Supporting Information

Catalytic Enantioselective Construction of β-Quaternary Carbons via a Conjugate Addition of Cyanide to β,β-Disubstituted α,β-Unsaturated Carbonyl Compounds

Yuta Tanaka, Motomu Kanai,* and Masakatsu Shibasaki*

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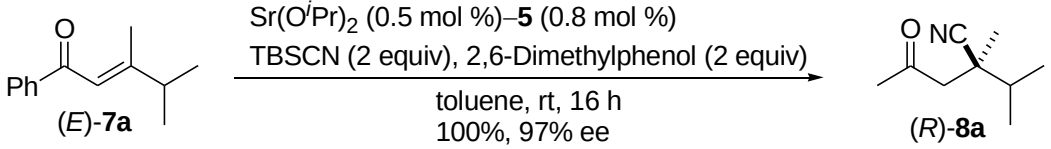
1. General Method: ^{1}H NMR spectra were recorded on a JEOL JNM-LA500 spectrometer, operating at 500 MHz for ^{1}H NMR and 125.65 MHz for ^{13}C NMR. Chemical shifts were reported downfield from TMS (δ = 0 ppm) for ^{1}H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to the solvent used as an internal reference. Optical rotations were measured on a JASCO P-1010 polarimeter. ESI-TOF mass spectra were measured on JEOL JMS-T100LC. Column chromatographies were performed with silica gel Merck 60 (230-400 mesh ASTM). The enantiomeric excess (ee) was determined by HPLC or GC analysis. HPLC analysis was performed on JASCO HPLC systems consisting of the following: pump, 880-PU or PU-980; detector, 875-UV, UV-970, or RI930, measured at 254 nm or RI; mobile phase, hexane–2-propanol. GC analysis was performed Shimazu GC-14A with Varian Chirasil DEX CB column (0.25 mm x 25 m). In general, reactions were carried out under an argon atmosphere. $Sr(O^{i}Pr)_2$ was purchased from Kojundo Chemical Laboratory Co., Ltd. (Fax:

+81-492-84-1351, sales@kojundo.co.jp). Chiral ligand **1** was prepared by reported methods.[1]

2. General Procedure for the Catalytic Enantioselective Conjugate Addition of Cyanide to β,β-Disubstituted Enones and β,β-Disubstituted α,β-Unsaturated *N*-acylpyrroles (Table 2, entry 1):

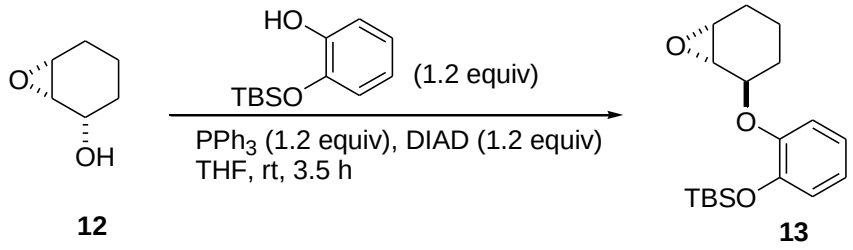


To a solution of ligand **5** (3.9 mg, 8.3 μmol) in THF (500 μL), Sr(O*i*Pr)$_2$ (0.10 M solution in THF, 50 μL, 5 μmol) was added at room temperature. Then, the solvent was evaporated. After drying the resulting pre-catalyst under reduced pressure (<5 mmHg) for 1 h, toluene (1 mL) was added, and the mixture was stirred for 30 min at room temperature. 100 μL of the catalyst solution was transferred to a reaction vessel using a gas-tight syringe, and was used for the asymmetric cyanation reaction. To the catalyst solution, (*E*)-**7a** (19.0 μL, 18.8 mg, 0.10 mmol) was added. A solution prepared by mixing TBSCN (28.3 mg, 0.20 mmol) and 2,6-dimethylphenol (22.4 mg, 0.20 mmol) in toluene (0.1 mL) at room temperature for 20 minutes, was added to the reaction mixture. After stirring the reaction mixture at room temperature for 16 h, the reaction mixture was directly loaded on column in a well-ventilated hood (caution! Highly toxic HCN is generated), and purified by flash column chromatography (silica gel, AcOEt-hexane, 1:10) to afford the **8a** (22.3 mg, 0.104 mmol) in 100% yield as a colorless oil. The enantiomeric excess of the product was determined by HPLC analysis to be 97% ee.

3. Ligand Synthesis

(3-A) Synthesis of 2 and 3

(1*R*,2*R*,6*R*)-2-(2'-*t*Butyldimethylsilyloxyphenoxy)-7-oxabicyclo[4.1.0] heptane (13)

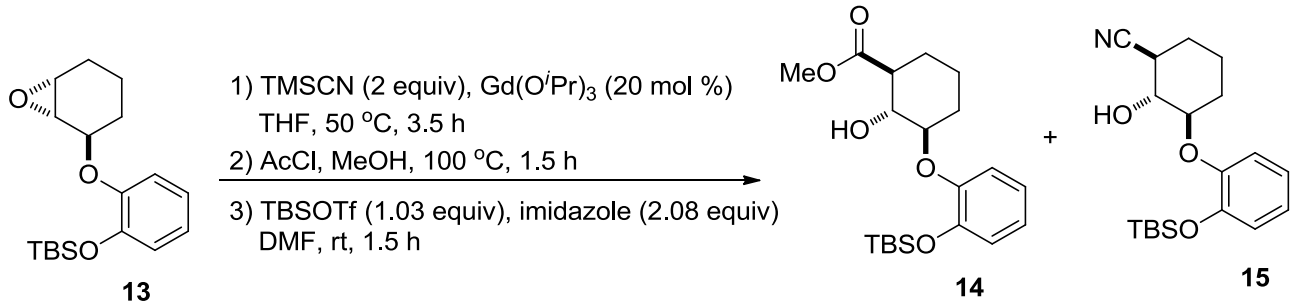


12 was prepared by reported methods (>99% ee).[1] To a solution of PPh_3 (136 mg, 0.52 mmol, 1.2 equiv) and 2-*t*-butyldimethylsilyloxyphenol (117 mg, 0.52 mmol, 1.2 equiv) in THF (1.5 mL), DIAD (diisopropyl azodicarboxylate, 102 μL, 0.52 mmol, 1.2 equiv) was added dropwise with cooling in an ice bath. Epoxy alcohol **12** (49 mg, 0.43 mmol) in THF (0.5 mL) was added dropwise to the mixture, and the mixture was warmed to room temperature. After stirring for 3.5 h, water was added, and the organic layer was separated. The aqueous layer was extracted with EtOAc twice, and the combined organic layers were washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (silica gel, hexane-EtOAc, 200:1) to afford **13** (122 mg, 0.38 mmol) as a

[1] Fujimori, I.; Mita, T.; Maki, K.; Shiro, M.; Sato, A.; Furusho, S.; Kanai, M.; Shibasaki, M. *Tetrahedron* **2007**, *63*, 5820.

colorless oil in 89% yield. ^{1}H NMR ($CDCl_3$): δ = 6.99-6.95 (m, 1H), 6.92-6.81 (m, 3H), 4.46 (dd, J = 8.9, 5.5 Hz, 1H), 3.24 (brs, 1H), 3.21 (d, *J* = 3.7 Hz, 1H), 2.11-2.03 (m, 1H), 1.97-1.88 (m, 1H), 1.85-1.77 (m, 1H), 1.58-1.40 (m, 2H), 1.34-1.24 (m, 1H), 0.99 (s, 9H), 0.16 (s, 3H), 0.15 (s, 3H); ^{13}C NMR ($CDCl_3$): δ = 148.6, 145.8, 121.8, 121.6, 121.5, 115.5, 72.2, 53.8, 53.1, 26.7, 25.7, 24.2, 18.4, 14.7, –4.5; IR (neat): 3420, 2928, 1500 cm^{-1}; MS (ESI): m/z 343 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{18}H_{28}O_3SiNa$ $[M+Na]^+$ 343.1705. Found 343.1701; $[\alpha]_D^{27}$ = +9 (*c* = 0.48, $CHCl_3$) for 99% ee.

(1*R*,2*R*,6*S*)-6-Methoxycarbonyl-2-(2'-*t*-butyldimethylsilyloxyphenoxy)cyclohexanol (14) and (1*R*,2*R*,3*R*)-3 -(2'-^{t}Butyldimethylsilyloxyphenoxy)-2-hydroxycyclohexanecarbonitrile (15)



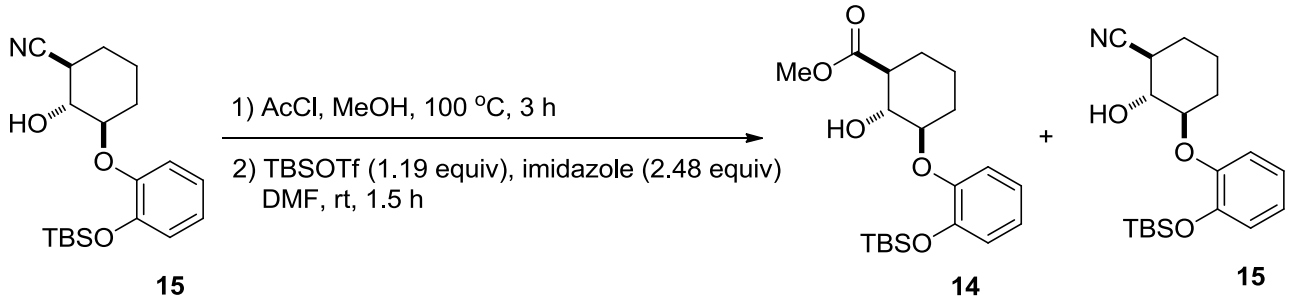
To a solution of **13** (7.24 g, 22.6 mmol) in THF (110 mL), Gd(O^{i}Pr)$_3$ (1.51 g, 4.52 mmol, 20 mol %) in THF (22.6 mL) was added at rt. TMSCN (6.03 mL, 45.2 mmol, 2 equiv) was added to the reaction mixture, and the mixture was warmed to 50 °C. After stirring for 3.5 h, water was added, and the organic layer was separated. The aqueous layer was extracted with EtOAc twice, and the combined organic layers were washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure. To the residue, HCl solution in MeOH (4 M, prepared by mixing AcCl (10 mL) and MeOH (25 mL) on ice bath) was added at rt, and the mixture was warmed to 100 °C in the sealed tube. After stirring for 1.5 h, the reaction mixture was poured into satd. $NaHCO_3$. The aqueous layer was extracted with EtOAc three times, and the combined organic layers were washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was dissolved in DMF (100 mL), and imidazole (9.04 g, 46.9 mmol, 2.08 equiv) was added to the mixture at rt. To the reaction mixture, TBSOTf (5.36 mL, 23.3 mmol, 1.03 equiv) was added with cooling in an ice bath, and the mixture was warmed to rt. After stirring for 1.5 h, water was added, and the organic layer was separated. The aqueous layer was extracted with EtOAc twice, and the combined organic layers were washed with water. The organic layer was further washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (silica gel, hexane-Et_2O, 4:1) to afford **14** (1.50 g, 3.94 mmol) as a colorless oil in 17% yield and **15** (2.95 g, 8.50 mmol) as a colorless oil in 38% yield for 3 steps.

14: ^{1}H NMR ($CDCl_3$): δ = 6.97-6.93 (m, 1H), 6.89-6.81 (m, 3H), 3.98-3.84 (m, 1H), 3.72 (s, 3H), 3.27 (s, 1H), 2.48-2.40 (m 1H), 2.20-2.12 (m, 1H), 1.95-1.87 (m, 1H), 1.85-1.76 (m, 1H), 1.57-1.41 (m, 2H), 1.39-1.28 (m, 1H), 0.99 (s, 9H), 0.18 (s, 3H), 0.16 (s, 3H); ^{13}C NMR ($CDCl_3$): δ = 174.2, 149.7, 146.5, 122.5, 122.1, 121.4, 118.1, 84.1, 74.5, 51.8, 49.1, 30.0, 28.0, 25.7, 23.1, 18.3, –4.4; IR (neat): 3484, 2950, 1740, 1499, 1264 cm^{-1}; MS (ESI): m/z 403 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{20}H_{32}O_5SiNa$ $[M+Na]^+$ 403.1917. Found 403.1899; $[\alpha]_D^{27}$ = –19 (*c* = 3.10, $CHCl_3$) for 99% ee.

15: ^{1}H NMR ($CDCl_3$): δ = 6.94-6.82 (m, 4H), 3.79-3.70 (m, 3H), 2.53-2.46 (m, 1H), 2.21-2.16 (m, 1H),

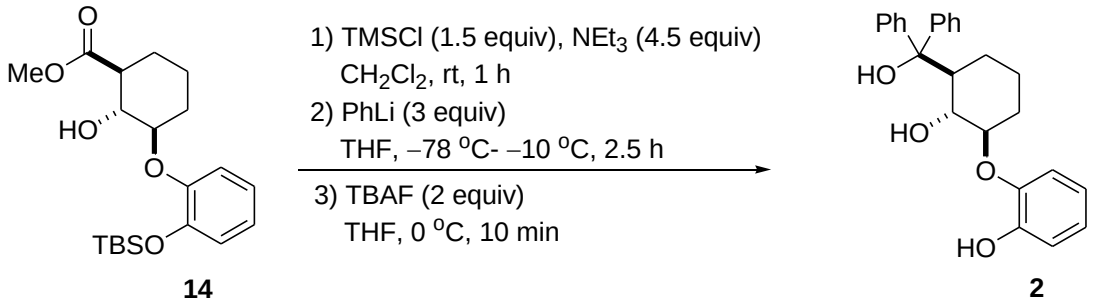
2.14-2.06 (m, 1H), 1.86-1.79 (m, 1H), 1.69-1.58 (m, 1H), 1.52-1.40 (m, 1H), 1.37-1.25 (m, 1H), 0.99 (s, 9H), 0.20 (s, 3H), 0.17 (s, 3H); ^{13}C NMR ($CDCl_3$): δ = 149.4, 146.5, 123.2, 122.2, 121.4, 120.2, 118.9, 84.4, 74.0, 34.8, 29.9, 28.3, 25.7, 22.7, 18.3, –4.3, –4.4; IR (neat): 3466, 2931, 2244, 1499, 1266 cm^{-1}; MS (ESI): m/z 370 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{19}H_{29}NO_3SiNa$ $[M+Na]^+$ 370.1814. Found 370.1807; $[\alpha]_D^{27}$ = –21 (*c* = 5.42, $CHCl_3$) for 99% ee.

15 can be converted to **14** by following procedure.



To **15** (2.95 g, 8.50 mmol), HCl solution in MeOH (4 M, prepared by mixing AcCl (10 mL) and MeOH (25 mL) on ice bath) was added at rt, and the mixture was warmed to 100 °C in a sealed tube. After stirring for 3 h, the reaction mixture was poured into satd. $NaHCO_3$. The aqueous layer was extracted with EtOAc three times, and the combined organic layers were washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was dissolved in DMF (40 mL), and imidazole (3.89 g, 20.2 mmol, 2.38 equiv) was added to the mixture at rt. To the reaction mixture, TBSOTf (2.32 mL, 10.1 mmol, 1.19 equiv) was added with cooling in an ice bath, and the mixture was warmed to rt. After stirring for 1.5 h, water was added, and the organic layer was separated. The aqueous layer was extracted with EtOAc twice, and the combined organic layers were washed with water. The organic layer was further washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (silica gel, hexane-Et_2O, 4:1) to afford **14** (1.13 g, 2.97 mmol) as a colorless oil in 35% yield and **15** (1.50 g, 4.32 mmol) as a colorless oil in 51% yield for 2 steps.

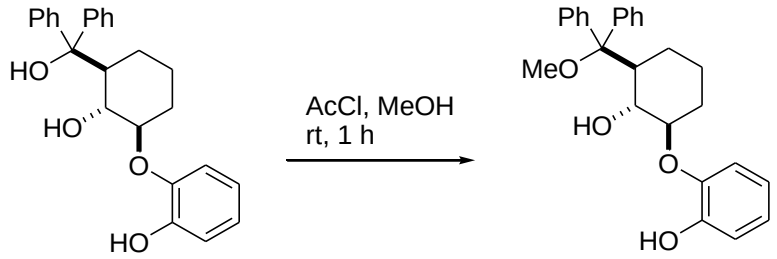
(1*R*,2*R*,6*S*)-6-Diphenylhydroxymethyl-2-(2'-hydroxyphenoxy)cyclohexanol (2)



To a solution of **14** (209 mg, 0.55 mmol) in CH_2Cl_2 (2.5 mL), triethylamine (341 μL, 2.46 mmol, 4.5 equiv) was added at rt. To the mixture, TMSCl (104 μL, 0.82 mmol, 1.5 equiv) was added at rt. After stirring for 1 h, water was added, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 twice, and the combined organic layers were washed with satd. NH_4Cl twice and brine. The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was dissolved in THF (2.5 mL), and PhLi (1.9 M solution in dibutylether, 0.87 mL, 1.65 mmol, 3 equiv) was added at –78 °C. The

reaction mixture was gradually warmed to −10 °C. After stirring for 2.5 h, satd. NH_4Cl was added, and the organic layer was separated. The aqueous layer was extracted with EtOAc twice, and the combined organic layers were washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was dissolved in THF (2.5 mL), and TBAF (1 M solution in THF, 1.1 mL, 1.1 mmol, 2 equiv) was added with cooling in an ice bath. After stirring for 10 min, satd. NH_4Cl was added and the organic layer was separated. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (silica gel, hexane-EtOAc, 5:1) to afford **2** (170 mg, 0.44 mmol) as a white powder in 79% yield for 3 steps. ^{1}H NMR ($CDCl_3$): δ = 7.46-7.29 (m, 10H), 7.00-6.89 (m, 3H), 6.74-6.69 (m, 1H), 5.62 (s, 1H), 3.69-3.62 (m, 1H), 3.56-3.49 (m, 1H), 3.00 (s, 1H), 2.71-2.64 (m ,1H), 2.71-2.62 (m, 1H), 1.78-1.64 (m, 2H), 1.38-1.22 (m, 2H), 1.01-0.90 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 149.8, 145.9, 144.8, 141.3, 128.8, 128.2, 128.0, 127.7, 127.6, 127.4, 125.0, 121.9, 119.3, 116.8, 88.1, 83.5, 75.2, 49.2, 30.6, 27.6, 22.8; IR (neat): 3358, 2941, 1592, 1495, 1264 cm^{-1}; MS (ESI): m/z 413 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{25}H_{26}O_4Na$ $[M+Na]^+$ 413.1729. Found 413.1710; $[\alpha]_D^{27}$ = +11 (*c* = 0.55, $CHCl_3$) for 99% ee.

(1*R*,2*R*,6*S*)-6-Diphenylmethoxymethyl-2-(2'-hydroxyphenoxy)cyclohexanol (3)

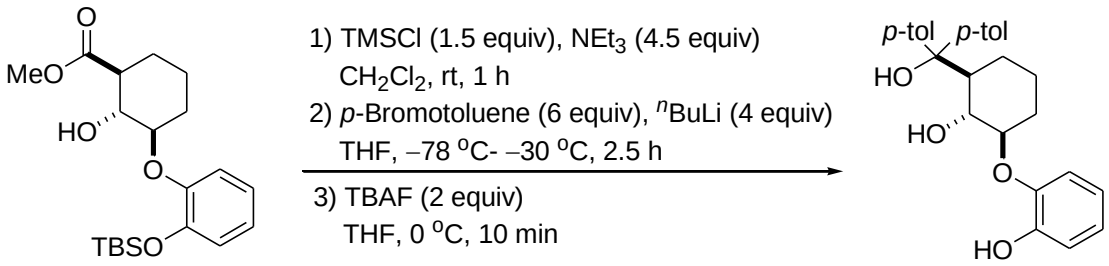


2 **3**

To **2** (128 mg, 0.33 mmol), HCl solution in MeOH (2 M, prepared by mixing AcCl (0.43 mL) and MeOH (2.57 mL) on ice bath) was added at rt. After stirring for 1 h, the reaction mixture was poured into satd. $NaHCO_3$. The aqueous layer was extracted with EtOAc three times. The combined organic layers were washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (silica gel, hexane-EtOAc, 10:1) to afford **3** (108 mg, 0.27 mmol) as a white powder in 81% yield. ^{1}H NMR ($CDCl_3$): δ = 9.27 (s, 1H), 7.47-7.32 (m, 10H), 7.01-6.93 (m, 2H), 6.92-6.88 (m, 1H), 6.72-6.66 (m, 1H), 6.55 (s, 1H), 3.60-3.51 (m, 1H), 3.21 (t, *J* = 9.3 Hz, 1H), 2.86 (s, 3H), 2.74-2.66 (m, 1H), 2.14-2.06 (m, 1H), 1.65-1.56 (m, 2H), 1.30-1.13 (m, 2H), 0.94-0.82 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 150.3, 146.3, 137.9, 136.0, 129.5, 129.2, 128.5, 128.2, 127.7, 125.3, 122.9, 119.0, 117.0, 90.5, 88.9, 75.1, 51.9, 49.4, 30.5, 26.6, 22.7; IR (neat): 3391, 2941, 1590, 1495, 1266 cm^{-1}; MS (ESI): m/z 427 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{26}H_{28}O_4Na$ $[M+Na]^+$ 427.1885. Found 427.1870; $[\alpha]_D^{27}$ = +6 (*c* = 1.00, $CHCl_3$) for 99% ee.

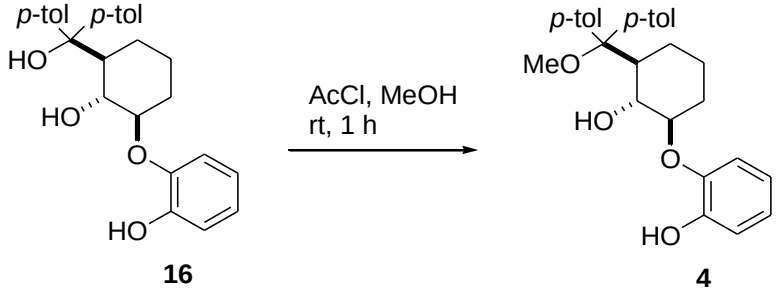
(3-B) Synthesis of 4 and 5

(1*R*,2*R*,6*S*)-6-Di-*para*-tolylhydroxymethyl-2-(2'-hydroxyphenoxy)cyclohexanol (16)



To a solution of **14** (1.76 g, 4.63 mmol) in CH_2Cl_2 (23 mL), triethylamine (2.89 mL, 20.84 mmol, 4.5 equiv) was added at rt. To the mixture, TMSCl (882 μL, 6.95 mmol, 1.5 equiv) was added at rt. After stirring for 1 h, water was added, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 twice, and the combined organic layers were washed with satd. NH_4Cl twice and brine. The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was dissolved in THF (6 mL), and was added to a tolyllithium solution in THF at −78 °C, prepared by adding ^{n}BuLi (2.76 M solution in hexane, 6.71 mL, 18.52 mmol, 4 equiv) to a solution of *para*-bromotoluene (3.42 mL, 27.78 mmol, 6 equiv) in THF (25 mL) at −78 °C followed by stirring for 2 h. The reaction mixture was gradually warmed to −30 °C. After stirring for 2.5 h, satd. NH_4Cl was added, and the organic layer was separated. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was dissolved in THF (23 mL), and TBAF (1 M solution in THF, 9.26 mL, 9.26 mmol, 2 equiv) was added with cooling in an ice bath. After stirring for 10 min, satd. NH_4Cl was added, and the organic layer was separated. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (silica gel, CH_2Cl_2) to afford **16** (1.69 g, 4.03 mmol) as a white powder in 87% yield for 3 steps. ^{1}H NMR ($CDCl_3$): δ = 8.84 (s, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 6.99-6.94 (m, 1H), 6.93-6.89 (m, 2H), 6.73-6.68 (m, 1H) 5.83 (s, 1H), 3.64-3.57 (m, 1H), 3.50 (t, *J* = 9.3 Hz, 1H), 2.91 (s,1H), 2.66-2.58 (m, 1H), 2.38 (s, 3H), 2.32 (s, 3H), 2.17-2.10 (m, 1H), 1.76-1.62 (m, 2H), 1.37-1.20 (m, 2H), 0.98-0.87 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 149.9, 146.0, 142.0, 138.2, 138.0, 137.2, 129.3, 128.3, 127.9, 127.3, 125.0, 122.2, 119.2, 116.8, 88.2, 83.3, 75.2, 49.0, 30.6, 27.5, 22.7, 21.0, 21.0; IR (neat): 3344, 2943, 1591, 1495, 1264 cm^{-1}; MS (ESI): m/z 441 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{27}H_{30}O_4Na$ $[M+Na]^+$ 441.2042. Found 441.2028; $[\alpha]_D^{27}$ = +19 (*c* = 2.97, $CHCl_3$) for 99% ee.

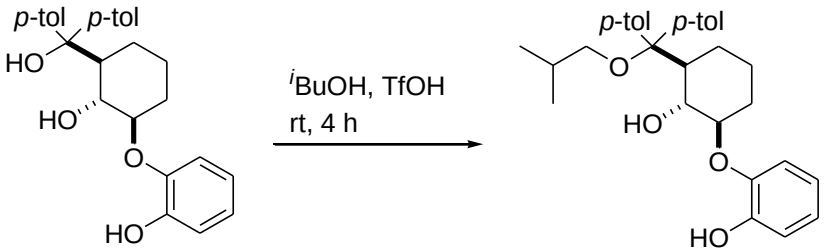
(1*R*,2*R*,6*S*)-6-Di-*para*-tolylmethoxymethyl-2-(2'-hydroxyphenoxy)cyclohexanol (4)



To **16** (126 mg, 0.30 mmol), HCl solution in MeOH (2 M, 3mL) was added at rt. After stirring for 1 h, the

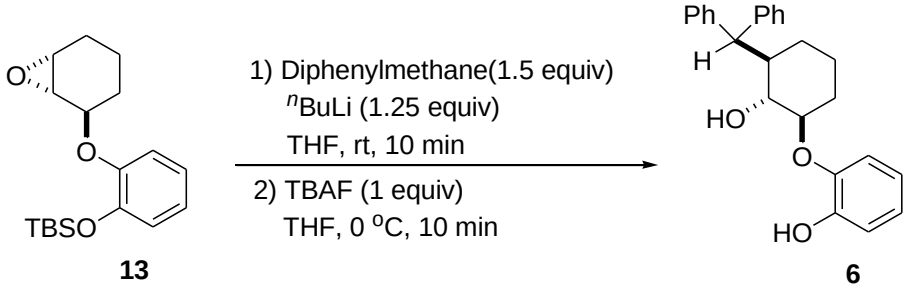
reaction mixture was poured into satd. $NaHCO_3$. The aqueous layer was extracted with EtOAc three times. The combined organic layers were washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (silica gel, hexane-EtOAc, 15:1) to afford **4** (104 mg, 0.24 mmol) as a white powder in 80% yield. ^{1}H NMR ($CDCl_3$): δ = 9.31 (s, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.27-7.21 (m, 4H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.01-6.97 (m, 2H), 6.92-6.88 (m, 1H), 6.71-6.66 (m, 1H), 6.59 (s, 1H), 3.58-3.51 (m, 1H), 3.21 (t, *J* = 9.3 Hz, 1H), 2.85 (s, 3H), 2.68-2.61 (m, 1H), 2.40 (s, 3H), 2.35 (s, 3H), 2.13-2.05 (m, 1H), 1.62-1.52 (m, 2H), 1.30-1.12 (m, 2H), 0.90-0.80 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 150.3, 146.3, 138.2, 137.3, 135.0, 133.0, 129.4, 129.1, 128.8, 128.3, 125.3, 122.9, 119.0, 117.0, 90.4, 89.0, 75.1, 51.7, 49.4, 30.5, 26.6, 22.7, 21.0; IR (neat): 3236, 2941, 1590, 1495, 1266 cm^{-1}; MS (ESI): m/z 455 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{28}H_{32}O_4Na$ $[M+Na]^+$ 455.2198. Found 455.2185; $[\alpha]_D^{27}$ = +9 (*c* = 1.60, $CHCl_3$) for 99% ee.

(1*R*,2*R*,6*S*)-6-Di-*para*-tolyl(2'-methyl-1'-propyloxy)methyl-2-(2'-hydroxyphenoxy)cyclohexanol (5)



To a solution of **16** (126 mg, 0.30 mmol) in 2-methyl-1-propanol (6 mL), trifluoromethansulfonic acid (26 μL, 0.3 mmol) was added at rt. After stirring for 4 h, satd. $NaHCO_3$ was added, and the organic layer was separated. The aqueous layer was extracted with EtOAc twice, and the combined organic layers were washed with water. The organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (silica gel, hexane-EtOAc, 50:1) to afford **5** (114 mg, 0.24 mmol) as a white powder in 80% yield. ^{1}H NMR ($CDCl_3$): δ = 9.35 (s, 1H), 7.31 (d, *J* = 8.2Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.00-6.93 (m, 1H), 6.91-6.88 (m, 1H), 6.81 (s, 1H), 6.71-6.66 (m, 1H), 3.59-3.52 (m, 1H), 3.25 (t, *J* = 9.3Hz, 1H), 3.02 (dd, *J* = 8.9, 6.1 Hz, 1H), 2.71-2.63 (m, 1H), 2.39 (s, 3H), 2.37-2.34 (m, 4H), 2.11-2.04 (m, 1H), 1.78-1.67 (m, 1H), 1.61-1.50 (m, 2H), 1.28-1.12 (m, 2H), 0.86-0.77 (m, 7H); ^{13}C NMR ($CDCl_3$): δ = 150.3, 146.2, 138.1, 137.2, 135.5, 133.4, 129.4, 129.2, 128.7, 128.2, 125.3, 122.9, 119.0, 117.0, 89.9, 88.8, 75.1, 70.6, 49.4, 30.3, 28.5, 26.5, 22.7, 21.0, 19.6, 19.6; IR (neat): 3251, 2955, 1590, 1495, 1266 cm^{-1}; MS (ESI): m/z 497 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{31}H_{38}O_4Na$ $[M+Na]^+$ 497.2668. Found 497.2665; $[\alpha]_D^{25}$ = +1 (*c* = 1.27, $CHCl_3$) for 99% ee.

(1*R*,2*R*,6*R*)-6-Diphenylmethyl-2-(2'-hydroxyphenoxy)cyclohexanol (6)

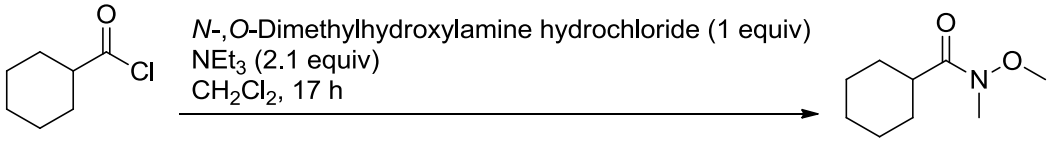


To a solution of diphenylmethane (388 μL, 2.33 mmol, 1.5 equiv) in THF (8 mL), ^{n}BuLi (2.76 M solution in hexane, 703 μL, 1.94 mmol, 1.25 equiv) was added at –78 °C. The reaction mixture was warmed to rt, and stirred for 1 h, followed by the addition of **13** (497 mg, 1.55 mmol) at rt. After stirring for 10 min, satd. NH_4Cl was added, and the organic layer was separated. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was dissolved in THF (3.5 mL), and TBAF (1 M solution in THF, 1.55 mL, 1.55 mmol, 1 equiv) was added with cooling in an ice bath. After stirring for 10 min, satd. NH_4Cl was added and the organic layer was separated. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (silica gel, hexane-EtOAc, 20:1) to afford **6** (228 mg, 0.61 mmol) as a white powder in 39% yield for 2 steps. ^{1}H NMR ($CDCl_3$): δ = 7.74 (s, 1H), 7.37-7.26 (m, 8H), 7.23-7.18 (m, 2H), 6.98-6.93 (m, 2H), 6.92-6.87 (m, 1H), 6.77-6.71 (m, 1H), 4.14 (d, *J* = 8.0 Hz, 1H), 3.69-3.60 (m, 2H), 2.48-2.37 (m, 1H), 2.22-2.16 (m, 2H), 1.75-1.64 (m, 2H), 1.49-1.39 (m, 1H), 1.27-1.16 (m, 1H), 1.04-0.93 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 149.2, 145.5, 143.3, 142.4, 129.0, 128.9, 128.6, 128.2, 126.9, 126.6, 124.7, 120.9, 119.5, 116.4, 86.7, 77.6, 55.1, 46.4, 30.7, 28.9, 22.7; IR (neat): 3405, 2939, 1594, 1496, 1262 cm^{-1}; MS (ESI): m/z 397 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{25}H_{26}O_3Na$ $[M+Na]^+$ 397.1780. Found 397.1772; $[\alpha]_D^{25}$ = 0 (*c* = 2.64, $CHCl_3$) for 99% ee.

4. Substrate Synthesis

(4-A) General Procedure for the Synthesis of Enones 7a-7e, 7g, 7h (Synthesis of 7e)

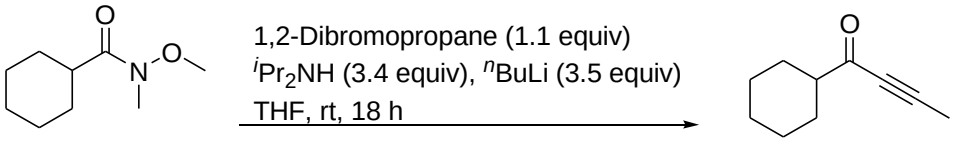
***N*-Methoxy-*N*-methylcyclohexanecarboxamide (17)**



17

To a solution of *N,O*-dimethylhydroxylamine hydrochloride (5.9 g, 60 mmol, 1 equiv) in CH_2Cl_2 (120 mL), triethylamine (17.6 mL, 126 mmol, 2.1 equiv) was added with cooling in an ice bath. To the mixture, cyclohexanecarbonylchloride (8.0 mL, 60 mmol) was added and the mixture was warmed to rt. After stirring for 17 h, water was added, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 twice. The combined organic layers were washed with 1 M HCl, satd. $NaHCO_3$ and brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure to afford crude **17** (9.6 g, 56 mmol) as a colorless oil (ca. 93% yield), and crude **17** was used in the next reaction without purification.

1-Cyclohexyl-2-butyn-1-one (18)



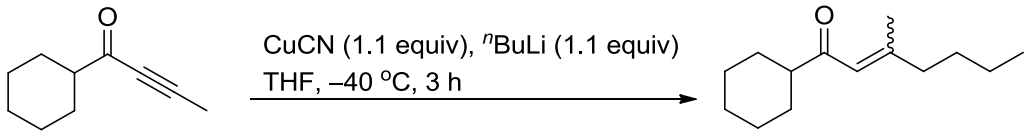
17 **18**

To di-*i*-propylamine (26.7 mL, 190.4 mmol, 3.4 equiv), ^{n}BuLi (1.59 M solution in hexane, 123 mL, 196 mmol, 3.5 equiv) was added with cooling in an ice bath. After stirring for 15 min, the mixture was cooled to –78 °C, and THF (140 mL) was added. 1,2-Dibromopropane (6.41 mL, 61.6 mmol, 1.1 equiv) was added to

the mixture dropwise at −78 °C, and the reaction mixture was warmed to 0 °C. After stirring for 30 min, the mixture was cooled to −78 °C, and crude **17** (9.6 g, 56 mmol) was added. The mixture was gradually warmed to rt. After stirring for 16 h, the mixture was cooled to 0 °C, and 3 M HCl was added. The organic layer was separated, and the aqueous layer was extracted with AcOEt twice. The combined organic layers were washed successively with satd. $NaHCO_3$ and brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (silica gel, hexane-Et_2O, 20:1) to afford **18** (5.84 g, 38.9 mmol) as a colorless oil in 69% yield. Without further purification, **18** was used in the next reaction.

(*E*)-1-Cyclohexyl-3-methyl-2-hepten-1-one ((*E*)-7e) and

(*Z*)-1-Cyclohexyl-3-methyl-2-hepten-1-one ((*Z*)-7e)



18 **7e**

To a solution of CuCN (3.83 g, 42.8 mmol, 1.1 equiv) in THF (400 mL), ^{n}BuLi (1.59 M solution in hexane, 26.9 mL, 42.8 mmol, 1.1 equiv) was added at −40 °C. After stirring for 15 min, the mixture was cooled to −78 °C, and **18** (5.84 g, 38.9 mmol) in THF (20 mL) was added. The reaction mixture was gradually warmed to −40 °C. After stirring for 3 h, satd. NH_4Cl was added and the organic layer was separated. The aqueous layer was extracted with Et_2O twice. The combined organic layers were washed with brine, and dried over Na_2SO_4. Solvent was removed under reduced pressure. The residue was passed through a short pad column chromatography (silica gel, AcOEt), and the solvent was removed under reduced pressure. The residue (mixture of *E*- and *Z*-isomers) was purified by Rover column (silica gel, Hexane-Et_2O, 50:1) to afford (*E*)-**7e** (3.23 g, 15.5 mmol) as a colorless oil in 40% yield and (*Z*)-**7e** (3.01 g, 14.4 mmol) as a colorless oil in 37% yield.

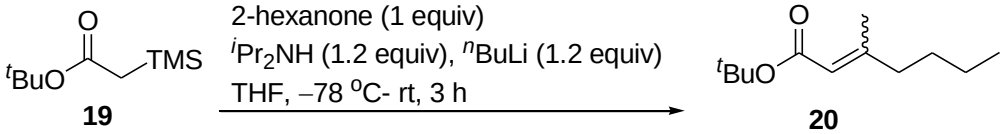
(*E*)-**7e**: ^{1}H NMR ($CDCl_3$): δ = 6.05 (s, 1H), 2.30-2.23 (m, 1H), 2.10-2.05 (m, 5H), 1.82-1.70 (m, 4H), 1.66-1.59 (m, 1H), 1.45-1.38 (m, 2H), 1.33-1.10 (m, 7H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 204.3, 159.0, 122.2, 51.6, 41.0, 29.7, 28.6, 25.9, 25.8, 22.3, 19.2, 13.8; IR (neat): 2929, 1685, 1617 cm^{-1}; MS (ESI): m/z 231 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{14}H_{24}ONa$ $[M+Na]^+$ 231.1725. Found 231.1731.

(*Z*)-**7e**: ^{1}H NMR ($CDCl_3$): δ = 6.03 (s, 1H), 2.52 (t, *J* = 7.7 Hz, 2H), 2.29-2.21 (m, 1H), 1.83 (s, 3H), 1.81-1.71 (m, 4H), 1.67-1.58 (m, 1H), 1.41-1.10 (m, 9H), 0.87 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 203.8, 159.6, 122.9, 51.6, 33.3, 30.4, 28.6, 25.9, 25.8, 25.5, 22.9, 13.9; IR (neat): 2929, 1684, 1617 cm^{-1}; MS (ESI): m/z 231 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{14}H_{24}ONa$ $[M+Na]^+$ 231.1725. Found 231.1735.

Enones **7f**[2] and **7i**[3] were synthesized following the reported procedures.

(4-B) General Procedure for the Synthesis of α, β-Unsaturaned *N*-Acylpyrroles 9 (Synthesis of 9a)

3-Methyl-2-heptenoicacid 1,1-dimethylethylester (20)

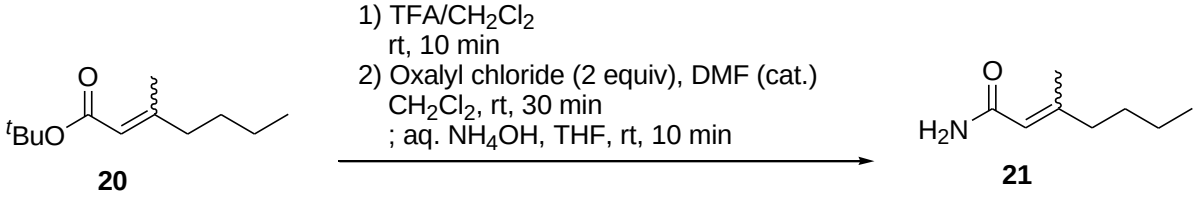


19 **20**

[2] Martin, N. J. A.; List, B. *J. Am. Chem. Soc.* **2006**, *128*, 13368.
[3] Hudlicky, T.; Srnak, T. *Tetrahedron Lett.* **1981**, *22*, 3351.

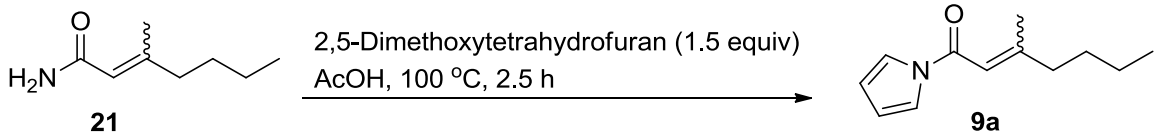
19 was synthesized following reported procedure.[4] To di-*i*-propylamine (3.36 mL, 24.0 mmol, 1.2 equiv), ^{n}BuLi (2.76 M solution in hexane, 8.70 mL, 24.0 mmol, 1.2 equiv) was added with cooling in an ice bath. After stirring for 15 min, the mixture was cooled to −78 °C, and THF (50 mL) was added. **19** (3.77 g, 20.0 mmol) was added to the mixture dropwise at −78 °C. After stirring for 10 min, 2-hexanone (2.47 mL, 20.0 mmol, 1 equiv) was added and the reaction mixture was gradually warmed to rt. Aftrer stirring for 3 h, satd. NH_4Cl was added, and the organic layer was separated. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with satd. NH_4Cl and brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure to afford a (*E*)- and (*Z*)-mixture of crude **20** (3.62 g, 18.3 mmol, *E/Z* = 1/1) as a colorless oil (ca. 91% yield). Crude **20** was used in the next reaction without purification.

3-Methyl-2-heptenamide (21)



To a solution of crude **20** (3.62 g, 18.3 mmol) in CH_2Cl_2 (18 mL), trifluoroacetic acid (18 mL) was added at rt. After stirring for 10 min, water was added, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 twice. The combined organic layers were washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (75 mL), and oxalyl chloride (2.84 mL, 36.6 mmol, 2 equiv) was added at rt. One drop of DMF was added to the reaction mixture at rt. After stirring for 0.5 h, the mixture was evaporated, and the residue was dissolved in THF (30 mL). To the mixture, aq. NH_4OH (30 % v/v, 18 mL) was added at rt. After stirring for 10 min, the organic layer was separated. The aqueous layer was extracted with AcOEt twice. The combined organic layers were successively washed with satd. NH_4Cl and brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure to afford crude **21** (2.43 g, 15.1 mmol: ca. 83% yield). Crude **21** was used in the next reaction without purification.

(*E*)-3-Methyl-1-(pyrrol-1-yl)-2-hepten-1-one ((*E*)-9a) and
(*Z*)-3-Methyl-1-(pyrrol-1-yl)-2-hepten-1-one ((*Z*)-9a)



To a solution of crude **21** (2.43 g, 15.1 mmol) in AcOH (60 mL), 2,5-dimethyltetrahydrofuran (2.9 mL, 22.7 mmol, 1.5 equiv) was added at rt, and the mixture was heated at 100 °C. After stirring for 2.5 h, water and AcOEt was added, and the organic layer was separated. The aqueous layer was extracted with AcOEt twice, and the combined organic layers were washed with satd. $NaHCO_3$ five times. The organic layer was further washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (silica gel, hexane-CH_2Cl_2, 6:1) to afford (*E*)-**9a** (1.08 g, 5.7 mmol) as a colorless oil in 37% yield and (*Z*)-**9a** (0.77 g, 4.0 mmol) as a colorless oil in 27% yield.

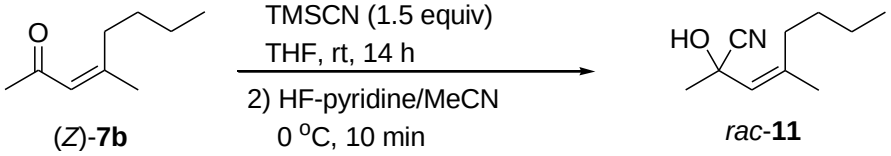
[4] Ager, D. J. *Organic Reactions*, **1990**, *38*.

(*E*)-**9a**: ^{1}H NMR ($CDCl_3$): δ = 7.33 (t, *J* = 2.3 Hz, 2H), 6.32-6.29 (m, 1H), 6.27 (t, *J* = 2.3 Hz, 2H), 2.24 (t, *J* = 7.8 Hz, 2H), 2.19 (s, 3H), 1.55-1.47 (m, 2H), 1.39-1.30 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 163.3, 119.1, 114.3, 112.6, 41.1, 29.6, 22.3, 19.6, 13.9; IR (neat): 3381, 2957, 2931, 1696, 1631, 1467, 1277 cm^{-1}; MS (ESI): m/z 214 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{12}H_{17}NONa$ $[M+Na]^+$ 214.1208. Found 214.1205.

(*Z*)-**9a**: ^{1}H NMR ($CDCl_3$): δ = 7.33 (t, *J* = 2.1 Hz, 2H), 6.29 (s, 1H), 6.26 (t, *J* = 2.1 Hz, 2H), 2.62 (t, *J* = 7.8 Hz, 2H), 1.99 (s, 3H), 1.53-1.45 (m, 2H), 1.42-1.33 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 163.8, 162.8, 119.1, 114.8, 112.6, 34.0, 30.3, 25.6, 22.9, 13.9; IR (neat): 3371, 2958, 2931, 1697, 1630, 1467, 1274 cm^{-1}; MS (ESI): m/z 214 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{12}H_{17}NONa$ $[M+Na]^+$ 214.1208. Found 214.1206.

(4-C) Synthesis of *rac*-11

(*Z*)-2,4-Dimethyl-2-hydroxy-3-octenenitrile (11)



(*Z*)-**7b** *rac*-**11**

To a solution of *rac*-FujiCAPO[1] (153 mg, 0.375 mmol, 7.5 mol %) in THF (12.5 mL), a solution of Gd(O^{i}Pr)$_3$ (83.8 mg, 0.25 mmol, 5 mol %) in THF (1.25 mL) was added at rt. The mixture was heated at 50 °C. After stirring for 20 min, the mixture was cooled to rt, and (*Z*)-**7b** (815 μL, 5 mmol) was added, followed by the addition of TMSCN (1.0 mL, 7.5 mmol, 1.5 equiv). After stirring for 14 h, water was added, and the organic layer was separated. The aqueous layer was extracted with AcOEt twice. The combined organic layers were washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was dissolved in MeCN (4 mL), and HF-pyridine (0.2 mL) was added with cooling in an ice bath. After stirring for 10 min, water was added, and the organic layer was separated. The aqueous layer was extracted with AcOEt twice. The combined organic layers were washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (silica gel, hexane-AcOEt, 20:1) to afford *rac*-**11** (659 mg, 3.94 mmol) as a colorless oil in 79% yield. ^{1}H NMR ($CDCl_3$): δ = 5.26 (s, 1H), 2.83-2.77 (m, 1H), 2.40-2.27 (m, 2H), 1.73 (d, *J* = 1.6 Hz, 3H), 1.67 (s, 3H), 1.50-1.31 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 145.7, 125.0, 122.0, 65.1, 32.5, 30.3, 29.7, 23.6, 22.8, 13.9; IR (neat): 3423, 2959, 2238, 1656, 1457, 1378, 1120 cm^{-1}; MS (ESI): m/z 190 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{10}H_{17}NONa$ $[M+Na]^+$ 190.1208. Found 190.1201.

5. Characterization of New Compounds

(*E*)-3,4-Dimethyl-1-phenyl-2-penten-1-one ((*E*)-7a)

^{1}H NMR ($CDCl_3$): δ = 7.90 (d, *J* = 7.0 Hz, 2H), 7.50 (dd, *J* = 7.0, 7.0 Hz, 1H), 7.42 (dd, *J* = 7.0 Hz, 2H), 6.72 (s, 1H), 2.51-2.42 (m, 1H), 2.15 (s, 3H), 1.13 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR ($CDCl_3$): δ = 192.2, 165.4, 139.5, 132.2, 128.4, 128.1, 118.5, 38.5, 21.0, 17.3; IR (neat): 2964, 1661, 1609, 1239 cm^{-1}; MS (ESI): m/z 211 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{13}H_{16}ONa$ $[M+Na]^+$ 211.1099. Found 211.1103.

(*Z*)-3,4-Dimethyl-1-phenyl-2-penten-1-one ((*Z*)-7a)

^{1}H NMR ($CDCl_3$): δ = 7.91 (d, *J* = 7.0 Hz, 2H), 7.50 (dd, *J* = 7.0, 7.0 Hz, 1H), 7.42 (dd, *J* = 7.0 Hz, 2H), 6.59 (s, 1H), 3.80-3.71 (m, 1H), 1.90 (s, 3H), 1.06 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR ($CDCl_3$): δ = 191.5, 164.8, 139.3, 132.3, 128.4, 128.3, 120.9, 30.1, 20.7, 19.7; IR (neat): 2924, 1660, 1609, 1239 cm^{-1}; MS (ESI): m/z 211 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{13}H_{16}ONa$ $[M+Na]^+$ 211.1099. Found 211.0954.

(*E*)-4-Methyl-3-octen-2-one ((*E*)-7b)

^{1}H NMR ($CDCl_3$): δ = 6.02 (s, 1H), 2.13 (s, 3H), 2.09-2.05 (m, 5H), 1.45-1.37 (m, 2H), 1.32-1.23 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 198.8, 158.9, 123.4, 40.9, 31.7, 29.6, 22.3, 19.2, 13.8; IR (neat): 3412, 2932, 1688, 1617 cm^{-1}; MS (ESI): m/z 163 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_9H_{16}ONa$ $[M+Na]^+$ 163.1099. Found 163.1095.

(*Z*)-4-Methyl-3-octen-2-one ((*Z*)-7b)

^{1}H NMR ($CDCl_3$): δ = 6.01 (s, 1H), 2.53 (t, *J* = 7.6 Hz, 2H), 2.11 (s, 3H), 1.82 (d, *J* = 1.6 Hz, 3H), 1.42-1.27 (m, 4H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 198.2, 159.6, 123.9, 33.3, 31.7, 30.3, 25.3, 22.8, 13.9; IR (neat): 3413, 2959, 1688, 1616 cm^{-1}; MS (ESI): m/z 163 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_9H_{16}ONa$ $[M+Na]^+$ 163.1099. Found 163.1096.

(*E*)-4,5-Dimethyl-3-hexen-2-one ((*E*)-7c)

^{1}H NMR ($CDCl_3$): δ = 6.04 (s, 1H), 2.34-2.25 (m, 1H), 2.15 (s, 3H), 2.06 (s, 3H), 1.03 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$): δ = 199.3, 164.0, 121.4, 38.2, 31.8, 20.9, 16.8; IR (neat): 3413, 2965, 1686, 1616 cm^{-1}; MS (ESI): m/z 149 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_8H_{14}ONa$ $[M+Na]^+$ 149.0942. Found 149.0944.

(*Z*)-4,5-Dimethyl-3-hexen-2-one ((*Z*)-7c)

^{1}H NMR ($CDCl_3$): δ = 5.95 (s, 1H), 3.92-3.82 (m, 1H), 2.11 (s, 3H), 1.75 (s, 3H), 0.97 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$): δ = 198.3, 164.2, 123.5, 31.9, 29.1, 20.9, 19.3; IR (neat): 3412, 2966, 1688, 1612 cm^{-1}; MS (ESI): m/z 149 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_8H_{14}ONa$ $[M+Na]^+$ 149.0942. Found 149.0945.

(*E*)- 5-Methyl-1-phenyl-4-nonen-3-one ((*E*)-7d)

^{1}H NMR ($CDCl_3$): δ = 7.27-7.23 (m, 2H), 7.19-7.14 (m, 3H), 6.02 (s, 1H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.13-2.08 (m, 5H), 1.46-1.38 (m, 2H), 1.33-1.26 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 199.9, 159.2, 141.4, 128.3, 128.3, 125.9, 122.8, 45.8, 40.9, 30.1, 29.6, 22.3, 19.3, 13.8; IR (neat): 2930, 1686, 1617 cm^{-1}; MS (ESI): m/z 253 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{16}H_{22}ONa$ $[M+Na]^+$ 253.1568. Found 253.1555.

(*Z*)- 5-Methyl-1-phenyl-4-nonen-3-one ((*Z*)-7d)

^{1}H NMR ($CDCl_3$): δ = 7.27-7.23 (m, 2H), 7.19-7.14 (m, 3H), 6.01 (s, 1H), 2.89 (t, *J* = 7.7 Hz, 2H), 2.71 (t, *J* = 7.7 Hz, 2H), 2.57 (t, *J* = 7.7 Hz, 2H), 1.85 (s, 3H), 1.44-1.30 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 199.3, 159.9, 141.4, 128.3, 128.2, 125.8, 123.4, 45.8, 33.5, 30.3, 30.0, 25.4, 22.9, 13.9; IR (neat): 2929, 1686, 1616 cm^{-1}; MS (ESI): m/z 253 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{16}H_{22}ONa$ $[M+Na]^+$ 253.1568. Found 253.1555.

(*E*)-4-Phenyl-3-hexen-2-one ((*E*)-7h)

^{1}H NMR ($CDCl_3$): δ = 7.46-7.41 (m, 2H), 7.39-7.33 (m, 3H), 6.36 (s, 1H), 3.03 (q, *J* = 7.6 Hz, 2H), 2.26 (s, 3H), 1.04 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 198.4, 160.4, 141.3, 128.9, 128.5, 126.8, 124.1, 32.2, 24.4, 13.5; IR (neat): 2968, 1682, 1597 cm^{-1}; MS (ESI): m/z 197 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{12}H_{14}ONa$ $[M+Na]^+$ 197.0942. Found 197.0936.

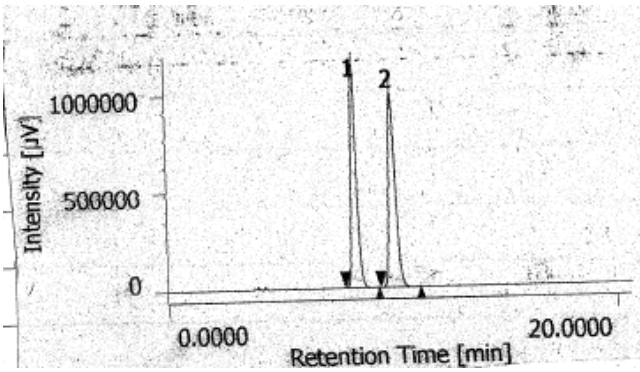
(*Z*)-4-Phenyl-3-hexen-2-one ((*Z*)-7h)

^{1}H NMR ($CDCl_3$): δ = 7.38-7.30 (m, 3H), 7.16-7.12 (m, 2H), 6.06 (s, 1H), 2.45 (q, *J* = 7.3 Hz, 2H), 1.75 (s, 3H), 1.03 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 200.8, 158.5, 140.4, 128.4, 128.1, 127.4, 127.1, 33.5, 30.2, 12.2; IR (neat): 2969, 1656 cm^{-1}; MS (ESI): m/z 197 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{12}H_{14}ONa$ $[M+Na]^+$ 197.0942. Found 197.0954.

(*R*)-2-Methyl-2-(1-methylethyl)-4-oxo-4-phenylbutanenitrile (8a)

^{1}H NMR ($CDCl_3$): δ = 7.95-7.90 (m, 2H), 7.60-7.54 (m, 1H), 7.46 (dd, *J* = 7.6, 7.6 Hz, 2H), 3.35 (d, *J* = 17.1 Hz, 1H) , 3.15 (d, *J* = 17.1 Hz, 1H), 2.19-2.09 (m, 1H), 1.45 (s, 3H), 1.11 (d, *J* = 6.7 Hz, 3H), 1.06 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 195.6, 136.8, 133.6, 128.7, 128.0, 123.2, 43.7, 38.6, 34.6, 21.2, 18.3, 17.5; IR (neat): 2971, 2233, 1690 cm^{-1}; MS (ESI): m/z 238 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{14}H_{17}NONa$ $[M+Na]^+$ 238.1208. Found 238.1194; $[\alpha]_D^{26}$ = +3 (*c* = 1.09, $CHCl_3$) for 97% ee; HPLC condition: Chiralpak AS-H column, flow rate: 1.0 mL / min, *n*-hexane / *i*-PrOH = 4 / 1, t = 7.5 min (*S*, minor), 8.9 min (*R*, major). λ = 254 nm.

HPLC chart of *rac*-**8a**



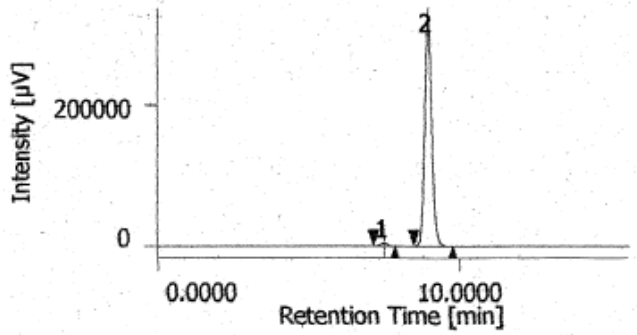
ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%
1	Unknown	8.275	19541079	1140998	48.820
2	Unknown	9.950	20485690	992080	51.180

コメント

システム名 HPLC-1

HPLC chart of (*R*)-**8a**



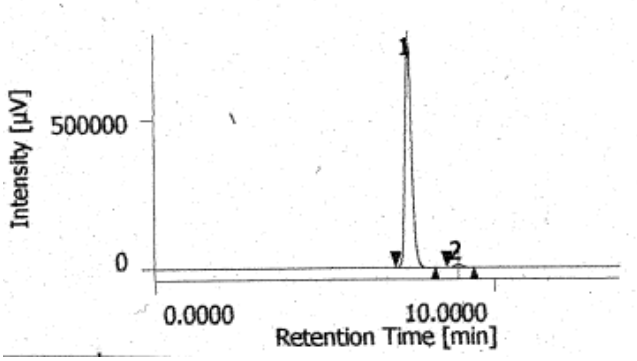
ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%
1	Unknown	7.467	73369	5027	1.383
2	Unknown	8.908	5230376	320857	98.617

from (*E*): 97% ee (*R*)

システム名 HPLC-2

HPLC chart of (*S*)-**8a**



ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%
1	Unknown	7.450	10197535	750574	98.460
2	Unknown	8.917	159472	10279	1.540

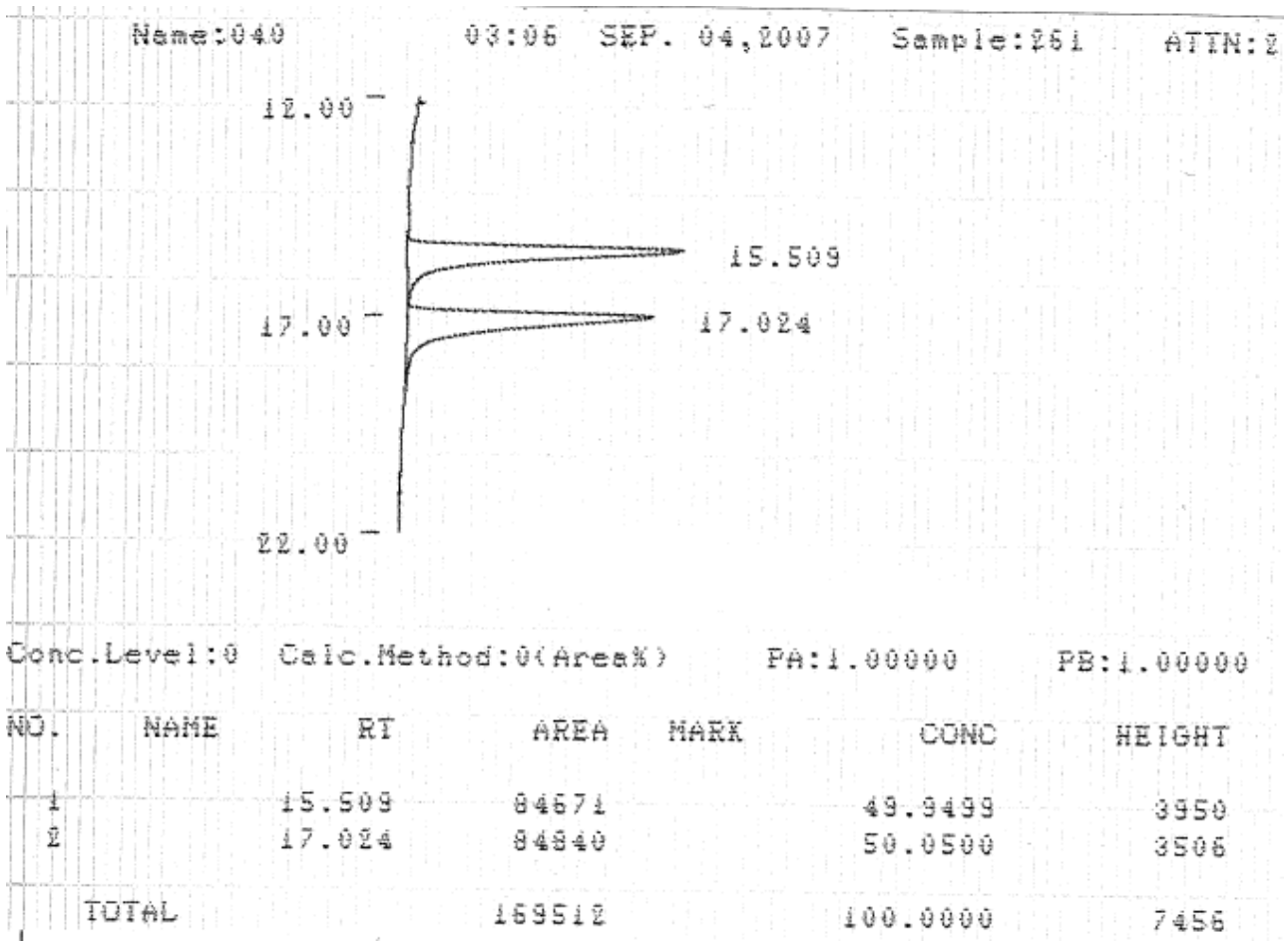
from (*Z*): 97% ee (*S*)

システム名 HPLC-2

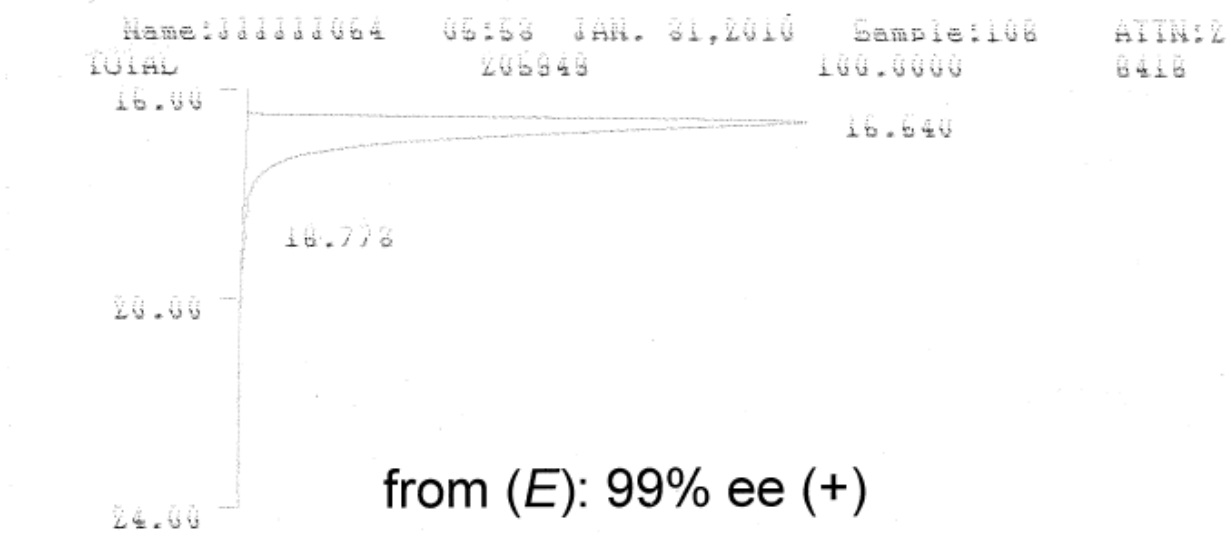
2-Butyl-2-methyl-4-oxo-pentanenitrile (8b)

^{1}H NMR ($CDCl_3$): δ = 2.75 (d, *J* = 17.1 Hz, 1H) , 2.58 (d, *J* = 17.1 Hz, 1H), 2.18 (s, 3H), 1.72-1.65 (m, 1H), 1.57-1.49 (m, 1H), 1.46-1.39 (m, 2H), 1.38 (s, 3H), 1.37-1.29 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 203.9, 123.6, 50.8, 38.9, 33.7, 30.8, 26.9, 24.0, 22.6, 13.8; IR (neat): 2959, 2234, 1720 cm^{-1}; MS (ESI): m/z 190 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{10}H_{17}NONa$ $[M+Na]^+$ 190.1208. Found 190.1205; $[\alpha]_D^{26}$ = +14 (*c* = 0.74, $CHCl_3$) for 99% ee; GC condition: Chirasil DEX CB, injector temp. = 200 °C, detector temp. = 250 °C, column temp. = 95 °C (isothermic), t = 16.6 min (major), 18.8 min (minor).

