Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

For

Convenient thioacid precursor, α-methylphenacyl thioester

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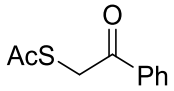
Compounds	Expt.	Spectra
Scheme 1	-	-
***S*-Phenacyl thioacetate (2a)**	SI-4	-
***S*-α-Methylphenacyl thioacetate (2b)**	SI-4	SI-29
***S*-α,α-Dimethylphenacyl thioacetate (2c)**	SI-5	SI-31
Phenacylthiol (3a)	SI-5	-
α-Methylphenacylthiol (3b)	SI-5	SI-33
α,α-Dimethylphenacylthiol (3c)	SI-5	SI-35
***S*-Phenacyl *N*-*tert*-butoxycarbonyl-L-thiotryptophanate (4a)**	SI-6	SI-37
***S*-α-Methylphenacyl *N*-*tert*-butoxycarbonyl-L-thiotryptophanate (4b)**	SI-6	SI-39
***S*-(α,α-Dimethylphenacyl) *N*-*tert*-butoxycarbonyl-L-thiotryptophanate (4c)**	SI-7	SI-41
Table 1	-	-
***S*-Benzyl *N*-*tert*-butoxycarbonyl-L-thiotryptophanate (5a-c)**	SI-8	SI-43
Table 2 7a-i	-	-
***S*-α-Methylphenacyl thiobenzoate (7a)**	SI-9	SI-45
***S*-α-Methylphenacyl thiodecanoate (7b)**	SI-9	SI-47
***S*-α-Methylphenacyl *N*-*tert*-butoxycarbonyl-L-thiophenylalainate (7c)**	SI-9	SI-49
***S*-α-Methylphenacyl *N*-*tert*-butoxycarbonylthioglycinate (7d)**	SI-10	SI-51
***S*-α-Methylphenacyl *N*-*tert*-butoxycarbonyl-*O*-benzyl-L-thioserinate (7e)**	SI-10	SI-53
***S*-α-Methylphenacyl *N*-*tert*-butoxycarbonyl-*O*-benzyl-L-thiothreonate (7f)**	SI-11	SI-55
***S*-α-Methylphenacyl *N*-fluorenylmethyloxycarbonyl-L-thiotryptophanate (7g)**	SI-11	SI-57
***S*$^{\alpha}$-α-Methylphenacyl *S*$^{\gamma}$-9-fluorenylmethyl *N*-*tert*-butoxycarbonyl-L-dithioglutamate (7h)**	SI-12	SI-59
***S*$^{\alpha}$-α-Methylphenacyl *S*$^{\gamma}$-2,4,6-trimethoxybenzyl *N*-(9-fluorenylmethyloxycarbonyl)-L-dithioglutamate (7i)**	SI-12	SI-61
Scheme SI-1	-	-
***S*$^{\alpha}$-α-Methylphenacyl *O*$^{\gamma}$-allyl *N*-*tert*-butoxycarbonyl-L-α-thioglutamate (S2)**	SI-13	SI-63
***S*$^{\alpha}$-α-Methylphenacyl *N*-*tert*-butoxycarbonyl-L-α-thioglutamate (S3)**	SI-14	SI-65
***S*$^{\alpha}$-α-Methylphenacyl *O*$^{\gamma}$-*tert*-butyl *N*-(9-fluorenylmethyloxycarbonyl)-L-α-thioglutamate (S5)**	SI-14	SI-67

General Methods

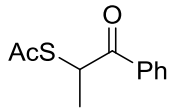
Analytical thin layer chromatography (TLC) was performed using Merck KGaA TLC 60F-254 plates (0.25 mm), and visualization was accomplished with a 2.5% solution of *p*-anisaldehyde in $AcOH/H_2SO_4/H_2O$, and a 1% solution of ninhydrin in EtOH, followed by heating or UV irradiation (254 nm). Silica gel column chromatography was performed on FUJI SILYSIA CHEMICAL Ltd. Silica Gel PSQ60B 46-50 μm (spherical, neutral). Specific rotations were measured on an automatic polarimeter with a path length of 50 mm in the solvent specified. Concentrations are given in g/100 mL. Optical rotations were measured on a JASCO P-2200 photoelectric polarimeter. ^1H and ^{13}C NMR spectra were recorded on a JEOL Ltd. JNM-ECP400 series (400 MHz). ^1H NMR data are reported as follows: chemical shift in parts par million (ppm) downfield or upfield from tetramethylsilane (δ 0.00) or $CDCl_3$ (δ 7.26), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. Chemical shifts in ^{13}C NMR are reported in ppm downfield or upfield from $CDCl_3$ (δ 77.36). High-resolution mass spectra (HRMS) were recorded on a JEOL Ltd. AccuTOFCS JIMS-T100CS with an electrospray ionization (ESI) source coupled.

General procedure for preparation of S-phenacyl thioacetates.

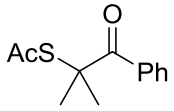
To a phenacyl bromide in DMF (1.0 M) was added *S*-potassium thioacetate (1.05 equiv.) at 0 °C. The reaction mixture was stirred for 30 min, and the reaction was quenched with water. The mixture was extracted with CH_2Cl_2, and the combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give an *S*-phenacyl thioacetate.



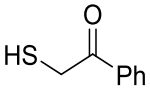
***S*-Phenacyl thioacetate** (**2a**). Phenacyl bromide (**1a**, 1.1 g, 5.7 mmol) was used as a bromide. Yellow solid. Data were in agreement with a known literature.[1]



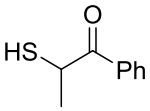
***S*-α-Methylphenacyl thioacetate** (**2b**). 2-Bromopropiophenone (**1b**, 14 g, 66 mmol) was used as a bromide. Brown oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, $J_{o,m}$ = 7.6 Hz, 2H, Ar-H_o), 7.51 (t, $J_{m,p}$ = 7.6 Hz, 1H, Ar-H_p),7.40 (dd, $J_{o,m}$ = 7.6 Hz, $J_{m,p}$ = 7.6 Hz, 2H, Ar-H_m), 5.23 (q, $J_{\alpha,\beta}$ = 7.2 Hz, 1H, CH), 2.30 (s, 3H, CH_3), 1.49 (d, $J_{\alpha,\beta}$ = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 194.0, 134.9, 133.6 128.7, 128.6, 42.4, 30.3, 17.8; ESIHRMS: *m/z* calcd. for $C_{11}H_{12}O_2SNa$ $(M + Na)^+$ 231.0456, found 231.0462.



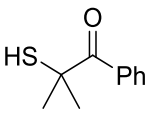
***S*-α,α-Dimethylphenacyl thioacetate** (**2c**). 2-Bromo-2-methylpropiophenone[2] (**1c**, 15 g, 66 mmol) was used as a bromide. Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, $J_{o,m}$ = 7.6 Hz, 2H, Ar-H$_o$), 7.44 (t, $J_{m,p}$ = 7.2 Hz, 1H, Ar-H$_p$), 7.36 (dd, $J_{o,m}$ = 7.6 Hz, $J_{m,p}$ = 7.2 Hz, 2H, Ar-H$_m$), 2.11 (s, 3H, CH_3), 1.70 (s, J = 7.2 Hz, 6H, CH_3 x 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.8, 194.2, 136.3, 131.7, 129.4, 128.8, 128.2, 127.8, 55.5, 30.2, 26.9; ESIHRMS: *m/z* calcd. for $C_{12}H_{14}O_2SNa$ $(M + Na)^+$ 245.0613, found 245.0626.



Phenacylthiol (**3a**). **2a** (0.23 g, 1.2 mmol) in MeOH (2.4 mL) were degassed, and NaOMe (12 mg, 0.23 mmol) was added at room temperature. The reaction mixture was degassed again and stirred for 30 min, and the reaction was quenched with HCl aq. (3.0 M, 10 mL). The mixture was extracted with CH_2Cl_2 (7 mL x 3), and the combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give the title compound as a yellow oil. Data were in agreement with a known literature.[1]

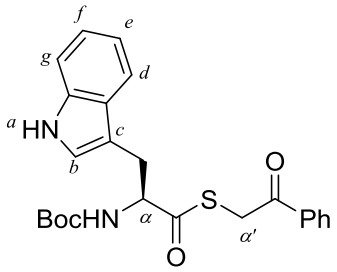


α-Methylphenacylthiol (**3b**). To a degassed solution of **2b** (14 mL, 66 mmol) in MeCN (66 mL) was added $H_2NNH_2 \cdot H_2O$ (3.4 mL, 66 mmol) at 0 °C. The reaction mixture was degassed again and stirred for 15 min. Then, the reaction was quenched with HCl aq. (1.0 M, 300 mL). The mixture was extracted with CH_2Cl_2 (100 mL x 3), and the combined organic layer was washed with brine (300 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give the title compound as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, $J_{o,m}$ = 7.2 Hz, 2H, Ar-H$_o$), 7.53 (t, $J_{m,p}$ = 7.2 Hz, 1H, Ar-H$_p$),7.43 (dd, $J_{o,m}$ = 7.2 Hz, $J_{m,p}$ = 7.2 Hz, 2H, Ar-H$_m$), 4.36 (qd, $J_{\alpha,\beta}$ =6.6 Hz, $J_{\alpha,SH}$ = 9.5 Hz, 1H, CH), 2.00 (d, $J_{\alpha,SH}$ = 9.5 Hz, 1H, SH), 1.58 (d, $J_{\alpha,\beta}$ = 6.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 134.8, 133.4, 128.8, 128.7, 36.7, 21.0; FABHRMS: *m/z* calcd. for $C_9H_{11}OS$ $(M + H)^+$ 167.0531, found 167.0522.

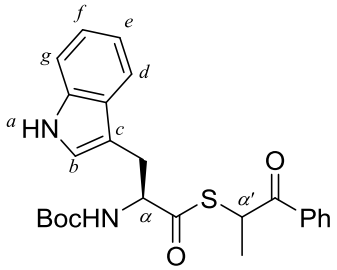


α,α-Dimethylphenacylthiol (**3c**). To a degassed solution of **2c** (15 g, 66 mmol) in MeCN (66 mL) was added $H_2NNH_2 \cdot H_2O$ (3.4 mL, 66 mmol) at 0 °C. The reaction mixture was degassed again and stirred for 15 min. Then, the reaction was quenched with HCl aq. (1.0 M, 300 mL). The mixture was extracted with CH_2Cl_2 (100 mL x 3), and the combined organic layer was washed with brine (300

mL), dried over Na_2SO_4, and concentrated *in vacuo* to give the title compound as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, $J_{o,m}$ = 7.6 Hz, 2H, Ar-H$_o$), 7.42 (t, $J_{m,p}$ = 7.6 Hz, 1H, Ar-H$_p$), 7.35 (dd, $J_{o,m}$ = 7.6 Hz, $J_{m,p}$ = 7.6 Hz, 2H, Ar-H$_m$), 2.30 (s, 1H, SH), 1.62 (s, 6H, CH_3 x 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8, 136.5, 131.7, 129.3, 128.1, 49.0, 30.2. Data were in agreement with a known literature.[3]

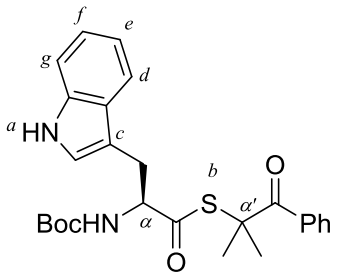


***S*-Phenacyl *N*-*tert*-butoxycarbonyl-L-thiotryptophanate** (**4a**). To Boc-L-Trp-OH (199 mg, 0.66 mmol) and phenacylthiol (120 mg, 0.79 mmol) in CH_2Cl_2 (1.3 mL) were added EDCI (151 mg, 0.79 mmol) and DMAP (8 mg, 0.06 mmol) at room temperature. The reaction mixture was stirred for 1 h, and the reaction was quenched with water (10 mL). The mixture was extracted with CH_2Cl_2 (7 mL x 3), and the combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (10 g, hexane/EtOAc = 9/1 to 4/1) to afford the corresponding thioester as a yellow foam (244 mg, 85%). $[\alpha]^{20}_D$ = -75.2 (*c* = 0.75, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (br s, 1H, NH$_a$), 7.93 (d, $J_{o,m}$ = 7.6 Hz, 2H, Ar-H$_o$), 7.65-7.52 (m, 2H, Ar-H, In-H), 7.45 (dd, $J_{o,m}$ = 7.6 Hz, $J_{m,p}$ = 7.6 Hz, 2H, Ar-H$_m$), 7.33 (d, $J_{d,e}$ = 8.0 Hz, H$_d$), 7.19 (dd, $J_{e,f}$ = 8.0 Hz, $J_{f,g}$ = 8.0 Hz, 1H, H$_f$), 7.12 (dd, $J_{d,e}$ = 8.0 Hz, $J_{e,f}$ = 8.0 Hz, 1H, H$_e$), 7.01 (s, 1H, H$_b$), 5.29 (br d, $J_{\alpha,NH}$ = 8.0 Hz, 1H, NH), 4.77 (td, $J_{\alpha,NH}$ = 8.0 Hz, $J_{\alpha,\beta}$ = 4.8 Hz, 1H, H$_\alpha$), 4.35 & 4.12 (ABq, *J* = 16.0 Hz, 1H each, $CH_{2\alpha'}$), 3.32 (d, $J_{\alpha,\beta}$ = 4.8 Hz, 2H, $CH_{2\beta}$), 1.44 (s, 9 H, ^{t}Bu); ^{13}C NMR (100MHz, $CDCl_3$) δ 201.1, 193.7, 155.6, 136.4, 135.7, 133.9, 127.7, 123.7, 122.2, 119.6, 118.6, 111.7, 109.1, 80.6, 61.1, 36.9, 28.5, 28.0; ESIHRMS: *m/z* calcd. for $C_{24}H_{26}N_2O_4SNa$ $(M + Na)^+$ 461.1511, found 461.1512.



***S*-α-Methylphenacyl *N*-*tert*-butoxycarbonyl-L-thiotryptophanate** (**4b**). To Boc-L-Trp-OH (599 mg, 2.0 mmol) and α-methylphenacylthiol (399 mg, 2.4 mmol) in CH_2Cl_2 (4.0 mL) were added EDCI (364 mg, 1.9 mmol) and DMAP (24 mg, 0.2 mmol) at room temperature. The reaction mixture

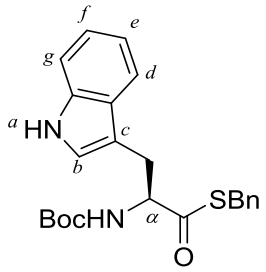
was stirred for 1 h, and the reaction was quenched with water (20 mL). The mixture was extracted with CH_2Cl_2 (10 mL x 3), and the combined organic layer was washed with brine (20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (15 g, hexane/EtOAc = 9/1 to 4/1) to afford the title compound as a yellow foam (840 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (br s, 0.5H each, NH_a), 7.96 (d, $J_{o,m}$ = 7.2 Hz, 2H, Ar-H_o), 7.60 (t, $J_{m,p}$ = 7.2 Hz, 1H, Ar-H_p), 7.55 (d, $J_{d,e}$ = 6.8 Hz, 1H, H_d), 7.43 (dd, $J_{o,m}$ = 7.2 Hz, $J_{m,p}$ = 7.2 Hz ,2H, Ar-H_m), 7.34 (dd, $J_{d,e}$ = 6.8 Hz, $J_{e,f}$ = 7.2 Hz, 1H, H_e), 7.16 (d, $J_{f,g}$ = 7.2 Hz, 1H, H_g), 7.14 (dd, $J_{e,f}$ = 7.2 Hz, $J_{f,g}$ = 7.2 Hz, 1H, H_f), 6.93 (s, 0.5H each, H_b), 5.45-5.25 (br d, $J_{\alpha,NH}$ = 10.8 Hz, 1H, NH), 5.21 (q, $J_{\alpha',\beta'}$ = 4.9 Hz, 1H, $H_{\alpha'}$), 4.70 (ddd, $J_{\alpha,\beta}$ = 4.8 Hz each, $J_{\alpha,NH}$ = 10.8 Hz, 1H, H_α), 3.31 & 3.29 (dd, $J_{\alpha,\beta}$ = 4.8 Hz, $J_{\beta,\beta}$ =12.8 Hz, 2H, $CH_{2\beta}$), 1.50 (d, $J_{\alpha',\beta'}$ = 4.9 Hz, 3H, $CH_{3\beta'}$), 1.46&1.39 (s, 4.5H each, ^{t}Bu); ^{13}C NMR (100MHz, $CDCl_3$) δ 200.1, 200.8, 198.3, 198.1, 155.6, 155.5, 136.5, 135.1, 133.9, 127.6, 122.3, 119.7, 118.7, 118.7, 111.8, 109.1, 80.7, 77.8, 77.6, 77.5, 77.2, 61.3, 61.2, 61.1, 42.8, 42.7, 28.4, 17.8, 17.5; ESIHRMS: *m/z* calcd. for $C_{25}H_{28}N_2O_4SNa$ $(M + Na)^+$ 475.1668, found 475.1692.



***S*-(α,α-Dimethylphenacyl) *N*-*tert*-butoxycarbonyl-L-thiotryptophanate** (**4c**). To Boc-L-Trp-OH (500 mg, 1.6 mmol) and α,α-dimethylphenacylthiol (356 mg, 1.9 mmol) in CH_2Cl_2 (3.2 mL) were added EDCI (364 mg, 1.9 mmol) and DMAP (24 mg, 0.2 mmol) at room temperature. The reaction mixture was stirred for 1 h, and the reaction was quenched with water (20 mL). The mixture was extracted with CH_2Cl_2 (10 mL x 3), and the combined organic layer was washed with brine (20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (15 g, hexane/EtOAc = 9/1 to 4/1) to afford the corresponding thioester as a greenish foam (745 mg, 97%). $[\alpha]^{20}_D$ = -52.1 (*c* = 1.23, $CHCl_3$); ^{1}H NMR (400 MHz $CDCl_3$) δ 8.46 (br s, 1H, NH_α), 8.02 (d, $J_{o,m}$ = 8.0 Hz, 2H, Ar-H_o), 7.54-7.44 (m, 2H, Ar-H, In-H), 7.34 (dd, $J_{o,m}$ = 8.0 Hz, $J_{m,p}$ = 7.6 Hz, 2H, Ar-H_m), 7.32 (d, $J_{f,g}$ = 8.0 Hz, 1H, H_g), 7.18 (dd, $J_{f,g}$ = 8.0 Hz, $J_{e,f}$ = 7.6 Hz, 1H, H_f), 7.11 (dd, $J_{e,f}$ = 7.6 Hz, $J_{d,e}$ = 8.0 Hz, 1H, H_e), 6.60 (s, 1H, H_b), 4.98 (br d, $J_{\alpha,NH}$ = 8.4 Hz, 1H, NH), 4.53 (td, $J_{\alpha,\beta}$ = 7.2 Hz, $J_{\alpha,NH}$ = 8.4 Hz, 1H, H_α), 2.99 (d, $J_{\alpha,\beta}$ = 7.2 Hz, 2H, $CH_{2\beta}$), 1.70 (s, 6H, $CH_{3\beta'}$ x 2), 1.43 (s, 9H, ^{t}Bu); ^{13}C NMR (100MHz, $CDCl_3$) δ 201.2, 200.5, 155.2, 136.2, 136.2, 129.1, 127.7, 122.2, 119, 7, 118.6, 111.5, 109.1, 80.4, 60.7, 55.1, 28.4, 28.2, 27.4, 27.0; ESIHRMS: *m/z* calcd. for $C_{26}H_{30}N_2O_4SNa$ $(M + Na)^+$ 489.1824, found 489.1804.

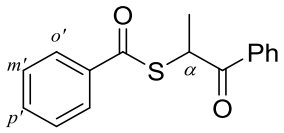
General procedure for deprotection followed by benzylation in Table 1.

Thiotriptophanates (0.12 mmol) in 90% AcOH aq. (0.1 M) was degassed, and 50 equiv. of freshly washed Zn was added to the solution. The mixture was degassed again and stirred, followed by concentration under high vacuum. The residue was suspended in $CHCl_3$/MeOH (5/1), and then filtrated through silicagel pad. The filtrate was concentrated *in vacuo*. To the residue in DMF (0.1 M) were added 3.0 equiv. of Cs_2CO_3 and BnBr, and the reaction mixture was stirred for 30 min. The reaction was quenched with water (10 mL). The mixture was extracted with CH_2Cl_2 (7 mL x 3), and the combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford the corresponding benzyl thioester.

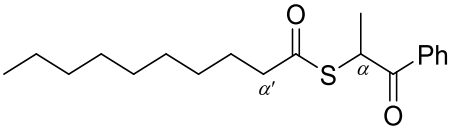


***S*-Benzyl *N*-*tert*-butoxycarbonyl-L-thiotryptophanate** (**5**). Colorless solid; mp: 127.5-130.0 °C; $[\alpha]^{20}_D$ = -53.6 (*c* = 0.53, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (br s, 1H, NH_a), 7.57 (br, 1H, In-H), 7.34 (d, $J_{d,e}$ = 8.0 Hz, 1H, H_d), 7.31-7.17 (m, 6H, In-H, Ar-H x5), 7.12 (dd, $J_{d,e}$ = 8.0 Hz, $J_{e,f}$ = 7.2 Hz, 1H, H_e), 6.82 (s, 1H, H_b), 5.06 (br d, $J_{\alpha,NH}$ = 8.0 Hz, NH), 4.73 (ddd, $J_{\alpha,NH}$ = 8.0 Hz, $J_{\alpha,\beta}$ = 5.6 Hz each, 1H, H_α), 4.10 & 4.04 (ABq, *J* = 12.4 Hz, 1H each, CH_2Ph), 3.36 & 3.33 & 3.28 & 3.25 (ddd, $J_{\alpha,\beta}$ = 5.6 Hz each, $J_{\beta,\beta}$ = 17.6 Hz, 2H, $CH_{2\beta}$), 1.42 (s, 9H, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 155.3, 137.3, 136.2, 128.6, 127.1, 122.3, 119.8, 118.9, 111.3, 109.6, 80.4, 65.4, 60.6, 33.5, 28.4, 28.2; ESIHRMS: *m/z* calcd. for $C_{23}H_{26}N_2O_3SNa$ $(M + Na)^+$ 433.1562, found 433.1567.

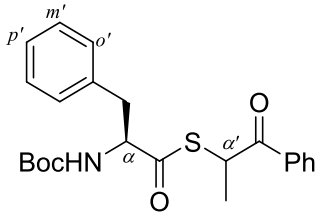
General procedure for preparation of S-α-Methylphenacyl thioester 7a-i (Table 2) To a carboxylic acid and 1.2 equiv. of α-methylphenacylthiol in CH_2Cl_2 (0.5 M) were added 1.2 equiv. of EDCI and 0.1 equiv. of DMAP at room temperature. The reaction mixture was stirred for 1 h, and the reaction was quenched with water (20 mL). The mixture was extracted with CH_2Cl_2 (10 mL x 3), and the combined organic layer was washed with brine (20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford the corresponding Mpa thioester.



***S*-α-Methylphenacyl thiobenzoate** (**7a**). Benzoic acid (**6a**, 168 mg, 1.4 mmol) was used as a carboxylic acid. Purification was performed by silica gel column chromatography (10 g, hexane to hexane/EtOAc = 9/1) to afford the title compound as a yellow syrup (335 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, $J_{o,m}$ = 7.6 Hz, 2H, Ar-H$_o$), 7.89 (d, $J_{o',m'}$ = 7.7 Hz, 2H, Ar-H$_{o'}$), 7.48 (t, $J_{m,p}$ = 7.7 Hz, 1H, Ar-H$_p$), 7.46 (t, $J_{m',p'}$ = 7.2 Hz, 1H, Ar-H$_{p'}$), 7.38 (dd, $J_{o,m}$ = 7.6 Hz, $J_{m,p}$ = 7.7 Hz, 2H, Ar-H$_m$), 7.33 (dd, $J_{o',m'}$ = 7.7 Hz, $J_{m',p'}$ = 7.2 Hz, 2H, Ar-H$_{m'}$), 5.46 (q, $J_{\alpha,\beta}$ = 7.0 Hz, 1H, H$_\alpha$), 1.16 (d, $J_{\alpha,\beta}$ = 7.0 Hz, 3H, CH$_{3\beta}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 190.0, 136.2, 135.0, 134.0, 133.6, 128.9, 128.8, 128.7, 127.5, 42.5, 17.9; ESIHRMS: *m/z* calcd. for $C_{16}H_{14}O_2SNa$ $(M + Na)^+$ 293.0613, found 293.0616.

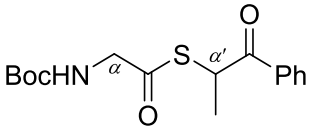


***S*-α-Methylphenacyl thiodecanoate** (**7b**). Capric acid (**6b**, 219 mg, 1.3 mmol) was used as a carboxylic acid. Purfication was performed by silica gel column chromatography (10 g, hexane to hexane/EtOAc = 19/1) to afford the title compound as a yellow syrup (377 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, $J_{o,m}$ = 7.6 Hz, 2H, Ar-H$_o$), 7.49 (t, $J_{m,p}$ = 7.2 Hz, 1H, Ar-H$_p$), 7.38 (dd, $J_{o,m}$ = 7.6 Hz, $J_{m,p}$ = 7.2 Hz, 2H, Ar-H$_m$), 5.23 (q, $J_{\alpha,\beta}$ = 7.0 Hz, 1H, H$_\alpha$), 2.49 (t, $J_{\alpha',\beta'}$ = 7.6 Hz, 2H, $COCH_2$), 1.59 (t, $J_{\alpha',\beta'}$ = 6.8 Hz, 2H, CH_2), 1.49 (d, $J_{\alpha,\beta}$ = 7.0 Hz, 3H, CH_3), 1.29-1.10 (m, 12H, CH_2 x6), 0.82 (t, J = 6.8 Hz, 3H, CH$_{3\beta}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 197.2, 135.0, 133.4, 128.7, 128.6, 43.7, 41.9, 31.9, 29.4, 29.3, 29.2, 28.9, 25.6, 22.7, 17.7, 14.2; ESIHRMS: *m/z* calcd. for $C_{19}H_{28}O_2SNa$ $(M + Na)^+$ 343.1708, found 343.1705.

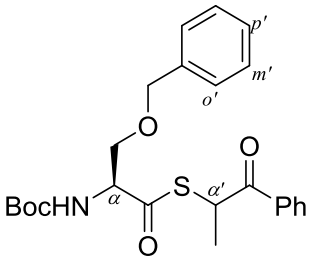


***S*-α-Methylphenacyl *N*-*tert*-butoxycarbonyl-L-thiophenylalainate** (**7c**). Boc-L-Phe-OH (**6c**, 99 mg, 0.37 mmol) was used as a carboxylic acid. Purification was performed by silica gel column chromatography (10 g, hexane/EtOAc = 9/1) to afford the title compound as a yellow syrup (147 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, $J_{o,m}$ = 7.6 Hz, 2H, Ar-H$_o$), 7.52 (t, $J_{m,p}$ = 7.6 Hz, 1H, Ar-H$_p$), 7.42 (dd, $J_{o,m}$ = 7.6 Hz, $J_{m,p}$ = 7.6 Hz, 2H, Ar-H$_m$), 7.23-7.13 (m, 3H, Ar-H), 7.08 (dd, $J_{o',m'}$ = 9.6 Hz, $J_{m',p'}$ = 9.6 Hz, 2H, Ar-H$_{m'}$), 5.21 (q, $J_{\alpha',\beta'}$ = 6.8 Hz, 1H, H$_{\alpha'}$), 5.04 & 4.99 (br d, $J_{\alpha,NH}$ = 8.0 Hz, 0.5H each, NH), 4.63 (td, $J_{\alpha,\beta}$ = 6.8 Hz, $J_{\alpha,NH}$ = 8.0 Hz, 1H, H$_\alpha$), 3.15-2.95 (m, 2H, CH$_{2\beta}$), 1.49

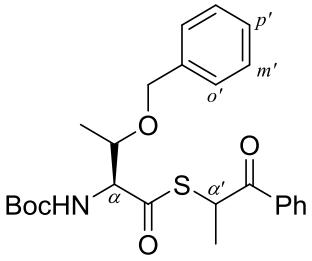
(d, $J_{\alpha',\beta'}$ = 6.8 Hz, 3H, $CH_{3\beta'}$), 1.35 & 1.30 (s, 4.5H each, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 199.7, 197.5, 197.3, 196.0, 196.9, 155.1, 155.0, 135.6, 135.0, 133.7, 129.4, 129.4, 129.0, 128.9, 128.8, 128.7, 127.2, 80.5, 80.4, 61.3, 61.2, 48.0, 42.4, 42.3, 38.2, 38.0, 28.3, 28.3, 28.0, 17.8, 17.6, 16.9, 16.5; ESIHRMS: *m/z* calcd. for $C_{23}H_{27}NO_4SNa$ $(M + Na)^+$ 436.1559, found 436.1551.



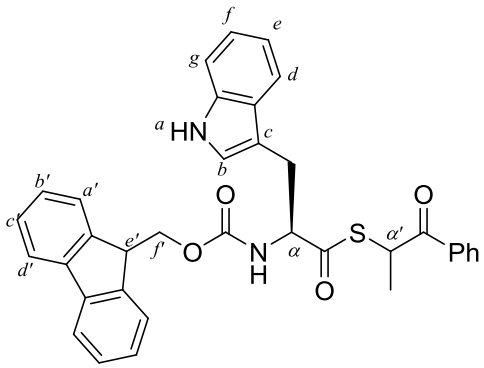
***S*-α-Methylphenacyl *N*-*tert*-butoxycarbonylthioglycinate** (**7d**). Boc-Gly-OH (**6d**, 604 mg, 3.5 mmol) was used as a carboxylic acid. Purification was performed by silica gel column chromatography (20 g, hexane/EtOAc = 9/1) to afford the title compound as a white foam (1.1 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, $J_{o,m}$ = 7.2 Hz, 2H, Ar-H_o), 7.41 (t, $J_{m,p}$ = 7.2 Hz, 1H, Ar-H_p), 7.29 (dd, $J_{o,m}$ = 7.2 Hz, $J_{m,p}$ = 7.2 Hz, 2H, Ar-H_m), 5.73 & 5.64 (br d, $J_{\alpha,NH}$ = 10.8 Hz, 0.5H each, NH), 5.11 (q, $J_{\alpha',\beta'}$ = 6.4 Hz, 1H, $H_{\beta'}$), 3.87 (ddd, $J_{\alpha,\beta}$ = 17.2 Hz, $J_{\alpha,NH}$ = 10.8 Hz each, 2H, $CH_{2\alpha}$), 1.37 (d, $J_{\alpha',\beta'}$ = 6.4 Hz, 3H, $H_{\alpha'}$), 1.28 & 1.20 (s, 4.5H each, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 197.6, 155.8, 134.7, 133.7, 133.5, 128.8, 128.7. 128.5, 80.2, 50.2, 42.2, 42.0, 28.3, 17.7; ESIHRMS: *m/z* calcd. for $C_{16}H_{21}NO_4SNa$ $(M + Na)^+$ 346.1089, found 346.1083.



***S*-α-Methylphenacyl *N*-*tert*-butoxycarbonyl-*O*-benzyl-L-thioserinate** (**7e**). Boc-L-Ser-OH (**6e**, 303 mg, 1.0 mmol) was used as a carboxylic acid. Purification was performed by silica gel column chromatography (15 g, hexane/EtOAc = 9/1) to afford the title compound as a yellow syrup (448 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 & 7.92 (d, $J_{o,m}$ = 6.8 Hz, 1H each, Ar-H_o), 7.50 & 7.48 (t, $J_{m,p}$ = 7.2 Hz, 0.5H each, Ar-H_p), 7.39 & 7.37 (dd, $J_{o,m}$ = 6.8 Hz, $J_{m,p}$ = 7.2 Hz, 1H each, Ar-H_m), 7.30-7.12 (m, 5H, Ar-H), 5,59 & 5.56 (br d, $J_{\alpha,NH}$ = 8.0 Hz, 0.5H each, NH), 5.23 (q, $J_{\alpha',\beta'}$ = 7.2 Hz, 1H, $H_{\alpha'}$), 4.51 & 4.49 (ddd, $J_{\alpha,NH}$ = 8.0 Hz, $J_{\alpha,\beta}$ = 8.0 Hz each, 0.5H each, H_α), 4.44 & 4.38 (ABq, J = 12.4 Hz, 1H each, CH_2Ph), 3.93 & 3.60 (dd, $J_{\alpha,\beta}$ = 8.0 Hz, $J_{\beta,\beta}$ = 11.2 Hz, 1H each, $CH_{2\beta}$), 1.52 (d, $J_{\alpha',\beta'}$ = 7.2 Hz, 3H, $CH_{3\beta'}$), 1.44 & 1.38 (s, 4.5H each, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 199.1, 197.4, 197.3, 155.3, 155.2, 135.0, 134.9, 133.7, 133.6, 133.52, 128.7, 128.6, 128.5, 128.0, 127.9, 127.7, 127.5, 80.6, 80.5, 73.5, 73.4, 73.3, 60.7, 60.5, 60.4, 42.6, 42.4, 28.4, 18.0, 18.0, 17.6, 17.6; ESIHRMS: *m/z* calcd. for $C_{24}H_{29}NO_5SNa$ $(M + Na)^+$ 466.1664, found 466.1664.

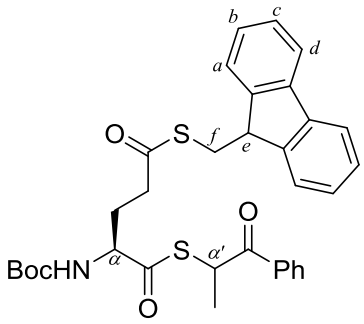


***S*-α-Methylphenacyl *N*-*tert*-butoxycarbonyl-*O*-benzyl-L-thiothreonate** (**7f**). Boc-L-Thr-OH (**6f**, 312 mg, 1.5 mmol) was used as a carboxylic acid. Purification was performed by silica gel column chromatography (15 g, hexane/EtOAc = 9/1) to afford the title compound as a yellow syrup (523 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 & 7.94 (d, $J_{o,m}$ = 7.6 Hz, 1H each, Ar-H_o), 7.54 & 7.49 (t, $J_{m,p}$ = 7.2 Hz, 0.5H each, Ar-H_p), 7.42 & 7.37 (dd, $J_{o,m}$ = 7.6 Hz, $J_{m,p}$ = 7.2 Hz, 1H each, Ar-H_m), 7.35-7.05 (m, 5H, Ar-H), 5.42 & 5.41 (br, 0.5H each, NH), 5.24 (q, $J_{\alpha',\beta'}$ = 6.4 Hz, 1H, $H_{\alpha'}$), 4.55-4.23 (m, 4H, CH_2Ph, H_α, H_β), 1.54 (d, $J_{\alpha',\beta'}$ = 6.4 Hz, 3H, $CH_{3\beta'}$), 1.47 & 1.40 (s, 4.5H each, ^{t}Bu), 1.23 (m, 3H, $CH_{3\gamma}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.8, 200.3, 197.7, 197.5, 155.9, 155.8, 137.8, 137.7, 135.1, 134.9, 133.7, 133.6, 80.6, 80.6, 74.9, 74.4, 71.6, 65.2, 65.1, 42.5, 42.4, 28.4, 28.3, 18.0, 17.5, 16.9, 16.7; ESIHRMS: *m/z* calcd. for $C_{24}H_{29}NO_5SNa$ $(M + Na)^+$ 480.1821, found 480.1850.

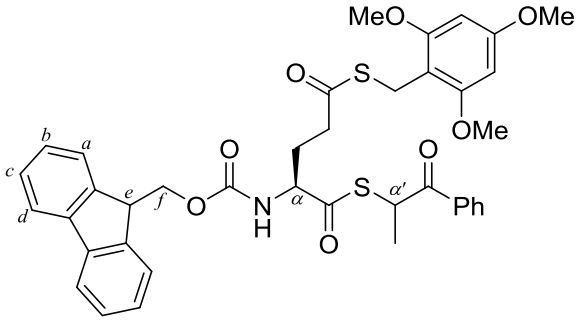


***S*-α-Methylphenacyl *N*-fluorenylmethyloxycarbonyl-L-thiotryptophanate** (**7g**). Fmoc-L-Trp-OH (**6g**, 500 mg, 1.2 mmol) was used as a carboxylic acid. Purification was performed by silica gel column chromatography (15 g, hexane/EtOAc = 9/1 to 4/1) to afford the corresponding thioester as a white foam (662 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (br, 1H, NH_a), 8.00-7.92 (m, 2H, Ar-H), 7.79-7.72 (m, 2H, Fm-H), 7.63-7.10 (m, 13H, Ar-H x 3, Fm-H x 6, In-H x 4), 6.88 & 6.83 (s, 0.5H each, H_b), 5.32 (br d, $J_{\alpha,NH}$ = 7.6 Hz, 1H, NH), 5.21 (q, $J_{\alpha',\beta'}$ = 7.2 Hz, 1H, $H_{\alpha'}$), 4.82 (ddd, $J_{\alpha,NH}$ = 7.6 Hz, $J_{\alpha,\beta}$ = 5.6 Hz each, 1H, H_α), 4.35 (dd, $J_{e',f'}$ = 7.2 Hz each, 2H, $CH_{2f'}$), 4.17 & 4.11 (t, $J_{e',f'}$ = 7.2 Hz, 1H, $H_{e'}$), 3.30 (ddd, $J_{\alpha,\beta}$ = 5.6 Hz each, $J_{\beta,\beta}$ = 15.6 Hz, 2H, $CH_{2\beta}$), 1.51 & 1.48 (d, $J_{\alpha',\beta'}$ = 7.2 Hz, 1.5H each, $CH_{3\beta'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 155.9, 143.8, 143.7, 141.4, 136.2, 135.1, 135.0, 133.7, 128.9, 128.8, 127.9, 127.2, 125.5, 123.4, 122.5, 118.6, 118.5, 111.5, 111.5,

109.2, 109.0, 67.4, 67.4, 61.2, 47.2, 43.0, 42.7, 28.2, 27.8, 17.7, 17.4; ESIHRMS: *m/z* calcd. for $C_{35}H_{30}N_2O_4SNa$ $(M + Na)^+$ 597.1824, found 597.1852.



***S*$^{\alpha}$-α-Methylphenacyl *S*$^{\gamma}$-9-fluorenylmethyl *N*-*tert*-butoxycarbonyl-L-dithioglutamate** (**7h**). To a Boc-L-Glu(OH)-SMpa (**S3**, 0.74 g, 1.86 mmol) and 9-fluorenylmethylthiol (0.47 g, 2.23 mmol)[4] in CH_2Cl_2 (4.0 mL) were added EDCI (0.43g, 2.23 mmol) and DMAP (23 mg, 0.19 mmol) at room temperature. The reaction mixture was stirred for 1 h, and the reaction was quenched with water (100 mL). The mixture was extracted with CH_2Cl_2 (30 mL x 3), and the combined organic layer was washed with brine (100 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purfication of the residue by flash chromatography (silica gel 20g, hexane/EtOAc = 19/1 to 9/1) gave a yellow foam (0.81 g, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, $J_{o,m}$ = 7.2 Hz, 2H, Ar-H$_o$), 7.73 (d, $J_{c,d}$ = 7.6 Hz, 2H, H$_d$), 7.60 (d, $J_{a,b}$ = 8.0 Hz, 2H, H$_a$), 7.54 (t, $J_{m,p}$ = 7.2 Hz, 1H, Ar-H$_p$), 7.43 (dd, $J_{b,c}$ = 7.6 Hz, $J_{c,d}$ = 7.6 Hz, 2H, H$_c$), 7.38 (dd, $J_{a,b}$ = 8.0 Hz, $J_{b,c}$ = 7.6 Hz, 2H, H$_b$), 7.30 (dd, $J_{o,m}$ = 7.2 Hz, $J_{m,p}$ = 7.2 Hz, 2H, Ar-H$_m$), 5.19 (q, $J_{\alpha',\beta'}$ = 7.2 Hz, 1H, H$_{\alpha'}$), 5.10-5.00 (br m, 1H, NH), 4.35-4.21 (m, 1H, H$_\alpha$), 4.15 (t, $J_{e,f}$ = 5.6 Hz, 2H, H$_f$), 3.52 (d, $J_{e,f}$ = 5.6 Hz, 2H, H$_e$), 2.58-2.48 (m, 2H, $CH_{2\gamma}$), 2.17-2.05 & 1.91-1.78 (m, 1H each, $CH_{2\beta}$), 1.53 (d, $J_{\alpha',\beta'}$ = 7.2 Hz, 3H, $CH_{3\beta'}$), 1.41 (s, 9H, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 198.1, 155.1, 145.3, 141.2, 135.0, 133.7, 128.8, 128.6, 127.9, 127.2, 124.7, 120.0, 80.8, 59.8, 46.7, 42.7, 39.8, 32.4, 28.4, 27.7, 17.6; ESIHRMS: *m/z* calcd. for $C_{33}H_{35}NO_5S2Na$ $(M + Na)^+$ 612.1854, found 612.1836.



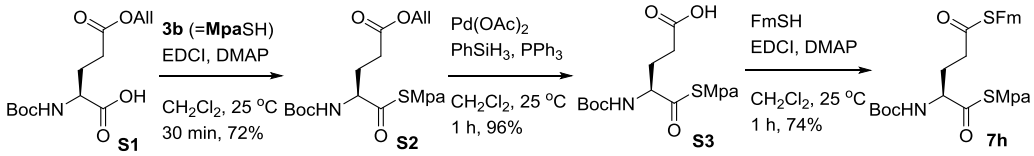
***S*$^{\alpha}$-α-Methylphenacyl *S*$^{\gamma}$-2,4,6-trimethoxybenzyl *N*-(9-fluorenylmethyloxycarbonyl)-L-dithioglutamate** (**7i**).

To a Fmoc-L-Glu(OH)-SMpa (**S6**, 90 mg, 0.17 mmol) and 2,4,6-trimethoxybenzylthiol (45 mg, 0.21 mmol) in CH_2Cl_2 (1.7 mL) were added EDCI (40 mg, 0.21 mmol) and DMAP (2.1 mg, 0.02 mmol)

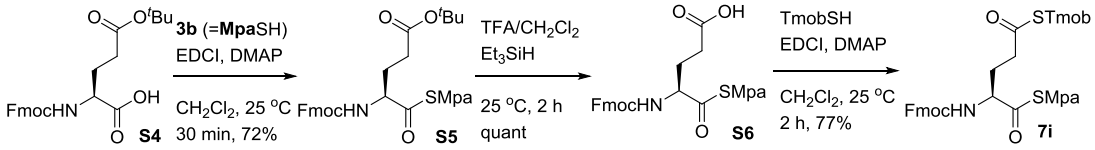
at room temperature. The reaction mixture was stirred for 1 h, and the reaction was quenched with water (10 mL). The mixture was extracted with CH_2Cl_2 (7 mL x 3), and the combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purfication of the residue by flash chromatography (silica gel 10 g, hexane/EtOAc = 9/1 to 2/1) gave a colorless foam (93 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 & 7.92 (d, $J_{o,m}$ = 7.6 Hz, 1H each, Ar-H$_o$), 7.74 (d, $J_{c,d}$ = 7.6 Hz, 2H, H$_d$), 7.61 & 7.57 (d, $J_{a,b}$ = 7.2 Hz, 1H each, H$_a$), 7.53 (t, $J_{m,p}$ = 7.2 Hz, 1H, Ar-H$_p$), 7.44 (dd, $J_{o,m}$ = 7.6 Hz, $J_{m,p}$ = 7.2 Hz, 2H, Ar-H$_m$), 7.38 (dd, $J_{b,c}$ = 7.6 Hz, $J_{c,d}$ = 7.2 Hz, 2H, H$_c$), 7.30 (dd, $J_{a,b}$ = 7.6 Hz, $J_{b,c}$ = 7.2 Hz, 2H, H$_b$), 6.08 (s, 2H, Ar-H), 5.71 & 5.76 (br d, $J_{\alpha,NH}$ = 8.4 Hz, 0.5H each, NH), 5.21 (q, $J_{\alpha',\beta'}$ = 6.8 Hz, 1H, H$_{\alpha'}$), 4.50-4.32 (m, 3H, H$_\alpha$, CH_{2f}), 4.25 & 4.21 (ABq, J = 12.4 Hz, 2H, CH_2Ph), 4.15 (t, $J_{e,f}$ = 6.8 Hz, 1H, H$_e$), 3.77 (s, 9H, OCH_3 x 3), 2.68 & 2.52 (m, 2H, $CH_{2\gamma}$), 2.28-2.18 & 2.08-1.95 (m, 1H each, $CH_{2\beta}$), 1.54 (d, $J_{\alpha',\beta'}$ = 6.4 Hz, 3H, $CH_{3\beta'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 199.5, 199.1, 197.5, 197.2, 161.0, 159.2, 156.0, 155.8, 143.9, 143.8, 143.7, 143.7, 141.4, 141.3, 135.0, 134.8, 133.7, 128.8, 128.6, 127.8, 127.2, 125.2, 125.2, 120.1, 120.1, 104.5, 90.6, 67.4, 67.3, 60.5, 60.5, 55.9, 55.4, 47.2, 47.2, 42.9, 42.7, 39.4, 27.8, 27.7, 22.5, 17.8, 17.6; ESIHRMS: *m/z* calcd. for $C_{39}H_{39}NO_8S_2Na$ $(M + Na)^+$ 736.2015, found 762.2008.

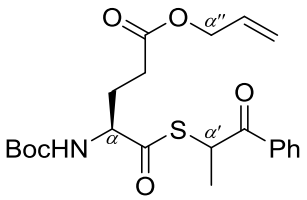
Scheme SI-1. Preparations of Mpa thioesters **7h** and **7i**.

7h



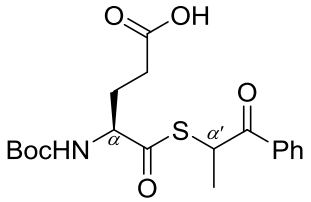
7i





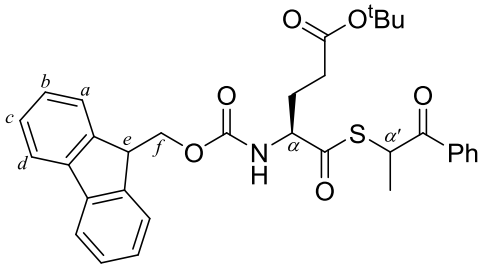
***S*$^{\alpha}$-α-Methylphenacyl *O*$^{\gamma}$-allyl *N*-*tert*-butoxycarbonyl-L-α-thioglutamate** (**S2**). To a Boc-L-Glu(OAll)-OH[6] (2.0 g, 6.9 mmol) and methylphenacylthiol (1.4 g, 8.3 mmol) in CH_2Cl_2 (13 mL) were added EDCI (1.6 g, 8.3 mmol) and DMAP (85 mg, 0.69 mmol) at room temperature. The reaction mixture was stirred for 1 h, and the reaction was quenched with water (100 mL). The

mixture was extracted with CH_2Cl_2 (50 mL x 3), and the combined organic layer was washed with brine (100 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purfication of the residue by flash chromatography (silica gel 20 g, hexane/EtOAc = 19/1 to 9/1) gave a yellow syrup (2.2 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, $J_{o,m}$ = 7.2 Hz, 2H, Ar-H$_o$), 7.56 & 7.55 (t, $J_{m,p}$ = 7.2 Hz, 0.5H each, Ar-H$_p$), 7.44 (dd, $J_{o,m}$ =7.2 Hz, $J_{m,p}$ =7.2 Hz, 2H, Ar-H$_m$), 5.87 (m, 1H, H$_{\beta''}$), 5.37-5.12 (m, 4H, $CH_{2\gamma''}$, H$_{\alpha'}$, NH), 4.53-4.66 (m, 2H, $CH_{2\alpha''}$), 4.45-4.30 (m, 1H, H$_\alpha$), 2.46-2.35 (m, 2H, $CH_{2\gamma}$), 2.23-2.11 & 1.96-1.85 (m, 1H each, $CH_{2\beta}$), 1.53 (d, $J_{\alpha',\beta'}$ = 6.8 Hz, 3H, $CH_{3\beta'}$), 1.43 & 1.37(s, 4.5H each, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 197.6, 172.4, 155.2, 134.9, 133.7, 132.0, 128.8, 128.6, 118.6, 80.7, 65.6, 60.0, 42.7, 42.6, 30.2, 28.4, 27.5, 27.3, 17.8, 17.6; ESIHRMS: *m/z* calcd. for $C_{22}H_{29}NO_6SNa$ $(M + Na)^+$ 458.1613, found 458.1628.



***S*$^{\alpha}$-α-Methylphenacyl *N*-*tert*-butoxycarbonyl-L-α-thioglutamate** (**S3**).

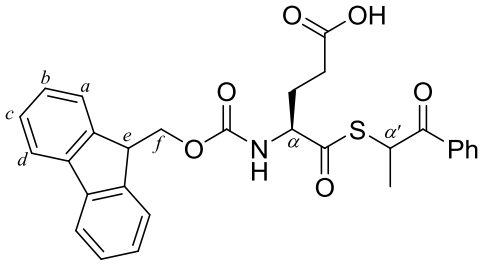
Triphenylphosphine (286 mg, 1.1 mmol) and palladium (II) acetate (49 mg, 0.21 mmol) in CH_2Cl_2 (9.0 mL) were added to Boc-L-Glu(OAll)-SMpa (**S2**, 1.9 g, 4.36 mmol). The mixture was degassed, and then phenylsilane (0.27 mL, 2.2 mmol) was added. After stirring for 1 h, the resulting solution was concentrated *in vacuo.* Purification of the residue by flash chromatography (silica gel 20 g, $CHCl_3$/MeOH = 39/1 to 19/1) gave a yellow form (1.65 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (br, 1H, CO_2H), 7.93 (d, $J_{o,m}$ = 7.2 Hz, 2H, Ar-H$_o$), 7.55 (t, $J_{m,p}$ = 7.2 Hz, 1H, Ar-H$_p$), 7.44 (dd, $J_{o,m}$ = 7.2 Hz, $J_{m,p}$ = 7.2 Hz, 2H, Ar-H$_m$), 5.33-5.22 (br m, 1H, NH), 5.21 (q, $J_{\alpha',\beta'}$ = 6.8 Hz, 1H, H$_{\alpha'}$), 4.45-4.09 (m, 1H, H$_\alpha$), 2.53-2.33 (m, 2H, $CH_{2\gamma}$), 2.24-2.05 & 1.98-1.81 (m, 1H each, $CH_{2\beta}$), 1.52 (d, $J_{\alpha',\beta'}$ = 6.8 Hz, 3H, $CH_{3\beta'}$), 1.42 & 1.40 (s, 4.5H each, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200..8, 197.5, 197.2, 155.3, 134.9, 133.7, 128.8, 128.7, 80.9, 59.9, 42.8, 30.1, 28.4, 27.3, 17.8, 17.6; ESIHRMS: *m/z* calcd. for $C_{19}H_{25}NO_6SNa$ $(M + Na)^+$ 418.1300, found 418.1312.



***S*$^{\alpha}$-α-Methylphenacyl *O*$^{\gamma}$-*tert*-butyl *N*-(9-fluorenylmethyloxycarbonyl)-L-α-thioglutamate** (**S5**).

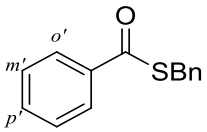
To a Fmoc-L-Glu(O^{t}Bu)-OH·H_2O (1.0 g, 2.3 mmol) and α-methylphenacylthiol (0.47 g, 2.8 mmol) in CH_2Cl_2 (4.7 mL) were added EDCI (0.54 g, 2.8 mmol) and DMAP (29 mg, 0.23 mmol) at room temperature. The reaction mixture was stirred for 1 h, and the reaction was quenched with water

(100 mL). The mixture was extracted with CH_2Cl_2 (50 mL x 3), and the combined organic layer was washed with brine (100 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purfication of the residue by flash chromatography (silica gel 20g, hexane/EtOAc = 9/1 to 4/1) gave a yellow foam (1.3 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 & 7.92 (d, $J_{o,m}$ = 8.0 Hz, 1H each, Ar-H$_o$), 7.74 & 7.73 (d, $J_{c,d}$ = 8.0 Hz, 1H each, H$_d$), 7.61 & 7.55 (d, $J_{a,b}$ = 7.6 Hz, 1H each, H$_a$), 7.53 & 7.51 (t, $J_{m,p}$ = 7.6 Hz, 0.5H each, Ar-H$_p$), 7.43 (dd, $J_{o,m}$ = 8.0 Hz, $J_{m,p}$ = 7.6 Hz, 2H, Ar-H$_m$), 7.37 (dd, $J_{b,c}$ = 7.6 Hz, $J_{c,d}$ = 8.0 Hz, 2H, H$_c$), 7.29 (dd, $J_{a,b}$ = 7.6 Hz, $J_{b,c}$ = 7.6 Hz, 2H, H$_b$), 5.95 & 5.86 (br d, $J_{\alpha,NH}$ = 8.0 Hz, 0.5H each, NH), 5.21 (q, $J_{\alpha',\beta'}$ = 6.0 Hz, 1H, H$_{\alpha'}$), 4.53-4.42 (m, 2H, CH_{2f}), 4.32 (ddd, $J_{\alpha,NH}$ = 8.0 Hz, $J_{\alpha,\beta}$ = 7.6 Hz each, 1H, H$_\alpha$), 4.21 & 4.13 (t, $J_{e,f}$ = 6.8 Hz, 0.5H each, H$_e$), 2.38-2.23 (m, 2H, $CH_{2\gamma}$), 2.15 & 1.93 (dt, $J_{\alpha,\beta}$ = 7.6 Hz, $J_{\beta,\gamma}$ = 6.8 Hz, 1H each, $CH_{2\beta}$), 1.55 & 1.54 (d, $J_{\alpha',\beta'}$ = 6.0 Hz, 1.5H each, $CH_{3\beta'}$), 1.45 & 1.44 (s, 4.5H each, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 199.4, 197.6, 197.2, 172.4, 172.3 156.0, 155.9, 143.9, 143.9, 143.7, 143.7, 141.4, 141.3, 135.0, 134.9, 133.7, 128.8, 128.8, 128.7, 127.9, 127.8, 127.2, 127.2, 125.2, 125.1, 120.1, 120.1, 81.2, 67.3, 67.3, 60.7, 60.7, 47.2, 47.2, 42.8, 42.6, 31.5, 28.2, 27.4, 27.2, 17.8, 17.6; ESIHRMS: *m/z* calcd. for $C_{33}H_{35}NO_6SNa$ $(M + Na)^+$ 596.2083, found 596.2106.

