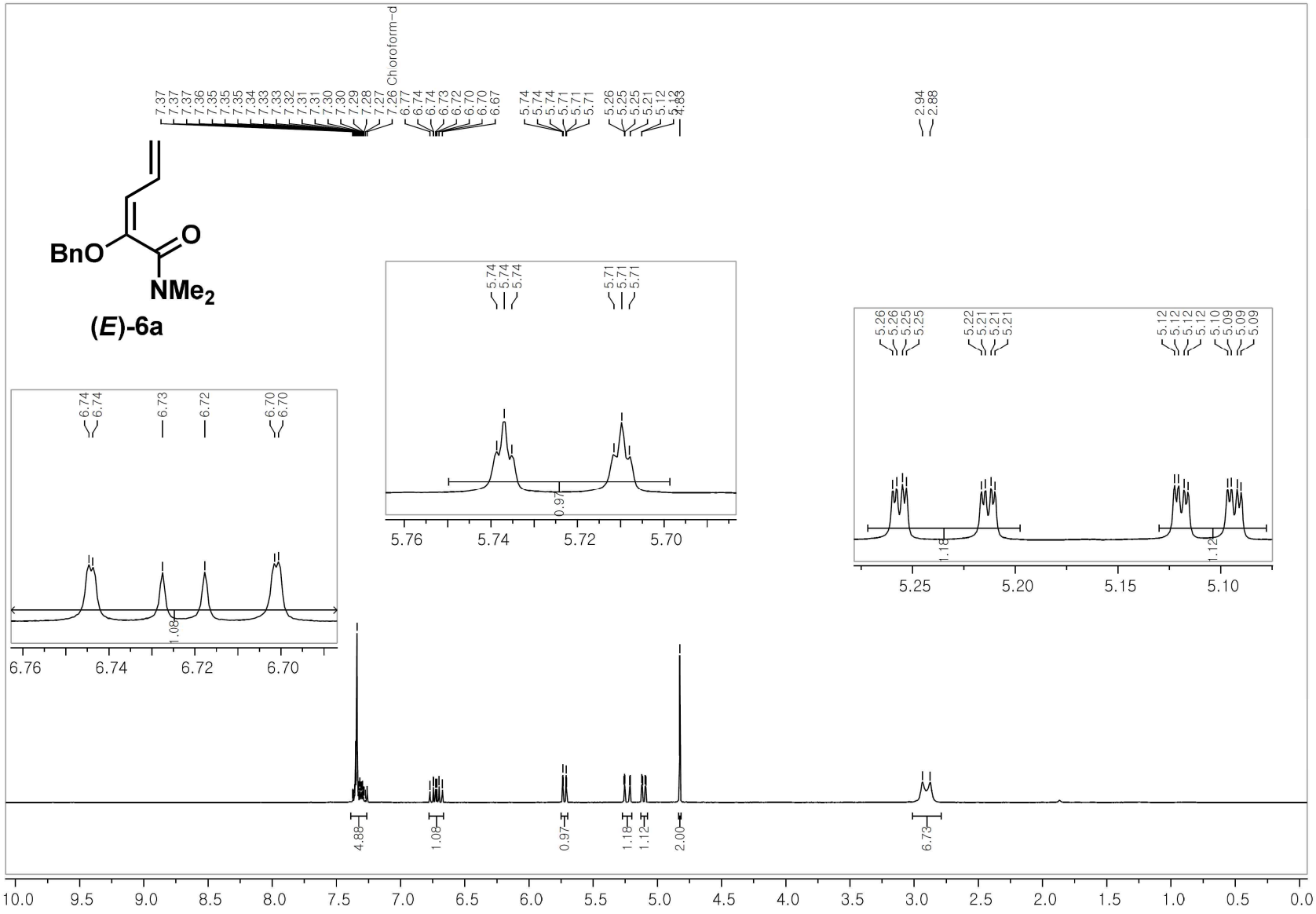
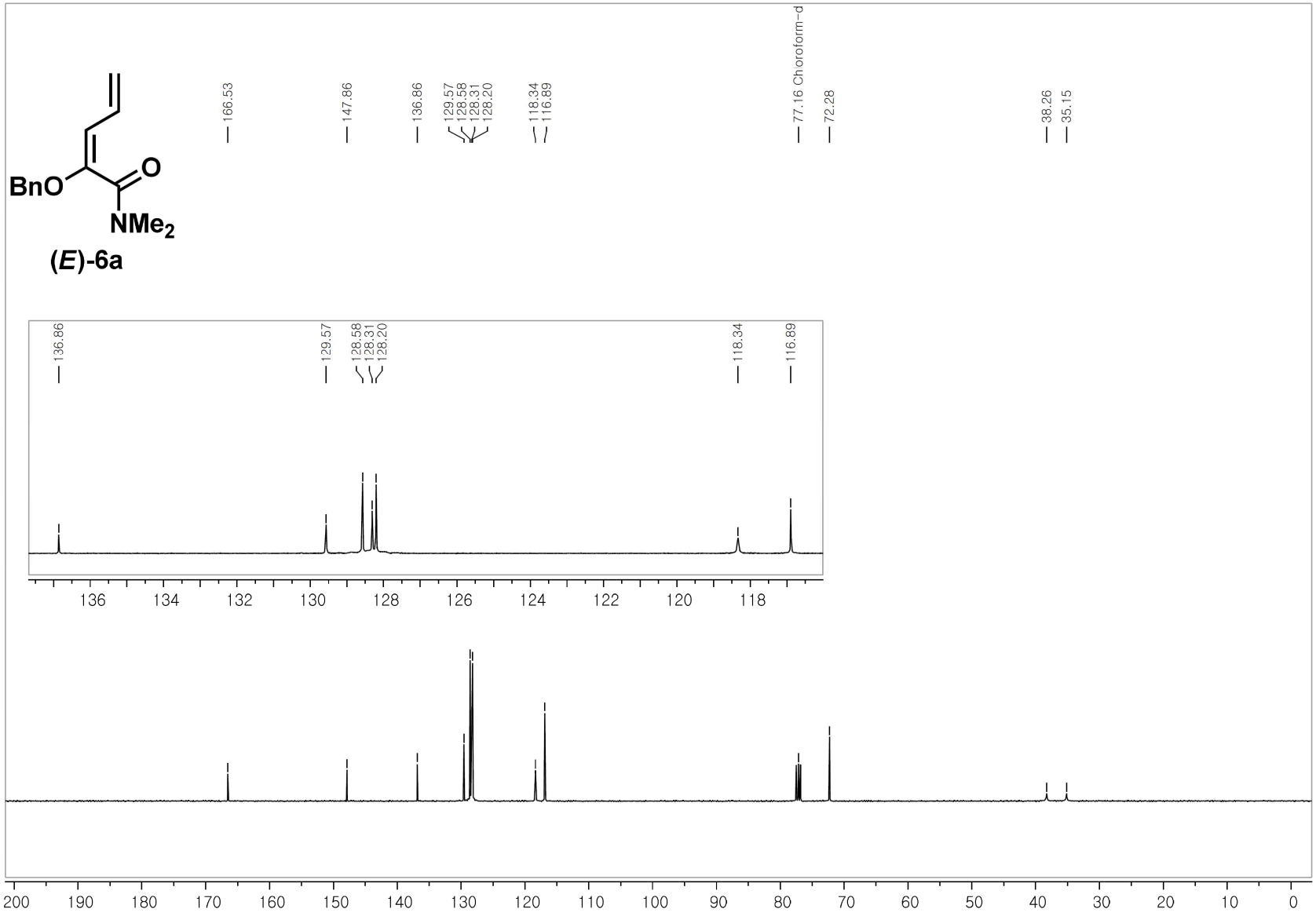
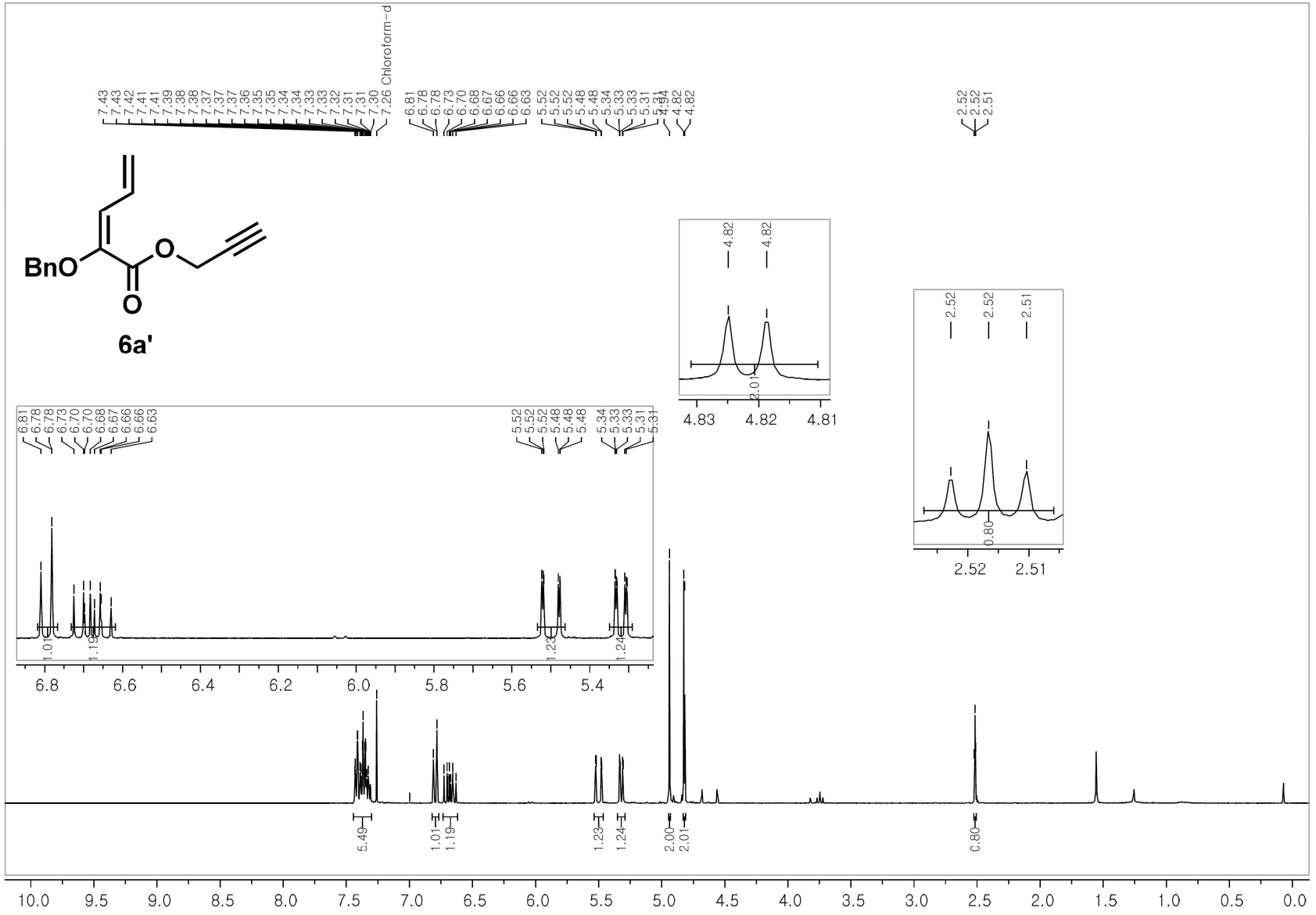
-61.40
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230

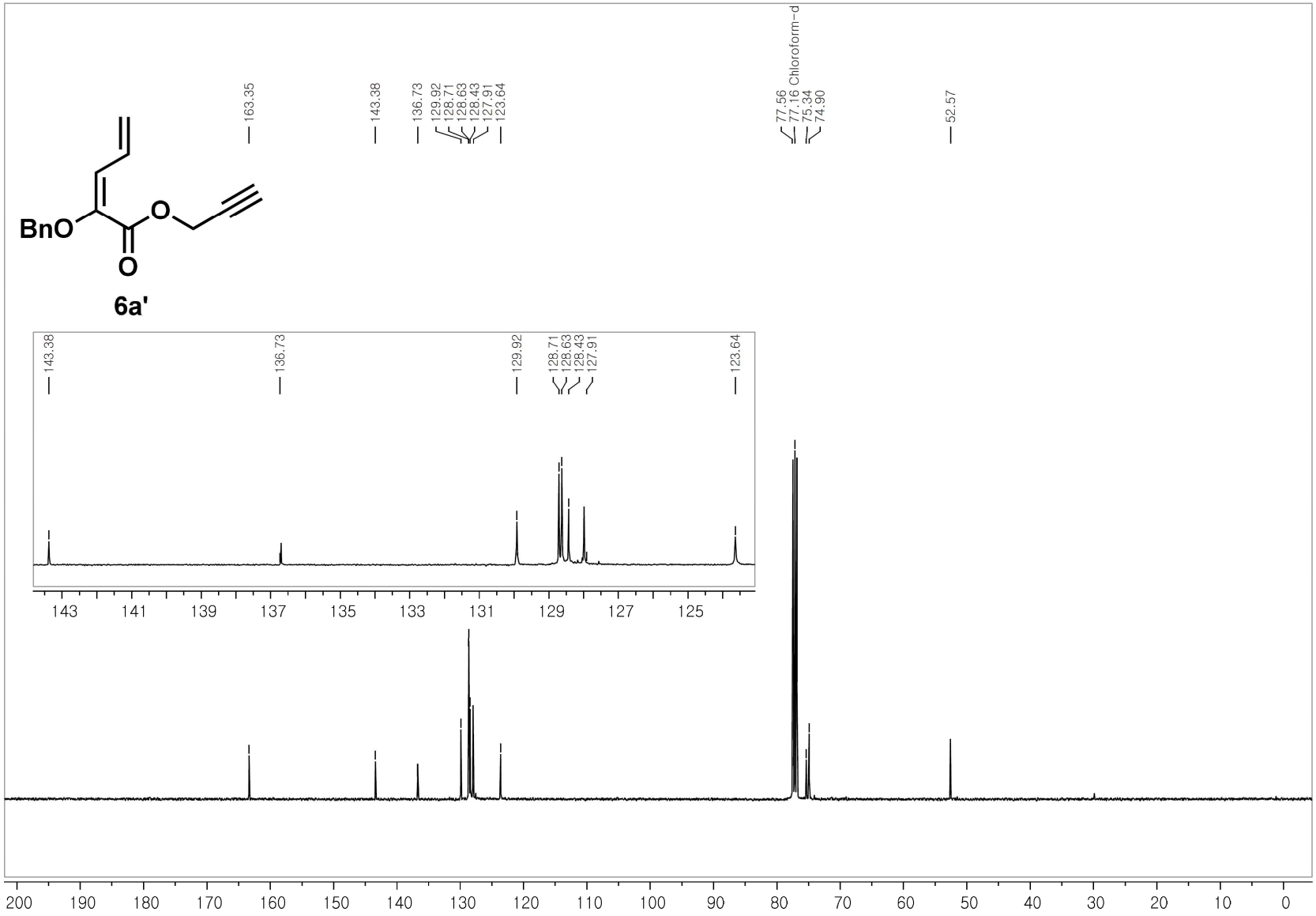

7.37
7.36
7.35
7.33
7.32
7.32
7.31
7.30
7.29
7.28
7.26 Chloroform-d
4.60
3.76
3.75
3.74
3.74
3.73
3.73
3.67
3.67
3.66
3.65
3.64
BnO
Cl
1'
1.99
1.97
3.75
3.70
3.65
5.66
2.00
1.99
1.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

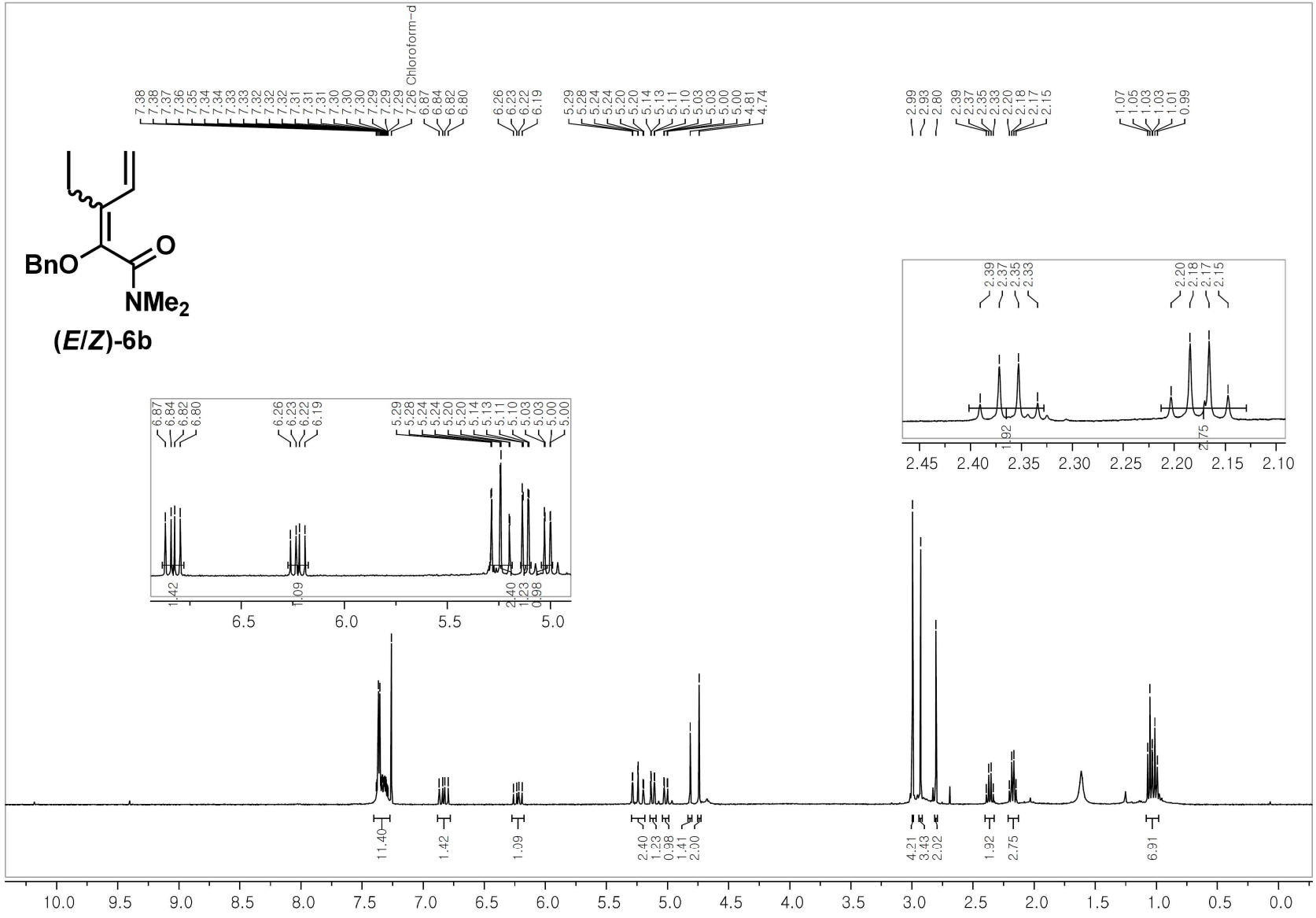

137.83
128.57
127.94
127.83
77.16 Chloroform-d
73.32
70.19
43.00
BnO
Cl
1'
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

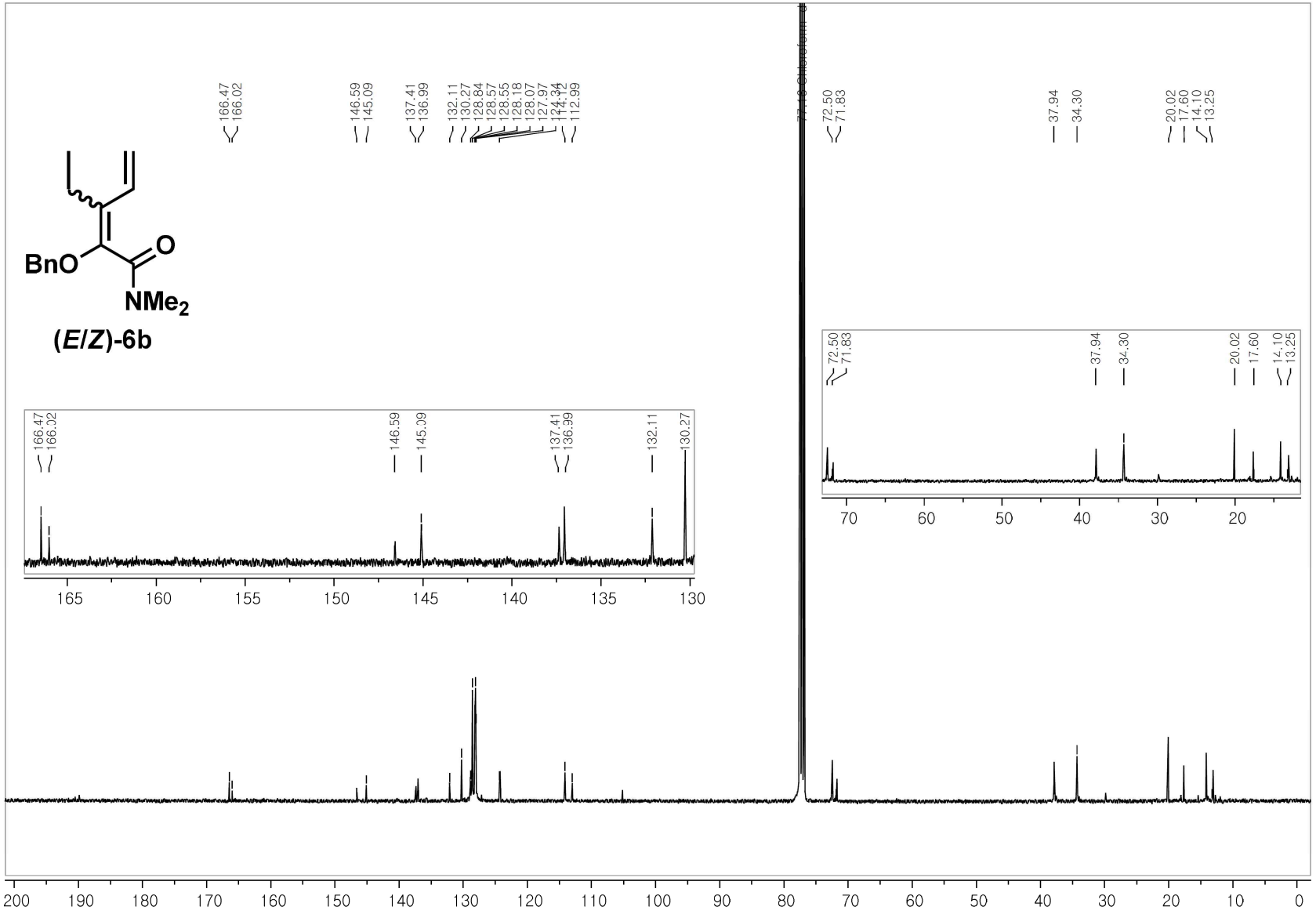

(E)-6a
BnO
O
NMe2
Choroform-d
4.88
1.08
0.97
1.18
1.12
2.00
6.73

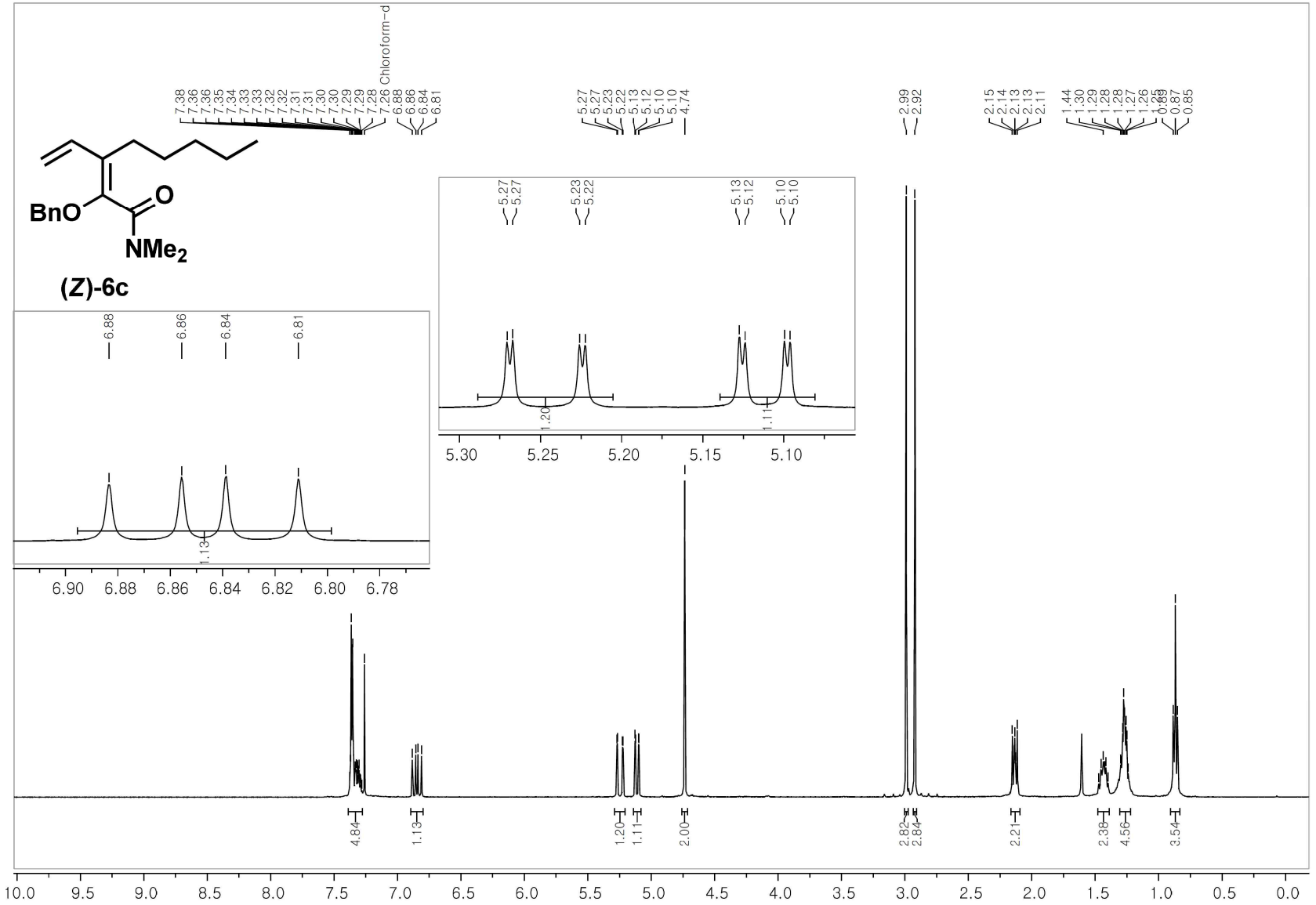

BnO
O
NMe2
(E)-6a
166.53
147.86
136.86
129.57
128.58
128.31
128.20
118.34
116.89
77.16 Chloroform-d
72.28
38.26
35.15
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
136
134
132
130
128
126
124
122
120
118

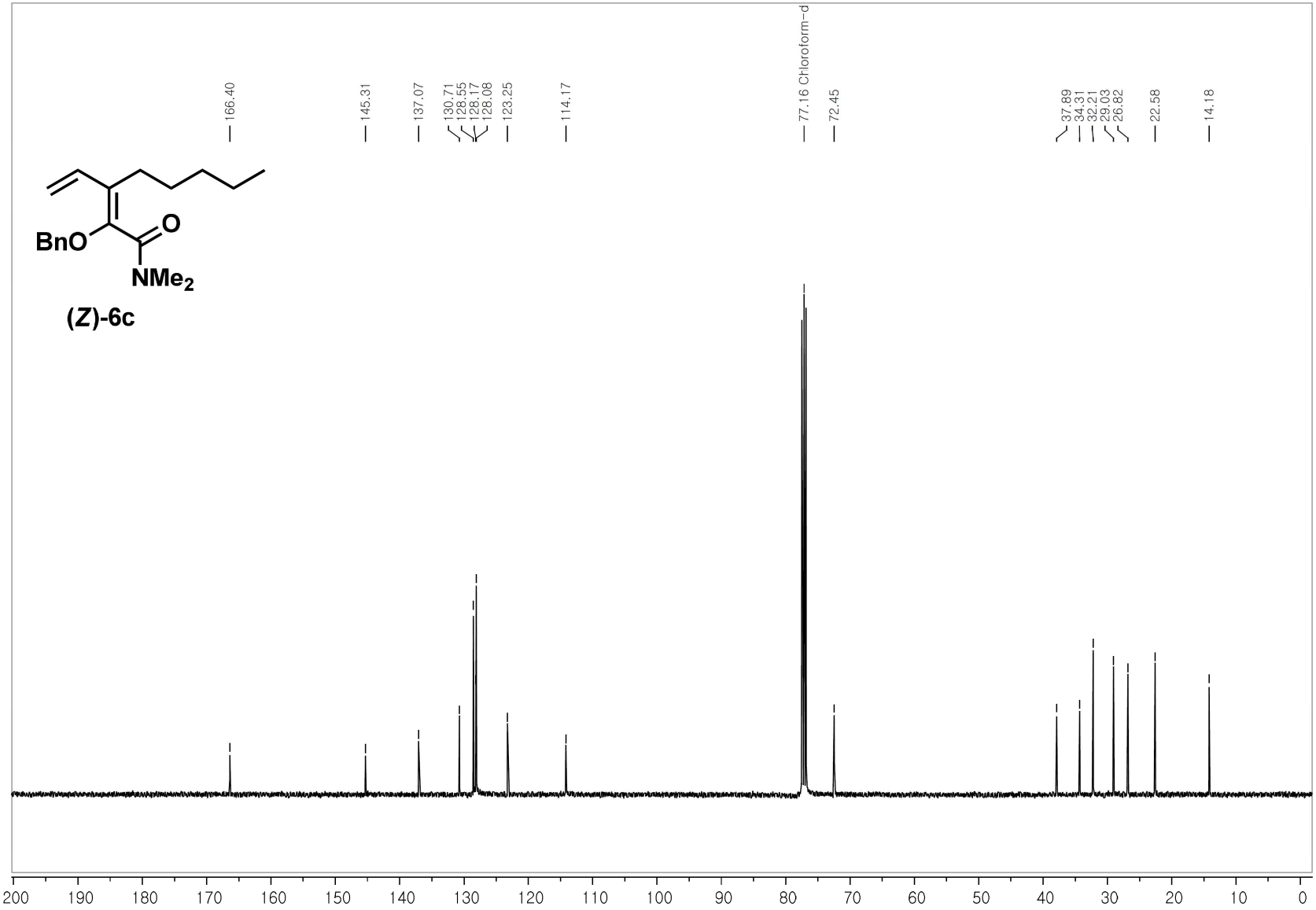

Chloroform-d
BnO
O
O
6a'

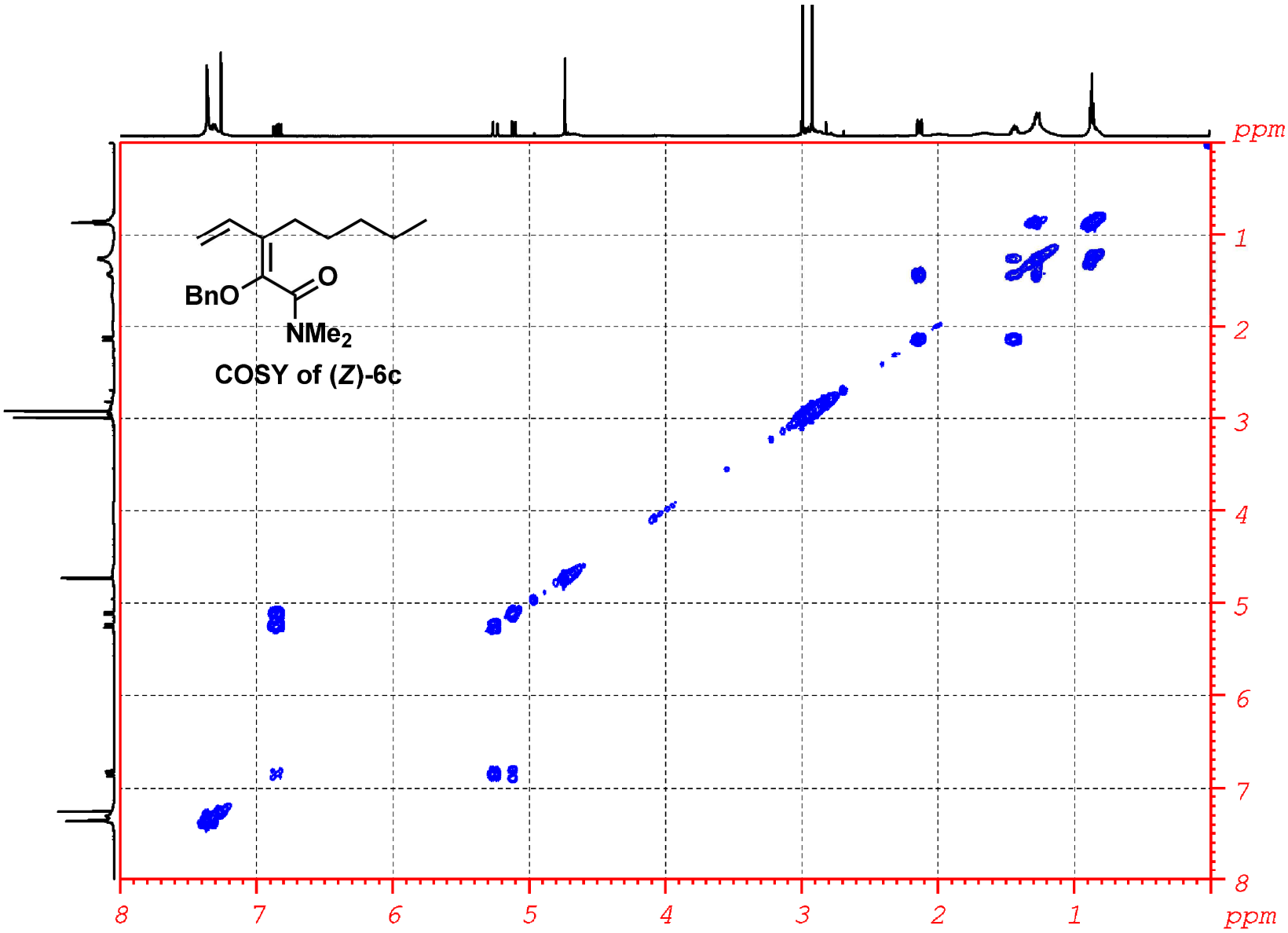

BnO
O
O
6a'
163.35
143.38
136.73
129.92
128.71
128.63
128.43
127.91
123.64
77.56
77.16 Chloroform-d
75.34
74.90
52.57
143
141
139
137
135
133
131
129
127
125
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


BnO
O
NMe2
(E/Z)-6b
Chloroform-d


BnO
O
NMe2
(E/Z)-6b
166.47
166.02
146.59
145.09
137.41
136.99
132.11
130.27
128.84
128.57
128.55
128.18
128.07
127.97
112.99
72.50
71.83
37.94
34.30
20.02
17.60
14.10
13.25


BnO
O
NMe2
(Z)-6c
Chloroform-d


166.40
145.31
137.07
130.71
128.55
128.17
128.08
123.25
114.17
77.16 Chloroform-d
72.45
37.89
34.31
32.21
29.03
26.82
22.58
14.18
BnO
O
NMe2
(Z)-6c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


BnO
O
NMe2
COSY of (Z)-6c
ppm
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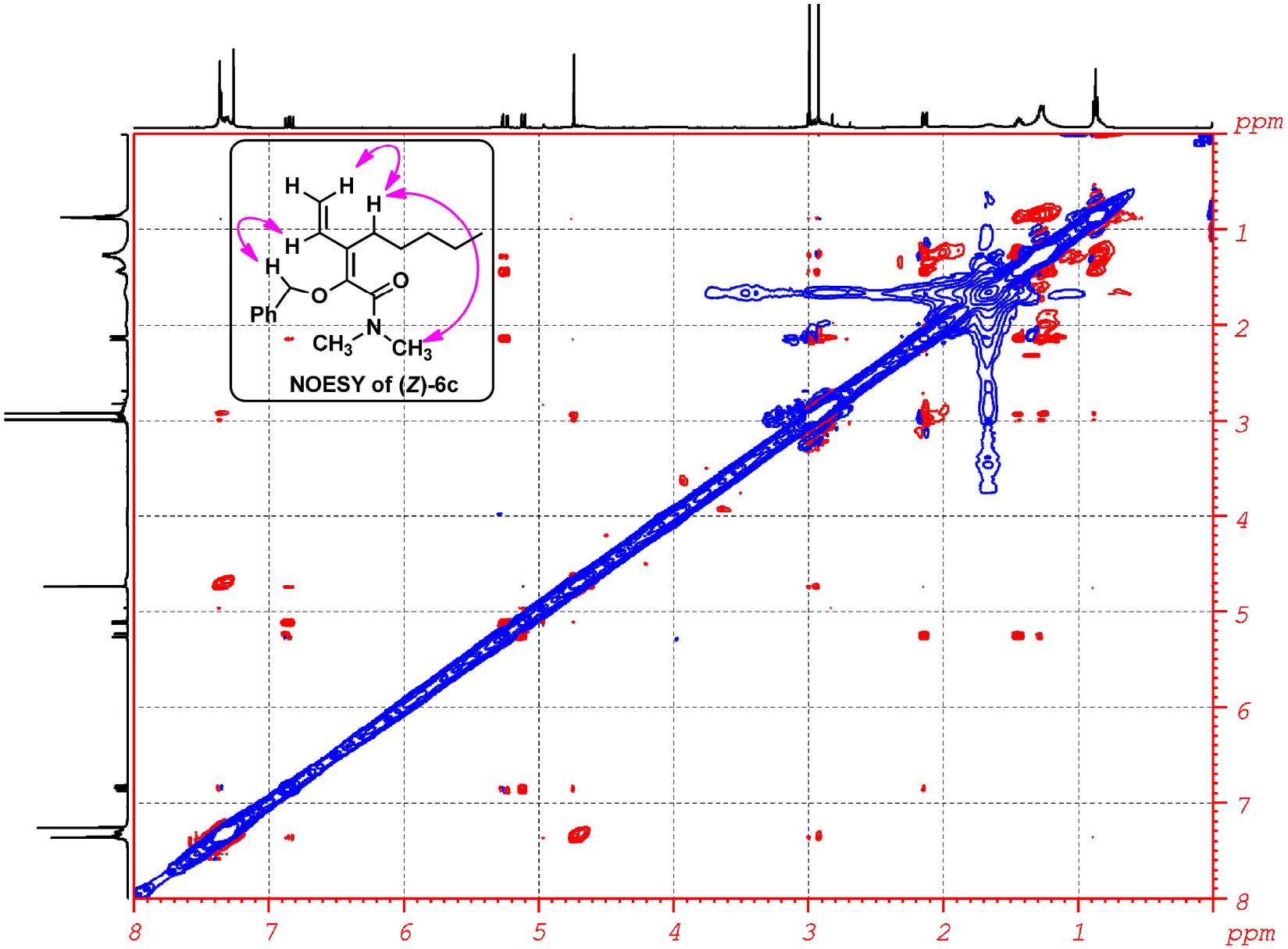
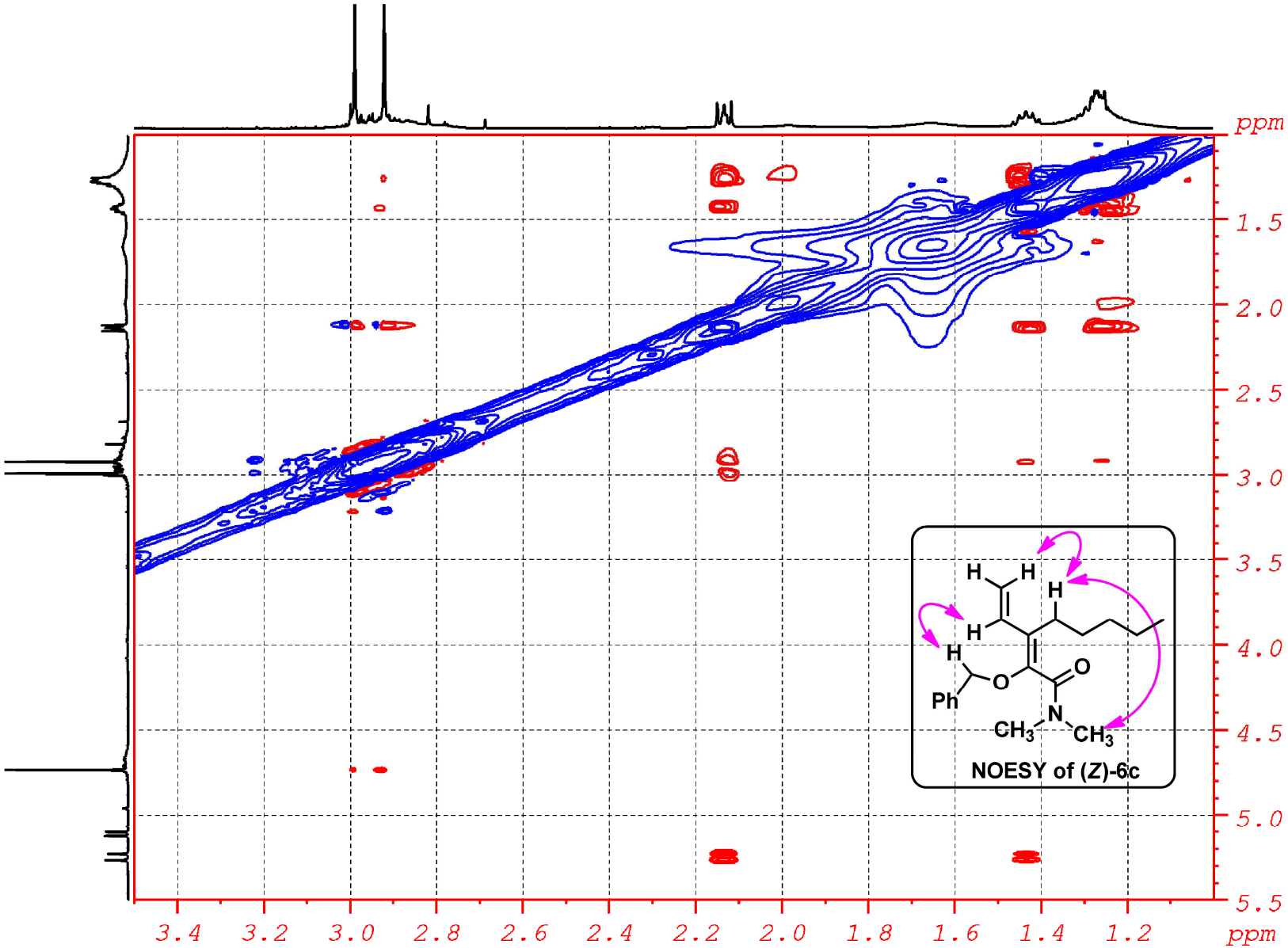
2
3
4
5
6
7
8
8
7
6
5
4
3
2
1
ppm


ppm
1
2
3
4
5
6
7
8
8
7
6
5
4
3
2
1
ppm
H
H
H
H
H
O
O
Ph
N
CH3
CH3
NOESY of (Z)-6c


ppm
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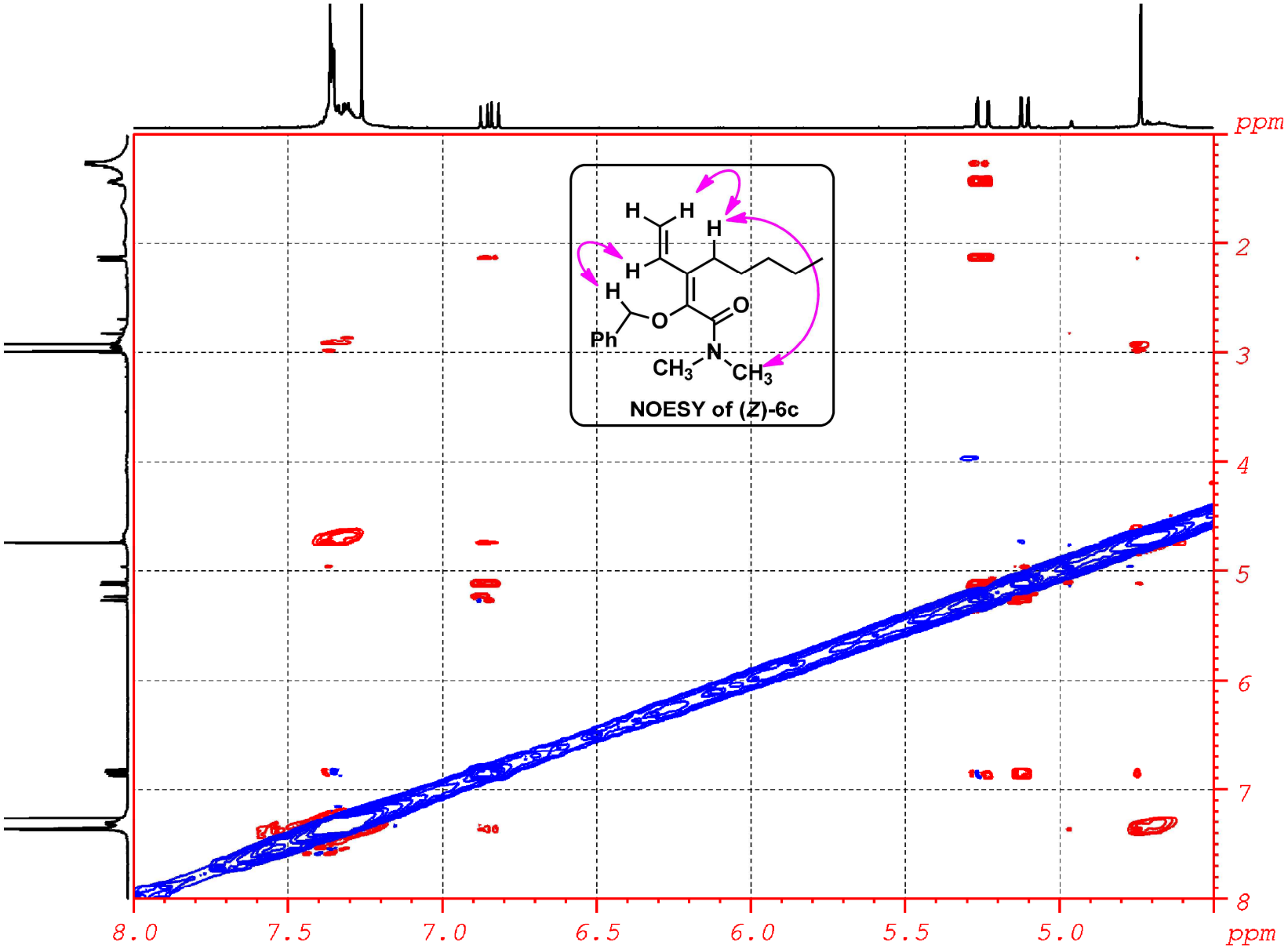
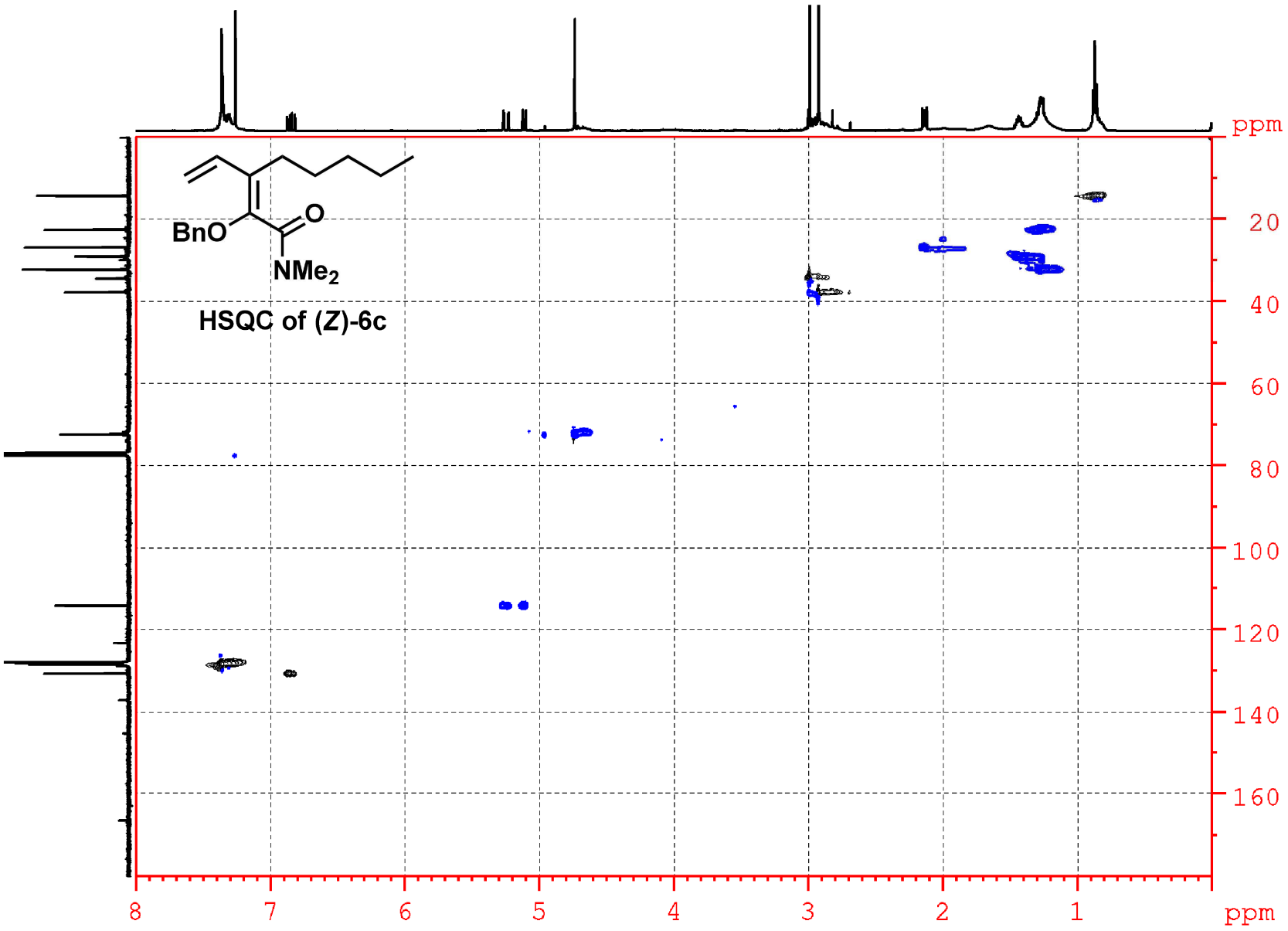
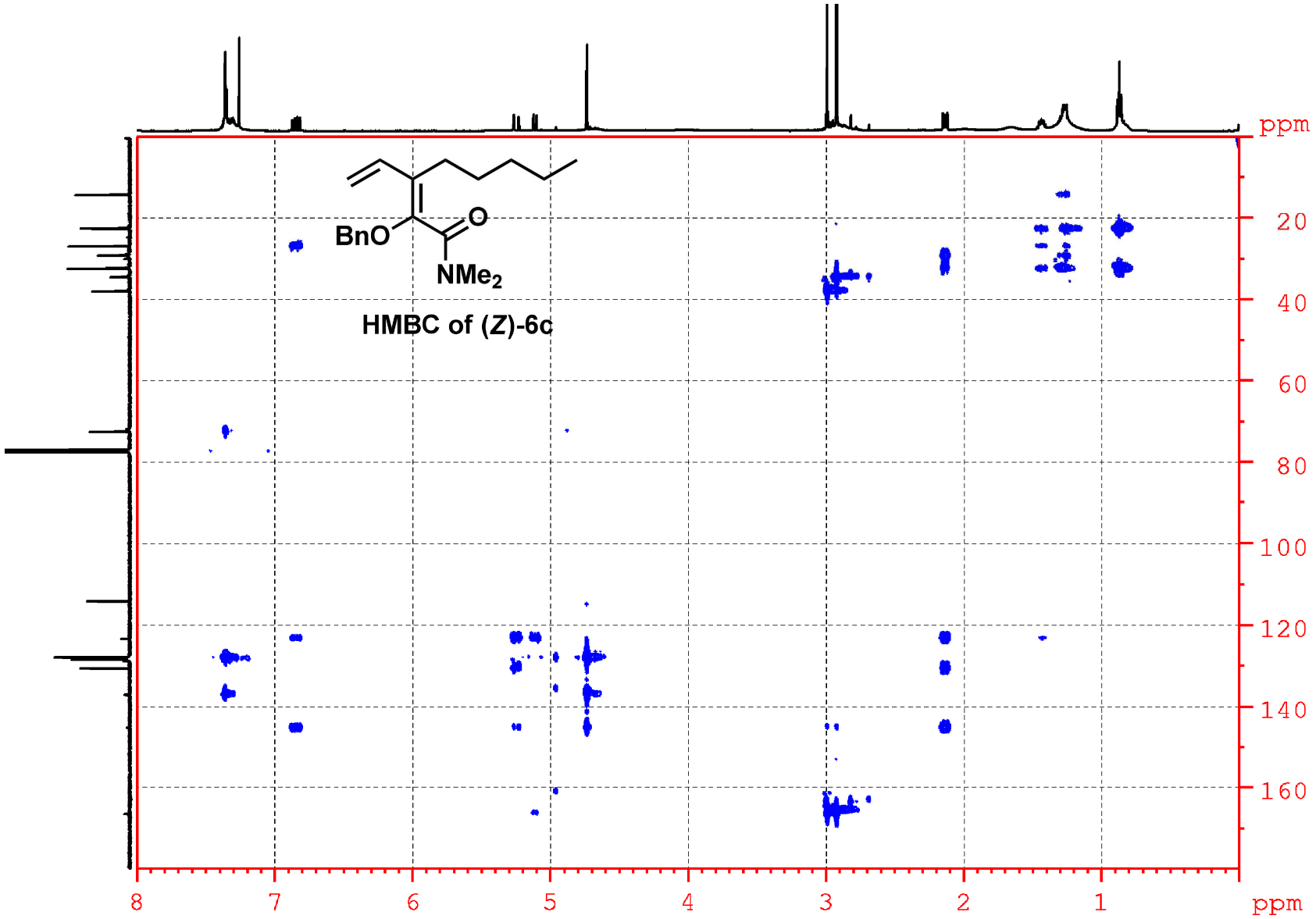
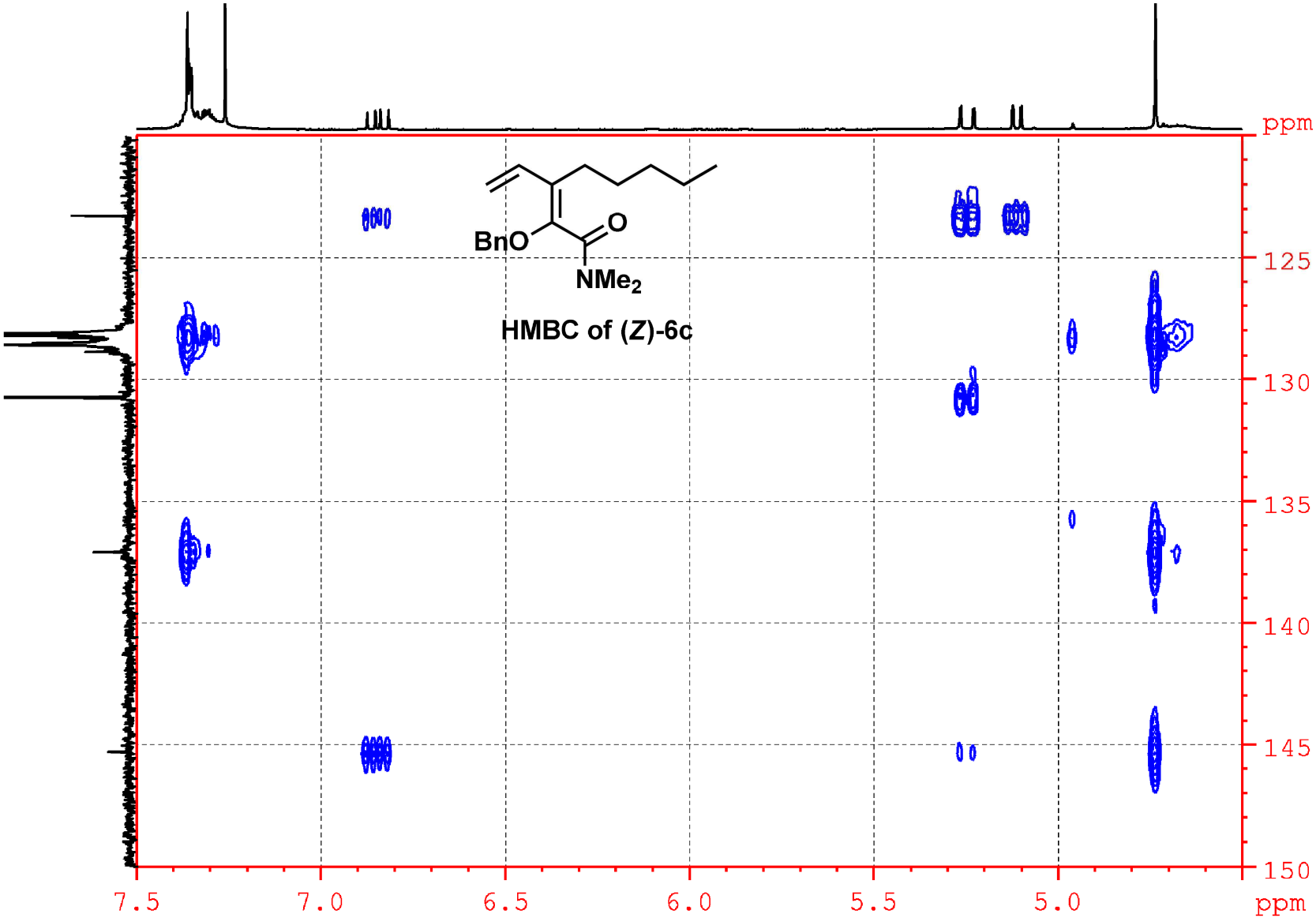
2.5
3.0
3.5
4.0
4.5
5.0
5.5
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
ppm
H
H
H
H
H
O
O
Ph
N
CH3
CH3
NOESY of (Z)-6c


ppm
2
3
4
5
6
7
8
8.0
7.5
7.0
6.5
6.0
5.5
5.0
ppm
H
H
H
H
H
O
O
Ph
N
CH3
CH3
NOESY of (Z)-6c


