Supplementary Material (ESI) for Chemical Communications

# Highly enantioselective intramolecular aza-spiroannulation onto indoles using chiral rhodium catalysis: asymmetric entry to spiro-β-lactam core of chartellines

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## Supporting Information

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## General Experimental Procedures:

All reactions were carried out under an atmosphere of argon unless otherwise specified. Anhydrous solvents were transferred via syringe to flame-dried glassware, which had been cooled under a stream of dry nitrogen. Ethereal solvents and dichloromethane (anhydrous; Kanto Chemical Co., Inc) were used as received. All other solvents were dried and distilled by standard procedures. Yields refer to chromatographically and spectroscopically ($^1$H NMR) homogeneous materials unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification unless otherwise stated.

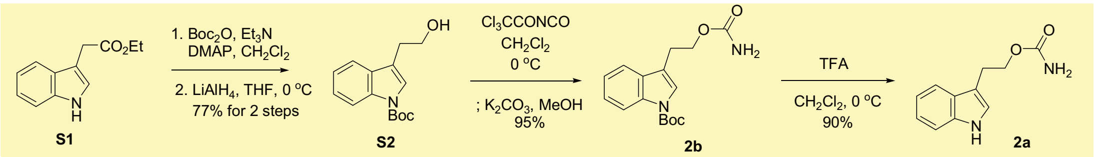
Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel plates (60F-254) using UV light as visualizing agent and p-anisaldehyde in ethanol/aqueous $H_2SO_4/CH_3CO_2H$ for staining. Column chromatography was performed using silica gel 60 particle size 0.063-0.210 mm. The eluents employed are reported as volume : volume percentages.

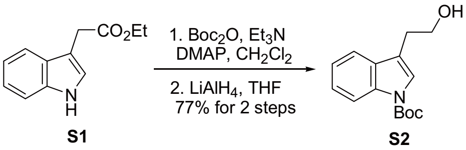
Proton nuclear magnetic resonance ($^1$H NMR) spectra were recorded using a JEOL JMN-AL400 (400 MHz), and a JEOL 500 (500 MHz) spectrometers. For $^1$H-NMR spectra, chemical shift (δ) are given from TMS (0.00 ppm) in $CDCl_3$ and from residual non-deuterated solvent peak in other solvent (DMSO-*d*$_6$: 2.49 ppm, methanol-*d*$_4$: 3.30 ppm) as internal standard. Coupling constants (*J*) are reported in Hz. Multiplicities are reported using the following abbreviations: s, singlet; d. doublet; t, triplet; q, quartet; m, multiplet; br, broad; app, Apparent. Carbon-13 nuclear magnetic resonance ($^{13}$C NMR) spectra were recorded using a JEOL JMN-AL400 spectrometer at 100 MHz, and JEOL JNM-ECP-500 at 125 MHz. For $^{13}$C-NMR spectra, chemical shift (δ) are given from $CDCl_3$ (77.0 ppm), DMSO-*d*$_6$ (39.5 ppm), methanol-*d*$_4$ (49.0 ppm) as internal standard.

Melting points were determined using Yazawa BY-2 melting point apparatus and are reported uncorrected. Infrared spectra were obtained on a JASCO FT-IR-410 at 4.0 cm$^{-1}$ resolution and are reported in wavenumbers. High resolution mass spectra (HRMS) were recorded on a JMS-AX500 or JMS-700 using electron impact (EI). Low resolution mass spectra (MS) were recorded on JEOL JMS-DX303. Elemental analyses were performed using Yanaco CHN CORDER MT-6. Analytical chiral HPLC was performed on CHIRALPAK AD-H obtained from Daicel Chemical Industries, ltd.

## Preparation of indoyl carbamates and sulfamate esters

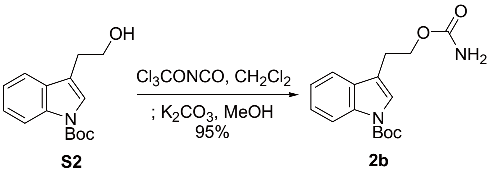
### Preparation of 2a and 2b





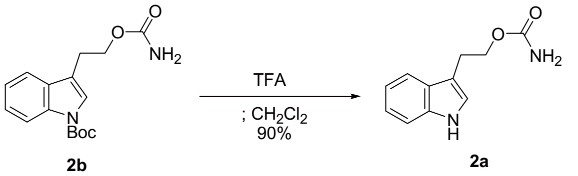
**Ethyl (1-*tert*-butoxycarbonyl-1H-indol-3-yl)-acetate (S2)** : To a solution of indole **S1** (500 mg, 2.46 mmol) in $CH_2Cl_2$ (4.9 ml) at rt was added $Et_3N$ (0.52 ml, 3.69 mmol, 1.5 eq.), $Boc_2O$ (0.85 ml, 3.69 mmol, 1.5 eq.) and DMAP (30 mg, 0.25 mmol, 10 mol%). After the reaction mixture was stirred for 10 min, water was added and the resultant solution was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo* to provide a Boc-protected product that was carried on without further purification. To a solution of $LiAlH_4$ (112 mg, 2.95 mmol, 1.2 eq.) in THF (2.4 ml) at 0 °C was added a solution of the crude mixture in THF (2.5 ml). After the reaction mixture was stirred for 5 min, the reaction was quenched with $H_2O$ (10 ml), filtered through Celite, and concentrated *in vacuo*. The resulting mixture was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo*. The residue was purified by column chromatography (1:2 AcOEt:hexane) to give alcohol **S2** as yellow oil (493 mg, 1.89 mmol, 77% for 2 steps).

IR (neat) : 3429, 2979, 2933, 1731, 1454, 1380 $cm^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 8.14 (d, $J$ = 7.6 Hz, 1H), 7.54 (d, $J$ = 7.8 Hz, 1H), 7.47 (s, 1H), 7.33 (dd, $J$ = 7.1, 7.1 Hz, 1H), 7.24 – 7.22 (m, 1H), 3.93 (t, $J$ = 6.4 Hz, 2H), 2.97 (t, $J$ = 6.4 Hz, 2H), 1.67 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 149.7, 135.6, 130.5, 124.5, 123.6, 122.5, 118.9, 117.0, 115.3, 83.5, 62.0, 28.5, 28.2 ; MS *m/z* : 261 ($M^+$), 130 (100%) ; HRMS Calcd. $C_{15}H_{19}O_3N$ : 261.1365, Found : 261.1367



**1-*tert*-Butoxycarbonyl-3-(2-carbamoyloxy-ethyl)-1*H*-indole (2b)** : To a solution of alcohol **S2** (473 mg, 1.81 mmol) in $CH_2Cl_2$ (9 ml) at 0 °C was added trichloroacetyl isocyanate (0.26 ml, 2.17 mmol, 1.2 eq.) and the mixture was stirred for 5 min. When TLC indicated consumption of the alcohol, MeOH (9 ml) and $K_2CO_3$ (50 mg, 138.21 mmol, 0.2 eq.) was added to the reaction mixture. The mixture was allowed to warm to rt and stirred for 4 h. Then, water was added and the resultant solution was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo*, and the crude products was purified by recrystallization from MeOH/ Hexane to give carbamate **2b** as colorless solid (523 mg, 1.72 mmol, 95%). An analytical sample was obtained by recrystallization from MeOH./hexane;

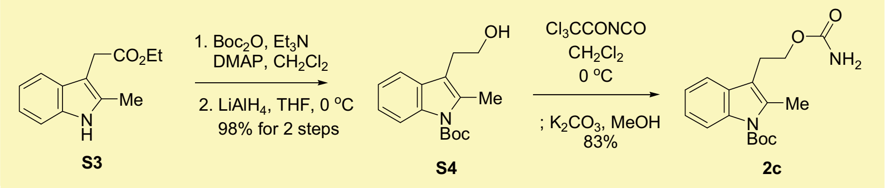
Mp = 102 - 103°C (MeOH/ Hexane, plate). ; IR (neat) : 3470, 3366, 2979, 1730, 1604, 1454, 1371 $cm^{-1}$ ; $^1H$-NMR (400 MHz, $CDCl_3$) δ: 8.11 (d, $J$ = 6.3 Hz, 1H ), 7.54 (d, $J$ = 7.6 Hz, 1H), 7.44 (s, 1H), 7.33 – 7.29 (m, 1H), 7.25 – 7.22 (m, 1H), 4.59 (br, 2H ), 4.36 (t, $J$ = 7.0 Hz, 2H), 3.03 (t, $J$ = 7.0 Hz, 2H ), 1.67 (s, 9H) ; $^{13}C$-NMR (100 MHz, $CDCl_3$) δ: 156.8, 149.7, 135.4, 130.5, 124.4, 123.3, 122.4, 118.9, 116.7, 115.3, 83.5, 64.3, 28.2, 24.8 ; MS *m/z* : 304 ($M^+$), 143 (100%) ; HRMS Calcd. $C_{16}H_{20}O_4N_2$ : 304.1423, Found : 304.1438

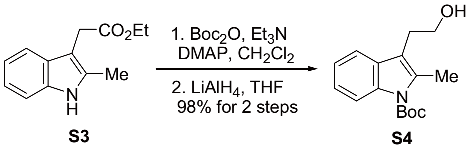


**3-(2-Carbamoyloxy-ethyl)-1*H*-indole (2a)** : To a solution of indole **2b** (37 mg, 0.120 mmol) in $CH_2Cl_2$ (0.6 ml) at 0 °C was added TFA (0.36 mmol, 4.8 mmol, 40 eq.). After the reaction mixture was stirred for 2.5 h, benzene was added and the resultant solution was concentrated *in vacuo*. After this manipulation was repeated three times, the product was collected and washed with methanol, benzene, $CH_2Cl_2$ to give carbamate **2a** as white solid (22 mg, 0.108 mmol, 90%).

mp = 132 - 133°C ( MeOH ). IR (neat) : 3448, 3213, 1719, 1455, 1429 $cm^{-1}$ ; $^1H$-NMR (400 MHz, DMDO-$d_6$) δ: 8.08 (d, $J$ = 8.3 Hz, 1H ), 7.62 (d, $J$ = 7.8 Hz, 1H), 7.52 (s, 1H), 7.32 – 7.28 (m, 1H), 7.25 – 7.21 (m, 1H), 6.47 (br, 2H ), 4.18 (t, $J$ = 6.8 Hz, 2H), 2.94 (t, $J$ = 6.8 Hz, 2H ) ; $^{13}C$-NMR (100 MHz, $CDCl_3$) δ: 156.8, 136.1, 127.1, 123.0, 120.9, 118.2, 111.3, 110.3, 63.5, 24.9 ; MS *m/z* : 204 ($M^+$), 143 (100%) ; HRMS Calcd. $C_{11}H_{12}O_2N_2$ : 204.0899, Found : 204.0893

**Preparation of 2c**

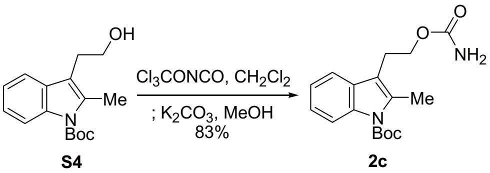




**2-(1-*tert*-Butoxycarbonyl-2-methyl-1*H*-indol-3-yl)-ethanol (S3)** : To a solution of indole **S3**[1] (21.2 g, 97.6 mmol) in $CH_2Cl_2$ (97.6 ml) at rt was added $Et_3N$ (34.1 ml, 243.9 mmol, 2.5 eq.), $Boc_2O$ (29.1 ml, 126.8 mmol, 1.3 eq.) and DMAP (596 mg, 4.88 mmol, 5 mol%). After the reaction mixture was stirred for 30 min, water was added and the resultant solution was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo* to provide a Boc-protected product that was carried on without further purification. To a solution of $LiAlH_4$ (3.70 g, 97.6 mmol, 1.0 eq.) in THF (97.6 ml) at 0 °C was added a solution of the crude mixture in THF (97.6 ml). After the reaction mixture was stirred for 5 min, the reaction was quenched with $H_2O$ (50 ml), filtered through Celite, and concentrated *in vacuo*. The resulting mixture was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo*. The residue was purified by column chromatography (1:2 AcOEt:hexane) to give alcohol **S4** as yellow oil (26.4 g, 95.9 mmol, 98% for 2 steps).

IR (neat) : 3366, 2978, 2932, 1730 cm$^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 8.09 (d, $J$ = 7.1 Hz, 1H), 7.45 (d, $J$ = 7.3 Hz, 1H), 7.26 – 7.18 (m, 2H), 3.82 (t, $J$ = 6.3 Hz, 2H), 2.95 (t, $J$ = 6.6 Hz, 2H), 2.57 (s, 3H), 1.68 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 150.6, 135.7, 134.5, 129.8, 123.4, 122.4, 117.7, 115.4, 114.3, 83.6, 62.4, 28.4, 27.6, 14.1 ; MS *m/z* : 275 (M$^+$), 144 (100%) ; HRMS Calcd. $C_{16}H_{21}O_3N$ : 275.1521, Found : 275.1503

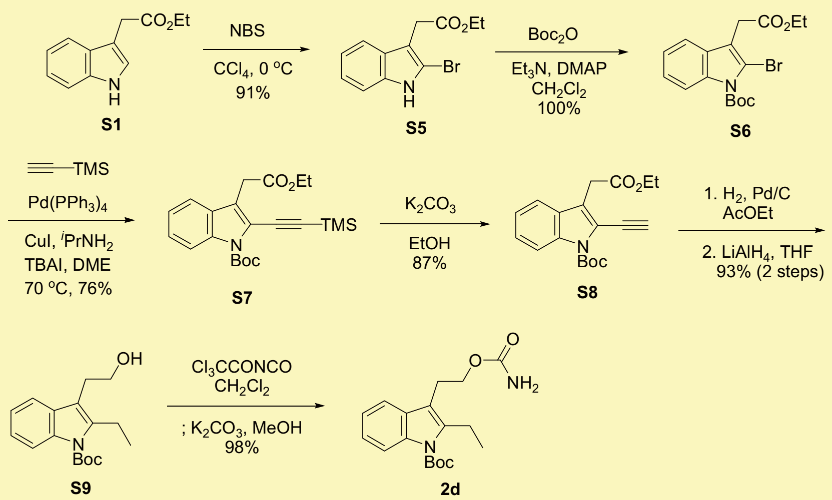
Ref.1) Sengupta, A.K.; Gupta, A. A. *Indian J. Chem.* **1983**, *22B*, 263.

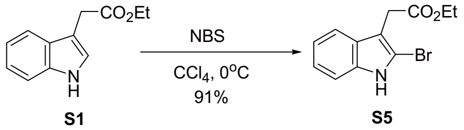


**1-*tert*-Butoxycarbonyl-3-(2-carbamoyloxy-ethyl)-2-methyl-1*H*-indole (2c)** : To a solution of alcohol **S4** (7.26 g, 26.1 mmol) in $CH_2Cl_2$ (52 ml) at 0 ˚C was added trichloroacetyl isocyanate (3.74

ml, 31.3 mmol, 1.2 eq.) and the mixture was stirred for 5 min. When TLC indicated consumption of the alcohol, MeOH (52 ml) and $K_2CO_3$ (723 mg, 5.22 mmol, 0.2 eq.) was added to the reaction mixture. The mixture was allowed to warm to rt and stirred for 4 h. Then, water was added and the resultant solution was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo*, and the crude products was purified by recrystallization from MeOH to give carbamate **2c** as colorless needle (5.78 g, 18.2 mmol, 69%); mp = 150 - 152°C ( MeOH ).
IR (neat) : 3424, 3330, 3272, 2970, 1723, 1701, 1607 cm$^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 8.09 (dd, *J* = 2.0, 6.7 Hz, 1H ), 7.45 (dd, *J* = 2.0, 6.5 Hz, 1H), 7.24 – 7.20 (m, 2H), 4.77 (br, 2H ), 4.20 (t, *J* = 7.3 Hz, 2H), 3.00 (t, *J* = 7.1 Hz, 2H ), 2.55 (s, 3H), 1.68 (s, 9H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 156.9, 150.7, 135.6, 1, 34.4, 129.8, 123.4, 122.4, 117.6, 115.4, 113.9, 83.5, 64.3, 28.2, 23.9, 13.9 ; MS *m/z* : 318 ($M^+$), 201 (100%) ; HRMS Calcd. $C_{17}H_{22}O_4N_2$ : 318.1580, Found : 318.1593

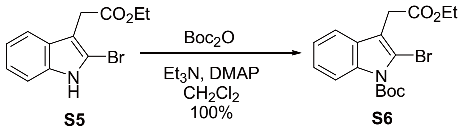
**Preparation of 2d**





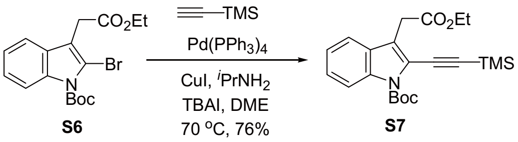
**Ethyl (2-bromo-1*H*-indol-3yl)-acetate (S5)** : To a solution of indole **S1** (3.0 g, 14.8 mmol) in $CCl_4$ (29.5 ml) at 0 °C was added recrystallized NBS (2.63 g, 14.8 mmol, 1.0 eq.) in 5 portions. After the reaction mixture was stirred for 2 h, the precipitate was filtered and the filtrate was concentrated *in vacuo.* The residue was purified by column chromatography (1:6 AcOEt:hexane) to give bromo indole **S5** as purple oil (3.77 g, 13.4 mmol, 91%).
IR (neat) : 3330, 2981, 1722 cm$^{-1}$ ; H-NMR (400 MHz, $CDCl_3$) δ: 8.25 (br, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.17 – 7.08 (m, 3H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.72 (s, 2H), 1.24 (t, *J* = 7.1 Hz, 3H) ; $^{13}$C-NMR

(100 MHz, $CDCl_3$) δ: 171.1, 136.0, 127.5, 122.4, 120.3, 118.3, 110.5, 110.3, 110.0, 108.6, 61.0, 31.1, 14.2 ; MS m/z : 281 ($M^+$), 208 (100%) ; HRMS Calcd. $C_{12}H_{12}BrO_2N$ : 281.0051, Found : 281.003



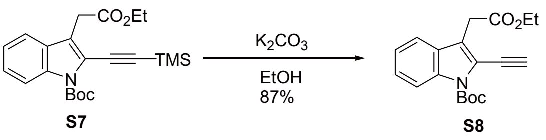
**Ethyl (1-*tert*-butoxycarbonyl-2-bromo-1*H*-indol-3-yl) acetate (S6)** : To a solution of indole **S5** (3.77 g, 13.4 mmol) in $CH_2Cl_2$ (26.7 ml) at rt was added $Et_3N$ (4.9 ml, 34.8 mmol, 2.5 eq.), $Boc_2O$ (4.0 ml, 17.4 mmol, 1.3 eq.) and DMAP (82 mg, 0.669 mmol, 5 mol%). After the reaction mixture was stirred for 30 min, water was added and the resultant solution was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo*, and the crude products was purified by column chromatography (1:20 AcOEt-Hexane) to give indole **S6** as yellow oil (5.11 g, 13.4 mmol, 100%);

IR (neat) : 2980, 1738cm$^{-1}$ ; H-NMR (400 MHz, $CDCl_3$) δ: 8.08 (d, $J$ = 8.3 Hz, 1H), 7.47 (d, $J$ = 7.6 Hz, 1H), 7.31 – 7.21 (m, 2H), 4.16 (q, $J$ = 7.1 Hz, 2H), 3.76 (s, 2H), 1.70 (s, 9H), 1.24 (t, $J$ = 7.1 Hz, 3H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 169.9, 148.9, 136.3, 128.5, 124.5, 122.9, 118.2, 116.4, 115.3, 110.8, 85.0, 61.1, 31.6, 28.2, 14.3 ; MS m/z : 381 ($M^+$), 57 (100%) ; HRMS Calcd. $C_{17}H_{22}BrO_4N$ : 381.0576, Found : 381.0587



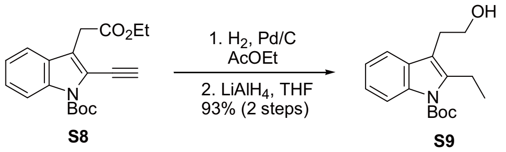
**Ethyl (1-*tert*-butoxycarbonyl-2-trimethylsilylethynyl-1*H*-indol-3-yl) acetate (S7)** : To a 2-necked flask were added tetrabutylammonium iodide (2.90 g, 7.86 mmol, 3.0 eq.), CuI (249 mg, 1.31 mmol, 0.5 eq.) and $Pd(PPh_3)_4$ (907 mg, 0.786 mmol, 0.3 eq.) and then was degassed. To this flask were added DME (3 ml), $^iPrNH_2$ (2.25 ml, 26.2 mmol, 10 eq.), bromo indole **S6** (1.0 g, 2.62 mmol) in DME (10 ml) and trimethylsilyl acetylene (0.56 ml, 3.93 mmol, 1.5 eq.). After the reaction mixture was stirred for 1 h at 70 °C, $Et_2O$ was added and filtered through Celite. $H_2O$ was added to the filtrate and the resultant solution was extracted with $Et_2O$. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo*, and the crude products was purified by column chromatography (1:30 AcOEt-Hexane) to give indole **S7** as purple oil (790 mg, 1.98 mmol, 76%)

IR (neat) : 2980, 2148, 1736 cm$^{-1}$ ; $^1$H-NMR (400 MHz, CDCl$_3$) δ: 8.21 (d, *J* = 8.3 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.37 (ddd, *J* = 1.2, 7.6, 7.6 Hz, 1H), 7.26 – 7.23 (m, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.83 (s, 2H), 1.69 (s, 9H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.28 (s, 9H) ; $^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 170.3, 149.4, 135.8, 128.4, 126.0, 123.1, 122.9, 119.3, 119.2, 115.6, 104.8, 95.9, 84.5, 60.9, 31.4, 28.1, 14.2 ; MS m/z : 399 (M$^+$), 226 (100%) ; HRMS Calcd. $C_{22}H_{29}O_4NSi$ : 306.1866, Found : 399.1860



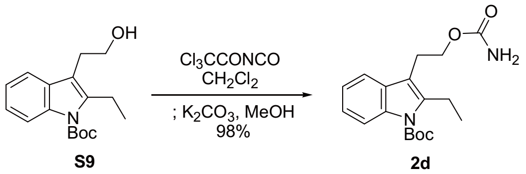
**Ethyl (1-*tert*-butoxycarbonyl-2-ethynyl-1*H*-indol-3-yl)-acetate (S8)** : To a solution of acetylene **S7** (790 mg, 1.98 mmol) in EtOH (9.9 ml) at rt was added $K_2CO_3$ (410 mg, 2.97 mmol, 1.5 eq.). After the reaction mixture was stirred for 2 h, water was added and the resultant solution was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo*, and the crude products was purified by column chromatography (1:30 AcOEt-Hexane) to give indole **S8** as purple oil (562 mg, 1.72 mmol 87%)

IR (neat) : 3273, 2987, 1734 cm$^{-1}$ ; $^1$H-NMR (400 MHz, CDCl$_3$) δ: 8.14 (d, *J* = 8.5 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.37 (ddd, *J* = 1.2, 8.0, 8.5 Hz, 1H), 7.28 – 7.24 (m, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 2H), 3.67 (s, 1H), 1.68 (s, 9H), 1.24 (t, *J* = 7.1 Hz, 3H) ; $^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 170.3, 149.3, 135.7, 128.3, 126.1, 123.2, 122.9, 119.4, 118.5, 115.7, 86.7, 84.8, 75.0, 61.0, 31.2, 28.1 ; MS m/z : 327 (M$^+$), 154 (100 %) ; HRMS Calcd. $C_{19}H_{21}O_4N$ : 327.1471, Found : 327.1451



**2-(1-*tert*-Butoxycarbonyl-2-ethyl-1*H*-indol-3-yl)-ethanol (S9)** : A solution of acetylene **S8** (579 mg, 1.77mmol) in AcOEt (8.9 ml) was hydrogenated in the presence of 10% Pd/C (58 mg) under atmospheric pressure of $H_2$. After the reaction mixture was stirred for 5 h, the mixture was filtered through Celite. The filtrate was concentrated *in vacuo* to provide an alkane product that was carried on without further purification. To a solution of crude product in THF (8.9 ml) at 0 °C was added $LiAlH_4$ (67.1 mg, 1.77 mmol, 1.0 eq.). After the reaction mixture was stirred for 5 min, the reaction was quenched with $H_2O$, filtered through Celite, and concentrated *in vacuo*. The resulting mixture was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo*. The residue was purified by column chromatography (1:4 AcOEt:hexane) to give alcohol **S9** as yellow oil (475 mg, 1.64 mmol, 93% for 2 steps).

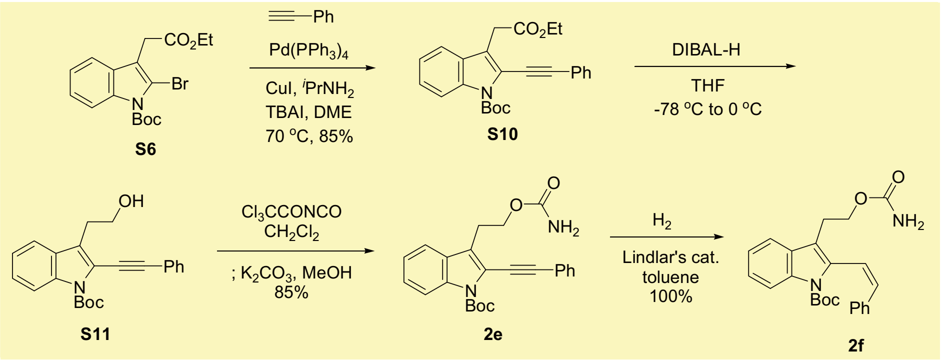
IR (neat) : 3349, 2978, 2934, 1730 cm$^{-1}$ ; $^1$H-NMR (400 MHz, CDCl$_3$) δ: 811 (dd, *J* = 1.3, 7.4 Hz, 1H), 7.49 – 7.47 (m, 1H), 7.25 (ddd, *J* = 1.4, 7.5, 8.0 Hz, 1H), 7.23 – 7.19 (d, *J* = 1.4, 7.5, 8.0 Hz, 1H), 3.84 (br, 2H), 3.05 (q, *J* = 7.6 Hz, 2H), 2.96 (t, *J* = 6.6 Hz, 2H), 1.69 (s, 9H), 1.23 (t, *J* = 7.6 Hz, 3H) ; $^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 140.5, 136.0, 129.9, 123.6, 122.5, 117.9, 116.9, 115.6, 113.8, 83.6, 62.5, 28.2, 27.6, 20.1, 15.1 ; MS m/z : 289 (M$^+$), 158 (100%) ; HRMS Calcd. $C_{17}H_{23}O_3N$ : 289.1678, Found : 289.1668

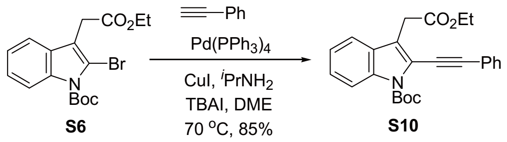


**1-*tert*-Butoxycarbonyl-3-(2-carbamoyloxy-ethyl)-2-ethyl-1*H*-indole (2d)** : To a solution of alcohol **S9** (395 mg, 1.37 mmol) in CH$_2$Cl$_2$ (6.8 ml) at 0 ˚C was added trichloroacetyl isocyanate (0.195 ml, 1.64 mmol, 1.2 eq.) and the mixture was stirred for 5 min. When TLC indicated consumption of the alcohol, MeOH (6.8 ml) and K$_2$CO$_3$ (19 mg, 0.137 mmol, 0.2 eq.) was added to the reaction mixture. The mixture was allowed to warm to rt and stirred for 10 h. Then, water was added and the resultant solution was extracted with AcOEt. The organic layer was washed with brine, dried over MgSO$_4$, concentrated *in vacuo*, and the residue was purified by column chromatography (1:3 AcOEt:hexane) to give carbamate **2d** as colorless solid (432 mg, 1.34 mmol, 98%). An analytical sample was obtained by recrystallization from AcOEt/hexane;

mp = 132-134°C ( AcOEt/ Hexane, needle) ; IR (neat) : 3491, 3364, 2978, 1731, 1601 cm$^{-1}$ ; $^1$H-NMR (400 MHz, CDCl$_3$) δ: 8.11 (dd, *J* = 1.8, 7.1 Hz, 1H), 7.50 – 7.48 (m, 1H), 7.26 – 7.18 (m, 2H), 4.77 (br, 2H), 4.23 (t, *J* = 7.2 Hz, 2H), 3.04 (t, *J* = 7.5 Hz, 2H), 3.00 (q, *J* = 7.2 Hz, 2H), 1.68 (s, 9H), 1.24 (t, *J* = 7.2 Hz, 3H) ; $^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 156.7, 150.4, 140.2, 135.9, 129.8, 123.5, 22.5, 117.9, 115.6, 113.5, 83.6, 64.6, 28.2, 24.0, 20.0, 15.1 ; MS m/z : 332 (M$^+$), 215 (100%) ; HRMS Calcd. $C_{18}H_{24}O_4N_2$ : 332.1736, Found : 332.1733

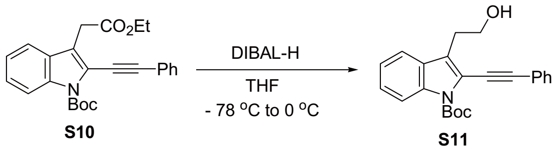
## Preparation of 2e and 2f





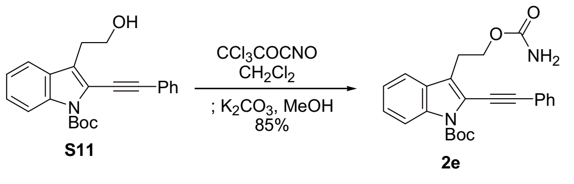
**Ethyl (1-*tert*-butoxycarbonyl-2-phenylethynyl-1*H*-indol-3-yl) acetate (S10)** : To a 2-necked flask were added tetrabutylammonium iodide (2.90 g, 7.86 mmol, 3.0 eq.), CuI (149 mg, 0.786 mmol, 0.3 eq.) and $Pd(PPh_3)_4$ (302 mg, 0.39 mmol, 0.1 eq.) and then was degassed. To this flask were added DME (3 ml), $^iPrNH_2$ (2.25 ml, 26.2 mmol, 10 eq.), bromo indole **S6** (1.0 g, 2.62 mmol) in DME (10 ml) and phenyl acetylene (0.43 ml, 3.93 mmol, 1.5 eq.). After the reaction mixture was stirred for 1 h at 70 °C, $Et_2O$ was added and filtered through Celite. $H_2O$ was added to the filtrate and the resultant solution was extracted with $Et_2O$. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo*, and the crude products was purified by column chromatography (1:30 AcOEt-Hexane) to give indole **S10** as purple oil (898 mg, 2.22 mmol, 85%).

IR (neat) : 2980, 2930, 1732cm$^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 8.20 (d, *J* = 8.6 Hz, 1H), 7.58 – 7.52 (m, 3H), 7.38 – 7.34 (m, 4H), 7.26 – 7.25 (m, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.91 (s, 2H), 1.68 (s, 9H), 1.22 (t, *J* = 7.0 Hz, 3H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 170.4, 149.5, 136.0, 131.4, 128.6, 128.4, 125.8, 123.1, 121.6, 119.4, 119.1, 115.6, 98.3, 84.2, 81.0, 61.0, 31.4, 28.2, 14.1 ; MS m/z : 403 ($M^+$), 230 (100%) ; HRMS Calcd. $C_{25}H_{25}O_4N$ : 403.1784, Found : 403.1785

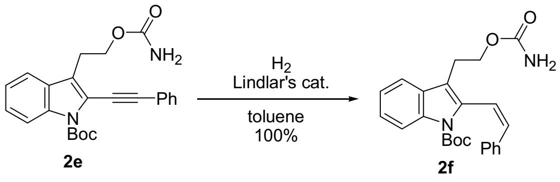


**2-(1-*tert*-Butoxycarbonyl-2-phenylethynyl-1*H*-indol-3-yl)-ethanol (S11)** :To a solution of ester **S10** (162 mg, 0.402 mmol) in THF (3.0 ml) at -78 °C was added DIBAL-H (1.0 M in toluene, 1.21 ml, 1.21 mmol, 3.0 eq.) dropwise over 10 min. After the reaction mixture was stirred for 1 h, the reaction mixtuere was gradually allowed to warm up to 0 °C. Then, the reaction was quenched with satirated $NH_4Cl$ and MeOH. The resultant solution was filtered through Celite, and concentrated *in vacuo*. The resulting mixture was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo*. The residue was purified by column chromatography (1:4 AcOEt:hexane) to give alcohol **S11** as yellow oil (119 mg, 0.329 mmol, 82%).

IR (neat) : 3390, 2980, 1731 cm$^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 8.20 (d, *J* = 8.3 Hz, 1H), 7.59 – 7.55 (m, 3H), 7.38 – 7.36 (m, 4H), 7.29 – 7.26 (m, 1H), 3.98 (t, *J* = 6.6 Hz, 2H), 3.19 (t, *J* = 6.6 Hz, 2H), 1.69 (s, 9H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 149.5, 130.1, 131.4, 129.1, 128.5, 128.4, 125.8, 125.6, 123.1, 123.0, 118.9, 118.7, 115.7, 84.1, 81.4, 62.3, 28.8, 28.3 ; MS m/z : 361 ($M^+$), 361 (100%) ; HRMS Calcd. $C_{23}H_{23}O_3N$ : 361.1678, Found : 361.1660



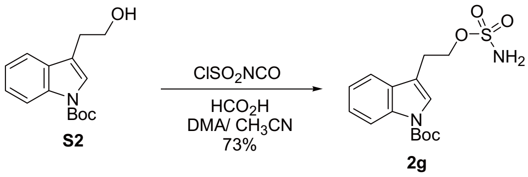
**1-*tert*-Butoxycarbonyl-3-(2-carbamoyloxy-ethyl)-2-phenylethynyl-1*H*-indole (2e)** : To a solution of alcohol **S11** (117 mg, 0.324 mmol) in $CH_2Cl_2$ (1.6 ml) at 0 °C was added trichloroacetyl isocyanate (0.058 ml, 0.486 mmol, 1.2 eq.) and the mixture was stirred for 5 min. When TLC indicated consumption of the alcohol, MeOH (1.6 ml) and $K_2CO_3$ (8.9 mg, 0.0648 mmol, 0.2 eq.) was added to the reaction mixture. The mixture was allowed to warm to rt and stirred for 5 h. Then, water was added and the resultant solution was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo*, and the residue was purified by column chromatography (1:2 AcOEt:hexane) to give carbamate **2e** as colorless solid (125 mg, 0.309 mmol, 96%). An analytical sample was obtained by recrystallization from AcOEt/hexane.;
mp = 154-156 °C ( AcOEt/ Hexane, plate) ; IR (neat) : 3514, 3384, 3340, 1731, 1715, 1702, 1580 $cm^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 8.20 (d, $J$ = 8.3 Hz, 1H), 7.58 – 7.57 (m, 3H), 7.37 – 7.34 (m, 4H), 7.28 – 7.25 (m, 1H), 4.71 (br, 2H), 4.37 (t, $J$ = 7.1 Hz, 2H), 3.23 (t, $J$ = 7.1 Hz, 2H), 1.69 (s, 9H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 156.8, 149.5, 136.0, 131.4, 129.0, 128.5, 128.4, 125.7, 125.0, 123.1, 118.9, 118.8, 115.7, 97.9, 84.1, 81.2, 63.9, 28.3, 25.1 ; MS m/z : 404 ($M^+$), 243 (100%) ; HRMS Calcd. $C_{24}H_{24}O_4N_2$ : 404.1736, Found : 404.1744



**(1'*Z*)-1-*tert*-Butoxycarbonyl-3-(2-carbamoyloxy-ethyl)-2-phenylvinyl-1*H*-indole (2f)** : A solution of acetylene **2e** (45 mg, 0.111 mmol) in toluene (1.1 ml) was hydrogenated in the presence of 5% Lindlar's cat. (9.0 mg) under atmospheric pressure of $H_2$. After the reaction mixture was stirred for 8 h, the mixture was filtered through Celite. The filtrate was concentrated *in vacuo*, and the residue was purified by column chromatography (1:2 AcOEt:hexane) to give alkene **2f** as colorless amorphous (45 mg, 0.111 mmol, 100%).

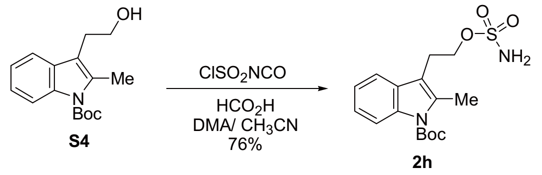
IR (neat) : 3485, 3380, 2979, 1729, 1599 cm$^{-1}$ ; $^1$H-NMR (400 MHz, CDCl$_3$) δ: 8.19 (d, *J* = 8.3 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.33 – 7.15 (m, 7H), 6.73 (d, *J* = 11.8 Hz, 1H), 6.62 (d, *J* = 11.8 Hz, 1H), 4.52 (br, 2H), 3.85 (t, *J* = 7.1 Hz, 2H), 2.67 (t, *J* = 7.2 Hz, 2H), 1.62 (s, 9H) ; $^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 156.7, 150.2, 136.9, 136.1, 133.6, 131.8, 130.0, 128.3, 127.6, 124.3, 122.6, 121.7, 119.0, 115.5, 114.9, 84.0, 63.5, 28.1, 24.3 ; MS m/z : 406 (M$^+$), 232 (100%) ; HRMS Calcd. $C_{24}H_{26}O_4N_2$ : 406.1893, Found : 406.1882

**Preparation of sulfamate esters 2g and 2h**



**1-*tert*-Butoxycarbonyl-3-(2-sulfamoyloxy-ethyl)-1*H*-indole (2g) :** Formic acid (0.18 ml, 4.78 mmol, 2.5 eq.) was added dropwise to neat chlorosulfonylisocyanate (0.42 ml, 4.78 mmol, 2.5 eq) at 0 °C with rapid stirring. Vigorous gas evolution was observed during the addition process. MeCN (5.0 ml) was added and the solution was stirred 8 h at rt. The reaction mixture was cooled to 0 °C and a solution of alcohol **S2** (500 mg, 1.91 mmol) in DMA (5.0 ml) was added dropwise. The reaction mixture was warmed to 25 °C. After the reaction mixture was stirred for 30 min, saturated NaHCO$_3$ was added and the resultant solvent was extracted with AcOEt. The organic layer was washed with brine, dried over MgSO$_4$, concentrated *in vacuo*. The residue was purified by column chromatography (1:1 AcOEt:hexane) to give sulfamate ester **2g** as white solid (476 mg, 1.40 mmol, 73%). An analytical sample was obtained by recrystallization from CHCl$_3$/hexane.

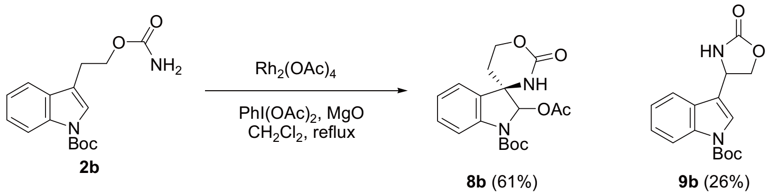
Mp : 124 – 125 °C (CHCl$_3$/Hexane, needle) ; IR (neat) : 3353, 3259, 1721, 1455, 1363, 1346 cm$^{-1}$ ; $^1$H-NMR (400 MHz, CDCl$_3$) δ:8.13 (d, *J* = 8.1 Hz, 1H), 7.53 (d, *J* = 7.3 Hz, 1H), 7.49 (s, 1H), 7.35 – 7.31 (m, 1H), 7.28 – 7.24 (m, 1H), 4.65 (s, 2H), 4.48 (t, *J* = 6.8 Hz, 2H), 3.16 (dt, *J* = 0.97, 6.8 Hz, 2H), 1.67 (s, 9H) ; $^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 149.7, 135.4, 130.1, 124.6, 123.8, 122.6, 118.6, 115.4, 115.3, 83.9, 70.0, 28.2, 24.8 ; MS m/z : 340 (M$^+$), 143 (100%) ; HRMS Calcd. $C_{15}H_{20}O_5N_2S$ : 340.3947, Found : 340.1100



**1-*tert*-Butoxycarbonyl-3-(2-carbamoyloxy-ethyl)-2-methyl-1*H*-indole (2h) :** Formic acid (0.034 ml, 0.907 mmol, 2.5 eq.) was added dropwise to neat chlorosulfonylisocyanate (0.079 ml, 0.907 mmol, 2.5 eq) at 0 °C with rapid stirring. Vigorous gas evolution was observed during the addition process. MeCN (1.8 ml) was added and the solution was stirred 8 h at rt. The reaction mixture was cooled to 0 °C and a solution of alcohol **S4** (100 mg, 0.363 mmol) in DMA was added dropwise. The reaction mixture was warmed to 25 °C. After the reaction mixture was stirred for 30 min, saturated $NaHCO_3$ was added and the resultant solvent was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo*. The residue was purified by column chromatography (1:1 AcOEt:hexane) to give sulfamate ester **2h** as white solid (98 mg, 0.277 mmol, 76%). An analytical sample was obtained by recrystallization from $CHCl_3$/hexane.

Mp 124 – 125 °C ($CHCl_3$/hexane, powder) : IR (neat) :3724, 3271, 1709, 1463, 1364 $cm^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ:8.09 (d, $J$ = 8.8 Hz, 1H), 7.42 (d, $J$ = 7.1 Hz, 1H), 7.25 – 7.19 (m, 2H), 4.79 (s, 2H), 4.28 (t, $J$ = 7.3 Hz, 2H), 3.10 (t, $J$ = 7.3 Hz, 2H), 2.54 (s, 3H), 1.67 (s, 9H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 150.6, 135.7, 135.0, 129.3, 123.6, 122.6, 117.4, 115.5, 112.5, 83.4, 70.0, 28.2, 24.0, 13.9 ; MS m/z : 354 ($M^+$), 144 (100%) ; HRMS Calcd. $C_{16}H_{22}O_5N_2S$ : 354.1249, Found : 354.1252

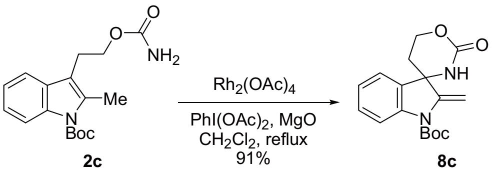
## Spirocyclization of indoyl carbamates and sulfamate esters with $Rh_2(OAc)_4$



**1-*tert*-Butoxycarbonyl-2-(methylcarbonyloxy)-spiro[*3H*-indol-3,6'-[1',3']oxazinan-2'-one (8b)** and **4-(1-*tert*-Butoxycarbonyl-1*H*-indol-3-yl)-oxazolidin-2-one (9b)** : To a solution of carbamate **2b** (88 mg, 0.289 mmol) in $CH_2Cl_2$ (2.9 ml) at rt was added MgO (29.1 mg, 0.723 mmol, 2.5 eq.), $PhI(OAc)_2$ (130 mg, 0.405 mmol, 1.4 eq.) and $Rh_2(OAc)_4$ (6.4 mg, 0.014 mmol, 5 mol%). The reaction mixture was stirred vigorously at reflux for 10 h. The mixture was allowed to cool to rt and filtered through Celite. The filtrate was concentrated *in vacuo*, and the residue was purified by column chromatography (1:1 AcOEt:hexane) to give cyclic carbamate **9b** as colorless oil (23 mg, 0.075 mmol, 26%) and cyclic carbamate **8b** as white amorphous (64 mg, 0.177 mmol, 61%).

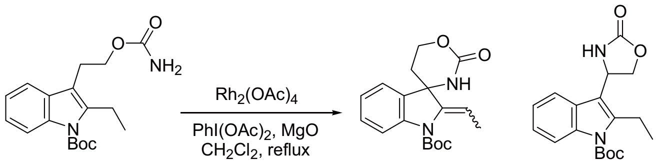
**8b** : IR (neat) : 3238, 3130, 2979, 2930, 1744, 1712, 1604, 1481, 1387 $cm^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 7.83 (br, 1H), 7.35 (dd, *J* = 6.2, 6.2 Hz, 1H), 7.30 (d, *J* = 6.2 Hz, 1H), 7.12 (dd, *J* = 6.1, 6.1 Hz, 1H), 6.55 (s, 1H), 5.69 (br, 1H), 4.68 - 4.62 (m, 1H), 4.37 (dt, *J* = 3.4, 11.7 Hz, 1H), 2.13 (s, 3H), 2.13 – 2.10 (m, 2H), 1.55 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 169.9, 153.3, 151.1, 131.5, 130.5, 124.1, 123.0, 115.2, 86.6, 82.9, 63.7, 62.5, 32.3, 28.1, 20.7 ; MS *m/z* : 362 ($M^+$), 202 (100 %) ; HRMS Calcd. $C_{16}H_{22}O_8N_2$ : 362.1478, Found : 362.1454

**9b** : IR (neat) : 3281, 2979, 2931, 1757, 1737, 1454, 1371 $cm^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 8.17 (d, *J* = 8.3 Hz, 1H), 7.61 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.37 (dd, *J* = 8.3, 8.3 Hz, 1H), 7.28 - 7.24 (m, 1H), 6. 00 (br, 1H), 5.20 (dd, *J* = 7.8, 7.8 Hz, 1H), 4.76 (dd, *J* = 8.8, 8.8 Hz, 1H), 4.41 (dd, *J* = 6.7, 8.5 Hz, 1H), 1.67 (s, 9H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 159.4, 149.3, 136.2, 127.2, 123.7, 123.0, 118.8, 118.6, 115.7, 84.3, 70.4, 49.6, 28.1 ; MS *m/z* : 302 ($M^+$), 57 (100%) ; HRMS Calcd. $C_{16}H_{18}O_2N_4$ : 302.3942, Found : 302.1249



**(3*R*)-1-*tert*-Butoxycarbonyl-2-methylen-spiro[*3H*-indol-3,6'-[1',3']oxazinan-2'-one (8c)** : To a solution of carbamate **2c** (5 g, 15.7 mmol) in $CH_2Cl_2$ (157 ml) at rt was added MgO (1.58 g, 39.3 mmol, 2.5 eq.), $PhI(OAc)_2$ (7.08 g, 22.0 mmol, 1.4 eq.) and $Rh_2(OAc)_4$ (347 mg, 0.785 mmol, 5 mol%). The reaction mixture was stirred vigorously at reflux for 10 h. The mixture was allowed to cool to rt and filterd through Celite. The filtrate was concentrated *in vacuo*, and the residue was purified by column chromatography (1:1 AcOEt:hexane) to give cyclic carbamate **8c** as white amorphous (4.52 g, 14.3 mmol, 91% ).

IR (neat) : 2979, 2933, 1788, 1716, 1654, 1604 $cm^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 8.8 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.12 (dd, *J* = 7.5, 7.5 Hz, 1H), 5.82 (d, *J* = 1.4 Hz, 1H), 5.64 (br, 1H), 5.00 (d, *J* = 1.7 Hz, 1H), 4.56 – 4.50 (m, 1H), 4.41 – 4.36 (m, 1H), 2.08 (t, *J* = 5.8 Hz, 2H), 1.64 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 153.2, 151.1, 150.6, 140.3, 132.0, 130.0, 124.0, 122.6, 116.0, 97.4, 83.4, 62.5, 62.2, 35.5, 28.3 ; MS *m/z* : 316 ($M^+$), 57 (100 %) ; HRMS Calcd. $C_{17}H_{20}O_4N_2$ : 316.3518, Found : 316.1402

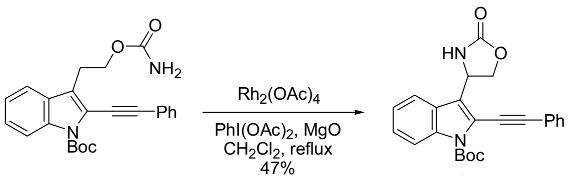


**2d** **8d** (85%) **9d** (10%)

**(2*E/Z*)-1-*tert*-Butoxycarbonyl-2-ethyliden-spiro[*3H*-indol-3,6'-[1',3']oxazinan-2'-one (8d)** and **4-(1-*tert*-Butoxycarbonyl-2-ethyl-1*H*-indol-3-yl-oxazolidin-2-one (9d)** : To a solution of carbamate **2d** (105 mg, 0.316 mmol) in $CH_2Cl_2$ (3.2 ml) at rt was added MgO (31.8 mg, 0.79 mmol, 2.5 eq.), $PhI(OAc)_2$ (142 mg, 0.442 mmol, 1.4 eq.) and $Rh_2(OAc)_4$ (7.7 mg, 0.0158 mmol, 5 mol%). The reaction mixture was stirred vigorously at reflux for 18 h. The mixture was allowed to cool to rt and filterd through Celite. The filtrate was concentrated *in vacuo*, and the residue was purified by column chromatography (1:2 AcOEt:hexane) to give cyclic carbamate **9d** as colorless oil (10.7 mg, 0.0323 mmol, 10% ) and . cyclic carbamate **8d** as white amorphous (87.9 mg, 0.267 mmol, 85%).

**9d** : IR (neat) : 3269, 2979, 2933, 1735, 1604 $cm^{-1}$ ; $^1H$-NMR (400 MHz, $CDCl_3$) δ: 8.12 (d, *J* = 8.3 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.30 – 7.20 (m, 2H), 5.49 (br, 1H), 5.31 – 5.27 (m, 1H), 4.71 – 4.67 (m, 1H), 4.51 – 4.47 (m, 1H), 3.11 (dt, *J* = 14.5, 7.4 Hz, 1H), 3.00 (dt, *J* = 14.5, 7.4 Hz, 1H), 1.72 (s, 9H), 1.22 (t, *J* = 7.4 Hz, 3H) ; $^{13}C$-NMR (100 MHz, $CDCl_3$) δ: 159.1, 149.9, 141.5, 136.2, 126.3, 124.1, 123.0, 118.6, 115.8, 113.4, 84.5, 69.7, 48.9, 28.2, 19.8, 15.8 ; MS m/z : 330 ($M^+$), 57 (100%) ; HRMS Calcd. $C_{18}H_{22}O_4N_2$ : 330.1580, Found : 330.1582

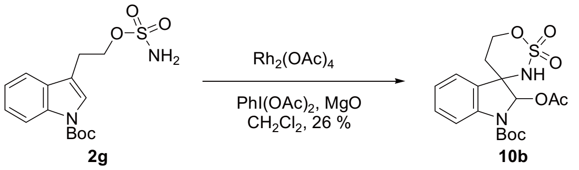
**8d** : IR (neat) : 3244, 2979, 2927, 1707 $cm^{-1}$ ; $^1H$-NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, *J* = 8.5 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 0.9H), 7.33 – 7.27 (m, 3.8H), 7.15 – 7.08 (m, 1.9H), 6.52 (q, *J* = 7.7 Hz, 1H), 5.66 (br, 1H), 5.45 (q, *J* = 7.0 Hz, 0.9H) , 5.36 (br, 0.9H), 4.54 (dt, *J* = 16.0, 5.6 Hz, 1H), 4.48 – 4.39 (m. 1.9H), 4.31 (dt, 11.2, 4.0 Hz, 0.9 H), 2.53 – 2.45 (m, 1H), 1.95 (d, *J* = 7.7 Hz, 3H), 1.74 (d, *J* = 7.7 Hz, 2.8H), 1.62 (s, 9H), 1.58 (s, 8.1 H) ; $^{13}C$-NMR (100 MHz, $CDCl_3$) δ:153.9, 153.5, 151.8, 150.8, 143.2, 141.5, 141.5, 140.0, 134.1, 133.3, 129.5, 129.4, 124.4, 123.5, 122.8, 122.0, 117.2, 116.5, 112.4, 111.7, 82.8, 82.4, 63.3, 62.7, 61.6, 60.3, 33.3, 33.1, 28.3, 28.1, 14.4, 11.7 ; MS m/z : 330 ($M^+$), 57 (100 %) ; HRMS Calcd. $C_{18}H_{22}O_4N_2$ : 330.1580, Found : 330.1588



**2e** **9e**

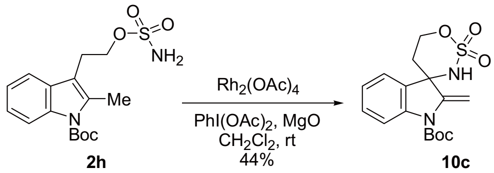
**4-(1-*tert*-Butoxycarbonyl-2-phenylethynyl-1*H*-indol-3-yl)-oxazolidin-2-one (9e)** : To a solution of carbamate **2e** (70 mg, 0.173 mmol) in $CH_2Cl_2$ (1.7 ml) at rt was added MgO (17.4 mg, 0.435 mmol, 2.5 eq.), $PhI(OAc)_2$ (78 mg, 0.242 mmol, 1.4 eq.) and $Rh_2(OAc)_4$ (3.8 mg, 8.7 μmol, 5 mol%). The reaction mixture was stirred vigorously at reflux for 24 h. The mixture was allowed to cool to rt and filterd through Celite. The filtrate was concentrated *in vacuo*, and the residue was purified by column chromatography (1:1 AcOEt:hexane) to give cyclic carbamate **9e** as brown oil (32.9 mg, 0.109 mmol, 47% ).

IR (neat) : 3272, 2981, 1747 cm$^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 8.22 (d, *J* = 8.6 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.56 – 7.53 (m, 2H), 7.41 – 7.39 (m, 4H), 7.31 – 7.27 (m, 2H), 5.57 – 5.53 (dd, *J* = 7.0, 9.0 Hz, 1H), 5.36 (br, 1H), 4.81 (t, *J* = 9.0 Hz, 1H), 4.55 (dd, *J* = 7.0, 8.8 Hz, 1H), 1.68 (s, 9H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 158.9, 149.0, 136.0, 131.4, 129.1, 126.3, 125.6, 124.1, 123.6, 122.1, 119.4, 119.1, 115.9, 99.3, 84.9, 79.6, 69.6, 49.5, 28.3 ; MS m/z : 402 (M$^+$), 41 (100%) ; HRMS Calcd. $C_{24}H_{22}O_4N_2$ : 402.1580, Found : 402.1587



**1-*tert*-Butoxycarbonyl-2-(methylcarbonyloxy)-spiro[*3H*-indol-3,4'-[1',2',3']oxathiazinan-2',2'-dione (10b) :** To a solution of sulfamate ester **2g** (70 mg, 0.206 mmol) in $CH_2Cl_2$ (2.1 ml) at rt was added MgO (19 mg, 0.473 mmol, 2.3 eq.), $PhI(OAc)_2$ (73 mg, 0.226 mmol, 1.1 eq.) and $Rh_2(OAc)_4$ (1.8 mg, 4.1 µmol, 2 mol%). The reaction mixture was stirred vigorously at rt for 2 h. The mixture was filterd through Celite. The filtrate was concentrated *in vacuo*, and the residue was purified by column chromatography (1:2 AcOEt:hexane) to give cyclic sulfamate ester **10b** as colorless oil (21 mg, 0.0527 mmol, 26%).

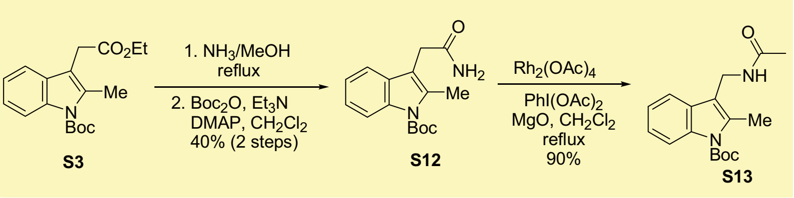
IR (neat) : 3267, 2980, 1763, 1718, 1605, 1483, 1389, 1308 cm$^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ:7.79 (d, *J* = 7.3 Hz, 1H), 7.45 – 7.43 (m, 1H), 7.37 – 7.33 (m, 1H), 7.13 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.93 (s, 1H), 5.02 (s, 1H), 4.97 (ddd, *J* = 2.4, 12, 12 Hz, 1H), 4.63 (ddd, *J* = 2.4, 4.9, 12 Hz, 1H), 2.31 (ddd, *J* = 4.9 , 12.0, 15.0 Hz, 1H), 2.10 (s, 3H), 2.05 – 2.01 (m, 1H), 1.56 (s, 9H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 167.9, 151.1, 139.9, 131.1, 130.8, 124.2, 123.1, 115.6, 83.3, 83.1, 69.8, 66.7, 32.5, 28.2, 20.9 ; MS *m/z* : 398 (M$^+$), 144 (100 %) ; HRMS Calcd. $C_{17}H_{22}O_8N_2O_7S$ : 398.1148, Found : 3398.1150



**1-*tert*-Butoxycarbonyl-2-methylen-spiro[*3H*-indol-3,4'-[1',2',3']oxathiazinan-2',2'-dione (10c)** : To a solution of sulfamate ester **2h** (50 mg, 0.141 mmol) in $CH_2Cl_2$ (1.4 ml) at rt was added MgO (13 mg, 0.324 mmol, 2.3 eq.), $PhI(OAc)_2$ (50 mg, 0.156 mmol, 1.1 eq.) and $Rh_2(OAc)_4$ (1.2 mg, 2.8 μmol, 2 mol%). The reaction mixture was stirred vigorously at rt for 2 h. The mixture was filterd through Celite. The filtrate was concentrated *in vacuo*, and the residue was purified by column chromatography (1:2 AcOEt:hexane) to give cyclic sulfamate ester **10c** as white amorphous (22 mg, 0.0624 mmol, 44%)

IR (neat) : 3272, 2979, 2930, 1715, 1480, 1355 $cm^{-1}$ ; $^1H$-NMR (400 MHz, $CDCl_3$) δ: 7.82 (m, 2H), 7.37 – 7.33 (m, 2H), 7.15 (dd, $J$ = 7.6, 7.6 Hz, 1H), 5.94 (d, $J$ = 2.1 Hz, 1H), 5.27 (d, $J$ = 2.1 Hz, 1H), 4.87 (ddd, $J$ = 4.3, 8.7, 11.6 Hz, 1H), 4.81 – 4.69 (m, 1H), 2.40 (ddd, $J$ = 5.1, 8.7, 15.0 Hz, 1H), 2.30 (ddd, $J$ = 4.5, 5.6, 15.0 Hz, 1H), 1.64 (s, 9H) ; $^{13}C$-NMR (100 MHz, $CDCl_3$) δ: 151.0, 150.4, 140.3, 130.7, 130.2, 124.2, 124.1, 116.0, 97.6, 83.7, 68.3, 65.4, 34.5, 28.3 ; MS *m/z* : 352 ($M^+$), 57 (100 %) ; HRMS Calcd. $C_{16}H_{20}O_5N_2S$ : 352.1093, Found : 352.1084

## Preparation of acetamide S13 and reaction of S13 with $Rh_2(OAc)_4$ and $PhI(OAc)_2$



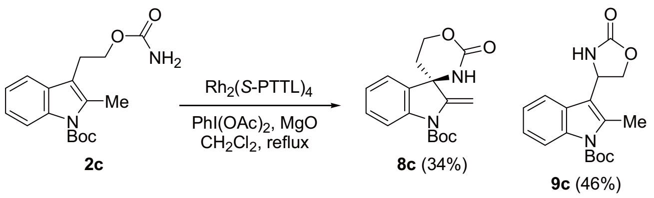
**2-(1-*tert*-Butoxycarbonyl-2-methyl-1*H*-indol-3-yl)-acetamide (S12) :** To a sealed-tube was added ester **S3** (1.4 g, 4.41 mmol) in saturated $NH_3$/MeOH. The reaction mixture was stirred at reflux for 5 days. The mixture was allowed to cool to rt and the solvent was removed *in vacuo* to provide a amide product that was carried on without further purification. To a solution of crude mixture in $CH_2Cl_2$ (54 ml) at rt was added $Et_3N$ (1.9 ml, 13.4 mmol, 2.5 eq.), $Boc_2O$ (1.9 ml, 8.1 mmol, 1.5 eq.) and DMAP (66 mg, 0.54 mmol, 10 mol%). After the reaction mixture was stirred for 30 min, water was added and the resultant solution was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo*, and the crude products was purified by column chromatography (2:1 AcOEt-Hexane) to give acetamide **S12** as yellow oil (514 mg, 1.78 mmol, 40% for 2 steps):

IR (neat) :3355, 3272, 3260, 2986, 1720, 1646, 1455, 1363, 1347 $cm^{-1}$ ; $^1H$-NMR (400 MHz, $CDCl_3$) δ: 8.11 (d, $J$ = 7.8 Hz, 1H), 7.44 (d, $J$ = 7.1 Hz, 1H), 7.30 – 7.22 (m, 2H), 5.50 (br, 2H), 3.64 (s, 2H), 2.58 (s, 3H), 1.69 (s, 9H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 172.9, 150.5, 135.8, 135.4, 129.1, 124.1, 123.0, 117.7, 115.6, 111.8, 84.1, 31.8, 28.3, 14.0 ; MS *m/z* : 288.1 ($M^+$), 144.1 (100 %) ; HRMS Calcd. $C_{16}H_{20}O_3N_2$ : 288.1474, Found : 288.1460

***N*-(1-*tert*-Butoxycarbonyl-2-methylindol-3-yl)-methylacetamide (S13) :** To a solution of acetamide **S12** (25 mg, 0.0867 mmol) in $CH_2Cl_2$ (2.0 ml) at rt was added MgO (8.7 mg, 0.217 mmol, 2.5 eq.), $PhI(OAc)_2$ (39.1 mg, 0.121 mmol, 1.4 eq.) and $Rh_2(OAc)_4$ (1.9 mg, 4.3 μmol, 5 mol%). The reaction mixture was stirred vigorously at reflux for 10 h. The mixture was allowed to cool to rt and filterd through Celite. The filtrate was concentrated *in vacuo*, and the residue was purified by column chromatography (2:1 AcOEt:hexane) to give acetamide **S13** as yellow oil (23.6 mg, 0.0824 mmol, 90% ) :

IR (neat) :3463, 3336, 3196, 2979, 2931, 1730, 1668, 1457, 1357, 1324 cm$^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 8.10 (d, $J$ = 7.7 Hz, 1H), 7.49 (d, $J$ = 7.0 Hz, 1H), 7.29 – 7.21 (m, 2H), 5.48 (br, 1H), 4.54 (s, 1H), 4.52 (s, 1H), 2.60 (s, 3H), 2.00 (s, 3H), 1.68 (s, 9H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 169.7, 150.4, 135.6, 135.5, 128.7, 123.8, 122.8, 117.7, 115.5, 114.4, 84.0, 33.6, 28.3, 23.3, 14.0 ; MS *m/z* : 302.2 ($M^+$), 143.1 (100 %) ; HRMS Calcd. $C_{17}H_{22}O_3N_2$ : 302.1630, Found : 302.1630

## Enantioselective spirocyclization

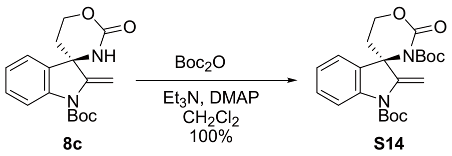


**4-(1-*tert*-Butoxycarbonyl-2-methyl-1*H*-indol-3-yl)-oxazolidin-2-one (9c)** : To a solution of carbamate **2c** (100 mg, 0.314 mmol) in $CH_2Cl_2$ (3.1 ml) at rt was added MgO (31.7 mg, 0.785 mmol, 2.5 eq.), $PhI(OAc)_2$ (142 mg, 0.440 mmol, 1.4 eq.) and $Rh_2$(*S*-PTTL)$_4$ (19.6 mg, 15.7 μmol, 5 mol%). The reaction mixture was stirred vigorously at reflux for 21 h. The mixture was allowed to cool to rt and filterd through Celite. The filtrate was concentrated *in vacuo*, and the residue was purified by column chromatography (1:1 AcOEt:hexane) to give oxazolidinone **9c** as white amorphous (46.2 mg, 0.146 mmol, 46%) and cyclic carbamate **8c** as white amorphous (33.9 mg, 0.107 mmol, 34%).

