Electronic Supplementary Information:

Asymmetric β-boration of α,β-unsaturated carbonyl compounds promoted by chiral rhodium–bisoxazolinylphenyl catalysts

Takushi Shiomi, Takahiro Adachi, Kenji Toribatake, Li Zhou and Hisao Nishiyama*

Department of Applied Chemistry, Graduate School of Engineering,

Nagoya University, Chikusa, Nagoya, 464-8603, Japan.

Fax:+81-52-789-3209; E-mail: hnishi@apchem.nagoya-u.ac.jp

Table of Contents

1. Typical reactions.

Asymmetric β-borylation of (*E*)-isopropyl cinnamate and the oxidation (one pot procedure, Table 1, Entry 6). Rh(Phebox-*sb*) **1b** (2.8 mg, 0.0050 mmol), bis(pinacolato)diboron (152 mg, 0.60 mmol, 1.2 equiv.), NaO*t*-Bu (2.8 mg, 0.029 mmol) were placed in a flask with a stirring bar. Under an argon atmosphere, the cinnamate (94.8 mg, 0.50 mmol) and toluene (1.0 mL) were added. The mixture was stirred at 80 °C for 0.5 h; the borylated product, R_f = 0.52, ethyl acetate/hexane = 1:5. At room temperature, the solvent was removed under reduced pressure. Then, THF (1.0 mL), water (1.0 mL), and $NaBO_3(H_2O)_4$ (384 mg, 2.5 mmol) were added. The mixture was stirred for room temperature for 0.5 h; the hydroxy product, R_f = 0.34, ethyl acetate/hexane = 1:3. Water was added, and the mixture was extracted with ethyl acetate. The combined organic layer was washed with brine and was dried over $MgSO_4$. After concentration, the residue was purified by silica gel column chromatography with hexane/ethyl acetate as eluent to give the β-hydroxyester **5** (92.4 mg, 0.444 mmol) in 89% yield; 93% ee measured by chiral LC.

(*E*)-*tert*-Butyl cinnamate (101.2 mg, 0.50 mmol) was subjected to the similar procedure to give the corresponding β-hydroxyester **6** (82.9 mg, 0.373 mmol) in 75%; 85% ee measured by chiral LC (Table 1, Entry 10).

(*Z*)-Ethyl cinnamate (84.2 mg, 0.48 mmol) was subjected to the similar procedure with **1a** (2.6 mg, 0.0048 mmol), bis(pinacolato)diboron (147 mg, 0.58 mmol), NaO*t*-Bu (2.4 mg, 0.024 mmol), in toluene (1.0 mL) at 80 °C for 0.5 h to give **3** (112 mg, 0.368 mmol) in 77%. Oxidation of **3** (70.9 mg, 0.23 mmol) was carried out with $NaBO_3(H_2O)_4$ (246 mg, 1.6 mmol), THF (1.0 mL), water (1.0 mL), at room temperature for 3 h to give the β-hydroxyester (44.0 mg, 0.227 mmol) in 97% yield; 93% ee by chiral LC.

Asymmetric β-borylation of (*E*)-ethyl 5-phenylpent-2-enoate and the oxidation. Rh(Phebox-*sb*) **1b** (2.8 mg, 0.0050 mmol), bis(pinacolato)diboron (140 mg, 0.55 mmol, 1.1 equiv.), NaO*t*-Bu (2.4 mg, 0.025 mmol) were placed in a flask with a stirring bar. Under an argon atmosphere, the phenylpentenoate (102 mg, 0.50 mmol, a mixture of *E* and *Z*, 97:3) and toluene (1.0 mL) were added. The mixture was stirred at 80°C for 0.5

h. At room temperature, the mixture was directly charged to a silica-gel column with eluent of hexane/ethyl acetate (20:1) to give the borylated product **9** in 90% (149 mg, 0.45 mmol). The solution of **9** (67 mg, 0.20 mmol) and $NaBO_3(H_2O)_4$ (156 mg, 1.0 mmol) in THF (1.0 ml) and H_2O (1.0 mL) was stirred at room temperature for 0.5 h. The mixture was extracted with ethyl acetate. After concentration of the extract, the residue was purified by silica gel column chromatography with hexane/ethyl acetate as eluent to give the β-hydroxyester (42 mg, 0.188 mmol) in 94% yield; 90% ee by chiral LC.

Use of Rh(Phebox-*ip*) **1a** (2.7 mg, 0.0050 mmol), bis(pinacolato)diboron (152 mg, 0.60 mmol, 1.2 equiv.), NaO*t*-Bu (2.4 mg, 0.025 mmol), the pentenoate (102.5 mg, 0.50 mmol), toluene (1.0 mL), 80°C, 0.5 h: **9** (149 mg, 0.448 mmol), 90%; oxidation of **9** (80.9 mg, 0.24 mmol), $NaBO_3(H_2O)_4$ (185 mg, 1.2 mmol), THF (1.0 mL), water (1.0 mL), at room temperature, 3 h: the β-hydroxyester (50.6 mg, 0.228 mmol) in 98% yield; 86% ee by chiral LC.

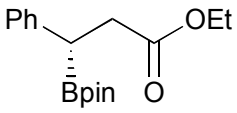
Asymmetric β-borylation of (*E*)-benzyl but-2-enoate and the oxidation. Rh(Phebox-*sb*) **1b** (2.8 mg, 0.0050 mmol), bis(pinacolato)diboron (140 mg, 0.55 mmol, 1.1 equiv.), NaO*t*-Bu (2.4 mg, 0.025 mmol) were placed in a flask with a stirring bar. Under an argon atmosphere, the butenoate (88.1 mg, 0.50 mmol) and toluene (1.0 mL) were added. The mixture was stirred at 80°C for 0.5 h. At room temperature, the mixture was directly charged to a silica-gel column with eluent of hexane/ethyl acetate (20:1) to give the borylated product **10** in 87% (132 mg, 0.434 mmol). The solution of **10** (44.3 mg, 0.146 mmol) and $NaBO_3(H_2O)_4$ (112 mg, 0.72 mmol) in THF (0.8 ml) and H_2O (0.8 mL) was stirred at room temperature for 0.5 h. The mixture was extracted with ethyl acetate. After concentration of the extract, the residue was purified by silica gel column chromatography with hexane/ethyl acetate as eluent to give the β-hydroxyester (26.3 mg, 0.135 mmol) in 92% yield; 84% ee by chiral LC.

Use of Rh(Phebox-*ip*) **1a** (2.7 mg, 0.0050 mmol), bis(pinacolato)diboron (152 mg, 0.60 mmol, 1.2 equiv.), NaO*t*-Bu (2.4 mg, 0.025 mmol), the butenoate (88.1 mg, 0.50 mmol), toluene (1.0 mL), 80°C, 0.5 h: **10** (134 mg, 0.44 mmol), 88%; oxidation of **10** (96 mg, 0.32 mmol), $NaBO_3(H_2O)_4$ (246 mg, 1.6 mmol), THF (1.0 mL), water (1.0 mL), at room temperature, 3 h: the β-hydroxyester (55.9 mg, 0.288 mmol) in 91% yield; 82%

ee by chiral LC.

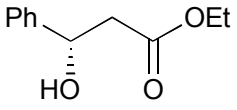
Asymmetric β-borylation of (*E*)-*N*,*N*-dimethylcinnamamide and the oxidation. Rh(Phebox-*ip*) **1a** (2.7 mg, 0.0050 mmol), bis(pinacolato)diboron (152 mg, 0.60 mmol, 1.2 equiv.), NaO*t*-Bu (2.4 mg, 0.025 mmol) were placed in a flask with a stirring bar. Under an argon atmosphere, the cinnamamide (87.6 mg, 0.50 mmol) and toluene (1.0 mL) were added. The mixture was stirred at 80 °C for 0.5 h. At room temperature, the mixture was directly charged to a silica-gel column with eluent of hexane/ethyl acetate to give the borylated product **13** in 70% (106 mg, 0.35 mmol). The solution of **13** (68.7 mg, 0.227 mmol) and $NaBO_3(H_2O)_4$ (177 mg, 1.14 mmol) in THF (1.0 ml) and H_2O (1.0 mL) was stirred at room temperature for 3 h. The mixture was extracted with ethyl acetate (15 mL x 3). After concentration of the extract, the residue was purified by silica gel column chromatography with hexane/ethyl acetate as eluent to give the β-hydroxyester (36.5 mg, 0.189 mmol) in 83% yield; 97% ee by chiral LC.

2. Characterization data of the products.



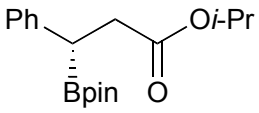
3

(*S*)-Ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-phenylpropanoate: colorless oil. IR (film): 2978, 1731, 1371, 1323, 1141, 847, 701 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.18 (s, 6H), 1.23 (s, 6H), 1.23 (t, *J* = 7.2 Hz, 3H), 2.62-2.77 (m, 2H), 2.89 (dd, *J* = 15.3, 9.6 Hz, 1H), 4.11 (m, 2H), 7.11-7.31 (m, 5H) ppm; ^{13}C NMR (75 MHZ, $CDCl_3$): δ 14.4, 24.6, 24.7, 28.2 (*C*B, broad), 37.4, 60.4, 83.5, 125.4, 128.0, 128.2, 141.1, 173.0; FAB-HRMS: $[M^{\bullet+}]$ *m/z*, found: 304.1840; calcd ($C_{17}H_{25}O_4B$): 304.1849; $[\alpha]_D^{27}$ = +20.7 (c = 1.07, $CHCl_3$), corresponding to 93% ee of **4** from (*Z*)-cinnamate.



4

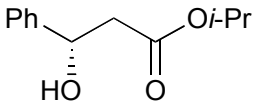
(*S*)-Ethyl 3-hydroxy-3-phenylpropanoate: colorless oil. IR (film): 3471 (broad), 2982, 1730, 1195, 1037, 760 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.27 (t, *J* = 7.2 Hz, 3H), 2.88 (m, 2H), 3.30 (d, *J* = 3.3 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 5.14 (m, 1H), 7.22-7.42 (m, 5H) ppm; ^{13}C NMR (75 MHZ, $CDCl_3$): δ 14.3, 43.4, 60.9, 70.3, 125.5, 127.6, 128.3, 142.2, 172.1. Chromatography: DAICEL CHIRALCEL OD-H, hexane/2-propanol (90:10, 0.5 mL/min), retention time: 15.2 min (major), 18.3 min (minor), 96.6% ee (*S*); FAB-HRMS: $[M+H^+]$ *m/z*, found: 195.1029; calcd ($C_{11}H_{15}O_3$): 195.1021; $[\alpha]_D^{26}$ = –46.5 (c = 1.04, $CHCl_3$), 96.6% ee determined by chiral LC; from (*Z*)-cinnamate: $[\alpha]_D^{25}$ = –43.6 (c = 1.0, $CHCl_3$), 93% ee determined by chiral LC; Lit.[S1], $[\alpha]_D^{28}$ = –45.8 (c = 0.25, $CHCl_3$), 90% ee (*S*); Lit.[S2], $[\alpha]_D$ = –52 (c = 1, $CHCl_3$).



the borylation product from isopropyl cinnamate

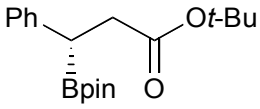
(*S*)-Isopropyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-phenylpropanoate**:**

colorless oil. IR (film): 2979, 1725, 1371, 1139, 970, 768, 706 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.18 (s, 6H), 1.19 (d, *J* = 6.3 Hz, 6H), 1.28 (s, 6H), 2.62 (dd, *J* = 5.7, 15.3 Hz, 1H), 2.73 (dd, *J* = 5.7, 9.6 Hz, 1H), 2.85 (dd, *J* = 9.6, 15.3 Hz, 1H), 4.98 (m, 1H), 7.15-7.30 (m, 5H) ppm; ^{13}C NMR (75 MHZ, $CDCl_3$): δ 22.2, 24.8, 24.9, 67.8, 83.6, 125.5, 128.2, 128.4, 141.3, 172.8; *C*[B] was not detected; FAB-HRMS: [M+H^+] *m/z*, found: 319.2085; calcd ($C_{18}H_{28}O_4B$): 319.2084.



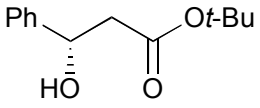
5

(*S*)-Isopropyl 3-hydroxy-3-phenylpropanoate: colorless oil. IR (film): 3060 (broad), 1729, 1107 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.24 (d, *J* = 6.0 Hz, 3H), 1.25 (d, *J* = 6.3 Hz, 3H), 2.62-2.80 (m, 3H), 3.40 (b, 1H), 5.06 (m, 1H, C*H*(CH_3)$_2$), 5.12 (m, C*H*OH), 7.23-7.43 (m, 5H) ppm; ^{13}C NMR (75 MHZ, $CDCl_3$): δ 22.3, 44.0, 68.8, 70.1, 125.9, 127.9, 128.7, 142.6, 172.0. Chromatography: DAICEL CHIRALPAK AS-H, hexane/2-propanol (97:3, 0.5 mL/min), retention time: 23.1 min (minor), 24.8 min (major), 93% ee; absolute configuration was tentatively assigned to *S*, as analogy of the ethyl ester; FAB-HRMS: [M+H^+] *m/z*, found: 209.1179; calcd ($C_{12}H_{17}O_3$): 209.1178; $[\alpha]_D^{24}$ = –39.6 (c = 0.94, $CHCl_3$), 93% ee determined by chiral LC; Lit.[S3], $[\alpha]^{20}_D$ = +39.4 (c = 1.1, $CHCl_3$) for *R*.



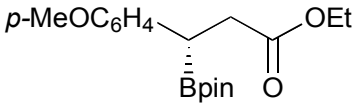
the borylation product from *tert*-butyl cinnamate

(*S*)-*tert*-Butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-phenylpropanoate: colorless oil. IR (film): 2977, 1728, 1369, 1140, 846, 701 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.17 (s, 6H), 1.23 (s, 6H), 1.41 (S, 9H), 2.60 (dd, *J* = 5.5, 15.0 Hz, 1H), 2.68 (dd, *J* = 5.5, 9.9 Hz, 1H), 2.80 (dd, *J* = 9.9, 15.0 Hz, 1H), 7.05-7.30 (m, 5H) ppm; ^{13}C NMR (75 MHZ, $CDCl_3$): δ 24.8, 24.9, 28.4, 38.6, 80.2, 83.5, 125.4, 128.2, 128.3, 141.3, 172.6; *C*[B] was not detected; FAB-HRMS: [M+H^+] *m/z*, found: 333.2244; calcd ($C_{19}H_{30}O_4B$): 333.2241.



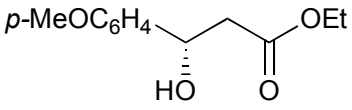
6

(*S*)-*tert*-Butyl 3-hydroxy-3-phenylpropanoate: colorless oil. IR (film): 3443 (broad), 1730, 1368, 1149 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.46 (s, 9H), 2.60-2.74 (m, 2H), 3.45 (d, *J* = 3.3 Hz, 1H), 5.09 (ddd, *J* = 3.3, 4.5, 7.8 Hz, 1H, O*H*), 7.26-7.42 (m, 5H) ppm; ^{13}C NMR (75 MHZ, $CDCl_3$): δ 28.4, 44.5, 70.5, 81.7, 125.7, 127.6, 128.4, 142.5, 171.7; Chromatography: DAICEL CHIRALPAK AS-H, hexane/2-propanol (99:1, 1.0 mL/min), retention time: 41.4 min (minor), 45.2 min (major), 86% ee (Table 1, entry 9); FAB-HRMS: [M+H^+] *m/z*, found: 223.1337; calcd ($C_{13}H_{19}O_3$): 223.1334; $[\alpha]_D^{24}$ = –37.7 (c = 1.2, $CHCl_3$), 85% ee (Table 1, entry 10) determined by chiral LC.



7

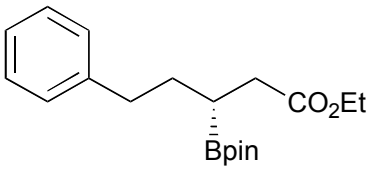
(*S*)-Ethyl 3-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propanoate): colorless oil. IR (film): 2981, 1731, 1369, 1249, 1033, 840 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.18 (s, 6H), 1.23 (s, 6H), 1.23 (t, *J* = 7.2 Hz, 3H), 2,58-2.73 (m, 2H), 2.80-2.90 (m, 1H), 3.77 (s, 3H), 4.10 (m, 2H), 6.81 (m, 2H), 7.14 (m, 2H) ppm; ^{13}C NMR (75 MHZ, $CDCl_3$): δ 14.5, 24.7, 24.8, 37.8, 55.2, 60.4, 83.4, 113.7, 128.9, 133.1, 157.3, 173.1; *C*[B] was not observed; FAB-HRMS: [$M^{\bullet+}$] *m/z*, found: 334.1943; calcd ($C_{18}H_{27}O_5B$): 334.1955; $[\alpha]_D^{26}$ = +31.5 (c = 1.0, $CHCl_3$), 94% ee of the corresponding alcohol.



the alcohol from **7**

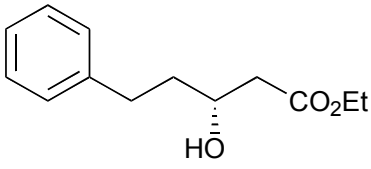
(*S*)-Ethyl 3-hydroxy-3-(4-methoxyphenyl)propanoate: colorless oil. IR (film): 3475 (broad), 2980, 1728, 1610, 1511, 1248, 1173, 1032, 838 cm^{-1}; ^1H NMR (300 MHz,

$CDCl_3$): δ 1.26 (t, *J* = 7.2 Hz, 3H), 2.60-2.80 (m, 2H), 3.80 (s, 3H), 4.17 (q, *J* = 7.2 Hz, 2H), 5.08 (m, 1H), 6.87 (m, 2H), 7.28 (m, 2H); ^{13}C NMR (75 MHZ, $CDCl_3$): δ 14.3, 42.4, 55.3, 60.8, 69.9, 113.7, 126.7, 134.5, 158.8, 172.0. Chromatography: DAICEL CHIRALPAK AS-H, hexane/2-propanol (95:5, 1.0 mL/min), retention time: 14.7 min (minor), 18.4 min (major), 94% ee; FAB-HRMS: [M+Na^+] *m/z*, found: 247.0944; calcd ($C_{12}H_{16}O_4Na$): 247.0946; $[\alpha]_D^{26}$ = –28.6 (c = 1.0, $CHCl_3$), 94% ee by chiral LC; Lit.[S4], $[\alpha]_D$ = +34 (c = 2.0, $CHCl_3$), 86% ee for *R*.



9

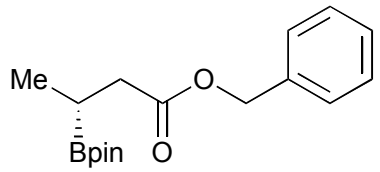
(*R*)-Ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-phenylpentanoate: colorless oil. IR (film): 2981, 2930, 1731, 1378, 1320, 1146 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (t, *J* = 7.2 Hz, 3H), 1.26 (s, 6H), 1.27 (s, 6H), 1.40 (m, 1H), 1.67 (m, 1H), 1.79 (m, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 7.12-7.20 (m, 3H), 7.22-7.30 (m, 2H) ppm; ^{13}C NMR (75 MHZ, $CDCl_3$): δ 14.5, 20.0 (*C*-B), 24.9, 25.0, 32.8, 35.2, 35.9, 60.3, 83.2, 125.5, 128.1, 128.2, 142.3, 173.5; FAB-HRMS: [M+H^+] *m/z*, found: 333.2244; calcd ($C_{19}H_{30}O_4B$): 333.2241; $[\alpha]_D^{26}$ = +3.18 (c = 1.03, $CHCl_3$), 86% ee of the corresponding alcohol.



the alcohol from **9**

(*R*)-Ethyl 3-hydroxy-5-phenylpentanoate: colorless oil. IR (film): 3454, 2980, 1726, 1186, 1034 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.28 (t, *J* = 6.9 Hz, 3H), 1.72-1.92 (m, 2H), 2.40-2.56 (m, 2H), 2.70 (m, 1H), 2.80 (m, 1H), 3.12 (d, *J* = 4.2 Hz, 1H), 4.02 (m, 1H), 4.17 (q, *J* = 6.9 Hz, 2H), 7.16-7.21 (m, 3H), 7.24-7.29 (m, 2H) ppm; ^{13}C NMR (75 MHZ, $CDCl_3$): δ 14.3, 31.9, 38.2, 41.4, 60.7, 67.2, 125.6, 128.1, 128.2, 141.5, 172.6. Chromatography: DAICEL CHIRALCEL OD-H, hexane/2-propanol (90:10, 1.0

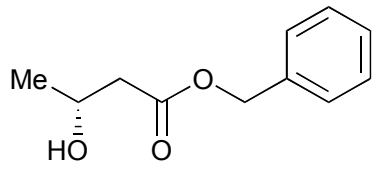
mL/min), retention time: 24.7 min (minor), 29.3 min (major), 90% ee; FAB-HRMS: [M+Na$^+$] *m/z*, found: 245.1148 ; calcd ($C_{13}H_{18}O_3Na$): 245.1154; $[\alpha]_D^{26}$ = +0.58 (c = 1.0, $CHCl_3$), 86% ee determined by chiral LC; Lit.[S5], $[\alpha]^{25}_D$ = +1.0 (c = 1.0, $CHCl_3$), 99% ee for *R*.



10

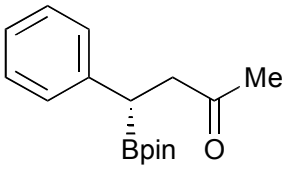
10

(*R*)-Benzyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate: colorless oil. IR (film): 2975, 1735, 1380, 1148 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.02 (d, *J* = 7.5 Hz, 3H), 1.22 (s, 6H), 1.23 (s, 6H), 1.42 (m, 1H), 2.42 (dd, *J* = 6.6, 16.5 Hz, 1H), 2.51 (dd, *J* = 7.8 Hz, 16.5 Hz, 1H), 5.08 (d, *J* = 14.4 Hz, 1H), 5.13 (d, *J* = 14.4 Hz, 1H), 7.25-7.40 (m, 5H) ppm; ^{13}C NMR (75 MHZ, $CDCl_3$): δ 15.3, 24.8, 24.9, 33.8 (*C*-B), 37.8, 66.0, 83.1, 127.8, 127.9, 128.2, 136.0, 173.3; FAB-HRMS: [M+H$^+$] *m/z*, found: 305.1938; calcd ($C_{17}H_{26}O_4B$): 305.1927; $[\alpha]_D^{27}$ = –2.38 (c = 0.99, $CHCl_3$), 82% ee of the corresponding alcohol.