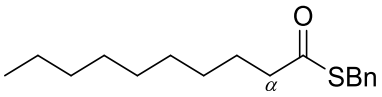


***S*$^{\alpha}$-α-Methylphenacyl *N*-fluorenylmethyloxycarbonyl-L-α-thioglutamate (S6).** To a solution of Fmoc-L-Glu(O^{t}Bu)-SMpa (**S5**, 115 mg, 0.20 mmol) in 40% TFA/CH_2Cl_2 (1.0 mL) was added Et_3SiH (38 μL, 0,24 mmol), and the reaction mixture was stirred for 1 h. The solution was concentrated *in vacuo*, and the residual TFA was removed by azeotropic distillation with toluene *in vacuo* which gave a colourless form (quantitive yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (br, 1H, CO_2H), 7.93 & 7.91 (d, $J_{o,m}$ = 8.4 Hz, 1H each, Ar-H$_o$), 7.72 (d, $J_{c,d}$ = 7.2 Hz, 2H, H$_d$), 7.61-7.50 (m. 3H, Ar-H, Fm-H x 2), 7.45-7.23 (m, 6H, ArH x 2, FmH x 4), 5.80 & 5.73 (br d, $J_{\alpha,NH}$ = 6.8 Hz, 0.5H each, NH), 5.21 (q, $J_{\alpha',\beta'}$ = 6.8 Hz, 1H, H$_{\alpha'}$), 4.53-4.30 (m, 3H, CH_{2f}, H$_\alpha$), 4.18 & 4.14 (t, $J_{e,f}$ = 6.8 Hz, 0.5H each, H$_e$), 2.46-2.28 (m, 2H, $CH_{2\gamma}$), 2.26-2.13 & 1.95-1.82 (m, 1H each, $CH_{2\beta}$), 1.52 (d, $J_{\alpha',\beta'}$ = 6.8 Hz, 3H, $CH_{3\beta'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 199.3, 197.8, 197.4, 177.9, 177.8 156.2, 156.1, 143.8, 143.8, 143.7, 143.7, 141.4, 134.9, 134.8, 133.8, 128.9, 128.7, 127.9, 127.2, 125.2, 125.1, 120.1, 67.4, 67.3, 60.4, 60.3, 47.2, 43.2, 43.0, 30.1, 27.4, 27.2, 17.7, 17.6; ESIHRMS: *m/z* calcd. for $C_{29}H_{27}NO_6SNa$ $(M + Na)^+$ 540.1457, found 540.1449.

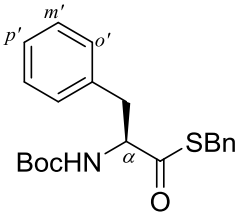
General procedure for deprotection followed by derivatization to S-benzyl thioesters 8a-i (Table 2). *S*-α-Methylphenacyl thioesters in 90% AcOH aq. (0.1 M) was degassed, and 50 equiv. of freshly washed Zn was added to the solution. The mixture was degassed again and stirred at room temperature, followed by concentration under high vacuum. The residue was suspended in $CHCl_3$/MeOH (5/1), and then filtrated through silica gel pad. The filtrate was concentrated *in vacuo*. To the residue in DMF (0.1 M) were added 3.0 equiv. of Cs_2CO_3 and BnBr, and the reaction mixture was stirred for 30 min. The reaction was quenched with water (10 mL). The mixture was extracted with CH_2Cl_2 (7 mL x 3), and the combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford the corresponding benzyl thioester.



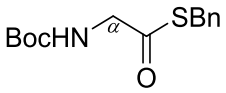
***S*-Benzyl thiobenzoate** (**8a**). BzSMpa (**7a**, 60 mg, 0.22 mmol) was used as a *S*-α-methylphenacyl thioester. Purification was performed by silica gel column chromatography (10 g, hexane to hexane/EtOAc = 19/1) to afford the title compound as a colorless syrup (41 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, $J_{o,m}$ = 7.6 Hz, 2H, SBn(Ar-H)), 7.57 (t, $J_{m,p}$ = 7.3 Hz, 1H, SBn(Ar-H)), 7.50-7.20 (m, 7H, the other Ar-H), 4.38-4.28 (m, 2H, CH_2Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 137.6, 136.9, 133.5, 129.1, 128.74, 128.72, 127.4, 127.4, 33.1; Anal. Calcd for ($C_{14}H_{12}OS$): C, 73.65; H, 5.30; O, 7.01; S, 14.04. Found: C, 73.37; H, 5.39.



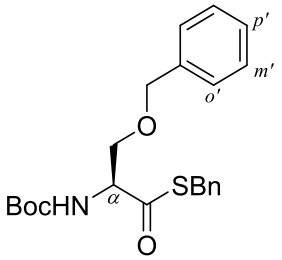
***S*-Benzyl thiodecanoate** (**8b**). ^{n}C_9H_{19}COSMpa (**7b**, 50 mg, 0.16 mmol) was used as a *S*-α-methylphenacyl thioester. Purfication was performed by silica gel column chromatography (10 g, hexane to hexane/ toluene = 4/1) to give the title compound as a colorless syrup (40 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.17 (m, 5H, Ar-H), 4.24-4.16 (m, 2H, CH_2Ph), 2.56 (t, $J_{\alpha,\beta}$ = 7.6 Hz, 2H, $CH_{2\beta}$), 1.67 (m, 2H, CH_2), 1.38-1.16 (m, 12H, CH_2), 0.88 (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 137.9, 128.9, 128.7, 127.2, 43.9, 33.2, 31.9, 29.5, 29.3, 29.0, 25.7, 22.8, 14.2; ESIHRMS: *m/z* calcd. for $C_{17}H_{26}O_2SNa$ $(M + Na)^+$ 301.1602, found 301.1621.



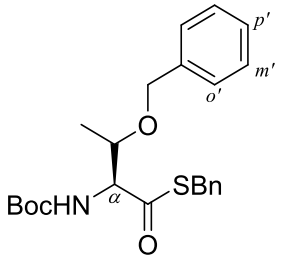
***S*-Benzyl *N*-*tert*-butoxycarbonyl-L-thiophenylalaninate** (**8c**). Boc-L-Phe-SMpa (**7c**, 55 mg, 0.13 mmol) was used as a *S*-α-methylphenacyl thioester. Purification was performed by silica gel column chromatography (10 g, hexane/EtOAc = 19/1) to afford the title compound as a colorless solid (41 mg, 83%). $[\alpha]^{20}_{D}$ = -11.0 (*c* = 0.36, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.21 (m, 8H, Ar-H), 7.14-7.04 (m, 2H, Ar-H), 4.89 (br d, $J_{\alpha,NH}$ = 4.0 Hz, 1H, NH), 4.65 (ddd, $J_{\alpha,\beta}$ = 6.4 Hz each, $J_{\alpha,NH}$ = 4.0 Hz, 1H, H_α), 4.17 & 4.04 (ABq, *J* = 13.6 Hz, 1H each, CH_2Ph), 3.11 (dd, $J_{\alpha,\beta}$ = 6.4 Hz, $J_{\beta,\beta}$ = 19.2 Hz, 2H, $CH_{2\beta}$), 1.43 & 1.39 (s, 4.5H each, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 155.0, 137.2, 135.5, 129.5, 129.0, 128.9, 128.7, 127.4, 127.1, 80.5, 38.4, 33.4, 28.5, 28.4; ESIHRMS: *m/z* calcd. for $C_{21}H_{25}NO_3SNa$ $(M + Na)^+$ 394.1453, found 394.1479.



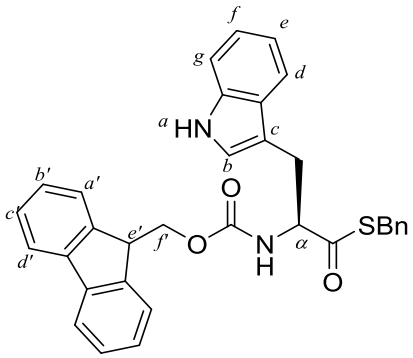
***S*-Benzyl *N*-*tert*-butoxycarbonylthioglycinate** (**8d**). Boc-Gly-SMpa (**7d**, 183 mg, 0.57 mmol) was used as a *S*-α-methylphenacyl thioester. Purification was performed by silica gel column chromatography (15 g, hexane/EtOAc = 19/1) to afford the title compound as a yellow foam (132 mg, 83 %). mp: 72.4-76.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.21 (m, 5H, Ar-H), 5.10 (br d, $J_{\alpha,NH}$ = 6.2 Hz, NH), 4.15 & 4.12 (ABq, *J* = 12.4 Hz, 2H, CH_2Ph), 4.05 (d, $J_{\alpha,NH}$ = 6.2 Hz, 2H, $CH_{2\alpha}$), 1.45 (s, 9H, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$), δ 197.8, 137.1, 129.0, 128.7, 127.5, 127.0, 80.5, 50.3, 33.0, 28.4; ESIHRMS: *m/z* calcd. for $C_{14}H_{19}NO_3SNa$ $(M + Na)^+$ 304.0984, found 304.0996.



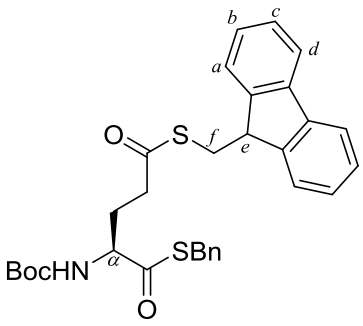
***S*-Benzyl *N*-*tert*-butoxycarbonyl-*O*-benzyl-L-thioserinate** (**8e).** Boc-L-Ser(OBn)-SMpa (**7e**, 61 mg, 0.14 mmol) was used as a *S*-α-methylphenacyl thioester. Purification was performed by silica gel column chromatography (10 g, hexane/EtOAc = 19/1) to afford the title compound as a colorless oil (43 mg, 78%). $[\alpha]^{20}_{D}$ = -1.7 (*c* = 0.53, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.17 (m, 10H, Ar-H), 5.49 (br, d, $J_{\alpha,NH}$ = 8.8 Hz, 1H, NH), 4.49 (ddd, $J_{\alpha,NH}$ = 8.8 Hz, $J_{\alpha,\beta}$ =3.6 Hz each, 1H, H_α), 4.47-4.42 (m, 2H, SCH_2Ph), 4.19 & 4.08 (ABq, *J* = 14.0 Hz, 1H each, OCH_2Ph), 4.00 & 3.98 (dd, $J_{\alpha,\beta}$ = 3.6 Hz, $J_{\beta,\beta}$ = 9.6 Hz, 1H, $CH_{2\beta}$), 3.67 & 3.64 (dd, $J_{\alpha,\beta}$ = 3.6 Hz, $J_{\beta,\beta}$ = 9.6 Hz, 1H, $CH_{2\beta}$), 1.46 (s, 9H, ^{t}Bu); ^{13}C NMR(100 MHz, $CDCl_3$) δ 200.2, 155.4, 137.5, 137.2, 129.0, 128.7, 128.5, 127.9, 127.7, 127.4, 80.5, 73.5, 70.4, 60.4, 33.6, 28.4; ESIHRMS: *m/z* calcd. for $C_{22}H_{27}NO_4SNa$ $(M + Na)^+$ 424.1559, found 424.1572.



***S*-Benzyl *N*-*tert*-butoxycarbonyl-*O*-benzyl-L-thiothreonate** (**8f**). Boc-L-Thr(OBn)-SMpa (**7f**, 51 mg, 0.11 mmol) was used as a *S*-α-methylphenacyl thioester. Purification was performed by silica gel column chromatography (10 g, hexane/EtOAc = 19/1) to afford the title compound as a colorless solid (33 mg, 73%). mp: 90.2-93.2 °C; $[\alpha]^{20}_{D}$ = -17.0 (*c* = 0.48, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.05 (m, 10H, Ar-H), 5.42 (br d, *J* = 9.2 Hz, 1H, NH), 4.43 & 4.30 (ABq, *J* = 11.6 Hz, 1H each, SCH_2Ph), 4.33-4.25 (m, 2H, H_α, H_β), 4.20 & 4.03 (ABq, *J* = 13.6 Hz, 1H each, OCH_2Ph), 1.46 (s, 9H, ^{t}Bu), 1.24 (d, $J_{\beta,\gamma}$ = 6.0 Hz, $CH_{3\gamma}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 156.0, 137.9 , 137.4, 129.0, 128.7, 128.4, 127.8, 127.3, 80.4, 74,8, 71.7, 65.1, 33.6, 28.4, 16.9; ESIHRMS: *m/z* calcd. for $C_{23}H_{29}NO_3SNa$ $(M + Na)^+$ 438.1715, found 438.1725.

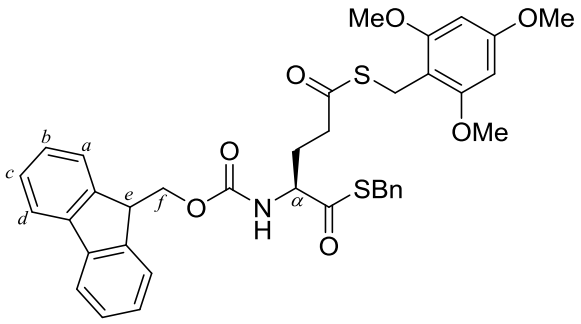


***S*-Benzyl *N*-fluorenylmethyloxycarbonyl-L-thiotryptophanate** (**8g**). Fmoc-L-Trp-SMpa (**7g**, 80 mg, 0.09 mmol) was used as a *S*-α-Methylphenacyl thioester. Purification was performed by silica gel column chromatography (10 g, hexane/EtOAc = 9/1 to 2/1) to afford the title compound as a white foam (43 mg, 85%). $[\alpha]^{20}_{D}$ = -47.9 (*c* = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (br, 1H, NH_a), 7.75 (d, $J_{c',d'}$ = 7.2 Hz, 2H, $H_{d'}$), 7.59 (d, $J_{d,e}$ = 7.6 Hz, 1H, H_d), 7.52 (dd, $J_{b',c'}$ = 7.6 Hz, $J_{c',d'}$ = 7.2 Hz, 2H, $H_{c'}$), 7.43-7.18 (m, 11H, Fm-H x4, InH x2, Ar-H x5), 7.15 (dd, $J_{d,e}$ = 7.6 Hz, $J_{e,f}$ = 7.2 Hz, 1H, H_e), 6.79 (s, 1H, H_b), 5.32 (br d, $J_{\alpha,NH}$ = 8.8 Hz, 1H, NH), 4.82 (ddd, $J_{\alpha,NH}$ = 8.8 Hz, $J_{\alpha,\beta}$ = 5.2 Hz each, 1H, H_α), 4.35 (dd, $J_{e',f'}$ = 7.2 Hz each, 2H, $CH_{2f'}$), 4.18 (t, $J_{e',f'}$ = 7.2 Hz, 1H, $H_{e'}$), 4.11 & 4.07 (ABq, *J* = 13.6 Hz, 1H each, CH_2Ph), 3.34 (ddd, $J_{\alpha,\beta}$ = 5.2 Hz each, $J_{\beta,\beta}$ = 14.8 Hz, 2H, $CH_{2\beta}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 155.8, 143.9, 143.8, 141.4, 137.1, 136.2, 129.1, 128.7, 127.8, 127.4, 127.2, 125.2, 123.3, 122.5, 120.0, 118.7, 111.4, 109.4, 67.3, 61.1, 47.2, 33.6, 28.2; ESIHRMS: *m/z* calcd. for $C_{33}H_{28}N_2O_3SNa$ $(M + Na)^+$ 555.1719, found 555.1709.



S^{α}-Benzyl S^{γ}-9-fluorenylmethyl *N*-*tert*-butoxycarbonyl-L-dithioglutamate (8h).

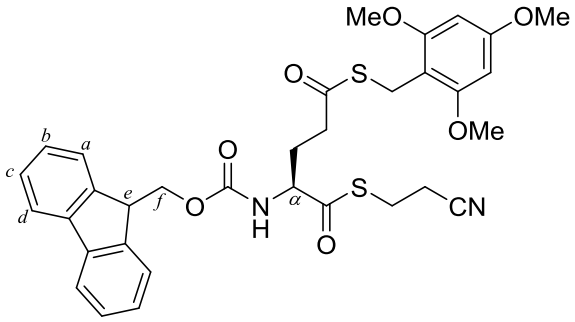
Boc-L-Glu(SFm)-SMpa (**7h**, 110 mg, 0.19 mmol) was used as a *S*-α-Methylphenacyl thioester. Purification was performed by silica gel column chromatography (10 g, hexane/Acetone = 9/1 to 4/1) to afford the title compound as a colourless foam (79 mg, 78%). $[\alpha]^{20}_{D}$ = 3.26 (*c* = 0.31, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, $J_{c,d}$ = 7.6 Hz, 2H, H_d), 7.62 (d, $J_{a,b}$ = 7.2 Hz, 2H, H_a), 7.34 (dd, $J_{b,c}$ = 7.2 Hz, $J_{c,d}$ = 7.6 Hz, 2H, H_c), 7.31 (dd, $J_{a,b}$ = 7.2 Hz, $J_{b,c}$ = 7.2 Hz, 2H, H_b), 7.30-7.22 (m, 5H, Ar-H), 5.09 (br, 1H, NH), 4.36-4.26 (m, 1H, H_α), 4.16 (t, $J_{e,f}$ = 5.6 Hz, 1H, H_e), 4.19-4.04 (m, 2H, CH_2Ph), 3.53 (d, $J_{e,f}$ = 5.6 Hz, 2H, CH_{2f}), 2.65-2.48(m, 2H, $CH_{2\gamma}$), 2.22-2.17 & 2.04-1.80 (m, 1H each, $CH_{2\beta}$), 1.43 (s, 9H, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 198.1, 155.2, 145.4, 141.2, 137.0, 129.0, 128.7, 127.9, 127.5, 127.2, 124.7, 124.7, 120.0, 80.6, 59.8, 46.8, 40.0, 33.4, 32.4, 28.4, 28.1; ESIHRMS: *m/z* calcd. for $C_{31}H_{33}NO_4S2Na$ $(M + Na)^+$ 570.1749, found 570.1771



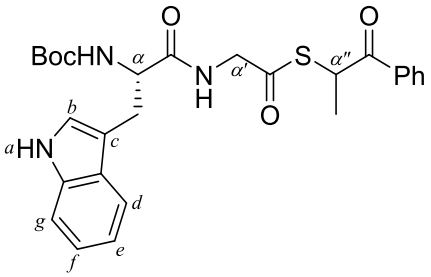
S^{α}-Benzyl S^{γ}-2,4,6-trimethoxybenzyl *N*-(9-fluorenylmethyloxycarbonyl)-L-dithioglutamate (**8i**)**.**

Fmoc-L-Glu(STmob)-SMpa (**7i**, 50 mg, 0.07 mmol) was used as a *S*-α-Methylphenacyl thioester. Purification was performed by silica gel column chromatography (10 g, hexane/EtOAc = 9/1 to 2/1) to afford the title compound as a colorless soild (38 mg, 81%). mp: 103.0-106.2 °C; $[\alpha]^{20}_{D}$ = -3.0 (*c* = 0.43 , $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, $J_{c,d}$ = 7.2 Hz, 2H, H_d), 7.60 (d, $J_{a,b}$ = 7.2 Hz, 2H, H_a), 7.38 (dd, $J_{b,c}$ = 6.8 Hz, $J_{c,d}$ = 7.2 Hz, 2H, H_c), 7.29 (m, 7H, Fm-H, Ar-H x 5), 6.08 (s, 2H, Ar-H), 5.58 (br d, $J_{\alpha,NH}$ = 8.4 Hz, 0.5H each, NH), 4.50-4.35 (m, 3H, H_α, CH_{2f}), 4.26-4.18 (m, 3H, CH_2Ph, H_e), 4.13 & 4.09 (ABq, *J* = 13.6 Hz, 2H, CH_2Ph), 3.77 (s, 9H, OCH_3 x 3), 2.70-2.54 (m, 2H, $CH_{2\gamma}$), 2.32-2.23 & 2.10-1.98 (m, 1H each, $CH_{2\beta}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 199.6, 161.0, 159.2, 155.9, 143.9, 143.8, 143.7, 141.3, 136.8, 129.0, 128.8, 127.8, 127.5, 127.2, 125.2,

120.0, 104.6, 90.6, 67.3, 60.5, 55.9, 55.4, 47.3, 39.5, 33.5, 28.0, 22.4; ESIHRMS: *m/z* calcd. for $C_{37}H_{37}NO_7S_2Na$ $(M + Na)^+$ 694.1909, found 694.1899.



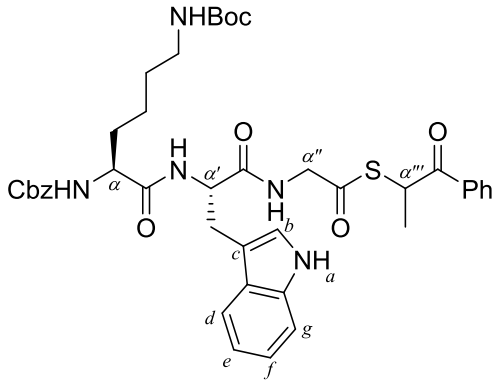
***S*$^{\alpha}$-Cyanoethyl *S*$^{\gamma}$-(2,4,6-trimethoxybenzyl) *N*-(9-fluorenylmethyloxycarbonyl)-L-dithioglutamate** (**8j**). Fmoc-L-Glu(STmob)-SMpa (**7i**, 48 mg, 0.07 mmol) was used as a *S*-α-Methylphenacyl thioester. Purification was performed by silica gel column chromatography (10 g, hexane/EtOAc = 2/1) to afford the title compound as a colorless form (33 mg, 77%). $[\alpha]^{20}_D$ = 6.9 (*c* = 0.15, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, $J_{c,d}$ = 7.6 Hz, 2H, H_d), 7.61 (m, 2H, Fm-H), 7.39 (dd, $J_{b,c}$ = 7.2 Hz, $J_{c,d}$ = 7.6 Hz, 2H, H_c), 7.31 (dd, $J_{b,c}$ = 7.2 Hz, $J_{a,b}$ = 7.2 Hz, 2H, H_b), 6.08 (s, 2H, Ar-H), 5.68 (br d, $J_{\alpha,NH}$ = 8.4 Hz, 1H, NH), 4.55-4.45 (m, 1H, H_α), 4.45-4.35 (m, 2H, CH_{2f}), 4.28-4.17 (m, 3H, CH_2Ph, H_e), 3.77 (s, 9H, OCH_3 x 3), 3.08 (q, *J* = 6.4 Hz, 2H, CH_2), 2.75-2.50 (m, 4H, CH_2, $CH_{2\gamma}$), 2.30-2.20 & 2.13-1.98 (m, 1H each, $CH_{2\beta}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 199.7, 161.0, 159.2, 156.0, 143.8, 143.6, 141.4, 128.8, 127.8, 127.2, 125.2, 125.2, 120.1, 117.8, 104.5, 90.6, 67.4, 60.7, 55.9, 55.4, 47.3, 39.4, 27.4, 24.6, 22.5, 18.4; ESIHRMS: *m/z* calcd. for $C_{33}H_{34}N_2O_7S_2Na$ $(M + Na)^+$ 657.1705, found 657.1679.



***S*-α-Methylphenacyl *N*-*tert*-butoxycarbonyl-L-tryptophanylthioglycinate** (**9**).

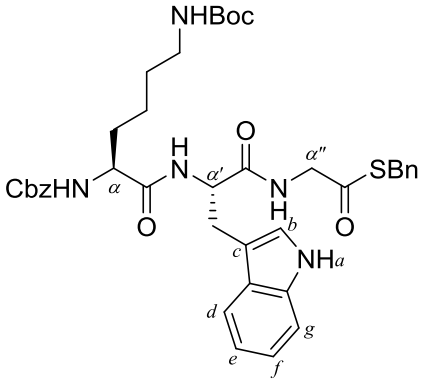
Boc-Gly-SMpa (**7c**, 472 mg, 1.5 mmol) was dissolved in 40% TFA/CH_2Cl_2 (15 mL), and the solution was stirred for 10 min. The solution was concentrated *in vacuo*, and the residual TFA was removed by azeotropic distillation with toluene *in vacuo*. In another flask, Boc-L-Trp-OH (667 mg, 2.2 mmol), and *N*-methylmorphiline (192 μL, 1.8 mmol) were suspended in CH_2Cl_2 (3.0 mL), and HOBt·H_2O (355 mg, 2.6 mmol) and EDCI (336 mg, 1.8 mmol) were added. The reaction mixture was stirred for 15 min, and it was added to a solution of the residue in CH_2Cl_2 (3.0 mL). The reaction mixture was stirred for further 1 h, and the reaction was quenched with water (20 mL). The mixture was extracted with CH_2Cl_2 (10 mL x 3), and the combined organic layer was washed with brine (20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the residue by flash

chromatography (silica gel 20 g, hexane/EtOAc = 4/1 to 1/1) gave an orange foam (588 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (br s, 1H, NH_a), 7.95 & 7.94 (d, $J_{o,m}$ = 7.6 Hz, 1H each, Ar-H_o), 7.59 (t, $J_{m,p}$ = 7.6 Hz, 1H, Ar-H_p), 7.58 (d, $J_{d,e}$ = 6.8 Hz, 1H, H_d), 7.46 (dd, $J_{o,m}$ = 7.6 Hz, $J_{m,p}$ = 7.6 Hz, 2H, Ar-H_m), 7.32 (dd, $J_{d,e}$ = 6.8 Hz, $J_{e,f}$ = 8.0 Hz ,1H, H_e), 7.16 (dd, $J_{e,f}$ = 8.0 Hz, $J_{f,g}$ = 7.6 Hz, 1H, H_f), 7.09 & 7.08 (d, $J_{f,g}$ = 7.6 Hz, 0.5H each, H_g), 7.00 (s, 1H, H_b), 6.59 (br s, 1H, NH), 5.21 & 5.20 (q, $J_{\alpha'',\beta''}$ = 6.8 Hz, 0.5H each, $H_{\alpha''}$), 5.12 (br s, 1H, NH), 4.51 (m, 1H, H_α), 4.04 (m, 2H, $CH_{2\alpha'}$), 3.21 (m, 2H, $CH_{2\beta}$), 1.49 (d, $J_{\alpha'',\beta''}$ = 6.8 Hz, 3H, $CH_{3\beta''}$), 1.39 (s, 9H, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 195.8, 172.4, 172.4, 156.5, 155.6, 136.3, 134.8, 133.9, 128.9, 128.7, 127.6, 123.7, 123.6, 122.3, 119.8, 118.7, 111.4, 110.2, 110.0, 55.4, 55.3, 55.2, 48.9, 42.5, 28.4, 28.0, 17.9, 17.8; ESIHRMS: *m/z* calcd. for $C_{27}H_{31}N_3O_5SNa$ $(M + Na)^+$ 532.1882, found 532.1895.

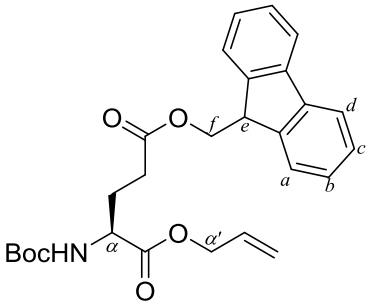


***S*-α-Methylphenacyl *N*$^{\alpha}$-benzyloxycarbonyl-*N*$^{\varepsilon}$-*tert*-butoxycarbonyl-L-lysyl-L-tryptophanylthio glycinate** (**10**). Boc-L-Trp-Gly-SMpa (**9**, 526 mg, 1.1 mmol) was dissolved in 40% TFA/CH_2Cl_2 (11 mL), and the solution was stirred for 20 min. The solution was concentrated *in vacuo*, and the residual TFA was removed by azeotropic distillation with toluene *in vacuo*. In another flask, Cbz-L-Lys(Boc)-OH (605 mg, 1.6 mmol), and *N*-methylmorphiline (140 μL, 1.3 mmol) were suspended in CH_2Cl_2 (2.1 mL), and HOBt·H_2O (258 mg, 1.9 mmol) and EDCI (244 mg, 1.3 mmol) were added. The reaction mixture was stirred for 10 min, and it was added to a solution of the residue in CH_2Cl_2 (1 mL). The reaction mixture was stirred for further 1 h, and the reaction was quenched with water (20 mL). The mixture was extracted with CH_2Cl_2 (10 mL x 3), and the combined organic layer was washed with brine (20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the residue by flash chromatography (silica gel 20 g, hexane/EtOAc = 4/1 to 1/1) gave an orange foam (662 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 & 8.66 (br s, 0.5H each, NH_a), 7.94 & 7.90 (d, $J_{o,m}$ = 7.6 Hz, 1H each, Ar-H_o), 7.56 (t, $J_{m,p}$ = 7.6 Hz, 1H, Ar-H_p), 7.54 (d, $J_{d,e}$ = 6.8 Hz, 1H, H_d), 7.45 & 7.39 (dd, $J_{o,m}$ = 7.6 Hz, $J_{m.p}$ = 7.6 Hz, 1H each, Ar-H_m), 7.35-7.18 (m, 7H, Ar-H x5, InH x2), 7.13 (dd, $J_{e,f}$ = 6.8 Hz, $J_{f,g}$ = 6.8 Hz, 1H, H_f), 7.08 (d, $J_{f,g}$ = 6.8 Hz, 1H, H_g), 7.01 & 6.94 (s, 0.5H each, H_b), 6.80-6.73 (br, 1H, NH), 5.63 & 5.59 (br, 0.5H each, NH), 5.22 (q, $J_{\alpha''',\beta'''}$ = 6.8 Hz, 1H, $H_{\alpha'''}$), 5.05-4.65 (m, 4H, $PhCH_2$, H_α, NH), 4.25-4.10 (m, 1H, $H_{\alpha''}$), 3.96 (m, 2H,

$CH_{2\alpha''}$), 3.39-3.17 (m, 2H, $CH_{2\beta'}$), 3.08-2.80 (m, 2H, $CH_{2\beta}$), 1.49 (d, $J_{\alpha''',\beta'''}$ = 6.8 Hz, 3H, $CH_{3\beta'''}$), 1.39 (s, 9H, ^{t}Bu), 1.38-1.27 (m, 4H, CH_2 x2), 1.16-1.03 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 197.7, 172.0, 156.9, 156.7, 156.6, 136.3, 136.0, 134.7, 134.0, 133.8, 129.0, 128.9, 128.8, 128.7, 128.6, 128.6, 128.4, 128.3, 127.6, 124.0, 123.7, 122.2, 119.8, 118.4, 118.3, 111.6, 110.0, 79.5, 77.3, 67.4, 67.3, 54.0, 49.1, 42.6, 29.8, 28.5, 18.1; ESIHRMS: *m/z* calcd. for $C_{41}H_{49}N_5O_8SNa$ $(M + Na)^+$ 794.3200, found 794.3186.

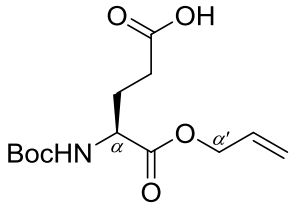


***S*-Benzyl N^{α}-benzyloxycarbonyl-N^{ε}-*tert*-butoxycarbonyl-L-lysyl-L-tryptophenylthioglycinate** (**11**). Cbz-L-Lys(Boc)-L-Trp-Gly-SMpa (**10**, 62 mg, 0.08 mmol) in 90% AcOH (0.8 mL) was degassed, and freshly washed Zn (268 mg, 4.1 mmol) was added to the solution. The mixture was degassed again and stirred for 1 h at 40 °C, followed by concentration under high vacuum. The residue was suspended in $CHCl_3$/MeOH (5/1), and then filtrated through silica gel pad. The filtrate was concentrated *in vacuo*. To the residue in DMF (0.8 ml) were added Cs_2CO_3 (79 mg, 0.25 mmol) and BnBr, and the reaction mixture was stirred for 15 min. The reaction was quenched with water (10 mL). The mixture was extracted with EtOAc (7 mL x 3), and the combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purfication of the residue by flash chromatography (silica gel 10 g, $CHCl_3$ to $CHCl_3$/EtOAc = 1/1) gave the title compound as a colorless solid (50 mg, 89%). mp: 132.8-138.8 °C; $[\alpha]^{20}_D$ = -25.1 (*c* = 0.63, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (br, 1H, NH_a), 7.53 (d, $J_{d,e}$ = 7.8 Hz, 1H, H_d), 7.37-7.16 (m, 11H, In-H, Ar-H x10), 7.12 (dd, $J_{d,e}$ = 7.8 Hz, $J_{e,f}$ = 7.7 Hz, 1H, H_e), 7.05 (dd, $J_{e,f}$ = 7.7 Hz, $J_{f,g}$ = 7.0 Hz 1H, H_f), 6.94 (s, 1H, H_b), 6.87 (br, 1H, NH), 5.73 (br, 1H, NH), 4.97 & 4.92 (ABq, *J* = 12.0 Hz, 1H each, $PhCH_2$), 4.82 (m, 1H, H_α), 4.71 (br, 1H, NH), 4.16-3.87 (m, 5H, CH_2Ph, $CH_{2\alpha''}$, $H_{\alpha'}$), 3.32-3.17 (m, 2H, $CH_{2\beta'}$), 3.30-2.87 (m, 2H, $CH_{2\beta}$), 1.40 (s, 9H, ^{t}Bu), 1.32-1.20 (m, 4H, CH_2 x2), 1.15-1.00 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 172.1, 171.9, 156.8, 156.6, 137.1, 136.3, 136.1, 129.0, 128.6, 128.4, 128.2, 127.5, 123.6, 122.1, 119.7, 118.5, 111.5, 110.0, 79.5, 77.3, 67.3, 55.8, 53.9, 49.0, 39.6, 33.0, 31.2, 29.7, 28.5, 27.3, 22.1; ESIHRMS: *m/z* calcd. for $C_{39}H_{47}N_5O_7SNa$ $(M + Na)^+$ 752.3094, found 752.3100.



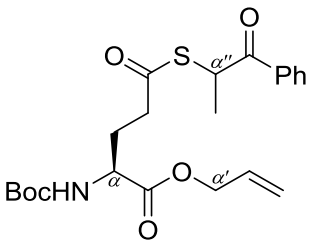
***O*$^{\alpha}$-Allyl *O*$^{\gamma}$-(9-fluorenylmethyl) *N*-*tert*-butoxycarbonyl-L-glutamate** (**13**).

To Boc-L-Glu(OFm)-OH[5] (**12**, 1.4 g, 3.3 mmol) in DMF (6.6 mL) were added AllBr (0.34 mL 4.0 mmol) and K_2CO_3 (0.55 g, 4.0 mmol) at room temperature. The reaction mixture was stirred for 3 h, and then poured to water (100 mL). The mixture was extracted with CH_2Cl_2 (50 mL x 3), and the combined organic layer was washed with brine (100 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purfication of the residue by flash chromatography (silica gel 10 g, hexane/EtOAc = 9/1 to 4/1) gave the title compound as a colorless syrup (1.5 g, 97%). $[\alpha]^{20}_D$ = 5.9 (*c* = 0.78, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, $J_{c,d}$ = 7.2 Hz, 2H, H_d), 7.57 (d, $J_{a,b}$ = 7.6 Hz, 2H, H_a), 7.38 (dd, $J_{b,c}$ = 7.2 Hz, $J_{a,b}$ = 7.6 Hz, 2H, H_b), 7.30 (dd, $J_{c,d}$ = 7.2 Hz, $J_{b,c}$ = 7.2 Hz, 2H, H_c), 5.90 (dddd, $J_{\alpha',\beta'}$ = 5.2 Hz each, $J_{\beta',\gamma'(E)}$ = 16.8 Hz, $J_{\beta',\gamma'(Z)}$ = 10.4 Hz, 1H, $H_{\beta'}$), 5.38 (ddd, $J_{\beta',\gamma'(E)}$ = 16.8 Hz, $J_{\beta',\gamma'(Z)}$ = 10.4 Hz, $J_{\gamma',\gamma'}$ = 1.2 Hz, 2H, $CH_{2\gamma'}$), 5.30-5.18 (br, 1H, NH), 4.63 (dd, $J_{\alpha',\beta'}$ = 5.2 Hz each, 2H, $CH_{2\alpha'}$), 4.4-4.33 (m, 3H, CH_{2f}, H_α), 4.19 (t, $J_{e,f}$ = 6.8 Hz, 1H, H_e), 2.49 (td, $J_{\beta,\gamma}$ = 6.8 Hz, $J_{\gamma,\gamma}$ = 16.0 Hz, 2H, $CH_{2\gamma}$), 2.21 & 1.97 (dtd, $J_{\beta,\beta}$ = 20.8 Hz, $J_{\beta,\gamma}$ = 6.8 Hz each, 1H each, $CH_{2\beta}$), 1.41 (s, 9H, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 171.9, 155.5, 143.8, 143.8, 141.4, 131.6, 127.9, 127.2, 125.1, 120.1, 119.0, 80.1, 66.6, 66.1, 53.1, 46.9, 30.4, 28.4, 27.8; ESIHRMS: *m/z* calcd. for $C_{27}H_{31}NO_6Na$ $(M + Na)^+$ 488.2049, found 488.2053.



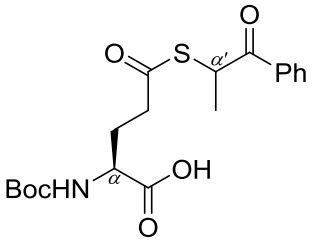
***O*$^{\alpha}$-Allyl *N*-*tert*-butoxycarbonyl-L-glutamic acid** (**14**). Boc-L-Glu(OFm)-OAll (**13**, 0.89 g, 1.9 mmol) was added 20% piperidine in DMF (7.3 mL) at room temperature, and the reaction mixture was stirred 20 min, followed by concentration under high vacuum. Purfication of the residue by flash chromatography (silica gel 20 g, hexane/EtOAc = 4/1 to EtOAc) gave the title compound as a colorless syrup (470 mg, 85%). $[\alpha]^{20}_D$ = 1.5 (*c* = 1.55, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30-8.30 (br, 1H, CO_2H), 5.88 (dddd, $J_{\alpha',\beta'}$ = 5.6 Hz each, $J_{\beta',\gamma'(E)}$ = 17.2 Hz, $J_{\beta',\gamma'(Z)}$ = 10.8 Hz, 1H, $H_{\beta'}$), 5.28 (ddd, $J_{\beta',\gamma'(E)}$ = 17.2 Hz, $J_{\beta',\gamma'(Z)}$ = 10.8 Hz, $J_{\gamma',\gamma'}$ = 1.6 Hz, 2H, $CH_{2\gamma'}$), 5.22-5.16 (br d, $J_{\alpha,NH}$ = 8.0 Hz, 1H, NH), 4.61 (dd, $J_{\alpha',\beta'}$ = 5.6 Hz each, 2H, $CH_{2\alpha'}$), 4.35 (ddd, $J_{\alpha,NH}$ = 8.0 Hz, $J_{\alpha,\beta}$ = 6.8

Hz each, 1H, H_{α}), 2.44 (ttd, $J_{\beta,\gamma}$ = 6.8 Hz each, $J_{\gamma,\gamma}$ = 7.2 Hz, 2H, $CH_{2\gamma}$), 2.18 & 1.95 (tdd, $J_{\alpha,\beta}$ = 6.8 Hz, $J_{\beta,\gamma}$ = 6.8 Hz, $J_{\beta,\beta}$ = 14.4 Hz, 1H each, $CH_{2\beta}$), 1.44 (s, 9H, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 172.0, 155.6, 131.5, 119.1, 80.3, 66.2, 52.9, 30.2, 28.3, 27.7; ESIHRMS: *m/z* calcd. for $C_{13}H_{21}NO_6Na$ $(M + Na)^+$ 310.1267, found 310.1251.



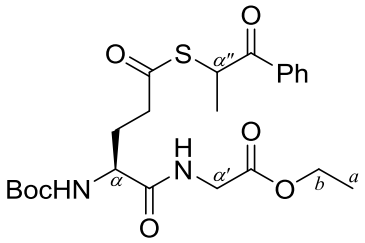
***O*$^{\alpha}$-Allyl *S*$^{\gamma}$-α-methylphenacyl *N*-*tert*-butoxycarbonyl-L-γ-thioglutamate** (**15**).

To Boc-L-Glu(OH)-OAll (**14**, 710 mg, 2.5 mmol) and *S*-α-methylphenacylthiol (500 mg, 3.0 mmol) in CH_2Cl_2 (5.0 mL) were added EDCI (570 mg, 3.0 mmol) and DMAP (30 mg, 0.25 mmol) at room temperature. The reaction mixture was stirred for 2 h, and the reaction was quenched with water (30 mL). The mixture was extracted with CH_2Cl_2 (15 mL x 3), and the combined organic layer was washed with brine (20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purfication of the residue by flash chromatography (silica gel 20 g, hexane/EtOAc = 9/1 to 4/1) gave a yellow syrup (870 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, $J_{o,m}$ = 7.2 Hz, 2H, Ar-H_o), 7.56 & 7.54 (t, $J_{m,p}$ = 7.2 Hz, 0.5H each, Ar-H_p), 7.44 (dd, $J_{o,m}$ =7.2 Hz, $J_{m,p}$ =7.2 Hz, 2H, Ar-H_m), 5.86 (m, 1H, $H_{\beta'}$), 5.36-5.17 (m, 3H, $CH_{2\gamma'}$, $H_{\alpha''}$), 5.16-5.02 (br, 1H, NH), 4.54-4.65 (m, 2H, $CH_{2\alpha'}$), 4.37-4.25 (m, 1H, H_{α}), 2.73-2.52 (m, 2H, $CH_{2\gamma}$), 2.28-2.12 & 2.05-1.87 (m, 1H each, $CH_{2\beta}$), 1.53 & 1.52 (d, $J_{\alpha'',\beta''}$ = 6.8 Hz, 1.5H each, $CH_{3\beta''}$), 1.40 & 1.39 (s, 4.5H each, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 196.8, 196.7, 171.3, 155.3, 134.9, 133.7, 131.5, 128.8, 128.6, 119.2, 80.2, 66.2, 66.2, 52.8, 52.7, 42.4, 42.4, 39.6, 39.5, 28.3, 28.2, 28.1, 17.8, 17.8; ESIHRMS: *m/z* calcd. for $C_{22}H_{29}NO_6SNa$ $(M + Na)^+$ 458.1614, found 458.1630.



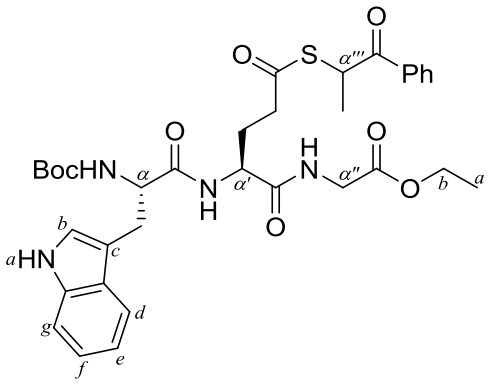
***S*$^{\gamma}$-α-Methylphenacyl *N*-*tert*-butoxycarbonyl-L-γ-thioglutamic acid** (**16**). Triphenylphosphine (29 mg, 0.11 mmol) and palladium (II) acetate (5.0 mg, 0.02 mmol) in CH_2Cl_2 (2.3 mL) were added to a solution of Boc-L-Glu(SMpa)-OAll (**15**, 490 mg, 1.1 mmol) in CH_2Cl_2 (2.3 mL). The mixture was degassed, and then phenylsilane (0.07 mL, 0.56 mmol) was added. After stirring for 1 h, the resulting solution was concentrated *in vacuo*. Purification of the residue by flash chromatography (silica gel

15 g, $CHCl_3$/EtOAc = 9/1 to 4/1) gave a yellow form (436 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, $J_{o,m}$ = 8.0 Hz, 2H, Ar-H_o), 7.55 (t, $J_{m,p}$ = 7.6 Hz, 1H, Ar-H_p), 7.43 (dd, $J_{o,m}$ = 8.0 Hz, $J_{m,p}$ = 7.6 Hz, 2H, Ar-H_m), 5.32 (br, 1H, NH), 5.25 (q, $J_{\alpha',\beta'}$ = 6.8 Hz, 1H, $H_{\alpha'}$), 4.36-4.09 (m, 1H, H_α), 2.78-2.55 (m, 2H, $CH_{2\gamma}$), 2.30-2.13 & 2.09-2.00 (m, 1H each, $CH_{2\beta}$), 1.51 (d, $J_{\alpha',\beta'}$ = 6.8 Hz, 3H, $CH_{3\beta'}$), 1.39 (s, 9H, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 197.5, 197.2, 197.1, 197.1, 155.9, 155.8, 134.9, 133.8, 128.8, 128.6, 80.5, 80.4, 42.5, 39.7, 39.6, 39.6, 29.8, 28.4, 27.8, 27.8, 17.8, 17.8; ESIHRMS: *m/z* calcd. for $C_{19}H_{25}NO_6SNa$ $(M + Na)^+$ 418.1301, found 418.1329.

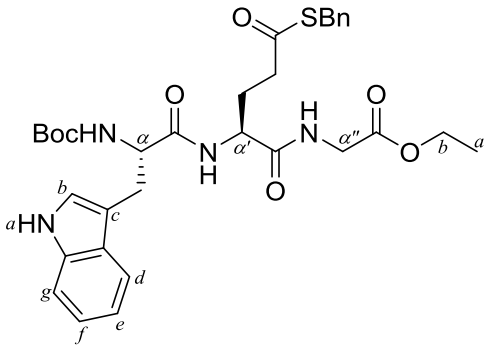


Ethyl *N-tert*-butoxycarbonyl-L-*S*$^\gamma$-α-methylphenacyl-γ-thioglutamylglycinate (**17**).

Boc-L-Glu(SMpa)-OH (**16**, 210 mg, 0.52 mmol), and HOBt·H_2O (120 mg, 0.79 mmol) were suspended in CH_2Cl_2 (5.0 mL), and EDCI (120 mg, 0.63 mmol) and *N*-methylmorphiline (68 μL, 0.63 mmol) were added. The mixture was stirred for 10 min, and then H_2N-Gly-OEt·HCl (88 mg, 0.63 mmol) was added. The reaction mixture was stirred for further 3 h, and then quenched with water (20 mL). The mixture was extracted with CH_2Cl_2 (10 mL x 3), and the combined organic layer was washed with brine (20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the residue by flash chromatography (silica gel 15 g, hexane/EtOAc = 4/1 to 1/1) gave a yellow foam (210 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, $J_{o,m}$ = 7.2 Hz, 2H, Ar-H_o), 7.53 (t, $J_{m,p}$ = 7.2 Hz, 1H, Ar-H_p), 7.42 (dd, $J_{o,m}$ = 7.2 Hz, $J_{m,p}$ = 7.2 Hz, 2H, Ar-H_m), 6.99 (br, 1H, NH), 5.41 (br, 1H, NH), 5.23 (q, 1H, $J_{\alpha'',\beta''}$ = 6.8 Hz, $H_{\alpha''}$), 4.27-4.16 (m, 1H, H_α), 4.14 (q, $J_{a,b}$ = 6.8 Hz, 2H, CH_{2b}), 3.87-4.03 (m, 2H, $CH_{2\alpha'}$), 2.68 (m, 2H, $CH_{2\gamma}$), 2.14 & 1.95 (m, 1H each, $CH_{2\beta}$), 1.50 (d, $J_{\alpha'',\beta''}$ = 6.8 Hz, 3H, $CH_{3\beta''}$), 1.37 (s, 9H, ^{t}Bu), 1.21 (t, $J_{a,b}$ = 6.8 Hz, 3H, CH_{3a}); ^{13}C NMR (100MHz, $CDCl_3$) δ 197.4, 197.3, 197.3, 171.7, 169.6, 169.6, 155.7, 134.9, 134.9, 133.6, 128.8, 128.6, 80.3, 61.5, 53.4, 53.2, 41.1, 39.7, 39.5, 28.4, 28.1, 17.8, 17.7, 14.2; ESIHRMS: *m/z* calcd. for $C_{23}H_{32}N_2O_7SNa$ $(M + Na)^+$ 503.1828, found 503.1851.



Ethyl *N*-*tert*-Butoxycarbonyl-L-tryptophanyl-*S*$^{\gamma}$-α-methylphenacyl-L-thioglutamylglycinate (**18**). Boc-L-Glu(SMpa)-Gly-OEt (**17**, 87 mg, 0.18 mmol) was dissolved in 40% TFA/CH_2Cl_2 (0.9 mL), and the solution was stirred for 15 min. The solution was concentrated *in vacuo*, and the residual TFA was removed by azeotropic distillation with toluene *in vacuo*. In another flask, Boc-L-Trp-OH (66 mg, 0.22 mmol) and *N*-methylmorphiline (24 μL, 0.22 mmol) were suspended in CH_2Cl_2/DMF (1/1, 1.0 mL), and HOBt·H_2O (42 mg, 0.27 mmol) and EDCI (42 mg, 0.22 mmol) were added. The reaction mixture was stirred for 10 min, and it was added to a solution of the residue in CH_2Cl_2/DMF (1/1, 1.0 mL). The reaction mixture was stirred for further 1 h, and then quenched with water (10 mL). The mixture was extracted with CH_2Cl_2 (5 mL x 3), and the combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the residue by silica gel column chromatography (10 g, $CHCl_3$ to $CHCl_3$/MeOH = 9/1) gave a colorless form (87 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 & 8.59 (br, 0.5H each, NH_a), 7.98 & 7.94 (d, $J_{o,m}$ = 7.2 Hz, 1H each, Ar-H_o), 7.64-7.54 (m, 2H, Ar-H, In-H), 7.48 & 7.45 (dd, $J_{o,m}$ = 7.2 Hz, $J_{m,p}$ = 7.6 Hz, 1H each, Ar-H_m), 7.30 (m, 1H, In-H), 7.16-7.03 (m, 2H, In-H), 6.99-6.82 (m, 3H, In-H, NH x 2), 5.30 & 5.28 (br, 1H, NH), 5.19 & 5.18 (q, $J_{\alpha''',\beta'''}$ = 6.8 Hz, 0.5H each, $H_{\alpha'''}$), 4.49-4.40 (m, 1H, H_{α}), 4.38-4.26 (m, 1H, $H_{\alpha'}$), 4.13 & 4.12 (q, $J_{a,b}$ = 7.2 Hz, 1H each, CH_{2b}), 3.90-3.60 (m, 2H, $CH_{2\alpha''}$), 3.35-3.23 & 3.19-3.08 (m, 1H each, $CH_{2\beta}$), 2.50-2.38 & 2.27-2.18 (m, 1H each, $CH_{2\gamma'}$), 2.10-1.98 & 1.97-1.76 (m, 1H each, $CH_{2\beta'}$), 1.50 & 1.49 (d, $J_{\alpha''',\beta'''}$ = 6.8 Hz, 1.5H each, $CH_{3\beta'''}$), 1.40 (s, 9H, ^{t}Bu), 1.23 & 1.22 (t, $J_{a,b}$ = 7.2 Hz, 1.5H each, CH_{3a}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 198.2, 197.9, 197.8, 172.5, 172.4, 171.0, 170.9, 169.5, 162.9, 156.0, 156.0, 155.9, 136.3, 136.3, 135.1, 134.9, 133.8, 133.8, 129.0, 128.9, 128.7, 128.7, 127.5, 127.4, 126.7, 126.1, 123.6, 123.5, 122.2, 119.7, 118.7, 118.6, 111.6, 111.6, 109.7, 80.6, 61.5, 61.5, 56.0, 52.3, 52.1, 43.0, 43.0, 41.3, 39.1, 39.0, 36.7, 31.6, 28.4, 28.0, 27.9, 27.3, 17.5, 17.5, 14.2; ESIHRMS: *m/z* calcd. for $C_{34}H_{42}N_4O_8SNa$ $(M + Na)^+$ 689.2621, found 689.2614.



Ethyl *N*-*tert*-butoxycarbonyl-L-tryptophanyl-*S*$^{\gamma}$-benzyl-L-γ-thioglutamylglycinate(19).

