Supporting Information

A novel flurine-metal exchange reaction of pentafluorocrotonate with organocuprate – Generation of β-metallated tetrafluorocrotonate and its cross-coupling reaction

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Experimental

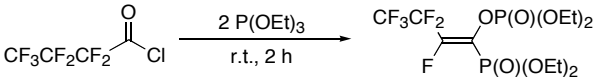
1. Measurements and materials

^{1}H and ^{13}C NMR spectra were measured with a Bruker DRX-500 (500.13 MHz for ^{1}H and 125.75 MHz for ^{13}C) spectrometer in a chloroform-*d* ($CDCl_3$) solution with tetramethylsilane as an internal reference. A JEOL JNM-AL400 (376.05 MHz) was used to measure ^{19}F NMR spectra in $CDCl_3$ using trichlorofluoromethane as an internal standard. Infrared spectra (IR) were determined in a liquid film or KBr disk method with a AVATAR-370DTGS spectrometer (Thermo ELECTRON) or a FT/IR-4100 (JASCO). High resolution mass spectra were taken with a JEOL JMS-700 MS spectrometer. Elemental analyses were conducted with a Yanaco CHN CORDER MT-5 instrument. Column chromatography was carried out on silica gel (Wako gel C-200) and TLC analysis was performed on silica gel TLC plates (Merck, Silica gel 60 F_{254}).

Anhydrous tetrahydrofuran (THF) and diethyl ether waere purchased from Wako chemicals. All chemicals were of reagent grade and, if necessary, were purified in the usual manner prior to use. All reactions were carried out under an atomosphere of argon.

2. Preparation of fluoroinated substrate 1a-c

2.1. Preparation of diethyl (Z)-1-(diethoxyphosphinyl)oxy-1-perfluorobutenephosphonate[1]



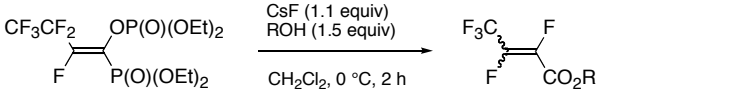
In a two-necked round-bottomed flask, equipped with a teflon stirrer bar, a rubber septum, and an inlet tube for argon, was placed 20 mmol of triethyl phosphite. After the flask was cooled by immersing in an ice-methanol bath, 10 mmol of freshly prepared perfluorobutanoic acid chloride **5**, prepared according to literature method[2], was intoruduced to it via a syringe at such rate that the mixture was stirred at room temperature for 2 h. To this mixture, recooled to 0 °C, was gradually added 50 mL of water by use of a syringe. The resultant solution was subjected to extraction with diethyl ether (50 mL × 3) and the ethereal extracts were washed with 5% aqueous sodium hydrogen carbonate, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was chromatographed on

silica gel (hexane/AcOEt = 1 : 1) to give pure (*Z*)-1-(diethoxyphosphinyl)oxy-1-perfluorobutenephosphonate as a viscous oil.

2.1.1. (*Z*)-1-(diethoxyphosphinyl)oxy-1-perfluorobutenephosphonate

Yield: 50%; ^{1}H NMR ($CDCl_3$) δ 1.25 ~ 1.31 (m, 12H), 4.14 ~ 4.22 (m, 8H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ -137.45 ~ -137.32 (m, 1F), -119.55 ~ -119.45 (m, 2F), -84.05 ~ -83.95 (m, 3F); ^{31}P NMR ($CDCl_3$, H_3PO_4) δ 2.07 (d, *J* = 10.2 Hz, 1P), -7.22 (dd, *J* = 10.2, 2.4 Hz, 1P), IR (neat) 3412 (m), 2990 (m), 1764 (m), 1481 (m), 1363 (s), 1274 (s), 1216 (s), 1149 (s), 1031 (vs), 870 (m) cm^{-1}; HRMS (FAB) Calcd for (M+H) $C_{12}H_{21}F_6O_7P_2$: 453.0667, Found 453.0678.

2.2. Typical procedure for the preparation of benzyl 2,3,4,4,4-pentafluorocrotonate (1a)



1 : R = Bn (**a**)
R = $PhCH_2CH_2$ (**b**)
R = (*E*)-PhCH=$CHCH_2$ (**c**)

Compounds **1a**, **1b**, and **1c** was prepared by slight modifications of the previously reported methods,[3] as follows: A two-necked round-bottomed flask, equipped with a teflon stirrer bar, a rubber septum, and an inlet tube for argon was charged with a suspended solution of CsF (1.1 equiv, 5.5 mmol) and benzyl alcohol (1.5 equiv, 7.5 mmol) in CH_2Cl_2 (10 mL). After the flask was cooled by immersing in an ice-methanol bath, vinyl phosphonate (5.0 mmol) was intoruduced to it *via* a syringe at such rate that the mixture was stirred at 0 °C for 2 h. The resultant solution was poured into ice-cooled water (30 mL), followed by extraction with diethyl ether (30 mL × 3) and the organic layers were dried over anhydrous sodium sulfate, filtered and concentrated with a rotary evaporator under reduced pressure. Column chromatography of the residue using hexane/benzene (5:1) gave pure product, benzyl 2,3,4,4,4-pentafluorocrotonate (**1a**) as a mixture of the *E*/*Z* isomers (*E*/*Z* = ~90/10).

2.2.1. Benzyl 2,3,4,4,4-pentafluorocrotonate (**1a**)

Yield: 50%; *E*-**1a** : ^{1}H NMR ($CDCl_3$) δ 5.37 (s, 2H), 7.35 ~ 7.42 (m, 5H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ -153.84 (dq, *J* = 138.6, 18.8 Hz, 1F), -150.63 (dq, *J* = 138.6, 6.6 Hz, 1F), -68.91 (dd,

J = 18.8, 6.6 Hz, 3F); ^{13}C NMR ($CDCl_3$) δ 68.36, 118.16 (qdd, *J* = 274.8, 31.4, 4.0 Hz), 128.46, 128.69, 128.86, 134.10, 141.59 (ddq, *J* = 230.0, 32.8, 2.4 Hz), 145.08 (ddd, *J* = 273.2, 41.0, 41.0 Hz), 157.27 (dd, *J* = 30.4, 6.2 Hz); *Z*-**1a** : ^{1}H NMR ($CDCl_3$) δ 5.344 (s, 2H), 7.35 ~ 7.42 (m, 5H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ -136.00 ~ -137.00 (m, 2F), -65.67 (dd, *J* = 8.8, 8.8 Hz, 3F); IR (neat) 3038 (w), 2966 (w), 1751 (vs), 1458 (m), 1372 (s), 1273 (vs), 1224 (vs), 1162 (vs), 960 (m) cm^{-1}; HRMS (EI) Calcd for (M+) $C_{11}H_7F_5O_2$: 266.0366, Found 266.0356; Anal. Calcd for $C_{11}H_7F_5O_2$: C, 49.64: H, 2.65. Found: C, 49.60; H, 2.75.

2.2.2. 2-Phenylethyl 2,3,4,4,4-pentafluorocrotonate (**1b**)

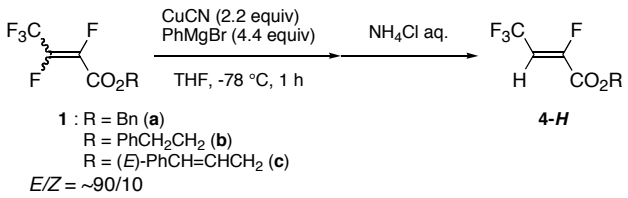
E-**1b** : ^{1}H NMR ($CDCl_3$) δ 3.05 (t, *J* = 6.9 Hz, 2H), 4.55 (t, *J* = 6.9Hz, 2H), 7.23 ~ 7.30 (m, 3H), 7.31 ~ 7.37 (m, 2H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ -153.70 (dq, *J* = 139.1, 22.1 Hz, 1F), -151.16 (dq, *J* = 139.1, 9.8 Hz, 1F), -68.88 (dd, *J* = 22.1, 9.8 Hz, 3F); ^{13}C NMR ($CDCl_3$) δ 34.73, 67.44, 118.07 (qdd, *J* = 274.9, 34.9, 3.6 Hz), 126.95, 128.66, 128.90, 136.66, 141.49 (ddq, *J* = 262.8, 33.1, 2.4 Hz), 145.01 (ddq, *J* = 273.6, 41.0, 41.0 Hz), 157.43 (dd, *J* = 30.7, 6.2 Hz); *Z*-**1b** : ^{1}H NMR ($CDCl_3$) δ 3.03 (t, *J* = 6.5 Hz, 2H), 4.53 (t, *J* = 6.5 Hz, 2H), 7.23 ~ 7.30 (m, 3H), 7.31 ~ 7.37 (m, 2H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ -137.15 ~ -136.75 (m, 1F), -136.45 ~ -136.10 (m, 1F), -65.67 (dd, *J* = 9.4, 9.4 Hz, 3F); IR (neat) 3031 (m), 2964 (m), 1750 (vs), 1702 (m), 1605 (w), 1498 (m), 1375 (s), 1276 (vs), 1227 (vs), 1163 (vs), 984 (s) cm^{-1}; HRMS (FAB) Calcd for (M+H) $C_{12}H_{10}F_5O_2$: 281.0602, Found 281.0594.

2.2.3. 3-Phenyl-2-propen-1-yl 2,3,4,4,4-pentafluorocrotonate (**1c**)

E-**1c** : ^{1}H NMR ($CDCl_3$) δ 5.00 (dd, *J* = 6.6, 0.8 Hz, 2H), 6.31 (dt, *J* = 15.8, 6.6 Hz, 1H), 6.76 (d, *J* = 15.8 Hz, 1H), 7.27 ~ 7.37 (m, 3H), 7.39 ~ 7.44 (m, 2H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ -153.61 (dq, *J* = 139.1, 21.8 Hz, 1F), -150.99 (dq, *J* = 139.1, 9.8 Hz, 1F), -68.88 (dd, *J* = 21.8, 9.8 Hz, 3F); ^{13}C NMR ($CDCl_3$) δ 67.44, 118.07 (qdd, *J* = 275.0, 35.3, 3.8 Hz), 120.84, 126.77, 128.55, 128.69, 136.32, 136.58, 141.54 (ddq, *J* = 230.4, 32.9, 2.4 Hz), 145.09 (ddq, *J* = 273.7, 40.9, 40.9 Hz), 157.34 (dd, *J* = 30.2, 6.2 Hz); *Z*-**1c** : ^{1}H NMR ($CDCl_3$) δ 4.98 (dd, *J* = 6.9, 0.9 Hz, 2H), 6.29 (dt, *J* = 15.9, 6.9 Hz, 1H), 6.75 (d, *J* = 15.9 Hz, 1H), 7.27 ~ 7.37 (m, 3H), 7.39 ~ 7.44 (m, 2H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ -136.85 ~ -136.55 (m, 1F), -136.40 ~ -136.15 (m, 1F), -65.65 (dd, *J* = 9.4, 9.4 Hz, 3F); IR (neat) 3029 (m), 2957 (w),

1749 (vs), 1701 (m), 1495 (m), 1371 (s), 1270 (vs), 1222 (vs), 1162 (vs), 966 (s) cm^{-1}; HRMS (FAB) Calcd for (M+) $C_{13}H_9F_5O_2$: 292.0523, Found 292.0530.

3. Typical procedure for the preparation of benzyl 2,4,4,4-tetrafluorocrotonate (4a-H)



A 30 mL-two necked round bottomed flask equipped with a magnetic stirrer bar, a rubber septum and an inlet tube for argon was charged with a suspended solution of CuCN (2.2 equiv) in THF (1 mL). To this solution was slowly added a solution of phenylmagnesium bromide (4.4 equiv) in THF *via* a syringe at -78 °C. The whole was warmed up at -20 °C and stirred for 15 min. To the resulting solution was added benzyl 2,3,4,4,4-pentafluoro-2-butenoate (**2a**, 1.0 equiv) *via* a syringe at -78 °C. After being stirred for 1 h, the reaction mixture was poured into ice-cooled saturated aqueous NH_4Cl (30 mL), followed by extraction with ether (30 mL × 5). The organic layers were dried over anhydrous sodium sulfate, filtered and concentrated with a rotary evaporator. Column chromatography of the residue using hexane/benzene (5:1) yielded pure benzyl 2,4,4,4-tetrafluorocrotonate (**4a-*H***).

3.1. (*Z*)-Benzyl 2,4,4,4-tetrafluorocrotonate (**4a-*H***)

Yield: 50%; ^{1}H NMR ($CDCl_3$) δ 5.33 (s, 2H), 6.28 (dq, *J* = 28.1, 7.5 Hz, 1H), 7.35 ~ 7.41 (m, 5H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ -111.08 (dq, *J* = 28.1, 17.3 Hz, 1F), -59.80 (dd, *J* = 17.3, 7.5 Hz, 1F); ^{13}C NMR ($CDCl_3$) δ 68.63, 106.95 (qd, *J* = 37.2, 5.6 Hz), 121.07 (q, *J* = 270.5 Hz), 128.69, 128.80, 129.05, 133.99, 158.55 (d, *J* = 34.1 Hz), 151.99 (dq, *J* = 284.4, 5.0 Hz); IR (neat) 3038 (w), 2963 (w), 1753 (vs), 1697 (s), 1458 (m), 1365 (s), 1283 (vs), 1178 (vs), 1073 (m), 947 (w) cm^{-1}; HRMS (EI) Calcd for (M+) $C_{11}H_8F_4O_2$: 248.0460, Found 248.0458.

3.2. 2-Phenylethyl 2,4,4,4-tetrafluorocrotonate (**4b-*H***)

Yield: 50%; ^{1}H NMR ($CDCl_3$) δ 3.02 (t, *J* = 7.0 Hz, 2H), 4.87 (t, *J* = 7.0 Hz, 2H), 6.20 (dq, *J* = 28.1, 7.5 Hz, 1H), 7.20 ~ 7.37 (m, 5H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ -111.24 (dq, *J* = 28.1,

16.9 Hz, 1F), -59.80 (dd, *J* = 16.9, 7.5 Hz, 1F); ^{13}C NMR ($CDCl_3$) δ 34.73, 67.32, 106.72 (qd, *J* = 37.0, 5.6 Hz), 121.08 (q, *J* = 270.5 Hz), 126.97, 128.70, 128.84, 136.63, 151.99 (dq, *J* = 284.8, 4.9 Hz), 158.57 (d, *J* = 33.9 Hz); IR (neat) 3031 (w), 2963 (w), 1753 (vs), 1697 (vs), 1498 (m), 1396 (s), 1368 (s), 1287 (vs), 1183 (vs), 1141 (vs), 1076 (s), 910 (s) cm^{-1}; HRMS (EI) Calcd for (M+) $C_{12}H_{10}F_4O_2$: 262.0617, Found 262.0608.

3.3. 3-Phenyl-2-propen-1-yl 2,4,4,4-tetrafluorocrotonate (**4c-*H***)

Yield: 42%; ^{1}H NMR ($CDCl_3$) δ 4.95 (dd, *J* = 6.8, 1.0 Hz, 2H), 6.30 (dq, *J* = 28.1, 7.5 Hz, 1H), 6.30 (dt, *J* = 15.8, 6.8 Hz, 1H), 6.74 (d, *J* = 15.8 Hz, 1H), 7.25 ~ 7.38 (m, 3H), 7.39 ~ 7.43 (m, 2H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ -111.17 (dq, *J* = 28.1, 16.9 Hz, 1F), -59.79 (dd, *J* = 16.9, 7.5 Hz, 1F); IR (neat) 3030 (m), 2957 (m), 1752 (vs), 1696 (vs), 1496 (s), 1449 (s), 1365 (vs), 1276 (vs), 1138 (vs), 1073 (vs), 967 (s) cm^{-1}; HRMS (FAB) Calcd for (M+) $C_{13}H_{10}F_4O_2$: 274.0617, Found 274.0615.

