Electronic Supplementary Information

Dearomative *ipso*-iodocyclization/desymmetrization sequence leading to optically active tricyclic piperazine scaffolds

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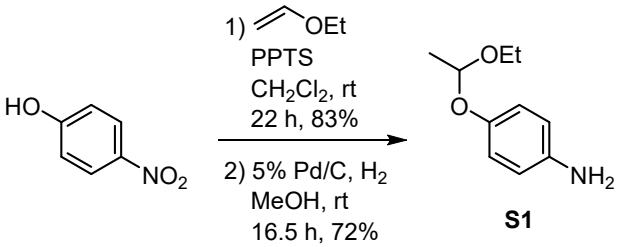
General. Melting point was measured by Yanagimoto micro melting point apparatus. Optical rotations were measured on a JASCO P-2200 polarimeter ($[\alpha]_D$ values are in units of 10^{-1} deg cm^2 g^{-1}). Unless otherwise noted, IR spectra were measured on a Perkin Elmer Spectrum 100 FT-IR spectrometer using $CHCl_3$. ^1H NMR and ^{13}C NMR spectra were determined on a Varian Mercury-300 or a Varian VXR-500 or a Brucker-600 superconducting FT-NMR spectrometer, respectively. Chemical shifts (δ) are reported in ppm relative to tetramethylsilane as internal reference ($CDCl_3$: δ = 0 ppm for ^1H) and residual solvent signal ($CDCl_3$: δ = 77.0 ppm for ^{13}C). *J*-Values are given in Hz. MS was performed on an Exactive Orbitrap mass spectrometer. Column chromatography was performed using Kanto Silica Gel 60 N (spherical, neutral). Microwave reactions were performed in a sealed vessel using a Biotage Initiator and reaction temperatures were measured using IR. Reaction times refer to the hold time at the desired set temperature and not to total irradiation time. All reaction was carried out under argon atmosphere. All reagents were directly used as obtained commercially.

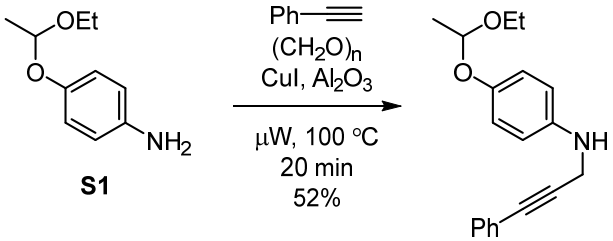
4-(1-Ethoxyethoxy)aniline (S1)



To a mixture of 4-nitrophenol (13.9 g, 100 mmol) and PPTS (2.51 g, 10.0mmol) in dry CH_2Cl_2 (500 mL) was added ethyl vinyl ether (17.2 mL, 180 mmol) and stirred at rt for 22 h. After the reaction was completed, the mixture was quenched with a saturated aqueous solution of $NaHCO_3$, extracted with CH_2Cl_2, dried over Na_2SO_4, filtered, and evaporated *in vacuo*. The residue was purified by flash column chromatography on silica gel eluting with hexane/EtOAc = 20:1 to give 1-(1-ethoxyethoxy)-4-nitrobenzene (17.5 g, 83%) as pale yellow oil. IR ν_{max}: 2983, 1594, 1516, 1344 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.2 Hz, 2H), 7.06 (d, *J* = 7.2 Hz, 2H), 5.52 (q, *J* = 5.1 Hz, 1H), 3.82-3.65 (m, 1H), 3.60-3.45 (m, 1H), 1.56 (d, *J* = 5.1 Hz, 3H), 1.20 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.0, 125.6, 116.7, 99.5, 61.1, 19.8, 15.2.

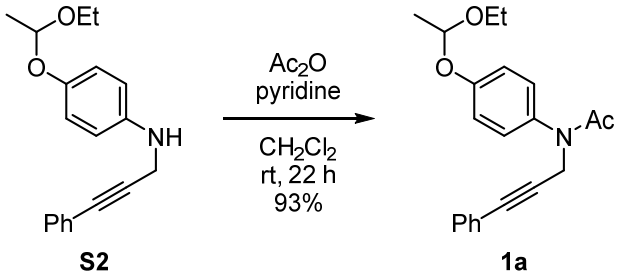
To a solution of 1-(1-ethoxyethoxy)-4-nitrobenzene (16.7 g, 79.1 mmol) in MeOH (158 mL) at rt was added 5% Pd/C (1.67 g). The reaction mixture was purged with H_2 gas, and was vigorously stirred at rt for 16.5 h. After the reaction was completed, the mixture was filtrated on Celite pad. The filtrate was evaporated *in vacuo*, and the residue was purified by flash column chromatography on silica gel eluting with hexane/EtOAc = 7:3 to give **S1** (10.3 g, 72%) as brown oil. IR ν_{max}: 3445, 3370, 3011, 1622 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.86-6.77 (m, 2H), 6.65-6.55 (m, 2H), 5.18 (q, *J* = 5.1 Hz, 1H), 3.85-3.70 (m, 1H), 3.60-3.35 (m, 3H), 1.43 (d, *J* = 5.1 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4, 141.2, 119.4, 116.0, 100.8, 61.7, 20.5, 15.3; HR-ESIMS calcd for $C_{10}H_{16}NO_2$ $[M+H]^+$ 182.1176. Found 182.1175.

4-(1-Ethoxyethoxy)-*N*-(3-phenylprop-2-yn-1-yl)aniline (S2)



According to the literature,[1] a mixture of **S1** (5.44 g, 30.0 mmol), ethynylbenzene (3.29 mL, 30.0 mmol), paraformaldehyde (0.901 g, 30.0 mmol), CuI (1.71 g, 9.00 mmol) and Al_2O_3 (3.00 g) was sealed and was stirred at 100 °C for 20 min in a microwave reactor. After cooling to rt, the mixture was filtrated on Celite pad, washed with EtOAc. The filtrate was evaporated *in vacuo*, and the residue was purified by flash column chromatography on silica gel eluting with hexane/EtOAc = 6:1: to give **S2** (4.64 g, 52%) as pale yellow oil. IR ν_{max}: 3021, 3012, 1615, 1599 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45-7.35 (m, 2H), 7.30-7.20 (m, 3H), 6.98-6.85 (m, 2H), 6.98-6.88 (m, 2H), 6.75-6.62 (m, 2H), 5.22 (q, *J* = 5.4 Hz, 1H), 4.10 (s, 2H), 3.92-3.70 (m, 2H), 3.65-3.48 (m, 1H), 1.44 (d, *J* = 5.4 Hz, 3H), 1.21 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.5, 142.4, 131.6, 128.2, 128.1, 122.8, 119.4, 114.7, 100.8, 85.6, 83.2, 61.7, 35.2, 20.5, 15.2; HR-ESIMS calcd for $C_{19}H_{22}NO_2$ $[M+H]^+$ 296.1645. Found 296.1646.

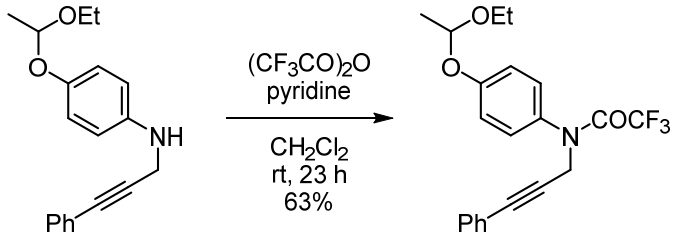
***N*-(4-(1-Ethoxyethoxy)phenyl)-*N*-(3-phenylprop-2-yn-1-yl)acetamide (1a)**



To a solution of **S2** (443 mg, 1.50 mmol), pyridine (0.485 mL, 6.00 mmol) in dry CH_2Cl_2 (6.0 mL) at 0 °C was added Ac_2O (0.284 mL, 3.00 mmol). The reaction mixture was allowed to rt, and was stirred for 22 h. After the reaction was completed, the reaction mixture was diluted with water, extracted with CH_2Cl_2. The organic layer was washed with a saturated aqueous solution of NH_4Cl, dried over Na_2SO_4, filtered and evaporated *in vacuo*. The residue was purified by flash column chromatography on silica gel eluting with hexane/acetone = 3:1 to give **1a** (469 mg, 93%) as pale yellow oil.

IR ν_{max}: 3012, 1652, 1599 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38-7.16 (m, 7H), 7.03 (d, *J* = 8.7 Hz, 2H), 5.40 (q, *J* = 5.1 Hz, 1H), 4.67 (s, 2H), 3.82-3.72 (m, 1H), 3.62-3.48 (m, 1H), 1.88 (s, 3H), 1.52 (d, *J* = 5.1 Hz, 3H), 1.21 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.9, 156.4, 135.7, 131.4, 129.2, 128.0, 122.7, 117.9, 99.4, 84.7, 84.0, 61.2, 39.1, 22.6, 20.3, 15.4; HR-ESIMS calcd for $C_{21}H_{24}NO_3$ $[M+H]^+$ 338.1751. Found 338.1749.

***N*-(4-(1-Ethoxyethoxy)phenyl)-2,2,2-trifluoro-*N*-(3-phenylprop-2-yn-1-yl)acetamide (1b)**

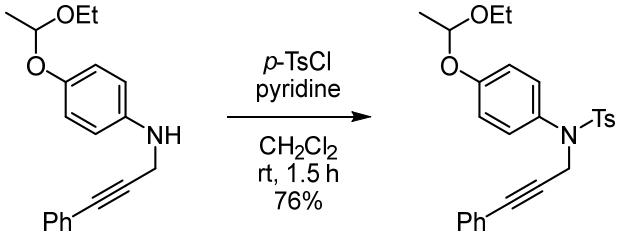


S2 **1b**

To a solution of **S2** (443 mg, 1.50 mmol), pyridine (0.485 mL, 6.00 mmol) in dry CH_2Cl_2 (6.0 mL) at 0 °C was added trifluoroacetic anhydride (0.417 mL, 3.00 mmol). The reaction mixture was allowed to rt, and was stirred for 23 h. After the reaction was completed, the reaction mixture was diluted with water, extracted with CH_2Cl_2. The organic layer was washed with a saturated aqueous solution of NH_4Cl, dried over Na_2SO_4, filtered and evaporated *in vacuo*. The residue was purified by flash column chromatography on silica gel eluting with hexane/acetone = 10:1 to give **1b** (369 mg, 63%) as pale yellow oil.

IR ν_{max}: 2982, 2242, 1670, 1605 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.38-7.34 (m, 2H), 7.33-7.25 (m, 5H), 7.05 (d, *J* = 8.4 Hz, 2H), 5.43 (q, *J* = 5.4 Hz, 1H), 4.71 (s, 2H), 3.80-3.74 (m, 1H), 3.59-3.53 (m, 1H), 1.52 (d, *J* = 5.4 Hz, 3H), 1.20 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.6, 156.7 (q, *J* = 36.0 Hz), 131.7, 131.6, 129.8, 128.6, 128.3, 122.2, 117.5, 116.3 (q, *J* = 286.5 Hz), 99.4, 85.6, 82.3, 61.1, 41.8, 20.0, 15.1; HR-ESIMS calcd for $C_{21}H_{20}F_3NNaO_3$ $[M+Na]^+$ 414.1287. Found 414.1282.

***N*-(4-(1-Ethoxyethoxy)phenyl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1c)**

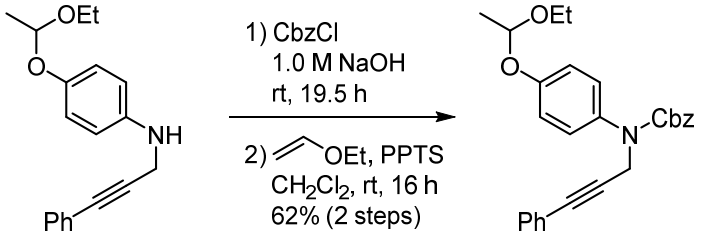


S2 **1c**

To a solution of **S2** (443 mg, 1.50 mmol), pyridine (0.600 mL, 7.42 mmol) in dry CH_2Cl_2 (3.0 mL) at rt was added *p*-TsCl (343 mg, 1.80 mmol). The reaction mixture was stirred at rt for 1.5 h. After the reaction was completed, the reaction mixture was quenched with 1 M HCl, extracted with Et_2O. The organic layer was washed with brine, dried over Na_2SO_4, filtered and evaporated *in vacuo*. The residue was purified by flash column chromatography on silica gel eluting with hexane/acetone = 5:1 to give **1c** (514 mg, 76%) as pale yellow oil.

IR ν_{max}: 3030, 1599, 1350, 1163 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.30-7.10 (m, 9H), 6.91 (d, *J* = 9.0 Hz, 2H), 5.36 (q, *J* = 5.4 Hz, 1H), 4.61 (s, 2H), 3.80-3.69 (m, 1H), 3.62-3.45 (m, 1H), 2.35 (s, 3H), 1.48 (d, *J* = 5.4 Hz, 3H), 1.19 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3, 143.1, 135.7, 132.9, 131.1, 129.7, 128.9, 128.1, 127.9, 127.8, 122.1, 117.1, 99.2, 85.4, 83.6, 61.2, 42.3, 21.6, 20.2, 15.3; HR-ESIMS calcd for $C_{26}H_{27}NNaO_4S$ $[M+Na]^+$ 472.1553. Found 472.1551.

Benzyl (4-(1-ethoxyethoxy)phenyl)(3-phenylprop-2-yn-1-yl)carbamate (1d)



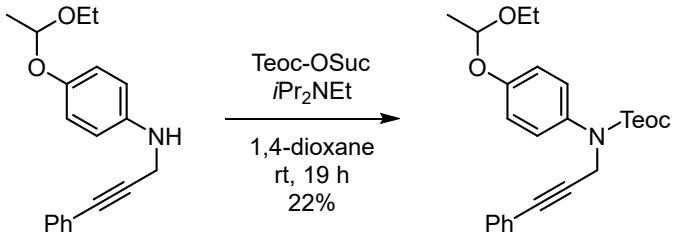
S2 **1d**

To a mixture of **S2** (398 mg, 1.35 mmol) in 1.0 M NaOH (1.35 mL) at rt was added CbzCl (290 μL, 2.03 mmol), and the mixture was stirred at this temperature for 19.5 h. After the reaction was completed, the mixture was diluted with water, extracted with EtOAc, dried over Na_2SO_4, filtered and evaporated *in vacuo*. The residue was purified by flash column chromatography on silica gel eluting with hexane/EtOAc = 2:1 to give benzyl (4-hydroxyphenyl)(3-phenylprop-2-yn-1-yl)carbamate (478 mg).

To a mixture of benzyl (4-hydroxyphenyl)(3-phenylprop-2-yn-1-yl)carbamate (478 mg) and PPTS (35.2 mg, 0.140 mmol) in dry CH_2Cl_2 (2.8 mL) was added ethyl vinyl ether (239 μL, 2.50 mmol) and stirred at rt for 16 h. After the reaction was completed, the mixture was quenched with a saturated aqueous solution of $NaHCO_3$, extracted with CH_2Cl_2, dried over Na_2SO_4, filtered, and evaporated *in vacuo*. The residue was purified by flash column chromatography on silica gel eluting with hexane/EtOAc = 6:1 to give **1d** (374 mg, 62% in 2 steps) as pale yellow oil.

IR ν_{max}: 3014, 1701, 1600 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40-7.10 (m, 12H), 6.98 (d, J = 9.0 Hz, 2H), 5.37 (q, J = 5.1 Hz, 1H), 5.18 (br s, 2H), 4.60 (s, 2H), 3.82-3.68 (m, 1H), 3.61-3.49 (m, 1H), 1.50 (d, J = 5.1 Hz, 3H), 1.20 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.5, 154.9, 136.3, 135.1, 131.4, 128.2 (2C), 128.04, 127.97, 127.6, 127.3, 122.6, 117.4, 99.6, 85.0, 84.2, 67.5, 61.3, 41.3, 20.4, 15.4; HR-ESIMS calcd for $C_{27}H_{27}NNaO_4$ $[M+Na]^+$ 452.1832. Found 452.1830.

2,2,2-Trichloroethyl (4-(1-ethoxyethoxy)phenyl)(3-phenylprop-2-yn-1-yl)carbamate (1e)



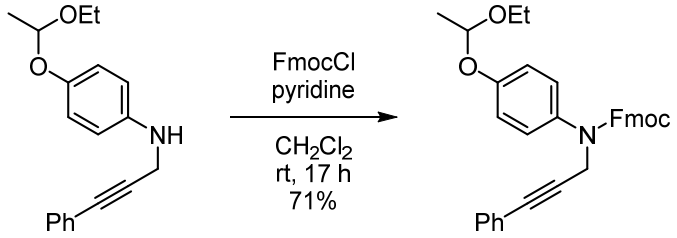
S2 **1e**

To a solution of **S2** (295 mg, 1.00 mmol), *i*Pr$_2$NEt (524 μL, 1.50 mmol) in dry 1,4-dioxane (2.0 mL) at rt was added Teoc-OSuc (142 mg, 1.10 mmol). The reaction mixture was stirred at rt for 19 h. After the reaction was completed, the reaction mixture was diluted with water, extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, filtered and evaporated *in vacuo*. The residue was purified by flash column chromatography on silica gel eluting with hexane/acetone = 10/1 to give **1e** (95.7 mg, 22%) as pale yellow oil.

IR ν_{max}: 3012, 1693, 1600 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38-7.30 (m, 2H), 7.29-7.16 (m, 5H), 6.97 (d, J = 9.0 Hz, 2H), 5.36 (q, J = 5.1 Hz, 1H), 4.58 (s, 2H), 4.22 (br t, J = 8.1 Hz, 2H), 3.83-3.72 (m, 1H), 3.59-3.48 (m, 1H), 1.50 (d, J = 5.1 Hz, 3H), 1.20 (t, J = 6.9 Hz, 3H), 0.97 (br s, 2H), -0.03 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3, 135.0, 131.3, 128.1, 128.0 (2C), 122.6, 117.3 (2C), 99.5, 85.1, 83.9, 64.3, 61.3, 41.0, 20.3, 17.8, 15.3, -1.3; HR-ESIMS calcd for $C_{25}H_{33}NNaO_4Si$ $[M+Na]^+$ 462.2071. Found

462.2073.

(9*H*-Fluoren-9-yl)methyl (4-(1-ethoxyethoxy)phenyl)(3-phenylprop-2-yn-1-yl)carbamate (1f)

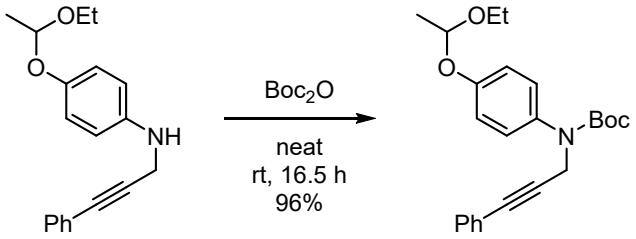


S2 **1f**

To a solution of **S2** (443 mg, 1.50 mmol), pyridine (243 μL, 3.00 mmol) in dry CH_2Cl_2 (4.5 mL) at 0 °C was added FmocCl (427 mg, 1.65 mmol). The reaction mixture was stirred at rt for 17 h. After the reaction was completed, the reaction mixture was diluted water, extracted with CH_2Cl_2, dried over Na_2SO_4, filtered and evaporated *in vacuo*. The residue was purified by flash column chromatography on silica gel eluting with hexane/EtOAc = 3/1 to give **1f** (550 mg, 71%) as pale yellow oil.

IR ν_{max}: 3013, 1701, 1607 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.2 Hz, 2H), 7.42-7.10 (m, 13H), 7.05 (d, *J* = 9.0 Hz, 2H), 5.42 (q, *J* = 5.1 Hz, 1H), 4.63 (s, 2H), 4.37 (s, 2H), 4.07 (s, 1H) 3.88-3.75 (m, 1H), 3.65-3.50 (m, 1H), 1.53 (d, *J* = 5.1 Hz, 3H), 1.22 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.1, 155.2, 143.7, 141.2, 134.7, 131.6, 129.0, 128.3, 128.2, 127.5, 126.9, 125.2, 122.7, 119.8, 117.6, 99.6, 84.8, 84.3, 67.9, 61.3, 47.0, 41.0, 20.2, 15.2; HR-ESIMS calcd for $C_{34}H_{31}NNaO_4$ $[M+Na]^+$ 540.2145. Found 540.2151.

***tert*-Butyl (4-(1-ethoxyethoxy)phenyl)(3-phenylprop-2-yn-1-yl)carbamate (1g)**

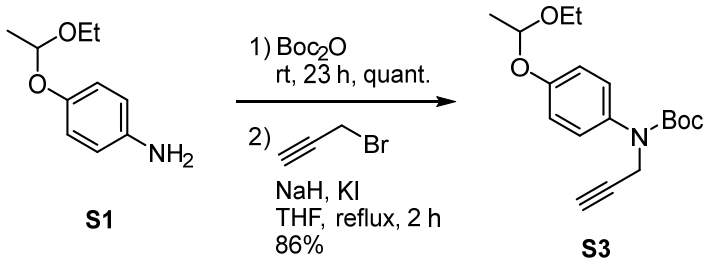


S2 **1g**

According to the literature,[2] Boc_2O (230 μL, 1.00 mmol) was added to **S2** (295 mg, 1.00 mmol) at rt, and the reaction mixture was stirred for 16.5 h. After the reaction was completed, the reaction mixture was directly purified by flash column chromatography on silica gel eluting with hexane/EtOAc = 15:1 to give **1g** (380 mg, 96%) as pale yellow oil.

IR ν_{max}: 3013, 1692, 1599 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40-7.30 (m, 2H), 7.29-7.18 (m, 5H), 6.96 (d, *J* = 8.7 Hz, 2H), 5.35 (q, *J* = 5.4 Hz, 1H), 4.53 (s, 2H), 3.83-3.72 (m, 1H), 3.59-3.50 (m, 1H), 1.50 (s, 9H), 1.48 (d, *J* = 5.4 Hz, 3H), 1.20 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.0, 154.2, 135.9, 131.4, 128.0, 127.9, 127.7, 122.8, 117.3, 99.7, 85.6, 83.7, 80.7, 61.4, 40.9, 28.5, 20.4, 15.4; HR-ESIMS calcd for $C_{24}H_{29}NNaO_4$ $[M+Na]^+$ 418.1989. Found 418.1988.

***tert*-Butyl (4-(1-ethoxyethoxy)phenyl)(prop-2-yn-1-yl)carbamate (S3)**

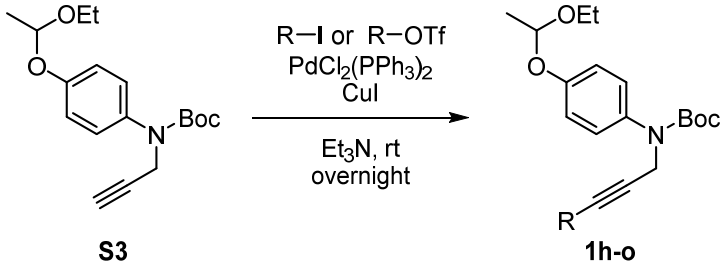


According to the literature,[2] Boc_2O (3.45 mL, 15.0 mmol) was added to **S1** (2.72 g, 15.0 mmol) at rt, and the reaction mixture was stirred for 23 h. After the reaction was completed, the reaction mixture was evaporated *in vacuo* to give *tert*-butyl (4-(1-ethoxyethoxy)phenyl)carbamate (4.22 g, quant.) as colorless oil.

To a solution of *tert*-butyl (4-(1-ethoxyethoxy)phenyl)carbamate (4.22 g, 15.0 mmol) in dry THF (50 mL) at 0 °C was added NaH (60% in mineral oil, 0.660 g, 16.5 mmol, and was stirred at 0 °C for 10 min. Then, propargyl bromide (1.36 mL, 18.0 mmol) was added, and was stirred at rt for 19 h. KI (3.74 g, 22.5 mmol) was added to the mixture, and was heated under reflux for 2 h. After the reaction was completed, the mixture was cooled to rt, the reaction mixture was diluted with a saturated aqueous solution of NH_4Cl, extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, filtered and evaporated *in vacuo*. The residue was purified by flash column chromatography on silica gel eluting with hexane/acetone = 10:1 to give **S3** (4.13 g, 86%) as colorless oil.

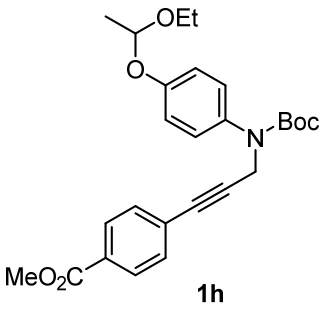
IR ν_{max}: 3308, 2982, 2124, 1694, 1608 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 5.35 (q, J = 5.1 Hz, 1H), 4.30 (s, 2H), 3.82-3.70 (m, 1H), 3.60-3.47 (m, 1H), 2.24 (d, J = 2.7 Hz, 1H), 1.49 (d, J = 5.1 Hz, 3H), 1.44 (s, 9H), 1.20 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9, 153.9, 135.7, 127.4, 117.2, 99.5, 80.7, 79.9, 71.6, 61.3, 40.0, 28.3, 20.3, 15.3; HR-ESIMS calcd for $C_{18}H_{25}NNaO_4$ $[M+Na]^+$ 342.1676. Found 342.1673.

General Procedure for Sonogashira Coupling (GP1)



A solution of **S3** (319 mg, 1.00 mmol), aryl iodide or vinyl triflate (1.20 mmol), $PdCl_2(PPh_3)_2$ (14.0 mg, 0.0200 mmol), CuI (3.8 mg, 0.0200 mmol) in Et_3N (5.5 mL) was stirred at rt overnight. After the reaction was completed, the mixture was filtrated with Celite, and the filtrate was evaporated *in vacuo*. The residue was diluted with a saturated aqueous solution of NH_4Cl, and extracted with Et_2O. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated *in vacuo*. The residue was purified by flash column chromatography on silica gel to give **1h-o**.

Methyl 4-(3-((*tert*-butoxycarbonyl)(4-(1-ethoxyethoxy)phenyl)amino)prop-1-yn-1-yl)benzoate (1h)

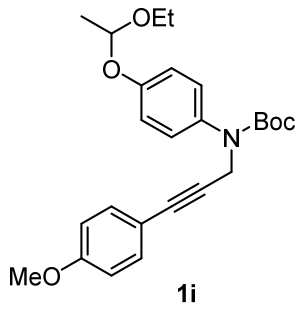


1h

According to **GP1**, **1h** (411 mg, 91%) was obtained from methyl 4-iodobenzoate (315 mg, 1.20 mmol). Eluent: hexane/EtOAc = 6/1.

Yellow oil; IR ν_{max}: 2982, 1707, 1607 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 8.7 Hz, 2H), 7.26 (br d, *J* = 9.3 Hz, 2H), 6.99 (d, *J* = 9.0 Hz, 2H), 5.37 (q, *J* = 5.4 Hz, 1H), 4.57 (s, 2H), 3.91 (s, 3H), 3.84-3.73 (m, 1H), 3.60-3.48 (m, 1H), 1.50 (d, *J* = 5.4 Hz, 3H), 1.47 (br s, 9H), 1.20 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 155.2, 154.4, 135.9, 131.5, 129.5, 129.4, 127.8, 127.6, 117.5, 99.6, 88.7, 83.0, 80.9, 61.3, 52.2, 40.7, 28.3, 20.2, 15.1; HR-ESIMS calcd for $C_{26}H_{31}NNaO_6$ $[M+Na]^+$ 476.2044. Found 476.2047.

***tert*-Butyl (4-(1-ethoxyethoxy)phenyl)(3-(4-methoxyphenyl)prop-2-yn-1-yl)carbamate (1i)**

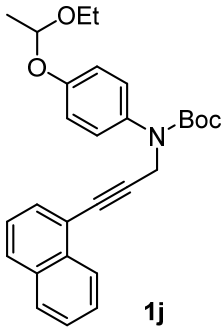


1i

According to **GP1**, **1i** (412 mg, 97%) was obtained from 4-iodoanisole (281 μL, 1.20 mmol). Eluent: hexane/EtOAc = 6/1.

Pale yellow oil; IR ν_{max}: 3010, 2245, 1691, 1606 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38-7.20 (m, 4H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 5.35 (q, *J* = 5.1 Hz, 1H), 4.51 (s, 2H), 3.82-3.70 (m, 4H), 3.60-3.48 (m, 1H), 1.49 (d, *J* = 5.1 Hz, 3H), 1.46 (s, 9H), 1.20 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 154.8, 154.1, 135.9, 132.7, 127.6, 117.2, 114.9, 113.6, 99.6, 84.0, 83.4, 80.6, 61.4, 55.3, 40.8, 28.4, 20.4, 15.3; HR-ESIMS calcd for $C_{25}H_{31}NNaO_5$ $[M+Na]^+$ 448.2094. Found 448.2093.

***tert*-Butyl (4-(1-ethoxyethoxy)phenyl)(3-(naphthalen-1-yl)prop-2-yn-1-yl)carbamate (1j)**

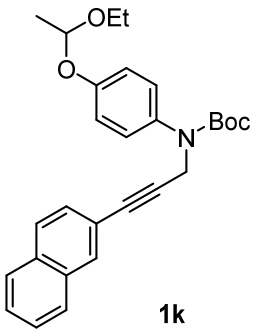


1j

According to **GP1**, **1j** (441 mg, 99%) was obtained from 1-iodonaphthalene (175 μL, 1.20 mmol). Eluent: hexane/EtOAc = 6/1.

Pale yellow oil; IR ν_{max}: 3016, 2364, 1691, 1606, 1587 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.20-8.11 (br m, 1H), 7.85-7.73 (m, 2H), 7.60 (d, *J* = 6.9 Hz, 1H), 7.54-7.43 (m, 2H), 7.42-7.26 (m, 3H), 7.00 (d, *J* = 9.0 Hz, 2H), 5.36 (q, *J* = 5.1 Hz, 1H), 4.71 (s, 2H), 3.83-3.71 (m, 1H), 3.59-3.47 (m, 1H), 1.60-1.40 (m, 12H), 1.19 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.2, 154.4, 136.0, 133.3, 133.0, 130.2, 128.6, 128.1, 127.9, 126.6, 126.3, 126.1, 125.1, 120.5, 117.4, 99.7, 90.4, 81.8, 80.8, 61.3, 40.9, 28.3, 20.2, 15.1; HR-ESIMS calcd for $C_{28}H_{31}NNaO_4$ $[M+Na]^+$ 468.2145. Found 468.2149.

***tert*-Butyl (4-(1-ethoxyethoxy)phenyl)(3-(naphthalen-2-yl)prop-2-yn-1-yl)carbamate (1k)**



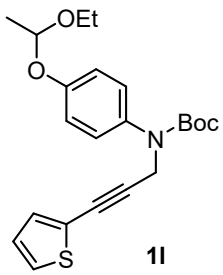
1k

According to **GP1**, **1k** (345 mg, 79%) was obtained from 2-iodonaphthalene (305 mg, 1.20 mmol). Eluent: hexane/EtOAc = 7/1.

Pale yellow oil; IR ν_{max}: 2982, 1693, 1598 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.81-7.73 (m, 3H), 7.49-7.44 (m, 2H), 7.41 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.30 (br d, *J* = 8.1 Hz, 2H), 7.00 (d, *J* = 9.0 Hz, 2H), 5.37 (q, *J* = 5.4 Hz, 1H), 4.60 (s, 2H), 3.85-3.72 (m, 1H), 3.60-3.48 (m, 1H), 1.50 (d, *J* = 5.4 Hz, 3H), 1.48 (br s, 9H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.2, 154.5, 136.1, 132.8, 132.7, 131.4, 128.4, 127.9, 127.7, 127.62 (2C), 126.6, 126.5, 120.2, 117.5, 99.7,

85.9, 84.0, 80.8, 61.4, 40.8, 28.3, 20.2, 15.1; HR-ESIMS calcd for $C_{28}H_{31}NNaO_4$ $[M+Na]^+$ 468.2145. Found 468.2143.

***tert*-Butyl (4-(1-ethoxyethoxy)phenyl)(3-(thiophen-2-yl)prop-2-yn-1-yl)carbamate (1l)**

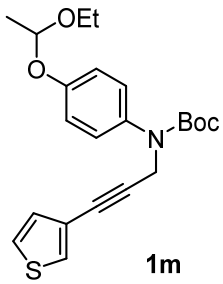


1l

According to **GP1**, **1l** (374 mg, 93%) was obtained from 2-iodothiophene (122 μL, 1.20 mmol). Eluent: hexane/acetone = 10/1.

Pale yellow oil; IR ν_{max}: 3020, 1693, 1608 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.26-7.16 (m, 3H), 7.13 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.98-6.91 (m, 3H), 5.35 (q, *J* = 5.1 Hz, 1H), 4.53 (s, 2H), 3.88-3.72 (m, 1H), 3.61-3.48 (m, 1H), 1.49 (d, *J* = 5.1 Hz, 3H), 1.46 (s, 9H), 1.20 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9, 154.1, 135.8, 131.7, 127.6, 126.7, 126.6, 122.7, 117.3, 99.6, 89.5, 87.1, 80.8, 61.4, 41.1, 28.5, 20.4, 15.4; HR-ESIMS calcd for $C_{22}H_{27}NNaO_4S$ $[M+Na]^+$ 424.1553 . Found 424.1550.

***tert*-Butyl (4-(1-ethoxyethoxy)phenyl)(3-(thiophen-3-yl)prop-2-yn-1-yl)carbamate (1m)**

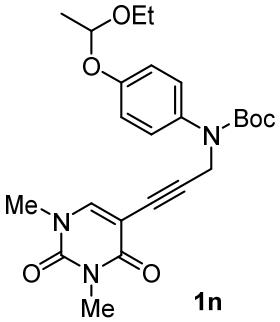


1m

According to **GP1**, **1m** (399 mg, 99%) was obtained from 3-iodothiophene (122 μL, 1.20 mmol). Eluent: hexane/EtOAc = 6/1.

Pale yellow oil; IR ν_{max}: 3020, 2366, 1693, 1608 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.31-7.19 (m, 3H), 7.03 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.95 (d, *J* = 9.0 Hz, 2H), 5.35 (q, *J* = 5.1 Hz, 1H), 4.51 (s, 2H), 3.88-3.70 (m, 1H), 3.60-3.47 (m, 1H), 1.49 (d, *J* = 5.1 Hz, 3H), 1.46 (s, 9H), 1.20 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9, 154.2, 135.8, 129.6, 128.4, 127.6, 125.0, 121.8, 117.3, 99.6, 85.1, 80.8, 78.7, 61.4, 40.9, 28.5, 20.4, 15.4; HR-ESIMS calcd for $C_{22}H_{27}NNaO_4S$ $[M+Na]^+$ 424.1553. Found 424.1554.

***tert*-Butyl (3-(1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)prop-2-yn-1-yl) (4-(1-ethoxyethoxy)phenyl)carbamate (1n)**

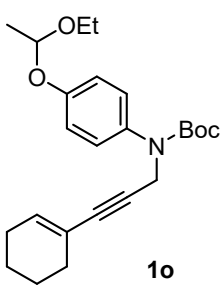


1n

According to **GP1**, **1n** (325 mg, 71%), was obtained from 5-iodo-1,3-dimethyluracil (319 mg, 1.20 mmol). Eluent: hexane/EtOAc = 1/1.

Pale yellow oil; IR ν_{max}: 3013, 2235, 1711, 1692, 1660, 1608 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.26 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 9.0 Hz, 2H), 5.36 (q, *J* = 5.4 Hz, 1H), 4.53 (s, 2H), 3.84-3.72 (m, 1H), 3.60-3.48 (m, 1H), 3.40 (s, 3H), 3.35 (s, 3H), 1.49 (d, *J* = 5.4 Hz, 3H), 1.45 (s, 9H), 1.20 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.6, 155.0, 154.1, 150.7, 145.6, 135.9, 127.6, 117.3, 99.5, 98.3, 89.6, 80.6, 74.8, 61.2, 40.6, 37.1, 28.1 (2C), 20.1, 15.0; HR-ESIMS calcd for $C_{24}H_{31}N_3NaO_6$ $[M+Na]^+$ 480.2105. Found 480.2101.

***tert*-Butyl (3-(cyclohex-1-en-1-yl)prop-2-yn-1-yl)(4-(1-ethoxyethoxy)phenyl)carbamate (1o)**

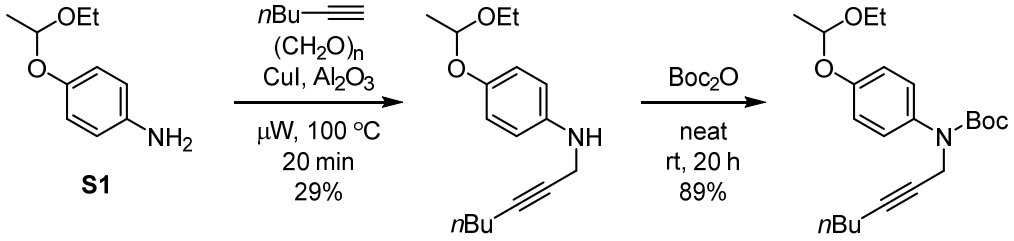


1o

According to **GP1**, **1o** (366 mg, 92%) was obtained from 1-cyclohexenyl trifluoromethanesulfonate (210 mg, 1.20 mmol). Eluent: hexane/EtOAc = 15/1.

Colorless oil; IR ν_{max}: 3011, 2224, 1692, 1606 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.20 (br d, J = 8.7 Hz, 2H), 6.94 (d, J = 9.0 Hz, 2H), 6.01 (br s, 1H), 5.34 (q, J = 5.4 Hz, 1H), 4.41 (s, 2H), 3.82-3.70 (m, 1H), 3.60-3.48 (m, 1H), 2.10-2.02 (br m, 4H), 1.62-1.52 (m, 4H), 1.49 (d, J = 5.1 Hz, 3H), 1.45 (s, 9H), 1.20 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8, 154.1, 135.9, 134.3, 127.6, 120.2, 117.2, 99.6, 85.4, 82.7, 80.6, 61.4, 40.7, 29.3, 28.5, 25.7, 22.4, 21.6, 20.4, 15.4; HR-ESIMS calcd for $C_{24}H_{33}NNaO_4$ $[M+Na]^+$ 422.2302. Found 422.2301.

***tert*-Butyl (4-(1-ethoxyethoxy)phenyl)(hept-2-yn-1-yl)carbamate (1p)**

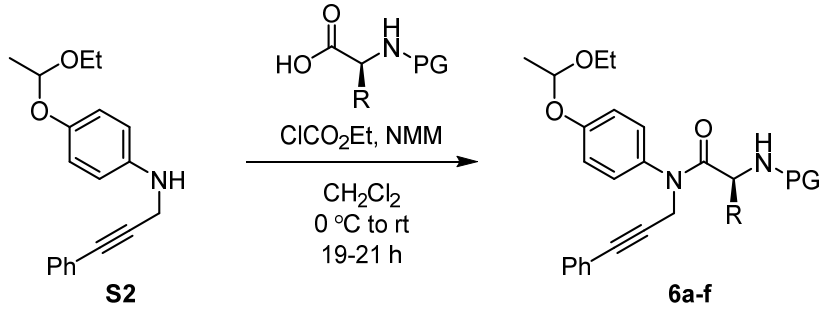


According to the literature,[1] a mixture of **S1** (363 mg, 2.00 mmol), 1-hexyne (230 μL, 2.00 mmol), paraformaldehyde (60.1 mg, 2.00 mmol), CuI (114 mg, 0.600 mmol) and Al_2O_3 (200 mg) was sealed and was stirred at 100 °C for 20 min in a microwave reactor. After cooling to rt, the mixture was filtrated on Celite pad, washed with EtOAc. The filtrate was evaporated *in vacuo*, and the residue was purified by flash column chromatography on silica gel eluting with hexane/EtOAc = 4:1: to give **S4** (79.2 mg, 29%) as yellow oil. IR ν_{max}: 3423, 2934, 2232, 1615 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.99 (d, J = 8.7 Hz, 2H), 6.62 (d, J = 8.7 Hz, 2H), 5.21 (q, J = 5.4 Hz, 1H), 3.90-3.77 (m, 3H), 3.66 (br s, 1H), 3.62-3.49 (m, 1H), 2.16 (tt, J = 6.9, 1.8 Hz, 2H), 1.51-1.30 (m, 7H), 1.21 (t, J = 6.9 Hz, 3H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.3, 142.7, 119.4, 114.6, 100.8, 83.7, 77.0, 61.7, 34.8, 30.7, 21.8, 20.5, 18.3, 15.2, 13.6; HR-ESIMS calcd for $C_{17}H_{26}NO_2$ $[M+H]^+$ 276.1958. Found 276.1959.

According to the literature,[2] Boc_2O (66.1 μL, 0.288 mmol) was added to **S4** (79.2 mg, 0.288 mmol) at rt, and the reaction mixture was stirred for 2.5 h. Then, Boc_2O (66.1 μL, 0.288 mmol) was added again, and the reaction mixture was stirred for 17.5 h. After the reaction was almost completed, the reaction mixture was evaporated *in vacuo*, and the residue was purified by flash column chromatography on silica gel eluting with hexane/EtOAc = 10:1 to give **1p** (96.6 g, 89%) as yellow oil.

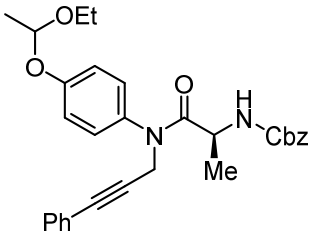
IR ν_{max}: 2934, 2223, 1693, 1608 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.21 (br d, J = 7.0 Hz, 1H), 6.95 (d, J = 9.0 Hz, 2H), 5.36 (q, J = 5.0 Hz, 1H), 4.29 (s, 2H), 3.82-3.75 (m, 1H), 3.58-3.51 (m, 1H), 2.16 (tt, J = 7.0, 2.0 Hz, 2H), 1.49 (d, J = 5.0 Hz, 3H), 1.48-1.32 (m, 13H), 1.21 (t, J = 7.0 Hz, 3H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.0, 154.4, 136.3, 127.7, 117.3, 99.7, 84.0, 80.5, 76.1, 61.4, 40.3, 30.7, 28.3, 21.8, 20.2, 18.3, 15.1, 13.5; HR-ESIMS calcd for $C_{22}H_{33}NNaO_4$ $[M+Na]^+$ 398.2302. Found 398.2314.

General Procedure for the Preparation of 6a-f (GP2)



To a solution of *N*-protected amino acid (1 equiv) and *N*-methylmorpholine (1 equiv) in dry CH_2Cl_2 (0.12 M) was treated at 0 °C with ethyl chloroformate (1 equiv). After 20 min at 0 °C, **S2** (1 equiv) in dry CH_2Cl_2 (1.5 mL) was added *via* cannula. The reaction mixture was stirred at 0 °C for 0.5 h, and then stirred at room temperature overnight (19-21 h). The reaction mixture was quenched with a saturated aqueous solution of NH_4Cl, and was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtered, and evaporated *in vacuo*. The residue was purified by flash column chromatography on silica gel to give **6**.

Benzyl ((2*S*)-1-((4-(1-ethoxyethoxy)phenyl)-(3-phenylprop-2-yn-1-yl)amino)-1-oxopropan-2-yl)carbamate (6a)

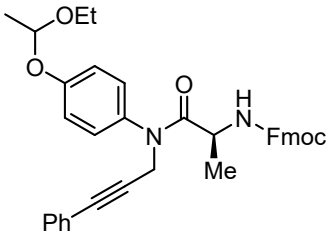


6a

According to **GP2**, **6a** (114 mg, 76%) was obtained from **S2** (88.6 mg, 0.300 mmol), *N*-Cbz-L-Ala-OH (67.0 mg, 0.300 mmol), ethyl chloroformate (28.6 μL, 0.300 mmol) and *N*-methylmorpholine (33.0 μL, 0.300 mmol). Eluent: hexane/acetone = 3:1.

Pale yellow oil; $[\alpha]_D^{25}$ +62.2 (*c* 1.02, $CHCl_3$); IR ν_{max}: 3429, 3020, 1717, 1658, 1600 cm^{-1}; The ^1H and ^{13}C NMR spectra of **6a** showed the presence of two rotamers (1:1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.40-7.18 (m, 12H), 7.05 (d, *J* = 8.7 Hz, 2H), 5.63 (br d, *J* = 7.8 Hz, 1H), 5.48-5.34 (m, 1H), 5.08 (d, *J* = 12.0 Hz, 1H), 5.02 (d, *J* = 12.0 Hz, 1H), 4.71 (d, *J* = 17.1 Hz, 1H), 4.62 (d, *J* = 17.1 Hz, 1H), 4.45-4.29 (m, 1H), 3.86-3.72 (m, 1H), 3.68-3.50 (m, 1H), 1.52 (d, *J* = 5.1 Hz, 3H), 1.32-1.12 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 157.0, 155.3, 136.3, 133.6, 131.5, 129.6, 128.3, 128.2, 128.1, 127.9, 127.8, 122.6, 117.9, 99.5, 99.3, 84.6, 84.1, 66.6, 61.3, 61.1, 47.6, 39.8, 20.2, 20.1, 19.1, 15.2; HR-ESIMS calcd for $C_{30}H_{32}N_2NaO_5$ $[M+Na]^+$ 523.2203. Found 523.2206.

(9*H*-Fluoren-9-yl)methyl ((2*S*)-1-((4-(1-ethoxyethoxy)phenyl)(3-phenylprop-2-yn-1-yl)amino)-1-oxopropan-2-yl)carbamate (6b)



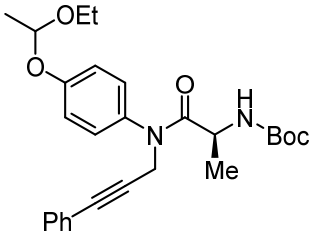
6b

According to **GP2**, **6b** (426 mg, 60%) was obtained from **S2** (354 mg, 1.20 mmol), *N*-Fmoc-L-Ala-OH (435 mg, 1.32 mmol), ethyl chloroformate (126 μL, 1.32 mmol) and *N*-methylmorpholine (145 μL, 1.32 mmol). Eluent: hexane/acetone = 4:1.

Colorless amorphous solid; $[\alpha]_D^{26}$ +68.0 (*c* 0.600, $CHCl_3$); IR ν_{max}: 3427, 3018, 1718, 1659, 1600 cm^{-1}; The ^1H and ^{13}C NMR spectra of **6b** showed the presence of two rotamers (1:1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 6.6 Hz, 2H), 7.42-7.22 (m, 11H), 7.07 (d, *J* = 8.4 Hz, 2H), 5.68 (d, *J* = 8.4 Hz, 1H), 5.46-5.36 (m, 1H), 4.73 (d, *J* = 17.1 Hz, 1H), 4.66 (d, *J* = 17.1 Hz, 1H), 4.45-4.26 (m, 3H), 4.19 (t, *J* = 7.2 Hz, 1H), 3.85-3.71 (m, 1H), 3.63-3.50 (m,

1H), 1.52 (d, *J* = 5.4 Hz, 3H), 1.26-1.12 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 157.2, 157.1, 155.4, 143.9, 143.8, 141.2, 133.5, 131.6, 129.7, 128.3, 128.2, 127.6, 127.0, 125.1, 122.6, 119.9, 117.9, 99.5, 99.3, 84.6, 84.0, 66.8, 61.3, 61.1, 47.5, 47.1, 39.7, 20.03, 19.99, 19.0, 15.1; HR-ESIMS calcd for $C_{37}H_{36}N_2NaO_5$ $[M+Na]^+$ 611.2516. Found 611.2516.

***tert*-Butyl ((2*S*)-1-((4-(1-ethoxyethoxy)phenyl)(3-phenylprop-2-yn-1-yl)amino)-1-oxopropan-2-yl)carbamate (6c)**

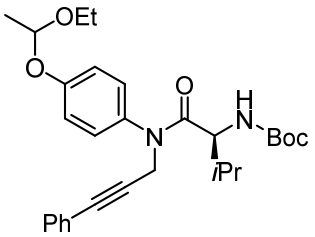


6c

According to **GP2**, **6c** (336 mg, 60%) was obtained from **S2** (354 mg, 1.20 mmol), *N*-Boc-L-Ala-OH (250 mg, 1.32 mmol), ethyl chloroformate (126 μL, 1.32 mmol) and *N*-methylmorpholine (145 μL, 1.32 mmol). Eluent: hexane/acetone = 8:1.

Colorless amorphous solid; $[\alpha]_D^{26}$ +68.0 (*c* 1.32, $CHCl_3$); IR ν_{max}: 3435, 2982, 1707, 1658, 1599 cm^{-1}; The ^{1}H and ^{13}C NMR spectra of **6c** showed the presence of two rotamers (1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.19 (m, 7H), 7.04 (d, *J* = 8.7 Hz, 2H), 5.46-5.35 (m, 1H), 5.30 (br d, *J* = 7.8 Hz, 1H), 4.70 (d, *J* = 17.1 Hz, 1H), 4.62 (d, *J* = 17.1 Hz, 1H), 4.38-4.22 (m, 1H), 3.86-3.72 (m, 1H), 3.63-3.50 (m, 1H), 1.52 (d, *J* = 5.4 Hz, 3H), 1.41 (s, 9H), 1.23 (t, *J* = 6.9 Hz, 1.5H), 1.22 (t, *J* = 6.9 Hz, 1.5H), 1.15 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 157.10, 157.05, 154.9, 133.7, 131.6, 129.7, 128.3, 128.2, 122.7, 117.9, 99.5, 99.3, 84.5, 84.2, 79.4, 61.4, 61.1, 47.0, 39.7, 28.3, 20.1, 20.0, 19.1, 15.2; HR-ESIMS calcd for $C_{27}H_{34}N_2NaO$ $[M+Na]^+$ 489.2360. Found 489.2360.

***tert*-Butyl ((2*S*)-1-((4-(1-ethoxyethoxy)phenyl)(3-phenylprop-2-yn-1-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate (6d)**

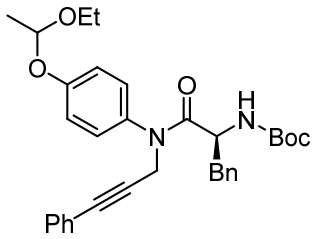


6d

According to **GP2**, **6d** (234 mg, 39%) was obtained from **S2** (354 mg, 1.20 mmol), *N*-Boc-L-Val-OH (287 mg, 1.32 mmol), ethyl chloroformate (126 μL, 1.32 mmol) and *N*-methylmorpholine (291 μL, 2.64 mmol). Eluent: hexane/EtOAc = 8:1.

Colorless amorphous solid; $[\alpha]_D^{26}$ +144 (*c* 1.14, $CHCl_3$); IR ν_{max}: 3435, 2980, 1709, 1655, 1601 cm^{-1}; The ^{1}H and ^{13}C NMR spectra of **6d** showed the presence of two rotamers (1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.20 (m, 7H), 7.04 (dd, *J* = 8.7, 1.8 Hz, 2H), 5.46-5.36 (m, 1H), 5.17 (br d, *J* = 8.7 Hz, 1H), 4.78 (d, *J* = 17.1 Hz, 1H), 4.53 (d, *J* = 17.1 Hz, 1H), 4.28-4.18 (br m, 1H), 3.84-3.71 (m, 1H), 3.62-3.48 (m, 1H), 1.94-1.80 (m, 1H), 1.51 (d, *J* = 5.1 Hz, 3H), 1.42 (s, 9H), 1.25-1.17 (m, 3H), 0.82 (d, *J* = 6.9 Hz, 3H), 0.76 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.7, 156.6, 156.5, 155.1, 134.0, 131.4, 129.4, 128.01, 127.96, 122.6, 117.8, 117.7, 99.5, 99.2, 84.4, 84.2, 79.2, 61.4, 61.0, 55.7, 39.9, 31.5, 28.5, 20.3, 20.2, 19.7, 17.2, 15.4; HR-ESIMS calcd for $C_{29}H_{38}N_2NaO_5$ $[M+Na]^+$ 517.2673. Found 517.2671.

***tert*-Butyl ((2*S*)-1-((4-(1-ethoxyethoxy)phenyl)(3-phenylprop-2-yn-1-yl)amino)-1-oxo-3-phenylpropan-2-yl)carbamate (6e)**

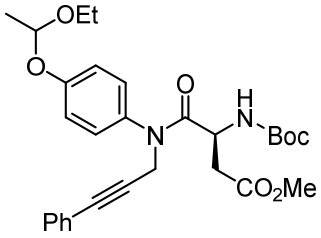


6e

According to **GP2**, **6e** (426 mg, 65%) was obtained from **S2** (354 mg, 1.20 mmol), *N*-Boc-L-Phe-OH (435 mg, 1.32 mmol), ethyl chloroformate (126 μL, 1.32 mmol) and *N*-methylmorpholine (145 μL, 1.32 mmol). Eluent: hexane/acetone = 3:1.

Colorless oil; $[\alpha]_D^{25}$ +69.4 (*c* 1.01, $CHCl_3$); IR ν_{max}: 3434, 3012, 1709, 1655, 1603 cm^{-1}; The ^1H and ^{13}C NMR spectra of **6e** showed the presence of some rotamers; ^1H NMR (300 MHz, $CDCl_3$) δ 7.36-7.22 (m, 5H), 7.20-7.12 (m, 3H), 7.04-6.80 (m, 6H), 5.44-5.34 (m, 1H), 5.19 (br d, *J* = 6.9 Hz, 1H), 4.72 (d, *J* = 17.1 Hz, 1H), 4.56-4.43 (m, 2H), 3.85-3.71 (m, 1H), 3.62-3.50 (m, 1H), 2.93 (dd, *J* = 12.9, 6.9 Hz, 1H), 2.72 (br dd, *J* = 12.9, 6.6 Hz, 1H), 1.52 (d, *J* = 5.4 Hz, 3H), 1.37 (s, 7.5H), 1.26-1.15 (m, 4.5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 156.64, 156.60, 154.4, 136.2, 133.7, 131.4, 129.4, 129.3, 128.1, 128.0, 126.5, 122.6, 117.8, 117.7, 99.5, 99.2, 84.4, 84.2, 79.5, 61.4, 61.1, 52.5, 39.8, 28.4, 20.3, 20.2, 15.4; HR-ESIMS calcd for $C_{33}H_{38}N_2NaO_5$ $[M+Na]^+$ 565.2673. Found 565.2675.

Methyl (3*S*)-3-((*tert*-butoxycarbonyl)amino)-4-((4-(1-ethoxyethoxy)phenyl)(3-phenylprop-2-yn-1-yl)amino)-4-oxobutanoate (6f)

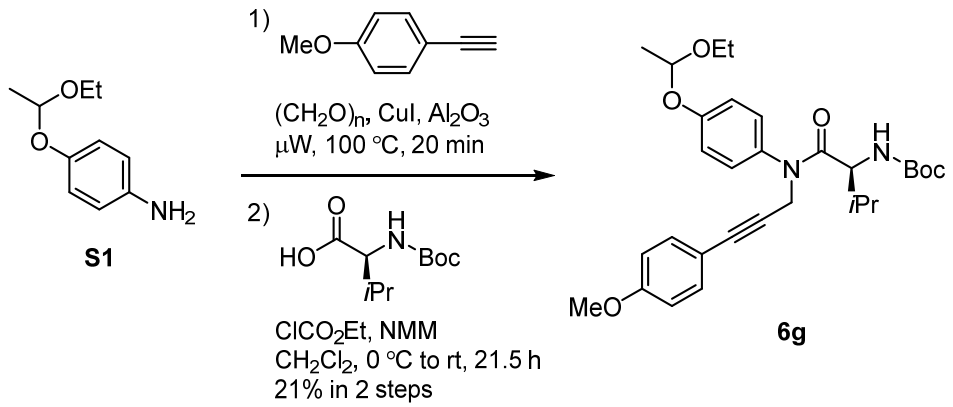


6f

According to **GP2**, **6f** (123 mg, 20%) was obtained from **S2** (354 mg, 1.20 mmol), *N*-Boc-L-Asp(OMe)-OH (326 mg, 1.32 mmol), ethyl chloroformate (126 μL, 1.32 mmol) and *N*-methylmorpholine (145 μL, 1.32 mmol). Eluent: hexane/acetone = 3:1 to 2:1.

Yellow oil; $[\alpha]_D^{26}$ +15.7 (*c* 1.05, $CHCl_3$); IR ν_{max}: 3433, 2982, 1733, 1713, 1662, 1599 cm^{-1}; The ^1H and ^{13}C NMR spectra of **6f** showed the presence of two rotamers (1:1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.36-7.21 (m, 7H), 7.04 (dd, *J* = 8.7, 0.9 Hz, 2H), 5.45-5.26 (m, 2H), 4.74-4.55 (m, 3H), 3.86-3.72 (m, 1H), 3.61 (s, 3H), 3.60-3.50 (m, 1H), 2.68 (br d, *J* = 15.0 Hz, 1H), 2.46 (ddd, *J* = 15.3, 6.0, 1.5 Hz, 1H), 1.52 (d, *J* = 5.1 Hz, 3H), 1.39 (s, 9H), 1.27-1.17 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 170.0, 156.8, 154.2, 133.5, 131.4, 129.4, 128.1, 128.0, 122.6, 117.9, 99.5, 99.4, 84.6, 84.1, 79.8, 61.4, 61.3, 51.8, 48.4, 40.1, 37.4, 28.4, 20.3, 15.4; HR-ESIMS calcd for $C_{29}H_{36}N_2NaO_7$ $[M+Na]^+$ 547.2415. Found 547.2408.

***tert*-Butyl ((2*S*)-1-((4-(1-ethoxyethoxy)phenyl)(3-(4-methoxyphenyl)prop-2-yn-1-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate (6g)**



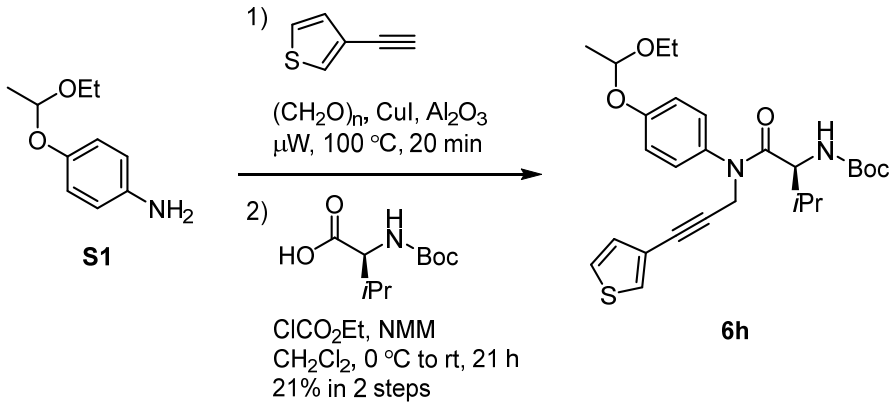
According to the literature,[1] a mixture of **S1** (439 mg, 2.42 mmol), 4-ethynylanisole (320 mg, 2.42 mmol),

paraformaldehyde (72.7 mg, 2.42 mmol), CuI (138 mg, 0.726 mmol) and Al_2O_3 (242 mg) was sealed and was stirred at 100 °C for 20 min in a microwave reactor. After cooling to rt, the mixture was filtrated on Celite pad, washed with EtOAc. The filtrate was evaporated *in vacuo*, and the residue was purified by flash column chromatography on silica gel eluting with hexane/EtOAc = 6:1: to give 4-(1-ethoxyethoxy)-*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)aniline (370 mg) as pale yellow oil.

According to **GP2**, **6g** (266 mg, 21% in 2 steps) was obtained from 4-(1-ethoxyethoxy)-*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)aniline (370 mg, 1.14 mmol), *N*-Boc-L-Val-OH (272 mg, 1.25 mmol), ethyl chloroformate (119 μL, 1.25 mmol) and *N*-methylmorpholine (276 μL, 2.50 mmol). Eluent: hexane/EtOAc = 5:1 to 4:1.

Colorless oil; $[\alpha]_D^{27}$ +101 (*c* 1.10, $CHCl_3$); IR ν_{max}: 3435, 2979, 1708, 1655, 1606 cm^{-1}; The ^1H and ^{13}C NMR spectra of **6g** showed the presence of two rotamers (1:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.31-7.26 (m, 4H), 7.06 (d, *J* = 9.0 Hz, 1H), 7.05 (d, *J* = 9.0 Hz, 1H), 6.80 (d, *J* = 9.0 Hz, 2H), 5.46-5.39 (m, 1H), 5.22-5.15 (br m, 1H), 4.77 (d, *J* = 17.0 Hz, 1H), 4.53 (d, *J* = 17.0 Hz, 1H), 4.27-4.20 (br m, 1H), 3.83-3.75 (m, 1H), 3.79 (s, 3H), 3.61-3.53 (m, 1H), 1.90-1.82 (m, 1H), 1.52 (d, *J* = 5.0 Hz, 3H), 1.42 (s, 9H), 1.22 (t, *J* = 7.0 Hz, 1.5H), 1.21 (t, *J* = 7.0 Hz, 1.5H), 0.82 (d, *J* = 7.0 Hz, 3H), 0.76 (d, *J* = 7.0 Hz, 1.5H), 0.75 (d, *J* = 7.0 Hz, 1.5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.1, 169.5, 159.5, 156.82, 156.75, 155.4, 134.3, 134.2, 129.6, 117.9, 117.8, 114.8, 113.8, 99.6, 99.2, 84.1, 83.0, 79.2, 61.4, 61.0, 55.52, 55.49, 55.22, 55.20, 39.8, 31.3, 28.3, 20.1, 20.0, 19.5, 16.9, 15.1; HR-ESIMS calcd for $C_{30}H_{40}N_2NaO_6$ $[M+Na]^+$ 547.2779. Found 547.2772.

tert-Butyl ((2*S*)-1-((4-(1-ethoxyethoxy)phenyl)(3-(thiophen-3-yl)prop-2-yn-1-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate (6h)



According to the literature,[1] a mixture of **S1** (453 mg, 2.50 mmol), 3-ethynylthiophene (270 mg, 2.50 mmol), paraformaldehyde (75.1 mg, 2.50 mmol), CuI (143 mg, 0.750 mmol) and Al_2O_3 (250 mg) was sealed and was stirred at 100 °C for 20 min in a microwave reactor. After cooling to rt, the mixture was filtrated on Celite pad, washed with EtOAc. The filtrate was evaporated *in vacuo*, and the residue was purified by flash column chromatography on silica gel eluting with hexane/EtOAc = 7:1: to give 4-(1-ethoxyethoxy)-*N*-(3-(thiophen-3-yl)prop-2-yn-1-yl)aniline (389 mg) as pale yellow oil.

According to **GP2**, **6h** (260 mg, 21% in 2 steps) was obtained from 4-(1-ethoxyethoxy)-*N*-(3-(thiophen-3-yl)prop-2-yn-1-yl)aniline (389 mg, 1.29 mmol), *N*-Boc-L-Val-OH (308 mg, 1.42 mmol), ethyl chloroformate (135 μL, 1.42 mmol) and *N*-methylmorpholine (313 μL, 2.84 mmol). Eluent: hexane/EtOAc = 6:1 to 5:1.

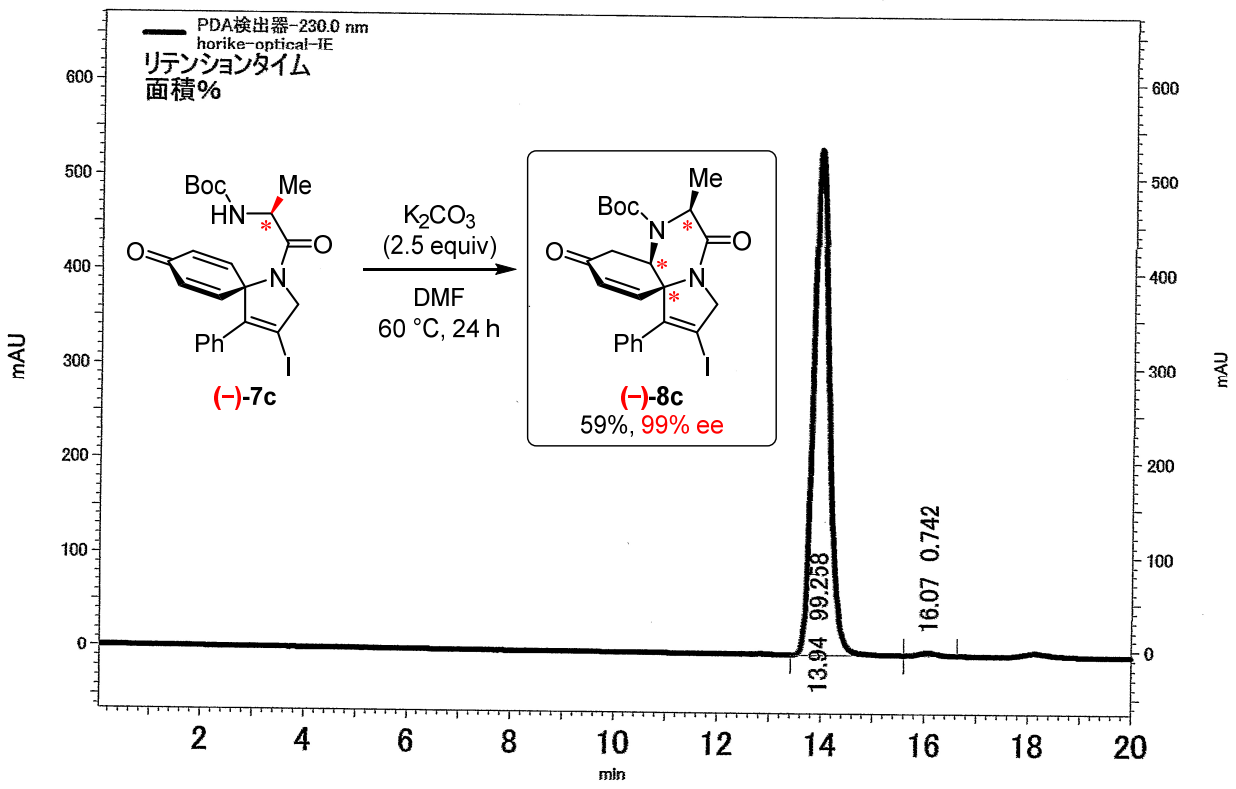
Colorless oil; $[\alpha]_D^{26}$ +115 (*c* 1.00, $CHCl_3$); IR ν_{max}: 3436, 2980, 1709, 1656, 1606 cm^{-1}; The ^1H and ^{13}C

NMR spectra of **6h** showed the presence of two rotamers (1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 3.0, 0.9 Hz, 1H), 7.28 (d, *J* = 9.0 Hz, 2H), 7.23 (dd, *J* = 5.1, 3.0 Hz, 1H), 7.10-7.01 (m, 3H), 5.48-5.38 (m, 1H), 5.19 (br d, *J* = 8.1 Hz, 1H), 4.76 (d, *J* = 17.1 Hz, 1H), 4.53 (d, *J* = 17.1 Hz, 1H), 4.24 (dd, *J* = 9.6, 5.7 Hz, 1H), 3.86-3.73 (m, 1H), 3.63-3.50 (m, 1H), 1.93-1.80 (m, 1H), 1.52 (d, *J* = 5.4 Hz, 3H), 1.43 (s, 9H), 1.22 (t, *J* = 6.9 Hz, 1.5H), 1.21 (t, *J* = 6.9 Hz, 1.5H), 0.82 (d, *J* = 6.9 Hz, 3H), 0.75 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.1, 156.8, 156.7, 155.4, 134.14, 134.09, 129.8, 129.5, 128.8, 125.2, 121.7, 117.8, 117.7, 99.5, 99.1, 84.0, 79.3, 79.2, 61.4, 60.9, 55.4, 39.8, 31.3, 28.3, 20.1, 20.0, 19.5, 16.9, 15.1; HR-ESIMS calcd for $C_{27}H_{36}N_2NaO_5S$ $[M+Na]^+$ 523.2237. Found 523.2233.

References

1) Kabalka, G. W.; Zhou, L.-L.; Wang, L.; Pagni, R. M. *Tetrahedron* **2006**, *62*, 857.
2) Jia, X.; Huang, Q.; Li, J.; Li, S.; Yang, Q. *Synlett* **2007**, 806.