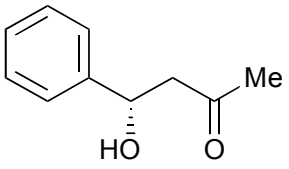
the alcohol from **10**

(*R*)-Benzyl 3-hydroxybutanoate: colorless oil. IR (film): 3430, 2970, 1729, 1382, 1290, 1172 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.24 (d, *J* = 6.3 Hz, 3H), 2.44-2.59 (m, 2H), 2.98 (broad, 1H), 4.22 (m, 1H), 5.16 (s, 2H), 7.33-7.40 (m, 5H) ppm; ^{13}C NMR (75 MHZ, $CDCl_3$): δ 22.6, 42.9, 64.3, 66.5, 128.0, 128.2, 128.4, 135.3, 172.3. Chromatography: DAICEL CHIRALCEL OD-H, hexane/2-propanol (98:2, 0.5 mL/min), retention time: 39.5 min (major), 56.1 min (minor), 82% ee; FAB-HRMS: [M+H$^+$] *m/z*, found: 195.1017; calcd ($C_{11}H_{15}O_3$): 195.1021; $[\alpha]_D^{27}$ = –26.0 (c = 1.0, $CHCl_3$), 82% ee; Lit.[S6], $[\alpha]_D$ = +29.0 (c = 1.0, $CHCl_3$), 94% ee for *S*.



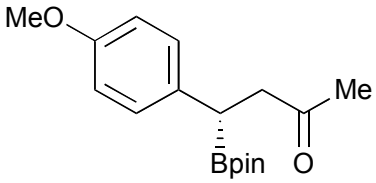
11

(*S*)-4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-4-phenylbutan-2-one: colorless oil. IR (film): 2981, 1711, 1365, 1321, 1145, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.17 (S, 6H), 1.23 (s, 6H), 2.15 (s, 3H), 2.64 (m, 1H), 2.84 (dd, *J* = 5.1, 18.3 Hz, 1H), 3.05 (dd, *J* = 11.0, 18.3 Hz, 1H), 7.10-7.30 (m, 5H) ppm; ^{13}C NMR (75 MHZ, $CDCl_3$): δ 24.67, 24.69, 29.8, 47.6, 83.4, 125.3, 128.0, 128.3, 141.4, 207.9; *C*[B] was not observed; FAB-HRMS: [M+H^+] *m/z*, found: 275.1818; calcd ($C_{16}H_{24}O_3B$): 275.1822; $[\alpha]_D^{26}$ = +21.1 (c = 1.0, $CHCl_3$), 56% ee of the corresponding alcohol.



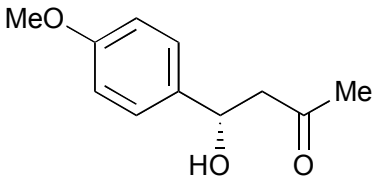
the alcohol from **11**

(*S*)-4-Hydroxy-4-phenylbutan-2-one: colorless oil. IR (film): 3452 (broad), 1707, 1362, 1059, 754, 697 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.21 (s, 3H), 2.80-2.90 (m, 2H), 3.29 (broad s, 1H), 5.16 (m, 1H), 7.20-7.40 (m, 5H) ppm; ^{13}C NMR (75 MHZ, $CDCl_3$): δ 30.9, 52.0, 69.8, 125.4, 127.5, 128.3, 142.4, 208.7. Chromatography: DAICEL CHIRALPAK AS-H, hexane/2-propanol (95:5, 1.5 mL/min), retention time: 10.8 min (minor), 12.6 min (major), 56% ee; FAB-HRMS: [M+Na^+] *m/z*, found: 187.0742; calcd ($C_{10}H_{12}O_2Na$): 187.0735; $[\alpha]_D^{26}$ = –35.6 (c = 1.0, $CHCl_3$), 56% ee; Lit.[S7], $[\alpha]^{20}_D$ = -51.3 (c = 1.0, $CHCl_3$), 79% ee for *S*; also see, Lit.[S8].



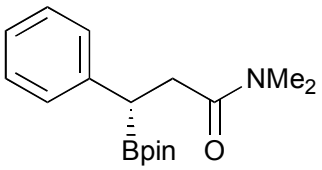
12

(*S*)-4-(4-Methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-one: colorless oil. IR (film): 2981, 1710, 1364, 1249, 1145, 833 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.29 (s, 6H), 1.35 (s, 6H), 2.25 (s, 3H), 2.70 (dd, *J* = 5.4, 10.5 Hz , 1H), 2.92 (dd, *J* = 5.4, 18.0 Hz, 1H), 3.11 (dd, *J* = 10.5, 18.0 Hz, 1H), 3.89 (s, 3H), 6.92 (m, 2H), 7.24 (m, 2H) ppm; ^{13}C NMR (75 MHZ, $CDCl_3$): δ 24.61, 24.63, 25.8 (broad, *C*[B]), 29.7, 47.6, 55.1, 83.2, 113.7, 128.8, 133.2, 157.2, 208.0; FAB-HRMS: [$M^{\bullet+}$] *m/z*, found: 304.1844; calcd ($C_{17}H_{25}O_4B$): 304.1849; $[\alpha]_D^{26}$ = +23.3 (c = 1.0, $CHCl_3$), 70% ee of the corresponding alcohol.



the alcohol from **12**

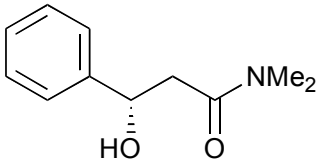
(*S*)-4-Hydroxy-4-(4-methoxyphenyl)butan-2-one. colorless oil. IR (film): 3500 (broad), 2929, 1707, 1513, 1249, 1173, 832 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.20 (s, 3H), 2.78 (dd, *J* = 3.6, 17.7 Hz, 1H), 2.89 (dd, *J* = 9.0, 17.7 Hz, 1H), 3.80 (s, 3H), 5.10 (m, 1H), 6.87 (m, 2H), 7.27 (m, 2H) ppm; ^{13}C NMR (75 MHZ, $CDCl_3$): δ 30.9, 52.0, 55.3, 69.5, 113.7, 126.7, 134.6, 158.8, 208.7. Chromatography: DAICEL CHIRALPAK AD-H, hexane/2-propanol (95:5, 1.5 mL/min), retention time: 29.7 min (minor), 33.2 min (major), 70% ee; FAB-HRMS: [$M^{\bullet+}$] *m/z*, found: 194.0940; calcd ($C_{11}H_{14}O_3$): 194.0943; $[\alpha]_D^{26}$ = –33.9 (c = 1.0, $CHCl_3$), 70% ee by chiral LC.



13

(*S*)-*N*,*N*-Dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-phenylpropanamide: white solids. IR (KBr): 2978, 1642, 1361, 1139, cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.14 (s, 12H), 2.60 (m, 1H), 2.83 (m, 1H), 2.95 (m, 1H), 2.99 (s, 3H), 3.01 (s, 3H), 7.05-7.16 (m, 5H) ppm; ^{13}C NMR (75 MHZ, $CDCl_3$): δ 24.8, 24.9, 30.8 (*C*-B), 36.1, 37.3, 38.2, 82.0, 124.8, 127.9, 128.1, 142.8, 174.4; FAB-HRMS: [$M^{\bullet+}$]

m/z, found: 303.2011; calcd ($C_{17}H_{26}O_3NB$): 303.2009; $[\alpha]_D^{27}$ = +38.4 (c = 1.0, $CHCl_3$), 97.3% ee of the corresponding alcohol.



the alcohol from **13**

(*S*)-3-Hydroxy-*N*,*N*-dimethyl-3-phenylpropanamide: colorless oil. IR (film): 3413 (broad), 1623, 1406 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.80-2.88 (m, 3H), 2.95 (s, 3H), 2.99 (s, 3H), 4.80 (s, 1H, O*H*), 5.14 (m, 1H, C*H*OH), 7.24-7.46 (m, 5H) ppm; ^{13}C NMR (75 MHZ, $CDCl_3$): δ 35.3, 37.2, 42.0, 70.4, 125.5, 127.3, 128.2, 142.7, 171.9. Chromatography: DAICEL CHIRALCEL OD-H, hexane/2-propanol (95:5, 0.5 mL/min), retention time: 44.0 min (major), 51.6 min (minor), 97% ee; FAB-HRMS: $[M^+H^+]$ *m/z*, found: 194.1175; calcd ($C_{11}H_{16}NO_2$): 194.1181; $[\alpha]_D^{26}$ = –90.5 (c = 1.07, $CHCl_3$), 97.3% ee; Lit.[S9], $[\alpha]_D^{24}$ = –87.9 (c = 0.40, $CHCl_3$), 96% ee for *S*.

References:

S1 J.-E. Lee, J. Yun, *Angew. Chem. Int. Ed.*, 2008, **47**, 145-147; (*b*) H.-S. Sim, X. Feng, J. Yun, *Chem. Eur. J.*, 2009, **15**, 1939-1943.

S2 V. Raovelomanana-Vidal, C. Girard, R. Touati, J. P. Tranchier, B. B. Hassine, J. P. Genêt, *Adv. Synth. Catal.,* 2003, **345**, 261-274.

S3 C. Xu, C. Yuan, *Tetrahedron,* 2005, **61**, 2169-2186.

S4 M. Á, Fernández-Ibáñez, B. Maciá, A. J. Minnaard, B. L. Feringa, *Angew. Chem. Int. Ed.,* 2008, **47**, 1317-1319.

S5 S.-I. Kiyooka, M. A. Hena, *Tetrahedron: Asymmetry*, 1996, **7**, 2181-2184.

S6 C. Medson, A. J. Smallridge, M. A. Trewhella, *Tetrahedron: Asymmetry*, 1997, **8**, 1049-1054.

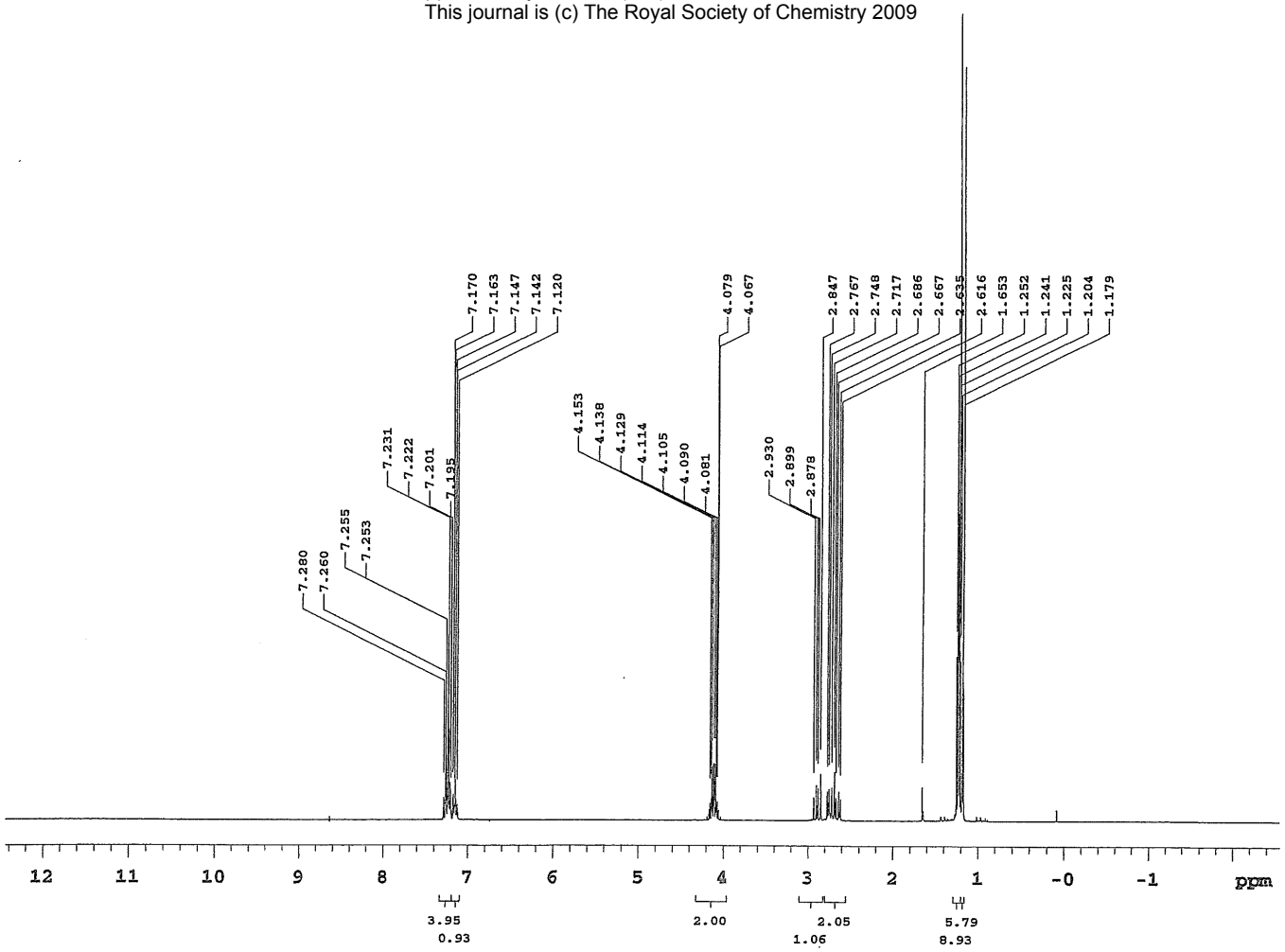
S7 V. D'Elia, H. Zwicknagel, O. Reiser, *J. Org. Chem.,* 2008, **73**, 3262-3265.

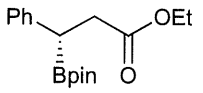
S8 H.-S. Sim, X. Feng, J. Yun, *Chem. Eur. J.*, 2009, **15**, 1939-1943.

S9 H. Chea, H.-S. Sim, J. Yun, *Adv. Synth. Catal.*, 2009, **351**, 855-858.

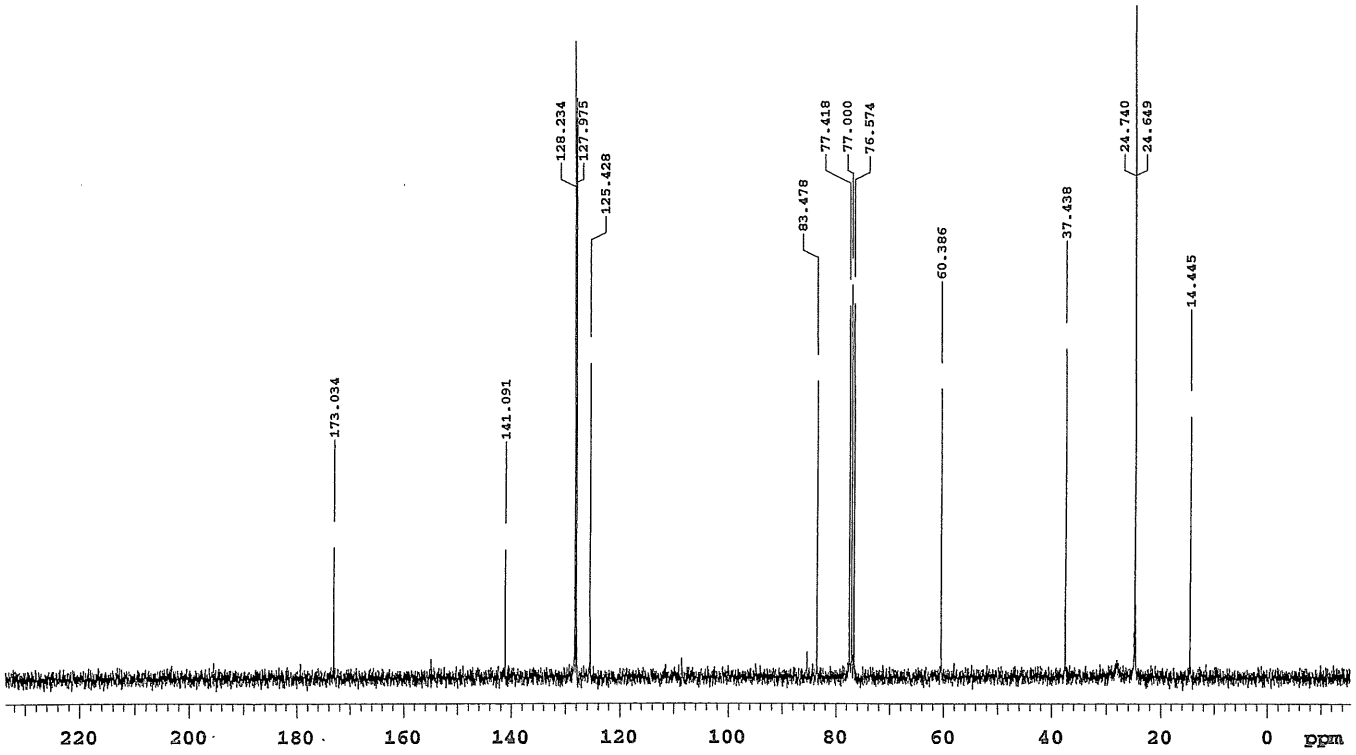
---

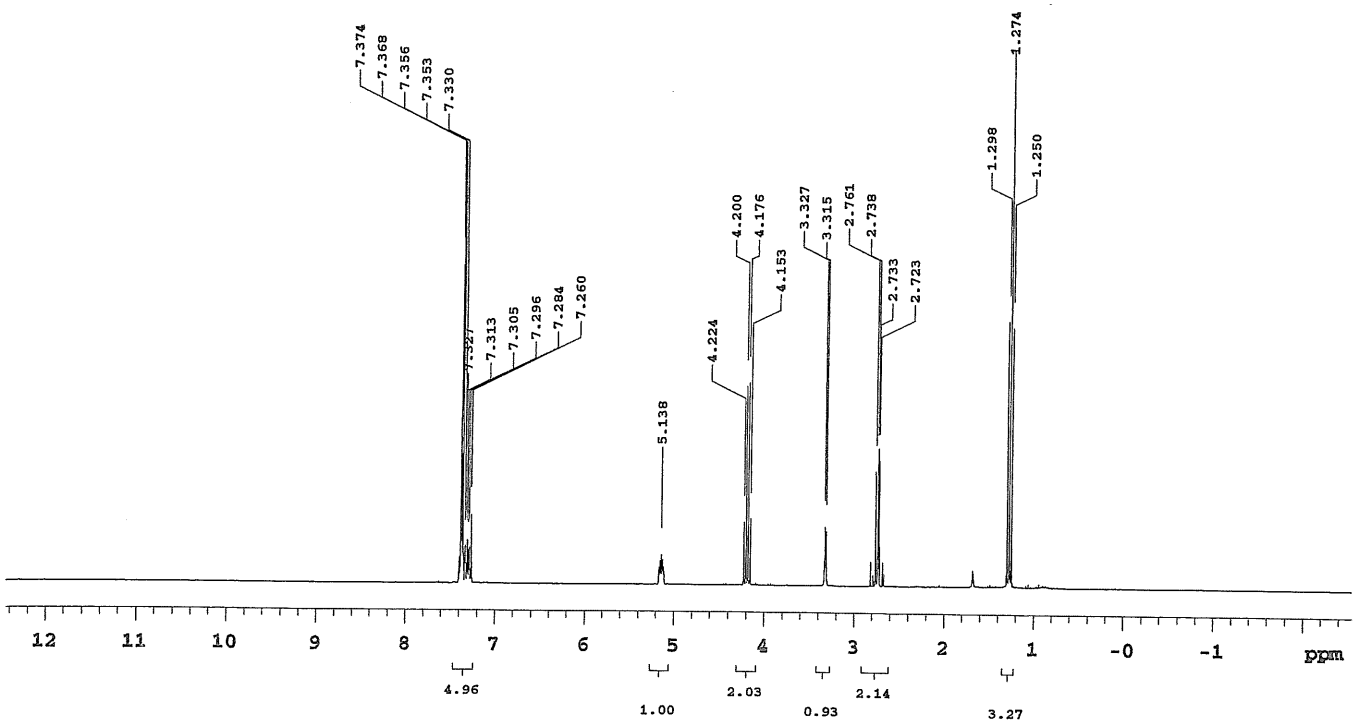
3. ^{1}H and ^{13}C NMR spectra of the products.