BnO
O
NMe2
HSQC of (Z)-6c
ppm
20
40
60
80
100
120
140
160
8
7
6
5
4
3
2
1
ppm


BnO
O
NMe2
HMBC of (Z)-6c
ppm
20
40
60
80
100
120
140
160
8
7
6
5
4
3
2
1
ppm


BnO
O
NMe2
HMBC of (Z)-6c
ppm
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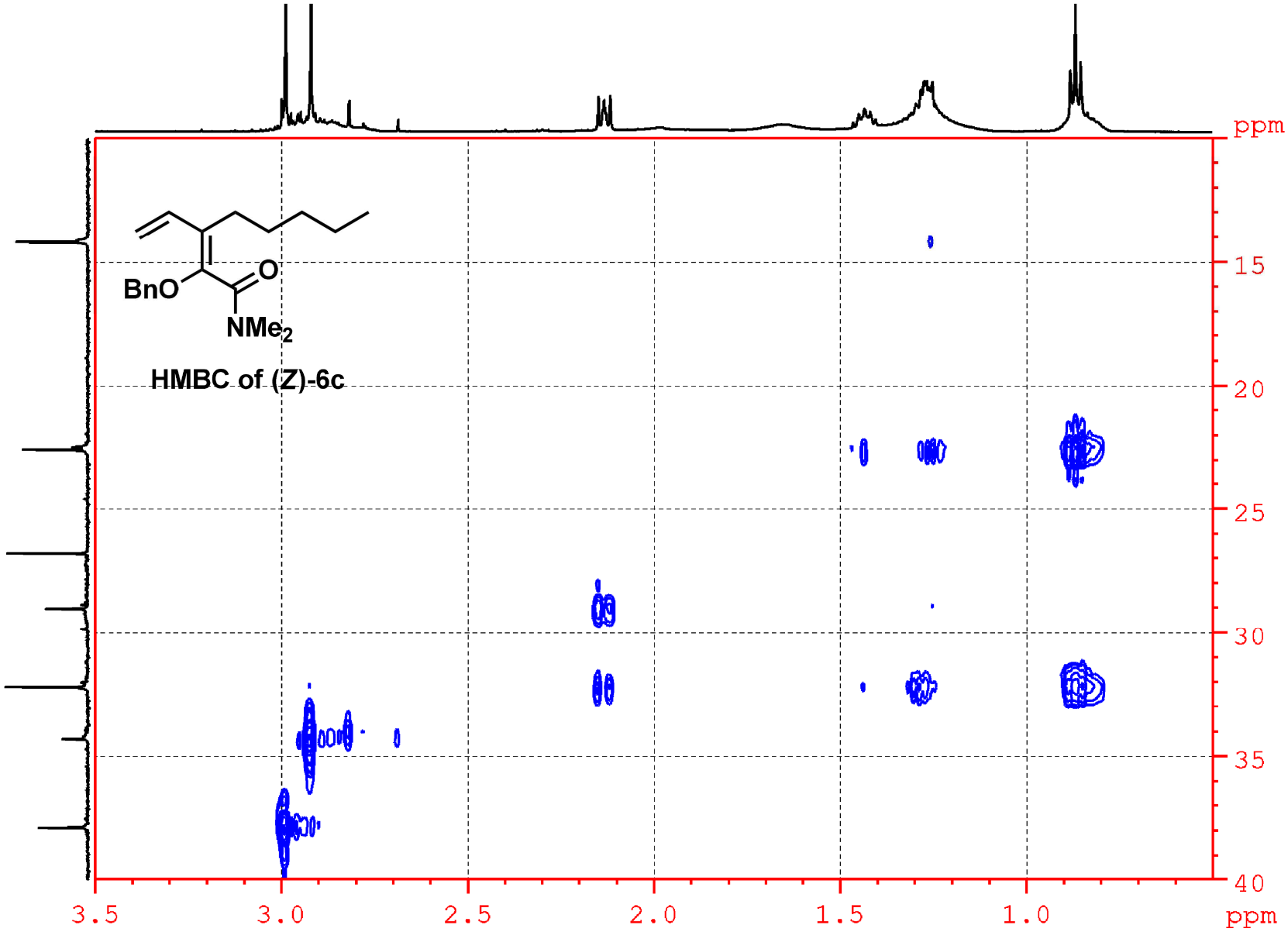
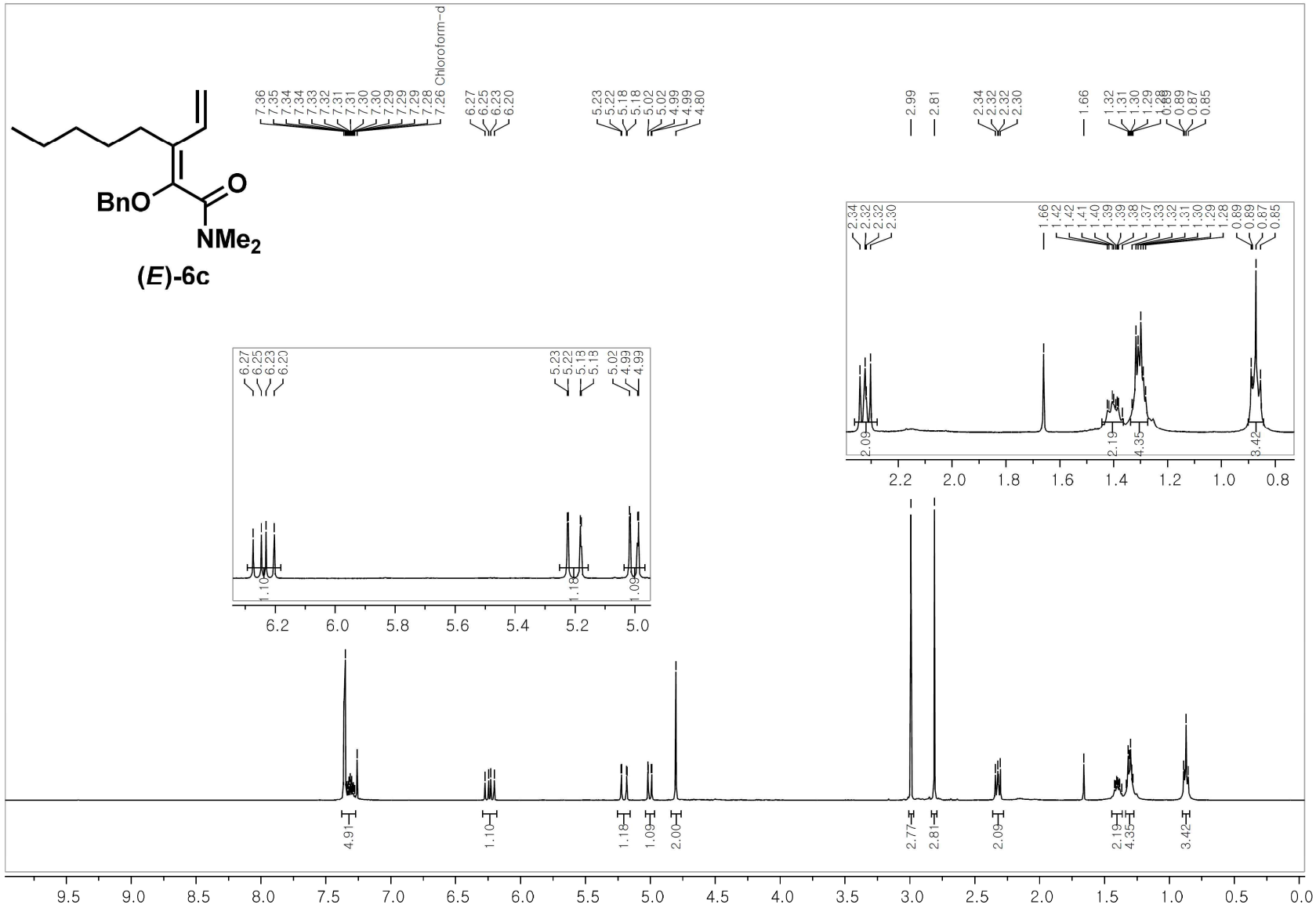
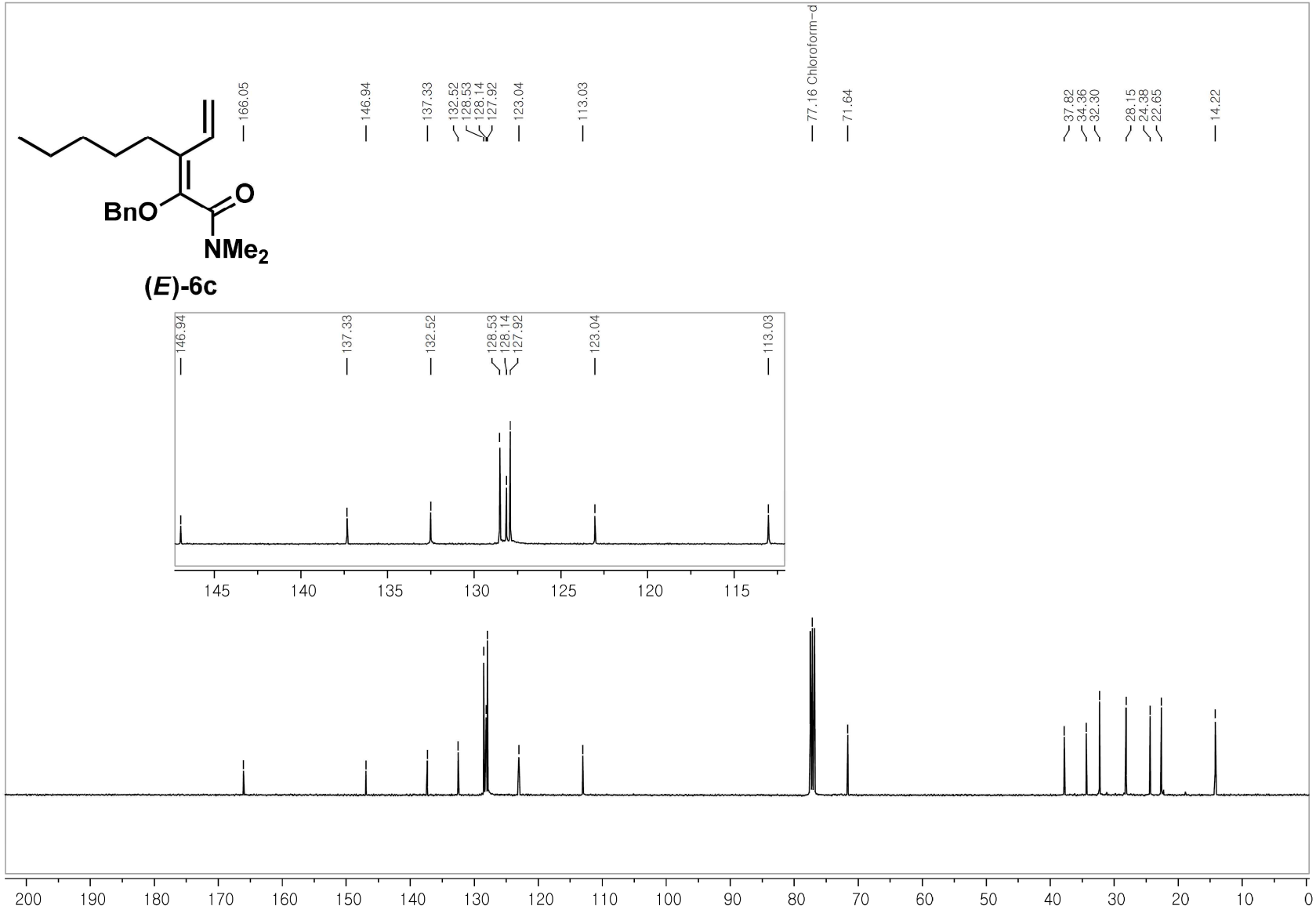
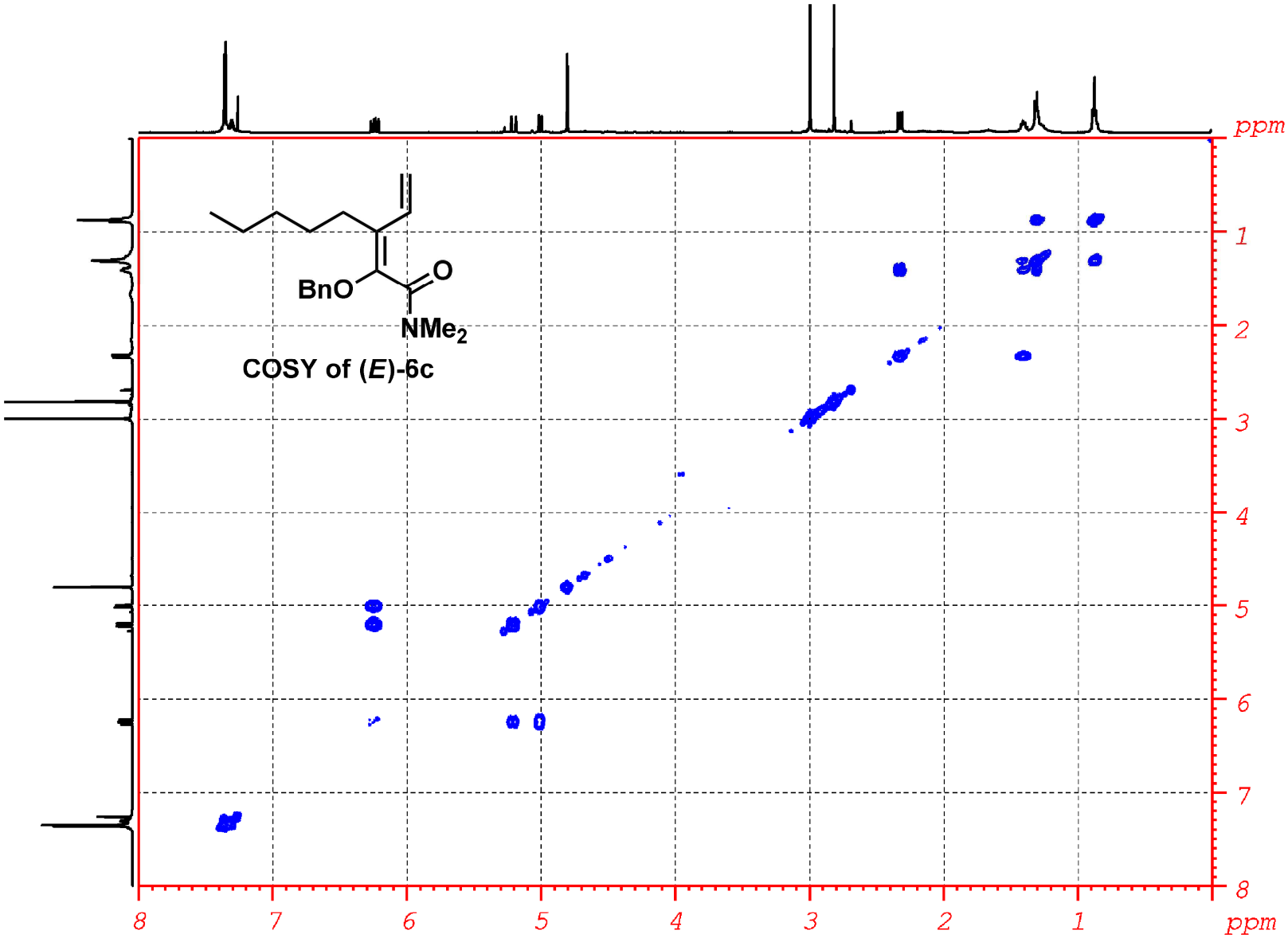
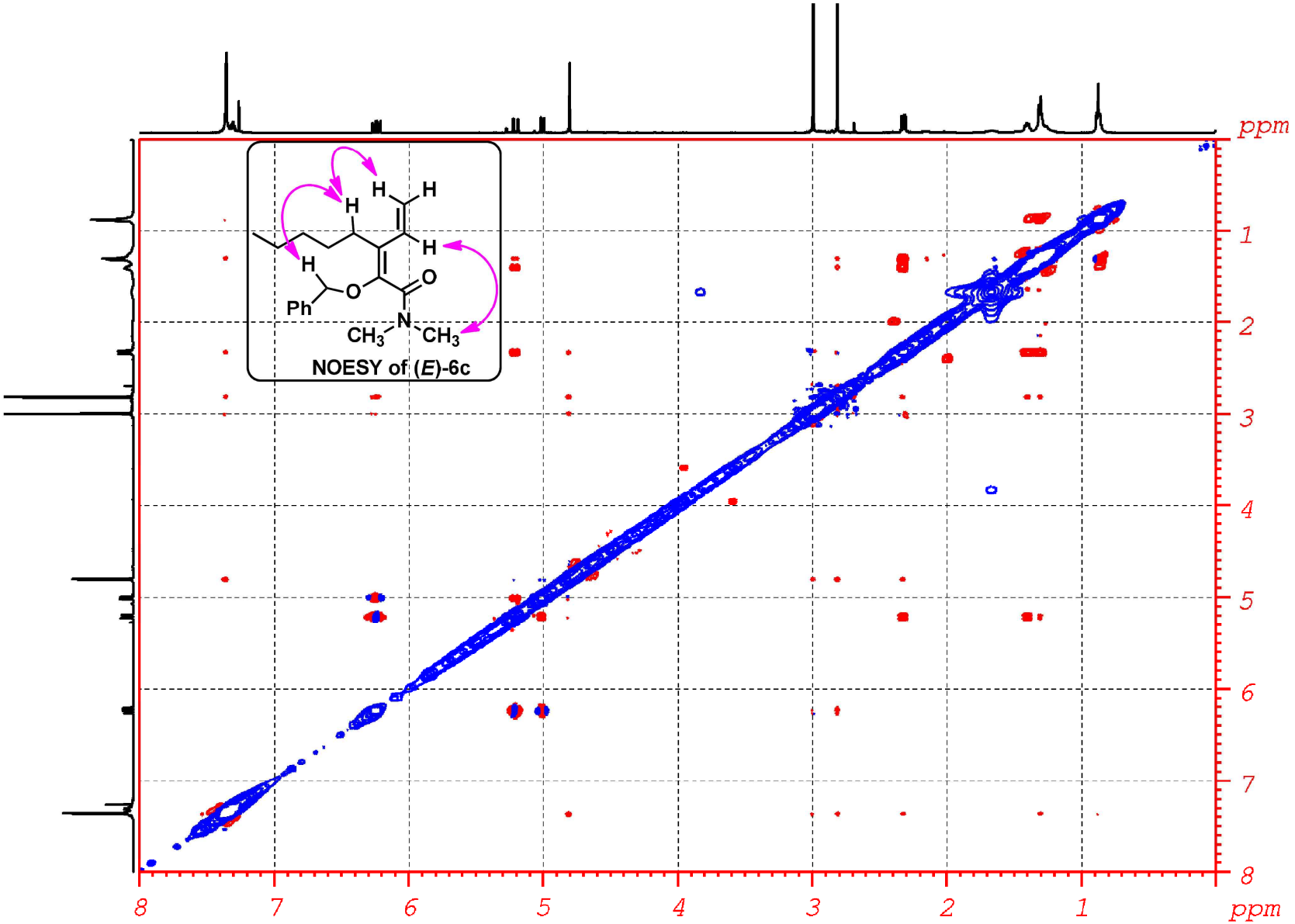
130
135
140
145
150
7.5
7.0
6.5
6.0
5.5
5.0
ppm

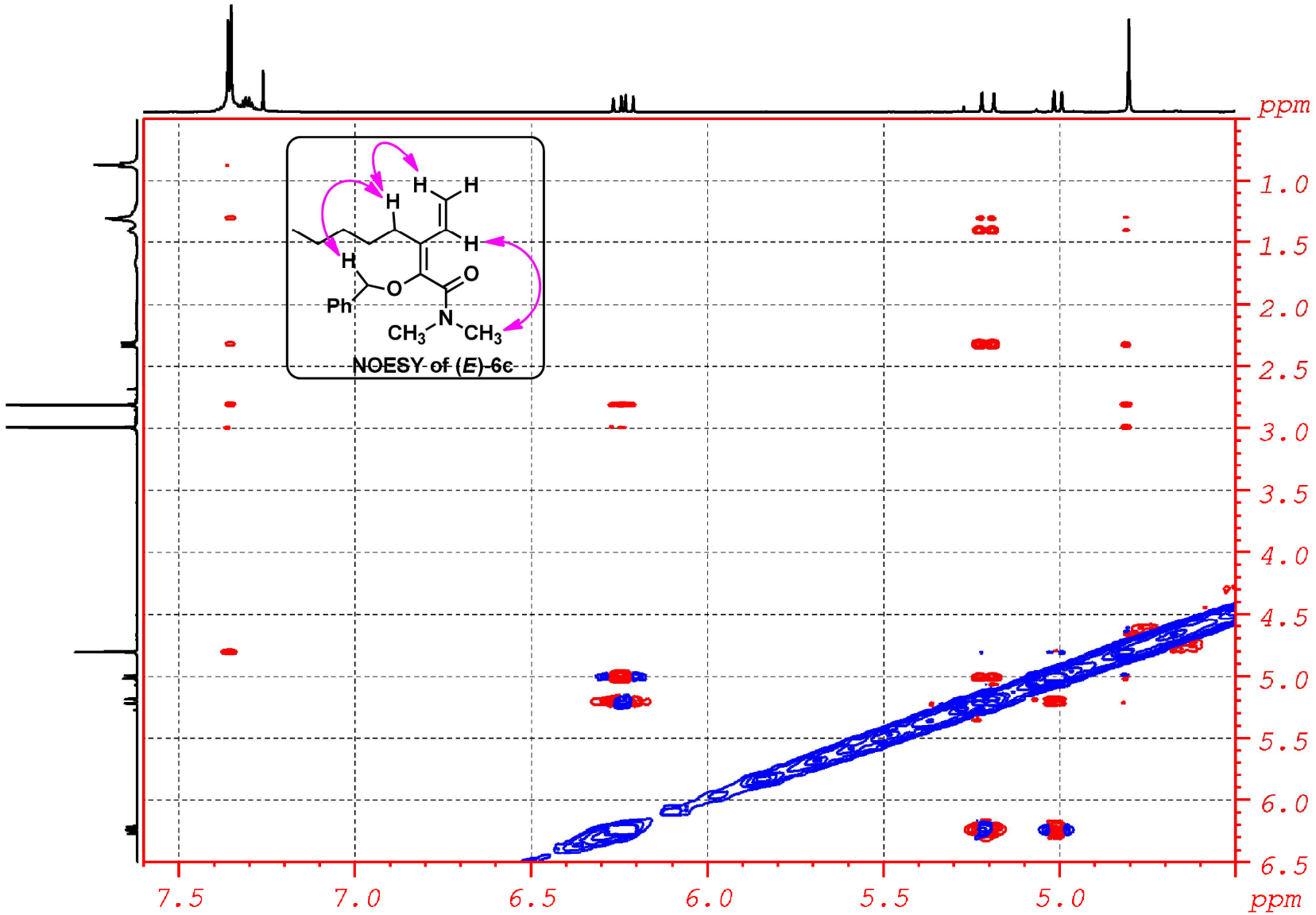

BnO
O
NMe2
HMBC of (Z)-6c
ppm
15
20
25
30
35
40
3.5
3.0
2.5
2.0
1.5
1.0
ppm

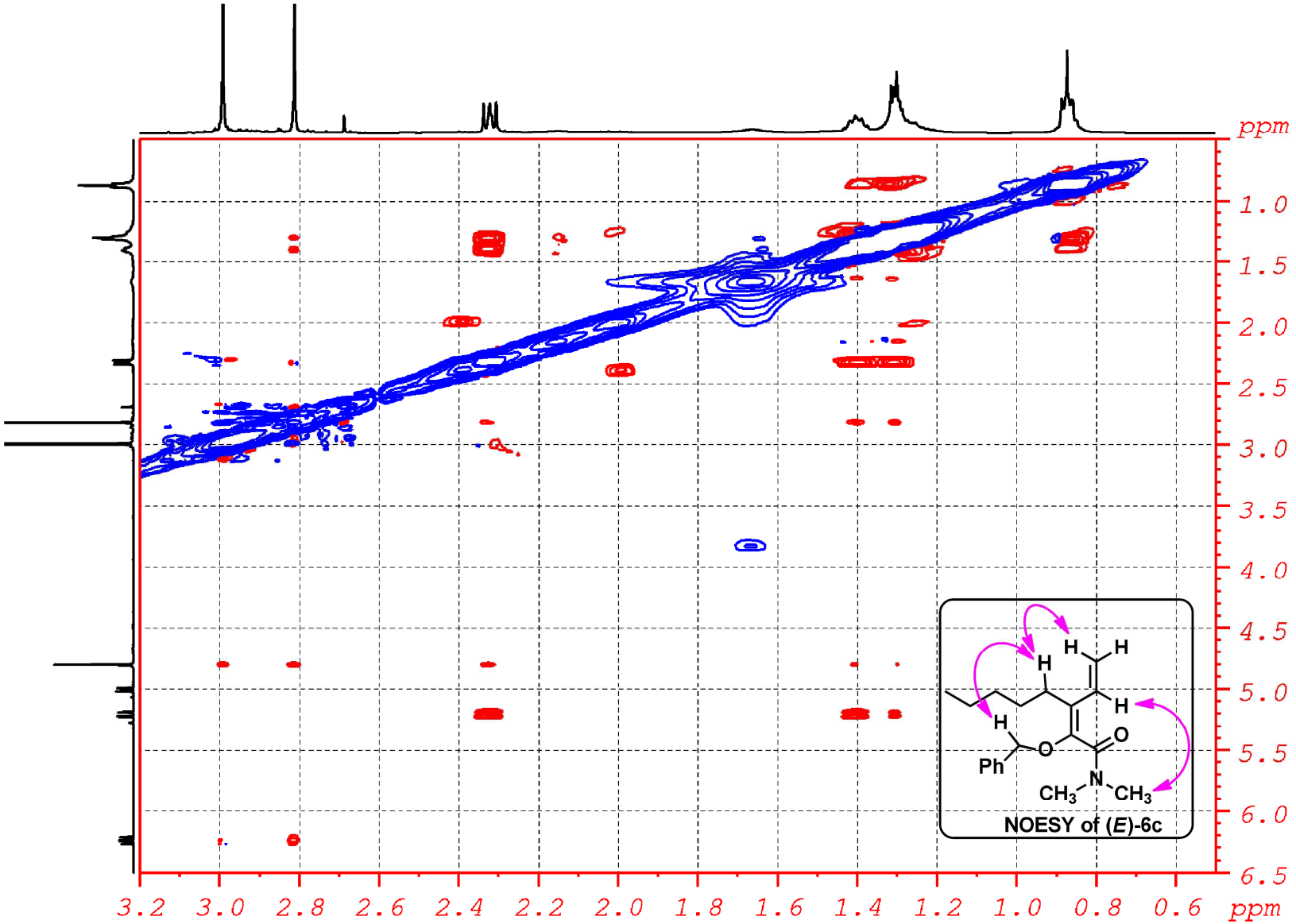

BnO
O
NMe2
(E)-6c
Chloroform-d

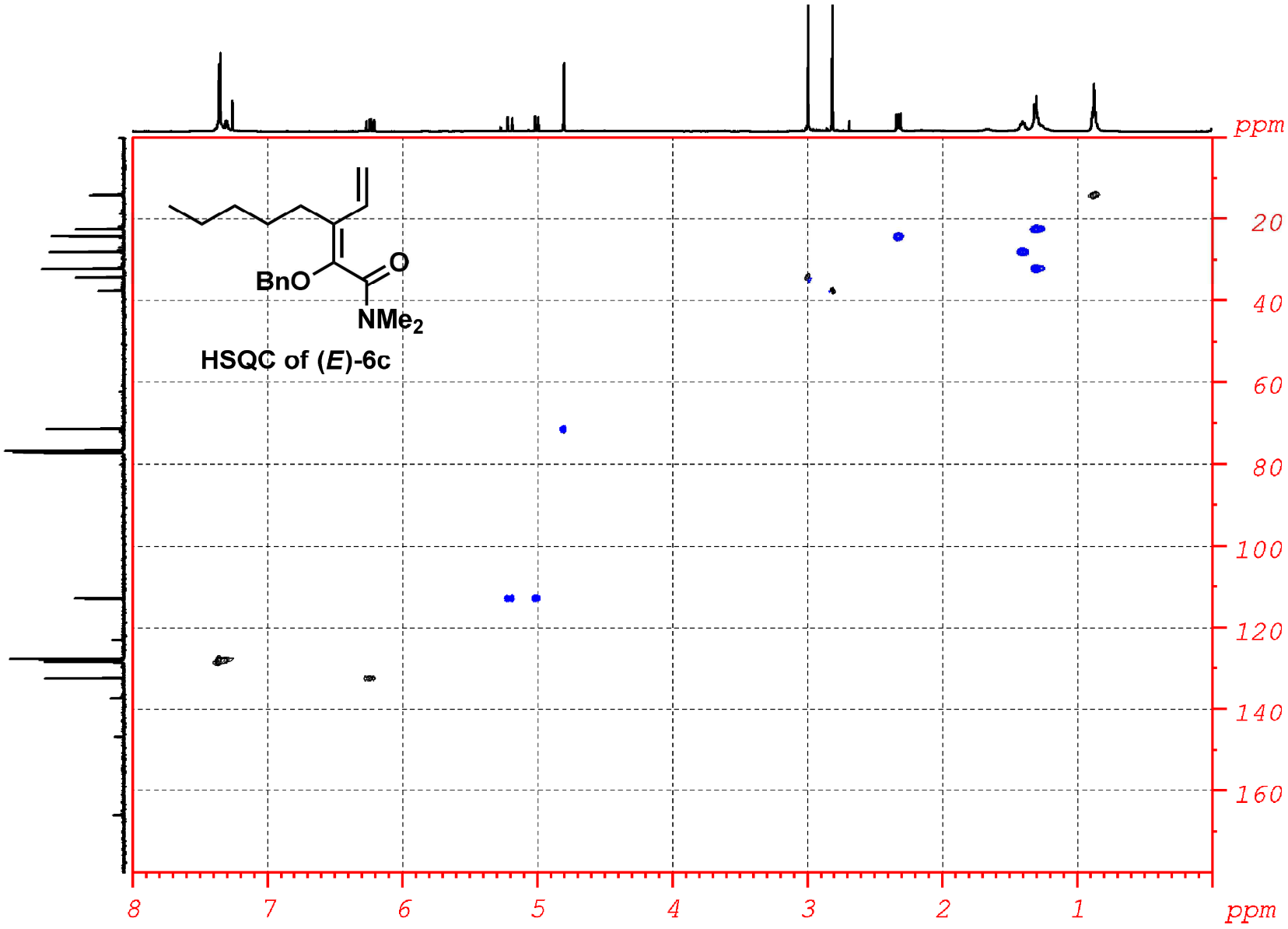

166.05
146.94
137.33
132.52
128.53
128.14
127.92
123.04
113.03
77.16 Chloroform-d
71.64
37.82
34.36
32.30
28.15
24.38
22.65
14.22
BnO
O
NMe2
(E)-6c

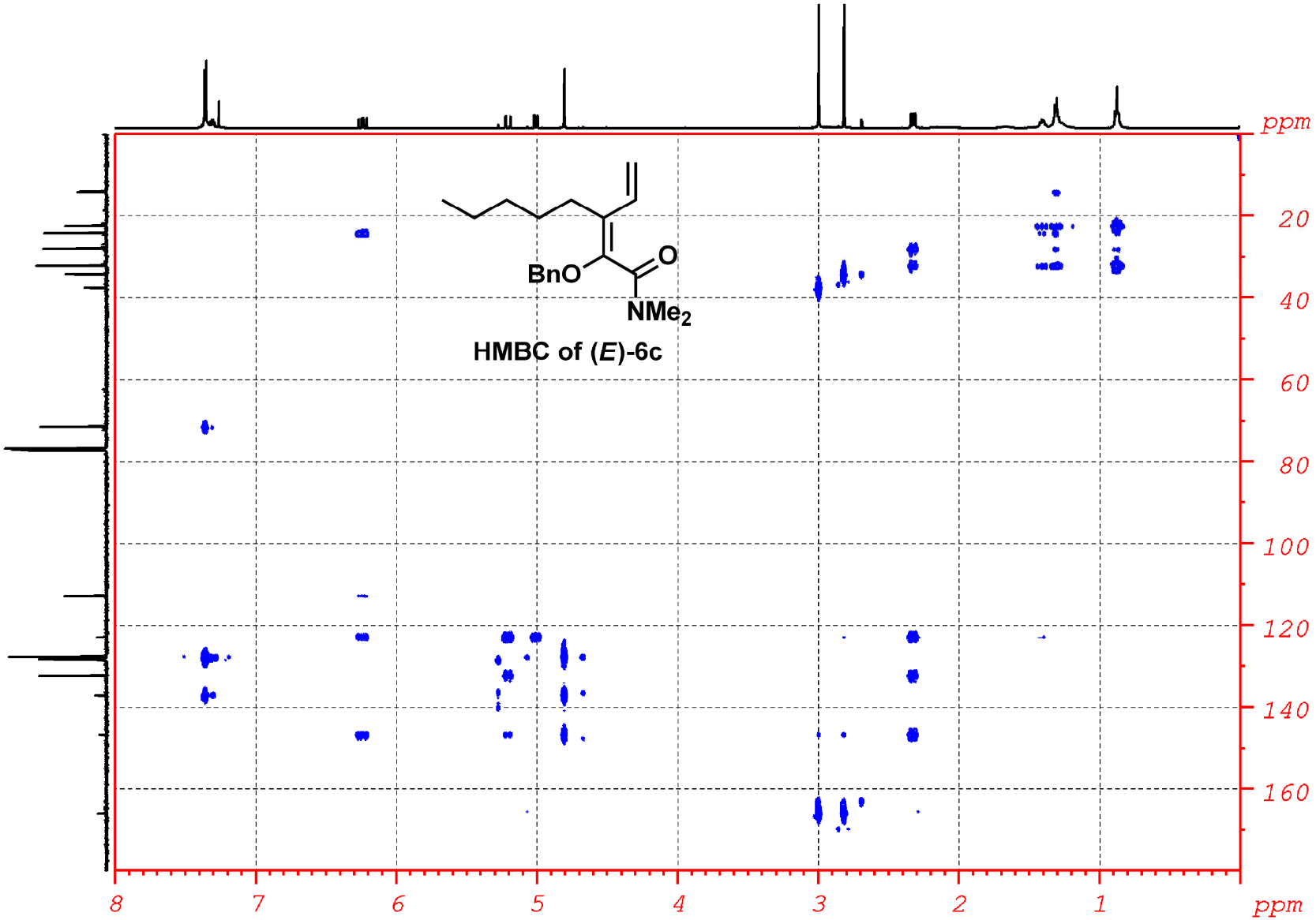

BnO
O
NMe2
COSY of (E)-6c
ppm
1
2
3
4
5
6
7
8
8
7
6
5
4
3
2
1
ppm

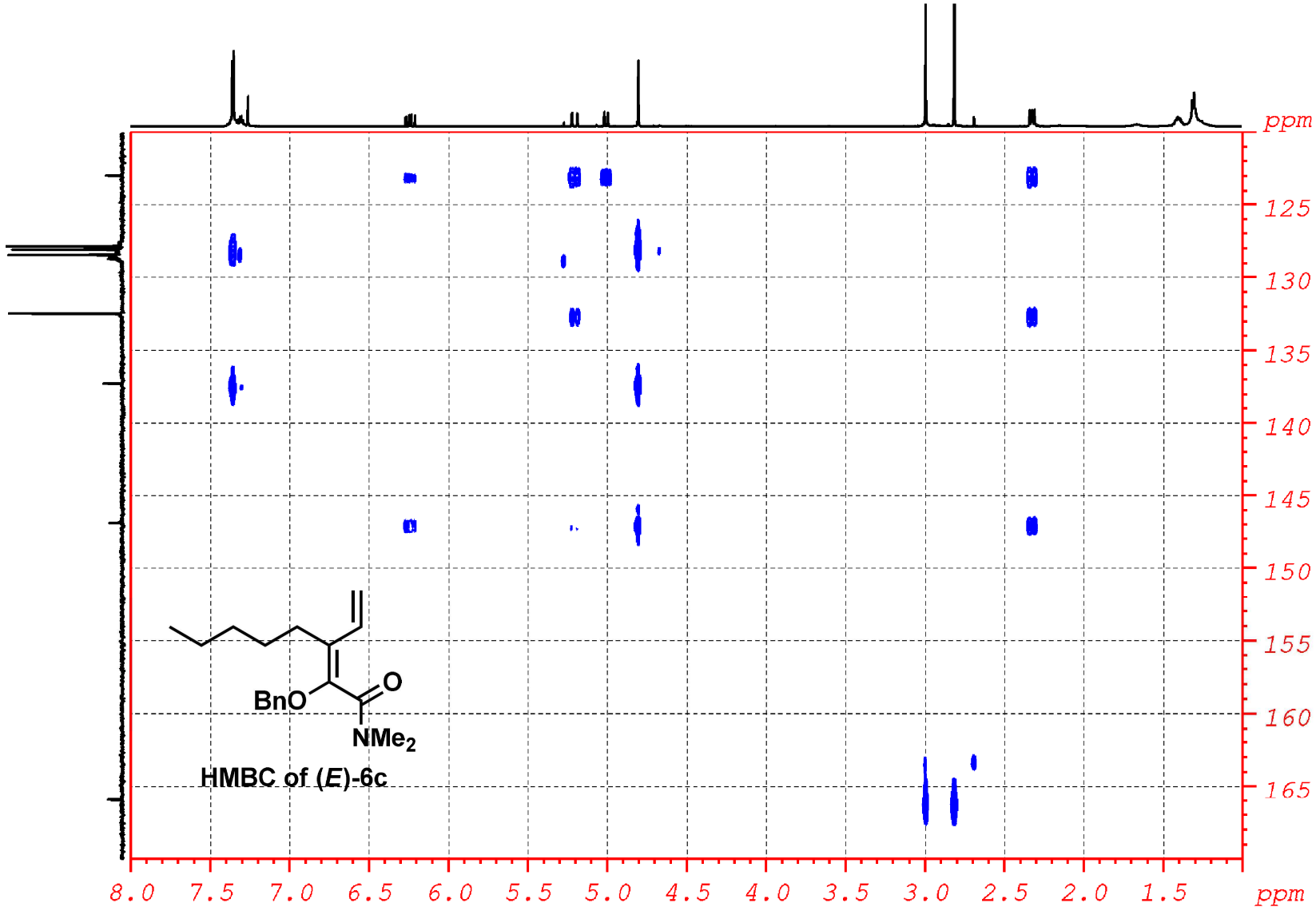

ppm
1
2
3
4
5
6
7
8
8
7
6
5
4
3
2
1
ppm
H
H
H
H
H
O
Ph
O
N
CH3
CH3
NOESY of (E)-6c


ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.5
7.0
6.5
6.0
5.5
5.0
ppm
H
H
H
H
H
O
O
Ph
N
CH3
CH3
NOESY of (E)-6c

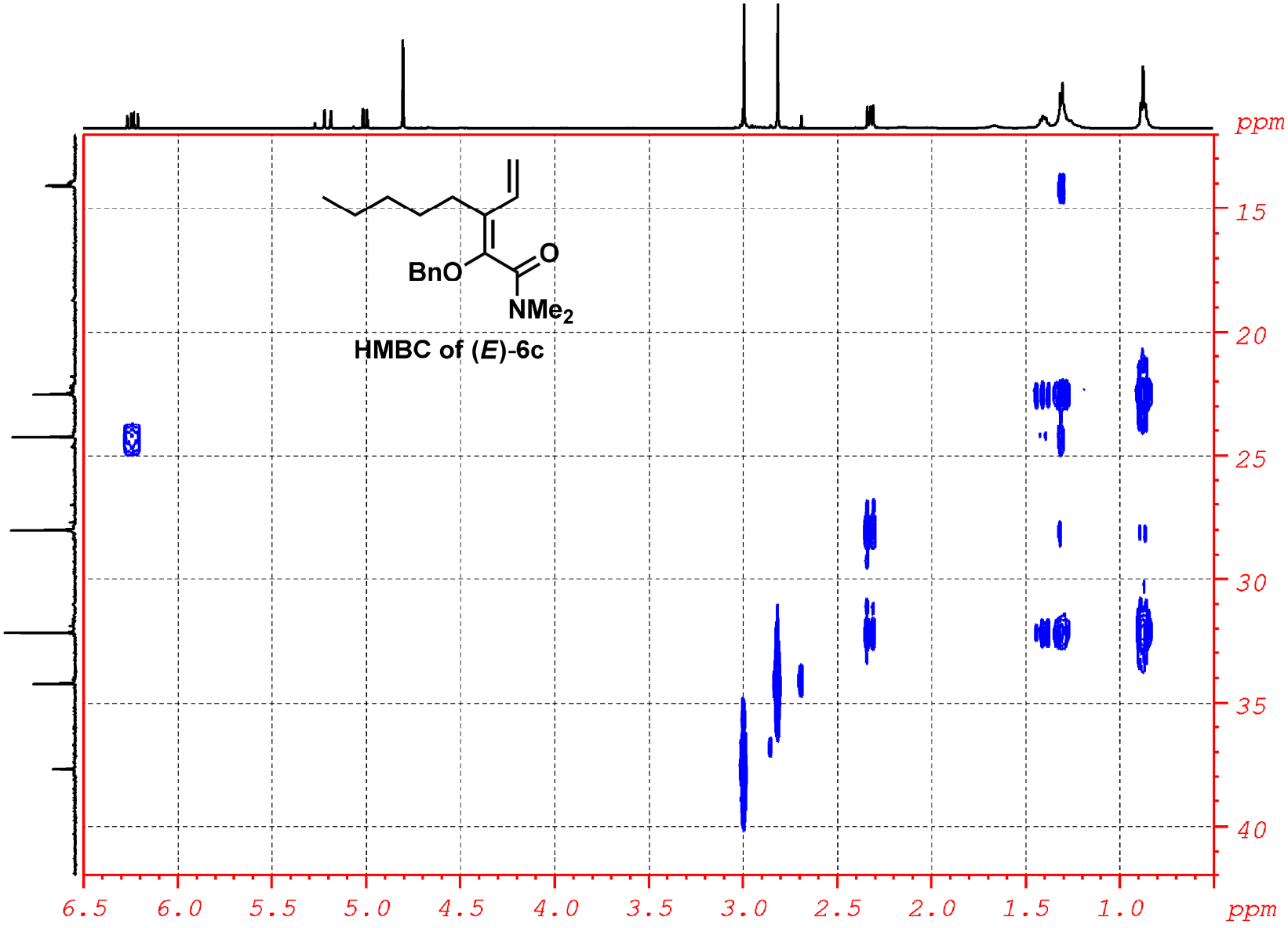

ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
ppm
H
H
H
H
H
O
O
Ph
N
CH3
CH3
NOESY of (E)-6c