Boc-L-Trp-L-Glu(SMpa)-Gly-OEt (**18**, 40 mg, 0.06 mmol) in 90% AcOH (0.6 mL) was degassed, and freshly washed Zn (198 mg, 3.0 mmol) was added to the solution. The mixture was degassed again and stirred for 6 h at 40 °C, followed by concentration under high vacuum. The residue was suspended in $CHCl_3$/MeOH (5/1), and then filtrated through silica gel pad. The filtrate was concentrated *in vacuo*. To the residue in DMF (0.6 ml) were added Cs_2CO_3 (60 mg, 0.18 mmol) and BnBr, and the reaction mixture was stirred for 15 min. The reaction was quenched with water (10 mL). The mixture was extracted with EtOAc (5 mL x 3), and the combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purfication of the residue by silica gel column chromatography (10 g, $CHCl_3$ to $CHCl_3$/MeOH = 9/1) gave the title compound as a white foam (30 mg, 79%). $[\alpha]^{20}_D$ = -41.3 (*c* = 0.45, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.00 (br, 1H, NH_a), 7.90 (d, $J_{d,e}$ = 7.6 Hz, 1H, H_d), 7.35-7.23 (m, 6H, In-H, Ar-H x 5), 7.15 (dd, $J_{d,e}$ = 7.6 Hz, $J_{e,f}$ = 7.2 Hz, 1H, H_e), 7.09 (dd, $J_{e,f}$ = 7.2 Hz, $J_{f,g}$ = 7.6 Hz, 1H, H_f), 6.97 (m, 1H, In-H), 6.90-6.79 (m, 2H, NH x 2), 5.16 (br d, $J_{\alpha,NH}$ = 5.6 Hz, 1H, NH), 4.41 (ddd, $J_{\alpha,\beta}$ = 5.6 Hz each, $J_{\alpha,NH}$ = 5.6 Hz, 1H, H_α), 4.33 (ddd, $J_{\alpha',\beta'}$ = 7.6 Hz each, $J_{\alpha',NH}$ = 6.4 Hz, 1H, $H_{\alpha'}$), 4.16 (q, $J_{a,b}$ = 7.2 Hz, 2H, CH_{2b}), 4.06 & 4.02 (ABq, *J* = 14.0 Hz, 1H each, CH_2Ph), 3.90 & 3.71 (dd, $J_{\alpha'',NH}$ = 6.0 Hz, $J_{\alpha'',\alpha''}$ = 18.0 Hz, 1H, $CH_{2\alpha''}$), 3.32 & 3.14 (dd, $J_{\alpha,\beta}$ = 5.6 Hz, $J_{\beta,\beta}$ = 14.4 Hz, 1H each, $CH_{2\beta}$), 2.49 & 2.20 (td, $J_{\beta',\gamma'}$ = 6.8 Hz, $J_{\gamma',\gamma'}$ = 16.4 Hz, 1H each, $CH_{2\gamma'}$), 1.98 & 1.87 (dtd, $J_{\alpha',\beta'}$ = 7.6 Hz, $J_{\beta',\gamma'}$ = 6.8 Hz, $J_{\beta',\beta'}$ = 12.8 Hz, 1H each, $CH_{2\beta'}$), 1.42 (s, 9H, ^{t}Bu), 1.25 (t, $J_{a,b}$ = 7.2 Hz, 3H, CH_{3a}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 172.3, 171.0, 169.5, 137.6, 136.2, 129.0, 128.8, 127.5, 127.4, 123.4, 122.4, 119.9, 118.9, 111.4, 110.0, 80.6, 61.5, 55.7, 52.5, 41.3, 39.2, 33.4, 29.8, 29.7, 28.4, 28.0, 27.1, 14.2; ESIHRMS: *m/*z calcd. for $C_{32}H_{40}N_4O_7SNa$ $(M + Na)^+$ 647.2516, found 647.2533.

References

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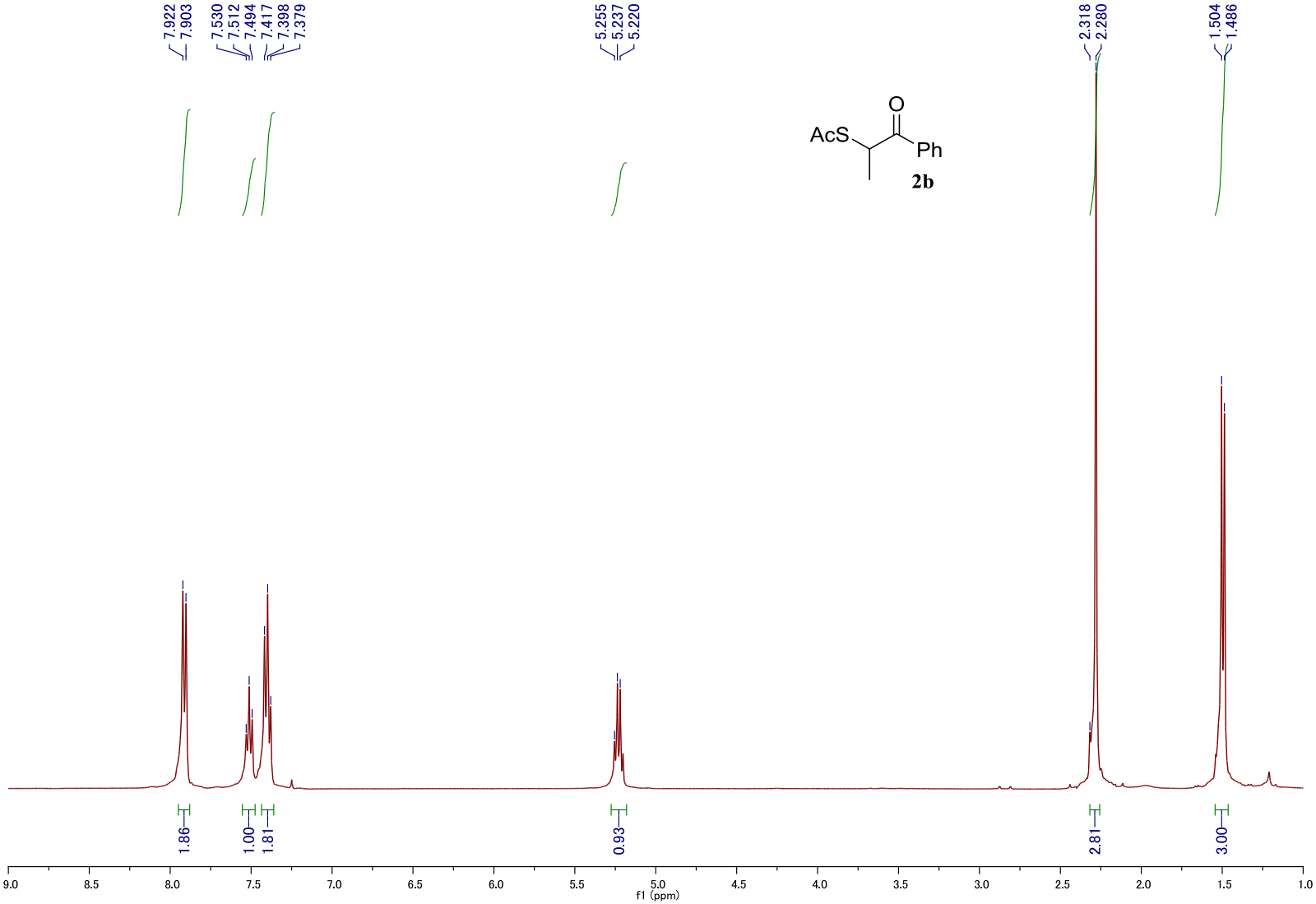
***S*-α-Methylphenacyl thioacetate (2b)** ^{1}H NMR (400 MHz, $CDCl_3$)



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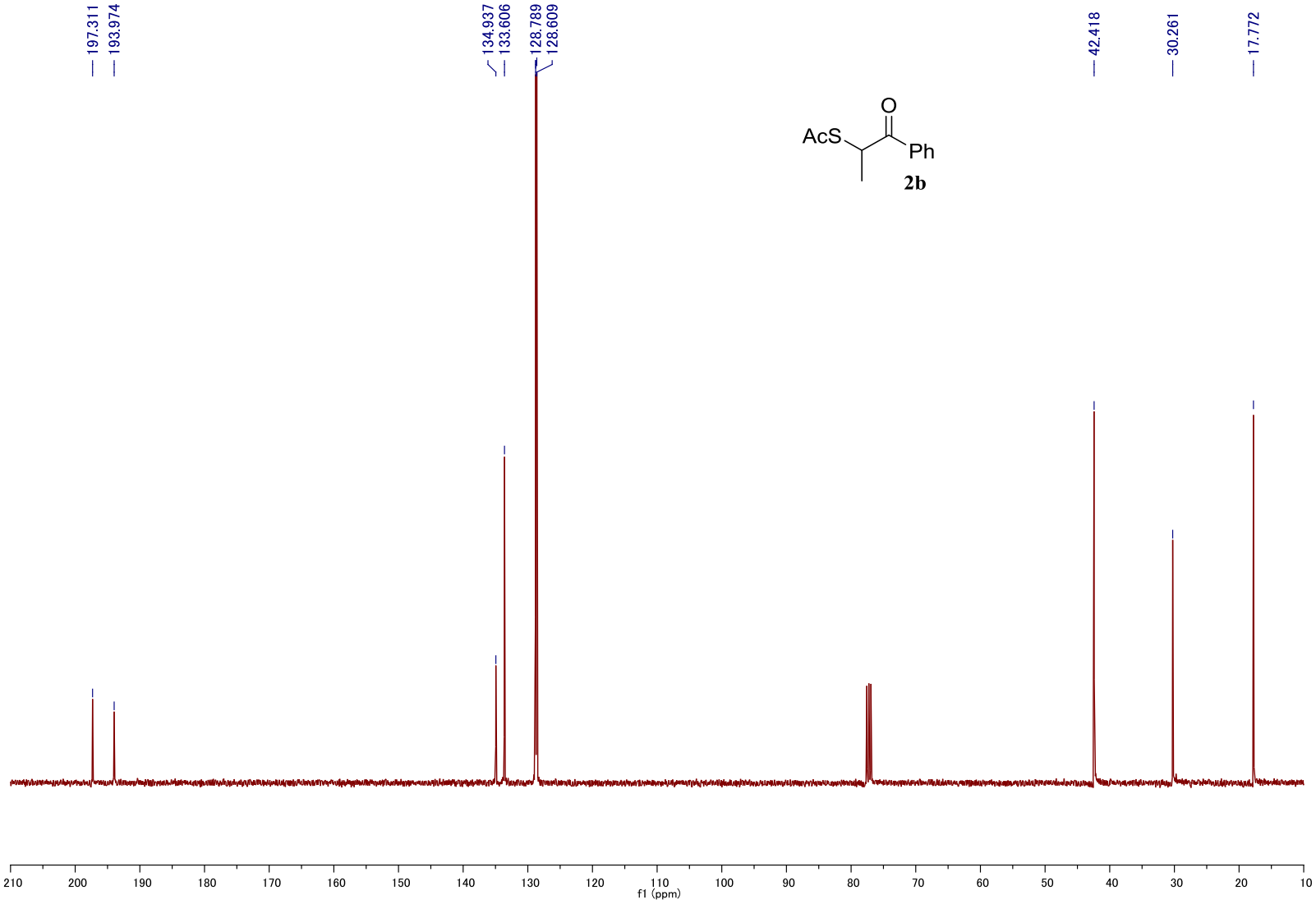

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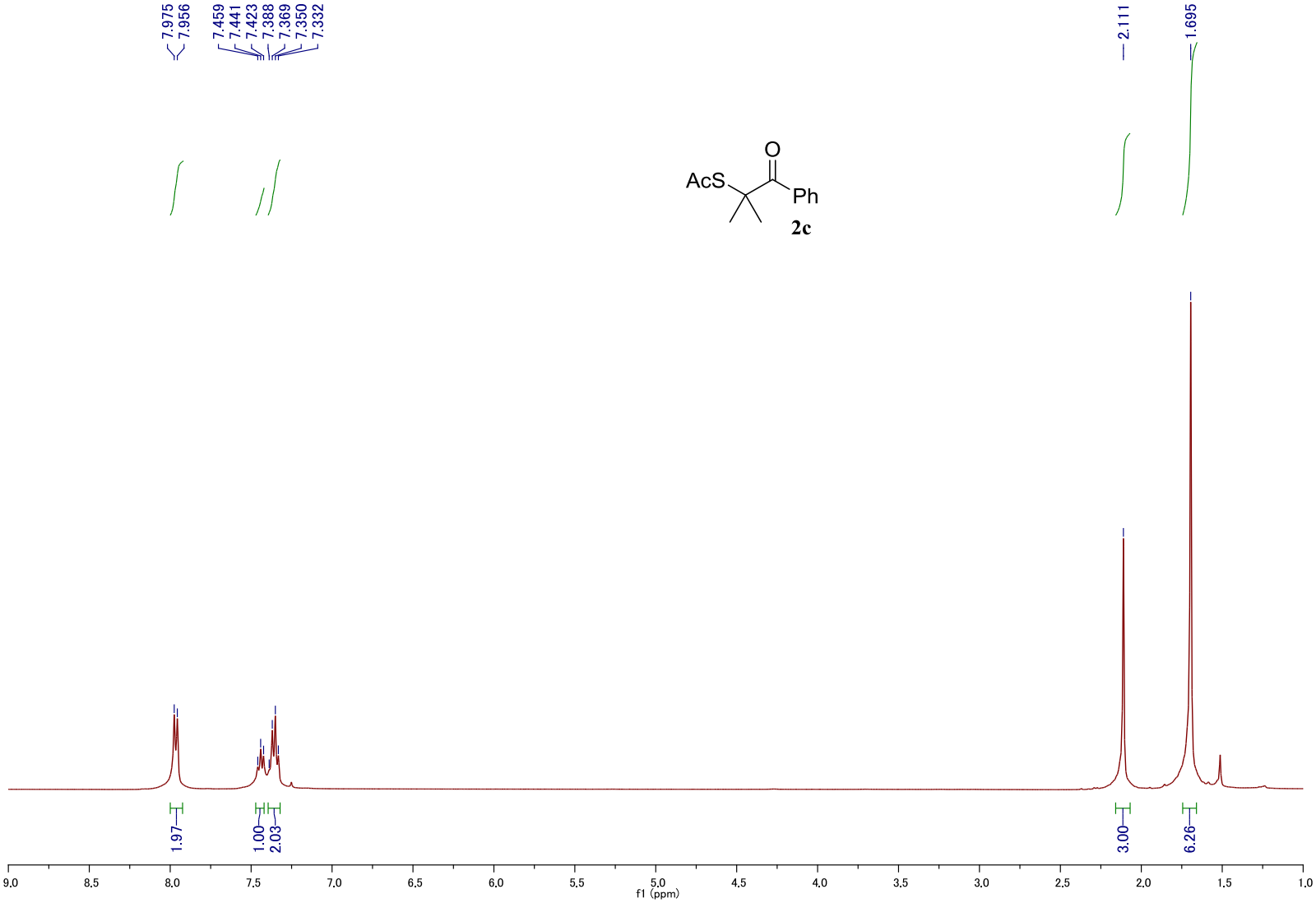

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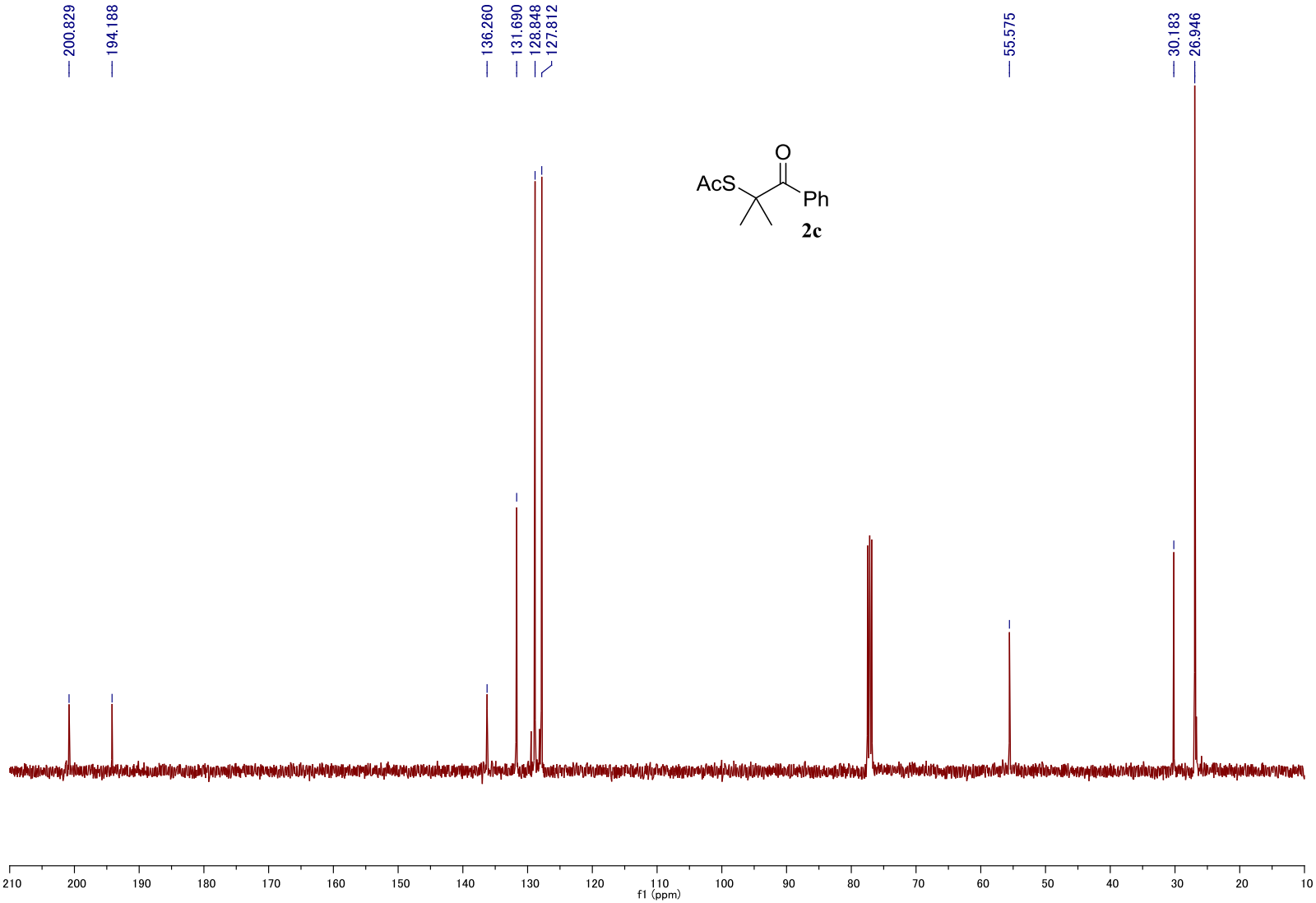
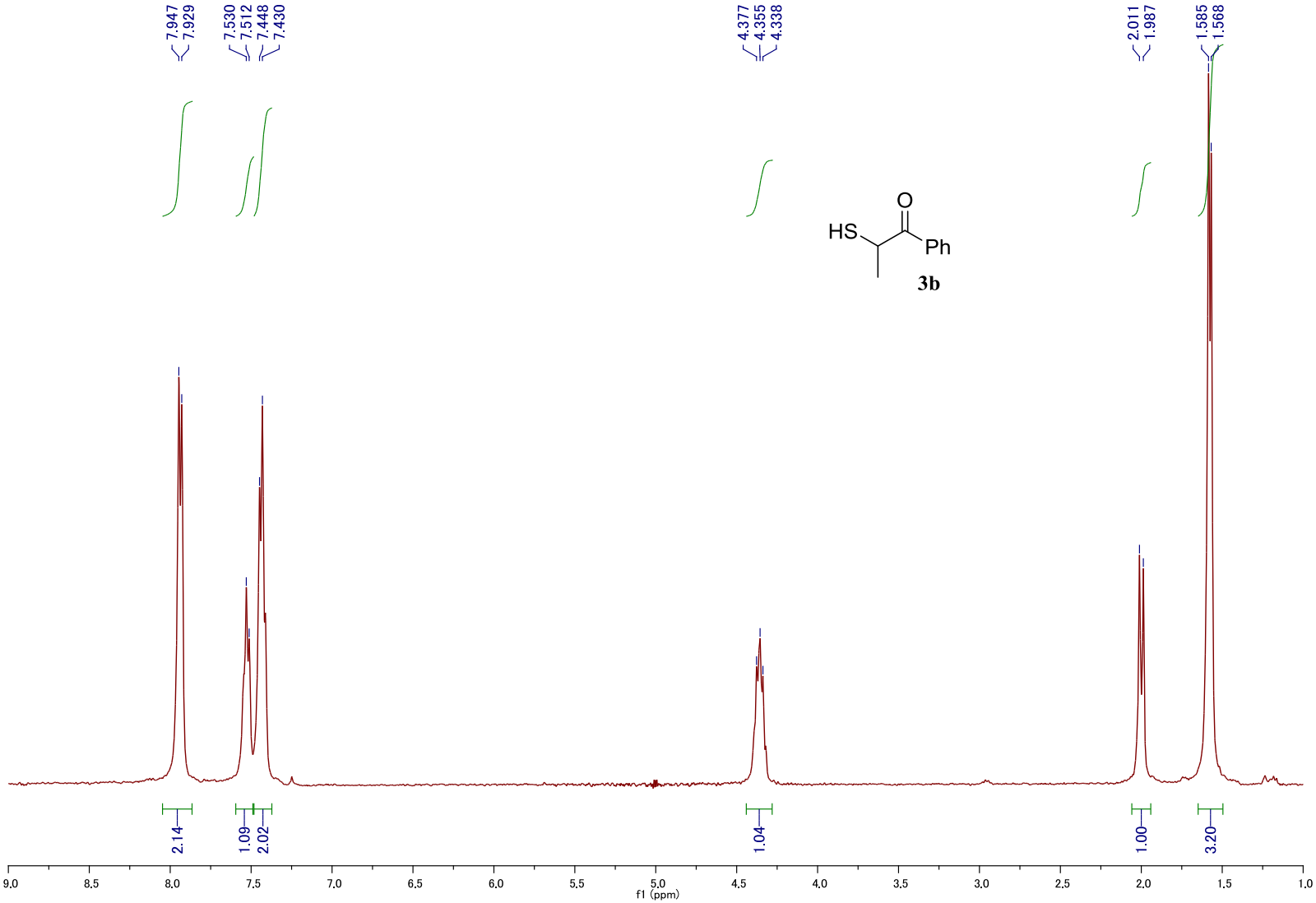
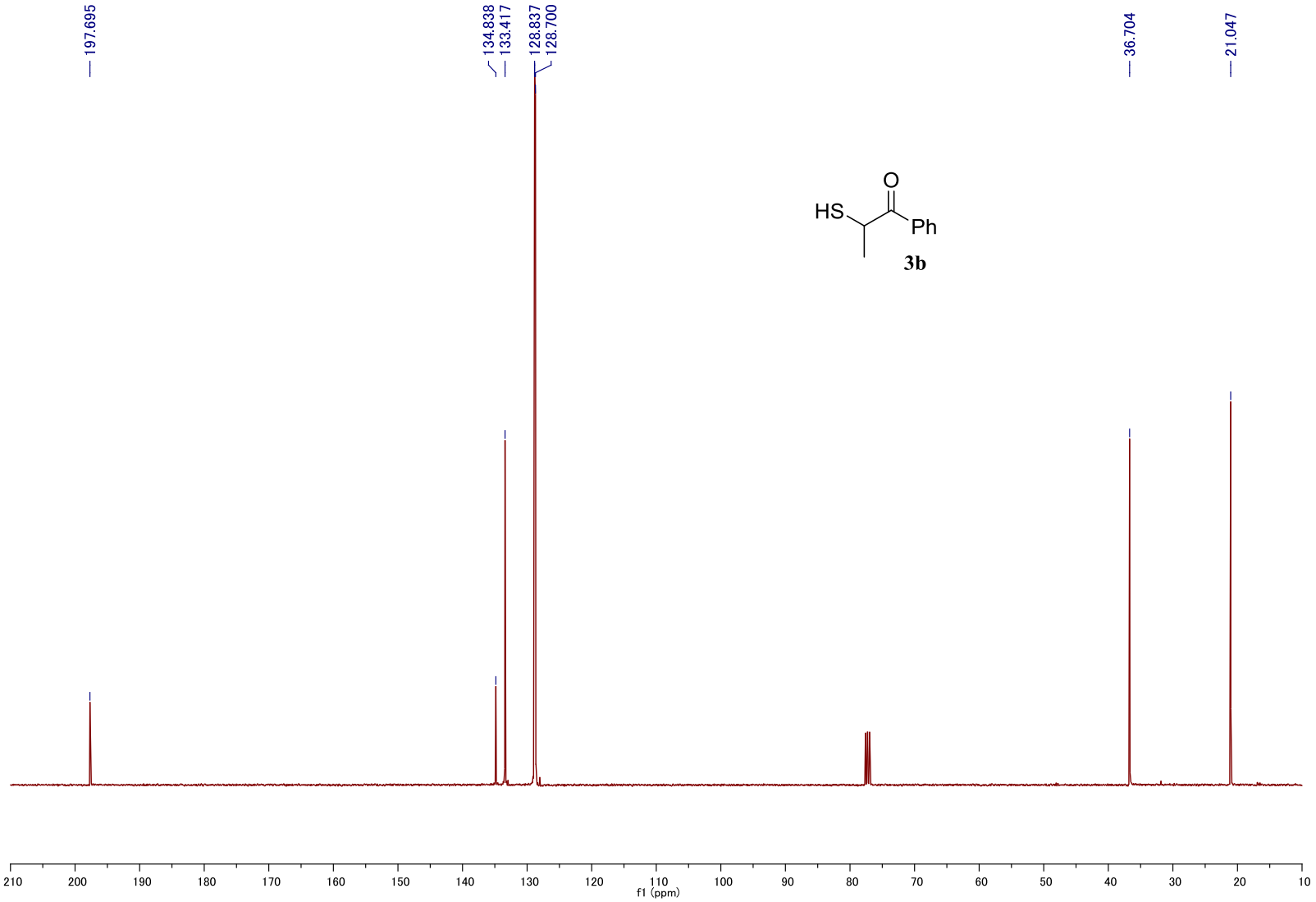


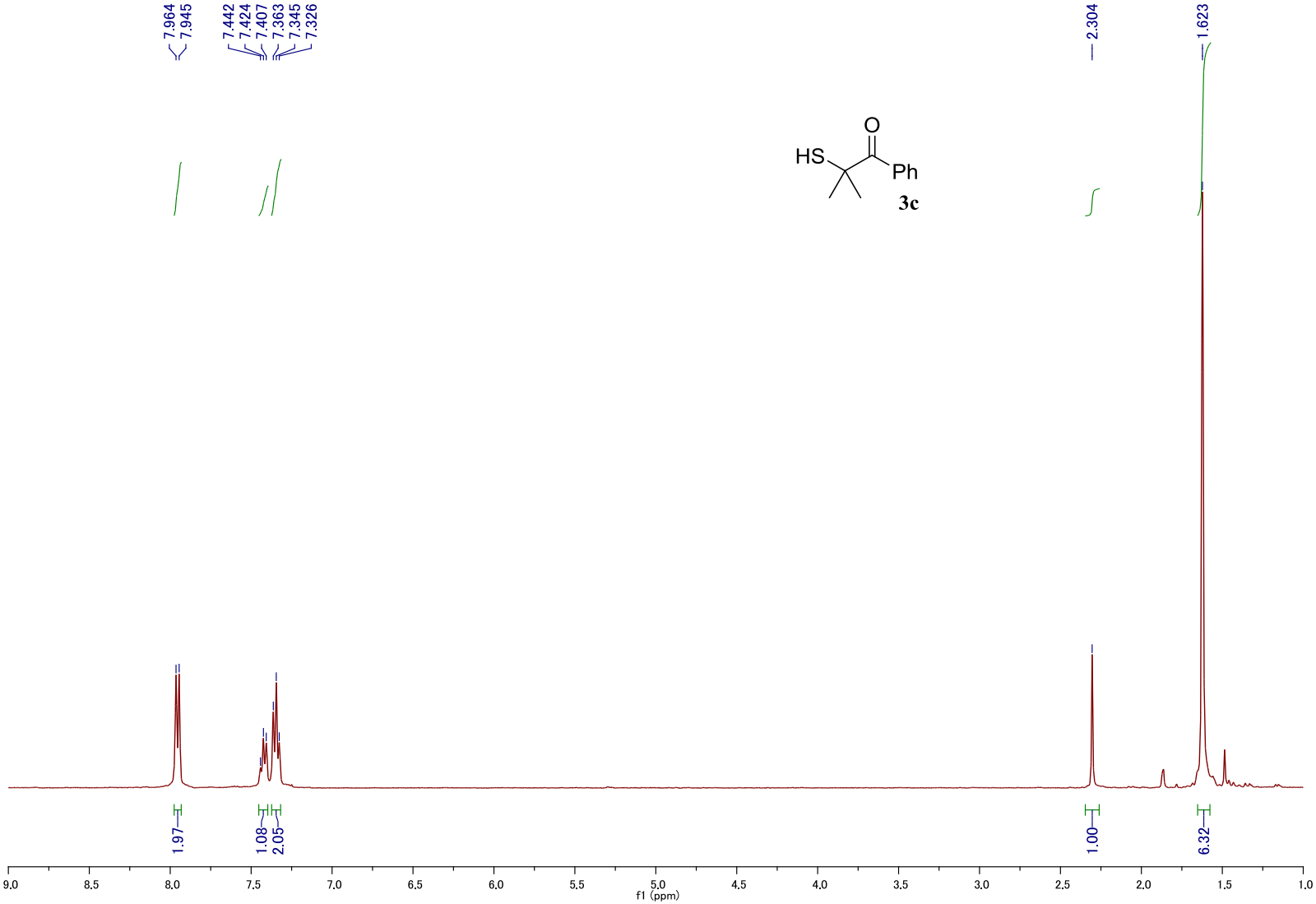
α-Methylphenacylthiol (**3b**) ^{1}H NMR (400 MHz, $CDCl_3$)



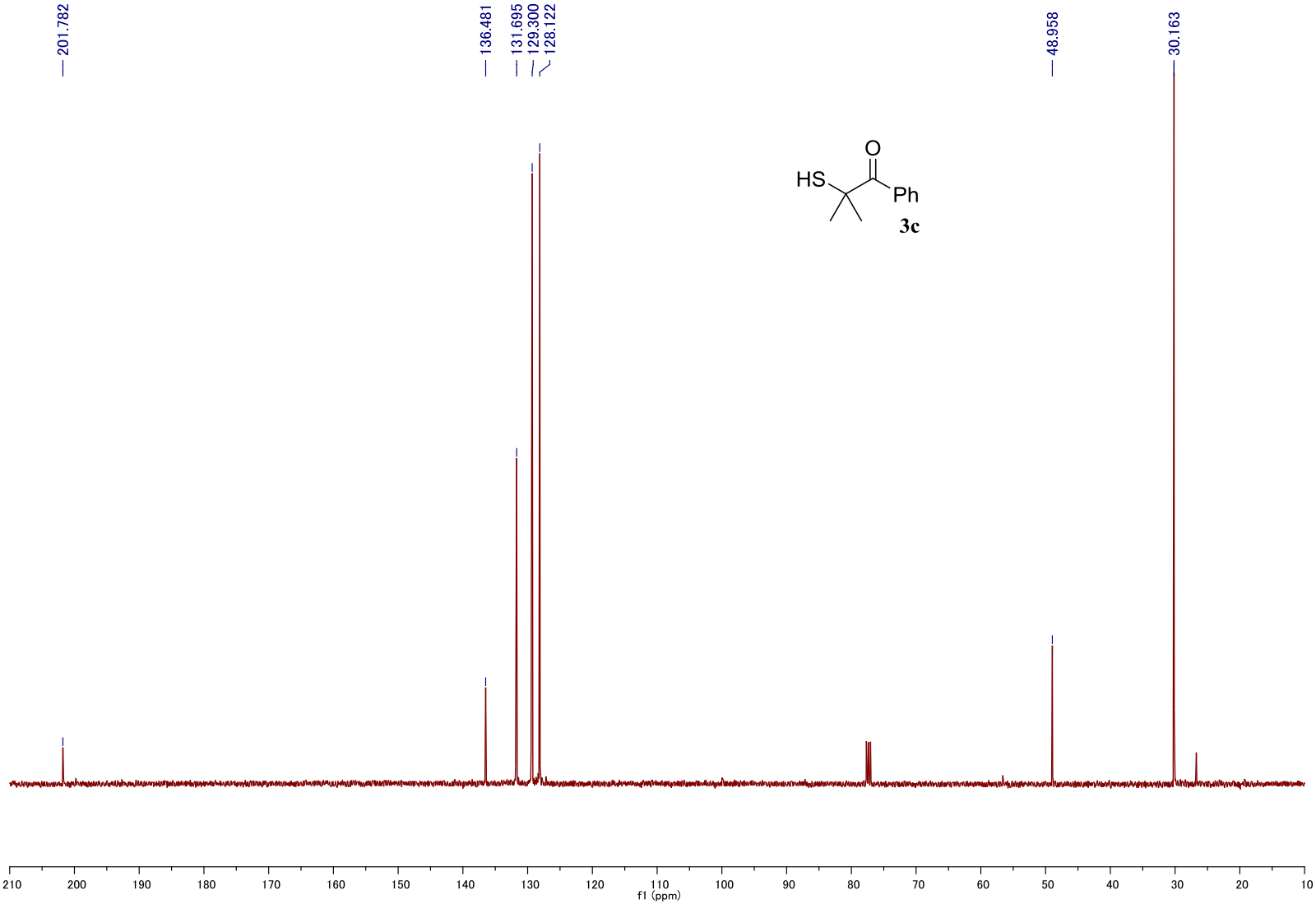
α-Methylphenacylthiol (**3b**) ^{13}C NMR (100 MHz, $CDCl_3$)



α,α-Dimethylphenacylthiol (3c) ^{1}H NMR (400 MHz, $CDCl_3$)



α,α-Dimethylphenacylthiol (3c) ^{13}C NMR (100 MHz, $CDCl_3$)



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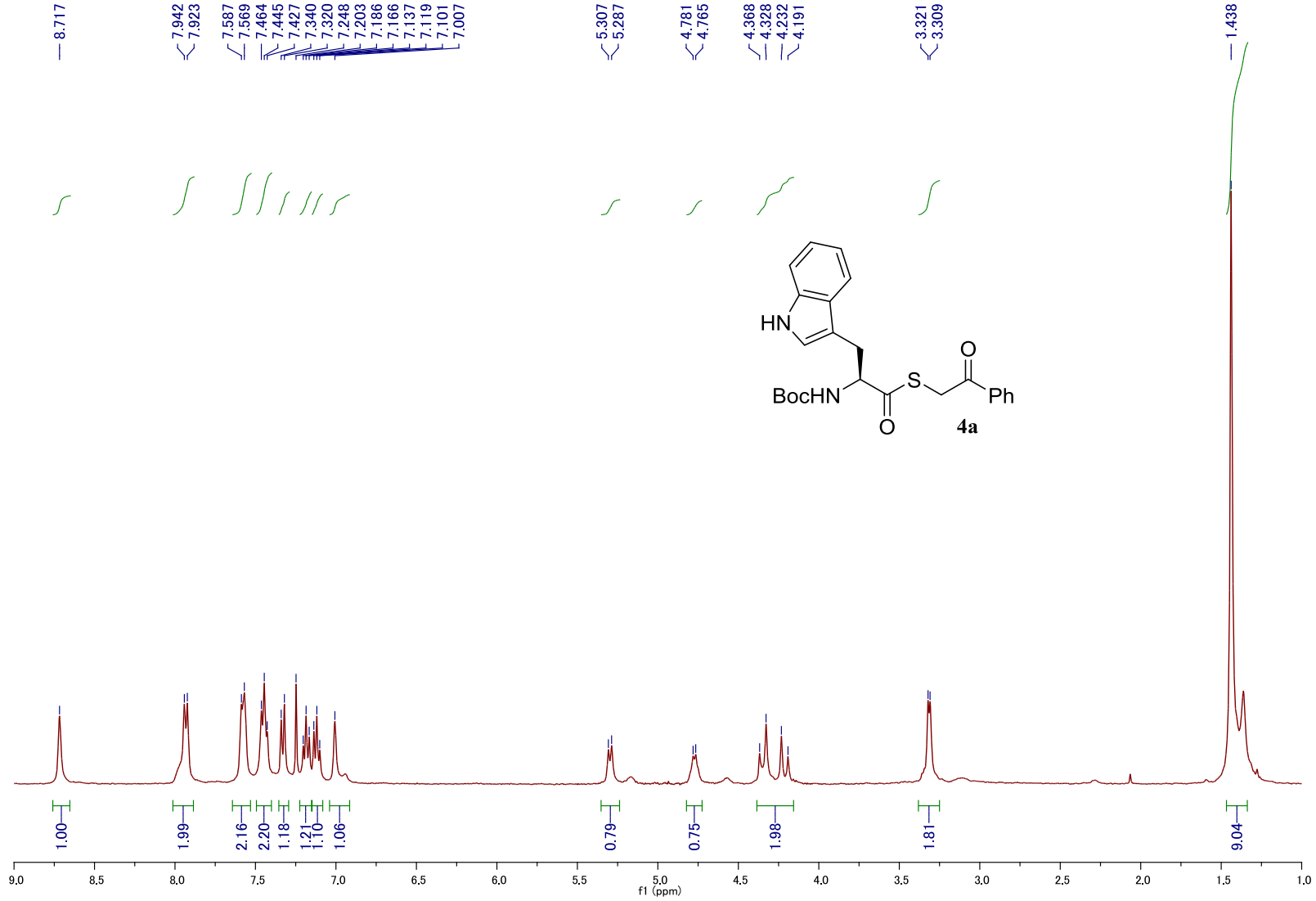

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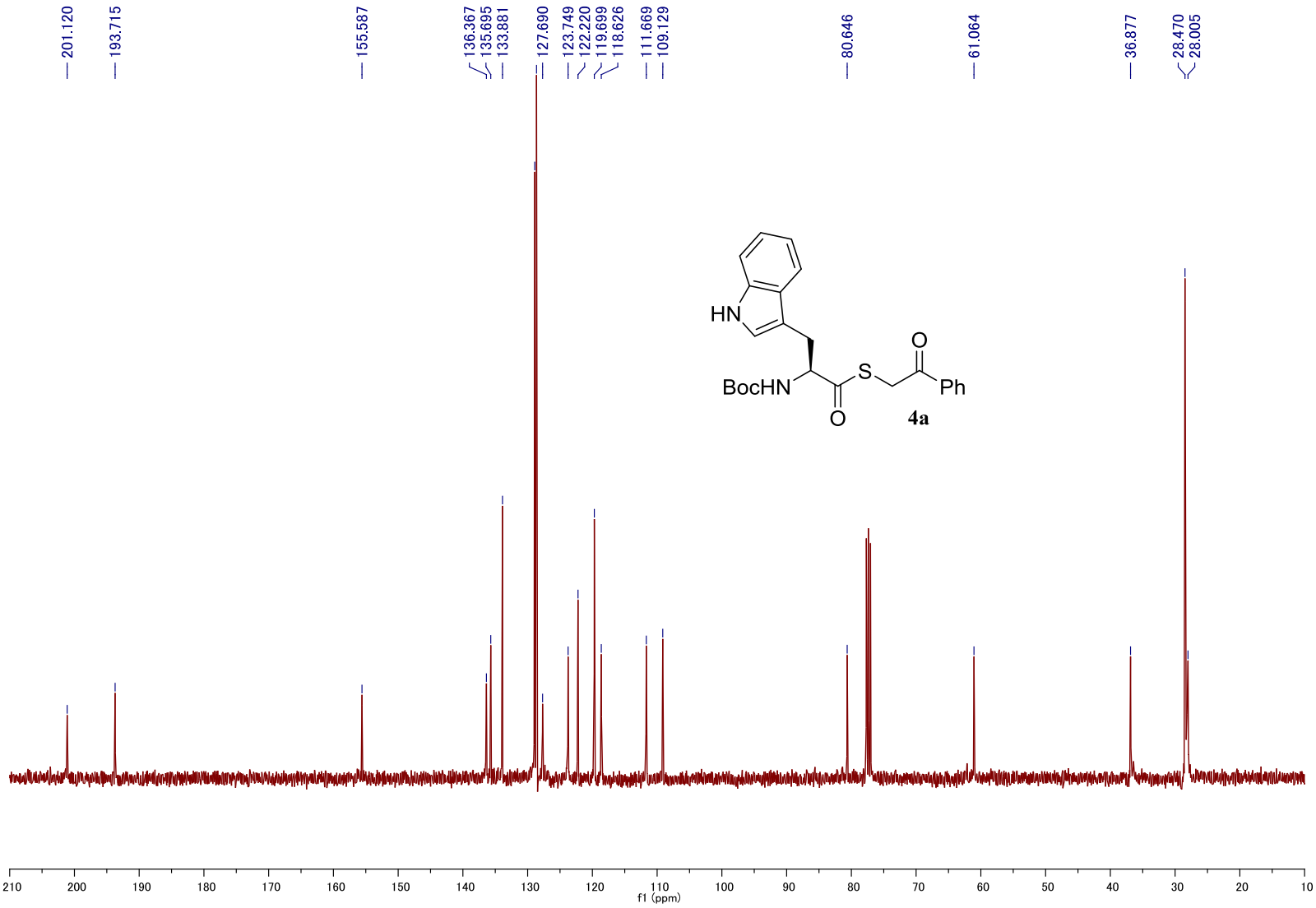

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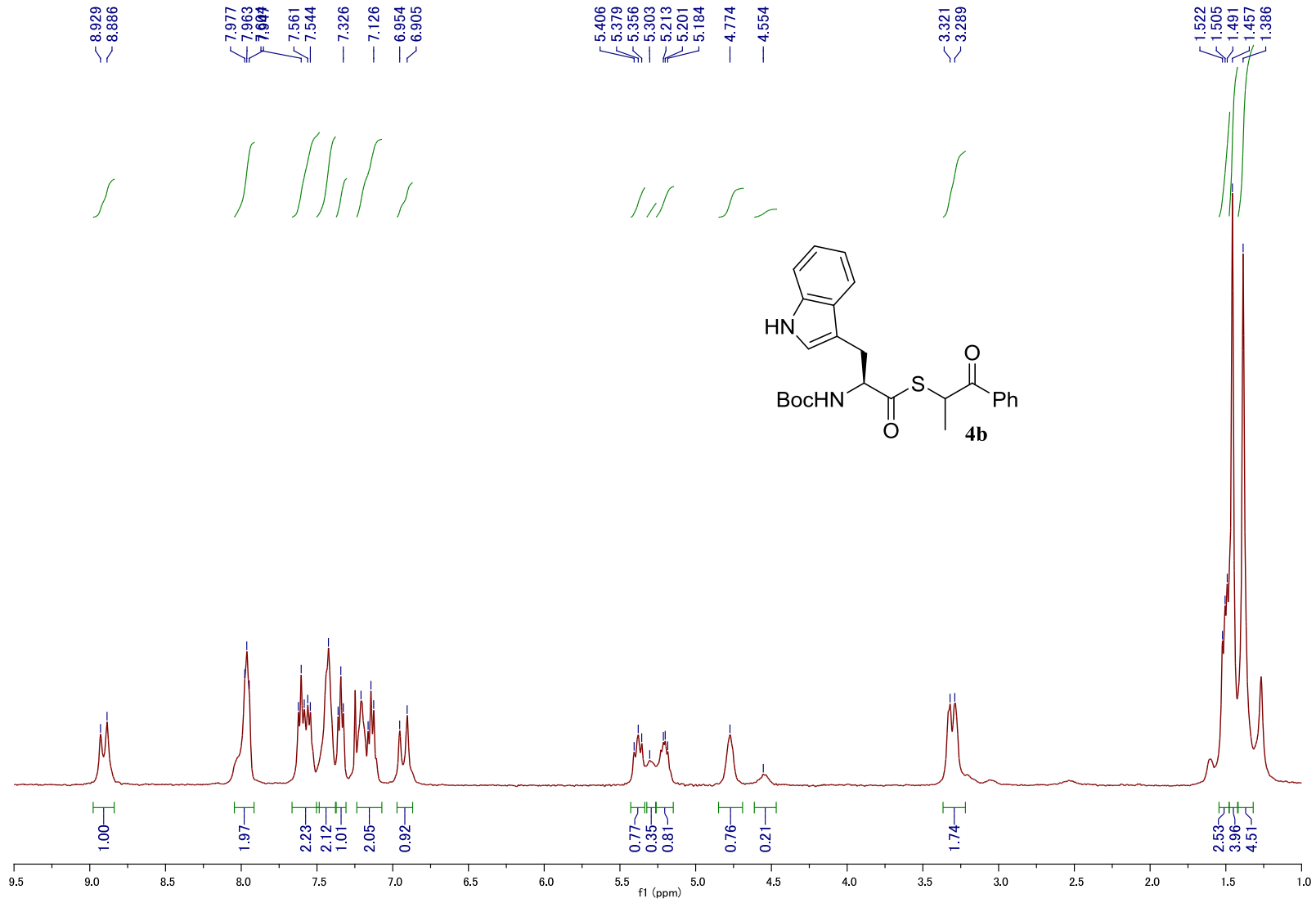

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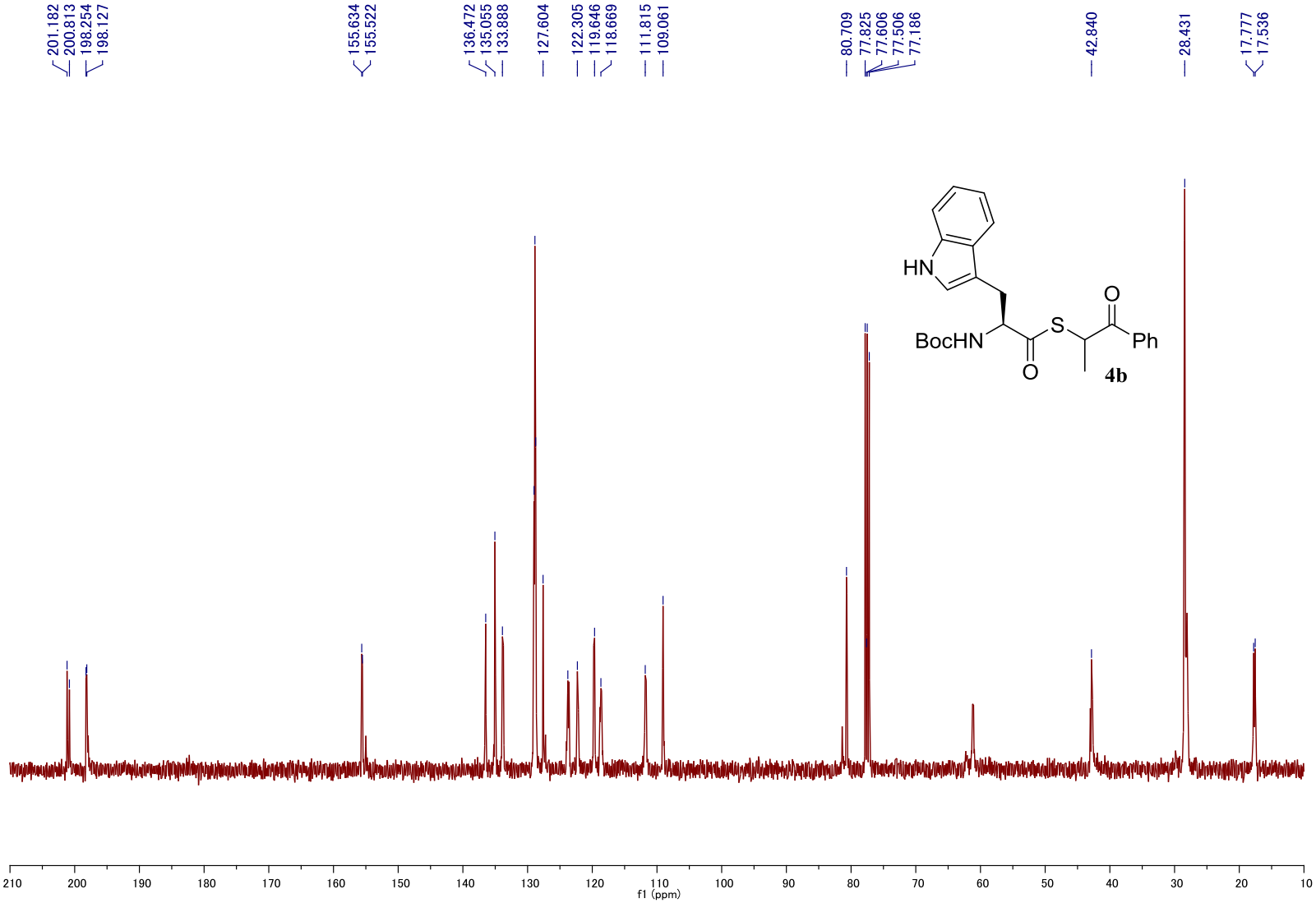
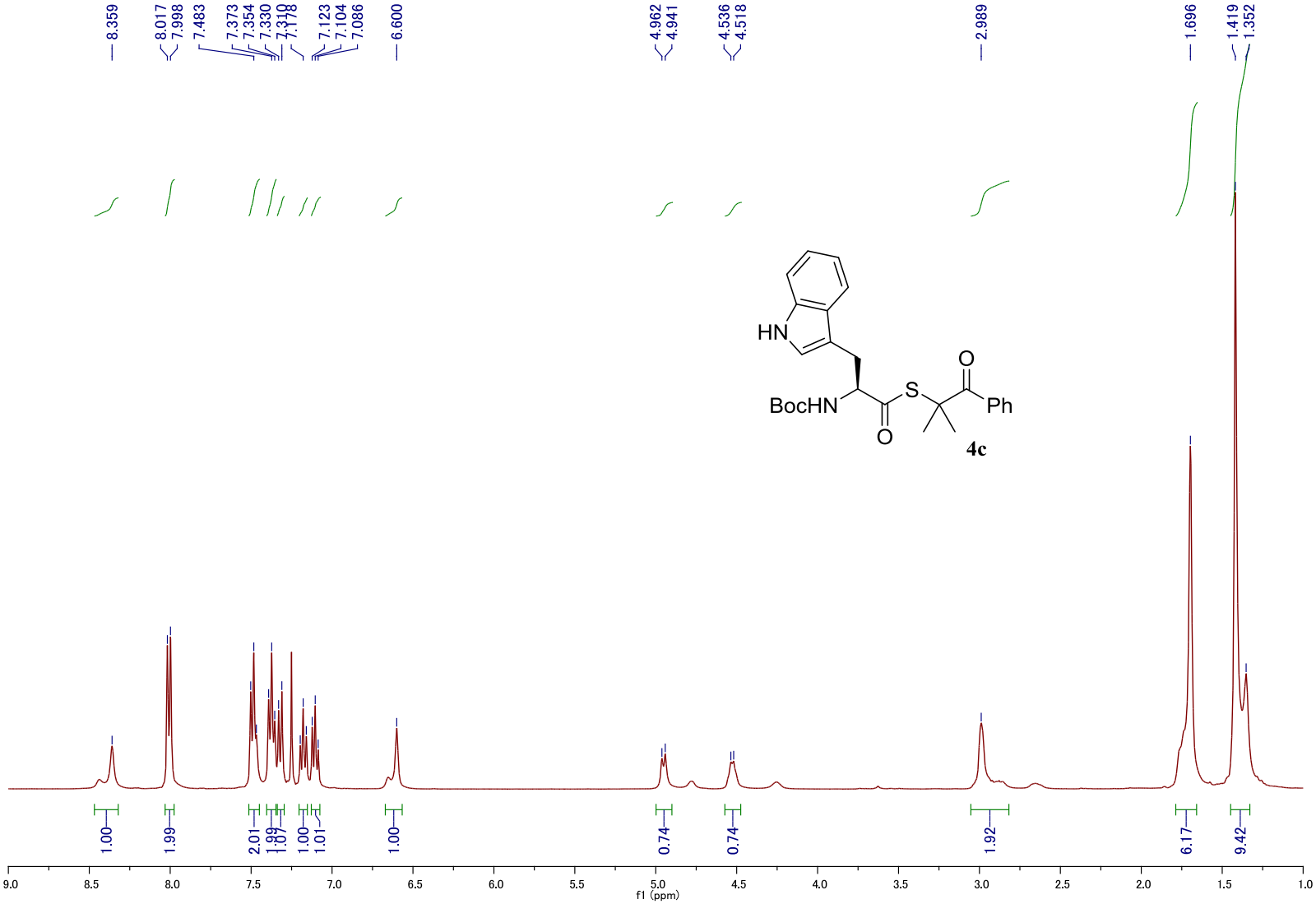


