Supporting Information

for

Stereoselective Construction of Substituted Chromans by Palladium-Catalyzed Cyclization of Propargylic Carbonates with 2-(2-Hydroxyphenyl)acetates

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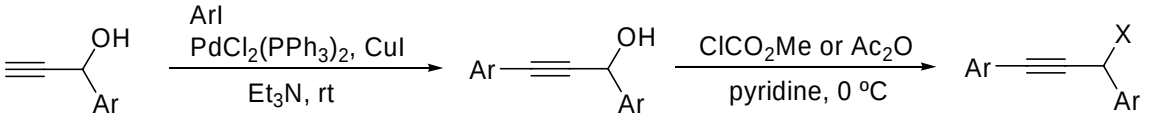
General. All nonaqueous reactions were carried out under a positive atmosphere of argon in dried glassware unless otherwise indicated. Materials were obtained from commercial suppliers and used without further purification except when otherwise noted. Solvents were dried and distilled according to standard protocol. The phrase 'residue upon workup' refers to the residue obtained when the organic layer was separated and dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. 2-(2-Hydroxyphenyl)acetates **2a**,[1] **2b**,[2] and propargyl alcohols **S-1b**,[3] **S-1c**[4] were prepared according to the procedures described in the literature.

Preparation of Propargylic Carbonates and Esters 1 (Scheme S-1)

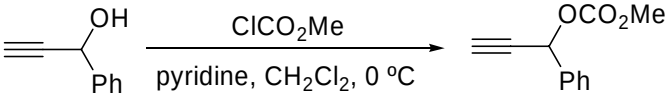
Scheme S-1



S-1a Ar = Ph
S-1b Ar = 4-F-Ph
S-1c Ar = 4-MeO-Ph

S-2a Ar = Ph 96%
S-2b Ar = 4-F-Ph 74%
S-2c Ar = 4-MeO-Ph 84%

1a Ar = Ph X = OCO_2Me 87%
1b Ar = 4-F-Ph X = OCO_2Me 96%
1c Ar = 4-MeO-Ph X = OAc quant

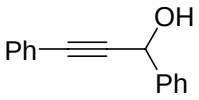


S-1a **1d** quant

General procedure for the synthesis of propargylic carbonates.

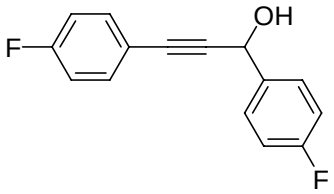
Synthesis of S-2a. To a stirred solution of PhI (1.5 mL, 13.6 mmol) in Et_3N (20 mL) were added 1-phenyl-2-propyn-1-ol **S-1a** (500 mg, 3.8 mmol), $PdCl_2(PPh_3)_2$ (186 mg, 265 μmol) and CuI (101 mg, 530 μmol) at rt, and stirring was continued for 2 h at the same temperature. After filtration of the reaction mixture using small amount of silica gel followed by concentration, the residue was chromatographed on silica gel with hexane-AcOEt (9:1 v/v) as eluent to give propargylic alcohol **S-2a** (754 mg, 96%) as a brown oil.

1,3-Diphenylprop-2-yn-1-ol (S-2a).



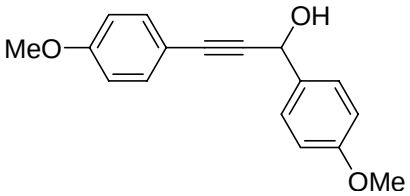
Brown oil; IR (neat) 3364, 1598, 1489, 1031, 961, 757 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.24 (1H, d, *J* = 6.4 Hz), 5.70 (1H, d, *J* = 6.4 Hz), 7.30−7.38 (4H, m), 7.39−7.44 (2H, m), 7.47−7.49 (2H, m), 7.62−7.64 (2H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 65.1 (CH), 86.6 (Cq), 88.7 (Cq), 122.4 (Cq), 126.7 (CH×2), 128.3 (CH×2), 128.4 (CH), 128.6 (CH), 128.6 (CH×2), 131.7 (CH×2), 140.6 (Cq); HRMS (ESI) *m/z* calcd for $C_{15}H_{13}O$ $[M+H]^+$ 209.0966, found 209.0962.

1,3-Bis(4-fluorophenyl)prop-2-yn-1-ol (S-2b).



Pale yellow oil; IR (neat) 3324, 1602, 1507, 1224, 1157, 837 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.26 (1H, d, *J* = 6.0 Hz), 5.67 (1H, d, *J* = 6.0 Hz), 7.00−7.05 (2H, m), 7.06−7.12 (2H, m), 7.43−7.48 (2H, m), 7.57−7.60 (2H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 64.3 (CH), 85.8 (Cq), 88.2 (Cq), 115.5 (CH×2, d, *J* = 21.5 Hz), 115.6 (CH×2, d, *J* = 22.3 Hz), 118.3 (Cq, d, *J* = 4.2 Hz), 128.5 (CH×2, d, *J* = 8.3 Hz), 133.6 (CH×2, d, *J* = 8.3 Hz), 136.4 (Cq, d, *J* = 3.3 Hz), 162.7 (Cq, d, *J* = 246.1 Hz), 162.7 (Cq, d, *J* = 248.6 Hz); HRMS (ESI) *m/z* calcd for $C_{15}H_{10}OF_2Na$ $[M+Na]^+$ 267.0597, found 267.0593.

1,3-Bis(4-methoxyphenyl)prop-2-yn-1-ol (S-2c).

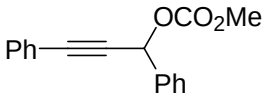


Pale yellow oil; IR (neat) 3241, 2837, 1606, 1507, 1248, 1172, 1033, 832 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.17 (1H, d, *J* = 6.4 Hz), 3.82 (3H, s), 3.83 (3H, s), 5.64 (1H, d, *J* = 6.4 Hz), 6.85 (2H, d, *J* = 8.8

Hz), 6.93 (2H, d, J = 8.8 Hz), 7.41 (2H, d, J = 8.8 Hz) , 7.55 (2H, d, J = 8.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 55.2 (CH_3), 55.3 (CH_3), 64.7 (CH), 86.4 (Cq), 87.6 (Cq), 113.9 (CH×2), 113.9 (CH×2), 114.5 (Cq), 128.1 (CH×2), 133.1 (CH×2), 133.2 (Cq), 159.6 (Cq), 159.7 (Cq); HRMS (ESI) *m/z* calcd for $C_{17}H_{17}O_3Na$ $[M+H]^+$ 269.1178, found 269.1175.

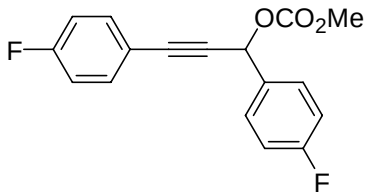
Synthesis of 1a. To a stirred solution of propargylic alcohol **S-2a** (750 mg, 3.6 mmol) in CH_2Cl_2 (20 mL) were added pyridine (0.87 mL, 10.8 mmol) and methyl chloroformate (0.33 mL, 4.3 mmol) at 0 °C, and stirring was continued for 1 h at the same temperature. The reaction mixture was diluted with aqueous NH_4Cl and extracted with AcOEt. The combined extracts were washed with brine. The residue upon work up was chromatographed on silica gel with hexane-AcOEt (8:2 v/v) as eluent to give propargylic carbonate **1a** (836 mg, 87%) as a pale yellow oil.

1,3-Diphenylprop-2-ynyl methyl carbonate (1a).



Pale yellow oil; IR (neat) 2956, 1750, 1490, 1442, 1261, 930, 758, 692 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.83 (3H, s), 6.53 (1H, s), 7.28−7.36 (3H, m), 7.36−7.44 (3H, m), 7.47−7.49 (2H, m), 7.61−7.63 (2H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 55.1 (CH_3), 70.2 (CH), 84.8 (Cq), 88.0 (Cq), 121.9 (Cq), 127.8 (CH×2), 128.3 (CH×2), 128.7 (CH×2), 128.9 (CH), 129.2 (CH), 131.9 (CH×2), 136.5 (Cq), 154.9 (Cq); HRMS (ESI) *m/z* calcd for $C_{17}H_{14}O_3Na$ $[M+Na]^+$ 289.0841, found 289.0840.

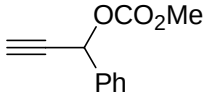
1,3-Bis(4-fluorophenyl)prop-2-ynyl methyl carbonate (1b).



Colorless oil; IR (neat) 2959, 1748, 1602, 1442, 1265, 1158, 837, 790 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$)

δ 3.82 (3H, s), 6.48 (1H, s), 7.01 (2H, dd, *J* = 8.4 and 8.8 Hz), 7.09 (2H, dd, *J* = 8.4 Hz and 8.8 Hz), 7.46 (2H, dd, *J* = 8.8 and 5.2 Hz), 7.59 (2H, dd, *J* = 8.8 and 5.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 55.1 (CH_3), 69.4 (CH), 84.3 (Cq), 87.1 (Cq), 115.6 (CH×2, d, *J* = 22.3 Hz), 115.7 (CH×2, d, *J* = 21.5 Hz), 117.8 (Cq, d, *J* = 4.1 Hz), 129.8 (CH×2, d, *J* = 9.1 Hz), 132.4 (Cq, d, *J* = 3.3 Hz), 133.9 (CH×2, d, *J* = 8.2 Hz), 154.8 (Cq), 162.9 (Cq, d, *J* = 249.4 Hz), 163.2 (Cq, d, *J* = 246.9 Hz); HRMS (ESI) *m/z* calcd for $C_{17}H_{13}O_3F_2$ $[M+H]^+$ 303.0833, found 303.0828.

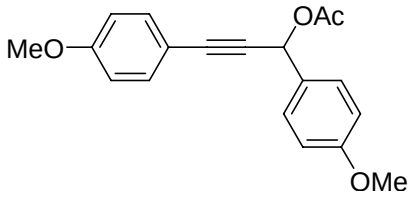
Methyl 1-phenylprop-2-ynyl carbonate (1d)



Pale yellow oil; IR (neat) 3290, 2958, 1750, 1442, 1260, 931, 697 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.72 (1H, d, *J* = 2.4 Hz), 3.82 (3H, s), 6.29 (1H, d, *J* = 2.4 Hz), 7.38−7.43 (3H, m), 7.54−7.57 (2H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 55.2 (CH_3), 69.3 (CH), 76.5 (CH), 79.6 (Cq), 127.6 (CH×2), 128.7 (CH×2), 129.3 (CH), 135.8 (Cq), 154.7 (Cq); HRMS (ESI) *m/z* calcd for $C_{11}H_{10}O_3Na$ $[M+Na]^+$ 213.0528, found 213.0529.

Synthesis of 1c. To a stirred solution of propargylic alcohol **S-2c** (400 mg, 1.5 mmol) in CH_2Cl_2 (7.5 mL) were added pyridine (0.87 mL, 10.8 mmol), 4-DMAP (18.2 mg, 0.15 mmol) and acetic anhydride (0.21 mL, 2.2 mmol) at 0 °C, and stirring was continued for 2 h at the same temperature. The reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with brine. The residue upon work up was chromatographed on silica gel with hexane-AcOEt (8:2 v/v) as eluent to give propargylic acetate **1c** (617 mg, quant) as a pale yellow oil.

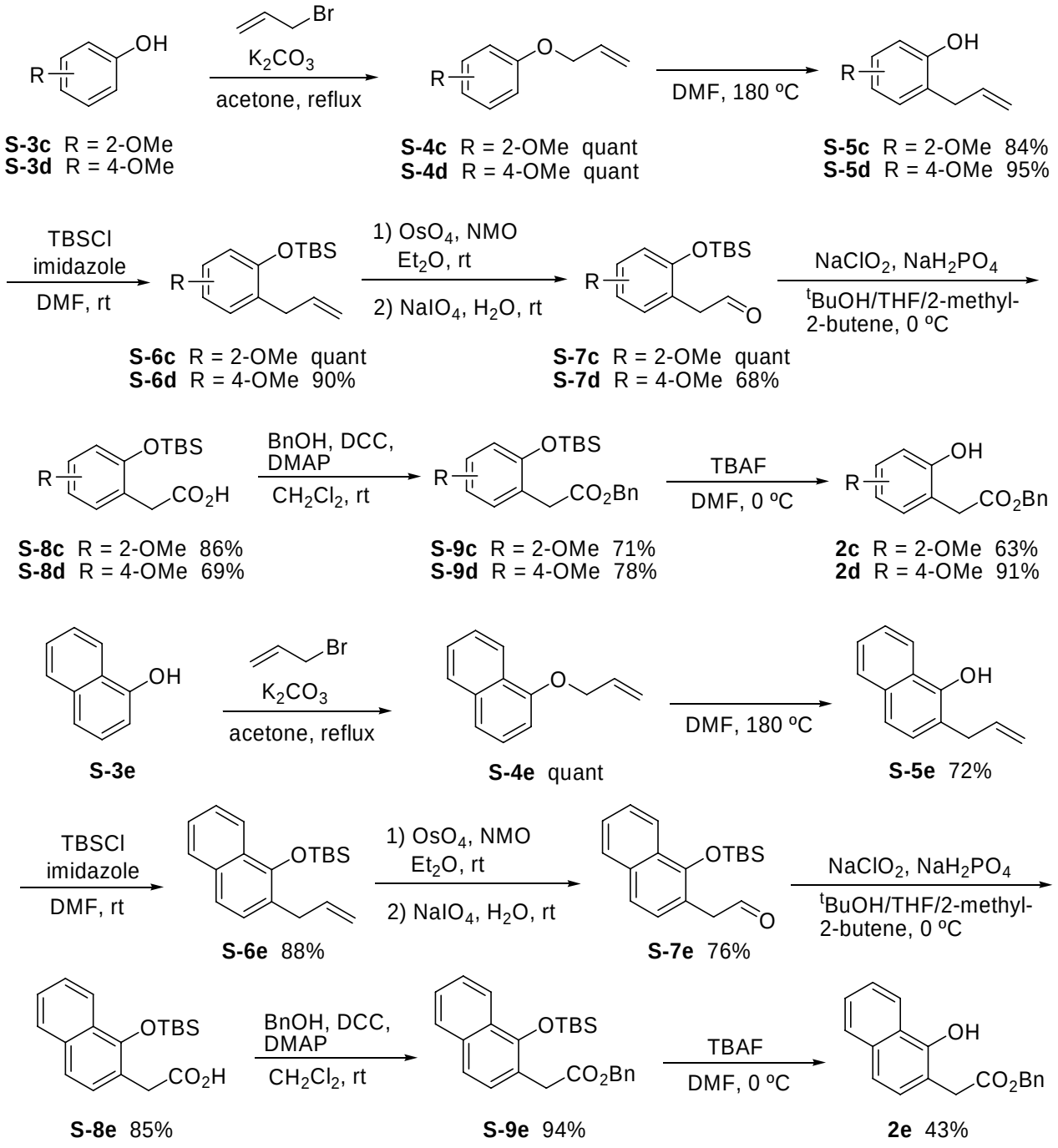
1,3-Bis(4-methoxyphenyl)prop-2-ynyl acetate (1c).



Pale yellow oil; IR (neat) 2935, 2883, 1739, 1606, 1506, 1369, 1221, 1033, 949, 833 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.11 (3H, s), 3.81 (3H, s), 3.82 (3H, s), 6.64 (1H, s), 6.84 (2H, d, *J* = 8.8 Hz), 6.92 (2H, d, *J* = 8.8 Hz), 7.42 (2H, d, *J* = 8.8 Hz) , 7.53 (2H, d, *J* = 8.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.2 (CH_3), 55.3 (CH_3), 55.3 (CH_3), 65.9 (CH), 84.4 (Cq), 86.9 (Cq), 113.9 (CH×2), 114.0 (CH×2), 114.2 (Cq), 129.3 (CH×2), 129.6 (Cq), 133.4 (CH×2), 159.9 (Cq), 160.0 (Cq), 169.9 (Cq); HRMS (ESI) *m/z* calcd for $C_{19}H_{18}O_4$ $[M]^+$ 310.1205, found 310.1203.

Preparation of 2-(2-Hydroxyphenyl)acetates 2 (Scheme S-2)

Scheme S-2

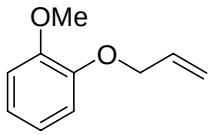


General procedure for the synthesis of 2-(2-hydroxyphenyl)acetates.

Synthesis of S-4d. To a stirred solution of 4-methoxyphenol (**S-3d**) (1.0 g, 8.1 mmol) in acetone (40 mL) were added K_2CO_3 (2.2 g, 16.1 mmol) and allyl bromide (0.8 mL, 9.7 mmol) at rt, and stirring was

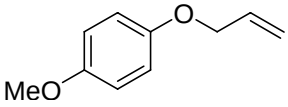
continued for 2 h under reflux condition. After filtration of the reaction mixture using Celite followed by concentration, the residue was chromatographed on silica gel with hexane-AcOEt (9:1 v/v) as eluent to give allyl ether **S-4d** (1.45g, quant) as a colorless oil.

1-(Allyloxy)-2-methoxybenzene (S-4c).



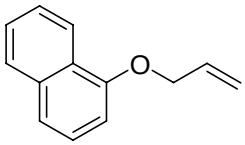
Colorless oil; IR (neat) 2935, 1592, 1506, 1124, 1027, 927, 742 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.89 (3H, s), 4.62 (2H, td, *J* = 1.6 and 5.6 Hz), 5.29 (1H, ddd, *J* = 1.6, 2.8 and 10.8 Hz), 5.41 (1H, ddd, *J* = 1.6, 2.8 and 17.2 Hz), 6.10 (1H, tdd, *J* = 5.6, 10.8 and 17.2 Hz), 6.86−6.96 (4H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 55.8 (CH_3), 69.8 (CH_2), 111.7 (CH), 113.5 (CH), 117.9 (CH_2), 120.7 (CH), 121.2 (CH), 133.4 (CH), 148.0 (Cq), 149.4 (Cq); HRMS (ESI) *m/z* calcd for $C_{10}H_{12}O_2Na$ $[M+Na]^+$ 187.0735, found 187.0735.

1-(Allyloxy)-4-methoxybenzene (S-4d).



Colorless oil; IR (neat) 2834, 1508, 1464, 1231, 1039, 824 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.77 (3H, s), 4.49 (2H, td, *J* = 1.6 and 5.2 Hz), 5.27 (1H, ddd, *J* = 1.6, 2.8 and 10.8 Hz), 5.42 (1H, ddd, *J* = 1.6, 2.8 and 17.6 Hz), 6.05 (1H, tdd, *J* = 5.2, 10.8 and 17.6 Hz), 6.81−6.88 (4H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 55.5 (CH_3), 69.3 (CH_2), 114.5 (CH×2), 115.6 (CH×2), 117.2 (CH_2), 133.6 (CH), 152.6 (Cq), 153.8 (Cq); HRMS (ESI) *m/z* calcd for $C_{10}H_{12}O_2Na$ $[M+Na]^+$ 187.0735, found 187.0737.

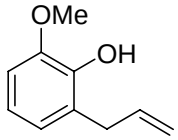
1-(Allyloxy)naphthalene (S-4e).



Pale yellow oil; IR (neat) 3053, 1628, 1581, 1509, 1401, 1268, 1098, 770, 571 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.73 (2H, d, *J* = 5.2 Hz), 5.34 (1H, dd, *J* = 1.6 and 10.4 Hz), 5.27 (1H, dd, *J* = 1.6 and 17.2 Hz), 6.19 (1H, tdd, *J* = 5.2, 10.4 and 17.2 Hz), 6.82 (1H, d, *J* = 7.6 Hz), 7.36 (1H, t, *J* = 8.0 Hz), 7.43 (1H, d, *J* = 8.0 Hz), 7.45−7.52 (2H, m), 7.79−7.82 (1H, m), 8.30−8.32 (1H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 68.9 (CH_2), 105.1 (CH), 117.3 (CH_2), 120.4 (CH), 122.1 (CH), 125.2 (CH), 125.8 (CH), 125.8 (Cq), 126.4 (CH), 127.4 (CH), 133.3 (CH), 134.5 (Cq), 154.3 (Cq); HRMS (ESI) *m/z* calcd for $C_{13}H_{12}O$ $[M]^+$ 184.0888, found 184.0889.

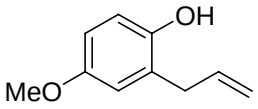
Synthesis of S-5d. Allyl ether **S-4d** (1.4 g, 8.5 mmol) in DMF (6 mL) was heated at 180 °C for 12 h in sealed tube. The reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with brine. The residue upon work up was chromatographed on silica gel with hexane-AcOEt (9:1 v/v) as eluent to give 2-allyl phenol **S-5d** (1.3g, 95%) as a colorless oil.

2-Allyl-6-methoxyphenol (S-5c).



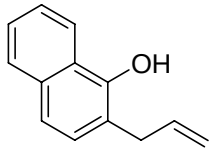
Colorless oil; IR (neat) 3522, 1479, 1270, 1078, 912, 739 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.42 (2H, d, *J* = 6.8 Hz), 3.88 (3H, s), 5.03−5.11 (2H, m), 5.69 (1H, s), 5.96−6.06 (1H, m), 6.74−6.82 (3H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 33.8 (CH_2), 56.0 (CH_3), 108.6 (CH), 115.4 (CH_2), 119.4 (CH), 122.2 (CH), 125.8 (Cq), 136.6 (CH), 143.4 (Cq), 146.3 (Cq); HRMS (ESI) *m/z* calcd for $C_{10}H_{12}O_2$ $[M]^+$ 164.0837, found 164.0833.

2-Allyl-4-methoxyphenol (S-5d).



Colorless oil; IR (neat) 3408, 1638, 1506, 1201, 1039, 915, 808 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.38 (2H, d, *J* = 6.4 Hz), 3.76 (3H, s), 4.58 (1H, s), 5.14−5.15 (1H, m), 5.17−5.18 (1H, m), 5.96−6.06 (1H, m), 6.67−6.70 (2H, m), 6.74−6.77 (1H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 35.1 (CH_2), 55.7 (CH_3), 112.5 (CH), 115.9 (CH), 116.4 (CH), 116.4 (CH_2), 126.7 (Cq), 136.2 (CH), 147.9 (Cq), 153.6 (Cq); HRMS (ESI) *m/z* calcd for $C_{10}H_{12}O_2Na$ $[M+Na]^+$ 187.0735, found 187.0738.

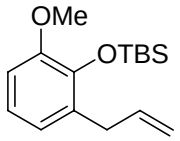
2-Allylnaphthalen-1-ol (S-5e).



Brown oil; IR (neat) 3339, 1661, 1575, 1387, 1099, 917, 809, 756 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.58 (2H, d, *J* = 6.4 Hz), 5.25 (1H, d, *J* = 8.0 Hz), 5.26 (1H, d, *J* = 18.8 Hz), 5.53 (1H, s), 6.08 (1H, tdd, *J* = 6.4, 8.0 and 18.8 Hz), 7.22 (1H, d, *J* = 8.4 Hz), 7.41 (1H, d, *J* = 8.0 Hz), 7.43−7.49 (2H, m), 7.77−7.79 (1H, m), 8.16−8.18 (1H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 35.7 (CH_2), 117.0 (CH_2), 117.8 (Cq), 120.4 (CH), 121.3 (CH), 124.8 (Cq), 125.3 (CH), 125.8 (CH), 127.5 (CH), 128.4 (CH), 133.8 (Cq), 136.1 (CH), 149.6 (Cq); HRMS (ESI) *m/z* calcd for $C_{13}H_{12}O$ $[M]^+$ 184.0888, found 187.0884.

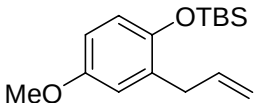
Synthesis of S-6d. To a stirred solution of 2-allyl phenol **S-5d** (1.2 g, 7.5 mmol) in DMF (40 mL) were added imidazole (1.7 g, 11.2 mmol) and *tert*-butyldimethylsilyl chloride (1.5 g, 22.5 mmol) at rt, and stirring was continued for 3 h. The reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with brine. The residue upon work up was chromatographed on silica gel with hexane-AcOEt (9:1 v/v) as eluent to give silyl ether **S-6d** (1.9g, 90%) as a colorless oil.

2-Allyl-1-(*tert*-butyldimethylsiloxy)-6-methoxybenzene (S-6c).



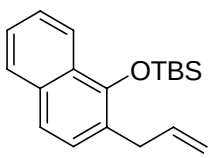
Colorless oil; IR (neat) 2929, 1480, 1288, 1084, 918, 781 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.18 (6H, s), 0.99 (9H, s), 3.41 (2H, d, *J* = 6.4 Hz), 3.78 (3H, s), 5.02−5.03 (1H, m), 5.05−5.07 (1H, m), 5.91−6.01 (1H, m), 6.72 (1H, dd, *J* = 1.6 and 8.0 Hz), 6.74 (1H, dd, *J* = 1.6 and 7.6 Hz), 6.84 (1H, dd, *J* = 7.6 and 8.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ −3.9 (CH_3×2), 18.9 (Cq), 26.1 (CH_3×3), 34.3 (CH_2), 54.8 (CH_3), 109.4 (CH), 115.5 (CH_2), 120.7 (CH), 121.9 (CH), 131.4 (Cq), 137.1 (CH), 142.6 (Cq), 150.0 (Cq); HRMS (ESI) *m/z* calcd for $C_{16}H_{27}O_2Si$ $[M+H]^+$ 279.1780, found 279.1778.

2-Allyl-1-(*tert*-butyldimethylsiloxy)-4-methoxybenzene (S-6d).



Colorless oil; IR (neat) 2858, 1497, 1227, 1045, 839 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.20 (6H, s), 1.00 (9H, s), 3.34 (2H, d, *J* = 6.8 Hz), 3.75 (3H, s), 5.03−5.04 (1H, m), 5.07−5.08 (1H, m), 5.90−6.01 (1H, m), 6.62 (1H, dd, *J* = 3.2 and 8.8 Hz), 6.70 (1H, d, *J* = 3.2 Hz), 6.71 (1H, d, *J* = 8.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ −4.2 (CH_3×2), 18.2 (Cq), 25.8 (CH_3×3), 34.6 (CH_2), 55.5 (CH_3), 111.7 (CH), 115.6 (CH), 115.7 (CH_2), 118.9 (CH), 131.5 (Cq), 136.8 (CH), 147.1 (Cq), 153.8 (Cq); HRMS (ESI) *m/z* calcd for $C_{16}H_{27}O_2Si$ $[M+H]^+$ 279.1780, found 279.1782.

2-Allyl-1-(*tert*-butyldimethylsiloxy)naphthalene (S-6e).

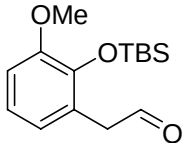


Pale yellow oil; IR (neat) 2930, 1570, 1472, 1386, 1261, 1086, 916, 830, 778 cm^{-1}; ^{1}H-NMR (400 MHz,

$CDCl_3$) δ 0.18 (6H, s), 1.13 (9H, s), 3.55 (2H, d, *J* = 6.8 Hz), 5.07−5.14 (2H, m), 5.90−6.00 (1H, m), 7.29 (1H, d, *J* = 8.8 Hz), 7.38−7.44 (2H, m), 7.45 (1H, d, *J* = 7.6 Hz), 7.74−7.77 (1H, m), 8.05−8.09 (1H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ −3.2 (CH_3×2), 18.7 (Cq), 26.1 (CH_3×3), 34.5 (CH_2), 116.0 (CH_2), 121.5 (CH), 123.1 (CH), 124.8 (Cq), 124.8 (CH), 125.3 (CH), 127.5 (CH), 128.2 (Cq), 128.2 (CH), 133.8 (Cq), 137.1 (CH), 148.0 (Cq); HRMS (ESI) *m/z* calcd for $C_{19}H_{27}OSi$ $[M+H]^+$ 299.1831, found 299.1831.

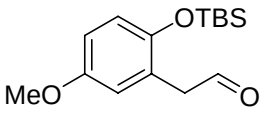
Synthesis of S-7d. To a stirred solution of silyl ether **S-6d** (100 mg, 360 μmol) in Et_2O (7 mL) were added OsO_4 (2 w/v% in H_2O, 0.9 mL, 72 μmol) and 4-methylmorpholine *N*-oxide (42.2 mg, 360 μmol) at rt, and stirring was continued for 12 h. Then water (7 mL) and $NaIO_4$ (770 mg, 3.6 mmol) was added to the reaction mixture, and further stirring was continued for 1 h. The reaction mixture was quenched with sat. Na_2SO_3 aq. and extracted with AcOEt. The combined extracts were washed with brine. The residue upon work up was chromatographed on silica gel with hexane-AcOEt (9:1 v/v) as eluent to give aldehyde **S-7d** (69 mg, 68%) as a pale yellow oil.

2-[2-(*tert*-Butyldimethylsilyloxy)-3-methoxyphenyl] acetaldehyde (S-7c).



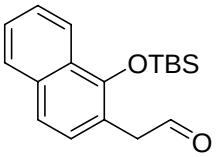
Colorless oil; IR (neat) 2930, 1727, 1585, 1251, 1083, 912, 840, 782 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.19 (6H, s), 0.97 (9H, s), 3.68 (2H, d, *J* = 2.0 Hz), 3.81 (3H, s), 6.73 (1H, dd, *J* = 2.0 and 7.6 Hz), 6.83 (1H, dd, *J* = 2.0 and 8.0 Hz), 6.90 (1H, dd, *J* = 7.6 and 8.0 Hz), 9.68 (1H, t, *J* = 2.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ −3.8 (CH_3×2), 18.8 (Cq), 26.0 (CH_3×3), 45.3 (CH_2), 54.7 (CH_3), 110.9 (CH), 121.2 (CH), 122.9 (CH), 123.9 (Cq), 143.5 (Cq), 150.1 (Cq), 200.2 (CH); HRMS (ESI) *m/z* calcd for $C_{15}H_{24}O_3NaSi$ $[M+Na]^+$ 303.1392, found 303.1396.

2-[2-(*tert*-Butyldimethylsilyloxy)-5-methoxyphenyl]acetaldehyde (S-7d).



Pale yellow oil; IR (neat) 2859, 1727, 1500, 1229, 1047, 895, 840 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.21 (6H, s), 0.98 (9H, s), 3.60 (2H, d, *J* = 2.0 Hz), 3.76 (3H, s), 6.79 (1H, d, *J* = 2.8 Hz), 6.73 (1H, dd, *J* = 2.8 and 8.4 Hz), 6.79 (1H, d, *J* = 8.4 Hz), 6.79 (1H, d, *J* = 8.4 Hz), 9.68 (1H, t, *J* = 2.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ −4.3 (CH_3×2), 18.1 (Cq), 25.7 (CH_3×3), 45.7 (CH_2), 55.6 (CH_3), 113.5 (CH), 116.7 (CH), 118.9 (CH), 123.9 (Cq), 147.8 (Cq), 153.9 (Cq), 199.8 (CH); HRMS (ESI) *m/z* calcd for $C_{15}H_{24}O_3NaSi$ $[M+Na]^+$ 303.1392, found 303.1392.

2-[1-*tert*-Butyldimethylsilyloxy)naphthalen-2-yl]acetaldehyde (S-7e).

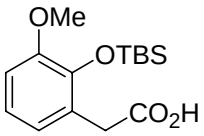


Pale yellow oil; IR (neat) 2926, 1718, 1507, 772, 668 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.17 (6H, s), 1.12 (9H, s), 3.83 (2H, d, *J* = 2.4 Hz), 7.23 (1H, d, *J* = 8.4 Hz), 7.44−7.48 (2H, m), 7.52 (1H, d, *J* = 8.4 Hz), 7.78−7.82 (1H, m), 8.06−8.10 (1H, m), 9.73 (1H, t, *J* = 2.4 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ −3.1 (CH_3×2), 18.7 (Cq), 26.1 (CH_3×3), 45.6 (CH_2), 117.7 (Cq), 122.2 (CH), 123.1 (CH), 125.2 (CH), 126.0 (CH), 127.8 (CH), 128.1 (Cq), 128.4 (CH), 134.5 (Cq), 149.6 (Cq), 200.1 (CH); HRMS (ESI) *m/z* calcd for $C_{18}H_{24}O_2Si$ $[M]^+$ 300.1546, found 300.1547.

Synthesis of S-8d. To a stirred solution of aldehyde **S-7d** (898 mg, 3.2 mmol), NaH_2PO_4 and 2-methyl-2-butene (3 mL, 28.4 mmol) in THF-^{t}BuOH-water (1:3:5) (27 mL) were added $NaClO_2$ (2.0 g, 22.4 mmol) at 0 °C, and stirring was continued for 4 h. The reaction mixture was quenched with 1 N HCl aq. and extracted with AcOEt. The combined extracts were washed with brine. The residue upon work up

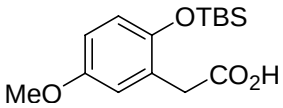
was chromatographed on silica gel with hexane-AcOEt (8:2 v/v) as eluent to give carboxylic acid **S-8d** (652 mg, 69%) as a pale yellow oil.

2-[2-(*tert*-Butyldimethylsilyloxy)-3-methoxyphenyl]acetic acid (S-8c).



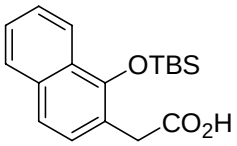
Colorless crystals; mp 60.9−61.1 °C (recrystallized from hexane); IR (KBr) 3400, 1714, 1489, 1247, 1085, 915 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.20 (6H, s), 0.99 (9H, s), 3.71 (2H, d, *J* = 7.6 Hz), 3.79 (3H, s), 6.80 (2H, d, *J* = 7.6 Hz), 6.89 (1H, t, *J* = 7.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ −3.8 (CH_3×2), 18.8 (Cq), 26.0 (CH_3×3), 35.8 (CH_2), 54.7 (CH_3), 110.7 (CH), 120.8 (CH), 122.7 (CH), 125.0 (Cq), 143.2 (Cq), 149.8 (Cq), 177.9 (Cq); HRMS (ESI) *m/z* calcd for $C_{15}H_{24}O_4NaSi$ $[M+Na]^+$ 319.1342, found 319.1343.

2-[2-(*tert*-Butyldimethylsilyloxy)-5-methoxyphenyl]acetic acid (S-8d).



Colorless crystals; mp 67.8−68.6 °C (recrystallized from hexane); IR (KBr) 2958, 1710, 1608, 1498, 1221, 1037, 886 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.21 (6H, s), 0.98 (9H, s), 3.62 (2H, s), 3.75 (3H, s), 6.71 (1H, dd, *J* = 2.8 and 8.4 Hz), 6.75 (1H, d, *J* = 8.4 Hz), 6.76 (1H, d, *J* = 2.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ −4.3 (CH_3×2), 18.1 (Cq), 25.7 (CH_3×3), 36.1 (CH_2), 55.6 (CH_3), 113.5 (CH), 116.6 (CH), 118.7 (CH), 125.1 (Cq), 147.6 (Cq), 153.6 (Cq), 177.9 (Cq); HRMS (ESI) *m/z* calcd for $C_{15}H_{24}O_4NaSi$ $[M+Na]^+$ 319.1342, found 319.1339.

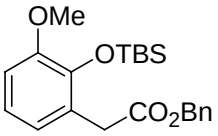
2-[1-(*tert*-Butyldimethylsilyloxy)naphthalen-2-yl]acetic acid (S-8e).



Yellow crystals; mp 116.3−117.0 °C (recrystallized from hexane); IR (KBr) 2928, 1720, 1569, 1465, 1382, 1324, 1218, 1096, 814, 742 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.17 (6H, s), 0.11 (9H, s), 3.85 (2H, s), 7.33 (1H, d, *J* = 8.4 Hz), 7.42−7.45 (2H, m), 7.48 (1H, d, *J* = 8.4 Hz), 7.75−7.79 (1H, m), 8.04−8.07 (1H, m); ^{13}C-NMR (75 MHz, $CDCl_3$) δ −3.3 (CH_3×2), 18.7 (Cq), 26.0 (CH_3×3), 35.7 (CH_2), 118.8 (Cq), 121.8 (CH), 123.2 (CH), 125.0 (CH), 125.9 (CH), 127.7 (CH), 127.9 (Cq), 128.4 (CH), 134.4 (Cq), 149.0 (Cq), 177.4 (Cq); HRMS (ESI) *m/z* calcd for $C_{18}H_{24}O_3NaSi$ $[M+Na]^+$ 339.1392, found 339.1392.

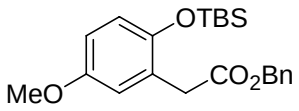
Synthesis of S-9d. To a stirred solution of carboxylic acid **S-8d** (410 mg, 1.4 mmol) in CH_2Cl_2 (6 mL) were added benzyl alcohol (0.2 mL, 2.1 mmol), DCC (570 mg, 2.8 mmol) and DMAP (16.9 mg, 0.1 mmol) at 0 °C, and stirring was continued for 1 h. After filtration of the reaction mixture using Celite followed by concentration, the residue was chromatographed on silica gel with hexane-AcOEt (9:1 v/v) as eluent to give benzyl ester **S-9d** (415 mg, 78%) as colorless crystals.

Benzyl 2-[2-(*tert*-butyldimethylsilyloxy)-3-methoxyphenyl]acetate (S-9c).



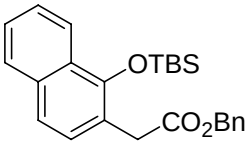
Colorless crystals; mp 43.4−43.9 °C (recrystallized from hexane); IR (KBr) 2926, 1744, 1588, 1491, 1080, 924, 734, 697 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.16 (6H, s), 0.96 (9H, s), 3.72 (2H, s), 3.78 (3H, s), 5.12 (2H, s), 6.77−6.80 (2H, m), 6.86 (1H, t, *J* = 8.0 Hz), 7.30−7.34 (5H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ −3.9 (CH_3×2), 18.8 (Cq), 26.0 (CH_3×3), 35.8 (CH_2), 54.7 (CH_3), 66.3 (CH_2), 110.5 (CH), 120.7 (CH), 122.7 (CH), 125.5 (Cq), 128.0 (CH), 128.1 (CH×2), 128.4 (CH×2), 136.0 (Cq), 143.2 (Cq), 149.8 (Cq), 171.4 (Cq); HRMS (ESI) *m/z* calcd for $C_{22}H_{30}O_4NaSi$ $[M+Na]^+$ 409.1811, found 409.1815.

Benzyl 2-[2-(*tert*-butyldimethylsilyloxy)-5-methoxyphenyl]acetate (S-9d).



Colorless oil; IR (KBr) 2930, 1742, 1501, 1229, 1044, 892, 697 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.18 (6H, s), 0.96 (9H, s), 3.73 (3H, s), 3.64 (2H, s), 5.12 (2H, s), 6.69 (1H, dd, *J* = 2.8 and 8.8 Hz), 6.73 (1H, d, *J* = 8.8 Hz), 6.75 (1H, d, *J* = 2.8 Hz), 7.30−7.32 (5H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ −4.3 (CH_3×2), 18.2 (Cq), 25.7 (CH_3×3), 36.2 (CH_2), 55.6 (CH_3), 66.4 (CH_2), 113.4 (CH), 116.4 (CH), 118.8 (CH), 125.6 (Cq), 128.1 (CH), 128.2 (CH×2), 128.4 (CH×2), 136.0 (Cq), 147.6 (Cq), 153.6 (Cq), 171.3 (Cq); HRMS (ESI) *m/z* calcd for $C_{22}H_{30}O_4NaSi$ $[M+Na]^+$ 409.1811, found 409.1810.

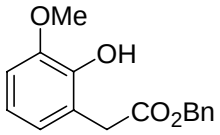
Benzyl 2-[1-(*tert*-butyldimethylsilyloxy)naphthalen-2-yl]acetate (S-9e).



Yellow oil; IR (KBr) 2930, 2858, 1739, 1572, 1225, 1155, 1089, 829 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.14 (6H, s), 1.10 (9H, s), 3.87 (2H, s), 5.15 (2H, s), 7.26−7.34 (6H, m), 7.41−7.48 (3H, m), 7.76−7.80 (1H, m), 8.04−8.07 (1H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ −3.4 (CH_3×2), 18.6 (Cq), 26.0 (CH_3×3), 35.9 (CH_2), 66.5 (CH_2), 119.4 (Cq), 121.7 (CH), 123.2 (CH), 124.9 (CH), 125.7 (CH), 127.6 (CH), 128.0 (Cq), 128.1 (CH), 128.1 (CH×2), 128.4 (CH×2), 128.5 (CH), 134.3 (Cq), 135.9 (Cq), 148.9 (Cq), 171.5 (Cq); HRMS (ESI) *m/z* calcd for $C_{25}H_{31}O_3Si$ $[M+H]^+$ 407.2042, found 407.2037.

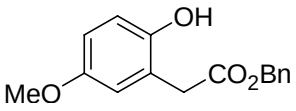
Synthesis of 2d. To a stirred solution of benzyl ester **S-9d** (410 mg, 1.4 mmol) in THF (5 mL) were added TBAF (1.0 M in THF, 1.6 mL, 1.6 mmol) at 0 °C, and stirring was continued for 1 h. The reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with brine. The residue upon work up was chromatographed on silica gel with hexane-AcOEt (8:2 v/v) as eluent to give 2-(2-hydroxyphenyl)acetate **2d** (266 mg, 91%) as a pale yellow oil.

Benzyl 2-(2-hydroxy-3-methoxyphenyl)acetate (2c).



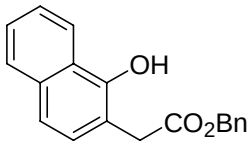
Pale yellow oil; IR (neat) 3522, 2941, 1733, 1595, 1481, 1272, 1076, 743 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.73 (2H, s), 3.89 (3H, s), 5.16 (2H, s), 5.86 (1H, s), 6.81 (3H, s), 7.30−7.37 (5H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 35.3 (CH_2), 56.0 (CH_3), 66.5 (CH_2), 109.8 (CH), 119.5 (CH), 120.2 (Cq), 123.0 (CH), 128.0 (CH×2), 128.1 (CH), 128.4 (CH×2), 136.0 (Cq), 144.0 (Cq), 146.6 (Cq), 171.6 (Cq); HRMS (ESI) *m/z* calcd for $C_{16}H_{16}O_4Na$ $[M+Na]^+$ 295.0946, found 295.0942.

Benzyl 2-(2-hydroxy-5-methoxyphenyl)acetate (2d).



Pale yellow oil; IR (neat) 3409, 2947, 1712, 1516, 1205, 1038, 816, 752, 700 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.69 (2H, s), 3.74 (3H, s), 5.17 (2H, s), 6.66 (1H, d, J = 2.8 Hz), 6.75 (1H, dd, J = 2.8 and 8.8 Hz), 6.82 (1H, s), 6.88 (1H, d, J = 8.8 Hz), 7.35−7.38 (5H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 37.9 (CH_2), 55.7 (CH_3), 67.5 (CH_2), 114.2 (CH), 116.3 (CH), 118.3 (CH), 121.6 (Cq), 128.4 (CH×2), 128.5 (CH), 128.6 (CH×2), 135.1 (Cq), 148.8 (Cq), 153.7 (Cq), 173.4 (Cq); HRMS (ESI) *m/z* calcd for $C_{16}H_{16}O_4Na$ $[M+Na]^+$ 295.0949, found 295.0946.

Benzyl 2-(1-hydroxynaphthalen-2-yl)acetate (2e).

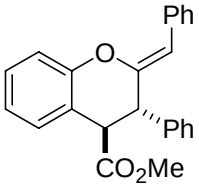


Yellow oil; IR (neat) 3310, 1701, 1510, 1384, 772, 424 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.87 (2H, s), 5.19 (2H, s), 7.17 (1H, d, J = 8.4 Hz), 7.34−7.39 (6H, m), 7.45−7.51 (2H, m), 7.75−7.78 (1H, m), 8.31−8.34 (1H, m), 8.38 (1H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 38.4 (CH_2), 67.9 (CH_2), 113.4 (Cq),

120.4 (CH), 122.3 (CH), 125.4 (CH), 126.0 (Cq), 126.3 (CH), 127.3 (CH), 128.4 (CH×2), 128.6 (CH), 128.7 (CH×2), 134.3 (Cq), 134.8 (Cq), 151.3 (Cq), 174.4 (Cq); HRMS (ESI) *m/z* calcd for $C_{19}H_{17}O_3$ $[M+H]^+$ 293.1178, found 293.1181.

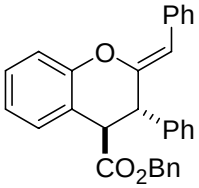
General procedure for the reaction of propargylic esters with phenols using palladium catalyst. Synthesis of 3aa (Table 1, entry 3). To a stirred solution of propargylic carbonate **1a** (25.0 mg, 94 μmol) in DMSO (2.0 mL) were added 2-(2-hydroxyphenyl)acetate **2a** (18.6 mg, 112 μmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (4.9 mg, 4.7 μmol) and dppf (10.4 mg, 18.8 μmol) at rt, and stirring was continued for 30 min at the same temperature under argon atomosphere. The reaction mixture was then allowed to heat to 120 °C, and stirred for 5 min. After filtration of the reaction mixture using small amount of silica gel followed by concentration, the residue was chromatographed on silica gel with hexane-AcOEt (9:1 v/v) as eluent to give **3aa** (34.0 mg, 99%) as a pale yellow oil.

(3*S,4*R**,*Z*)-Methyl 2-benzylidene-3-phenylchroman-4-carboxylate (3aa).**



Pale yellow oil; IR (neat) 1734, 1653, 1617, 1489, 1457, 1241, 755, 695 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.66 (3H, s), 4.16 (1H, d, *J* = 5.2 Hz), 4.35 (1H, d, *J* = 5.2 Hz), 5.47 (1H, s), 6.97 (1H, dt, *J* = 1.2 and 7.2 Hz), 7.10−7.34 (11H, m), 7.67 (2H, d, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 45.4 (CH), 48.1 (CH), 52.5 (CH_3), 109.2 (CH), 116.5 (CH), 118.4 (Cq), 122.1 (CH), 126.3 (CH), 127.2 (CH), 127.7 (CH×2), 128.2 (CH×2), 128.7 (CH×2), 128.8 (CH×2), 129.2 (CH), 129.5 (CH), 135.1 (Cq), 139.3 (Cq), 148.6 (Cq), 151.9 (Cq), 172.0 (Cq); HRMS (ESI) *m/z* calcd for $C_{24}H_{21}O_3$ $[M+H]^+$ 357.1496, found 357.1491.

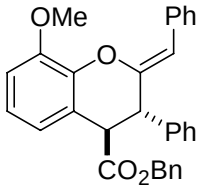
(3*S,4*R**,*Z*)-2-Benzylidene-3-phenylchroman-4-carboxylate (3ab).**



Pale yellow oil; IR (neat) 1734, 1483, 1241, 752, 695 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.21 (1H, d, *J*

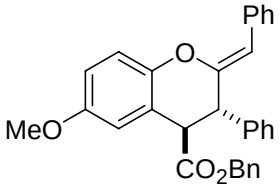
= 5.6 Hz), 4.34 (1H, d, *J* = 5.6 Hz), 5.10 (2H, s), 5.40 (1H, s), 6.95 (1H, dd, *J* = 7.2 and 7.6 Hz), 7.09 (1H, d, *J* = 7.6 Hz), 7.13−7.28 (13H, m), 7.32 (2H, t, *J* = 7.6 Hz), 7.65 (2H, d, *J* = 7.6 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 45.4 (CH), 48.2 (CH), 67.0 (CH_2), 109.2 (CH), 116.5 (CH), 118.4 (Cq), 122.1 (CH), 126.3 (CH), 127.2 (CH), 127.8 (CH×2), 128.0 (CH×2), 128.1 (CH), 128.2 (CH×2), 128.4 (CH×2), 128.7 (CH×2), 128.9 (CH×2), 129.2 (CH), 129.4 (CH), 135.0 (Cq), 135.4 (Cq), 139.1 (Cq), 148.6 (Cq), 151.9 (Cq), 171.4 (Cq); HRMS (ESI) *m/z* calcd for $C_{30}H_{24}O_3Na$ $[M+Na]^+$ 455.1623, found 455.1622.