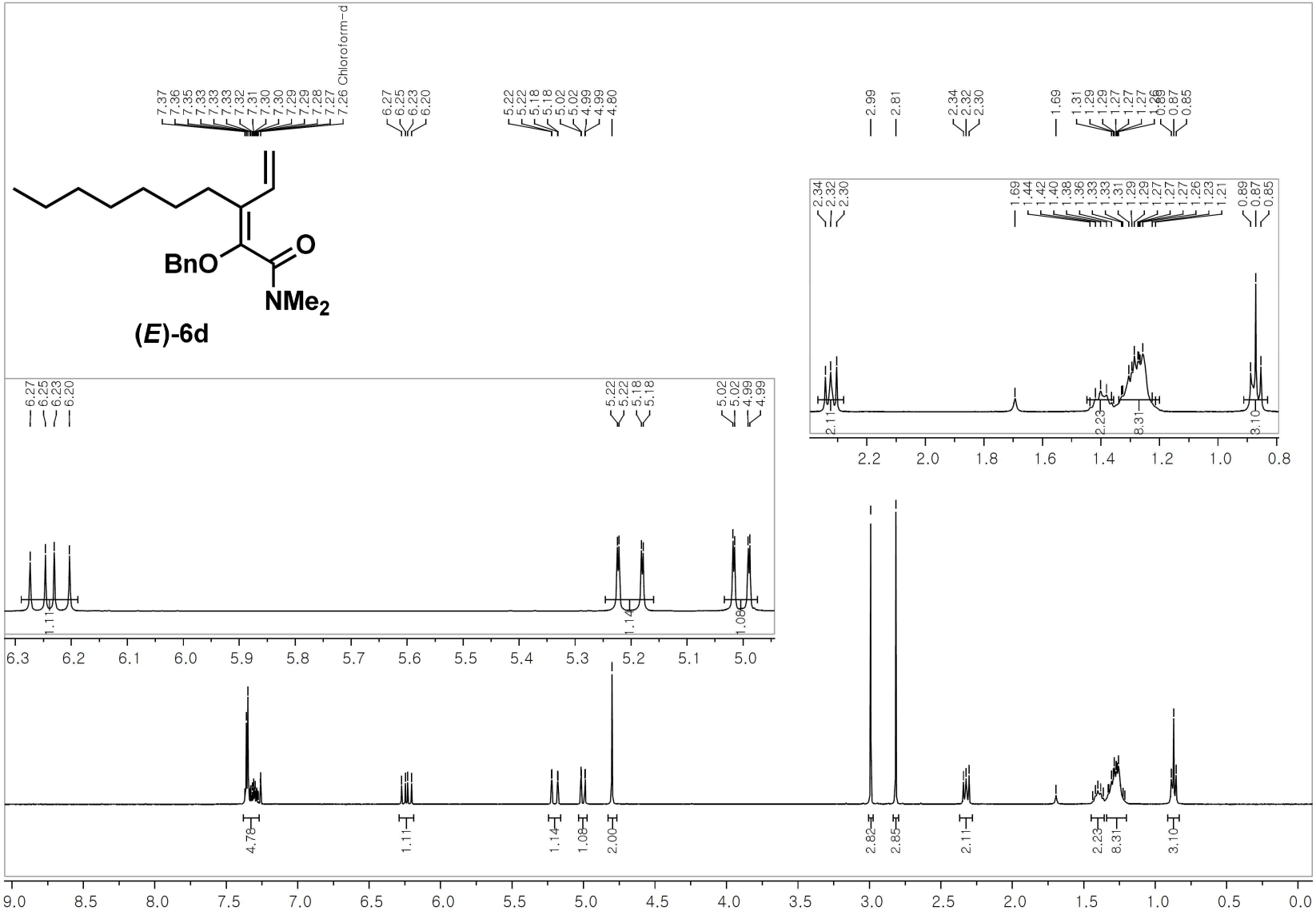

BnO
O
NMe2
HSQC of (E)-6c
ppm
20
40
60
80
100
120
140
160
8
7
6
5
4
3
2
1
ppm

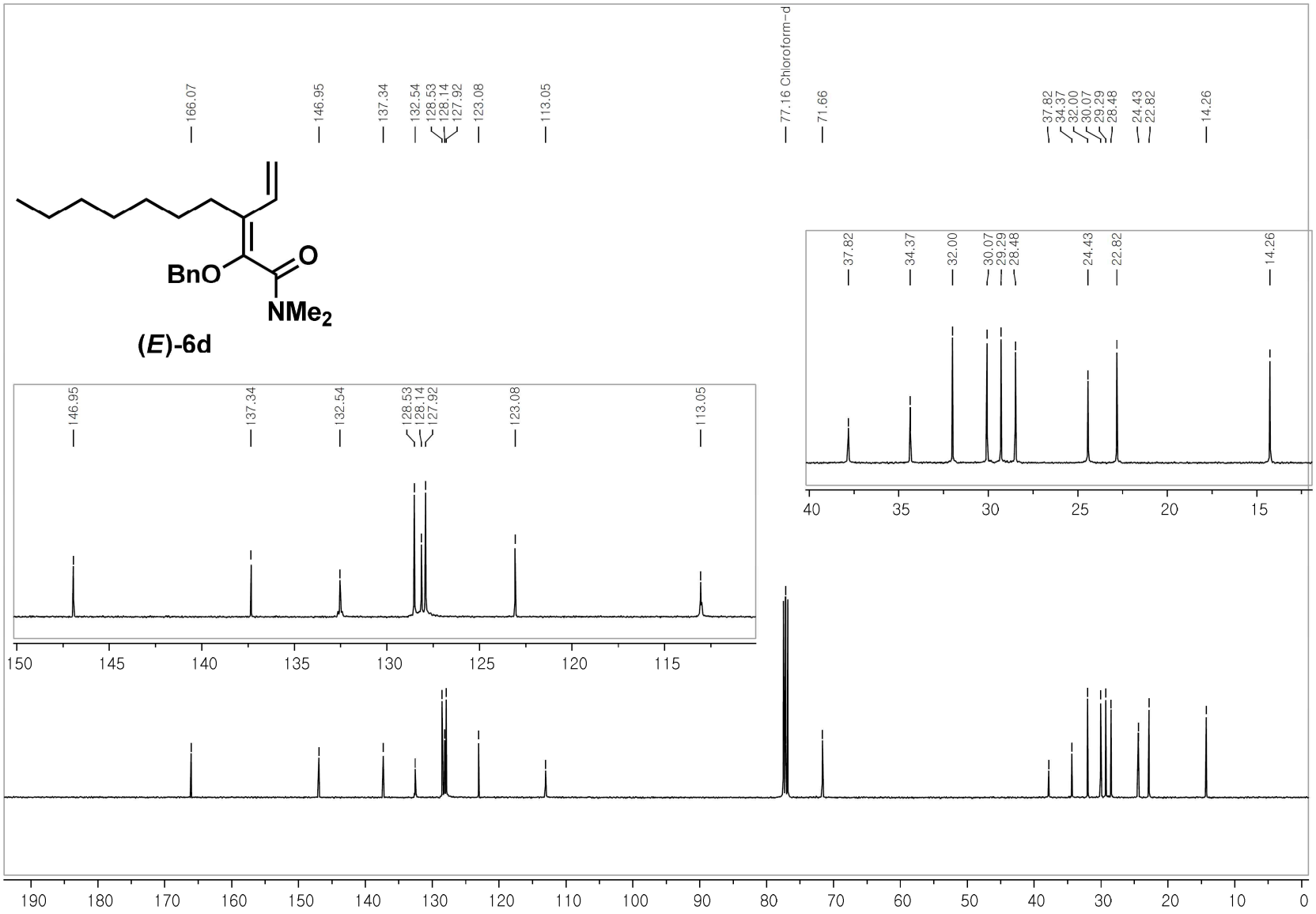

BnO
O
NMe2
HMBC of (E)-6c
ppm
20
40
60
80
100
120
140
160
8
7
6
5
4
3
2
1
ppm

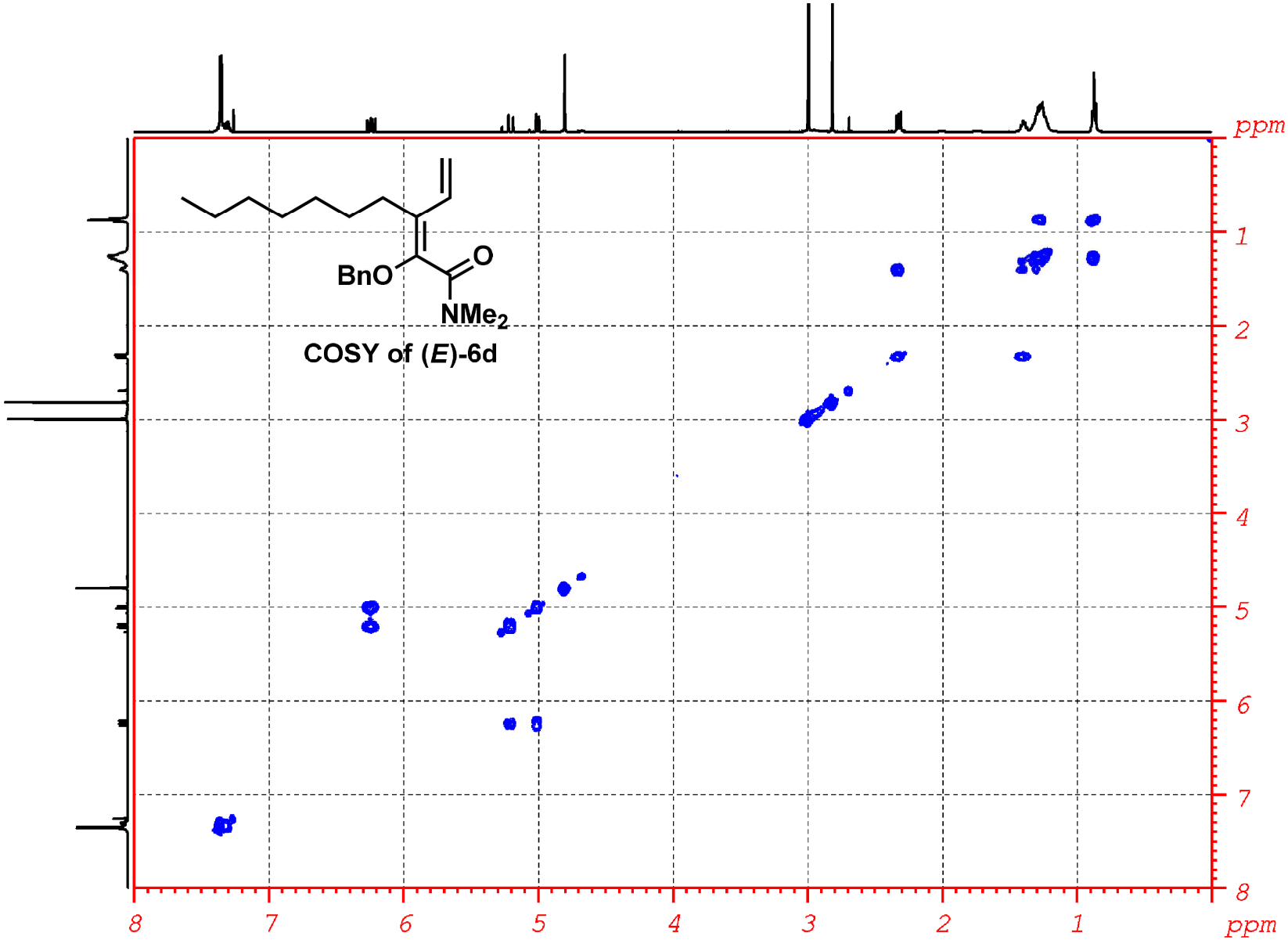

ppm
125
130
135
140
145
150
155
160
165
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
BnO
O
NMe2

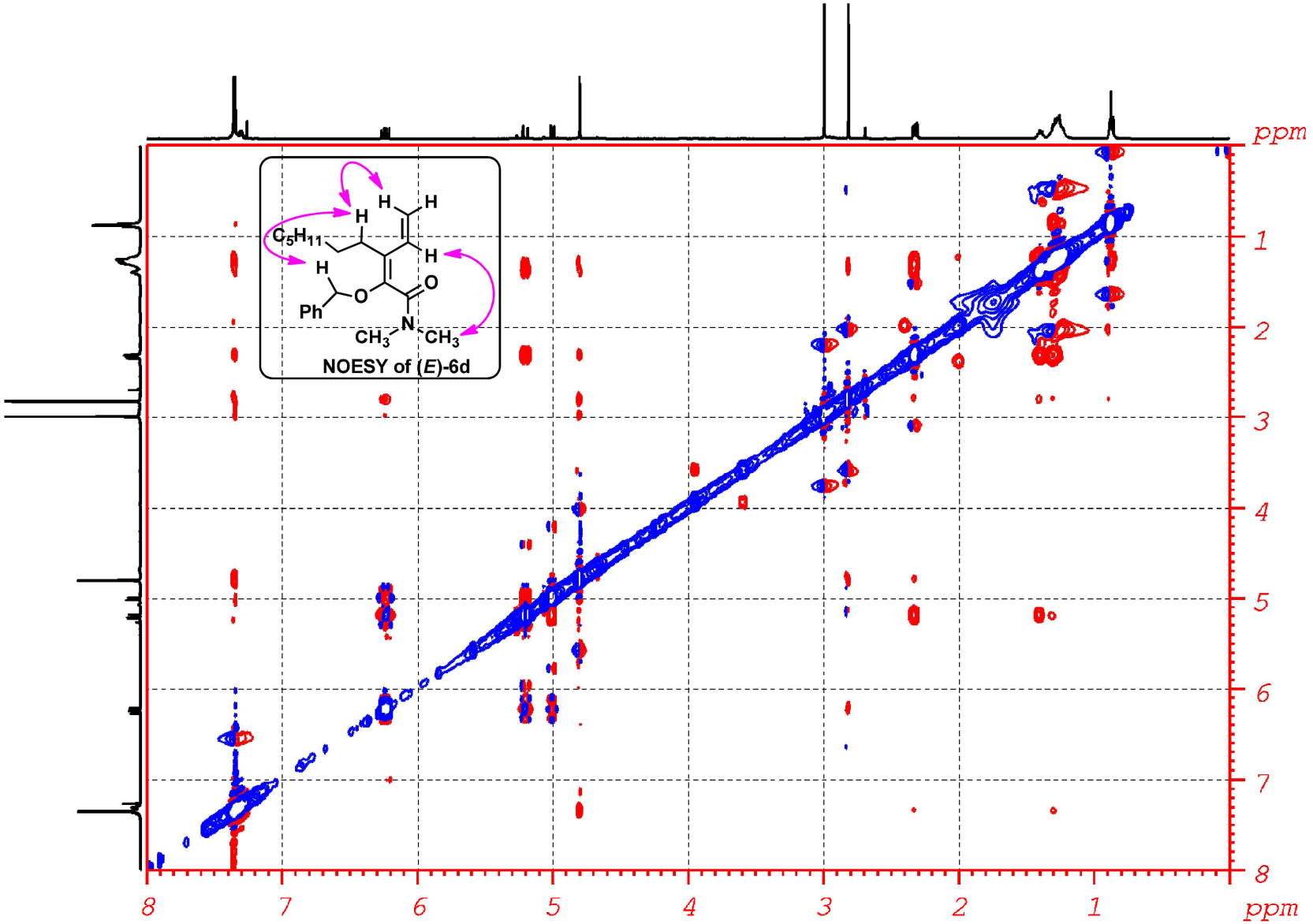
HMBC of (*E*)-6c

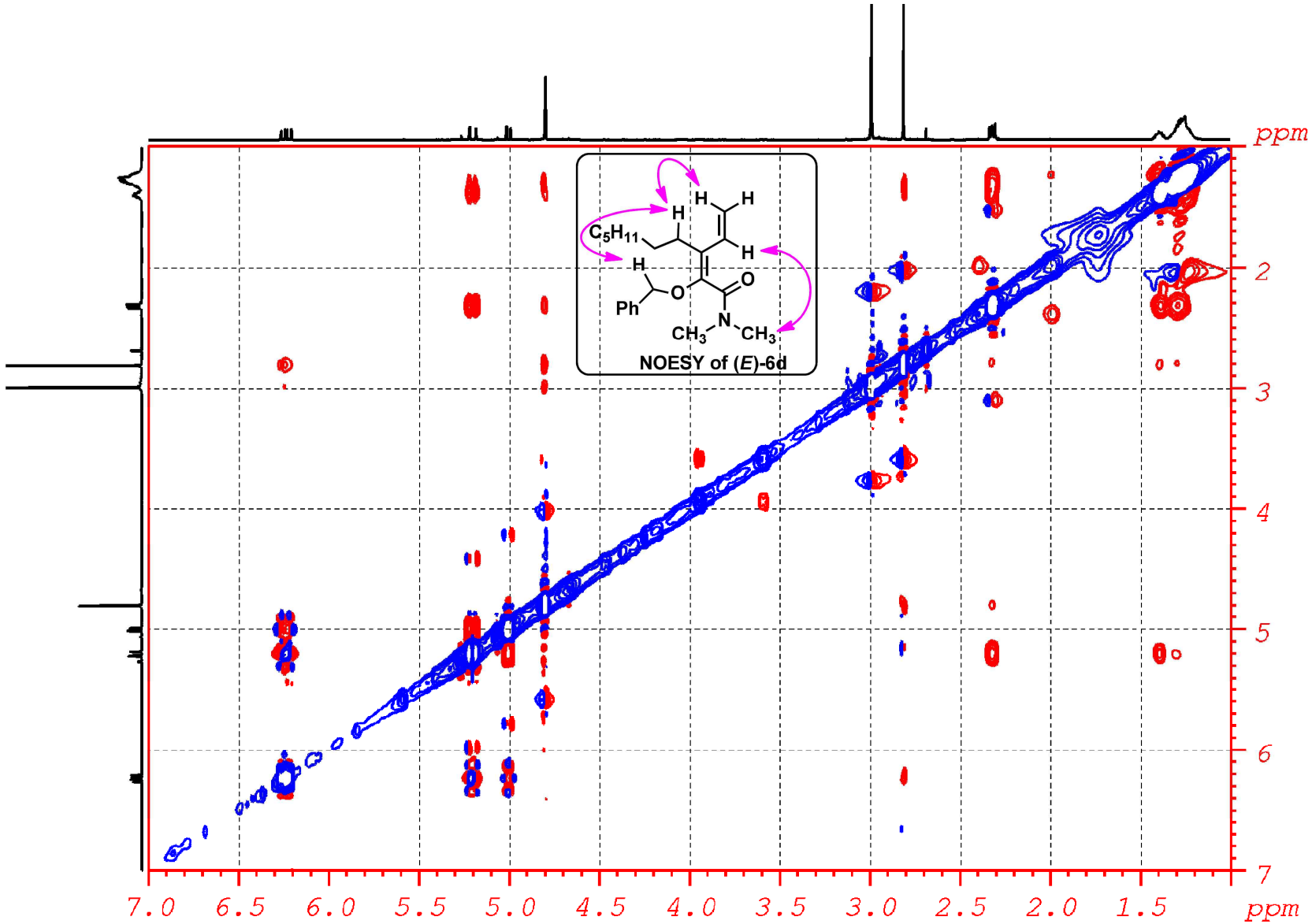

BnO
O
NMe2
HMBC of (E)-6c
ppm
15
20
25
30
35
40
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

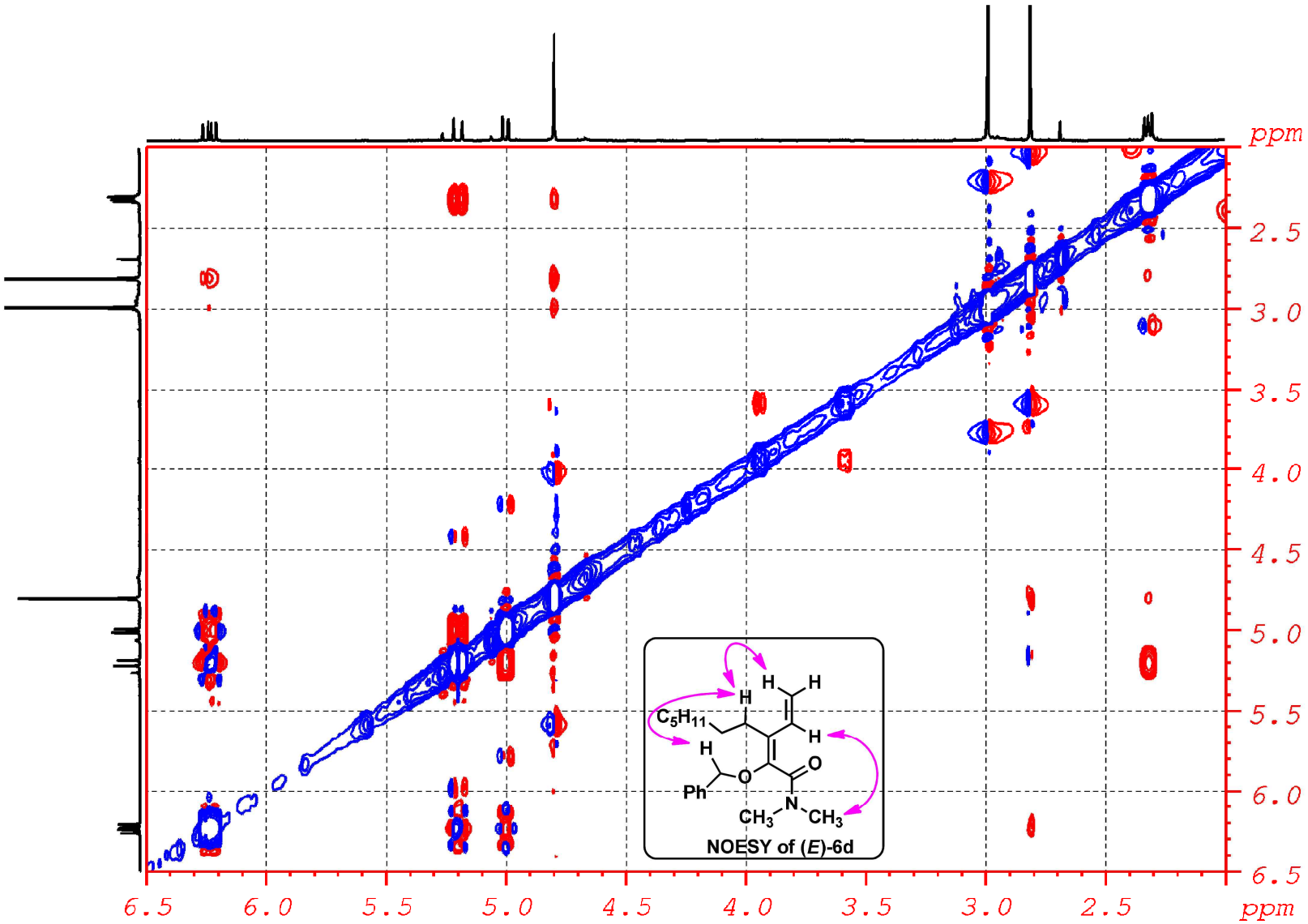

BnO
O
NMe2
(E)-6d
Chloroform-d

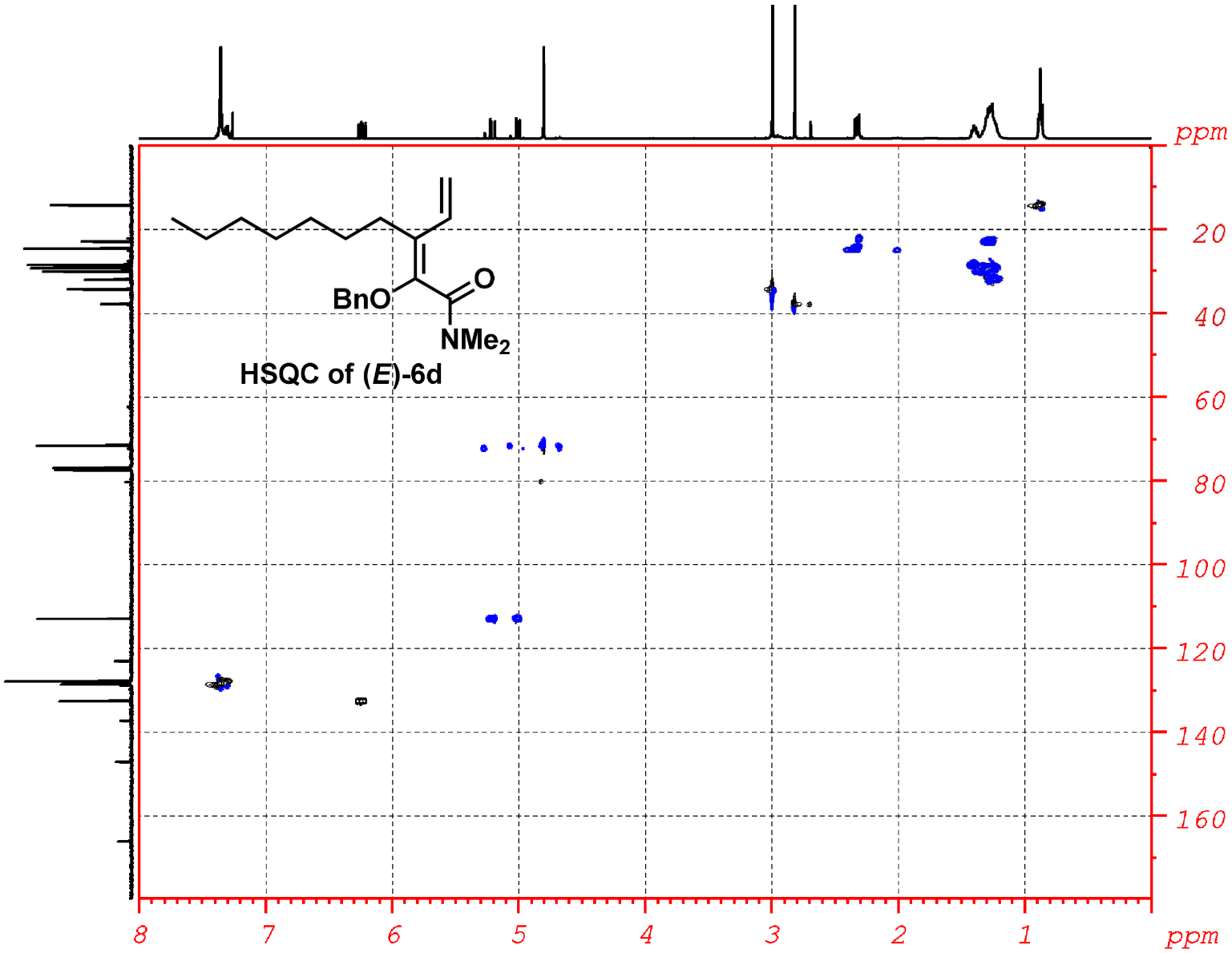

166.07
146.95
137.34
132.54
128.53
128.14
127.92
123.08
113.05
77.16 Chloroform-d
71.66
37.82
34.37
32.00
30.07
29.29
28.48
24.43
22.82
14.26
BnO
O
NMe2
(E)-6d

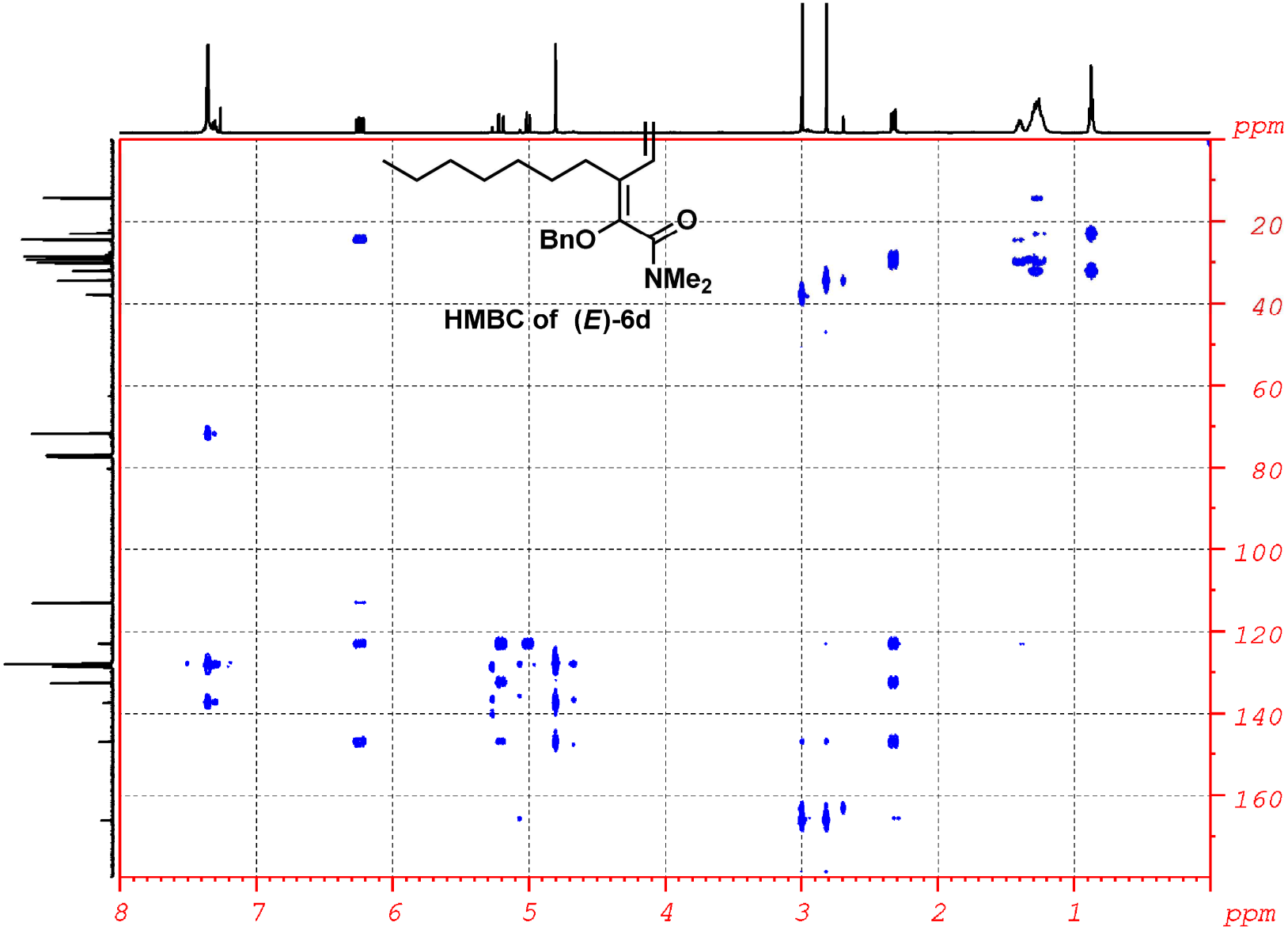

BnO
O
NMe2
COSY of (E)-6d
ppm
1
2
3
4
5
6
7
8
8
7
6
5
4
3
2
1
ppm

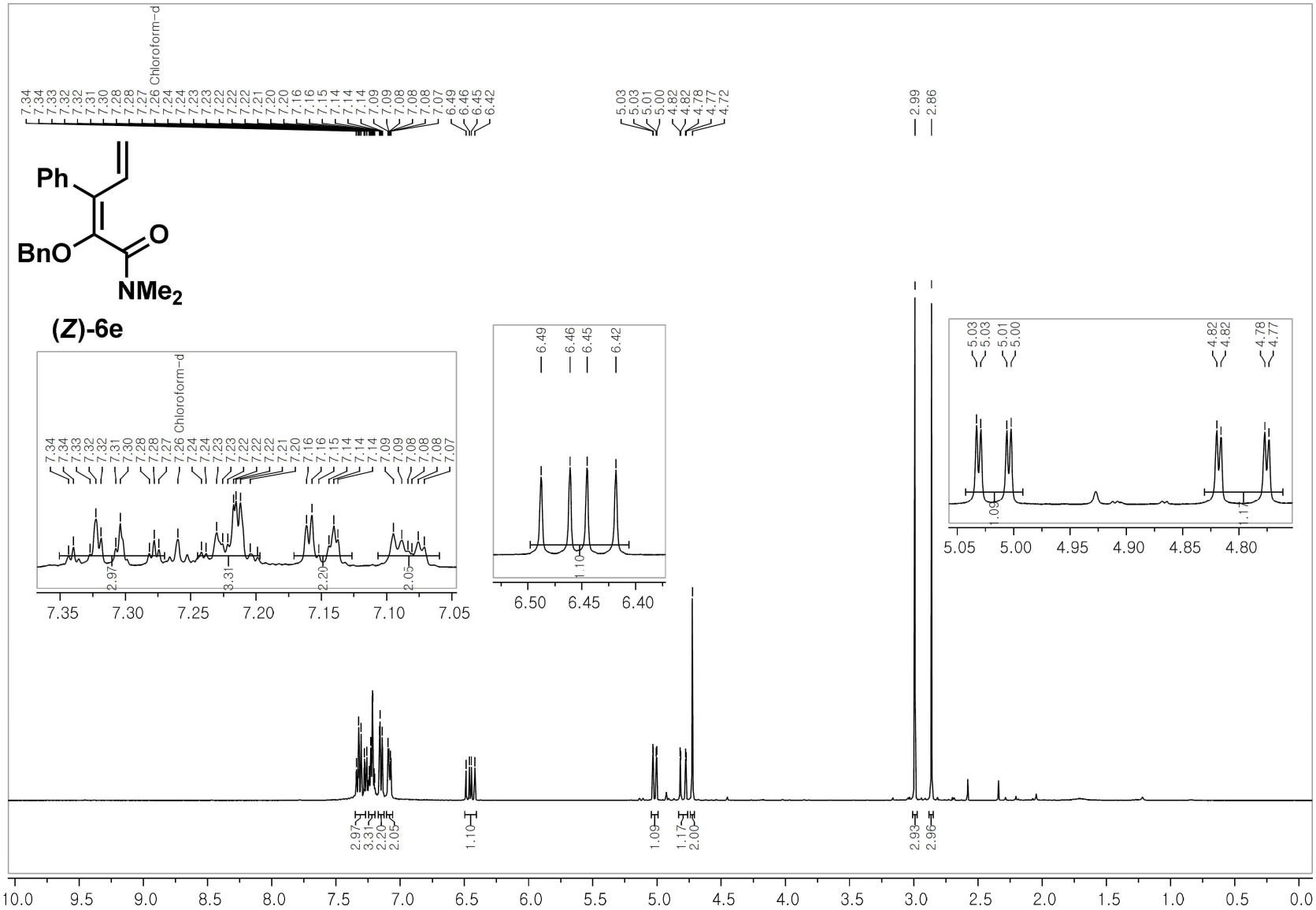

NOESY of (E)-6d
ppm
ppm

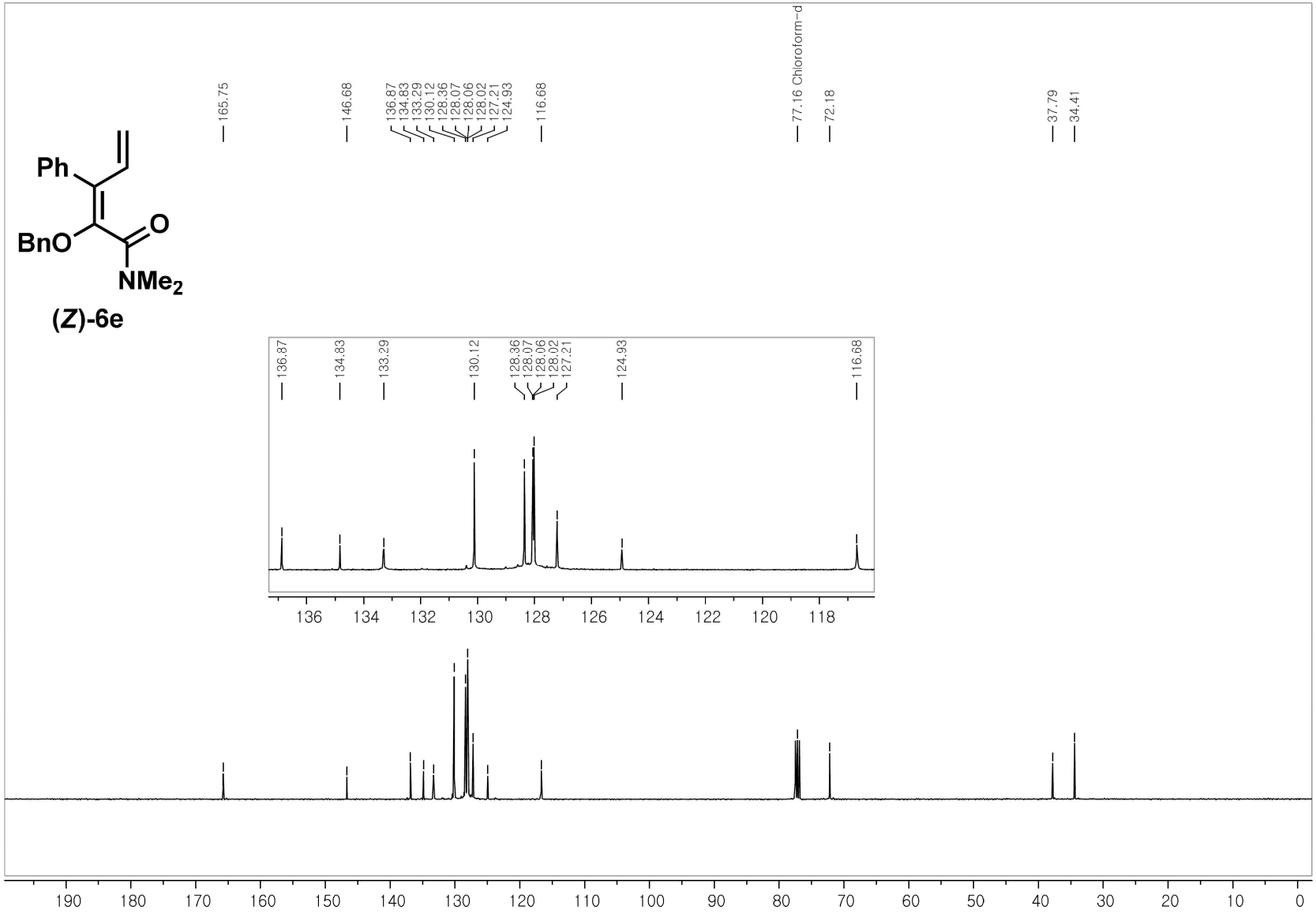

ppm
2
3
4
5
6
7
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
H
H
H
H
C5H11
H
O
O
Ph
N
CH3
CH3
NOESY of (E)-6d

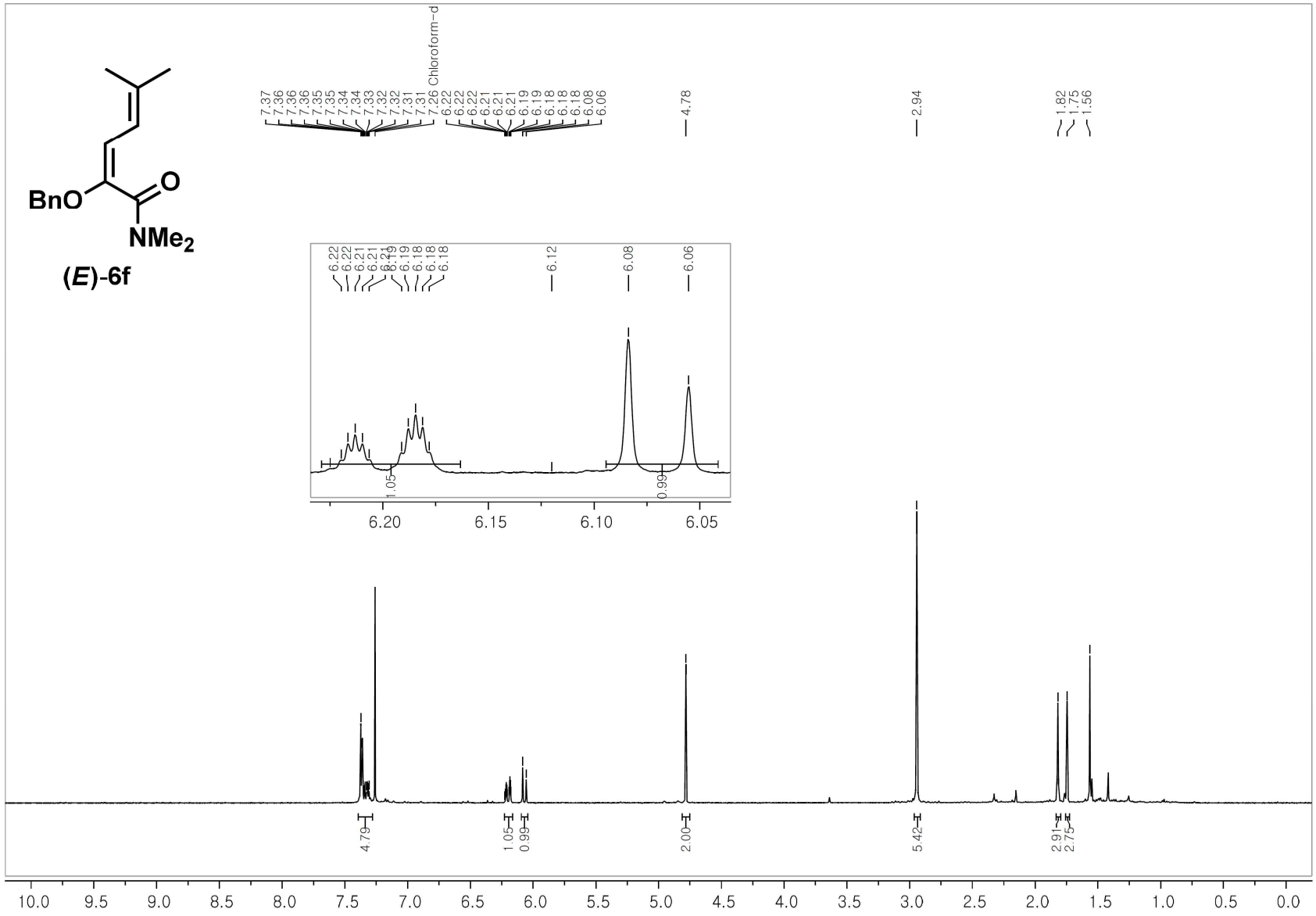

ppm
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
H
H
H
C5H11
H
H
O
Ph
O
N
CH3
CH3
NOESY of (E)-6d

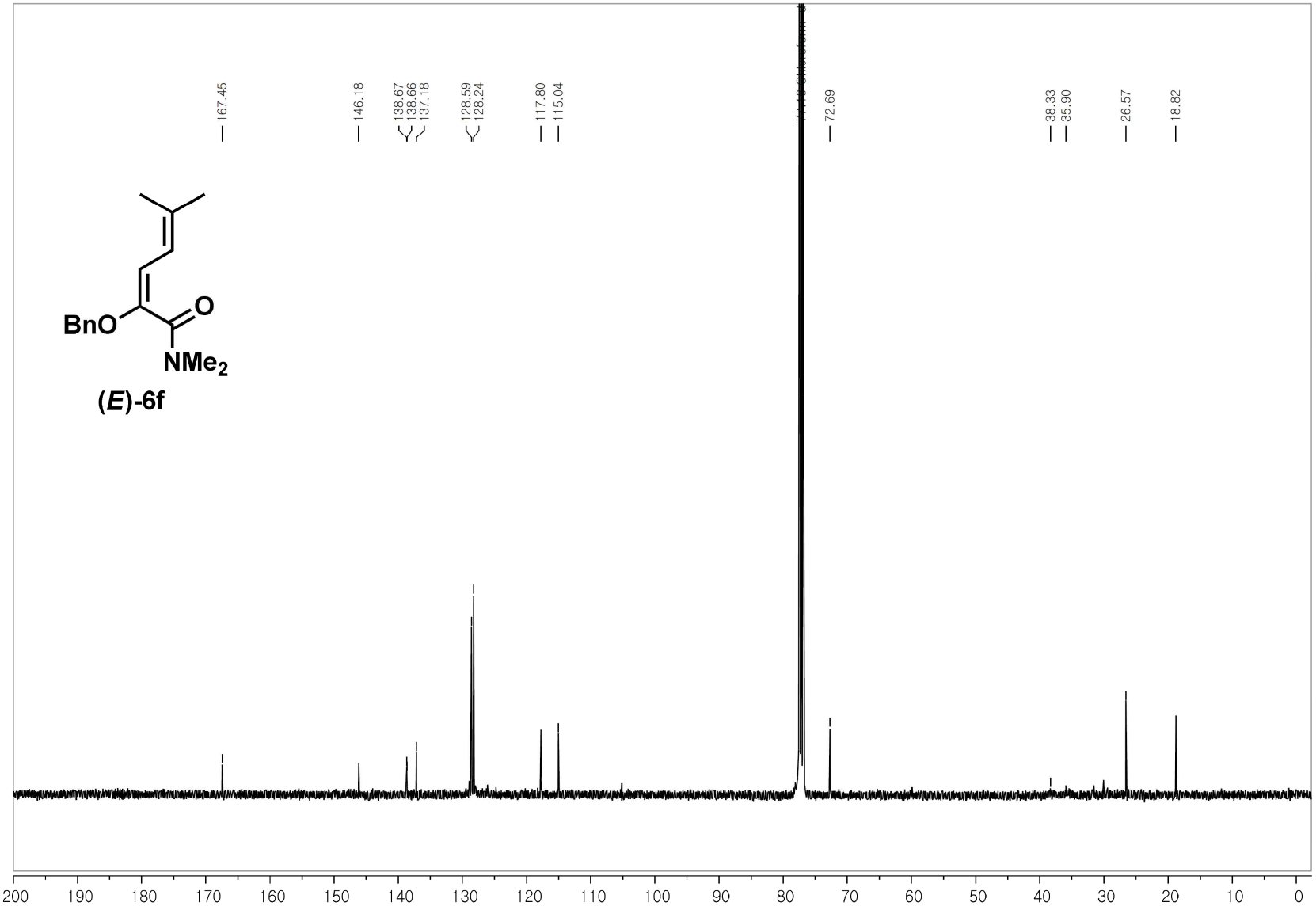

BnO
O
NMe2
HSQC of (E)-6d
ppm
20
40
60
80
100
120
140
160
8
7
6
5
4
3
2
1
ppm

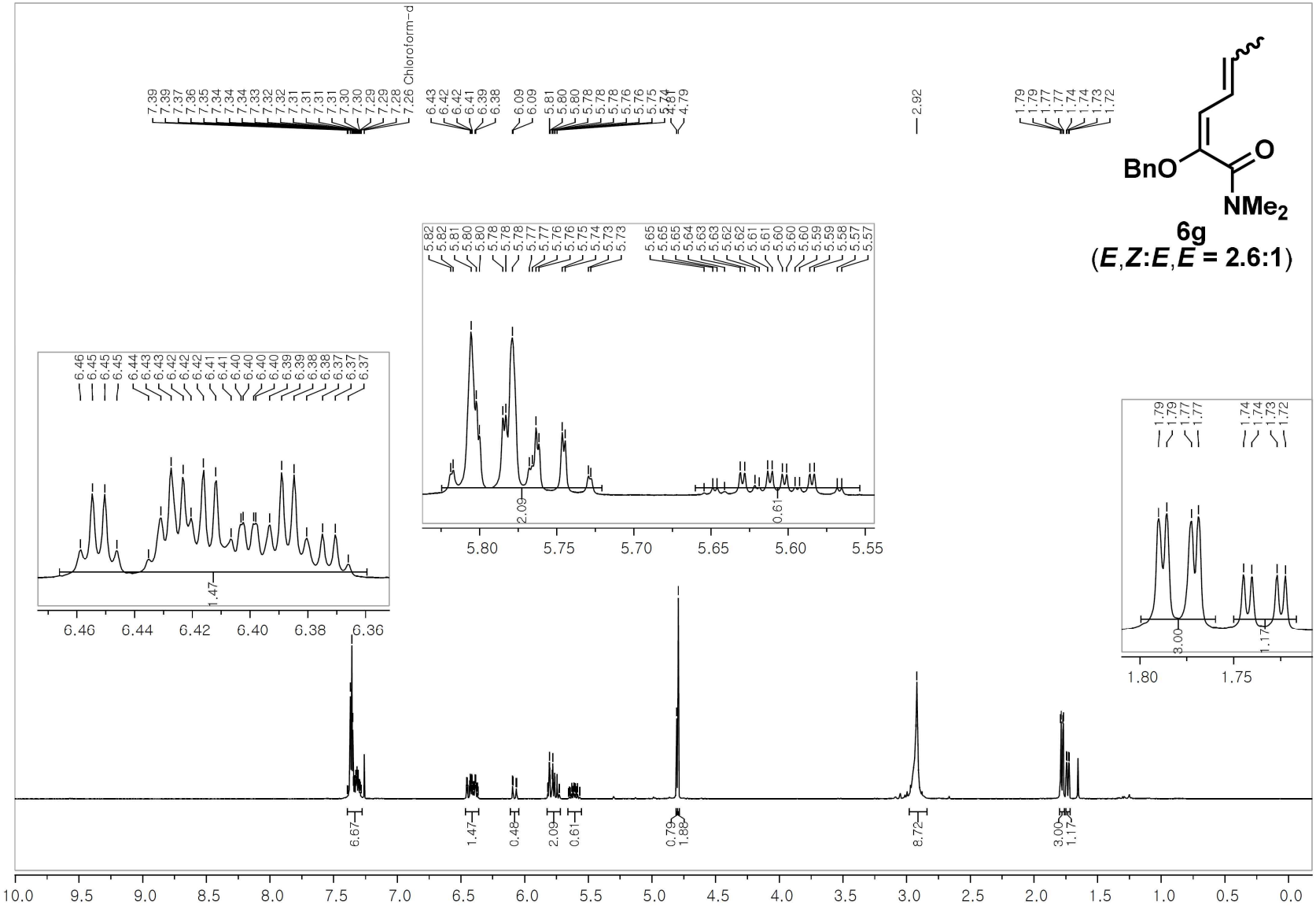

BnO
O
NMe2
HMBC of (E)-6d
ppm
20
40
60
80
100
120
140
160
8
7
6
5
4
3
2
1
ppm

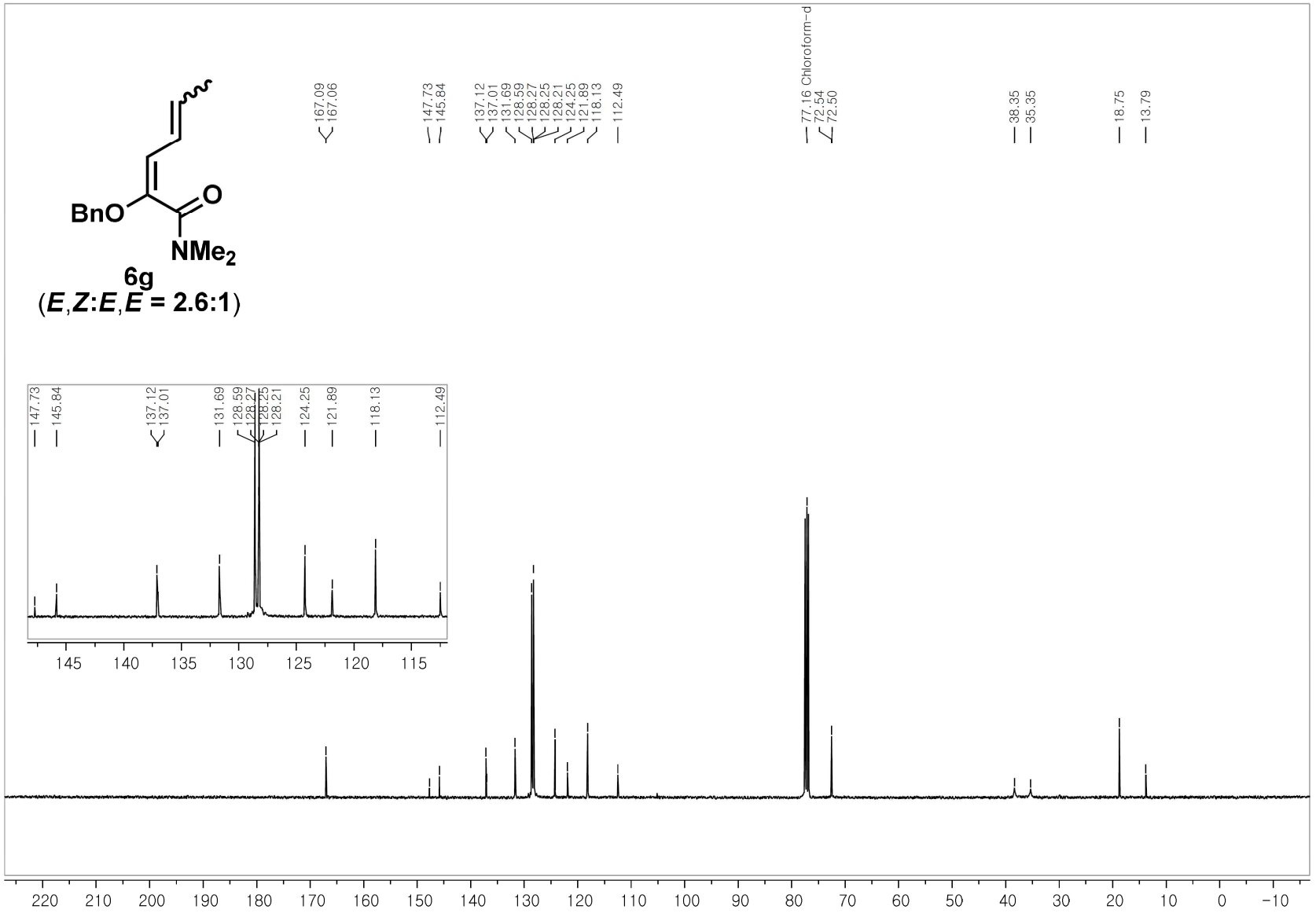

Ph
BnO
O
NMe2
(Z)-6e
Chloroform-d
2.97
3.31
2.20
2.05
1.10
1.09
1.17
2.00
2.93
2.96