GC chart of *rac*-**8b**

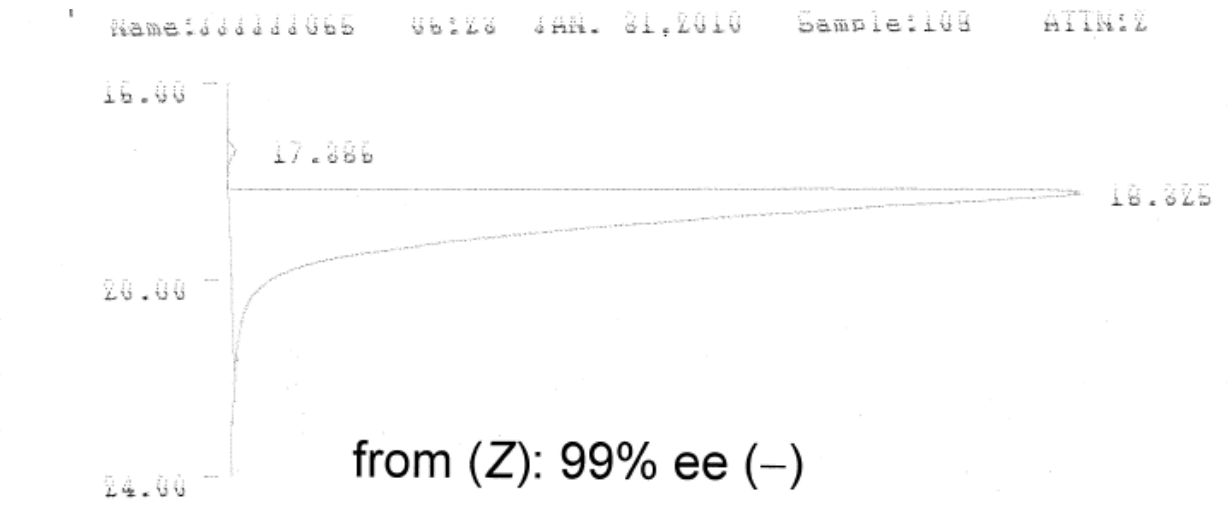


GC chart of (+)-**8b**



NO.	NAME	RT	AREA	MARK	CONC	HEIGHT
1		16.640	205118	V	99.7128	8366
2		18.778	588	V	0.2871	88
TOTAL			205706		100.0000	8454

HPLC chart of (–)-**8b**

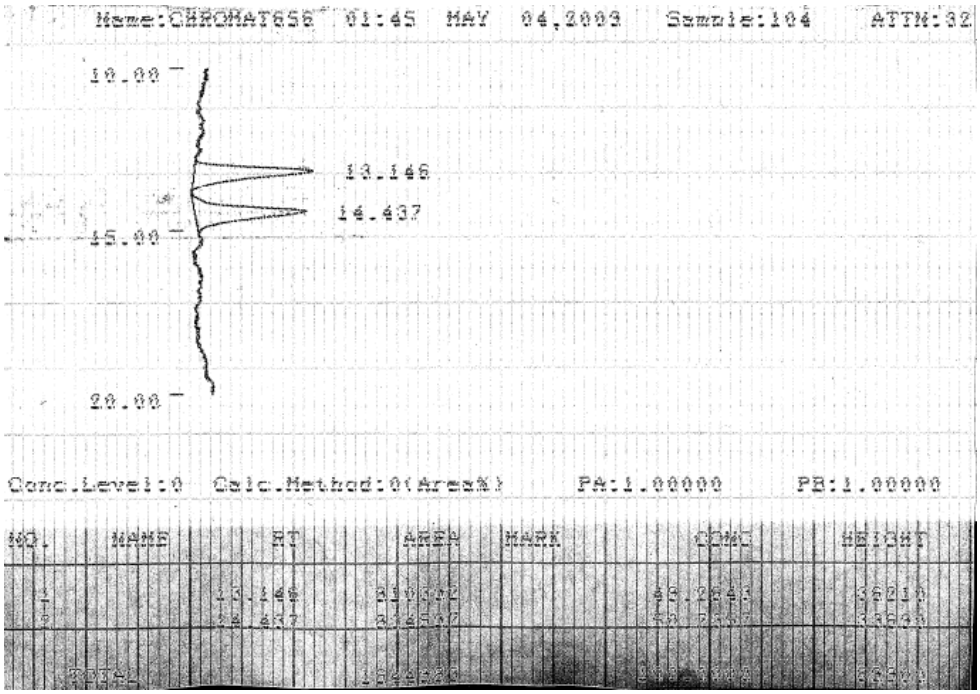


NO.	NAME	RT	AREA	MARK	CONC	HEIGHT
1		17.866	2167	V	0.3302	124
2		18.825	654043	V	99.6697	18508
TOTAL			656210		100.0000	18632

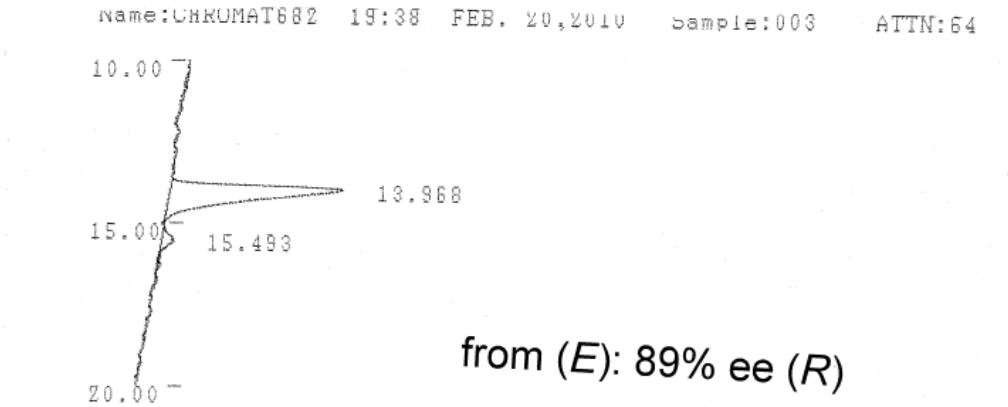
(*S*)-2-Methyl-2-(1-methylethyl)-4-oxo-pentanenitrile (8c)

^{1}H NMR ($CDCl_3$): δ = 2.80 (d, *J* = 16.8 Hz, 1H) , 2.56 (d, *J* = 16.8 Hz, 1H), 2.20 (s, 3H), 2.01-1.92 (m, 1H), 1.36 (s, 3H), 1.04 (d, *J* = 6.7 Hz, 3H), 1.01 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 204.2, 123.0, 48.8, 38.2, 34.7, 31.0, 20.8, 18.1, 17.4; IR (neat): 3428, 2922, 2233, 1720 cm^{-1}; MS (ESI): m/z 176 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_9H_{15}NONa$ $[M+Na]^+$ 176.1051. Found 176.1056; $[\alpha]_D^{25}$ = –32 (*c* = 0.56, $CHCl_3$) for 99% ee; HPLC condition: Chiralpak AS-H column, flow rate: 1.0 mL / min, *n*-hexane / *i*-PrOH = 20 / 1, t = 13.1 min (*R*, minor), 14.4min (*S*, major). RI detection.

HPLC chart of *rac*-**8c**



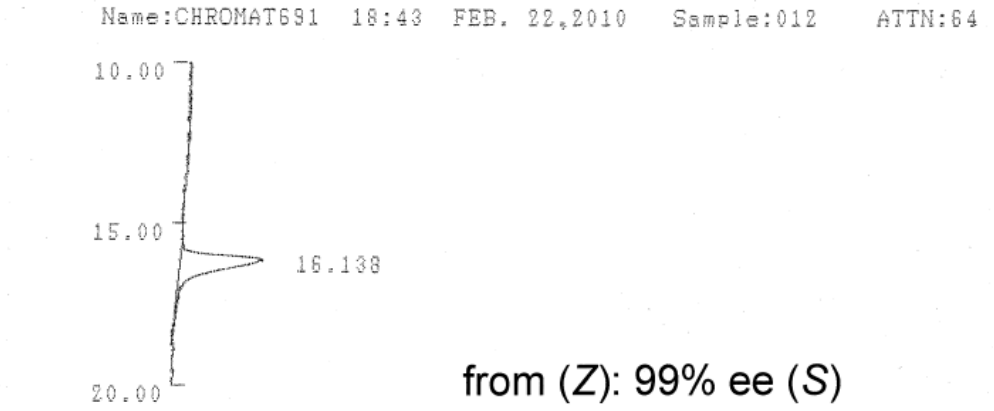
HPLC chart of (*R*)-**8c**



Conc.Level:0 Calc.Method:0(Area%) FA:1.00000 FB:1.00000

NO.	NAME	RT	AREA	MARK	CONC	HEIGHT
1		13.968	3172030		94.6057	107767
2		15.493	180865		5.3942	6584
	TOTAL		3352895		100.0000	114351

HPLC chart of (*S*)-**8c**



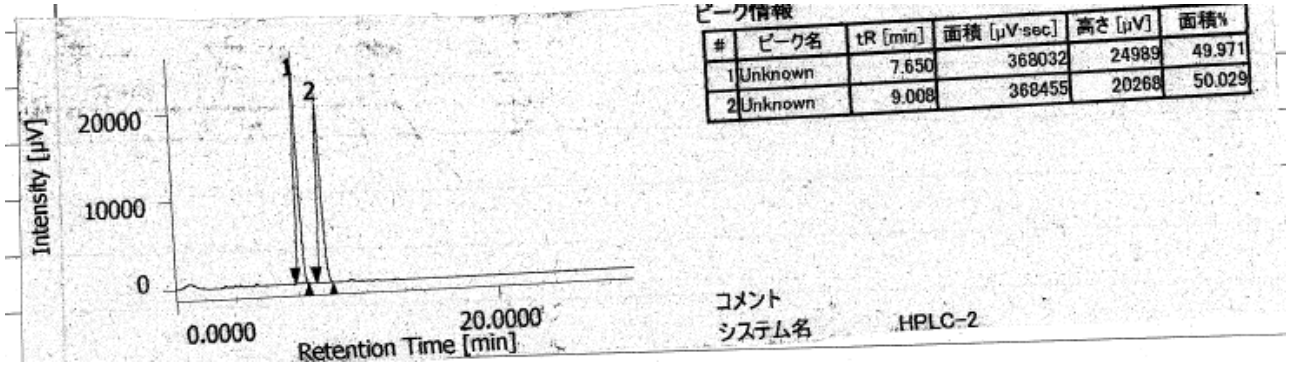
Conc.Level:0 Calc.Method:0(Area%) PA:1.00000 PB:1.00000

NO.	NAME	RT	AREA	MARK	CONC	HEIGHT
1		16.138	1595090		100.0000	50622
	TOTAL		1595090		100.0000	50622

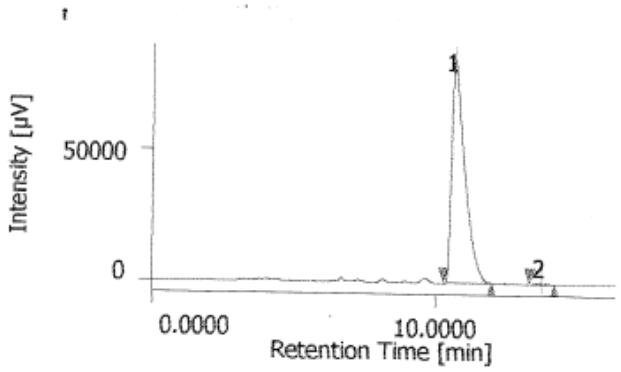
2-Butyl-2-methyl-4-oxo-6-phenylhexanenitrile (8d)

^{1}H NMR ($CDCl_3$): δ = 7.26 (t, *J* = 7.5 Hz, 2H), 7.20-7.14 (m, 3H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.78-2.72 (m, 2H), 2.67 (d, *J* = 17.1 Hz, 1H) , 2.51 (d, *J* = 17.1 Hz, 1H), 1.69-1.61 (m, 1H), 1.53-1.45 (m, 1H), 1.42-1.28 (m, 7H), 0.90 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 205.4, 140.5, 128.5, 128.3, 126.2, 123.6, 50.2, 45.0, 38.9, 33.7, 29.6, 26.8, 24.0, 22.6, 13.8; IR (neat): 2933, 2234, 1719 cm^{-1}; MS (ESI): m/z 280 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{17}H_{23}NONa$ $[M+Na]^+$ 280.1677. Found 280.1671; $[\alpha]_D^{26}$ = –6 (*c* = 2.02, $CHCl_3$) for 99% ee; HPLC condition: Chiralpak AS-H column, flow rate: 1.0 mL / min, *n*-hexane / *i*-PrOH = 9 / 1, t = 10.6 min (major), 13.7 min (minor). λ = 254 nm.

HPLC chart of *rac*-**8d**



HPLC chart of (–)-**8d**



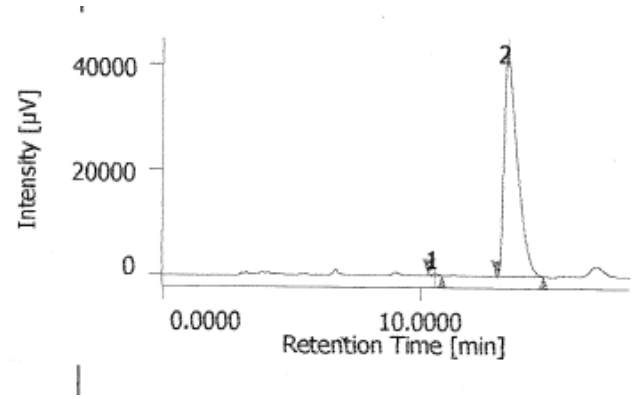
ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%
1	Unknown	10.558	2693219	85400	99.449
2	Unknown	13.667	14925	601	0.551

from (*E*): 99% ee (–)

システム名 HPLC-1

HPLC chart of (+)-**8d**



ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%
1	Unknown	10.508	5704	331	0.379
2	Unknown	13.250	1498636	42612	99.621

from (*Z*): 99% ee (+)

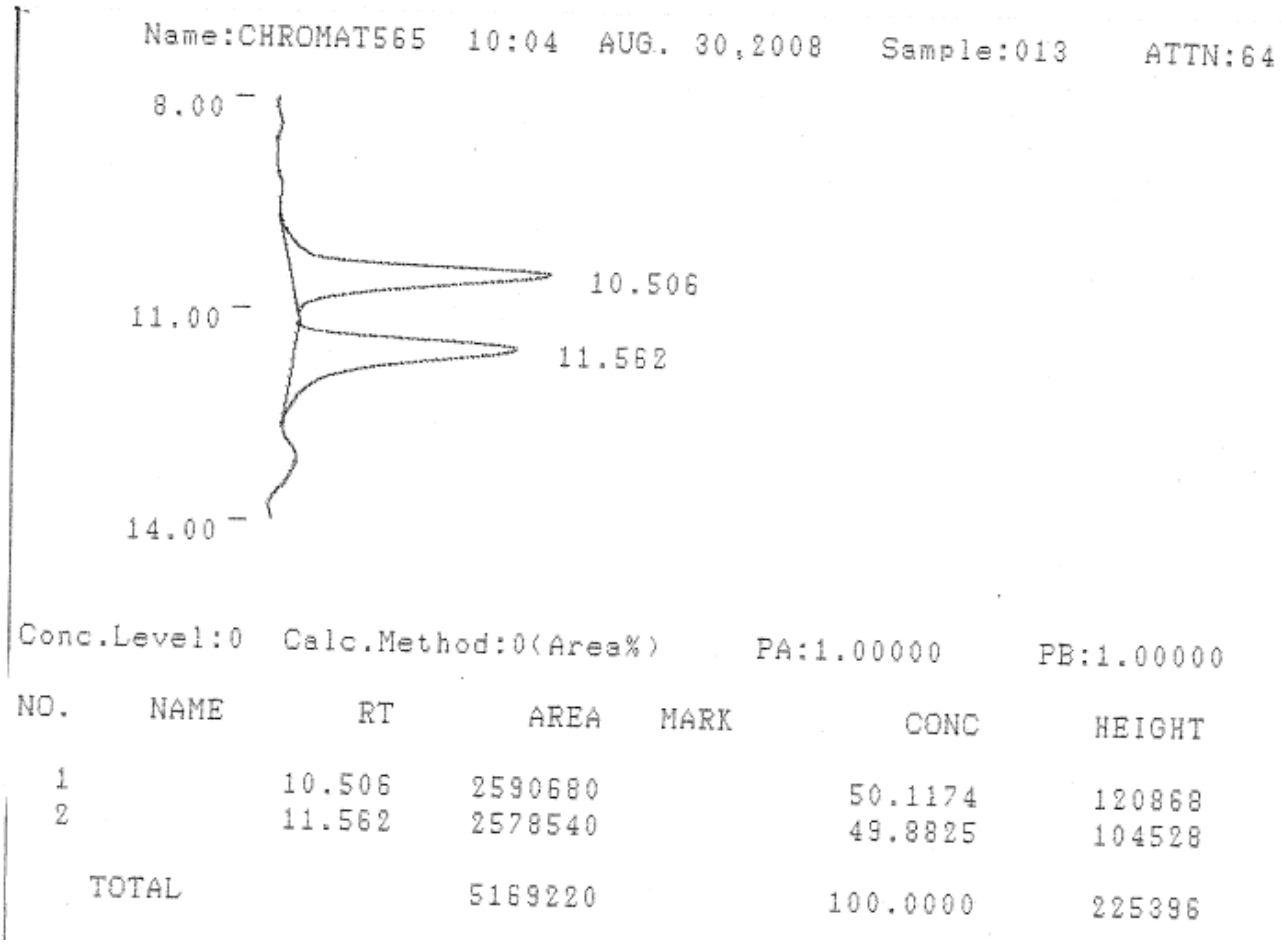
システム名 HPLC-1

測定日 2010/02/24 13:13:13

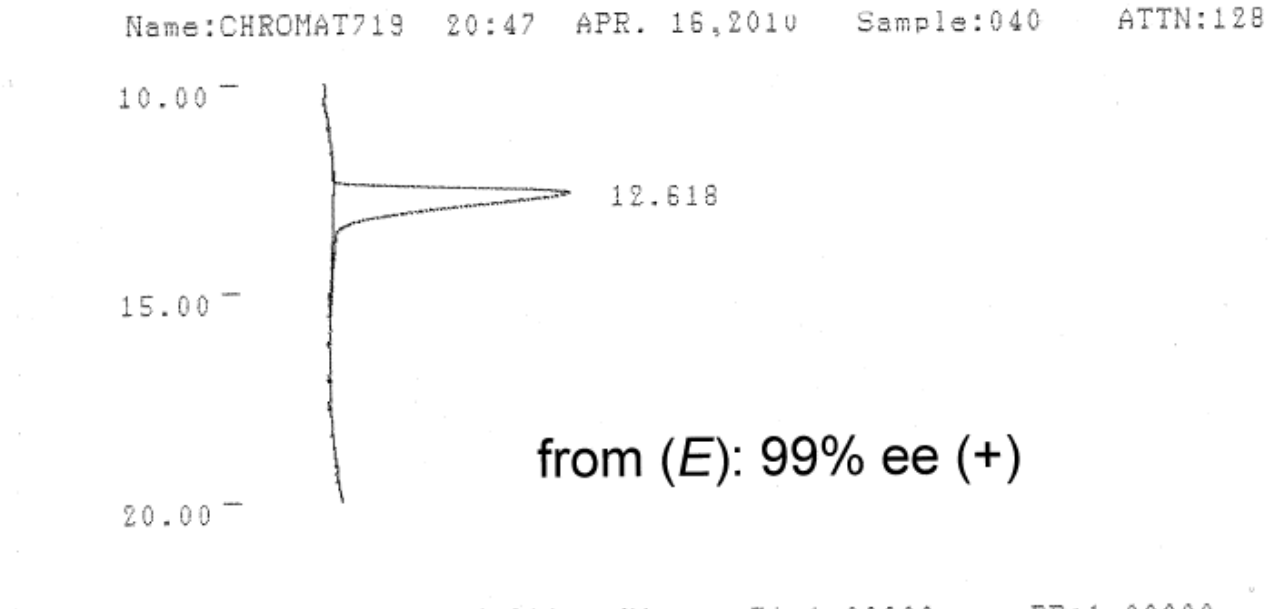
2-Butyl-4-cyclohexyl-2-methyl-4-oxo-butanenitrile (8e)

^{1}H NMR ($CDCl_3$): δ = 2.74 (d, *J* = 17.1 Hz, 1H) , 2.59 (d, *J* = 17.1 Hz, 1H), 2.34-2.26 (m, 1H), 1.84-1.60 (m, 6H), 1.57-1.46 (m, 1H), 1.45-1.11 (m, 12H), 0.89 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 209.4, 123.8, 51.2, 47.8, 38.8, 33.7, 28.3, 28.1, 26.9, 25.7, 25.5, 25.4, 24.0, 22.6, 13.8; IR (neat): 2931, 2234, 1712 cm^{-1}; MS (ESI): m/z 258 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{15}H_{25}NONa$ $[M+Na]^+$ 258.1834. Found 258.1817; $[\alpha]_D^{25}$ = +9 (*c* = 1.26, $CHCl_3$) for 99% ee; HPLC condition: Chiralpak AS-H column, flow rate: 1.0 mL / min, *n*-hexane / *i*-PrOH = 99 / 1, t = 12.7min (major), 14.1 min (minor). RI detection.

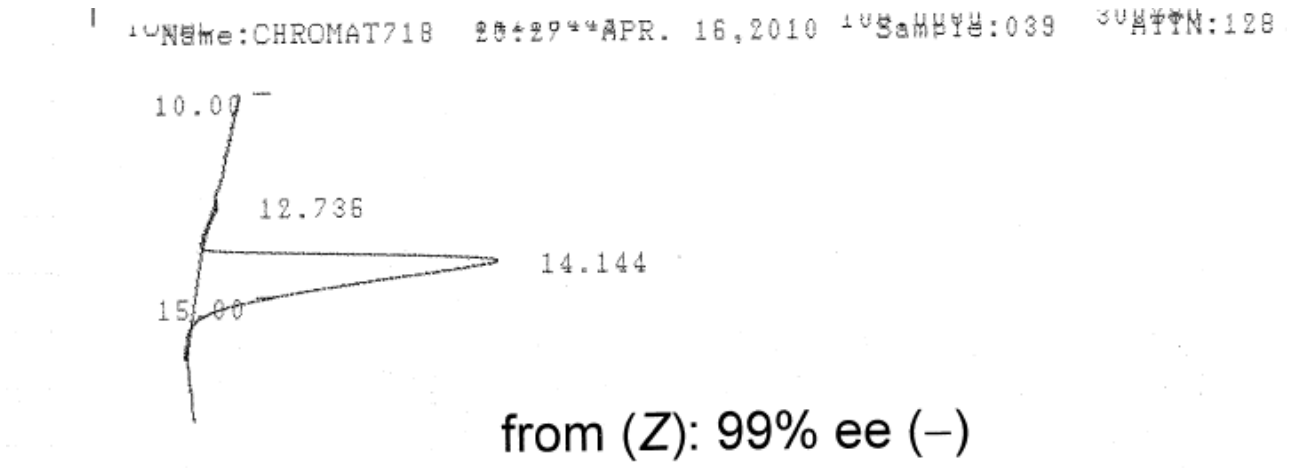
HPLC chart of *rac*-**8e**



HPLC chart of (+)-**8e**



HPLC chart of (−)-**8e**



Conc.Level:0 Calc.Method:0(Area%) PA:1.00000 PB:1.00000

NO.	NAME	RT	AREA	MARK	CONC	HEIGHT
1		12.736	28790		0.2039	2500
2		14.144	14085600		99.7960	296563
	TOTAL		14114390		100.0000	299063

2-Methyl-4-oxo-2-phenylpentanenitrile (8f)

^{1}H NMR ($CDCl_3$): δ = 7.45 (d, *J* = 8.0 Hz, 2H), 7.37 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.29 (dd, *J* = 8.0, 8.0 Hz, 1H), 3.12 (d, *J* = 17.0 Hz, 1H) , 3.01 (d, *J* = 17.0 Hz, 1H), 2.09 (s, 3H), 1.78 (s, 3H); ^{13}C NMR ($CDCl_3$): δ = 202.9, 139.6, 129.0, 128.0, 125.3, 122.7, 53.4, 38.7, 30.6, 27.3; IR (neat): 2983, 2238, 1719 cm^{-1}; MS (ESI): m/z 210 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{12}H_{13}NONa$ $[M+Na]^+$ 210.0895. Found 210.0893; $[\alpha]_D^{26}$ = –4 (*c* = 0.60, $CHCl_3$) for 99% ee; HPLC condition: Chiralpak AS-H column, flow rate: 1.0 mL / min, *n*-hexane / *i*-PrOH = 4 / 1, t = 10.2 min (major), 13.1 min (minor). λ = 254 nm.

2,4-Diphenyl-2-methyl-4-oxobutanenitrile (8g)

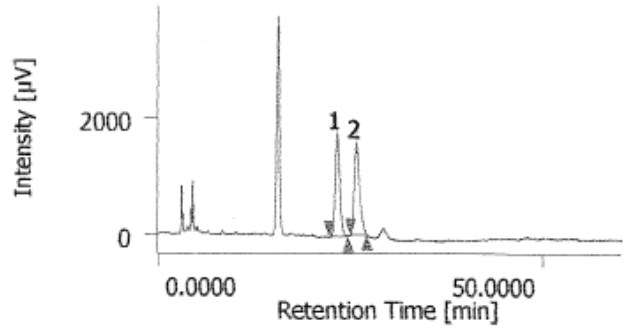
^{1}H NMR ($CDCl_3$): δ = 7.87 (d, *J* = 7.4 Hz, 2H), 7.58-7.50 (m, 3H), 7.43 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.37 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.29 (dd, *J* = 7.4, 7.4 Hz, 1H), 3.72 (d, *J* = 17.7 Hz, 1H) , 3.56 (d, *J* = 17.7 Hz, 1H), 1.89 (s, 3H); ^{13}C NMR ($CDCl_3$): δ = 194.2, 140.0, 136.1, 133.6, 129.0, 128.7, 127.9, 127.9, 125.4, 122.9, 48.7, 38.9, 27.6; IR (neat): 3061, 2238, 1689, 1448, 1225 cm^{-1}; MS (ESI): m/z 272 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{17}H_{15}NONa$ $[M+Na]^+$ 272.1051. Found 272.1040; $[\alpha]_D^{25}$ = –58 (*c* = 1.31, $CHCl_3$) for 99% ee; HPLC condition: Chiralpak AS-H column, flow rate: 1.0 mL / min, *n*-hexane / *i*-PrOH = 4 / 1, t = 12.1 min (major), 13.1 min (minor). λ = 254 nm.

2-Ethyl-4-oxo-2-phenylpentanenitrile (8h)

^{1}H NMR ($CDCl_3$): δ = 7.40 (d, *J* = 7.8 Hz, 2H), 7.36 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.28 (dd, *J* = 7.8 Hz, 1H), 3.12 (d, *J* = 17.1 Hz, 1H) , 3.07 (d, *J* = 17.1 Hz, 1H), 2.19-2.09 (m, 1H), 2.05 (s, 3H), 1.95-1.87 (m, 1H), 0.89 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 202.9, 137.5, 128.9, 127.9, 125.9, 121.5, 52.5. 44.9, 33.8, 30.6, 9.3; IR (neat): 2973, 2237, 1718 cm^{-1}; MS (ESI): m/z 224 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{13}H_{15}NONa$ $[M+Na]^+$ 224.1051. Found 224.1051; $[\alpha]_D^{26}$ = –36 (*c* = 0.57, $CHCl_3$) for 89% ee; HPLC condition: Chiralpak AS-H column, flow rate: 1.0 mL / min, *n*-hexane / *i*-PrOH = 20 / 1, t = 22.7min (major),

25.9 min (minor). λ = 254 nm.

HPLC chart of *rac*-**8h**

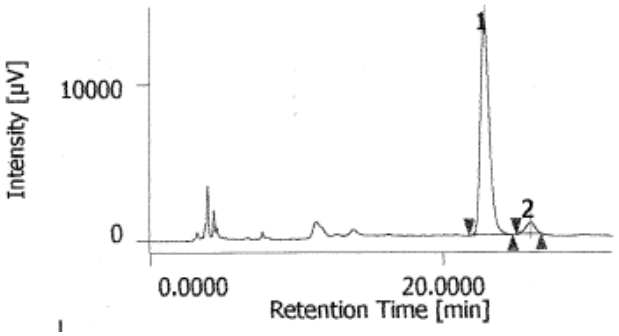


ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%
1	Unknown	23.142	68944	1750	48.214
2	Unknown	25.608	74053	1567	51.786

コメント
システム名 HPLC-2

HPLC chart of (–)-**8h**



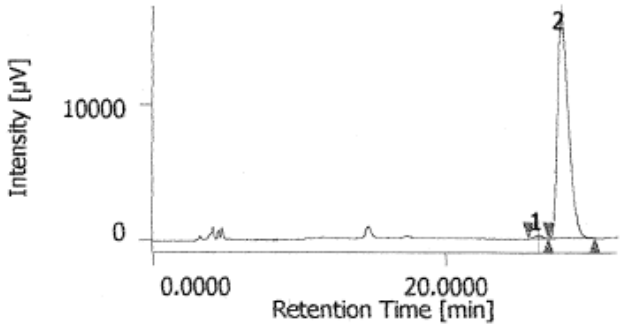
ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%
1	Unknown	22.683	570660	13950	94.317
2	Unknown	25.850	34386	732	5.683

from (*E*): 89% ee (–)

システム名 HPLC-2

HPLC chart of (+)-**8h**



ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%
1	Unknown	26.158	9613	266	1.121
2	Unknown	27.708	847554	16346	98.879

from (*Z*): 98% ee (+)

システム名 HPLC-1

***cis*-2-Acetyl-1-methylcyclohexanecarbonitrile (8i)**

^{1}H NMR ($CDCl_3$): δ = 2.23 (dd, *J* = 12.5, 3.1 Hz, 1H), 2.18 (s, 3H), 2.02-1.86 (m, 3H), 1.77-1.59 (m, 3H), 1.26-1.36 (m, 5H); ^{13}C NMR ($CDCl_3$): δ = 207.4, 122.5, 59.0, 38.7, 35.4, 28.9, 26.7, 25.2, 25.1, 22.7; IR (neat): 2935, 2232, 1712 cm^{-1}; MS (ESI): m/z 188 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{10}H_{15}NONa$ $[M+Na]^+$ 188.1051. Found 188.1047; $[\alpha]_D^{26}$ = +113 (*c* = 0.60, $CHCl_3$) for 99% ee; GC condition: Chirasil DEX CB, injector temp. = 200 °C, detector temp. = 250 °C, column temp. = 90 °C (isothermic), t = 43.7 min (minor), 46.8 min (major).

(*E*)-3,4-Dimethyl-1-(pyrrol-1-yl)-2-penten-1-one ((*E*)-9b)

^{1}H NMR ($CDCl_3$): δ = 7.33 (t, *J* = 2.3 Hz, 2H), 6.32 (s, 1H), 6.26 (t, *J* = 2.3 Hz, 2H), 2.51-2.42 (m, 1H), 2.16 (s, 3H), 1.12 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$): δ = 168.1, 163.6, 119.1, 112.5, 38.4, 20.9, 17.2; IR (neat): 2965, 1697, 1627, 1467, 1276 cm^{-1}; MS (ESI): m/z 200 $[M+Na]^+$; HRMS (ESI): m/z calcd for

$C_{11}H_{15}NONa$ $[M+Na]^+$ 200.1051. Found 200.1045.

(*Z*)-3,4-Dimethyl-1-(pyrrol-1-yl)-2-penten-1-one ((*Z*)-9b)

^1H NMR ($CDCl_3$): δ = 7.32 (t, *J* = 2.5 Hz, 2H), 6.26 (t, *J* = 2.5 Hz, 2H), 6.19 (s, 1H), 3.79-3.68 (m, 1H), 1.91 (d, *J* = 1.5 Hz, 3H), 1.07 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR ($CDCl_3$): δ = 167.4, 162.9, 119.2, 114.4, 112.6, 30.3, 20.6, 19.7; IR (neat): 2965, 1692, 1623, 1281 cm^{-1}; MS (ESI): m/z 200 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{11}H_{15}NONa$ $[M+Na]^+$ 200.1051. Found 200.1043.

(*E*)-3-phenyl-1-(pyrrol-1-yl)-2-buten-1-one ((*E*)-9c)

^1H NMR ($CDCl_3$): δ = 7.33-7.21 (m, 7H), 6.45-6.43 (q, *J* = 1.6 Hz, 1H), 6.21 (t, *J* = 2.3 Hz, 2H), 2.30 (d, *J* = 1.6 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 163.5, 155.4, 139.9, 128.3, 128.2, 126.8, 119.3, 117.4, 112.8, 26.7; IR (neat): 3146, 3056, 2977, 1700, 1627, 1468, 1281 cm^{-1}; MS (ESI): m/z 234 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{14}H_{13}NONa$ $[M+Na]^+$ 234.0895. Found 234.0908.

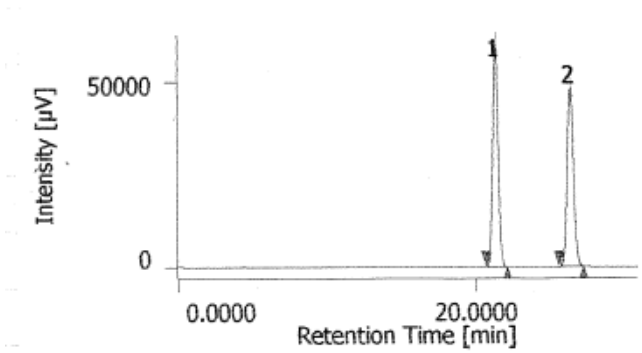
(*Z*)-3-phenyl-1-(pyrrol-1-yl)-2-buten-1-one ((*Z*)-9c)

^1H NMR ($CDCl_3$): δ = 7.57-7.50 (m, 2H), 7.46-7.38 (m, 5H), 6.74 (s, 1H), 6.31 (t, *J* = 2.3 Hz, 2H), 2.61 (d, *J* = 1.3 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 163.3, 157.9, 142.0, 129.4, 128.7, 126.3, 119.2, 115.9, 112.9, 18.9; IR (neat): 3148, 3059, 1688, 1613, 1467, 1292, 1245 cm^{-1}; MS (ESI): m/z 234 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{14}H_{13}NONa$ $[M+Na]^+$ 234.0895. Found 234.0891.

2-Butyl-2-methyl-4-oxo-4-(pyrrol-1-yl)butanenitrile (10a)

^1H NMR ($CDCl_3$): δ = 7.32-7.23 (brs, 2H), 6.30 (t, *J* = 2.3 Hz, 2 H), 3.15 (d, *J* = 16.8 Hz, 1H) , 3.00 (d, *J* = 16.8 Hz, 1H), 1.89-1.81 (m, 1H), 1.69-1.62 (m, 1H), 1.53-1.44 (m, 5H), 1.41-1.33 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 165.8, 123.1, 118.9, 113.7, 42.2, 38.9, 34.4, 27.0, 24.2, 22.6, 13.8; IR (neat): 2959, 2236, 1722, 1470, 1366, 1278 cm^{-1}; MS (ESI): m/z 241 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{13}H_{18}N_2ONa$ $[M+Na]^+$ 241.1317. Found 241.1298; $[\alpha]_D^{25}$ = –1 (*c* = 1.09, $CHCl_3$) for 98% ee; HPLC condition: Chiralpak IC column, flow rate: 1.0 mL / min, *n*-hexane / *i*-PrOH = 20 / 1, t = 23.6 min (minor), 29.2 min (major). λ = 254 nm

HPLC chart of *rac*-**10a**



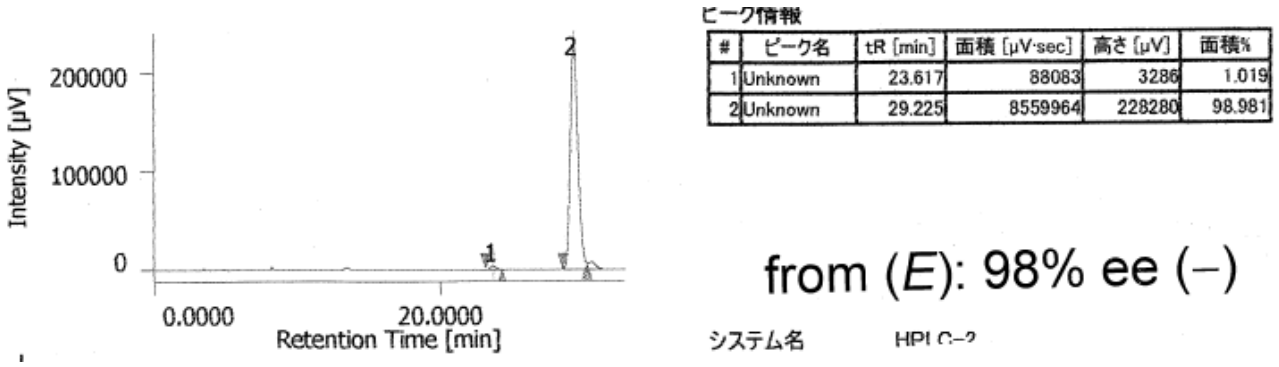
ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%
1	Unknown	21.225	1473477	59678	50.109
2	Unknown	26.242	1467046	47916	49.891

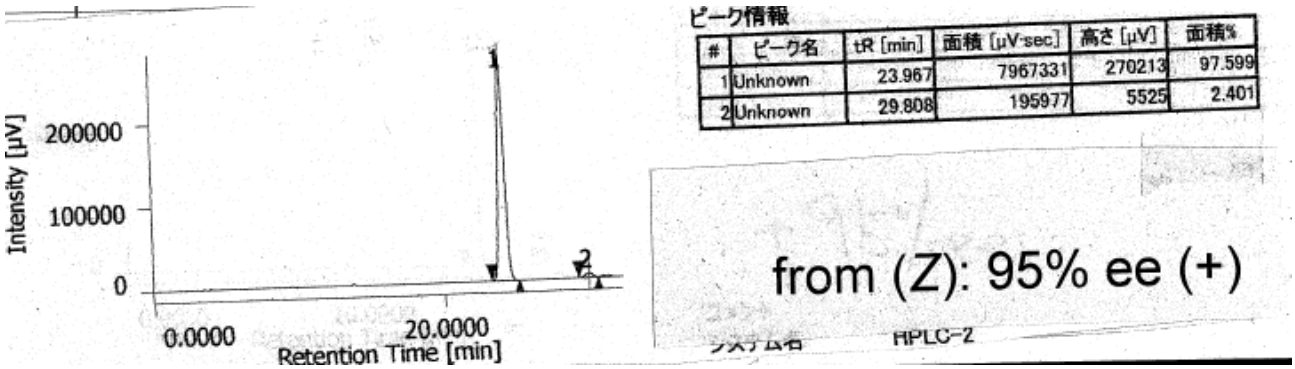
コメント

システム名 HPLC-2

HPLC chart of (–)-**10a**



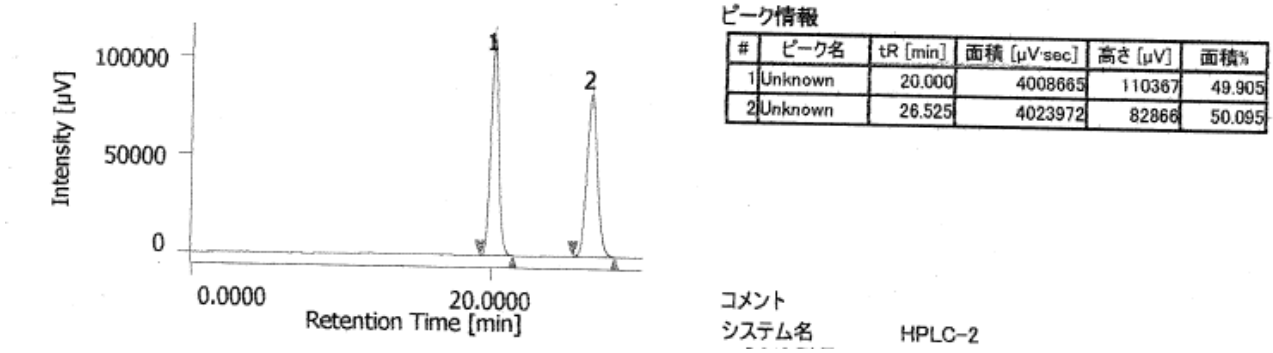
HPLC chart of (+)-**10a**



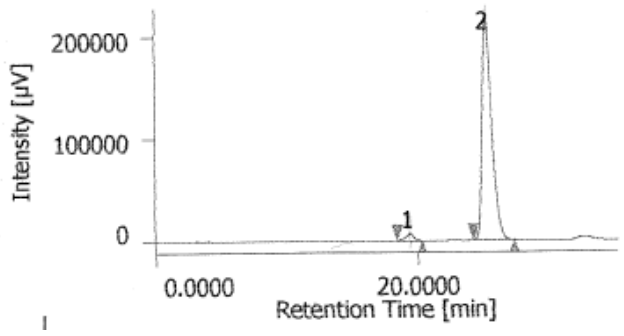
(*R*)-2-Methyl-2-(1-methylethyl)-4-oxo-4-(pyrrol-1-yl)butanenitrile (10b)

^{1}H NMR ($CDCl_3$): δ = 7.32-7.23 (brs, 2H), 6.30 (t, *J* = 2.3 Hz, 2 H), 3.19 (d, *J* = 16.5 Hz, 1H) , 2.99 (d, *J* = 16.5 Hz, 1H), 2.19-2.10 (m, 1H), 1.49 (s, 3H), 1.11 (d, *J* = 6.7 Hz, 3H), 1.07 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 166.1, 122.5, 118.9, 113.7, 40.2, 38.9, 34.6, 21.2, 18.3, 17.5; IR (neat): 2972, 2235, 1720, 1470, 1363, 1277 cm^{-1}; MS (ESI): m/z 227 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{12}H_{16}N_2ONa$ $[M+Na]^+$ 227.1160. Found 227.1163; $[\alpha]_D^{26}$ = +2 (*c* = 0.92, $CHCl_3$) for 95% ee; HPLC condition: Chiralpak AS-H column, flow rate: 1.0 mL / min, *n*-hexane / *i*-PrOH = 9 / 1, t = 19.3 min (*S*, minor), 25.1 min (*R*, major). λ = 254 nm

HPLC chart of *rac*-**10b**



HPLC chart of (*R*)-**10b**



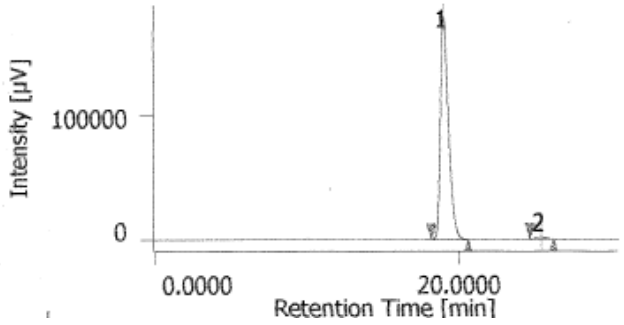
ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%
1	Unknown	19.283	277173	6951	2.495
2	Unknown	25.067	10831387	216515	97.505

from (*E*): 95% ee (*R*)

システム名 HPLC-1

HPLC chart of (*S*)-**10b**



ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%
1	Unknown	18.883	6509109	179028	98.766
2	Unknown	25.267	81357	1922	1.234

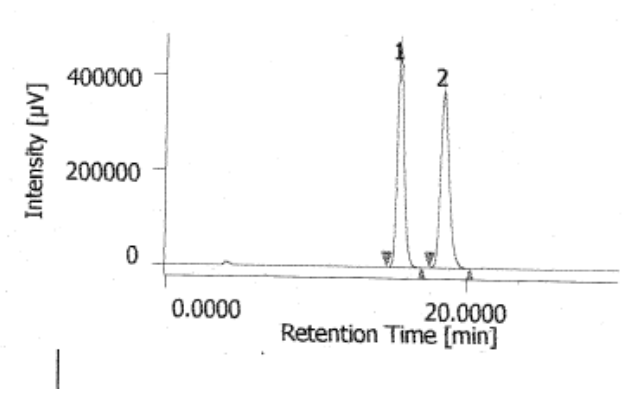
from (*Z*): 98% ee (*S*)

システム名 HPLC-1

2-Methyl-4-oxo-2-phenyl-4-(pyrrol-1-yl)butanenitrile (10c)

^{1}H NMR ($CDCl_3$): δ = 7.51 (d, *J* = 7.6 Hz, 2H), 7.39 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.32 (dd, *J* = 7.6 Hz, 1H), 7.23-7.17 (brs, 2H), 6.26 (t, *J* = 2.4 Hz, 2 H), 3.51 (d, *J* = 16.8 Hz, 1H) , 3.41 (d, *J* = 16.8 Hz, 1H), 1.92 (s, 3H); ^{13}C NMR ($CDCl_3$): δ = 165.2, 139.2, 129.1, 128.3, 125.3, 122.3, 118.8, 113.7, 45.1, 39.2, 27.3; IR (neat): 3147, 2240, 1719, 1470, 1365, 1277 cm^{-1}; MS (ESI): m/z 261 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_{15}H_{14}N_2ONa$ $[M+Na]^+$ 261.1004. Found 261.0990; $[\alpha]_D^{25}$ = –45 (*c* = 1.18, $CHCl_3$) for 99% ee; HPLC condition: Chiralpak AS-H column, flow rate: 1.0 mL / min, *n*-hexane / *i*-PrOH = 9 / 1, t = 24.9 min (major), 32.3 min (minor). λ = 254 nm

HPLC chart of *rac*-**10c**



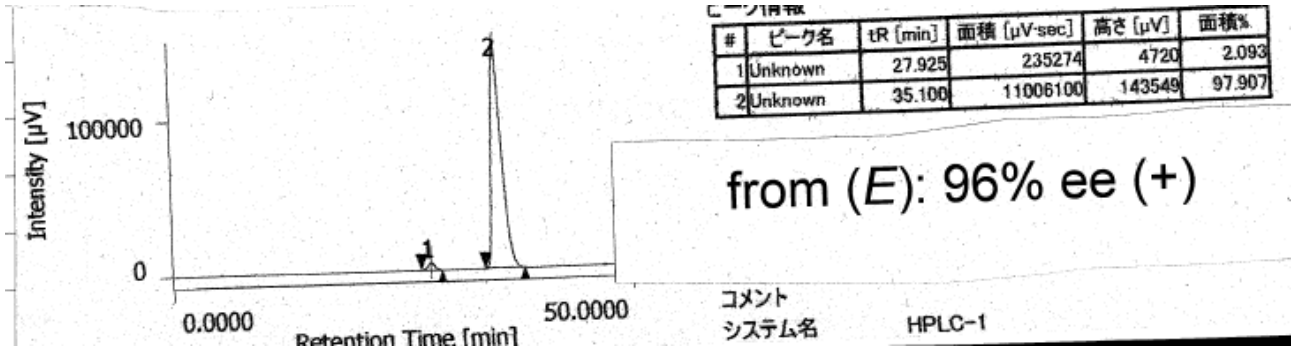
ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%
1	Unknown	15.425	14564894	462062	49.925
2	Unknown	18.342	14608458	372489	50.075

コメント

システム名 HPLC-2

HPLC chart of (+)-**10c**

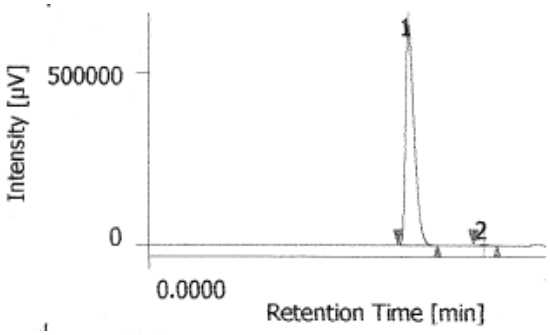


#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%
1	Unknown	27.925	235274	4720	2.093
2	Unknown	35.100	11006100	143549	97.907

from (*E*): 96% ee (+)

コメント
システム名 HPLC-1

HPLC chart of (–)-**10c**

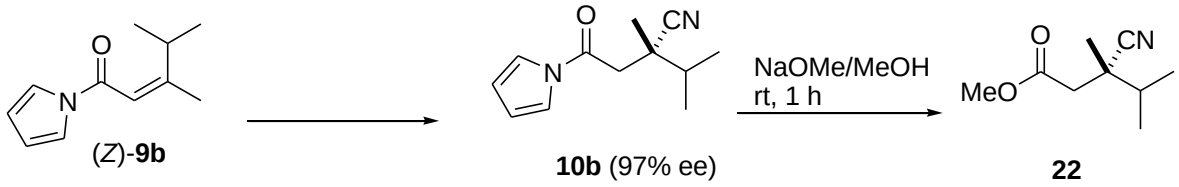


#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%
1	Unknown	24.933	36621144	636678	99.509
2	Unknown	32.250	180745	3155	0.491

from (*Z*): 99% ee (–)

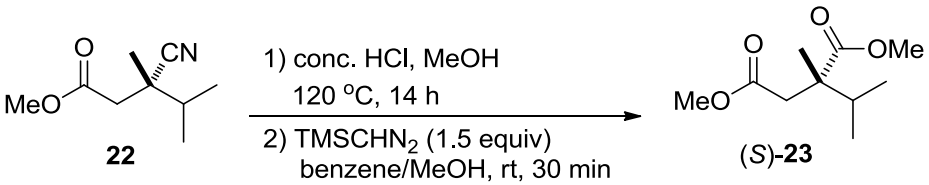
コメント
システム名 HPLC-2

6. Synthetically Useful Conversions of 10 and Determination of the Absolute Configuration



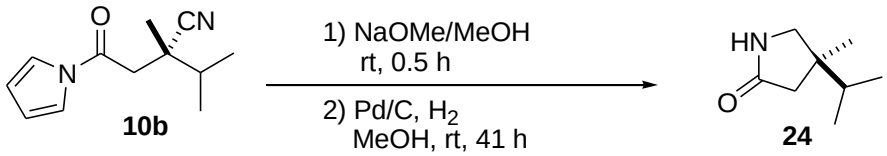
Catalytic enantioselective conjugate addition of cyanide to α,β-unsaturated *N*-acylpyrrole

To a solution of **10b** (97% ee, obtained from (*Z*)-**9b**, 46 mg, 0.225 mmol) in MeOH (2 mL), NaOMe (108 mg, 2 mmol) was added at rt. After stirring for 1 h, satd. NH_4Cl and AcOEt were added, and the organic layer was separated. The aqueous layer was extracted with AcOEt twice, and the combined organic layers were washed with brine. The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure to afford crude **22** (36 mg, 0.190 mmol) as a colorless oil (ca. 85% yield). Crude **22** was used in the next reaction without purification.



Crude **22** was dissolved in MeOH (1.5 mL), and conc. HCl (1.5 mL) was added at rt. The mixture was heated at 120 °C in a sealed tube. After stirring for 14 h, the reaction mixture was cooled in an ice bath, and water and AcOEt were added. The organic layer was separated. The aqueous layer was extracted with AcOEt twice, and the combined organic layers were washed with brine. The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was dissolved in benzene (4 mL) and MeOH (1 mL). To the mixture, TMSdiazomethane (2 M in hexane, 138 μL, 0.276 mmol, 1.5 equiv) was added at rt.

After stirring for 30 min, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (silica gel, hexane-AcOEt, 20:1) to afford (*S*)-**23** (7.7 mg, 0.038 mmol) as a colorless oil in 20% yield. $[\alpha]_D^{23}$ = +8 (*c* = 0.72, $CHCl_3$). The structure and the absolute configuration of (*S*)-**23** was determined by referring to the reported data.[5]

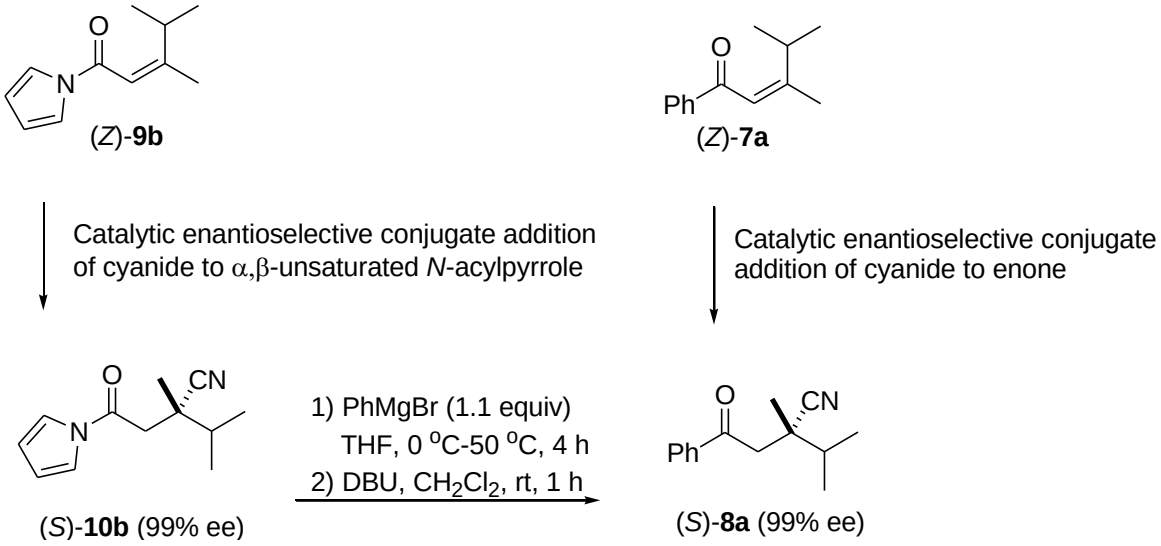


To a solution of **10b** (99% ee, obtained from (*Z*)-**9b**, 4.1 mg, 0.02 mmol) in MeOH (0.2 mL), NaOMe (11 mg, 0.2 mmol) was added at rt. After stirring for 0.5 h, satd. NH_4Cl and AcOEt were added, and the organic layer was separated. The aqueous layer was extracted with AcOEt twice, and the combined organic layers were washed with brine. The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure to afford crude **22** (3.4 mg, 0.02 mmol) as a colorless oil (ca. 100% yield). Crude **22** was used in the next reaction without purification. Crude **22** was dissolved in MeOH (0.2 mL), and Pd/C (15 mg) was added. Under H_2 atmosphere (1 atm) at rt, the mixture was stirred for 41 h. After filtration, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (silica gel, hexane-AcOEt, 2:1, then, CH_2Cl_2-MeOH, 20:1) to afford (*R*)-**24** (2.0 mg, 0.014 mmol) as a colorless crystal in 71% yield. The enantiometric excess of the product was determined by GC analysis to be 99% ee.

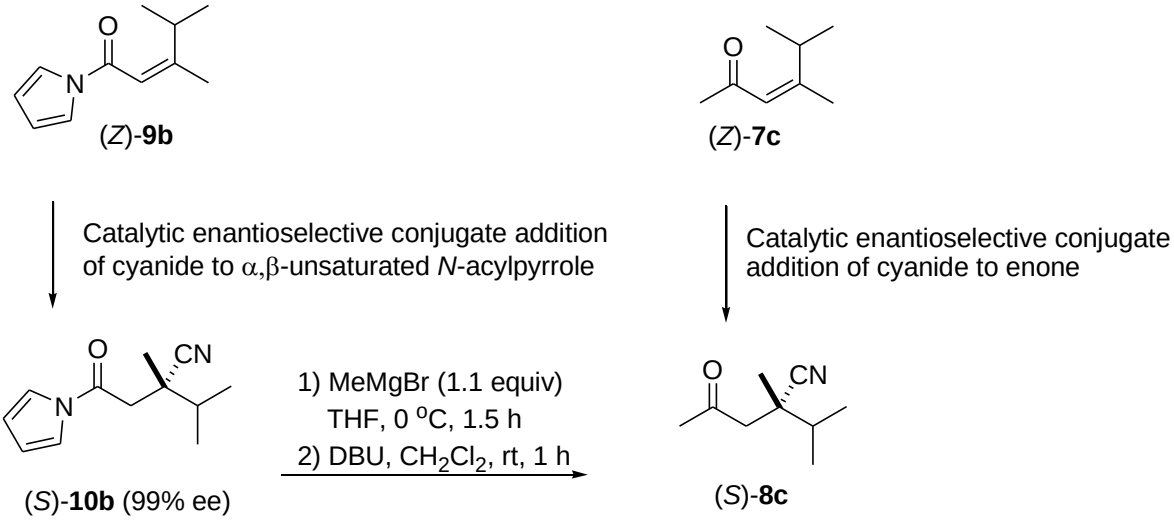
(*R*)-4-Methyl-4-(1-methylethyl)-2-pyrrolidinone (24)

^{1}H NMR ($CDCl_3$): ^{1}H NMR ($CDCl_3$): δ = 6.02-5.88 (brs, 1H), 3.18 (d, *J* = 9.5 Hz, 1H), 2.97 (d, *J* = 9.5 Hz, 1H), 2.21 (d, *J* = 16.5 Hz, 1H), 1.98 (d, *J* = 16.5 Hz, 1H), 1.70-1.60 (m, 1H), 1.02 (s, 3H), 0.87 (d, *J* = 7.1 Hz, 3H), 0.83 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 177.9, 53.8, 43.5, 42.5, 36.7, 20.5, 18.0, 17.4; IR (neat): 3189, 2956, 1668 cm^{-1}; MS (ESI): m/z 164 $[M+Na]^+$; HRMS (ESI): m/z calcd for $C_8H_{15}NONa$ $[M+Na]^+$ 164.1051. Found 164.1053; $[\alpha]_D^{23}$ = −18 (*c* = 0.07, $CHCl_3$) for 99% ee; GC condition: Chirasil DEX CB, injector temp. = 200 °C, detector temp. = 250 °C, column temp. = initial 20 min: 120 °C, then the temp. was elevated at the ratio 1 °C/min. until 140 °C, t = 35.6 min (minor), 36.7 min (major).

[5] Kulkarni, M. V.; Eisenbraun, E. J. *J. Org. Chem.* **1968**, *33*, 1661.



To a solution of (*S*)-**10b** (99% ee, 10 mg, 0.05 mmol) in THF (0.5 mL), PhMgBr (1.08 M solution in THF, 51 μL, 0.055 mmol, 1.1 equiv) was added with cooling in an ice bath, and the reaction mixture was warmed to 50 °C. After stirring for 4 h, satd. NH_4Cl was added, and the organic layer was separated. The aqueous layer was extracted with AcOEt twice, and the combined organic layers were washed with brine. The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (1 mL), and one drop of DBU was added to the mixture at rt. After stirring for 1 h, satd. NH_4Cl was added, and the organic layer was separated. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (silica gel, hexane-Et_2O, 20:1) to afford (*S*)-**8a** (4.1 mg, 0.019 mmol) as a colorless oil in 38% yield. The enantiometric excess of the product was determined by HPLC analysis to be 99% ee.

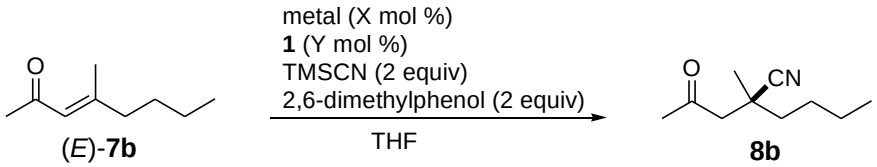


To a solution of (*S*)-**10b** (99% ee, 20 mg, 0.10 mmol) in THF (1 mL), MeMgBr (3 M solution in Et_2O, 37 μL, 0.11 mmol, 1.1 equiv) was added with cooling in an ice bath. After stirring for 1.5 h, satd. NH_4Cl was added, and the organic layer was separated. The aqueous layer was extracted with AcOEt twice, and the combined organic layers were washed with brine. The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (1 mL), and one drop of DBU was added to the mixture at rt. After stirring for 1 h, satd. NH_4Cl was added, and the organic layer was separated.

The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (silica gel, hexane-EtOAc, 20:1) to afford (*S*)-**8c** (7.2 mg, 0.047 mmol) as a colorless oil in 47% yield. $[\alpha]_D^{25} = -24$ (*c* = 0.52, $CHCl_3$).

7. Study of Catalytic Metals

Table S-1 Study of catalytic metals in combination with ligand **1**



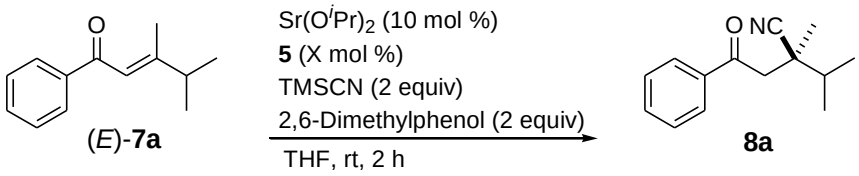
(*E*)-**7b** **8b**

entry	metal (X mol %)	**1** (Y mol %)	temp	time (h)	yield (%)	ee (%)
1	$Ca(O^iPr)_2$ (30 mol %)	30	rt	15	5	22
2	$Sr(O^iPr)_2$ (30 mol %)	30	rt	15	82	54
3	$Sr(HMDS)_2$-2DME (30 mol %)	30	rt	15	90	53
4	$Ba(O^iPr)_2$ (30 mol %)	30	rt	15	5	3
5	$Ti(O^iPr)_4$ (20 mol %)	40	rt-60 ºC	36	0	-
6	$Zr(O^iPr)_4$ (20 mol %)	40	rt-60 ºC	36	<5	1
7	$Hf(O^iPr)_4$ (20 mol %)	40	rt-60 ºC	36	<4	2
8	$Al(O^iPr)_3$ (20 mol %)	30	rt-50 ºC	15	trace	2
9	$Ga(O^iPr)_3$ (20 mol %)	30	rt-50 ºC	15	0	-
10	$In(O^iPr)_3$ (20 mol %)	30	rt-50 ºC	15	0	-
11	BEt_3 (10 mol %)	15	rt-55 ºC	24	0	-
12	$AlEt_3$ (10 mol %)	15	rt-55 ºC	24	0	-
13[a]	$Pr(O^iPr)_3$ (10 mol %)	15	rt	24	14	22
14[a]	$Nd(O^iPr)_3$ (10 mol %)	15	rt	24	16	8
15[a]	$Sm(O^iPr)_3$ (10 mol %)	15	rt	24	28	26
16[a]	$Gd(O^iPr)_3$ (10 mol %)	15	rt	24	26	34

[a] TBSCN was used instead of TMSCN

8. Ee vs Sr/ligand Ratio

Table S-2 Catalytic asymmetric conjugate cyanation of (*E*)-**7a** performed at different Sr/ligand ratio

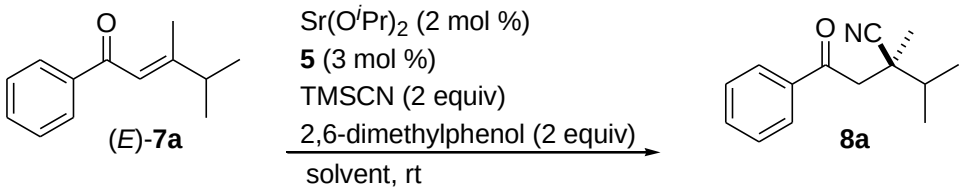


entry	ligand (X mol %)	metal : ligand ratio	yield (%)	ee (%)
1	10	1 : 1	100	96
2	15	2 : 3	100	98
3	20	1 : 2	100	98
4	25	2 : 5	100	98

The enantioselectivity was constantly high (>96% ee) regardless of the Sr:ligand ratio.