(3*S,4*R**,*Z*)-Methyl 2-benzylidene-8-methoxy-3-phenylchroman-4-carboxylate (3ac).**



Pale yellow oil; IR (neat) 1734, 1486, 1271, 770, 696 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.95 (3H, s), 4.21 (1H, d, *J* = 5.6 Hz), 4.34 (1H, d, *J* = 5.6 Hz), 5.09 (2H, s), 5.41 (1H, s), 6.70 (1H, dd, *J* = 3.2 and 5.6 Hz), 6.87−6.90 (2H, m), 7.15−7.26 (11H, m), 7.32 (2H, t, *J* = 7.6 Hz), 7.80 (2H, d, *J* = 7.6 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 45.2 (CH), 48.1 (CH), 56.3 (CH_3), 67.0 (CH_2), 109.7 (CH), 111.6 (CH), 119.1 (Cq), 120.7 (CH), 121.6 (CH), 126.3 (CH), 127.2 (CH), 127.8 (CH×2), 128.0 (CH×2), 128.1 (CH), 128.2 (CH×2), 128.4 (CH×2), 128.7 (CH×2), 129.0 (CH×2), 135.1 (Cq), 135.4 (Cq), 139.2 (Cq), 141.6 (Cq), 148.1 (Cq), 148.4 (Cq), 171.4 (Cq); HRMS (ESI) *m/z* calcd for $C_{31}H_{26}O_4Na$ $[M+Na]^+$ 485.1729, found 485.1734.

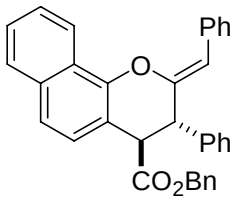
(3*S,4*R**,*Z*)-Methyl 2-benzylidene-6-methoxy-3-phenylchroman-4-carboxylate (3ad).**



Pale yellow oil; IR (neat) 1734, 1497, 1222, 754, 696 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.68 (3H, s), 4.16 (1H, d, *J* = 5.2 Hz), 4.31 (1H, d, *J* = 5.2 Hz), 5.08 (1H, d, *J* = 12.4 Hz), 5.12 (1H, d, *J* = 12.4 Hz),

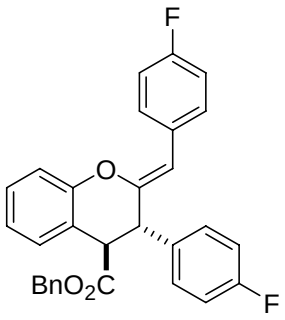
5.37 (1H, s), 6.60 (1H, d, J = 2.8 Hz), 6.82 (1H, dd, J = 2.8 and 8.8 Hz), 7.07 (1H, d, J = 8.8 Hz), 7.18−7.33 (13H, m), 7.64 (2H, d, J = 7.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 45.5 (CH), 48.5 (CH), 55.6 (CH_3), 67.0 (CH_2), 108.8 (CH), 113.8 (CH), 115.3 (CH), 117.2 (CH), 118.8 (Cq), 126.2 (CH), 127.2 (CH), 127.8 (CH×2), 128.1 (CH×2), 128.2 (CH×3), 128.4 (CH×2), 128.7 (CH×2), 128.8 (CH×2), 135.2 (Cq), 135.4 (Cq), 139.3 (Cq), 146.1 (Cq), 148.8 (Cq), 154.5 (Cq), 171.2 (Cq); HRMS (ESI) *m/z* calcd for $C_{31}H_{26}O_4Na$ $[M+Na]^+$ 485.1729, found 485.1724.

(3*S,4*R**,*Z*)-Methyl 2-benzylidene-3-phenyl-3,4-dihydro-2*H*-benzo[*h*]chromene-4-carboxylate (3ae).**



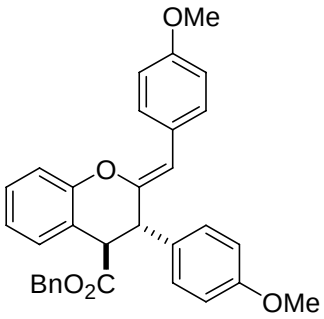
Pale yellow oil; IR (neat) 1748, 1457, 1262, 770, 695 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.32 (1H, d, J = 4.8 Hz), 4.45 (1H, d, J = 4.8 Hz), 5.12 (2H, s), 5.59 (1H, s), 7.18−7.29 (12H, m), 7.39 (2H, t, J = 7.6 Hz), 7.45 (1H, d, J = 8.8 Hz), 7.51−7.60 (2H, m), 7.76 (2H, d, J = 7.6 Hz), 7.81 (1H, d, J = 7.6 Hz), 8.42 (1H, d, J = 8.4 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 45.2 (CH), 48.4 (CH), 67.1 (CH_2), 110.2 (CH), 112.3 (Cq), 121.7 (CH), 121.8 (CH), 124.2 (Cq), 126.2 (CH), 126.5 (CH), 126.6 (CH), 126.6 (CH), 127.2 (CH), 127.6 (CH×2), 127.7 (CH), 128.0 (CH×2), 128.2 (CH), 128.3 (CH×2), 128.4 (CH×2), 128.7 (CH×2), 129.0 (CH×2), 134.2 (Cq), 135.0 (Cq), 135.5 (Cq), 139.4 (Cq), 147.3 (Cq), 148.4 (Cq), 171.6 (Cq); HRMS (ESI) *m/z* calcd for $C_{34}H_{26}O_3Na$ $[M+Na]^+$ 505.1780, found 505.1785.

(3*S,4*R**,*Z*)-Benzyl 2-(4-fluorobenzylidene)-3-(4-fluorophenyl)chroman-4-carboxylate (3bb).**



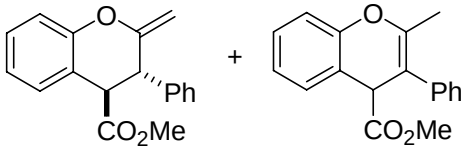
Pale yellow oil; IR (neat) 1734, 1603, 1507, 1456, 1229, 1160, 754, 698 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.15 (1H, d, *J* = 5.6 Hz), 4.28 (1H, d, *J* = 5.6 Hz), 5.09 (1H, d, *J* = 12.8 Hz), 5.12 (1H, d, *J* = 12.8 Hz), 5.31 (1H, s), 6.91−7.03 (5H, m), 7.09−7.30 (10H, m), 7.60 (2H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 44.7 (CH), 48.3 (CH), 67.1 (CH_2), 108.1 (CH), 115.1 (CH×2, d, *J* = 21.4 Hz), 115.6 (CH×2, d, *J* = 20.7 Hz), 116.5 (CH), 118.4 (Cq), 122.3 (CH), 128.1 (CH×2), 128.2 (CH), 128.4 (CH×2), 129.4 (CH×2), 129.4 (CH×2, d, *J* = 17.3 Hz), 130.4 (CH×2, d, *J* = 7.4 Hz), 131.0 (Cq, d, *J* = 3.3 Hz), 134.6 (Cq, d, *J* = 3.3 Hz), 135.3 (Cq), 148.1 (Cq), 151.7 (Cq), 161.3 (Cq, d, *J* = 244.5 Hz), 161.9 (Cq, d, *J* = 245.3 Hz), 171.2 (Cq); HRMS (ESI) *m/z* calcd for $C_{30}H_{22}O_3F_2Na$ $[M+Na]^+$ 491.1435, found 491.1432.

(3*S,4*R**,*Z*)-Benzyl 2-(4-methoxybenzylidene)-3-(4-methoxyphenyl)chroman-4-carboxylate (3cb).**



Pale yellow oil; IR (neat) 1734, 1511, 1457, 722 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.76 (3H, s), 3.82 (3H, s), 4.17 (1H, d, *J* = 6.0 Hz), 4.25 (1H, d, *J* = 6.0 Hz), 5.08 (1H, d, *J* = 12.4 Hz), 5.11 (1H, d, *J* = 12.4 Hz), 5.30 (1H, s), 6.78 (2H, d, *J* = 8.8 Hz), 6.86 (2H, d, *J* = 8.8 Hz), 6.94 (1H, t, *J* = 7.2 Hz), 7.07−7.17 (6H, m), 7.22−7.33 (4H, m), 7.59 (2H, d, *J* = 8.8 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 44.7 (CH), 48.4 (CH), 55.2 (CH_3), 55.2 (CH_3), 66.9 (CH_2), 108.5 (CH), 113.6 (CH×2), 114.0 (CH×2), 116.5 (CH), 118.8 (Cq), 121.9 (CH), 127.9 (Cq), 128.0 (CH×2), 128.1 (CH), 128.4 (CH×2), 129.0 (CH×2), 129.1 (CH), 129.2 (CH), 130.1 (CH×2), 131.0 (Cq), 135.5 (Cq), 147.5 (Cq), 152.0 (Cq), 158.0 (Cq), 158.6 (Cq), 171.6 (Cq); HRMS (ESI) *m/z* calcd for $C_{32}H_{28}O_5Na$ $[M+Na]^+$ 515.1834, found 515.1835.

(3*R,4*S**)-Methyl 2-methylene-3-phenylchroman-4-carboxylate (3da) + methyl 2-methyl-3-phenyl-4*H*-chromene-4-carboxylate (5).**

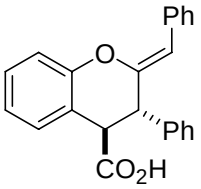


Pale yellow oil; IR (neat) 2951, 1733, 1588, 1489, 1456, 1245, 1039, 846, 756 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.83 (1.5H, s), 3.66 (1.5H, s), 3.93 (1.5H, s), 4.11 (0.5H, d, *J* = 6.4 Hz), 4.16 (0.5H, s), 4.23 (0.5H, d, *J* = 6.4 Hz), 4.80 (0.5H, s), 5.63 (0.5H, s), 6.74 (0.5H, d, *J* = 8.0 Hz), 6.86−7.00 (2H, m), 7.05−7.07 (1H, m), 7.08−7.37 (5.5H, m); HRMS (ESI) *m/z* calcd for $C_{18}H_{16}O_3Na$ $[M+Na]^+$ 280.1099, found 280.1095.

Hydrolysis of (3*S,4*R**,*Z*)-Methyl 2-benzylidene-3-phenylchroman-4-carboxylate (3aa). (Scheme 3)**

To a stirred solution of **3aa** (33.5 mg, 94 μmol) in THF/H_2O (1.5+0.5mL) were added $LiOH·H_2O$ (7.9 mg, 188 μmol) at rt, and stirring was continued for 2.5 h. The reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with brine, and the residue upon workup was chromatographed on silica gel with hexane-AcOEt (8:2 v/v) as eluent to give **4** (30.3 mg, 94%) as colorless crystals.

(3*R,4*S**,*Z*)-2-Benzylidene-3-phenylchroman-4-carboxylic acid (4).**

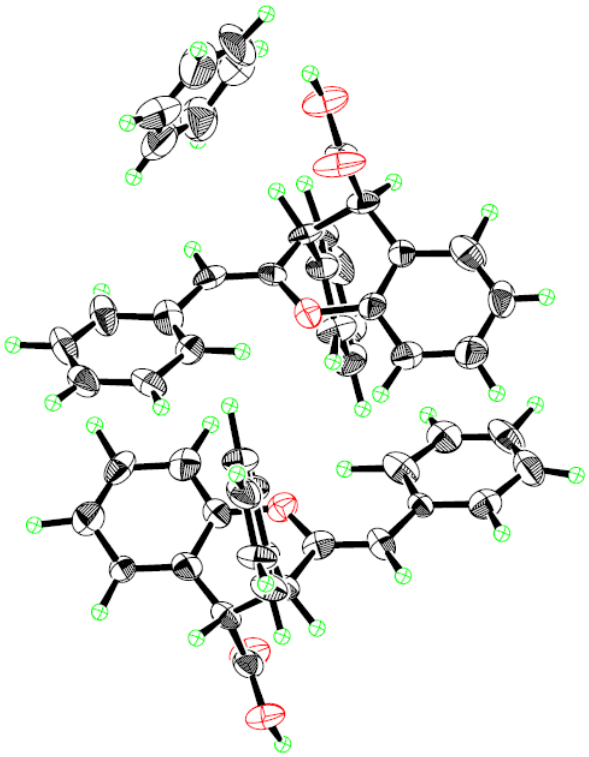


Colorless crystals; mp 122.8−125.4 °C (recrystallized from benzene); IR (neat) 3026, 1711, 1588, 1489, 1456, 1241, 753, 695 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.19 (1H, d, *J* = 4.8 Hz), 4.38 (1H, d, *J* = 4.8 Hz), 5.51 (1H, s), 6.98 (1H, t, *J* = 7.2 Hz), 7.14−7.35 (11H, m), 7.68 (2H, d, *J* = 7.6 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 45.0 (CH), 44.7 (CH), 109.5 (CH), 116.6 (CH), 117.5 (Cq), 122.2 (CH), 126.4 (CH),

127.3 (CH), 127.5 (CH×2), 128.2 (CH×2), 128.7 (CH×2), 128.9 (CH×2), 129.5 (CH), 129.9 (CH), 135.0 (Cq), 139.3 (Cq), 147.9 (Cq), 151.9 (Cq), 176.4 (Cq); HRMS (ESI) *m/z* calcd for $C_{23}H_{18}O_3Na$ $[M+Na]^+$ 365.1155, found 365.1154.

X-Ray crystallographic analysis of compound 4. A colorless block crystal having approximate dimensions of 0.50 x 0.40 x 0.30 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Kα radiation. The structure was solved by direct methods (SIR97) and expanded using Fourier techniques (DIRDIF99). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F was based on 9139 observed reflections ($I > 0.00\sigma(I)$) and 565 variable parameters, and converged (largest parameter shift was 4.02 times its esd) with unweighted and weighted agreement factors of $R = 0.084$ and $R_W = 0.191$. Crystal data for **4**: $C_{26}H_{21}O_3$, M = 381.45, triclinic, space group P1, a = 8.4452(8) Å, b = 10.6647(9) Å, c = 11.566(1) Å, $\alpha = 82.230(2)^\circ$, $\beta = 89.149(2)^\circ$, $\gamma = 77.425(2)^\circ$, V = 1007.3(2) $Å^3$, Z = 2, $D_c = 1.258$ g/cm^3, F(000) = 402, μ(MoKα) = 0.81 cm^{-3}.

Figure S-1. ORTEP drawing of **4** (as a dimer·benzene complex)



Procedure for the reaction of propargylic ester with phenol using (*S*)-SEGPHOS and palladium catalyst. Synthesis of (3*S*,4*R*)-3ab (Table 3, entry 7). To a stirred solution of propargylic carbonate **1a** (20.0 mg, 75 μmol) in DMSO (2.0 mL) were added 2-(2-hydroxyphenyl)acetate **2b** (21.8 mg, 90 μmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (3.9 mg, 3.8 μmol) and (*S*)-SEGPHOS (9.2 mg, 15 μmol) at rt, and stirring was continued for 30 min at the same temperature under argon atomosphere. The reaction mixture was then allowed to heat to 60 °C, and stirred for 3 h. After filtration of the reaction mixture using small amount of silica gel followed by concentration, the residue was chromatographed on silica gel with hexane-AcOEt (9:1 v/v) as eluent to give (3*R*,4*S*)-**3ab** (19.1 mg, 59%; 96 % ee) as a pale yellow oil.

(3*S*,4*R*,*Z*)-2-Benzylidene-3-phenylchroman-4-carboxylate [(3*S*,4*R*)-3ab]. $[\alpha]_D^{30}$ = −43.3 (c 1.10 in $CHCl_3$); enantiomeric excess was determined by HPLC analysis [CHIRALCEL AS-H column,

hexane-^{i}PrOH (9:1 v/v), 0.5 mL/min, λ = 254 nm, retention time 17.3 min (3*S*,4*R*) and 22.6 min (3*R*,4*S*)]. Other spectral data coincides with those of the racemic **3ab**.

Determination of Absolute Configuration

Absolute configuration of (3*R*,4*S*)-**3ab** was determined as follows (Scheme S-3). The product (3*R*,4*S*)-**3ab** was subjected to hydrolysis in the presence of $LiOH{\cdot}H_2O$ to give the carboxylic acid. The product was transformed to (*S*)- and (*R*)-PGME ester by the reaction with (*S*)- and (*R*)-phenylglycine methyl ester.[5] On the basis of the $\Delta\delta$ values ($\Delta\delta = \delta_{(S)\text{-amide}} - \delta_{(R)\text{-amide}}$) (Figure S-1), the absolute configuration of **3ab** was determined as 3*S*, 4*R*.

Scheme S-3

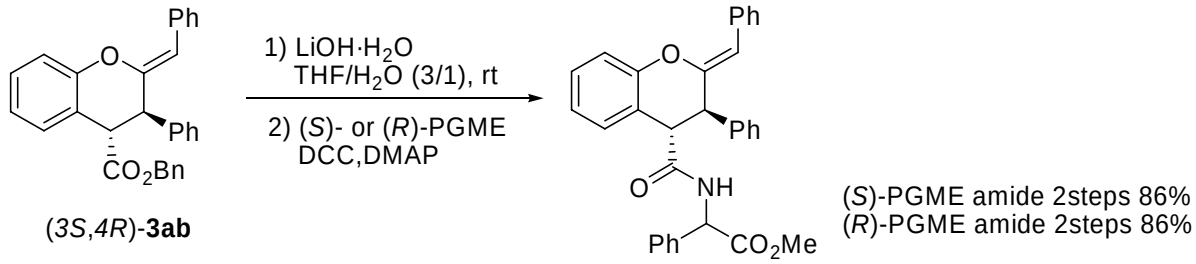
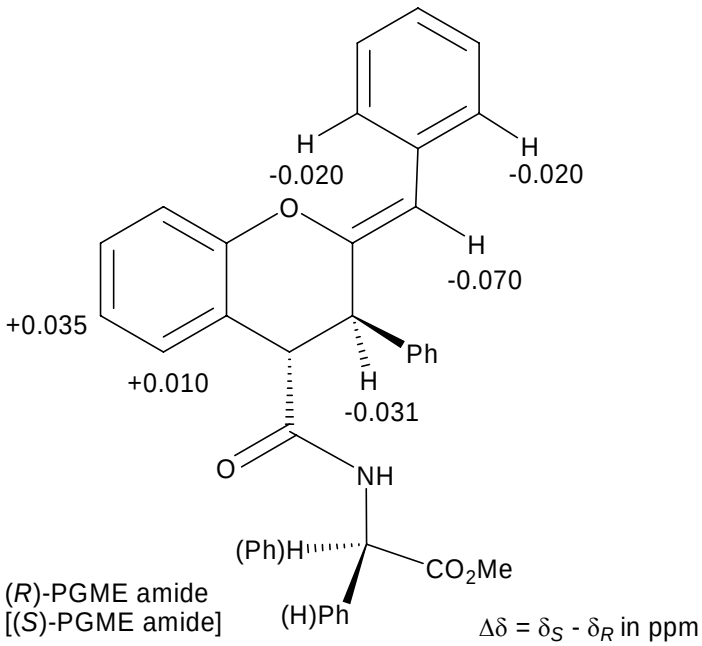
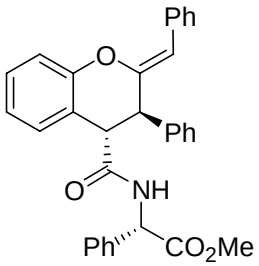


Figure S-2



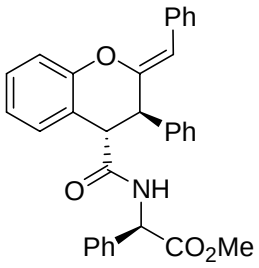
Experimental Details of Scheme S-1.

(*S*)-Methyl 2-[(3*R*,4*S*,*Z*)-2-benzylidene-3-phenylchroman-4-carboxamido]-2-phenylacetate [(*S*)-PGME amide].



To a stirred solution of (3*R*,4*S*)-**3ab** (0.5 mg, 1.2 μmol) in THF/H_2O (0.1+0.03 mL) were added LiOH·H_2O (0.6 mg, 14 μmol) at rt, and stirring was continued for 2.5 h. The reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with brine, and the residue upon workup was chromatographed on silica gel with hexane-AcOEt (8:2 v/v) as eluent to give carboxylic acid as colorless crystals. To a stirred solution of this carboxylic acid in CH_2Cl_2 (0.5 mL) were added (*S*)-phenylglycine methyl ester (0.4 mg, 2.2 μmol), DCC (0.6 mg, 3.0 μmol) and DMAP (0.1 mg, 0.8 μmol) at 0 °C, and stirring was continued for 30 min. After filtration of the reaction mixture using Celite followed by concentration, the residue was chromatographed on silica gel with hexane-AcOEt (9:1 v/v) as eluent to give the (*S*)-PGME amide (1.9 mg, 86% in 2 steps) as a white solid. Mp 64.5−65.8 °C; IR (neat) 3310, 2926, 1742, 1654, 1489, 1455, 1241, 756, 696 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.63 (3H, s), 4.06 (1H, d, *J* = 2.4 Hz), 4.48 (1H, d, *J* = 2.4 Hz), 5.50 (1H, d, *J* = 6.8 Hz), 5.54 (1H, s), 6.58 (1H, d, *J* = 6.8 Hz), 6.84 (2H, t, *J* = 7.6 Hz), 7.03−7.09 (4H, m), 7.12−7.30 (8H, m), 7.33−7.38 (3H, m), 7.68 (2H, d, *J* = 7.6 Hz); HRMS (ESI) *m/z* calcd for $C_{32}H_{28}NO_4$ $[M+H]^+$ 490.2018, found 490.2019.

(*R*)-Methyl 2-[(3*R*,4*S*,*Z*)-2-benzylidene-3-phenylchroman-4-carboxamido]-2-phenylacetate [(*R*)-PGME amide].



By following the same procedure described for (*S*)-PGME amide, (*R*)-PGME amide was prepared from (3*R*,4*S*)-**3ab** and (*R*)-phenylglycine methyl ester: 94% yield in 2 steps; white solid; White solid; mp 63.1−65.3 °C; IR (neat) 3295, 2927, 1746, 1655 1490, 1455, 1243, 769, 696 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.54 (3H, s), 4.07 (1H, d, *J* = 4.0 Hz), 4.51 (1H, d, *J* = 4.0 Hz), 5.44 (1H, d, *J* = 6.8 Hz), 5.61 (1H, s), 6.61 (1H, d, *J* = 6.8 Hz), 7.03 (1H, t, *J* = 7.6 Hz), 7.12−7.36 (15H, m), 7.68 (2H, d, *J* = 7.2 Hz); HRMS (ESI) *m/z* calcd for $C_{32}H_{28}NO_4$ $[M+H]^+$ 490.2018, found 490.2018.

References

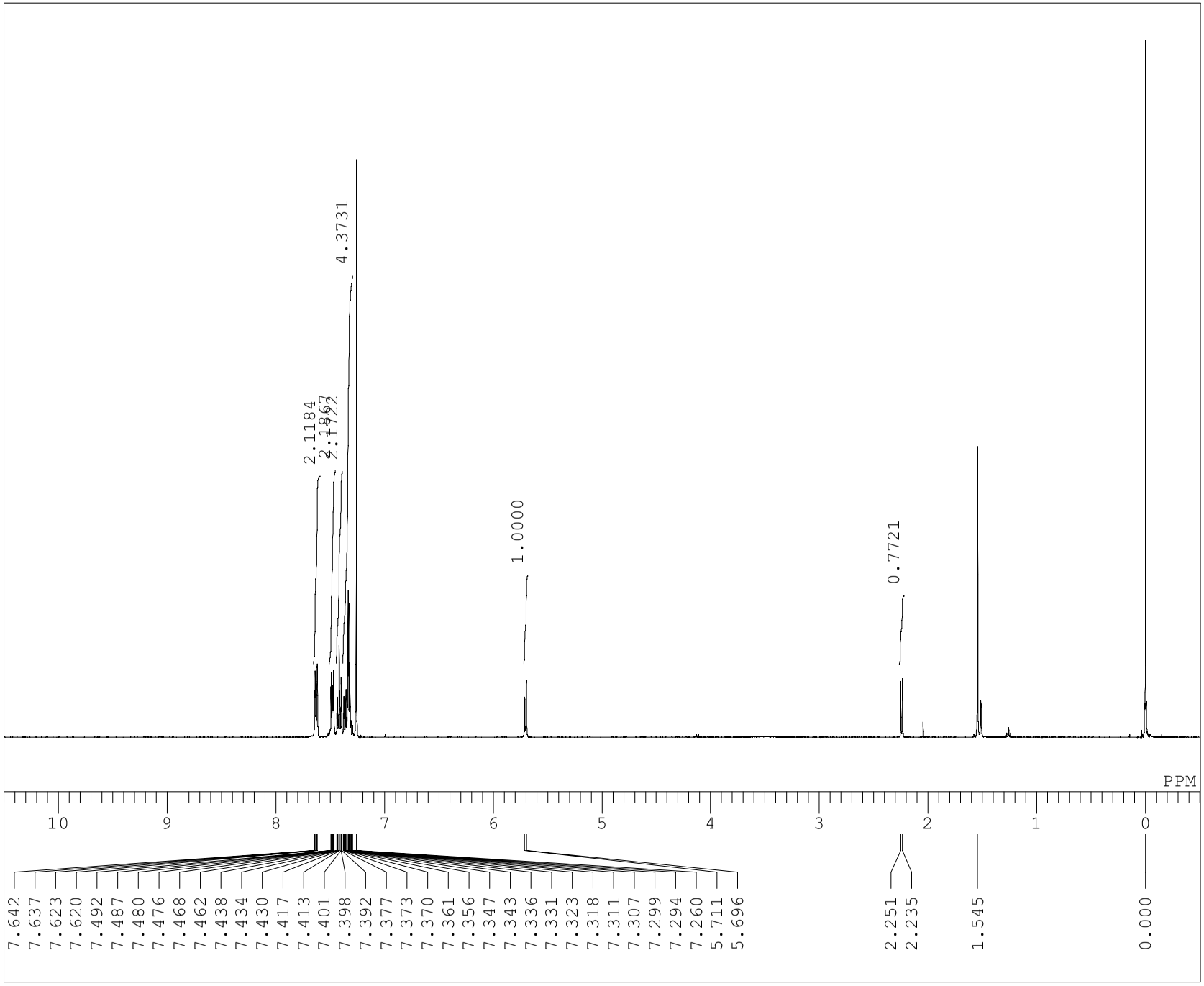
1) J. Lin, B. S. Gerstenberger, N. T. Stessman, J. P. Konopelski, *Org. Lett.* **2008**, *10*, 3969.

2) P. Nussbaumer, M. Bilban, *J. Org. Chem.* **2000**, *65*, 7660.

3) V. É. Trépanier, E. Fillion, *Organometallics*, **2007**, *26*, 30.

4) S. Chassaing, M. Kueny-Stotz, G. Isorez, R. Brouillard, *Eur. J. Org. Chem.* **2007**, 2438.

5) Y. Nagai and T. Kusumi, *Tetrahedron Lett.* **1995**, *36*, 1853.

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RGAIN            22
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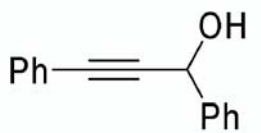
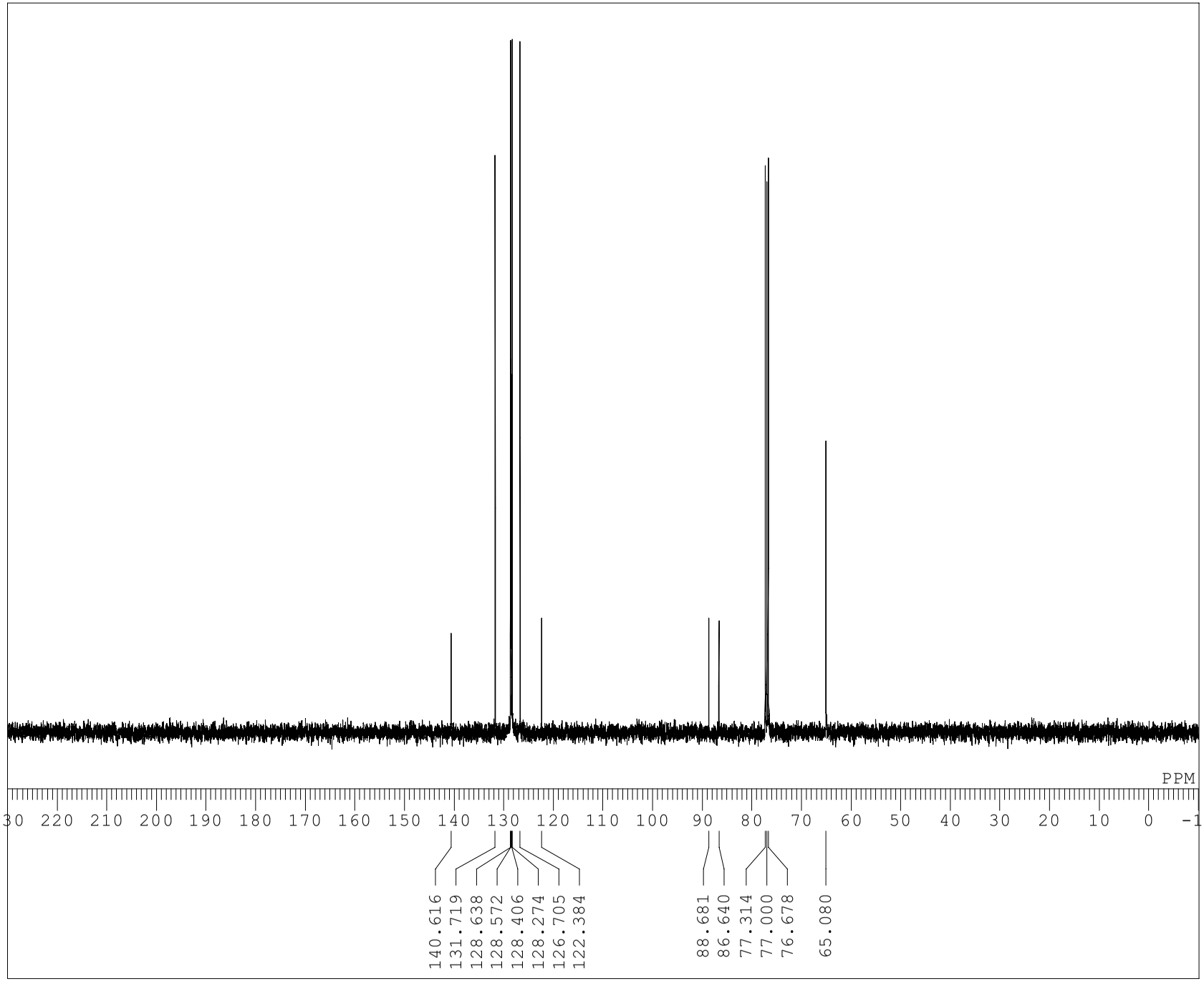


S-2a



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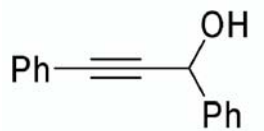
RGAIN 23



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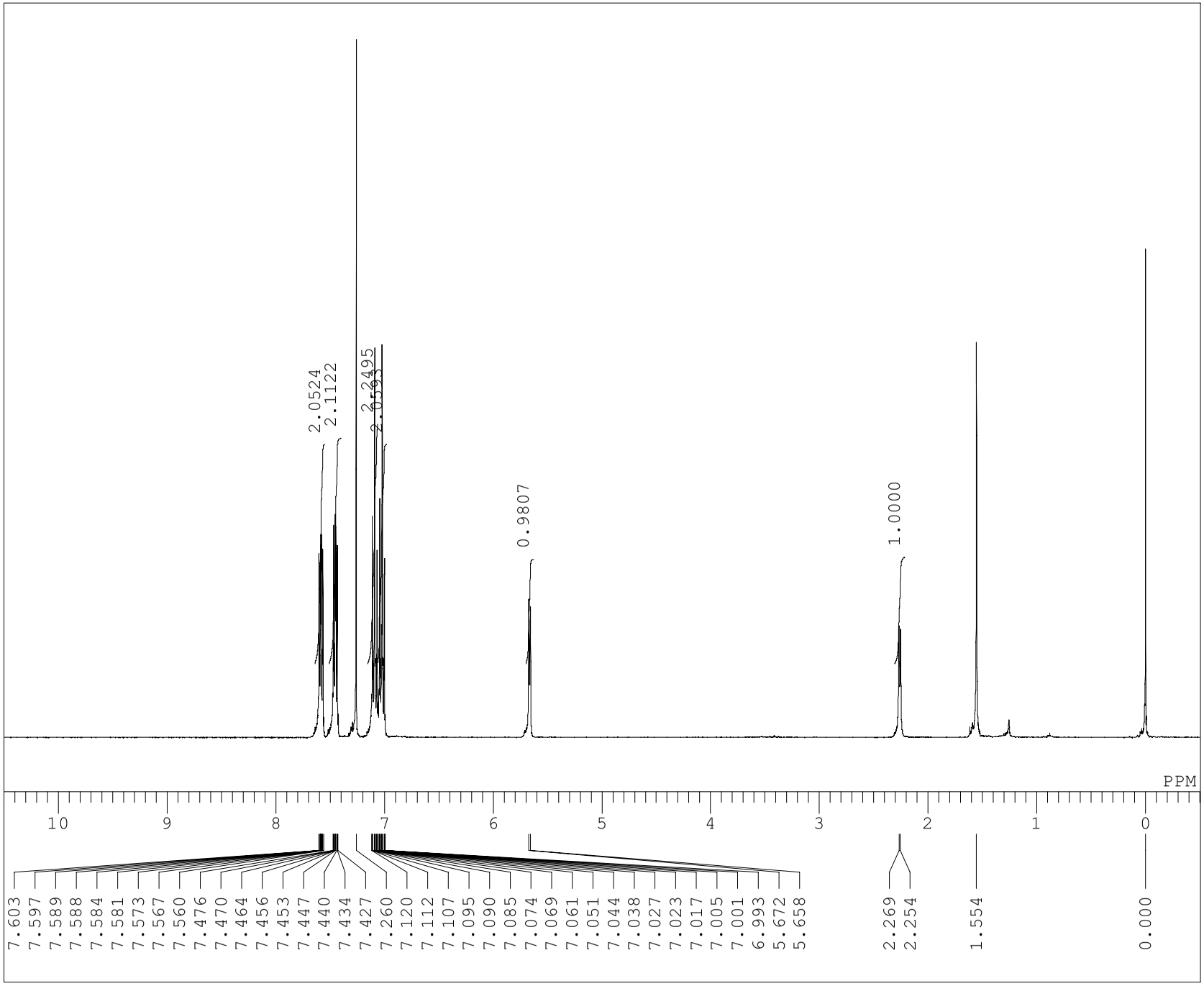


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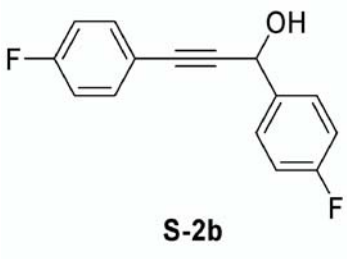

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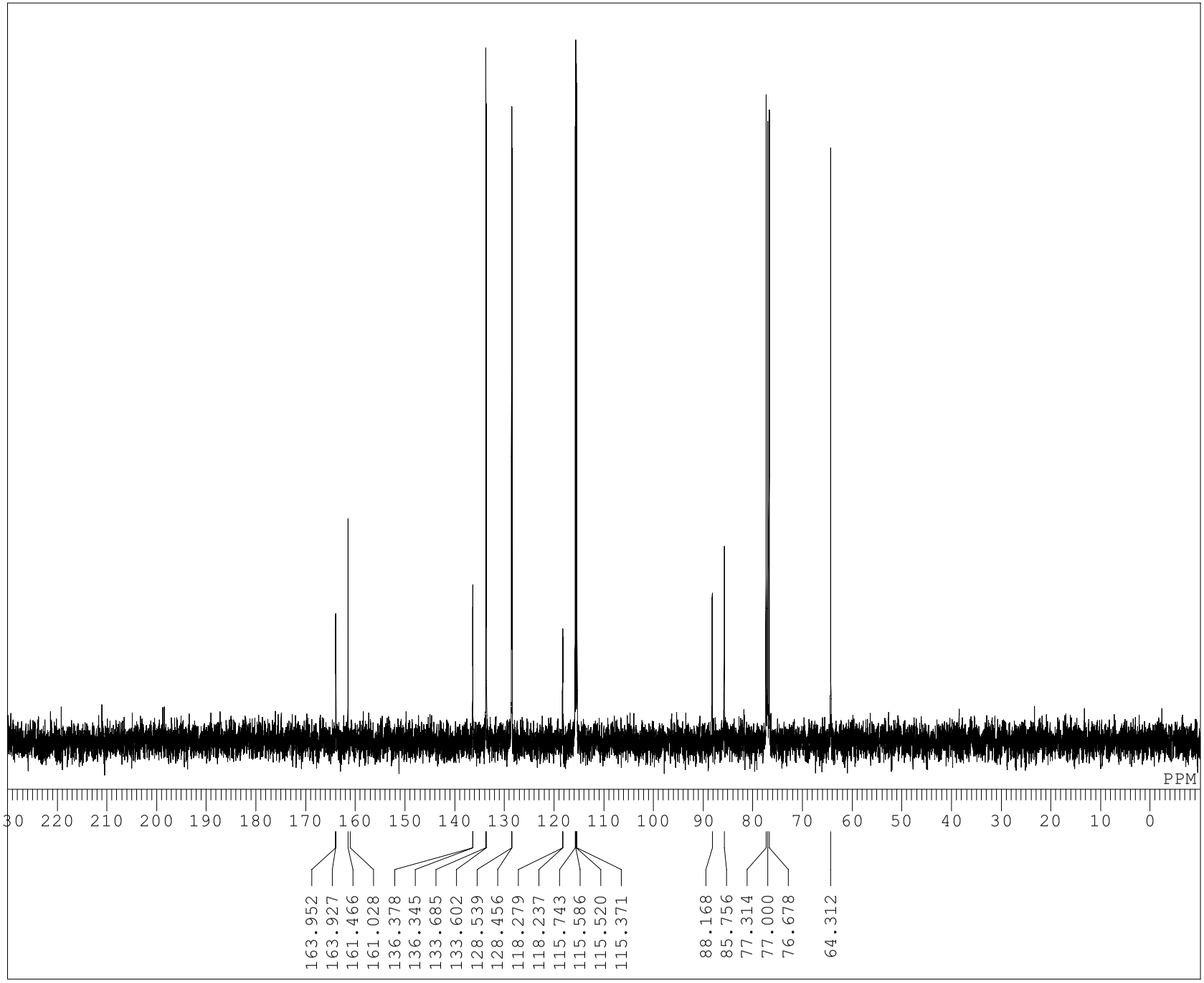


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RGAIN             23
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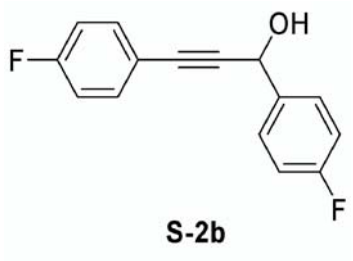

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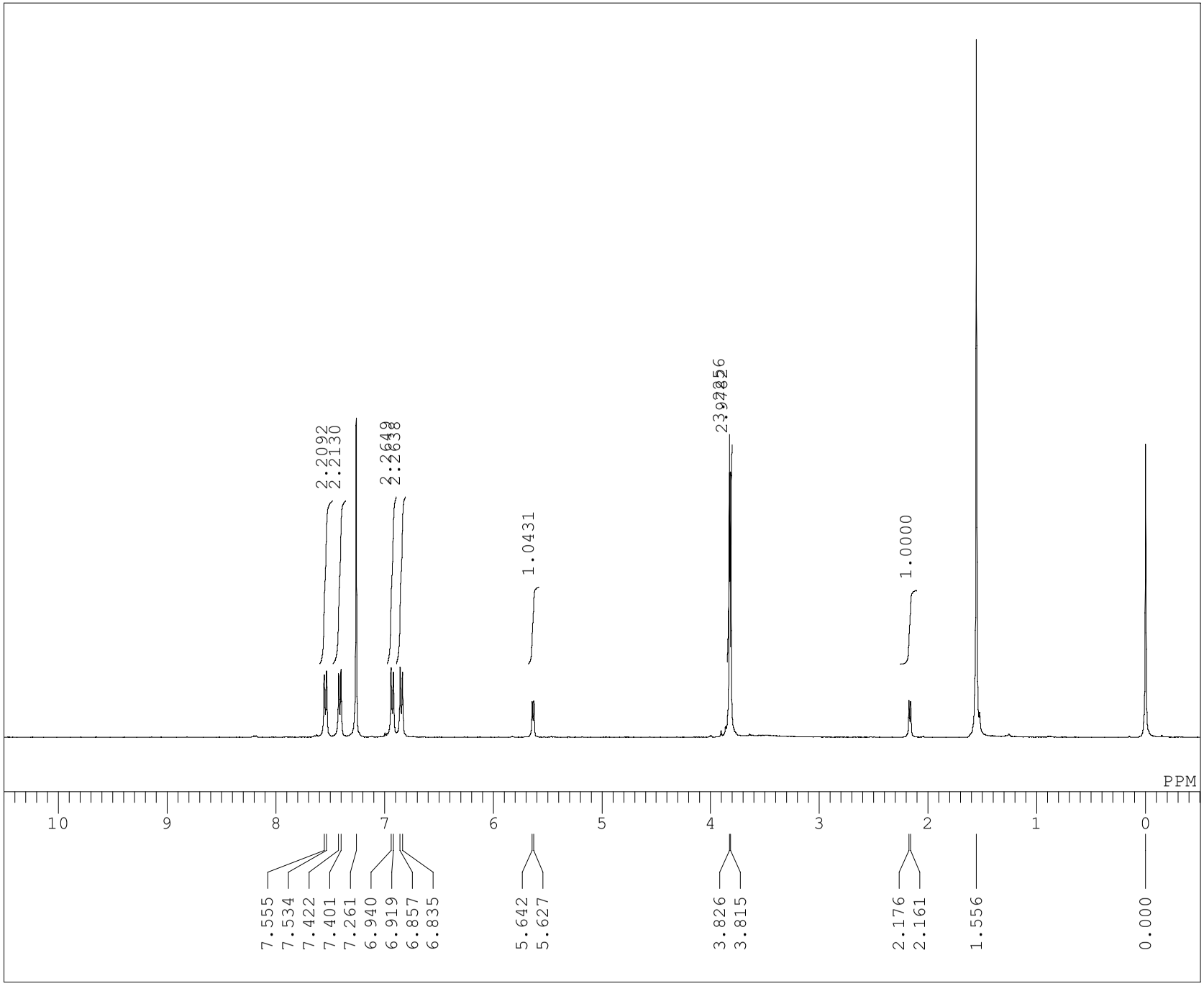

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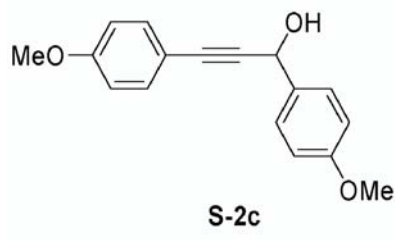

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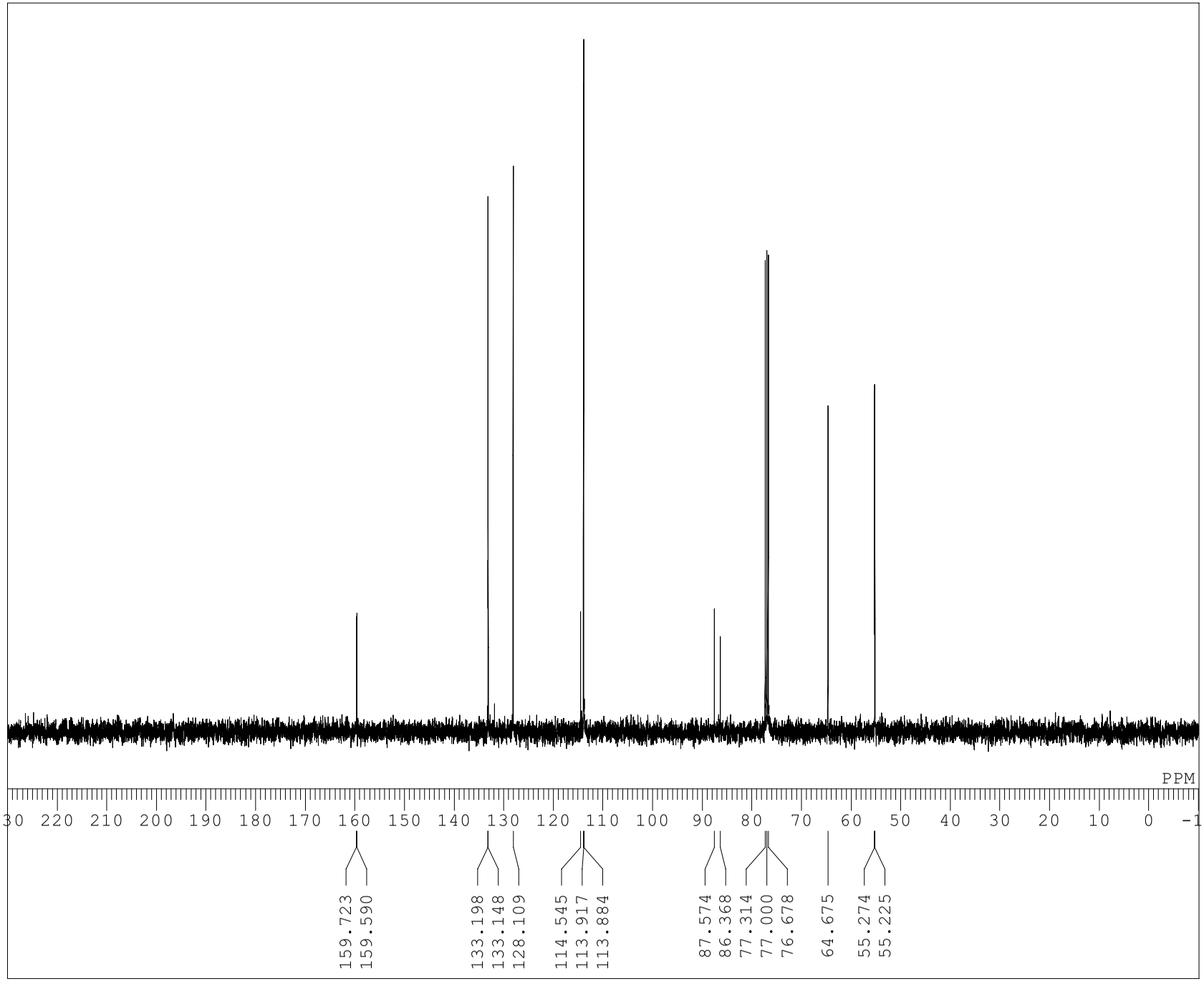