***S*-(α,α-Dimethylphenacyl) *N*-*tert*-butoxycarbonyl-L-thiotryptophanate (4c)** ^{1}H NMR (400 MHz, $CDCl_3$)



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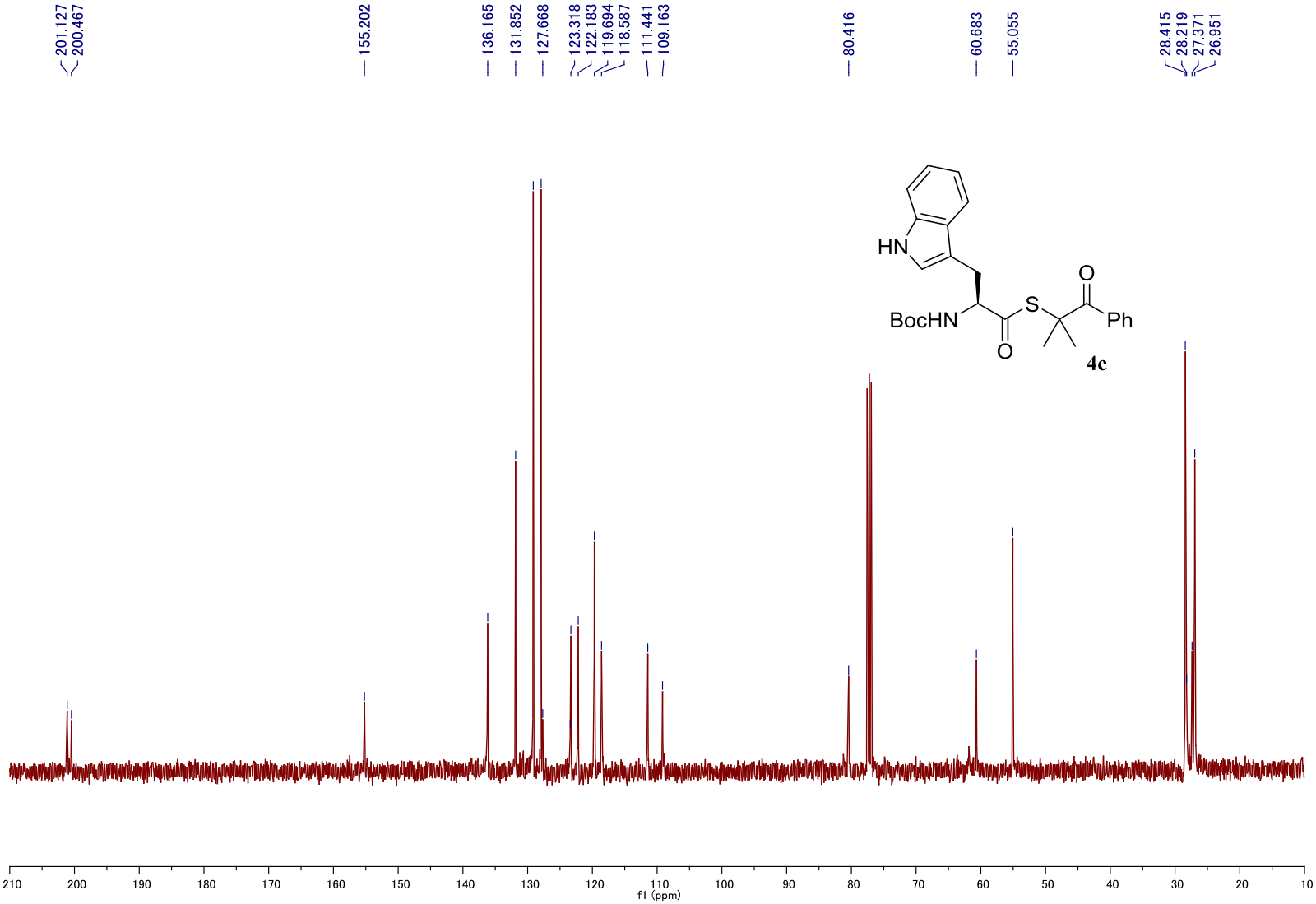
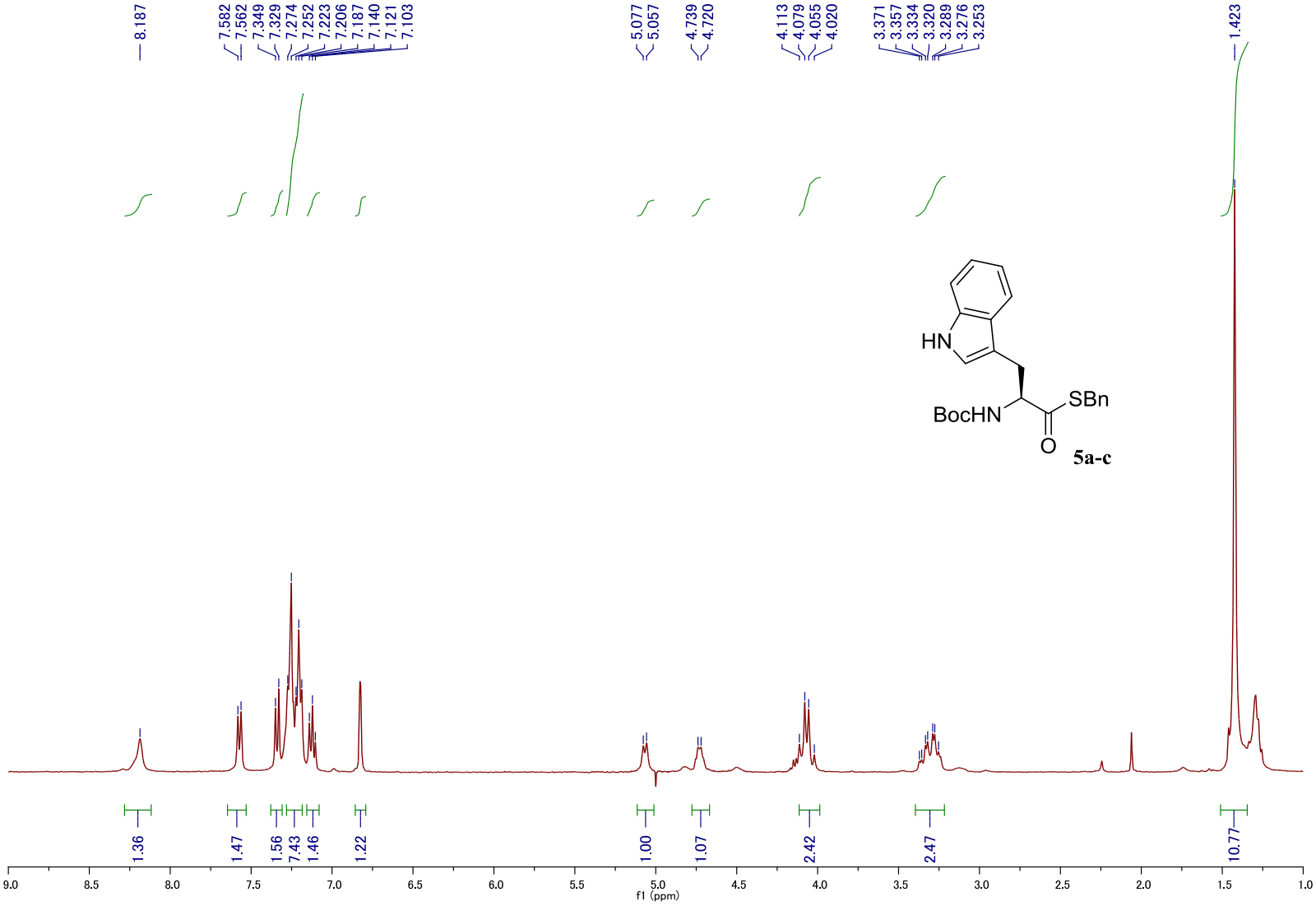
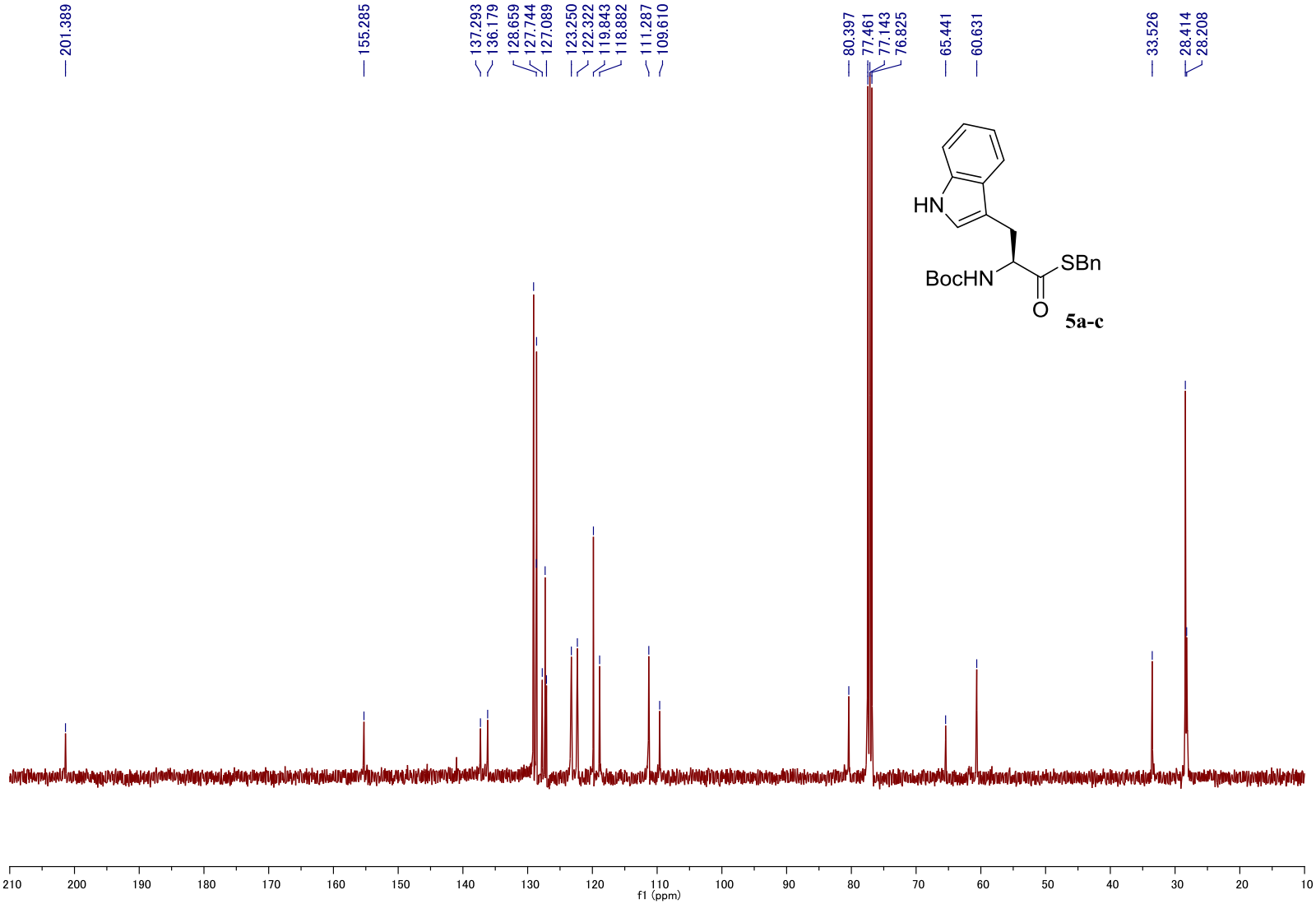


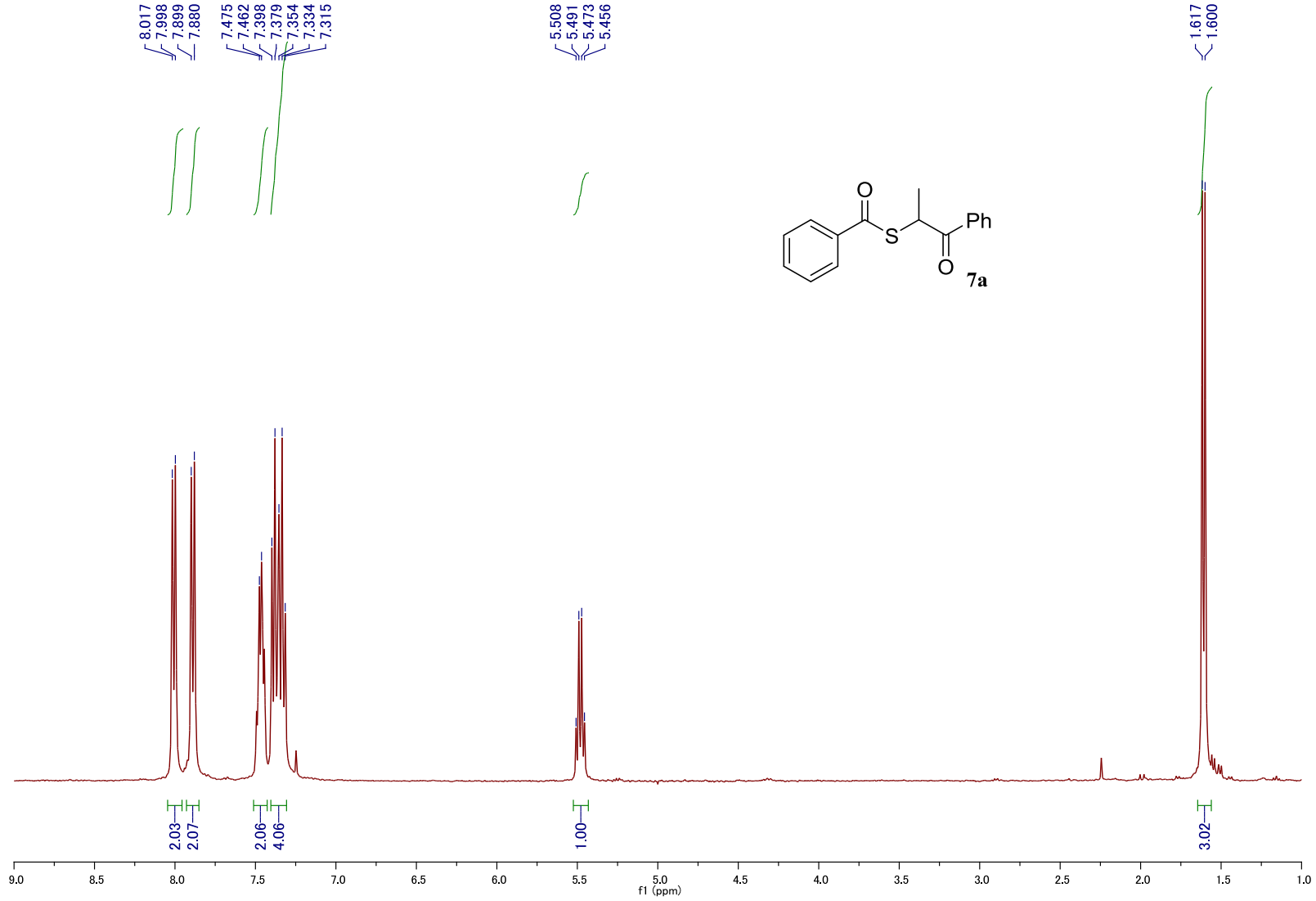
_S_-Benzyl _N-tert_-butoxycarbonyl-L-thiotryptophanate (5a-c) ^{1}H NMR (400 MHz, $CDCl_3$)



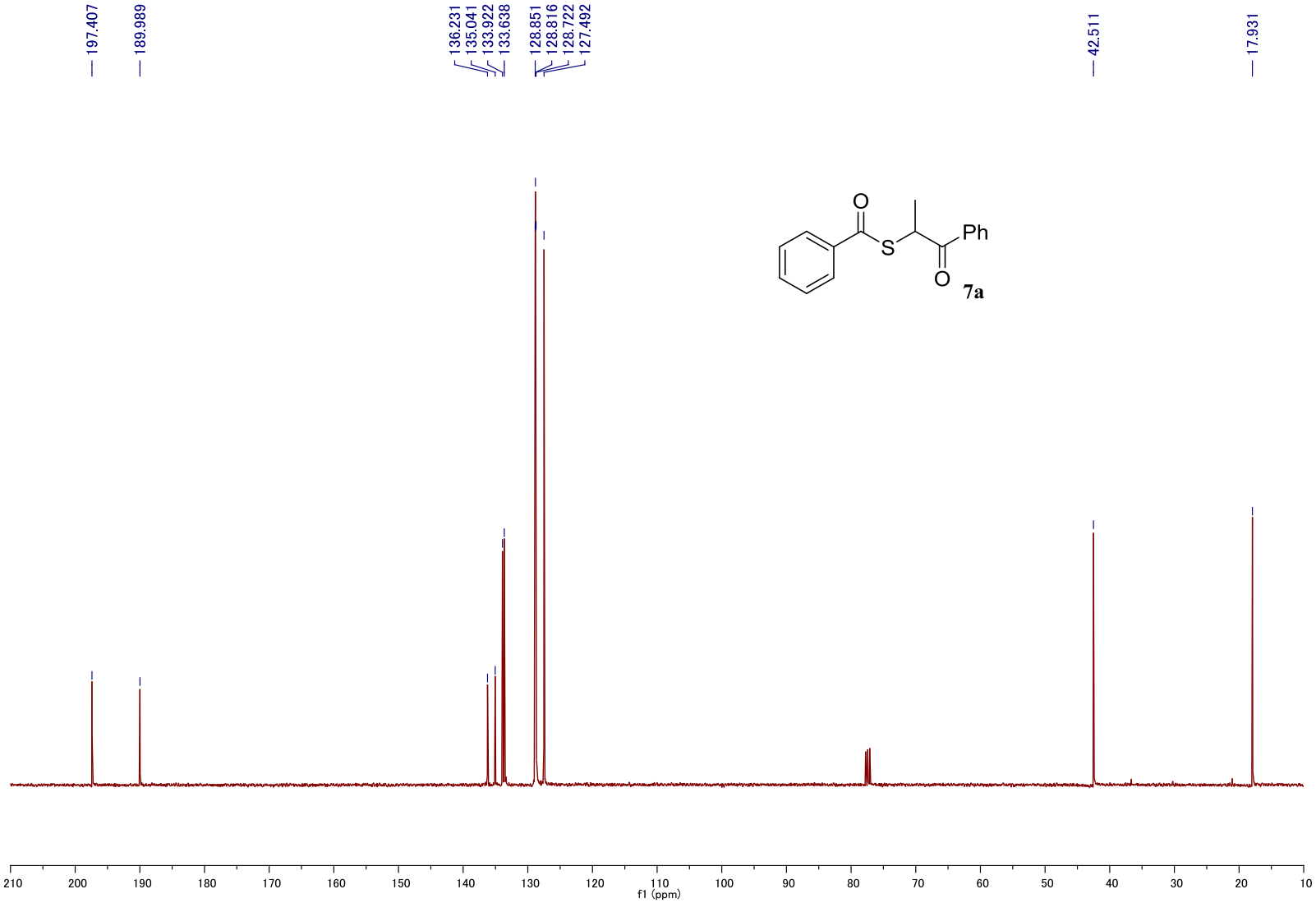
S-Benzyl *N-tert*-butoxycarbonyl-L-thiotryptophanate (5a-c) ^{13}C NMR (100 MHz, $CDCl_3$)



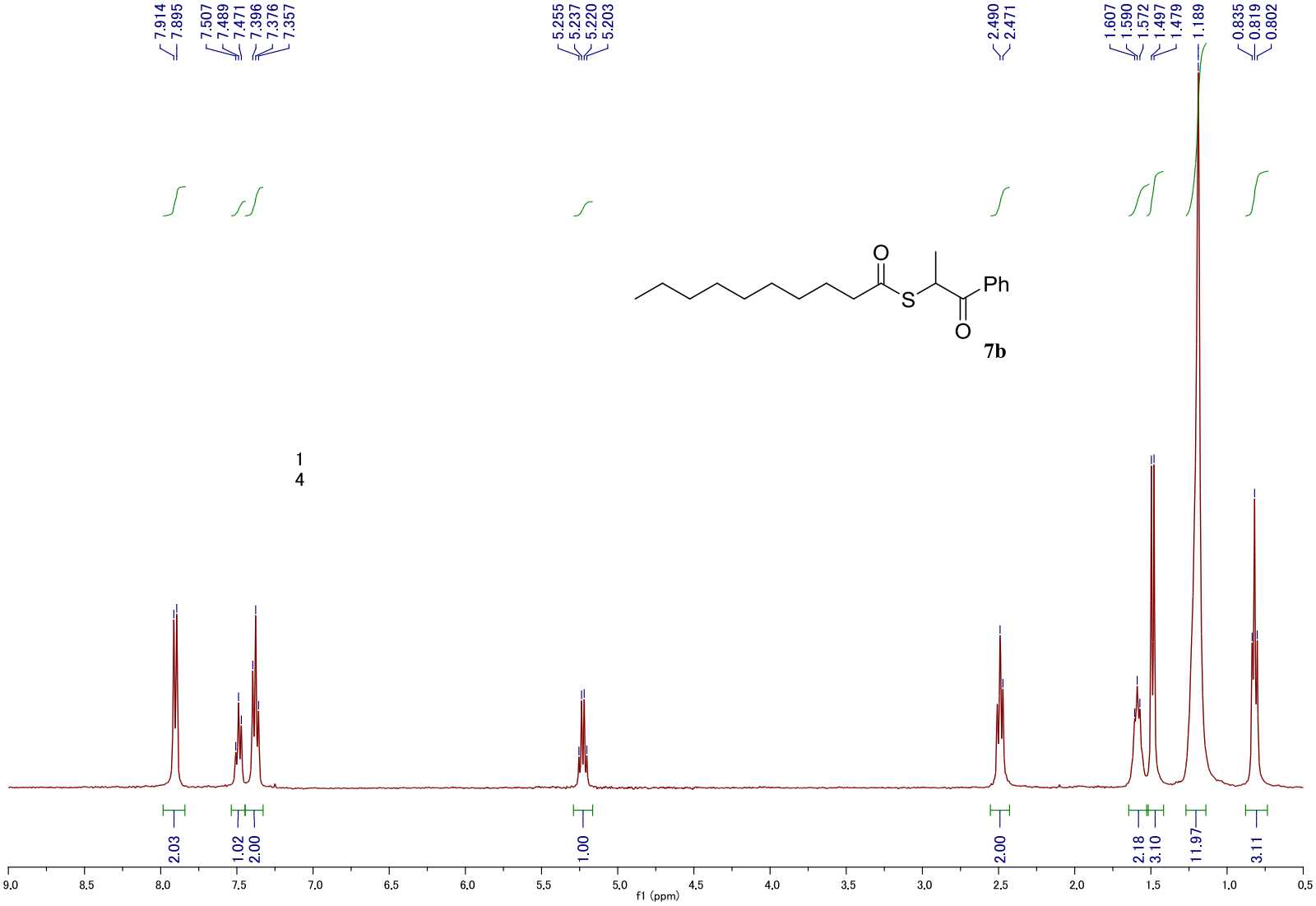
S-α-Methylphenacyl thiobenzoate (7a) ^{1}H NMR (400 MHz, $CDCl_3$)



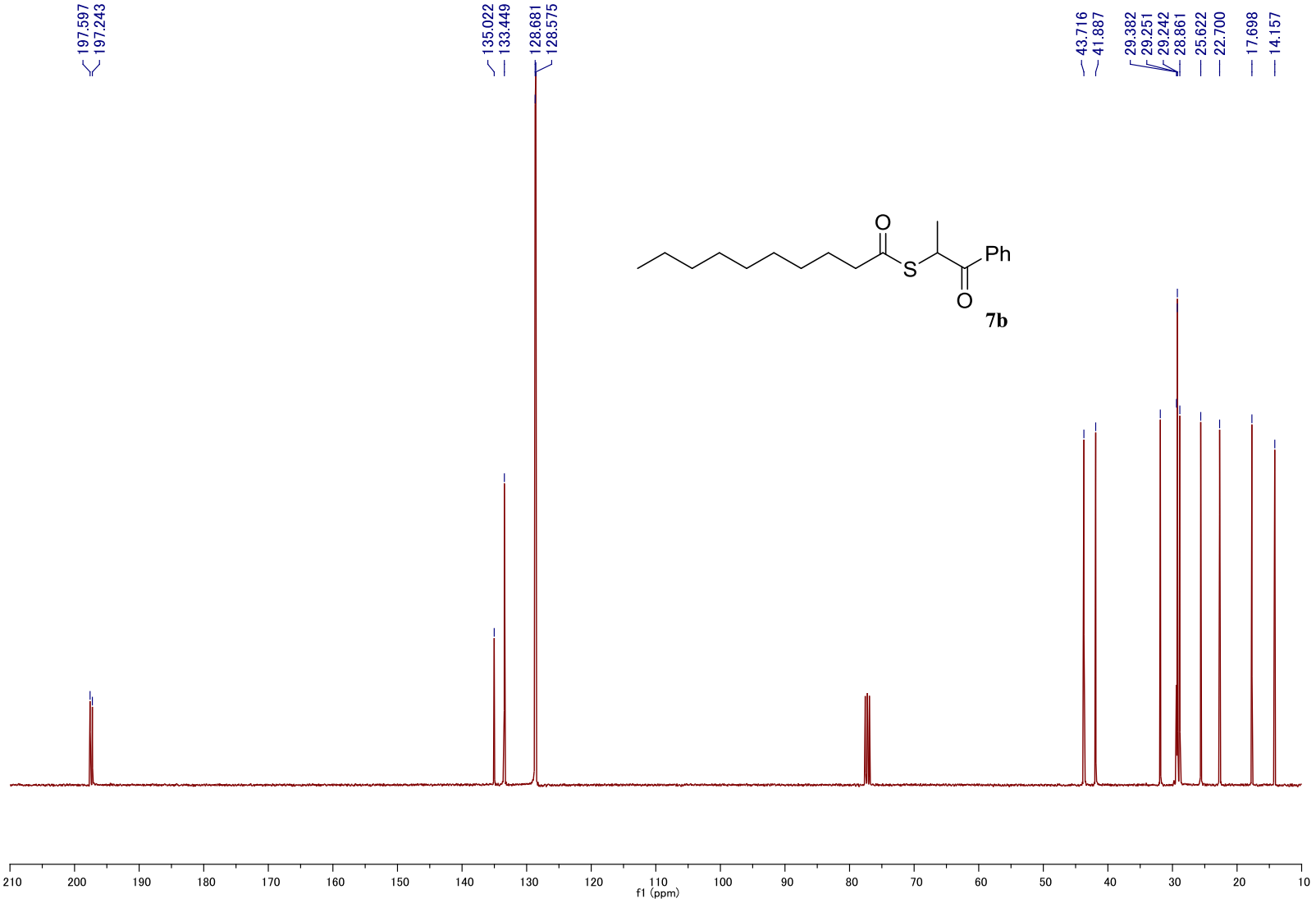
***S*-α-Methylphenacyl thiobenzoate (7a)** ^{13}C NMR (100 MHz, $CDCl_3$)



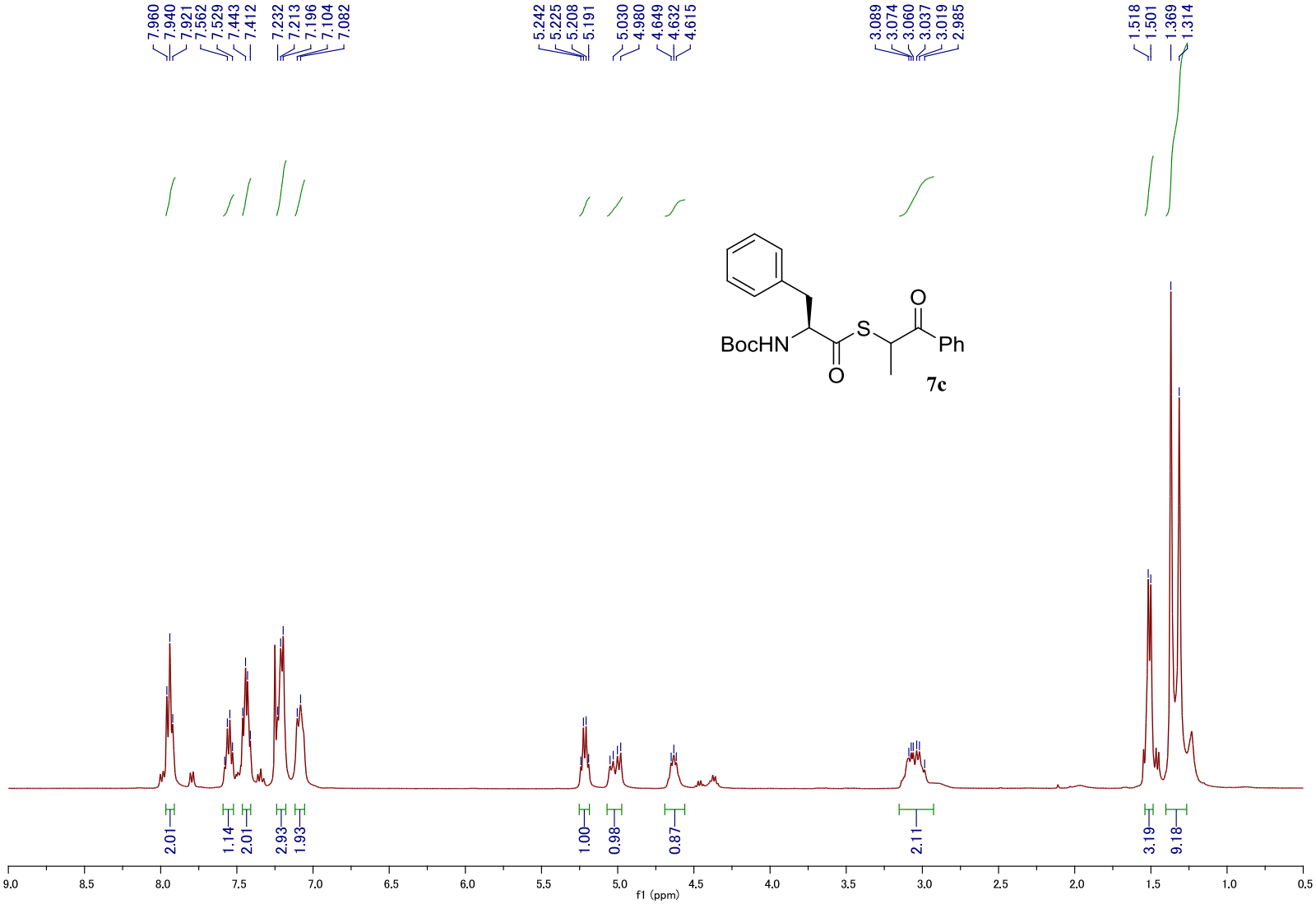
S-α-Methylphenacyl thiodecanoate (7b) ^{1}H NMR (400 MHz, $CDCl_3$)



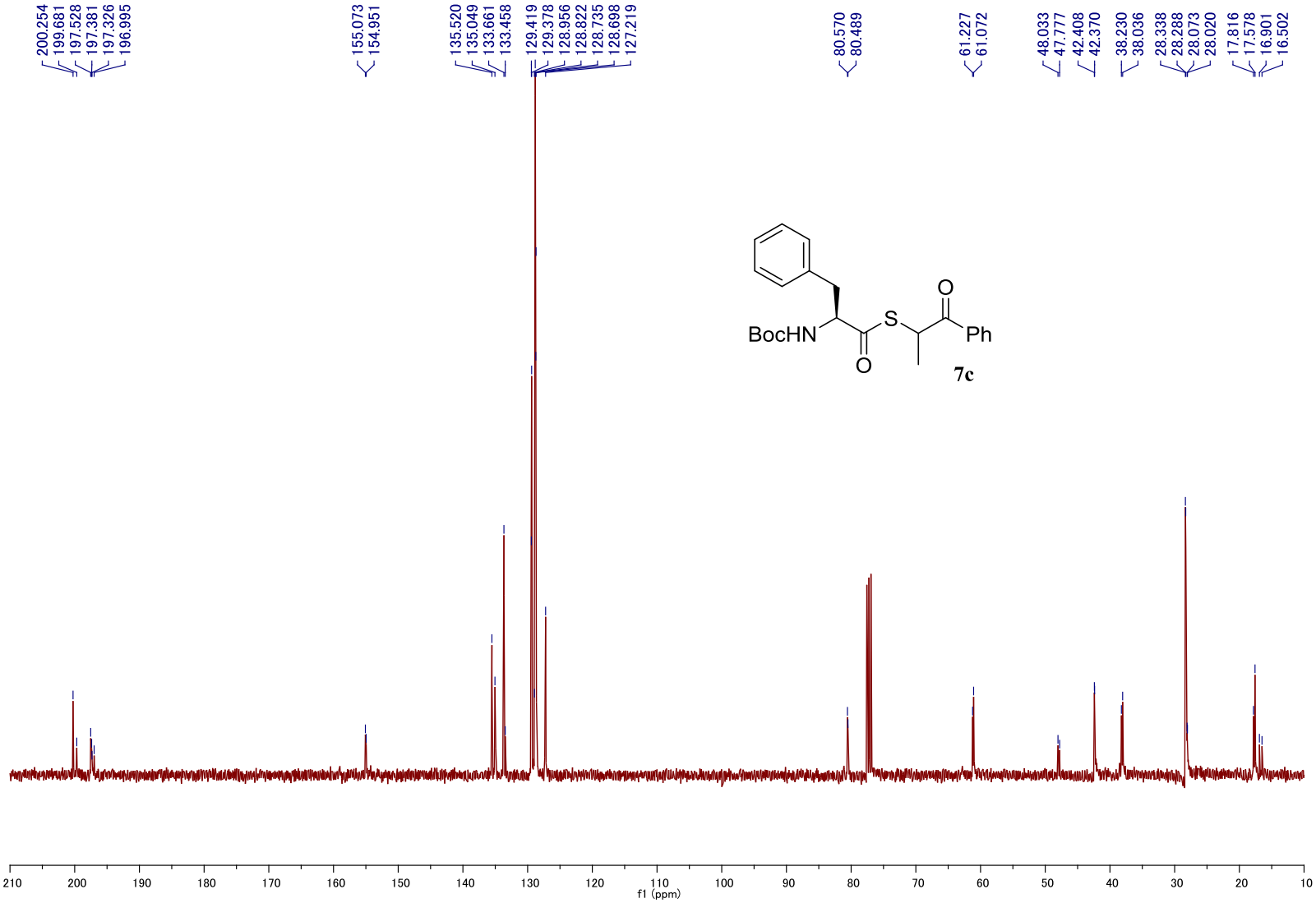
***S*-α-Methylphenacyl thiodecanoate (7b)** ^{13}C NMR (100 MHz, $CDCl_3$)



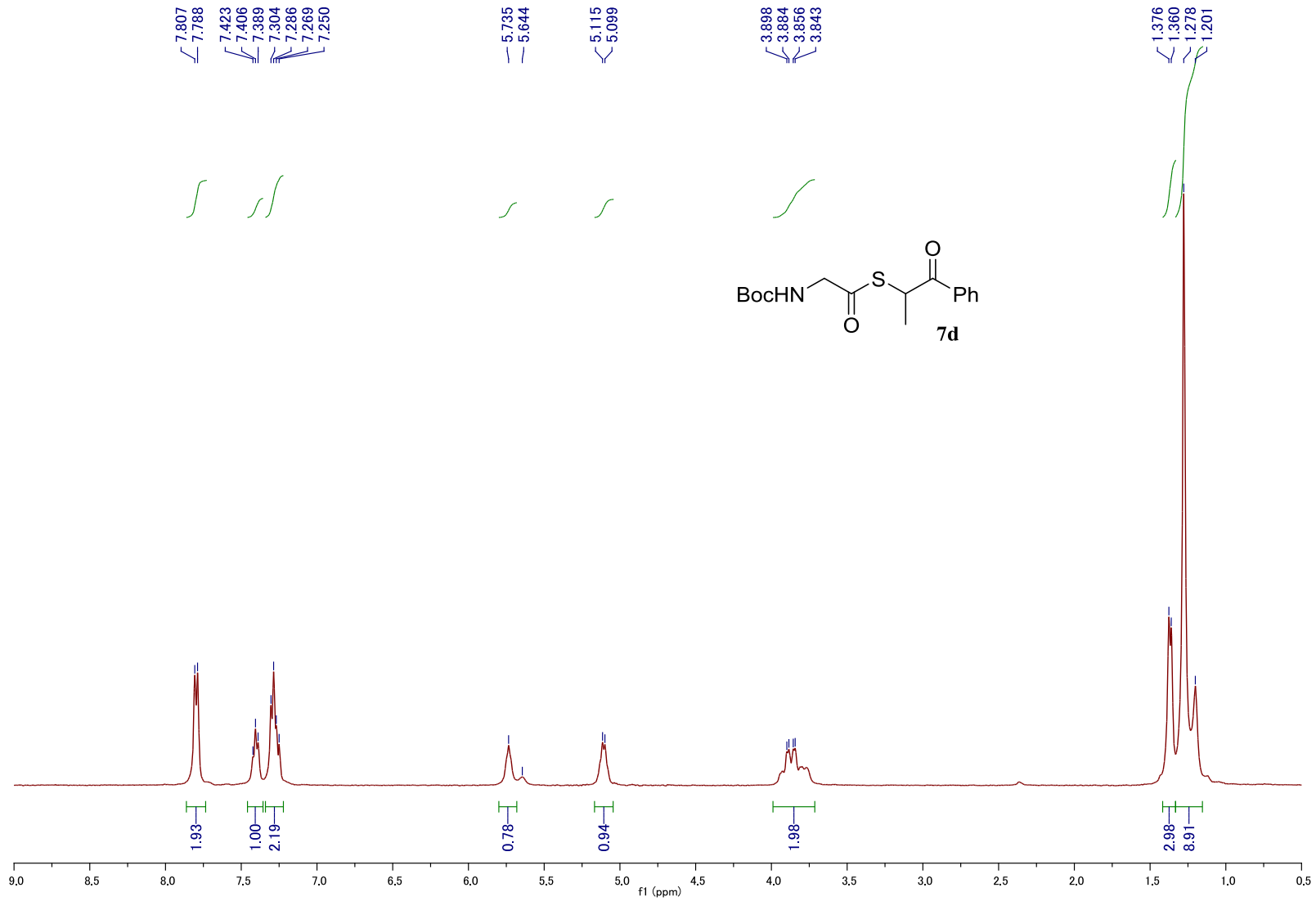
S-α-Methylphenacyl *N-tert*-butoxycarbonyl-L-thiophenylalainate (7c) ^{1}H NMR (400 MHz, $CDCl_3$)



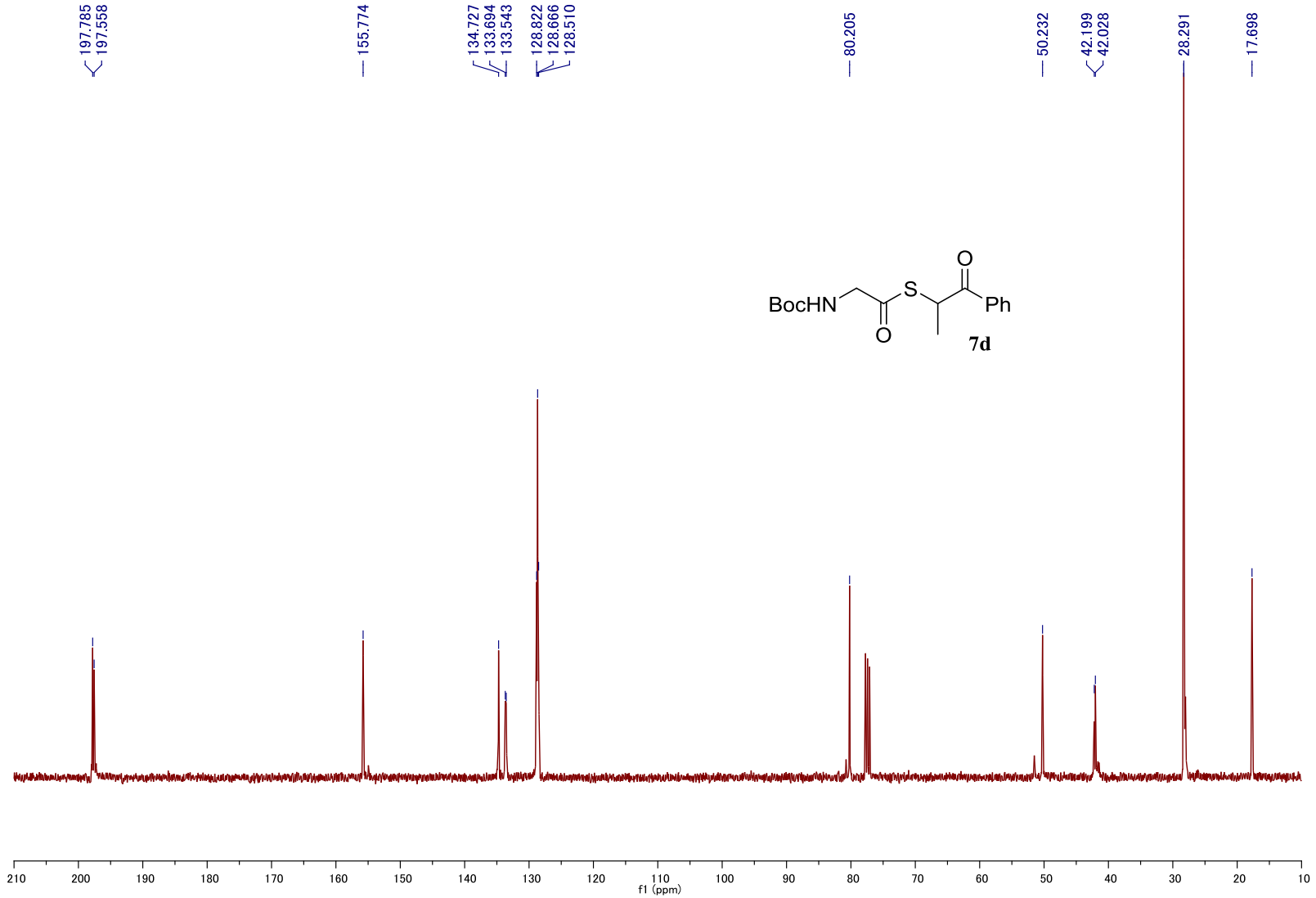
S-α-Methylphenacyl *N-tert*-butoxycarbonyl-L-thiophenylalainate (7c) ^{13}C NMR (100 MHz, $CDCl_3$)



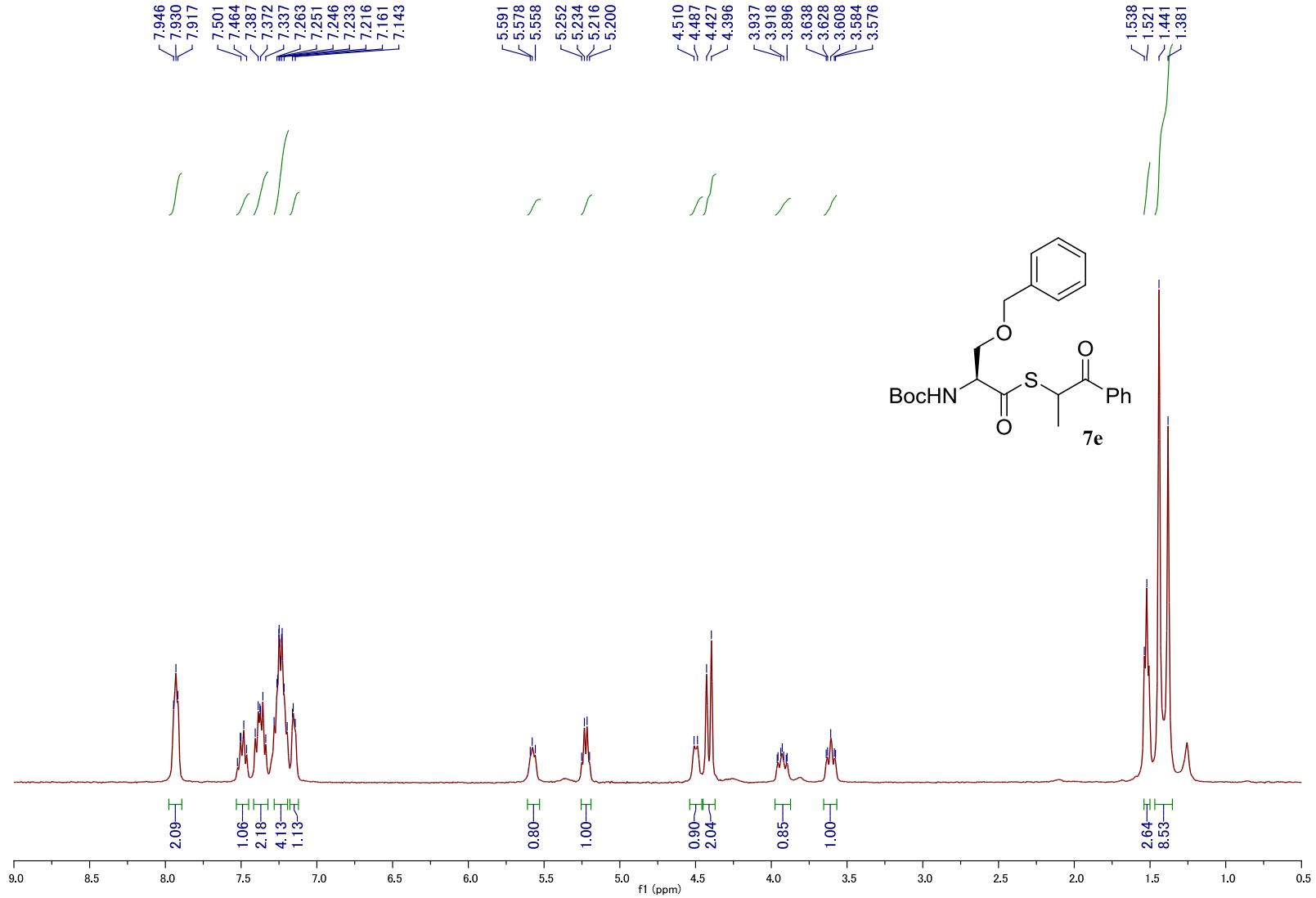
_S_-α-Methylphenacyl _N-tert_-butoxycarbonyl-thioglycinate (7d) ^{1}H NMR (400 MHz, $CDCl_3$)



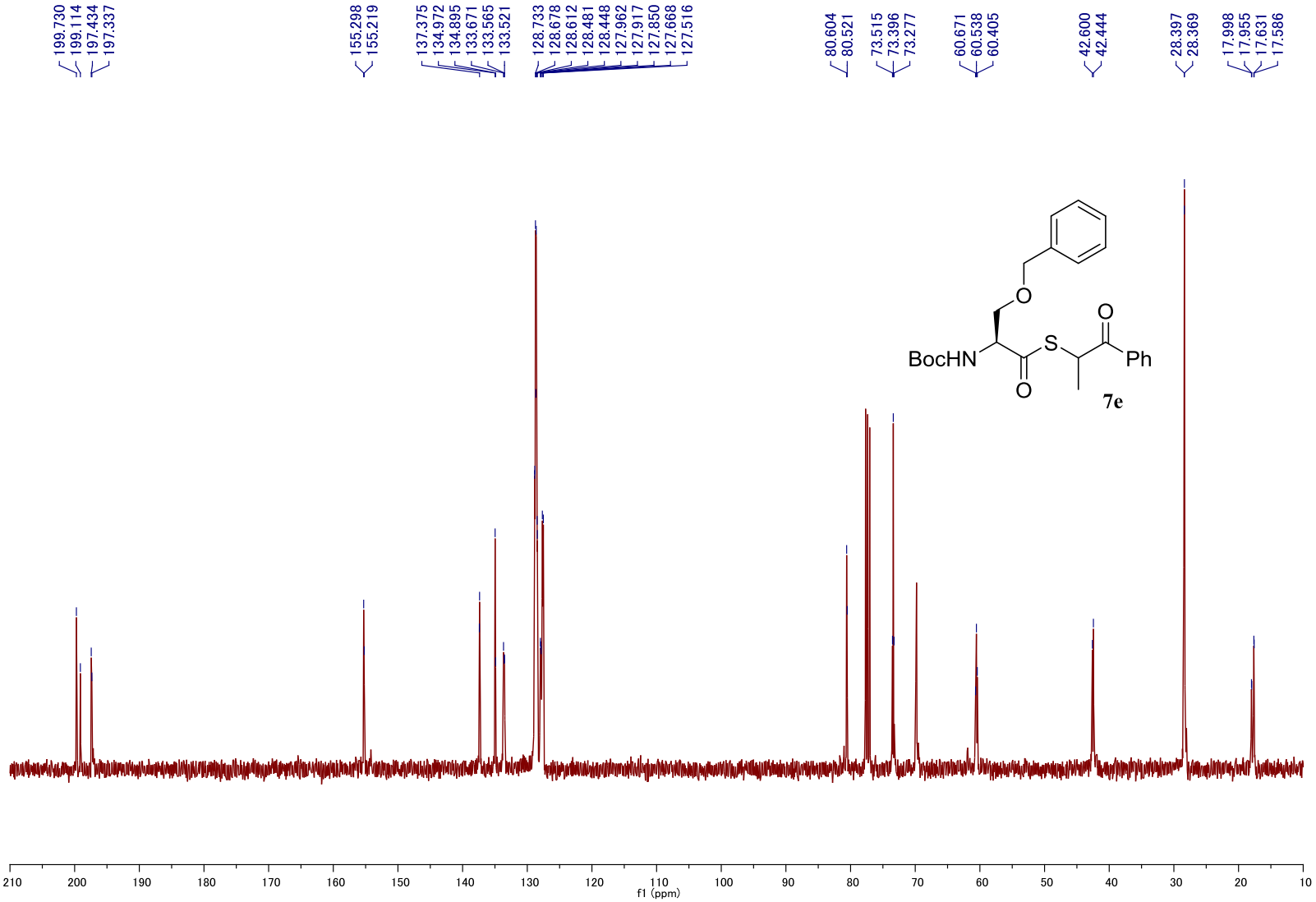
_S_-α-Methylphenacyl _N-tert_-butoxycarbonylthioglycinate (7d) ^{13}C NMR (100 MHz, $CDCl_3$)



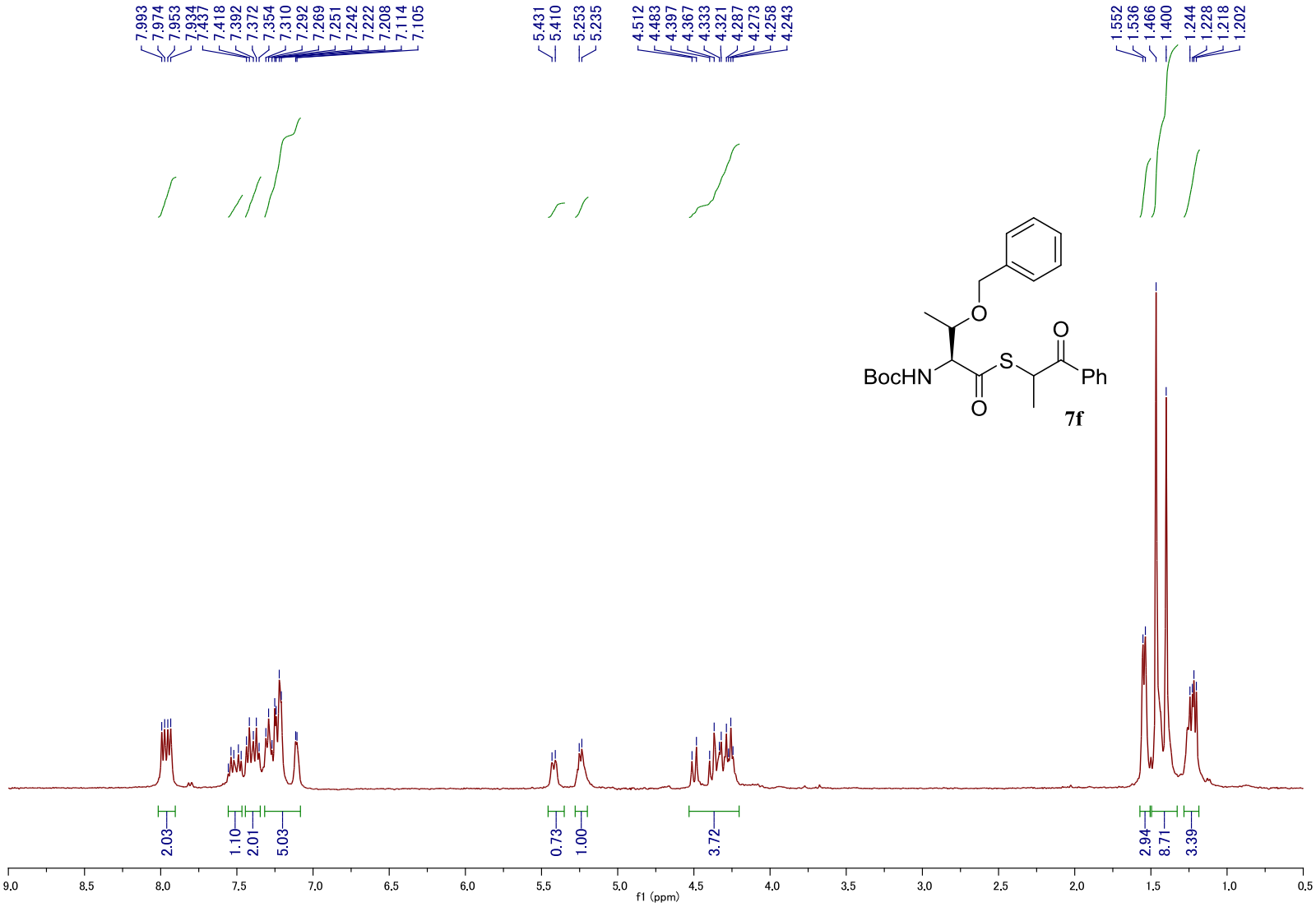
S-α-Methylphenacyl *N-tert*-butoxycarbonyl-*O*-benzyl-L-thioserinate (7e) ^{1}H NMR (400 MHz, $CDCl_3$)