Chiral HPLC Charts of **8c**



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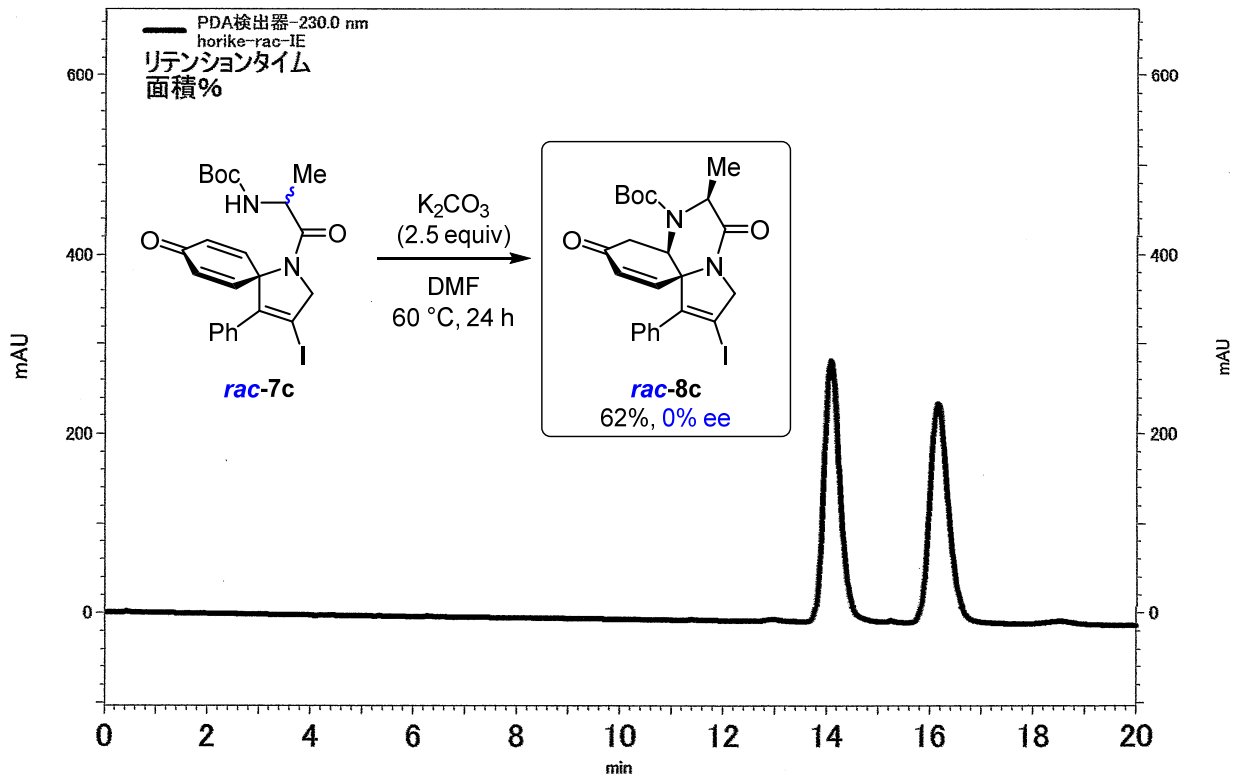

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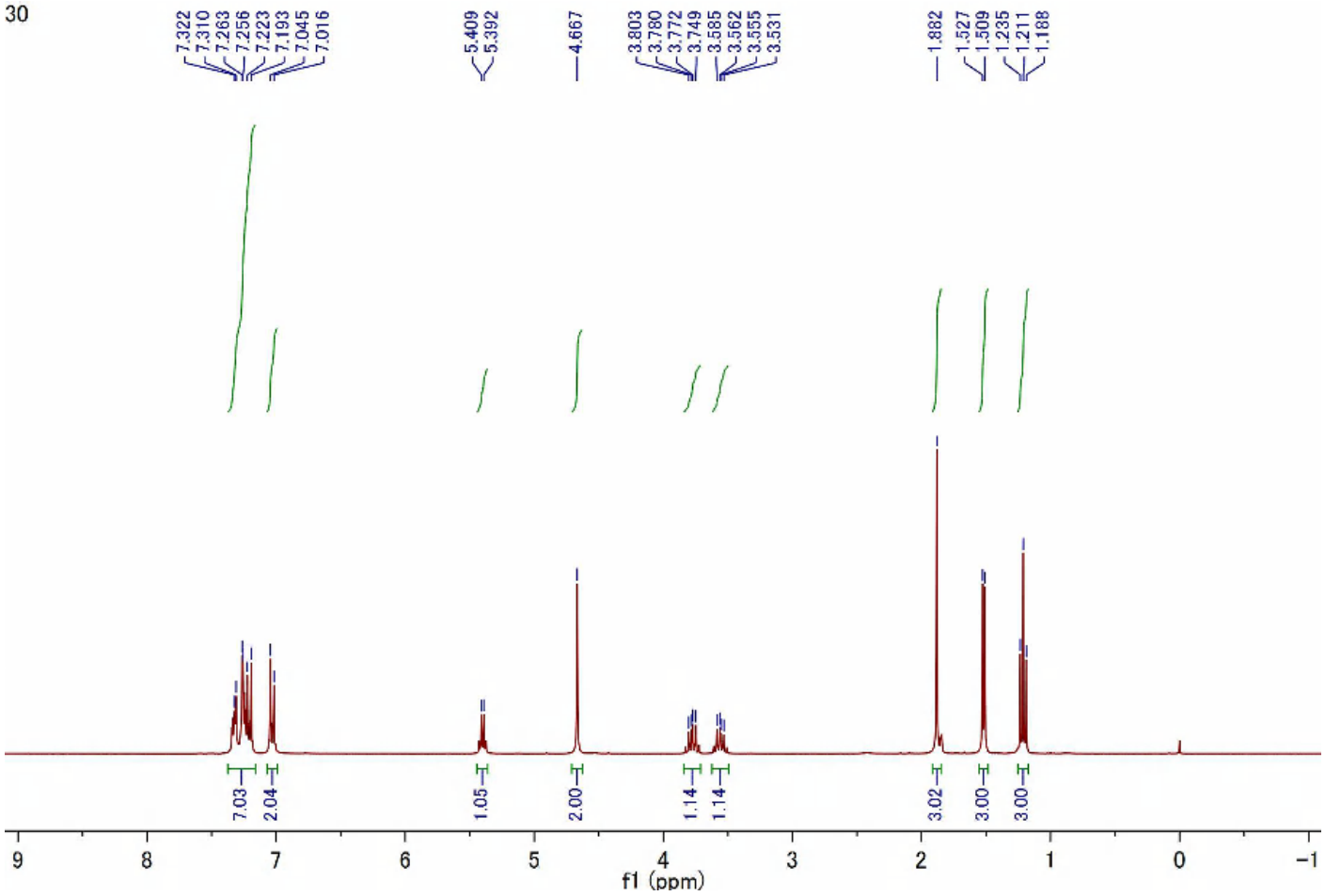
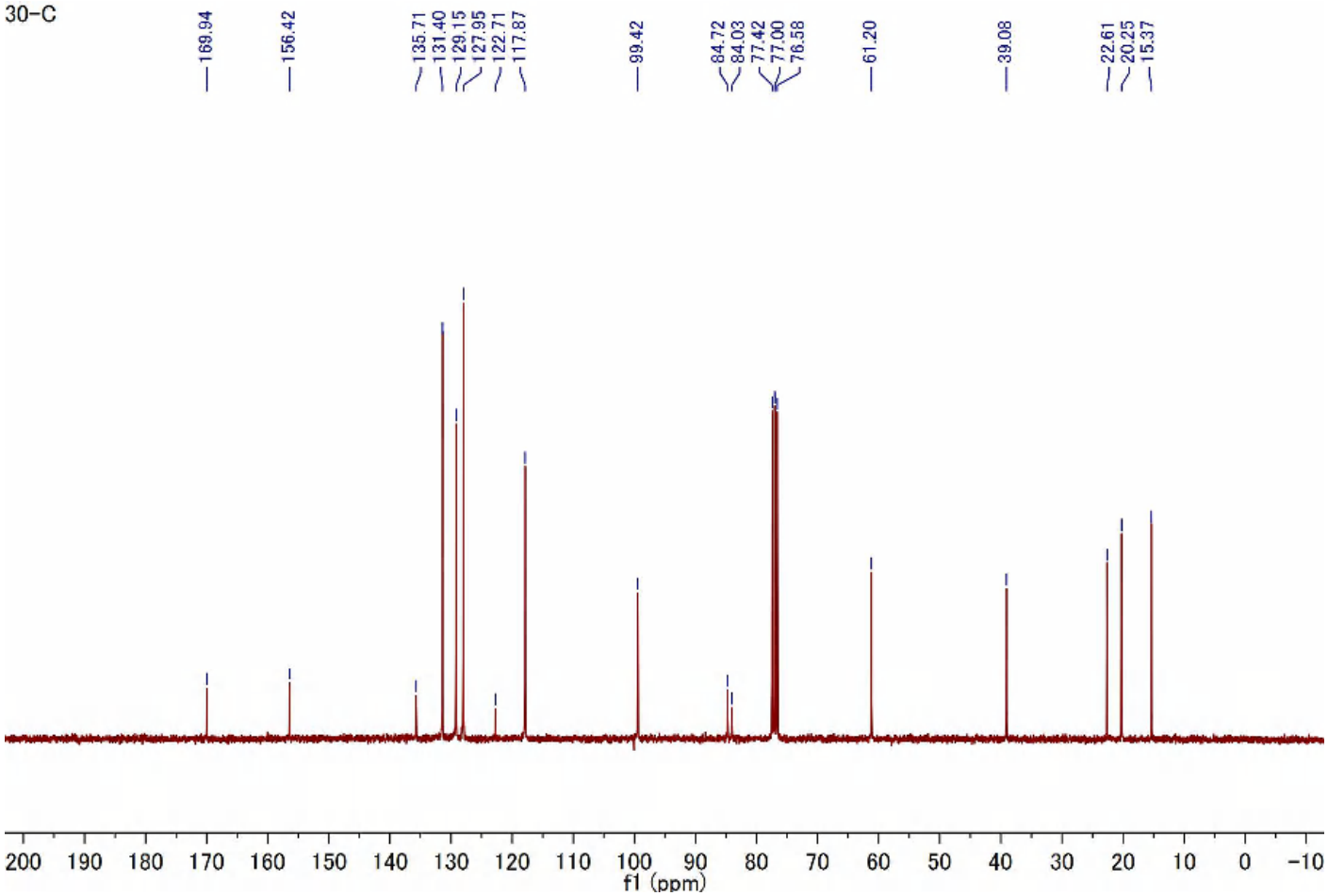
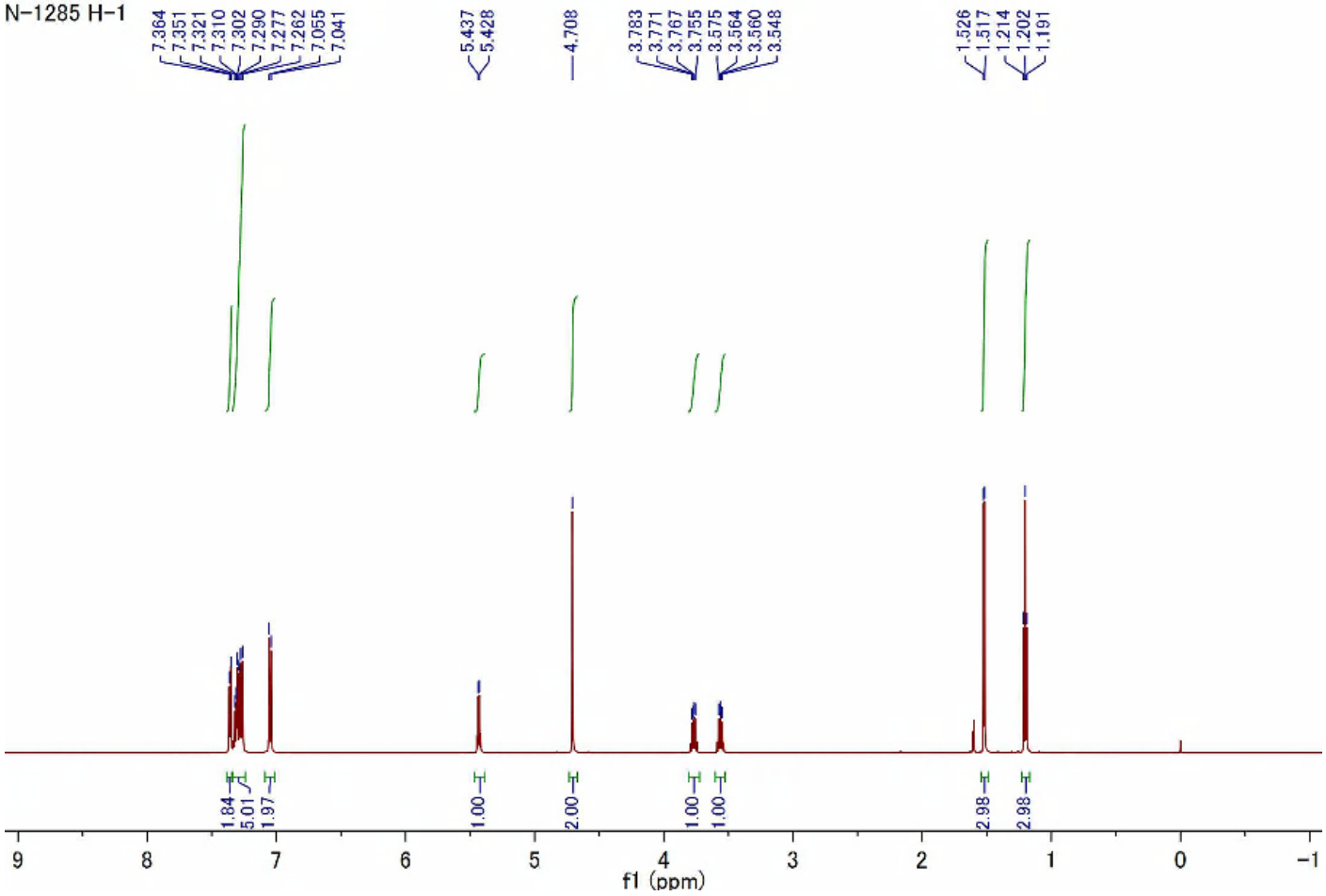
Compound **1a** (^{1}H NMR, 300 MHz, $CDCl_3$)



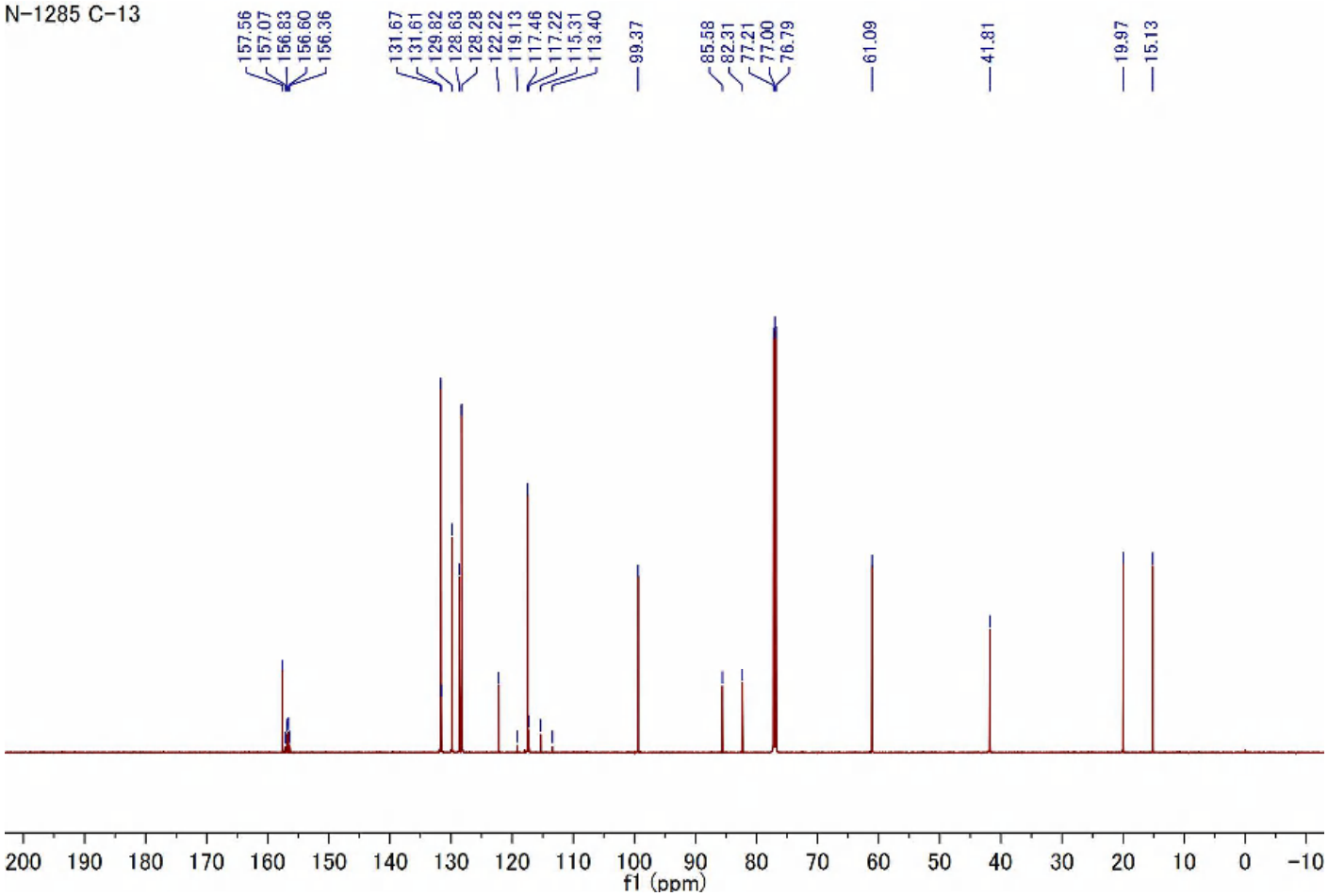
Compound **1a** (^{13}C NMR, 75 MHz, $CDCl_3$)



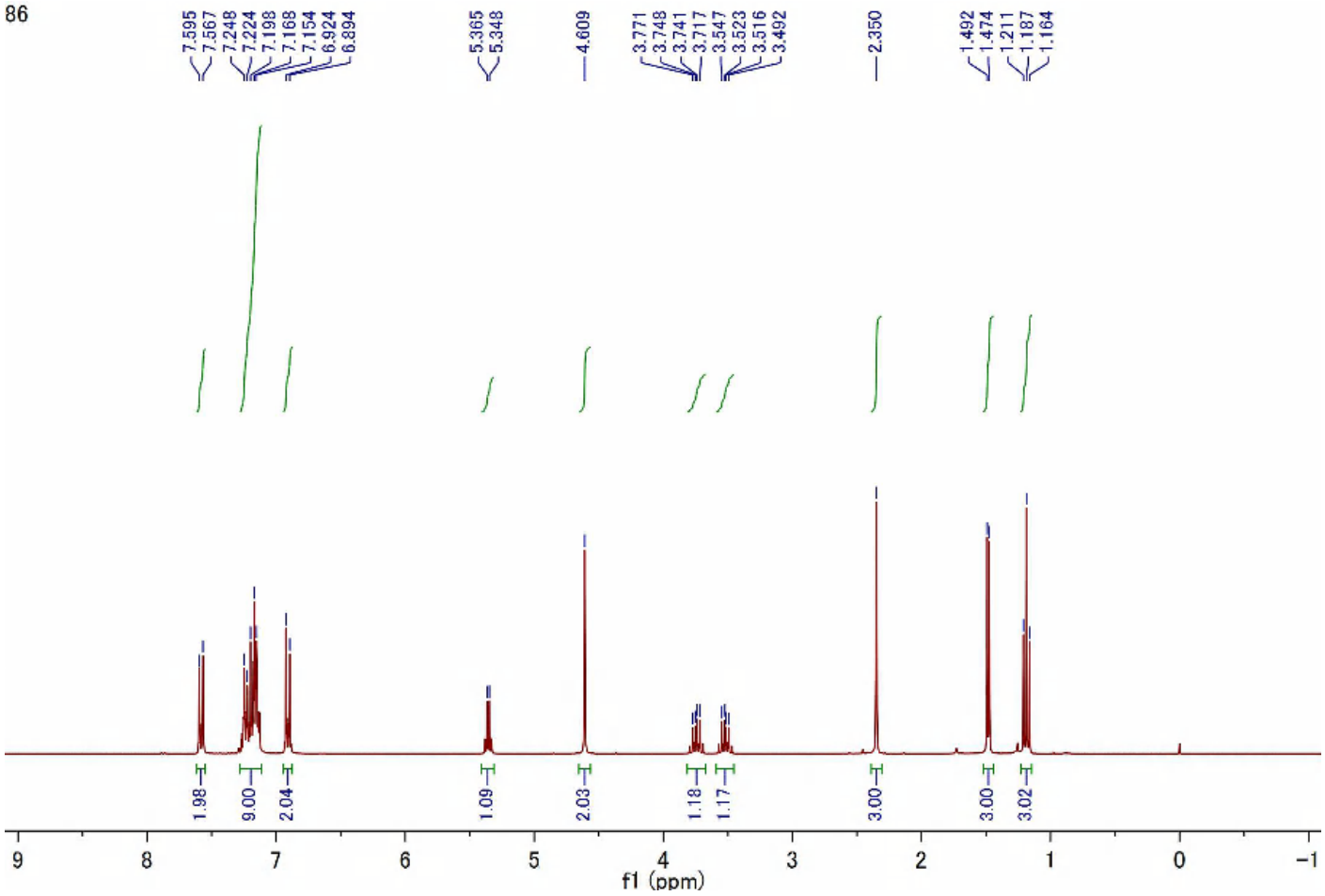
Compound **1b** (^{1}H NMR, 600 MHz, $CDCl_3$)



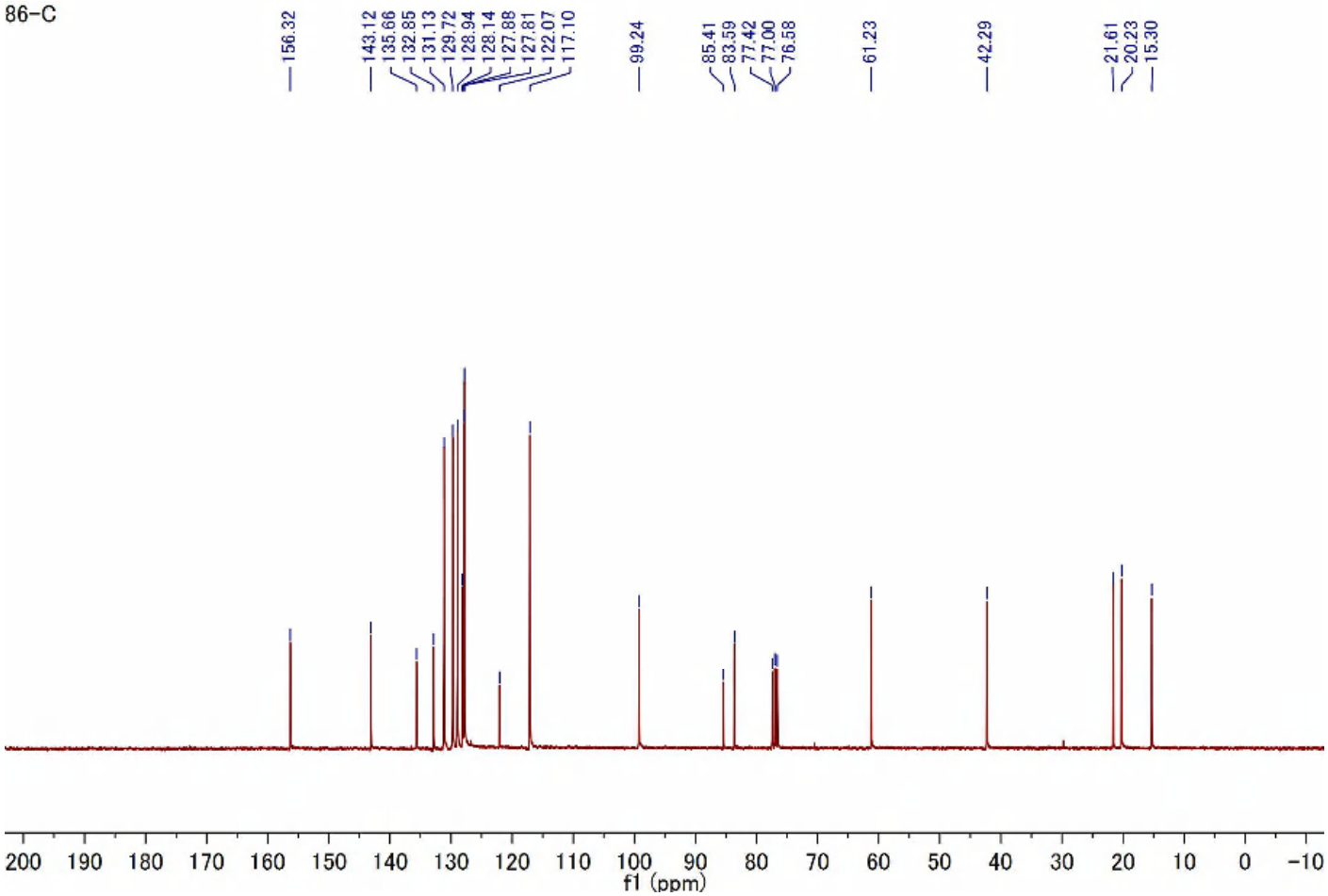
Compound **1b** (^{13}C NMR, 150 MHz, $CDCl_3$)



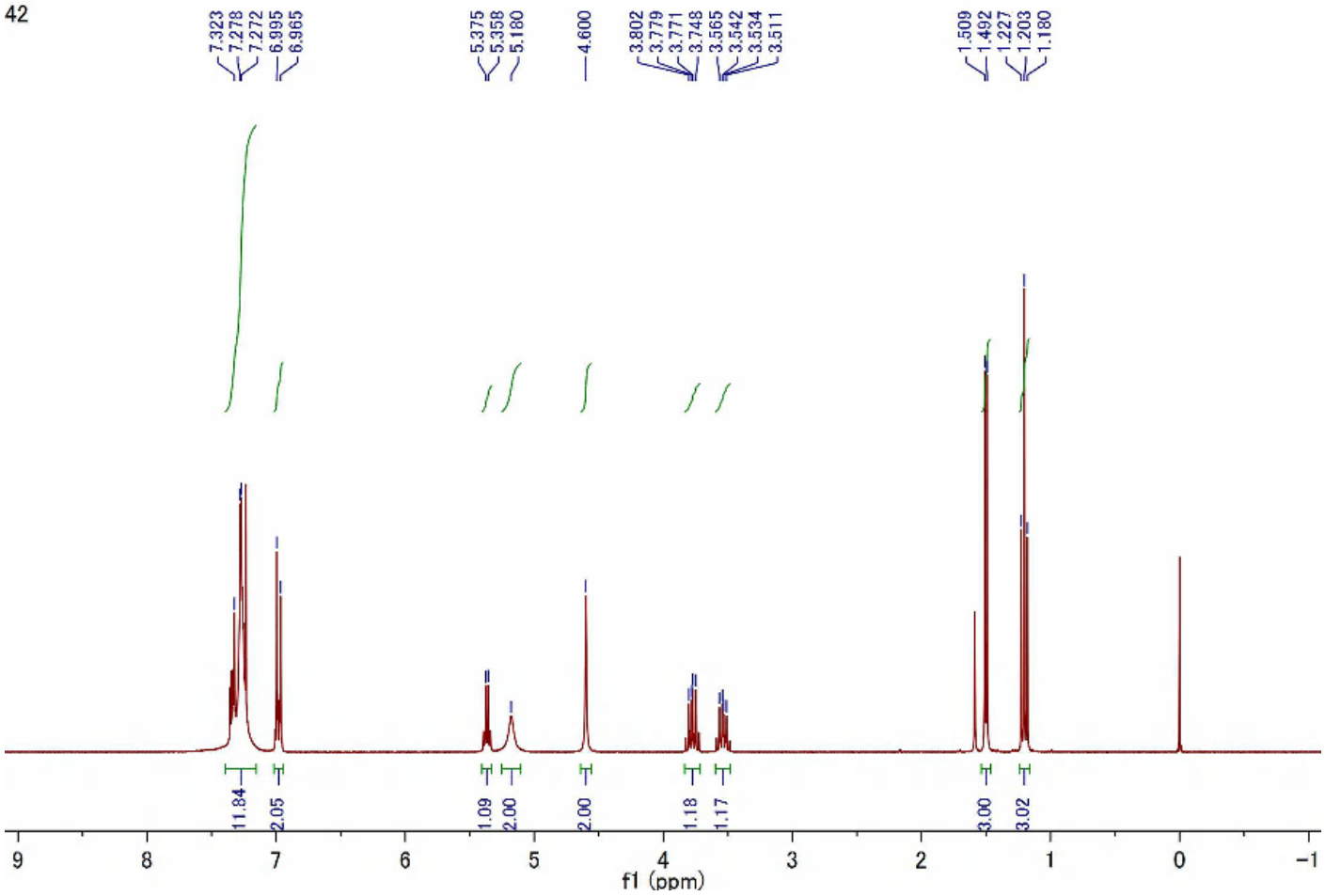
Compound **1c** (^{1}H NMR, 300 MHz, $CDCl_3$)



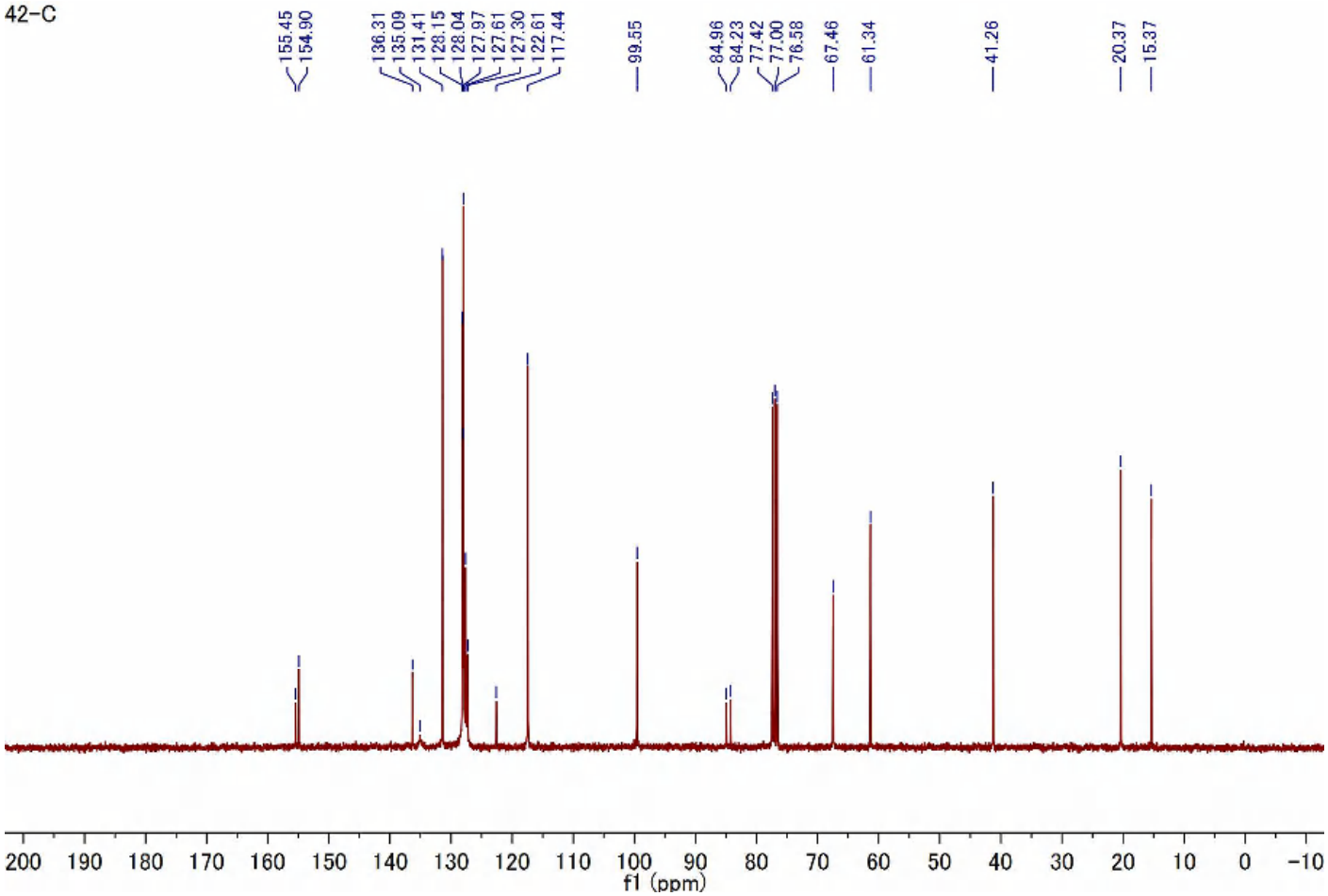
Compound **1c** (^{13}C NMR, 75 MHz, $CDCl_3$)



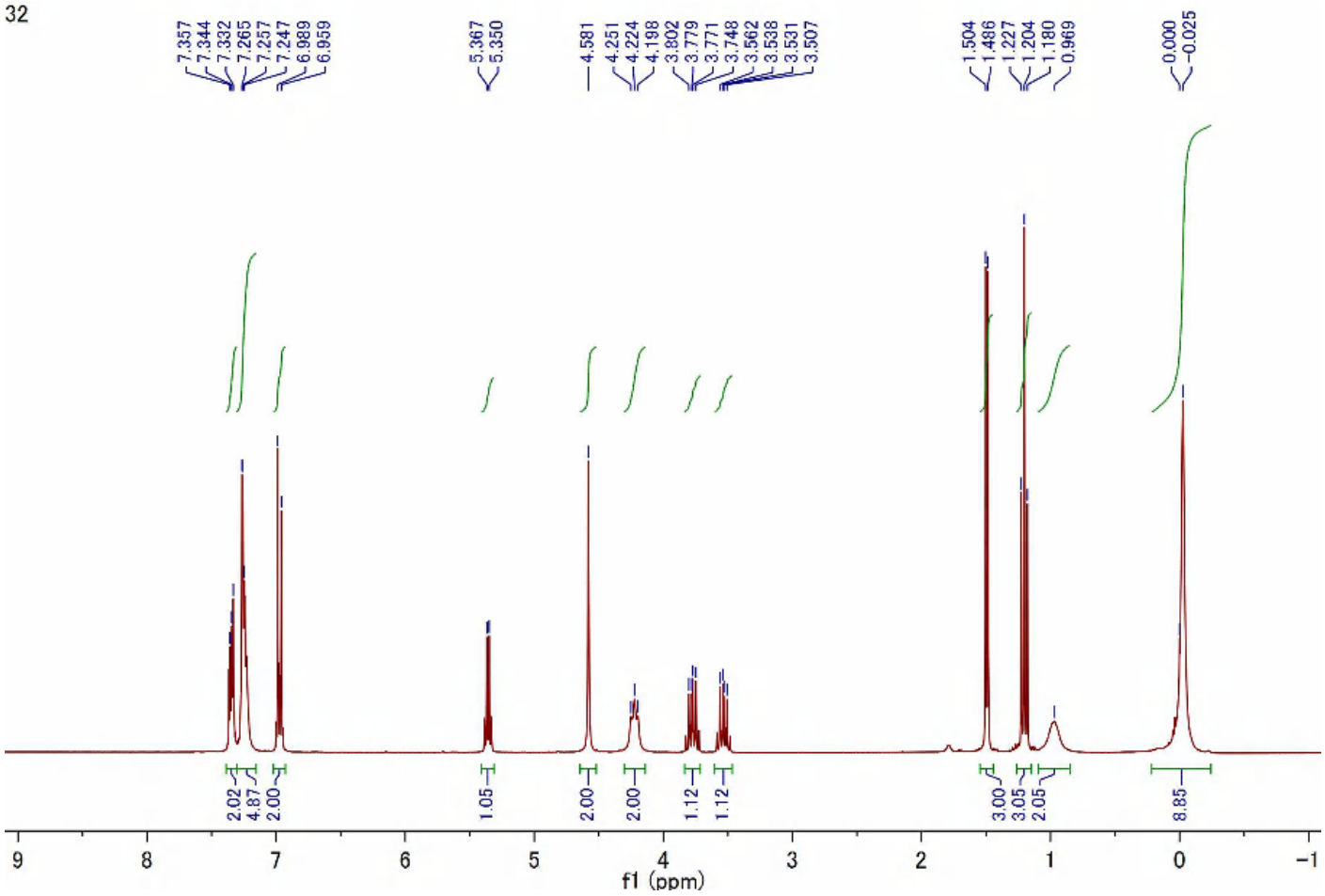
Compound **1d** (^{1}H NMR, 300 MHz, $CDCl_3$)



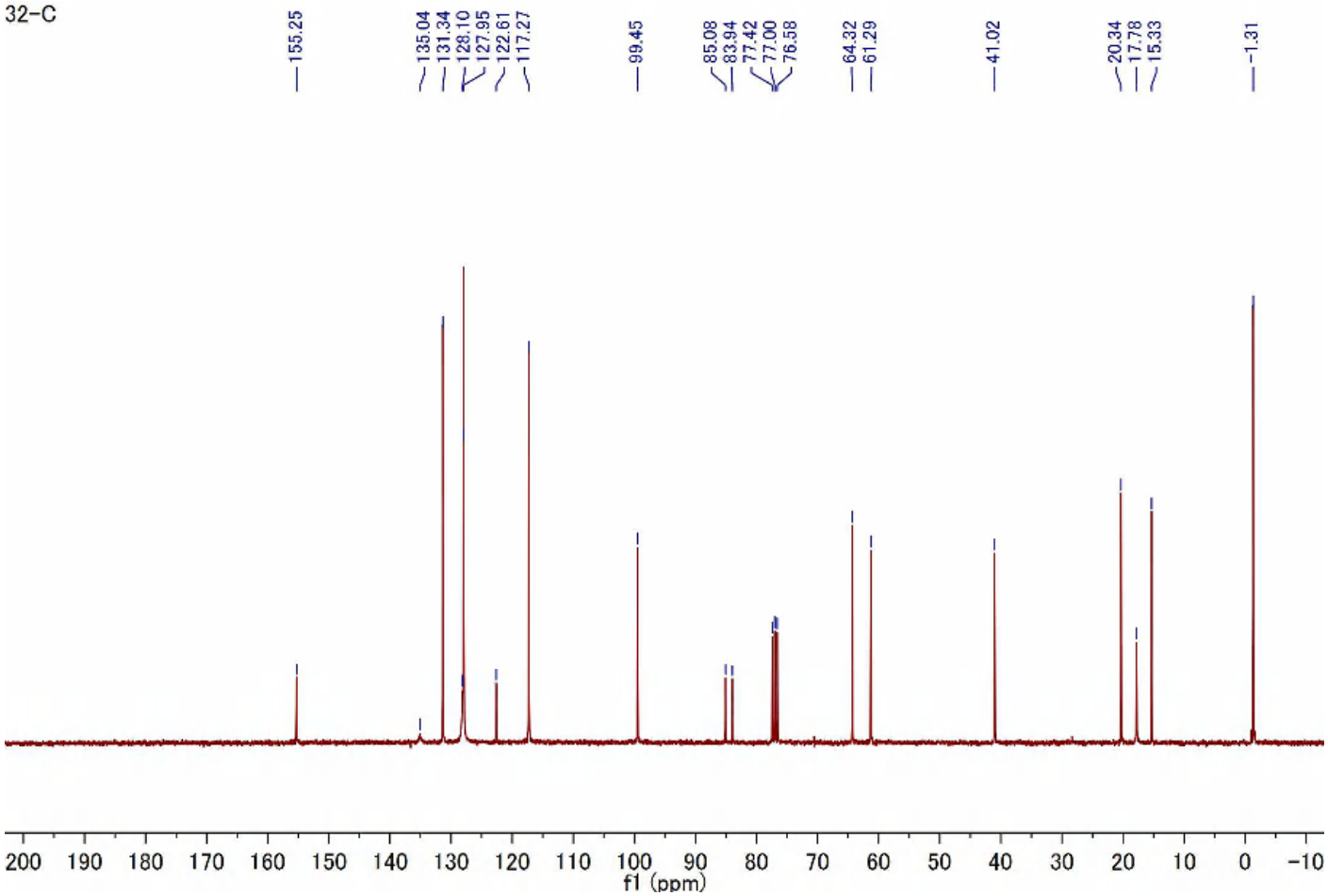
Compound **1d** (^{13}C NMR, 75 MHz, $CDCl_3$)



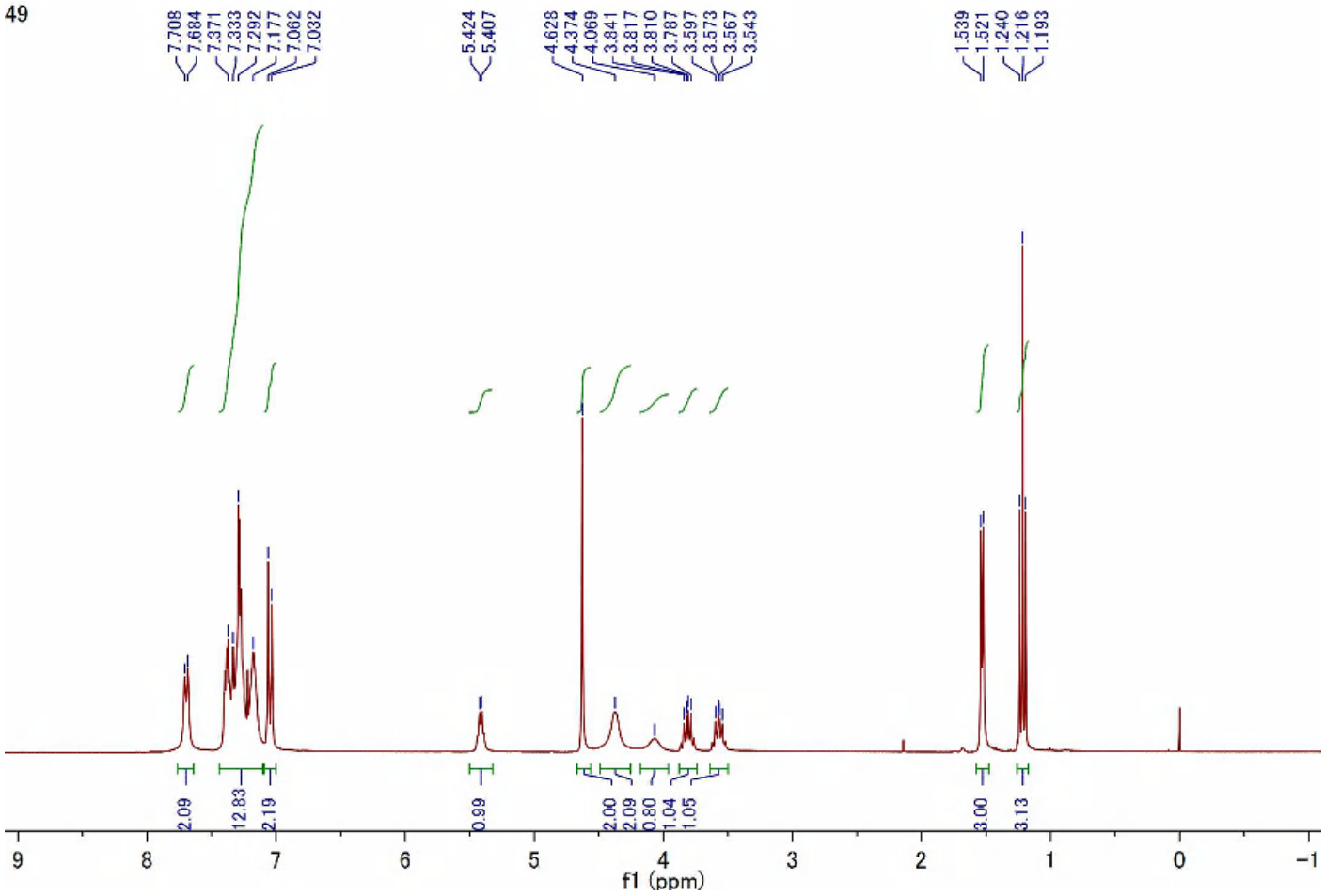
Compound **1e** (^{1}H NMR, 300 MHz, $CDCl_3$)



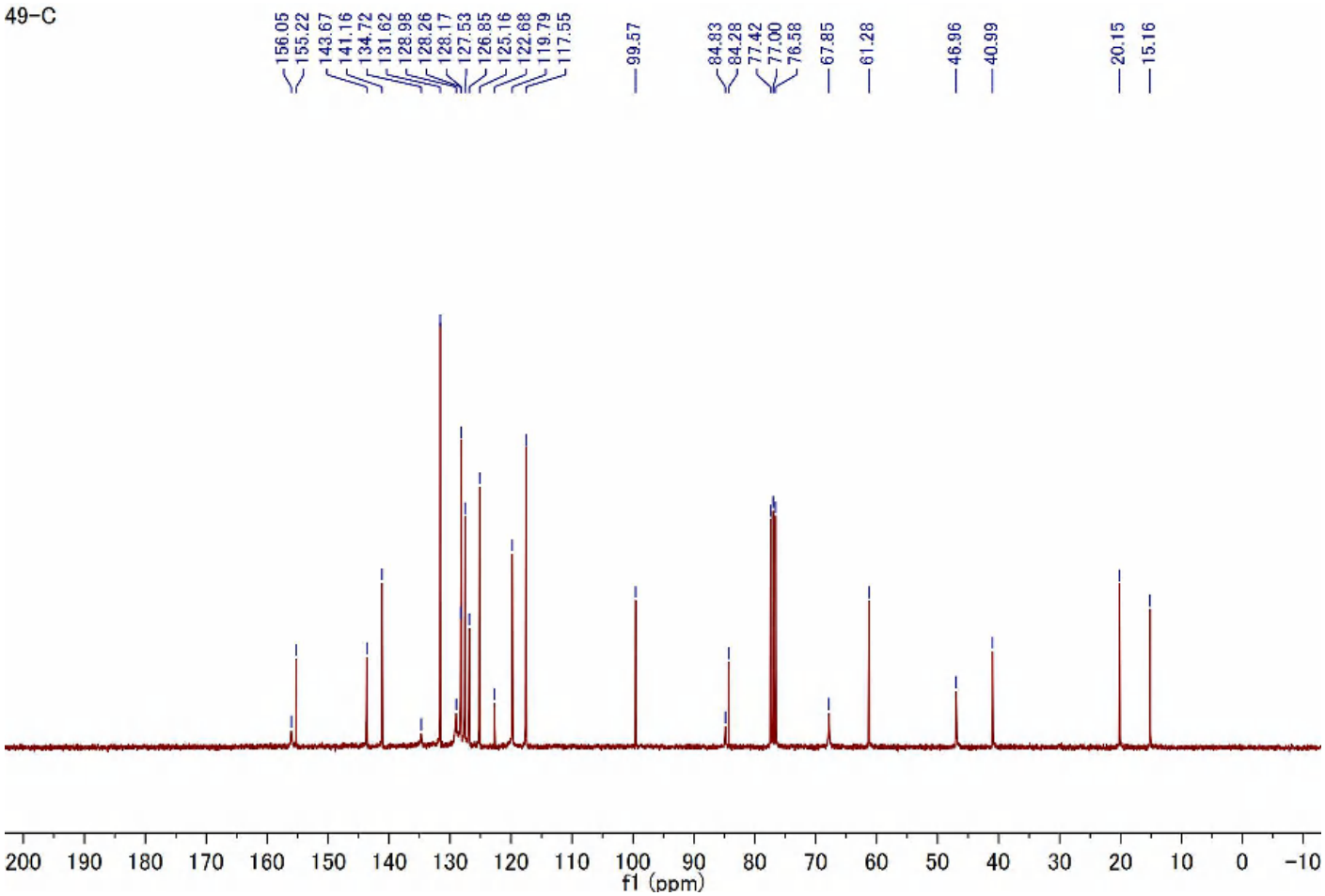
Compound **1e** (^{13}C NMR, 75 MHz, $CDCl_3$)



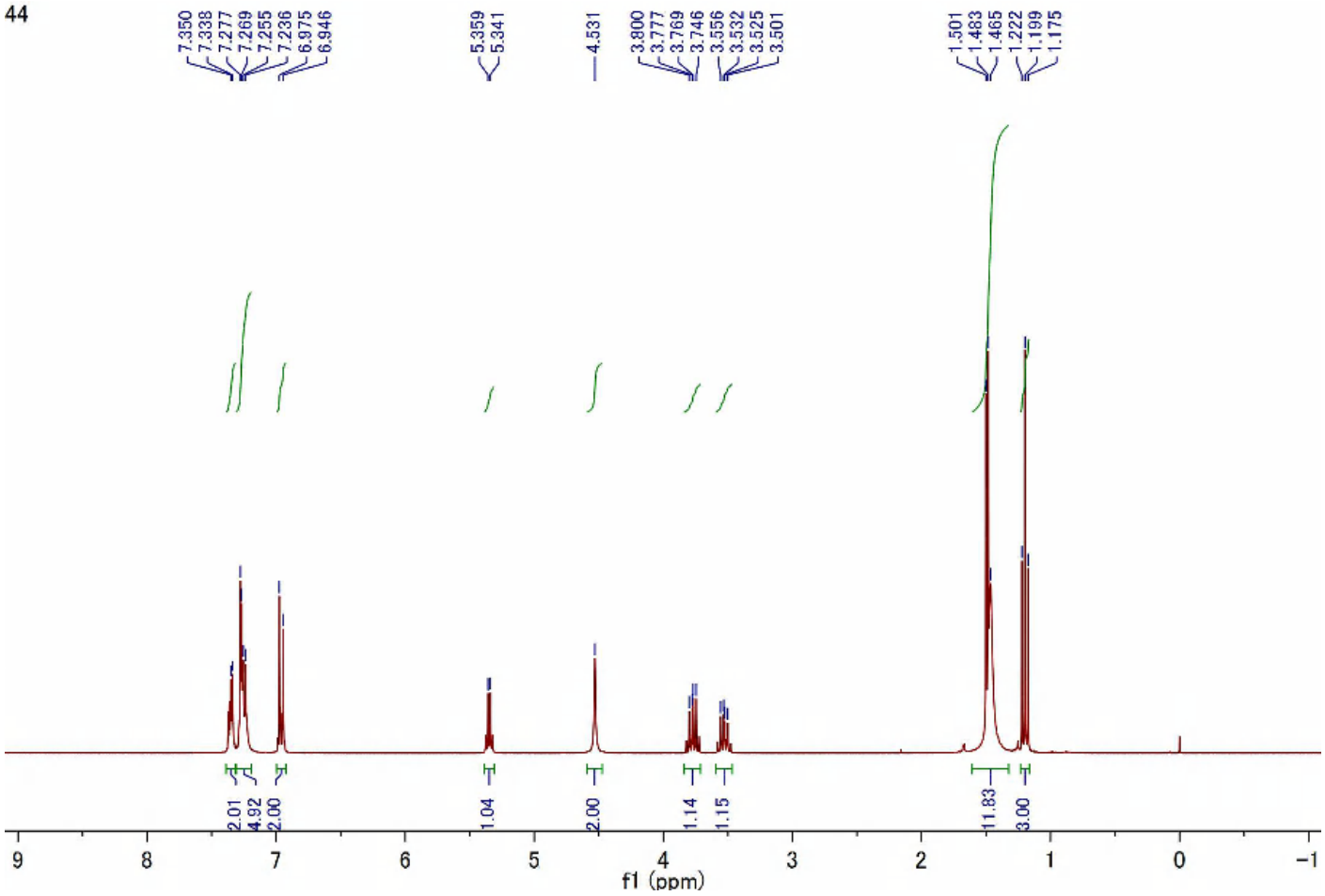
Compound **1f** (^{1}H NMR, 300 MHz, $CDCl_3$)



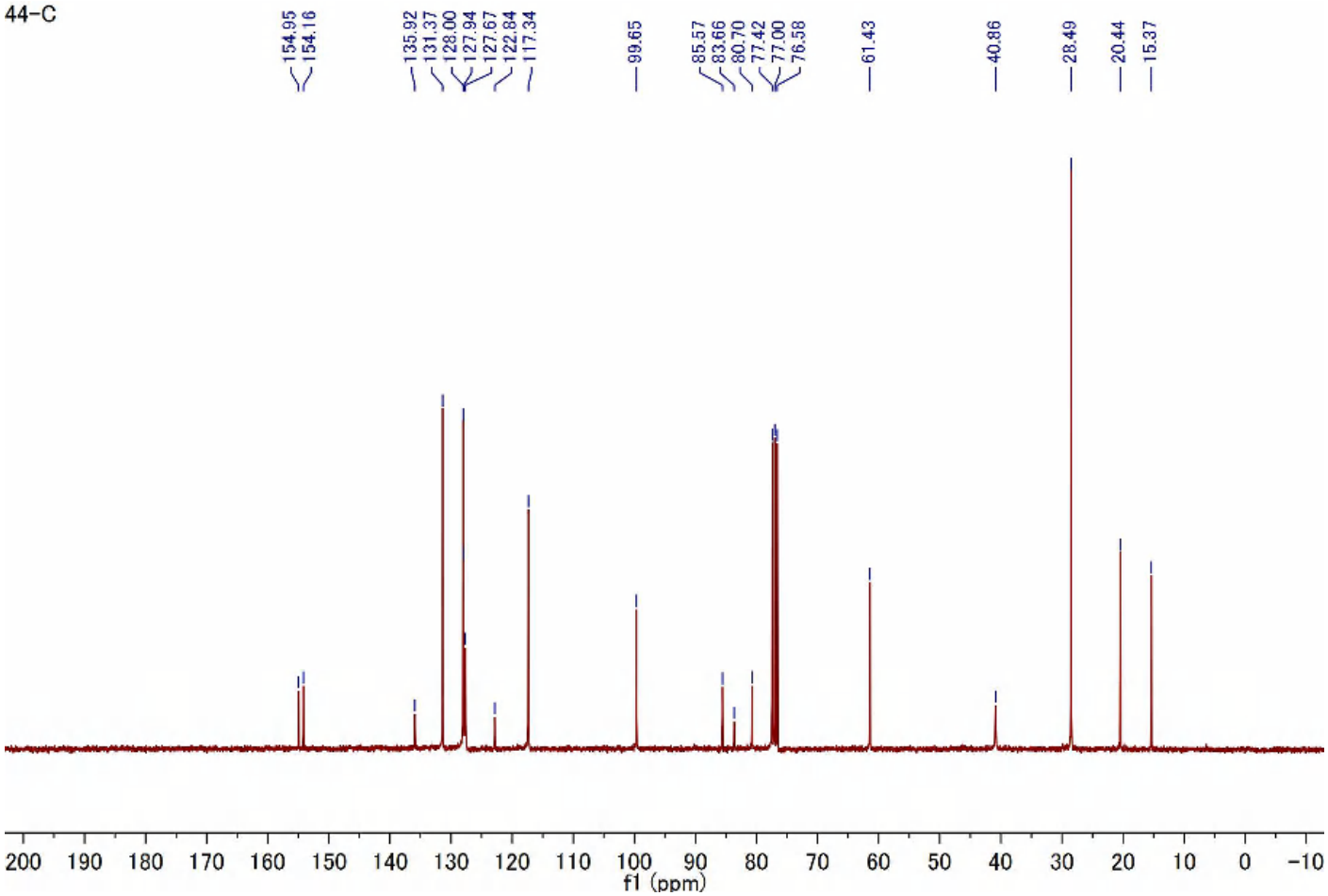
Compound **1f** (^{13}C NMR, 75 MHz, $CDCl_3$)



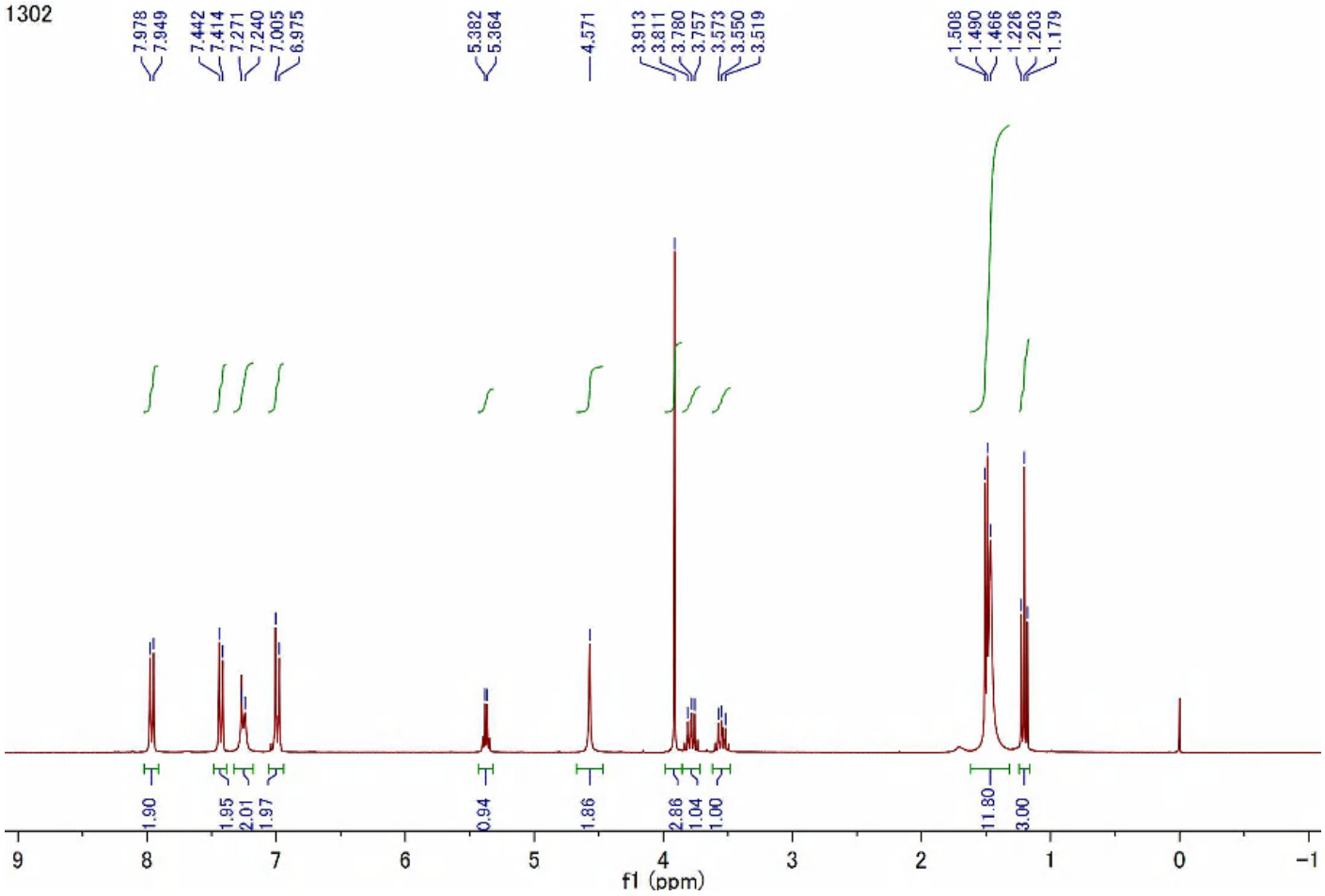
Compound **1g** (^{1}H NMR, 300 MHz, $CDCl_3$)



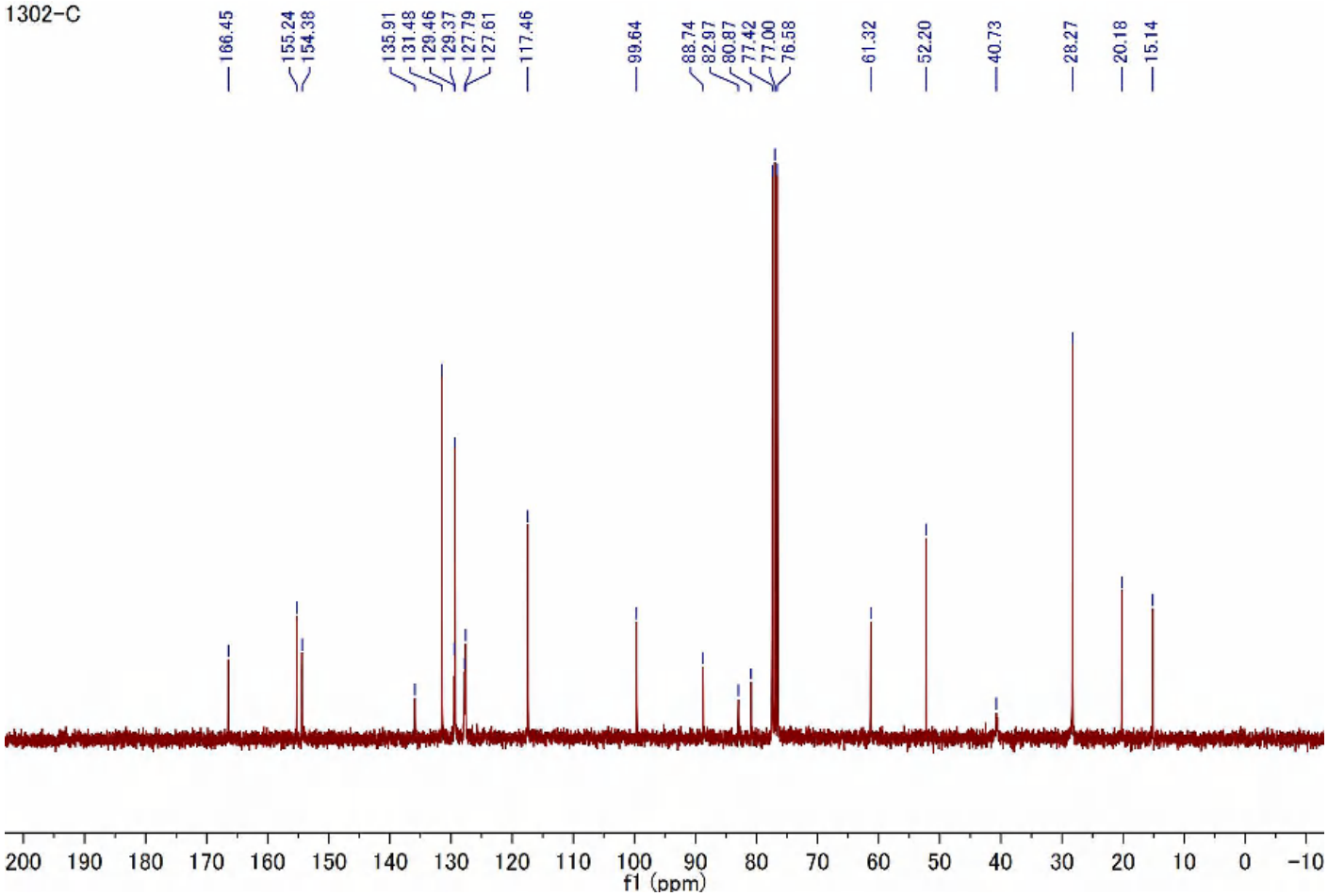
Compound **1g** (^{13}C NMR, 75 MHz, $CDCl_3$)



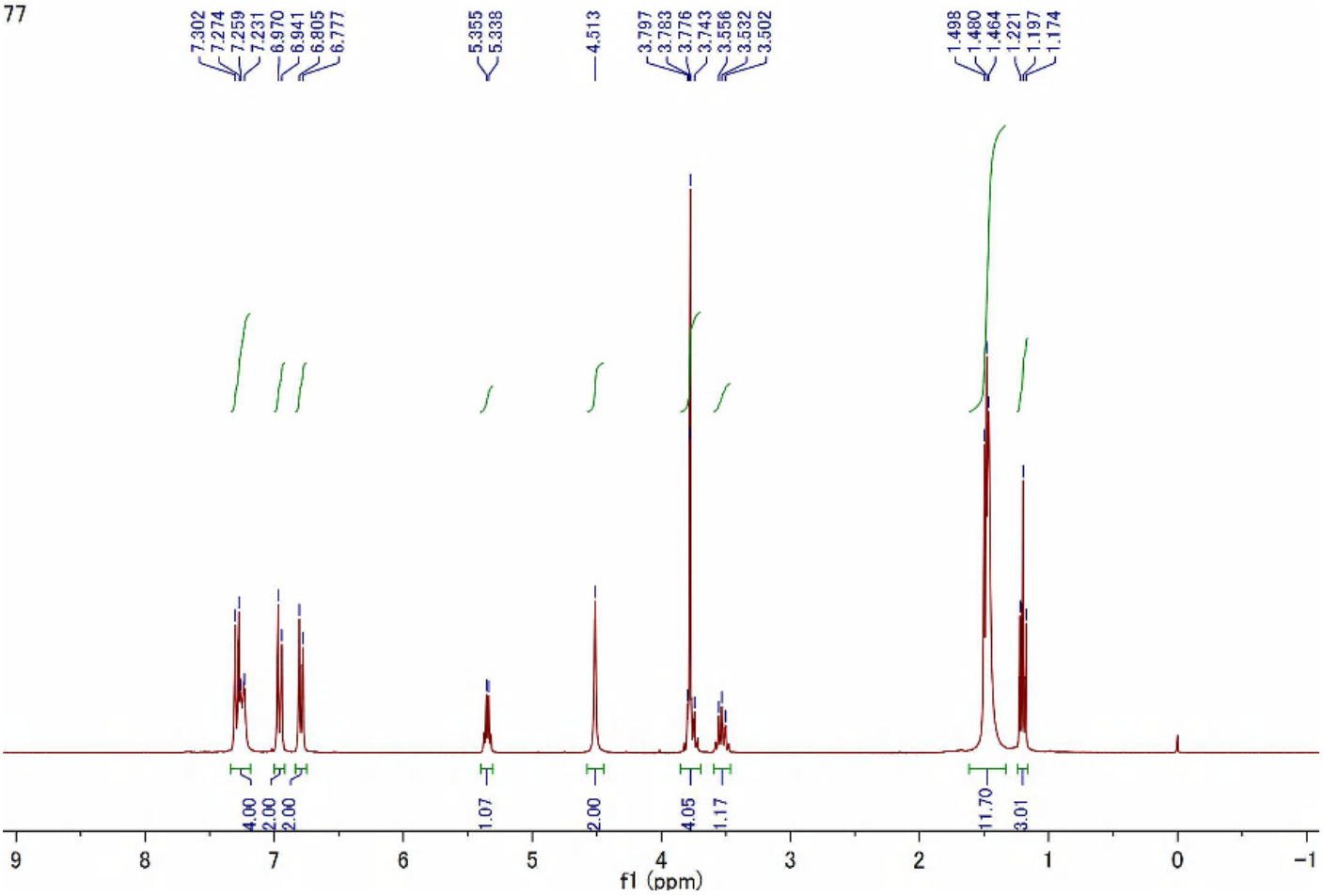
Compound **1h** (^{1}H NMR, 300 MHz, $CDCl_3$)



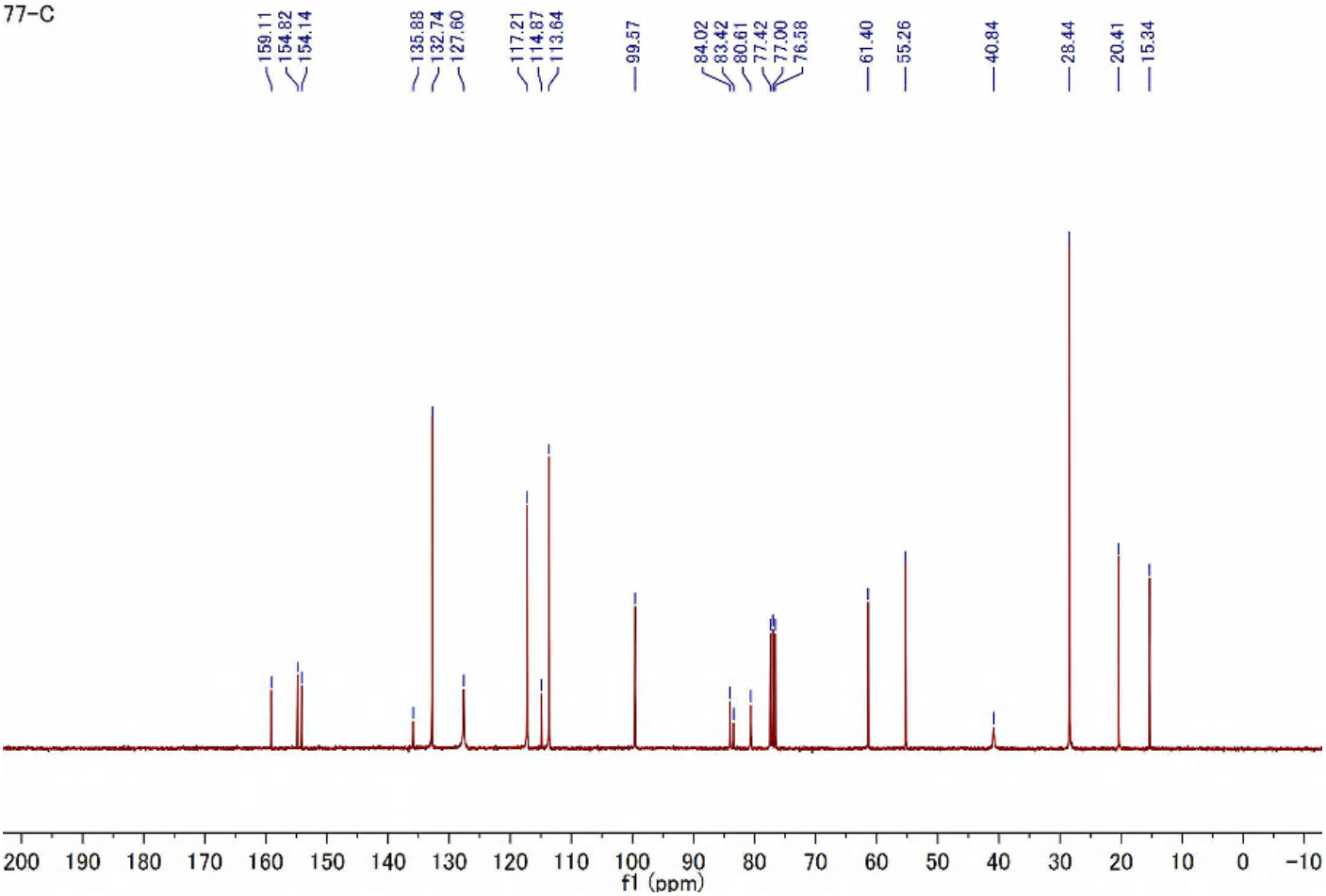
Compound **1h** (^{13}C NMR, 75 MHz, $CDCl_3$)