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RGAIN            25
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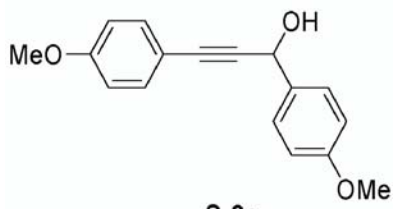

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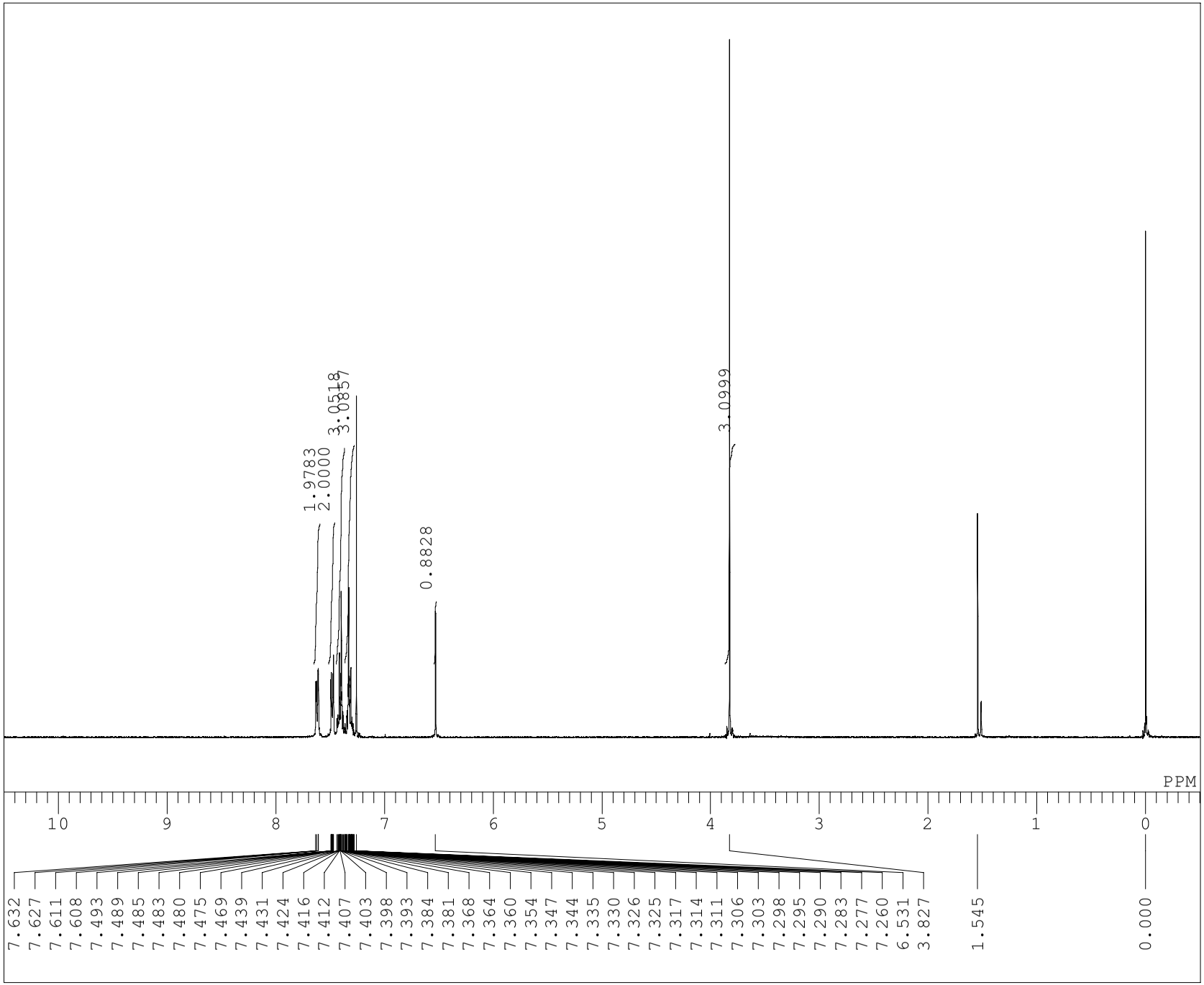


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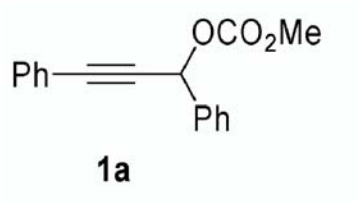

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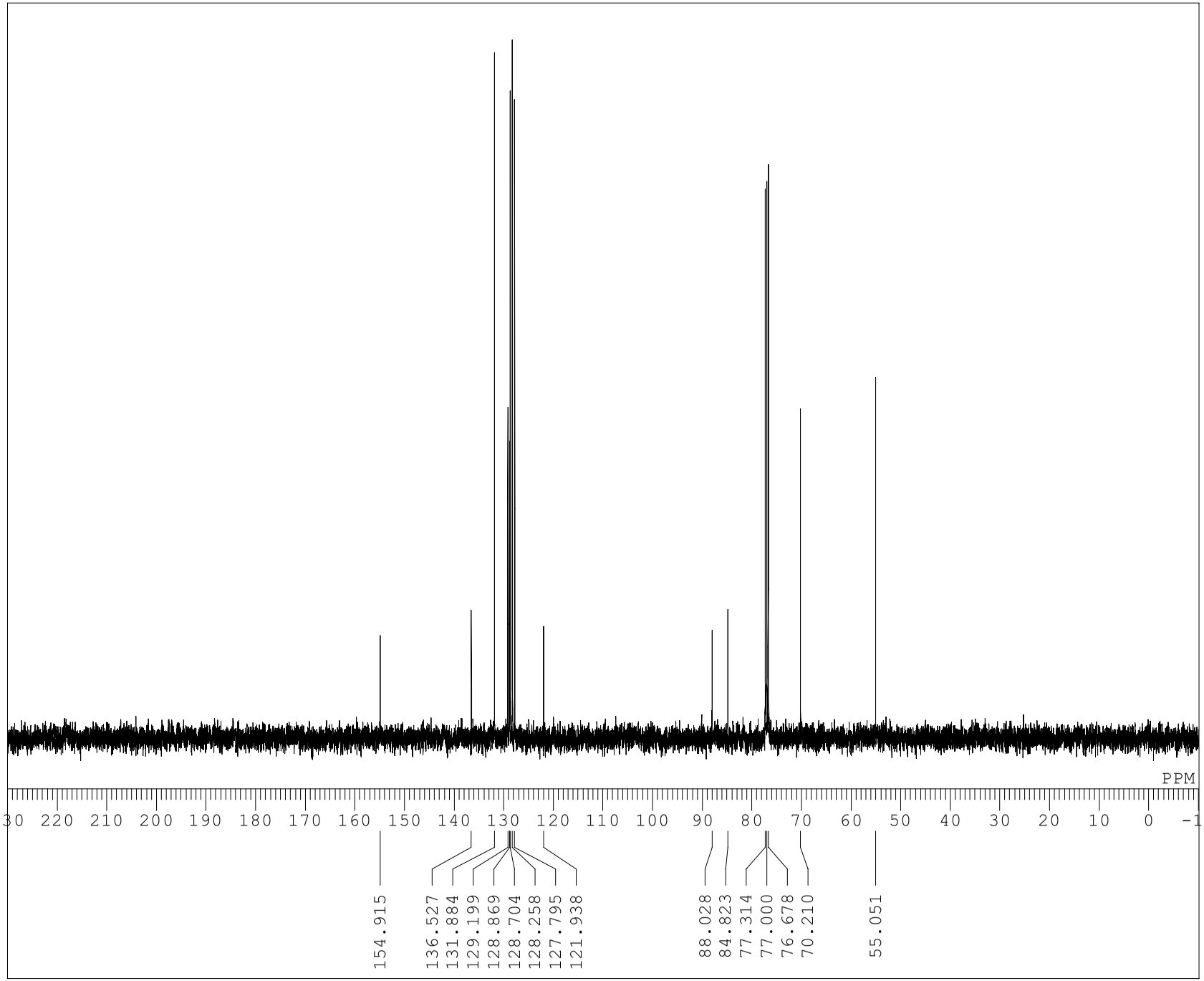


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RGAIN            23
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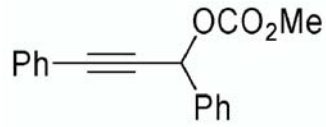

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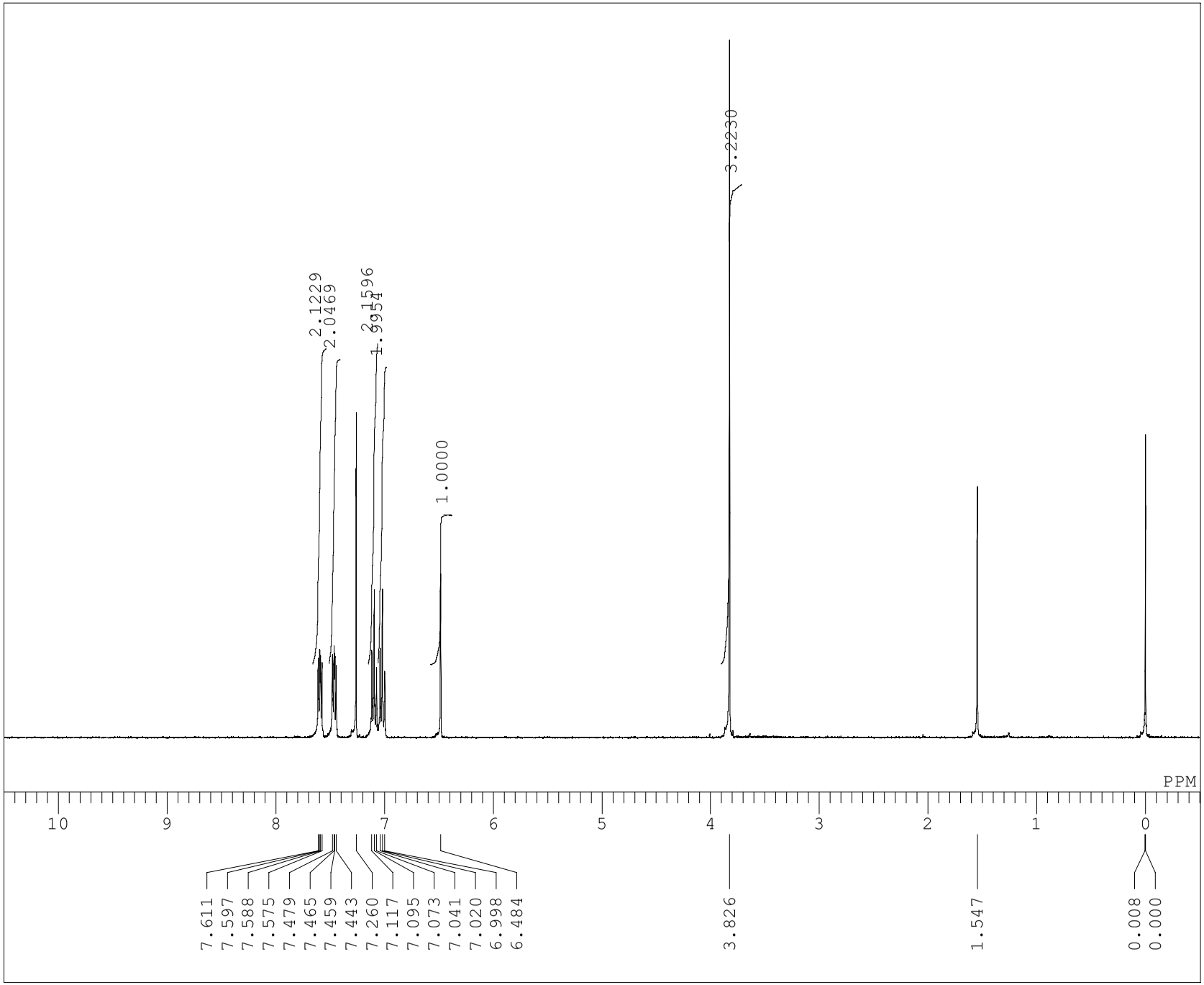


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ACQTM         4.100 sec
PD            2.901 sec
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CTEMP          24.7 c
SLVNT  CDCL3
EXREF          0.00 ppm
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RGAIN            21
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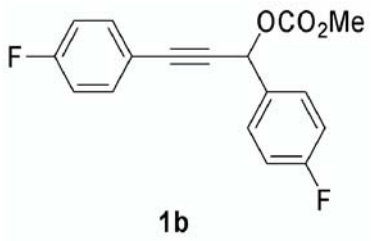

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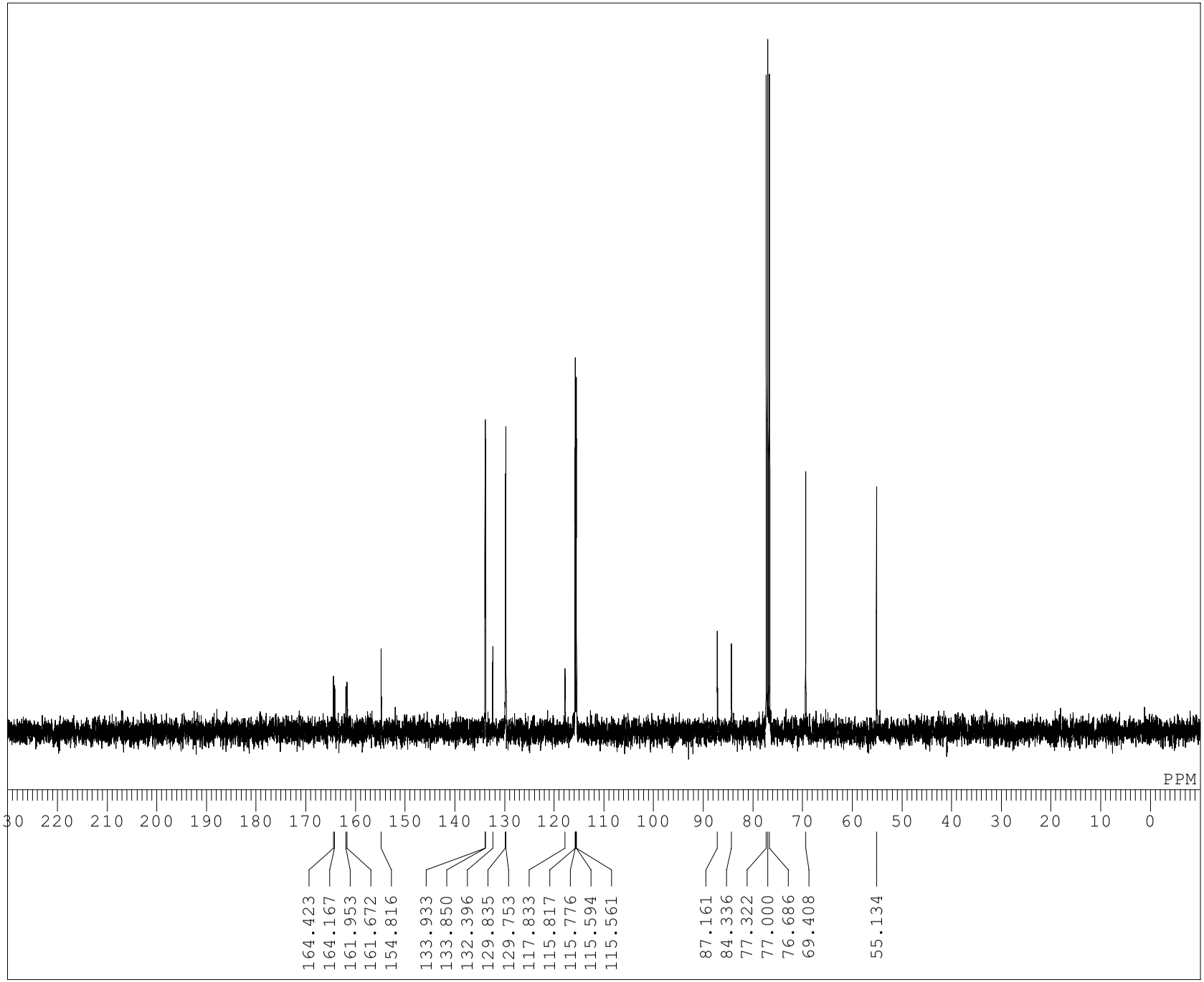


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PD           1.794 sec
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CTEMP         26.1 c
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EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            25
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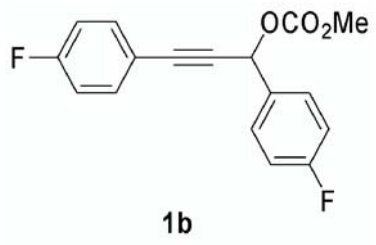

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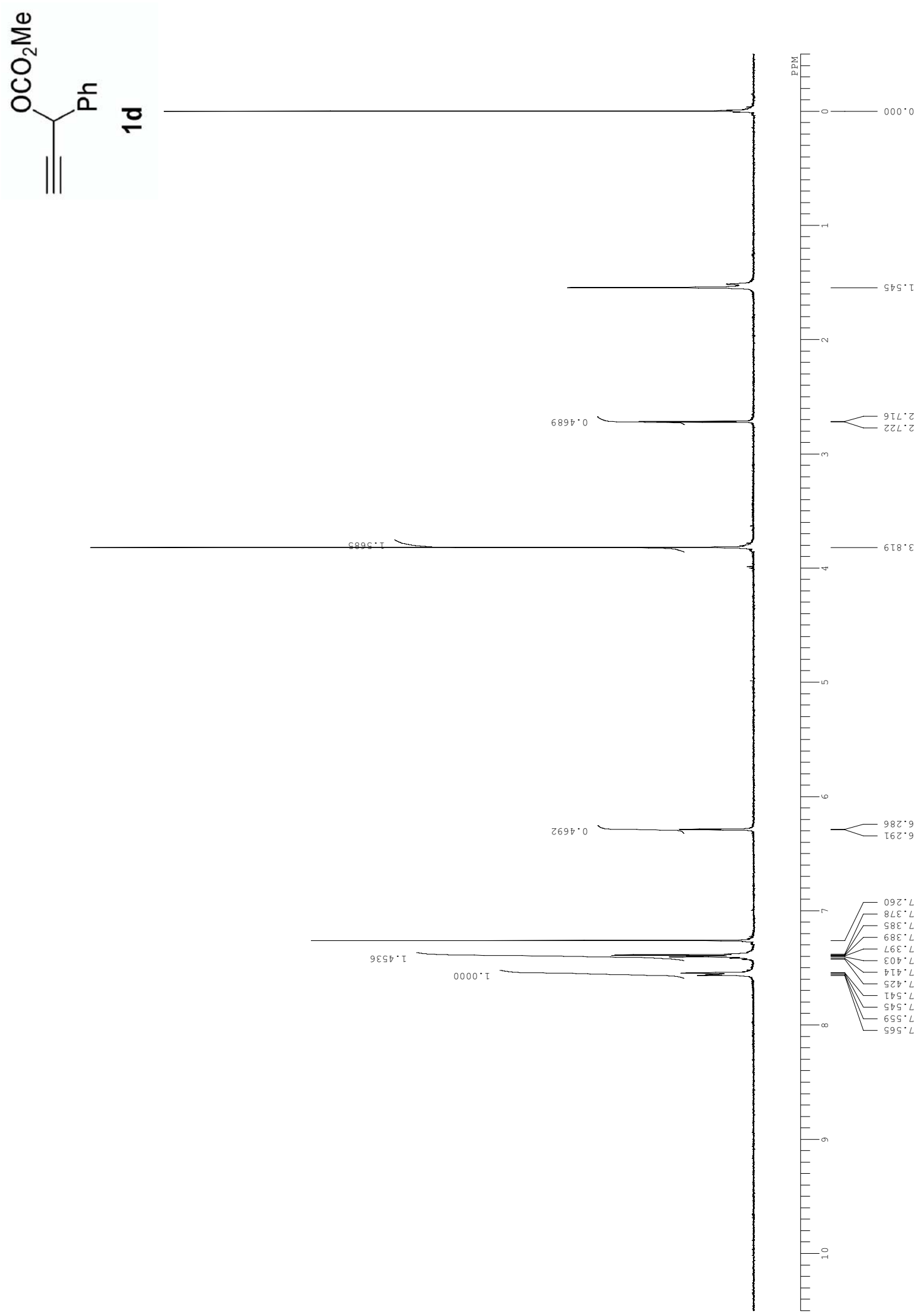
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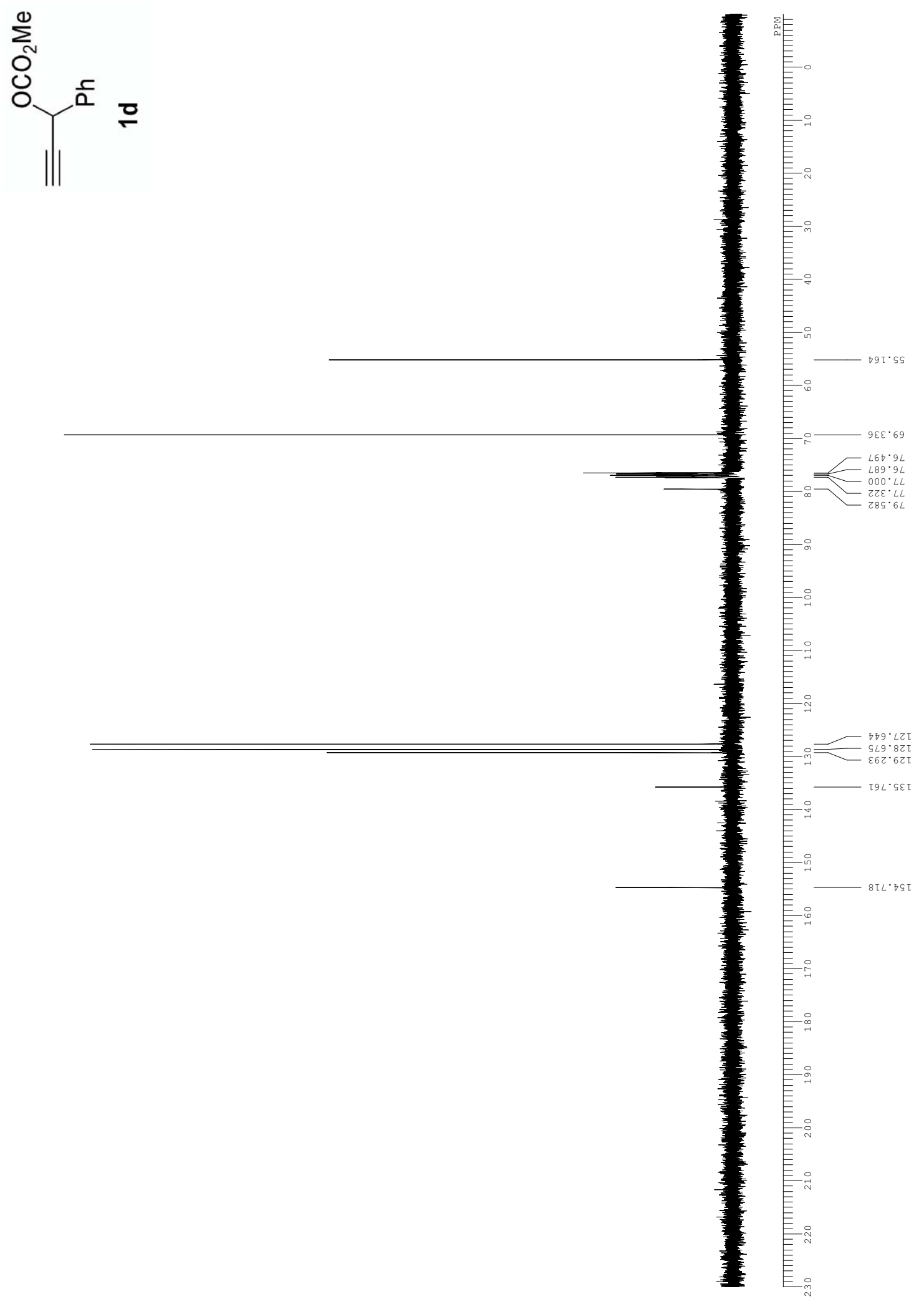
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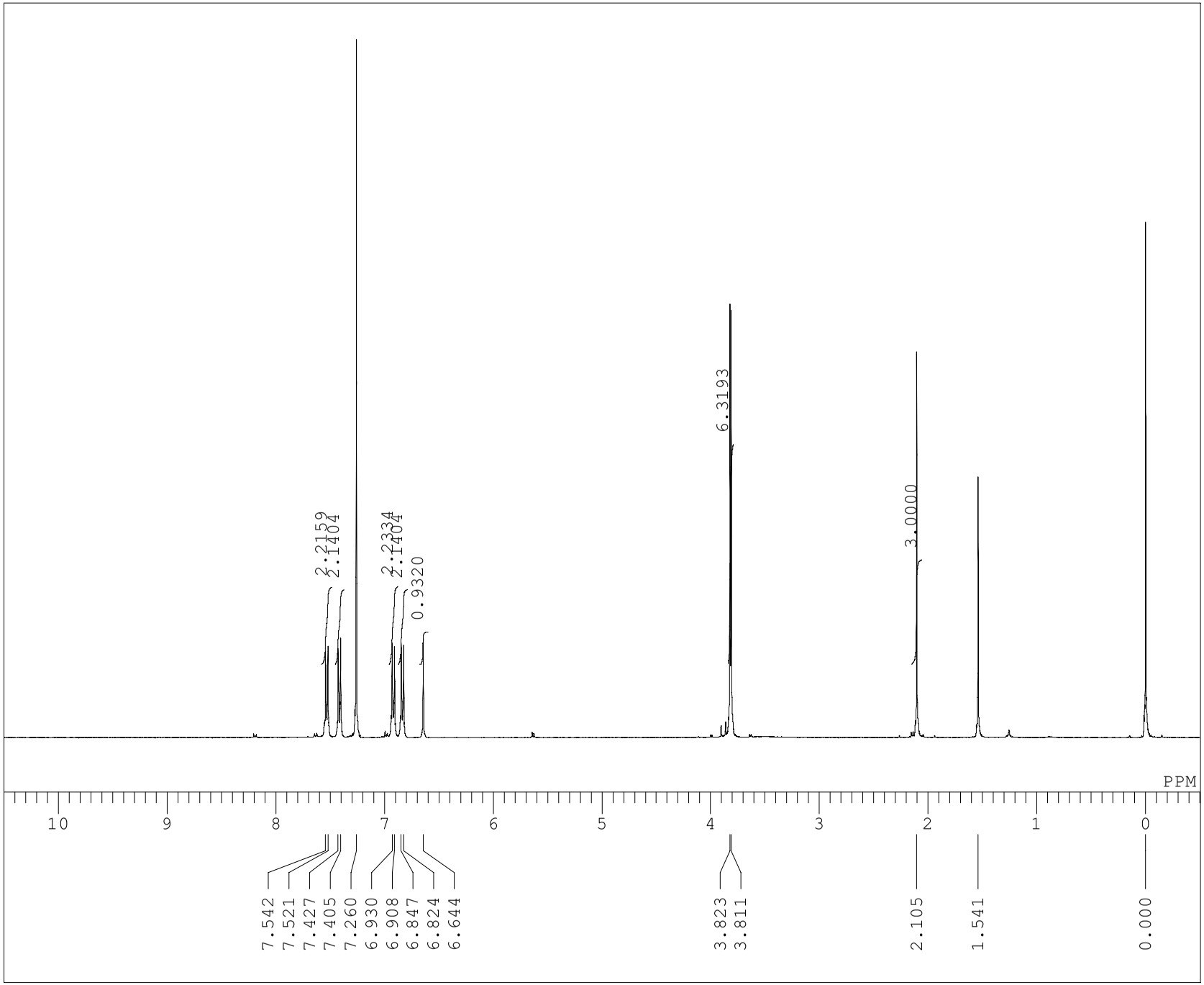

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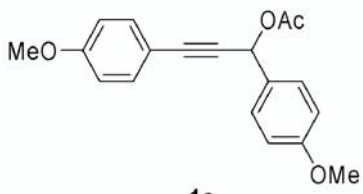
BF 0.12 Hz
RGAIN 21



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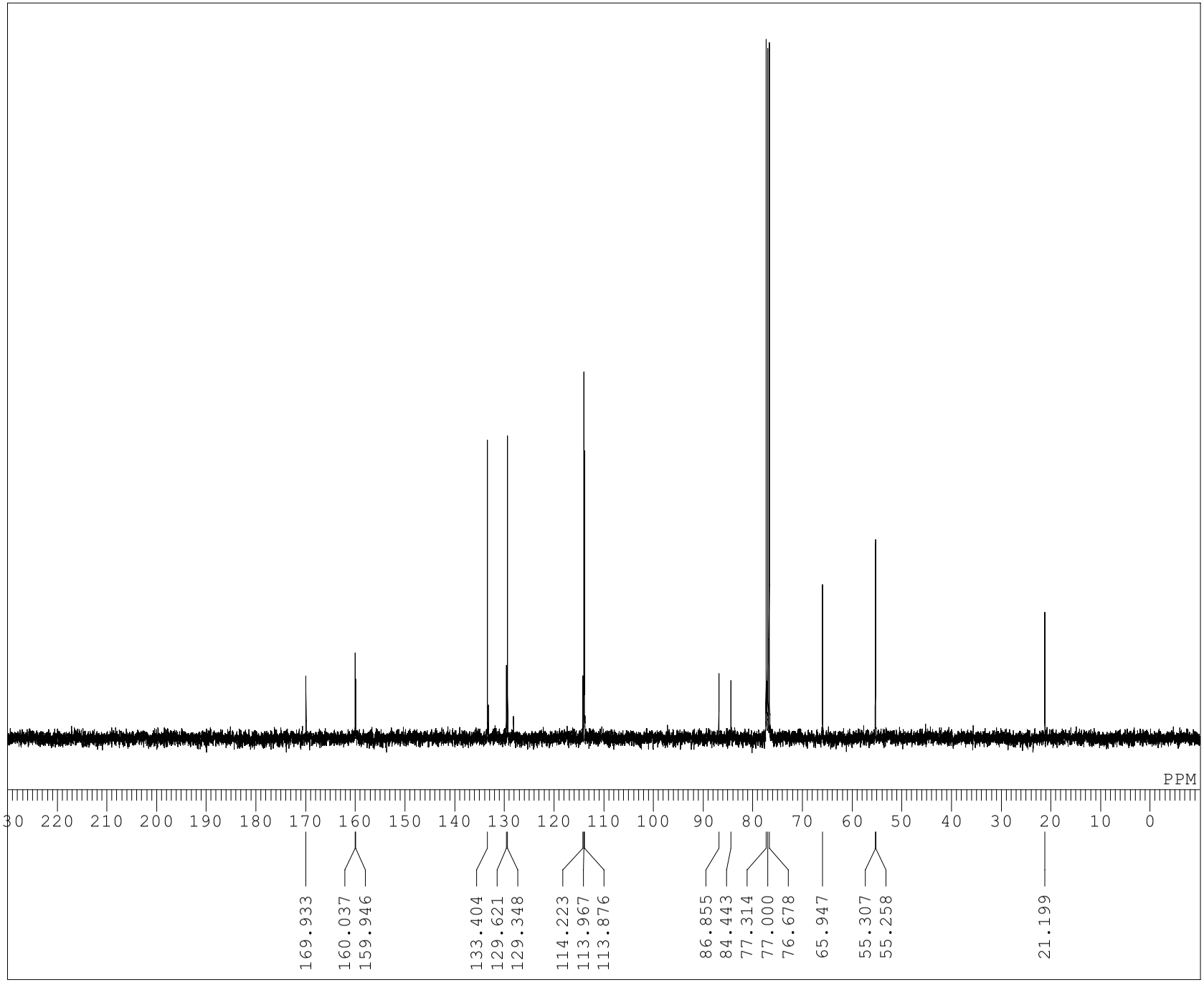

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POINT 32768
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SCANS 253
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IRNUC 1H
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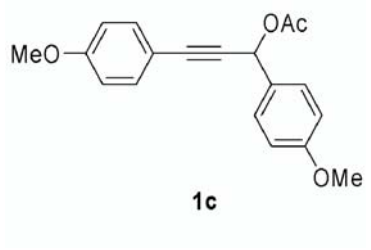
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 23



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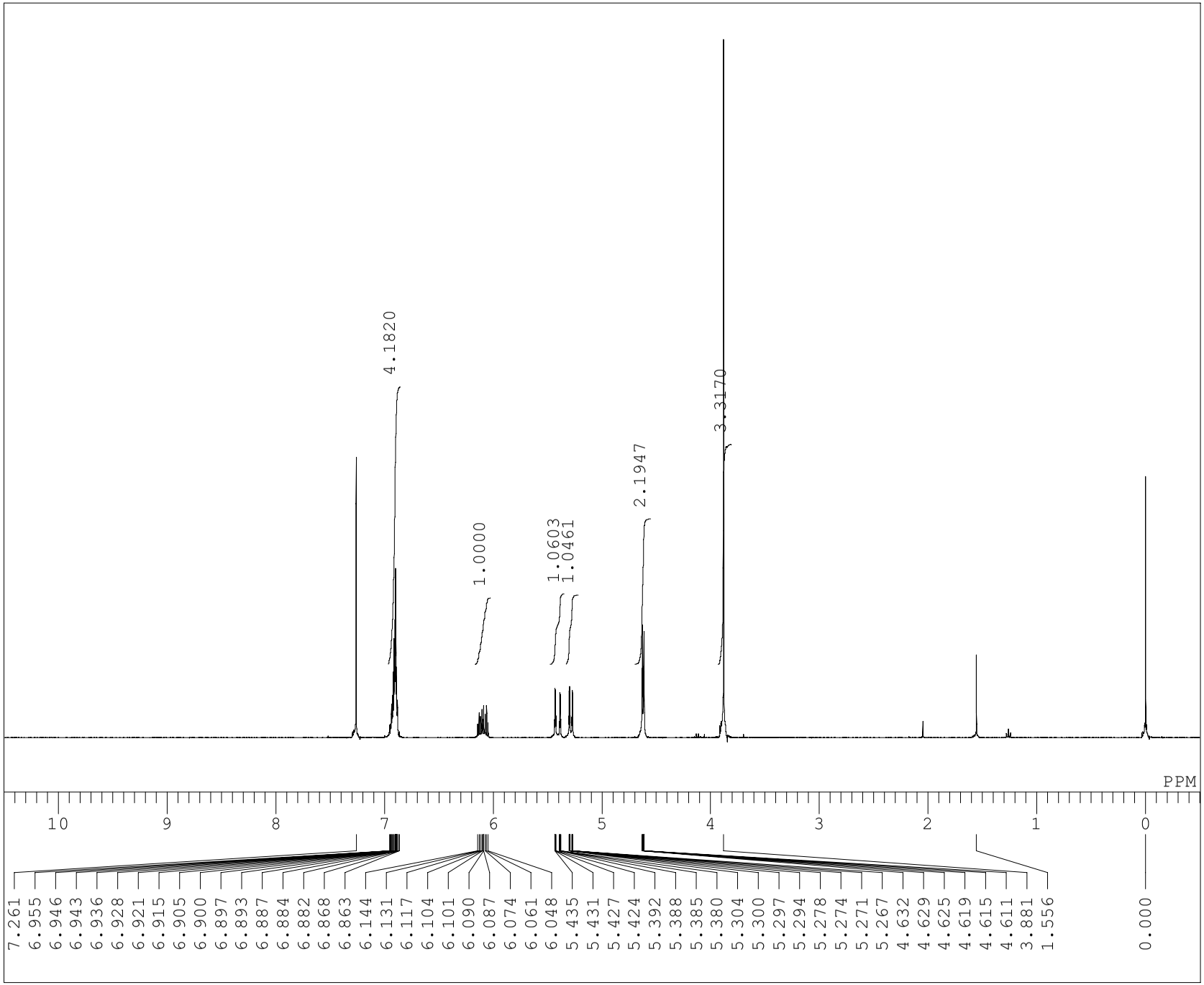


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RGAIN             19
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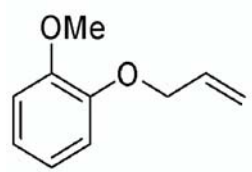
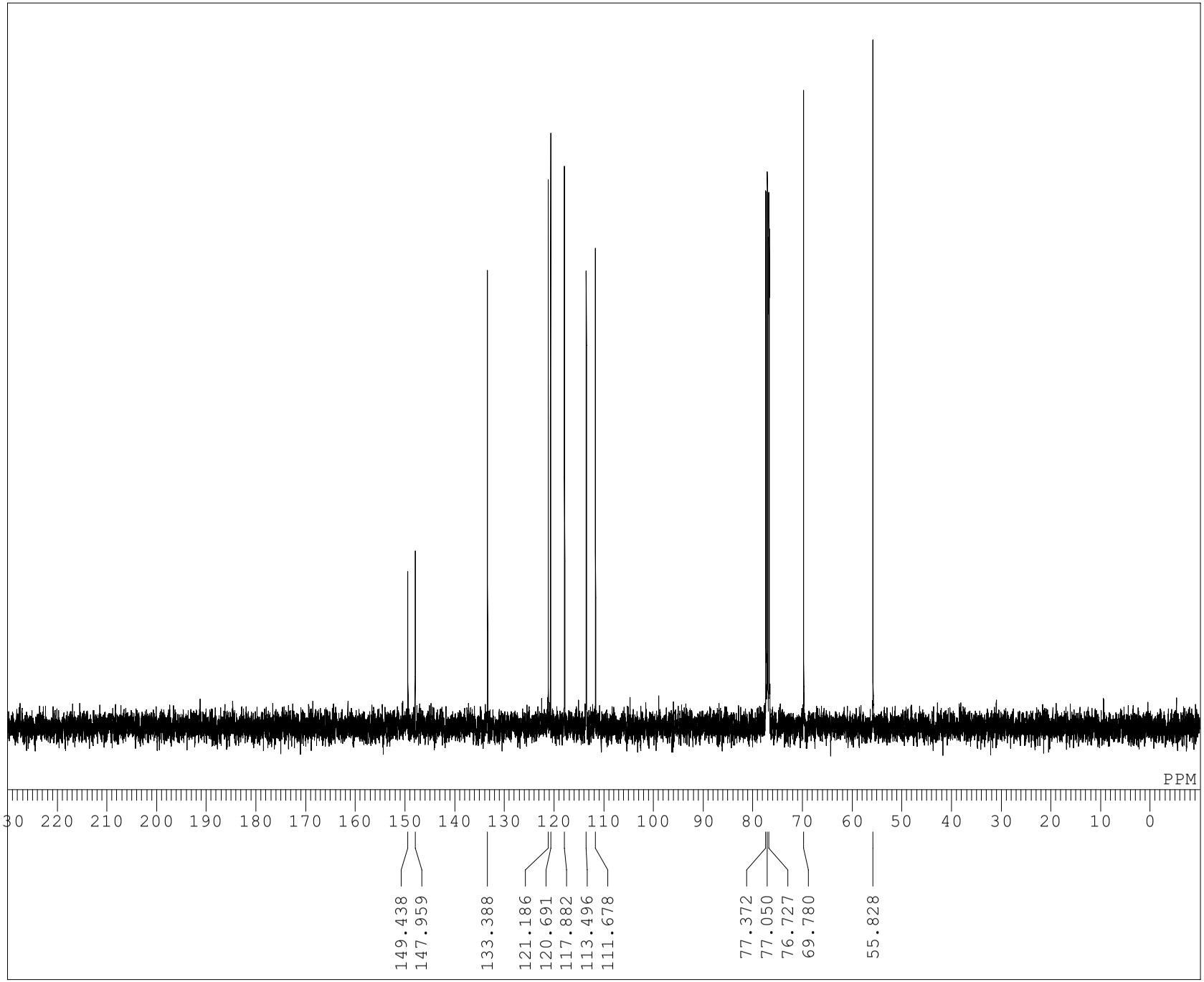


S-4c

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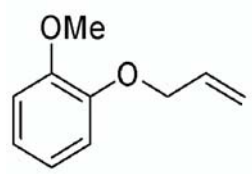
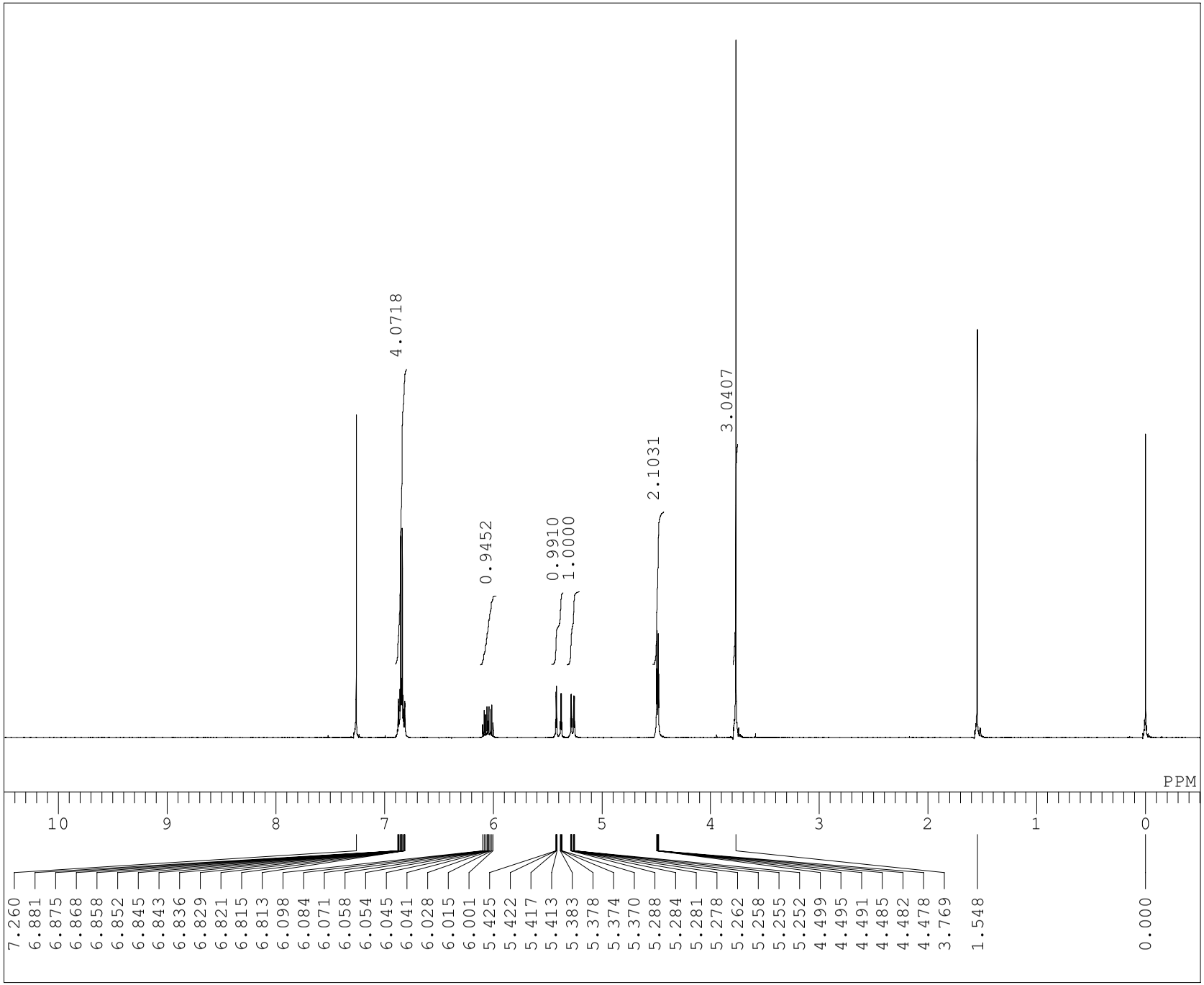
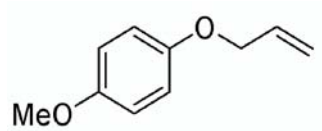
OBFIN       10500.0 Hz
POINT         32768
FREQU       27210.9 Hz
SCANS           160
ACQTM         1.204 sec
PD            1.794 sec
PW1             6.1 us
IRNUC  1H
CTEMP          21.6 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            23
```



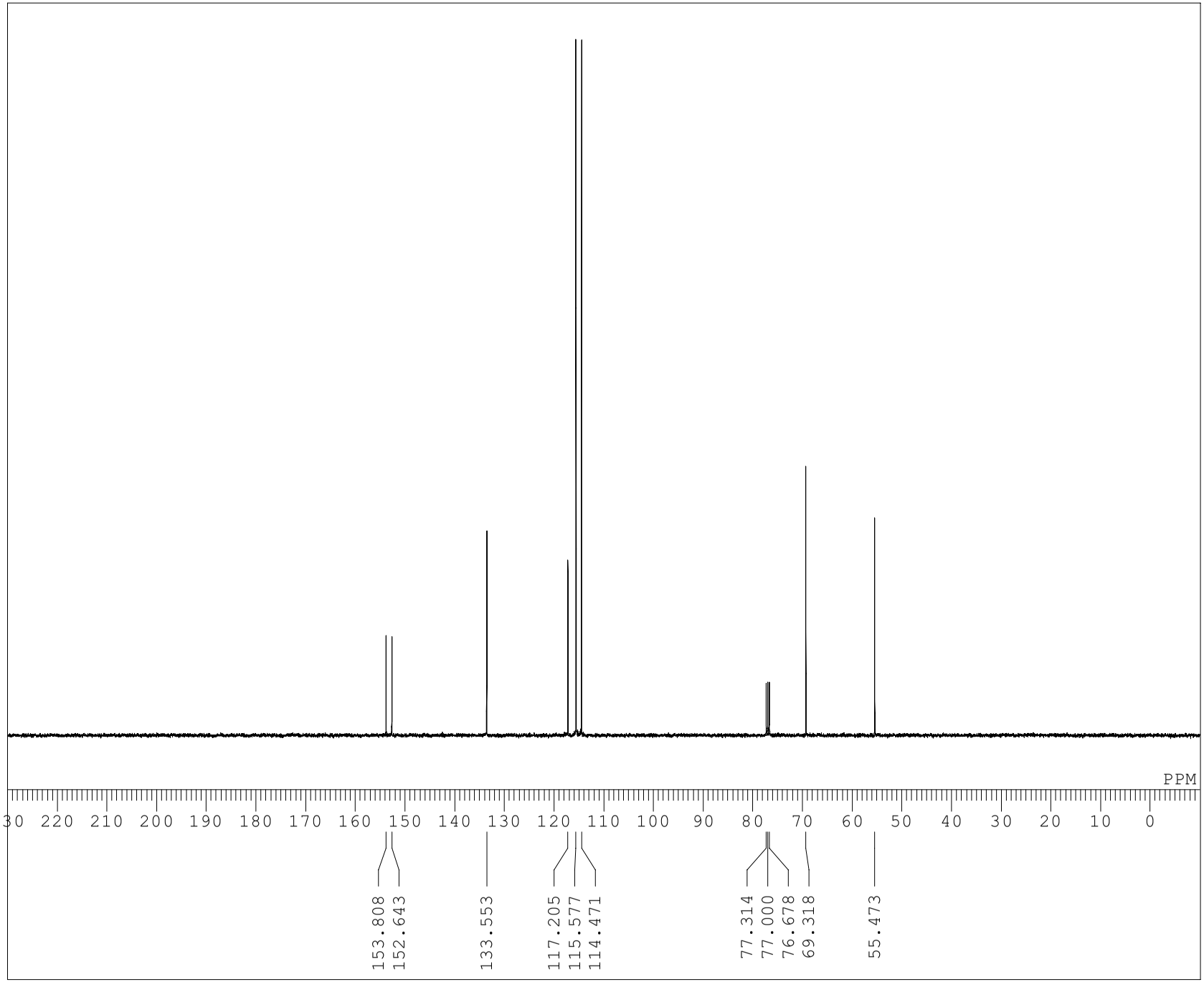
S-4c



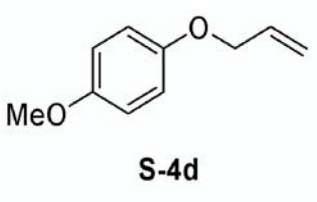

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Wed May 20 09:30:13 2009
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU        7992.0 Hz
SCANS              4
ACQTM          4.100 sec
PD             2.901 sec
PW1              6.3 us
IRNUC  1H
CTEMP           25.3 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             20
```