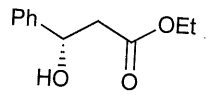

7.280
7.260
7.255
7.253
7.231
7.222
7.201
7.195
7.170
7.163
7.147
7.142
7.120
4.153
4.138
4.129
4.114
4.105
4.090
4.081
4.079
4.067
2.930
2.899
2.878
2.847
2.767
2.748
2.717
2.686
2.667
2.635
2.616
1.653
1.252
1.241
1.225
1.204
1.179
12 11 10 9 8 7 6 5 4 3 2 1 -0 -1 ppm
3.95
0.93
2.00
2.05
1.06
5.79
8.93


Ph
OEt
Bpin
O

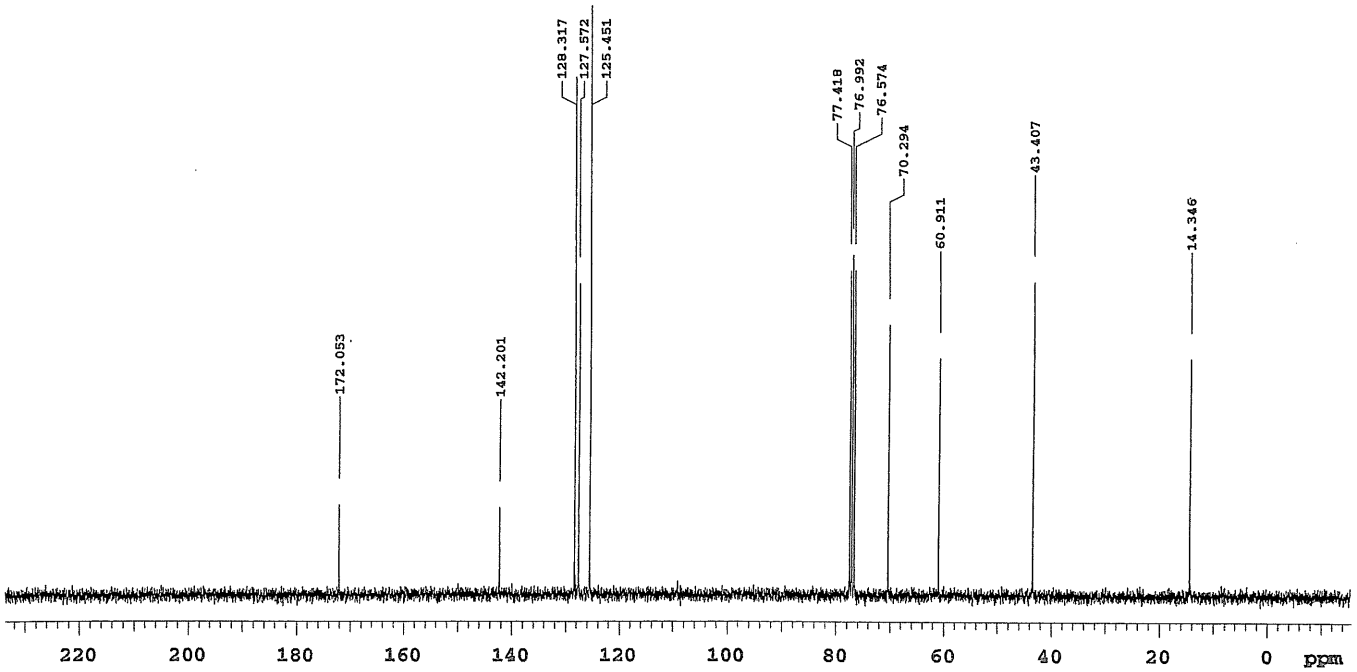
3

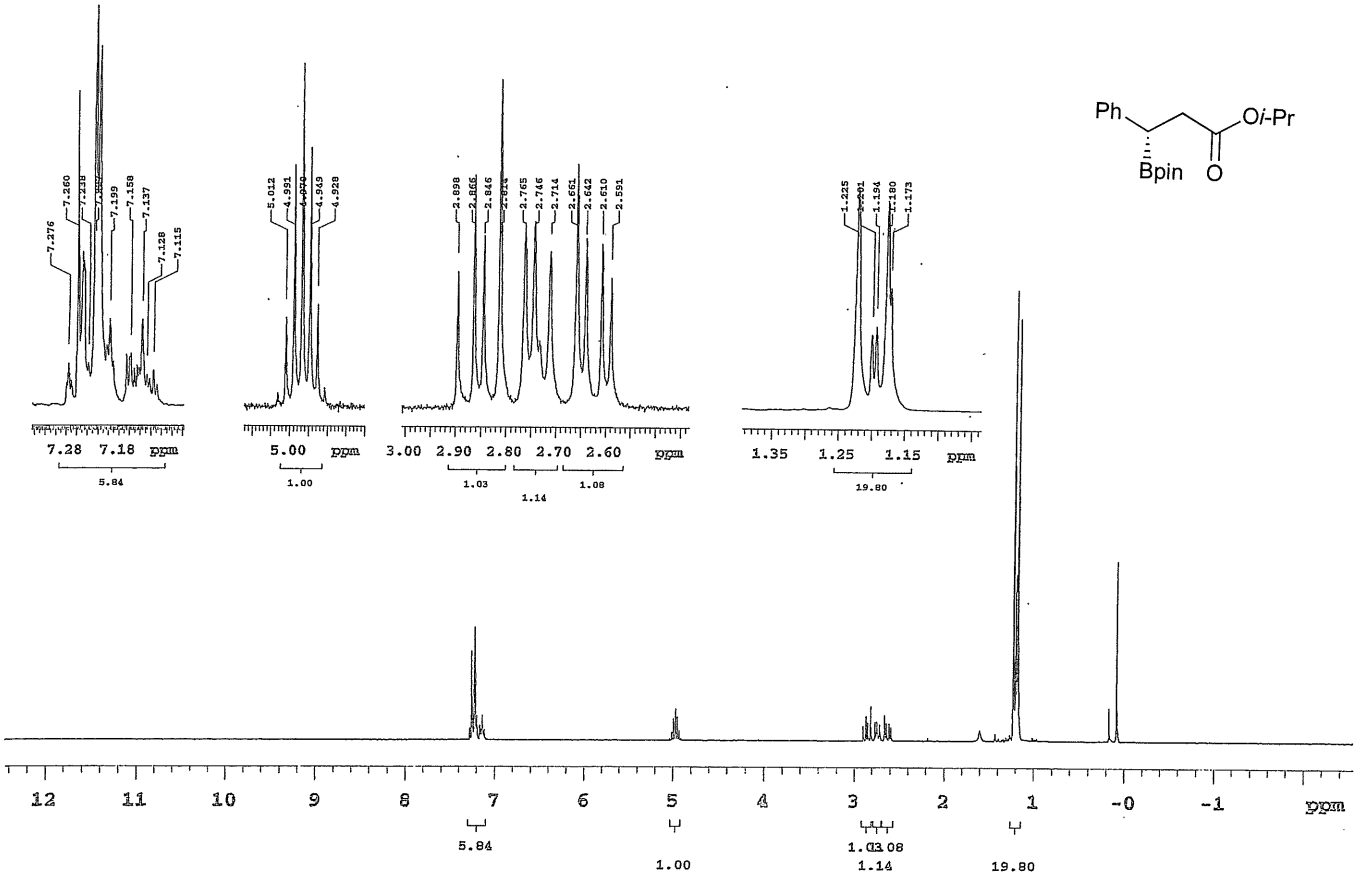

173.034
141.091
128.234
127.975
125.428
83.478
77.418
77.000
76.574
60.386
37.438
24.740
24.649
14.445
220 200 180 160 140 120 100 80 60 40 20 0 ppm

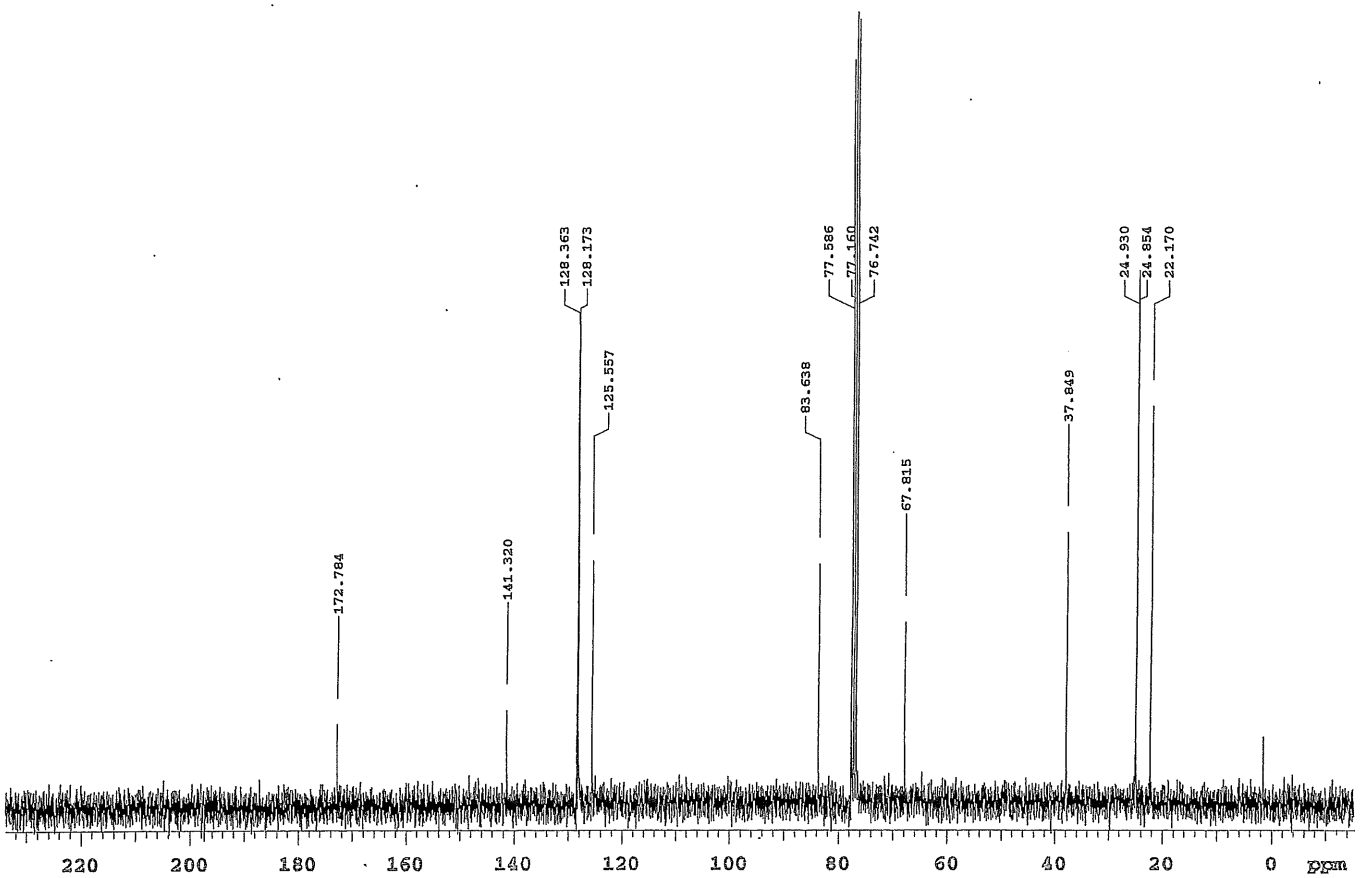

7.374
7.368
7.356
7.353
7.330
7.327
7.313
7.305
7.296
7.284
7.260
5.138
4.224
4.200
4.176
4.153
3.327
3.315
2.761
2.738
2.733
2.723
1.298
1.274
1.250
12 11 10 9 8 7 6 5 4 3 2 1 -0 -1 ppm
4.96
1.00
2.03
0.93
2.14
3.27

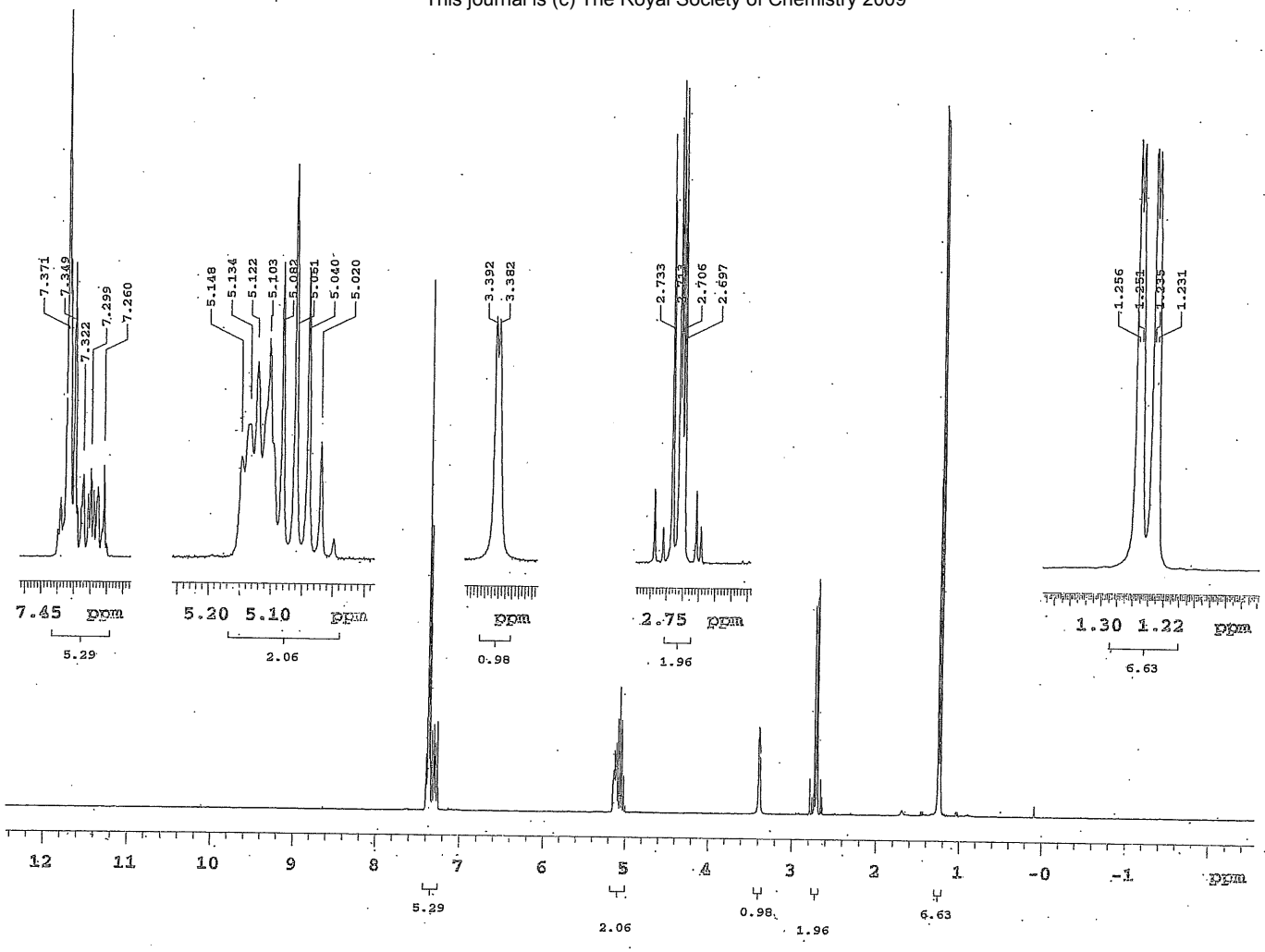

Ph
OEt
HO
O

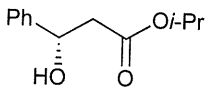
4


172.053
142.201
128.317
127.572
125.451
77.418
76.992
76.574
70.294
60.911
43.407
14.346
220 200 180 160 140 120 100 80 60 40 20 0 ppm

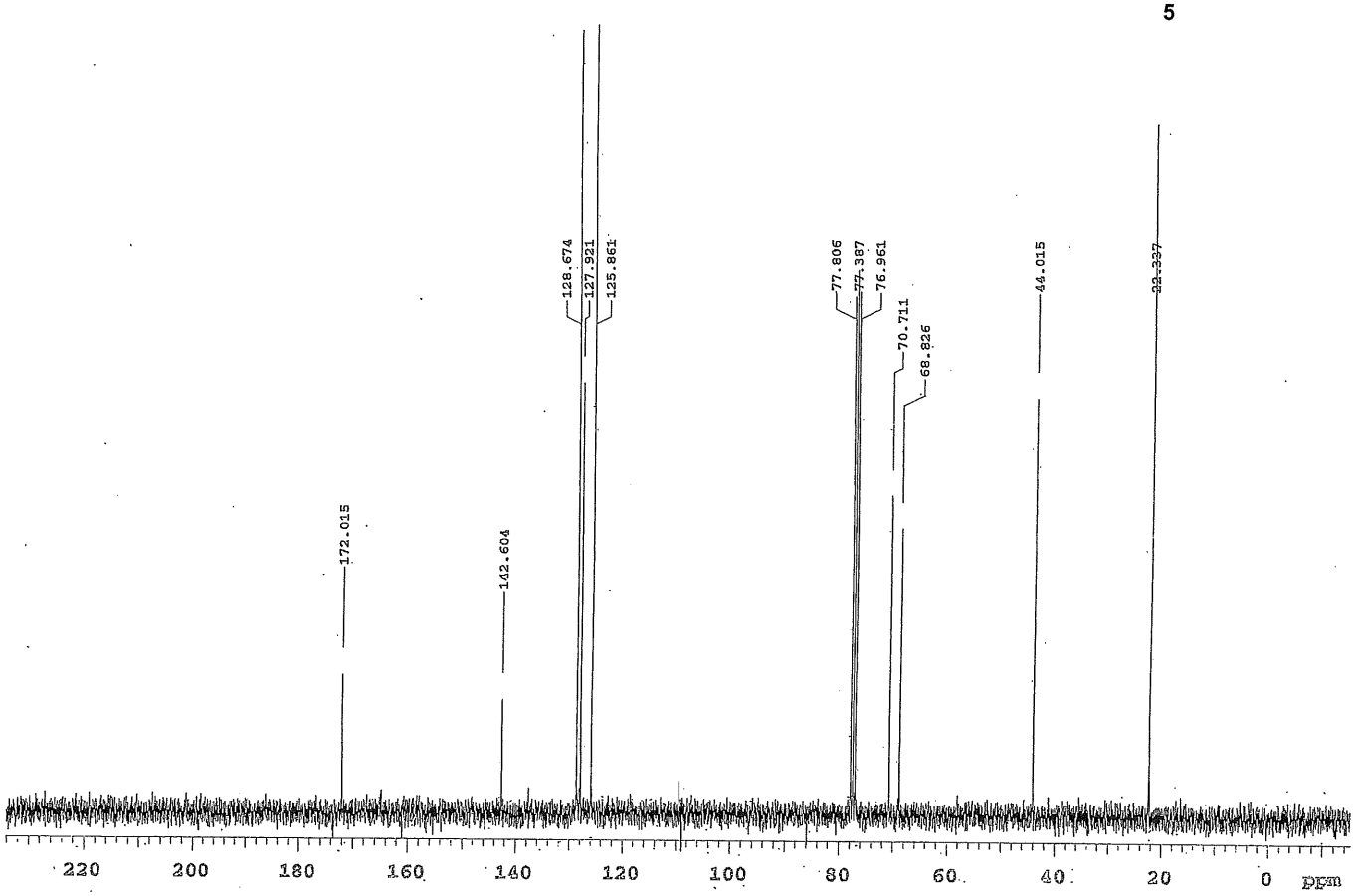

Ph
O*i*-Pr
Bpin
O
7.28 7.18 ppm
5.84
5.00 ppm
1.00
3.00 2.90 2.80 2.70 2.60 ppm
1.03
1.14
1.08
1.35 1.25 1.15 ppm
19.80
12 11 10 9 8 7 6 5 4 3 2 1 -0 -1 ppm
5.84
1.00
1.14
19.80

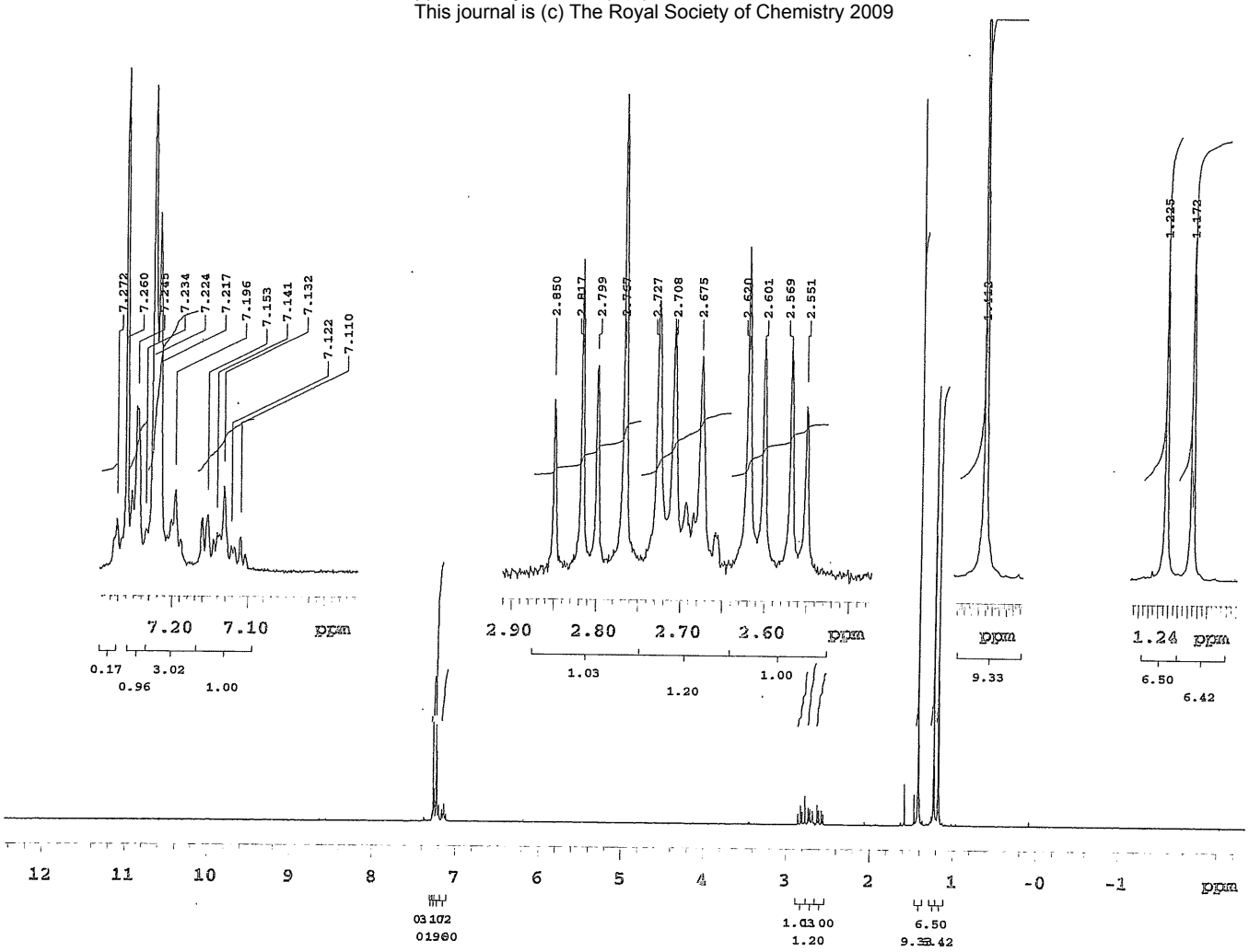

172.784
141.320
128.363
128.173
125.557
83.638
77.586
77.160
76.742
67.815
37.849
24.930
24.854
22.170
220 200 180 160 140 120 100 80 60 40 20 0 ppm