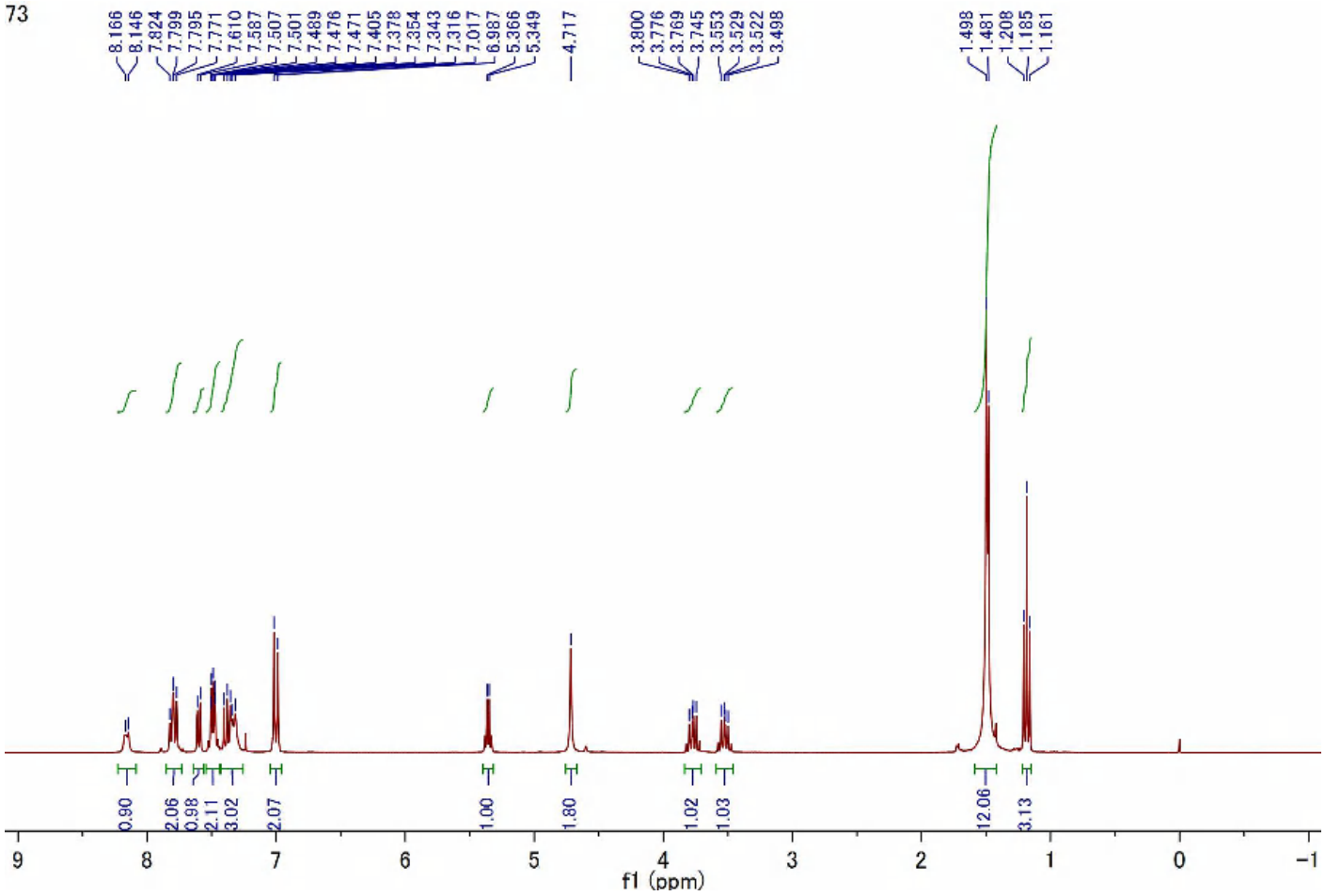
Compound **1i** (^{1}H NMR, 300 MHz, $CDCl_3$)



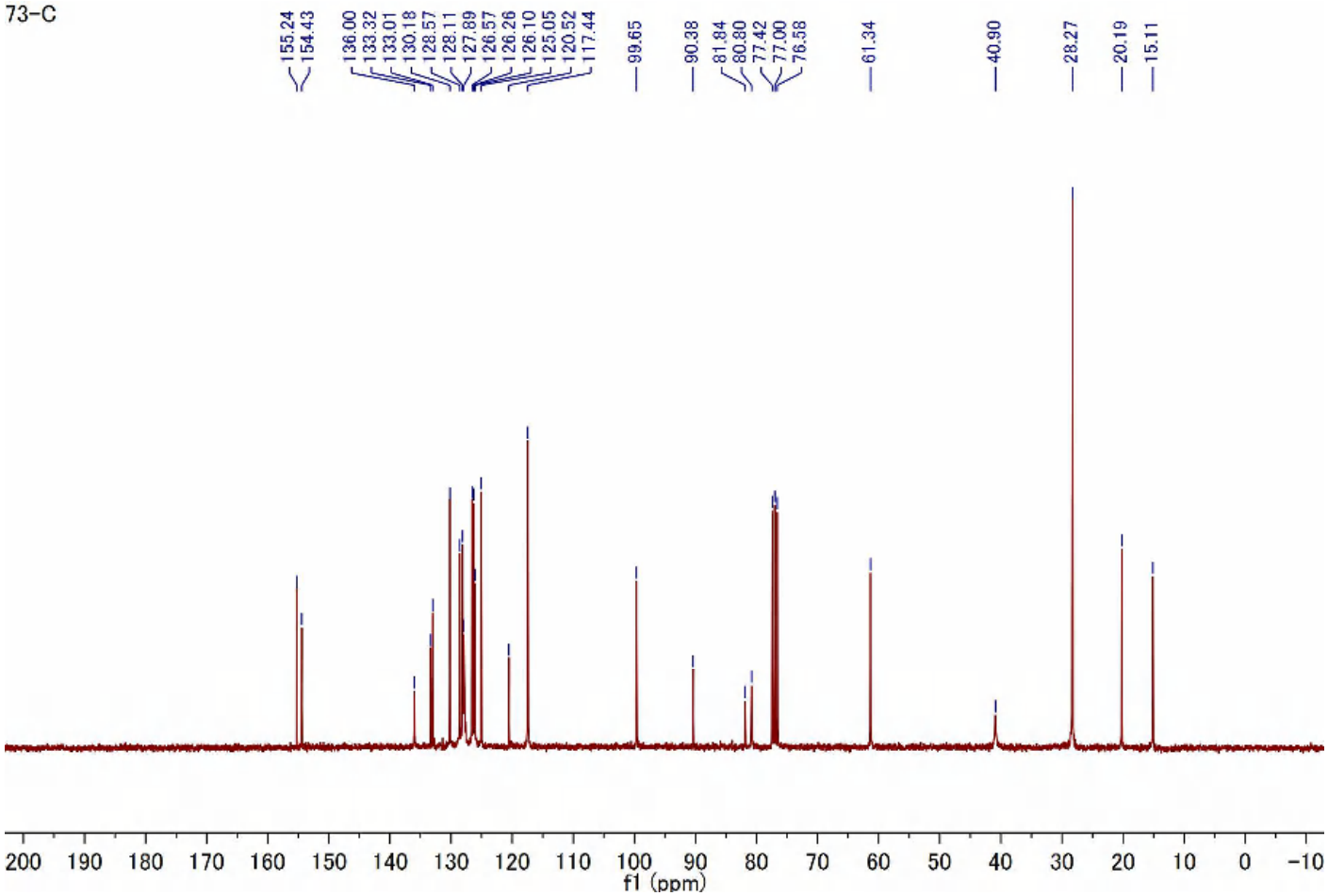
Compound **1i** (^{13}C NMR, 75 MHz, $CDCl_3$)



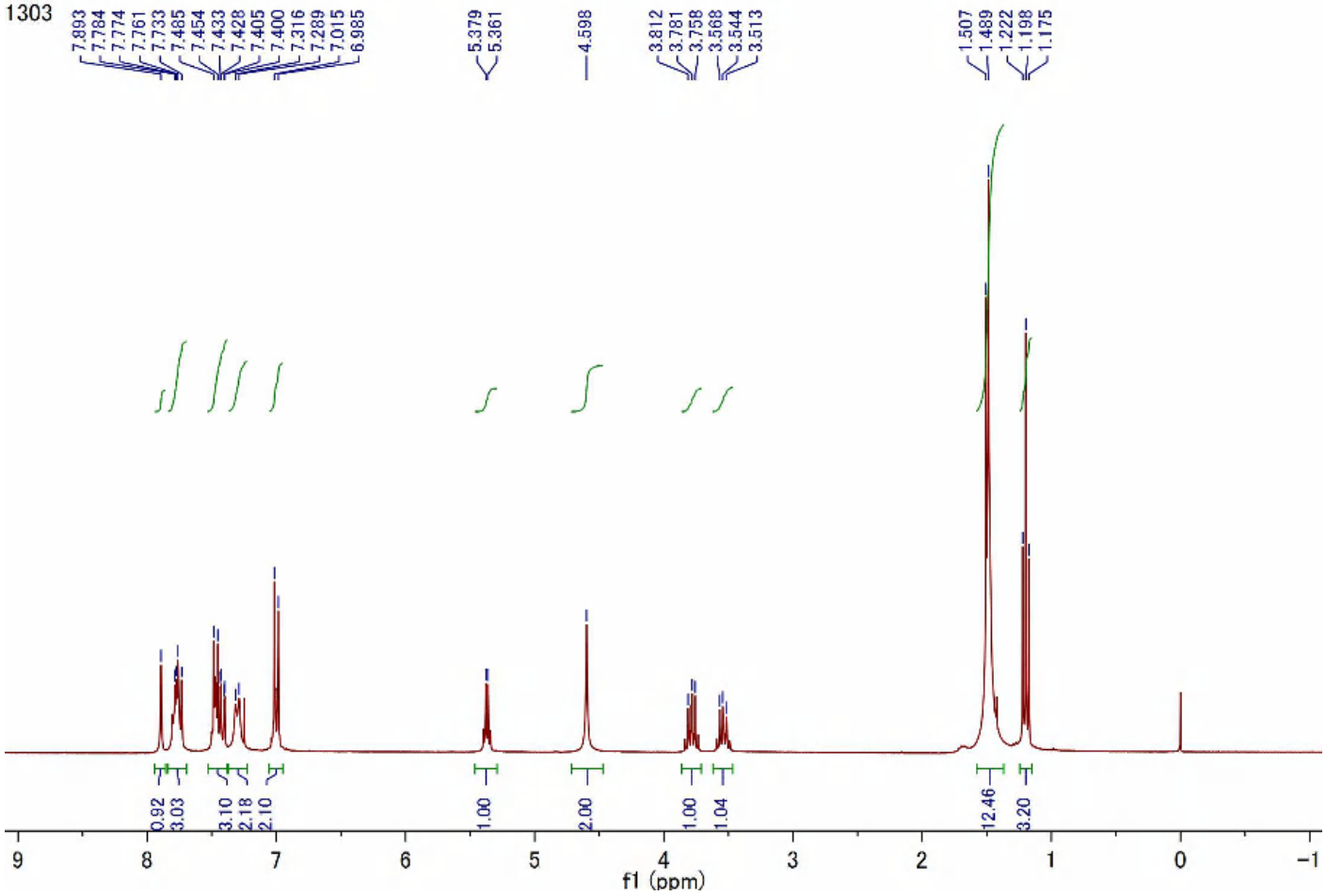
Compound **1j** (^{1}H NMR, 300 MHz, $CDCl_3$)



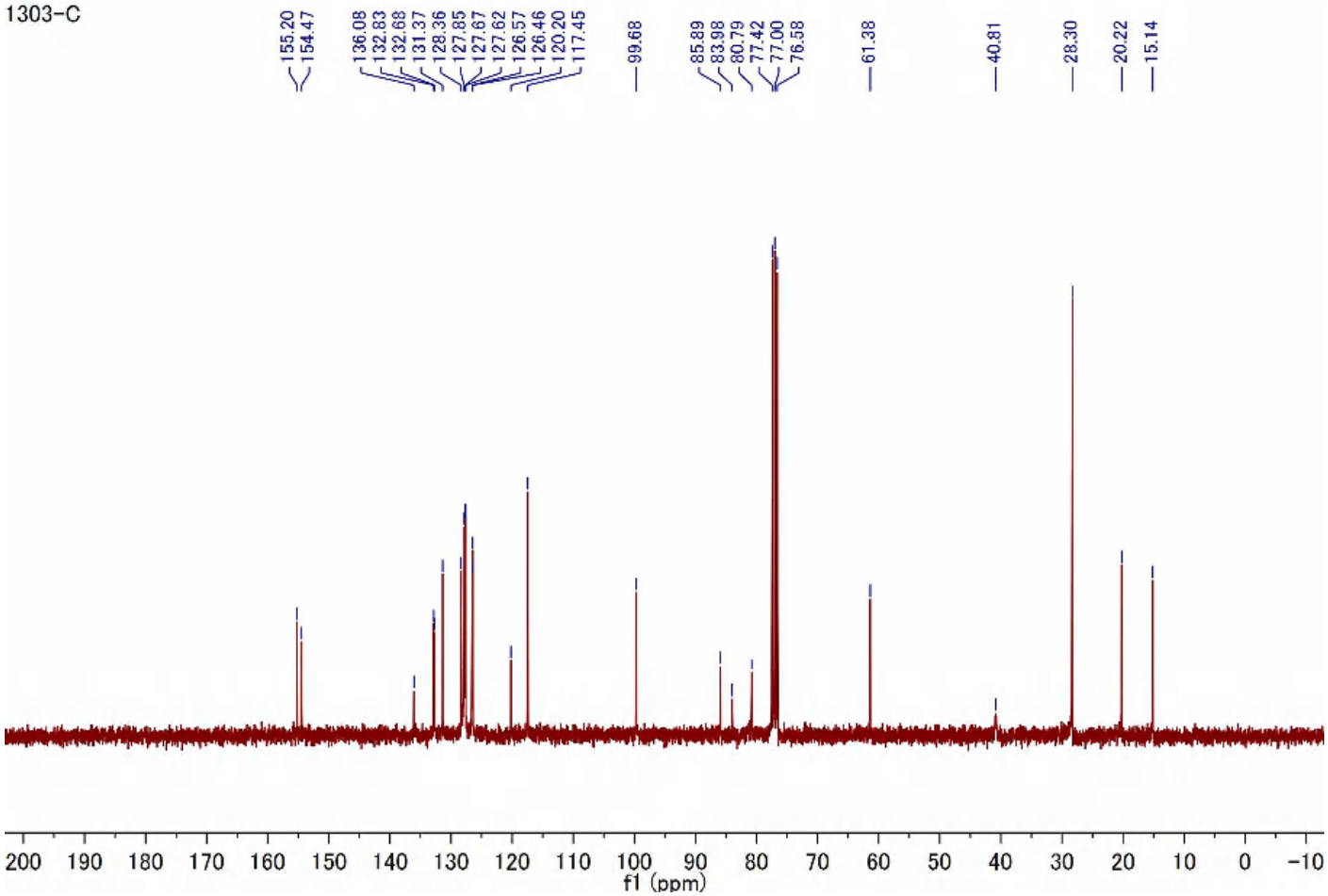
Compound **1j** (^{13}C NMR, 75 MHz, $CDCl_3$)



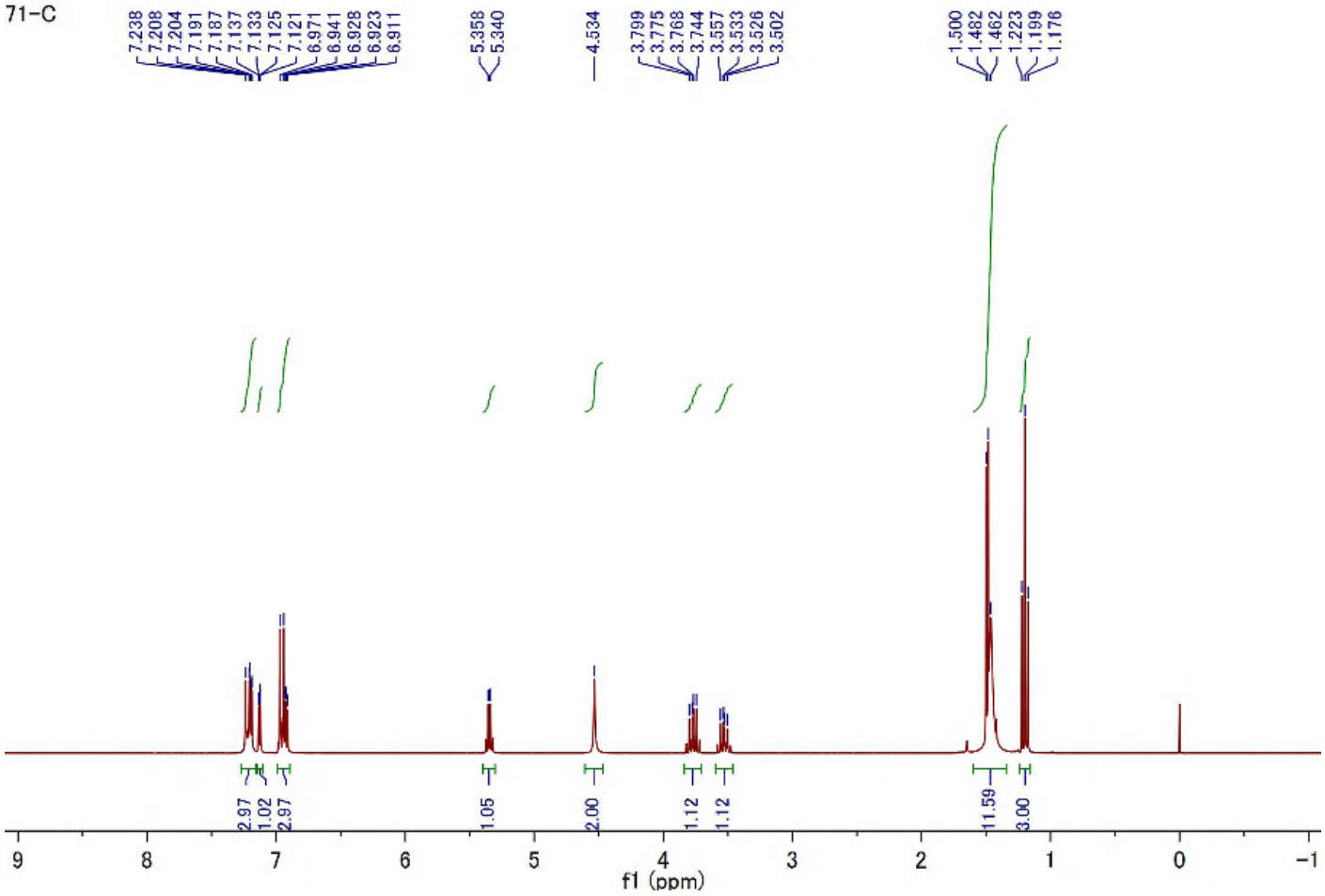
Compound **1k** (^{1}H NMR, 300 MHz, $CDCl_3$)



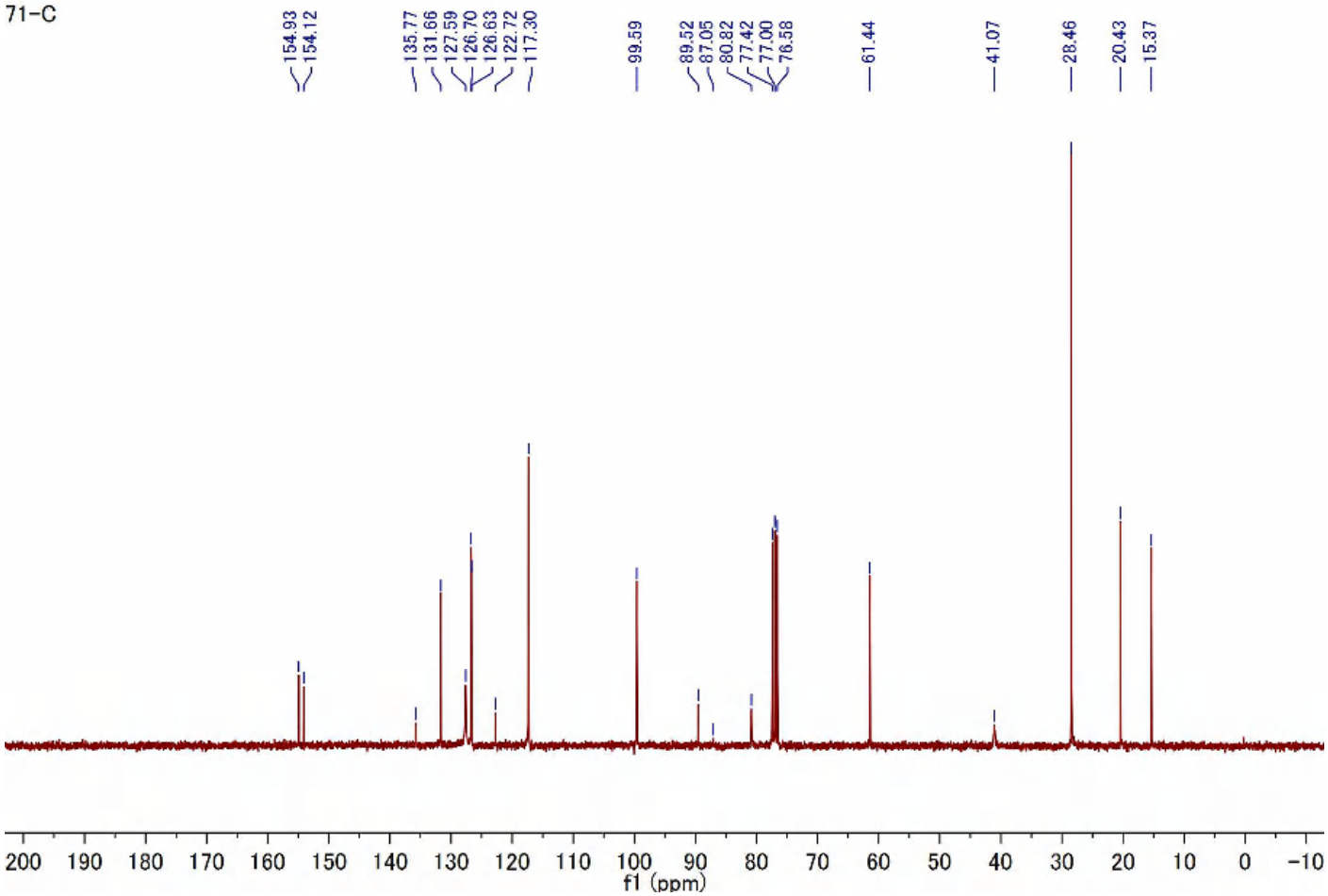
Compound **1k** (^{13}C NMR, 75 MHz, $CDCl_3$)



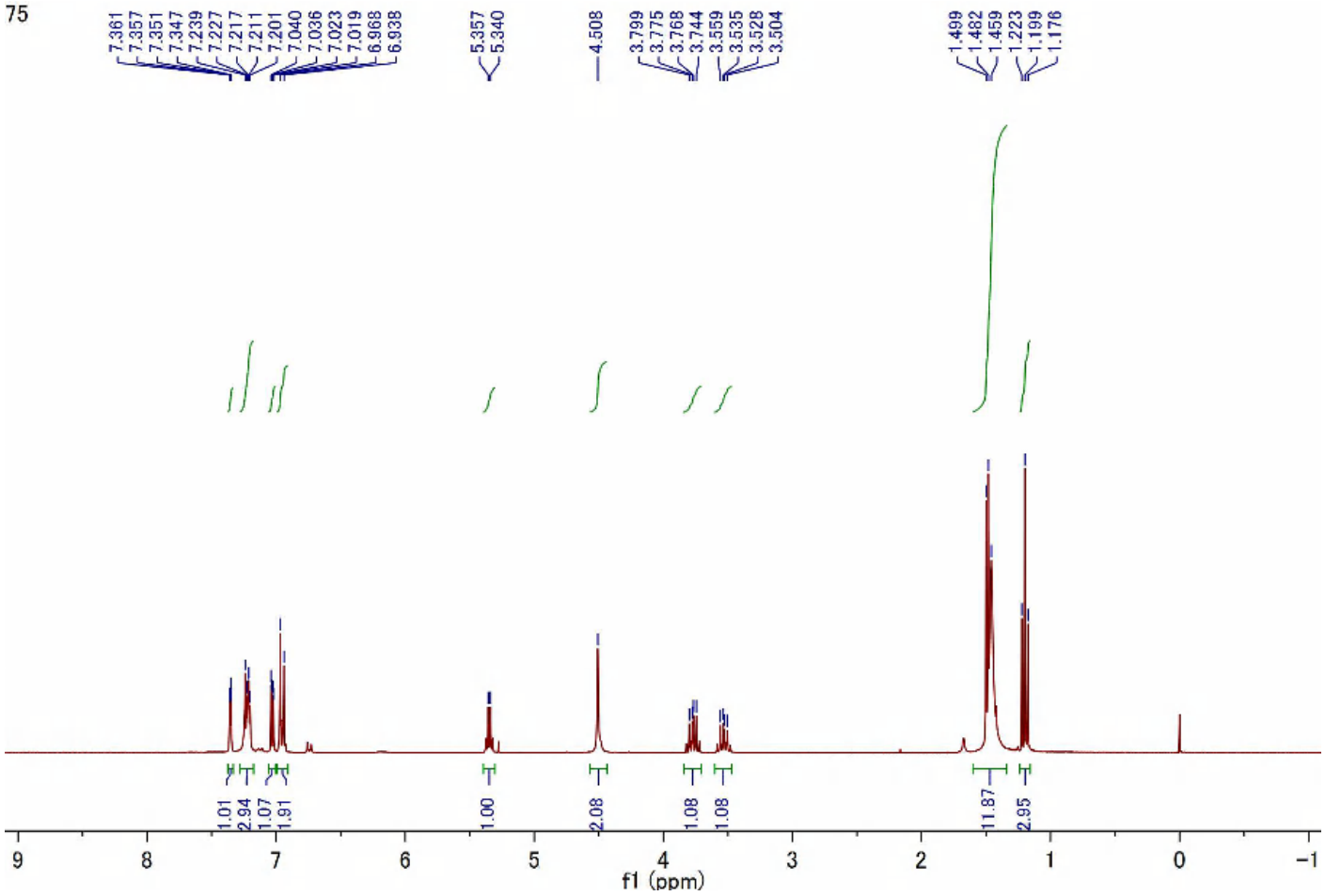
Compound **1l** (^{1}H NMR, 300 MHz, $CDCl_3$)



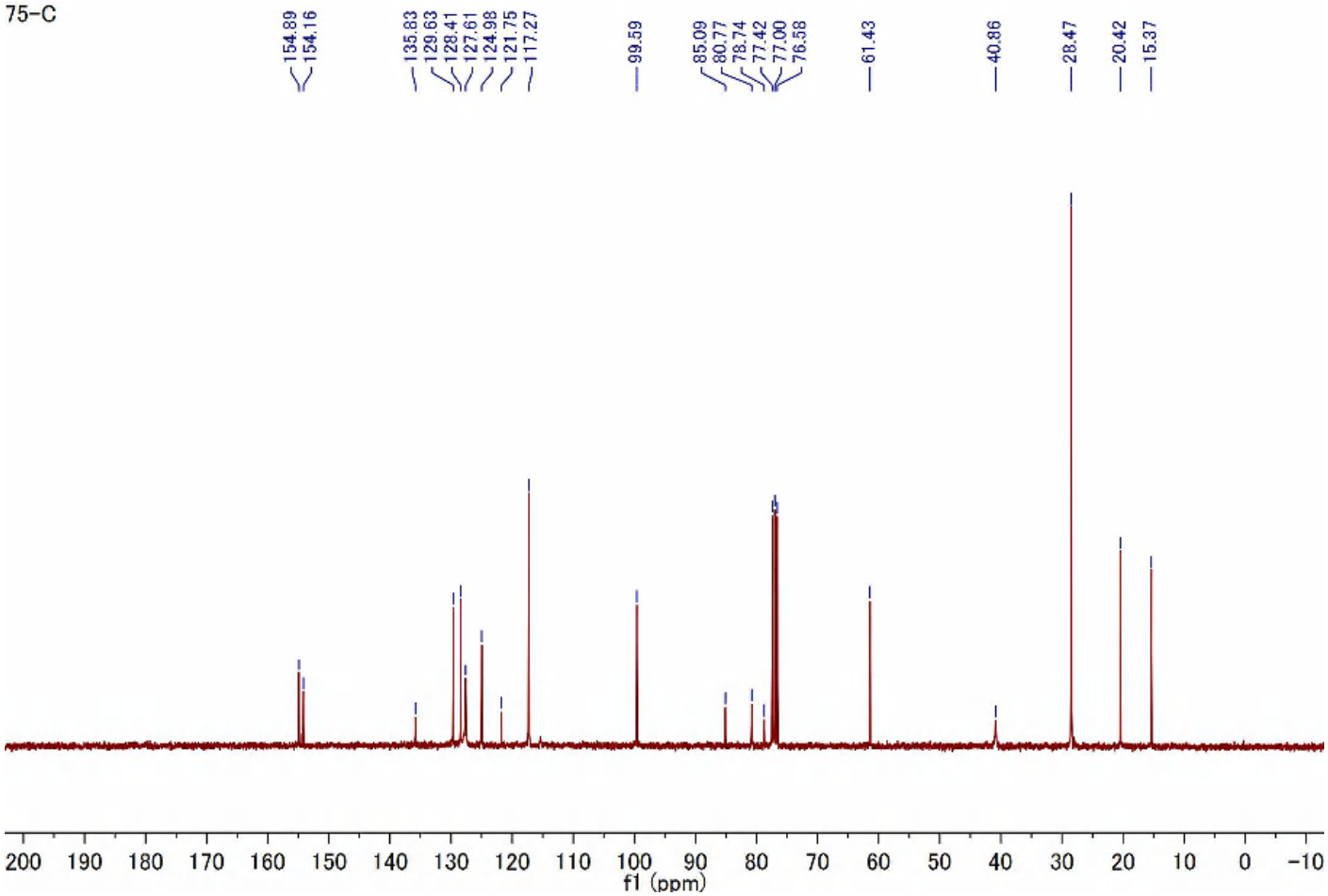
Compound **1l** (^{13}C NMR, 75 MHz, $CDCl_3$)



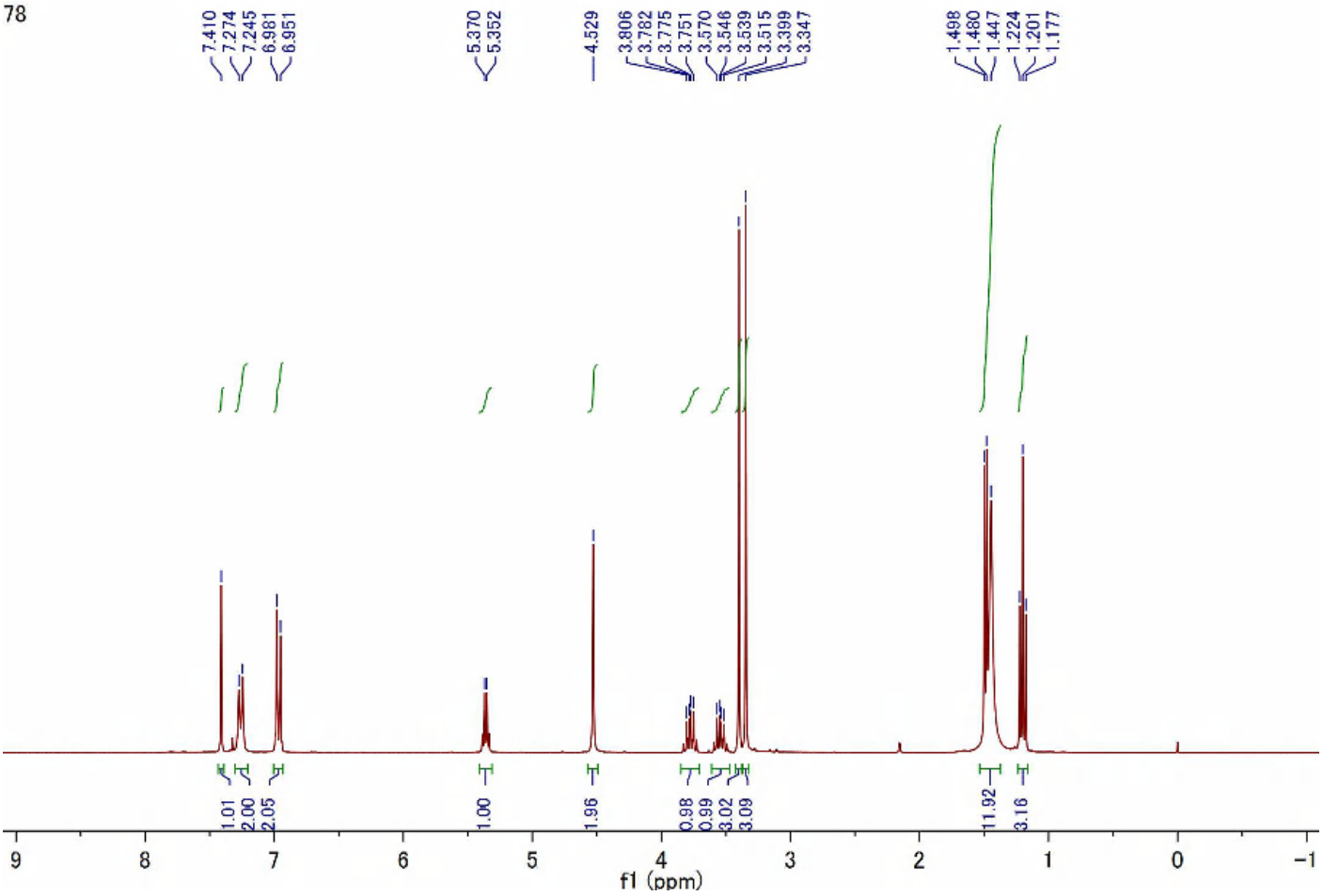
Compound **1m** (^{1}H NMR, 300 MHz, $CDCl_3$)



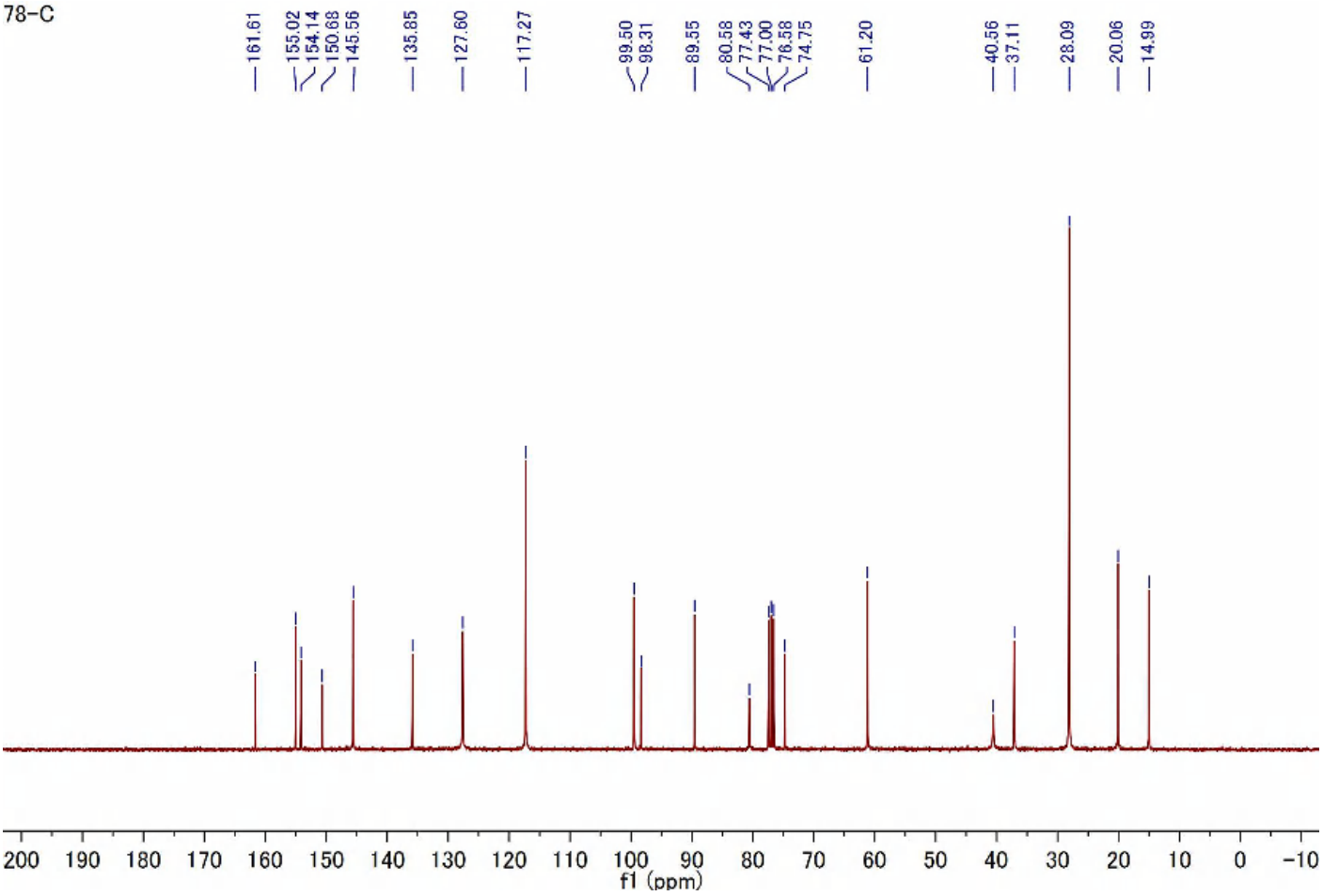
Compound **1m** (^{13}C NMR, 75 MHz, $CDCl_3$)



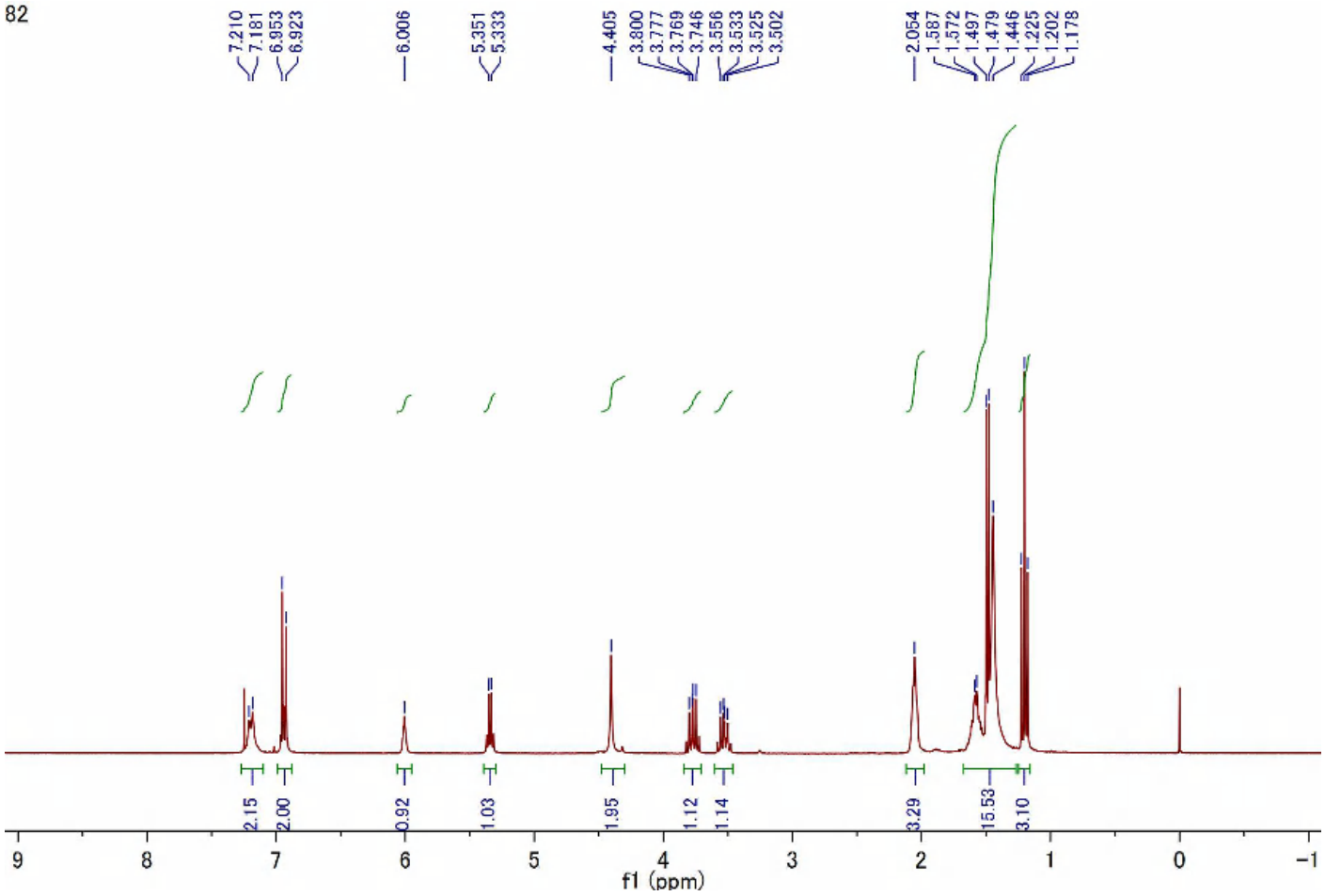
Compound **1n** (^{1}H NMR, 300 MHz, $CDCl_3$)



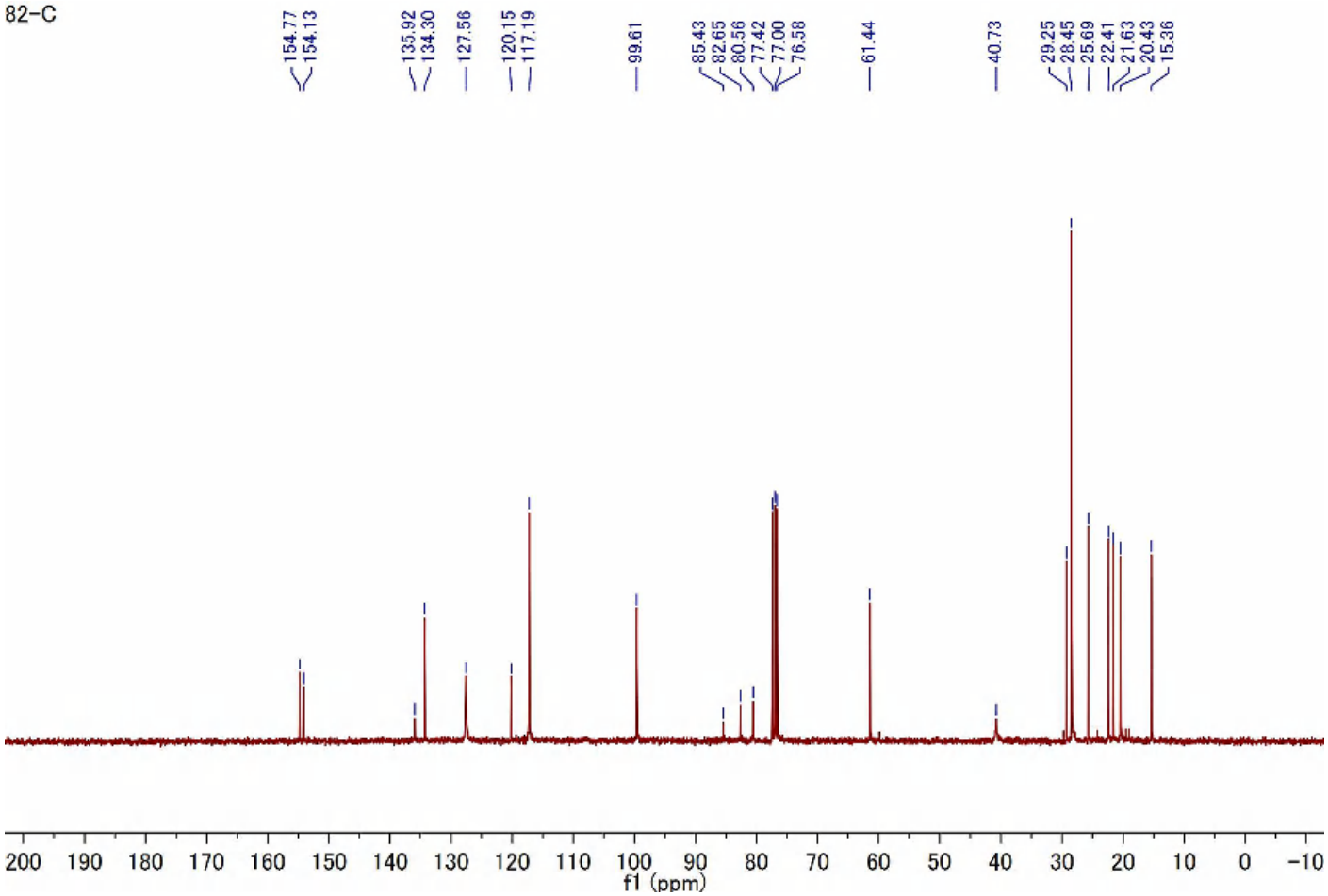
Compound **1n** (^{13}C NMR, 75 MHz, $CDCl_3$)



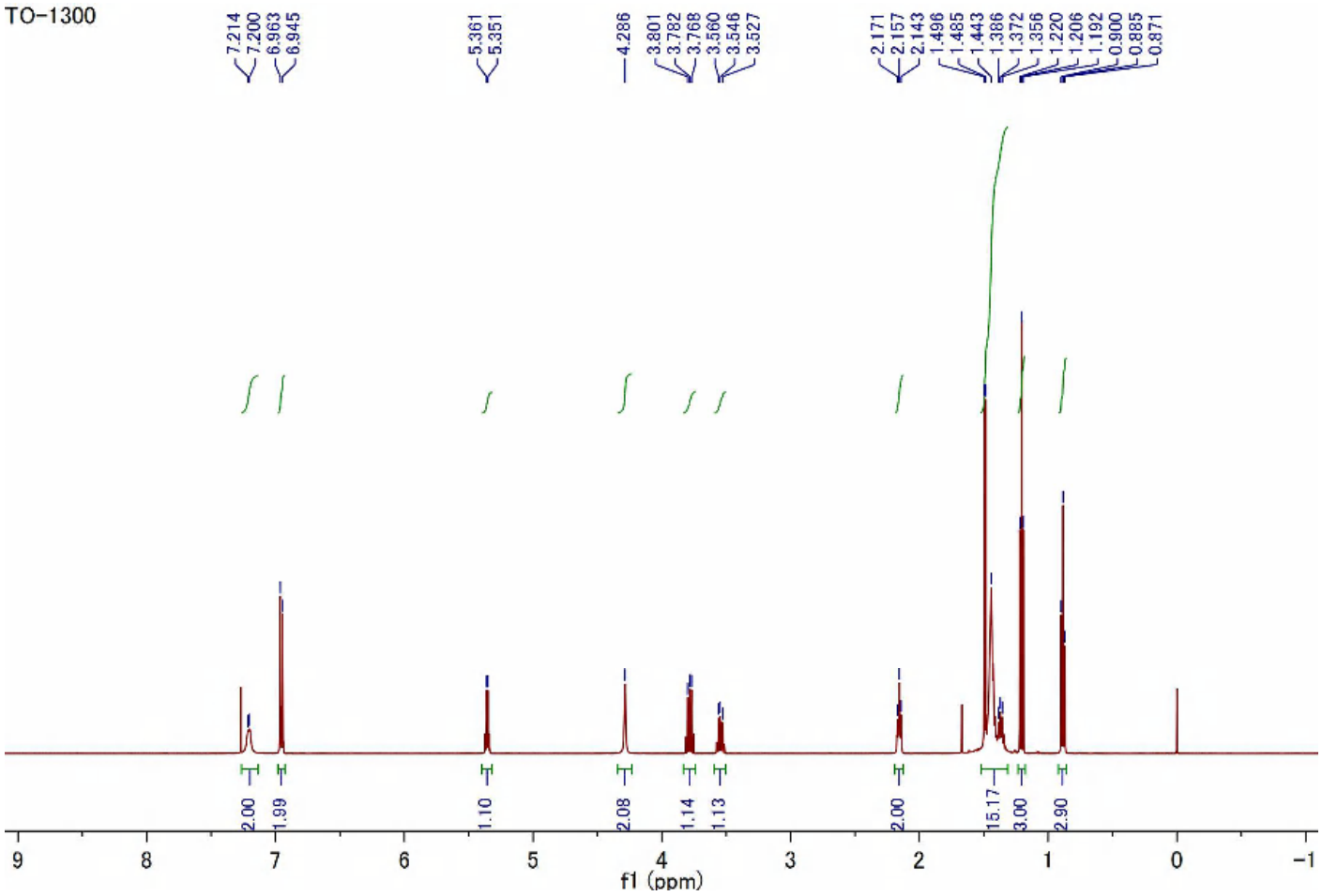
Compound **1o** (^{1}H NMR, 300 MHz, $CDCl_3$)



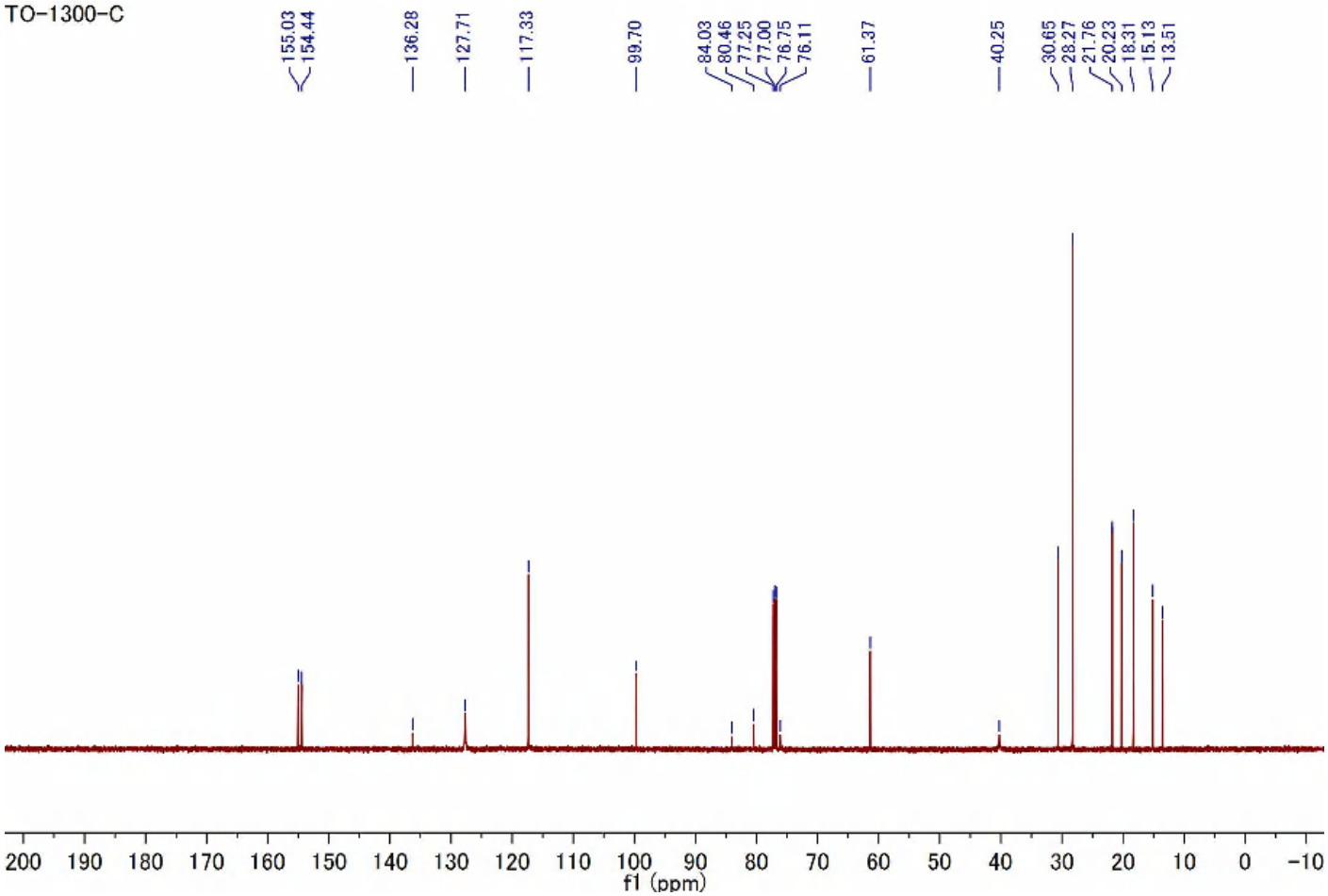
Compound **1o** (^{13}C NMR, 75 MHz, $CDCl_3$)



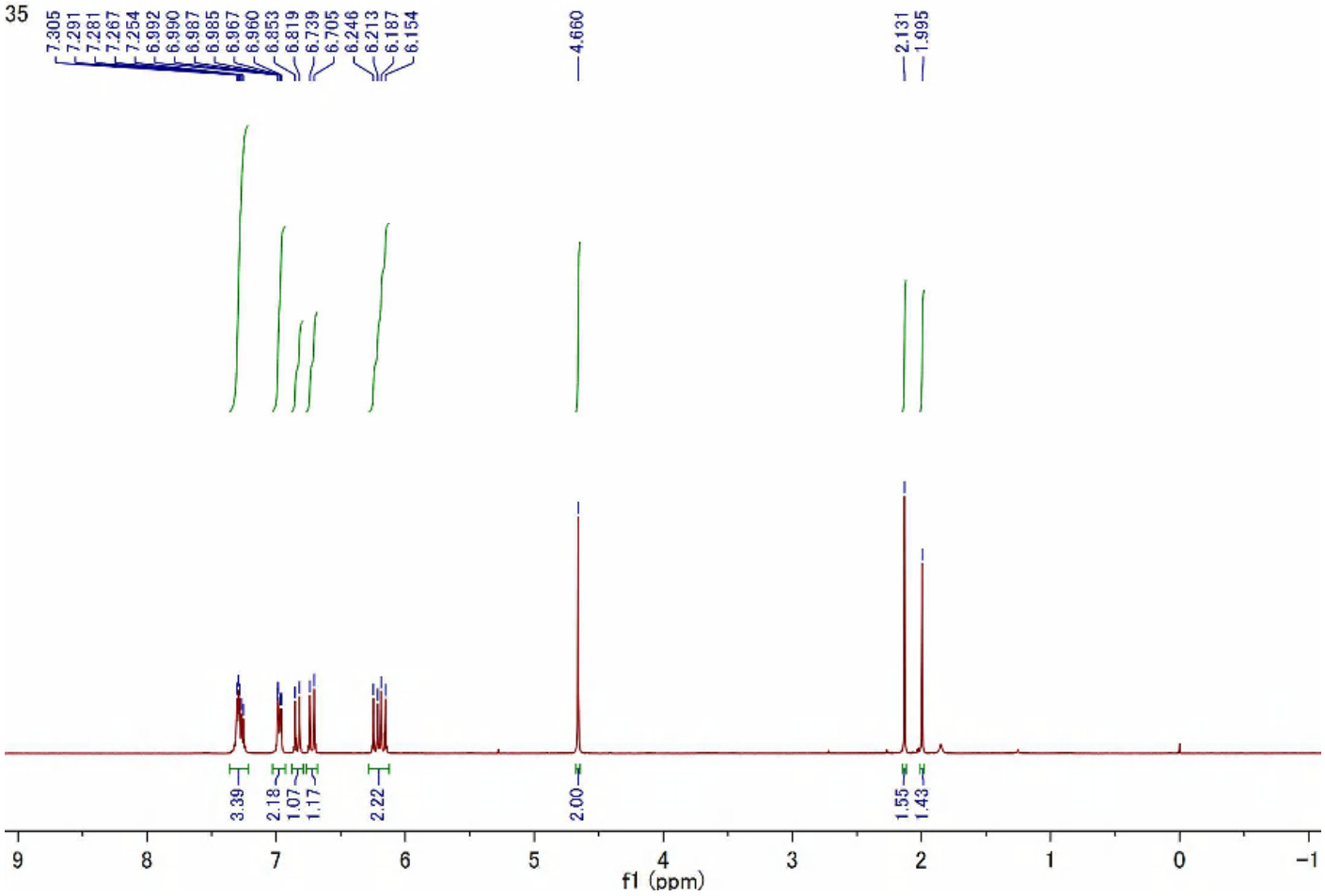
Compound **1p** (^{1}H NMR, 500 MHz, $CDCl_3$)



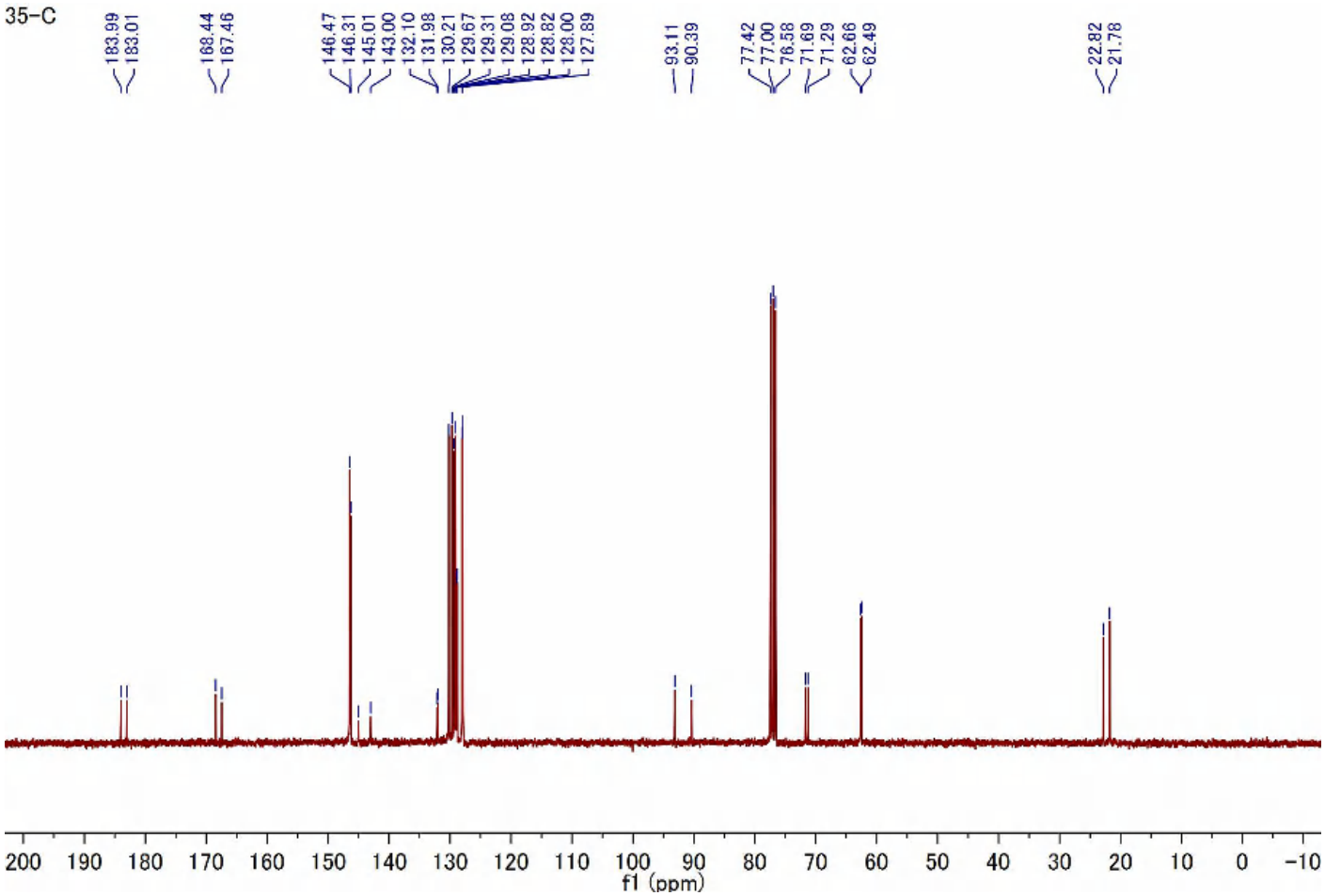
Compound **1p** (^{13}C NMR, 125 MHz, $CDCl_3$)



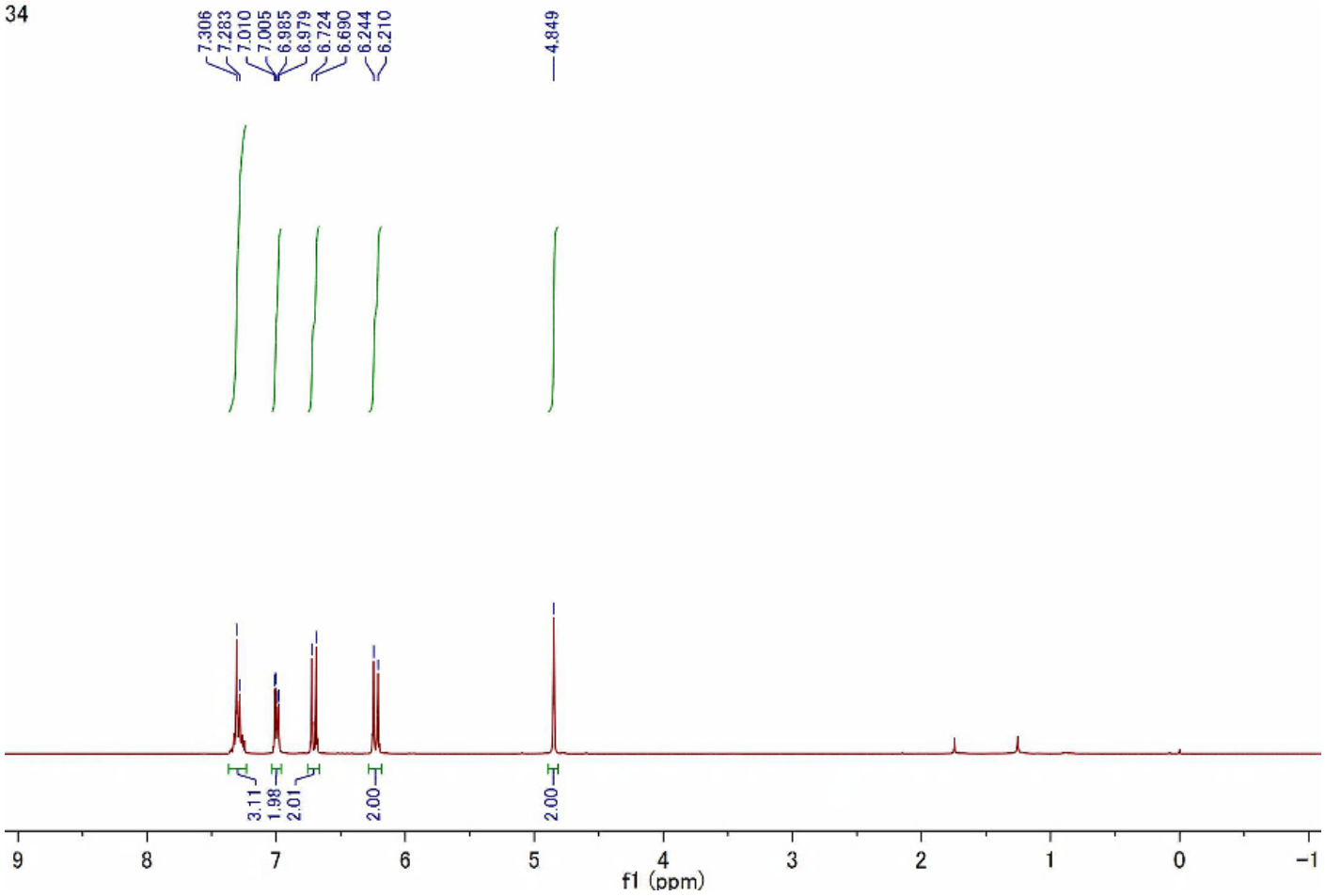
Compound **2a** (^{1}H NMR, 300 MHz, $CDCl_3$)



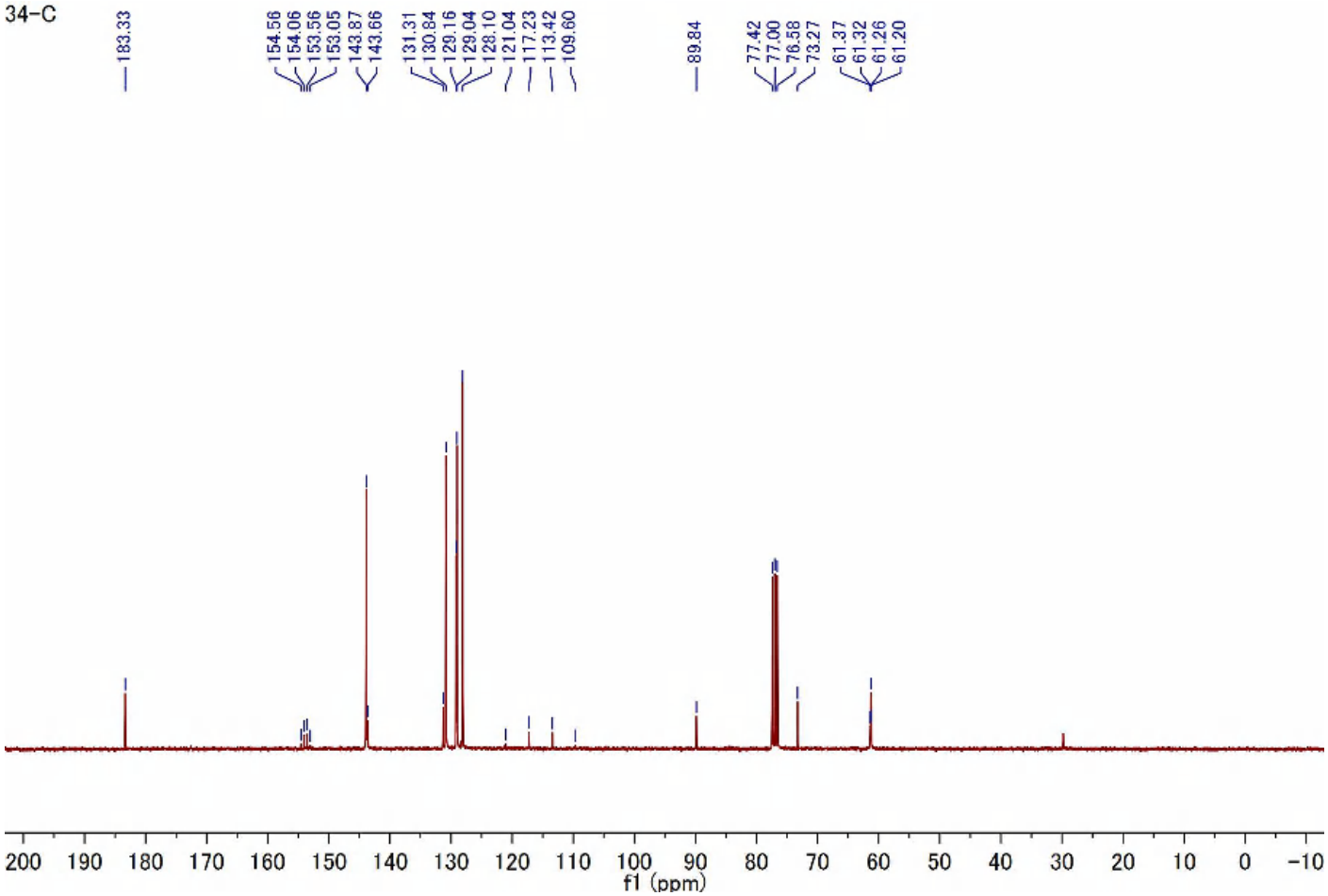
Compound **2a** (^{13}C NMR, 75 MHz, $CDCl_3$)