**8c** : $[\alpha]_D^{30}$ + 82.9° (*c* 0.44, $CHCl_3$)

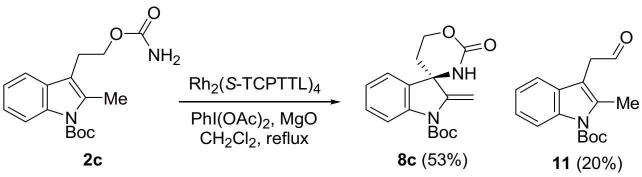
**9c** : IR (neat) : 3237, 2979, 2932, 1768, 1717, 1606 cm$^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 8.12 (d, $J$ = 8.5 Hz, 1H), 7.60 (d, $J$ = 7.7 Hz, 1H), 7.31 – 7.29 (m, 1H), 7.22 (dd, $J$ = 7.6, 7.6 Hz, 1H), 5.62 (br, 1H), 5.29 (dd, $J$ = 8.3, 8.3 Hz, 1H), 4.69 (dd, $J$ = 9.1, 9.1 Hz, 1H), 4.48 (dd, $J$ = 8.1, 8.1 Hz, 1H), 2.57 (s, 3H), 1.69 (s, 9H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 159.3, 150.3, 136.1, 135.6, 126.5, 123.0, 118.4, 115.7, 114.4, 84.4, 69.6, 48.8, 28.2, 13.8 ; MS *m/z* : 316 ($M^+$), 260 (100%) ; HRMS Calcd. $C_{17}H_{20}O_4N_2$ : 316.3518, Found : 316.1401

## Determination of enantio excess



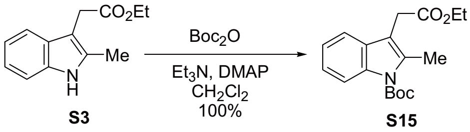
**(3*R*)-1,1'-Di-*tert*-butoxycarbonyl-2-methylene-spiro[3*H*-indole-3,6'-[1',3']oxazinan]-2'-one (S14)** : To a solution of cyclic carbamate **8c** (80 mg, 0.253 mmol) in $CH_2Cl_2$ (1.3 ml) at rt was added $Et_3N$ (0.11 ml, 0.759 mmol, 3 eq.), $Boc_2O$ (0.083 ml, 0.380 mmol, 1.5 eq.) and DMAP (3.1 mg, 25.3 μmol, 10 mol%). After the reaction mixture was stirred for 1 h, water was added and the resultant solution was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo*. The residue was purified by column chromatography (1:2 AcOEt:hexane) to give cyclic carbamate **S14** as white amorphous (105 mg, 0.253 mmol 100%).

$[\alpha]_D^{31}$ -5.6° (*c* 0.50, $CHCl_3$) ; IR (neat) : 2979, 1788, 1716, 1654, 1604 $cm^{-1}$ ; $^1H$-NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 8.5 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.10 (dd, *J* = 7.6, 7.6 Hz, 1H), 5.78 (d, *J* = 2.2 Hz, 1H), 4.88 (d, *J* = 2.2 Hz, 1H), 4.56 – 4.51 (m, 1H), 4.42 – 4.36 (m, 1H), 2.25 (dd, *J* = 5.1, 5.5 Hz, 2H), 1.65 (s, 9H), 1.12 (s, 9H) ; $^{13}C$-NMR (100 MHz, $CDCl_3$) δ: 151.2, 150.0, 149.9, 140.1, 132.9, 129.3, 123.8, 121.3, 116.0, 94.3, 84.1, 83.5, 66.5, 61.5, 38.9, 28.3, 27.2 ; MS *m/z* : 416 ($M^+$), 216 (100%) ; HRMS Calcd. $C_{22}H_{28}O_6N_2$ : 416.1947, Found : 416.1959 ; HPLC: column, Daicel Chiralpak AD-H; eluent, *n*-hexane:*i*-PrOH 10:1; flow rate, 0.5 ml/min; retention time 24.9 min [(*R*)-**S14**] and 37.9 min [(*S*)-**S15**]



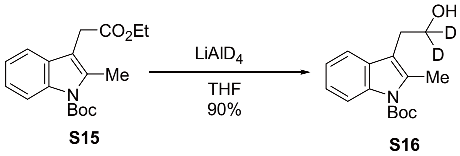
**(1-*tert*-Butoxycarbonyl-2-methyl-1*H*-indol-3-yl)-formaldehyde (11)** : To a solution of carbamate **2c** (70 mg, 0.220 mmol) in $CH_2Cl_2$ (22 ml) at rt was added MgO (22.2 mg, 0.55 mmol, 2.5 eq.), PhI$(OAc)_2$ (145 mg, 0.462 mmol, 2.1eq.) and $Rh_2$(*S*-TCPTTL$)_4$ (27.7 mg, 0.0154 mmol, 7 mol%). The reaction mixture was stirred vigorously at reflux for 48 h. The mixture was allowed to cool to rt and filterd through Celite. The filtrate was concentrated *in vacuo*, and the residue was purified by column chromatography (1:6 AcOEt:hexane) to give aldehyde **11** as brown oil (12.0 mg, 0.0439 mmol, 20%) and elution of the column of with AcOEt:hexane (1:1) gave cyclic carbamate **8c** (36.8 mg, 0.116 mmol, 53%).

**11** : IR (neat) : 3051, 2932, 1728 cm$^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 9.65 (t, *J* = 2.2 H, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.29 – 7.21 (m, 2H), 3.71 (d, *J* = 2.2 Hz, 2H), 2.56 (s, 3H), 1.69 (s, 9H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 198.4, 150.5, 135.8, 135.7, 129.5, 123.9, 122.8, 117.4, 115.6, 108.7, 84.0, 39.3, 28.3, 14.1 ; MS *m/z* : 273 (M$^+$), 144 (100%) ; HRMS Calcd. $C_{16}H_{19}O_3N$ : 273.1365, Found : 273.1351



**Ethyl (1-*tert*-butoxycarbonyl-2-methyl-1*H*-indol-3-yl)-acetate (S15)**: To a solution of indole **S3** (1.81 g, 8.43 mmol) in $CH_2Cl_2$ (21.1 ml) at rt was added $Et_3N$ (3.54 ml, 25.3 mmol, 3 eq.), $Boc_2O$ (2.90 ml, 12.6 mmol, 1.5 eq.) and DMAP (51.5 mg, 0.422 mmol, 5 mol%). After the reaction mixture was stirred for 30 min, water was added and the resultant solution was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo*. The residue was purified by column chromatography (1:10 AcOEt:hexane) to give indole **S15** as yellow oil (2.67 g, 8.43 mmol 100%).

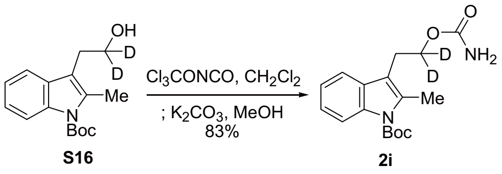
IR (neat) : 2979, 2933, 1733 cm$^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 8.09 (d, *J* = 7.5 Hz, 1H), 7.48 – 7.46 (m, 1H), 7.25 – 7.19 (m, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.66 (s, 2H), 2.58 (s, 3H), 1.68 (s, 9H), 1.23 (t, *J* = 7.1 Hz, 3H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 171.1, 150.6, 135.6, 135.1, 129.6, 123.5, 122.5, 117.9, 115.4, 111.4, 83.7, 60.9, 30.3, 28.3, 14.2, 14.1 ; MS *m/z* : 317 (M$^+$), 144 (100%) ; HRMS Calcd. $C_{18}H_{23}O_4N$ : 317.1627, Found : 317.1635



**2-(1-*tert*-Butoxycarbonyl-2-methyl-1*H*-indol-3-yl)-[1,1-$^2$H$_2$]-ethanol (S16)** : To a solution of $LiAlD_4$ (94 mg, 2.23 mmol, 1.0 eq.) in THF (5.5 ml) at 0 °C was added a solution of indole **S15** (708 mg, 2,23 mmol) in THF (5.5 ml). After the reaction mixture was stirred for 5 min, the reaction was quenched with $H_2O$. The resultant mixture was filtered through Celite, and concentrated *in vacuo*.

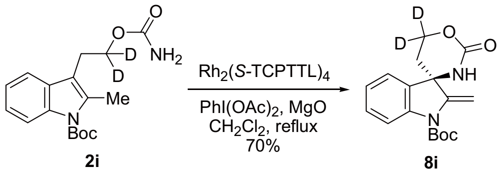
The resulting mixture was extracted with AcOEt, washed brine, dried over $MgSO_4$, concentrated *in vacuo*. The residue was purified by column chromatography (1:2 AcOEt:hexane) to give alcohol **S16** as yellow oil (557 mg, 2.01 mmol, 90%).

IR (neat) : 3366, 2978, 2931, 1729 $cm^{-1}$ ; $^1H$-NMR (400 MHz, $CDCl_3$) δ: 8.10 (d, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 7.3 Hz, 1H), 7.25 – 7.19 (m, 2H), 2.93 (m, 2H), 2.56 (s, 3H), 1.68 (s, 9H) ; $^{13}C$-NMR (100 MHz, $CDCl_3$) δ: 150.7, 135.8, 134.5, 129.9, 123.5, 122.5, 117.7, 115.4, 114.3, 83.6, 28.3, 27.3, 14.0 ; MS *m/z* : 277 ($M^+$), 144 (100%) ; HRMS Calcd. $C_{16}H_{19}D_2O_3N$ : 277.1645, Found : 277.1642



**1-*tert*-Butoxy-3-(2-carbamoyloxy-[2,2-$^2H_2$]-ethyl)-2-methyl-1*H*-indole (2i)** : To a solution of alcohol **S16** (557 mg, 1.98 mmol) in $CH_2Cl_2$ (9.9 ml) at 0 °C was added trichloroacetyl isocyanate (0.284 ml, 2.38 mmol, 1.2 eq.) and the mixture was stirred for 5 min. When TLC indicated consumption of the alcohol, MeOH (9.9 ml) and $K_2CO_3$ (27.4 mg, 0.198 mmol, 0.1 eq.) was added to the reaction mixture. The mixture was allowed to warm to rt and stirred for 8 h. Then, water was added and the resultant solution was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo*, and the crude products was purified by column chromatography (1:2 AcOEt:hexane) to give carbamate **2i** as colorless needle (547 mg, 1.71 mmol, 86%). An analytical sample was obtained by recrystallization from MeOH.

mp = 150 – 151 °C (MeOH) ; IR (neat) : 3421, 3332, 3272, 2979, 1722, 1699, 1605 $cm^{-1}$ ; $^1H$-NMR (400 MHz, $CDCl_3$) δ: 8.09 (d, *J* = 7.3 Hz, 1H), 7.48 (d, *J* = 6.3 Hz, 1H), 7.26 – 7.22 (m, 2H), 4.54 (br, 2H), 3.00 (s, 2H), 2.56 (s, 3H), 1.68 (s, 9H) ; $^{13}C$-NMR (100 MHz, $CDCl_3$) δ: 156.8, 150.7, 135.7, 134.4, 129.9, 123.4, 122.5, 117.6, 115.4, 114.0, 83.6, 28.3, 23.8, 13.9 ; MS *m/z* : 277 ($M^+$), 144 (100%) ; HRMS Calcd. $C_{16}H_{19}D_2O_3N$ : 277.1645, Found : 277.1639

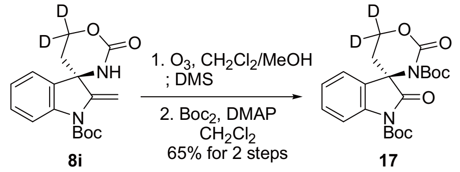


**(3*R*)-1-*tert*-Butoxycarbonyl-2-methylen-spiro[3*H*-indol-3,6’-[4’,4’-$^2H_2$]-[1’,3’]oxazinan-2’-one (8i) :** To a solution of carbamate **2i** (70 mg, 0.218 mmol) in $CH_2Cl_2$ (21.8 ml) at rt was added MgO (26.4 mg, 0.655 mmol, 3 eq.), $PhI(OAc)_2$ (113 mg, 0.351 mmol, 1.6 eq.) and $Rh_2$(*S*-TCPTTL)$_4$ (27.5

mg, 0.153 µmol, 7 mol%). The reaction mixture was stirred vigorously at reflux for 48 h. The mixture was allowed to cool to rt and filterd through Celite. The filtrate was concentrate *in vacuo*, and the residue was purified by column chromatography (1:2 AcOEt:hexane) to give cyclic carbamate **8i** as white amorphous (48.5 mg, 0.152 mmol, 70%).

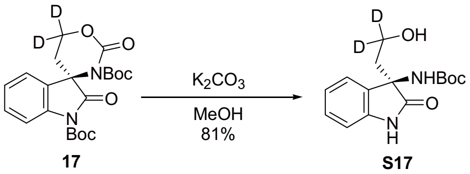
$[\alpha]_D^{25}$ + 52.7° (*c* 0.93, $CHCl_3$) ; IR (neat) : 3242, 3120, 2979, 1713, 1605 $cm^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 8.6 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.12 (dd, *J* = 7.4, 7.4 Hz, 1H), 5.82 (d, *J* = 1.7 Hz, 1H), 5.26 (br, 1H), 5.00 (d, *J* = 1.6 Hz, 1H), 2.08 (s, 2H), 1.64 (s, 9H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 153.4, 151.0, 150.6, 140.2, 132.0, 129.9, 123.9, 122.6, 115.9, 97.2, 83.3, 62.3, 35.3, 28.2 ; MS *m/z* : 318 ($M^+$), 57 (100%) ; HRMS Calcd. $C_{17}H_{18}D_2O_4N_2$ : 318.1547, Found : 318.1538

## Synthesis of chiral spiro-β-lactam 23



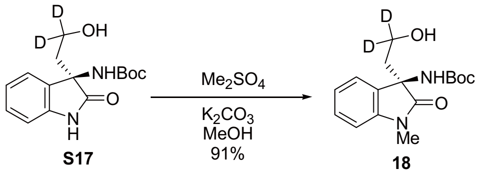
**1,1'-Di-*tert*-butoxycarbonyl-spiro[2,3-dihydro-1*H*-indol-3,6'-[4',4'-$^2$H2]-[1',3']oxazinan]-2,2'-dione (17)** : Cyclic carbamate **8i** (1.134 g, 3.56 mmol) was dissolved in $CH_2Cl_2$/MeOH (1:1 178 ml). The solution was cooled at -78 °C and ozone was introduced for 5 min and followed by argon gas for 20 min. The mixture was added $Me_2S$ (2.62 ml, 35.6 ml, 10 eq.), allowed to warm slowly at rt and stirred for overnight. The solution was concentrated *in vacuo*. To the crude mixture in $CH_2Cl_2$ (35.6 ml) was added $Boc_2O$ (1.23 ml, 5.34 mmol, 1.5 eq.) and DMAP (43.5 mg, 0.356 mmol, 10 mol%). After the reaction mixture was stirred for 10 min, water was added and the resultant solvent was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo*. The residue was purified by column chromatography (1:2 AcOEt:hexane) to give amide **17** as white amorphous (980 mg, 2.33 mmol, 65% for 2 steps)

$[\alpha]_D^{29}$ + 37.2° (*c* 1.19, $CHCl_3$) ; IR (neat) : 2982, 1794, 1733, 1608 $cm^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 7.93 (d, *J* = 8.2 Hz, 1H), 7.42 (ddd, *J* = 1.2, 7.5, 8.2 Hz, 1H), 7.33 (dd, *J* = 1.2, 7.5 Hz, 1H), 7.24 (ddd, *J* = 1.0, 7.5, 7.5 Hz, 1H), 2.34 (d, *J* = 14.8 Hz, 1H), 2.24 (d, *J* = 14.8 Hz, 1H), 1.66 (s, 9H), 1.15 (s, 9H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 173.1, 149.1, 148.8, 148.6, 138.3, 129.8, 129.1, 125.0, 121.4, 115.4, 85.1, 84.9, 63.4, 33.6, 27.9, 26.9 ; MS *m/z* : 420 ($M^+$), 220 (100%) ; HRMS Calcd. $C_{21}H_{24}D_2O_7N_2$ : 420.1864, Found : 420.1862



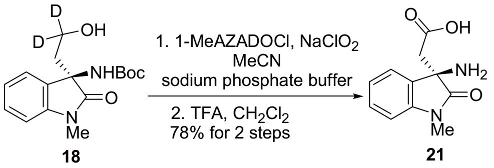
**(3*R*)-3-*tert*-Butoxycarbonylamino-3-(2-hydroxy-[2,2-$^2$H2]-ethyl)-2,3-dihydo-1*H*-indol-2-one (S17)** : To a solution of cyclic carbamate **17** (980 mg, 2.33 mmol) in MeOH (23.3 ml) was added $K_2CO_3$ (64.4 mg, 0.466 mmol, 0.2 eq.) at rt, and stirred for 13 h. The reaction was poured into saturated $NH_4Cl$, extracted with AcOEt, washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography (2:1 AcOEt:hexane) to give alcohol **18** as white amorphous (554 mg, 1.88 mmol, 81% );

$[\alpha]_D^{25}$ + 15.9° (*c* 0.60, $CHCl_3$) ; IR (neat) : 3314, 2979, 1722, 1621cm$^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 9.23 (br, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.18 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.01 (dd, *J* = 7.5, 7.7 Hz, 1H), 6.90 (br, 1H), 6.88 (d, *J* = 7.5 Hz, 1H), 2.10 (d, *J* = 14.7 Hz, 2H), 1.98 (d, *J* = 14.7 Hz, 1H), 1.26 (br, 9H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 180.1, 154.4, 140.4, 131.6, 128.6, 122.7, 122.5, 110.5, 80.4, 62.0 , 57.2, 38.6, 28.0 ; MS m/z : 294 ($M^+$), 147 (100%) ; HRMS Calcd. $C_{15}H_{18}D_2O_4N_2$ : 294.1547, Found : 294.1567

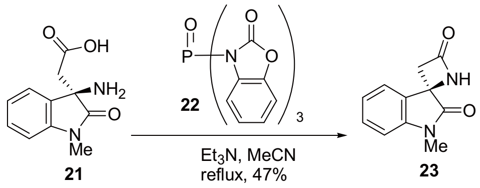


**(3*R*)-3-*tert*-Butoxycarbonylamino-3-(2-hydroxy-[2,2-$^2$H2]-ethyl)-1-methyl-2,3-dihyrdo-1*H*-indol-2-one (18)** : To a solution of alcohol **S17** (550 mg, 1.87 mmol) in acetone (9.3 ml) at rt was added $K_2CO_3$ (387 mg, 2.81 mmol, 1.5 eq.), and $Me_2SO_4$ (0.266 ml, 2.81 mmol, 1.5 eq.). The reaction mixture was stirred at reflux for 2 h. The mixture was allowed to cool to rt and poured into saturated $NH_4Cl$, extracted with AcOEt, washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography (2:1 AcOEt:hexane) to give alcohol **18** as white amorphous (525 mg, 1.70 mmol, 91% );

$[\alpha]_D^{24}$ + 28.4° (*c* 0.805, $CHCl_3$) ; IR (neat) : 3354, 2978, 2933, 1712, 1614cm$^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 7.32 - 7.28 (m, 2H), 7.07 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.32 (br, 1H), 3.24 (s, 3H), 1.98 (s, 2H), 1.23 (br, 9H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 177.6, 154.1, 142.6, 131.2, 128.4, 122.5, 122.5, 108.0, 79.9, 61.5, 38.5, 27.8, 26.3 ; MS m/z : 308 ($M^+$), 161 (100 %) ; HRMS Calcd. $C_{16}H_{20}D_2O_4N_2$ : 308.1703, Found : 308.1686



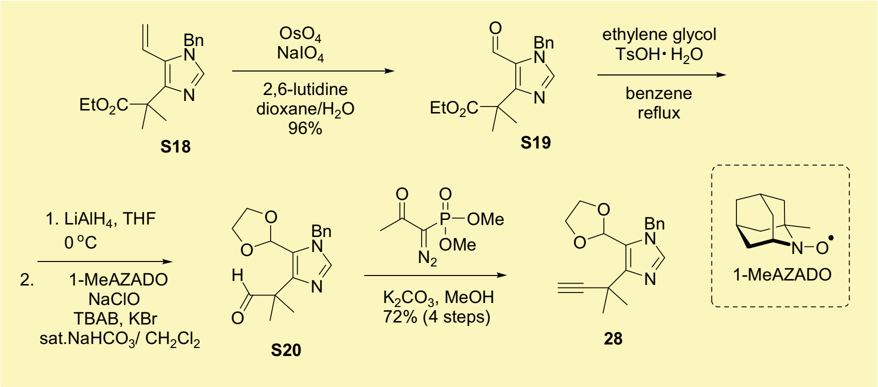
**(3*R*)-(3-Amino-1-methyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl)-acetic acid (20)** : To a solution of alcohol **18** (173 mg, 0.565 mmol) in MeCN (2.8 ml) and sodium phosphate buffer (pH 6.8, 1.0 M, 2.8 ml) was added NaClO$_2$ (80%, 192 mg, 1.70 mmol, 3.0 eq.) and 1-MeAZADOCl (**19**) (5.7 mg, 28.3 μmol, 5 mol%) at rt, and stirred for 1 h. The reaction was quenched with 2-methyl-2-butene, and the aqueous solution basified to pH 9 with 5% NaOH. The basic solution was washed with ether and then acidified to pH 5 with 10% HCl. The acidic solution was extracted with CHCl$_3$, washed with brine, dried over MgSO$_4$ and concentrated *in vacuo*. To a solution of crude mixture in CH$_2$Cl$_2$ (2.8 ml) at 0 $^o$C was added TFA (0.419 ml, 5.65, 10 eq.) and allowed to warm at rt. After the reaction was stirred for 3 h, benzene was added and concentrated *in vacuo*. This manipulation was repeated three times. The residue was neutralized with saturated NaHCO$_3$ and purified by ion-exchange resin (DOWEX, 50WX8, 200-400) to give β-amino acid **21** as white powder (97 mg, 0.440 mmol, 78% for 2 steps);
Mp : 123 - 126 $^o$C (MeCN) ; $[\alpha]_D^{25}$ + 76.0° (*c* 0.380, CHCl$_3$) ; IR (neat) : 2935, 1714, 1612cm$^{-1}$ ; $^1$H-NMR (500 MHz, D$_2$O) δ: 7.40 (d, *J* = 7.6 Hz, 1H), 7.37 (dd, *J* = 7.6, 7.8 Hz, 1H), 7.10 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 3.14 (s, 3H), 2.84 (d, *J* = 15.6 Hz, 1H), 2.76 (d, *J* = 15.6 Hz, 1H) ; $^{13}$C-NMR (125 MHz, D$_2$O ) δ: 177.9, 176.3, 144.1, 131.1, 128.4, 124.4, 124.2, 110.5, 59.3, 43.4, 27.1 ; FAB m/z : 221 (M+1)$^+$, 221 (100 %) ; HRFAB Calcd. C$_{11}$H$_{12}$O$_3$N$_2$ : 221.0926, Found : 221.0926

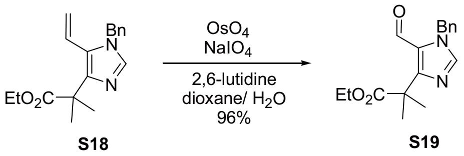


**(3*R*)-1-Methyl-spiro[2,3-dihydro-1*H*-3,4'-azelidin]-2,2'-dione (23)** : To a solution of **21** β-amino acid (30 mg, 0.136 mmol) in MeCN (13.6 ml) at rt was added Et$_3$N (0.057 ml, 0.408 mmol, 3.0 eq.), and **22** (91.8 mg, 0.204 mmol, 1.5 eq.). The reaction mixture was stirred at reflux for 6 h. The mixture was allowed to cool to rt and concentrated *in vacuo*. The residue was purified by column chromatography (1:1 AcOEt:hexane) to give β-lactam **23** as white powder (13 mg, 0.0643 mmol, 47% ); Mp : 236 – 238 $^o$C (CHCl$_3$/hexane) ;
$[\alpha]_D^{25}$ + 46.0° (*c* 0.470, CHCl$_3$) ; IR (neat) : 3276, 1774, 1686, 1616 cm$^{-1}$ ; $^1$H-NMR (400 MHz, CDCl$_3$) δ: 7.46 (dd, *J* = 0.7, 7.5 Hz, 1H), 7.39 (dt, *J* = 1.2, 7.7 Hz, 1H), 7.15 (dt, *J* = 0.7, 7.5 Hz, 1H),

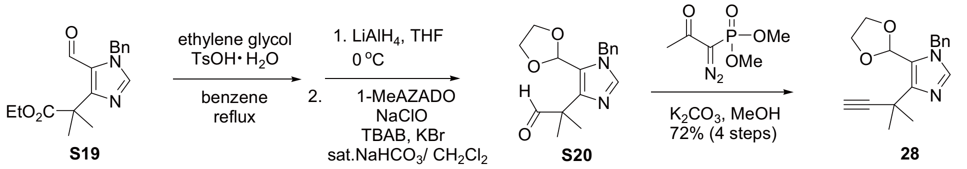
6.88 (d, $J$ = 8.0 Hz, 1H), 6.09 (br, 1H), 3.49 (dd, $J$ = 2.2, 14.5 Hz, 1H), 3.25 (s, 3H), 3.24 (dd, $J$ = 1.2, 14.5 Hz, 1H) ; $^{13}$C-NMR (125 MHz, $CDCl_3$) δ: 175.1, 166.4, 143.5, 130.4, 126.7, 123.4, 123.3, 108.7, 55.9, 50.9, 26.6 ; MS m/z : 202 ($M^+$), 202 (100 %) ; HRMS Calcd. $C_{11}H_{10}O_2N_2$ : 202.0742, Found : 202.0724

## Preparation of imidazole 28 and Sonogashira couping





**S19** : To a solution of imidazole **S18**[2] (1.0 g, 3.35 mmol) in dioxane (24 ml) and $H_2O$ (8 ml) at rt were added 2,6-lutidine (0.78 ml, 6.70 mmol, 2.0 eq.), $OsO_4$ (0.1965 M in THF, 0.512 ml, 0.101 mmol, 3.0 mol%) and $NaIO_4$ (2.87 g, 13.4 mmol, 4.0 eq.). After the reaction mixture was stirred for 2 h, water was added and the resultant solution was extracted with AcOEt. The organic layer was washed with 2% HCl and brine, dried over $MgSO_4$, concentrated *in vacuo*. The residue was purified by column chromatography (1:1 AcOEt:hexane) to give aldehyde **S19** as yellow oil (965 mg, 3.21 mmol 96%).
IR (neat) : 2982, 2937, 1730, 1666, 1519, 1499, 1455, 1353, 1323 cm$^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 9.85 (s, 1H), 7.53 (s, 1H), 7.37 – 7.30 (m, 3H), 7.17 – 7.15 (m, 2H), 5.49 (s, 2H), 4.15 (q, $J$ = 7.3 Hz, 2H), 1.68 (s, 6H), 1.18 (t, $J$ = 7.3 Hz, 3H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 179.3, 175.9, 158.1, 140.7, 135.6, 128.9, 128.2, 127.3, 125.7, 61.3, 50.8, 44.6, 27.0, 13.9 ; MS m/z : 300 ($M^+$), 271 (100 %) ; HRMS Calcd. $C_{17}H_{20}O_3N_2$ : 300.1474, Found : 300.1485
ref. 2) Korakas, P.; Chaffee, S.; Shotwell, J. B.; Duque, P.; Wood, J. L. *Proc. Natl. Acad. Sci. USA*, **2004**, *101*, 12054.



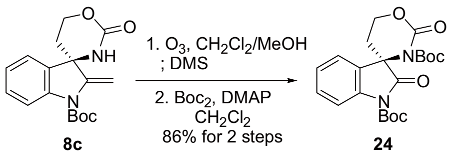
**28** : To a mixture of aldehyde **S19** (349 mg, 1.16 mmol) and ethylene glycol (0.32 ml, 5.81 mmol, 5.0 eq) in benzene (10 ml) was added *p*-TsOH·$H_2O$ (44 mg, 0.232 mmol, 0.2 eq.) and the mixture was heated to reflux for 36 h with azetropic removal of water. After being cooled to rt, the reaction mixture was quenched with saturated $NaHCO_3$ and the resultant solution was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo* to give corresponding crude acetal, which was used in the next step without further purification.

To a solution of crude product in THF (12 ml) at 0 °C was added $LiAlH_4$ (53 mg, 1.39 mmol, 1.2 eq.). After the reaction mixture was stirred for 20 min, the reaction was quenched with $H_2O$, filtered through Celite, and concentrated *in vacuo*. The resulting mixture was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo* to afford corresponding crude alcohol, which was used in the next step without further purification.

To a stirring mixture of crude alcohol and 1-Me-AZADO (5.8 mg, 3.5 μmol, 3 mol%) in $CH_2Cl_2$ (3.9 mL) and aqueous saturated $NaHCO_3$ (2.0 mL) containing KBr (14 mg, 0.12 mmol, 10 mol%) and $Bu_4NBr$ (19 mg, 0.058 mmol, 5 mol%) was added dropwise a premixed solutionof aqueous NaOCl (2.45 M in $H_2O$, 0.95 ml) and aqueous saturated $NaHCO_3$ (2.0 mL) at 0 °C over 5 min. The mixture was vigorously stirred for 5 min at 0 °C, then quenched with aqueous $Na_2SO_3$. The aqueous layer was separated and extracted with $CH_2Cl_2$. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo* to give corresponding crude aldehyde, which was used in the next step without further purification.

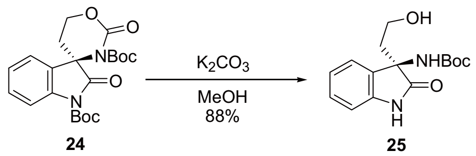
To a solution of crude aldehyde in MeOH (3 ml) at rt were added dimethyl-1-diazo-2-oxopropylphosphonate (223 mg, 1.16 mmol, 1.0 eq.) in MeOH (3 ml) and $K_2CO_3$ (240 mg, 1.74 mmol, 1.5 eq.). After the reaction mixture was stirred for 10 min, water was added and the resultant solution was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo*. The residue was purified by column chromatography (1:2 AcOEt:hexane) to give alkyne **28** as colorless oil (249 mg, 0.84 mmol 72% for 4 steps).

IR (neat) : 3286, 2979, 2932, 2893, 2108, 1719, 1568, 1501, 1455, 1395 $cm^{-1}$ ; $^1H$-NMR (400 MHz, $CDCl_3$) δ: 7.35 – 7.27 (m, 4H), 7.20 – 7.18 (m, 2H), 6.67 (s, 1H), 5.21 (s, 2H), 4.03- 3.93 (m, 4H), 2.29 (s, 1H), 1.66 (s, 6H) ; $^{13}C$-NMR (100 MHz, $CDCl_3$) δ: 147.1, 137.2, 136.4, 128.6, 127.8, 127.5, 120.2, 97.3, 91.0, 68.8, 64.7, 49.9, 31.2 ; MS m/z : 296 ($M^+$), 91 (100 %) ; HRMS Calcd. $C_{18}H_{20}O_2N_2$ : 296.1525, Found : 296.1522



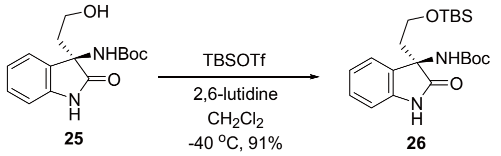
**1,1'-Di-*tert*-butoxycarbonyl-spiro[2,3-dihydro-1*H*-indol-3,6'-[1',3']oxazinan]2,2'-dione (24)** : Cyclic carbamate **8c** (100 mg, 0.316 mmol) was dissolved in $CH_2Cl_2$/MeOH (1:1 15.8 ml). The solution was cooled at -78 °C and ozone was introduced for 1 min and followed by argon gas for 5 min. The mixture was added $Me_2S$ (0.232 ml, 3.16 ml, 10 eq.), allowed to warm slowly at rt and stirred for overnight. The solution was concentrated *in vacuo*. To the crude mixture was added $Boc_2O$ (0.109 ml, 0.474 mmol, 1.5 eq.) and DMAP (3.9 mg, 31.6 μmol, 10 mol%). After the reaction mixture was stirred for 30 min, water was added and the resultant mixture was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo*. The residue was purified by column chromatography (1:2 AcOEt:hexane) to give amide **24** as white amorphous (114 mg, 0.272 mmol 86%).

IR (neat) : 2980 $cm^{-1}$, 2924 $cm^{-1}$, 1793$cm^{-1}$, 1733 $cm^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, *J* = 8.3 Hz, 1H), 7.40 (dd, *J* = 7.6, 8.3 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.22 (dd, *J* = 7.6, 7.6 Hz. 1H), 4.73 (ddd, *J* = 2.9, 8.5, 11.5 Hz, 1H), 4.32 (ddd, *J* = 3.4, 9.0, 11.5 Hz, 1H), 2.32 (ddd, *J* = 2.9, 5.9, 14.1 Hz, 1H), 2.23 (ddd, *J* = 3.4, 9.0, 14.1 Hz, 1H), 1.65 (s, 9H), 1.16 (s, 9H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 173.2, 149.3, 149.0, 148.8, 138.4, 130.0, 129.3, 125.1, 121.5, 115.6, 85.3, 85.0, 63.5, 61.7, 34.0, 28.0, 27.1 ; MS *m/z* : 418 ($M^+$), 218 (100%) ; HRMS Calcd. $C_{21}H_{26}O_7N_2$ : 418.1740, Found : 418.1748



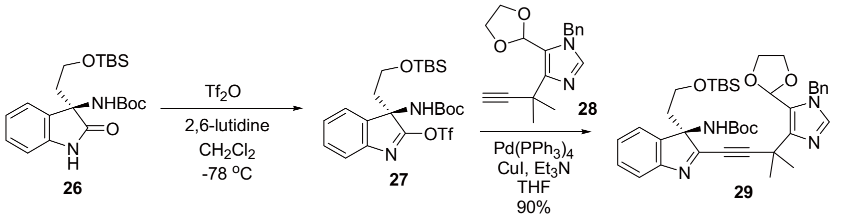
**3-*tert*-Butoxycarbonylamino-3-(2-hydroxyethyl)-2,3-dihydro-1*H*-indol-2-one (25)** : To a solution of cyclic carbamate **24** (235 mg, 0.562 mmol) in MeOH (5.6 ml) was added $K_2CO_3$ (77.6 mg, 0.562 mmol, 1.0 eq.) at rt. After the reaction mixture was stirred for 10 h, the reaction was quenched with a saturated aqueous solution of $NH_4Cl$. The mixture was extracted with AcOEt, washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography (2:1 AcOEt:hexane) to give alcohol **25** as white amorphous (145 mg, 0.496 mmol, 88%).

IR (neat) : 3323, 2978, 2930, 1722, 1621 $cm^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 8.13 (br, 1H), 7.29 – 7.26 (m, 1H), 7.22 (dd, *J* = 7.3, 7.6 Hz, 1H), 7.05 (dd, *J* = 7.3, 7.6 Hz, 1H), 6.86 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.55 (br, 1H), 3.96 (br, 1H), 3.86 (br, 1H), 2.06 – 2.00 (m, 2H), 1.26 (br, 9H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 180.2, 154.4, 140.4, 131.7 (br), 128.6, 122.7, 122.4, 110.5 (br), 80.3 (br), 62.0 (br), 57.7, 38.8, 28.0 (br) ; MS *m/z* : 292 ($M^+$), 147 (100%) ; HRMS Calcd. $C_{15}H_{20}O_4N_2$ : 292.1423, Found : 292.1418



**3-*tert*-Butoxycarbonylamino-3-(2-*tert*-buthyl-dimethylsiloxyethyl)-2,3-dihydro-1*H*-indol-2-one (26)** : To a solution of alcohol **25** (503 mg, 1.72 mmol) in $CH_2Cl_2$ (8.6 ml) were added 2,6-lutidine (0.60 ml, 5.16 mmol, 3.0 eq.) at - 40 °C. After the reaction mixture was stirred for 8 h, the reaction was quenched with a saturated $NaHCO_3$. The mixture was extracted with AcOEt, washed with 10% HCl and brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography (1:2 AcOEt:hexane) to give TBS ether **26** as white amorphous (640 mg, 1.57 mmol, 91%).

IR (neat) : 3374, 3292, 2954, 2929, 2857, 1724, 1622, 1472 $cm^{-1}$ ; $^1H$-NMR (400 MHz, $CDCl_3$) δ: 8.21 (br, 1H), 7.25 (d, *J* = 7.5 Hz), 7.20 (d, *J* = 7.5 Hz, 1H), 7.12 (br, 1H), 7.03 (dd, *J* = 7.2, 7.2 Hz), 6.85 (d, *J* = 7.5 Hz, 1H), 4.03 – 3.98 (m, 1H), 3.91 – 3.85 (m, 1H), 2.11 (ddd, *J* = 3.1, 8.9, 14.7 Hz), 1.75 – 1.69 (m, 1H), 1.32 (br, 9H), 0.98 (s, 9H), 0.16 (s, 3H), 0.14 (s, 3H) ; $^{13}C$-NMR (100 MHz, $CDCl_3$) δ: 179.0, 154.0, 140.4, 128.5, 122.9, 122.2, 112.7, 110.4, 79.6, 61.8, 59.0, 38.3, 28.2, 26.4, 25.8, 18.0, -5.7 ; MS *m/z* : 349 ($M^+$ - 57), 293 (100%) ; HRMS Calcd. $C_{17}H_{25}O_4N_2Si$ : 349.1584, Found : 349.1566

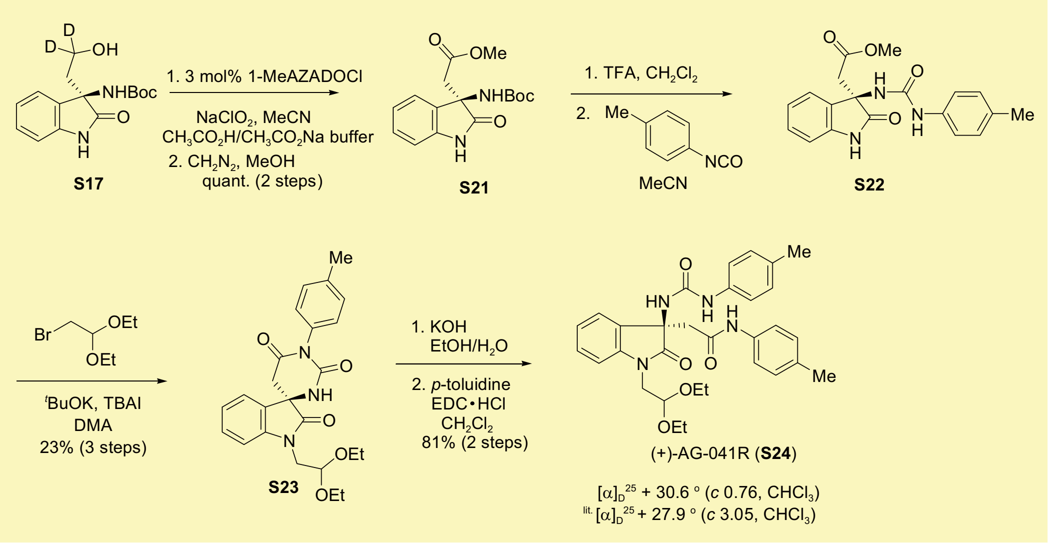


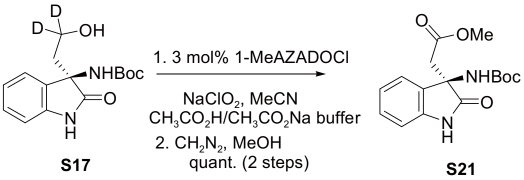
**29** : To a mixture of lactam **26** (190 mg, 0.467 mmol) and 2,6-lutidine (0.16 ml, 1.40 mmol, 3.0 eq.) in $CH_2Cl_2$ (4.7 ml) were added $Tf_2O$ (0.12 ml, 0.70 mmol, 1.5 eq.) at - 78 °C. After the reaction mixture was stirred for 1 h, 2-propanol (0.36 ml, 4.7 mmol, 10 eq.) was added and stirred for 30 min. The reaction was quenched with a saturated $NaHCO_3$. The mixture was extracted with AcOEt, washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography (Merck Silica gel 60 $F_{254}$, 1:2 AcOEt:hexane) to give triflate **00** as colorless oil, which was not fully characterized because of instability of triflate **27**. (caution : After the column chromatography, the solvent must not completely be removed. If the solvent was completely concentrated, triflate **27** was decomposed to lactam **26**).

To a solution of colorless oil of **27** in degassed THF (4.7 ml) were added $Et_3N$ (0.65 ml, 4.7 mmol, 10 eq.), alkyne **28** (125 mg, 0.420 mmol, 0.90 eq.), CuI (27 mg, 0.14 mmol, 30 mol%) and $Pd(PPh_3)_4$ (54 mg, 47 μmol, 10 mol%) at rt. After the reaction mixture was stirred for 2 h, water was added and the resultant mixture was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo*. The residue was purified by column chromatography (1:1 AcOEt:hexane) to give coupling product **29** as white amorphous (288 mg, 0.421 mmol, 90%).

IR (neat) : 3378, 2953, 2929, 2886, 2220, 1716, 1500, 1455 $cm^{-1}$ ; $^1$H-NMR (500 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 6.2 Hz, 1H), 7.35 – 7.21 (m, 10H), 6.69 (s, 1H), 5.23 (s, 2H), 4.01 – 3.96 (m, 4H), 3.78 (br, 2H), 2.27 (m, 1H), 1.77 (s, 6H), 1.46 (d, *J* = 11.4 Hz, 1H), 1.26 (br, 9H), 0.95 (s, 9H), 0.10 (s, 3H), 0.06 (s, 3H) ; $^{13}$C-NMR (125 MHz, $CDCl_3$) δ: 168.9, 153.7, 146.3, 139.5, 137.3, 136.4, 128.8, 128.7, 127.9, 127.7, 126.4, 121.9, 121.7, 120.9, 107.8, 97.3, 79.9, 75.6, 71.9, 64.9, 64.8, 59.7, 50.0, 37.8, 32.5, 30.8, 28.0, 26.0, 25.9, 18.0, - 5.58, - 5.60 ; MS (FAB) *m/z* : 685 ($M^+$ ), 91 (100%) ; HRMS Calcd. $C_{39}H_{52}O_6N_4Si$ : 685.3785, Found : 685.3792

## Synthesis of (+)-AG-041R and determination of absolute configuration

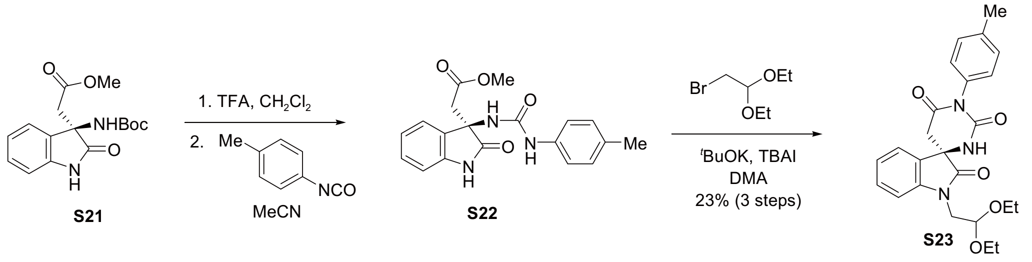




**Methyl (3*R*)-(3-*tert*-butoxycarbonyl-amino-2-oxo-2,3-dihydro-1*H*-indoyl-3-yl)- acetate (S21)** : To a solution of alchol **S17** (147 mg, 0.50 mmol) in MeCN (1.6 ml) and $CH_3CO_2H/CH_3CO_2Na$ buffer (1.6

ml) was added $NaClO_2$ (80%, 170 mg, 1.50 mmol, 3.0 eq.) and 1-MeAZADOCl (3.0 mg, 15 μmol, 3 mol%) at rt, and stirred for 2 h. The reaction was quenched with 2-methyl-2-butene, and water was added and the resultant solution was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo*. To a solution of crude mixture in MeOH (1.0 ml) at 0 $^{o}$C was added a solution of $CH_2N_2$ in $Et_2O$ (2.0 ml). The reaction was allowed to warm to rt and stirred for 1 h. The mixture was concentrated *in vacuo*. The residue was purified by column chromatography (1:2 AcOEt:hexane) to give methyl ester **S21** as white amorphous (160 mg, 0.50 mmol, 100% for 2 steps ) ;

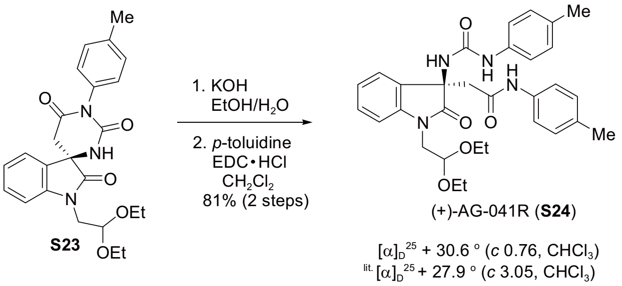
$[\alpha]_D^{29}$ +46.5° (*c* 1.38, $CHCl_3$) ; IR (neat) : 3285, 2979, 1726, 1622cm-1 ; $^1$H-NMR (400 MHz, CDCl3) δ: 8.63 (br, 1H), 7.24 – 7.19 (m, 2H), 7.00 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 6.45 (br, 1H), 3.71 (s, 3H), 2.93 (d, *J* = 15.1 Hz, 1H), 2.62 (d, *J* = 15.1 Hz, 1H), 1.30 (br, 9H) ; $^{13}$C-NMR (100 MHz, CDCl3) δ: 177.3, 170.3, 153.9, 140.5, 129.9, 129.2, 123.1, 122.6, 110.4, 80.6, 59.5, 52.2, 40.5, 28.0 ; MS m/z : 320 (M+), 264 (100%) ; HRMS Calcd. $C_{16}H_{20}O_5N_2$ : 320.1372, Found : 320.1349



**3-(4-Methoxyphenyl)-1'-(2,2-diethoxyethyl)-spiro[5,6-dihydroprymidin-6,3'-2',3'-dihydro-1*H*-indoyl]-2,2',4-trione (S23) :** To a solution of methyl ester **S21** (35 mg, 0.109 mmol) in $CH_2Cl_2$ (1.0 ml) was added TFA (0.112 ml, 1.51 mmol, 14 eq.) at 0 $^{o}$C, the mixture warmed to rt. The reaction was allowed to warm to rt and stirred for 2 h. The reaction was poured into $H_2O$ (5 ml), washed with $Et_2O$, and the aqueous solution basified with saturated $NaHCO_3$. The basic solution was extracted with $CHCl_3$ (3 × 20 ml), washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. To a solution of crude mixture in MeCN (1.0 ml) was added *p*-tosyl isocyanate (10.2 μl, 0.120 mmol, 1.1 eq.) at rt. After the reaction was stirred for 1h, the precipitation was collected, washed with MeCN, and dried under reduced pressure. To a solution of crude mixture in DMA (1.4 ml) was added potassium *tert*-butoxide (26.7 mg, 0.218 mmol, 2.0 eq), bromoacetaldehyde diethylacetal (19.7 μl, 0.131 mmol, 1.2 eq.), tetrabuthylammonium iodide (10.1 mg , 27.3 μmol, 25 mol%). The mixture was maintained at 80 $^{o}$C for 4 h then cooled to ambient temperature. Saturated $NH_4Cl$ (3 ml) was added and extracted with $Et_2O$. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography (1:1 AcOEt:hexane) to give cyclic urea **S23** as yellowish oil (15 mg, 0.0343 mmol, 23% for 3 steps ) ;

$[\alpha]_D^{24}$ +61.3° (*c* 1.28, $CHCl_3$) ; IR (neat) : 3272, 2977, 1737, 1689, 1614 cm$^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 7.42 – 7.38 (m, 2H), 7.30 – 7.23 (m, 4H), 7.18 – 7.12 (m, 2H), 5.57 (br, 1H), 4.71 (t, *J* = 5.3

Hz, 1H), 4.12 (dd, *J* = 5.3, 14.5 Hz, 1H), 3.39 – 3.71 (m, 3H), 3.55 – 3.48 (m, 2H), 3.22 (d, *J* = 16.4 Hz, 1H), 2.89 (dd, *J* = 1.7, 16.4 Hz, 1H), 2.39 (s, 3H), 1.15 (t, *J* = 7.0 Hz, 3H), 1.15 (t, *J* = 7.0 Hz, 3H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 175.3, 167.1, 154.3, 143.0, 138.6, 132.1, 130.8, 129.9, 128.4, 126.5, 123.7, 123.3, 111.0, 100.2, 63.7, 63.6, 43.6, 39.9, 21.3, 15.3, 15.2 ; MS *m/z* : 437 ($M^+$), 103 (100%) ; HRMS Calcd. $C_{24}H_{27}O_5N_3$ : 437.1951, Found : 437.1940



**2-[(*R*)-1-(2,2-Diethoxyethyl)-2-oxo-3-(3-*p*-tolylureido)-2,3-dihydro-1*H*-indol-3-yl]-*N*-*p*-tolylacetamide (AG-041R) (S24)** : To a solution of cyclic urea **S23** (15 mg, 0.0343 mmol) in EtOH/$H_2O$ (10:1, 1.9 ml) at 0 °C was added KOH (4.8 mg, 0.0858 mmol, 2.5 eq.) and the mixture was allowed to warm to rt and stirred for 10 h. The reaction was poured onto $H_2O$ and 10% HCl (5 ml), extracted with $CHCl_3$, washed with brine, dried over $MgSO_4$, concentrated *in vacuo*. To a solution of crude mixture in $CH_2Cl_2$ (1.0 ml) at 0 °C was added EDC•HCl (8.5 mg, 0.0446 mmol, 1.3 eq.) and *p*-toluidine (4.8 mg, 0.0446 mmol, 1.3 eq.) at 0 °C. The mixture was stirred for 40 min at 0 °C. The reaction was poured onto $H_2O$ and 10% HCl (5 ml), extracted with $CHCl_3$, washed with brine, dried over $MgSO_4$, concentrated *in vacuo*. The residue was purified by column chromatography (1:1 AcOEt:hexane) to give AG-041R **1** as white crystal (15.2 mg, 0.0279 mmol, 81% for 2 steps ) ;
$[\alpha]_D^{25}$ +30.6° (*c* 0.760, $CHCl_3$) ; IR (neat) : 3319, 2974, 2921, 1698, 1686, 1663, 1608 cm$^{-1}$ ; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 8.51 (s, 1H), 7.29 – 7.21 (m, 5H), 7.17 (s, 1H), 7.07 – 6.96 (m, 6H), 6.89 (d, *J* = 8.2 Hz, 2H), 4.75 (dd, *J* = 4.6, 5.5 Hz, 1H), 3.97 (dd, *J* = 5.9, 14.4 Hz, 1H), 3.78 (dd, *J* = 4.2, 14.5 Hz, 1H), 3.72 – 3.48 (m, 4H), 2.97 (d, *J* = 14.7 Hz, 1H), 2.63 (dd, *J* = 14.7 Hz, 1H), 2.28 (s, 3H), 2.20 (s, 3H), 1.13 (t, *J* = 7.0 Hz, 3H), 1.09 (t, *J* = 7.0 Hz, 3H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 177.6, 167.3, 154.0, 142.5, 135.9, 134.7, 134.5, 132.3, 130.0, 129.4, 129.2, 128.8, 122.9, 122.8, 120.7, 119.8, 110.2, 100.6, 63.4, 59.7, 43.9, 20.9, 20.7, 15.3 ; MS *m/z* : 544 ($M^+$), 103 (100 %) ; HRMS Calcd. $C_{31}H_{36}O_5N_4$ : 544.2686, Found : 544.2704

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1501−No1600¥No1561−No1570¥1562_09_3_10.als

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| PW1 | 5.80 usec |
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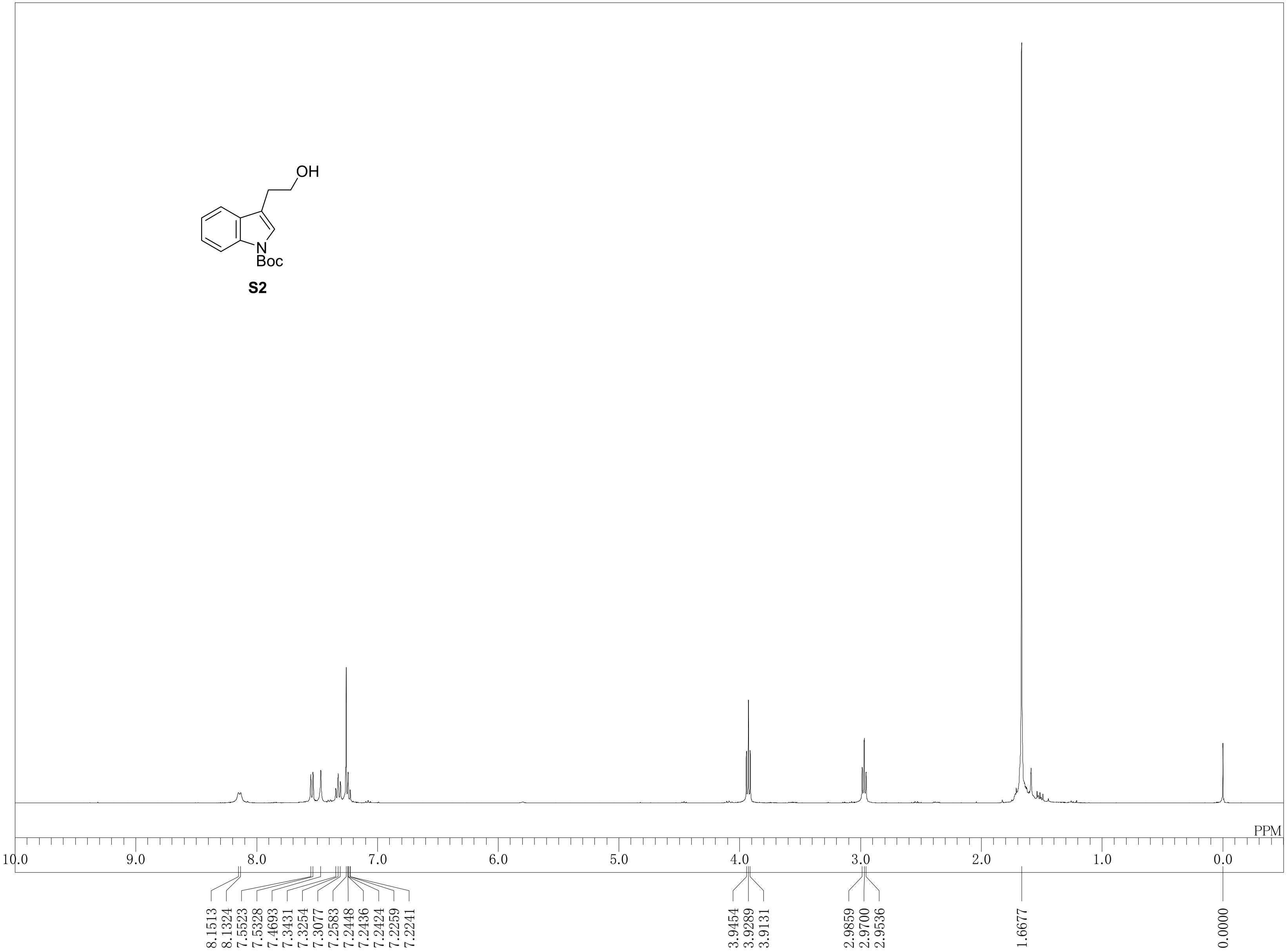

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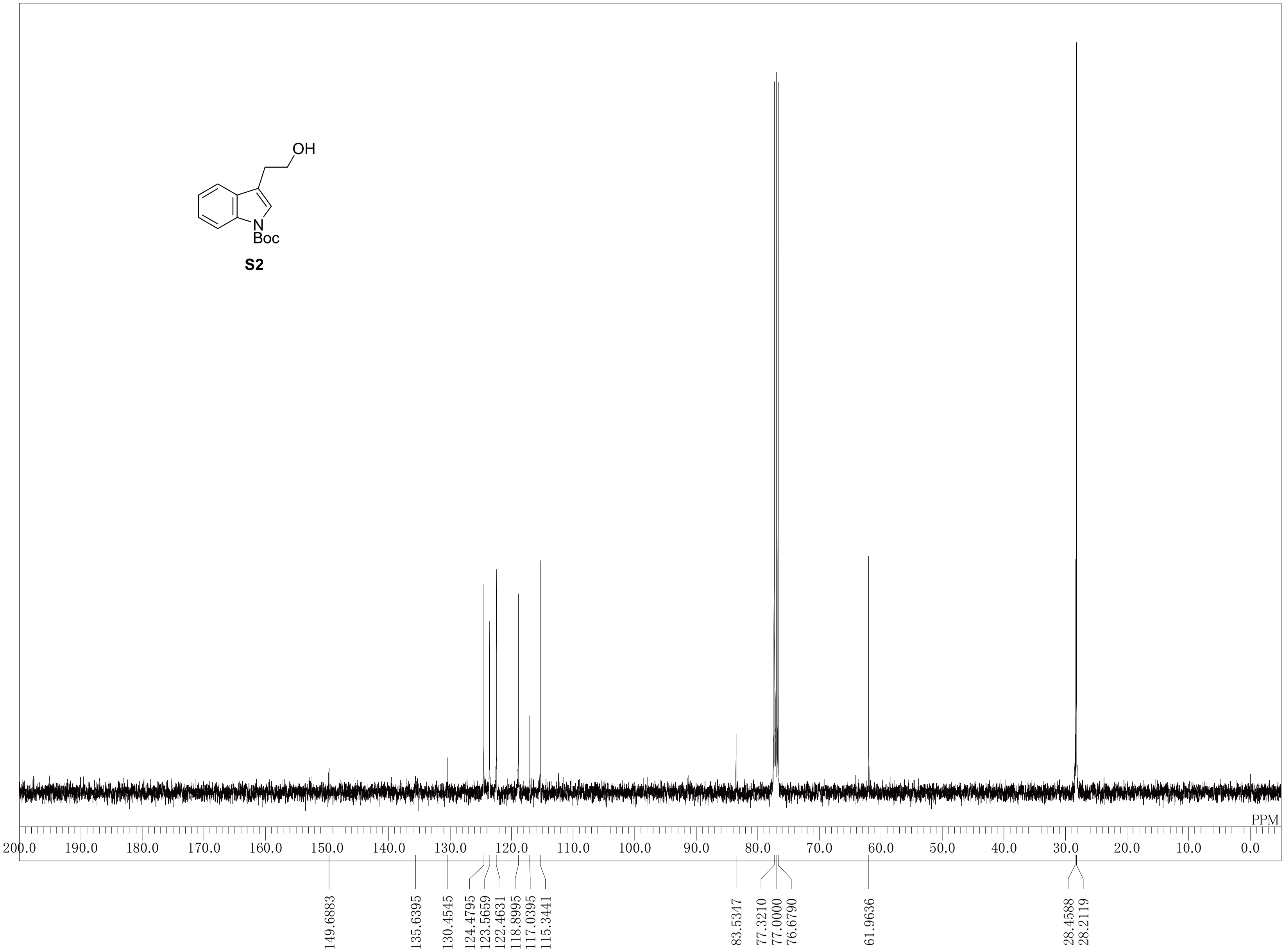

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| CTEMP | 27.1 c |
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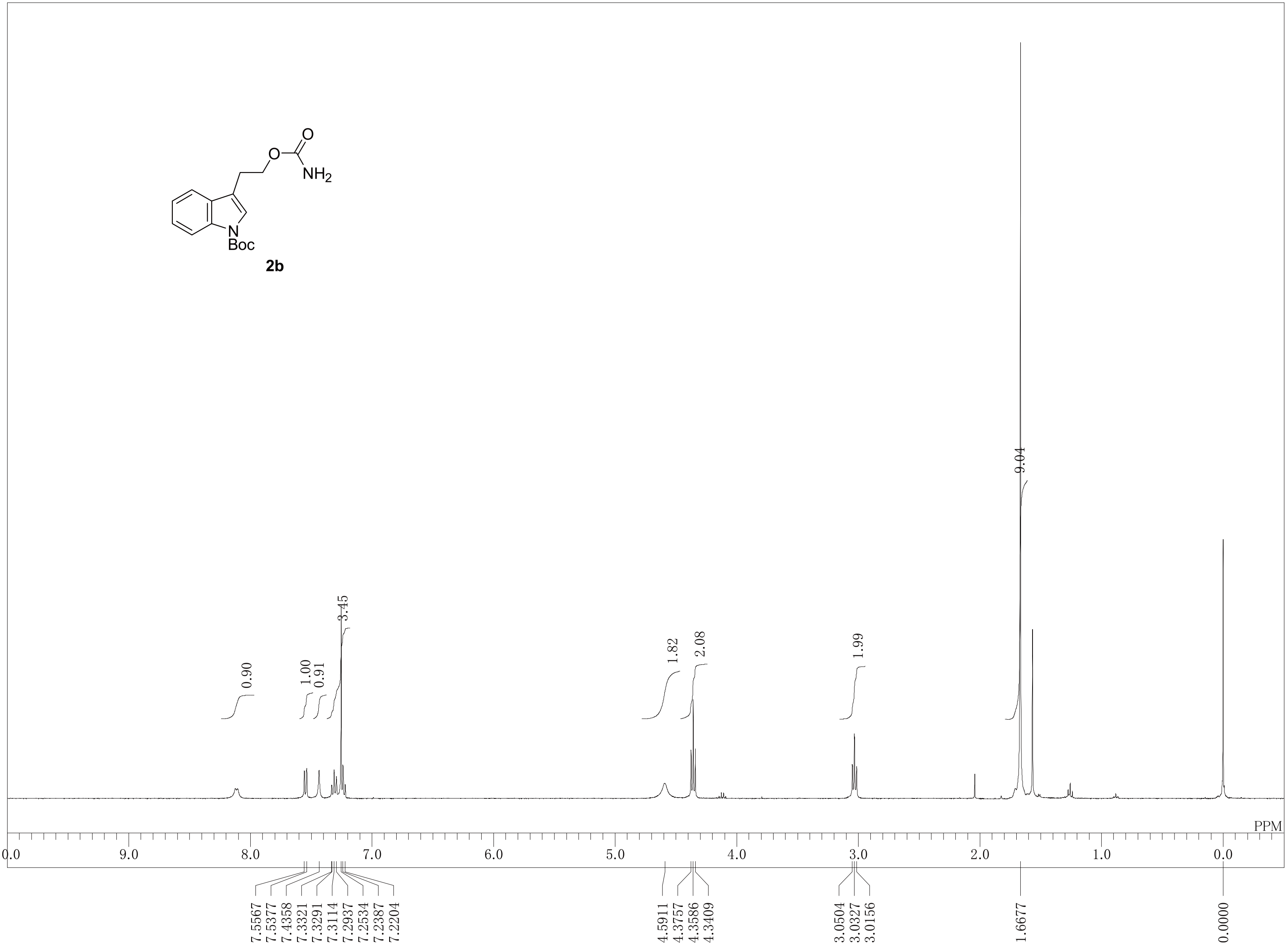

