Supporting Information

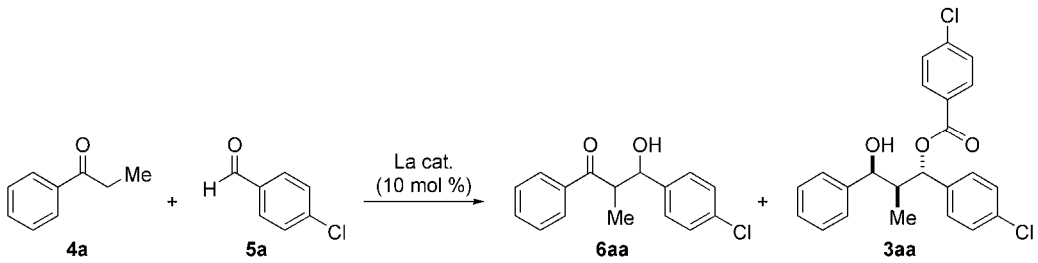
Direct Catalytic Asymmetric Aldol-Tishchenko Reaction

Vijay Gnanadesikan, Yoshihiro Horiuchi, Takashi Ohshima, and Masakatsu Shibasaki*
Graduate School of Pharmaceutical Sciences, The University of Tokyo
Tokyo 113-0033, Japan

Preliminary Studies on Reaction Mechanism

Reaction kinetics:

To get insight into the relationship between aldol product and aldol-Tishchenko product, we initially examined the ratio of aldol product and aldol-Tishchenko product and their stereoselectivities at different time. As shown in Table 1, the reaction consistently delivers racemic aldol products **6aa** with *no diastereoselectivity* and both enantio- and diastereoselectivity were independent of time. On the other hand, aldol-Tishchenko product **3aa** was found to have high levels of enantioselectivity (76-83% ee). These results imply the rapid retro-aldolization of **6aa** and *the aldol-Tishchenko product is not vulnerable for retro-aldol reaction.*

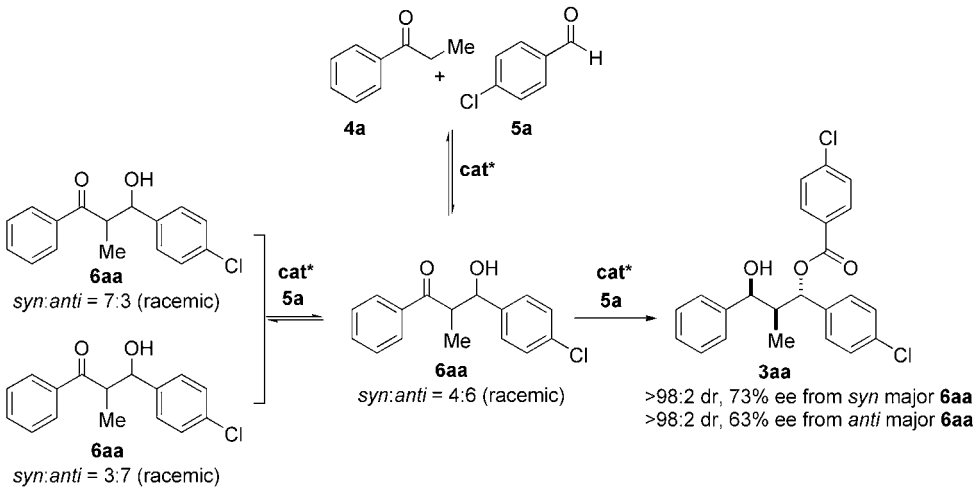


entry	time (d)	**4a**:**6aa**:**3aa** (%)[a]	**6aa** *syn*:*anti* (%)[a]	**6aa** *syn* ee, *anti* ee (%)[b]	**3aa** ee (%)[c]
1	1.5	76:16:8	1:1	racemic, racemic	83%
2	3.5	54:22:24	1:1	racemic, racemic	83%
3	6.5	32:28:40	1:1	racemic, racemic	76%

[a]Determined by ^{1}H NMR analysis of the crude sample. [c]Ee of **6aa** was determined by HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1 mL/min, t_R 18.4 min and 21.3 min (*syn*-aldol **6aa**), 30.8 min and 40.0 min (*anti*-aldol **6aa**), detection at 254 nm]. [c]Ee of **3aa** was determined by HPLC analysis after hydrolysis using NaOMe/MeOH to the corresponding diol **7aa**.

To confirm our interpretation, we next attempted the deliberate retro-aldolization of two independently prepared racemic *syn* or *anti* major aldol products **6aa**. Thus, *syn* major **6aa** (*syn*:*anti* = 7:3)[SI-1] was treated with 4-chlorobenzaldehyde (1.5 eq) in the presence of lanthanum catalyst (10 mol %). Interestingly, after 3.5 days, the reaction gave a mixture of ketone **4a**, aldol products **6aa** (*syn*:*anti* = 4:6, racemic), and Tishchenko product **3aa** (>98:2 dr, 73% ee) in a ratio of 28:36:36. As the reaction proceeded for longer time (6.5 days), ratio of **3aa**:**6aa** increased but the amount of ketone remained to be same.

Similar tendency was observed using *anti* major aldol product **6aa** (*syn*:*anti* = 3:7).[SI-1] After 3.5 days, the reaction gave 33:41:26 ratio of **4a**:**6aa** (*syn*:*anti* = 4:6, racemic):**3aa** (60% ee). These results clearly indicate that the aldol product **6aa** has the strong tendency towards retro-aldol reaction, whereas the aldol-Tishchenko product not only overcome the problematic retro-aldol reaction but also helps to keep the enantio- and diatereoselectivities intact.



From *syn* major **6aa** (*syn*:*anti* = 7:3):

entry	time (d)	**4a**:**6aa**:**3aa** (%)[a]	**6aa** *syn*:*anti* (%)[a]	**6aa** *syn* ee, *anti* ee (%)[b]	**3aa** ee (%)[c]
1	1.5	27:54:19	4:6	racemic, racemic	68%
2	3.5	28:36:36	4:6	racemic, racemic	73%
3	6.5	27:22:51	4:6	racemic, racemic	68%

[a]Determined by ^{1}H NMR analysis of the crude sample. [c]Ee of **6aa** was determined by HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1 mL/min, t_R 18.4 min and 21.3 min (*syn*-aldol **6aa**), 30.8 min and 40.0 min (*anti*-aldol **6aa**), detection at 254 nm]. [c]Ee of **3aa** was determined by HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1 mL/min, t_R 72.0 min (aldol-Tishchenko **3aa**, minor), 133.2 min (aldol-

Tishchenko **3aa**, major), detection at 254 nm].

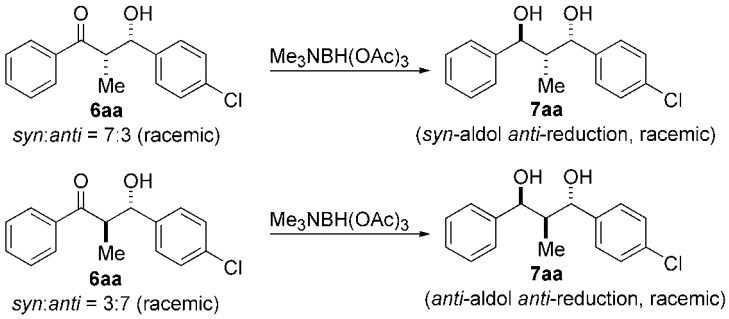
From *anti* major **6aa** (*syn*:*anti* = 3:7):

entry	time (d)	**4a**:**6aa**:**3aa** (%)[a]	**6aa** *syn*:*anti* (%)[a]	**6aa** *syn* ee, *anti* ee (%)[b]	**3aa** ee (%)[c]
1	1.5	28:57:15	4:6	racemic, racemic	56%
2	3.5	33:41:26	4:6	racemic, racemic	60%
3	6.5	31:30:39	4:6	racemic, racemic	63%

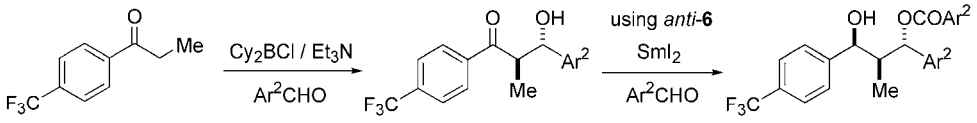
[a]Determined by ^{1}H NMR analysis of the crude sample. [c]Ee of **6aa** was determined by HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1 mL/min, t_R 18.4 min and 21.3 min (*syn*-aldol **6aa**), 30.8 min and 40.0 min (*anti*-aldol **6aa**), detection at 254 nm]. [c]Ee of **3aa** was determined by HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1 mL/min, t_R 72.0 min (aldol-Tishchenko **3aa**, minor), 133.2 min (aldol-Tishchenko **3aa**, major), detection at 254 nm].

Determination of relative configuration:

Relative configuration of **7aa** was assigned as follows. Both *syn*-aldol *anti*-Tishchenko and *anti*-aldol *anti*-Tishchenko products **7aa** were synthesized by *anti*-selective reduction[SI-2] of the corresponding *syn* and *anti* major aldol product **6aa**.[SI-1] The NMR of *anti*-aldol *anti*-Tishchenko products was identical with that obtained by chiral lanthanum catalyst.

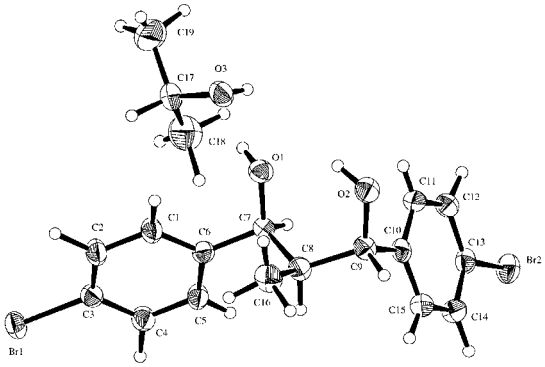


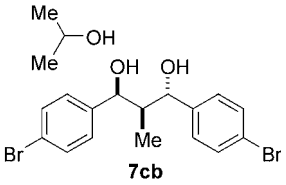
Relative configurations of **7bc**, **7be**, and **7bj** were assigned by following standard literature procedure, *anti*-aldol products **6** were prepared by Brown's aldol procedure[SI-3] and highly *anti*-selective reductions were achieved by Evans' Tishchenko reduction.[SI-4] Tishchenko products (**3bc**, **3be**, and **3bj**) were hydrolyzed using NaOMe in MeOH. The NMR and HPLC retention time of the corresponding 1,3-diols (**7bc**, **7be**, and **7bj**) were identical with those obtained by chiral lanthanum catalyst.



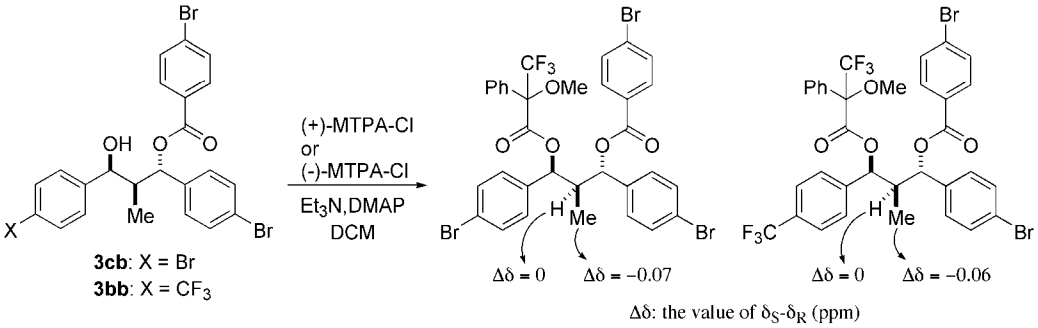
Determination of absolute configuration:

The high quality of the X-ray data set and the presence of the bromine heavy atom enabled determination of the absolute configuration of **7cb** from the anomalous X-ray scattering data.[SI-5] The (+)-enantiomer (major enantiomer) was assigned an (1*S*,3*S*)-stereochemistry with a corresponding Flack parameter of -0.00(3) [1.00(3) for the (1*R*,3*R*)-isomer].[SI-6] Data for the crystal of **7cb**•*i*-PrOH, which was recrystallized from *i*-PrOH/hexane: Crystal systems monoclinic Space group $P2_1$, a = 10.692(2) Å, b = 8.585(2) Å, c = 11.968(2) Å, β = 114.40(1)°, V = 1032.3(3) Å^3, Z = 2, R = 0.038, Rw = 0.055, goodness of fit = 1.001, Flack parameter = -0.00(3)

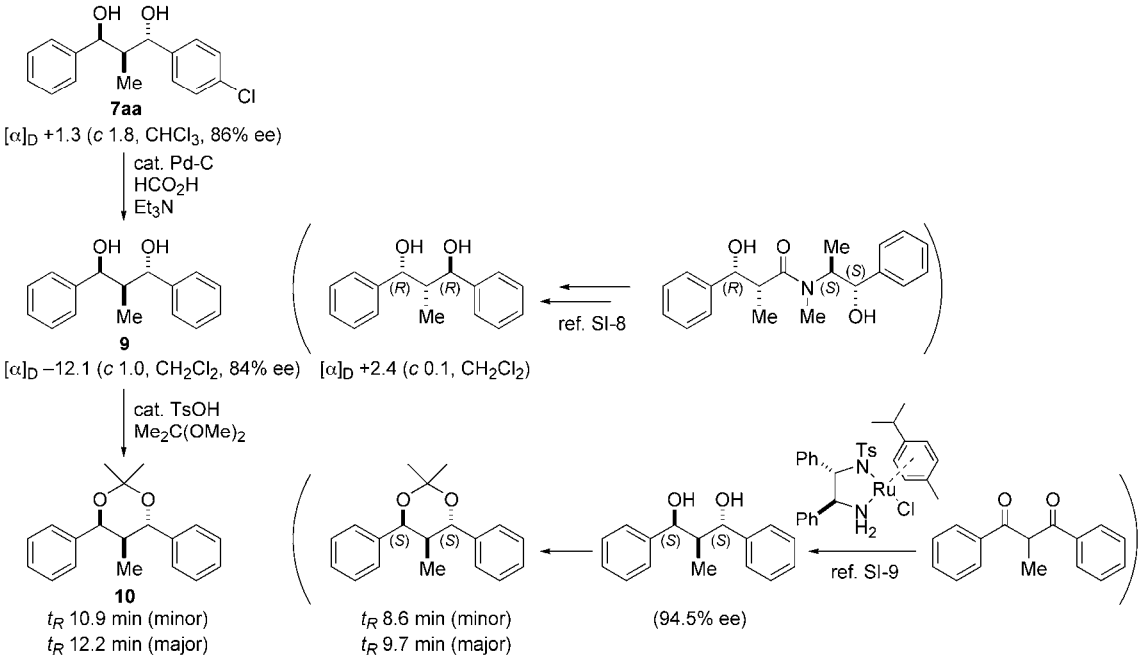




Following ^{1}H NMR studies using Mosher's method[SI-7] were also supported the above-mentioned absolute configuration.