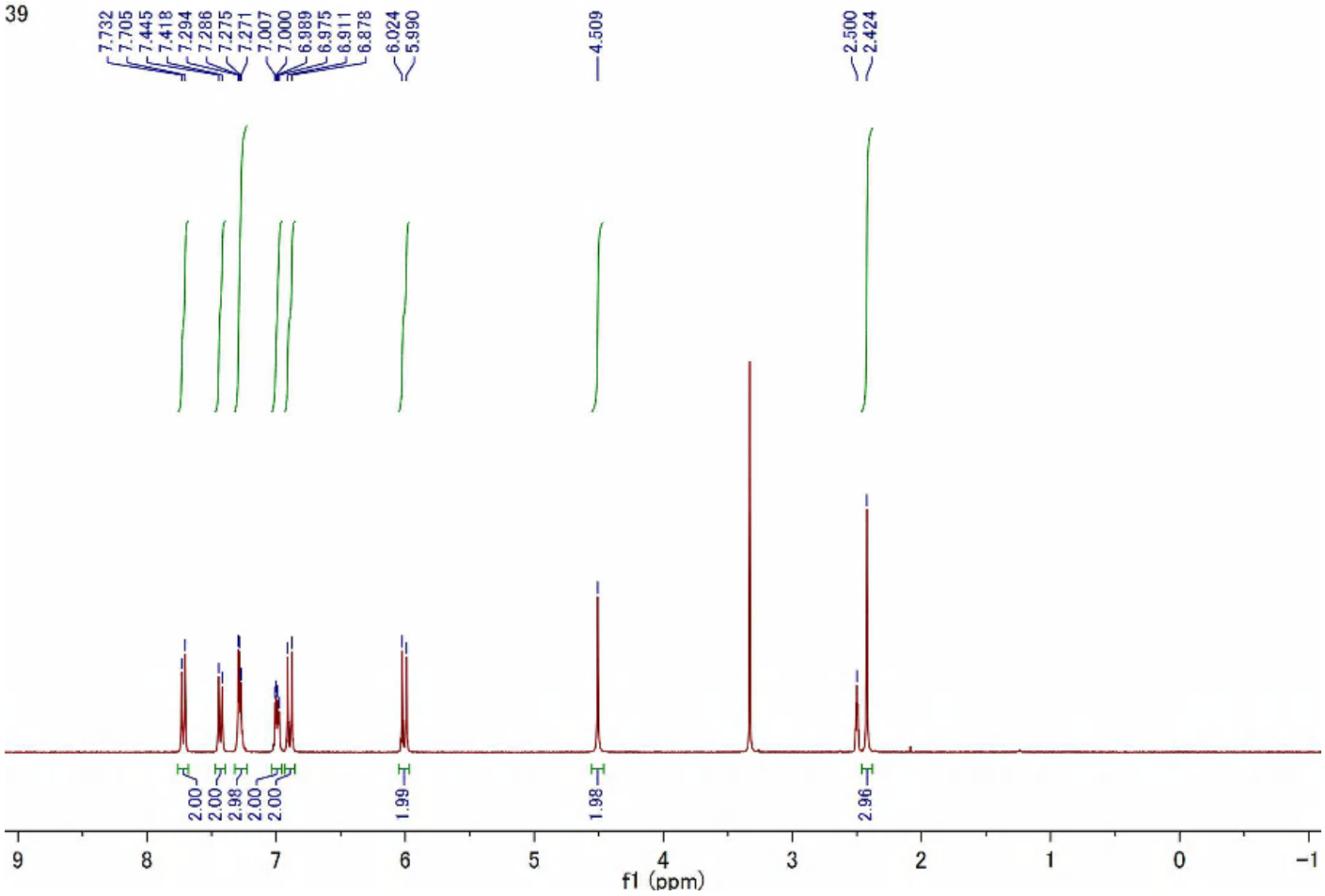
Compound **2b** (^{1}H NMR, 300 MHz, $CDCl_3$)



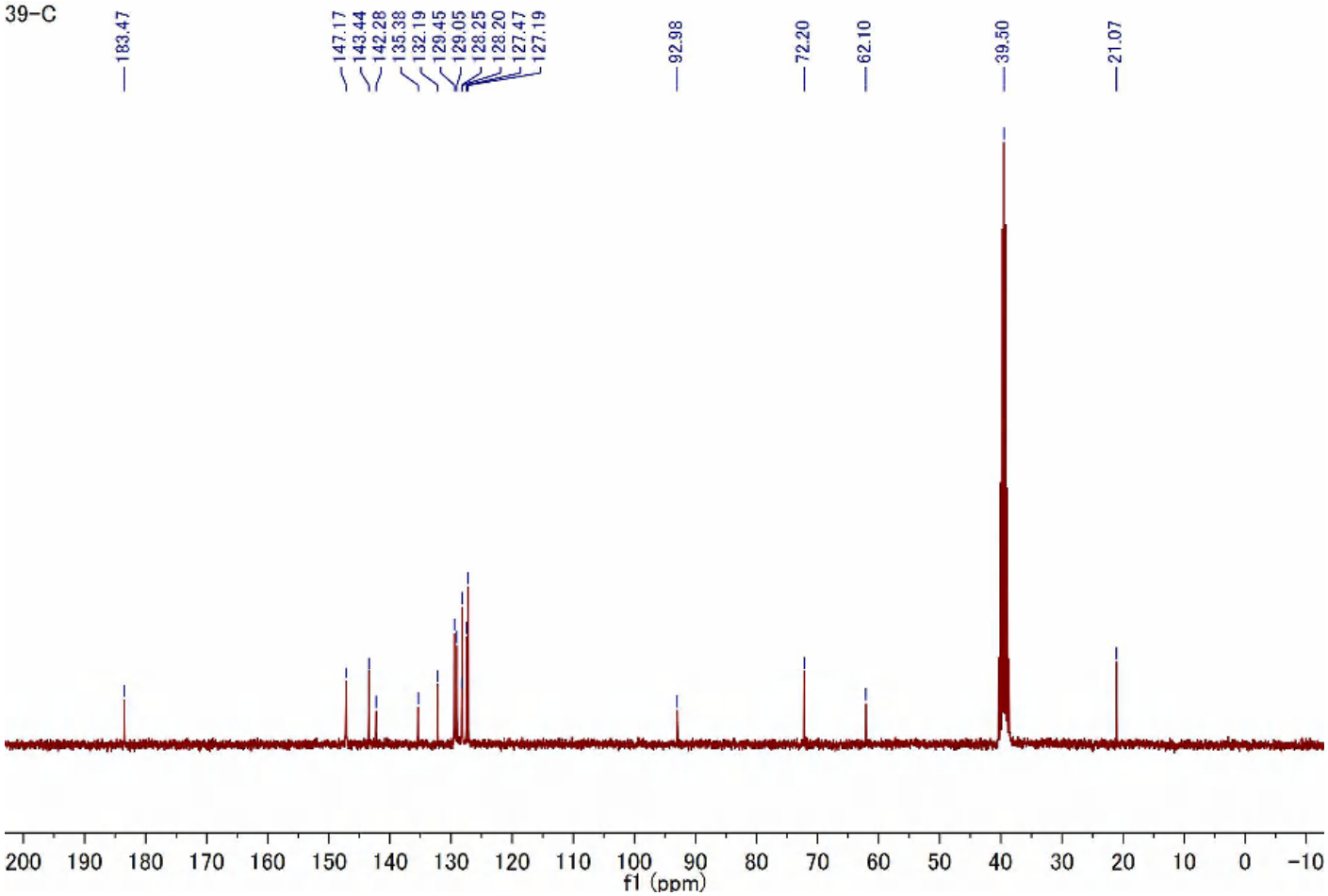
Compound **2b** (^{13}C NMR, 75 MHz, $CDCl_3$)



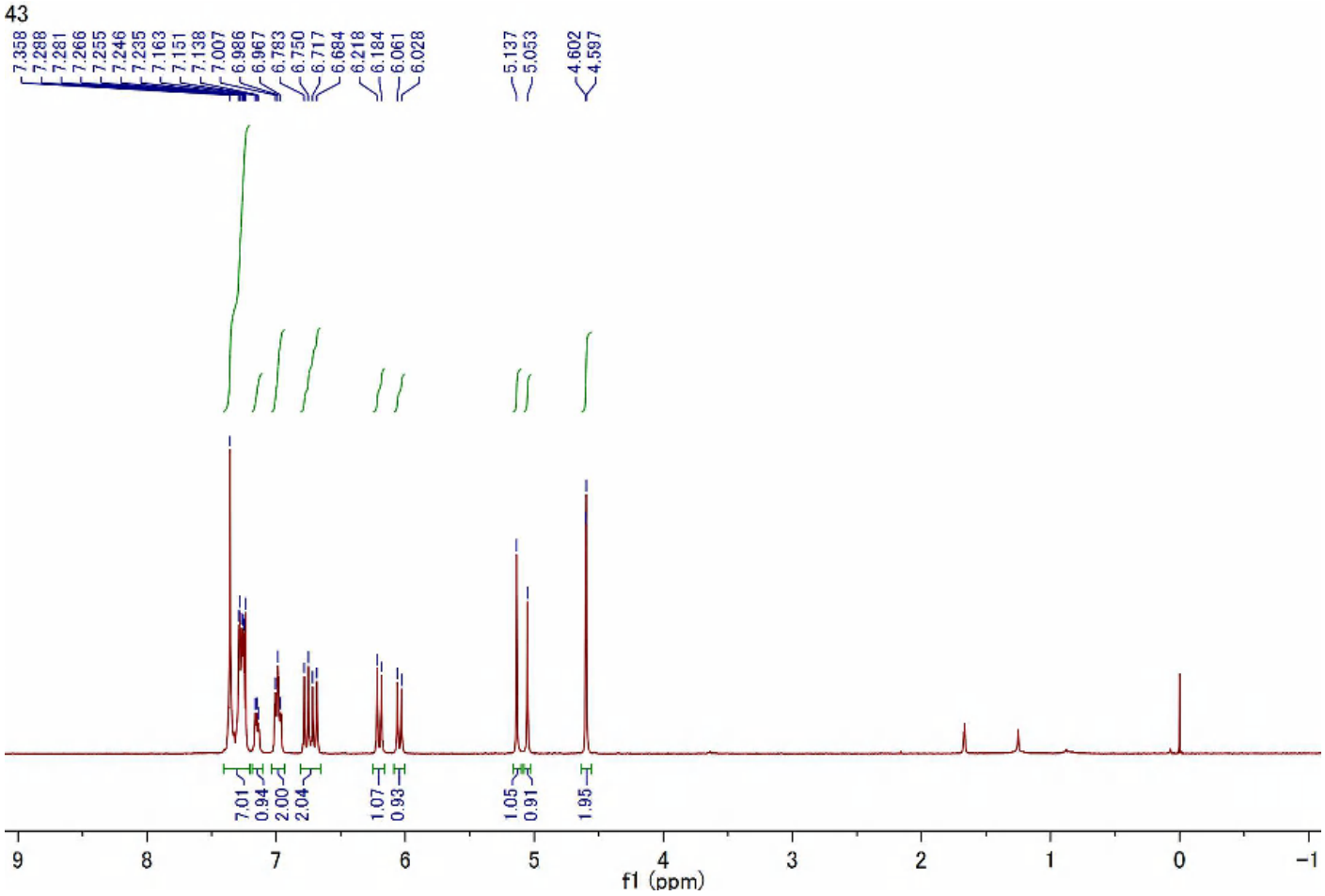
Compound **2c** (^{1}H NMR, 300 MHz, $CDCl_3$)



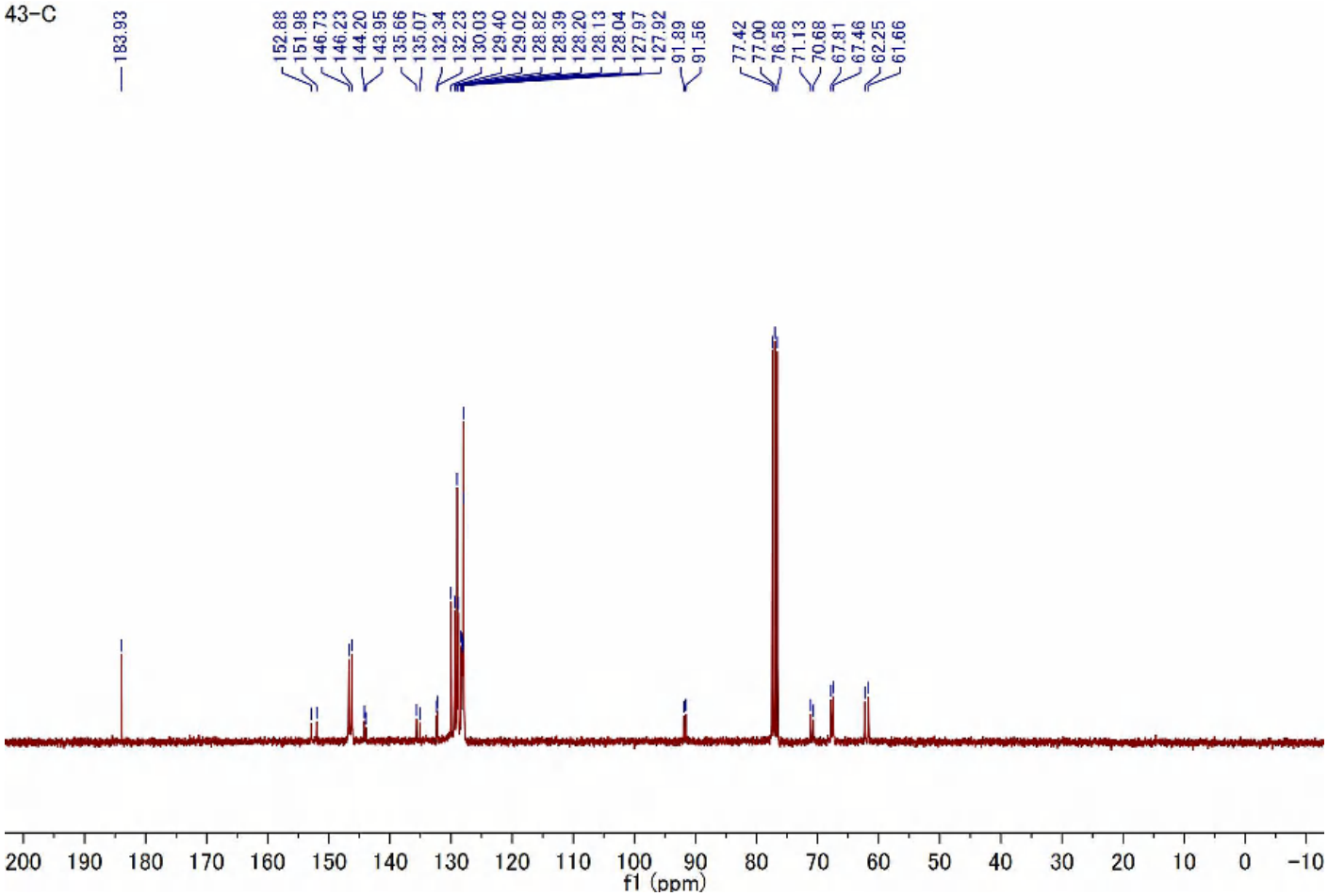
Compound **2c** (^{13}C NMR, 75 MHz, $CDCl_3$)



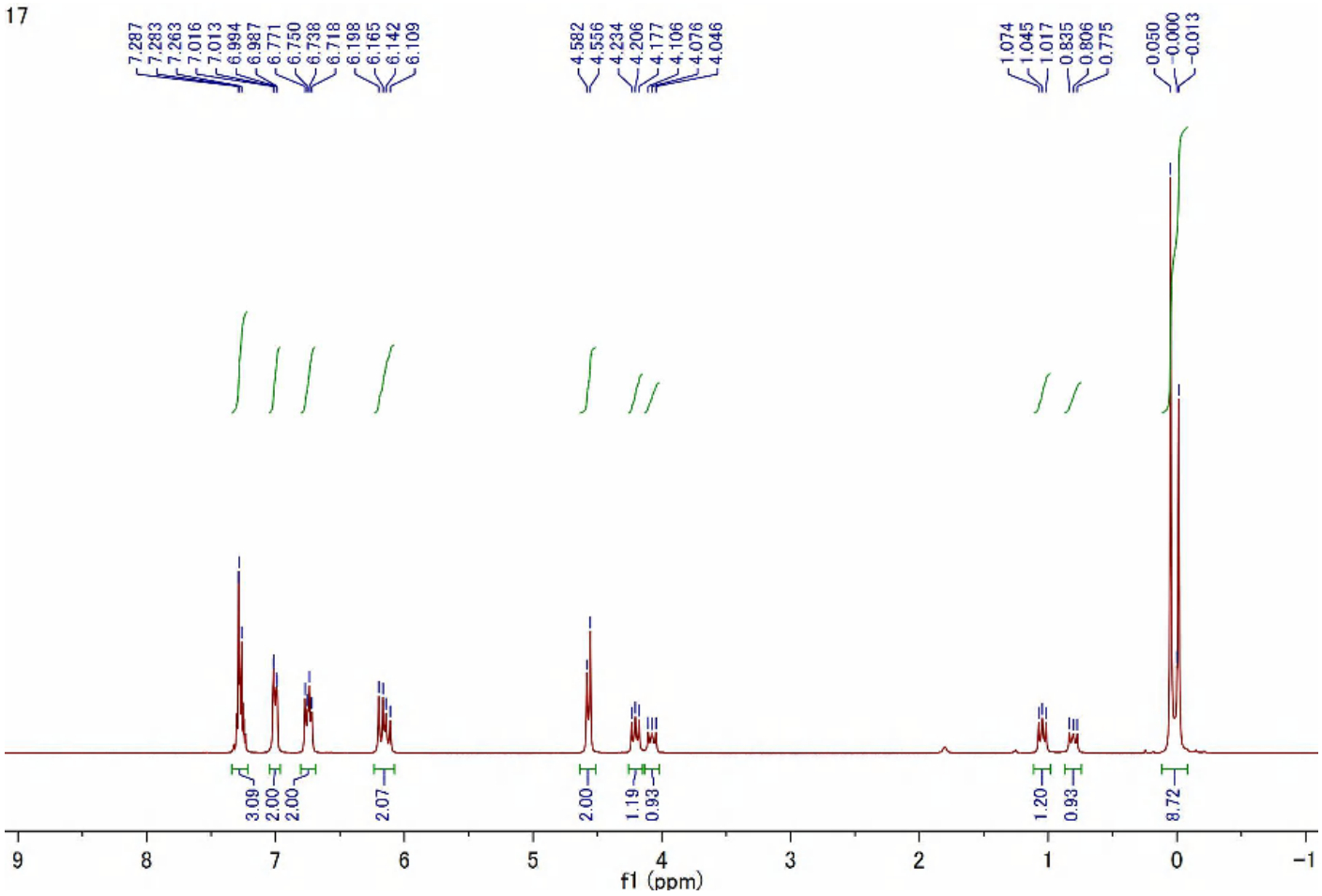
Compound **2d** (^{1}H NMR, 300 MHz, $CDCl_3$)



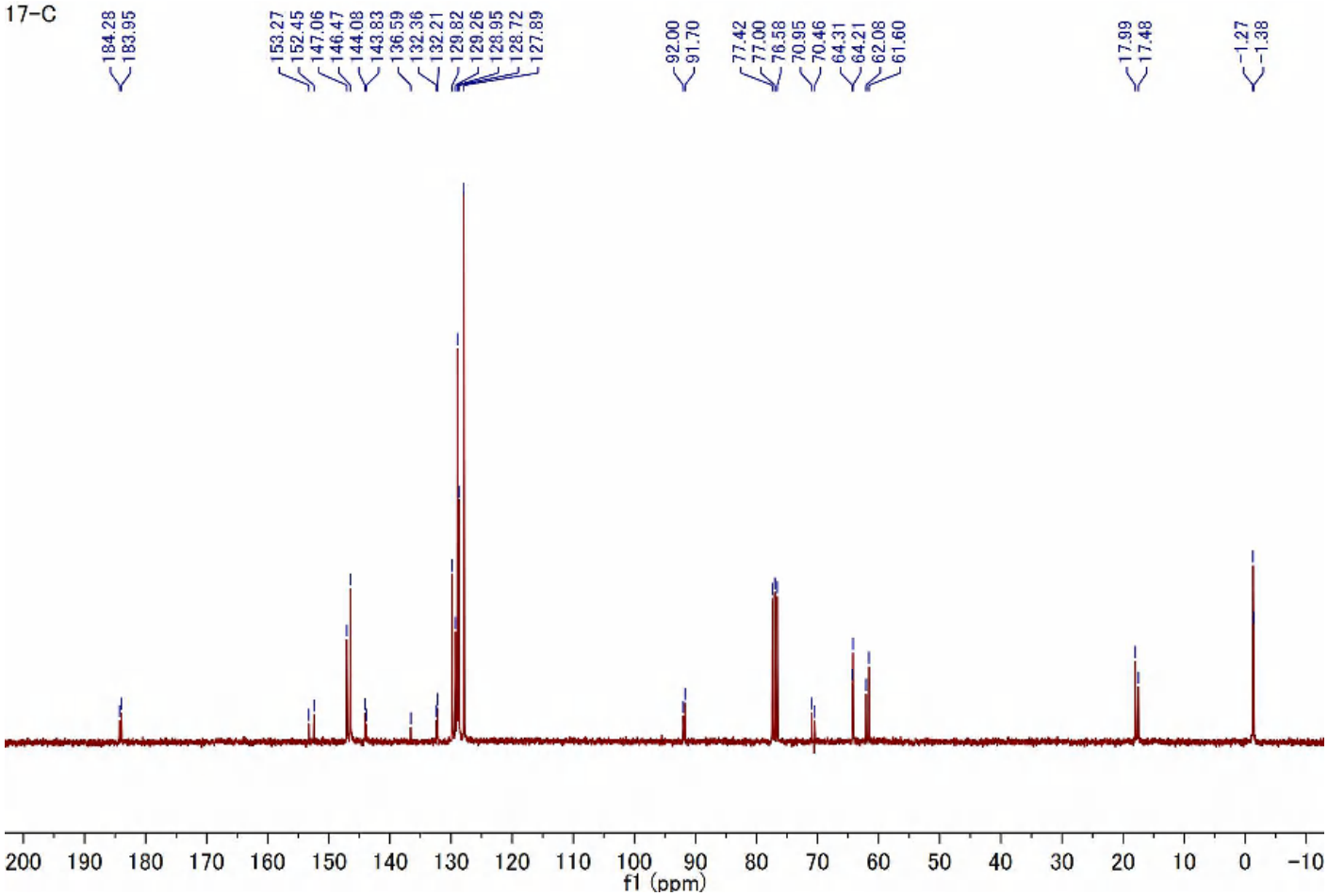
Compound **2d** (^{13}C NMR, 75 MHz, $CDCl_3$)



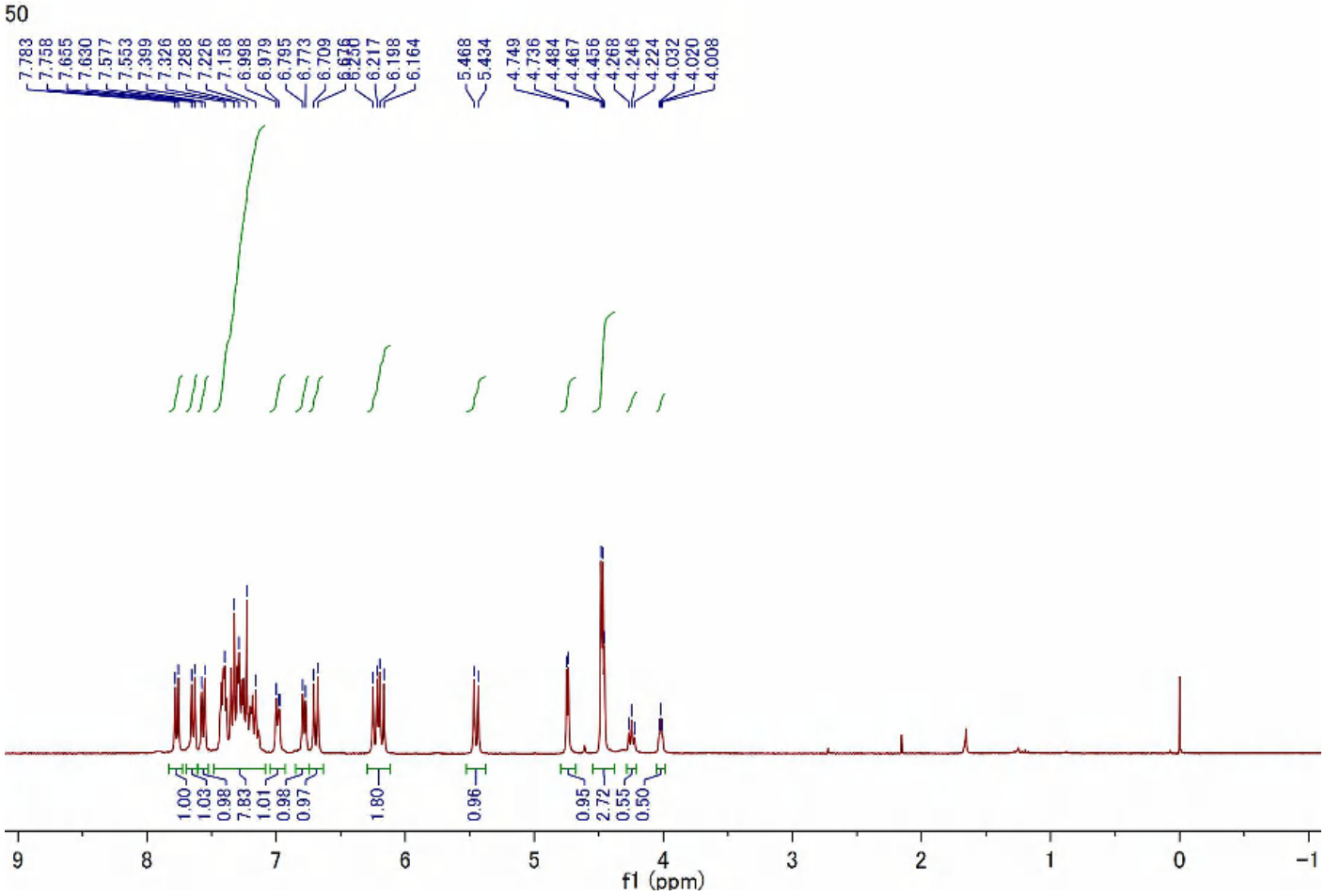
Compound **2e** (^{1}H NMR, 300 MHz, $CDCl_3$)



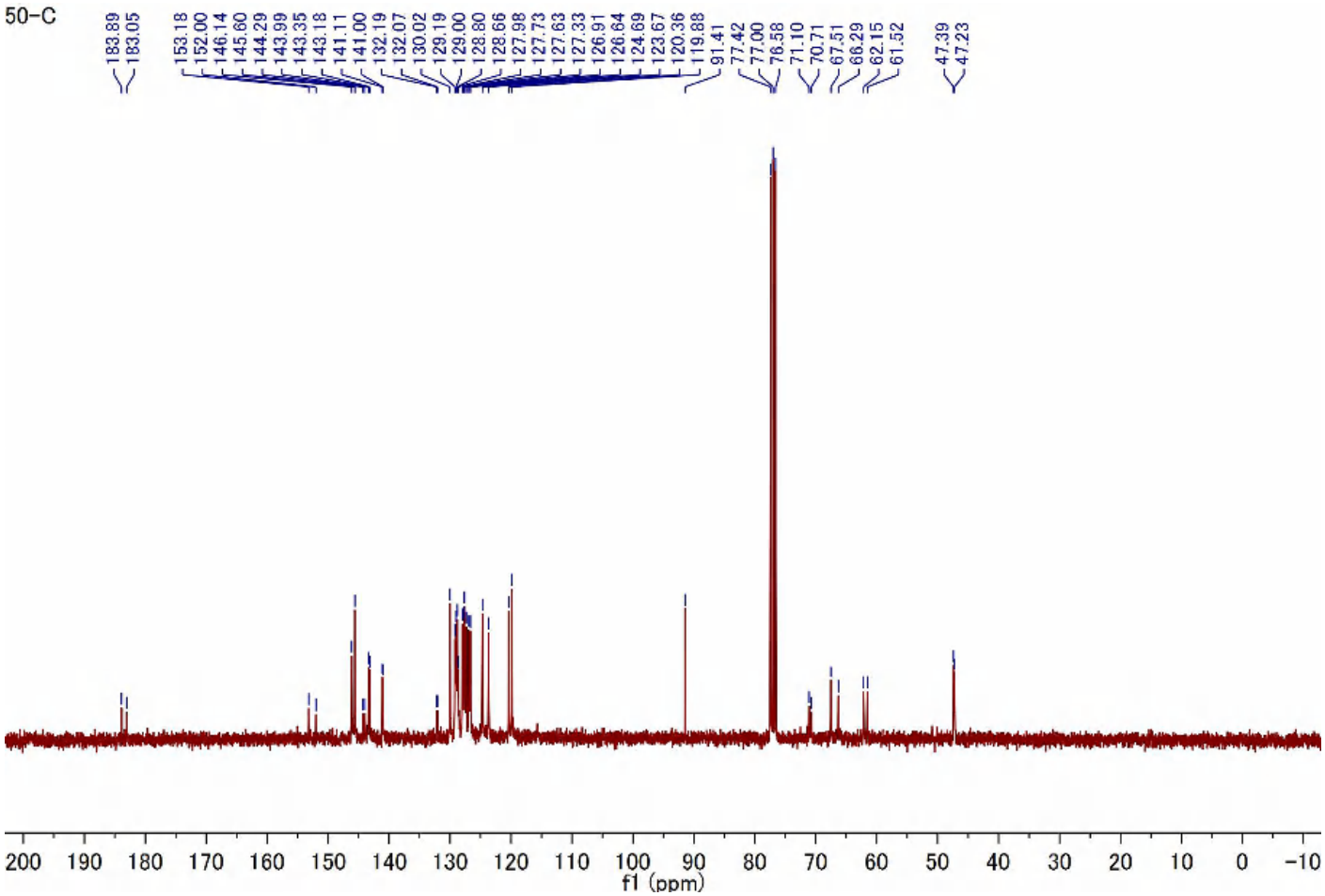
Compound **2e** (^{13}C NMR, 75 MHz, $CDCl_3$)



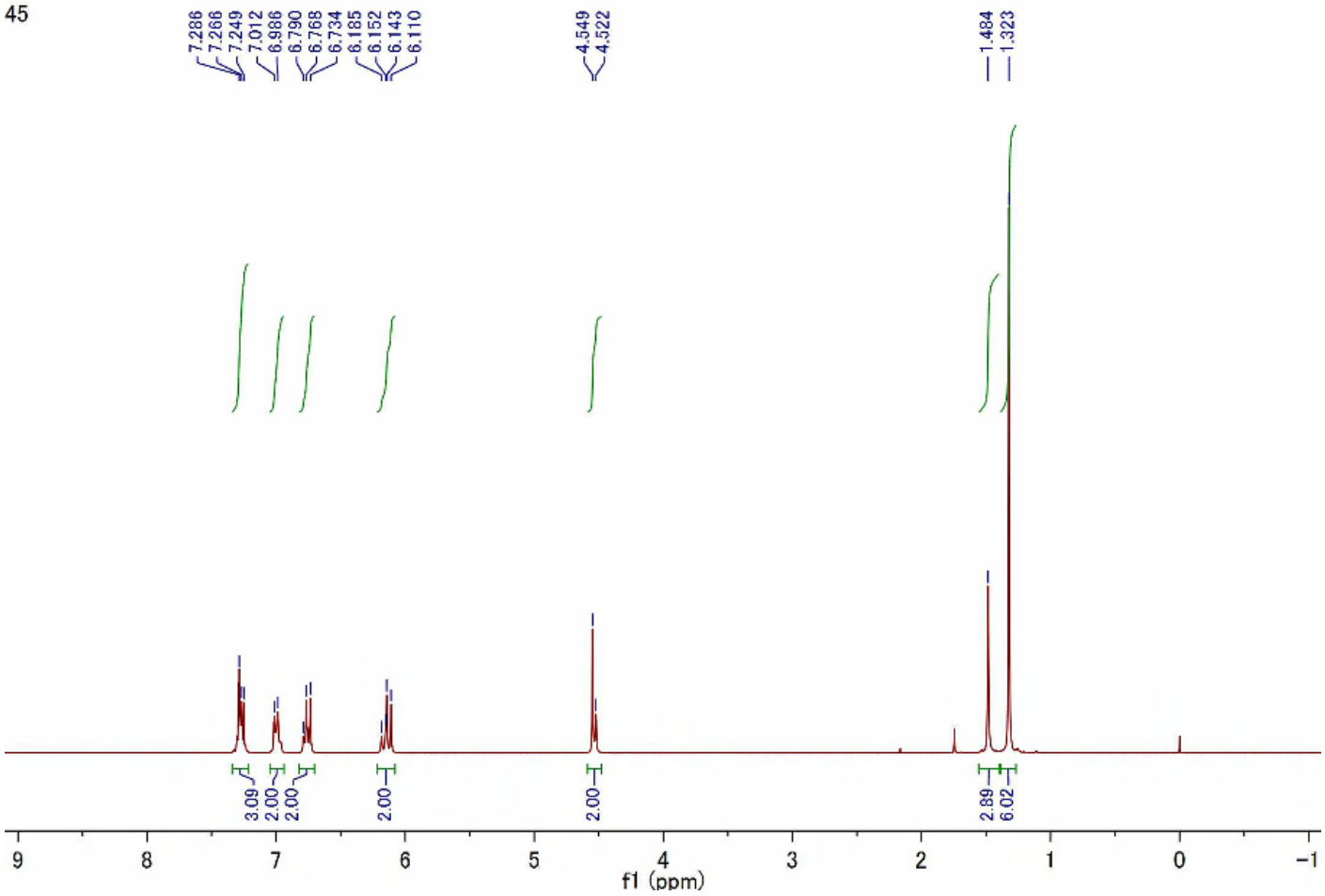
Compound **2f** (^{1}H NMR, 300 MHz, $CDCl_3$)



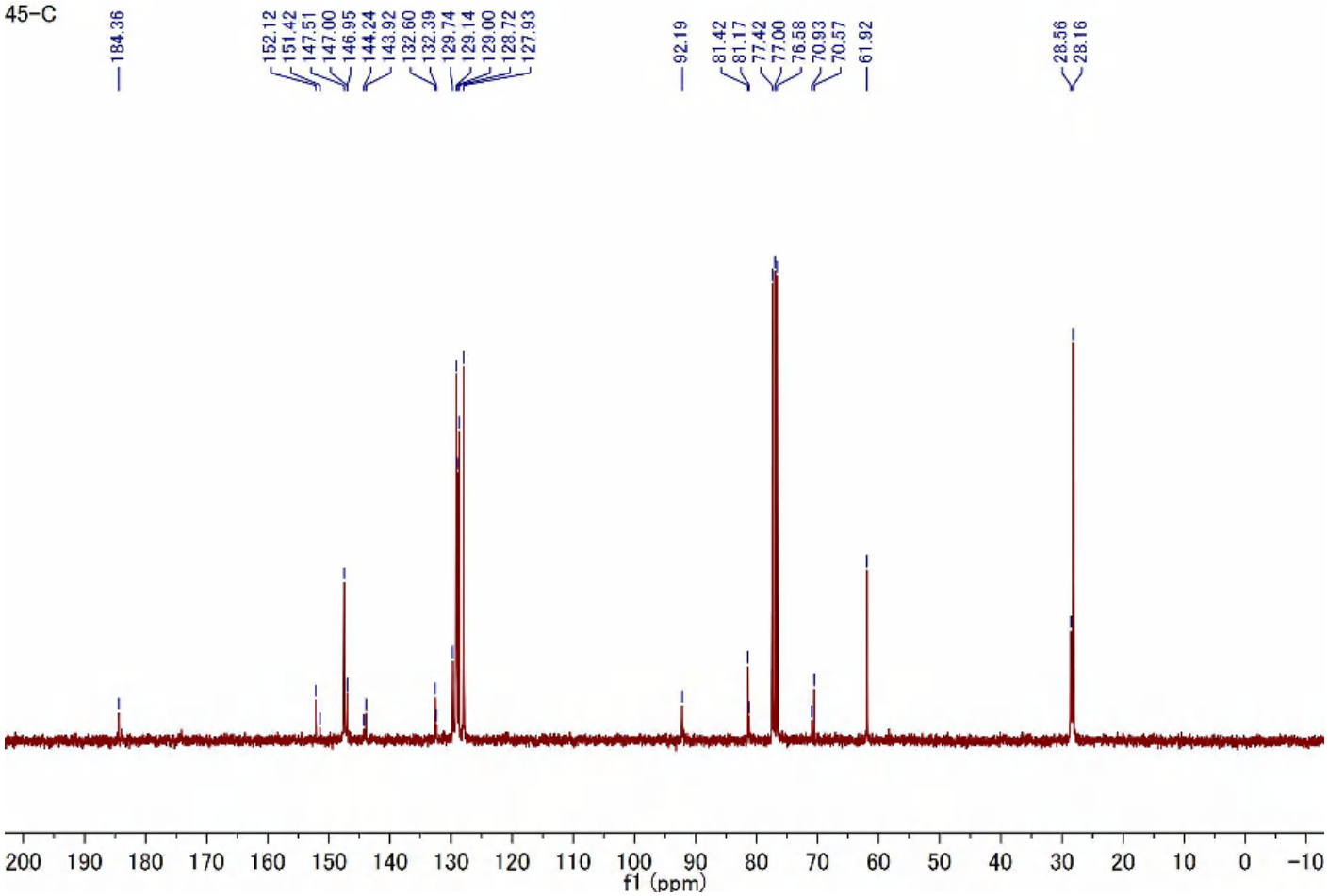
Compound **2f** (^{13}C NMR, 75 MHz, $CDCl_3$)



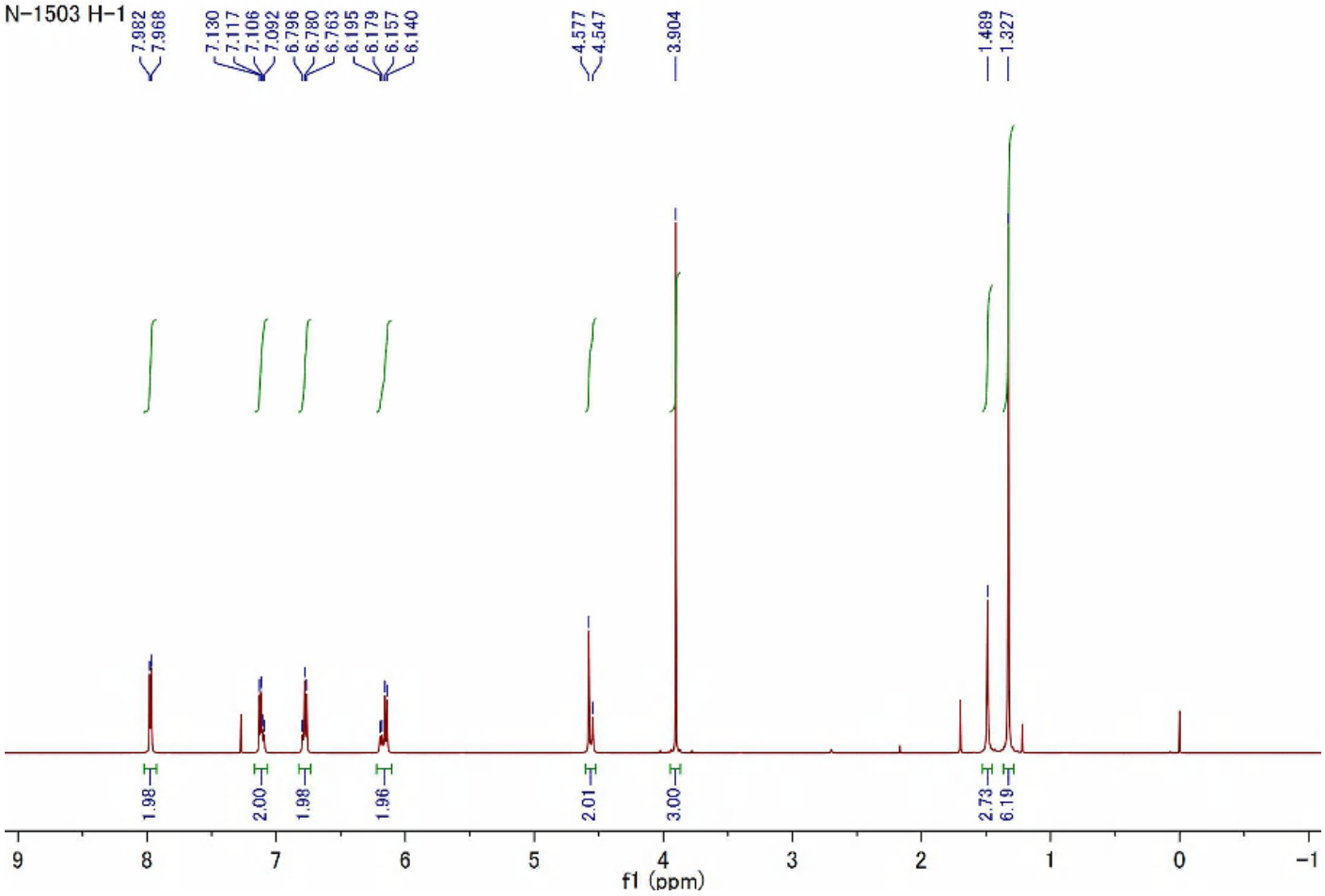
Compound **2g** (^{1}H NMR, 600 MHz, $CDCl_3$)



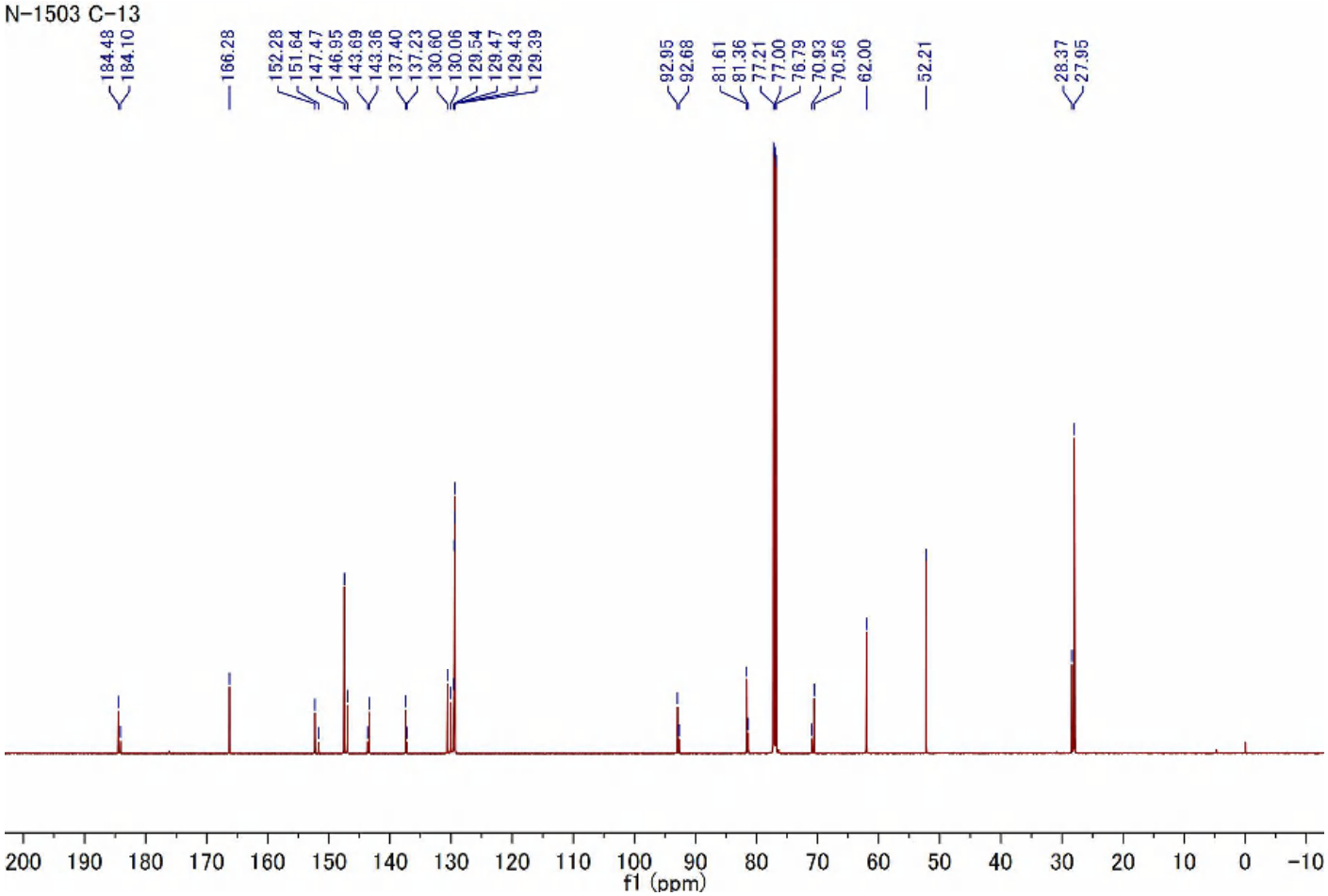
Compound **2g** (^{13}C NMR, 150 MHz, $CDCl_3$)



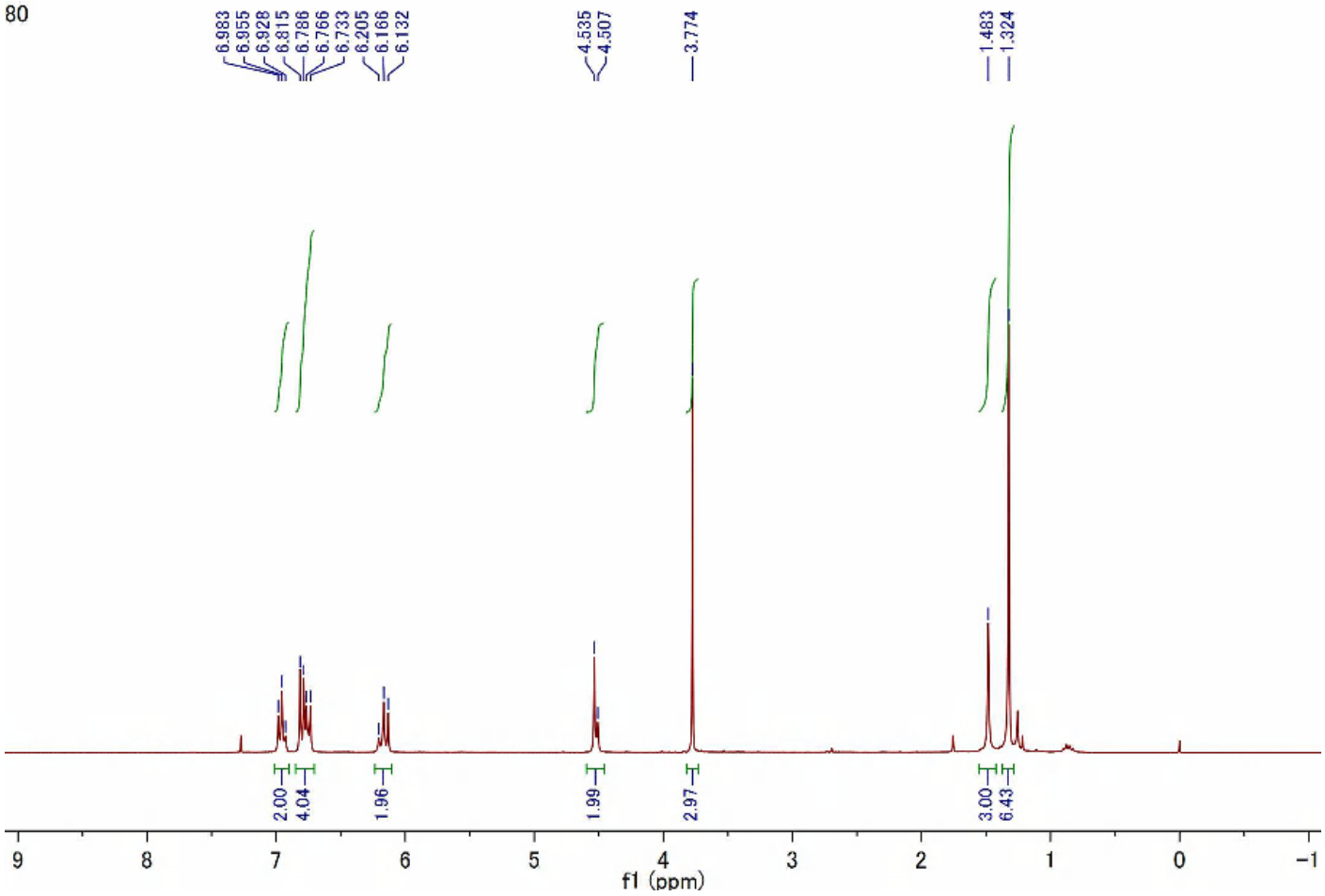
Compound **2h** (^{1}H NMR, 600 MHz, $CDCl_3$)



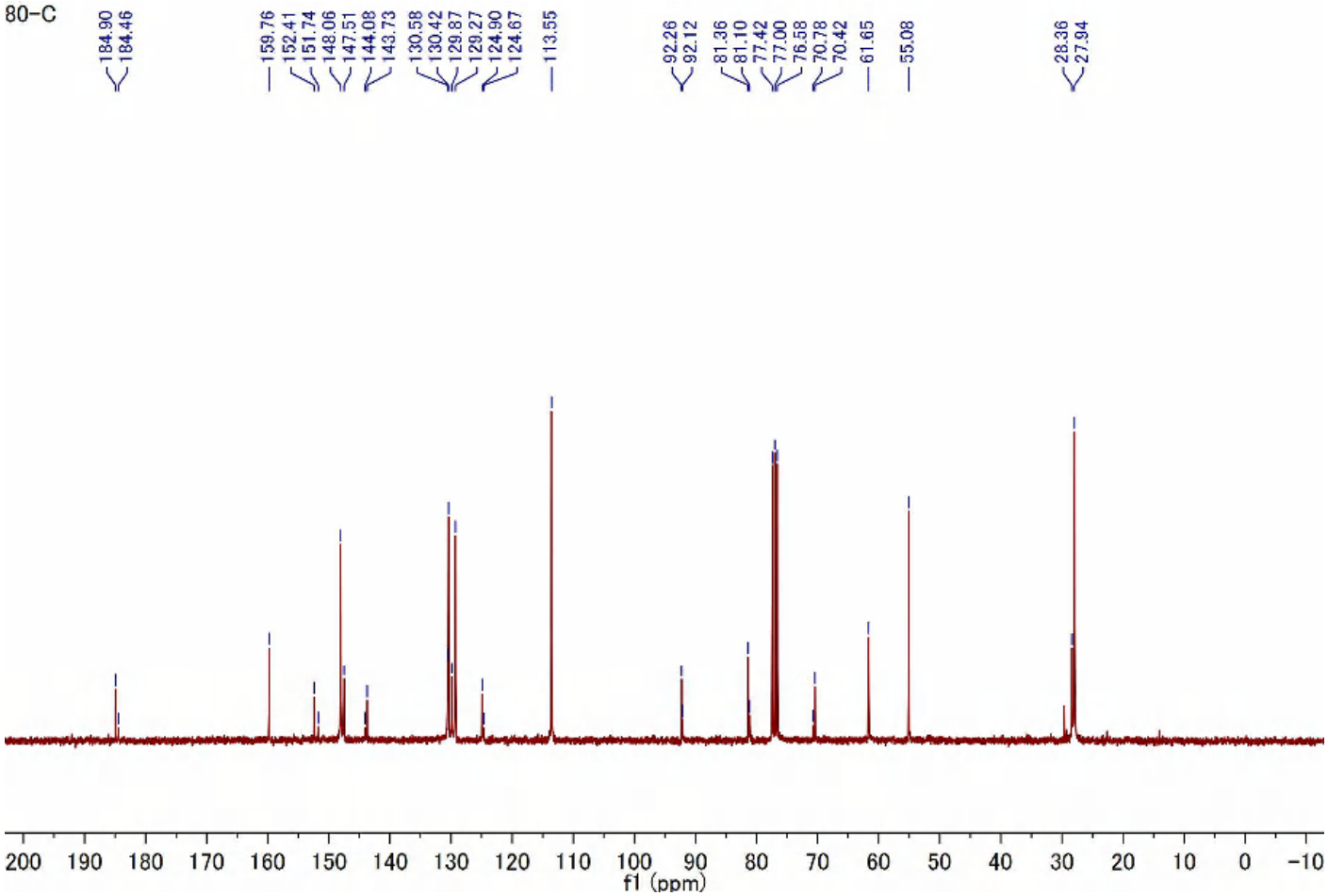
Compound **2h** (^{13}C NMR, 150 MHz, $CDCl_3$)



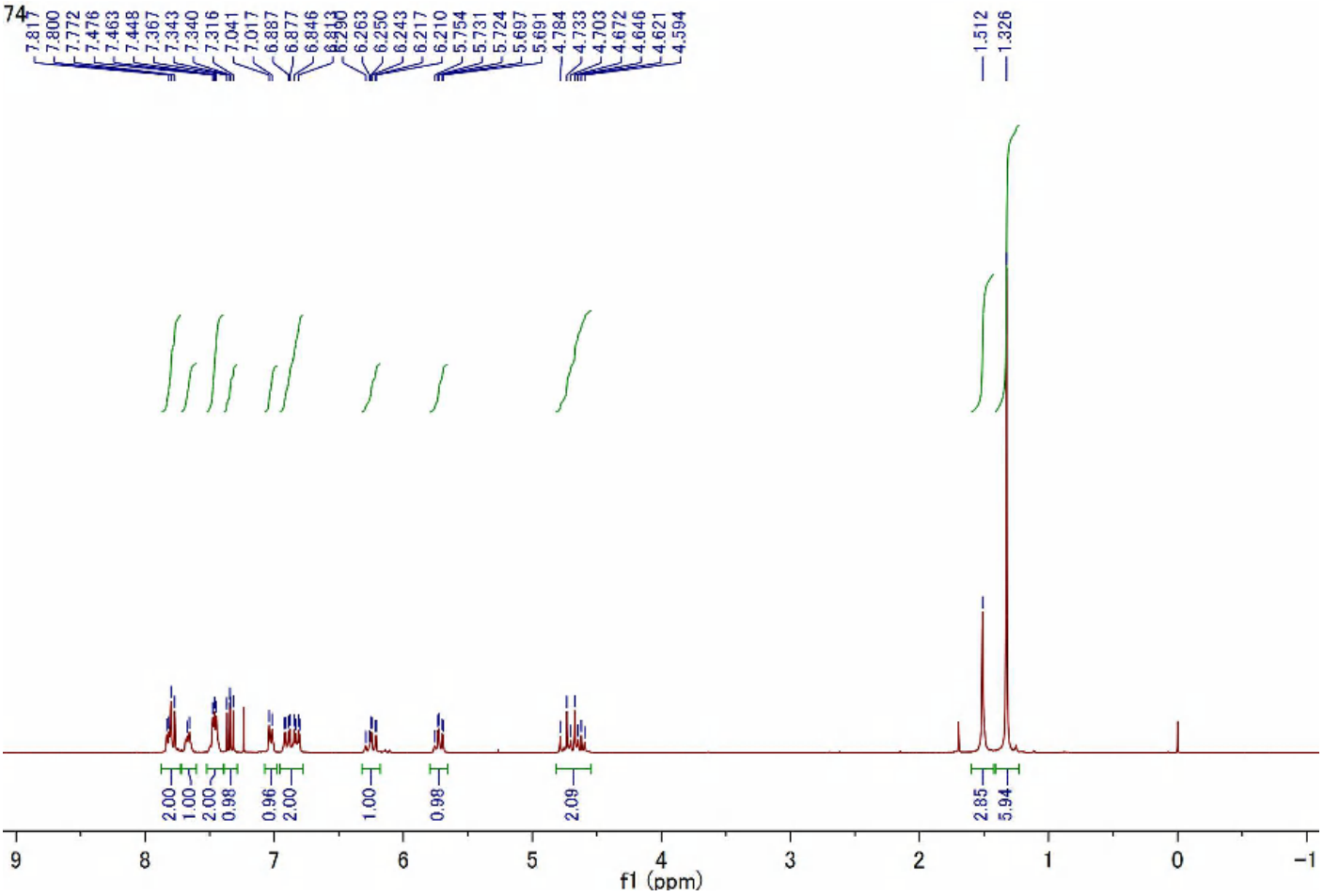
Compound **2i** (^{1}H NMR, 300 MHz, $CDCl_3$)



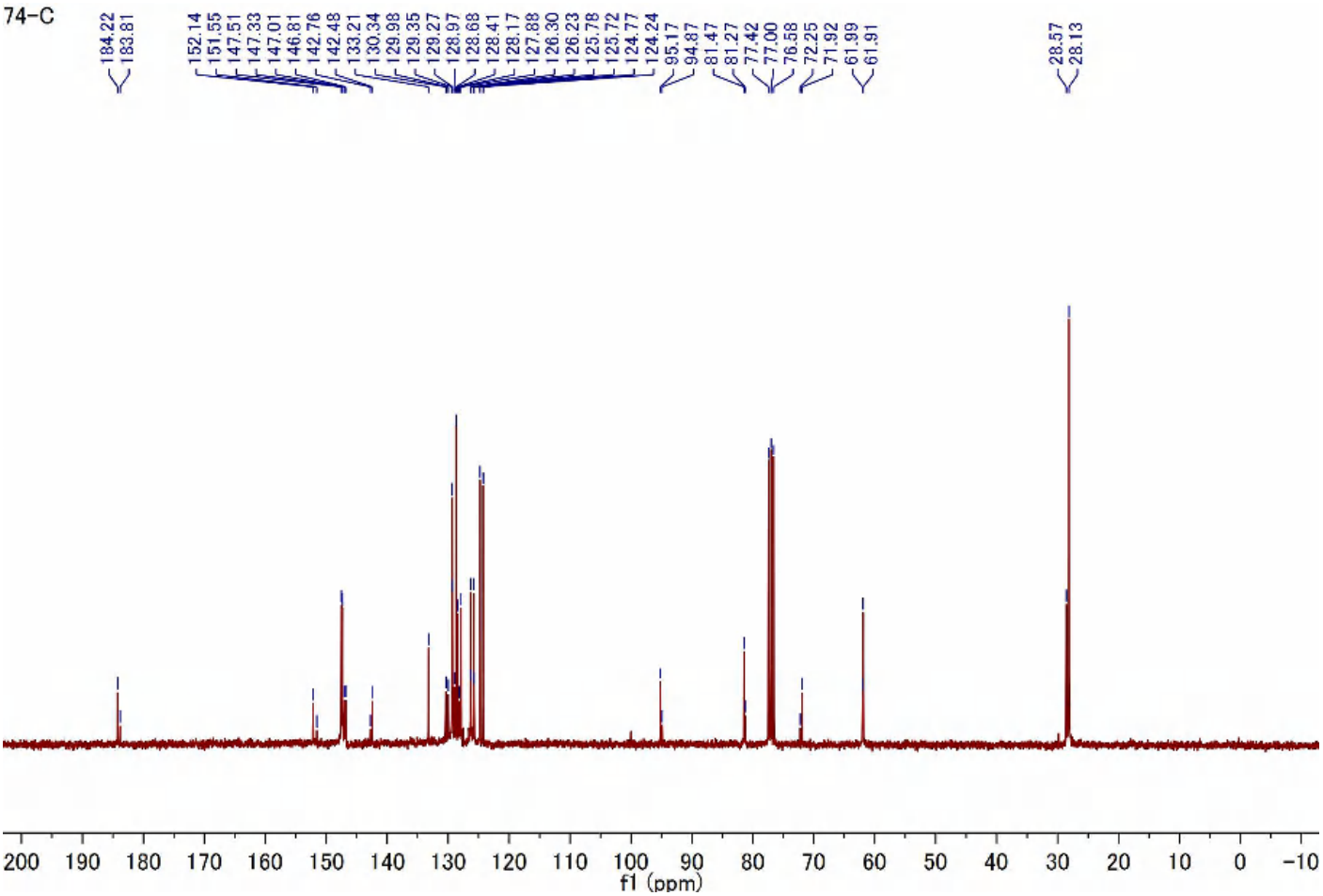
Compound **2i** (^{13}C NMR, 75 MHz, $CDCl_3$)



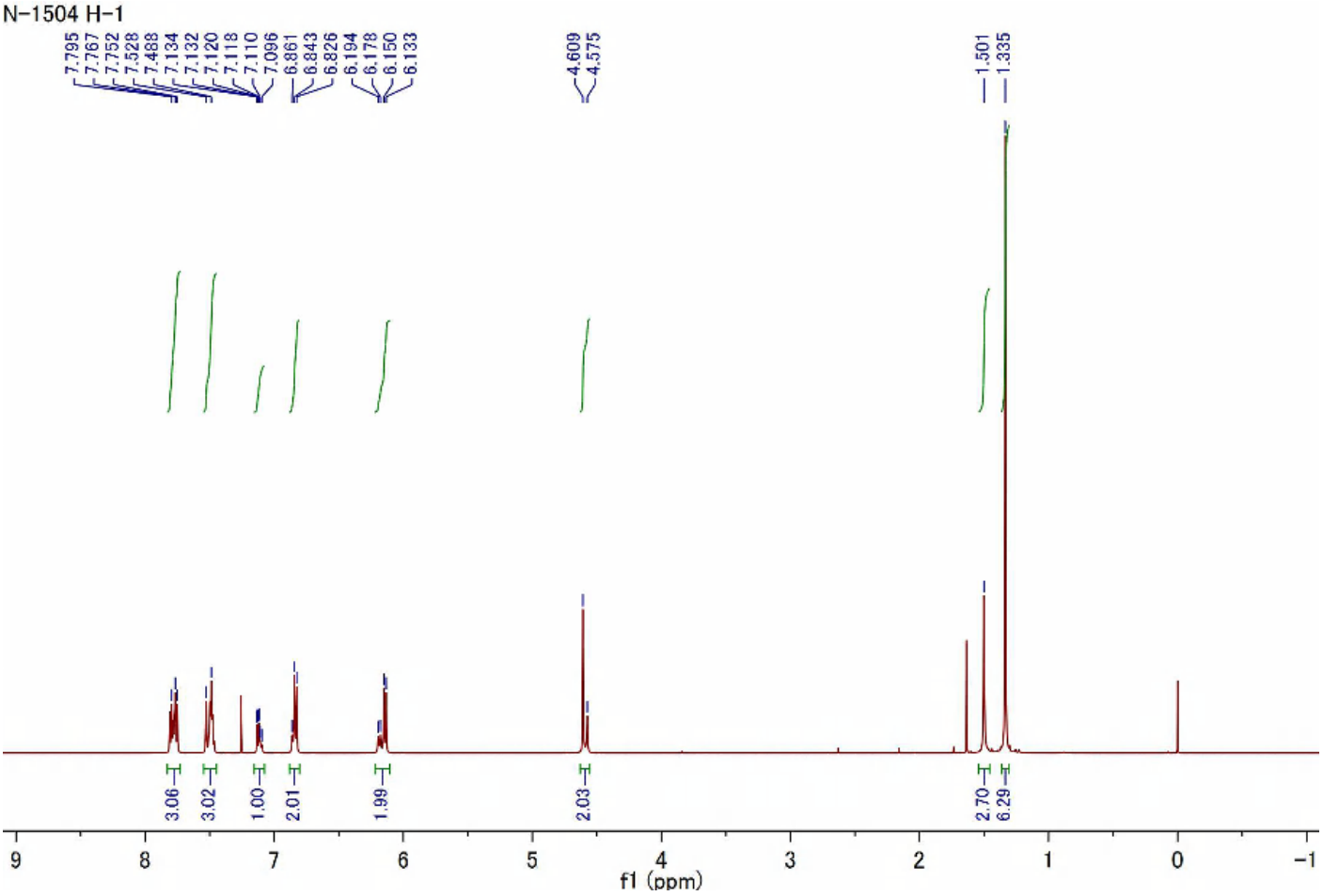
Compound **2j** (^{1}H NMR, 300 MHz, $CDCl_3$)



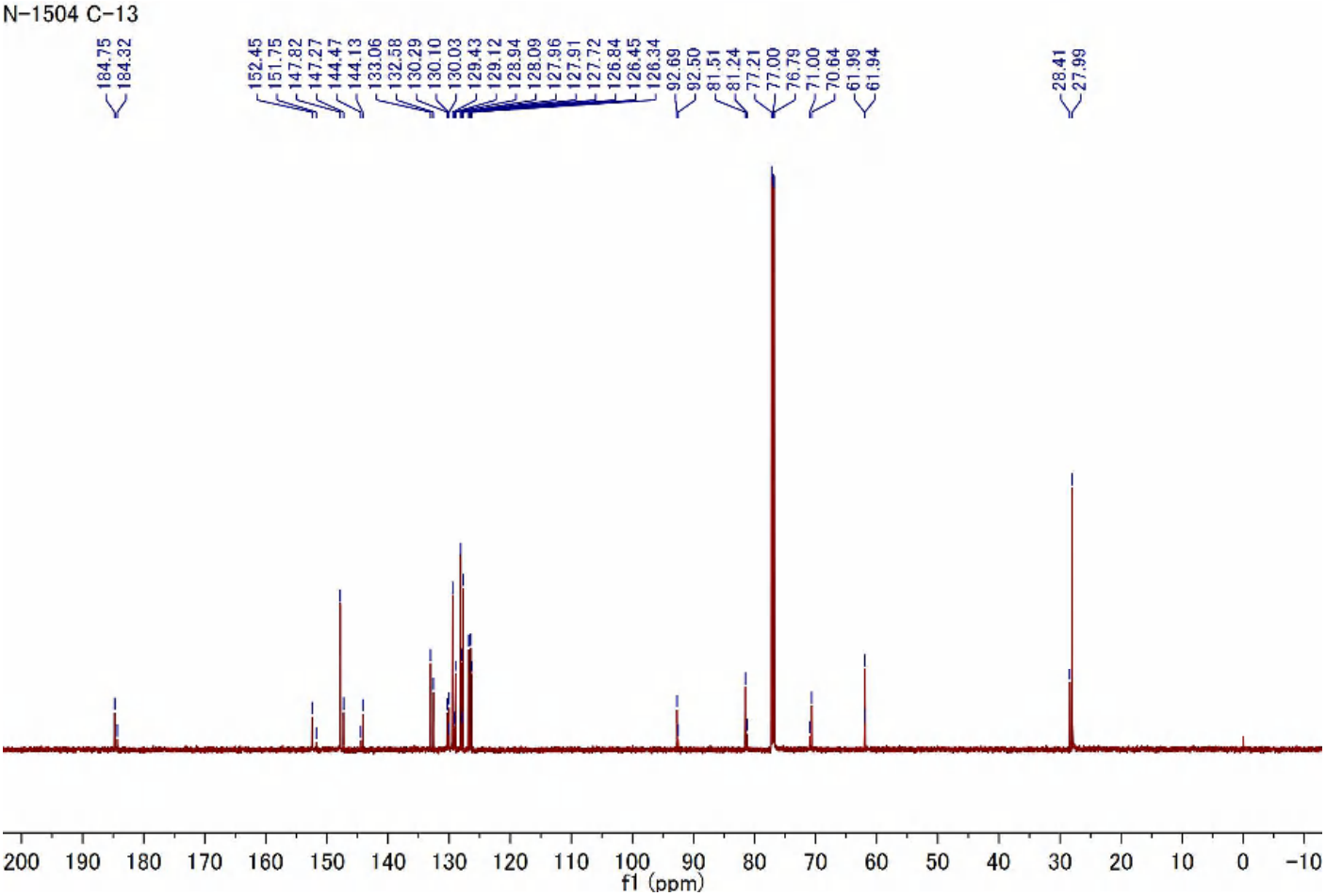
Compound **2j** (^{13}C NMR, 75 MHz, $CDCl_3$)