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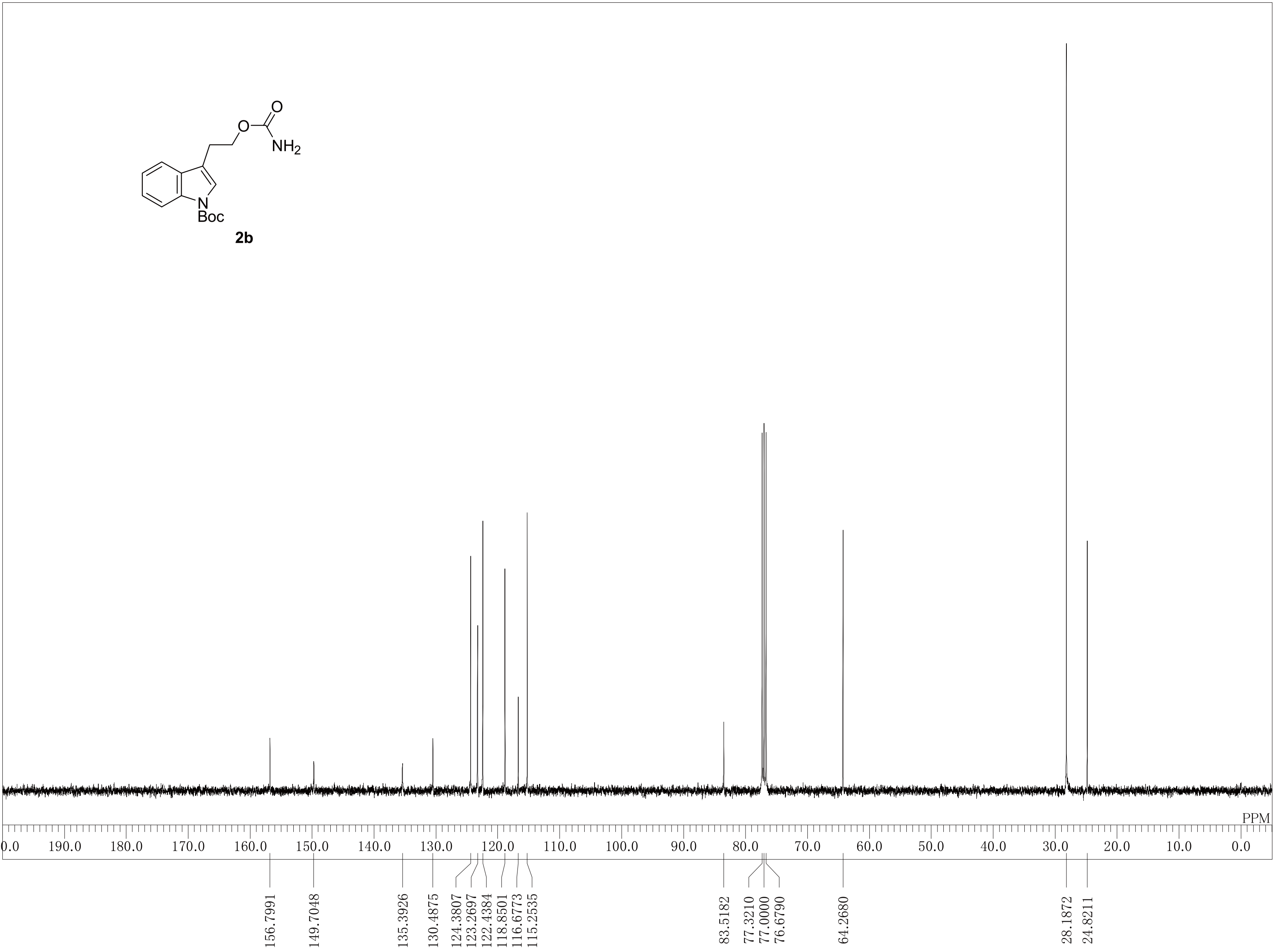

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| RGAIN | 24 |

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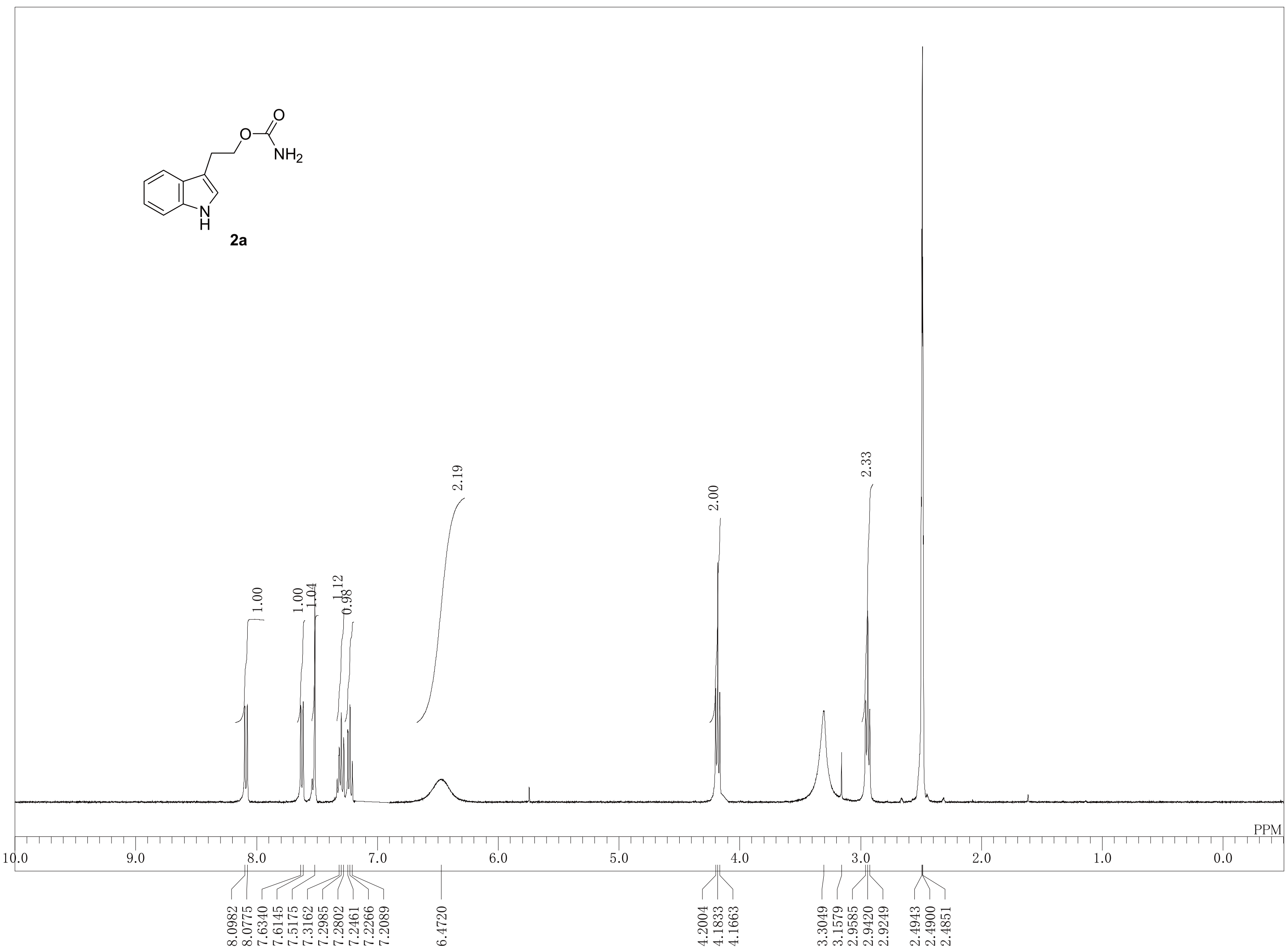

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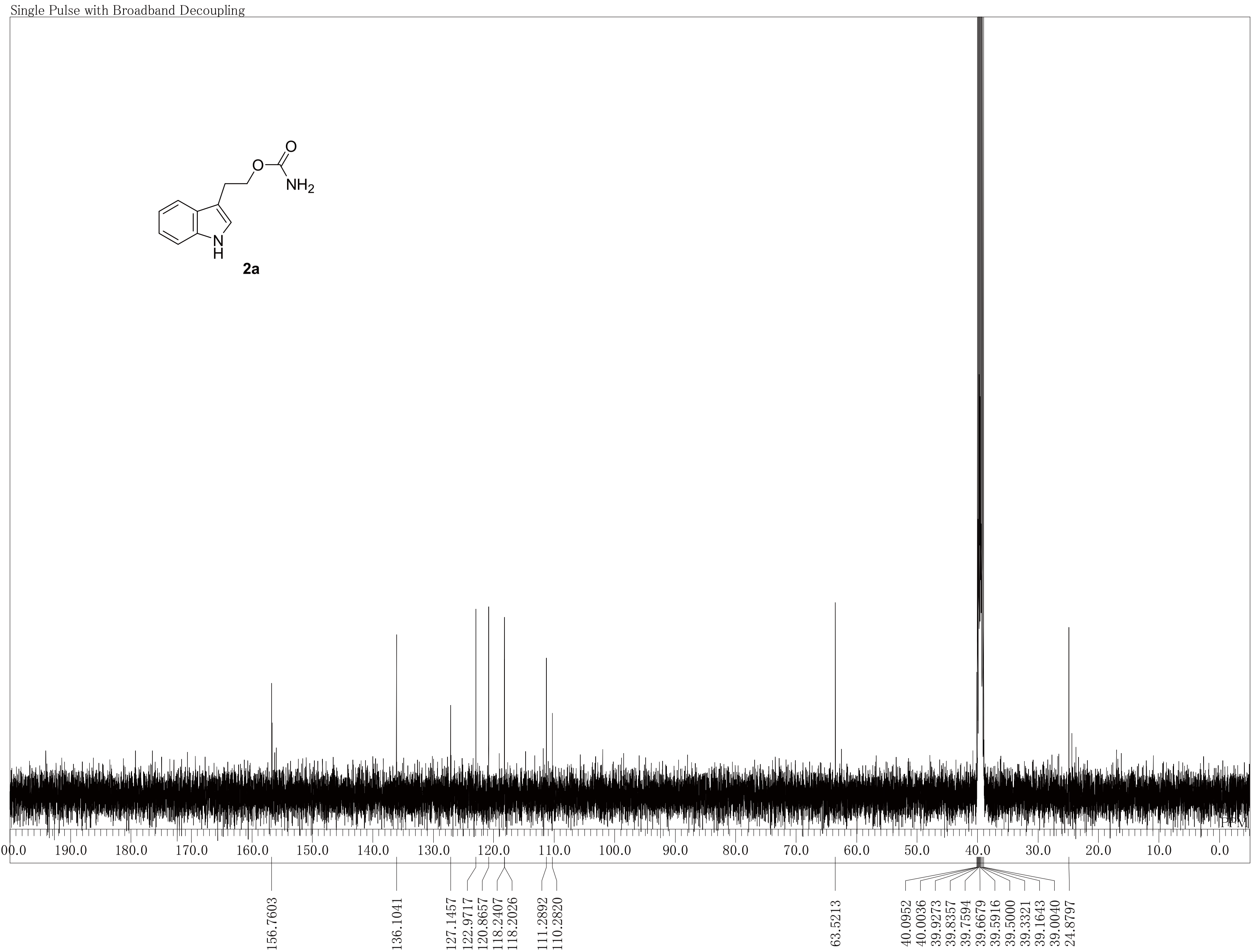

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| PW1 | 3.40 usec |
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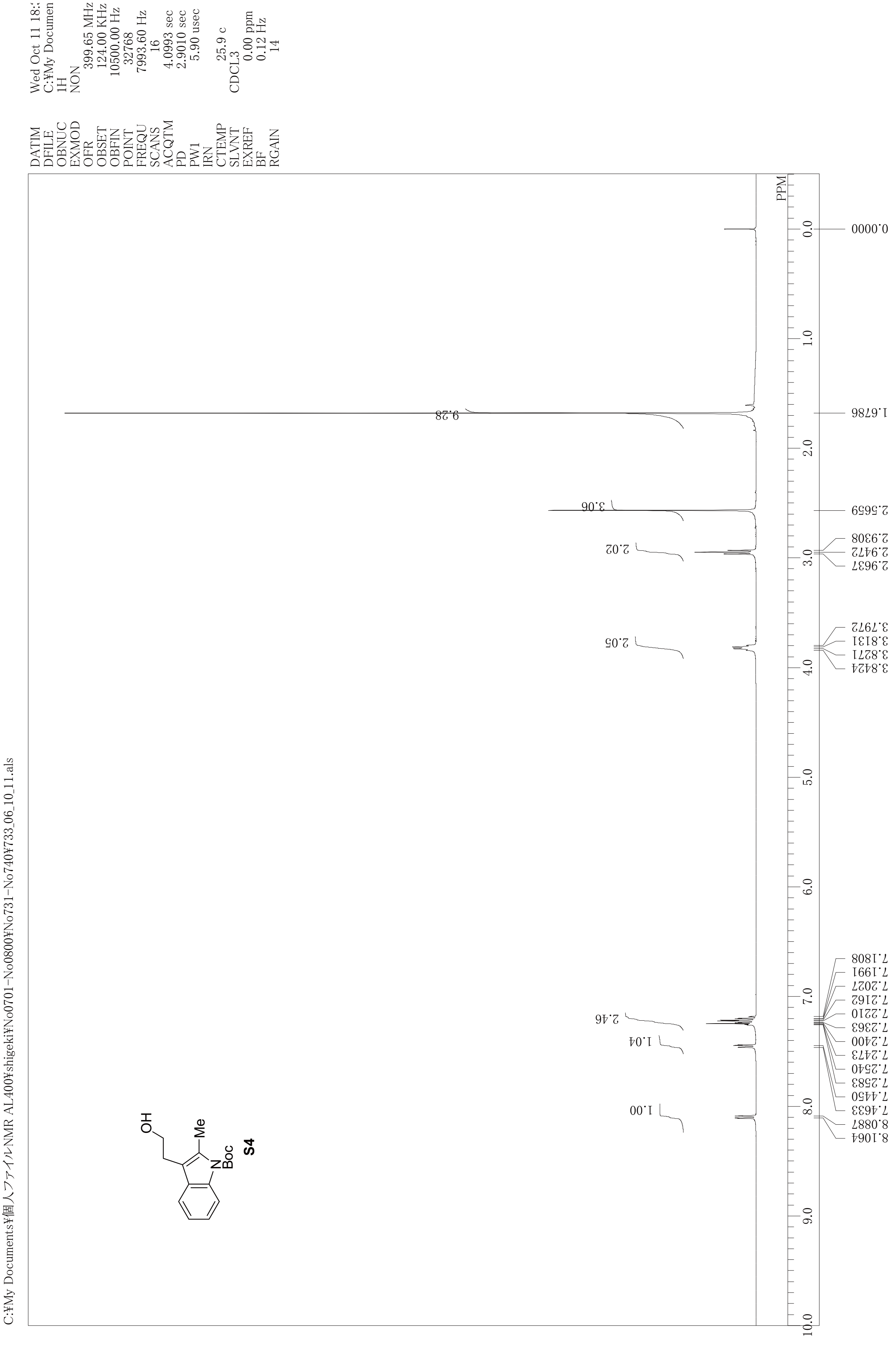
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PD 2.9010 sec
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N
Boc

**S4**

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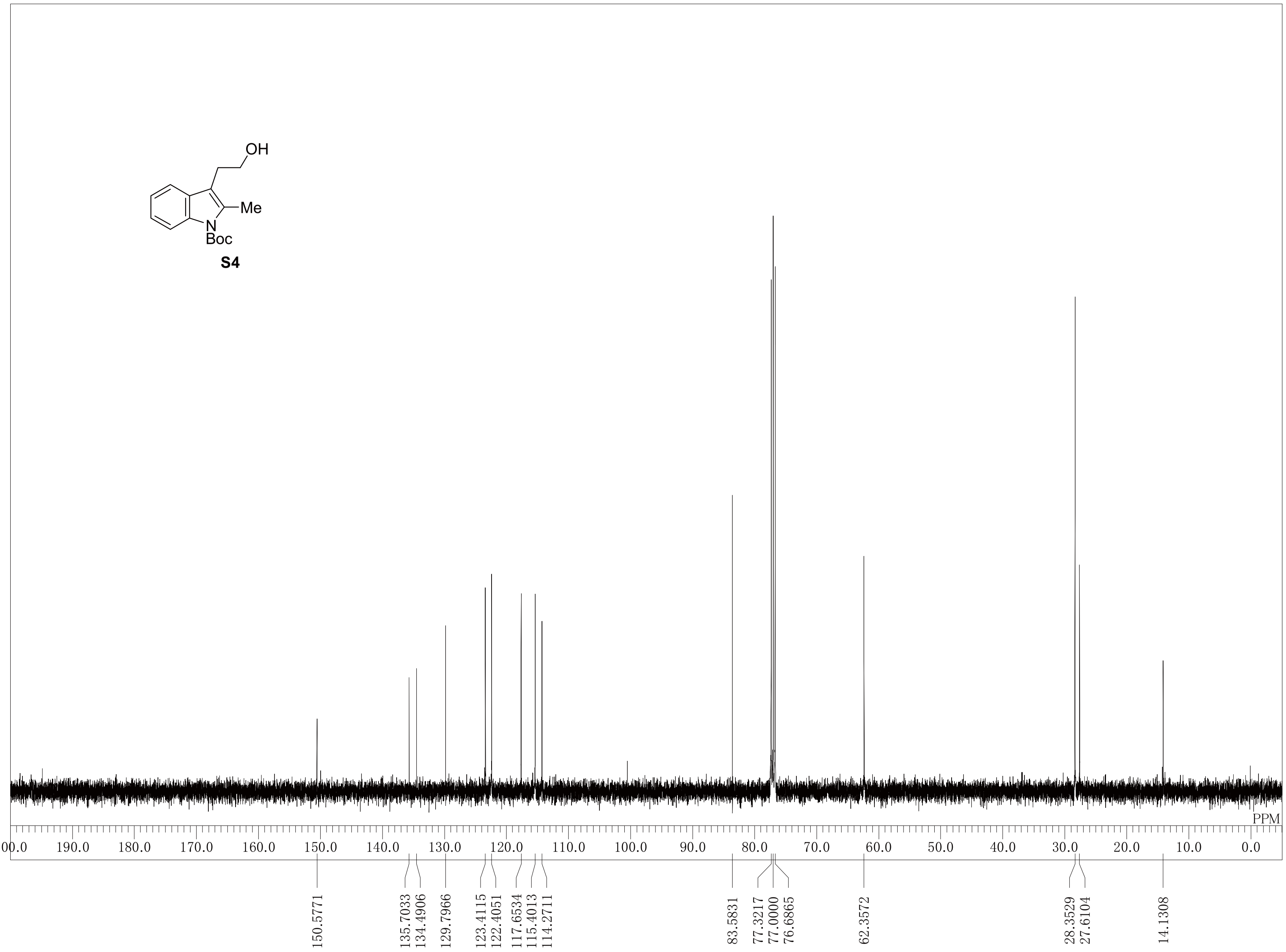

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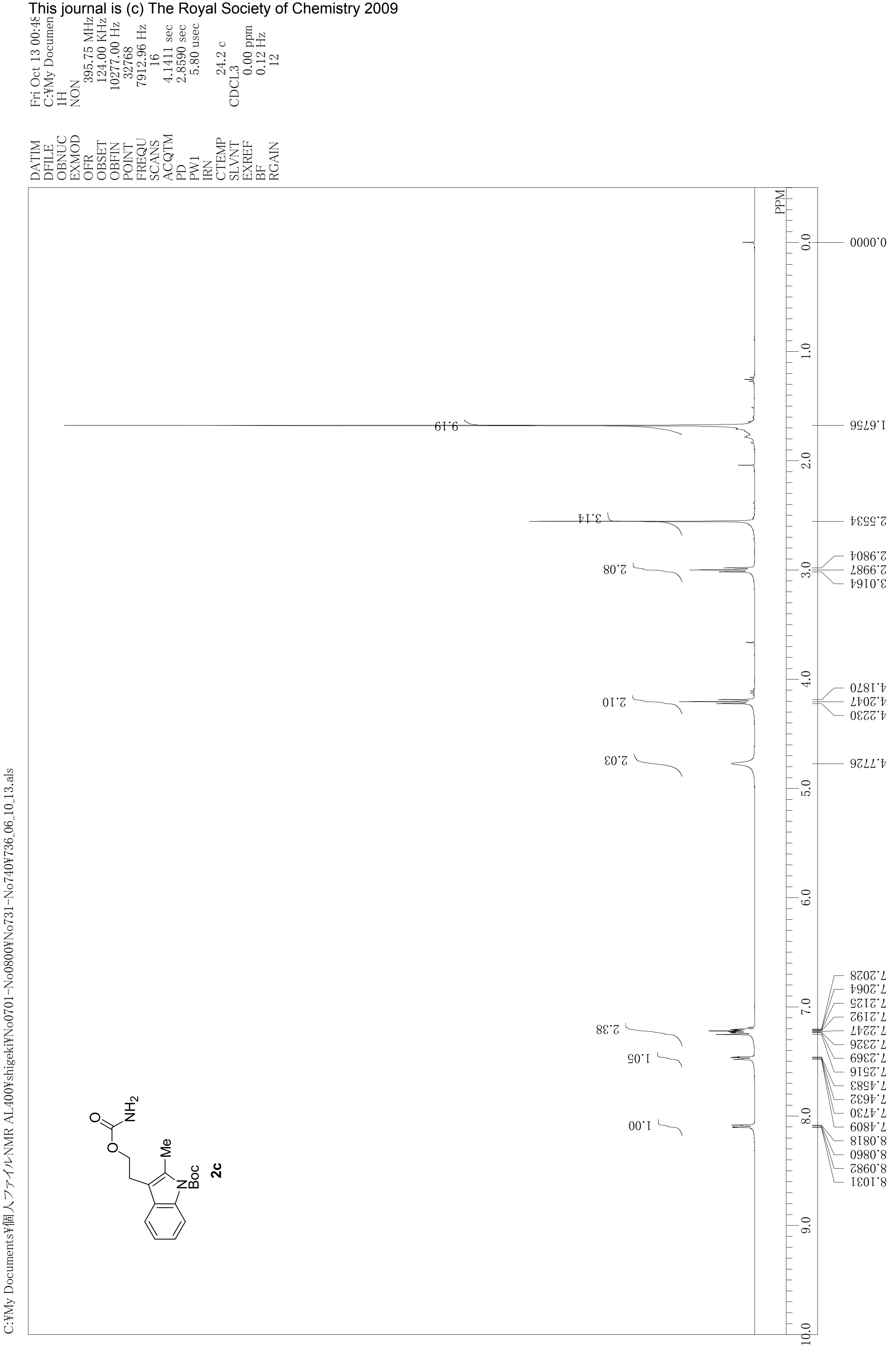
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Me
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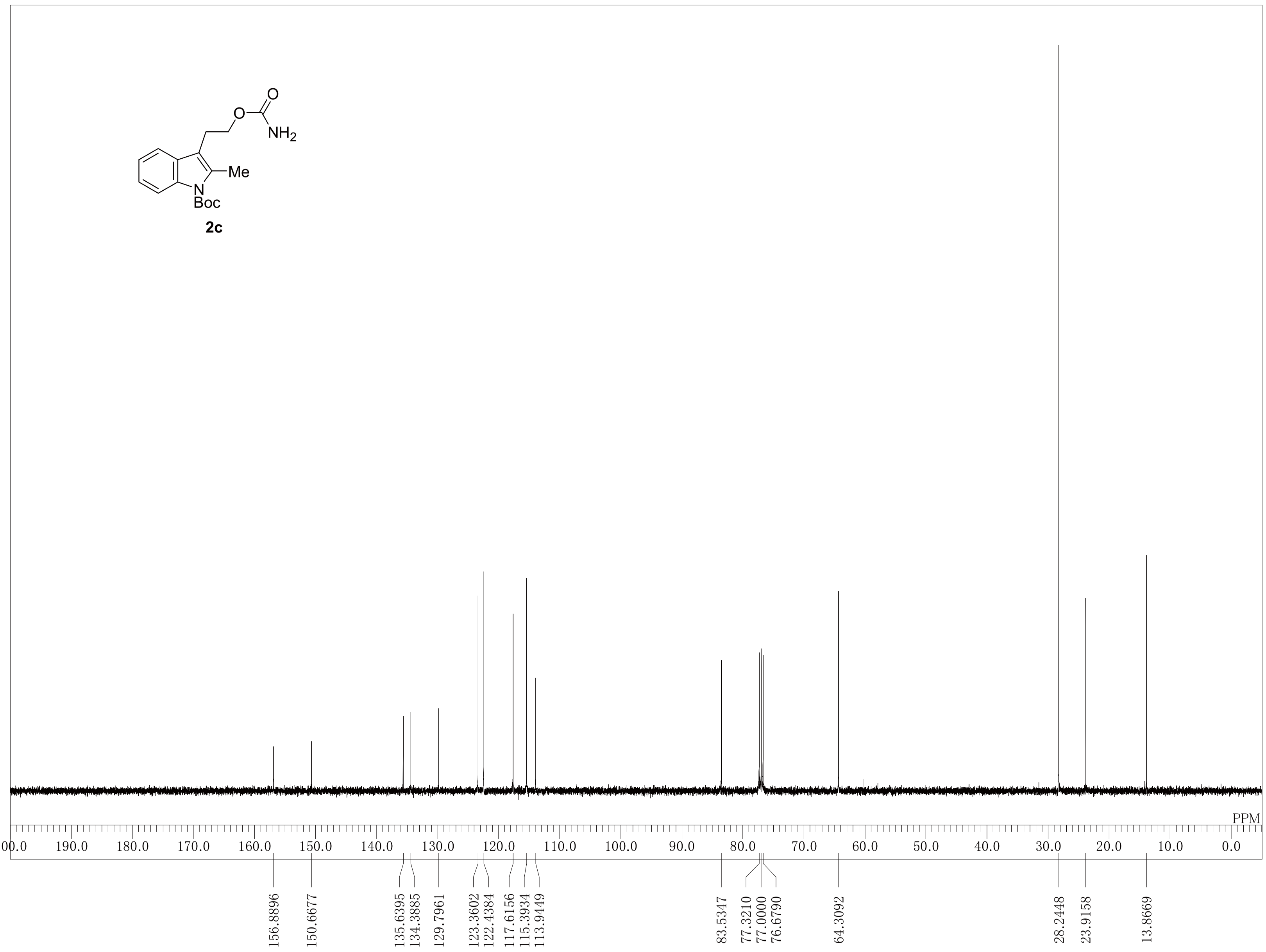
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IRN
CTEMP         26.2 c
SLVNT     CDCL3
EXREF        77.00 ppm
BF            0.12 Hz
RGAIN          24
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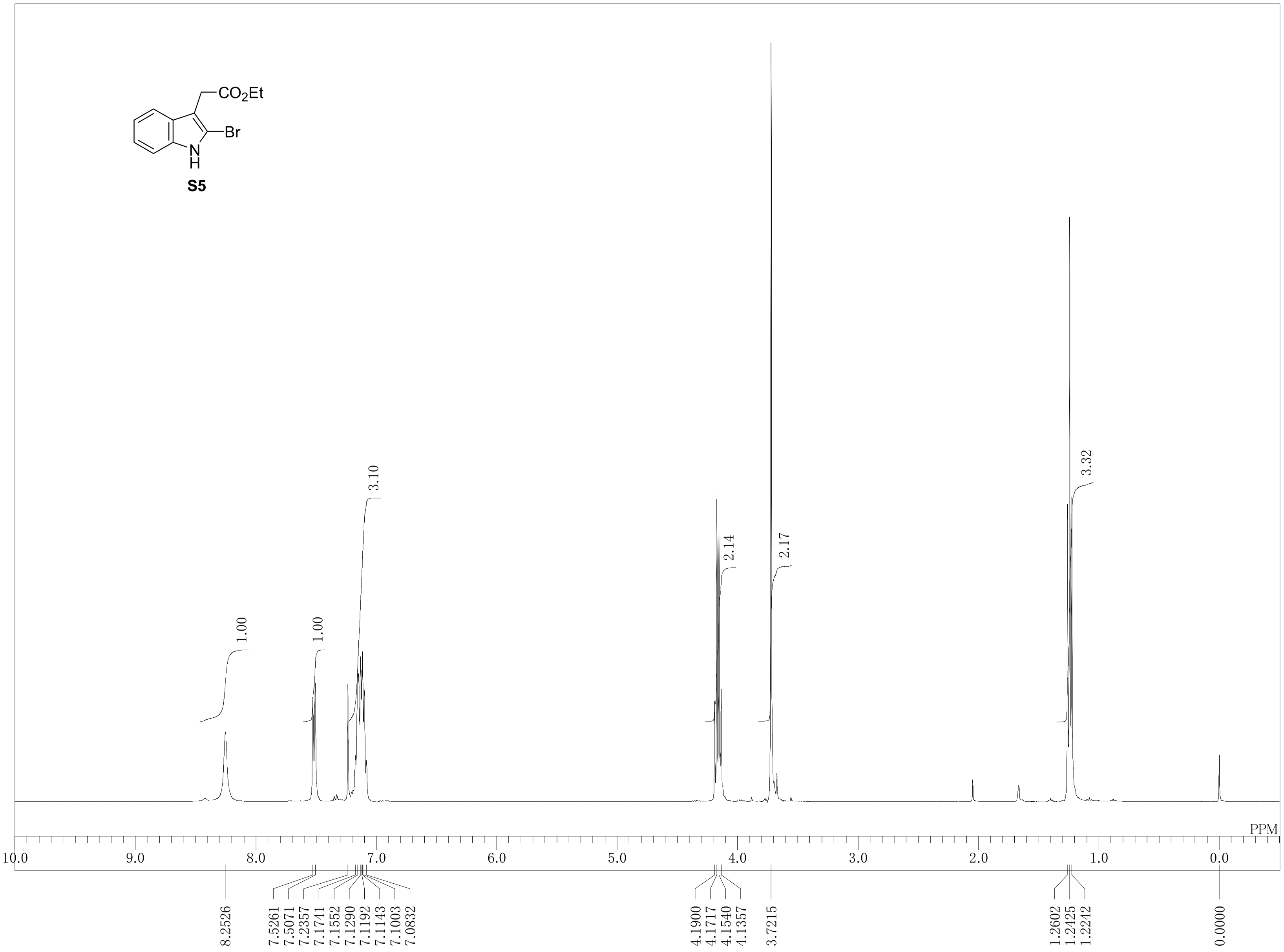

**S5**

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| OBFIN | 10277.00 Hz |
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| FREQU | 7912.96 Hz |
| SCANS | 16 |
| ACQTM | 4.1411 sec |
| PD | 2.8590 sec |
| PW1 | 5.80 usec |
| IRN | |
| CTEMP | 27.2 c |
| SLVNT | CDCL3 |
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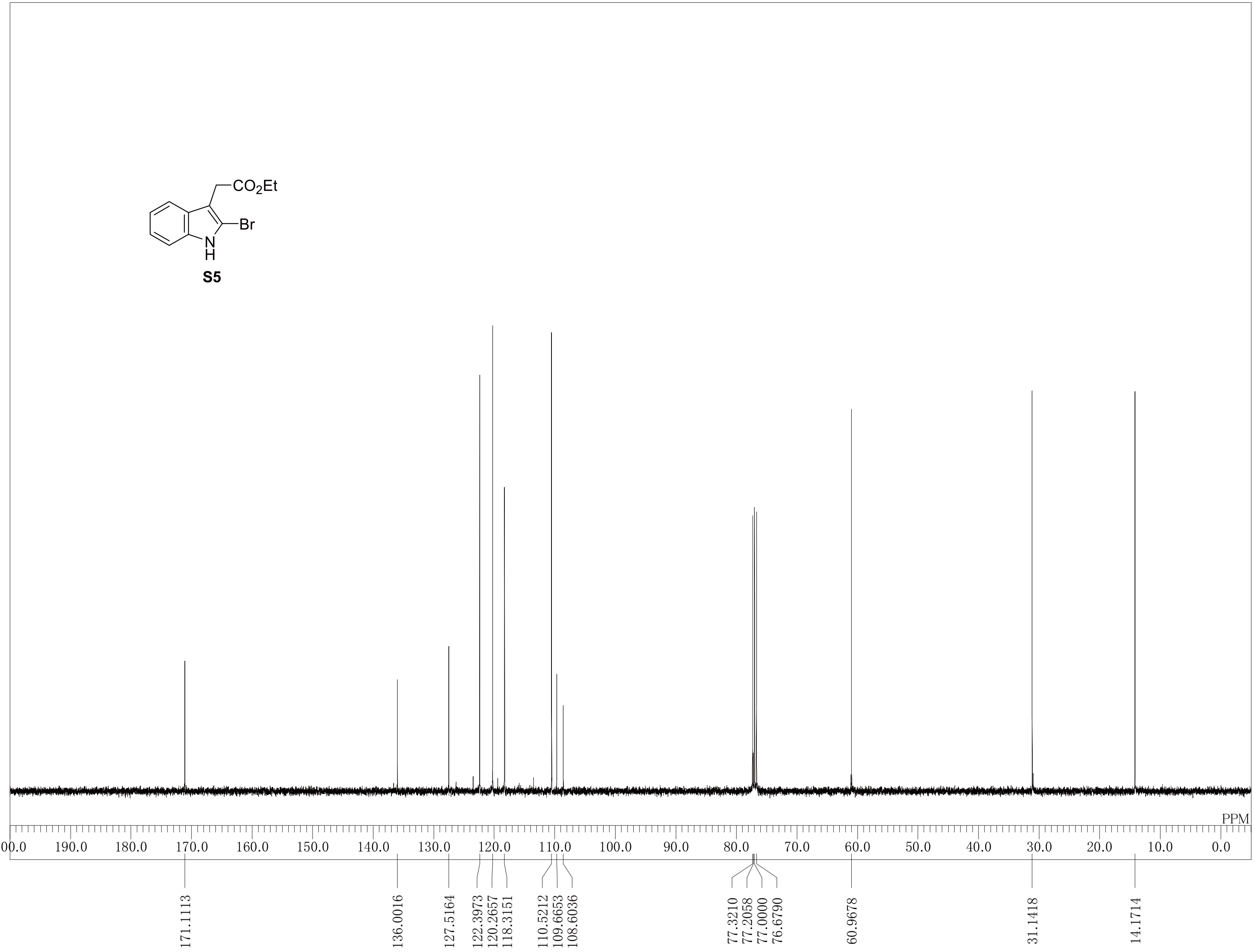
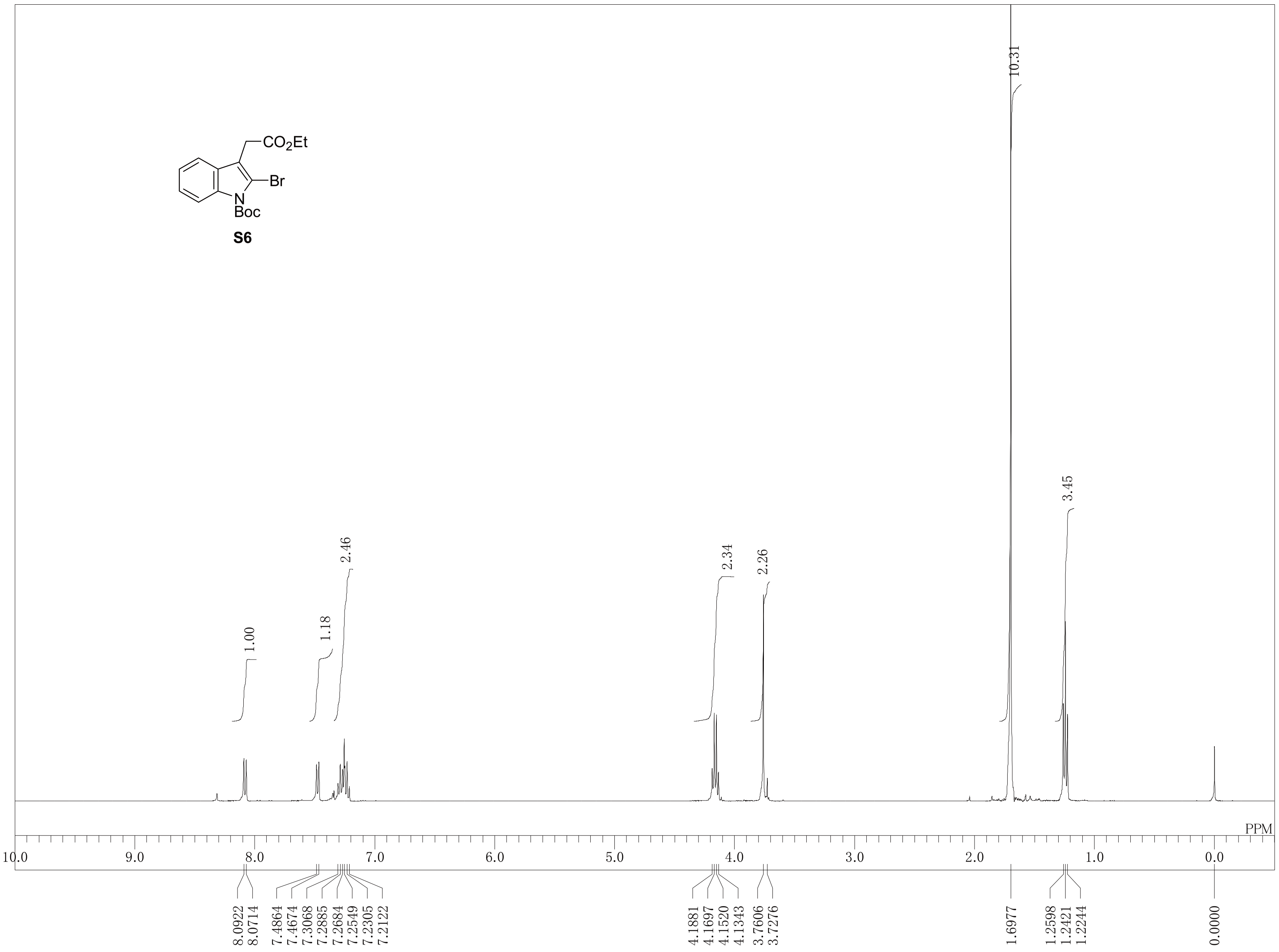
| BF | 0.42 Hz |
| RGAIN | 12 |

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1301-No1400¥No1321-No1330¥1322_07_12_6_13C.als

```
DATIM     Thu Dec 06 18:2
DFILE     C:¥My Documen
OBNUC     13C
EXMOD     BCM
OFR           99.45 MHz
OBSET         94.00 KHz
OBFIN      10309.00 Hz
POINT         32768
FREQU      26845.64 Hz
SCANS           416
ACQTM        1.2206 sec
PD           1.7790 sec
PW1            6.40 usec
IRN
CTEMP          28.1 c
SLVNT     CDCL3
EXREF         77.00 ppm
BF             0.42 Hz
RGAIN            24
```



| | |
|---|---|
| DATIM | Thu Mar 01 13:1 |
| DFILE | C:¥My Documen |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 399.65 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10500.00 Hz |
| POINT | 32768 |
| FREQU | 8000.00 Hz |
| SCANS | 16 |
| ACQTM | 4.0960 sec |
| PD | 2.9010 sec |
| PW1 | 5.90 usec |
| IRN | |
| CTEMP | 24.7 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 13 |


S6

Supplementary Material (ESI) for Chemical Communications
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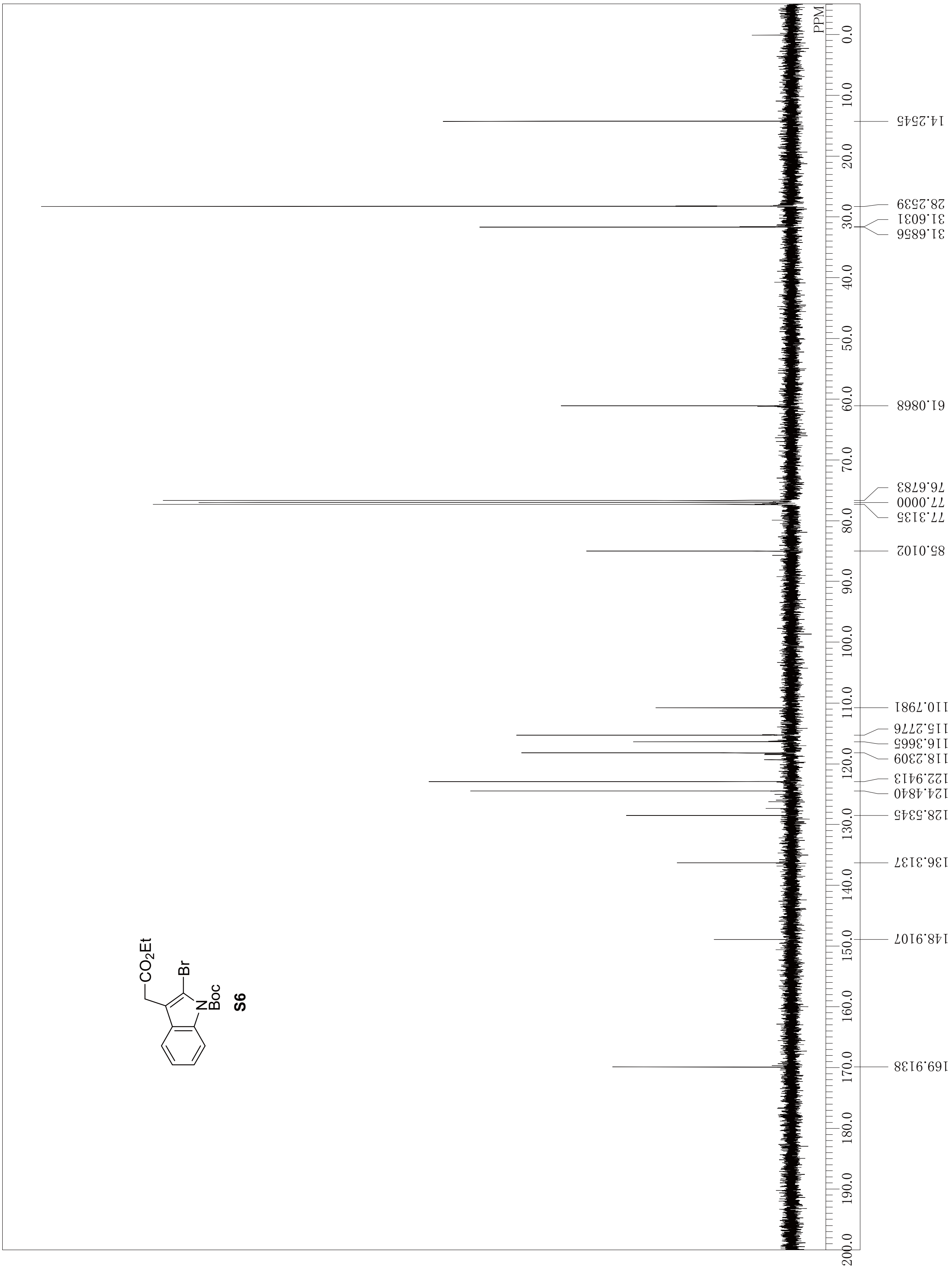
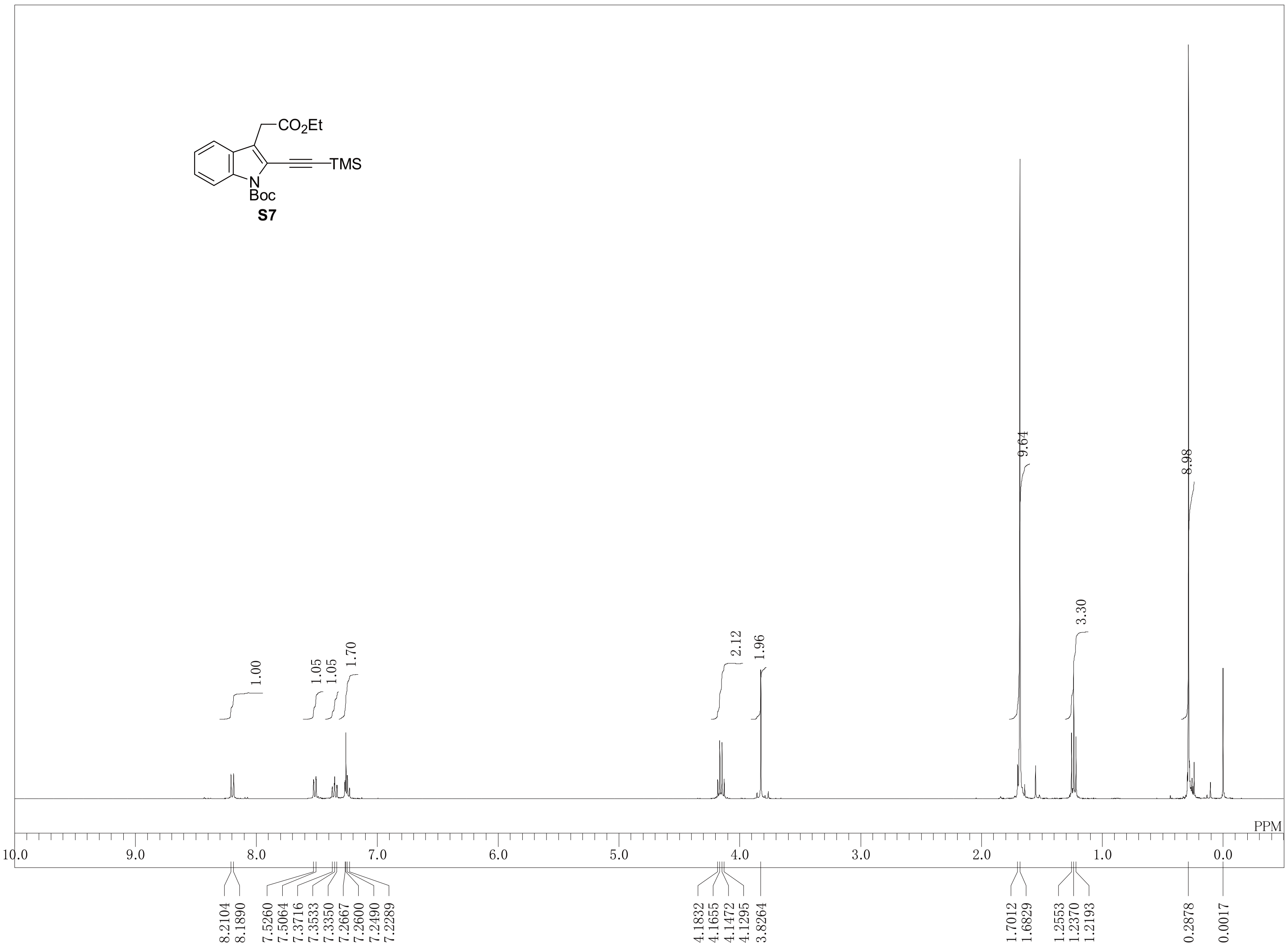
DATIM Thu Mar 01 13:4
DFILE C:¥My Documen
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 482
ACQTM 1.2059 sec
PD 1.7940 sec
PW1 5.90 usec
IRN
CTEMP 24.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 24



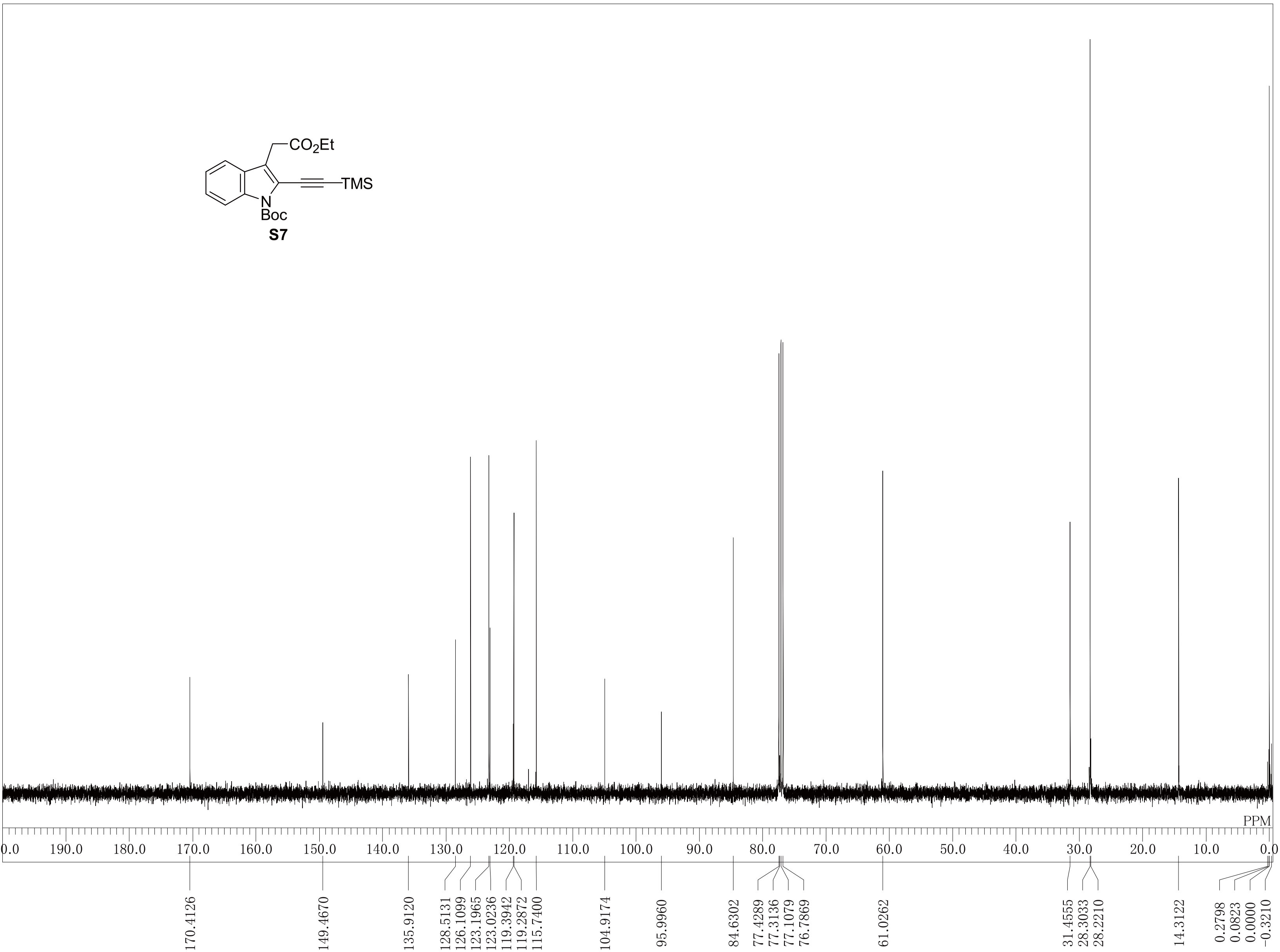
**S6**

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No0901-No1000¥No961-No970¥962_07_3_5.als


S7

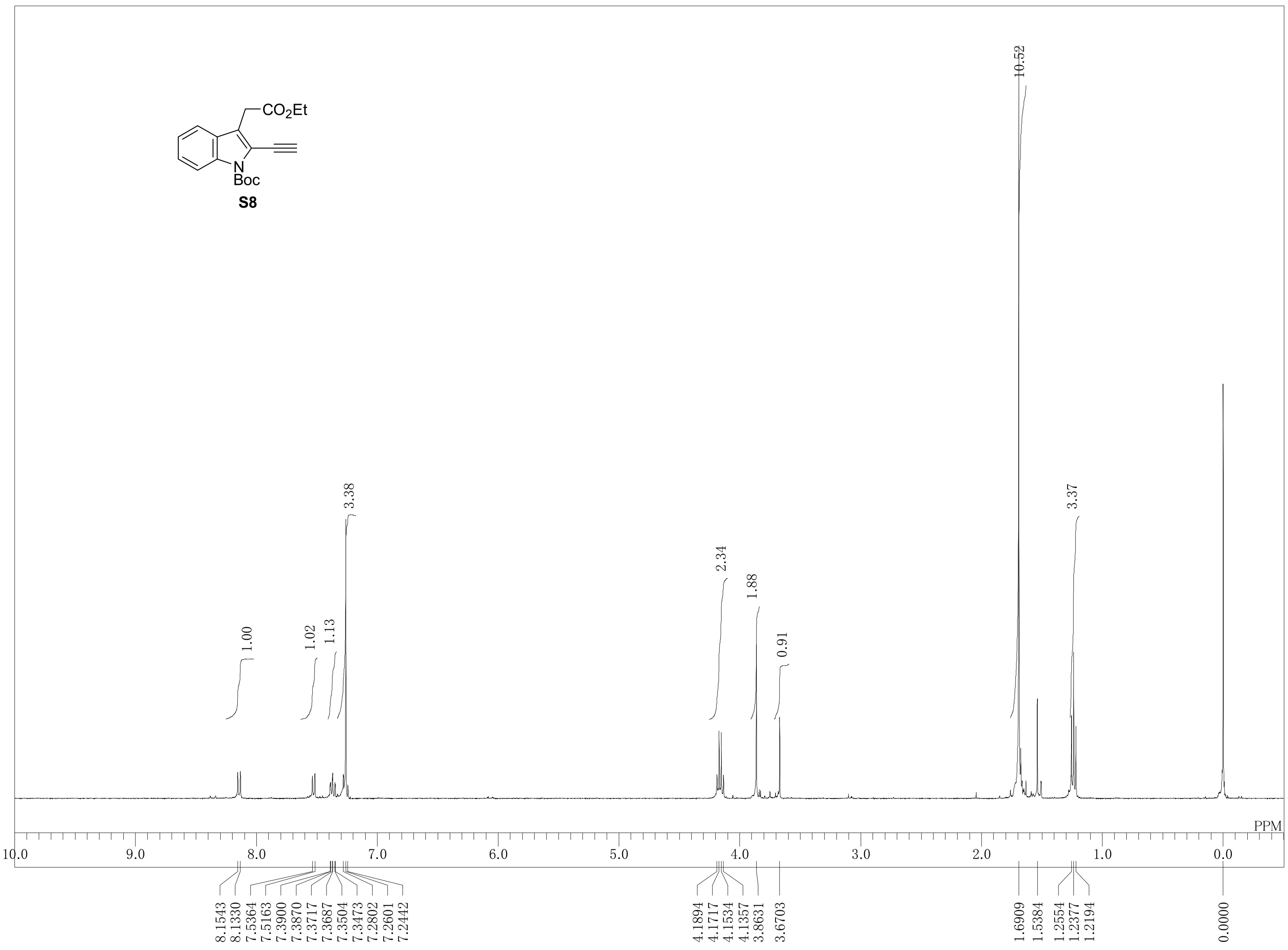
| | |
|---|---|
| DATIM | Mon Mar 05 20: |
| DFILE | C:¥My Documen |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 395.75 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10277.00 Hz |
| POINT | 32768 |
| FREQU | 7912.96 Hz |
| SCANS | 16 |
| ACQTM | 4.1411 sec |
| PD | 2.8590 sec |
| PW1 | 5.80 usec |
| IRN | |
| CTEMP | 25.2 c |
| SLVNT | CDCL3 |
| EXREF | 7.26 ppm |
| BF | 0.12 Hz |
| RGAIN | 16 |

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No0901-No1000¥No961-No970¥962_07_3_5_13C.als



| | |
|---|---|
| DATIM | Mon Mar 05 21: |
| DFILE | C:¥My Documen |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 468 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.50 usec |
| IRN | |
| CTEMP | 26.8 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 24 |

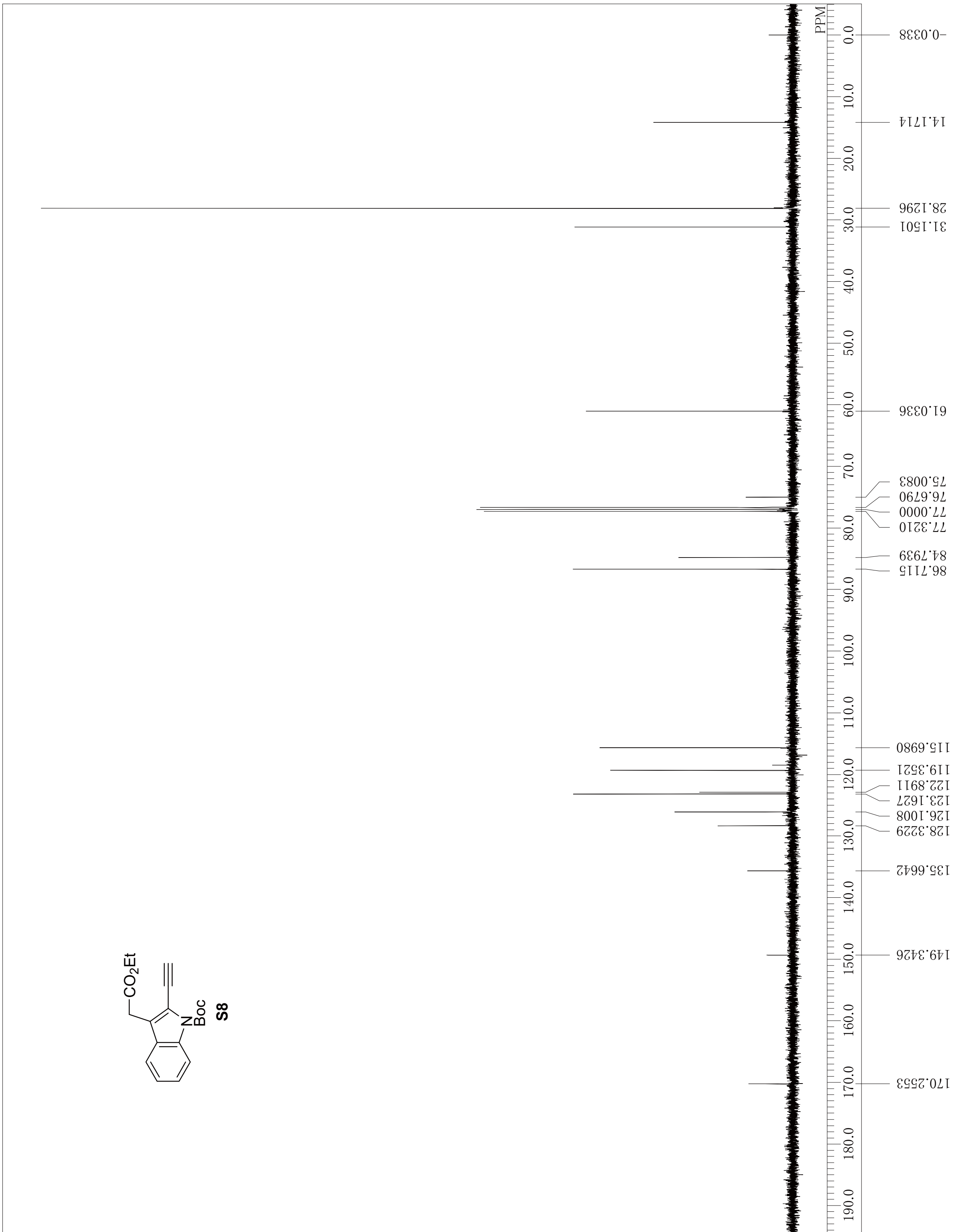
C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No0901-No1000¥No941-No950¥942_07_2_20.als



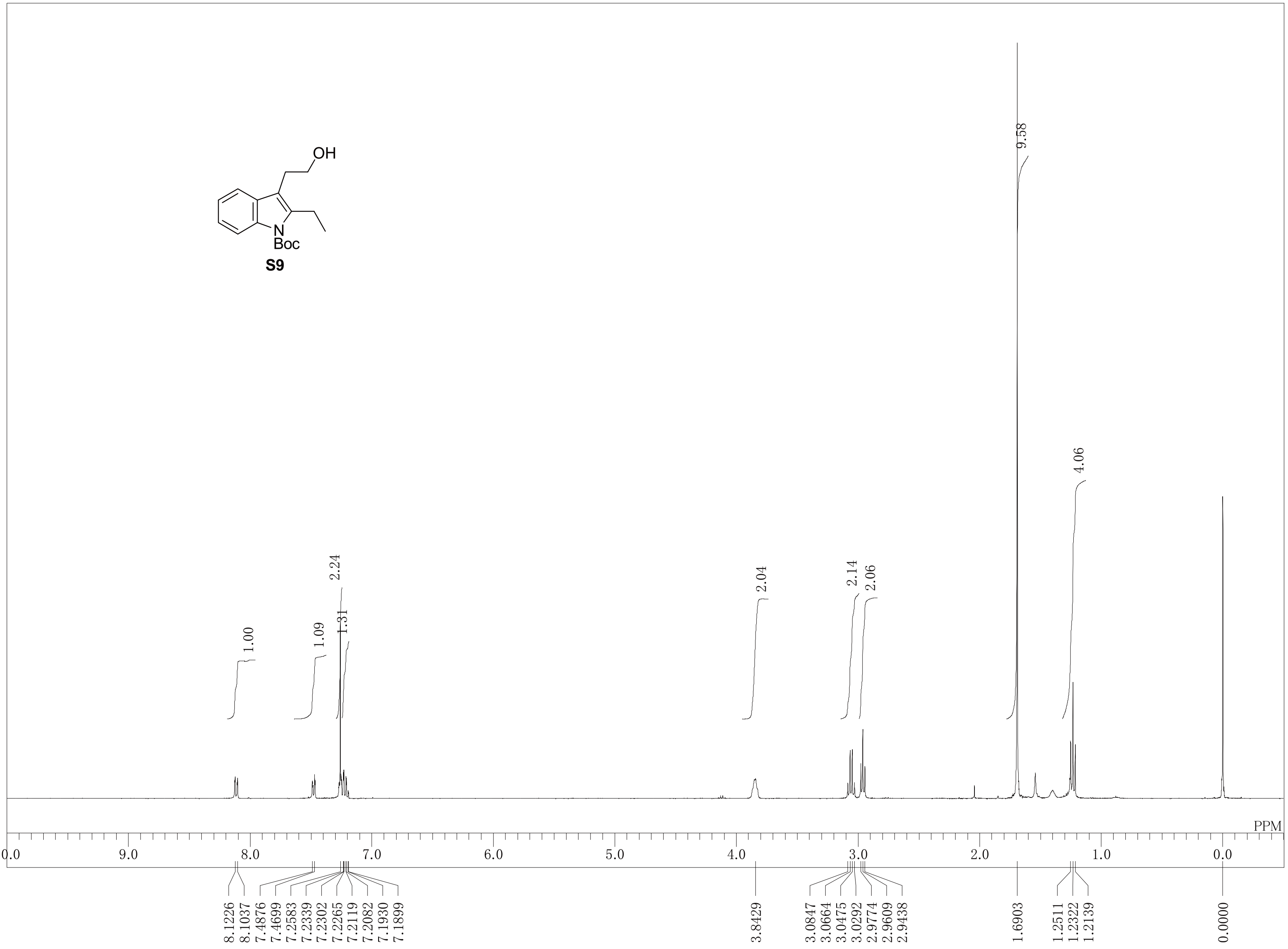
| | |
|---|---|
| DATIM | Tue Feb 20 21:3 |
| DFILE | C:¥My Documen |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 395.75 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10277.00 Hz |
| POINT | 32768 |
| FREQU | 7912.96 Hz |
| SCANS | 32 |
| ACQTM | 4.1411 sec |
| PD | 2.8590 sec |
| PW1 | 5.80 usec |
| IRN | |
| CTEMP | 25.1 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 21 |

C:¥My Documents¥個人ファイル¥NMR AL400¥shigeki¥No0901-No1000¥No961-No970¥964_07_3_6_13C.als

| | |
|---|---|
| DATIM | Tue Mar 06 21:4 |
| DFILE | C:¥My Documen |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 386 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.50 usec |
| IRN | |
| CTEMP | 26.7 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 24 |



C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No0901-No1000¥No941-No950¥948_07_3_2.als