9. Optimization of the Reaction Parameters

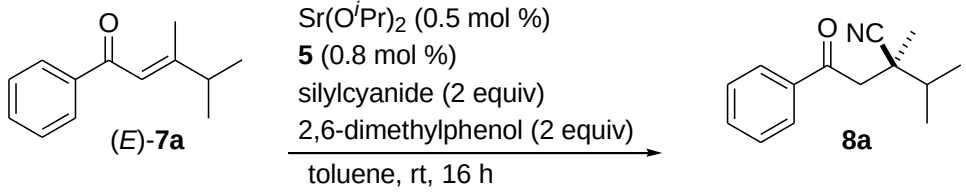
Table S-3 Catalytic asymmetric conjugate cyanation of (*E*)-**7a** performed using different solvents



entry	solvent	time (h)	yield (%)	ee (%)
1	THF	18	11	–1
2	dioxane	18	13	–13
3	Et_2O	1	82	–96.6
4	DME	18	79	–95.4
5	MeCN	18	34	–91.5
6	CH_2Cl_2	13	92	–93.1
7	toluene	1	99	–96.3

When the catalyst loading was reduced to 2 mol %, the use of THF gave significantly low yield and enantioselectivity. On the other hand, by the use of toluene as a solvent, the catalyst loading could be reduced to 2 mol % without any loss of yield nor enantioselectivity.

Table S-4 Catalytic asymmetric conjugate cyanation of (*E*)-**7a** performed using different silylcyanide

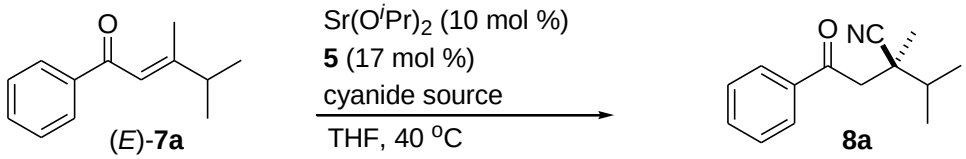


entry	silylcyanide	yield (%)	ee (%)
1	TMSCN	11	50
2	TBSCN	100	97

When the catalyst loading was reduced to 0.5 mol %, the use of TMSCN gave significantly low yield and enantioselectivity. On the other hand, by the use of TBSCN as a HCN source, the catalyst loading could be reduced to 0.5 mol % without any loss of yield nor enantioselectivity.

10. Catalytic Asymmetric Conjugate Cyanation Performed Using HCN

Table S-5 Catalytic asymmetric conjugate cyanation of (*E*)-**7a** performed using HCN

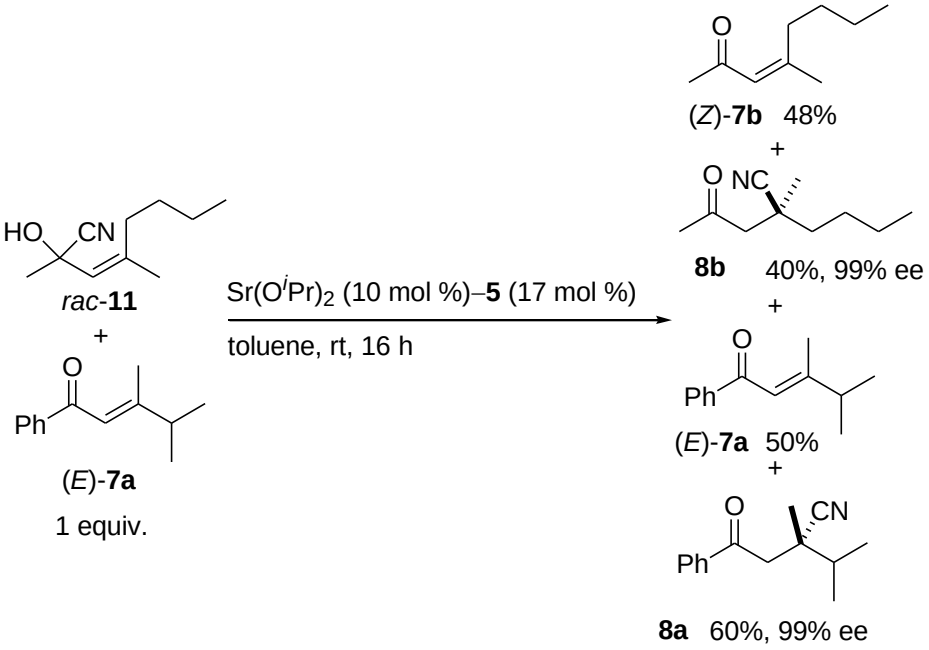


entry	cyanide source	time (h)	yield (%)	ee (%)
1	TMSCN (2 equiv) + 2,6-dimethylphenol (2 equiv)	1	100	97
2	TMSCN (2 equiv) + MeOH (2 equiv)	1	100	98
3	HCN (5M solution in toluene)	4	100	97

The use of HCN source other than silylcyanide + 2,6-dimethylphenol (entries 2 and 3) gave almost the same yield and enantioselectivity. Therefore, we assume that HCN should be the stoichiometric cyanide source, and silyl groups are not relevant to the catalytic cycle.

11. Crossover Experiment

Scheme S-1 Catalytic asymmetric rearrangement of cyanide using *rac*-**11** and (*E*)-**7a**



Treatment of racemic cyanohydrine **11** with the catalyst in the presence of enone (*E*)-**7a** produced enone (*Z*)-**7b** and 1,4-addition products **8b** and **8a** with the recovery of (*E*)-**7a**. This result indicates that catalytic asymmetric rearrangement of cyanide proceeds via intermolecular process.

12. ESI-MS Studies

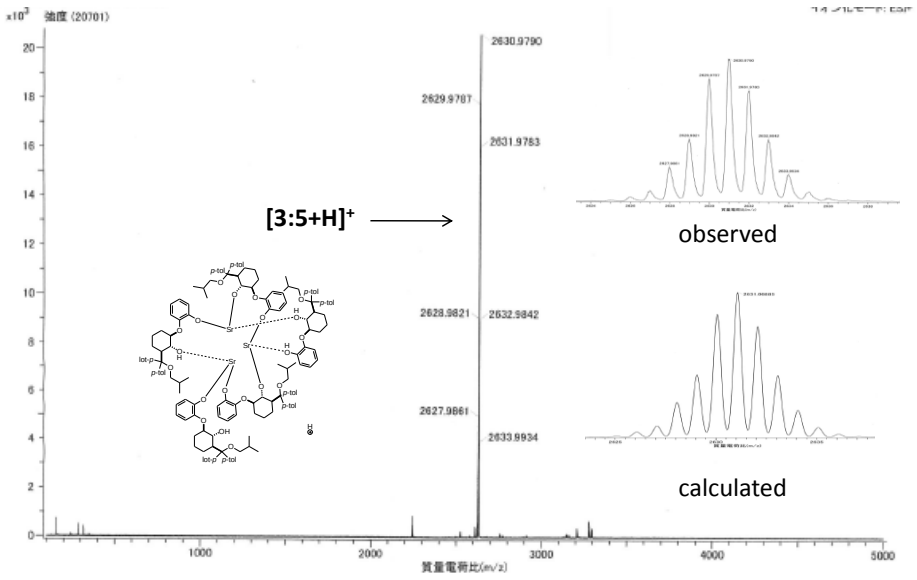


Figure S-1 Spectrum of Sr-**5** generated under the optimized catalyst preparation conditions (1:1.7 ratio).

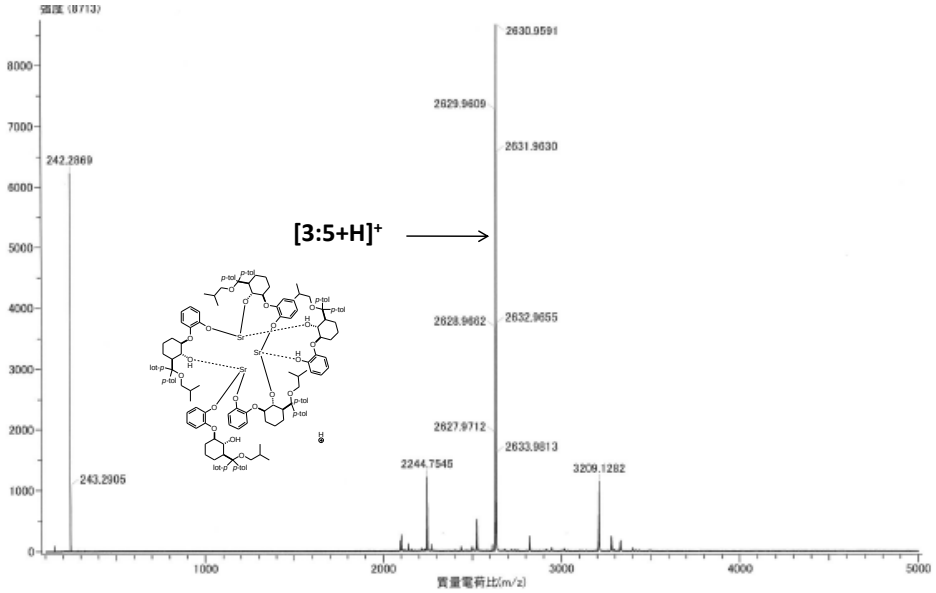


Figure S-2 Spectrum of Sr-**5** generated from 1:1 ratio.

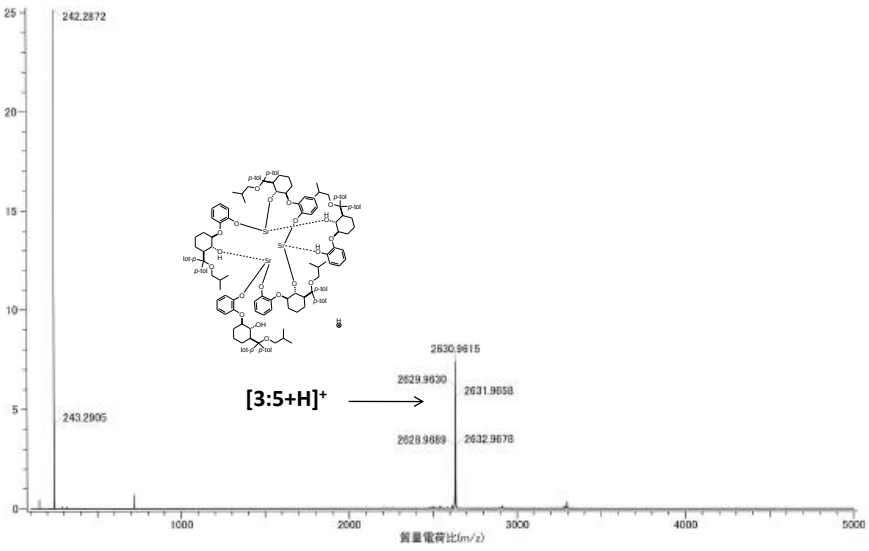


Figure S-3 Spectrum of Sr-**5** generated from 1:2.5 ratio.

There is only one species, which corresponds to a Sr:ligand = 3:5 complex in the MS chart (**Figure S-1**: catalyst prepared in a Sr:**5** = 1:1.7 ratio). That species was observed as a major component in the two MS charts (**Figure S-2**: catalyst prepared in a Sr:**5** = 1:1 ratio, and **Figure S-3**: catalyst prepared in a Sr:**5** = 1:2.5 ratio). The isotope distribution pattern of the MS peak completely matched with the calculated pattern. This fact, together with the independency of the product ee on the Sr:**5** ratio in catalyst preparation (**Table S-2**), strongly indicates that the active catalyst is a trimetallic Sr/**5** = 3:5 complex, and that this higher-order

structure is stable.

13. Proposed Catalytic Cycle

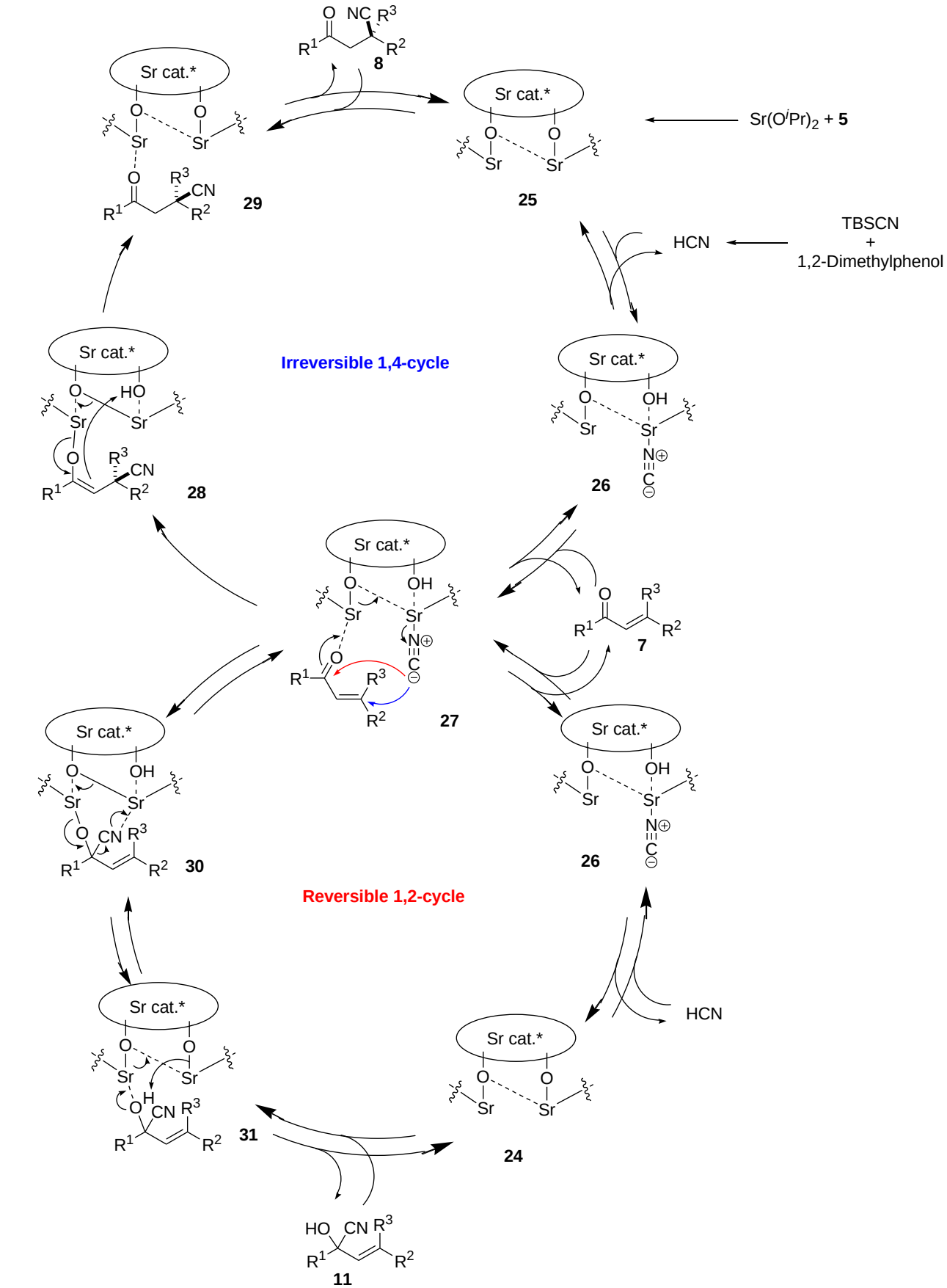


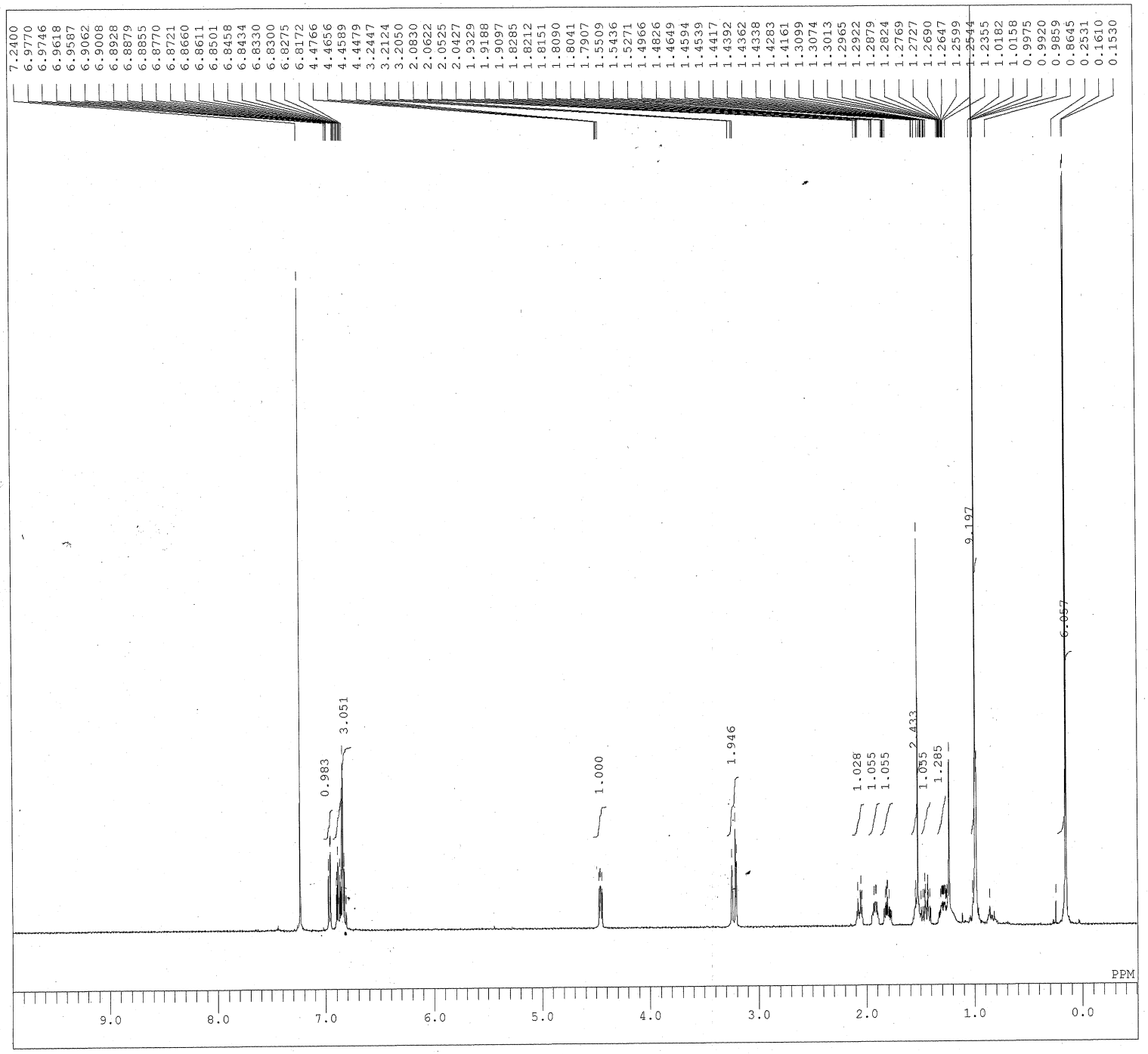
Figure S-4 Proposed catalytic cycle

On the hypothesis that the actual nucleophile is strontium isocyanide, which attacks to enone coordinated to strontium, we propose the catalytic cycle as depicted in **Figure S-4**. The active catalyst is Sr-**5** = 3:5 complex (**25**). HCN is generated from TBSCN and 2,6-dimethylphenol in situ. From catalyst **25** and HCN, strontium isocyanide (**26**) is formed. After the coordination of enone (**7**) to complex **26**, cyanation reaction proceeds through **27**. If 1,4-addition proceeds (blue arrow in **27**), resulting strontium enolate in **28** is protonated, and β-cyanoketone (**8**) is generated irreversibly accompanying the regeneration of the active catalyst (**25**). If 1,2-addition proceeds (red arrow in **27**), cyanohydrin (**11**) can be generated by protonation of the resulting alkoxide in **30**. However, this process is reversible, and cyanohydrin (**11**) coordinates to the active catalyst (**25**), forming **31**, followed by deprotonation of the cyanohydrin to generate complex **30**. Then, retro-1,2-cyanation proceeds through complex **27** accompanying regeneration of enone (**7**).

14. References for Catalytic Enantioseloective Conjugate Addition of Alkyl or Aryl Groups in Quaternary Ketone Synthesis (Supplement of ref 2 in the text)

(a) Lee, K.; Brown, M. K.; Hird, A. W.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2006**, *128*, 7182. (b) Brown, M. K.; May, T. L.; Baxter, C. A.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 1097. (c) May, T.; Brown, M. K.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 7358. (d) Martin, D.; Kehrli, S.; d'Augustin, M.; Clavier, H.; Mauduit, M.; Alexakis, A. *J. Am. Chem. Soc.* **2006**, *128*, 8416. (e) Palais, L.; Mikhel, I. S.; Bournaud, C.; Micouin, L.; Falciola, C. A.; d'Augustin, M.; Rosset, S.; Bernardinelli, G.; Alexakis, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 7462. (f) d'Augustin, M.; Alexakis, A. *Chem. Eur. J.* **2007**, *13*, 9647. (g) Hawner, C.; Li, K.; Cirriez, V.; Alexakis, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 8211. (h) Wilsily, A.; Fillion, E. *Org. Lett.* **2008**. *10*, 2801. (i) Shintani, R.; Duan, W.; Hayashi, T. *J. Am. Chem. Soc.* **2006**, *128*, 5628.

epox



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FREQU	10000.00 Hz
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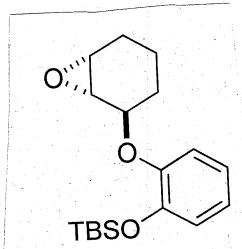
PD	3.7232 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	25.8 c
SLVNT	CDCL3
EXREF	7.24 ppm
BF	0.12 Hz
RGAIN	21



13

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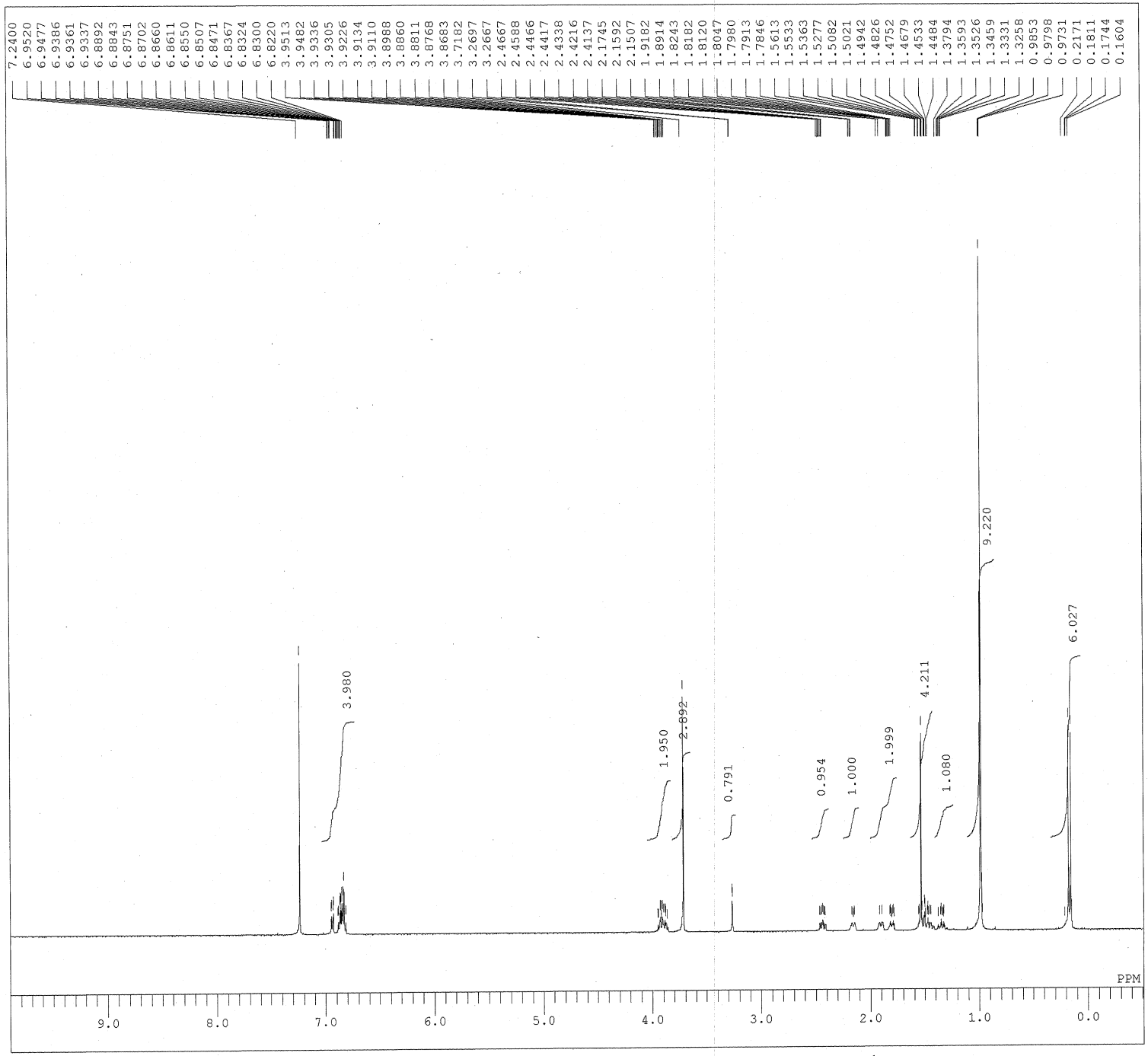


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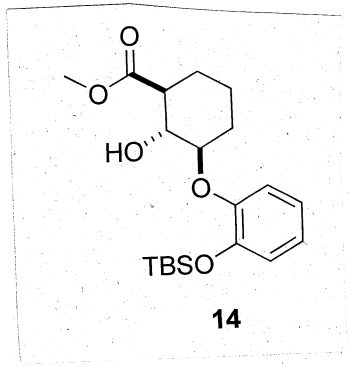

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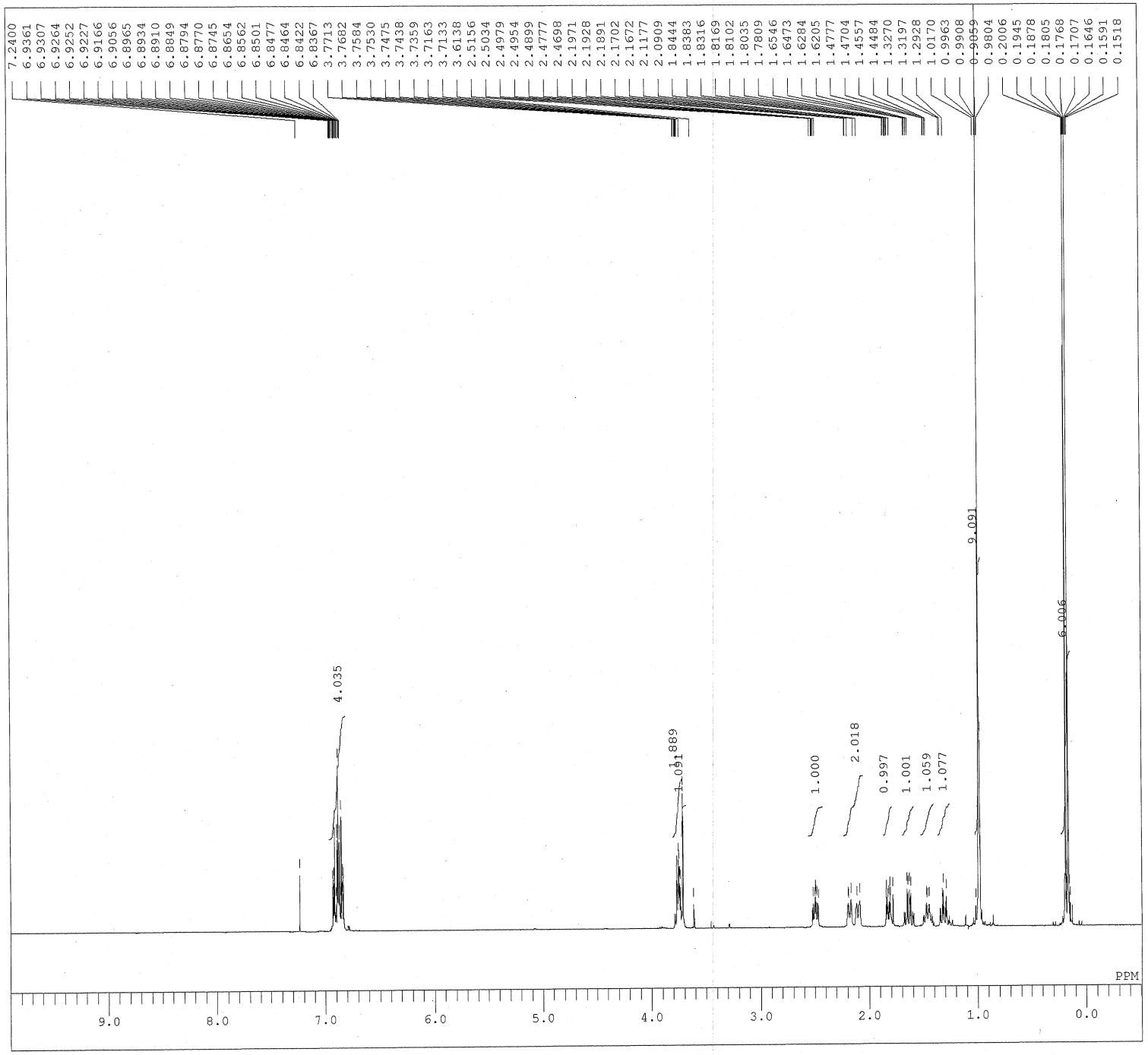

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FREQU 10000.00 Hz
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ACQTM 3.2768 sec
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IRNUC 1H
CTEMP 24.3 c
SLVNT CDCL3
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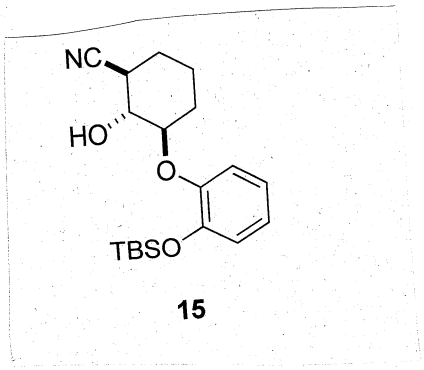
RGAIN 12



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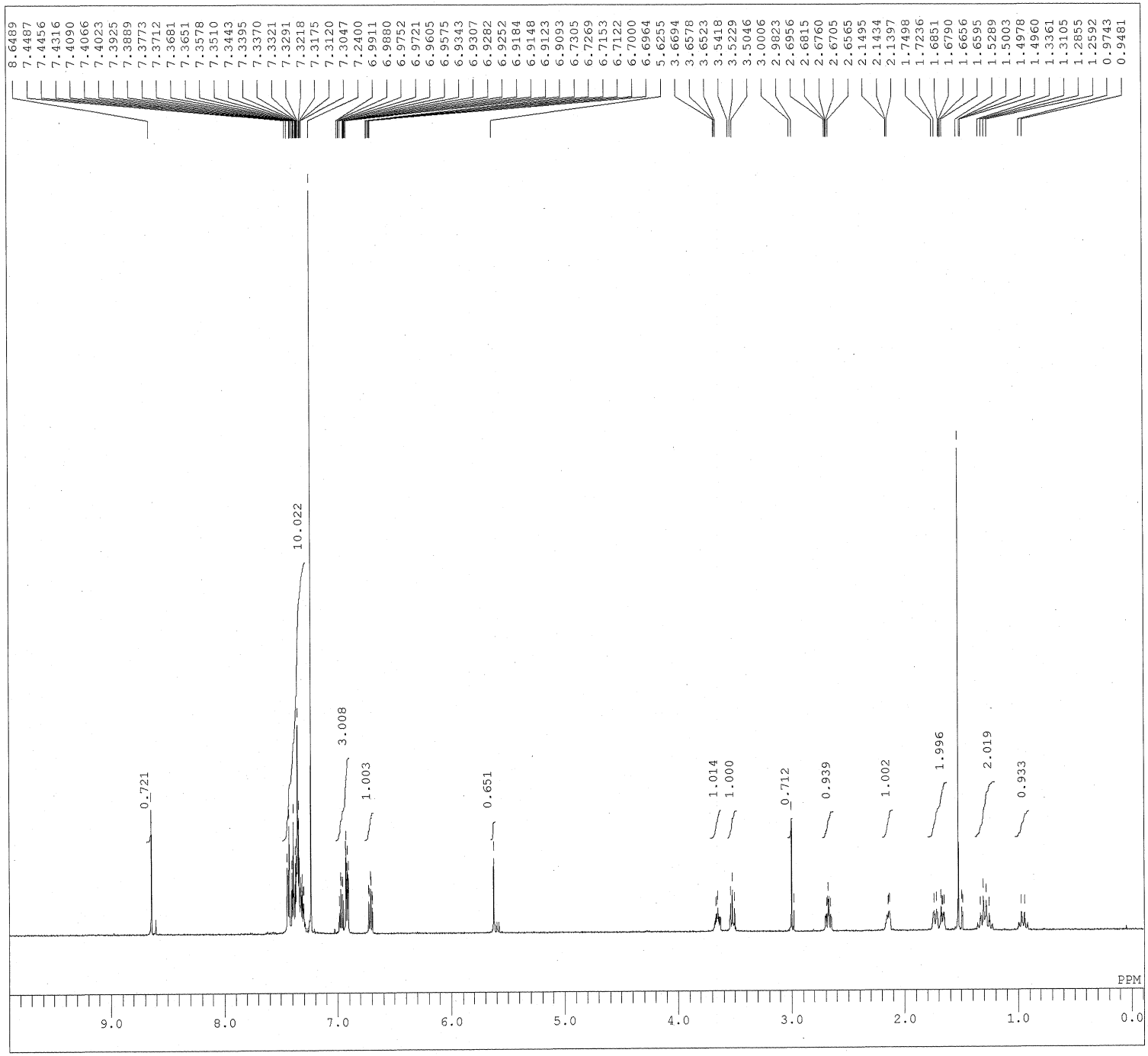


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PW1              6.50 usec
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RGAIN              23
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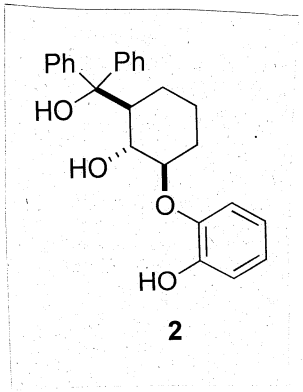

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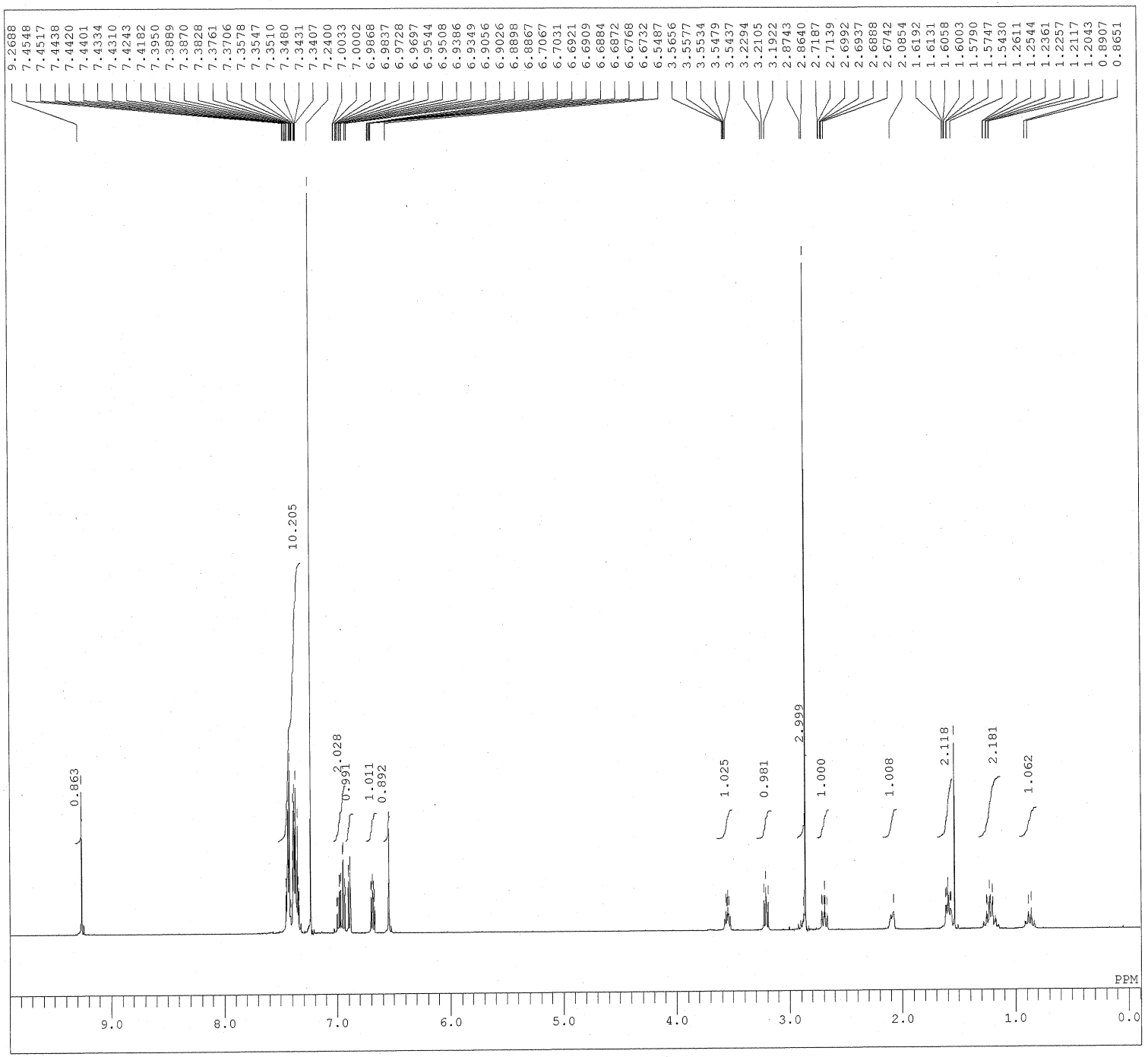

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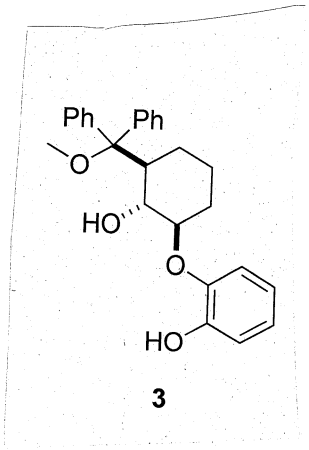
RGAIN	20



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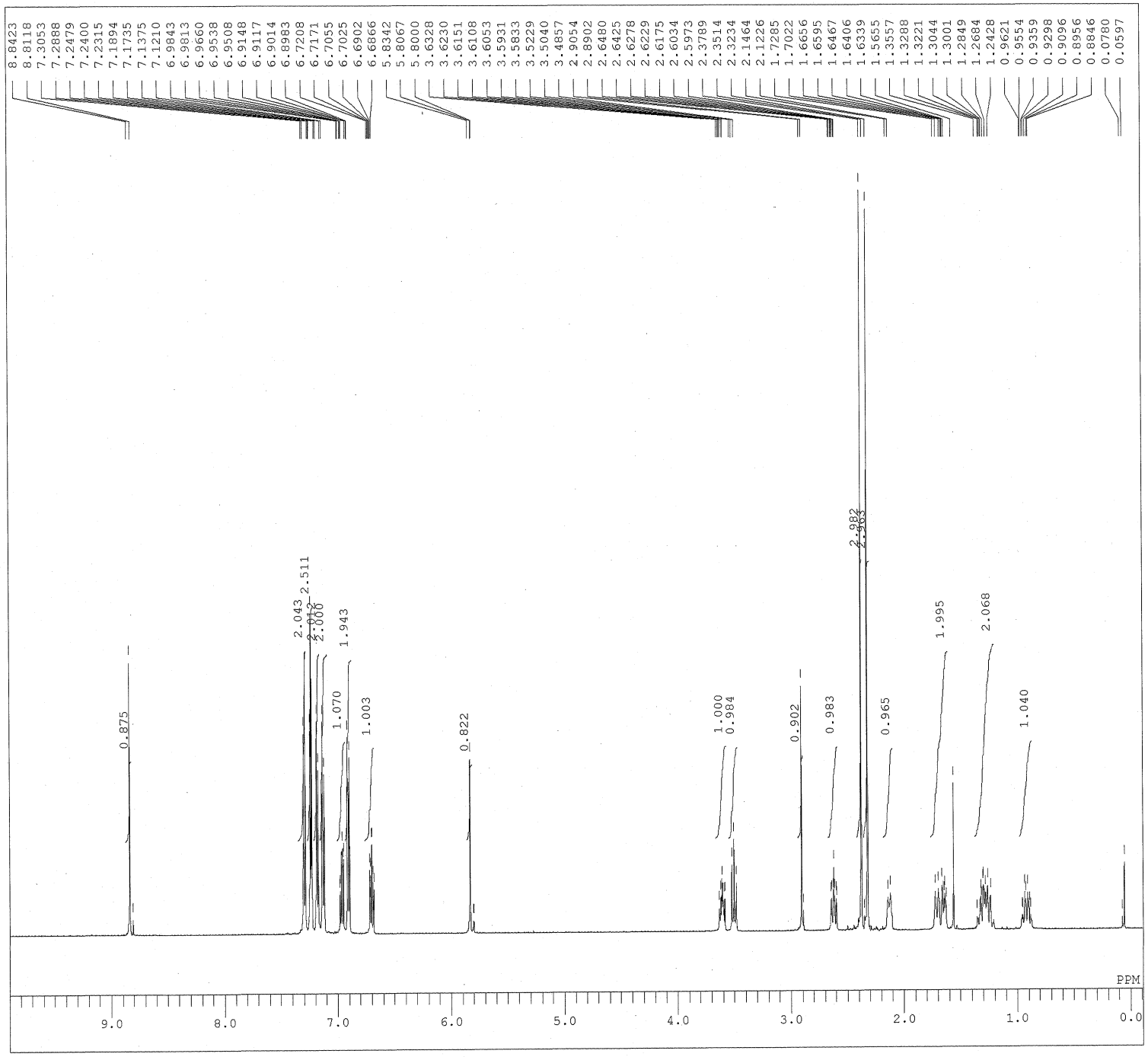


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RGAIN               17
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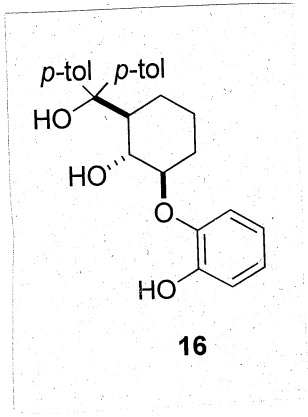

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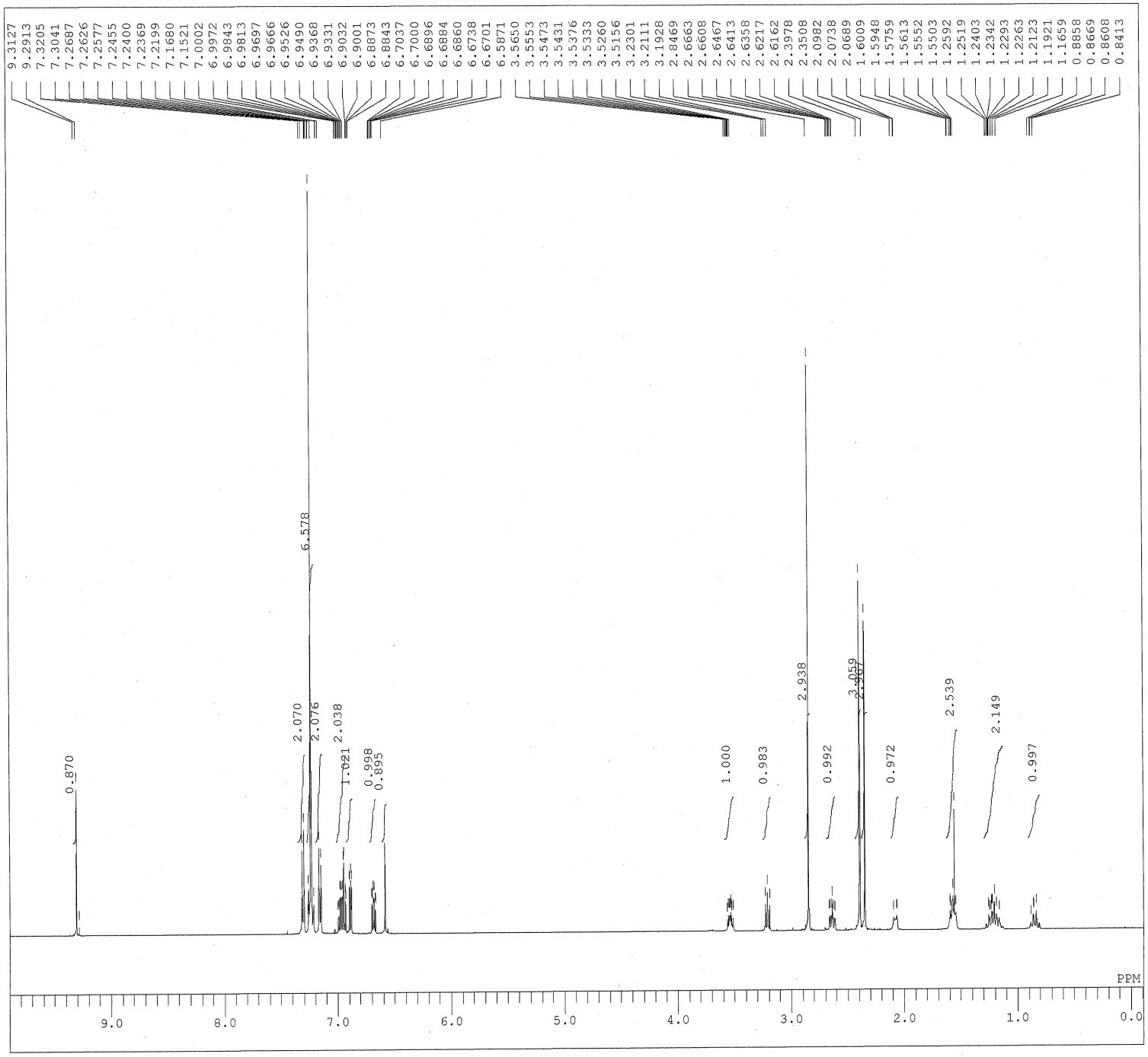


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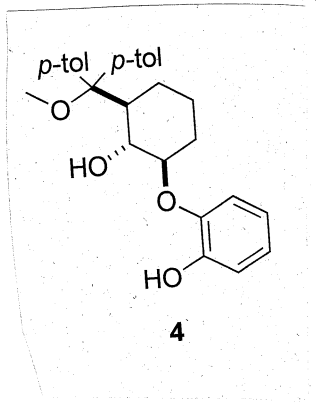

4

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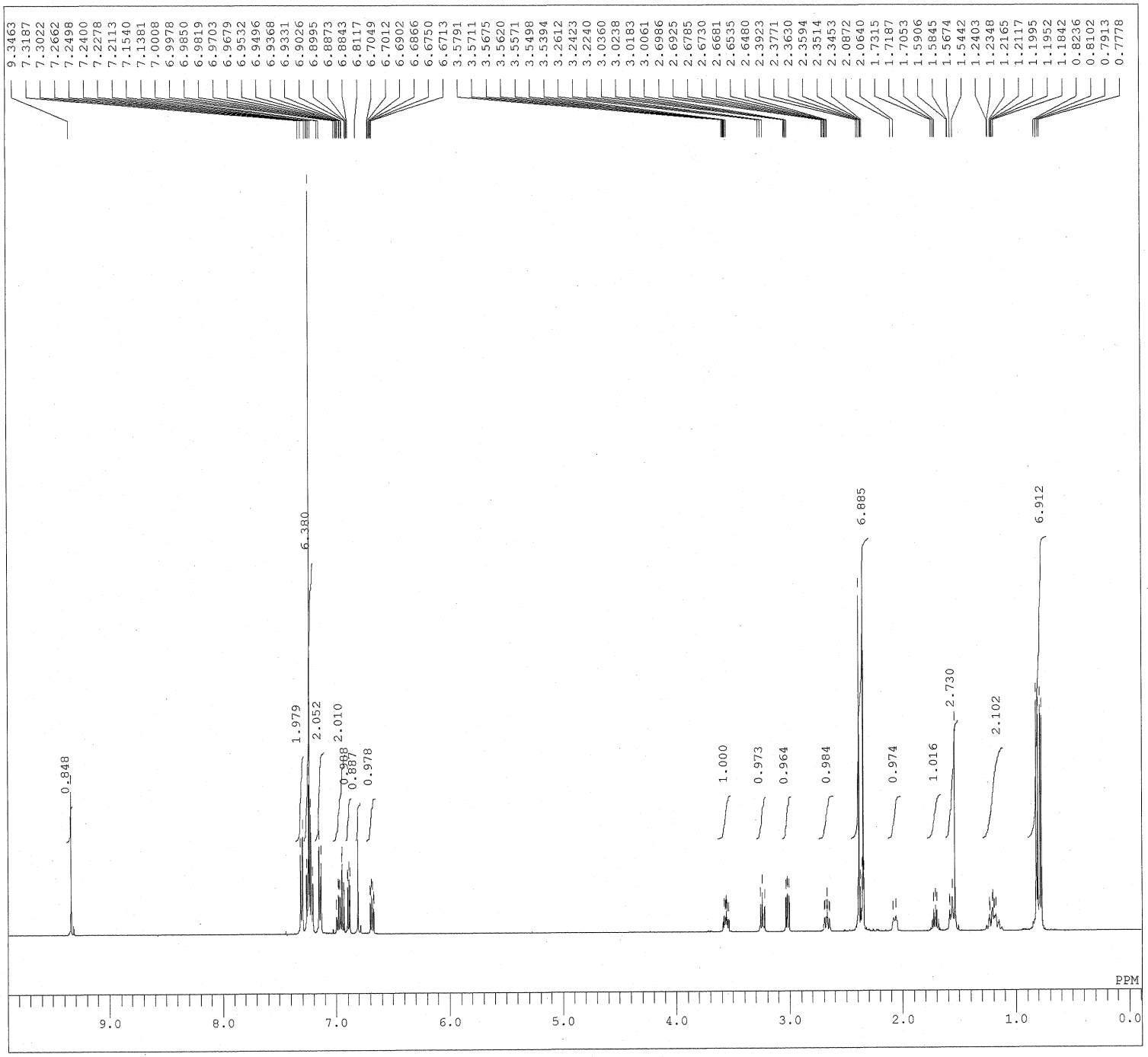


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RGAIN             19
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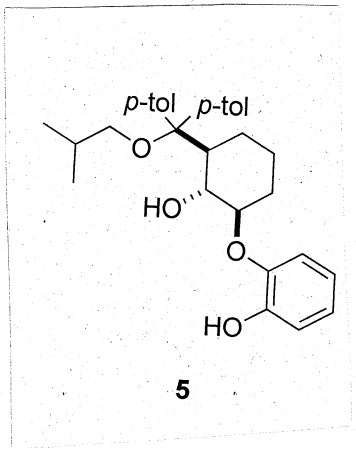

5

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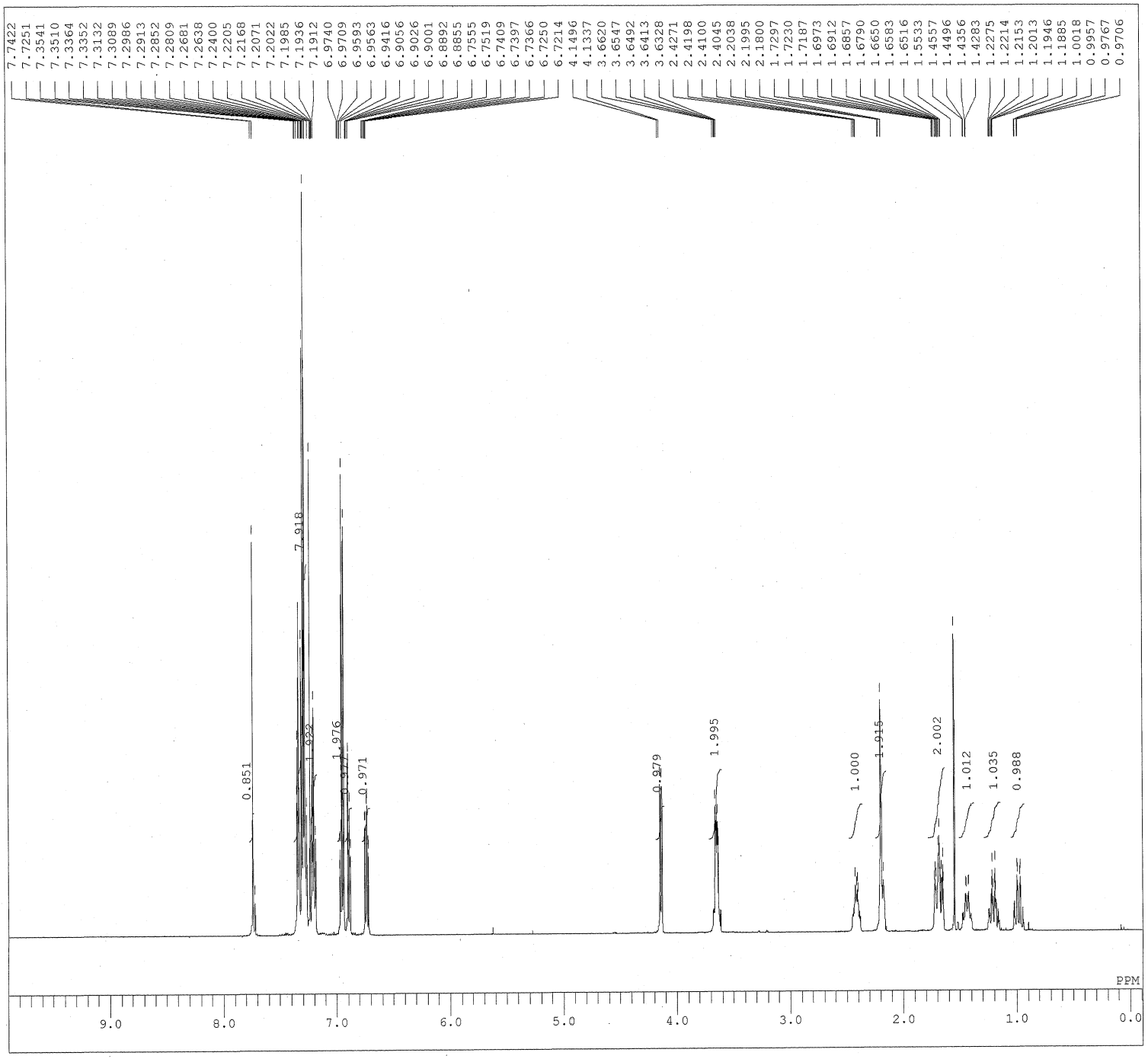

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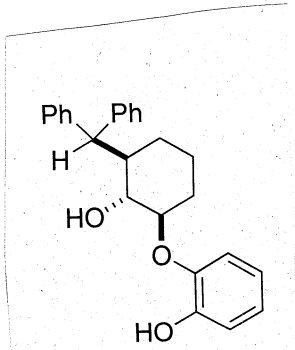
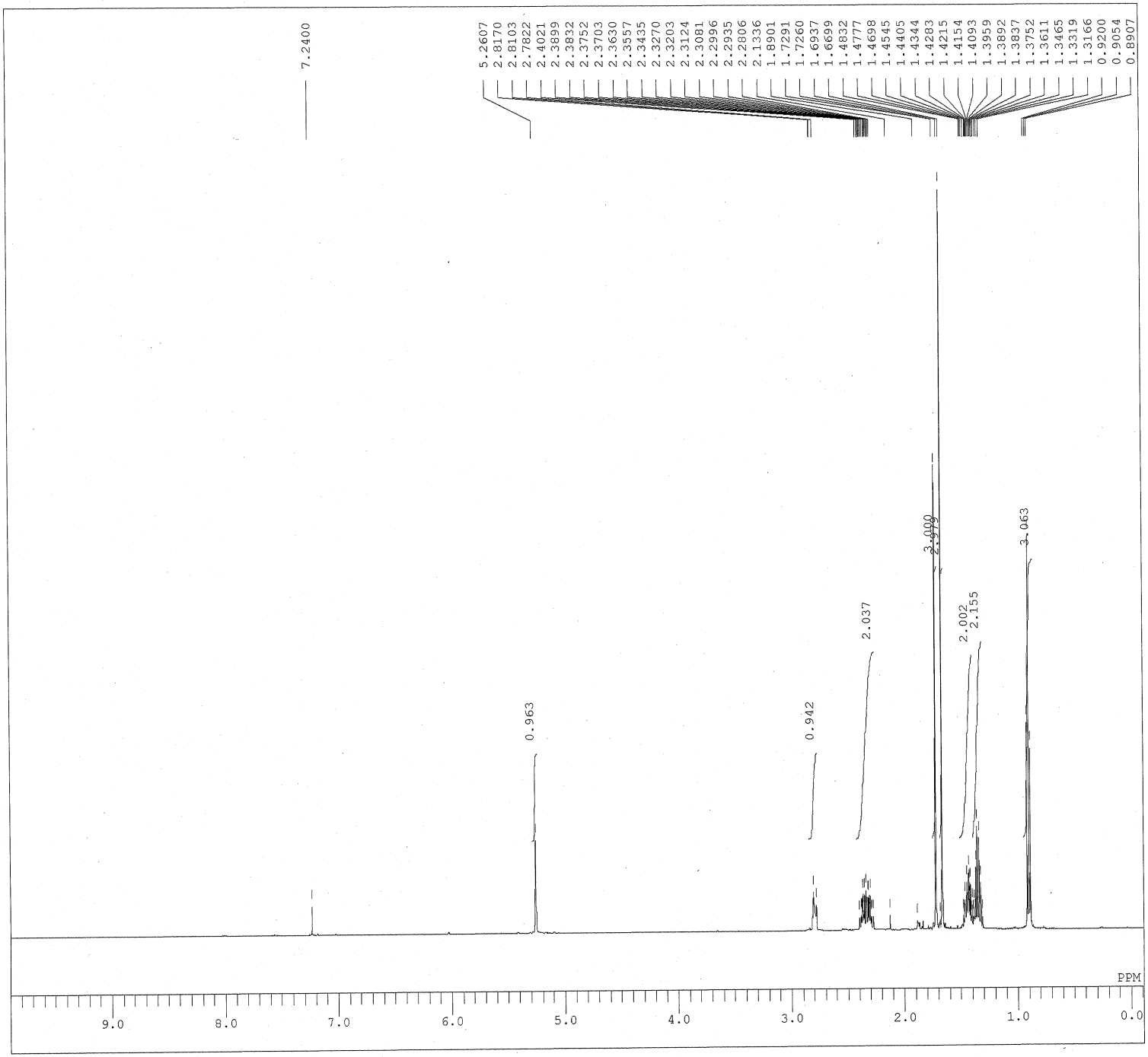
RGAIN 18



6

cyanohydrine

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RGAIN               12
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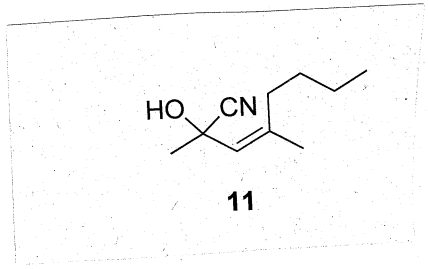

11

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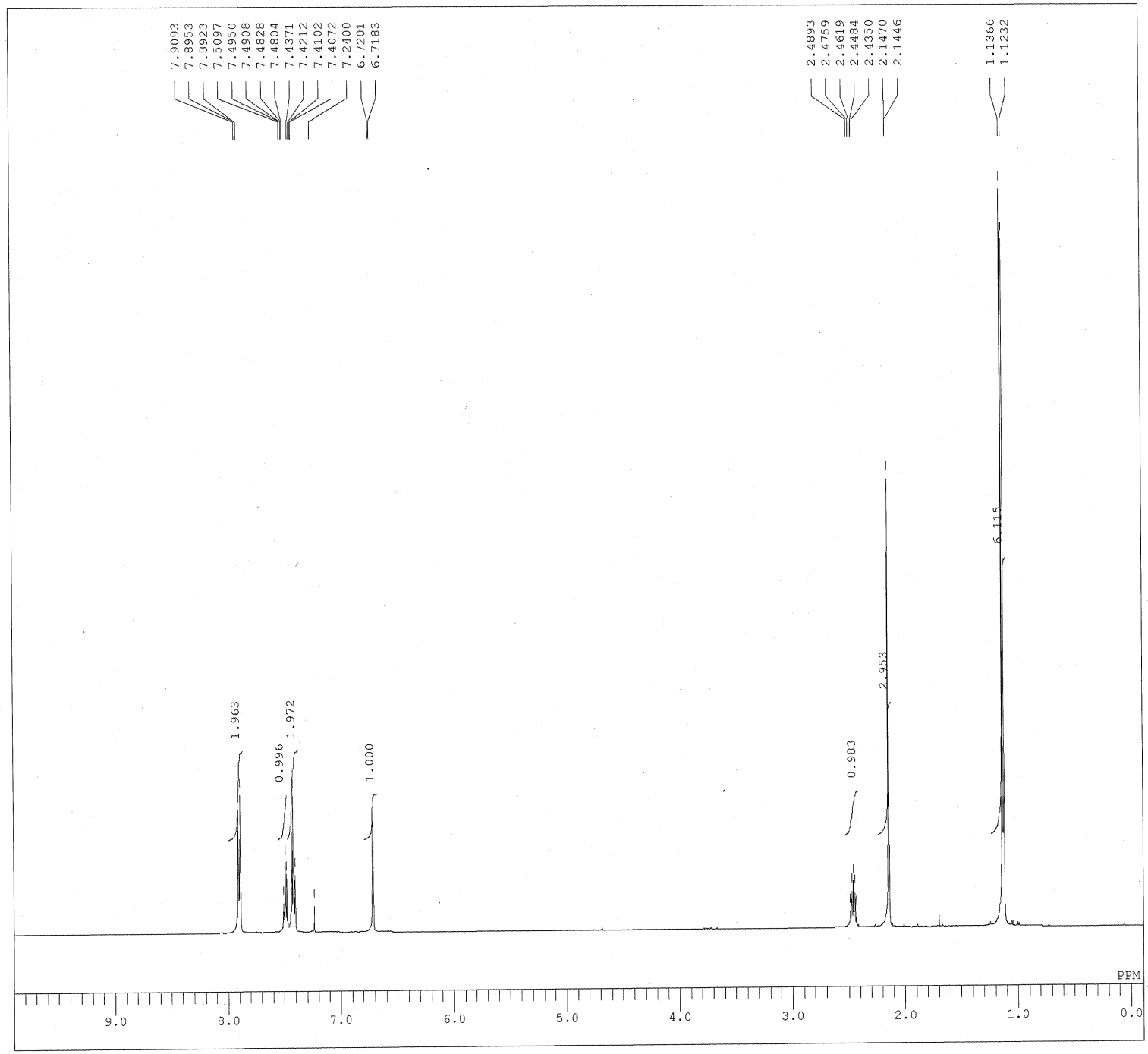