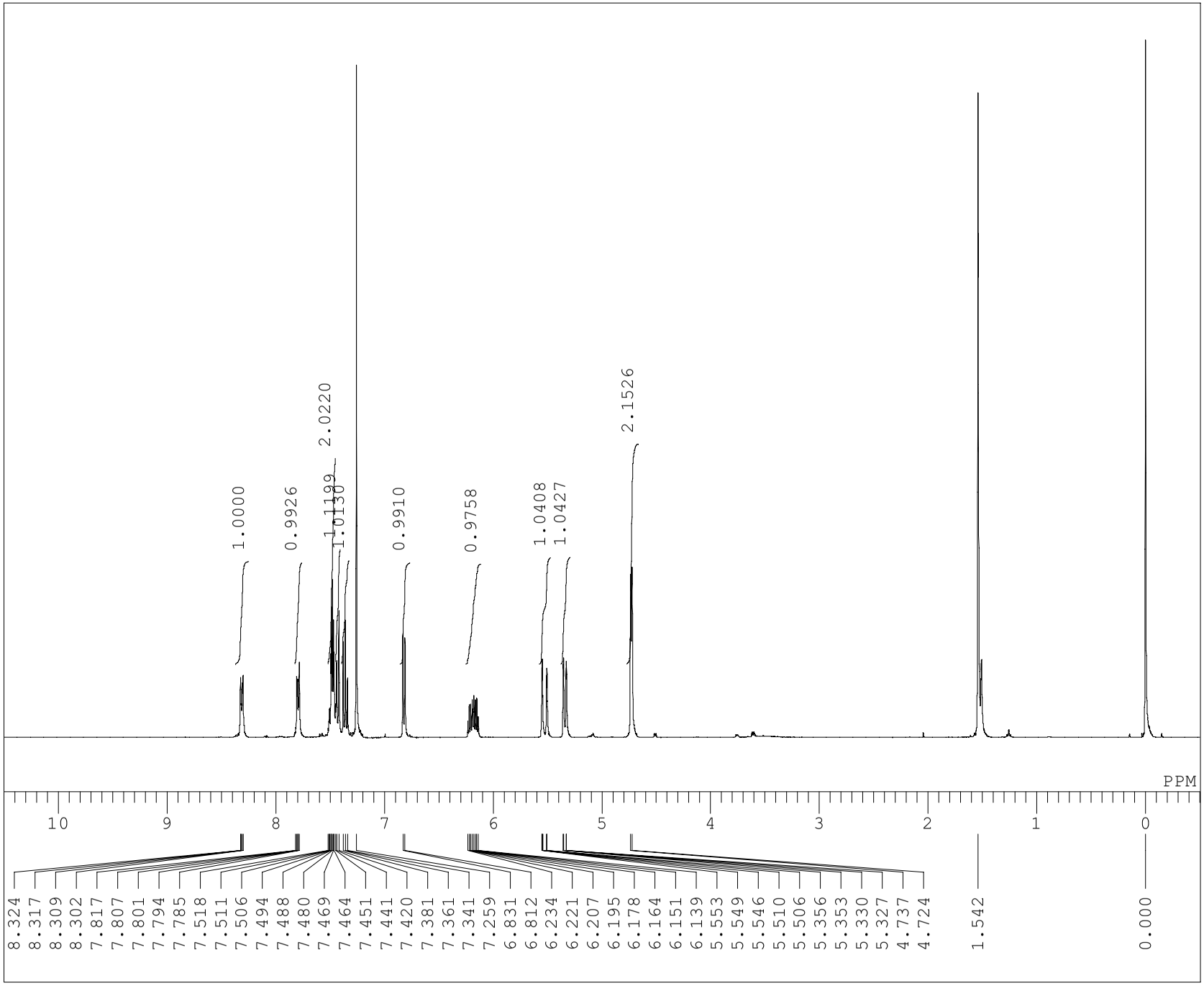
S-4d



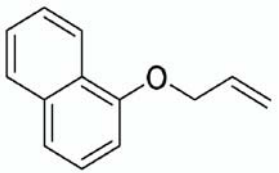

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Wed May 20 14:16:17 2009
OBNUC  13C
EXMOD  BCM
OBFRQ        100.40 MHz
OBSET        125.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU       27210.9 Hz
SCANS            80
ACQTM          1.204 sec
PD             1.794 sec
PW1              6.1 us
IRNUC  1H
CTEMP           25.8 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              1.20 Hz
RGAIN             22
```



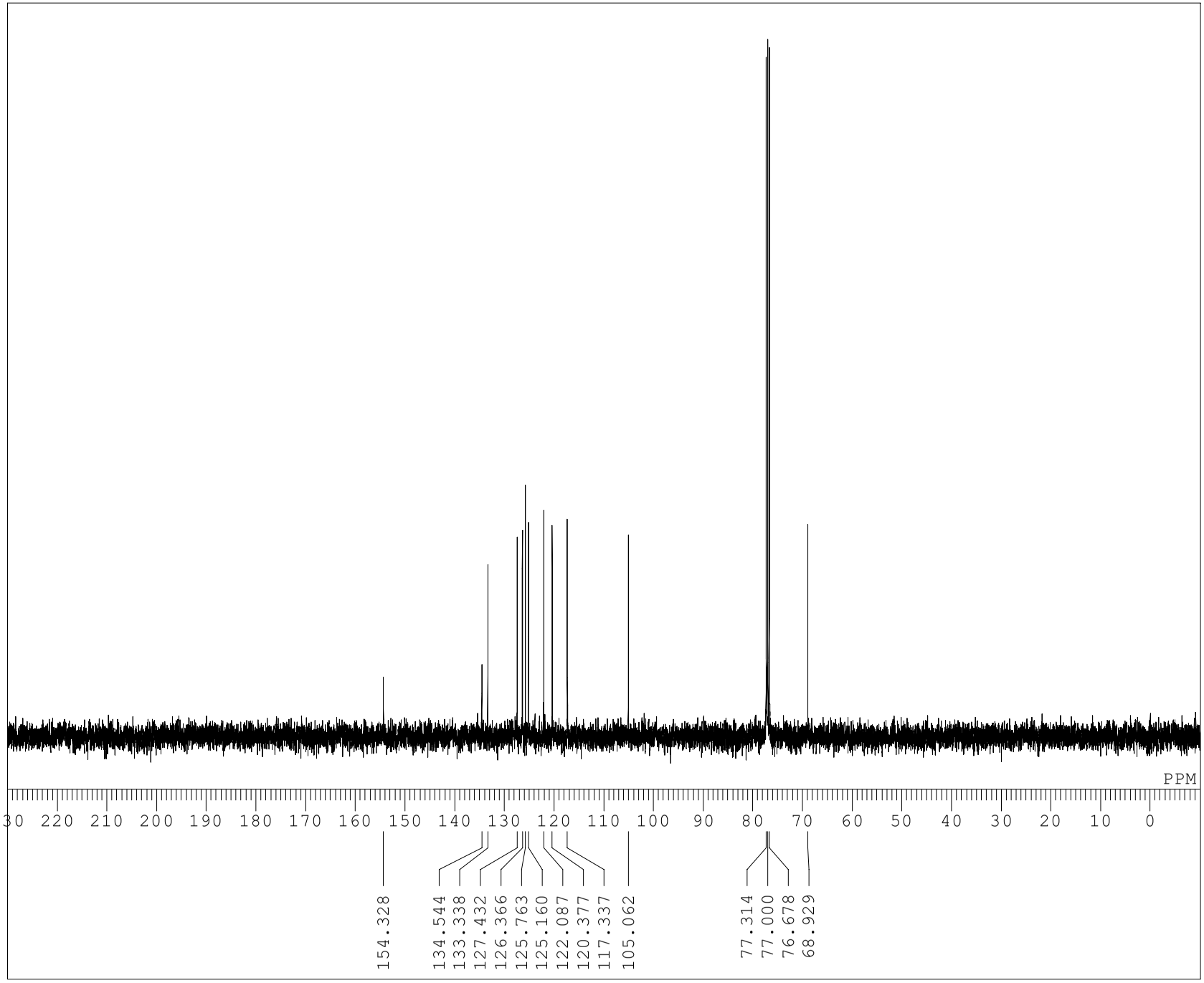
S-4d



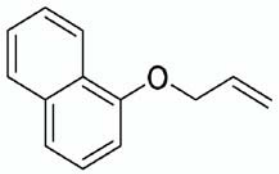

```
DFILE  \\150.59.248.165\data\NM
COMNT
DATIM  Sat Jul 04 17:28:43 2009
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU        7992.0 Hz
SCANS             32
ACQTM          4.100 sec
PD             2.901 sec
PW1              6.3 us
IRNUC  1H
CTEMP           25.9 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             23
```



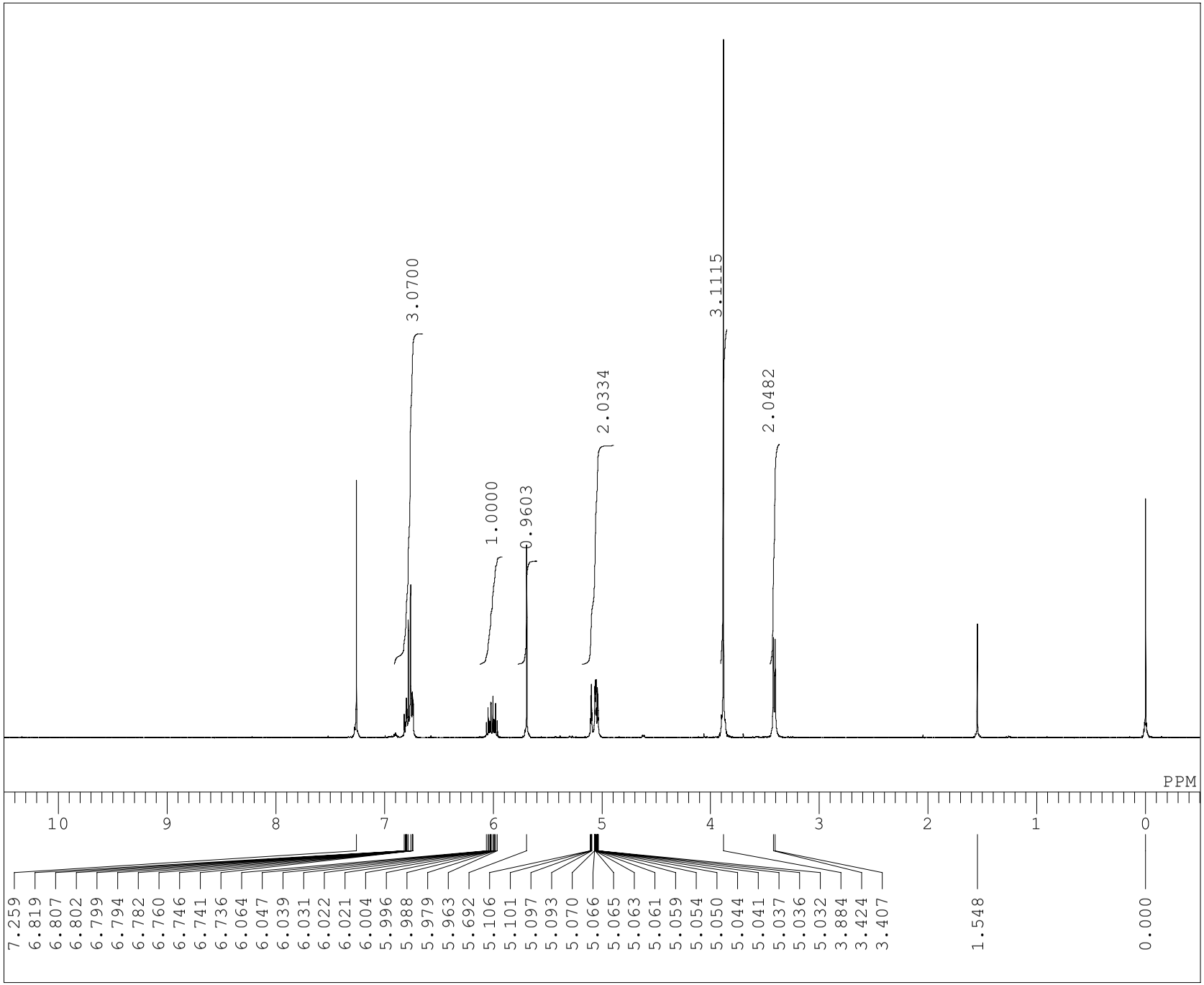
S-4e



DFILE \\150.59.248.165\data\NM
COMNT
DATIM Fri Feb 13 20:13:21 2009
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 27210.9 Hz
SCANS 104
ACQTM 1.204 sec
PD 1.794 sec
PW1 6.1 us
IRNUC 1H
CTEMP 27.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 23

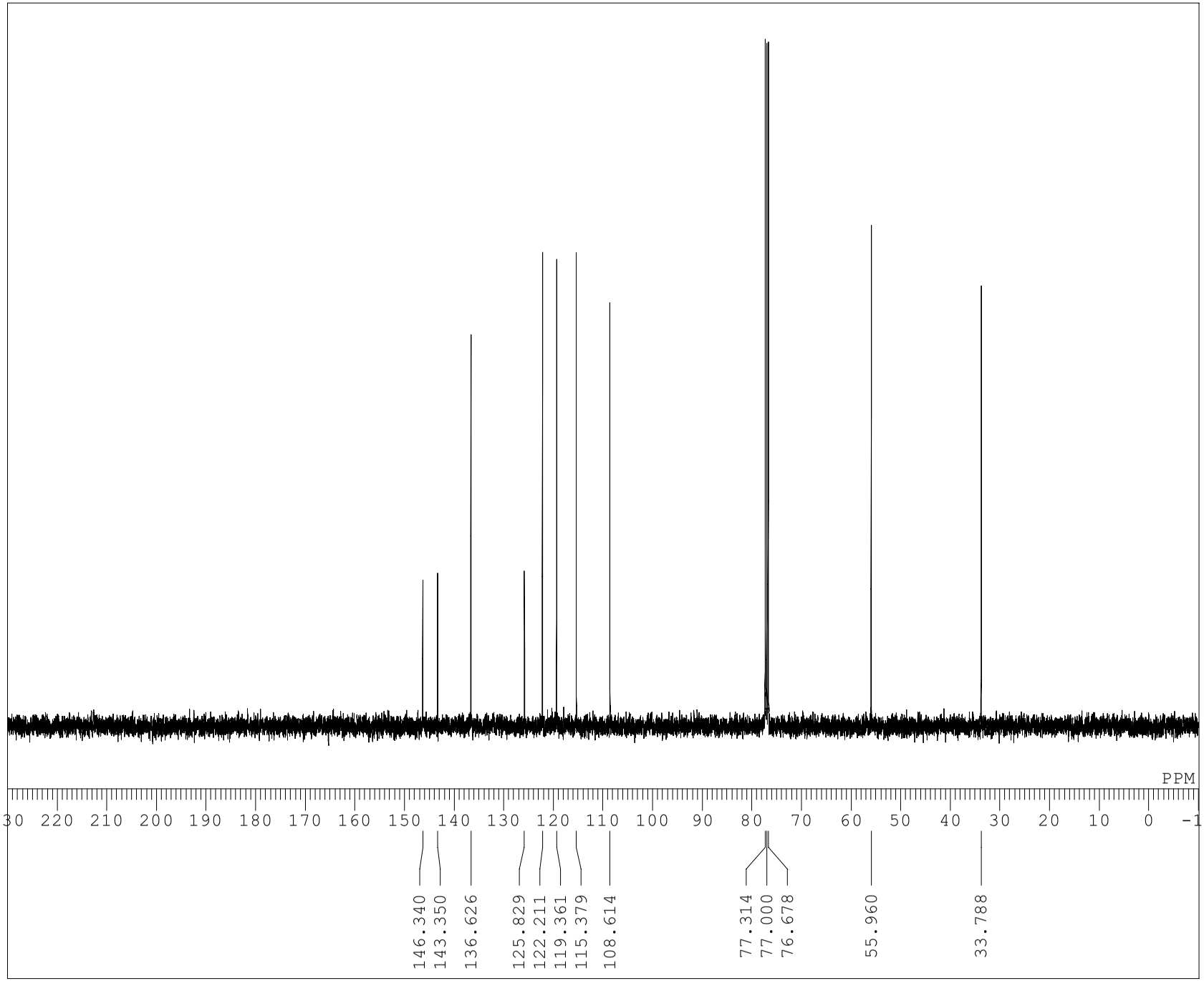


S-4e

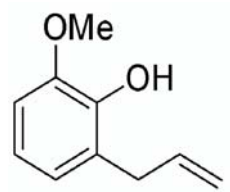



```
DFILE  \\150.59.248.165\data\NM
COMNT
DATIM  Wed Feb 04 16:44:12 2009
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU        7992.0 Hz
SCANS              4
ACQTM          4.100 sec
PD             2.901 sec
PW1              6.3 us
IRNUC  1H
CTEMP           21.4 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             19
```

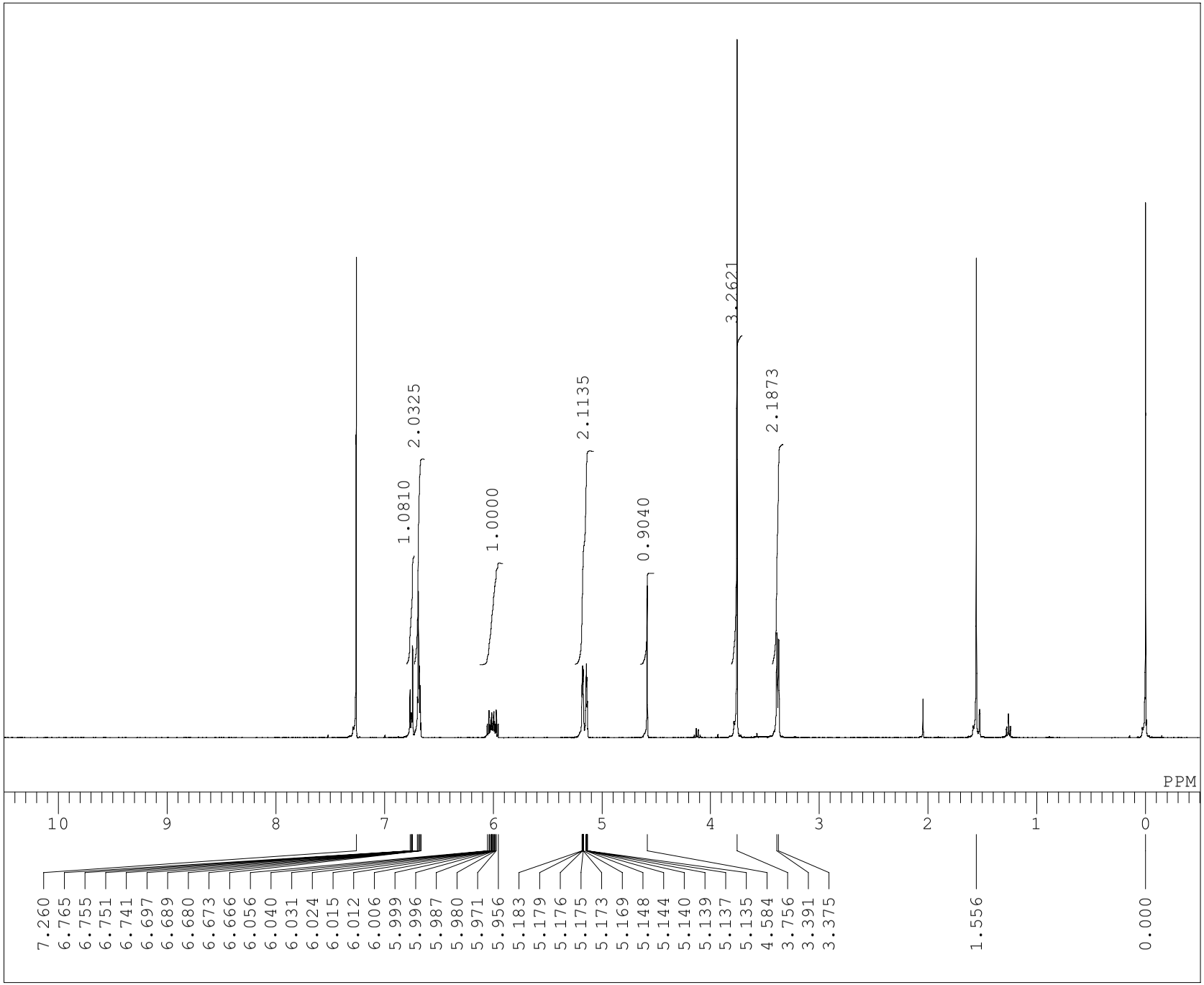
S-5c



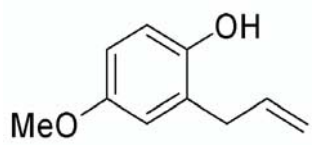

```
DFILE  \\150.59.248.165\data\NM
COMNT
DATIM  Wed Feb 04 16:54:17 2009
OBNUC  13C
EXMOD  BCM
OBFRQ        100.40 MHz
OBSET        125.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU       27210.9 Hz
SCANS           152
ACQTM         1.204 sec
PD            1.794 sec
PW1             6.1 us
IRNUC  1H
CTEMP          22.9 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            23
```



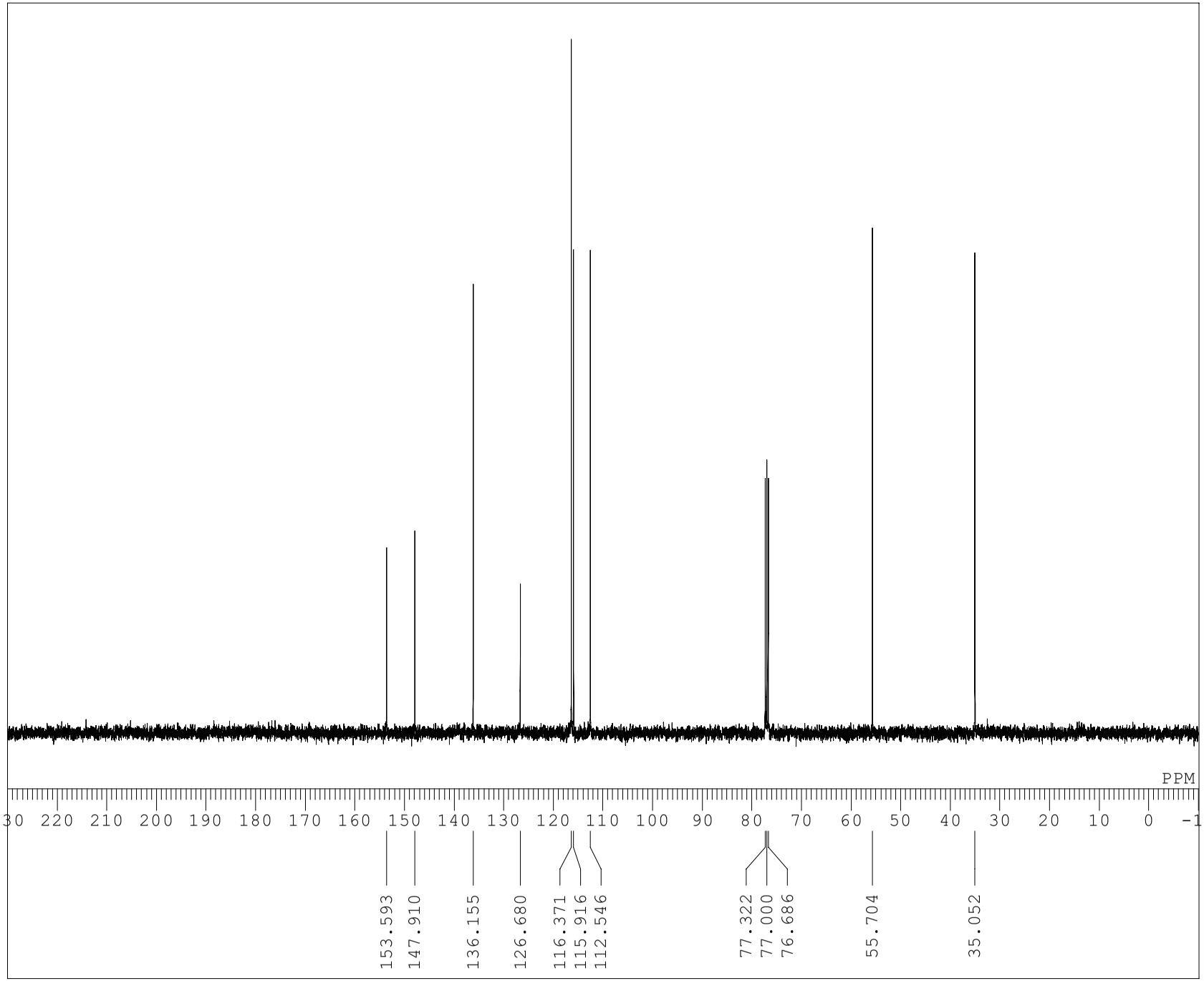
S-5c



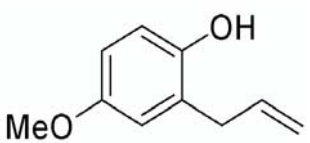
DFILE \\150.59.84.6\user\004BC
COMNT
DATIM Tue May 26 14:59:01 2009
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 7992.0 Hz
SCANS 32
ACQTM 4.100 sec
PD 2.901 sec
PW1 6.3 us
IRNUC 1H
CTEMP 24.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 22



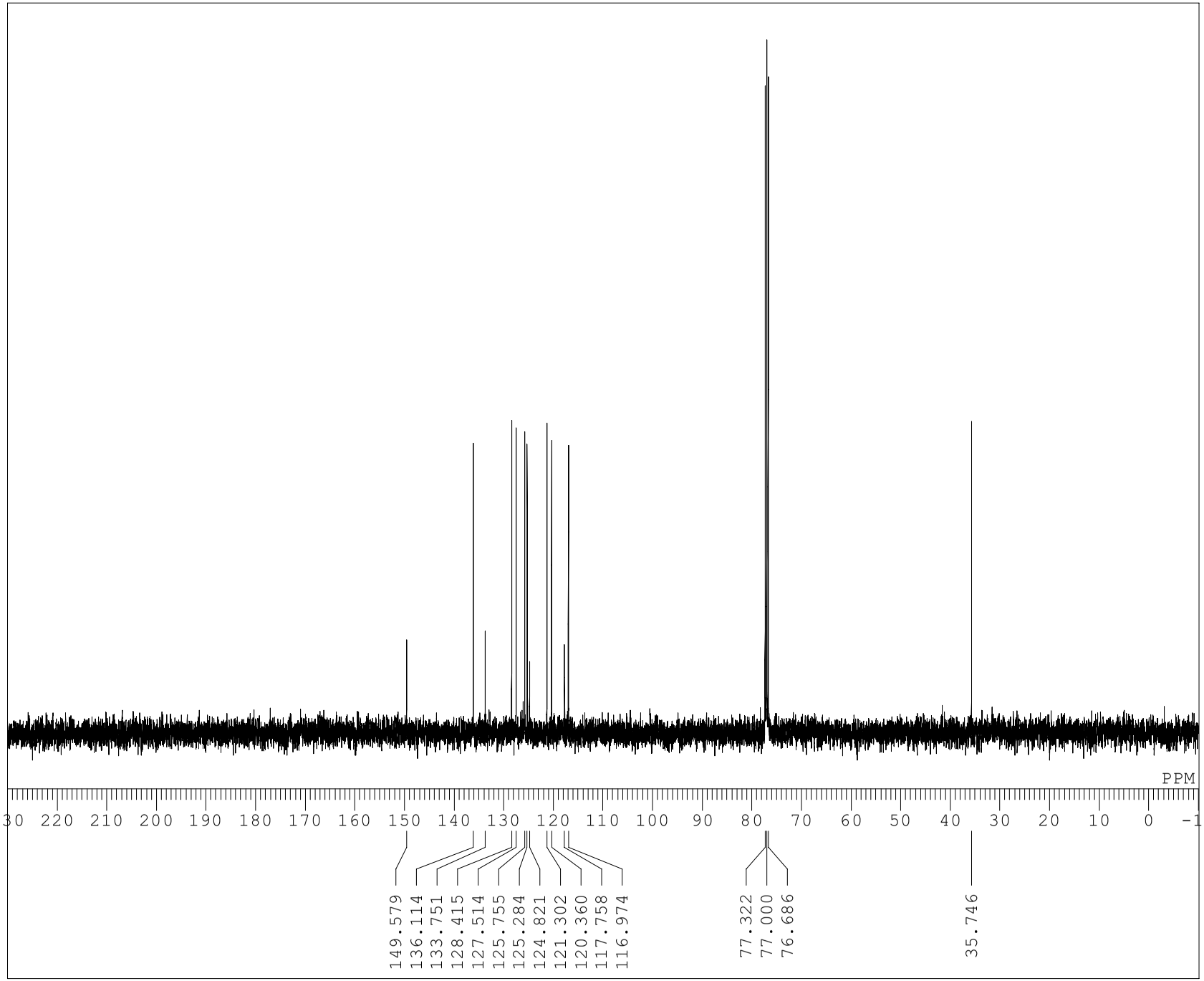
S-5d



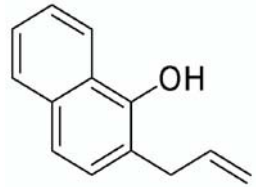

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Tue May 26 19:40:25 2009
OBNUC  13C
EXMOD  BCM
OBFRQ        100.40 MHz
OBSET        125.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU       27210.9 Hz
SCANS            56
ACQTM          1.204 sec
PD             1.794 sec
PW1              6.1 us
IRNUC  1H
CTEMP           25.9 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              1.20 Hz
RGAIN             23
```



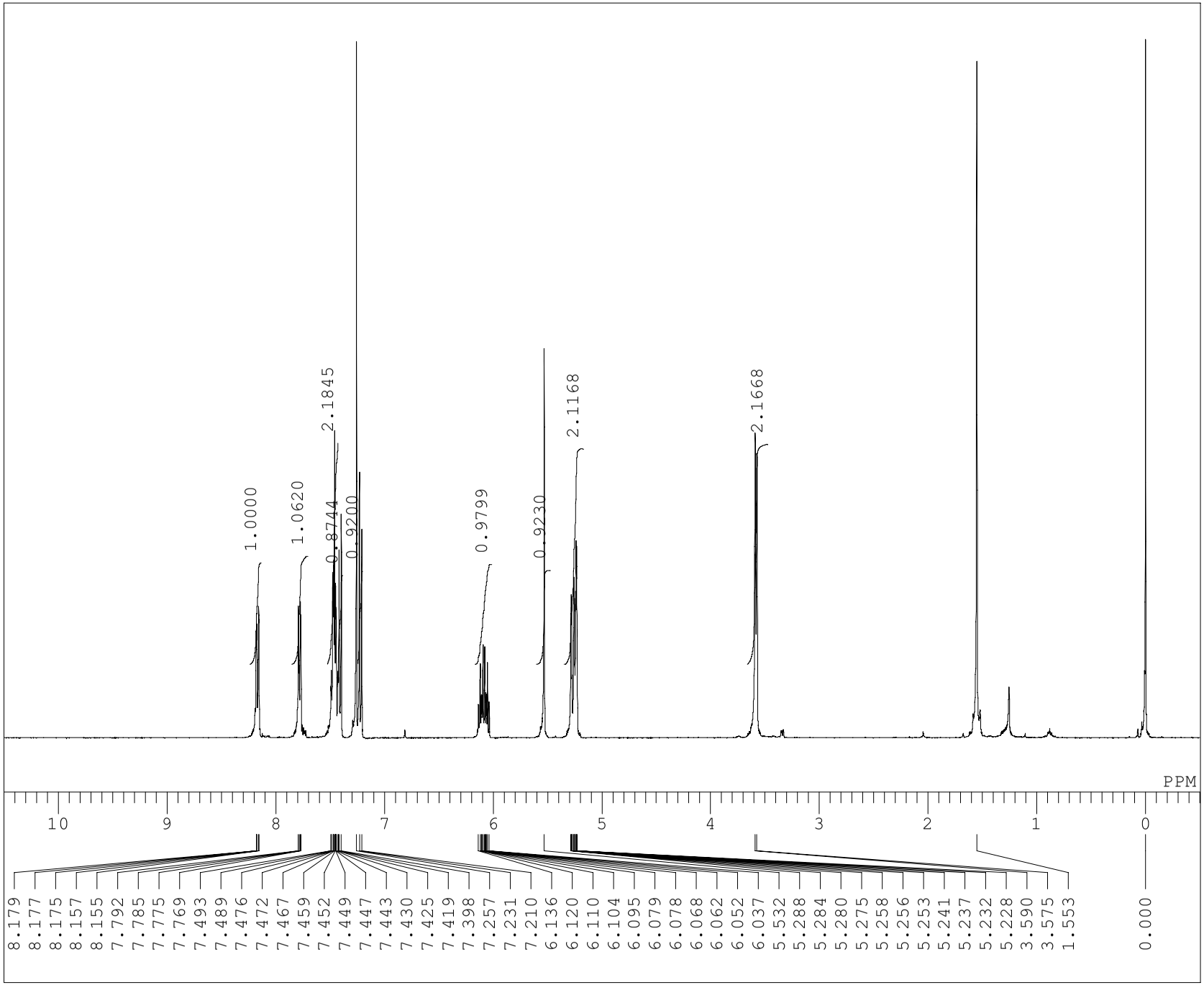
S-5d



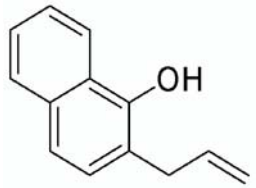

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Wed May 27 11:16:00 2009
OBNUC  13C
EXMOD  BCM
OBFRQ       100.40 MHz
OBSET       125.00 KHz
OBFIN      10500.0 Hz
POINT        32768
FREQU      27210.9 Hz
SCANS           92
ACQTM         1.204 sec
PD            1.794 sec
PW1             6.1 us
IRNUC  1H
CTEMP          25.7 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            23
```



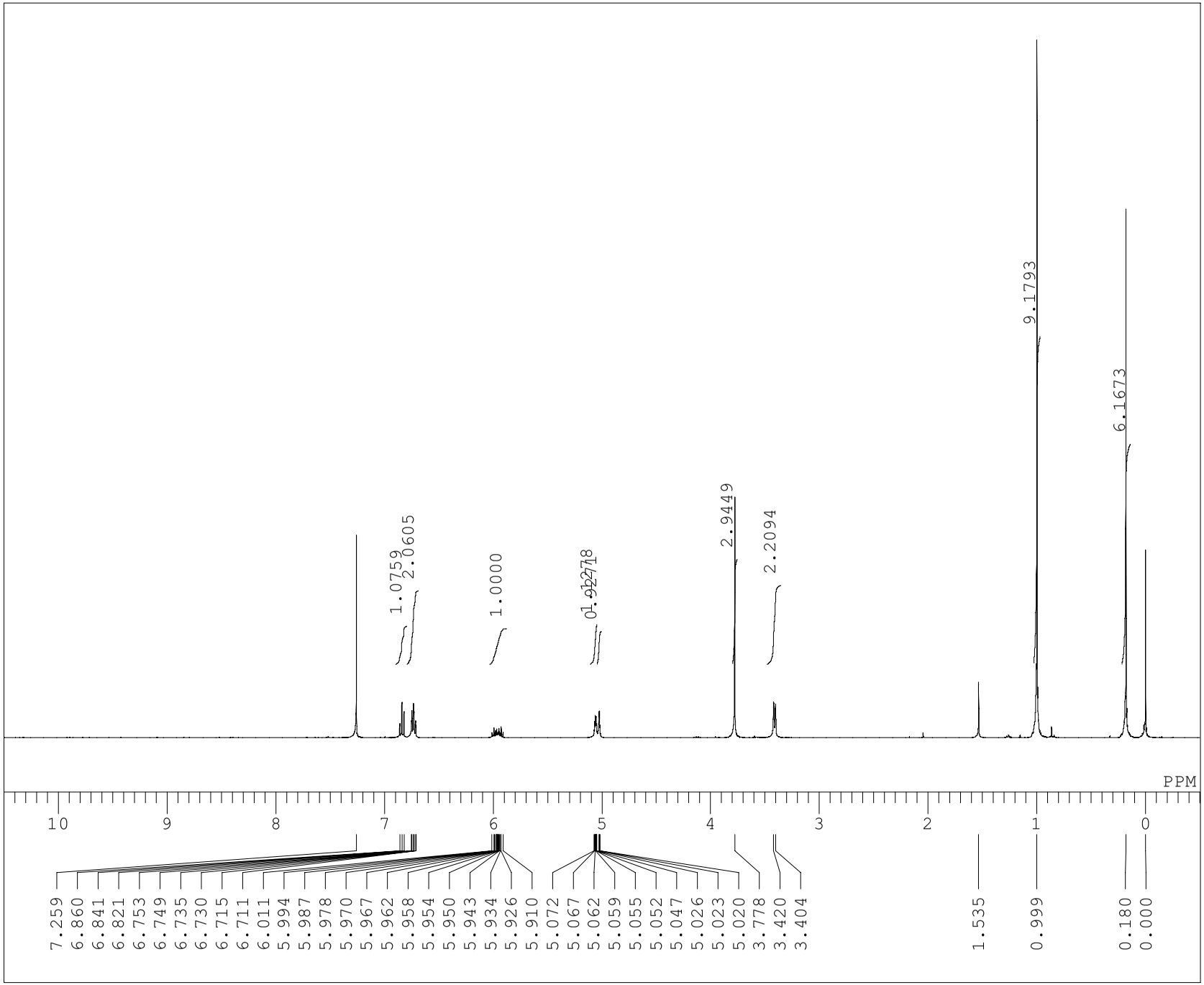
S-5e



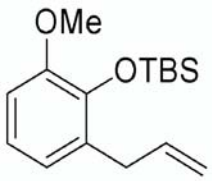

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Tue May 26 14:50:19 2009
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU        7992.0 Hz
SCANS            12
ACQTM         4.100 sec
PD            2.901 sec
PW1             6.3 us
IRNUC  1H
CTEMP          25.0 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            22
```



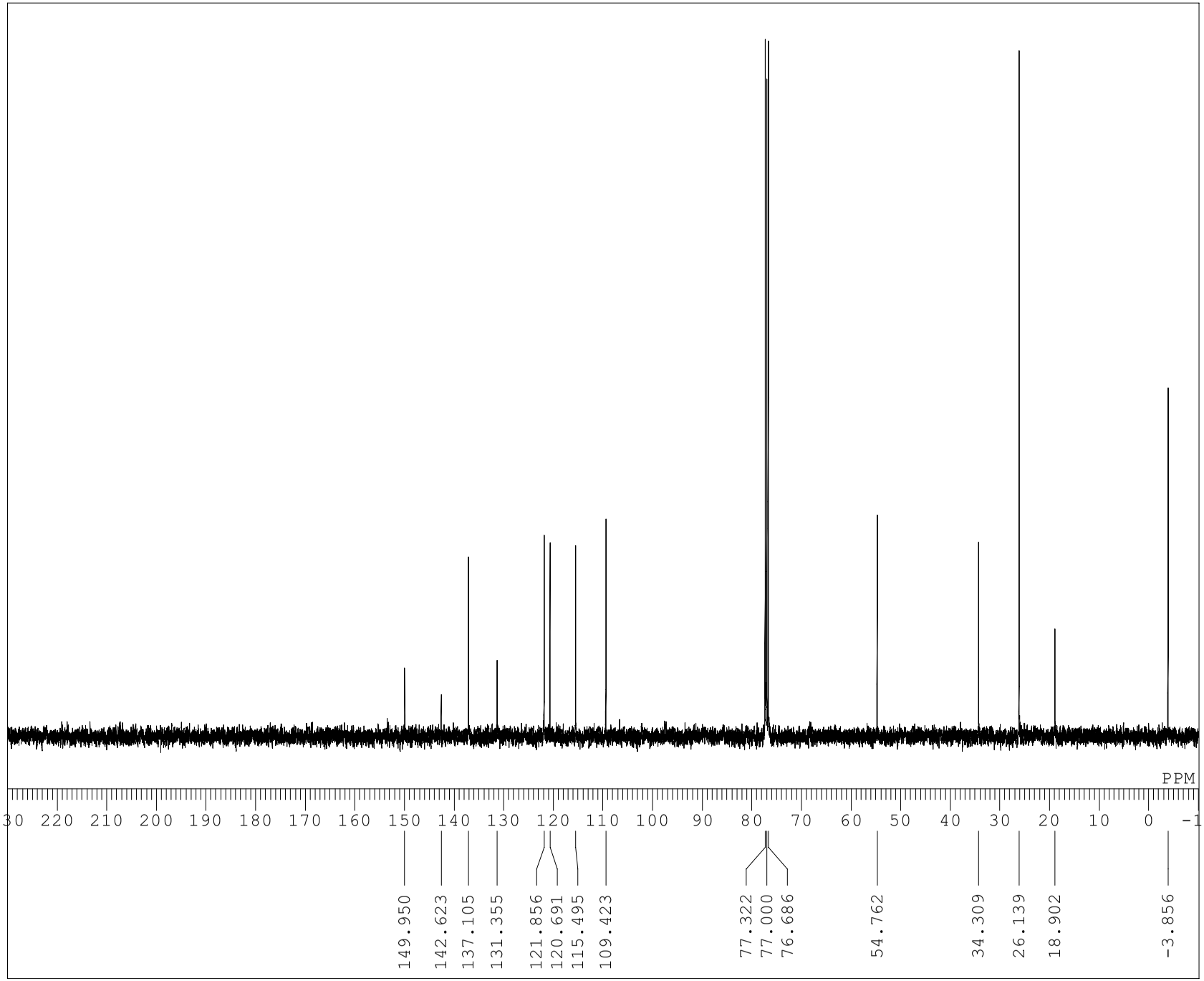
S-5e



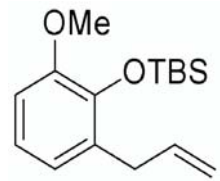

```
DFILE  \\150.59.248.165\data\NM
COMNT
DATIM  Thu Apr 30 13:48:16 2009
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU        7992.0 Hz
SCANS            16
ACQTM         4.100 sec
PD            2.901 sec
PW1             6.3 us
IRNUC  1H
CTEMP          25.2 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            19
```



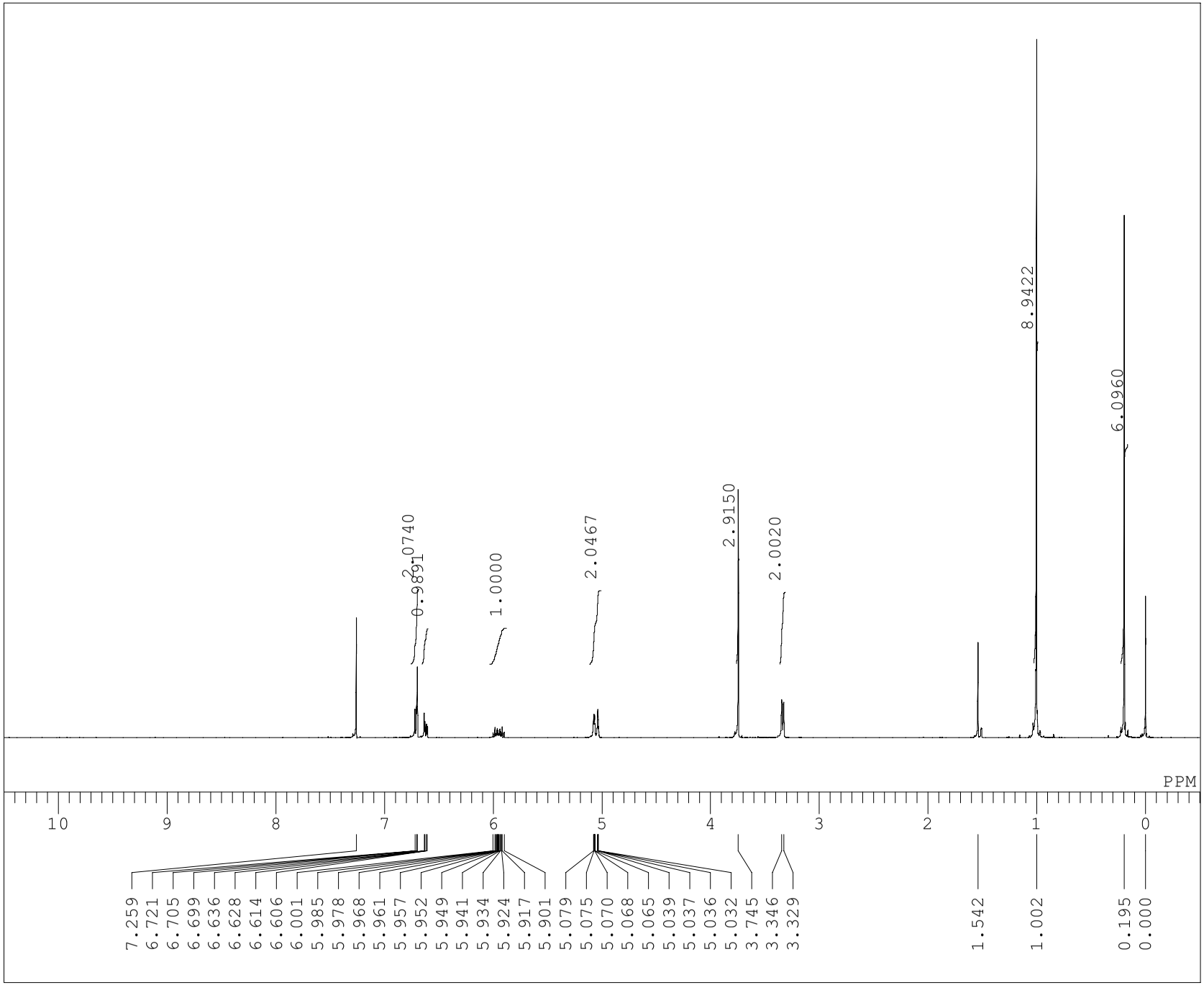
S-6c



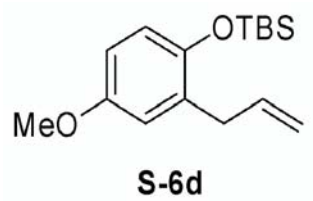

```
DFILE  \\150.59.248.165\data\NM
COMNT
DATIM  Thu Apr 30 14:03:09 2009
OBNUC  13C
EXMOD  BCM
OBFRQ       100.40 MHz
OBSET       125.00 KHz
OBFIN      10500.0 Hz
POINT        32768
FREQU      27210.9 Hz
SCANS          244
ACQTM        1.204 sec
PD           1.794 sec
PW1            6.1 us
IRNUC  1H
CTEMP         26.3 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            23
```