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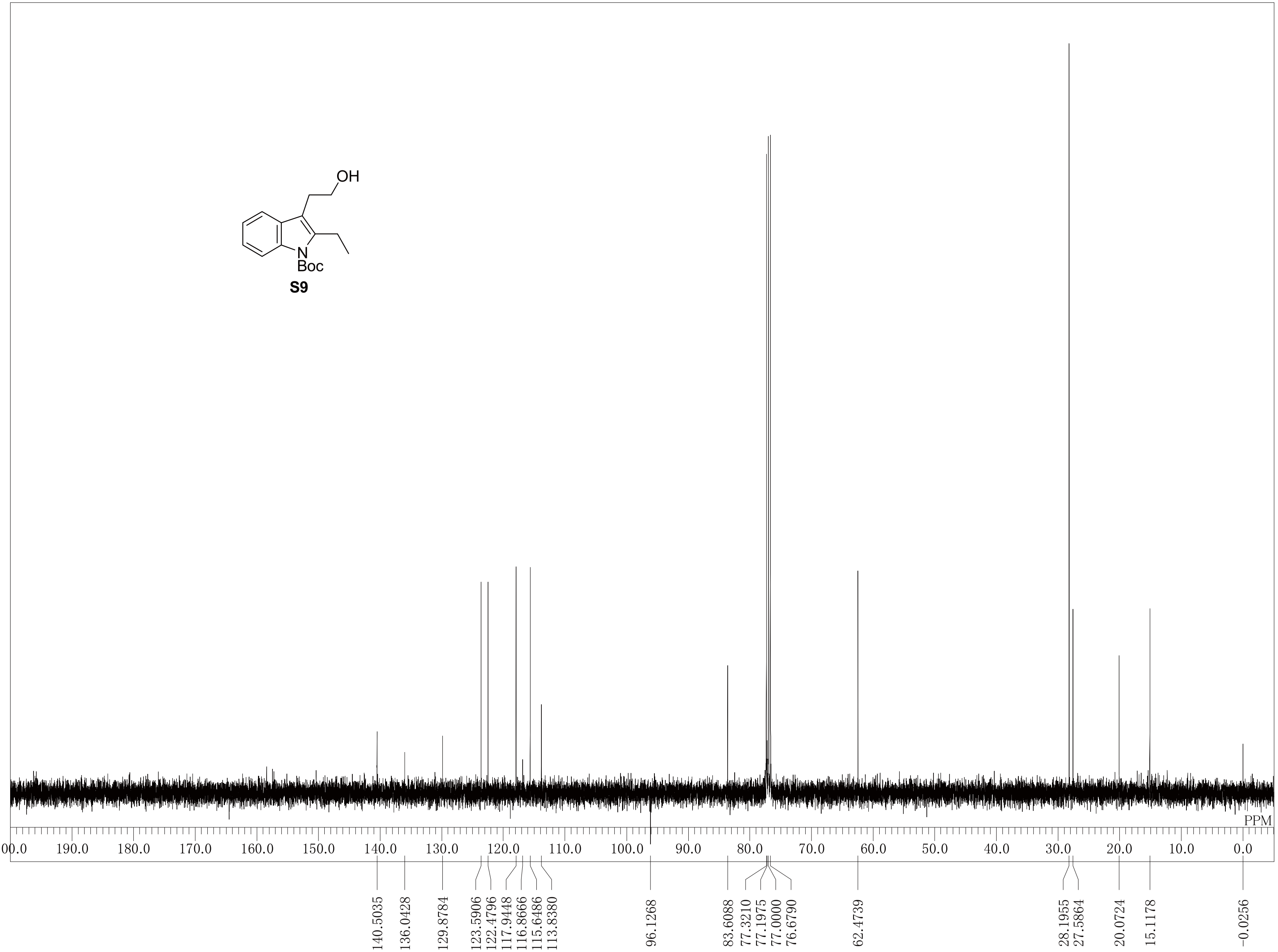
DATIM    Fri Mar 02 21:24
DFILE    C:¥My Documen
OBNUC    1H
EXMOD    NON
OFR        395.75 MHz
OBSET      124.00 KHz
OBFIN    10277.00 Hz
POINT        32768
FREQU      7912.96 Hz
SCANS           16
ACQTM       4.1411 sec
PD          2.8590 sec
PW1           5.80 usec
IRN
CTEMP         25.4 c
SLVNT    CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           19
```

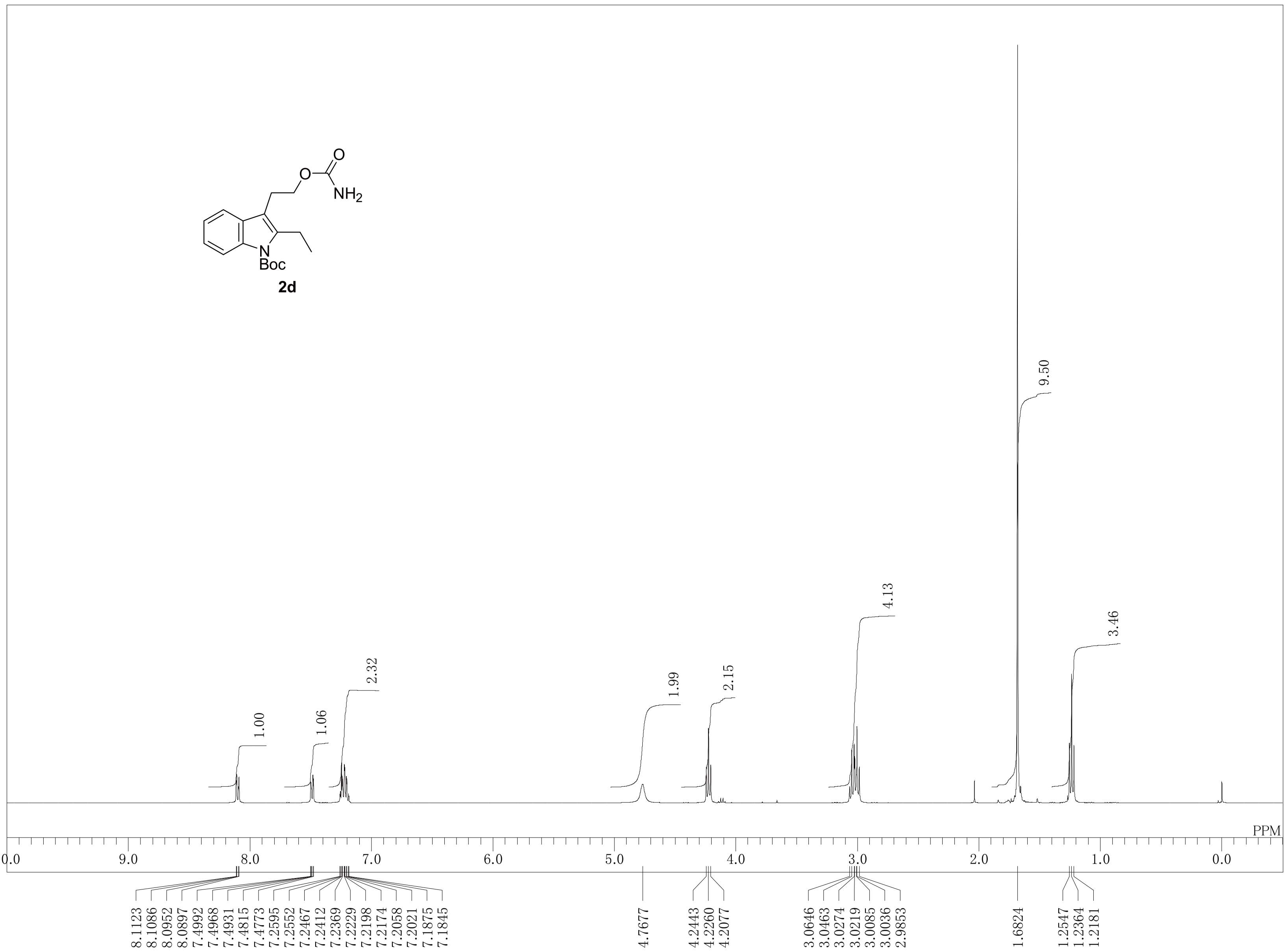
C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No0901-No1000¥No961-No970¥970_07_3_10_13C.als



**S9**

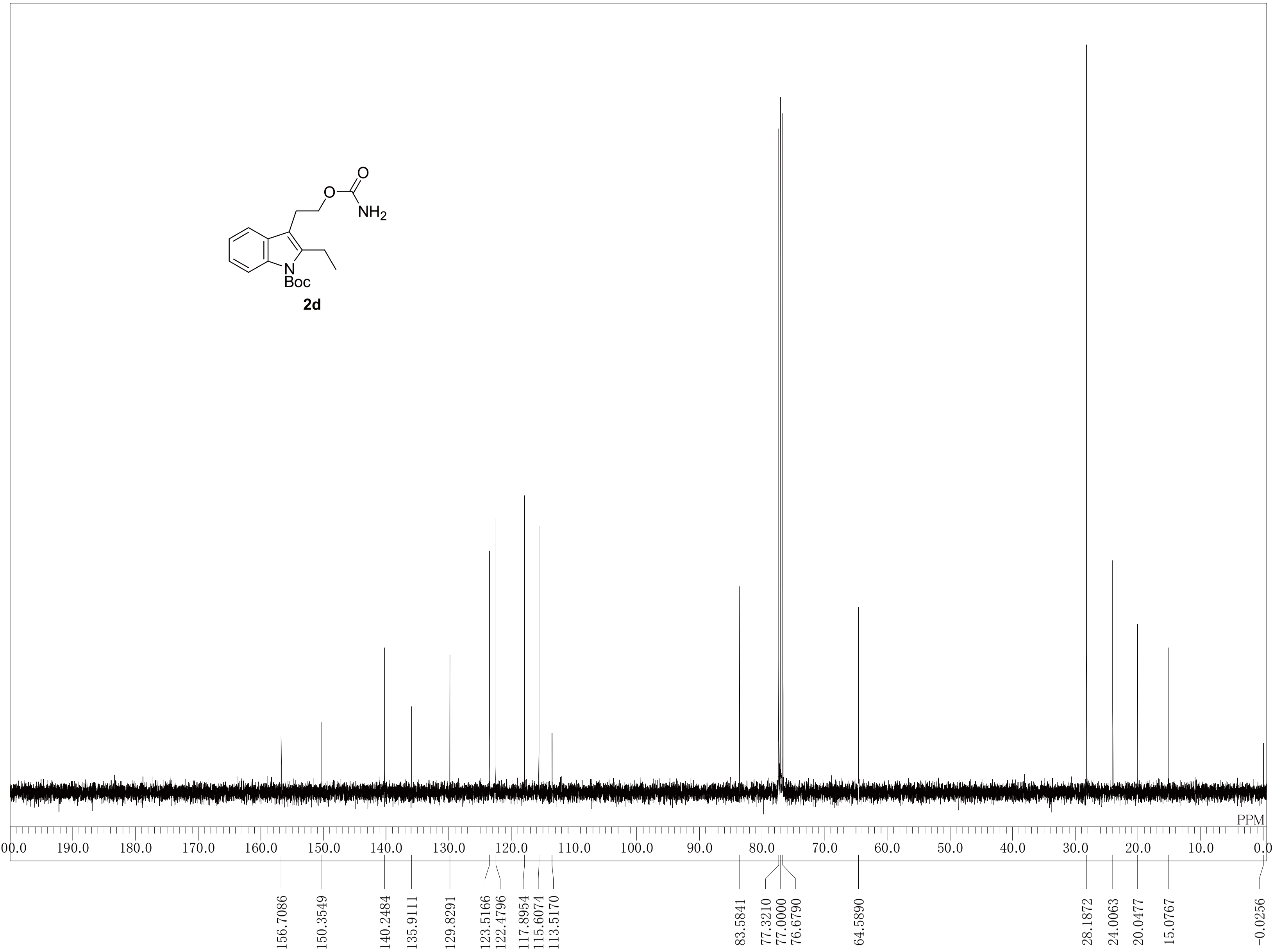
DATIM Sat Mar 10 10:4
DFILE C:¥My Documen
OBNUC 13C
EXMOD BCM
OFR 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 371
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRN
CTEMP 26.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 24

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1301-No1400¥No1331-No1340¥1338_07_12_14.als

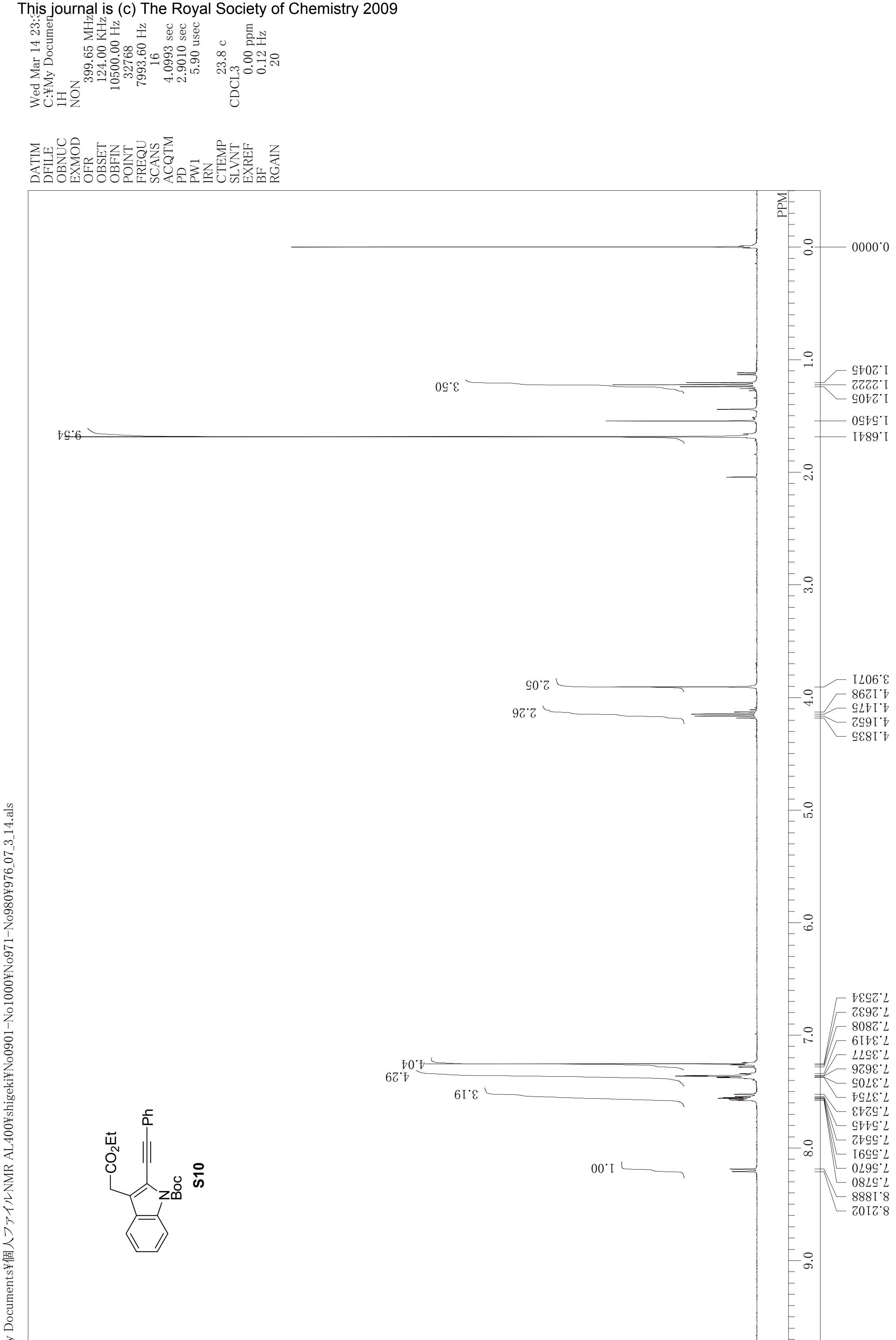


| | |
|---|---|
| DATIM | Fri Dec 14 13:07 |
| DFILE | C:¥My Documen |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 395.75 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10277.00 Hz |
| POINT | 32768 |
| FREQU | 7912.96 Hz |
| SCANS | 16 |
| ACQTM | 4.1411 sec |
| PD | 2.8590 sec |
| PW1 | 5.80 usec |
| IRN | |
| CTEMP | 26.1 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 0.42 Hz |
| RGAIN | 11 |

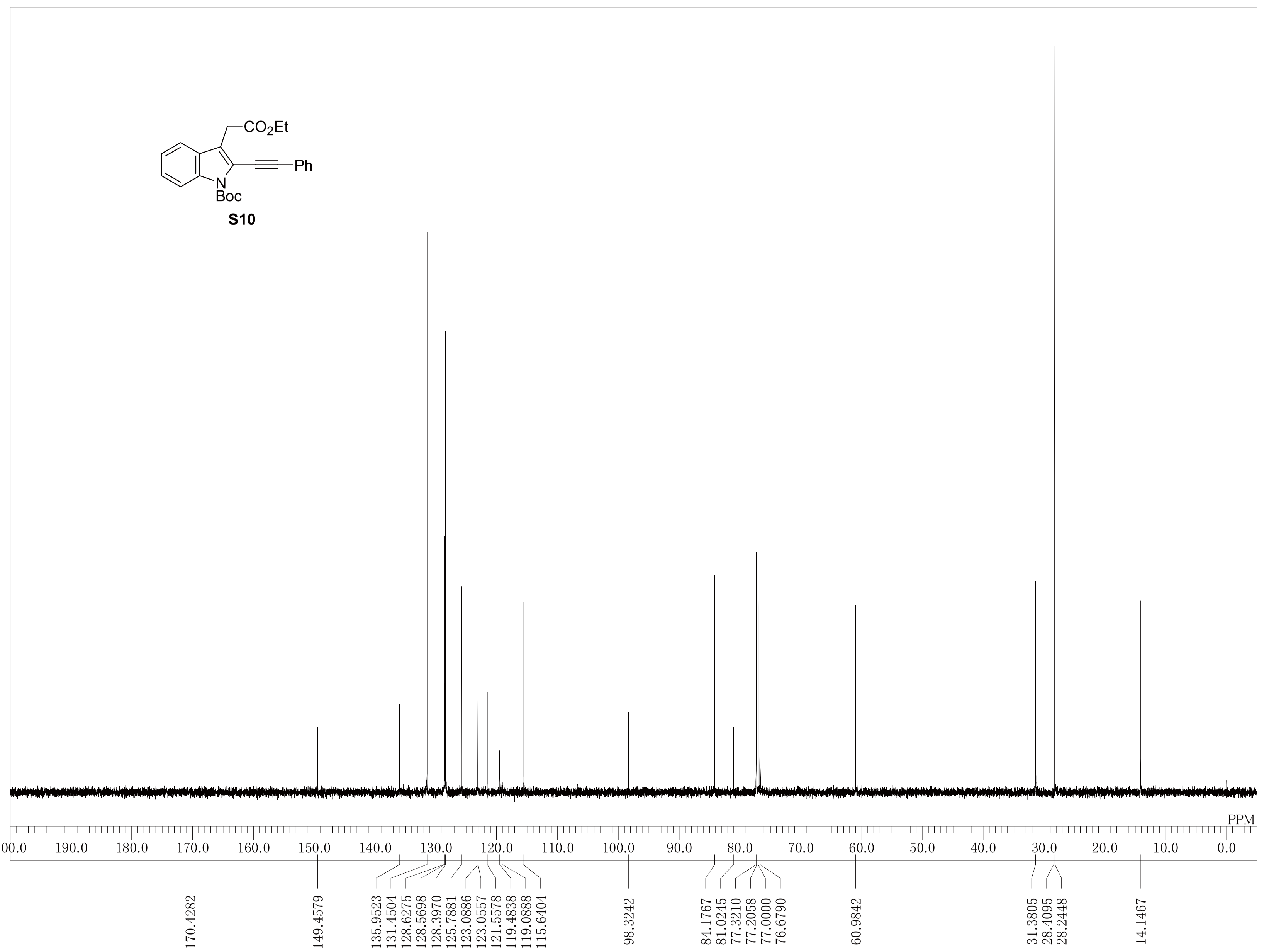
C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No0901-No1000¥No971-No980¥971_07_3_13_13C.als



| | |
|---|---|
| DATIM | Tue Mar 13 13:1 |
| DFILE | C:¥My Documen |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 452 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.50 usec |
| IRN | |
| CTEMP | 25.1 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 24 |

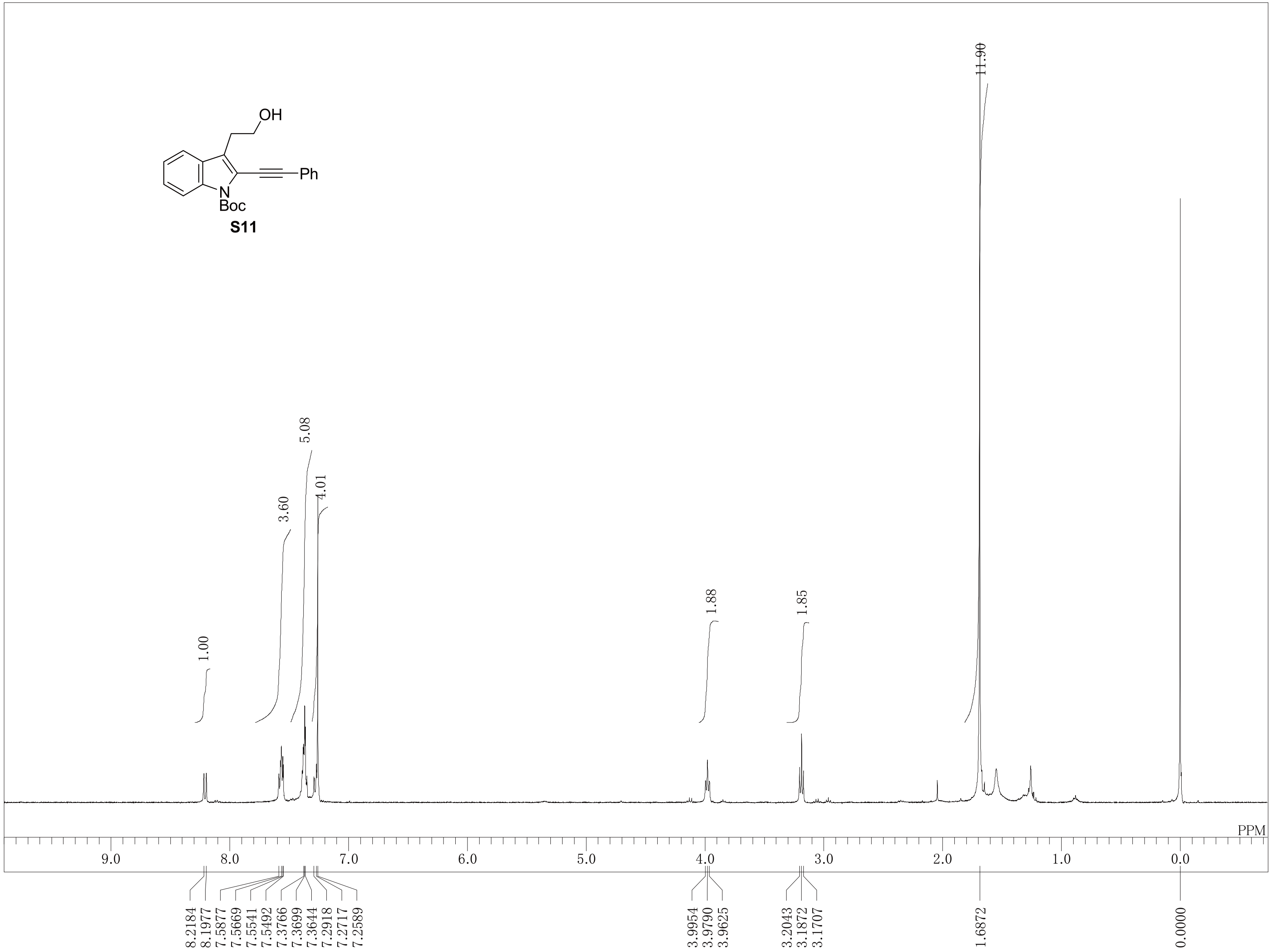

DATIM Wed Mar 14 23:
DFILE C:¥My Documen
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 16
ACQTM 4.0993 sec
PD 2.9010 sec
PW1 5.90 usec
IRN
CTEMP 23.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 20
C:¥My Documents¥個人ファイル¥NMR AL400¥shigeki¥No0901-No1000¥No971-No980¥976_07_3_14.als
PPM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
0.0000
1.2045
1.2222
1.2405
1.5450
1.6841
3.9071
4.1298
4.1475
4.1652
4.1835
7.2534
7.2632
7.2808
7.3419
7.3577
7.3626
7.3705
7.3754
7.5243
7.5445
7.5542
7.5591
7.5670
7.5780
8.1888
8.2102
3.50
9.54
2.05
2.26
4.04
4.29
3.19
1.00
CO2Et
Ph
N
Boc
S10

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No0901-No1000¥No971-No980¥976_07_3_15_13C.als



DATIM Thu Mar 15 09:5
DFILE C:¥My Documen
OBNUC 13C
EXMOD BCM
OFR 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 380
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRN
CTEMP 25.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 24

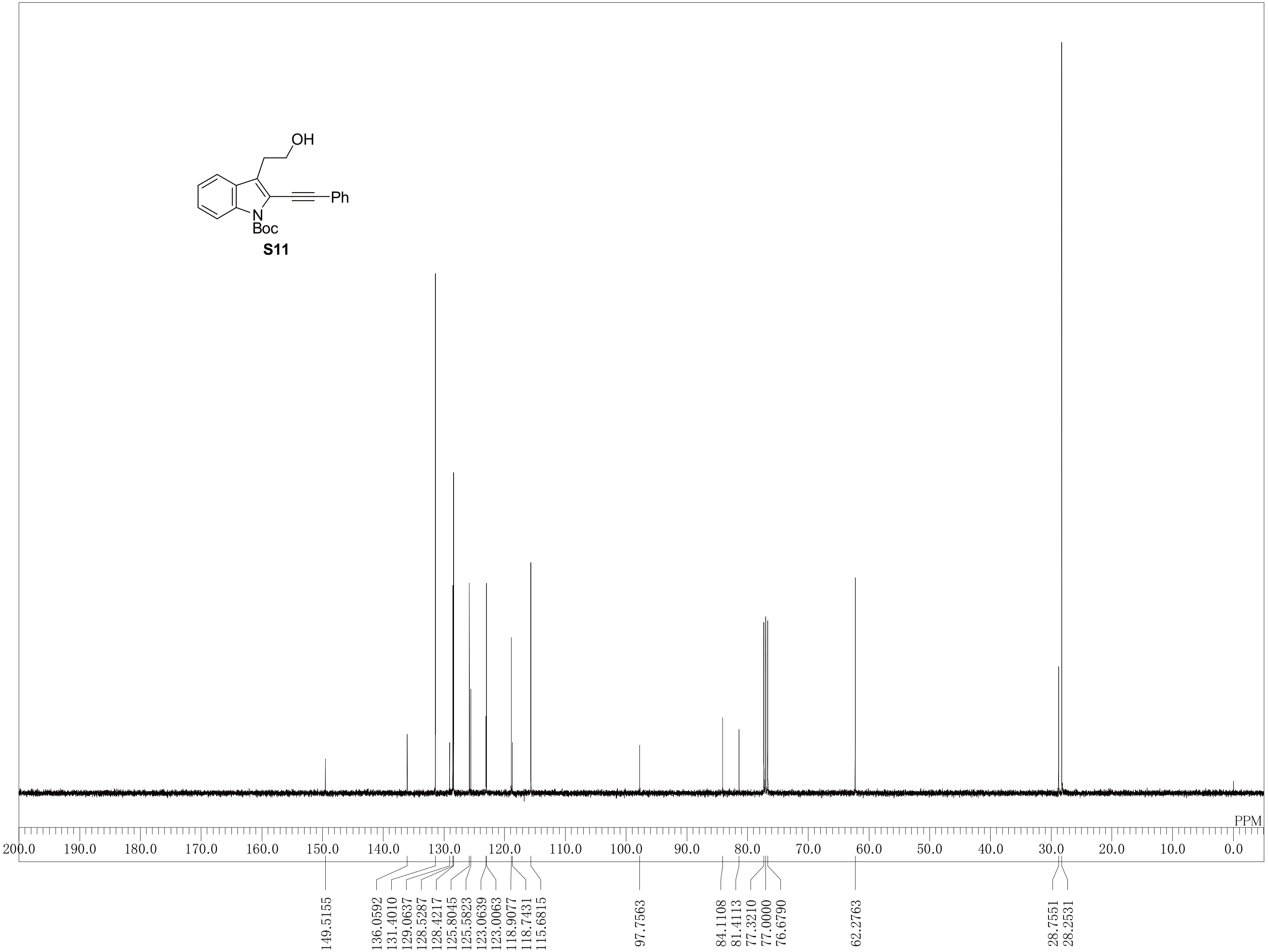
C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No0901-No1000¥No971-No980¥978_07_3_15.als



| | |
|---|---|
| DATIM | Thu Mar 15 18:5 |
| DFILE | C:¥My Documen |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 395.75 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10277.00 Hz |
| POINT | 32768 |
| FREQU | 7912.96 Hz |
| SCANS | 16 |
| ACQTM | 4.1411 sec |
| PD | 2.8590 sec |
| PW1 | 5.80 usec |
| IRN | |
| CTEMP | 24.8 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 20 |

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No0901-No1000¥No971-No980¥980_07_3_16_13C.als

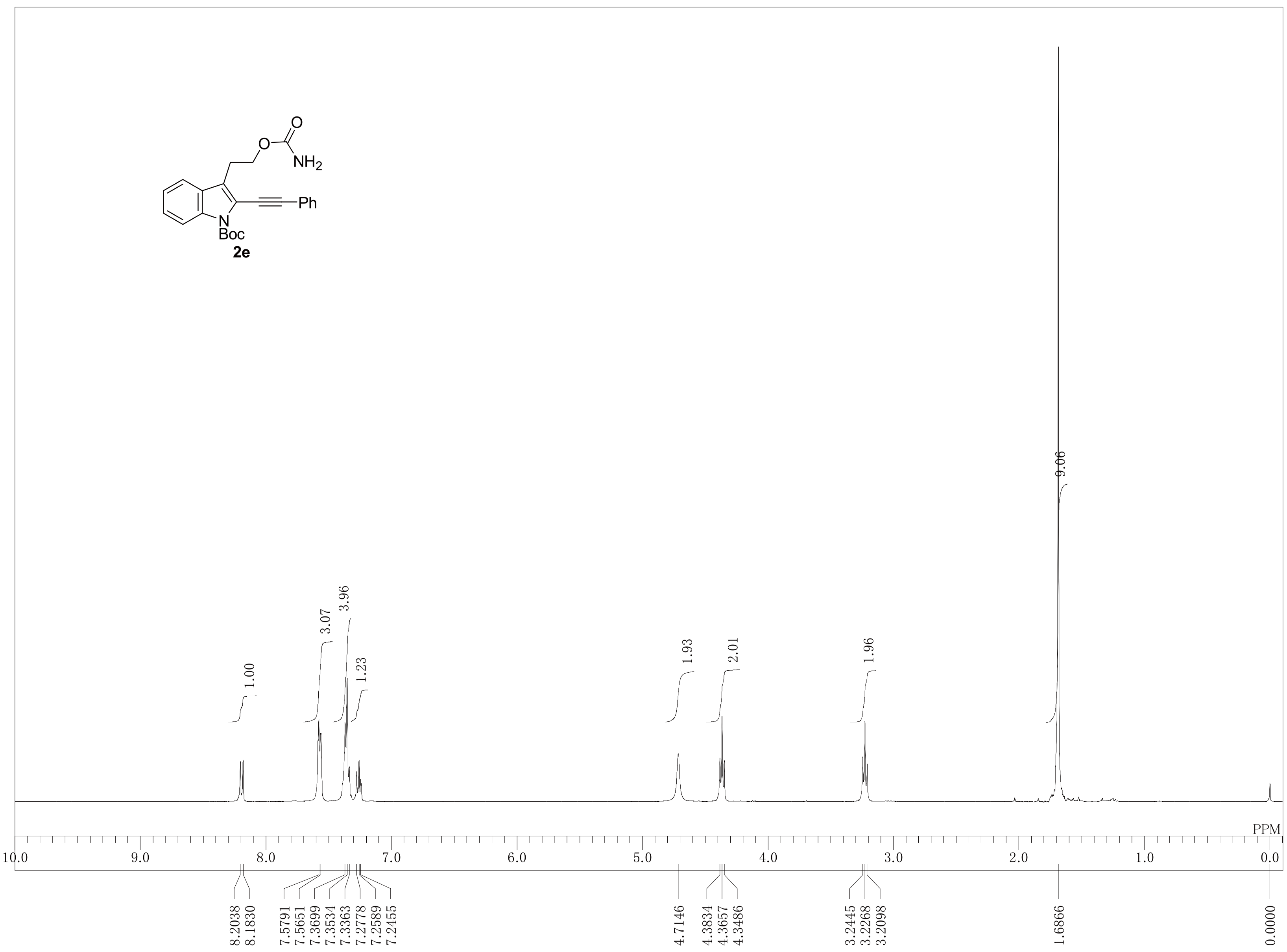
| | |
|---|---|
| DATIM | Fri Mar 16 09:34 |
| DFILE | C:¥My Documen |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 320 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.50 usec |
| IRN | |
| CTEMP | 26.0 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 24 |



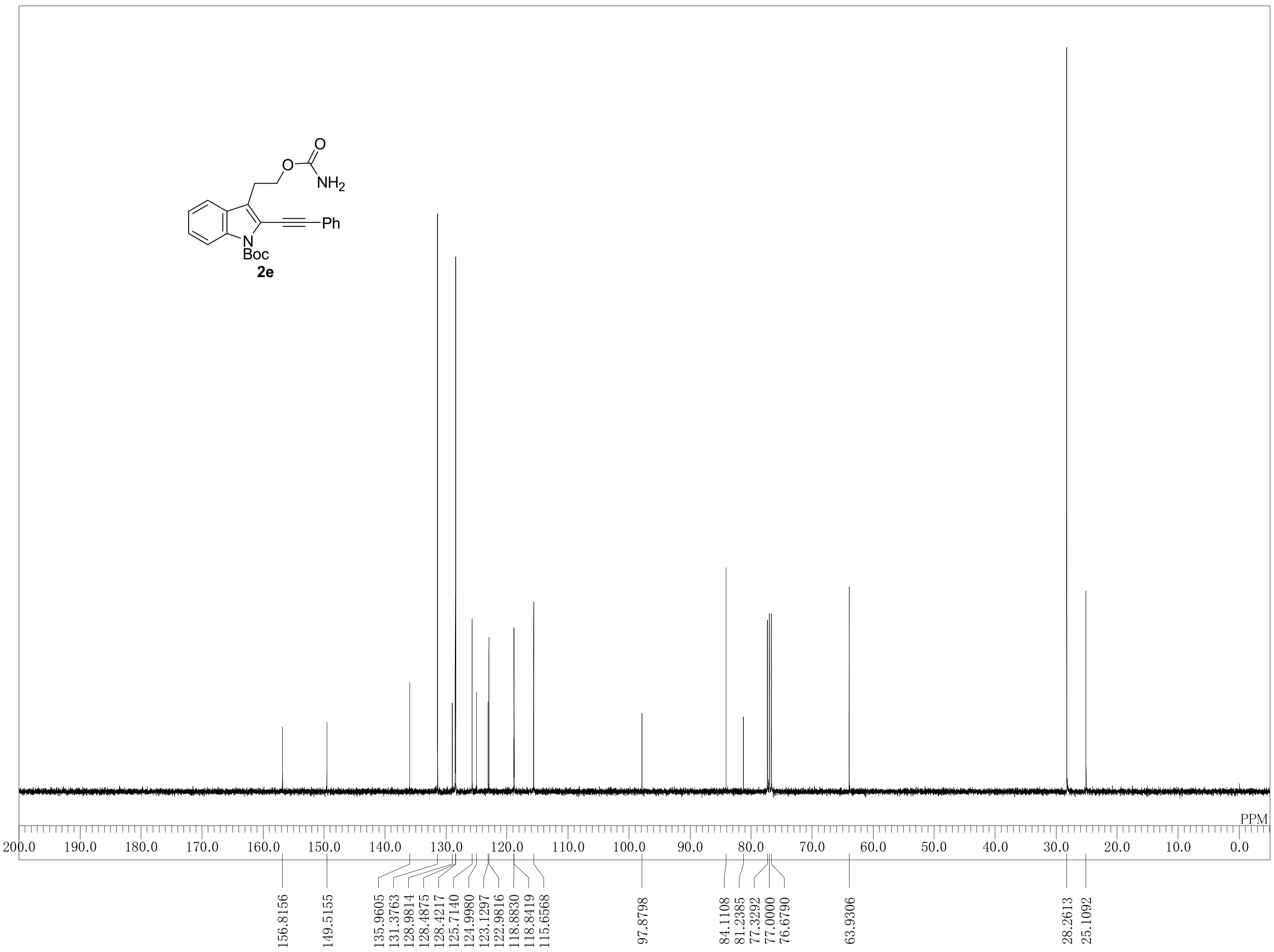
**S11**

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No0901-No1000¥No981-No990¥981_07_3_16.als

| | |
|---|---|
| DATIM | Fri Mar 16 23:04 |
| DFILE | C:¥My Documen |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 395.75 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10277.00 Hz |
| POINT | 32768 |
| FREQU | 7912.96 Hz |
| SCANS | 16 |
| ACQTM | 4.1411 sec |
| PD | 2.8590 sec |
| PW1 | 5.80 usec |
| IRN | |
| CTEMP | 24.2 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 12 |

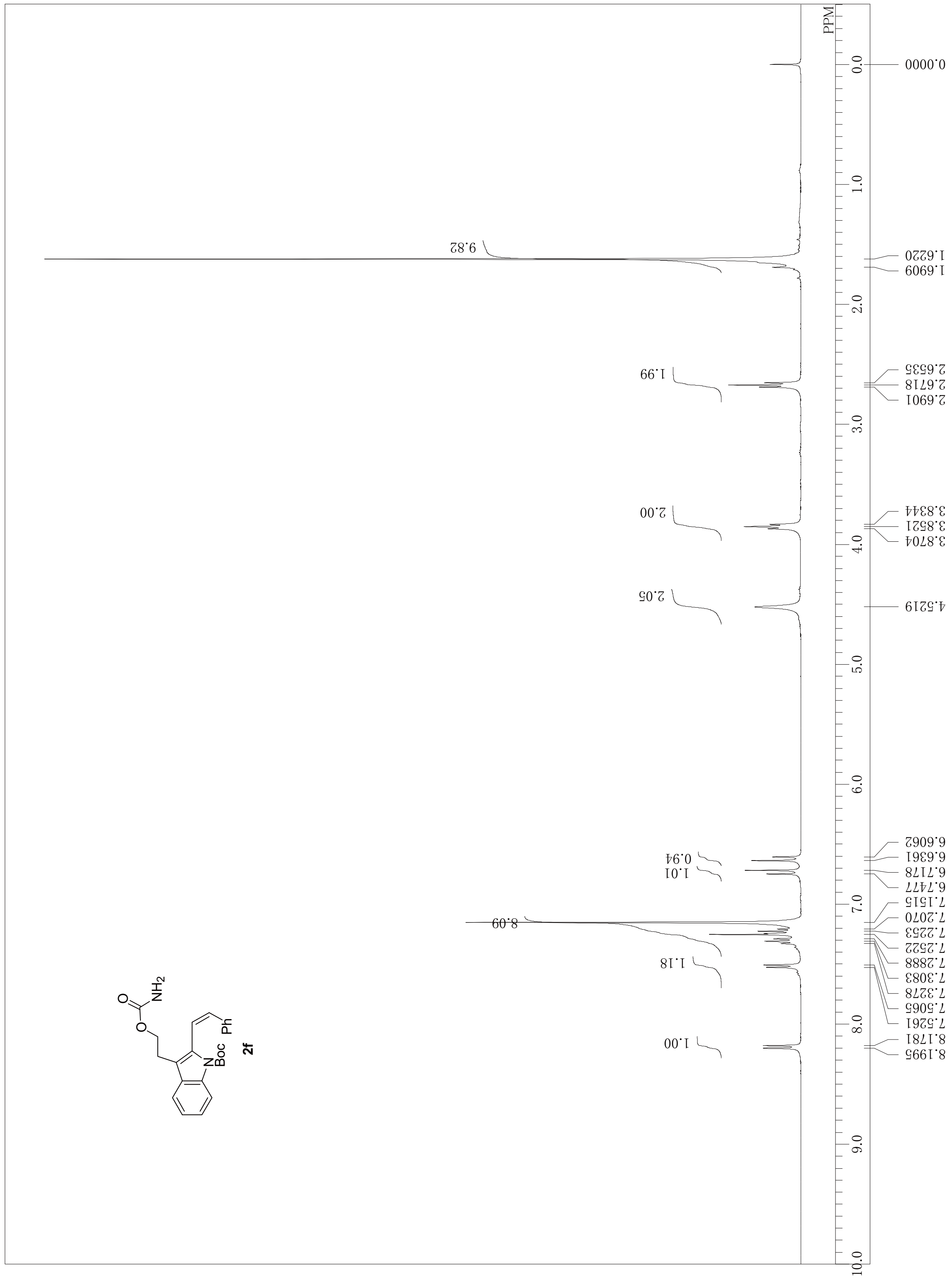


C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No0901-No1000¥No981-No990¥981_07_3_16_13C.als



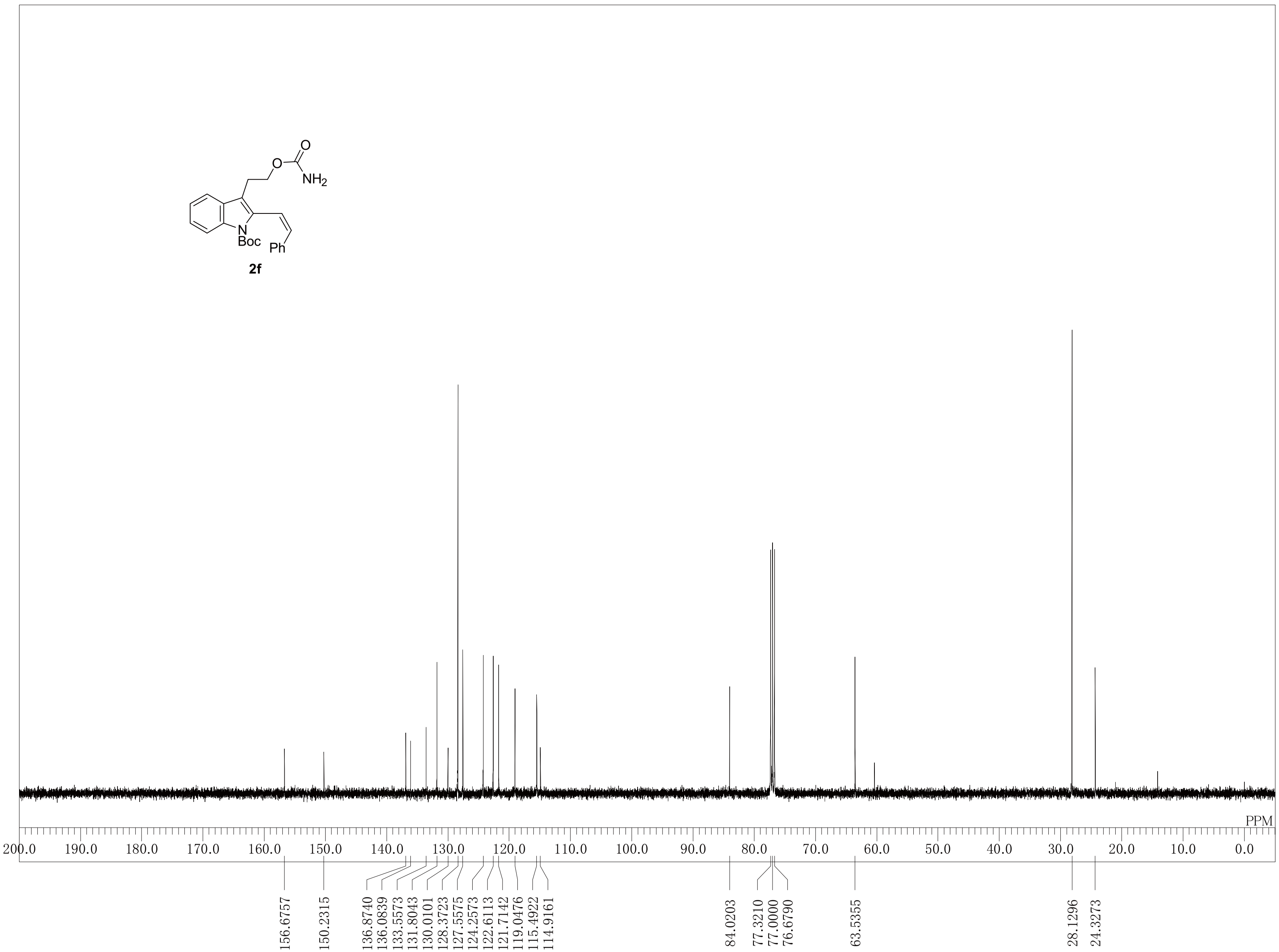
| | |
|---|---|
| DATIM | Fri Mar 16 23:27 |
| DFILE | C:¥My Documen |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 430 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.50 usec |
| IRN | |
| CTEMP | 26.2 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 24 |

DATIM Tue Mar 20 09:5
DFILE C:¥My Documen
OBNUC 1H
EXMOD NON
OFR 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 32768
FREQU 7912.96 Hz
SCANS 16
ACQTM 4.1411 sec
PD 2.8590 sec
PW1 5.80 usec
IRN
CTEMP 24.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 13



C:¥My Documents¥個人ファイル¥NMR AL400¥shigeki¥No0901-No1000¥No981-No990¥983_07_3_20.als

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No0901-No1000¥No981-No990¥983_07_3_20_13C.als


2f

| | |
|---|---|
| DATIM | Tue Mar 20 10:1 |
| DFILE | C:¥My Documen |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 344 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.50 usec |
| IRN | |
| CTEMP | 26.0 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 24 |

Supplementary Material (ESI) for Chemical Communications
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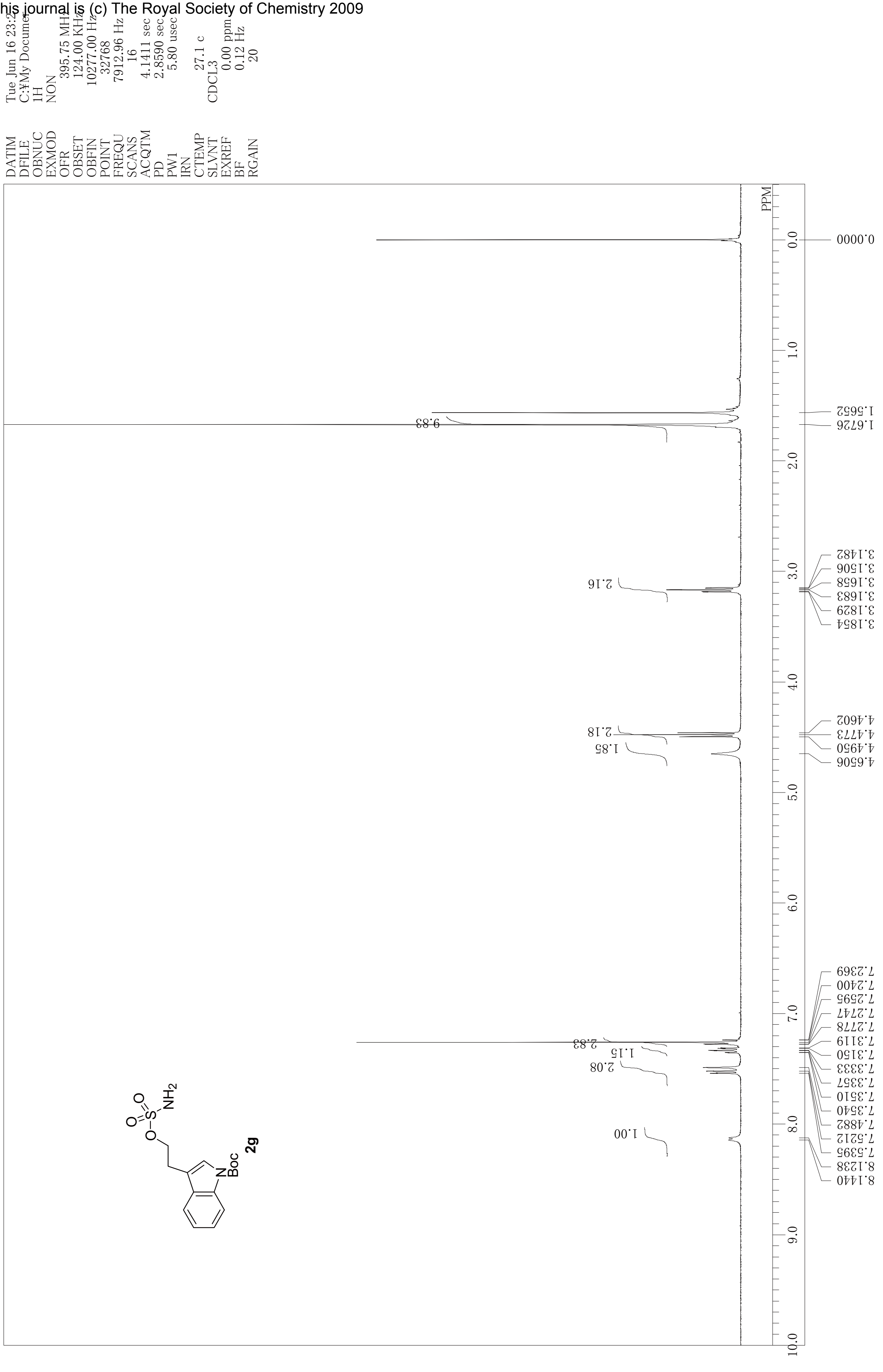
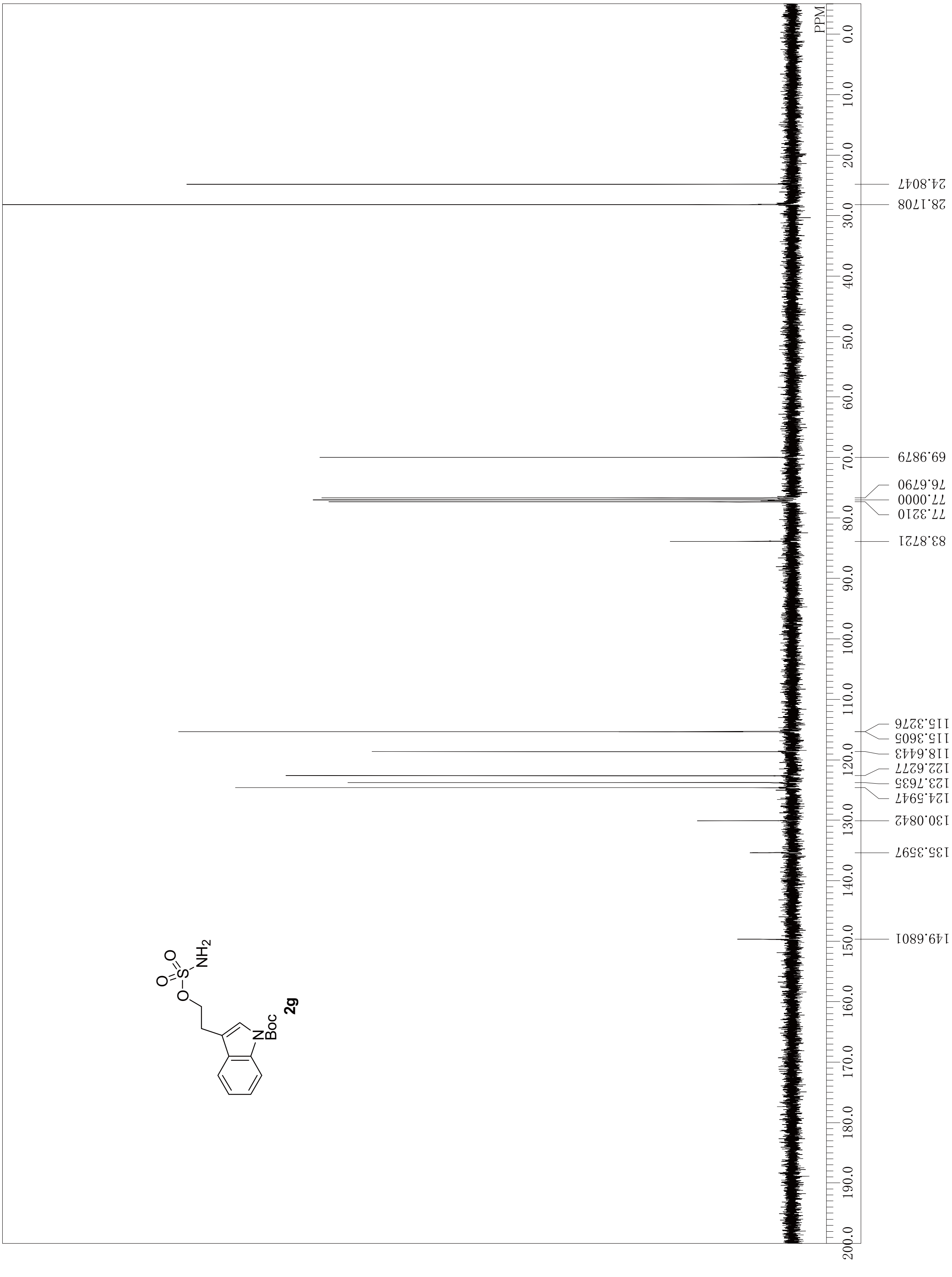
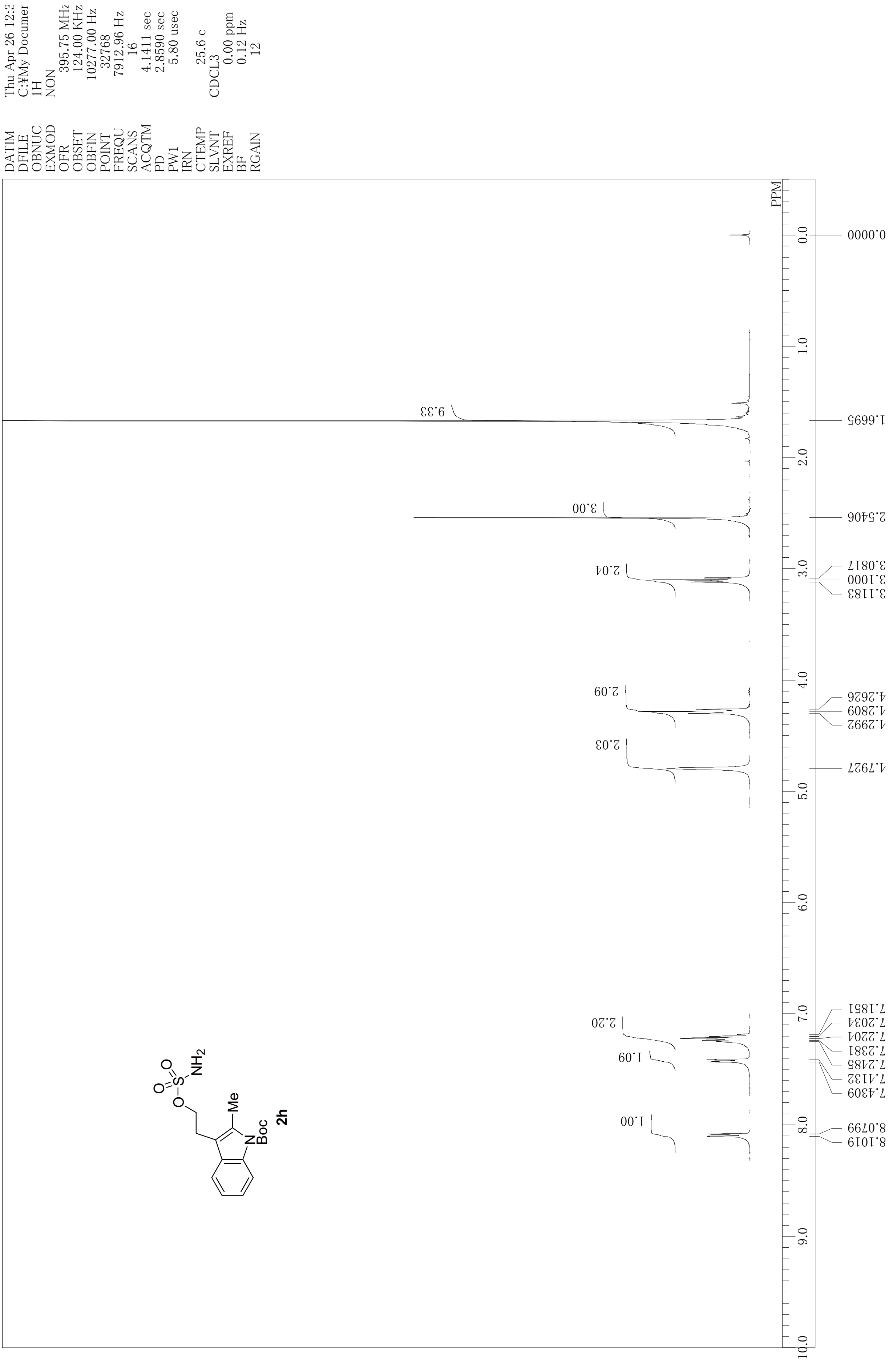


| | |
|---|---|
| DATIM | Fri Jun 19 18:52 |
| DFILE | C:¥My Documen |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 638 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.40 usec |
| IRN | |
| CTEMP | 26.7 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 24 |

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DFILE C:¥My Documer
OBNUC 1H
EXMOD NON
OFR 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 32768
FREQU 7912.96 Hz
SCANS 16
ACQTM 4.1411 sec
PD 2.8590 sec
PW1 5.80 usec
IRN
CTEMP 25.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 12
PPM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
0.0000
1.6695
2.5406
3.0817
3.1000
3.1183
4.2626
4.2809
4.2992
4.7927
7.1851
7.2034
7.2204
7.2381
7.2485
7.4132
7.4309
8.0799
8.1019
9.33
3.00
2.04
2.09
2.03
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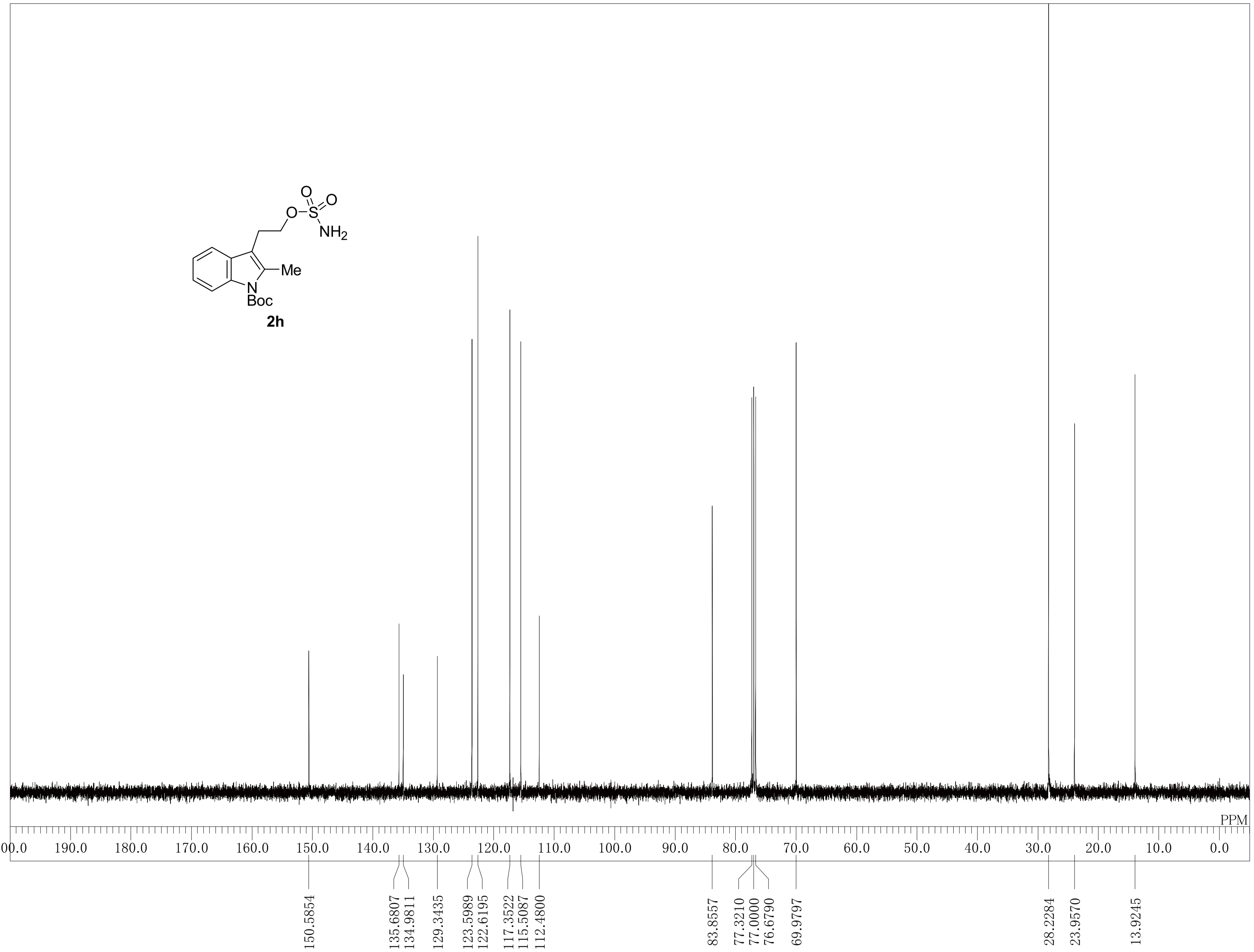
NH2
Me
N
Boc
2h

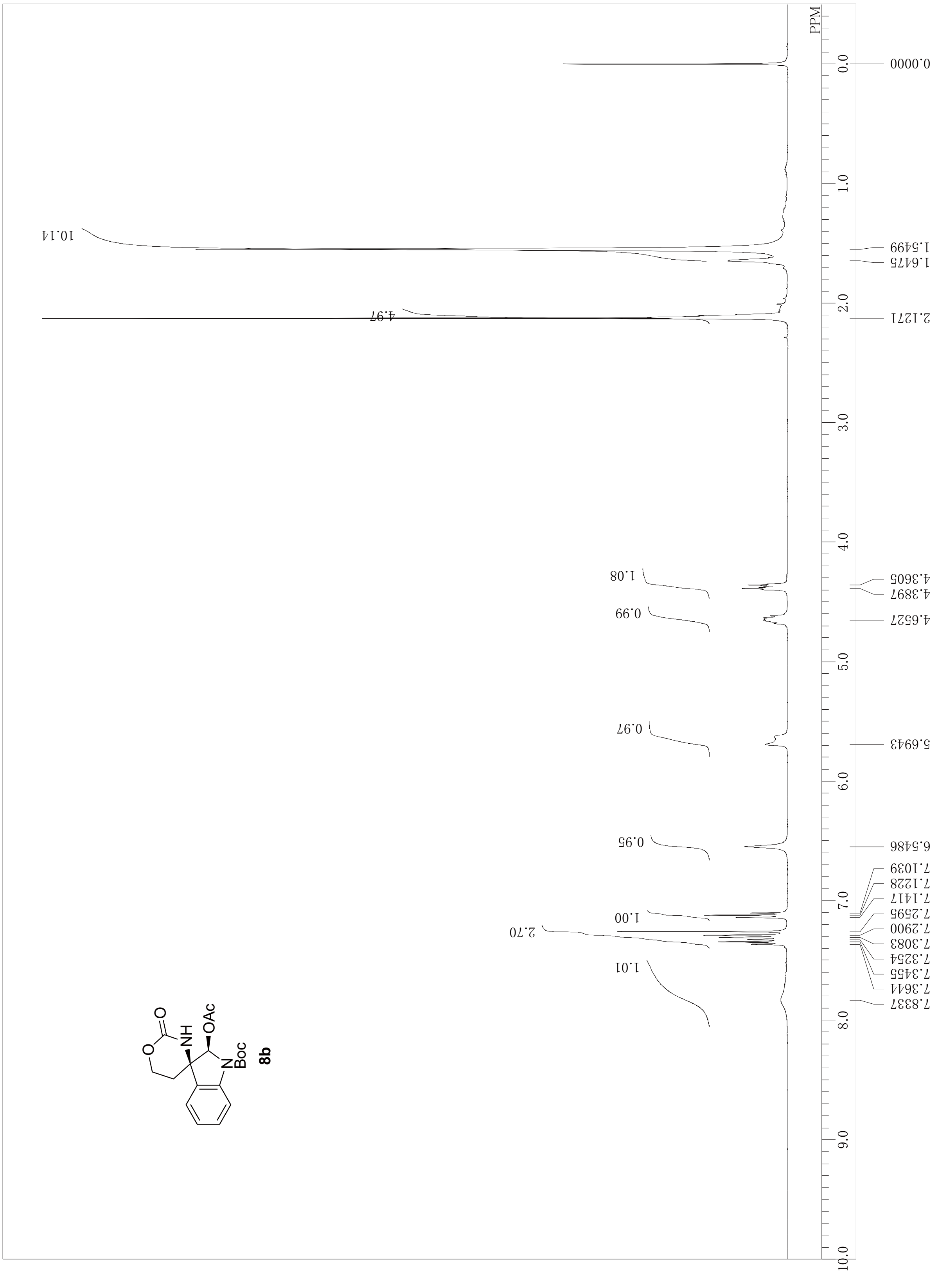


**2h**

| | |
|---|---|
| DATIM | Thu Apr 26 12:5 |
| DFILE | C:¥My Documer |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 451 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.40 usec |
| IRN | |
| CTEMP | 27.5 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 24 |

| | |
|---|---|
| DATIM | Wed Jun 18 17:1 |
| DFILE | C:¥My Documen |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 399.65 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10500.00 Hz |
| POINT | 32768 |
| FREQU | 7993.60 Hz |
| SCANS | 16 |
| ACQTM | 4.0993 sec |
| PD | 2.9010 sec |
| PW1 | 5.90 usec |
| IRN | |
| CTEMP | 25.8 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 1.02 Hz |
| RGAIN | 16 |

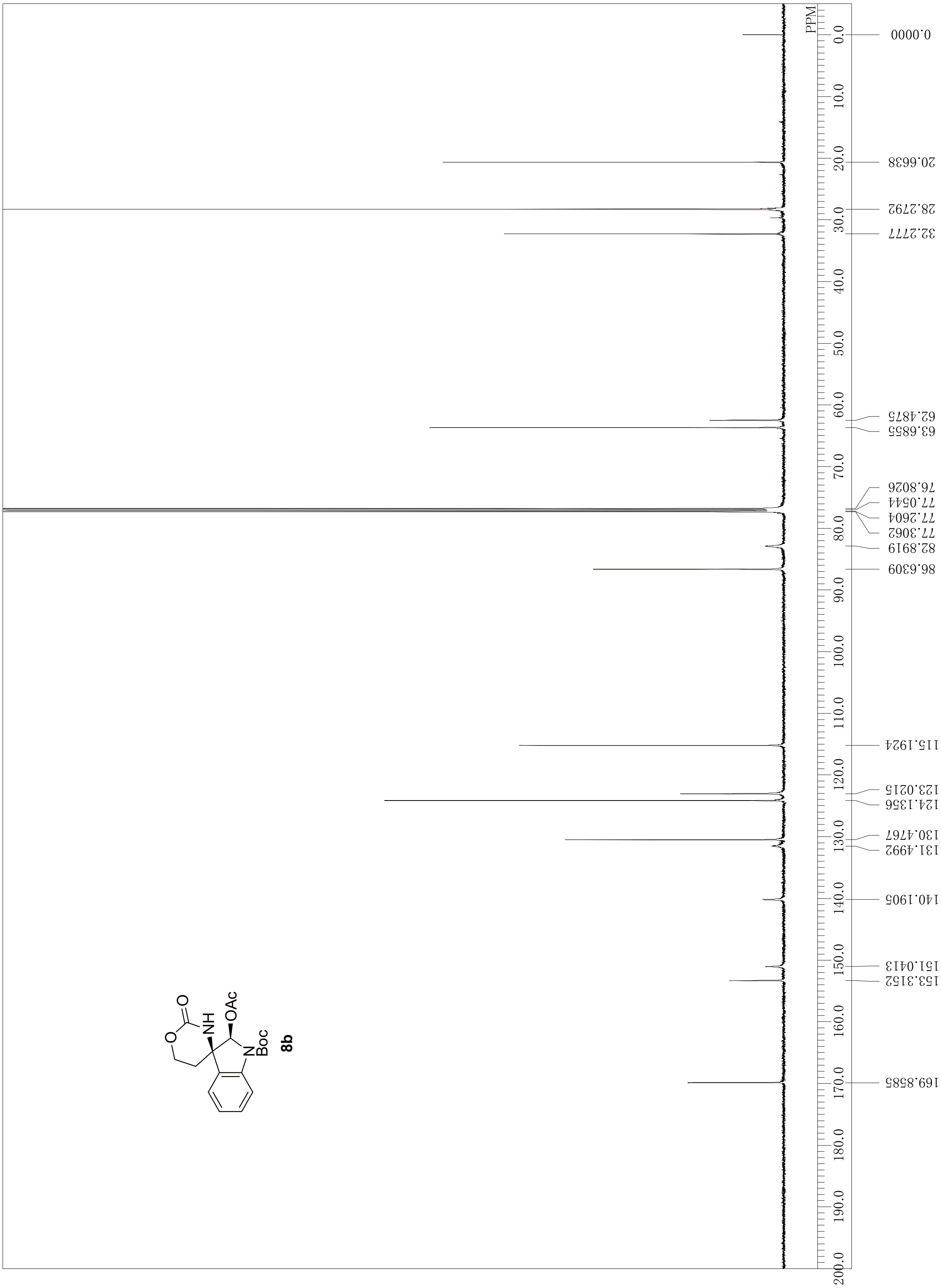
C:¥My Documents¥個人ファイル¥NMR AL400¥shigeki¥No1501-No1600¥No1561-No1570¥1564_06_18spot_2nd.als



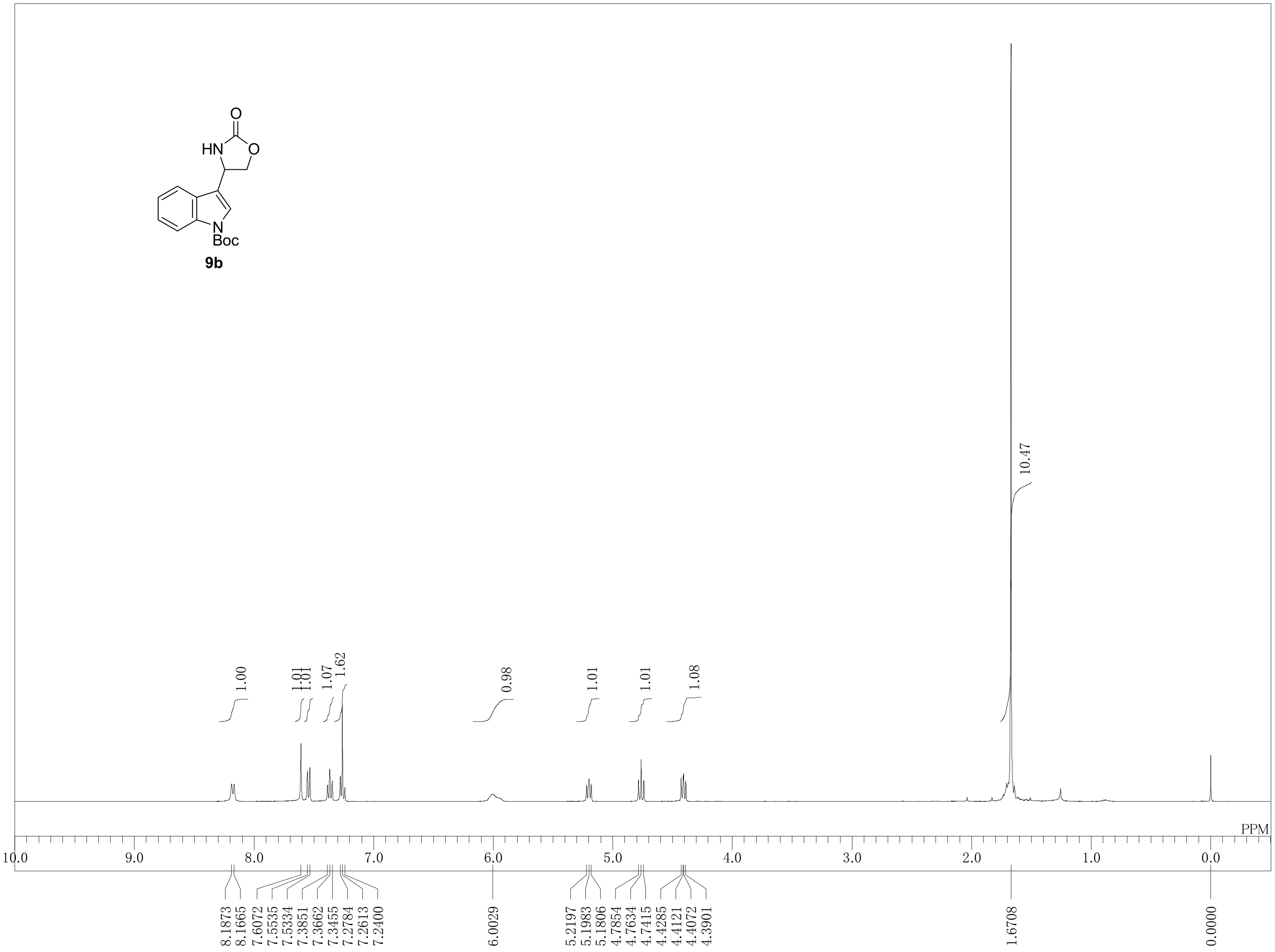
8b

| | |
|---|---|
| DATIM | 19-06-2008 07:3 |
| DFILE | C:¥My Documer |
| OBNUC | 13C |
| EXMOD | single_pulse_dec |
| OFR | 125.77 MH |
| OBSET | 7.87 KHz |
| OBFIN | 4.21 Hz |
| POINT | 32768 |
| FREQU | 31446.54 Hz |
| SCANS | 18000 |
| ACQTM | 1.0420 sec |
| PD | 1.0000 sec |
| PW1 | 3.40 usec |
| IRN | |
| CTEMP | 28.9 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 1.02 Hz |
| RGAIN | 26 |

C:¥My Documents¥個人ファイル¥NMR AL400¥shigeki¥No1501-No1600¥No1561-No1570¥1d_13c_COM_1564-spot_2nd_08_06_18.als



C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1501-No1600¥No1561-No1570¥1564_08_06_18_spot_1st.als

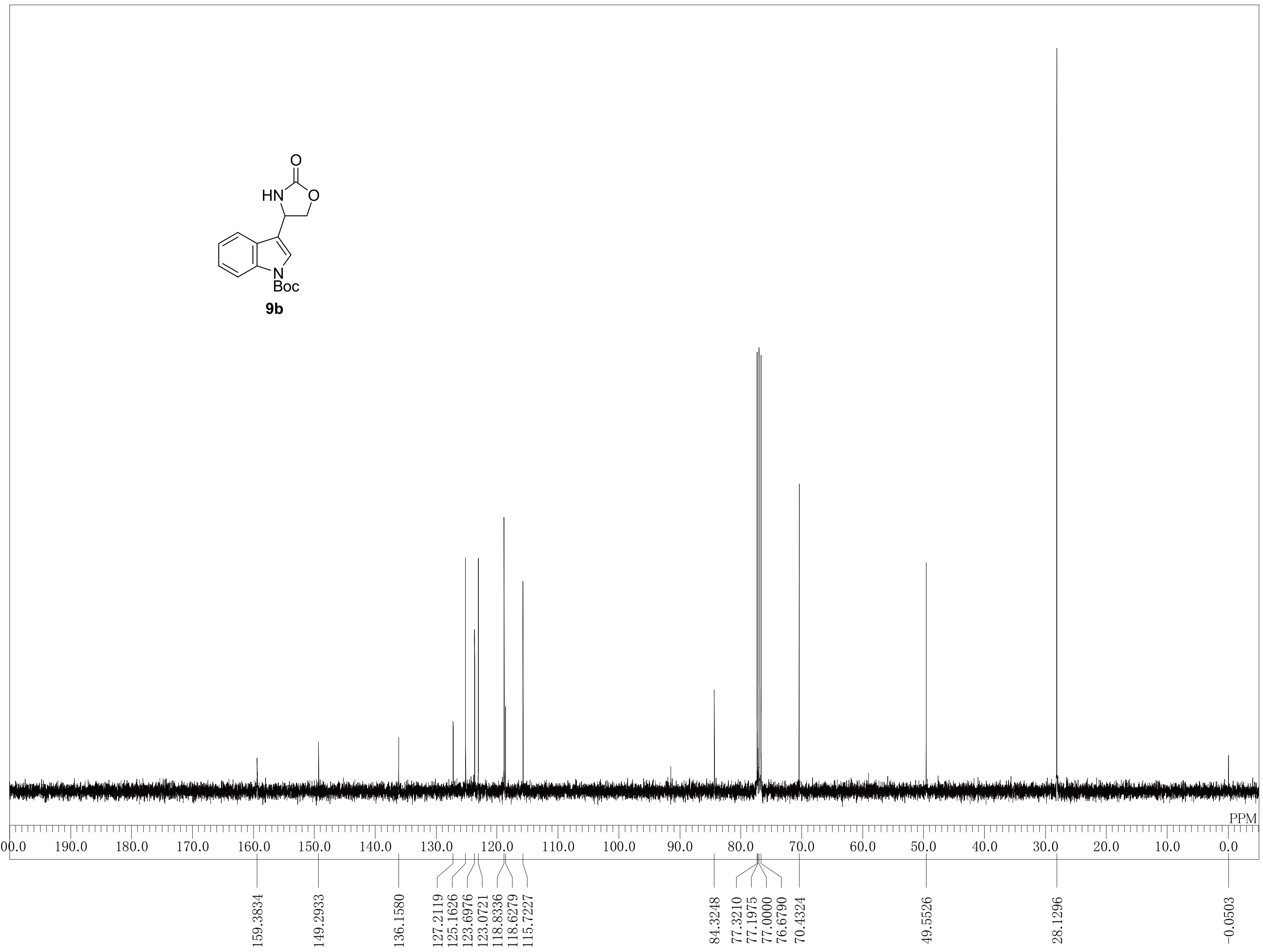


**9b**

| | |
|---|---|
| DATIM | Wed Jun 18 21:2 |
| DFILE | C:¥My Documen |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 395.75 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10277.00 Hz |
| POINT | 32768 |
| FREQU | 7912.96 Hz |
| SCANS | 8 |
| ACQTM | 4.1411 sec |
| PD | 2.8590 sec |
| PW1 | 5.80 usec |
| IRN | |
| CTEMP | 26.4 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 14 |

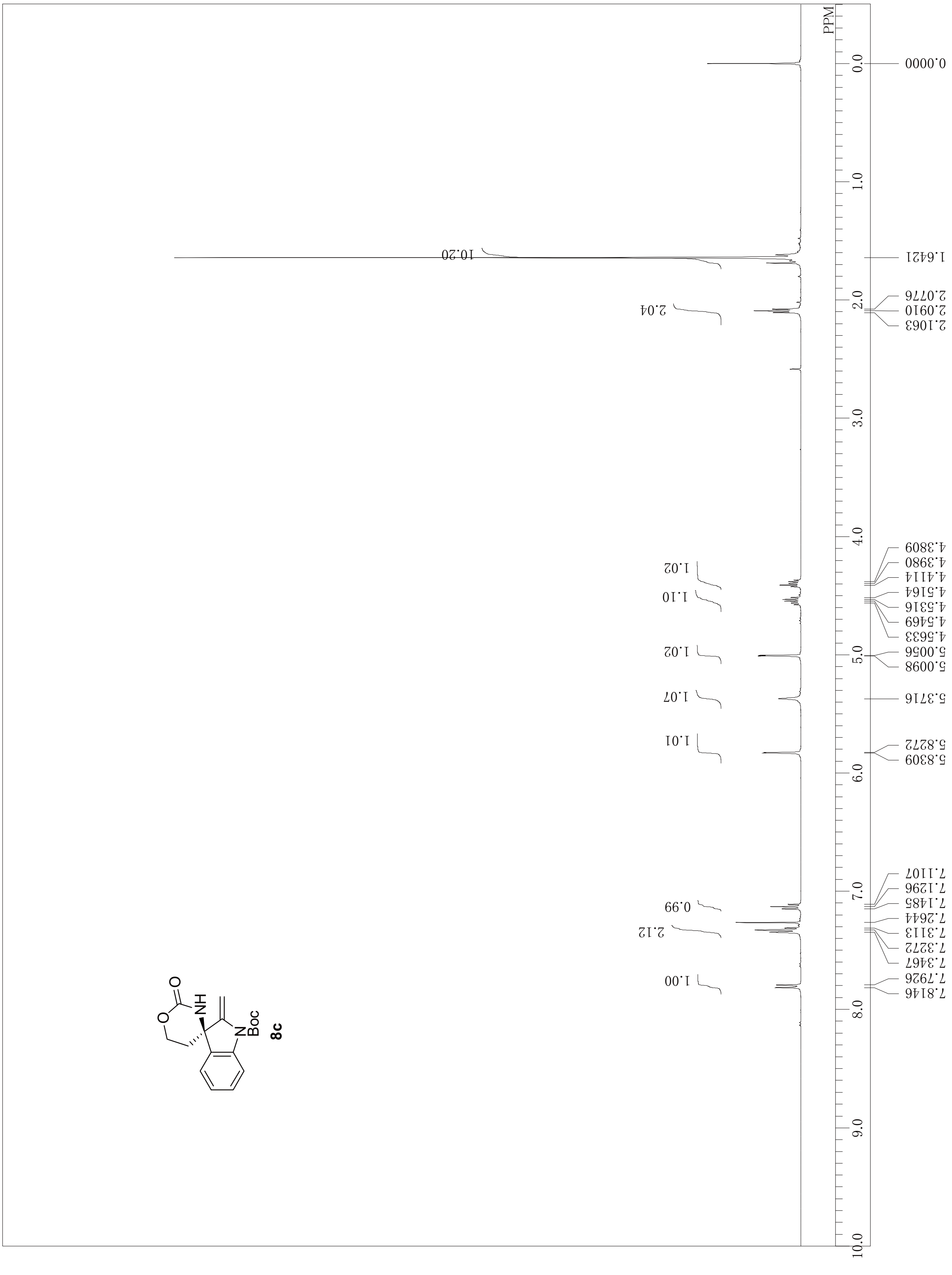
C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1501-No1600¥No1561-No1570¥1564_08_06_18_spot_1st_13C.als

| | |
|---|---|
| DATIM | Wed Jun 18 21:4 |
| DFILE | C:¥My Documen |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 434 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.40 usec |
| IRN | |
| CTEMP | 28.2 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 24 |



**9b**

| | |
|---|---|
| DATIM | Sat May 17 17:3 |
| DFILE | C:¥My Documer |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 395.75 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10277.00 Hz |
| POINT | 32768 |
| FREQU | 7912.96 Hz |
| SCANS | 16 |
| ACQTM | 4.1411 sec |
| PD | 2.8590 sec |
| PW1 | 5.80 usec |
| IRN | |
| CTEMP | 24.4 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 0.42 Hz |
| RGAIN | 17 |

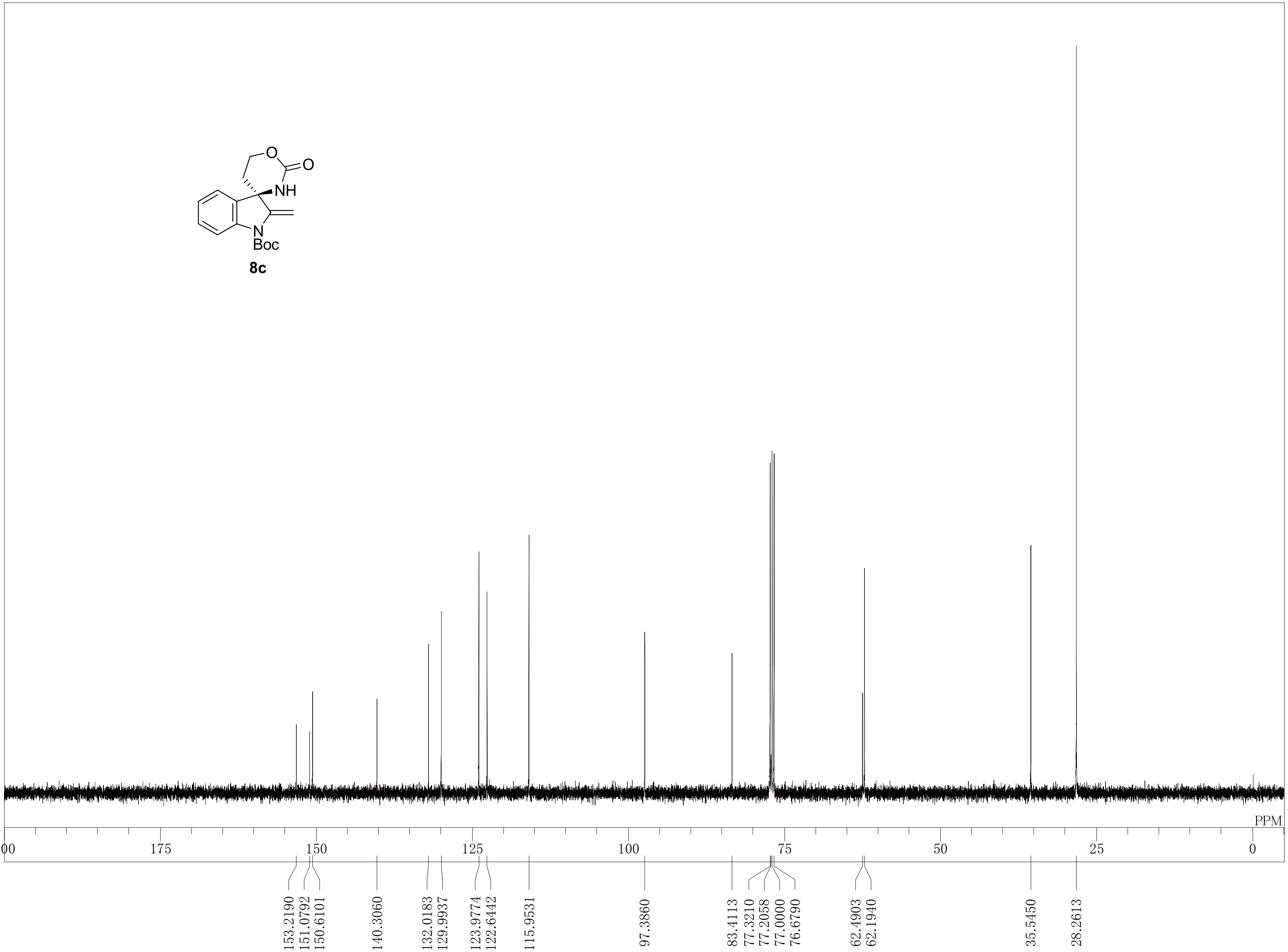


**8c**

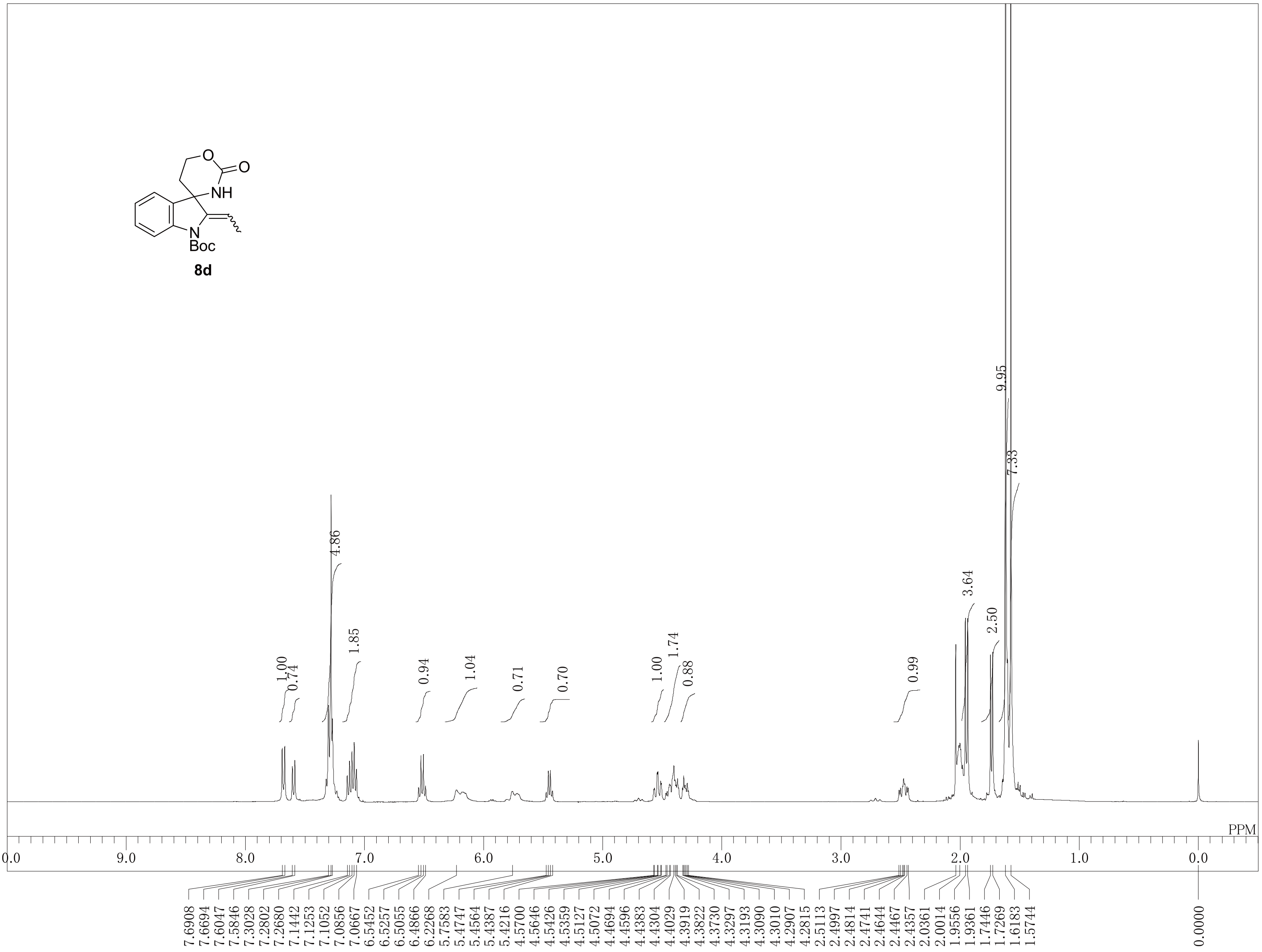
C:¥My Documents¥個人ファイル¥NMR AL400¥shigeki¥No1501-No1600¥No1510¥1508_08_05_17.als

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No0701-No0800¥No721-No730¥729_06_10_12_13C.als

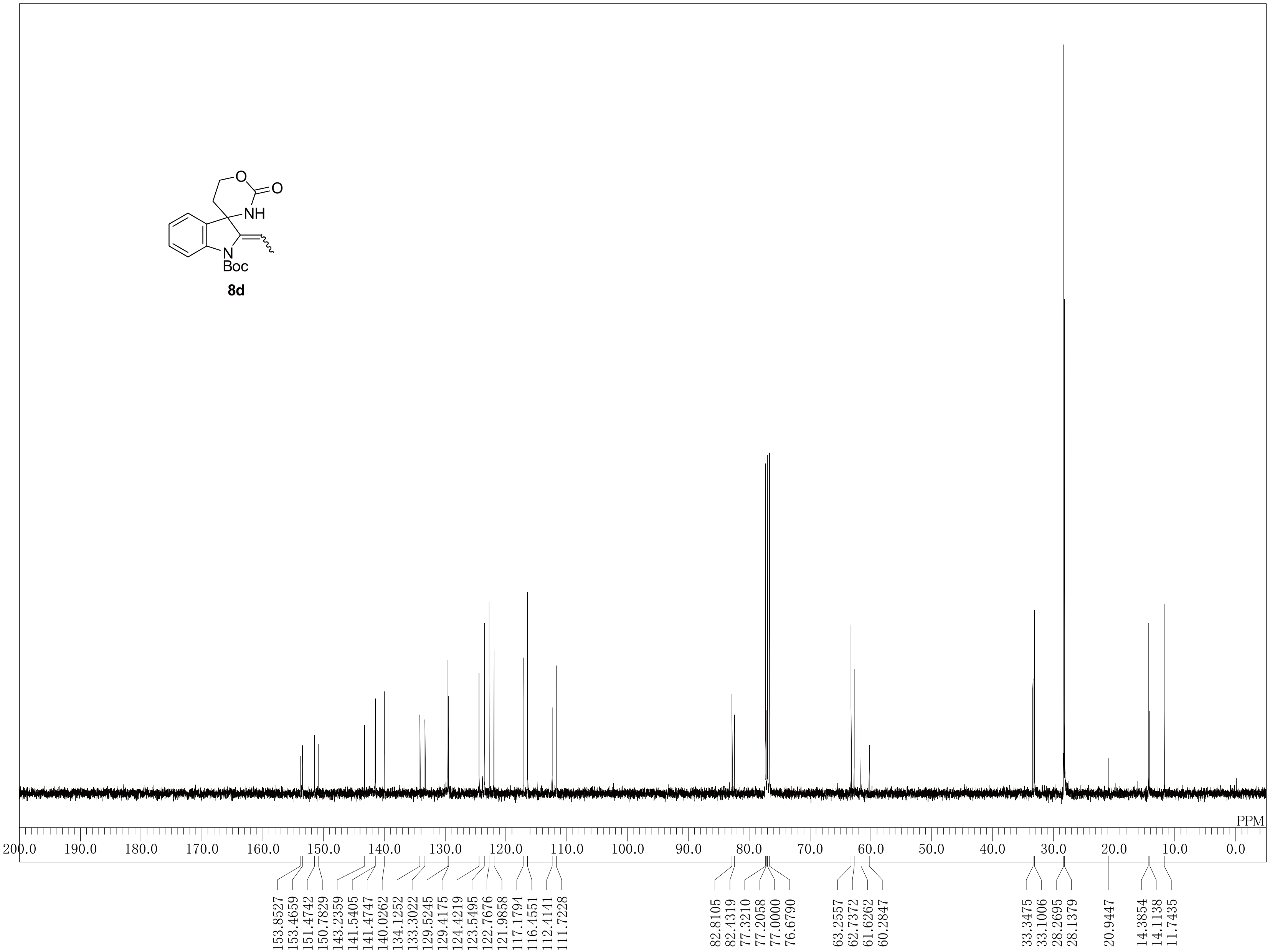
| | |
|---|---|
| DATIM | Thu Oct 12 19: |
| DFILE | C:¥My Docume |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MH |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 405 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.50 usec |