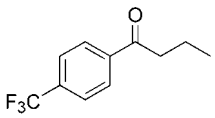
The absolute configuration of **7aa** was determined by comparing the measured optical rotation of the 1,3-diphenyl compound **9**[SI-8] and chiral stationary-phase HPLC analysis of the corresponding acetonide **10**.[SI-9] We thank Prof. Janine Cossy and Dr. Peter I. Dalko for kindly supplying detailed information about HPLC analysis of the acetonide compound **10**.


OH OH
Me
Cl
7aa
[α]D +1.3 (c 1.8, CHCl3, 86% ee)
cat. Pd-C
HCO2H
Et3N
9
[α]D –12.1 (c 1.0, CH2Cl2, 84% ee)
ref. SI-8
[α]D +2.4 (c 0.1, CH2Cl2)
cat. TsOH
Me2C(OMe)2
10
tR 10.9 min (minor)
tR 12.2 min (major)
tR 8.6 min (minor)
tR 9.7 min (major)
(94.5% ee)
ref. SI-9
(Daicel OD-H, hexane/i-PrOH 99.3:0.7, 0.4 mL/min, detected at 220 nm)

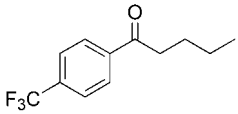
Experimental Procedures and Characterization of the Products

General: Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. NMR spectra were recorded on a JEOL JNM-LA500 spectrometer, operating at 500 MHz for ^{1}H NMR and 125.65 MHz for ^{13}C NMR. Chemical shifts in $CDCl_3$ were reported downfield from TMS (= 0 ppm) for ^{1}H NMR. For ^{13}C NMR, chemical shifts were reported downfield from TMS (= 0 ppm) or in the scale relative to $CHCl_3$ (77.00 ppm for ^{13}C NMR) as an internal reference. Optical rotations were measured on a JASCO P-1010 polarimeter. ESI mass spectra were measured on Waters micromass ZQ. The enantiomeric excess (ee) was determined by HPLC analysis. HPLC was performed on JASCO HPLC systems consisting of the following: pump, 880-PU or PU-980; detector, 875-UV or UV-970, measured at 254 nm; column, DAICEL CHIRALPAK AS–H, DAICEL CHIRALCEL AD–H; mobile phase, hexane–2-propanol; flow rate, 1 mL/min. Reactions were carried out in dry solvents under an argon atmosphere, unless otherwise stated. $Ln(OTf)_3$ and BuLi was purchased from Aldrich Chemical Laboratory Co., LTD., Other reagents were purified by the usual methods.

Synthesis of the ketones: To a solution of PrMgBr (11.04 g, 75 mmol) in THF (50 mL) at –78 ˚C was added slowly a mixture of 4-(trifluromethyl)benzonitrile (8.55 g, 50 mmol) and CuBr•Me_2S (205 mg, 1 mmol) in THF (50 mL) over 10 min. The reaction mixture was allowed to come to room temperature over 2 h and quenched with distilled water (20 mL). The organic layer was separated and the aqueous layer was extracted twice with ether. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated in *vacuo* to afford **4h** (9.73 g, 90%). **4i** was prepared by the same procedure.



1-(4-Trifluromethylphenyl)butane-1-one (4h): colorless oil; IR (neat) ν 2966, 2878, 1696, 1581, 1510, 1465, 1409, 1324, 1133, 1066 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.99 (t, *J* = 7.5, 3H), 1.76 (sextet, *J* = 7.5 Hz, 2H), 2.95 (t, *J* = 7.3 Hz, 2H), 7.69 (d, *J* = 8 Hz, 2H), 8.0 (d, *J* = 8Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.1, 17.0, 40.2, 123.4 (q, $J_{C\text{-}F}$ = 272.8 Hz), 125.1 (q, $J_{C\text{-}F}$ = 3.56 Hz), 127.9, 133.6 (q, $J_{C\text{-}F}$ = 32.3 Hz), 139.5, 198.3; ESI-MS *m/z* 217 [M+H$^+$]; Anal. calcd for $C_{11}H_{11}F_3O$: C 61.11, H 5.13; found C 61.00, H 4.94.



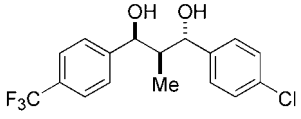
1-(4-Trifluromethylphenyl)pentane-1-one (4i): colorless oil; IR (neat) ν2961, 2874, 1694, 1409, 1325, 1066, 1014 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, *J* = 7.5 Hz, 3H), 1.39 (sextet, *J* = 7 Hz, 2H), 1.65 (quintet, *J* = 7.5 Hz, 2H), 2.91 (t, *J* = 7.5 Hz, 2H), 7.64 (d, *J* = 8 Hz, 2H), 7.98 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.8, 22.3, 26.1, 38.5, 123.6 (q, $J_{C\text{-}F}$ = 274 Hz), 125.7 (q, $J_{C\text{-}F}$ = 3.58 Hz), 128.31, 134.1 (q, $J_{C\text{-}F}$ = 32.3 Hz), 139.6, 199.4; ESI-MS *m/z* 231 [M+H$^+$]; Anal. calcd for $C_{12}H_{13}F_3O$: C

62.60, H 5.69; found C 62.55, H 5.55.
Other ketones are commercially available.

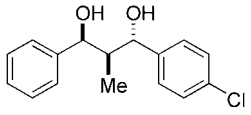
General procedure for the preparation of La(OTf)$_3$:(*R*)-BINOL:BuLi (1:3:5.6) complex: To a suspension of (*R*)-BINOL (429 mg, 1.5 mmol), La(OTf)$_3$ (293 mg, 0.5 mmol, Aldrich) in dry THF (2.5 mL) was slowly added 1.6 M hexane solution of BuLi (1.75 mL, 2.8 mmol, Aldrich) over 2 min at 4 ˚C. The ice-water bath was then removed and the reaction mixture was allowed to stir for 30 min at room temperature, by that time all the La(OTf)$_3$ was completely soluble and the reaction mixture became homogeneous. The reaction mixture was cooled to –78 ˚C using acetone-dry ice bath and the reaction mixture was concentrated slowly via a needle attached to a vacuum pump. After 1 min, the acetone-dry ice bath was removed and the reaction mixture was slowly allowed to come to room temperature under vacuum for over 30 min. After the reaction mixture became dry solid, the needle was removed and the reaction mixture was directly connected to vacuum. After 30 min, the vacuum was released with Argon gas and dry THF (2.5 mL) was added to make 0.2 M stock solution of the catalyst. The catalyst prepared by this method was directly used for the reaction. It can be stored at room temperature for a long time (at least one month) without any loss of reaction efficiency or enantioselectivity.

General procedure for the direct catalytic asymmetric propionate aldol-Tishchenko reaction: To a mixture of ketone **4b** (101 mg, 0.5 mmol), and aldehyde **5a** (170 mg, 1.25 mmol) in dry THF (0.25 mL) was slowly added a stock solution of the catalyst (0.25 mL, 0.2 M in THF) over 1 min at 4 ˚C. After being stirred for appropriate time at room temperature as described in the Table 2, the reaction mixture was diluted with ether (5 mL) and quenched with 1 M HCl (2 mL). The aqueous layer was extracted twice with ether (10 x 2 mL) and the combined organic layers were washed with brine (10 mL) and dried over sodium sulfate. After concentration in *vacuo*, the residue was purified by flash chromatography (SiO_2, hexane/ether = 5/1 to 4/1) to give **3ba** (272 mg, 95%) as a sticky oil. The product **3ba** was dissolved in MeOH (1 mL) and added NaOMe (27 mg, 0.5 mmol) and the resulting homogeneous mixture was stirred until the consumption of the starting material (generally from 20 min to 2 h), diluted with ethyl acetate (20 mL), and washed with water (5 mL). The aqueous layer was extracted twice with ethyl acetate (10 mL x 2) and the combined organic layers were washed with brine (10 mL) and dried over sodium sulfate. After concentration in *vacuo*, the residue was purified by flash chromatography (SiO_2, hexane/acetone = 10/1 to 8/1) to give diol **7ba** (185 mg, 95%, 2 steps) as a sticky oil.

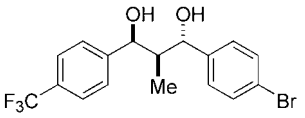
(1*S*,2*S*,3*S*)-1-(4-Chlorophenyl)-2-methyl-3-(4-trifluromethylphenyl)propane-1,3-diol (7ba): IR (neat) ν 3334,



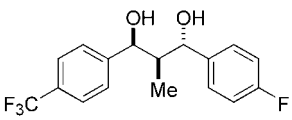
2977, 2899, 1619, 1490, 1415, 1326, 1164, 1125, 1068 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.74 (d, *J* = 6.5 Hz, 3H), 2.08-2.15 (m, 1H), 2.98 (d, *J* = 4 Hz, 1H), 3.29 (d, *J* = 4 Hz, 1H), 4.69 (dd, *J* = 7, 4 Hz, 1H), 5.05 (br-s, 1H), 7.30-7.38 (m, 6H), 7.57 (d, *J* = 8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.1, 45.4, 73.6, 77.1, 124.1 (q, $J_{C\text{-}F}$ = 274.1 Hz), 124.8 (q, $J_{C\text{-}F}$ = 3.6 Hz), 126.1, 127.4, 128.5, 129.2 (q, $J_{C\text{-}F}$ = 32.4 Hz), 133.3, 141.5, 146.3; ESI-MS *m/z* 367 [M+Na^+]. The enantiomeric excess of **7ba** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS-H, *i*-PrOH/hexane 5/95, flow rate 1 mL/min, t_R 15.0 min (major) and 19.6 min (minor), detection at 254 nm]; $[\alpha]_D^{23}$ +6.2 (*c* 0.935, $CHCl_3$, 93% ee); Anal. calcd for $C_{17}H_{16}ClF_3O_2$: C 59.23, H 4.68; found C 59.01, H 4.75.



(1*S*,2*S*,3*S*)-1-(4-Chlorophenyl)-2-methyl-3-phenylpropane-1,3-diol (7aa): white solid; IR(neat) ν 3329, 1489, 1451, 1090, 1013, 827, 755, 701 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.75 (d, *J* = 7.3 Hz, 3H), 2.15 (m, 1H), 2.85 (dd, *J* = 3.7, 11.3 Hz, 1H), 3.22 (dd, *J* = 4.0, 11.6 Hz, 1H), 4.69 (m, 1H), 5.02 (br-s, 1H), 7.23-7.37 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.3, 45.5, 74.5, 77.0, 125.9, 127.1, 127.6, 128.0, 128.4, 133.0, 142.0, 142.1; ESI-MS *m/z* 299 [M+Na^+]. The enantiomeric excess of **7aa** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1 mL/min, t_R 25.7 min (minor) and 32.6 min (major), detection at 254 nm]; $[\alpha]_D^{25}$ +1.3 (*c* 1.75, $CHCl_3$, 95% ee).



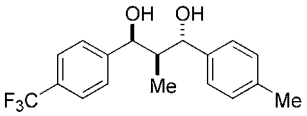
(1*S*,2*S*,3*S*)-1-(4-Bromophenyl)-2-methyl-3-(4-trifluromethylphenyl)propane-1,3-diol (7bb): sticky oil; IR (neat) ν 3594, 3387, 3053, 2985, 1618, 1486, 1419, 1326, 1265, 1166 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.75 (d, *J* = 7.45 Hz, 3H), 2.09-2.17 (m, 1H), 2.86 (d, *J* = 4 Hz, 1H), 3.16 (d, *J* = 4 Hz, 1H), 4.70 (dd, *J* = 6.3, 4 Hz, 1H), 5.08 (br-s, 1H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.1, 45.4, 73.6, 77.1, 121.4, 124.1 (q, $J_{C\text{-}F}$ = 274.1 Hz), 124.9 (q, $J_{C\text{-}F}$ = 3.6 Hz), 126.1, 127.7, 129.2 (q, $J_{C\text{-}F}$ = 32.4 Hz), 131.5, 142.1, 146.3; ESI-MS *m/z* 411, 413 [M+Na^+]. The enantiomeric excess of **7bb** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1 mL/min, t_R 16.5 min (minor) and 23.8 min (major), detection at 254 nm]; $[\alpha]_D^{23}$ +9.02 (*c* 0.820, $CHCl_3$, 95% ee); Anal. calcd for $C_{17}H_{17}BrF_3O_2$: C 52.46, H 4.14; found C 52.18, H 3.91.



