Supporting Information for "Asymmetric Synthesis of Neolignans (−)-*epi*-Conocarpan and (+)-Conocarpan via Rh(II)-Catalyzed C–H Insertion Process and Revision of the Absolute Configuration of (−)-*epi*-Conocarpan"

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Experimental Section

General. Melting points were determined on a capillary melting point apparatus and are uncorrected. Optical rotations were measured on a digital polarimeter at the sodium D line (589 nm). IR spectra were recorded on a FT/IR spectrometer and absorbance bands are reported in wavenumber (cm^{-1}). ^1H NMR spectra were recorded on a 270 MHz or a 400 MHz spectrometer. Chemical shifts are reported relative to internal standard (tetramethylsilane at 0.00 ppm, $CDCl_3$ at 7.26 ppm, or CD_3OD at 3.31 ppm). Data are presented as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant and integration. ^{13}C NMR spectra were recorded on a 67.5 MHz, a 100 MHz or a 125 MHz spectrometer. The following internal references were used ($CDCl_3$ at 77.0 ppm or CD_3OD at 49.0 ppm). Column chromatography was carried out on silica gel 60 N (63–210 mesh). Analytical thin layer chromatography (TLC) was carried out on silica gel 60 F_{254} plates. Visualization was accomplished with UV light, and anisaldehyde or phosphomolybdic acid stain solution followed by heating. Analytical high performance liquid chromatography (HPLC) was performed on an intelligent HPLC pump with intelligent UV/VIS detector. Detection was performed at 254 nm. Chiralcel OD-H, OJ-H, Chiralpak AD-H and IA columns (0.46 cm × 25 cm) were used.

All non-aqueous reactions were carried out in flame-dried glassware under Ar atmosphere unless otherwise noted. Reagents and solvents were purified by standard means. Dehydrated CH_2Cl_2 and THF were purchased from a commercial source. 4 Å molecular sieves were used after dried (150 °C, 1 mmHg, 12 h). Methyl 2-(5-bromo-2-hydroxyphenyl)acetate (**11**)[1], [(4-bromomethyl)phenoxy]triisopropylsilane (**12**)[2], 3,3-diethylpentanoic acid (**14**)[3] and (*S*)-4-benzyloxazolidin-2-one,[4] were prepared according to literature procedures.

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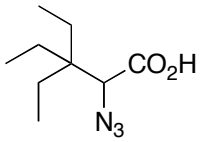
(1) Greenspan, P. D.; Fujimoto, R. A.; Marshall, P. J.; Raychaudhuri, A.; Lipson, K. E.; Zhou, H.; Doti, R. A.; Coppa, D. E.; Zhu, L.; Pelletier, R.; Uziel-Fusi, S.; Jackson, R. H.; Chin, M. H.; Kotyuk, B. L.; Fitt, J. J. *J. Med. Chem.* **1999**, *42*, 164–172.
(2) Ohshima, T.; Gnanadesikan, V.; Shibuguchi, T.; Fukuta, Y.; Nemoto, T.; Shibasaki, M. *J. Am. Chem. Soc.* **2003**, *125*, 11206–11207.
(3) Rabjohn, N.; Phillips, L. V.; Stapp, P. R. *J. Chem. Eng. Data* **1962**, *7*, 543–544.
(4) Gage, J. R.; Evans, D. A. *Org. Synth.* **1990**, *68*, 77–82.

I. Preparation of Rh_2(*S*-PTTEA)$_4$ (3b)

2-Azido-3,3-diethylpentanoic acid (15)

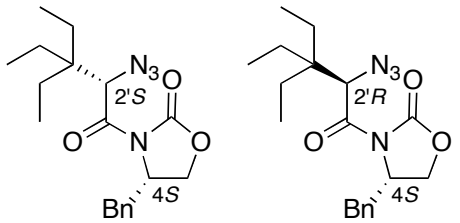


15

Phosphorus trichloride (0.50 mL, 5.67 mmol) was added to a mixture of 3,3-diethylpentanoic acid (**14**)[3] (15.0 g, 94.8 mmol) and bromine (5.58 mL, 114 mmol). After stirring at 50 °C for 2 h, the reaction mixture was heated at 100 °C for 1 h. The reaction mixture was evaporated in vacuo to furnish the crude product (24.5 g), which was used without further purification.

NaN_3 (18.5 g, 284 mmol) was added to a solution of the crude product in DMSO (75 mL), and the whole was heated at 90 °C for 2 h. After cooling, the reaction mixture was poured into water and acidified with 10% aqueous HCl. The solution was extracted with EtOAc (3 × 150 mL) and washed with brine (2 × 70 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product (18.2 g), which was purified by column chromatography (silica gel 150 g, 10:1→5:1 hexane/EtOAc) to provide carboxylic acid **15** (16.1 g, 85%) as a colorless oil: R_f 0.58 (5:1 benzene/Et_2O); IR (film) ν 2971, 2106, 1711, 1458, 1416 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.86 (t, J = 7.3 Hz, 9H), 1.40–1.55 (m, 6H), 4.03 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 8.0 (CH_3), 26.3 (CH_2), 43.1 (C), 68.5 (CH), 174.7 (C); HRMS (FAB) calcd for $C_9H_{17}N_3O_2Na$ (M^++Na) 222.1218, found 222.1212.

(4*S*,2′*S*)-2′-Azido-3′,3′-diethylpentanoyl-4-benzyloxazolidin-2-one (16) and (4*S*,2′*R*)-2′-azido-3′,3′-diethylpentanoyl-4-benzyloxazolidin-2-one (17)



16 **17**

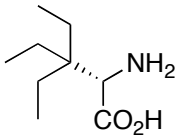
Oxalyl chloride (4.3 mL, 50.3 mmol) and DMF (0.1 mL, 1.3 mmol) were added to a solution of carboxylic acid **15** (6.68 g, 33.5 mmol) in CH_2Cl_2 (45 mL) at 0 °C. After stirring at 23 °C for 3 h, the reaction mixture was evaporated in vacuo to furnish the crude product (7.5 g), which was used without further purification.

n-BuLi (1.59 M solution in hexane, 21.1 mL, 33.5 mmol) was added to a solution of (*S*)-4-benzyloxazolidin-2-one[4] (5.94 g, 33.5 mmol) in THF (45 mL) at −78 °C, and the mixture was stirred at −78 °C for 30 min. A solution of the crude acid chloride in THF (15 mL) was added to the mixture at −78 °C. After stirring at −78 °C for 1 h, the mixture was poured into a two-layer mixture of Et_2O (60 mL) and 5% aqueous HCl (60 mL) at 0 °C. The aqueous layer was separated and extracted with EtOAc (120 mL). The combined organic layers were washed with H_2O (40 mL), saturated aqueous $NaHCO_3$ (40 mL) and brine (2 × 40 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product (11.4 g), which was purified by column chromatography (silica gel 300 g, 15:1→10:1 hexane/EtOAc) to provide less polar isomer **17** (5.18 g, 43%) as colorless oil and more polar isomer **16** (5.30 g, 44%) as a white solid. **16**: R_f 0.50 (2:1 hexane/EtOAc); mp

153.0–153.5 ºC (hexane/EtOAc); $[\alpha]_D^{24}$ +32.2 (*c* 1.10, $CHCl_3$); IR (film) ν 2968, 2101, 1780, 1704, 1455, 1388 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.3 Hz, 9H), 1.52 (q, *J* = 7.3 Hz, 6H), 2.87 (dd, *J* = 9.5, 13.2 Hz, 1H), 3.34 (dd, *J* = 3.2, 13.2 Hz, 1H), 4.17–4.25 (m, 2H), 4.69 (ddd, *J* = 3.2, 9.5, 12.2 Hz, 1H), 5.57 (s, 1H), 7.23–7.38 (m, 5H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 8.1 (CH_3), 26.1 (CH_2), 37.6 (CH_2), 44.0 (C), 55.9 (CH), 63.6 (CH), 66.1 (CH_2), 127.5 (CH), 129.0 (CH), 129.4 (CH), 134.8 (C), 153.1 (C), 169.4 (C); HRMS (FAB) calcd for $C_{19}H_{26}N_4O_3Na$ (M^++Na) 381.1903, found 381.1882. **17**: R_f 0.56 (2:1 hexane/EtOAc); $[\alpha]_D^{24}$ +52.1 (*c* 1.15, $CHCl_3$); IR (film) ν 2971, 2103, 1782, 1705, 1456, 1389 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.91 (t, *J* = 8.1 Hz, 9H), 1.45–1.66 (m, 6H), 2.63 (dd, *J* = 10.5, 13.2 Hz, 1H), 3.45 (dd, *J* = 3.5, 13.2 Hz, 1H), 4.15–4.75 (m, 2H), 4.79 (ddd, *J* = 3.5, 10.5, 14.6 Hz, 1H), 5.56 (s, 1H), 7.24–7.39 (m, 5H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 8.2 (CH_3), 26.2 (CH_2), 38.1 (CH_2), 44.5 (C), 55.6 (CH), 63.5 (CH), 66.3 (CH_2), 127.5 (CH), 129.0 (CH), 129.3 (CH), 135.0 (C), 153.3 (C), 169.5 (C); HRMS (FAB) calcd for $C_{19}H_{26}N_4O_3Na$ (M^++Na) 381.1910, found 381.1882.

The absolute configuration of **16** was established to be (4*S*,2′*S*) by a single-crystal X-ray analysis. Suitable crystals of **16** for X-ray crystallographic analysis were obtained by recrystallization from hexane/EtOAc.

(*S*)-Triethylalanine (18)

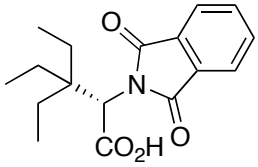


18

A 35% aqueous solution of H_2O_2 (5.6 mL, 58.0 mmol) and $LiOH{\cdot}H_2O$ (1.22 g, 29.0 mmol) were added to a solution of **16** (5.20 g, 14.5 mmol) in THF/H_2O (3:1, 150 mL) at 0 °C. After stirring at 0 °C for 3 h, the reaction was quenched by addition of 3 M aqueous Na_2SO_3 (20 mL) and saturated aqueous $NaHCO_3$ (200 mL). The mixture was extracted with CH_2Cl_2 (3 × 50 mL), and the water layer was acidified with 10% aqueous HCl. The solution was extracted with EtOAc (3 × 100 mL) and washed with brine (2 × 50 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product (2.32 g), which was used without further purification.

10% Pd/C (120 mg) was added to a solution of the crude product in AcOH/H_2O (2:1, 12 mL), and the resulting mixture was stirred vigorously under 1 atm of hydrogen at 23 °C for 20 h. The catalyst was filtered through a Celite pad, and the filtrate was evaporated in vacuo to furnish the crude product (2.4 g). The residue was dissolved in MeOH/H_2O (3:1, 20 mL) at 60 °C. The white solid formed at 23 °C after standing for 48 h, and were collected by suction, washed with ice-cold MeOH/H_2O (5:1, 6 mL) and dried in vacuo to give **18** (1.76 g, 70%): R_f 0.50 (19:1 EtOH/15% aqueous NH_3); mp >250 ºC (MeOH/H_2O); $[\alpha]_D^{23}$ +12.2 (*c* 0.1, MeOH); IR (KBr) ν 3527, 3120, 2967, 1638, 1603, 1526 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 0.89 (t, *J* = 7.3 Hz, 9H), 1.52 (dq, *J* = 7.3, 14.6 Hz, 6H), 3.39 (s, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 8.4 (CH_3), 27.0 (CH_2), 41.5 (C), 61.1 (CH), 173.4 (C); HRMS (ESI) calcd for $C_9H_{20}NO_2$ (M^++H) 174.1494, found 174.1485.

N-Phthaloyl-(S)-triethylalanine (19)

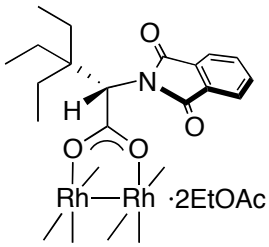


19

Triethylamine (173 mg, 1.71 mmol) was added to the mixture of (*S*)-**18** (740 mg, 4.27 mmol), phthalic anhydride (633 mg, 4.27 mmol) and toluene (40 mL). The mixture was heated to reflux, while the solvent was distilled off at a rate such that *ca*. 6 mL of the solvent was removed per hour. After heating the mixture for 2.5 h, the mixture was cooled to 23 °C. 5% aqueous HCl (10 mL) was added and resulting solution was extracted with EtOAc (2 × 30 mL). The combined organic layers were washed with brine (2 × 15 mL) and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product (1.33 g), which was purified by column chromatography (silica gel 60 g, 100:1→50:1 $CHCl_3$/MeOH) to provide **19** (1.19 g) as a white solid. The solid was dissolved in hexane/EtOAc (5:1, 12 mL) at 60 °C. Colorless needles formed at 23 °C after standing overnight, and were collected by suction, washed with ice-cold hexane/EtOAc (5:1, 4 mL) and dried in vacuo to give **19** (1.06 g, 82%): R_f 0.43 (10:1 $CHCl_3$/MeOH); mp 131.0–131.5 ºC (hexane/EtOAc); $[\alpha]_D^{22}$ −12.5 (*c* 1.01, EtOH); IR (KBr) ν 2967, 1719 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.89 (t, J = 7.3 Hz, 9H), 1.57 (dq, J = 7.3, 14.6 Hz, 3H), 1.75 (dq, J = 7.3, 14.6 Hz, 3H), 5.03 (s, 1H), 7.70–7.76 (m, 2H), 7.83–7.89 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 8.4 (CH_3), 27.4 (CH_2), 43.7 (C), 57.0 (CH), 123.5 (CH), 131.6 (C), 134.2 (CH), 168.3 (C), 174.8 (C); HRMS (FAB) calcd for $C_{17}H_{22}NO_4$ (M^++H) 304.1549, found 304.1577. Anal. Calcd for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98; N, 4.62. Found: C, 67.28; H, 7.01; N, 4.55.

The enantiopurity of **19** was determined to be >99% ee by comparison of HPLC retention time with the racemic sample after conversion to the corresponding methyl ester obtained by the treatment of **19** with diazomethane in ether [Chiralcel OJ-H (9:1 hexane/*i*-PrOH, 1.0 mL/min): t_R (major) = 8.3 min for (*S*)-**19**, t_R (minor) = 11.6 min for (*R*)-**19**.]

Dirhodium(II) tetrakis[N-phthaloyl-(S)-triethylalaninate] (3b)



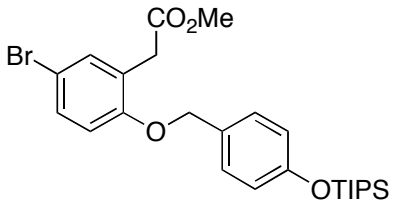
3b

A mixture of $Rh_2(OAc)_4$·2MeOH (202 mg, 0.40 mmol) and **19** (606 mg, 2.0 mmol) in chlorobenzene (30 mL) was heated at reflux with vigorous stirring, while the solvent was distilled off at a rate such that *ca*. 3 mL of the solvent was removed per hour. After 3 h, the remaining solvent was removed in vacuo, and the residue was dissolved in EtOAc (30 mL). The resulting solution was washed with saturated aqueous $NaHCO_3$ (2 × 5 mL) and brine (2 × 5 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished a green solid (798 mg), which was purified by column chromatography (silica gel 40 g, 2:1 hexane/EtOAc) to provide a green solid (680 mg). The solid was dissolved in EtOAc/hexane (3:2, 25 mL) at 60 °C. Green needles formed at 23 °C after standing overnight, and were collected by suction, washed with ice-cold hexane/EtOAc (3:1, 4 mL) and dried in vacuo to give **3b** (560 mg, 88%): R_f 0.53 (1:1 hexane/EtOAc); mp >280 ºC (hexane/EtOAc);

$[\alpha]_D^{22}$ +35.3 (*c* 0.052, $CDCl_3$); IR (KBr) ν 3432, 1967, 1884, 1780, 1721, 1607, 1381cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.85 (t, *J* = 7.3 Hz, 36H), 1.22 (t, *J* = 7.3 Hz, 6H), 1.45–1.71 (m, 24H), 2.02 (s, 6H), 4.09 (q, *J* = 7.3 Hz, 4H), 5.15 (s, 4H), 7.60–7.73 (m, 16H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 8.6 (CH_3), 14.1 (CH_3), 21.0 (CH_3), 27.1 (CH_2), 43.3 (C), 58.9 (CH), 60.6 (CH_2), 122.8 (CH), 123.5 (CH), 132.1 (C), 133.3 (CH), 133.7 (CH), 167.5 (C), 168.7 (C), 171.9 (C), 187.7 (C); HRMS (FAB) calcd for $C_{68}H_{80}N_4O_{16}Rh_2$ (M^+) 1414.3679, found 1414.3680. Anal. Calcd for $C_{68}H_{80}N_4O_{16}Rh_2$·2EtOAc: C, 57.36; H, 6.08; N, 3.52. Found: C, 57.14; H, 6.03; N, 3.78.
The enantiopurity of the methyl ester of **19** recovered from aqueous $NaHCO_3$ layers was determined to be >99% ee by HPLC, indicating that no racemization occurred during the ligand exchange reaction.

II. Asymmetric Synthesis of (−)-*epi*-Conocarpan (2) and (+)-Conocarpan (1)

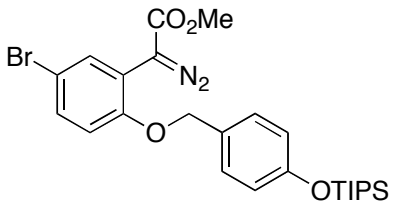
Methyl 2-[5-bromo-2-(4-triisopropylsilyloxybenzyloxy)phenyl]acetate (13)



13

A solution of [(4-bromomethyl)phenoxy]triisopropylsilane (**12**)[2] (1.10 g, 3.20 mmol) in THF (1.5 mL) was added to a suspension of methyl 2-(5-bromo-2-hydroxyphenyl)acetate (**11**)[1] (654 mg, 2.67 mmol) and K_2CO_3 (922 mg, 6.67 mmol) in THF (4 mL) at 0 °C. After stirring at 23 °C for 30 h, the reaction was quenched with water (10 mL). The mixture was extracted with EtOAc (50 mL), and the combined organic layer was washed with brine (2 × 15 mL) and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product (1.5 g), which was purified by column chromatography (silica gel 70 g, 40:1 hexane/EtOAc) to provide ester **13** (925 mg, 68%) as a white solid: R_f = 0.63 (4:1 hexane/EtOAc); mp 77.5–78.0 °C (hexane/EtOAc); IR (KBr) ν 1733 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (d, *J* = 7.3 Hz, 18H), 1.21–1.30 (m, 3H), 3.60 (s, 2H), 3.62 (s, 3H), 4.96 (s, 2H), 6.79 (d, *J* = 8.3 Hz, 2H), 6.86–6.88 (m, 2H), 7.21–7.23 (m, 2H), 7.31–7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.7 (CH), 18.0 (CH_3), 35.8 (CH_2), 51.9 (CH_3), 70.2 (CH_2), 112.7 (C), 113.5 (CH), 119.8 (CH), 125.5 (C), 128.5 (CH), 128.7 (C), 131.0 (CH), 133.5 (CH), 155.7 (C), 155.8 (C), 171.5 (C); HRMS (EI) calcd for $C_{25}H_{35}O_4SiBr$ (M^+) 506.1487, found 506.1478. Anal. Calcd for $C_{25}H_{35}O_4SiBr$: C, 59.16; H, 6.95; Br, 15.74. Found: C, 59.37; H, 6.92; Br, 15.81.

Methyl 2-diazo-2-[5-bromo-2-(4-triisopropylsilyloxybenzyloxy)phenyl]acetate (9a)



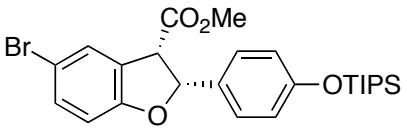
9a

A solution of ester **13** (1.30 g, 2.56 mmol) in THF (4 mL) was added to lithium bis(trimethylsilyl)amide (0.29 M in THF, 13.2 mL, 3.84 mmol) at −78 °C. After stirring at −78 °C for 30 min, 2,2,2-trifluoroethyltrifluoroacetate (0.55 mL, 4.10 mmol) was added in one portion. After stirring at −78 °C for 1 h, the

mixture was poured into a two-layer mixture of Et_2O (20 mL) and 5% aqueous HCl (20 mL) at 0 °C. The aqueous layer was separated and extracted with EtOAc (50 mL). The combined organic layer was washed with H_2O (15 mL), saturated aqueous $NaHCO_3$ (15 mL) and brine (2 × 15 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product (1.9 g), which was used without further purification.

A solution of methanesulfonyl azide (929 mg, 7.68 mmol) in CH_3CN (1 mL) was added to a solution of the crude product and triethylamine (1.3 mL, 9.33 mmol) in CH_3CN (3 mL). After stirring at 23 °C for 24 h, the mixture was poured into a two-layer mixture of Et_2O (20 mL) and 5% aqueous NaOH (20 mL). The aqueous layer was separated and extracted with EtOAc (50 mL). The combined organic layer was washed with water (15 mL), saturated aqueous NH_4Cl (15 mL) and brine (2 × 15 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product (1.7 g), which was purified by column chromatography (silica gel 200 g, 30:1 hexane/Et_2O) to provide α-diazo ester **9a** (1.02 g, 75%) as a yellow solid: R_f = 0.59 (4:1 hexane/EtOAc); mp 63.5–64.5 °C (hexane/EtOAc); IR ($CHCl_3$) ν 2108, 1698 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.10 (d, J = 6.6 Hz, 18H), 1.19–1.32 (m, 3H), 3.82 (s, 3H), 4.98 (s, 2H), 6.82 (d, J = 8.6 Hz, 1H), 6.89 (d, J = 7.9 Hz, 2H), 7.22 (d, J = 7.9 Hz, 2H), 7.29 (dd, J = 2.6, 8.6 Hz, 1H), 7.74 (d, J = 2.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.7 (CH), 18.0 (CH_3), 52.1 (CH_3), 70.9 (CH_2), 113.5 (C), 113.6 (CH), 116.1 (C), 120.0 (CH), 127.9 (C), 129.2 (CH), 130.6 (CH), 132.0 (CH), 153.3 (C), 156.1 (C), 166.0 (C); HRMS (FAB) calcd for $C_{25}H_{33}N_2O_4SiBrNa$ ($M+Na^+$) 555.1291, found 555.1306. Anal. Calcd for $C_{25}H_{33}N_2O_4SiBr$: C, 56.28; H, 6.23; N, 5.25; Br, 14.98. Found: C, 56.28; H, 6.15; N, 5.08; Br, 15.21.

(2*R*,3*S*)-5-Bromo-3-methoxycarbonyl-2-(4-triisopropylsilyloxyphenyl)-2,3-dihydrobenzofuran (8a, Table 1, entry 8)



8a

Rh_2(*S*-PTTEA)$_4$ (**3b**)·2EtOAc (47.7 mg, 0.03 mmol, 1 mol %) was added to a mixture of **9a** (1.60 g, 3.0 mmol) and 4 Å MS (1.60 g) in CH_2Cl_2 (30 mL) at −60 °C. After stirring at this temperature for 24 h, the 4 Å MS was filtrated through a Celite pad and the filtrate was concentrated in vacuo. The ratio of **8a**/**10a** was determined to be 97:3 by ^1H NMR of the crude product. The residue (1.7 g) was purified by column chromatography (silica gel 90 g, 25:1 hexane/Et_2O) to give **8a** (1.21 g, 80%) as a white solid and **10a** (31.0 mg, 2% yield, 6% ee) as a colorless oil. **8a**: R_f = 0.50 (6:1 hexane/Et_2O); mp 62.0–63.0 °C for 84 % ee; $[\alpha]_D^{21}$ −31.4 (c 1.15, $CHCl_3$) for 84% ee; IR ($CHCl_3$) ν 1738 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.08 (d, J = 7.2 Hz, 18H), 1.20–1.29 (m, 3H), 3.27 (s, 3H), 4.56 (d, J = 9.9 Hz, 1H), 5.94 (d, J = 9.9 Hz, 1H), 6.80–6.85 (m, 3H), 7.17 (d, J = 8.6 Hz, 2H), 7.33–7.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.6 (CH), 17.9 (CH_3), 51.8 (CH_3), 53.6 (CH), 86.1 (CH), 111.4 (CH), 112.8 (C), 119.7 (CH), 127.0 (C), 127.5 (CH), 128.9 (C), 129.0 (CH), 132.3 (CH), 156.3 (C), 159.6 (C), 169.7 (C); LRMS (EI) m/z 504 (M^+), 463, 433, 407,

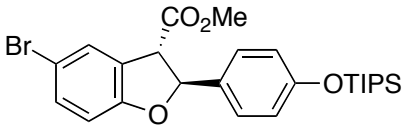
207, 134; HRMS (EI) calcd for $C_{25}H_{33}O_4SiBr$ (M^+) 504.1331, found 504.1332.

The enantiomeric excess of **8a** was determined to be 84% by HPLC with a Chiralcel OD-H column (100:1 hexane/*i*-PrOH, 0.5 mL/min): t_R (major) = 20.6 min for (2*R*,3*S*)-**8a**, t_R (minor) = 25.6 min for (2*S*,3*R*)-**8a**.

Recrystallization was performed by dissolving **8a** (520 mg, 1.03 mmol, 84% ee) in hexane (5 mL)–EtOAc (0.2 mL) at 40 °C. Colorless prisms formed at −20 °C after standing overnight, and were collected by suction, washed with ice-cold hexane (2 mL) and dried in vacuo to give enantiomerically pure **8a** (106 mg, 20%): mp 60.0–62.0 °C (hexane/EtOAc); $[\alpha]_D^{20}$ −38.7 (*c* 1.11, $CHCl_3$); Anal. Calcd for $C_{25}H_{33}O_4SiBr$: C, 59.40; H, 6.58; Br, 15.81. Found: C, 59.11; H, 6.36; Br, 16.11. The enantiopurity of **8a** was determined to be >99% ee by HPLC analysis.