| IRN | |
| CTEMP | 25.8 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 24 |

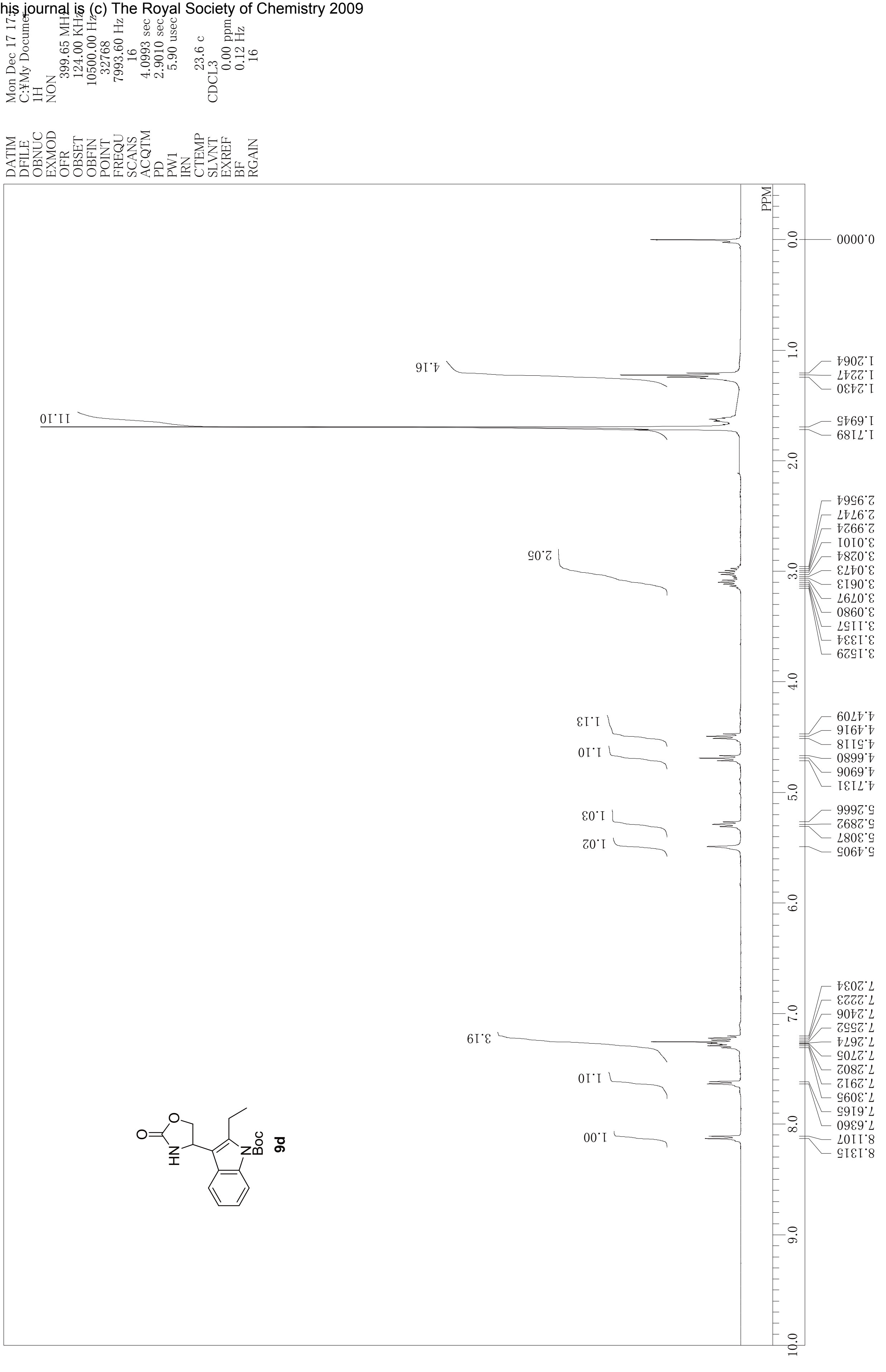


| | |
|---|---|
| DATIM | Mon Dec 17 18: |
| DFILE | C:¥My Documer |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 395.75 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10277.00 Hz |
| POINT | 32768 |
| FREQU | 7912.96 Hz |
| SCANS | 16 |
| ACQTM | 4.1411 sec |
| PD | 2.8590 sec |
| PW1 | 5.80 usec |
| IRN | |
| CTEMP | 23.7 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 0.42 Hz |
| RGAIN | 11 |


**8d**

| | |
|---|---|
| DATIM | Mon Dec 17 18 |
| DFILE | C:¥My Docume |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MH |
| OBSET | 94.00 KH |
| OBFIN | 10309.00 H |
| POINT | 32768 |
| FREQU | 26845.64 H |
| SCANS | 371 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.40 usec |
| IRN | |
| CTEMP | 25.3 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.42 Hz |
| RGAIN | 22 |




DATIM Mon Dec 17 17:
DFILE C:¥My Documen
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 16
ACQTM 4.0993 sec
PD 2.9010 sec
PW1 5.90 usec
IRN
CTEMP 23.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 16
PPM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
0.0000
1.2064
1.2247
1.2430
1.6945
1.7189
2.9564
2.9747
2.9924
3.0101
3.0284
3.0473
3.0613
3.0797
3.0980
3.1157
3.1334
3.1529
4.4709
4.4916
4.5118
4.6680
4.6906
4.7131
5.2666
5.2892
5.3087
5.4905
7.2034
7.2223
7.2406
7.2552
7.2674
7.2705
7.2802
7.2912
7.3095
7.6165
7.6360
8.1107
8.1315
4.16
11.10
2.05
1.13
1.10
1.03
1.02
3.19
1.10
1.00
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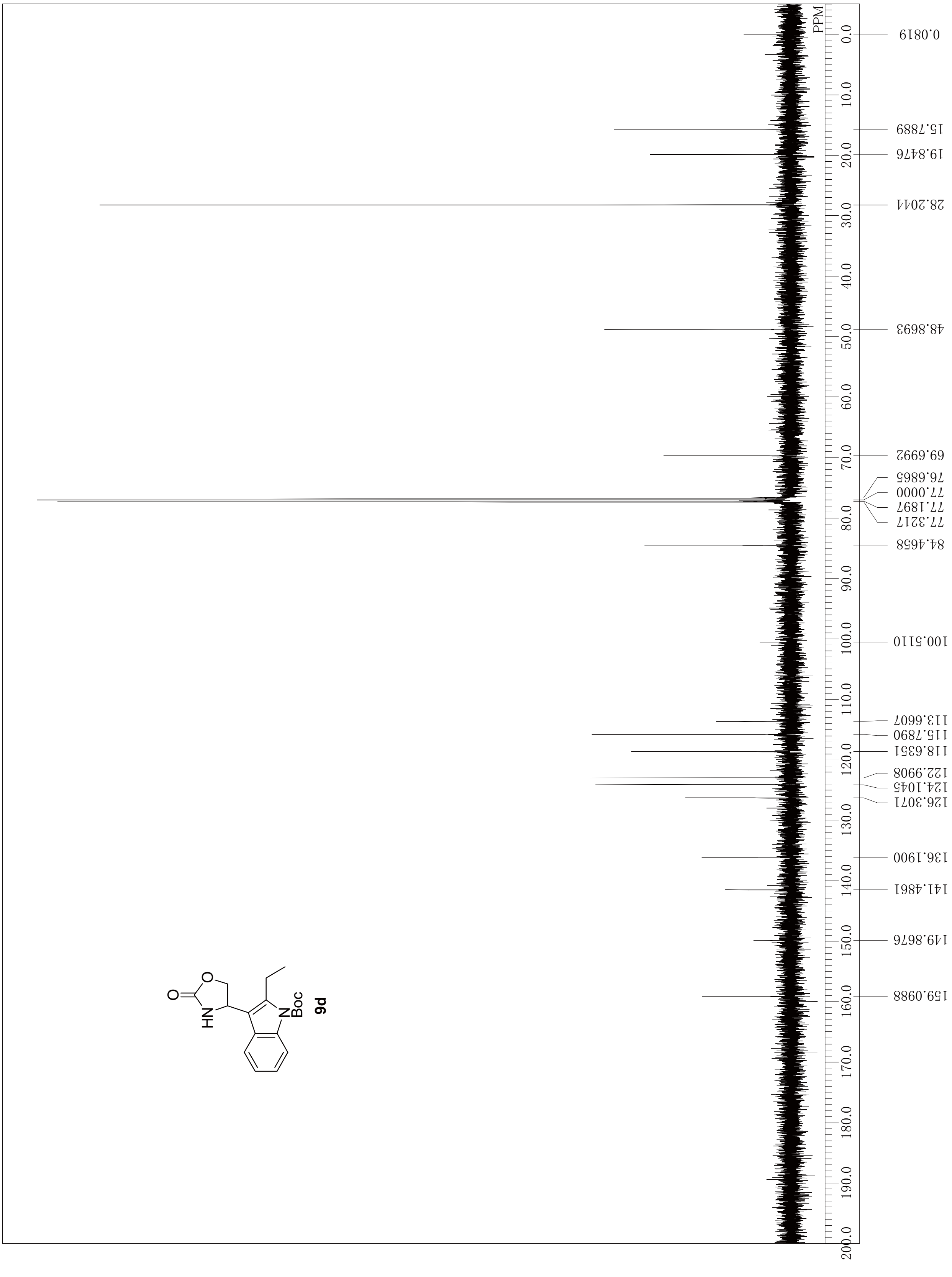
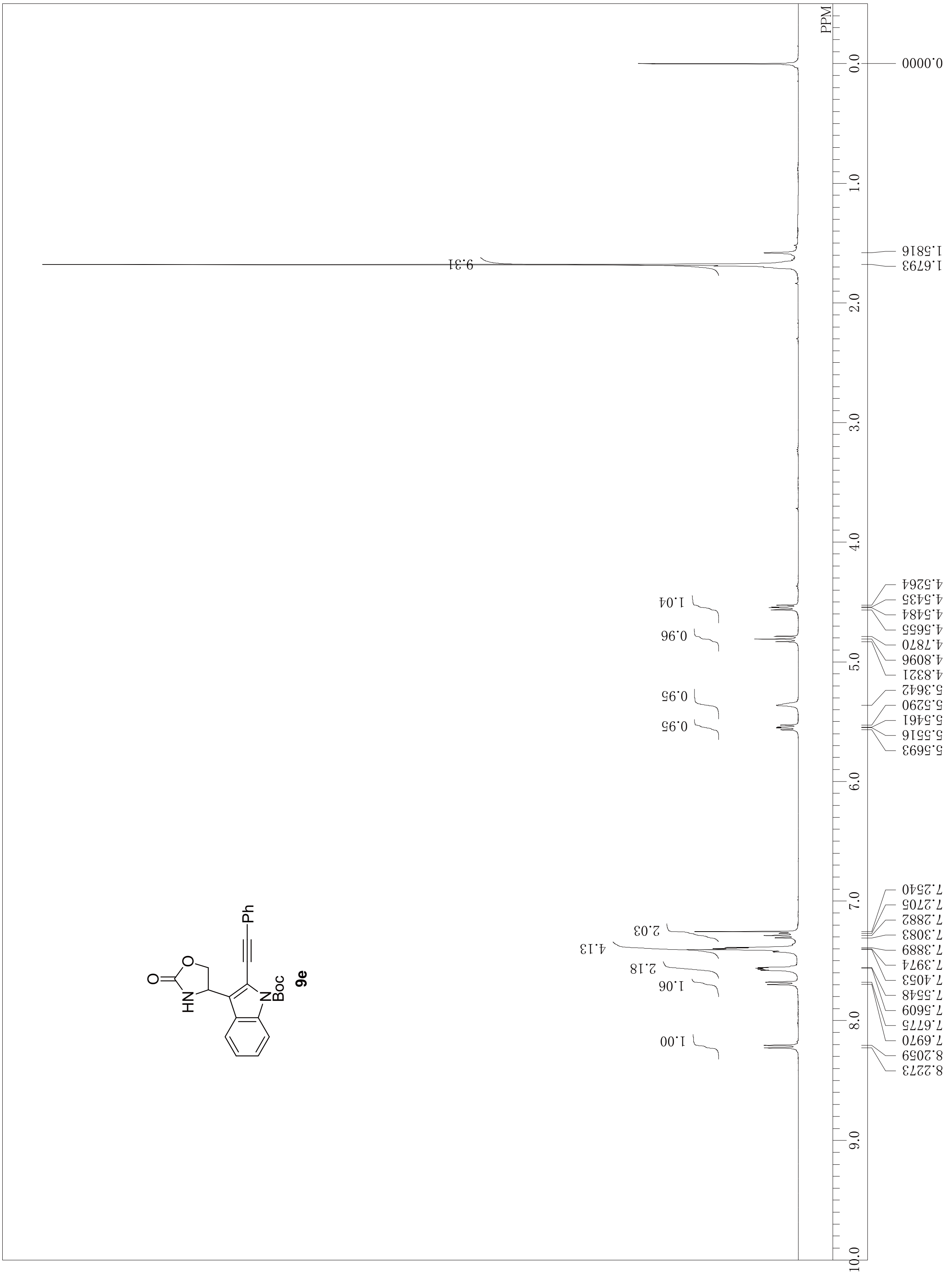
| | |
|---|---|
| DATIM | Mon Dec 17 17: |
| DFILE | C:¥My Documer |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 100.40 MHz |
| OBSET | 125.00 KHz |
| OBFIN | 10500.00 Hz |
| POINT | 32768 |
| FREQU | 27173.90 Hz |
| SCANS | 709 |
| ACQTM | 1.2059 sec |
| PD | 1.7940 sec |
| PW1 | 5.90 usec |
| IRN | |
| CTEMP | 23.7 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 24 |



9d

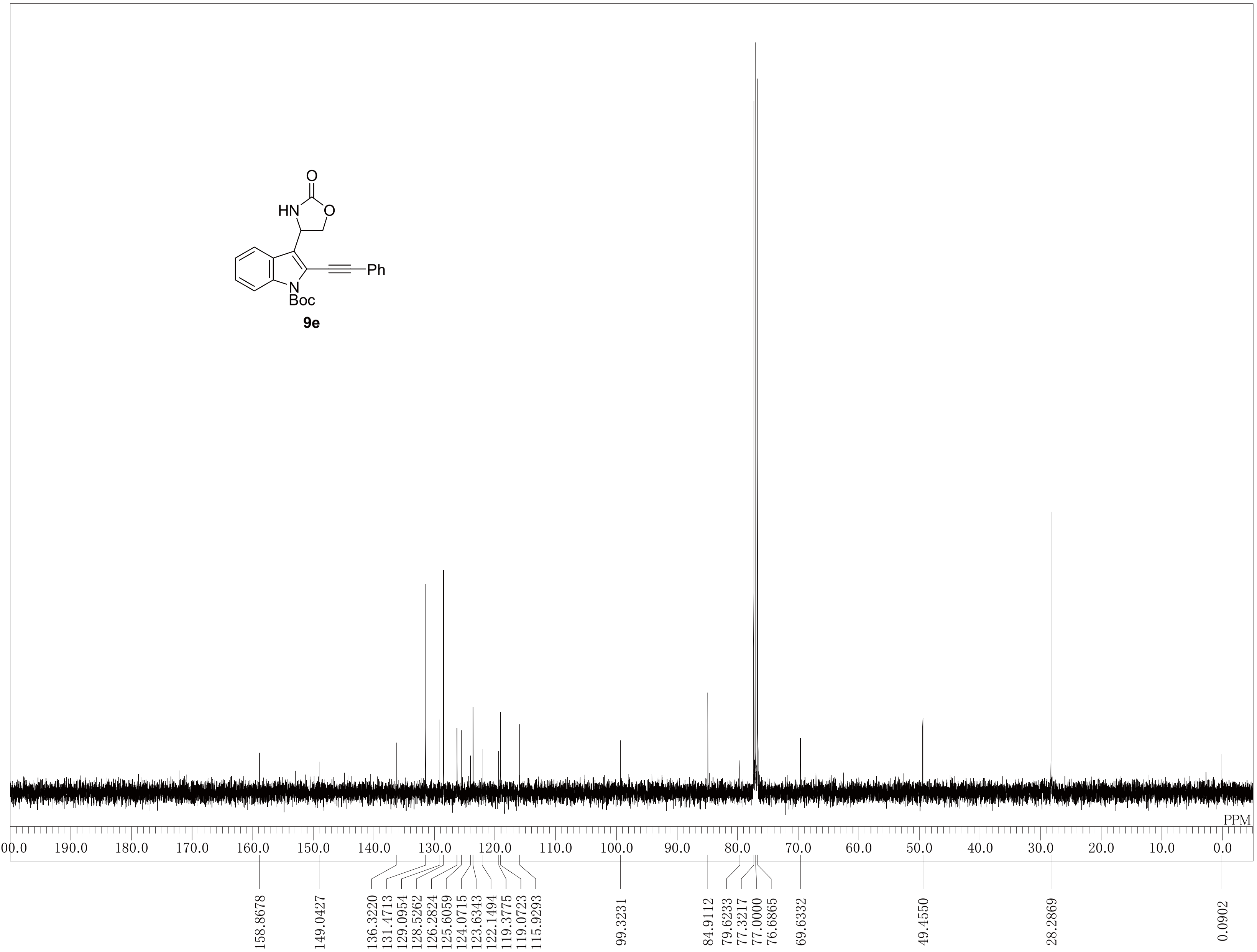
DATIM Sun Mar 18 17:
DFILE C:¥My Docume
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 32
ACQTM 4.0993 sec
PD 2.9010 sec
PW1 5.90 usec
IRN
CTEMP 24.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 17

C:¥My Documents¥個人ファイル¥NMR AL400¥shigeki¥No0901-No1000¥No981-No990¥982_07_3_18.als



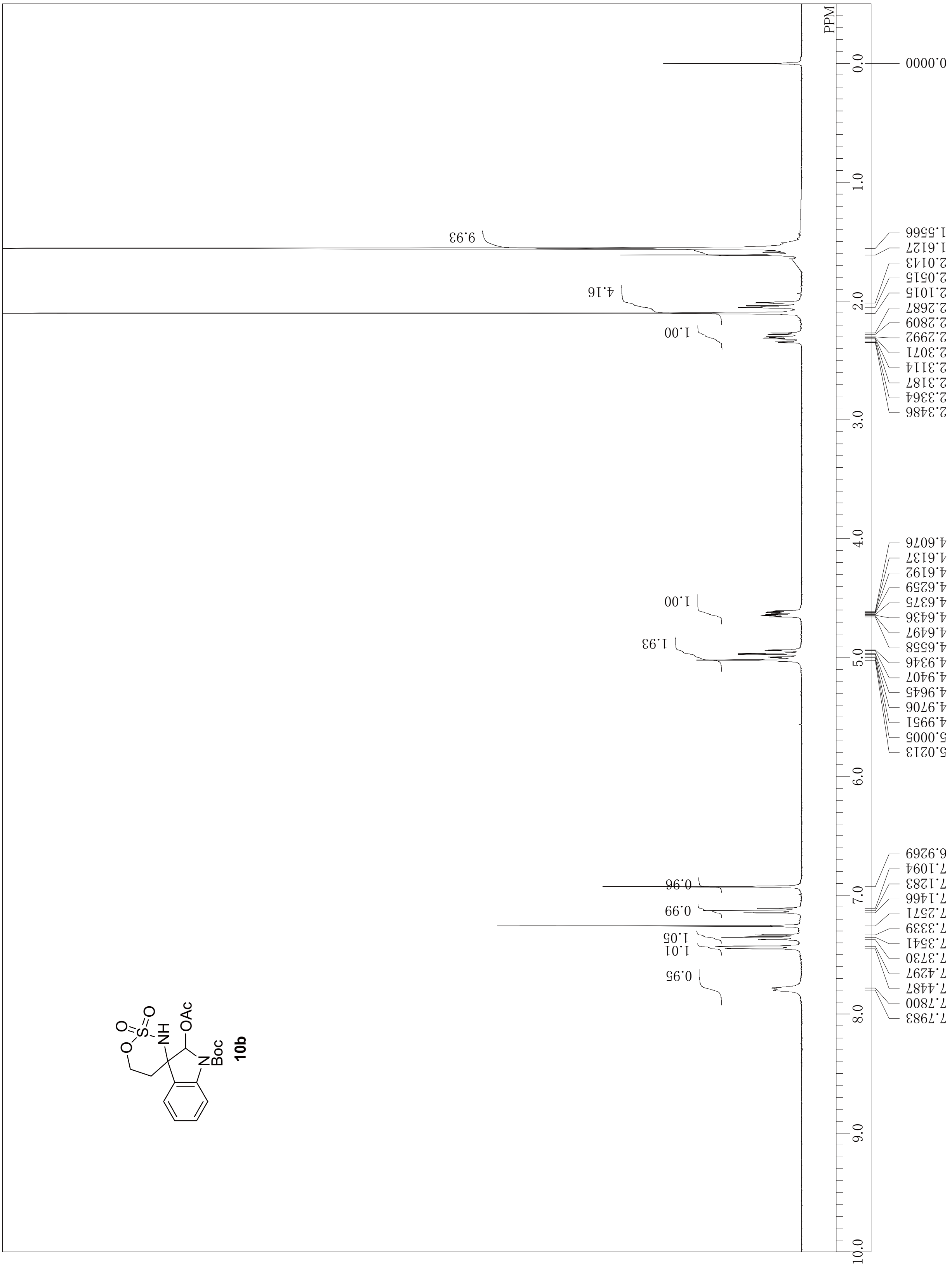
**9e**

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No0901-No1000¥No981-No990¥982_07_3_18_13C.als



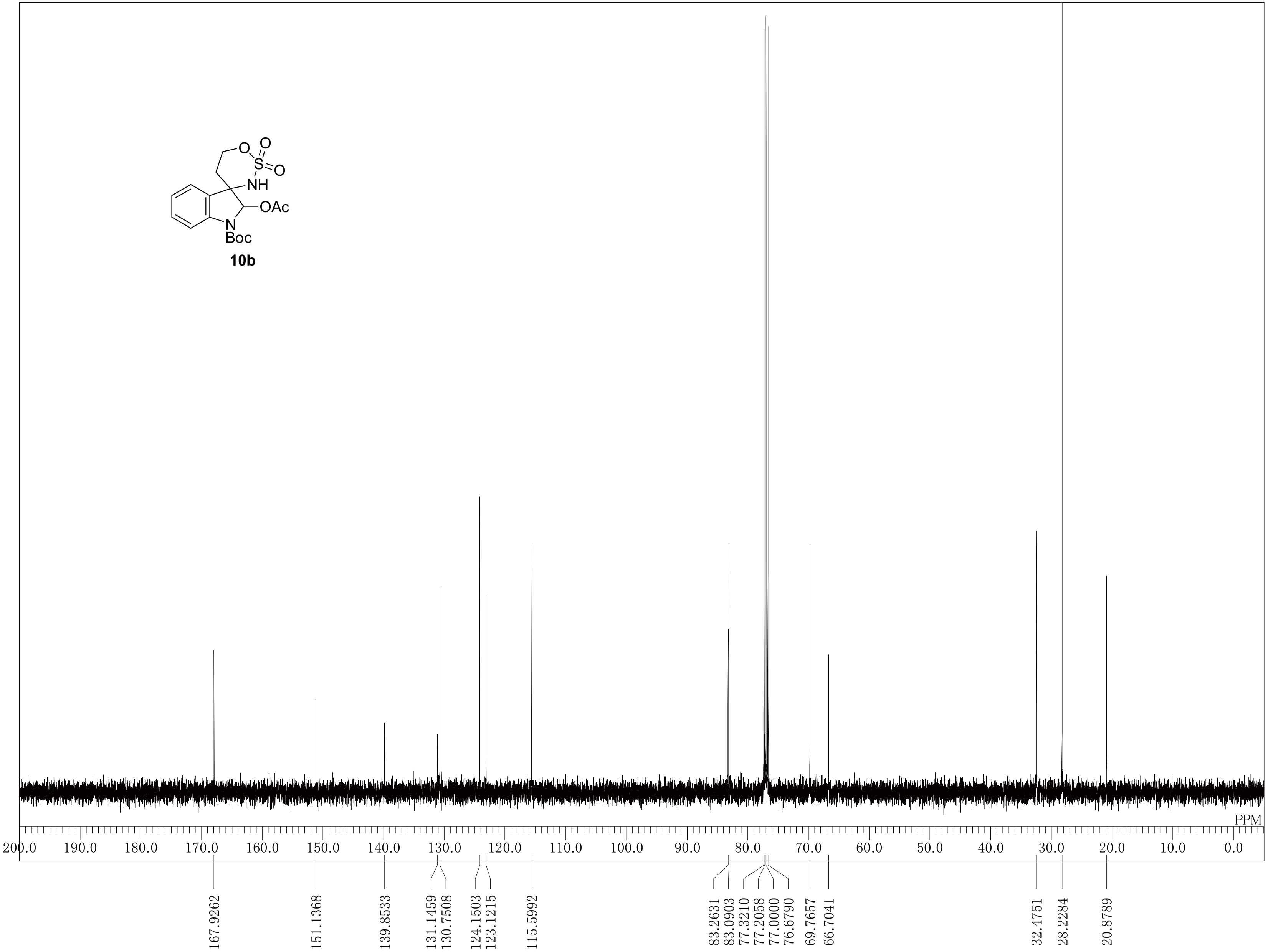
| | |
|---|---|
| DATIM | Sun Mar 18 17: |
| DFILE | C:¥My Documer |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 100.40 MHz |
| OBSET | 125.00 KHz |
| OBFIN | 10500.00 Hz |
| POINT | 32768 |
| FREQU | 27173.90 Hz |
| SCANS | 600 |
| ACQTM | 1.2059 sec |
| PD | 1.7940 sec |
| PW1 | 5.90 usec |
| IRN | |
| CTEMP | 23.5 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 23 |

| | |
|---|---|
| DATIM | Wed Jun 17 18:3 |
| DFILE | C:¥My Documer |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 399.65 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10500.00 Hz |
| POINT | 32768 |
| FREQU | 7993.60 Hz |
| SCANS | 16 |
| ACQTM | 4.0993 sec |
| PD | 2.9010 sec |
| PW1 | 5.90 usec |
| IRN | |
| CTEMP | 26.3 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 16 |



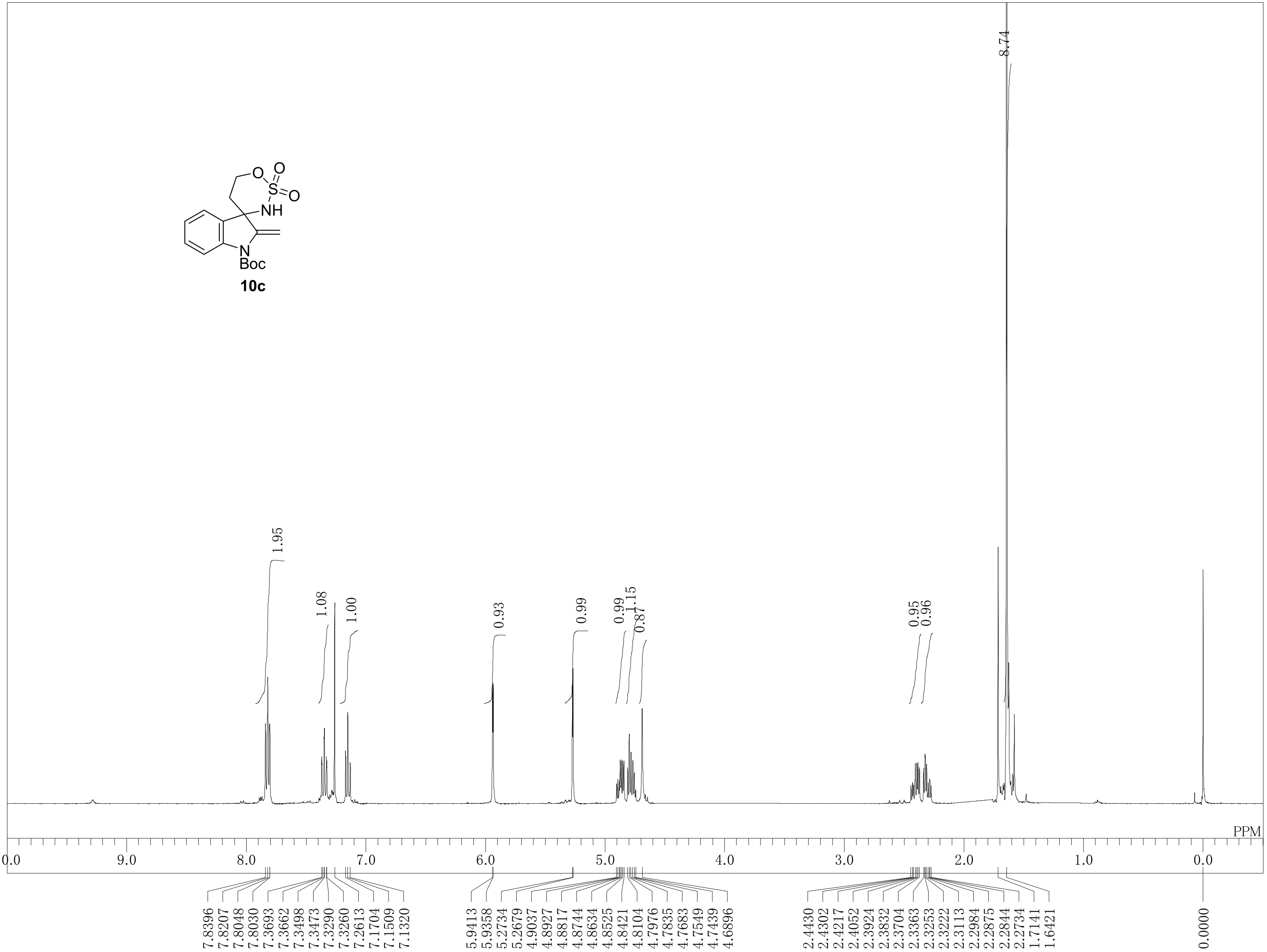
**10b**

DATIM Wed Jun 17 22:
DFILE C:¥My Documer
OBNUC 13C
EXMOD BCM
OFR 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 657
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.40 usec
IRN
CTEMP 27.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 24



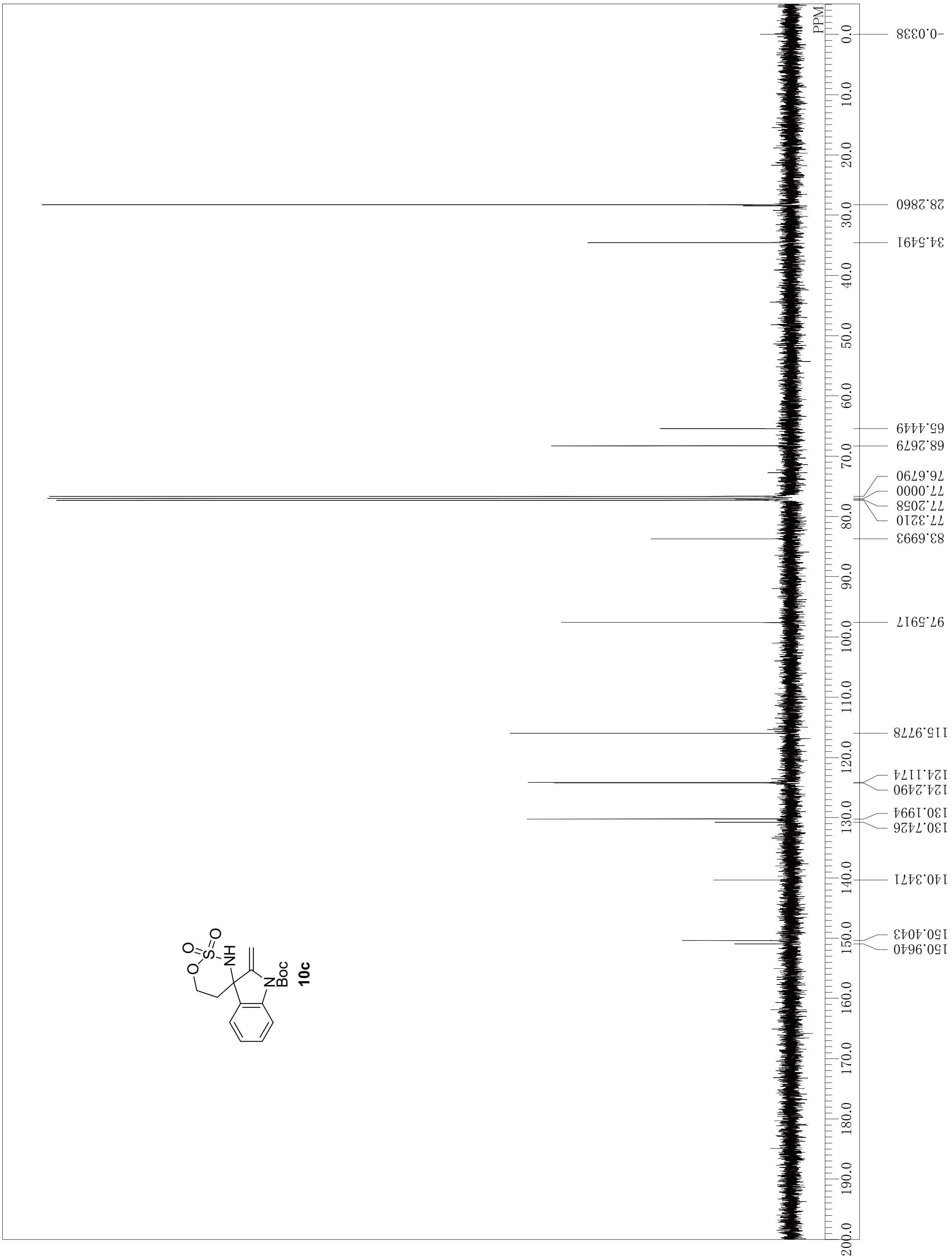
**10b**

DATIM Sat Apr 28 00:2(
DFILE C:¥My Documen
OBNUC 1H
EXMOD NON
OFR 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 32768
FREQU 7912.96 Hz
SCANS 16
ACQTM 4.1411 sec
PD 2.8590 sec
PW1 5.80 usec
IRN
CTEMP 24.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 16



**10c**

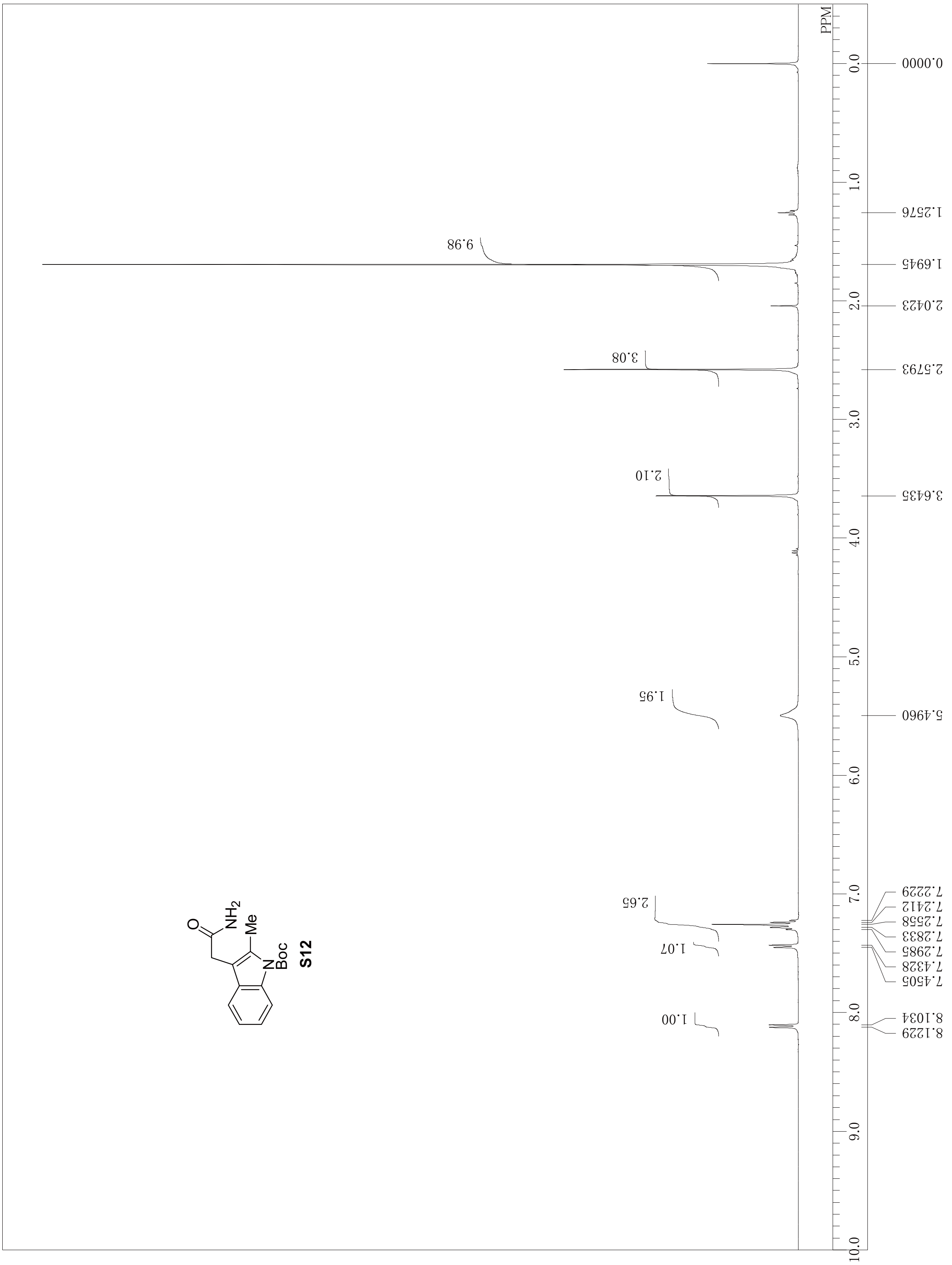
| | |
|---|---|
| DATIM | Tue May 01 10:: |
| DFILE | C:¥My Documer |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 456 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.40 usec |
| IRN | |
| CTEMP | 27.9 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.32 Hz |
| RGAIN | 25 |



**10c**

| | |
|---|---|
| DATIM | Wed Mar 05 22: |
| DFILE | C:¥My Documer |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 399.65 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10500.00 Hz |
| POINT | 32768 |
| FREQU | 7993.60 Hz |
| SCANS | 17 |
| ACQTM | 4.0993 sec |
| PD | 2.9010 sec |
| PW1 | 5.90 usec |
| IRN | |
| CTEMP | 23.3 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 0.82 Hz |
| RGAIN | 16 |

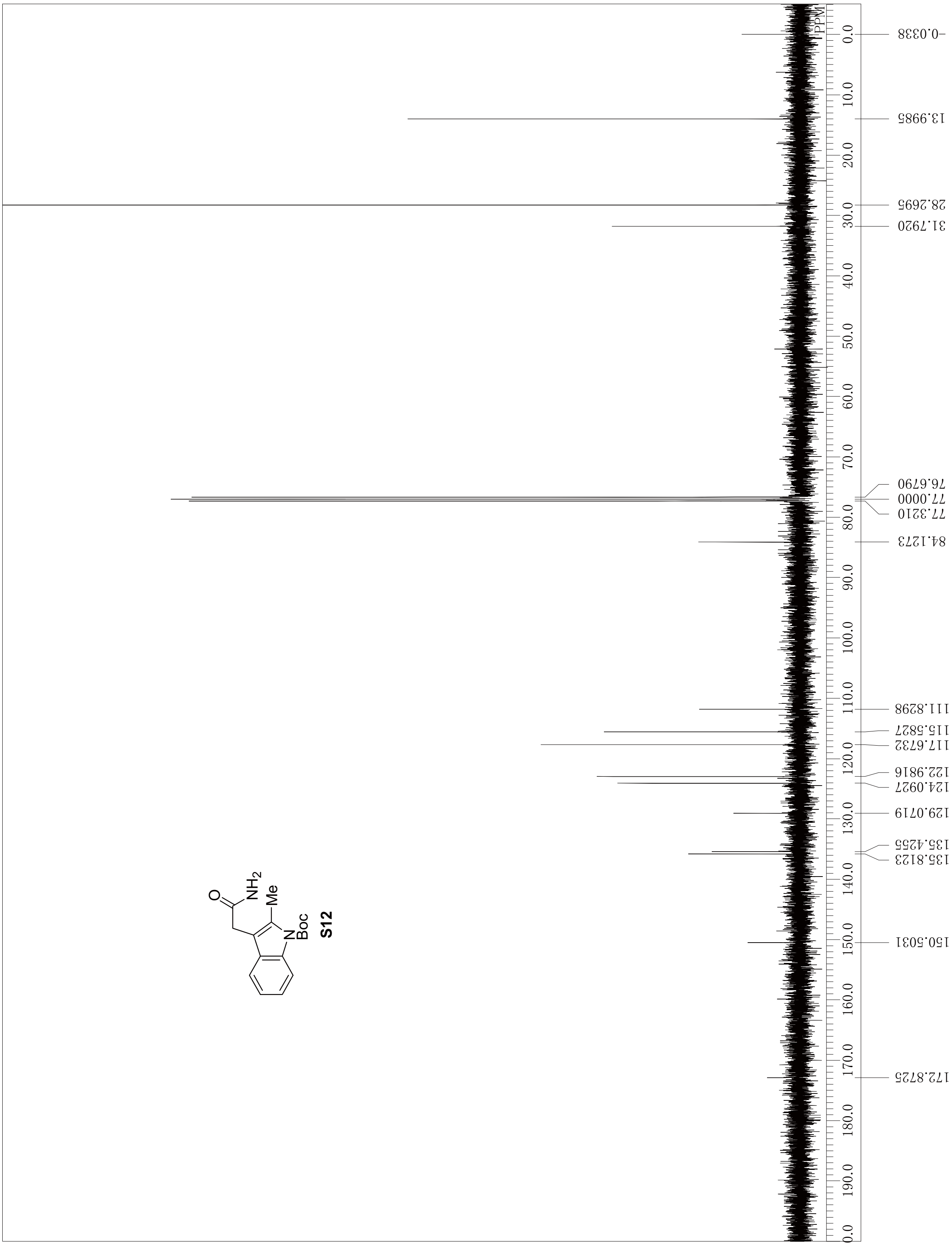
C:¥My Documents¥個人ファイル¥NMR AL400¥shigeki¥No1401-No1500¥No1431-No1440¥1439_08_03_05.als



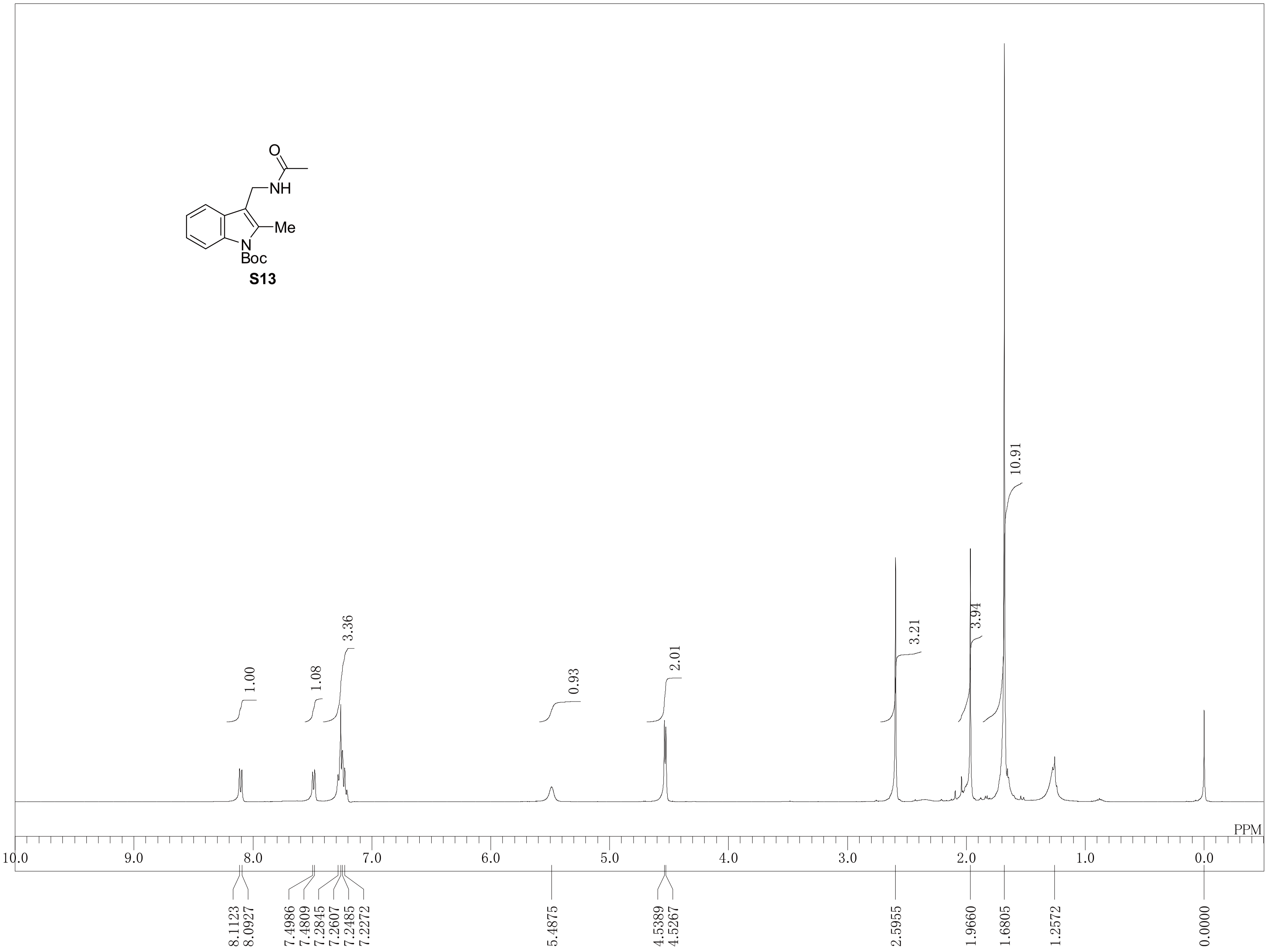
**S12**

| | |
|---|---|
| DATIM | Wed Mar 12 10: |
| DFILE | C:¥My Documer |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 456 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.40 usec |
| IRN | |
| CTEMP | 29.1 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 24 |

C:¥My Documents¥個人ファイル¥NMR AL400¥shigeki¥No1401-No1500¥No1441-No1450¥1446_08_03_12_13C.als

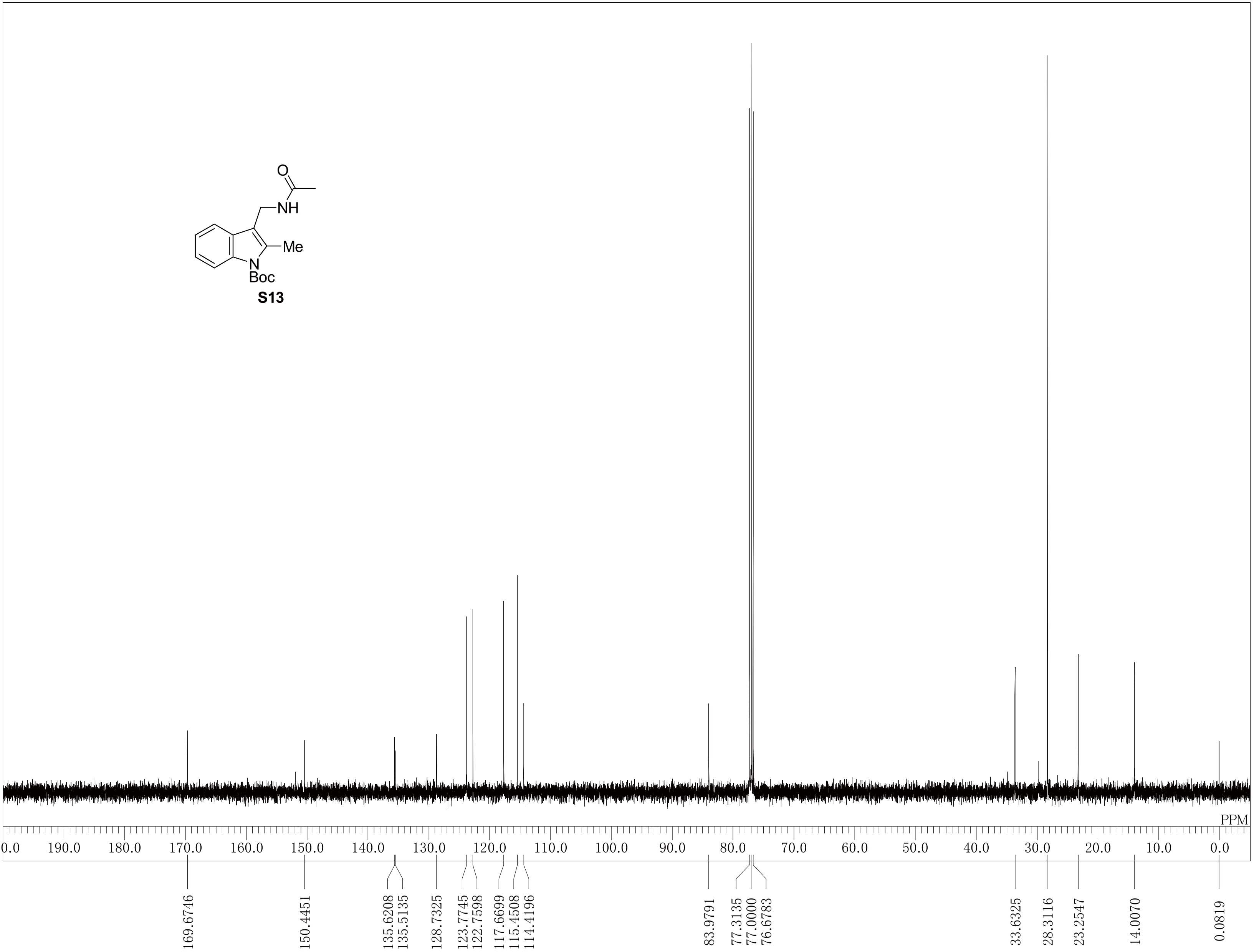


C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1401-No1500¥No1441-No1450¥1441_08_03_06.als



| | |
|---|---|
| DATIM | Fri Mar 07 10:1 |
| DFILE | C:¥My Documer |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 395.75 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10277.00 Hz |
| POINT | 32768 |
| FREQU | 7912.96 Hz |
| SCANS | 16 |
| ACQTM | 4.1411 sec |
| PD | 2.8590 sec |
| PW1 | 5.80 usec |
| IRN | |
| CTEMP | 26.3 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 1.02 Hz |
| RGAIN | 17 |

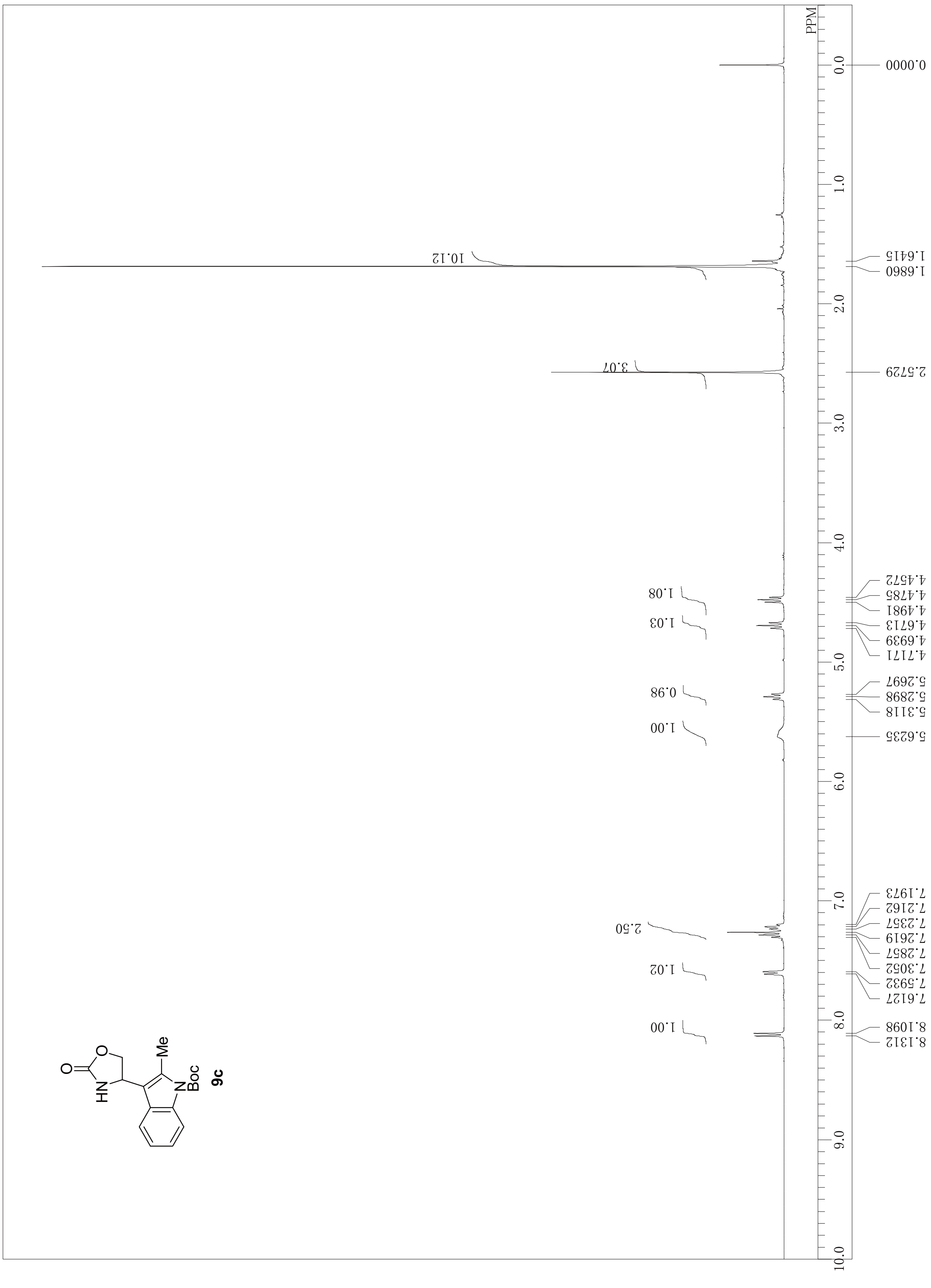
C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1401-No1500¥No1441-No1450¥1441_08_03_07_13C.als



| | |
|---|---|
| DATIM | Fri Mar 07 22:1 |
| DFILE | C:¥My Docume |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 100.40 MH |
| OBSET | 125.00 KH |
| OBFIN | 10500.00 Hz |
| POINT | 32768 |
| FREQU | 27173.90 Hz |
| SCANS | 769 |
| ACQTM | 1.2059 sec |
| PD | 1.7940 sec |
| PW1 | 5.90 usec |
| IRN | |
| CTEMP | 23.0 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 24 |

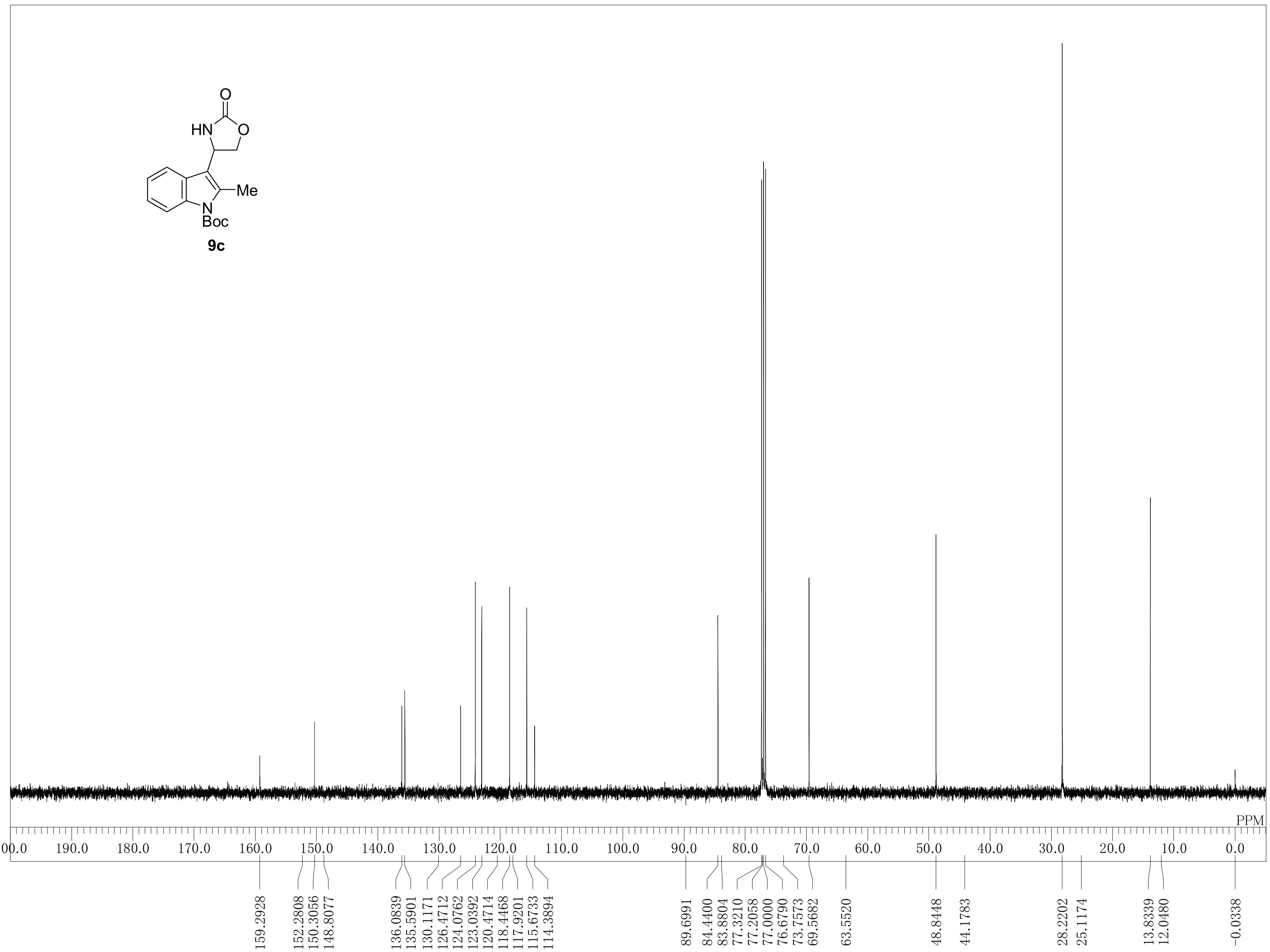
C:¥My Documents¥個人ファイル¥NMR AL400¥shigeki¥No1301-No1400¥No1321-No1330¥1325_07_12_8_insertion.als

| | |
|---|---|
| DATIM | Sun Dec 09 18:0 |
| DFILE | C:¥My Documen |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 395.75 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10277.00 Hz |
| POINT | 32768 |
| FREQU | 7912.96 Hz |
| SCANS | 16 |
| ACQTM | 4.1411 sec |
| PD | 2.8590 sec |
| PW1 | 5.80 usec |
| IRN | |
| CTEMP | 21.6 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 0.42 Hz |
| RGAIN | 15 |



**9c**

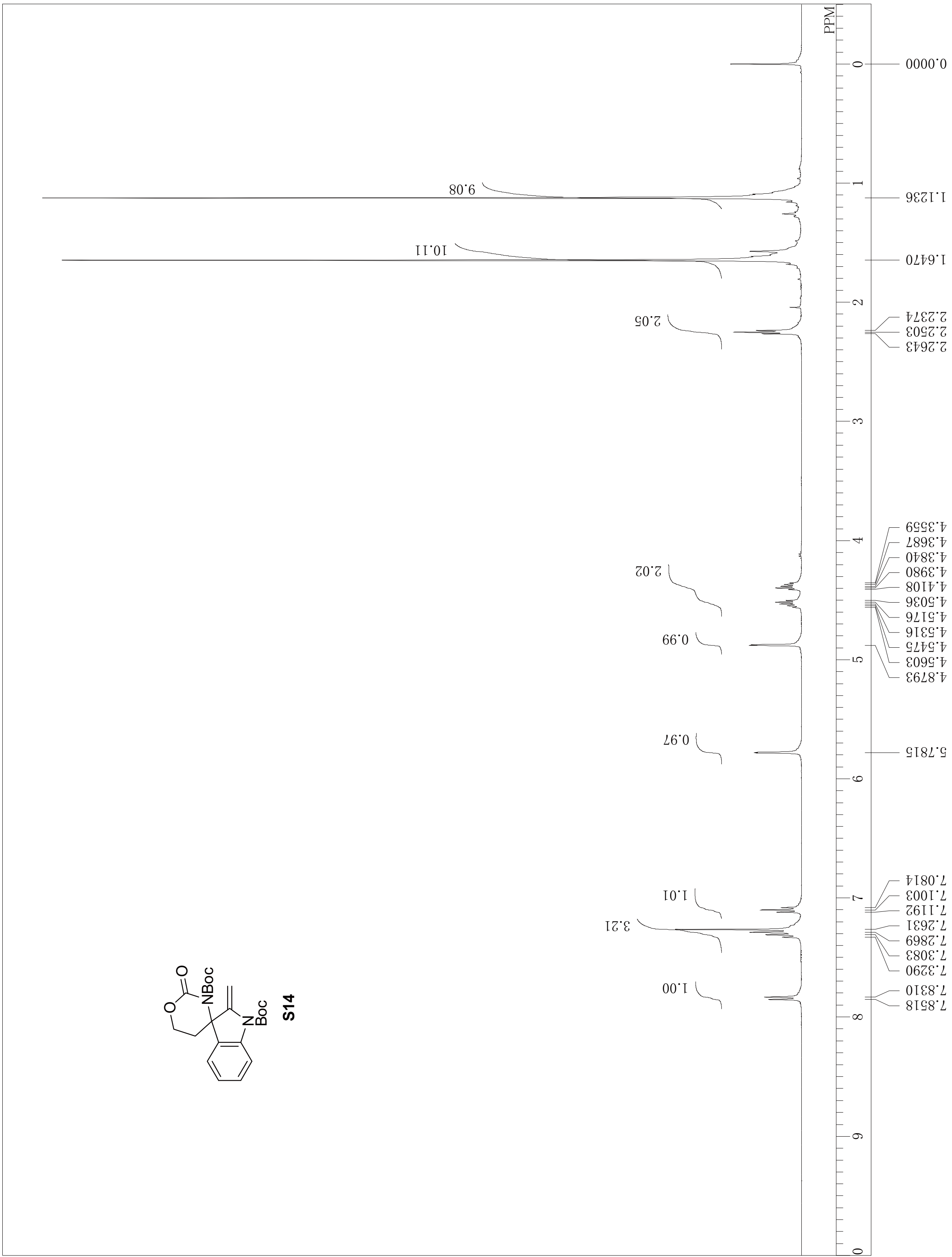
C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1301-No1400¥No1321-No1330¥1325_07_12_8_insertion_13C.als



| | |
|---|---|
| DATIM | Sun Dec 09 18:4 |
| DFILE | C:¥My Documen |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 780 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.40 usec |
| IRN | |
| CTEMP | 22.3 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.42 Hz |
| RGAIN | 24 |

C:¥My Documents¥個人ファイル¥NMR AL400¥shigeki¥No1401-No1500¥No1491-No1500¥1497_08_05_07.als

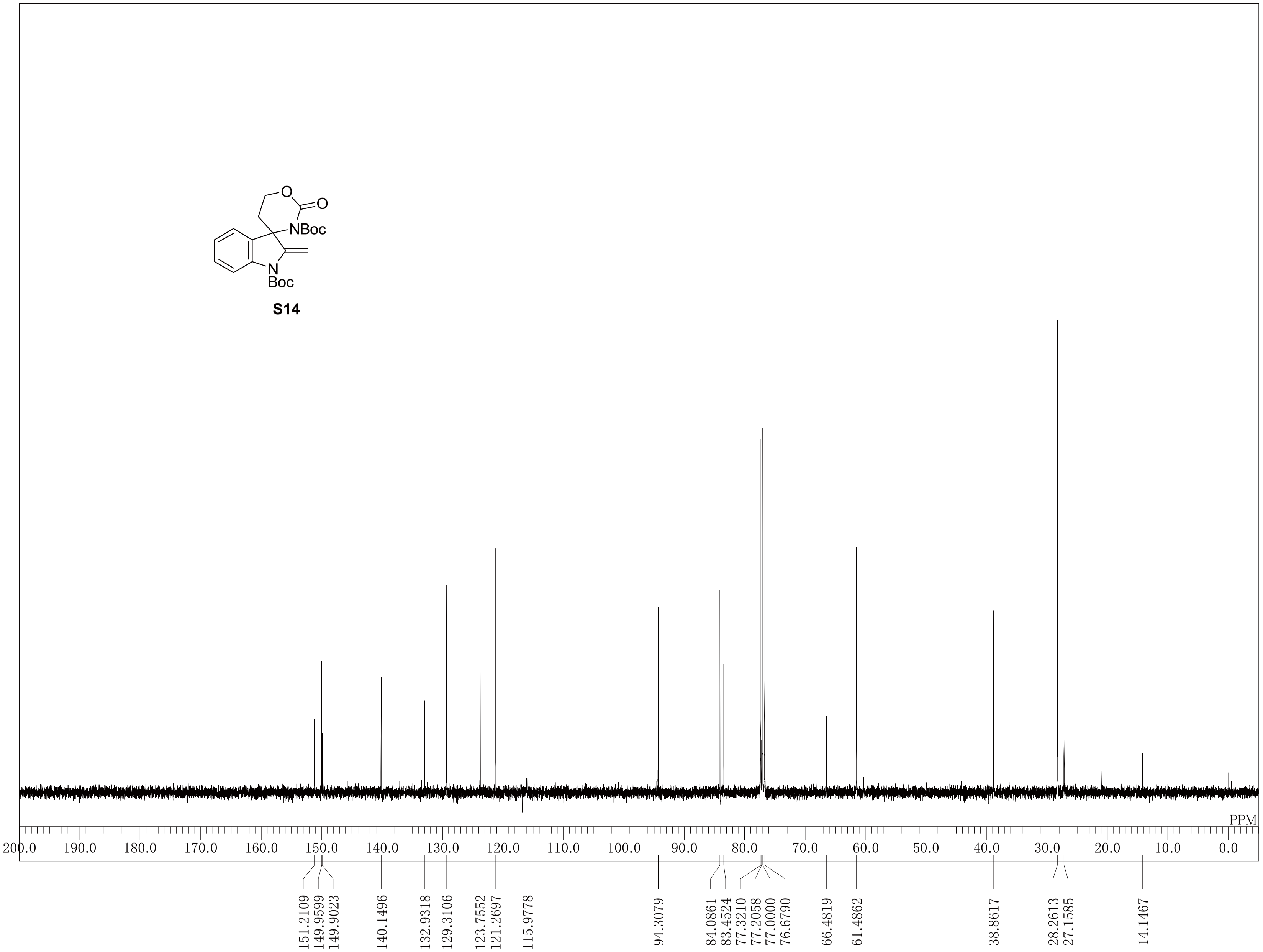
| | |
|---|---|
| DATIM | Wed May 07 23: |
| DFILE | C:¥My Documer |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 395.75 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10277.00 Hz |
| POINT | 32768 |
| FREQU | 7912.96 Hz |
| SCANS | 32 |
| ACQTM | 4.1411 sec |
| PD | 2.8590 sec |
| PW1 | 5.80 usec |
| IRN | |
| CTEMP | 27.5 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 0.42 Hz |
| RGAIN | 17 |



**S14**

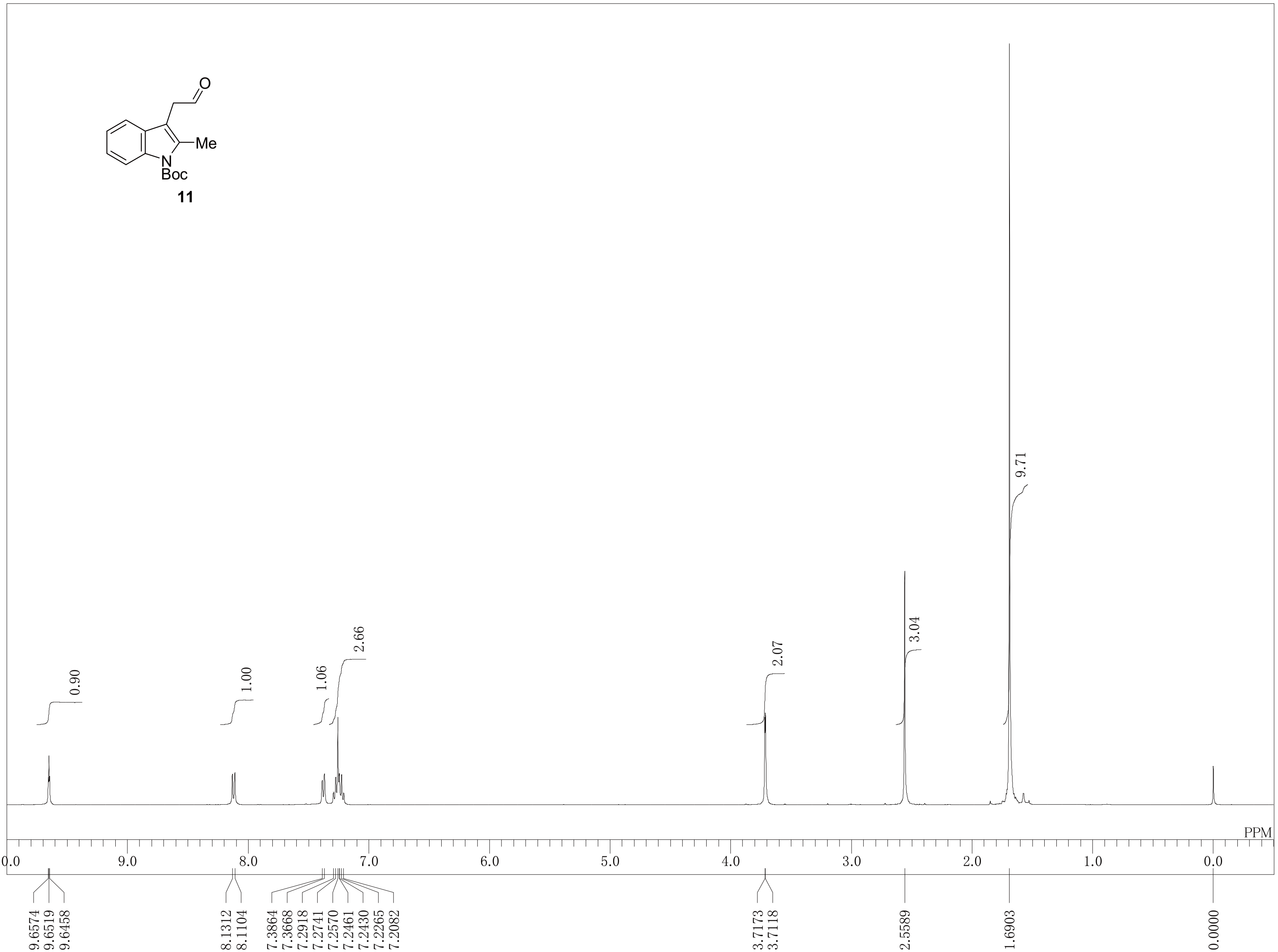
C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No0701-No0800¥No751-No760¥752_06_10_19_13C.als

| | |
|---|---|
| DATIM | Thu Oct 19 23:5 |
| DFILE | C:¥My Documer |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 436 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.50 usec |
| IRN | |
| CTEMP | 24.4 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 24 |



**S14**

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1201-No1300¥No1271-No1280¥1277_07_11_09_aldehyde.als



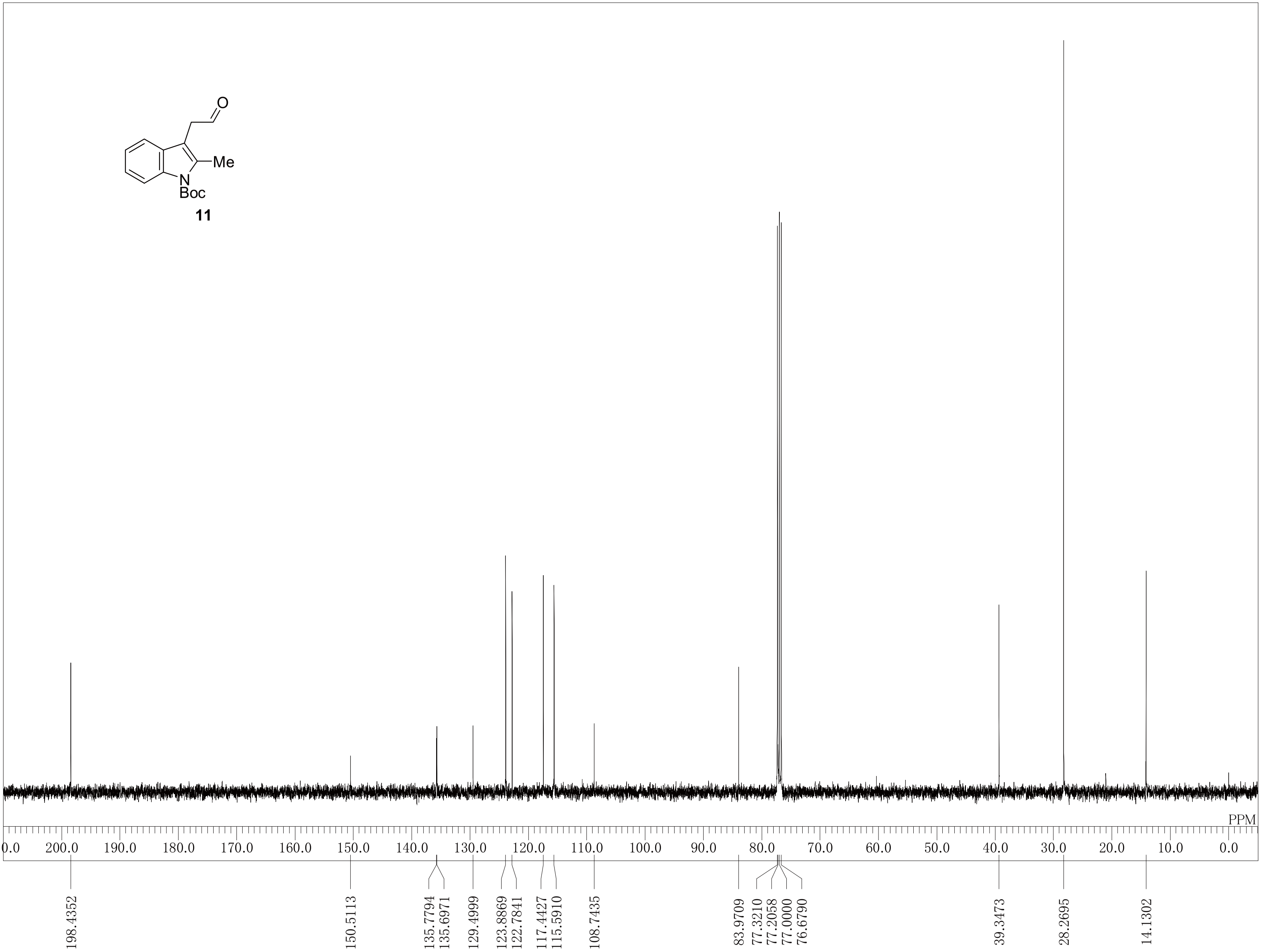
**11**

DATIM Fri Nov 09 23:0
DFILE C:¥My Documen
OBNUC 1H
EXMOD NON
OFR 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 32768
FREQU 7912.96 Hz
SCANS 8
ACQTM 4.1411 sec
PD 2.8590 sec
PW1 5.80 usec
IRN
CTEMP 24.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.92 Hz
RGAIN 14

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1201-No1300¥No1271-No1280¥1277_07_11_09_aldehyde_13C.als

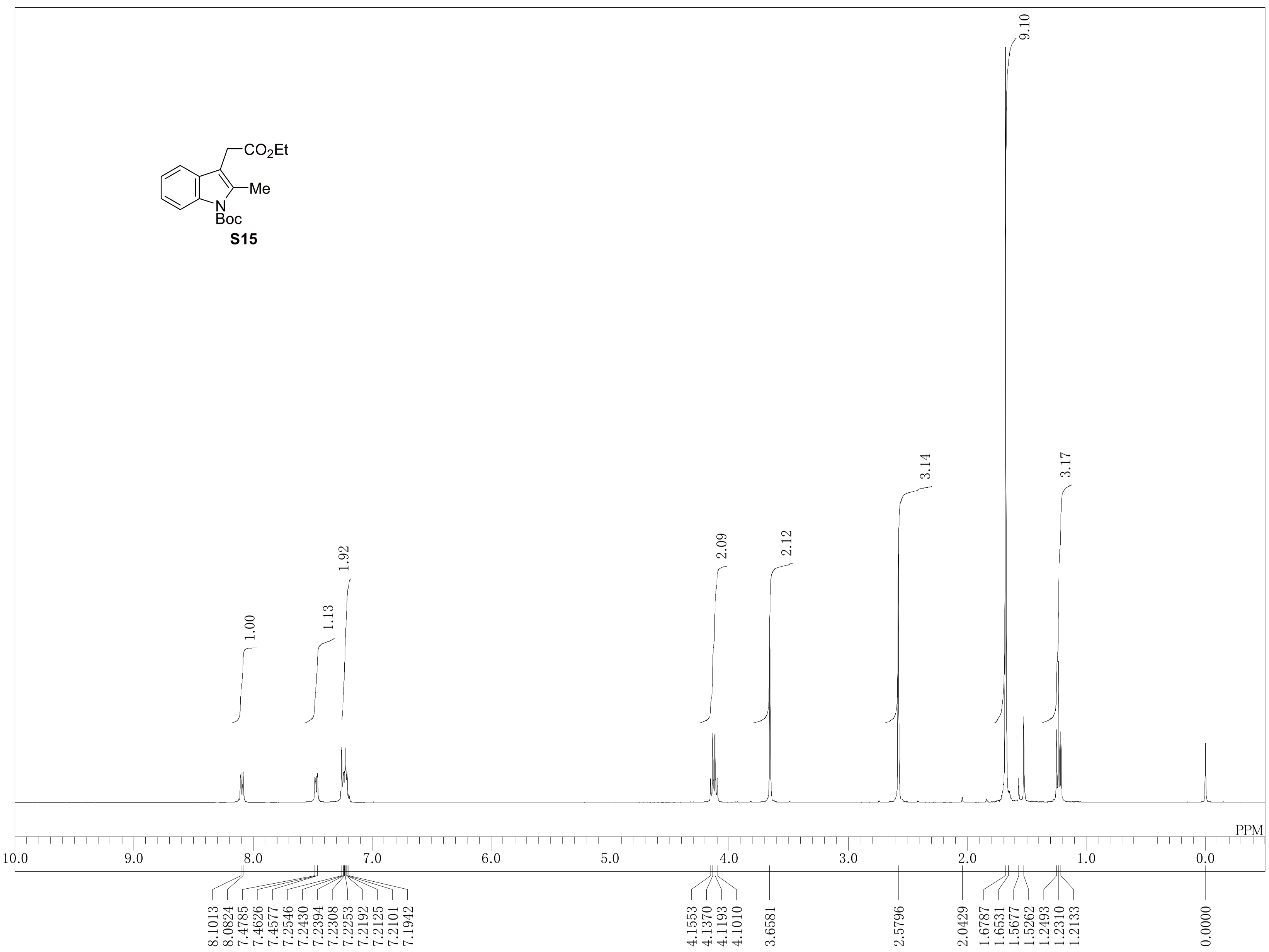
| | |
|---|---|
| DATIM | Fri Nov 09 23:2 |
| DFILE | C:¥My Documen |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 407 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.40 usec |
| IRN | |
| CTEMP | 25.5 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.92 Hz |
| RGAIN | 24 |

**11**



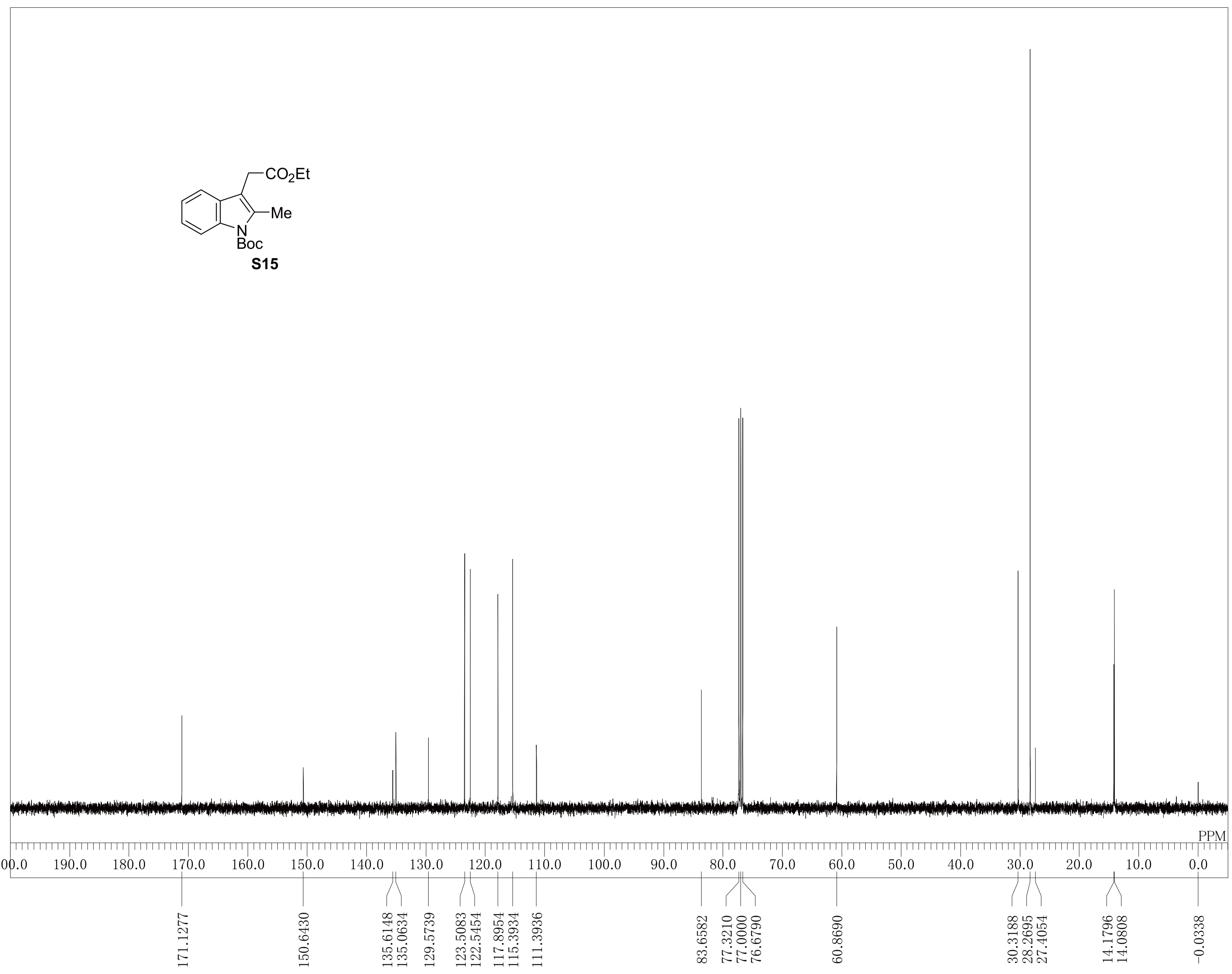
C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1301-No1400¥No1331-No1340¥1336_07_12_12.als

DATIM Wed Dec 12 21:
DFILE C:¥My Documer
OBNUC 1H
EXMOD NON
OFR 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 32768
FREQU 7912.96 Hz
SCANS 16
ACQTM 4.1411 sec
PD 2.8590 sec
PW1 5.80 usec
IRN
CTEMP 24.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 15



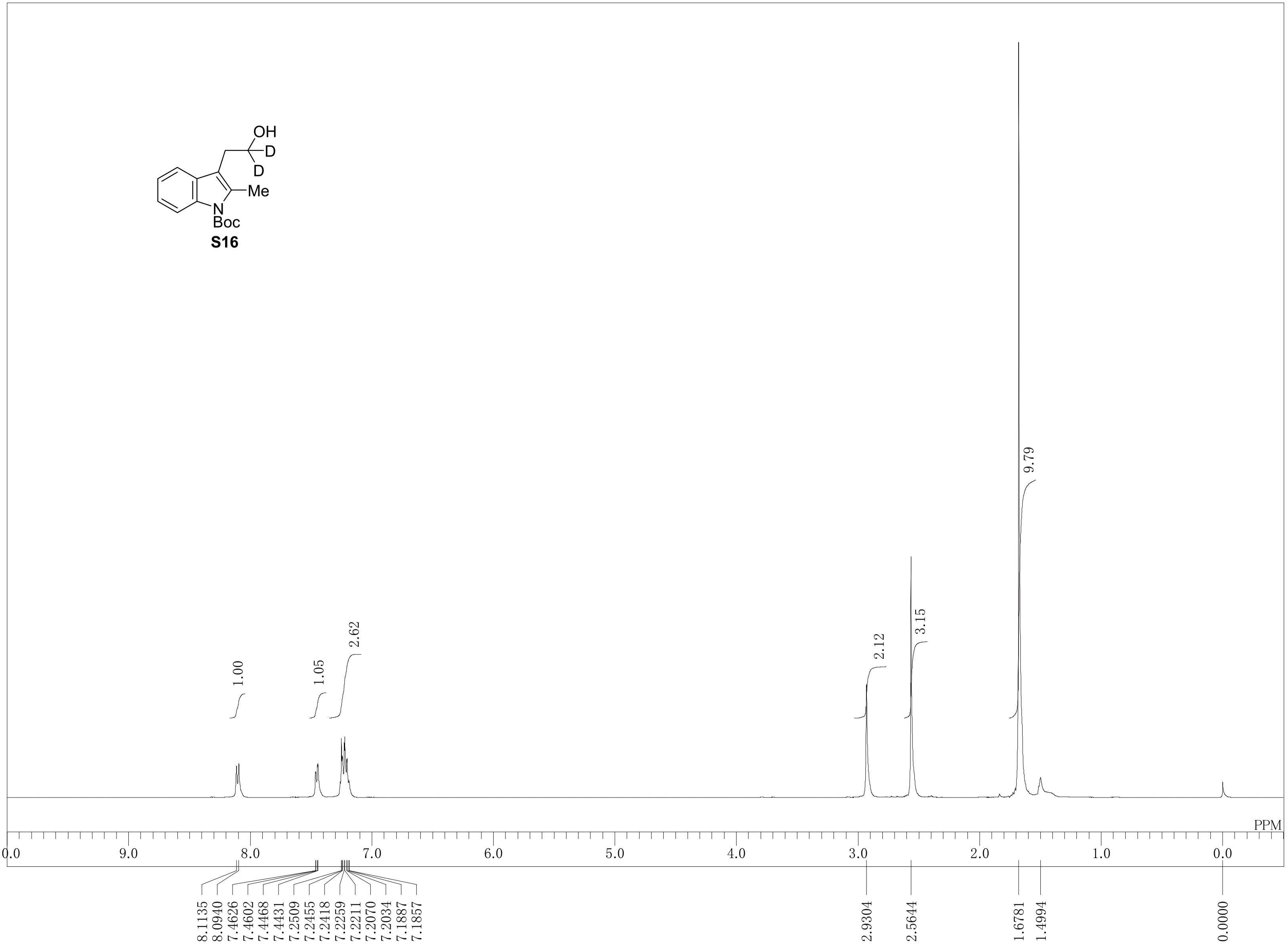
**S15**

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1301-No1400¥No1331-No1340¥1336_07_12_12_13C.als



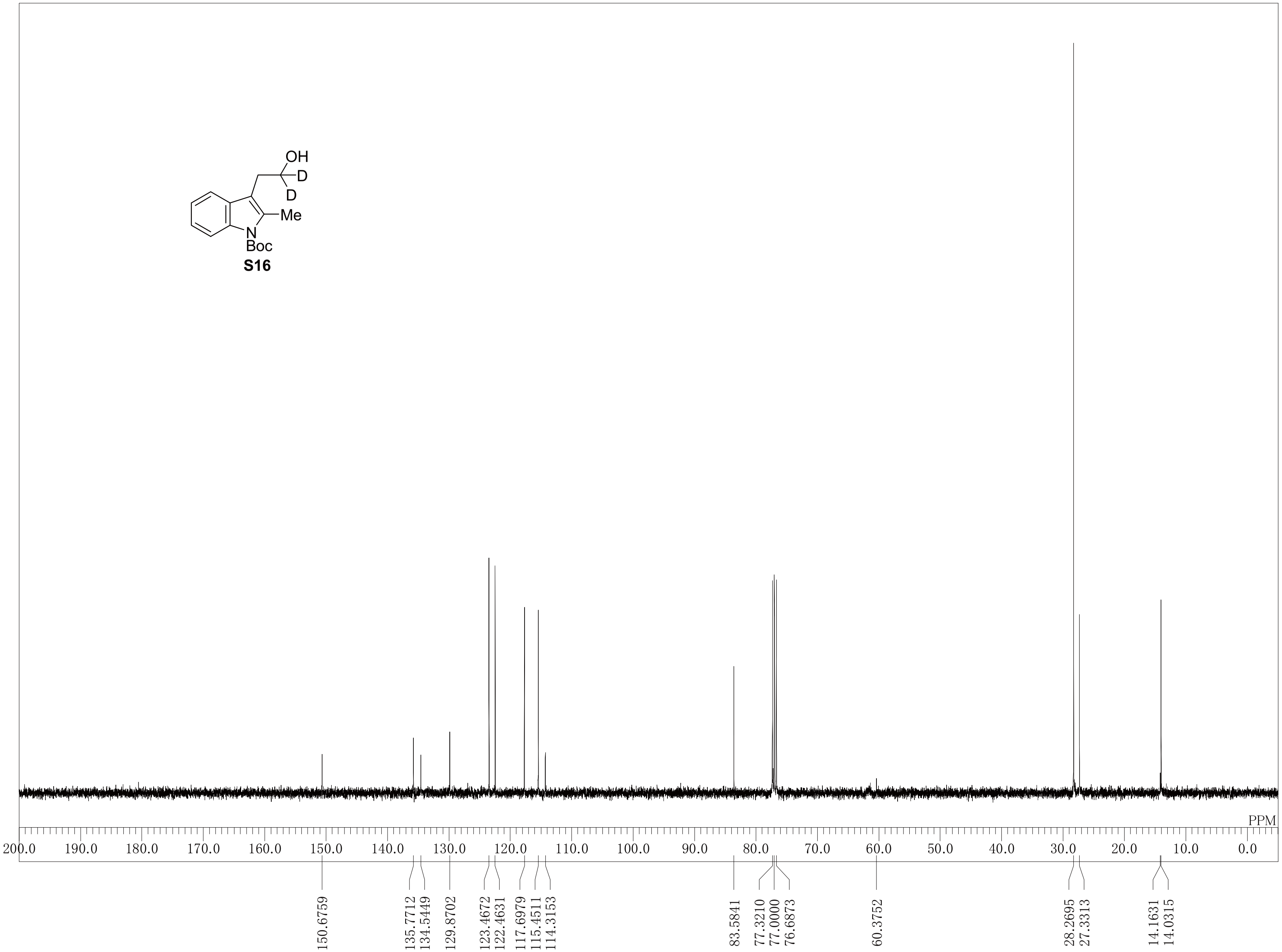
| | |
|---|---|
| DATIM | Wed Dec 12 21: |