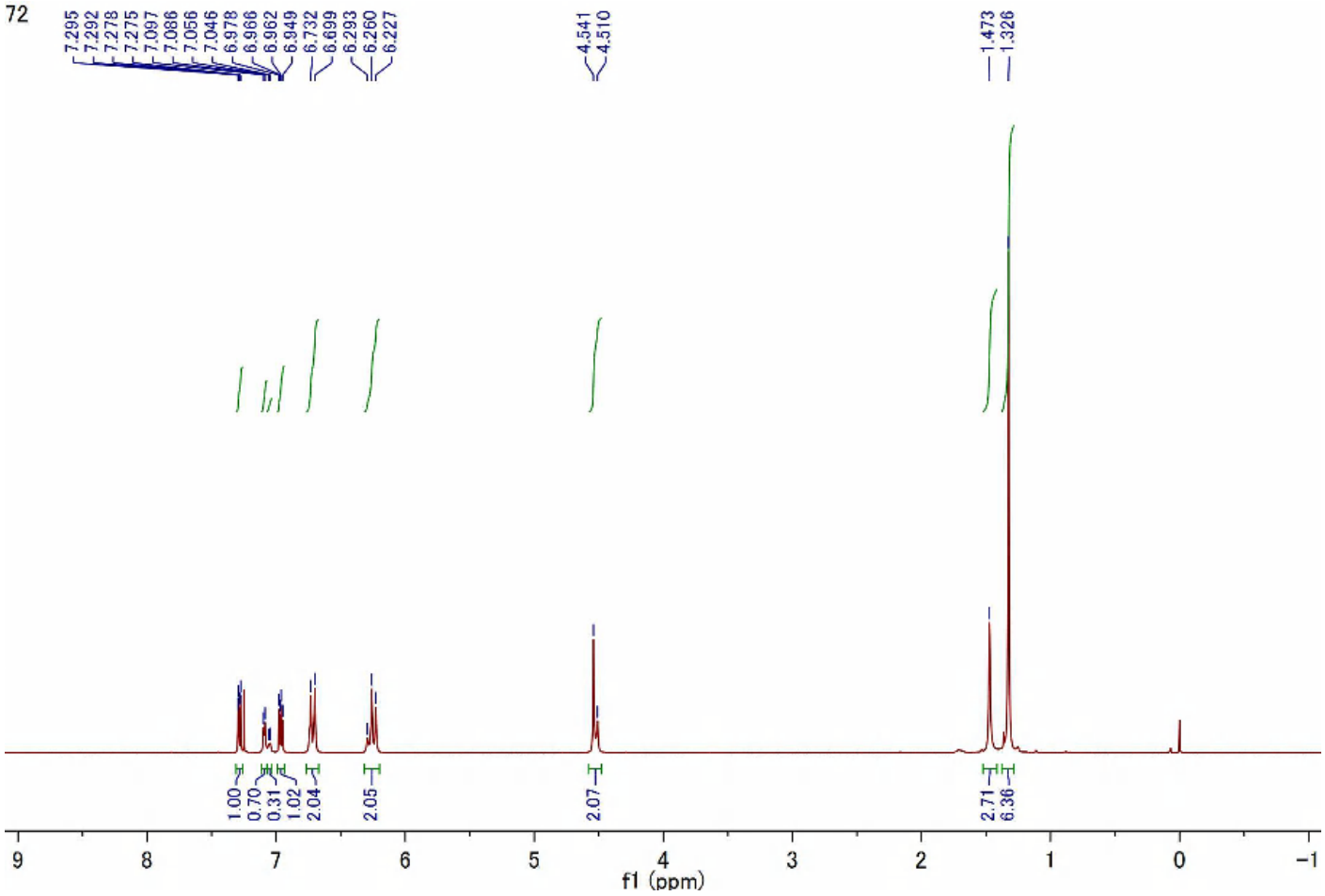
Compound **2k** (^{1}H NMR, 600 MHz, $CDCl_3$)



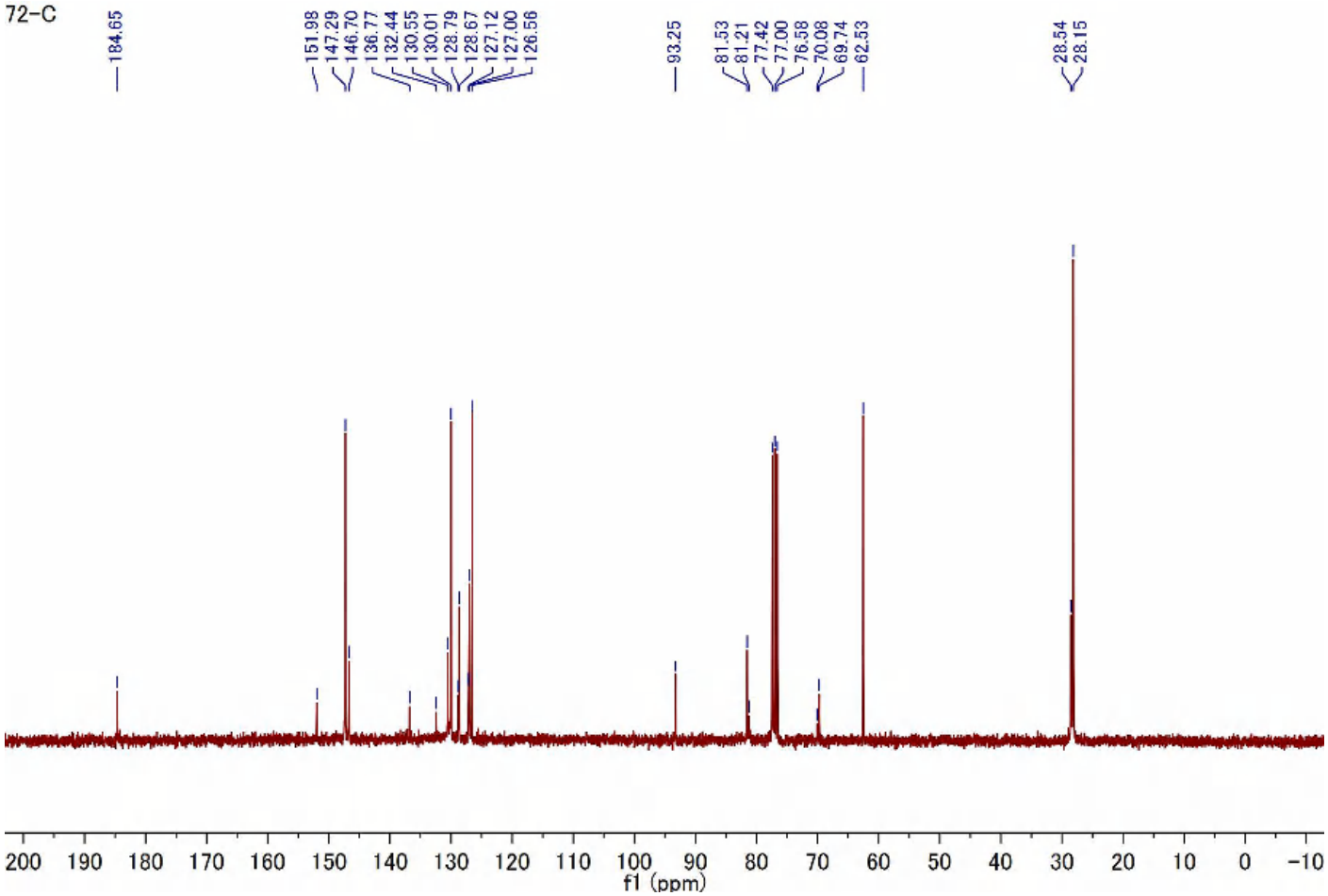
Compound **2k** (^{13}C NMR, 150 MHz, $CDCl_3$)



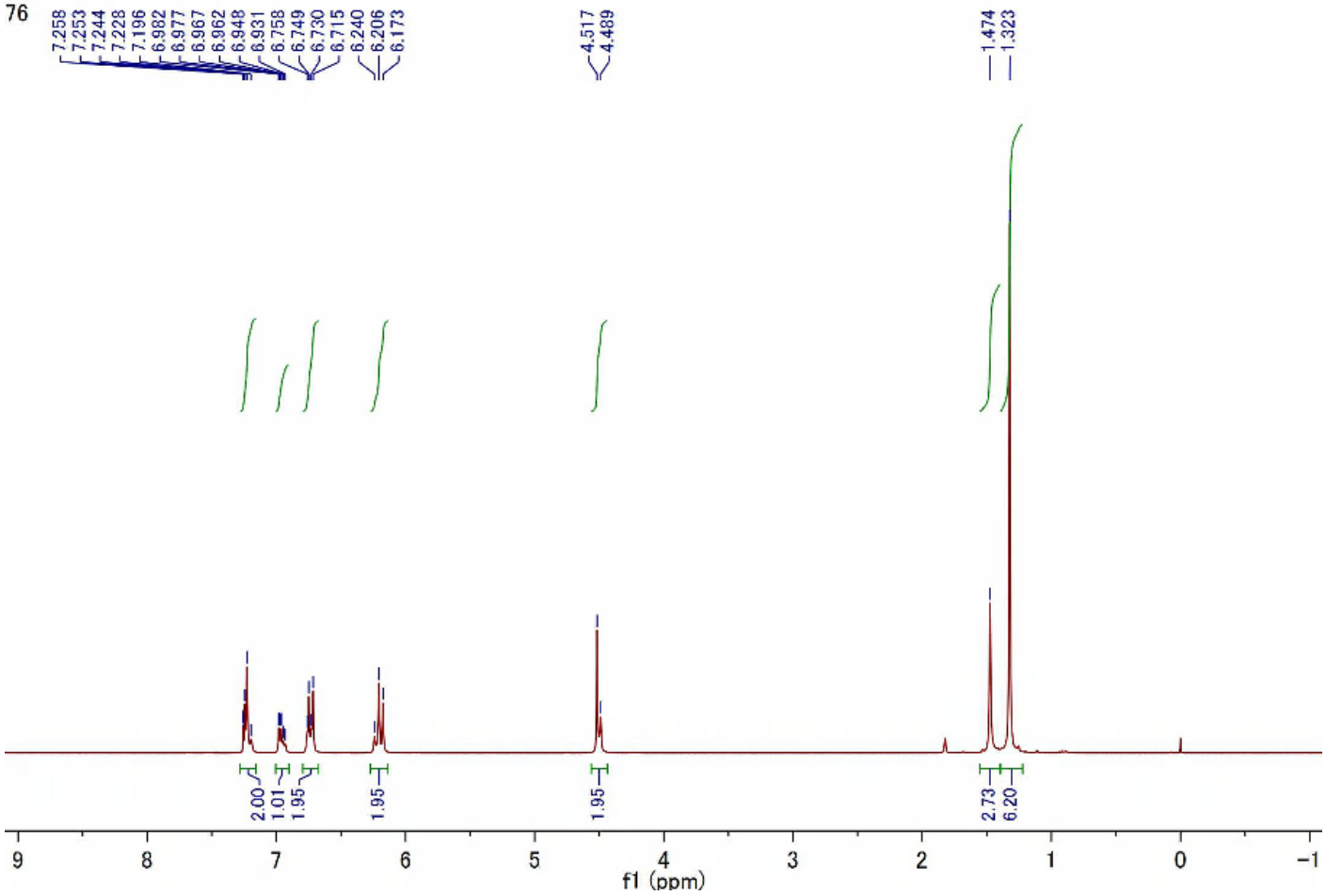
Compound **2l** (^{1}H NMR, 300 MHz, $CDCl_3$)



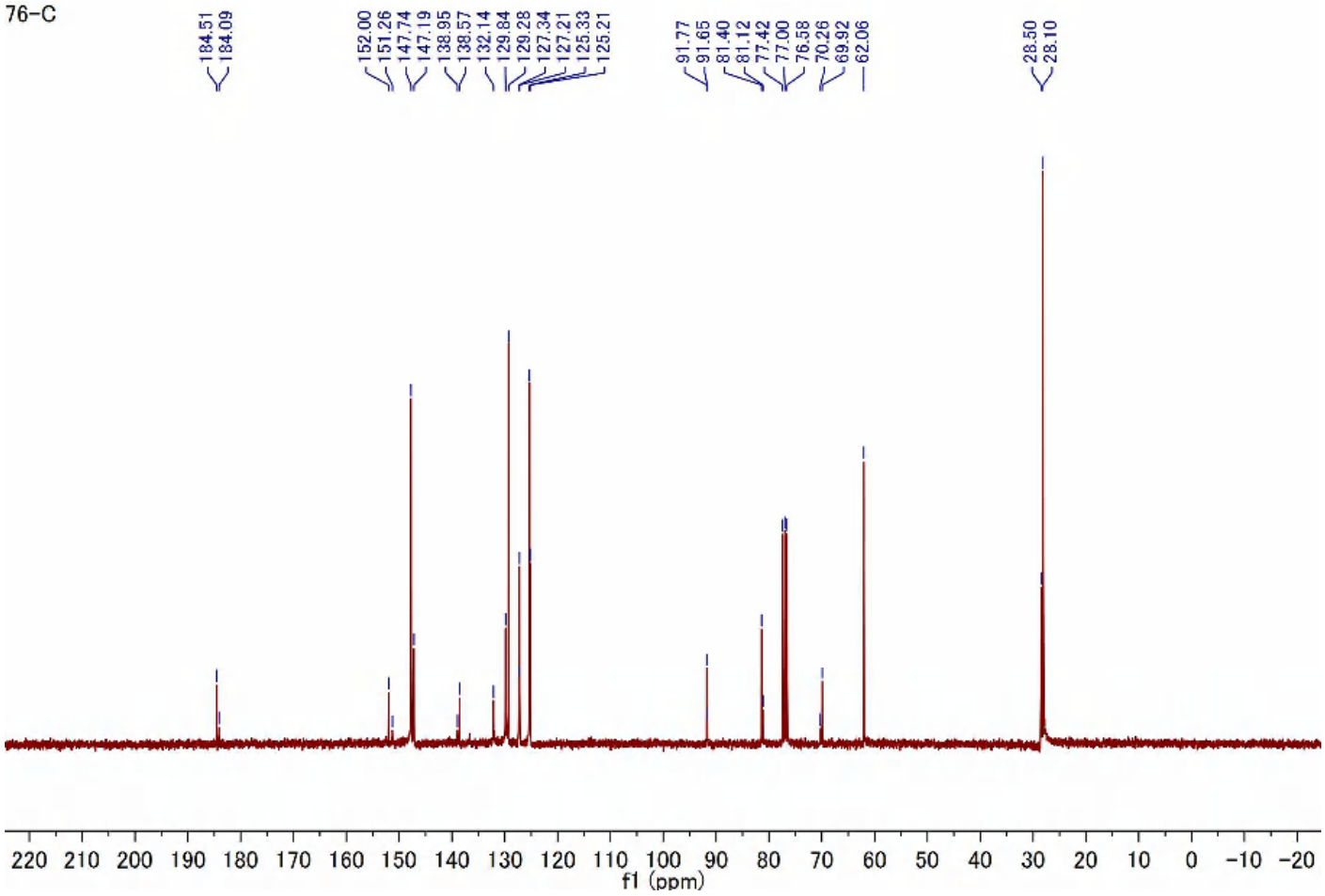
Compound **2l** (^{13}C NMR, 75 MHz, $CDCl_3$)



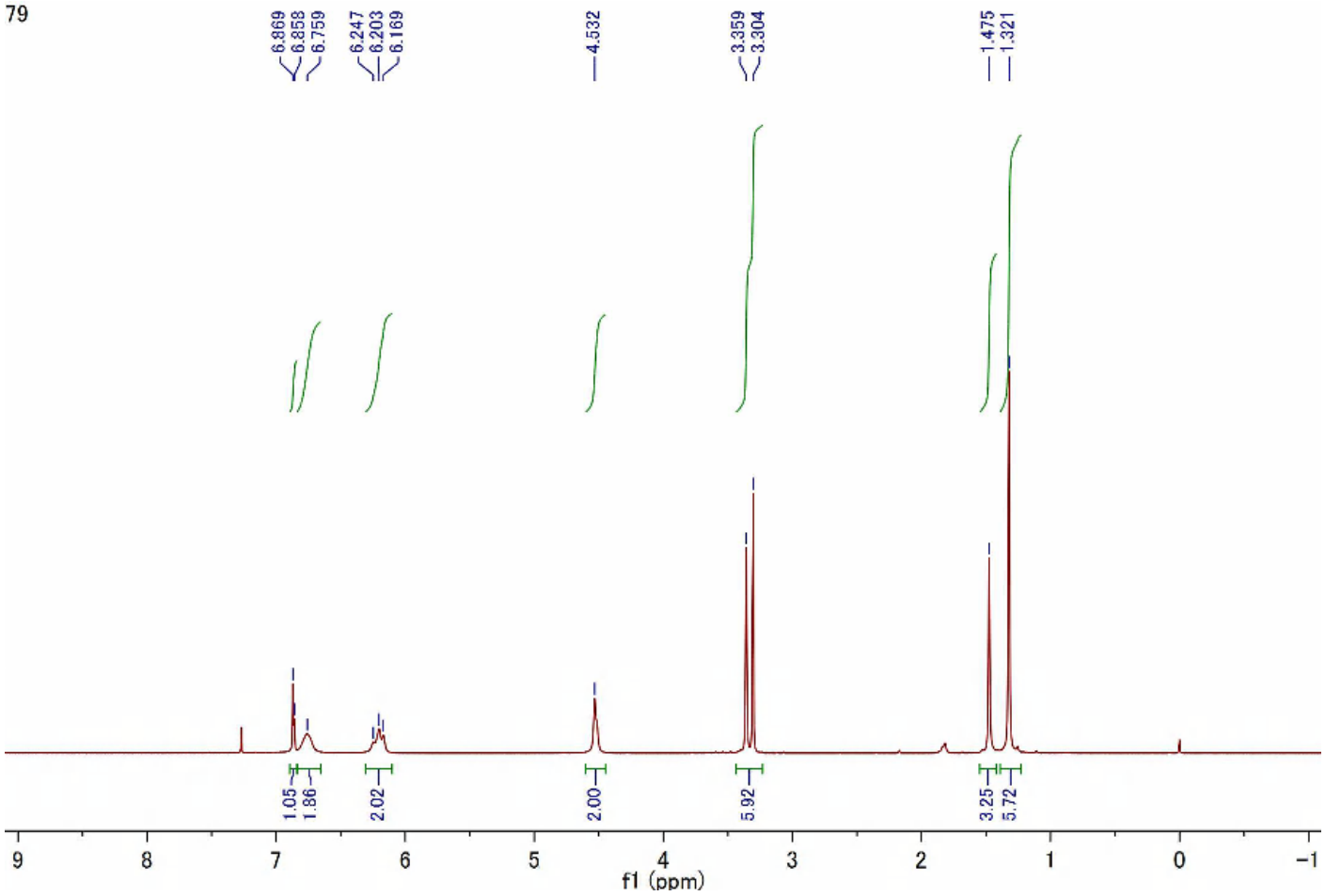
Compound **2m** (^{1}H NMR, 300 MHz, $CDCl_3$)



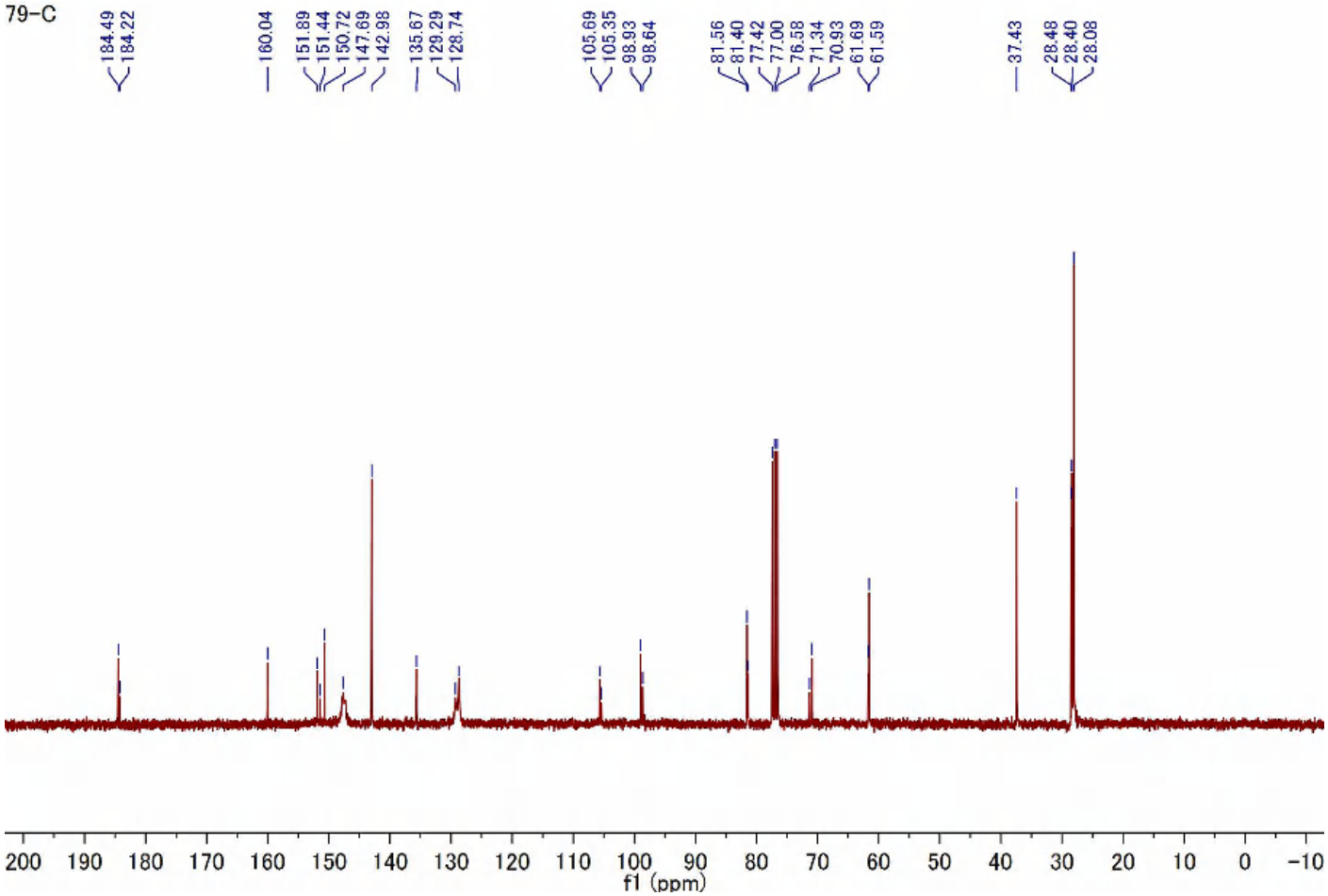
Compound **2m** (^{13}C NMR, 75 MHz, $CDCl_3$)



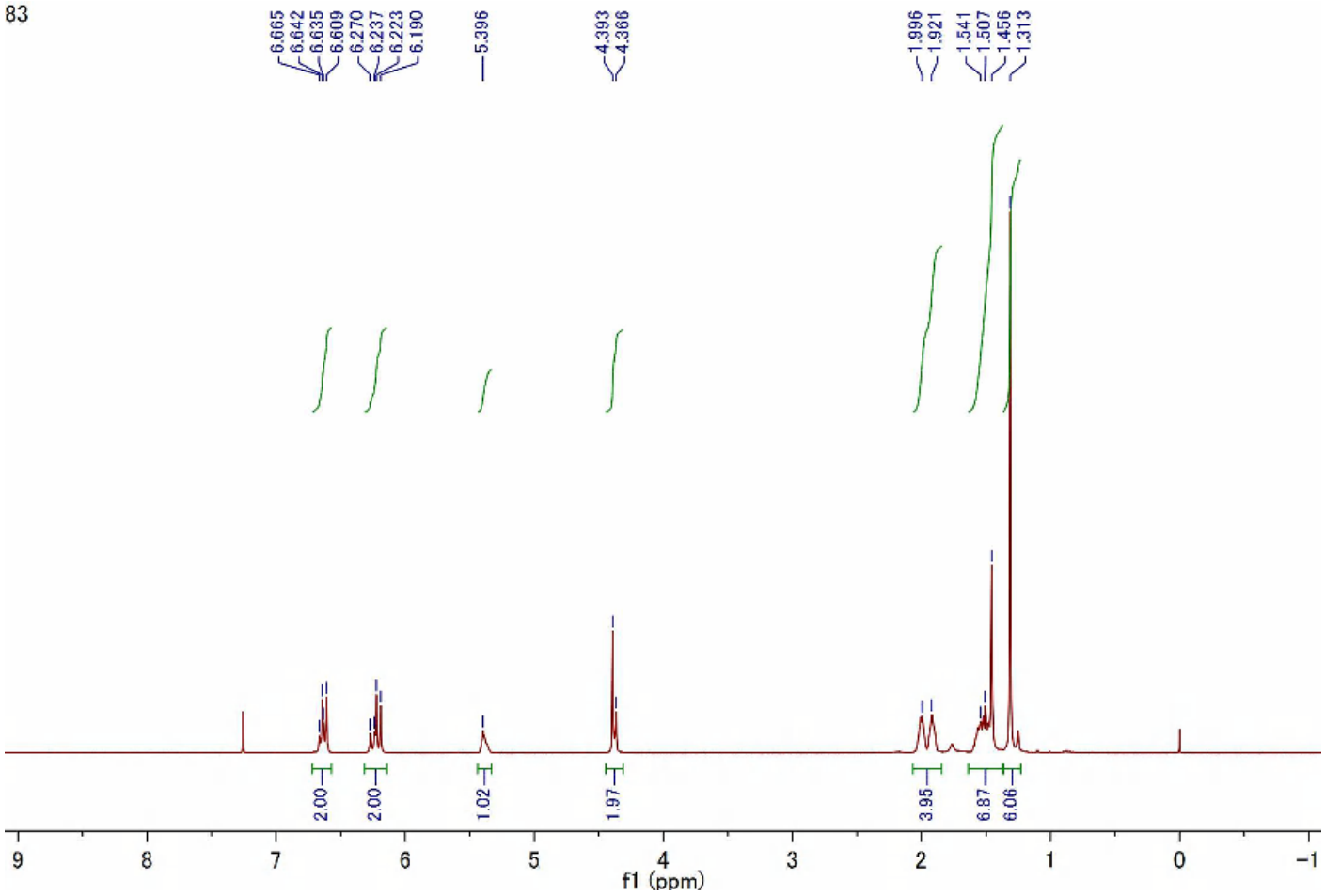
Compound **2n** (^{1}H NMR, 300 MHz, $CDCl_3$)



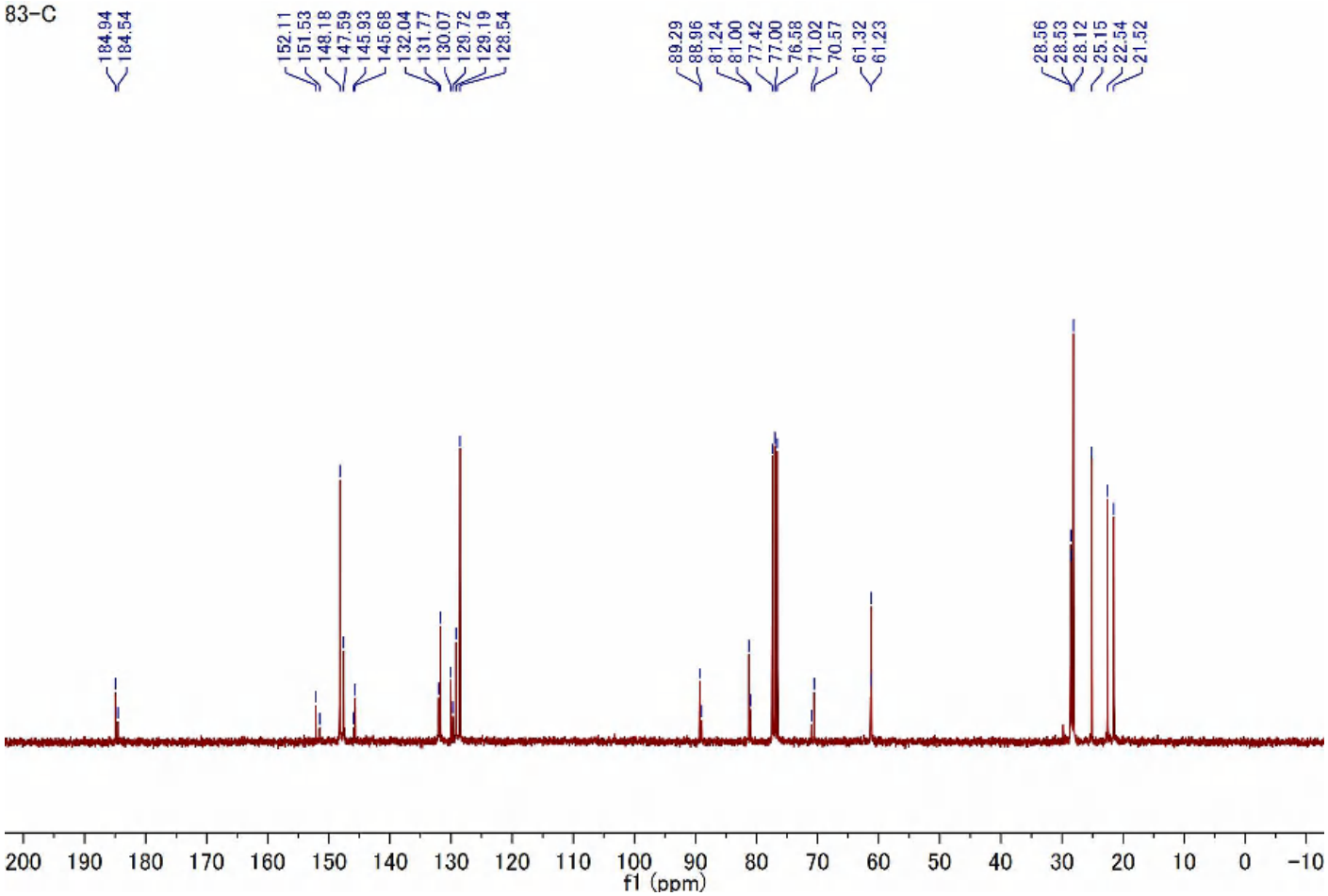
Compound **2n** (^{13}C NMR, 75 MHz, $CDCl_3$)



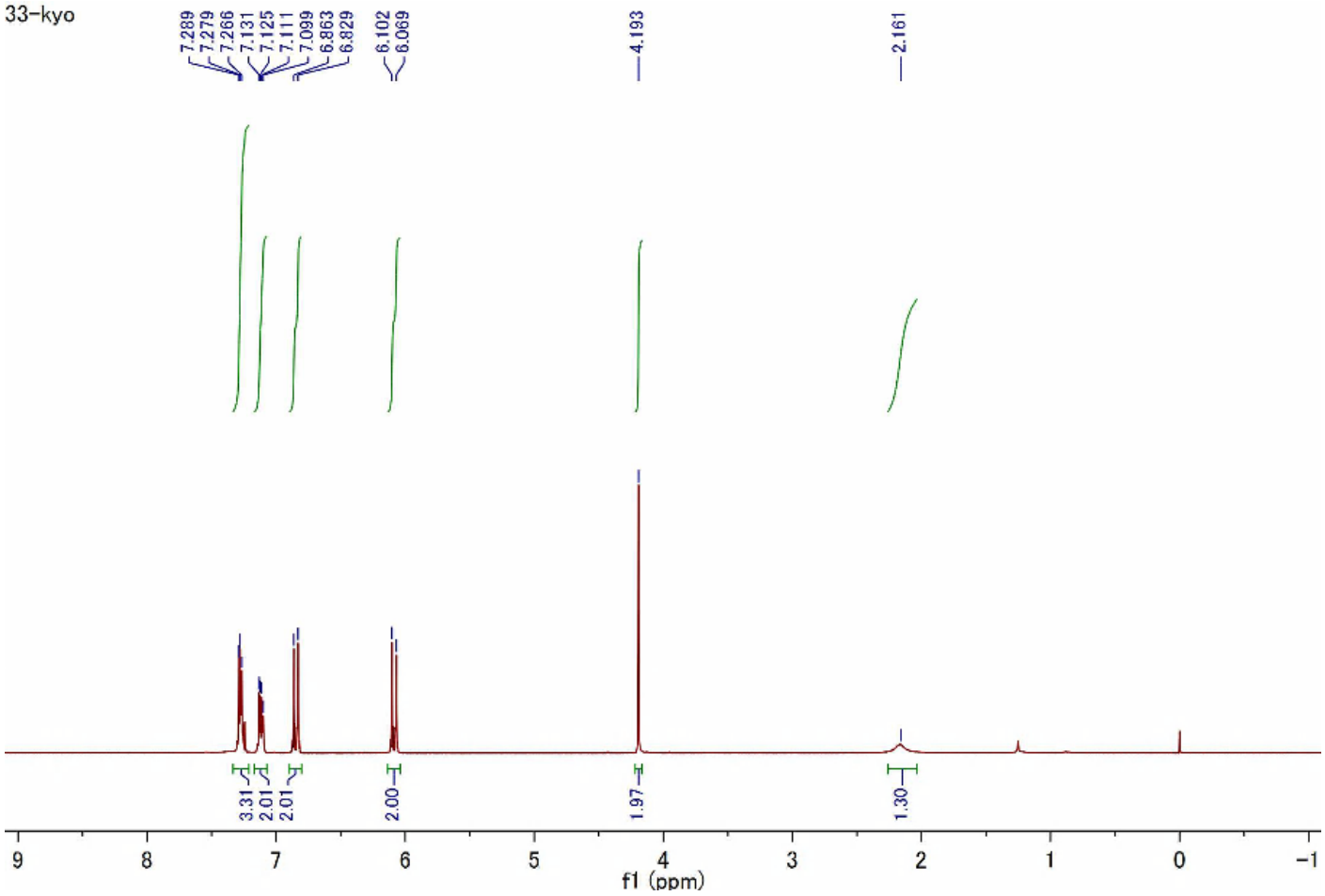
Compound **2o** (^{1}H NMR, 300 MHz, $CDCl_3$)



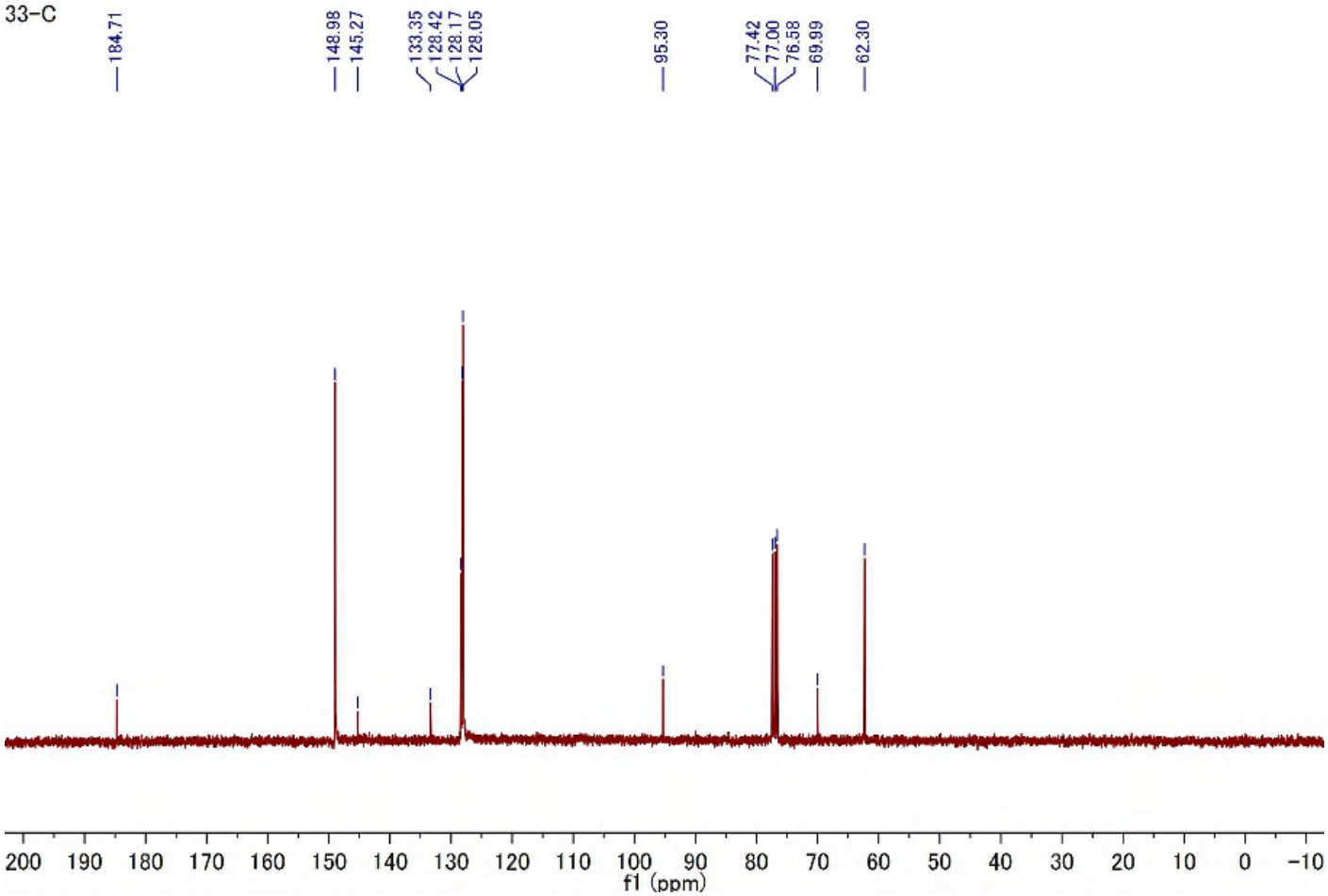
Compound **2o** (^{13}C NMR, 75 MHz, $CDCl_3$)



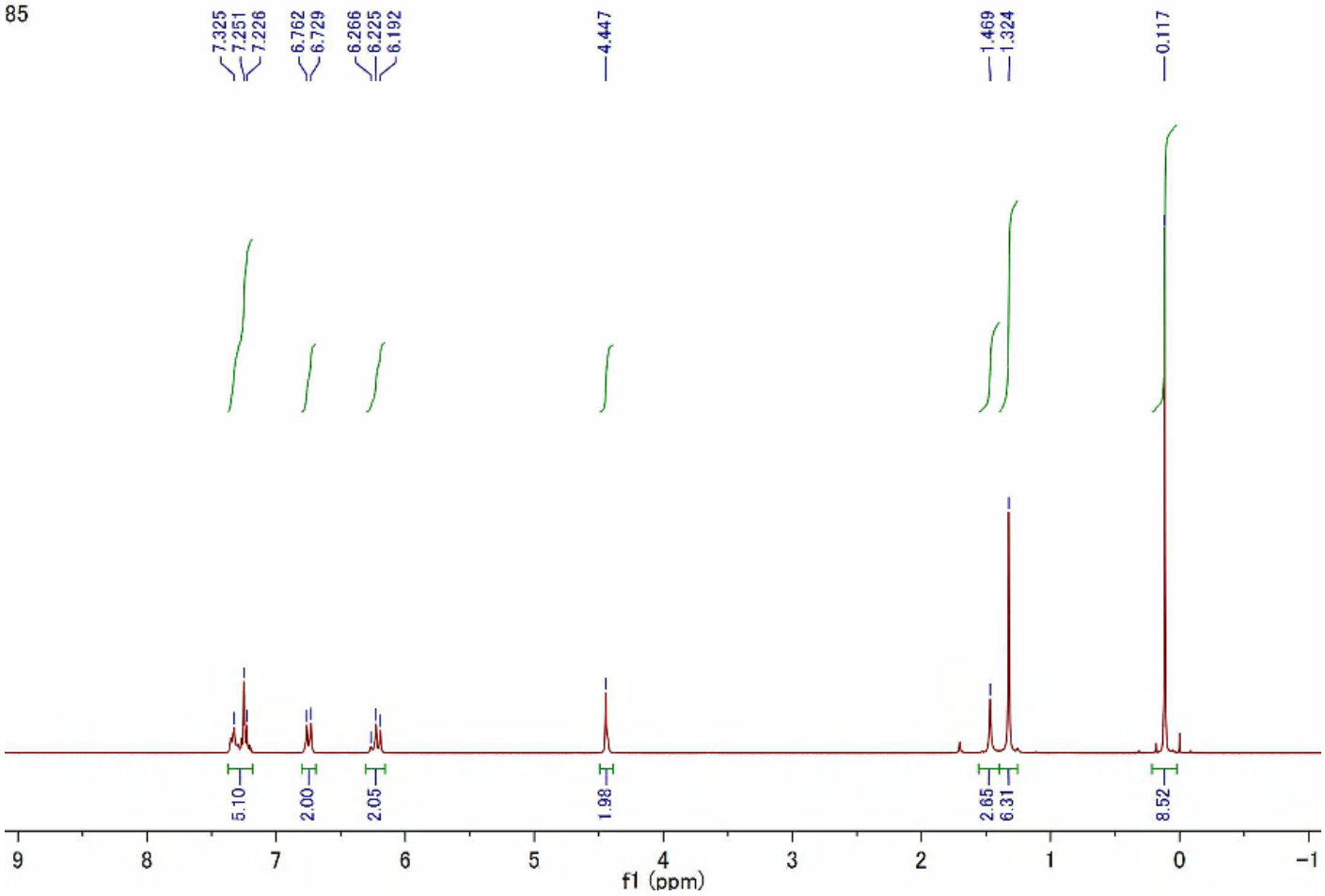
Compound **3** (^{1}H NMR, 300 MHz, $CDCl_3$)



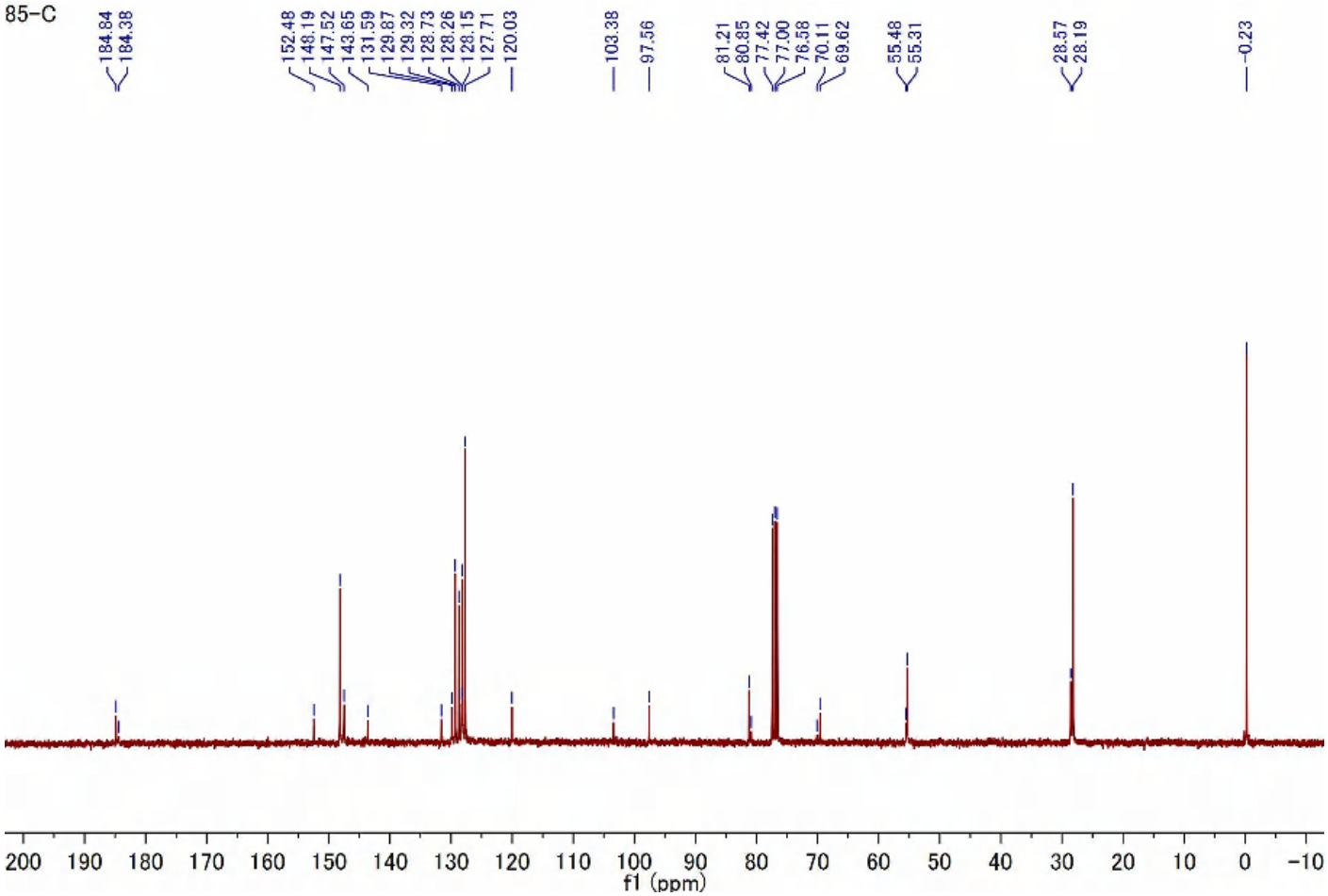
Compound **3** (^{13}C NMR, 75 MHz, $CDCl_3$)



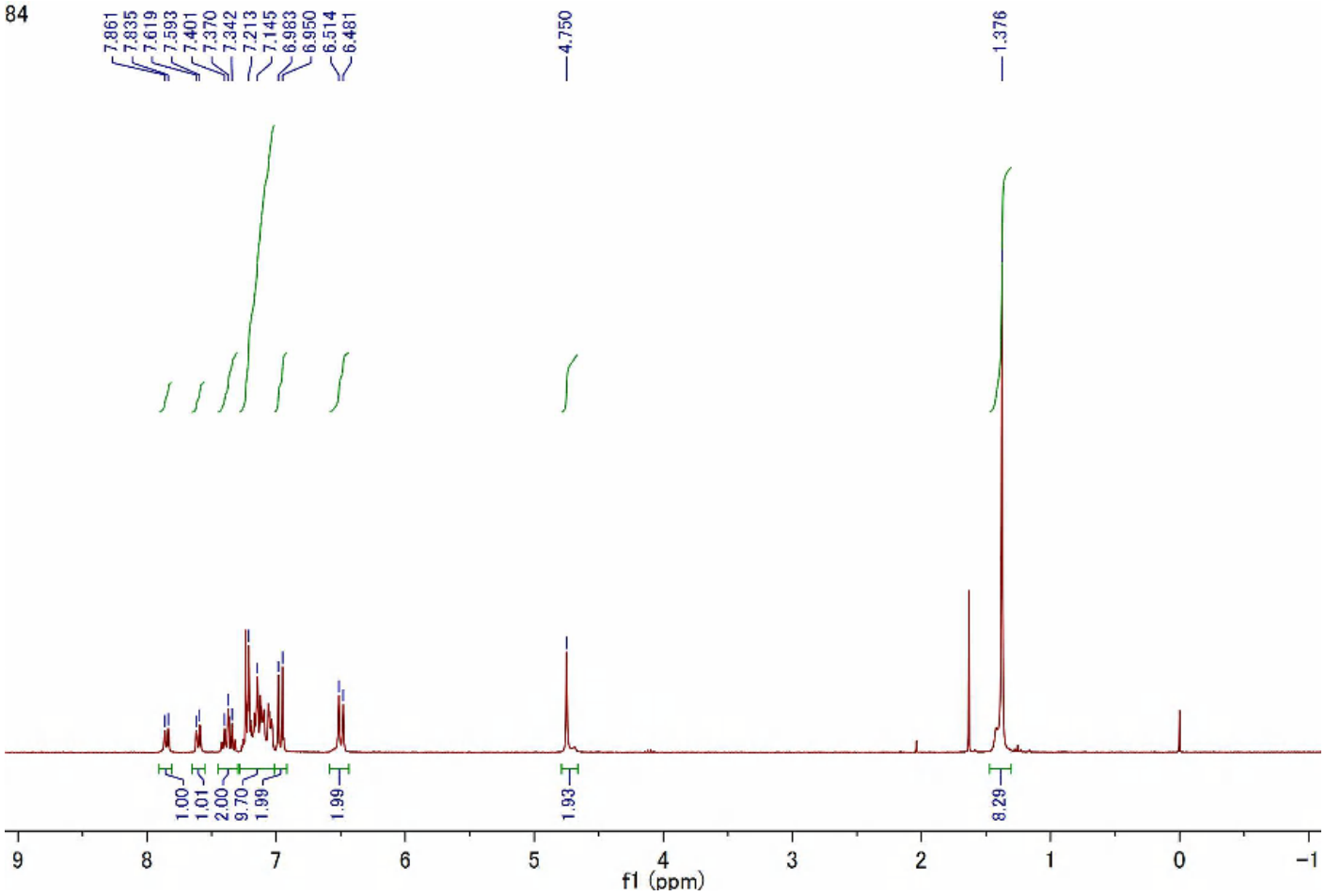
Compound **4** (^{1}H NMR, 300 MHz, $CDCl_3$)



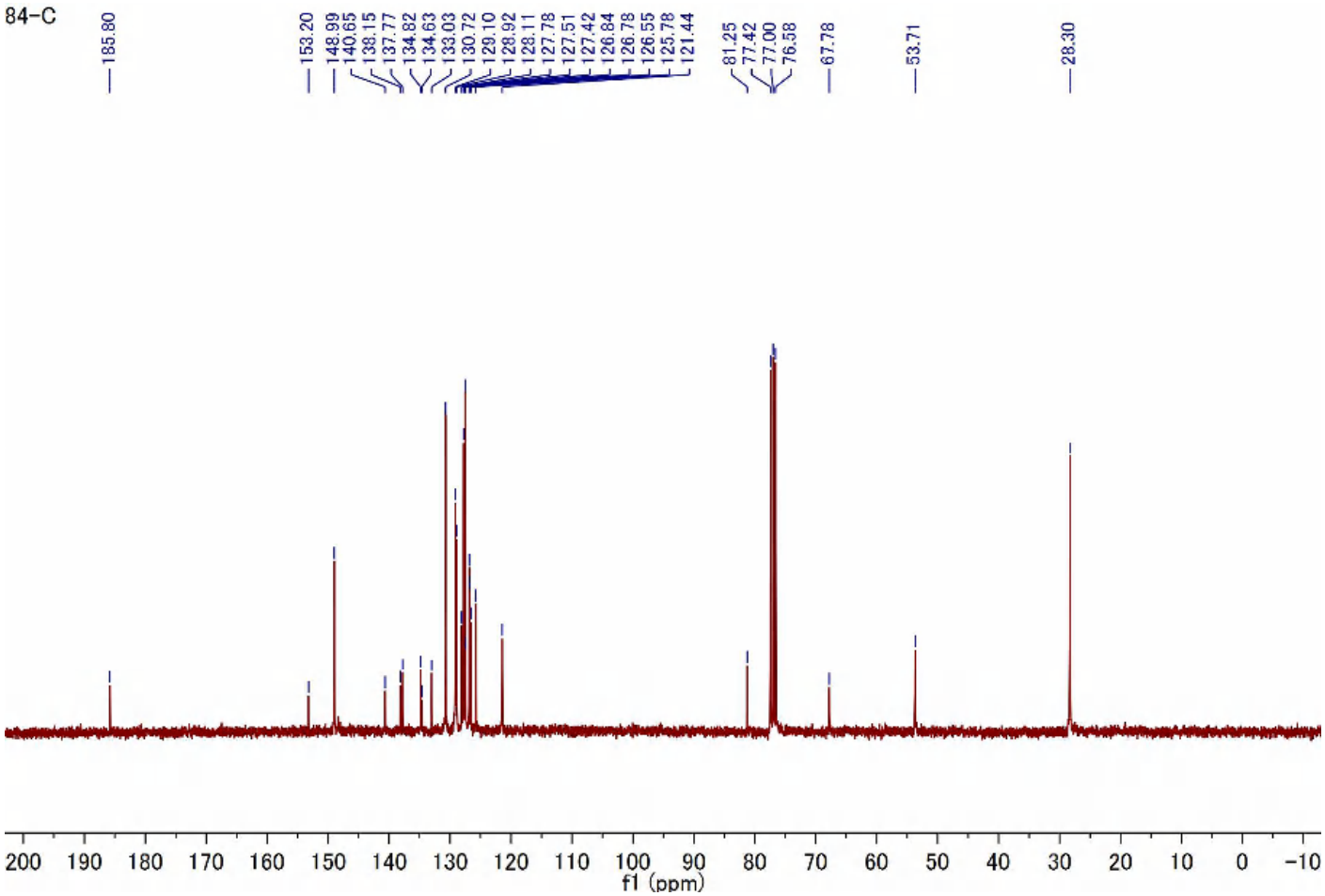
Compound **4** (^{13}C NMR, 75 MHz, $CDCl_3$)



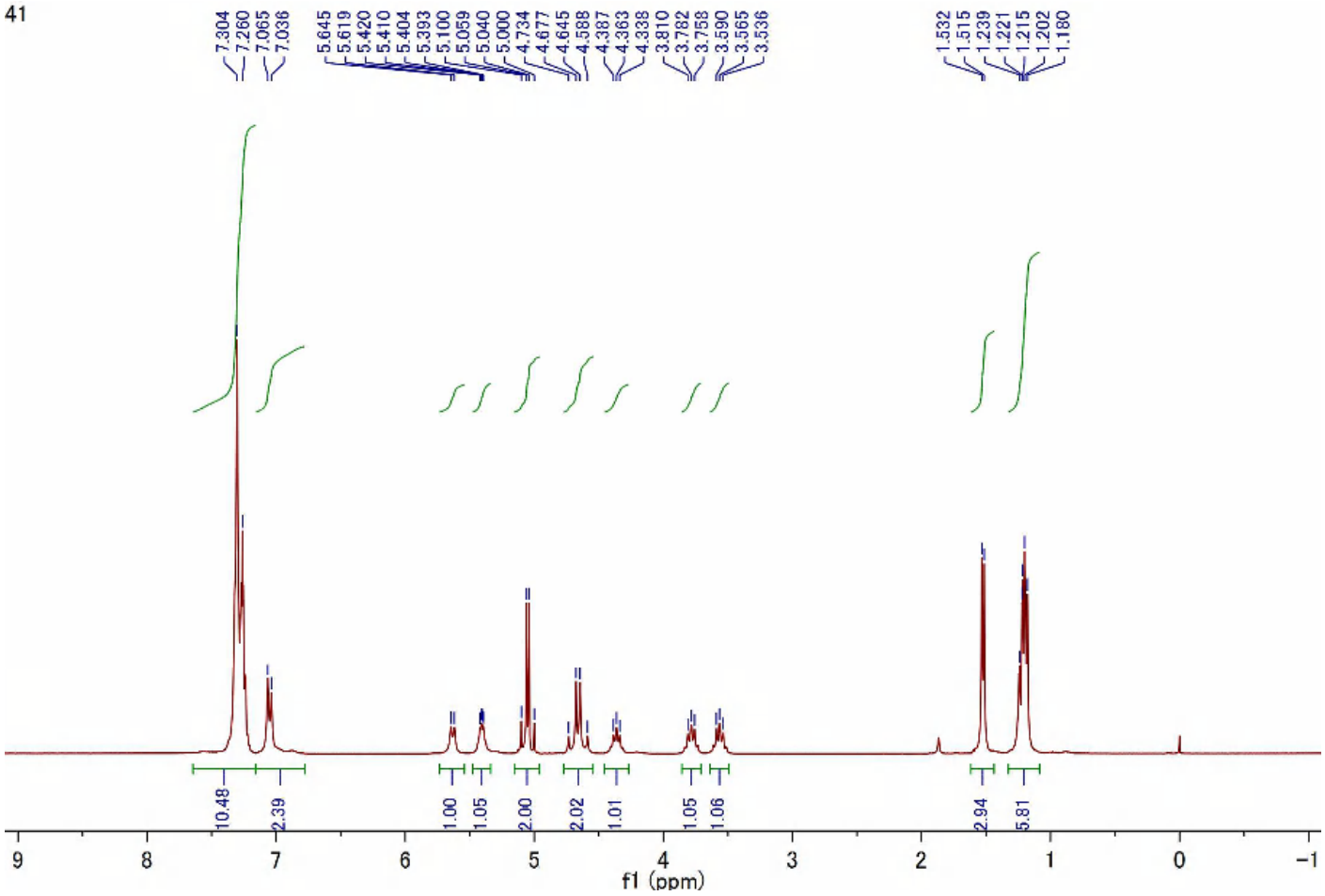
Compound **5** (^{1}H NMR, 300 MHz, $CDCl_3$)



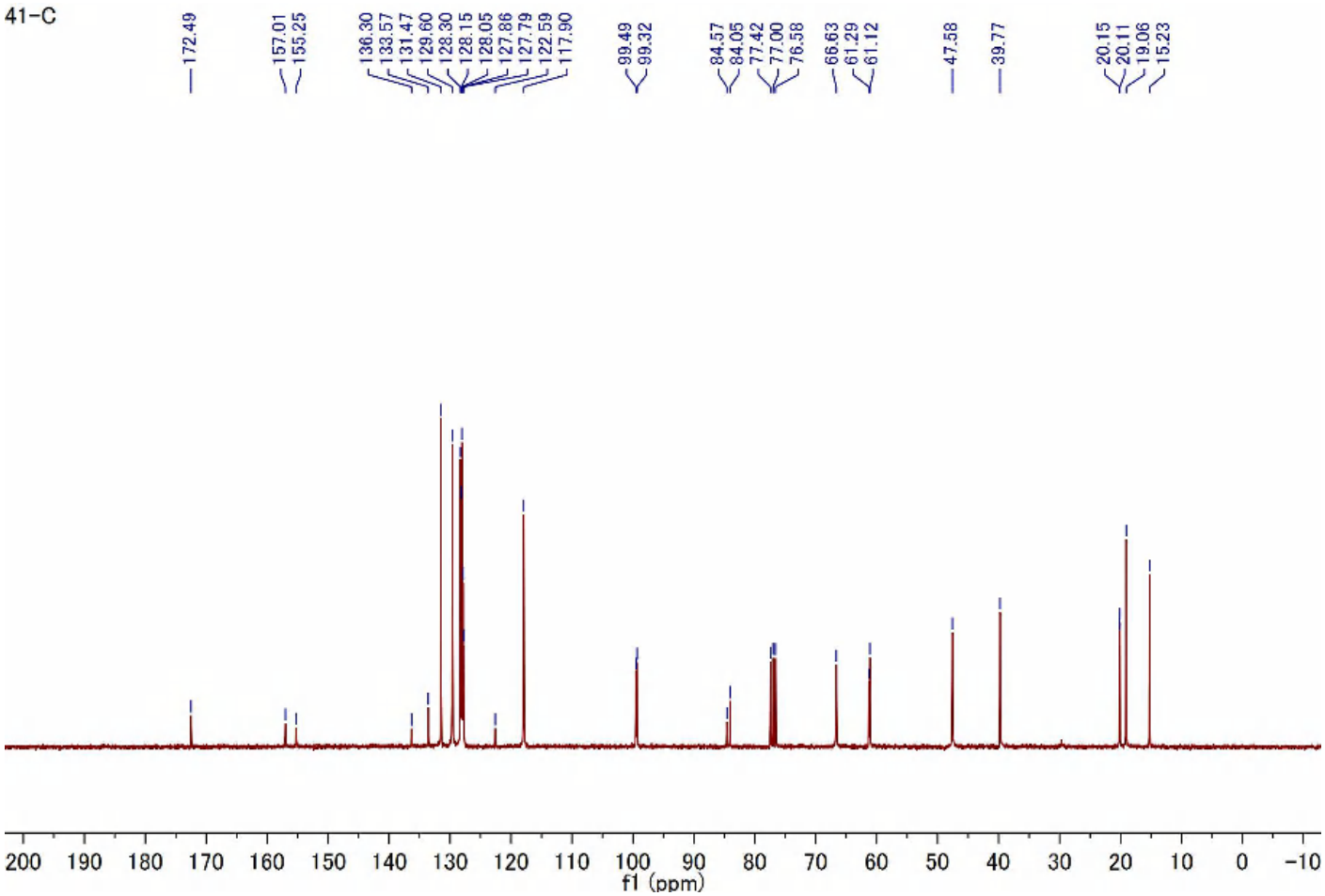
Compound **5** (^{13}C NMR, 75 MHz, $CDCl_3$)



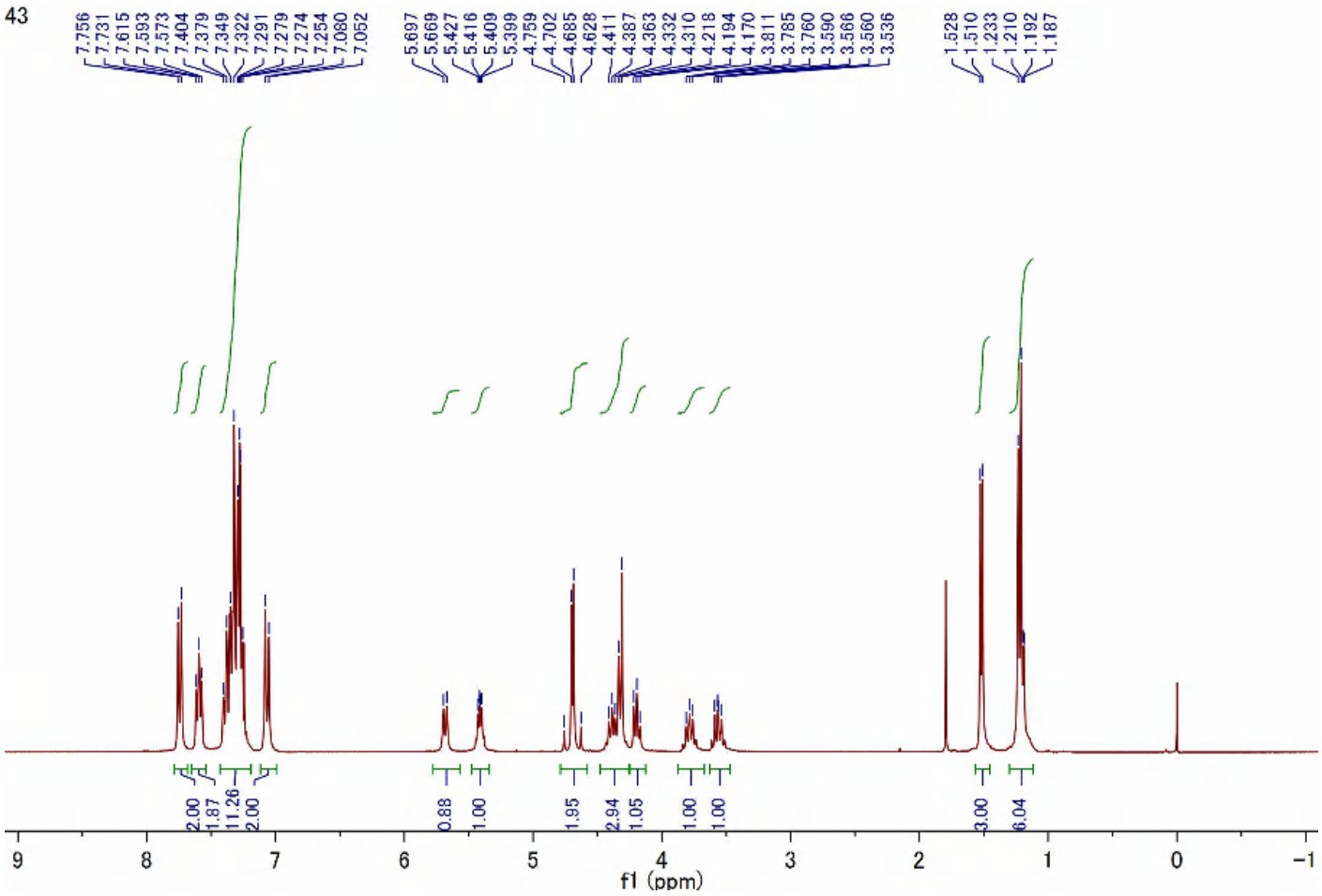
Compound **6a** (^{1}H NMR, 300 MHz, $CDCl_3$)



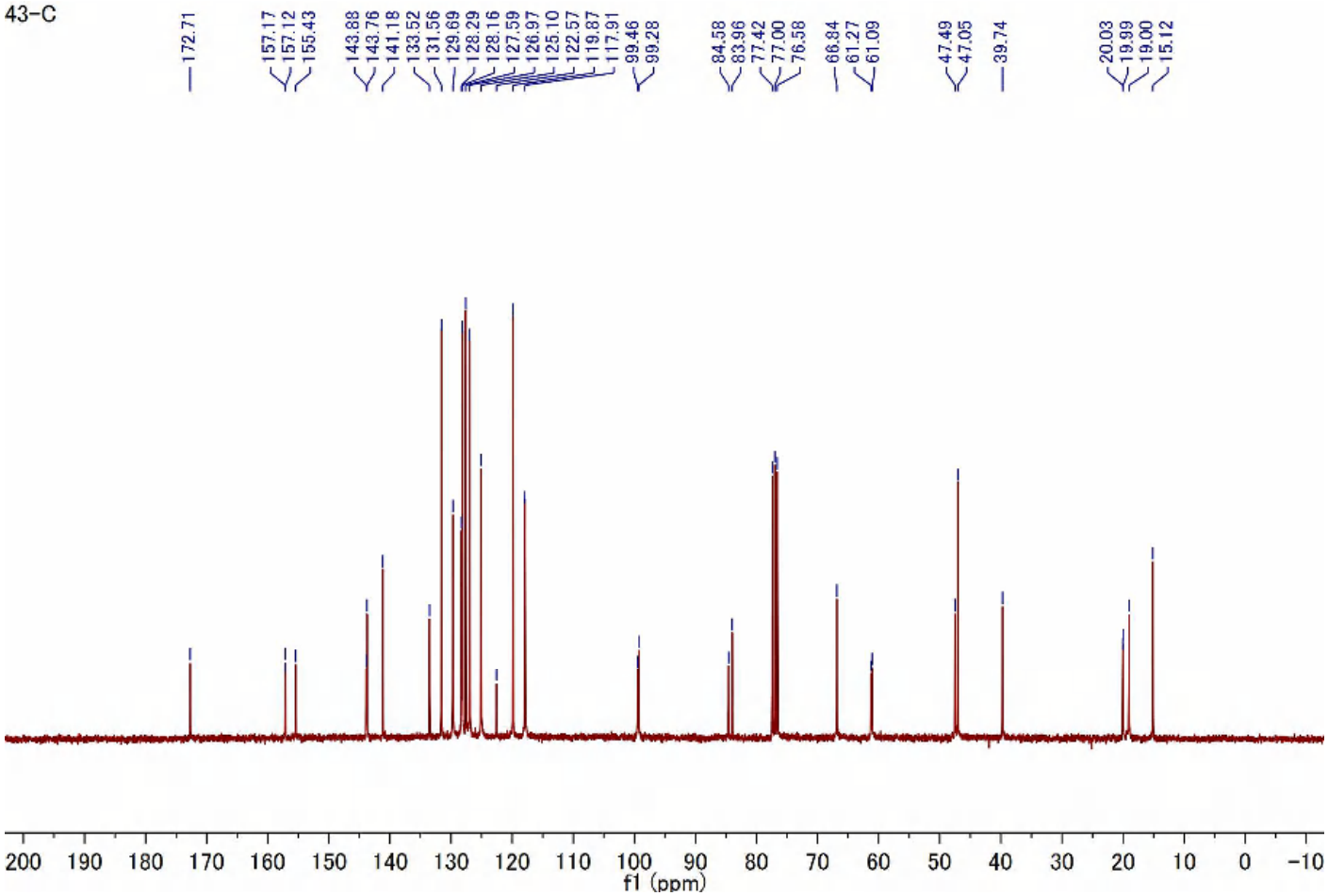
Compound **6a** (^{13}C NMR, 75 MHz, $CDCl_3$)