The preferred absolute configuration of **8a** was established as (2*R*,3*S*) by a single-crystal X-ray analysis. Suitable crystals of **8a** for X-ray crystallographic analysis were obtained by recrystallization from *i*-PrOH/H_2O.

(2*S*,3*S*)-5-Bromo-3-methoxycarbonyl-2-(4-triisopropylsilyloxyphenyl)-2,3-dihydrobenzofuran (10a, Table 1, entry 2)

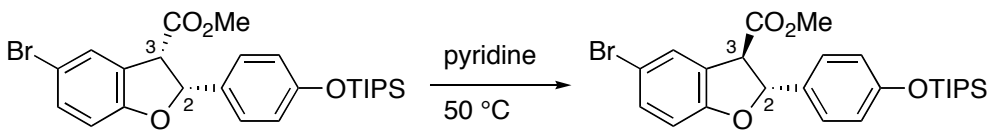


10a

Rh_2(*S*-PTTL)$_4$·2EtOAc (1.42 mg, 0.001 mmol, 1 mol %) was added to a solution of **9a** (53.4 mg, 0.10 mmol) in CH_2Cl_2 (1.0 mL) at −23 °C. After stirring at this temperature for 0.5 h, the mixture was concentrated in vacuo. The ratio of **8a**/**10a** was determined to be 89:11 by ^{1}H NMR of the crude product. The residue (56 mg) was purified by column chromatography (silica gel 5 g, 25:1 hexane/Et_2O) to give **8a** (31.8 mg, 63% yield, 75% ee) as a white solid and **10a** (4.4 mg, 9%) as a colorless oil. **10a**: R_f = 0.63 (6:1 hexane/Et_2O); $[\alpha]_D^{23}$ +26.5 (*c* 0.22, $CHCl_3$) for 32% ee; IR (neat) ν 1744 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (d, *J* = 7.3 Hz, 18H), 1.19–1.29 (m, 3H), 3.83 (s, 3H), 4.26 (d, *J* = 7.3 Hz, 1H), 6.05 (d, *J* = 7.3 Hz, 1H), 6.76 (d, *J* = 8.7 Hz, 1H), 6.84–6.88 (m, 2H), 7.20–7.24 (m, 2H), 7.33 (m, 1H), 7.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.6 (CH), 17.9 (CH_3), 52.9 (CH_3), 55.3 (CH), 86.1 (CH), 111.4 (CH), 112.5 (C), 120.1 (CH), 126.2 (C), 127.1 (CH), 128.1 (CH), 132.2 (C), 132.4 (CH), 156.4 (C), 158.4 (C), 170.7 (C); HRMS (EI) calcd for $C_{25}H_{33}O_4SiBr$ (M^+) 504.1331, found 504.1318. Anal. Calcd for $C_{25}H_{33}O_4SiBr$: C, 59.40; H, 6.58; Br, 15.81. Found: C, 59.41; H, 6.44; Br, 16.05.

The enantiomeric excess of **10a** was determined to be 32% by HPLC with a Chiralpak IA column (100:1 hexane/*i*-PrOH, 0.5 mL/min): t_R (minor) = 11.9 min for (2*R*,3*R*)-**10a**, t_R (major) = 15.0 min for (2*S*,3*S*)-**10a**.

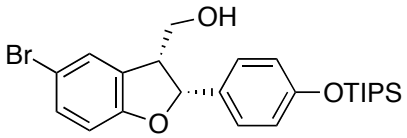
The preferred absolute configuration of **10a** was determined to be (2*S*,3*S*) by comparison of the sign of optical rotation with that of the compound obtained by epimerization of **8a** at the C3 stereocenter.



(2*R*,3*S*)-**8a** (2*R*,3*R*)-**10a**

Pyridine (0.5 mL) was added to (2*R*,3*S*)-**8a** (25.0 mg, 0.495 mmol, 84% ee) at 23 °C. After stirring for 15 h at 50 °C, the reaction was quenched with saturated aqueous NH_4Cl (1 mL). The whole was extracted with EtOAc (6 mL), and the organic layer was washed with water (2 mL) and brine (2 × 2 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product (38 mg), which was purified by column chromatography (silica gel 4 g, 25:1 hexane/Et_2O) to provide (2*R*,3*R*)-**10a** (23.0 mg, 93%) as a colorless oil: $[\alpha]_D^{23}$ −62.3 (*c* 1.08, $CHCl_3$) for 84% ee.

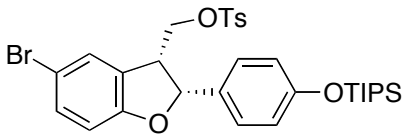
(2*R*,3*R*)-[5-Bromo-2-(4-triisopropylsilyloxyphenyl)-2,3-dihydrobenzofuran-3-yl]methanol (20)



20

DIBAL-H (1.0 M in toluene, 5.2 mL, 5.2 mmol) was added to a solution of ester **8a** (1.20 g, 2.38 mmol, 84% ee) in THF (24 mL) at −23 °C. After stirring at −23 °C for 30 min, the reaction was quenched by addition of methanol (1 mL) and 1 M aqueous potassium sodium tartrate (30 mL). The resulting mixture was stirred vigorously at 23 °C for 2 h, and the whole was extracted with EtOAc (2 × 60 mL). The organic layer was washed with brine (2 × 30 mL) and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product (1.4 g), which was purified by column chromatography (silica gel 30 g, 15:1 hexane/EtOAc) to provide alcohol **20** (1.10 g, 97%) as a colorless oil: R_f = 0.38 (4:1 hexane/EtOAc); $[\alpha]_D^{21}$ +25.1 (*c* 1.33, $CHCl_3$) for 84% ee; IR (neat) ν 3432 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.09 (d, *J* = 6.9 Hz, 18H), 1.18–1.31 (m, 3H), 3.38–3.51 (m, 2H), 3.72 (m, 1H), 5.85 (d, *J* = 8.6 Hz, 1H), 6.79 (d, *J* = 8.6 Hz, 1H), 6.89–6.93 (m, 2H), 7.24–7.27 (m, 2H), 7.30 (dd, *J* = 2.0, 8.2 Hz, 1H), 7.37 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.5 (CH), 17.8 (CH_3), 48.3 (CH), 62.6 (CH_2), 86.5 (CH), 111.0 (CH), 112.4 (C), 120.0 (CH), 127.2 (CH), 128.3 (CH), 128.7 (C), 130.9 (C), 131.4 (CH), 156.0 (C), 158.7 (C); HRMS (EI) calcd for $C_{24}H_{33}O_3SiBr$ (M^+) 476.1382, found 476.1382. Anal. Calcd for $C_{24}H_{33}O_3SiBr$: C, 60.37; H, 6.97; Br, 16.73. Found: C, 60.44; H, 6.89; Br, 16.88.

(2*R*,3*R*)-Methyl [5-bromo-2-(4-triisopropylsilyloxyphenyl)-2,3-dihydrobenzofuran-3-yl]-*p*-toluenesulfonate (21)



21

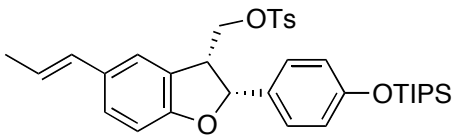
p-Toluenesulfonyl chloride (658 mg, 3.45 mmol) was added to a solution of alcohol **20** (1.10 g, 2.30 mmol) in pyridine (12 ml) at 0 °C. After stirring at 23 °C for 15 h, the reaction

was quenched with crushed ice. The whole was extracted with EtOAc (2 × 40 mL). The organic layer was washed with 5% aqueous HCl (2 × 20 mL), H_2O (20 mL), saturated aqueous $NaHCO_3$ (20 mL) and brine (2 × 20 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product (1.9 g), which was purified by column chromatography (silica gel 30 g, 12:1 hexane/EtOAc) to provide sulfonate **21** (1.39 g, 96%) as a white solid: R_f = 0.47 (4:1 hexane/EtOAc); mp 69.0–71.0 °C for 84 % ee; $[\alpha]_D^{21}$ +4.9 (*c* 1.18, $CHCl_3$) for 84% ee; IR (KBr) ν 1513, 1472 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.10 (d, *J* = 7.2 Hz, 18H), 1.20–1.30 (m, 3H), 2.42 (s, 3H), 3.71 (d, *J* = 7.2 Hz, 2H), 3.86 (dt, *J* = 7.2, 8.8 Hz, 1H), 5.79 (d, *J* = 8.8 Hz, 1H), 6.74 (d, *J* = 8.5 Hz, 1H), 6.83 (dt, *J* = 2.8, 8.5 Hz, 2H), 7.11 (dt, *J* = 2.8, 8.5 Hz, 2H), 7.24–7.29 (m, 4H), 7.53 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.7 (CH), 18.0 (CH_3), 21.7 (CH_3), 45.3 (CH), 69.2 (CH_2), 85.9 (CH), 111.2 (CH), 112.7 (C), 120.1 (CH), 127.2 (CH), 127.6 (CH), 127.7 (C), 128.5 (CH), 129.1 (C), 129.7 (CH), 132.0 (CH), 132.3 (C), 144.7 (C), 156.2 (C), 158.6 (C); HRMS (EI) calcd for $C_{31}H_{39}O_5SSiBr$ (M^+) 630.1470, found 630.1471.

The enantiomeric excess of **21** was determined to be 84% by HPLC with a Chiralpak AD-H column (50:1 hexane/*i*-PrOH, 1.0 mL/min): t_R (major) = 11.1 min for (2*R*,3*R*)-**21**, t_R (minor) = 14.6 min for (2*S*,3*S*)-**21**.

21 (1.39 g, 84% ee) was dissolved in hexane (15 mL)–EtOAc (2 mL) at 50 °C and stored at 23 °C overnight. Colorless prisms (238 mg, 17%, 6% ee) are removed by filtration, and the filtrate was concentrated in vacuo to afford enantiomerically pure **21** (1.15 g, 83%): mp 54.0–55.0 °C (hexane/EtOAc); $[\alpha]_D^{22}$ +6.2 (*c* 1.15, $CHCl_3$); Anal. Calcd for $C_{31}H_{39}O_5SSiBr$: C, 58.94; H, 6.22; S, 5.08; Br, 12.65. Found: C, 58.87; H, 6.09; S, 5.16, Br, 12.82. The enantiopurity of **21** was determined to be >99% ee by HPLC analysis.

(2*R*,3*R*)-Methyl {5-[(*E*)-propen-1-yl]-2-(4-triisopropylsilyloxyphenyl)-2,3-dihydrobenzo-furan-3-yl}-*p*-toluenesulfonate (22)

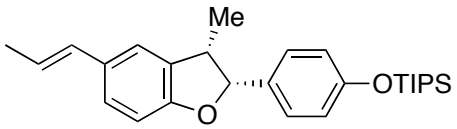


22

$PdCl_2(PPh_3)_2$ (27.2 mg, 3.88 μmol, 5 mol %) and K_2CO_3 (329 mg, 3.10 mmol) were added to a mixture of sulfonate **21** (490 mg, 0.776 mmol, >99% ee) and *trans*-1-propen-1-ylboronic acid (133 mg, 1.55 mmol) in THF/H_2O (4:1, 8 mL), and the mixture was heated at reflux for 7 h. After cooling, the reaction mixture was extracted with EtOAc (30 mL), and the organic layer was washed with water (2 × 5 mL) and brine (2 × 5 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product (580 mg), which was purified by column chromatography (silica gel 20 g, 1:2 hexane/toluene) to provide sulfonate **22** (350 mg, 76%) as a colorless oil: R_f = 0.46 (4:1 hexane/EtOAc); $[\alpha]_D^{21}$ −39.8 (*c* 0.90, $CHCl_3$) for >99% ee; IR (neat) ν 1609 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.10 (d, *J* = 6.6 Hz, 18H), 1.21–1.30 (m, 3H), 1.87 (dd, *J* = 1.7, 6.6 Hz, 3H), 2.41 (s, 3H), 3.68–3.92 (m, 3H) 5.78 (d, *J* = 8.6 Hz, 1H), 6.04 (dq, *J* = 6.6, 15.8 Hz,

1H), 6.31 (dd, J = 1.7, 15.8 Hz, 1H), 6.77–6.85 (m, 3H), 7.09–7.24 (m, 6H), 7.49–7.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.6 (CH), 17.9 (CH_3), 18.4 (CH_3), 21.6 (CH_3), 45.3 (CH), 69.5 (CH_2), 85.6 (CH), 109.4 (CH), 120.0 (CH), 122.7 (CH), 123.4 (CH), 126.8 (C), 127.2 (CH), 127.3 (CH), 127.7 (CH), 128.4 (C), 129.6 (CH), 130.4 (CH), 131.5 (C), 132.4 (C), 144.6 (C), 156.1 (C), 158.5 (C); HRMS (EI) calcd for $C_{34}H_{44}O_5SSi$ (M^+) 592.2678, found 592.2661. Anal. Calcd for $C_{34}H_{44}O_5SSi$: C, 68.88; H, 7.48; S, 5.41. Found: C, 68.81; H, 7.56; S, 5.42.

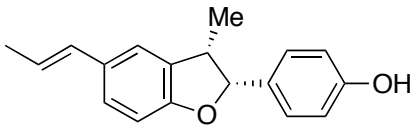
(2*R*,3*S*)-3-Methyl-5-[(*E*)-propen-1-yl]-2-(4-triisopropylsilyloxyphenyl)-2,3-dihydrobenzofuran (23)



23

$LiBEt_3H$ (1.09 M solution in THF, 2.1 mL, 2.29 mmol) was added to a solution of sulfonate **22** (340 mg, 0.573 mmol, >99% ee) in THF (3.0 mL) at 0 °C. After stirring at 23 °C for 10 h, the reaction was quenched by addition of water (3 mL). The whole was extracted with EtOAc (30 mL), and the organic layer was washed with water (5 mL) and brine (2 × 5 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product (379 mg), which was purified by column chromatography (silica gel 15 g, 30:1 hexane/EtOAc) to provide silyl ether **23** (213 mg, 88%) as a colorless oil: R_f = 0.46 (4:1 hexane/EtOAc); $[\alpha]_D^{21}$ −11.5 (c 0.95, $CHCl_3$) for >99% ee; IR (neat) ν 1610 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (d, J = 6.8 Hz, 3H), 1.08 (d, J = 7.2 Hz, 18H), 1.19–1.28 (m, 3H), 1.86 (dd, J = 1.8, 6.8 Hz, 3H), 3.58–3.66 (m, 1H), 5.75 (d, J = 8.6 Hz, 1H), 6.08 (dq, J = 6.8, 15.9 Hz, 1H), 6.36 (dd, J = 1.8, 15.9 Hz, 1H), 6.80–6.87 (m, 3H), 7.10–7.15 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.6 (CH), 16.7 (CH_3), 17.9 (CH_3), 18.4 (CH_3), 40.8 (CH), 87.9 (CH), 109.1 (CH), 119.7 (CH), 121.5 (CH), 122.9 (CH), 126.2 (CH), 127.4 (CH), 130.4 (C), 130.7 (CH), 131.2 (C), 133.1 (C), 155.6 (C), 158.3 (C); HRMS (EI) calcd for $C_{27}H_{38}O_2Si$ (M^+) 422.2641, found 422.2643. Anal. Calcd for $C_{27}H_{38}O_2Si$: C, 76.72; H, 9.06. Found: C, 76.83; H, 9.22.

(2*R*,3*S*)-*epi*-Conocarpan (2)



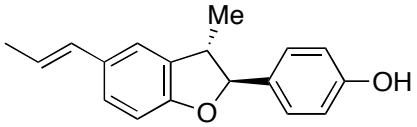
(–)-*epi*-conocarpan (**2**)

TBAF (0.4 M solution in THF, 0.8 mL, 0.32 mmol) was added to a solution of silyl ether **23** (90 mg, 0.213 mmol, >99% ee) in THF/AcOH (6;1, 1.4 mL) at 0 °C. After stirring at 23 °C for 8 h, the reaction was quenched with water (3 mL). The whole was extracted with EtOAc (30 mL), and the organic layer was washed with water (3 × 5 mL) and brine (2 × 5 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product (141 mg), which was purified by column chromatography (silica gel 8 g, 8:1 hexane/EtOAc) to provide (−)-*epi*-conocarpan (**2**) (53.3 mg, 94%) as a white amorphous solid: R_f 0.37 (3:1 hexane/EtOAc); $[\alpha]_D^{21}$ −9.7 (c 0.45, MeOH) for

>99% ee [lit.[5] $[\alpha]_D^{21}$ −33.3 (*c* 0.03, MeOH)]; IR (neat) ν 3388, 2964, 1614, 1015 cm^{-1}; CD (*c* 0.003, MeOH): $[\theta]_{209}$ 0, $[\theta]_{228}$ +54825, $[\theta]_{241}$ 0, $[\theta]_{262}$ −28671, $[\theta]_{278}$ 0, $[\theta]_{285}$ +6609 [lit.[5] CD (*c* 0.003, MeOH): $[\theta]_{218}$ 0, $[\theta]_{229}$ +14390, $[\theta]_{235}$ 0, $[\theta]_{243}$ −9923, $[\theta]_{275}$ 0, $[\theta]_{282}$ +2658]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.83 (d, *J* = 6.9 Hz, 3H), 1.86 (dd, *J* = 1.7, 6.9 Hz, 3H), 3.63 (m, 1H), 4.79 (s, 1H), 5.75 (d, *J* = 9.2 Hz, 1H), 6.08 (dq, *J* = 6.9, 15.5 Hz, 1H), 6.36 (dd, *J* = 1.7, 15.5 Hz, 1H), 6.80–6.83 (m, 3H), 7.11–7.19 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.7 (CH_3), 18.4 (CH_3), 40.7 (CH), 87.9 (CH), 109.1 (CH), 115.1 (CH), 121.5 (CH), 123.0 (CH), 126.2 (CH), 127.8 (CH), 130.0 (C), 130.7 (CH), 131.3 (C), 133.0 (C), 155.0 (C), 158.0 (C); LRMS (EI) m/z 266 (M^+), 251; HRMS (EI) calcd for $C_{18}H_{18}O_2$ (M^+) 266.1307, found 266.1304.

The enantiopurity of synthetic (−)-*epi*-conocarpan (**2**) was determined to be >99% ee by comparison of HPLC retention time (Chiralcel OD-H column, 9:1 hexane/*i*-PrOH, 1.0 mL/min) with the racemic sample: t_R = 10.1 min for (2*R*,3*S*)-**2**, t_R = 20.5 min for (2*S*,3*R*)-**2**.

(2*S*,3*S*)-Conocarpan (1)



(+)-conocarpan (**1**)

Na_2CO_3 (53.3 mg, 0.50 mmol) was added to a solution of (−)-**2** (53.3 mg, 0.20 mmol) in MeOH (2.0 mL) at 0 °C. After stirring at 23 °C for 1 h, the reaction was quenched with saturated aqueous NH_4Cl (3 mL). The whole was extracted with EtOAc (30 mL), and the organic layer was washed with water (5 mL) and brine (2 × 5 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product (64 mg), which was purified by column chromatography (silica gel 20 g, 8:1 hexane/EtOAc) to afford a 12:1 mixture of **1**/**2** (52.0 mg, 98%). The mixture was dissolved in hexane/EtOAc (5:1, 1.2 mL) at 60 °C. Colorless plates formed at 23 °C after standing overnight, and were collected by suction, washed with ice-cold hexane (1 mL) and dried in vacuo to give (+)-conocarpan (**1**) (37.7 mg, 71%): R_f = 0.37 (3:1 hexane/EtOAc); mp 137–139 °C (hexane/EtOAc) [lit.[6] mp 133–135 °C]; $[\alpha]_D^{22}$ +117 (*c* 1.18, MeOH) [lit.[6] $[\alpha]_D^{21}$ +122 (*c* 1.03, MeOH)]; IR (neat) ν 3376, 1615, 1599 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.39 (d, *J* = 6.8 Hz, 3H), 1.86 (d, *J* = 1.7, 6.6 Hz, 3H), 3.39 (m, 1H), 4.80 (s, 1H), 5.08 (d, *J* = 8.6 Hz, 1H), 6.09 (dq, *J* = 6.6, 15.5 Hz, 1H), 6.36 (dd, *J* = 1.7, 15.5 Hz, 1H), 6.76 (d, *J* = 8.0 Hz 1H), 6.83–6.85 (m, 3H), 7.11–7.14 (m, 2H), 7.29–7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9 (CH_3), 18.4 (CH_3), 45.2 (CH), 92.6 (CH), 109.3 (CH), 115.4 (CH), 120.7 (CH), 123.1 (CH), 126.3 (CH), 127.9 (CH), 130.7 (CH), 131.2 (C), 132.3 (C), 132.8 (C), 155.6 (C), 158.2 (C); LRMS (EI) m/z 266 (M^+), 251; HRMS (EI) calcd for $C_{18}H_{18}O_2$ (M^+) 266.1307, found 266.1304.

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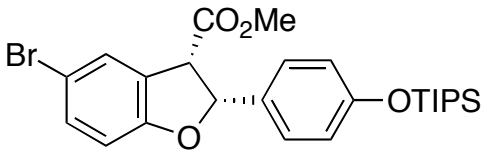
(5) Benevides, P. J. C.; Sartorelli, P.; Kato, M. J. *Phytochemistry* **1999**, *52*, 339–343.
(6) Achenbach, H.; Gross, J.; Dominguez, X. A.; Cano, G.; Star, J. V.; Brussolo, L. D. C.; Muñoz, G.; Salgado, F.; López, L. *Phytochemistry* **1987**, *26*, 1159–1166.



8a

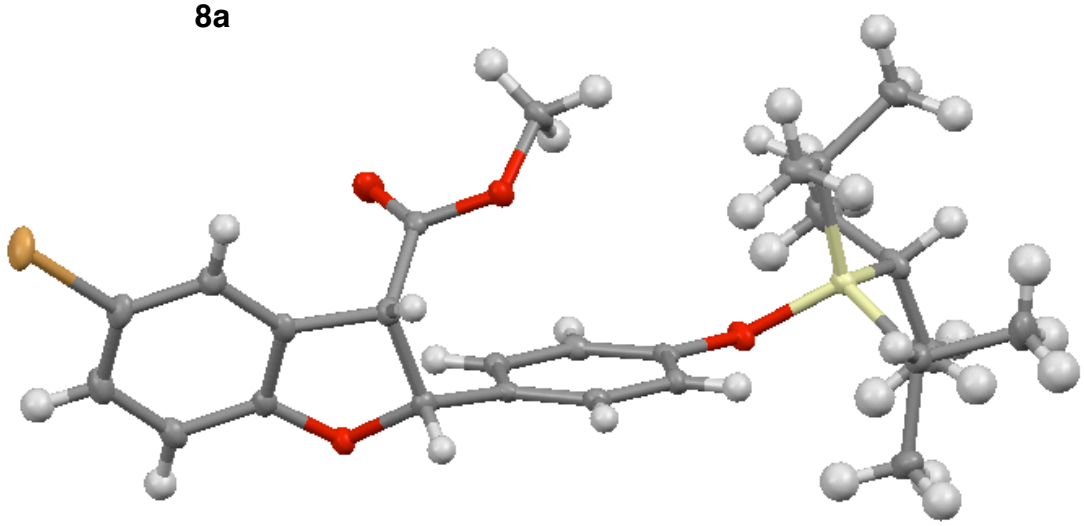
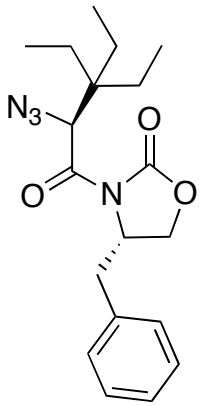


Figure 1. X-ray structure of **8a**.