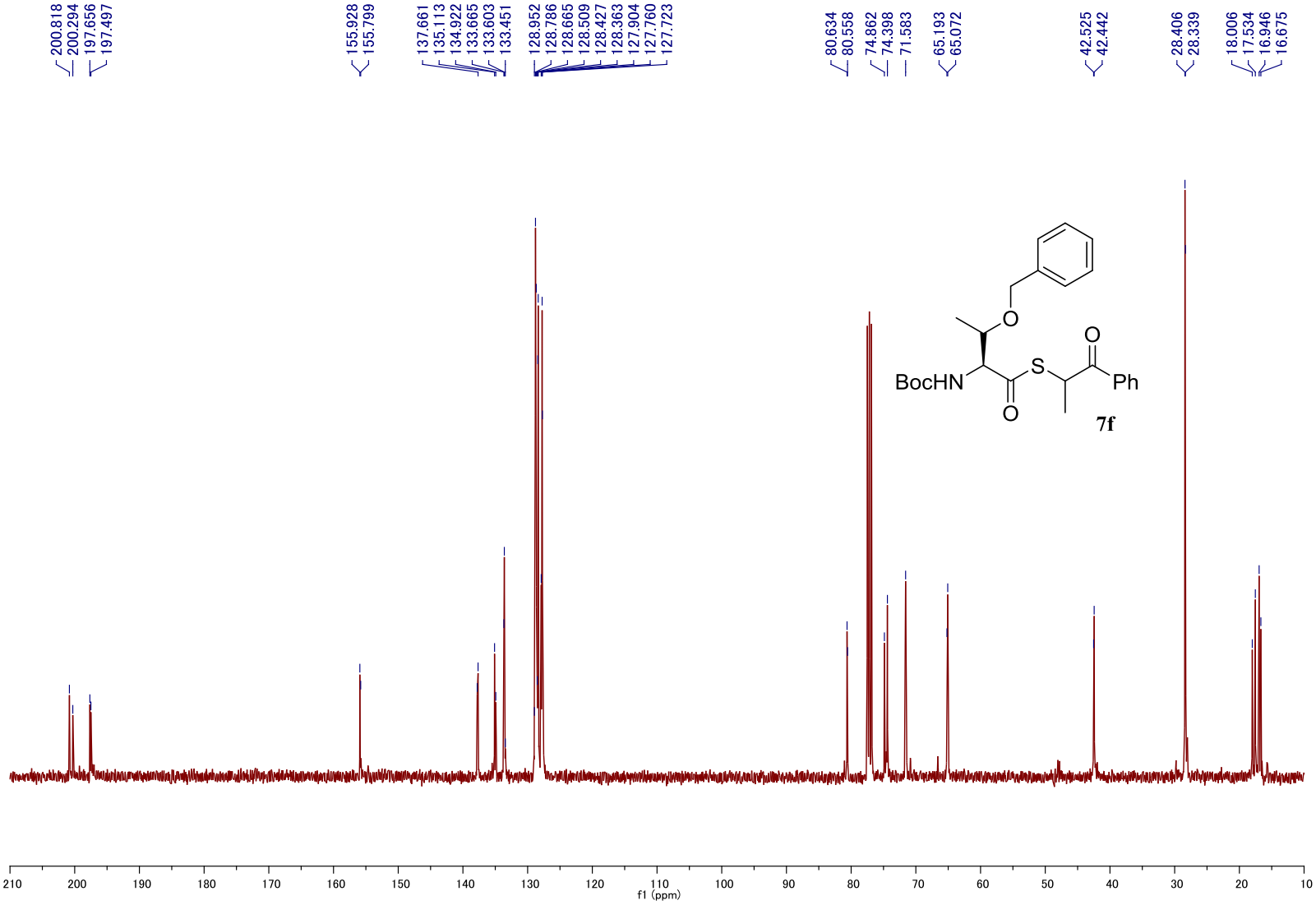
S-α-Methylphenacyl *N-tert*-butoxycarbonyl-*O*-benzyl-L-thioserinate (7e) ^{13}C NMR (100 MHz, $CDCl_3$)



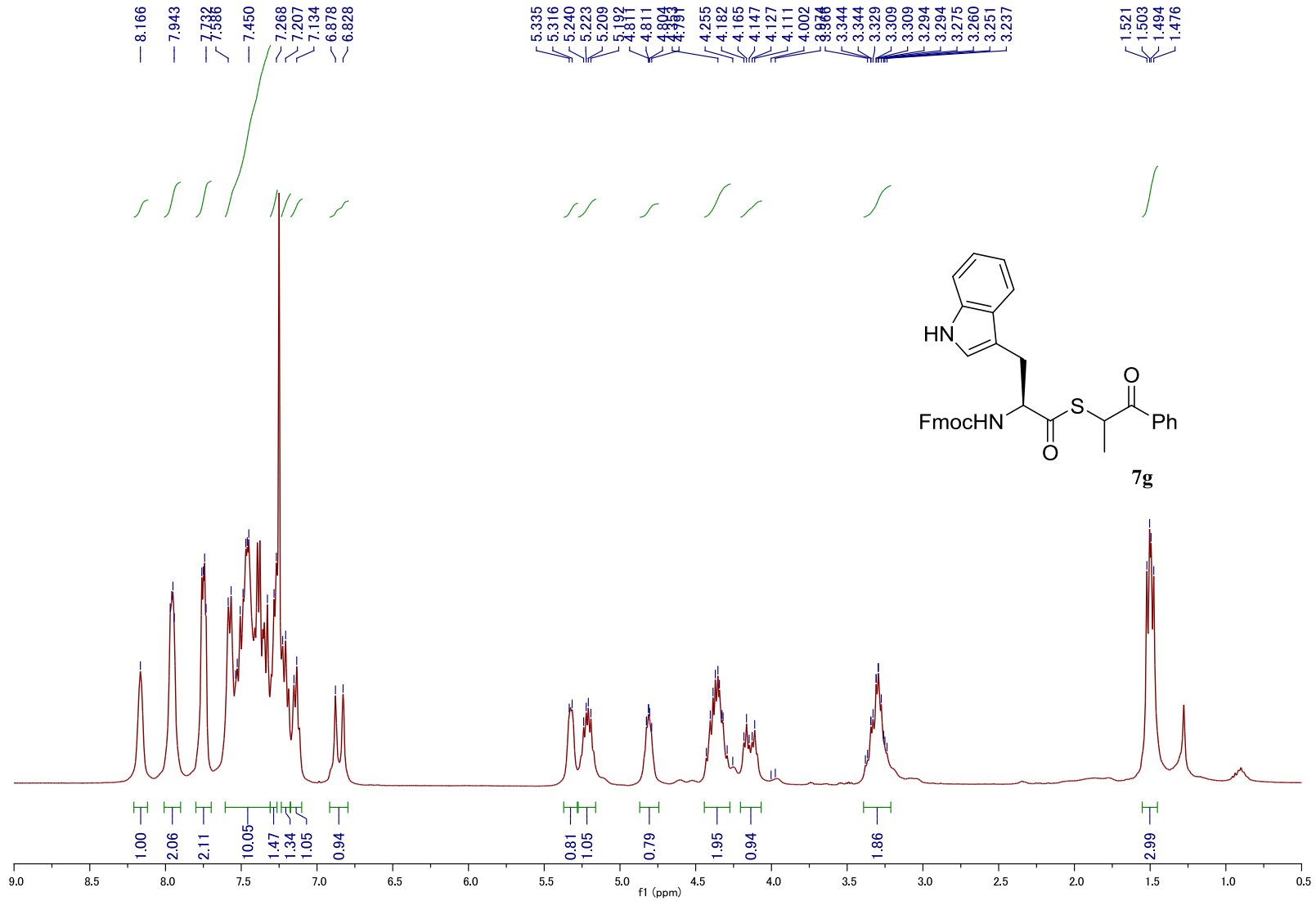
S-α-Methylphenacyl *N-tert*-butoxycarbonyl-*O*-benzyl-L-thiothreonate (7f) ^{1}H NMR (400 MHz, $CDCl_3$)



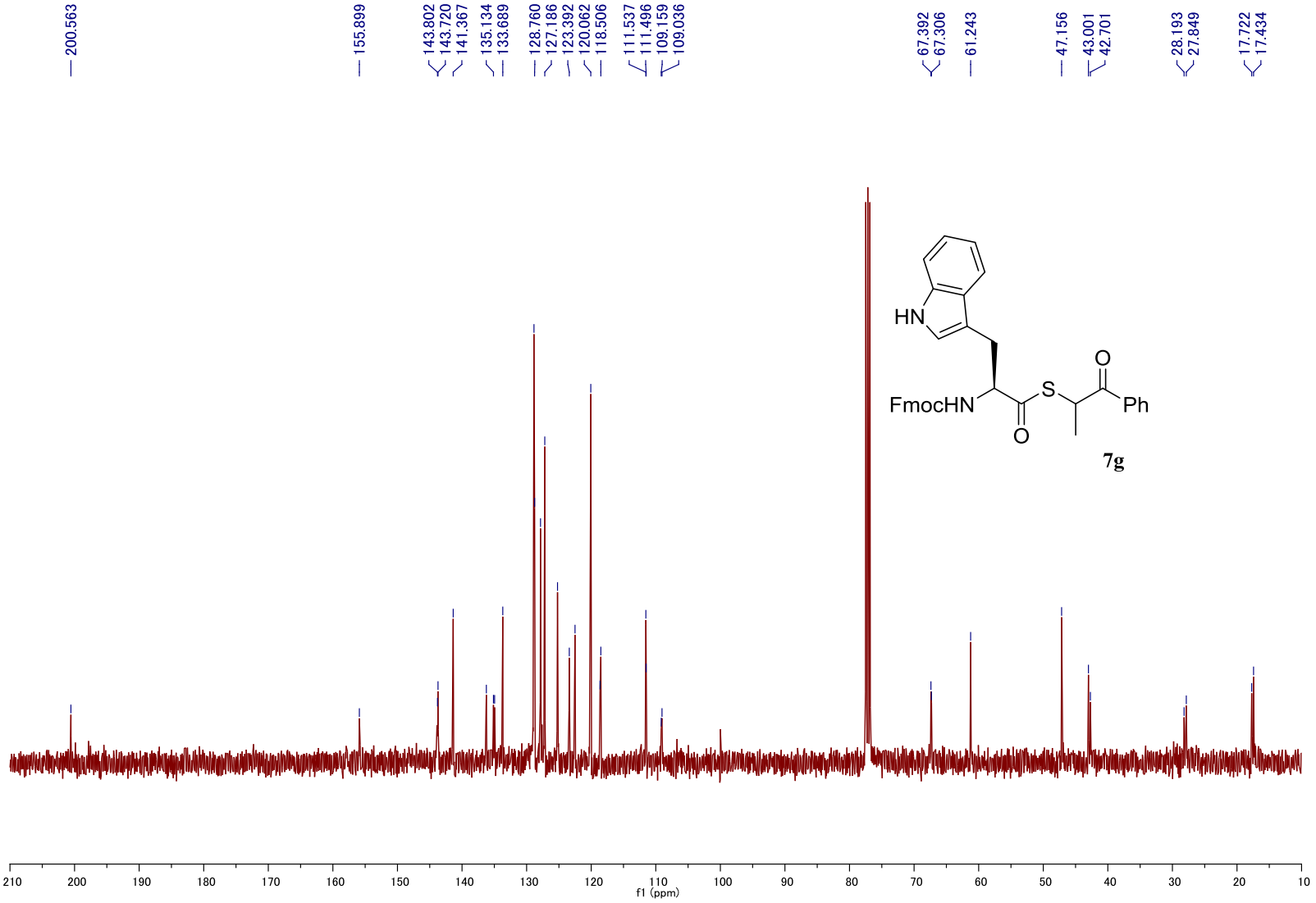
S-α-Methylphenacyl *N-tert*-butoxycarbonyl-*O*-benzyl-L-thiothreonate (7f) ^{13}C NMR (100 MHz, $CDCl_3$)



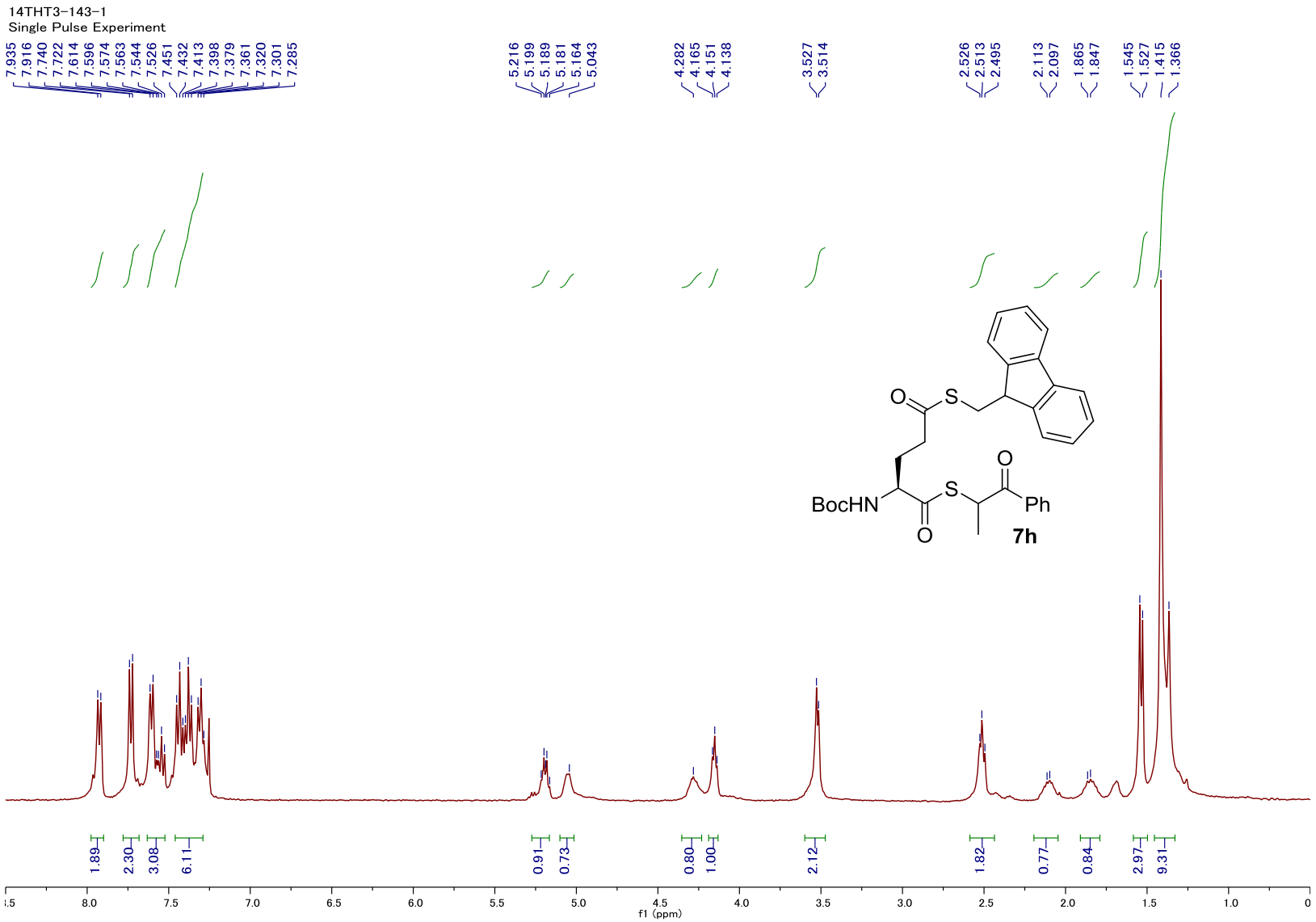
_S_-α-Methylphenacyl _N_-fluorenylmethyloxycarbonyl-L-thiotryptophanate (7g) ^{1}H NMR (400 MHz, $CDCl_3$)



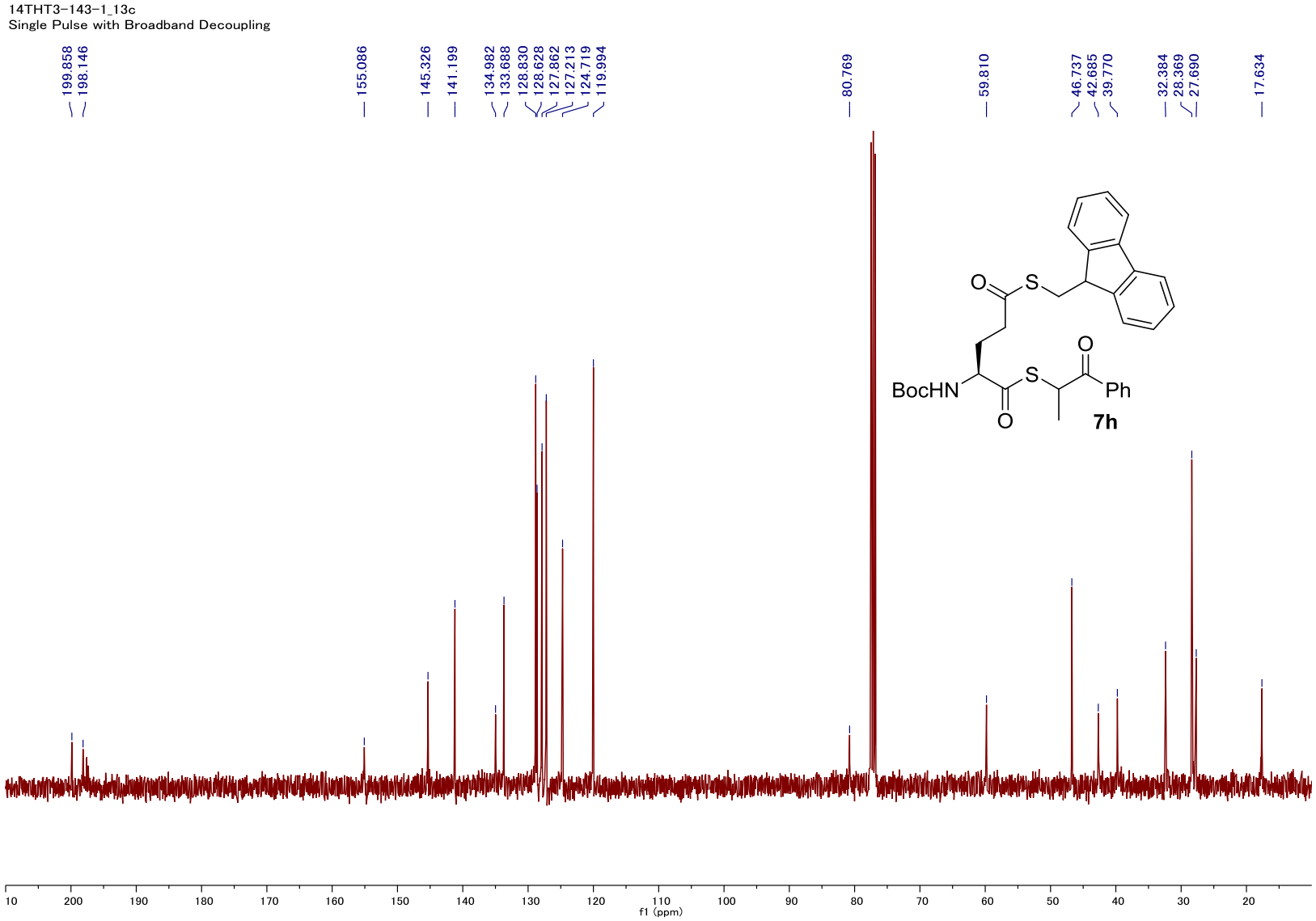
_S_-α-Methylphenacyl _N_-fluorenylmethyloxycarbonyl-L-thiotryptophanate (7g) ^{13}C NMR (100 MHz, $CDCl_3$)



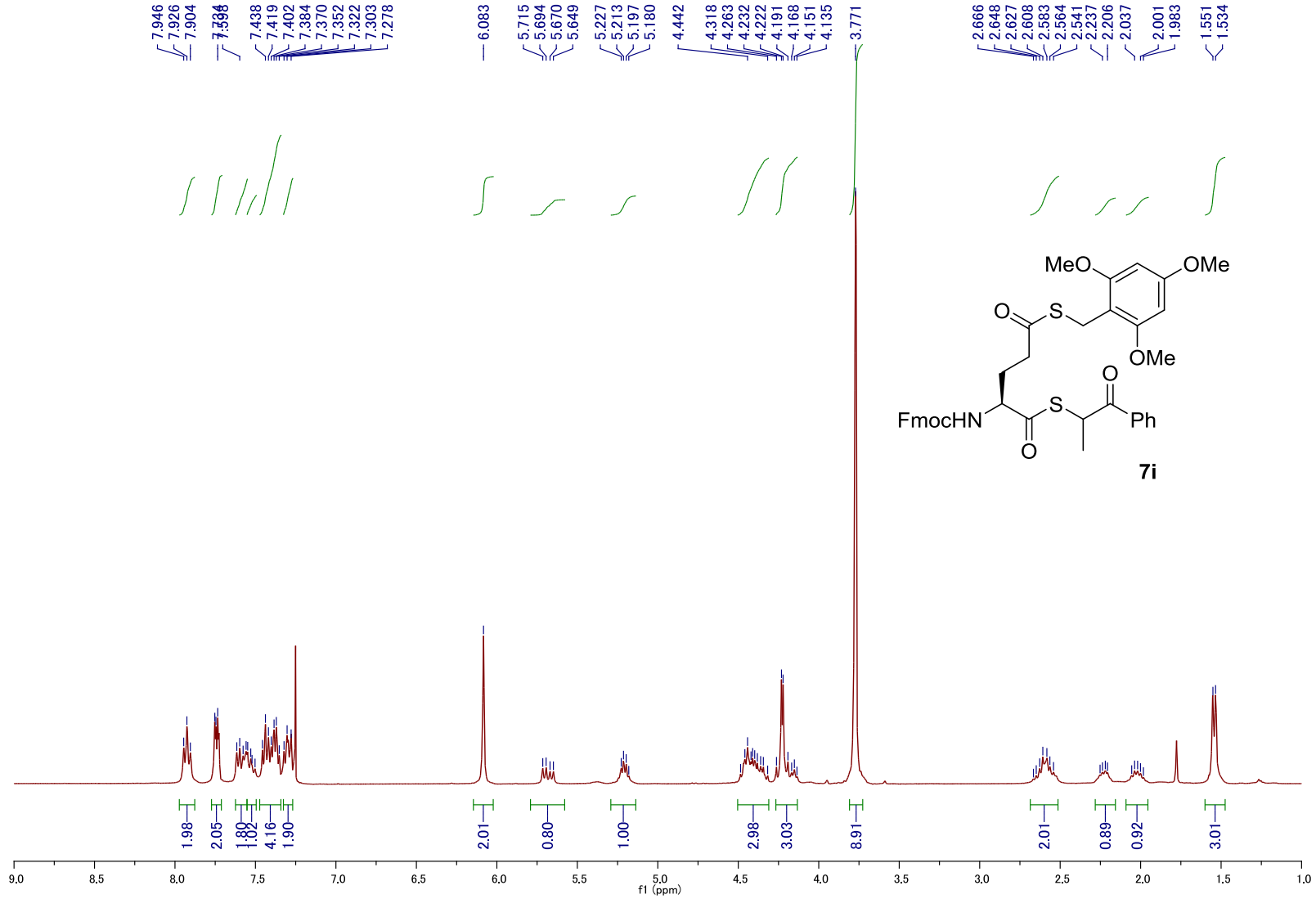
***S*$^{\alpha}$-α-Methylphenacyl *S*$^{\gamma}$-9-fluorenylmethyl *N*-*tert*-butoxycarbonyl-L-dithioglutamate (7h)** ^{1}H NMR (400 MHz, $CDCl_3$)



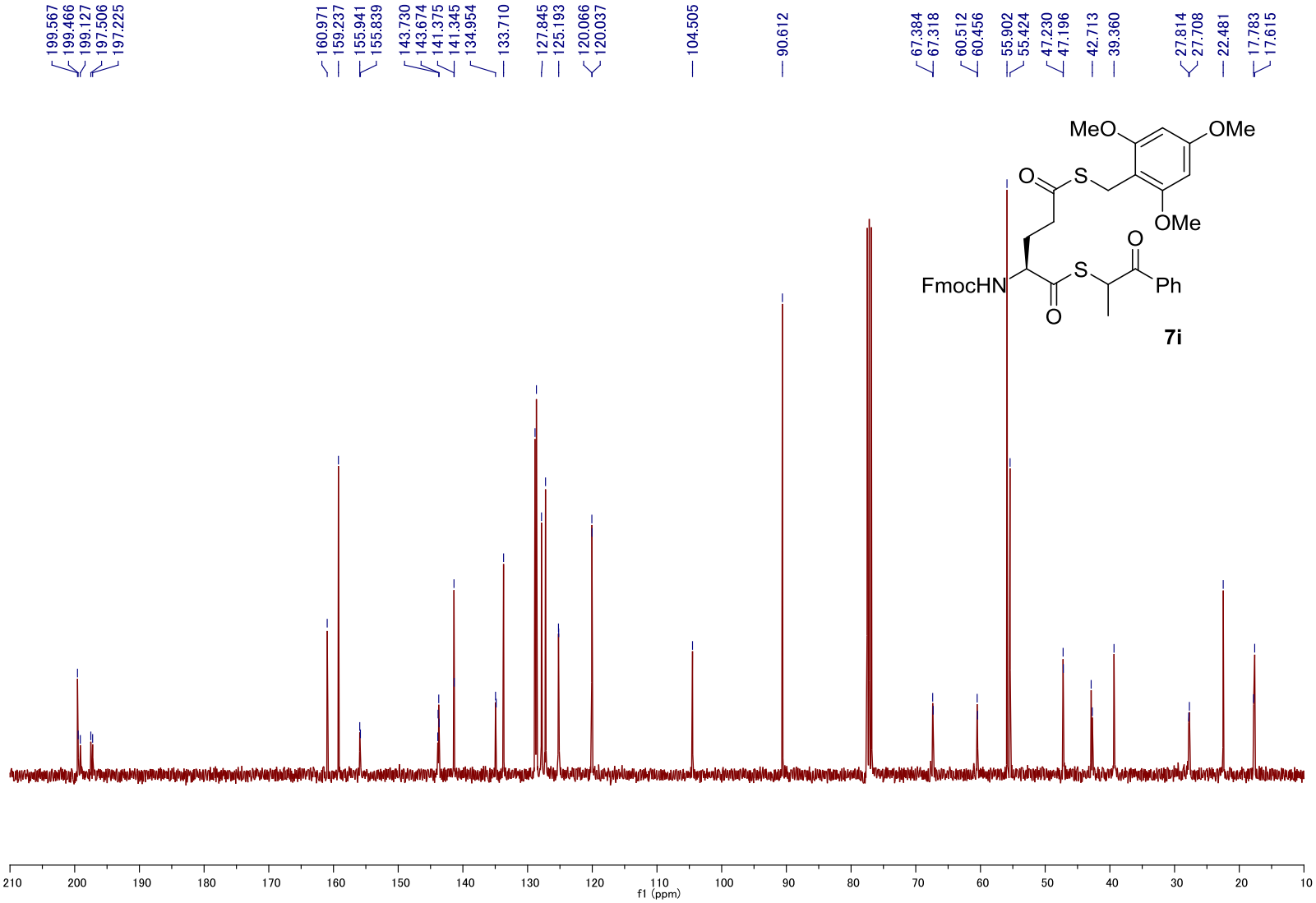
S^{α}-α-Methylphenacyl S^{γ}-9-fluorenylmethyl *N*-*tert*-butoxycarbonyl-L-dithioglutamate (7h) ^{13}C NMR (100 MHz, $CDCl_3$)



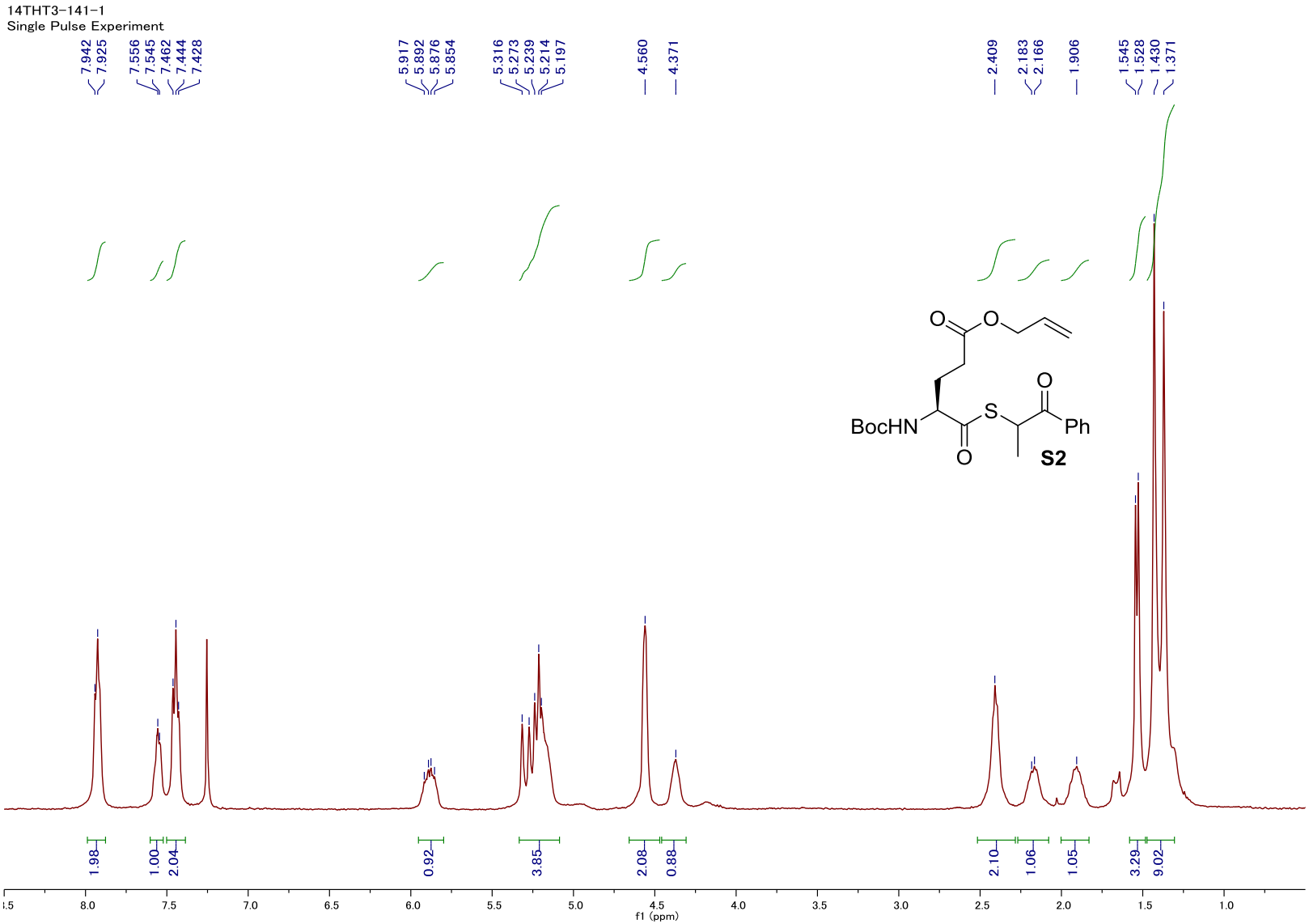
S^{α}-α-Methylphenacyl S^{γ}-2,4,6-trimethoxybenzyl *N*-(9-fluorenylmethyloxycarbonyl)-L-dithioglutamate (7i) ^{1}H NMR (400 MHz, $CDCl_3$)



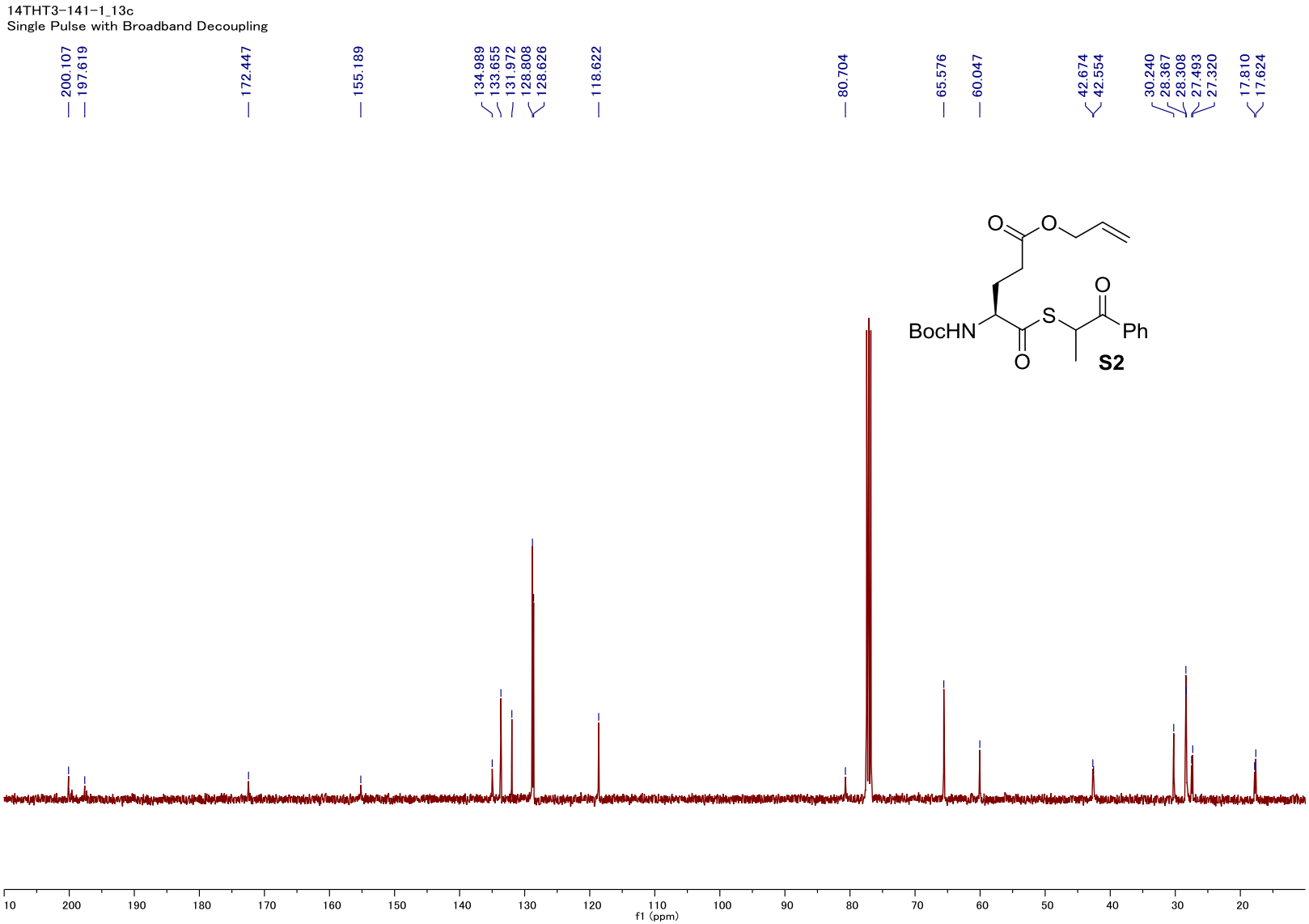
***S*$^{\alpha}$-α-Methylphenacyl *S*$^{\gamma}$-2,4,6-trimethoxybenzyl *N*-(9-fluorenylmethyloxycarbonyl)-L-dithioglutamate (7i)** ^{13}C NMR (100 MHz, $CDCl_3$)



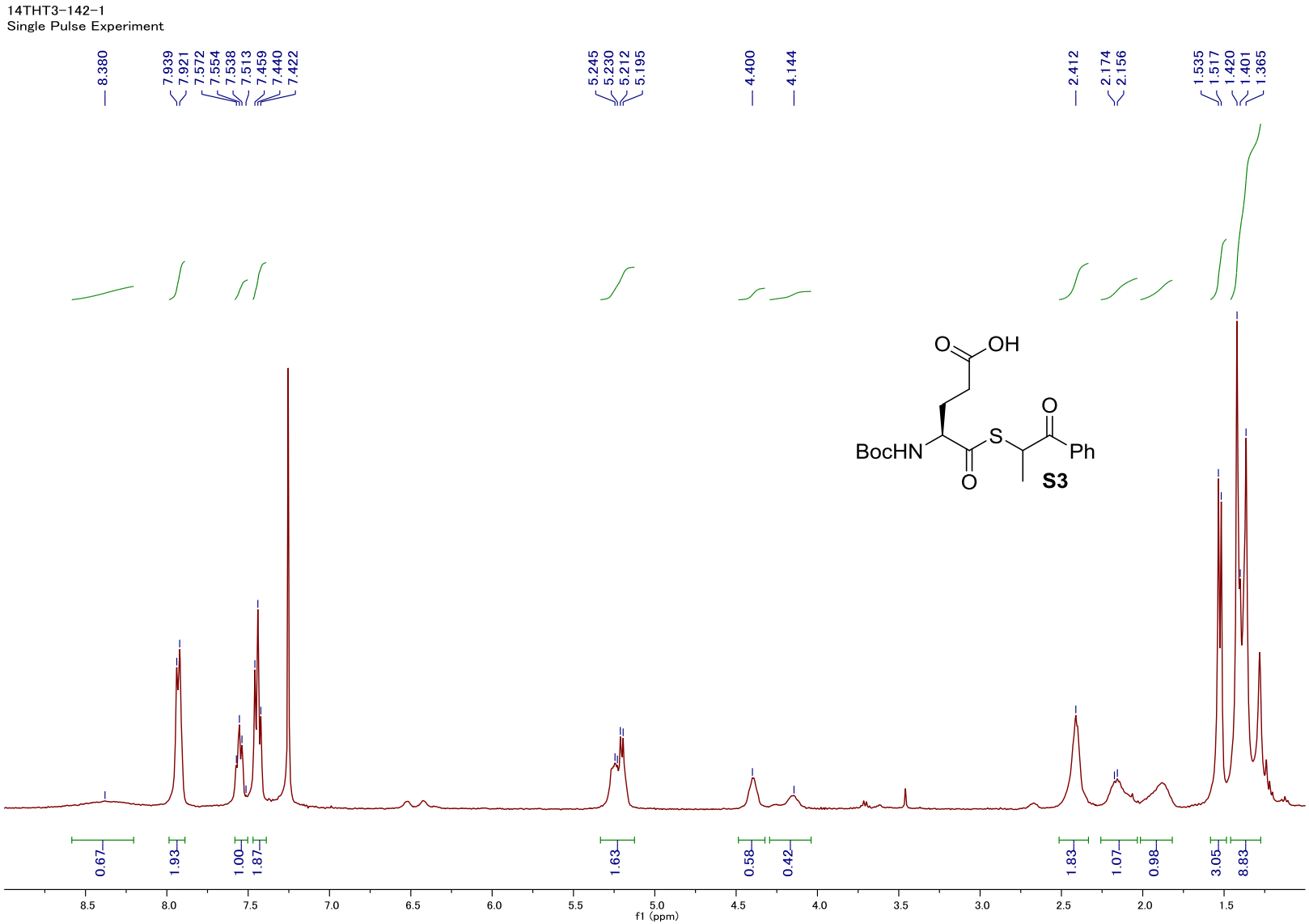
S^{α}-α-Methylphenacyl O^{γ}-allyl *N*-*tert*-butoxycarbonyl-L-α-thioglutamate (S2) ^{1}H NMR (400 MHz, $CDCl_3$)



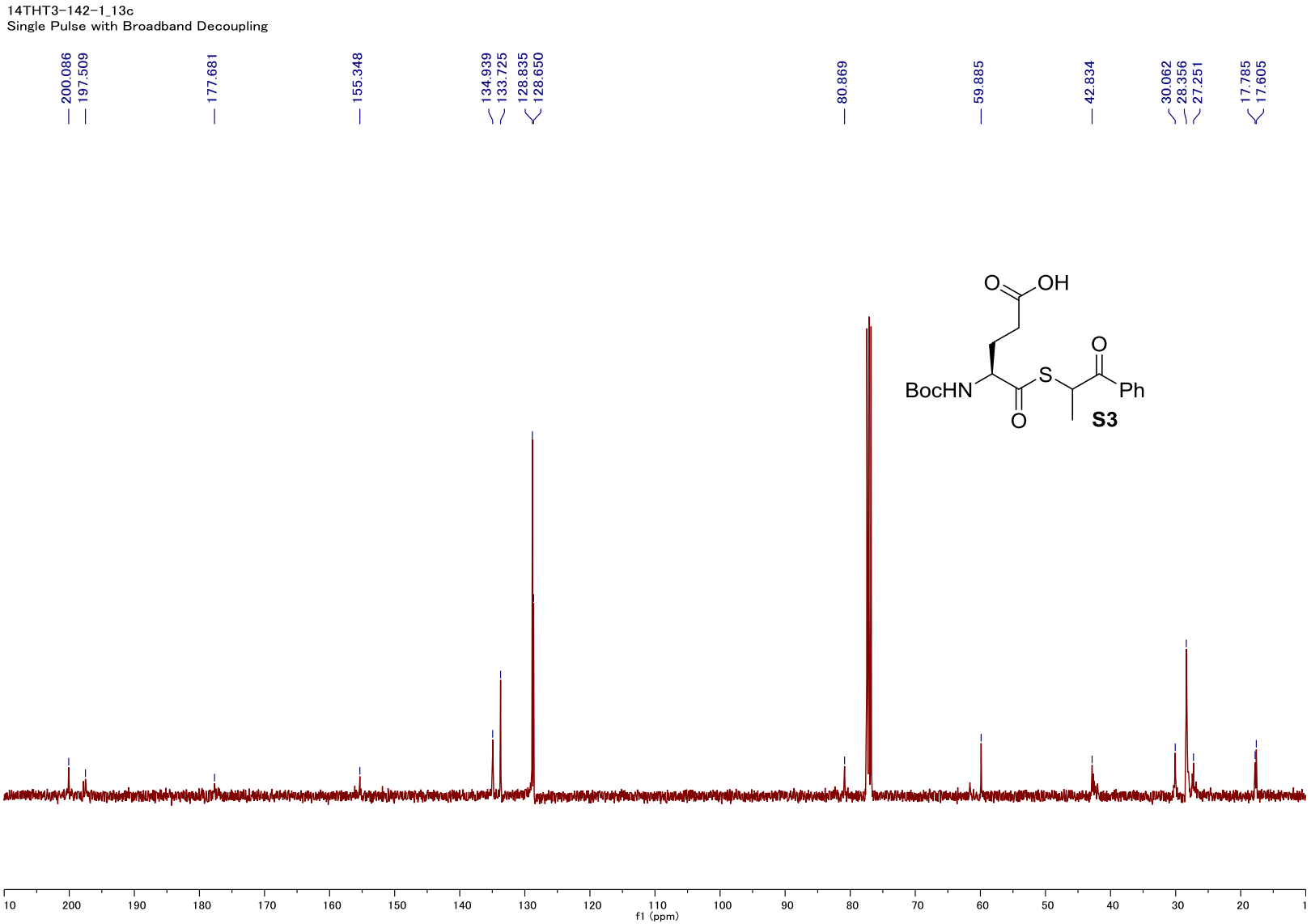
S^{α}-α-Methylphenacyl O^{γ}-allyl *N*-*tert*-butoxycarbonyl-L-α-thioglutamate (S2) ^{13}C NMR (100 MHz, $CDCl_3$)



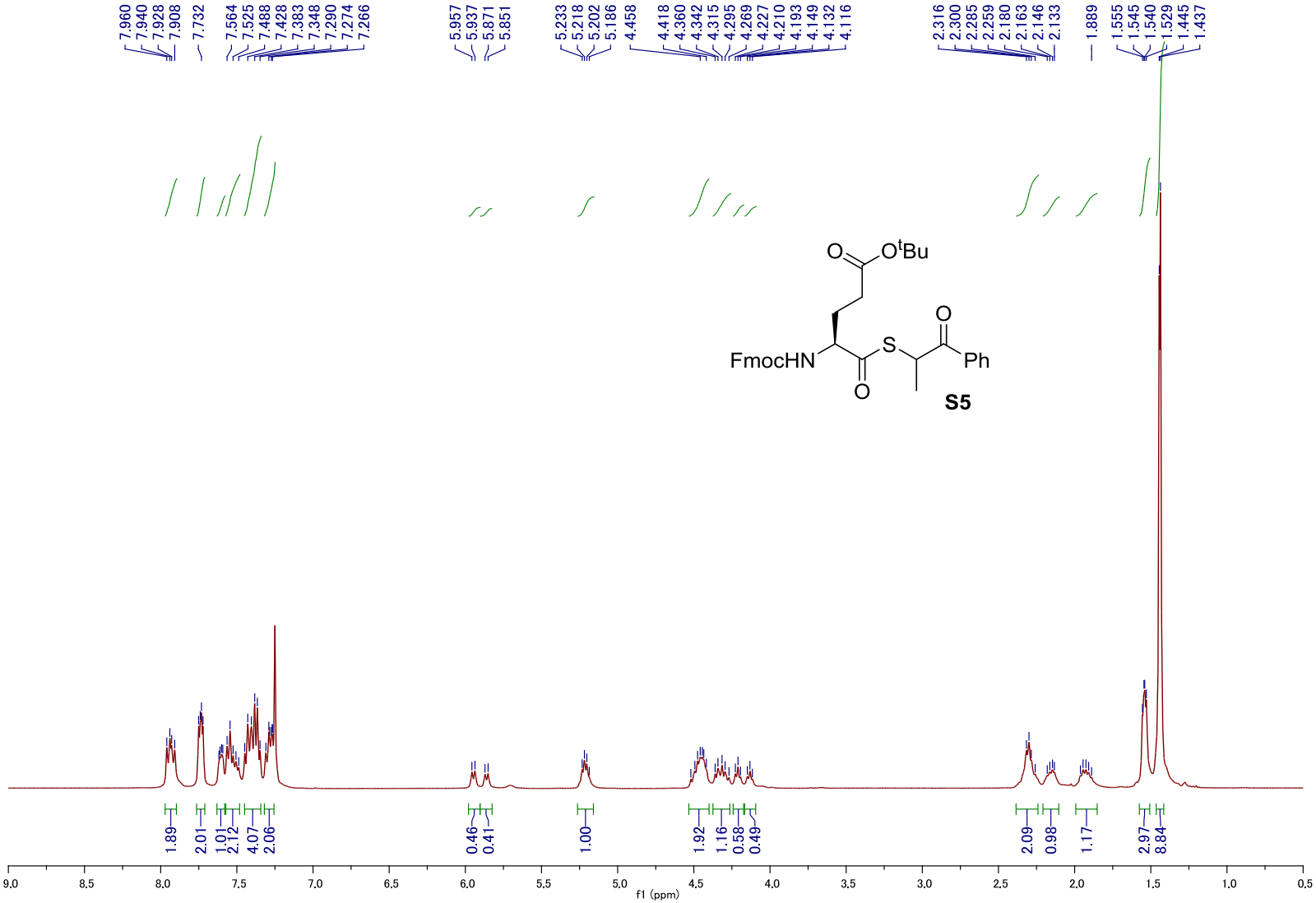
***S*$^{\alpha}$-α-Methylphenacyl *N*-*tert*-butoxycarbonyl-L-α-thioglutamate (S3)** ^{1}H NMR (400 MHz, $CDCl_3$)



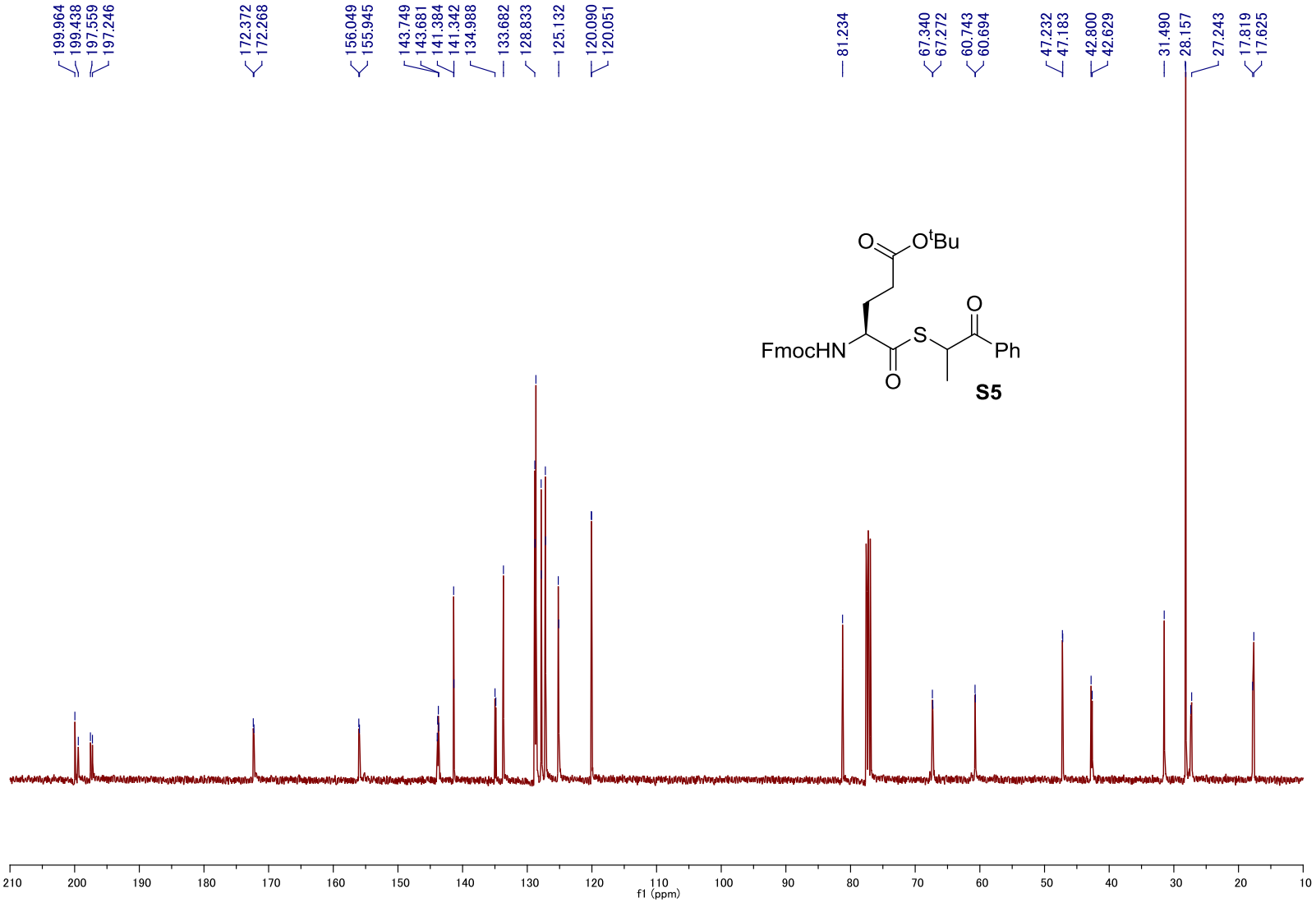
S^{α}-α-Methylphenacyl *N-tert*-butoxycarbonyl-L-α-thioglutamate (S3) ^{13}C NMR (100 MHz, $CDCl_3$)