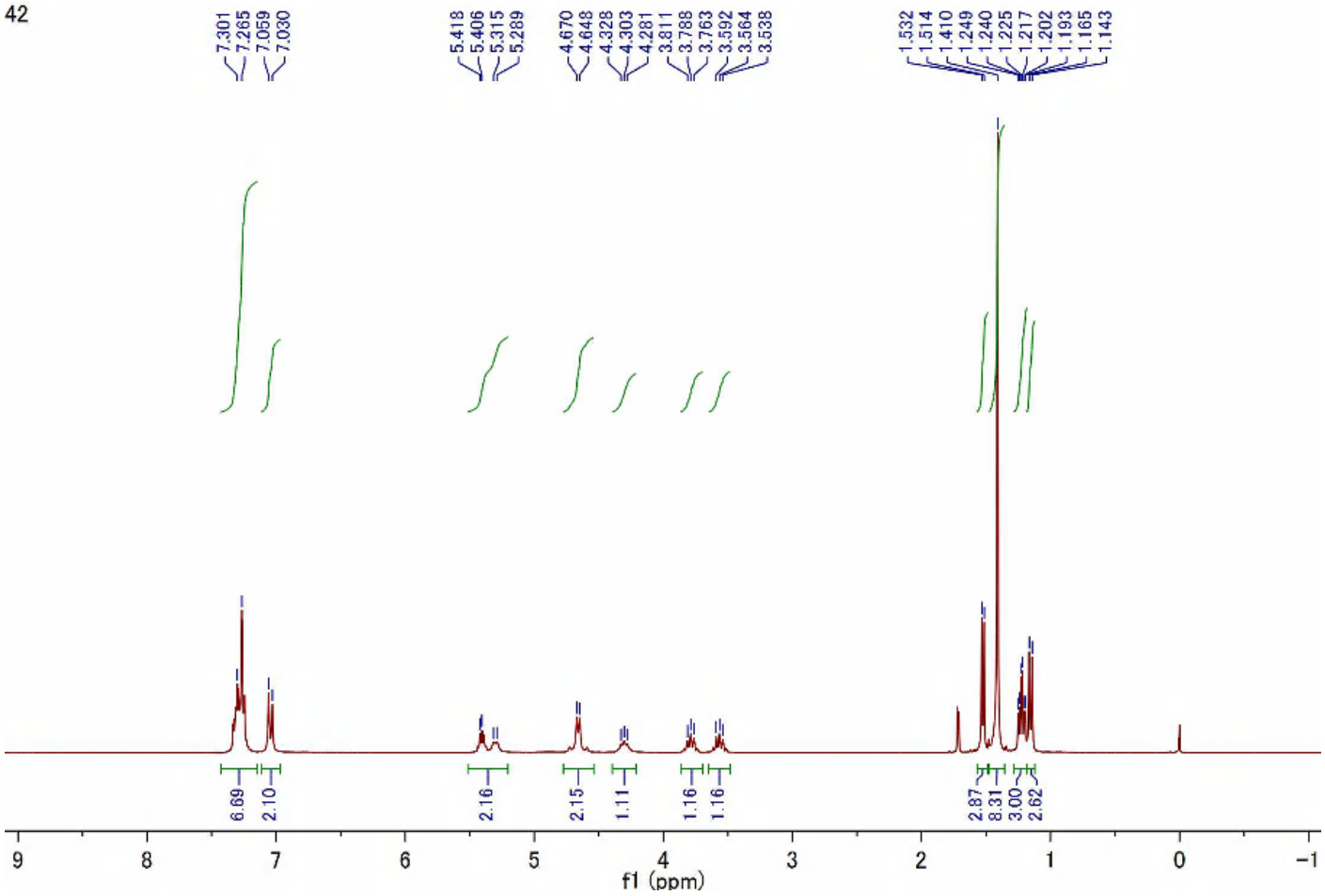
Compound **6b** (^{1}H NMR, 300 MHz, $CDCl_3$)



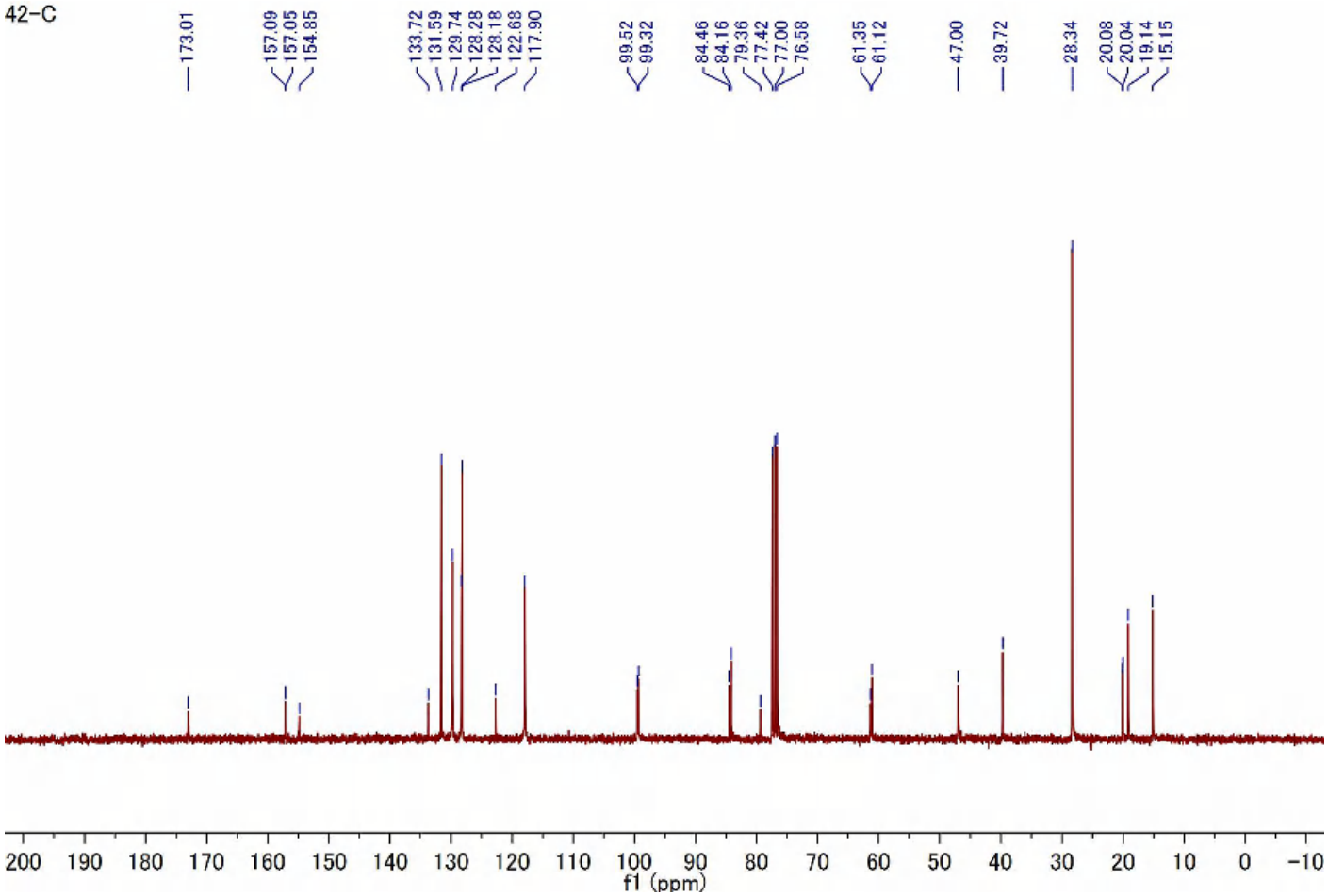
Compound **6b** (^{13}C NMR, 75 MHz, $CDCl_3$)



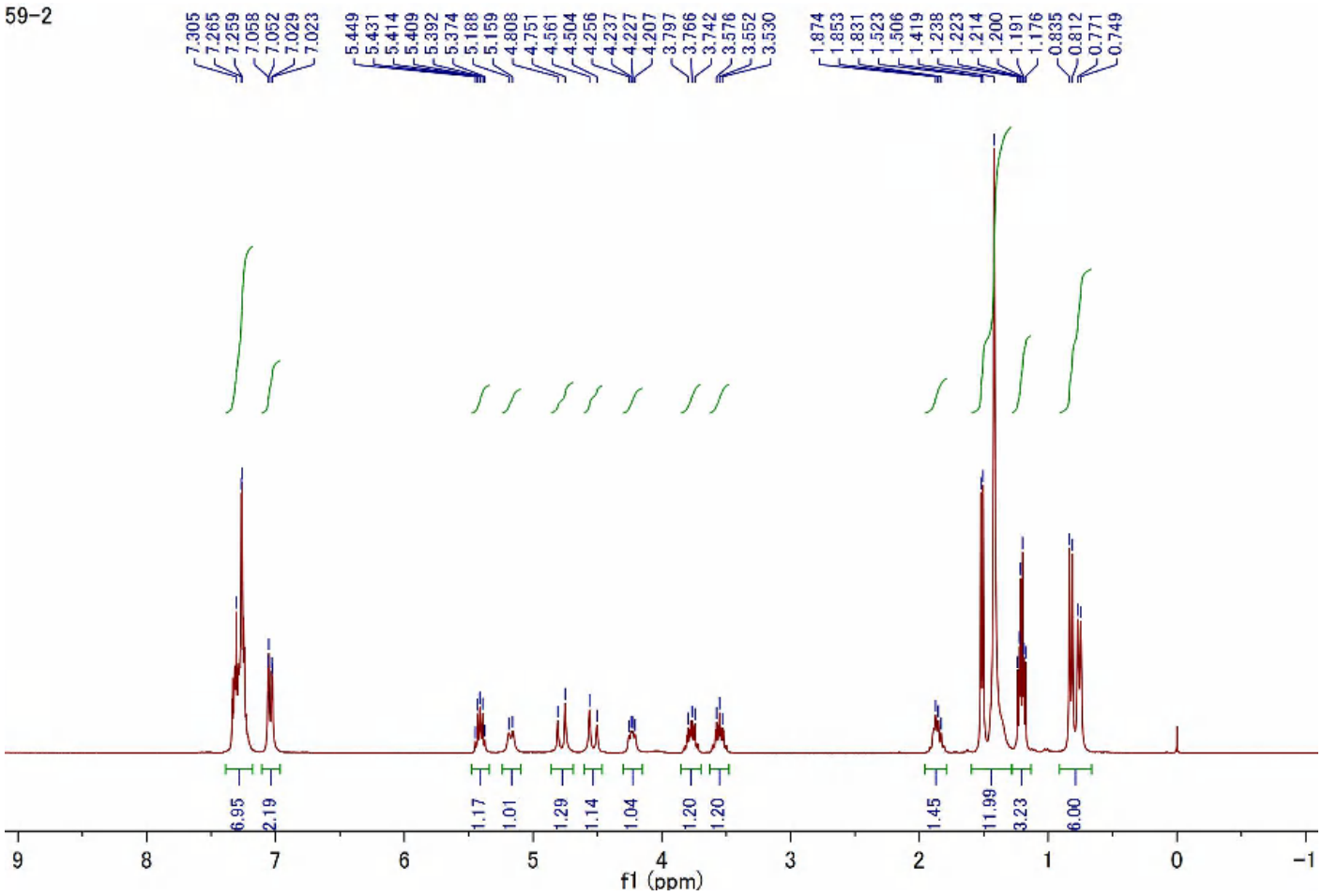
Compound **6c** (^{1}H NMR, 300 MHz, $CDCl_3$)



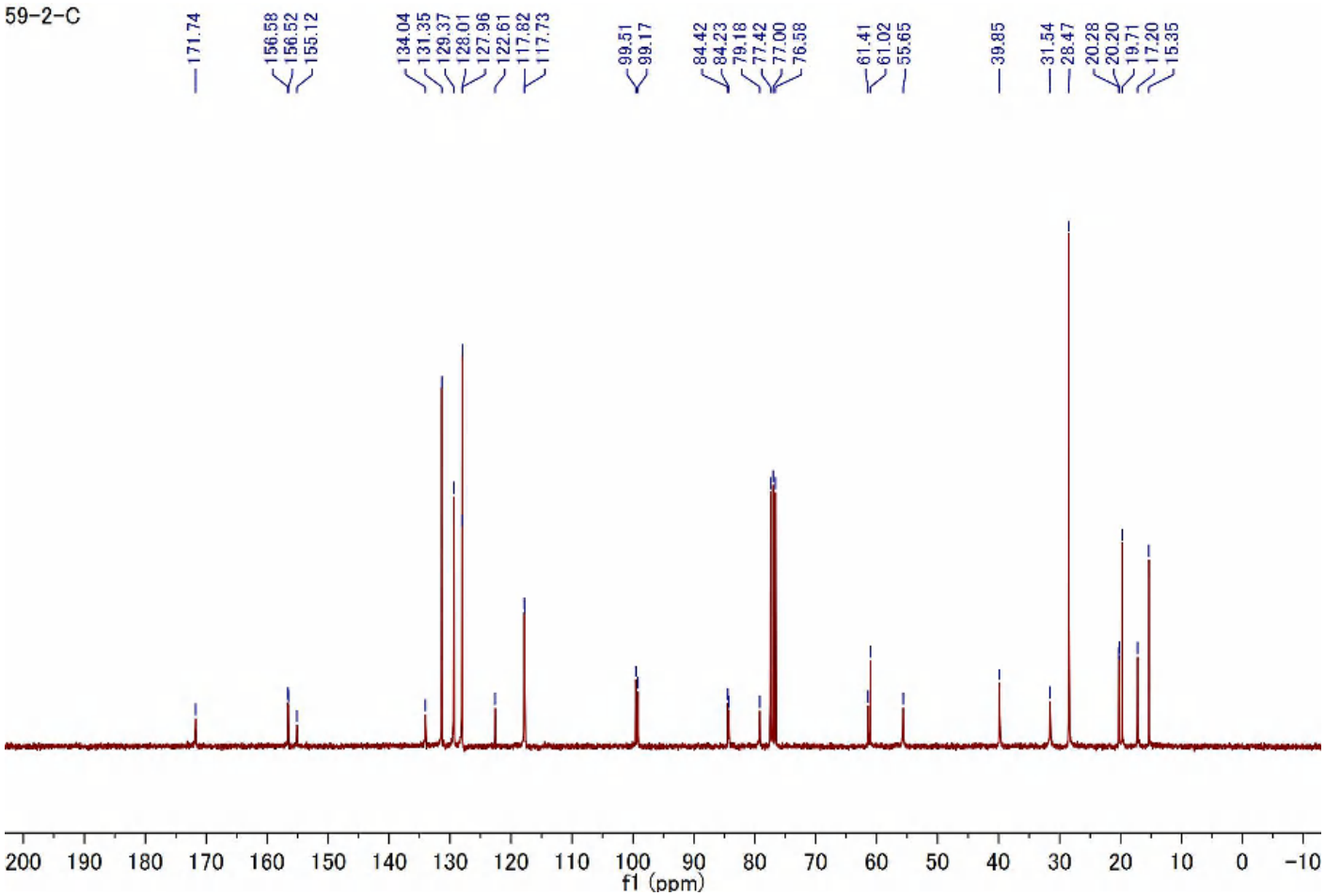
Compound **6c** (^{13}C NMR, 75 MHz, $CDCl_3$)



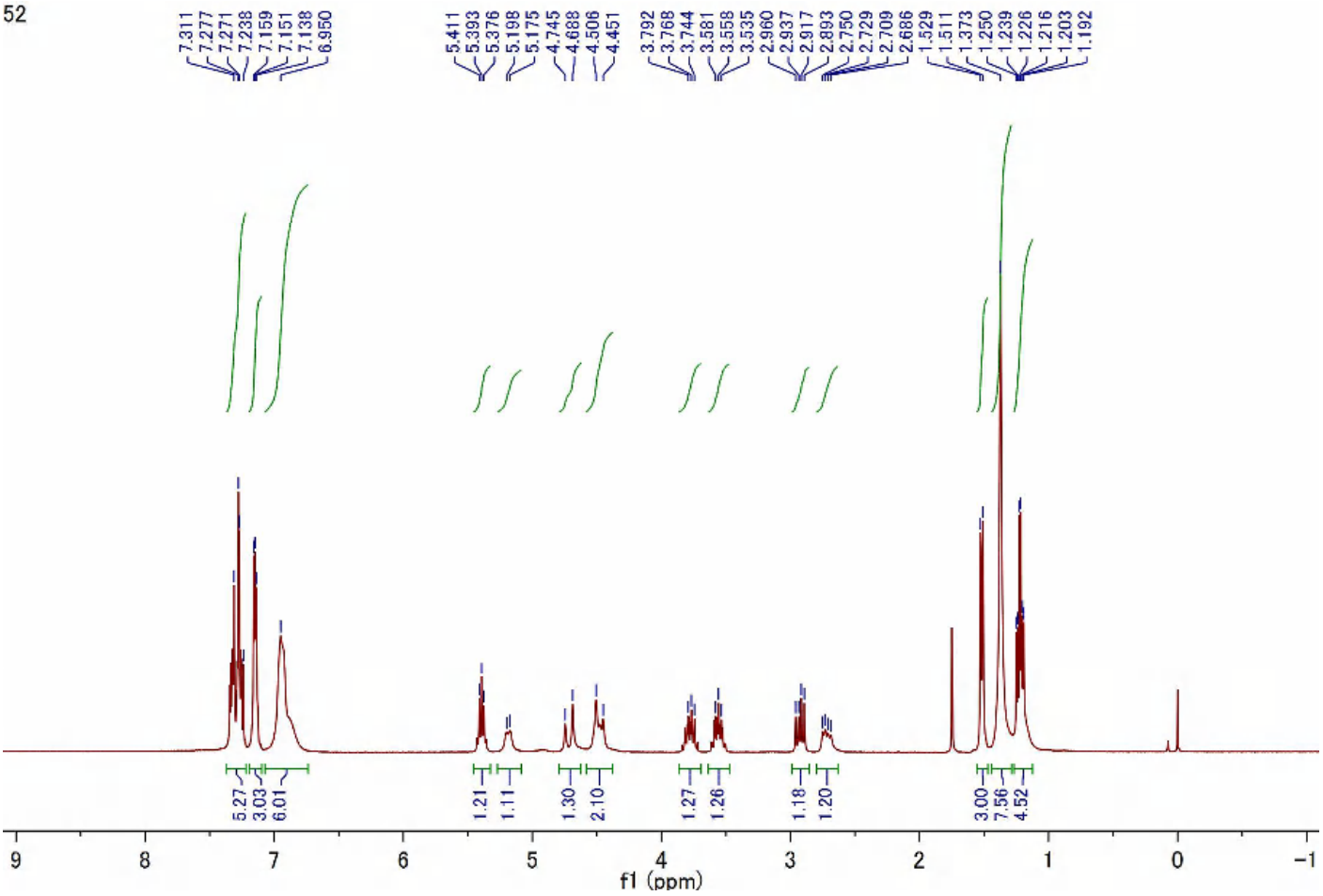
Compound **6d** (^{1}H NMR, 300 MHz, $CDCl_3$)



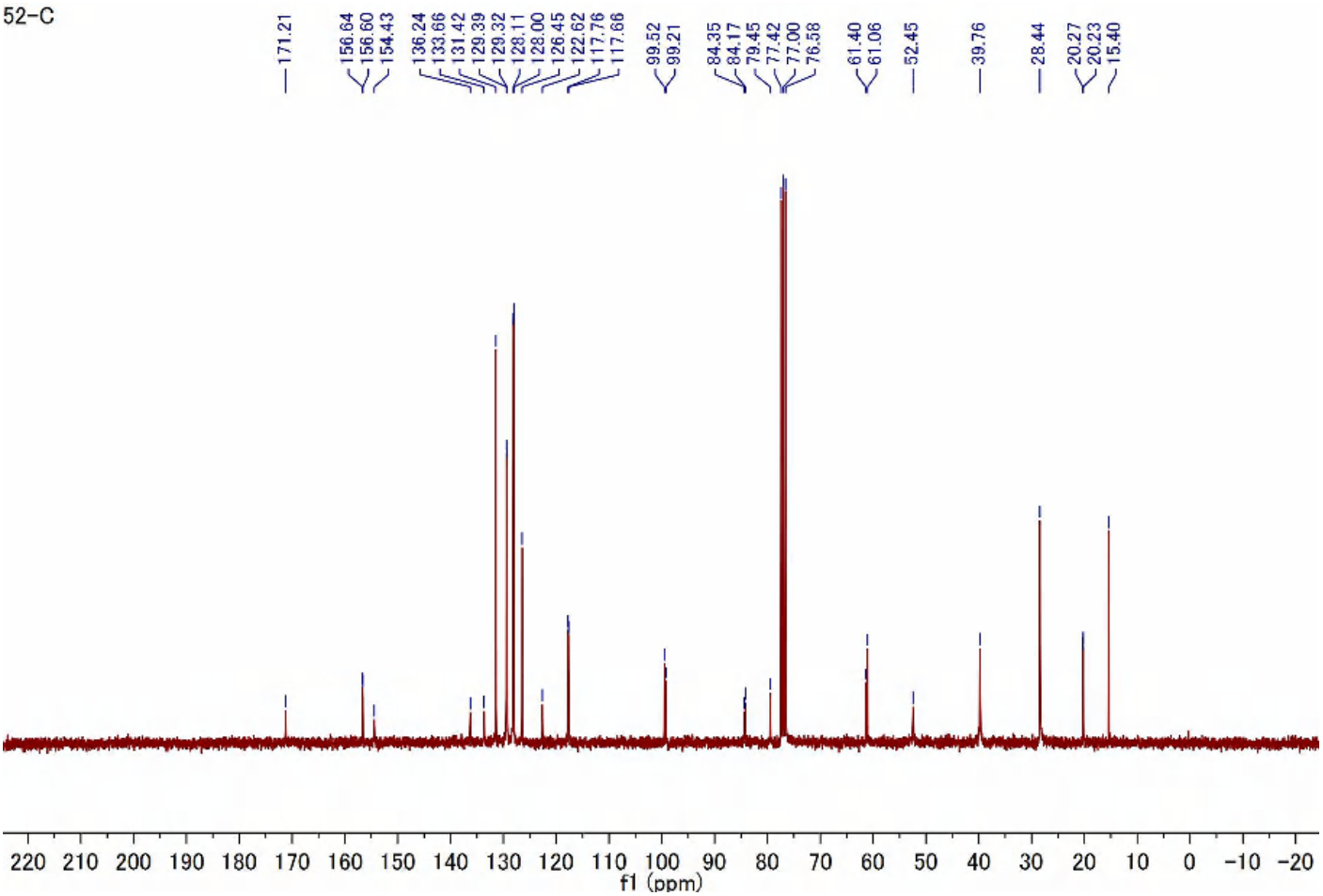
Compound **6d** (^{13}C NMR, 75 MHz, $CDCl_3$)



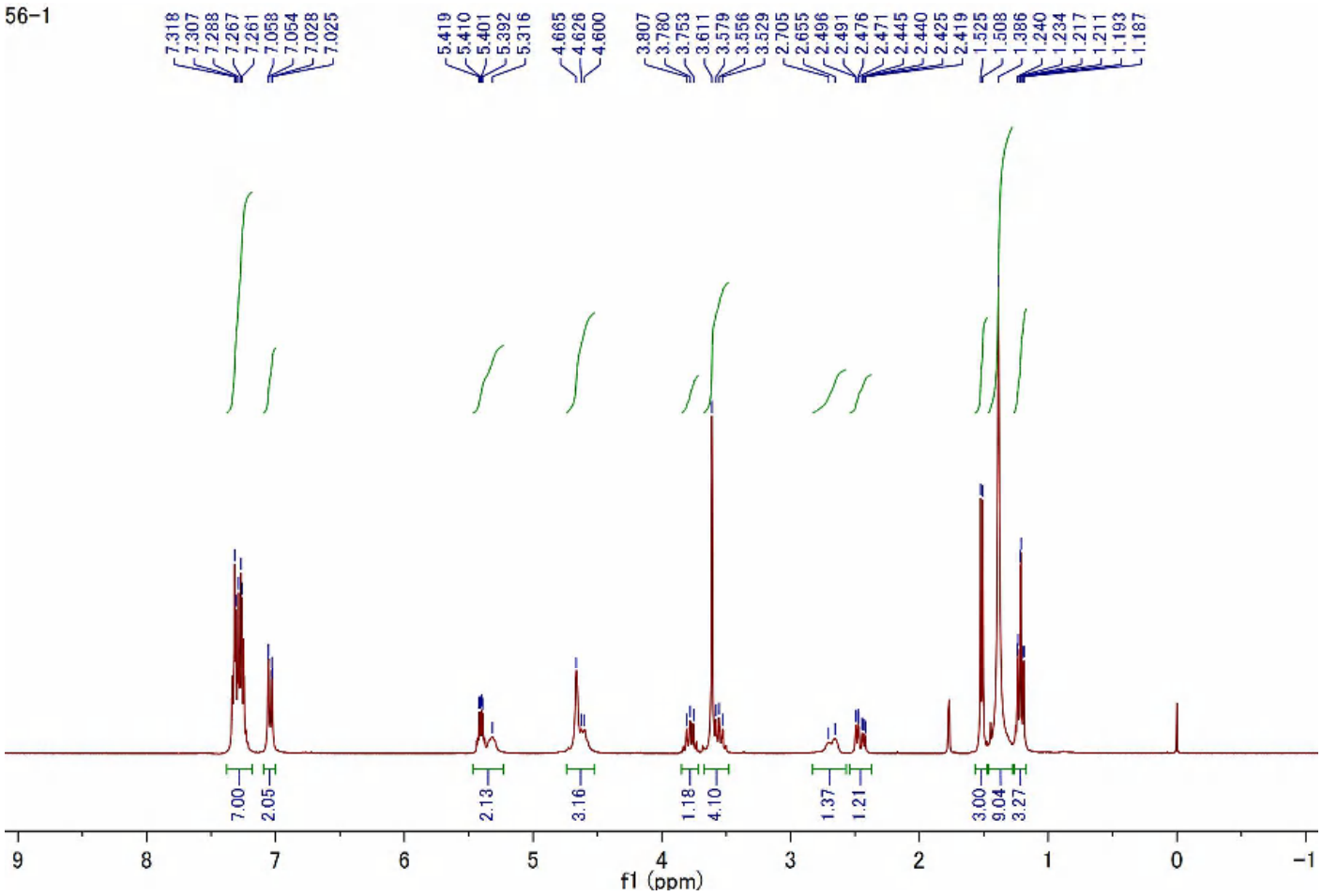
Compound **6e** (^{1}H NMR, 300 MHz, $CDCl_3$)



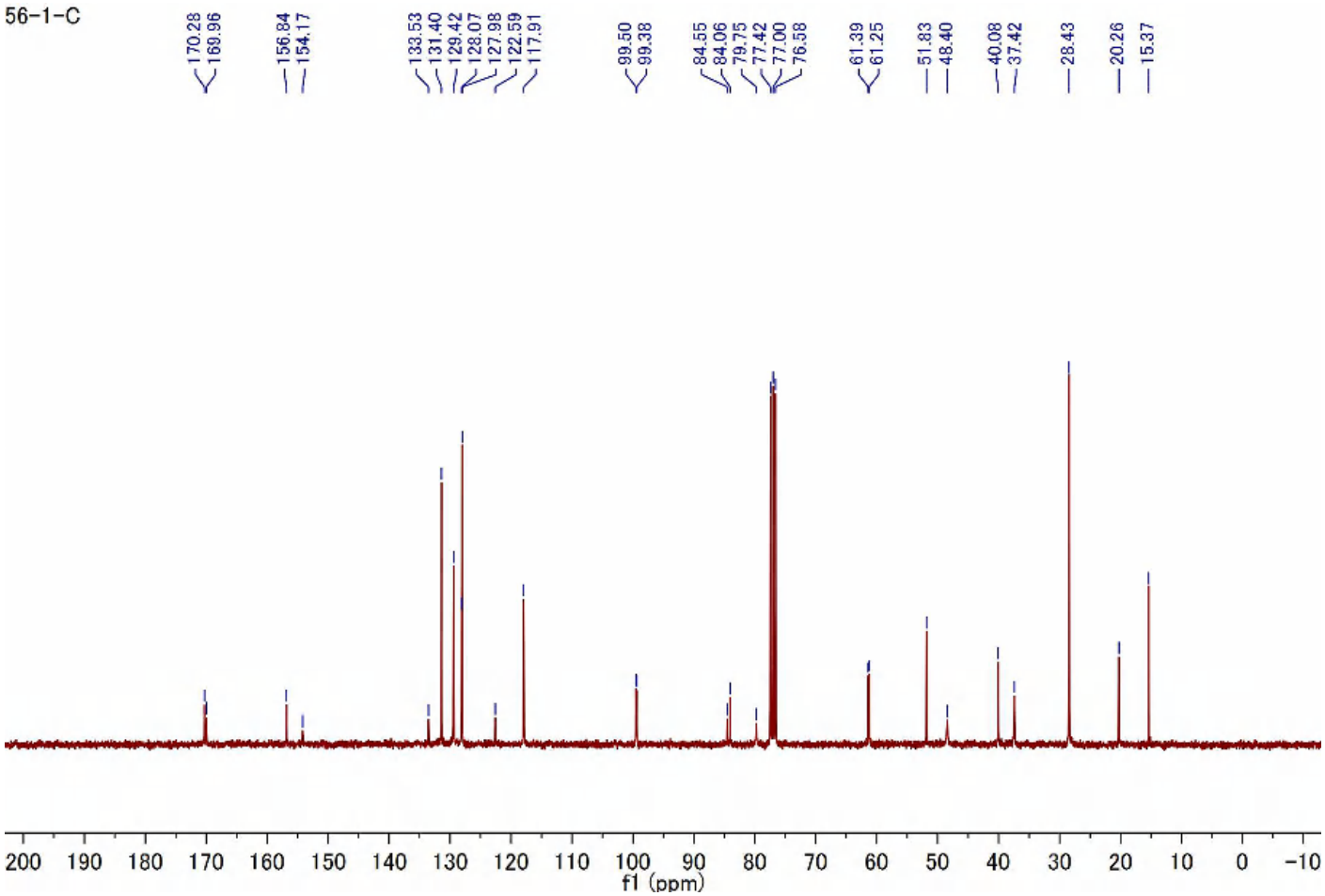
Compound **6e** (^{13}C NMR, 75 MHz, $CDCl_3$)



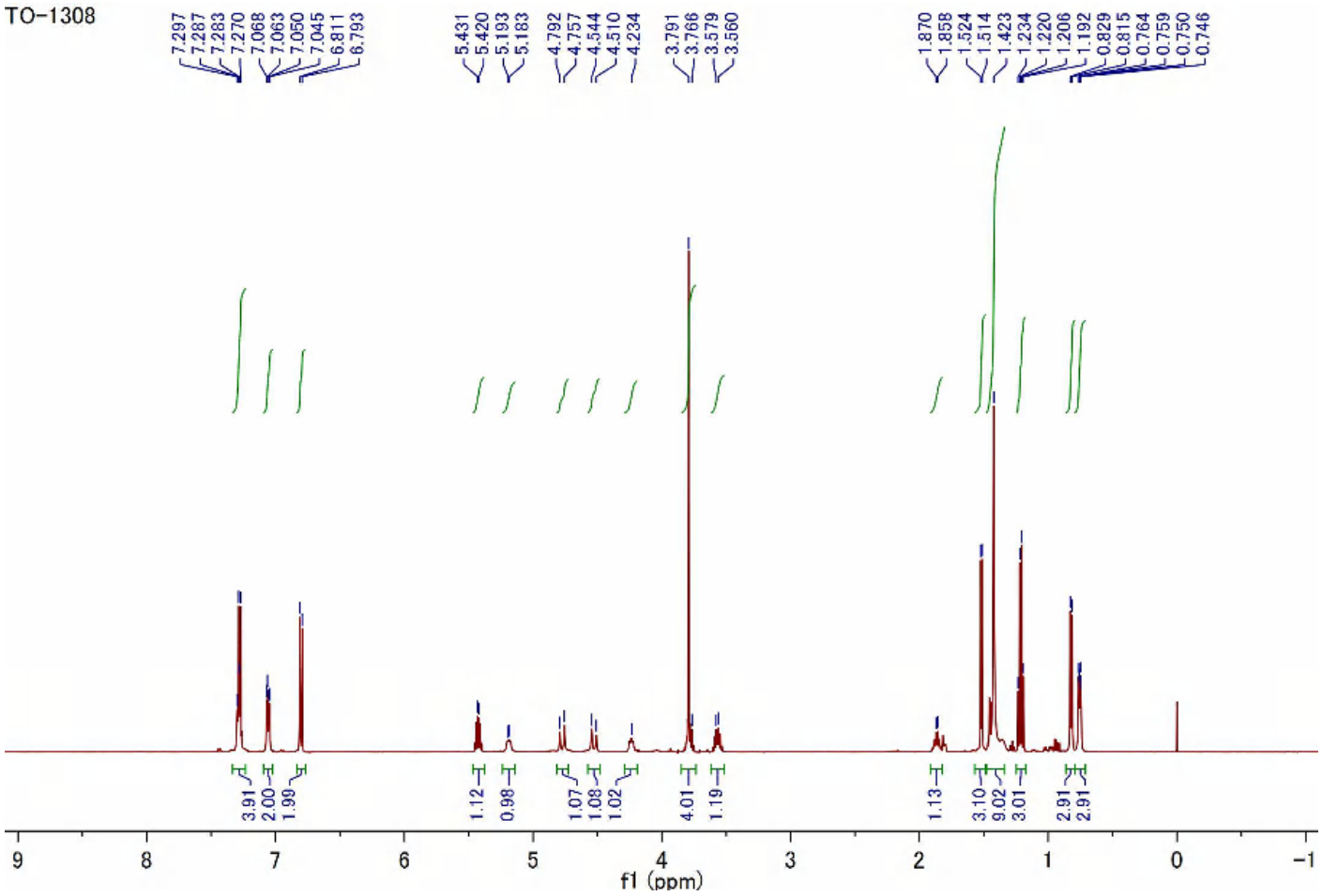
Compound **6f** (^{1}H NMR, 300 MHz, $CDCl_3$)



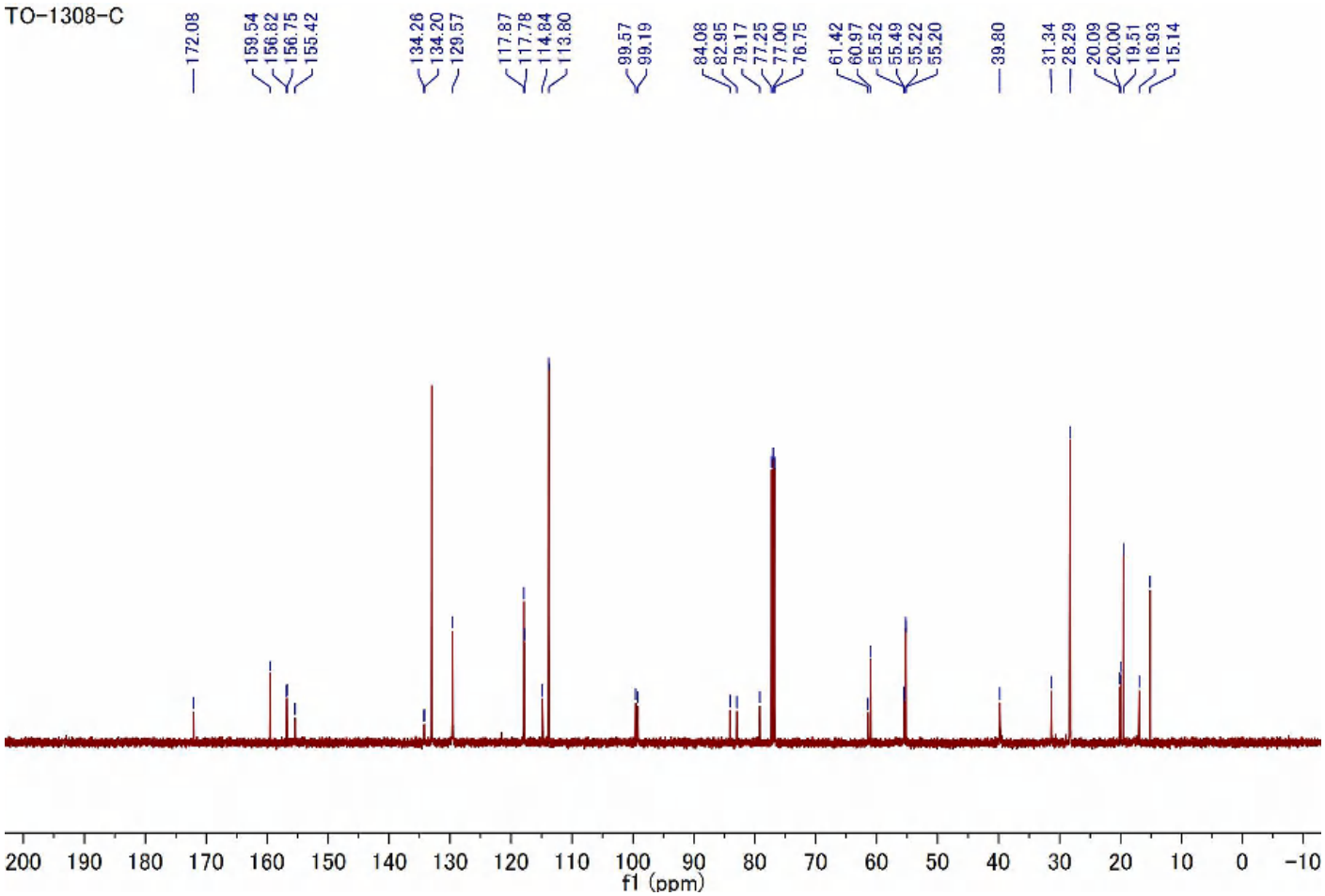
Compound **6f** (^{13}C NMR, 75 MHz, $CDCl_3$)



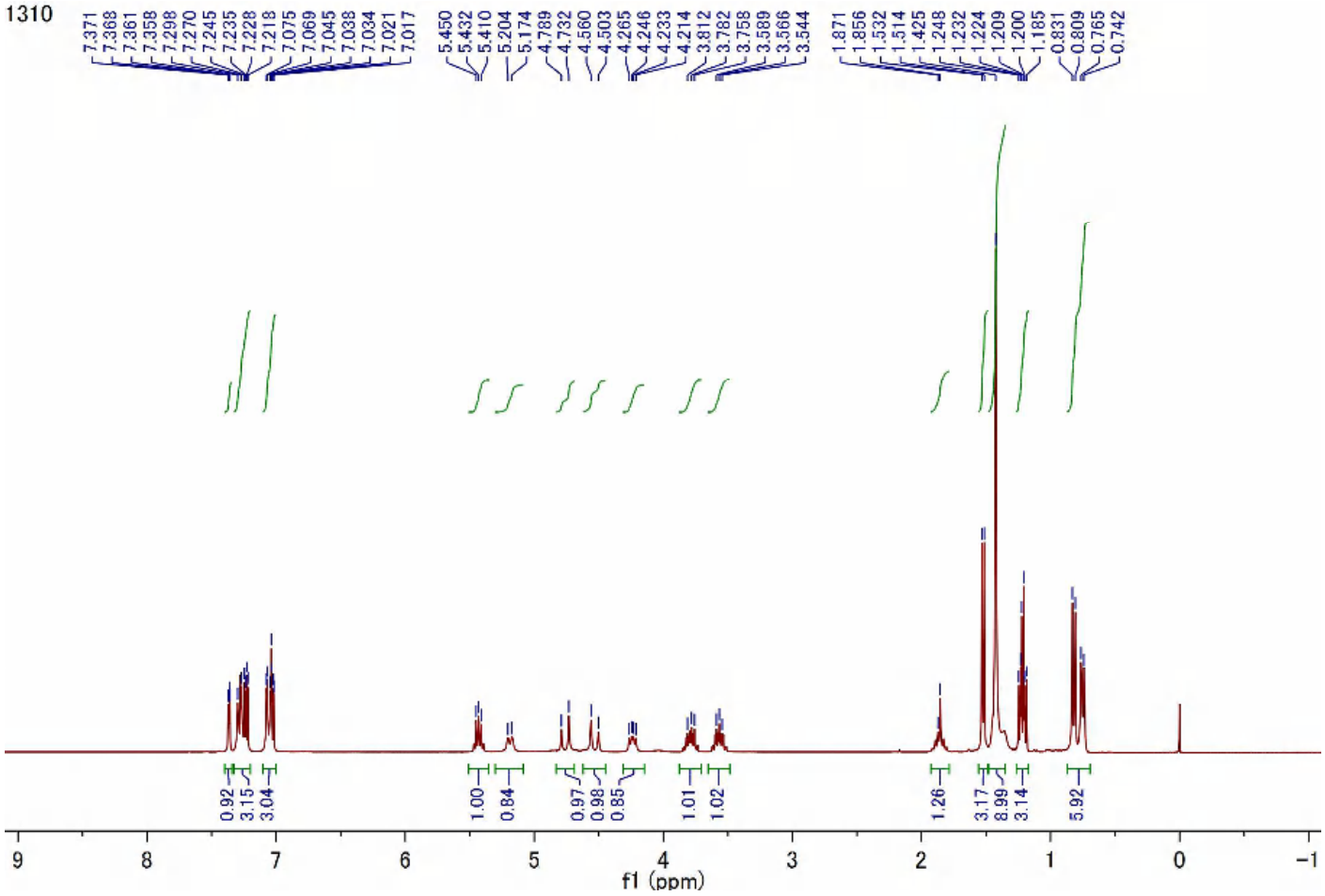
Compound **6g** (^{1}H NMR, 500 MHz, $CDCl_3$)



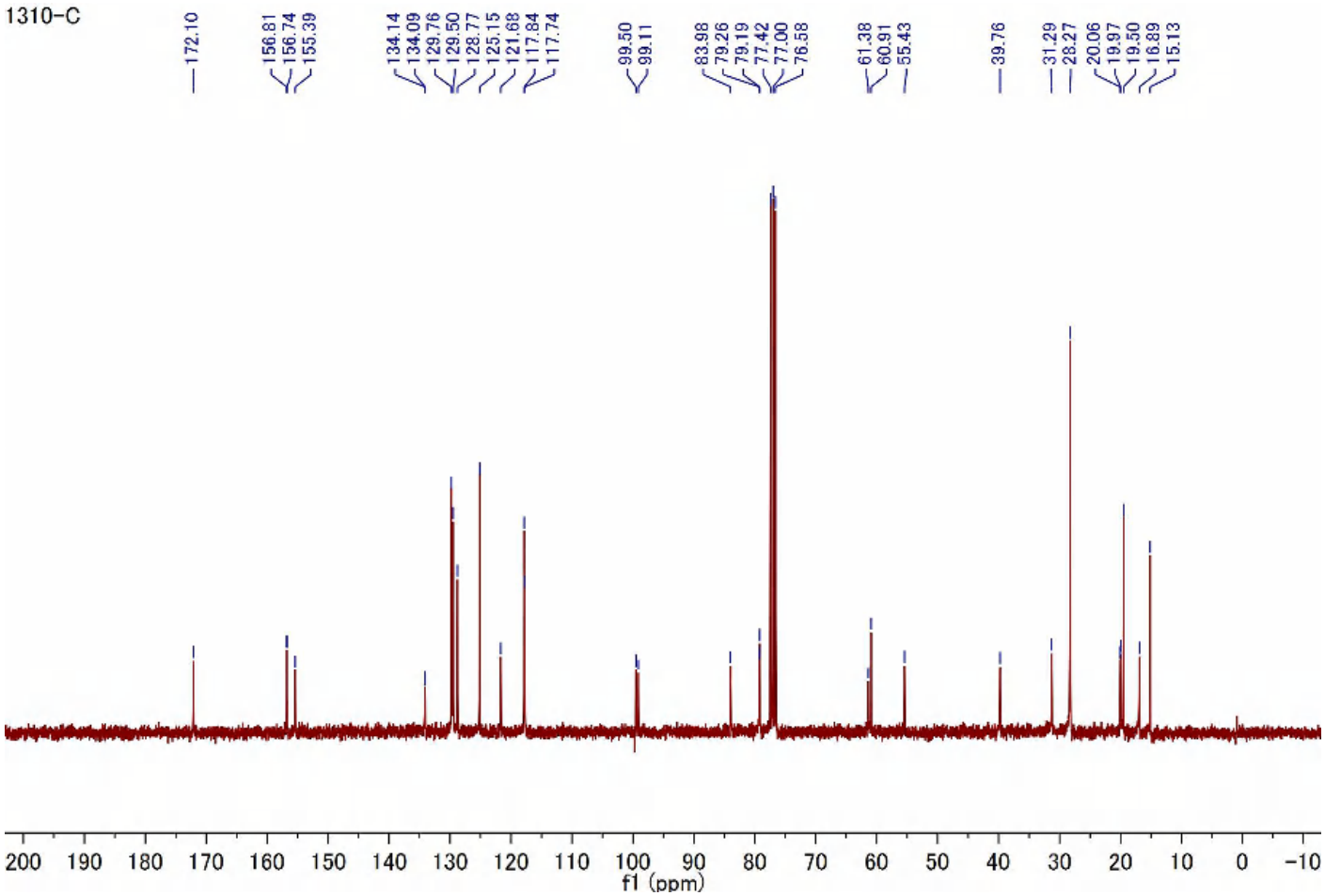
Compound **6g** (^{13}C NMR, 125 MHz, $CDCl_3$)



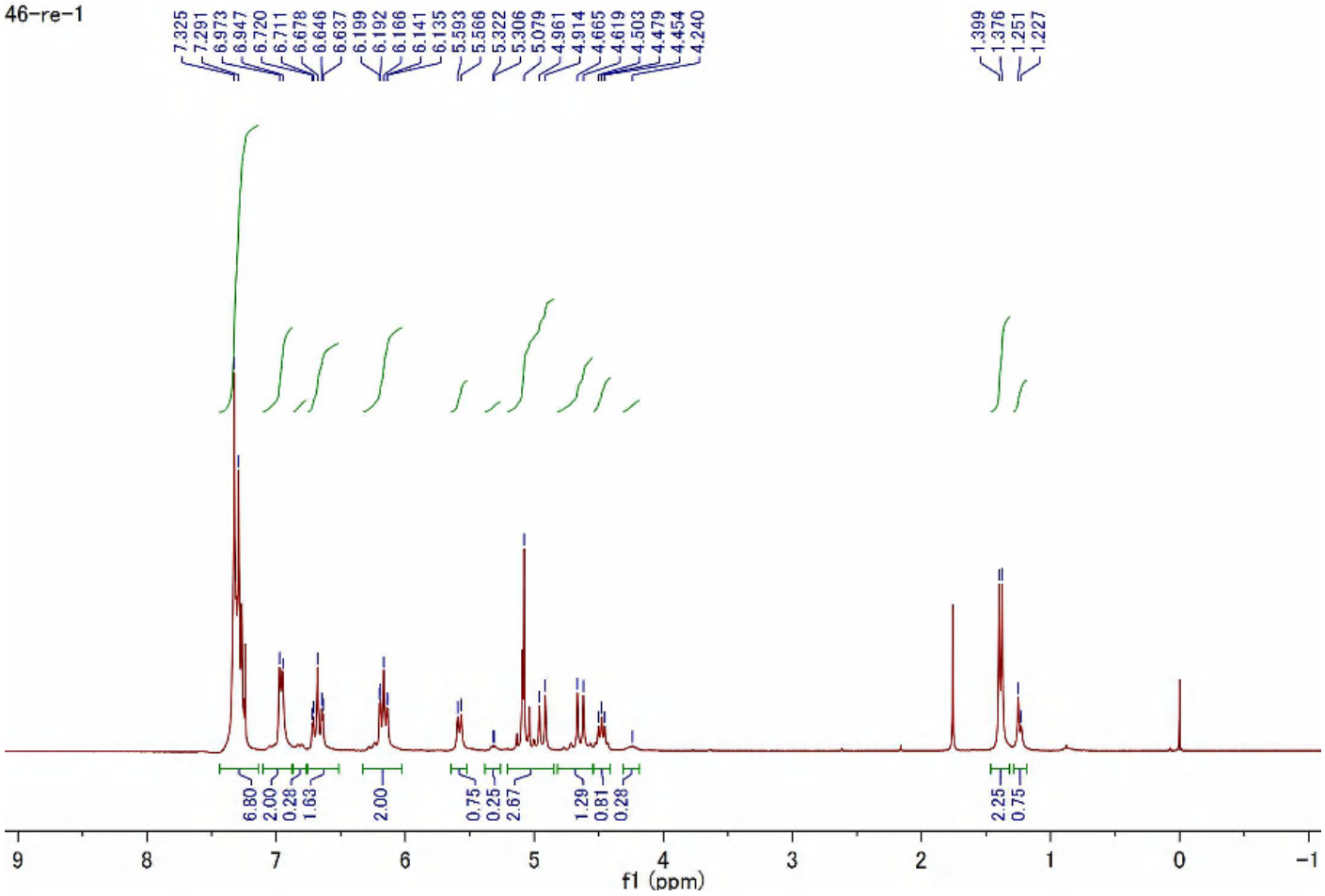
Compound **6h** (^{1}H NMR, 300 MHz, $CDCl_3$)



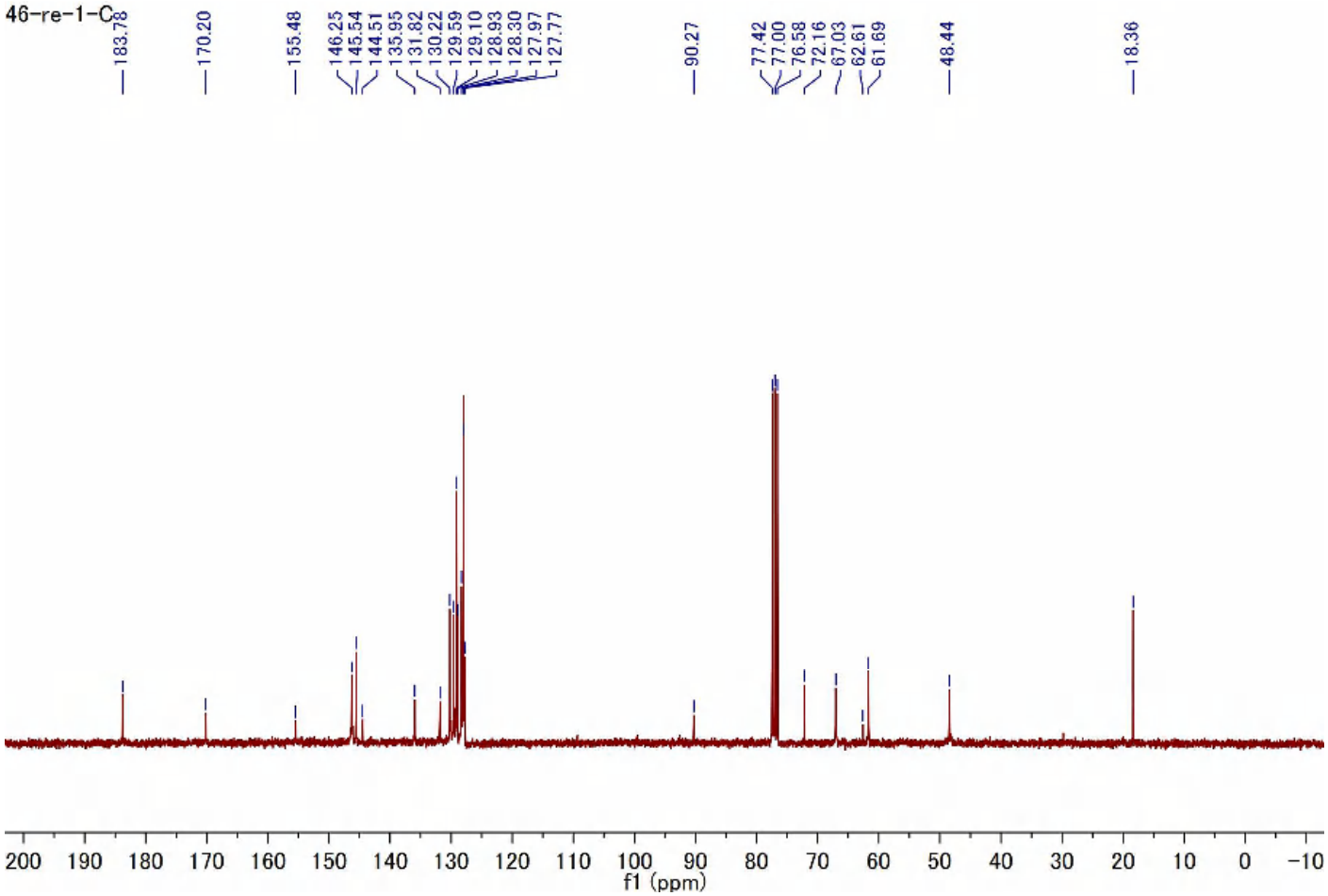
Compound **6h** (^{13}C NMR, 75 MHz, $CDCl_3$)



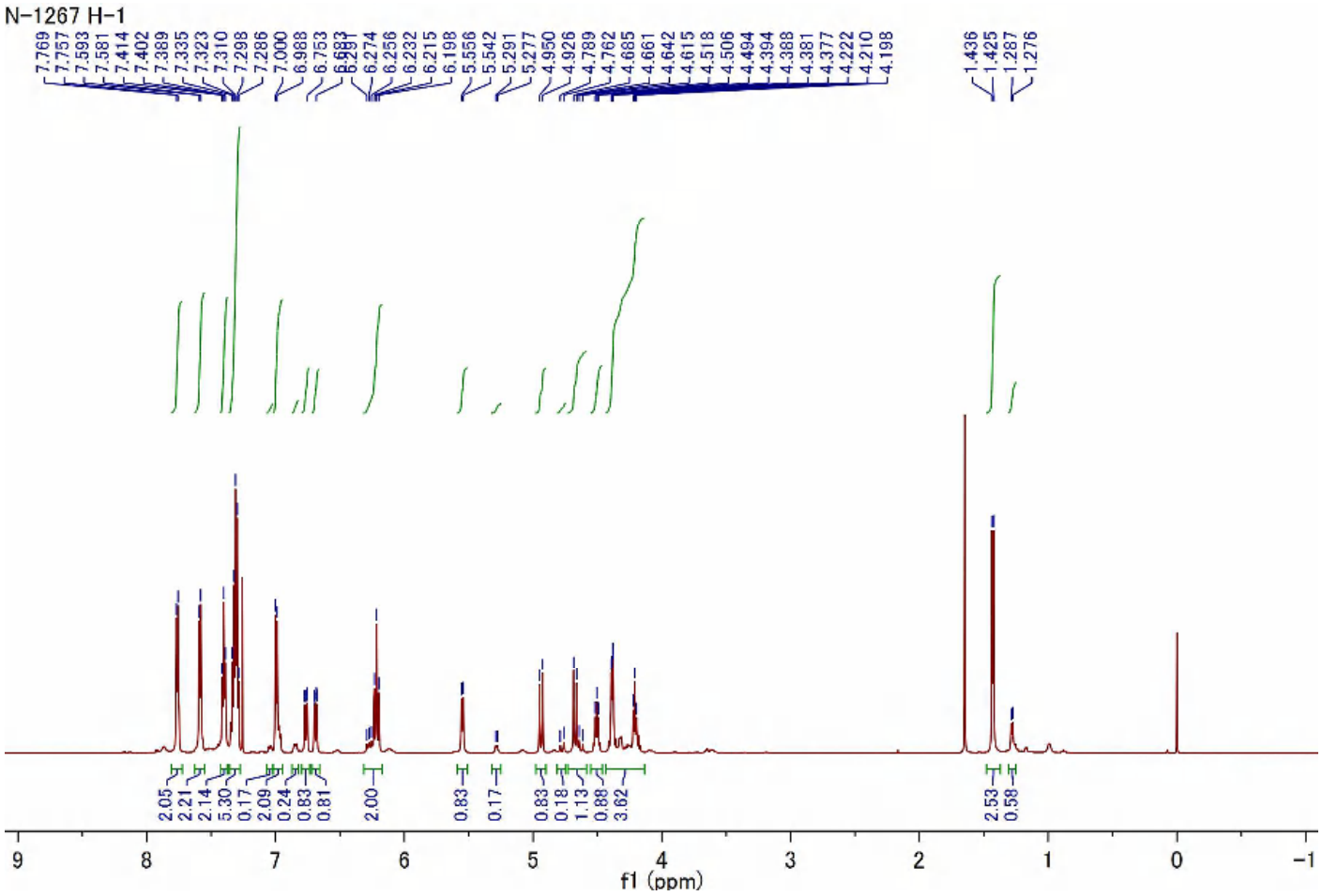
Compound **7a** (^{1}H NMR, 300 MHz, $CDCl_3$)



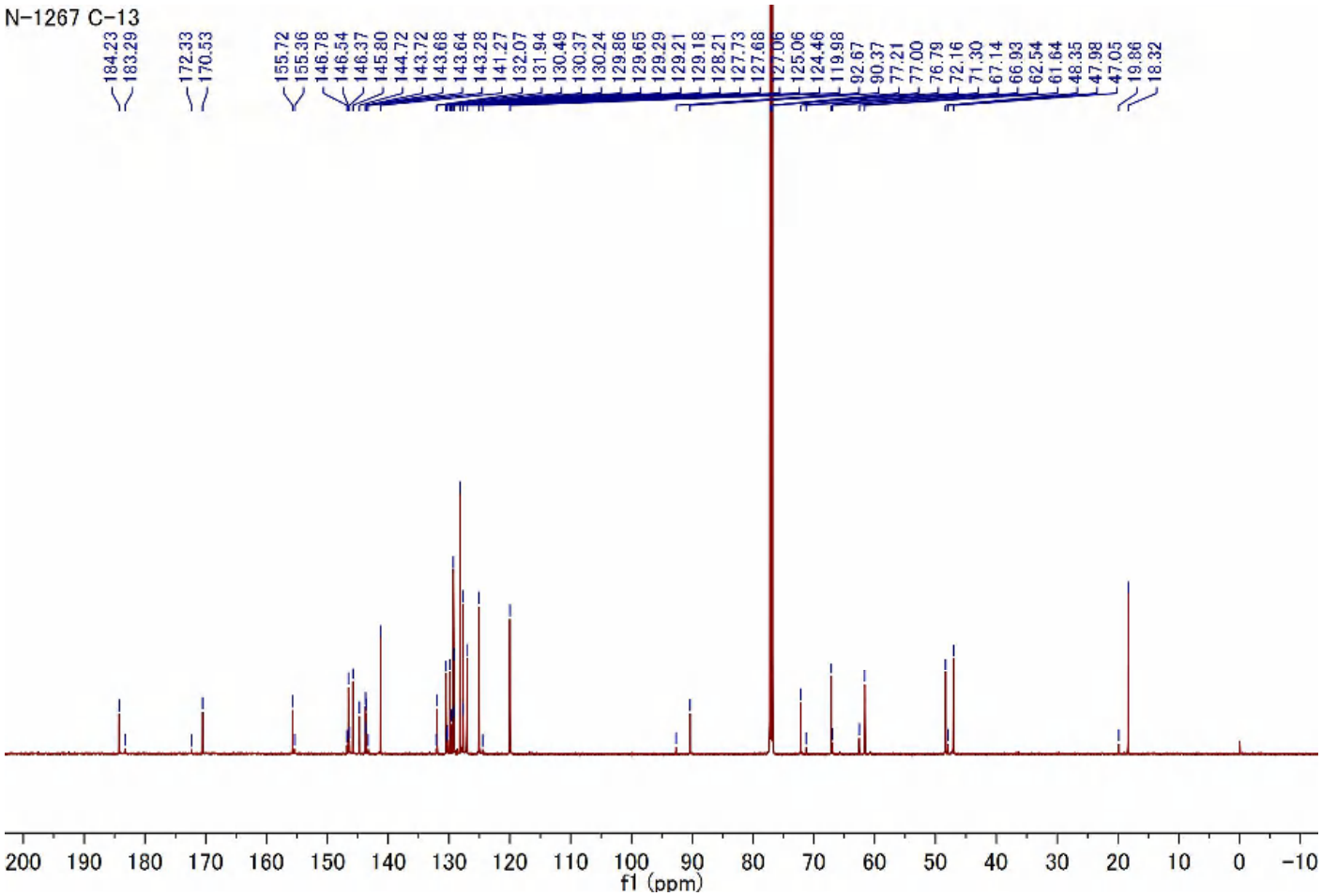
Compound **7a** (^{13}C NMR, 75 MHz, $CDCl_3$)



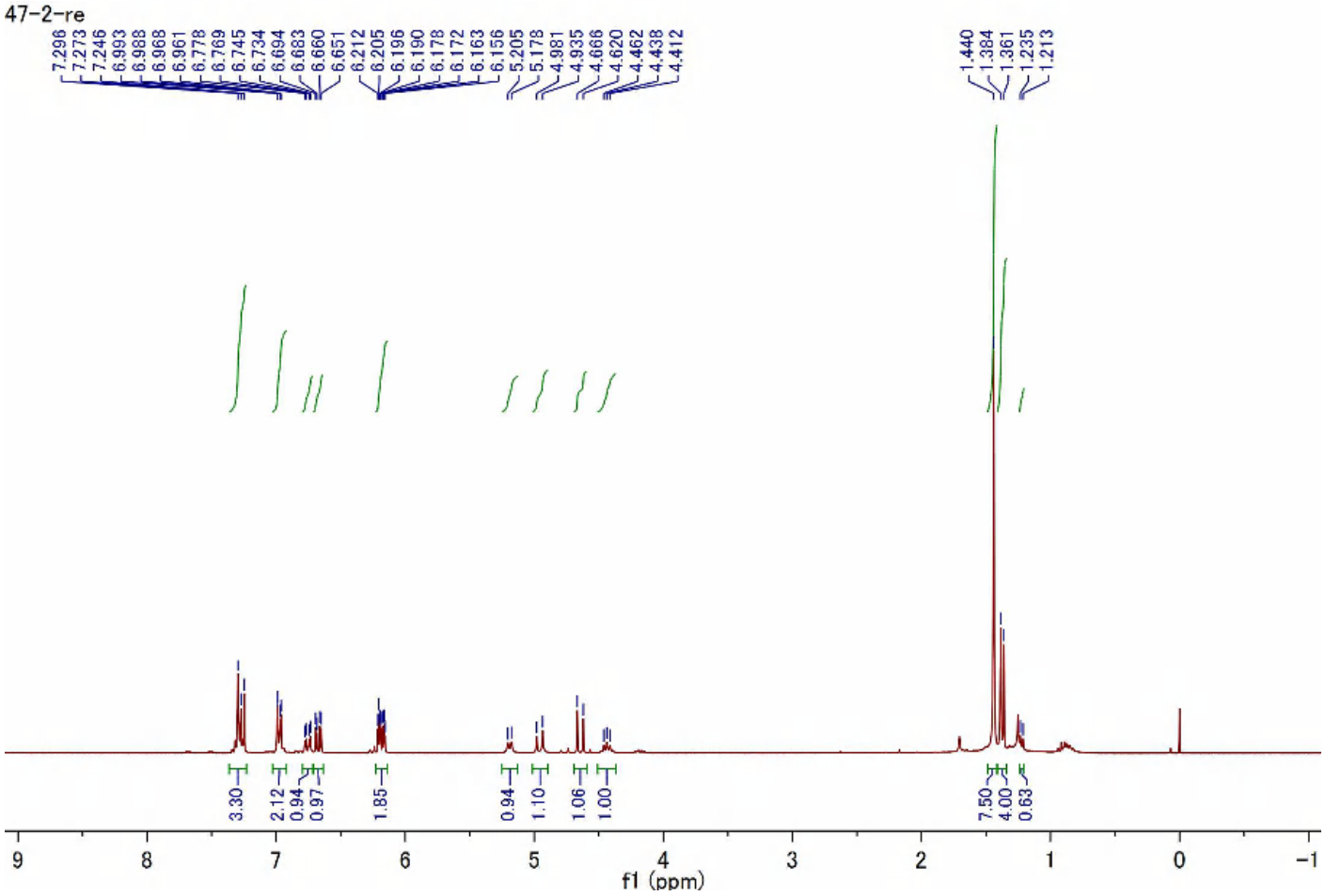
Compound **7b** (^{1}H NMR, 600 MHz, $CDCl_3$)



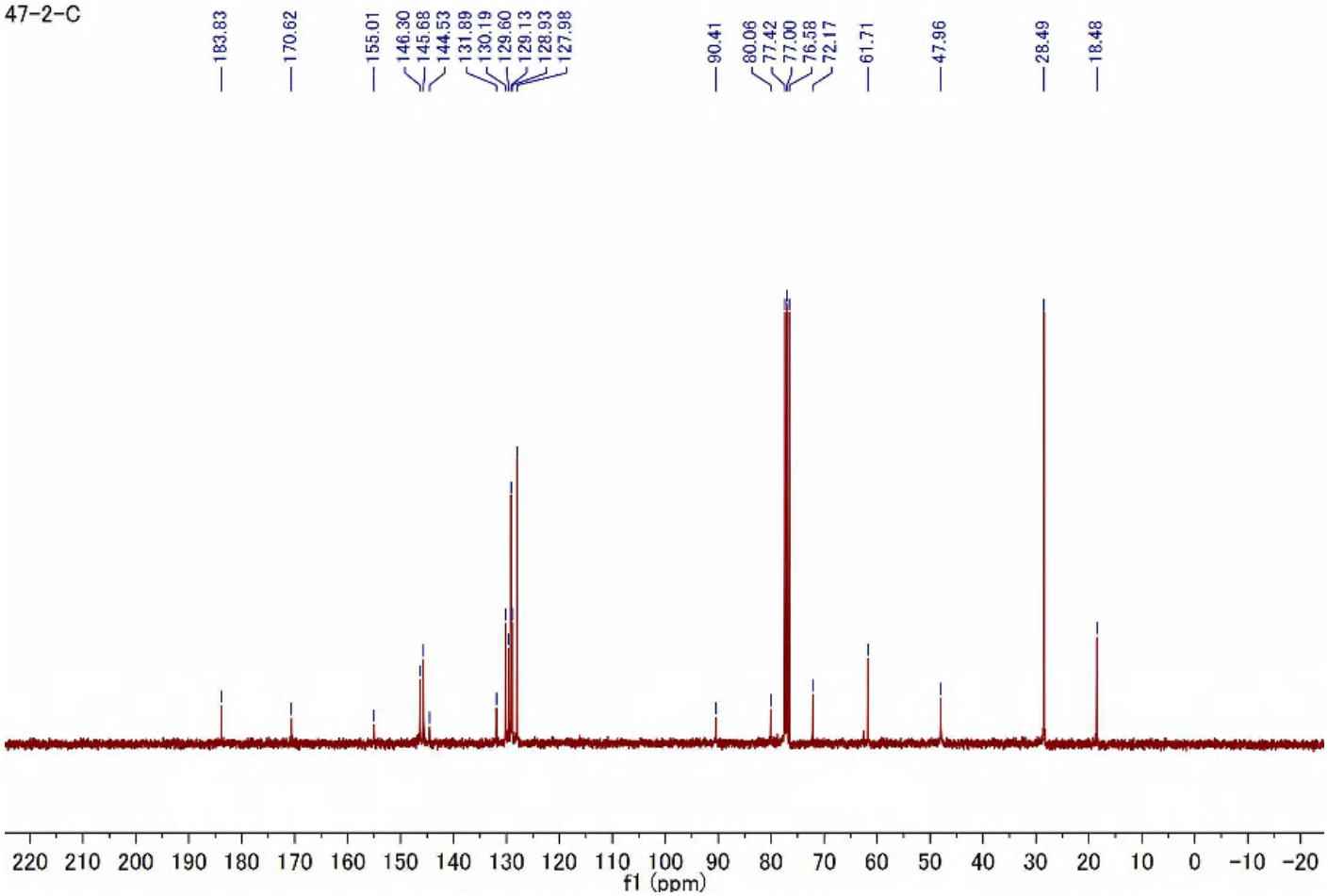
Compound **7b** (^{13}C NMR, 150 MHz, $CDCl_3$)