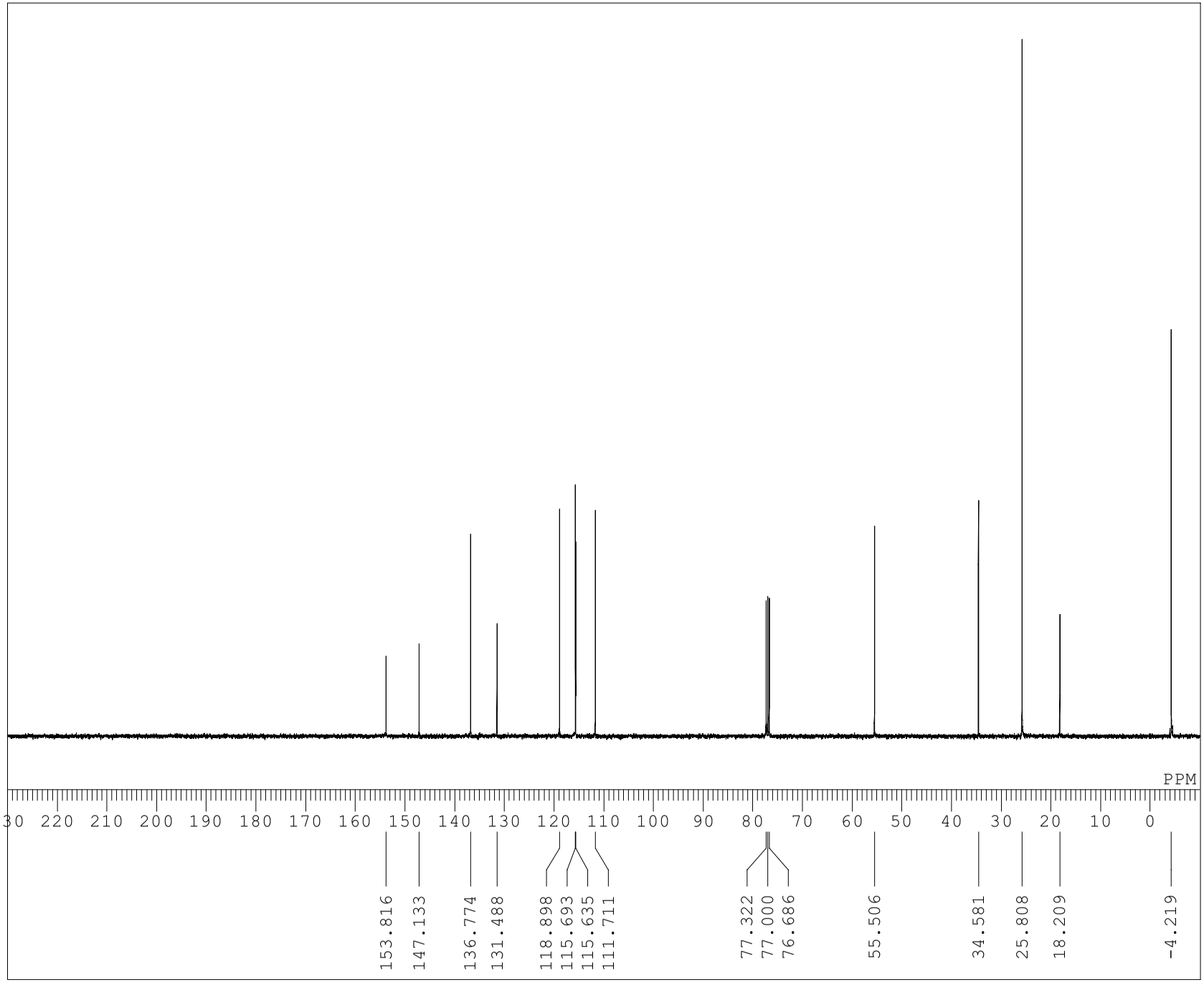
S-6c



DFILE \\150.59.84.6\user\004BC
COMNT
DATIM Sat May 16 15:53:47 2009
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 7992.0 Hz
SCANS 16
ACQTM 4.100 sec
PD 2.901 sec
PW1 6.3 us
IRNUC 1H
CTEMP 25.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 20



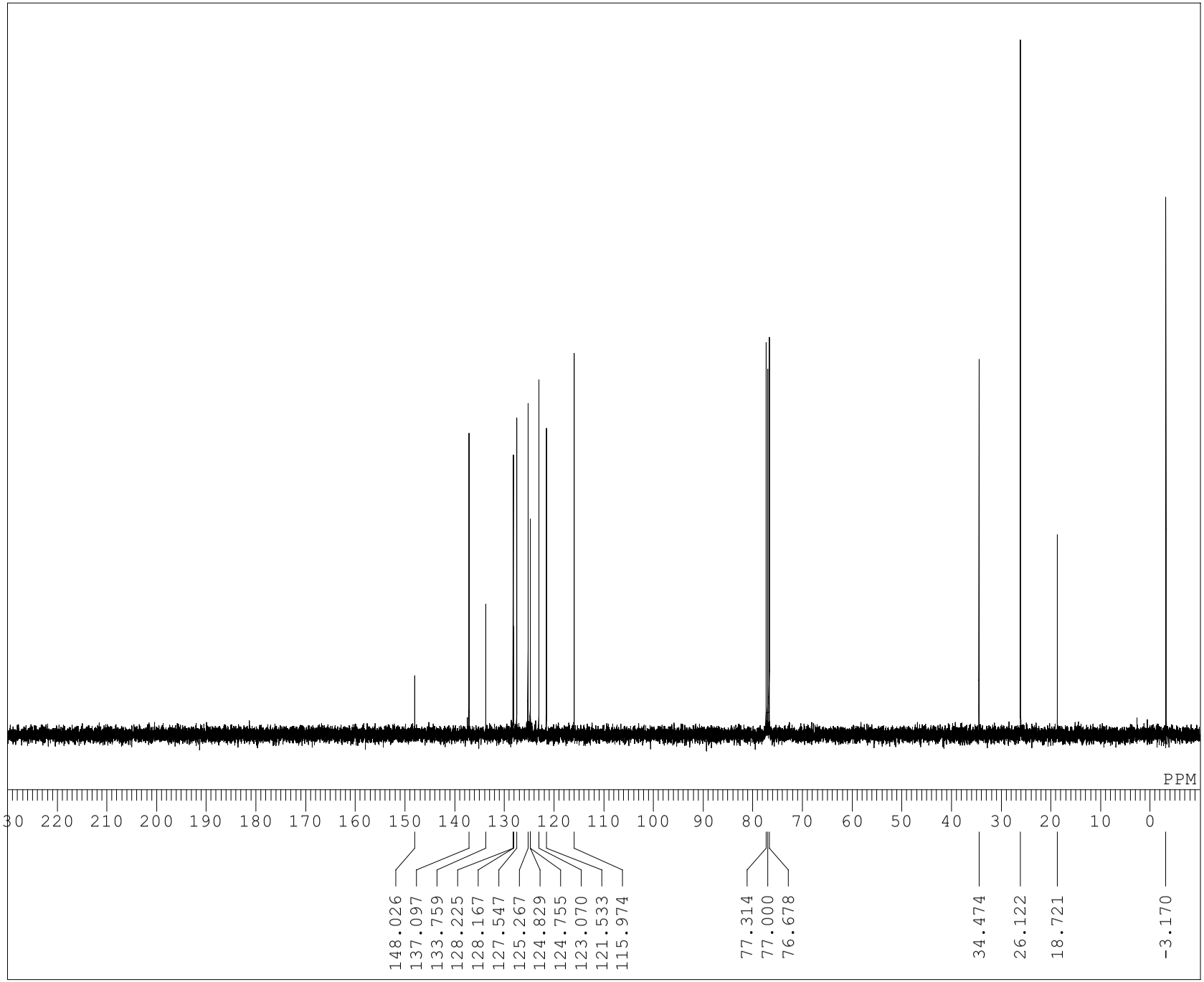
S-6d



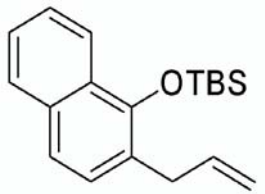

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Mon May 18 10:09:01 2009
OBNUC  13C
EXMOD  BCM
OBFRQ        100.40 MHz
OBSET        125.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU       27210.9 Hz
SCANS           141
ACQTM         1.204 sec
PD            1.794 sec
PW1             6.1 us
IRNUC  1H
CTEMP          25.7 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            23
```

S-6d

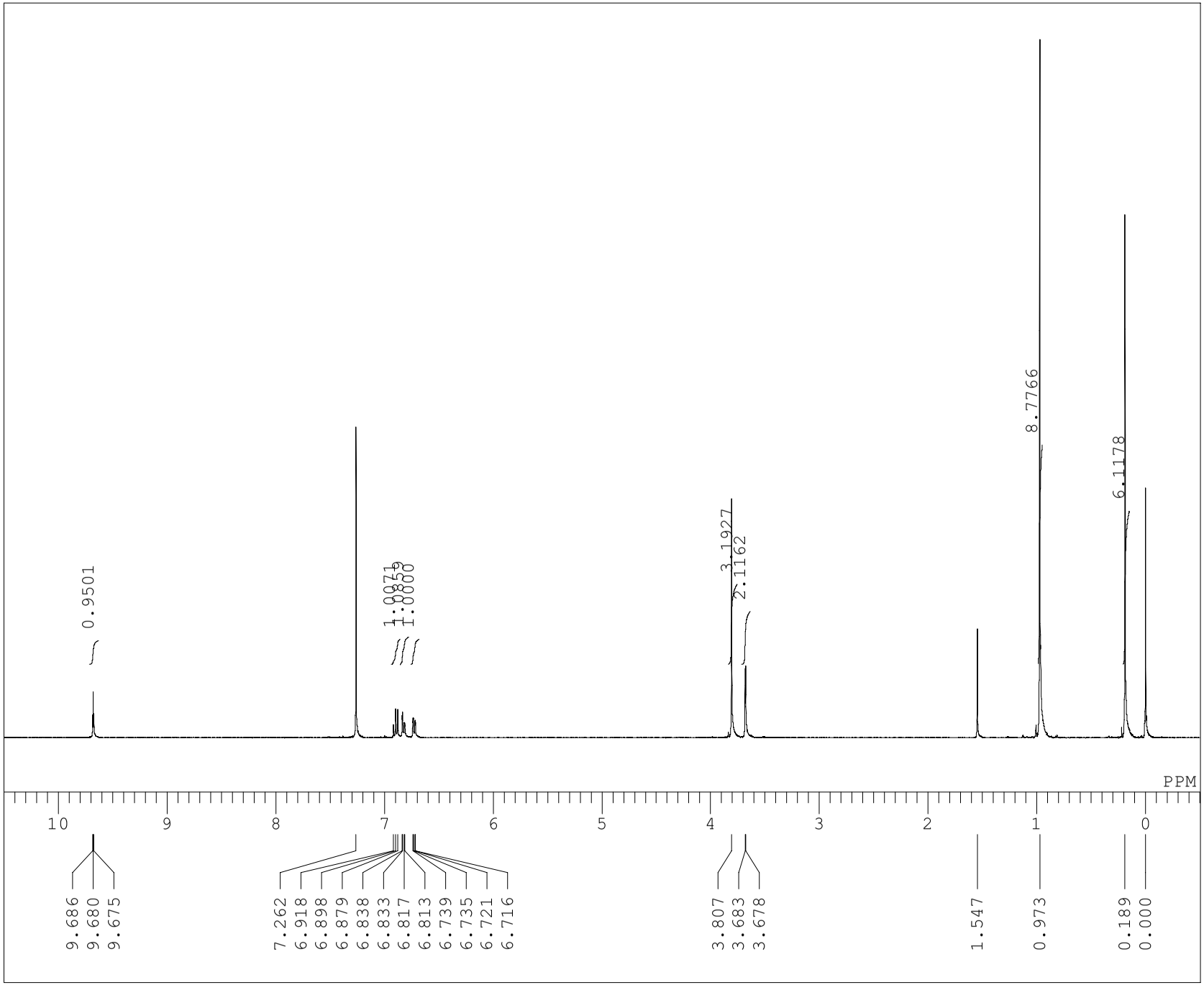
DFILE \\150.59.84.6\user\004BC
COMNT
DATIM Fri May 01 17:42:25 2009
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 7992.0 Hz
SCANS 28
ACQTM 4.100 sec
PD 2.901 sec
PW1 6.3 us
IRNUC 1H
CTEMP 24.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 20
OTBS
S-6e
PPM
0.000
0.178
1.128
1.539
3.542
3.559
5.074
5.078
5.082
5.087
5.092
5.096
5.103
5.107
5.111
5.130
5.134
5.139
5.143
5.904
5.920
5.929
5.937
5.945
5.962
5.971
5.979
5.988
6.004
7.259
7.279
7.301
7.378
7.383
7.395
7.400
7.410
7.419
7.425
7.437
7.443
7.464
7.739
7.748
7.753
7.756
7.761
7.767
7.771
8.054
8.065
8.071
8.078
8.087
6.0478
9.1324
2.1007
2.0958
0.9249
1.1404
1.0583
1.0992
0.9749
1.0000



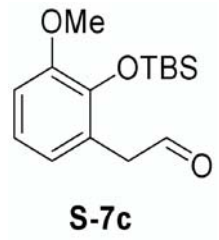

```
DFILE  \\150.59.248.165\data\NM
COMNT
DATIM  Fri May 01 19:07:04 2009
OBNUC  13C
EXMOD  BCM
OBFRQ        100.40 MHz
OBSET        125.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU       27210.9 Hz
SCANS           149
ACQTM         1.204 sec
PD            1.794 sec
PW1             6.1 us
IRNUC  1H
CTEMP          26.1 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.25 Hz
RGAIN            23
```



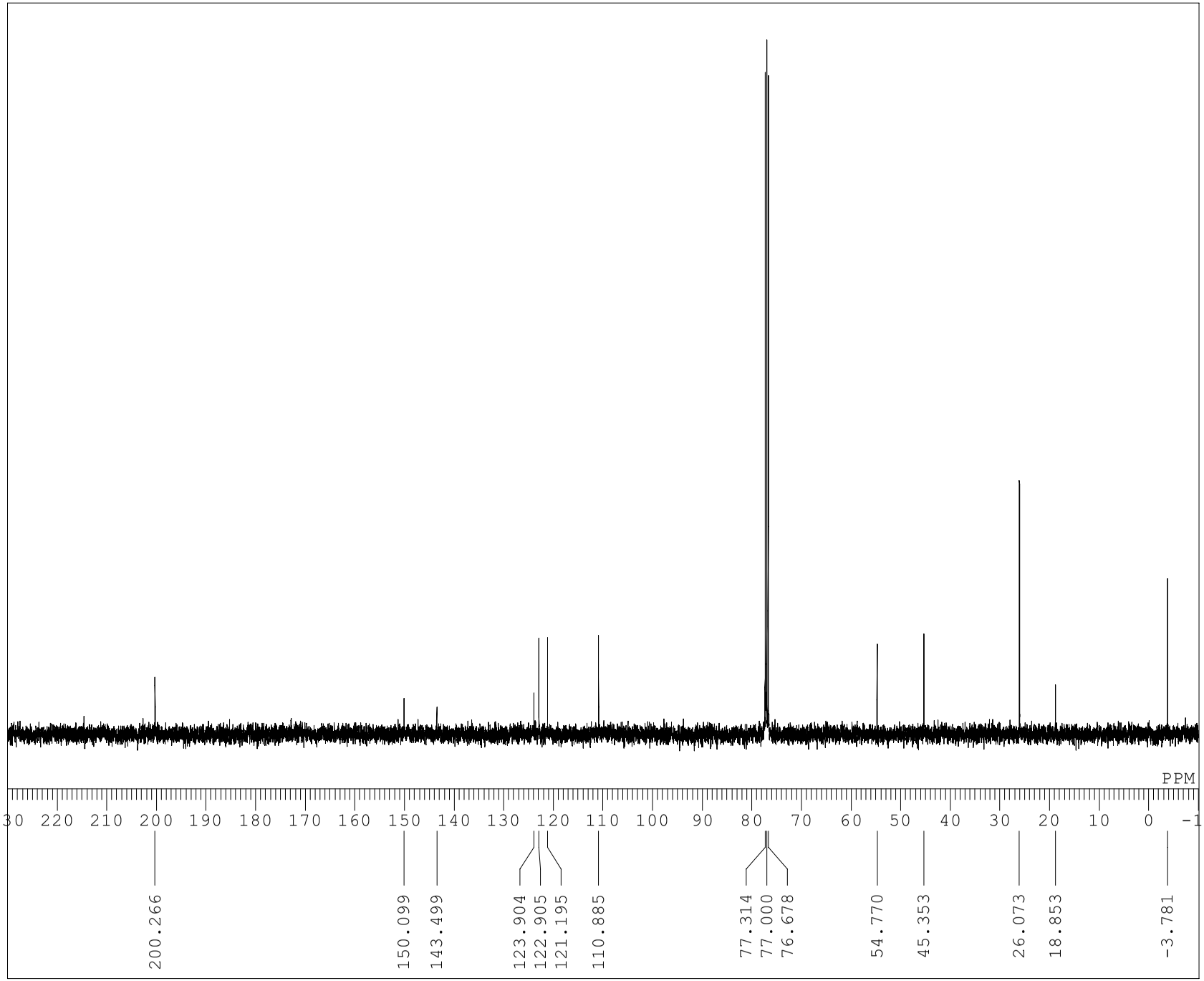
S-6e



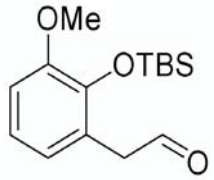

```
DFILE  \\150.59.248.165\data\NM
COMNT
DATIM  Fri Feb 06 21:41:53 2009
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU        7992.0 Hz
SCANS              4
ACQTM          4.100 sec
PD             2.901 sec
PW1              6.3 us
IRNUC  1H
CTEMP           22.5 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             20
```



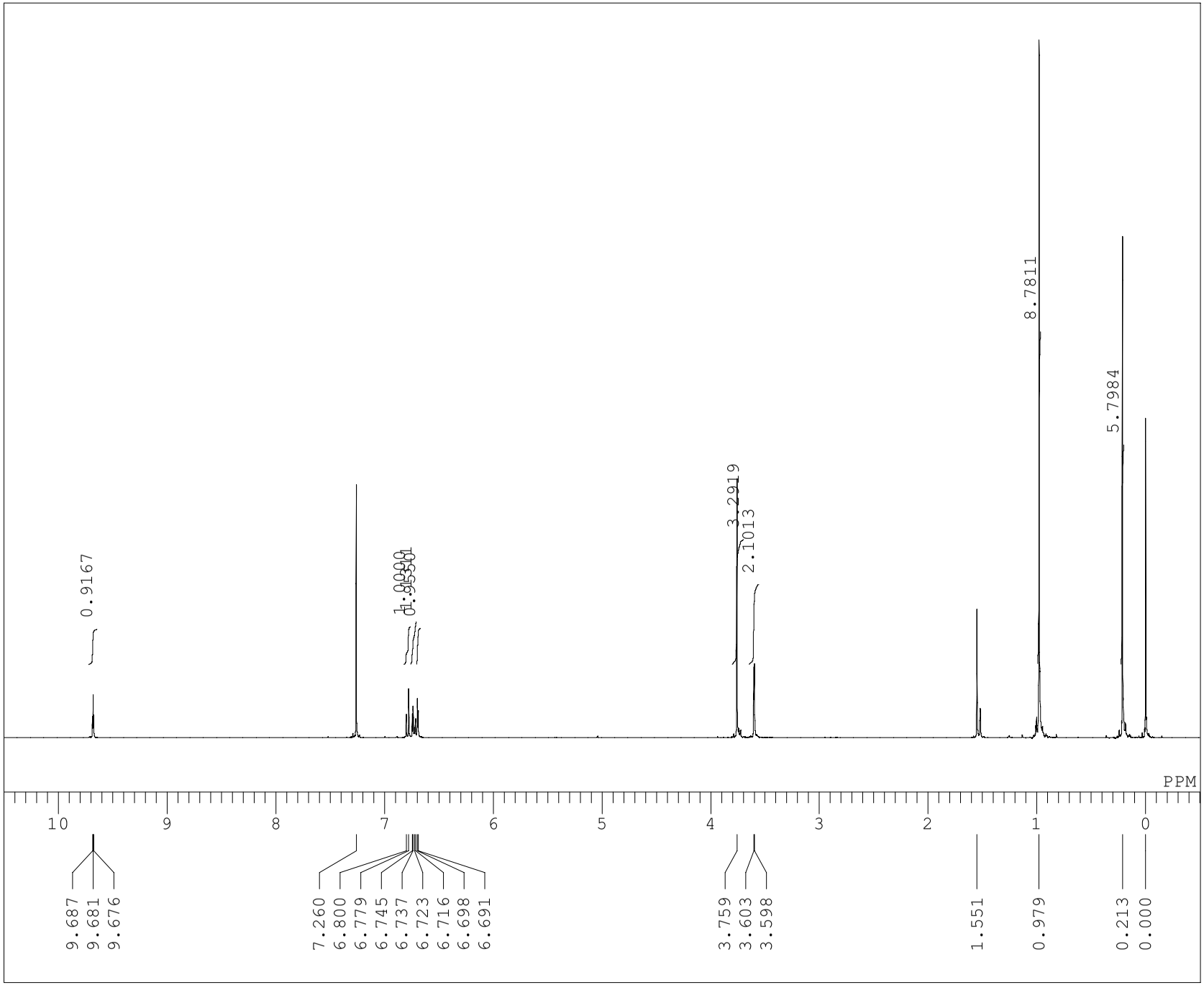
S-7c



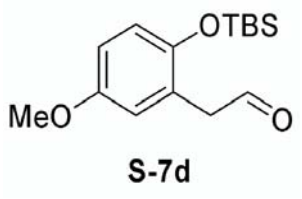
DFILE \\150.59.248.165\data\NM
COMNT
DATIM Fri Feb 06 21:53:26 2009
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 27210.9 Hz
SCANS 180
ACQTM 1.204 sec
PD 1.794 sec
PW1 6.1 us
IRNUC 1H
CTEMP 23.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 23



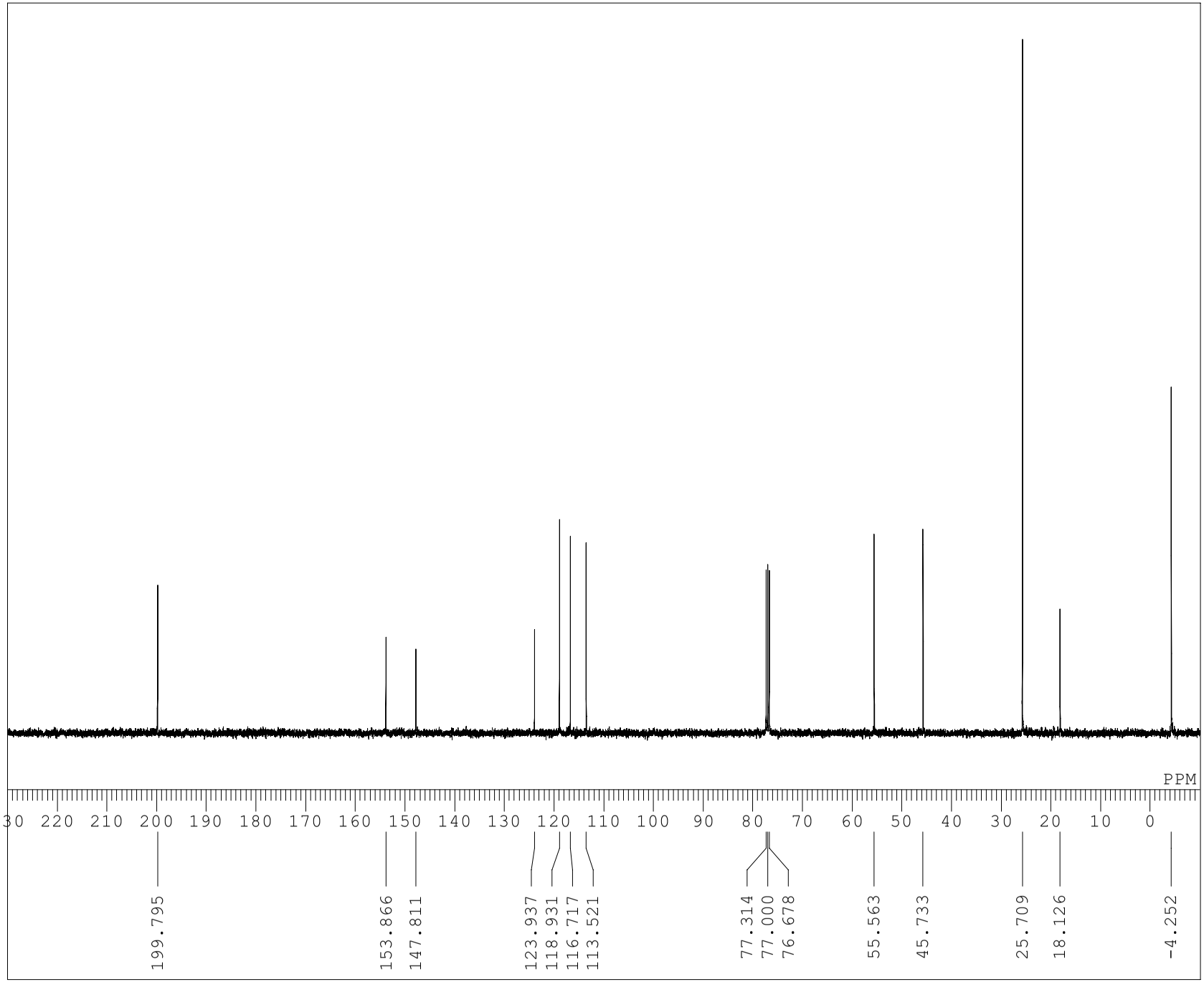
S-7c



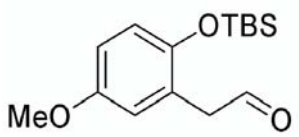

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Mon Jun 01 20:46:00 2009
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU        8000.0 Hz
SCANS            16
ACQTM         4.096 sec
PD            2.904 sec
PW1             5.7 us
IRNUC  1H
CTEMP          23.1 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            22
```



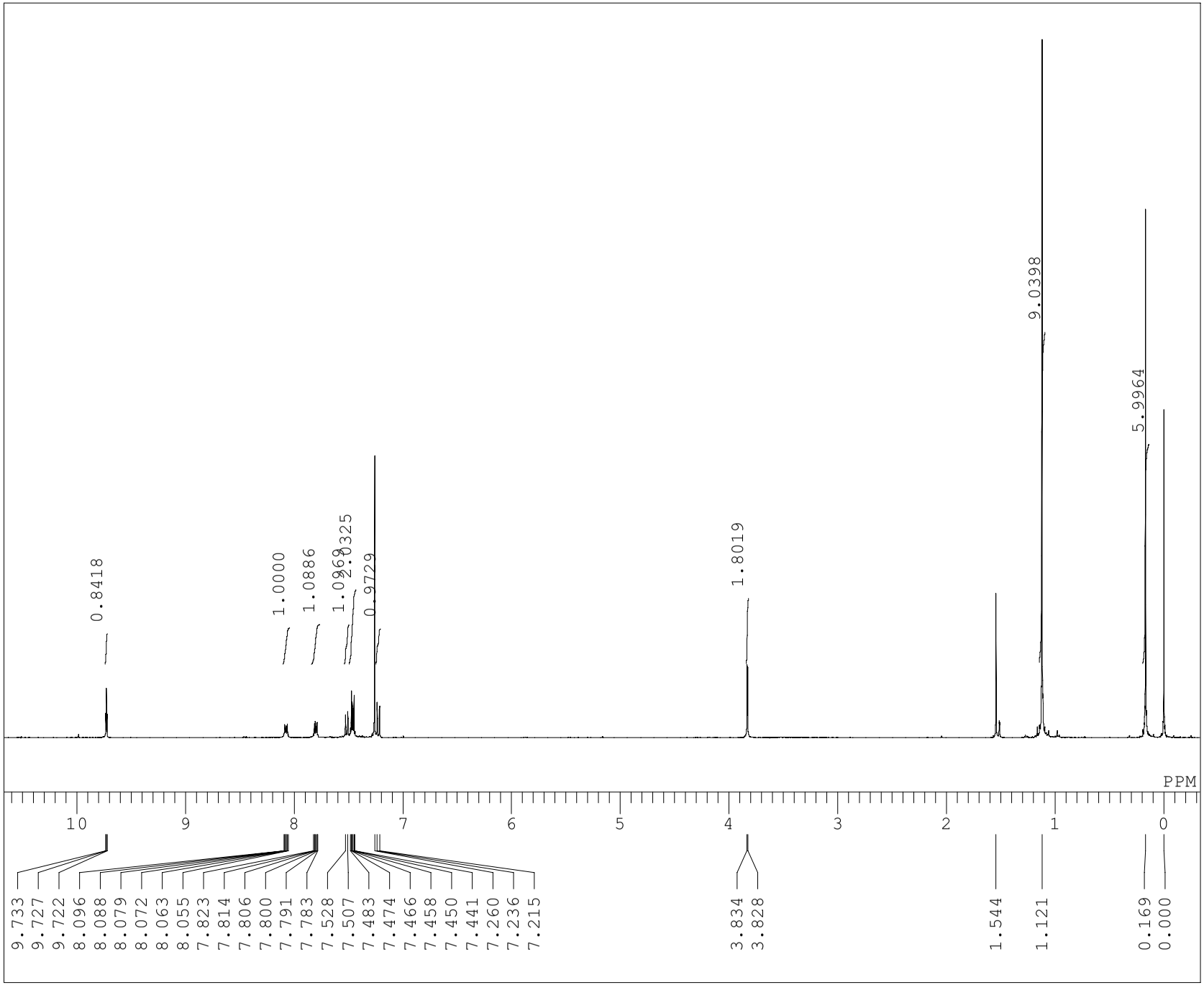
S-7d




```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Mon Jun 01 22:20:14 2009
OBNUC  13C
EXMOD  BCM
OBFRQ        100.40 MHz
OBSET        125.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU       27210.9 Hz
SCANS            66
ACQTM         1.204 sec
PD            1.794 sec
PW1             6.1 us
IRNUC  1H
CTEMP          26.3 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            23
```

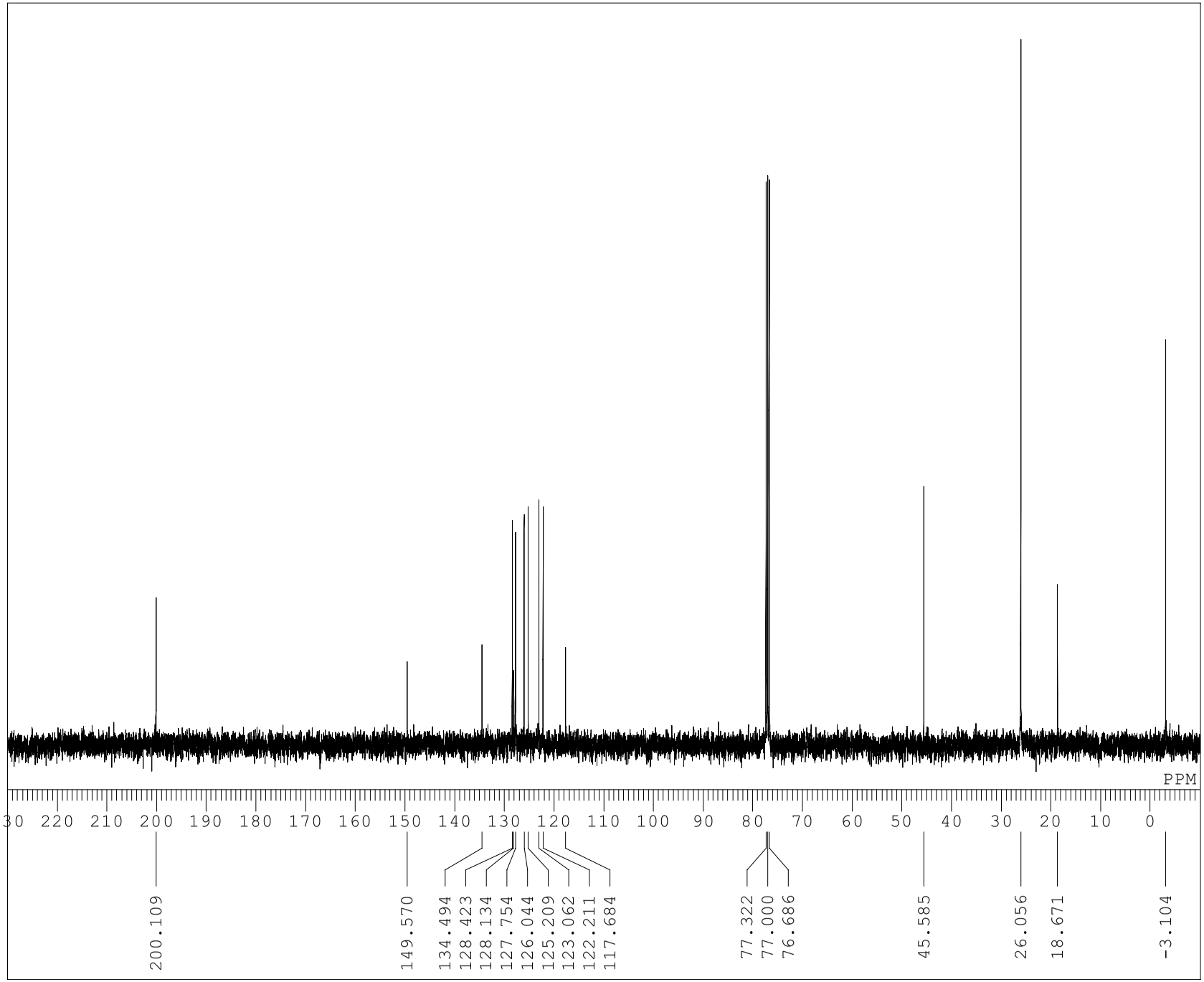


S-7d

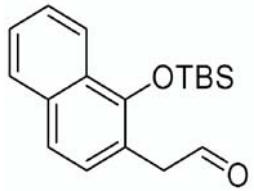



```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Fri May 15 15:27:06 2009
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU        7992.0 Hz
SCANS             32
ACQTM          4.100 sec
PD             2.901 sec
PW1              6.3 us
IRNUC  1H
CTEMP           24.7 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             21
```

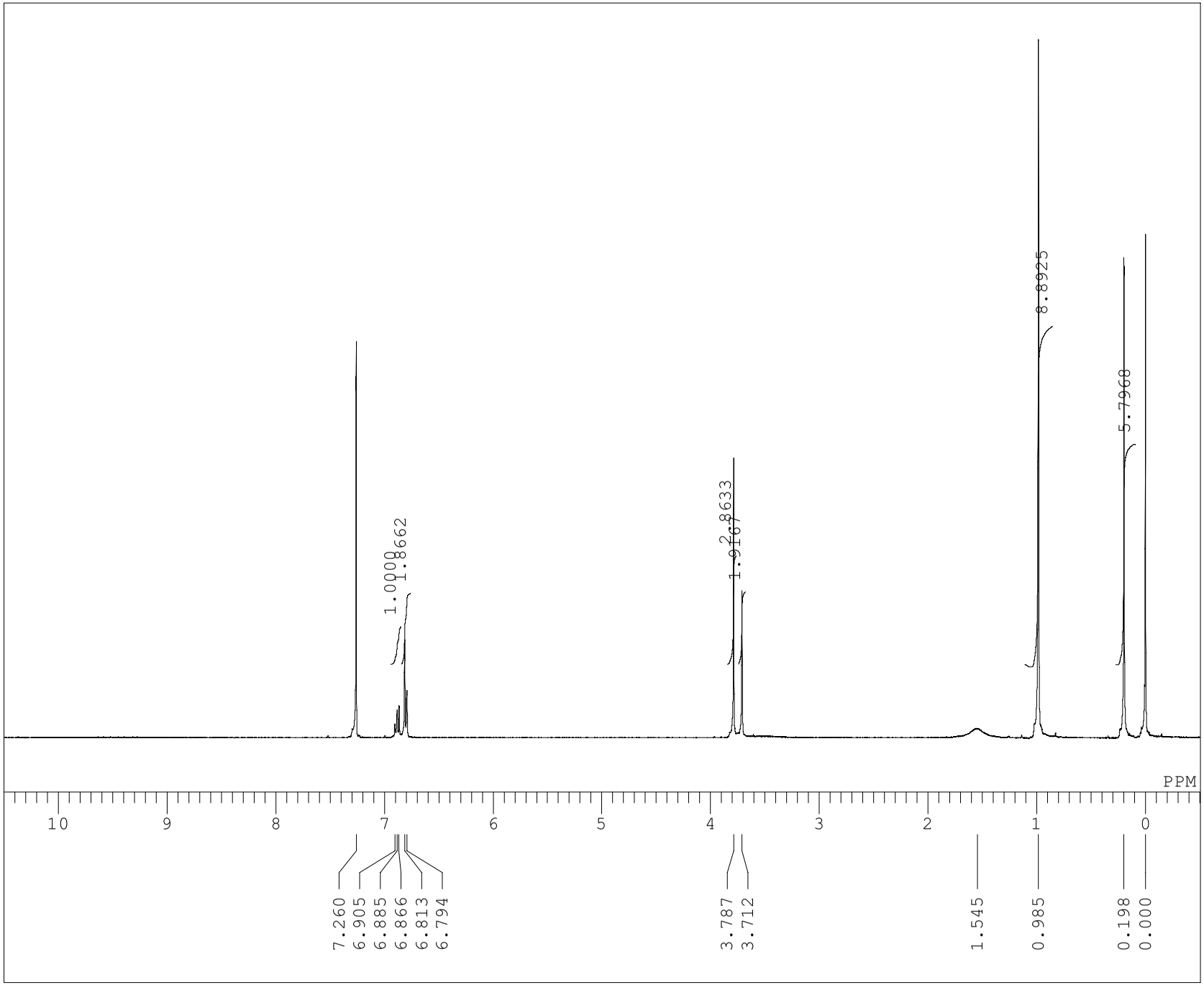
S-7e




```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Fri May 15 16:38:54 2009
OBNUC  13C
EXMOD  BCM
OBFRQ        100.40 MHz
OBSET        125.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU       27210.9 Hz
SCANS           188
ACQTM         1.204 sec
PD            1.794 sec
PW1             6.1 us
IRNUC  1H
CTEMP          25.7 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              1.20 Hz
RGAIN             23
```

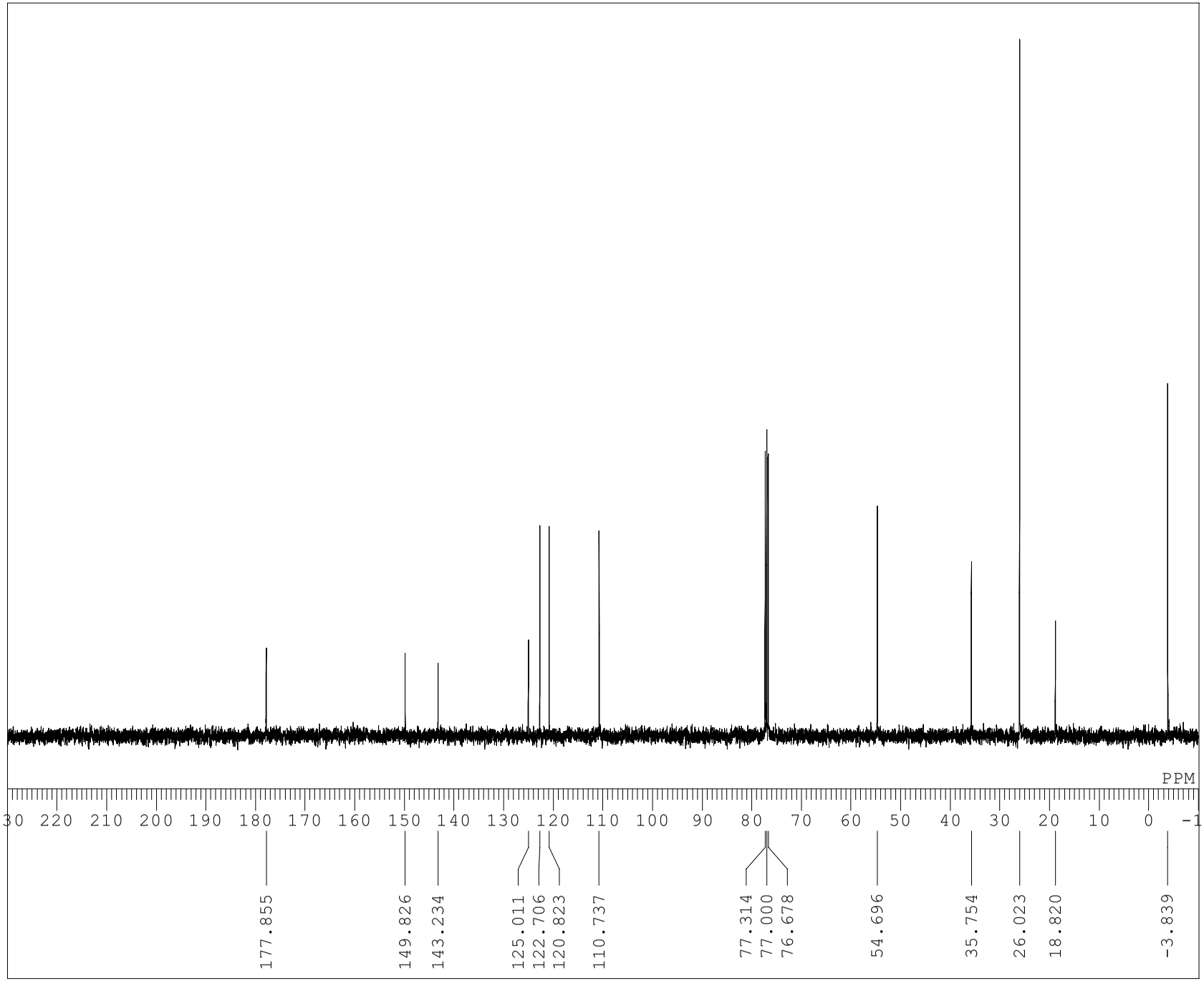


S-7e

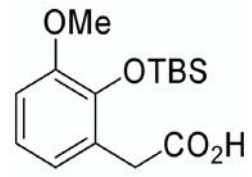



```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Wed Jun 10 20:59:55 2009
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU        7992.0 Hz
SCANS             32
ACQTM          4.100 sec
PD             2.901 sec
PW1              6.3 us
IRNUC  1H
CTEMP           25.1 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             22
```