16

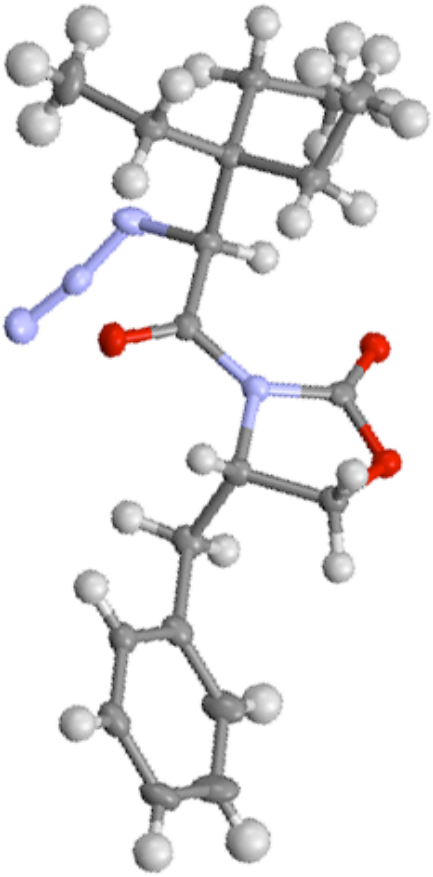
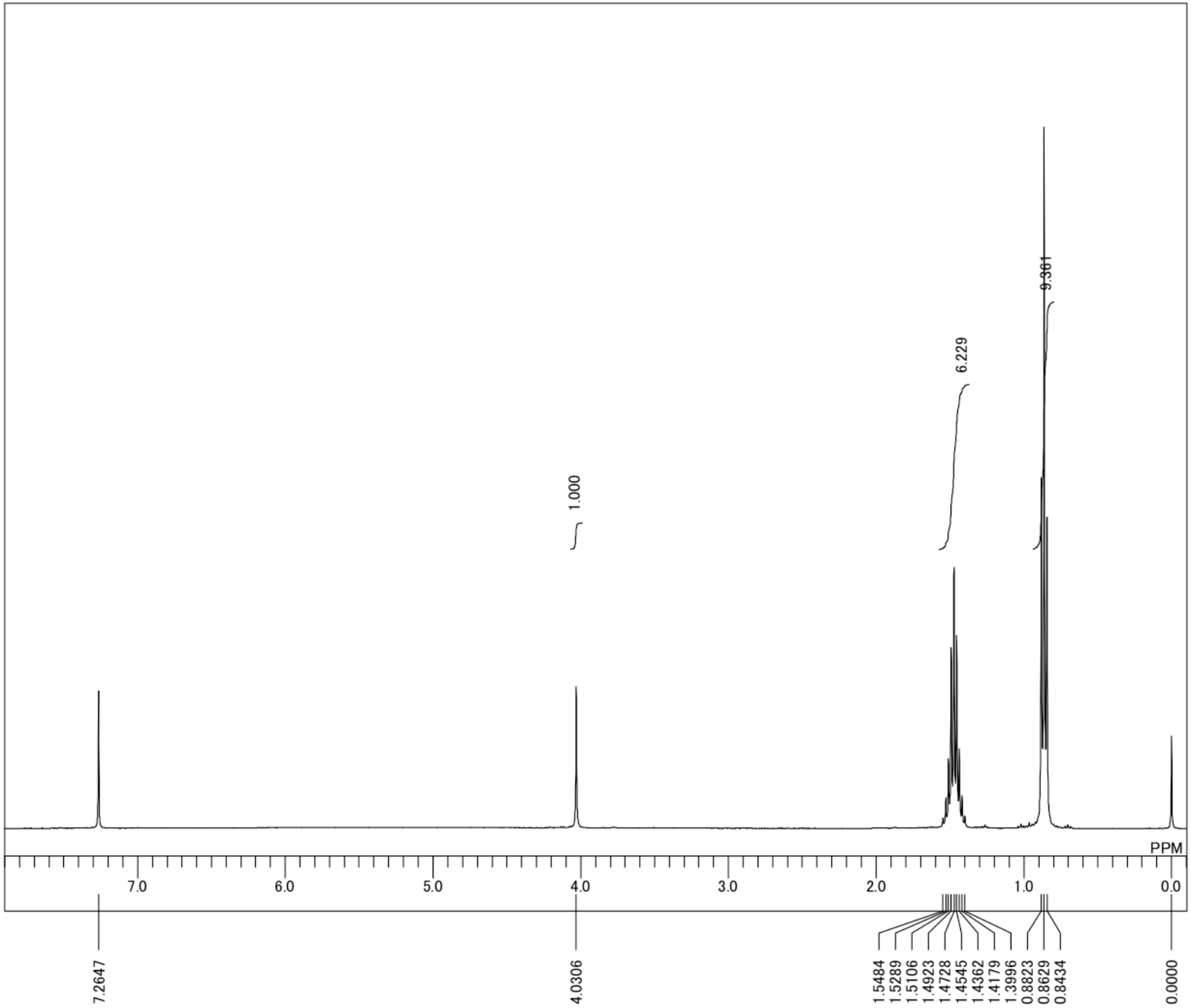
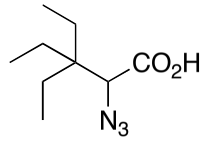


Figure 2. X-ray structure of **16**.

2-azide carboxylic acid

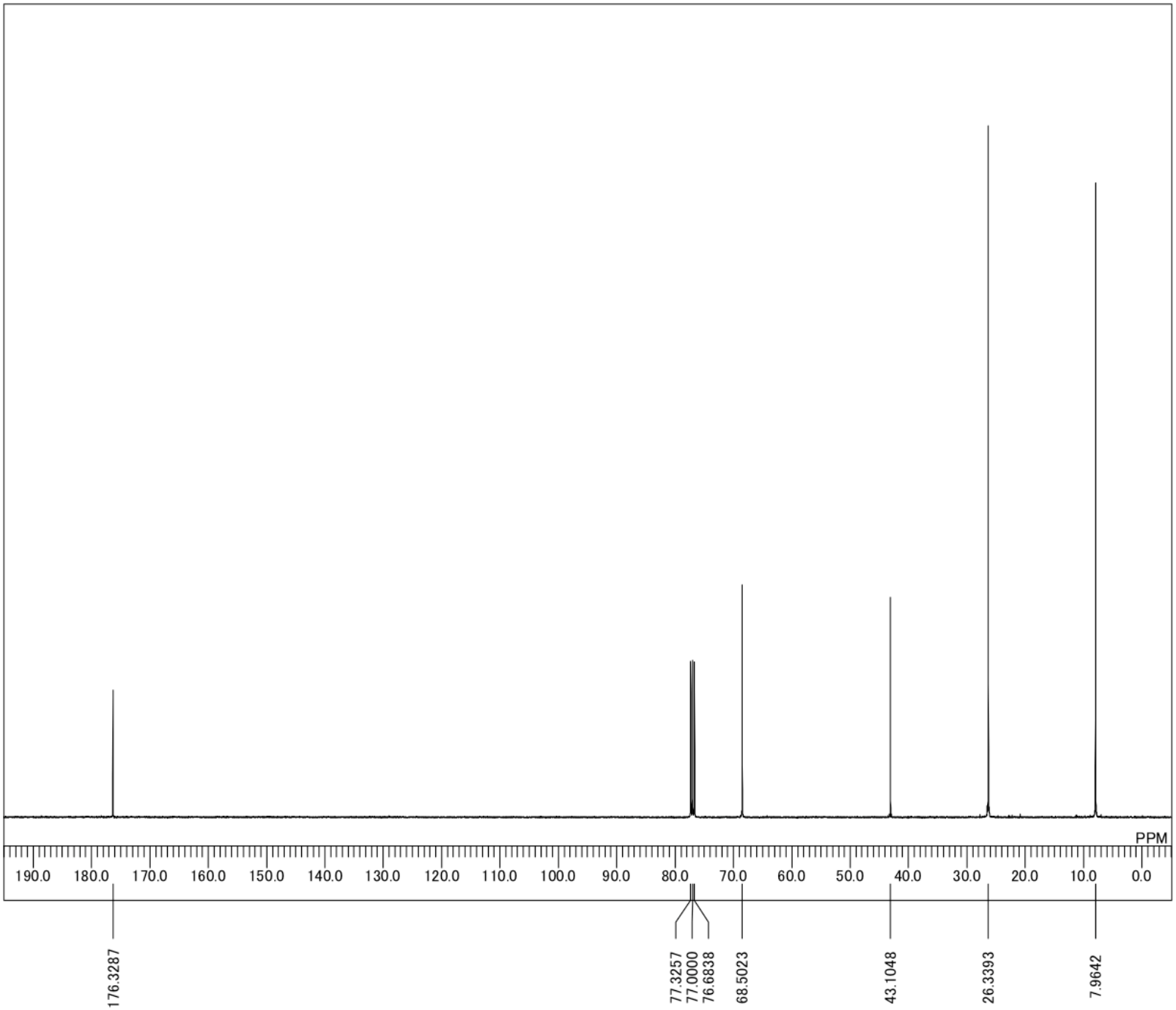


DFILE	2-azide carboxylic acid-1.als
COMNT	2-azide carboxylic acid
DATIM	19-09-2008 11:11:23
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	13107
FREQU	5938.15 Hz
SCANS	8
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	5.65 usec
IRNUC	1H
CTEMP	19.3 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.20 Hz
RGAIN	40

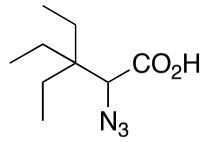


15

2-azide carboxylic acid_13C

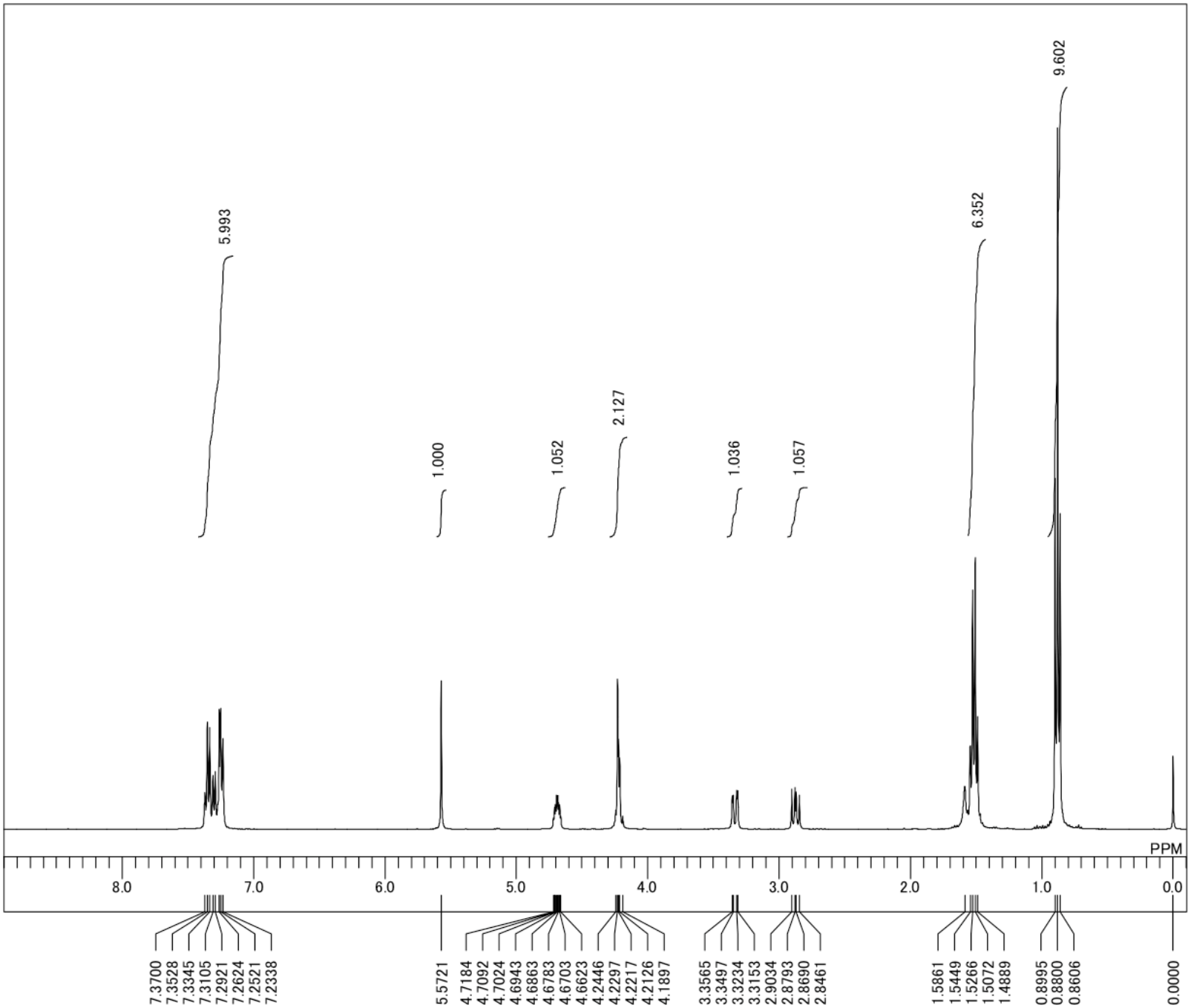


DFILE	2-azide carboxylic acid_13C-1.als
COMNT	2-azide carboxylic acid_13C
DATIM	19-09-2008 12:50:59
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	32768
FREQU	31250.00 Hz
SCANS	1450
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.17 usec
IRNUC	1H
CTEMP	19.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	58

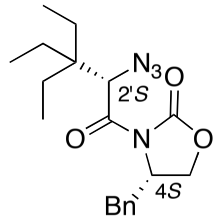


15

(S,S)-2-azide oxazolidinone_1H

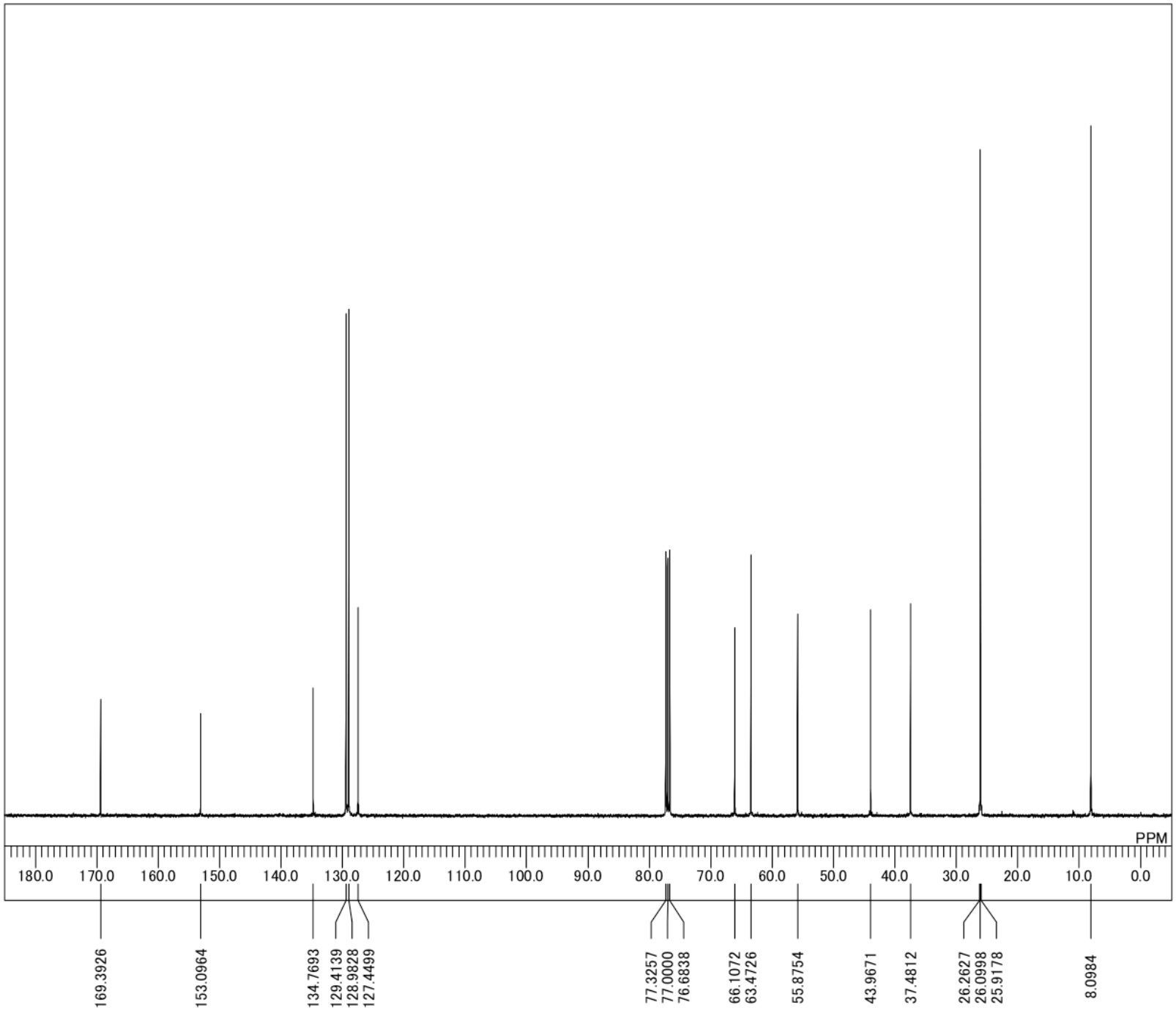


DFILE	(S,S)-2-azide oxazolidinone_1H-1.als
COMNT	(S,S)-2-azide oxazolidinone_1H
DATIM	19-09-2008 11:19:20
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	16384
FREQU	7422.80 Hz
SCANS	16
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	5.65 usec
IRNUC	1H
CTEMP	19.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.20 Hz
RGAIN	40



16

(S,S)-2-azide oxazolidinone_13C



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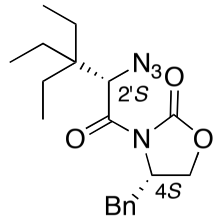
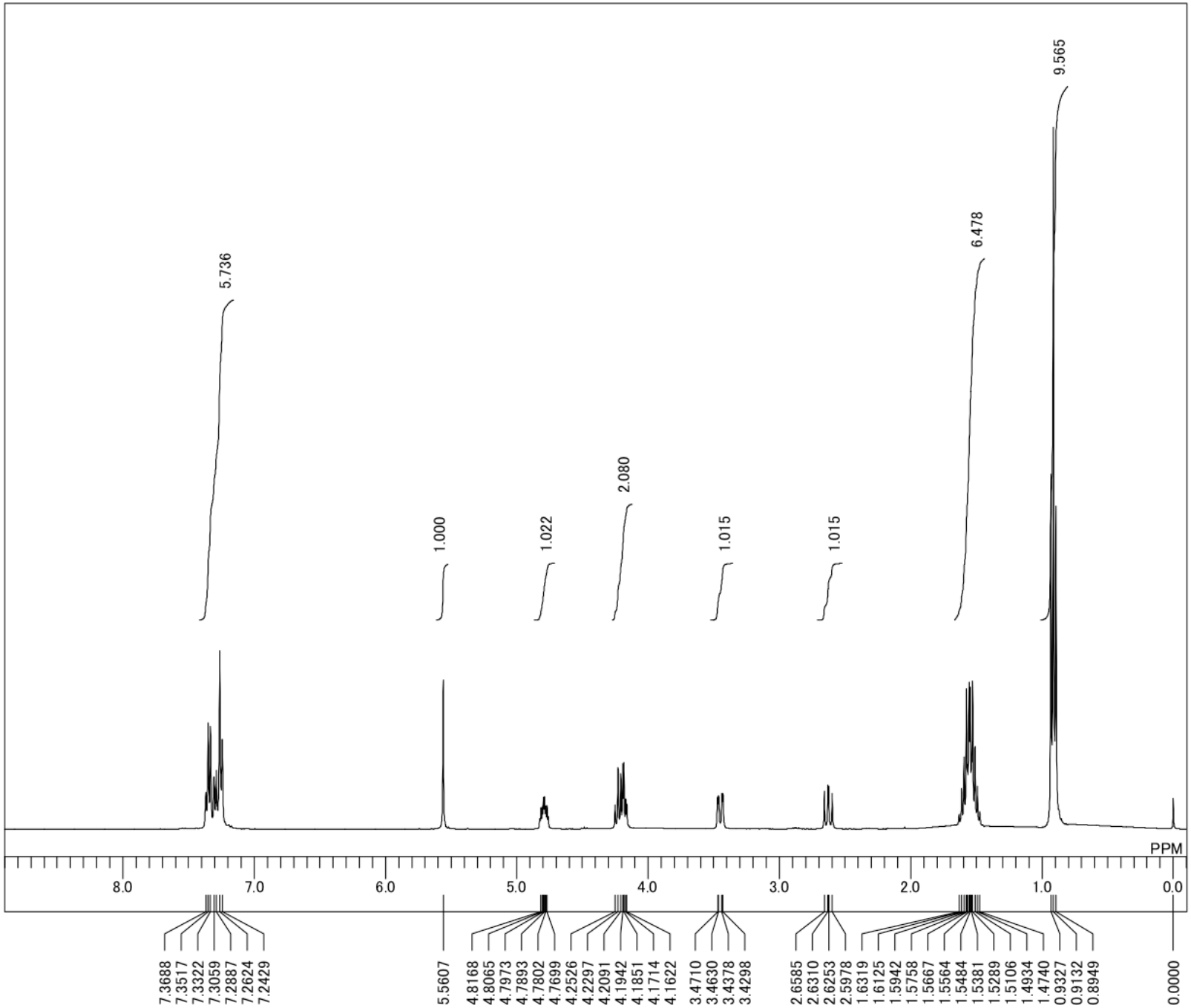
COMNT	(S,S)-2-azide oxazolidinone_13C
DATIM	19-09-2008 13:57:46
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	32768
FREQU	31250.00 Hz
SCANS	1145
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.17 usec
IRNUC	1H
CTEMP	19.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	60

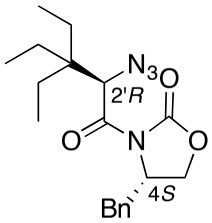


16

(2S,R)-2-azide oxazolidinone_1H

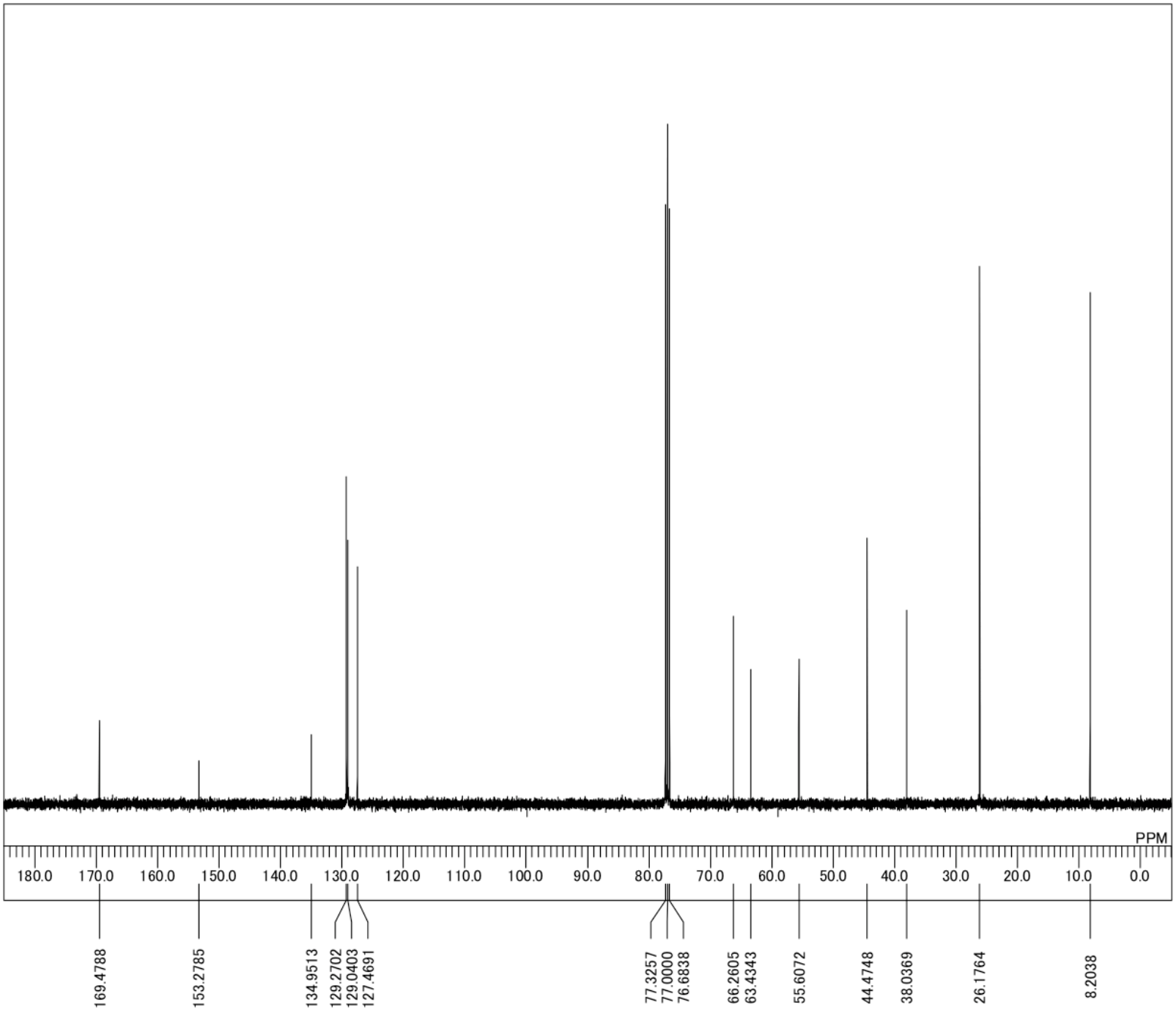


DFILE	(2S,R)-2-azide oxazolidinone_1H-1.als
COMNT	(2S,R)-2-azide oxazolidinone_1H
DATIM	19-09-2008 23:24:20
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	16384
FREQU	7422.80 Hz
SCANS	16
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	5.65 usec
IRNUC	1H
CTEMP	20.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.20 Hz
RGAIN	38

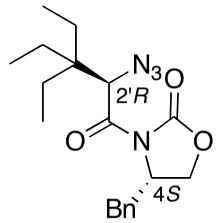


17

(2S,R)-2-azide oxazolidinone_13C



DFILE	(2S,R)-2-azide oxazolidinone_13C-1.als
COMNT	(2S,R)-2-azide oxazolidinone_13C
DATIM	26-09-2008 21:02:21
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	26214
FREQU	24999.62 Hz
SCANS	921
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.17 usec
IRNUC	1H
CTEMP	20.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	58