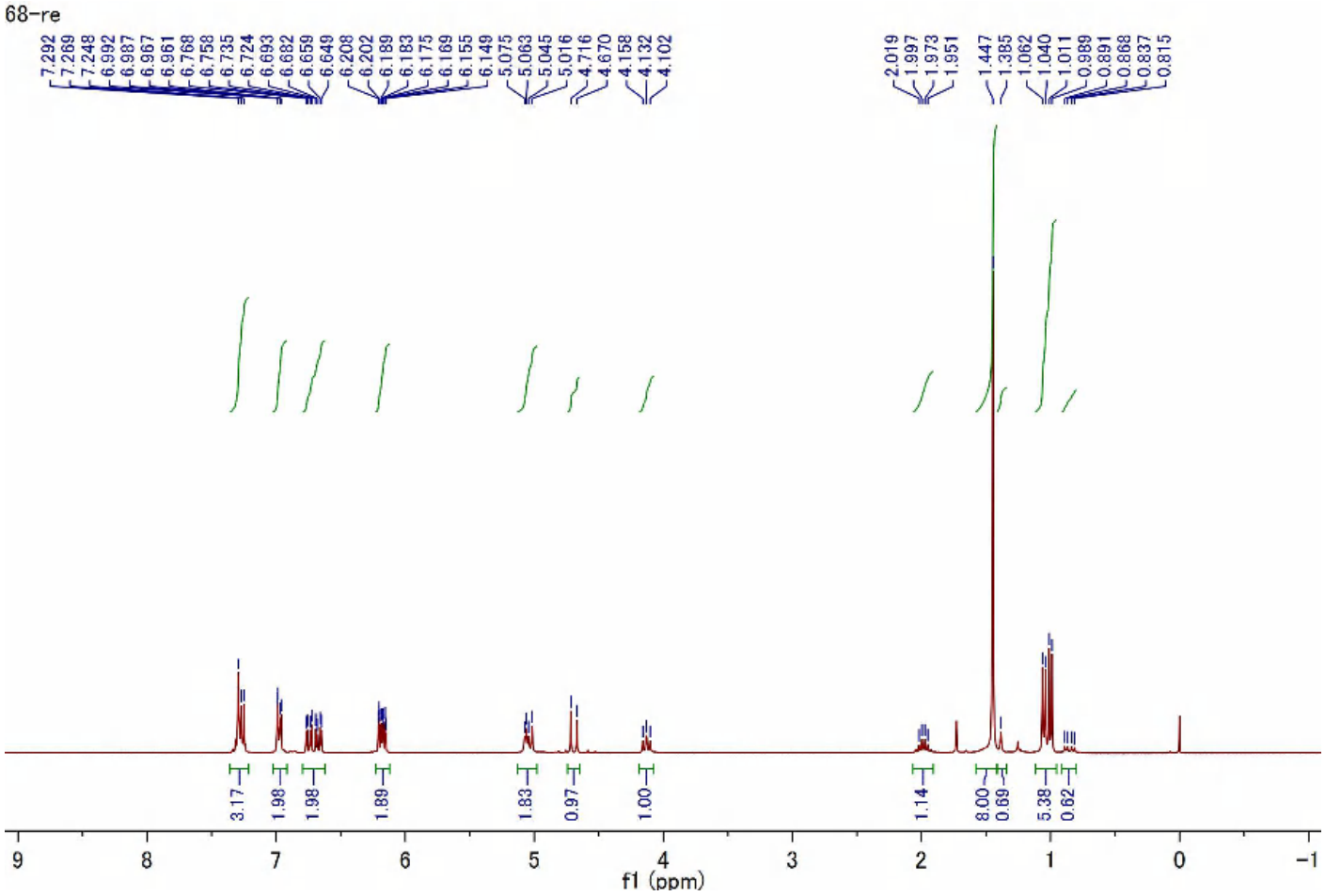
Compound **7c** (^{1}H NMR, 300 MHz, $CDCl_3$)



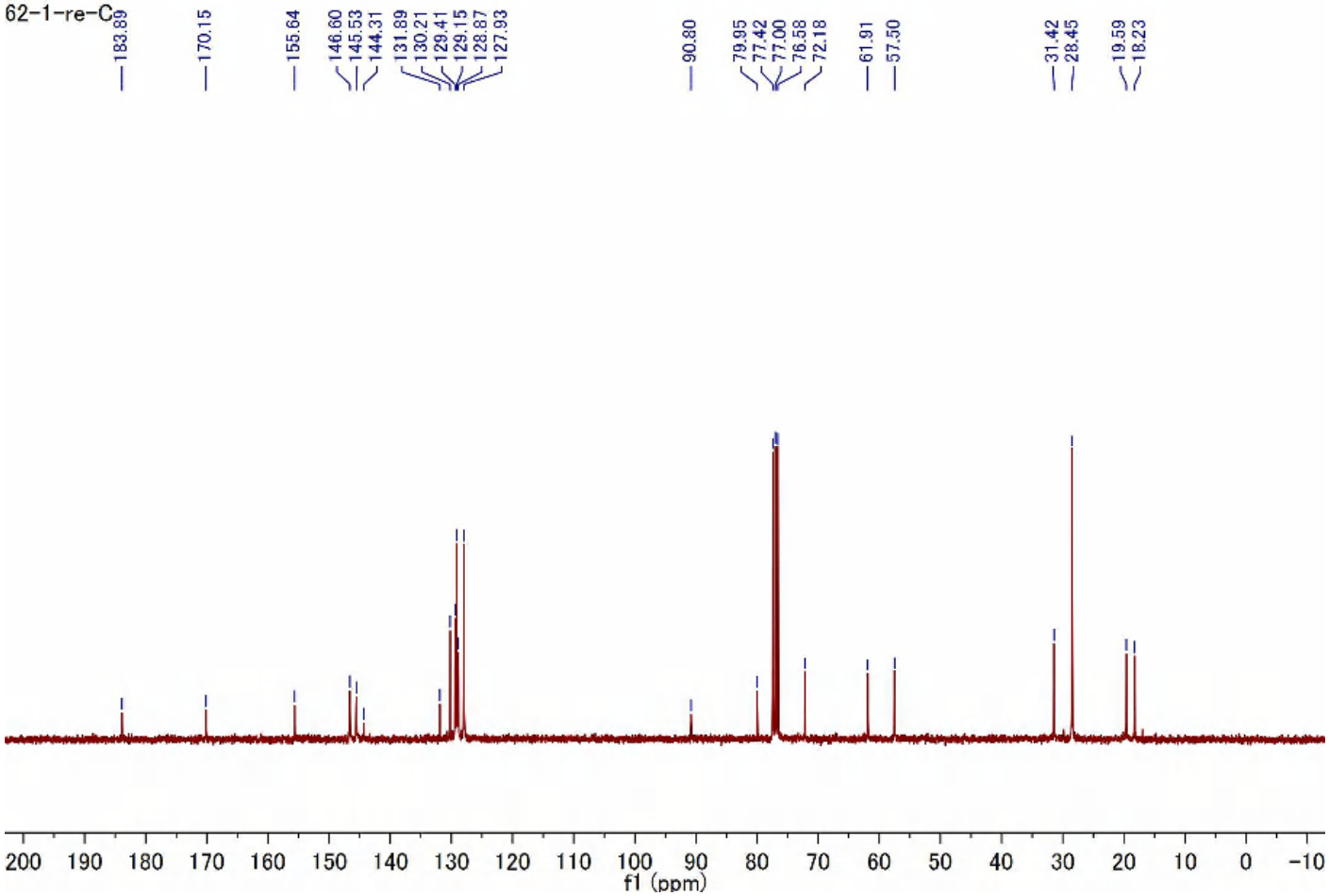
Compound **7c** (^{13}C NMR, 75 MHz, $CDCl_3$)



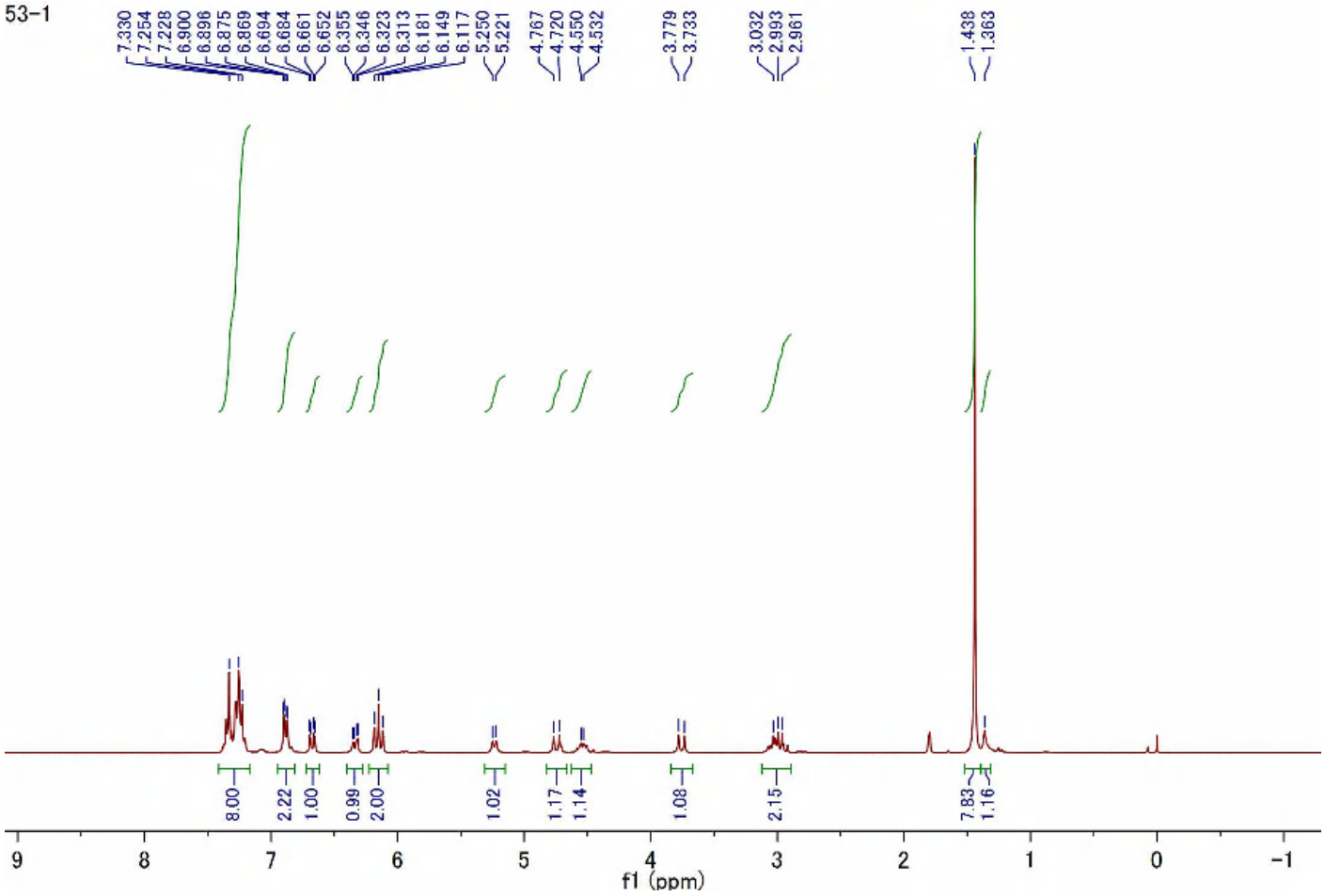
Compound **7d** (^{1}H NMR, 300 MHz, $CDCl_3$)



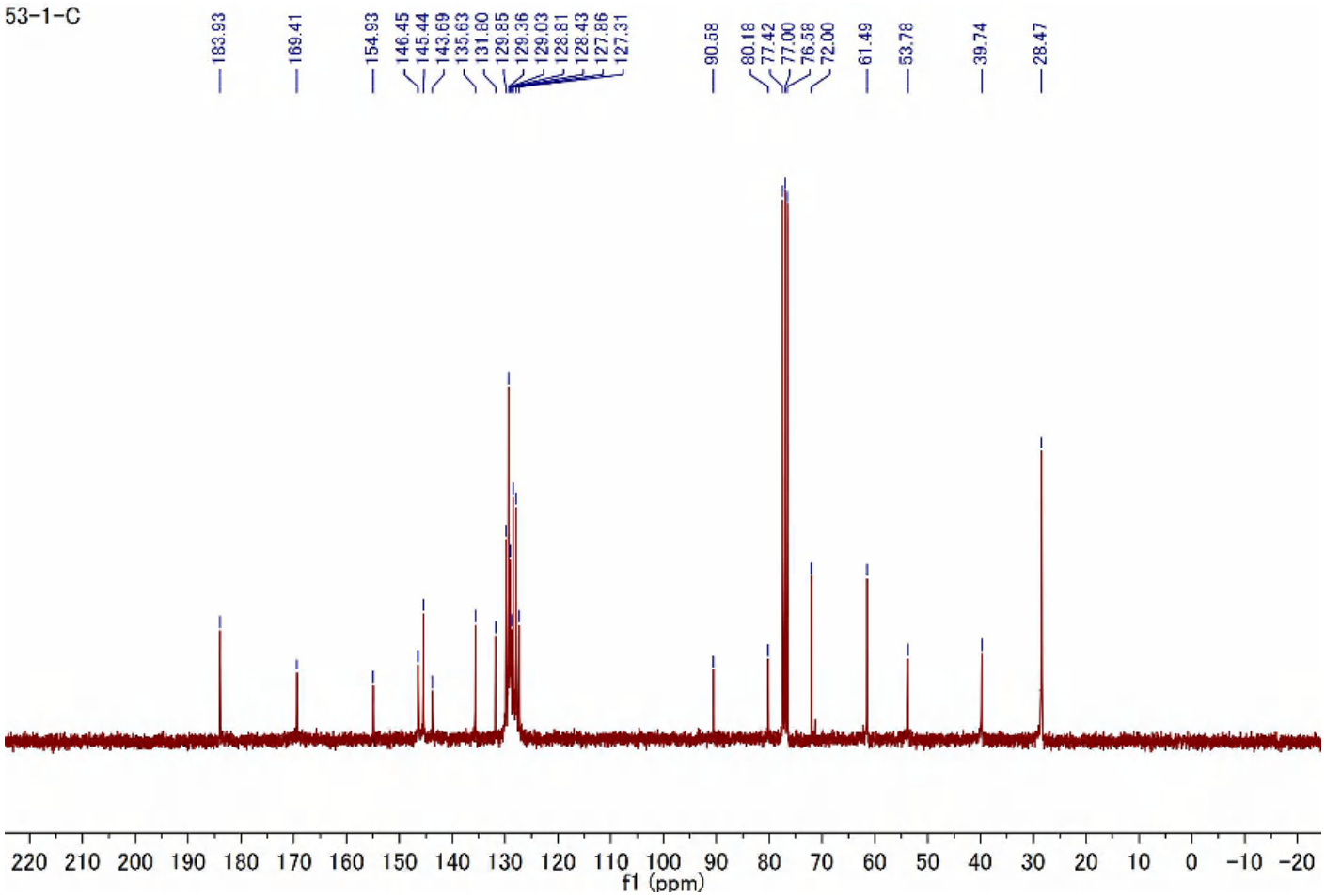
Compound **7d** (^{13}C NMR, 75 MHz, $CDCl_3$)



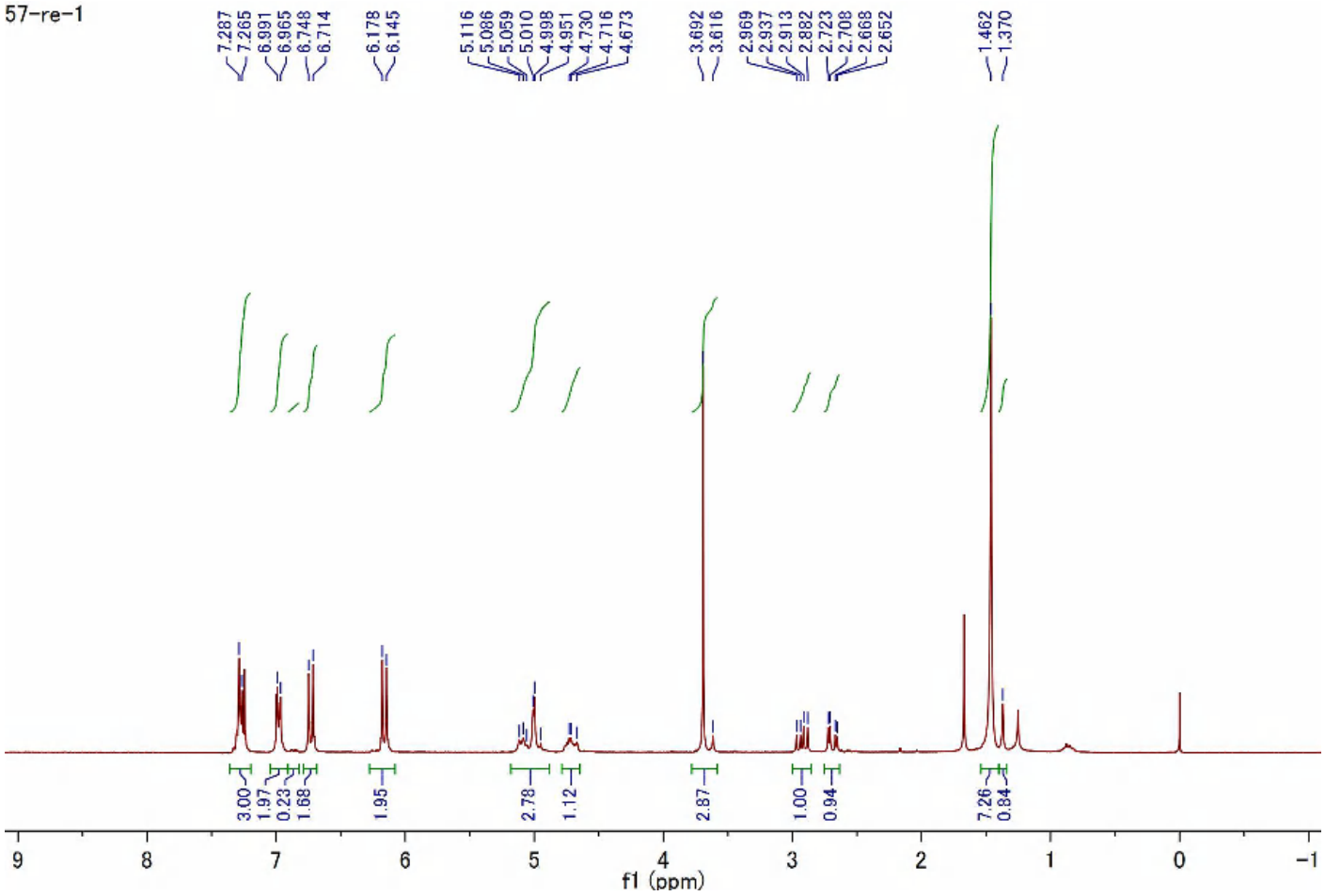
Compound **7e** (^{1}H NMR, 300 MHz, $CDCl_3$)



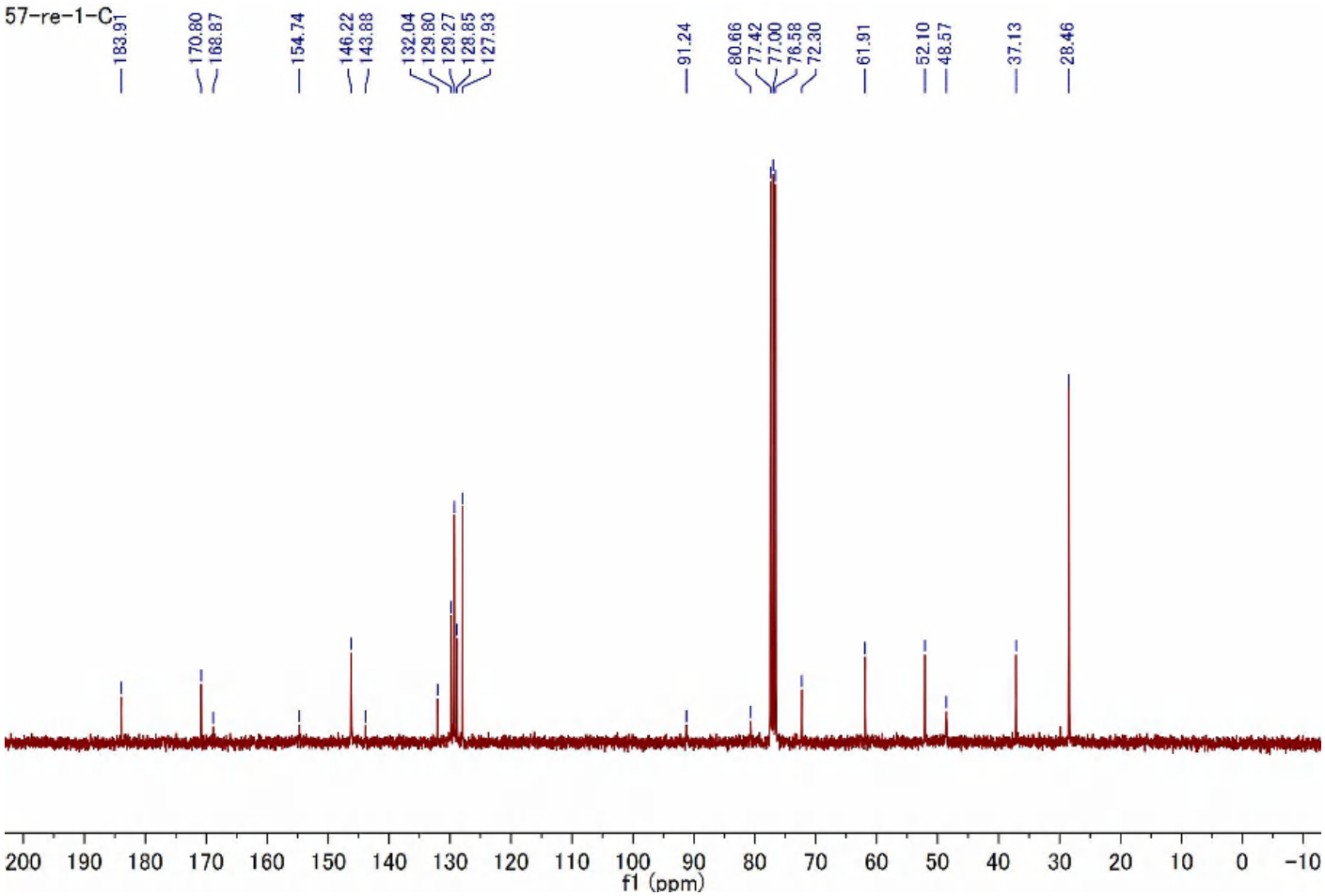
Compound **7e** (^{13}C NMR, 75 MHz, $CDCl_3$)



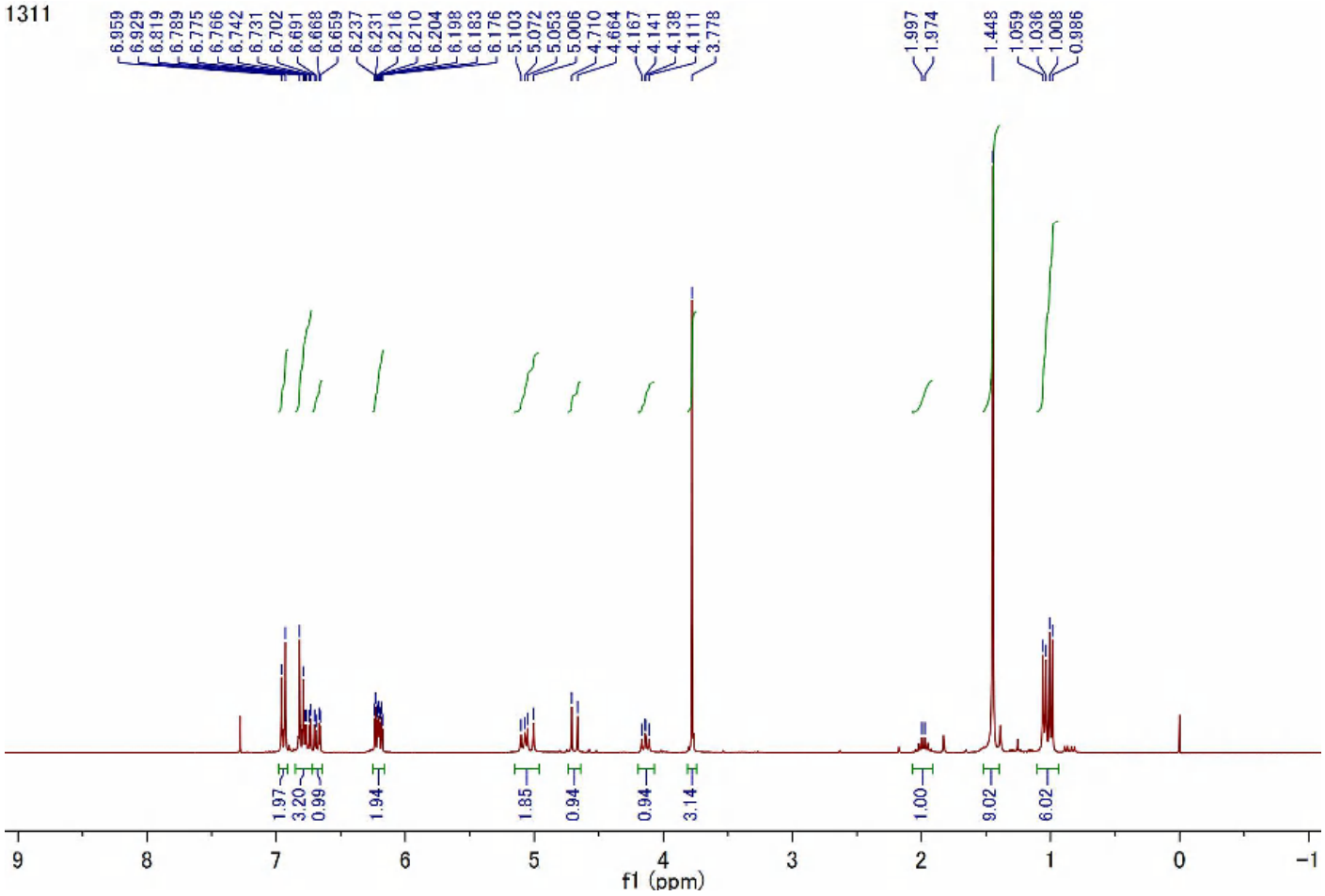
Compound **7f** (^{1}H NMR, 300 MHz, $CDCl_3$)



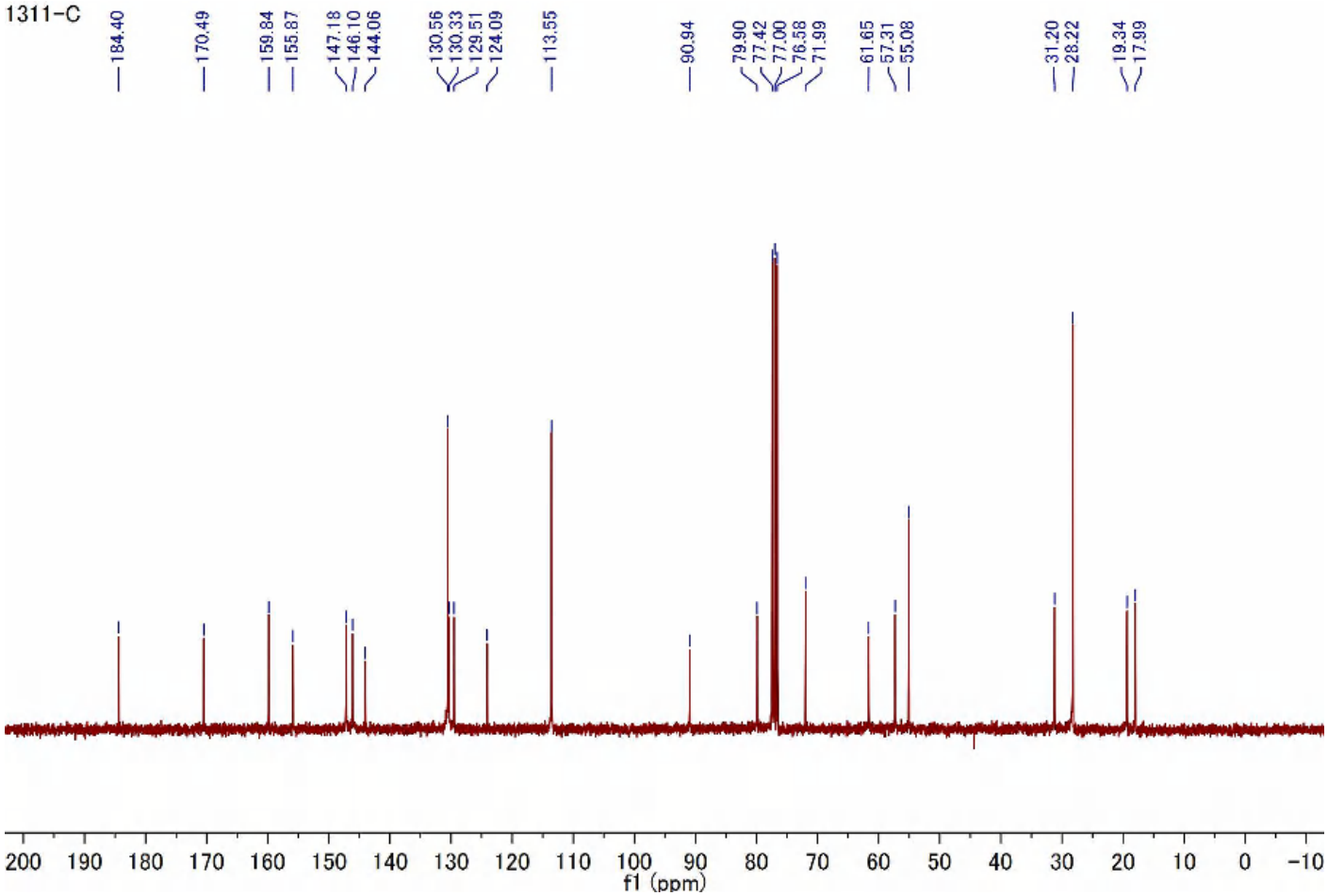
Compound **7f** (^{13}C NMR, 75 MHz, $CDCl_3$)



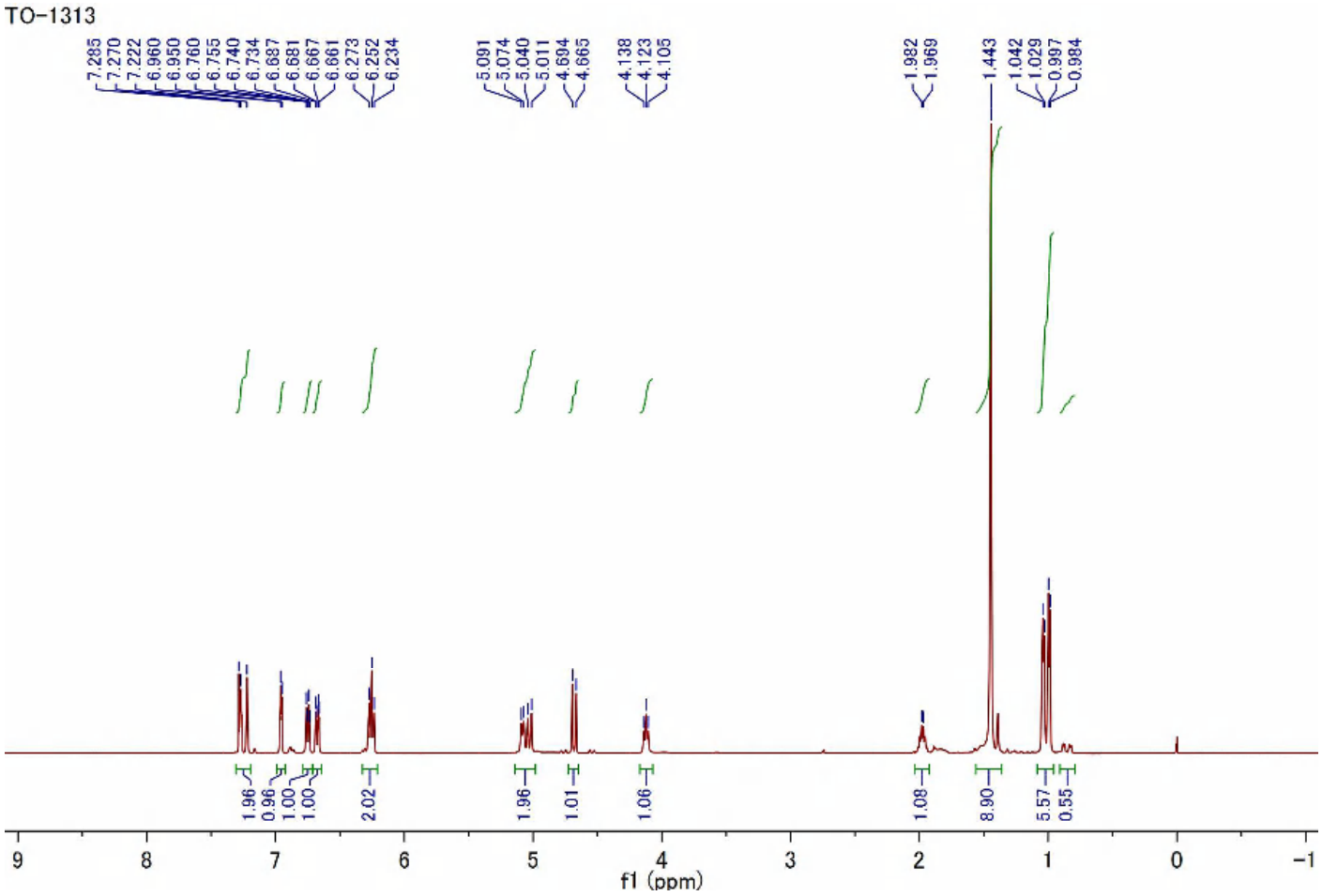
Compound **7g** (^{1}H NMR, 300 MHz, $CDCl_3$)



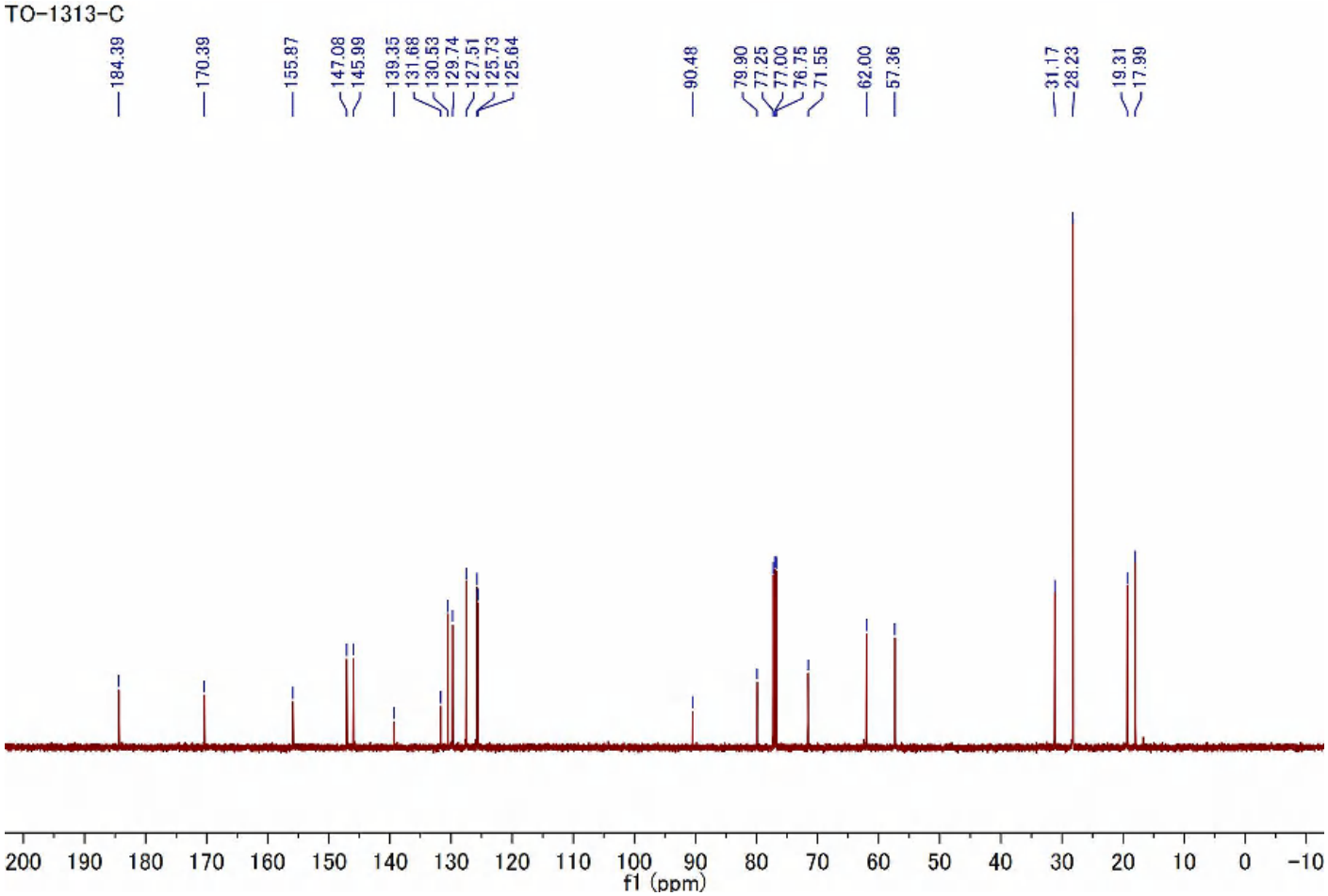
Compound **7g** (^{13}C NMR, 75 MHz, $CDCl_3$)



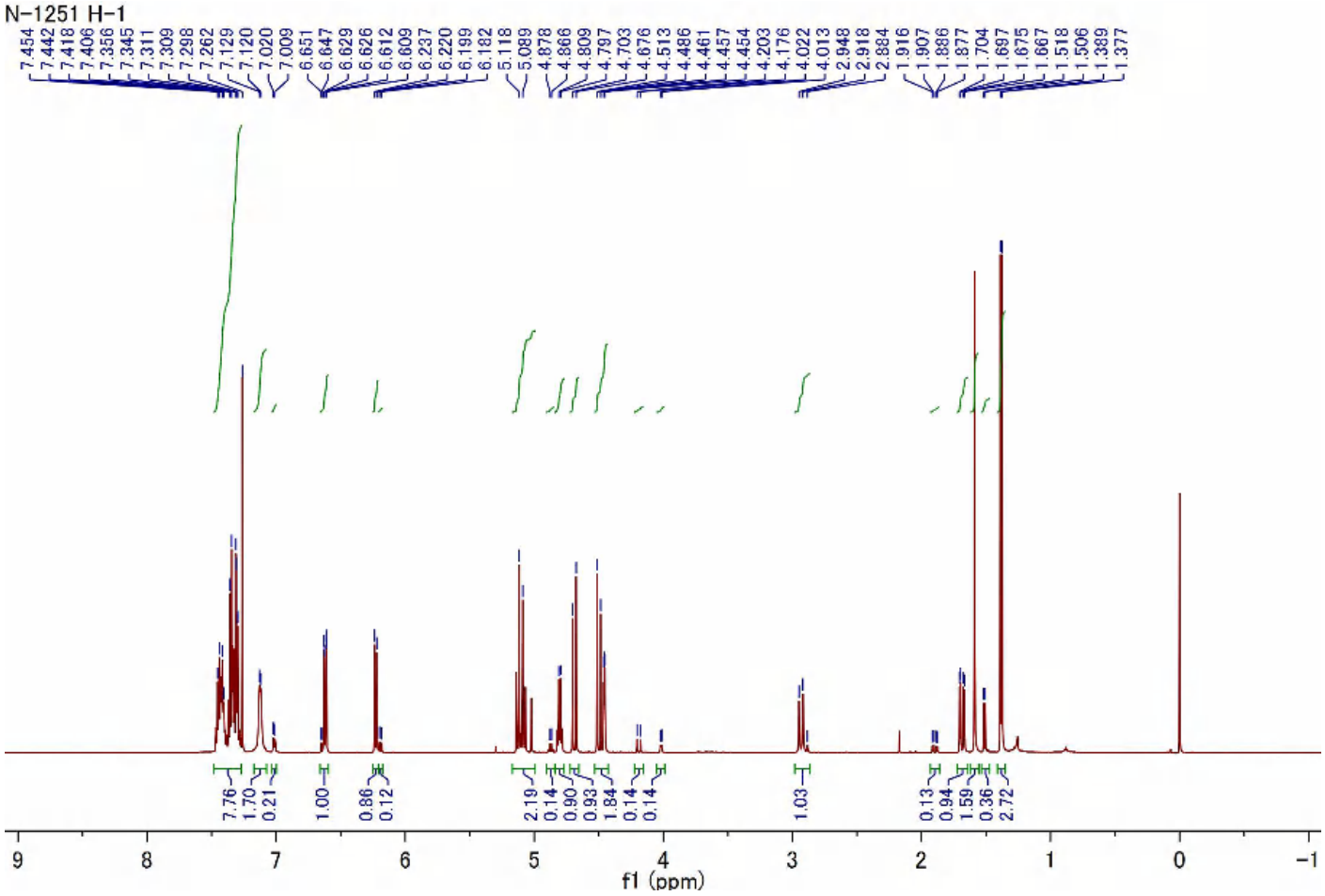
Compound **7h** (^{1}H NMR, 500 MHz, $CDCl_3$)



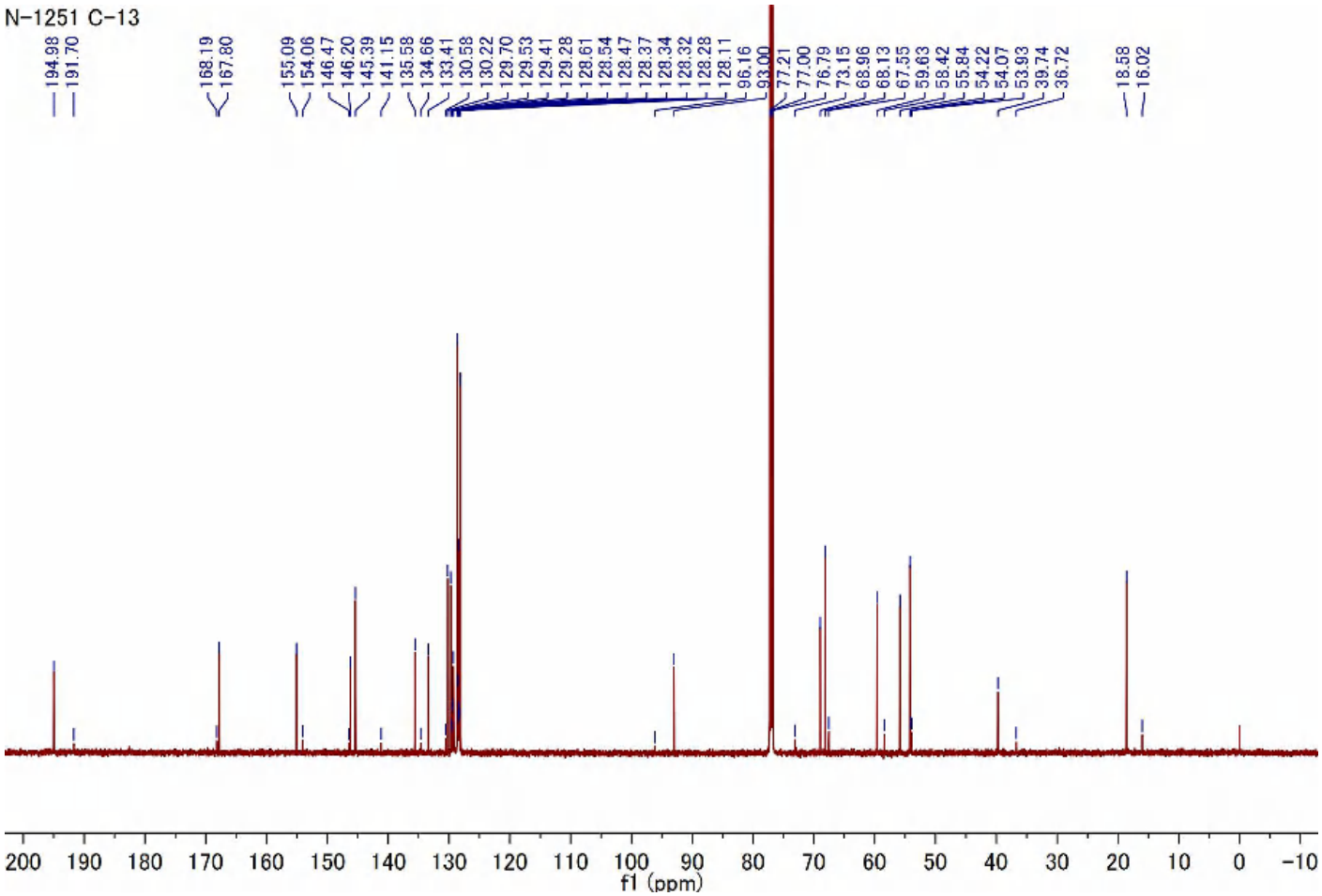
Compound **7h** (^{13}C NMR, 125 MHz, $CDCl_3$)



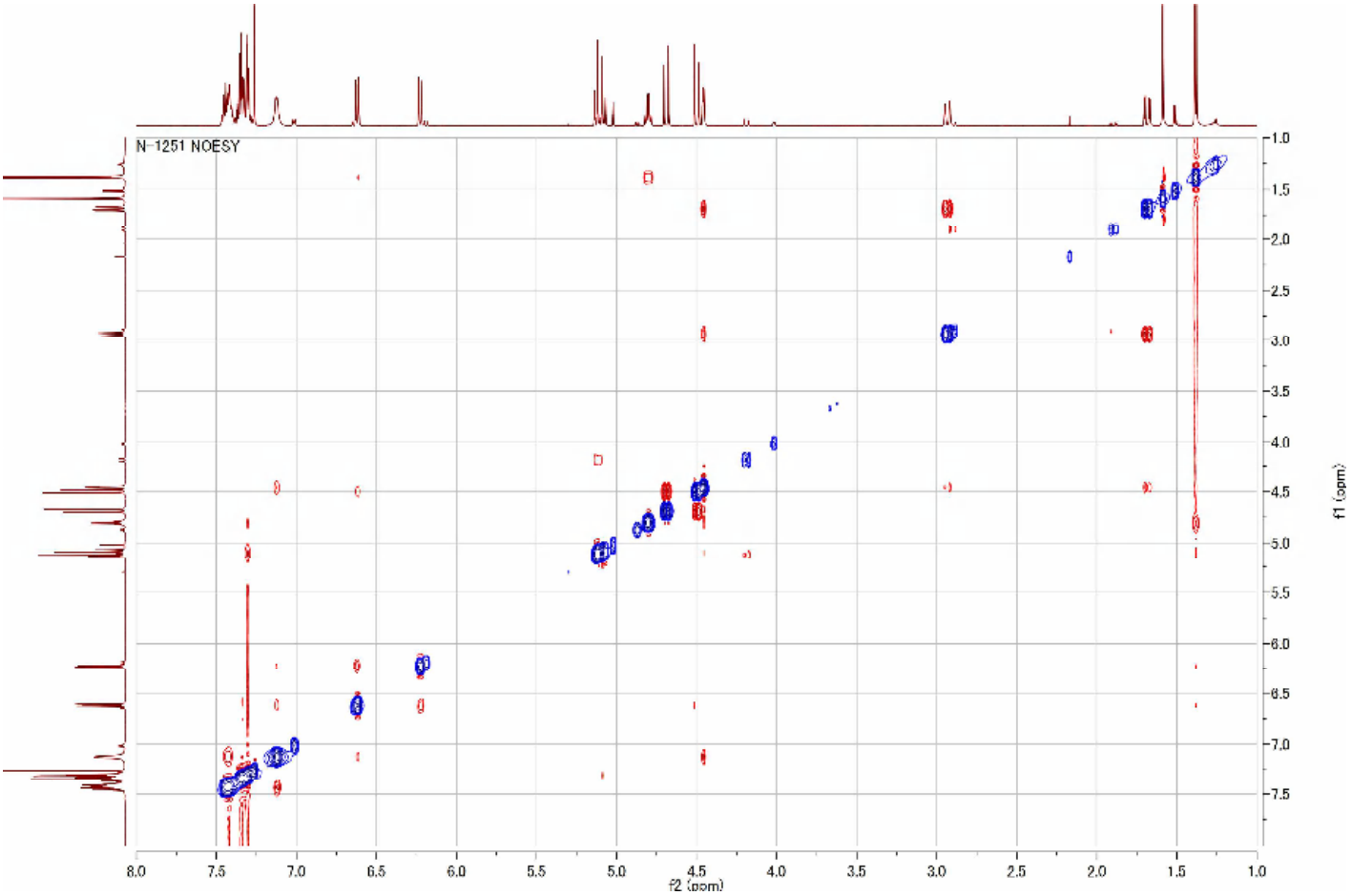
Compounds **8a** + **9a** (^{1}H NMR, 600 MHz, $CDCl_3$)



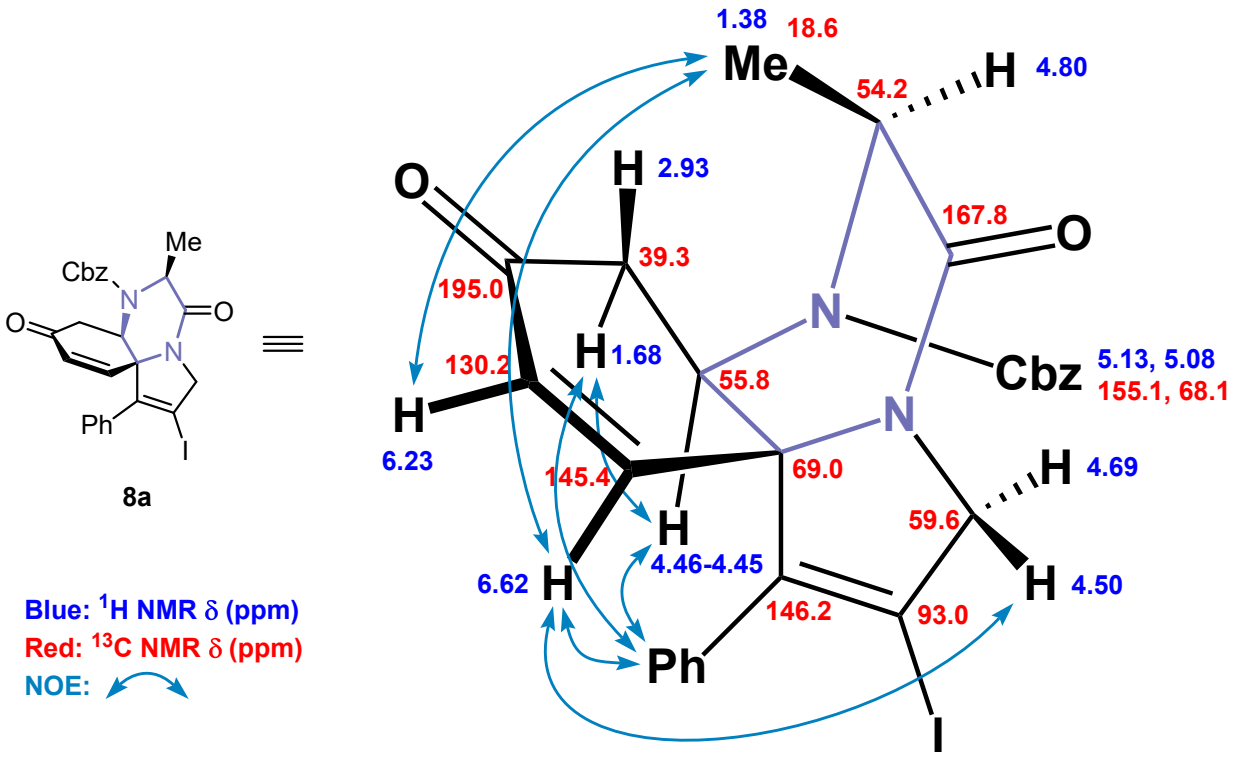
Compounds **8a** + **9a** (^{13}C NMR, 150 MHz, $CDCl_3$)



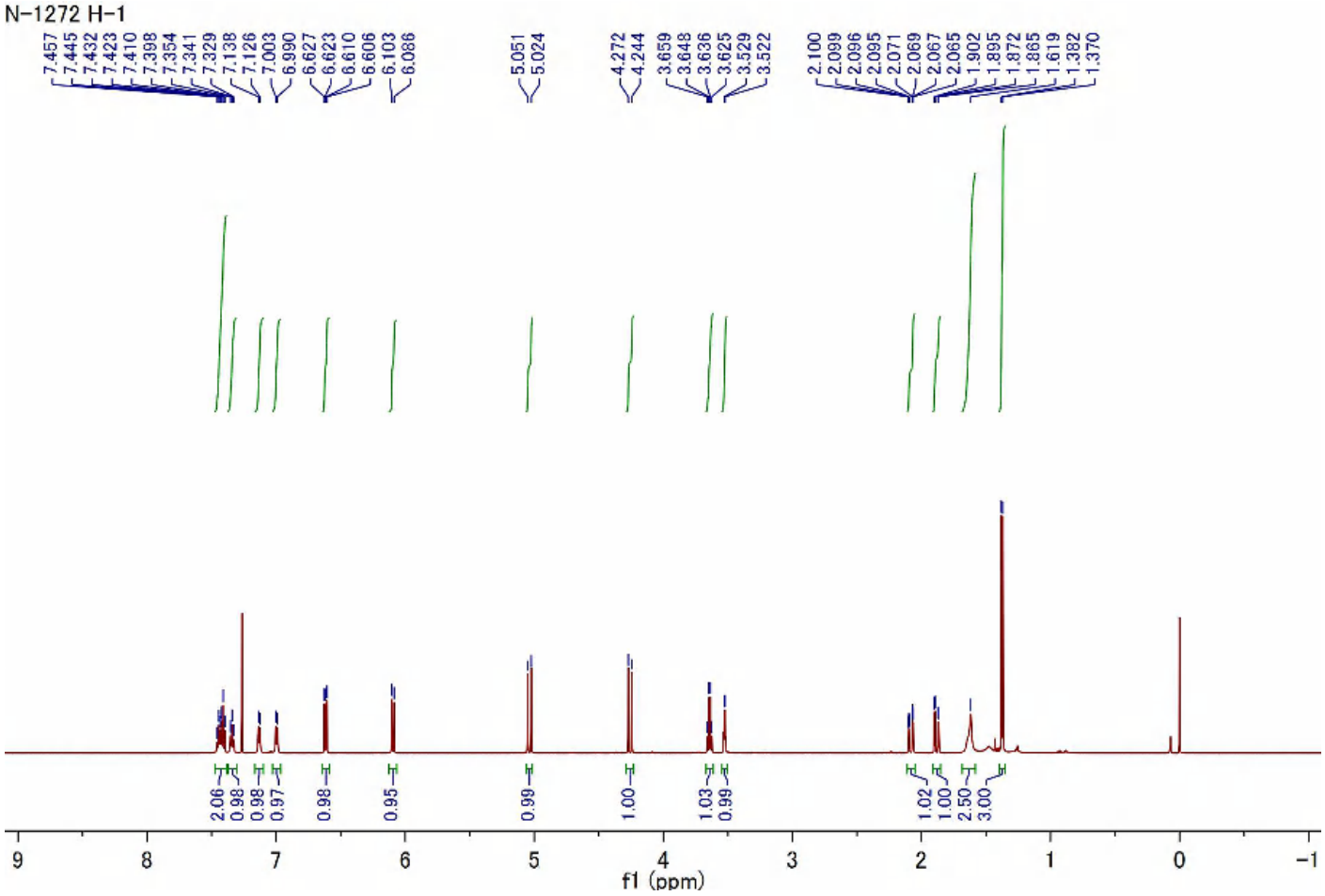
Compounds **8a** + **9a** (NOESY, $CDCl_3$)



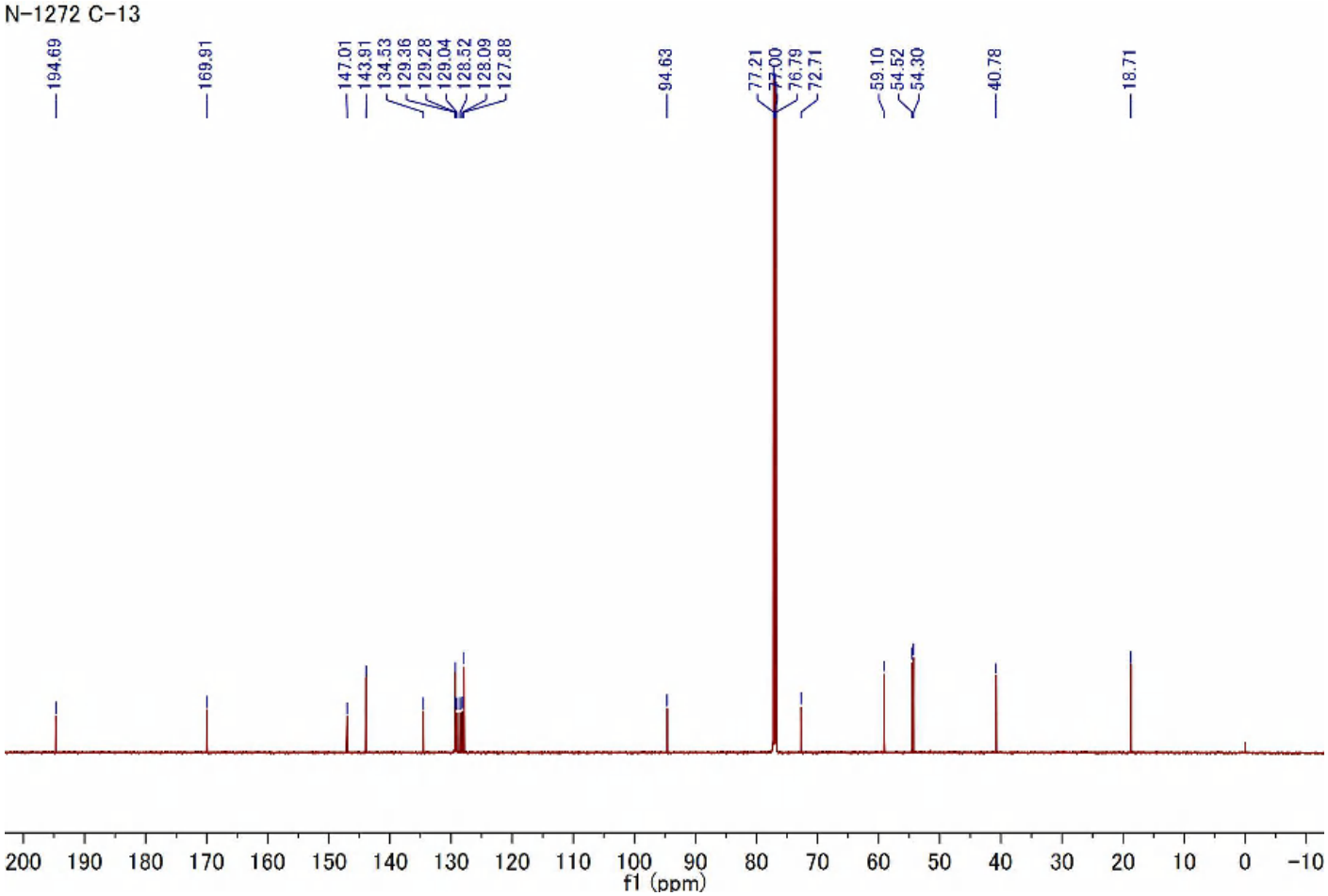
Structure Determination of Compound **8a**



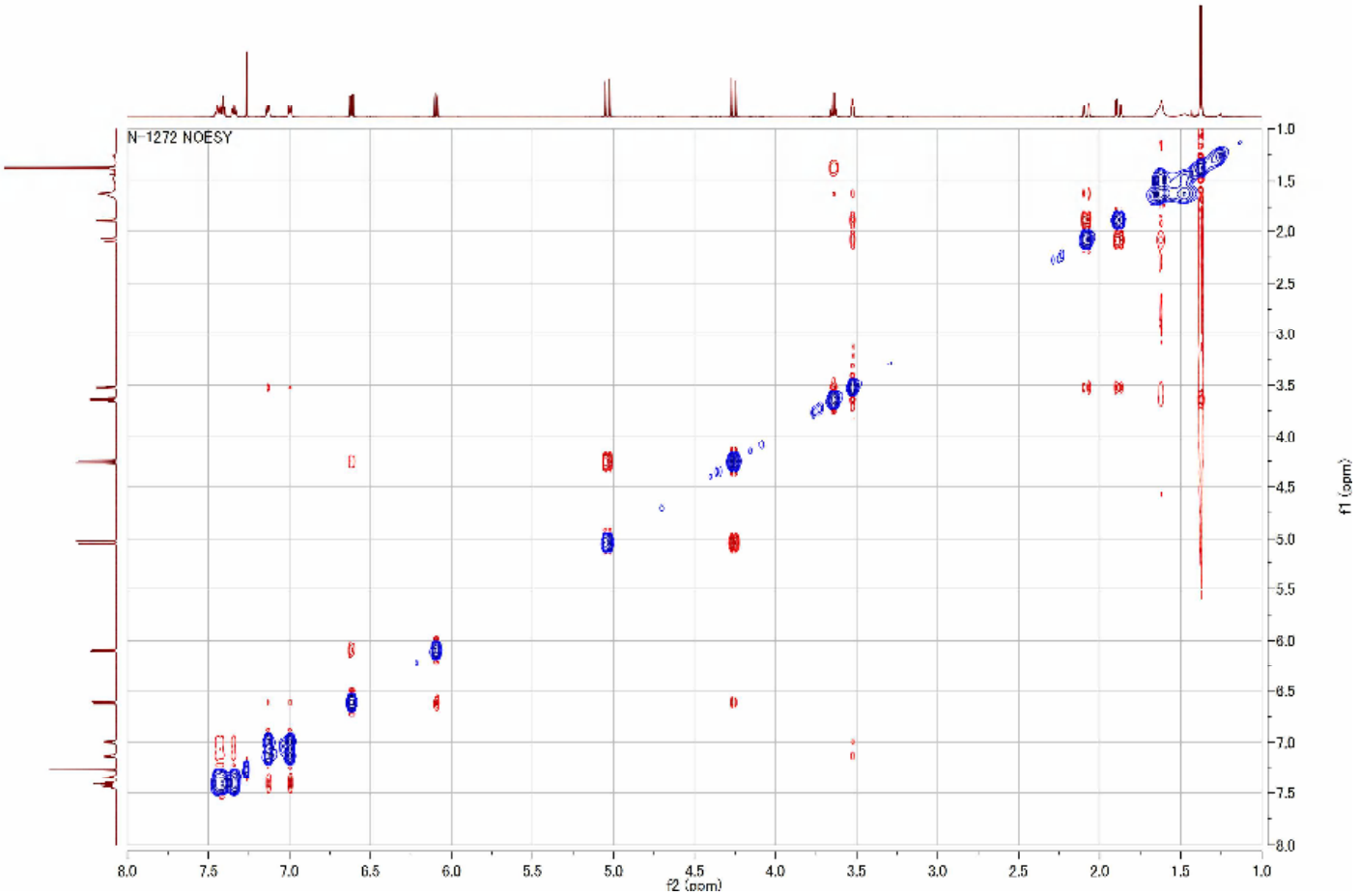
Compound **8b** (^{1}H NMR, 600 MHz, $CDCl_3$)



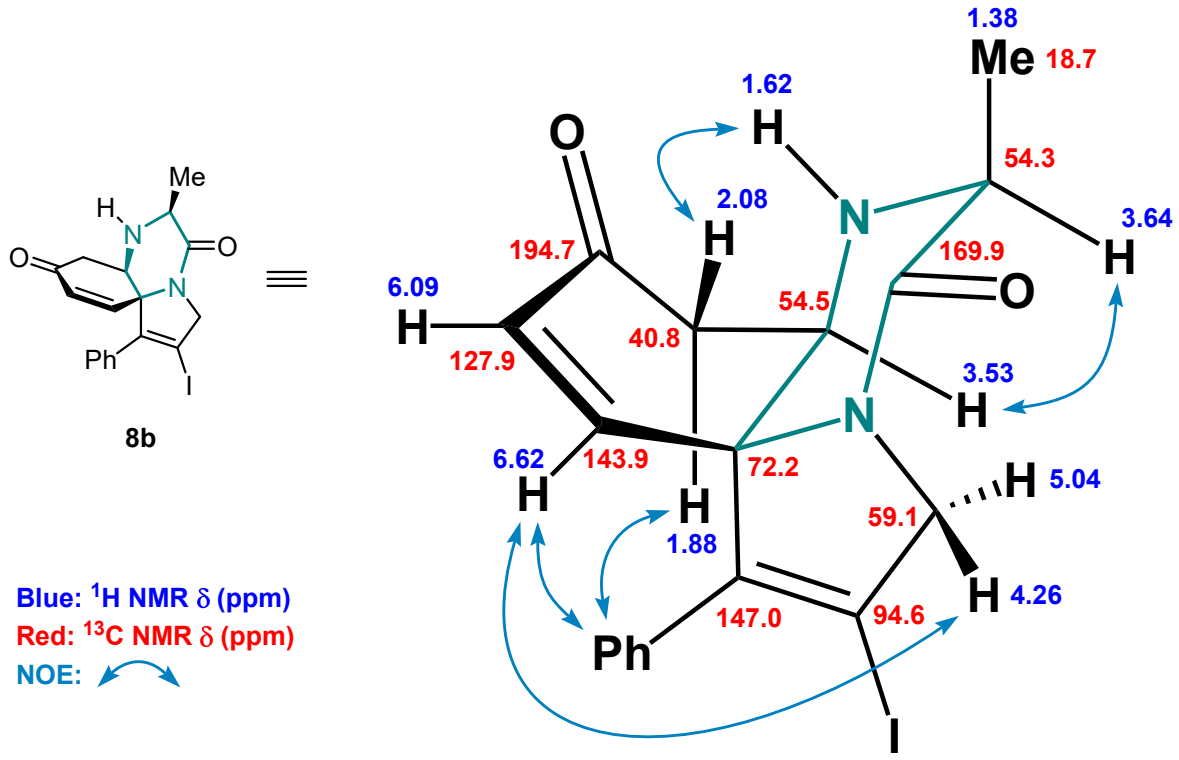
Compound **8b** (^{13}C NMR, 150 MHz, $CDCl_3$)



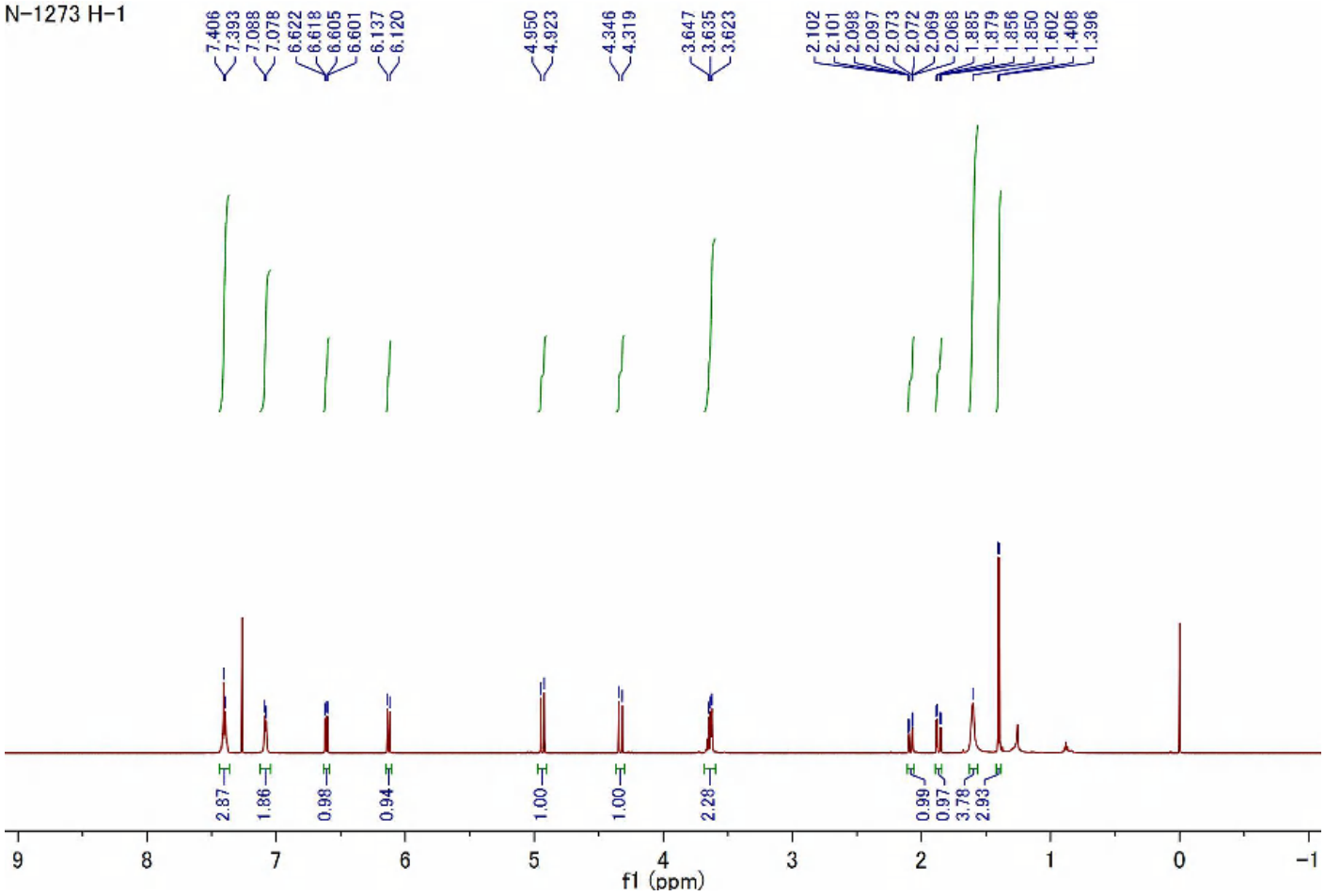
Compound **8b** (NOESY, $CDCl_3$)