| DFILE | C:¥My Documer |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 371 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.40 usec |
| IRN | |
| CTEMP | 26.1 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.42 Hz |
| RGAIN | 24 |

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1301-No1400¥No1311-No1320¥1319_07_12_5.als



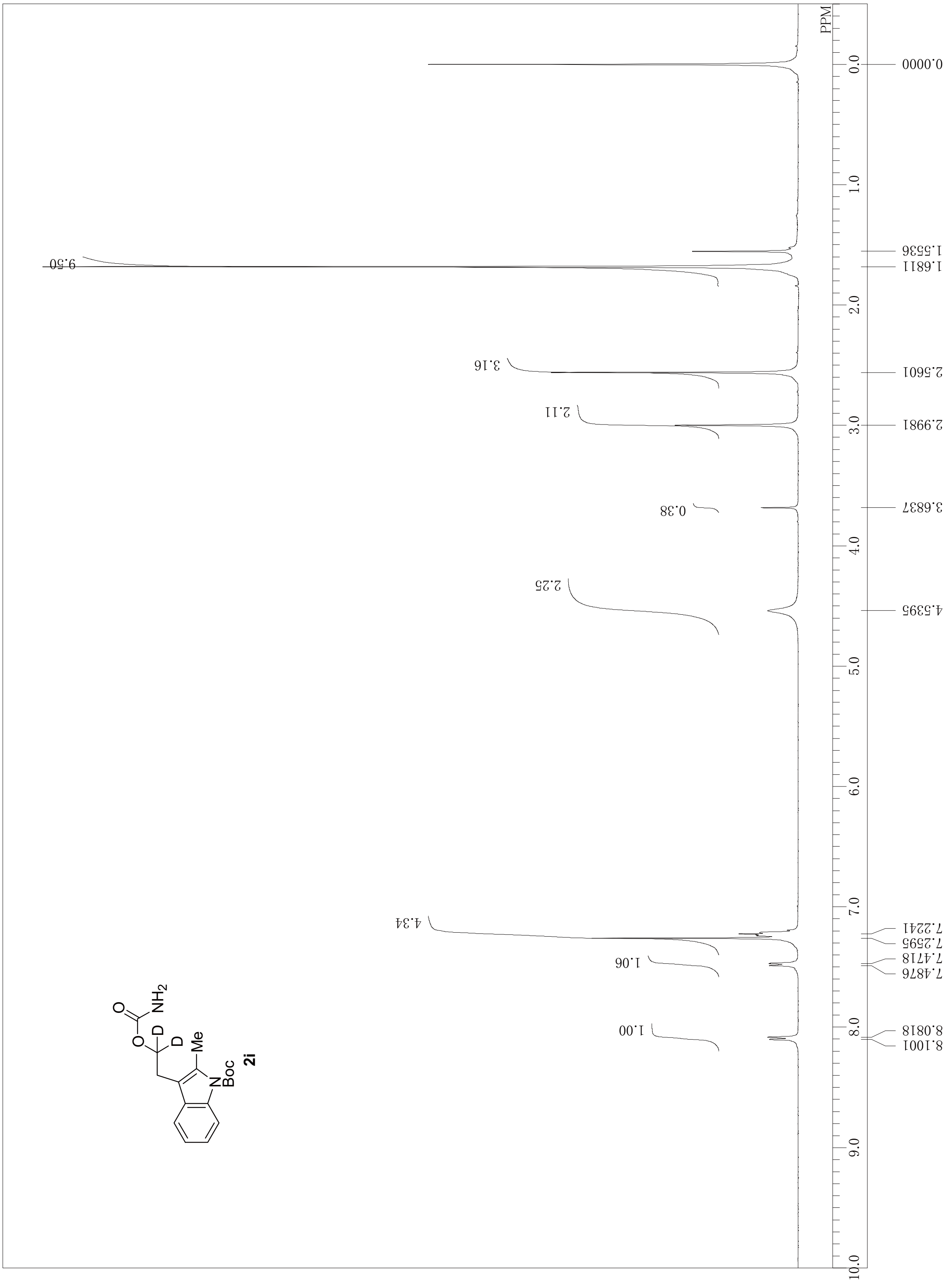
DATIM Wed Dec 05 23:(
DFILE C:¥My Documen
OBNUC 1H
EXMOD NON
OFR 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 32768
FREQU 7912.96 Hz
SCANS 8
ACQTM 4.1411 sec
PD 2.8590 sec
PW1 5.80 usec
IRN
CTEMP 23.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.52 Hz
RGAIN 12

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1301-No1400¥No1311-No1320¥1319_07_12_5_13C.als



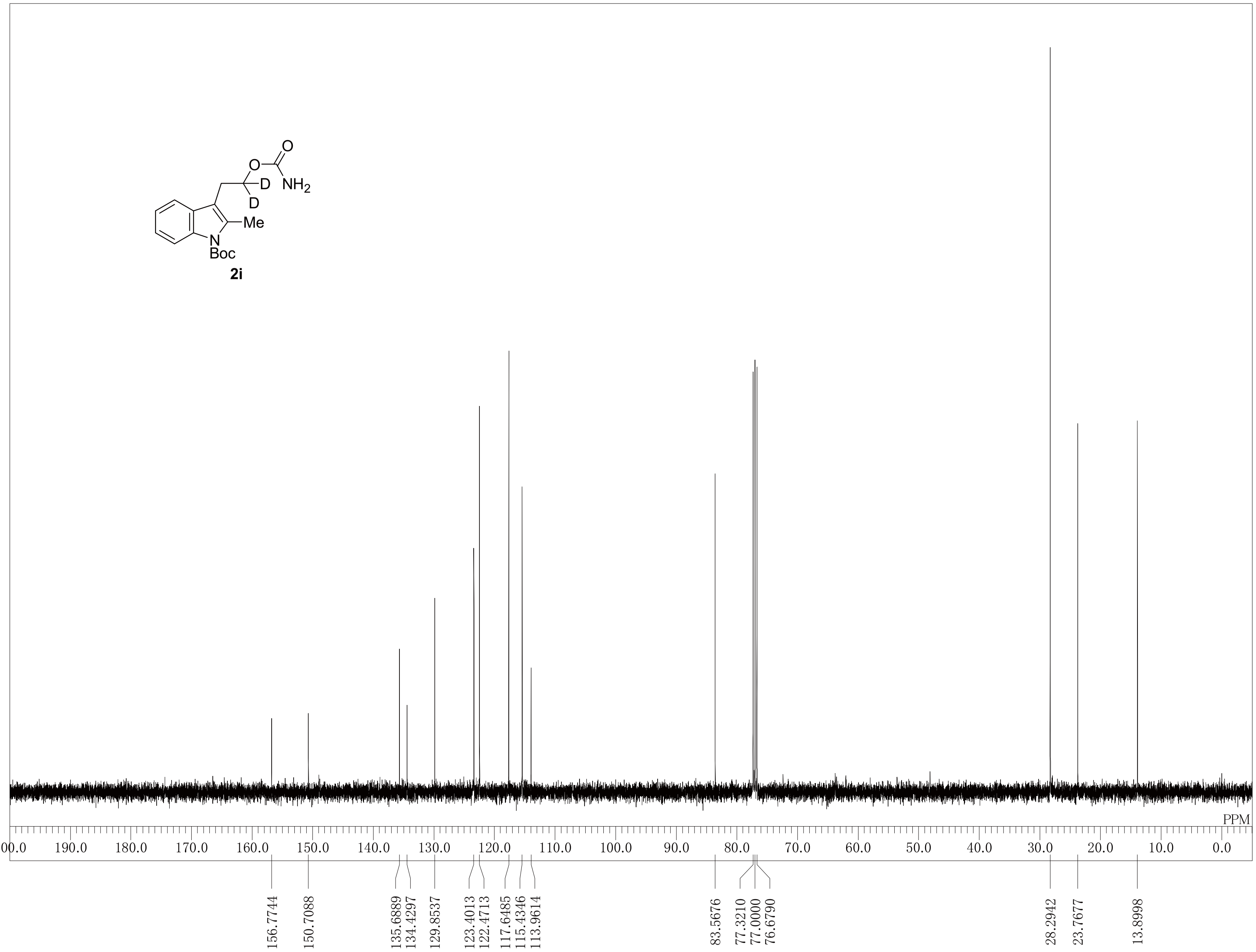
```
DATIM     Wed Dec 05 23:
DFILE     C:¥My Documen
OBNUC     13C
EXMOD     BCM
OFR          99.45 MHz
OBSET        94.00 KHz
OBFIN     10309.00 Hz
POINT        32768
FREQU     26845.64 Hz
SCANS          242
ACQTM       1.2206 sec
PD          1.7790 sec
PW1           6.40 usec
IRN
CTEMP         23.9 c
SLVNT     CDCL3
EXREF        77.00 ppm
BF            0.52 Hz
RGAIN           22
```

| | |
|---|---|
| DATIM | Mon Nov 19 15: |
| DFILE | C:¥My Documen |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 395.75 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10277.00 Hz |
| POINT | 32768 |
| FREQU | 7912.96 Hz |
| SCANS | 16 |
| ACQTM | 4.1411 sec |
| PD | 2.8590 sec |
| PW1 | 5.80 usec |
| IRN | |
| CTEMP | 23.4 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 0.93 Hz |
| RGAIN | 20 |



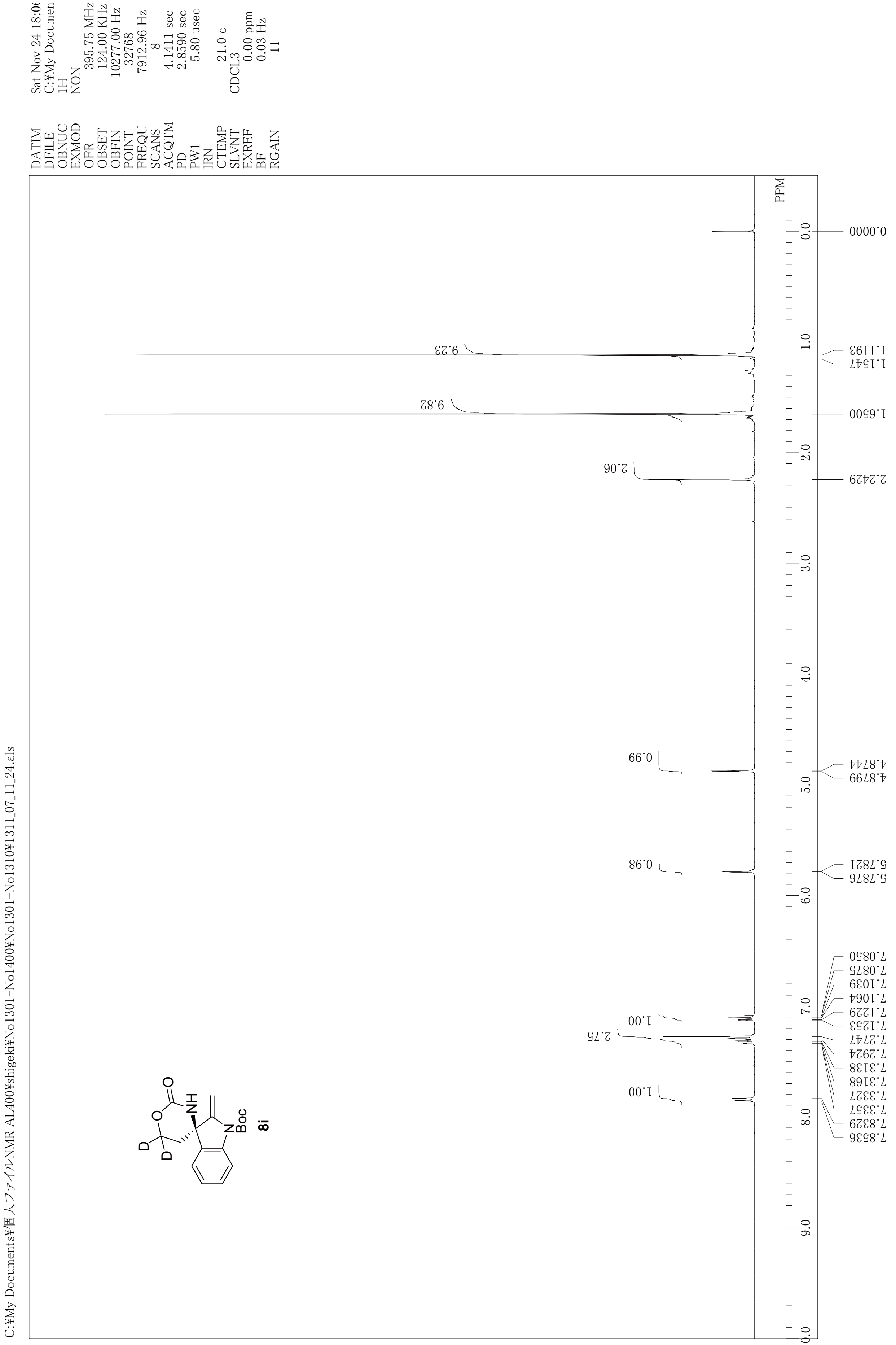
C:¥My Documents¥個人ファイル¥NMR AL400¥shigeki¥No1201-No1300¥No1291-No1300¥1298_07_11_19.als

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1301-No1400¥No1321-No1330¥1321_07_12_7_13C.als

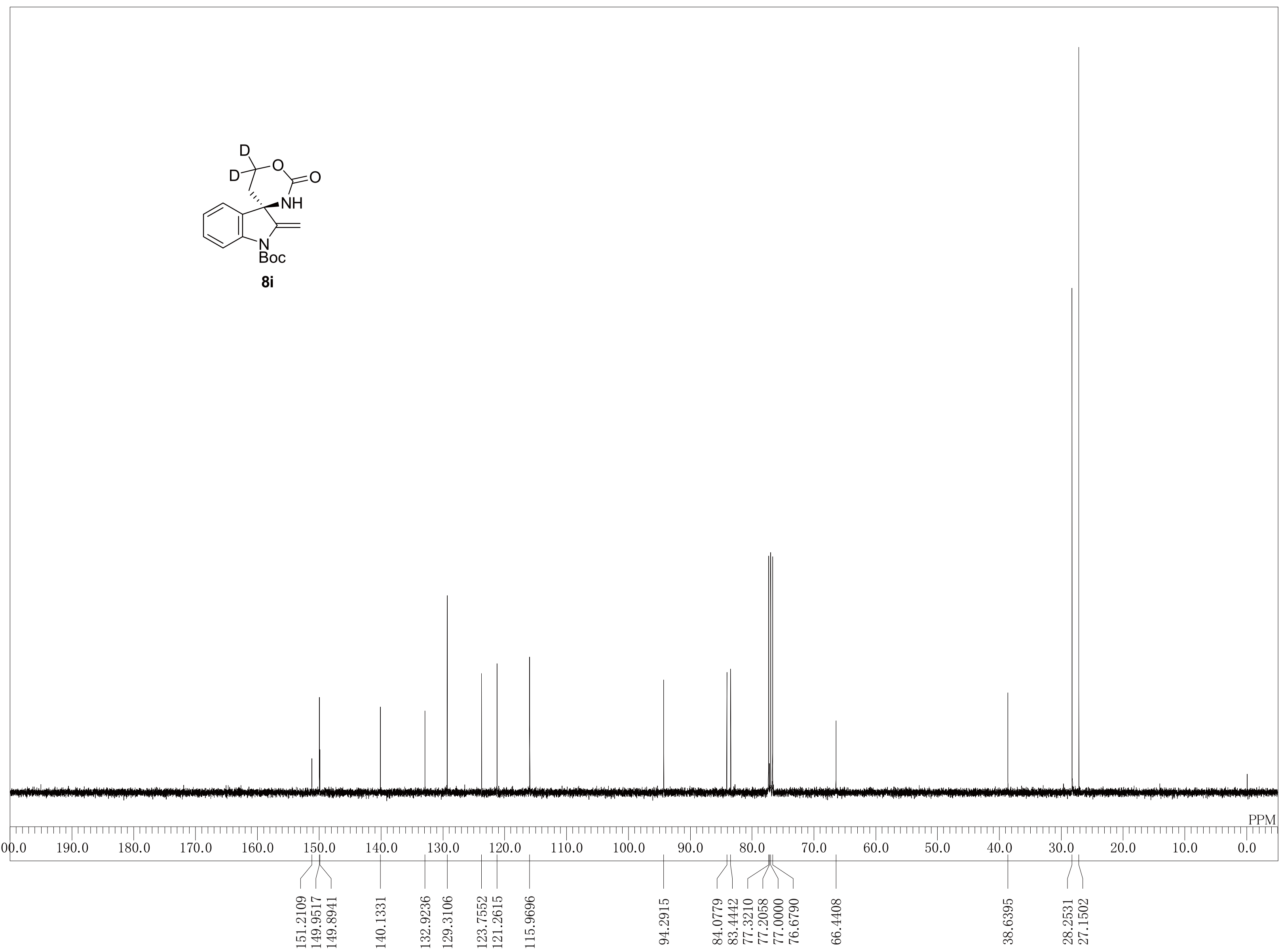


**2i**

| | |
|---|---|
| DATIM | Fri Dec 07 20:12 |
| DFILE | C:¥My Documen |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 428 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.40 usec |
| IRN | |
| CTEMP | 27.6 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 24 |


DATIM Sat Nov 24 18:0(
DFILE C:¥My Documen
OBNUC 1H
EXMOD NON
OFR 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 32768
FREQU 7912.96 Hz
SCANS 8
ACQTM 4.1411 sec
PD 2.8590 sec
PW1 5.80 usec
IRN
CTEMP 21.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.03 Hz
RGAIN 11
C:¥My Documents¥個人ファイル¥NMR AL400¥shigeki¥No1301-No1400¥No1301-No1310¥1311_07_11_24.als
PPM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
0.0000
1.1193
1.1547
1.6500
2.2429
4.8744
4.8799
5.7821
5.7876
7.0850
7.0875
7.1039
7.1064
7.1229
7.1253
7.2747
7.2924
7.3138
7.3168
7.3327
7.3357
7.8329
7.8536
9.23
9.82
2.06
0.99
0.98
1.00
2.75
1.00
D
D
O
O
NH
N
Boc
8i

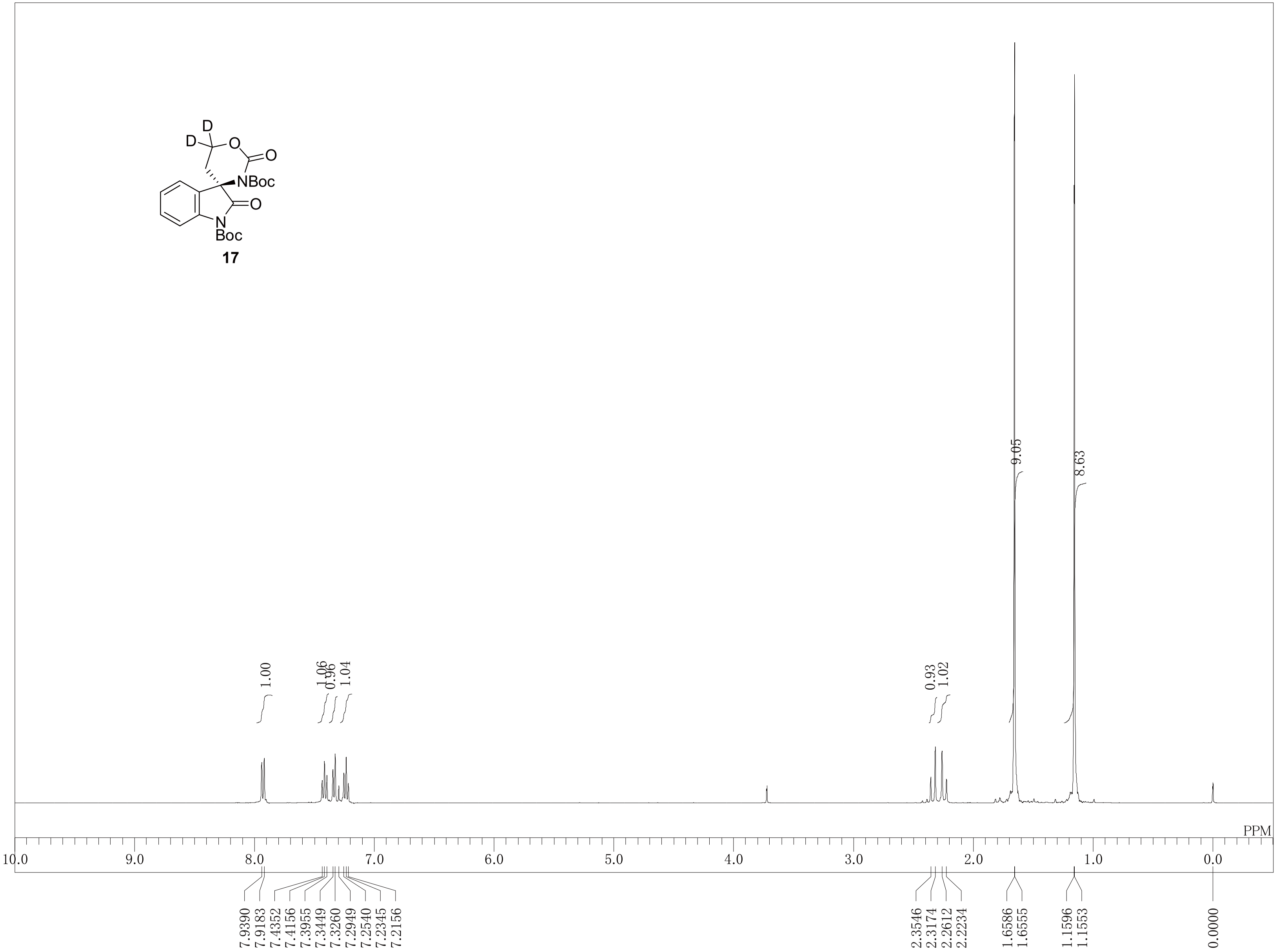
C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1301-No1400¥No1301-No1310¥1311_07_11_24_13C.als



**8i**

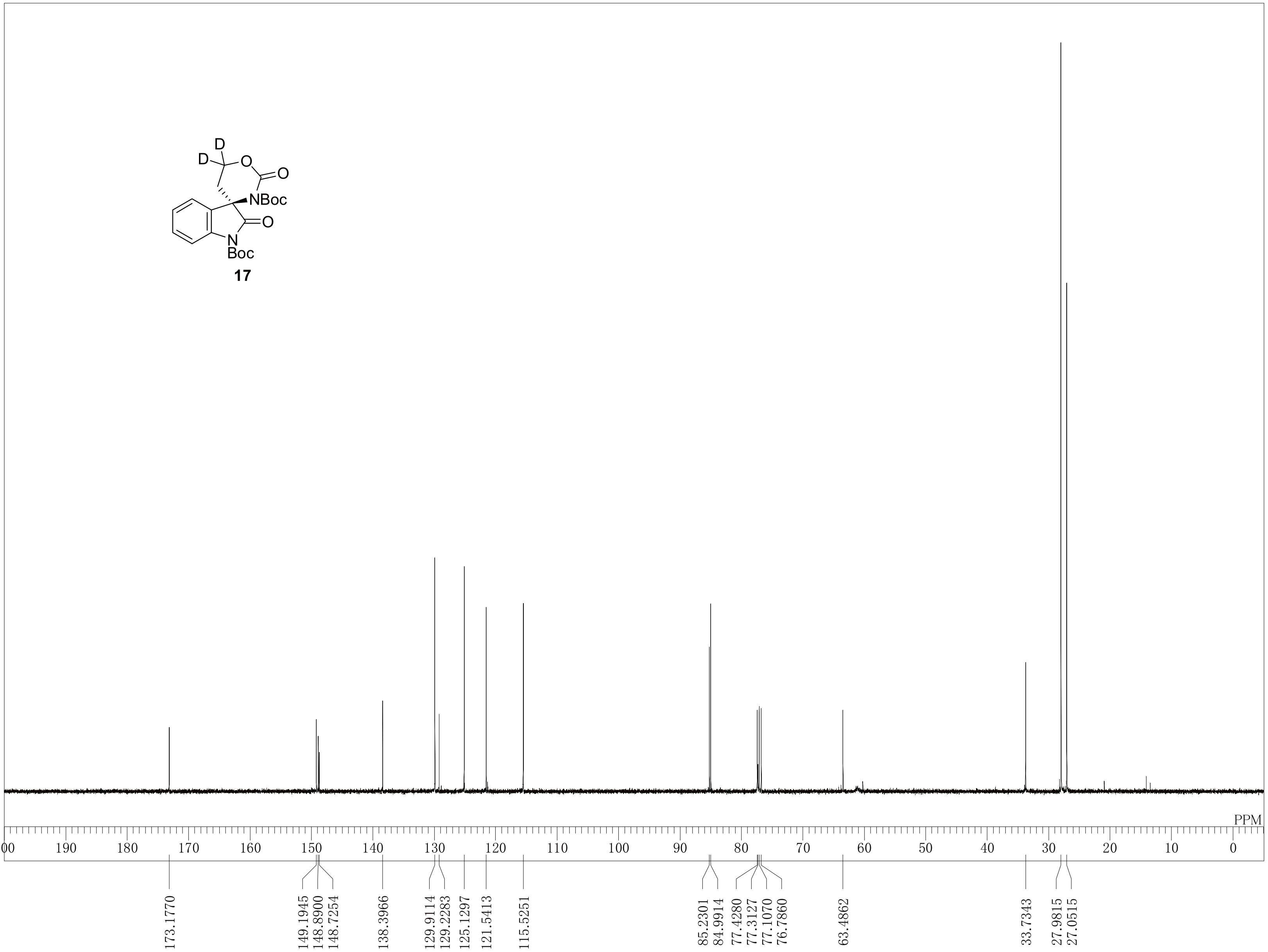
| | |
|---|---|
| DATIM | Sat Nov 24 18:27 |
| DFILE | C:¥My Documen |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 405 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.40 usec |
| IRN | |
| CTEMP | 22.4 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.03 Hz |
| RGAIN | 24 |

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1501-No1600¥No1511-No1520¥1518_08_05_28.als

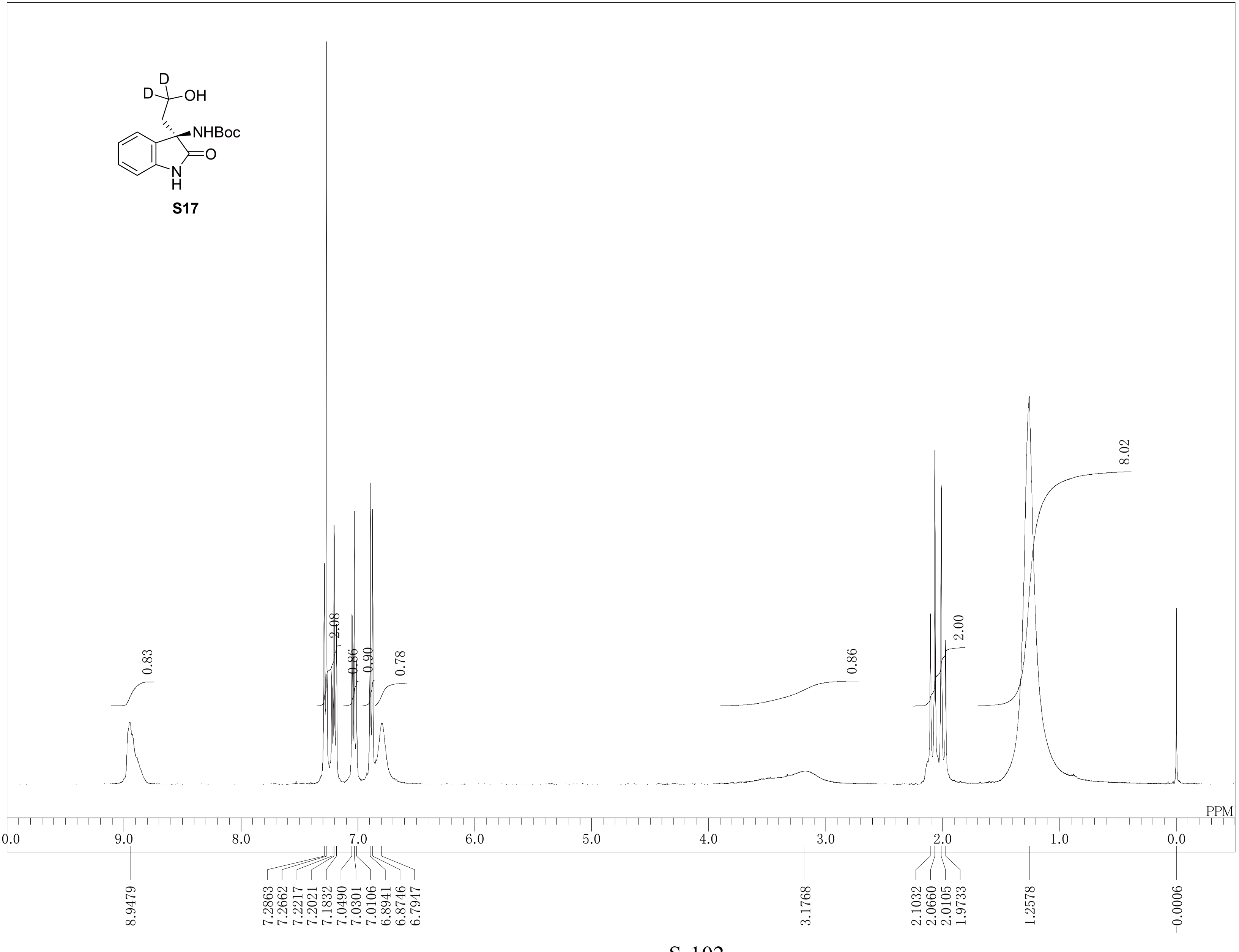


| | |
|---|---|
| DATIM | Wed May 28 09: |
| DFILE | C:¥My Documen |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 395.75 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10277.00 Hz |
| POINT | 32768 |
| FREQU | 7912.96 Hz |
| SCANS | 16 |
| ACQTM | 4.1411 sec |
| PD | 2.8590 sec |
| PW1 | 5.80 usec |
| IRN | |
| CTEMP | 25.9 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 0.21 Hz |
| RGAIN | 11 |

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1301-No1400¥No1341-No1350¥1344_07_12_19_13C.als



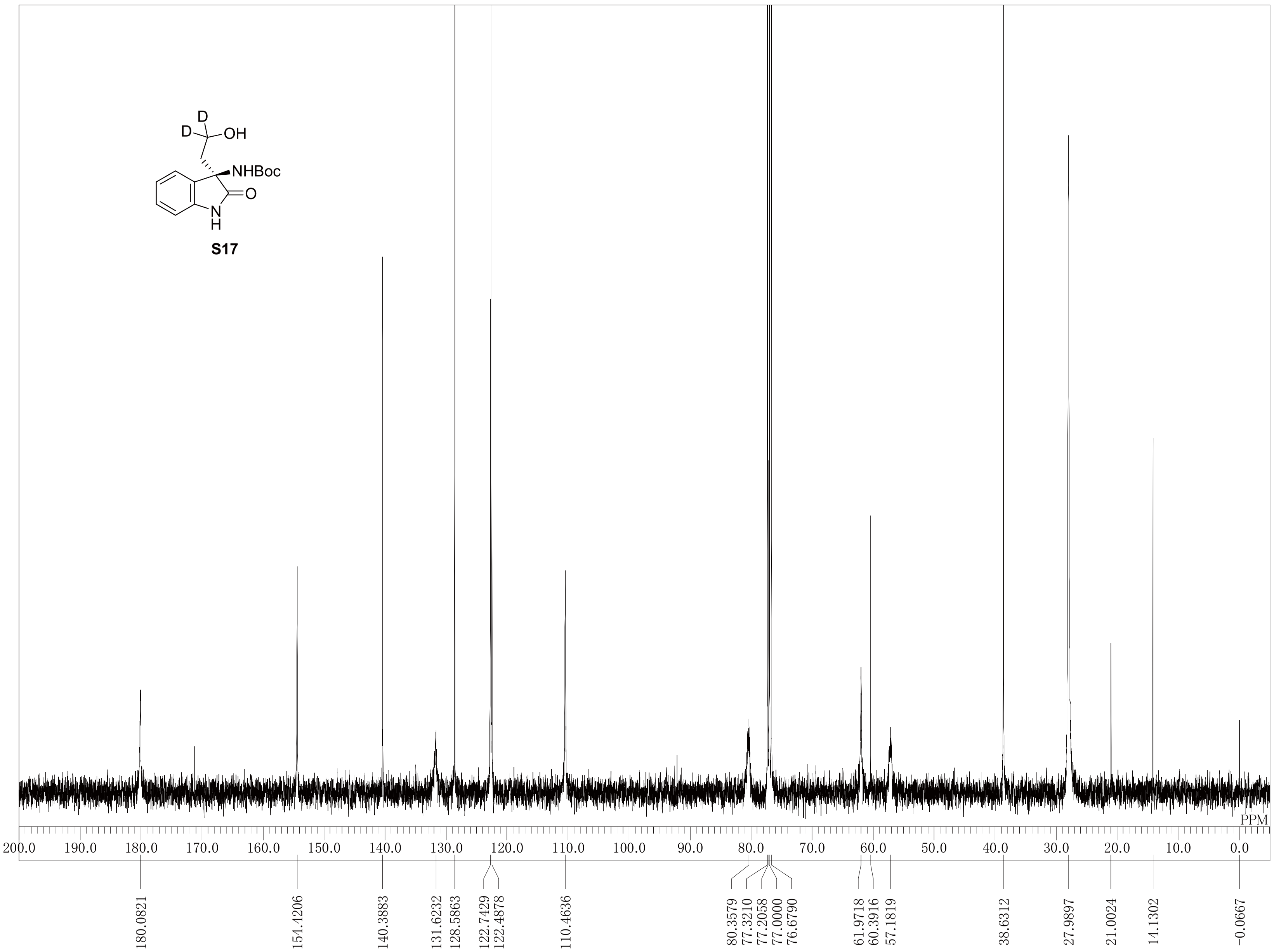
| | |
|---|---|
| DATIM | Wed Dec 19 18:: |
| DFILE | C:¥My Documen |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 437 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.40 usec |
| IRN | |
| CTEMP | 27.3 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.03 Hz |
| RGAIN | 22 |



**S17**

| | |
|---|---|
| DATIM | Thu May 29 20: |
| DFILE | C:¥My Documer |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 395.75 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10277.00 Hz |
| POINT | 32768 |
| FREQU | 7912.96 Hz |
| SCANS | 16 |
| ACQTM | 4.1411 sec |
| PD | 2.8590 sec |
| PW1 | 5.80 usec |
| IRN | |
| CTEMP | 25.4 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 0.43 Hz |
| RGAIN | 13 |

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1301-No1400¥No1351-No1360¥1352_07_12_20_13C.als

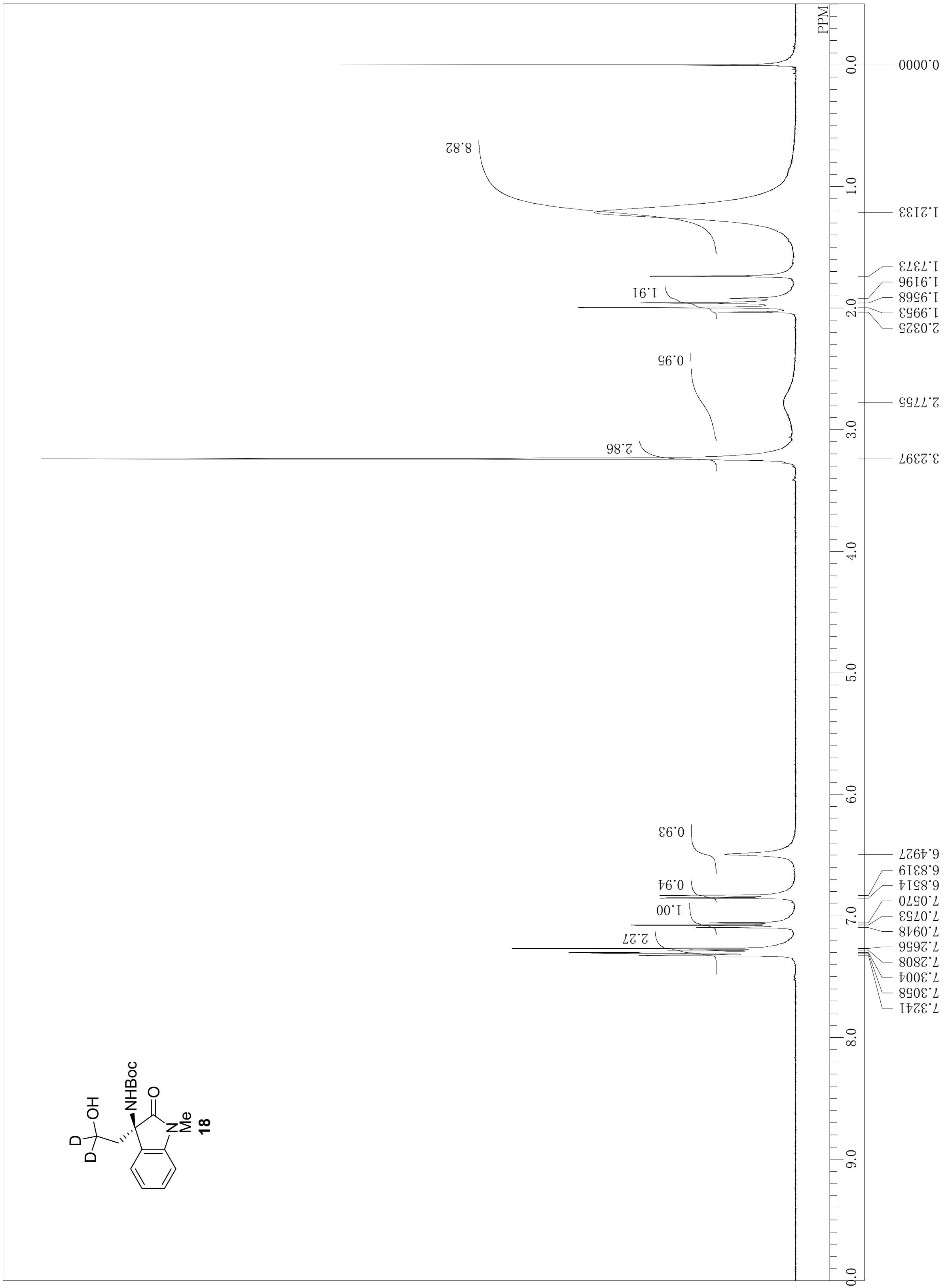


**S17**

| | |
|---|---|
| DATIM | Thu Dec 20 22:1 |
| DFILE | C:¥My Documen |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 562 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.40 usec |
| IRN | |
| CTEMP | 24.7 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.93 Hz |
| RGAIN | 24 |

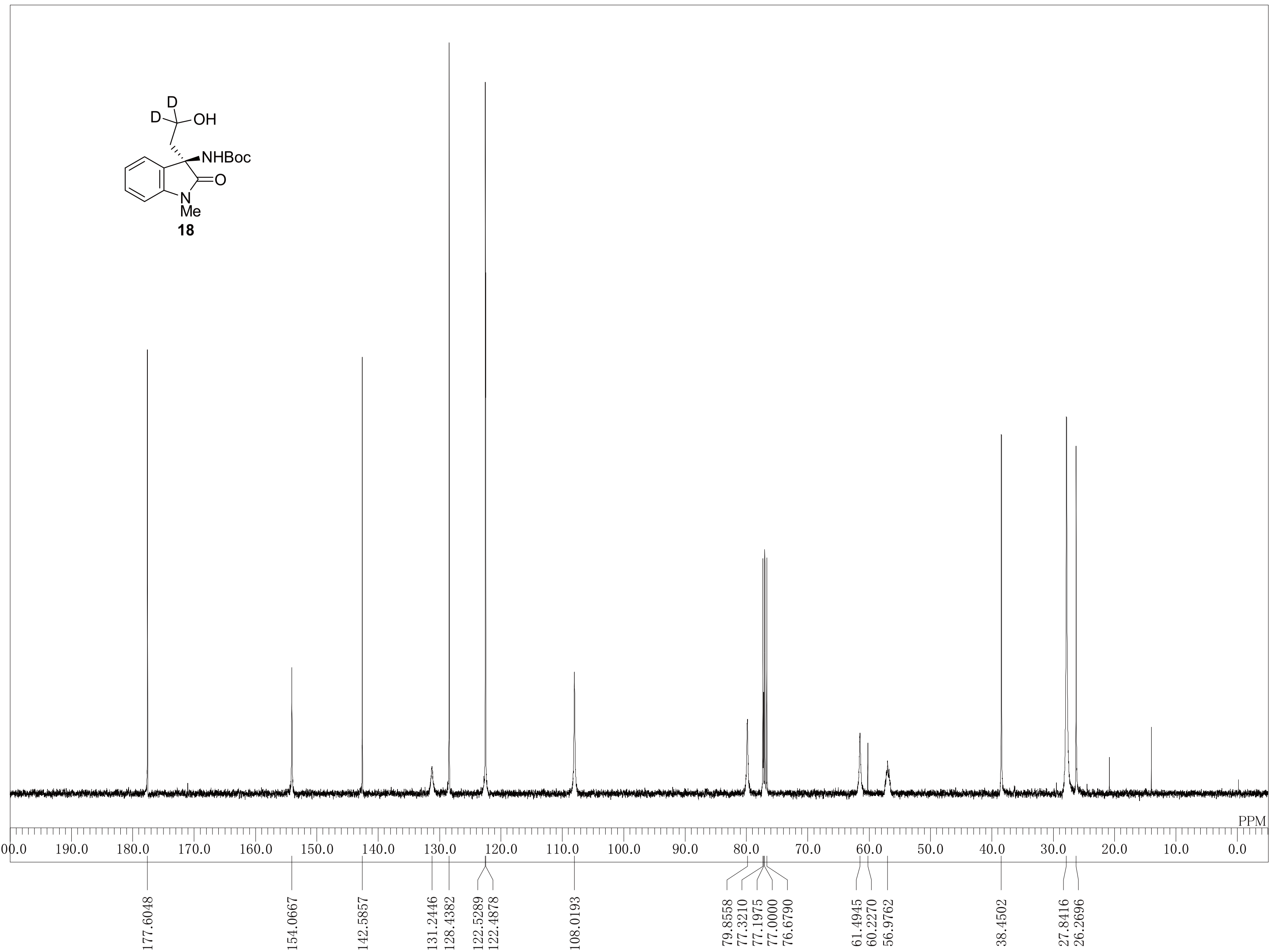
| | |
|---|---|
| DATIM | Mon Jun 02 10:0 |
| DFILE | C:¥My Documen |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 395.75 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10277.00 Hz |
| POINT | 32768 |
| FREQU | 7912.96 Hz |
| SCANS | 16 |
| ACQTM | 4.1411 sec |
| PD | 2.8590 sec |
| PW1 | 5.80 usec |
| IRN | |
| CTEMP | 23.9 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 16 |

C:¥My Documents¥個人ファイル¥NMR AL400¥shigeki¥No1301-No1400¥No1351-No1360¥1356_08_06_02.als



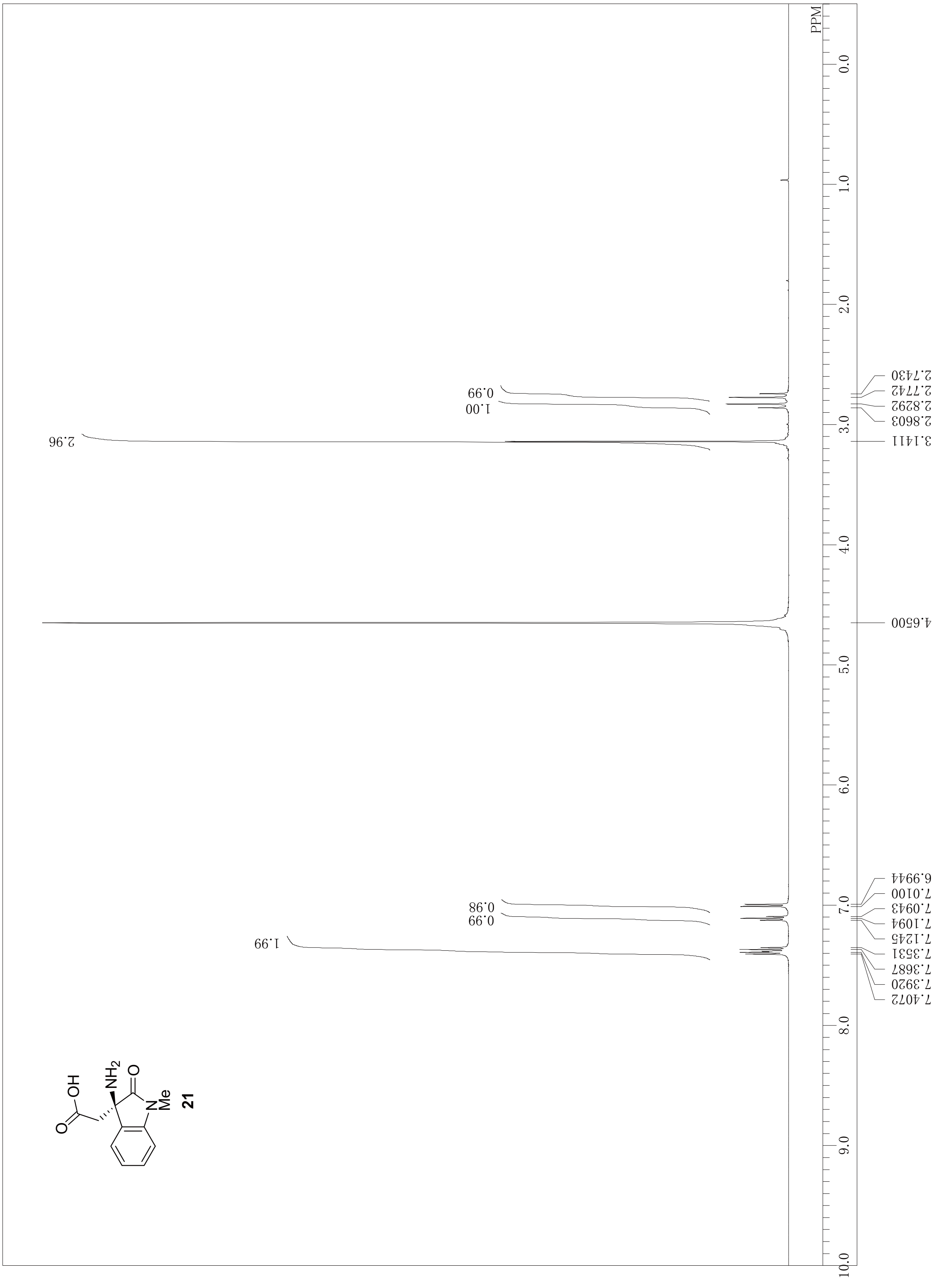
C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1301-No1400¥No1351-No1360¥1356_7_12_21_13C.als

| | |
|---|---|
| DATIM | Fri Dec 21 23:5 |
| DFILE | C:¥My Documen |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 391 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.40 usec |
| IRN | |
| CTEMP | 24.8 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.93 Hz |
| RGAIN | 23 |



| | |
|---|---|
| DATIM | 22-06-2007 15:5 |
| DFILE | C:¥My Documen |
| OBNUC | 1H |
| EXMOD | single_pulse.exp |
| OFR | 500.16 MHz |
| OBSET | 2.41 KHz |
| OBFIN | 6.01 Hz |
| POINT | 32768 |
| FREQU | 7507.51 Hz |
| SCANS | 16 |
| ACQTM | 4.3647 sec |
| PD | 4.0000 sec |
| PW1 | 5.80 usec |
| IRN | |
| CTEMP | 27.3 c |
| SLVNT | D2O |
| EXREF | 4.65 ppm |
| BF | 0.12 Hz |
| RGAIN | 14 |

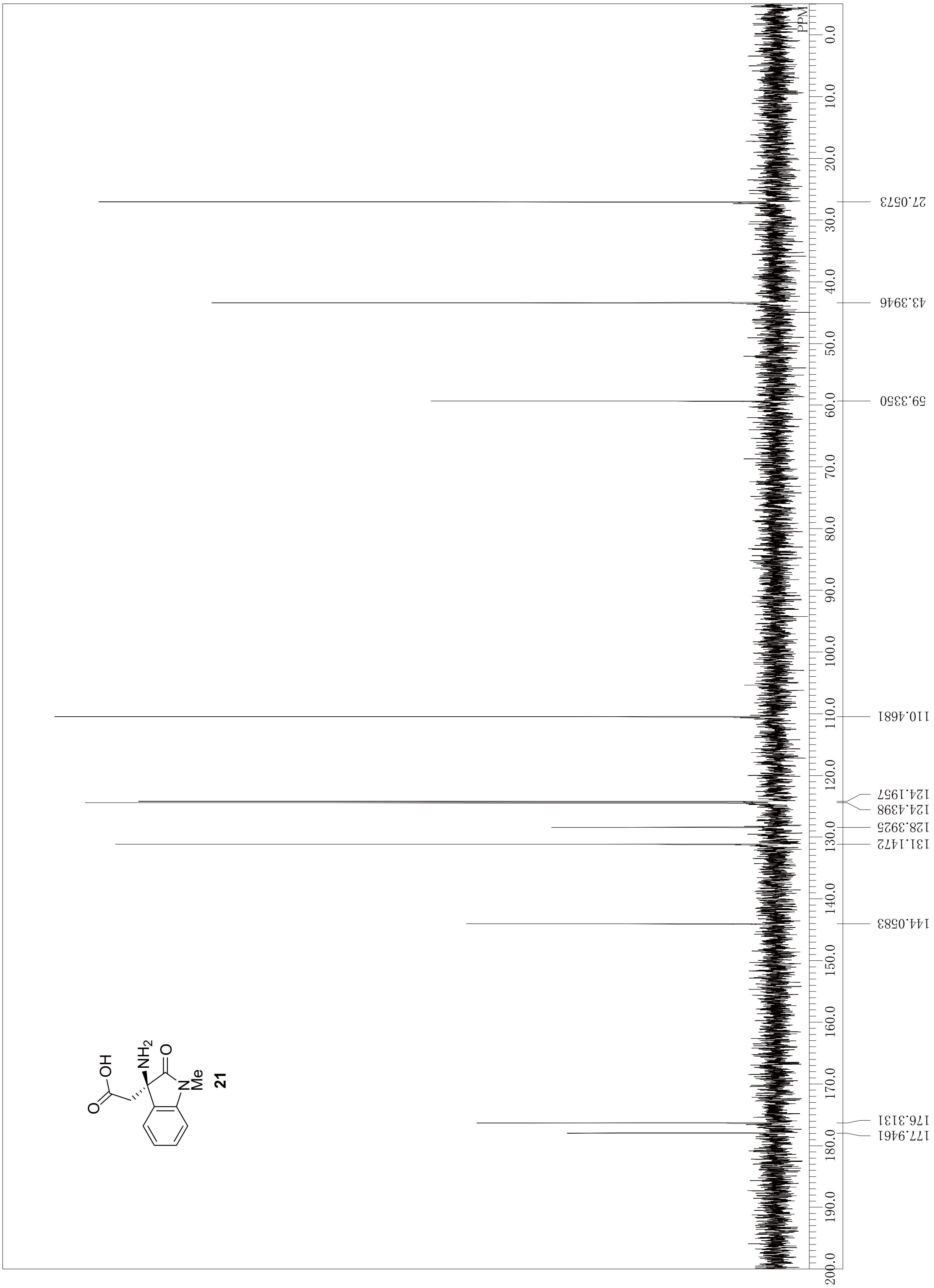
C:¥My Documents¥個人ファイル¥NMR AL400¥shigeki¥No1101-No1200¥No1101-No1110¥07_6_22_shigeki.als



**21**

| | |
|---|---|
| DATIM | 22-06-2007 15:3 |
| DFILE | C:¥My Document |
| OBNUC | 13C |
| EXMOD | single_pulse_dec |
| OFR | 125.77 MHz |
| OBSET | 7.87 KHz |
| OBFIN | 4.21 Hz |
| POINT | 32768 |
| FREQU | 31446.54 Hz |
| SCANS | 4200 |
| ACQTM | 1.0420 sec |
| PD | 1.0000 sec |
| PW1 | 3.40 usec |
| IRN | |
| CTEMP | 28.9 c |
| SLVNT | D2O |
| EXREF | 77.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 26 |

C:¥My Documents¥個人ファイル¥NMR AL400¥shigeki¥No1101-No1200¥No1101-No1110¥1d_13c_spectrum.2



Supplementary Material (ESI) for Chemical Communications
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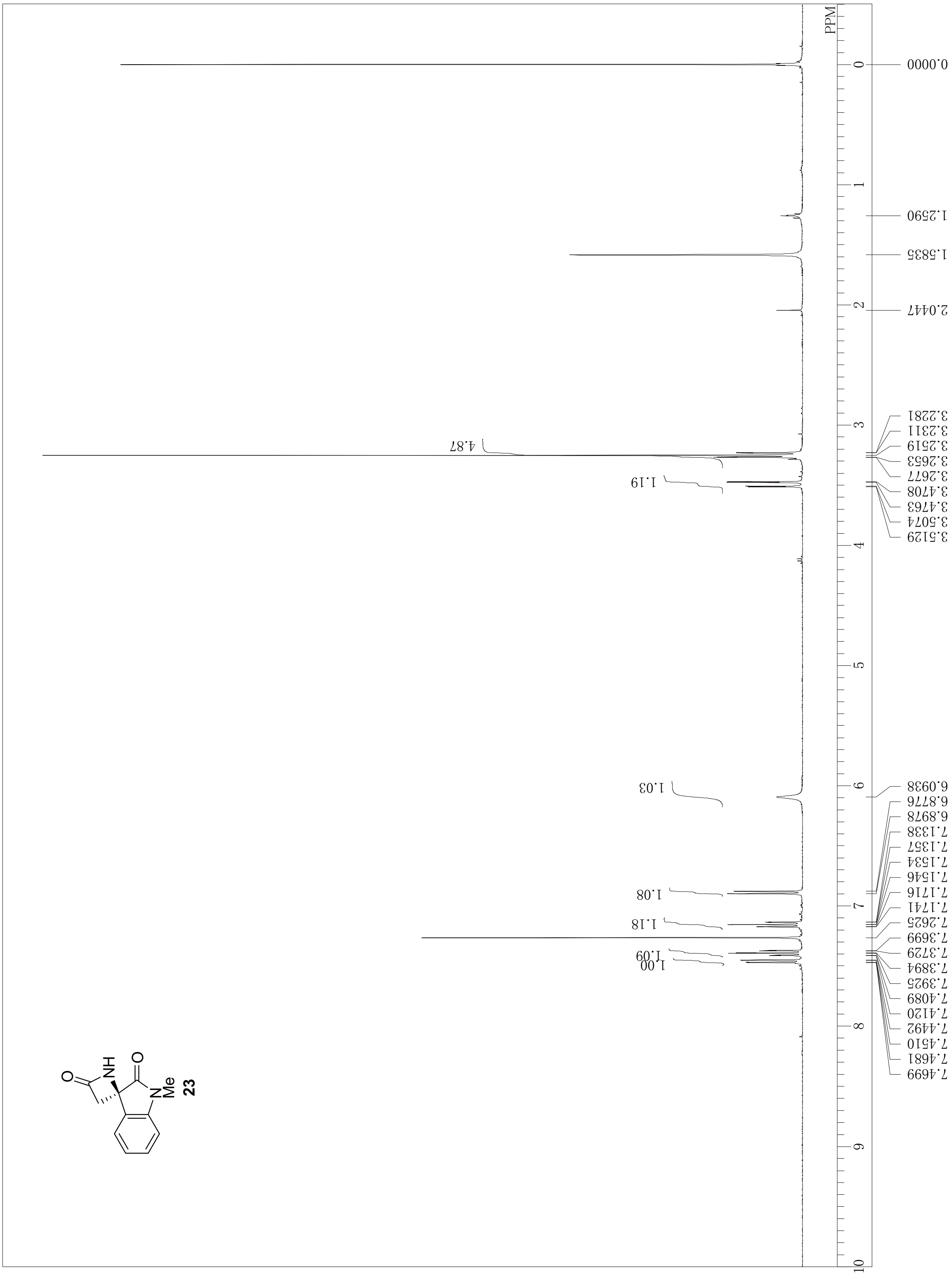
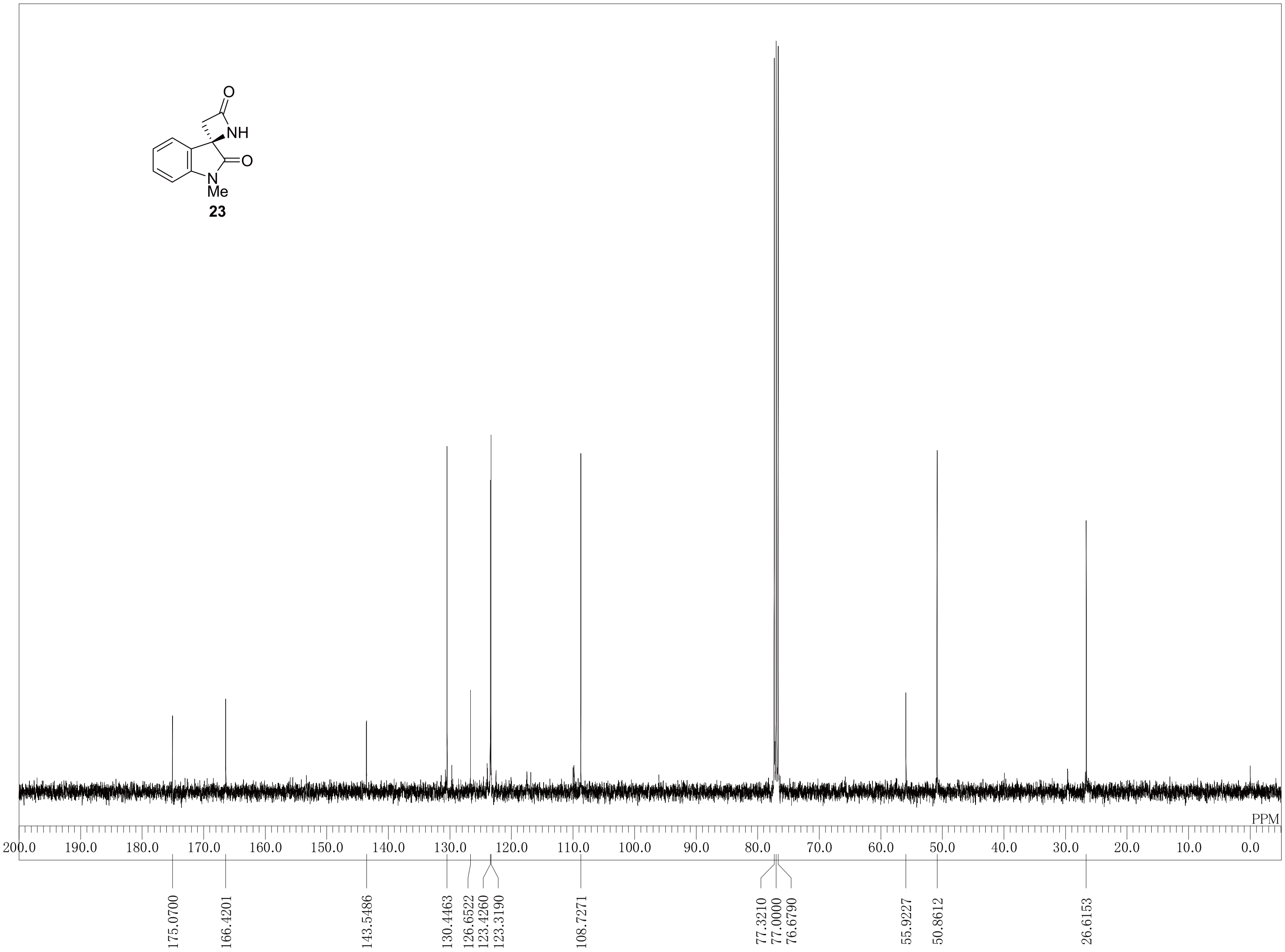
| | |
|---|---|
| DATIM | Wed Jun 27 20:5 |
| DFILE | C:¥My Documen |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 395.75 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10277.00 Hz |
| POINT | 32768 |
| FREQU | 7912.96 Hz |
| SCANS | 16 |
| ACQTM | 4.1411 sec |
| PD | 2.8590 sec |
| PW1 | 5.80 usec |
| IRN | |
| CTEMP | 24.1 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 0.32 Hz |
| RGAIN | 21 |

C:¥My Documents¥個人ファイル¥NMR AL400¥shigeki¥No1101-No1200¥No1111-No1120¥1116_07_6_27.als

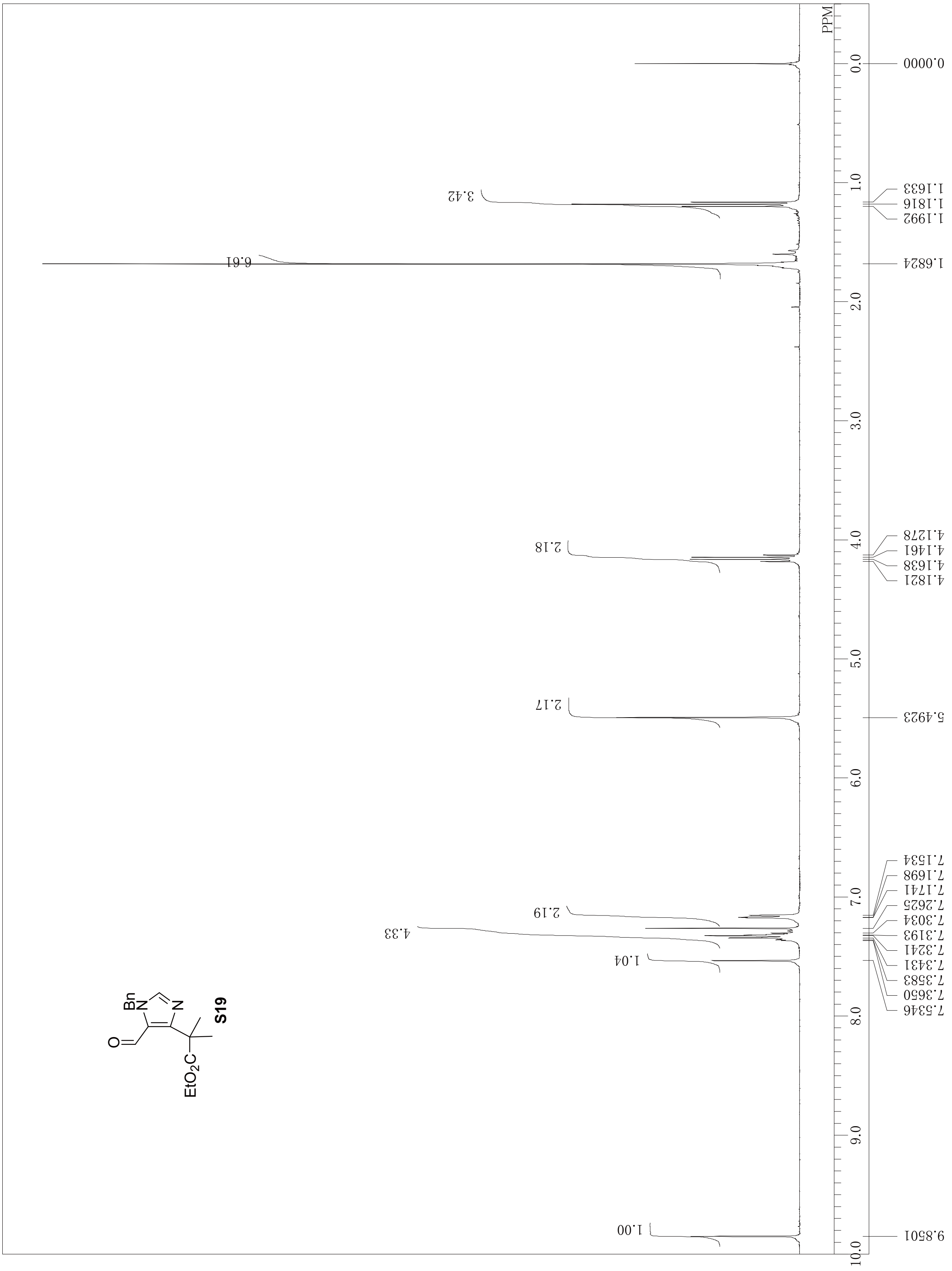


C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1301-No1400¥No1351-No1360¥1353_07_12_20_13C.als

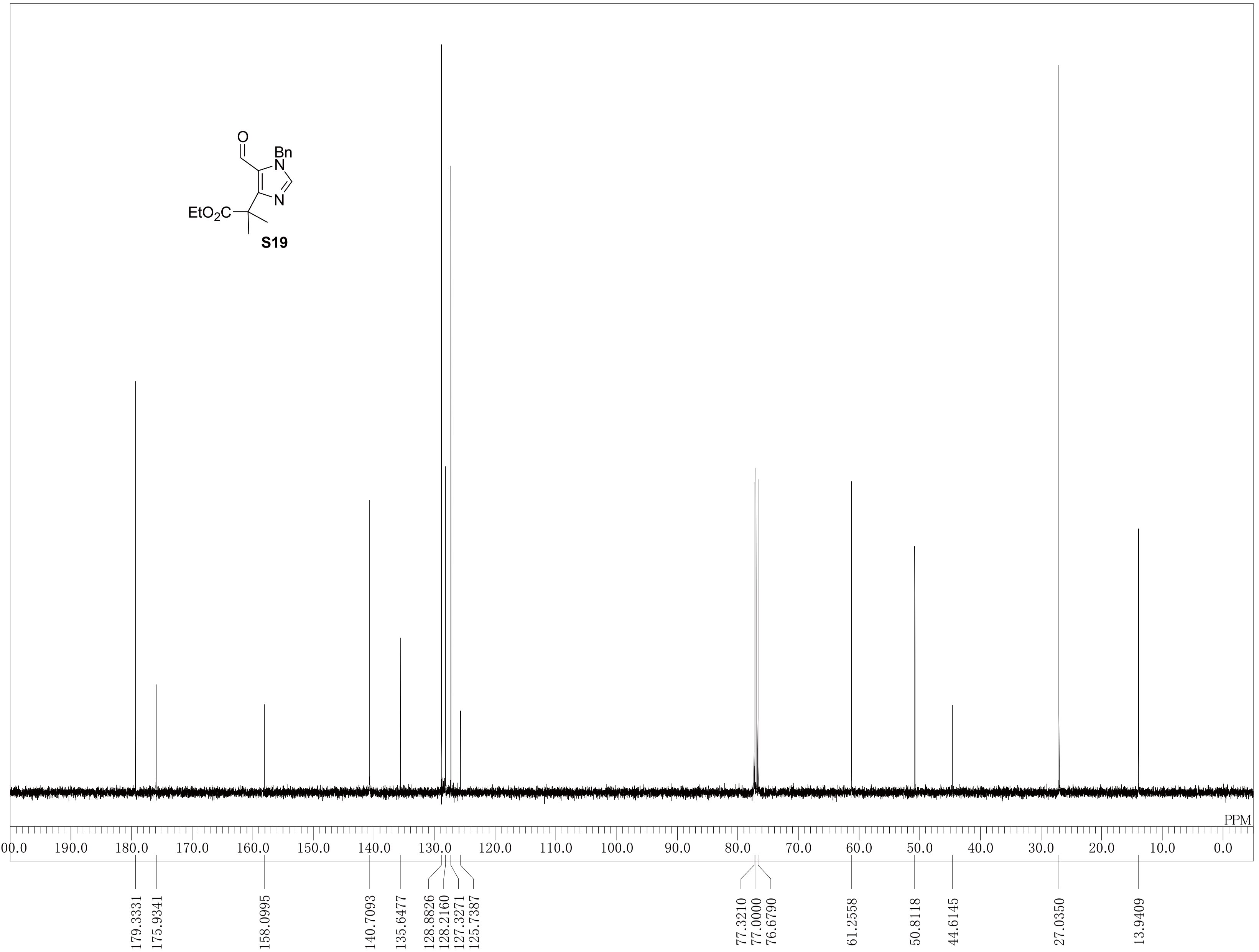


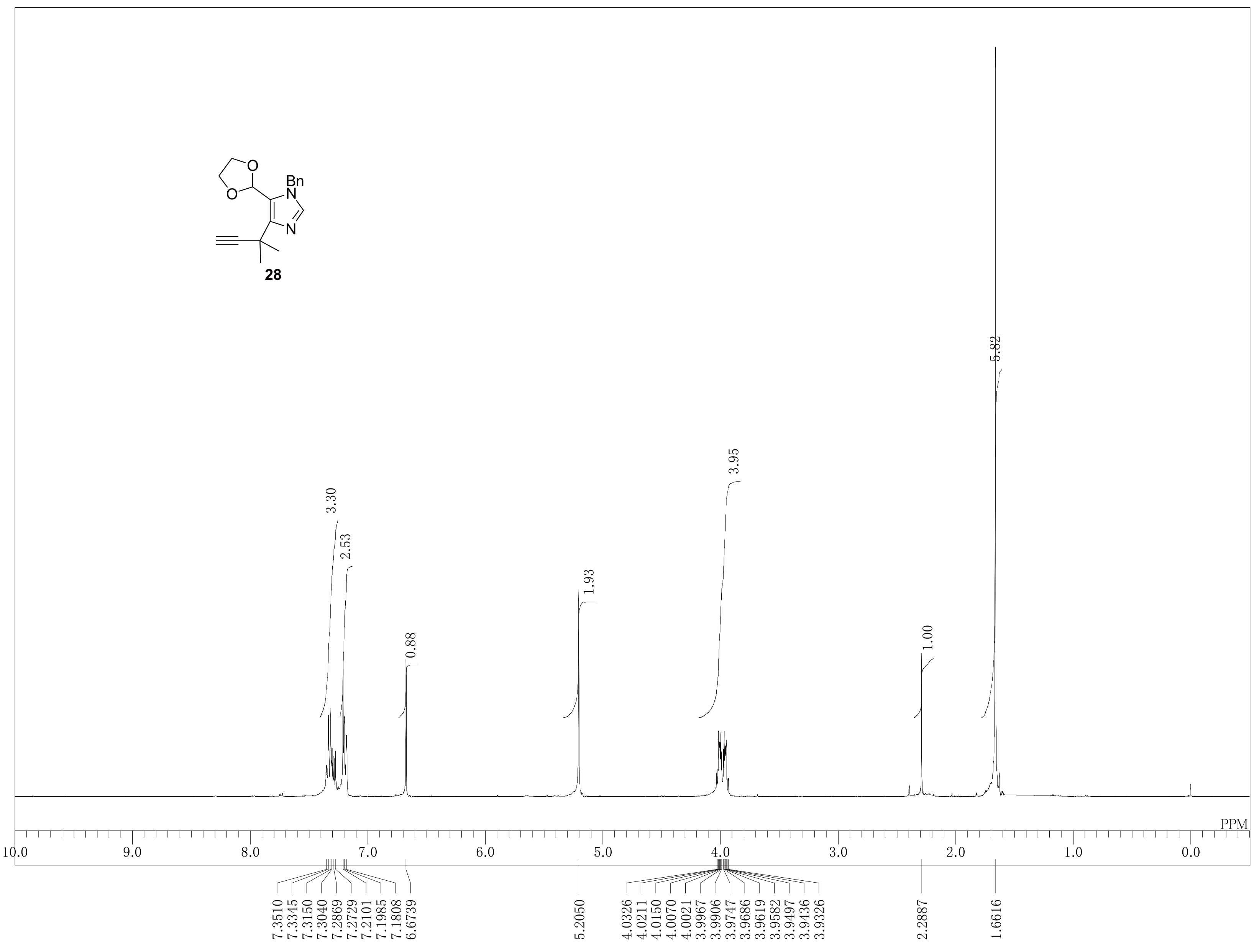
```
DATIM     Fri Dec 21 00:2
DFILE     C:¥My Documen
OBNUC     13C
EXMOD     BCM
OFR            99.45 MH
OBSET          94.00 KH
OBFIN       10309.00 H
POINT          32768
FREQU       26845.64 Hz
SCANS            435
ACQTM         1.2206 sec
PD            1.7790 sec
PW1             6.40 usec
IRN
CTEMP           24.2 c
SLVNT     CDCL3
EXREF          77.00 ppm
BF              0.93 Hz
RGAIN             24
```

| | |
|---|---|
| DATIM | Mon Jun 08 17:5 |
| DFILE | C:¥My Documen |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 395.75 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10277.00 Hz |
| POINT | 32768 |
| FREQU | 7912.96 Hz |
| SCANS | 16 |
| ACQTM | 4.1411 sec |
| PD | 2.8590 sec |
| PW1 | 5.80 usec |
| IRN | |
| CTEMP | 25.8 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 18 |



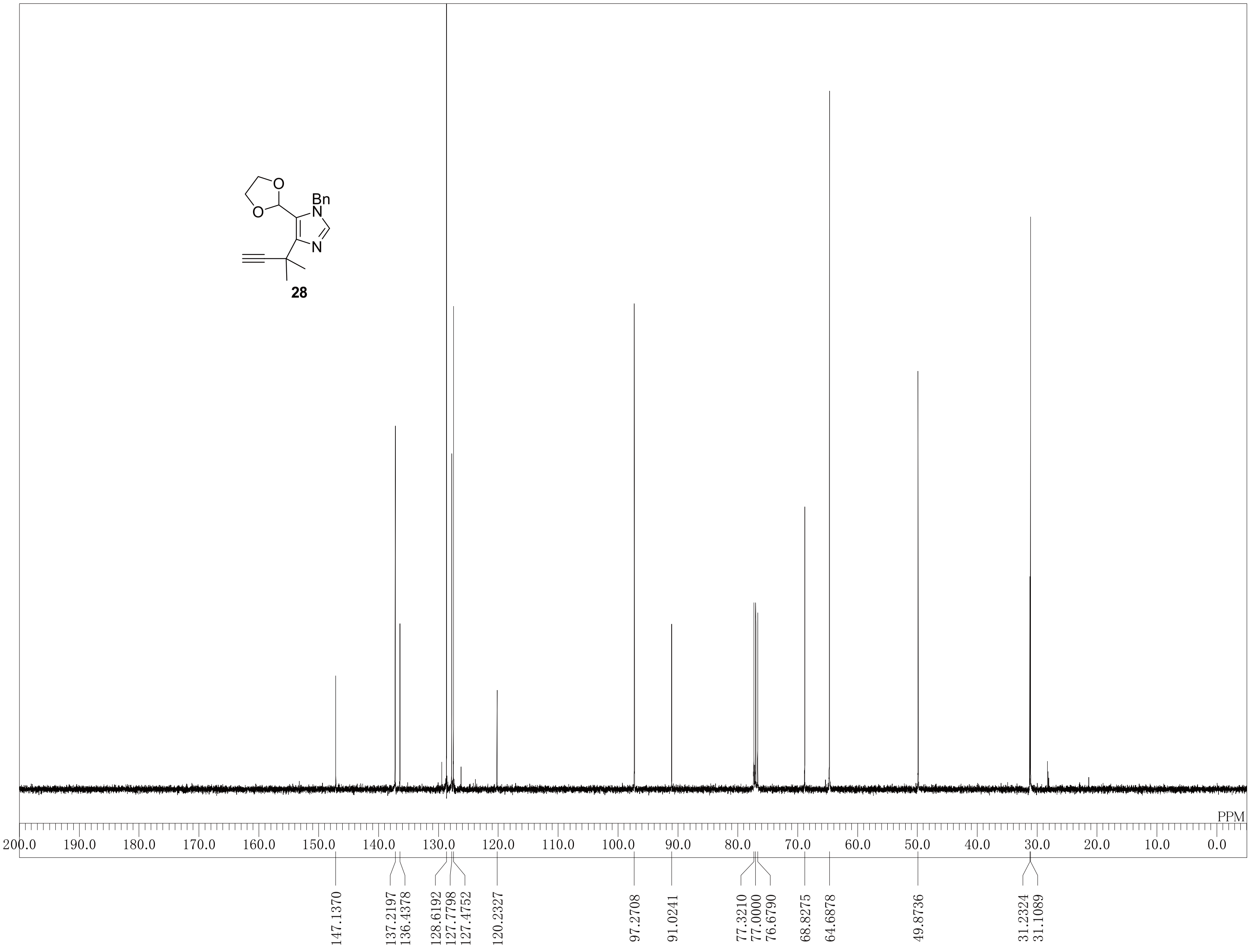
| | |
|---|---|
| DATIM | Tue Jun 09 16:1 |
| DFILE | C:¥My Documen |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 405 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.40 usec |
| IRN | |
| CTEMP | 28.0 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 24 |





| | |
|---|---|
| DATIM | Wed Jun 10 23:1 |
| DFILE | C:¥My Documer |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 395.75 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10277.00 Hz |
| POINT | 32768 |
| FREQU | 7912.96 Hz |
| SCANS | 8 |
| ACQTM | 4.1411 sec |
| PD | 2.8590 sec |
| PW1 | 5.80 usec |
| IRN | |
| CTEMP | 26.7 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 11 |

| | |
|---|---|
| DATIM | Wed Jun 10 23:4 |
| DFILE | C:¥My Documer |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 431 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.40 usec |
| IRN | |
| CTEMP | 28.2 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 22 |



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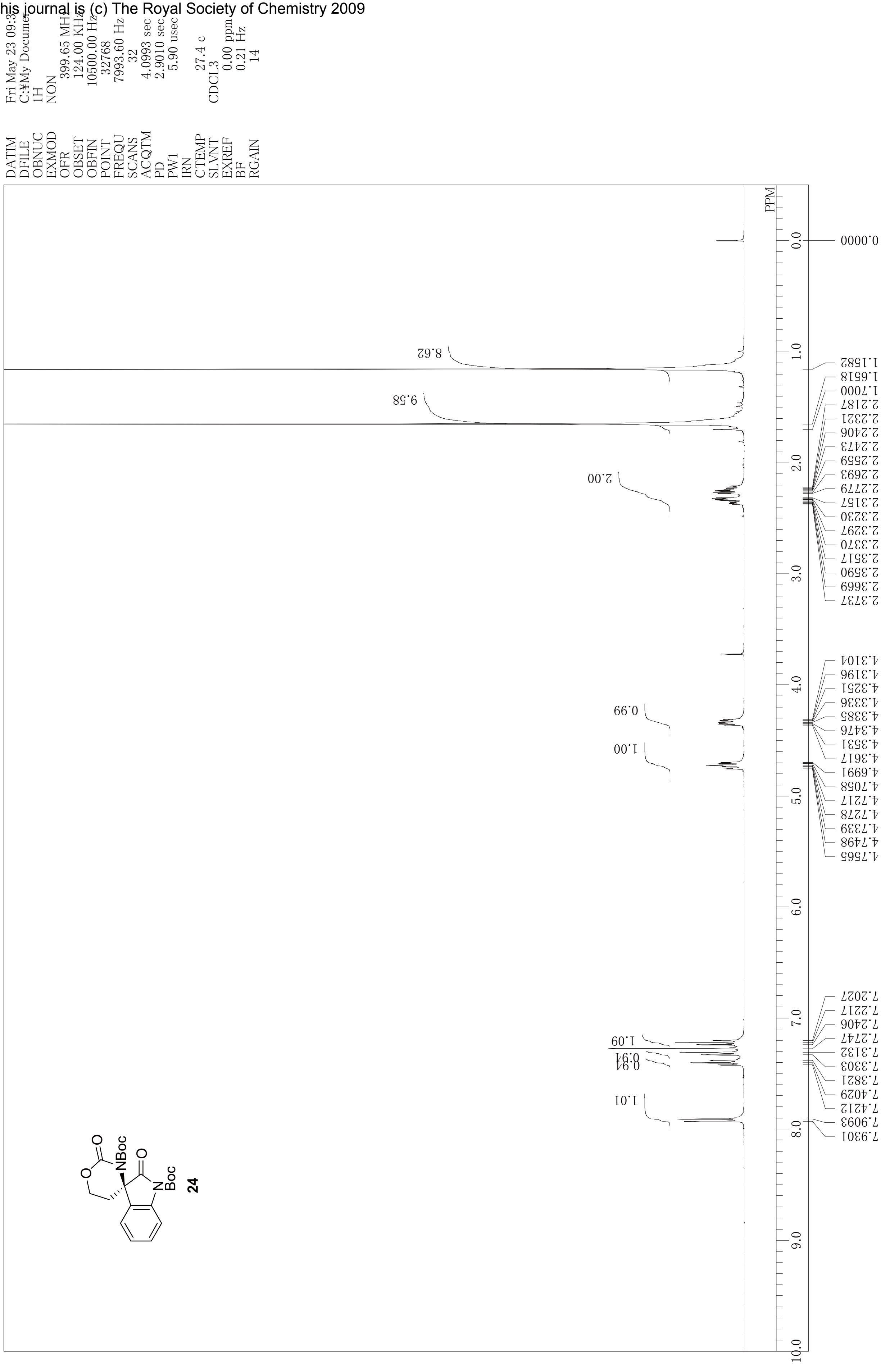
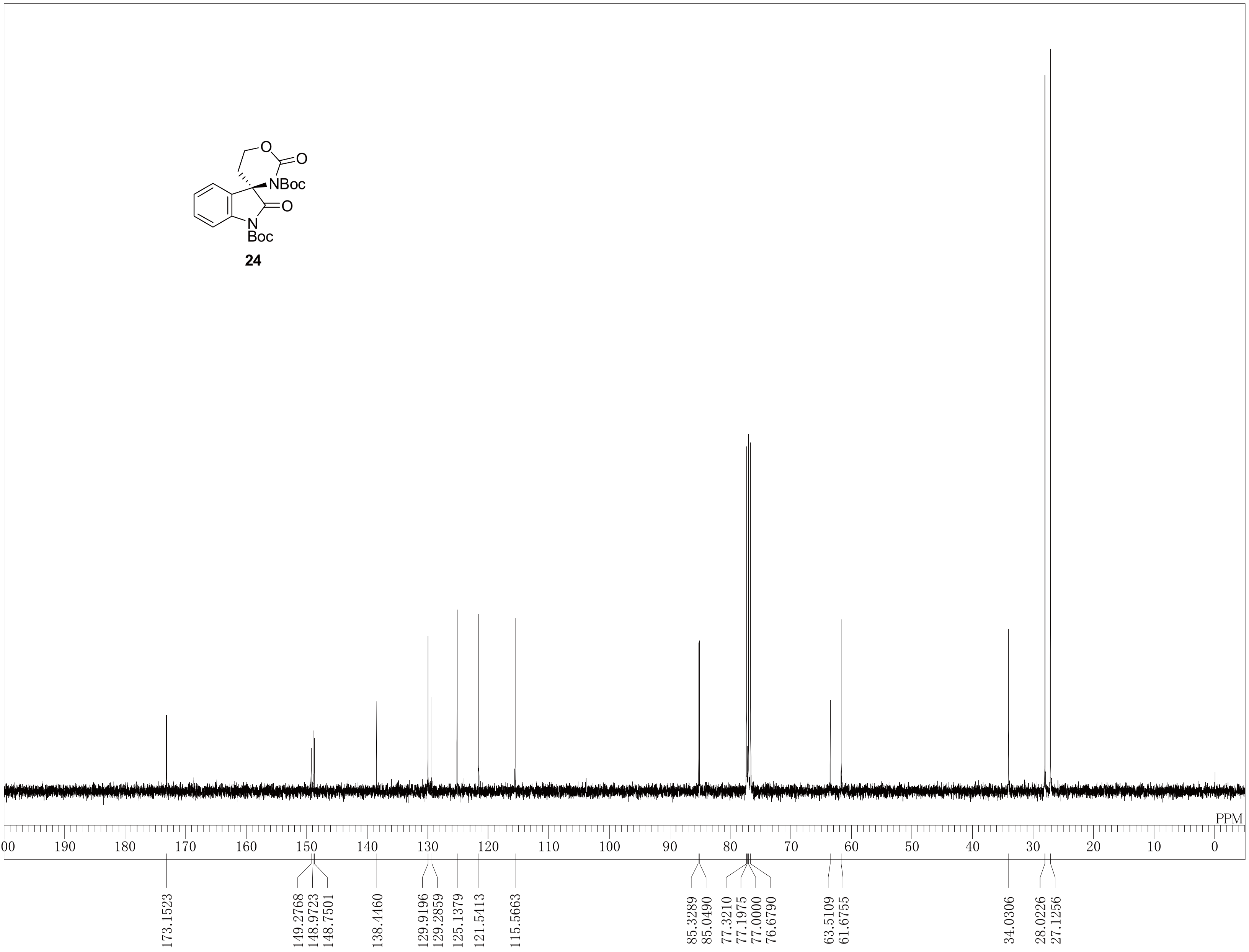