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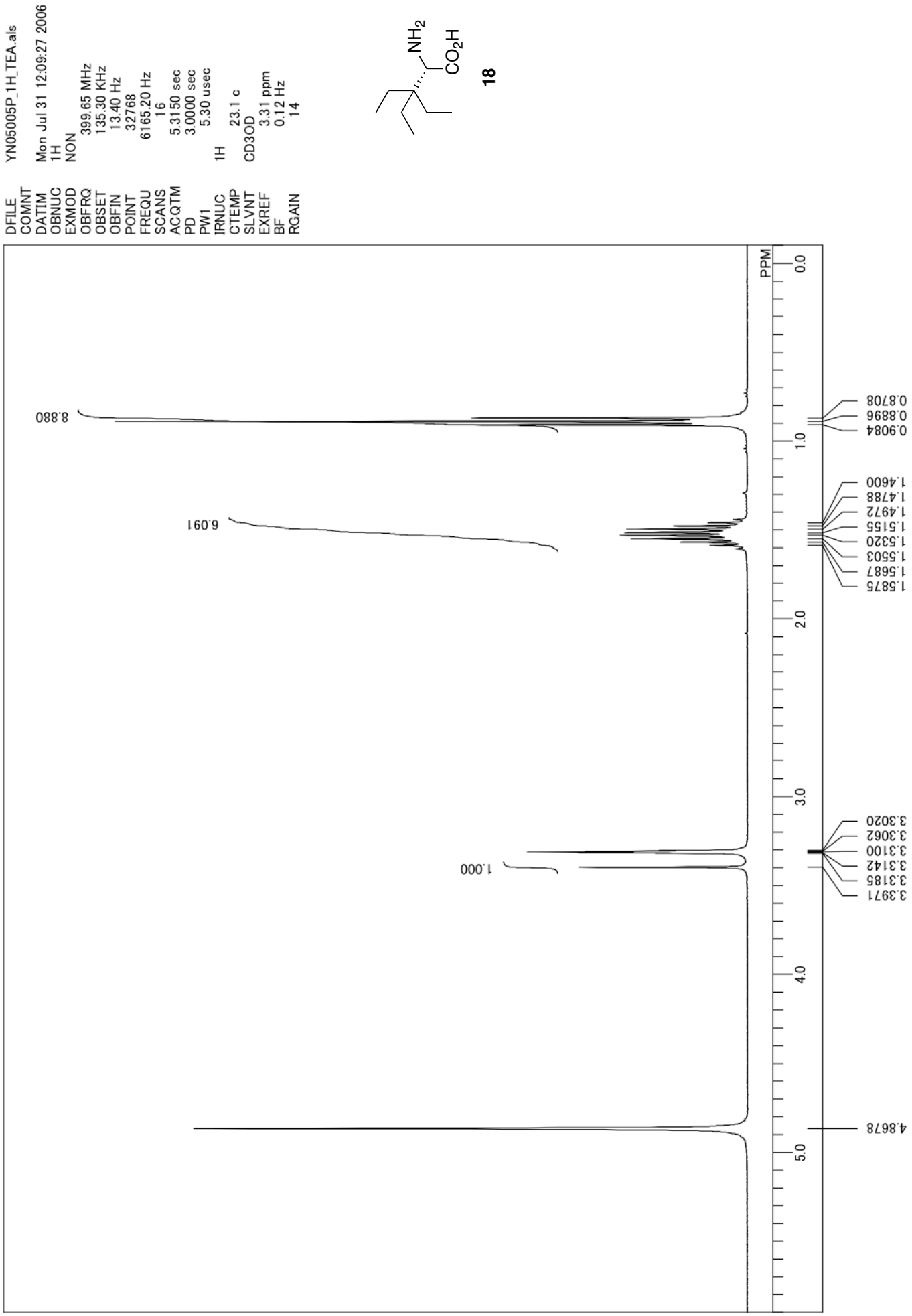
DFILE YN05005P_1H_TEA.als
COMNT
DATIM Mon Jul 31 12:09:27 2006
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 135.30 KHz
OBFIN 13.40 Hz
POINT 32768
FREQU 6165.20 Hz
SCANS 16
ACQTM 5.3150 sec
PD 3.0000 sec
PW1 5.30 usec
IRNUC 1H
CTEMP 23.1 c
SLVNT CD3OD
EXREF 3.31 ppm
BF 0.12 Hz
RGAIN 14
NH2
CO2H
18
PPM
0.0
1.0
2.0
3.0
4.0
5.0
8.880
6.091
1.000
0.8708
0.8896
0.9084
1.4600
1.4788
1.4972
1.5155
1.5320
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1.5875
3.3020
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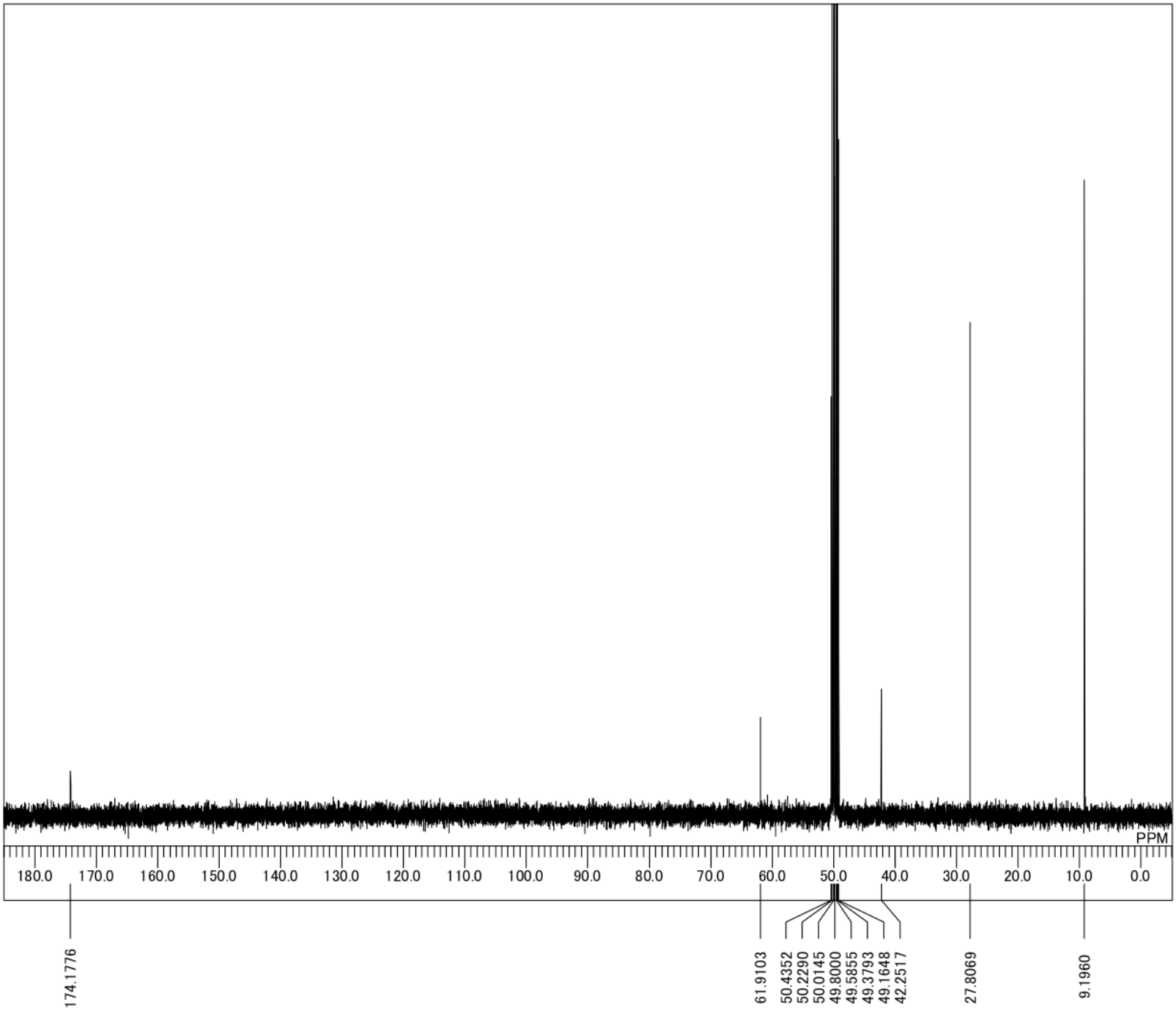
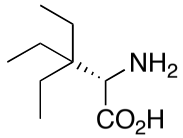
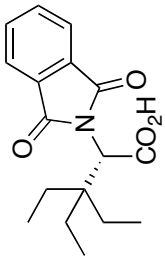
3.3142
3.3185
3.3971
4.8678



DFILE	YN05005P_13C_2.als
COMNT	
DATIM	Mon Jul 31 14:04:25 2006
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27173.90 Hz
SCANS	2266
ACQTM	1.2059 sec
PD	1.7940 sec
PW1	4.50 usec
IRNUC	1H
CTEMP	23.1 c
SLVNT	CD3OD
EXREF	49.80 ppm
BF	0.12 Hz
RGAIN	23



18



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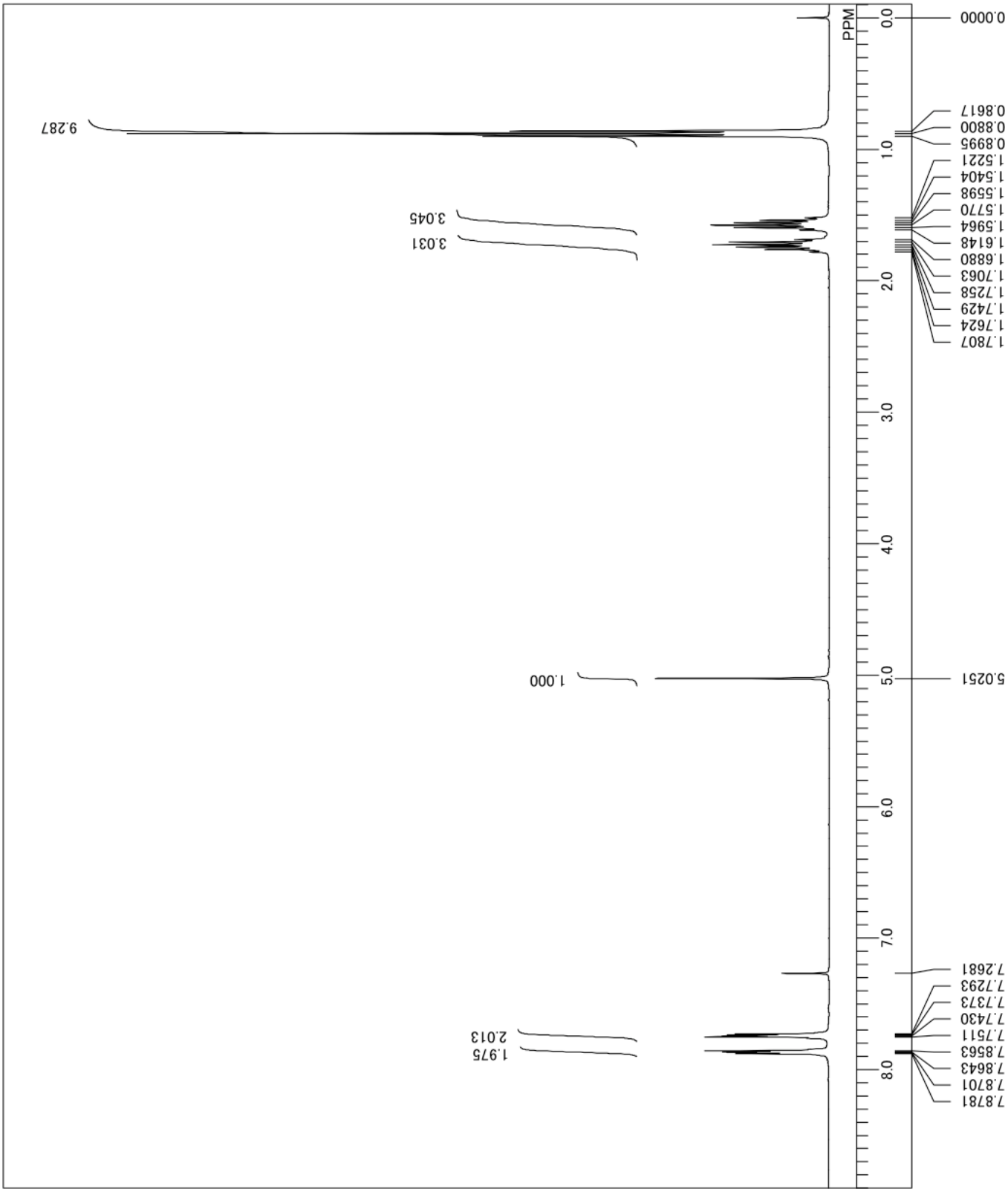
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COMNT
DATIM 19-09-2008 17:55:16
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 13107
FREQU 5938.15 Hz
SCANS 16
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 5.65 usec
IRNUC 1H
CTEMP 19.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 36
PPM
9.287
3.045
3.031
1.000
2.013
1.975
0.0000
0.8617
0.8800
0.8995
1.5221
1.5404
1.5598
1.5770
1.5964
1.6148
1.6880
1.7063
1.7258
1.7429
1.7624
1.7807
5.0251
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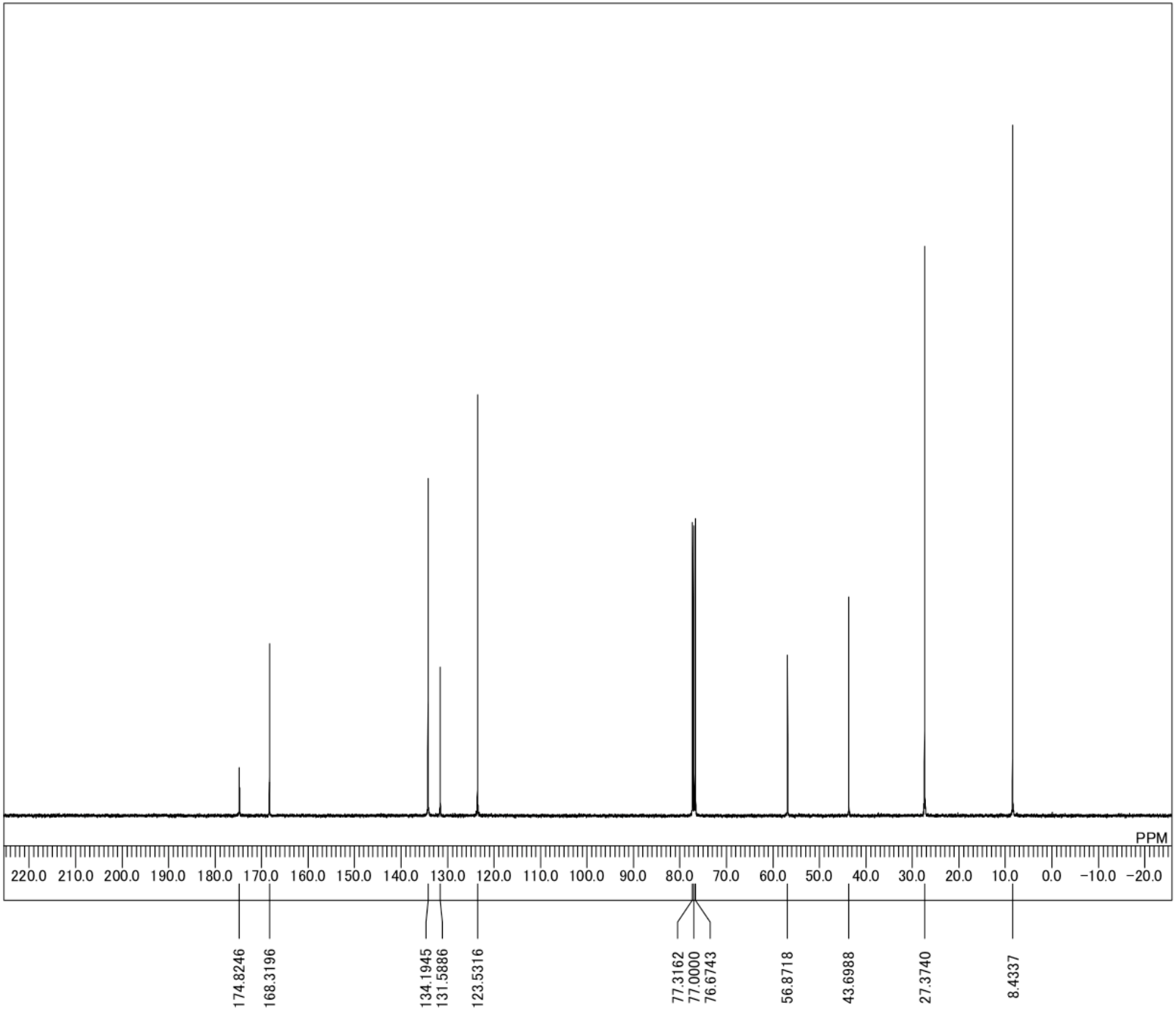
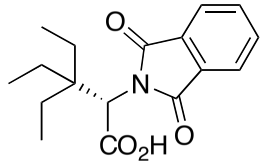
7.8643
7.8701
7.8781

PTTEA_13C

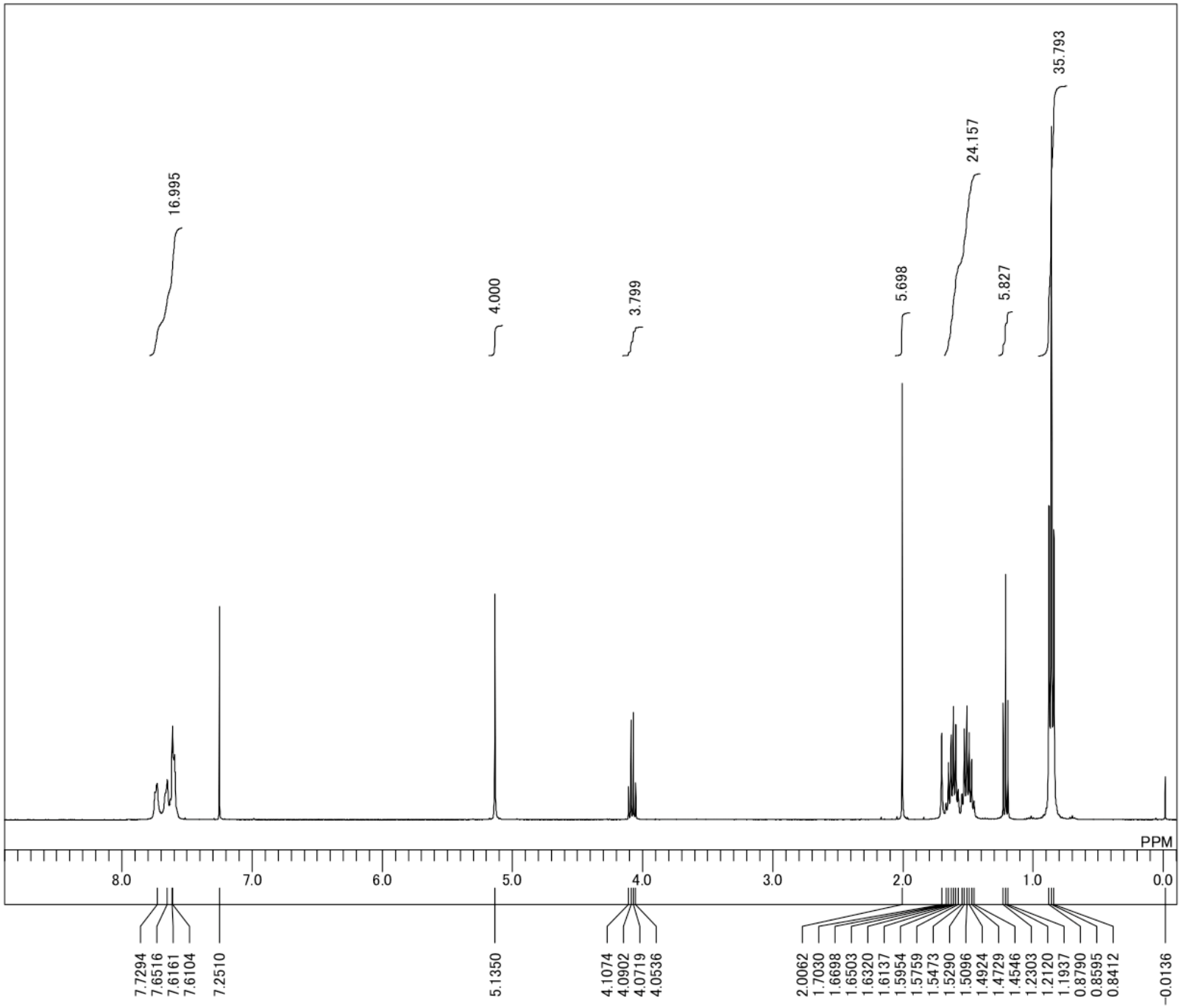


DFILE	PTTEA_13C-1.als
COMNT	PTTEA_13C
DATIM	19-09-2008 23:16:07
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	26214
FREQU	24999.62 Hz
SCANS	1287
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.17 usec
IRNUC	1H
CTEMP	20.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	56

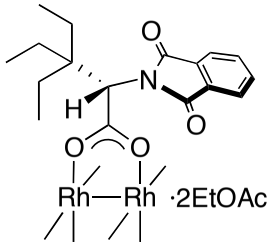


19

Rh2(S-PTTEA)4_5

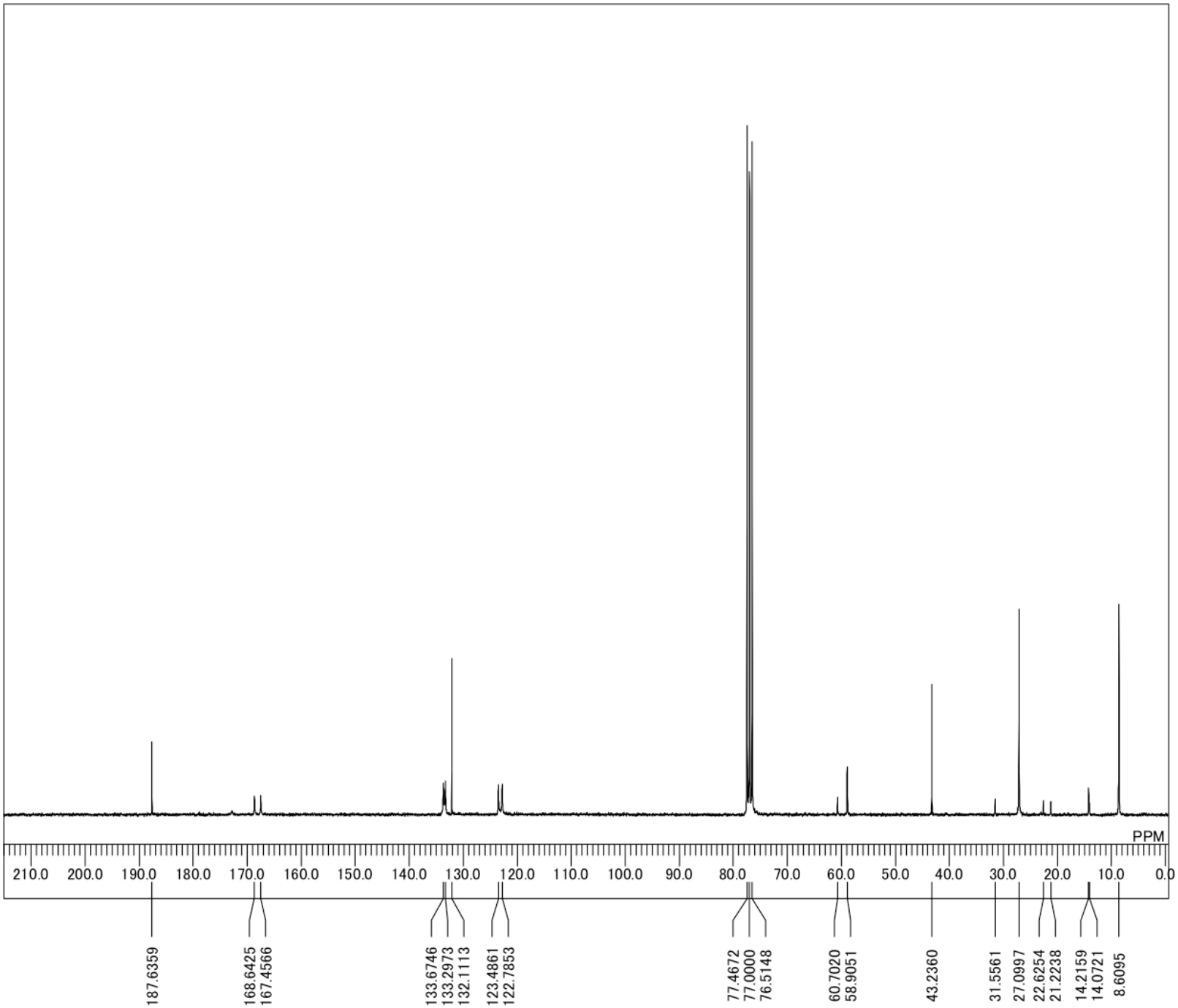


DFILE	Rh2(S-PTTEA)4.als
COMNT	Rh2(S-PTTEA)4_5
DATIM	28-10-2008 14:32:34
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	16384
FREQU	7422.80 Hz
SCANS	16
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	5.65 usec
IRNUC	1H
CTEMP	19.4 c
SLVNT	CDCL3
EXREF	12.50 ppm
BF	0.12 Hz
RGAIN	40