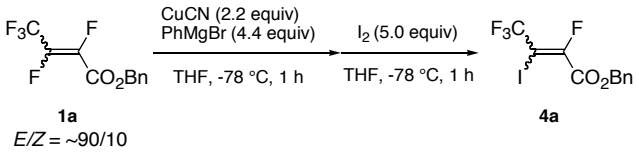
3.4. Benzyl 3-benzyl-2,4,4,4-tetrafluorocrfotonate **3a** (R^1=Bn)

Yield: 36%; *Z*-**3a** (R^1=Bn) : ^{1}H NMR ($CDCl_3$) δ 4.03 (s, 2H), 5.32 (s, 2H), 7.15 ~ 7.40 (m, 10H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ -110.33 (q, *J* = 19.5 Hz, 1F), -61.33 (d, *J* = 19.5 Hz, 3F); *E*-**3a** (R^1=Bn) : ^{1}H NMR ($CDCl_3$) δ 3.70 (d, *J* = 4.0 Hz, 2H), 5.31 (s, 2H), 7.15 ~ 7.40 (m, 10H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ -109.85 ~ -109.70 (m, 1F), -59.10 (d, *J* = 9.8 Hz, 3F); IR (neat) 3066 (w), 2962 (w), 1742 (vs), 1686 (m), 1497 (s), 1455 (s), 1347 (s), 1264 (vs), 1184 (vs), 1077 (m), 996 (w) cm^{-1}; HRMS (FAB) Calcd for (M+Na) $C_{18}H_{14}F_4O_2Na$: 361.0828, Found 361.0822.

3.5. Benzyl 4,4,4-trifluorobutynoate (**6a**)

^{1}H NMR ($CDCl_3$) δ 5.29 (s, 2H), 7.35 ~ 7.43 (m, 5H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ -52.69 (s, 3F); ^{13}C NMR ($CDCl_3$) δ 68.98, 70.38 (q, *J* = 54.9 Hz), 75.28 (q, *J* = 6.5 Hz), 113.34 (q, *J* = 260.3 Hz), 128.81, 128.81, 129.13, 133.64, 150.61 (q, *J* = 1.3 Hz); IR (neat) 3037 (w), 2965 (m), 1732 (vs), 1608 (m), 1457 (m), 1376 (m), 1270 (vs), 1163 (vs), 1094 (m), 999 (m) cm^{-1}; HRMS (EI) Calcd for (M+) $C_{11}H_7F_3O_2$: 228.0398, Found 228.0393.

4. Typical procedure for the preparation of benzyl 2,4,4,4-tetrafluoro-3-iodocrotonate (4a (El = I))



A 30 mL two-necked round bottomed flask equipped with a magnetic stirrer bar, a rubber septum and an inlet tube for argon was charged with a suspended solution of CuCN (2.2 equiv) in THF (1 mL). To this solution was slowly added a solution of phenylmagnesium bromide (4.4 equiv) in THF *via* a syringe at -78 °C. The whole was warmed up at -20 °C and stirred for 15 min. To the resulting solution was added benzyl 2,3,4,4,4-pentafluoro-2-butenoate (**1a**, 1.0 equiv) *via* a syringe at -78 °C. After being stirred at -78 °C for 1 h, the reaction mixture was treated with iodine (5.0 equiv) in THF at -78 °C for 1 h. After stirring for 1 h, the reaction mixture was poured into ice-cooled saturated aqueous NH_4Cl (30 mL), followed by extraction with ether (30 mL × 5). The organic layers were dried over anhydrous sodium sulfate, filtered and concentrated with a rotary evaporator. Column chromatography of the residue using hexane/benzene (2:1) yielded pure benzyl 2,4,4,4-tetrafluoro-3-iodo-2-butenoate (**4a** (*El* = I)).

5.1. (*E*)-Benzyl 2,4,4,4-tetrafluoro-3-iodocrotonate (**4a** (*El* = I))

Yield: 78%; ^{1}H NMR ($CDCl_3$) δ 5.35 (s, 2H), 7.35 ~ 7.50 (m, 5H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ -80.78 (q, *J* = 24.4 Hz, 1F), -58.25 (d, *J* = 24.4 Hz, 1F); ^{13}C NMR ($CDCl_3$) δ 68.81, 74.01 (qd, *J* = 30.7, 11.6 Hz), 120.87 (q, *J* = 274.9 Hz), 128.73, 128.74, 128.97, 133.89, 150.89 (dq, *J* = 294.1, 2.8 Hz), 158.51 (d, *J* = 33.6 Hz); IR (neat) 3069 (w), 2962 (w), 1743 (vs), 1627 (m), 1498 (m), 1312 (vs), 1237 (vs), 1187 (vs), 1147 (vs), 956 (s) cm^{-1}; HRMS (FAB) Calcd for (M+) $C_{11}H_7IF_4O_2$: 373.9427, Found 373.9438. Anal. Calcd for $C_{11}H_7F_4IO_2$: C, 35.32: H, 1.89. Found: C, 35.50; H, 1.92.

5.2. (*Z*)-Benzyl 3-allyl-2,4,4,4-tetrafluorocrotonate (**4a** (*El* = allyl))

Yield: 42%; ^{1}H NMR ($CDCl_3$) δ 3.39 (dd, *J* = 2.5, 1.5 Hz, 2H), 5.12 (dd, *J* = 10.0, 1.5 Hz, 1H), 5.14 (dd, *J* = 16.5, 1.5 Hz, 1H), 5.31 (s, 2H), 5.78 (dq, *J* = 16.5, 10.0 Hz, 1H), 7.35 ~ 7.44 (m, 5H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ -111.38 (q, *J* = 19.6 Hz, 1F), -62.10 (d, *J* = 19.6 Hz,

1F); ^{13}C NMR ($CDCl_3$) δ 29.18 (q, *J* = 1.6 Hz), 68.10, 117.86, 121.43 (qd, *J* = 30.5, 5.8 Hz),122.65 (q, *J* = 260.2 Hz), 128.56, 128.75, 128.88, 132.25 (d, *J* = 3.6 Hz), 134.27, 148.88 (dq, *J* = 281.4, 3.8 Hz), 159.35 (d, *J* = 32.9 Hz); IR (neat) 3070 (w), 2961 (w), 1739 (vs), 1672 (m), 1499 (m), 1348 (vs), 1274 (vs), 1186 (s), 1143 (vs), 1097 (s), 968 (m) cm^{-1}; HRMS (EI) Calcd for (M+) $C_{14}H_{12}F_4O_2$: 288.0773, Found 288.0760.

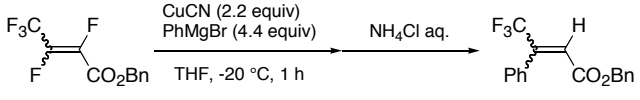
5.3. (*Z*)-Benzyl 2,4,4,4-tetrafluoro-3-methallylcrotonate (**4a** (*El* = methallyl))

Yield: 62%; ^{1}H NMR ($CDCl_3$) δ 1.73 (s, 3H), 3.35 (brs, 2H), 4.71 (brs, 1H), 4.86 (brs, 1H), 5.30 (s, 2H), 7.25 ~ 7.45 (m, 5H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ -110.29 (q, *J* = 19.5 Hz, 1F), -62.25 (d, *J* = 19.5 Hz, 1F); ^{13}C NMR ($CDCl_3$) δ 22.51, 32.65 (q, *J* = 3.8 Hz), 68.08, 112.06, 121.37 (qd, *J* = 29.6, 5.7 Hz), 122.54 (q, *J* = 276.8 Hz), 128.53, 128.73, 128.85, 134.25, 130.41 (d, *J* = 3.5 Hz), 149.47 (dq, *J* = 279.4, 2.8 Hz), 159.32 (d, *J* = 33.9 Hz); IR (neat) 3037 (w), 2975 (w), 1740 (vs), 1670 (m), 1456 (m), 1347 (s), 1277 (vs), 1220 (s), 1143 (vs), 1120 (m), 969 (w) cm^{-1}; HRMS (EI) Calcd for (M+) $C_{15}H_{14}F_4O_2$: 302.0930, Found 302.0920.

5.4. (*Z*)-Benzyl 3-crotyl-2,4,4,4-tetrafluorocrotonate (**4a** (*El* = crotyl))

Yield: 58%; ^{1}H NMR ($CDCl_3$) δ 1.65 (d, *J* = 6.4 Hz, 3H), 3.31 (d, *J* = 6.2 Hz, 2H), 5.31 (s, 2H), 5.37 (dt, *J* = 16.0, 6.2 Hz, 1H), 5.56 (dq, *J* = 16.0, 6.2 Hz, 1H), 7.35 ~ 7.45 (m, 5H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ -112.42 (q, *J* = 18.8 Hz, 1F), -61.99 (d, *J* = 18.8 Hz, 1F); ^{13}C NMR ($CDCl_3$) δ 17.83, 28.15 (q, *J* = 9.4 Hz), 68.00, 122.22 (qd, *J* = 29.6, 4.9 Hz), 122.67 (q, *J* = 274.9 Hz), 124.65 (d, *J* = 3.6 Hz), 128.56, 128.73, 128.84, 128.97, 134.34, 148.45 (dq, *J* = 272.1, 3.6 Hz), 159.45 (d, *J* = 33.9 Hz); IR (neat) 3035 (w), 2965 (w), 1740 (vs), 1672 (m), 1456 (m), 1348 (vs), 1266 (vs), 1210 (s), 1143 (vs), 1122 (vs), 1099 (s), 967 (s) cm^{-1}; HRMS (EI) Calcd for (M+) $C_{15}H_{14}F_4O_2$: 302.0930, Found 302.0935.

6. Typical procedure for the preparation of benzyl 4,4,4-trifluoro-3-phenylcrotonate (5a)



1a
E/*Z* = ~90/10

5a

A 30 mL-two necked round bottomed flask equipped with a magnetic stirrer bar, a rubber septum and an inlet tube for argon was charged with a suspended solution of CuCN (2.2

equiv) in THF (1 mL). To this solution was slowly added a solution of phenylmagnesium bromide (4.4 equiv) in THF *via* a syringe at -78 °C. The whole was warmed up at -20 °C and stirred for 15 min. To the resulting solution was added benzyl 2,3,4,4,4-pentafluoro-2-butenoate (**1a,** 1.0 equiv) *via* a syringe at -78 °C. After stirring at -20 °C for 1 h, the reaction mixture was poured into ice-cooled saturated aqueous NH_4Cl (30 mL), followed by extraction with ether (30 mL × 5). The organic layers were dried over anhydrous sodium sulfate, filtered and concentrated with a rotary evaporator. Column chromatography of the residue using hexane/benzene (2:1) yielded pure benzyl 4,4,4-trifluoro-3-phenylcrotonate (**5a**).

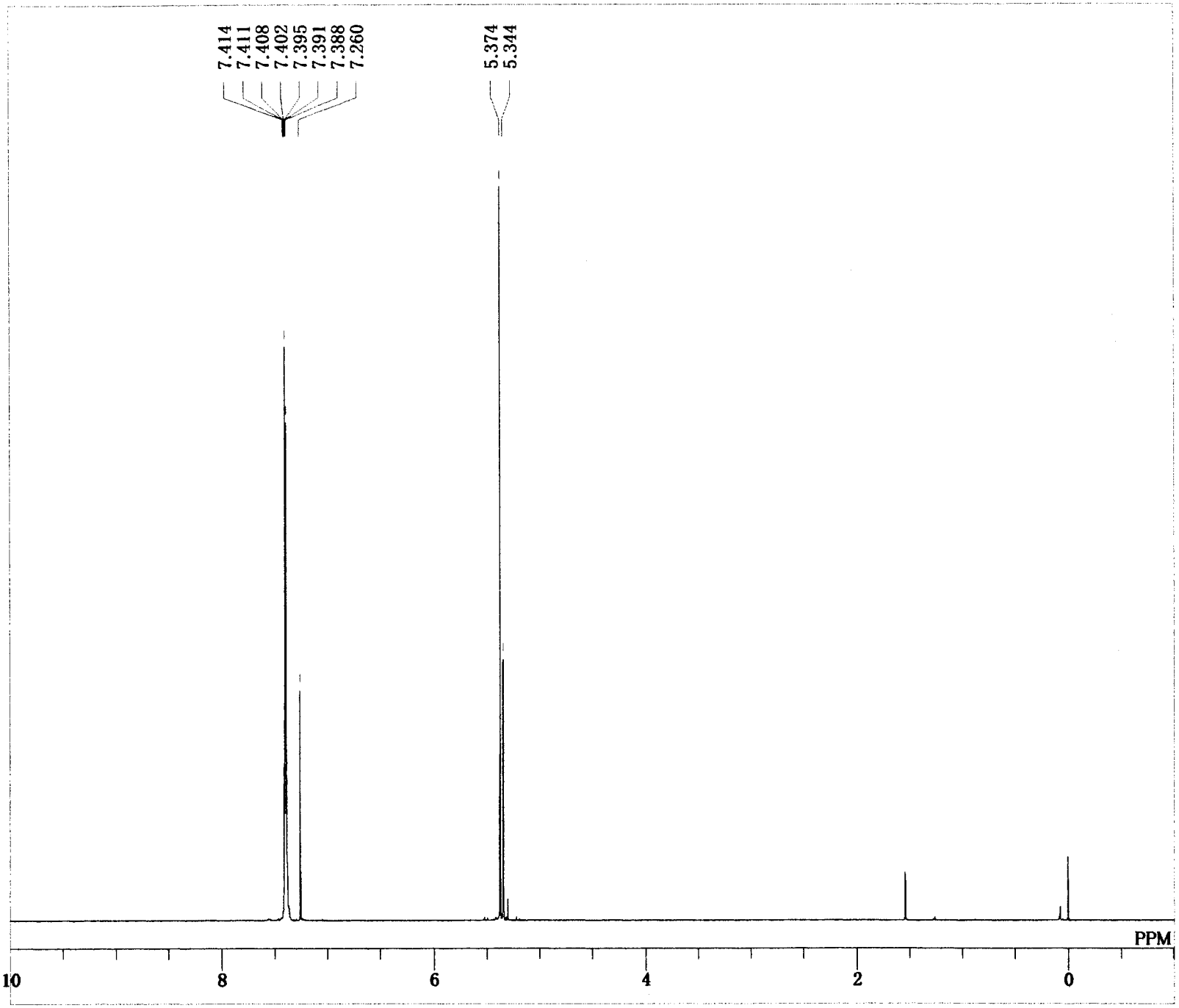
7.1. Benzyl 4,4,4-trifluoro-3-phenylcrotonate (**5a**)

Yield: 76%: *E*-**5a** : ^{1}H NMR ($CDCl_3$) δ 5.27 (s, 2H), 6.37 (s, 2H), 7.35 ~ 7.45 (m, 10H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ -60.52 (s, 3F); *Z*-**5a** : ^{1}H NMR ($CDCl_3$) δ 5.02 (s, 2H), 6.65 (q, *J* = 1.2 Hz, 2H), 7.35 ~ 7.45 (m, 10H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ -68.03 (s, 3F); IR (neat) 3065 (m), 3036 (m), 1736 (vs), 1656 (m), 1448 (s), 1364 (vs), 1284 (vs), 1170 (vs), 1128 (vs), 1003 (s), 949 (m) cm^{-1}; HRMS (FAB) Calcd for (M+H) $C_{17}H_{14}F_3O_2$: 307.0947, Found 307.0951.

Reference

(1) Ishihara, T.; Maekawa, T.;Yamasaki, Y.; Ando, T. *J. Fluorine Chem.* **1987**, *34*, 323-335.
(2) Tiers, G.V.D. *J. Org. Chem.* **1964**, *29*, 2038-2039.
(3) Ishihara, T.; Yamasaki, Y.; Ando, T. *Tetrahedron Lett*. **1986**, *27*, 2879-2880.