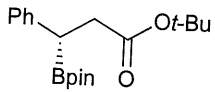

7.371
7.349
7.322
7.299
7.260
7.45 ppm
5.29
5.148
5.134
5.122
5.103
5.082
5.061
5.040
5.020
5.20 5.10 ppm
2.06
3.392
3.382
ppm
0.98
2.733
2.706
2.697
2.75 ppm
1.96
1.256
1.251
1.235
1.231
1.30 1.22 ppm
6.63
12 11 10 9 8 7 6 5 4 3 2 1 -0 -1 ppm
5.29
2.06
0.98
1.96
6.63

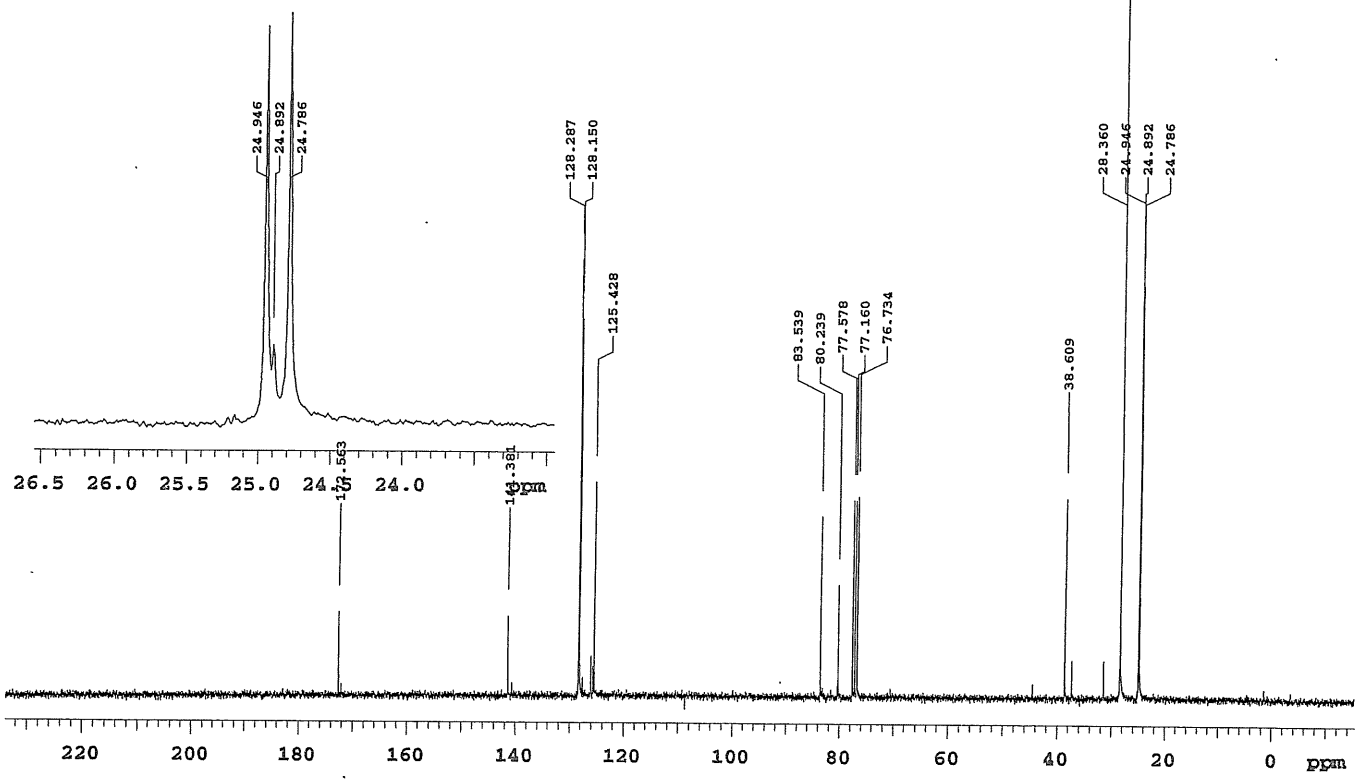

Ph
O*i*-Pr
HO
O

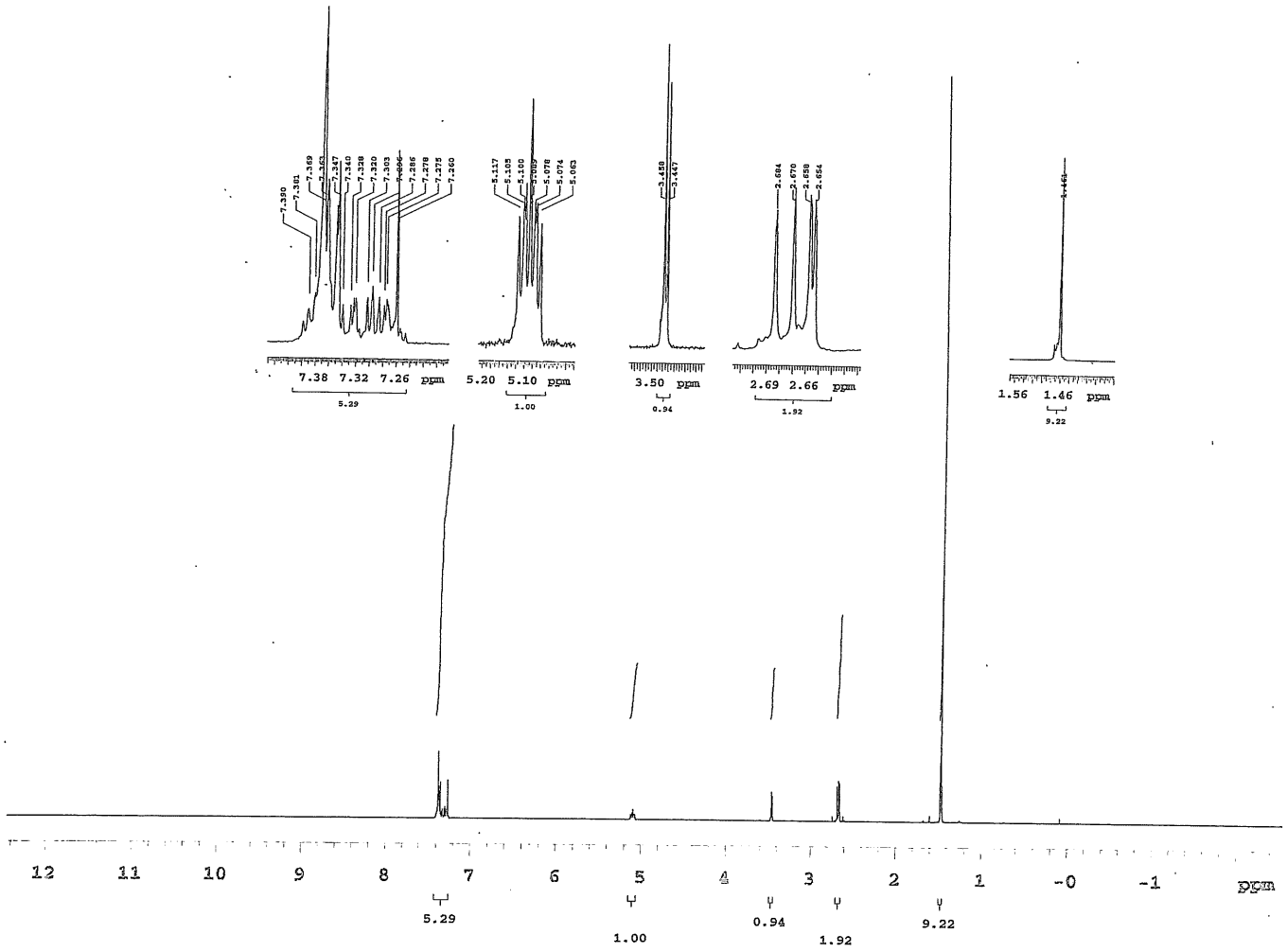
5

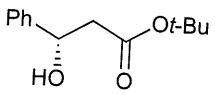

128.674
127.921
125.861
77.806
77.387
76.961
70.711
68.826
44.015
22.337
172.015
142.604
220 200 180 160 140 120 100 80 60 40 20 0 ppm


7.272
7.260
7.246
7.234
7.224
7.217
7.196
7.153
7.141
7.132
7.122
7.110
7.20
7.10
ppm
0.17
3.02
0.96
1.00
2.850
2.817
2.799
2.727
2.708
2.675
2.620
2.601
2.569
2.551
2.90
2.80
2.70
2.60
ppm
1.03
1.00
1.20
1.448
ppm
9.33
1.225
1.172
1.24 ppm
6.50
6.42
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm
03102
01960
1.03 00
1.20
6.50
9.33 42

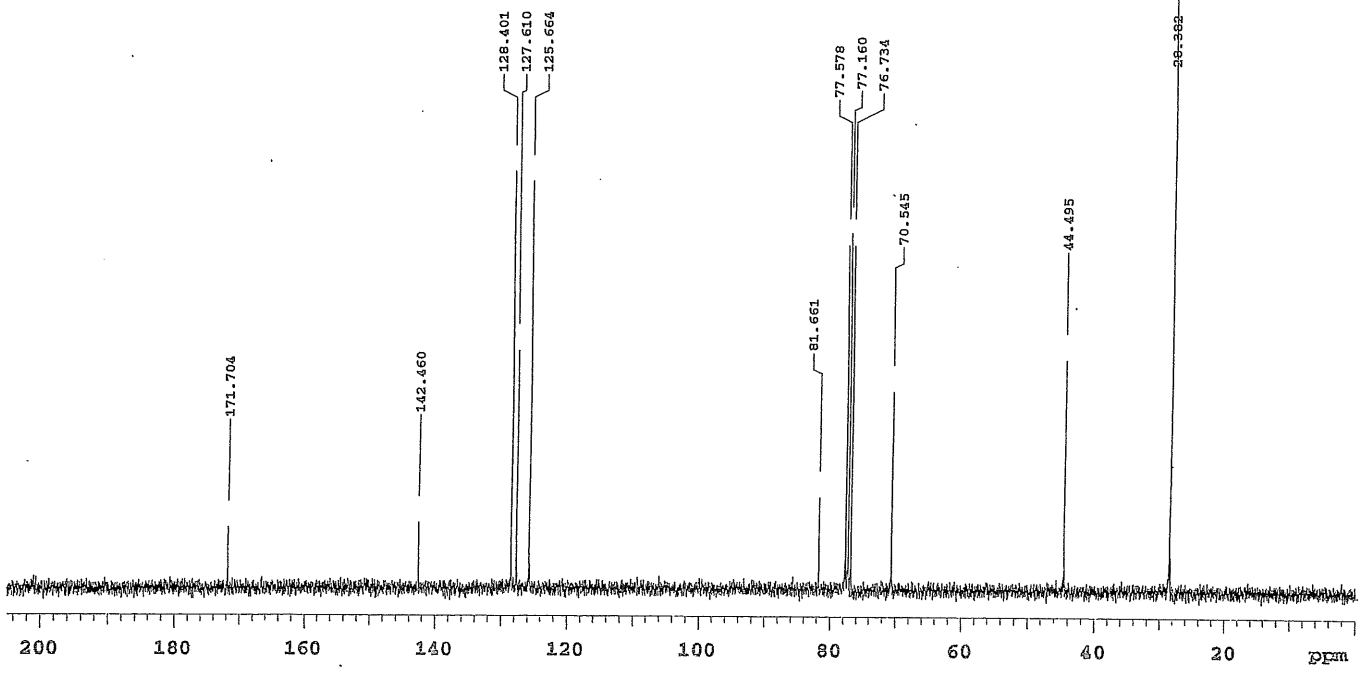

Ph
Ot-Bu
Bpin
O

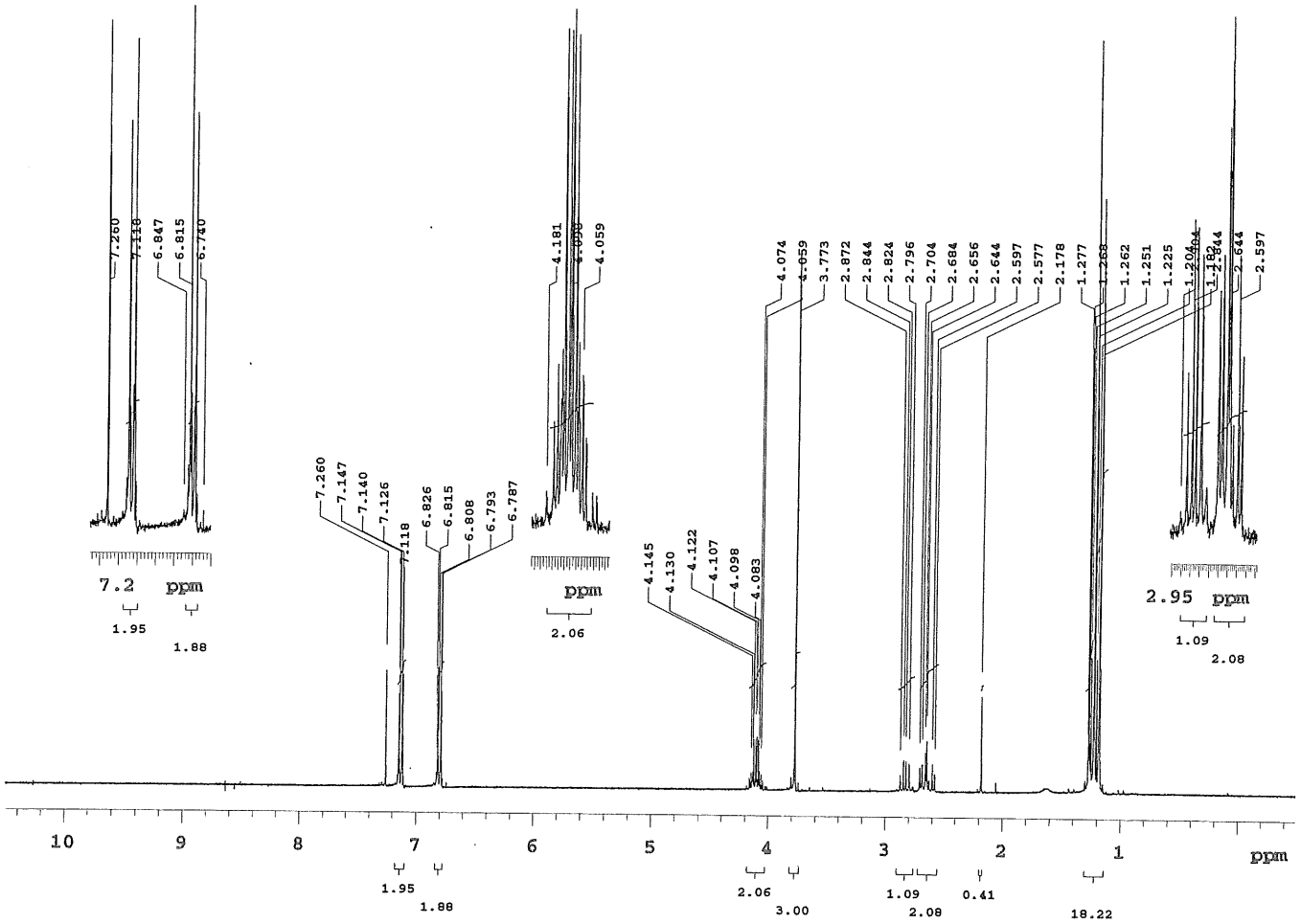

24.946
24.892
24.786
26.5
26.0
25.5
25.0
24.5
24.0
ppm
128.287
128.150
125.428
83.539
80.239
77.578
77.160
76.734
38.609
28.360
24.946
24.892
24.786
220
200
180
160
140
120
100
80
60
40
20
0
ppm

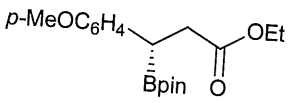

7.38 7.32 7.26 ppm
5.29
5.20 5.10 ppm
1.00
3.50 ppm
0.94
2.69 2.66 ppm
1.92
1.56 1.46 ppm
9.22
12 11 10 9 8 7 6 5 4 3 2 1 -0 -1 ppm
5.29
1.00
0.94
1.92
9.22


Ph
Ot-Bu
HO
O

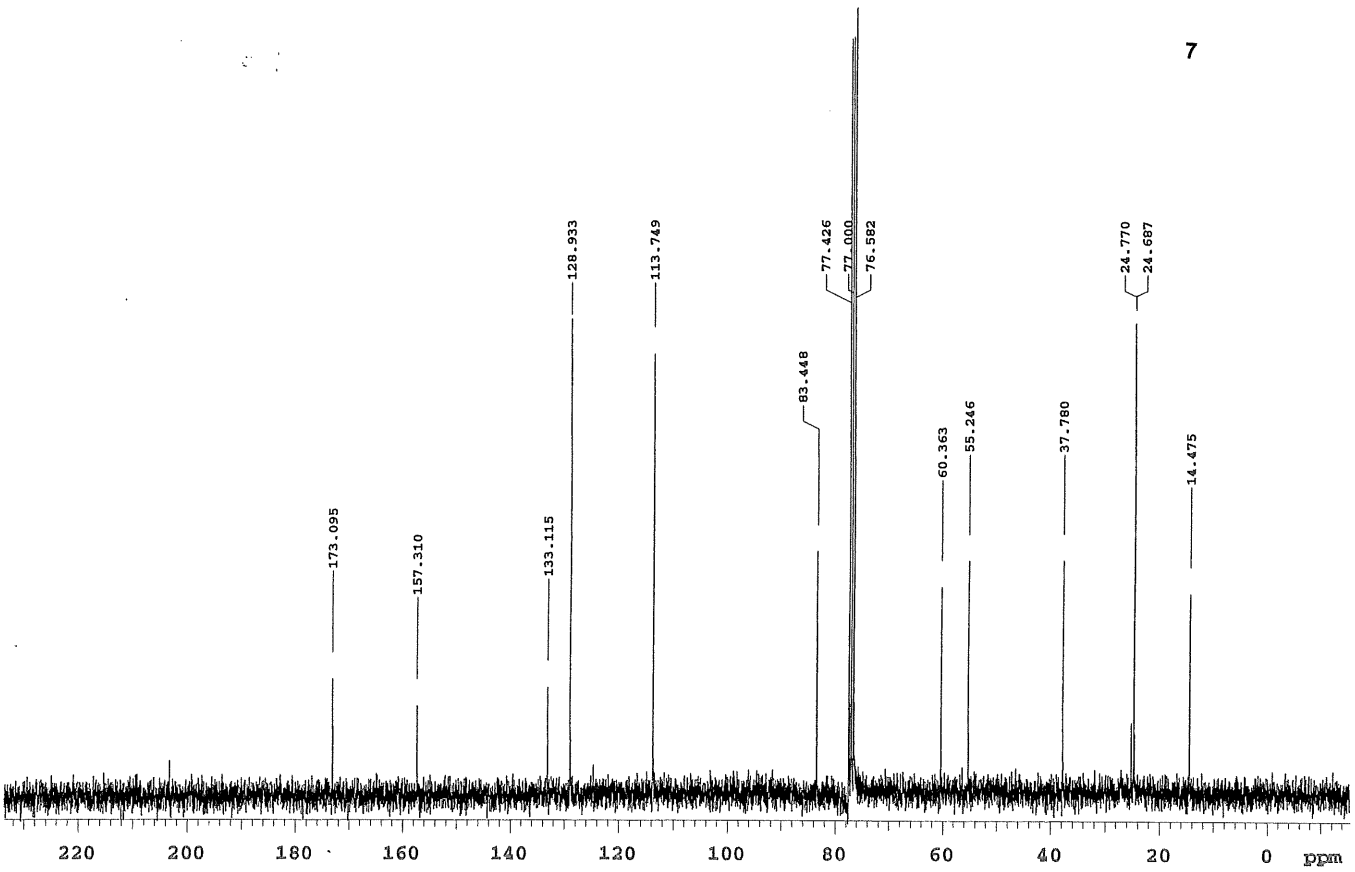
6

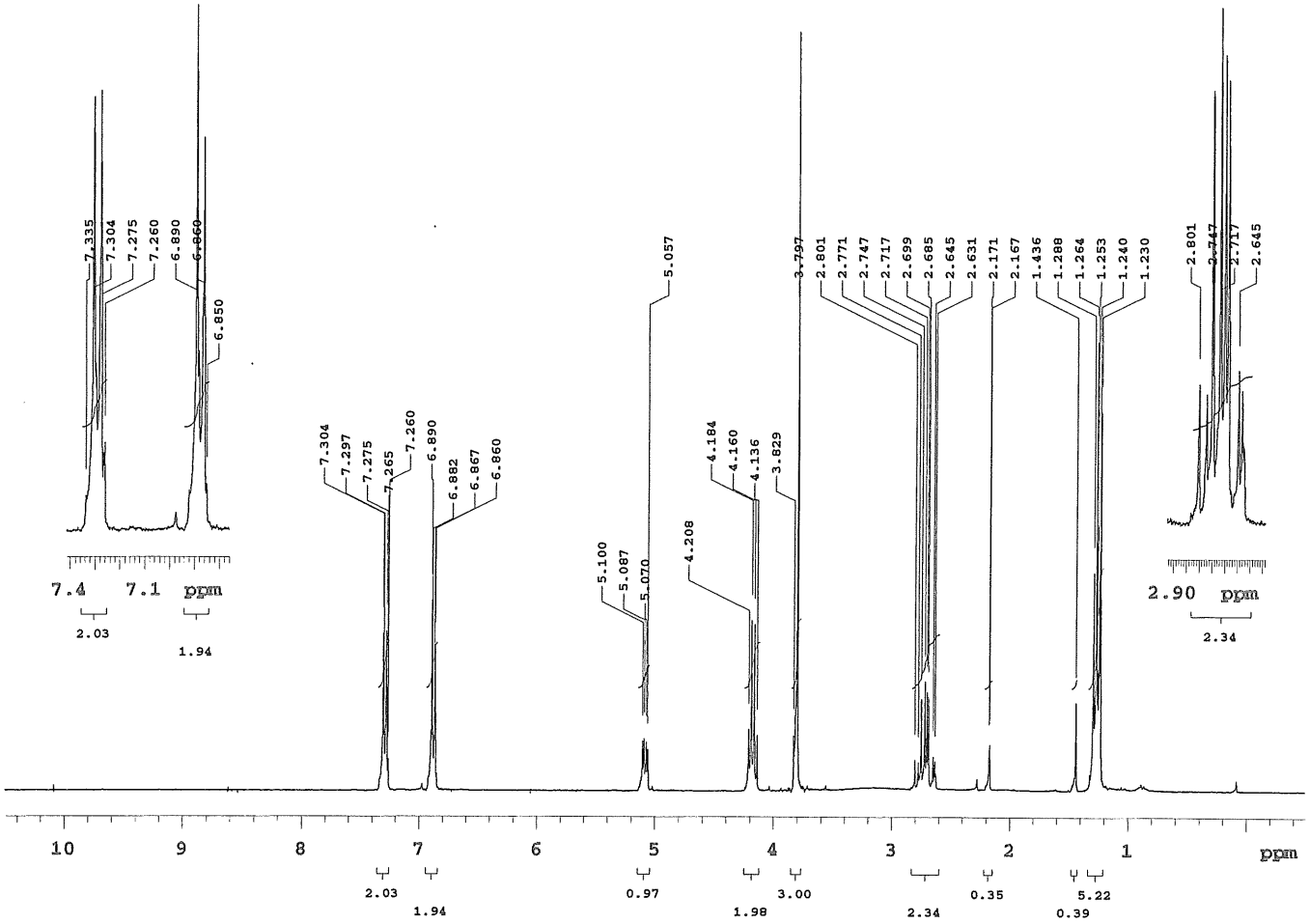

171.704
142.460
128.401
127.610
125.664
81.661
77.578
77.160
76.734
70.545
44.495
28.362
200 180 160 140 120 100 80 60 40 20 ppm