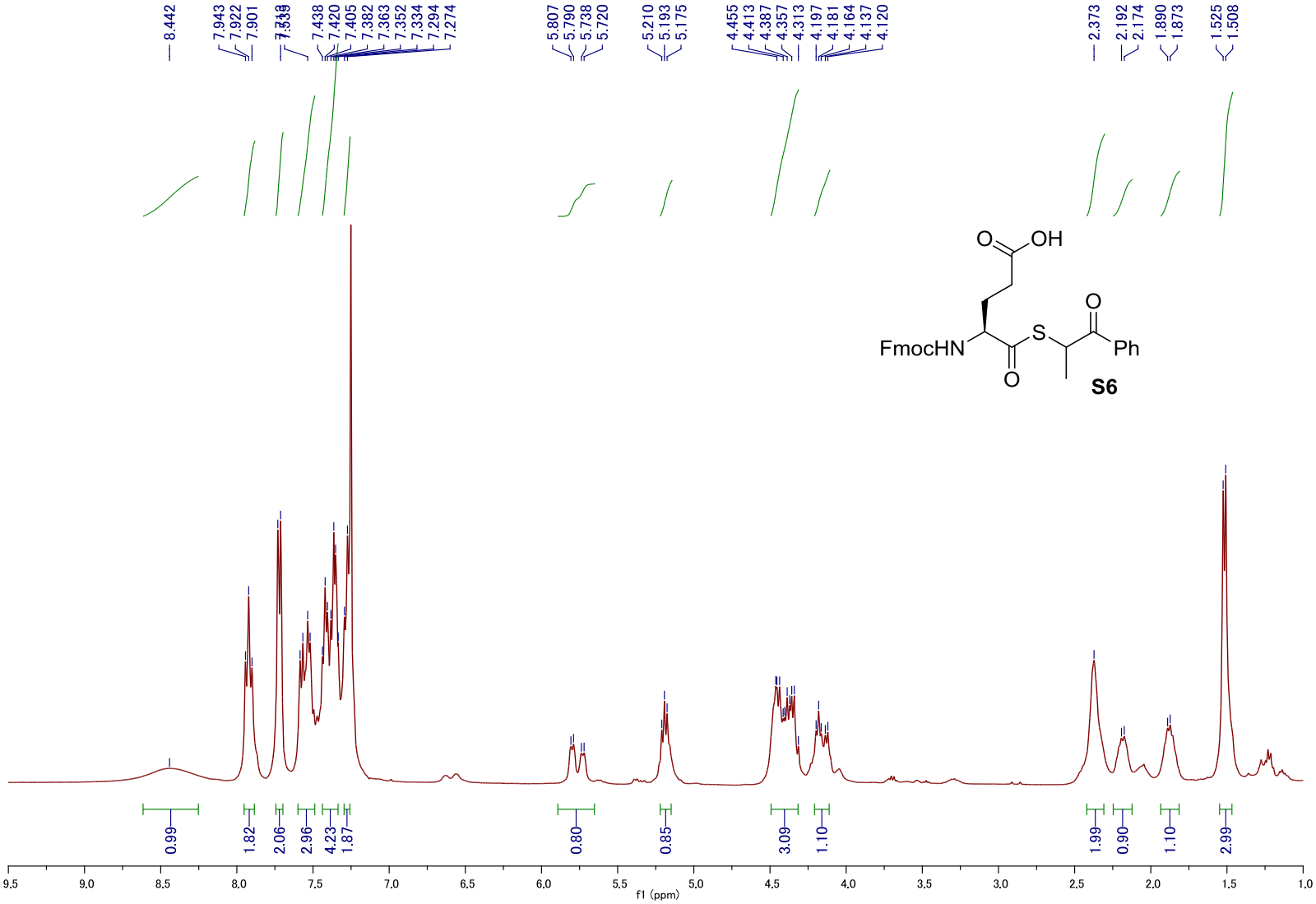
***S*$^{\alpha}$-α-Methylphenacyl *O*$^{\gamma}$-*tert*-butyl *N*-(9-fluorenylmethyloxycarbonyl)-L-α-thioglutamate (S5)** ^{1}H NMR (400 MHz, $CDCl_3$)



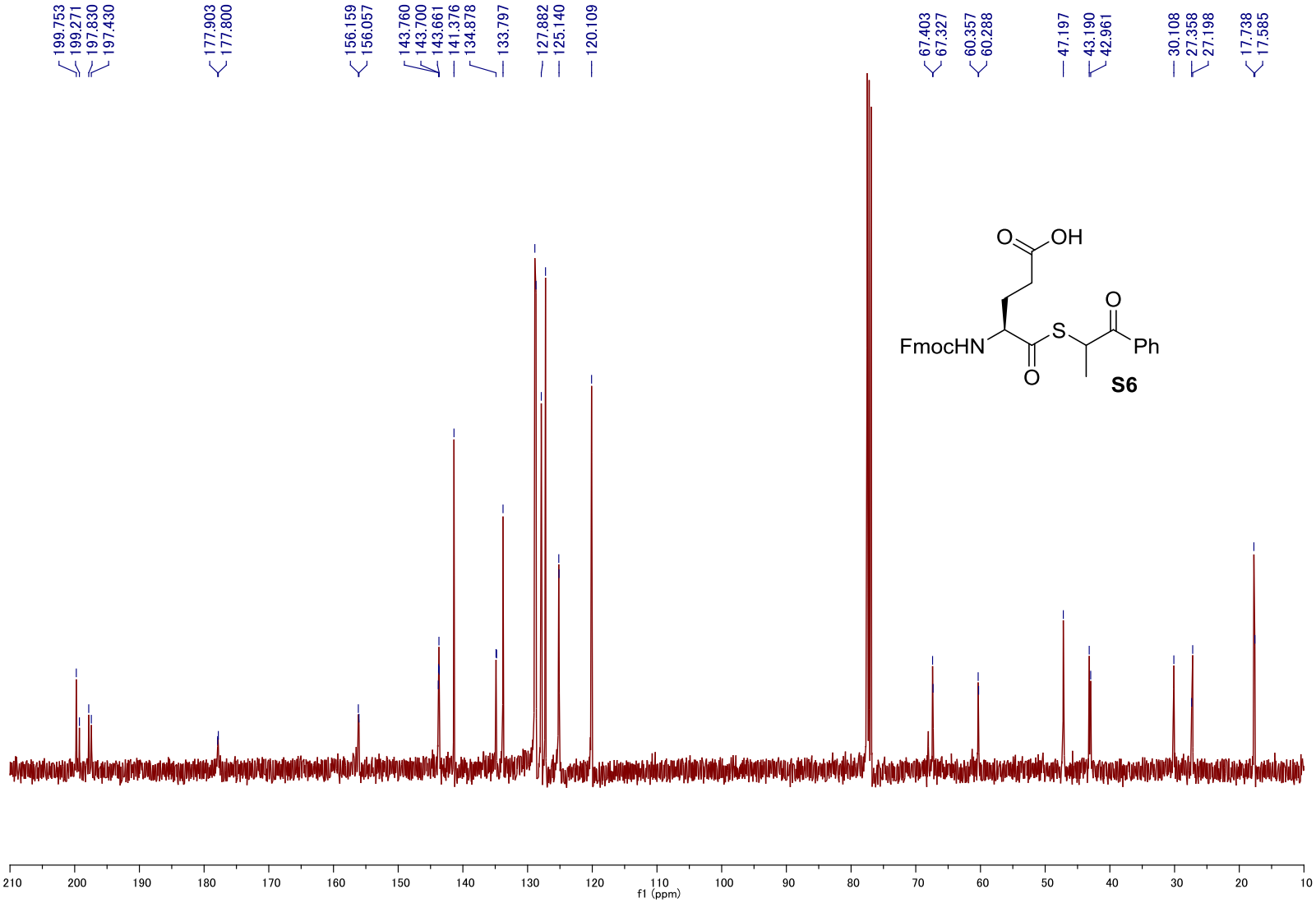
S^{α}-α-Methylphenacyl O^{γ}-*tert*-butyl *N*-(9-fluorenylmethyloxycarbonyl)-L-α-thioglutamate (S5) ^{13}C NMR (100 MHz, $CDCl_3$)



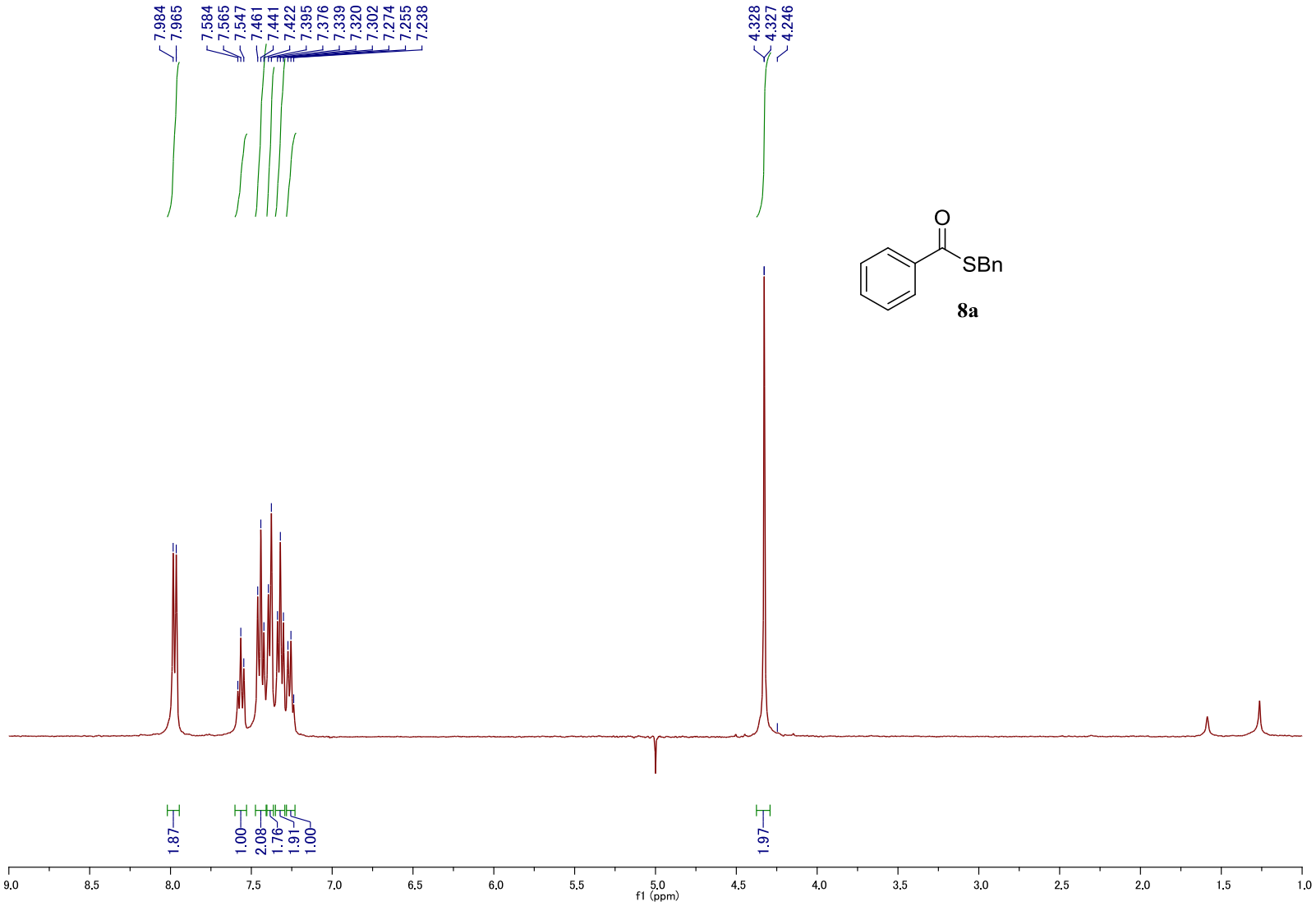
***S*$^{\alpha}$-α-Methylphenacyl *N*-fluorenylmethyloxycarbonyl-L-α-thioglutamate (S6)** ^{1}H NMR (400 MHz, $CDCl_3$)



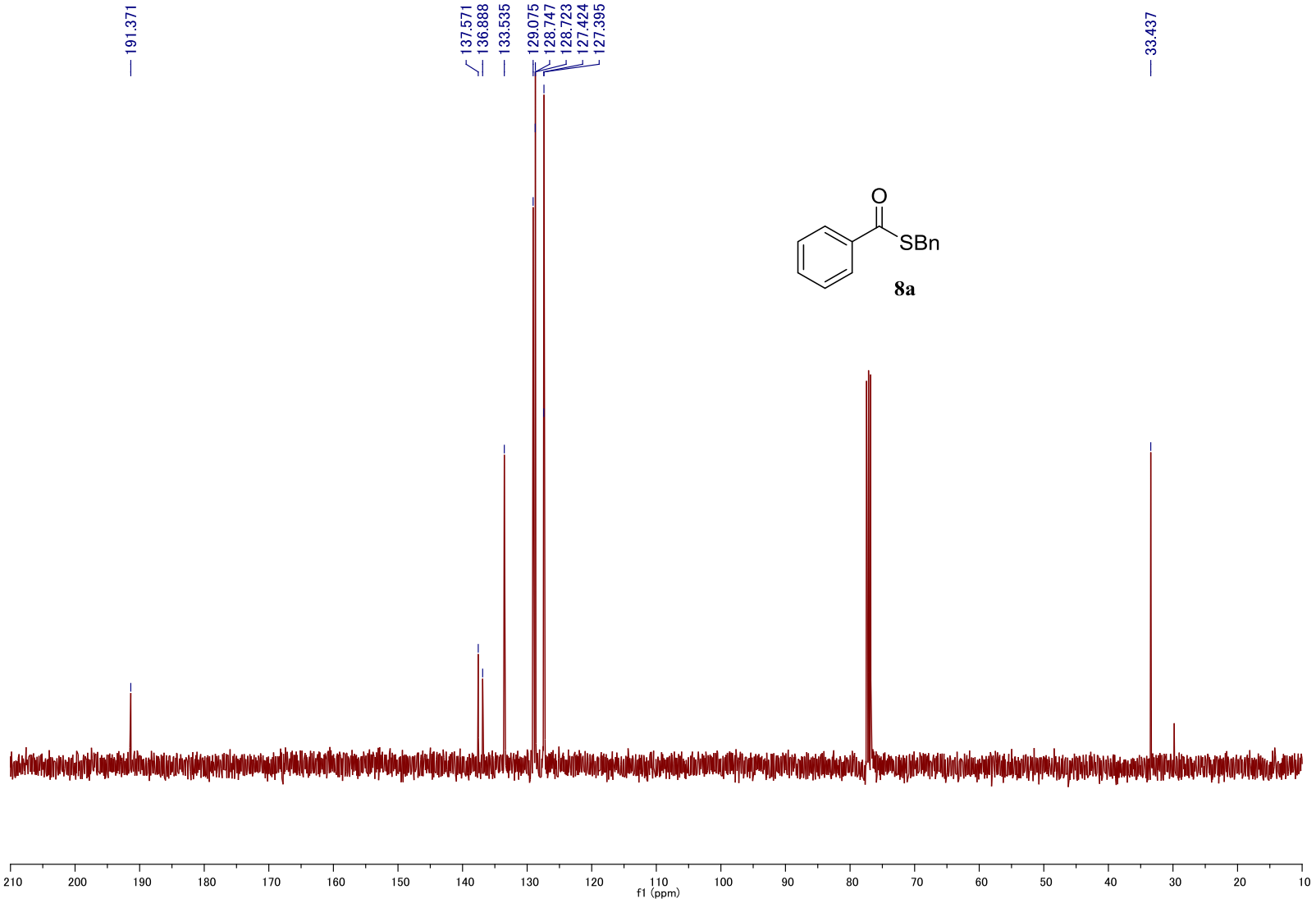
***S*$^{\alpha}$-α-Methylphenacyl *N*-fluorenylmethyloxycarbonyl-L-α-thioglutamate (S6)** ^{13}C NMR (100 MHz, $CDCl_3$)



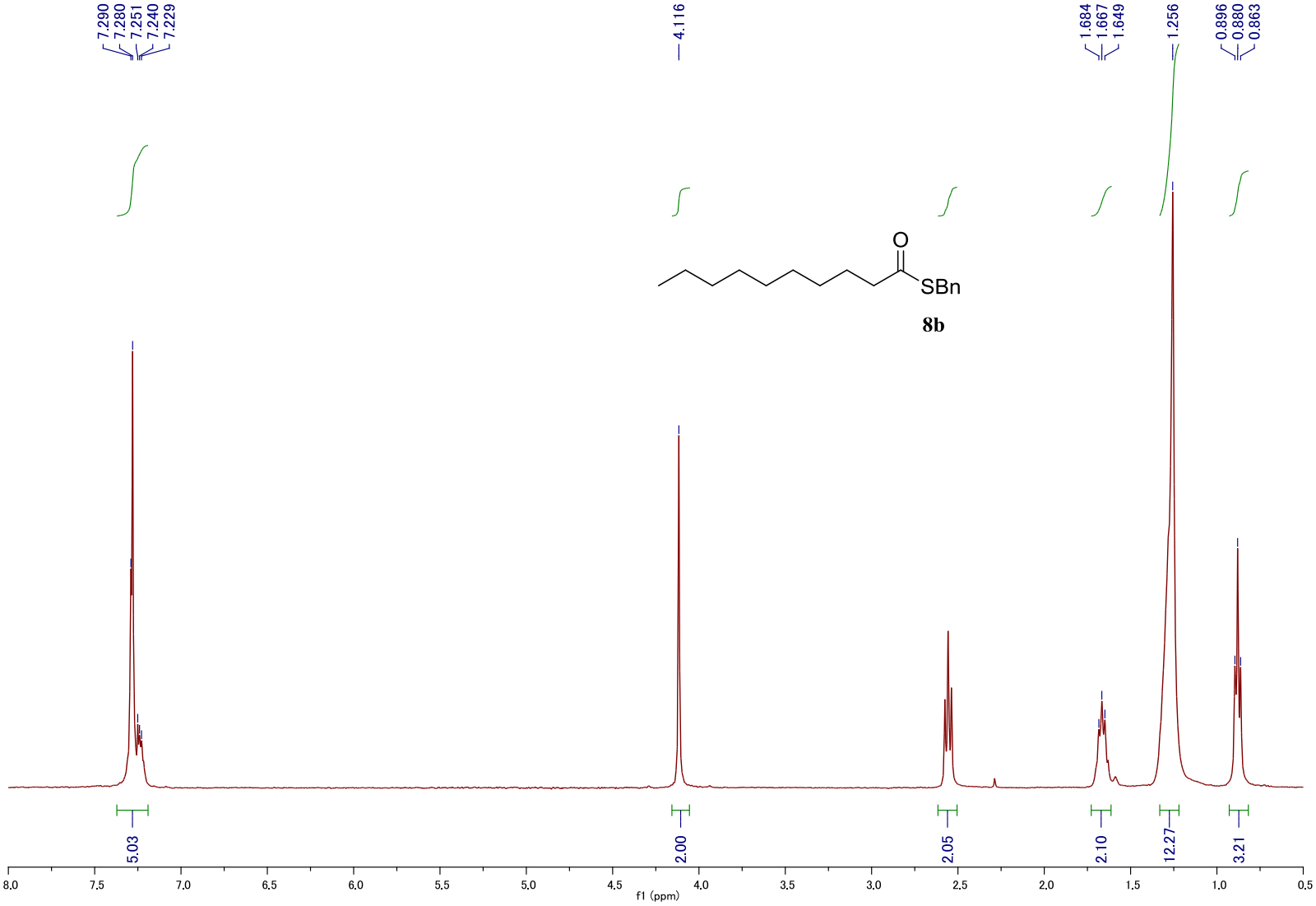
S-Benzyl thiobenzoate (8a) ^{1}H NMR (400 MHz, $CDCl_3$)



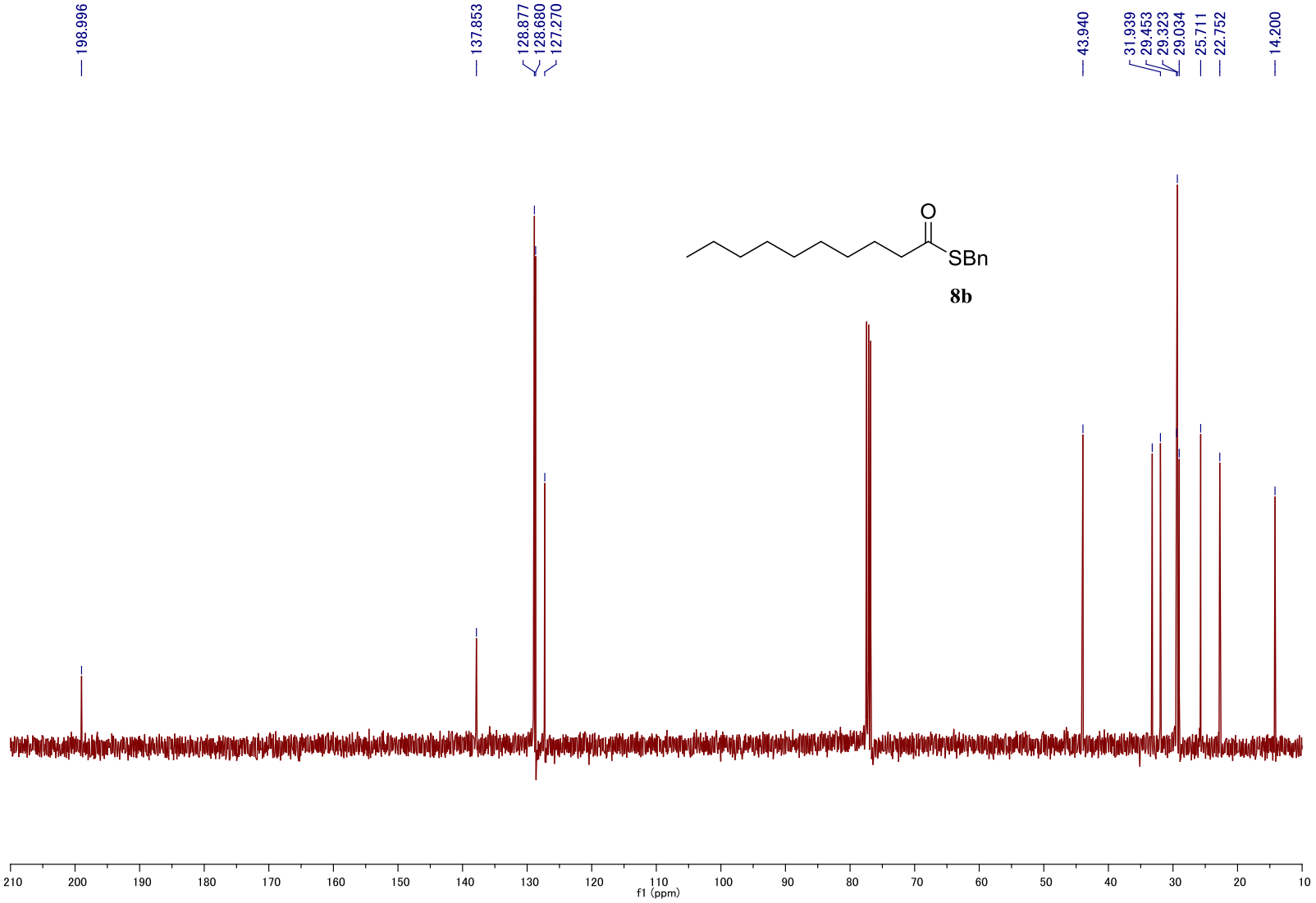
***S*-Benzyl thiobenzoate (8a)** ^{13}C NMR (100 MHz, $CDCl_3$)



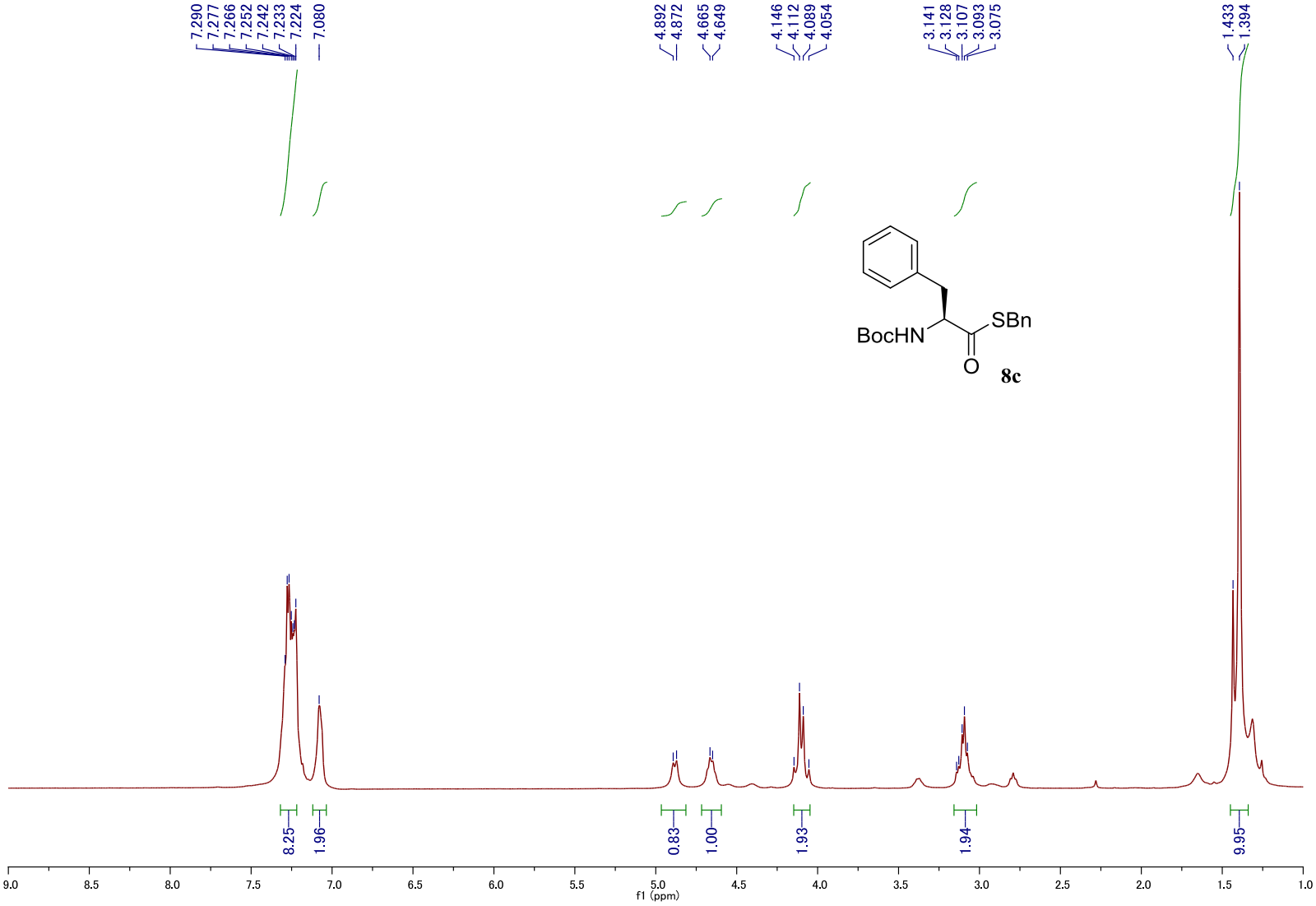
_S_-Benzyl thiodecanoate (8b) ^{1}H NMR (400 MHz, $CDCl_3$)



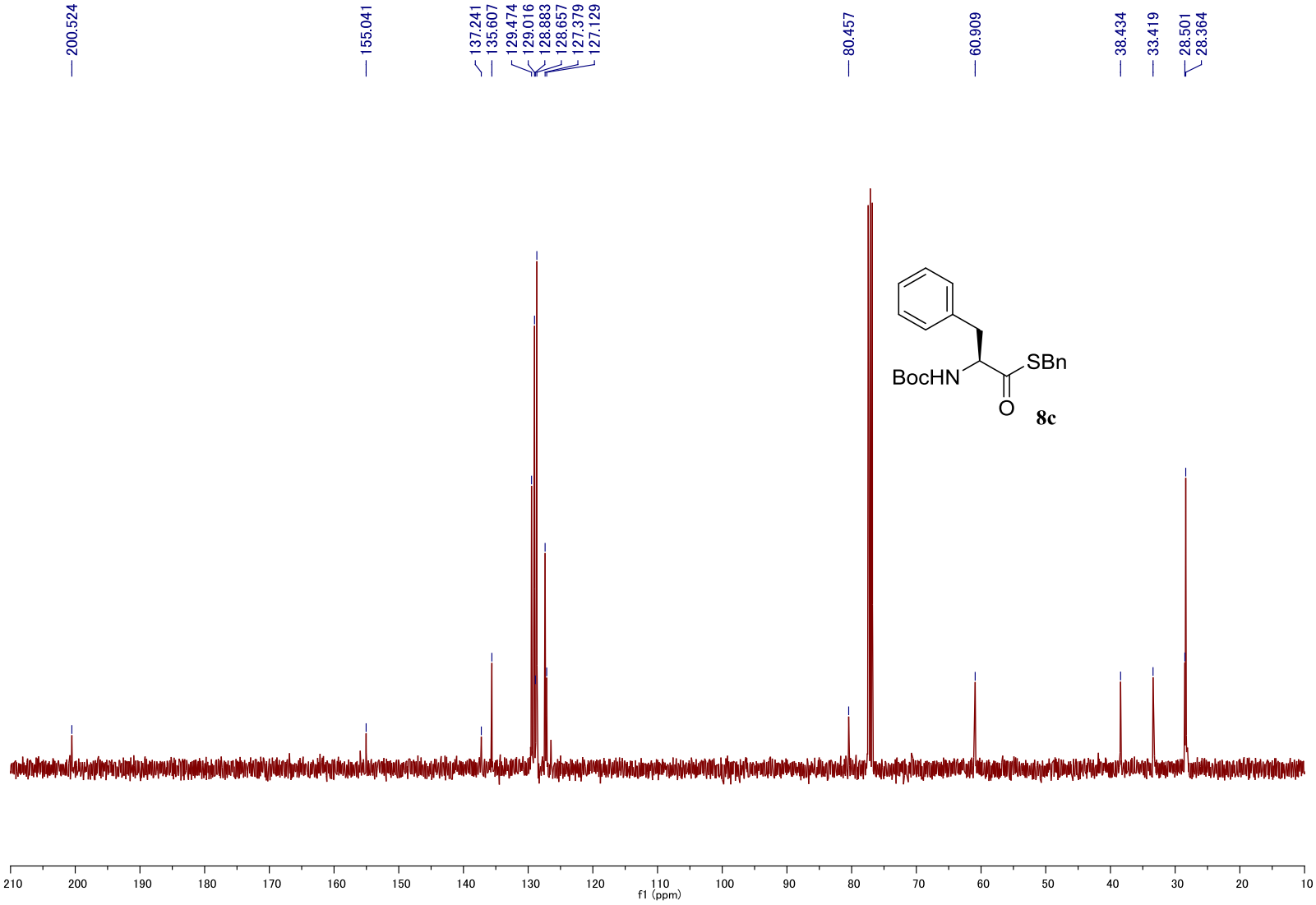
S-Benzyl thiodecanoate (8b) ^{13}C NMR (100 MHz, $CDCl_3$)



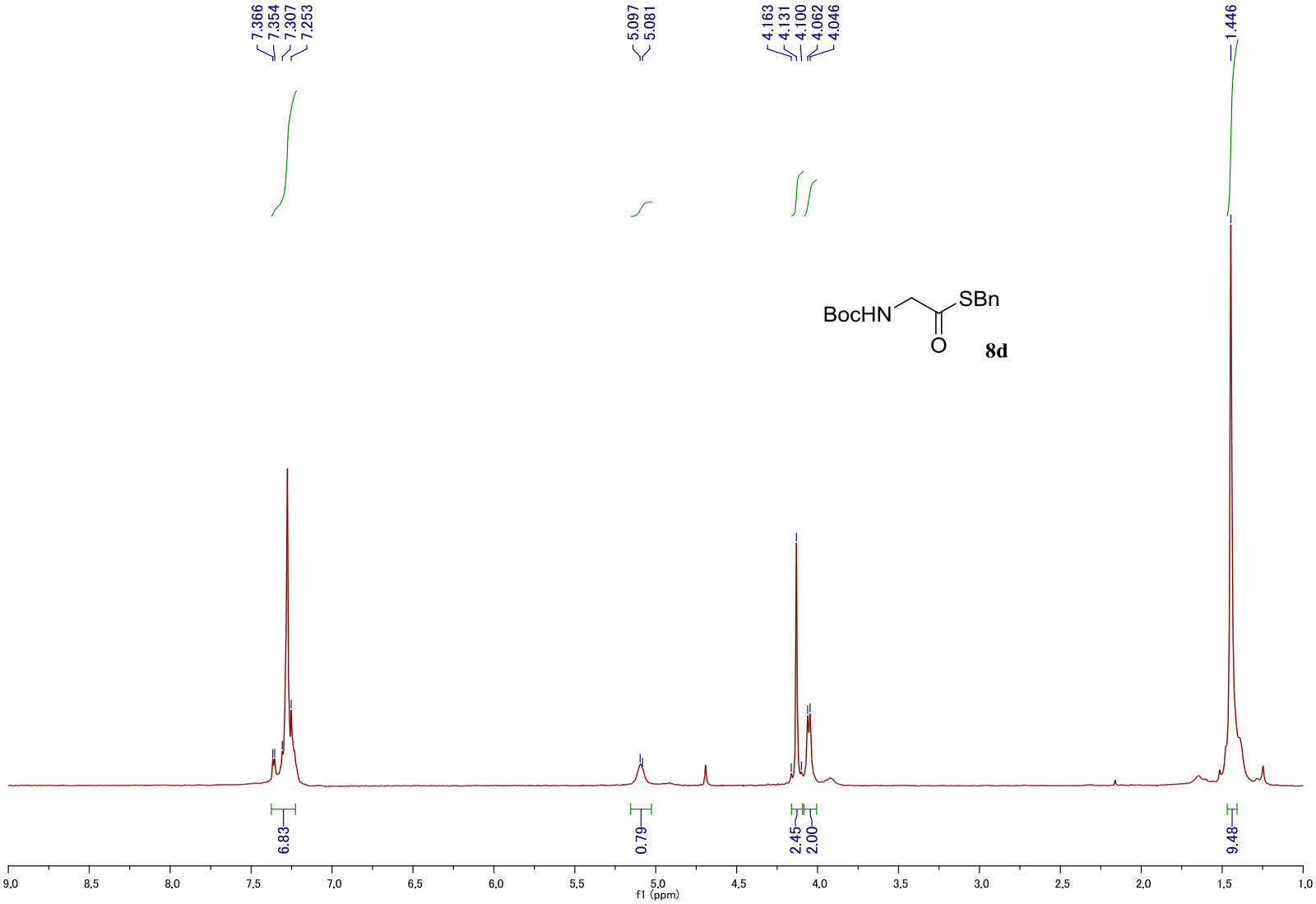
_S_-Benzyl _N-tert_-butoxycarbonyl-L-thiophenylalaninate (8c) ^{1}H NMR (400 MHz, $CDCl_3$)



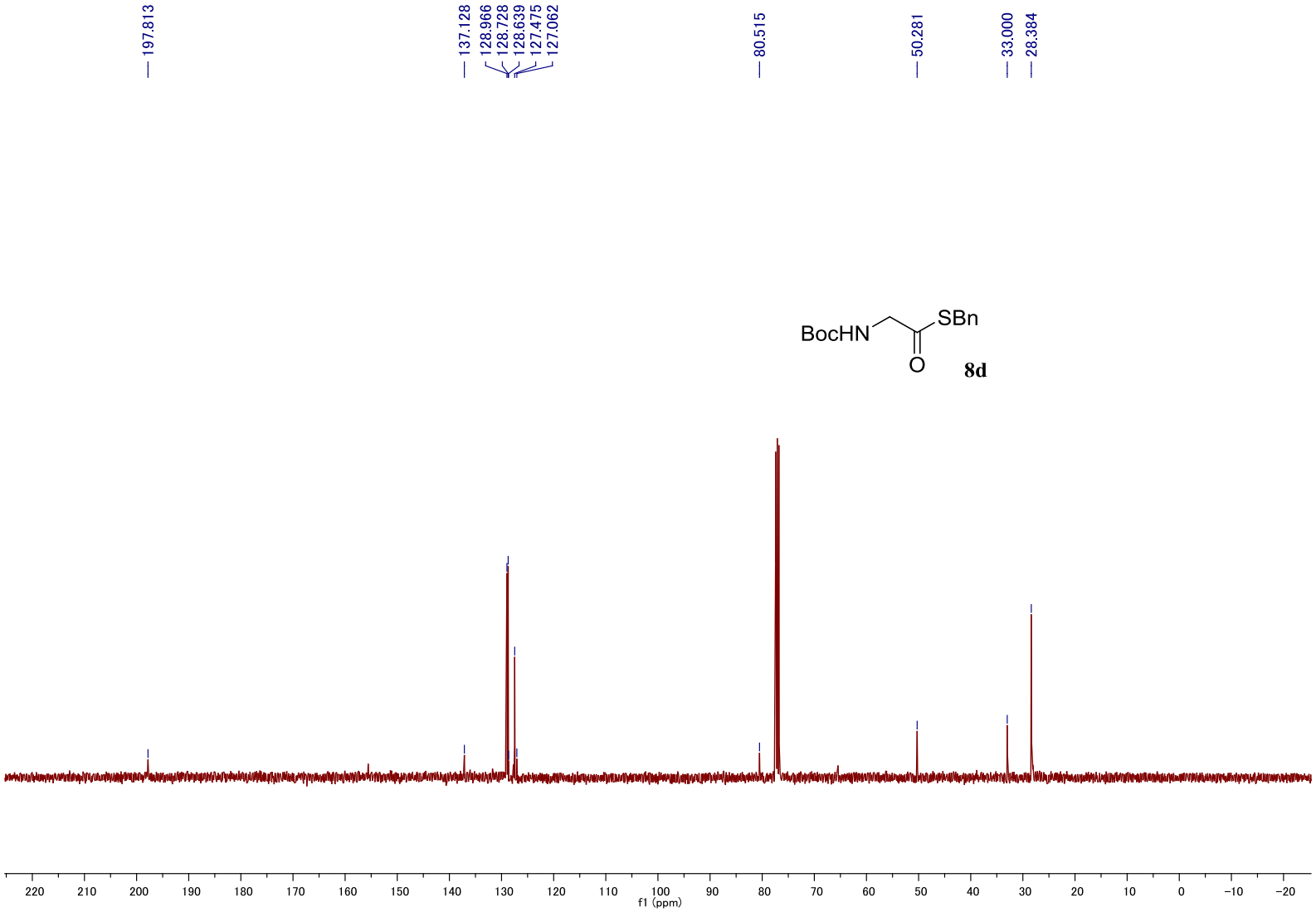
S-Benzyl *N-tert*-butoxycarbonyl-L-thiophenylalaninate (8c) ^{13}C NMR (100 MHz, $CDCl_3$)



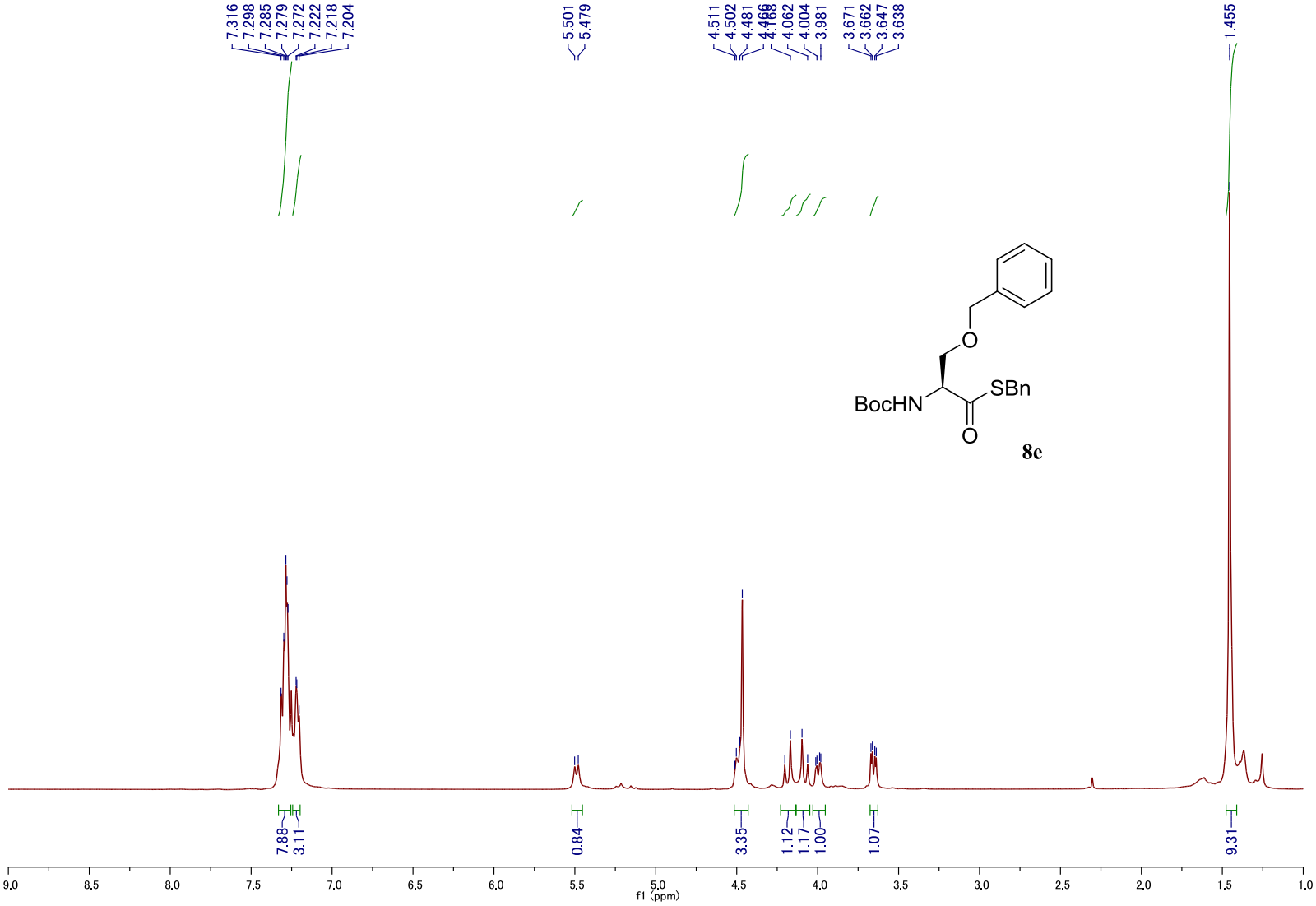
_S_-Benzyl _N-tert_-butoxycarbonylthioglycinate (8d) ^{1}H NMR (400 MHz, $CDCl_3$)



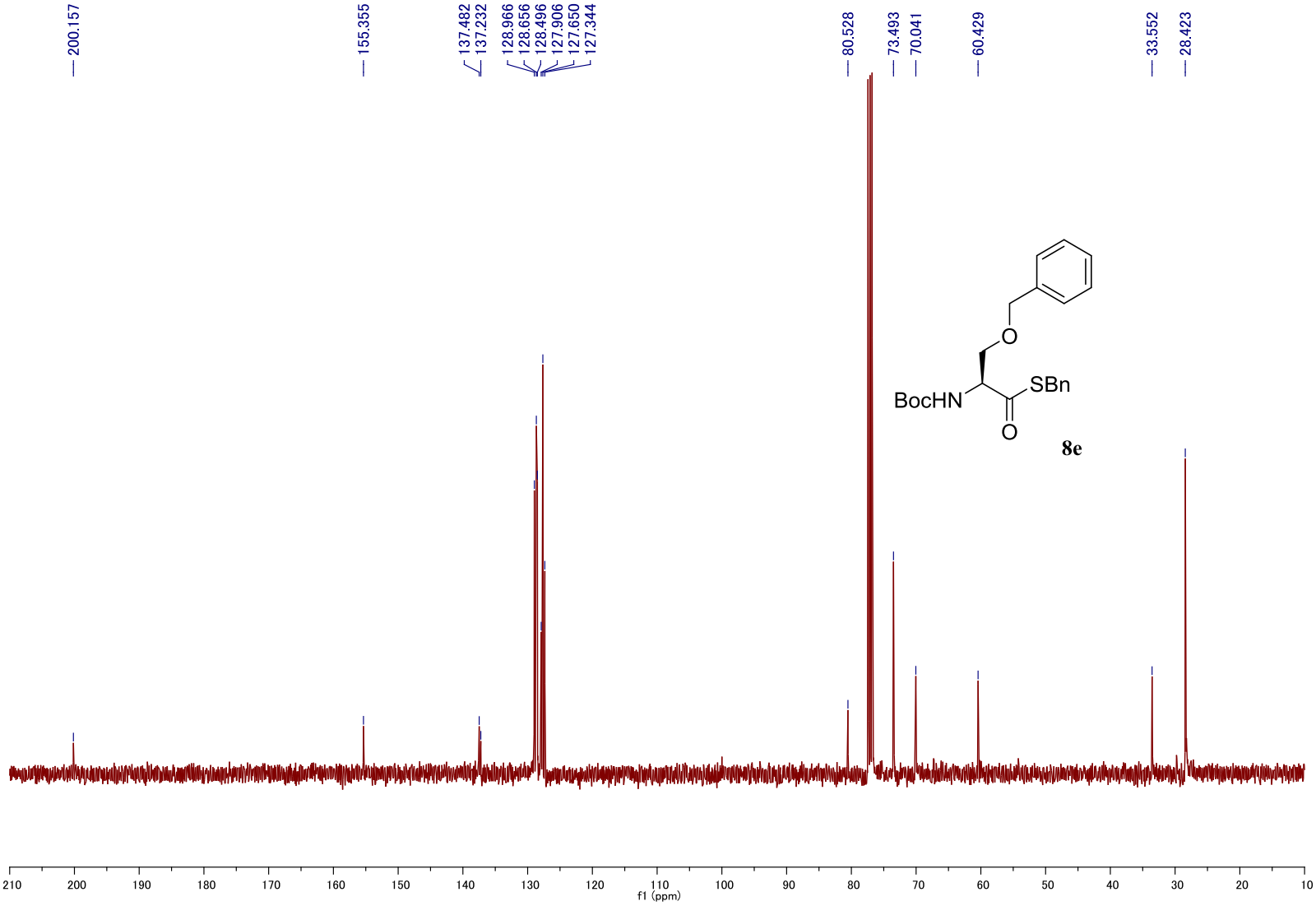
_S_-Benzyl _N-tert_-butoxycarbonylthioglycinate (8d) ^{13}C NMR (100 MHz, $CDCl_3$)



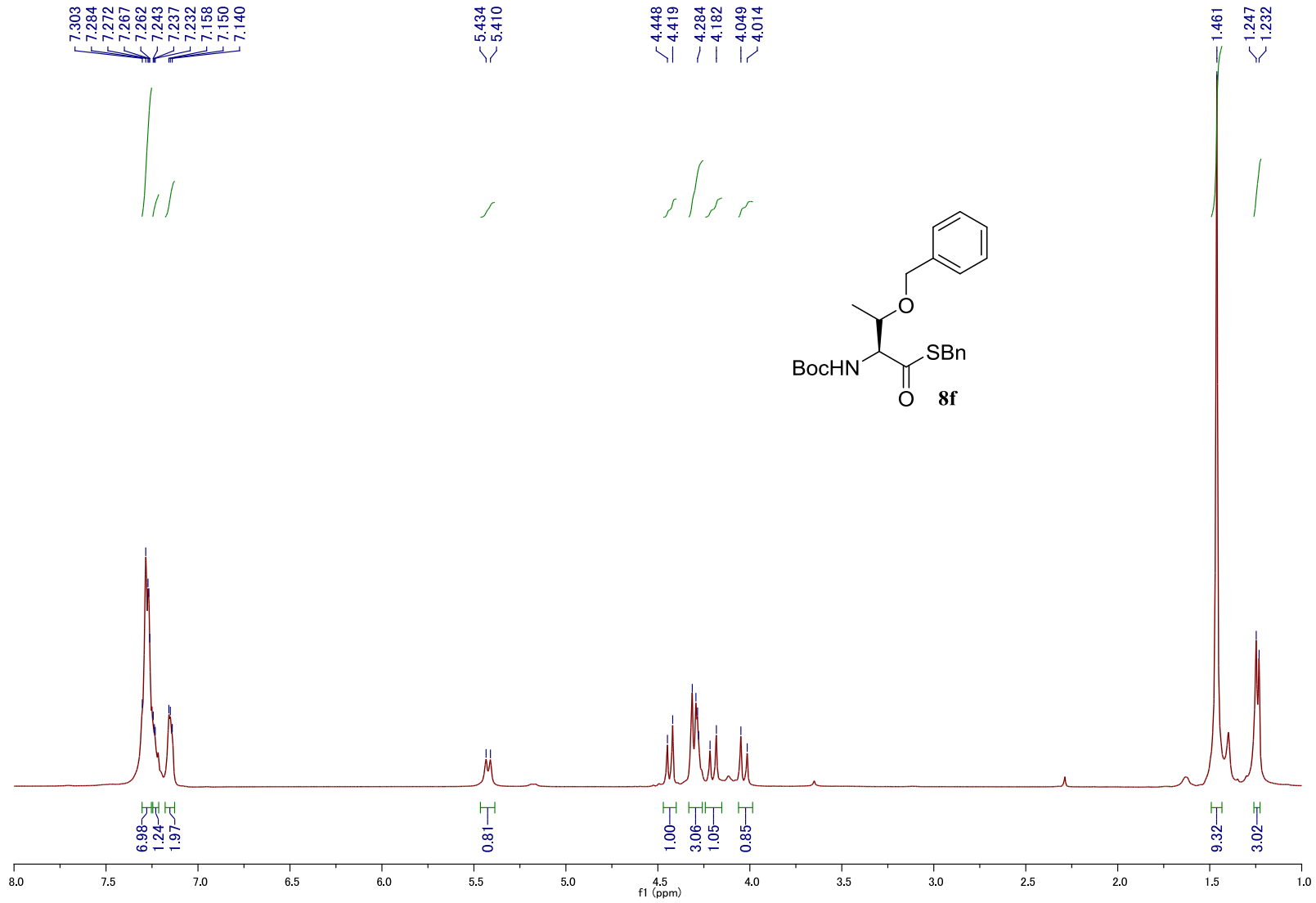
_S_-Benzyl _N-tert_-butoxycarbonyl-_O_-benzyl-L-thioserinate (8e) ^{1}H NMR (400 MHz, $CDCl_3$)



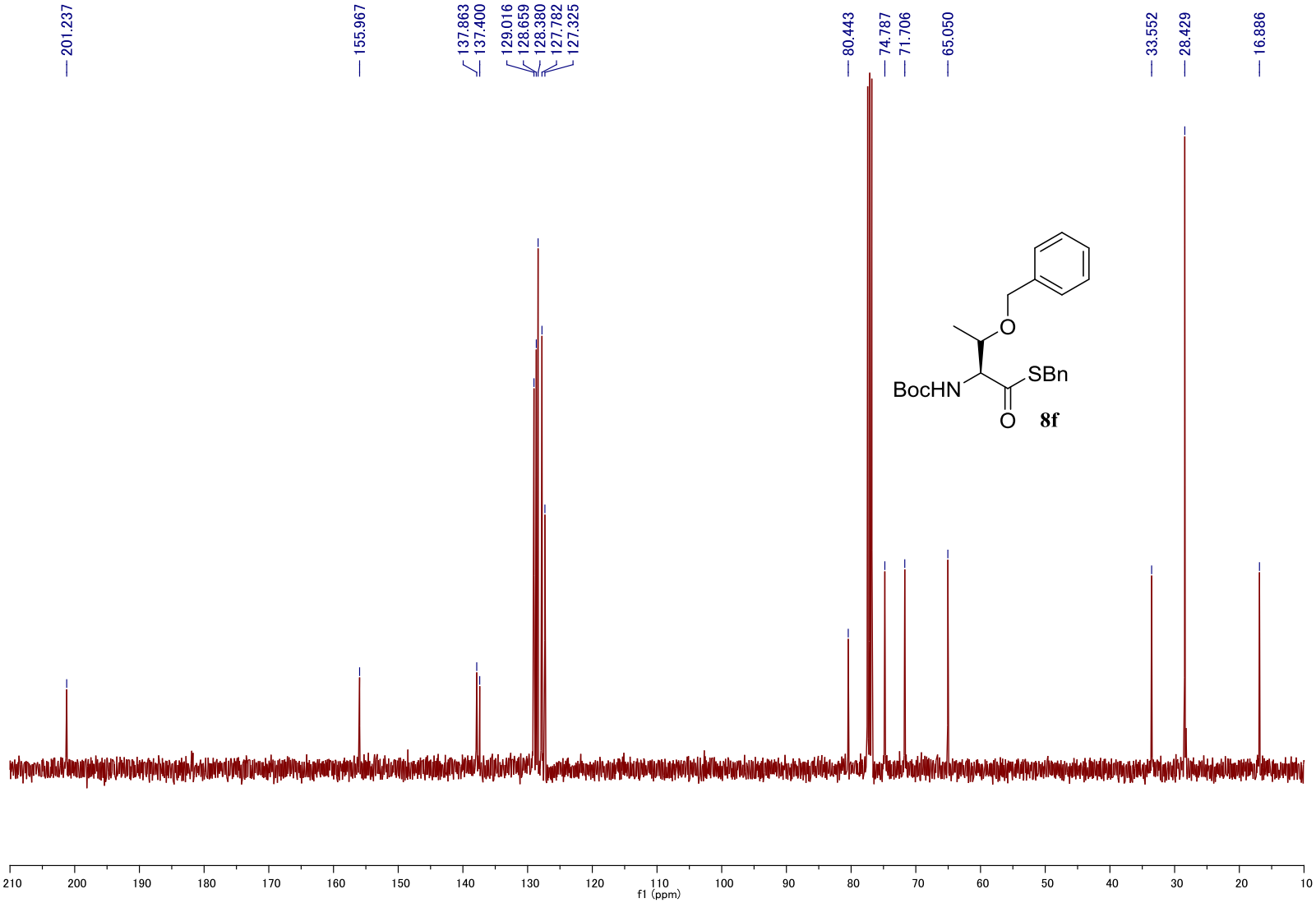
_S_-Benzyl _N-tert_-butoxycarbonyl-_O_-benzyl-L-thioserinate (8e) ^{13}C NMR (100 MHz, $CDCl_3$)