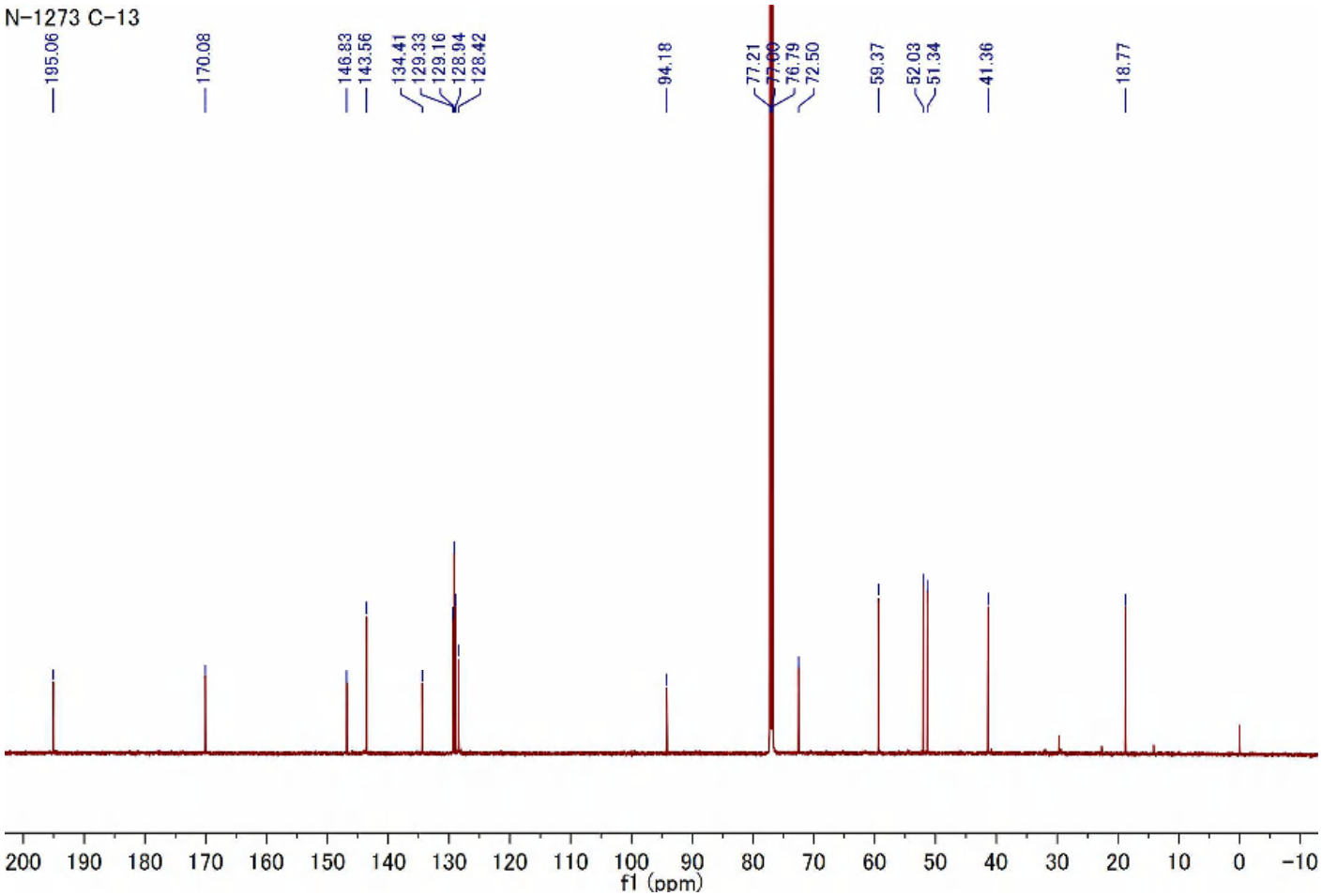
Structure Determination of Compound **8b**



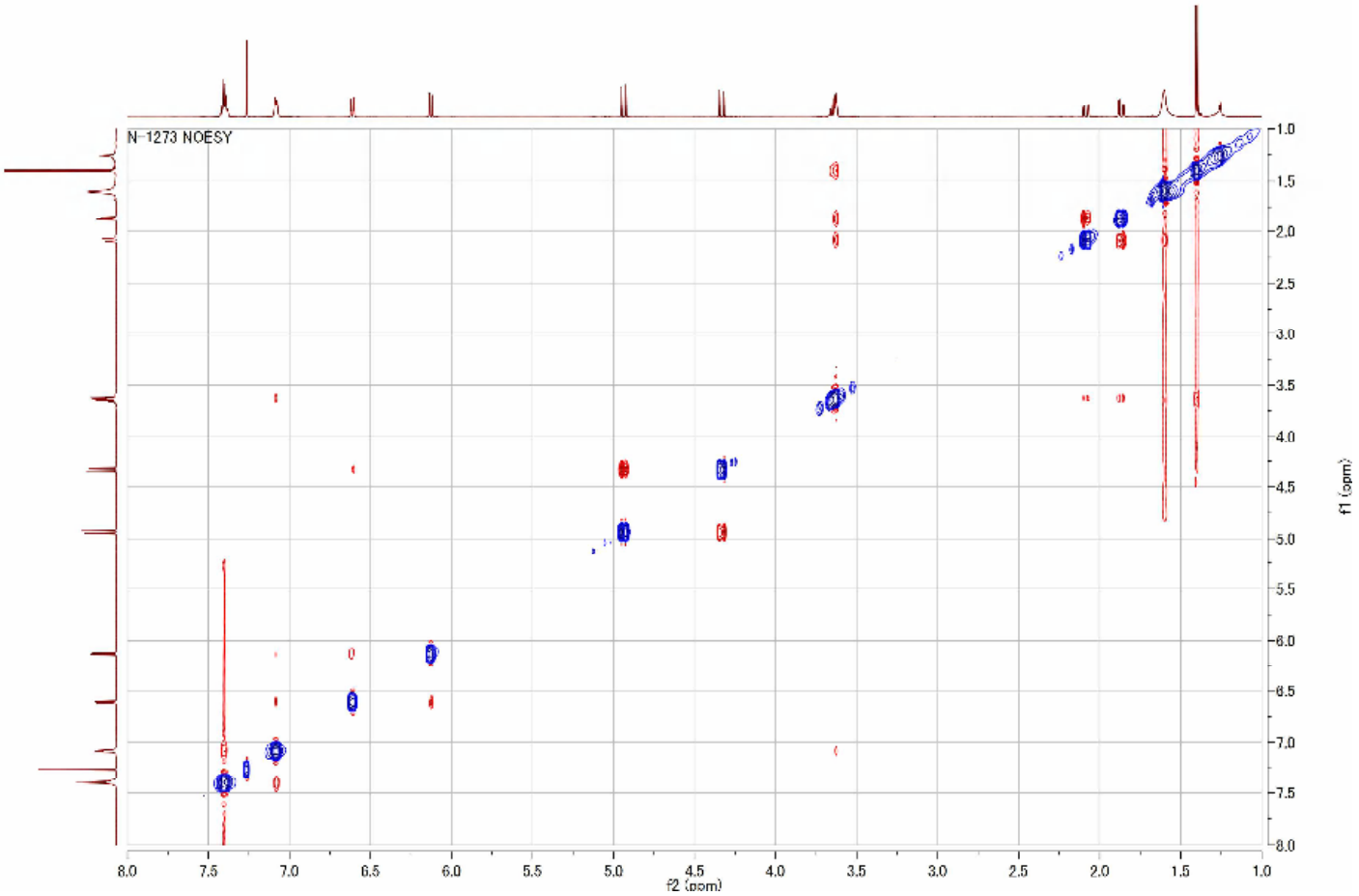
Compound **9b** (^{1}H NMR, 600 MHz, $CDCl_3$)



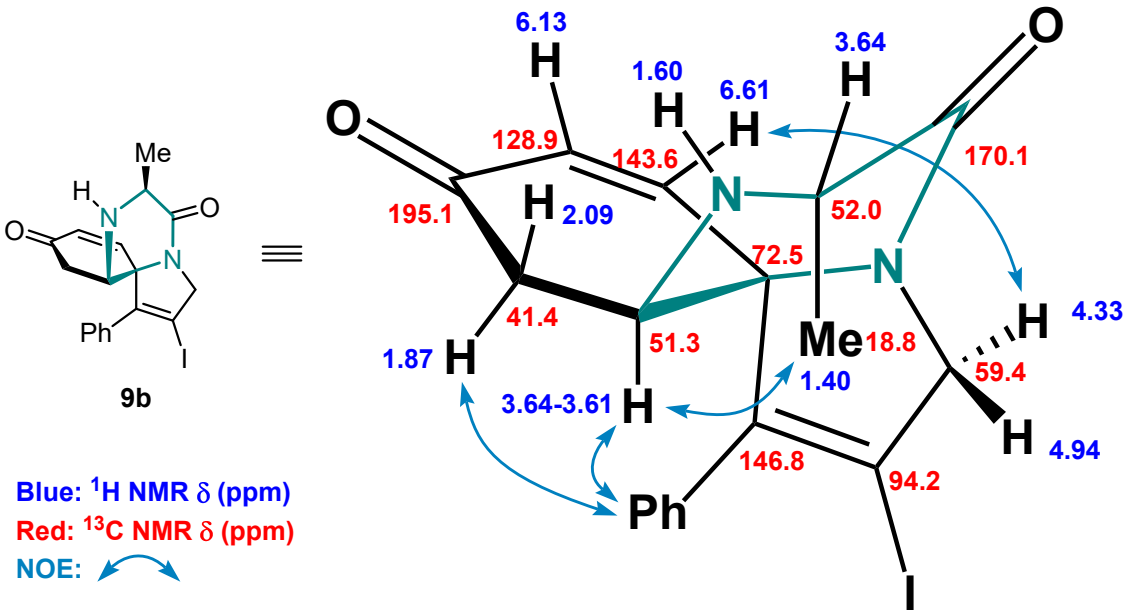
Compound **9b** (^{13}C NMR, 150 MHz, $CDCl_3$)



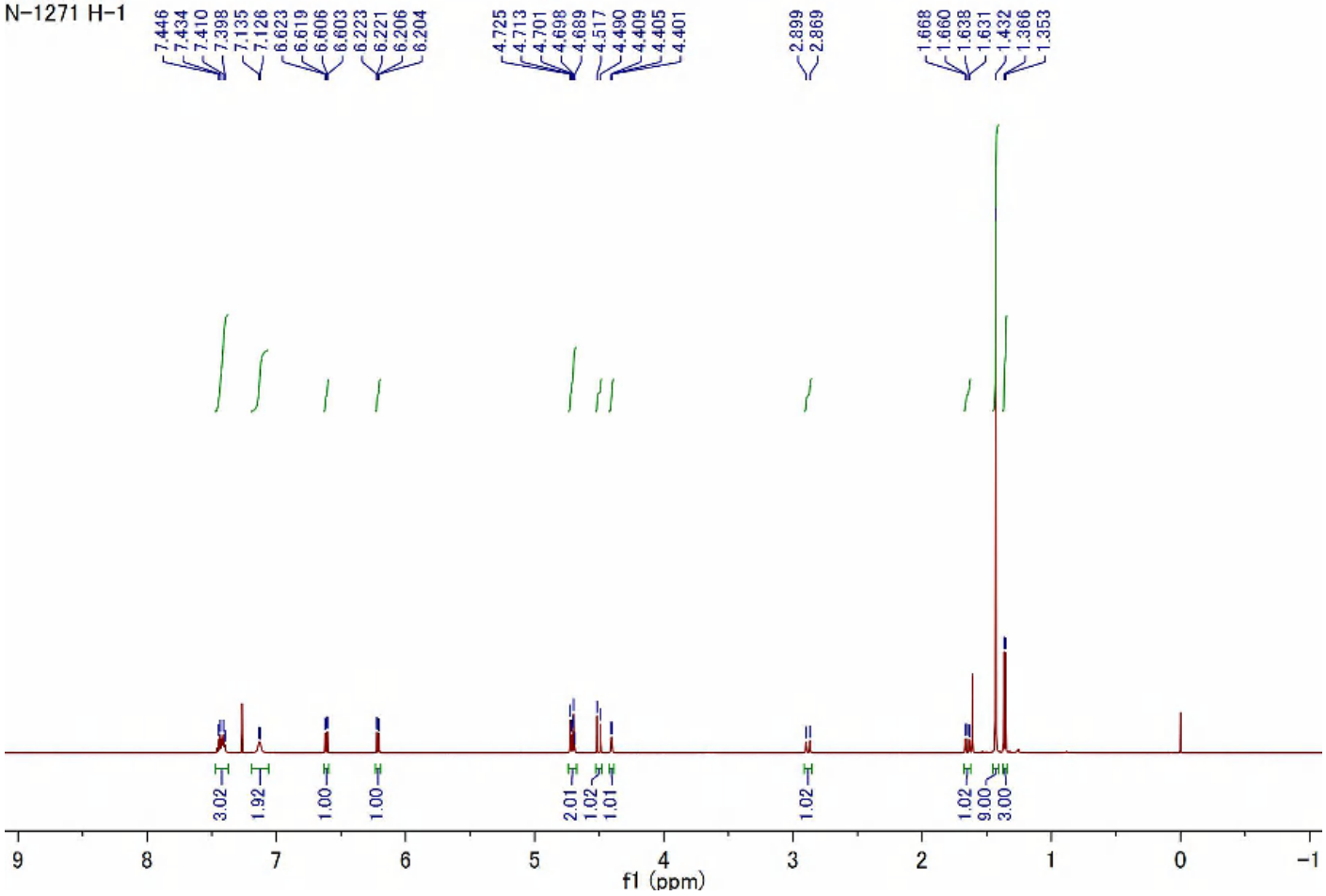
Compound **9b** (NOESY, $CDCl_3$)



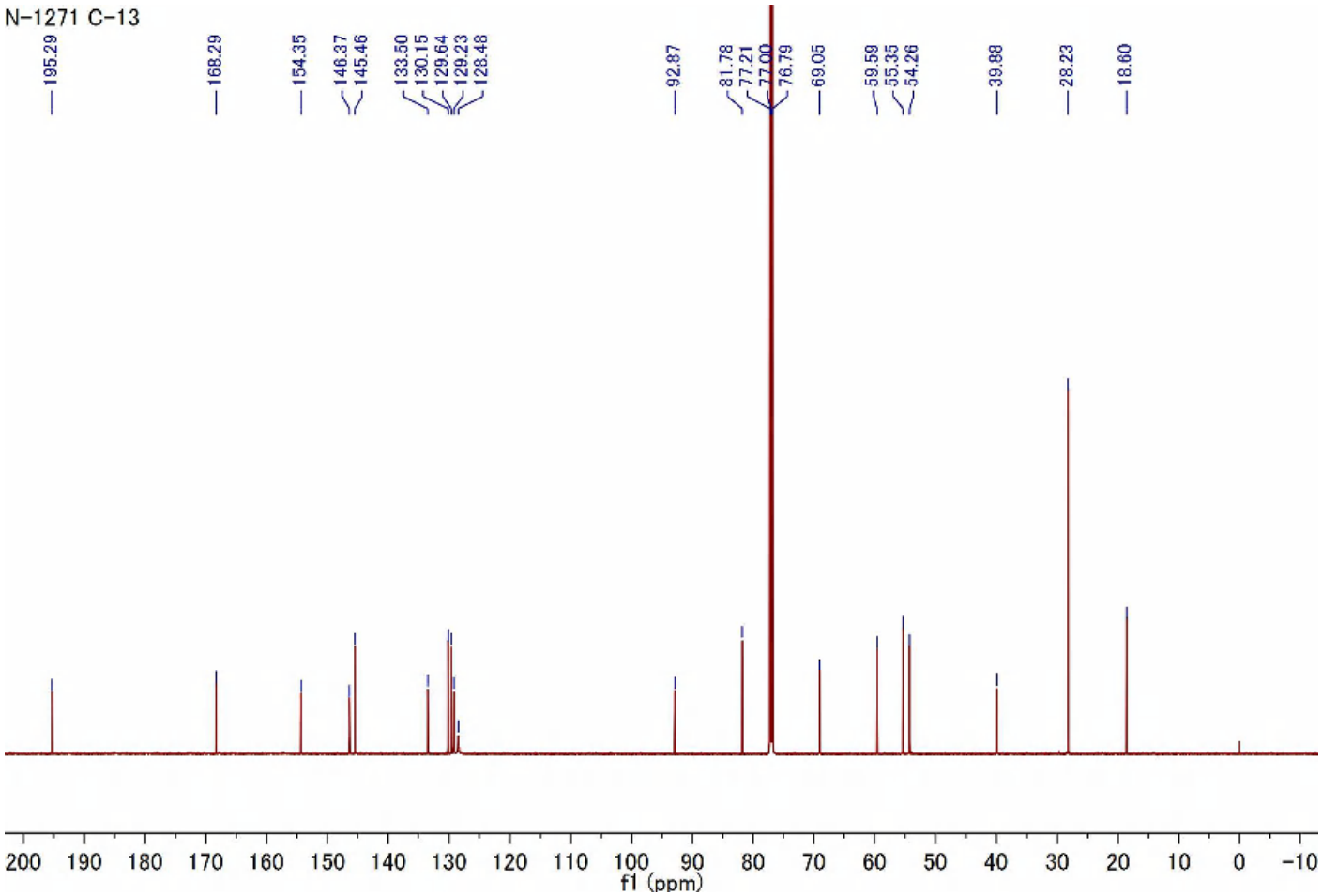
Structure Determination of Compound **9b**



Compound **8c** (^{1}H NMR, 600 MHz, $CDCl_3$)



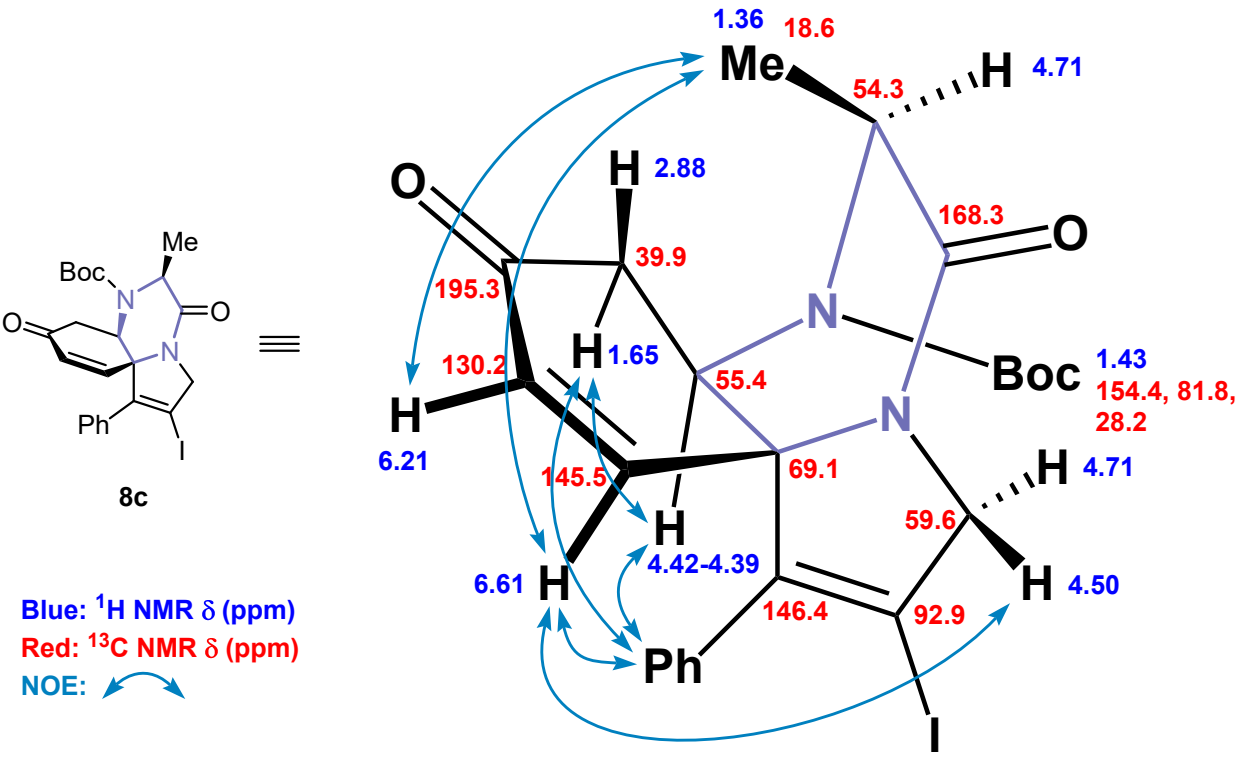
Compound **8c** (^{13}C NMR, 150 MHz, $CDCl_3$)



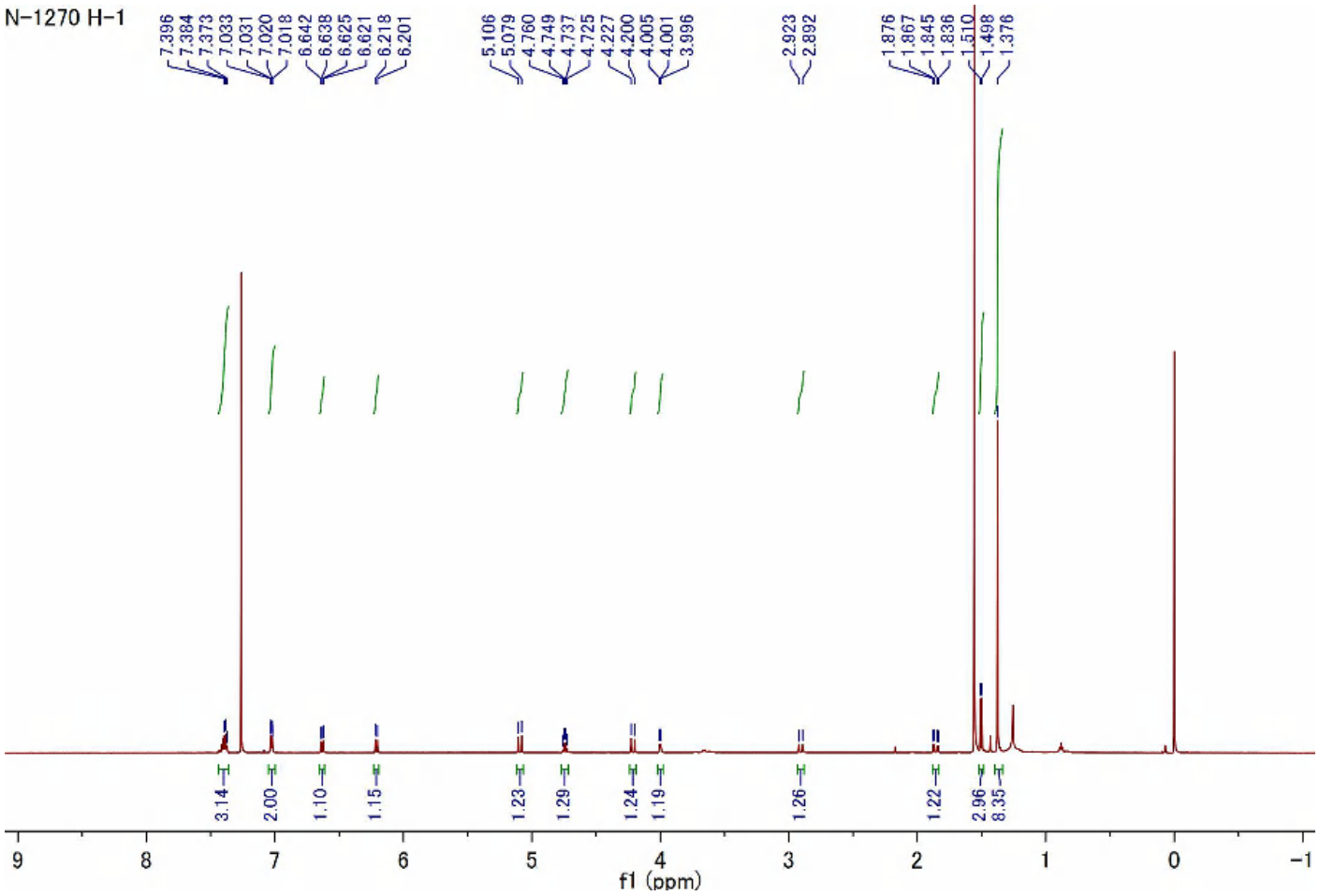
Compound **8c** (NOESY, $CDCl_3$)

Structure Determination of Compound **8c**

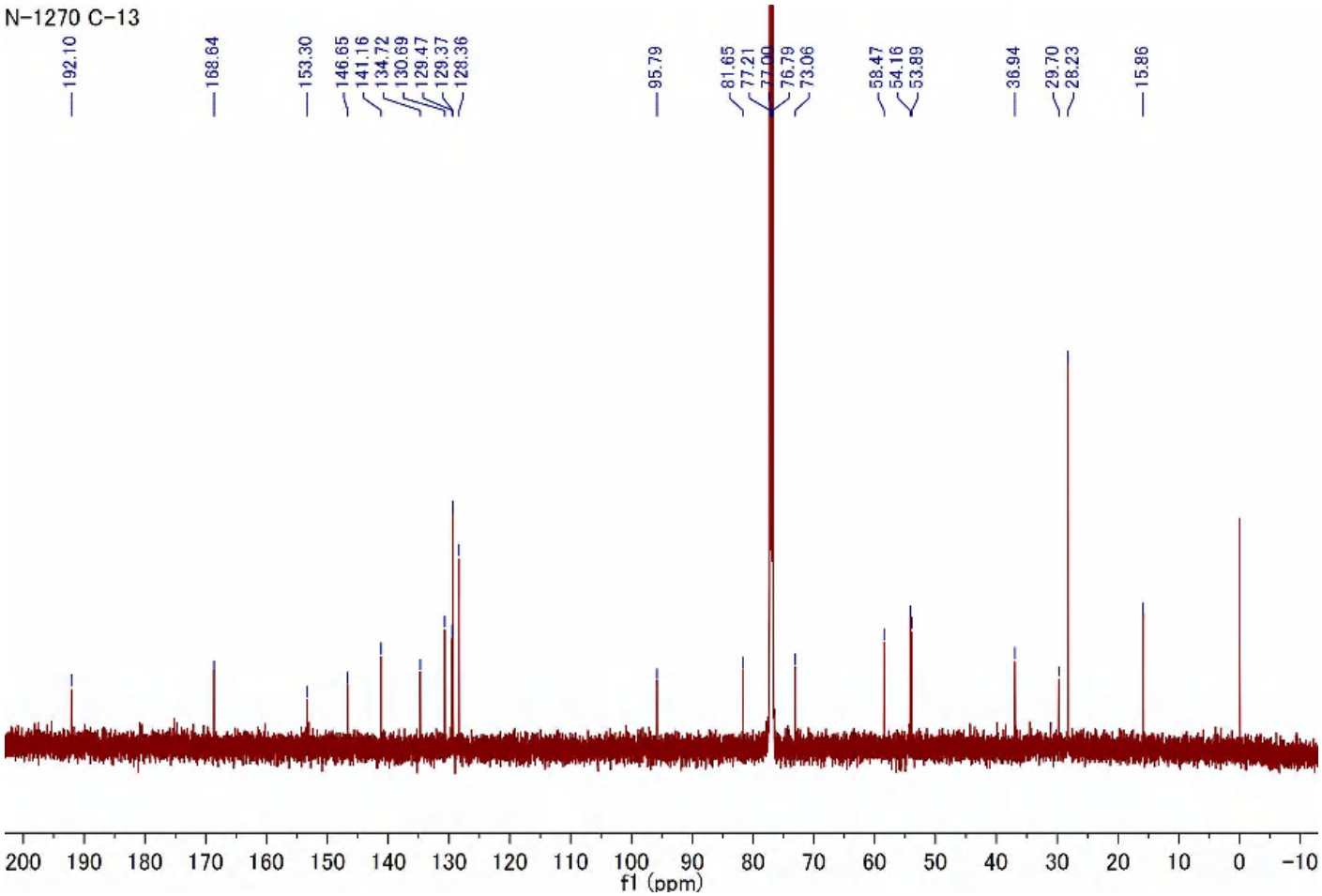
8c



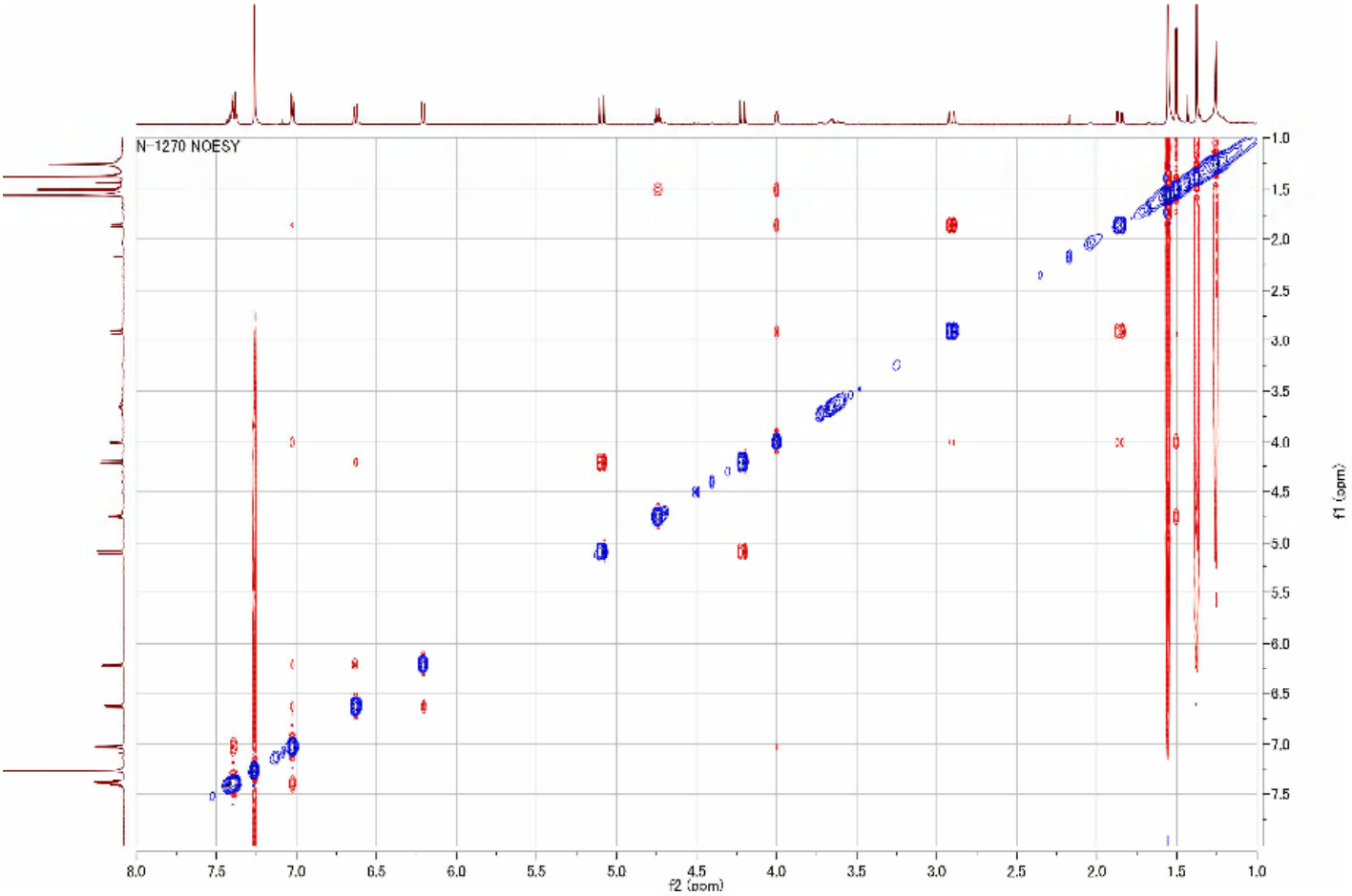
Compound **9c** (^{1}H NMR, 600 MHz, $CDCl_3$)



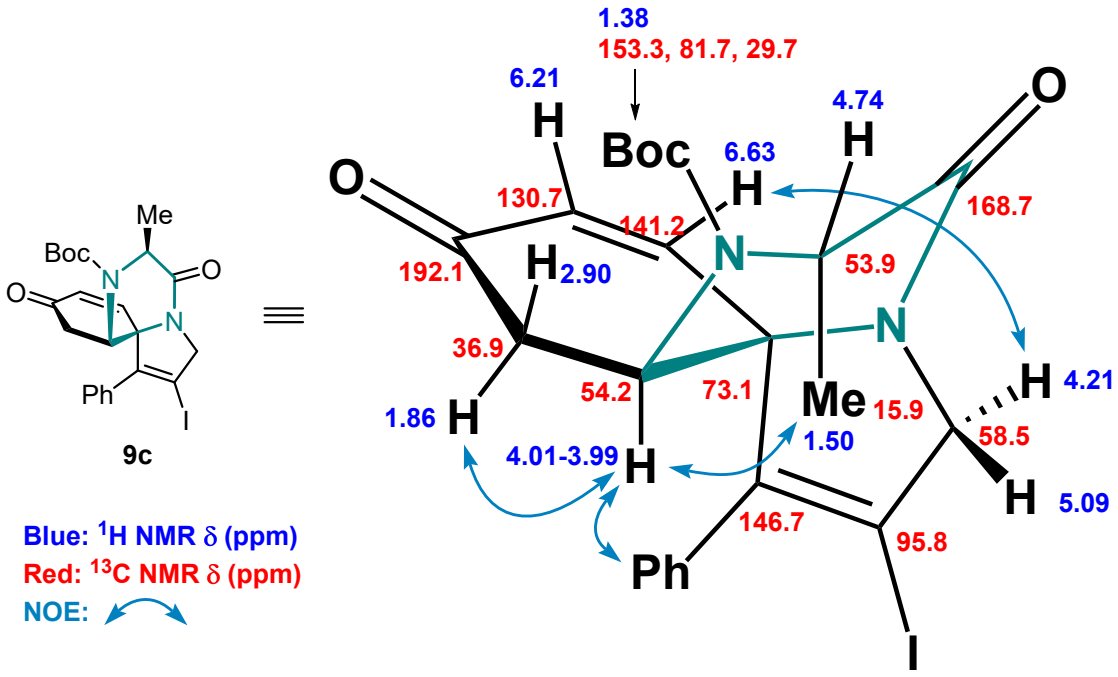
Compound **9c** (^{13}C NMR, 150 MHz, $CDCl_3$)



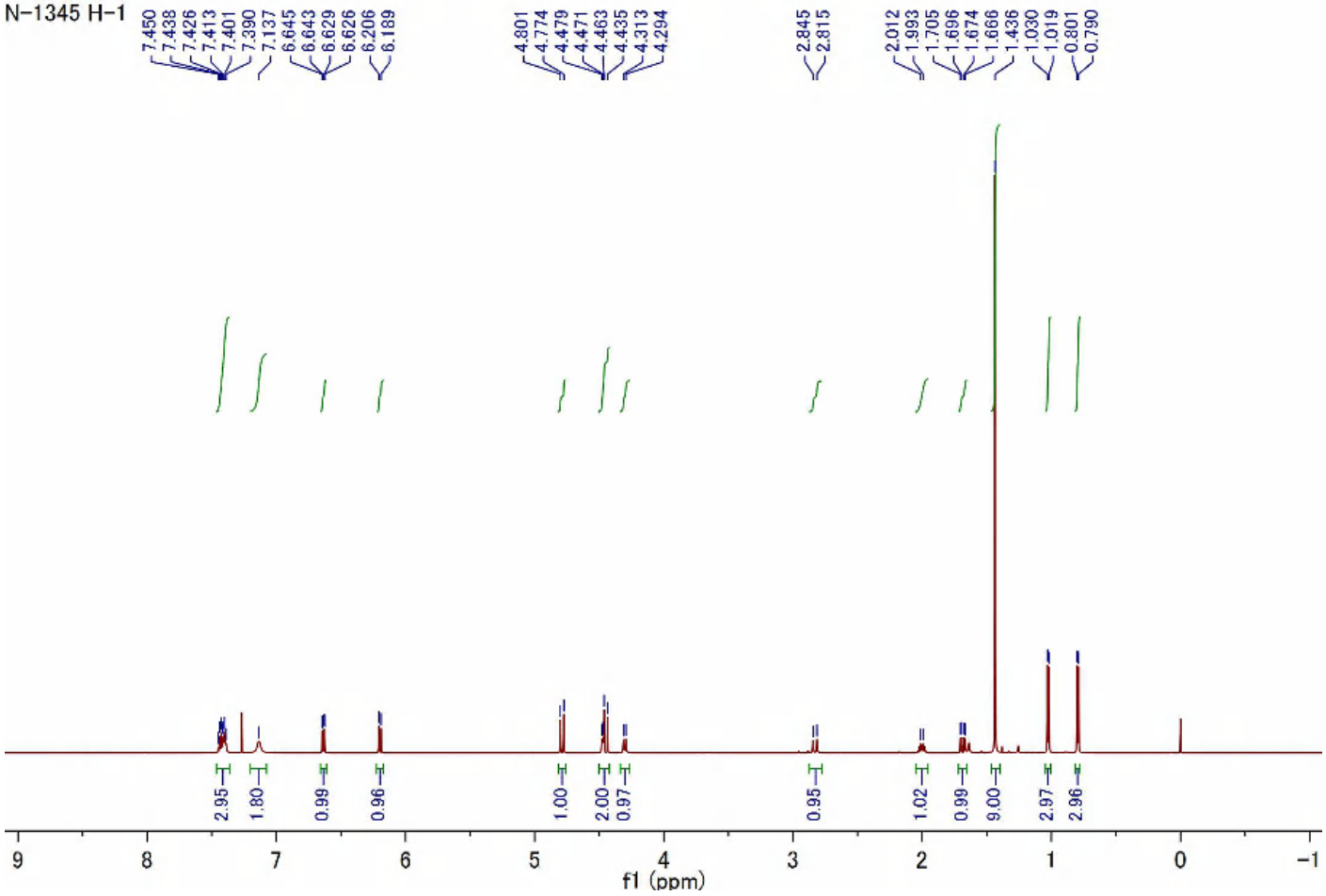
Compound **9c** (NOESY, $CDCl_3$)



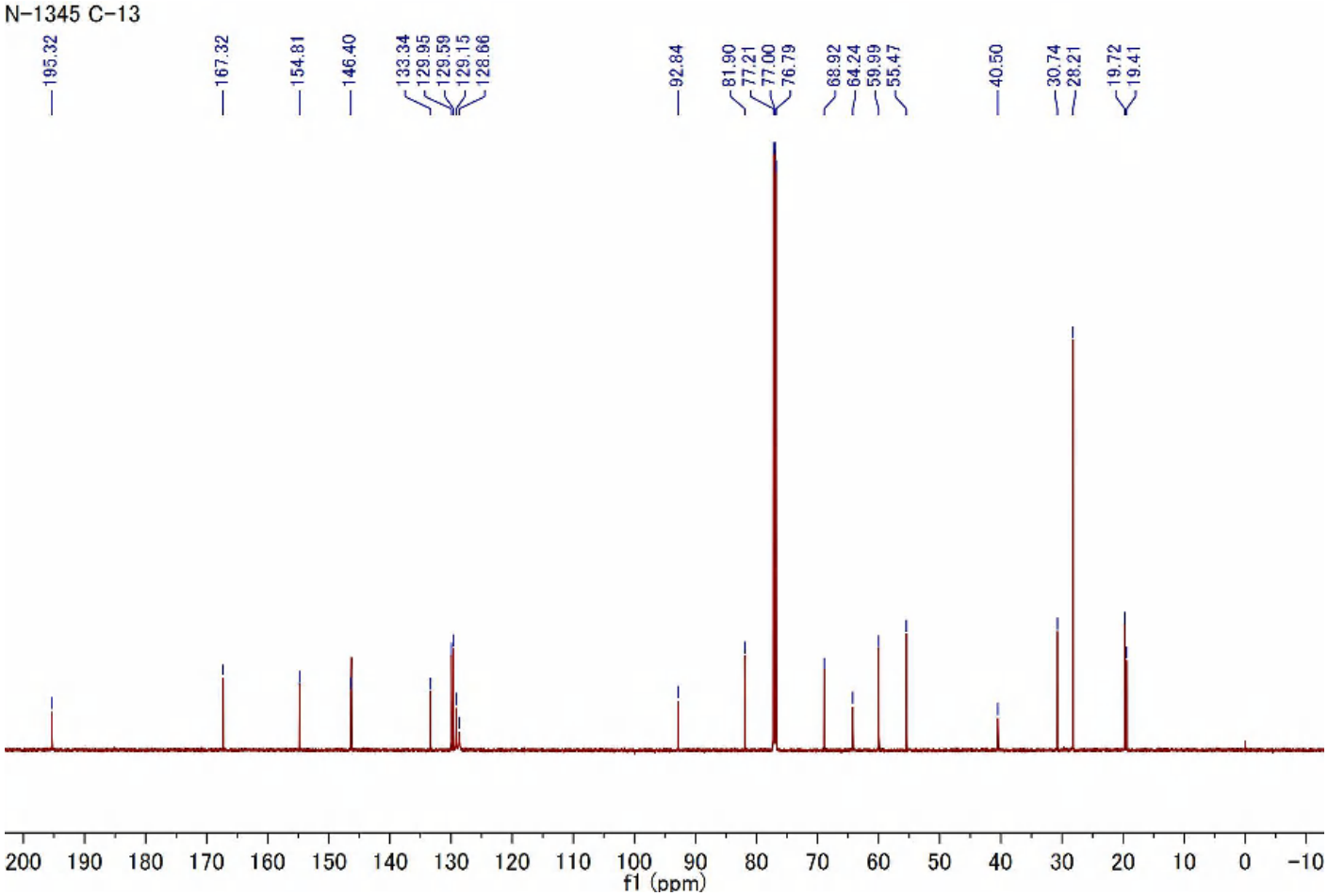
Structure Determination of Compound **9c**



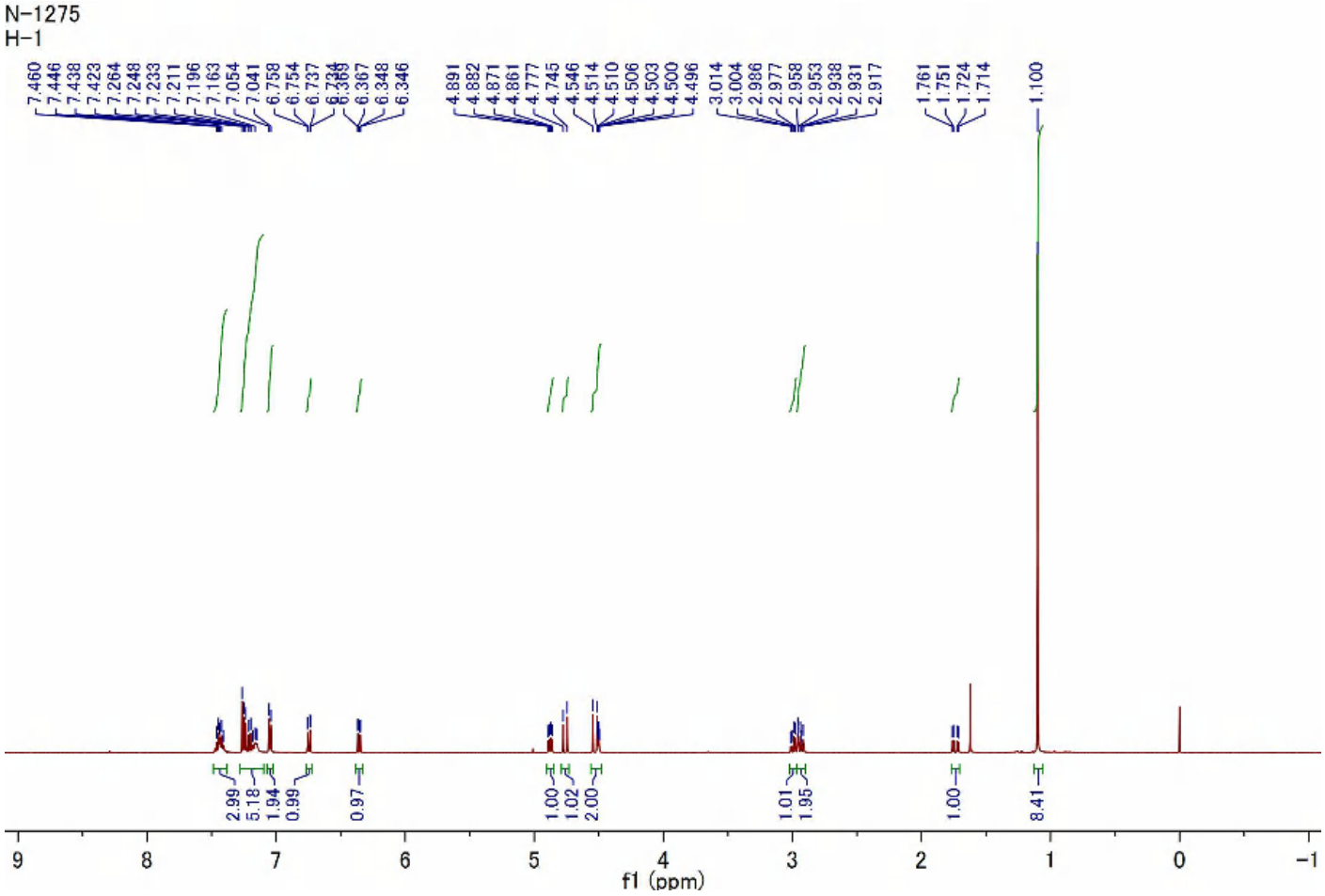
Compound **8d** (^{1}H NMR, 600 MHz, $CDCl_3$)



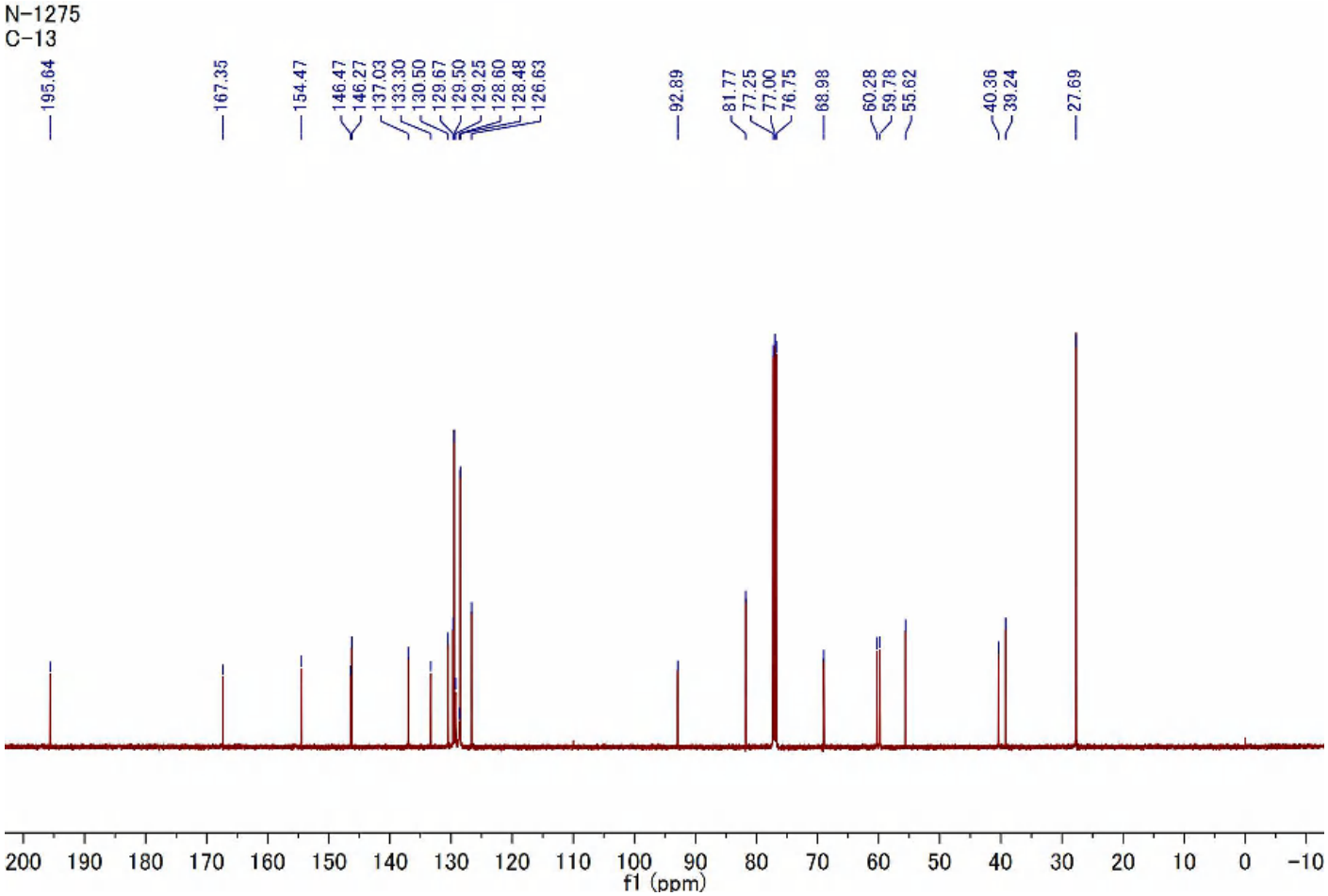
Compound **8d** (^{13}C NMR, 150 MHz, $CDCl_3$)



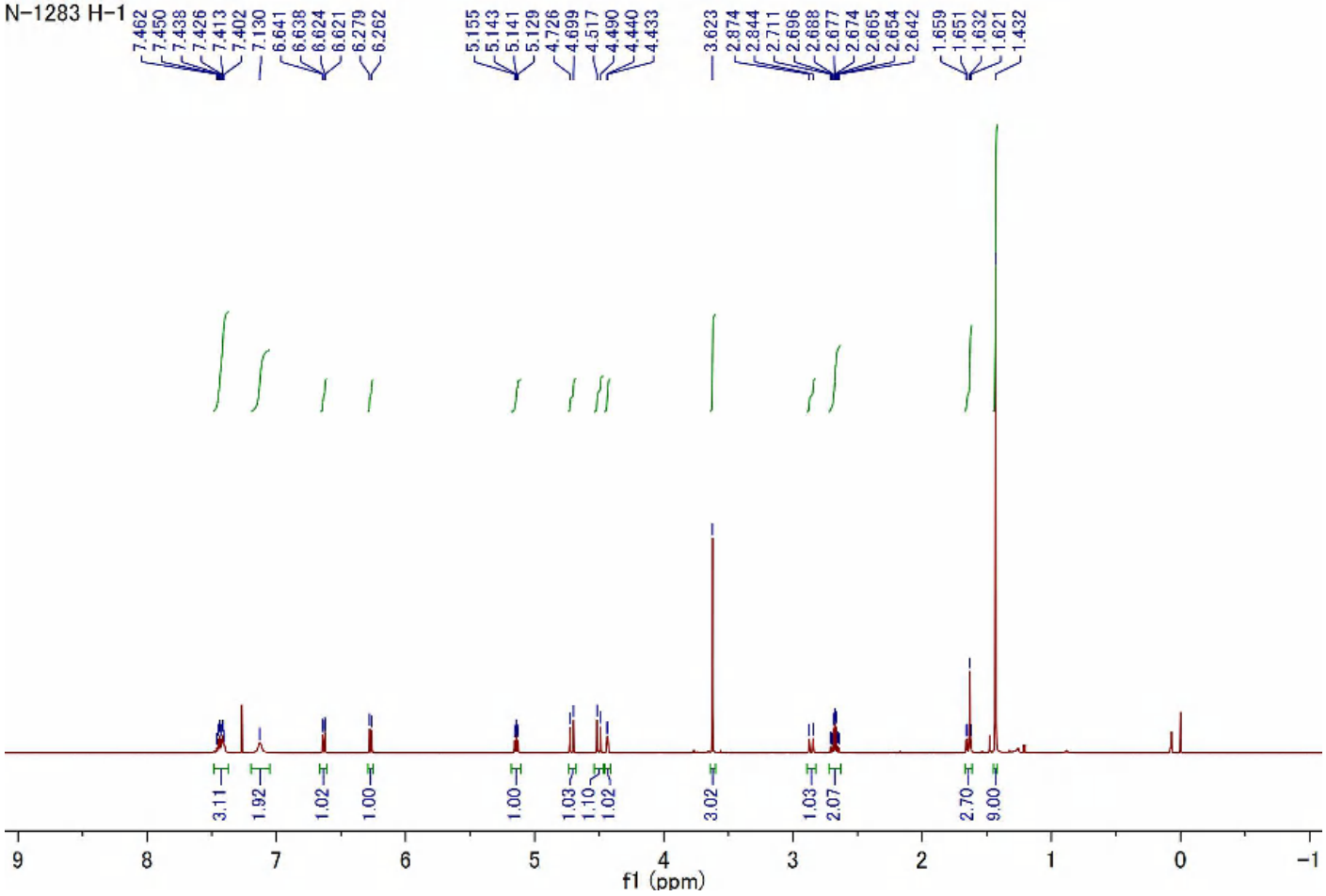
Compound **8e** (^{1}H NMR, 500 MHz, $CDCl_3$)



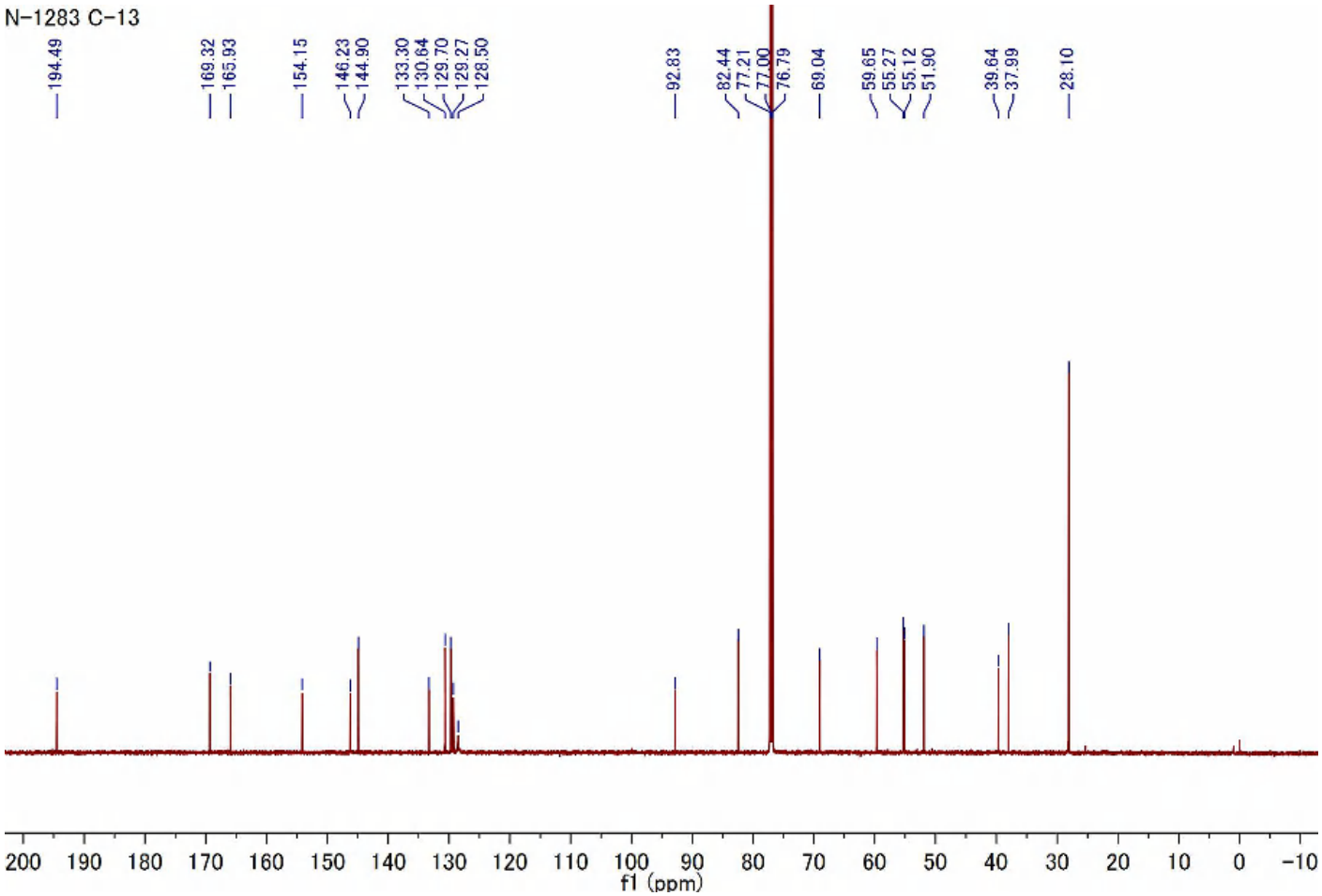
Compound **8e** (^{13}C NMR, 125 MHz, $CDCl_3$)



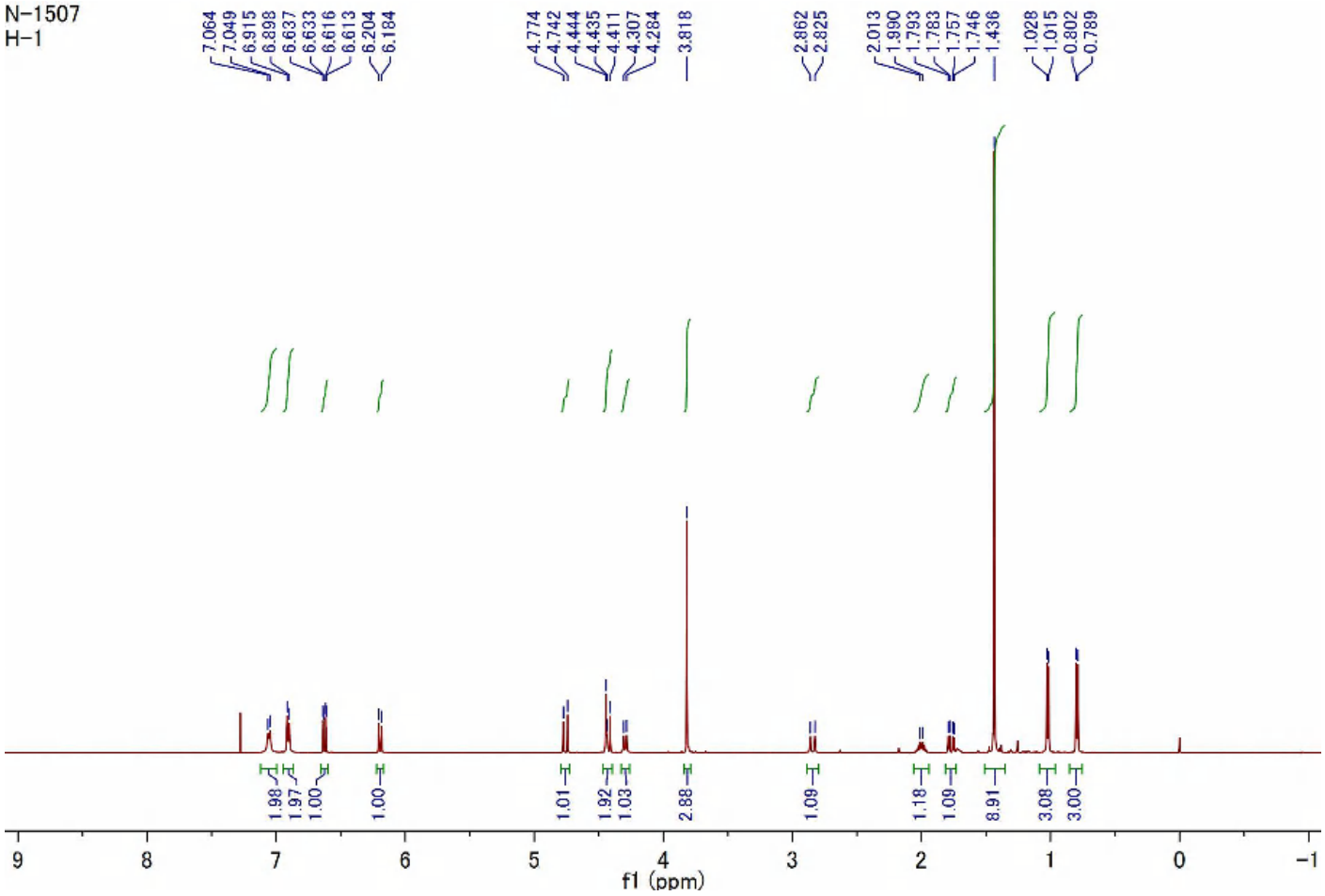
Compound **8f** (^{1}H NMR, 600 MHz, $CDCl_3$)



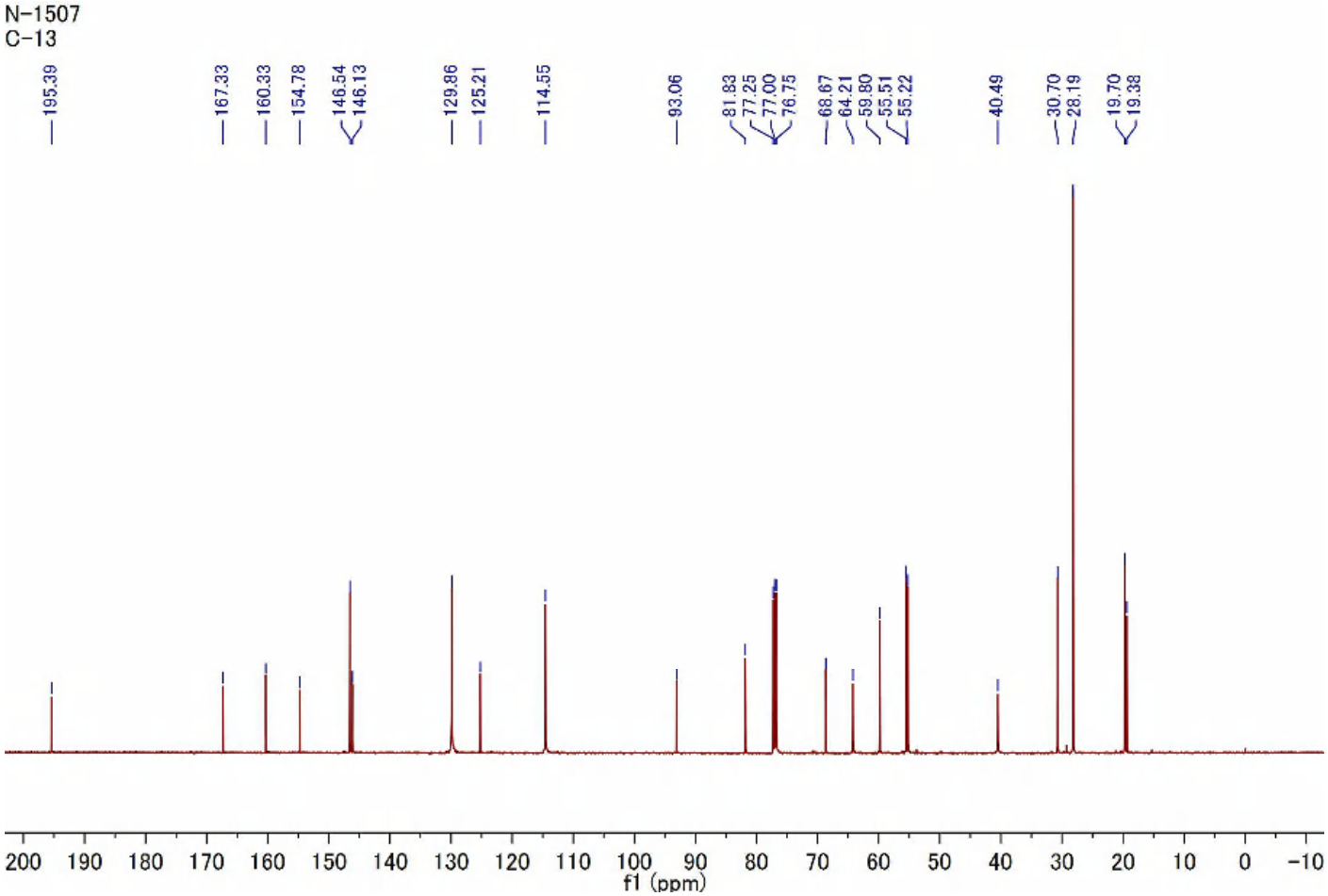
Compound **8f** (^{13}C NMR, 150 MHz, $CDCl_3$)



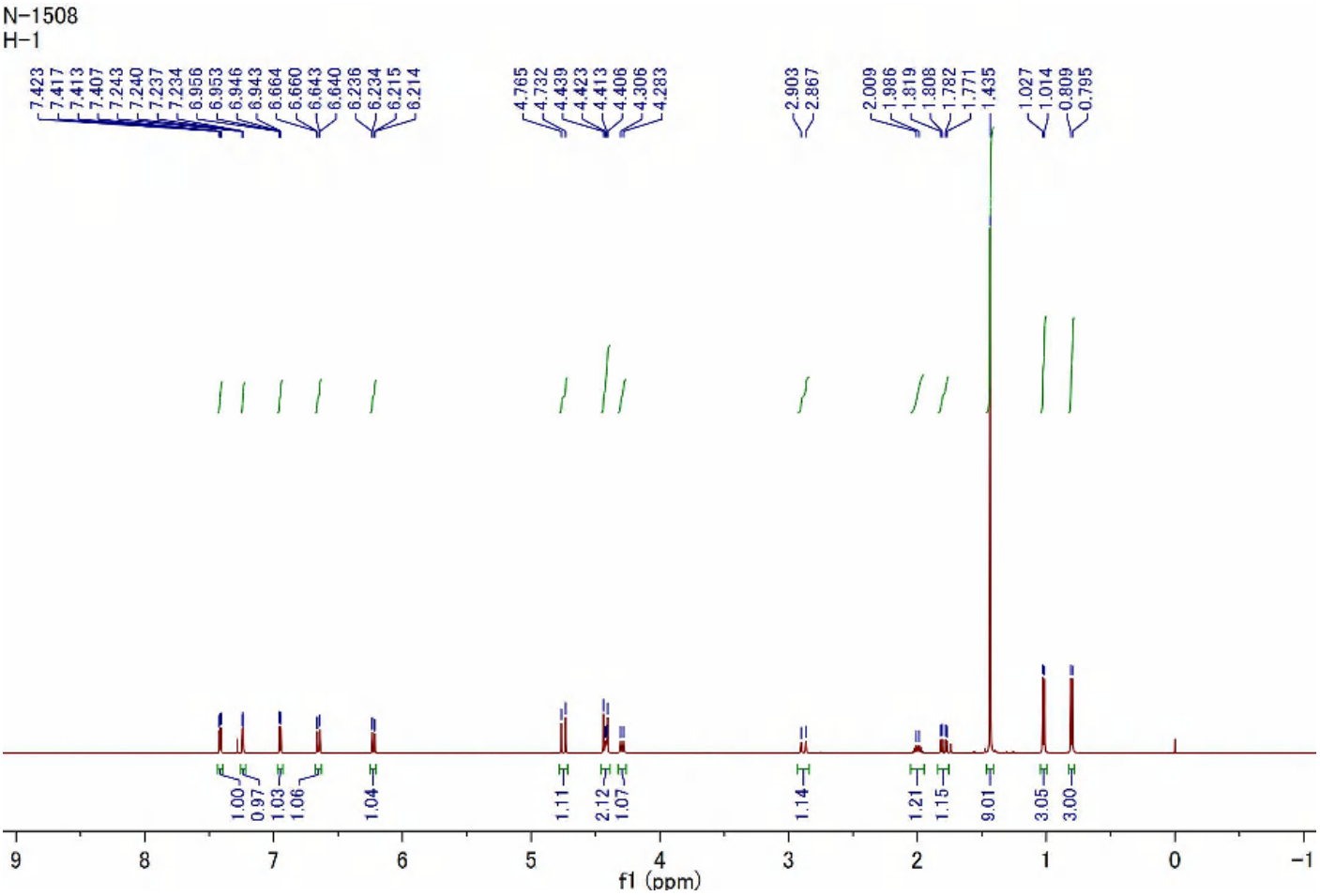
Compound **8g** (^{1}H NMR, 500 MHz, $CDCl_3$)



Compound **8g** (^{13}C NMR, 125 MHz, $CDCl_3$)



Compound **8h** (^{1}H NMR, 500 MHz, $CDCl_3$)



Compound **8h** (^{13}C NMR, 125 MHz, $CDCl_3$)