Benzyl ester(1a)



DFILE	FID
COMNT	Benzyl ester(1a)
DATIM	Sat Nov 26 18:06:28 2005
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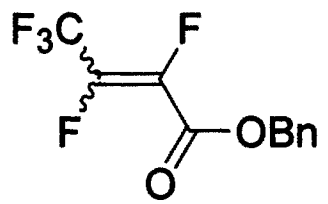
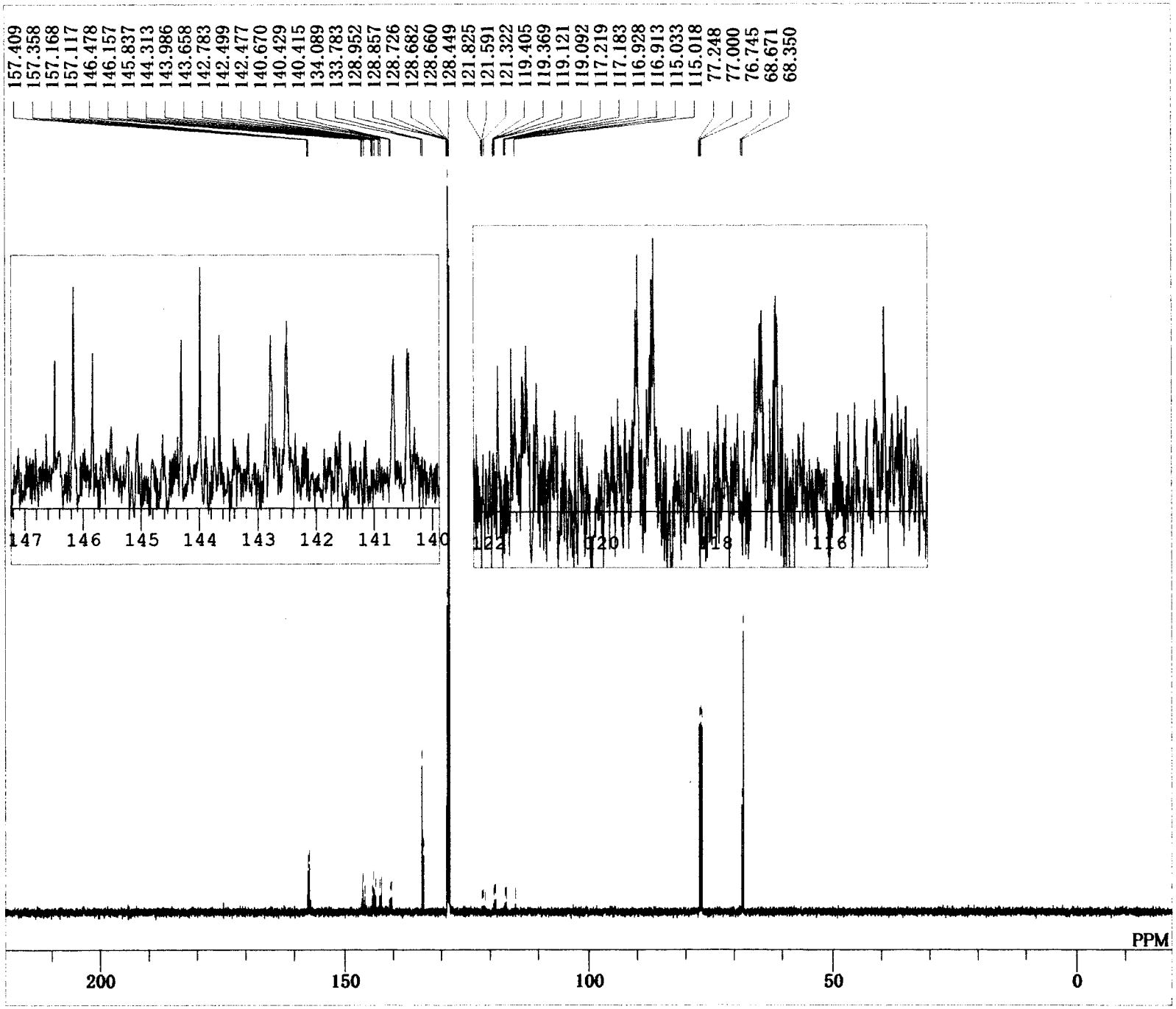
EXMOD	zg30
OBFRQ	500.13 MHz
OBSET	3.08 KHz
OBFIN	8.51 Hz
POINT	32768
FREQU	10330.58 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	297.1 c
SLVNT	CDCl3
EXREF	7.26 ppm
BF	0.10 Hz
RGAIN	574



1a

Benzyl Ester (1a)



DFILE	Benzyl ester(C).als
COMNT	Benzyl Ester (1a)
DATIM	Sat Nov 19 17:38:04 2005
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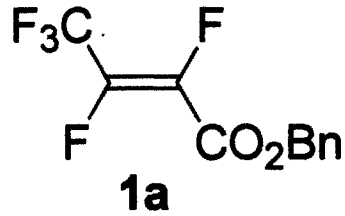
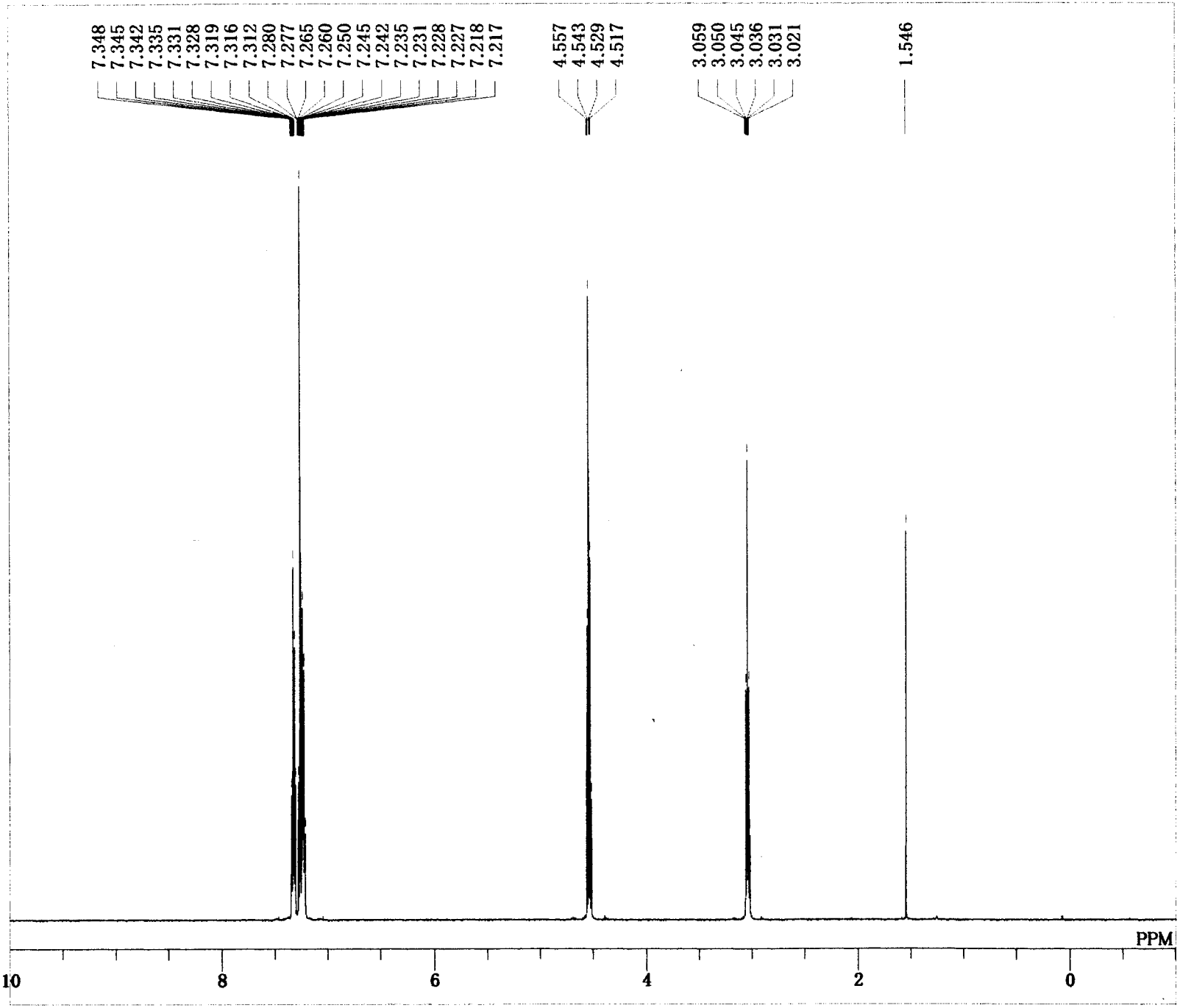
OBSET	0.36 KHz
OBFIN	4.30 Hz
POINT	32768
FREQU	30030.03 Hz
SCANS	256
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	297.0 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	1.00 Hz
RGAIN	3649

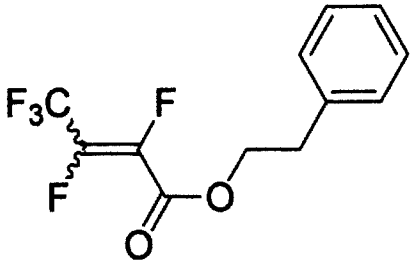


1a

Phenethyl ester(1b)

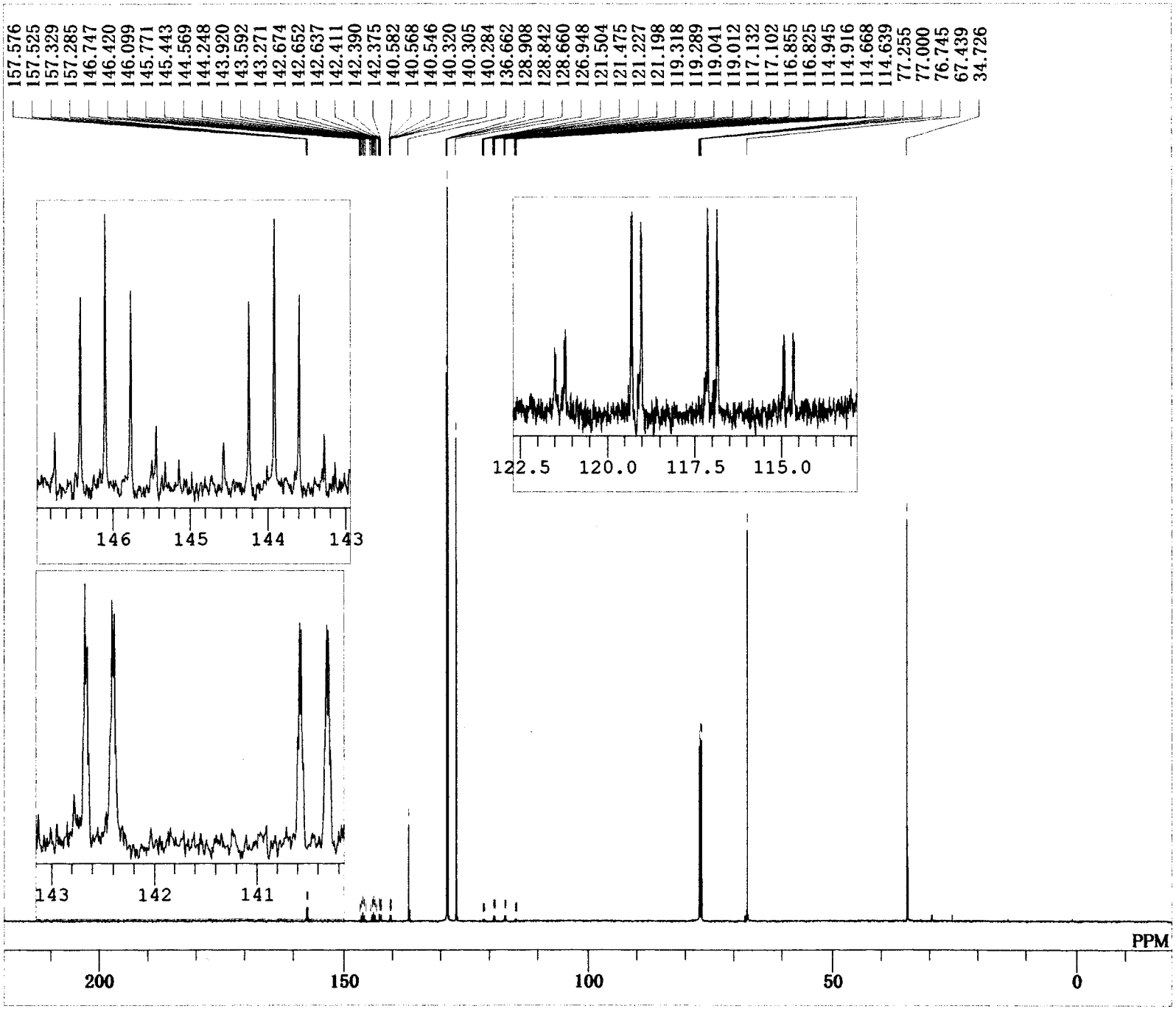


DFILE	fid
COMNT	Phenethyl ester(1b)
DATIM	Sat Feb 24 17:01:33 2007
OBNUC	1H
EXMOD	zg30
OBFRQ	500.13 MHz
OBSET	3.08 KHz
OBFIN	8.51 Hz
POINT	32768
FREQU	10330.58 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	294.1 c
SLVNT	CDCl3
EXREF	7.26 ppm
BF	0.10 Hz
RGAIN	812

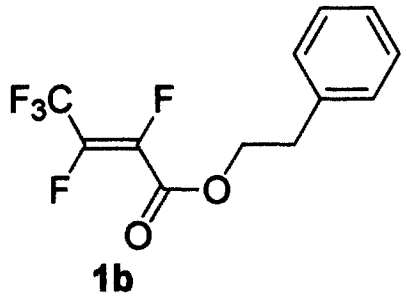


1b

Phenethyl ester(1b)

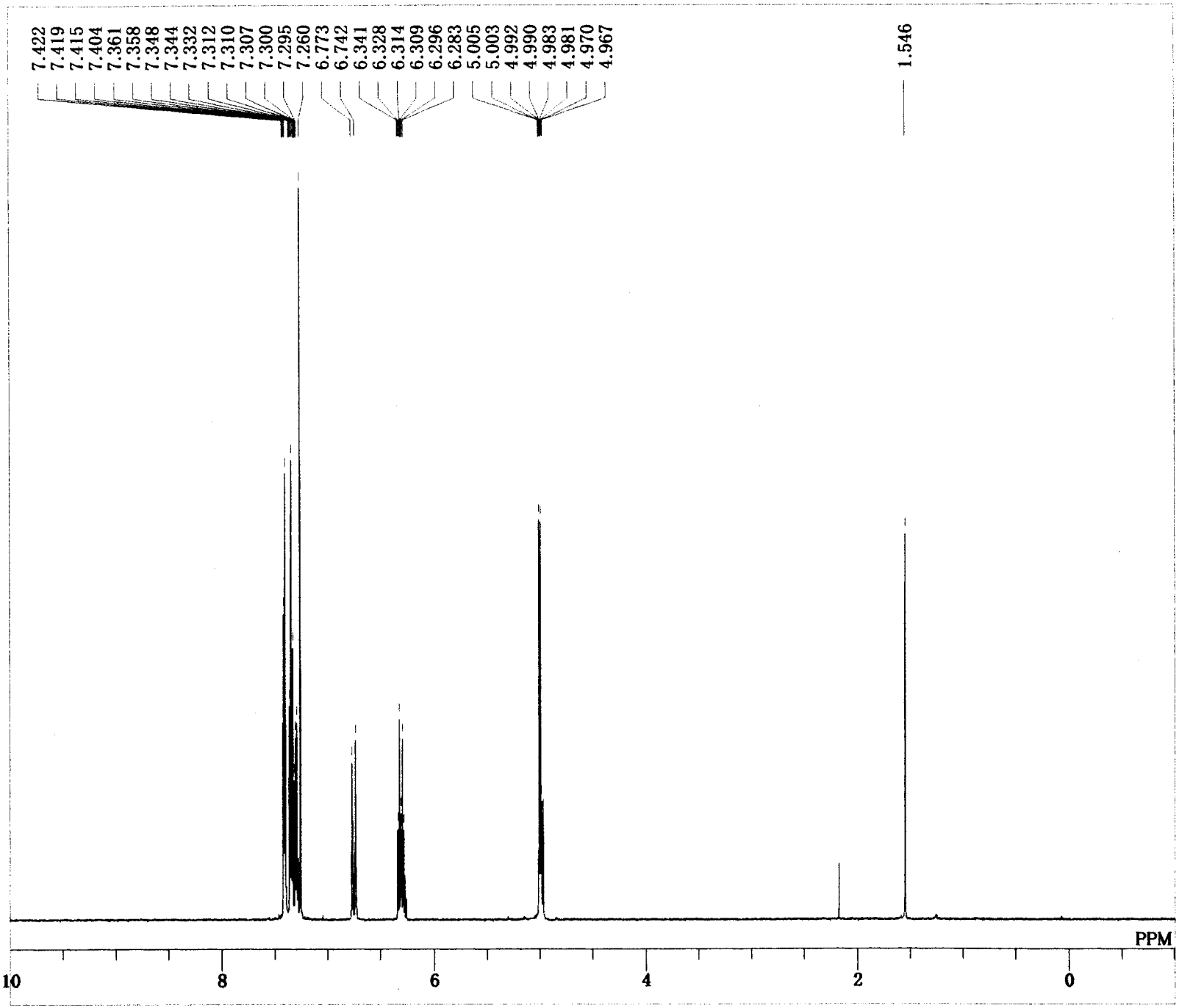


DFILE	phenethyl ester(C).als
COMNT	Phenethyl ester(1b)
DATIM	Wed Feb 21 09:22:11 200
OBNUC	13C
EXMOD	zgpg30
OBFRQ	125.77 MHz
OBSET	0.36 KHz
OBFIN	4.30 Hz
POINT	32768
FREQU	30030.03 Hz
SCANS	25600
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	294.1 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	1.00 Hz
RGAIN	1625