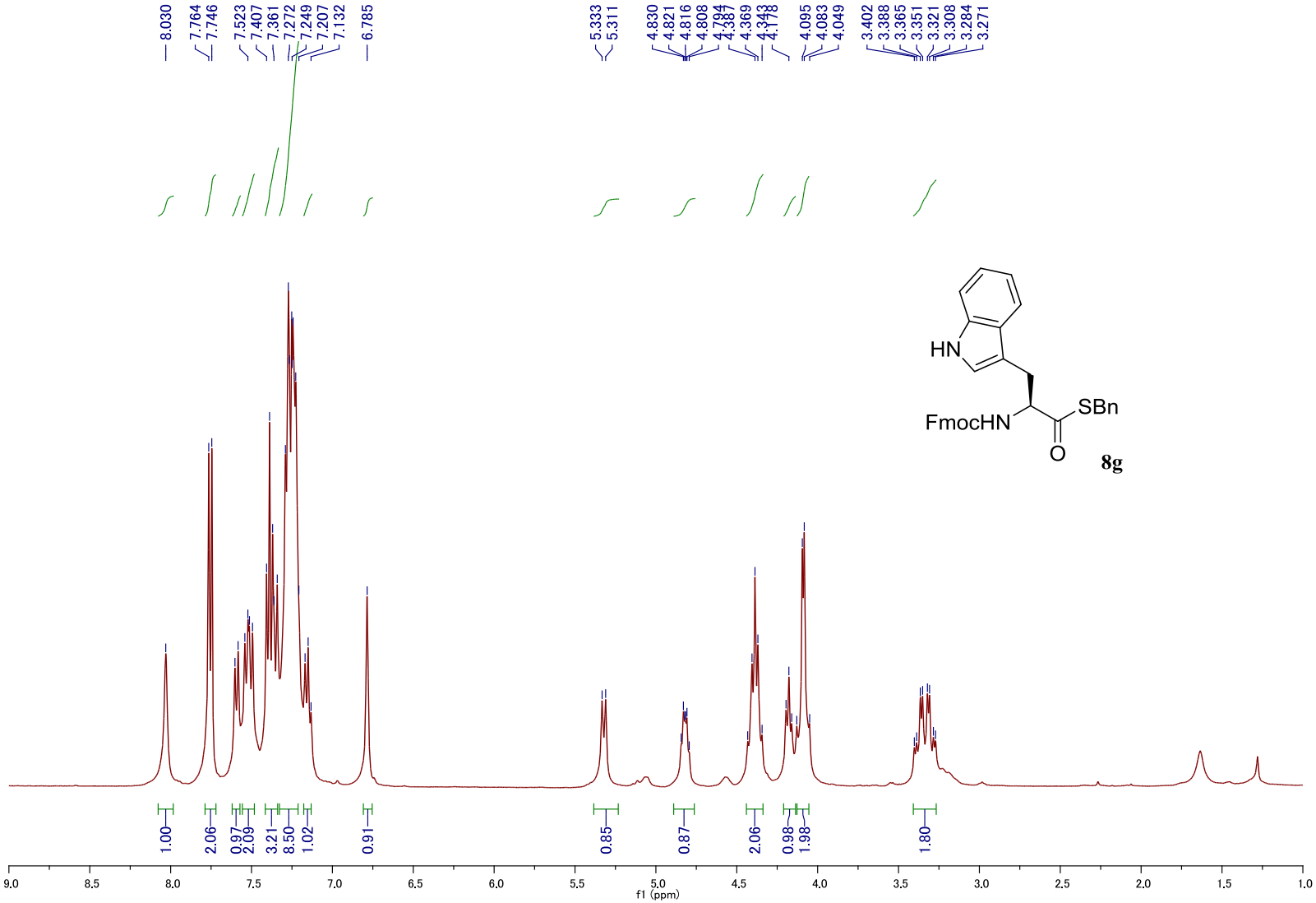
_S_-Benzyl _N-tert_-butoxycarbonyl-_O_-benzyl-L-thiothreonate (8f) ^{1}H NMR (400 MHz, $CDCl_3$)



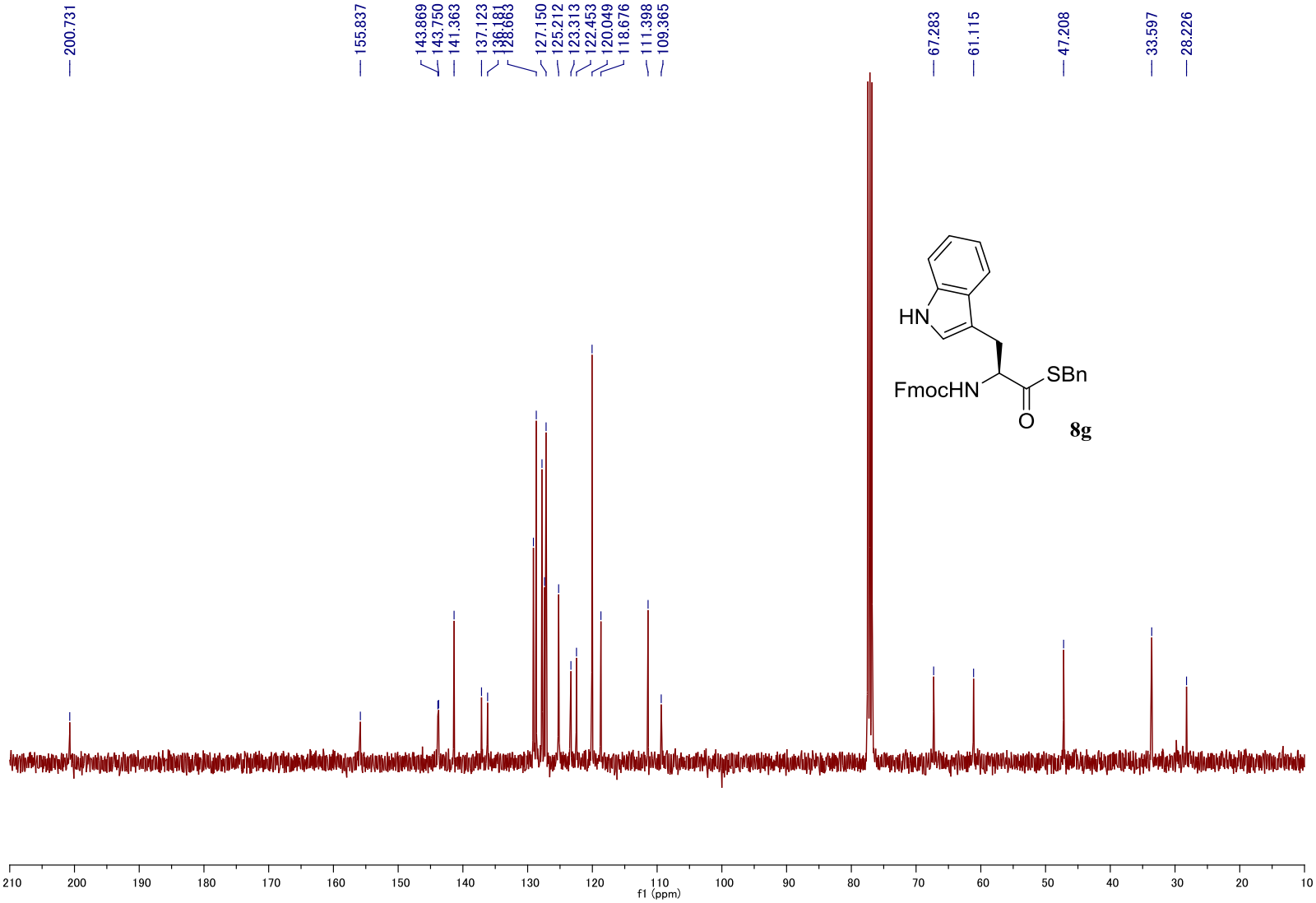
S-Benzyl *N-tert*-butoxycarbonyl-*O*-benzyl-L-thiothreonate (8f) ^{13}C NMR (100 MHz, $CDCl_3$)



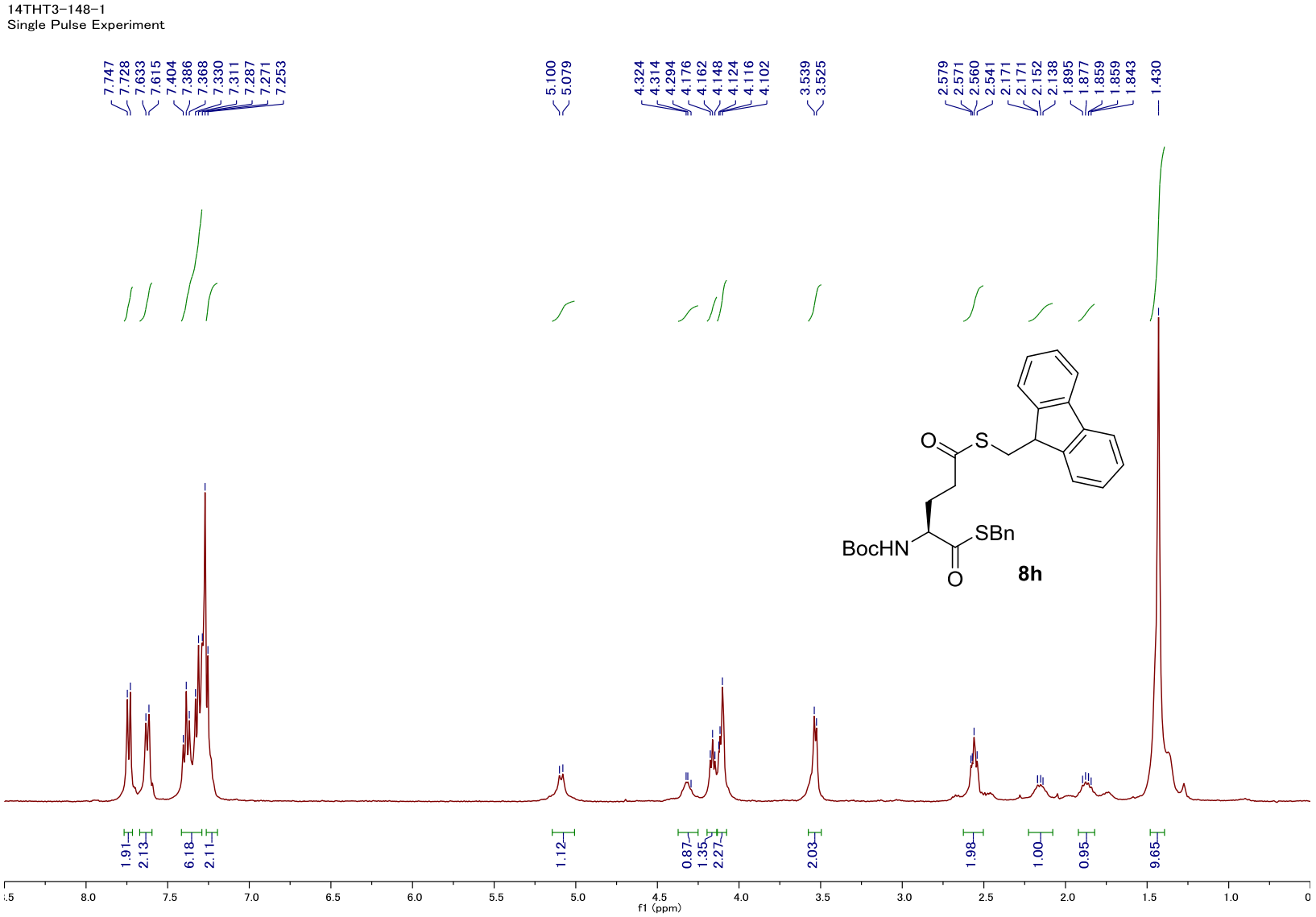
_S_-Benzyl _N_-fluorenylmethyloxycarbonyl-L-thiotryptophanate (8g) ^{1}H NMR (400 MHz, $CDCl_3$)



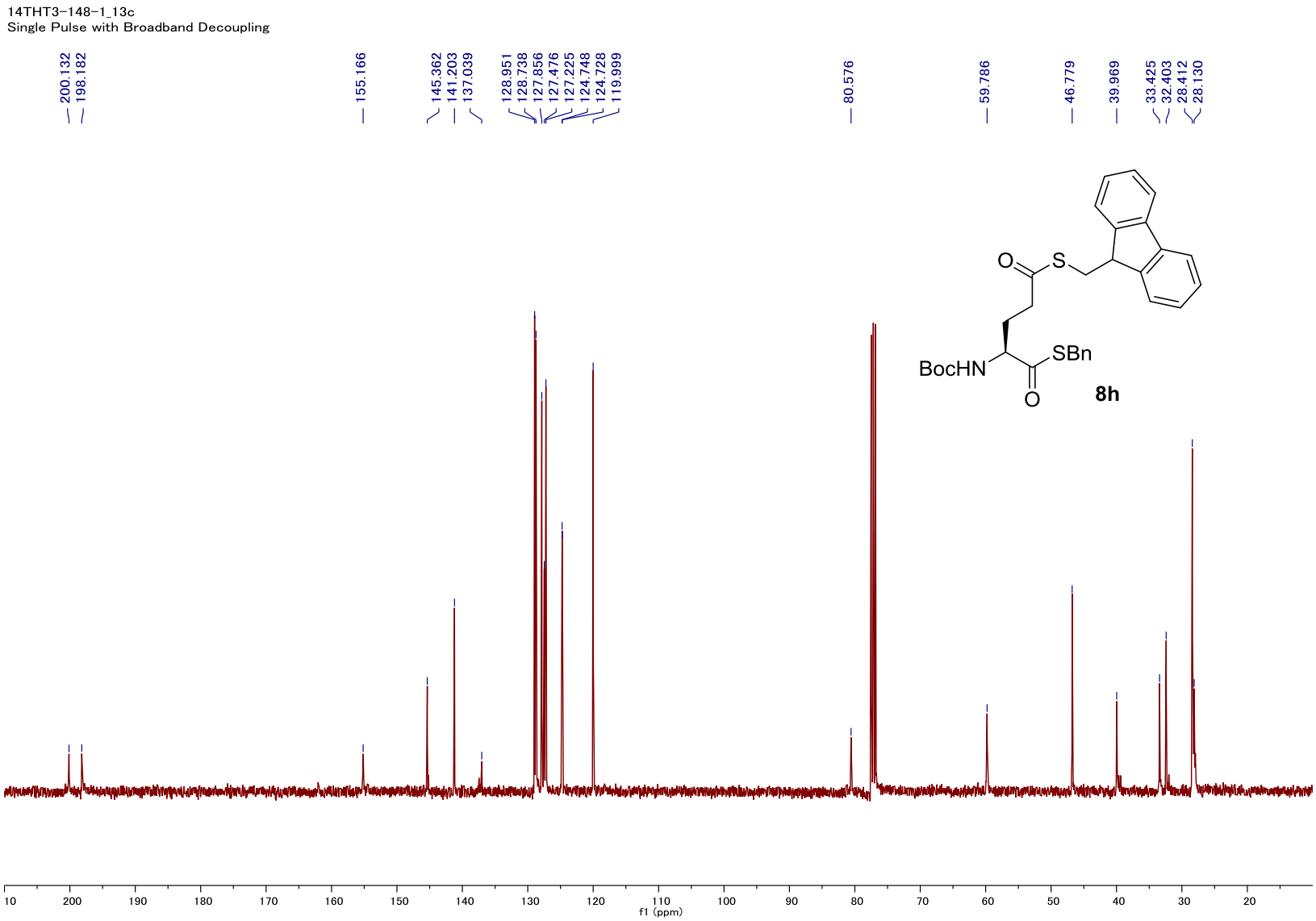
_S_-Benzyl _N_-fluorenylmethyloxycarbonyl-L-thiotryptophanate (8g) ^{13}C NMR (100 MHz, $CDCl_3$)



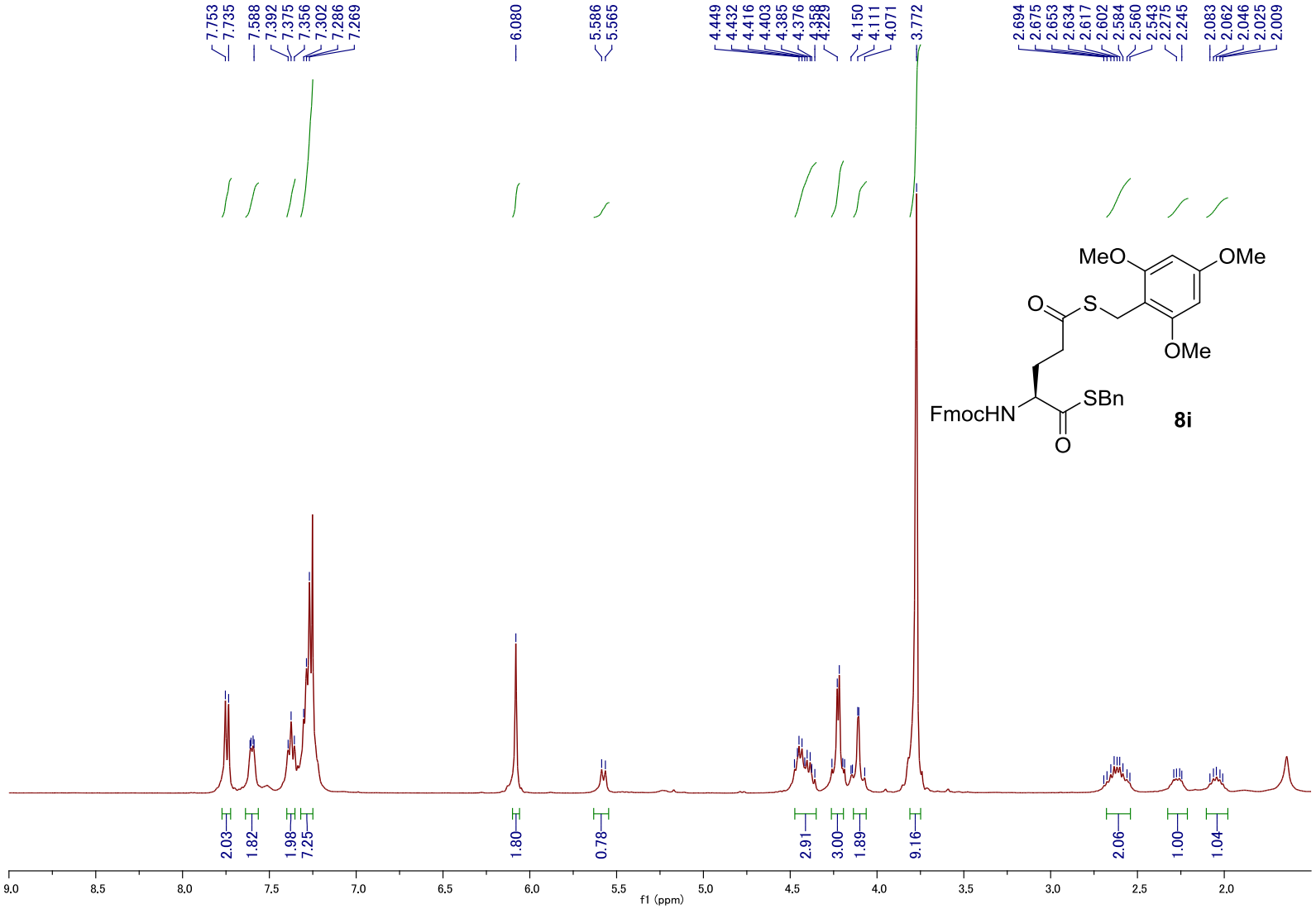
S^{α}-Benzyl S^{γ}-9-fluorenylmethyl *N*-*tert*-butoxycarbonyl-L-dithioglutamate (8h) ^{1}H NMR (400 MHz, $CDCl_3$)



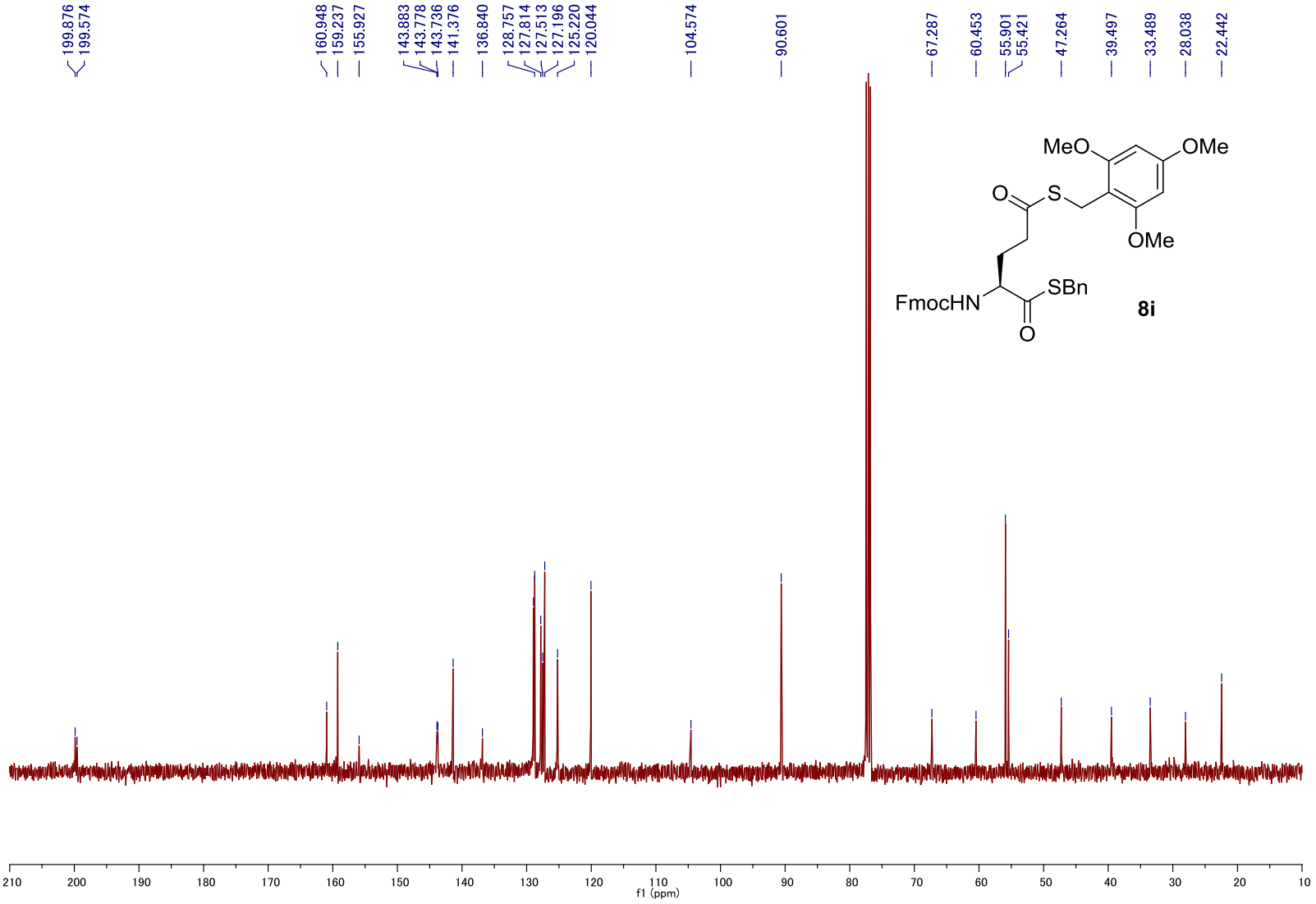
S^{α}-Benzyl S^{γ}-9-fluorenylmethyl *N-tert*-butoxycarbonyl-L-dithioglutamate (8h) ^{13}C NMR (100 MHz, $CDCl_3$)



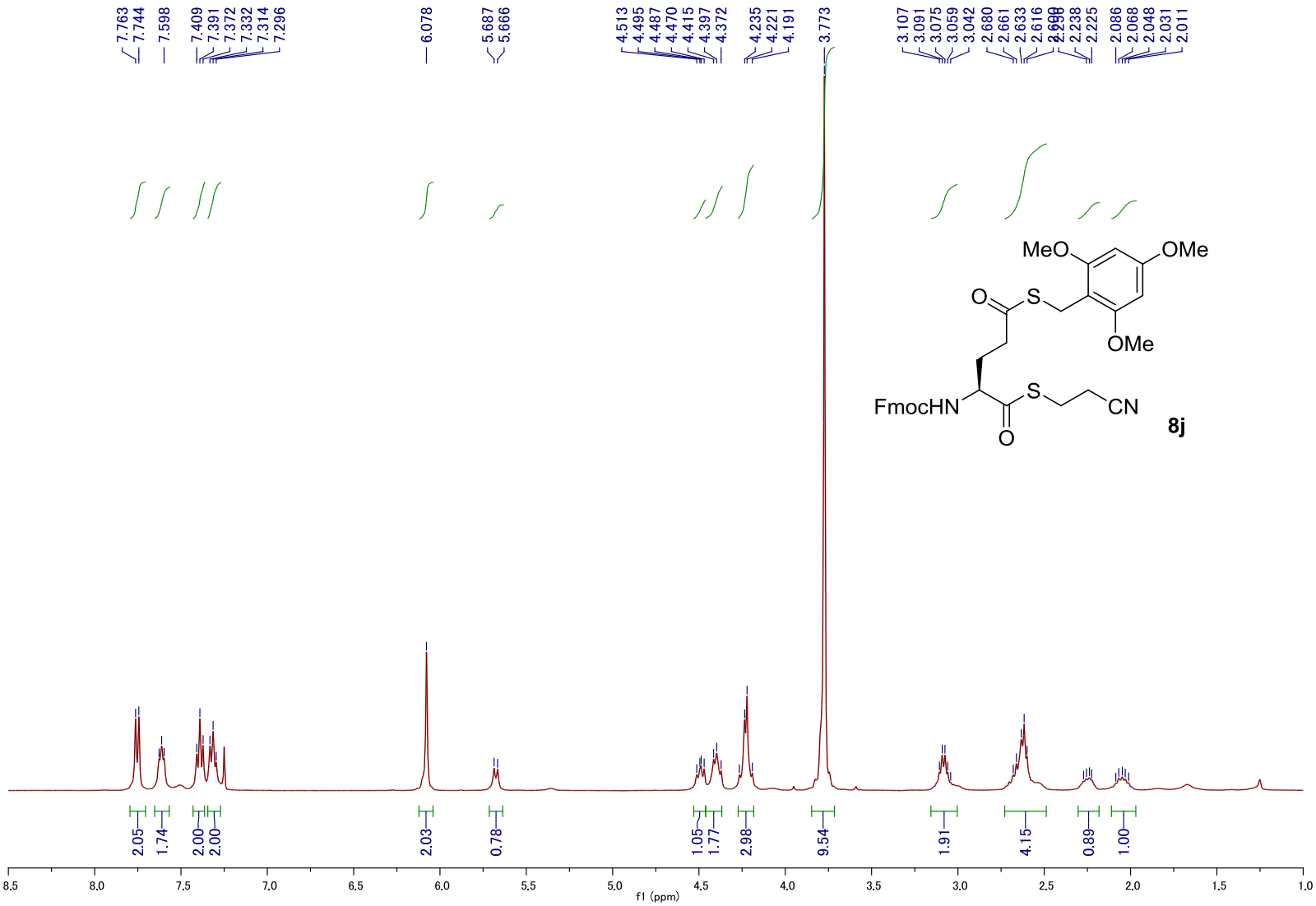
***S*$^{\alpha}$-Benzyl *S*$^{\gamma}$-2,4,6-trimethoxybenzyl *N*-(9-fluorenylmethyloxycarbonyl)-L-dithioglutamate (8i)** ^{1}H NMR (400 MHz, $CDCl_3$)



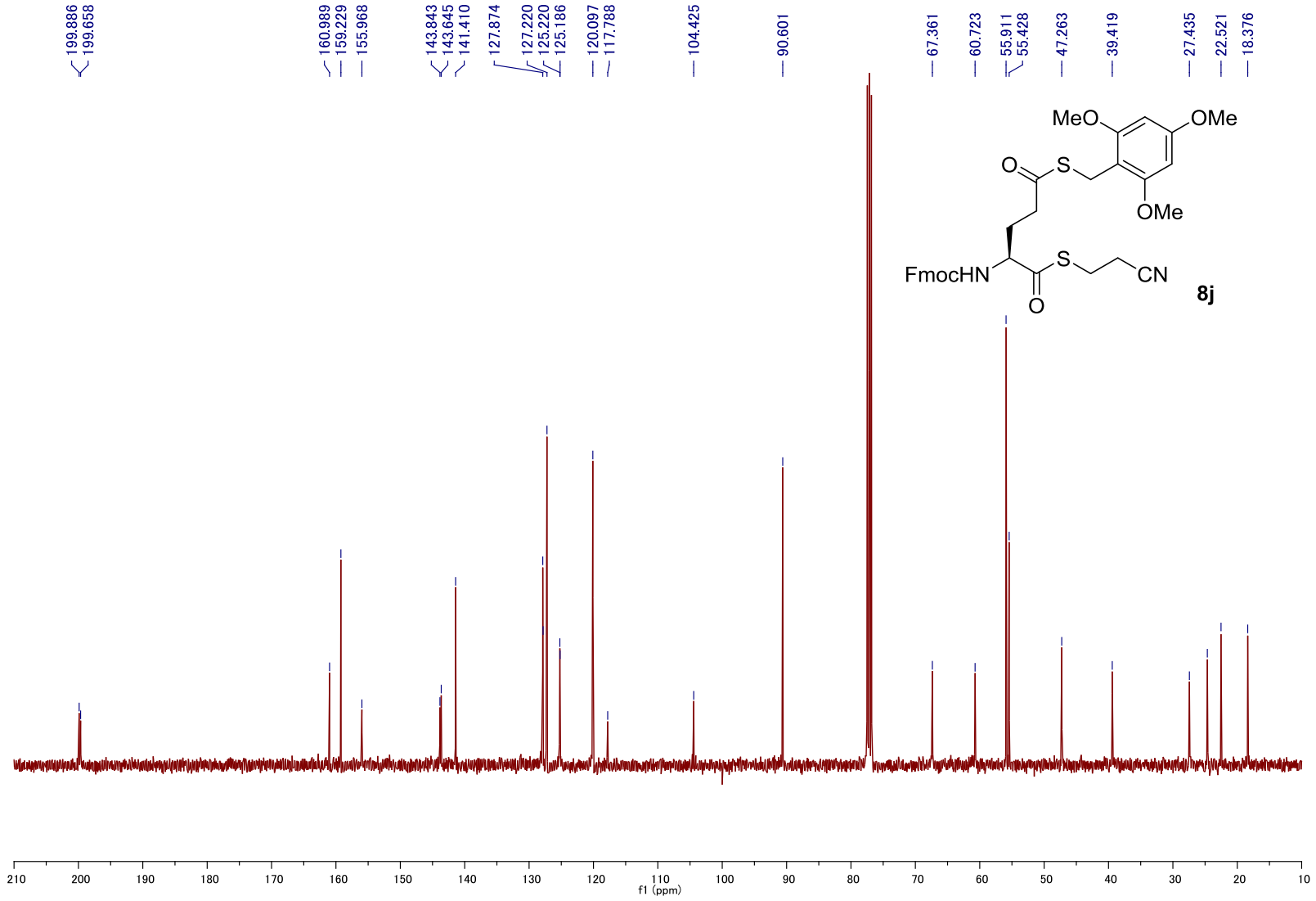
S^{α}-Benzyl S^{γ}-2,4,6-trimethoxybenzyl *N*-(9-fluorenylmethyloxycarbonyl)-L-dithioglutamate (8i) ^{13}C NMR (100 MHz, $CDCl_3$)



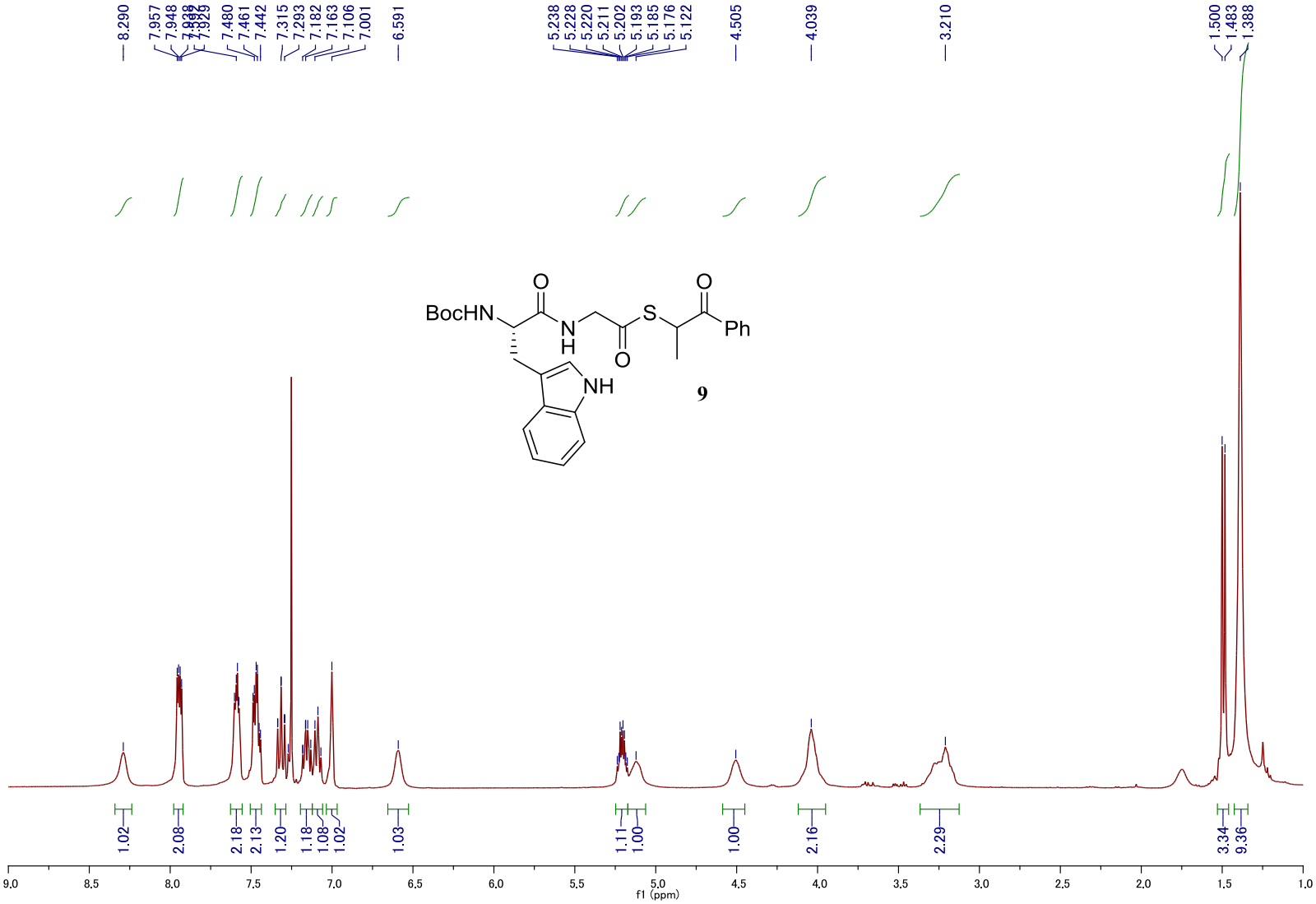
S^{α}-Cyanoethyl S^{γ}-(2,4,6-trimethoxybenzyl) *N*-(9-fluorenylmethyloxycarbonyl)-L-dithioglutamate (8j) ^{1}H NMR (400 MHz, $CDCl_3$)



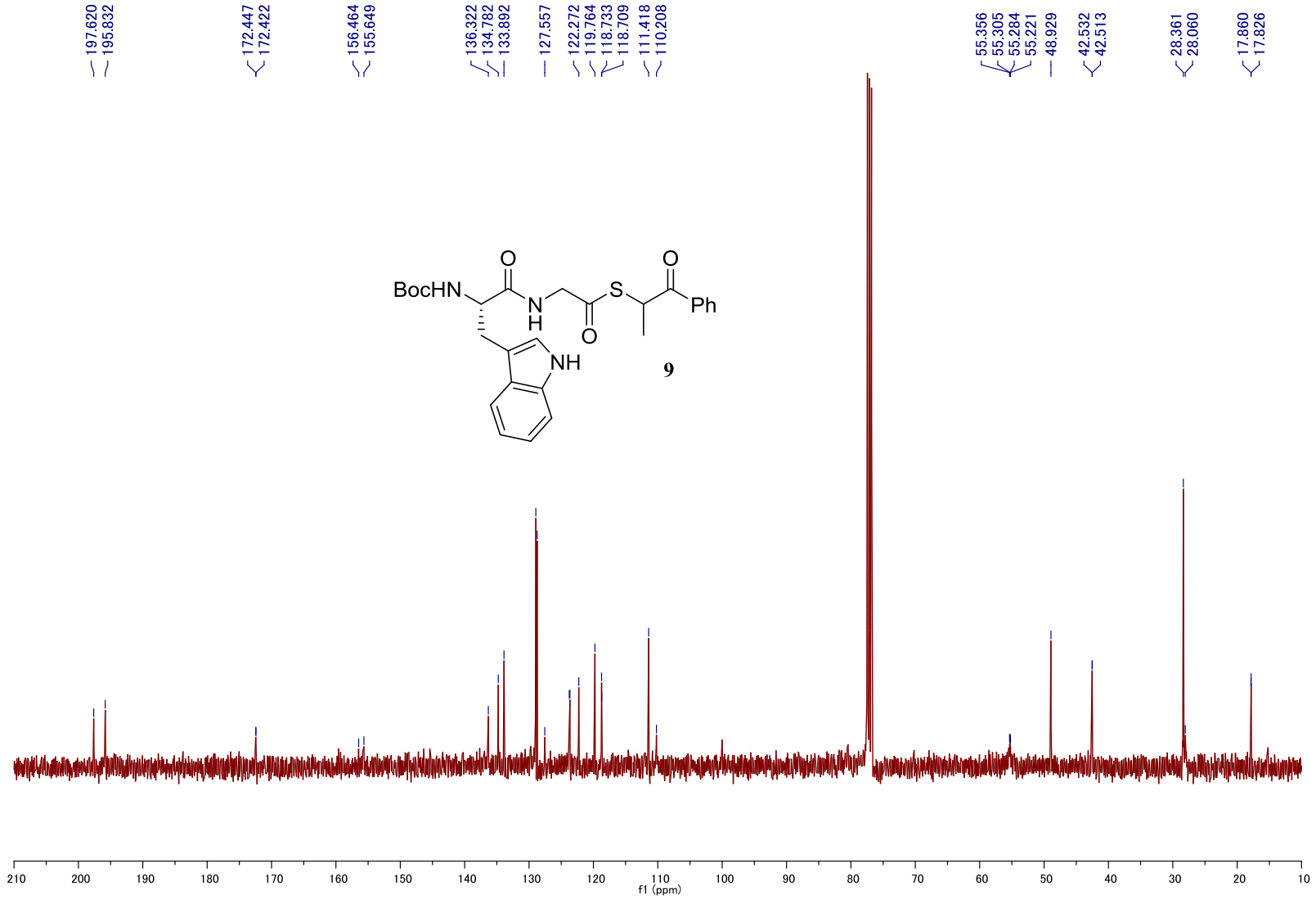
S^{α}-Cyanoethyl S^{γ}-(2,4,6-trimethoxybenzyl) *N*-(9-fluorenylmethyloxycarbonyl)-L-dithioglutamate (8j) ^{13}C NMR (100 MHz, $CDCl_3$)



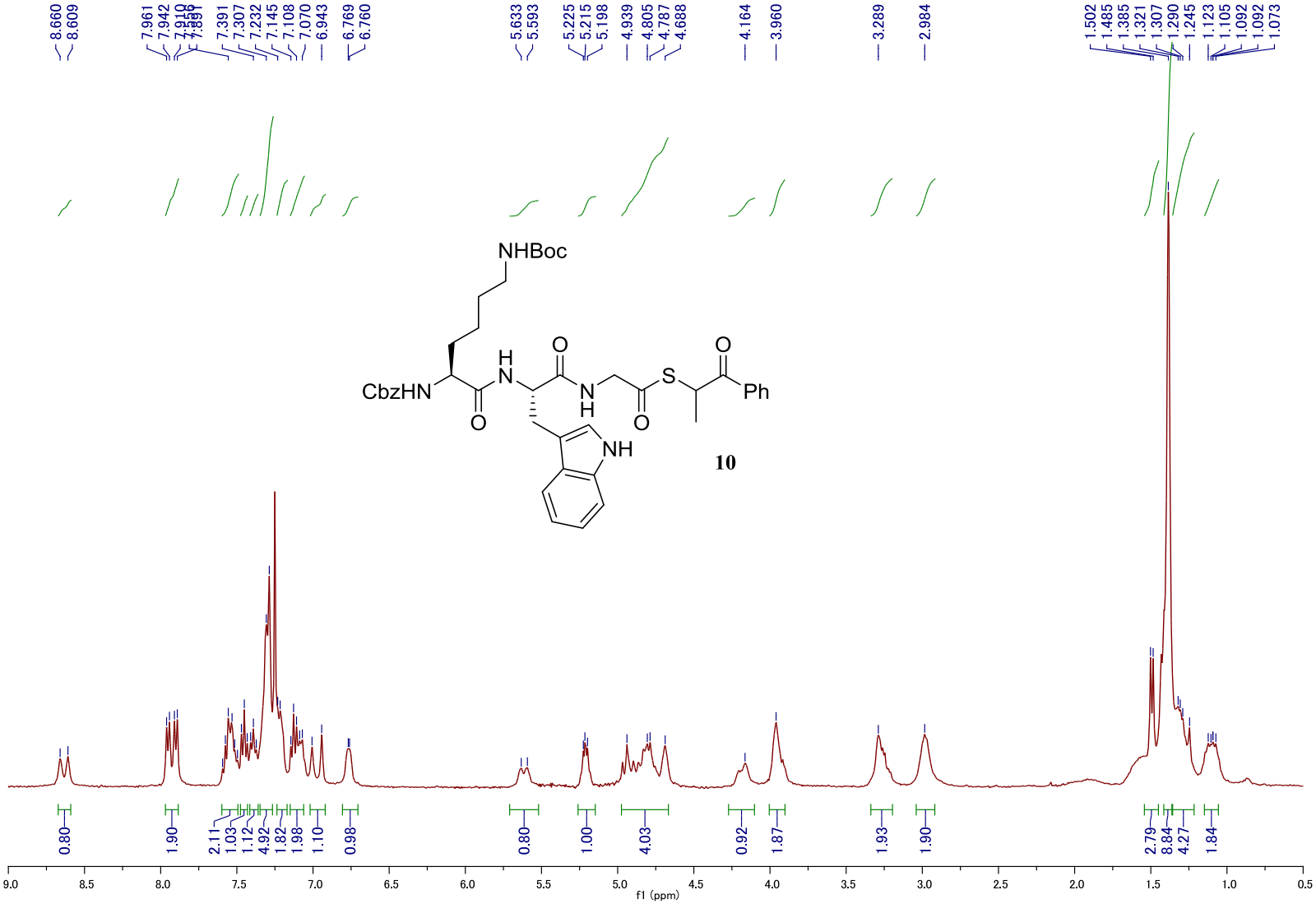
***S*-α-Methylphenacyl *N-tert*-butoxycarbonyl-L-tryptophanylthioglycinate (9)** ^{1}H NMR (400 MHz, $CDCl_3$)



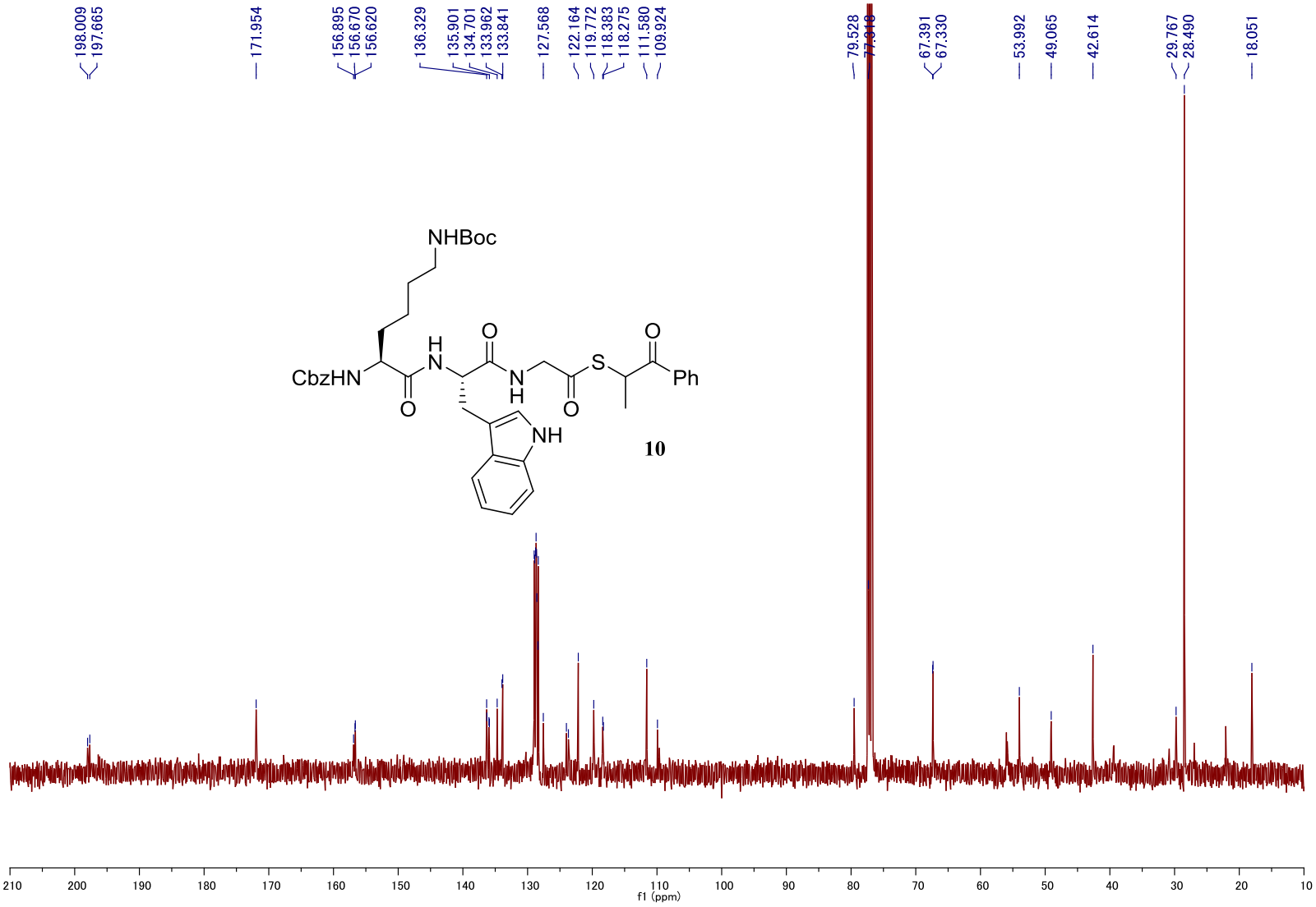
S-α-Methylphenacyl *N-tert*-butoxycarbonyl-L-tryptophanylthioglycinate (9) ^{13}C NMR (100 MHz, $CDCl_3$)



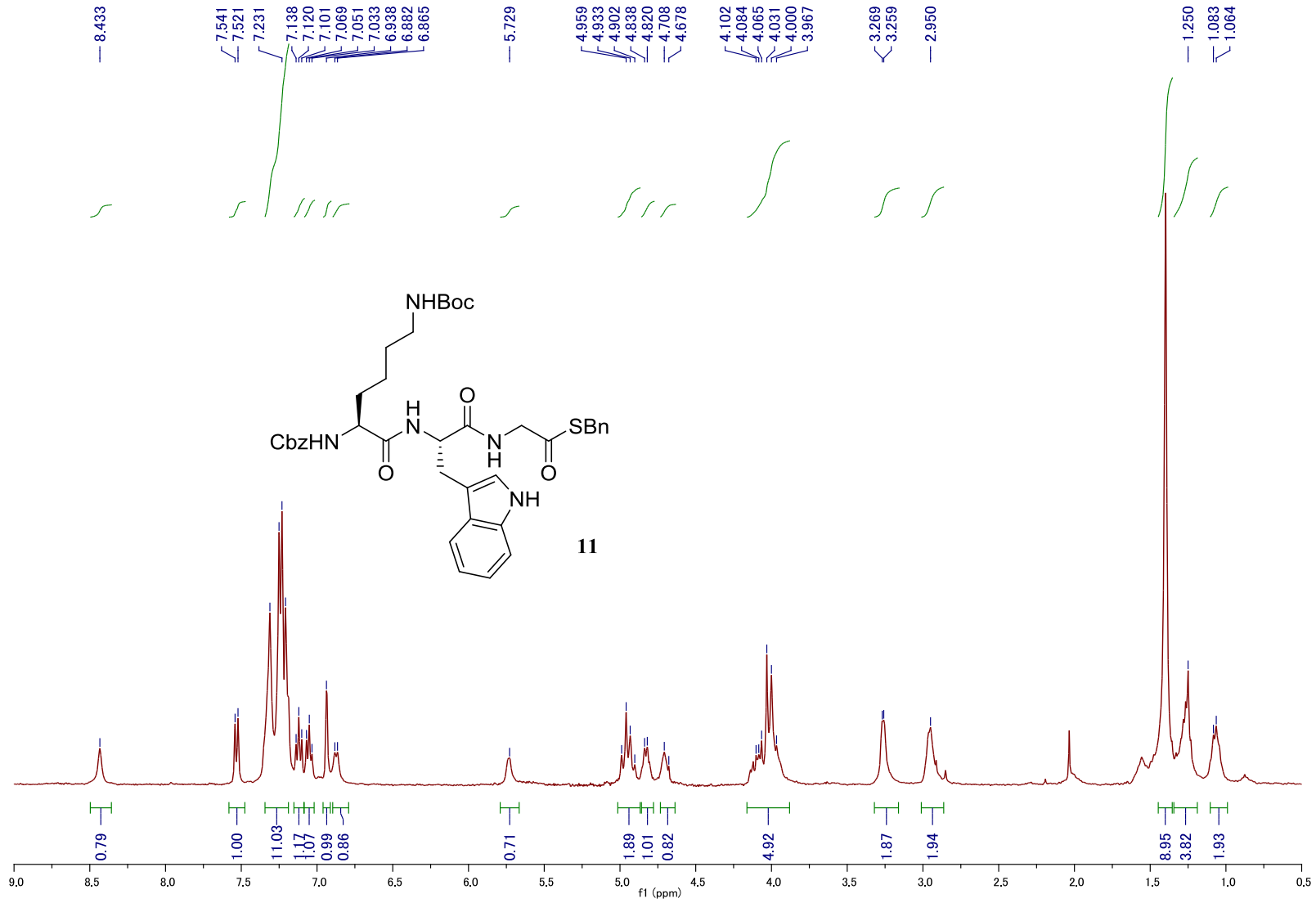
S-α-Methylphenacyl N^{α}-benzyloxycarbonyl-N^{ε}-*tert*-butoxycarbonyl-L-lysyl-L-tryptophanylthioglycinate (10) ^{1}H NMR (400 MHz, $CDCl_3$)



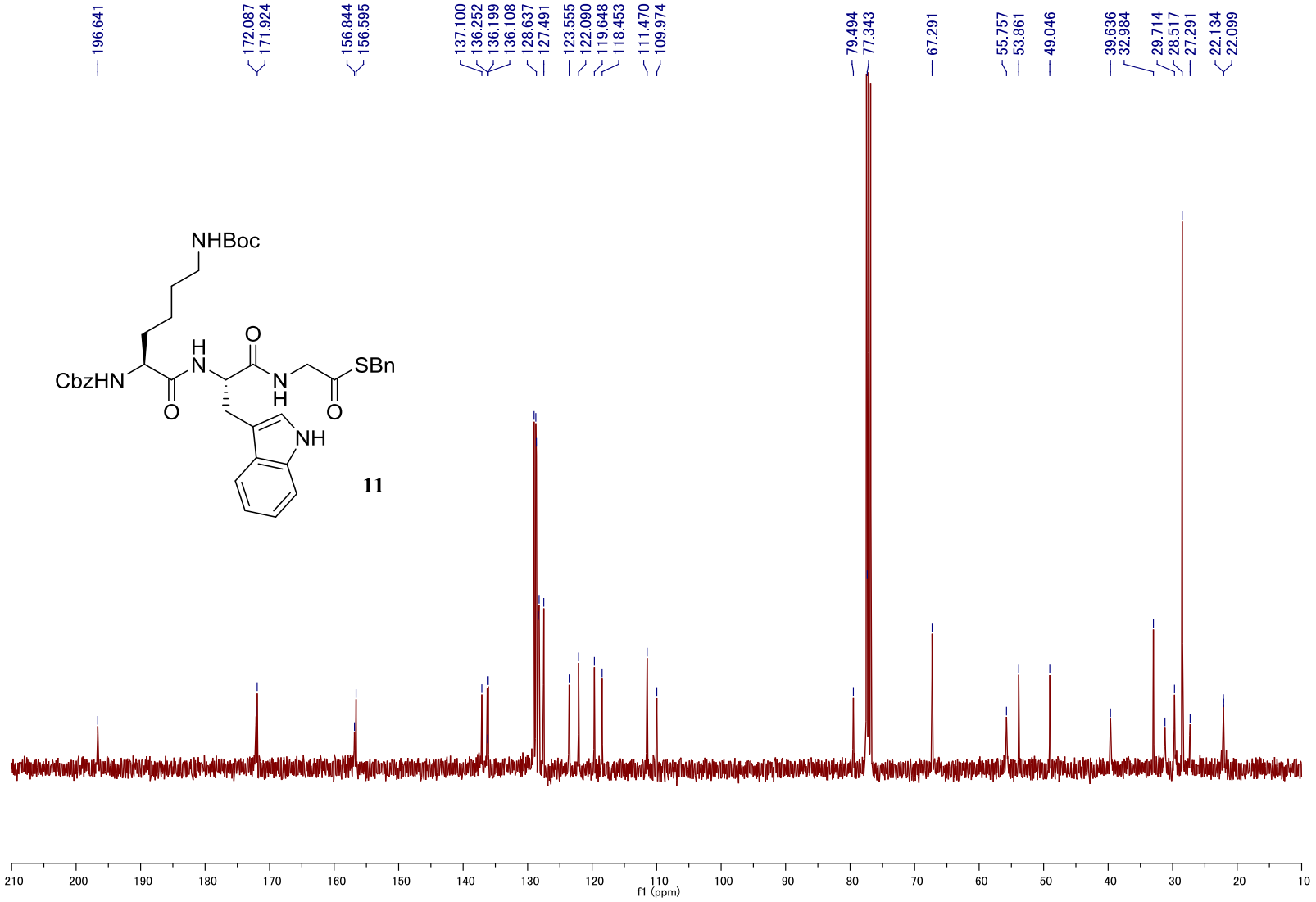
S-α-Methylphenacyl N^{α}-benzyloxycarbonyl-N^{ε}-*tert*-butoxycarbonyl-L-lysyl-L-tryptophanylthioglycinate (10) ^{13}C NMR (100 MHz, $CDCl_3$)