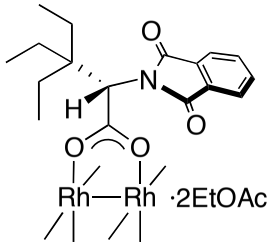


3b

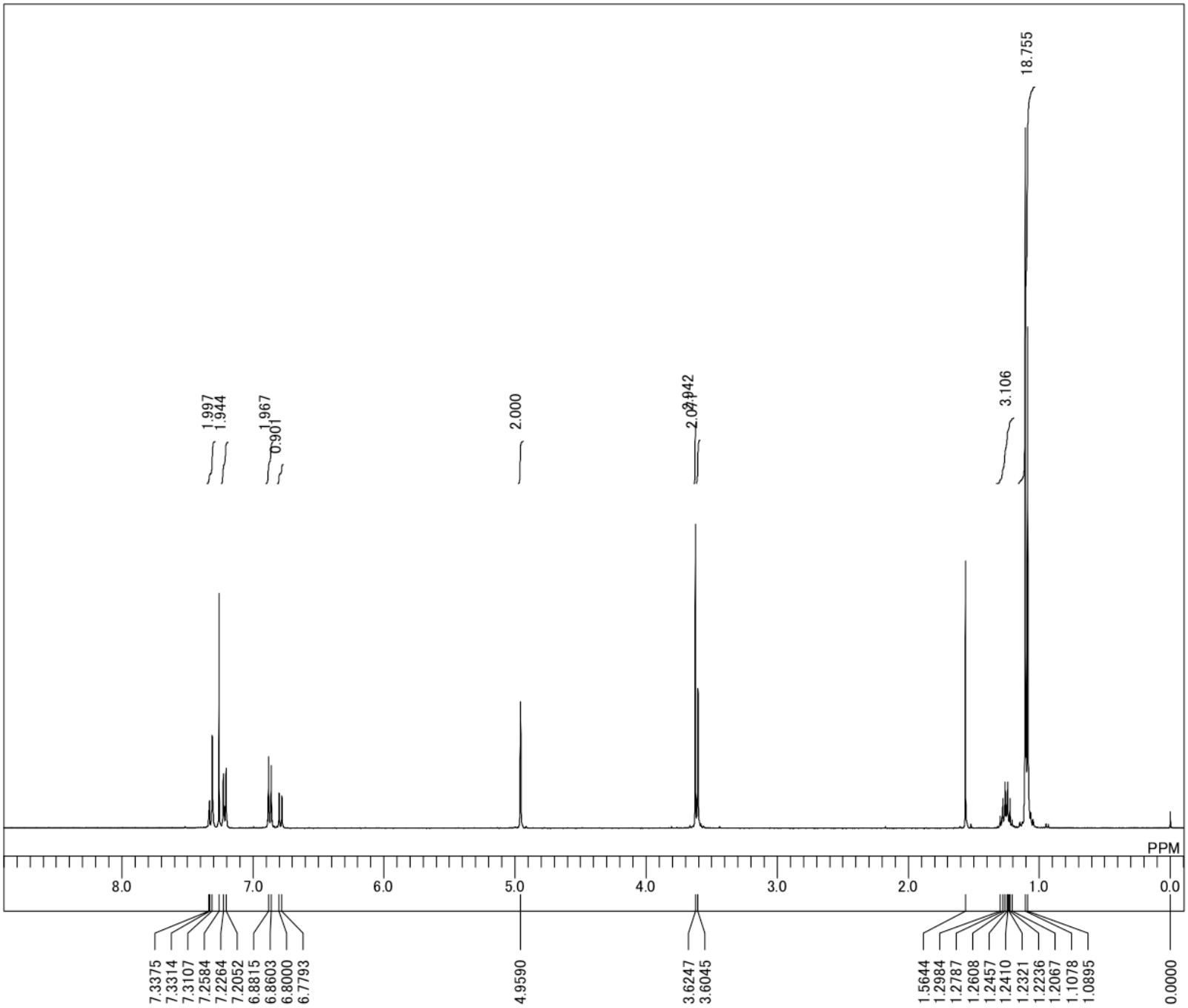
020409-1,RECRYST



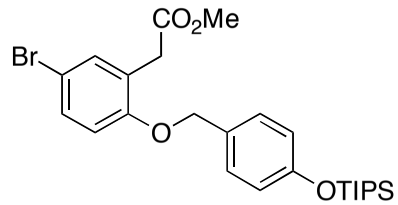
DFILE	Z01HT416C_Rh2(PTTEA)4.als
COMNT	020409-1,RECRYST
DATIM	17-APR-02 09:06:14
OBNUC	13C
EXMOD	BCM
OBFRQ	67.80 MHz
OBSET	135.00 KHz
OBFIN	5200.00 Hz
POINT	16384
FREQU	20000.00 Hz
SCANS	14421
ACQTM	0.8190 sec
PD	2.1810 sec
PW1	3.70 usec
IRNUC	1H
CTEMP	23.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	27



3b

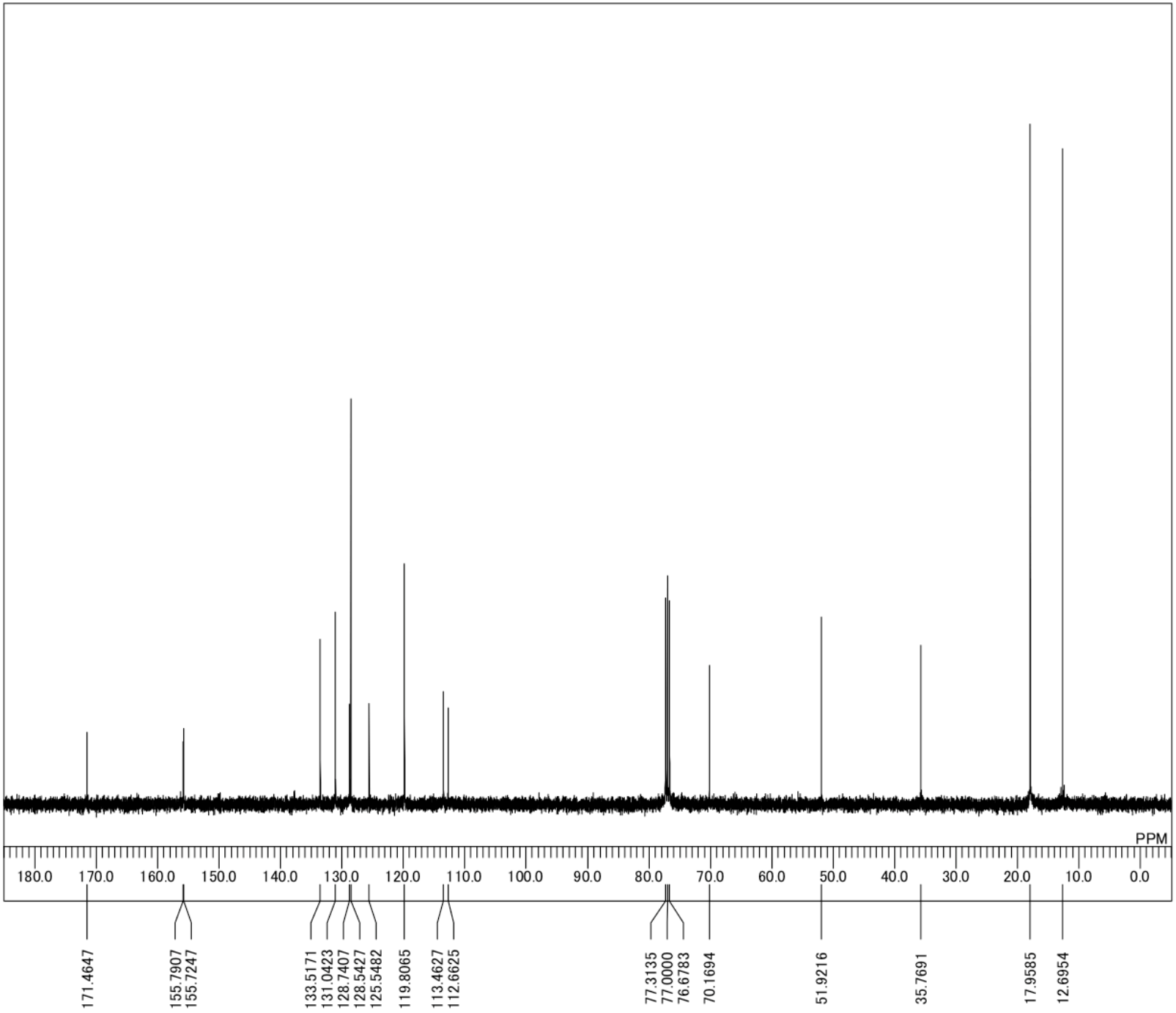


DFILE	YN06009Q.als
COMNT	
DATIM	Sat Nov 11 16:48:59 2006
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	135.30 KHz
OBFIN	13.40 Hz
POINT	32768
FREQU	6165.20 Hz
SCANS	16
ACQTM	5.3150 sec
PD	3.0000 sec
PW1	5.30 usec
IRNUC	1H
CTEMP	18.9 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	14

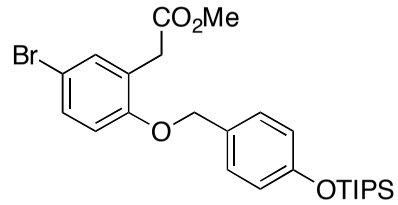


13

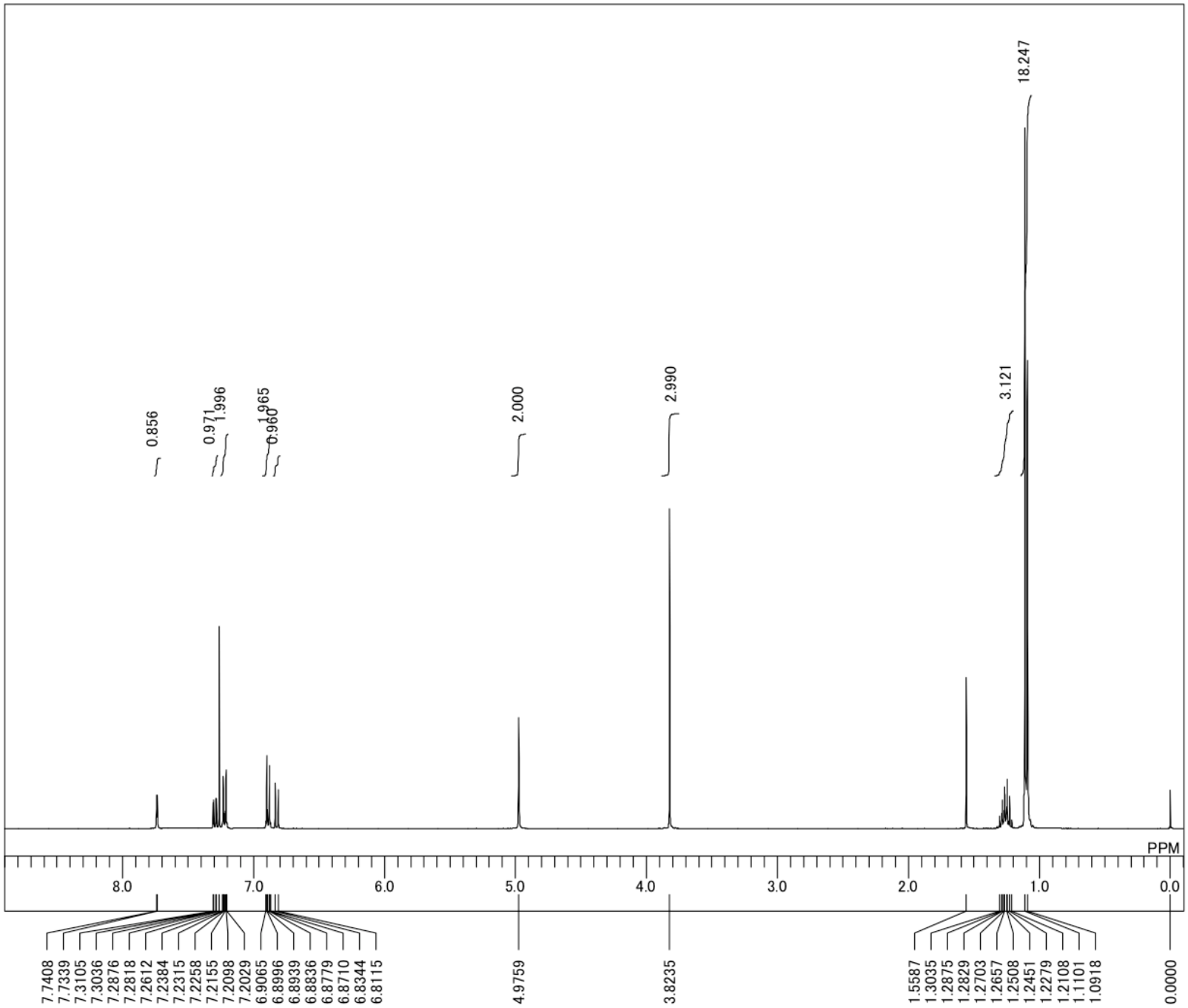
YN06021P_13C



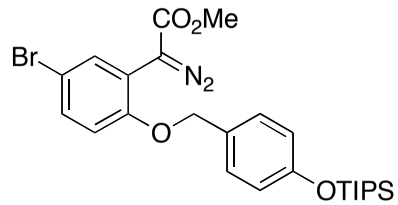
DFILE	YN06021P_13C.als
COMNT	YN06021P_13C
DATIM	Thu Dec 14 17:00:43 2006
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27173.90 Hz
SCANS	332
ACQTM	1.2059 sec
PD	1.7940 sec
PW1	4.50 usec
IRNUC	1H
CTEMP	19.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	23



13

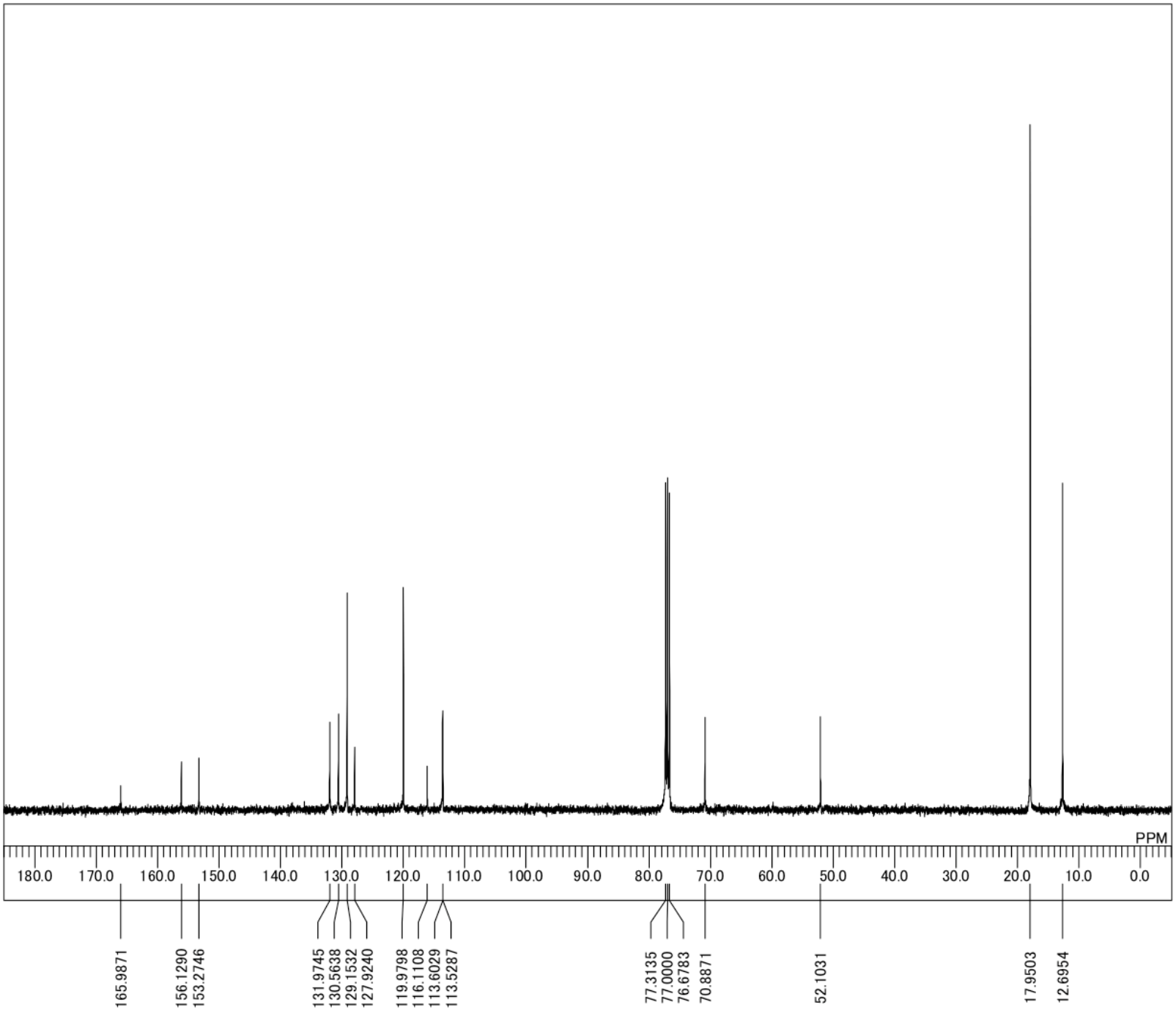


DFILE	YN_phenyldiazoacetate-1.jdf
COMNT	
DATIM	28-10-2008 21:38:15
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	16384
FREQU	7422.80 Hz
SCANS	16
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	5.65 usec
IRNUC	1H
CTEMP	20.7 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	40

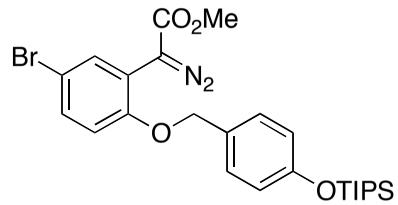


9a

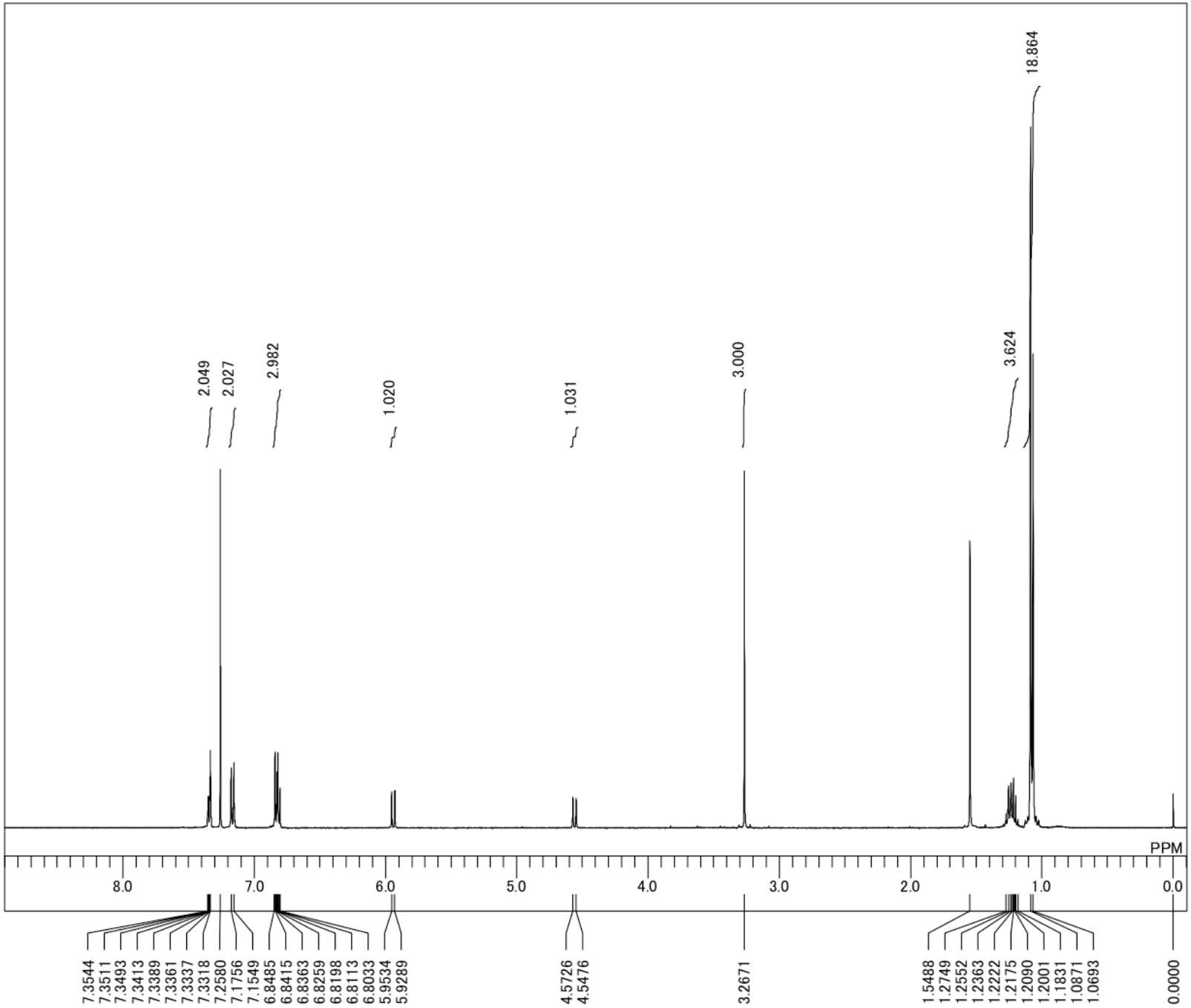
YN06027P_13C



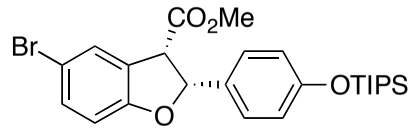
DFILE	YN06027P_13C.als
COMNT	YN06027P_13C
DATIM	Thu Dec 14 13:30:45 2006
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27173.90 Hz
SCANS	1016
ACQTM	1.2059 sec
PD	1.7940 sec
PW1	4.50 usec
IRNUC	1H
CTEMP	19.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	23



9a

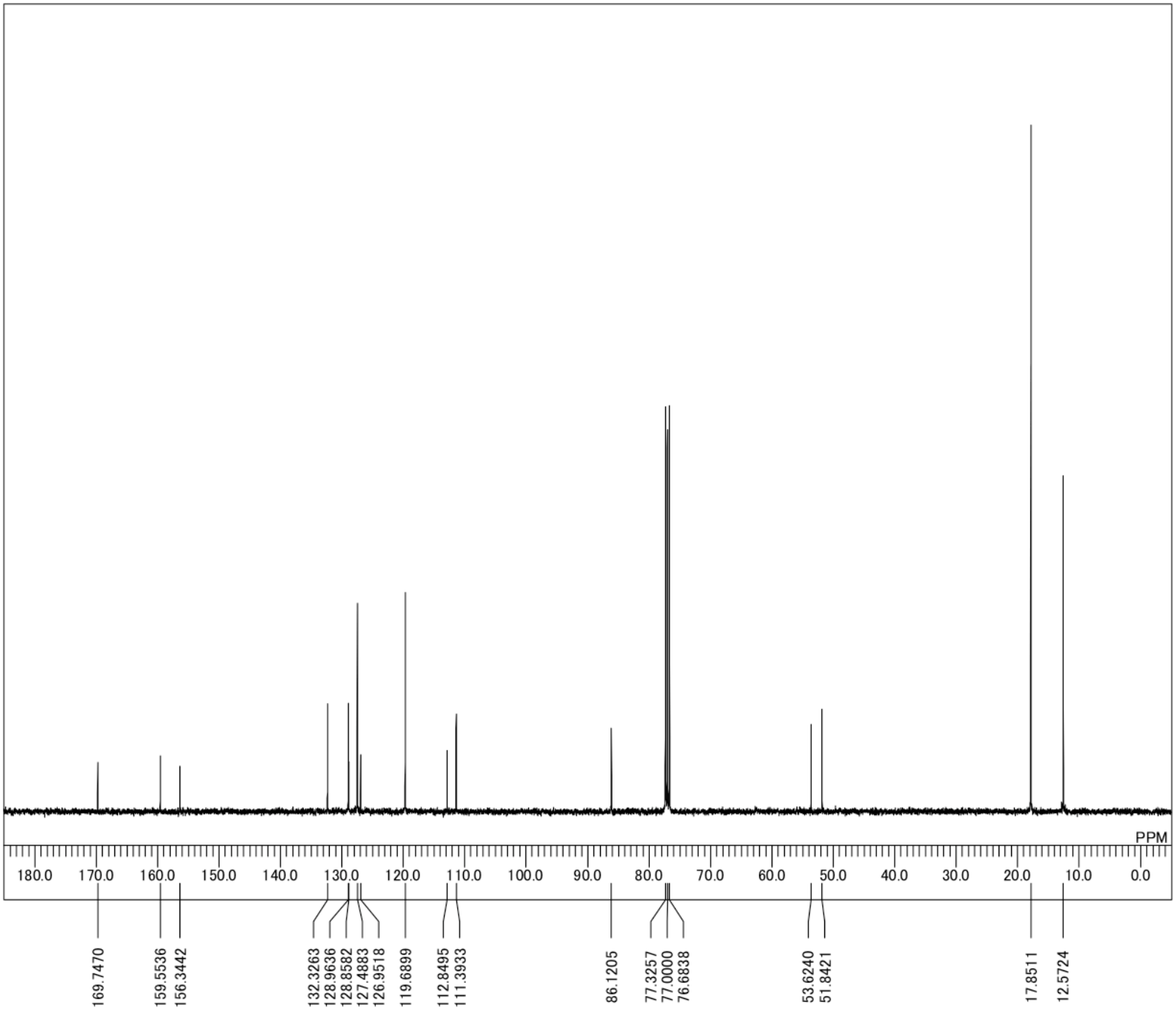


DFILE	YN04088P.als
COMNT	
DATIM	Mon Jun 19 00:16:39 2006
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	135.30 KHz
OBFIN	13.40 Hz
POINT	32768
FREQU	6165.20 Hz
SCANS	16
ACQTM	5.3150 sec
PD	3.0000 sec
PW1	5.30 usec
IRNUC	1H
CTEMP	21.8 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	14