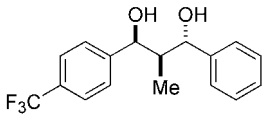
(1*S*,2*S*,3*S*)-1-(4-Flurophenyl)-2-methyl-3-(4-trifluromethylphenyl)propane-1,3-diol (7bc): sticky oil; IR (neat) ν 3499, 3000, 2968, 2922, 2252, 1712, 1363, 1325, 1223, 1125 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.72 (d, *J* = 7 Hz, 3H), 2.09-2.15 (m, 1H), 2.90 (d, *J* = 3.4 Hz, 1H), 3.36 (d, *J* = 4 Hz, 1H), 4.69 (dd, *J* = 6.8, 3.4 Hz, 1H), 5.07 (br-s, 1H), 7.05-

7.08 (m, 2H), 7.33-7.35 (m, 2H), 7.38 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.2, 45.6, 73.7, 77.0, 115.3 (d, $J_{C\text{-}F}$ = 21.6 Hz), 124.1 (q, $J_{C\text{-}F}$ = 274.1 Hz), 124.8 (q, $J_{C\text{-}F}$ = 3.6 Hz), 126.2, 127.6 (d, $J_{C\text{-}F}$ = 8.3 Hz), 129.2 (q, $J_{C\text{-}F}$ = 32.4 Hz), 138.8 (d, $J_{C\text{-}F}$ = 3.6 Hz), 146.4, 162.2 (d, $J_{C\text{-}F}$ = 247 Hz); ESI-MS *m/z* 351 [M+Na$^+$]. The enantiomeric excess of **7bc** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1 mL/min, t_R 14.6 min (minor) and 21.7 min (major), detection at 254 nm]; $[\alpha]_D^{24.5}$ –12.6 (*c* 2.78, $CHCl_3$, 92% ee); Anal. calcd for $C_{17}H_{17}F_4O_2$: C 62.19, H 4.97; found C 61.96, H 4.96.

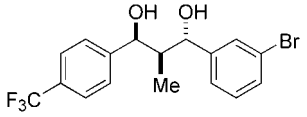
(1*S*,2*R*,3*S*)-2-Methyl-1-(4-tolyl)-3-(4-trifluromethylphenyl)propane-1,3-diol (7bd): stick oil; IR (neat) ν 3345, 2976, 2917, 1618, 1513, 1415, 1326, 1162, 1124, 1068 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.73 (d, J = 7 Hz, 3H), 2.13-2.19 (m, 1H), 2.36 (s, 3H), 2.63 (d, J = 3 Hz, 1H), 3.49 (d, J = 3 Hz, 1H), 4.68 (dd, J = 6.9, 3.4 Hz, 1H), 5.09 (br-s, 1H), 7.19 (d, J = 8 Hz, 2H), 7.26 (d, J = 7.5 Hz, 2H), 7.39 (d, J = 8 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.1, 21.0, 45.6, 73.5, 77.5, 124.2 (q, $J_{C\text{-}F}$ = 274.1 Hz), 124.7 (q, $J_{C\text{-}F}$ = 3.6 Hz), 126.0, 126.2, 128.9 (q, $J_{C\text{-}F}$ = 32.4 Hz), 129.1, 137.4, 140.0, 146.8; ESI-MS *m/z* 347 [M+Na$^+$]. The enantiomeric excess of **7bd** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1 mL/min, t_R 15.7 min (minor) and 23.1 min (major), detection at 254 nm]; $[\alpha]_D^{23.8}$ –1.75 (*c* 2.63, $CHCl_3$, 92% ee); Anal. calcd for $C_{18}H_{19}F_3O_2$: C 66.66, H 5.90; found C 66.57, H 5.81.



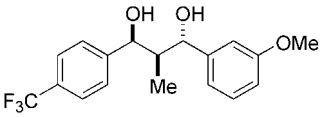
(1*S*,2*R*,3*S*)-2-Methyl-1-phenyl-3-(4-trifluromethylphenyl)propane-1,3-diol (7be): stick oil; IR (neat) ν 3345, 2984, 2895, 1618, 1455, 1415, 1326, 1164, 1124 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.74 (d, J = 7 Hz, 3H), 2.13-2.19 (m, 1H), 2.85 (d, J = 3.5 Hz, 1H), 3.51 (d, J = 4 Hz, 1H), 4.71 (dd, J = 6, 3.5 Hz, 1H), 5.07 (br-s, 1H), 7.29-7.34 (m, 1H), 7.36-7.40 (m, 6H), 7.56 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.1, 45.5, 73.5, 77.6, 124.2 (q, $J_{C\text{-}F}$ = 274.1 Hz), 124.8 (q, $J_{C\text{-}F}$ = 3.6 Hz), 126.0, 126.2, 127.7, 128.4, 129 (q, $J_{C\text{-}F}$ = 32.4 Hz), 143.0, 146.6; ESI-MS *m/z* 313 [M+Na$^+$]. The enantiomeric excess of **7be** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1 mL/min, t_R 14.6 min (minor) and 27.7 min (major), detection at 254 nm]; $[\alpha]_D^{23.7}$ –10.5 (*c* 2.44, $CHCl_3$, 91% ee); Anal. calcd for $C_{17}H_{17}F_3O_2$: C 65.80, H 5.52; found C 65.63, H 5.49.



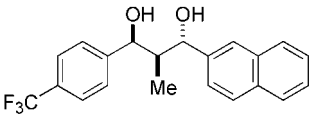
(1*S*,2*S*,3*S*)-1-(3-Bromophenyl)-2-methyl-3-(4-trifluromethylphenyl)propane-1,3-diol (7bf): sticky oil; IR



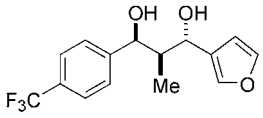
(neat) ν 3363, 3051, 2977, 2899, 1618, 1418, 1325, 1265, 1165, 1125, 1067, 1017 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.73 (d, *J* = 7.4 Hz, 3H), 2.06-2.12 (m, 1H), 3.56 (d, *J* = 4 Hz, 1H), 3.67 (d, *J* = 4 Hz, 1H), 4.61 (dd, *J* = 6.3, 4 Hz, 1H), 4.95 (br-s, 1H), 7.22-7.24 (m, 2H), 7.30 (d, *J* = 8 Hz, 2H), 7.40-7.43 (m, 1H), 7.52-7.54 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.1, 45.3, 73.6, 77.1, 124.1 (q, $J_{C\text{-}F}$ = 274.1 Hz), 122.6, 124.6, 124.8 (q, $J_{C\text{-}F}$ = 3.6 Hz), 126.1, 129.0, 129.1 (q, $J_{C\text{-}F}$ = 32.4 Hz), 130.0, 130.6, 145.5, 146.1; ESI-MS *m/z* 411, 413 [M+Na^+]. The enantiomeric excess of **7bf** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1 mL/min, t_R 14.1 min (minor) and 22.6 min (major), detection at 254 nm]; $[\alpha]_D^{24}$ +0.73 (*c* 3.54, $CHCl_3$, 86% ee); Anal. calcd for $C_{17}H_{16}BrF_3O_2$: C 52.46, H 4.14; found C 52.28, H 4.03.

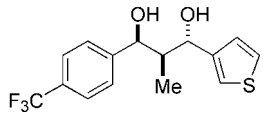
(1*S*,2*S*,3*S*)-1-(3-Methoxyphenyl)-2-methyl-3-(4-trifluromethylphenyl)propane-1,3-diol (7bg): 

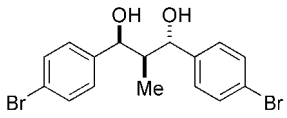
stick oil; IR (neat) ν 3436, 2953, 2837, 1722, 1600, 1488, 1455, 1435 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.77 (d, *J* = 7.5 Hz, 3H), 2.13-2.19 (m, 1H), 2.74 (d, *J* = 4 Hz, 1H), 3.35 (d, *J* = 4 Hz, 1H), 3.83 (s, 3H), 4.71 (dd, *J* = 6, 3.5 Hz, 1H), 5.10 (br-s, 1H), 6.84-6.86 (m, 1H), 6.95-6.96 (m, 2H), 7.28-7.32 (m, 1H), 7.39 (d, *J* = 4 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.9, 45.6, 55.1, 73.4, 77.6, 111.8, 112.8, 118.4, 124.2 (q, $J_{C\text{-}F}$ = 274.1 Hz), 124.8 (q, $J_{C\text{-}F}$ = 3.6 Hz), 126.2, 128.9 (q, $J_{C\text{-}F}$ = 32.4 Hz), 129.5, 144.8, 146.8, 159.7; ESI-MS *m/z* 363 [M+Na^+]. The enantiomeric excess of **7bg** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1 mL/min, t_R 20.6 min (minor) and 35.7 min (major), detection at 254 nm]; $[\alpha]_D^{24.6}$ –5.31 (*c* 2.26, $CHCl_3$, 85% ee); Anal. calcd for $C_{18}H_{19}F_3O_3$: C 63.52, H 5.63; found C 63.48, H 5.53.

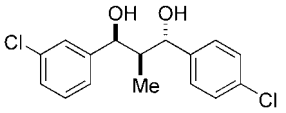
(1*S*,2*S*,3*S*)-2-Methyl-1-(napthalen-2-yl)-3-(4-trifluromethylphenyl)propane-1,3-diol (7bh): 

stick oil; IR (neat) ν 3433, 3059, 2974, 1718, 1629, 1508, 1468, 1436, 1414, 1354, 1325, 1290, 1231, 1199 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.79 (d, *J* = 7.5 Hz, 3H), 2.25-2.31 (m, 1H), 2.93 (d, *J* = 3.5 Hz, 1H), 3.45 (d, *J* = 4 Hz, 1H), 4.89 (dd, *J* = 6, 4 Hz, 1H), 5.10 (br-s, 1H), 7.37 (d, *J* = 8 Hz, 2H), 7.48-7.50 (m, 3H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.84-7.88 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.2, 45.4, 73.6, 77.9, 123.8, 124.7 (q, $J_{C\text{-}F}$ = 3.6 Hz), 125.0, 125.7 (q, $J_{C\text{-}F}$ = 274.1 Hz), 126.0, 126.1, 126.32, 127.6, 127.9, 128.4, 129 (q, $J_{C\text{-}F}$ = 32.4 Hz), 132.9, 133.1, 140.3, 146.6; ESI-MS *m/z* 383 [M+Na^+]. The enantiomeric excess of **7bh** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1 mL/min, t_R 22.5 min (minor) and 35.3 min (major), detection at 254 nm]; $[\alpha]_D^{24.2}$ +18.6 (*c* 1.72, $CHCl_3$, 88% ee); Anal. calcd for $C_{21}H_{19}F_3O_2$: C 69.99, H 5.31; found C 69.78, H 5.02.

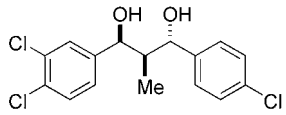
(1*S*,2*S*,3*S*)-1-(Furan-3-yl)-2-methyl-3-(4-trifluromethylphenyl)propane-1,3-diol (7bi):  sticky oil; IR (neat) ν 3347, 2977, 2899, 1619, 1503, 1415, 1326, 1162, 1124, 1067 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.79 (d, *J* = 7.45 Hz, 3H), 2.09-2.15 (m, 1H), 2.63 (d, *J* = 4 Hz, 1H), 3.28 (d, *J* = 4 Hz, 1H), 4.72 (dd, *J* = 6.3, 4 Hz, 1H), 5.17 (br-s, 1H), 6.42 (s, 1H), 7.42-7.45 (m, 4H), 7.59 (d, *J* = 8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.7, 44.6, 70.8, 73.5, 108.1, 124.1 (q, $J_{C\text{-}F}$ = 274.1 Hz), 124.9 (q, $J_{C\text{-}F}$ = 3.6 Hz), 126.2, 129.1 (q, $J_{C\text{-}F}$ = 32.4 Hz), 127.8, 139.5, 143.7, 146.7; ESI-MS *m/z* 323 [M+Na^+]. The enantiomeric excess of **7bi** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1 mL/min, t_R 17.5 min (minor) and 23.3 min (major), detection at 254 nm]; $[\alpha]_D^{23.8}$ –8.41 (*c* 2.14, $CHCl_3$, 93% ee); Anal. calcd for $C_{15}H_{15}F_3O_3$: C 60.00, H 5.04; found C 59.75, H 4.77.