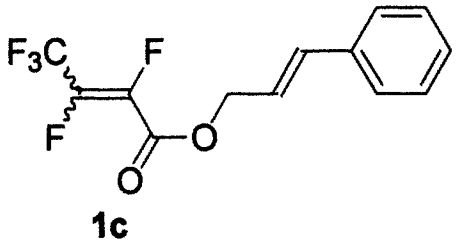


1b

Cinnamyl ester (1c)

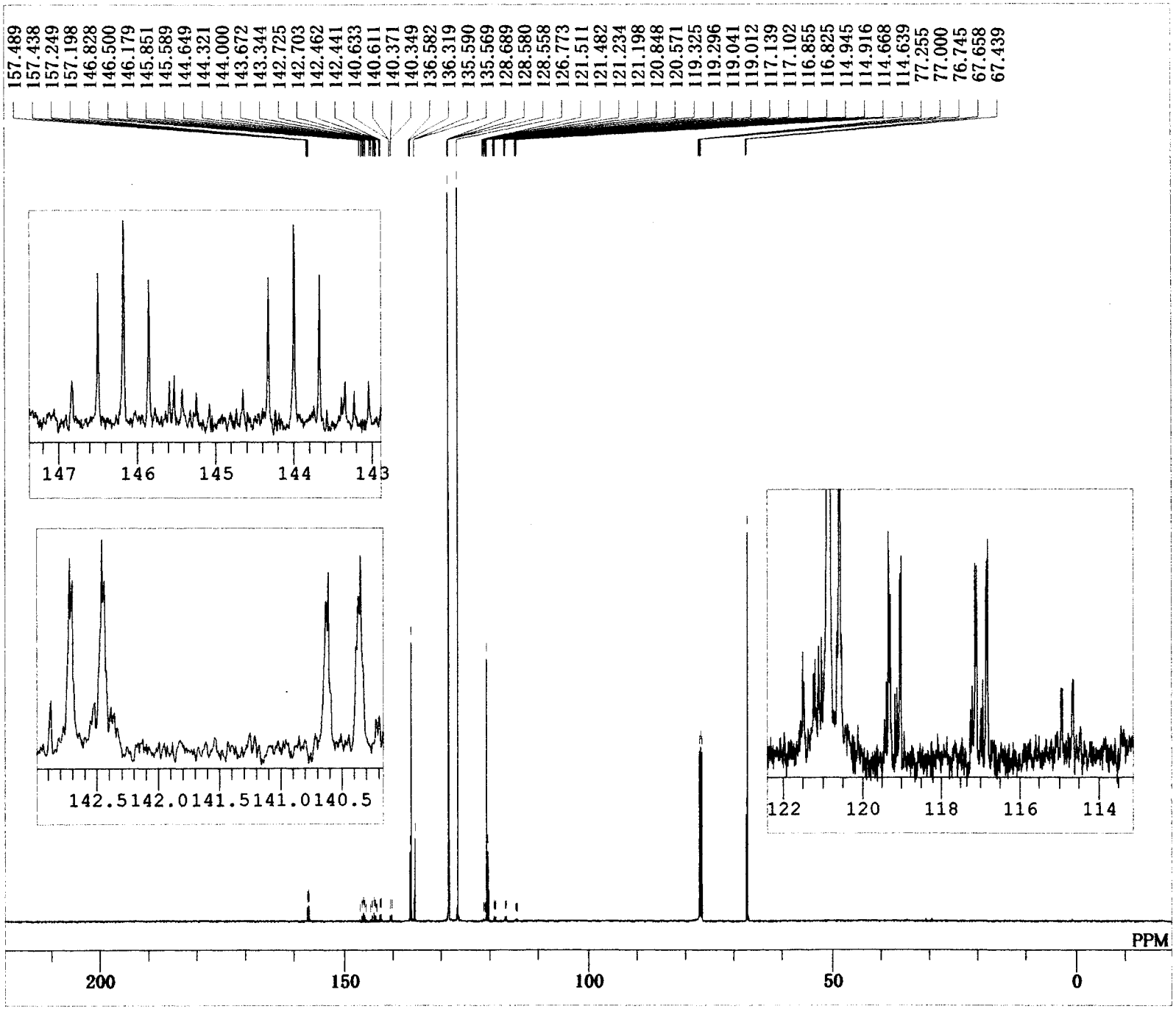


DFILE	fid
COMNT	Cinnamyl ester (1c)
DATIM	Wed Feb 21 21:14:33 200
OBNUC	1H
EXMOD	zg30
OBFRQ	500.13 MHz
OBSET	3.08 KHz
OBFIN	8.51 Hz
POINT	32768
FREQU	10330.58 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	294.4 c
SLVNT	CDCl3
EXREF	7.26 ppm
BF	0.10 Hz
RGAIN	1024

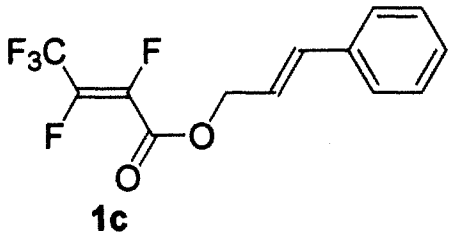


1c

Cinnamyl Ester(1c)

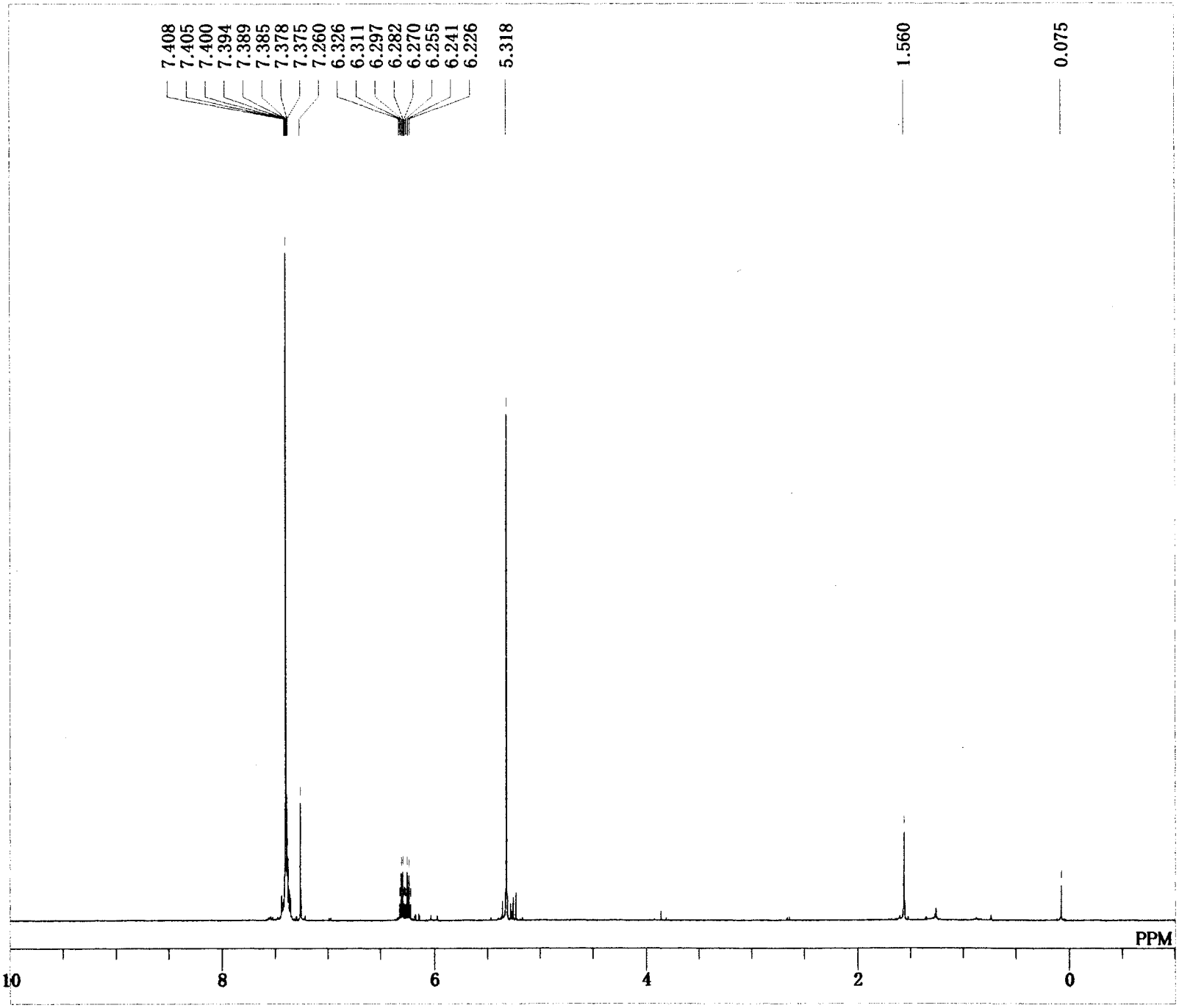


DFILE	cinnamyl ester(C).als
COMNT	Cinnamyl Ester(1c)
DATIM	Tue Feb 27 09:39:19 2007
OBNUC	13C
EXMOD	zgpg30
OBFRQ	125.77 MHz
OBSET	0.36 KHz
OBFIN	4.30 Hz
POINT	32768
FREQU	30030.03 Hz
SCANS	25600
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	294.8 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	1.00 Hz
RGAIN	3649

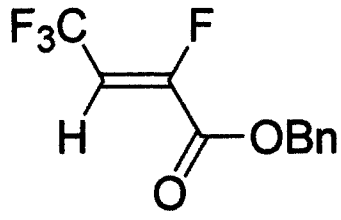


1c

Benzyl ester(reduction product)(4a-H)

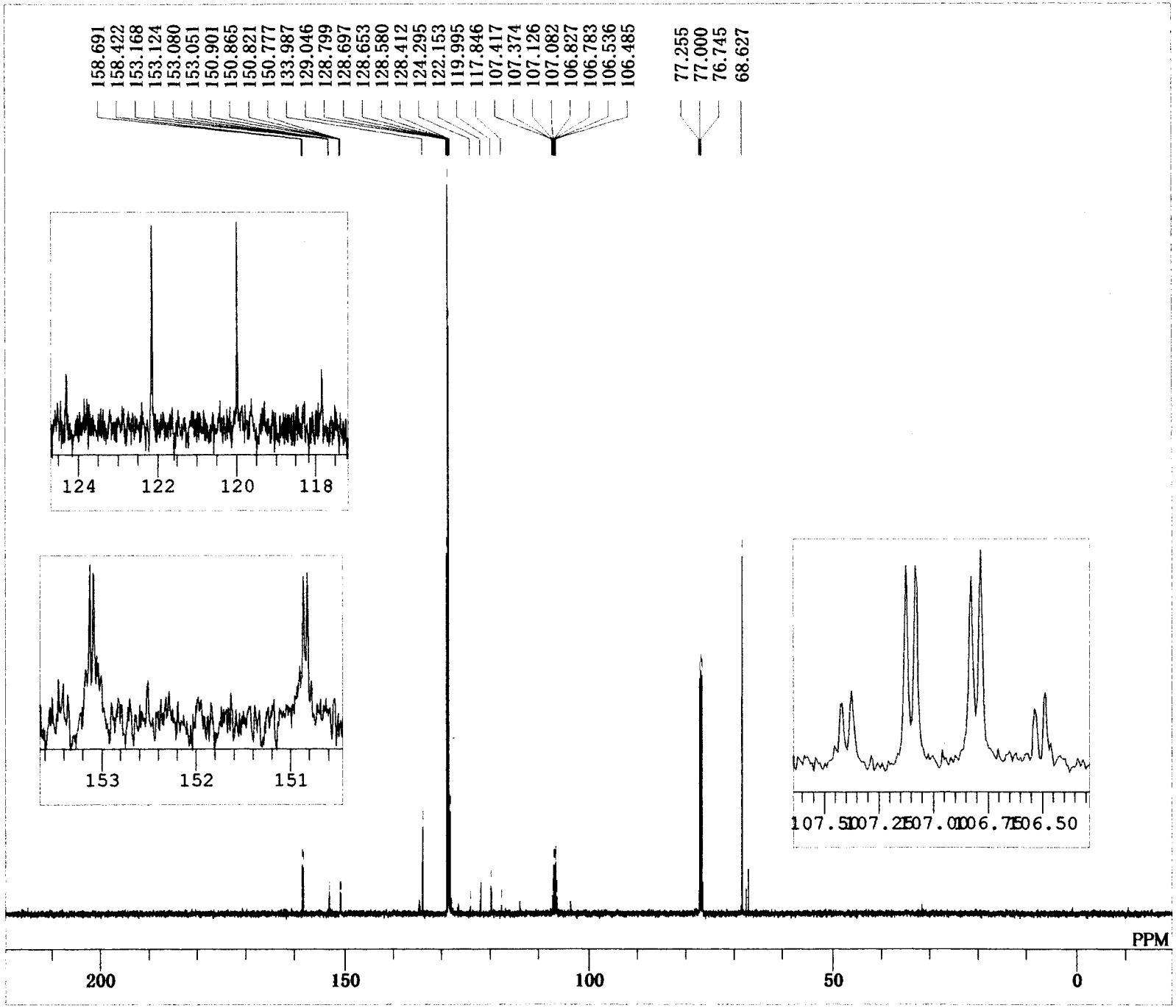


DFILE	FID
COMNT	Benzyl ester(reduction prc
DATIM	Wed Feb 22 20:45:19 200(
OBNUC	1H
EXMOD	zg30
OBFRQ	500.13 MHz
OBSET	3.08 KHz
OBFIN	8.51 Hz
POINT	32768
FREQU	10330.58 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	295.7 c
SLVNT	CDCl3
EXREF	7.26 ppm
BF	0.10 Hz
RGAIN	512

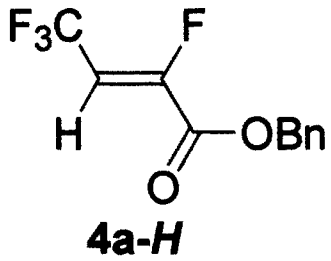


4a-*H*

Benzyl ester(reduction product)

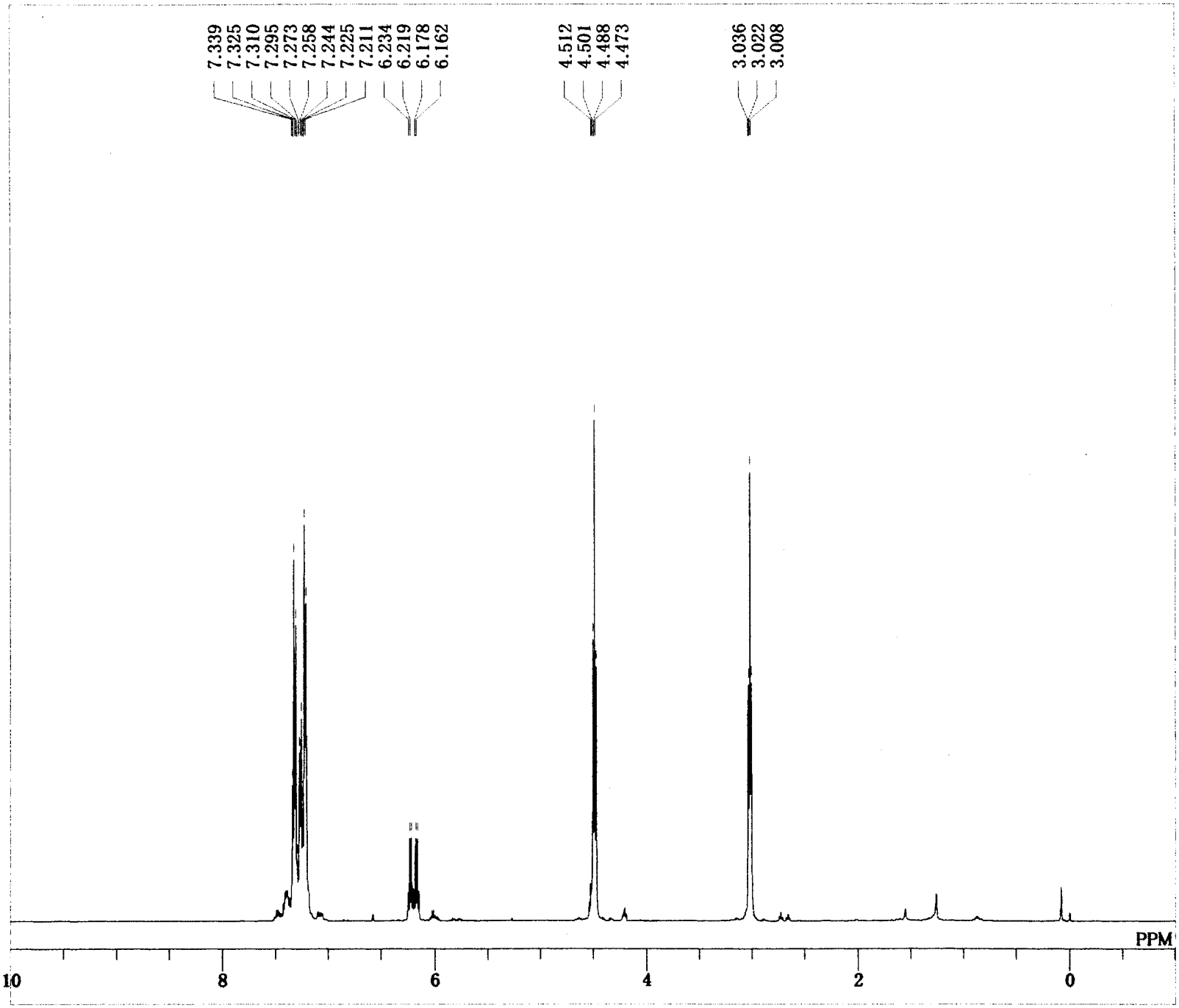


DFILE	Benzyl(reduction)(C).als
COMNT	Benzyl ester(reduction prc
DATIM	Sat Feb 25 20:33:54 2006
OBNUC	13C
EXMOD	zgpg30
OBFRQ	125.77 MHz
OBSET	0.36 KHz
OBFIN	4.30 Hz
POINT	32768
FREQU	30030.03 Hz
SCANS	256
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	295.9 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	1.00 Hz
RGAIN	3649