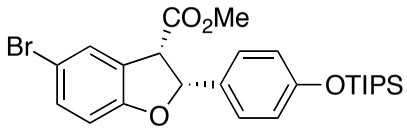


8a

13C

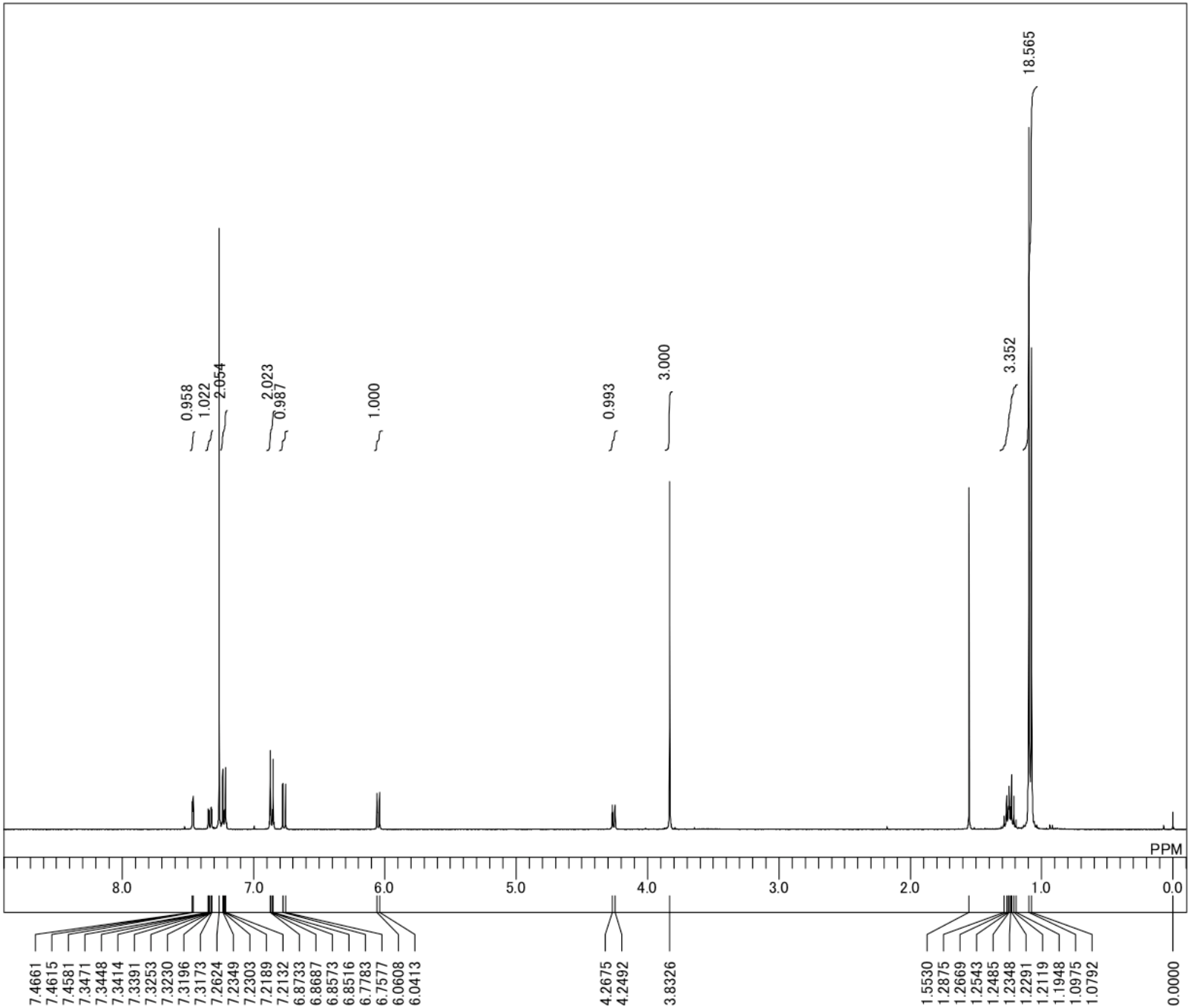


DFILE	YN06041P_13C.als
COMNT	13C
DATIM	25-01-2007 19:24:47
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	32768
FREQU	31250.00 Hz
SCANS	400
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.17 usec
IRNUC	1H
CTEMP	19.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	58

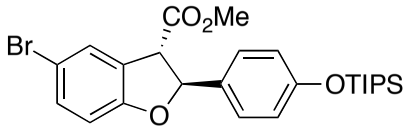


8a

YN06076P

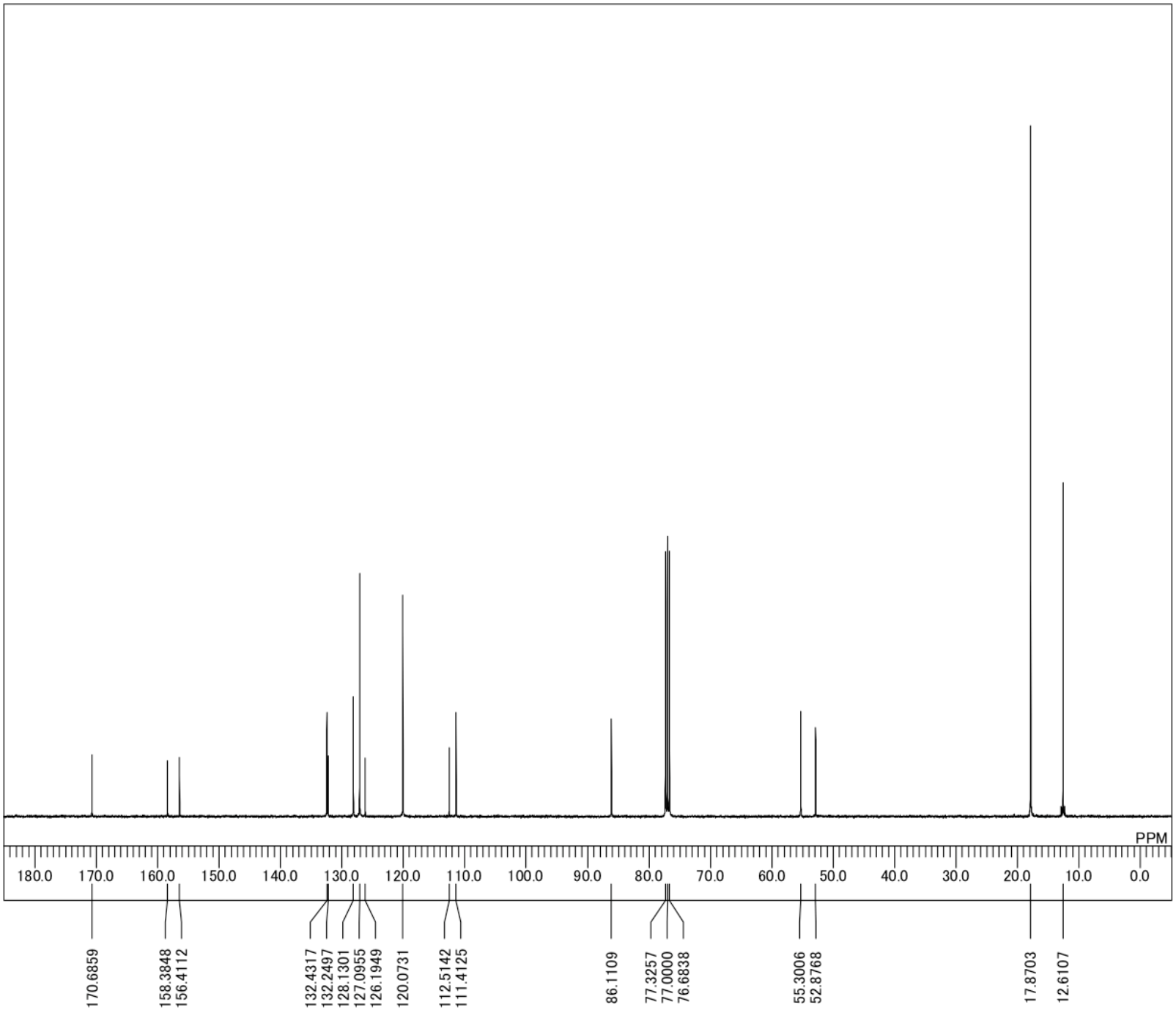


DFILE	YN06076P_trans-1.als
COMNT	YN06076P
DATIM	28-02-2007 13:59:59
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	13107
FREQU	5938.15 Hz
SCANS	8
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	5.65 usec
IRNUC	1H
CTEMP	19.5 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	44

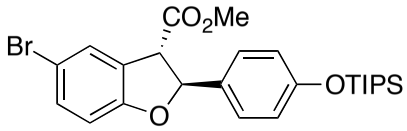


10a

YN06060Q_13C

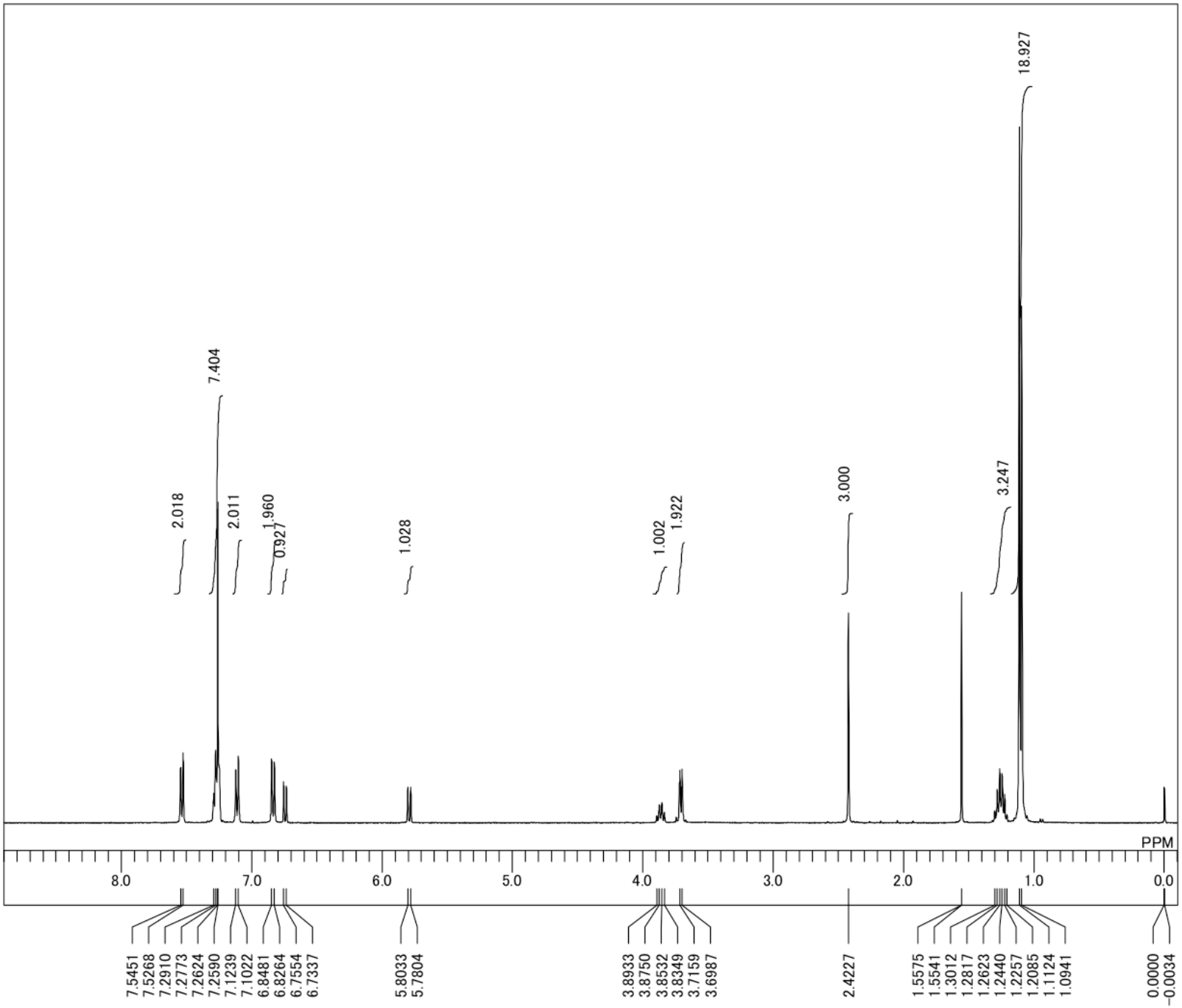


DFILE	YN06060Q_13C-1.als
COMNT	YN06060Q_13C
DATIM	12-01-2007 00:03:02
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	26214
FREQU	24999.62 Hz
SCANS	1715
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.17 usec
IRNUC	1H
CTEMP	19.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	60

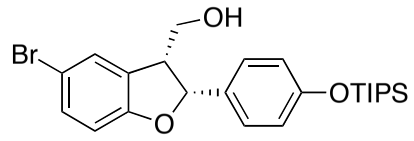


10a

YN06044P

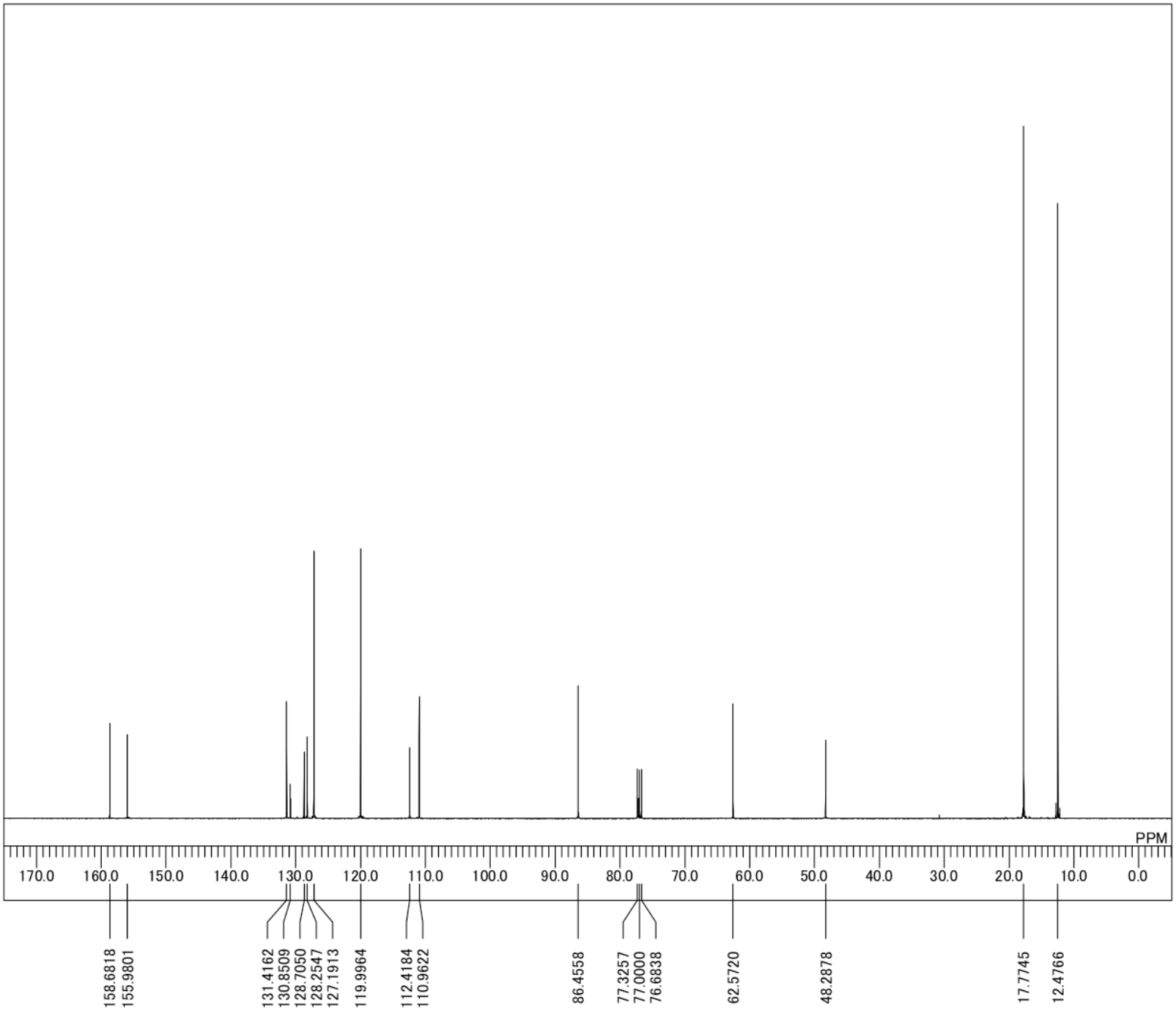


DFILE	YN06044P-1.als
COMNT	YN06044P
DATIM	25-12-2006 13:36:39
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	13107
FREQU	5938.15 Hz
SCANS	8
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	5.65 usec
IRNUC	1H
CTEMP	19.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	42

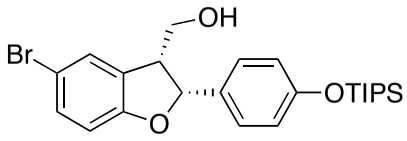


20

YN06061Q-13C

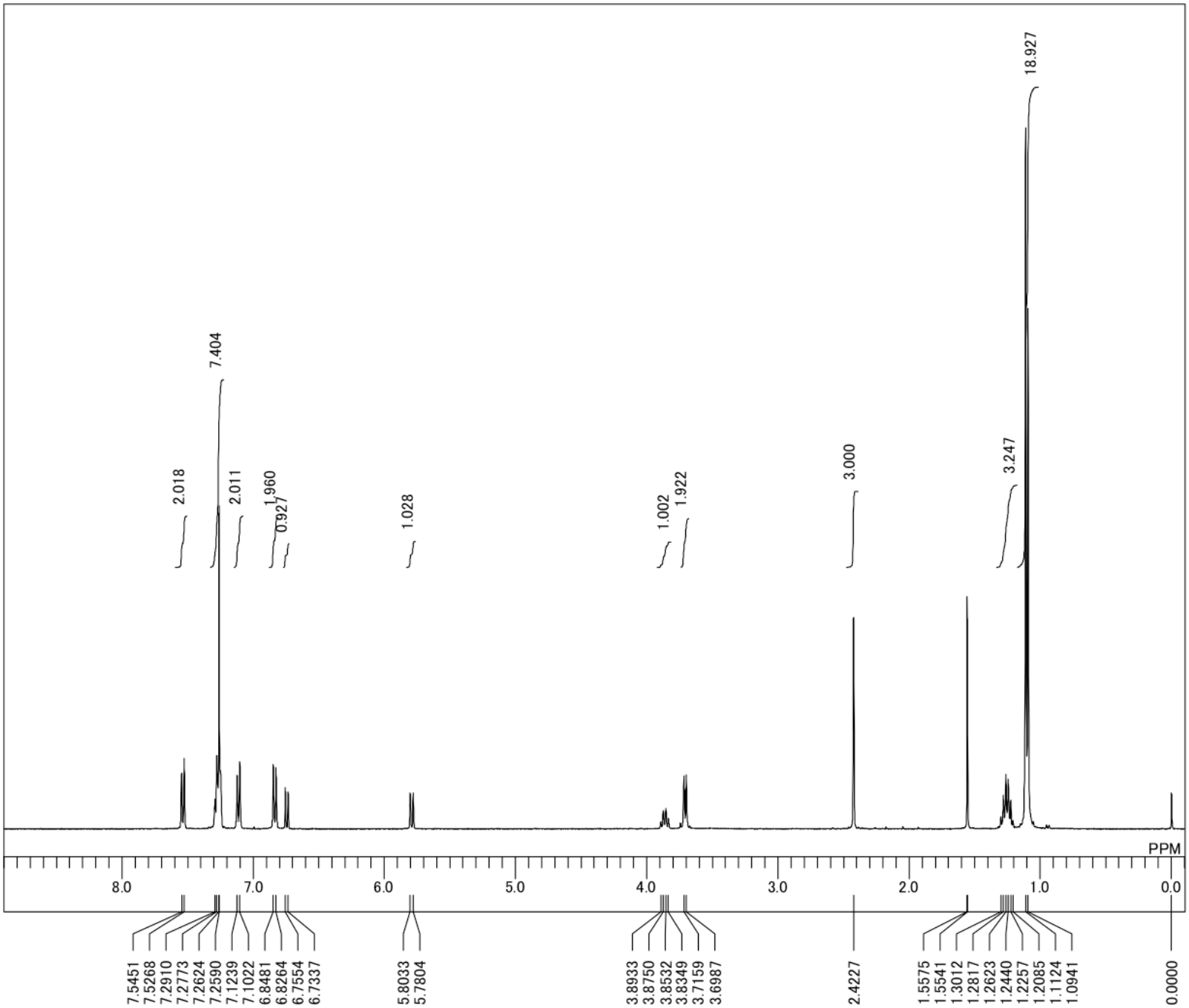


DFILE	YN06061Q_13C-1.als
COMNT	YN06061Q-13C
DATIM	13-01-2007 09:00:22
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	26214
FREQU	24999.62 Hz
SCANS	10000
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.17 usec
IRNUC	1H
CTEMP	19.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	58

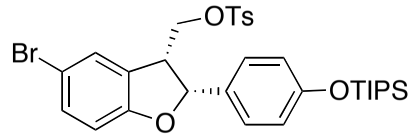


20

YN06044P

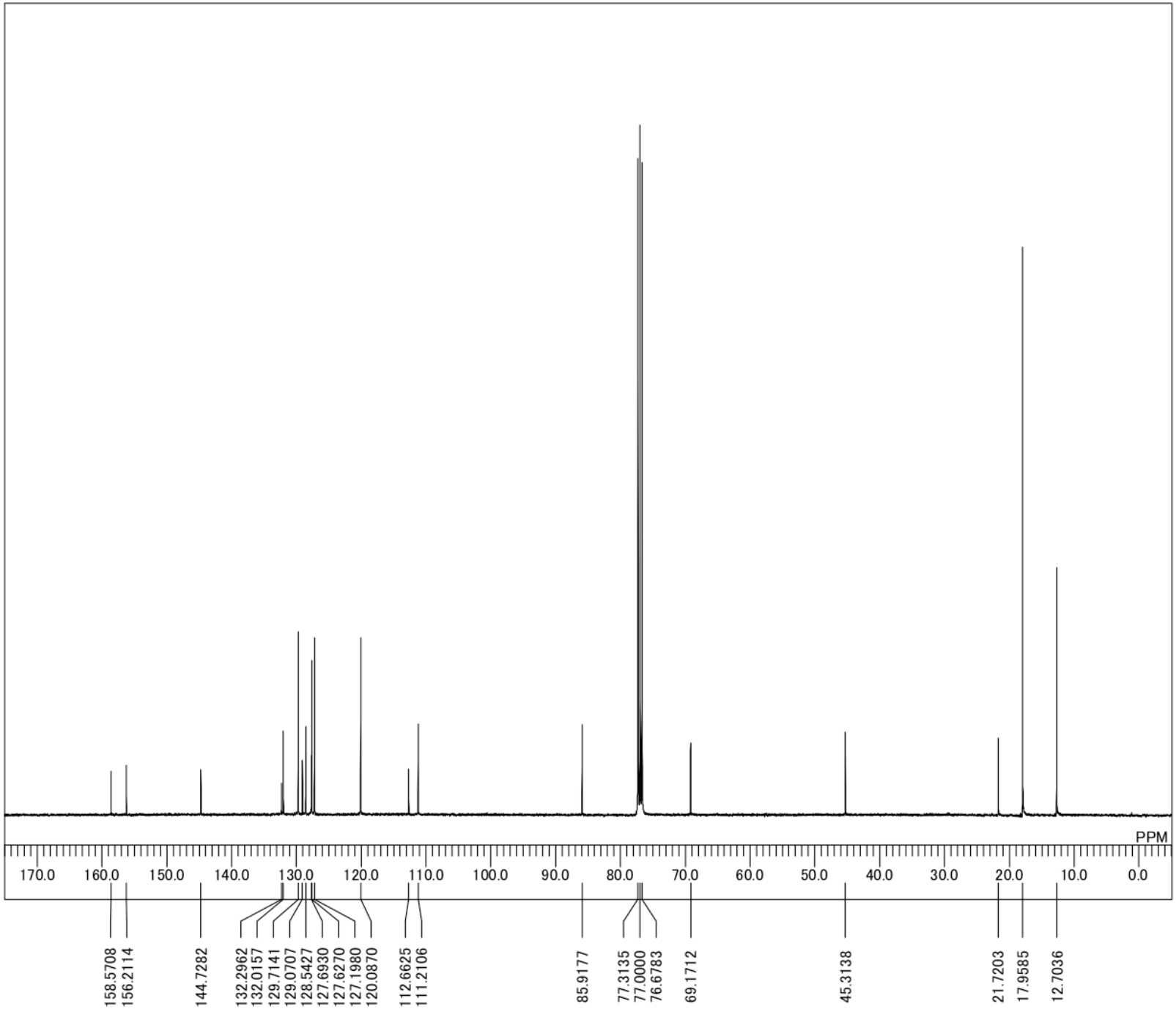


DFILE	YN06044P-1.als
COMNT	YN06044P
DATIM	25-12-2006 13:36:39
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	13107
FREQU	5938.15 Hz
SCANS	8
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	5.65 usec
IRNUC	1H
CTEMP	19.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	42