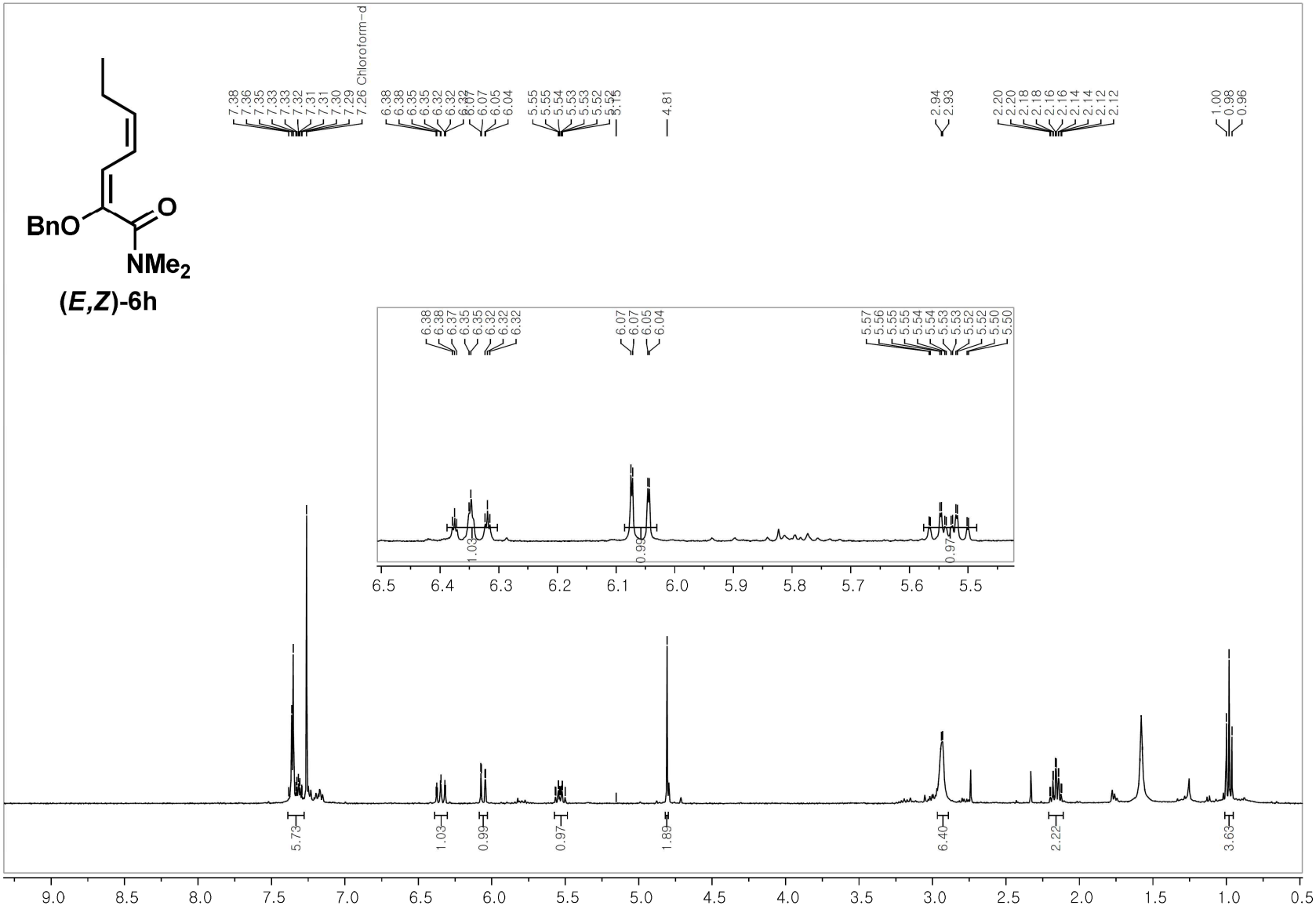

165.75
146.68
136.87
134.83
133.29
130.12
128.36
128.07
128.06
128.02
127.21
124.93
116.68
77.16 Chloroform-d
72.18
37.79
34.41
Ph
BnO
O
NMe2
(Z)-6e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
136 134 132 130 128 126 124 122 120 118

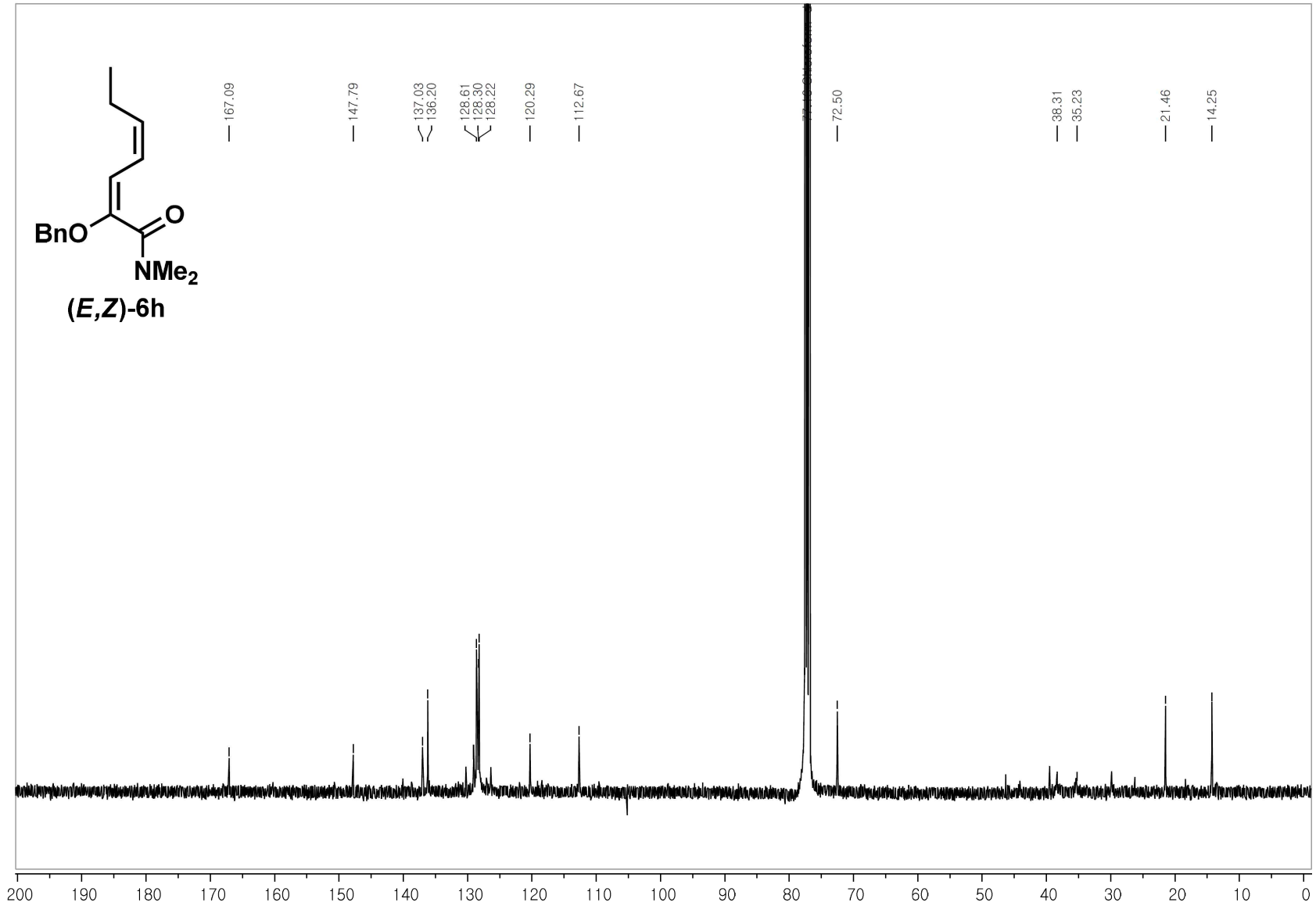

BnO
O
NMe2
(E)-6f
Chloroform-d
4.78
2.94
1.82
1.75
1.56
6.12
6.08
6.06
4.79
1.05
0.99
2.00
5.42
2.91
2.75

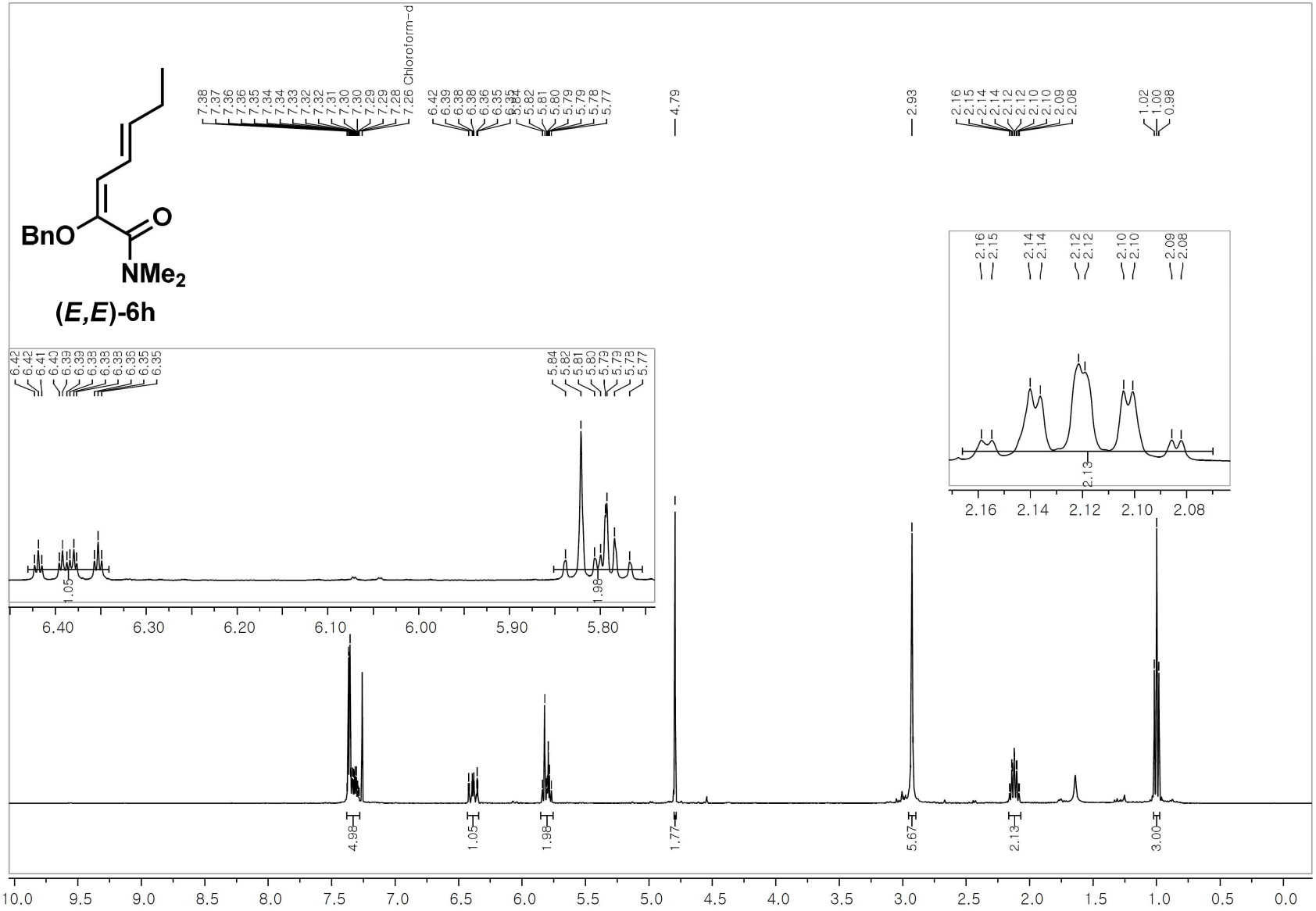

167.45
146.18
138.67
138.66
137.18
128.59
128.24
117.80
115.04
77.48
72.69
38.33
35.90
26.57
18.82
BnO
O
NMe2
(E)-6f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

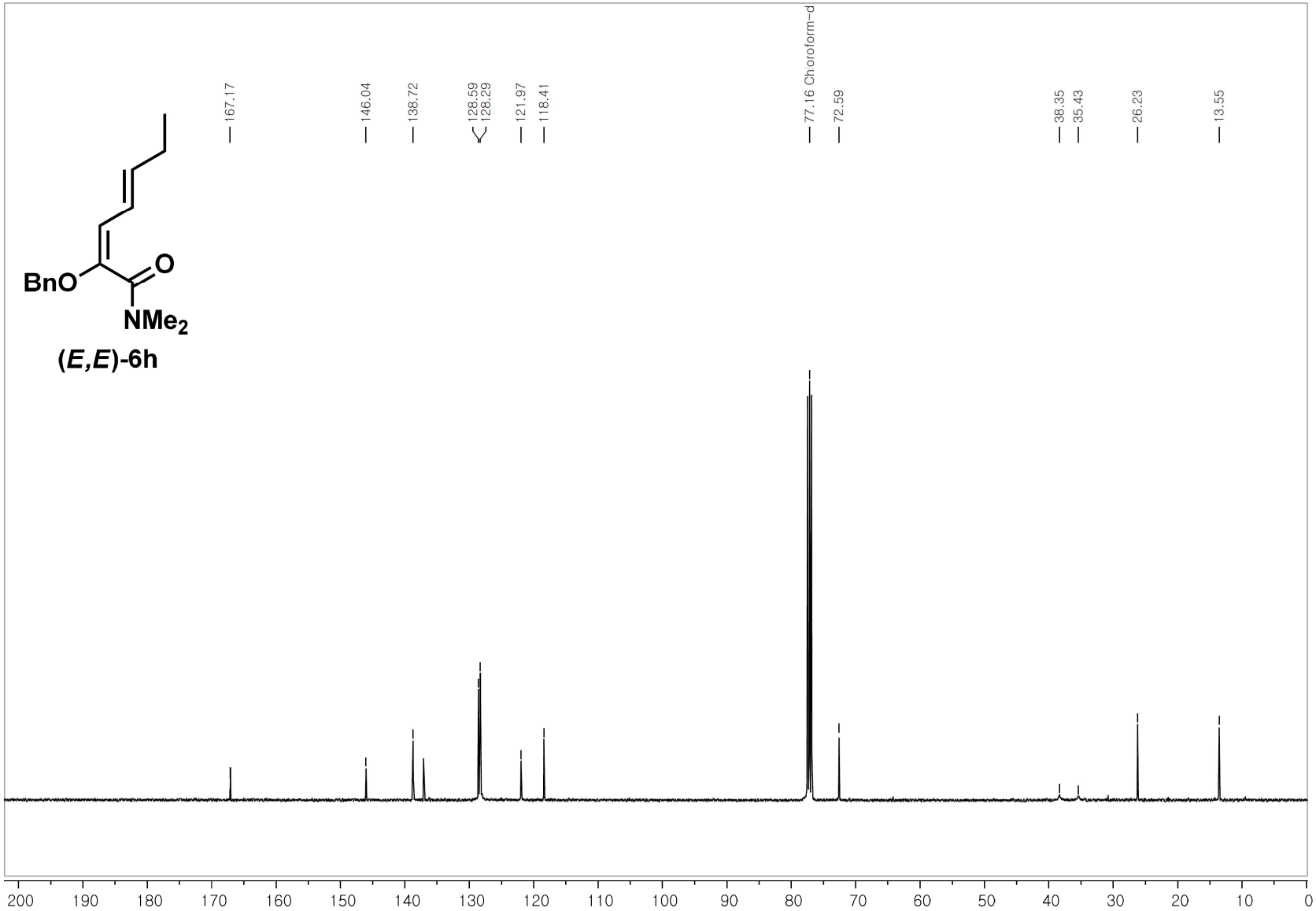

BnO
O
NMe2
6g
(E,Z:E,E = 2.6:1)
Chloroform-d
2.92

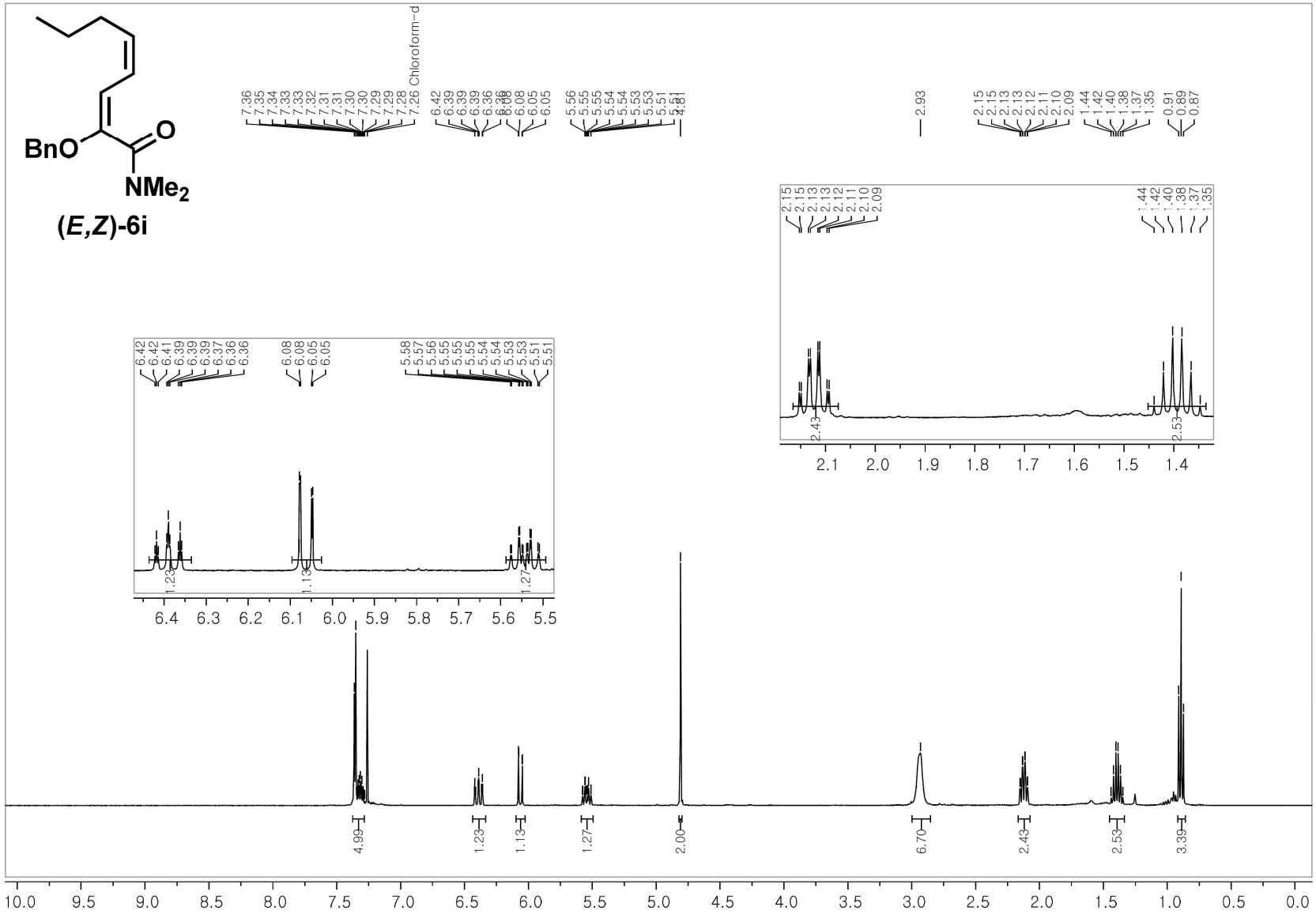

BnO
O
NMe2
6g
(E,Z:E,E = 2.6:1)
167.09
167.06
147.73
145.84
137.12
137.01
131.69
128.59
128.27
128.25
128.21
124.25
121.89
118.13
112.49
77.16 Chloroform-d
72.54
72.50
38.35
35.35
18.75
13.79

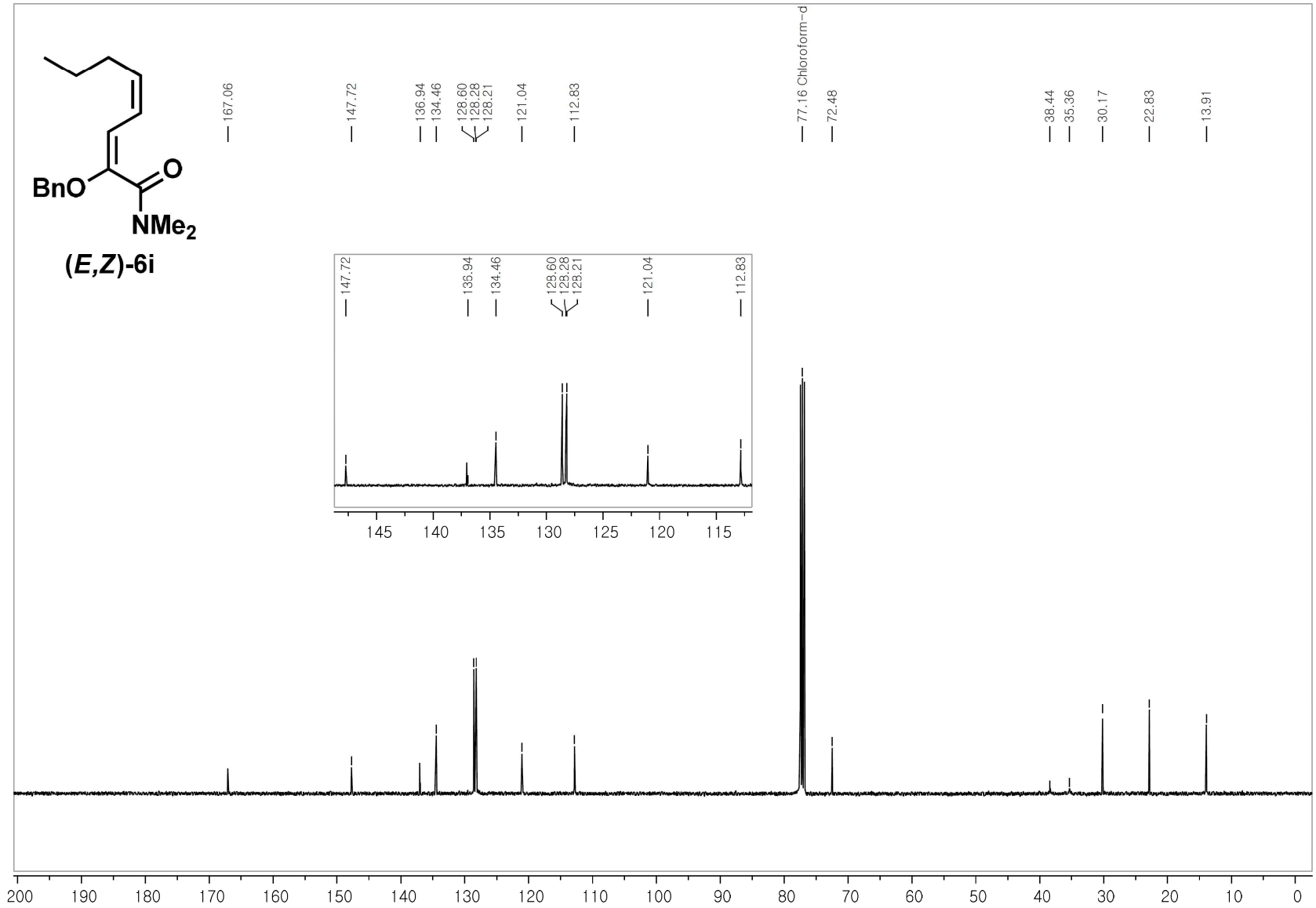

BnO
O
NMe2
(E,Z)-6h
Chloroform-d
7.38
7.36
7.35
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.26
6.38
6.38
6.35
6.35
6.32
6.32
6.32
6.07
6.07
6.05
6.04
5.55
5.55
5.54
5.53
5.53
5.52
5.52
5.15
4.81
2.94
2.93
2.20
2.20
2.18
2.18
2.16
2.16
2.14
2.14
2.12
2.12
1.00
0.98
0.96
5.73
1.03
0.99
0.97
1.89
6.40
2.22
3.63

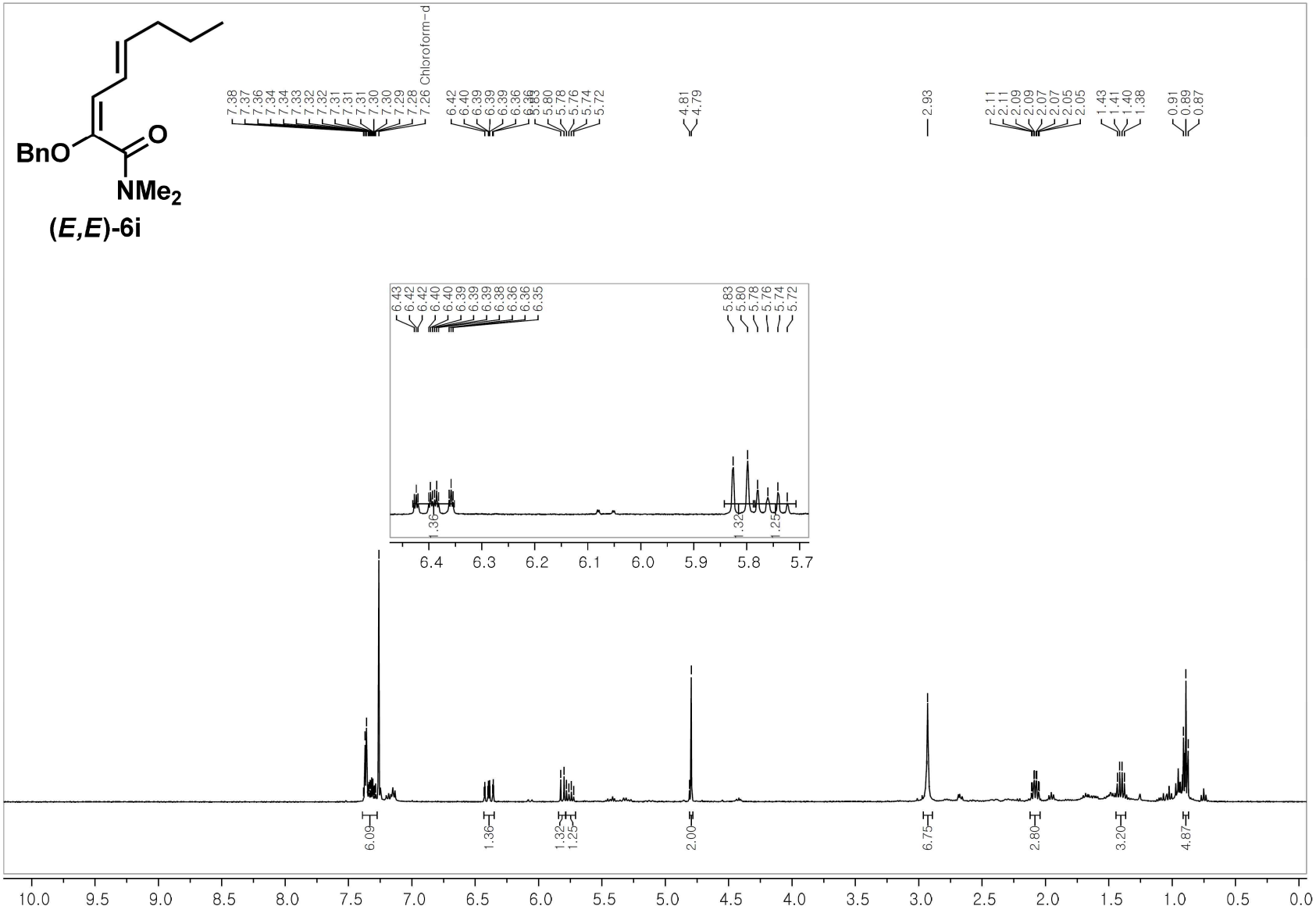

BnO
O
NMe2
(E,Z)-6h
167.09
147.79
137.03
136.20
128.61
128.30
128.22
120.29
112.67
77.16
72.50
38.31
35.23
21.46
14.25
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

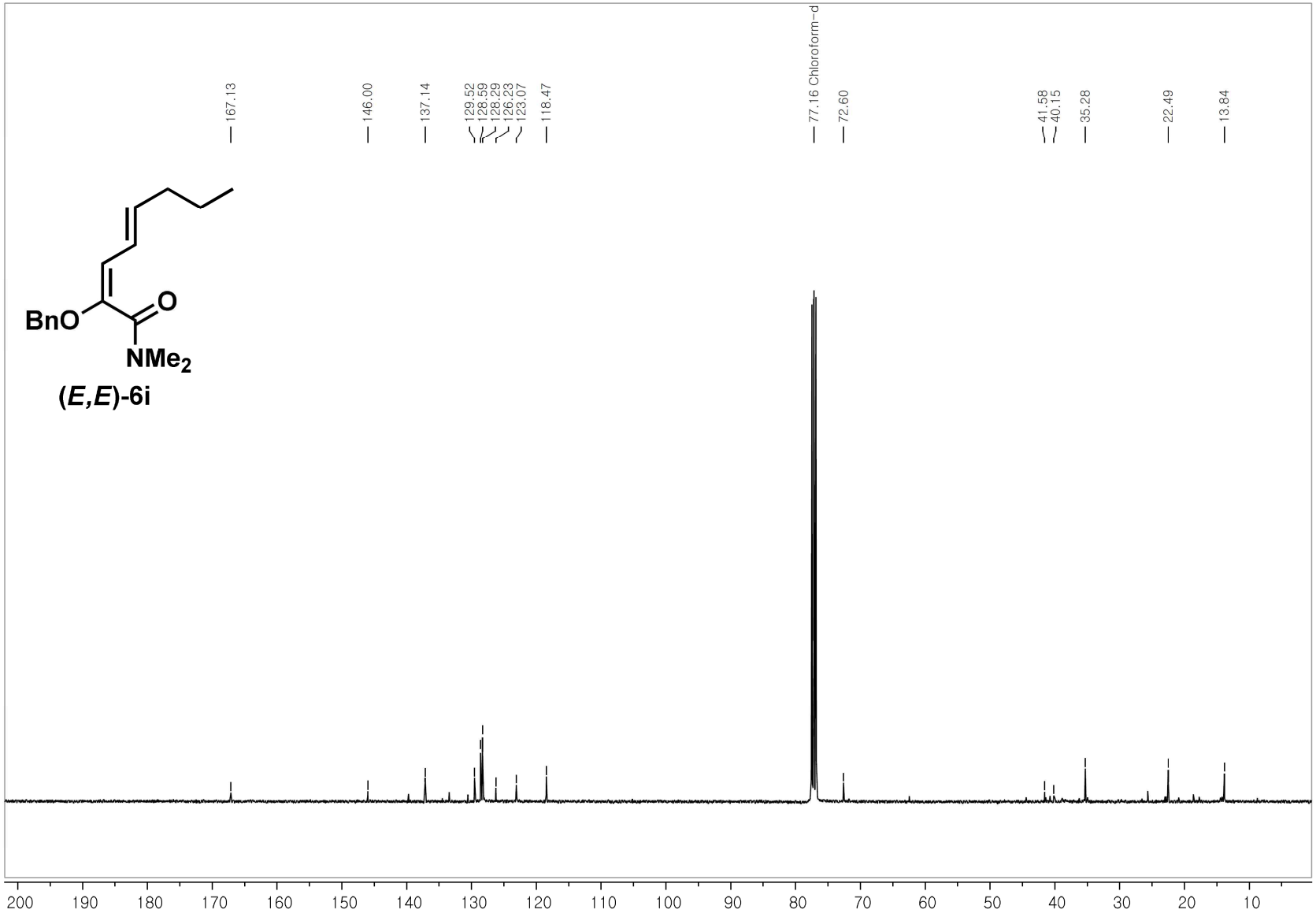

BnO
O
NMe2
(E,E)-6h
Chloroform-d
4.98
1.05
1.98
1.77
5.67
2.13
3.00

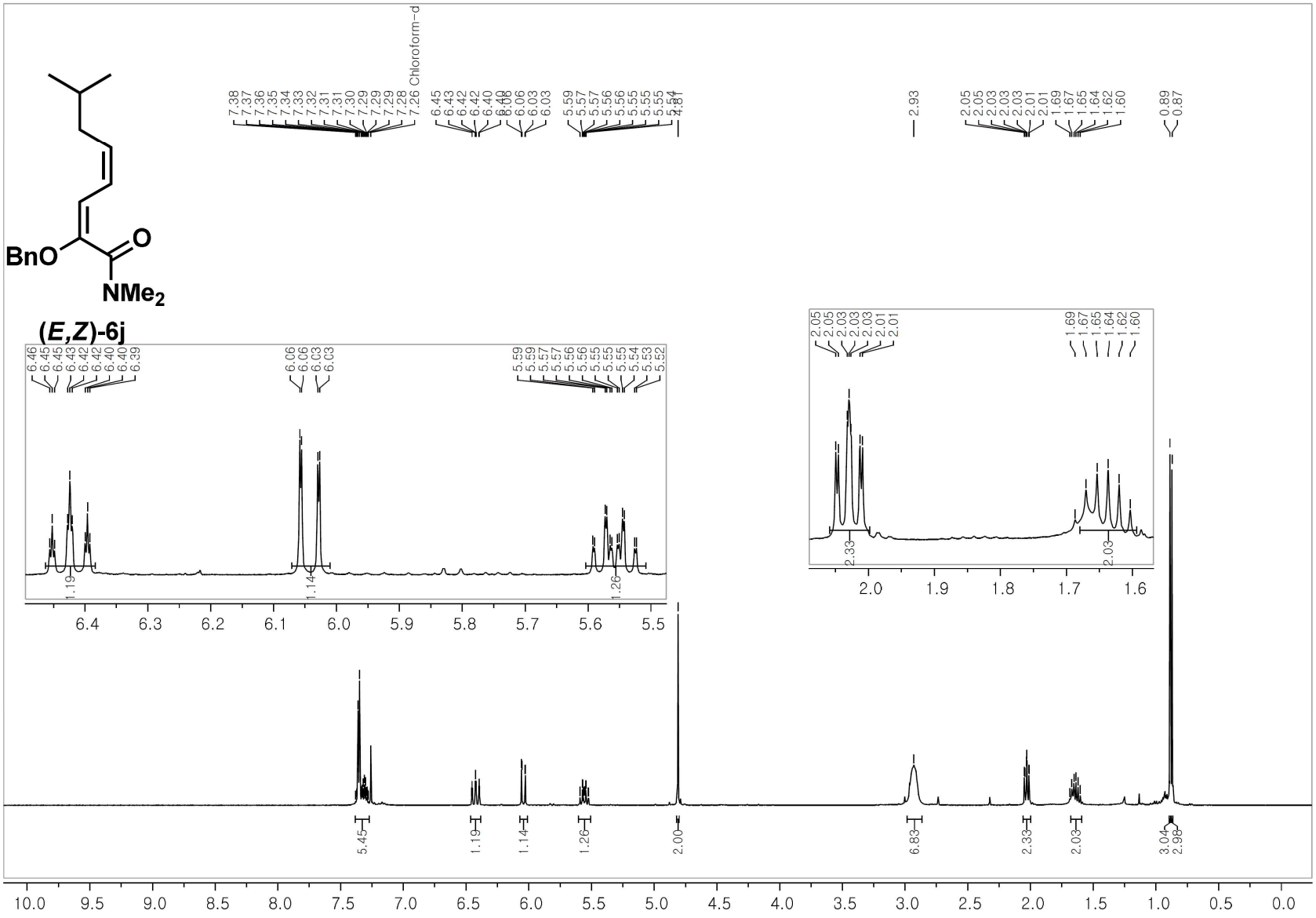

167.17
146.04
138.72
128.59
128.29
121.97
118.41
77.16 Choroform-d
72.59
38.35
35.43
26.23
13.55
BnO
O
NMe2
(E,E)-6h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

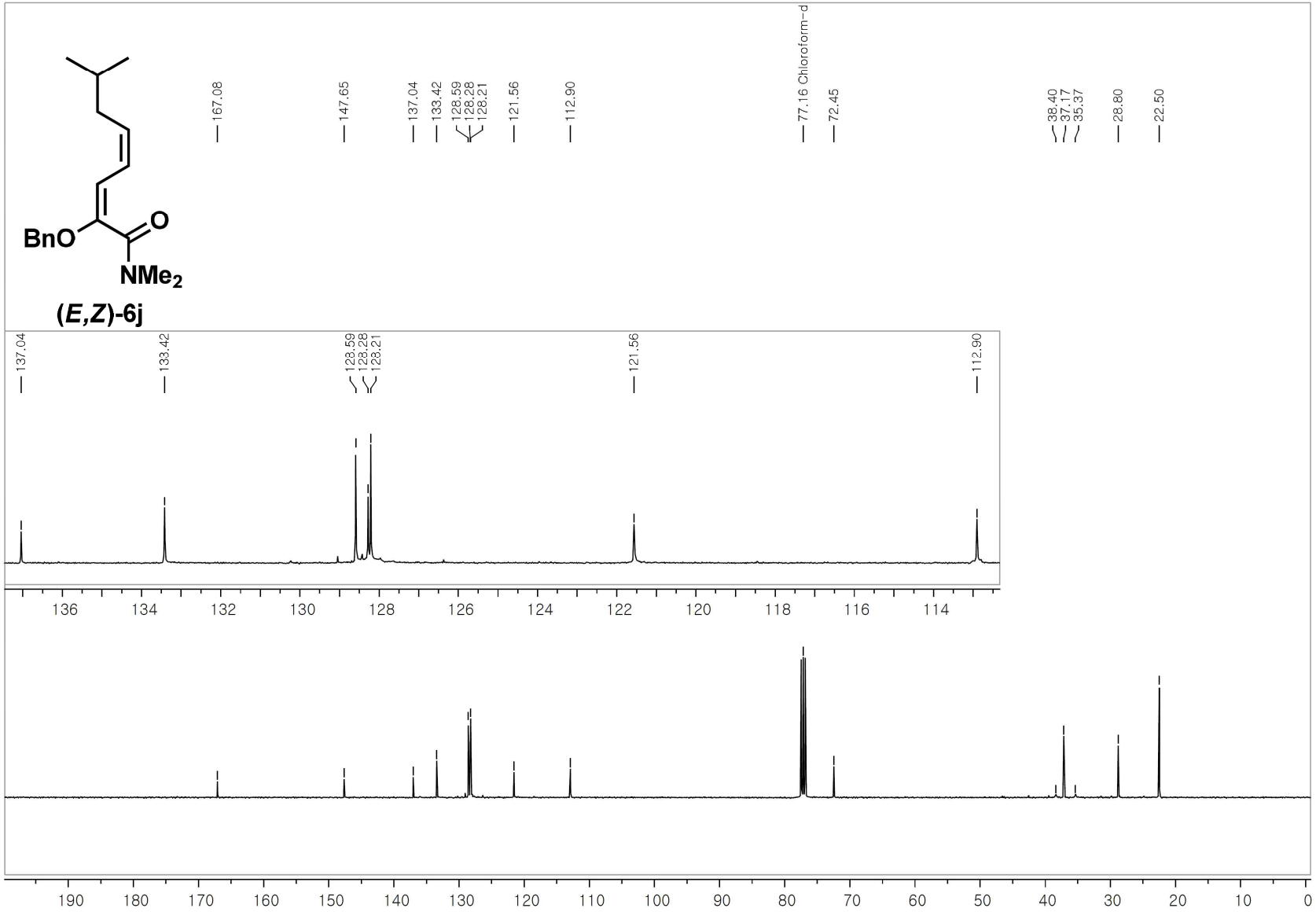

BnO
O
NMe2
(E,Z)-6i
Chloroform-d
4.99
1.23
1.13
1.27
2.00
6.70
2.43
2.53
3.39

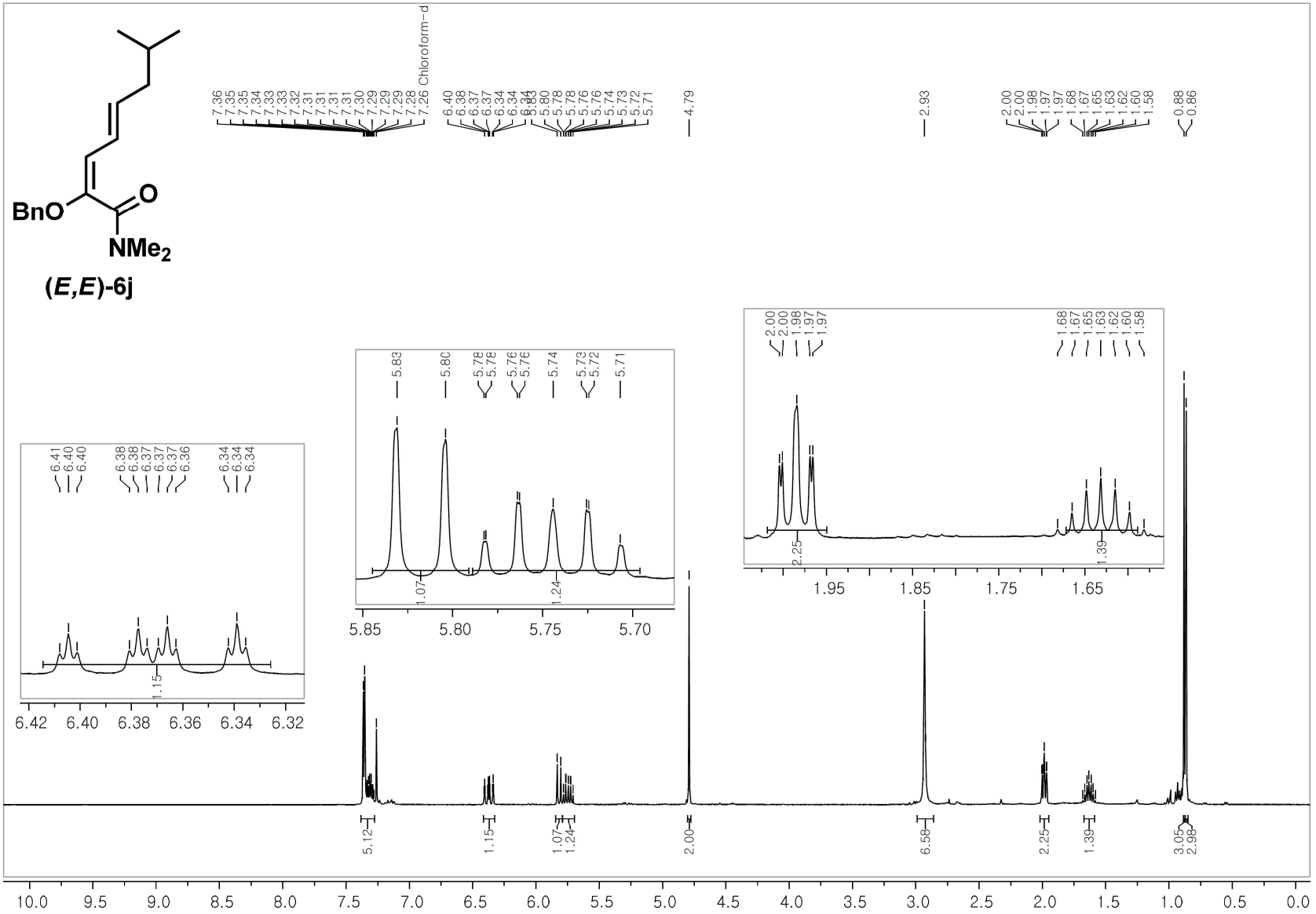

BnO
O
NMe2
(E,Z)-6i
167.06
147.72
136.94
134.46
128.60
128.28
128.21
121.04
112.83
77.16 Chloroform-d
72.48
38.44
35.36
30.17
22.83
13.91
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
145 140 135 130 125 120 115


BnO
O
NMe2
(E,E)-6i
Chloroform-d
7.38
7.37
7.36
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.31
7.30
7.30
7.29
7.28
7.26
6.42
6.40
6.39
6.39
6.39
6.36
6.36
6.35
5.80
5.78
5.76
5.74
5.72
4.81
4.79
2.93
2.11
2.11
2.09
2.09
2.07
2.07
2.05
2.05
1.43
1.41
1.40
1.38
0.91
0.89
0.87
6.43
6.42
6.42
6.40
6.40
6.39
6.39
6.39
6.38
6.36
6.36
6.35
5.83
5.80
5.78
5.76
5.74
5.72
1.36
1.32
1.25
6.4
6.3
6.2
6.1
6.0
5.9
5.8
5.7
6.09
1.36
1.32
1.25
2.00
6.75
2.80
3.20
4.87
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


167.13
146.00
137.14
129.52
128.59
128.29
126.23
123.07
118.47
77.16 Chloroform-d
72.60
41.58
40.15
35.28
22.49
13.84
BnO
O
NMe2
(E,E)-6i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


BnO
O
NMe2
(E,Z)-6j
Chloroform-d


BnO
O
NMe2
(E,Z)-6j
167.08
147.65
137.04
133.42
128.59
128.28
128.21
121.56
112.90
77.16 Chloroform-d
72.45
38.40
37.17
35.37
28.80
22.50
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
136 134 132 130 128 126 124 122 120 118 116 114