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RGAIN               13
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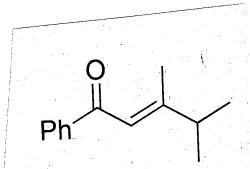
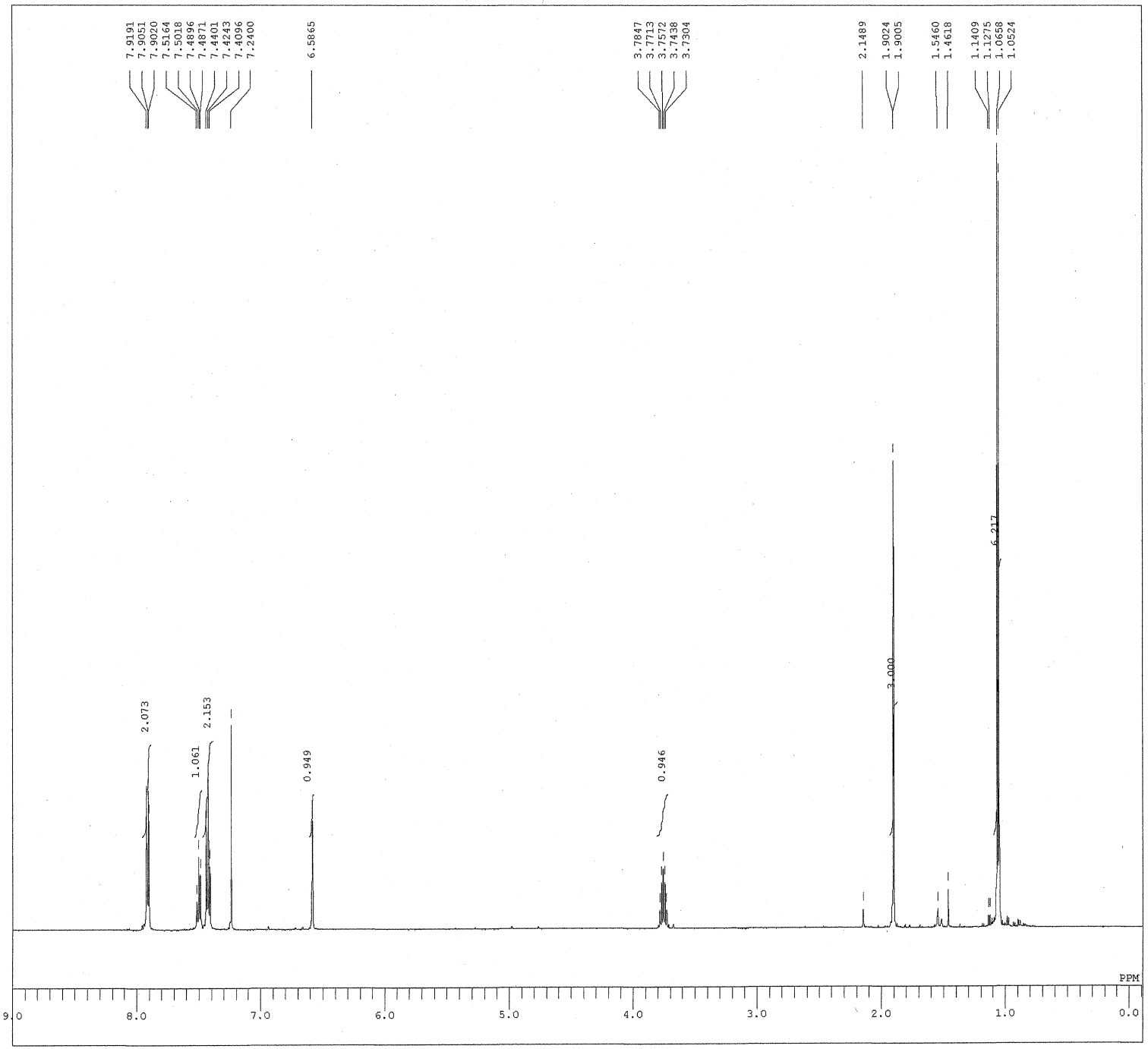
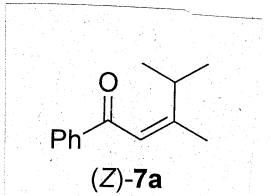


(*E*)-**7a**

phklpprot

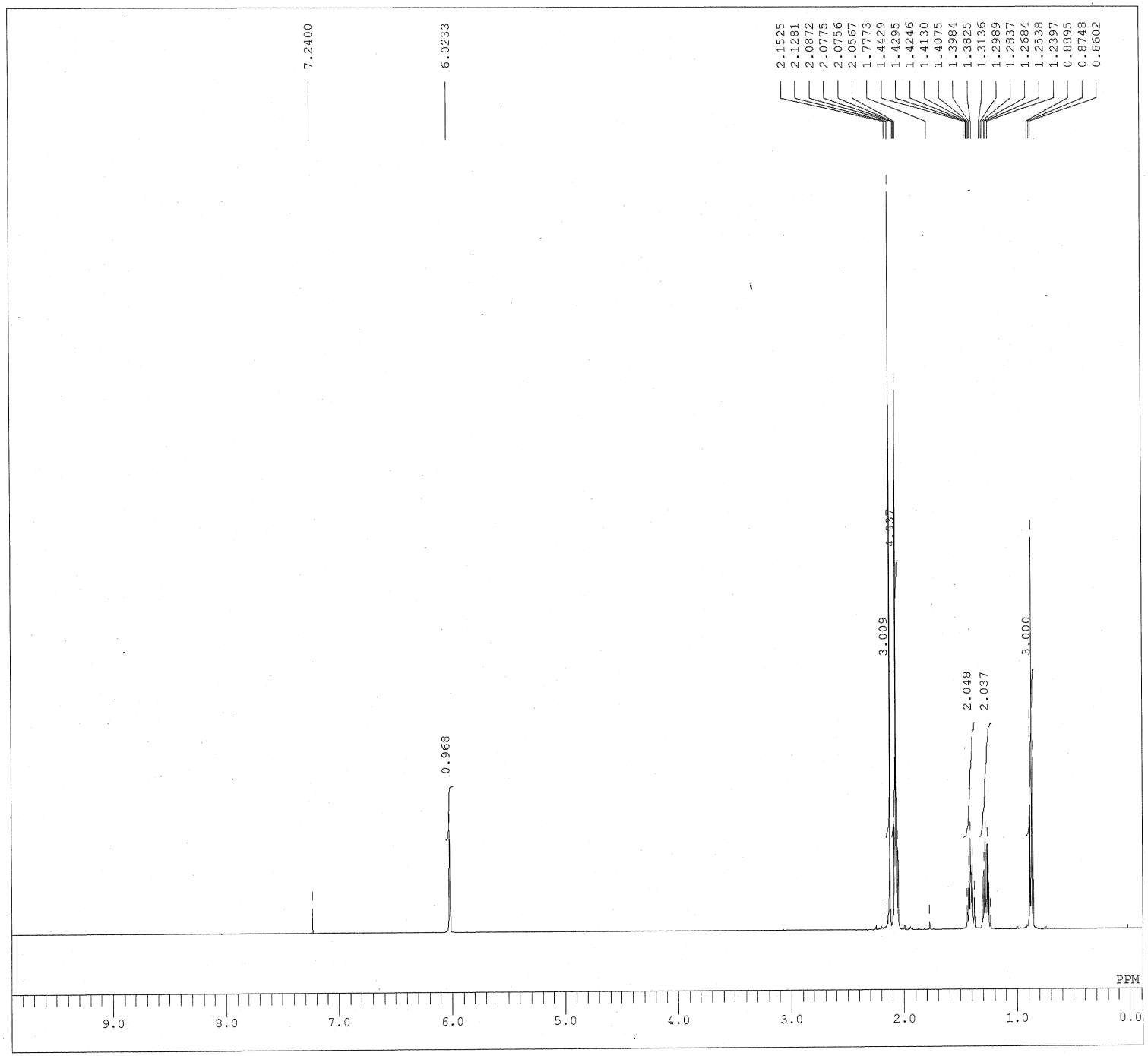


DFILE savedata03.nmdata
COMNT phklpprot
DATIM Tue Jan 12 13:51:41 2010
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 8
ACQTM 3.2768 sec
PD 3.7232 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 24.3 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 20

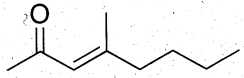


(*Z*)-**7a**

meknbutrans

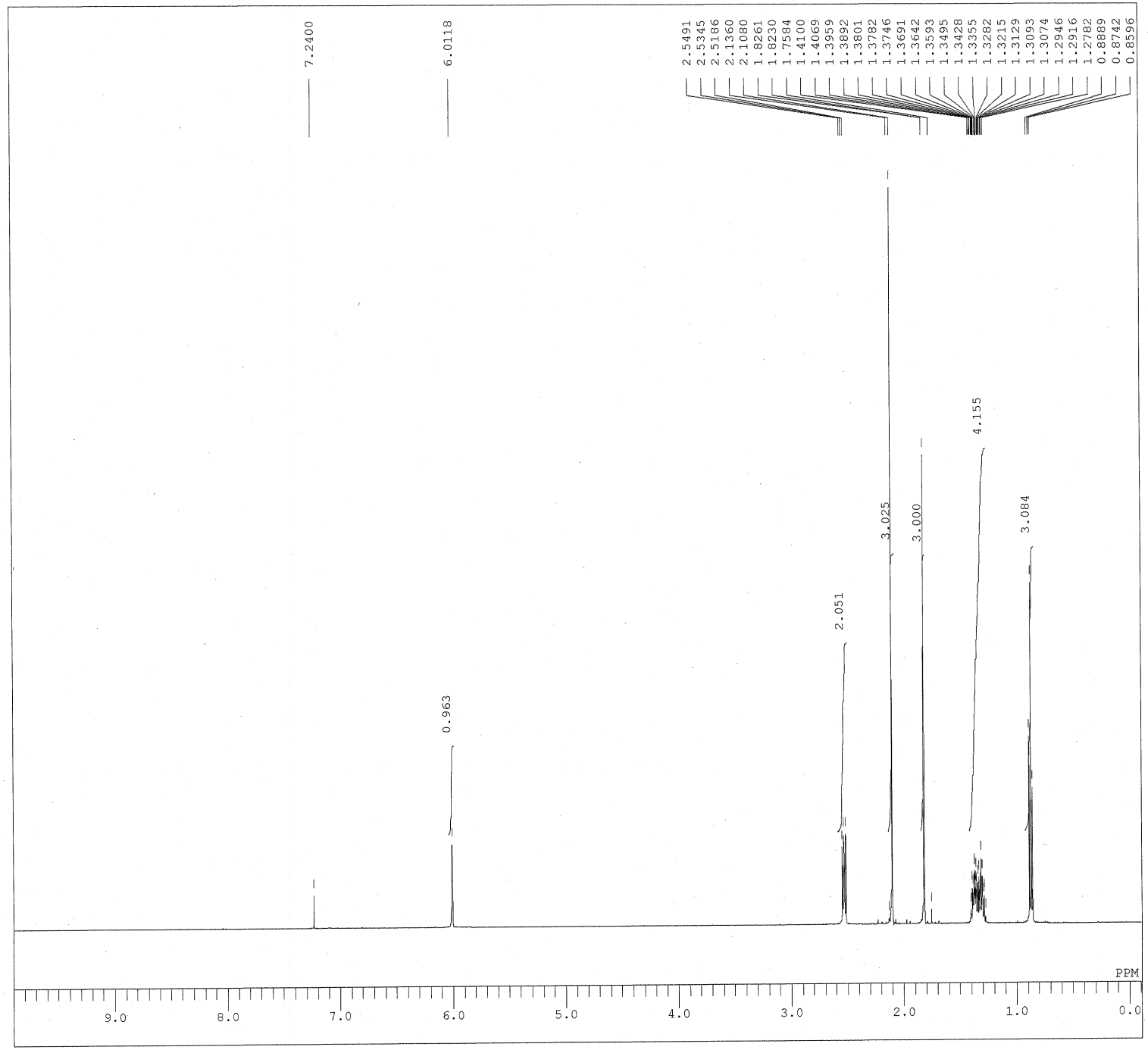


DFILE	savedata01.nmdata
COMNT	meknbutrans
DATIM	Sat Apr 17 09:39:10 2010
OBNUC	1H
EXMOD	non
OBFRQ	500.00 MHz
OBSET	160.00 KHz
OBFIN	2160.00 Hz
POINT	32768
FREQU	10000.00 Hz
SCANS	4
ACQTM	3.2768 sec
PD	3.7232 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	24.1 c
SLVNT	CDCL3
EXREF	7.24 ppm
BF	0.12 Hz
RGAIN	13

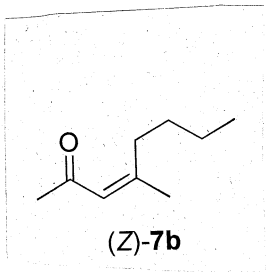


(*E*)-**7b**

meknbucis

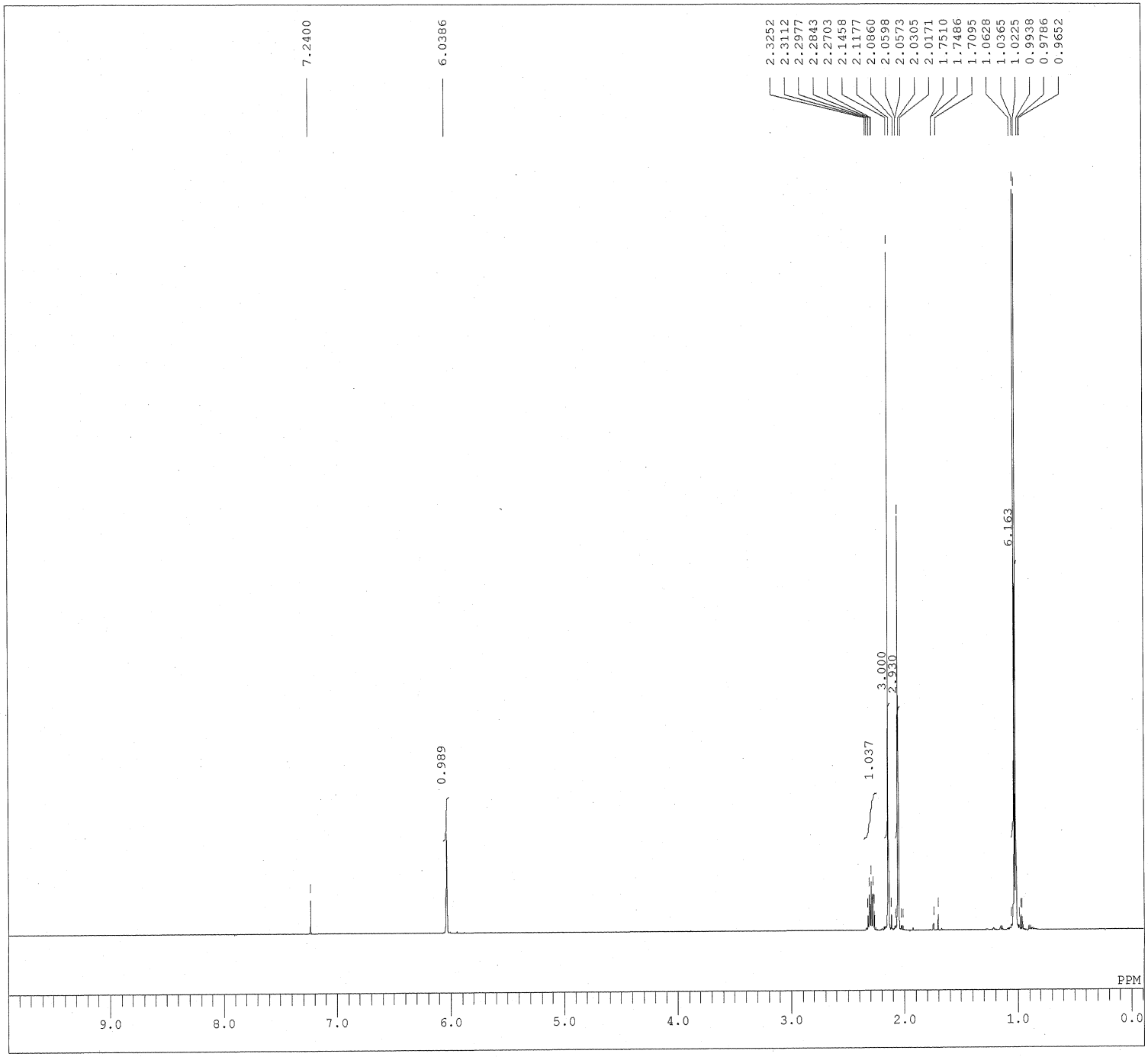


DFILE	savedata03.nmdata
COMNT	meknbucis
DATIM	Sat Apr 17 09:44:43 2010
OBNUC	1H
EXMOD	non
OBFRQ	500.00 MHz
OBSET	160.00 KHz
OBFIN	2160.00 Hz
POINT	32768
FREQU	10000.00 Hz
SCANS	6
ACQTM	3.2768 sec
PD	3.7232 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	25.0 c
SLVNT	CDCL3
EXREF	7.24 ppm
BF	0.12 Hz
RGAIN	13

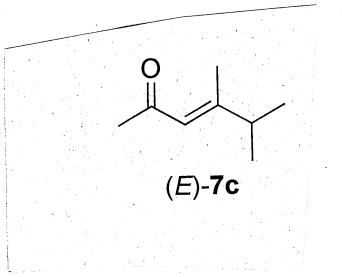


(*Z*)-**7b**

mekiprtrans

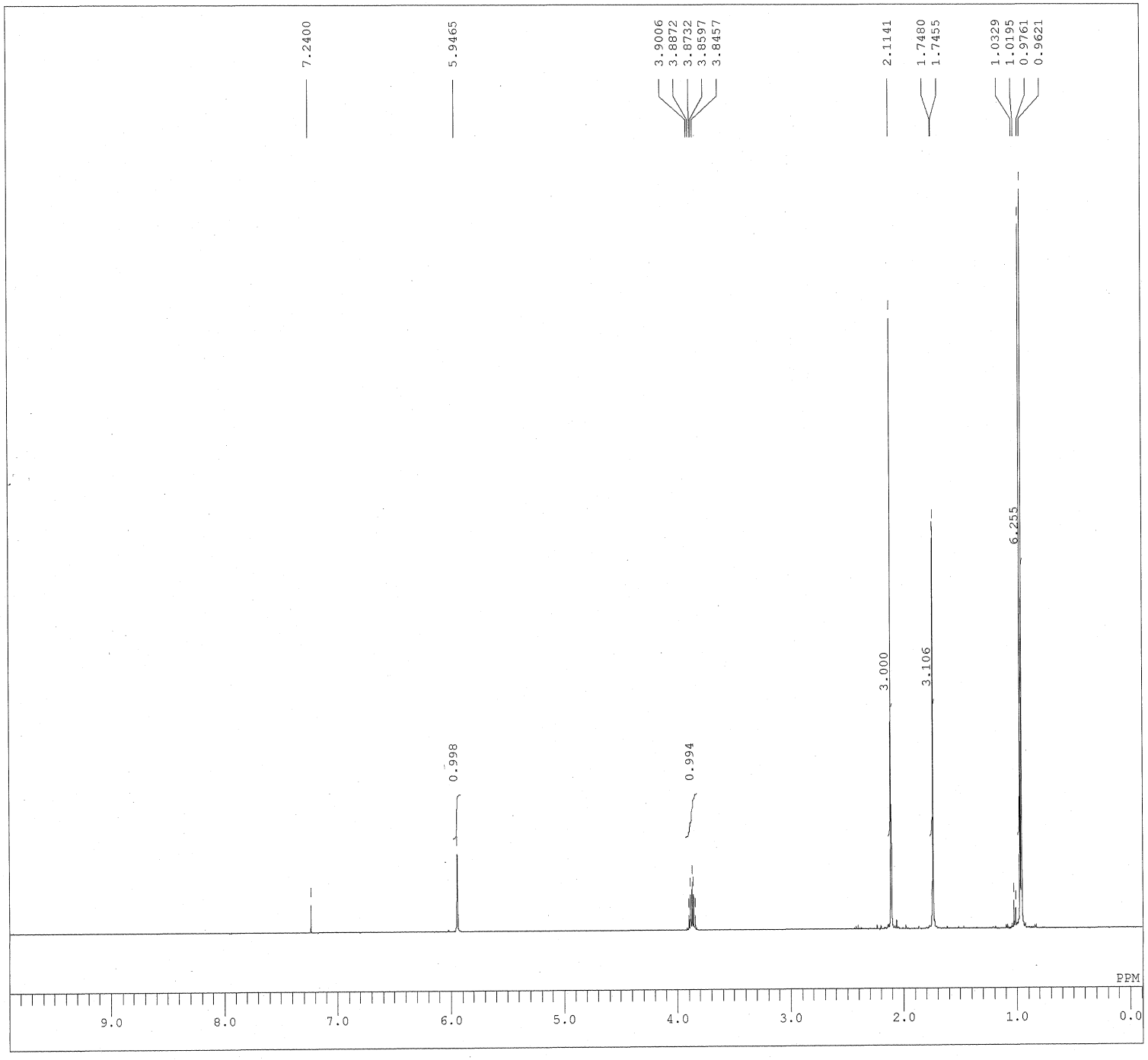


DFILE savedata05.nmdata
COMNT mekiprtrans
DATIM Sat Apr 17 09:50:03 2010
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 4
ACQTM 3.2768 sec
PD 3.7232 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 25.4 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 15

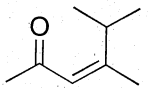


(*E*)-**7c**

mekiprcis

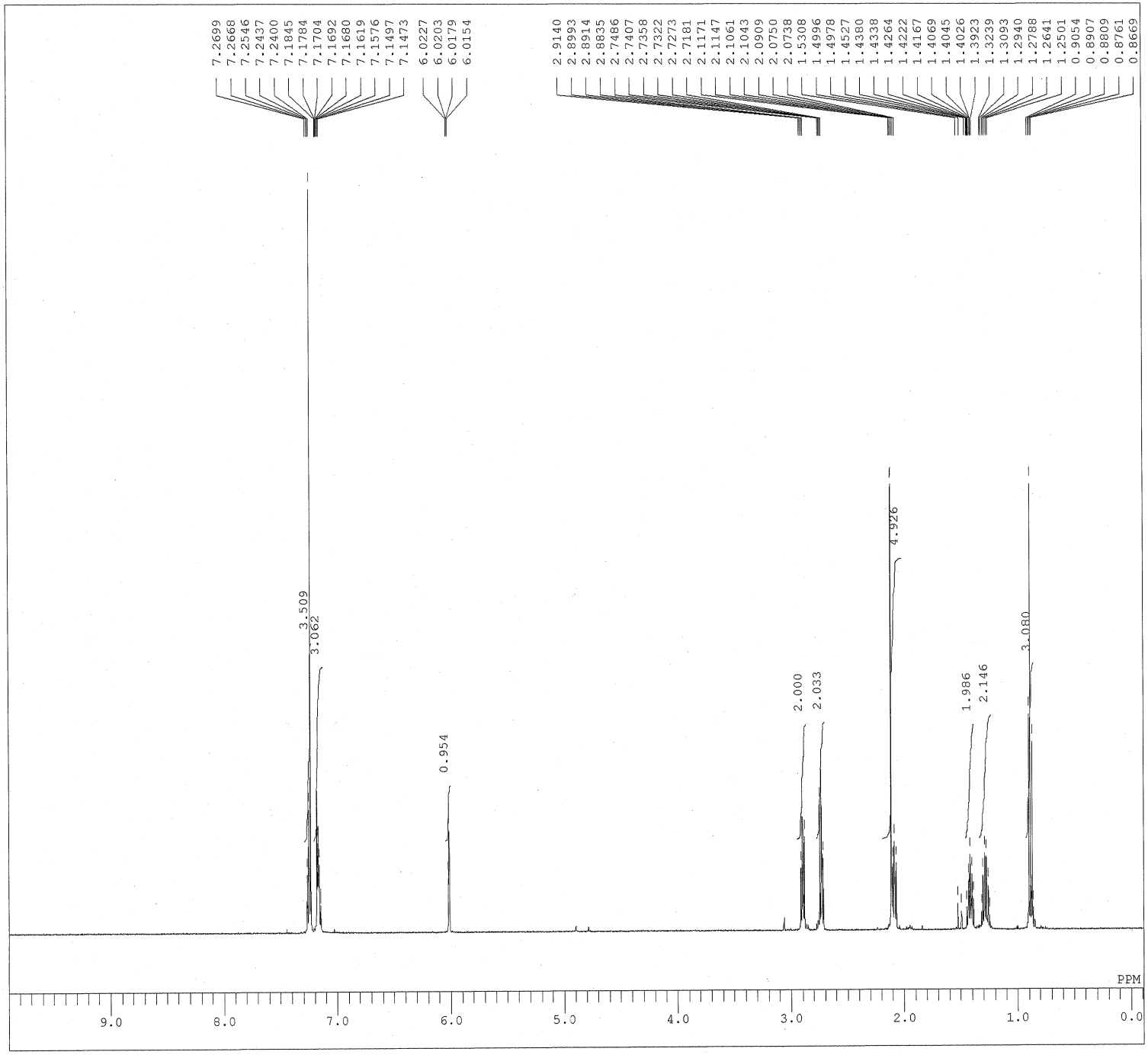



```
DFILE   savedata04.nmdata
COMNT   mekiprcis
DATIM   Sat Apr 17 09:59:40 2010
OBNUC   1H
EXMOD   non
OBFRQ         500.00 MHz
OBSET         160.00 KHz
OBFIN        2160.00 Hz
POINT          32768
FREQU       10000.00 Hz
SCANS              4
ACQTM          3.2768 sec
PD             3.7232 sec
PW1              6.50 usec
IRNUC   1H
CTEMP            25.6 c
SLVNT   CDCL3
EXREF             7.24 ppm
BF                0.12 Hz
RGAIN               14
```

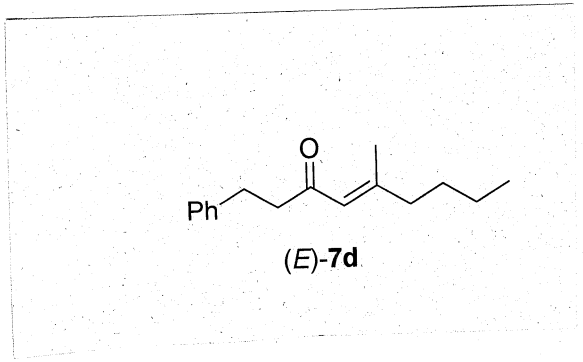


(*Z*)-**7c**

phetktrans

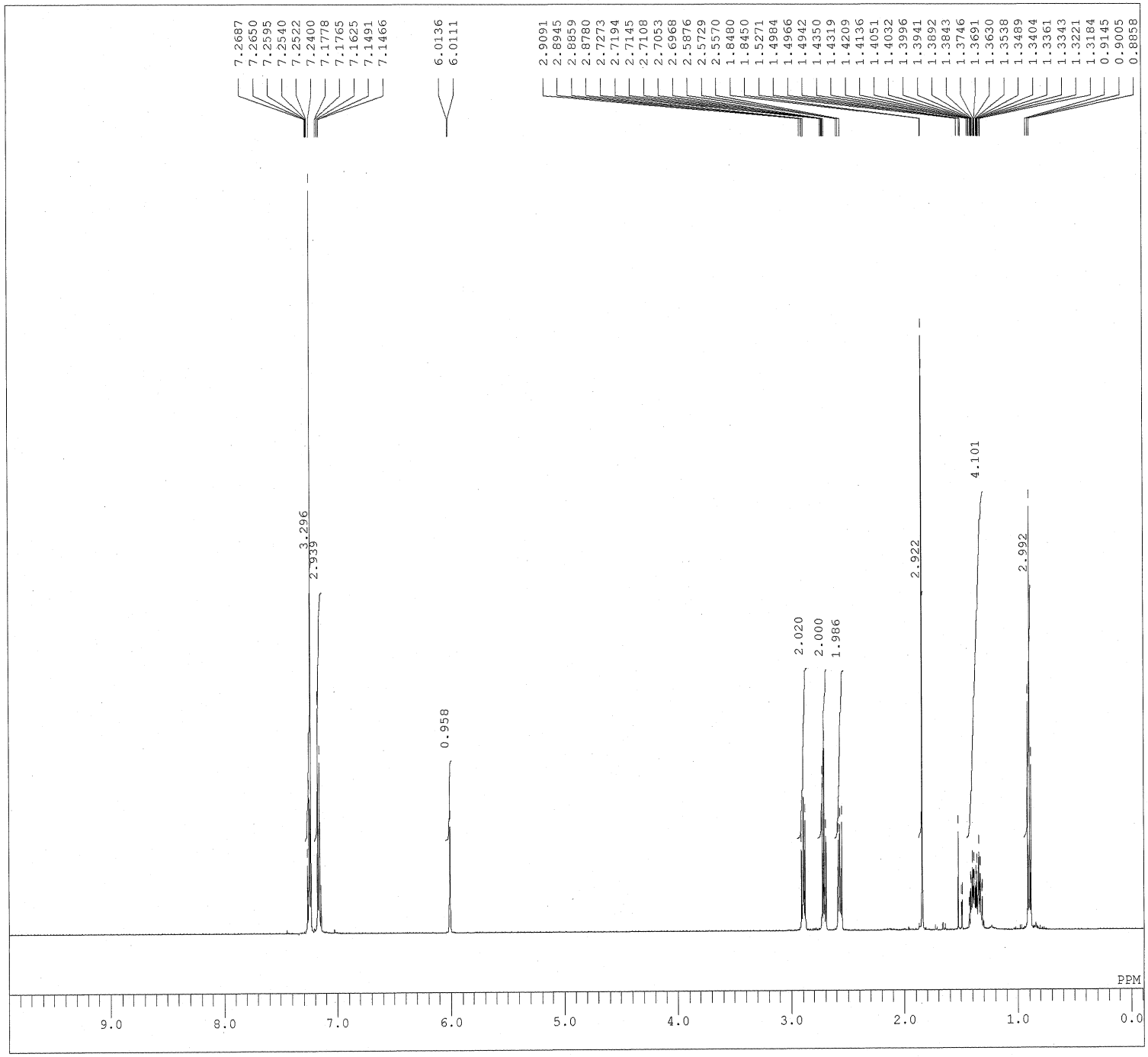



```
DFILE   savedata20.nmdata
COMNT   phetktrans
DATIM   Fri Apr 16 18:59:47 2010
OBNUC   1H
EXMOD   non
OBFRQ         500.00 MHz
OBSET         160.00 KHz
OBFIN        2160.00 Hz
POINT          32768
FREQU        10000.00 Hz
SCANS              4
ACQTM         3.2768 sec
PD            3.7232 sec
PW1             6.50 usec
IRNUC   1H
CTEMP           24.3 c
SLVNT   CDCL3
EXREF           7.24 ppm
BF              0.12 Hz
RGAIN             22
```

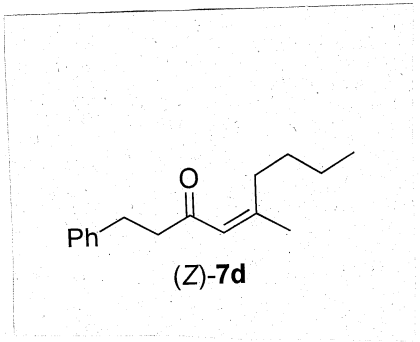


(*E*)-**7d**

phetkcis

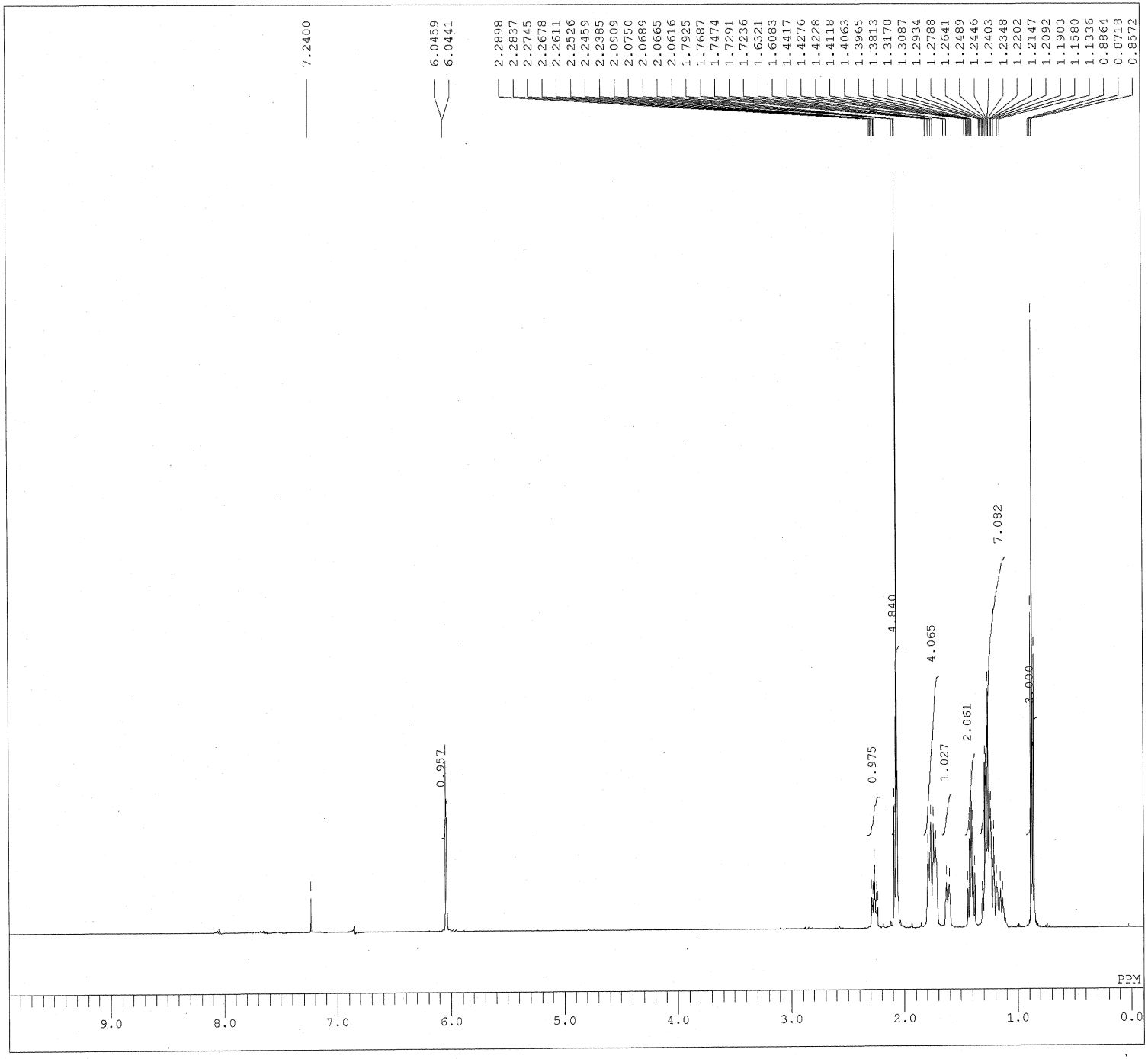



```
DFILE   savedata21.nmdata
COMNT   phetkcis
DATIM   Fri Apr 16 19:04:32 2010
OBNUC   1H
EXMOD   non
OBFRQ         500.00 MHz
OBSET         160.00 KHz
OBFIN        2160.00 Hz
POINT          32768
FREQU        10000.00 Hz
SCANS             14
ACQTM          3.2768 sec
PD             3.7232 sec
PW1               6.50 usec
IRNUC   1H
CTEMP            24.6 c
SLVNT   CDCL3
EXREF             7.24 ppm
BF                0.12 Hz
RGAIN               22
```

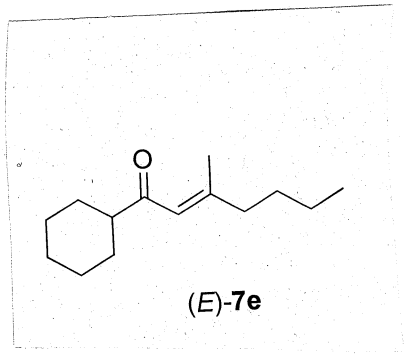


(*Z*)-**7d**

cyktrans

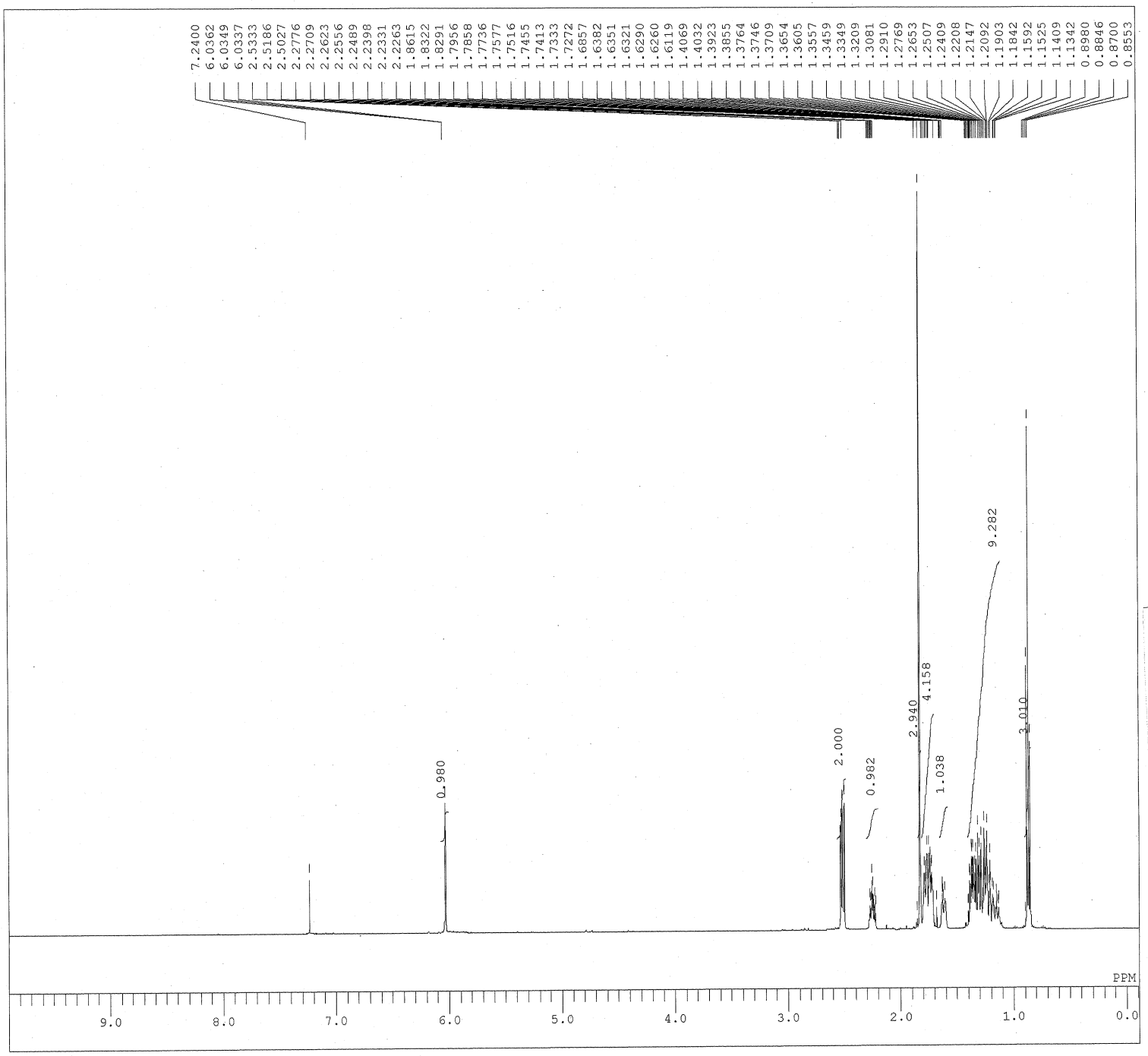



```
DFILE   savedata26.nmdata
COMNT   cyktrans
DATIM   Fri Apr 16 19:44:30 2010
OBNUC   1H
EXMOD   non
OBFRQ         500.00 MHz
OBSET         160.00 KHz
OBFIN        2160.00 Hz
POINT          32768
FREQU        10000.00 Hz
SCANS              5
ACQTM          3.2768 sec
PD             3.7232 sec
PW1               6.50 usec
IRNUC   1H
CTEMP             25.3 c
SLVNT   CDCL3
EXREF             7.24 ppm
BF                0.12 Hz
RGAIN               11
```

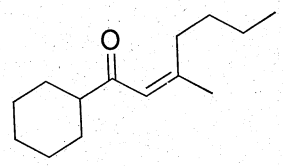


(*E*)-**7e**

cykcis

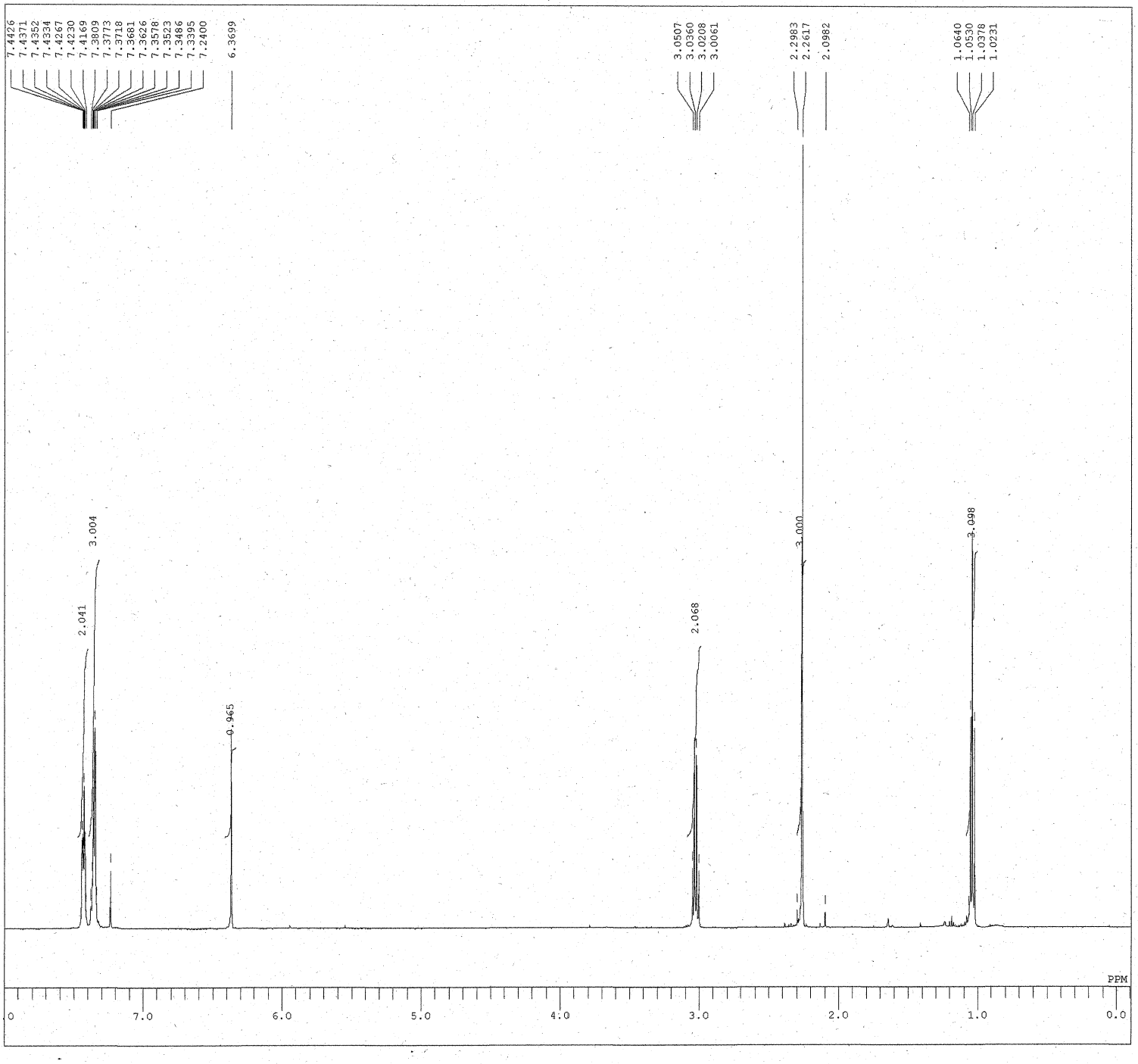



```
DFILE   savedata09.nmdata
COMNT   cykcis
DATIM   Sat Apr 17 10:06:32 2010
OBNUC   1H
EXMOD   non
OBFRQ         500.00 MHz
OBSET         160.00 KHz
OBFIN        2160.00 Hz
POINT          32768
FREQU       10000.00 Hz
SCANS              8
ACQTM          3.2768 sec
PD             3.7232 sec
PW1              6.50 usec
IRNUC   1H
CTEMP           25.9 c
SLVNT   CDCL3
EXREF            7.24 ppm
BF               0.12 Hz
RGAIN              12
```

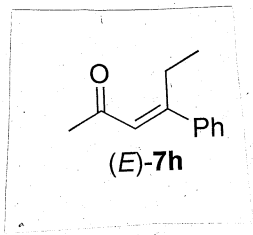


(Z)-**7e**

betaphetlpprot

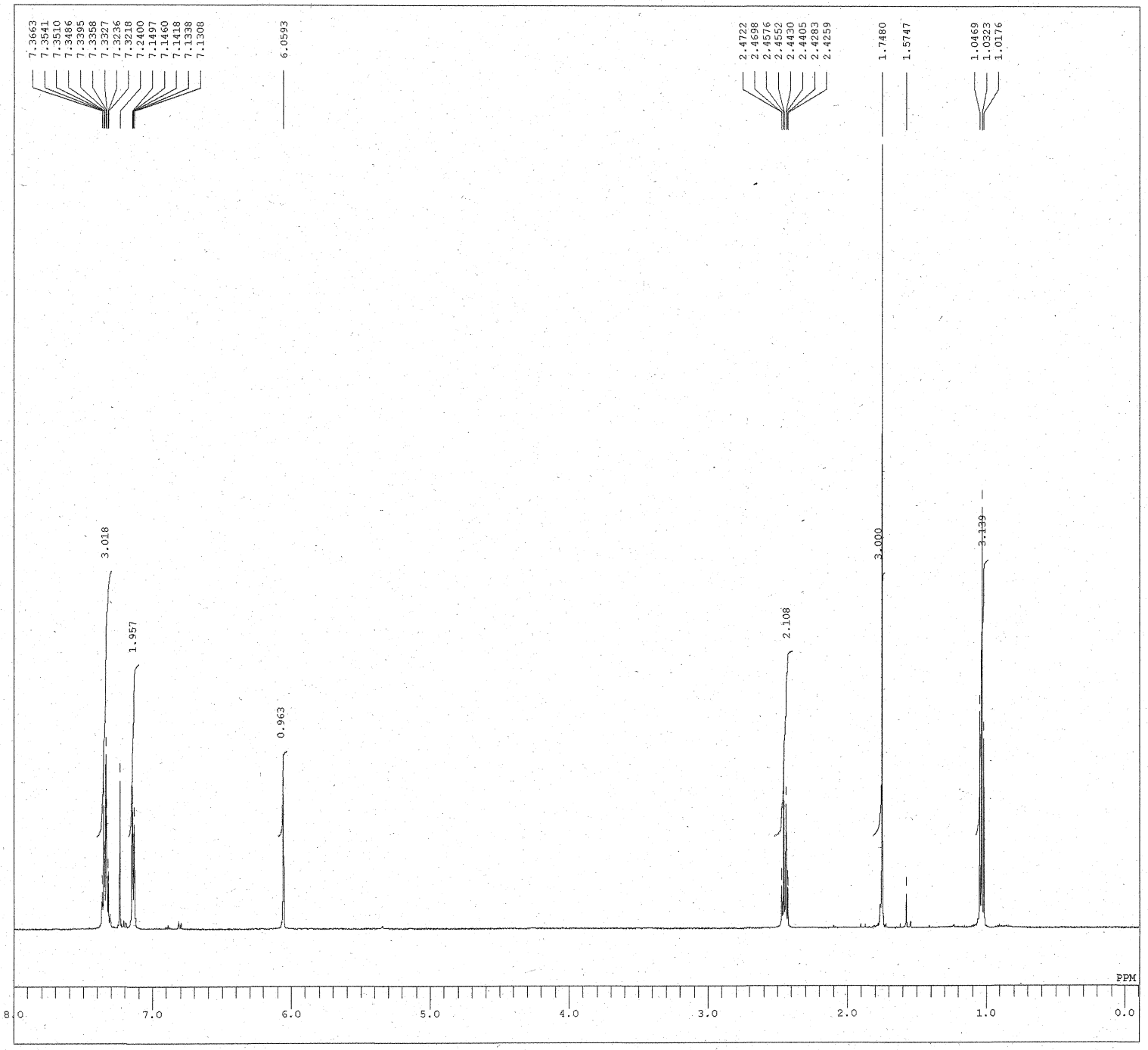



```
DFILE   savedata01.nmdata
COMNT   betaphetlpprot
DATIM   Mon Jan 11 16:53:46 2010
OBNUC   1H
EXMOD   non
OBFRQ         500.00 MHz
OBSET         160.00 KHz
OBFIN        2160.00 Hz
POINT          32768
FREQU        10000.00 Hz
SCANS              8
ACQTM         3.2768 sec
PD            3.7232 sec
PW1             6.50 usec
IRNUC   1H
CTEMP           24.0 c
SLVNT   CDCL3
EXREF           7.24 ppm
BF              0.12 Hz
RGAIN             16
```

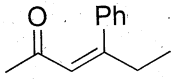


(*E*)-**7h**

betaphetmpprot

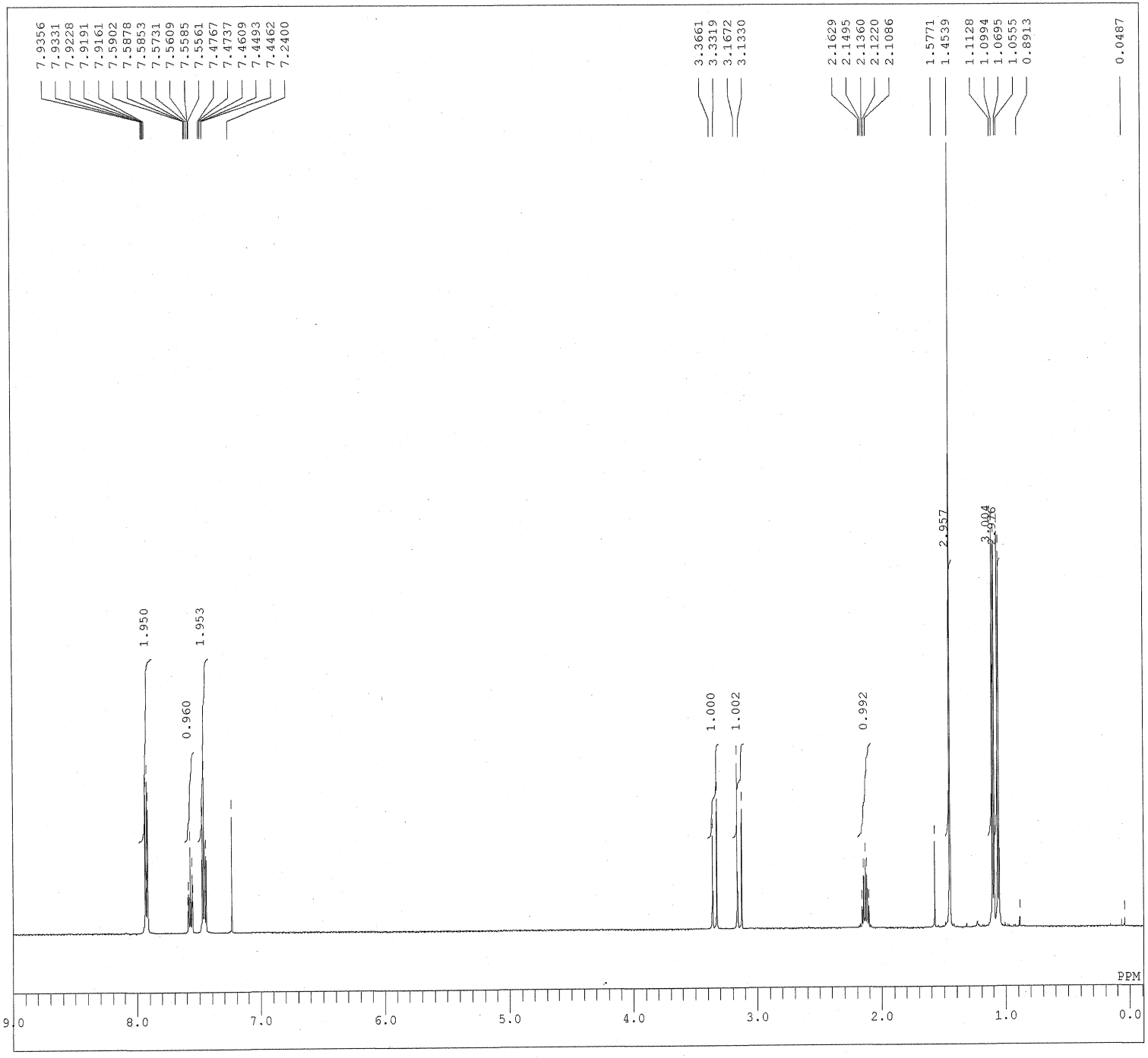



```
DFILE  savedata03.nmdata
COMNT  betaphetmpprot
DATIM  Mon Jan 11 17:03:23 2010
OBNUC  1H
EXMOD  non
OBFRQ        500.00 MHz
OBSET        160.00 KHz
OBFIN       2160.00 Hz
POINT         32768
FREQU      10000.00 Hz
SCANS             8
ACQTM        3.2768 sec
PD           3.7232 sec
PW1             6.50 usec
IRNUC  1H
CTEMP          25.0 c
SLVNT  CDCL3
EXREF          7.24 ppm
BF             0.12 Hz
RGAIN            18
```

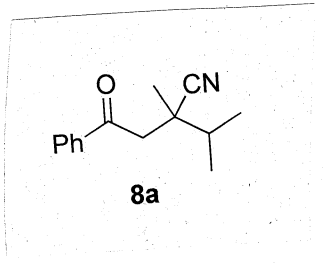


(*Z*)-**7h**

phtrans

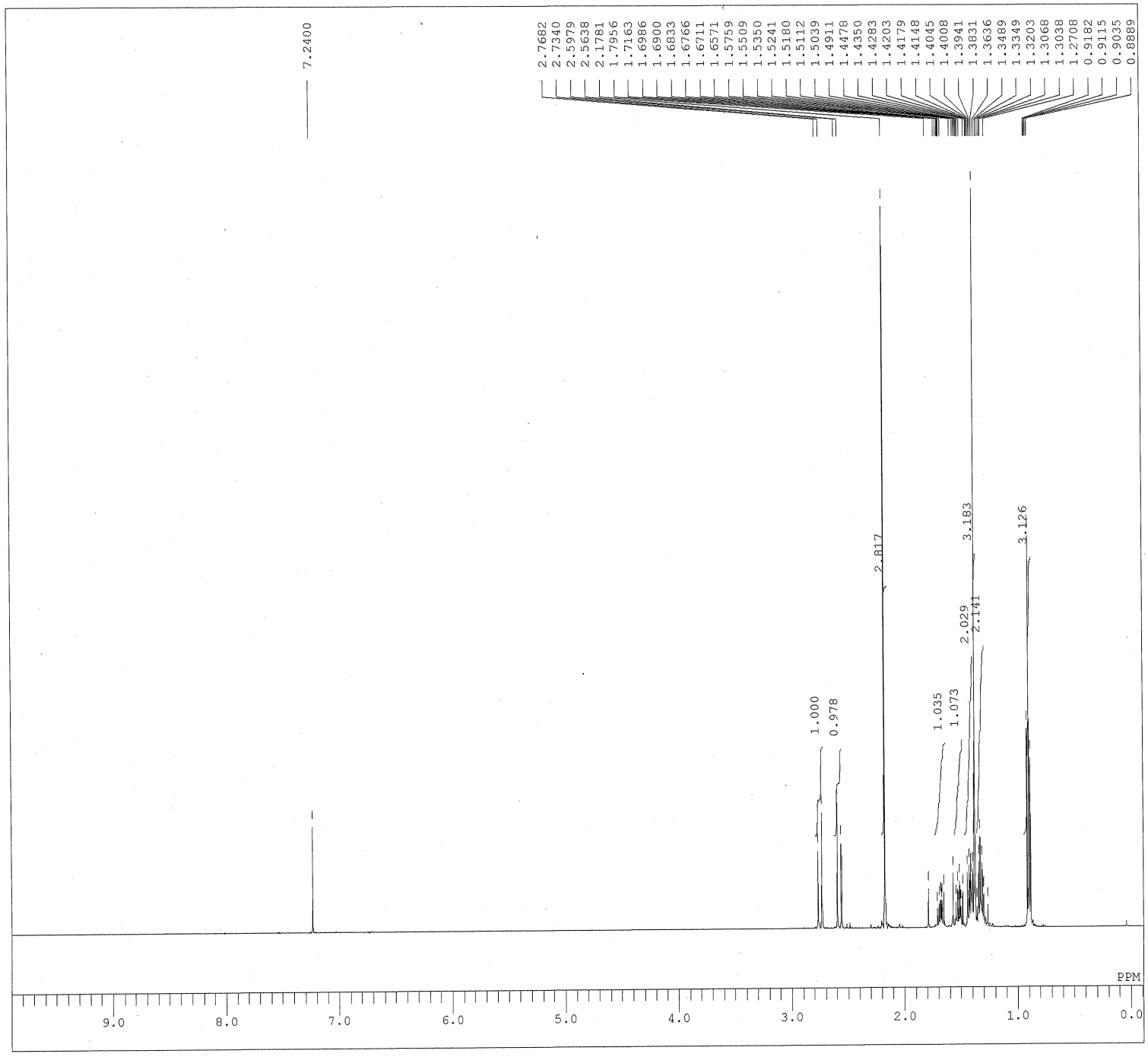



```
DFILE   savedata03.nmdata
COMNT   phtrans
DATIM   Sat Feb 13 16:12:17 2010
OBNUC   1H
EXMOD   non
OBFRQ         500.00 MHz
OBSET         160.00 KHz
OBFIN        2160.00 Hz
POINT          32768
FREQU        10000.00 Hz
SCANS              8
ACQTM          3.2768 sec
PD             3.7232 sec
PW1               6.50 usec
IRNUC   1H
CTEMP            25.3 c
SLVNT   CDCL3
EXREF             7.24 ppm
BF                0.22 Hz
RGAIN               17
```

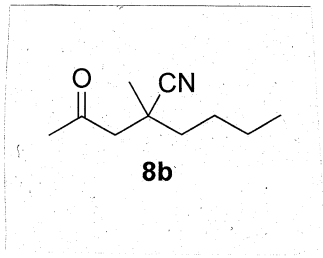


8a

meknbuproduct

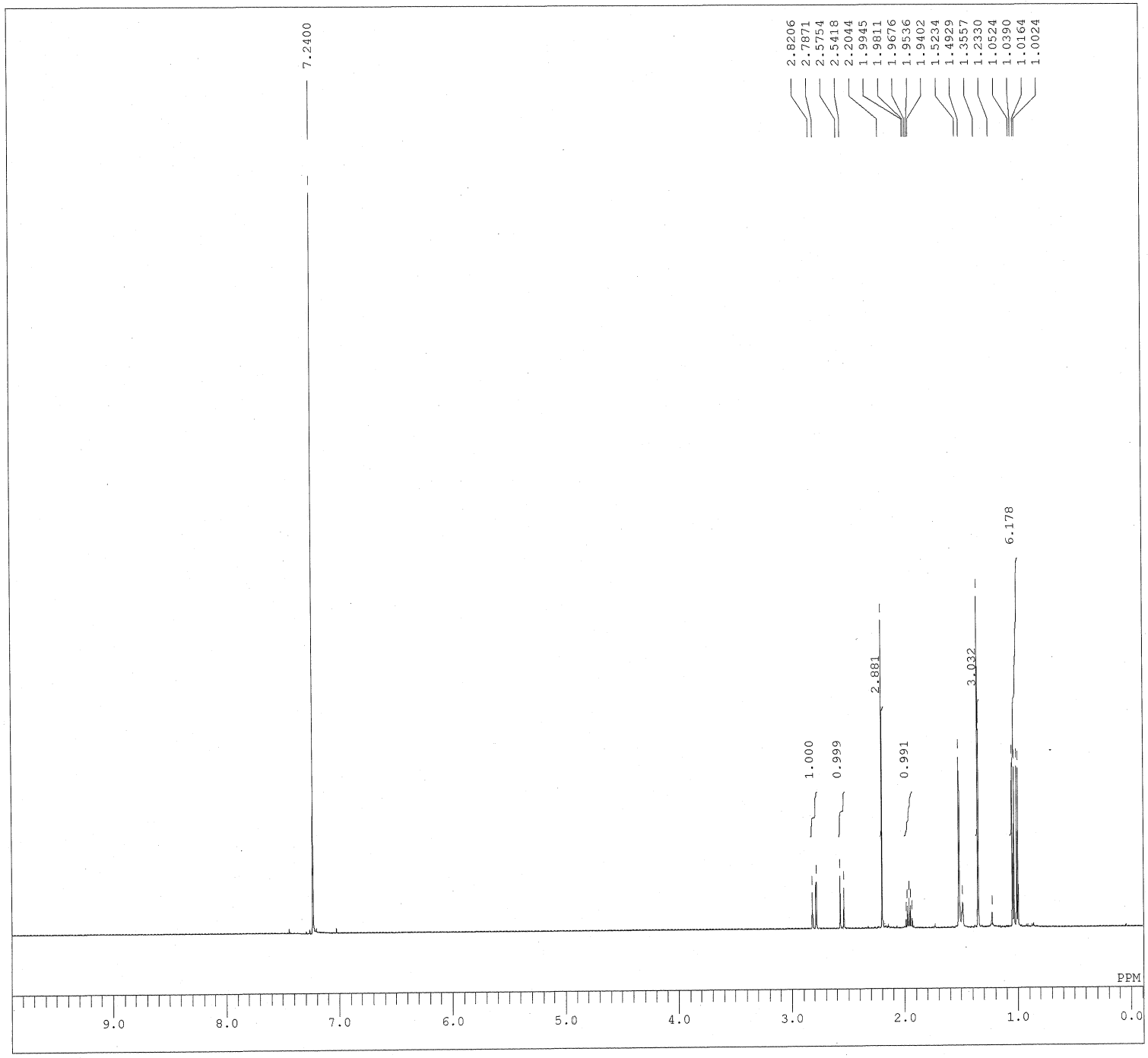


DFILE	savedata07.nmdata
COMNT	meknbuproduct
DATIM	Fri Apr 16 09:34:40 2010
OBNUC	1H
EXMOD	non
OBFRQ	500.00 MHz
OBSET	160.00 KHz
OBFIN	2160.00 Hz
POINT	32768
FREQU	10000.00 Hz
SCANS	4
ACQTM	3.2768 sec
PD	3.7232 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	25.4 c
SLVNT	CDCL3
EXREF	7.24 ppm
BF	0.12 Hz
RGAIN	17