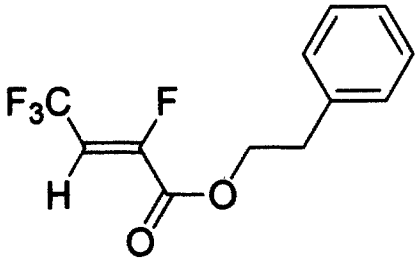


4a-*H*

Phenethyl ester(reduction product)(4b-H)

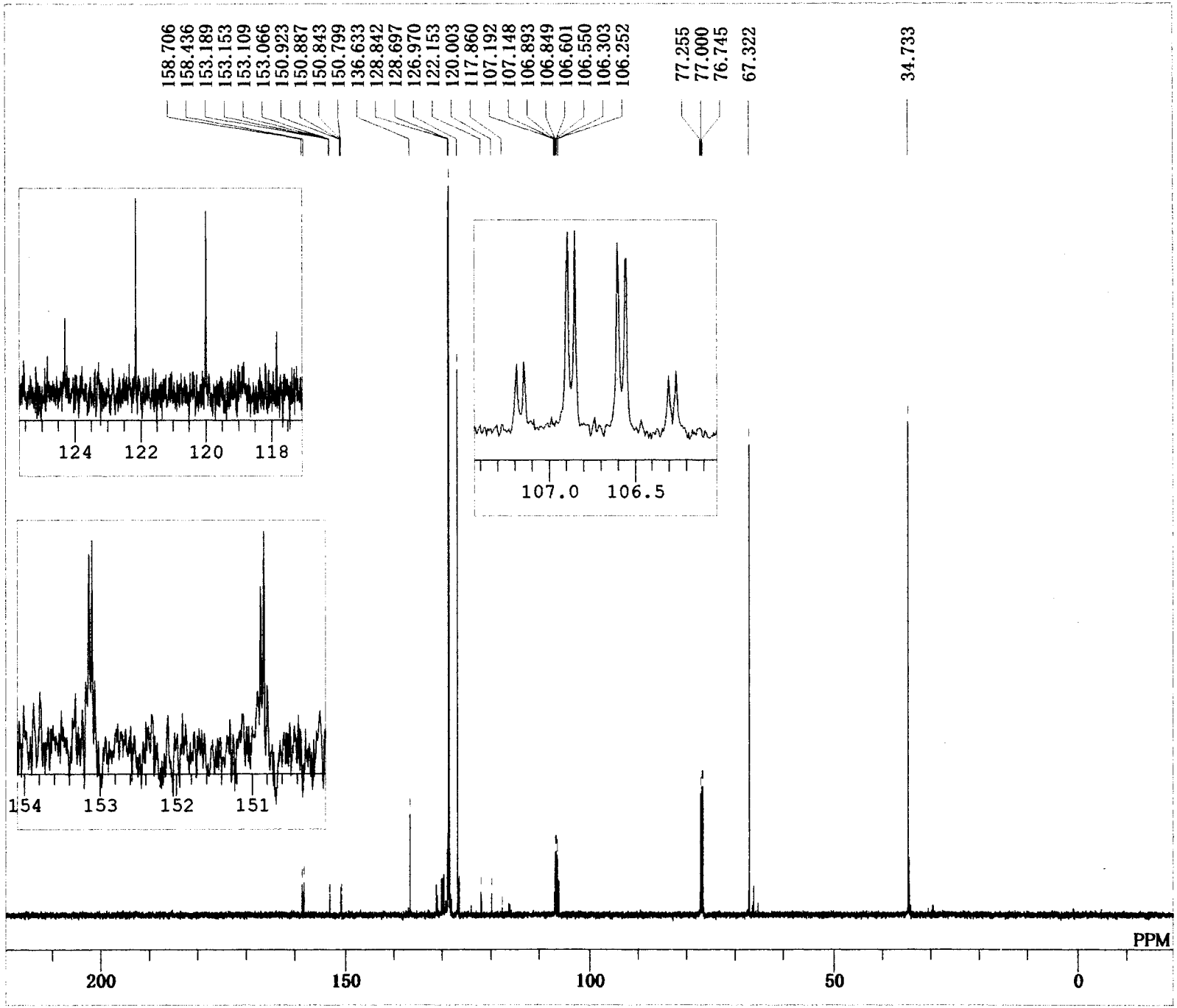


DFILE	fid
COMNT	Phenethyl ester(reduction
DATIM	Sat Feb 24 15:42:34 2007
OBNUC	1H
EXMOD	zg30
OBFRQ	500.13 MHz
OBSET	3.08 KHz
OBFIN	8.51 Hz
POINT	32768
FREQU	10330.58 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	294.3 c
SLVNT	CDCl3
EXREF	0.00 ppm
BF	1.00 Hz
RGAIN	128

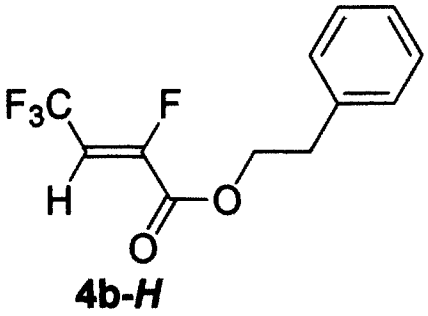


4b-*H*

Phenethyl ester(reduction product)(4b-H)

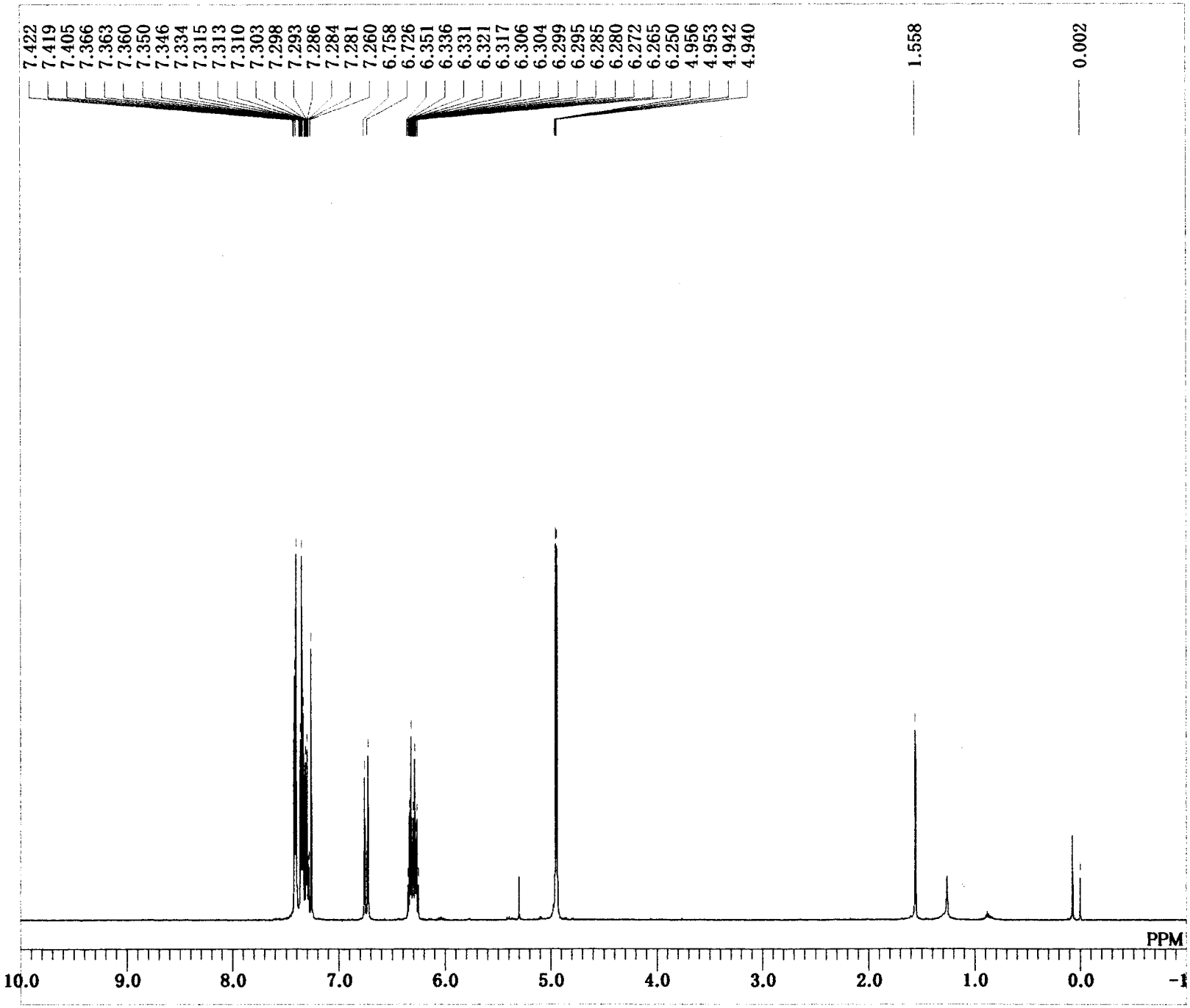


DFILE	Phenethyl(reduction)(C).al
COMNT	Phenethyl ester(reduction
DATIM	Sat Feb 24 15:51:23 2007
OBNUC	13C
EXMOD	zgpg30
OBFRQ	125.77 MHz
OBSET	0.36 KHz
OBFIN	4.30 Hz
POINT	32768
FREQU	30030.03 Hz
SCANS	256
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	294.7 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	1.00 Hz
RGAIN	3649

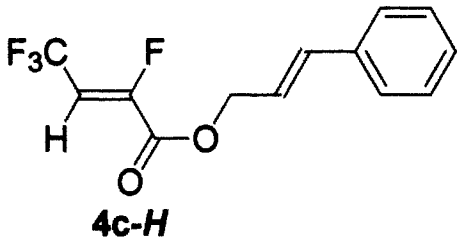


4b-*H*

Cinnamyl ester(reduction product)(4c-H)

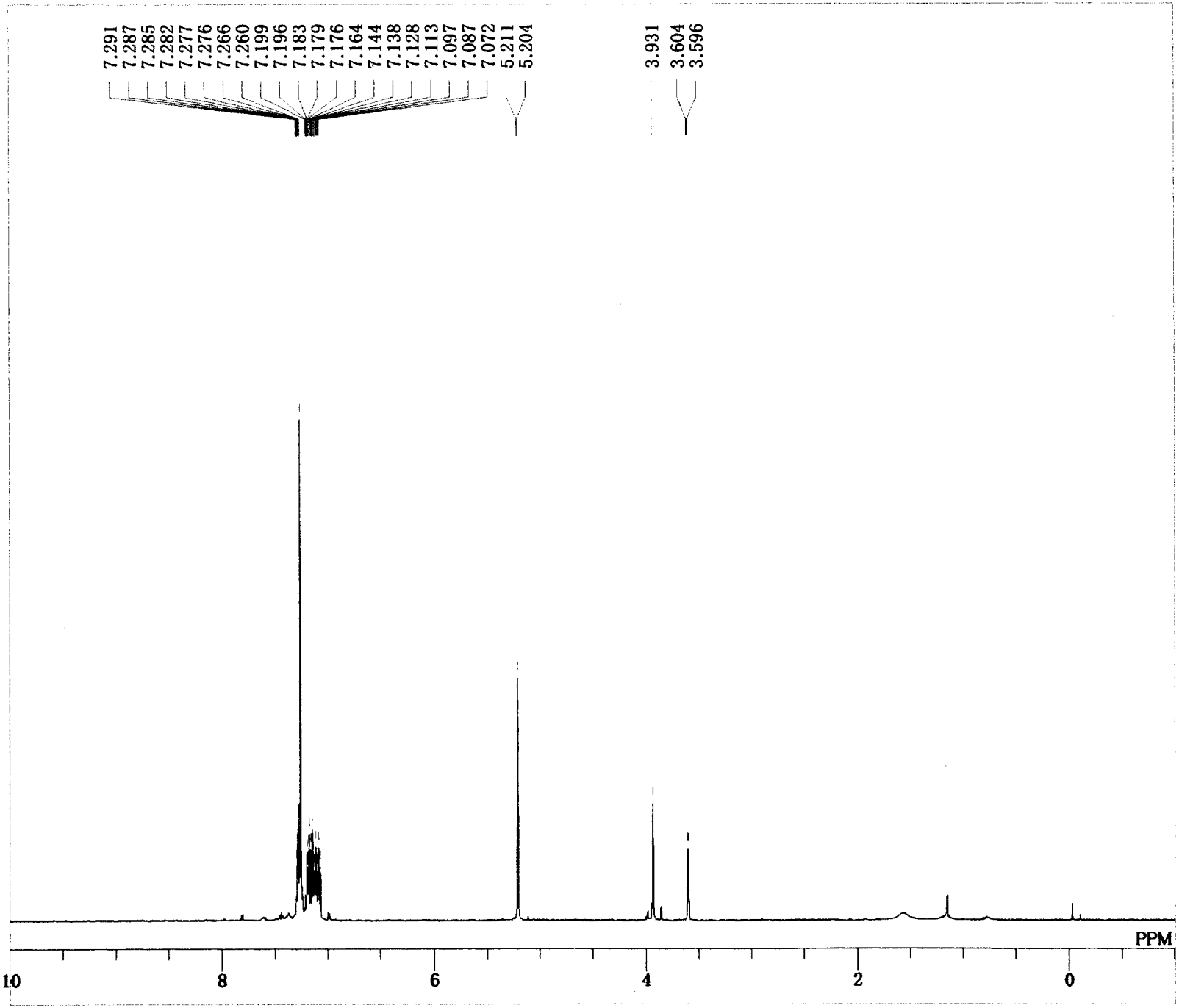


DFILE	fid
COMNT	Cinnamyl ester(reduction p
DATIM	Fri Feb 23 18:10:52 2007
OBNUC	1H
EXMOD	zg30
OBFRQ	500.13 MHz
OBSET	3.08 KHz
OBFIN	8.51 Hz
POINT	32768
FREQU	10330.58 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	294.7 c
SLVNT	CDCl3
EXREF	7.26 ppm
BF	0.10 Hz
RGAIN	512

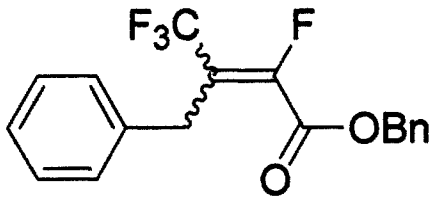


4c-*H*

Addition-elimination product(3a)