```
DATIM   Fri May 23 09:3
DFILE   C:¥My Documen
OBNUC   1H
EXMOD   NON
OFR     399.65 MHz
OBSET   124.00 KHz
OBFIN   10500.00 Hz
POINT   32768
FREQU   7993.60 Hz
SCANS   32
ACQTM   4.0993 sec
PD      2.9010 sec
PW1     5.90 usec
IRN
CTEMP   27.4 c
SLVNT   CDCL3
EXREF   0.00 ppm
BF      0.21 Hz
RGAIN   14
```

**24**

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1001-No1100¥No1081-No1090¥1086_07_6_7_spot_1_13C.als

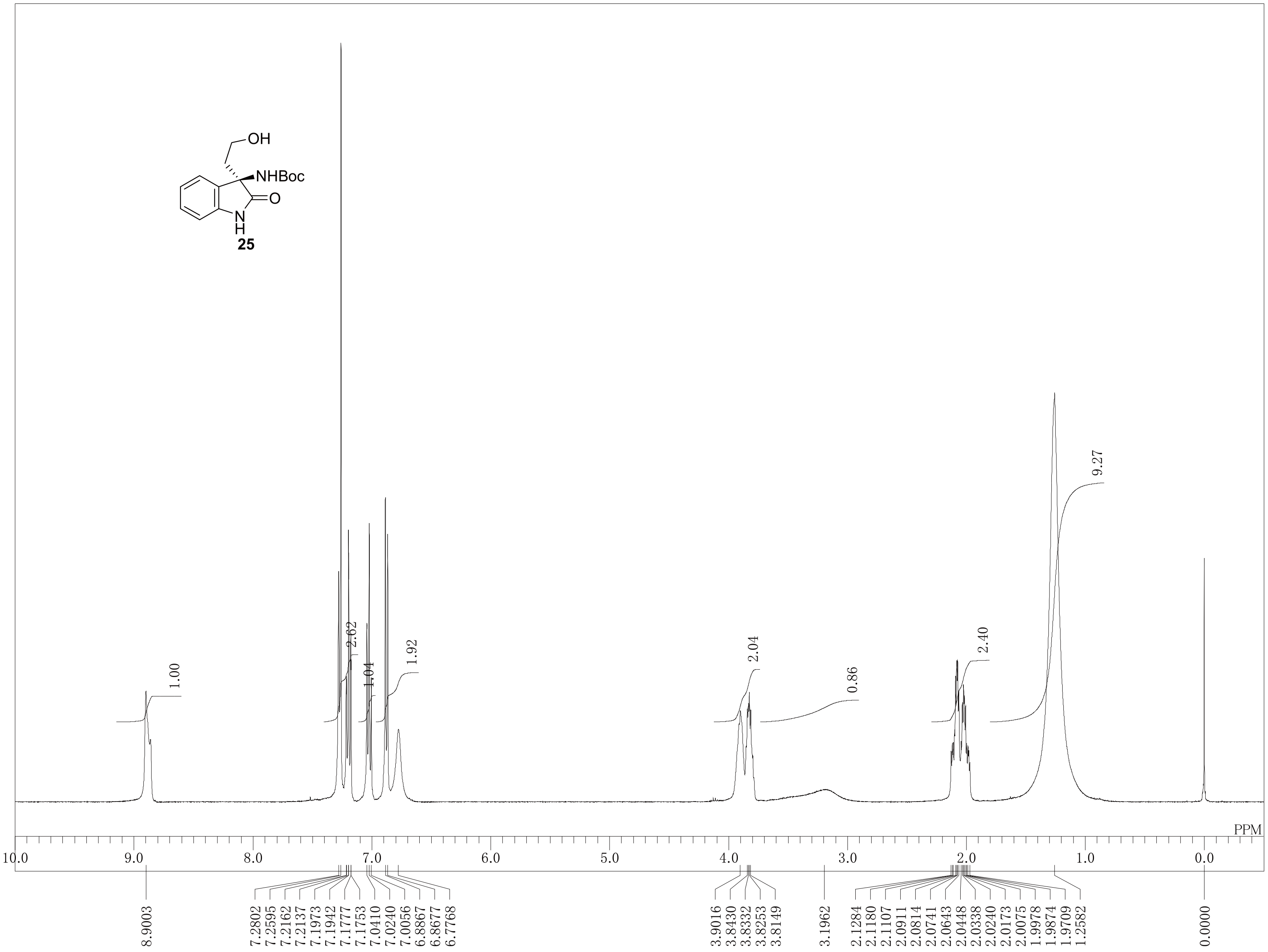


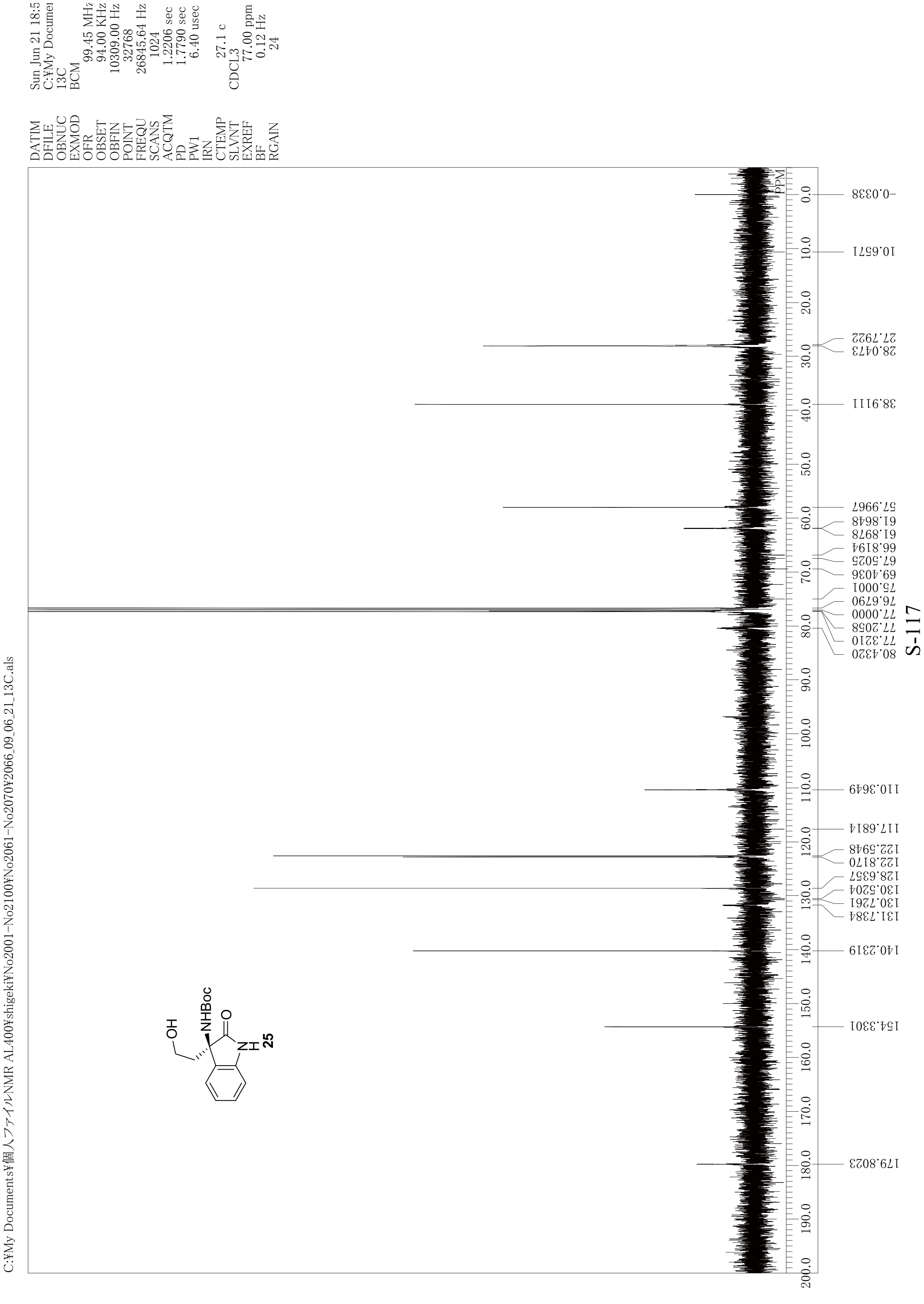
**24**

| | |
|---|---|
| DATIM | Thu Jun 07 23:2 |
| DFILE | C:¥My Documen |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 370 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.40 usec |
| IRN | |
| CTEMP | 27.0 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.42 Hz |
| RGAIN | 24 |

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1501-No1600¥No1531-No1540¥1534_08_06_04.als

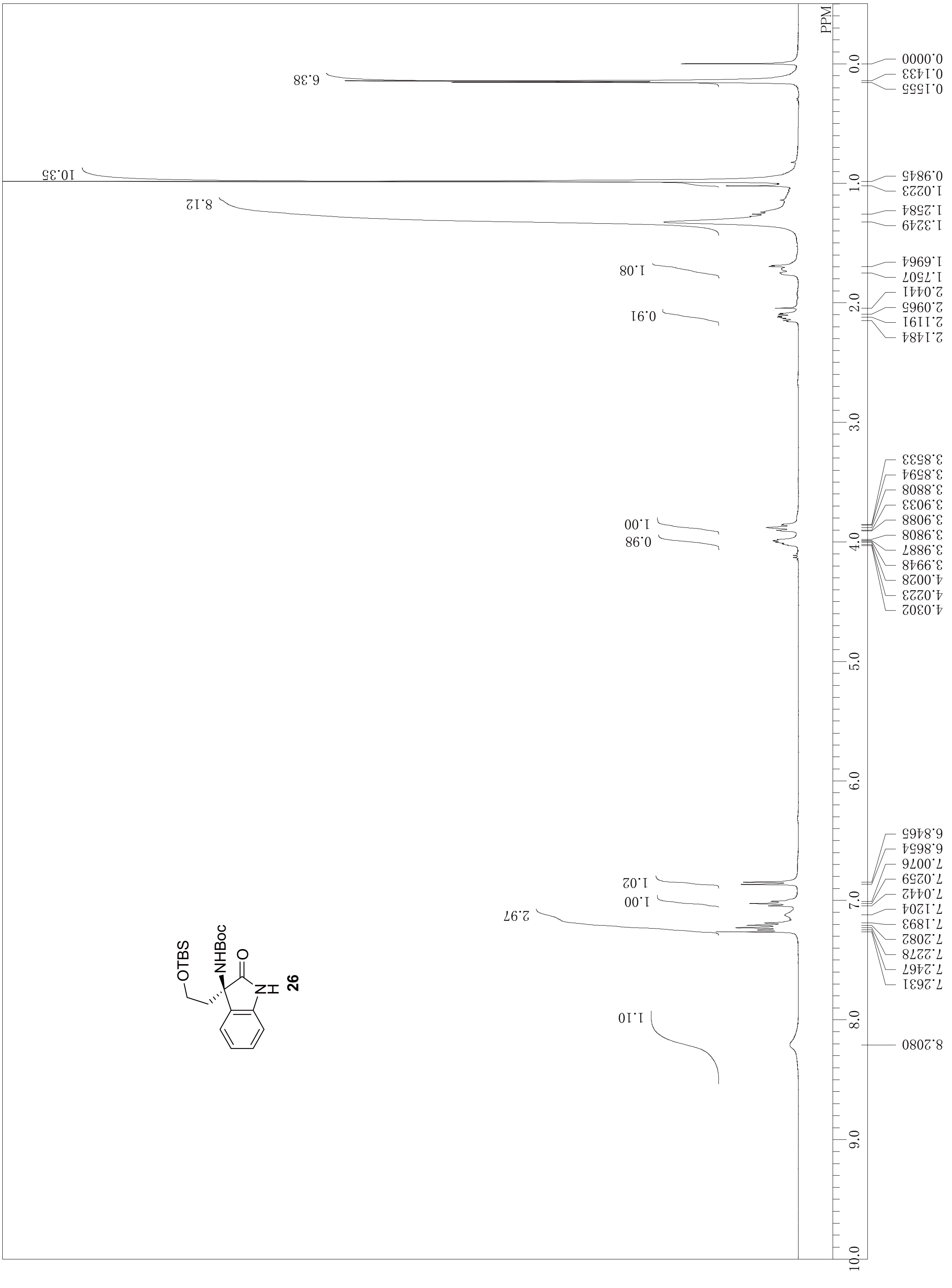
| | |
|---|---|
| DATIM | Wed Jun 04 15:4 |
| DFILE | C:¥My Documer |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 399.65 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10500.00 Hz |
| POINT | 32768 |
| FREQU | 7993.60 Hz |
| SCANS | 16 |
| ACQTM | 4.0993 sec |
| PD | 2.9010 sec |
| PW1 | 5.90 usec |
| IRN | |
| CTEMP | 27.4 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 14 |




DATIM Sun Jun 21 18:5
DFILE C:¥My Documer
OBNUC 13C
EXMOD BCM
OFR 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 1024
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.40 usec
IRN
CTEMP 27.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 24
PPM
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
200.0
-0.0338
10.6571
27.7922
28.0473
38.9111
57.9967
61.8648
61.8978
66.8194
67.5025
69.4036
75.0001
76.6790
77.0000
77.2058
77.3210
80.4320
110.3649
117.6814
122.5948
122.8170
128.6357
130.5204
130.7261
131.7384
140.2319
154.3301
179.8023
OH
NHBoc
O
N
H
25
C:¥My Documents¥個人ファイル¥NMR AL400¥shigeki¥No2001-No2100¥No2061-No2070¥2066_09_06_21_13C.als

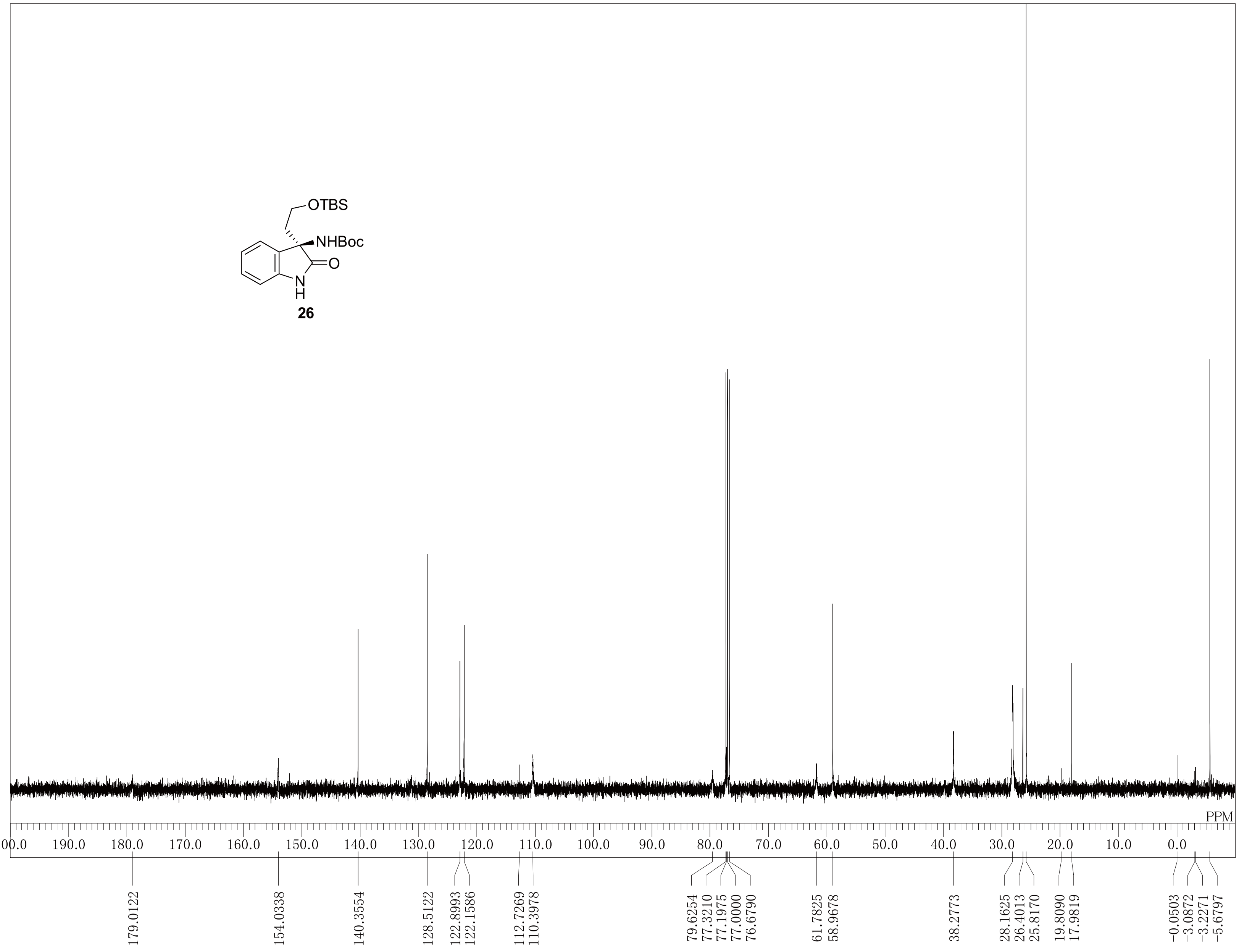
DATIM Wed Apr 09 20
DFILE C:¥My Docume
OBNUC 1H
EXMOD NON
OFR 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 32768
FREQU 7912.96 Hz
SCANS 16
ACQTM 4.1411 sec
PD 2.8590 sec
PW1 5.80 usec
IRN
CTEMP 25.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 13

C:¥My Documents¥個人ファイル¥NMR AL400¥shigeki¥No1401-No1500¥No1461-No1470¥1461_08_04_09.als



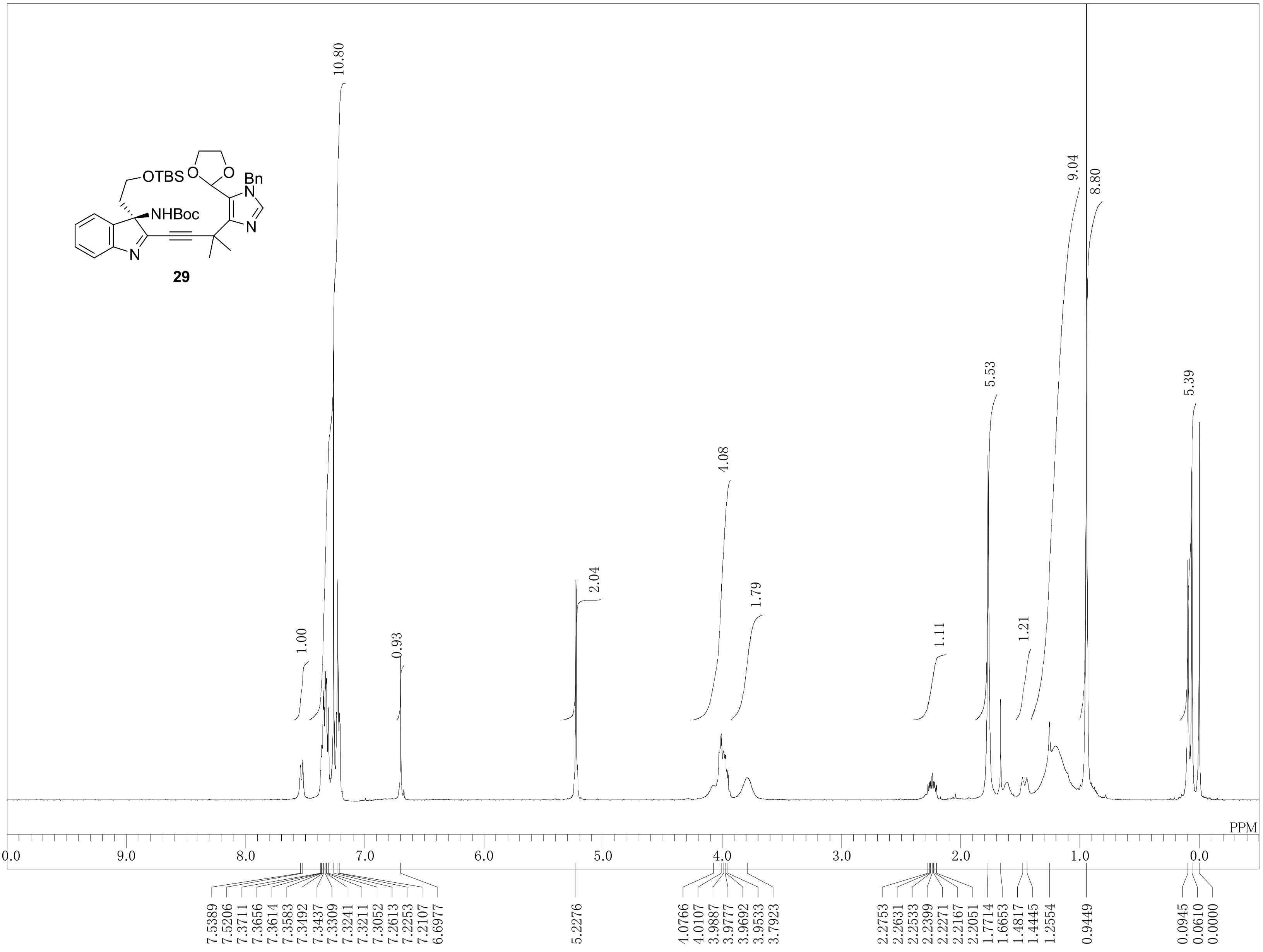
C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1401-No1500¥No1461-No1470¥1462_08_04_10_13C.als

| | |
|---|---|
| DATIM | Thu Apr 10 18:5 |
| DFILE | C:¥My Documer |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 502 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.40 usec |
| IRN | |
| CTEMP | 27.9 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 24 |



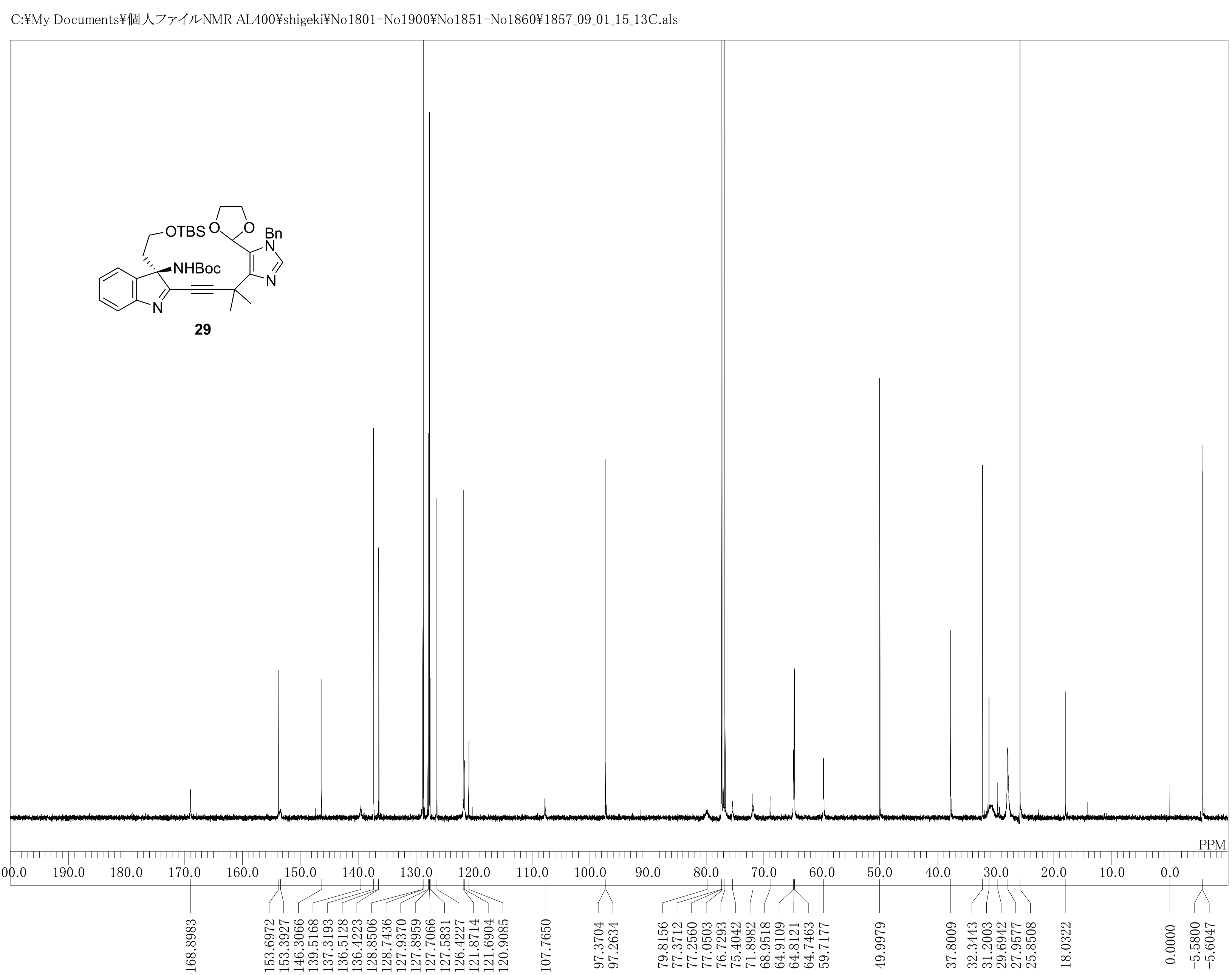
**26**

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1801-No1900¥No1851-No1860¥1857_09_01_15.als


**29**

DATIM Thu Jan 15 13:2
DFILE C:¥My Documer
OBNUC 1H
EXMOD NON
OFR 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 32768
FREQU 7912.96 Hz
SCANS 16
ACQTM 4.1411 sec
PD 2.8590 sec
PW1 5.80 usec
IRN
CTEMP 25.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.82 Hz
RGAIN 18

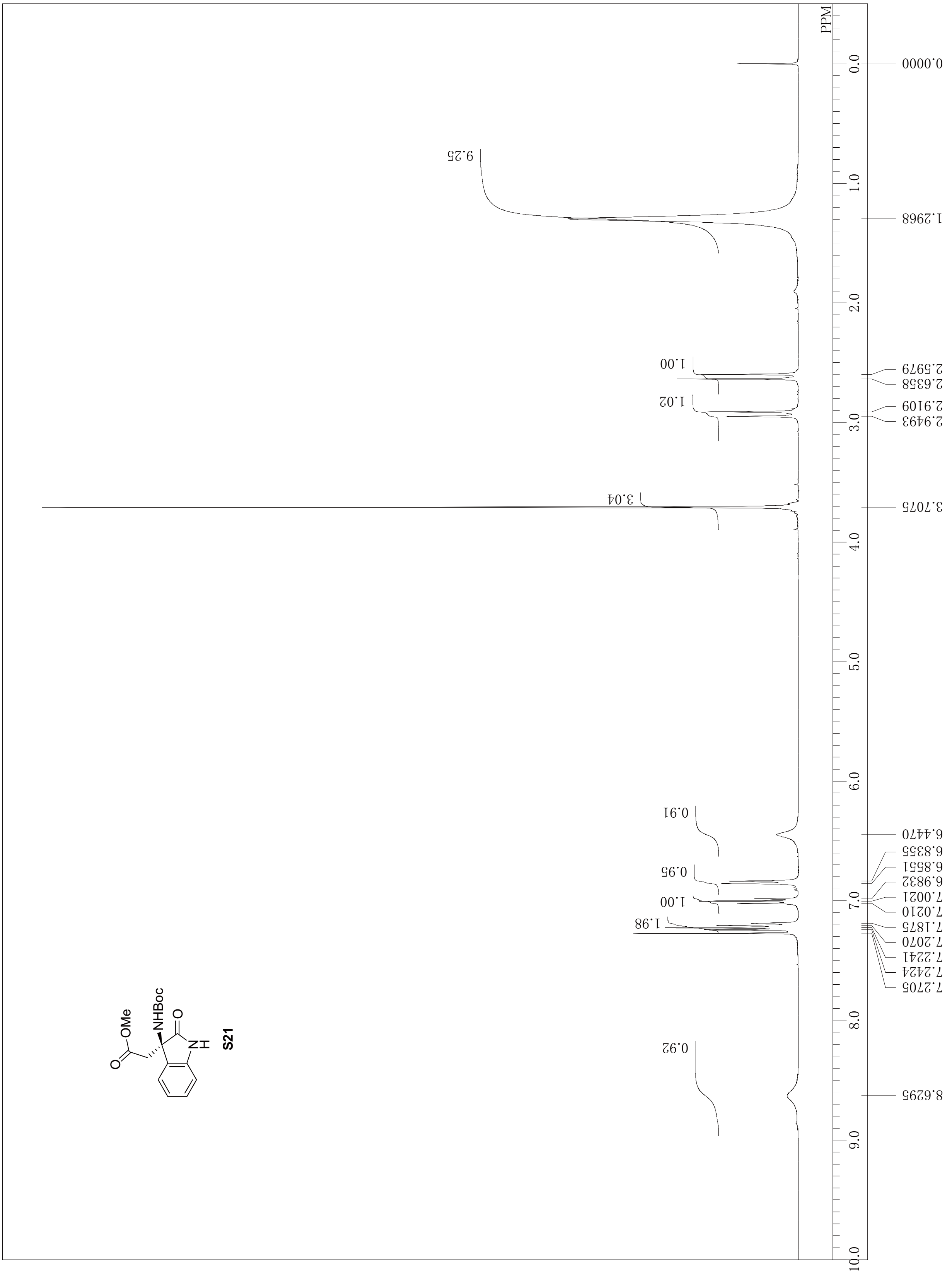
C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1801-No1900¥No1851-No1860¥1857_09_01_15_13C.als



**29**

DATIM Fri Jan 16 09:17
DFILE C:¥My Documer
OBNUC 13C
EXMOD BCM
OFR 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 12880
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.40 usec
IRN
CTEMP 24.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 24

| | |
|---|---|
| DATIM | Sat Jan 26 16:1 |
| DFILE | C:¥My Docume |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 395.75 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10277.00 Hz |
| POINT | 32768 |
| FREQU | 7912.96 Hz |
| SCANS | 16 |
| ACQTM | 4.1411 sec |
| PD | 2.8590 sec |
| PW1 | 5.80 usec |
| IRN | |
| CTEMP | 24.6 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 13 |



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DATIM   Sat Jan 26 16:4
DFILE   C:¥My Documen
OBNUC   13C
EXMOD   BCM
OFR       99.45 MHz
OBSET     94.00 KHz
OBFIN  10309.00 Hz
POINT     32768
FREQU  26845.64 Hz
SCANS       512
ACQTM    1.2206 sec
PD       1.7790 sec
PW1        6.40 usec
IRN
CTEMP      26.6 c
SLVNT   CDCL3
EXREF     77.00 ppm
BF         0.12 Hz
RGAIN        24
```
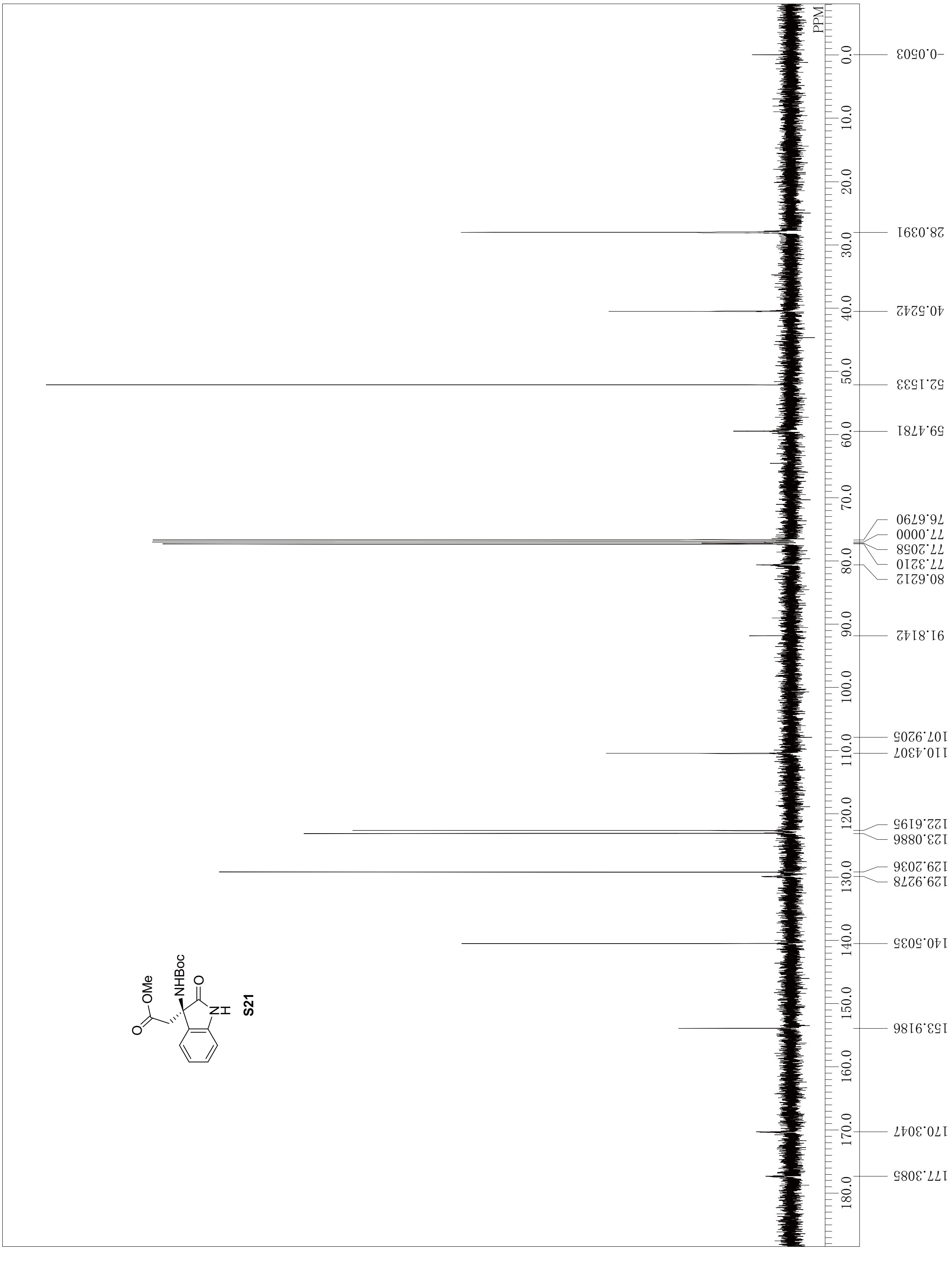
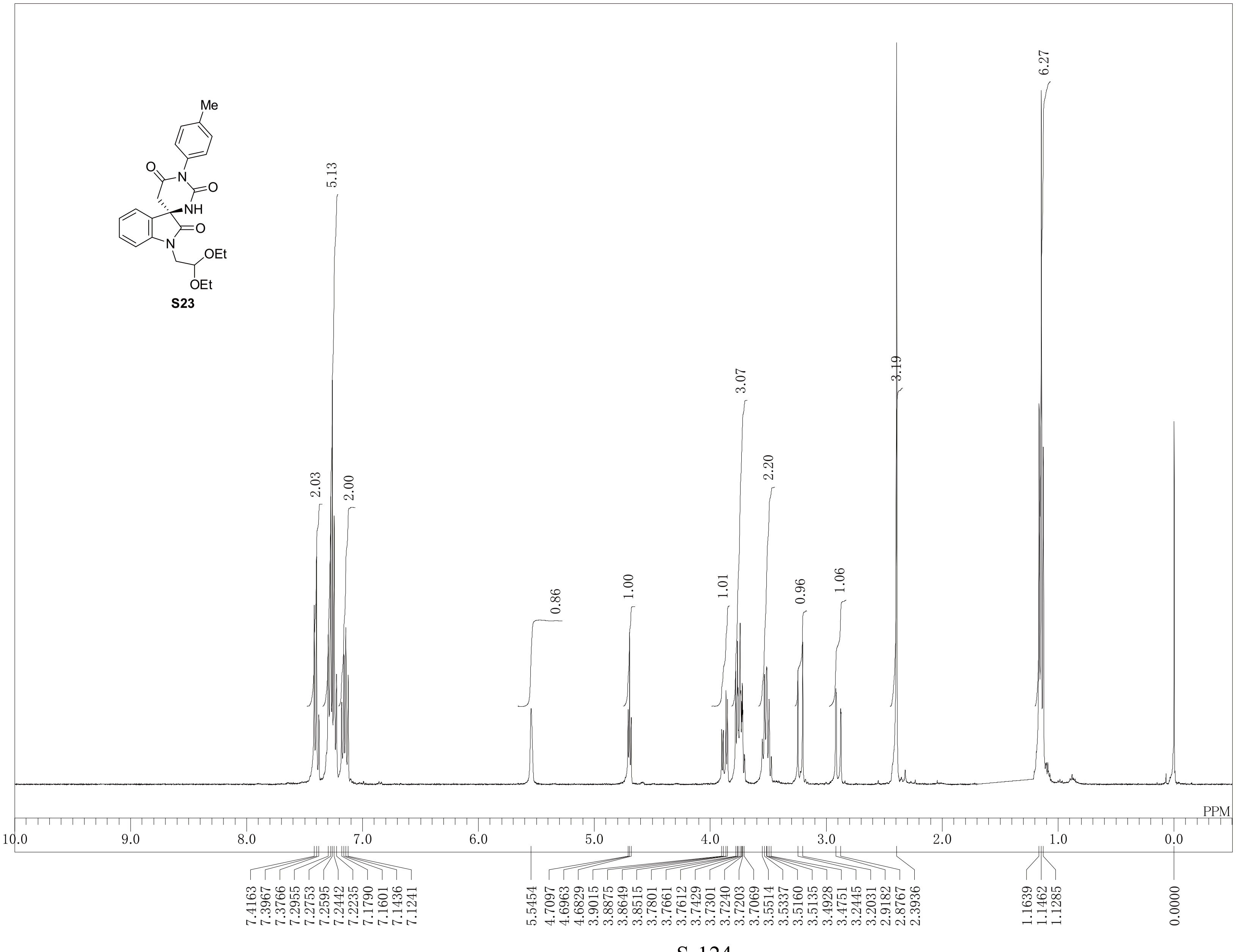
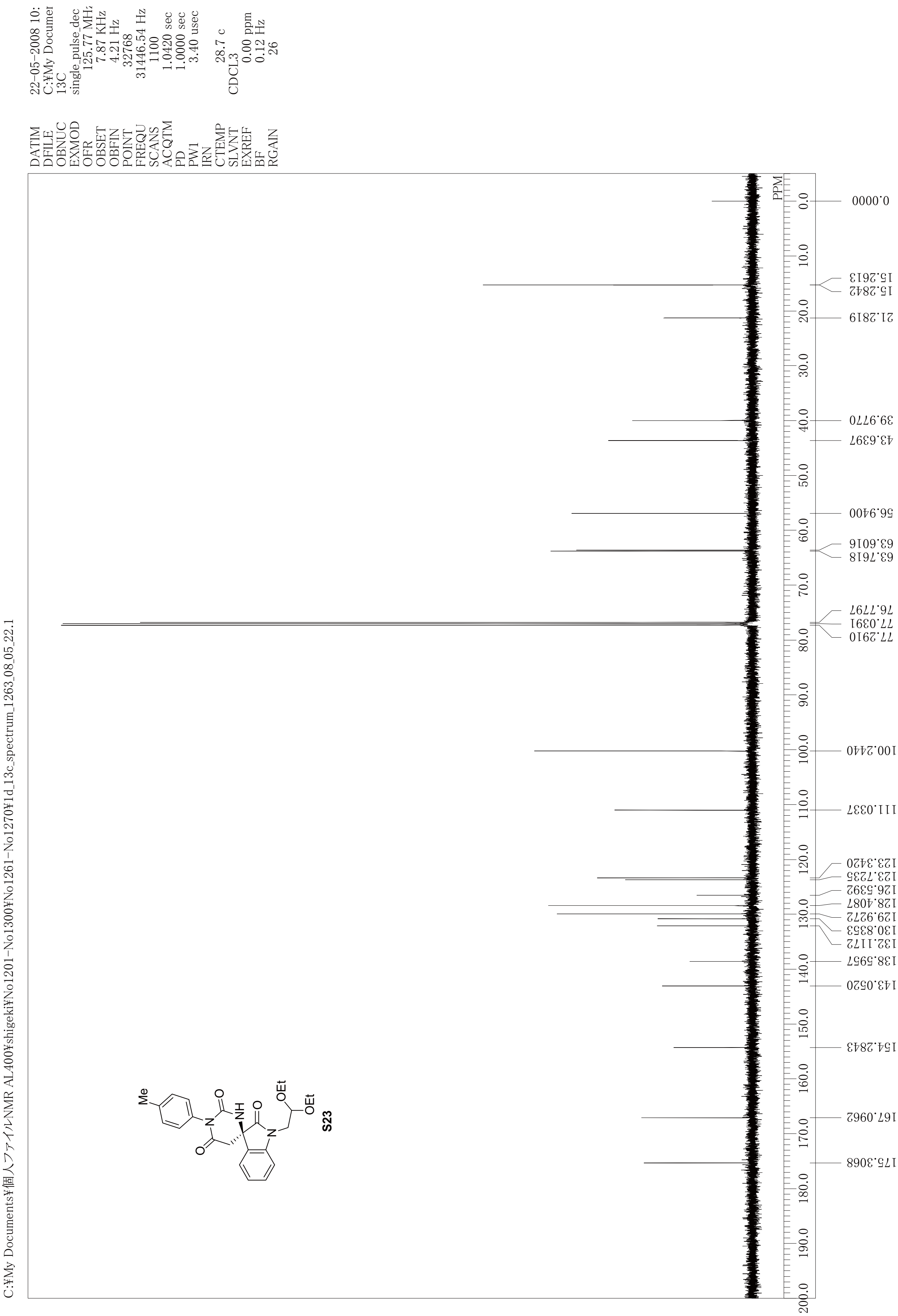