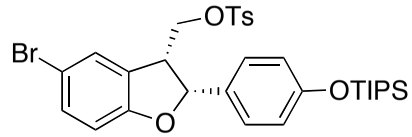


21

tosylate

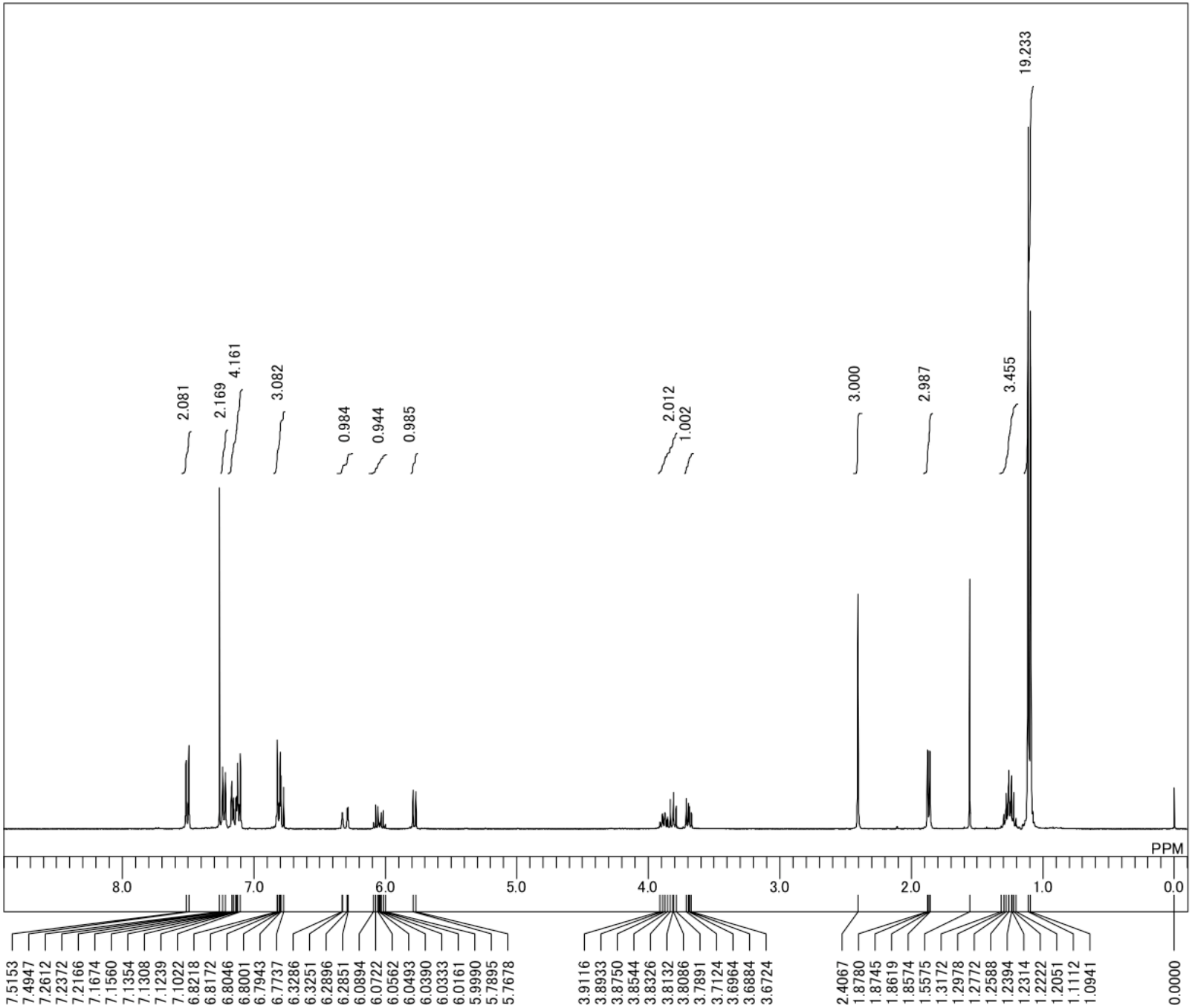


DFILE	YN04133R_C13.als
COMNT	tosylate
DATIM	Sun Jul 23 17:29:55 2006
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27173.90 Hz
SCANS	14688
ACQTM	1.2059 sec
PD	1.7940 sec
PW1	4.50 usec
IRNUC	1H
CTEMP	22.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	24

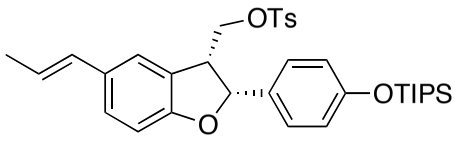


21

YN06054P

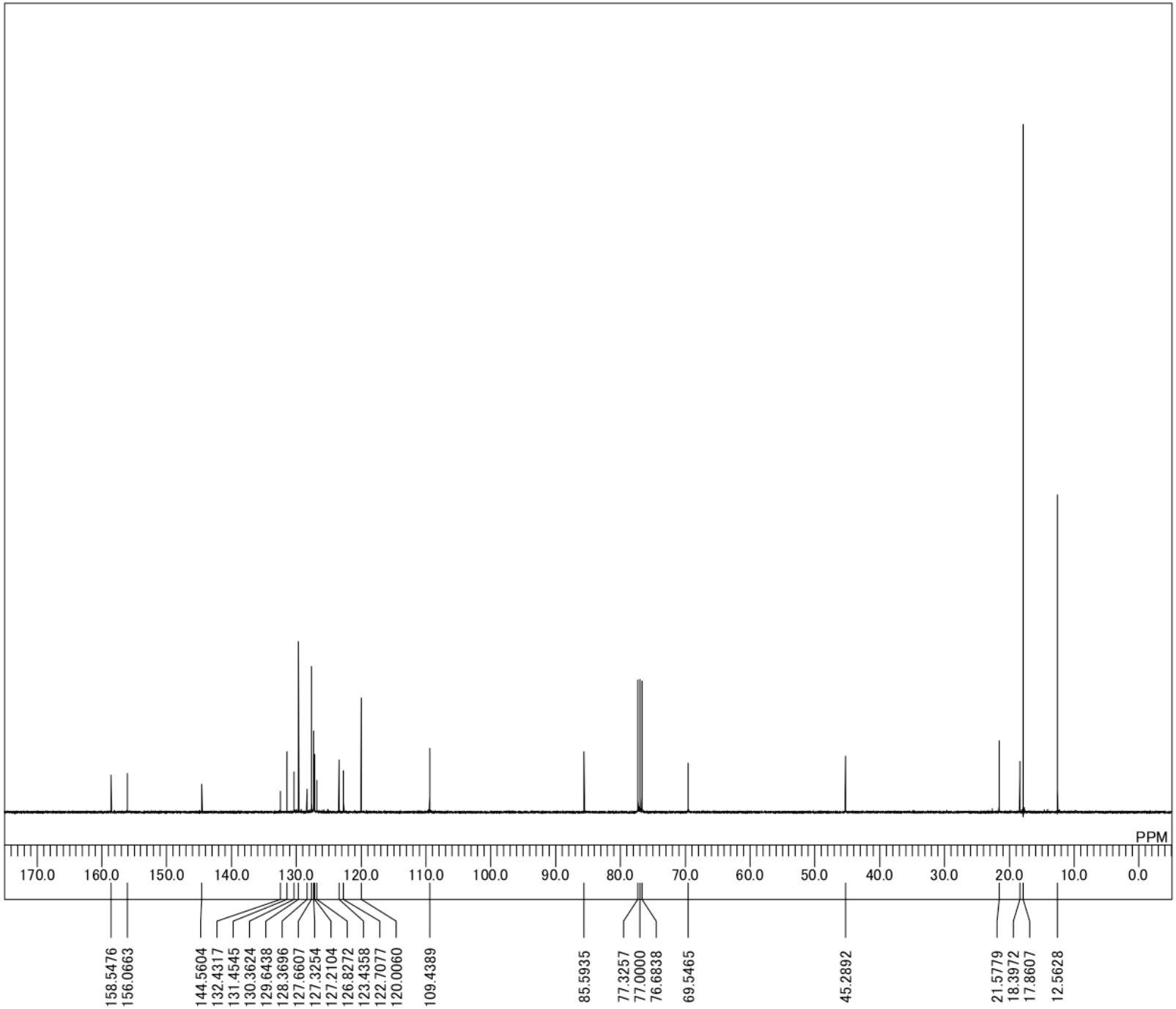


DFILE	YN06054P-1(DP).als
COMNT	YN06054P
DATIM	06-01-2007 11:23:22
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	13107
FREQU	5938.15 Hz
SCANS	8
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	5.65 usec
IRNUC	1H
CTEMP	19.6 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	40

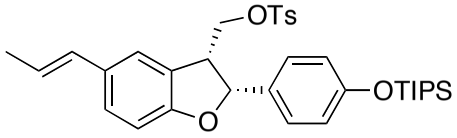


22

YN06054P_13C

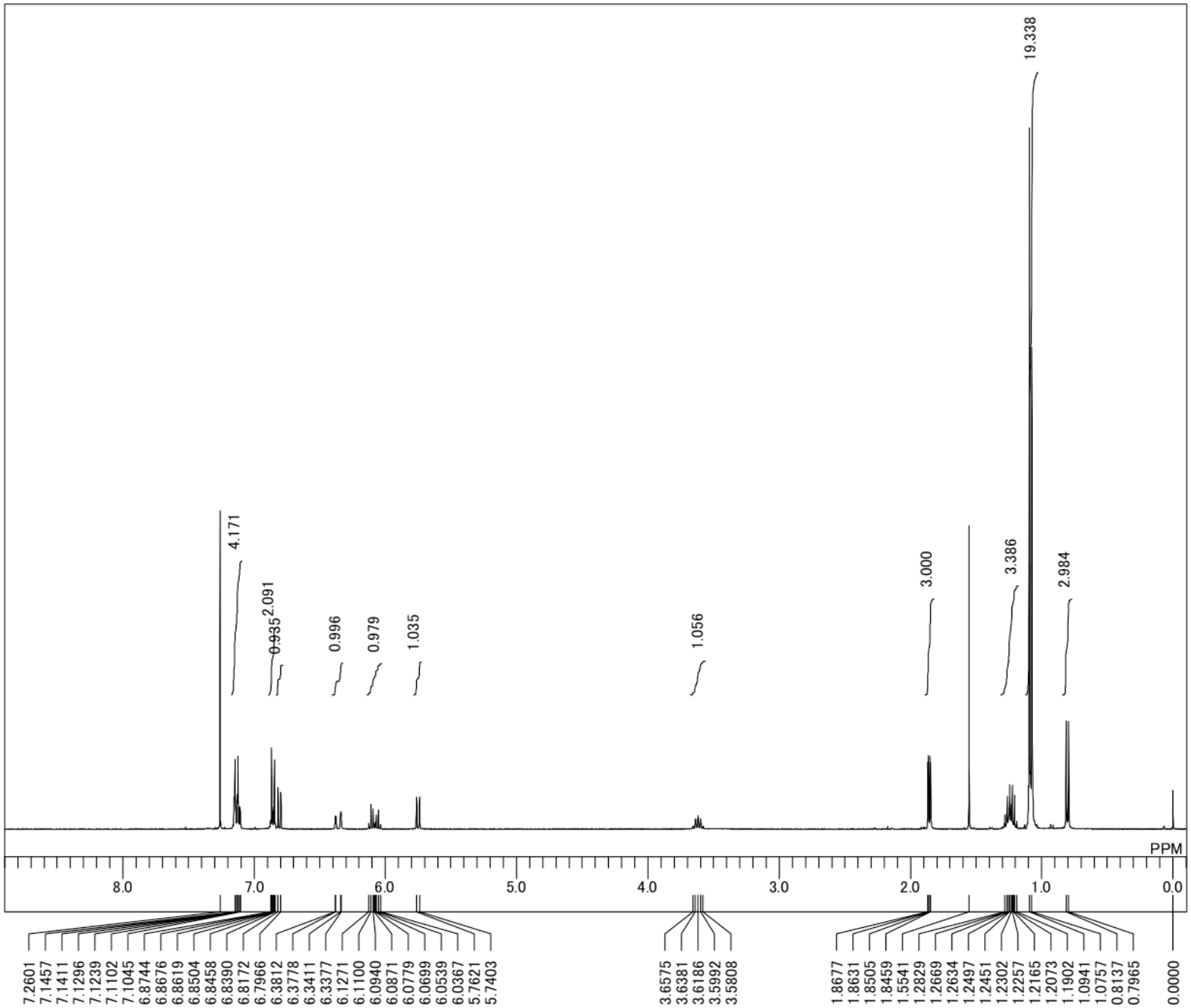


DFILE	YN06054P_13C-1(DP).als
COMNT	YN06054P_13C
DATIM	06-01-2007 12:46:38
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	26214
FREQU	24999.62 Hz
SCANS	1000
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.17 usec
IRNUC	1H
CTEMP	19.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

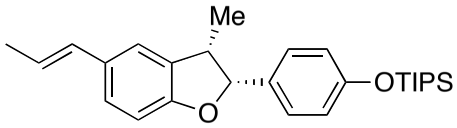


22

YN06055R_F10-12

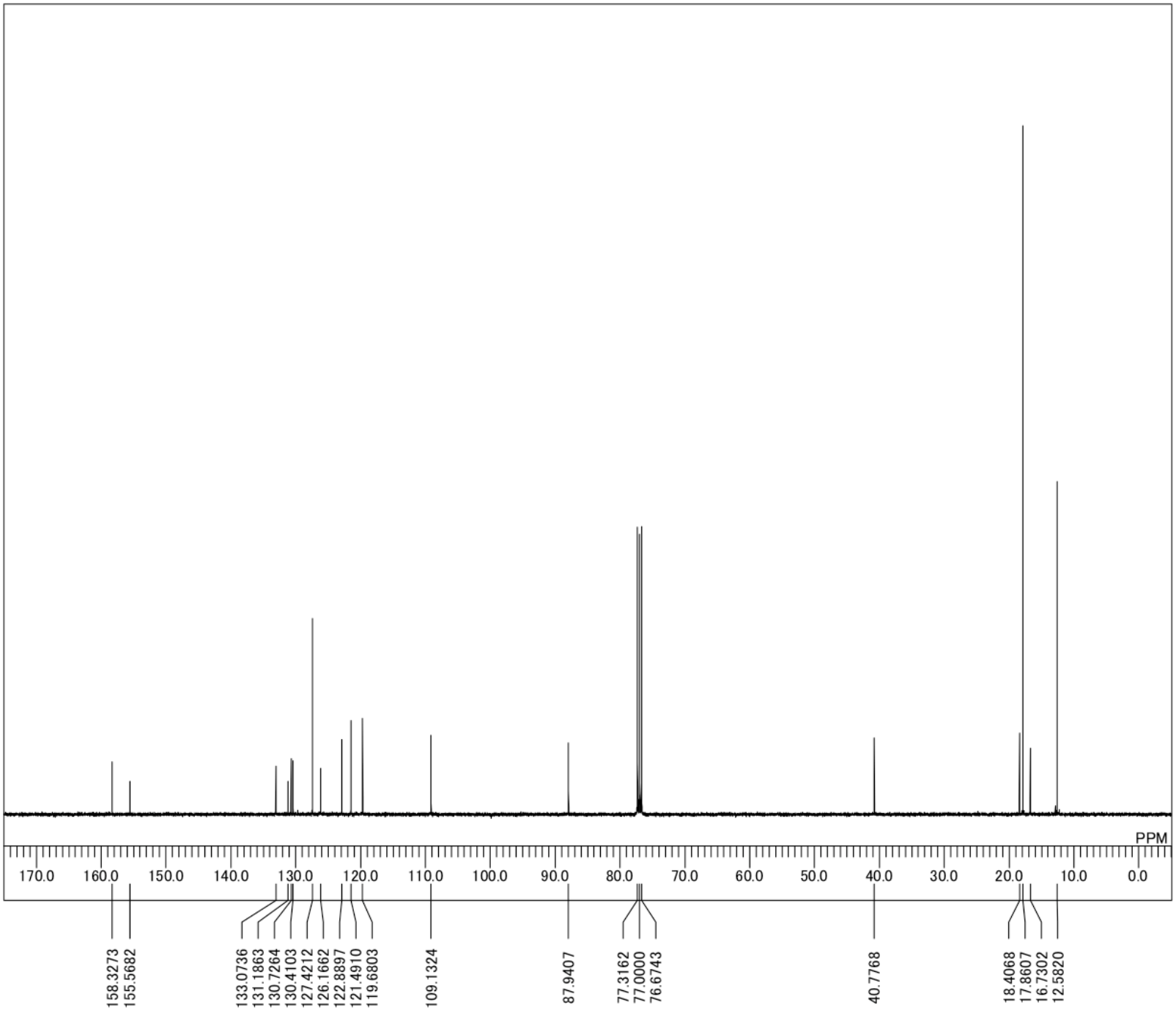


DFILE	YN06055R-1.als
COMNT	YN06055R_F10-12
DATIM	08-01-2007 08:36:06
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	13107
FREQU	5938.15 Hz
SCANS	8
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	5.65 usec
IRNUC	1H
CTEMP	19.9 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	40

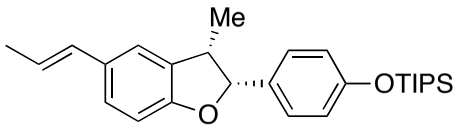


23

YN06055R_13C

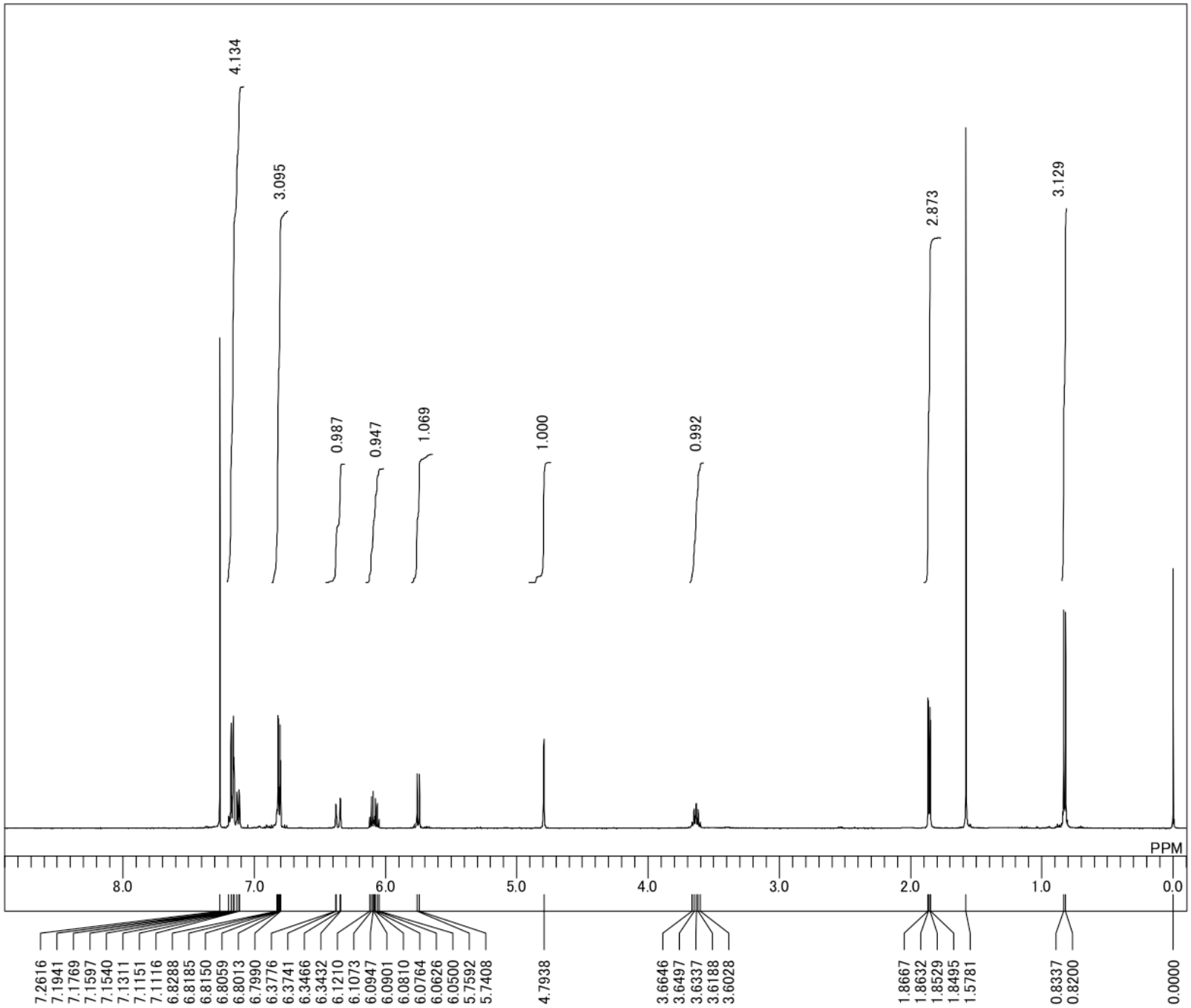


DFILE	YN06055R_13C-1.als
COMNT	YN06055R_13C
DATIM	08-01-2007 11:18:35
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	26214
FREQU	24999.62 Hz
SCANS	2265
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.17 usec
IRNUC	1H
CTEMP	19.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

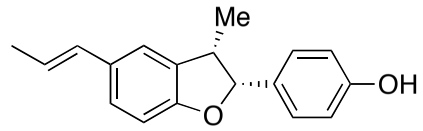


23

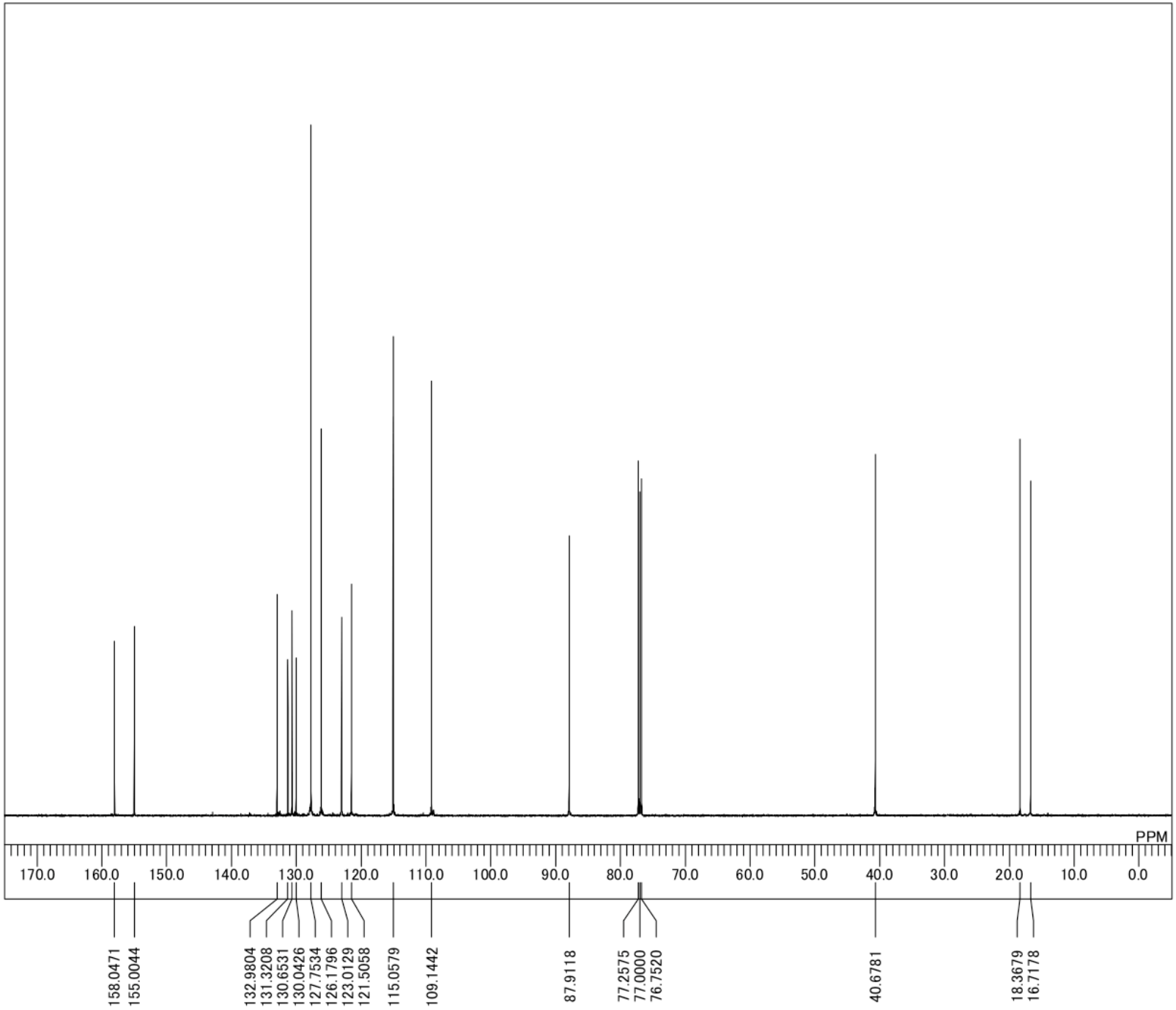
epi-conocarpan



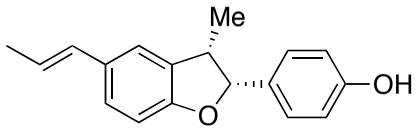
DFILE	YN12127P-1_(DP).als
COMNT	epi-conocarpan
DATIM	29-09-2008 18:38:27
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	16
ACQTM	1.7459 sec
PD	3.0000 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	20.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	50