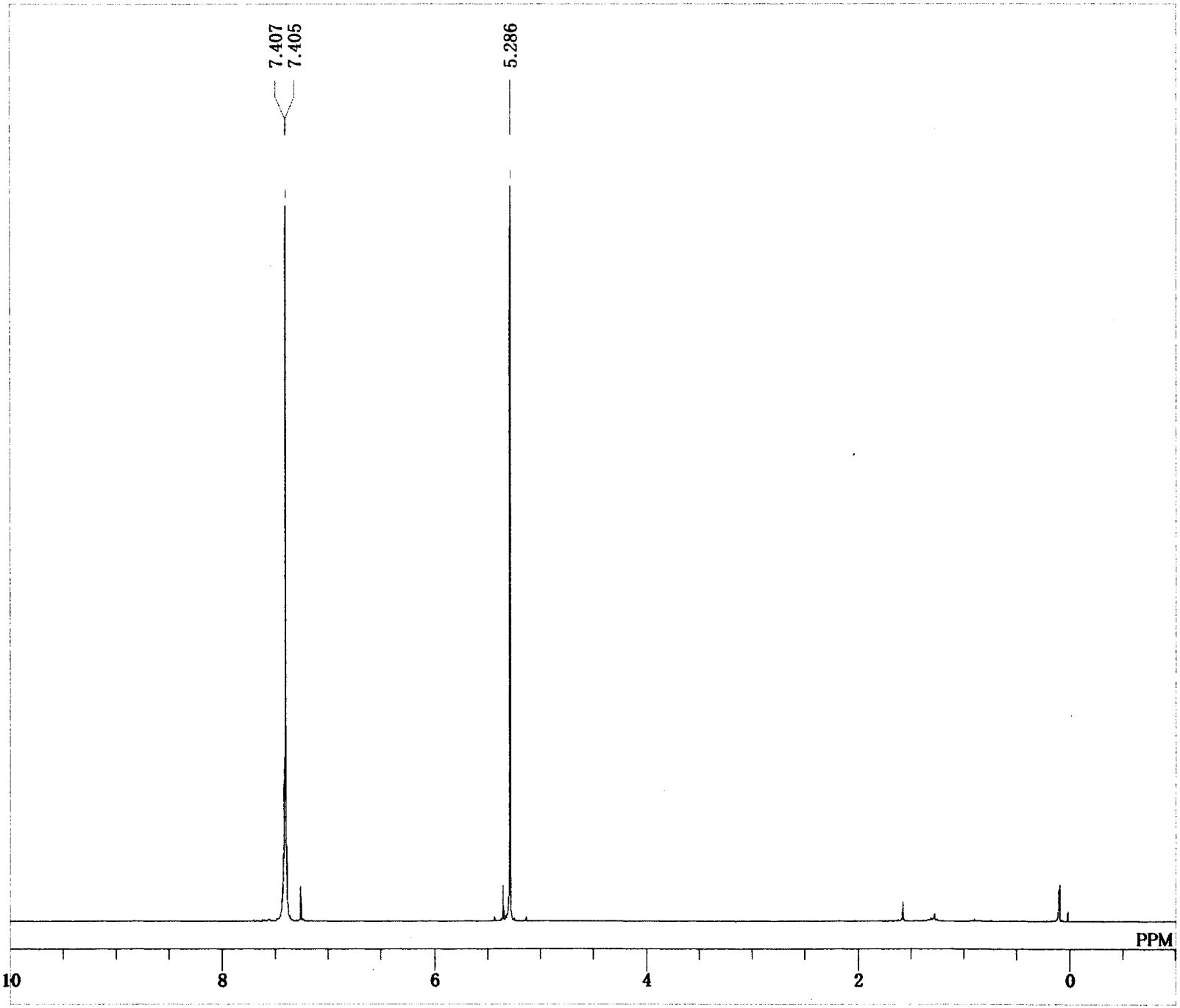


DFILE	FID
COMNT	Addition-elimination prodt
DATIM	Fri Jun 30 20:25:07 2006
OBNUC	1H
EXMOD	zg30
OBFRQ	500.13 MHz
OBSET	3.08 KHz
OBFIN	8.51 Hz
POINT	32768
FREQU	10330.58 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	299.6 c
SLVNT	CDCl3
EXREF	7.26 ppm
BF	0.10 Hz
RGAIN	287

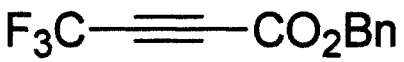


3a

Benzyl 4,4,4-trifluorobutynoate (6a)

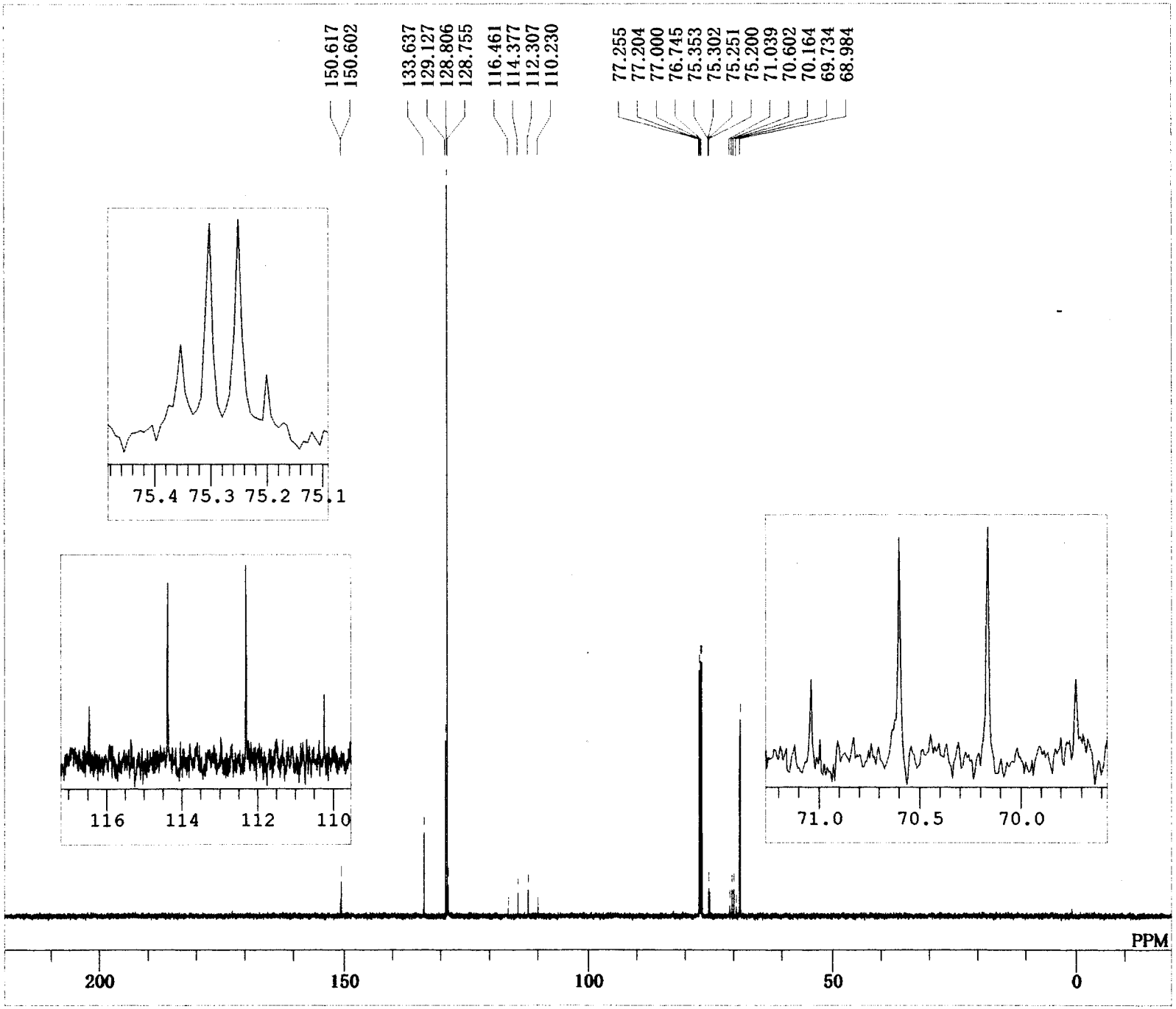


DFILE	FID
COMNT	Benzyl 4,4,4-trifluorobuty
DATIM	Mon Jan 30 17:15:00 2006
OBNUC	1H
EXMOD	zg30
OBFRQ	500.13 MHz
OBSET	3.08 KHz
OBFIN	8.51 Hz
POINT	32768
FREQU	10330.58 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	294.1 c
SLVNT	CDCl3
EXREF	7.26 ppm
BF	0.10 Hz
RGAIN	128

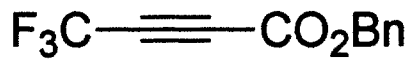


6a

Benzyl 4,4,4-trifluorobutynoate (6a)

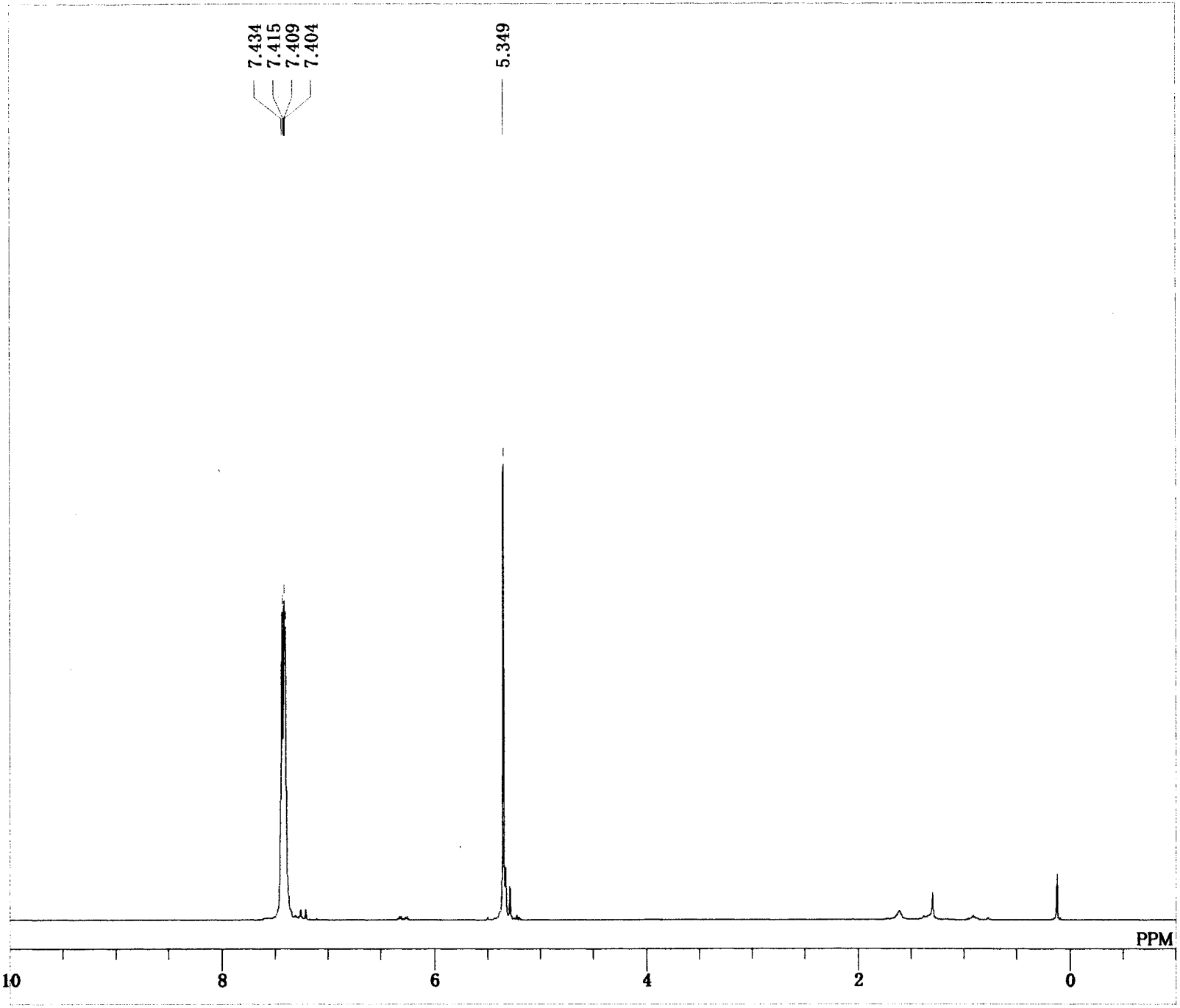


DFILE	FID
COMNT	Benzyl 4,4,4-trifluorobuty
DATIM	Mon Jan 30 17:22:47 2006
OBNUC	13C
EXMOD	zgpg30
OBFRQ	125.77 MHz
OBSET	0.36 KHz
OBFIN	4.30 Hz
POINT	32768
FREQU	30030.03 Hz
SCANS	256
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	295.1 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	1.00 Hz
RGAIN	3649

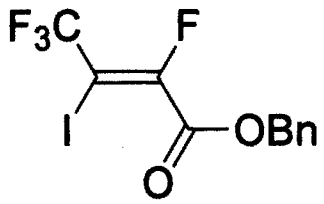


6a

iodide coupling

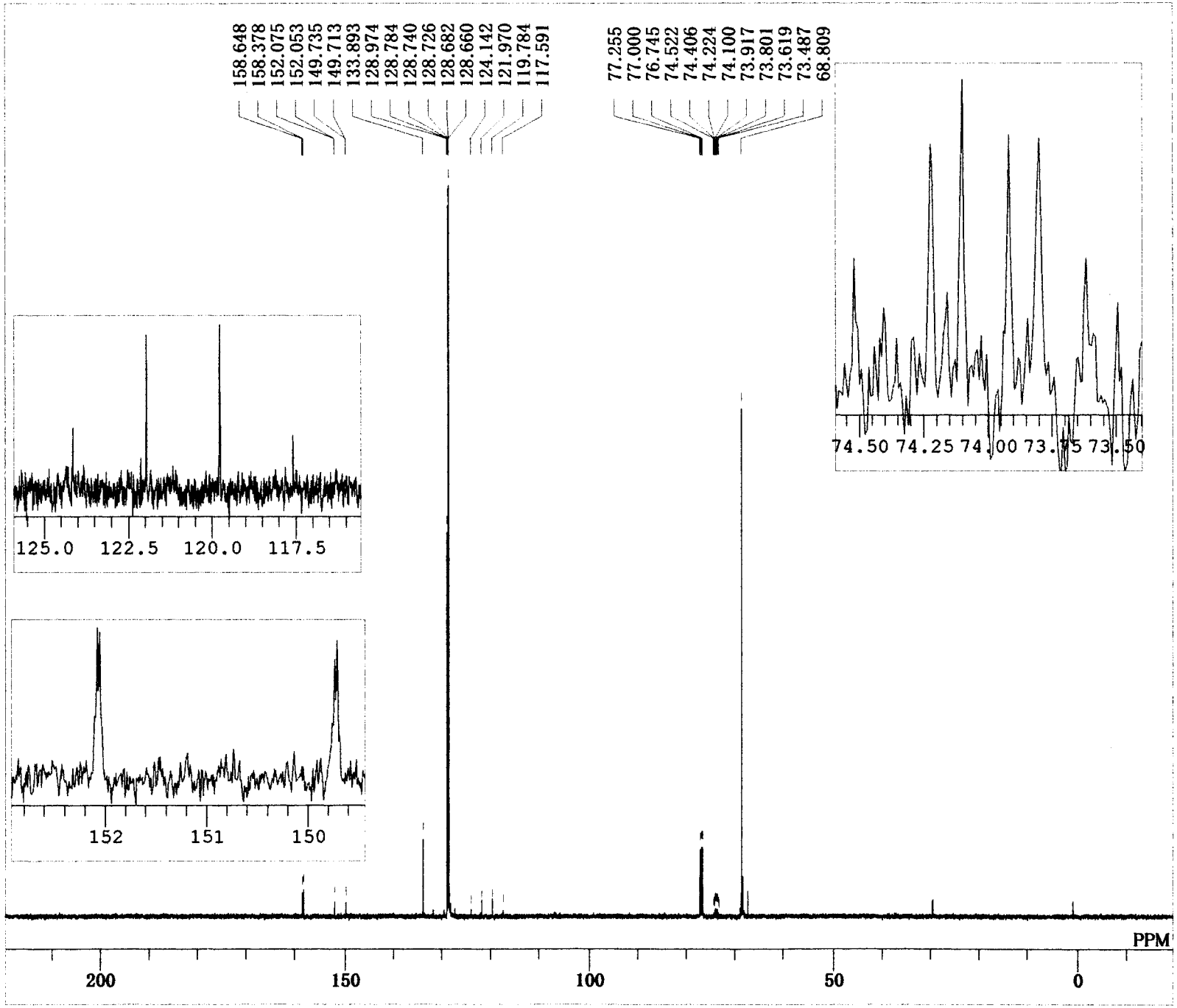


DFILE	FID
COMNT	iodide coupling
DATIM	Wed Jul 12 12:02:01 2006
OBNUC	1H
EXMOD	zg30
OBFRQ	500.13 MHz
OBSET	3.08 KHz
OBFIN	8.51 Hz
POINT	32768
FREQU	10330.58 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	299.7 c
SLVNT	CDCl3
EXREF	7.26 ppm
BF	0.10 Hz
RGAIN	128