**S21**

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1901-No2000¥No1921-No1930¥1924_09_02_20.als

| | |
|---|---|
| DATIM | Sat Feb 21 18:0 |
| DFILE | C:¥My Documer |
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 395.75 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10277.00 Hz |
| POINT | 32768 |
| FREQU | 7912.96 Hz |
| SCANS | 16 |
| ACQTM | 4.1411 sec |
| PD | 2.8590 sec |
| PW1 | 5.80 usec |
| IRN | |
| CTEMP | 24.1 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |
| BF | 0.12 Hz |
| RGAIN | 17 |




C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1201-No1300¥No1261-No1270¥1d_13c_spectrum_1263_08_05_22.1
DATIM 22-05-2008 10:
DFILE C:¥My Documer
OBNUC 13C
EXMOD single_pulse_dec
OFR 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 32768
FREQU 31446.54 Hz
SCANS 1100
ACQTM 1.0420 sec
PD 1.0000 sec
PW1 3.40 usec
IRN
CTEMP 28.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 26
PPM
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
200.0
0.0000
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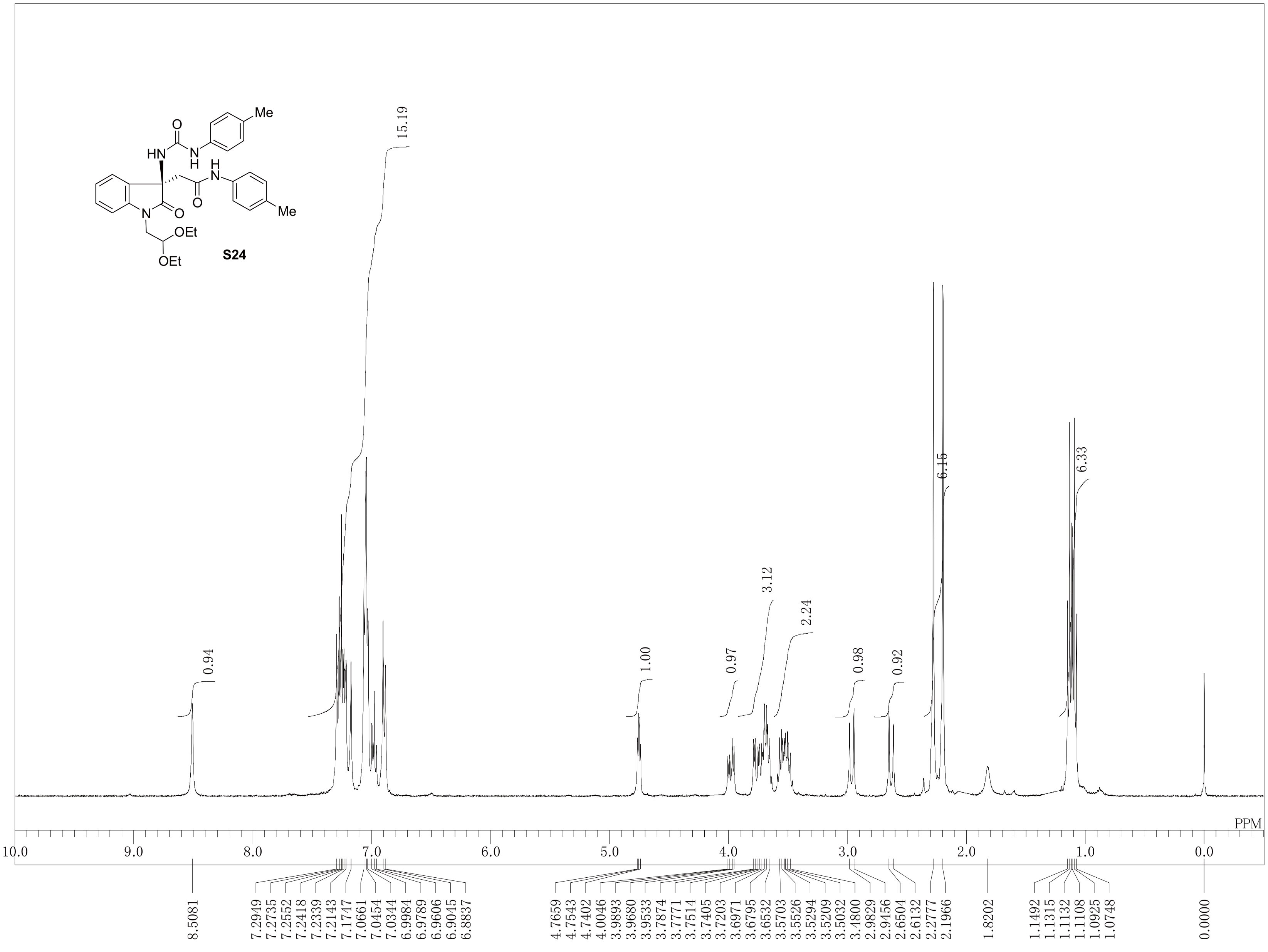
21.2819
39.9770
43.6397
56.9400
63.6016
63.7618
76.7797
77.0391
77.2910
100.2440
111.0337
123.3420
123.7235
126.5392
128.4087
129.9272
130.8353
132.1172
138.5957
143.0520
154.2843
167.0962
175.3068
Me
O
N
O
NH
O
N
OEt
OEt
O
S23

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1201-No1300¥No1271-No1280¥1275_07_11_06.als


**S24**

DATIM Tue Nov 06 23:
DFILE C:¥My Documer
OBNUC 1H
EXMOD NON
OFR 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 32768
FREQU 7912.96 Hz
SCANS 8
ACQTM 4.1411 sec
PD 2.8590 sec
PW1 5.80 usec
IRN
CTEMP 25.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.03 Hz
RGAIN 13

C:¥My Documents¥個人ファイルNMR AL400¥shigeki¥No1201-No1300¥No1271-No1280¥1275_07_11_06_13C.als

| | |
|---|---|
| DATIM | Tue Nov 06 23:3 |
| DFILE | C:¥My Document |
| OBNUC | 13C |
| EXMOD | BCM |
| OFR | 99.45 MHz |
| OBSET | 94.00 KHz |
| OBFIN | 10309.00 Hz |
| POINT | 32768 |
| FREQU | 26845.64 Hz |
| SCANS | 446 |
| ACQTM | 1.2206 sec |
| PD | 1.7790 sec |
| PW1 | 6.40 usec |
| IRN | |
| CTEMP | 25.9 c |
| SLVNT | CDCL3 |
| EXREF | 77.00 ppm |
| BF | 0.03 Hz |
| RGAIN | 24 |