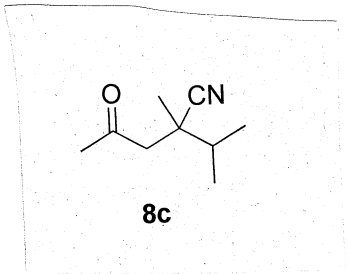


8b

ipr

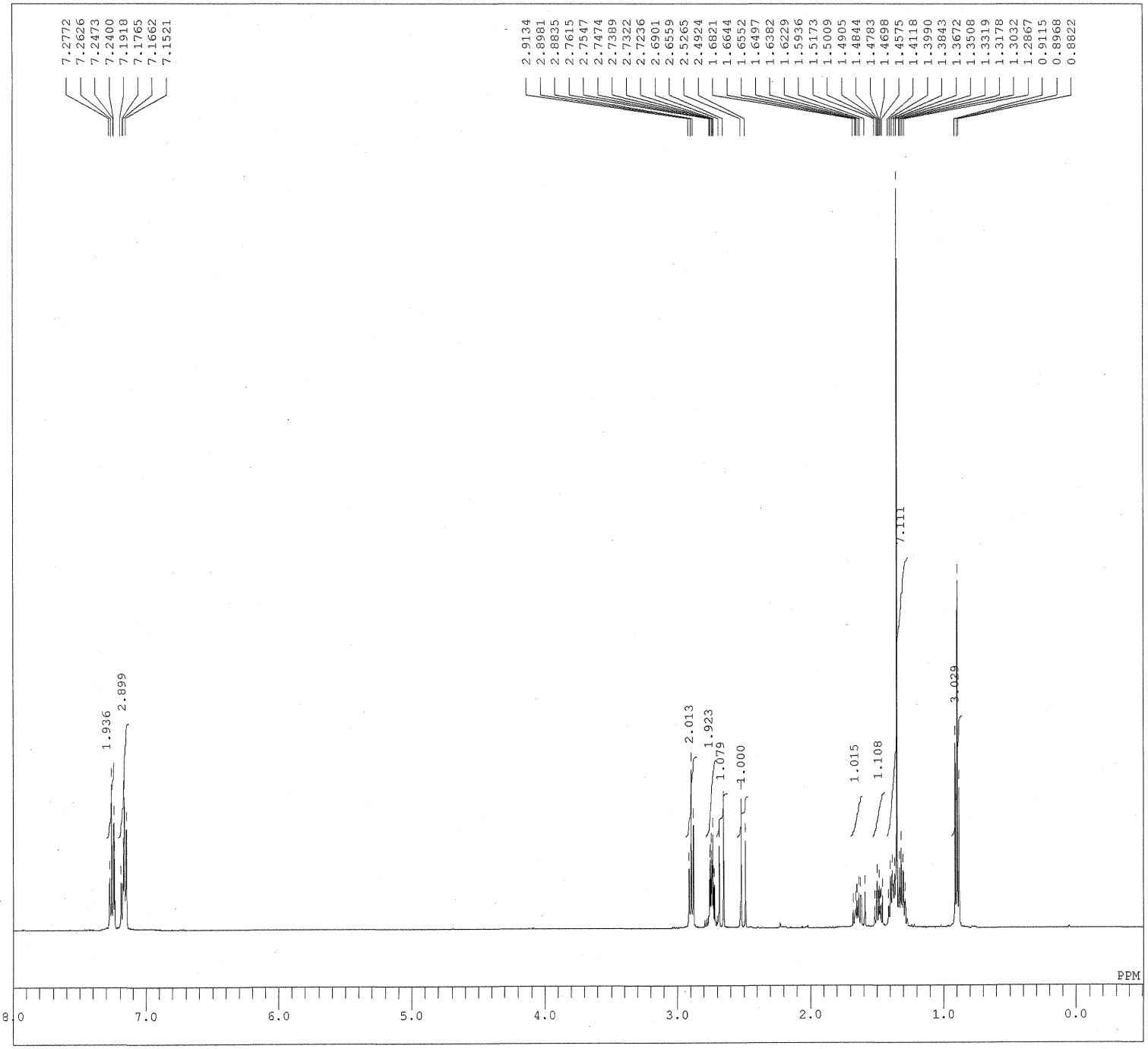



```
DFILE   savedata18.nmdata
COMNT   ipr
DATIM   Thu Apr 15 21:11:04 2010
OBNUC   1H
EXMOD   non
OBFRQ         500.00 MHz
OBSET         160.00 KHz
OBFIN        2160.00 Hz
POINT          32768
FREQU       10000.00 Hz
SCANS             16
ACQTM          3.2768 sec
PD             3.7232 sec
PW1               6.50 usec
IRNUC   1H
CTEMP             25.4 c
SLVNT   CDCL3
EXREF             7.24 ppm
BF                0.12 Hz
RGAIN               25
```

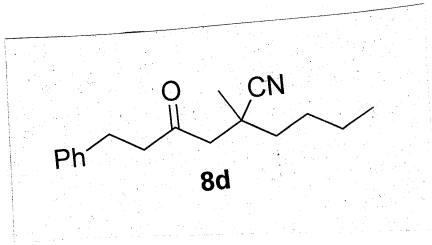


8c

phetktrans

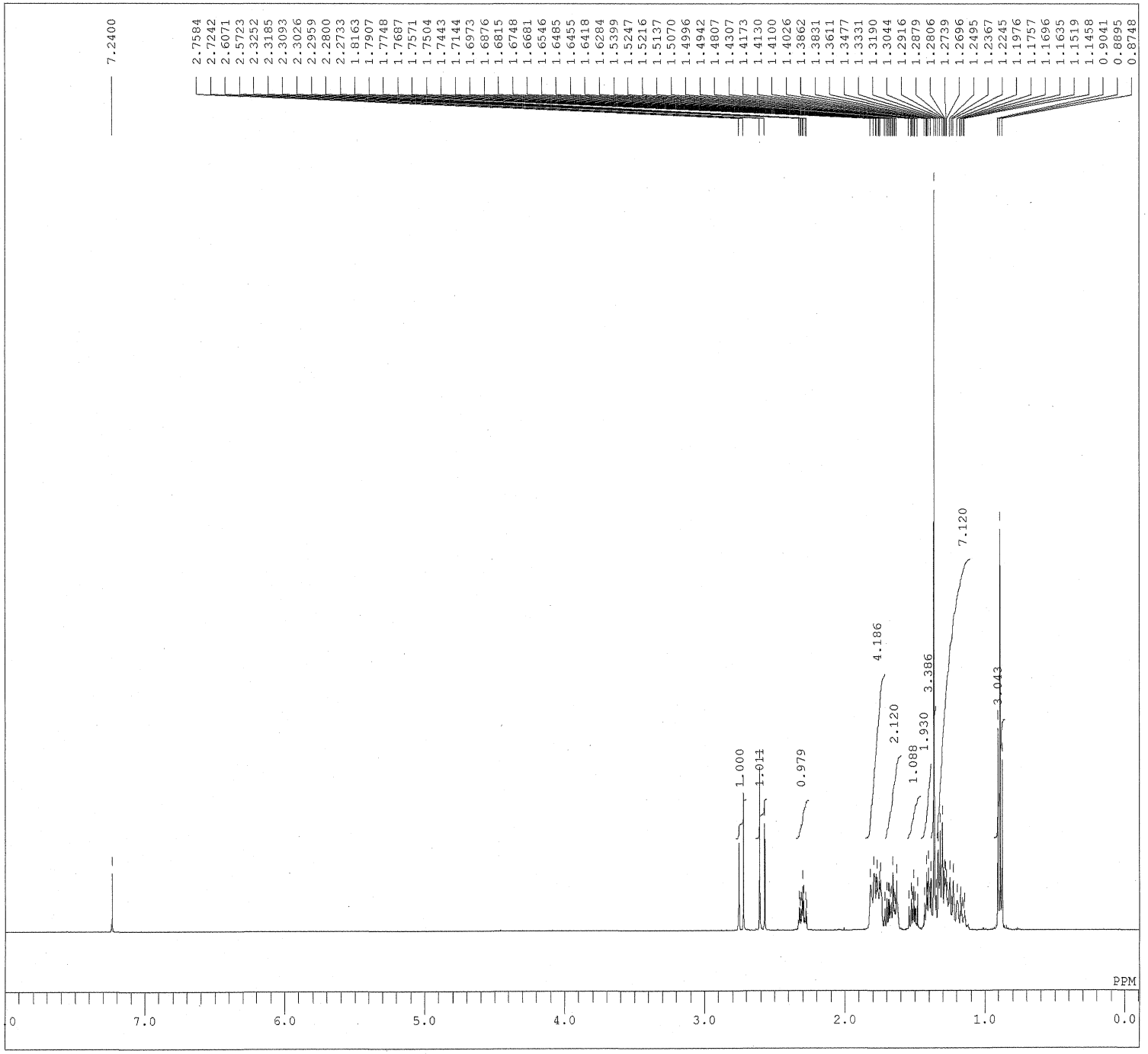


DFILE	savedata02.nmdata
COMNT	phetktrans
DATIM	Wed Feb 24 12:12:40 2010
OBNUC	1H
EXMOD	non
OBFRQ	500.00 MHz
OBSET	160.00 KHz
OBFIN	2160.00 Hz
POINT	32768
FREQU	10000.00 Hz
SCANS	6
ACQTM	3.2768 sec
PD	3.7232 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	24.1 c
SLVNT	CDCL3
EXREF	7.24 ppm
BF	0.12 Hz
RGAIN	15

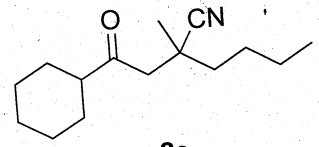


8d

cyktrans

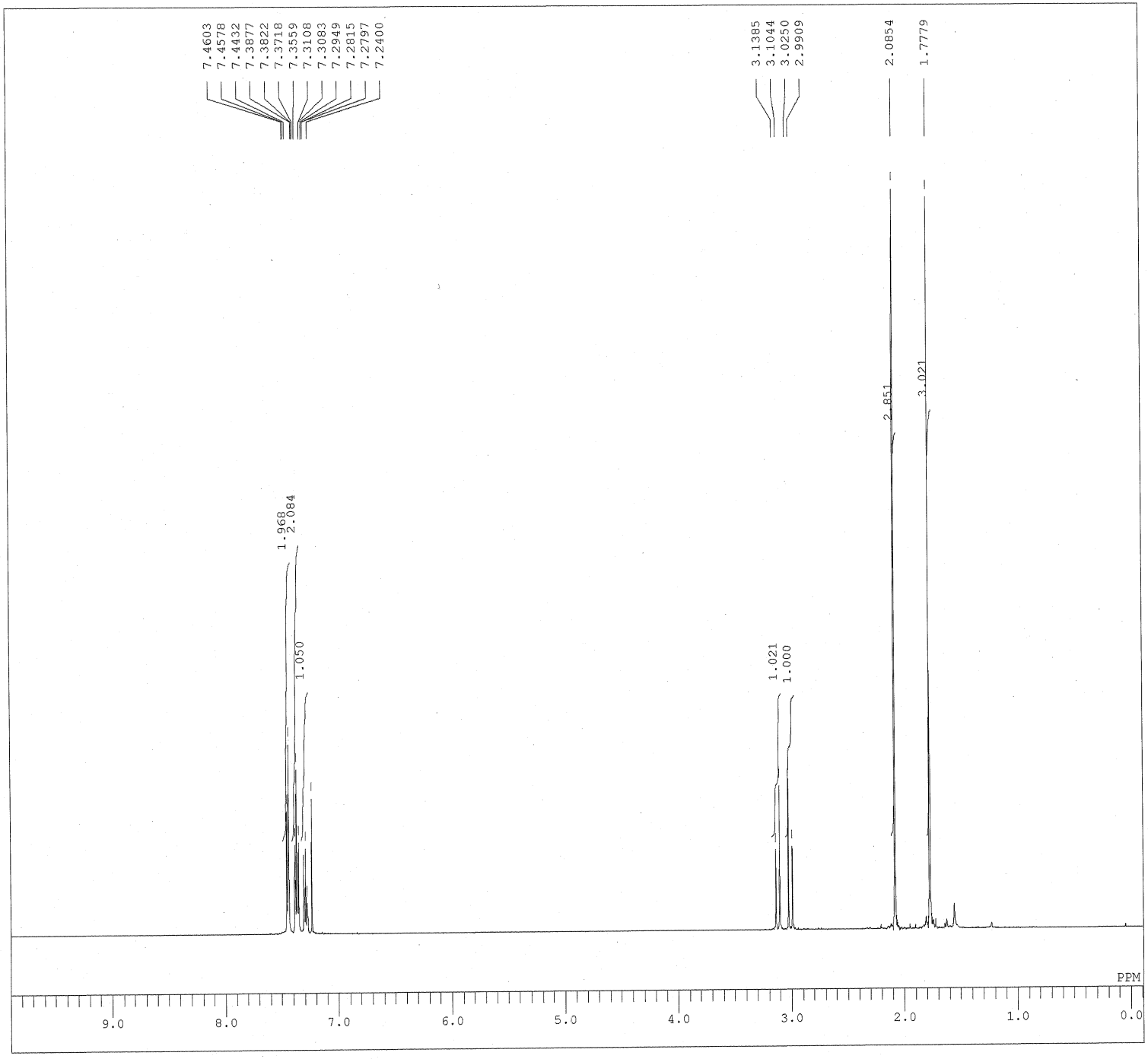



```
DFILE   savedata03.als
COMNT   cyktrans
DATIM   Sat Feb 20 19:16:02 2010
OBNUC   1H
EXMOD   non
OBFRQ         500.00 MHz
OBSET         160.00 KHz
OBFIN        2160.00 Hz
POINT          32768
FREQU       10000.00 Hz
SCANS              6
ACQTM          3.2768 sec
PD             3.7232 sec
PW1               6.50 usec
IRNUC   1H
CTEMP             23.7 c
SLVNT   CDCL3
EXREF             7.24 ppm
BF                0.10 Hz
RGAIN               13
```

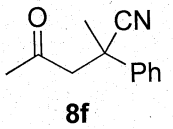


8e

mekbetaphproduct

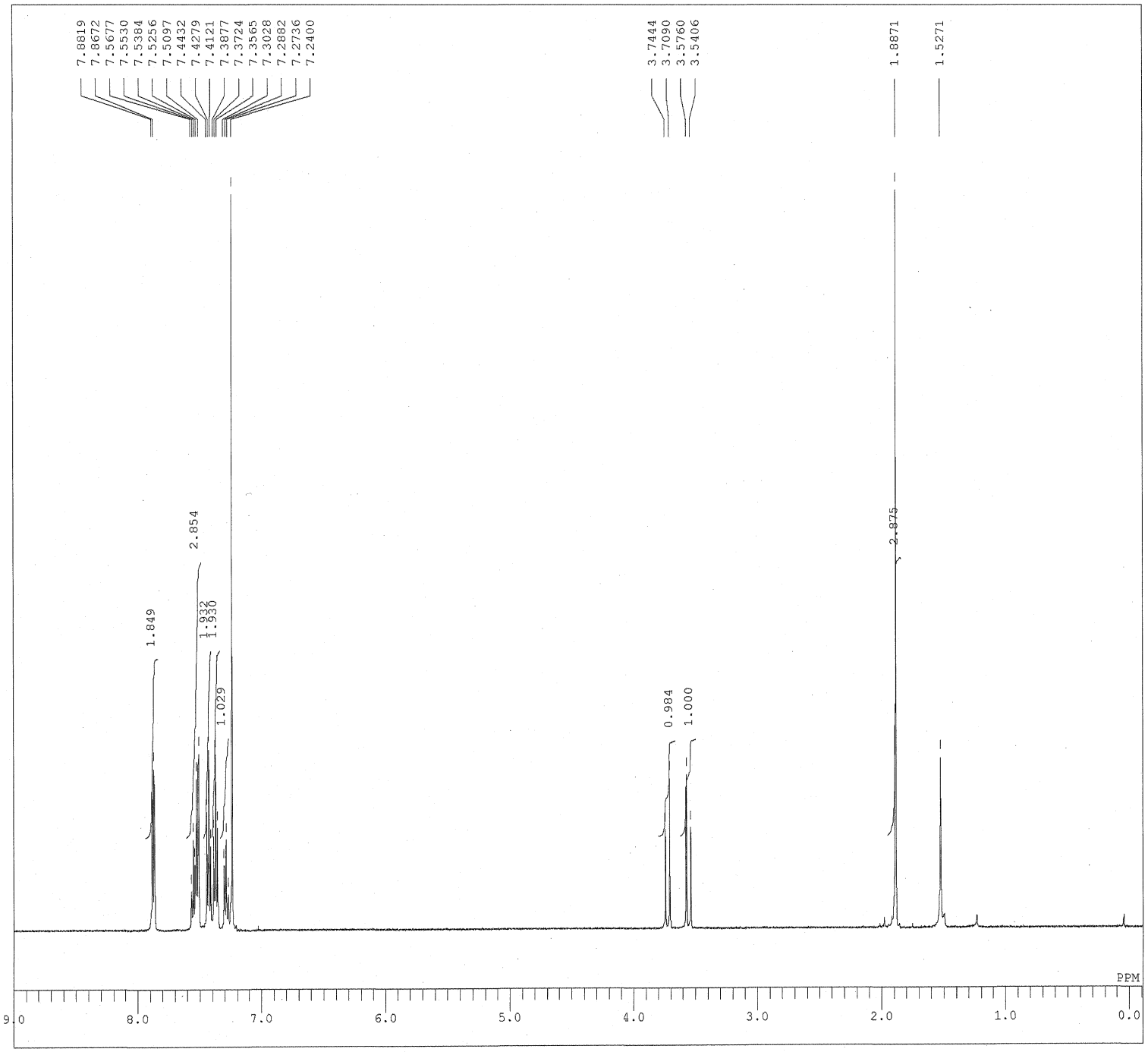


DFILE	savedata09.nmdata
COMNT	mekbetaphproduct
DATIM	Fri Apr 16 09:45:47 2010
OBNUC	1H
EXMOD	non
OBFRQ	500.00 MHz
OBSET	160.00 KHz
OBFIN	2160.00 Hz
POINT	32768
FREQU	10000.00 Hz
SCANS	4
ACQTM	3.2768 sec
PD	3.7232 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	25.7 c
SLVNT	CDCL3
EXREF	7.24 ppm
BF	0.12 Hz
RGAIN	19

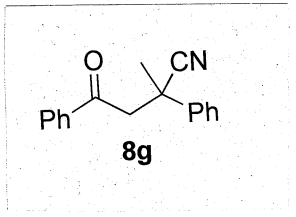


8f

chalc

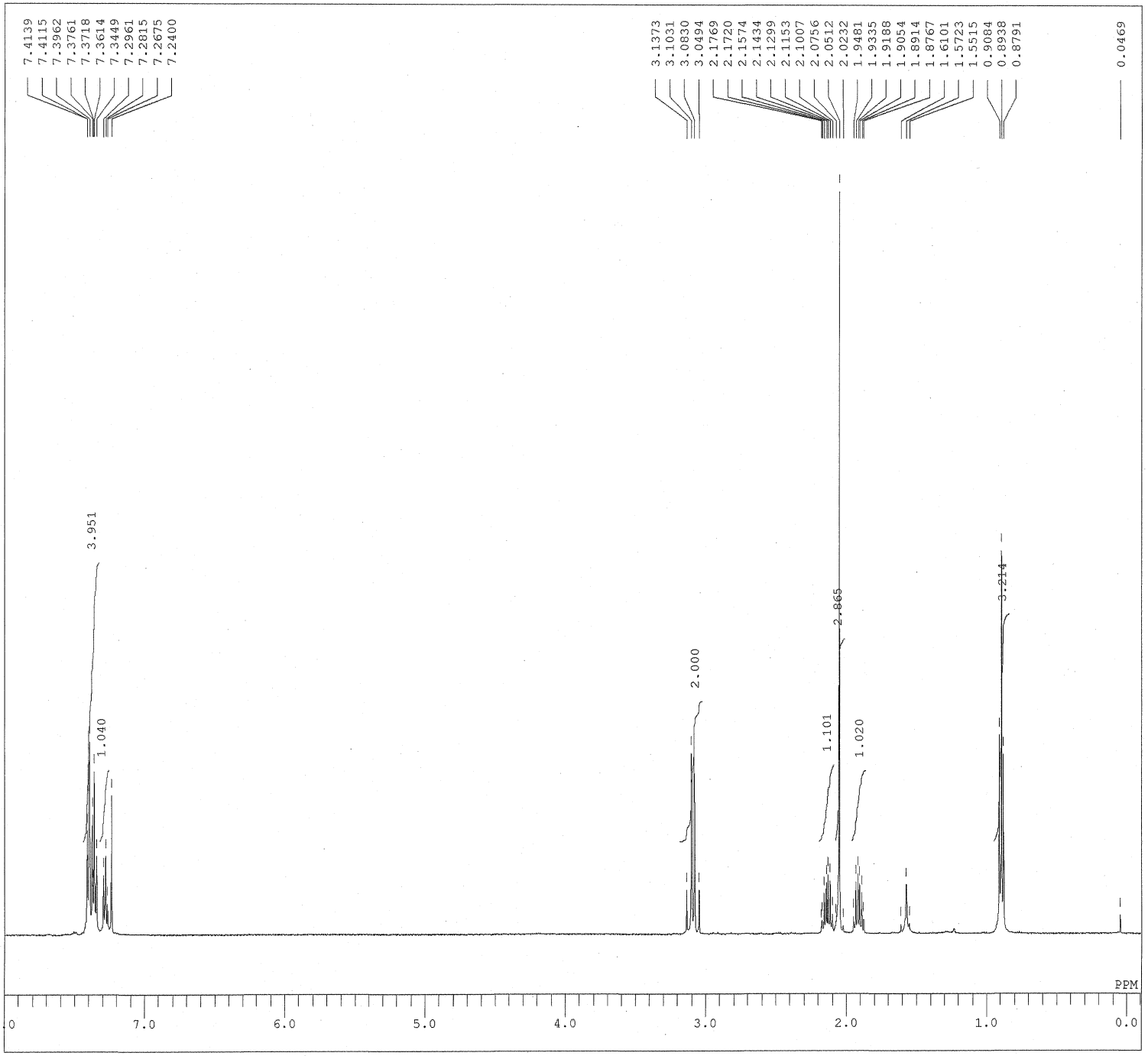



```
DFILE   savedata09.nmdata
COMNT   chalc
DATIM   Wed Feb 17 21:01:47 2010
OBNUC   1H
EXMOD   non
OBFRQ         500.00 MHz
OBSET         160.00 KHz
OBFIN        2160.00 Hz
POINT          32768
FREQU        10000.00 Hz
SCANS              8
ACQTM          3.2768 sec
PD             3.7232 sec
PW1               6.50 usec
IRNUC   1H
CTEMP             24.4 c
SLVNT   CDCL3
EXREF             7.24 ppm
BF                0.22 Hz
RGAIN               24
```

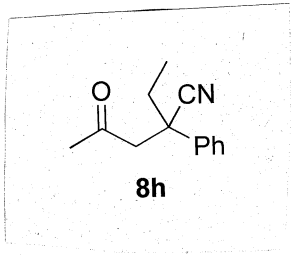


8g

betaettrans

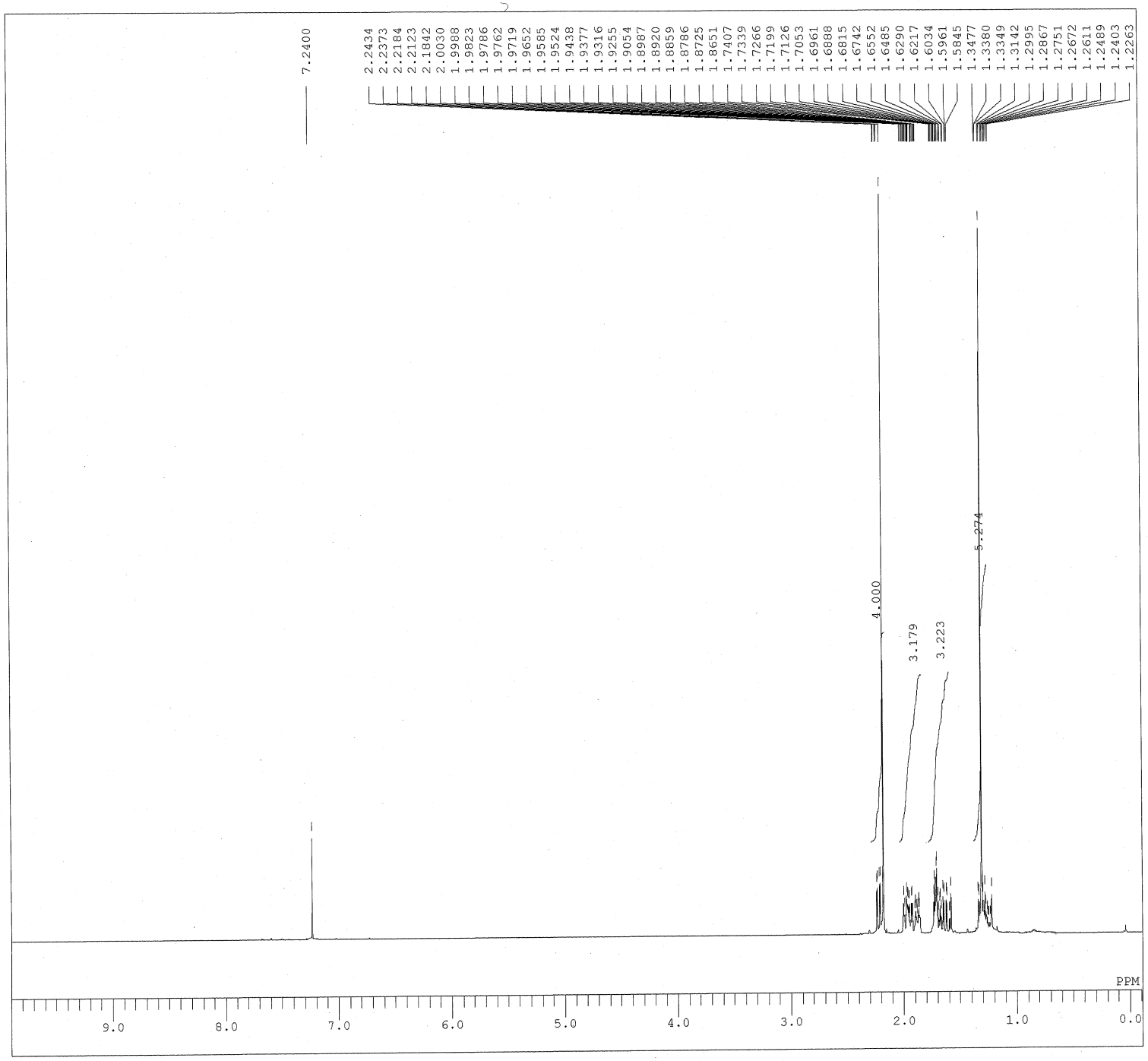


DFILE	savedata05.als
COMNT	betaettrans
DATIM	Wed Feb 24 20:46:17 2010
OBNUC	1H
EXMOD	non
OBFRQ	500.00 MHz
OBSET	160.00 KHz
OBFIN	2160.00 Hz
POINT	32768
FREQU	10000.00 Hz
SCANS	8
ACQTM	3.2768 sec
PD	3.7232 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	23.0 c
SLVNT	CDCL3
EXREF	7.24 ppm
BF	0.12 Hz
RGAIN	19

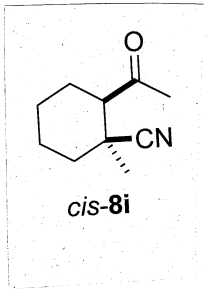


8h

alphacymp

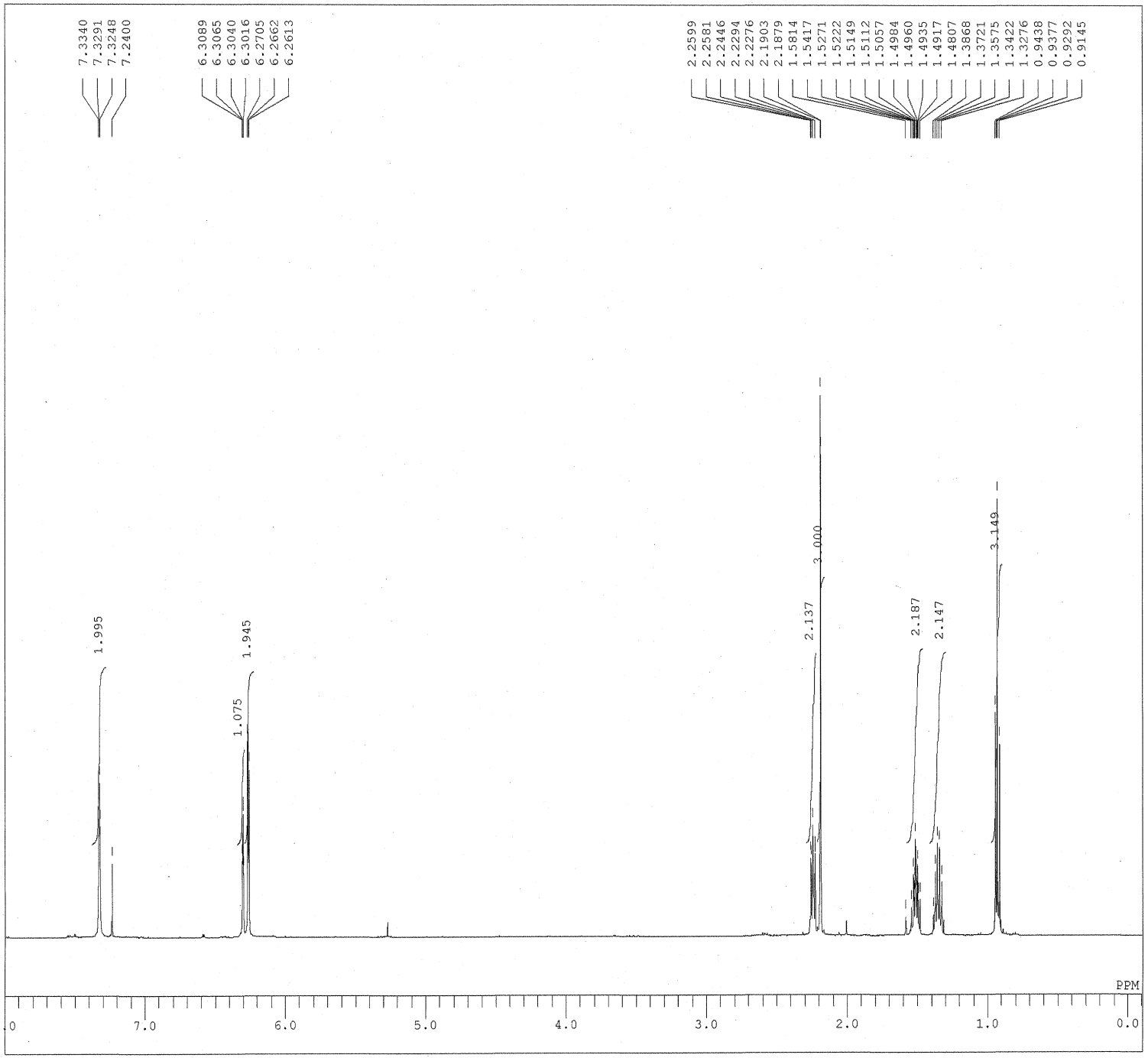



```
DFILE   savedata13.nmdata
COMNT   alphacymp
DATIM   Fri Apr 16 10:18:13 2010
OBNUC   1H
EXMOD   non
OBFRQ         500.00 MHz
OBSET         160.00 KHz
OBFIN        2160.00 Hz
POINT          32768
FREQU       10000.00 Hz
SCANS             27
ACQTM          3.2768 sec
PD             3.7232 sec
PW1               6.50 usec
IRNUC   1H
CTEMP            25.6 c
SLVNT   CDCL3
EXREF             7.24 ppm
BF                0.12 Hz
RGAIN               17
```

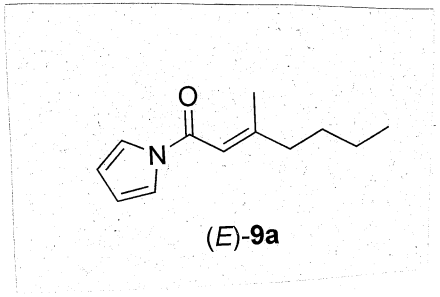


cis-**8i**

n

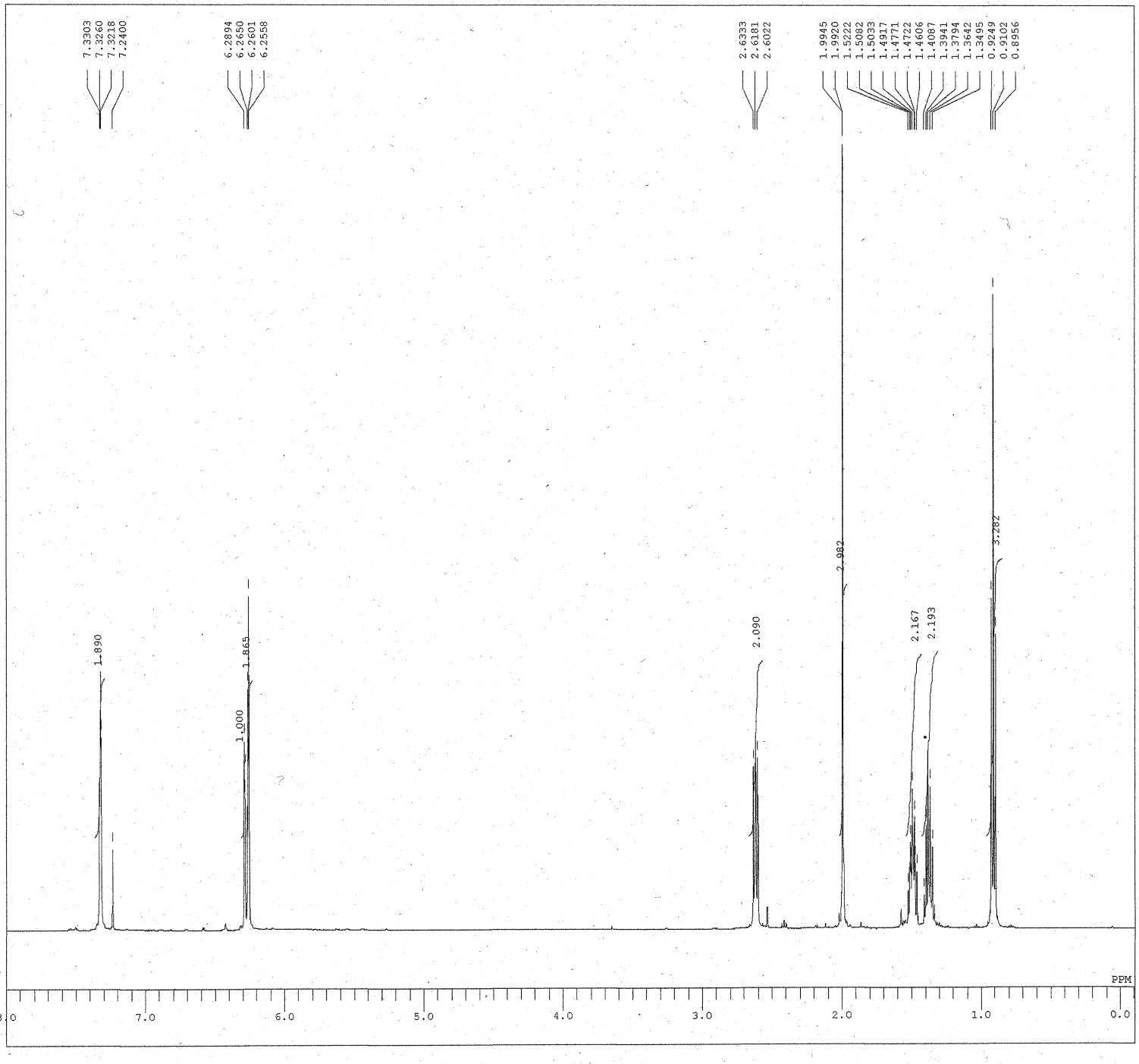



```
DFILE   savedata03.nmdata
COMNT   n
DATIM   Wed Feb  3 21:13:18 2010
OBNUC   1H
EXMOD   non
OBFRQ         500.00 MHz
OBSET         160.00 KHz
OBFIN        2160.00 Hz
POINT          32768
FREQU       10000.00 Hz
SCANS             16
ACQTM          3.2768 sec
PD             3.7232 sec
PW1               6.50 usec
IRNUC   1H
CTEMP            25.3 c
SLVNT   CDCL3
EXREF             7.24 ppm
BF                1.00 Hz
RGAIN               16
```

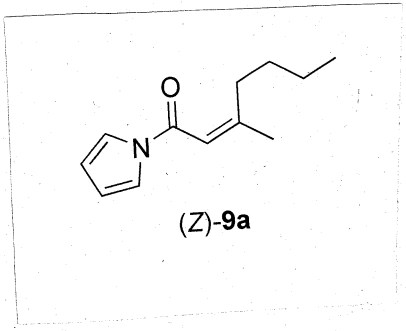


(*E*)-**9a**

nnbulpprot

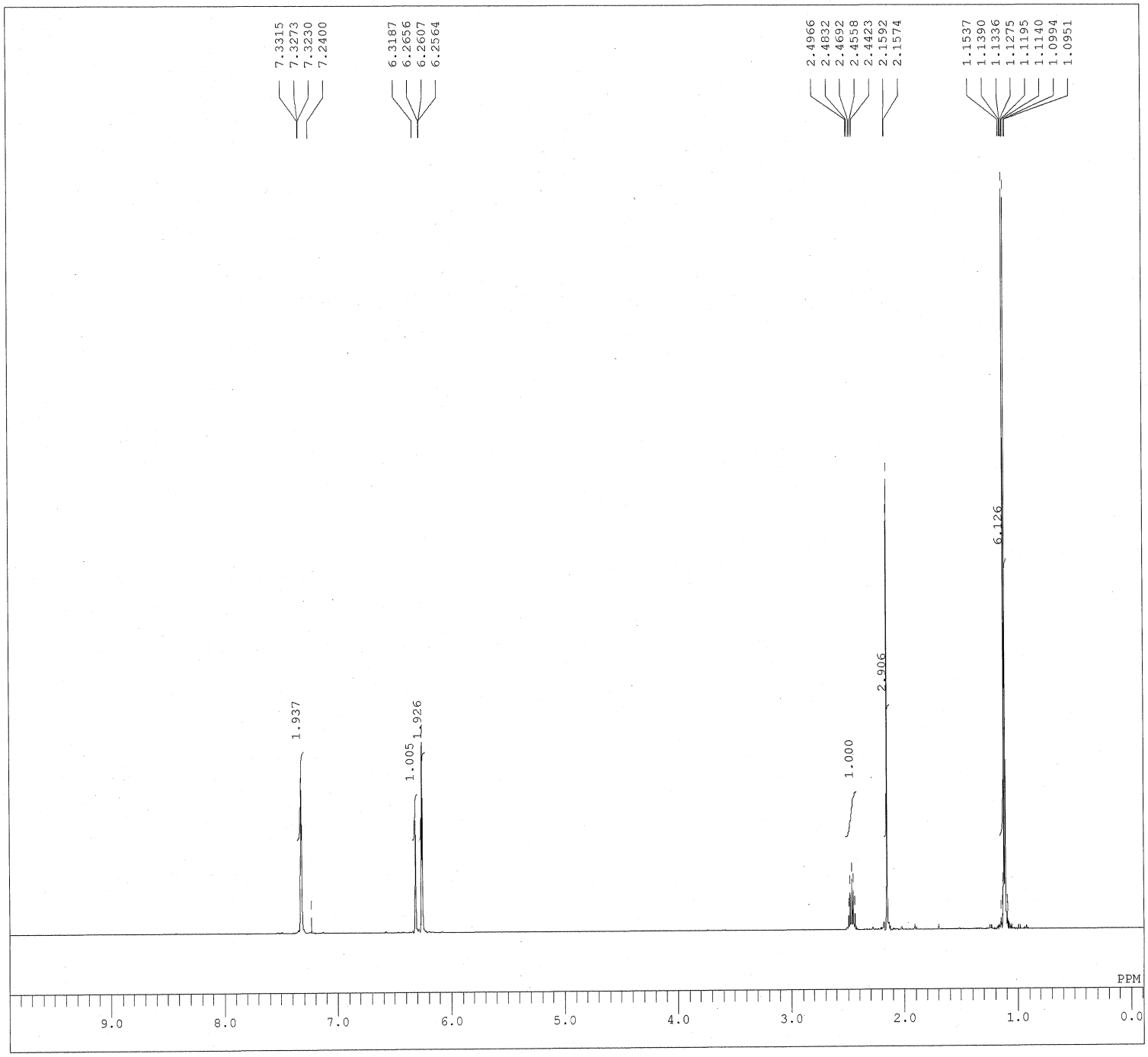



```
DFILE   savedata09.nmdata
COMNT   nnbulpprot
DATIM   Mon Jan 11 17:39:04 2010
OBNUC   1H
EXMOD   non
OBFRQ          500.00 MHz
OBSET          160.00 KHz
OBFIN         2160.00 Hz
POINT           32768
FREQU         10000.00 Hz
SCANS               8
ACQTM          3.2768 sec
PD             3.7232 sec
PW1              6.50 usec
IRNUC   1H
CTEMP           25.3 c
SLVNT   CDCL3
EXREF           7.24 ppm
BF              0.12 Hz
RGAIN             15
```

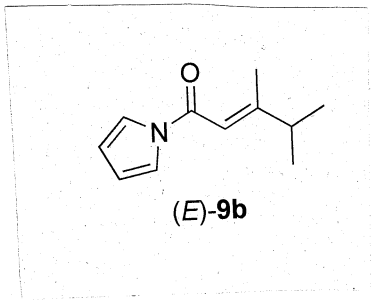


(*Z*)-**9a**

napiprtrans

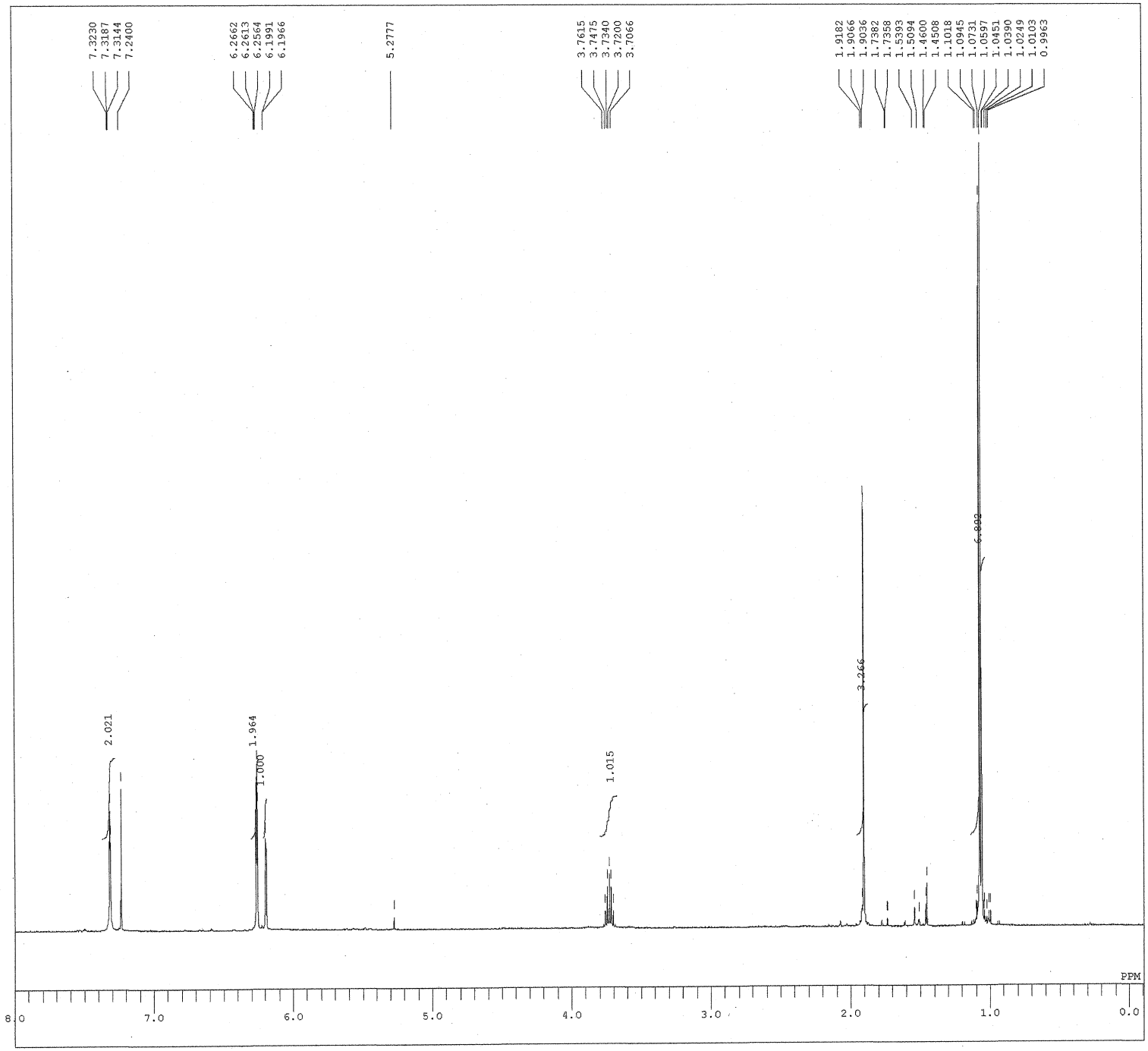



```
DFILE   savedata03.nmdata
COMNT   napiprtrans
DATIM   Fri Apr 16 09:16:20 2010
OBNUC   1H
EXMOD   non
OBFRQ         500.00 MHz
OBSET         160.00 KHz
OBFIN        2160.00 Hz
POINT          32768
FREQU       10000.00 Hz
SCANS              6
ACQTM          3.2768 sec
PD             3.7232 sec
PW1              6.50 usec
IRNUC   1H
CTEMP            25.3 c
SLVNT   CDCL3
EXREF             7.24 ppm
BF                0.12 Hz
RGAIN               12
```

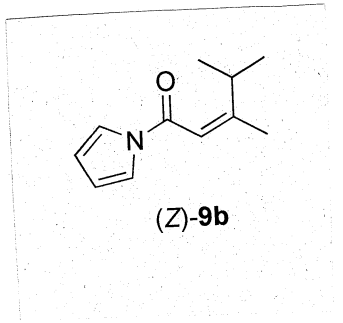


(*E*)-**9b**

niprlpprot

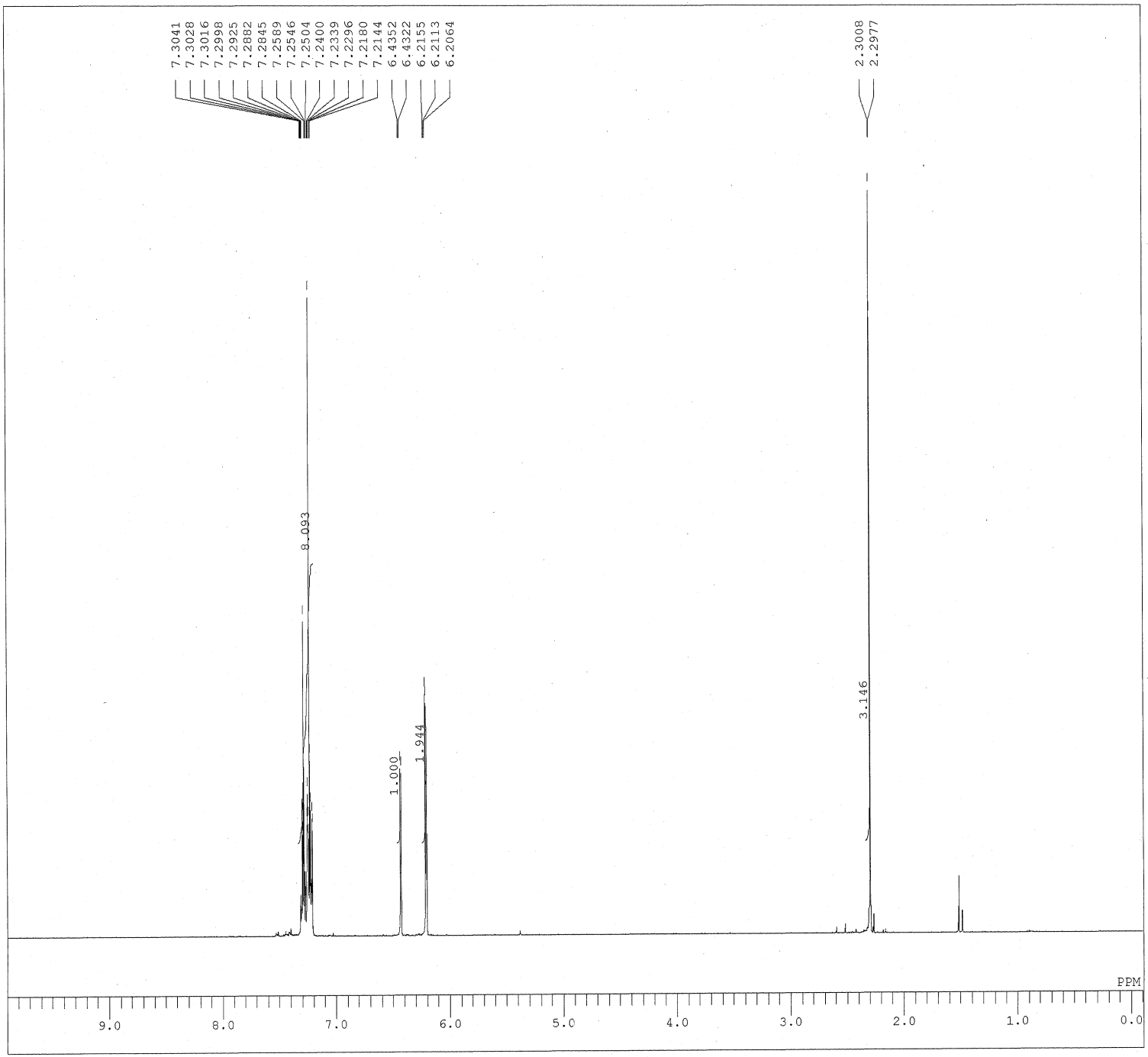



```
DFILE   savedata07.nmdata
COMNT   niprlpprot
DATIM   Tue Jan 12 14:36:18 2010
OBNUC   1H
EXMOD   non
OBFRQ         500.00 MHz
OBSET         160.00 KHz
OBFIN        2160.00 Hz
POINT          32768
FREQU       10000.00 Hz
SCANS              8
ACQTM          3.2768 sec
PD             3.7232 sec
PW1               6.50 usec
IRNUC   1H
CTEMP            24.8 c
SLVNT   CDCL3
EXREF             7.24 ppm
BF                0.12 Hz
RGAIN               19
```

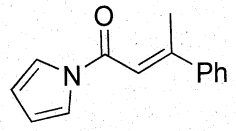


(*Z*)-**9b**

napbetaphtrans

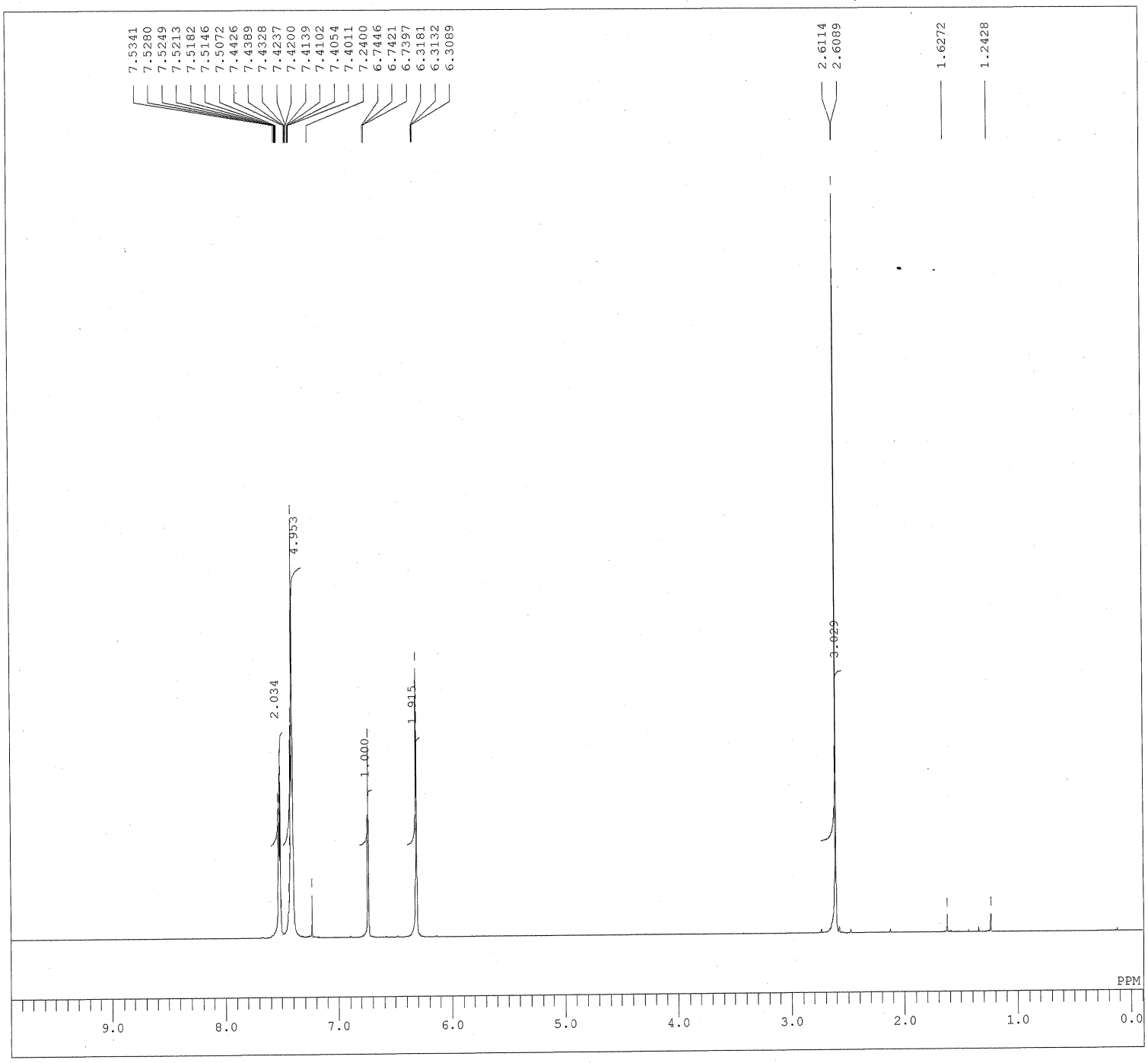



```
DFILE   savedata22.nmdata
COMNT   napbetaphtrans
DATIM   Fri Apr 16 19:10:01 2010
OBNUC   1H
EXMOD   non
OBFRQ         500.00 MHz
OBSET         160.00 KHz
OBFIN        2160.00 Hz
POINT          32768
FREQU       10000.00 Hz
SCANS             16
ACQTM          3.2768 sec
PD             3.7232 sec
PW1               6.50 usec
IRNUC   1H
CTEMP            24.6 c
SLVNT   CDCL3
EXREF             7.24 ppm
BF                0.12 Hz
RGAIN               22
```

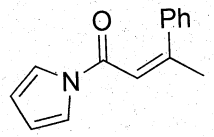


(*E*)-**9c**

napbetaphcis

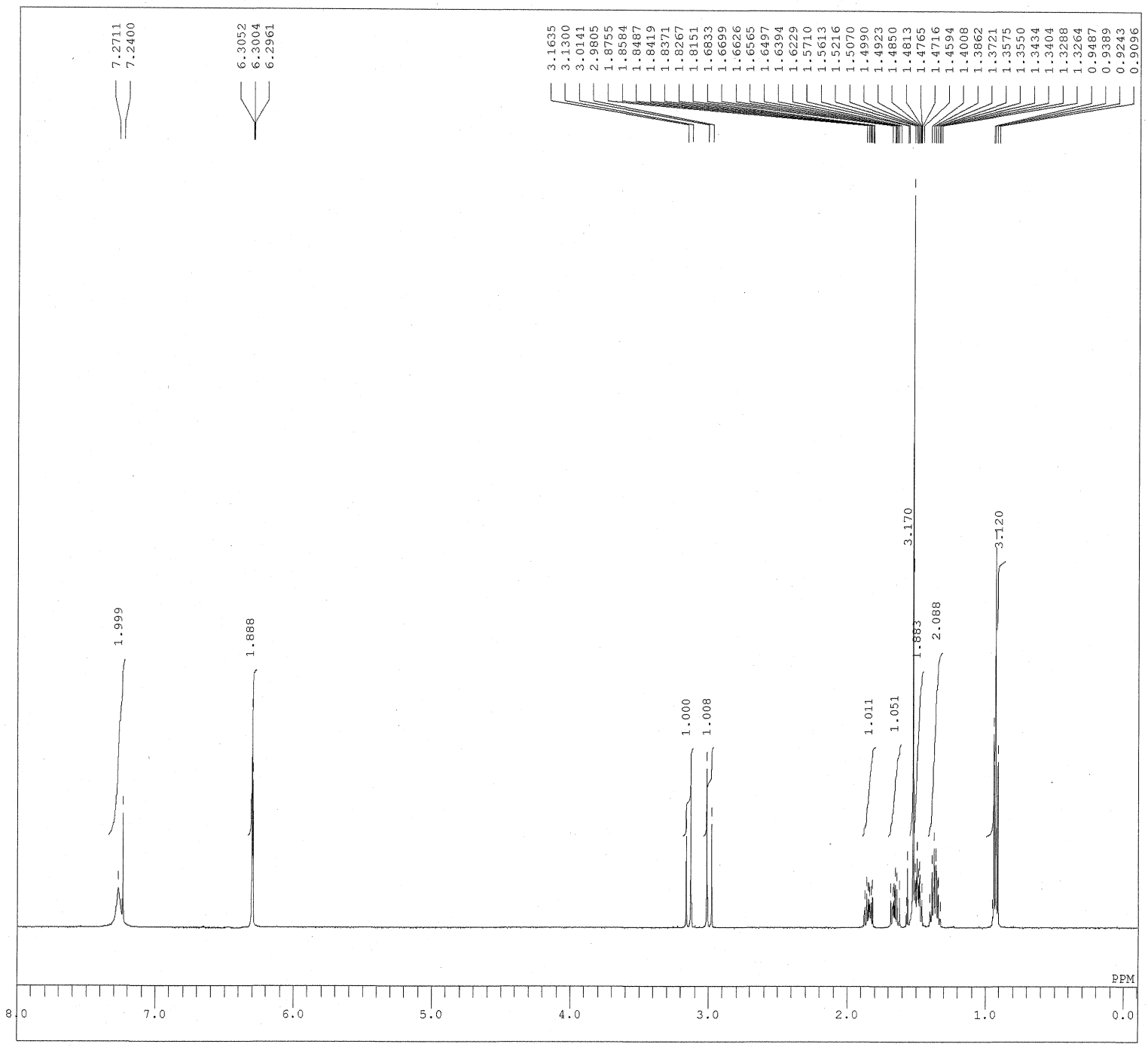


DFILE	savedata15.nmdata
COMNT	napbetaphcis
DATIM	Sat Apr 17 10:29:16 2010
OBNUC	1H
EXMOD	non
OBFRQ	500.00 MHz
OBSET	160.00 KHz
OBFIN	2160.00 Hz
POINT	32768
FREQU	10000.00 Hz
SCANS	6
ACQTM	3.2768 sec
PD	3.7232 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	25.5 c
SLVNT	CDCL3
EXREF	7.24 ppm
BF	0.12 Hz
RGAIN	14

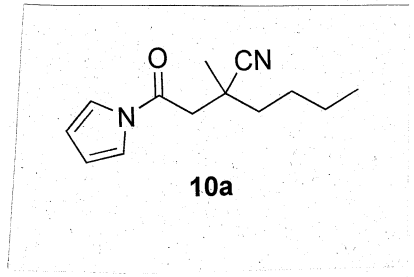


(*Z*)-**9c**

napnbutrans

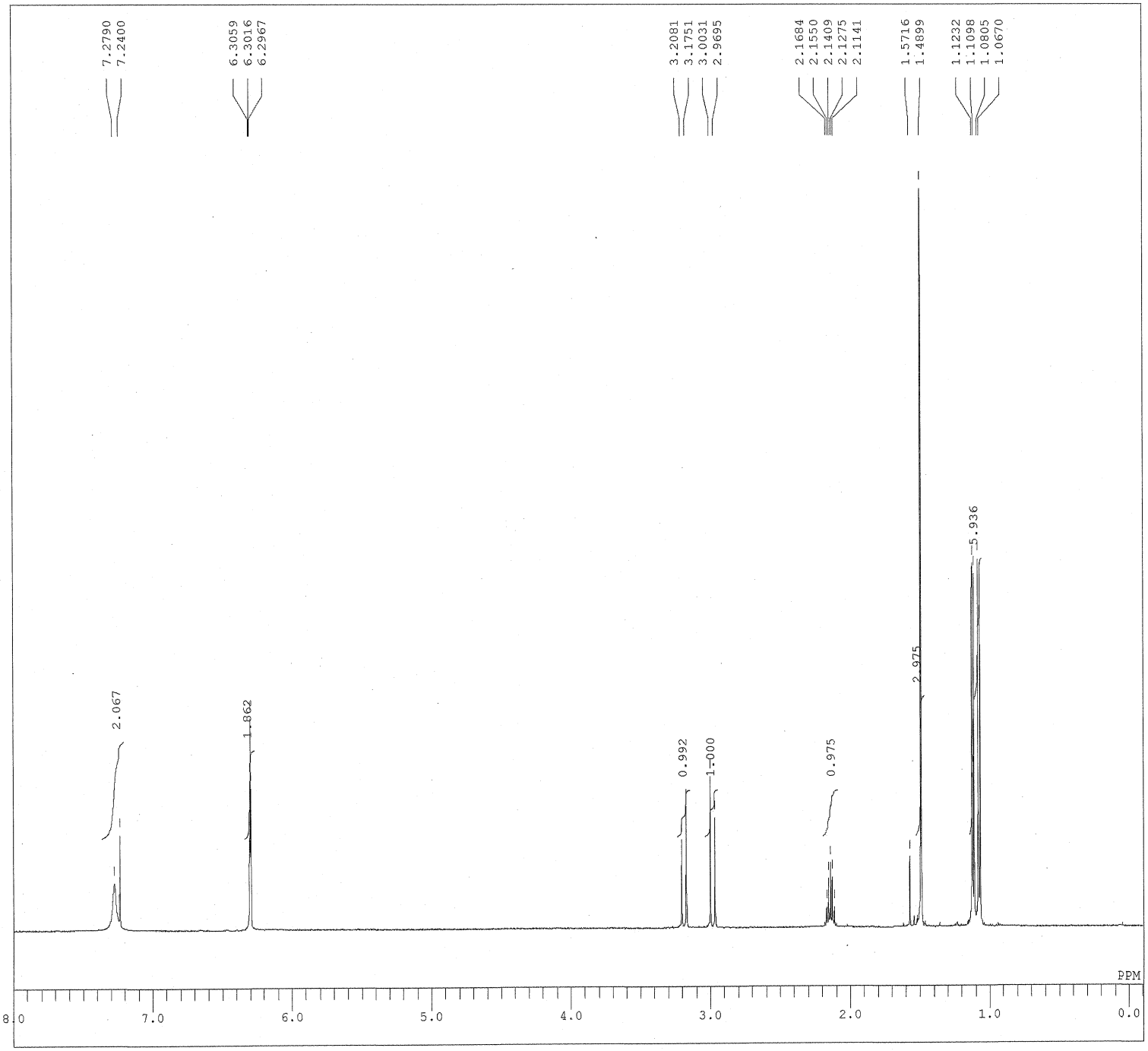


DFILE	savedata05.nmdata
COMNT	napnbutrans
DATIM	Sat Feb 20 19:24:09 2010
OBNUC	1H
EXMOD	non
OBFRQ	500.00 MHz
OBSET	160.00 KHz
OBFIN	2160.00 Hz
POINT	32768
FREQU	10000.00 Hz
SCANS	8
ACQTM	3.2768 sec
PD	3.7232 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	23.6 c
SLVNT	CDCL3
EXREF	7.24 ppm
BF	0.10 Hz
RGAIN	17