4a (*E*/ = I)

iodide-coupling



DFILE	iodine-coupling(C).als
COMNT	iodide-coupling
DATIM	Wed Jul 12 12:21:05 2006
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EXMOD	zgpg30
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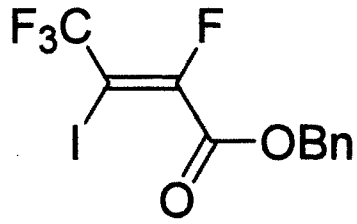
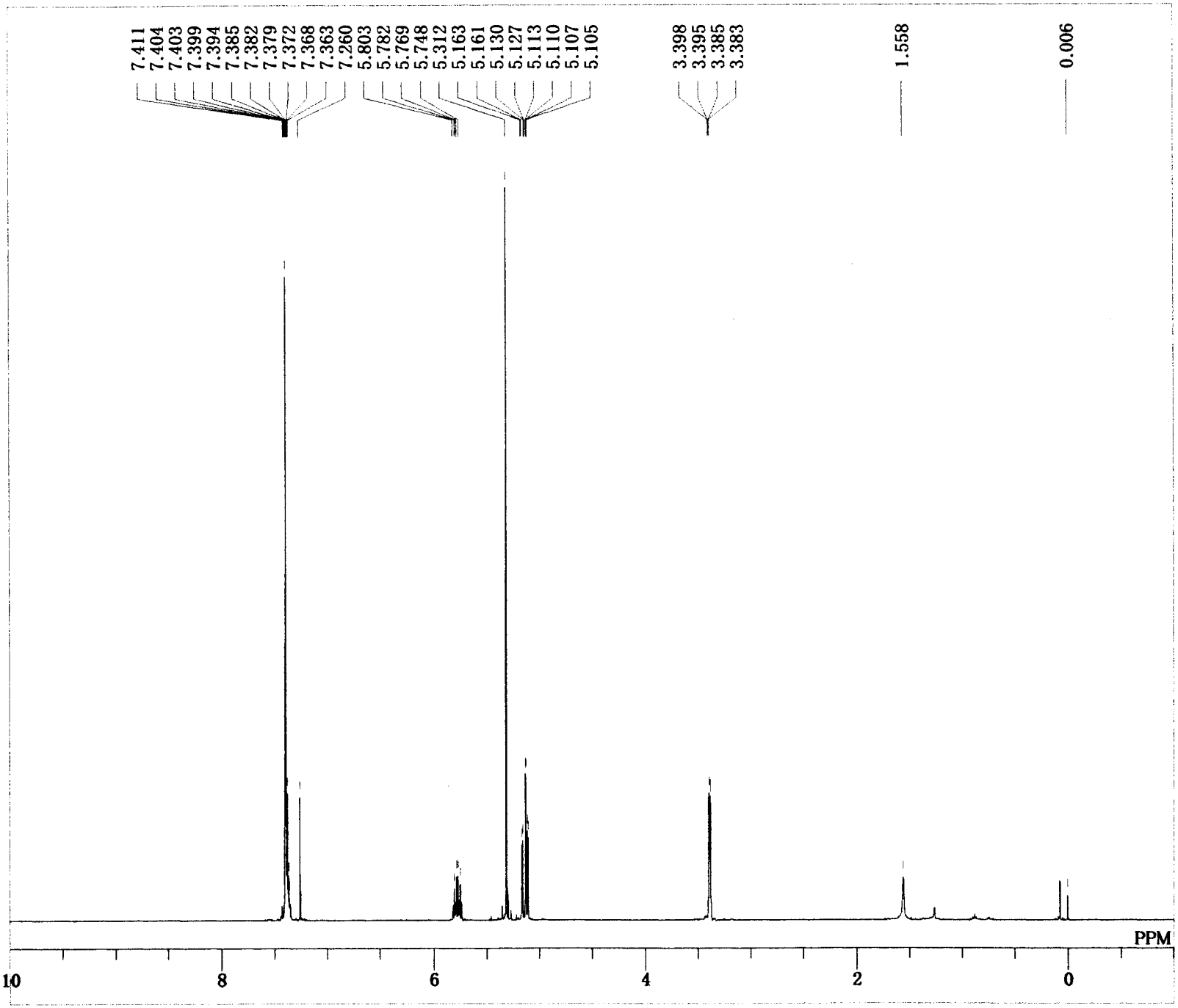
OBSET	0.36 KHz
OBFIN	4.30 Hz
POINT	32768
FREQU	30030.03 Hz
SCANS	256
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	300.0 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	1.00 Hz
RGAIN	2298

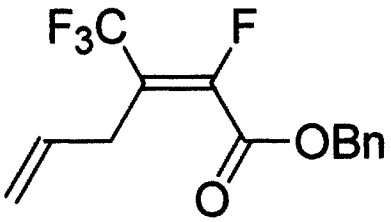


4a (*EI* = I)

allyl-coupling

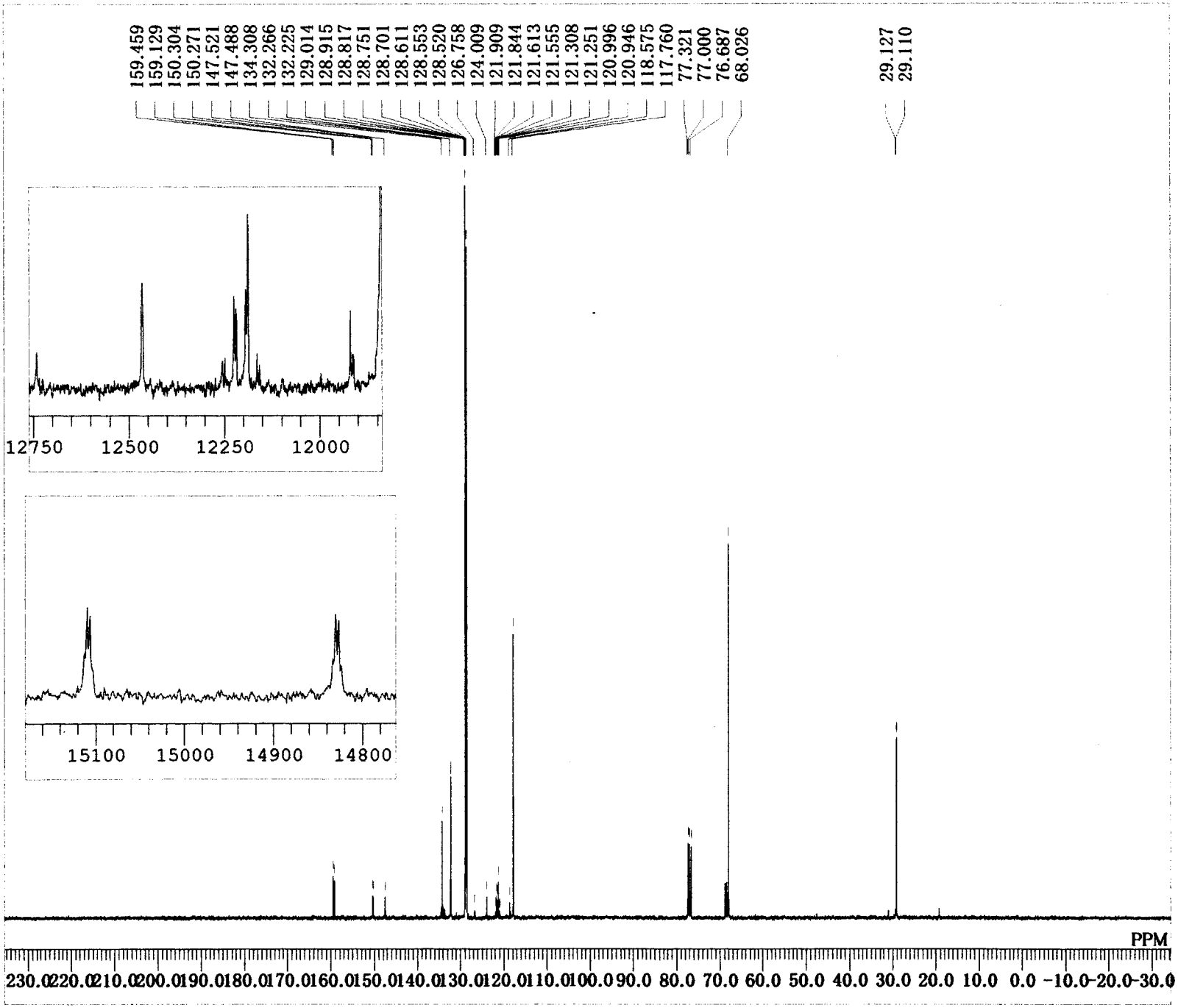


DFILE	FID
COMNT	allyl-coupling
DATIM	Mon May 22 10:54:22 200
OBNUC	1H
EXMOD	zg30
OBFRQ	500.13 MHz
OBSET	3.08 KHz
OBFIN	8.51 Hz
POINT	32768
FREQU	10330.58 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	300.2 c
SLVNT	CDCl3
EXREF	7.26 ppm
BF	0.10 Hz
RGAIN	362

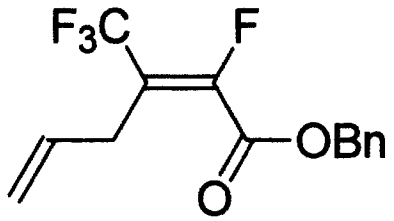


4a (*EI* = allyl)

allyl coupling

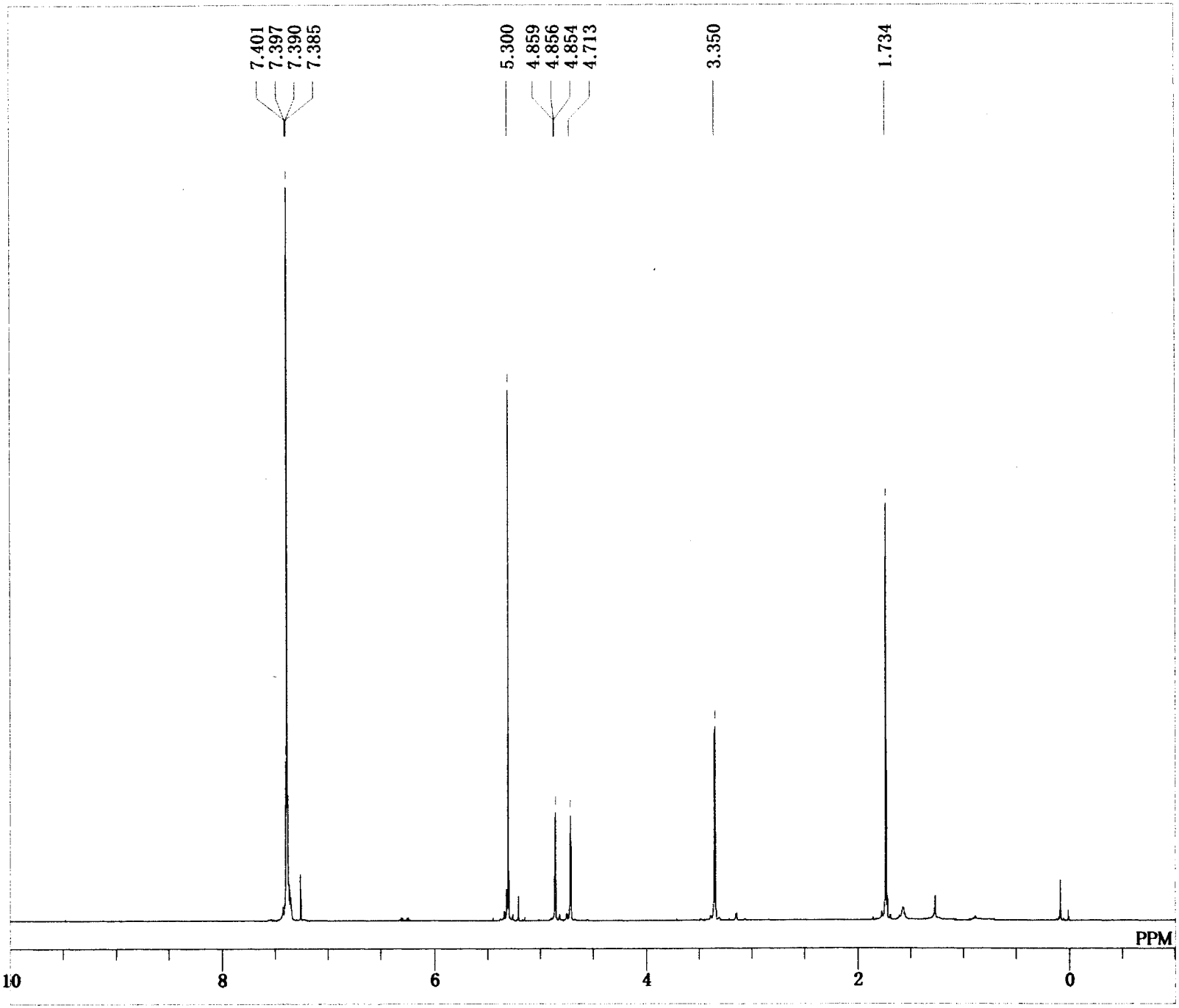


DFILE	allyl-coupling(C).als
COMNT	allyl coupling
DATIM	Wed Jun 06 14:20:43 2007
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27118.64 Hz
SCANS	256
ACQTM	1.2083 sec
PD	1.7920 sec
PW1	5.70 usec
IRNUC	1H
CTEMP	24.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.00 Hz
RGAIN	24

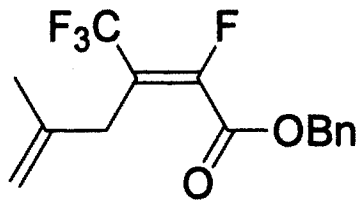


4a (*EI* = allyl)

methallyl coupling

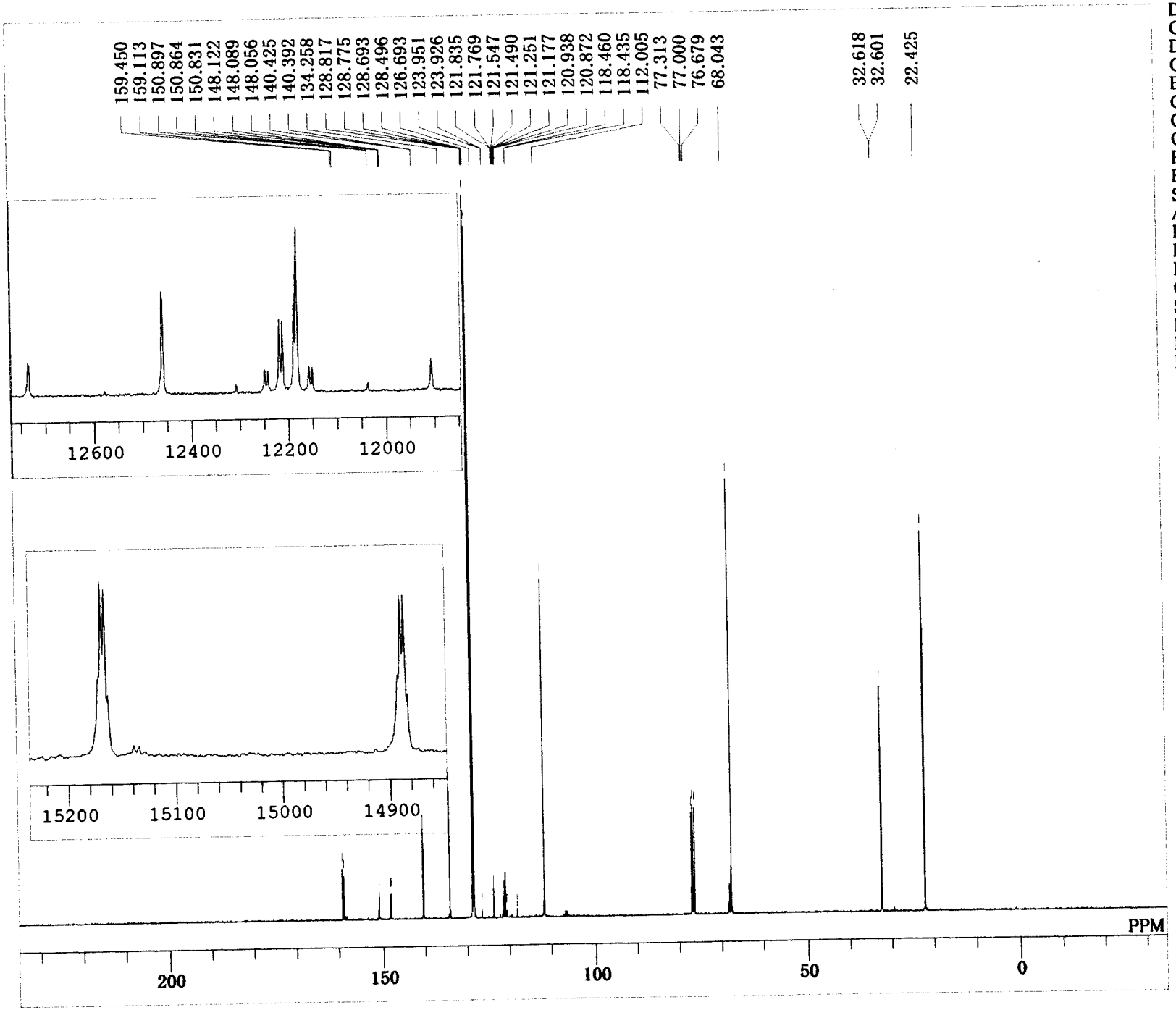


DFILE	FID
COMNT	methallyl coupling
DATIM	Tue May 23 09:19:22 200(
OBNUC	1H
EXMOD	zg30
OBFRQ	500.13 MHz
OBSET	3.08 KHz
OBFIN	8.51 Hz
POINT	32768
FREQU	10330.58 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	298.4 c
SLVNT	CDCl3
EXREF	7.26 ppm
BF	0.10 Hz
RGAIN	128