(1*S*,2*S*,3*S*)-2-Methyl-1-(thiophen-3-yl)-3-(4-trifluromethylphenyl)propane-1,3-diol (7bj):  sticky oil; IR (neat) ν 3346, 2975, 2900, 1619, 1415, 1326, 1163, 1124, 1067, 1016 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.78 (d, *J* = 7.5 Hz, 3H), 2.14-2.20 (m, 1H), 2.91 (d, *J* = 4 Hz, 1H), 3.44 (d, *J* = 3.5 Hz, 1H), 4.82 (dd, *J* = 5.5, 4 Hz, 1H), 5.07 (br-s, 1H), 7.08 (d, *J* = 5 Hz, 1H), 7.26 (s, 1H), 7.36-7.39 (m, 3H), 7.57 (d, *J* = 8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.7, 45.2, 73.5, 74.3, 121.3, 124.2 (q, $J_{C\text{-}F}$ = 274.1 Hz), 124.3 (q, $J_{C\text{-}F}$ = 3.6 Hz), 125.2, 126.1, 126.5, 129.1 (q, $J_{C\text{-}F}$ = 32.4 Hz), 144.7, 146.7; ESI-MS *m/z* 339 [M+Na^+]. The enantiomeric excess of **7bj** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1 mL/min, t_R 18.6 min (minor) and 26.9 min (major), detection at 254 nm]; $[\alpha]_D^{23.5}$ +1.48 (*c* 3.55, $CHCl_3$, 94% ee); Anal. calcd for $C_{15}H_{15}F_3O_2S$: C 56.95, H 4.78; found C 57.05, H 4.49.

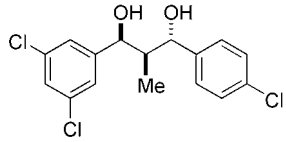
(1*S*,3*S*)-1,3-Bis(4-bromophenyl)-2-methylpropane-1,3-diol (7cb):  sticky oil; IR(neat) ν 3326, 1485, 1072, 1009, 822, 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.74 (d, *J* = 7.3 Hz, 3H), 2.09 (m, 1H), 3.01 (d, *J* = 4.0 Hz, 1H), 3.07 (d, *J* = 4.0 Hz, 1H), 4.66 (dd, *J* = 4.0, 5.5 Hz, 1H), 4.96 (br-s, 1H), 7.14 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 11.2, 45.3, 73.7, 77.0, 120.8, 121.3, 127.6, 127.8, 131.0, 131.4, 141.1, 142.2; ESI-MS *m/z* 421, 423, 425 [M+Na^+]. The enantiomeric excess of **7cb** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1 mL/min, t_R 29.6 min (minor) and 42.6 min (major), detection at 254 nm]; $[\alpha]_D^{24}$ +27.3 (*c* 1.48, $CHCl_3$, 85% ee); Anal. calcd for $C_{16}H_{16}Br_2O_2$: C 48.03, H 4.03; found C 47.97, H 4.07.

(1*S*,2*R*,3*S*)-1-(3-Chlorophenyl)-3-(4-chlorophenyl)-2-methylpropane-1,3-diol (7da): 

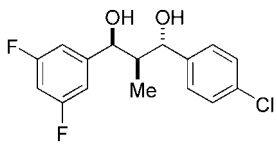
sticky oil; IR(neat) ν 3335, 1489, 1090, 1013 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.76 (d, *J* = 7.0 Hz, 3H), 2.11 (m, 1H), 2.92 (brs, 1H), 3.08 (brs, 1H), 4.70 (m, 1H), 4.99 (br-s, 1H), 7.13 (m, 1H), 7.21-7.28 (m, 3H), 7.31-7.36 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 11.2, 45.6, 73.5, 77.0, 124.0, 126.0, 127.1, 127.5, 128.6, 129.3, 133.3, 134.0, 141.7, 144.6; ESI-MS *m/z* 333, 335 [M+Na^+]. The enantiomeric excess of **7cb** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1 mL/min, t_R 22.7 min (minor) and 28.8 min (major), detection at 254 nm]; $[\alpha]_D^{25}$ +9.4 (*c* 1.0, $CHCl_3$, 84% ee); Anal calcd for $C_{16}H_{16}Cl_2O_2$: C 61.75, H 5.18; found C 61.51, H 5.16.

(1*S*,2*R*,3*S*)-1-(4-Chlorophenyl)-3-(3,4-dichlorophenyl)-2-methylpropane-1,3-diol (7ea): 

sticky oil; IR(neat) ν 3328, 1567, 1429, 1090, 798 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.75 (d, *J* = 7.0 Hz, 3H), 2.07 (m, 1H), 2.78 (brs, 1H), 3.22 (br-s, 1H), 4.70 (m, 1H), 4.97 (brs, 1H), 7.09 (m, 1H), 7.29-7.39 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 11.0, 45.6, 72.8, 77.1, 125.3, 127.4, 127.9, 128.7, 129.9, 130.8, 132.2, 133.4, 141.5, 142.9; ESI-MS *m/z* 367, 369, 371 [M+Na^+]. The enantiomeric excess of **7ea** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1 mL/min, t_R 21.1 min (minor) and 29.8 min (major), detection at 254 nm]; $[\alpha]_D^{25}$ +21.8 (*c* 0.99, $CHCl_3$, 88% ee); Anal calcd for $C_{16}H_{15}Cl_3O_2$: C 55.60, H 4.37; found C 55.52, H 4.44.

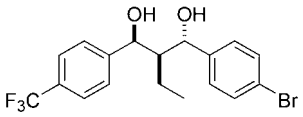
(1*S*,2*R*,3*S*)-1-(4-Chlorophenyl)-3-(3,5-dichlorophenyl)-2-methylpropane-1,3-diol (7fa): 

sticky oil; IR(neat) ν 3333, 1489, 1470, 1089, 814, 756 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.76 (d, *J* = 7.3 Hz, 3H), 2.07 (m, 1H), 2.68 (m, 1H), 3.21 (m, 1H), 4.71 (m, 1H), 4.97 (m, 1H), 7.14 (m, 1H), 7.22-7.26 (m, 3H), 7.31-7.37 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 10.9, 45.6, 72.7, 77.0, 124.4, 127.0, 127.4, 128.7, 133.4, 134.6, 141.4, 146.3; ESI-MS *m/z* 366.9, 369, 370.9 [M+Na^+]. The enantiomeric excess of **7fa** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1 mL/min, t_R 17.0 min (minor) and 23.9 min (major), detection at 254 nm]; $[\alpha]_D^{25}$ +9.5 (*c* 1.1, $CHCl_3$, 85% ee); Anal. calcd for $C_{16}H_{15}Cl_3O_2$: C 55.60, H 4.37; found C 55.46, H 4.40.

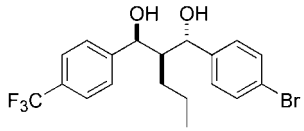
(1*S*,2*R*,3*S*)-1-(4-Chlorophenyl)-3-(3,5-diflurophenyl)-2-methylpropane-1,3-diol (7ga): 

sticky oil; IR(neat) ν 3335, 1624, 1595, 1456, 1116, 1090, 843 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.76 (d, *J* = 7.4 Hz, 3H), 2.08 (m, 1H), 2.74 (d, *J* = 4.0 Hz, 1H), 3.21 (d, *J* = 3.7 Hz, 1H), 4.71 (m, 1H), 4.98 (br-s, 1H), 6.67 (m, 1H), 6.80 (d, *J* = 6.1 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* =

8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 11.0, 45.4, 73.0, 76.8, 102.1 (t, $J_{C\text{-}F}$ = 50.6 Hz), 108.6 (dd, $J_{C\text{-}F}$ = 6.2, 19.6 Hz), 127.3, 128.5, 133.2, 141.5, 146.8 (t, $J_{C\text{-}F}$ = 8.3 Hz), 162.7 (dd, $J_{C\text{-}F}$ = 12.4, 248.0 Hz); ESI-MS *m/z* 335, 337 [M+Na$^+$]. The enantiomeric excess of **7ga** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1 mL/min, t_R 18.8 min (minor) and 23.7 min (major), detection at 254 nm]; $[\alpha]_D^{25}$ +4.0 (*c* 1.0, $CHCl_3$, 87% ee); Anal. calcd for $C_{16}H_{15}ClF_2O_2$: C 61.25, H 4.83; found C 61.29, H 4.87.

(1*S*,2*S*,3*S*)-1-(4-Bromophenyl)-2-ethyl-3-(4-trifluromethylphenyl)propane-1,3-diol (7hb): 

sticky oil; IR (neat) ν 3318, 2959, 2895, 1619, 1482, 1407, 1325, 1163, 1124 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85 (t, *J* = 7.5 Hz, 3H), 1.18-1.24 (m, 1H), 1.50-1.58 (m, 1H), 1.75-1.79 (m, 1H), 3.26 (d, *J* = 5.5 Hz, 1H), 3.54 (d, *J* = 3 Hz, 1H), 4.91 (brs, 1H), 4.93-4.95 (m, 1H), 7.26 (d, *J* = 6.8 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.0, 16.8, 55.3, 72.5, 73.9, 121.1, 124.1 (q, $J_{C\text{-}F}$ = 274.1 Hz), 124.8 (q, $J_{C\text{-}F}$ = 3.6 Hz), 125.8, 127.3, 129.1 (q, $J_{C\text{-}F}$ = 32.4 Hz), 131.5, 142.4, 146.3; ESI-MS *m/z* 425, 427 [M+Na$^+$]. The enantiomeric excess of **7hb** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1 mL/min, t_R 11.5 min (minor) and 17.3 min (major), detection at 254 nm]; $[\alpha]_D^{22.6}$ +23.2 (*c* 3.61, $CHCl_3$, 88% ee); Anal. calcd for $C_{18}H_{18}BrF_3O_2$: C 53.61, H 4.50; found C 53.60, H 4.36.

(1*S*,2*S*,3*S*)-1-(4-Bromophenyl)-2-propyl-3-(4-trifluromethylphenyl)propane-1,3-diol (7ib): 

sticky oil; IR (neat) ν 3312, 2959, 2932, 2872, 1618, 1486, 1415, 1325, 1164, 1126 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.77 (t, *J* = 6.9 Hz, 3H), 1.07-1.16 (m, 2H), 1.31-1.40 (m, 1H), 1.47-1.55 (m, 1H), 1.85-1.89 (m, 1H), 3.27 (d, *J* = 5.1 Hz, 1H), 3.54 (d, *J* = 3.4 Hz, 1H), 4.90-4.92 (m, 2H), 7.24-7.28 (m, 4H), 7.53 (d, *J* = 8Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 20.4, 25.8, 50.2, 72.5, 74.5, 121.1, 124.1 (q, $J_{C\text{-}F}$ = 274.1 Hz), 124.8 (q, $J_{C\text{-}F}$ = 3.6 Hz), 125.8, 127.3, 129.0 (q, $J_{C\text{-}F}$ = 32.4 Hz), 131.5, 142.4, 146.3; ESI-MS *m/z* 439, 441 [M+Na$^+$]. The enantiomeric excess of **7ib** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1 mL/min, t_R 11.2 min (minor) and 14.9 min (major), detection at 254 nm]; $[\alpha]_D^{23}$ +18 (*c* 3.15, $CHCl_3$, 87% ee); Anal. calcd for $C_{19}H_{20}BrF_3O_2$: C 54.69, H 4.83; found C 54.68, H 5.07.

References

SI-1 Aoki, Y.; Oshima, K.; Utimoto, K. *Chem. Lett.* **1995**, 463.

SI-2 Evans, D. A.; Chapman, K. T.; Carreira, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 3560.

SI-3 Brown, H. C.; Dhar, R. K.; Bakshi, R. K.; Pandiarajan, P. K., Singaram, B. *J. Am. Chem. Soc*. **1989**, *111*, 3441.

SI-4 Evans, D. A.; Hoveyda, A. H. *J. Am. Chem. Soc*. **1990**, *112*, 6447.

SI-5 Flack , H. D.; Bernardinelli, G. *J. Appl. Crystallogr*. **2000**, *33*, 1143.

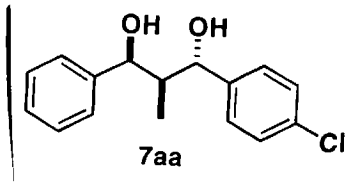
SI-6 Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; John Wiley & Sons: New York, 1994.