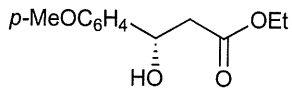

7.260
7.118
6.847
6.815
6.740
7.2 ppm
1.95
1.88
7.260
7.147
7.140
7.126
7.118
6.826
6.815
6.808
6.793
6.787
4.181
4.059
ppm
2.06
4.145
4.130
4.122
4.107
4.098
4.083
4.074
4.059
3.773
2.872
2.844
2.824
2.796
2.704
2.684
2.656
2.644
2.597
2.577
2.178
1.277
1.262
1.251
1.225
2.95 ppm
1.09
2.08
10 9 8 7 6 5 4 3 2 1 ppm
1.95
1.88
2.06
3.00
1.09
2.08
0.41
18.22

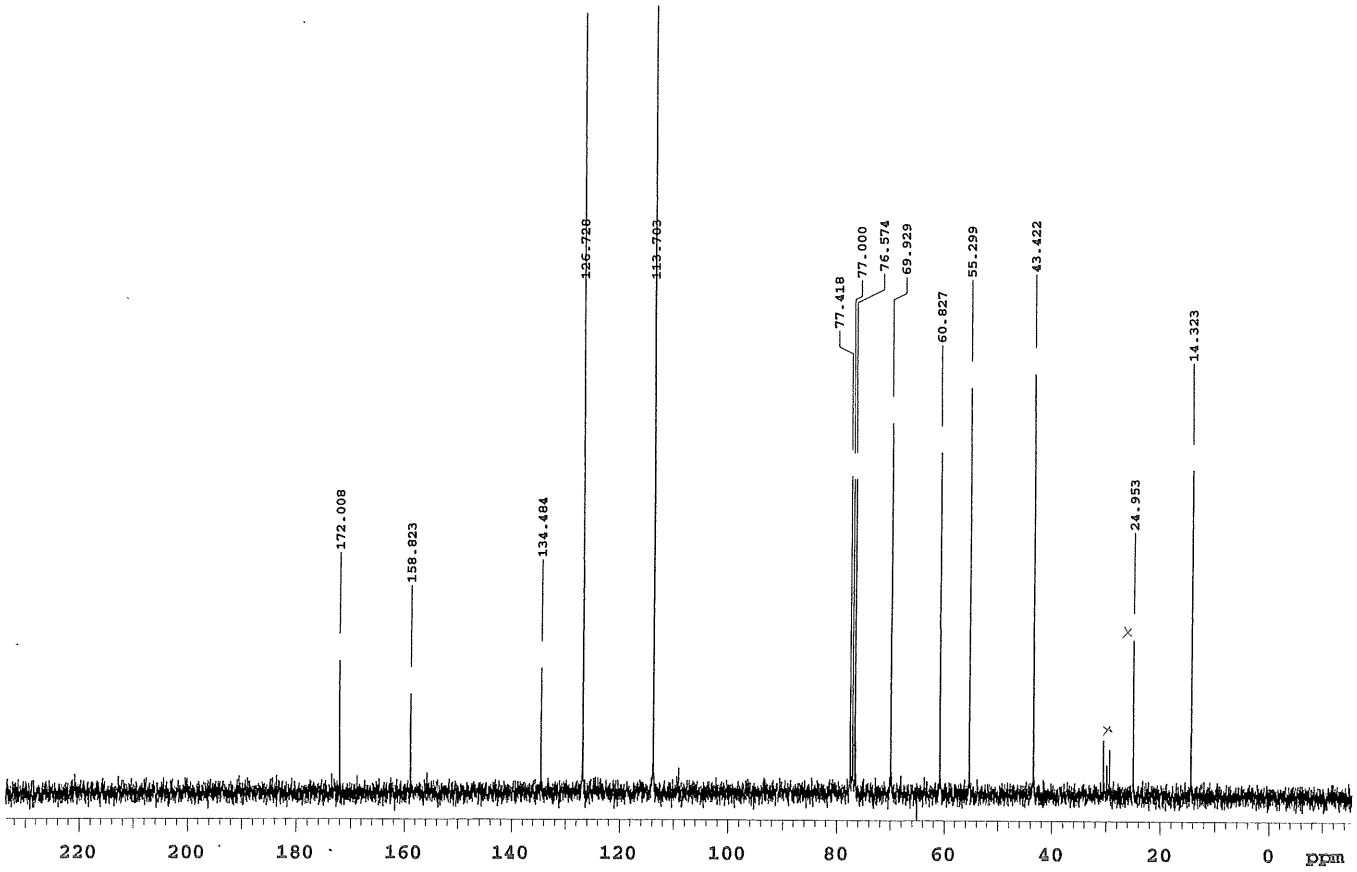

p-MeOC6H4
OEt
Bpin
O

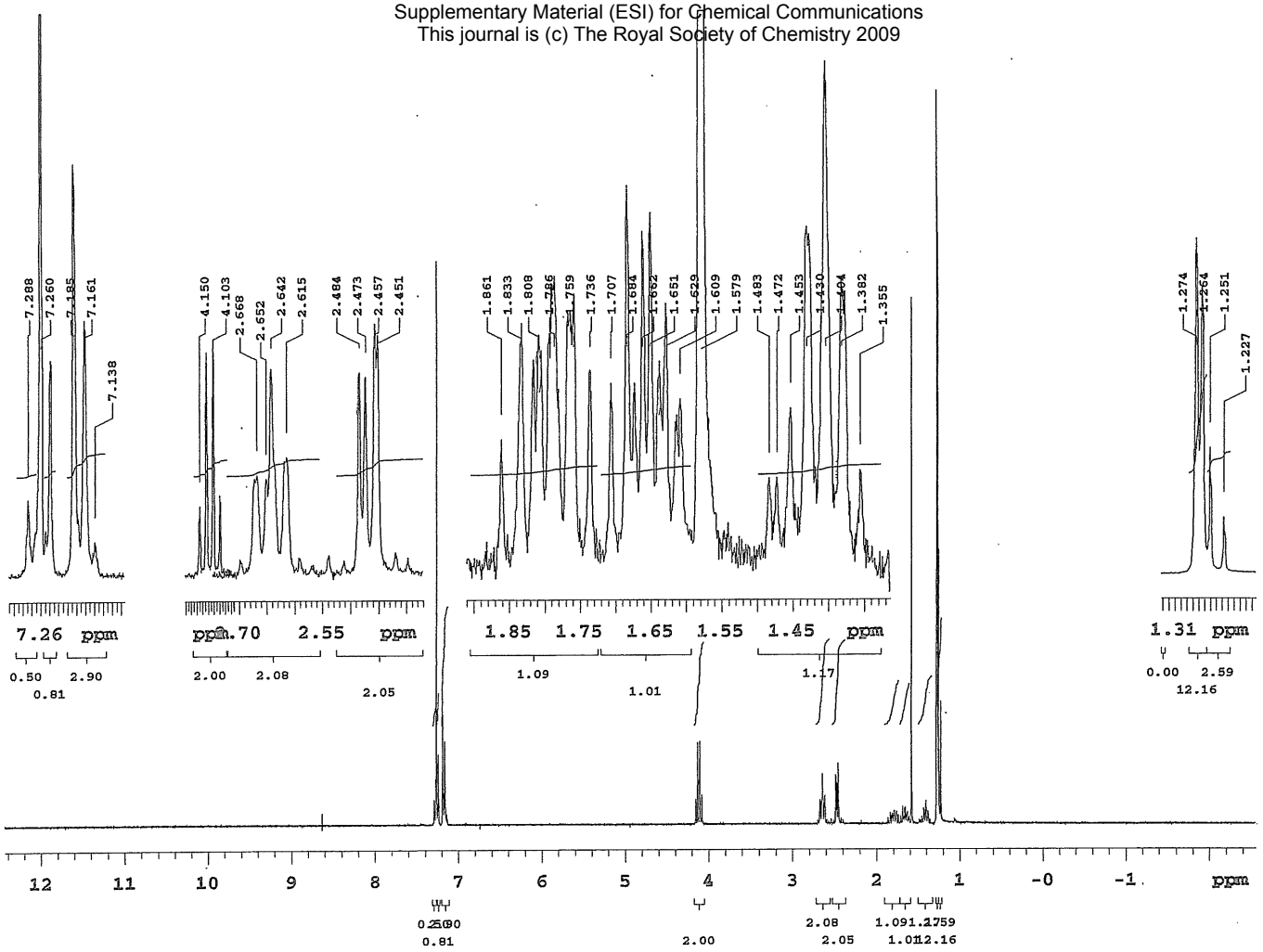
7

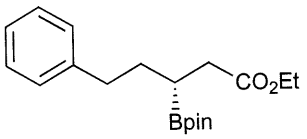

173.095
157.310
133.115
128.933
113.749
83.448
77.426
77.000
76.582
60.363
55.246
37.780
24.770
24.687
14.475
220 200 180 160 140 120 100 80 60 40 20 0 ppm


7.335
7.304
7.275
7.260
6.890
6.860
6.850
7.4
7.1
ppm
2.03
1.94
7.304
7.297
7.275
7.265
7.260
6.890
6.882
6.867
6.860
5.100
5.087
5.070
5.057
4.208
4.184
4.160
4.136
3.829
3.797
2.801
2.771
2.747
2.717
2.699
2.685
2.645
2.631
2.171
2.167
1.436
1.288
1.264
1.253
1.240
1.230
2.90
ppm
2.34
10
9
8
7
6
5
4
3
2
1
ppm
2.03
1.94
0.97
1.98
3.00
2.34
0.35
5.22
0.39

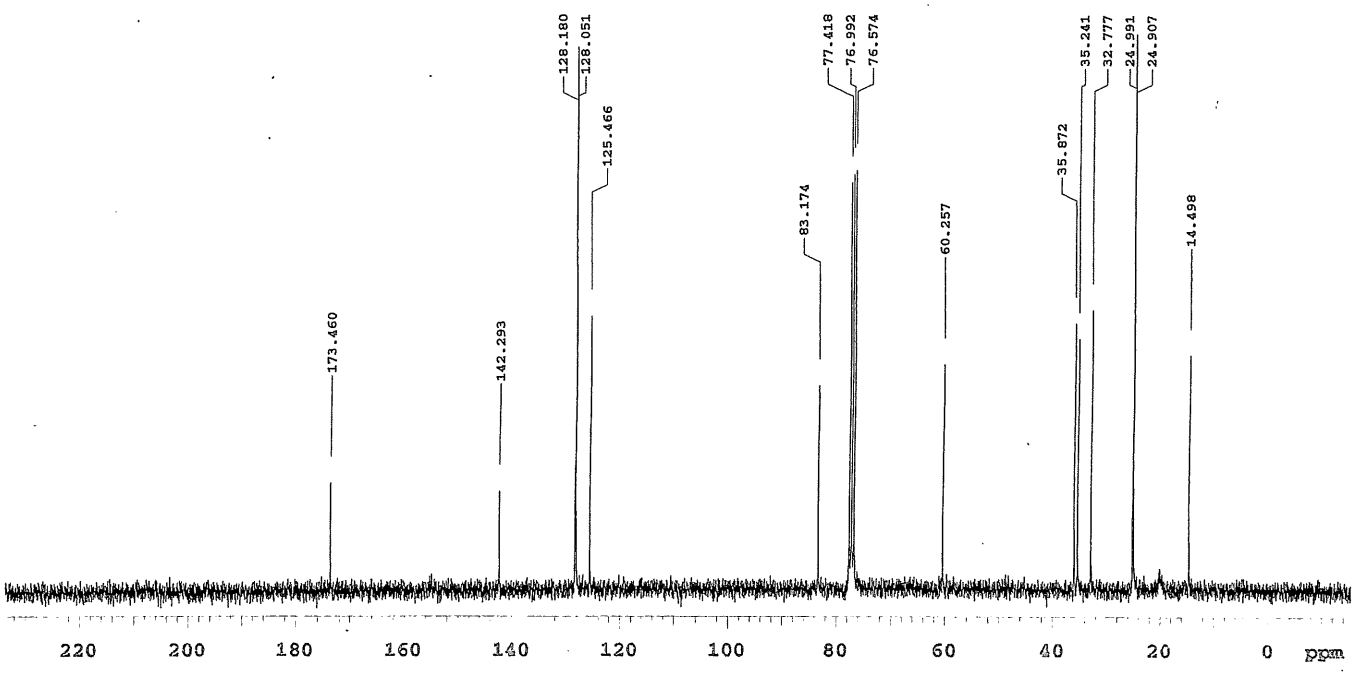

p-MeOC6H4
OEt
HO
O

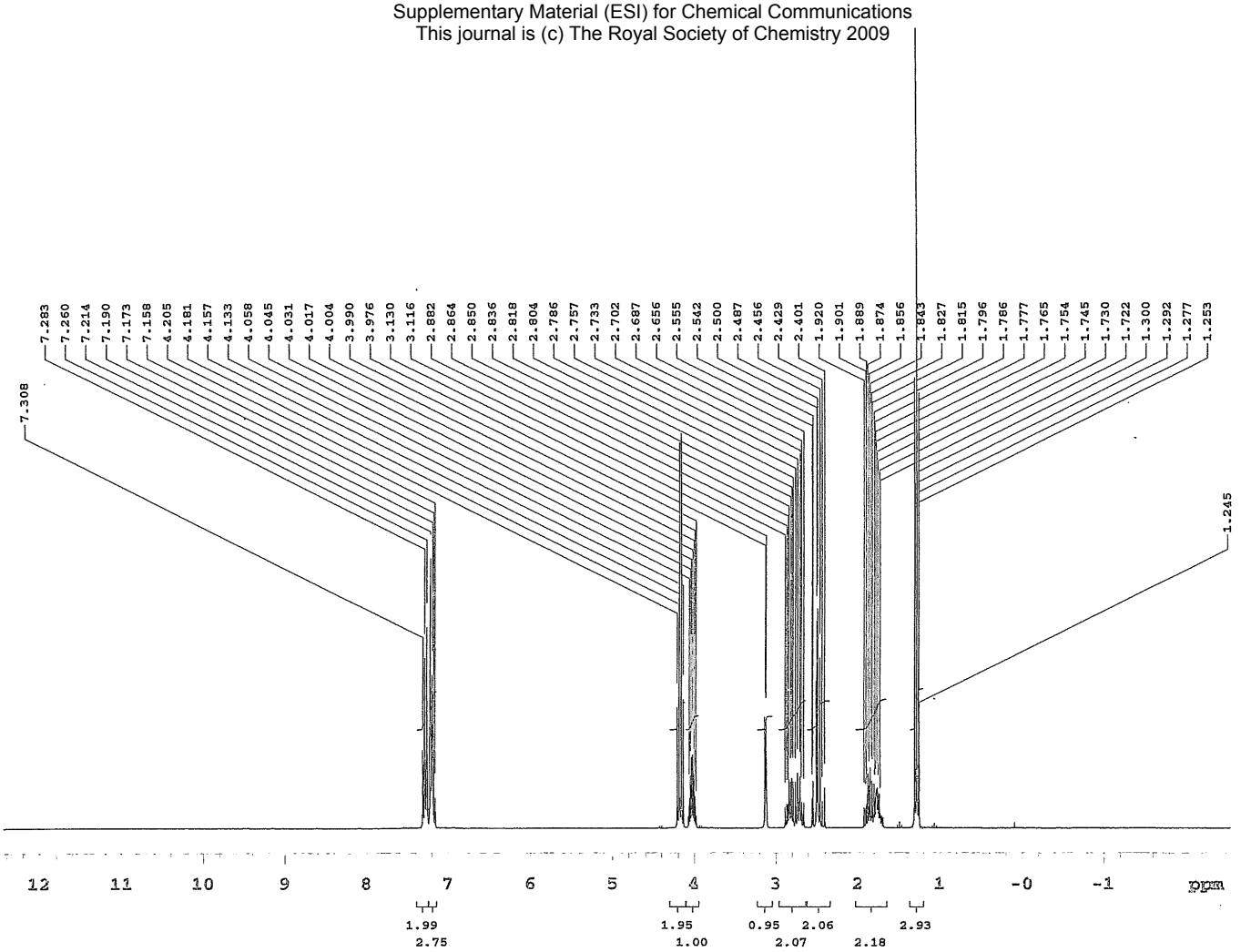

172.008
158.823
134.484
126.720
113.703
77.418
77.000
76.574
69.929
60.827
55.299
43.422
24.953
14.323
220
200
180
160
140
120
100
80
60
40
20
0
ppm

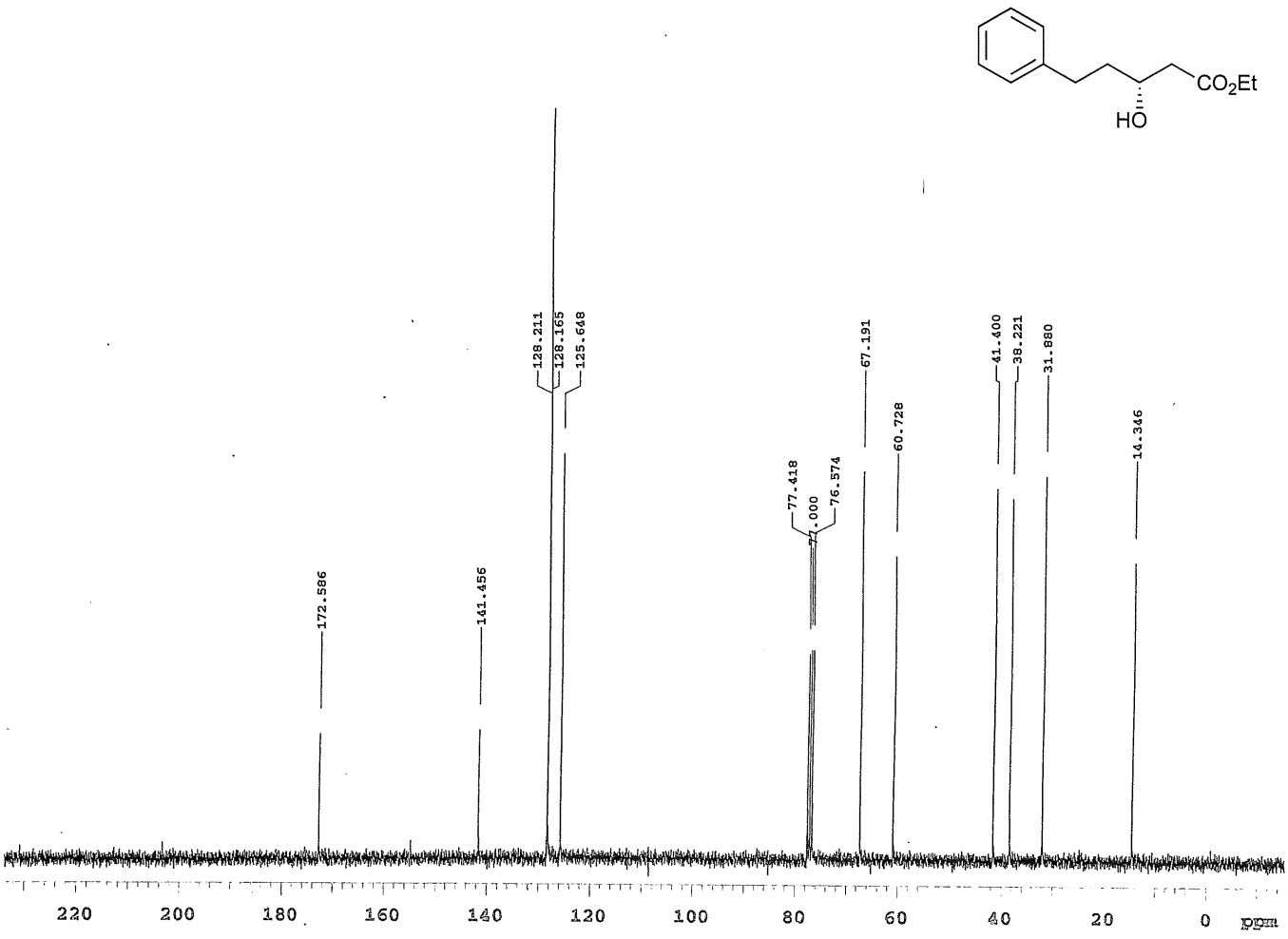

7.288
7.260
7.185
7.161
7.138
4.150
4.103
2.668
2.652
2.642
2.615
2.484
2.473
2.457
2.451
1.861
1.833
1.808
1.786
1.759
1.736
1.707
1.684
1.662
1.651
1.629
1.609
1.579
1.483
1.472
1.453
1.430
1.404
1.382
1.355
1.274
1.264
1.251
1.227
7.26 ppm
2.70 2.55 ppm
1.85 1.75 1.65 1.55 1.45 ppm
1.31 ppm
12 11 10 9 8 7 6 5 4 3 2 1 -0 -1 ppm