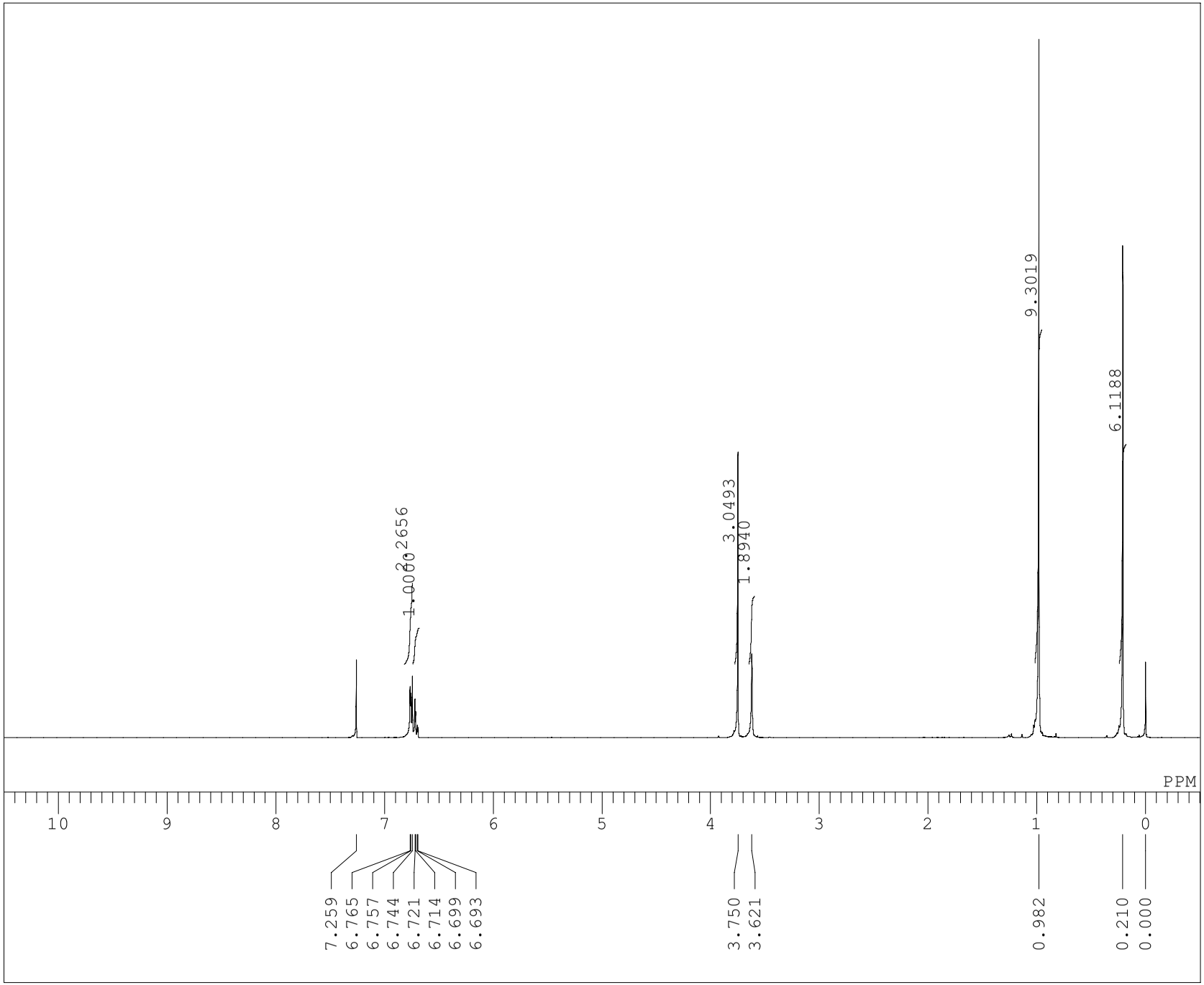
S-8c



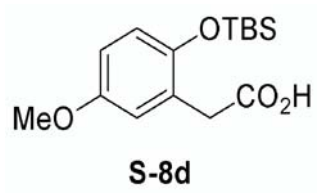

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Wed Jun 10 21:34:10 2009
OBNUC  13C
EXMOD  BCM
OBFRQ        100.40 MHz
OBSET        125.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU       27210.9 Hz
SCANS            73
ACQTM         1.204 sec
PD            1.794 sec
PW1             6.1 us
IRNUC  1H
CTEMP          26.0 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            25
```



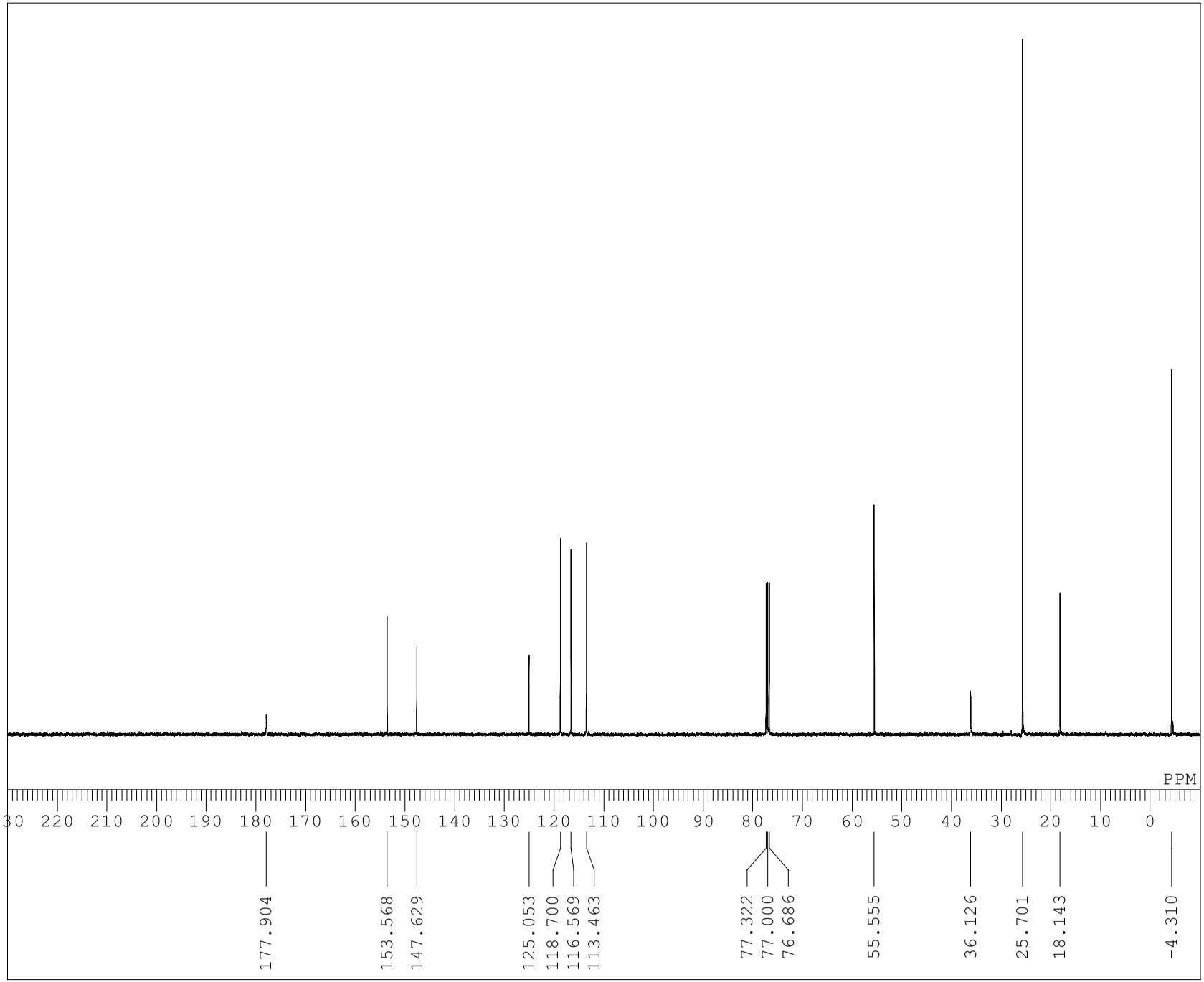
S-8c



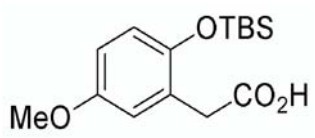

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Fri May 29 13:43:17 2009
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU        7992.0 Hz
SCANS             32
ACQTM         4.100 sec
PD            2.901 sec
PW1             6.3 us
IRNUC  1H
CTEMP          24.7 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            17
```



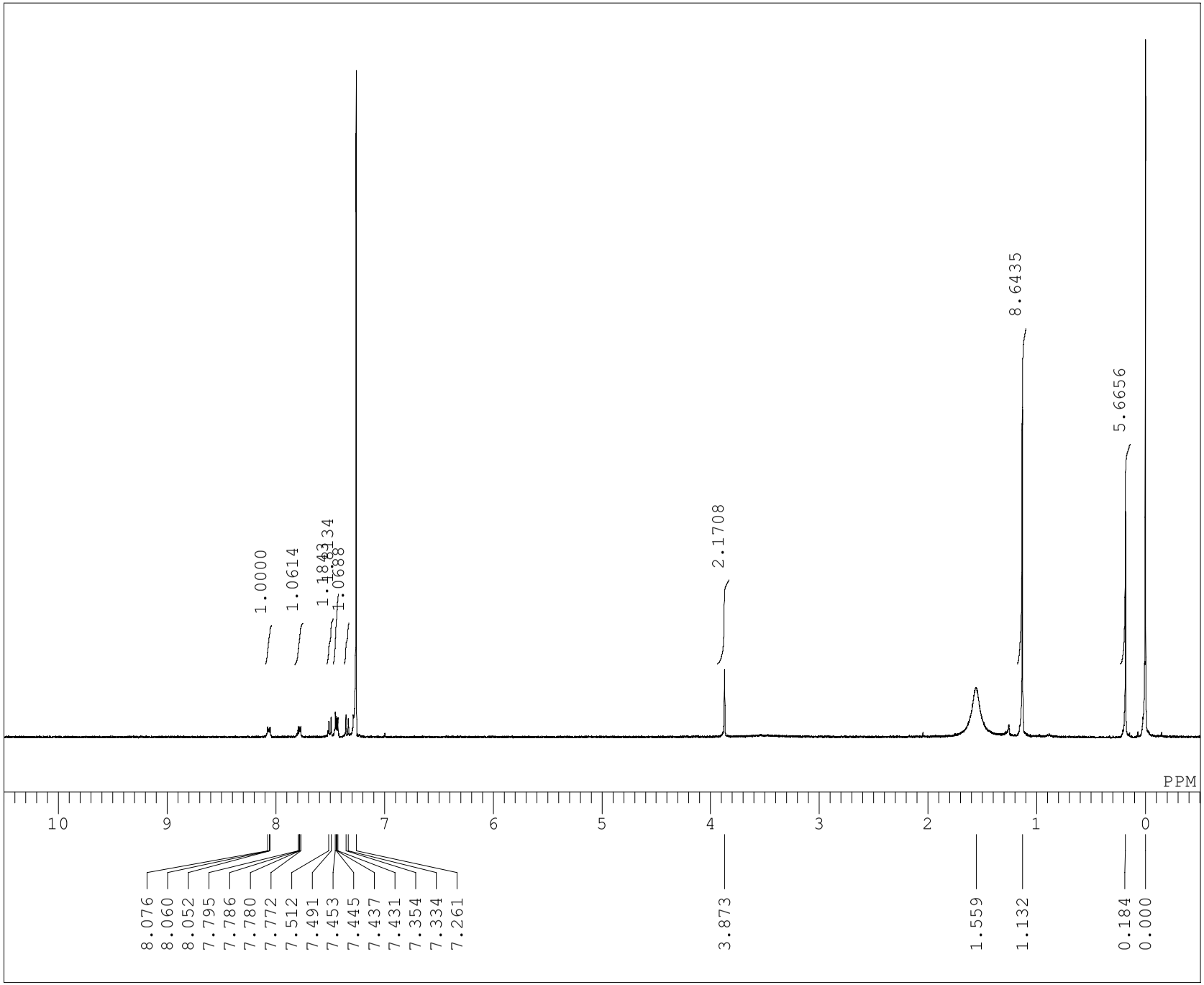
S-8d



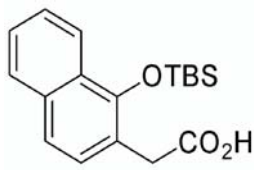
DFILE \\150.59.84.6\user\004BC
COMNT
DATIM Fri May 29 14:02:01 2009
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 27210.9 Hz
SCANS 321
ACQTM 1.204 sec
PD 1.794 sec
PW1 6.1 us
IRNUC 1H
CTEMP 25.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 23



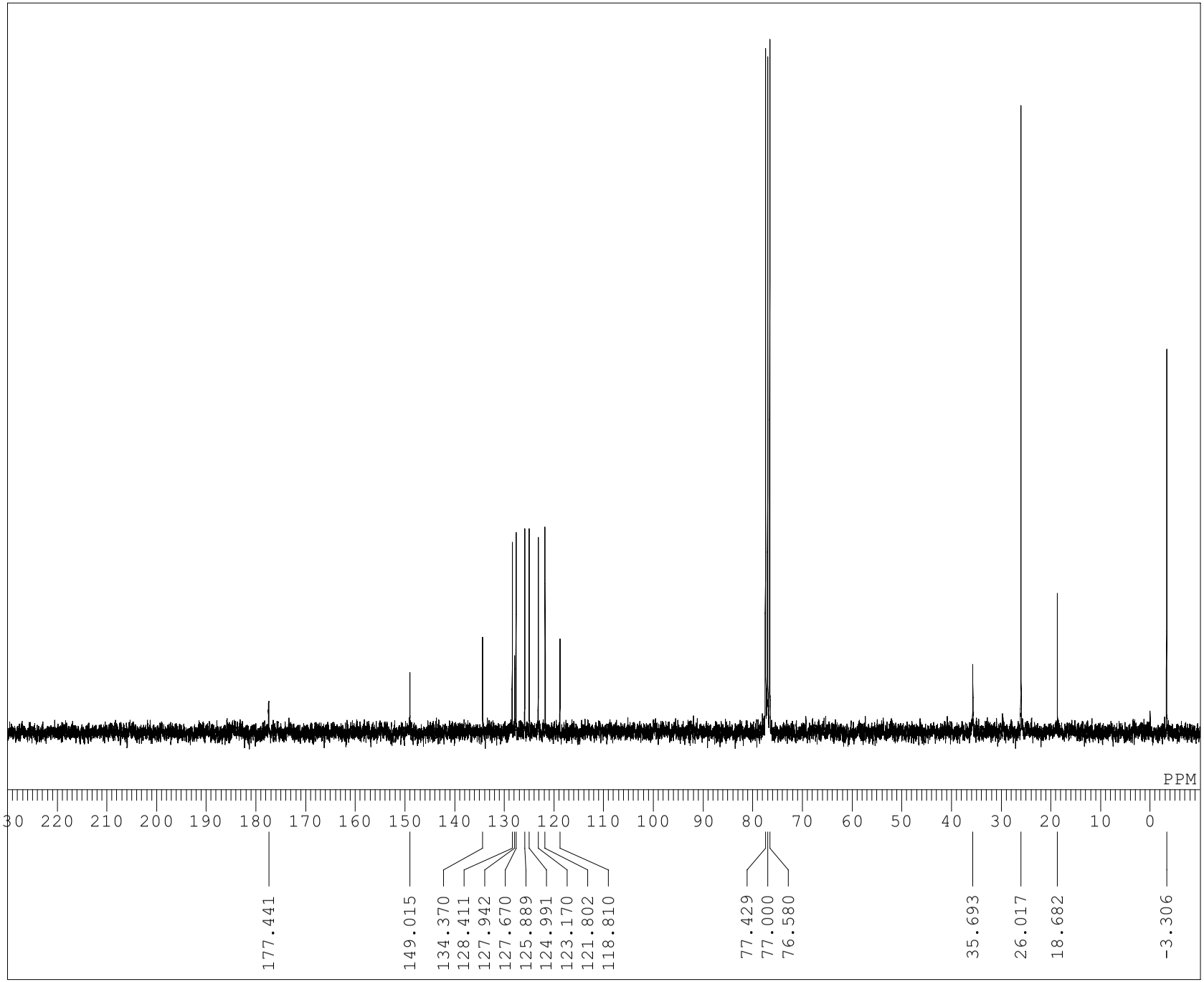
S-8d



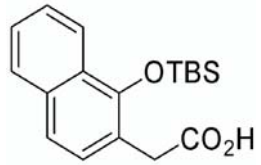

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Wed May 27 21:01:17 2009
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU        7992.0 Hz
SCANS             32
ACQTM          4.100 sec
PD             2.901 sec
PW1              6.3 us
IRNUC  1H
CTEMP           24.7 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             25
```



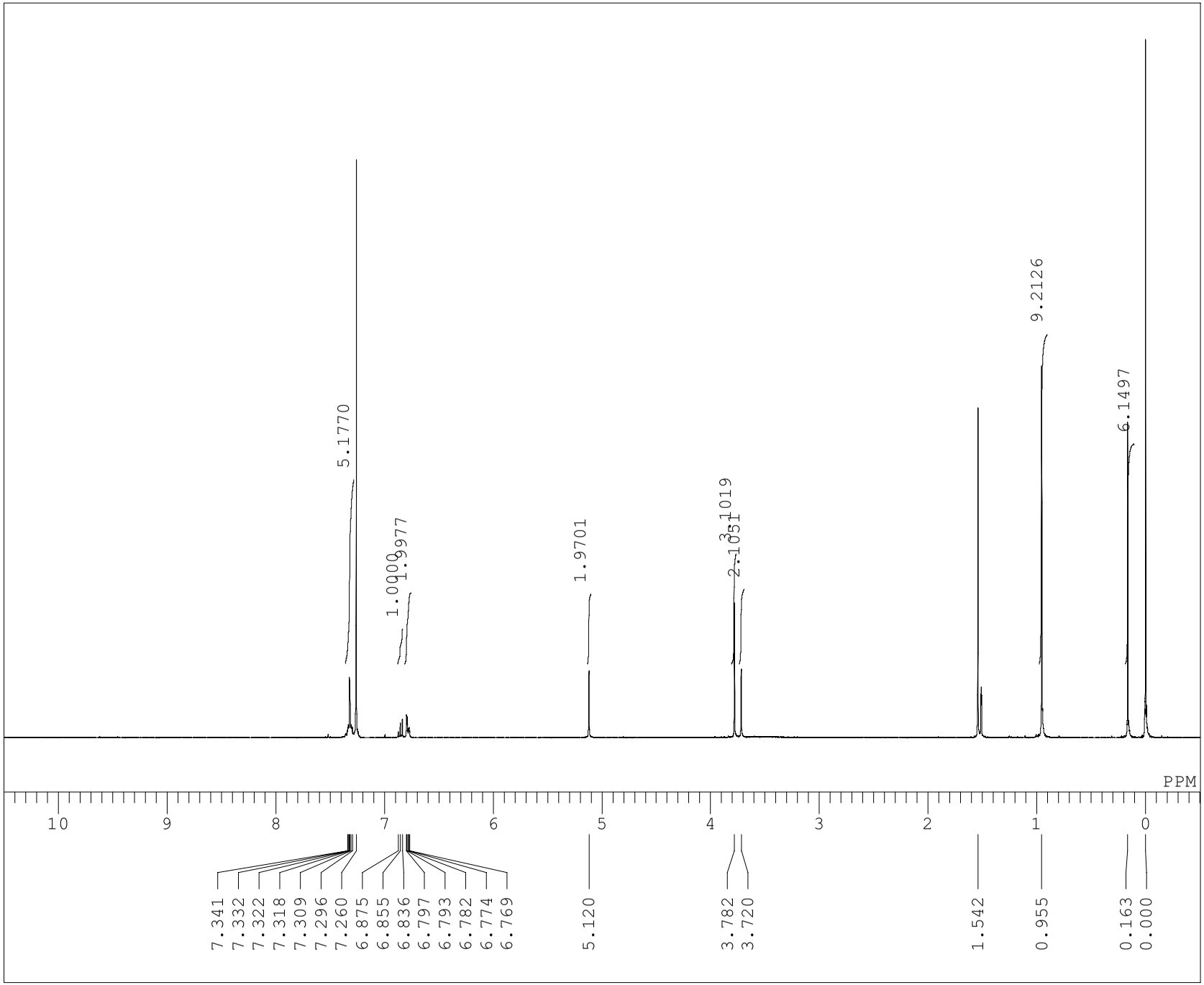
S-8e



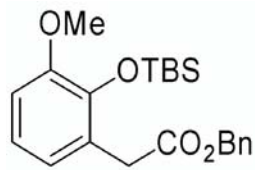
DFILE \\150.59.84.6\user\004BC
COMNT
DATIM Thu May 28 13:33:48 2009
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 740
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.5 us
IRNUC 1H
CTEMP 21.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 24



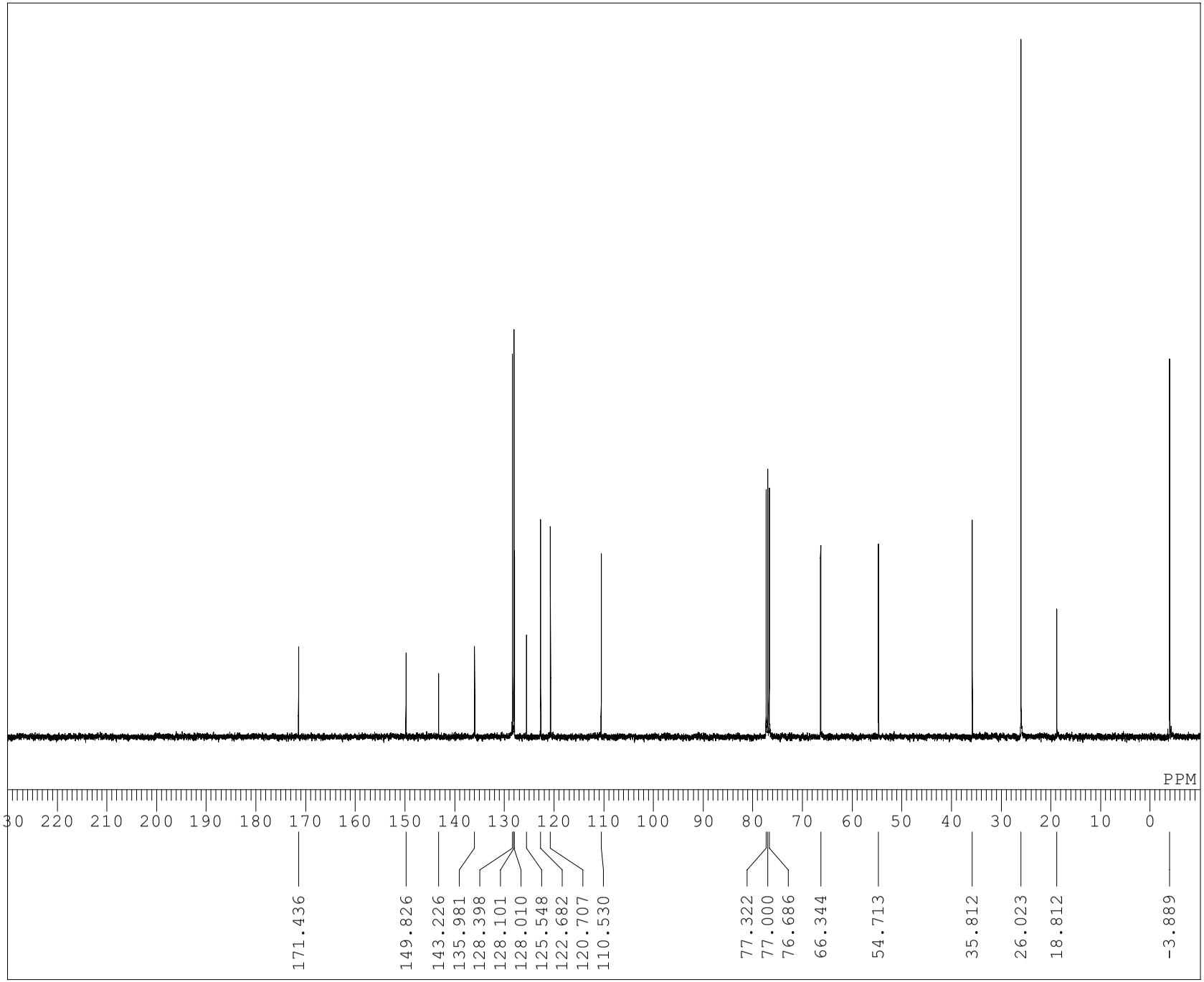
S-8e



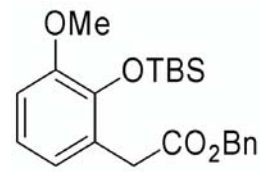

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Thu May 14 14:18:46 2009
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU        7992.0 Hz
SCANS            16
ACQTM         4.100 sec
PD            2.901 sec
PW1             6.3 us
IRNUC  1H
CTEMP          24.8 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            23
```



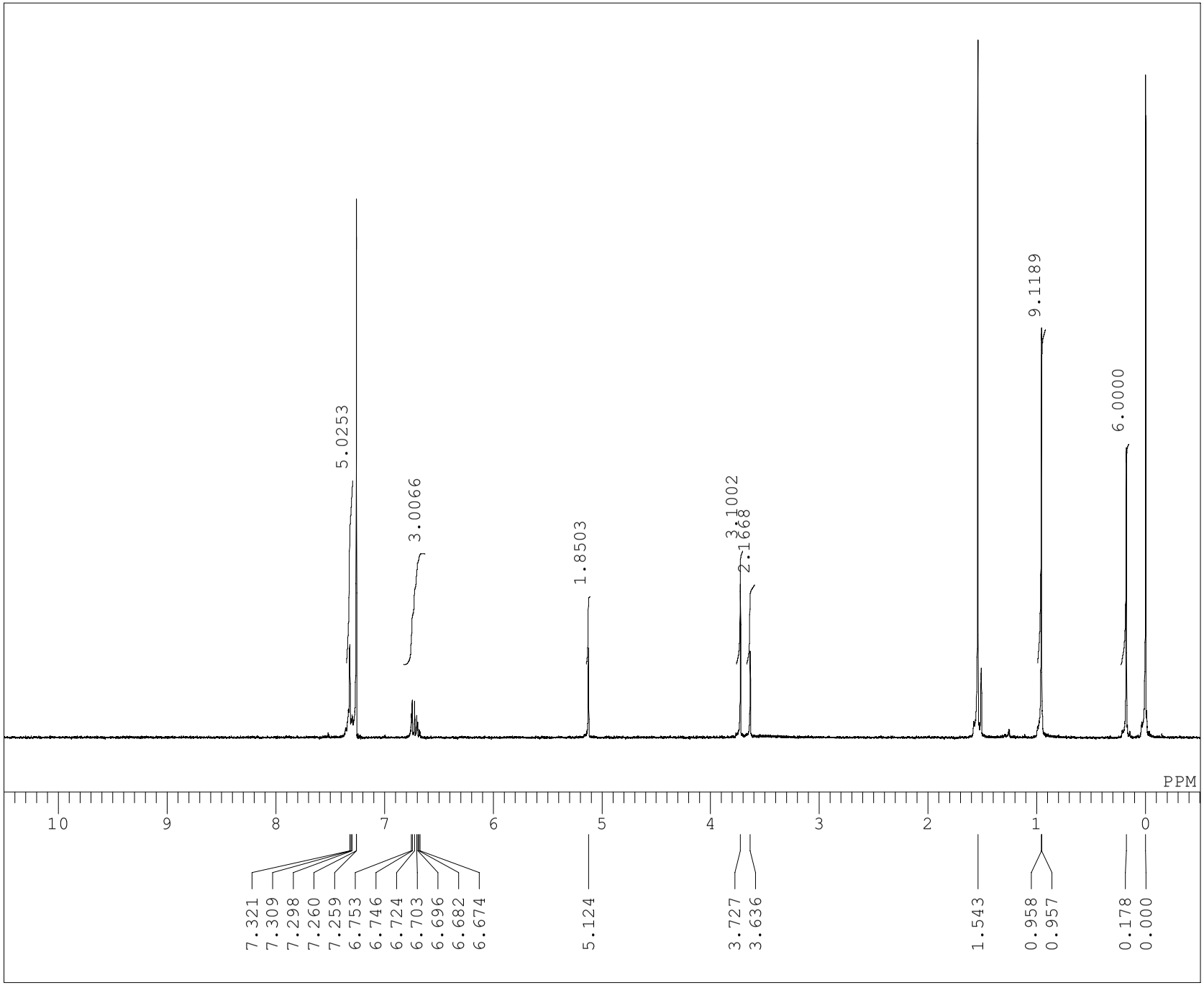
S-9c



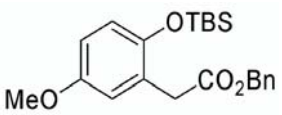

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Thu May 14 14:32:32 2009
OBNUC  13C
EXMOD  BCM
OBFRQ        100.40 MHz
OBSET        125.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU       27210.9 Hz
SCANS           212
ACQTM         1.204 sec
PD            1.794 sec
PW1             6.1 us
IRNUC  1H
CTEMP          26.0 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            23
```



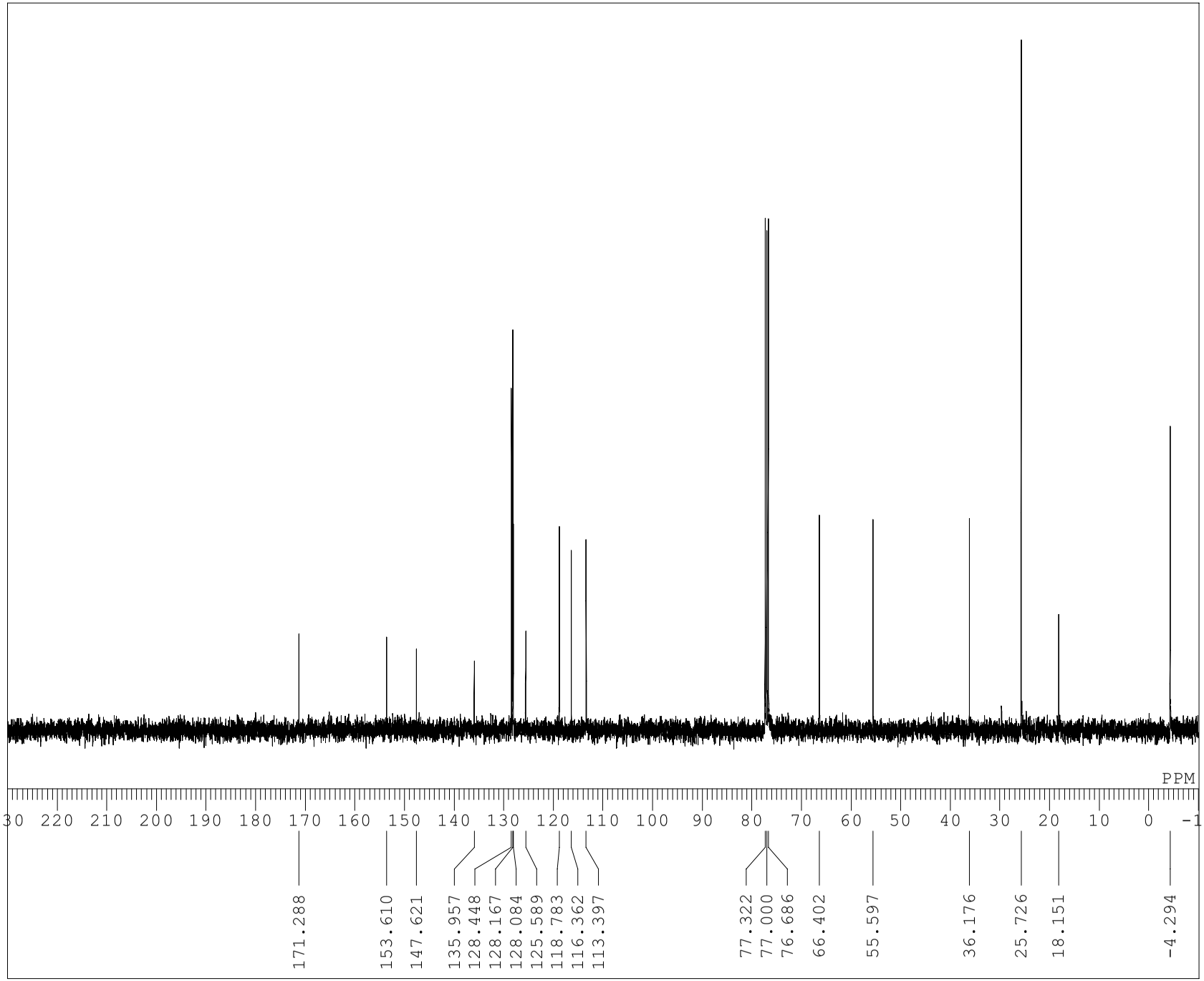
S-9c



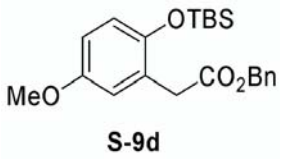

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Wed Jun 03 14:48:05 2009
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU        7992.0 Hz
SCANS              8
ACQTM         4.100 sec
PD            2.901 sec
PW1             6.3 us
IRNUC  1H
CTEMP          25.7 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            23
```



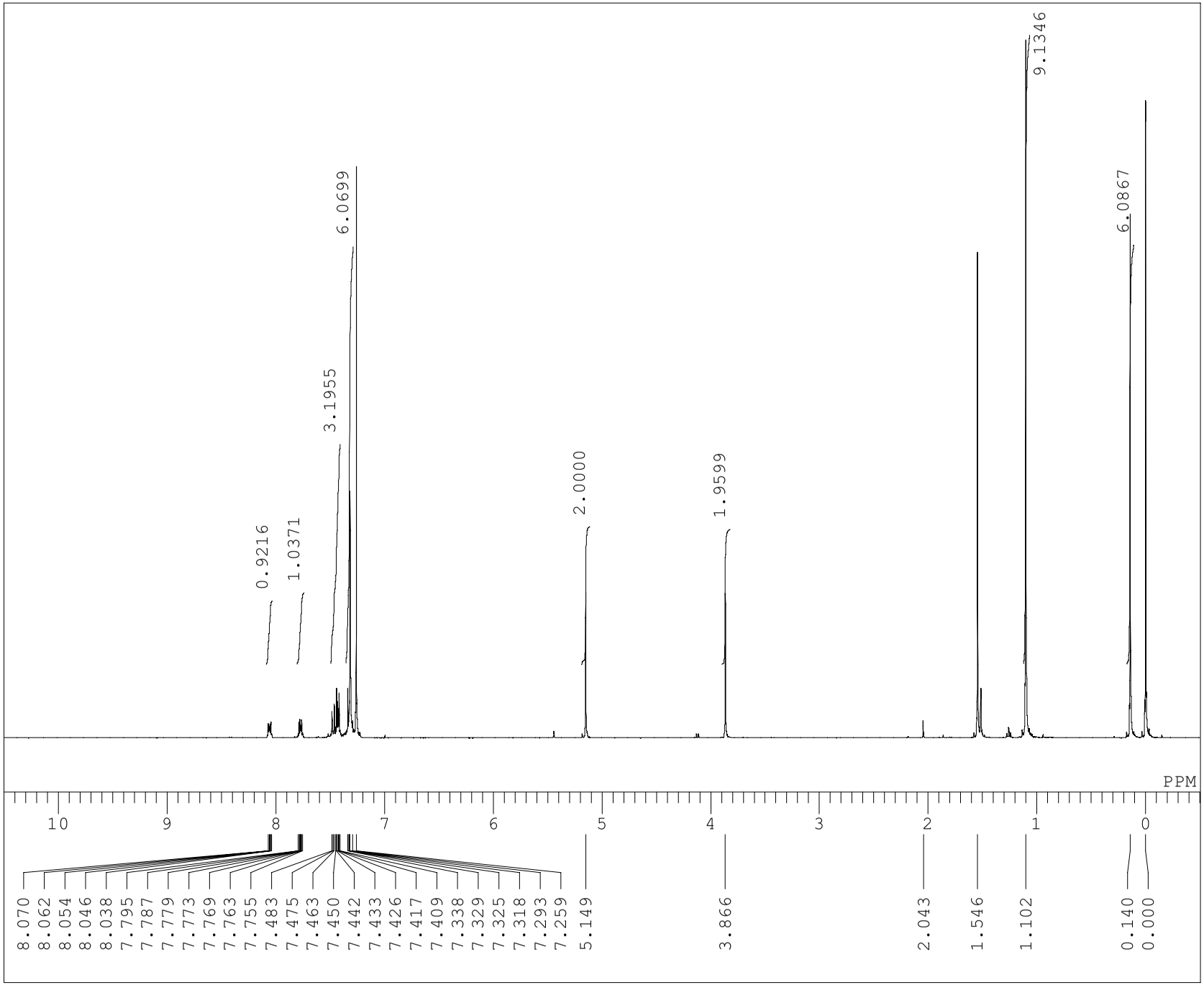
S-9d



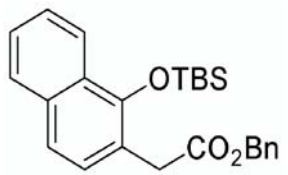

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Wed Jun 03 14:37:11 2009
OBNUC  13C
EXMOD  BCM
OBFRQ        100.40 MHz
OBSET        125.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU       27210.9 Hz
SCANS           100
ACQTM         1.204 sec
PD            1.794 sec
PW1             6.1 us
IRNUC  1H
CTEMP          26.9 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            23
```



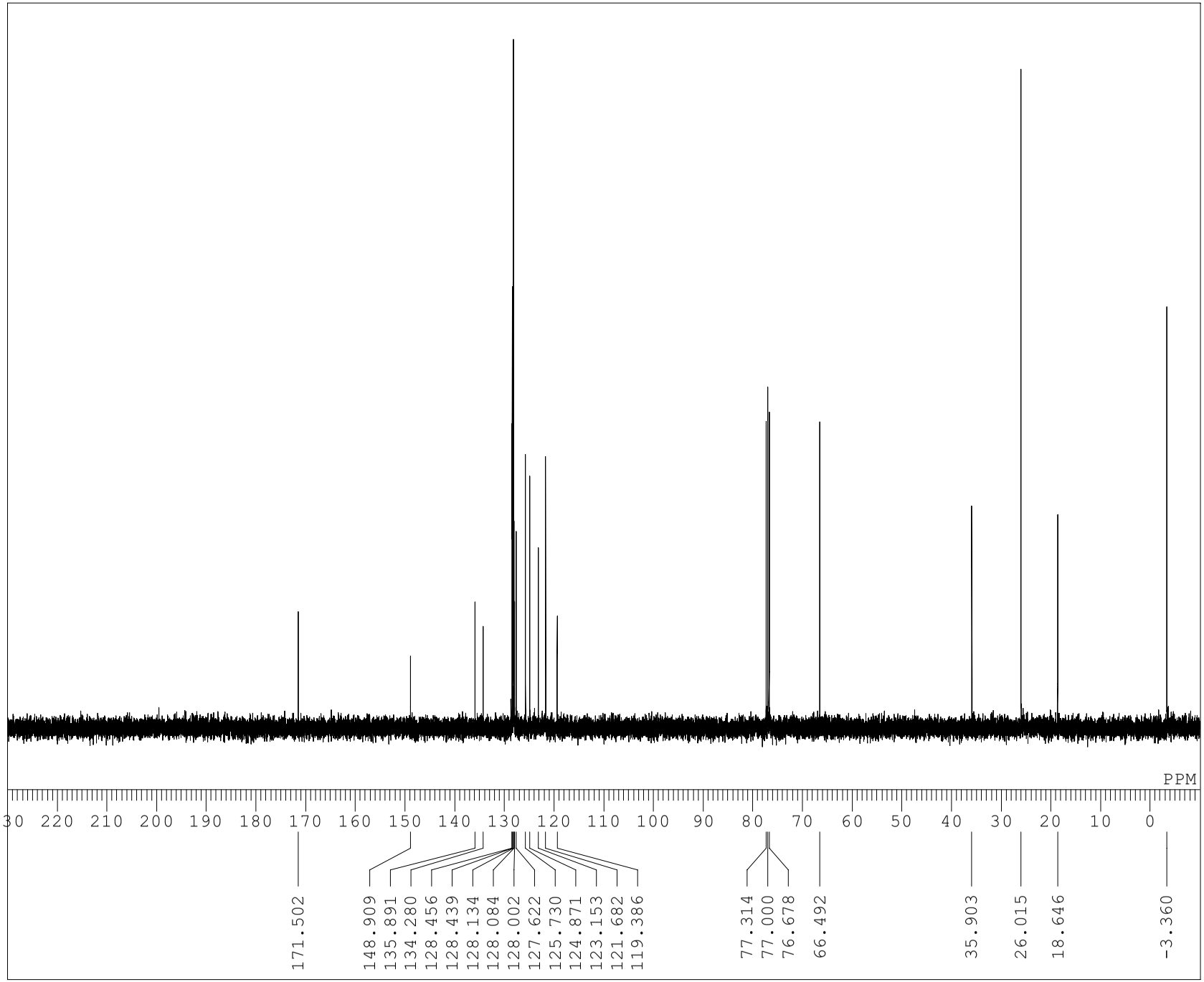
S-9d



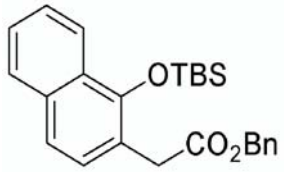

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Tue Jun 02 20:47:05 2009
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU        8000.0 Hz
SCANS              8
ACQTM          4.096 sec
PD             2.904 sec
PW1              5.7 us
IRNUC  1H
CTEMP           23.9 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             23
```



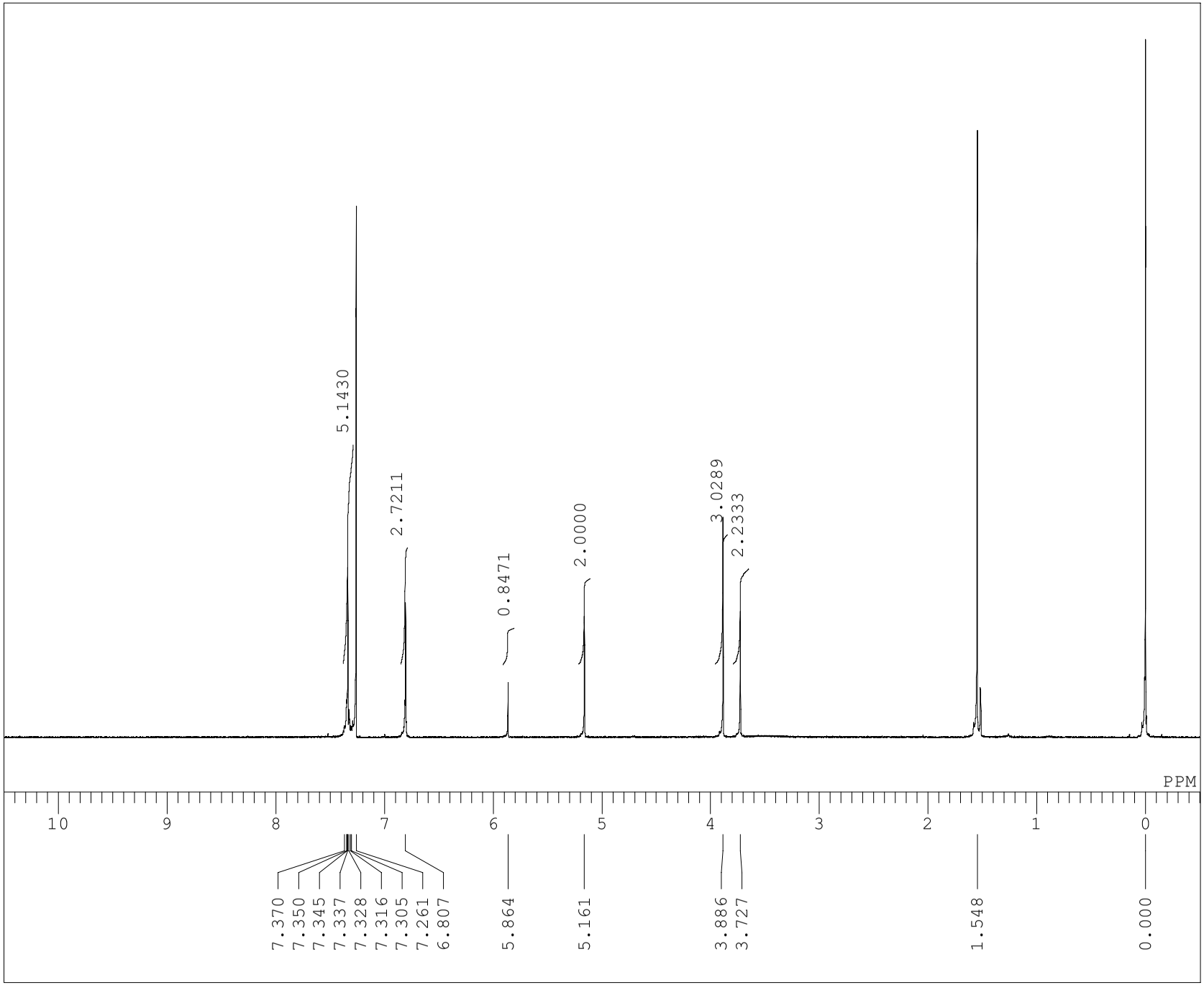
S-9e



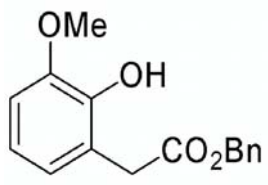

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Wed Jun 03 09:20:31 2009
OBNUC  13C
EXMOD  BCM
OBFRQ        100.40 MHz
OBSET        125.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU       27210.9 Hz
SCANS           112
ACQTM         1.204 sec
PD            1.794 sec
PW1             6.1 us
IRNUC  1H
CTEMP          25.9 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            23
```



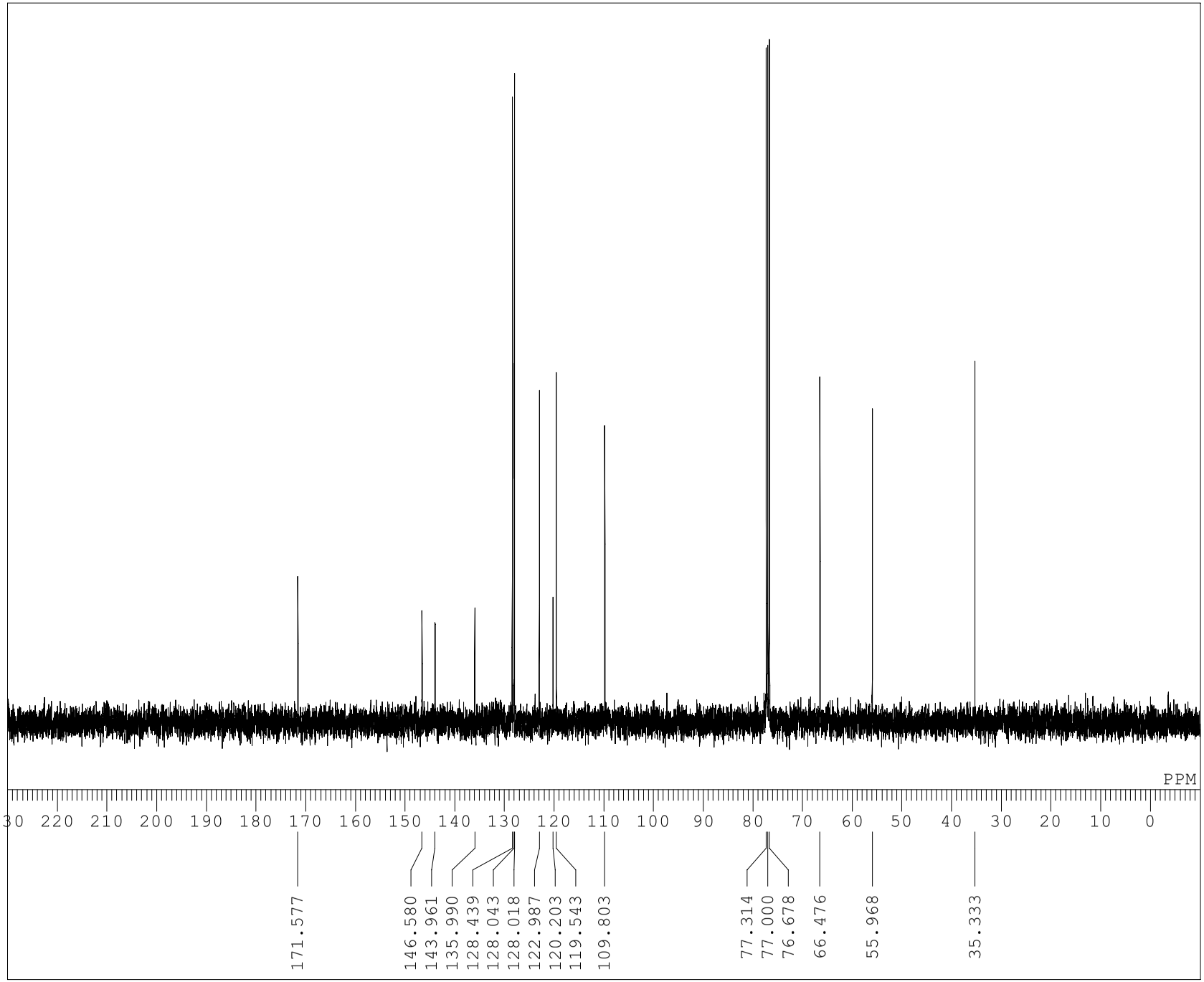
S-9e



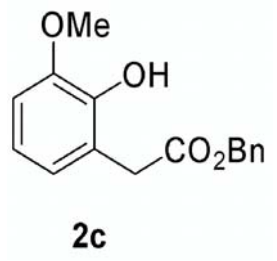

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Mon May 25 15:06:01 2009
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU        7992.0 Hz
SCANS            32
ACQTM         4.100 sec
PD            2.901 sec
PW1             6.3 us
IRNUC  1H
CTEMP          24.4 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            24
```