BnO
O
NMe2
(E,E)-6j
Chloroform-d
7.36 7.35 7.35 7.34 7.33 7.33 7.32 7.31 7.31 7.31 7.31 7.30 7.29 7.29 7.29 7.28 7.26
6.40 6.38 6.37 6.37 6.34 6.34 5.80 5.78 5.78 5.76 5.76 5.74 5.73 5.72 5.71
4.79
2.93
2.00 2.00 1.98 1.97 1.97 1.68 1.67 1.65 1.63 1.62 1.60 1.58
0.88 0.86
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6.34 6.34 6.34
1.15
6.42 6.40 6.38 6.36 6.34 6.32
5.83 5.80 5.78 5.78 5.76 5.76 5.74 5.73 5.72 5.71
1.07
1.24
5.85 5.80 5.75 5.70
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1.95 1.85 1.75 1.65
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1.15
1.07
1.24
2.00
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2.25
1.39
3.05
2.98
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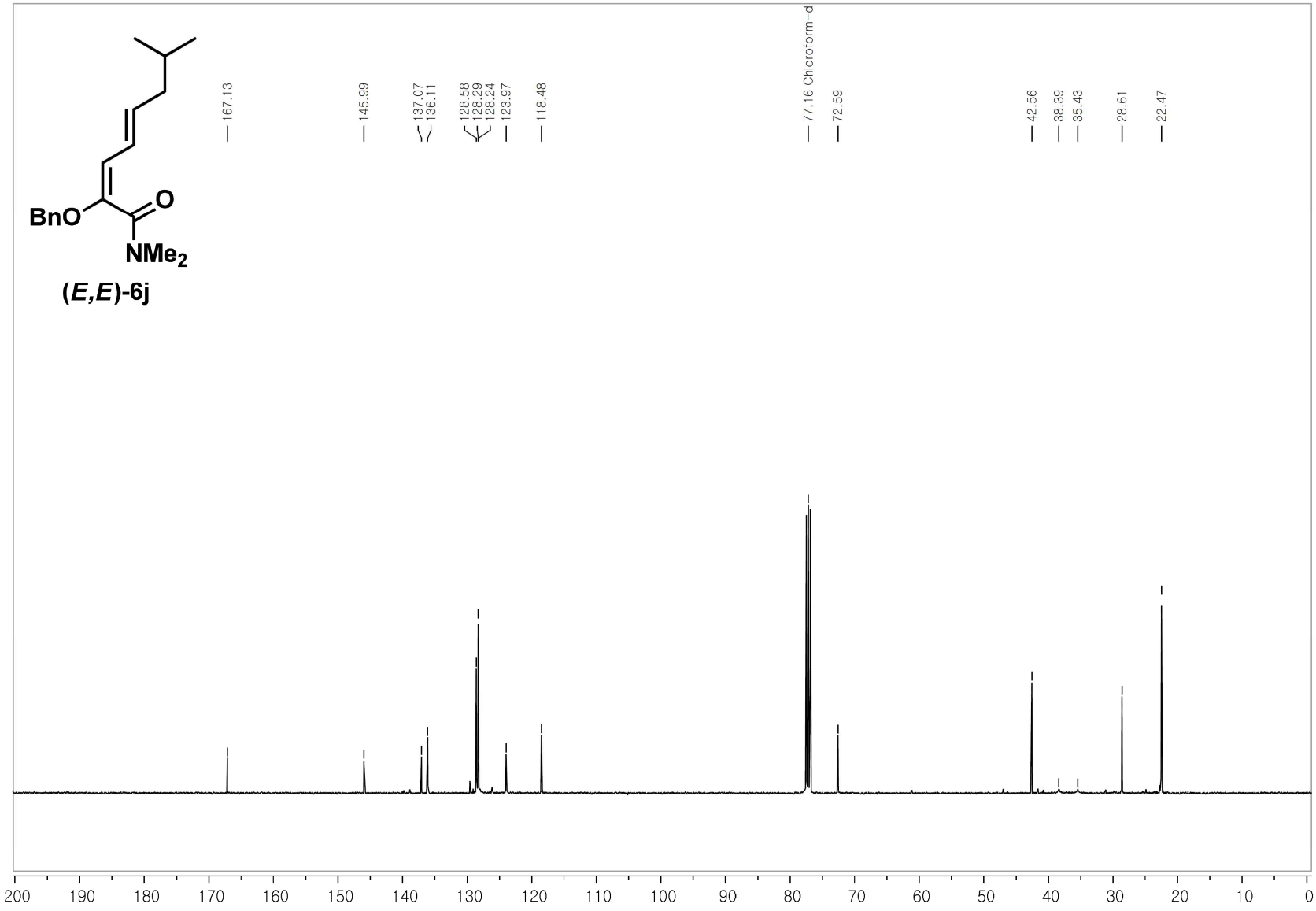
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118.48
77.16 Chloroform-d
72.59
42.56
38.39
35.43
28.61
22.47
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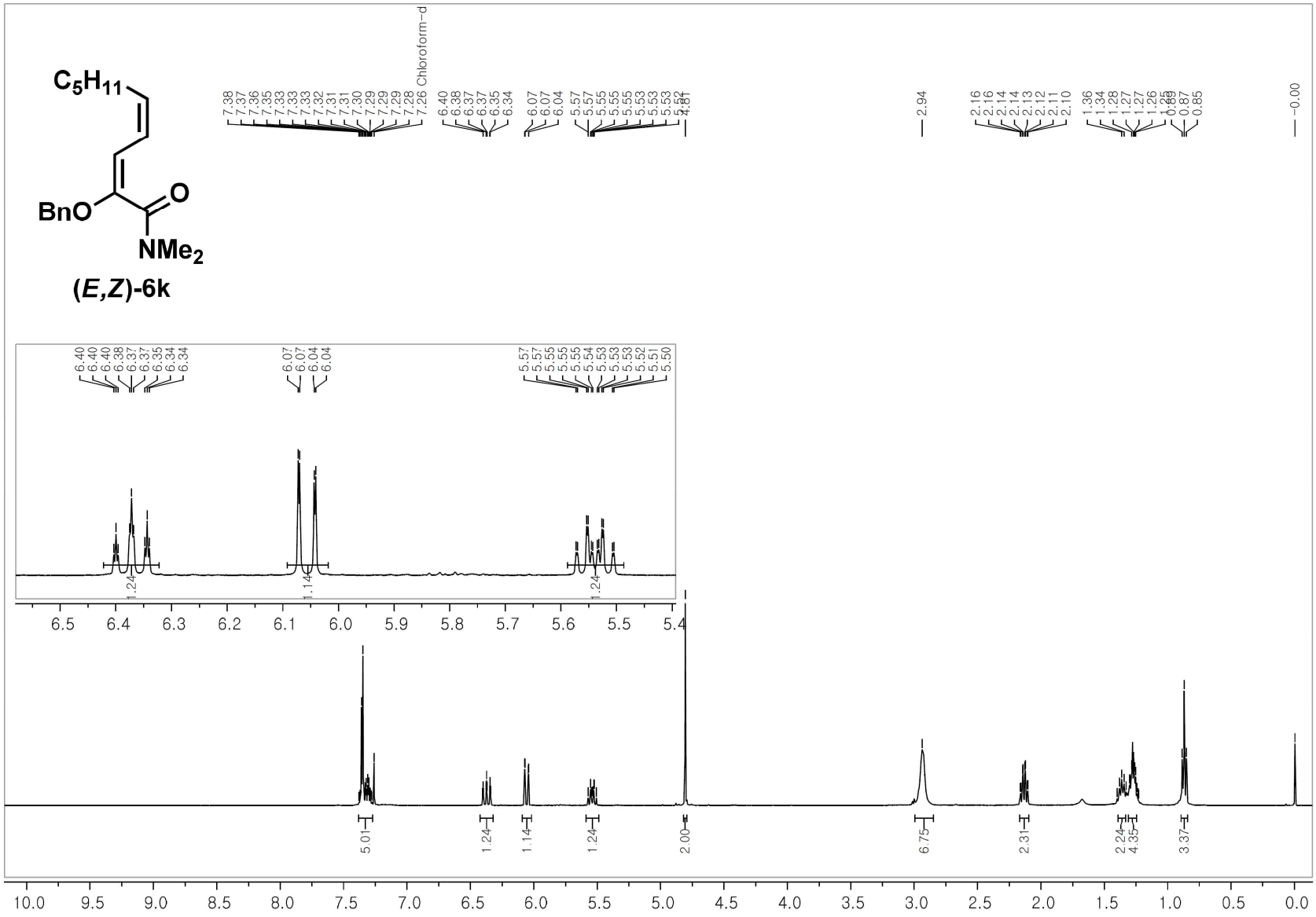
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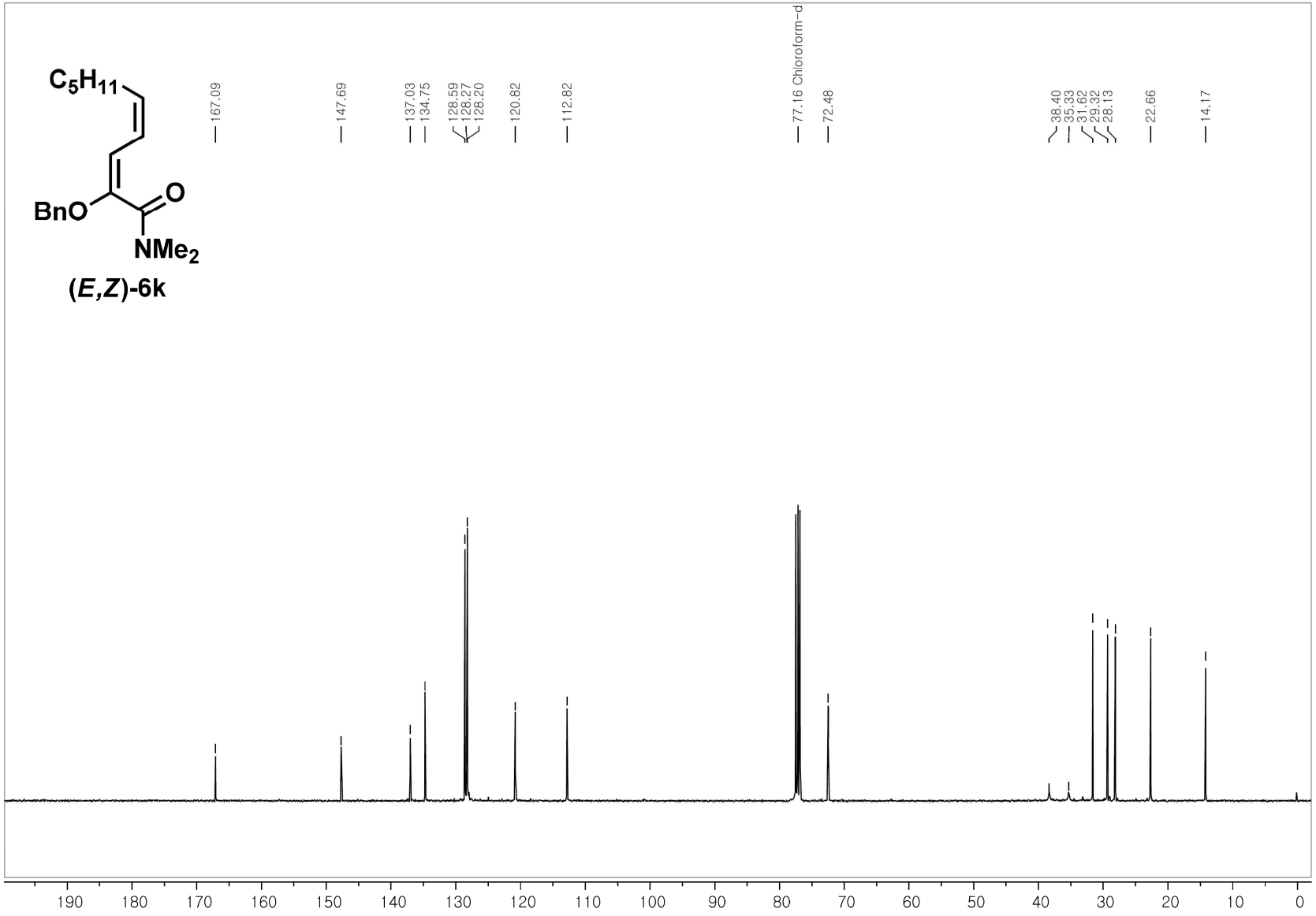
Chloroform-d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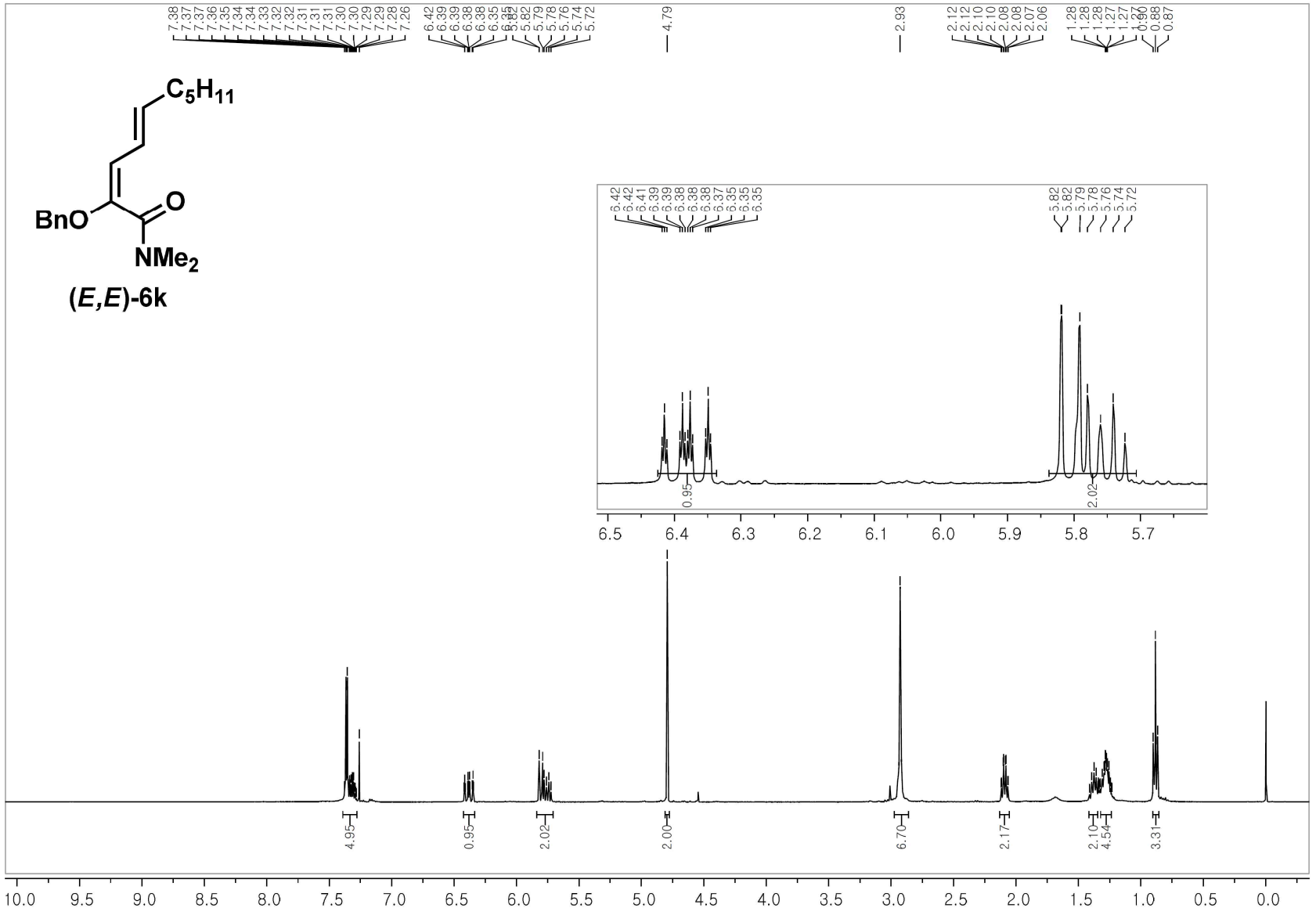
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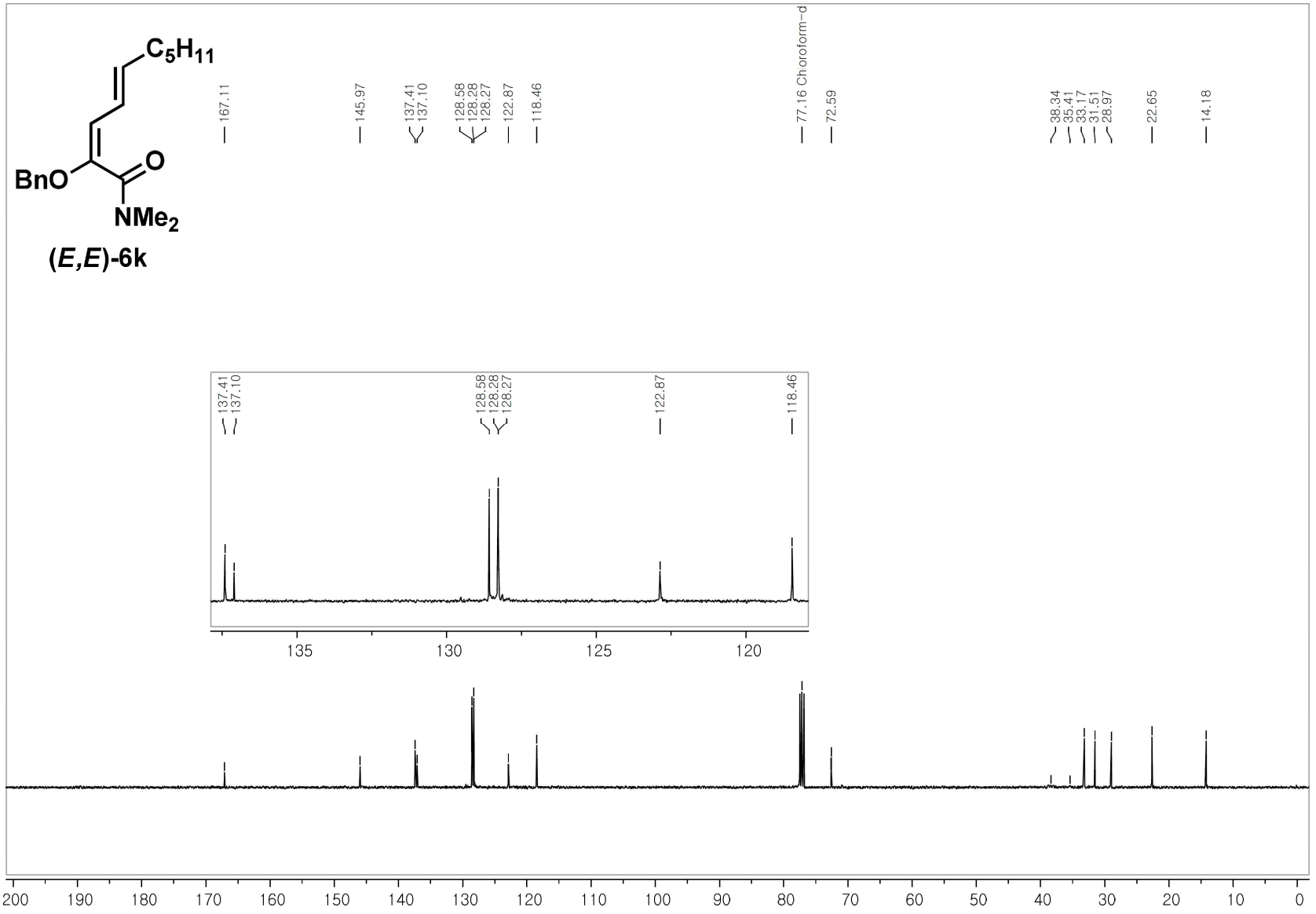
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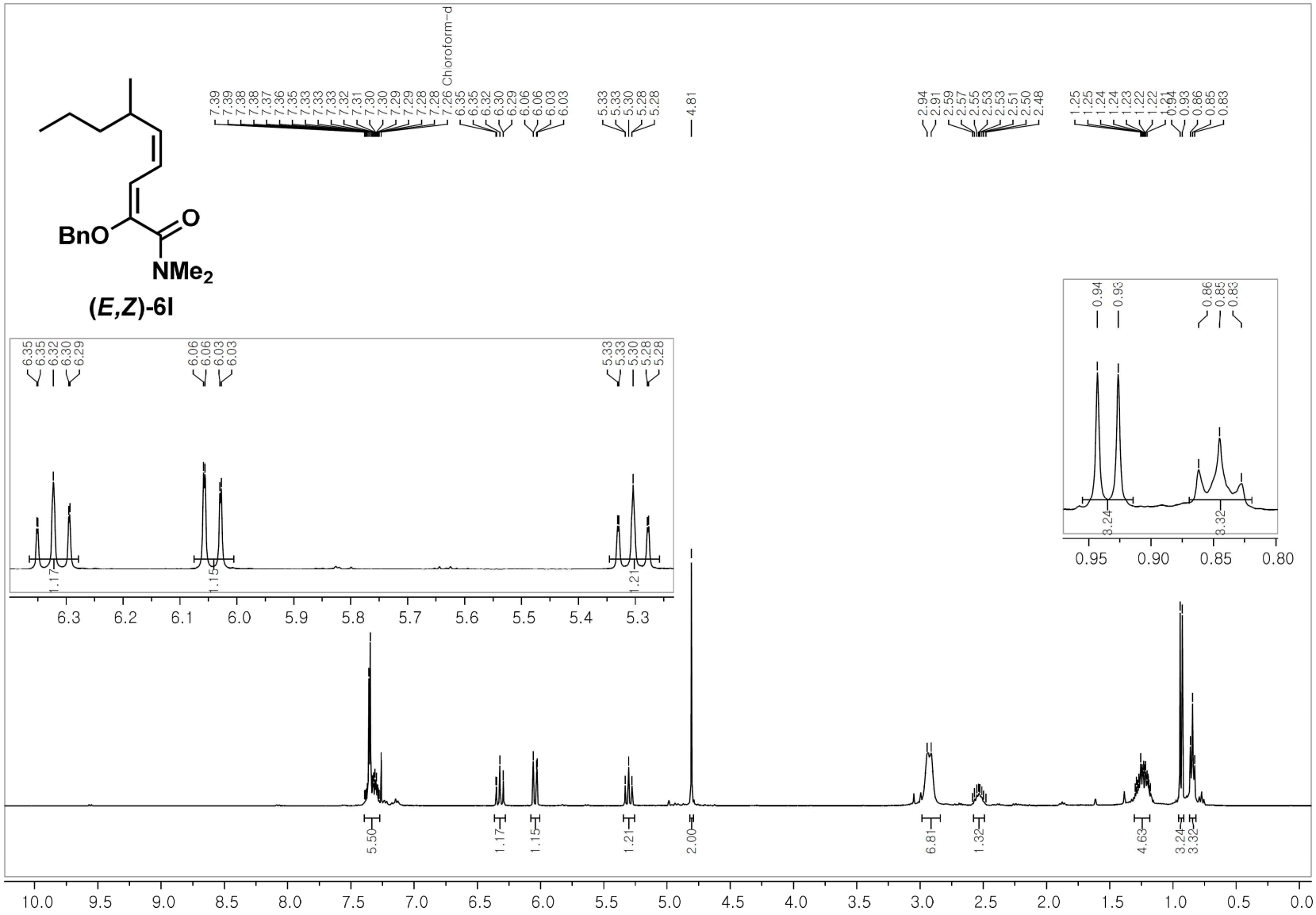
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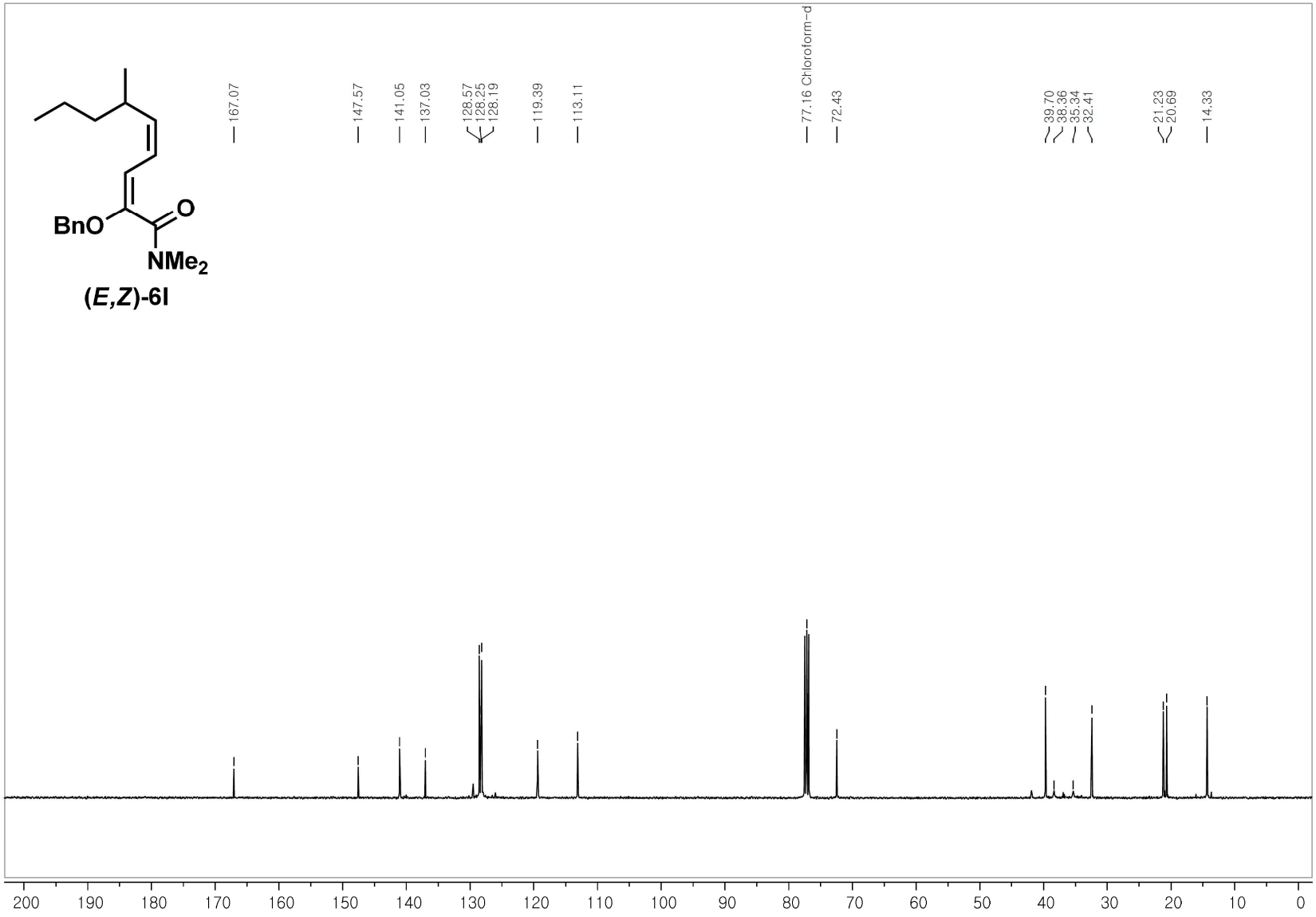
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38.36
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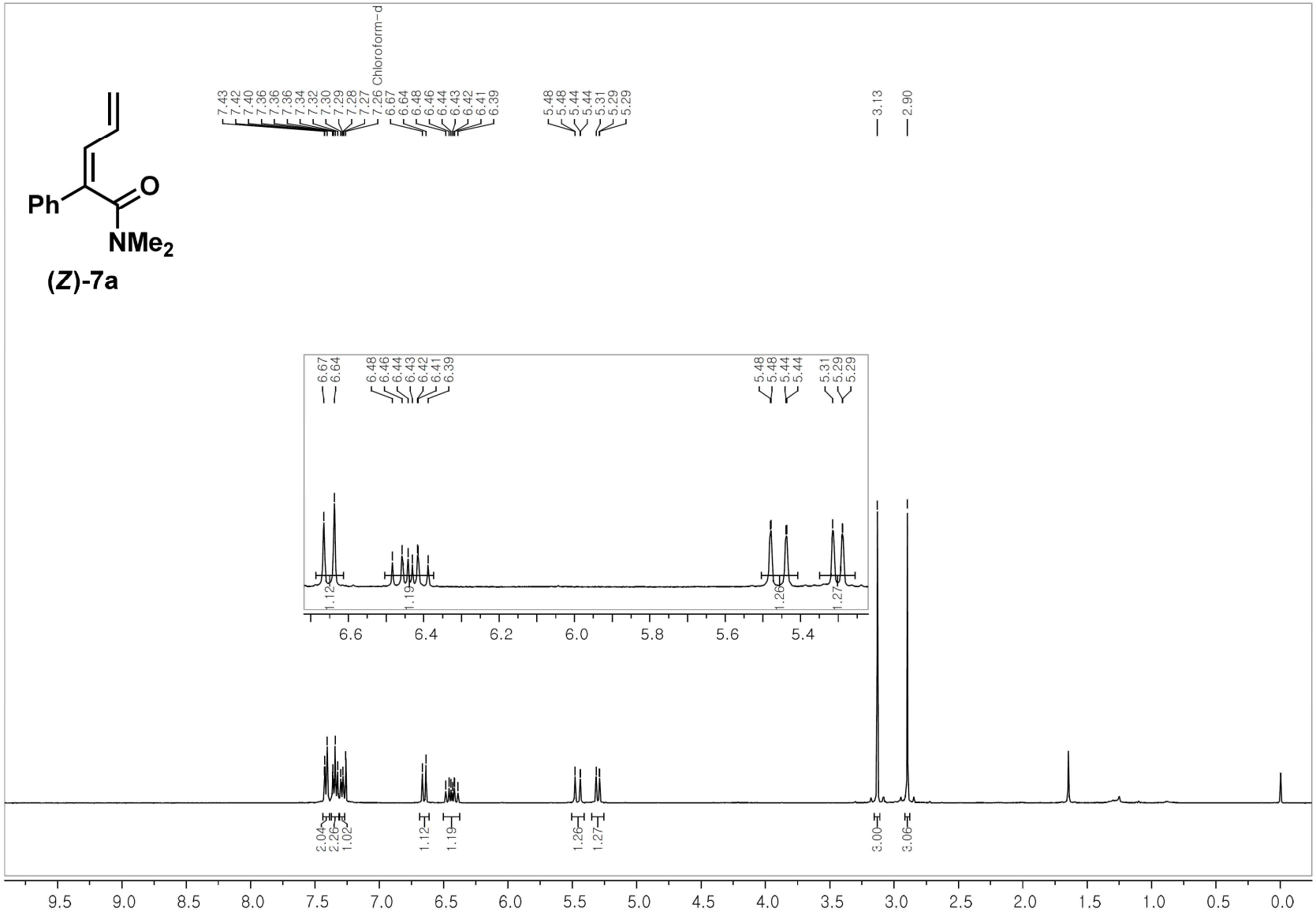
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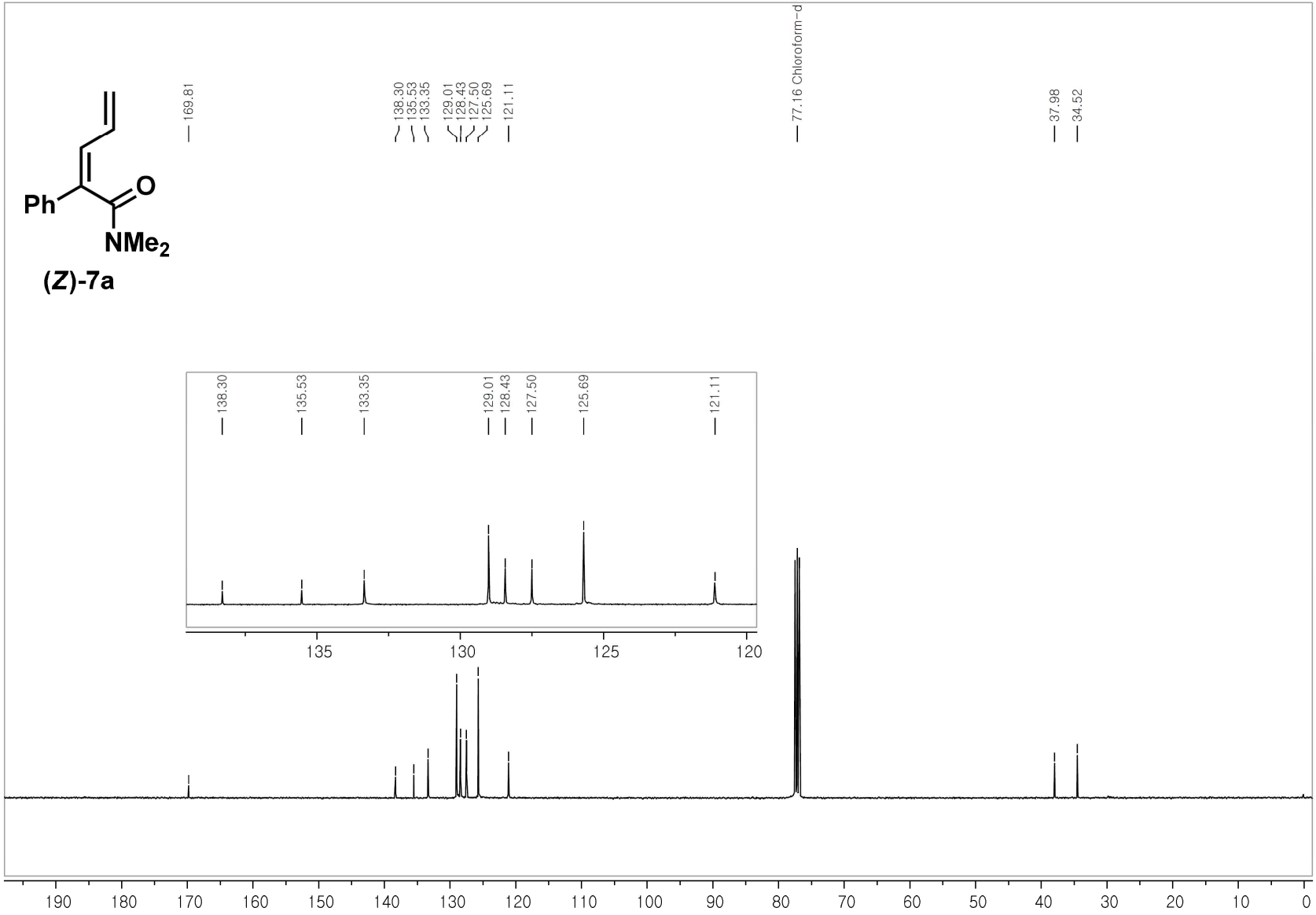
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180
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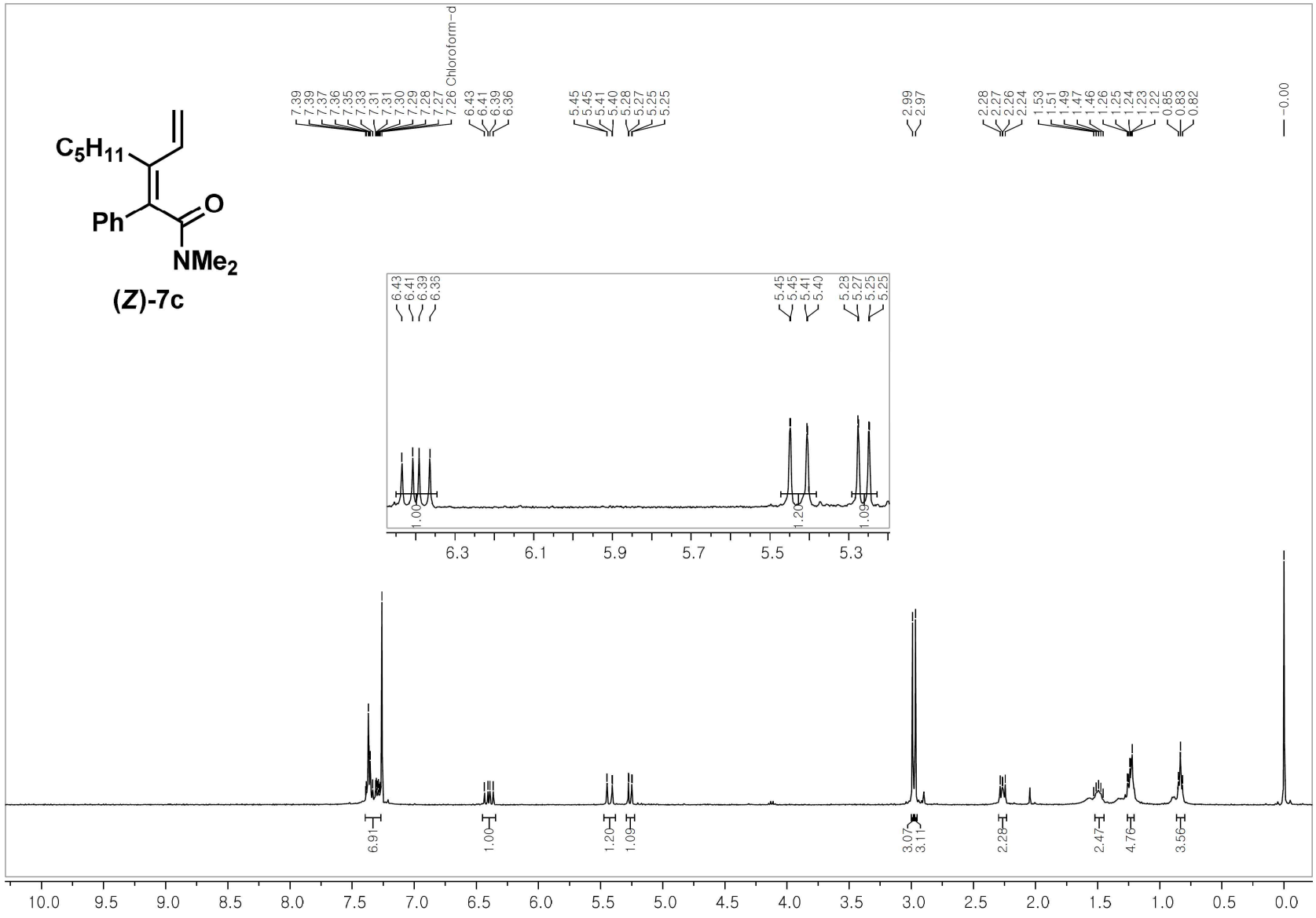
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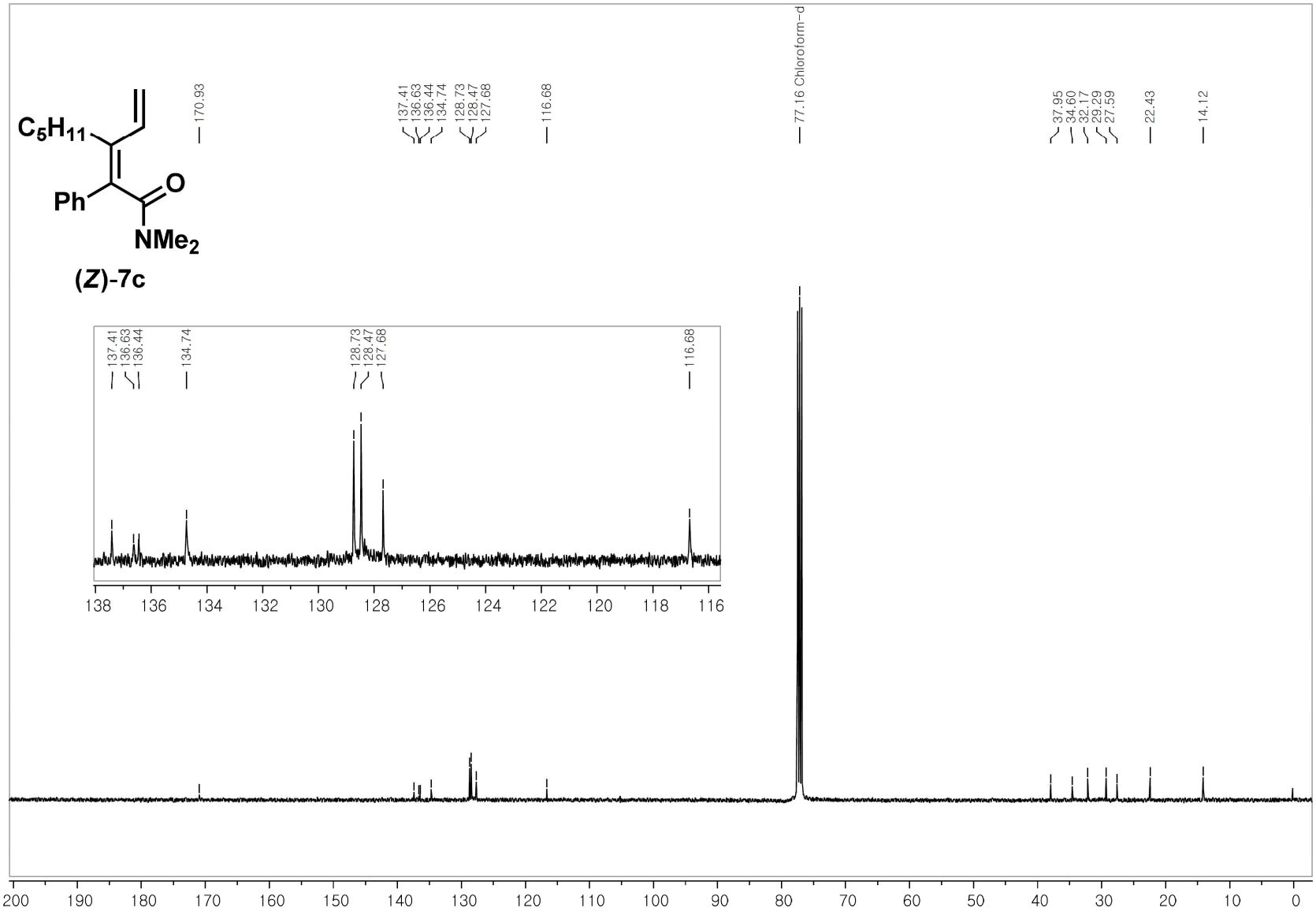
Chloroform-d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77.16 Chloroform-d
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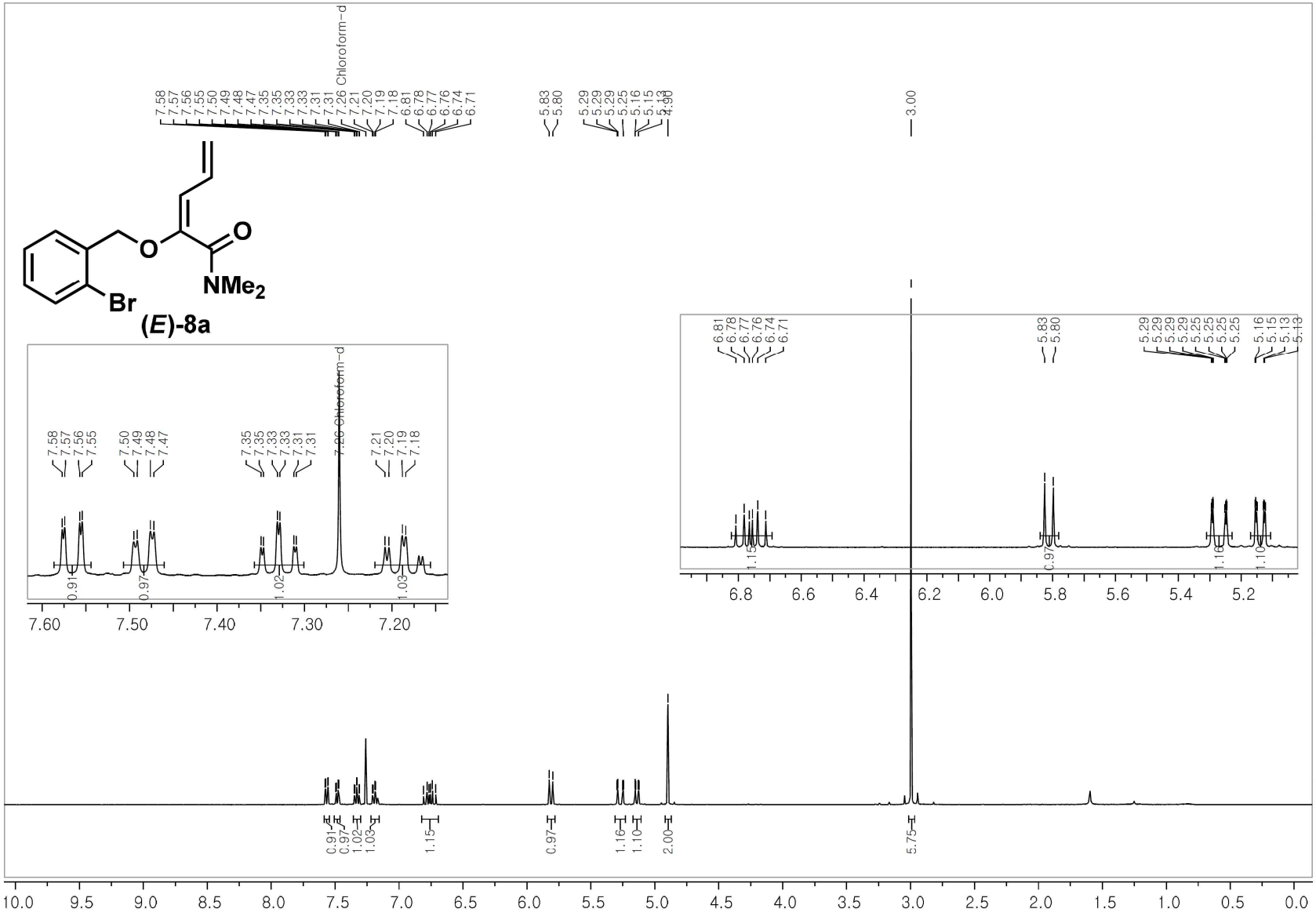
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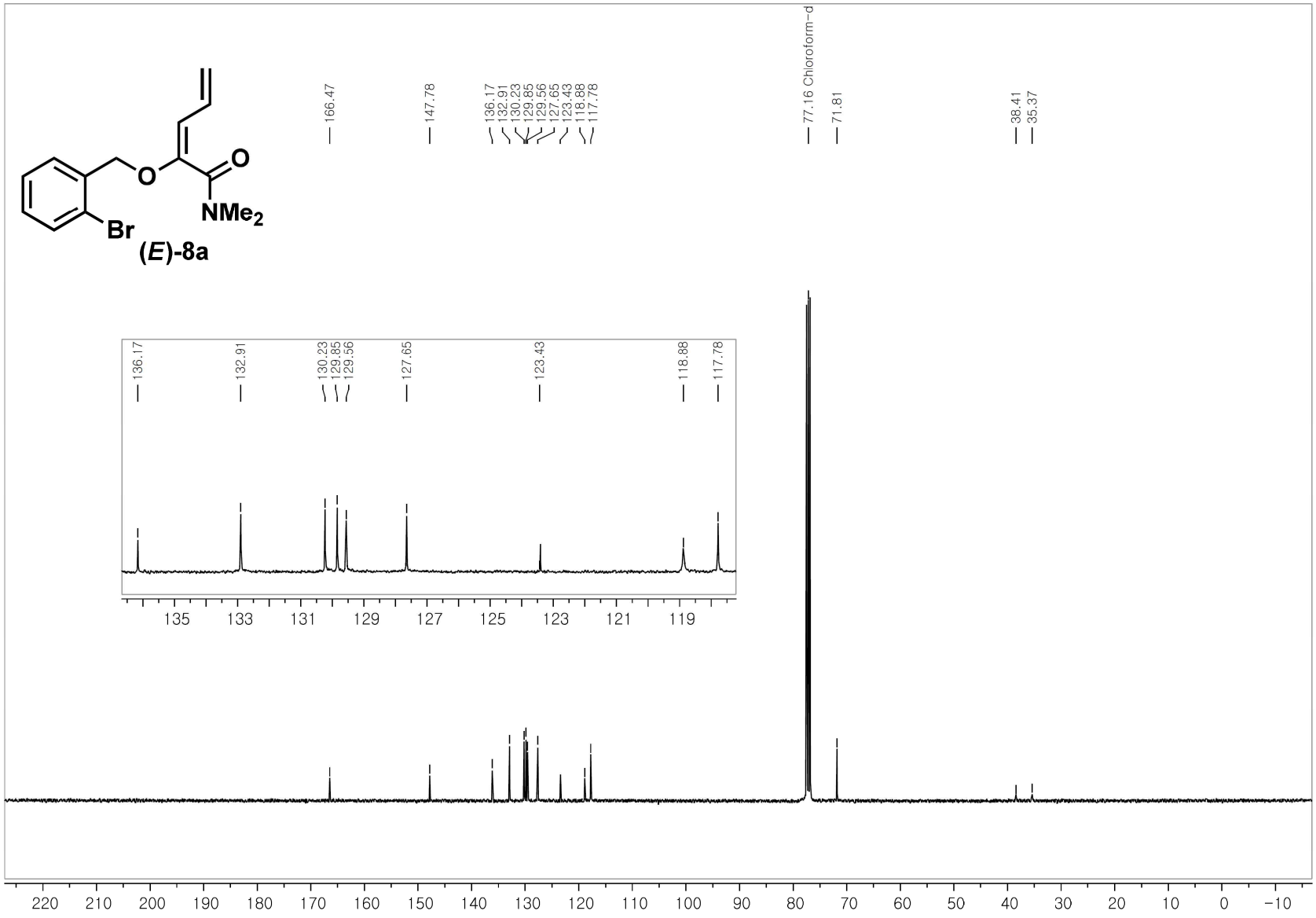
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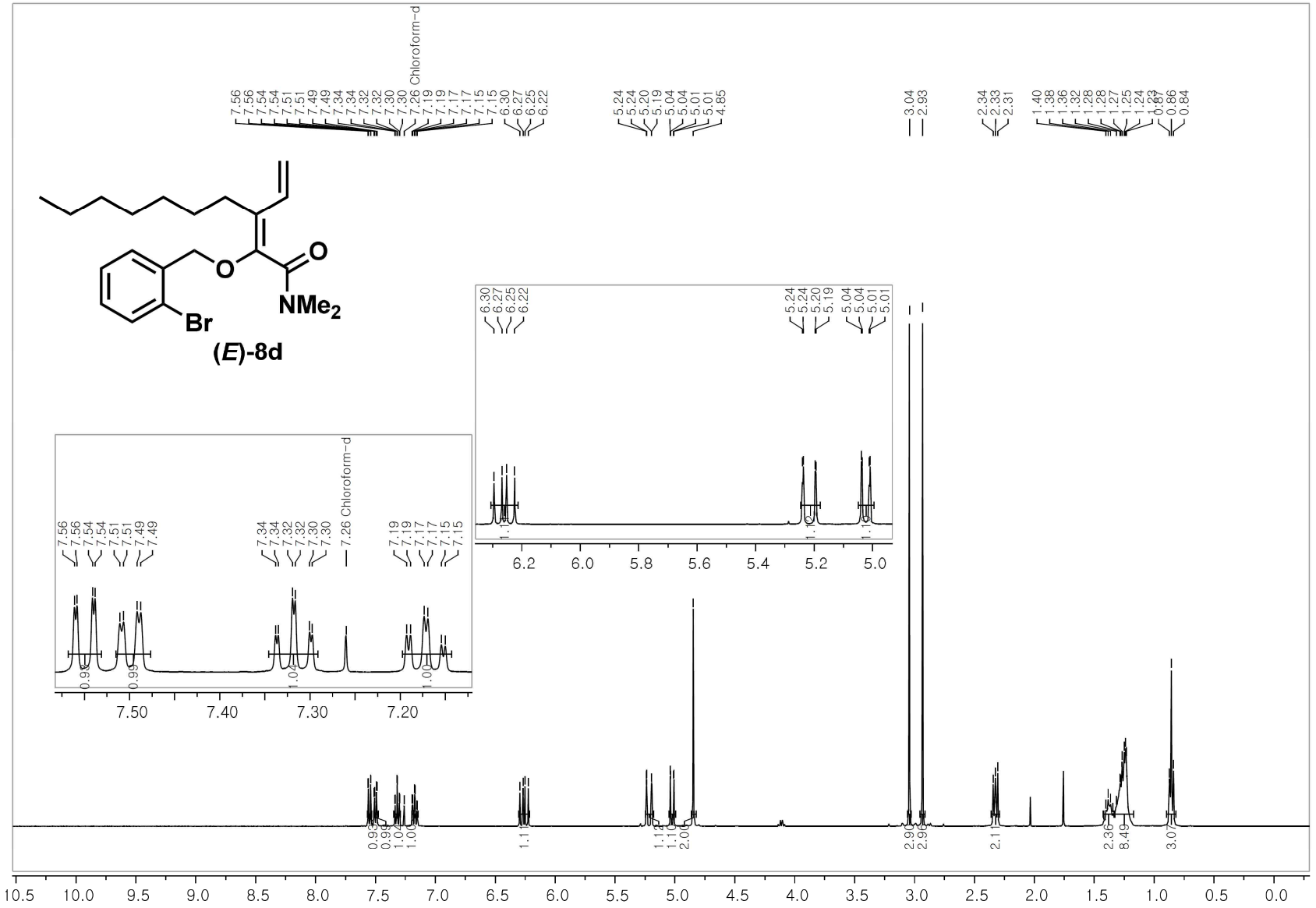
35.37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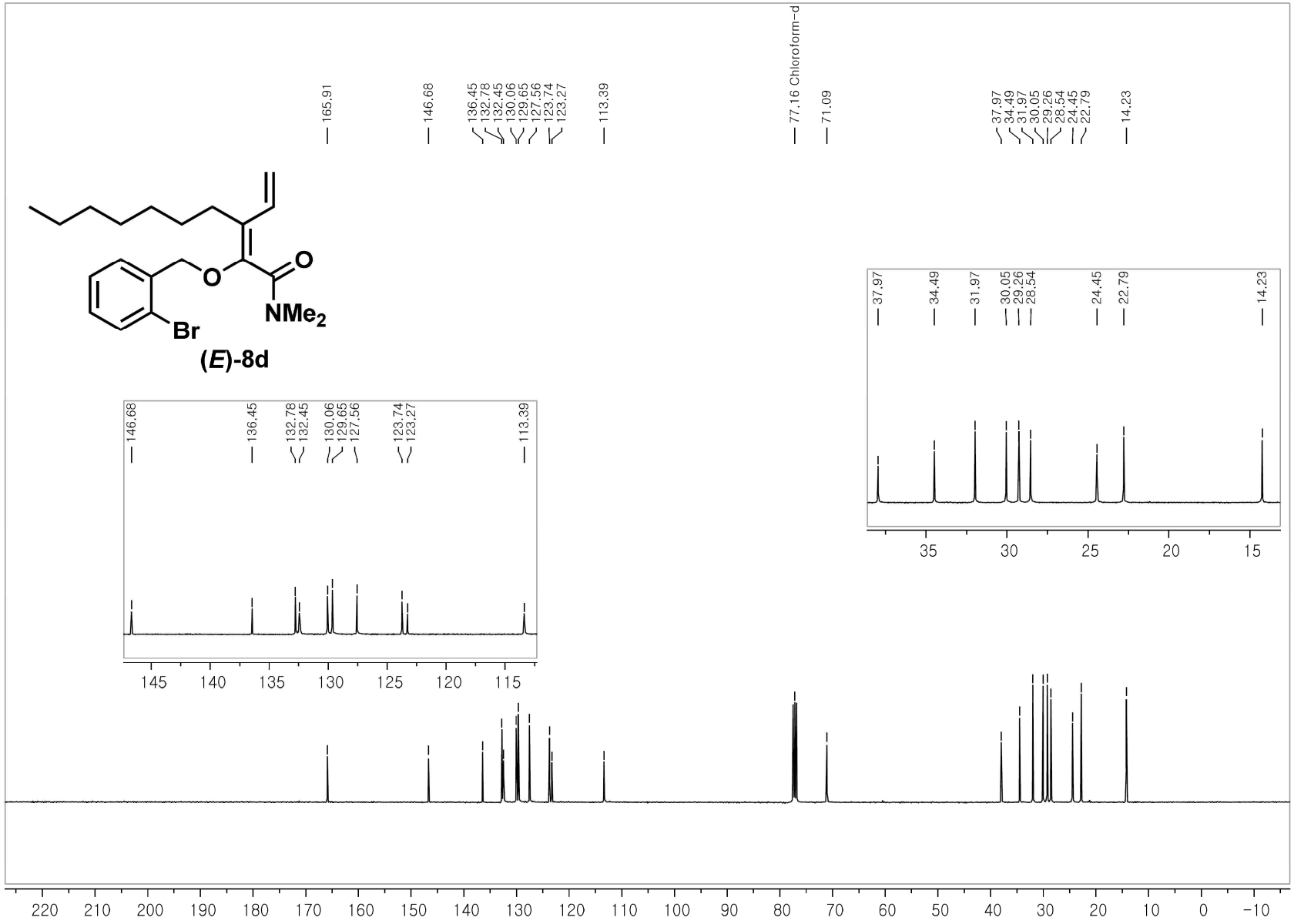
Br
O
O
NMe2
Chloroform-d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71.09