2

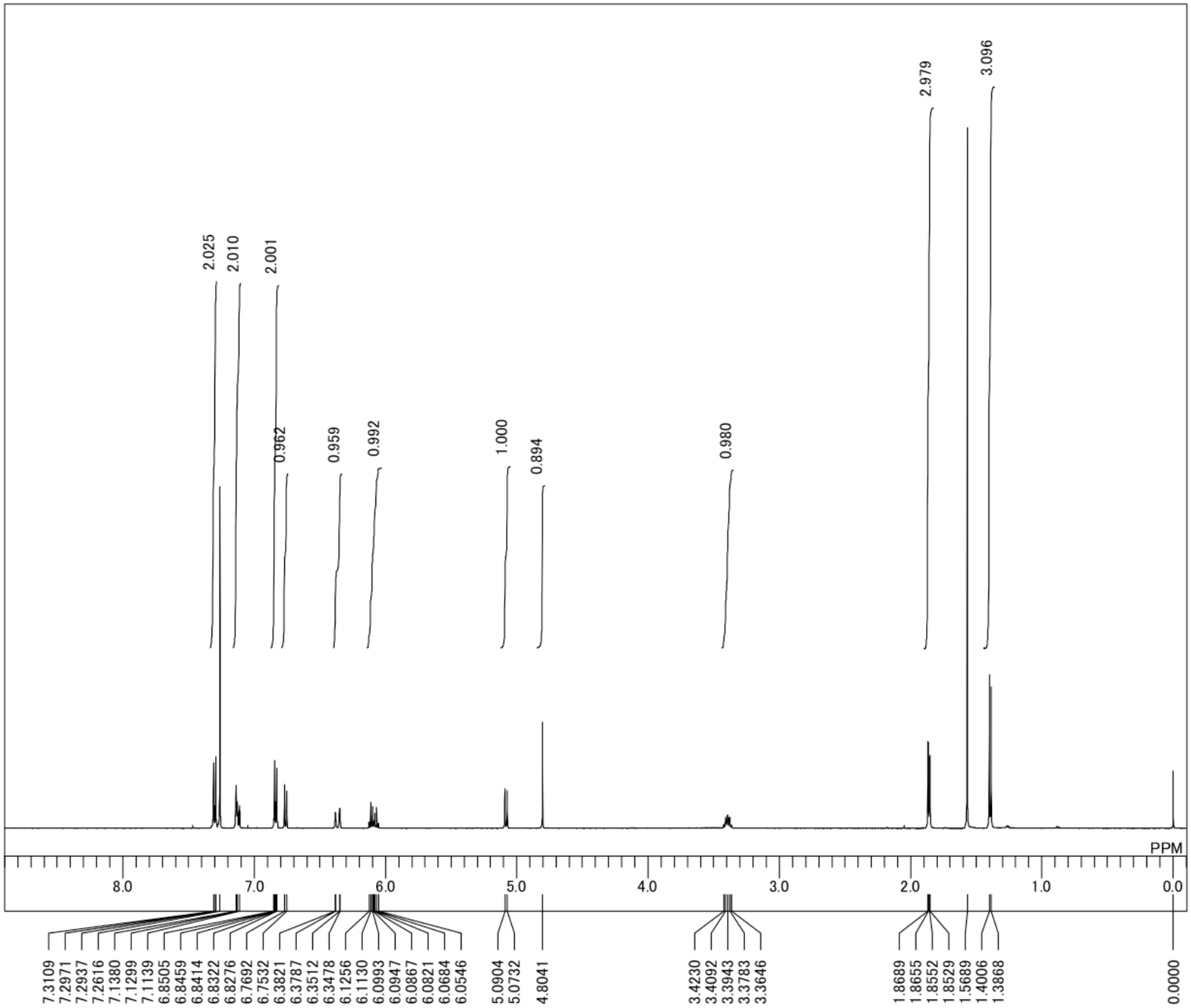


DFILE	YN12127P_3_13C-1.jdf
COMNT	
DATIM	30-09-2008 08:49:26
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	32768
FREQU	39308.18 Hz
SCANS	11551
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.33 usec
IRNUC	1H
CTEMP	20.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

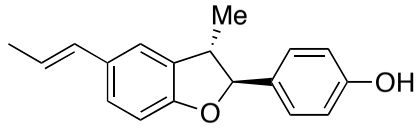


2

YN12135P_first crops

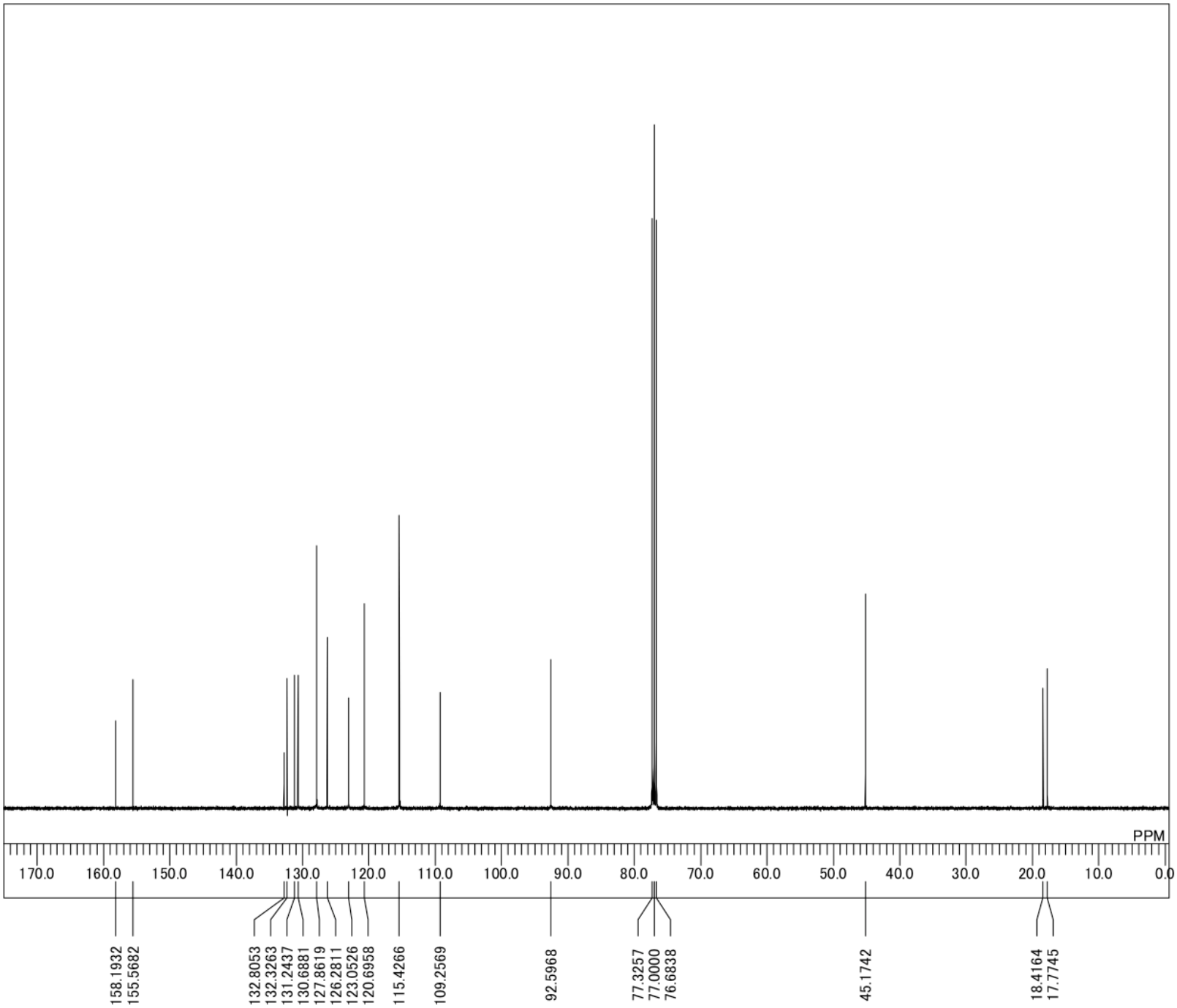


DFILE	YN12135P_first crops-1.als
COMNT	YN12135P_first crops
DATIM	06-10-2008 11:17:37
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	16
ACQTM	1.7459 sec
PD	3.0000 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	20.2 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	52

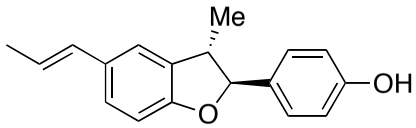


1

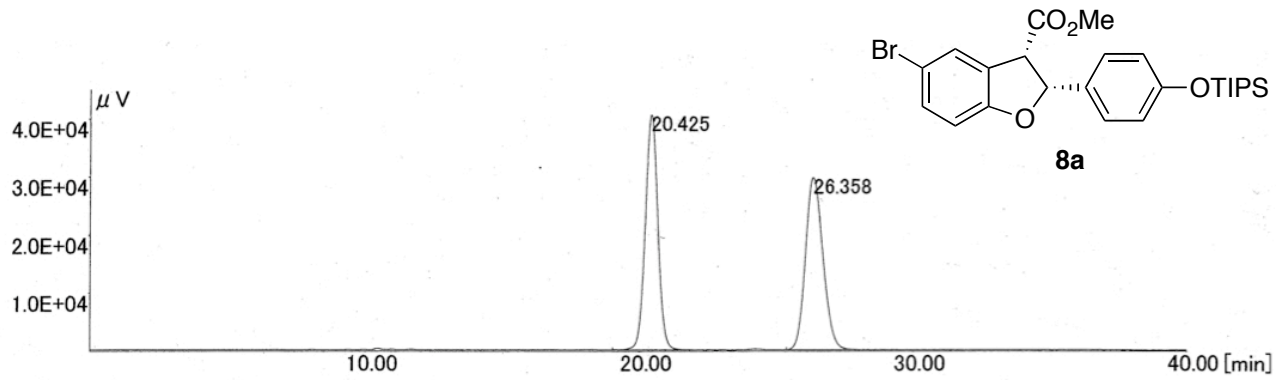
YN12135P_1st crops_13C



DFILE	YN12135P_1st crops_13C-1.als
COMNT	YN12135P_1st crops_13C
DATIM	07-10-2008 09:06:49
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	26214
FREQU	24999.62 Hz
SCANS	10154
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.17 usec
IRNUC	1H
CTEMP	19.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

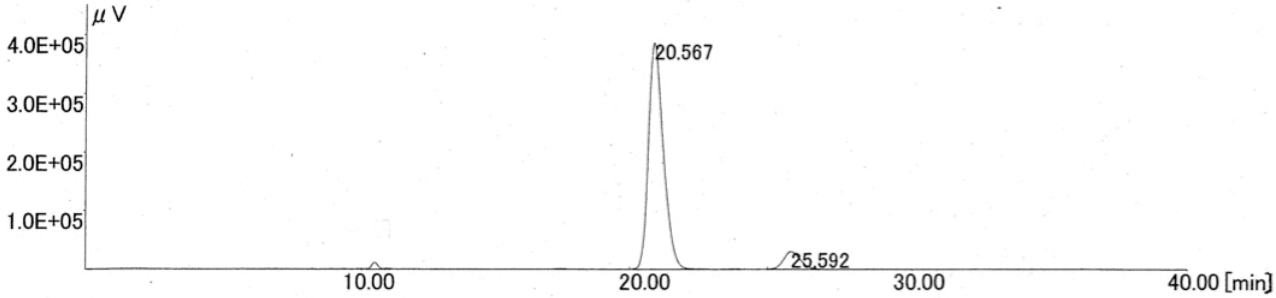


1



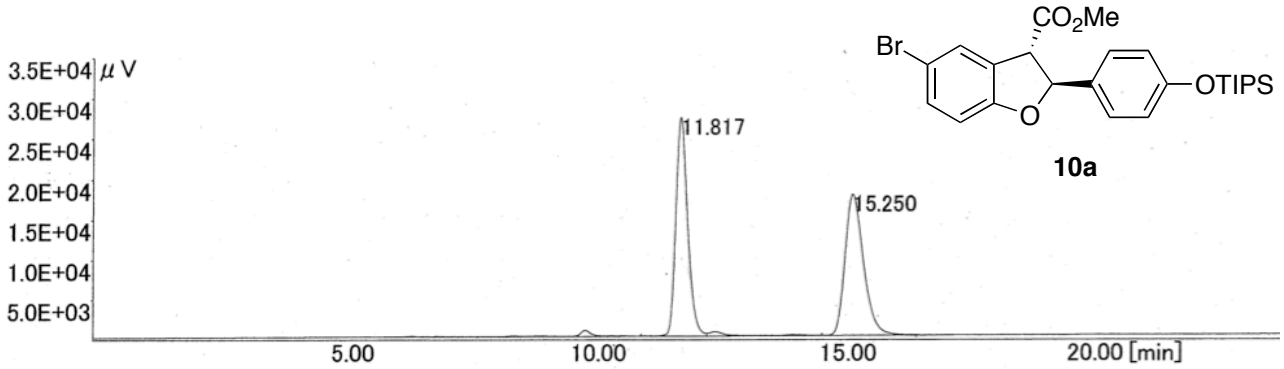
8a (racemate)

Peak No.	Time (min)	Area [μV˙sec]	Area %
1	20.43	1297146	50.21
2	26.36	1286267	49.79



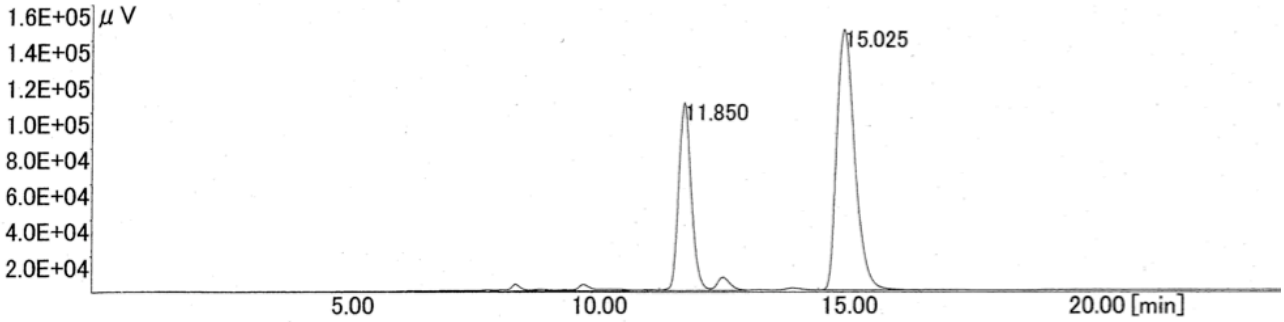
8a

Peak No.	Time (min)	Area [μV˙sec]	Area %
1	20.57	14611856	92.10
2	25.59	1253687	7.90



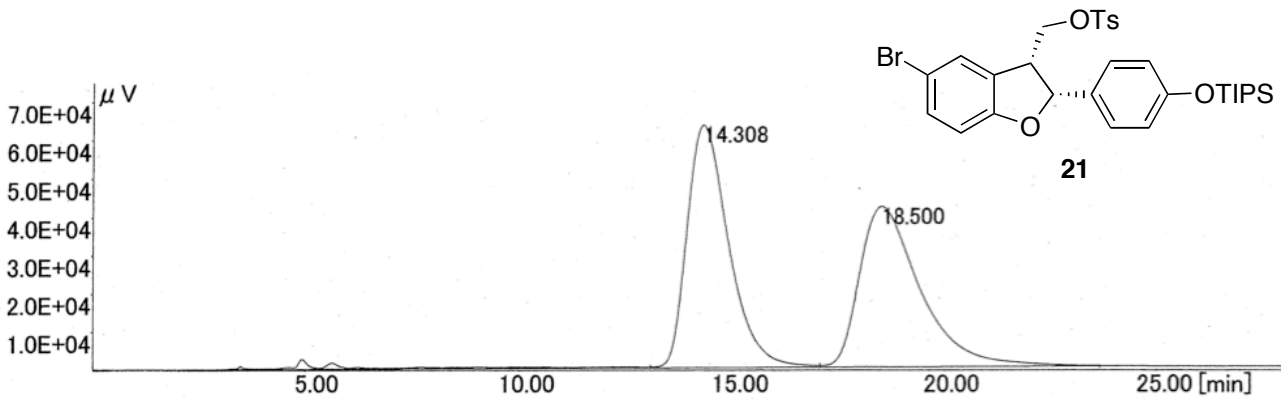
10a (racemate)

Peak No.	Time (min)	Area [μV˜sec]	Area %
1	11.82	452079	49.94
2	15.25	453180	50.06



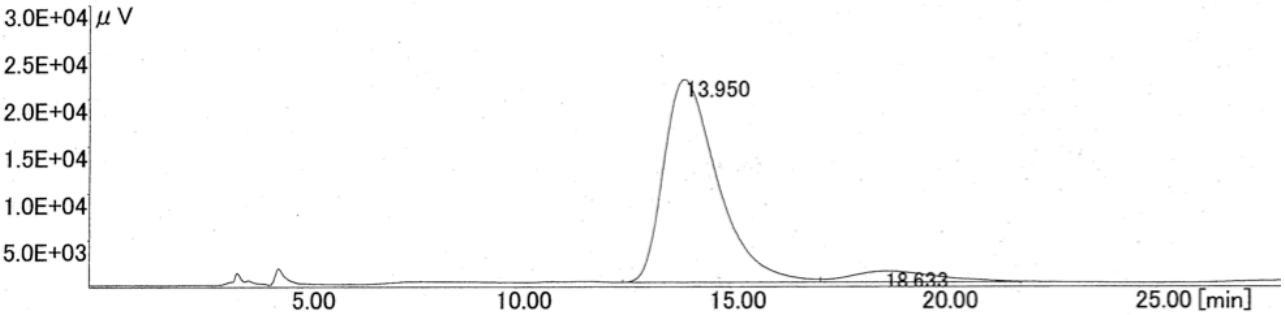
10a

Peak No.	Time (min)	Area [μV˜sec]	Area %
1	11.85	1826356	33.83
2	15.03	3572047	66.17



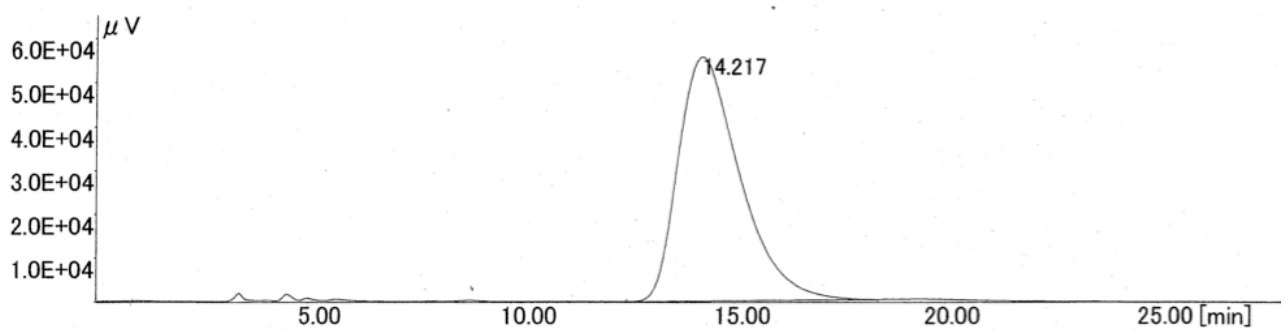
21 (racemate)

Peak No.	Time (min)	Area [μV˙sec]	Area %
1	14.31	4247935	50.01
2	18.50	4246675	49.99



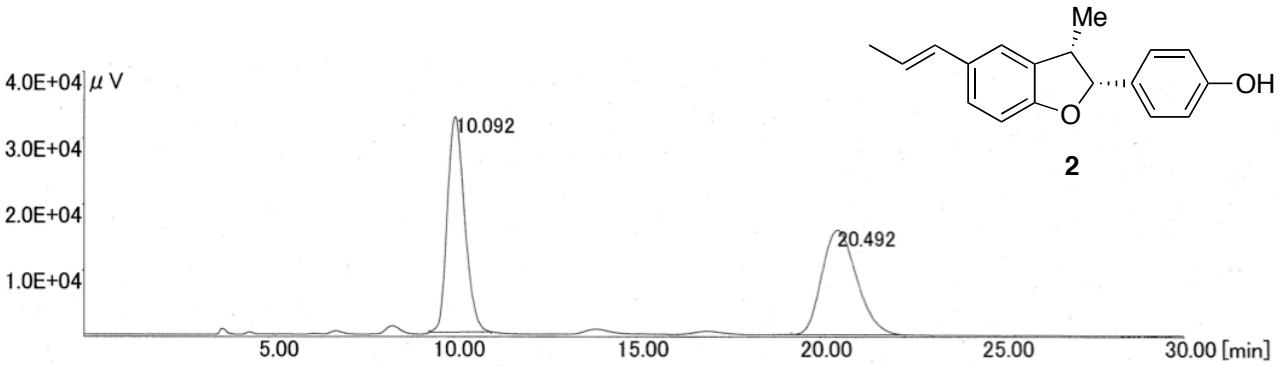
21

Peak No.	Time (min)	Area [μV˙sec]	Area %
1	13.95	1873743	92.11
2	18.63	160531	7.89



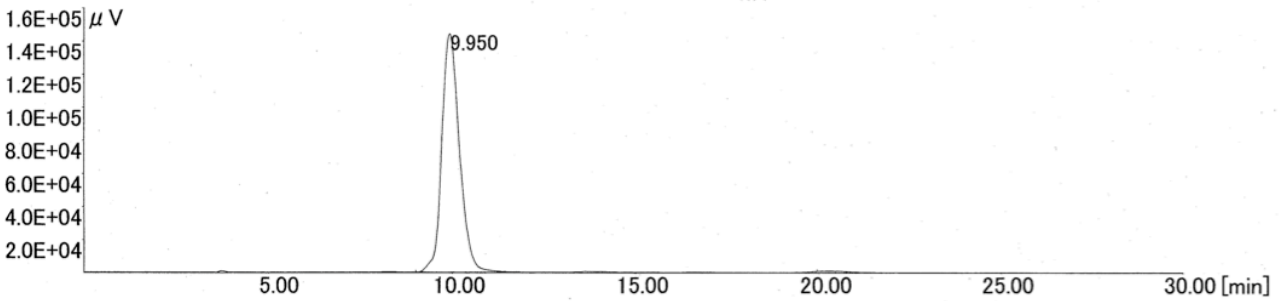
21 (optically pure)

Peak No.	Time (min)	Area [μV˙sec]	Area %
1	14.22	5576513	100.00



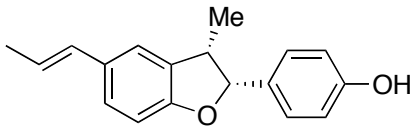
racemate of *epi*-conocarpan

Peak No.	Time (min)	Area [□V-sec]	Area %
1	10.09	1064994	50.22
2	20.49	1055461	49.78

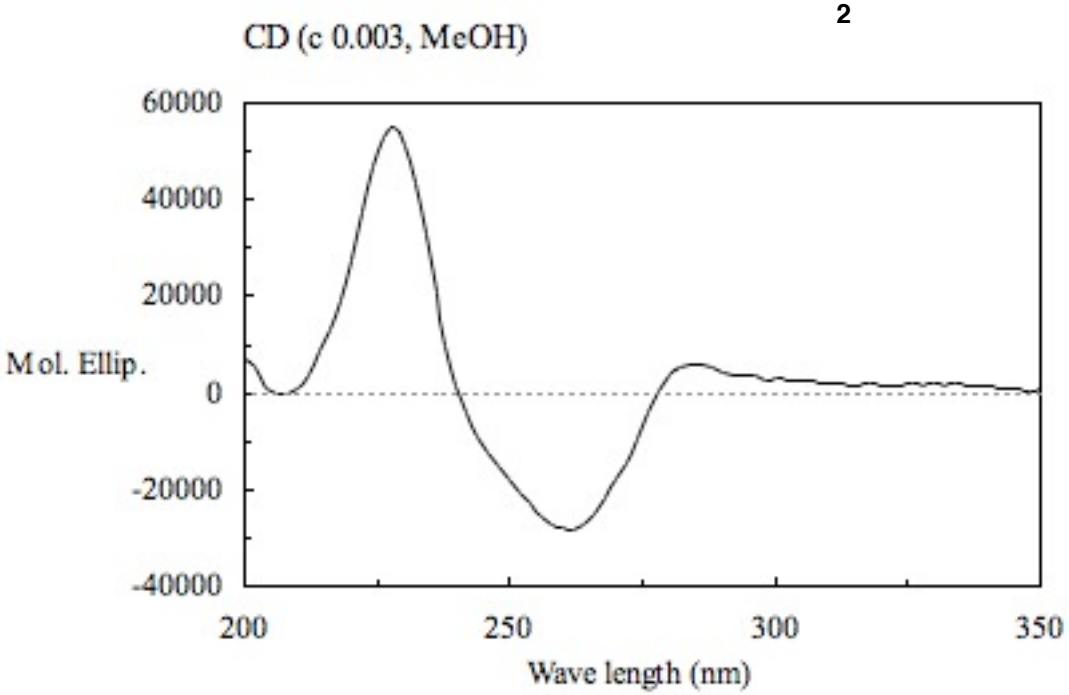


synthetic (–)-*epi*-conocarpan

Peak No.	Time (min)	Area [□V-sec]	Area %
1	9.95	4830618	100.00


Me
OH
O

2


CD (c 0.003, MeOH)
60000
40000
20000
Mol. Ellip.
0
-20000
-40000
200
250
300
350
Wave length (nm)