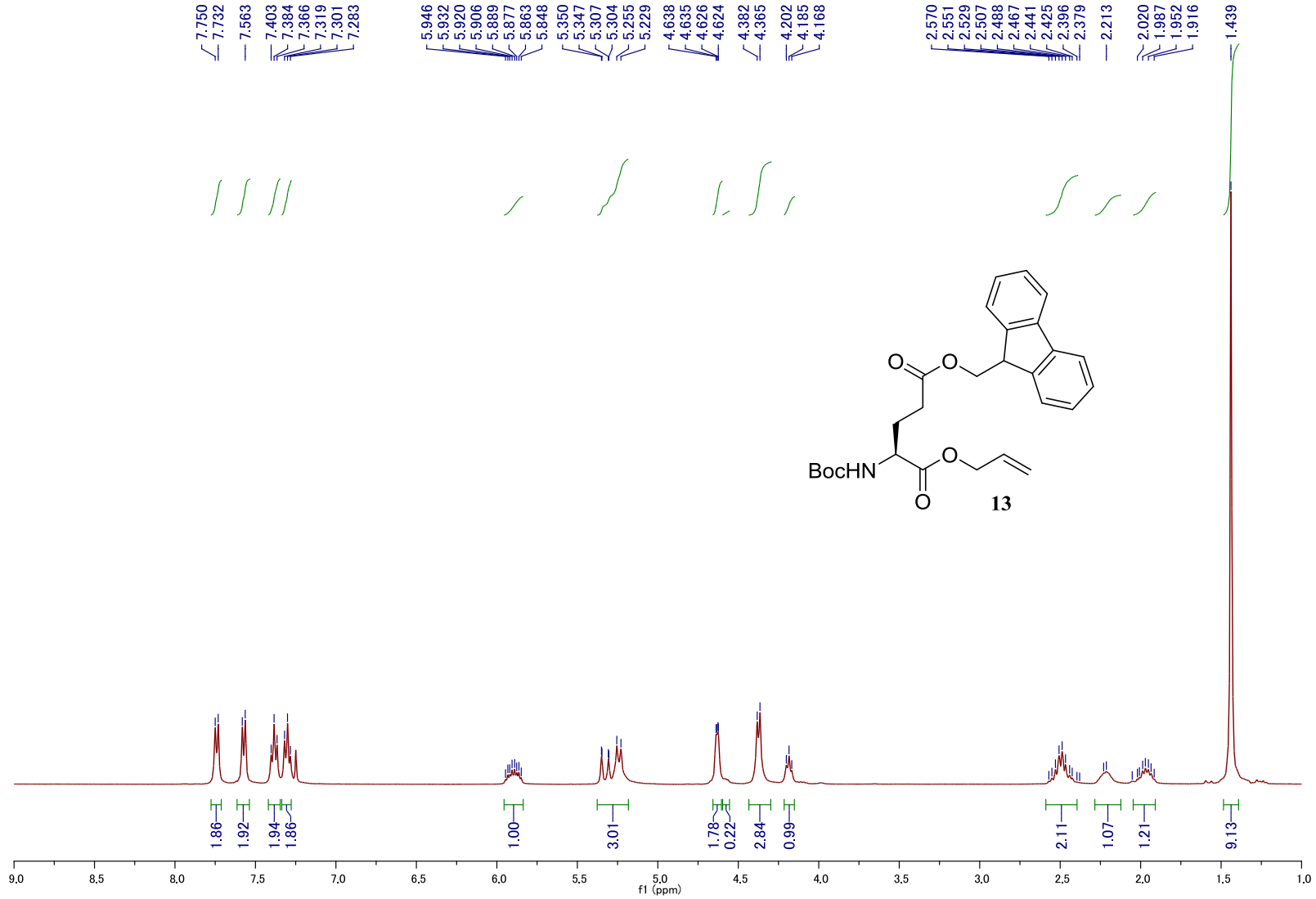
S-BenzylN^{α}-benzyloxycarbonyl-N^{ε}-*tert*-butoxycarbonyl-L-lysyl-L-tryptophenylthioglycinate (11) ^{1}H NMR (400 MHz, $CDCl_3$)



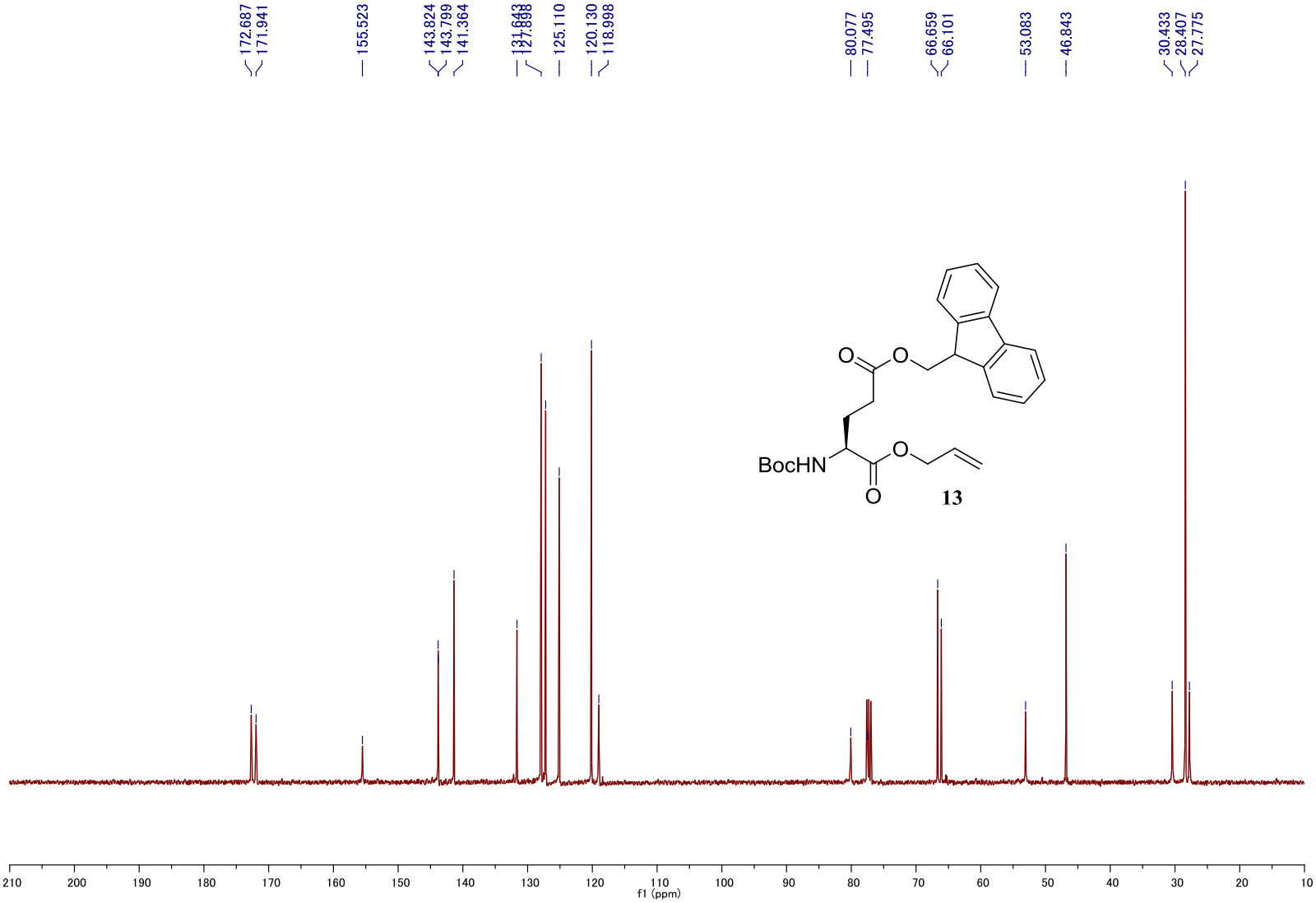
S-BenzylN^{α}-benzyloxycarbonyl-N^{ε}-*tert*-butoxycarbonyl-L-lysyl-L-tryptophenylthioglycinate (11) ^{13}C NMR (100 MHz, $CDCl_3$)



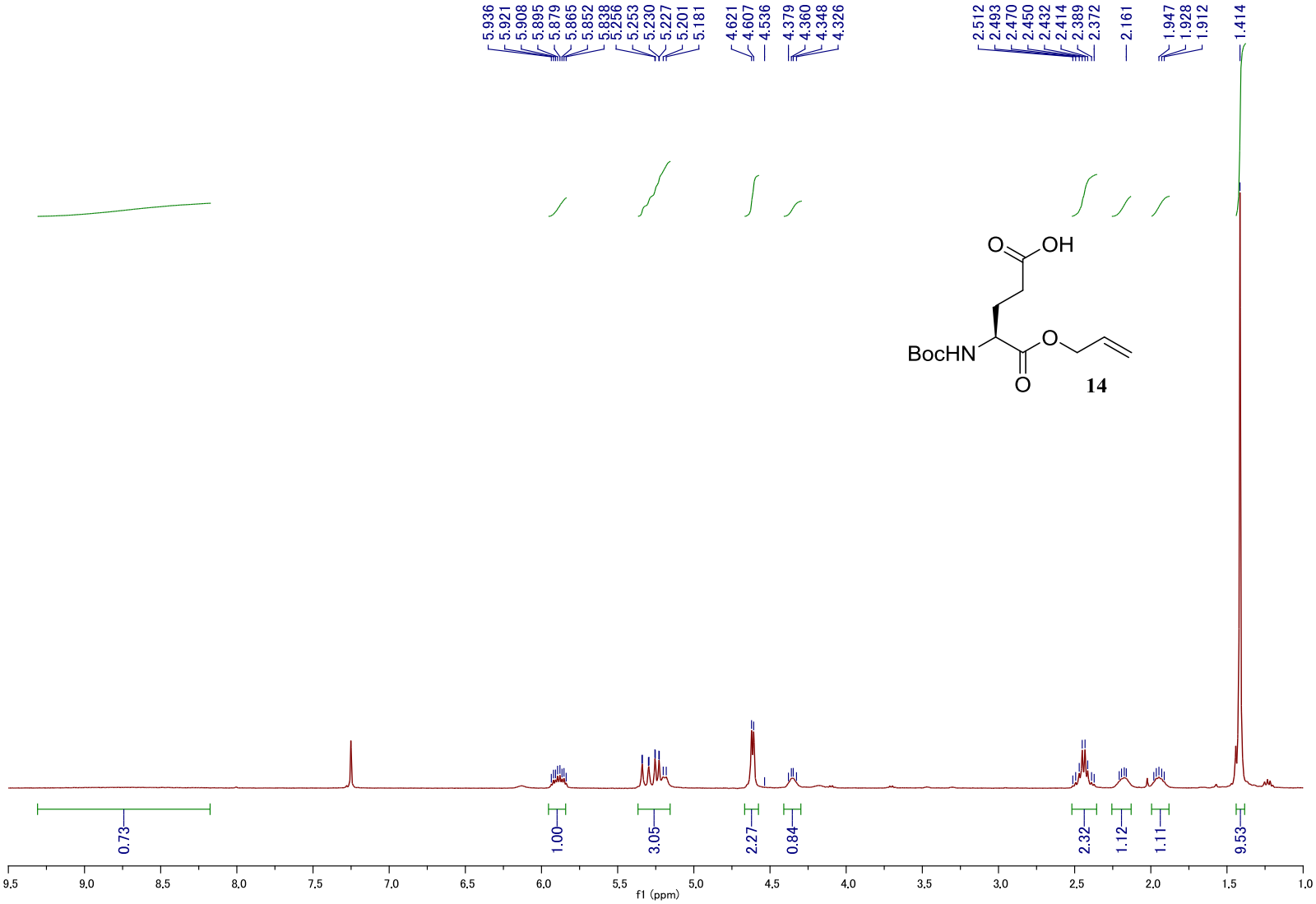
O^{α}-Allyl O^{γ}-(9-fluorenylmethyl) *N*-*tert*-butoxycarbonyl-L-glutamate (13) ^{1}H NMR (400 MHz, $CDCl_3$)



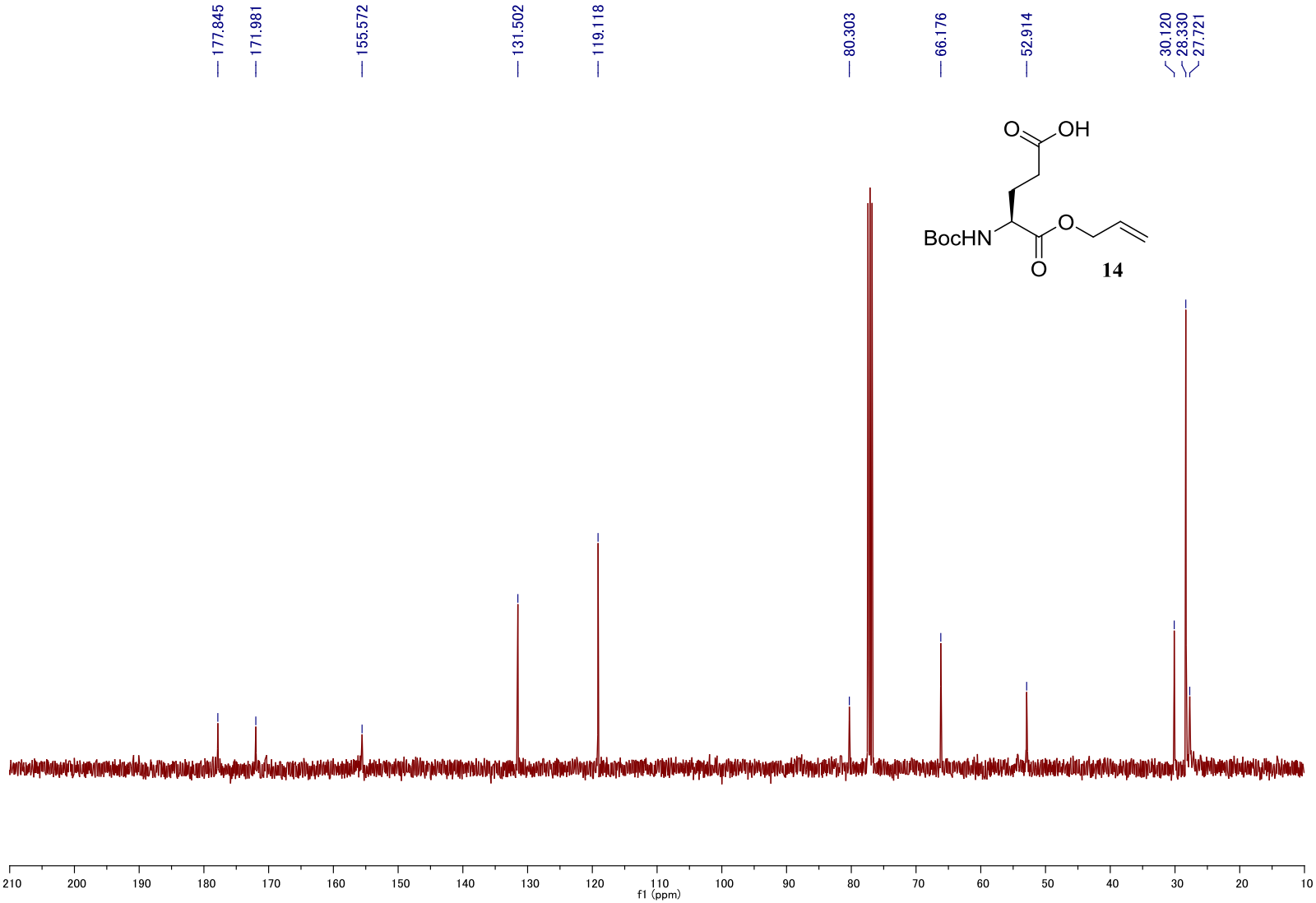
O^{α}-Allyl O^{γ}-(9-fluorenylmethyl) *N*-*tert*-butoxycarbonyl-L-glutamate (13) ^{13}C NMR (100 MHz, $CDCl_3$)



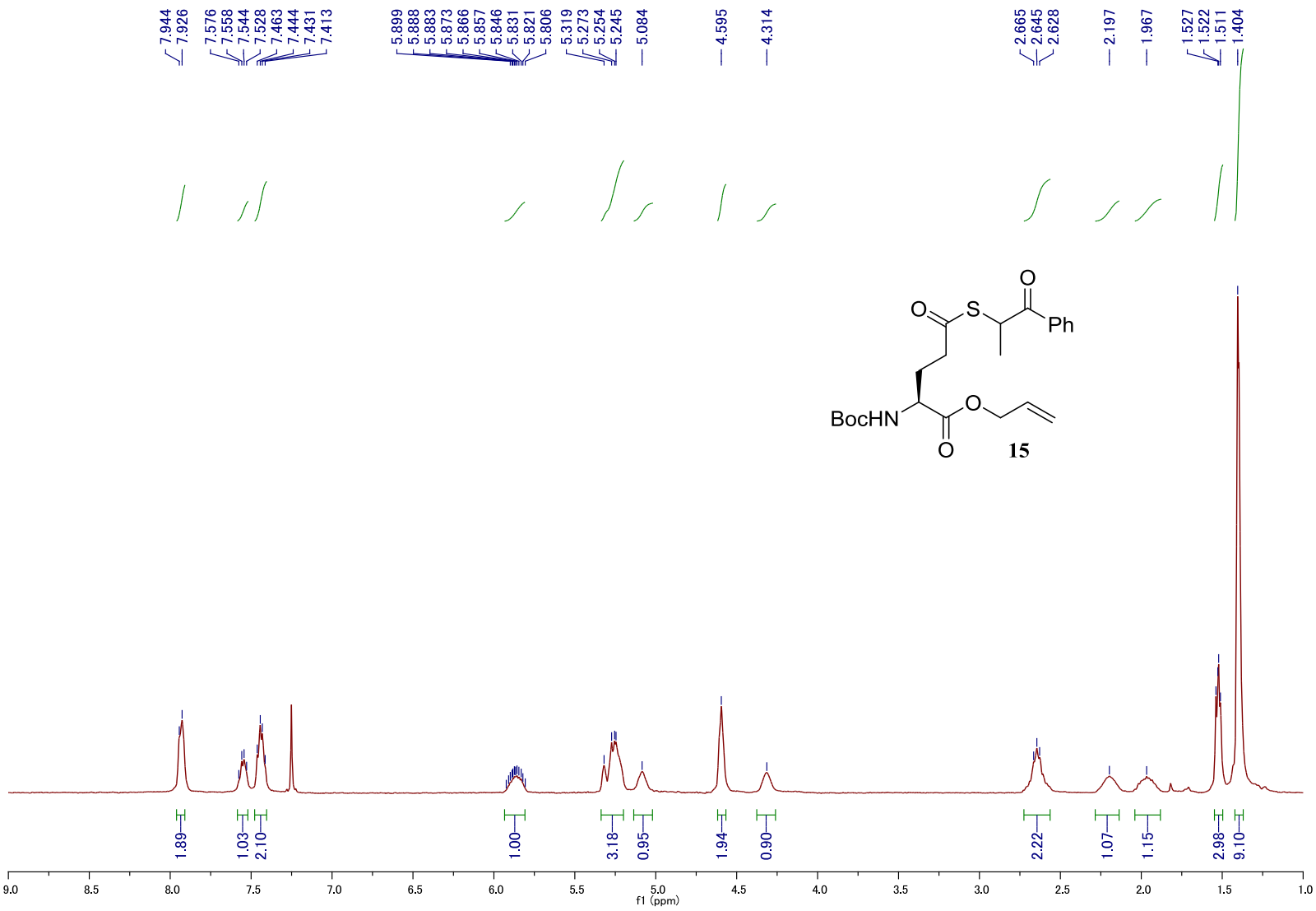
***O*$^{\alpha}$-Allyl *N*-*tert*-butoxycarbonyl-L-glutamic acid (14)** ^{1}H NMR (400 MHz, $CDCl_3$)



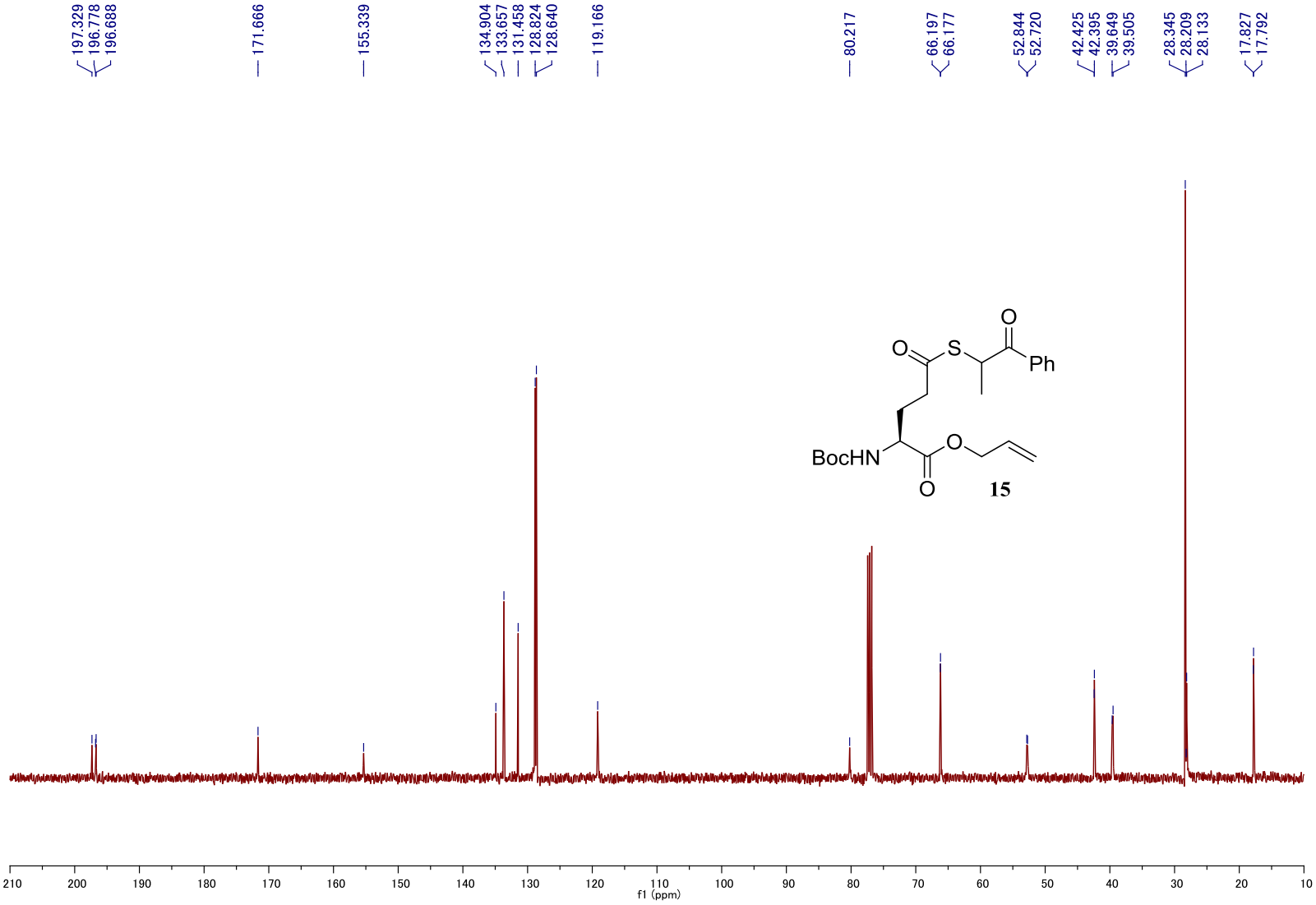
***O*$^{\alpha}$-Allyl *N*-*tert*-butoxycarbonyl-L-glutamic acid (14)** ^{13}C NMR (100 MHz, $CDCl_3$)



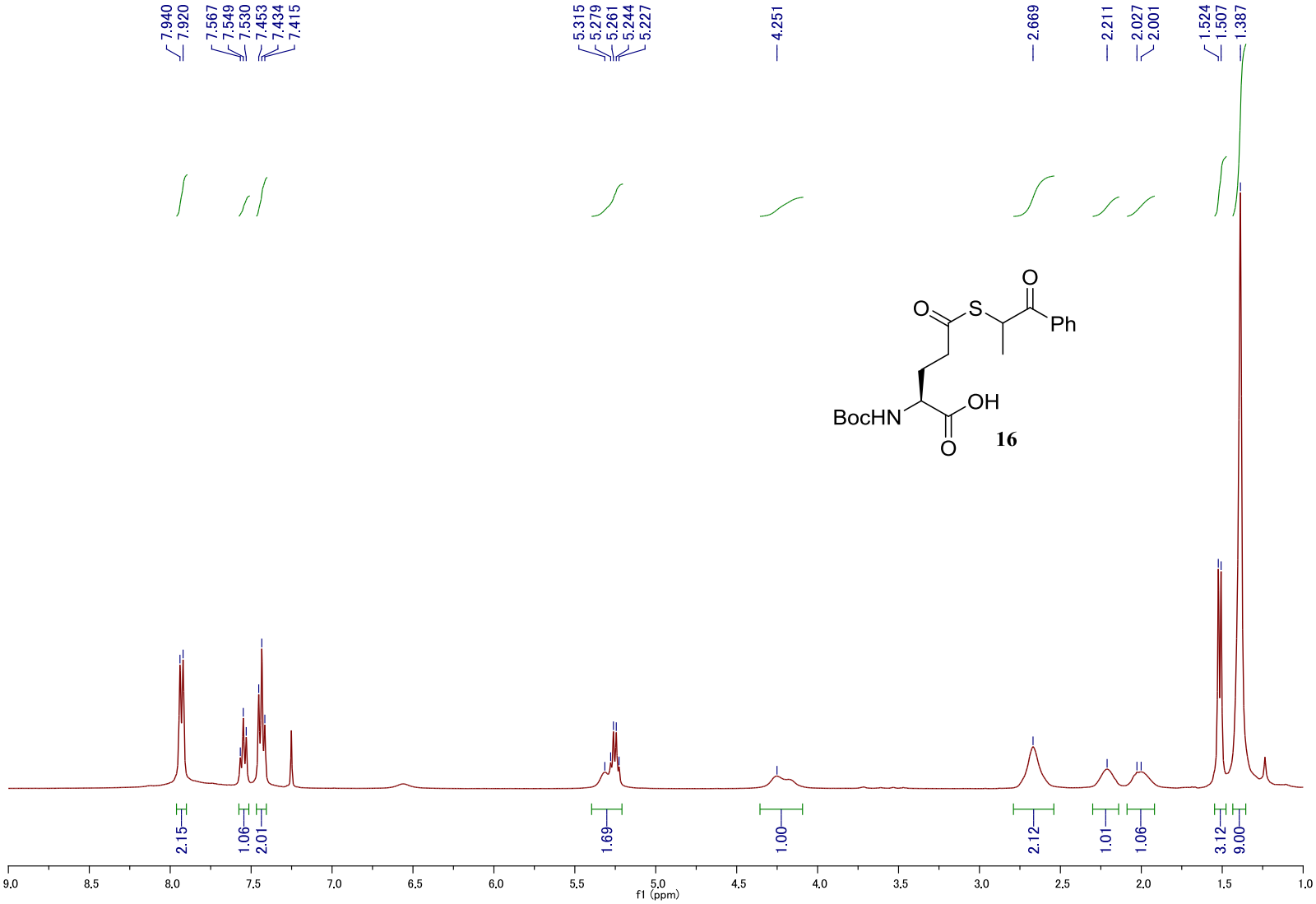
***O*$^{\alpha}$-Allyl *S*$^{\gamma}$-α-methylphenacyl *N*-*tert*-butoxycarbonyl-L-γ-thioglutamate (15)** ^{1}H NMR (400 MHz, $CDCl_3$)



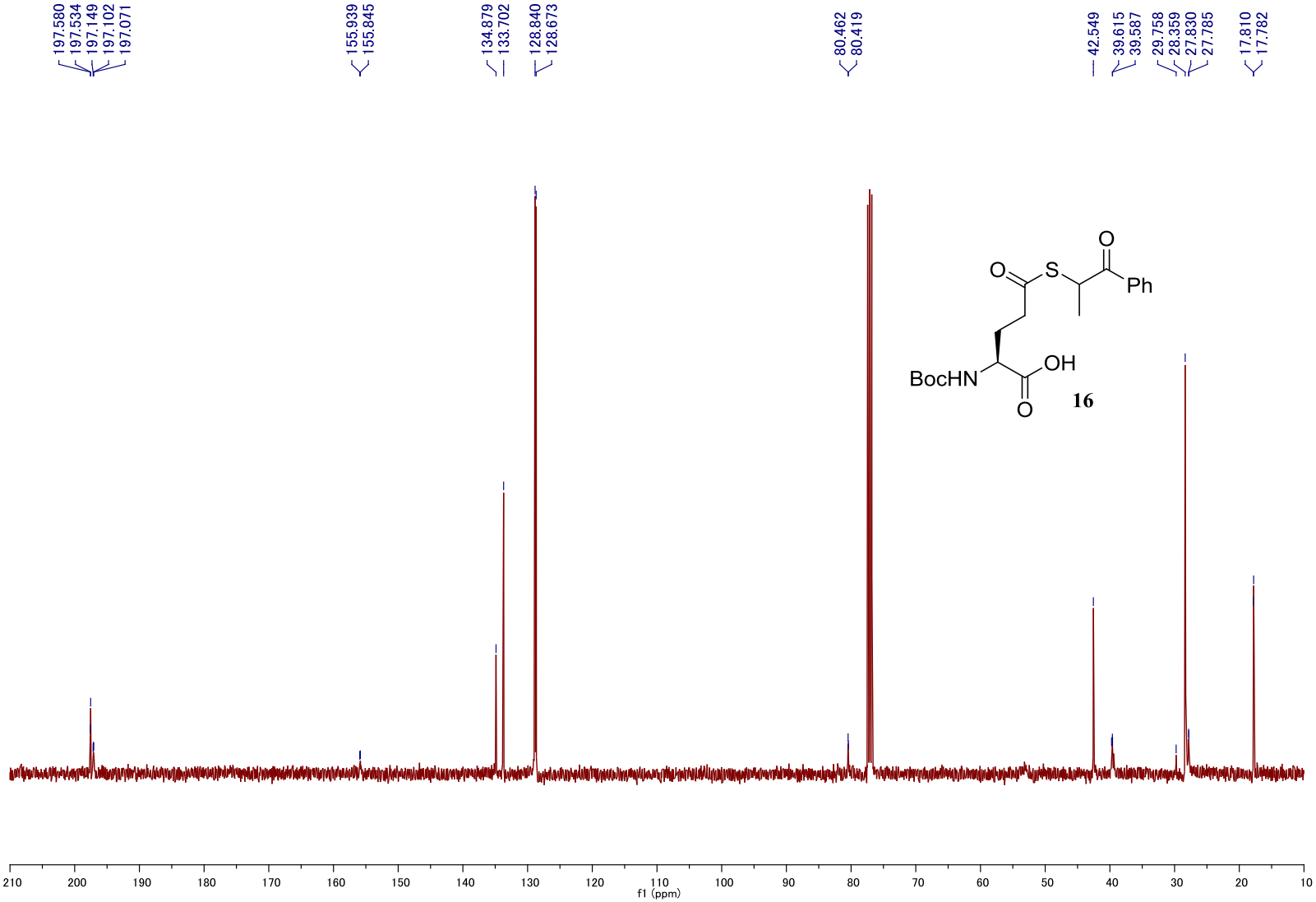
O^{α}-Allyl S^{γ}-α-methylphenacyl *N*-*tert*-butoxycarbonyl-L-γ-thioglutamate (15) ^{13}C NMR (100 MHz, $CDCl_3$)



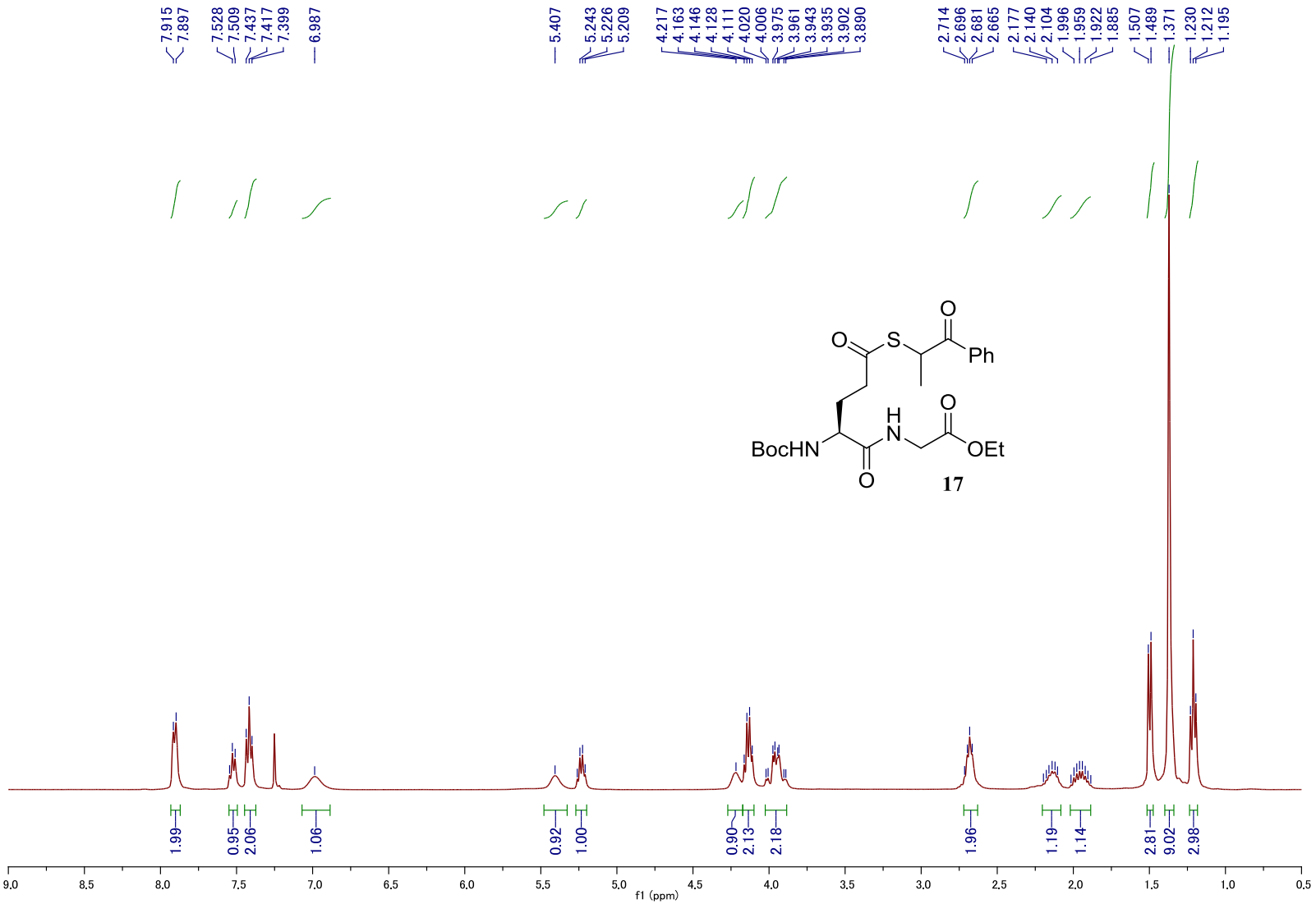
***S*$^{\gamma}$-α-Methylphenacyl *N*-*tert*-butoxycarbonyl-L-γ-thioglutamic acid (16)** ^{1}H NMR (400 MHz, $CDCl_3$)



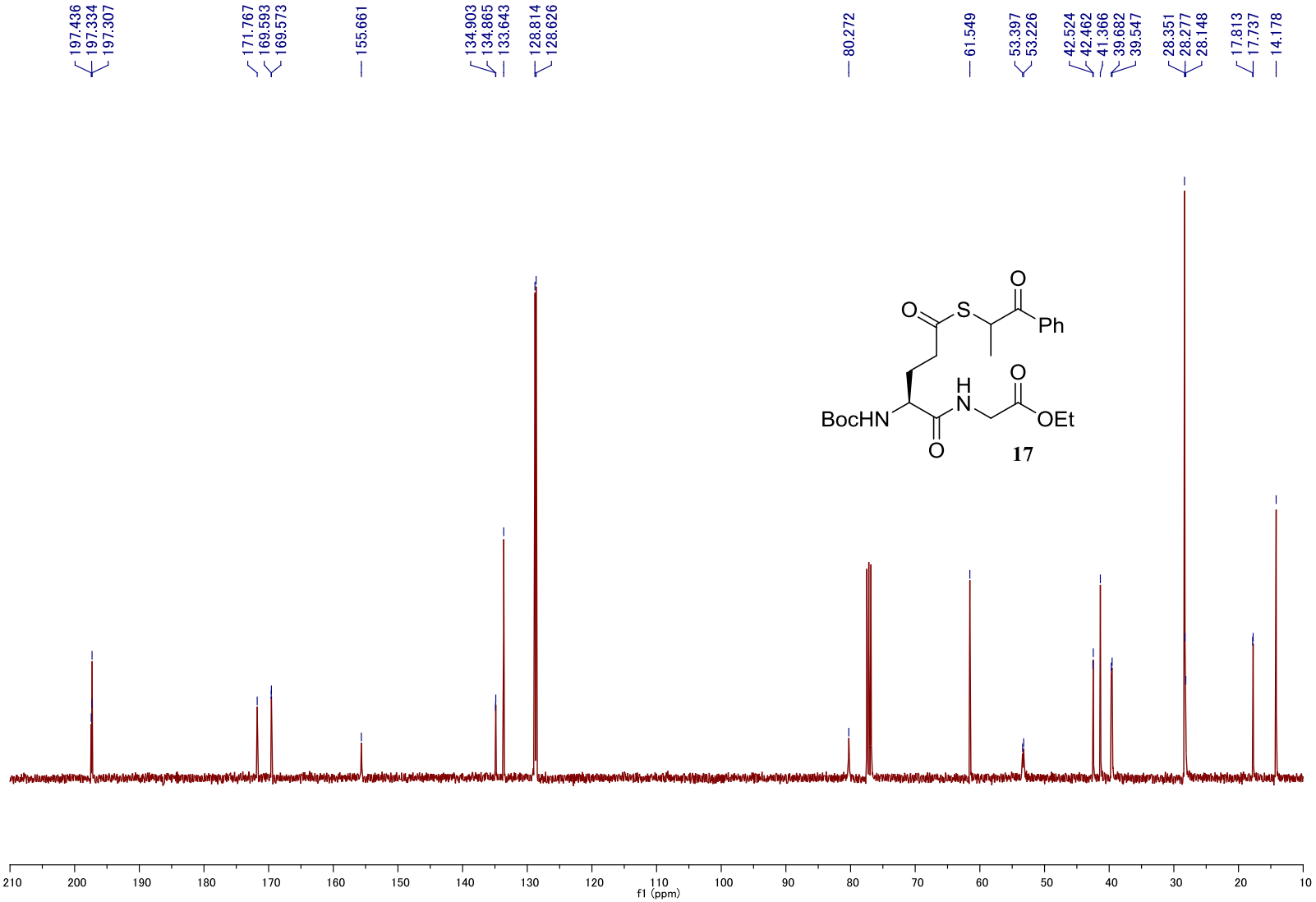
***S*$^{\gamma}$-α-Methylphenacyl *N*-*tert*-butoxycarbonyl-L-γ-thioglutamic acid (16)** ^{13}C NMR (100 MHz, $CDCl_3$)



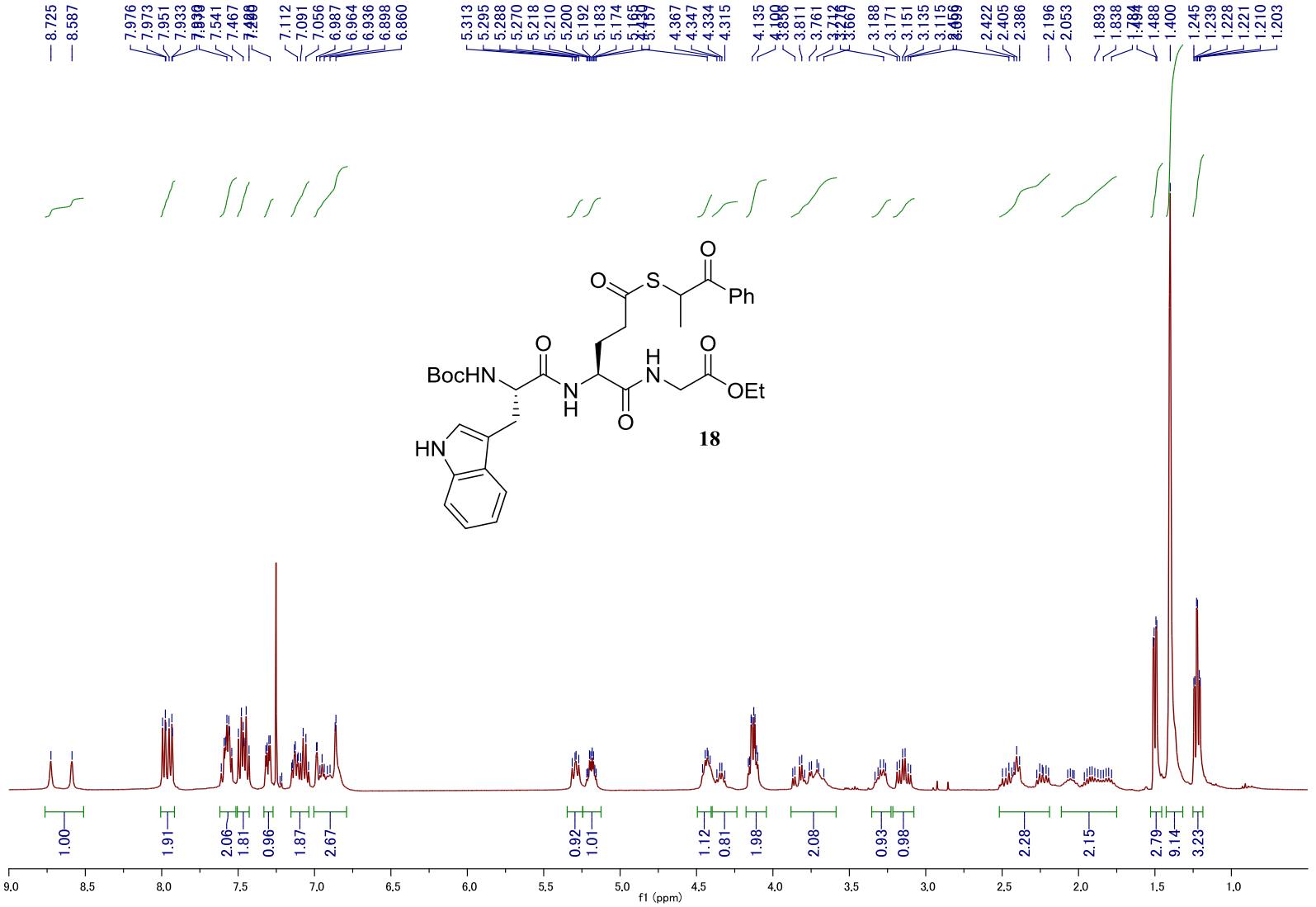
Ethyl *N*-*tert*-butoxycarbonyl-L-*S*$^{\gamma}$-α-metylphenacyl-γ-thioglutamylglycinate (17) ^{1}H NMR (400 MHz, $CDCl_3$)



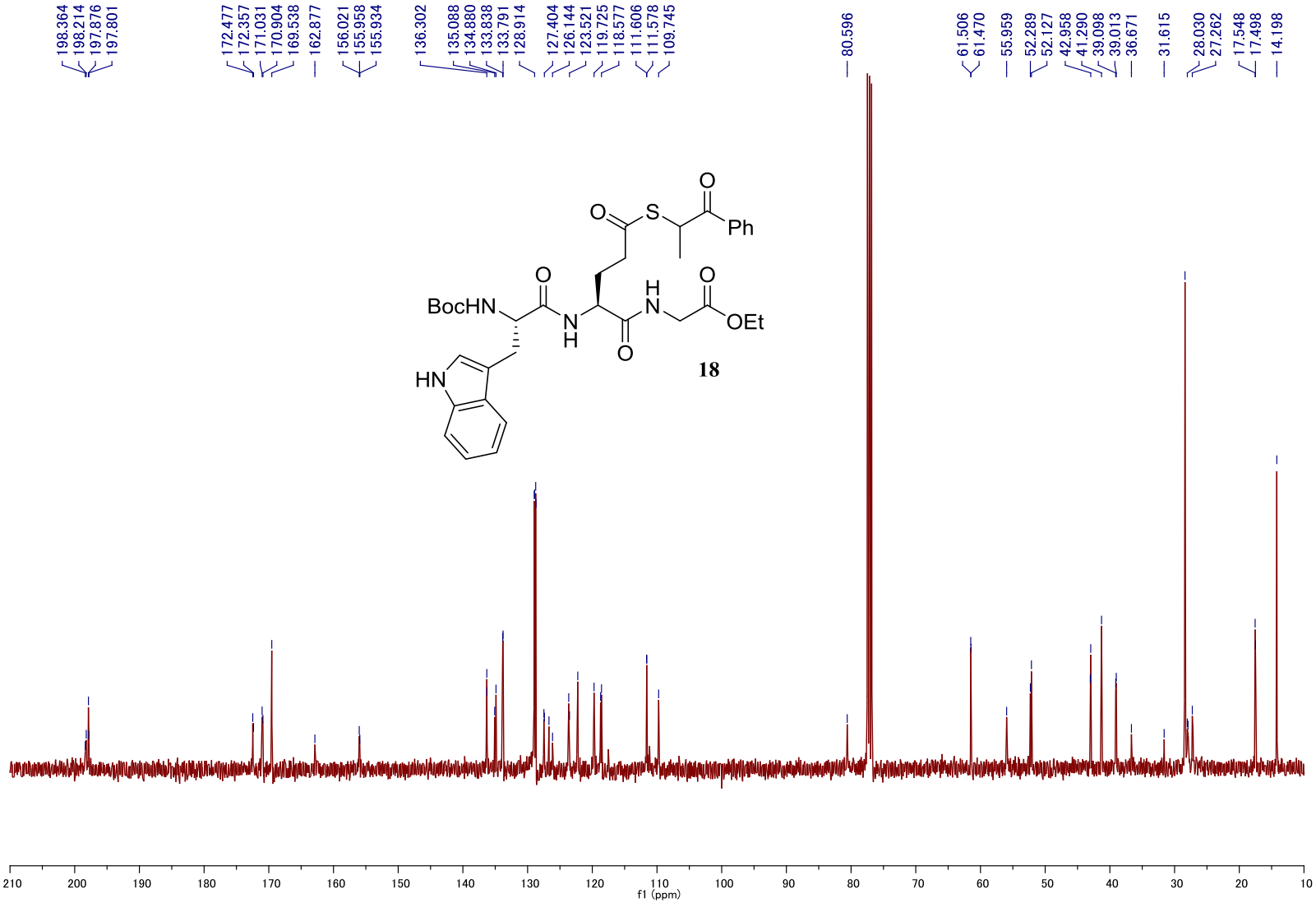
Ethyl *N*-*tert*-butoxycarbonyl-L-*S*$^{\gamma}$-α-metylphenacyl-γ-thioglutamylglycinate (17) ^{13}C NMR (100 MHz, $CDCl_3$)



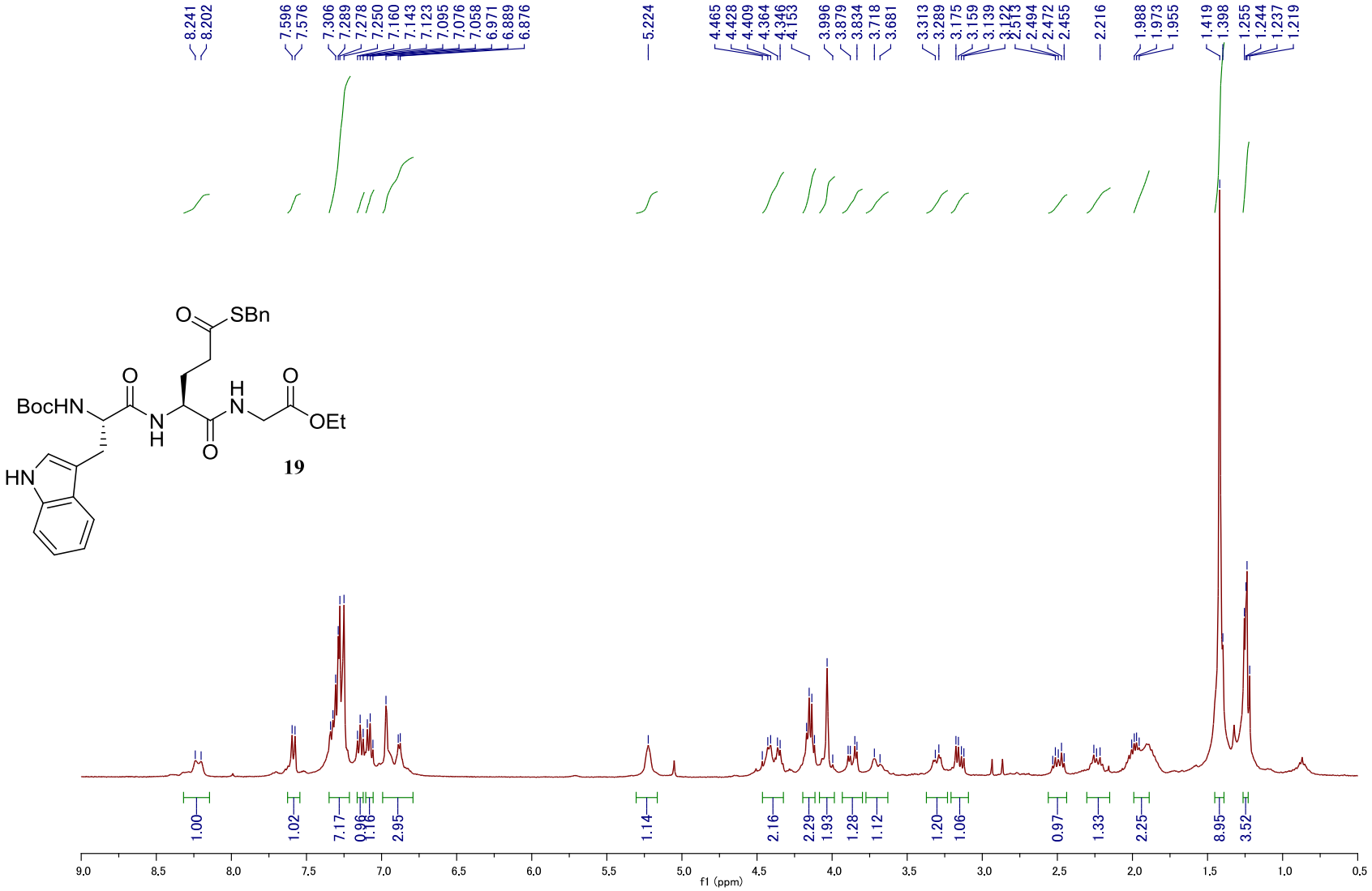
Ethyl *N*-*tert*-Butoxycarbonyl-L-tryptophanyl-*S*$^{\gamma}$-α-methylphenacyl-L-γ-thioglutamylglycinate (18) ^{1}H NMR (400 MHz, $CDCl_3$)



Ethyl *N*-*tert*-Butoxycarbonyl-L-tryptophanyl-*S*$^{\gamma}$-α-methylphenacyl-L-γ-thioglutamylglycinate (18) ^{13}C NMR (100 MHz, $CDCl_3$)



Ethyl *N*-*tert*-butoxycarbonyl-L-tryptophanyl-*S*$^{\gamma}$-benzyl-L-γ-thioglutamylglycinate (19) ^{1}H NMR (400 MHz, $CDCl_3$)



Ethyl *N*-*tert*-butoxycarbonyl-L-tryptophanyl-*S*$^{\gamma}$-benzyl-L-γ-thioglutamylglycinate (19) ^{13}C NMR (100 MHz, $CDCl_3$)