37.97
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O
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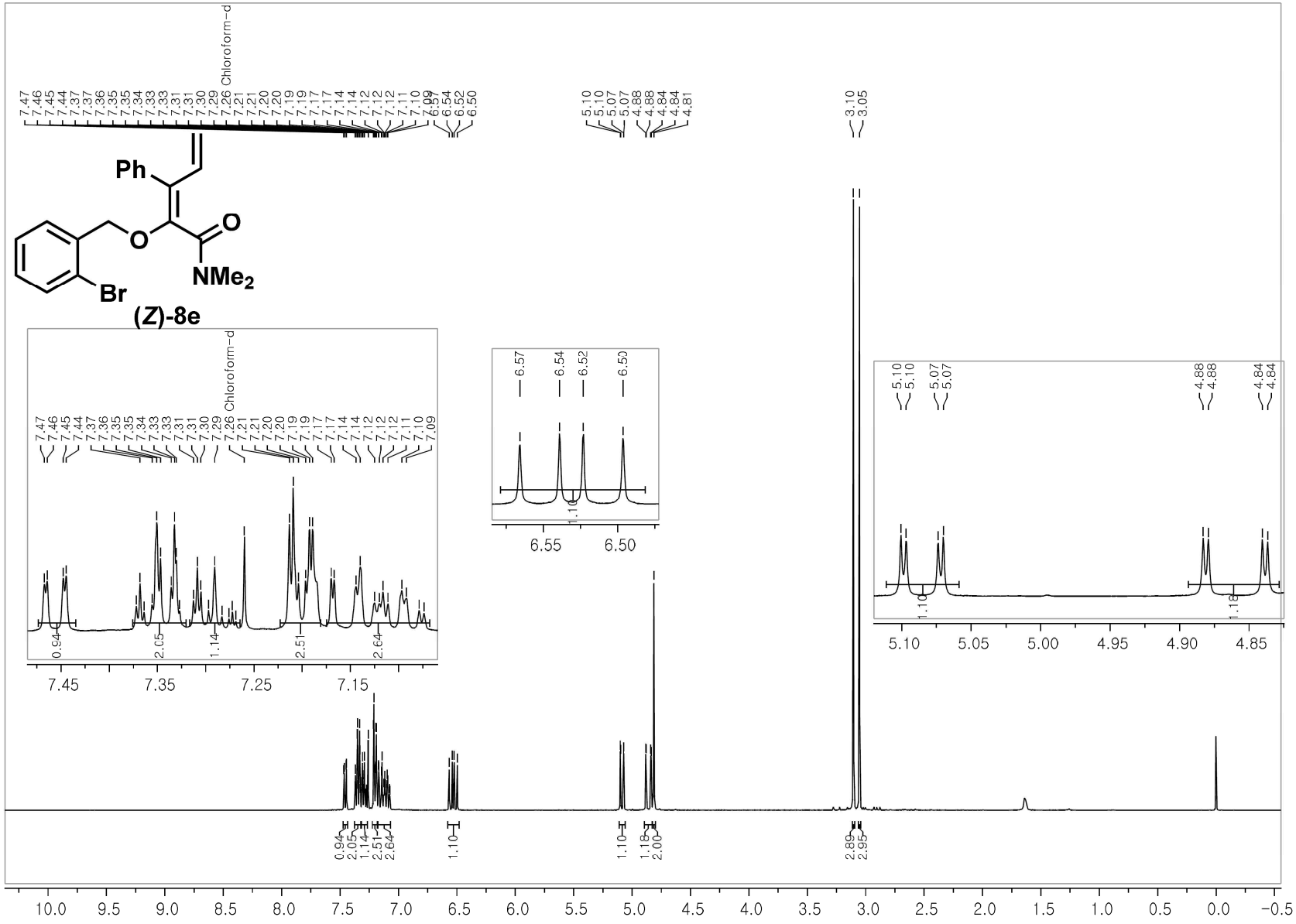
Br
(E)-8d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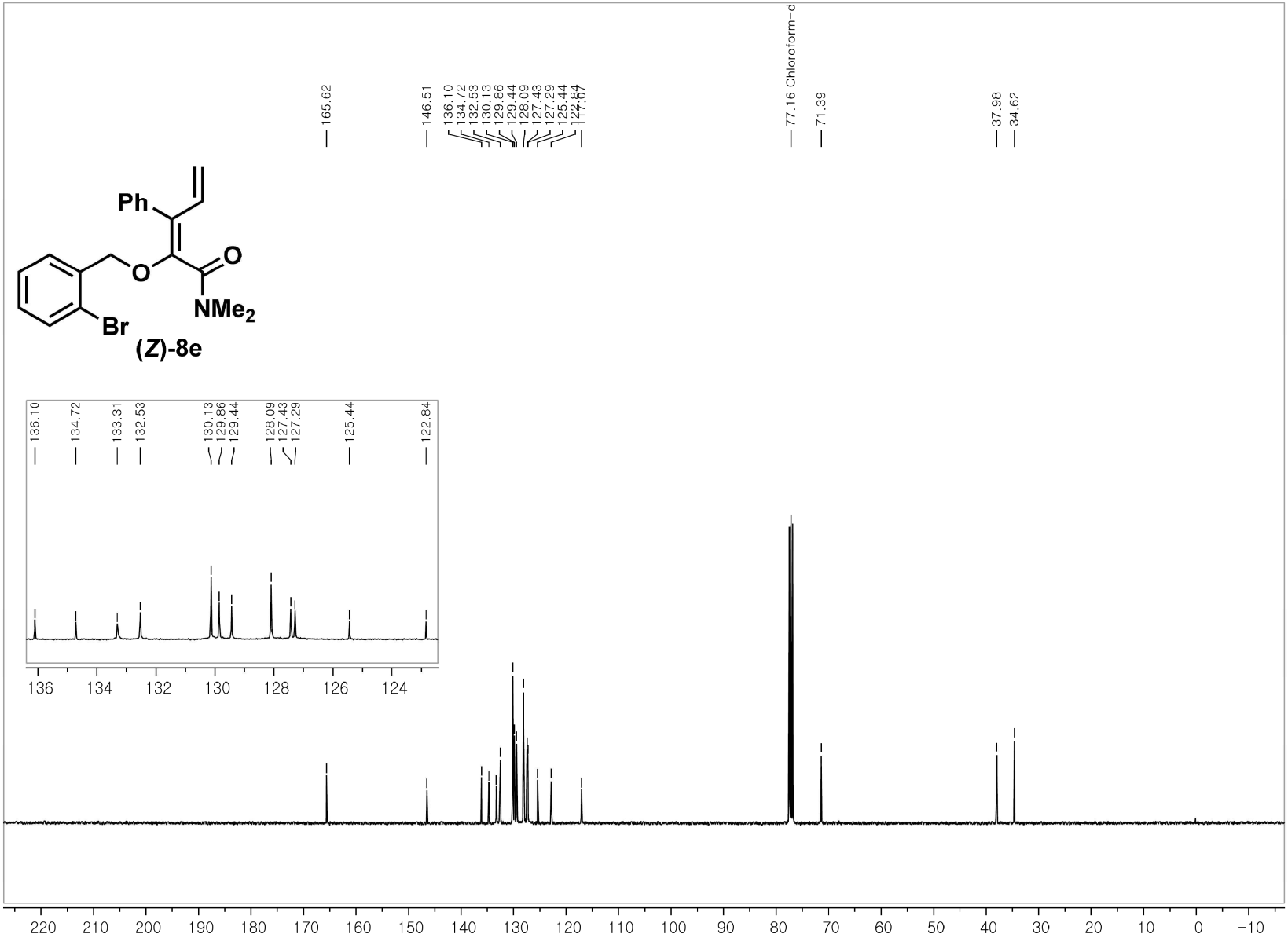
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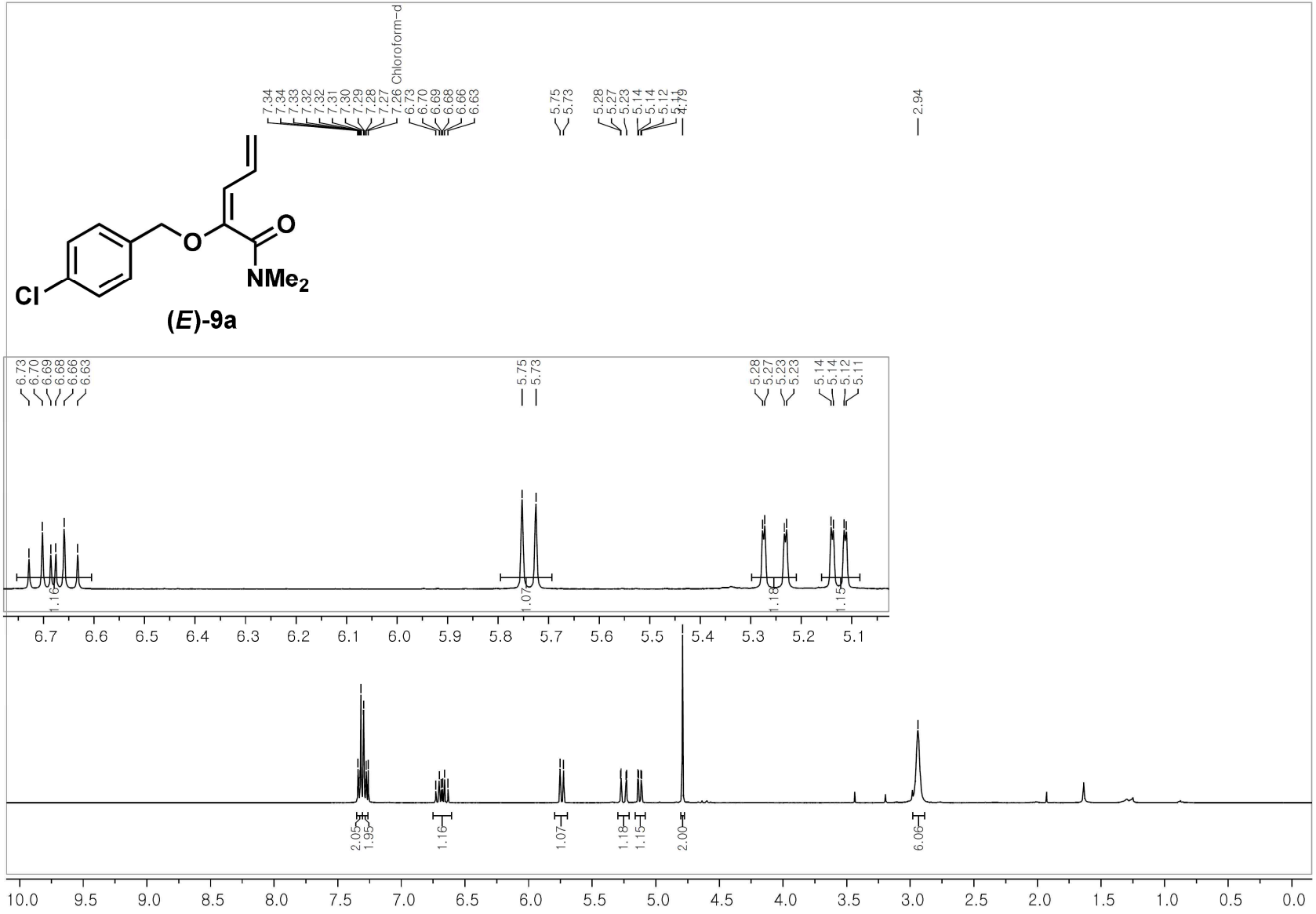
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6.70
6.69
6.68
6.66
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5.75
5.73
5.28
5.27
5.23
5.14
5.14
5.12
5.11
4.79
2.94
Cl
O
O
NMe2
(E)-9a
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1.07
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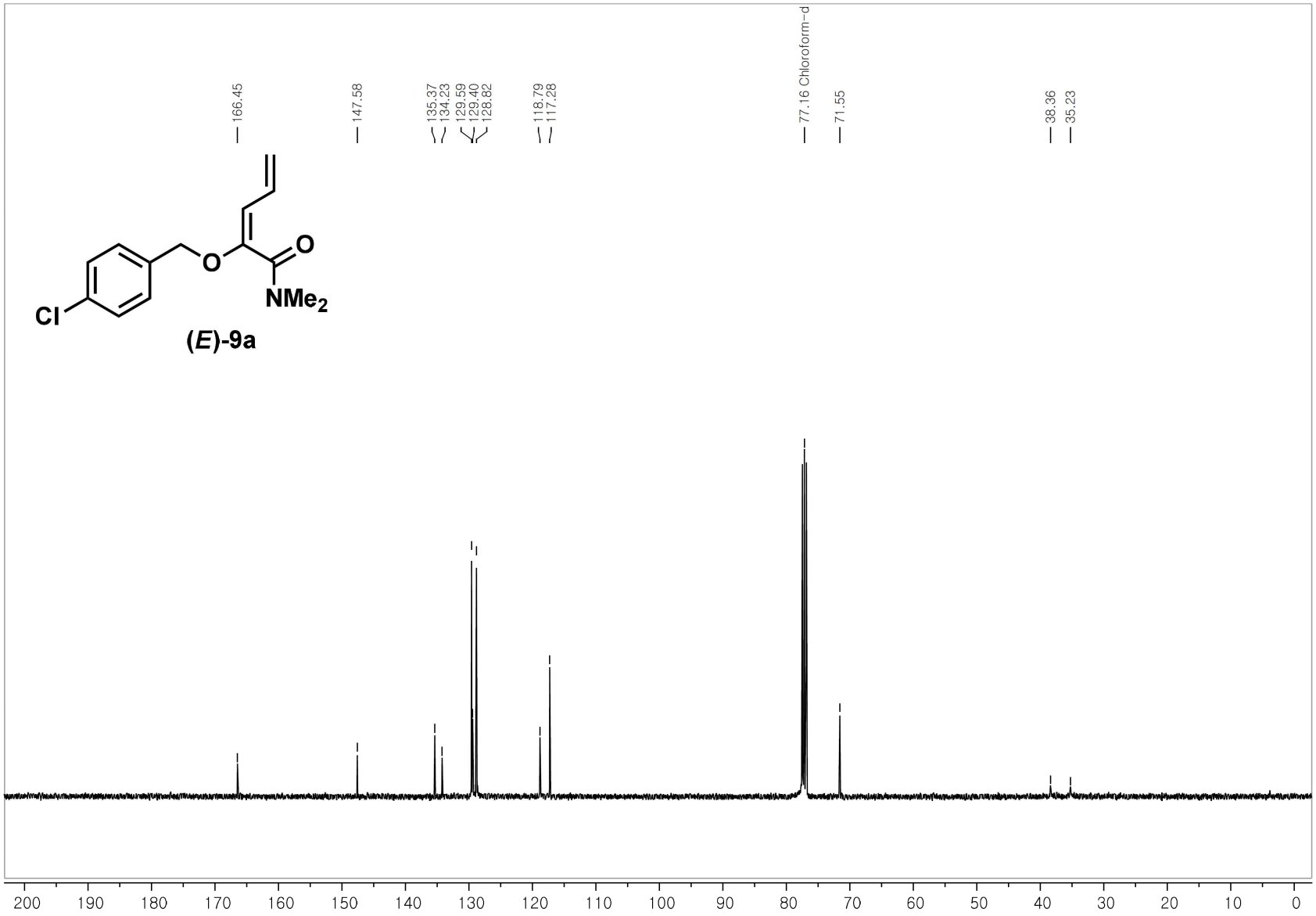
2.00
6.06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35.23
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O
NMe2
Cl
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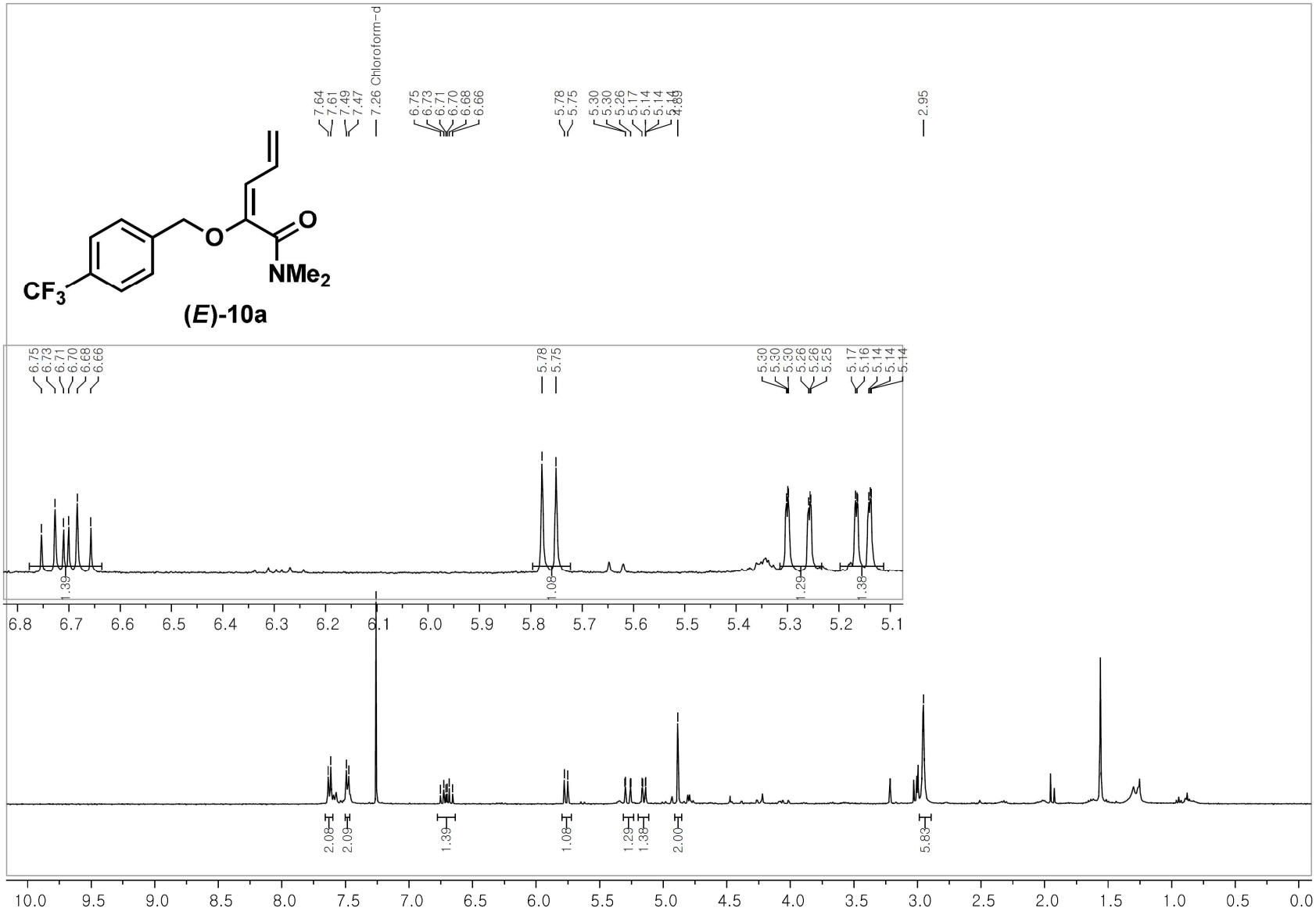
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5.17
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CF3
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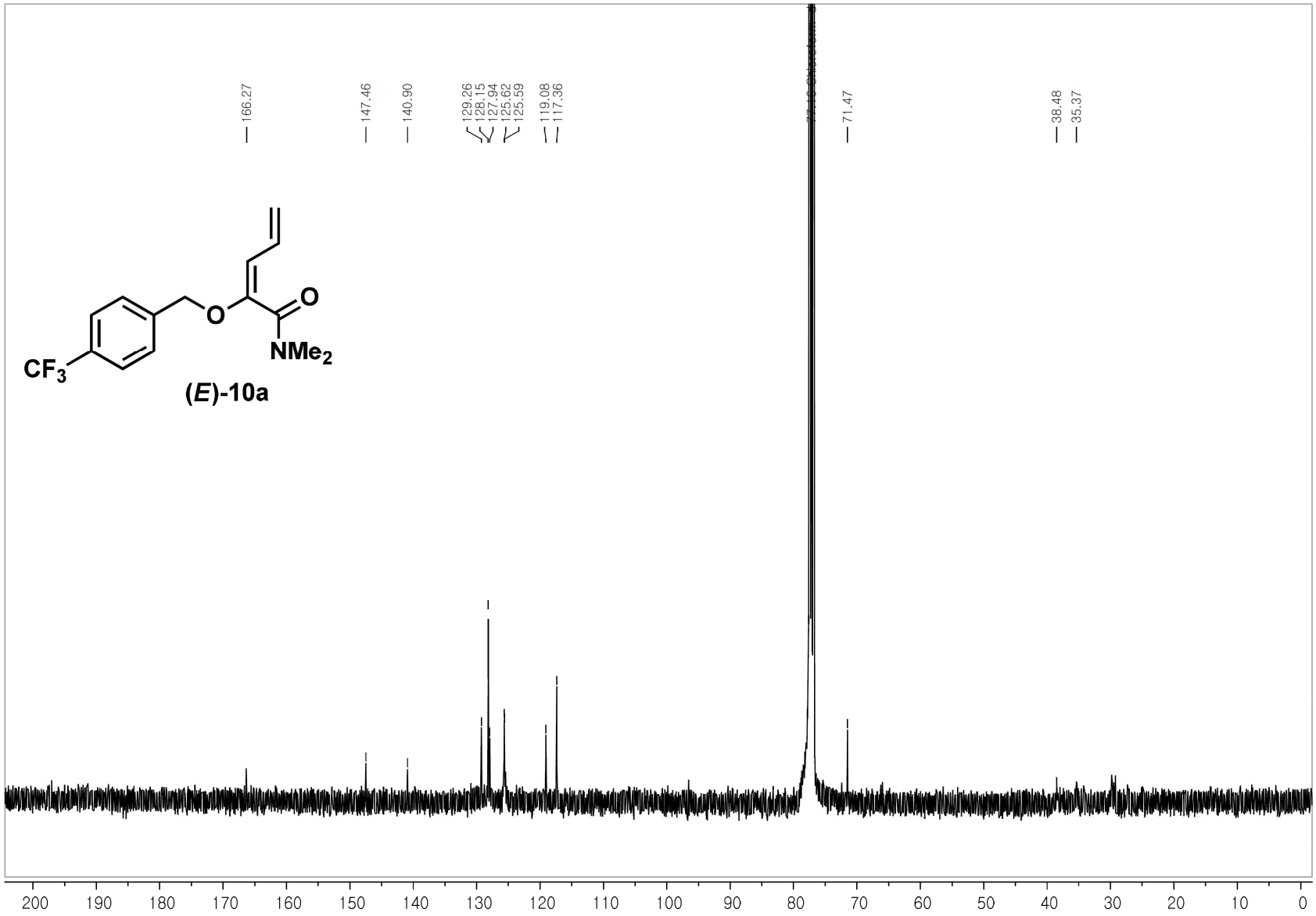
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O
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CF3
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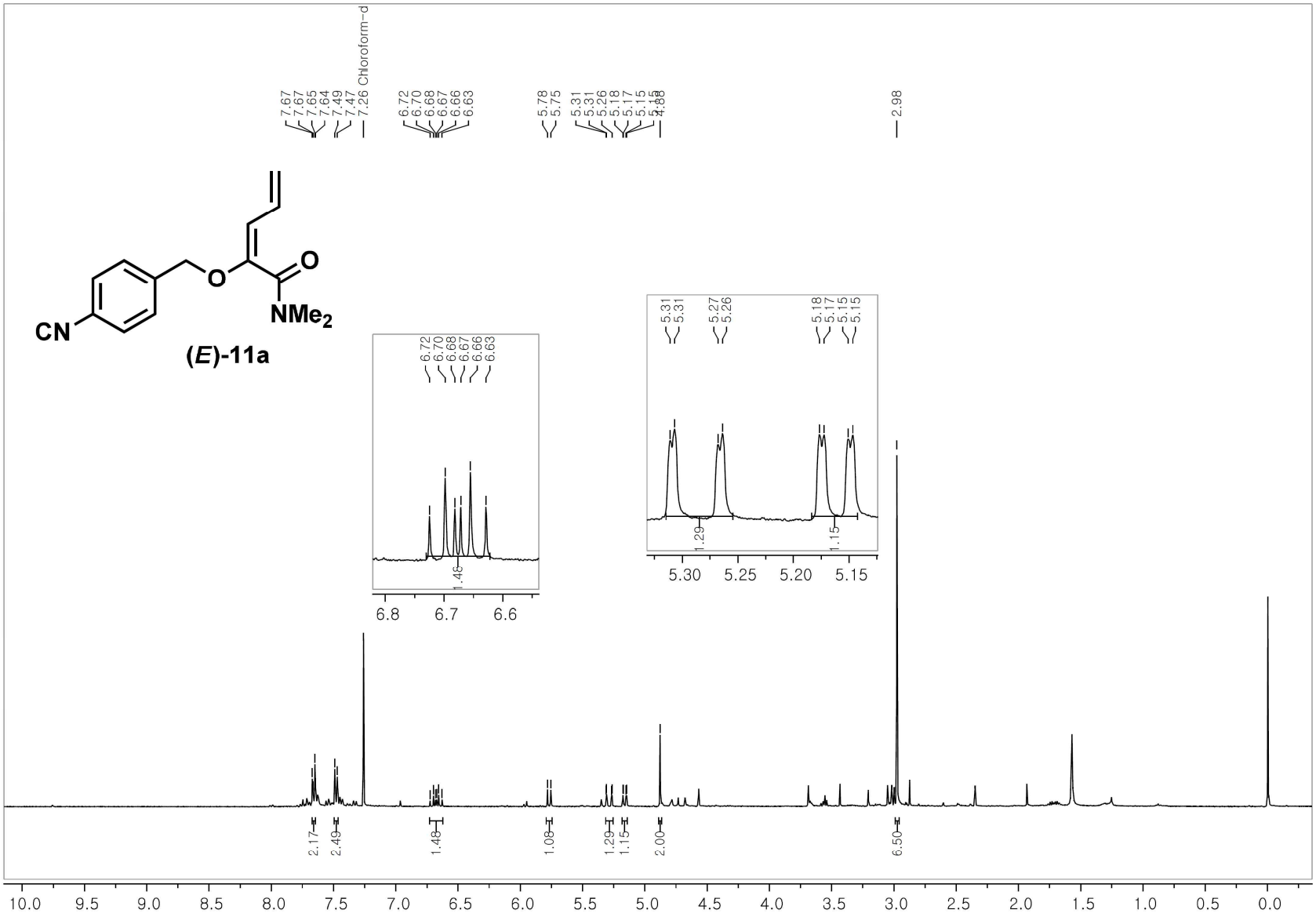
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O
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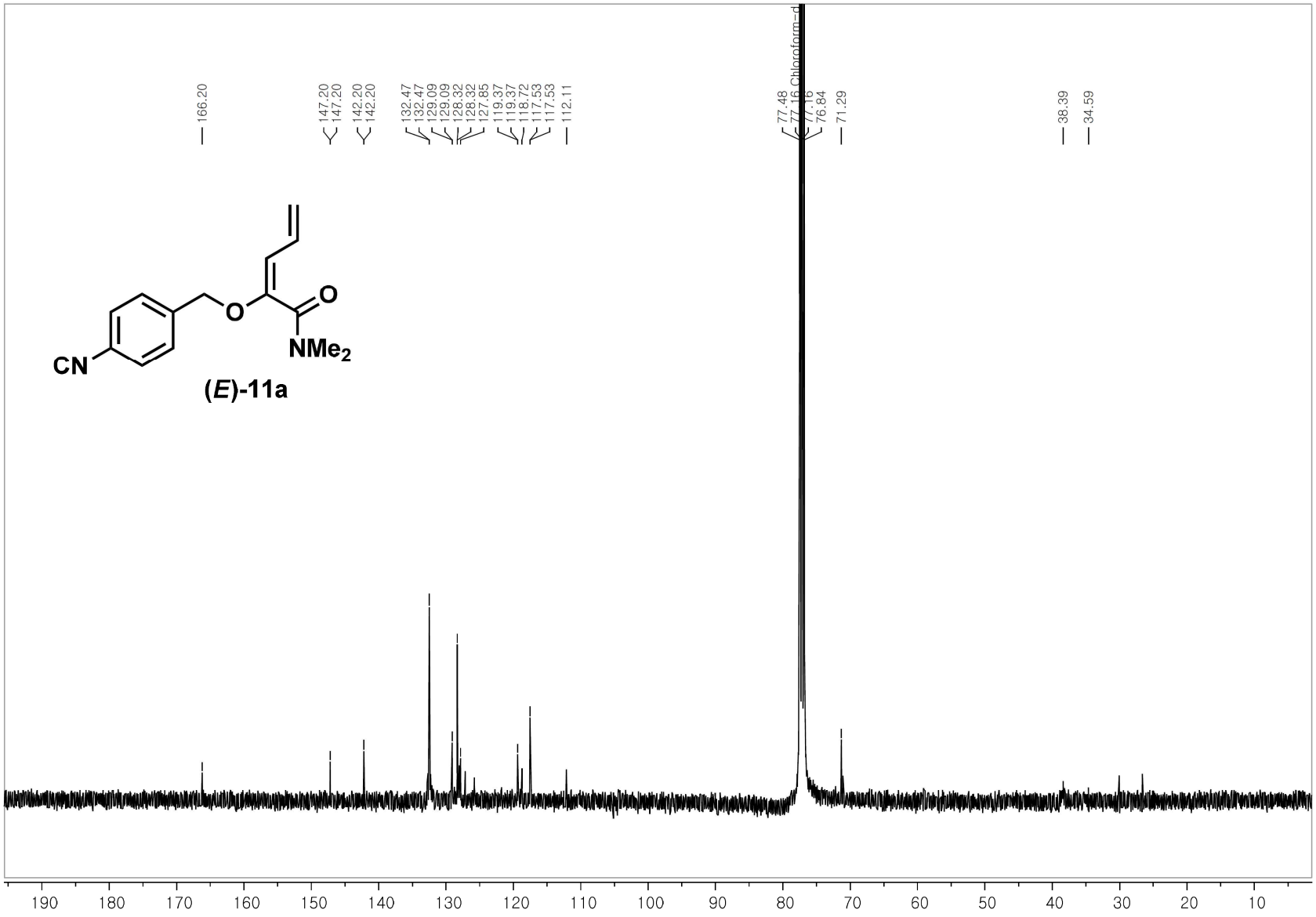
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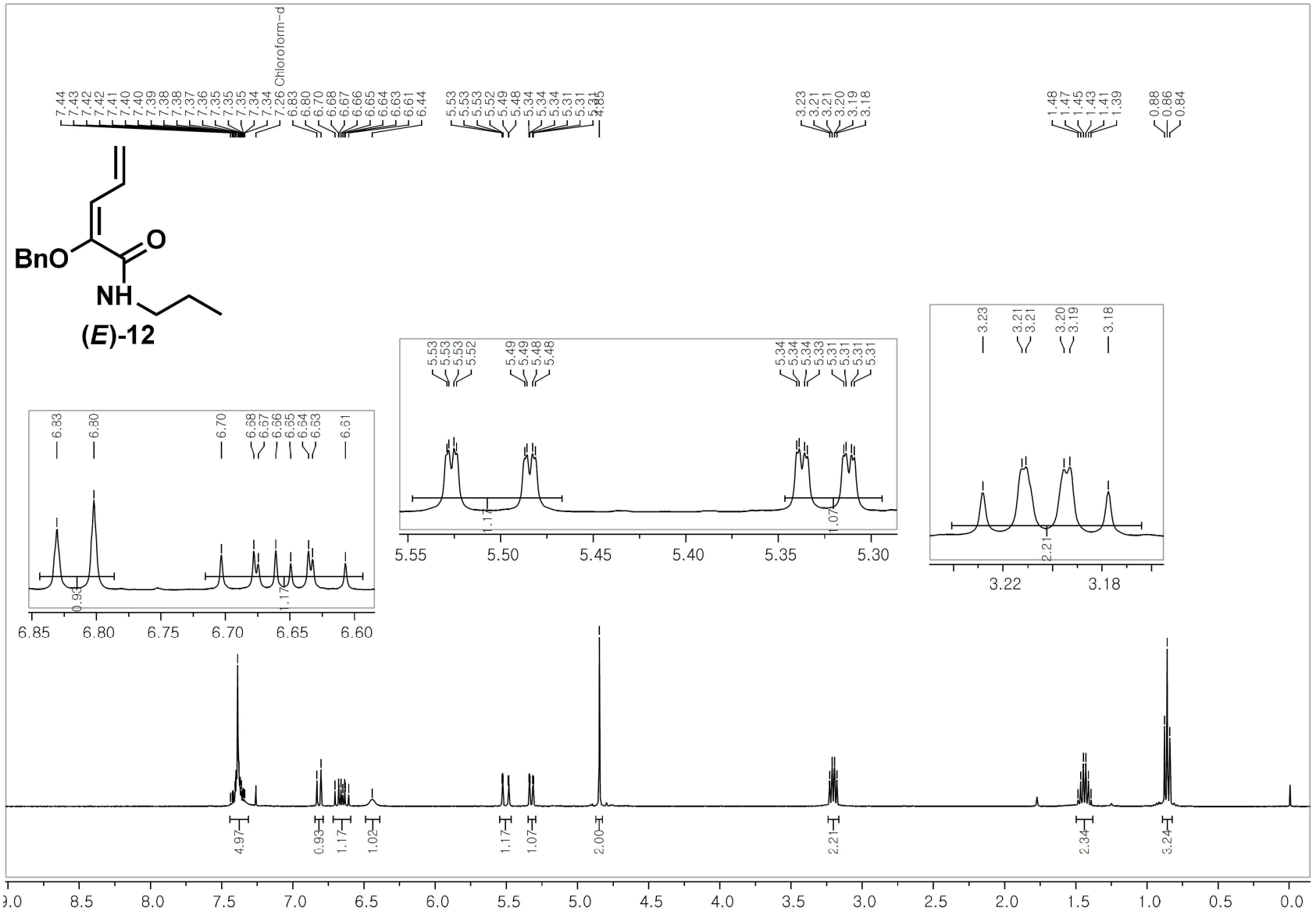
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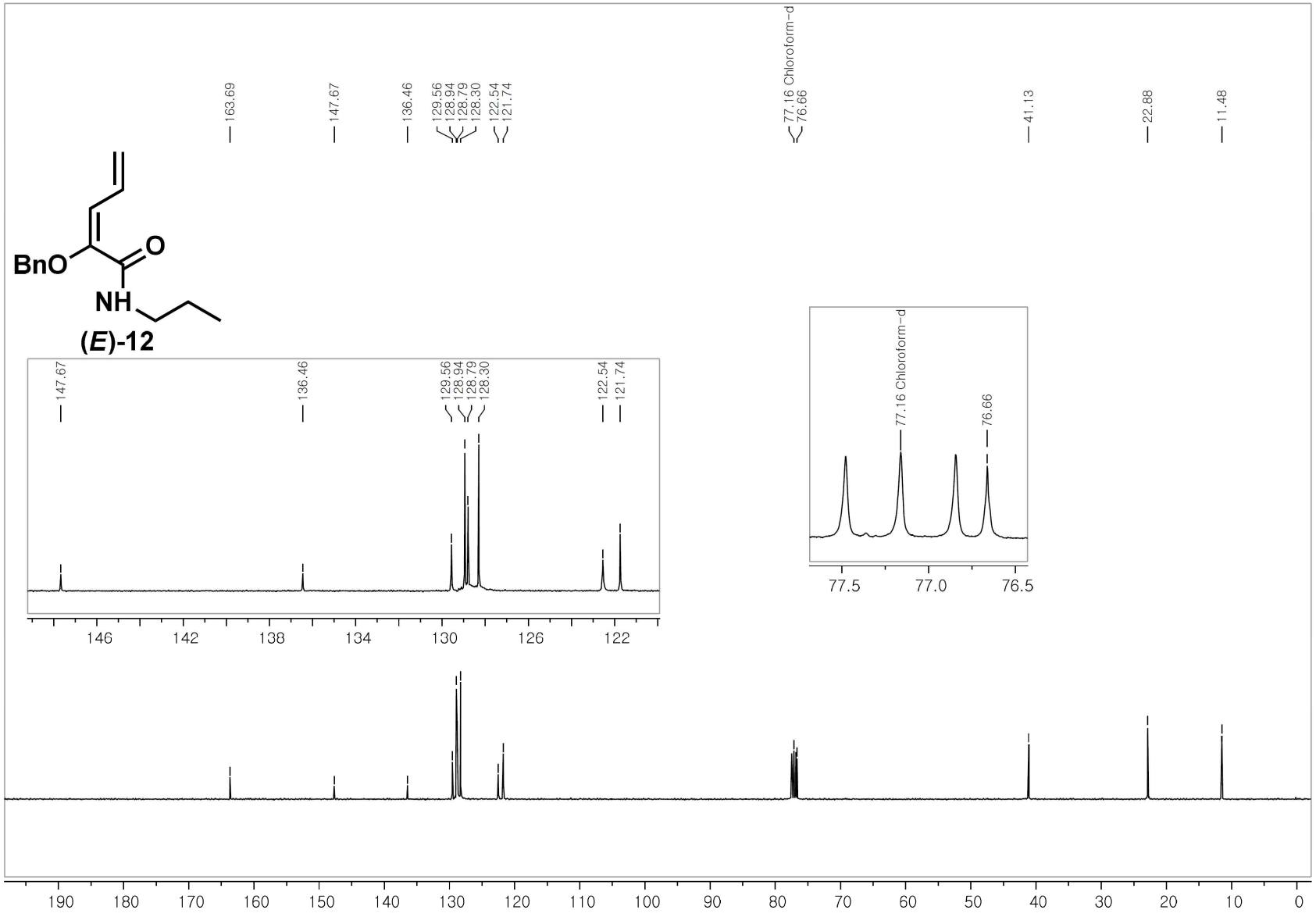
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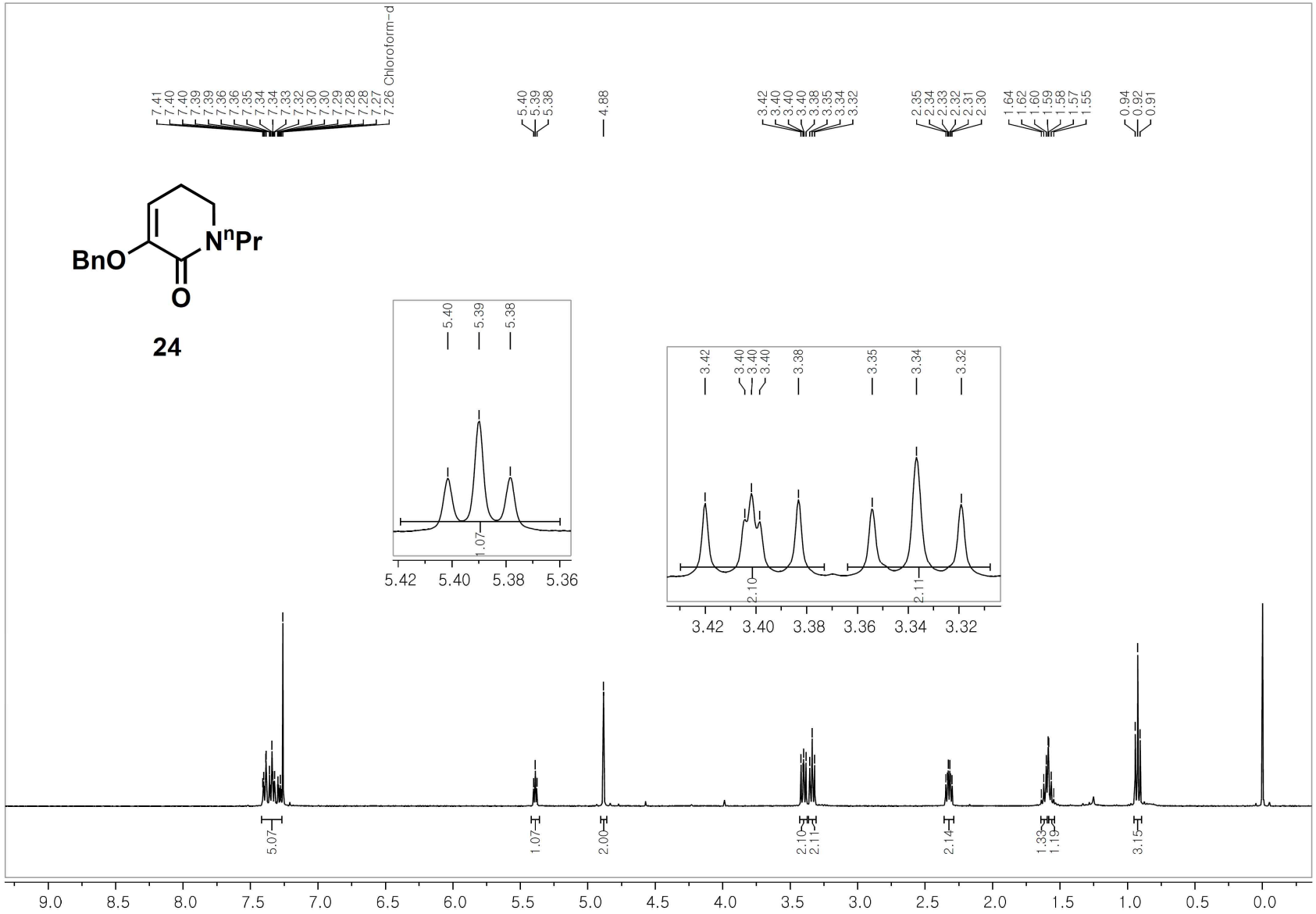
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N^nPr
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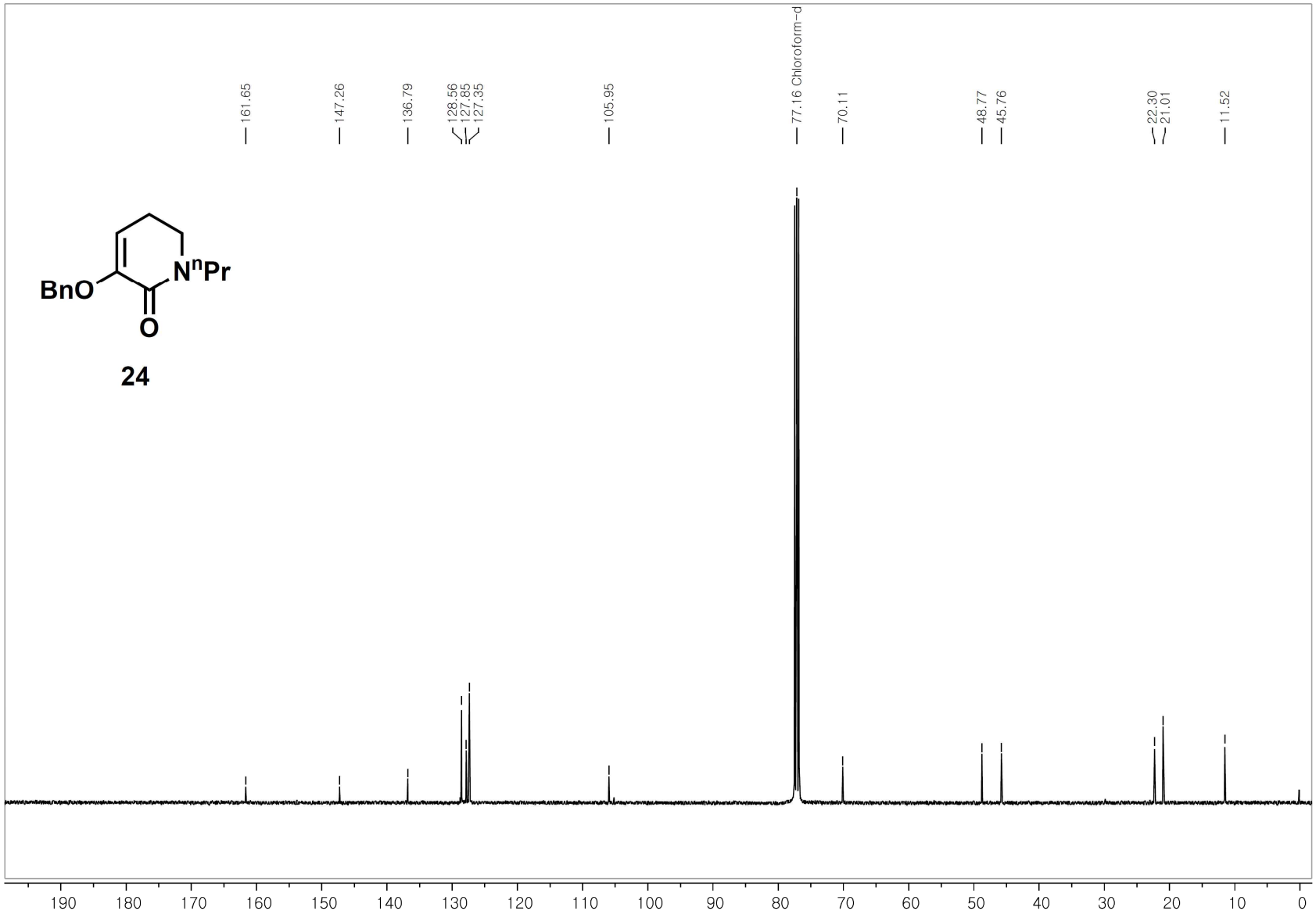
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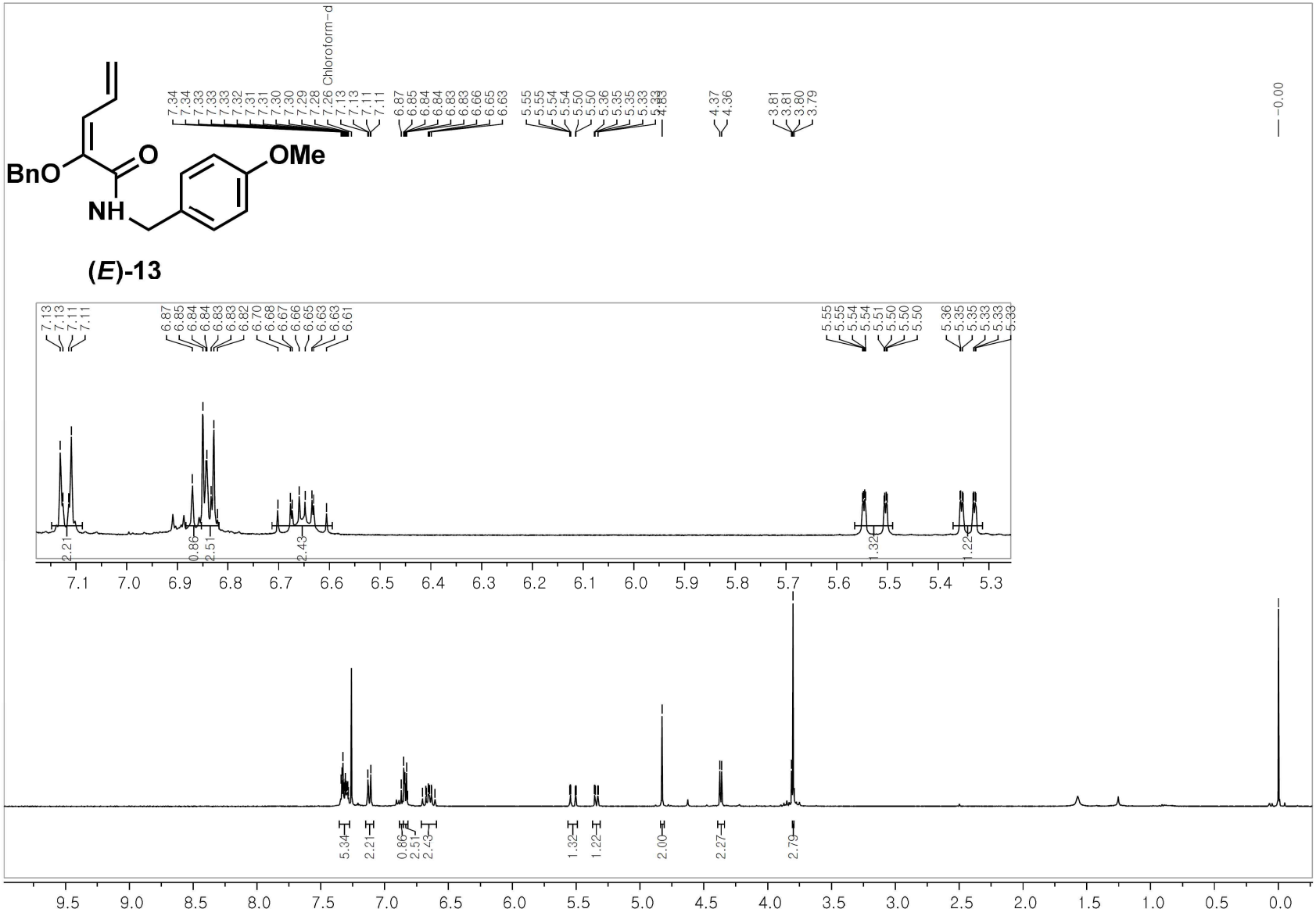
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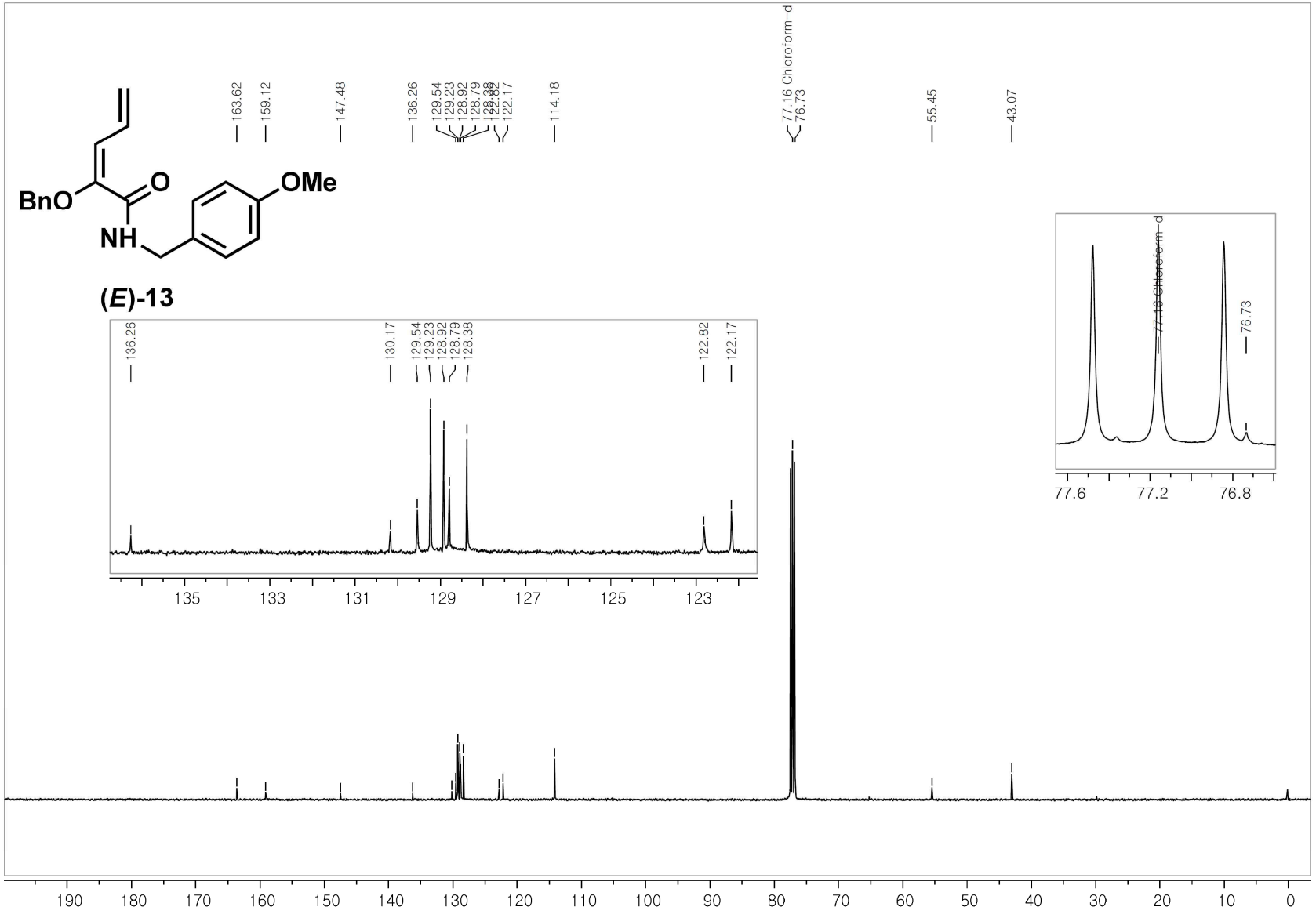
NH
OMe
(E)-13
Chloroform-d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NH
OMe
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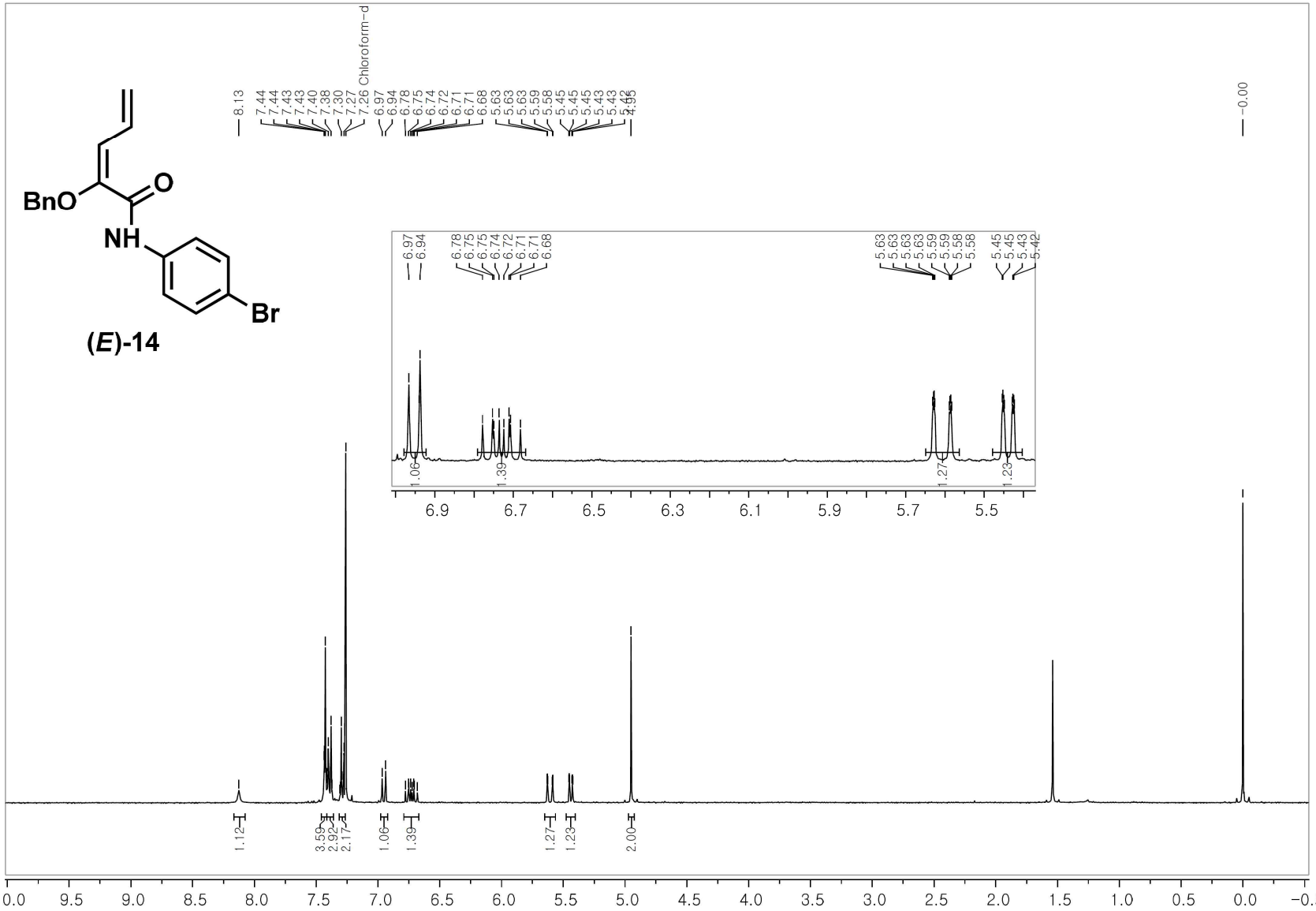
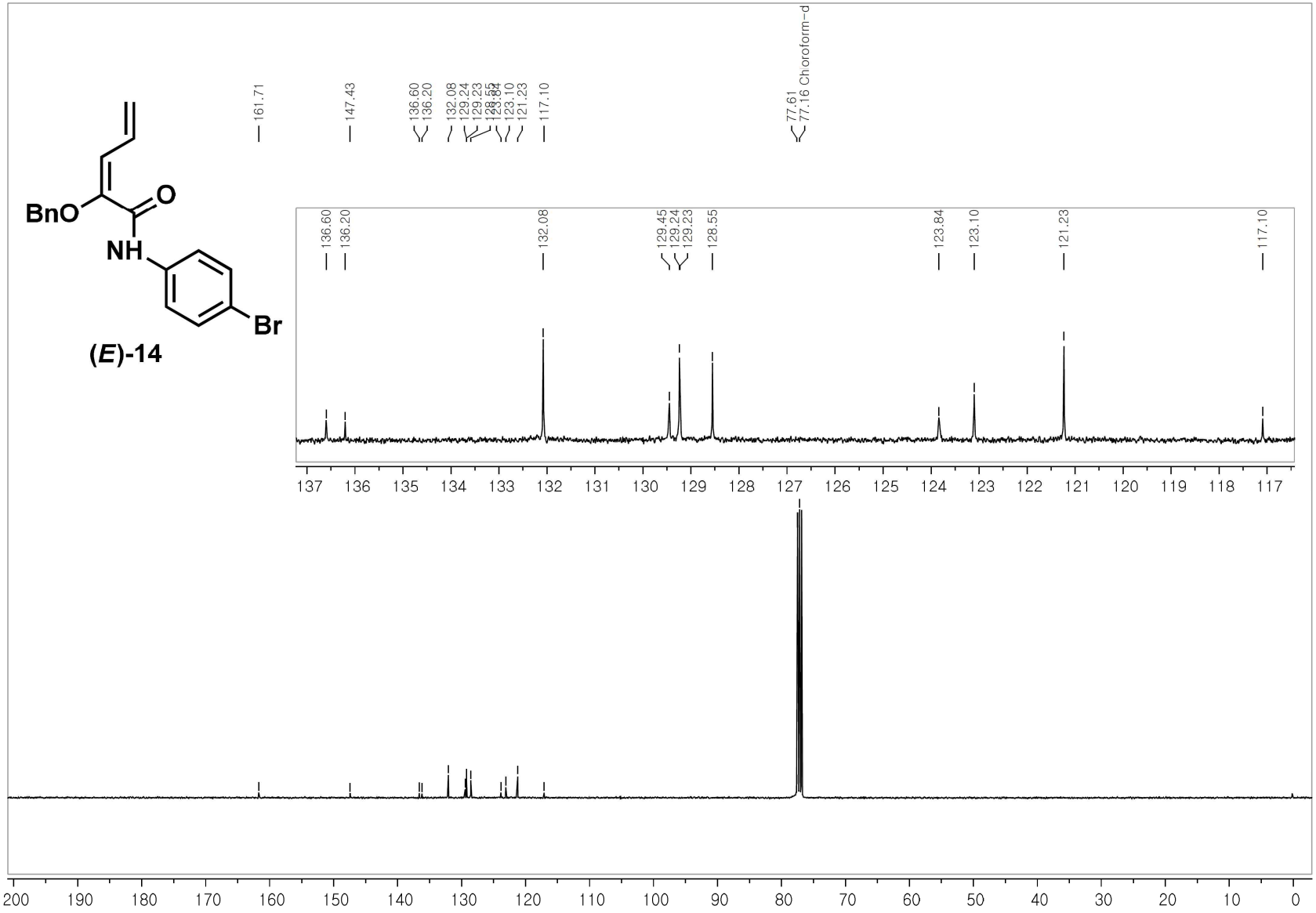
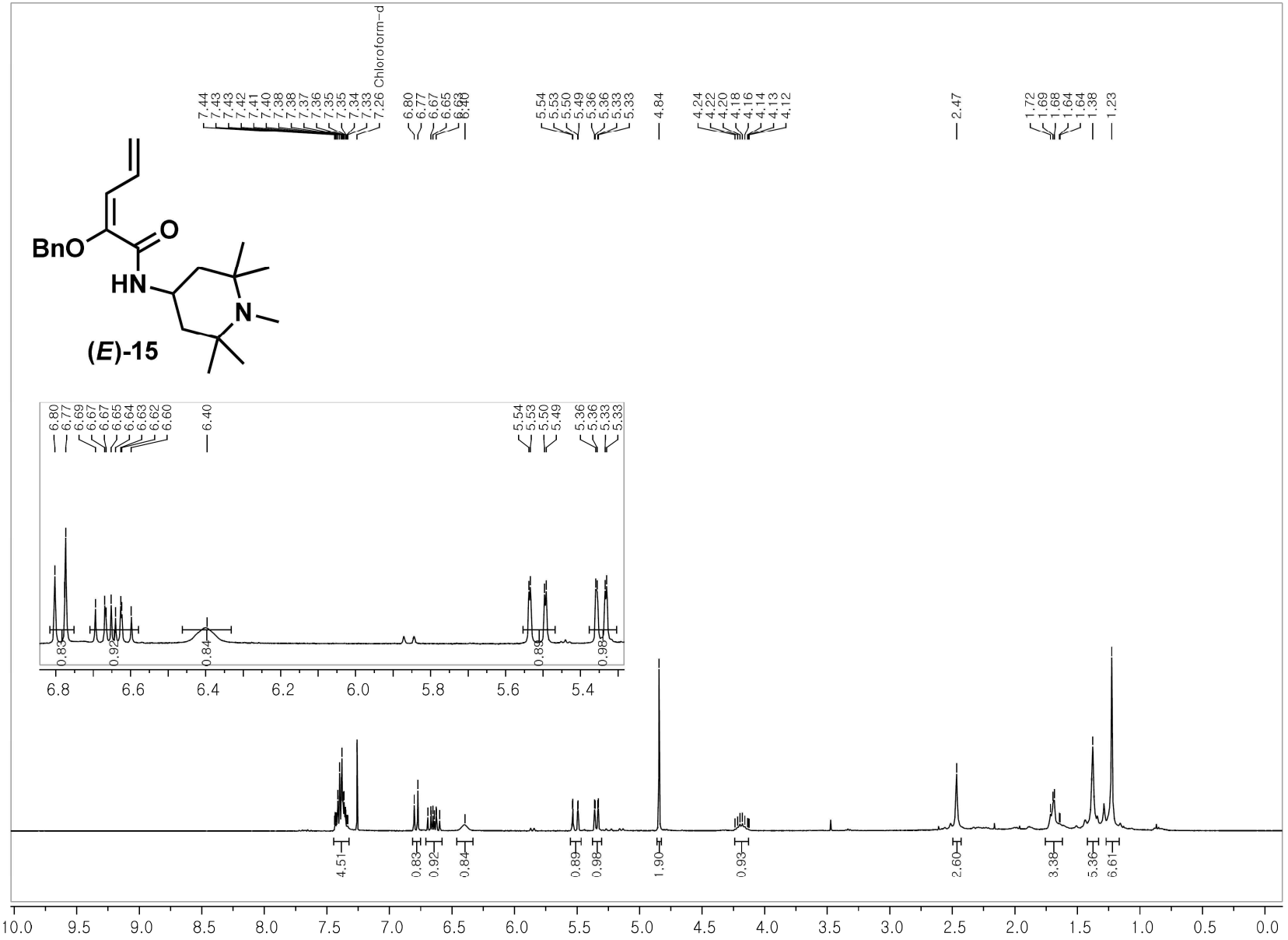
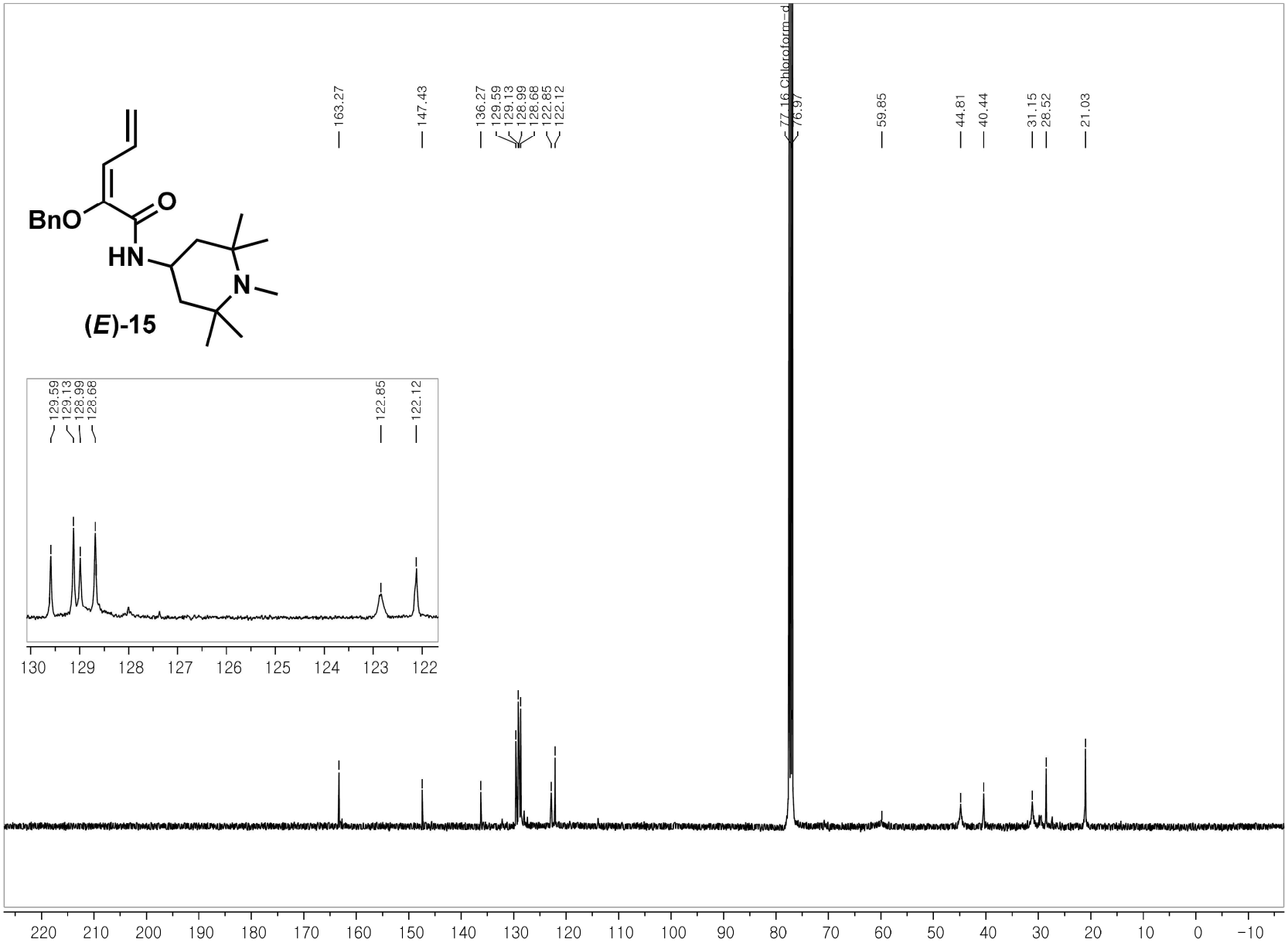
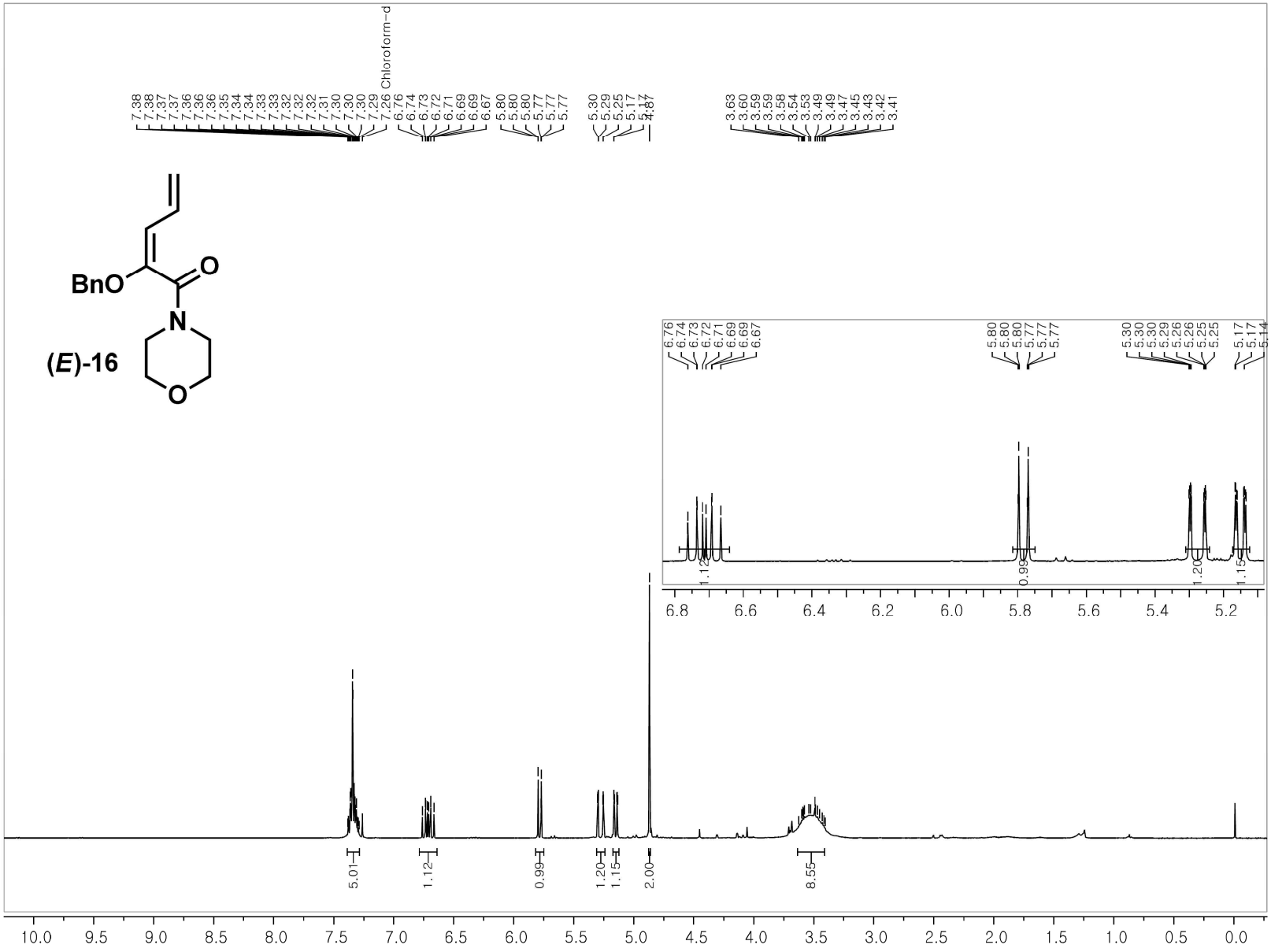
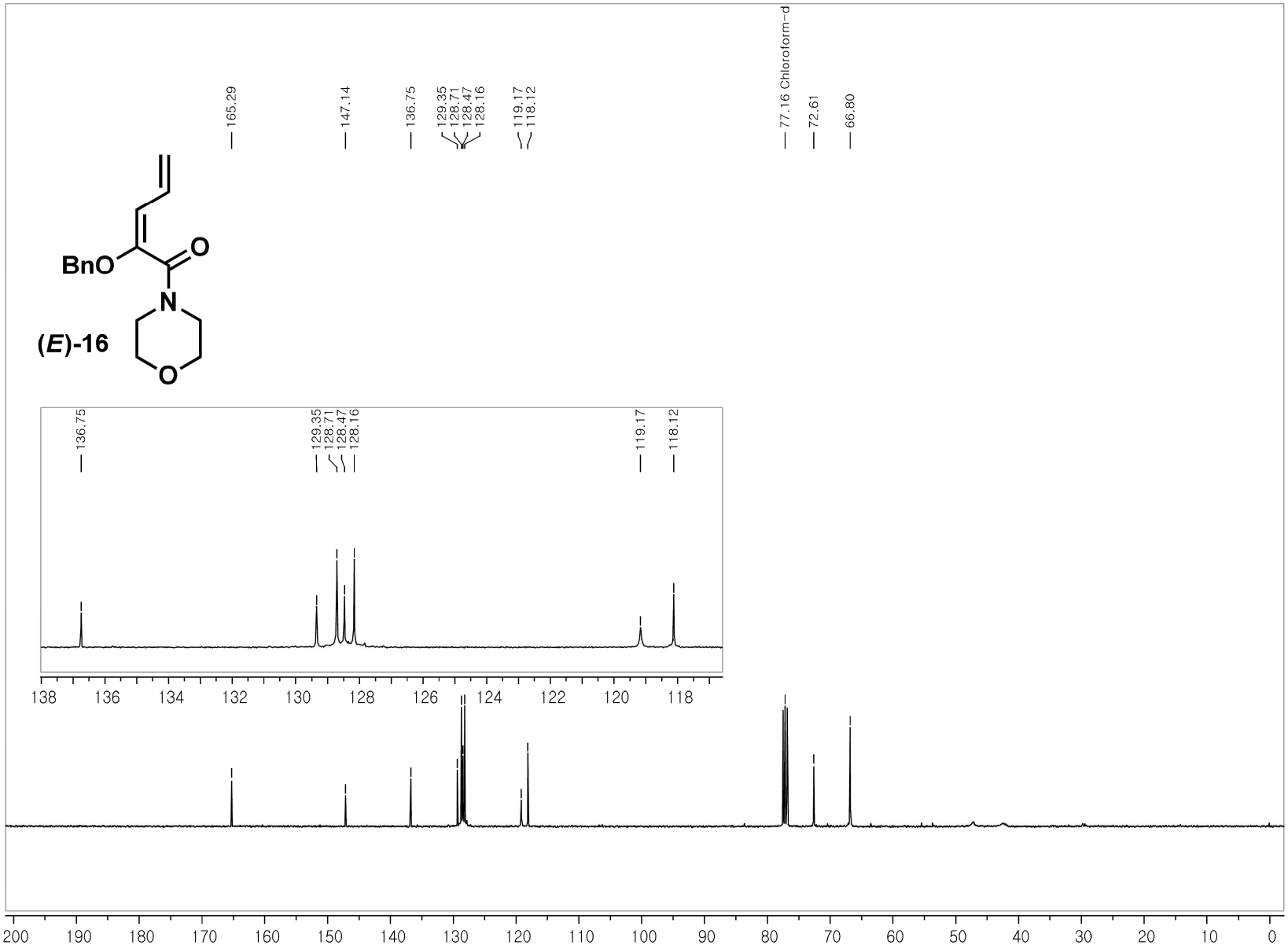