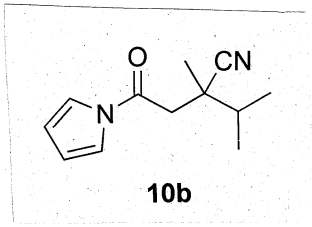


10a

napiprtrans

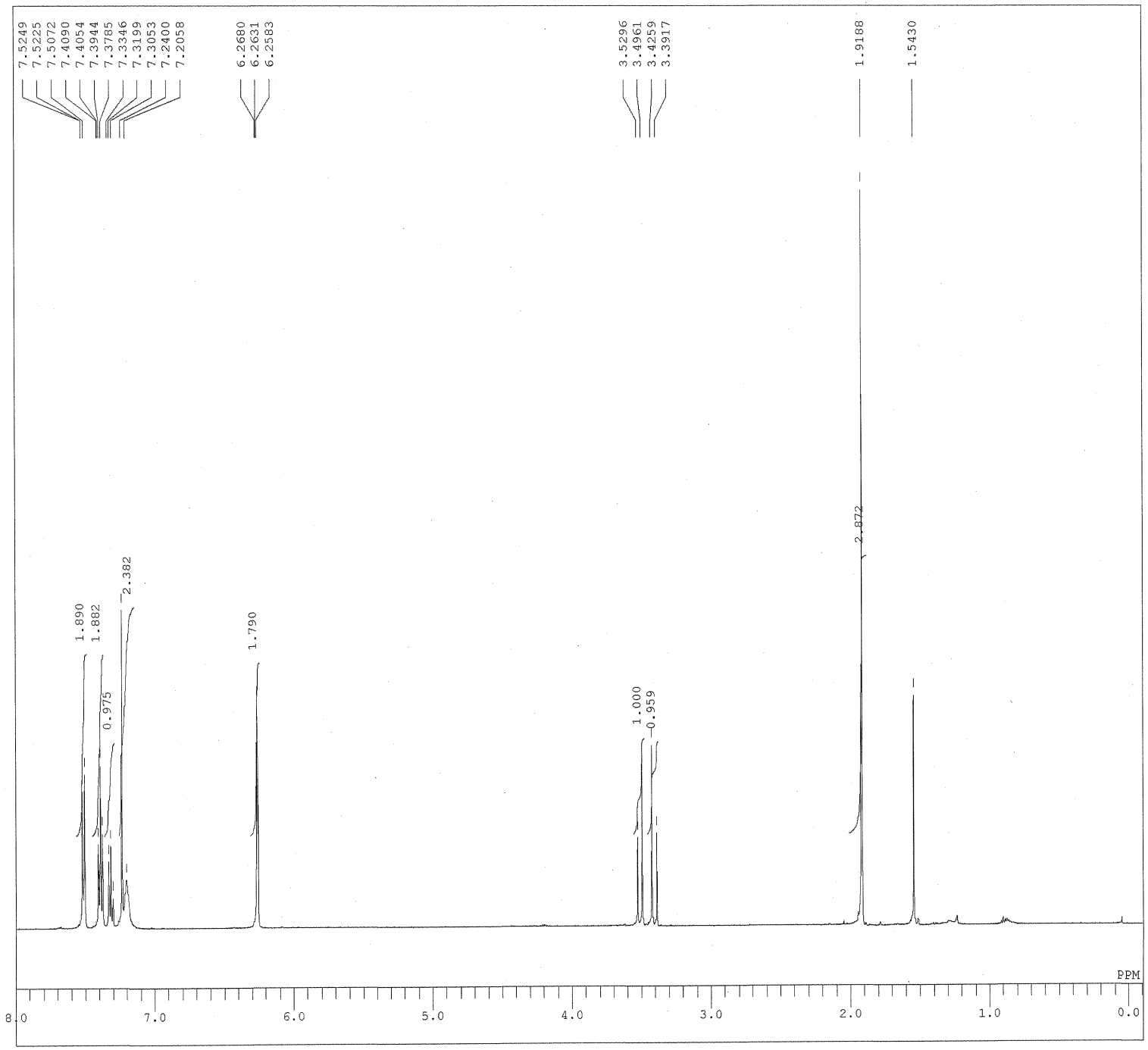



```
DFILE   savedata04.nmdata
COMNT   napiprtrans
DATIM   Wed Feb 24 12:21:11 2010
OBNUC   1H
EXMOD   non
OBFRQ         500.00 MHz
OBSET         160.00 KHz
OBFIN        2160.00 Hz
POINT          32768
FREQU       10000.00 Hz
SCANS              6
ACQTM          3.2768 sec
PD             3.7232 sec
PW1               6.50 usec
IRNUC   1H
CTEMP             23.9 c
SLVNT   CDCL3
EXREF             7.24 ppm
BF                0.12 Hz
RGAIN               17
```

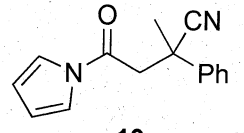


10b

napbetaph

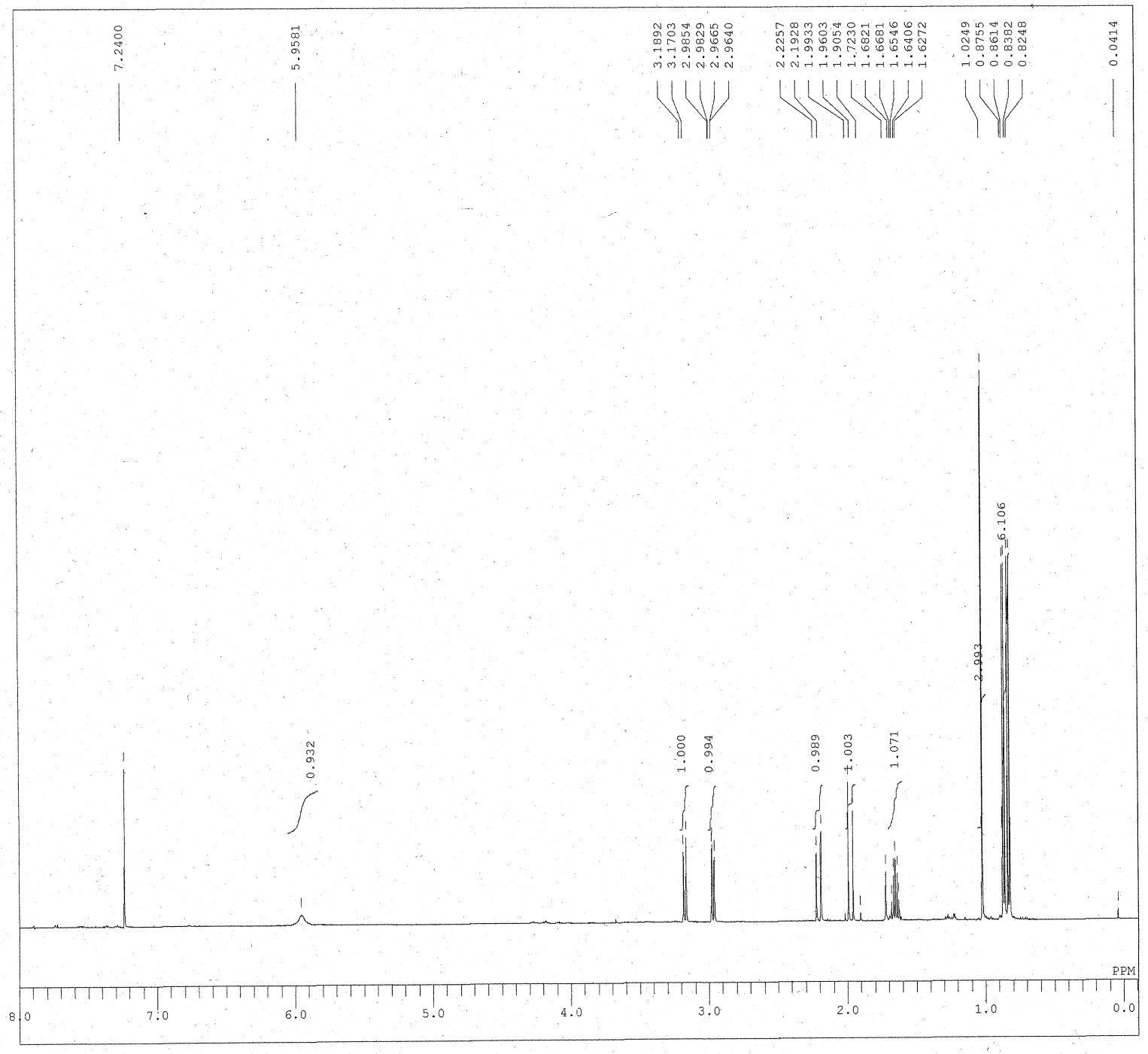



```
DFILE   savedata01.als
COMNT   napbetaph
DATIM   Wed Feb 24 19:38:12 2010
OBNUC   1H
EXMOD   non
OBFRQ         500.00 MHz
OBSET         160.00 KHz
OBFIN        2160.00 Hz
POINT          32768
FREQU       10000.00 Hz
SCANS              8
ACQTM          3.2768 sec
PD             3.7232 sec
PW1               6.50 usec
IRNUC   1H
CTEMP            23.5 c
SLVNT   CDCL3
EXREF             7.24 ppm
BF                0.12 Hz
RGAIN               22
```

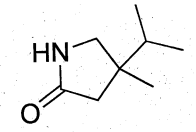


10c

1H Line

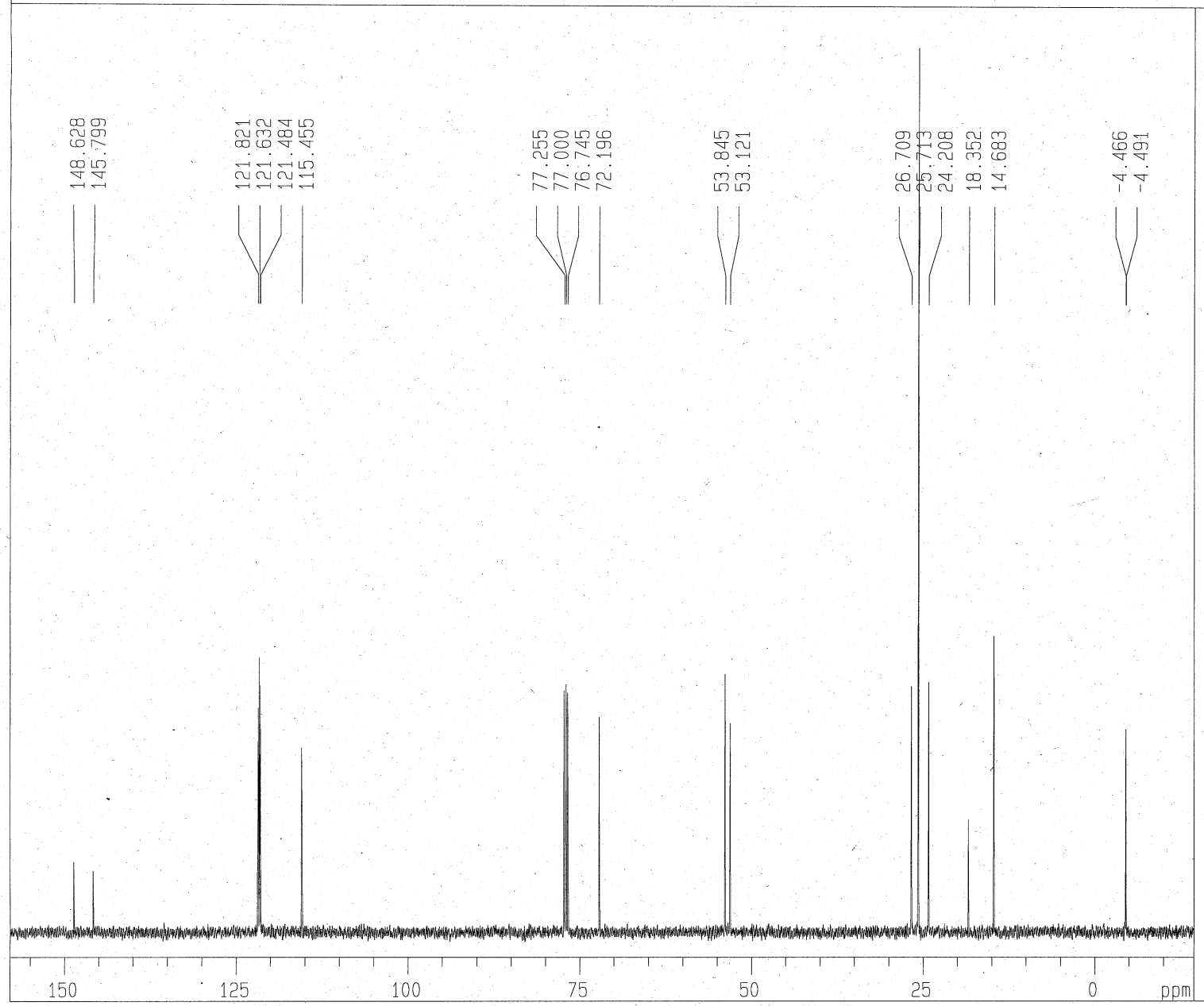


DFILE savedata03.nmdata
COMNT 1H Line
DATIM Thu Jun 3 16:45:09 2010
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 8
ACQTM 3.2768 sec
PD 3.7232 sec
PW1 5.90 usec
IRNUC 1H
CTEMP 24.5 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.01 Hz
RGAIN 19



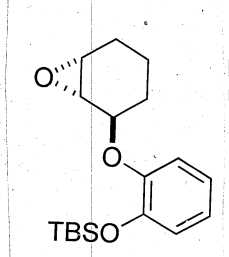
24

1H Line



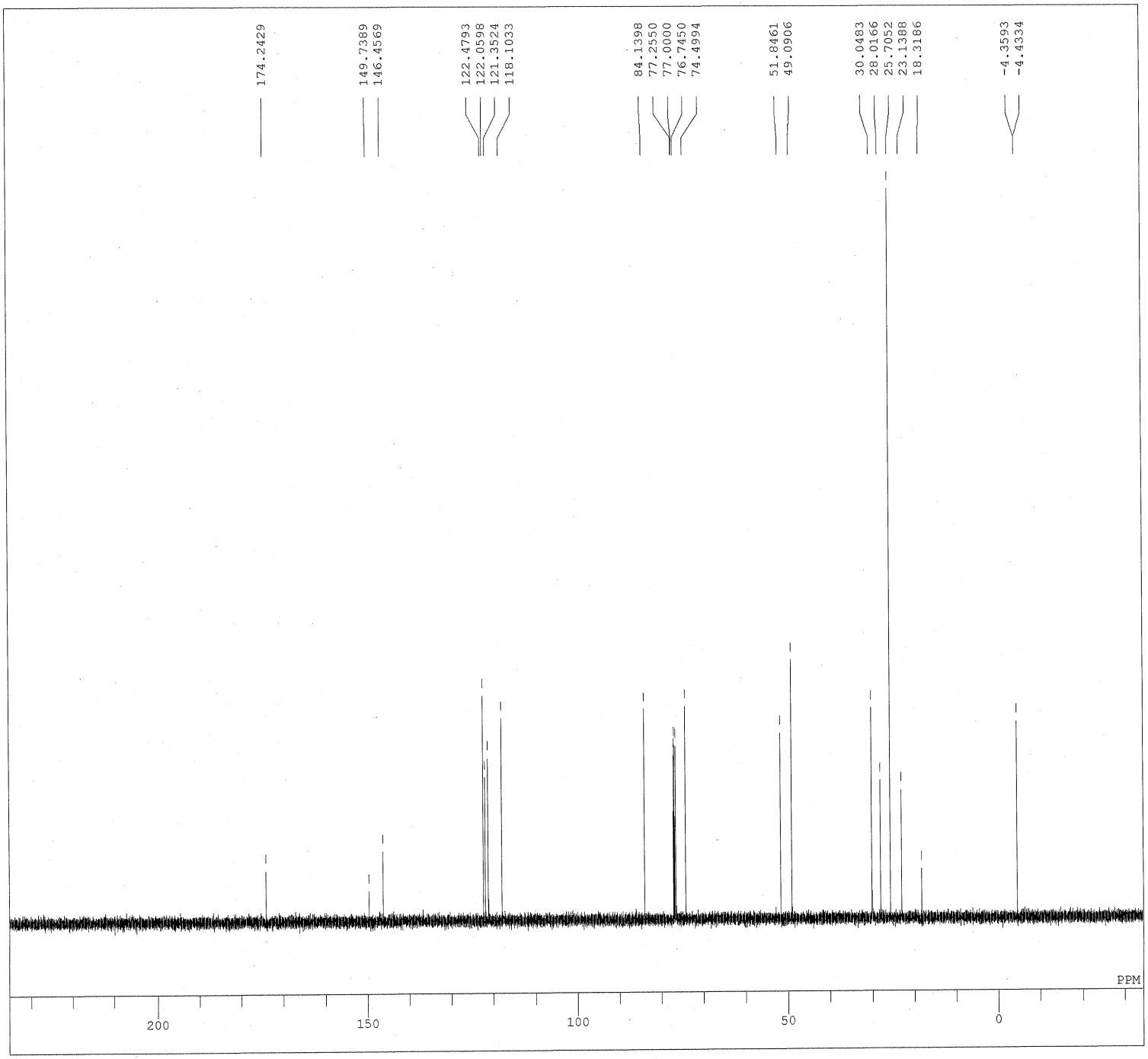
Date : Tue Dec 8 21:53:23 2009

FileName	:	.LoadingFID.nmdata
Comment	:	1H Line
SliceHistory	:	
EXMODE	:	bcm
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	33898.3 Hz
FILTR	:	16950 Hz
DELAY	:	11.8 usec
DEADT	:	10.0 usec
INTVL	:	29.5 usec
TIMES	:	6400 times
DUMMY	:	1 times
PD	:	2.0333 sec
ACQTM	:	966.6560 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	1.03 Hz
PW1	:	5.50 usec
OBNUC	:	13C
OBFRQ	:	125.65 MHz
OBSET	:	127958.00 Hz
RGAIN	:	31
IRNUC	:	1H
IRFRQ	:	500.00 MHz
IRSET	:	162160.00 Hz
IRRPW	:	50.0 usec
IRRNS	:	0
SCANS	:	75 times
SLVNT		
SPINNING		Hz
TEMP		C

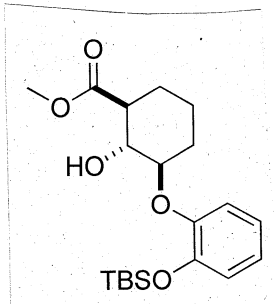


13

ligester

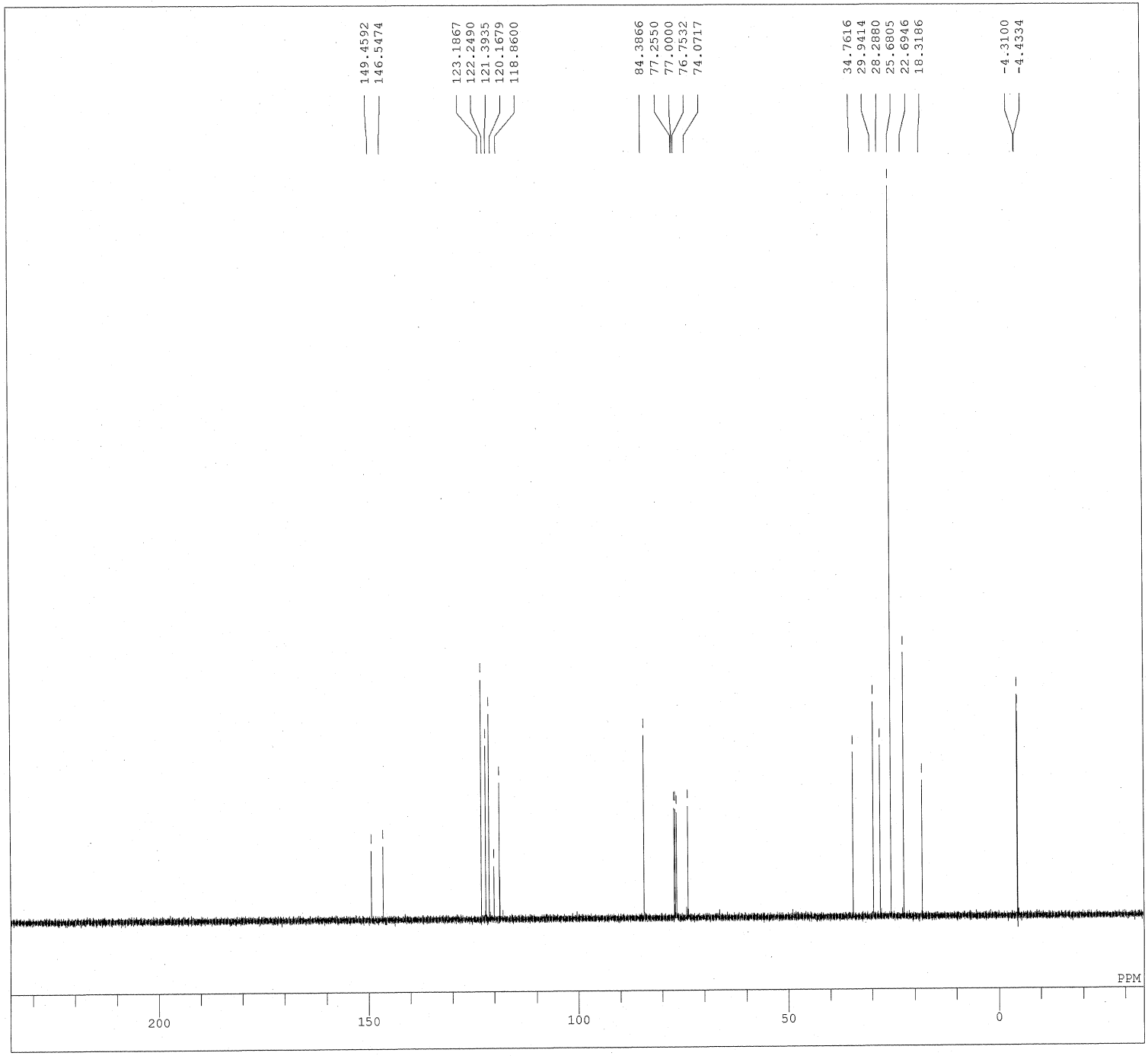



```
DFILE   savedata15.nmdata
COMNT   ligester
DATIM   Fri Apr 16 10:31:08 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS             47
ACQTM          0.9667 sec
PD             2.0333 sec
PW1               5.50 usec
IRNUC   1H
CTEMP            26.3 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.12 Hz
RGAIN              30
```

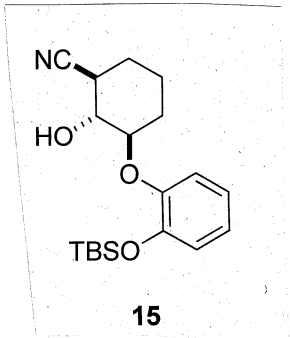


14

cnlig

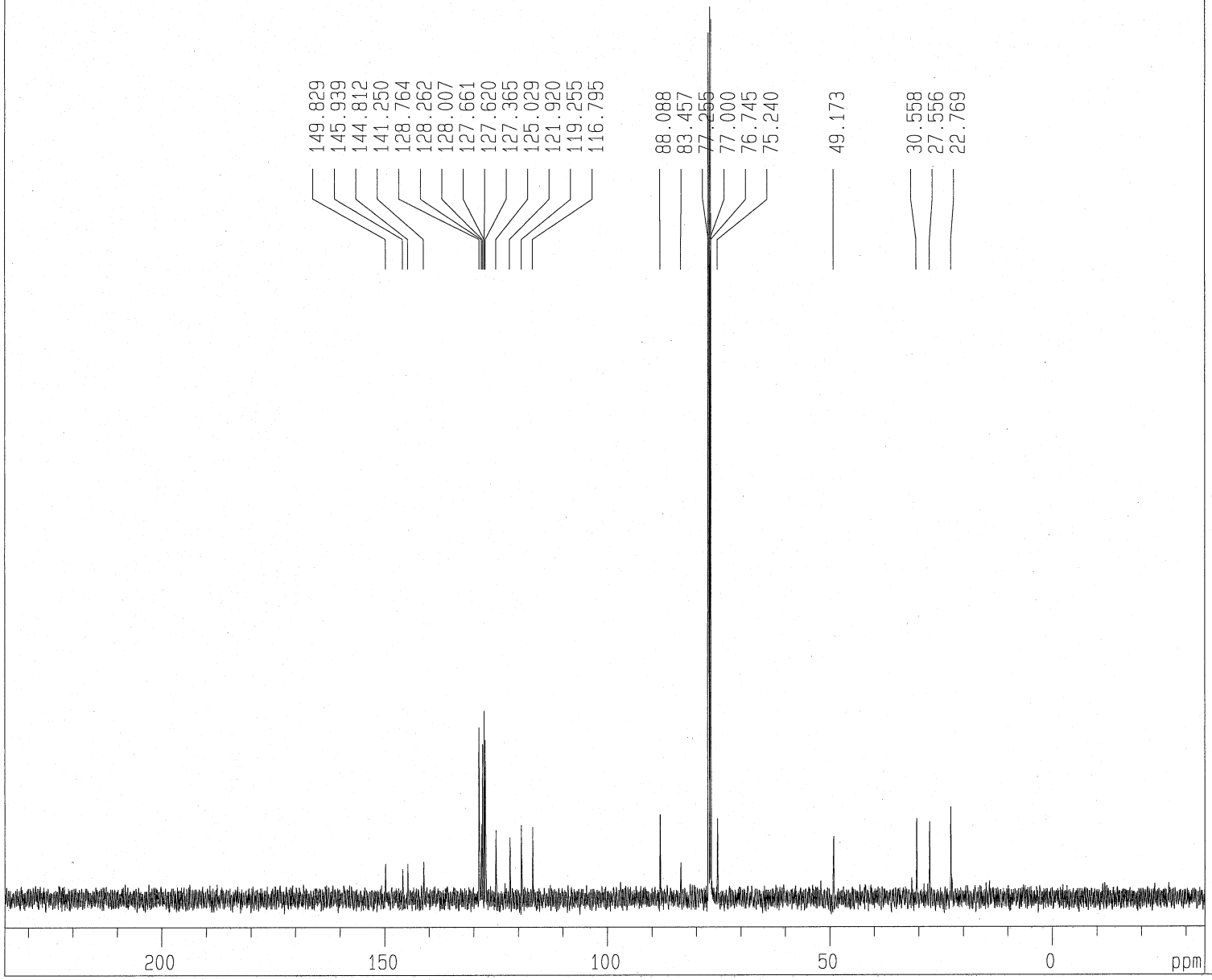



```
DFILE   savedata02.nmdata
COMNT   cnlig
DATIM   Fri Apr 16 09:11:52 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS            113
ACQTM          0.9667 sec
PD             2.0333 sec
PW1              5.50 usec
IRNUC   1H
CTEMP           25.6 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             30
```



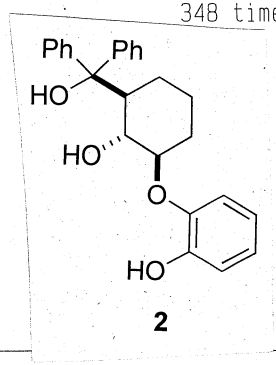
15

1H Line



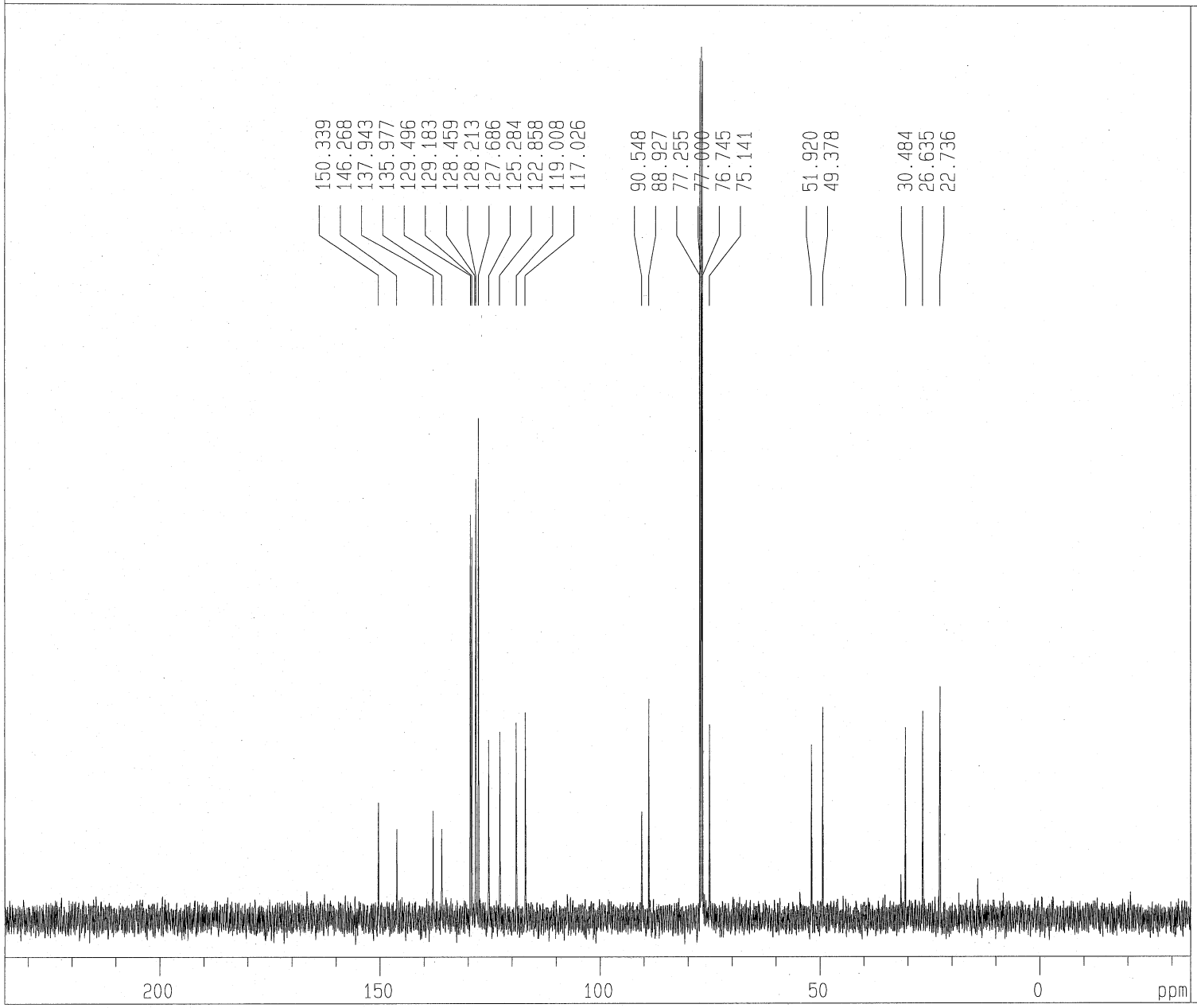
Date : Fri Dec 18 14:54:49 2009

FileName	:	.LoadingFID.nmdata
Comment	:	1H Line
SliceHistory	:	
EXMODE	:	bcm
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	33898.3 Hz
FILTR	:	16950 Hz
DELAY	:	11.8 usec
DEADT	:	10.0 usec
INTVL	:	29.5 usec
TIMES	:	8000 times
DUMMY	:	1 times
PD	:	2.0333 sec
ACQTM	:	966.6560 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	1.03 Hz
PW1	:	5.50 usec
OBNUC	:	13C
OBFRQ	:	125.65 MHz
OBSET	:	127958.00 Hz
RGAIN	:	30
IRNUC	:	1H
IRFRQ	:	500.00 MHz
IRSET	:	162160.00 Hz
IRRPW	:	50.0 usec
IRRNS	:	0
SCANS	:	348 times
SLVNT		
SPINNING		
TEMP		



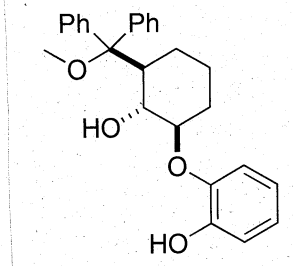
2

1H Line



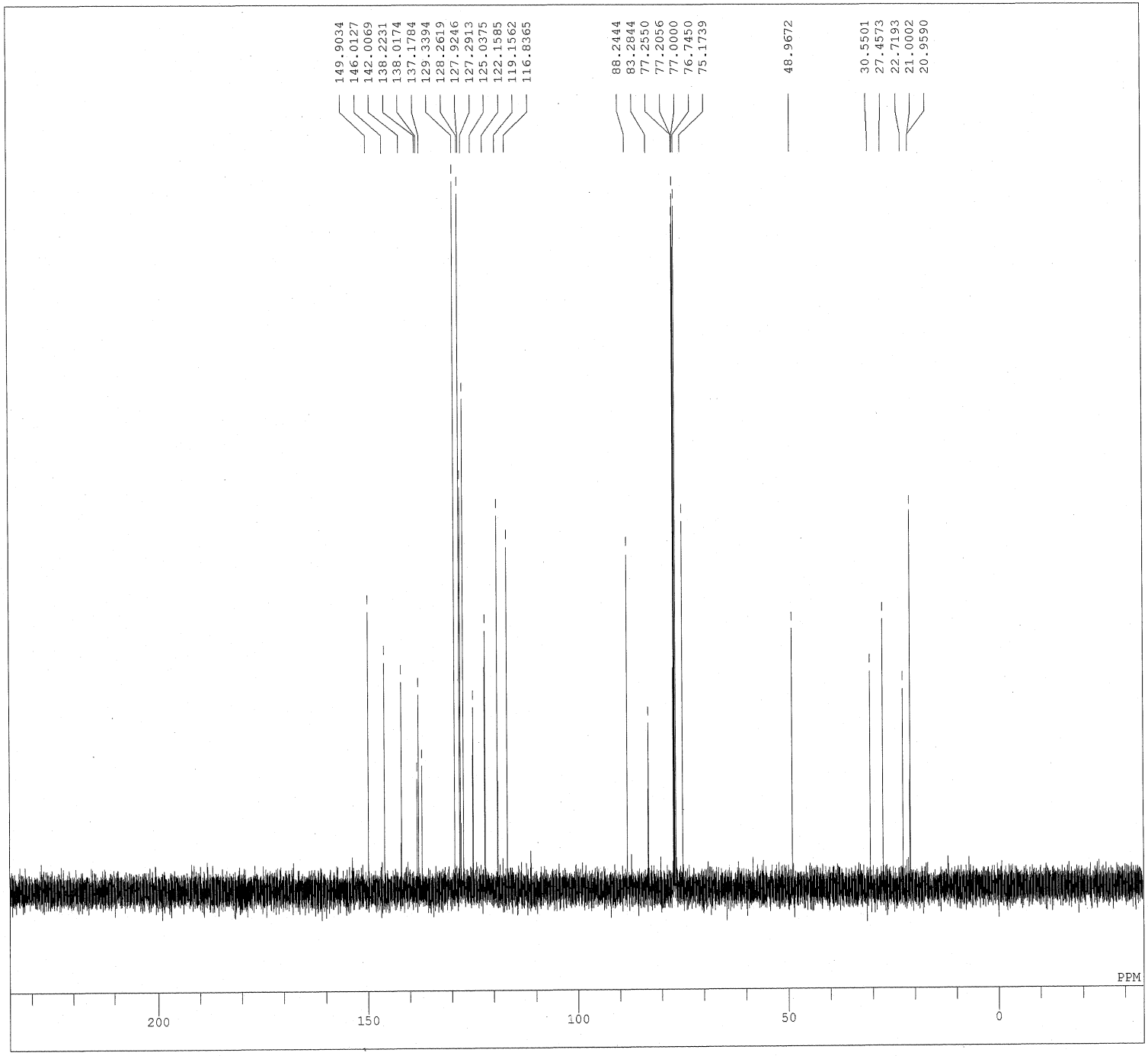
Date : Fri Dec 18 20:10:16 2009

FileName	:	.LoadingFID.nmdata
Comment	:	1H Line
SliceHistory	:	
EXMODE	:	bcm
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	33898.3 Hz
FILTR	:	16950 Hz
DELAY	:	11.8 usec
DEADT	:	10.0 usec
INTVL	:	29.5 usec
TIMES	:	12800 times
DUMMY	:	1 times
PD	:	2.0333 sec
ACQTM	:	966.6560 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	1.03 Hz
PW1	:	5.50 usec
OBNUC	:	13C
OBFRQ	:	125.65 MHz
OBSET	:	127958.00 Hz
RGAIN	:	30
IRNUC	:	1H
IRFRQ	:	500.00 MHz
IRSET	:	
IRRPW	:	
IRRNS	:	
SCANS	:	s
SLVNT	:	
SPINNING	:	
TEMP	:	

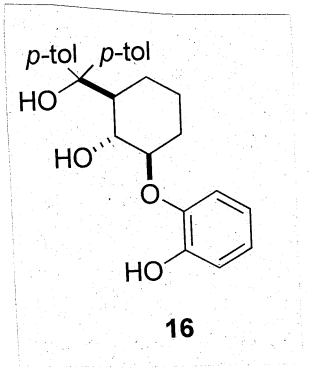


3

ptoloh

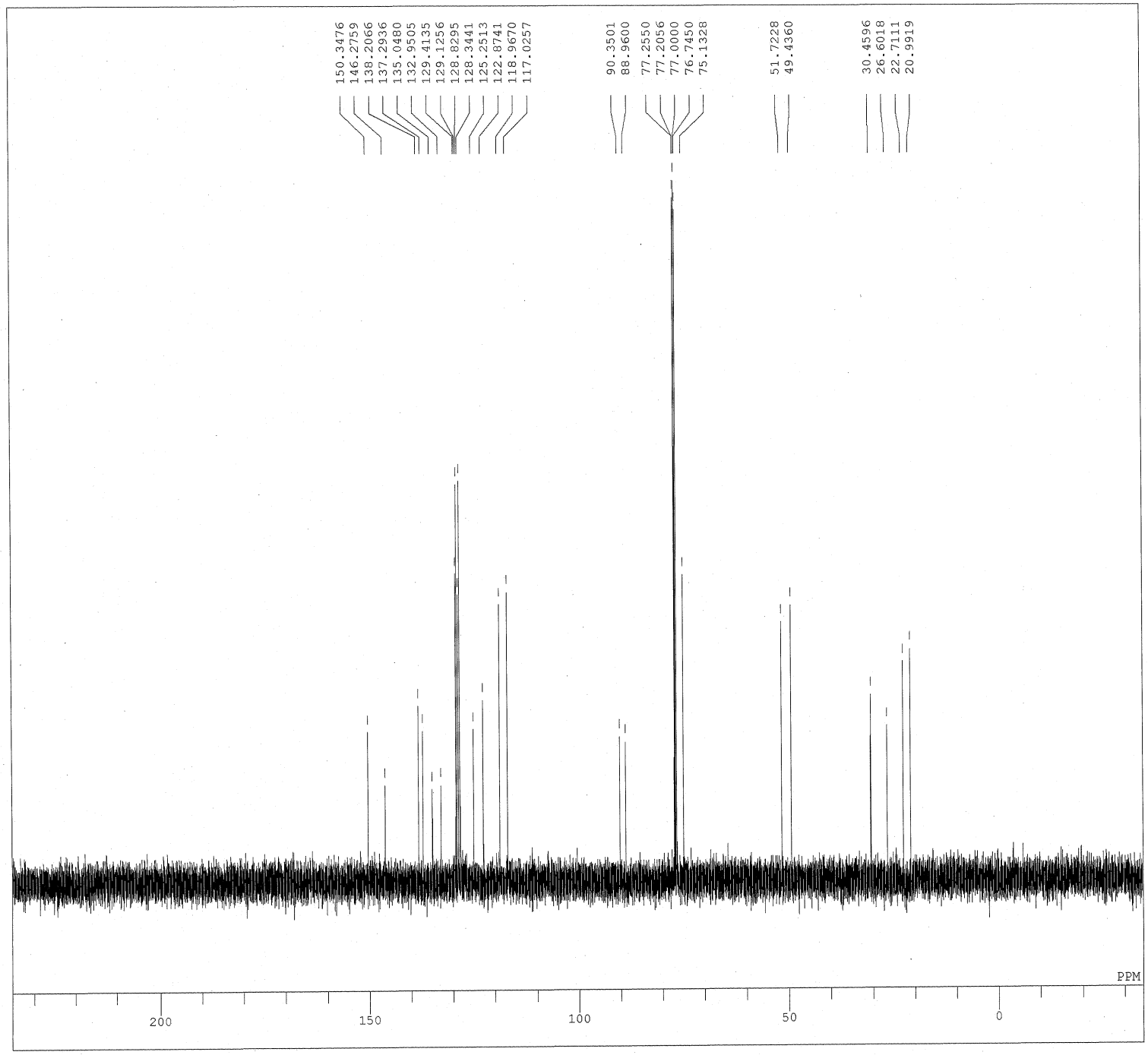



```
DFILE   savedata06.nmdata
COMNT   ptoloh
DATIM   Thu Apr 15 16:39:02 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS            116
ACQTM          0.9667 sec
PD             2.0333 sec
PW1              5.50 usec
IRNUC   1H
CTEMP           26.1 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             30
```

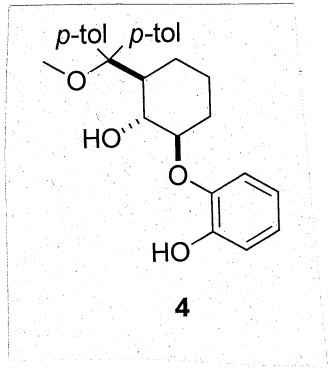


16

ptolmecarb

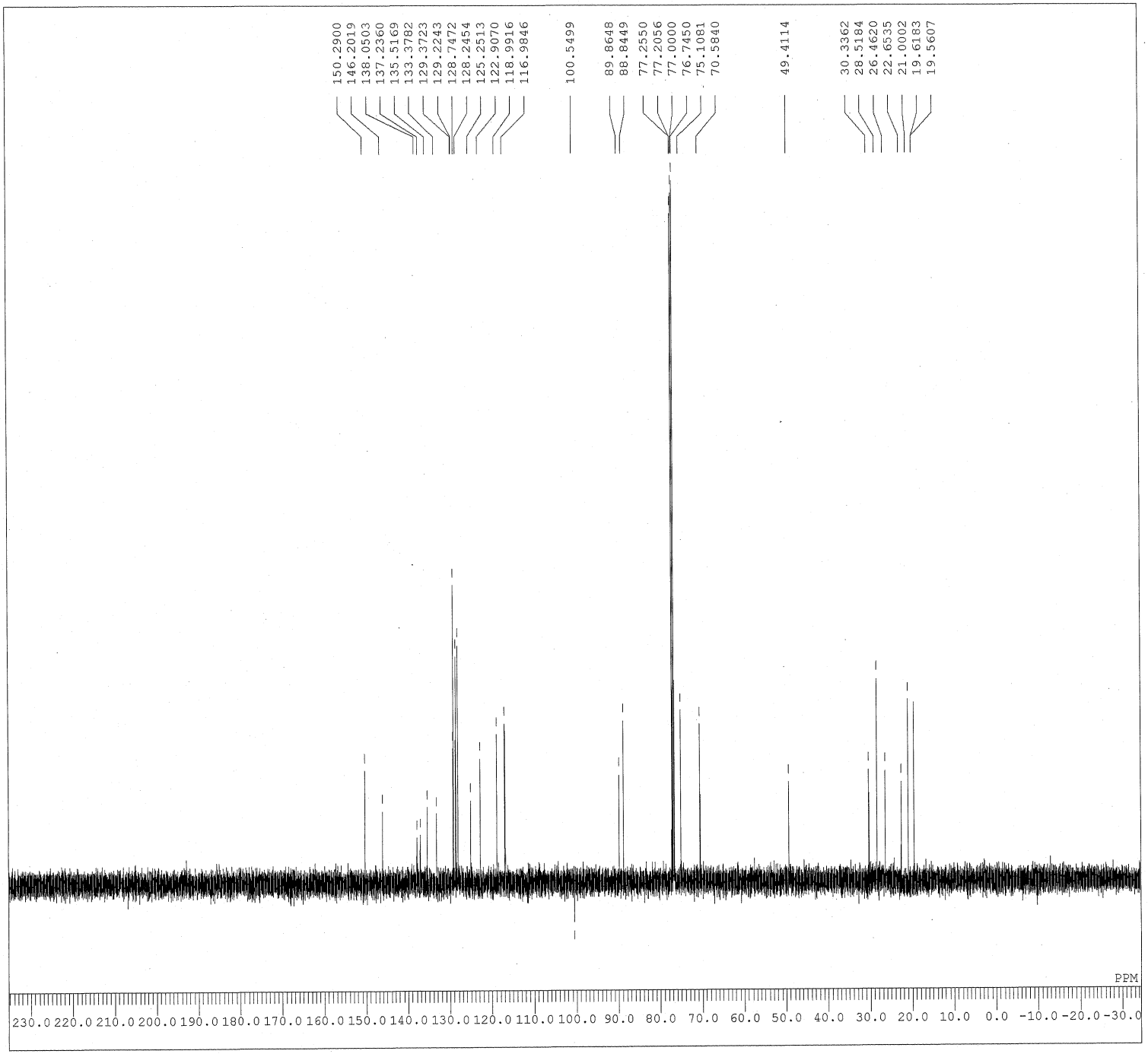



```
DFILE   savedata04.nmdata
COMNT   ptolmecarb
DATIM   Thu Apr 15 16:27:06 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS             86
ACQTM          0.9667 sec
PD             2.0333 sec
PW1              5.50 usec
IRNUC   1H
CTEMP            26.1 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.12 Hz
RGAIN              30
```

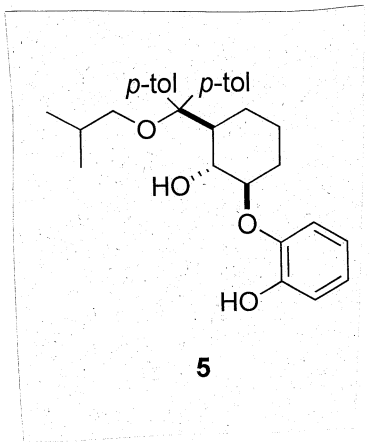


4

ptolibu

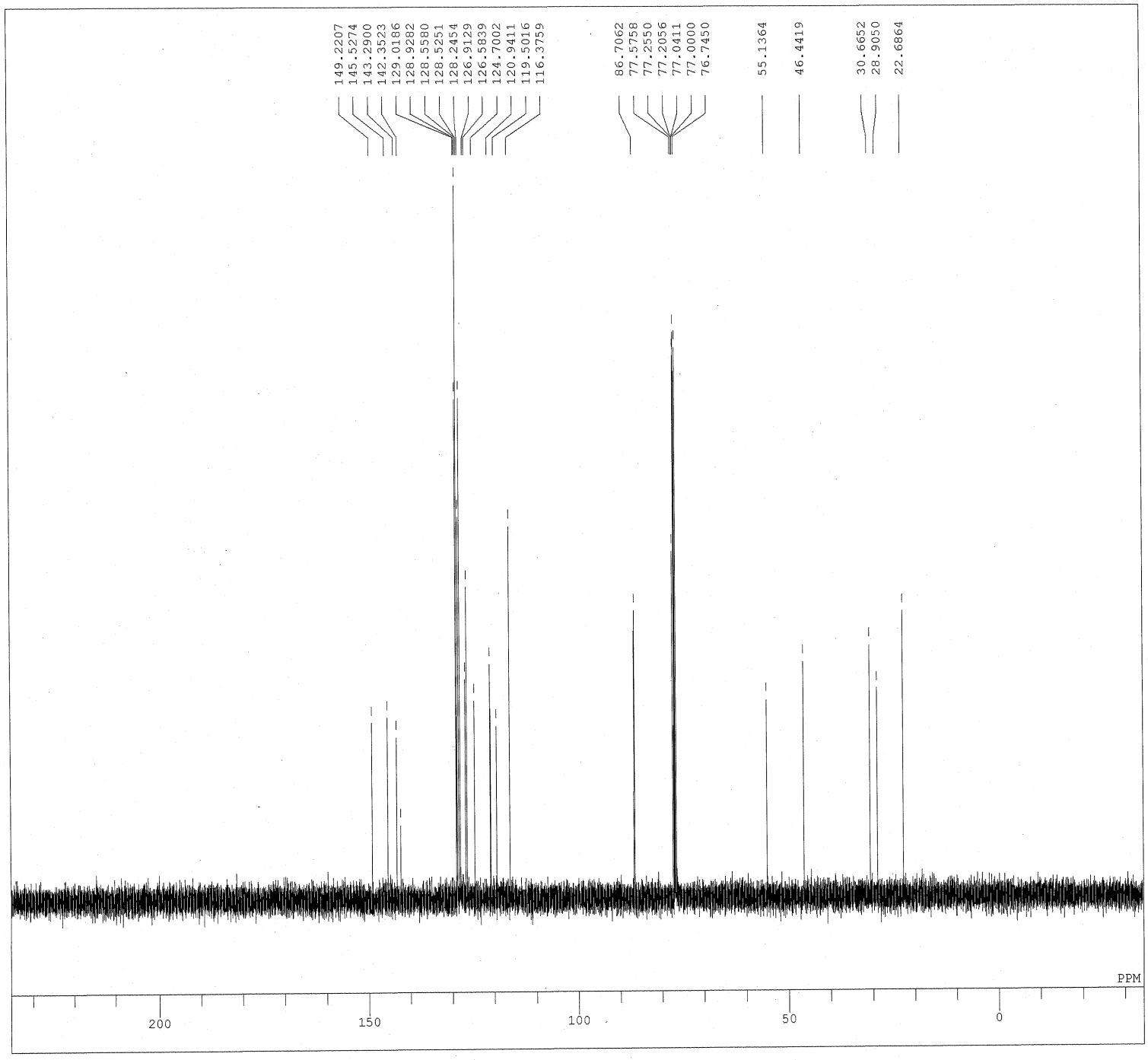


DFILE	savedata02.nmdata
COMNT	ptolibu
DATIM	Thu Apr 15 16:04:27 2010
OBNUC	13C
EXMOD	bcm
OBFRQ	125.65 MHz
OBSET	120.00 KHz
OBFIN	7958.00 Hz
POINT	32768
FREQU	33898.30 Hz
SCANS	230
ACQTM	0.9667 sec
PD	2.0333 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	26.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	30

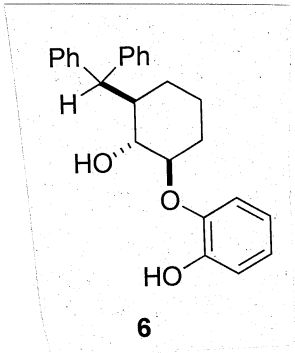


5

hcarb

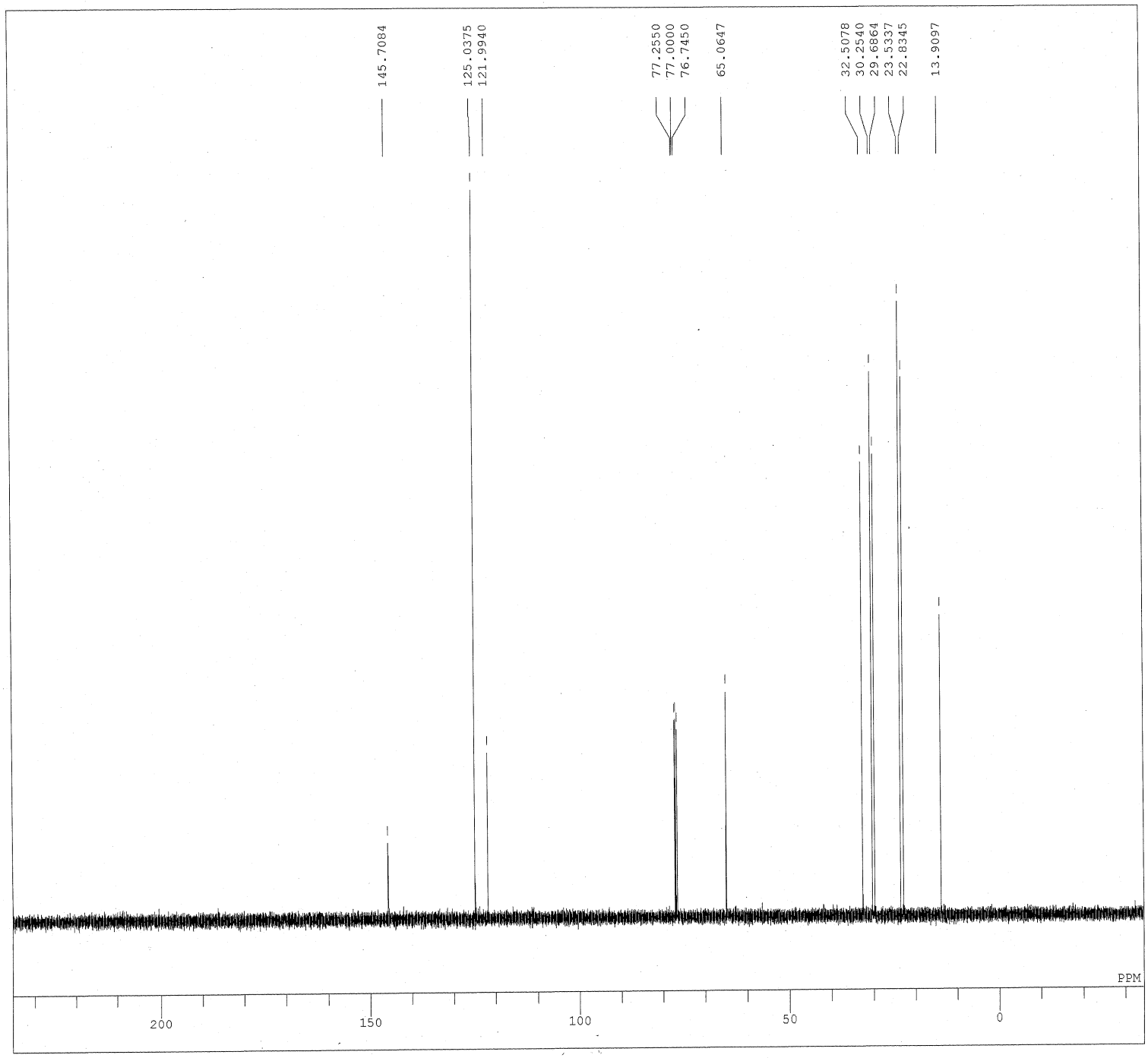



```
DFILE   savedata12.nmdata
COMNT   hcarb
DATIM   Thu Apr 15 17:44:09 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS            116
ACQTM          0.9667 sec
PD             2.0333 sec
PW1              5.50 usec
IRNUC   1H
CTEMP           26.4 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             30
```

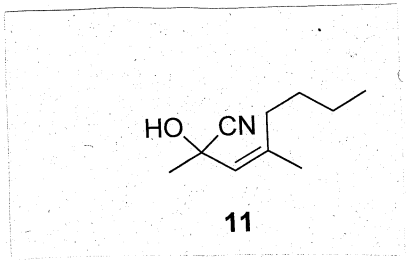


6

cyanohydrine

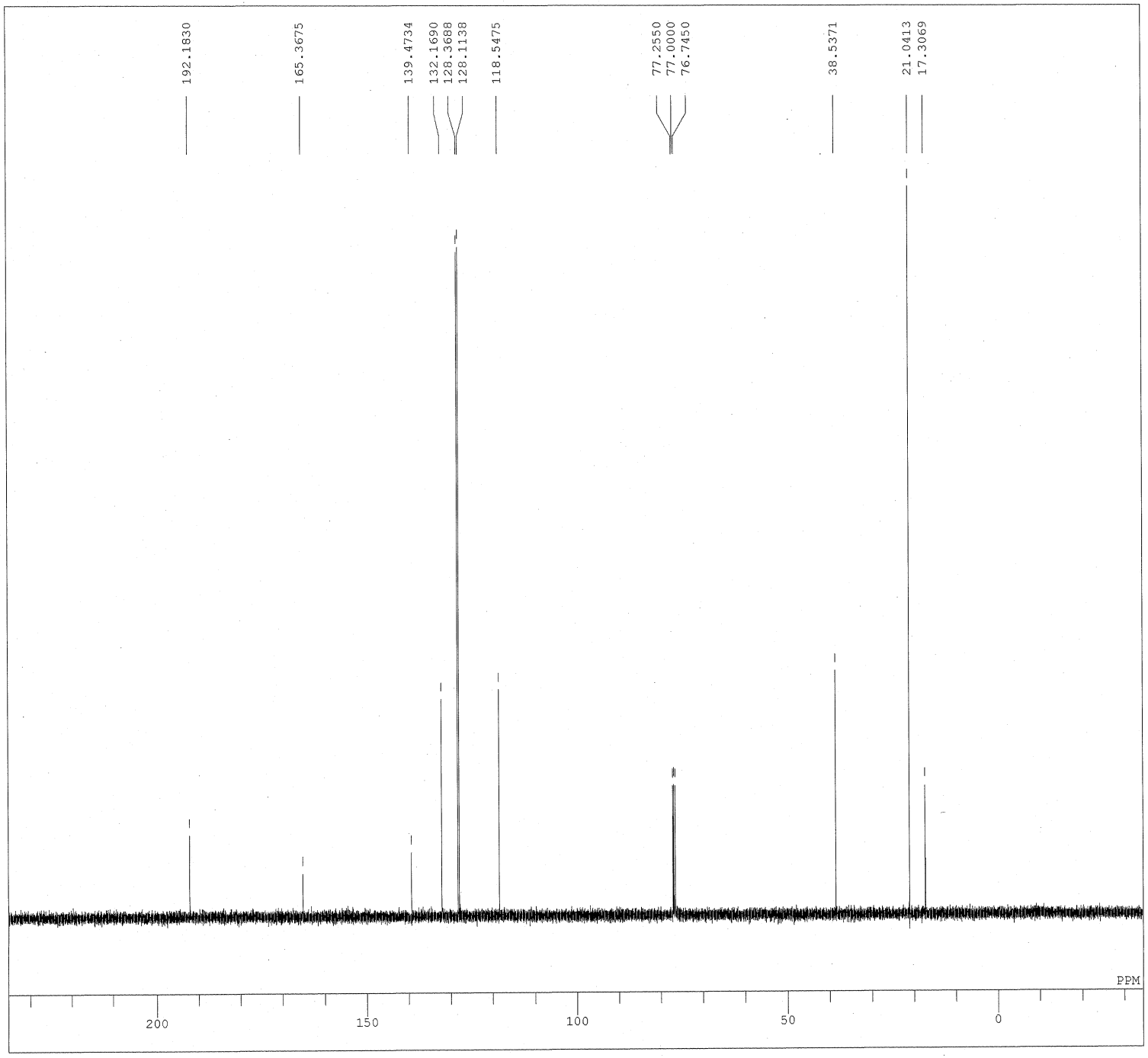



```
DFILE   savedata6.nmdata
COMNT   cyanohydrine
DATIM   Fri Apr 16 09:29:33 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS             63
ACQTM          0.9667 sec
PD             2.0333 sec
PW1              5.50 usec
IRNUC   1H
CTEMP            25.9 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.12 Hz
RGAIN              30
```

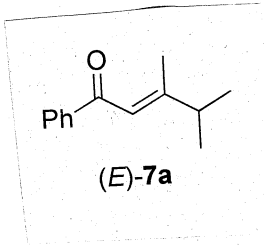


11

phkiprtrans

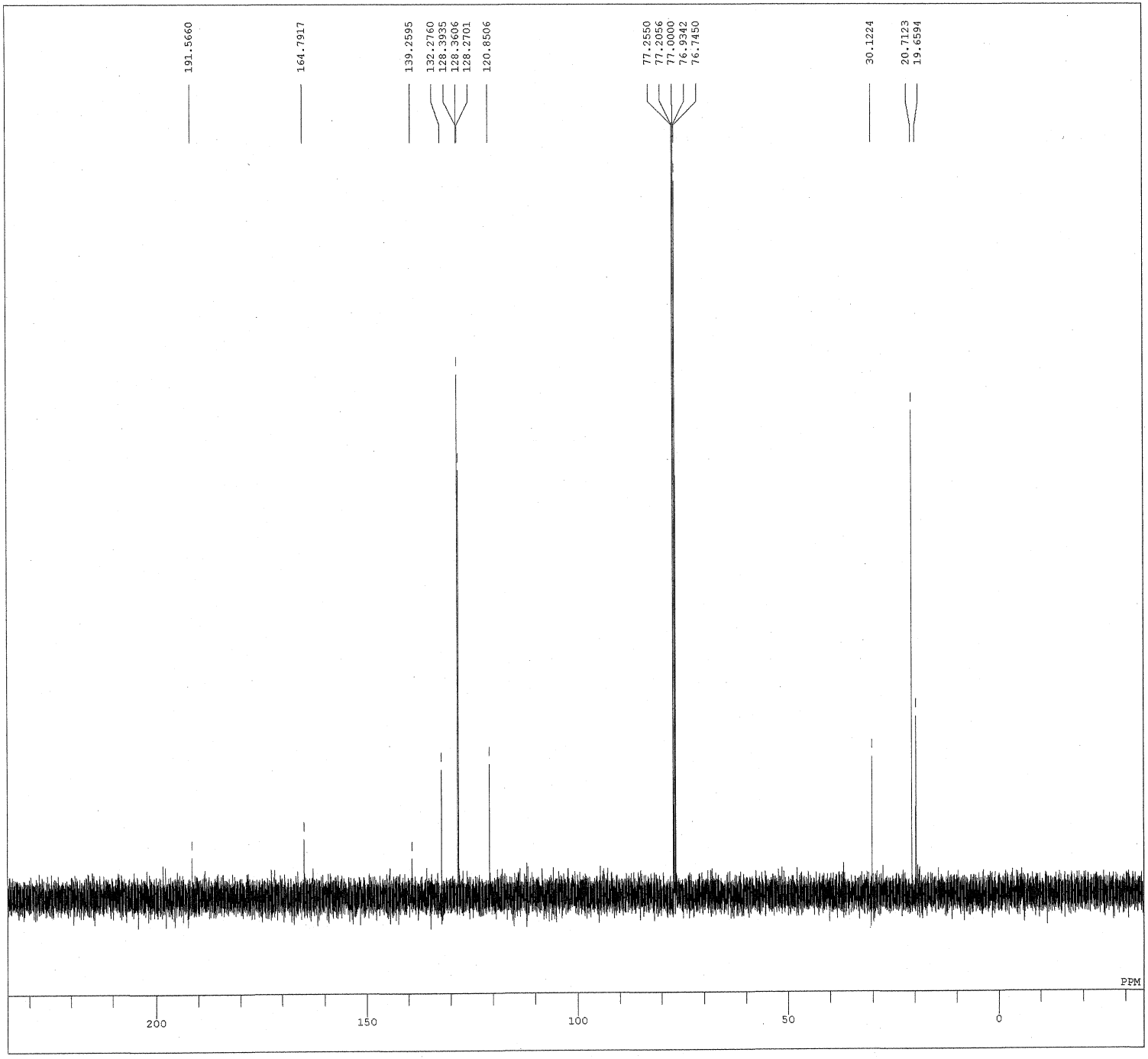



```
DFILE   savedata12.nmdata
COMNT   phkiprtrans
DATIM   Sat Apr 17 10:18:52 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS             55
ACQTM          0.9667 sec
PD             2.0333 sec
PW1              5.50 usec
IRNUC   1H
CTEMP            26.3 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.12 Hz
RGAIN              30
```