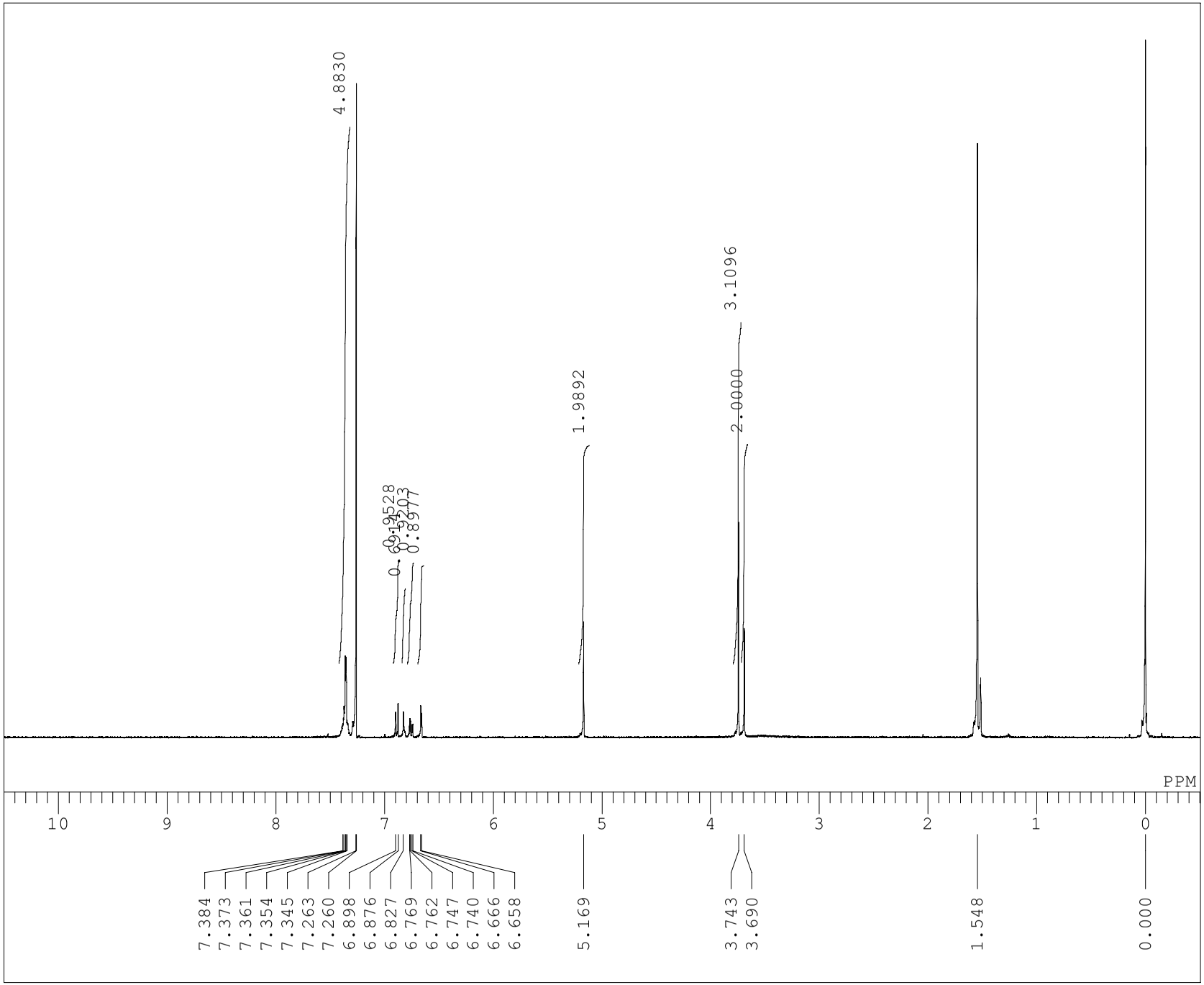
2c



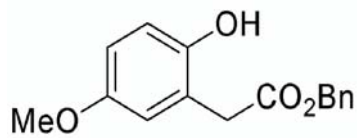

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Mon May 25 16:38:06 2009
OBNUC  13C
EXMOD  BCM
OBFRQ       100.40 MHz
OBSET       125.00 KHz
OBFIN      10500.0 Hz
POINT        32768
FREQU      27210.9 Hz
SCANS          109
ACQTM        1.204 sec
PD           1.794 sec
PW1            6.1 us
IRNUC  1H
CTEMP         26.0 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            25
```



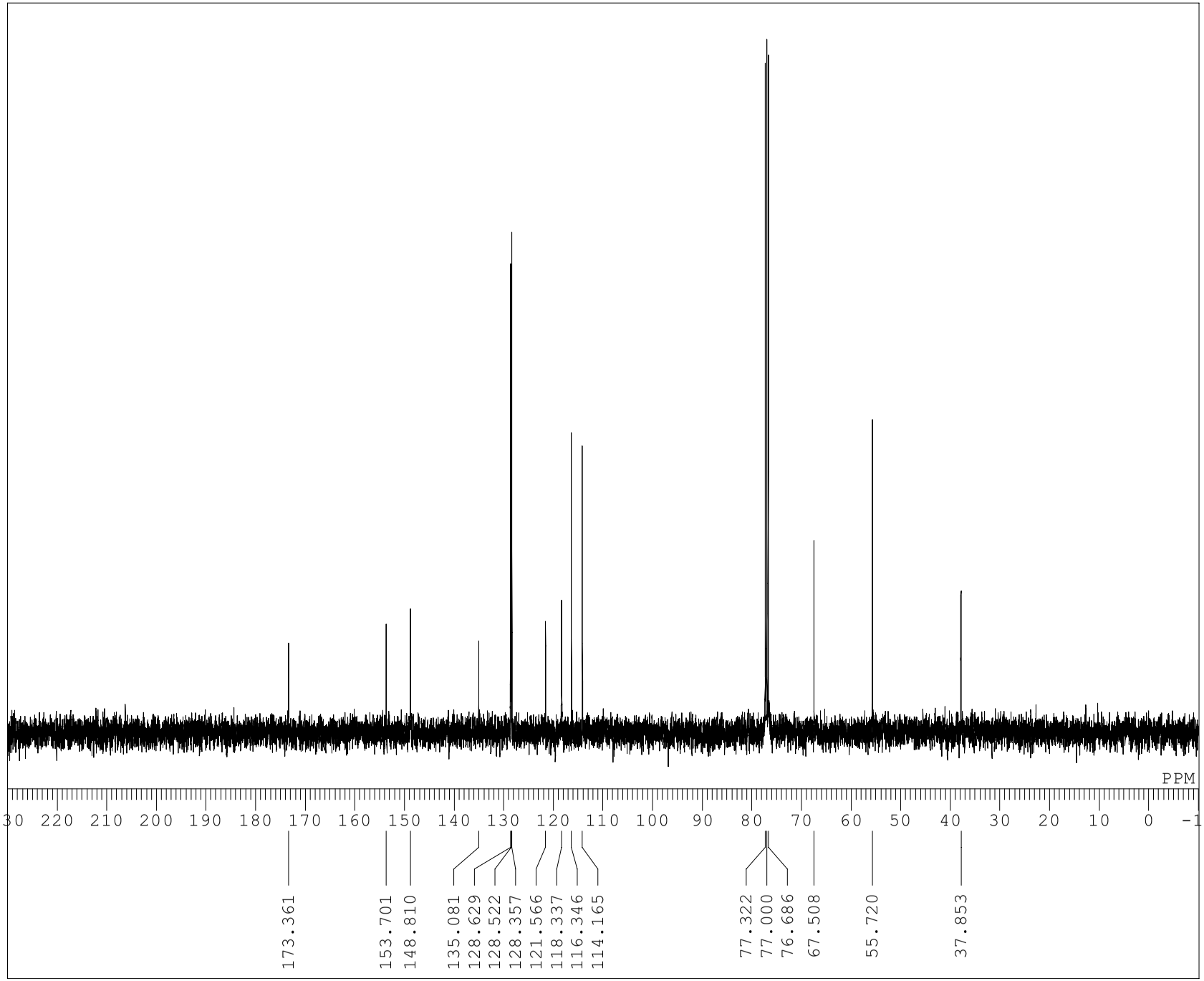
2c



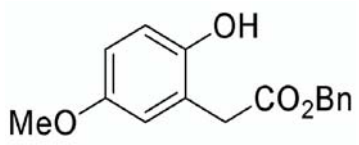
DFILE \\150.59.84.6\user\004BC
COMNT
DATIM Mon May 25 15:15:14 2009
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 7992.0 Hz
SCANS 28
ACQTM 4.100 sec
PD 2.901 sec
PW1 6.3 us
IRNUC 1H
CTEMP 24.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 24



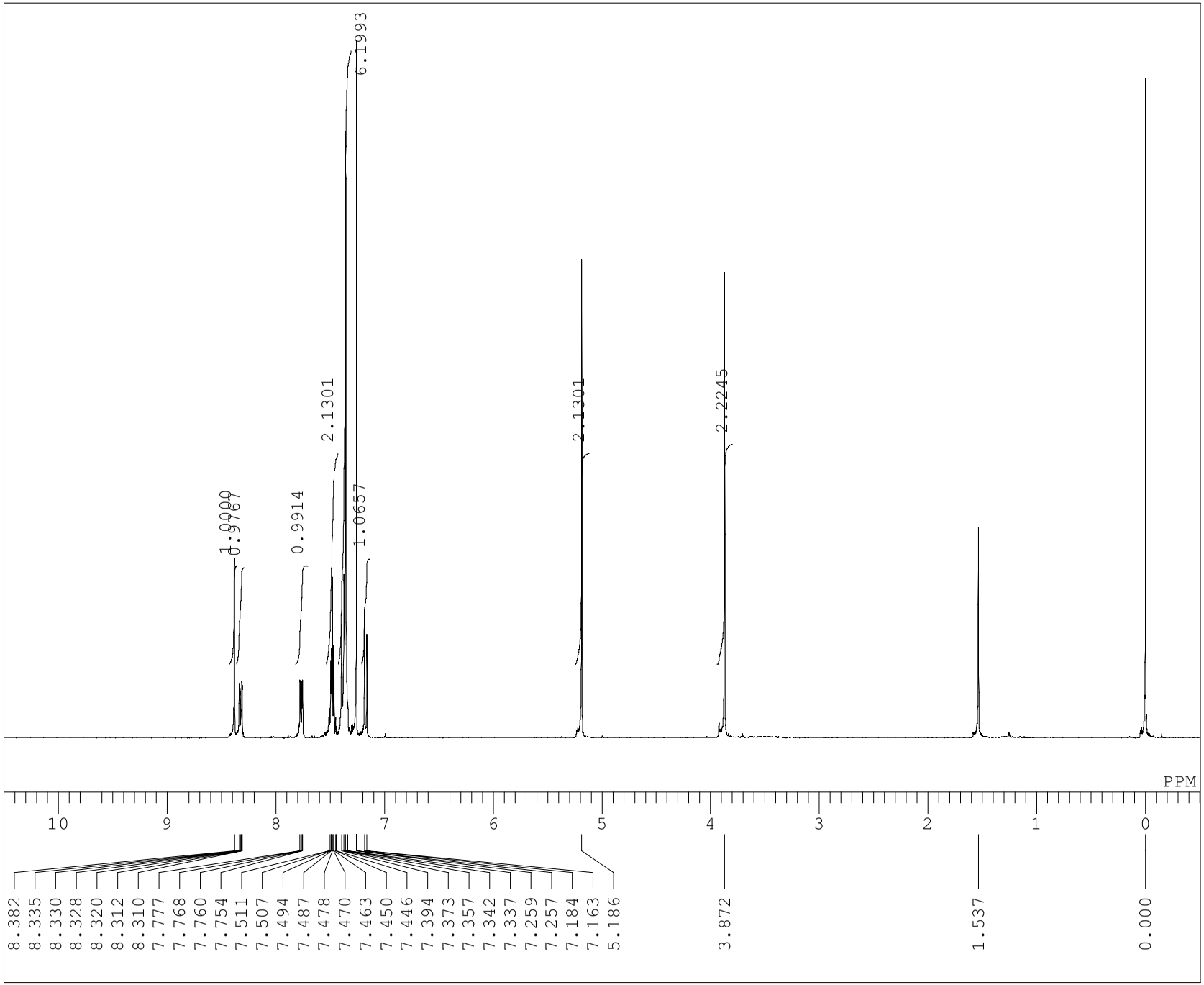
2d



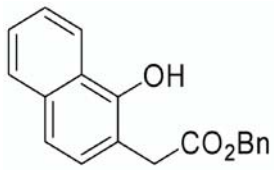

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Mon May 25 17:38:21 2009
OBNUC  13C
EXMOD  BCM
OBFRQ       100.40 MHz
OBSET       125.00 KHz
OBFIN      10500.0 Hz
POINT        32768
FREQU      27210.9 Hz
SCANS           77
ACQTM         1.204 sec
PD            1.794 sec
PW1             6.1 us
IRNUC  1H
CTEMP          25.9 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            24
```



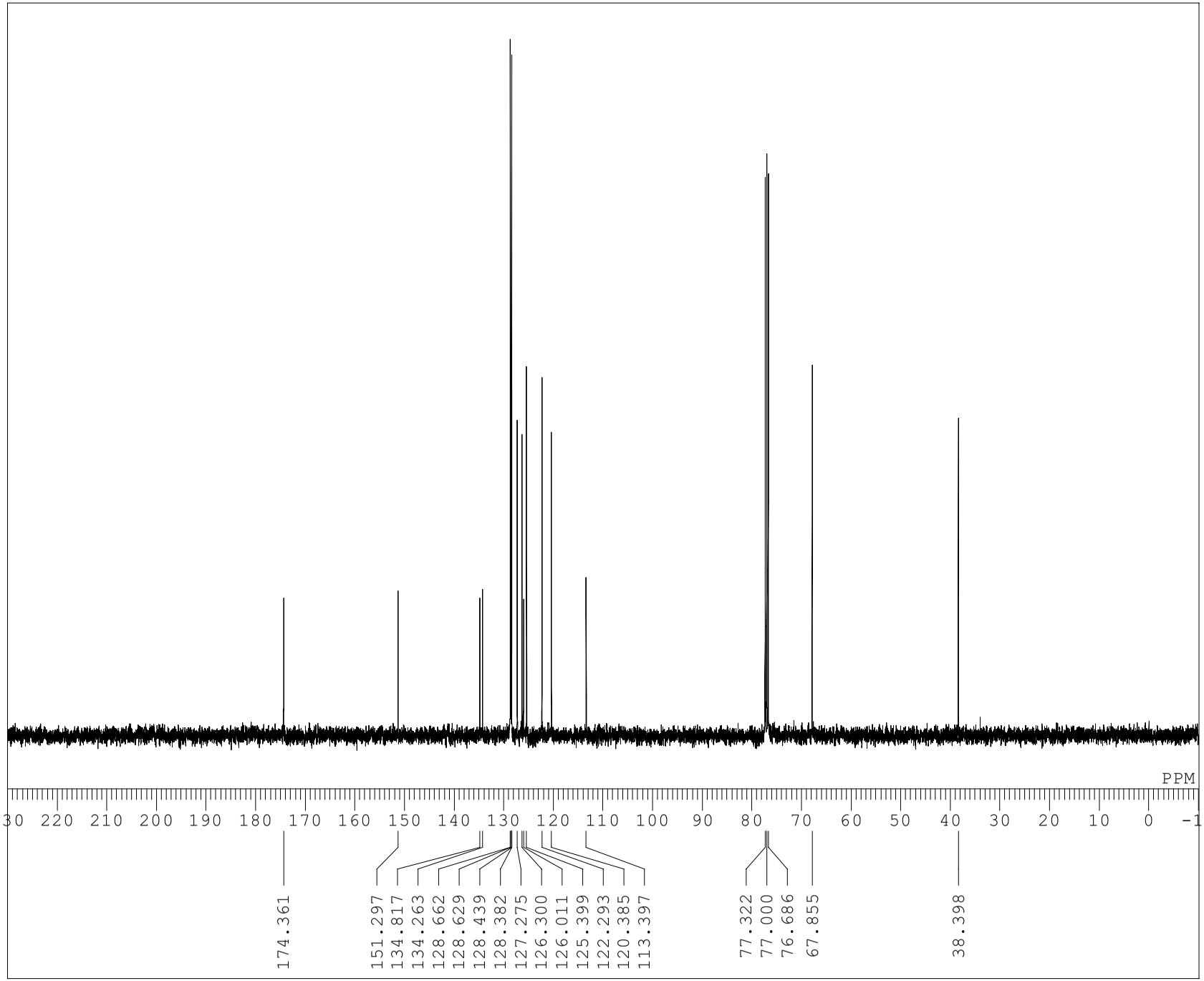
2d



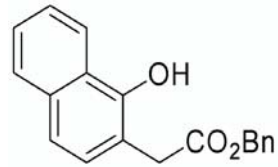

```
DFILE  \\150.59.248.165\data\NM
COMNT
DATIM  Wed Apr 22 15:20:51 2009
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU        7992.0 Hz
SCANS              4
ACQTM          4.100 sec
PD             2.901 sec
PW1              6.3 us
IRNUC  1H
CTEMP           25.5 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             21
```



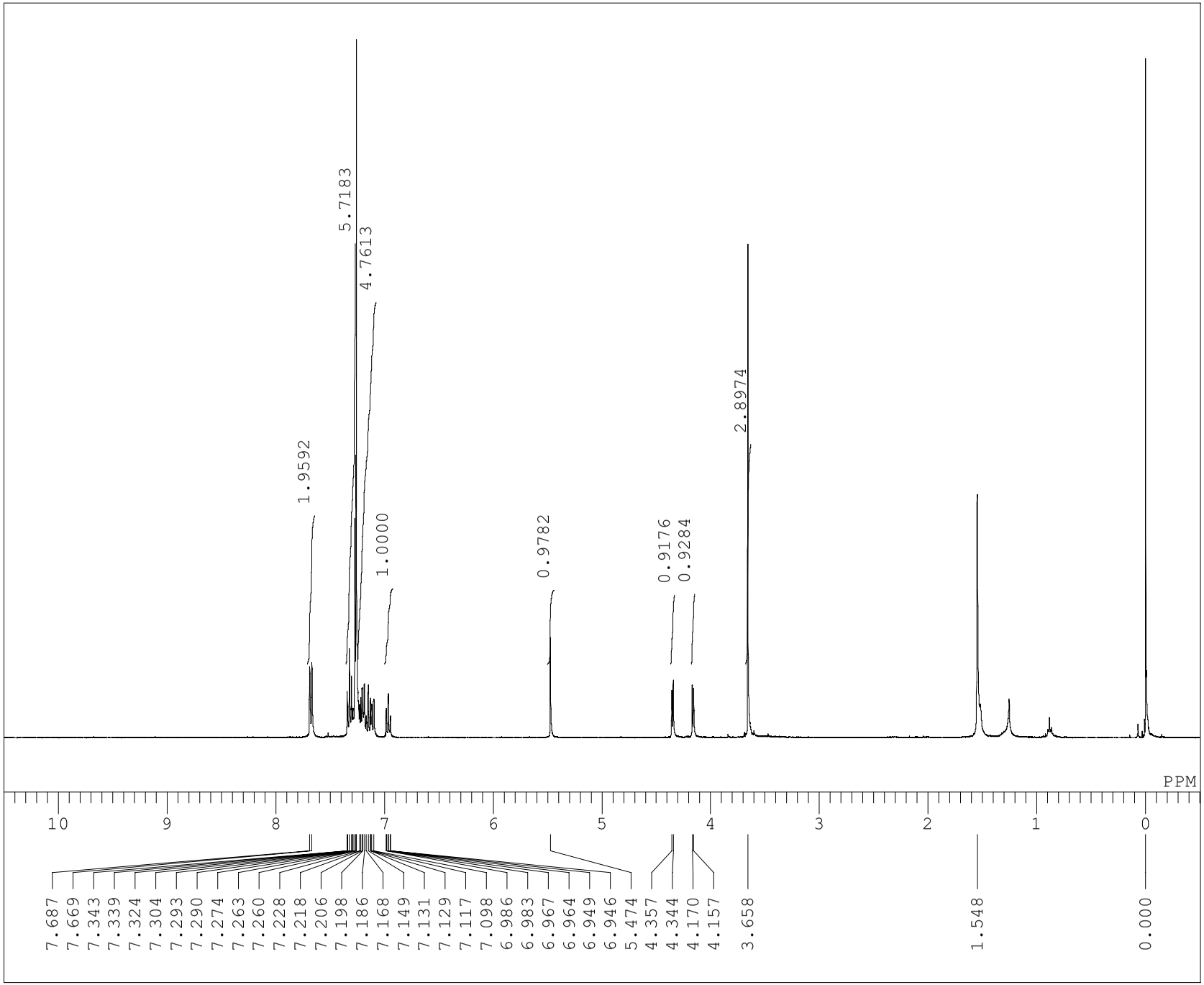
2e



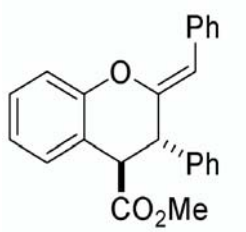

```
DFILE  \\150.59.248.165\data\NM
COMNT
DATIM  Wed Apr 22 15:49:04 2009
OBNUC  13C
EXMOD  BCM
OBFRQ       100.40 MHz
OBSET       125.00 KHz
OBFIN      10500.0 Hz
POINT        32768
FREQU      27210.9 Hz
SCANS          160
ACQTM        1.204 sec
PD           1.794 sec
PW1            6.1 us
IRNUC  1H
CTEMP         26.3 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            23
```



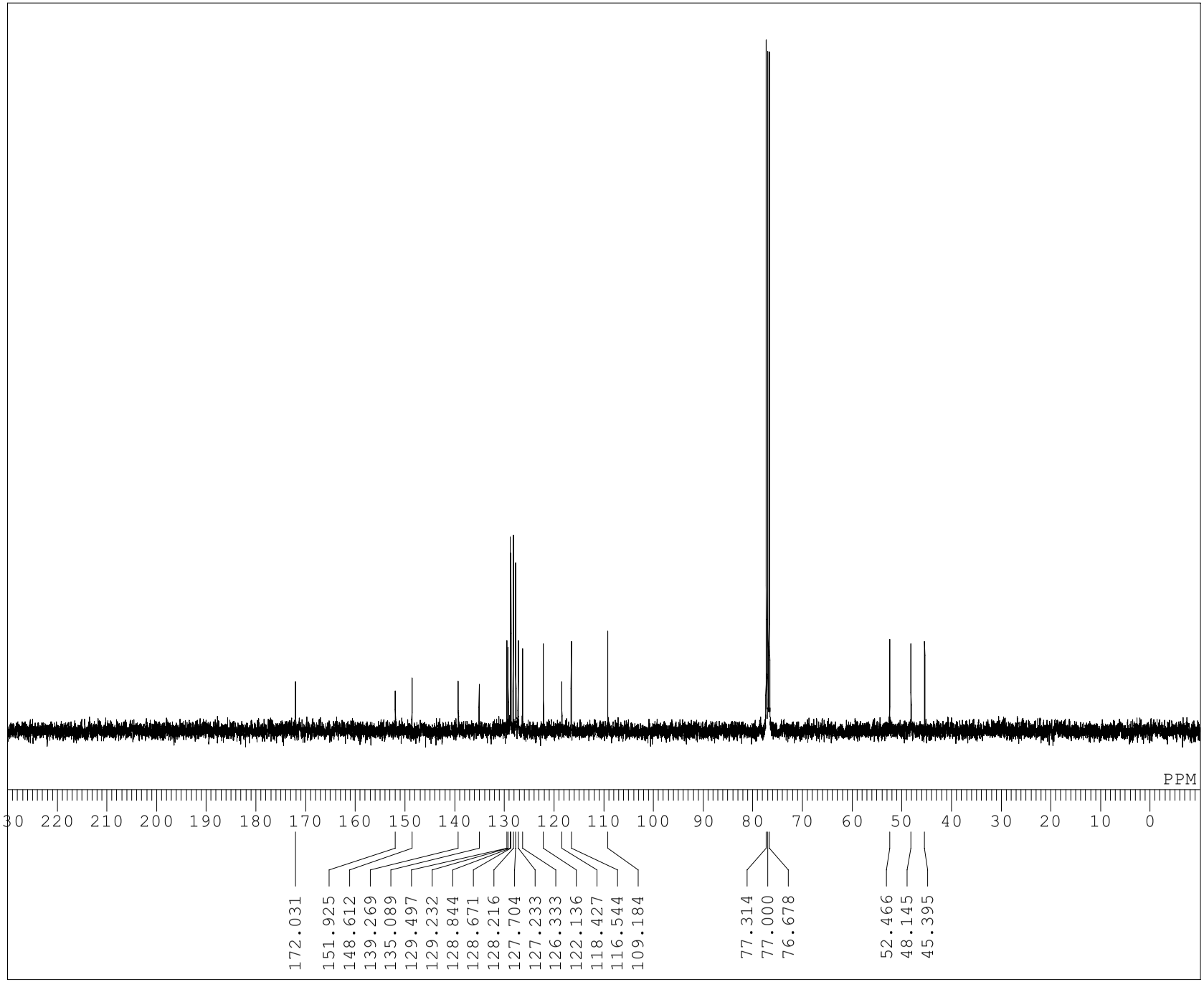
2e



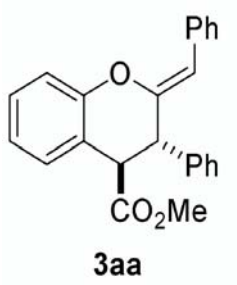
DFILE \\150.59.84.6\user\004BC
COMNT
DATIM Wed Jun 24 11:02:14 2009
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 7992.0 Hz
SCANS 32
ACQTM 4.100 sec
PD 2.901 sec
PW1 6.3 us
IRNUC 1H
CTEMP 24.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 21



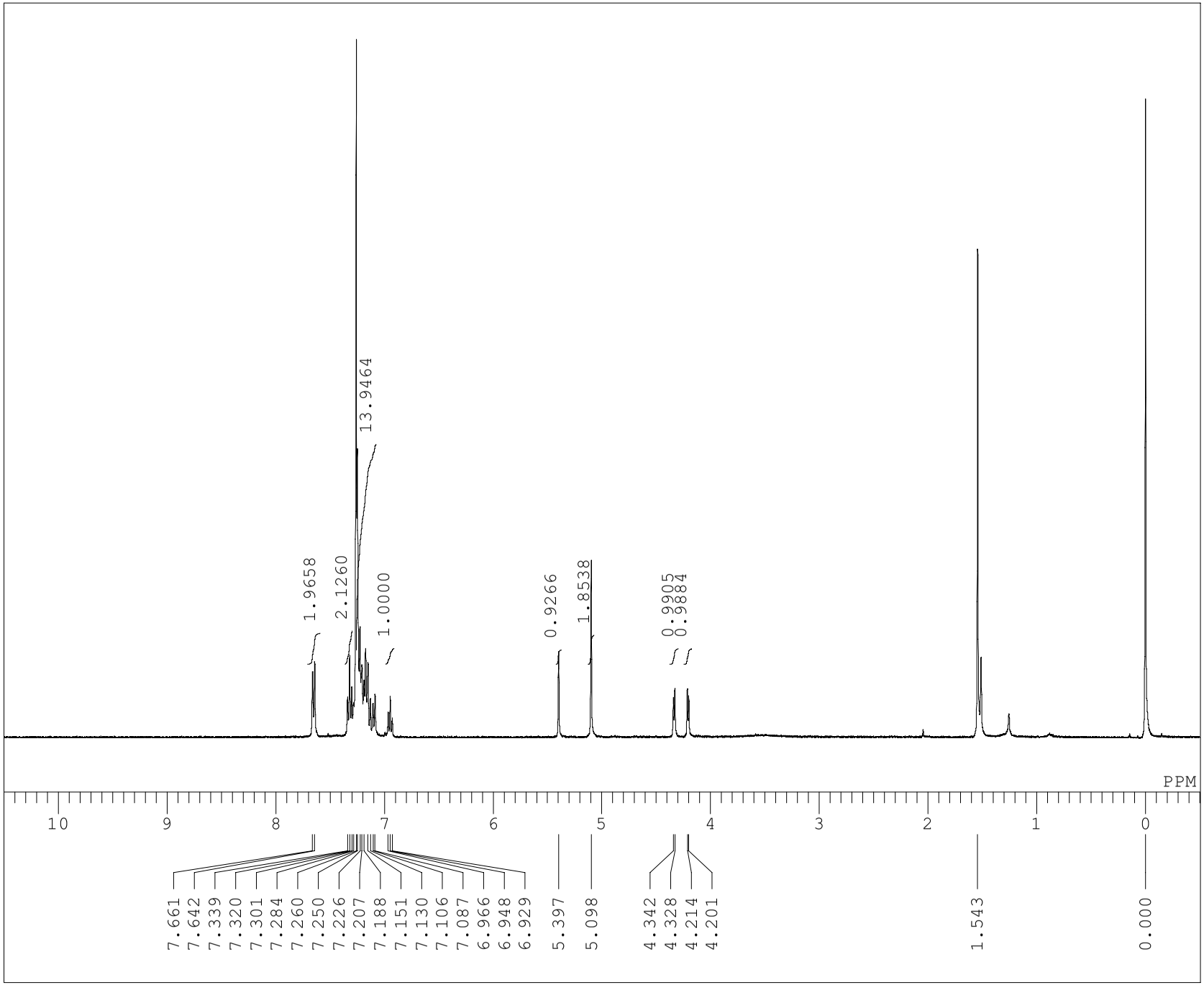
3aa



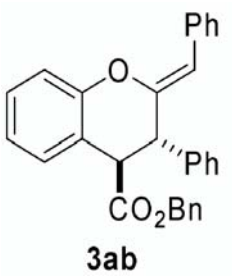

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Wed Jun 24 11:40:15 2009
OBNUC  13C
EXMOD  BCM
OBFRQ        100.40 MHz
OBSET        125.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU       27210.9 Hz
SCANS           300
ACQTM         1.204 sec
PD            1.794 sec
PW1             6.1 us
IRNUC  1H
CTEMP          26.0 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            23
```



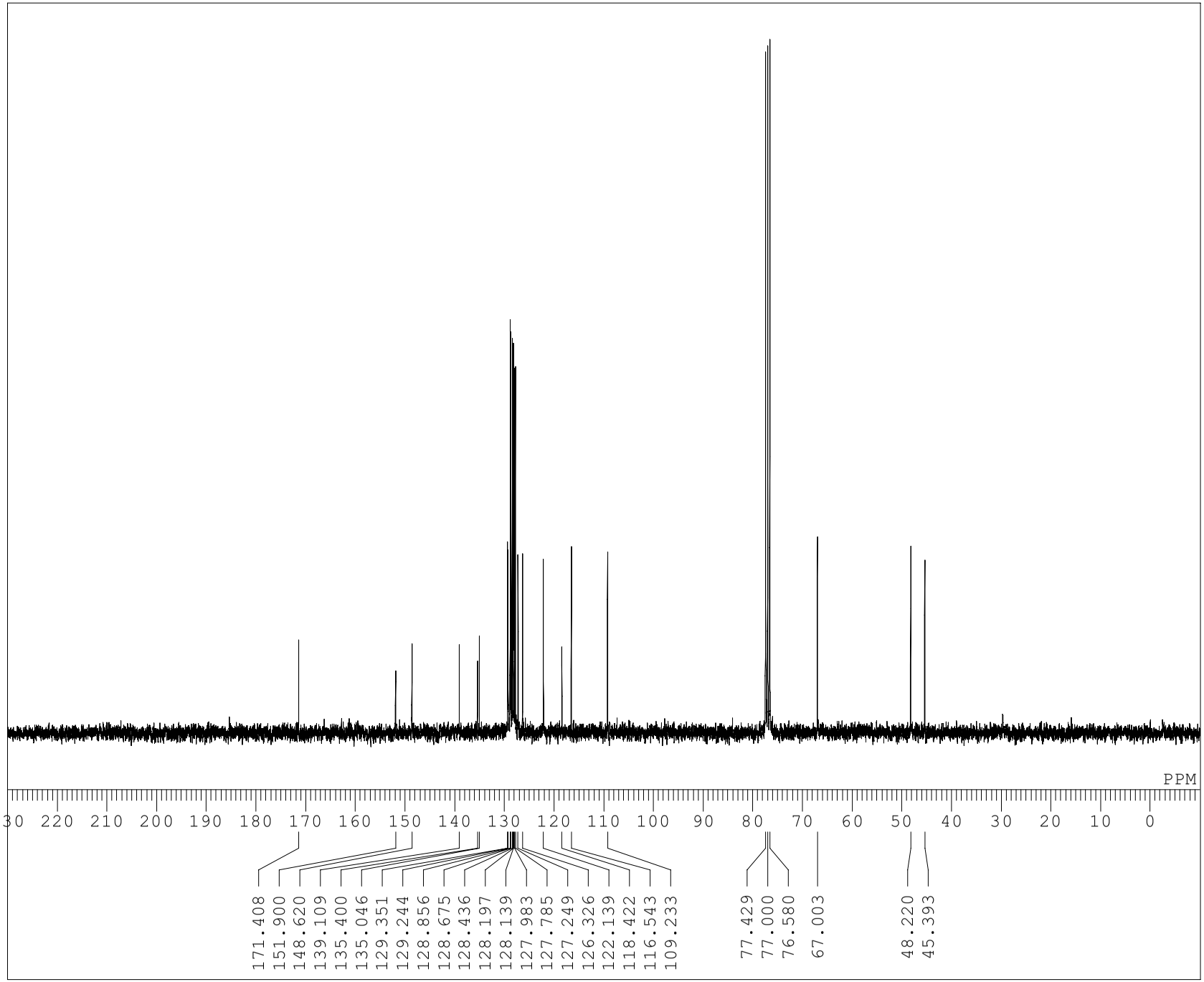
3aa



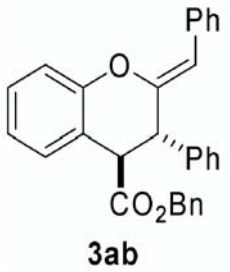

```
DFILE  \\150.59.84.6\user\004BC
COMNT  benzyl product 400MHz CD
DATIM  Fri Jun 12 16:31:11 2009
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU        7992.0 Hz
SCANS            32
ACQTM         4.100 sec
PD            2.901 sec
PW1             6.3 us
IRNUC  1H
CTEMP          24.8 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            22
```



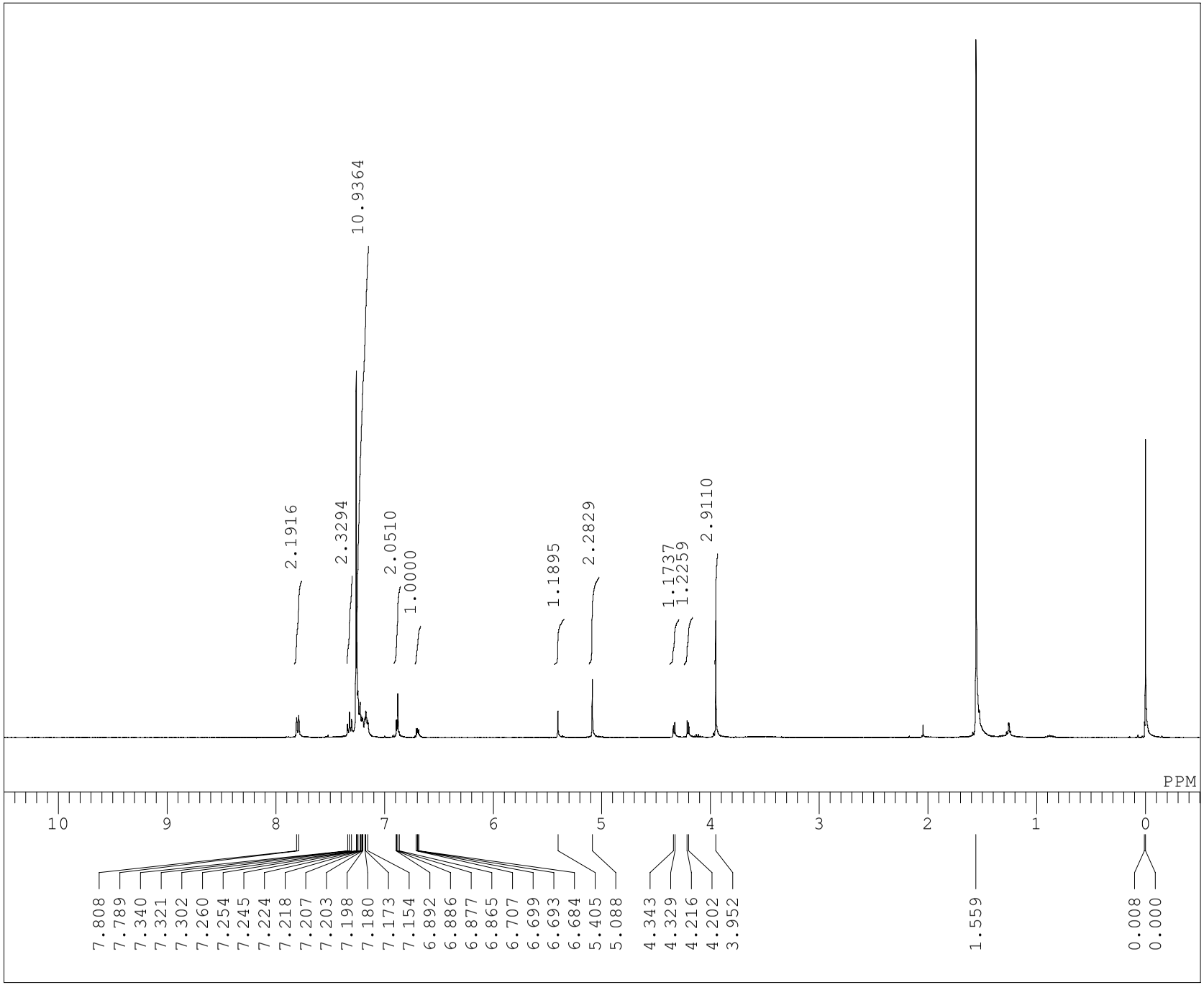
3ab



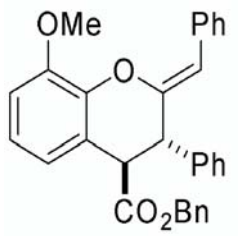

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Fri Jun 12 18:01:03 2009
OBNUC  13C
EXMOD  BCM
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN       1840.0 Hz
POINT         32768
FREQU      20408.1 Hz
SCANS           884
ACQTM         1.606 sec
PD            1.394 sec
PW1             4.5 us
IRNUC  1H
CTEMP          21.0 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            24
```



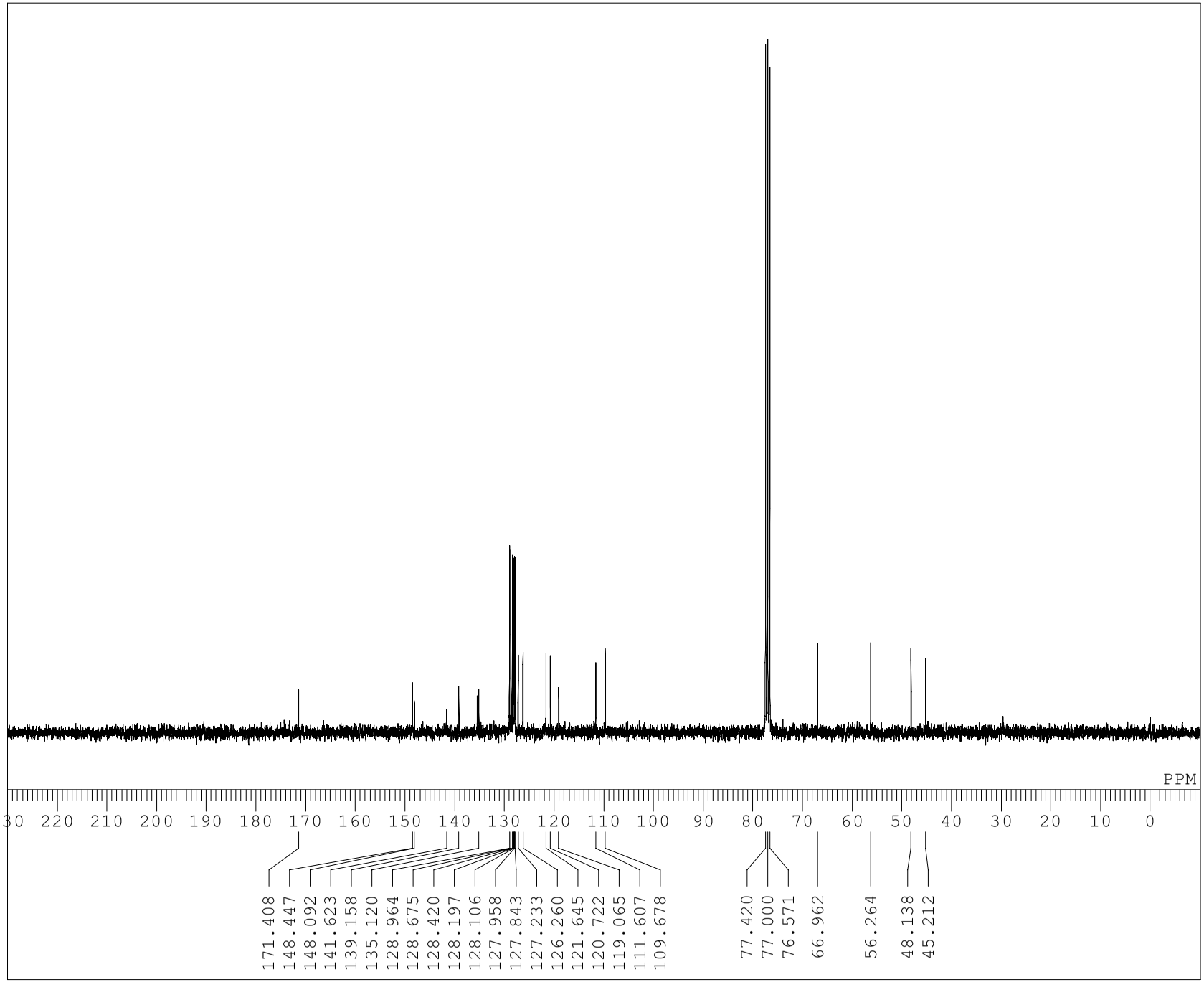
3ab



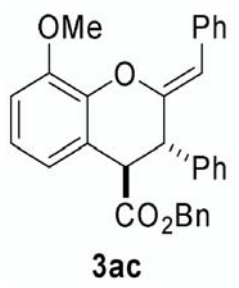
DFILE \\150.59.84.6\user\004BC
COMNT
DATIM Tue Jun 30 17:36:56 2009
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 7992.0 Hz
SCANS 64
ACQTM 4.100 sec
PD 2.901 sec
PW1 6.3 us
IRNUC 1H
CTEMP 24.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 22