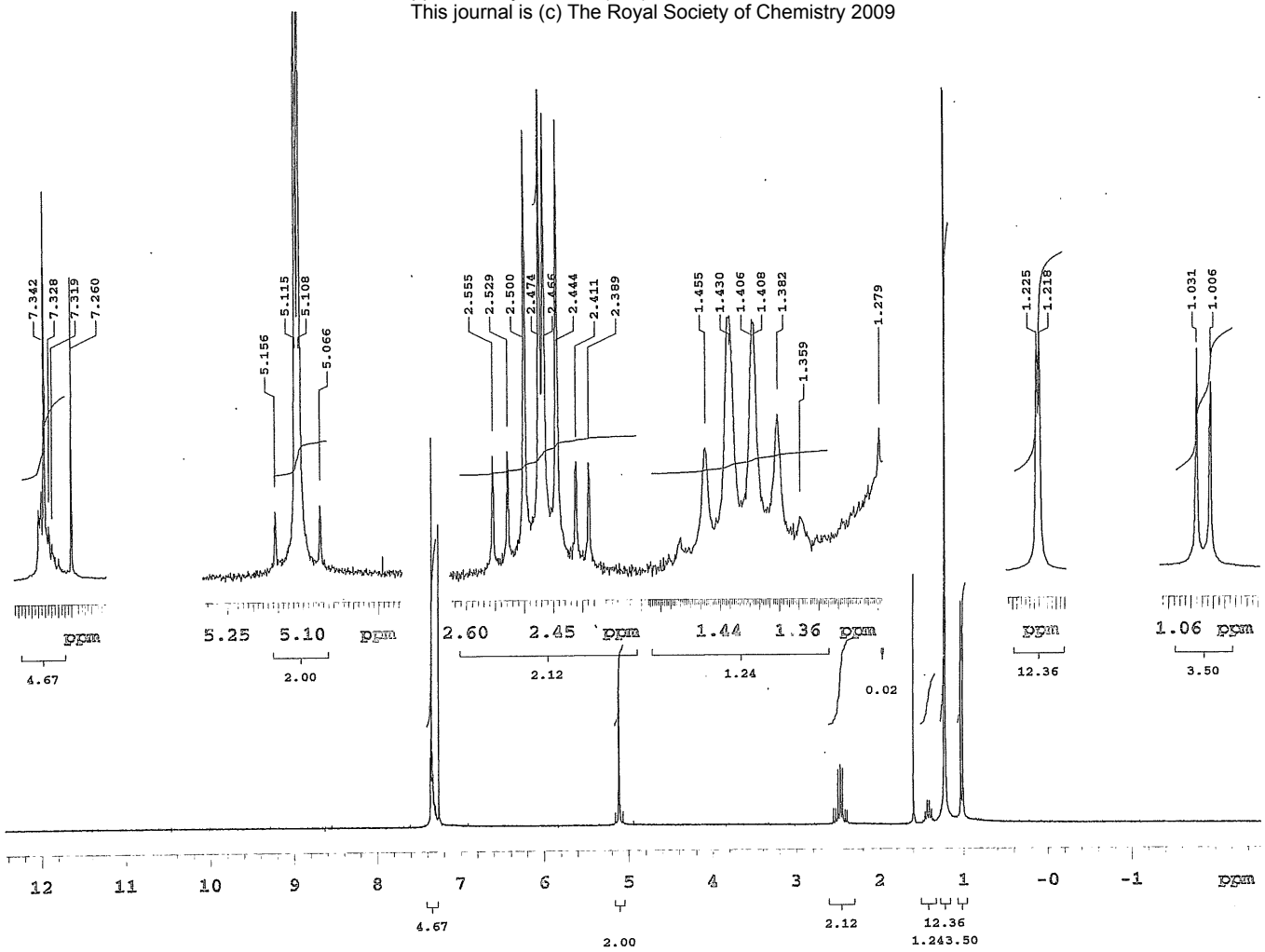

CO2Et
Bpin

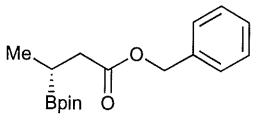
9


173.460
142.293
128.180
128.051
125.466
83.174
77.418
76.992
76.574
60.257
35.872
35.241
32.777
24.991
24.907
14.498
220 200 180 160 140 120 100 80 60 40 20 0 ppm

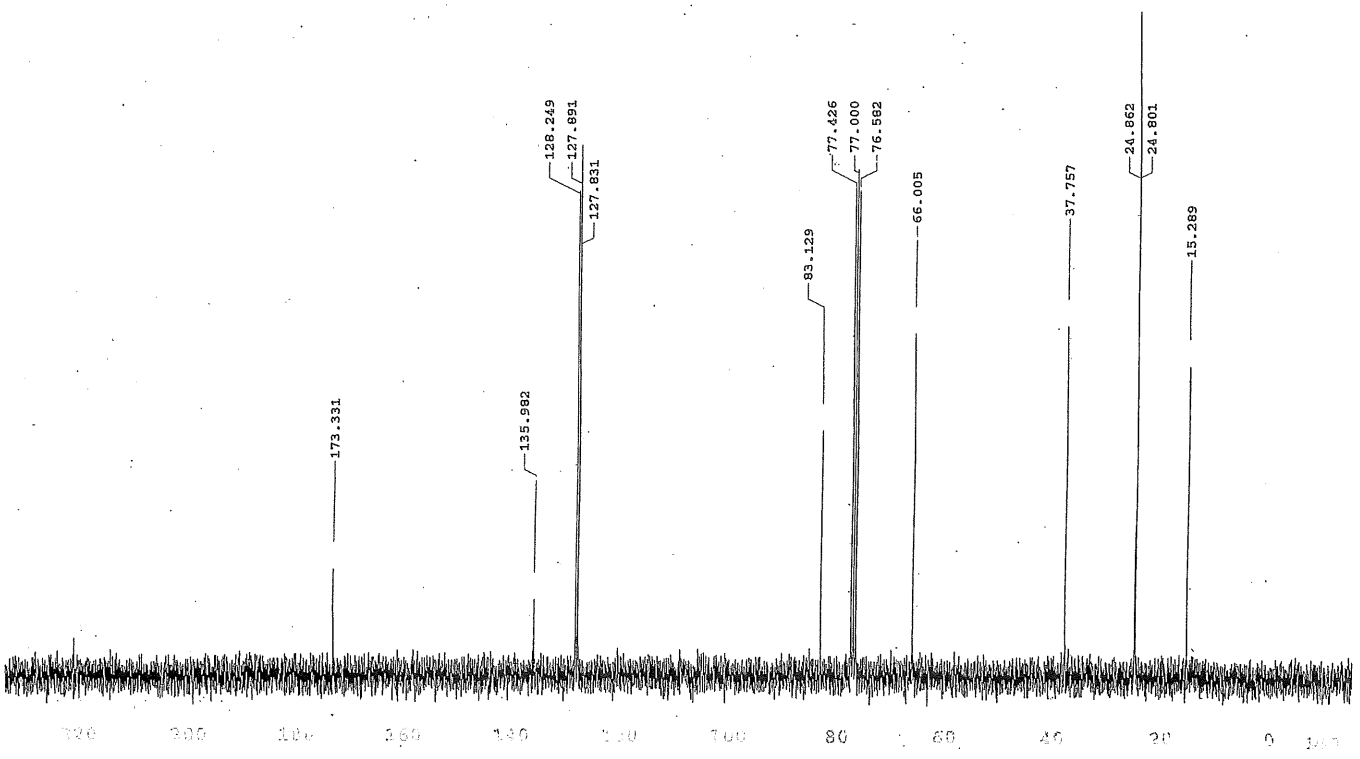

7.283
7.260
7.214
7.190
7.173
7.158
4.205
4.181
4.157
4.133
4.058
4.045
4.031
4.017
4.004
3.990
3.976
3.130
3.116
2.882
2.864
2.850
2.836
2.818
2.804
2.786
2.757
2.733
2.702
2.687
2.656
2.555
2.542
2.500
2.487
2.456
2.429
2.401
1.920
1.901
1.889
1.874
1.856
1.843
1.827
1.815
1.796
1.786
1.777
1.765
1.754
1.745
1.730
1.722
1.300
1.292
1.277
1.253
7.308
1.245
12 11 10 9 8 7 6 5 4 3 2 1 -0 -1 ppm
1.99
2.75
1.95
1.00
0.95
2.07
2.06
2.18
2.93

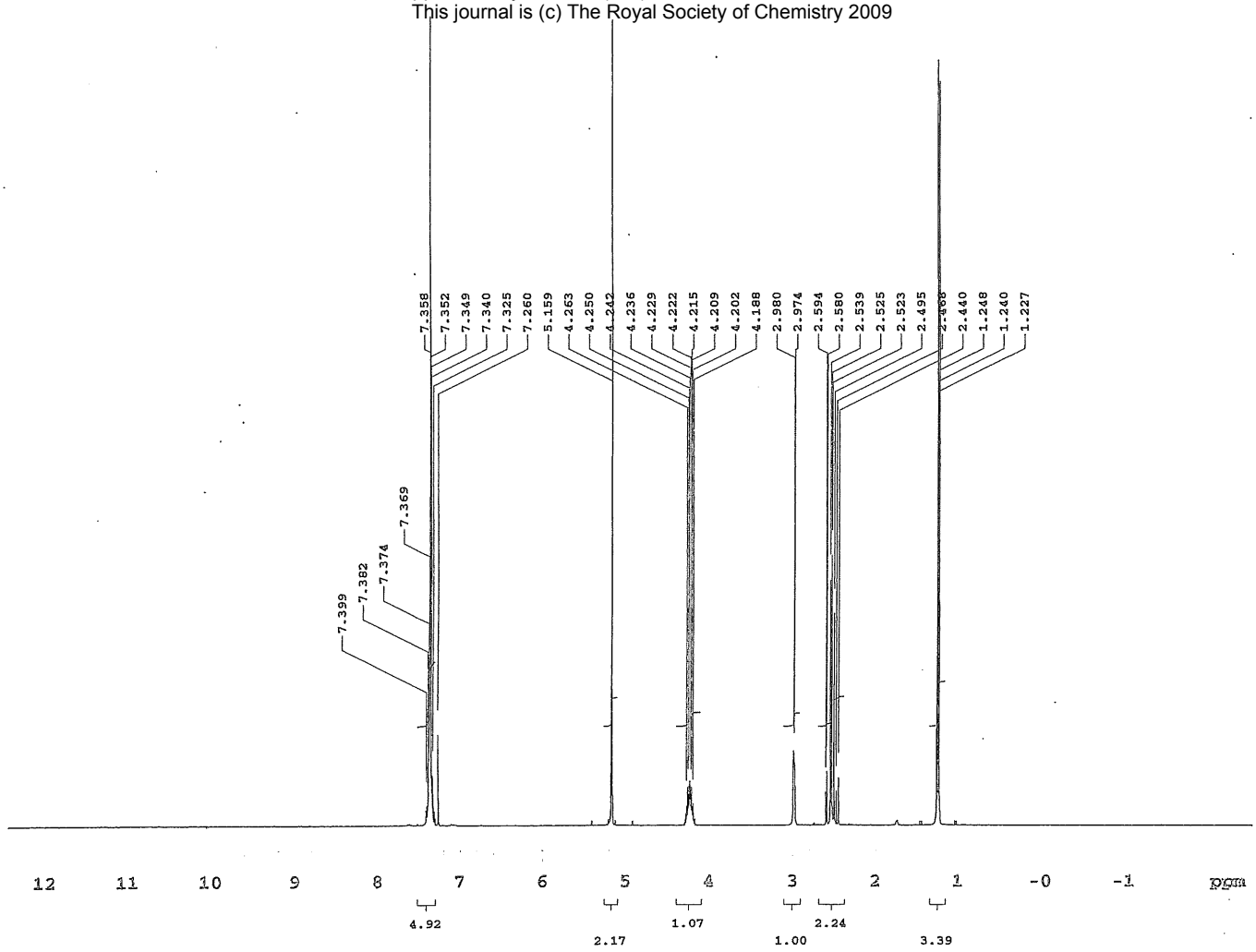

CO2Et
HO
172.586
141.456
128.211
128.165
125.648
77.418
77.000
76.574
67.191
60.728
41.400
38.221
31.880
14.346
220 200 180 160 140 120 100 80 60 40 20 0 ppm

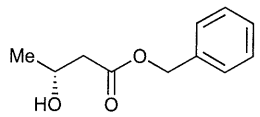

7.342
7.328
7.319
7.260
5.156
5.115
5.108
5.066
2.555
2.529
2.500
2.474
2.466
2.444
2.411
2.389
1.455
1.430
1.406
1.408
1.382
1.359
1.279
1.225
1.218
1.031
1.006
ppm
5.25 5.10 ppm
2.60 2.45 ppm
1.44 1.36 ppm
ppm
1.06 ppm
4.67
2.00
2.12
1.24
0.02
12.36
3.50
12 11 10 9 8 7 6 5 4 3 2 1 -0 -1 ppm
4.67
2.00
2.12
12.36
1.243.50

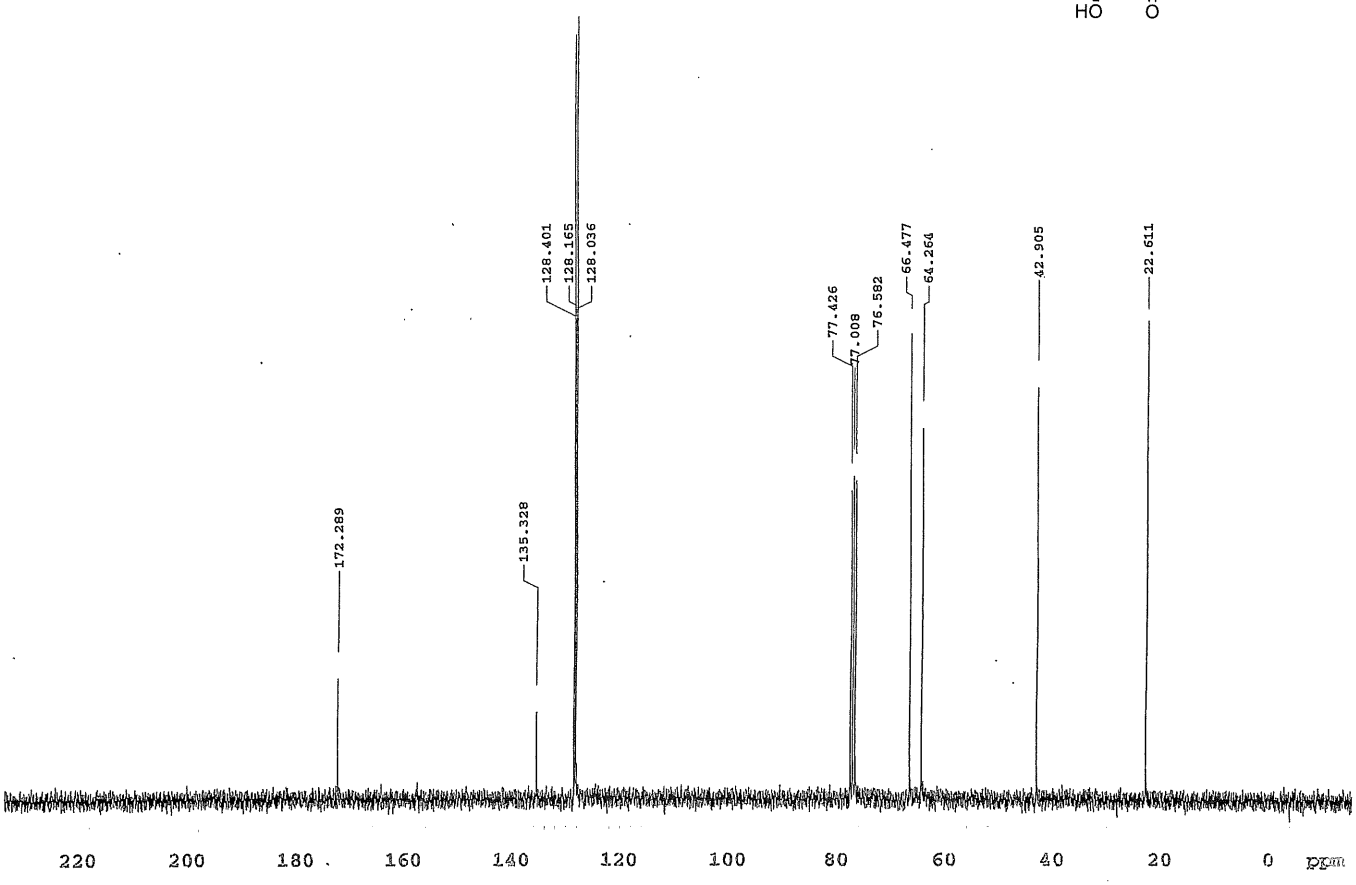

Me
O
Bpin
O

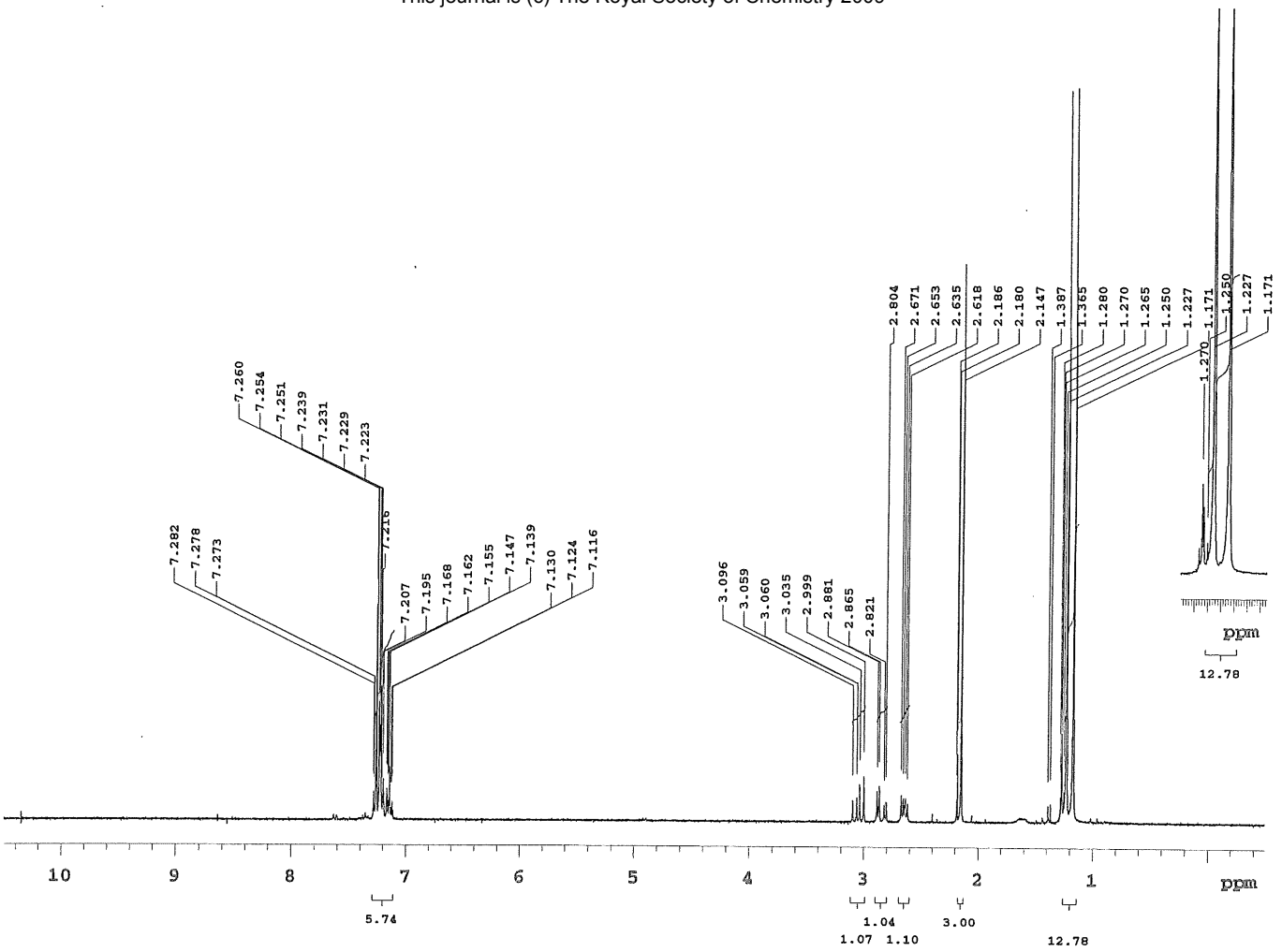
10

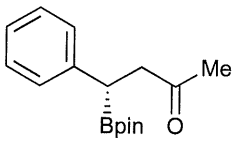

128.249
127.891
127.831
77.426
77.000
76.582
66.005
83.129
37.757
24.862
24.801
15.289
173.331
135.982


7.399
7.382
7.374
7.369
7.358
7.352
7.349
7.340
7.325
7.260
5.159
4.263
4.250
4.242
4.236
4.229
4.222
4.215
4.209
4.202
4.188
2.980
2.974
2.594
2.580
2.539
2.525
2.523
2.495
2.488
2.440
1.248
1.240
1.227
12 11 10 9 8 7 6 5 4 3 2 1 -0 -1 ppm
4.92
2.17
1.07
1.00
2.24
3.39