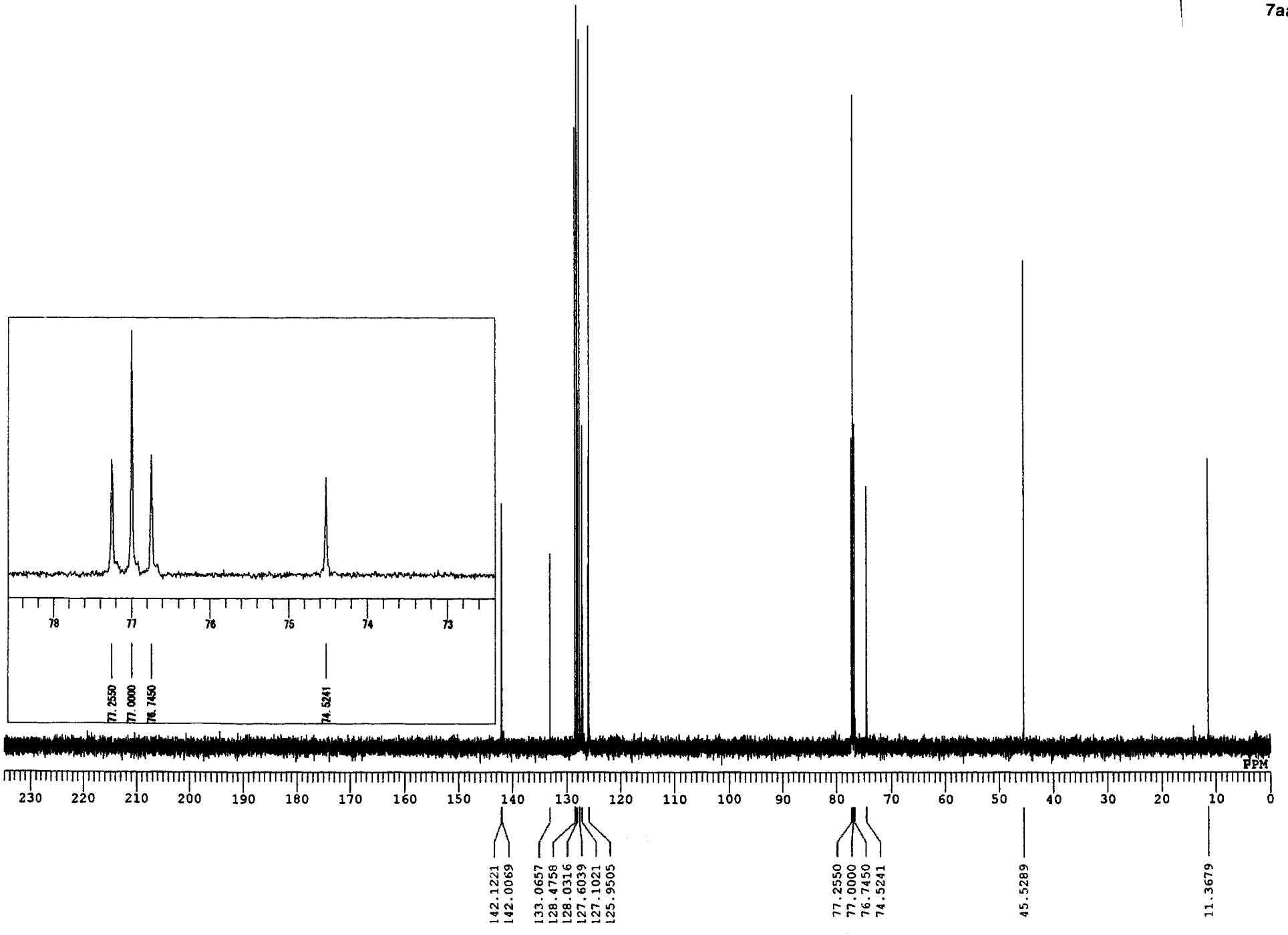
SI-7 Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Am. Chem. Soc*. **1991**, *113*, 4092.

SI-8 Vicario, J. L.; Badía, D.; Domínguez, E.; Rodríguez, M.; Carrillo, L. *J. Org. Chem.* **2000**, *65*, 3754.

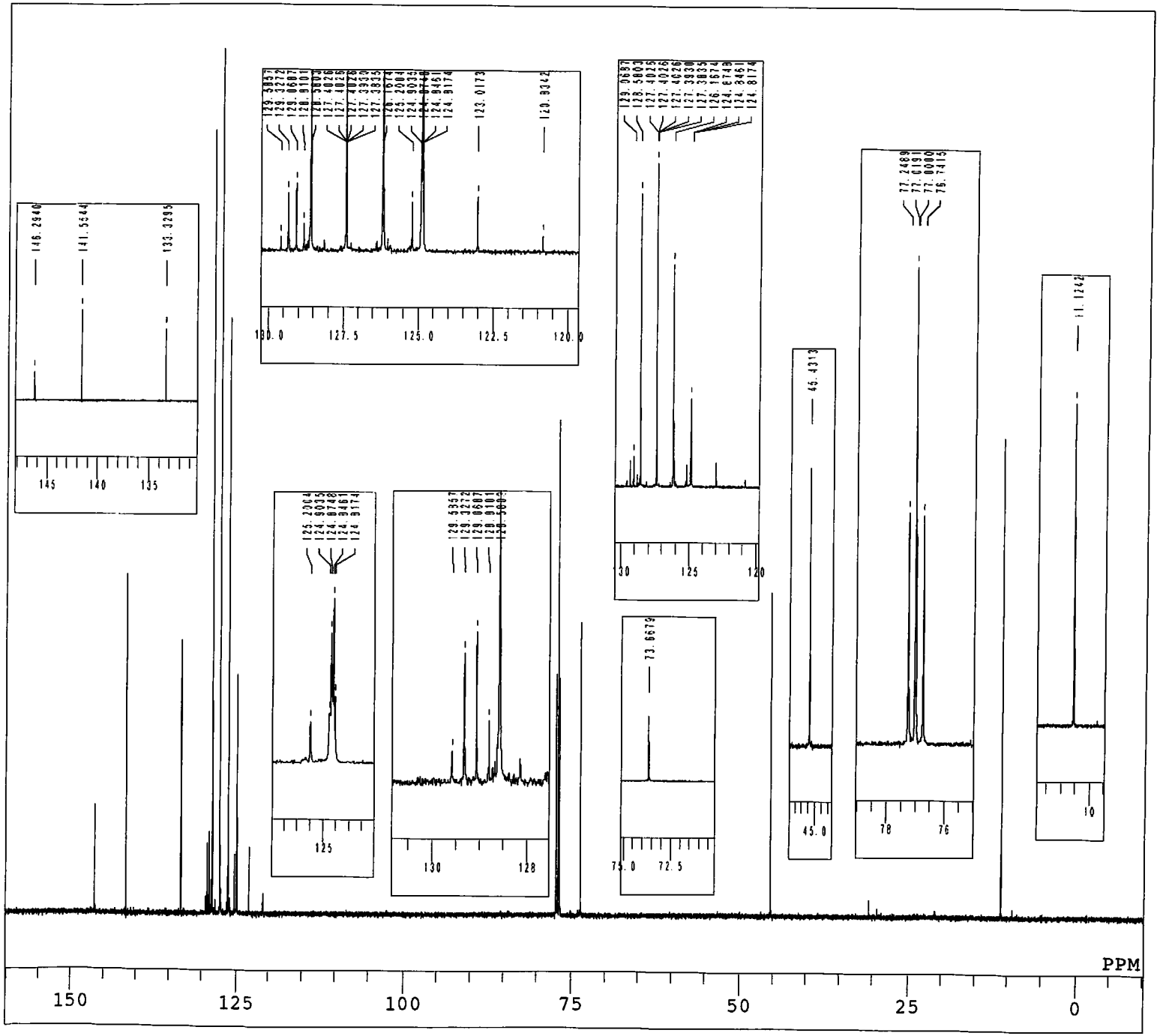
SI-9 Cossy, J.; Eustacheand, F.; Dalko, P. I. *Tetrahedron Lett.* **2001**, *42*, 5005.

D:\040317 H diol C13.als
1H Line

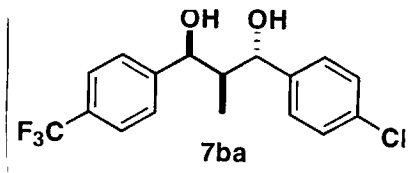




C:\My Documents\PGousei\vijay\vijay1-3.1

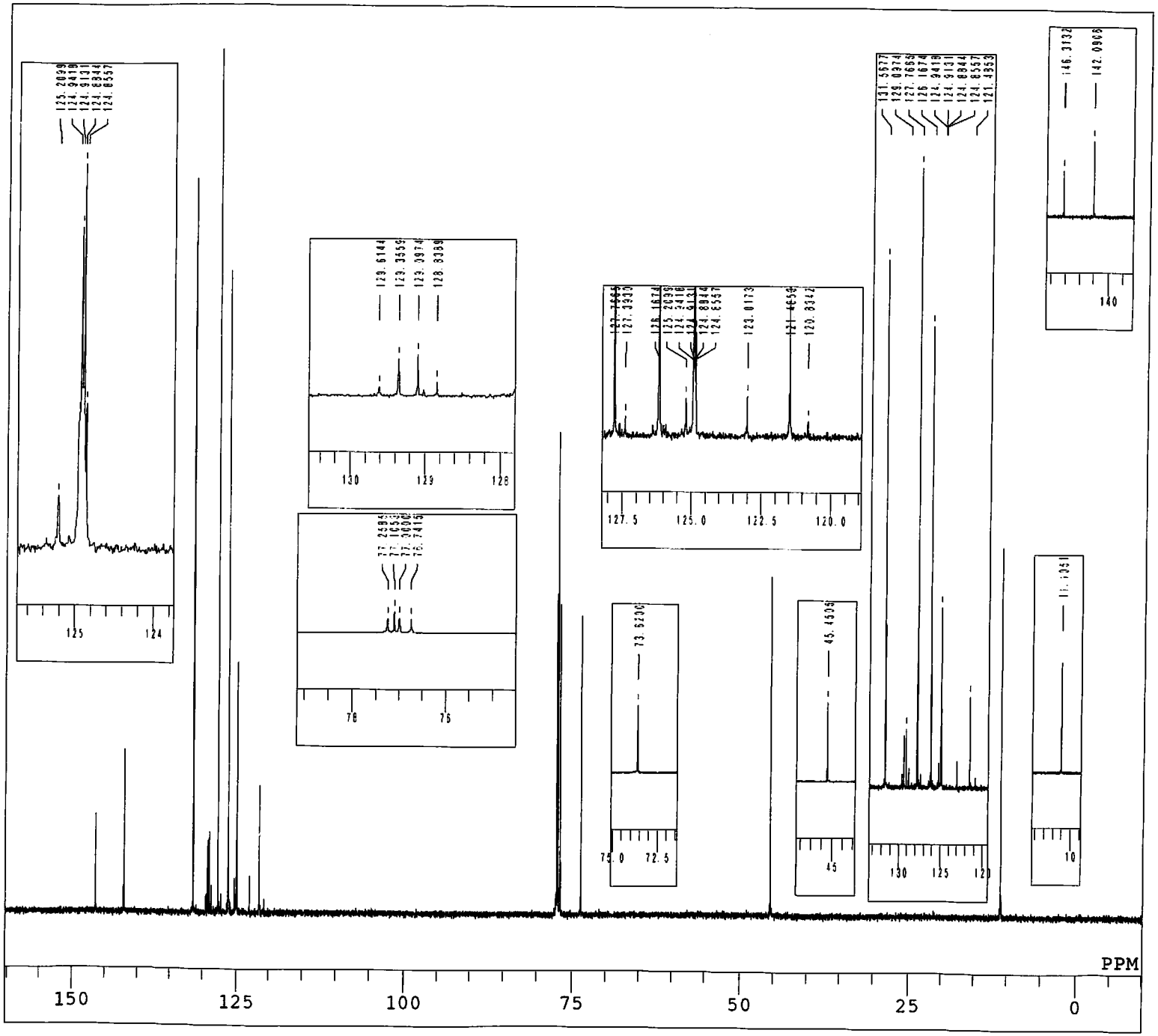


DFILE	C:\My Documents\PGousei\vij
COMNT	'4-Br13c
DATIM	18-03-2004 16:53:09
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	124.51 MHz
OBSET	3.45 KHz
OBFIN	6.0 Hz
POINT	32768
FREQU	39062.5 Hz
SCANS	568
ACQTM	0.839 sec
PD	2.000 sec
PW1	3.6 us
IRNUC	1H
CTEMP	23.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	50