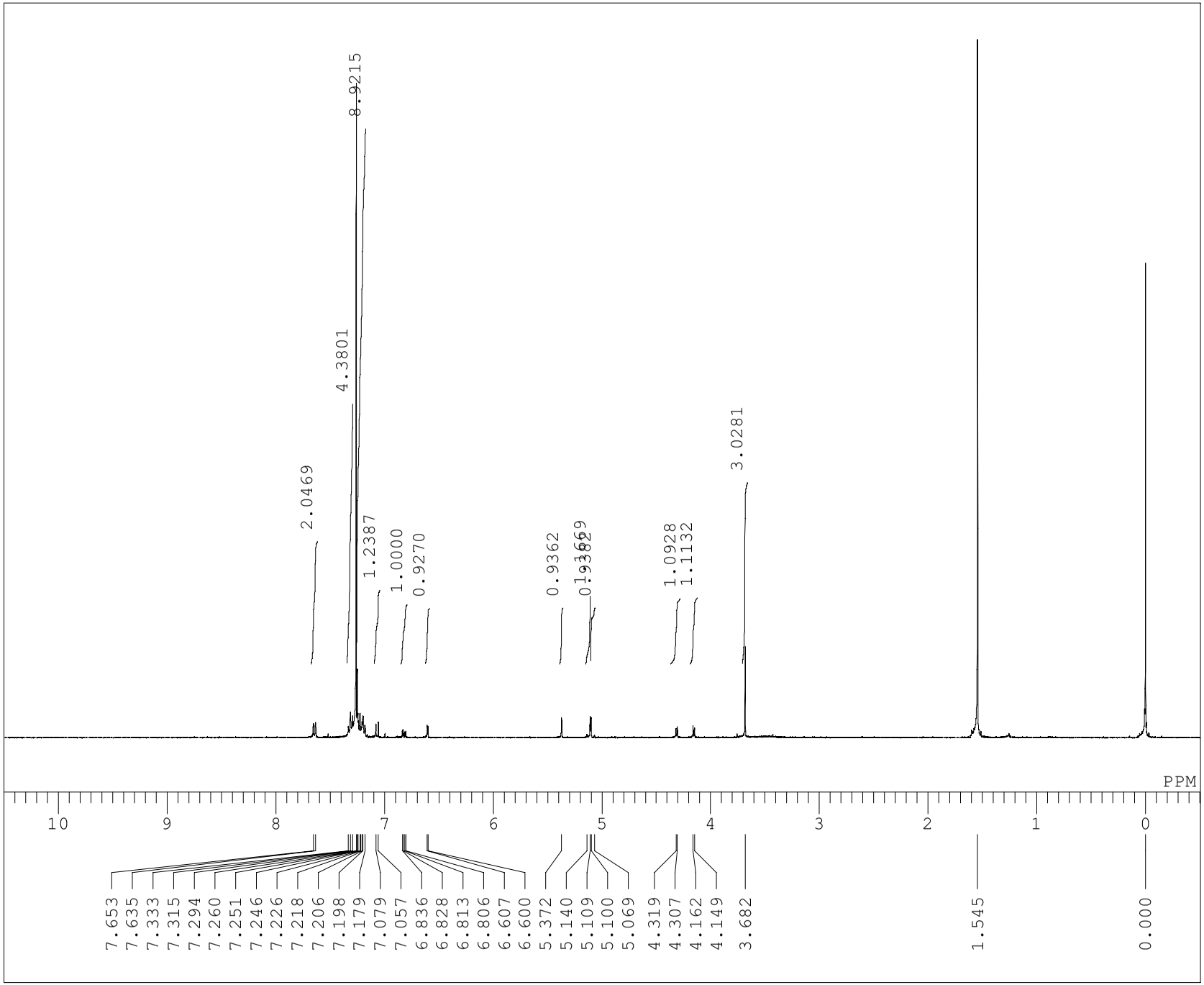
3ac



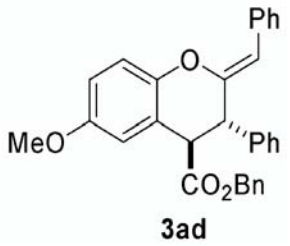

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Tue Jun 30 19:45:28 2009
OBNUC  13C
EXMOD  BCM
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN       1840.0 Hz
POINT         32768
FREQU      20408.1 Hz
SCANS          1000
ACQTM        1.606 sec
PD           1.394 sec
PW1            4.5 us
IRNUC  1H
CTEMP         21.8 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            24
```



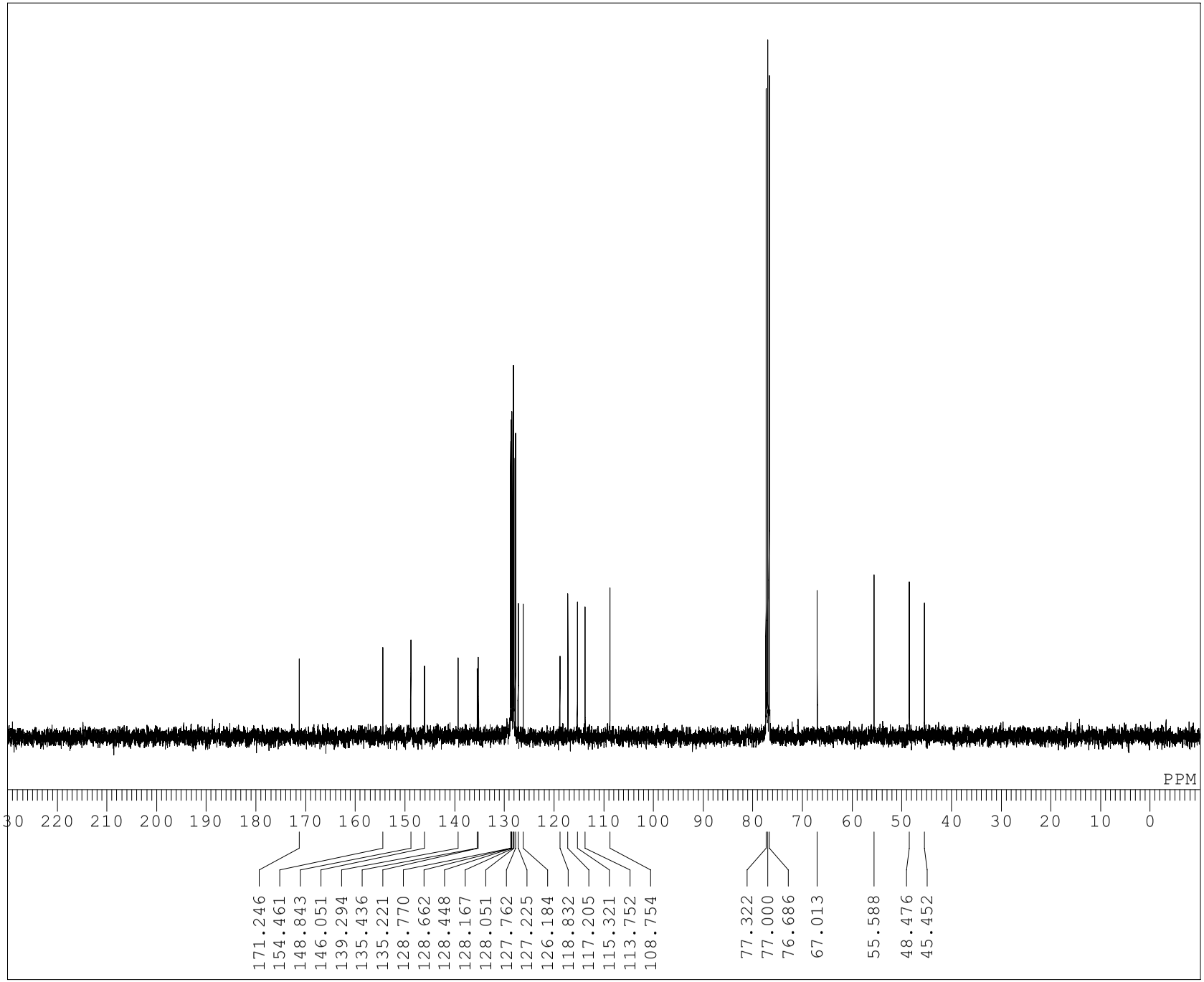
3ac



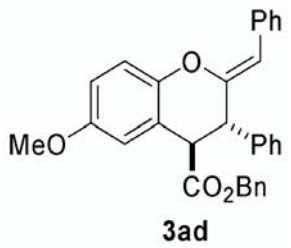
DFILE \\150.59.84.6\user\004BC
COMNT
DATIM Sat Apr 18 10:00:50 2009
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 7992.0 Hz
SCANS 12
ACQTM 4.100 sec
PD 2.901 sec
PW1 6.3 us
IRNUC 1H
CTEMP 25.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 23



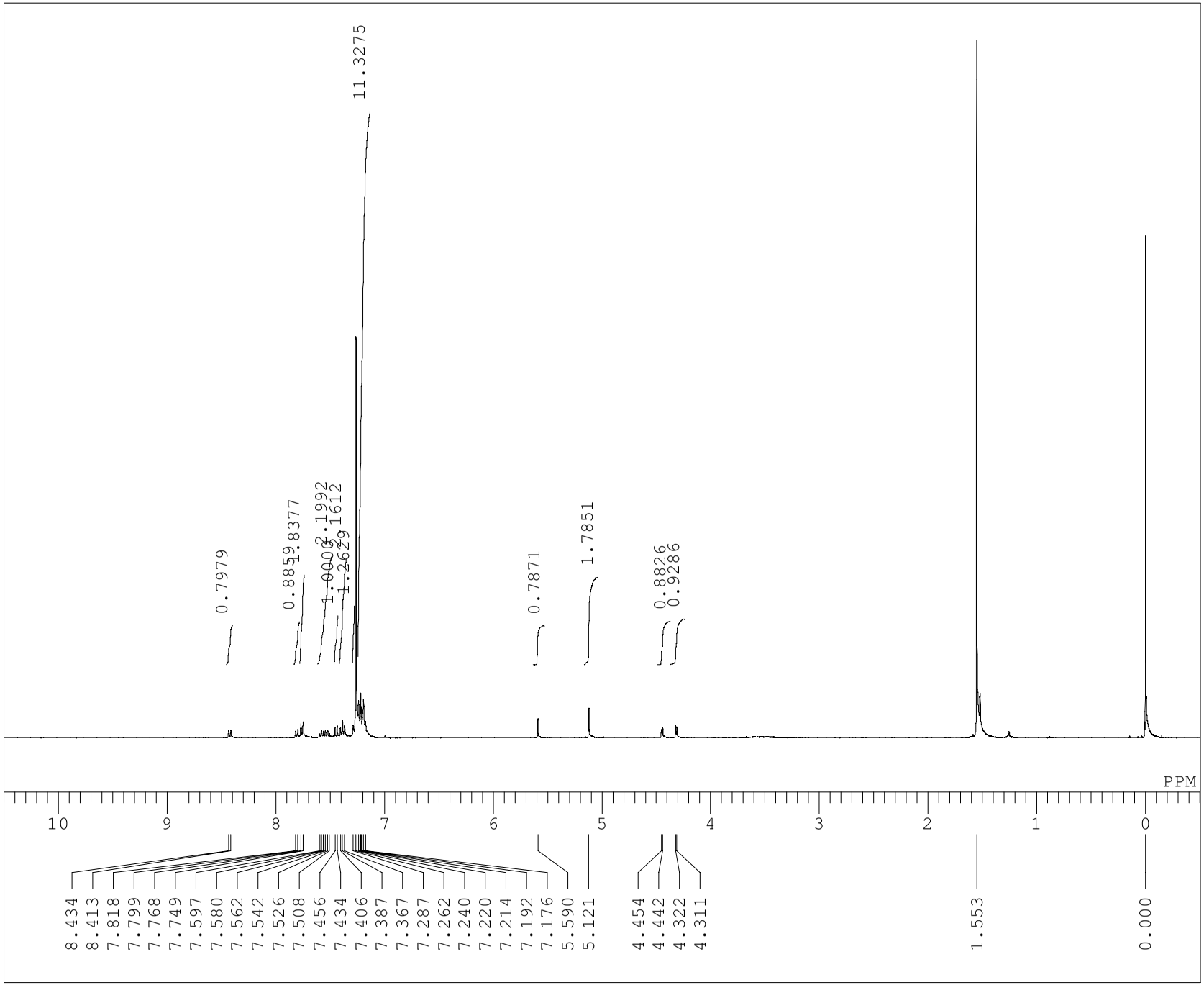
3ad



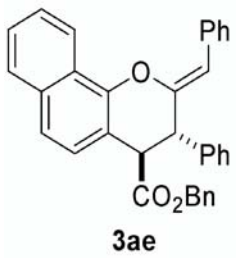

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Sat Apr 18 10:17:33 2009
OBNUC  13C
EXMOD  BCM
OBFRQ        100.40 MHz
OBSET        125.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU       27210.9 Hz
SCANS           256
ACQTM         1.204 sec
PD            1.794 sec
PW1             6.1 us
IRNUC  1H
CTEMP          26.5 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            24
```



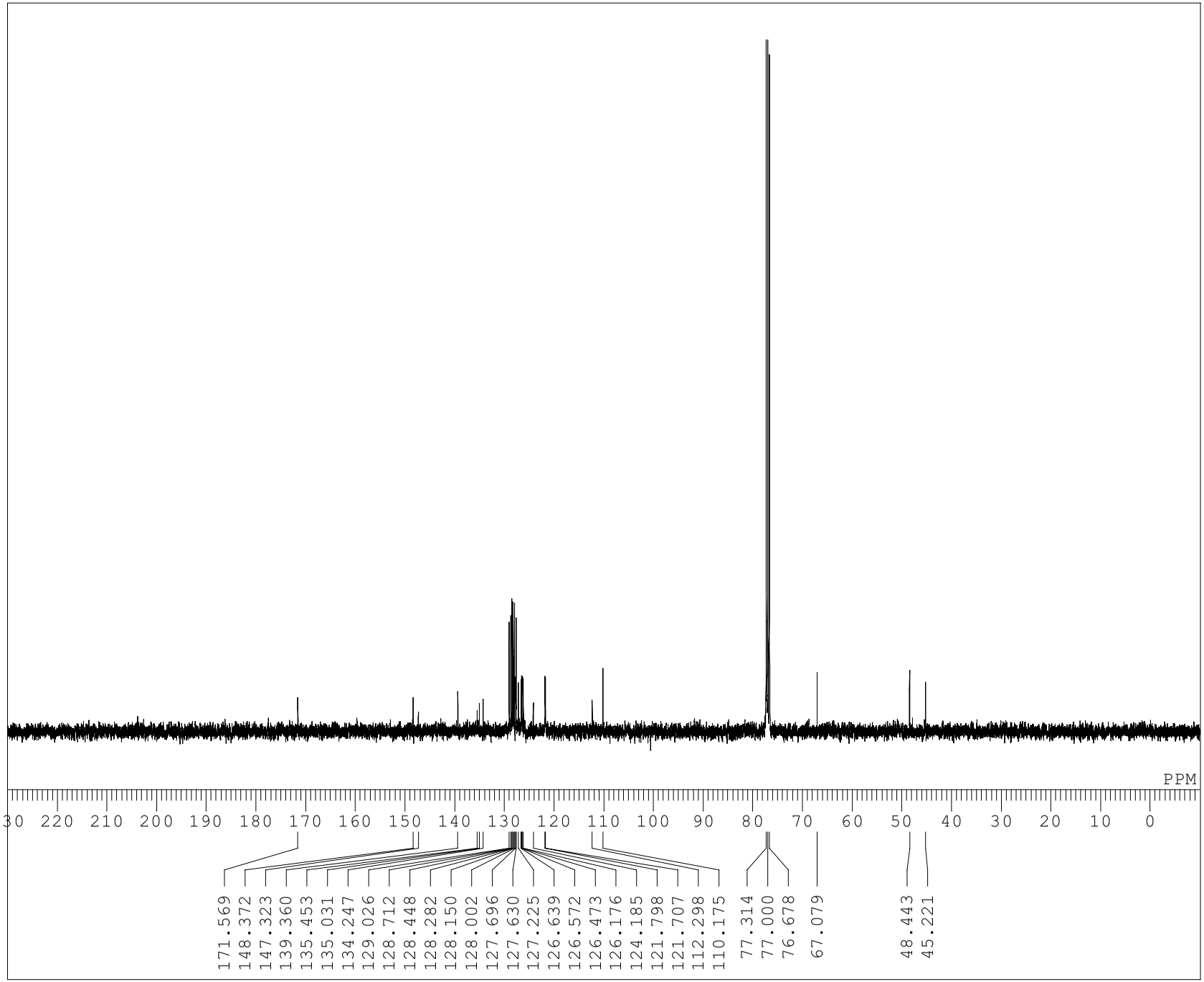
3ad



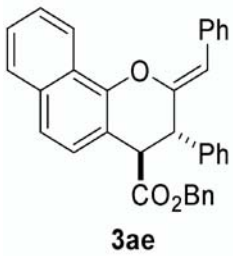

```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Fri Jun 26 19:03:30 2009
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU        7992.0 Hz
SCANS             32
ACQTM          4.100 sec
PD             2.901 sec
PW1              6.3 us
IRNUC  1H
CTEMP           24.3 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             23
```



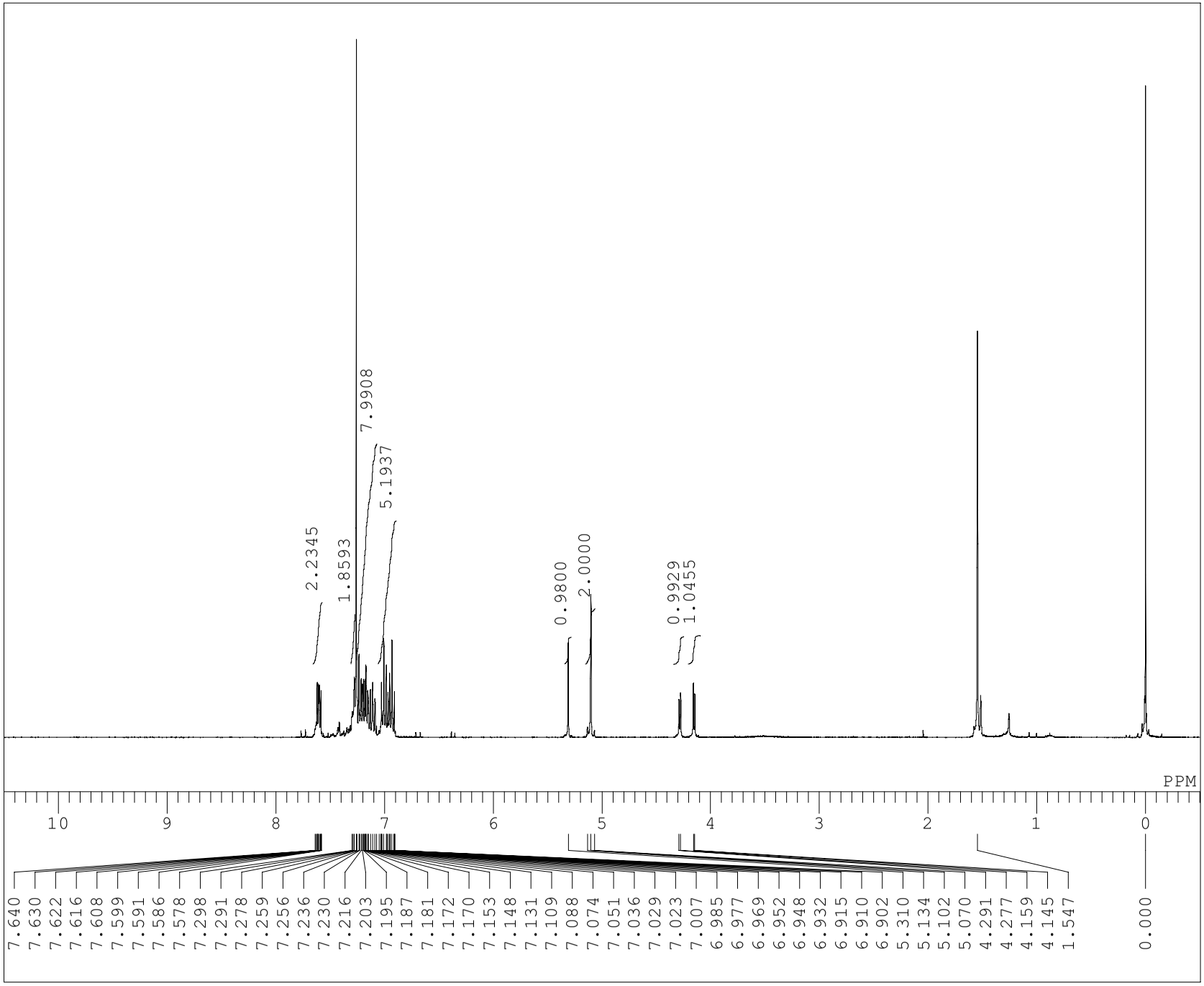
3ae




```
DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Fri Jun 26 13:16:06 2009
OBNUC  13C
EXMOD  BCM
OBFRQ        100.40 MHz
OBSET        125.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU       27210.9 Hz
SCANS           400
ACQTM         1.204 sec
PD            1.794 sec
PW1             6.1 us
IRNUC  1H
CTEMP          25.7 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            23
```

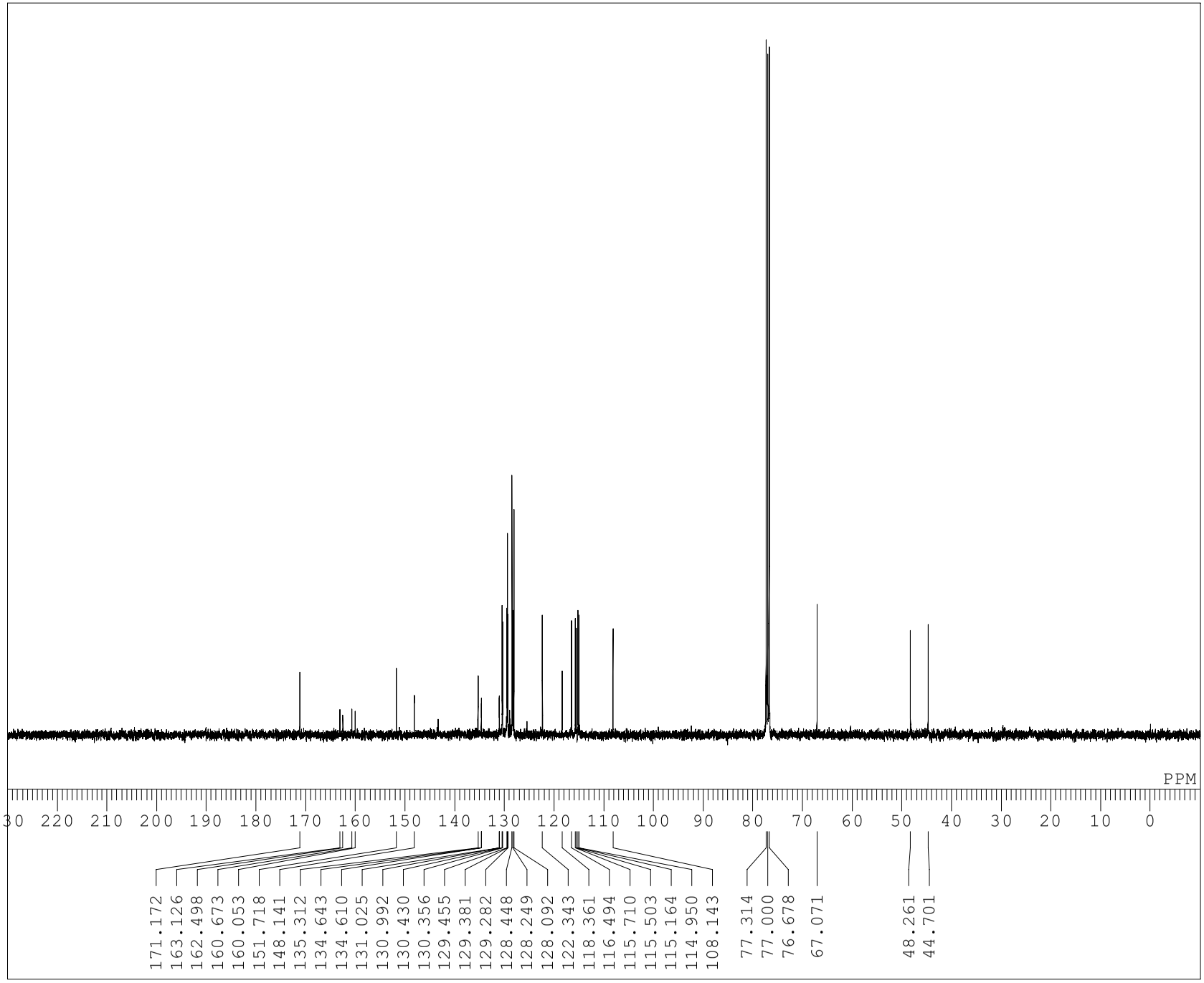


3ae

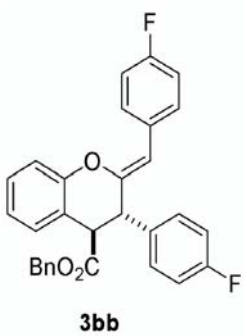


DFILE \\150.59.84.6\user\004BC
COMNT
DATIM Fri May 08 15:48:41 2009
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 7992.0 Hz
SCANS 24
ACQTM 4.100 sec
PD 2.901 sec
PW1 6.3 us
IRNUC 1H
CTEMP 24.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 21

3bb

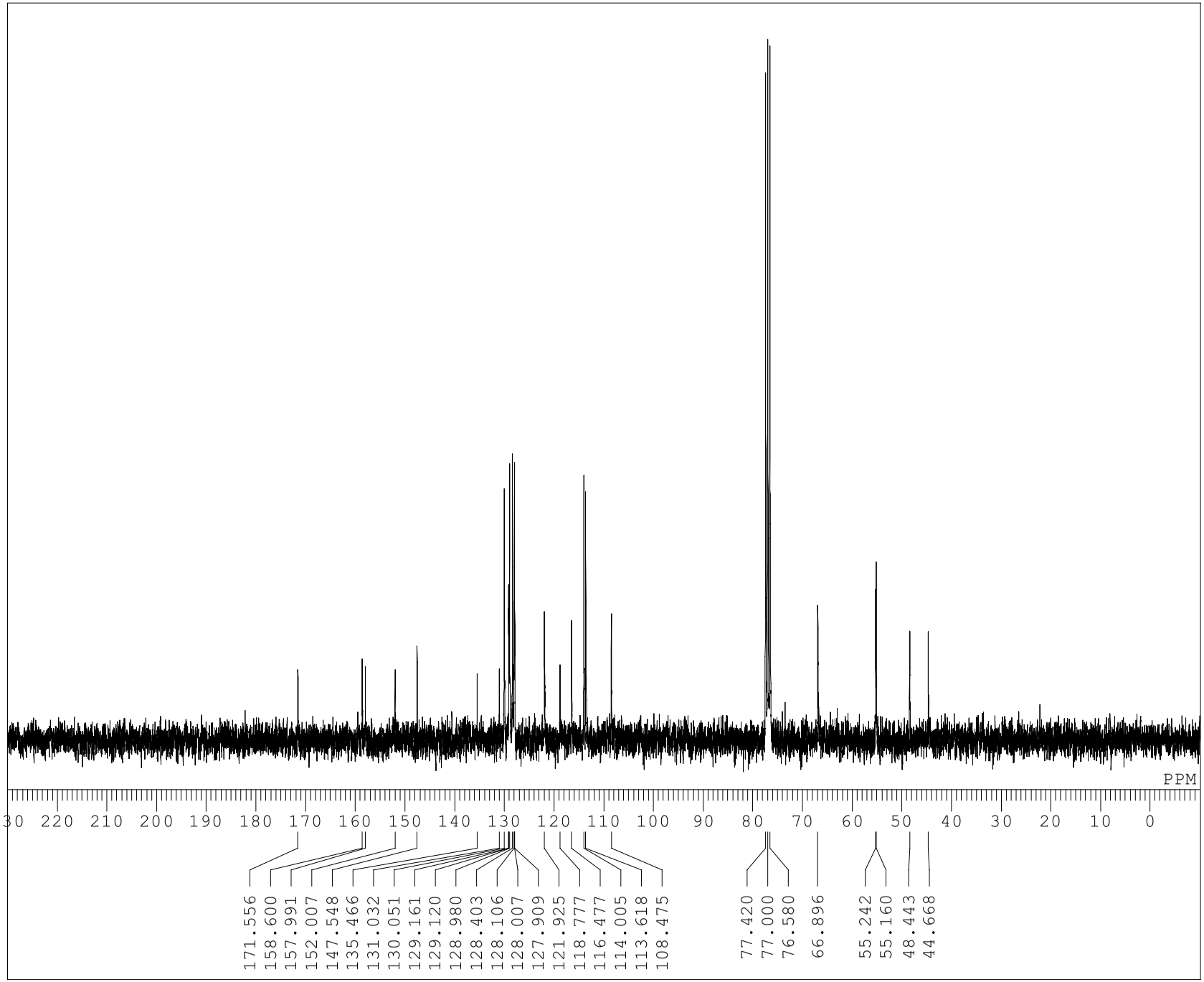


DFILE \\150.59.84.6\user\004BC
COMNT
DATIM Sat May 09 15:31:53 2009
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 27210.9 Hz
SCANS 756
ACQTM 1.204 sec
PD 1.794 sec
PW1 6.1 us
IRNUC 1H
CTEMP 25.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 23

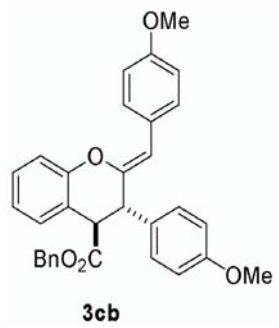


3bb

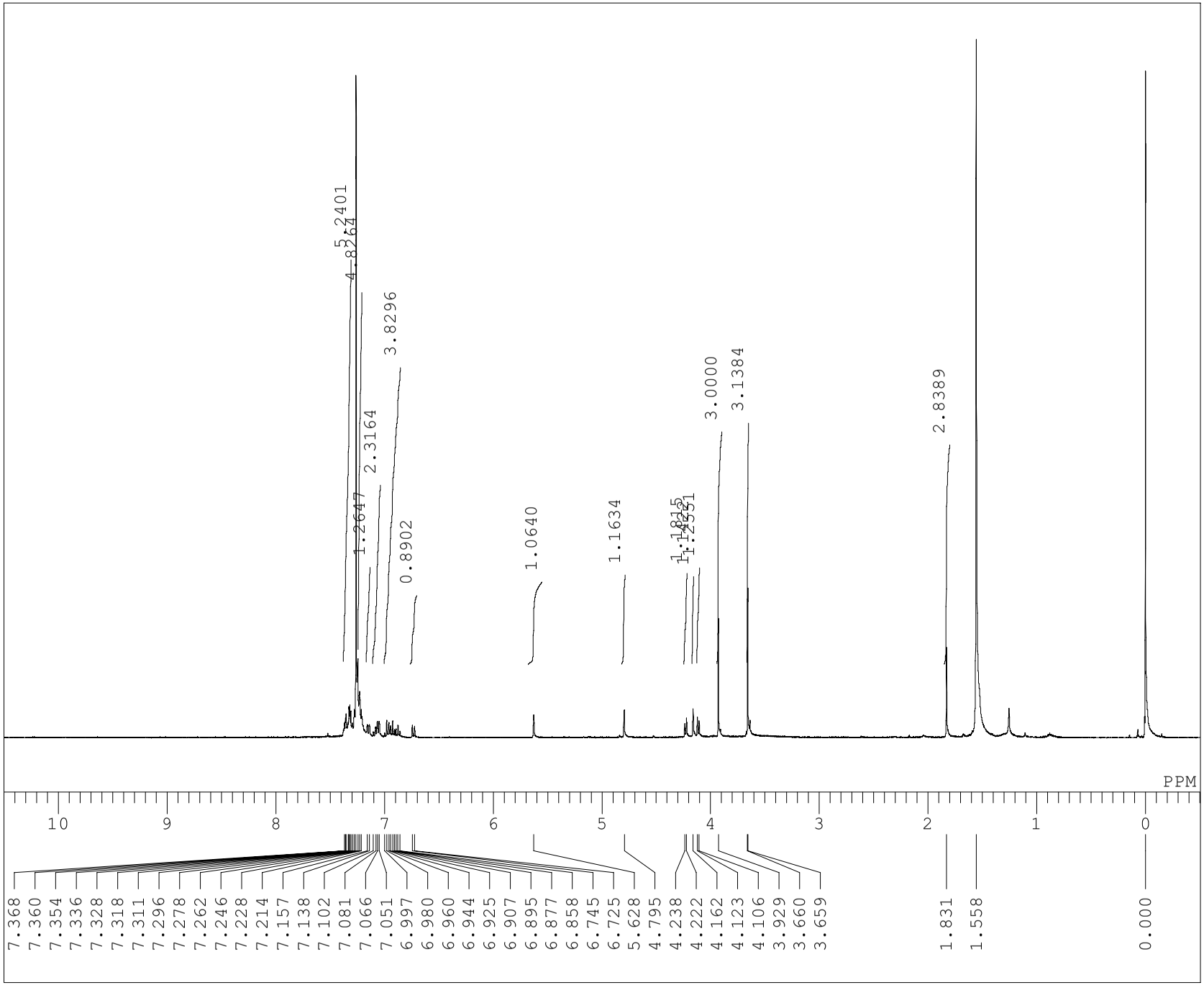
DFILE \\150.59.84.6\user\004BC
COMNT
DATIM Mon Jun 22 13:17:55 2009
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 7992.0 Hz
SCANS 32
ACQTM 4.100 sec
PD 2.901 sec
PW1 6.3 us
IRNUC 1H
CTEMP 24.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 22
OMe
OMe
BnO2C
3cb
PPM
0.000
1.554
2.9447
3.2926
0.9849
0.9788
2.1548
1.0052
1.0000
2.0599
2.0002
6.0909
3.2808
1.2134
2.0675
3.761
3.816
4.164
4.179
4.238
4.253
5.059
5.090
5.125
5.302
6.770
6.792
6.852
6.874
6.917
6.935
6.954
7.066
7.086
7.107
7.127
7.151
7.167
7.173
7.210
7.217
7.231
7.246
7.251
7.259
7.260
7.274
7.293
7.314
7.325
7.333
7.576
7.598



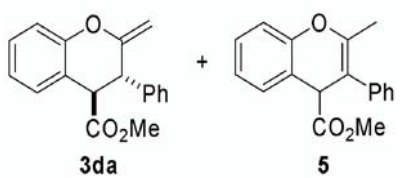
DFILE \\150.59.84.6\user\004BC
COMNT
DATIM Mon Jun 22 14:45:40 2009
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 540
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.5 us
IRNUC 1H
CTEMP 21.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 24



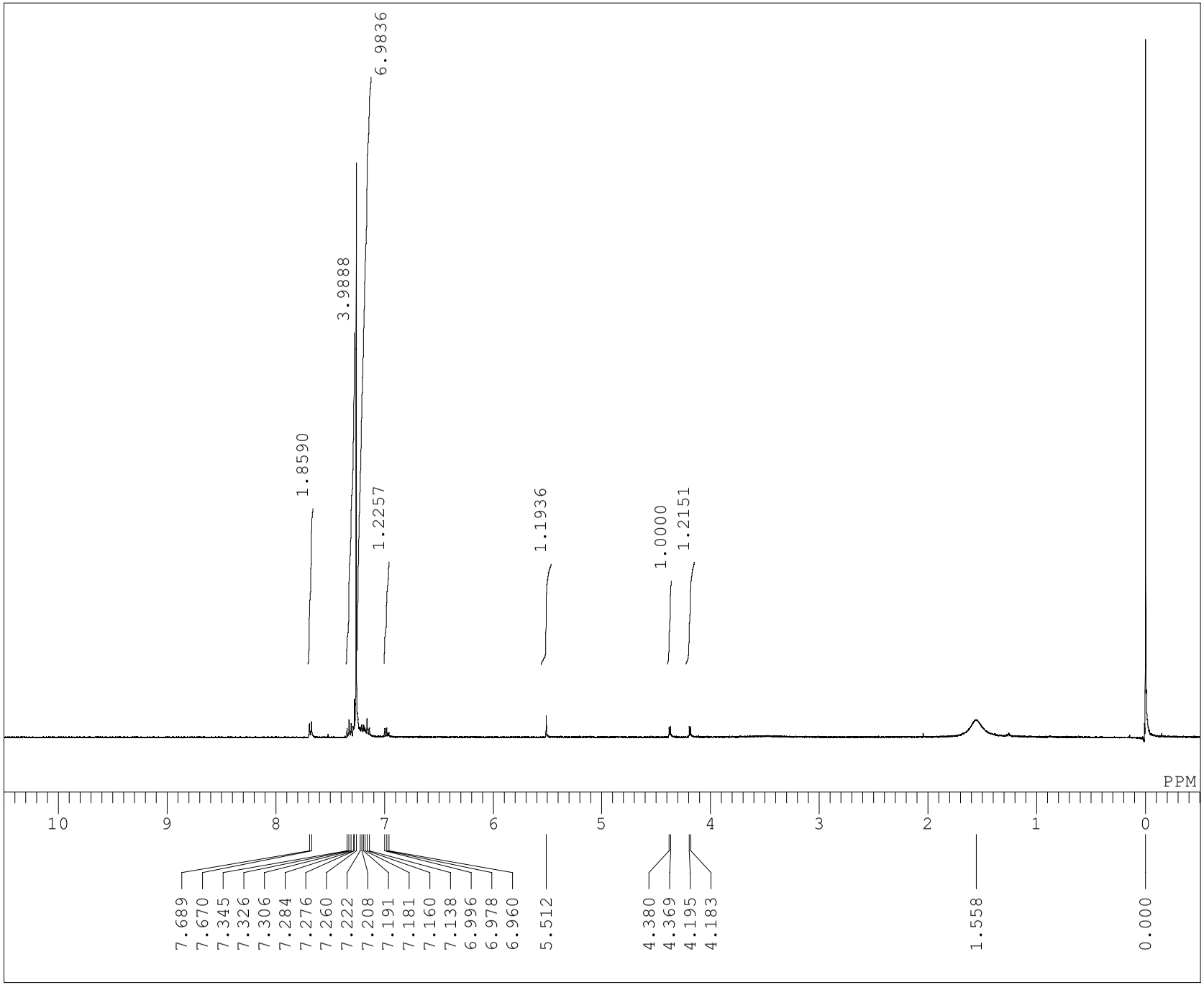
3cb



DFILE \\150.59.84.6\user\004BC
COMNT
DATIM Sat Jun 27 14:55:35 2009
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 7992.0 Hz
SCANS 60
ACQTM 4.100 sec
PD 2.901 sec
PW1 6.3 us
IRNUC 1H
CTEMP 24.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 23



3da **5**

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DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Fri Jul 03 22:45:30 2009
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU        7992.0 Hz
SCANS            16
ACQTM         4.100 sec
PD            2.901 sec
PW1             6.3 us
IRNUC  1H
CTEMP          25.7 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            24
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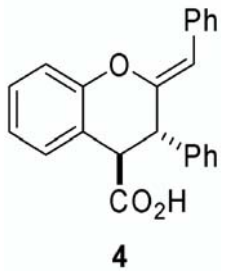
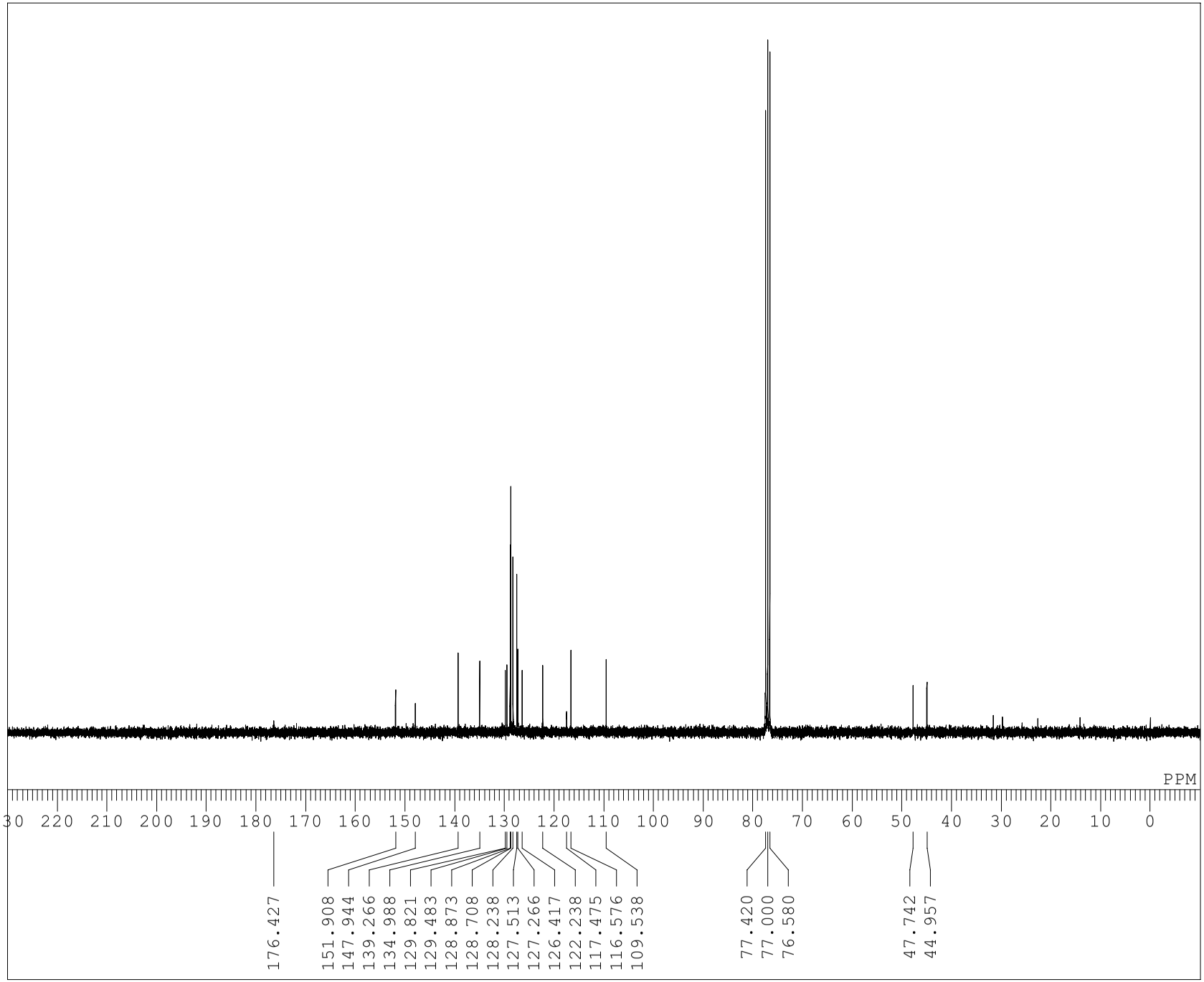


4

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DFILE  \\150.59.84.6\user\004BC
COMNT
DATIM  Sat Jul 04 23:46:41 2009
OBNUC  13C
EXMOD  BCM
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN       1840.0 Hz
POINT         32768
FREQU      20408.1 Hz
SCANS          7588
ACQTM         1.606 sec
PD            1.394 sec
PW1             4.5 us
IRNUC  1H
CTEMP          20.6 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            24
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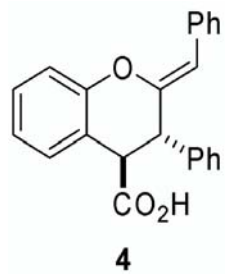

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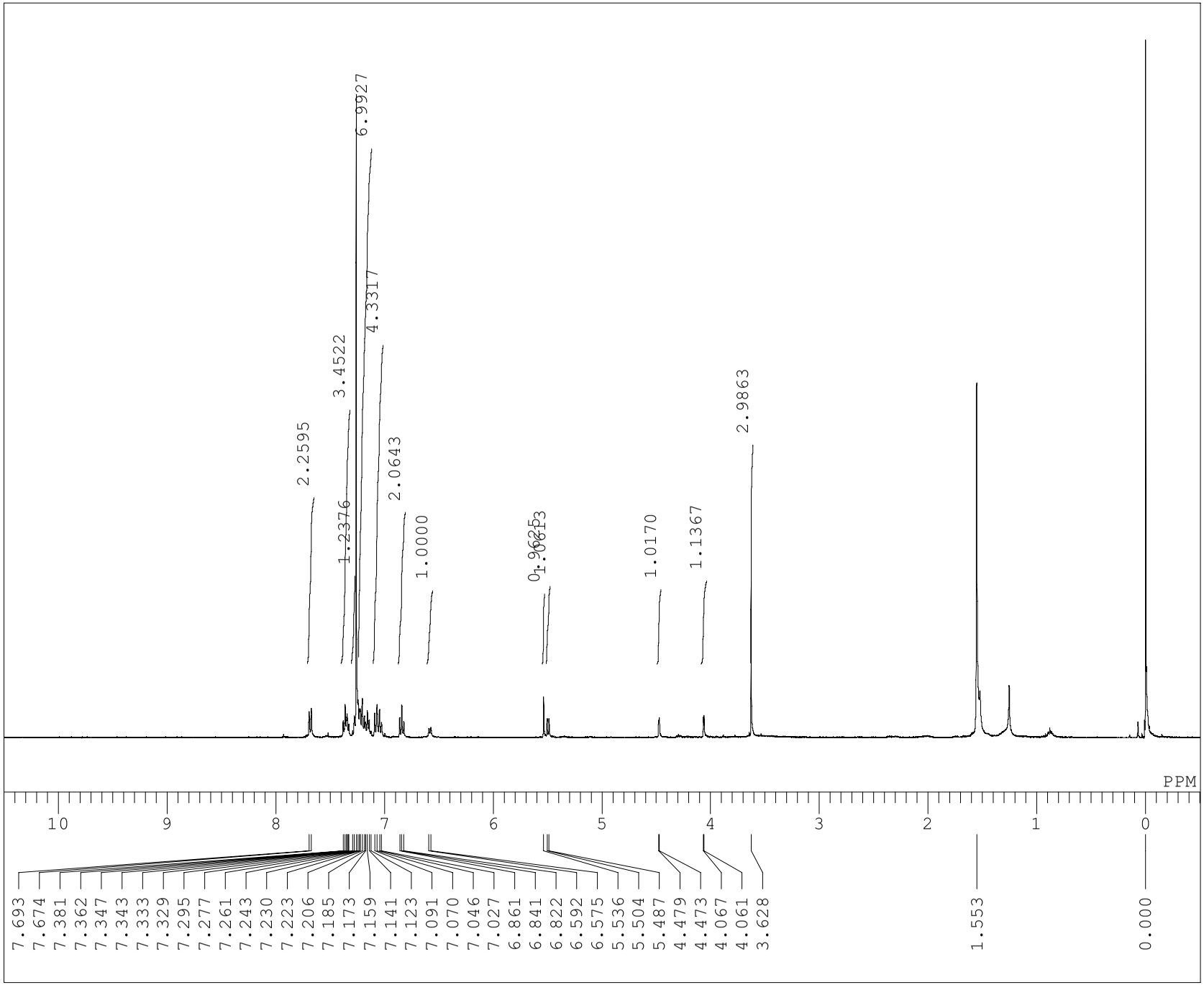
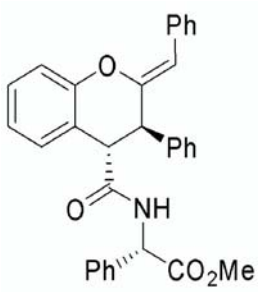
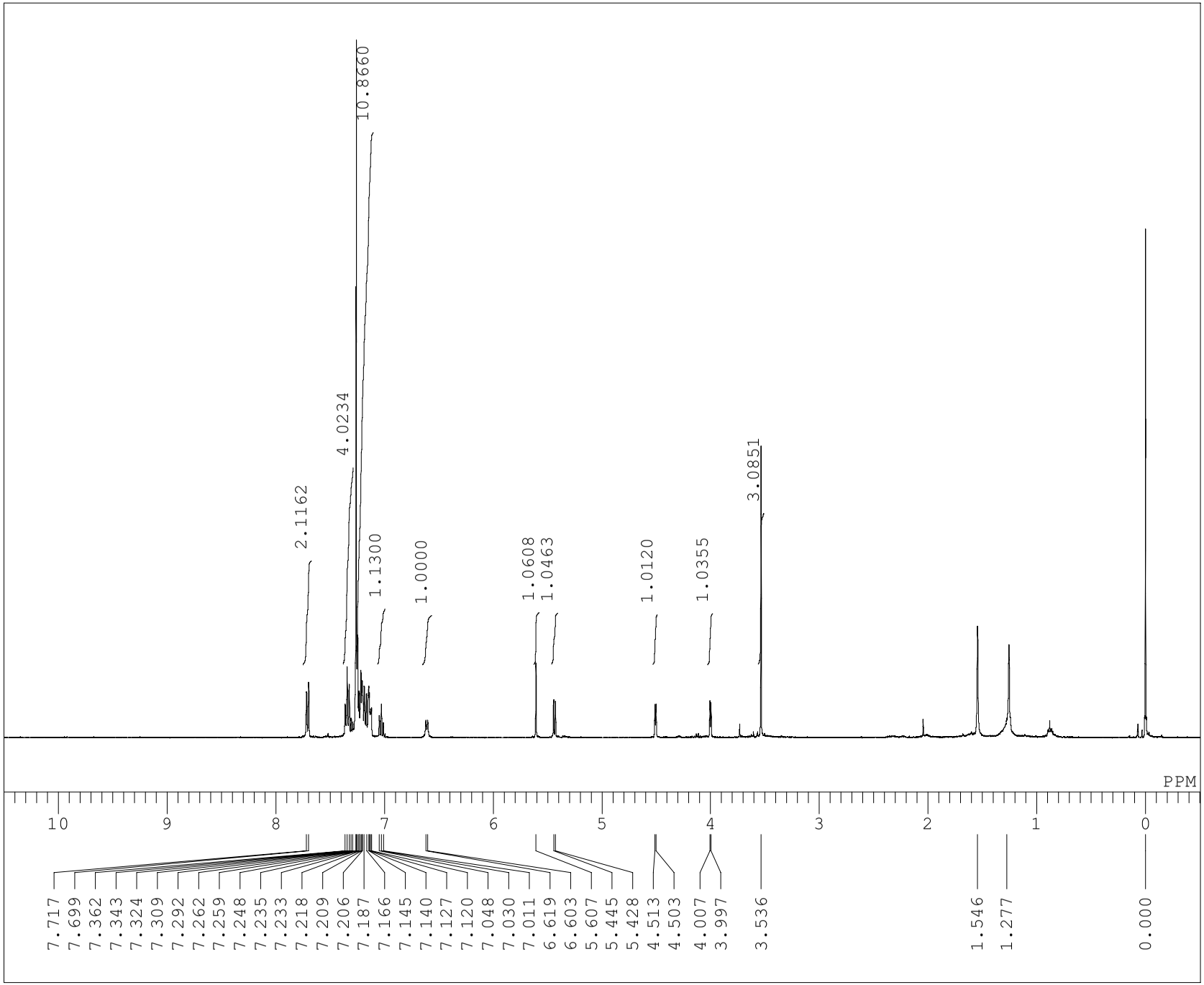


DFILE \\150.59.84.6\user\004BC
COMNT
DATIM Mon Jun 22 19:49:34 2009
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 7992.0 Hz
SCANS 32
ACQTM 4.100 sec
PD 2.901 sec
PW1 6.3 us
IRNUC 1H
CTEMP 24.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 23



(*S*)-PGME amide

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DFILE   \\150.59.248.165\data\NM
COMNT
DATIM   Thu Mar 19 11:56:43 2009
OBNUC   1H
EXMOD   NON
OBFRQ         399.65 MHz
OBSET         124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU         7992.0 Hz
SCANS            16
ACQTM          4.100 sec
PD             2.901 sec
PW1              6.3 us
IRNUC   1H
CTEMP           24.9 c
SLVNT   CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             21
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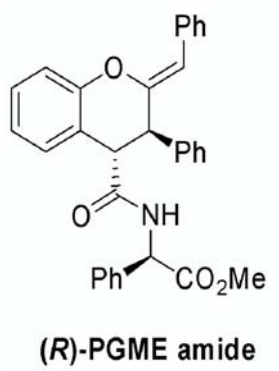

(*R*)-PGME amide