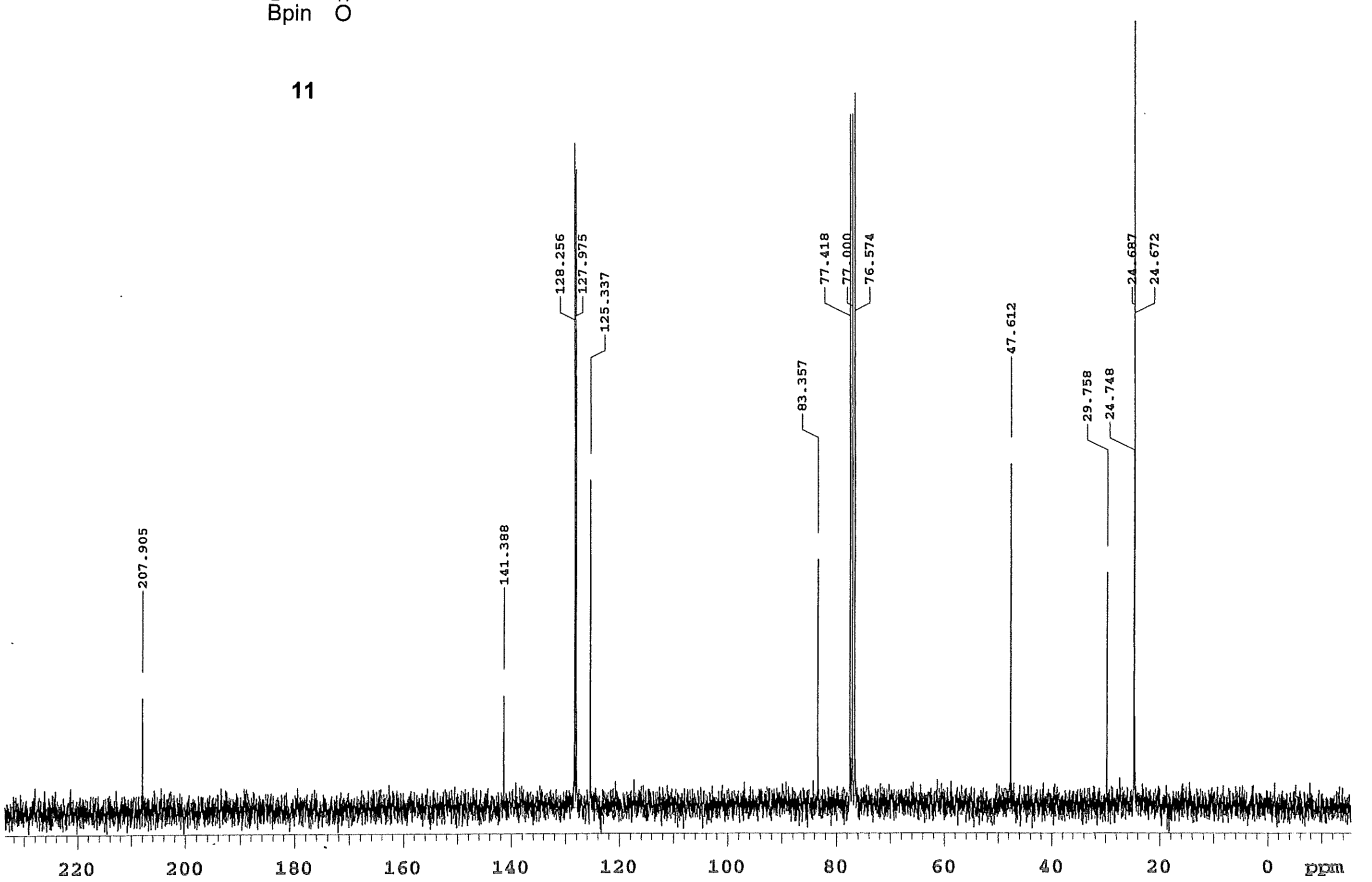

Me
HO
O
O

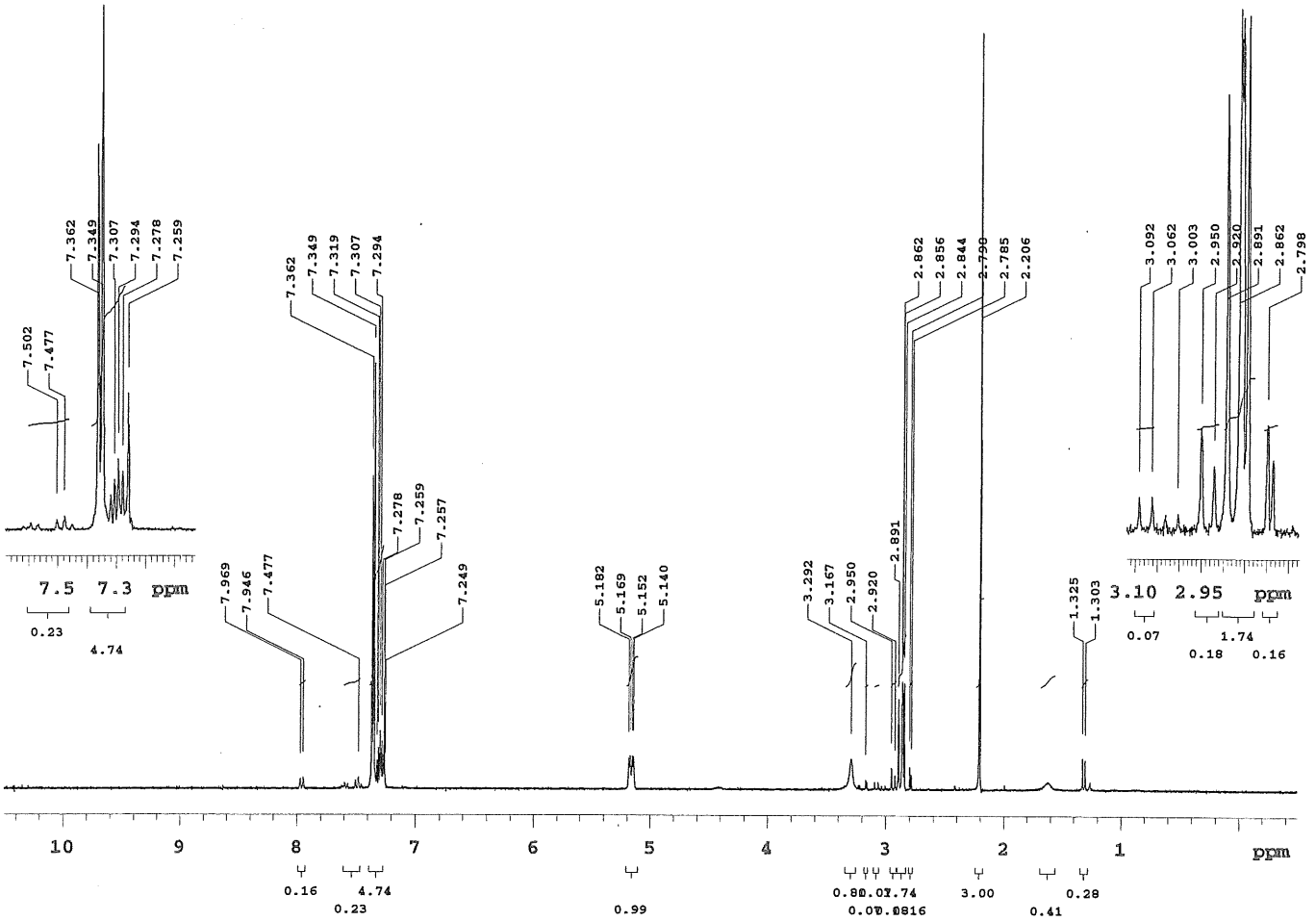

172.289
135.328
128.401
128.165
128.036
77.426
77.008
76.582
66.477
64.264
42.905
22.611
220 200 180 160 140 120 100 80 60 40 20 0 ppm

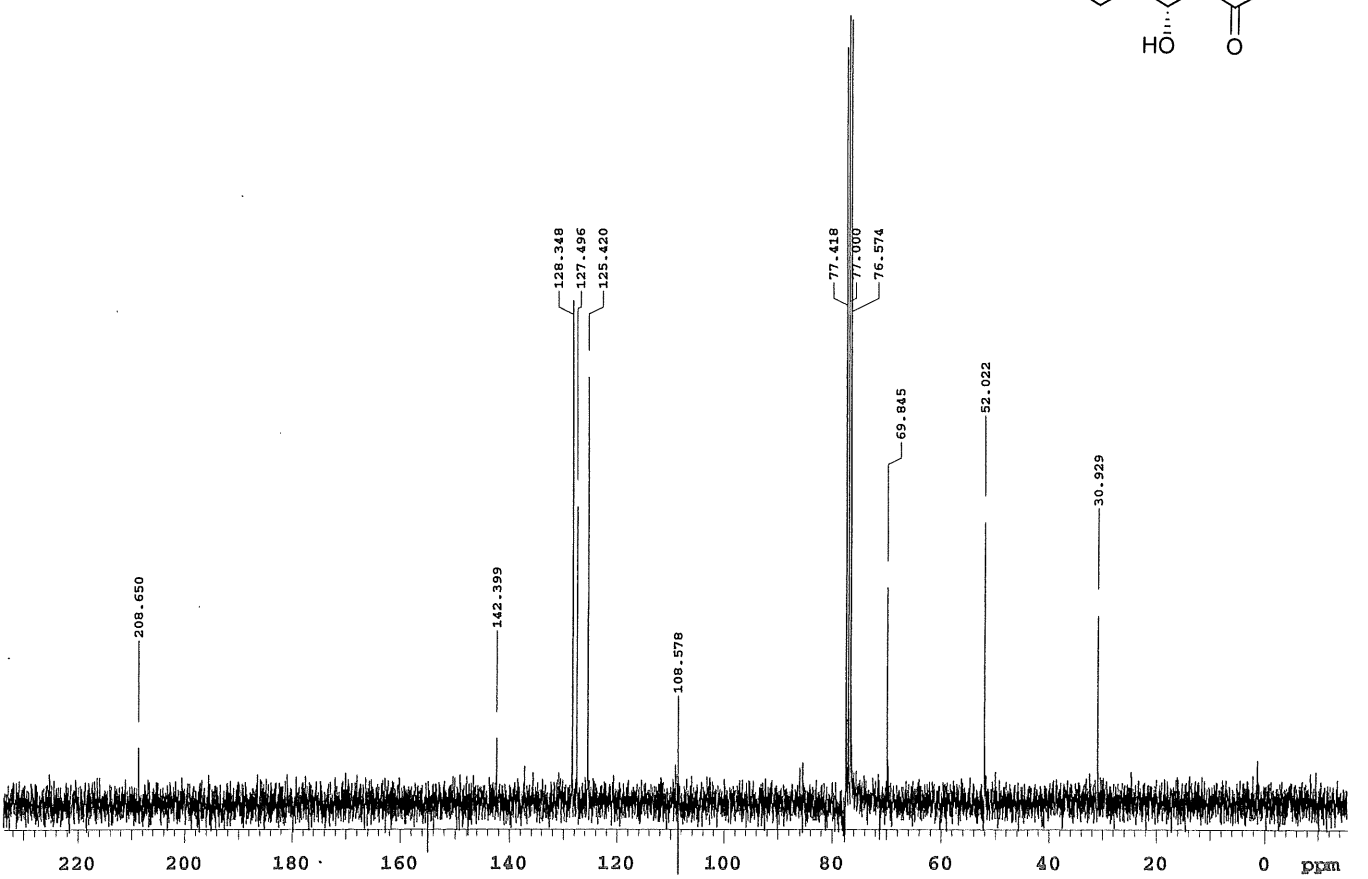

7.260
7.254
7.251
7.239
7.231
7.229
7.223
7.216
7.282
7.278
7.273
7.207
7.195
7.168
7.162
7.155
7.147
7.139
7.130
7.124
7.116
3.096
3.059
3.060
3.035
2.999
2.881
2.865
2.821
2.804
2.671
2.653
2.635
2.618
2.186
2.180
2.147
1.387
1.365
1.280
1.270
1.265
1.250
1.227
1.171
1.270
1.250
1.227
1.171
ppm
12.78
10
9
8
7
6
5
4
3
2
1
ppm
5.74
1.07
1.04
1.10
3.00
12.78

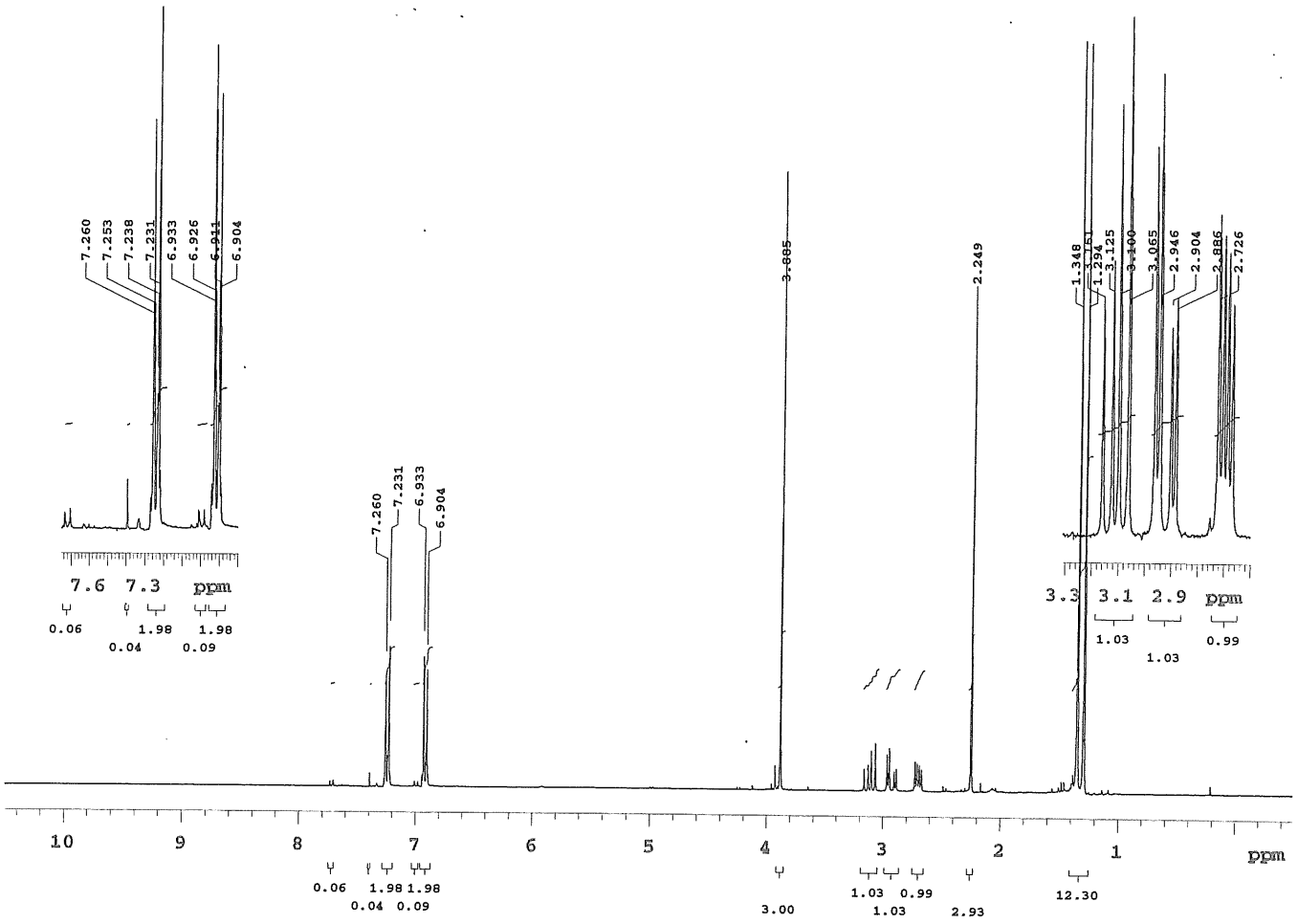

Me
Bpin
O

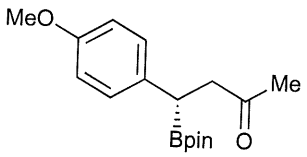
11


207.905
141.388
128.256
127.975
125.337
83.357
77.418
77.000
76.574
47.612
29.758
24.748
24.687
24.672
220
200
180
160
140
120
100
80
60
40
20
0
ppm

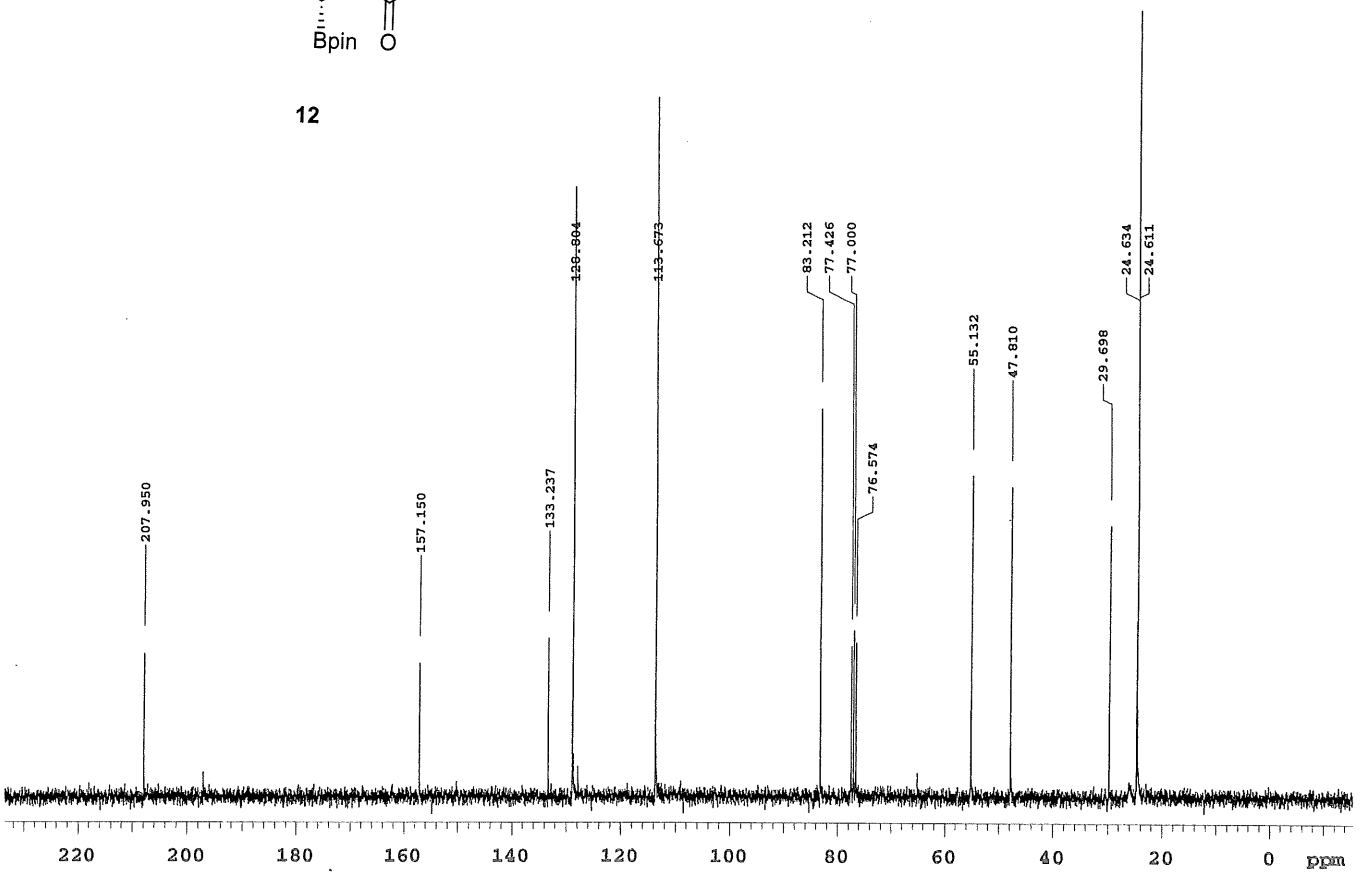

7.502
7.477
7.362
7.349
7.307
7.294
7.278
7.259
7.969
7.946
7.477
7.362
7.349
7.319
7.307
7.294
7.278
7.259
7.257
7.249
5.182
5.169
5.152
5.140
3.292
3.167
2.950
2.920
2.891
2.862
2.856
2.844
2.799
2.785
2.206
1.325
1.303
3.092
3.062
3.003
2.950
2.920
2.891
2.862
2.798
7.5 7.3 ppm
0.23
4.74
3.10 2.95 ppm
0.07
1.74
0.18
0.16
10 9 8 7 6 5 4 3 2 1 ppm
0.16
4.74
0.23
0.99
3.00
0.28
0.41

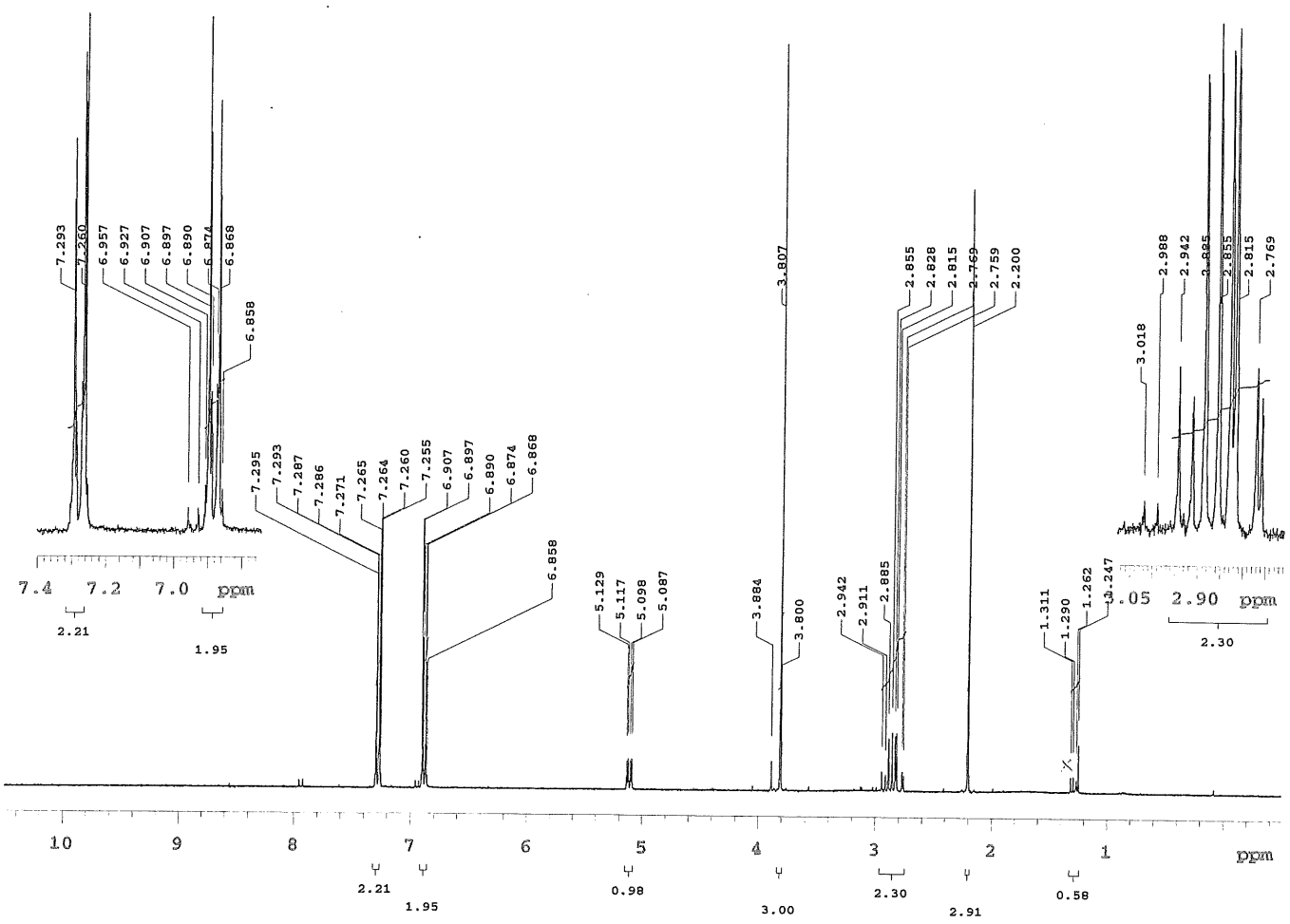

Me
HO
O
208.650
142.399
128.348
127.496
125.420
108.578
77.418
77.000
76.574
69.845
52.022
30.929
220 200 180 160 140 120 100 80 60 40 20 0 ppm