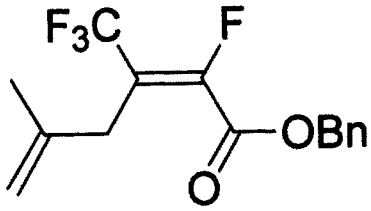


4a (*EI* = methallyl)

methallyl coupling

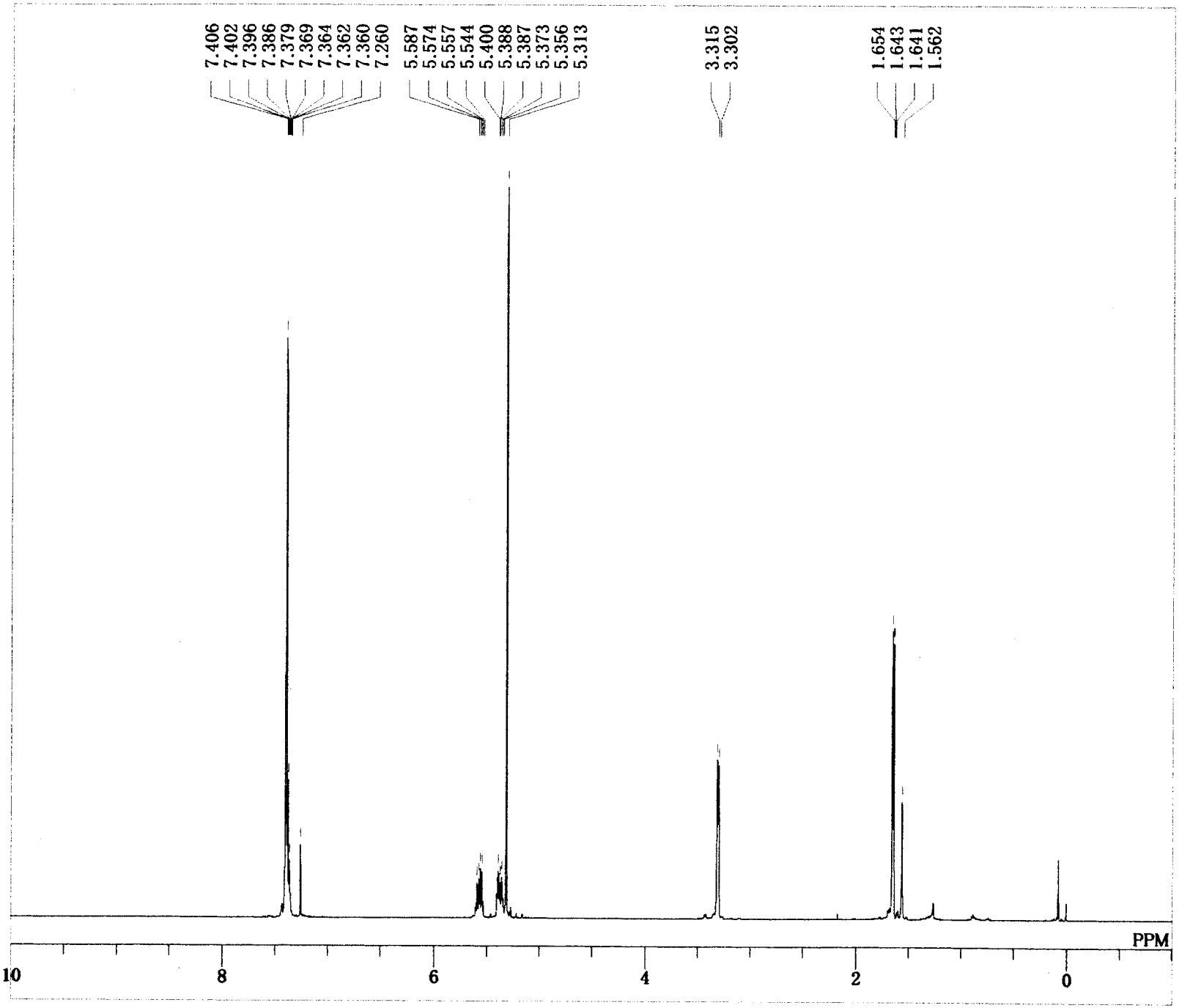


DFILE	methallyl-coupling(C).als
COMNT	methallyl coupling
DATIM	Tue Jun 05 08:16:10 2007
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27118.64 Hz
SCANS	13600
ACQTM	1.2083 sec
PD	1.7920 sec
PW1	5.70 usec
IRNUC	1H
CTEMP	22.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.00 Hz
RGAIN	24

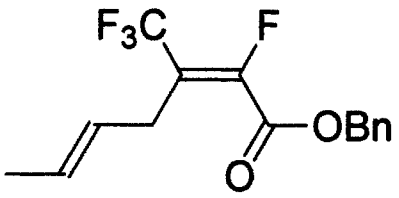


4a (*EI* = methallyl)

crotyl coupling

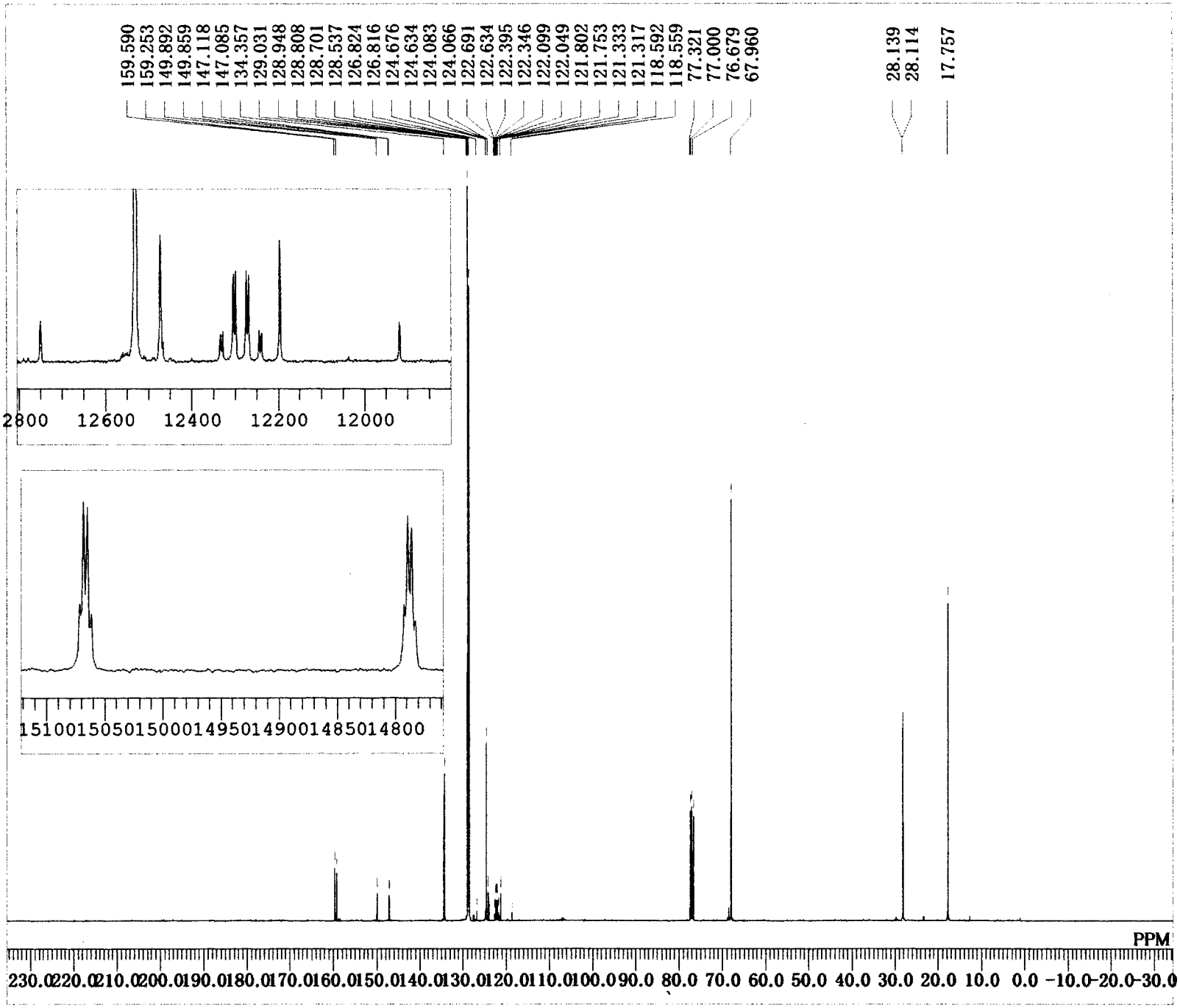


DFILE	FID
COMNT	crotyl coupling
DATIM	Tue May 23 09:36:09 200(
OBNUC	1H
EXMOD	zg30
OBFRQ	500.13 MHz
OBSET	3.08 KHz
OBFIN	8.51 Hz
POINT	32768
FREQU	10330.58 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	298.5 c
SLVNT	CDCl3
EXREF	7.26 ppm
BF	0.10 Hz
RGAIN	228

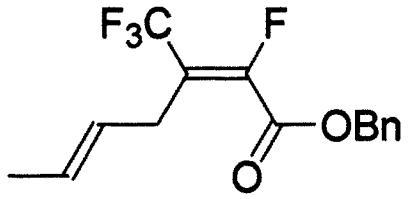


4a (*EI* = crotyl)

Crotyl coupling

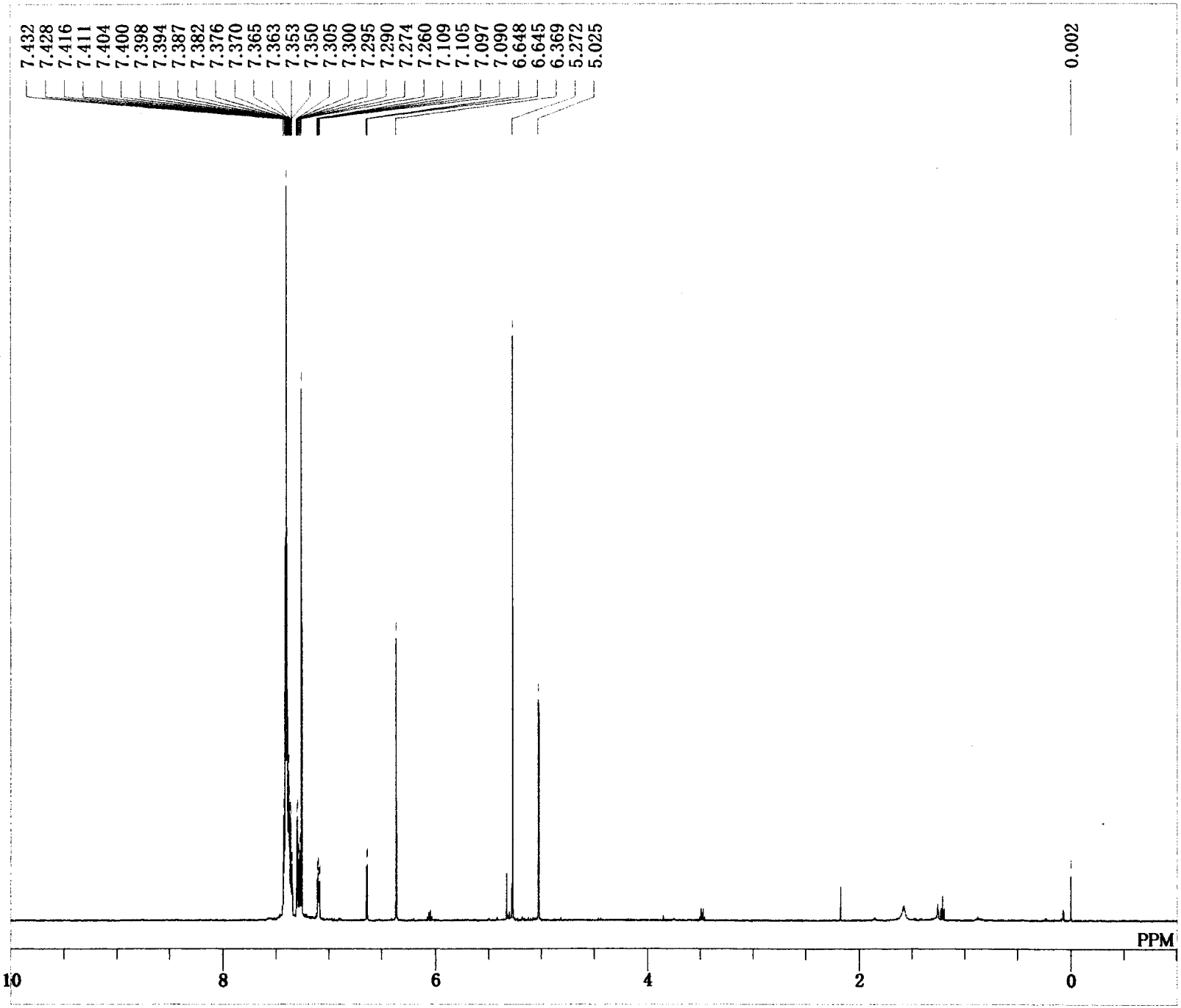


DFILE	crotyl-coupling(C).als
COMNT	Crotyl coupling
DATIM	Wed Jun 06 08:12:58 2007
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27118.64 Hz
SCANS	13600
ACQTM	1.2083 sec
PD	1.7920 sec
PW1	5.70 usec
IRNUC	1H
CTEMP	23.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.00 Hz
RGAIN	24

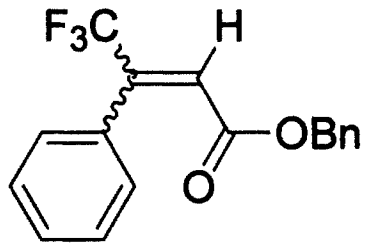


4a (*EI* = crotyl)

Benzyl 4,4,4-trifluoro-3-phenylcrotonate (5a)



DFILE	fid
COMNT	Benzyl 4,4,4-trifluoro-3-p
DATIM	Tue Jan 23 12:44:34 2007
OBNUC	1H
EXMOD	zg30
OBFRQ	500.13 MHz
OBSET	3.08 KHz
OBFIN	8.51 Hz
POINT	32768
FREQU	10330.58 Hz
SCANS	16
ACQTM	0.0000 sec
PD	0.0000 sec
PW1	10.00 usec
IRNUC	
CTEMP	293.8 c
SLVNT	CDCl3
EXREF	7.26 ppm
BF	0.10 Hz
RGAIN	645



5a