BnO
O
NH
Br
(E)-14
Chloroform-d

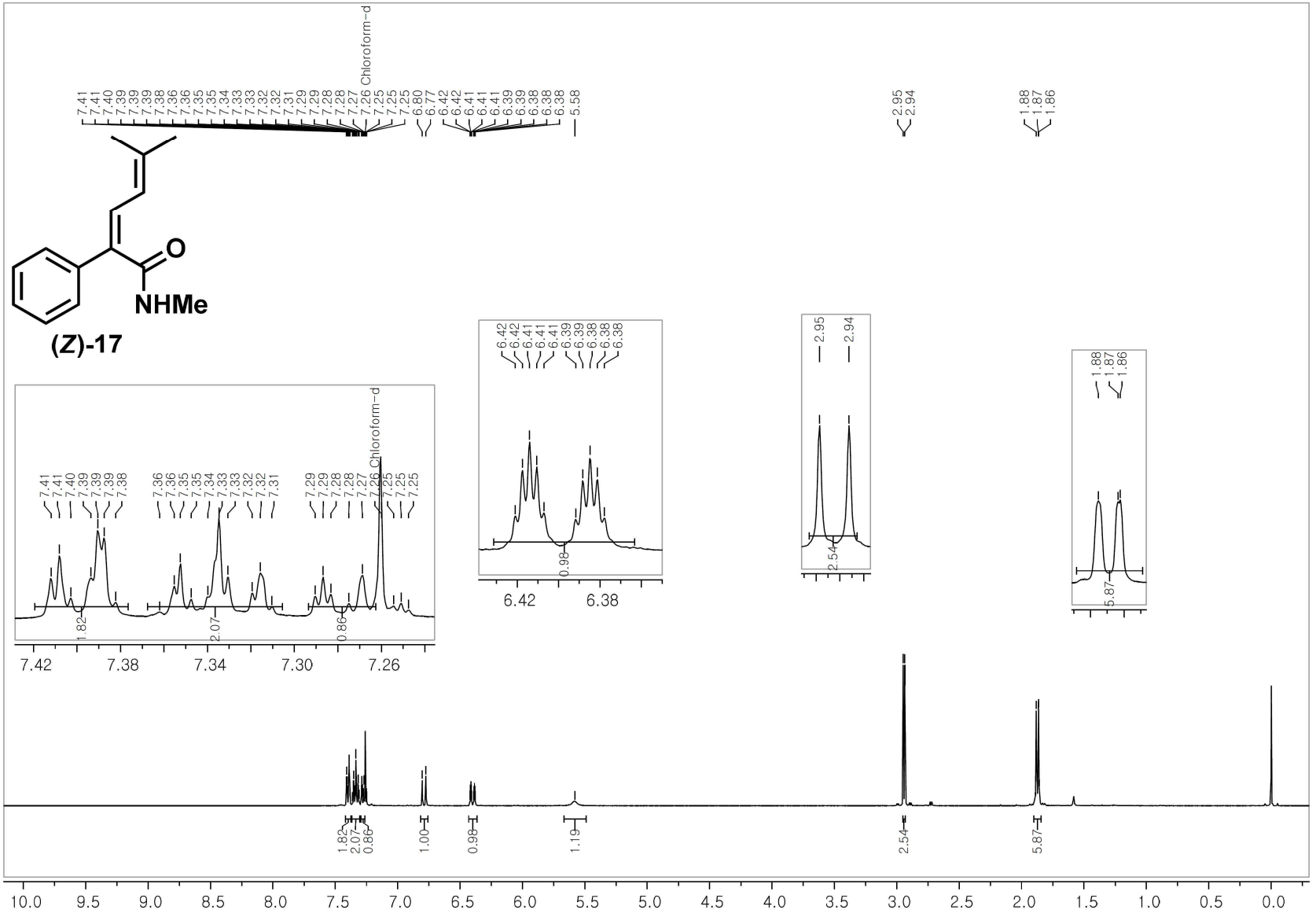

BnO
O
NH
Br
(E)-14
161.71
147.43
136.60
136.20
132.08
129.24
129.23
128.55
123.84
123.10
121.23
117.10
77.61
77.16 Chloroform-d

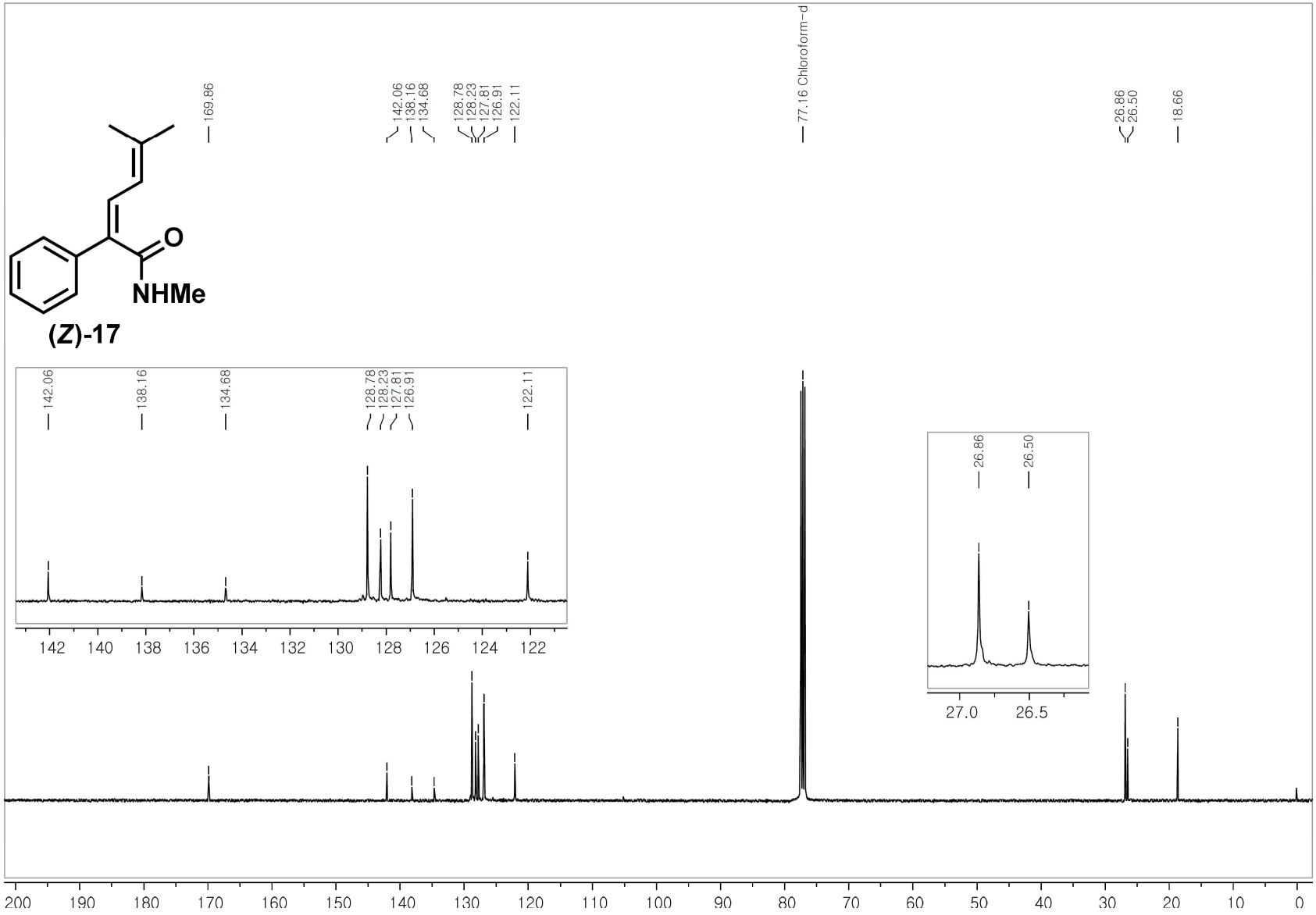

BnO
O
HN
N
(E)-15
Chloroform-d

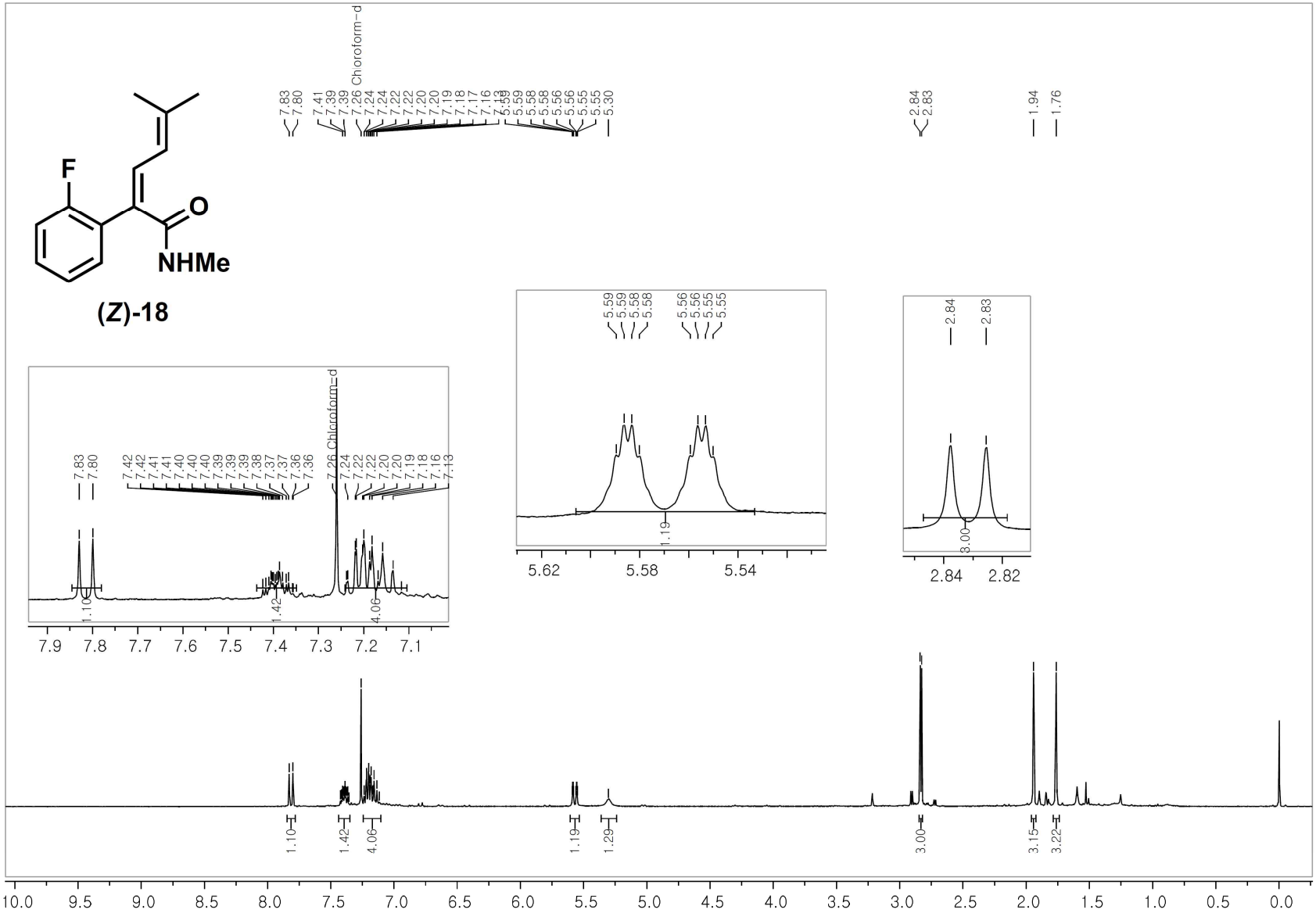

BnO
O
HN
N
(E)-15
163.27
147.43
136.27
129.59
129.13
128.99
128.68
122.85
122.12
77.16 Chloroform-d
76.97
59.85
44.81
40.44
31.15
28.52
21.03
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
130 129 128 127 126 125 124 123 122

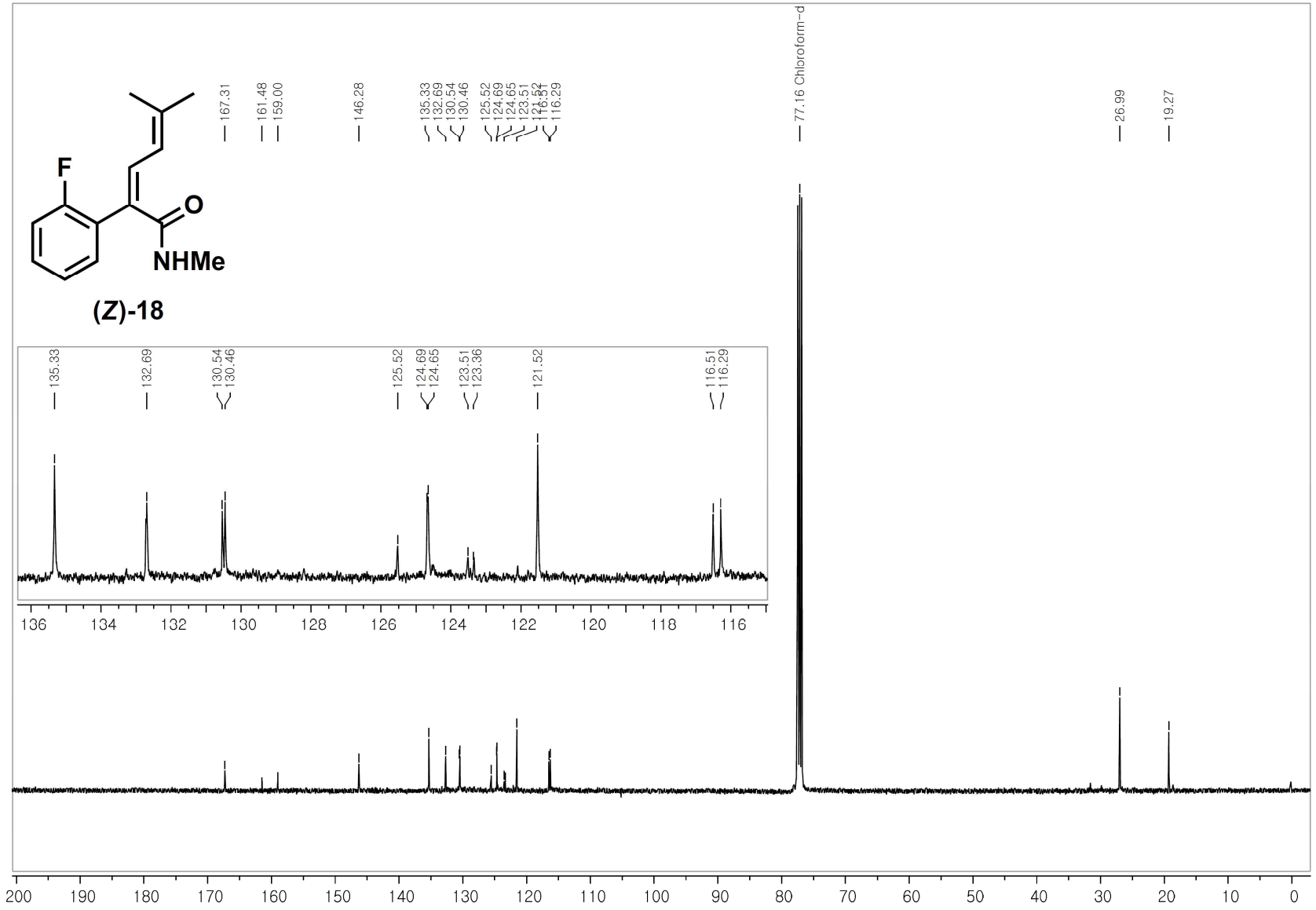

Chloroform-d
BnO
O
N
O
(E)-16
5.01
1.12
0.99
1.20
1.15
2.00
8.55

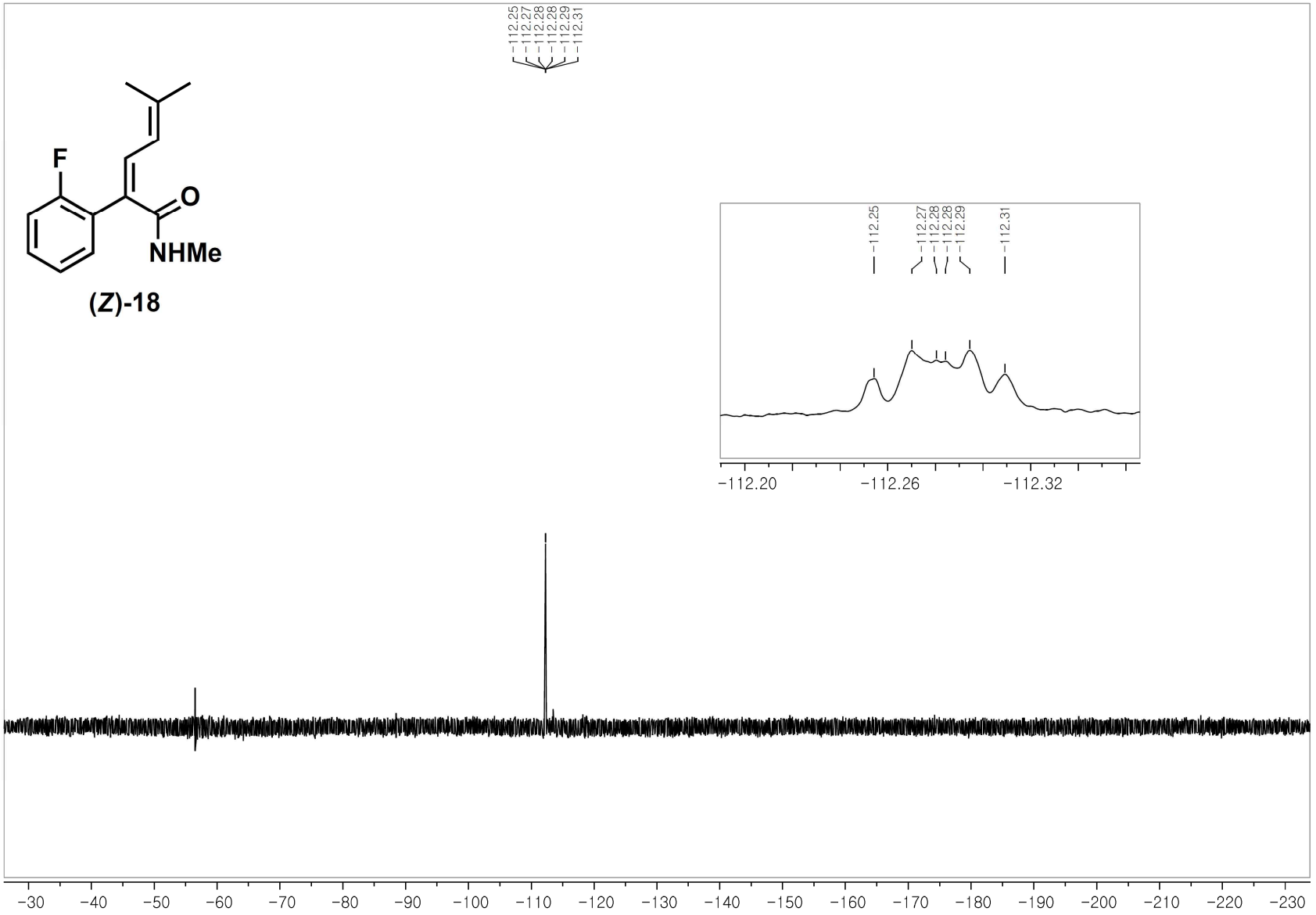

165.29
147.14
136.75
129.35
128.71
128.47
128.16
119.17
118.12
77.16 Chloroform-d
72.61
66.80
BnO
O
N
O
(E)-16
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
138 136 134 132 130 128 126 124 122 120 118


(Z)-17
NHMe
O
Chloroform-d
7.41 7.41 7.40 7.39 7.39 7.38 7.36 7.36 7.35 7.35 7.34 7.33 7.33 7.32 7.32 7.31 7.29 7.29 7.28 7.28 7.27 7.26 7.25 7.25 6.80 6.77 6.42 6.42 6.41 6.41 6.41 6.39 6.39 6.38 6.38 6.38 5.58
2.95 2.94
1.88 1.87 1.86
1.82 2.07 0.86 1.00 0.98 1.19 2.54 5.87
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


169.86
142.06
138.16
134.68
128.78
128.23
127.81
126.91
122.11
77.16 Chloroform-d
26.86
26.50
18.66
O
NHMe
(Z)-17
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
142 140 138 136 134 132 130 128 126 124 122
27.0 26.5


F
O
NHMe
(Z)-18
Chloroform-d


F
O
NHMe
(Z)-18
167.31
161.48
159.00
146.28
135.33
132.69
130.54
130.46
125.52
124.69
124.65
123.51
123.36
121.52
116.51
116.29
77.16 Chloroform-d
26.99
19.27
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
136 134 132 130 128 126 124 122 120 118 116


F
O
NHMe
(Z)-18
-112.25
-112.27
-112.28
-112.28
-112.29
-112.31
-112.20
-112.26
-112.32
-30
-40
-50
-60
-70
-80
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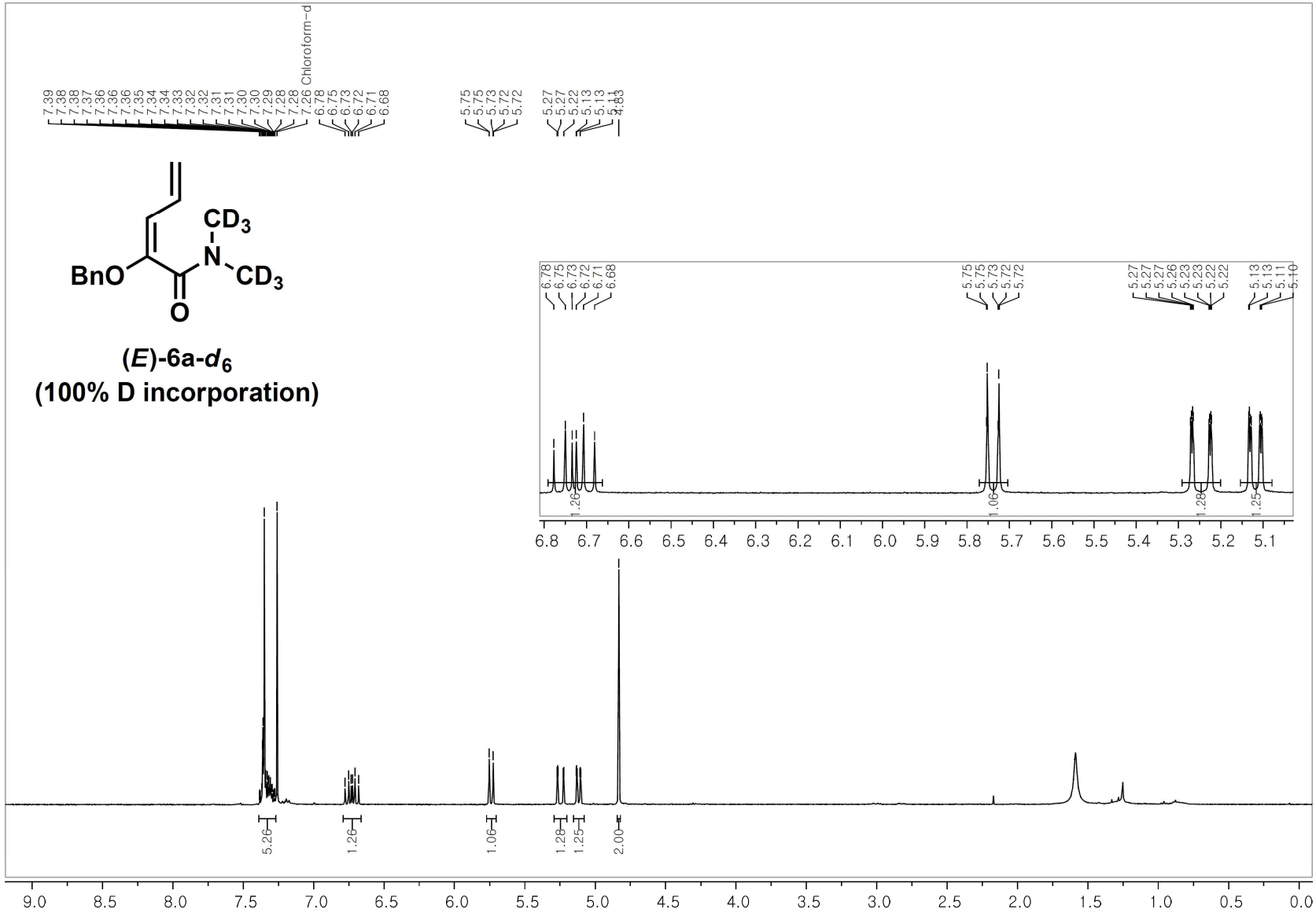
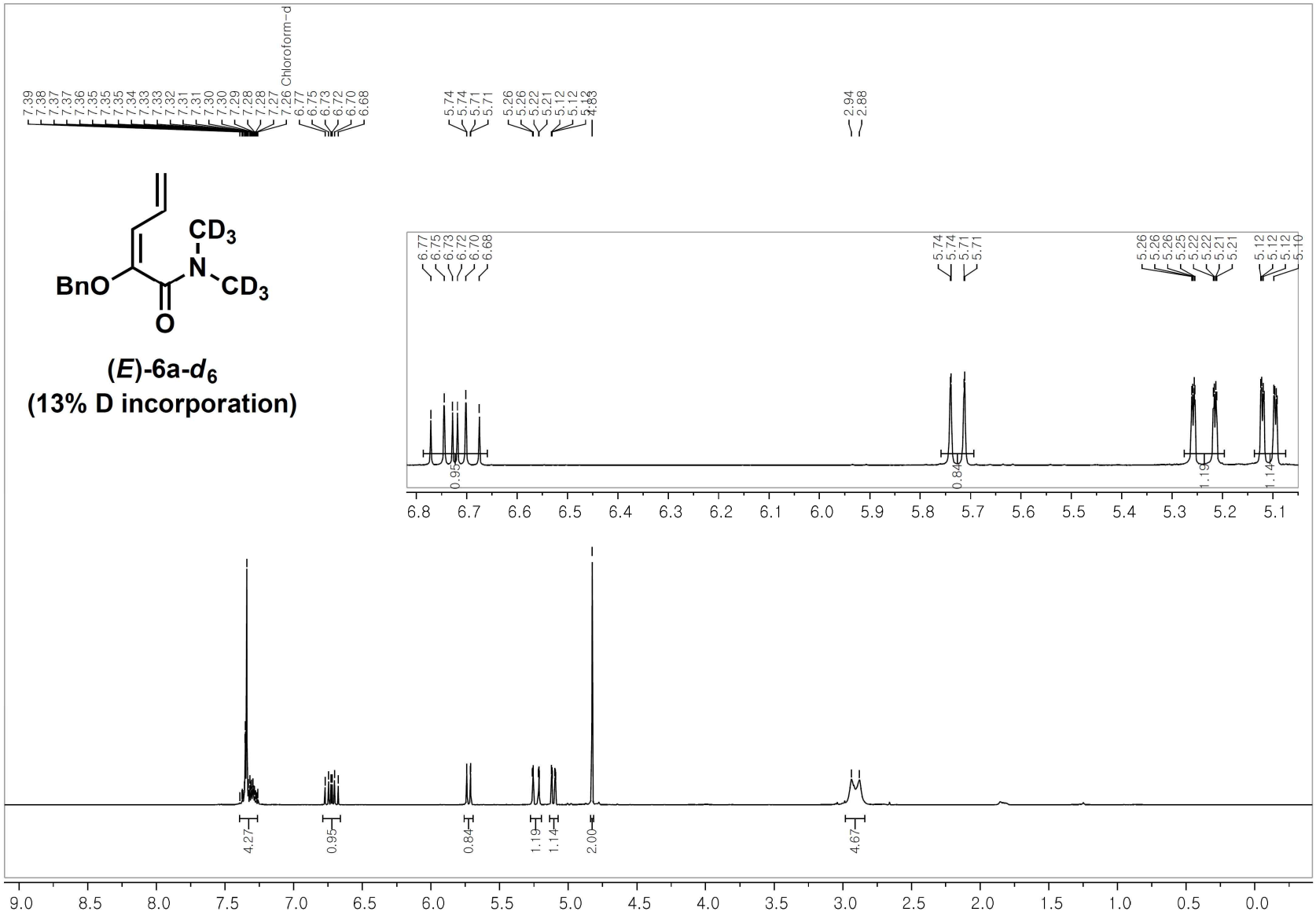
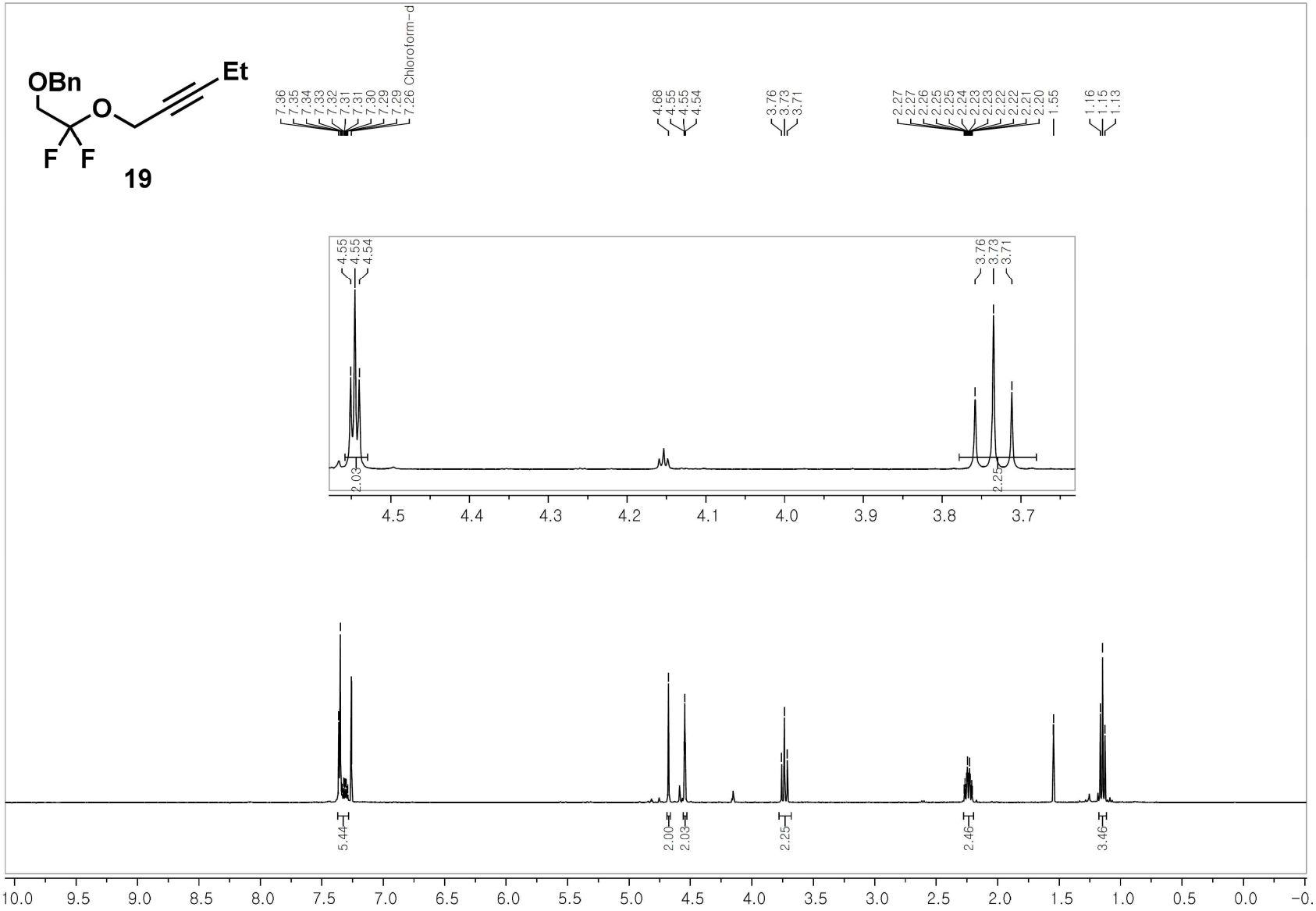

Chloroform-d
BnO
CD3
N
CD3
O
(E)-6a-d6
(100% D incorporation)


Chloroform-d
BnO
CD3
N
CD3
O
(E)-6a-d6
(13% D incorporation)


OBn
O
Et
F F
19
7.36
7.35
7.34
7.33
7.32
7.31
7.31
7.30
7.29
7.29
7.26 Chloroform-d
4.68
4.55
4.55
4.54
3.76
3.73
3.71
2.27
2.27
2.26
2.25
2.25
2.24
2.23
2.23
2.22
2.22
2.21
2.20
1.55
1.16
1.15
1.13
4.55
4.55
4.54
3.76
3.73
3.71
2.03
2.25
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
5.44
2.00
2.03
2.25
2.46
3.46
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
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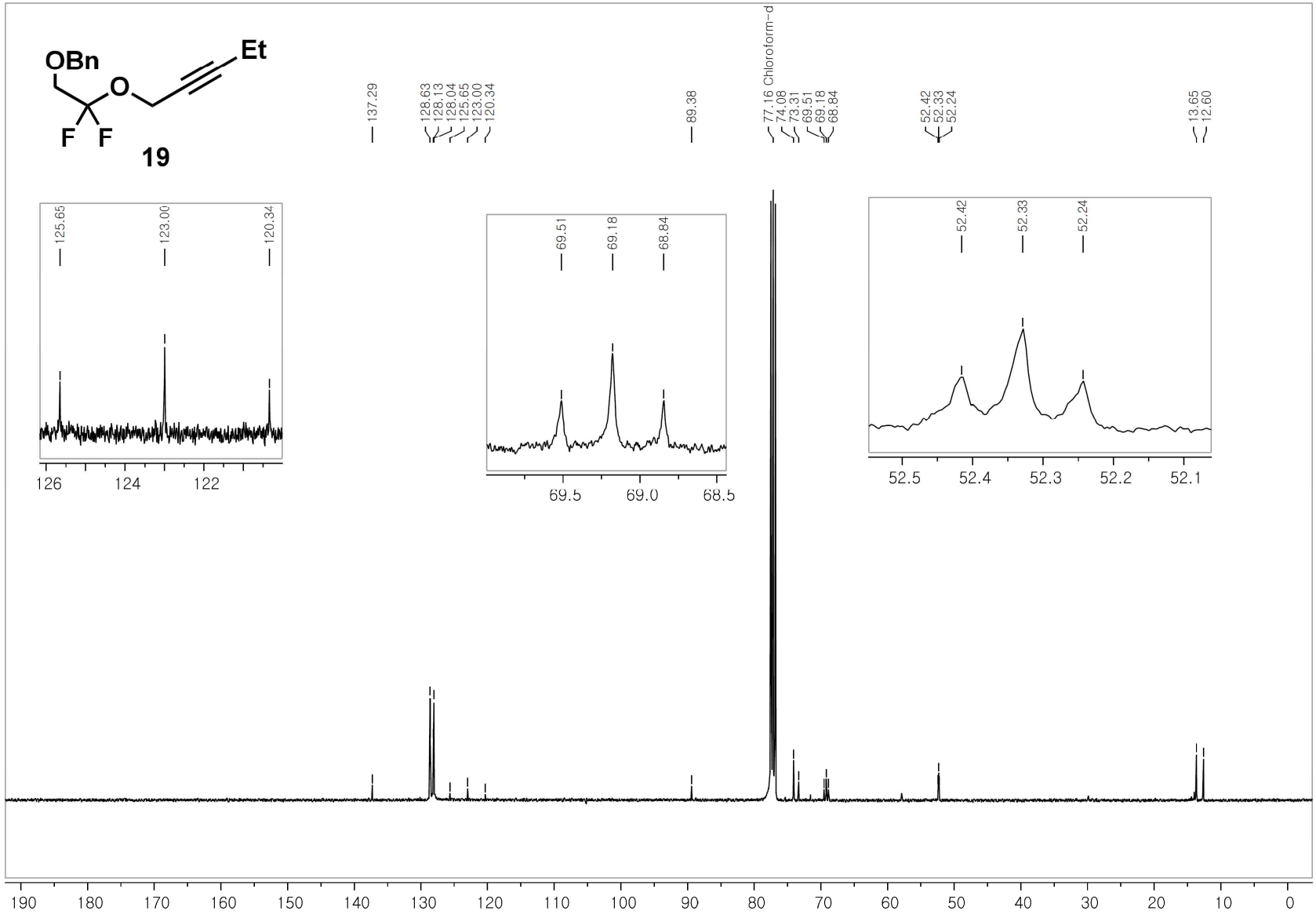
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.