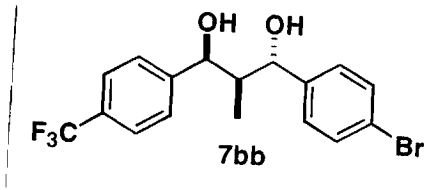


7ba

C:\My Documents\PGousei\vijay\vijay1-2.1

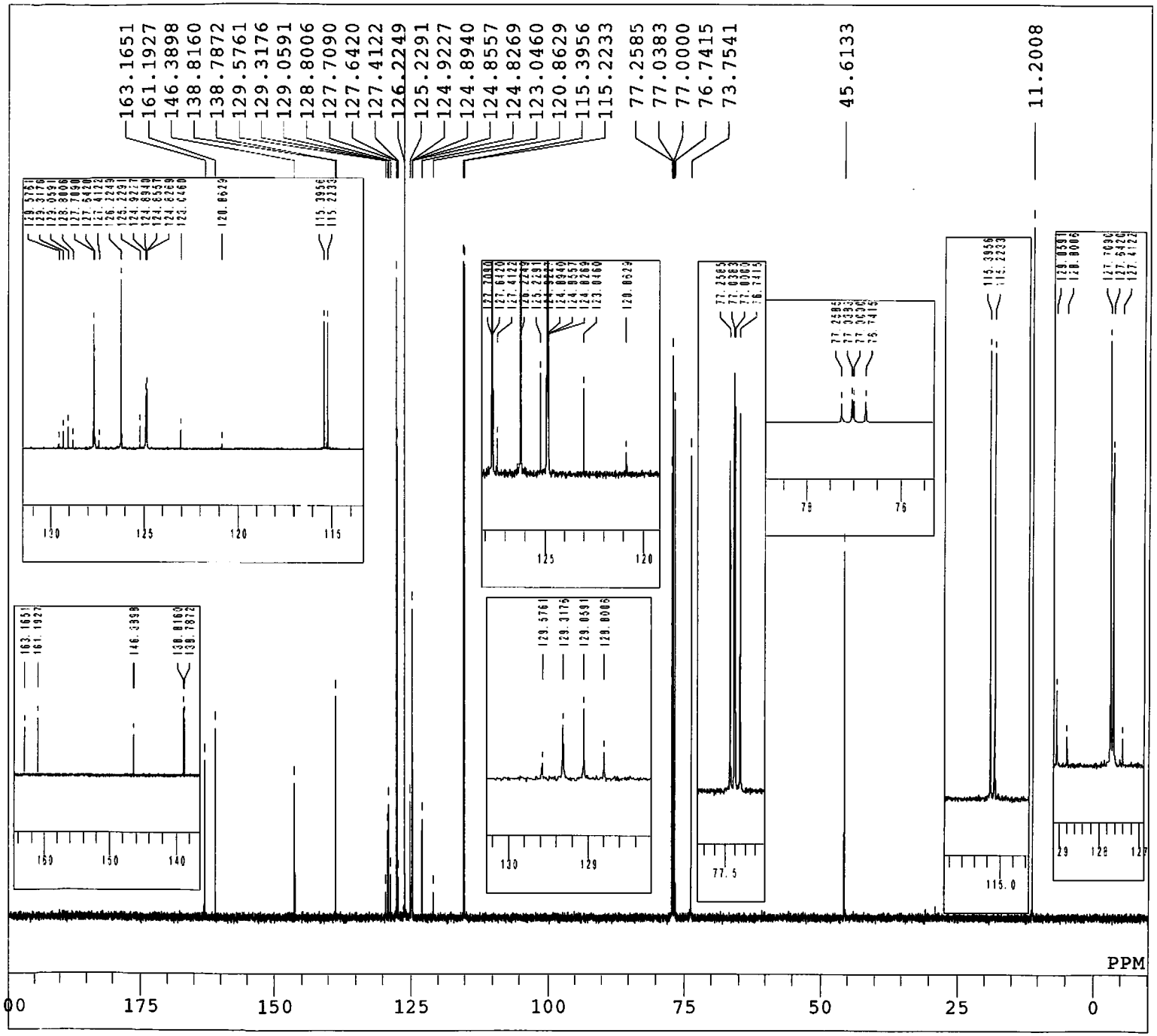


DFILE	C:\My Documents\PGousei\vij
COMNT	4-Cl13C
DATIM	18-03-2004 16:04:34
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	124.51 MHz
OBSET	3.45 KHz
OBFIN	6.0 Hz
POINT	32768
FREQU	39062.5 Hz
SCANS	921
ACQTM	0.839 sec
PD	2.000 sec
PW1	3.6 us
IRNUC	1H
CTEMP	23.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	50

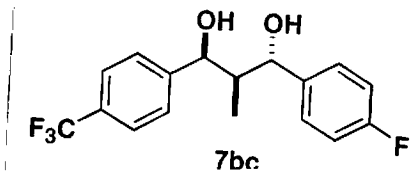


7bb

C:\My Documents\PGousei\vijay\vijay23.1
4F corbon 13 nmr



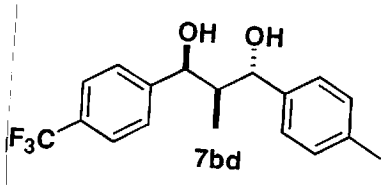
DFILE	C:\My Documents\PGousei\vij
COMNT	4F corbon 13 nmr
DATIM	26-03-2004 18:02:19
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	124.51 MHz
OBSET	3.45 KHz
OBFIN	6.0 Hz
POINT	32768
FREQU	39062.5 Hz
SCANS	669
ACQTM	0.839 sec
PD	2.000 sec
PW1	3.6 us
IRNUC	1H
CTEMP	21.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	50



7bc

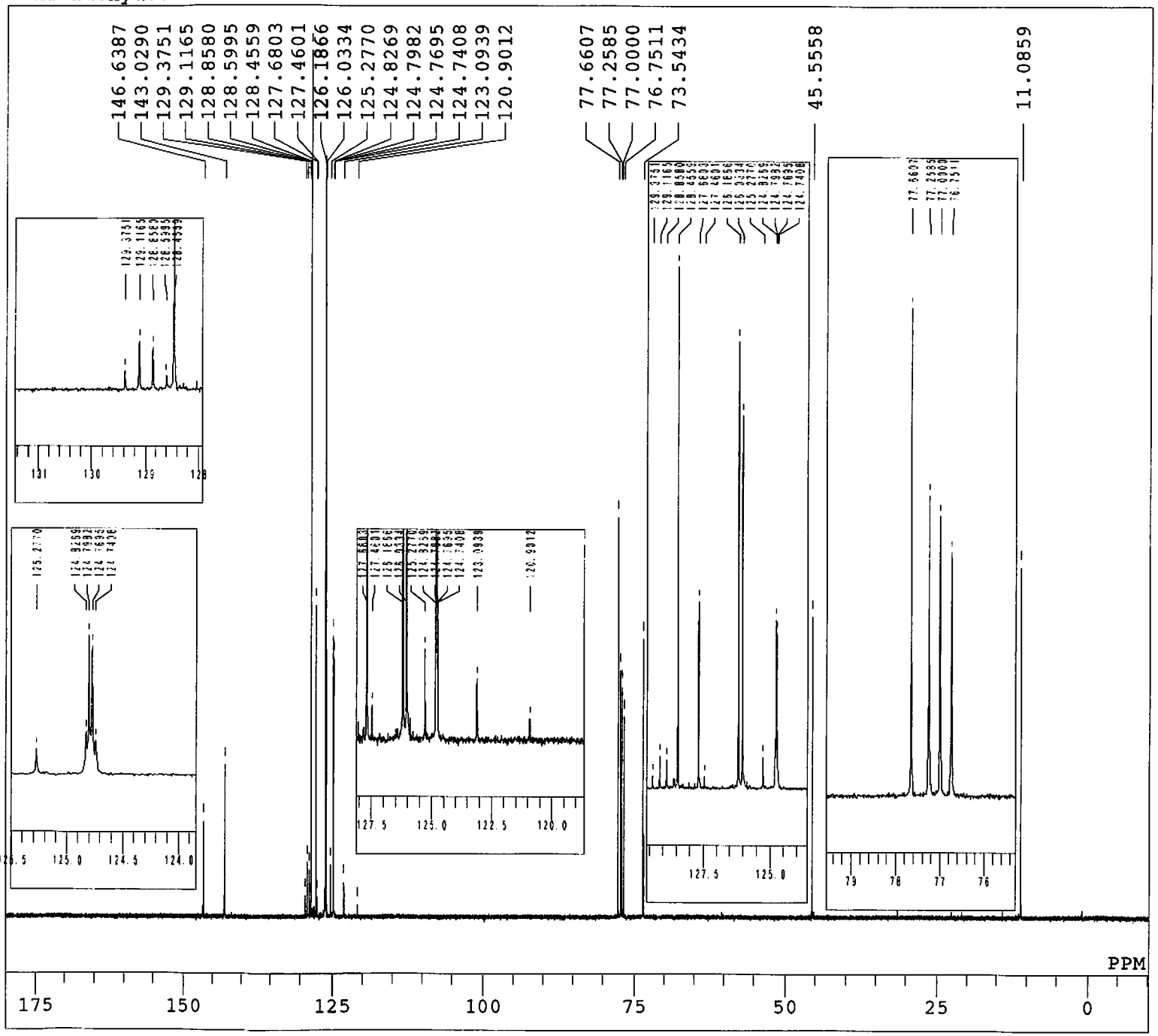
C:\My Documents\PGousei\vijay\vijay15.1
4Me Corbon 13 nmr

DFILE	C:\My Documents\PGousei\vij
COMNT	4Me Corbon 13 nmr
DATIM	24-03-2004 00:30:07
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	124.51 MHz
OBSET	3.45 KHz
OBFIN	6.0 Hz
POINT	32768
FREQU	39062.5 Hz
SCANS	587
ACQTM	0.839 sec
PD	2.000 sec
PW1	3.6 us
IRNUC	1H
CTEMP	21.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.00 Hz
RGAIN	50

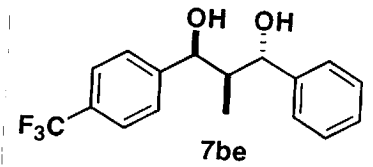


7bd

C:\My Documents\PGousei\vijay\vijay11.1
benzaldehydecorbon13



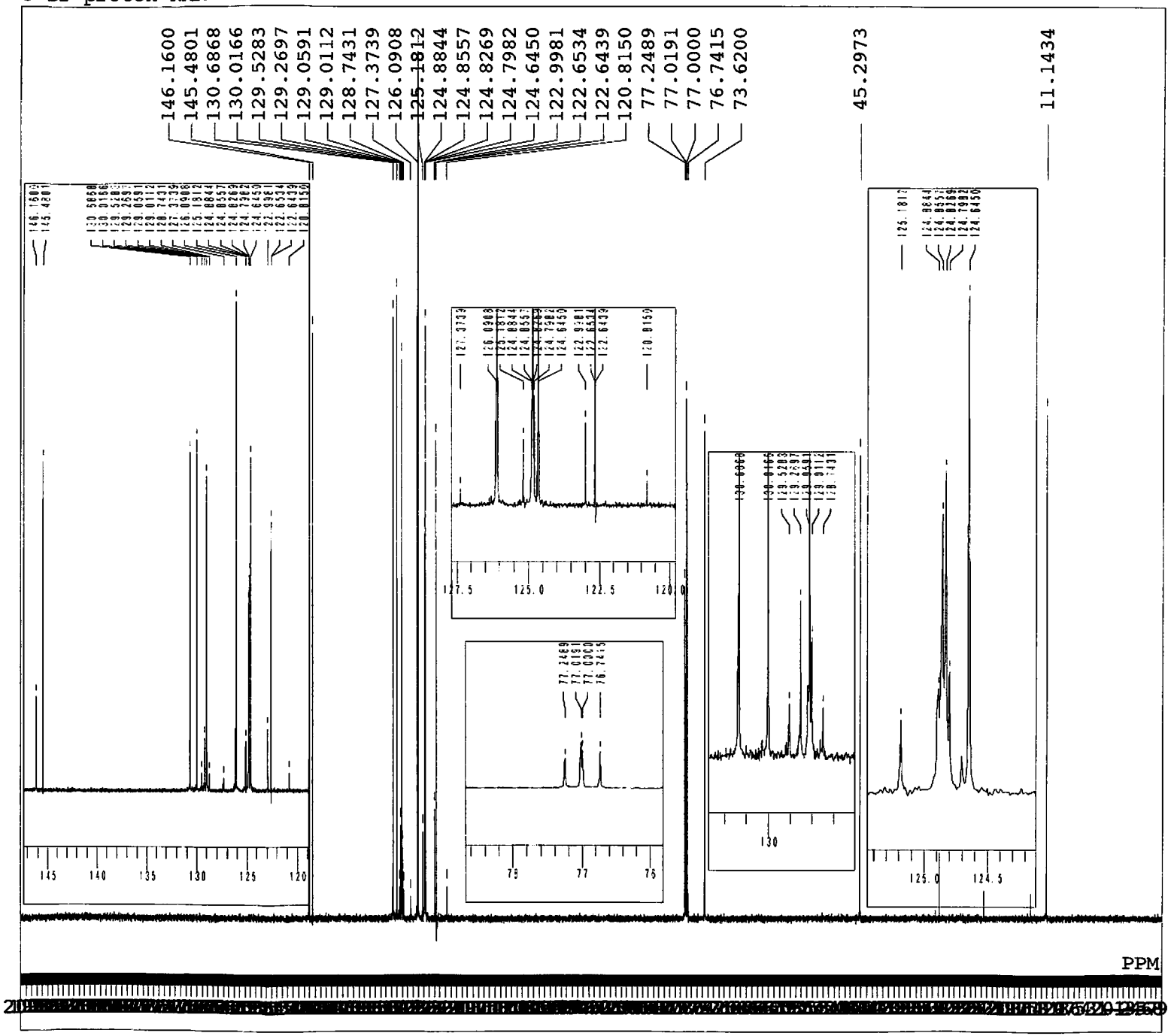
DFILE C:\My Documents\PGousei\vij
COMNT benzaldehydecorbon13
DATIM 22-03-2004 01:42:25
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 124.51 MHz
OBSET 3.45 KHz
OBFIN 6.0 Hz
POINT 32768
FREQU 39062.5 Hz
SCANS 495
ACQTM 0.839 sec
PD 2.000 sec
PW1 3.6 us
IRNUC 1H
CTEMP 21.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 50