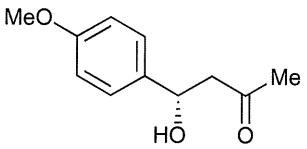

7.260
7.253
7.238
7.231
6.933
6.926
6.911
6.904
3.805
2.249
1.348
1.294
3.125
3.100
3.065
2.946
2.904
2.886
2.726
7.6 7.3 ppm
0.06 0.04 1.98 0.09 1.98
3.3 3.1 2.9 ppm
1.03 1.03 0.99
10 9 8 7 6 5 4 3 2 1 ppm
0.06 0.04 1.98 0.09 1.98
3.00
1.03 1.03 0.99
2.93
12.30

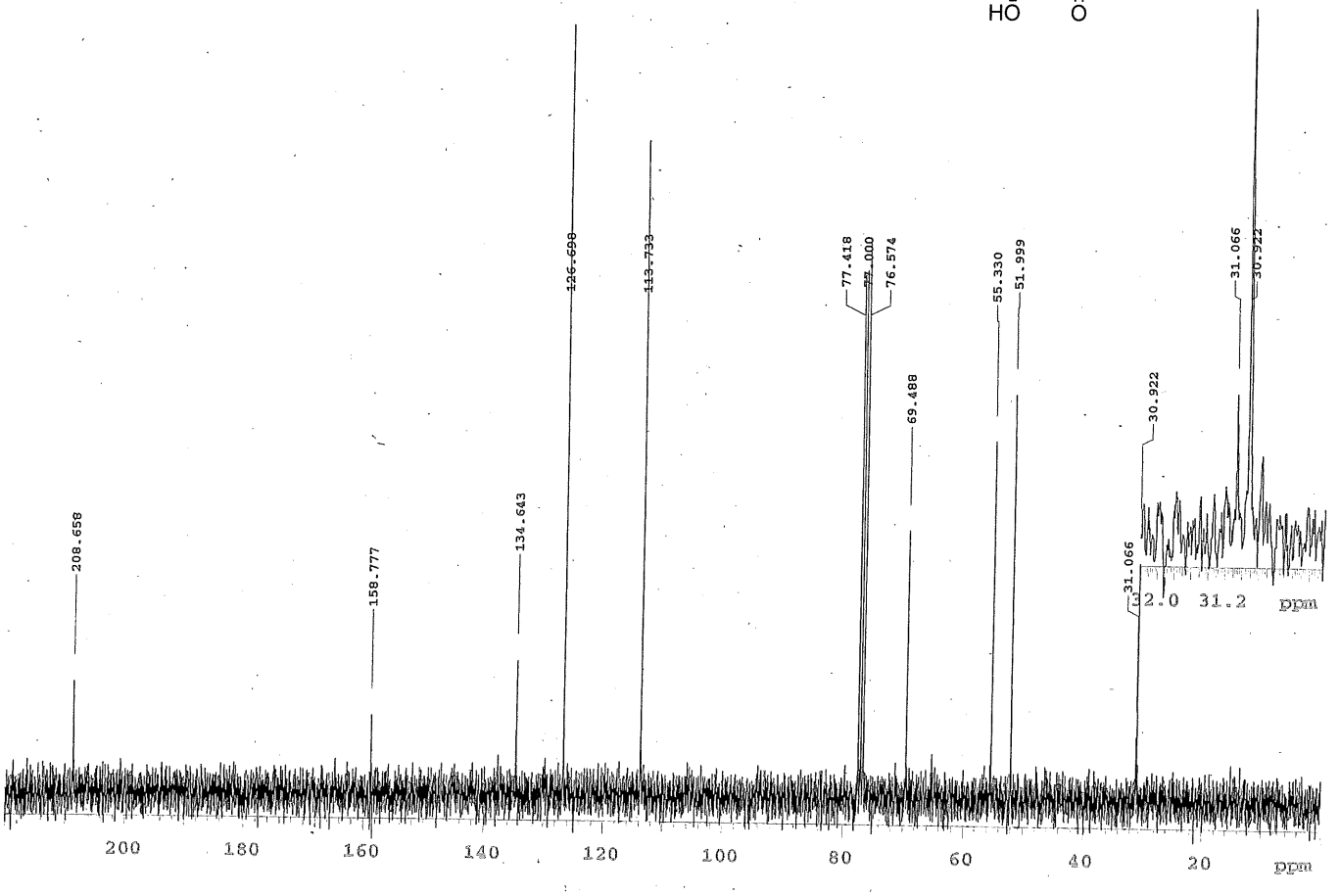

MeO
Me
Bpin
O

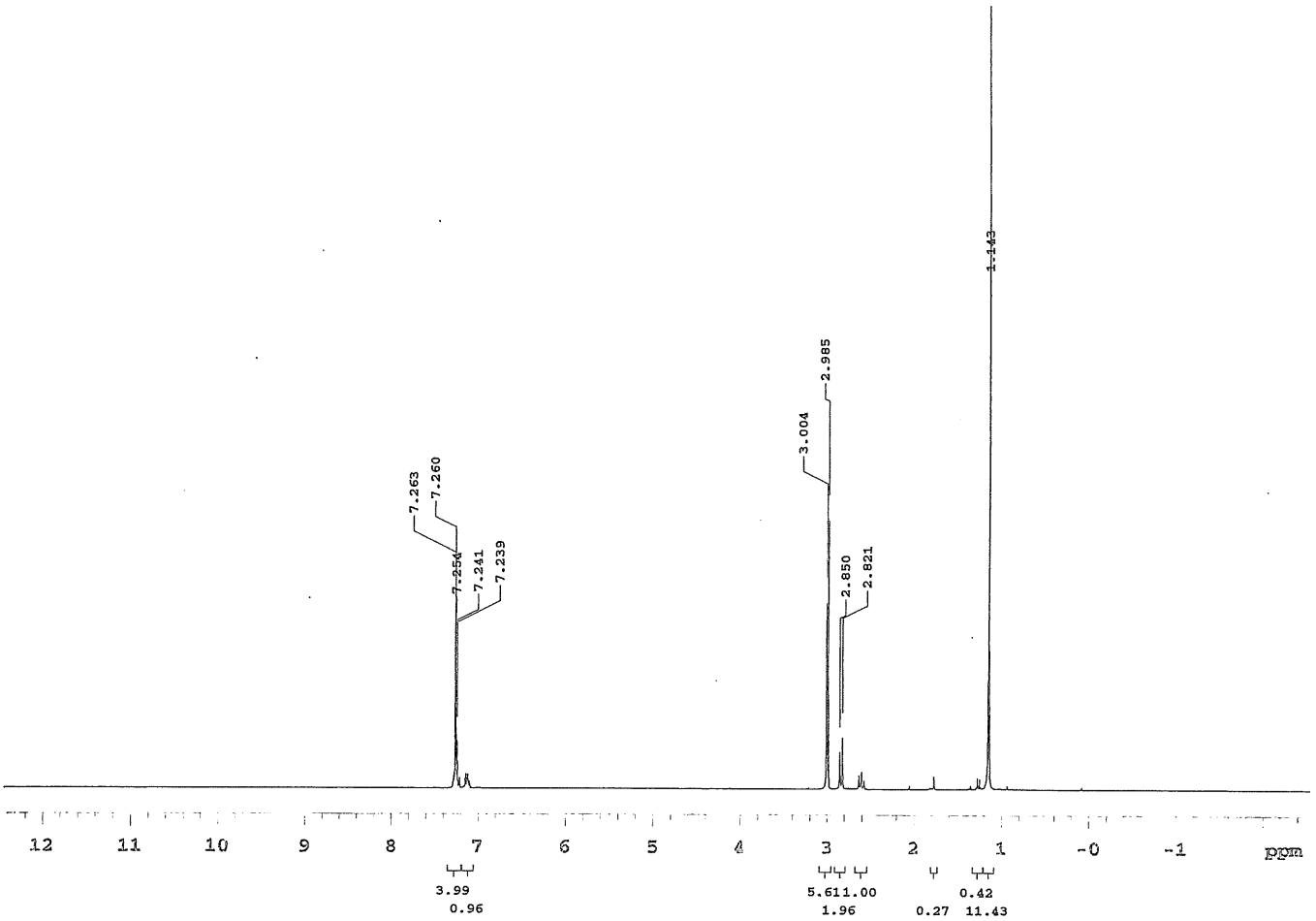
12

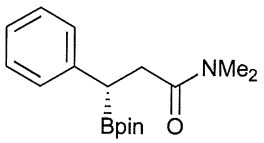

207.950
157.150
133.237
129.804
113.673
83.212
77.426
77.000
76.574
55.132
47.810
29.698
24.634
24.611
220 200 180 160 140 120 100 80 60 40 20 0 ppm


7.293
7.260
6.957
6.927
6.907
6.897
6.890
6.874
6.868
6.858
7.295
7.293
7.287
7.286
7.271
7.265
7.264
7.260
7.255
6.907
6.897
6.890
6.874
6.868
6.858
5.129
5.117
5.098
5.087
3.884
3.807
3.800
2.942
2.911
2.885
2.855
2.828
2.815
2.769
2.759
2.200
1.311
1.290
1.262
1.247
3.018
2.988
2.942
2.885
2.855
2.815
2.769
7.4 7.2 7.0 ppm
2.21
1.95
2.05 2.90 ppm
2.30
10 9 8 7 6 5 4 3 2 1 ppm
2.21
1.95
0.98
3.00
2.30
2.91
0.58

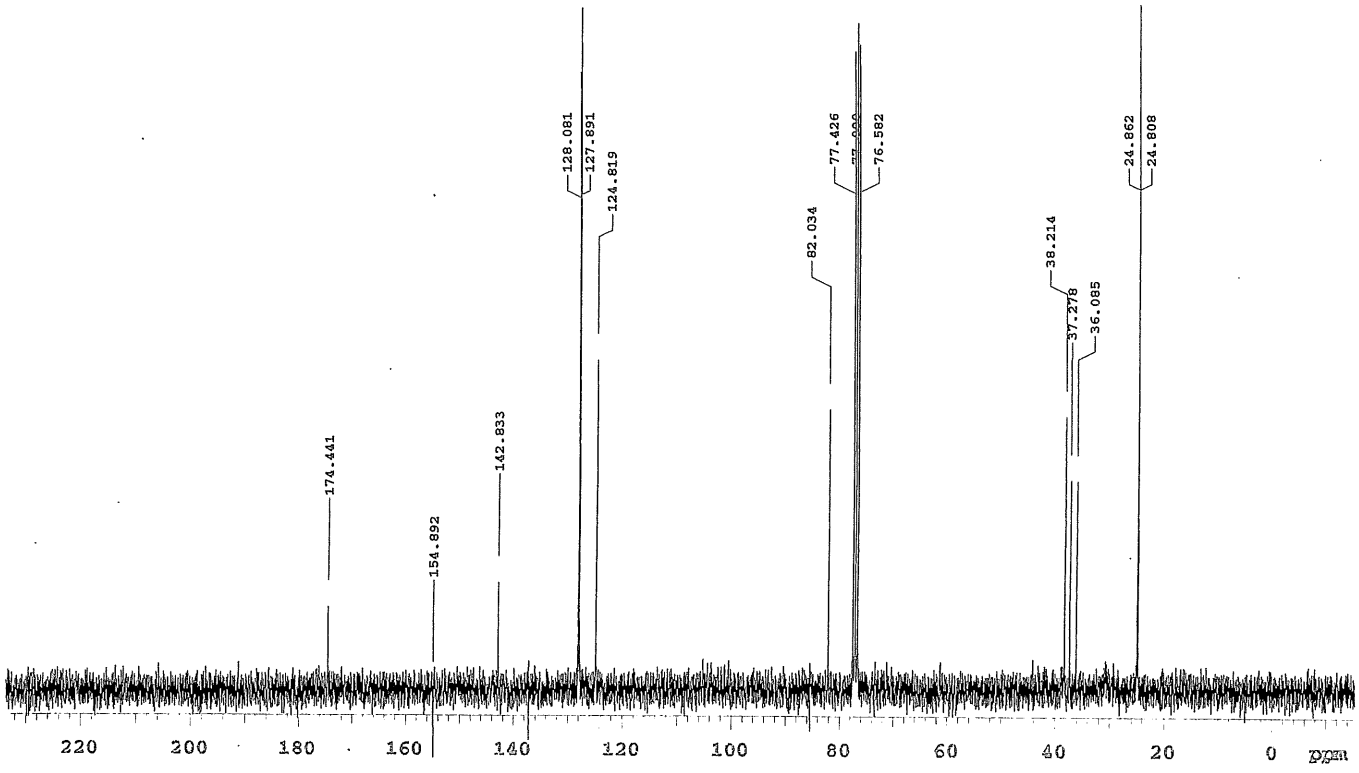

MeO
Me
HO
O

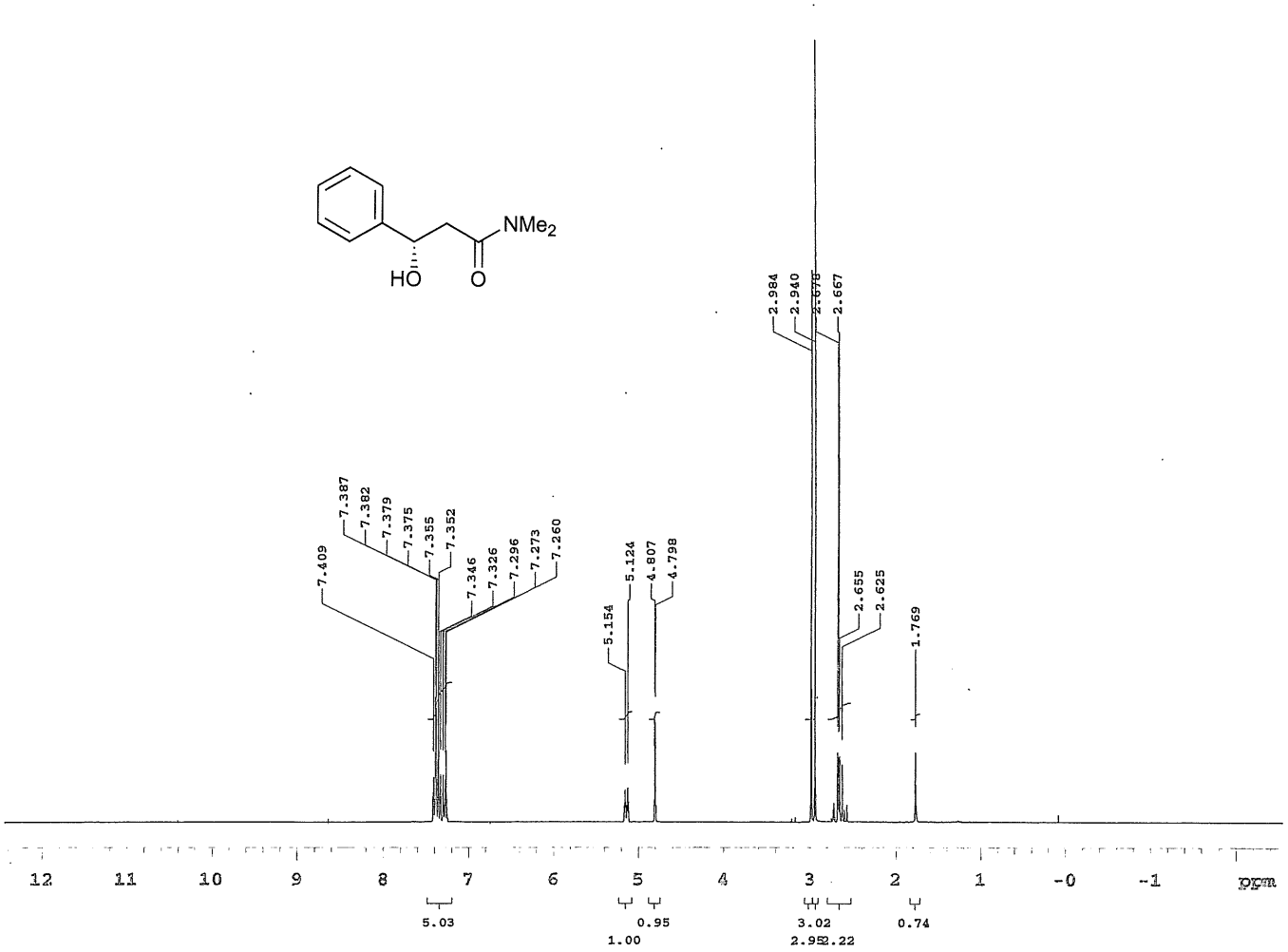

208.658
158.777
134.643
126.698
113.733
77.418
77.000
76.574
69.488
55.330
51.999
31.066
30.922
31.066
30.922
32.0 31.2 ppm
200 180 160 140 120 100 80 60 40 20 ppm

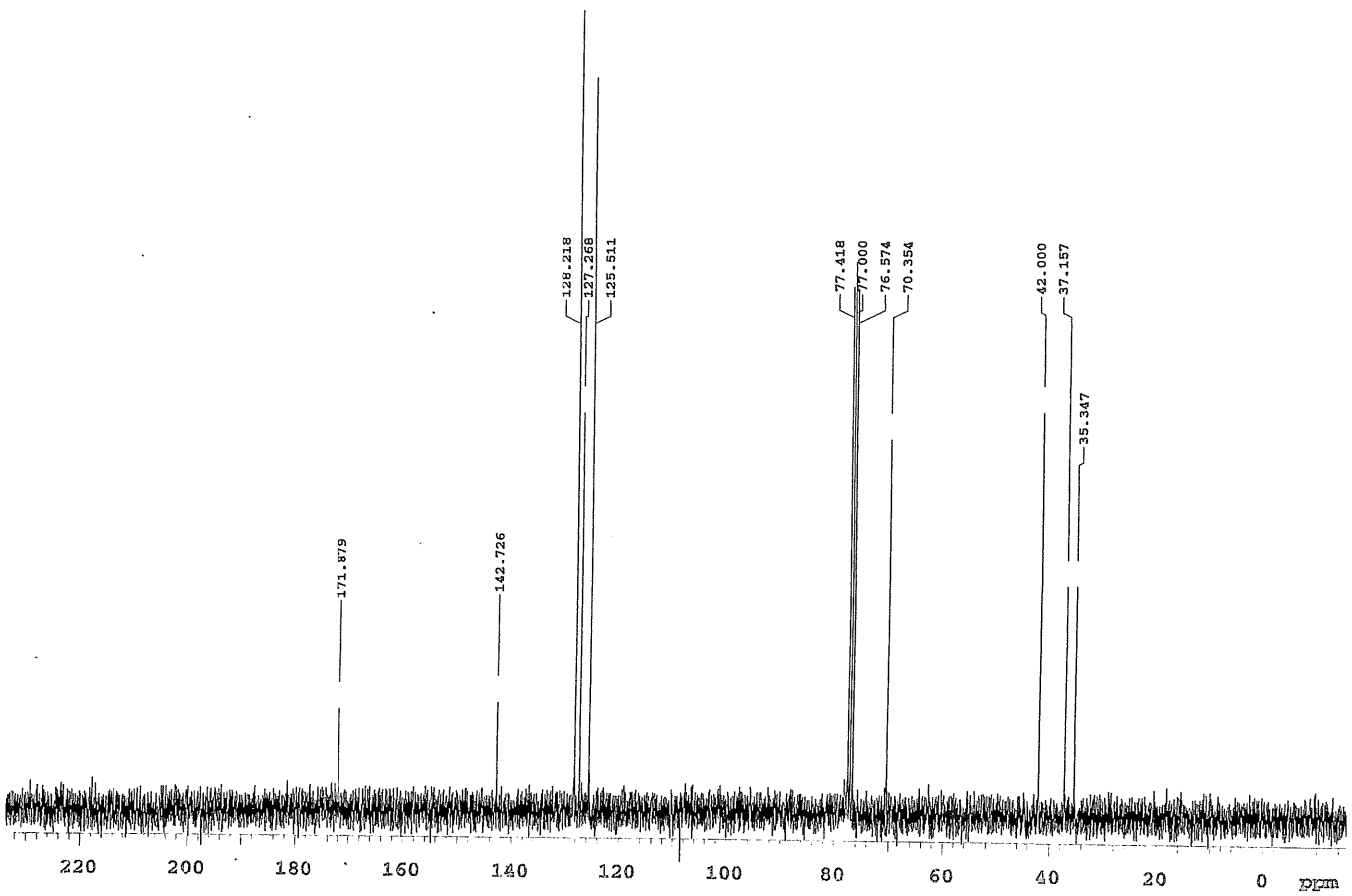

7.263
7.260
7.254
7.241
7.239
3.004
2.985
2.850
2.821
1.143
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm
3.99
0.96
5.61
1.96
1.00
0.27
0.42
11.43


NMe2
Bpin
O

13


174.441
154.892
142.833
128.081
127.891
124.819
82.034
77.426
76.582
38.214
37.278
36.085
24.862
24.808
220
200
180
160
140
120
100
80
60
40
20
0
ppm


NMe2
HO
O
2.984
2.940
2.878
2.667
7.387
7.382
7.379
7.375
7.355
7.352
7.409
7.346
7.326
7.296
7.273
7.260
5.154
5.124
4.807
4.798
2.655
2.625
1.769
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm
5.03
0.95
1.00
3.02
2.95
2.22
0.74


171.879
142.726
128.218
127.268
125.511
77.418
77.000
76.574
70.354
42.000
37.157
35.347
220
200
180
160
140
120
100
80
60
40
20
0
ppm