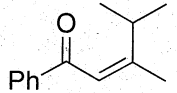


(*E*)-**7a**

phklpcarb

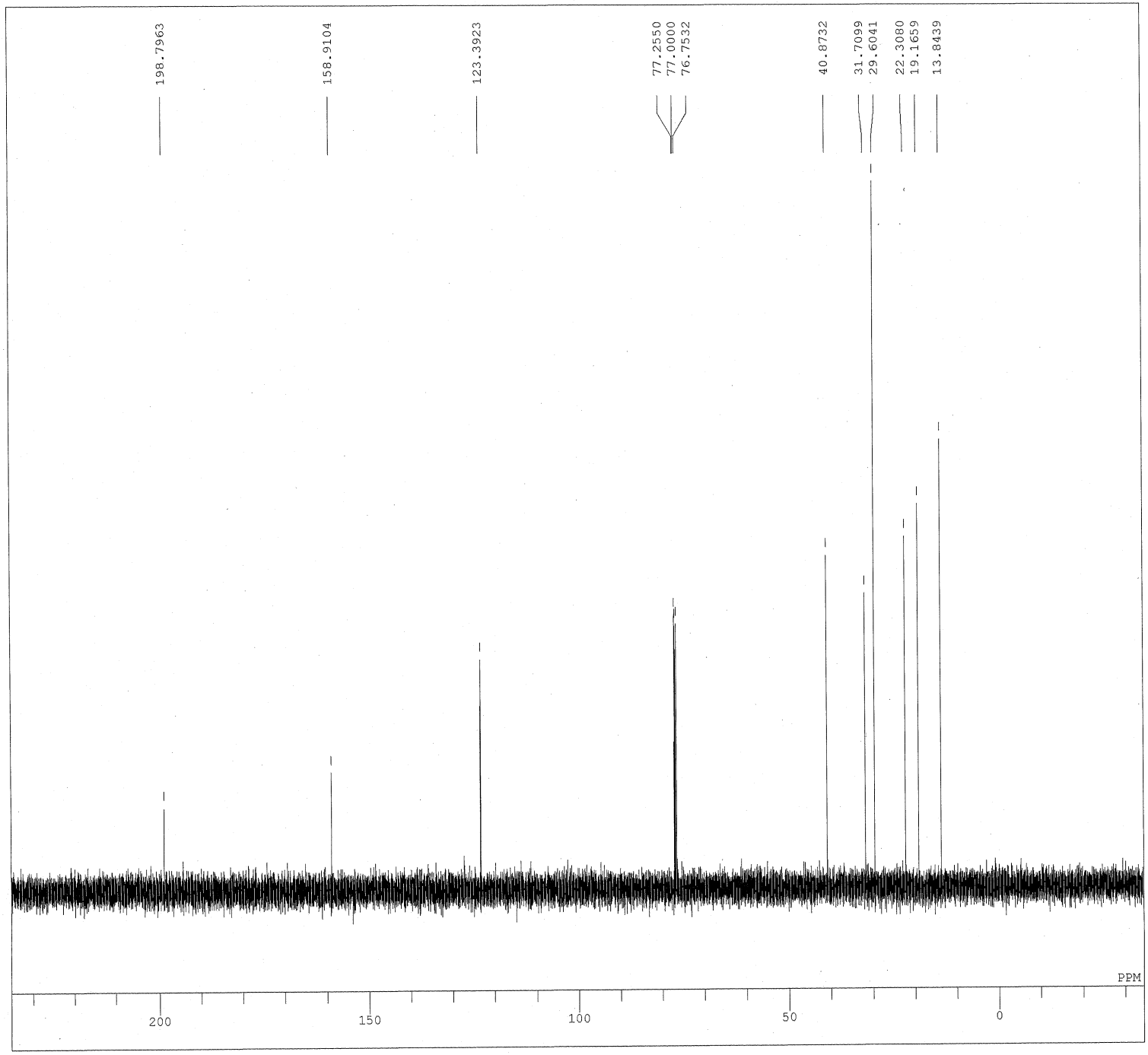



```
DFILE  savedata04.nmdata
COMNT  phklpcarb
DATIM  Tue Jan 12 14:03:29 2010
OBNUC  13C
EXMOD  bcm
OBFRQ        125.65 MHz
OBSET        120.00 KHz
OBFIN       7958.00 Hz
POINT         32768
FREQU      33898.30 Hz
SCANS          219
ACQTM         0.9667 sec
PD            2.0333 sec
PW1             5.50 usec
IRNUC  1H
CTEMP          25.9 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            30
```

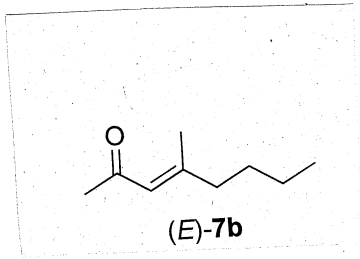


(*Z*)-**7a**

meknbutrans

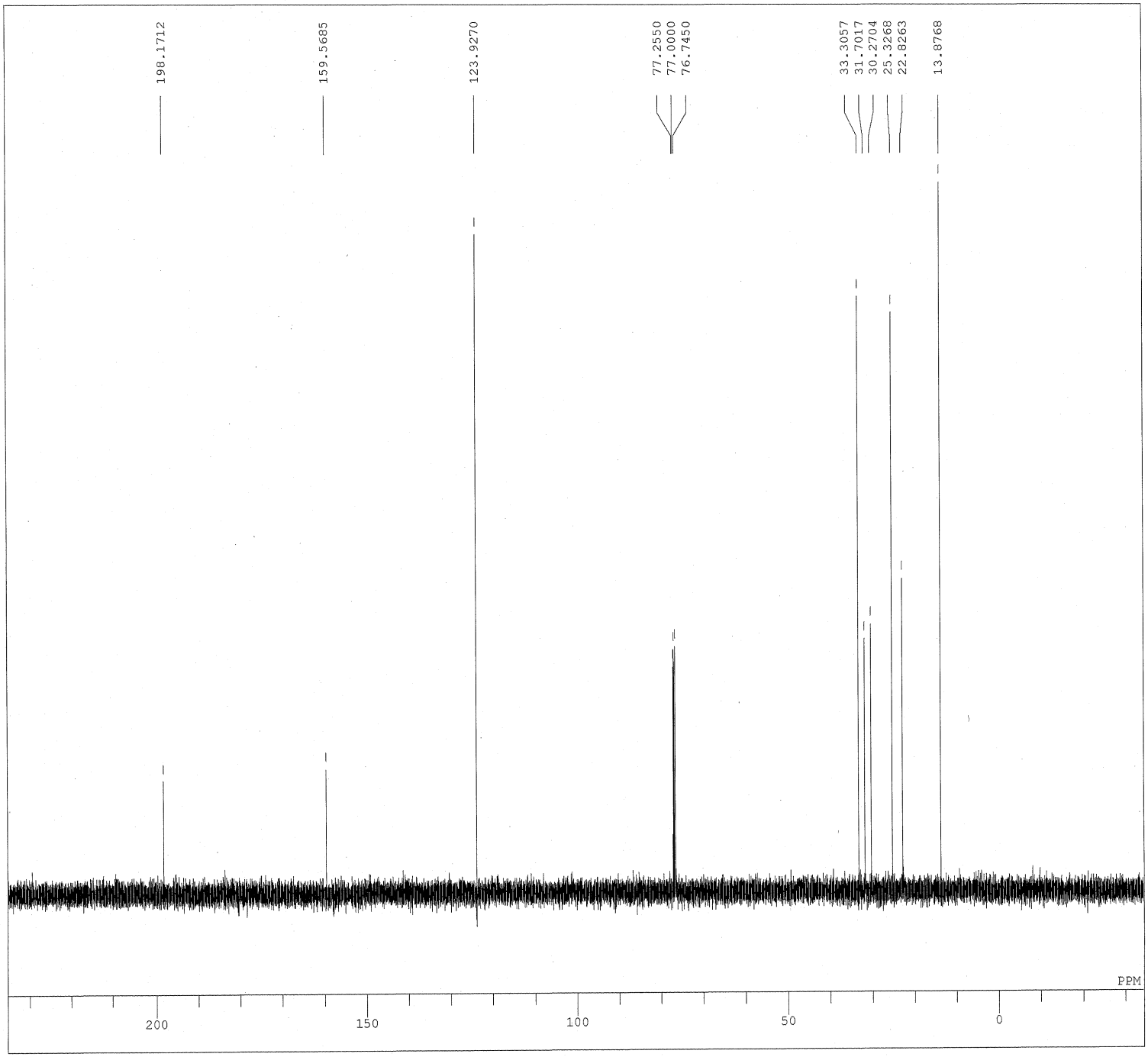


DFILE	savedata02.nmdata
COMNT	meknbutrans
DATIM	Sat Apr 17 09:40:45 2010
OBNUC	13C
EXMOD	bcm
OBFRQ	125.65 MHz
OBSET	120.00 KHz
OBFIN	7958.00 Hz
POINT	32768
FREQU	33898.30 Hz
SCANS	12
ACQTM	0.9667 sec
PD	2.0333 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	24.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	30

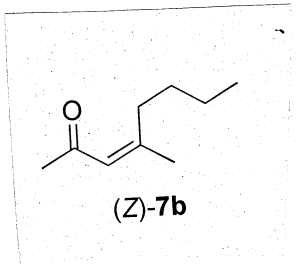


(*E*)-**7b**

meknbucis

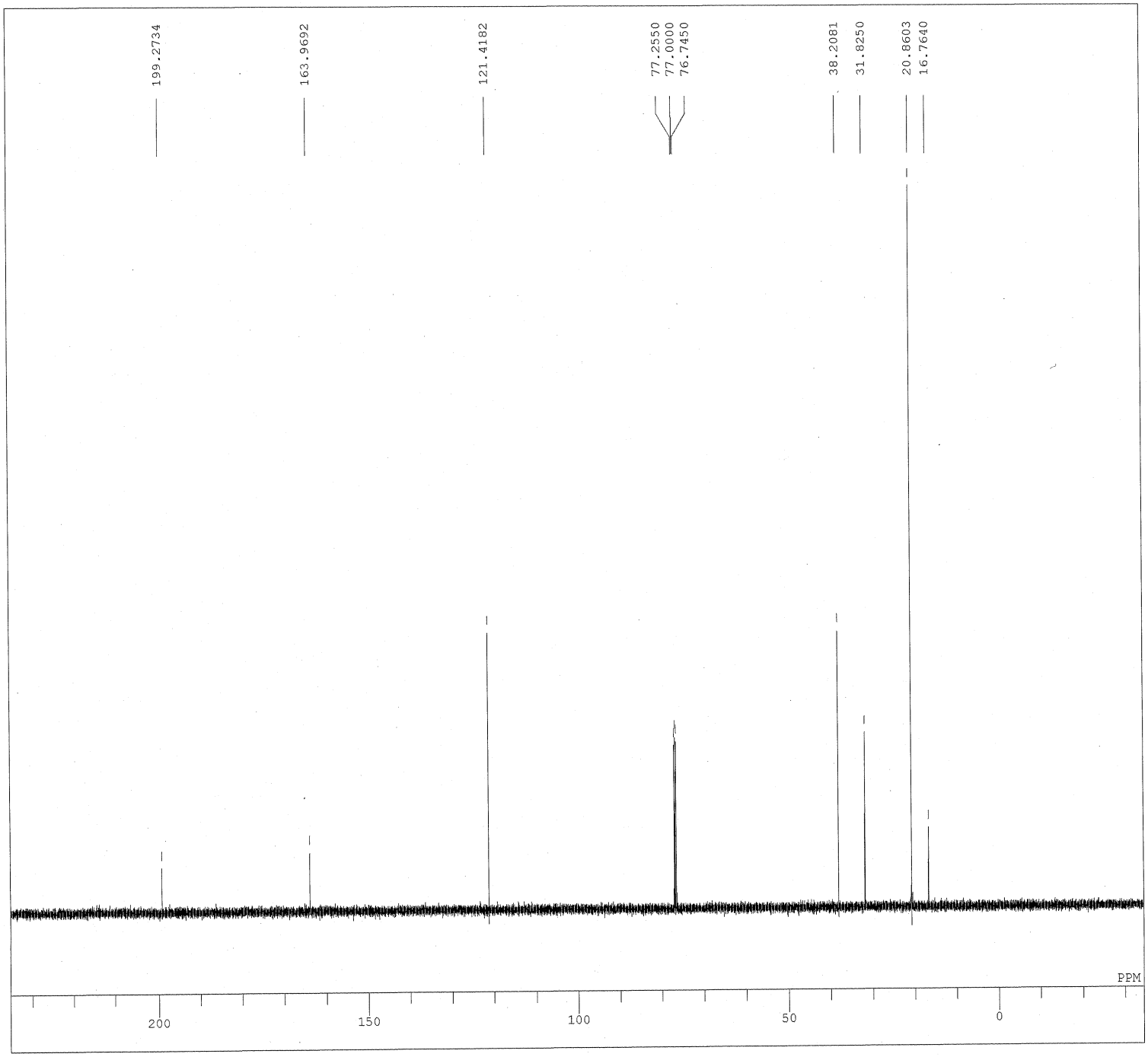


DFILE	savedata04.als	
COMNT	meknbucis	
DATIM	Sat Apr 17 09:46:48 2010	
OBNUC	13C	
EXMOD	bcm	
OBFRQ	125.65	MHz
OBSET	120.00	KHz
OBFIN	7958.00	Hz
POINT	32768	
FREQU	33898.30	Hz
SCANS	20	
ACQTM	0.9667	sec
PD	2.0333	sec
PW1	5.50	usec
IRNUC	1H	
CTEMP	25.5	c
SLVNT	CDCL3	
EXREF	77.00	ppm
BF	0.12	Hz
RGAIN	30	

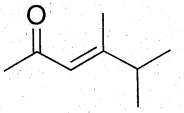


(Z)-**7b**

mekiprtrans

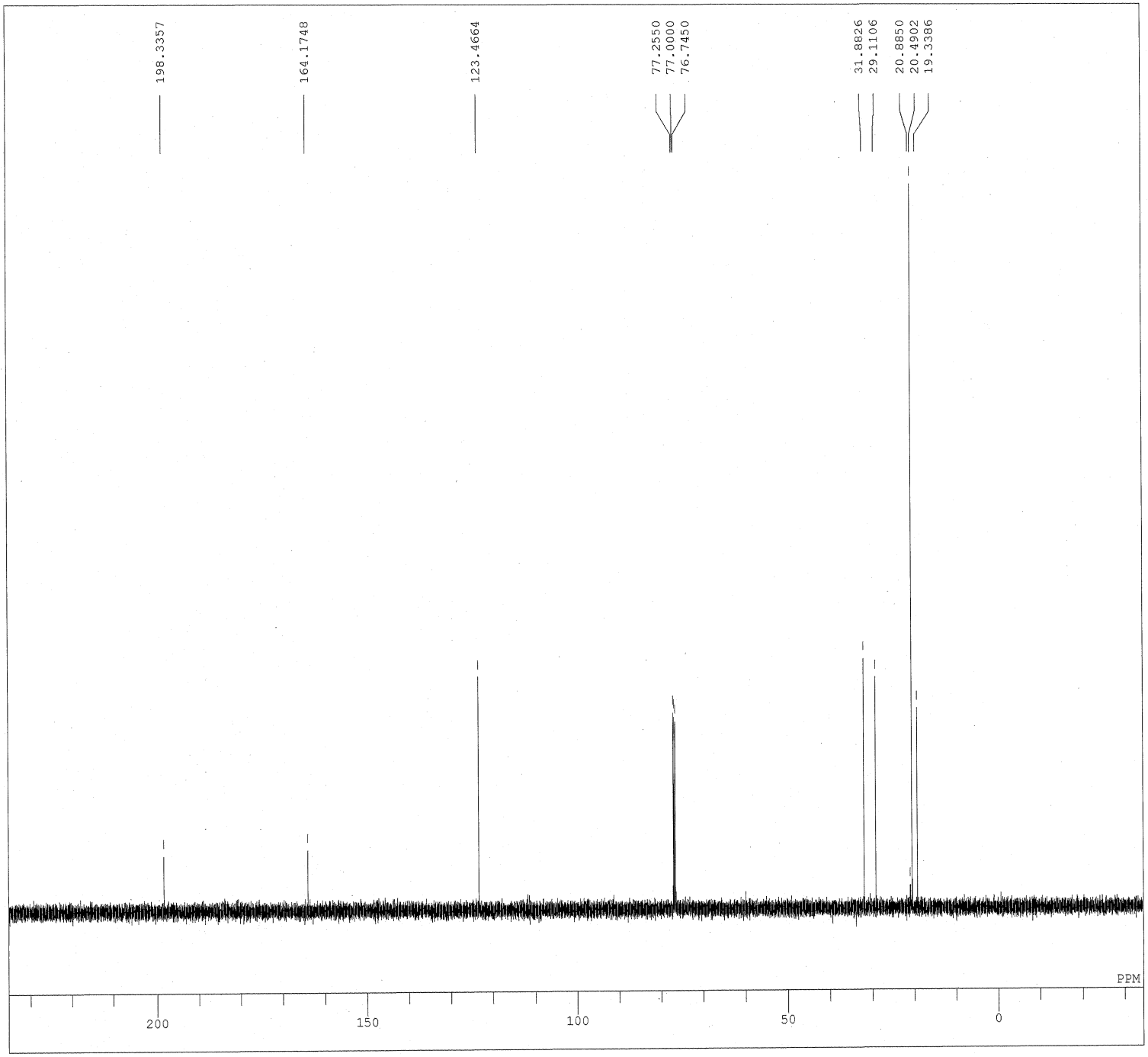



```
DFILE   savedata06.nmdata
COMNT   mekiprtrans
DATIM   Sat Apr 17 09:55:39 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS             92
ACQTM          0.9667 sec
PD             2.0333 sec
PW1              5.50 usec
IRNUC   1H
CTEMP            25.8 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.12 Hz
RGAIN              30
```

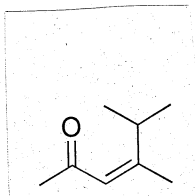


(*E*)-**7c**

mekiprcis

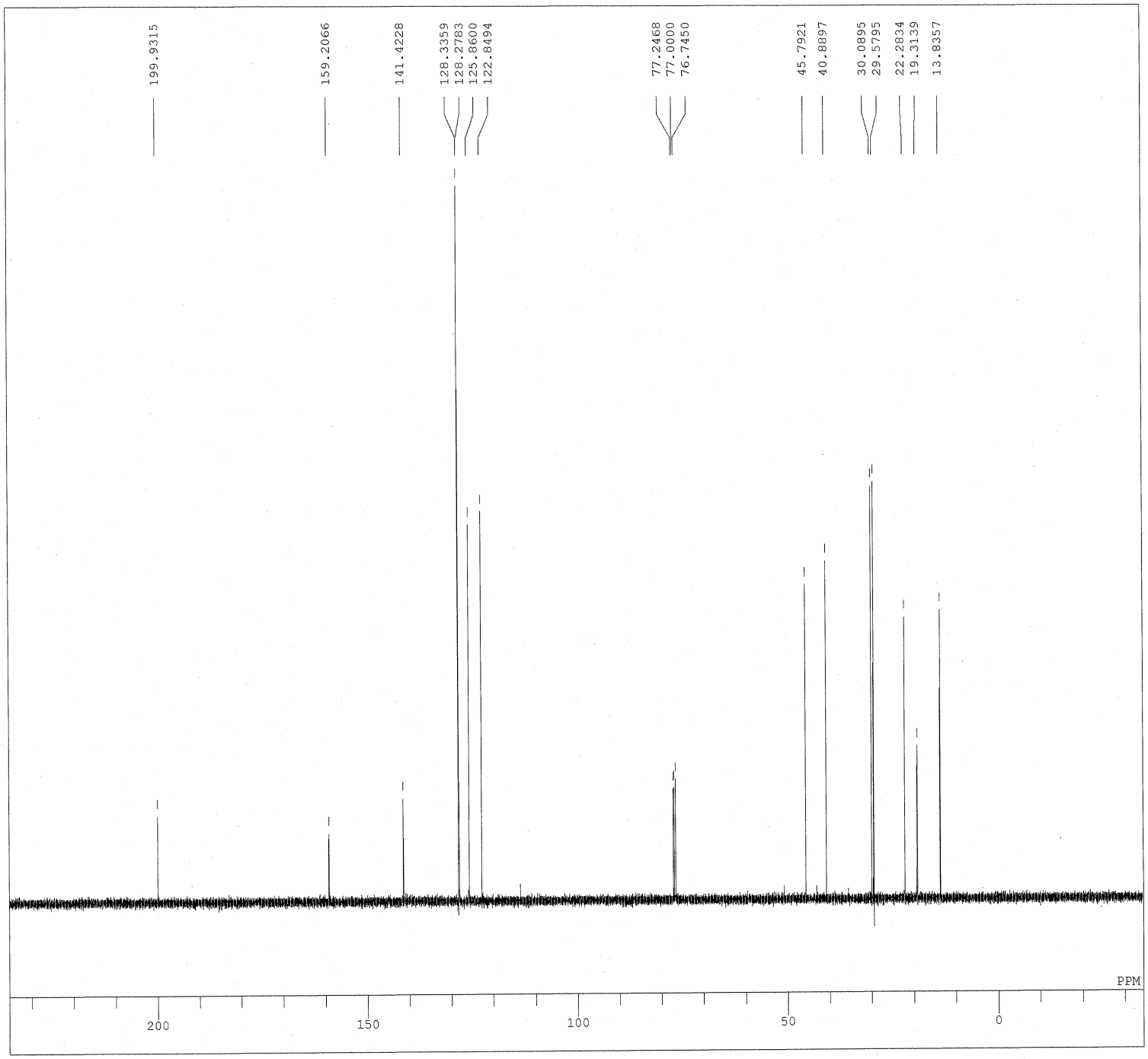



```
DFILE   savedata08.nmdata
COMNT   mekiprcis
DATIM   Sat Apr 17 10:02:31 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS             37
ACQTM          0.9667 sec
PD             2.0333 sec
PW1              5.50 usec
IRNUC   1H
CTEMP           26.1 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             30
```

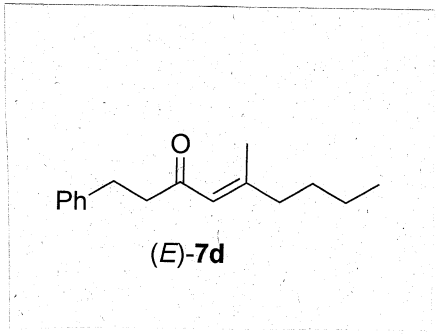


(*Z*)-**7c**

phetktrans

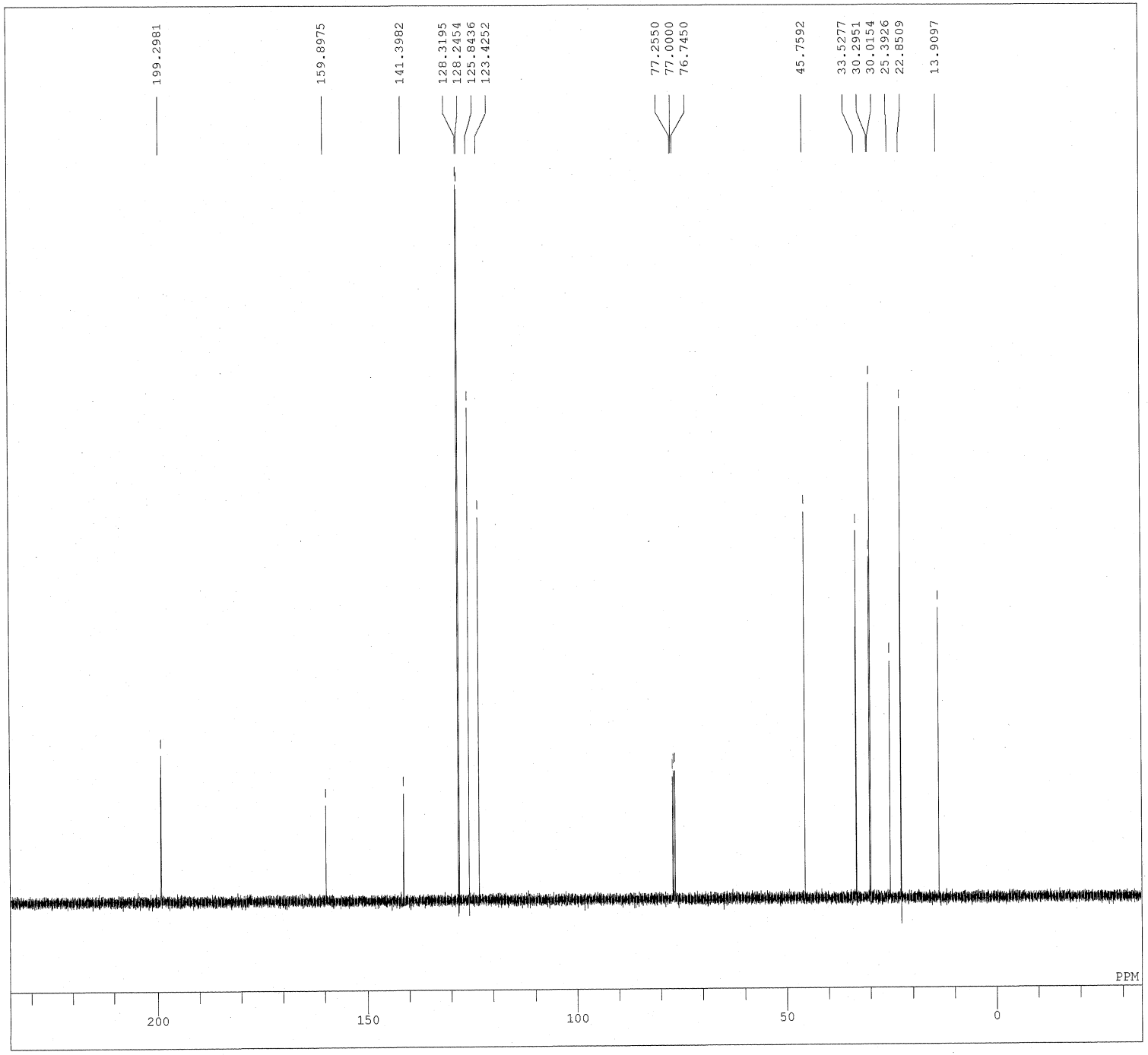


DFILE	savedata23.nmdata	
COMNT	phetktrans	
DATIM	Fri Apr 16 19:32:00 2010	
OBNUC	13C	
EXMOD	bcm	
OBFRQ	125.65	MHz
OBSET	120.00	KHz
OBFIN	7958.00	Hz
POINT	32768	
FREQU	33898.30	Hz
SCANS	52	
ACQTM	0.9667	sec
PD	2.0333	sec
PW1	5.50	usec
IRNUC	1H	
CTEMP	25.1	c
SLVNT	CDCL3	
EXREF	77.00	ppm
BF	0.12	Hz
RGAIN	30	

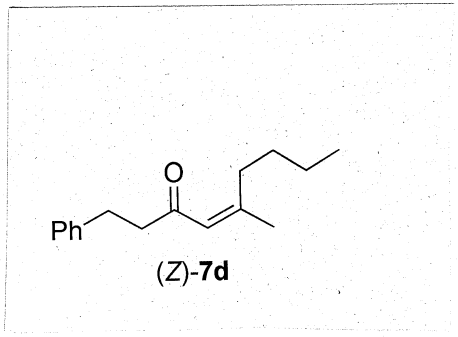


(*E*)-**7d**

phetkcis

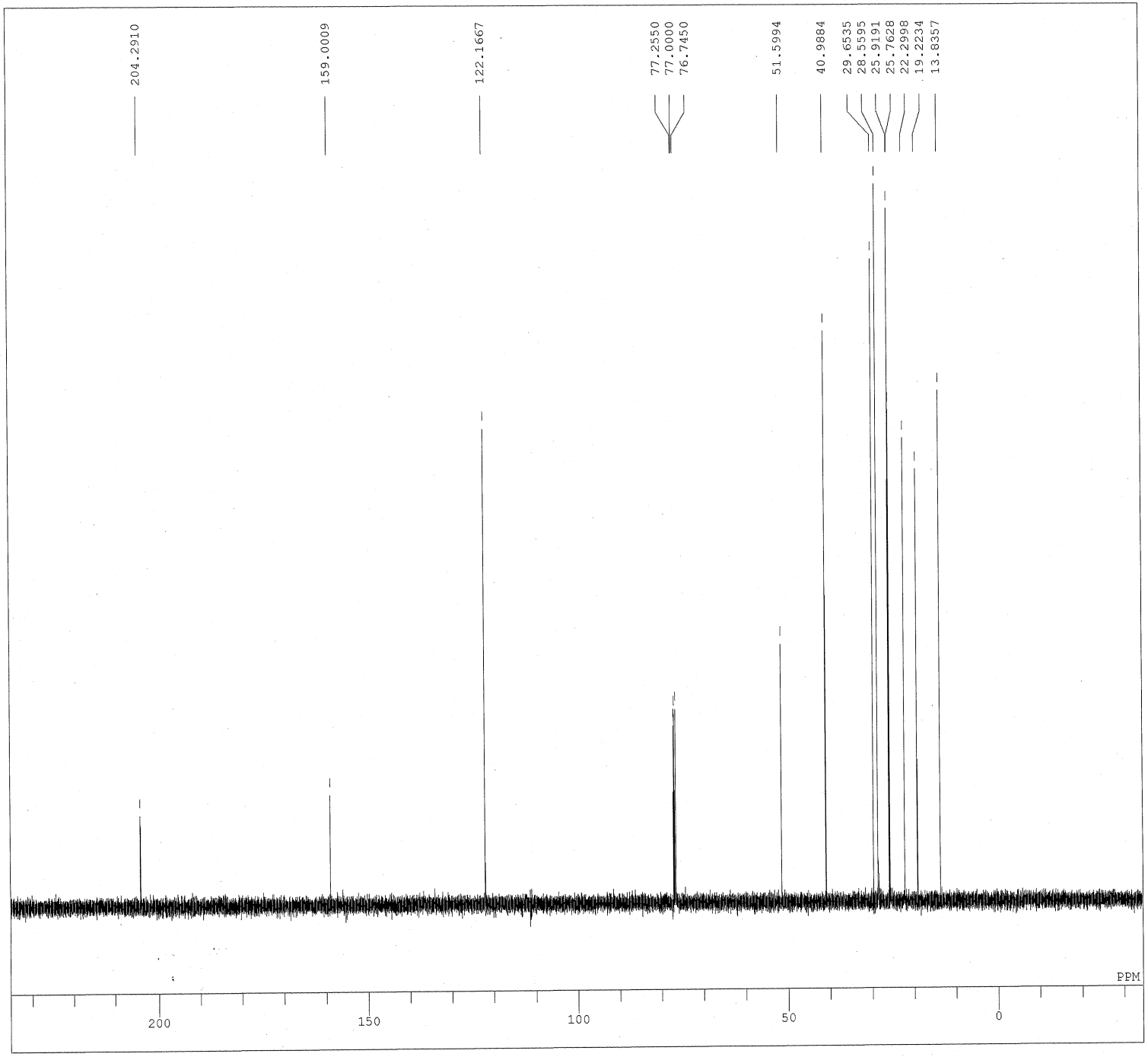



```
DFILE   savedata24.nmdata
COMNT   phetkcis
DATIM   Fri Apr 16 19:35:52 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS             36
ACQTM          0.9667 sec
PD             2.0333 sec
PW1              5.50 usec
IRNUC   1H
CTEMP            25.3 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.12 Hz
RGAIN              30
```

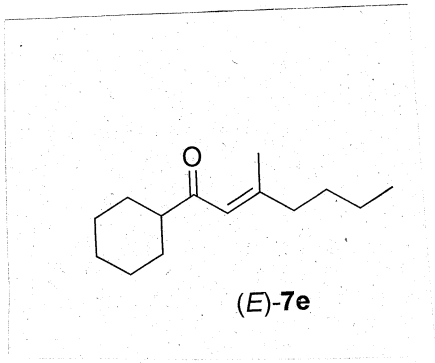


(*Z*)-**7d**

cyktrans

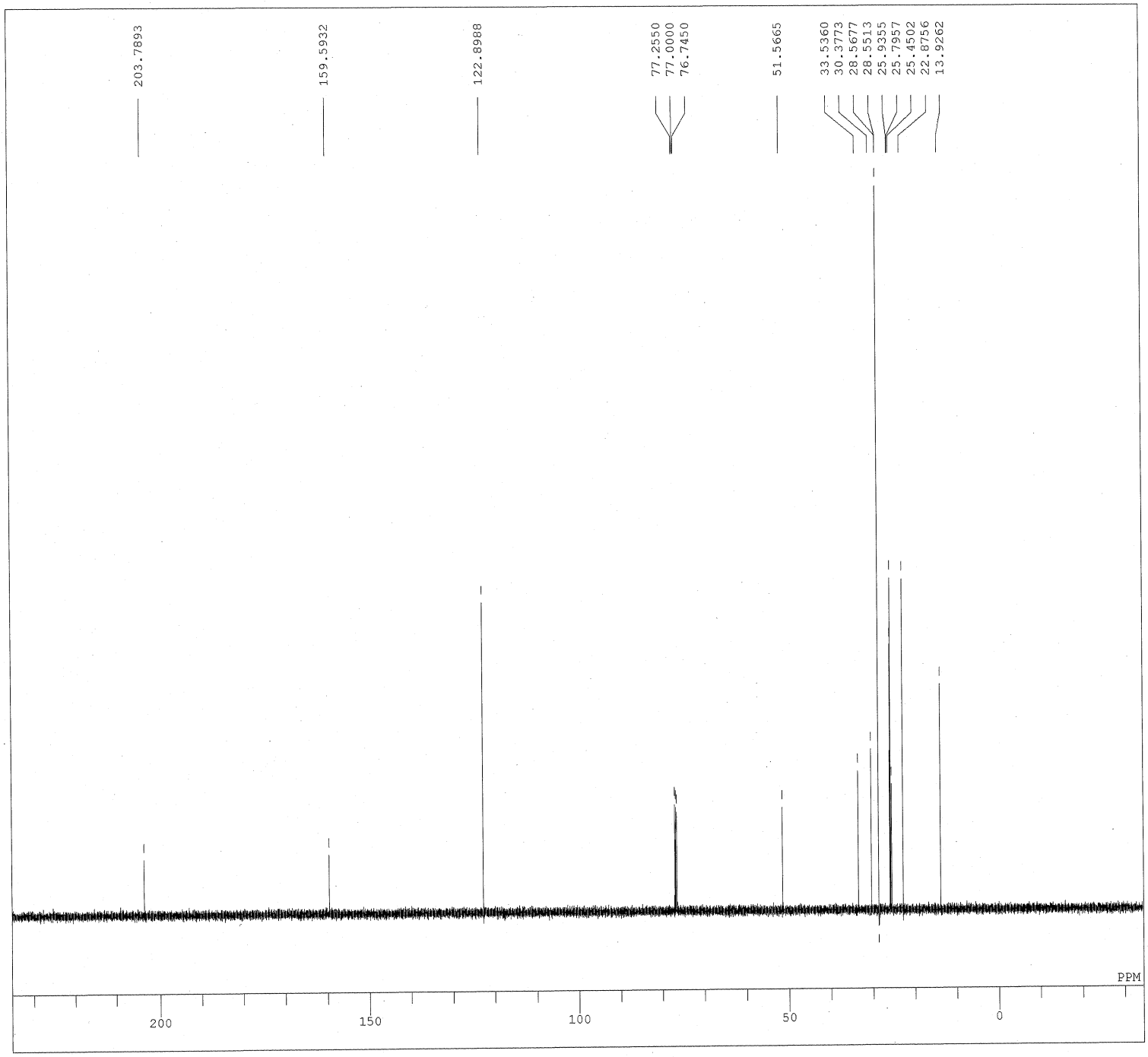



```
DFILE   savedata27.nmdata
COMNT   cyktrans
DATIM   Fri Apr 16 19:47:00 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS             29
ACQTM          0.9667 sec
PD             2.0333 sec
PW1              5.50 usec
IRNUC   1H
CTEMP            25.7 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.12 Hz
RGAIN              30
```

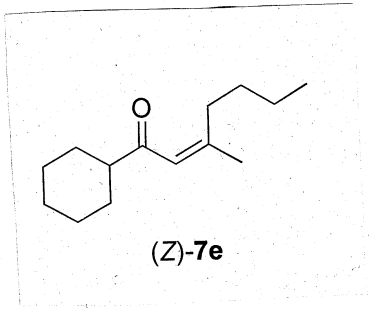


(*E*)-**7e**

cykcis

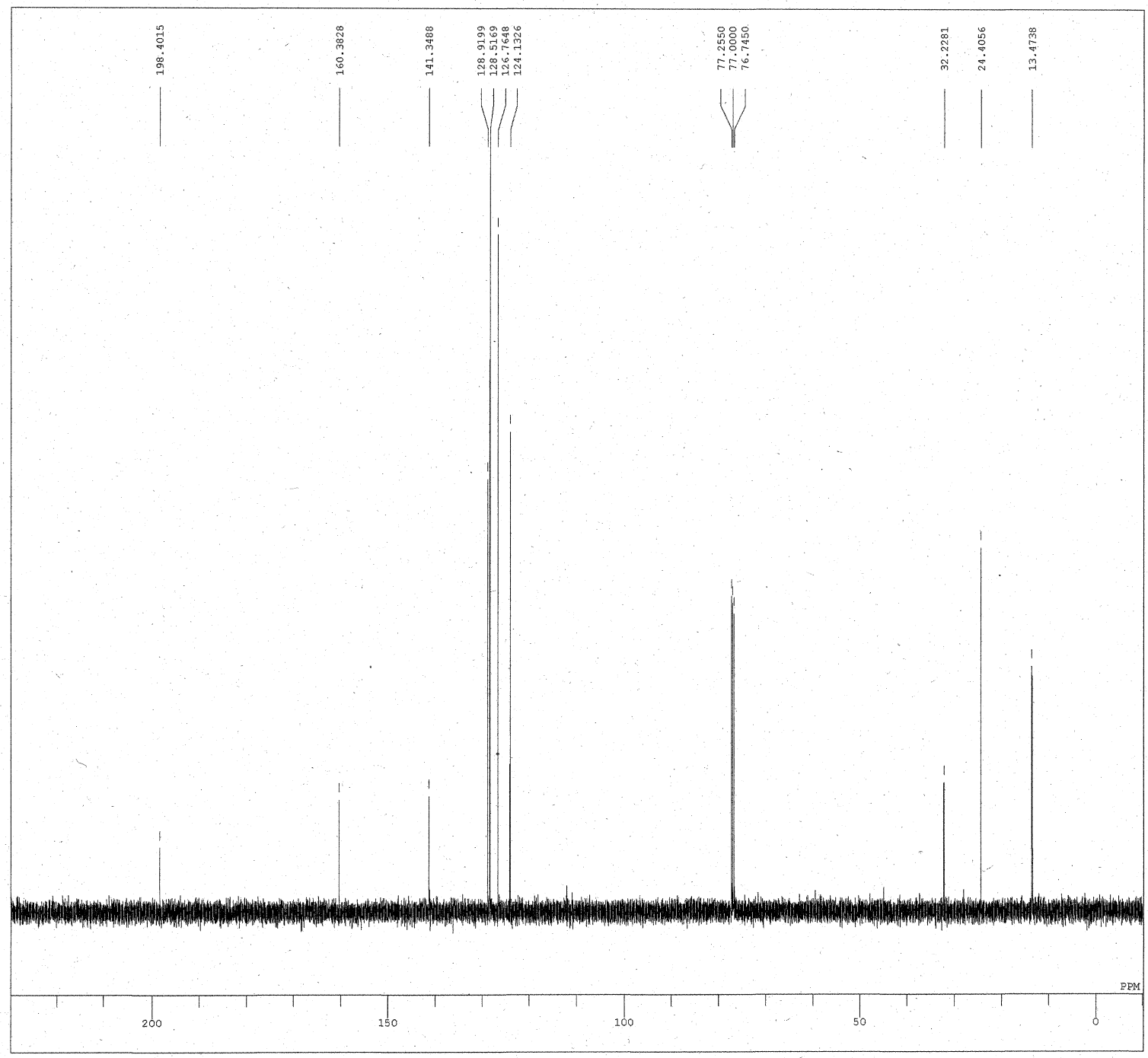



```
DFILE   savedata10.nmdata
COMNT   cykcis
DATIM   Sat Apr 17 10:09:22 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS             35
ACQTM          0.9667 sec
PD             2.0333 sec
PW1              5.50 usec
IRNUC   1H
CTEMP           26.1 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             30
```

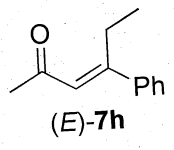


(*Z*)-**7e**

betaphetlpcarb

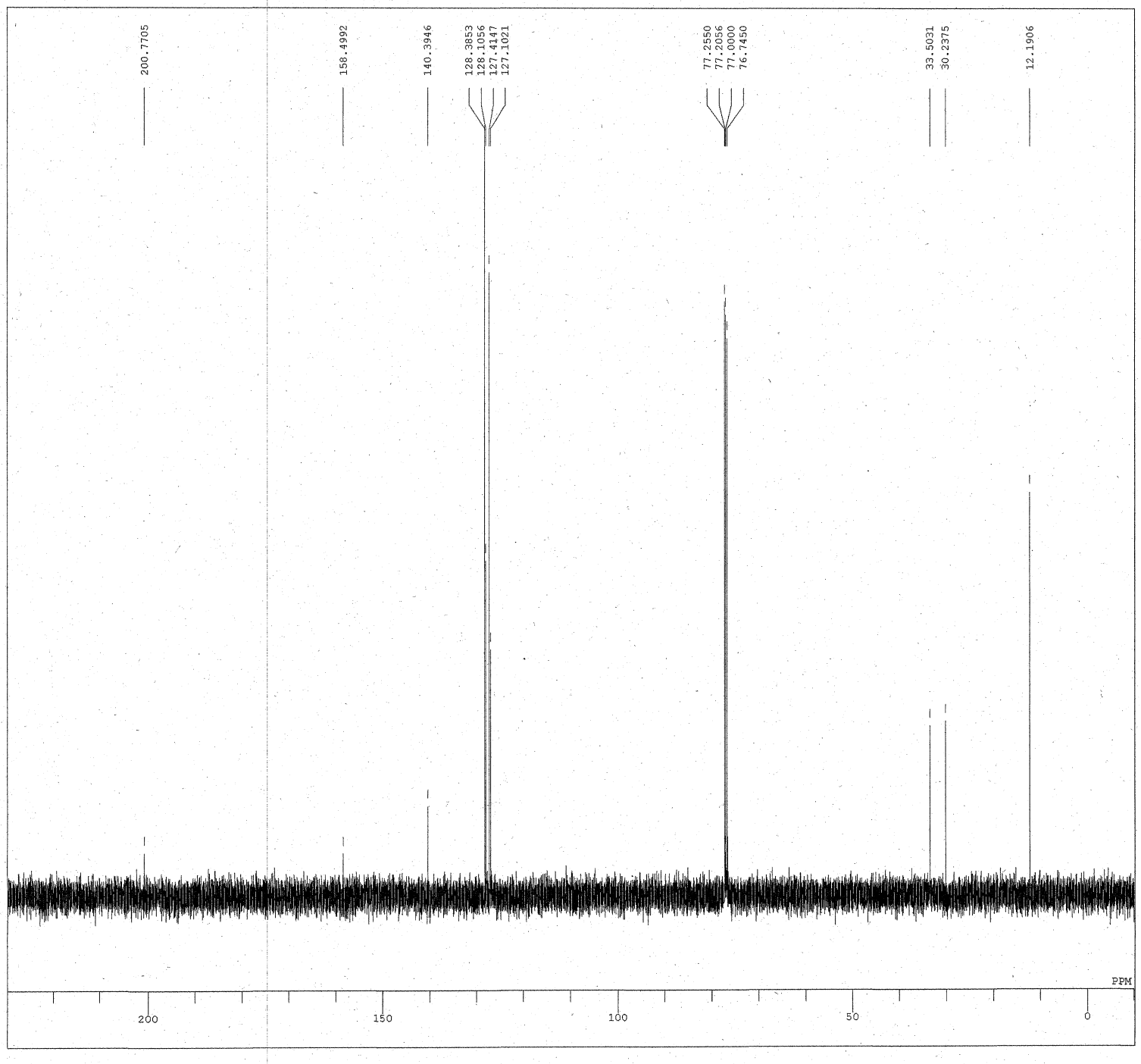



```
DFILE   savedata02.nmdata
COMNT   betaphetlpcarb
DATIM   Mon Jan 11 16:59:20 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS             87
ACQTM          0.9667 sec
PD             2.0333 sec
PW1             5.50 usec
IRNUC   1H
CTEMP           25.4 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.12 Hz
RGAIN              29
```

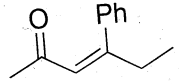


(*E*)-**7h**

betaphetmpcarb

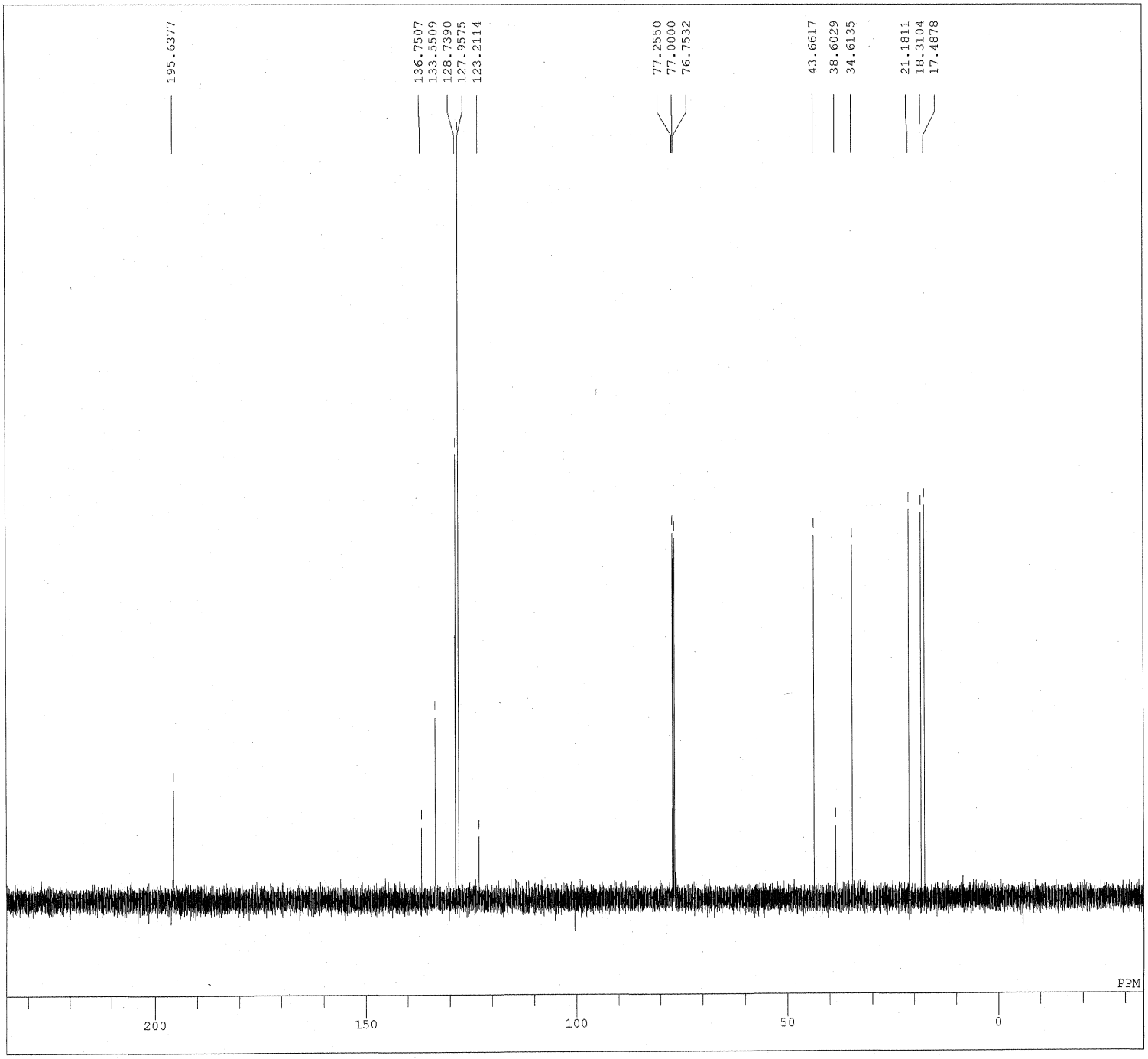



```
DFILE   savedata04.nmdata
COMNT   betaphetmpcarb
DATIM   Mon Jan 11 17:10:51 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS           125
ACQTM          0.9667 sec
PD             2.0333 sec
PW1              5.50 usec
IRNUC   1H
CTEMP           25.7 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             30
```

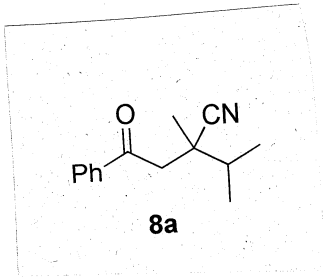


(Z)-**7h**

phipr

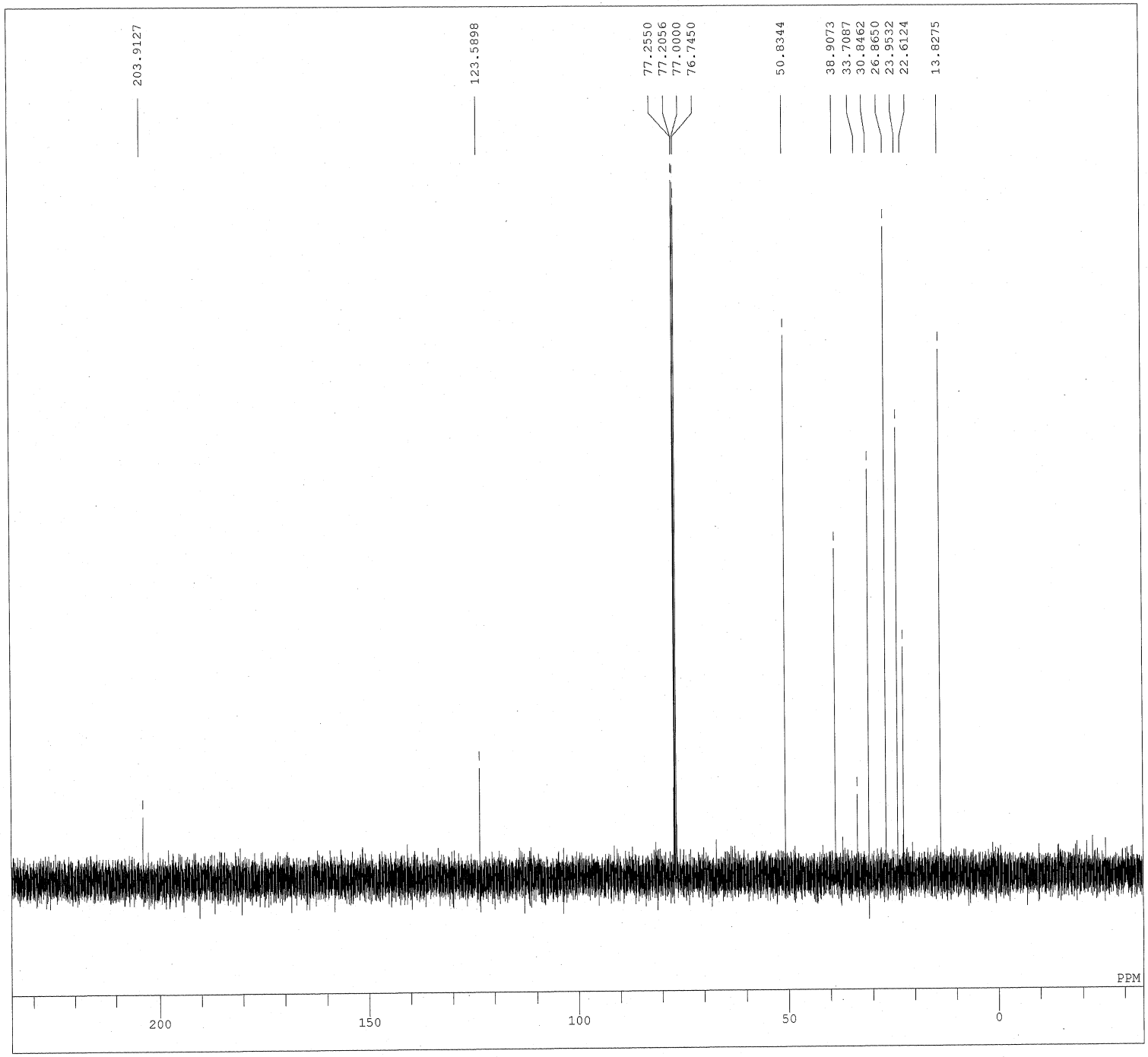



```
DFILE   savedata05.nmdata
COMNT   phipr
DATIM   Sat Feb 13 16:22:31 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS             89
ACQTM          0.9667 sec
PD             2.0333 sec
PW1               5.50 usec
IRNUC   1H
CTEMP            26.2 c
SLVNT   CDCL3
EXREF            77.00 ppm
BF                0.22 Hz
RGAIN               30
```

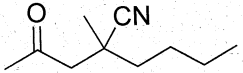


8a

meknbuproduct

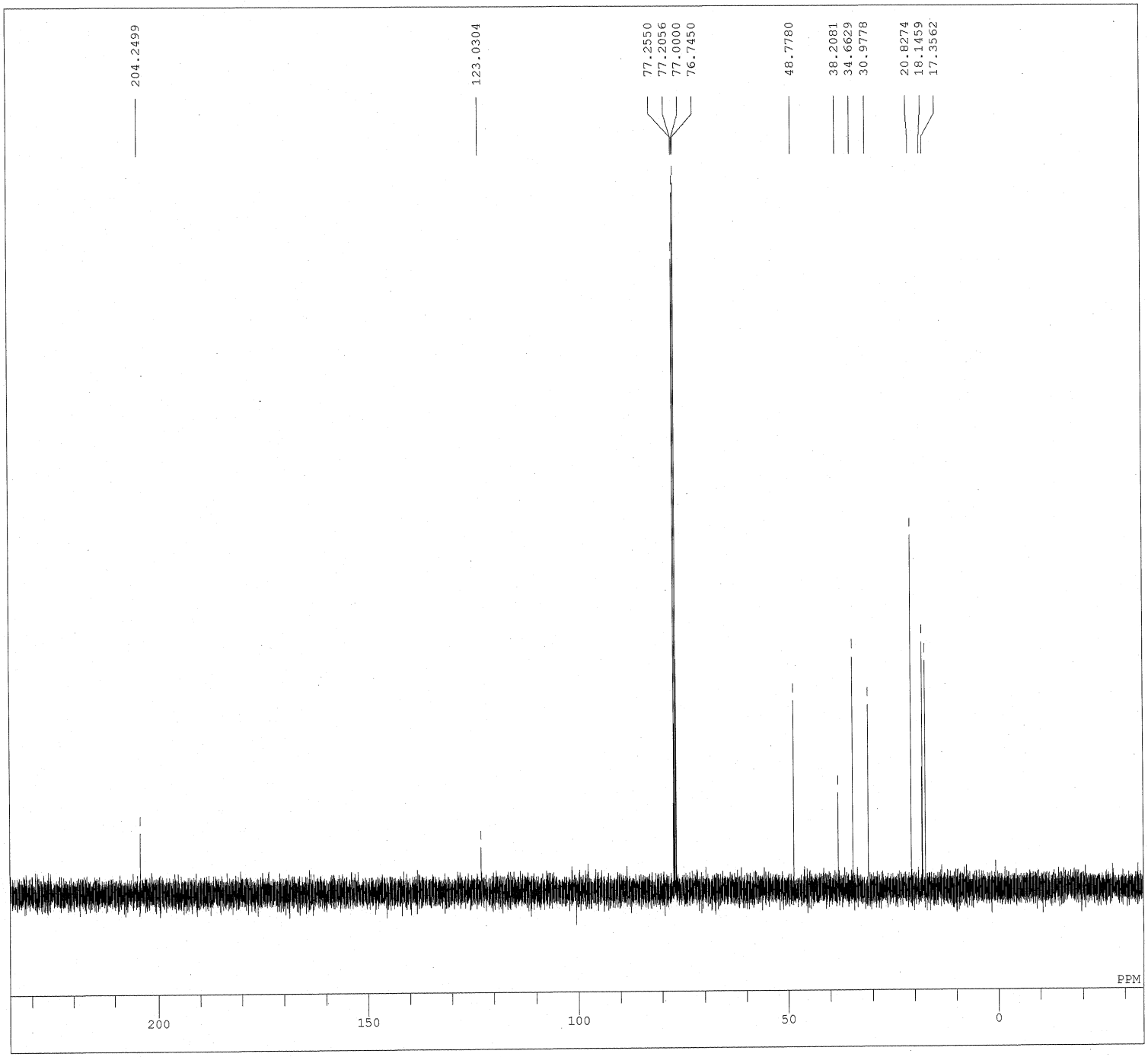


DFILE	savedata08.nmdata
COMNT	meknbuproduct
DATIM	Fri Apr 16 09:39:34 2010
OBNUC	13C
EXMOD	bcm
OBFRQ	125.65 MHz
OBSET	120.00 KHz
OBFIN	7958.00 Hz
POINT	32768
FREQU	33898.30 Hz
SCANS	77
ACQTM	0.9667 sec
PD	2.0333 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	25.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	30

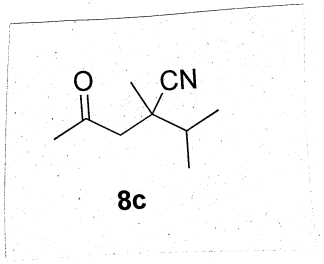


8b

mekiprproduct

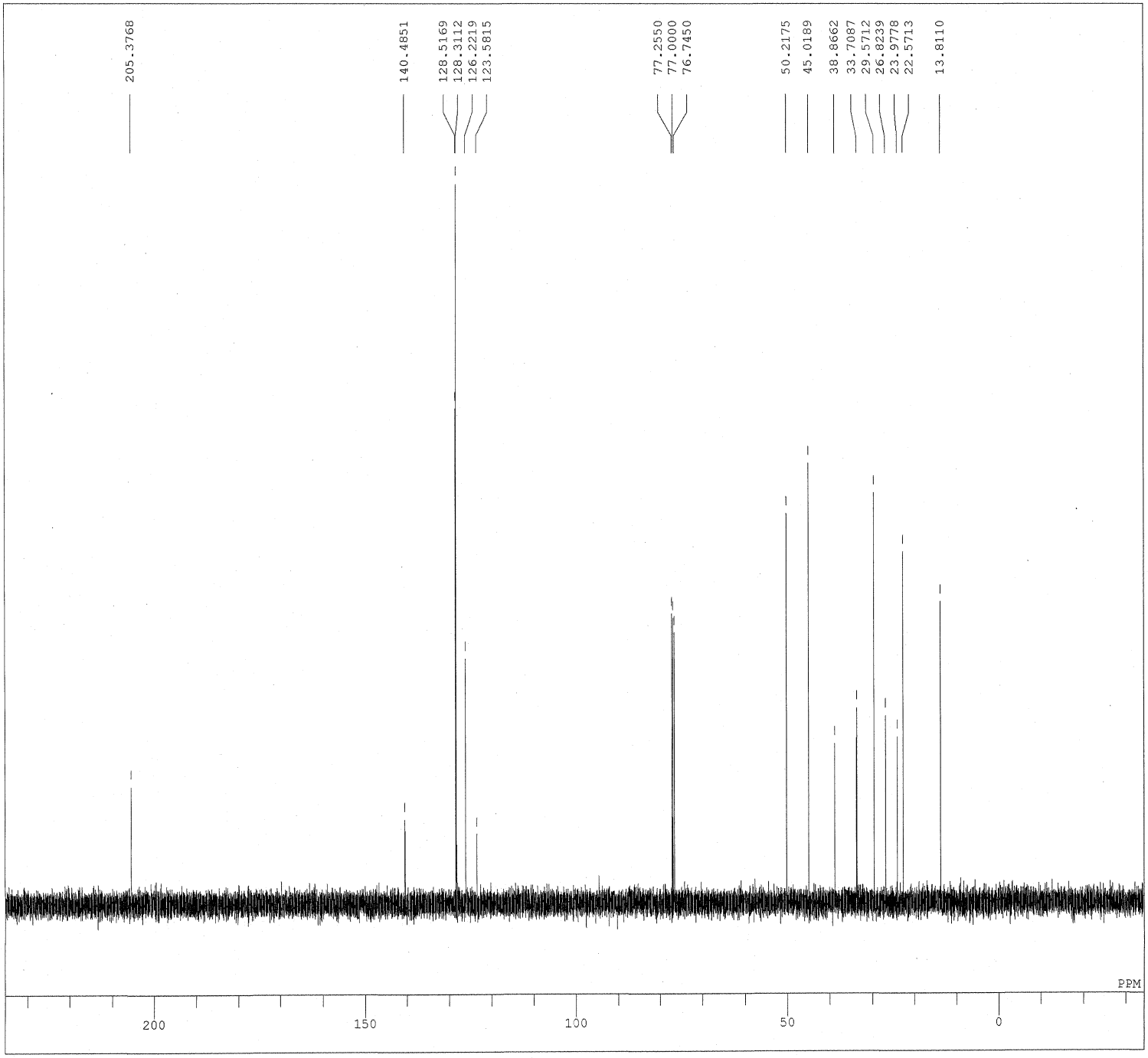


DFILE	savedata16.nmdata
COMNT	mekiprproduct
DATIM	Fri Apr 16 10:49:28 2010
OBNUC	13C
EXMOD	bcm
OBFRQ	125.65 MHz
OBSET	120.00 KHz
OBFIN	7958.00 Hz
POINT	32768
FREQU	33898.30 Hz
SCANS	260
ACQTM	0.9667 sec
PD	2.0333 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	26.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	30

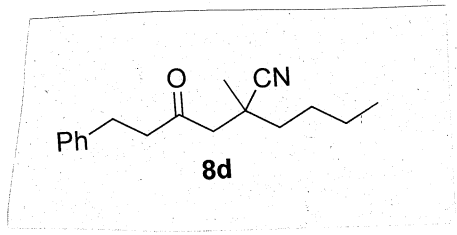


8c

phetk

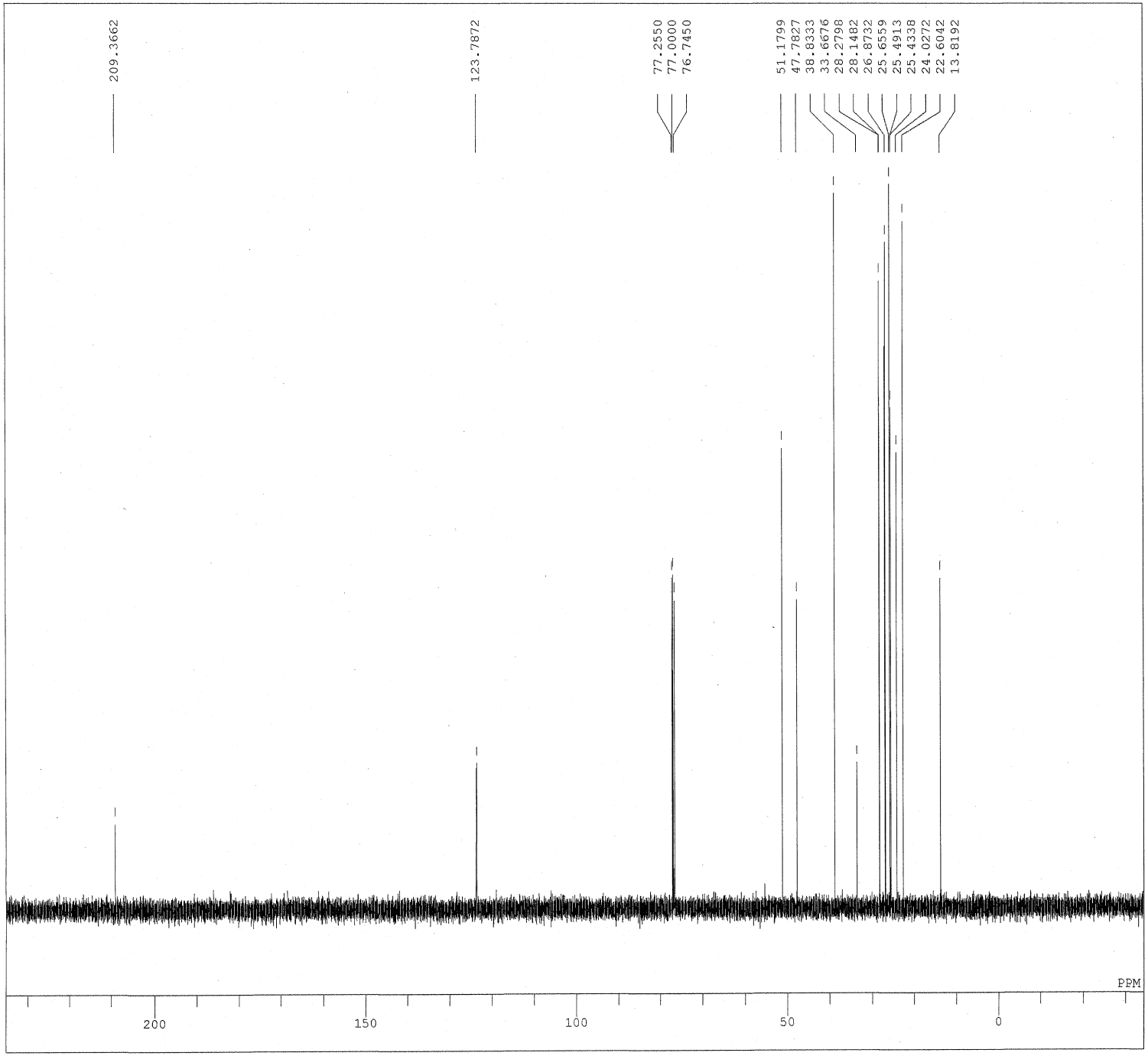



```
DFILE   savedata01.nmdata
COMNT   phetk
DATIM   Wed Feb 24 12:10:38 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS            28
ACQTM          0.9667 sec
PD             2.0333 sec
PW1              5.50 usec
IRNUC   1H
CTEMP           24.2 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             30
```