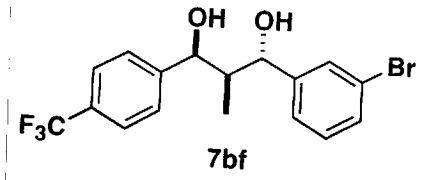
7be

C:\My Documents\PGousei\vijay\vijay 28.1

3 Br proton NMR

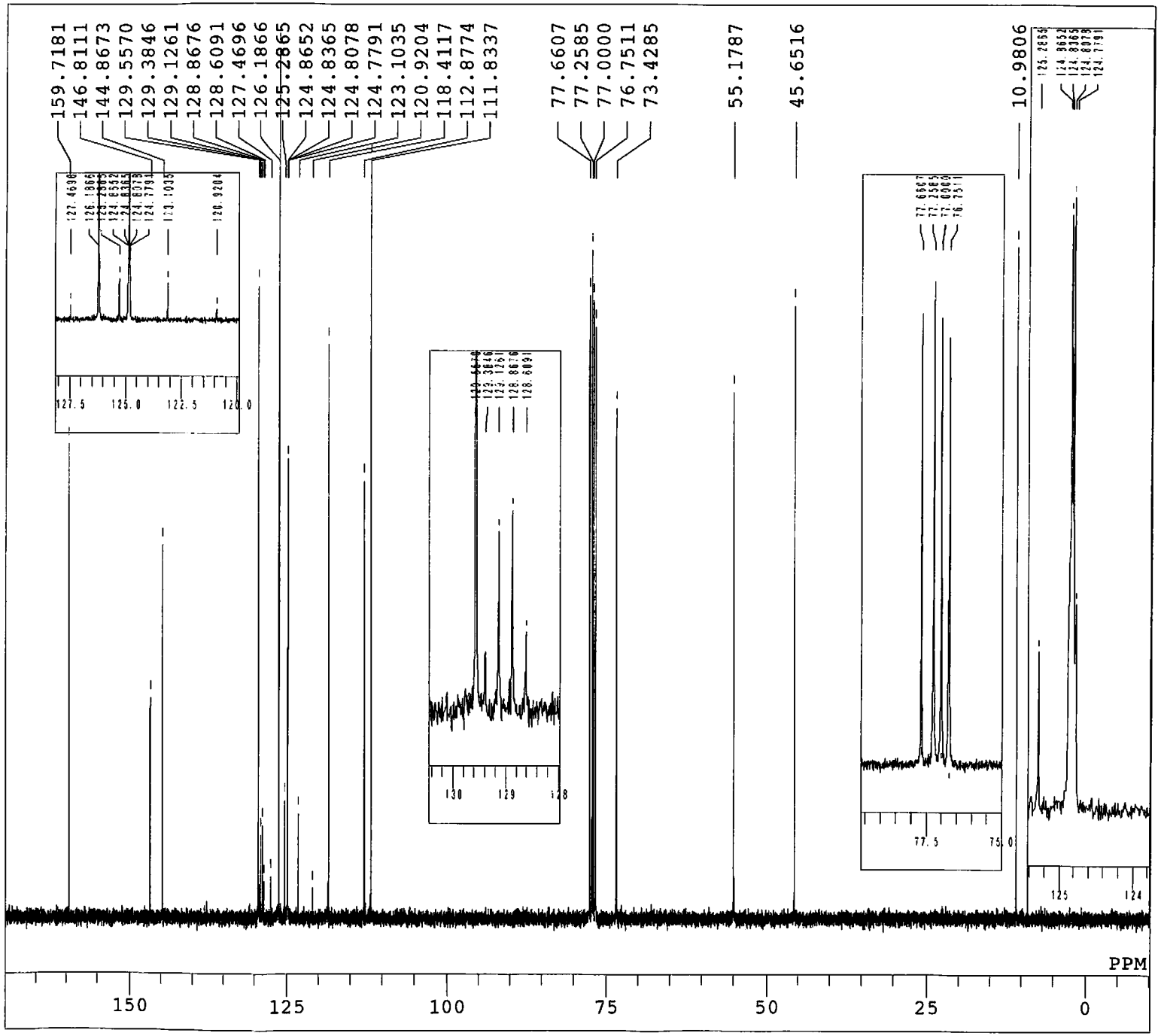


DFILE	C:\My Documents\PGousei\vij
COMNT	3 Br proton NMR
DATIM	05-04-2004 15:39:22
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	124.51 MHz
OBSET	3.45 KHz
OBFIN	6.0 Hz
POINT	32768
FREQU	39062.5 Hz
SCANS	606
ACQTM	0.839 sec
PD	2.000 sec
PW1	3.6 us
IRNUC	1H
CTEMP	21.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	50

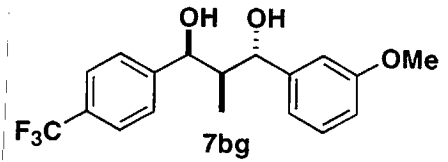


7bf

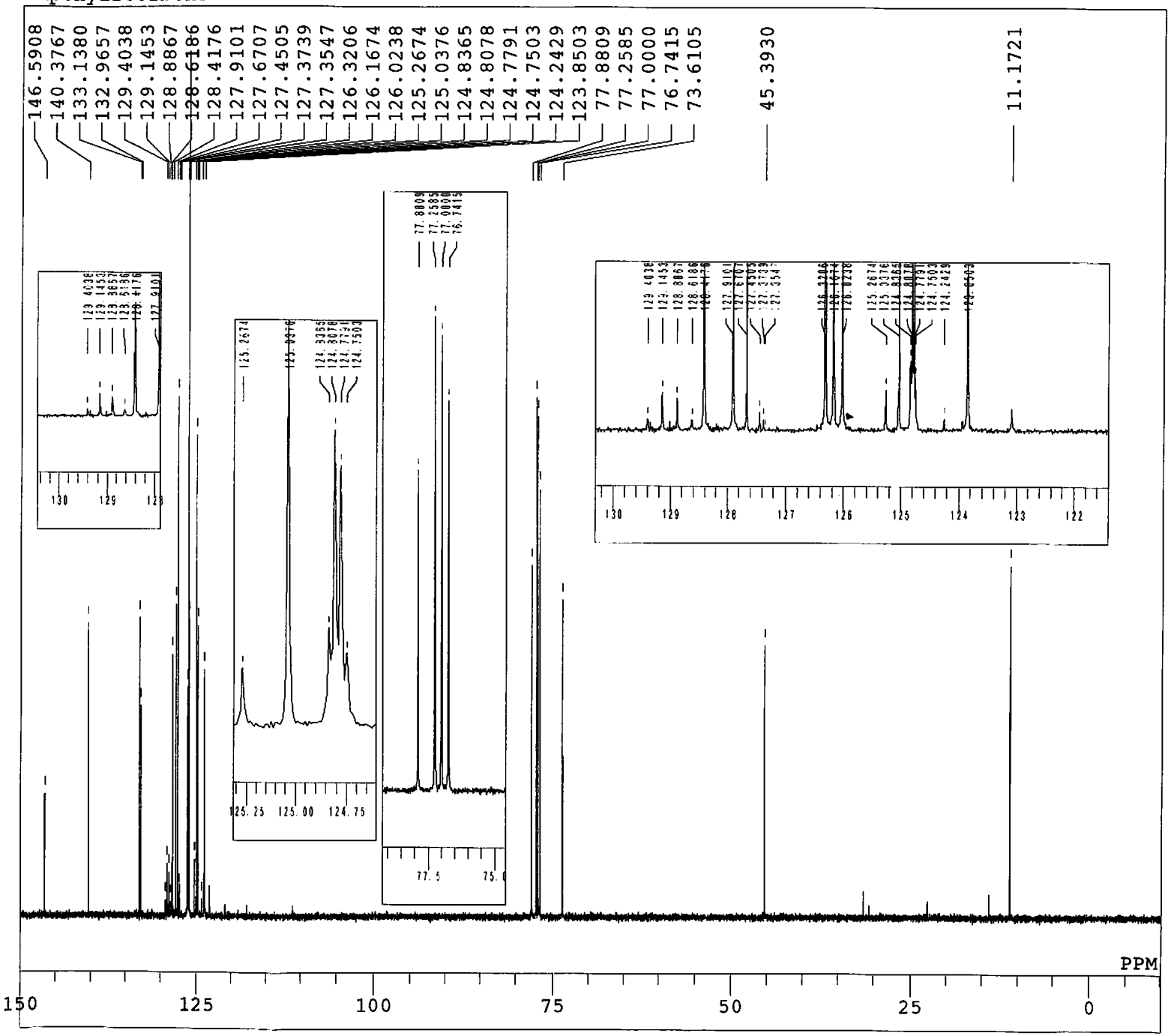
C:\My Documents\PGousei\vijay\vijay7.1
3OMeCorbon13



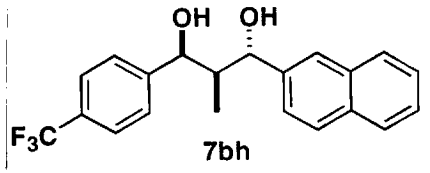
DFILE	C:\My Documents\PGousei\vij
COMNT	3OMeCorbon13
DATIM	20-03-2004 02:55:55
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	124.51 MHz
OBSET	3.45 KHz
OBFIN	6.0 Hz
POINT	32768
FREQU	39062.5 Hz
SCANS	614
ACQTM	0.839 sec
PD	2.000 sec
PW1	3.6 us
IRNUC	1H
CTEMP	22.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	50



C:\My Documents\PGousei\vijay\vijaynapthylC13.1
napthyl2Corbon13

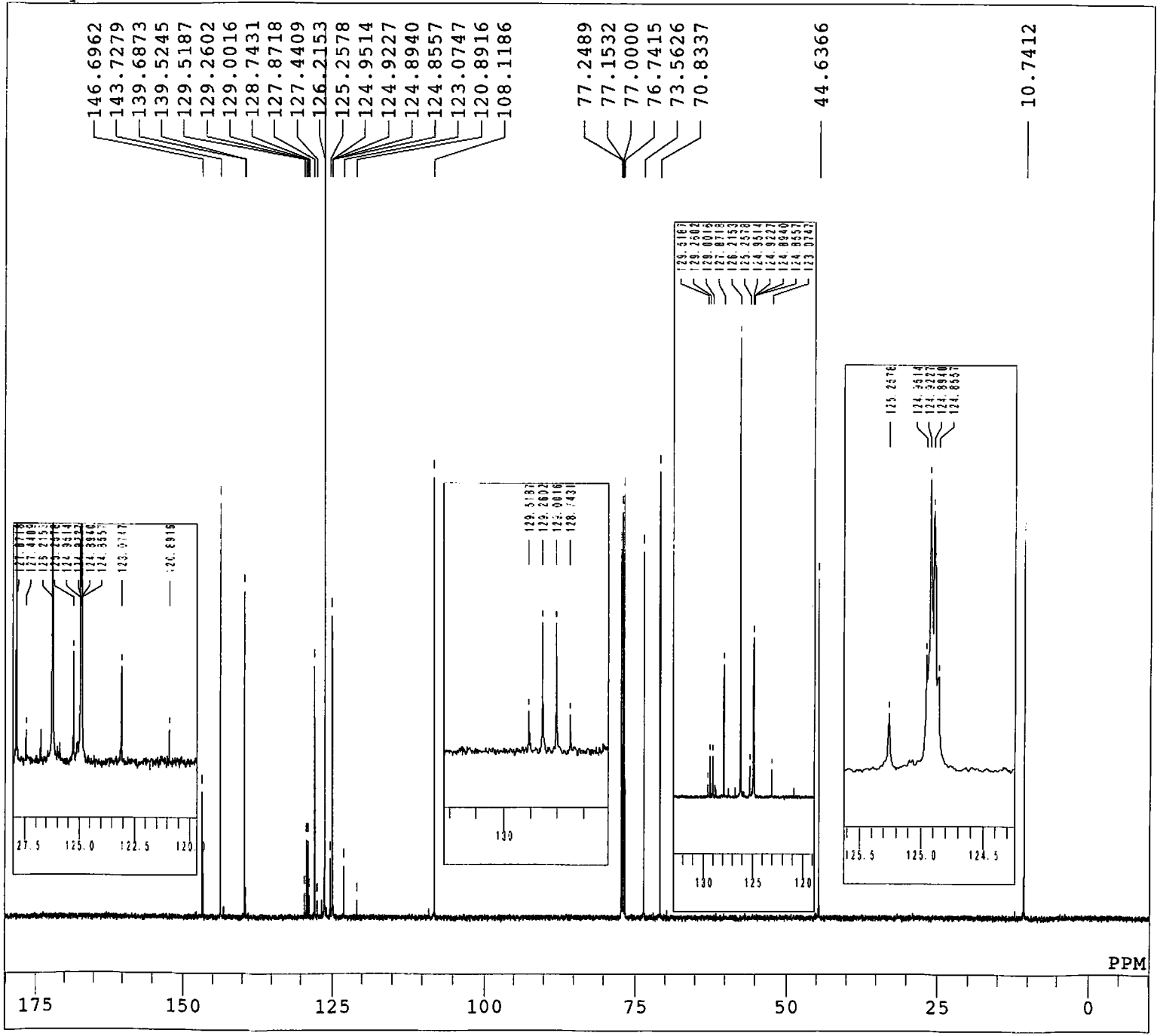


DFILE C:\My Documents\PGousei\vij
COMNT napthyl2Corbon13
DATIM 20-03-2004 02:13:37
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 124.51 MHz
OBSET 3.45 KHz
OBFIN 6.0 Hz
POINT 32768
FREQU 39062.5 Hz
SCANS 978
ACQTM 0.839 sec
PD 2.000 sec
PW1 3.6 us
IRNUC 1H
CTEMP 22.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 50