OBn
O
Et
F F
19
137.29
128.63
128.13
128.04
125.65
123.00
120.34
89.38
77.16 Chloroform-d
74.08
73.31
69.51
69.18
68.84
52.42
52.33
52.24
13.65
12.60
125.65
123.00
120.34
126
124
122
69.51
69.18
68.84
69.5
69.0
68.5
52.42
52.33
52.24
52.5
52.4
52.3
52.2
52.1
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180
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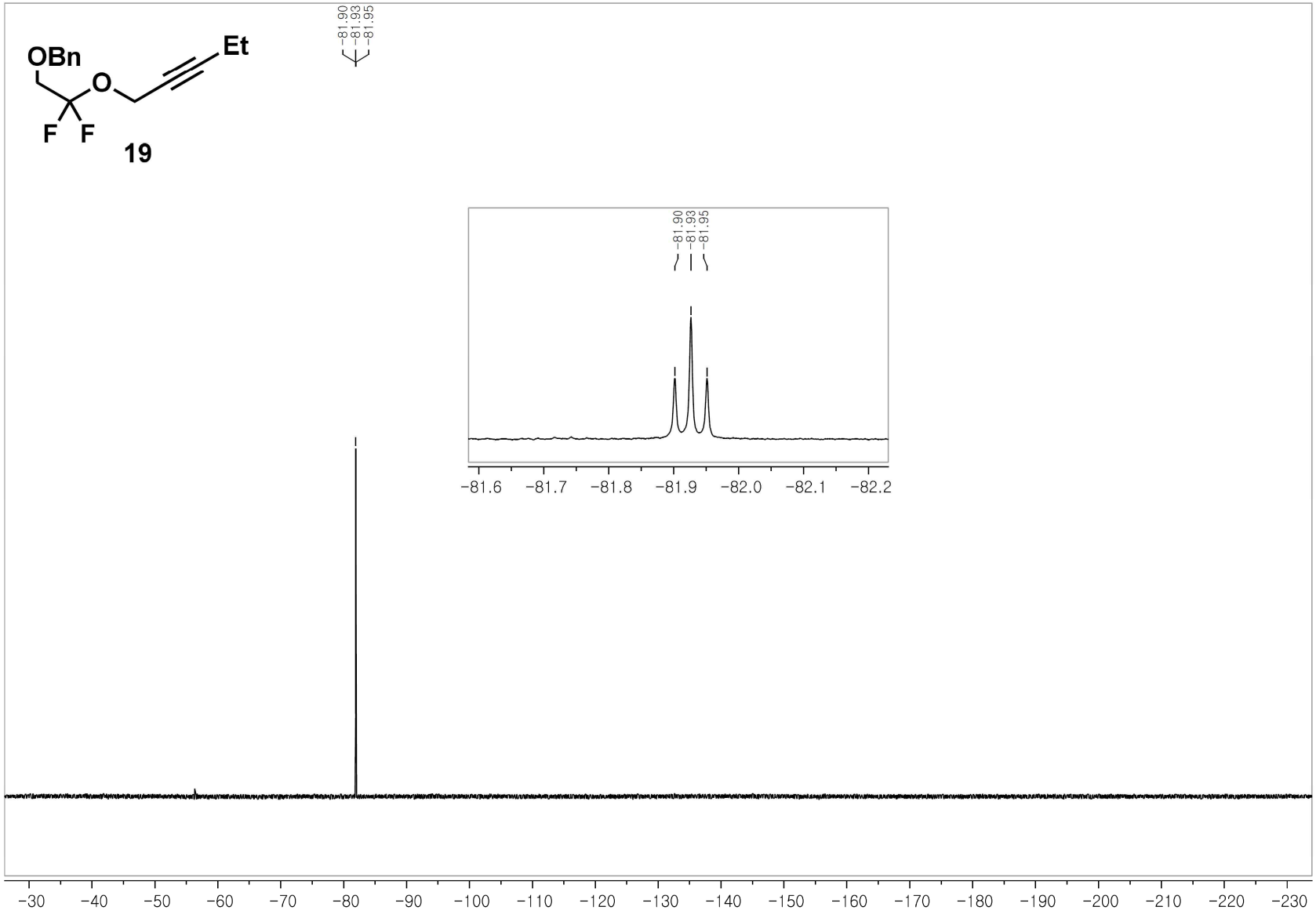
10
0


OBn
O
Et
F F
19
-81.90
-81.93
-81.95
-81.6
-81.7
-81.8
-81.9
-82.0
-82.1
-82.2
-30
-40
-50
-60
-70
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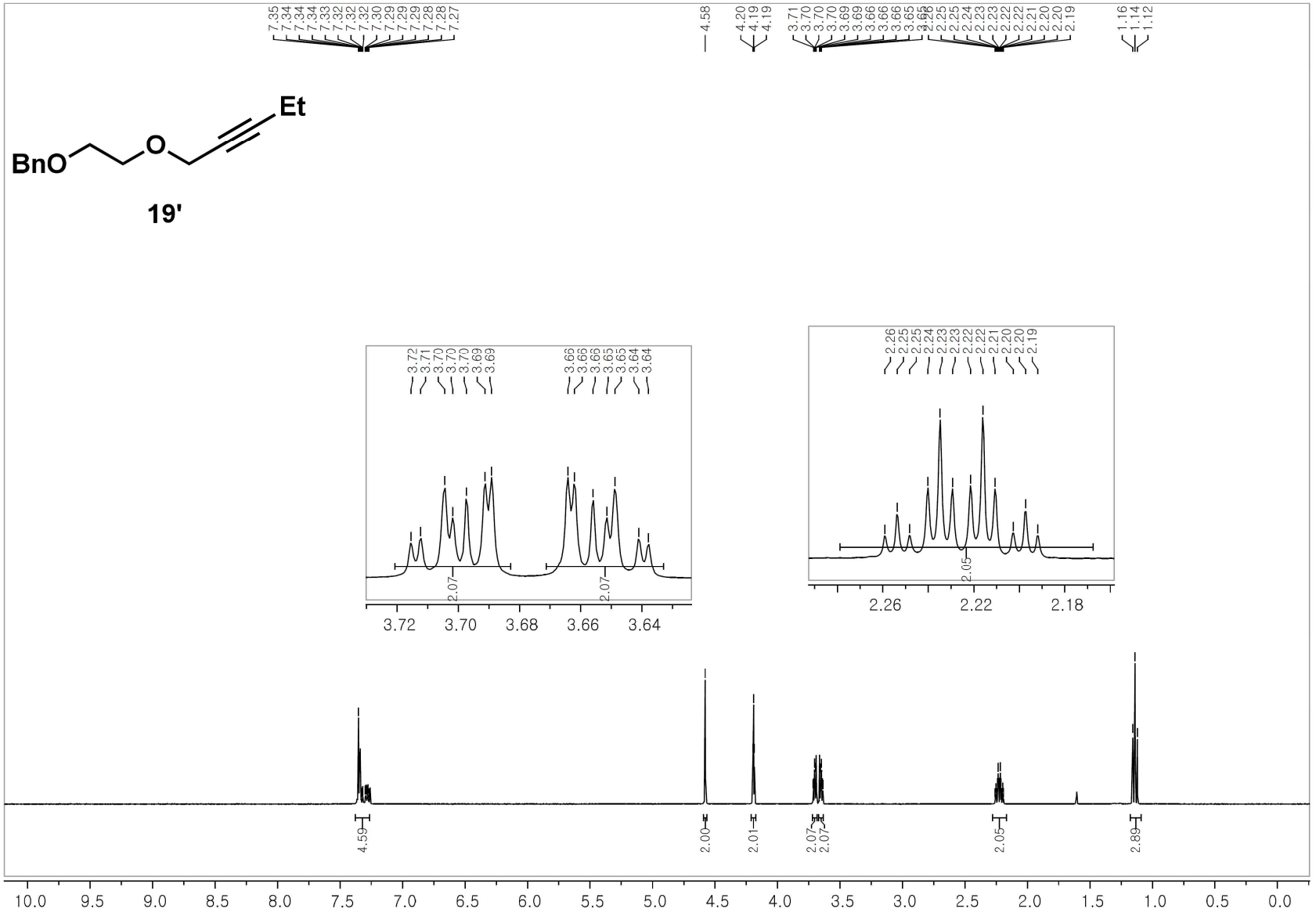
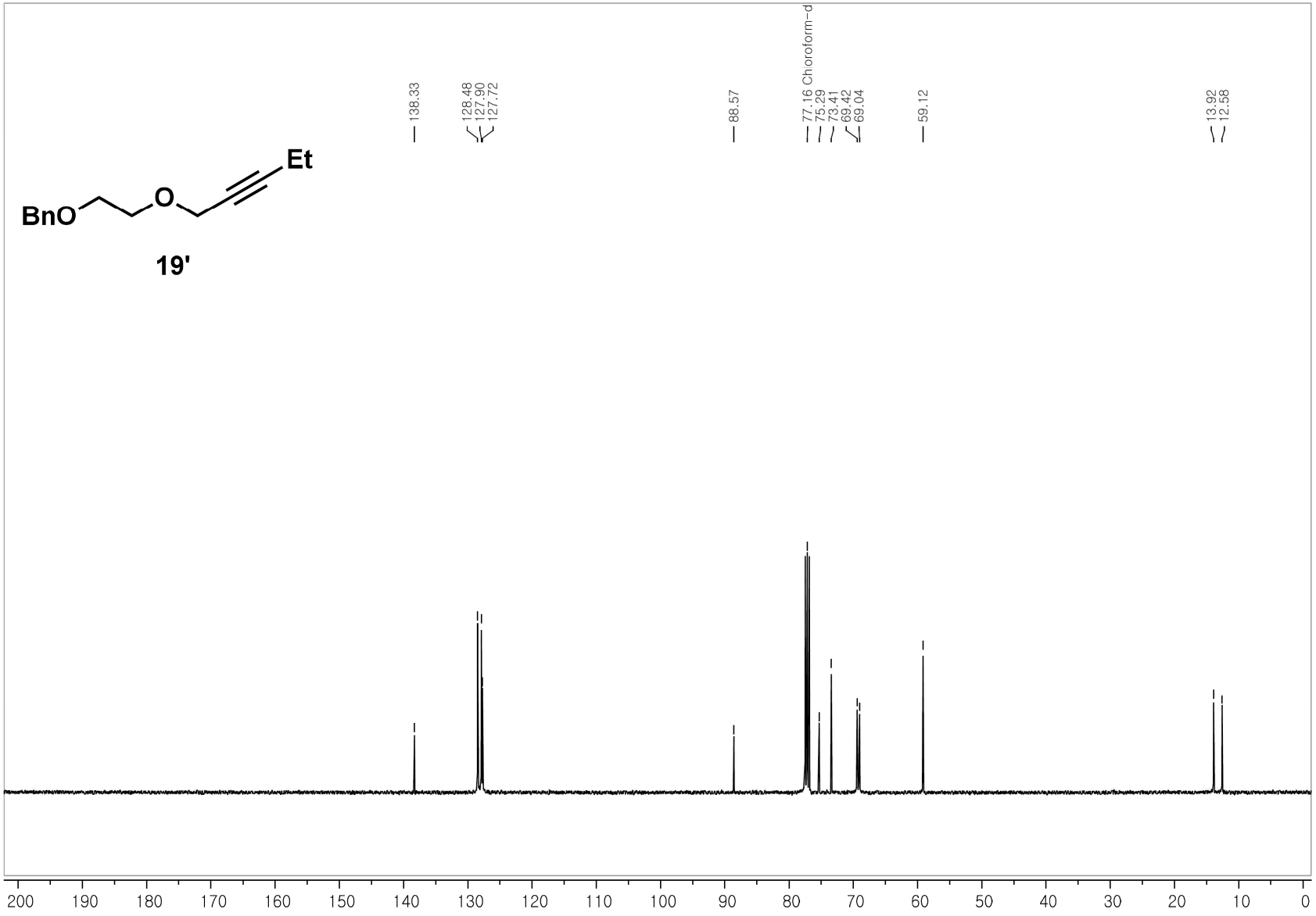
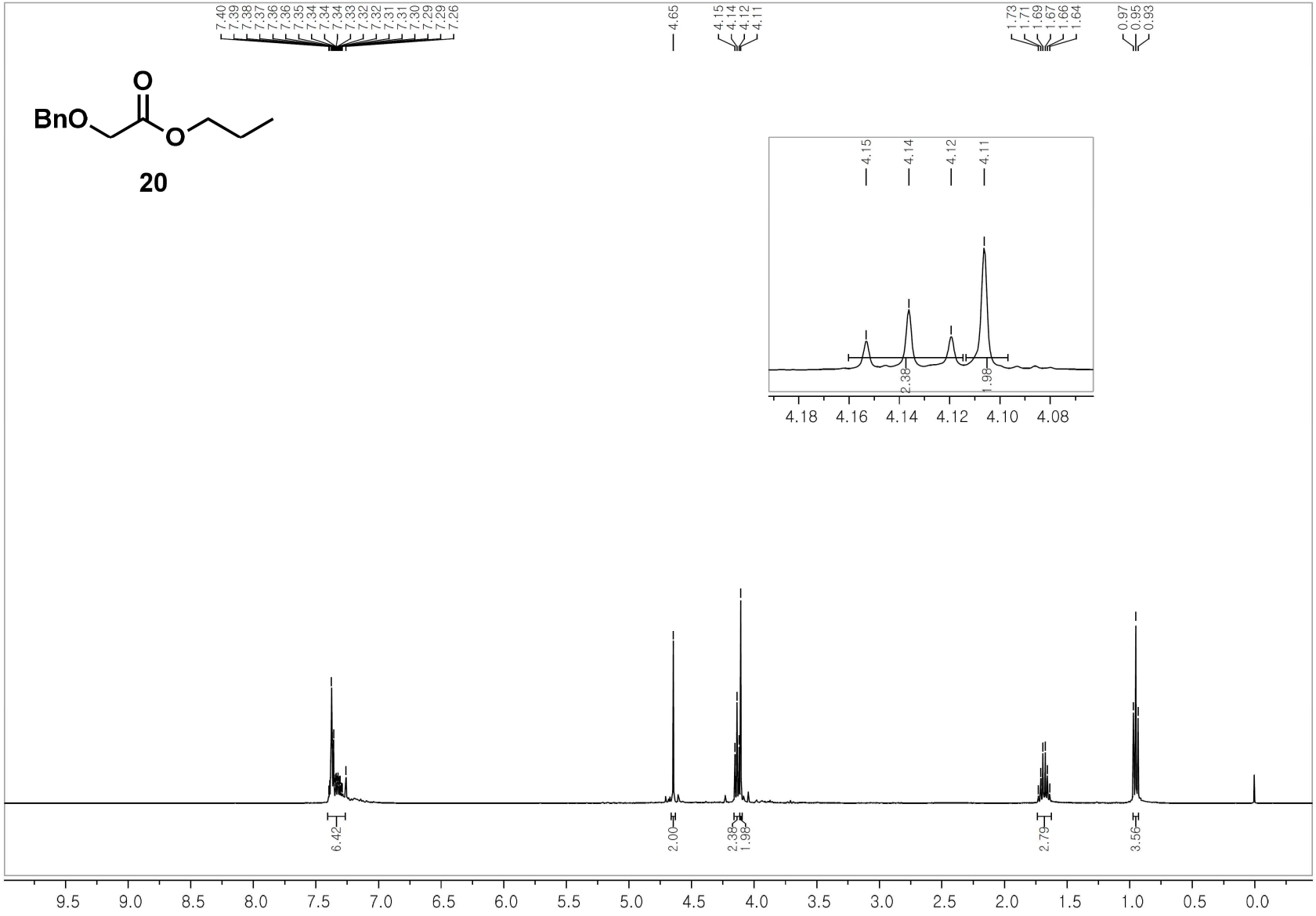

Et
BnO
O
19'


138.33
128.48
127.90
127.72
88.57
77.16 Chloroform-d
75.29
73.41
69.42
69.04
59.12
13.92
12.58
Et
O
BnO
19'
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


BnO
O
O
20
7.40 7.39 7.38 7.37 7.36 7.36 7.35 7.34 7.34 7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.29 7.29 7.26
4.65
4.15 4.14 4.12 4.11
1.73 1.71 1.69 1.67 1.66 1.64
0.97 0.95 0.93
4.15 4.14 4.12 4.11
2.38 1.98
4.18 4.16 4.14 4.12 4.10 4.08
6.42 2.00 2.38 1.98 2.79 3.56
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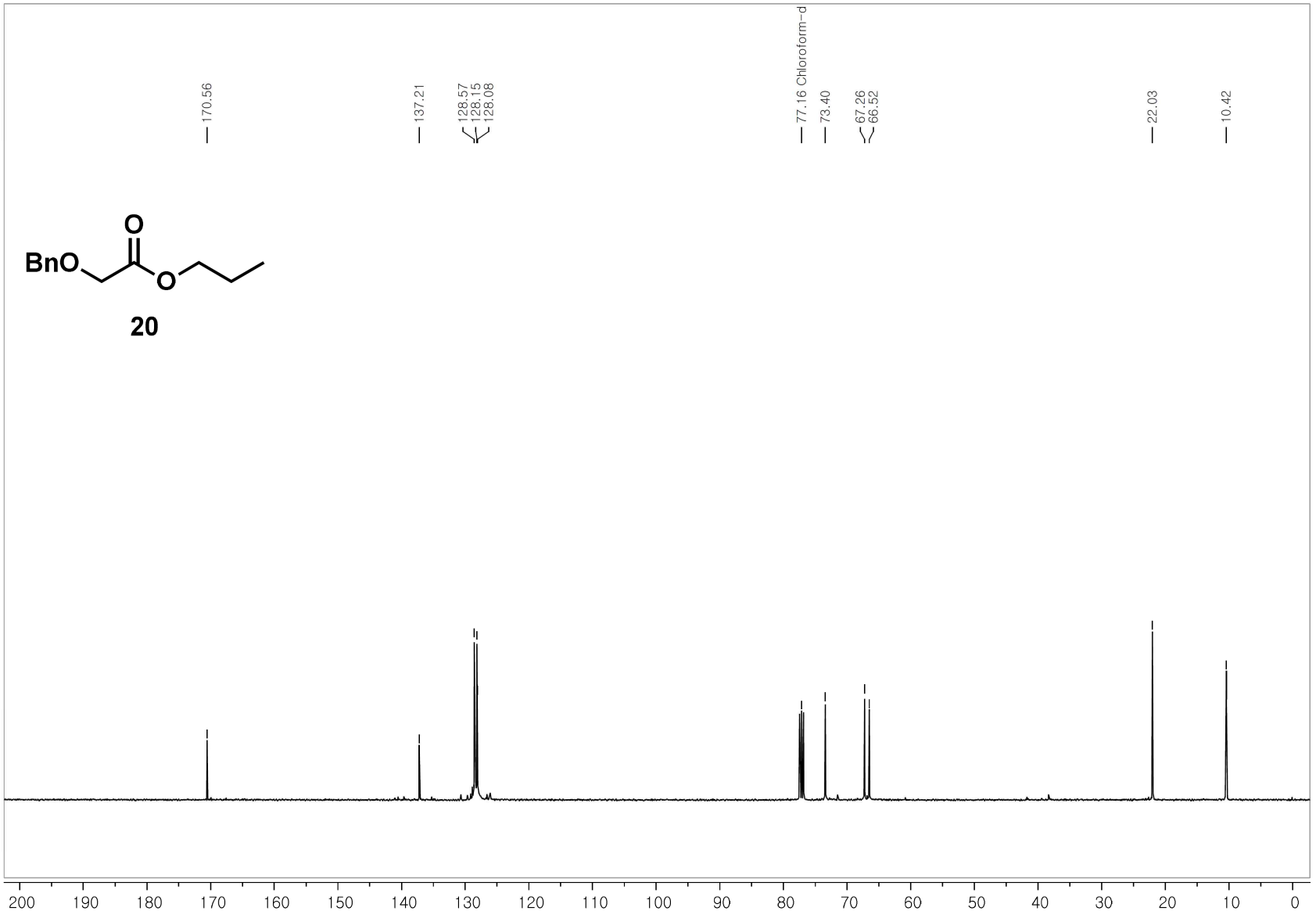
170.56
137.21
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128.15
128.08
77.16 Chloroform-d
73.40
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66.52
22.03
10.42
BnO
O
O
20
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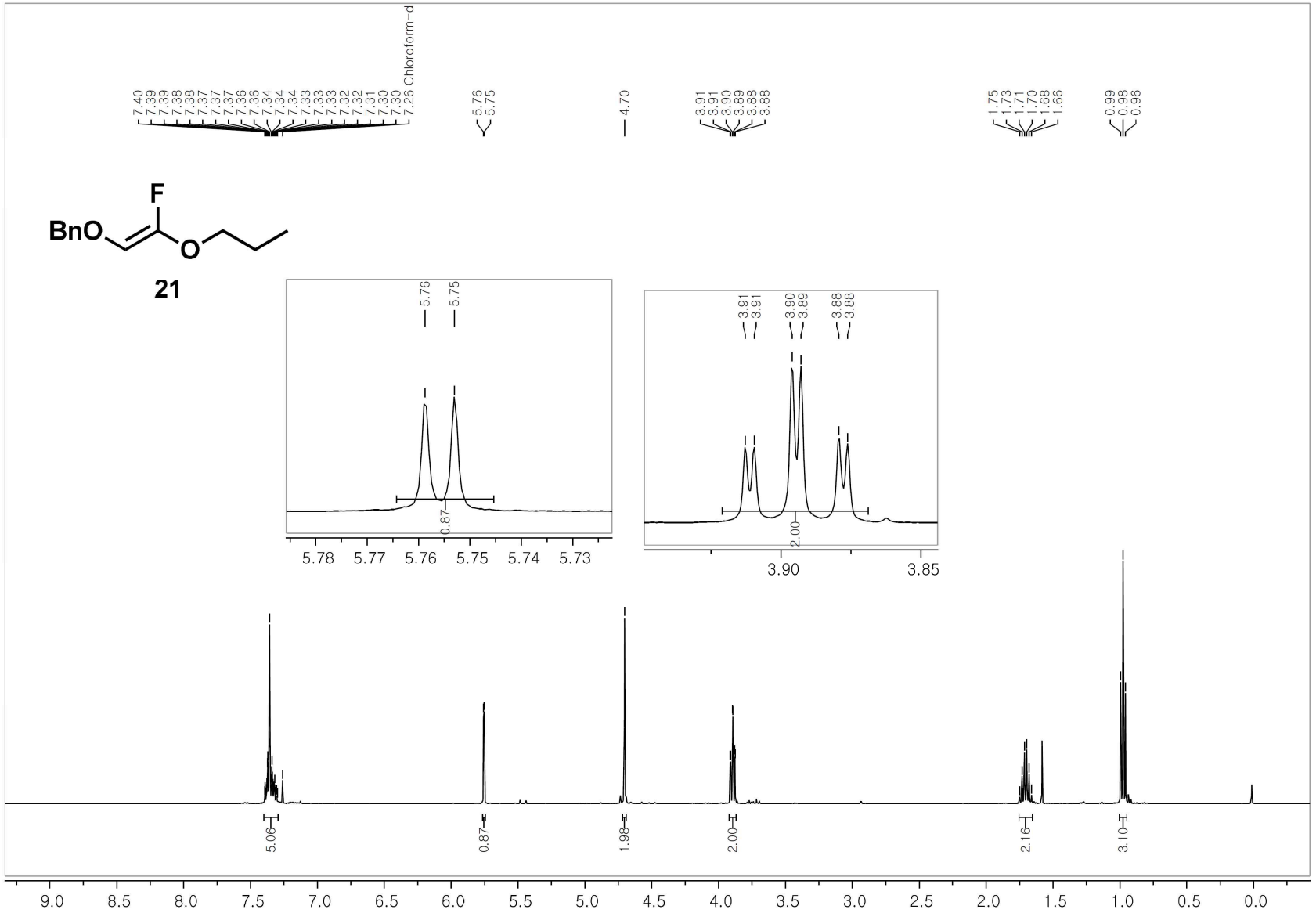
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7.34
7.33
7.33
7.33
7.32
7.32
7.31
7.30
7.30
7.26 Chloroform-d
5.76
5.75
4.70
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3.91
3.90
3.89
3.88
3.88
1.75
1.73
1.71
1.70
1.68
1.66
0.99
0.98
0.96
F
BnO
O
21
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0.87
5.78
5.77
5.76
5.75
5.74
5.73
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3.91
3.90
3.89
3.88
3.88
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3.90
3.85
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2.00
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8.0
7.5
7.0
6.5
6.0
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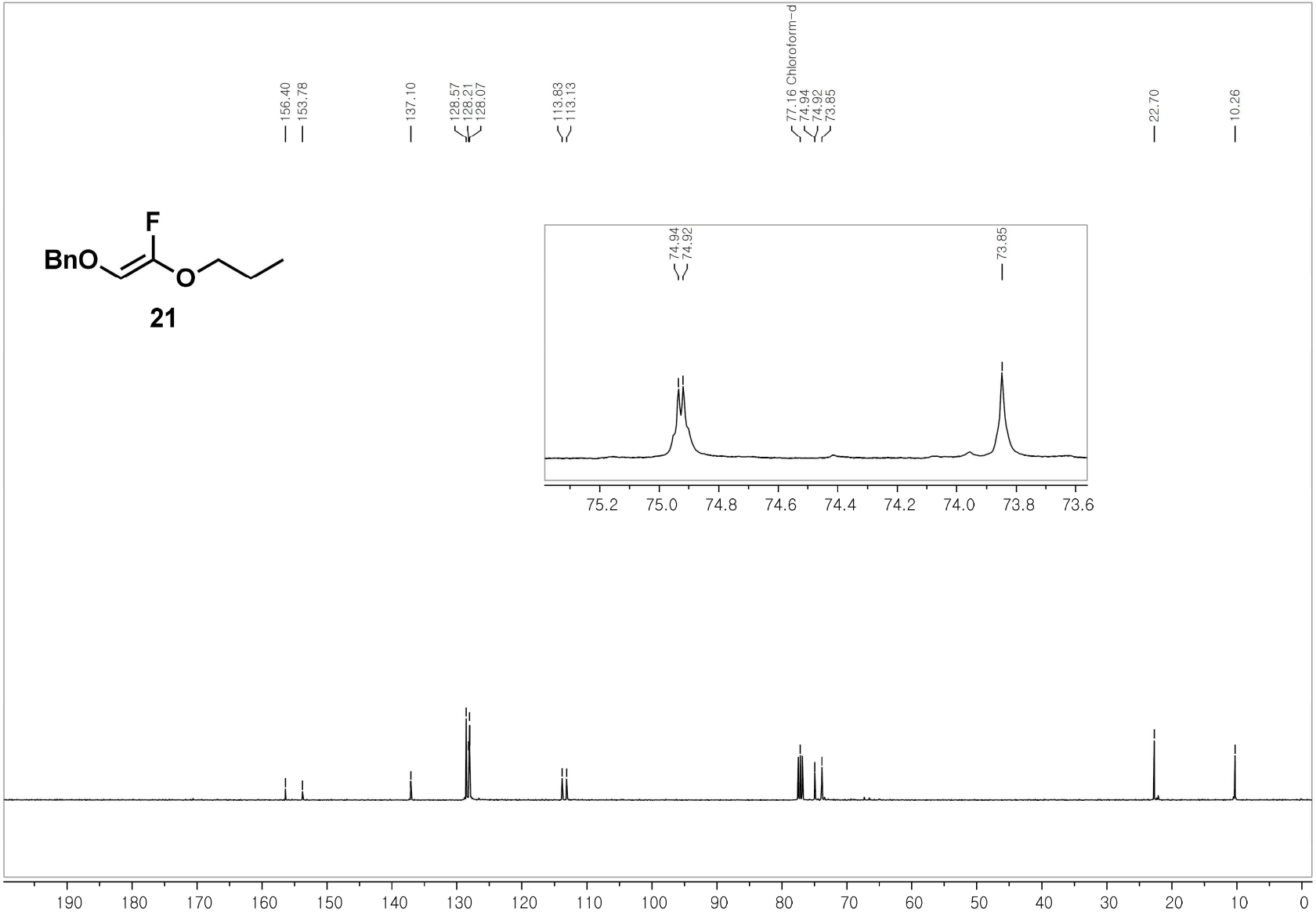
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128.07
113.83
113.13
77.16 Chloroform-d
74.94
74.92
73.85
22.70
10.26
F
BnO
O
21
74.94
74.92
73.85
75.2
75.0
74.8
74.6
74.4
74.2
74.0
73.8
73.6
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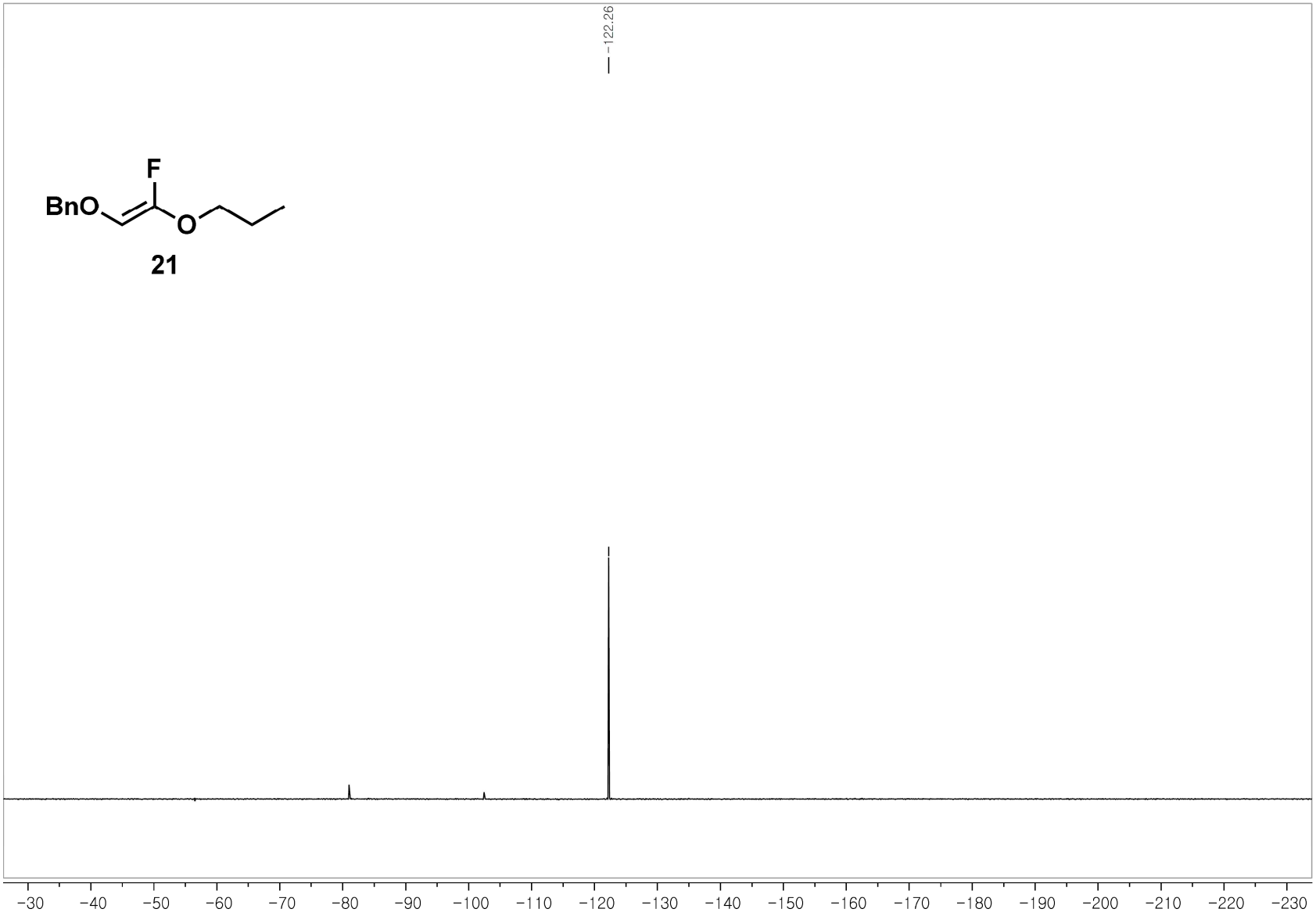
10
0


-122.26
F
BnO
O
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-50
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-70
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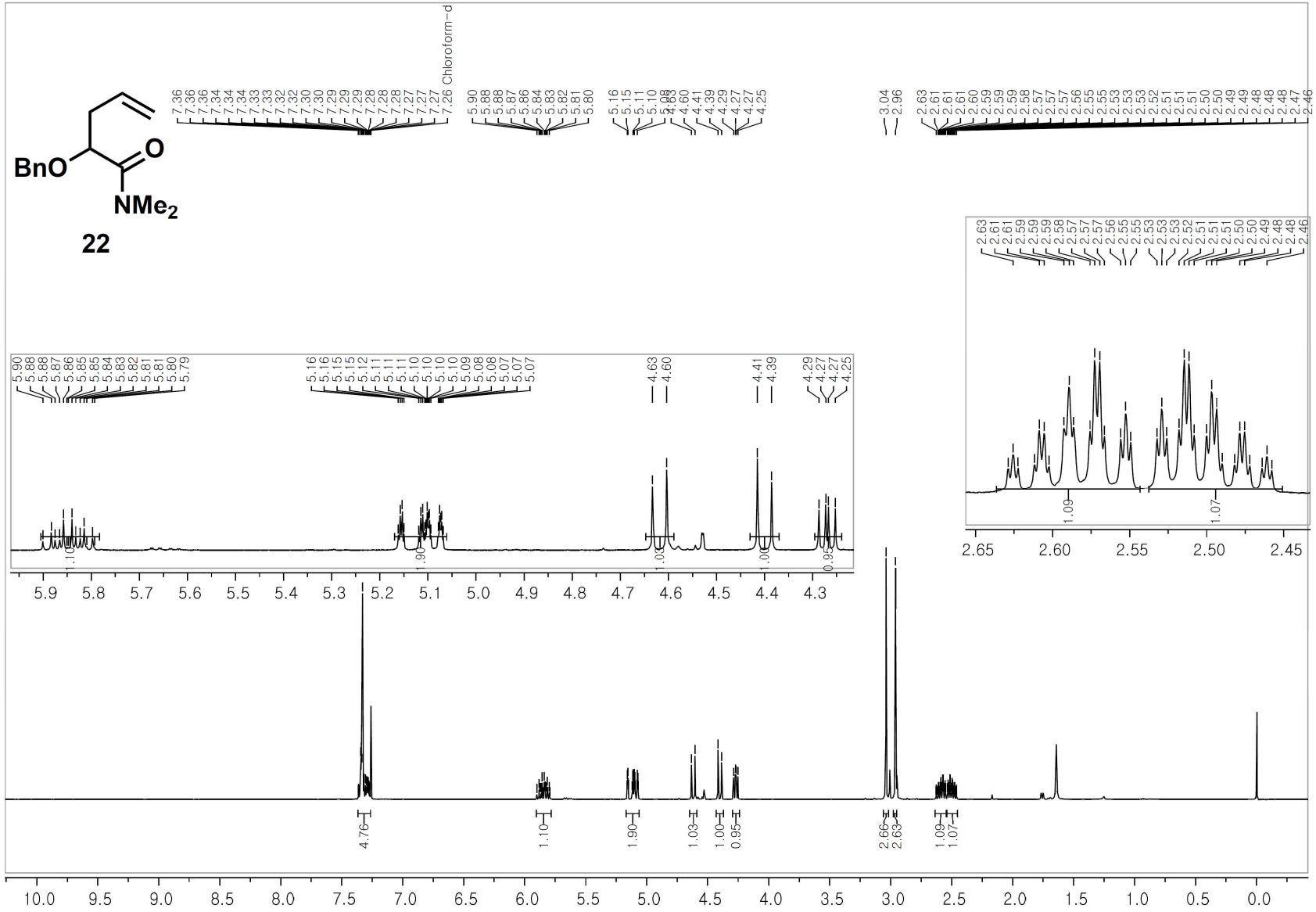
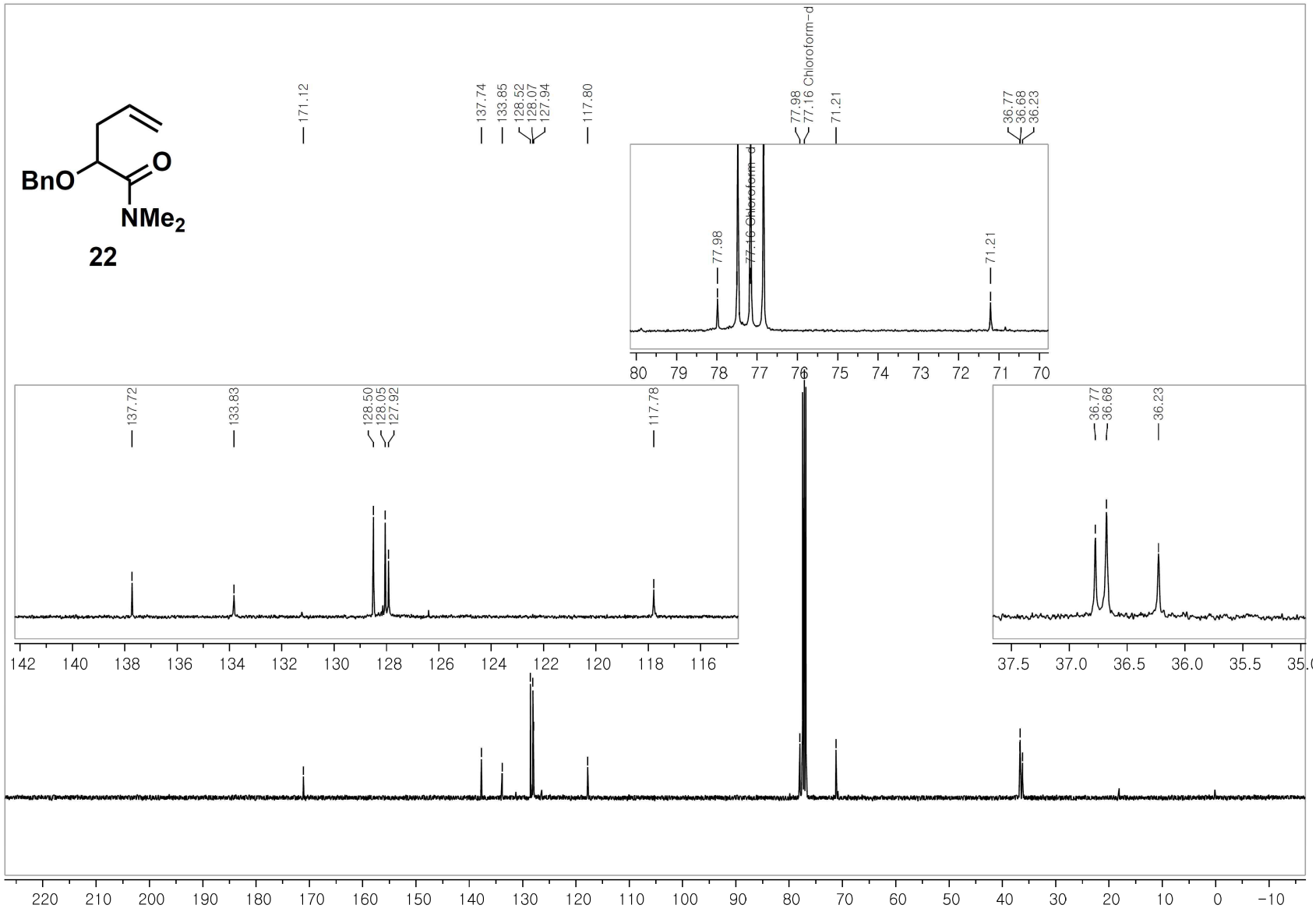

BnO
O
NMe2
22
Chloroform-d


BnO
O
NMe2
22
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128.52
128.07
127.94
117.80
77.98
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71.21
36.77
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36.23
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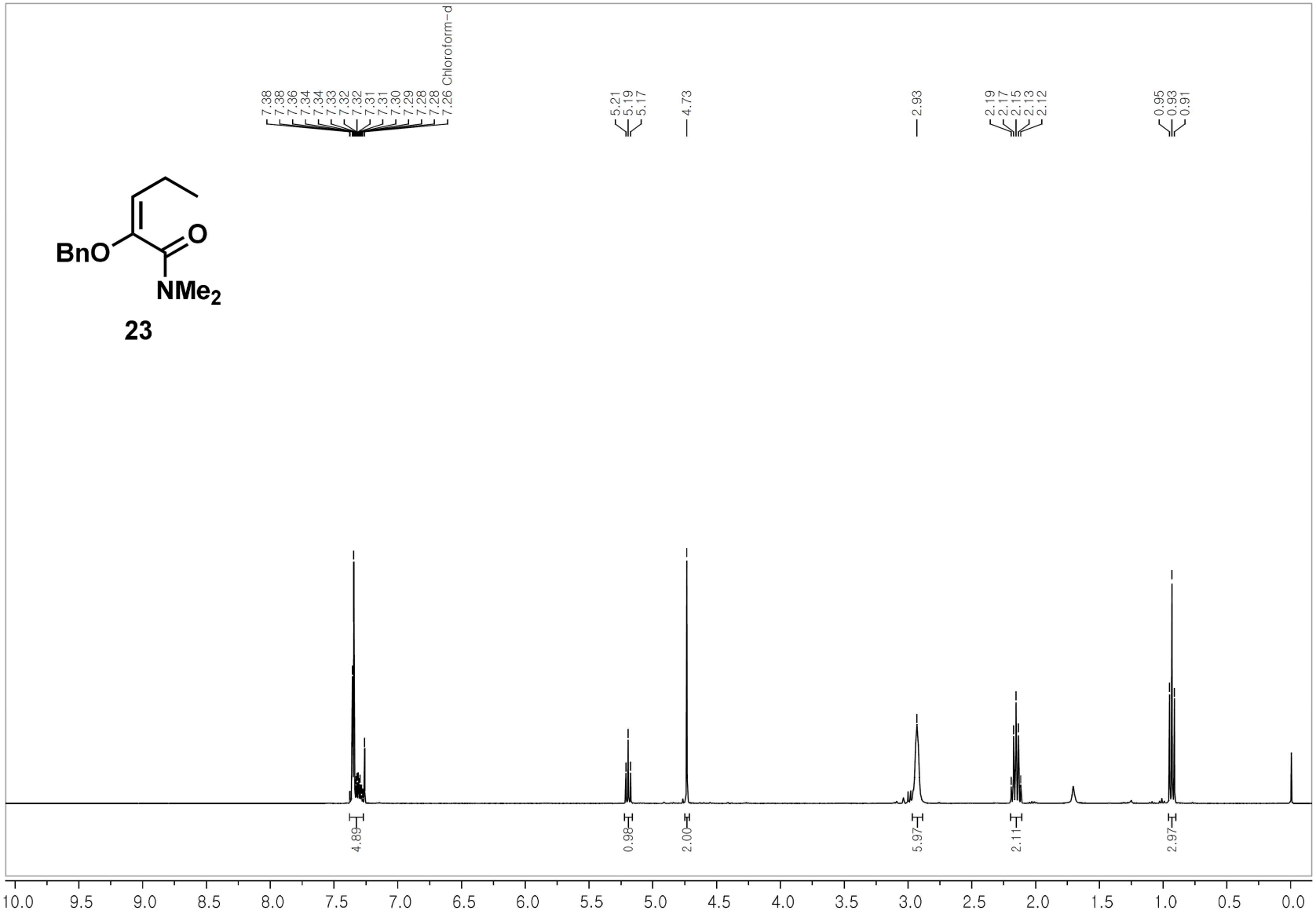
133.83
128.50
128.05
127.92
117.78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7.32
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7.28
7.28
7.26 Chloroform-d
5.21
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5.17
4.73
2.93
2.19
2.17
2.15
2.13
2.12
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0.93
0.91
BnO
O
NMe2
23
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5.97
2.11
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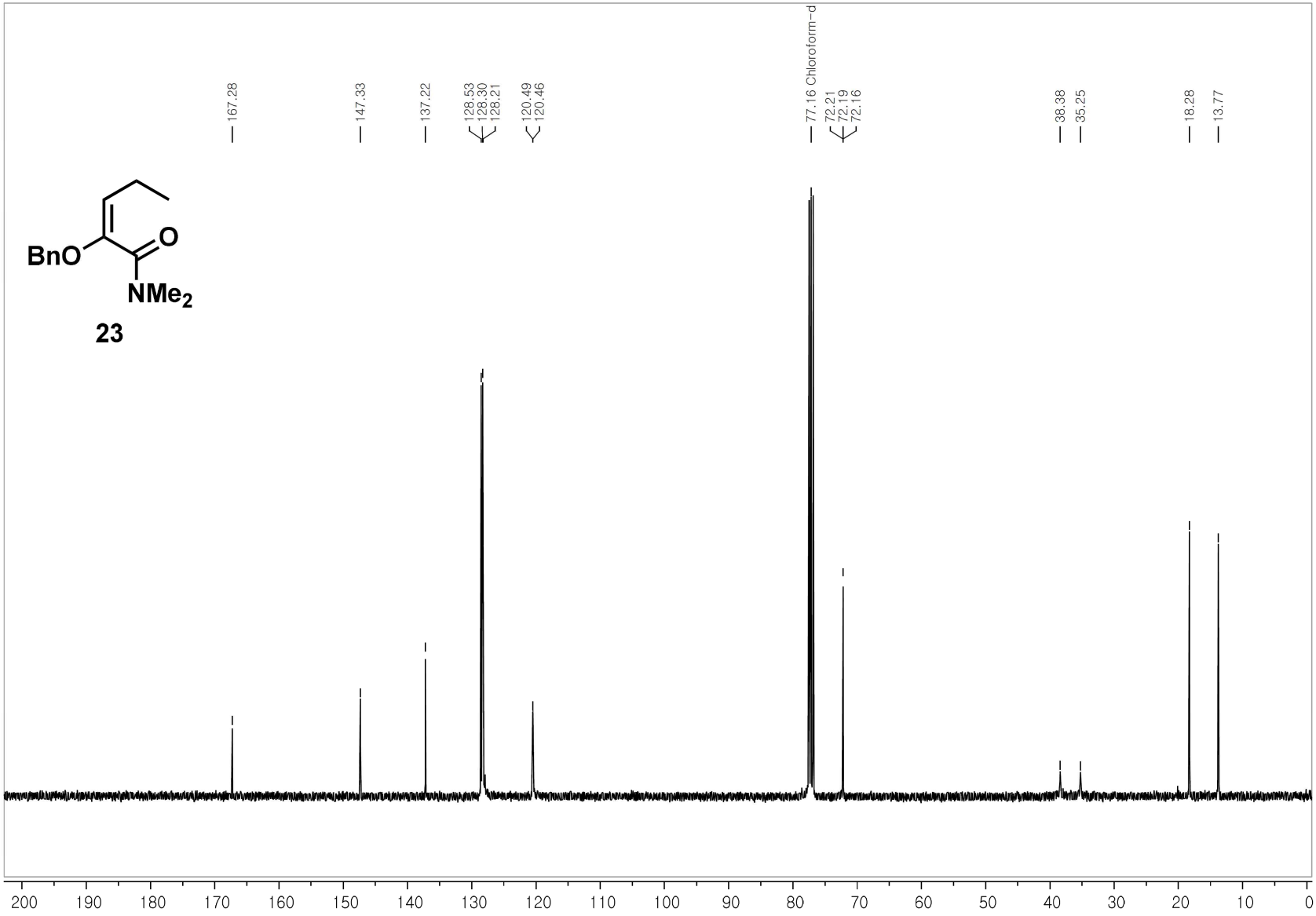
167.28
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120.46
77.16 Chloroform-d
72.21
72.19
72.16
38.38
35.25
18.28
13.77
BnO
O
NMe2
23
200
190
180
170
160
150
140
130
120
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100
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80
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40
30
20
10
0