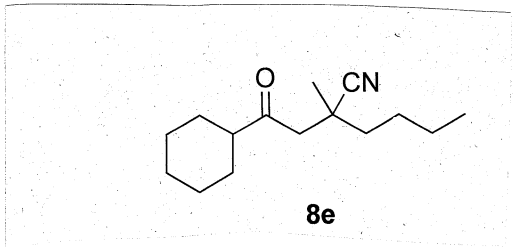


8d

cyk

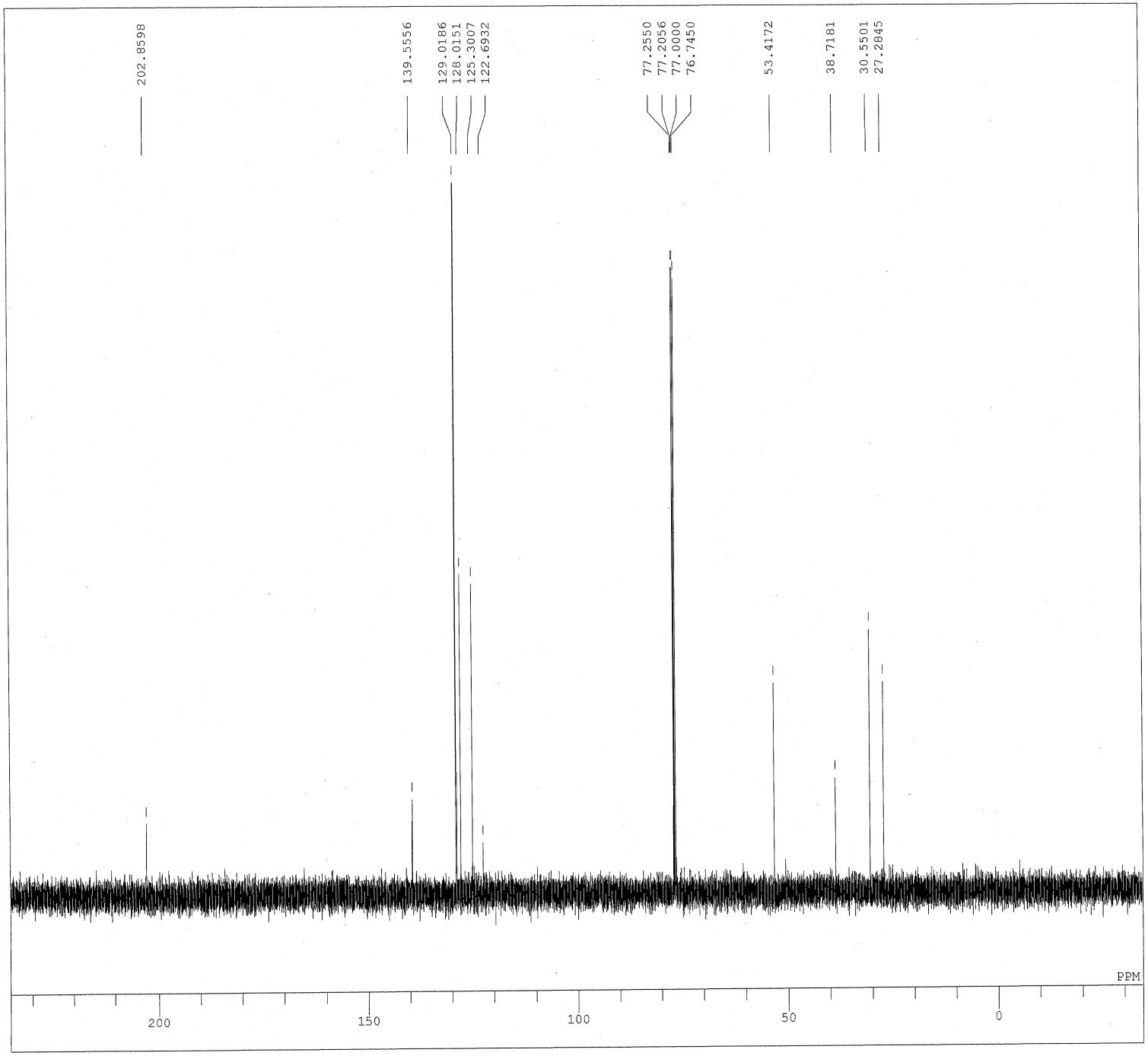


DFILE	savedata07.nmdata
COMNT	cyk
DATIM	Sat Feb 20 19:36:10 2010
OBNUC	13C
EXMOD	bcm
OBFRQ	125.65 MHz
OBSET	120.00 KHz
OBFIN	7958.00 Hz
POINT	32768
FREQU	33898.30 Hz
SCANS	72
ACQTM	0.9667 sec
PD	2.0333 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	24.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.10 Hz
RGAIN	30

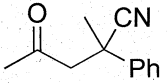


8e

mekbetaphproduct

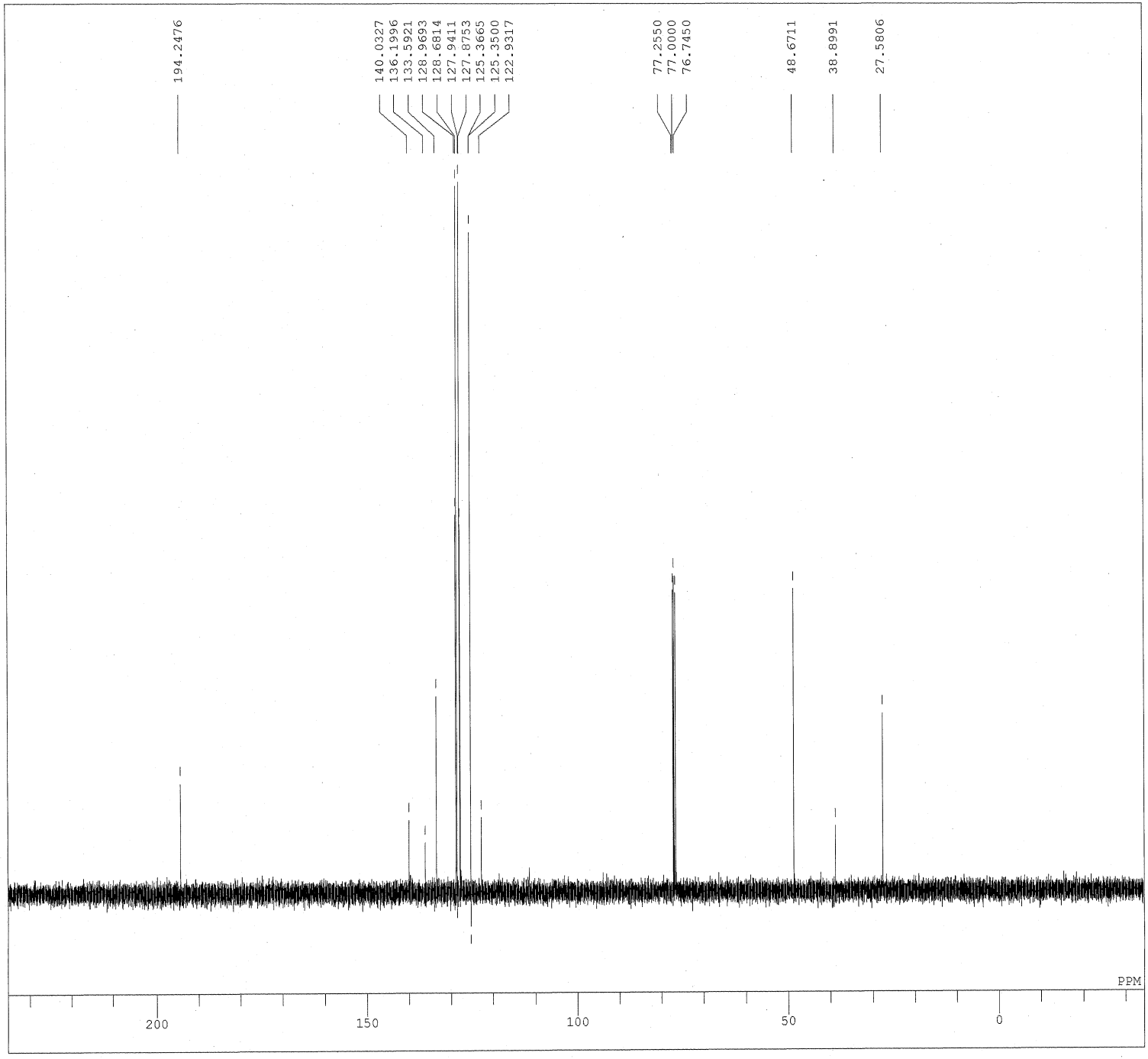


DFILE	savedata10.nmdata
COMNT	mekbetaphproduct
DATIM	Fri Apr 16 09:51:46 2010
OBNUC	13C
EXMOD	bcm
OBFRQ	125.65 MHz
OBSET	120.00 KHz
OBFIN	7958.00 Hz
POINT	32768
FREQU	33898.30 Hz
SCANS	100
ACQTM	0.9667 sec
PD	2.0333 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	26.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	30

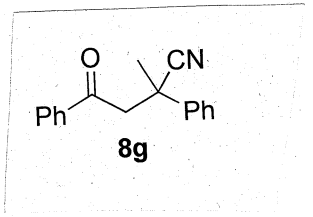


8f

chalcpro

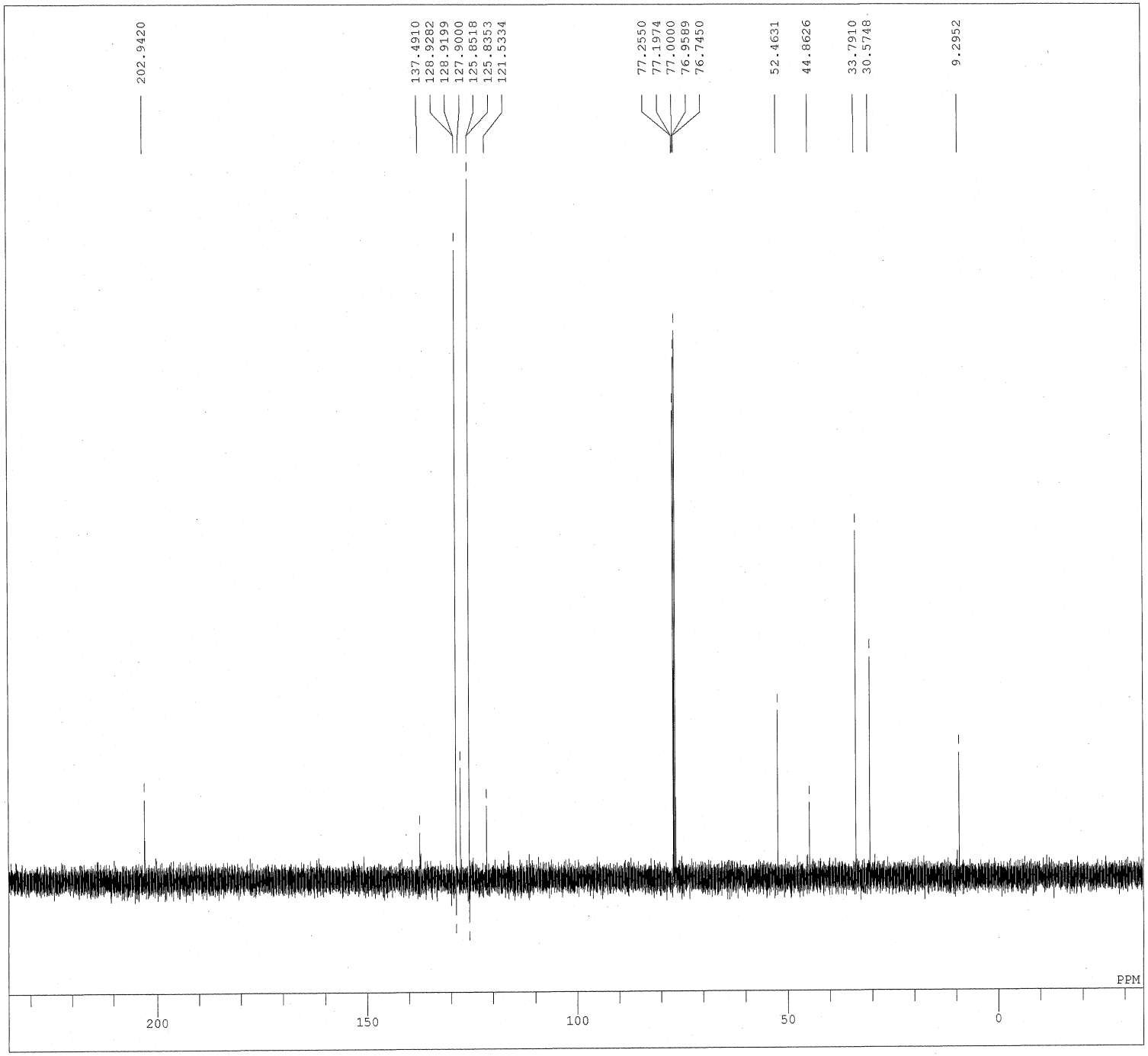



```
DFILE   savedata17.nmdata
COMNT   chalcpro
DATIM   Fri Apr 16 13:25:24 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS             56
ACQTM          0.9667 sec
PD             2.0333 sec
PW1               5.50 usec
IRNUC   1H
CTEMP            25.4 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.12 Hz
RGAIN              30
```

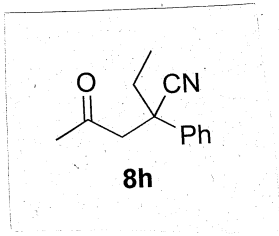


8g

betaetpro

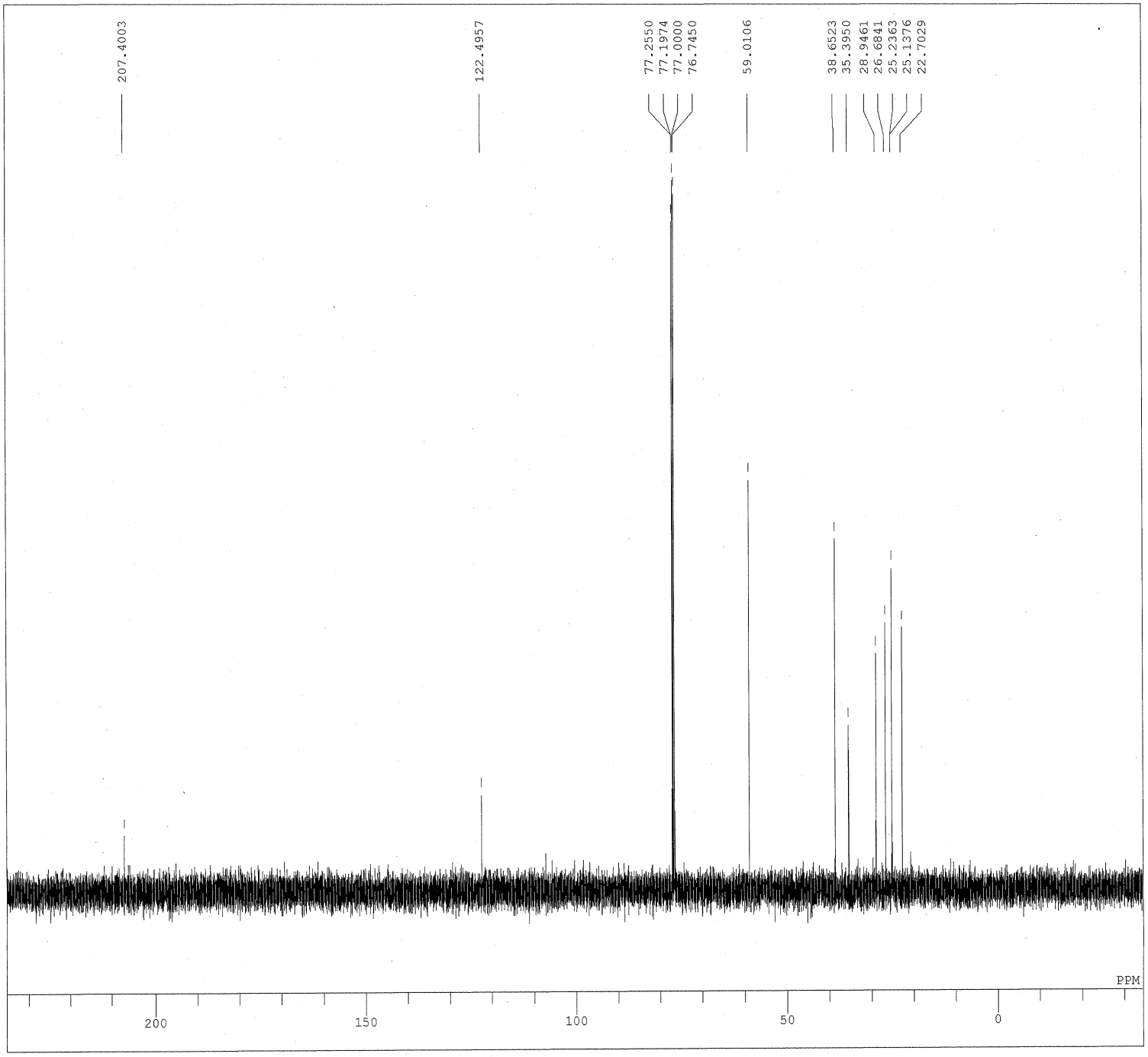


DFILE	savedata18.nmdata
COMNT	betaetpro
DATIM	Fri Apr 16 13:33:33 2010
OBNUC	13C
EXMOD	bcm
OBFRQ	125.65 MHz
OBSET	120.00 KHz
OBFIN	7958.00 Hz
POINT	32768
FREQU	33898.30 Hz
SCANS	113
ACQTM	0.9667 sec
PD	2.0333 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	26.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	30

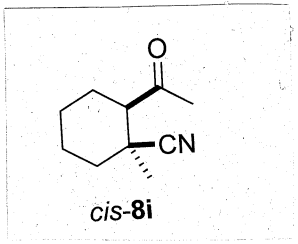


8h

alphacymp

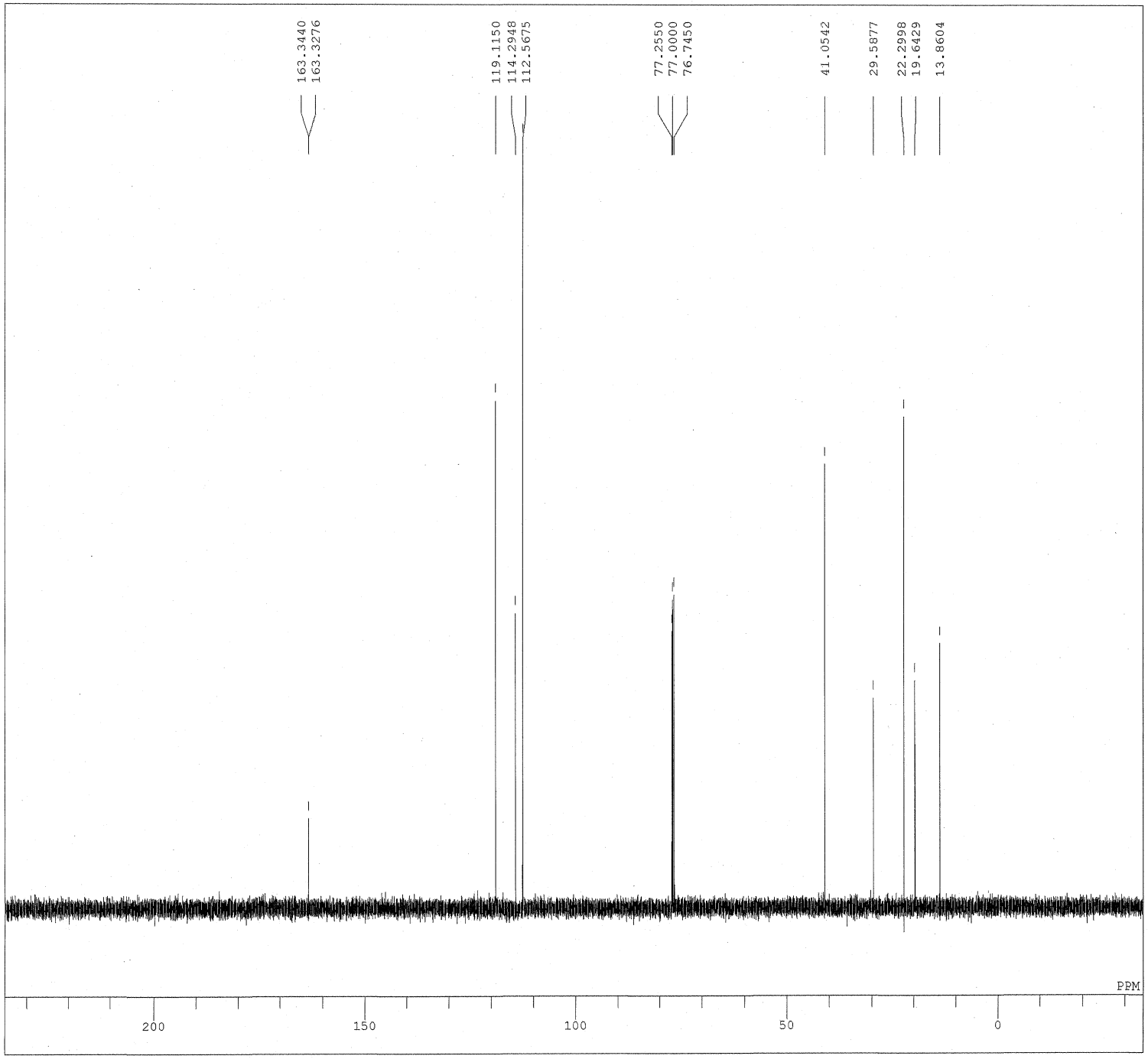


DFILE	savedata14.nmdata
COMNT	alphacymp
DATIM	Fri Apr 16 10:25:18 2010
OBNUC	13C
EXMOD	bcm
OBFRQ	125.65 MHz
OBSET	120.00 KHz
OBFIN	7958.00 Hz
POINT	32768
FREQU	33898.30 Hz
SCANS	122
ACQTM	0.9667 sec
PD	2.0333 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	26.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	30

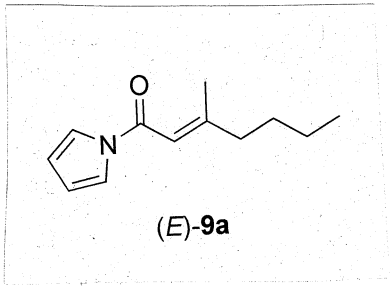


cis-**8i**

n

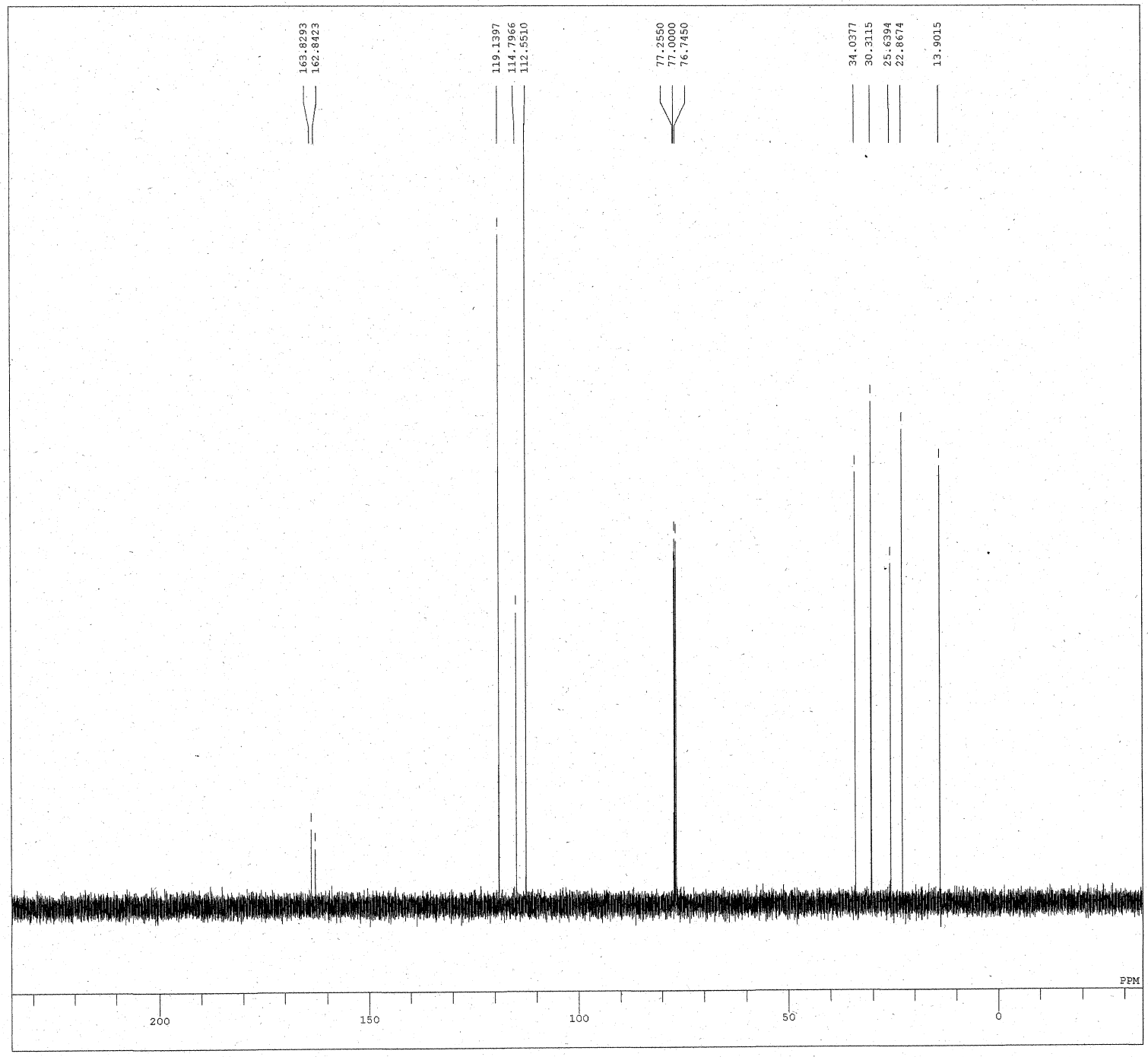


DFILE	savedata04.nmdata
COMNT	n
DATIM	Wed Feb 3 21:20:16 2010
OBNUC	13C
EXMOD	bcm
OBFRQ	125.65 MHz
OBSET	120.00 KHz
OBFIN	7958.00 Hz
POINT	32768
FREQU	33898.30 Hz
SCANS	114
ACQTM	0.9667 sec
PD	2.0333 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	26.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.00 Hz
RGAIN	30

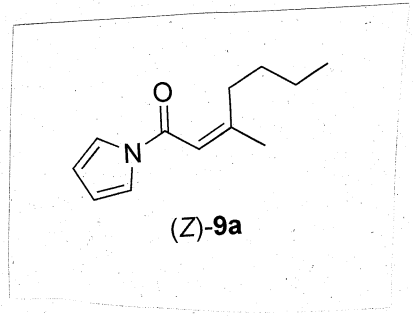


(*E*)-**9a**

nnbulpcarb

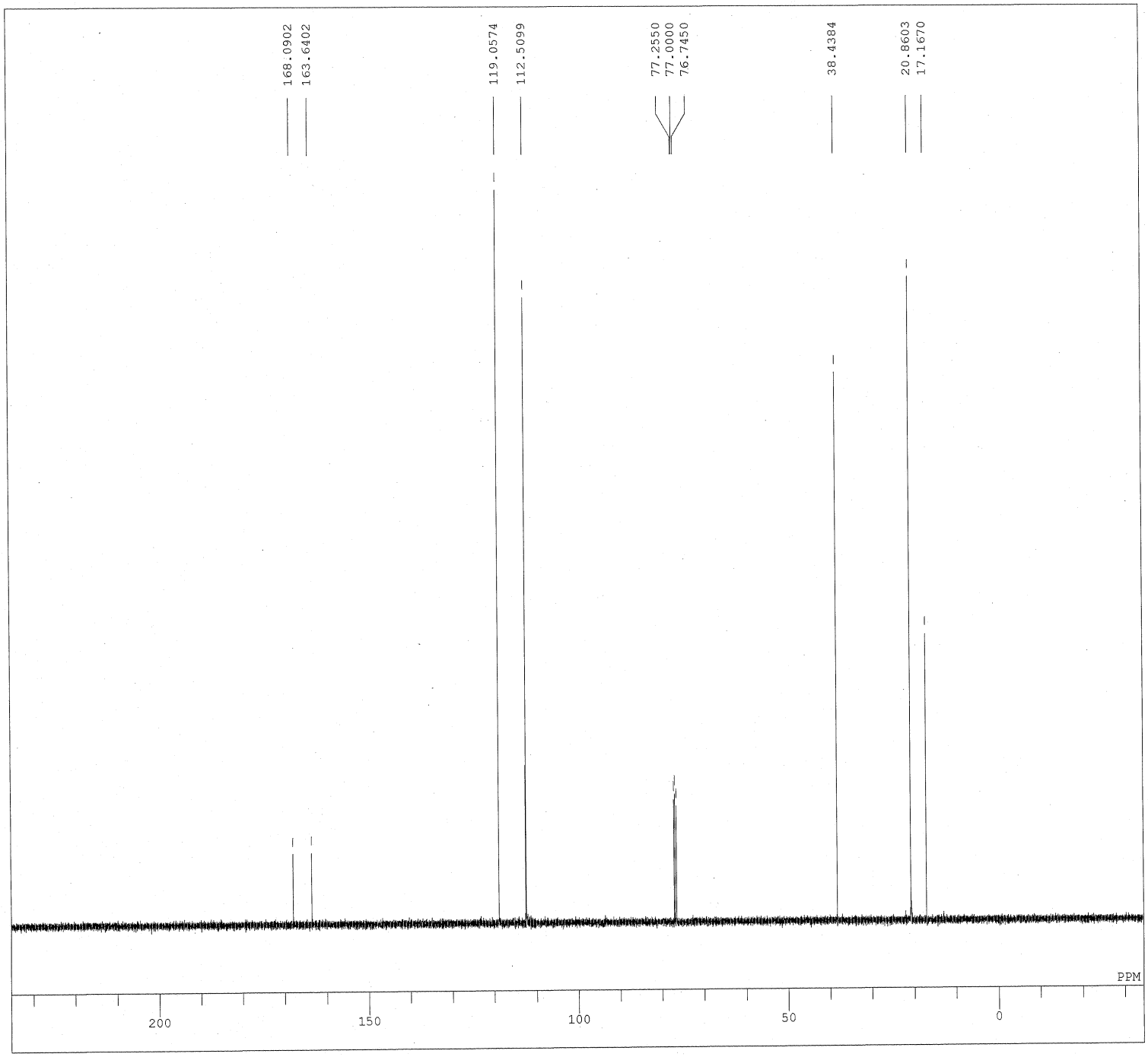



```
DFILE   savedata10.nmdata
COMNT   nnbulpcarb
DATIM   Mon Jan 11 17:45:28 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS            70
ACQTM          0.9667 sec
PD             2.0333 sec
PW1               5.50 usec
IRNUC   1H
CTEMP          25.9 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             30
```

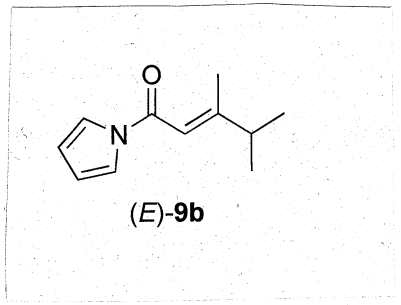


(*Z*)-**9a**

napiprtrans

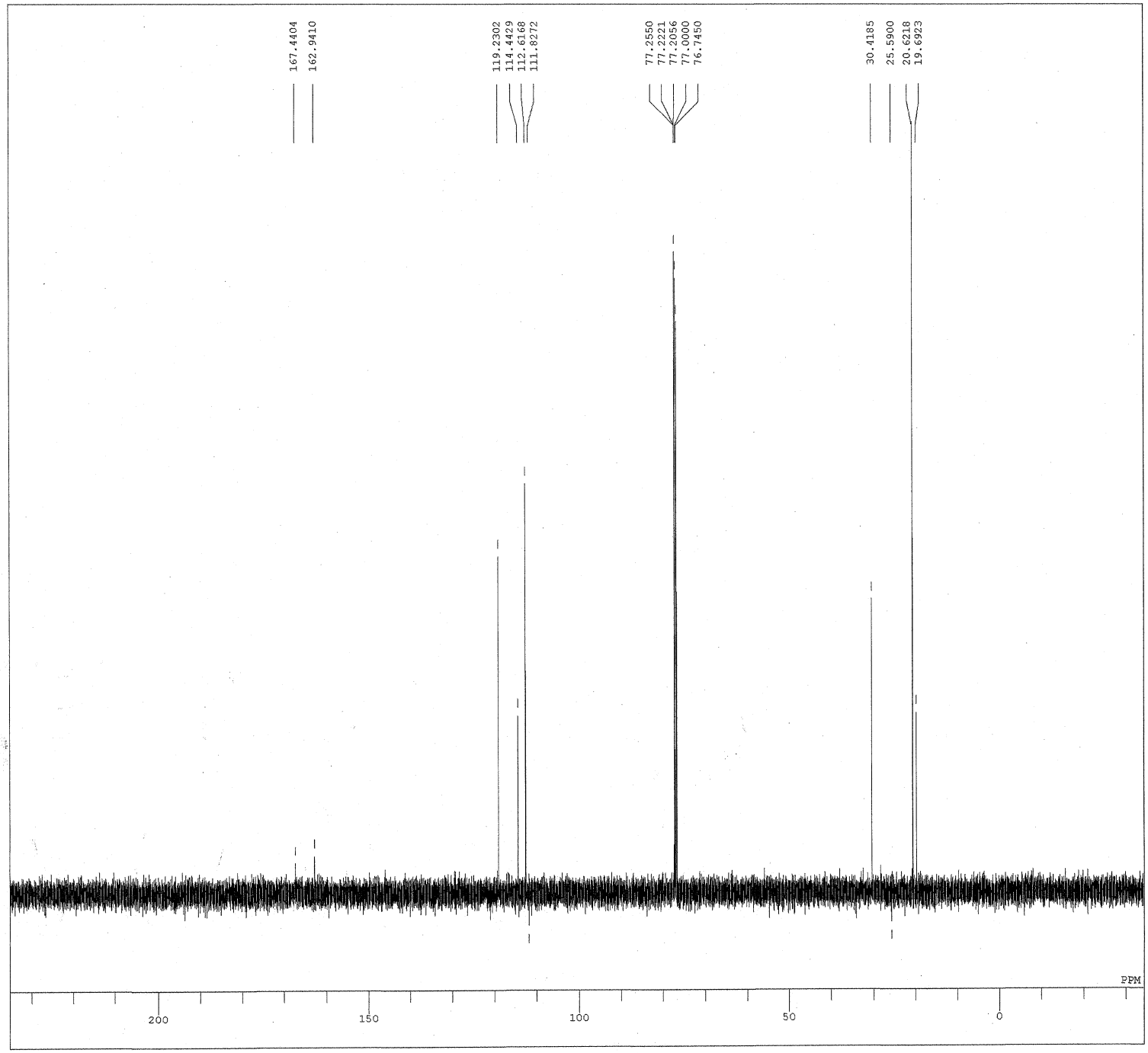



```
DFILE   savedata04.als
COMNT   napiprtrans
DATIM   Fri Apr 16 09:21:35 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS             83
ACQTM          0.9667 sec
PD             2.0333 sec
PW1              5.50 usec
IRNUC   1H
CTEMP            25.8 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.12 Hz
RGAIN              30
```

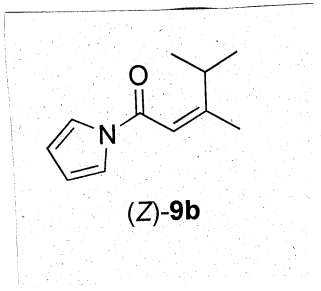


(*E*)-**9b**

niprlpcarb

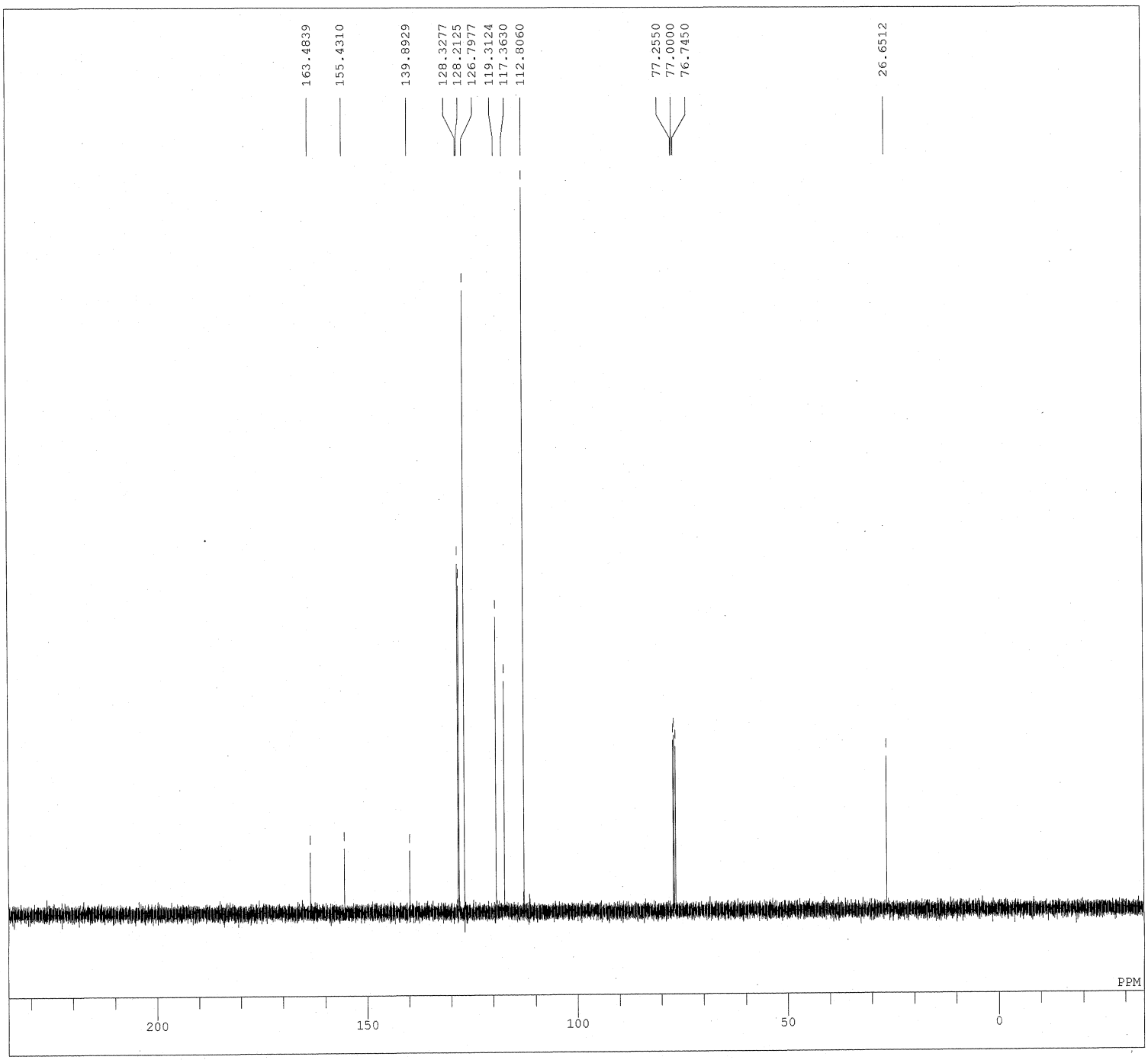



```
DFILE   savedata08.nmdata
COMNT   niprlpcarb
DATIM   Tue Jan 12 14:49:48 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS            249
ACQTM         0.9667 sec
PD            2.0333 sec
PW1             5.50 usec
IRNUC   1H
CTEMP          26.4 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             30
```

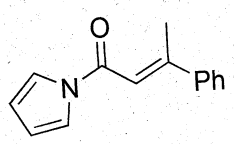


(*Z*)-**9b**

napbetaphtrans

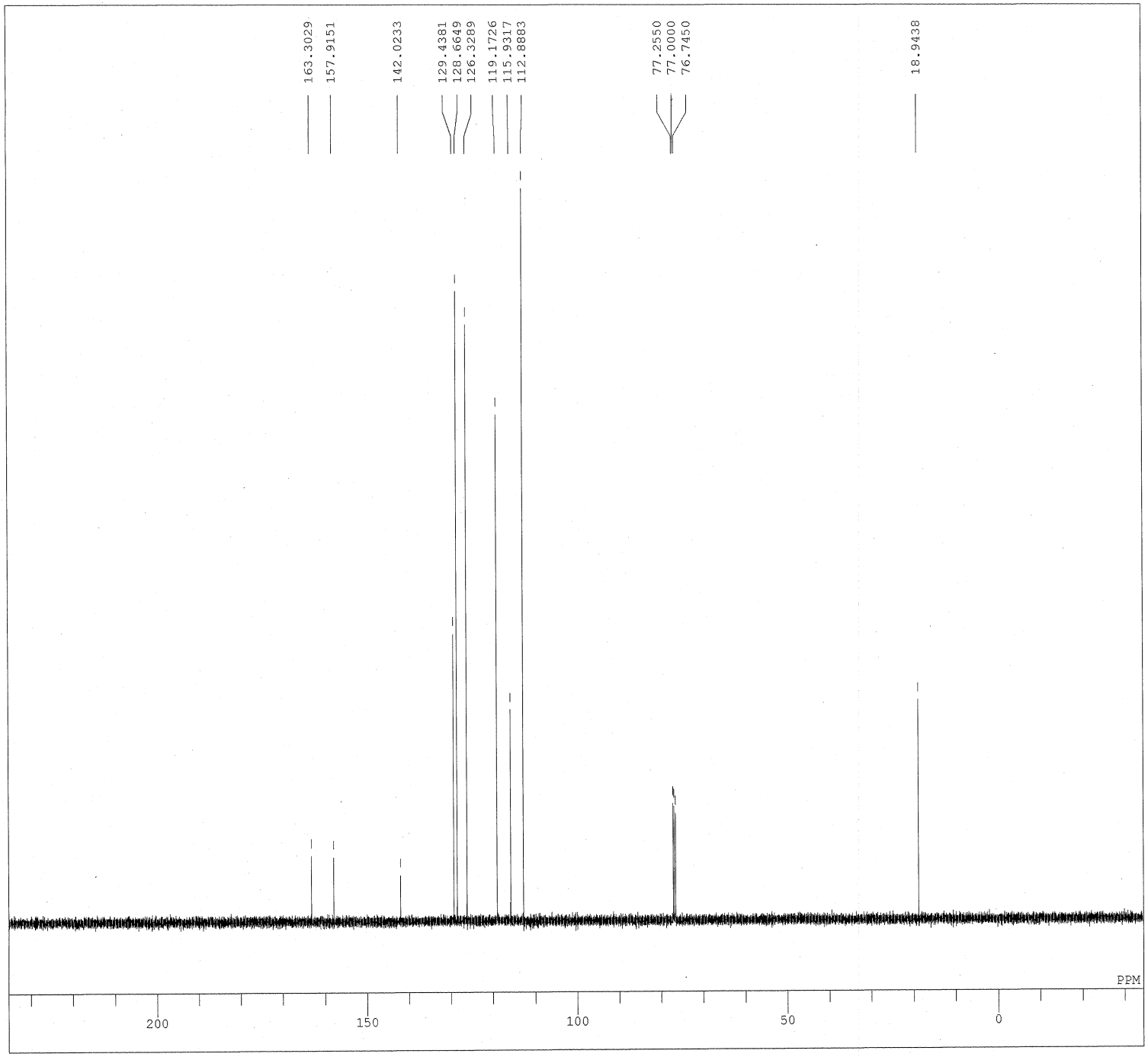



```
DFILE   savedata25.nmdata
COMNT   napbetaphtrans
DATIM   Fri Apr 16 19:39:39 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS             31
ACQTM          0.9667 sec
PD             2.0333 sec
PW1               5.50 usec
IRNUC   1H
CTEMP             25.5 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.12 Hz
RGAIN              30
```

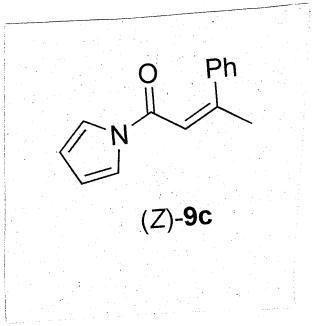


(*E*)-**9c**

napbetaphcis

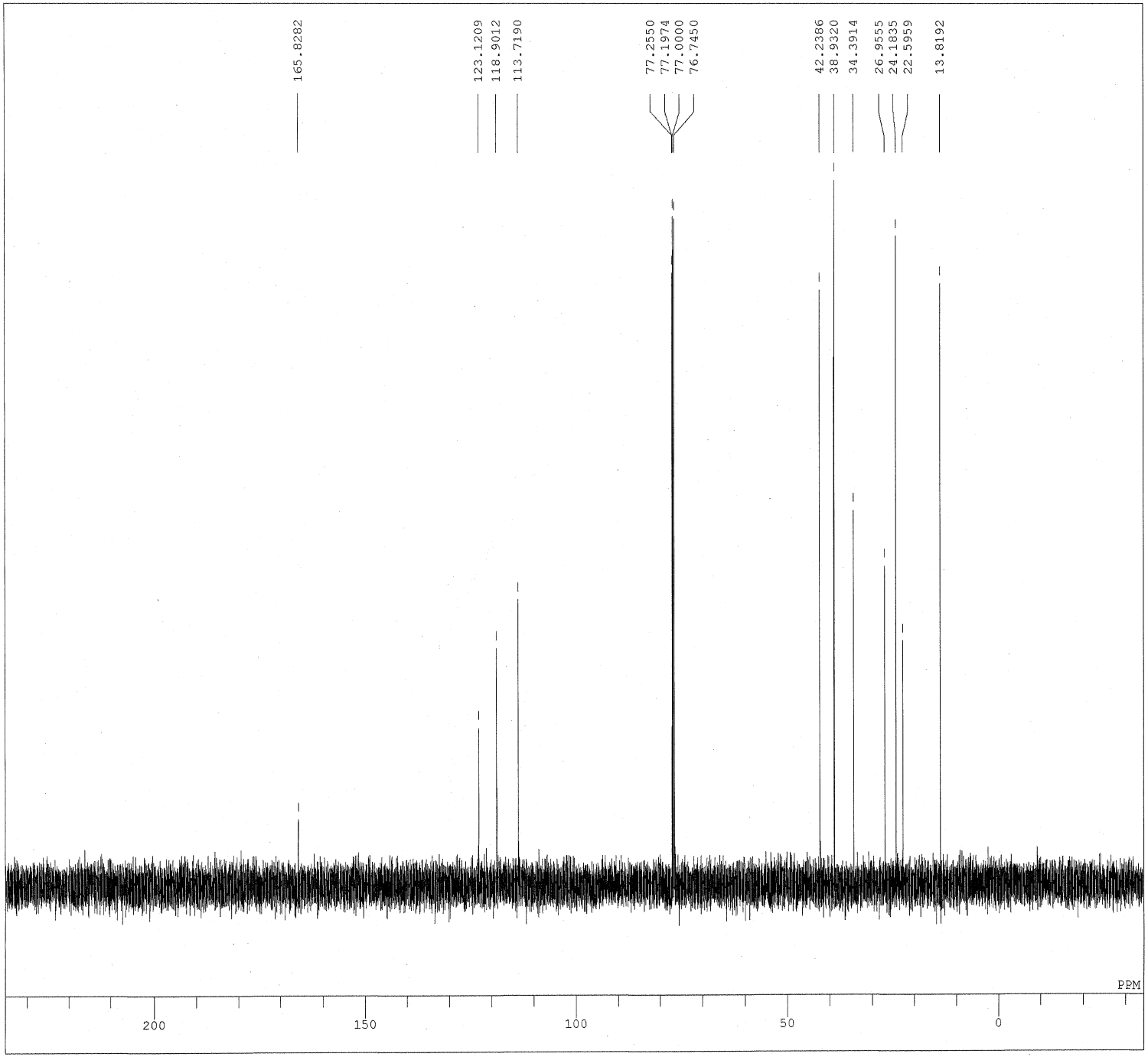



```
DFILE   savedata16.nmdata
COMNT   napbetaphcis
DATIM   Sat Apr 17 10:33:57 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS             63
ACQTM          0.9667 sec
PD             2.0333 sec
PW1              5.50 usec
IRNUC   1H
CTEMP            26.2 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.12 Hz
RGAIN              30
```

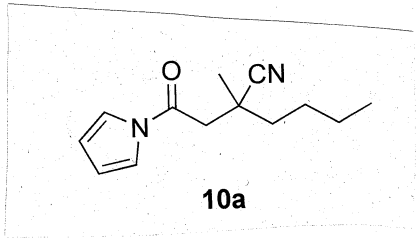


(*Z*)-**9c**

napnbu

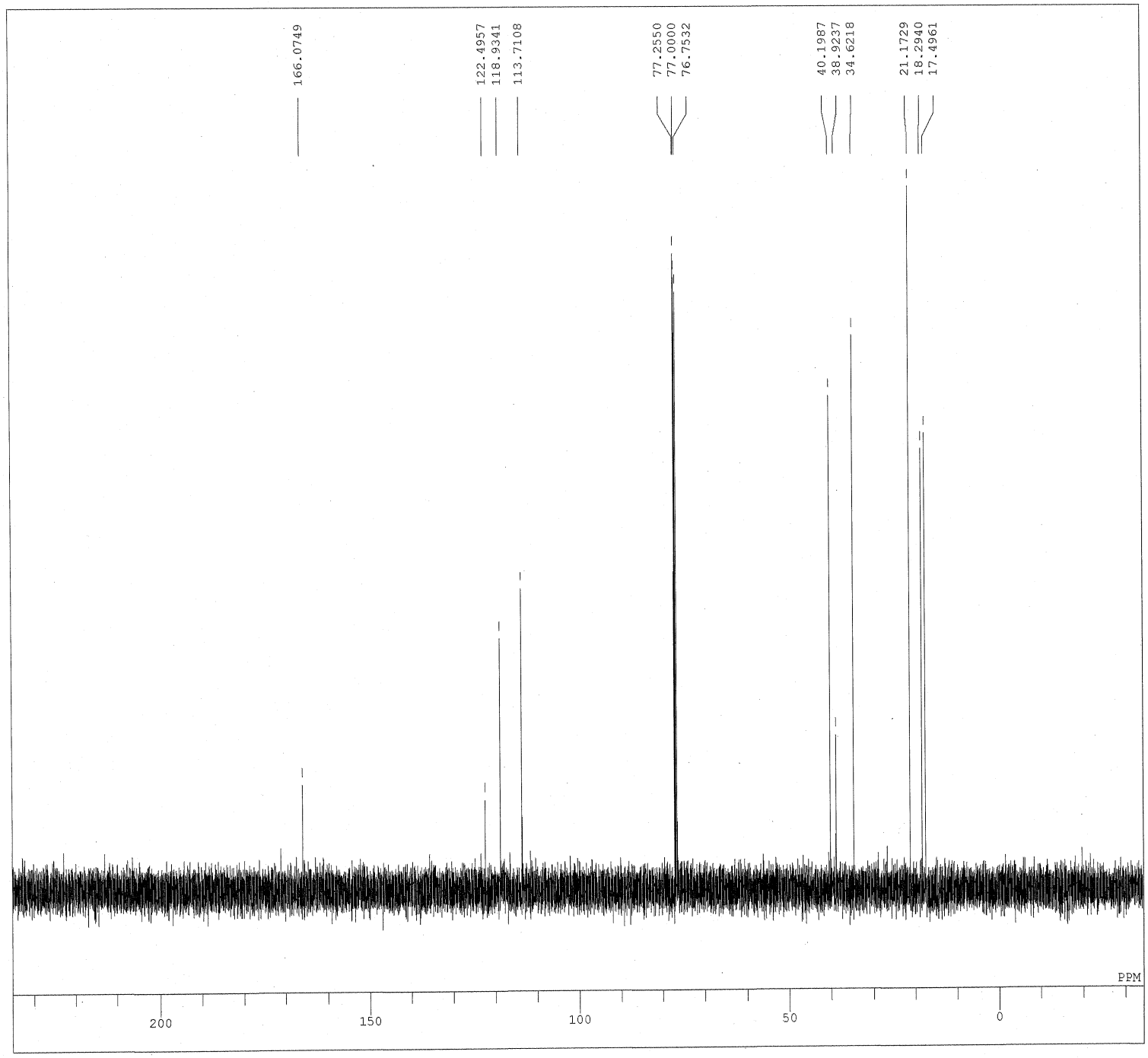



```
DFILE   savedata08.nmdata
COMNT   napnbu
DATIM   Sat Feb 20 19:41:56 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS             75
ACQTM          0.9667 sec
PD             2.0333 sec
PW1               5.50 usec
IRNUC   1H
CTEMP            24.9 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.10 Hz
RGAIN              30
```

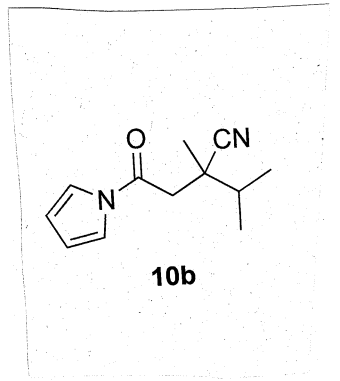


10a

napipr

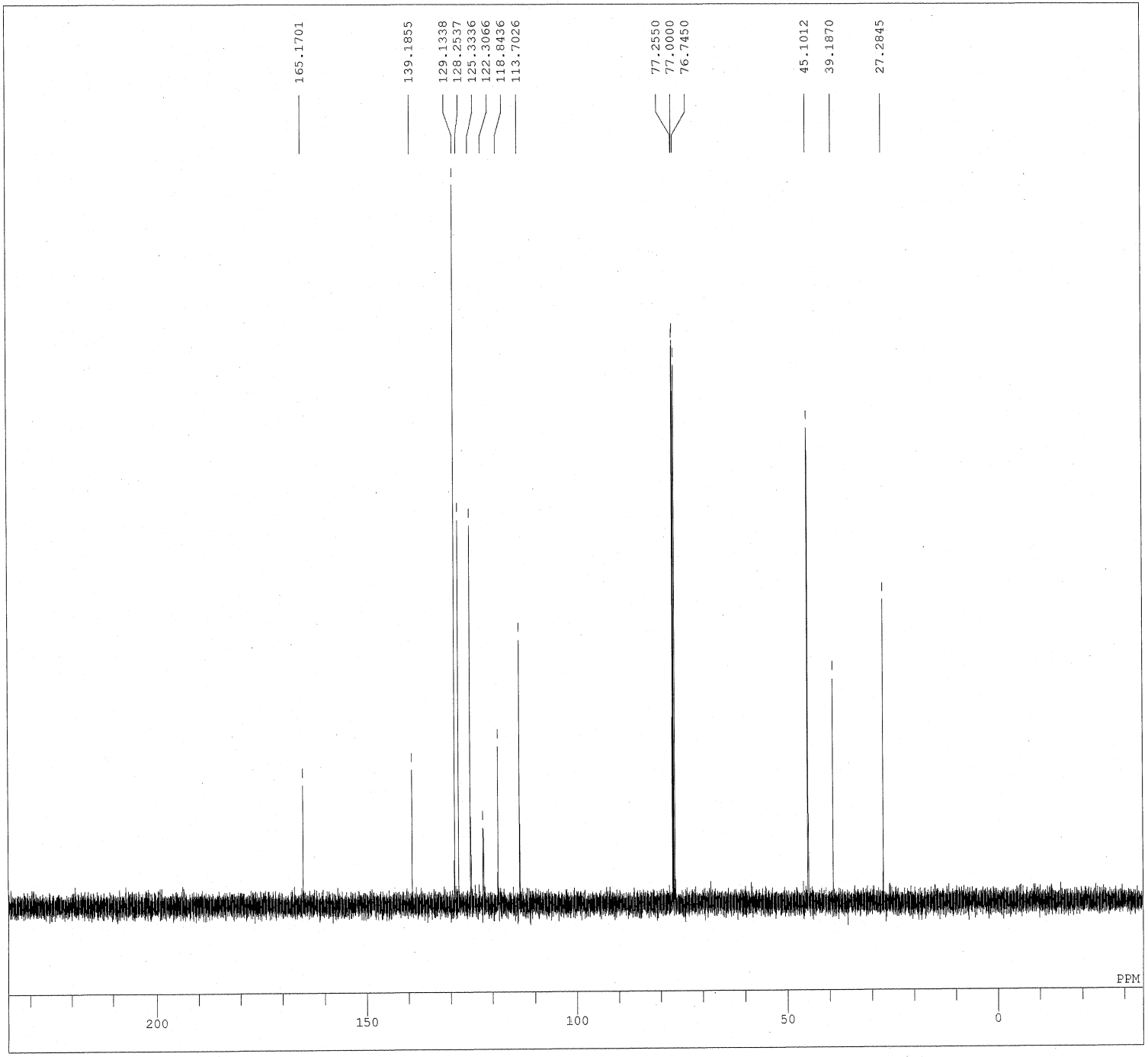



```
DFILE   savedata05.nmdata
COMNT   napipr
DATIM   Wed Feb 24 12:25:26 2010
OBNUC   13C
EXMOD   bcm
OBFRQ         125.65 MHz
OBSET         120.00 KHz
OBFIN        7958.00 Hz
POINT          32768
FREQU       33898.30 Hz
SCANS             66
ACQTM          0.9667 sec
PD             2.0333 sec
PW1               5.50 usec
IRNUC   1H
CTEMP            24.8 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.12 Hz
RGAIN              30
```

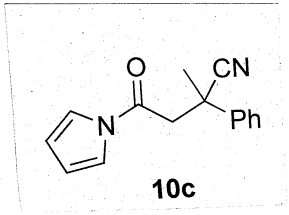


10b

napbetaphpro

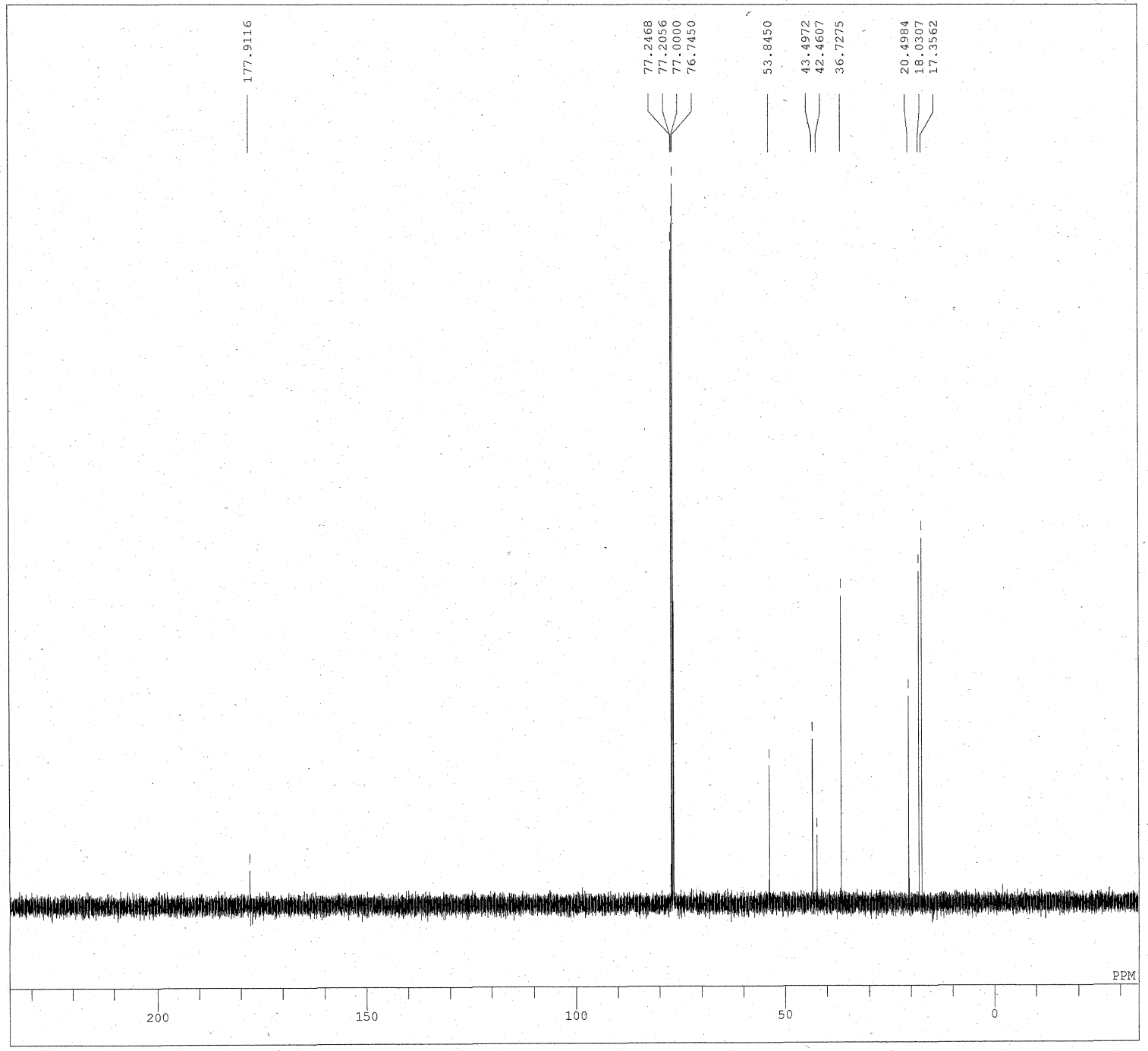


DFILE	savedata07.nmdata
COMNT	napbetaphpro
DATIM	Sat Apr 17 10:45:55 2010
OBNUC	13C
EXMOD	bcm
OBFRQ	125.65 MHz
OBSET	120.00 KHz
OBFIN	7958.00 Hz
POINT	32768
FREQU	33898.30 Hz
SCANS	162
ACQTM	0.9667 sec
PD	2.0333 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	26.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	30

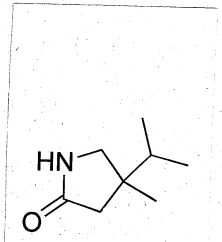


10c

c



DFILE	savedata04.nmdata	
COMNT	c	
DATIM	Thu Jun 3 17:09:09 2010	
OBNUC	13C	
EXMOD	bcm	
OBFRQ	125.65	MHz
OBSET	120.00	KHz
OBFIN	7958.00	Hz
POINT	32768	
FREQU	33898.30	Hz
SCANS	444	
ACQTM	0.9667	sec
PD	2.0333	sec
PW1	5.12	usec
IRNUC	1H	
CTEMP	27.3	c
SLVNT	CDCl3	
EXREF	77.00	ppm
BF	0.01	Hz
RGAIN	30	



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