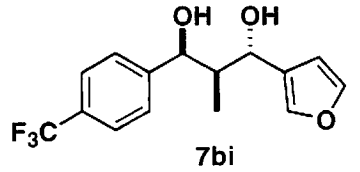


7bh

C:\My Documents\PGousei\vijay\vijay14.1
3 furyl corbon 13 nmr

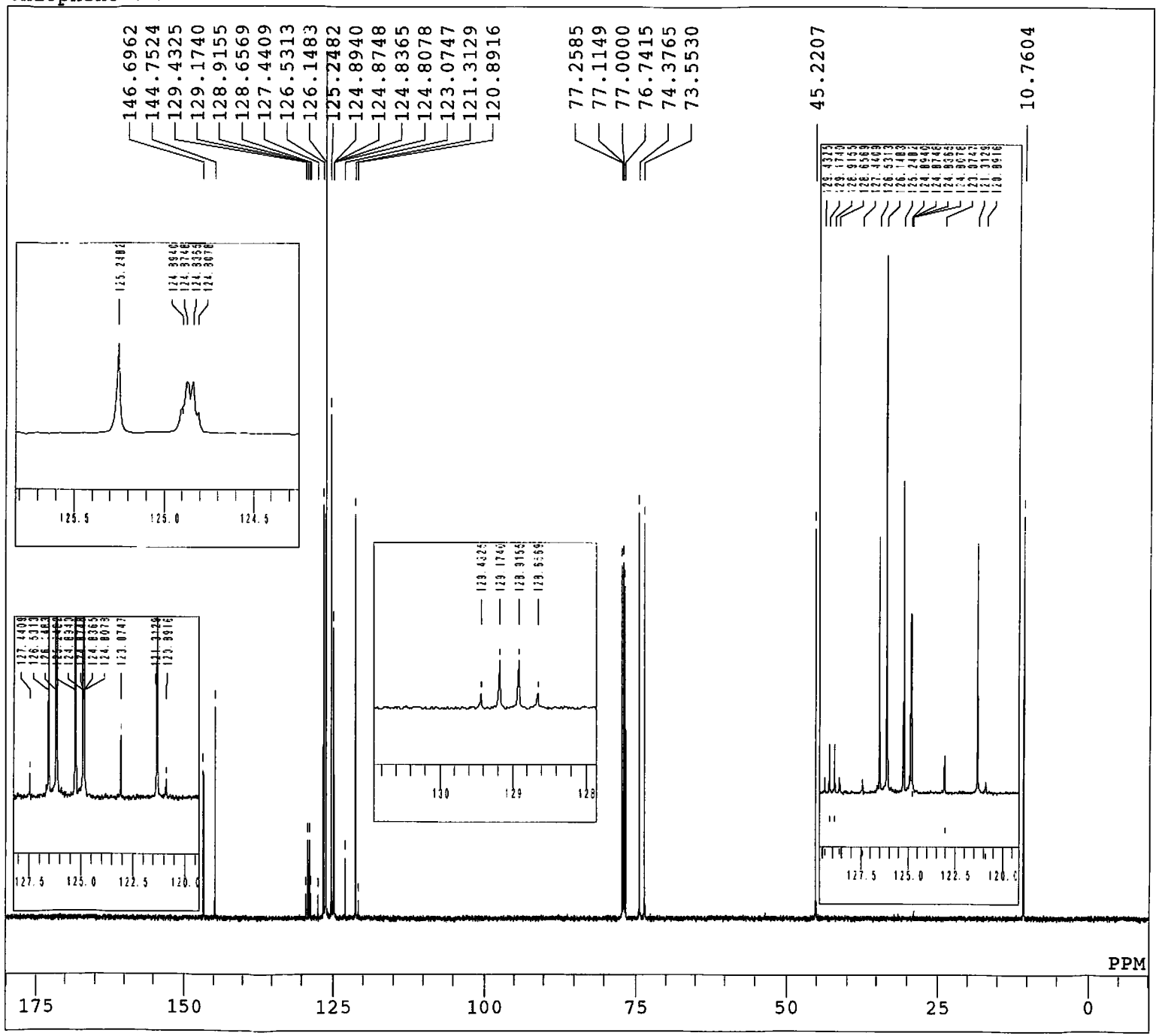


DFILE	C:\My Documents\PGousei\vij
COMNT	3 furyl corbon 13 nmr
DATIM	23-03-2004 23:54:09
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	124.51 MHz
OBSET	3.45 KHz
OBFIN	6.0 Hz
POINT	32768
FREQU	39062.5 Hz
SCANS	591
ACQTM	0.839 sec
PD	2.000 sec
PW1	3.6 us
IRNUC	1H
CTEMP	21.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.00 Hz
RGAIN	50

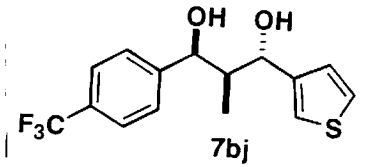


7bi

C:\My Documents\PGousei\vijay\vijay17.1
thiophene corbon 13 nmr

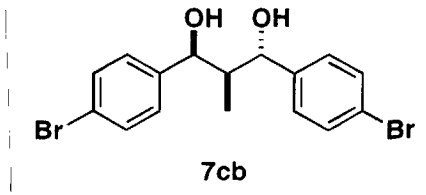


DFILE	C:\My Documents\PGousei\vij
COMNT	thiophene corbon 13 nmr
DATIM	24-03-2004 03:09:42
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	124.51 MHz
OBSET	3.45 KHz
OBFIN	6.0 Hz
POINT	32768
FREQU	39062.5 Hz
SCANS	728
ACQTM	0.839 sec
PD	2.000 sec
PW1	3.6 us
IRNUC	1H
CTEMP	21.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.00 Hz
RGAIN	50

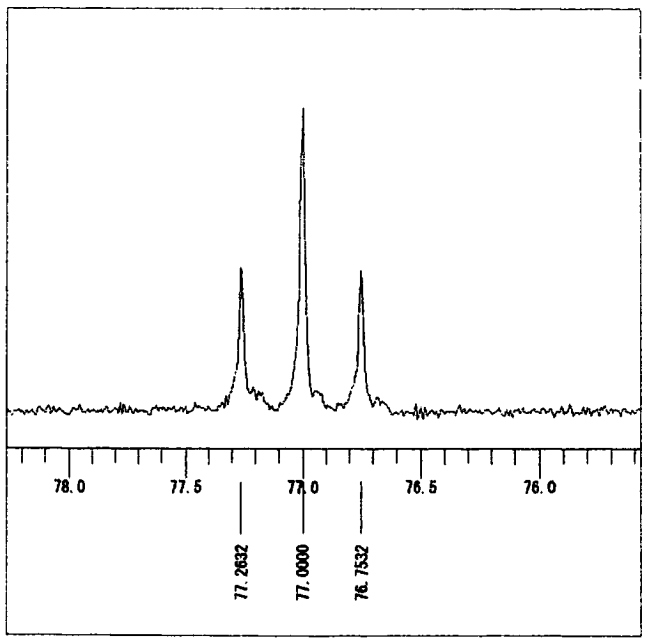


7bj

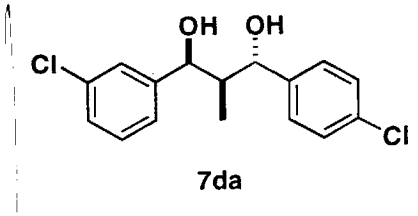
D:\040409 diol p-br+p-BrPhCHO C13.als
1H Line



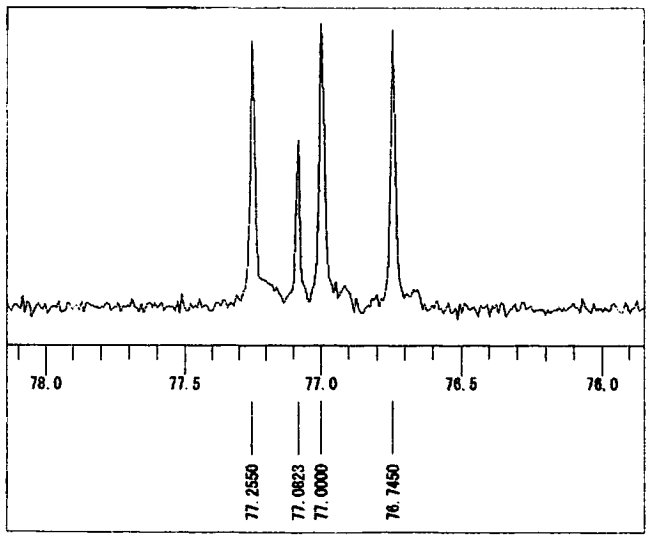
7cb



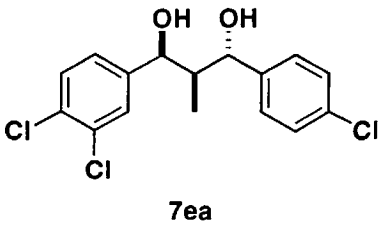
D:\040311 3-Cl-Cl diol C13.als
1H Line



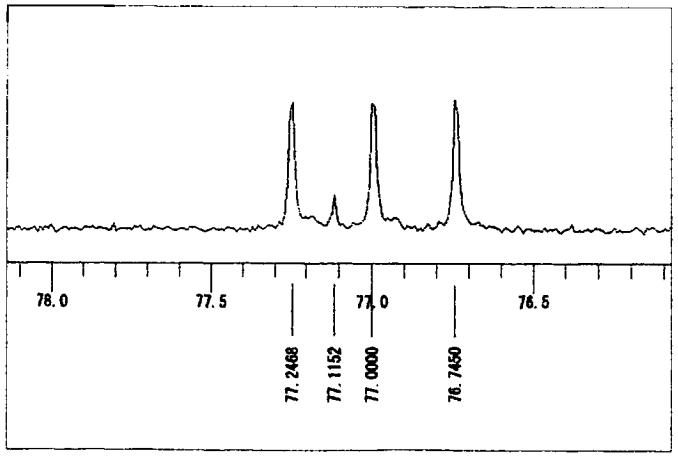
7da



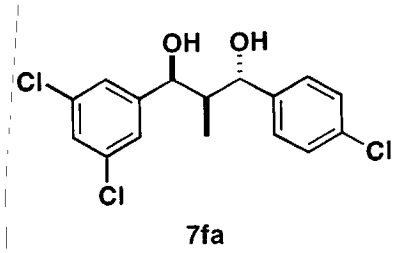
D:\040311 3,4-diCl-Cl diol C13.als
1H Line



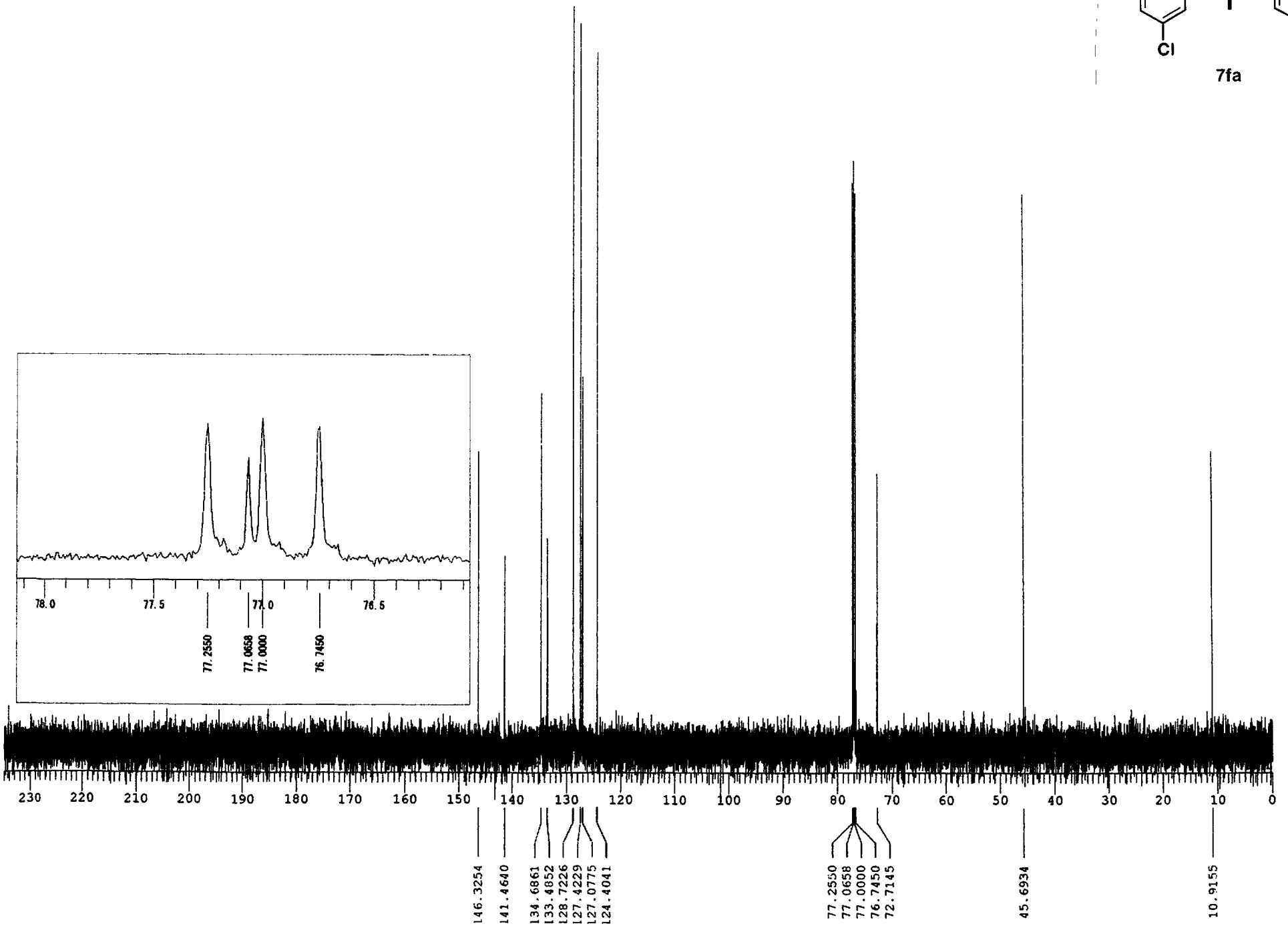
7ea



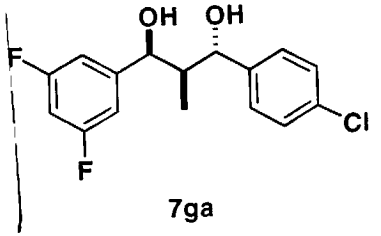
D:\040311 3,5-diCl-Cl diol C13.als
1H Line



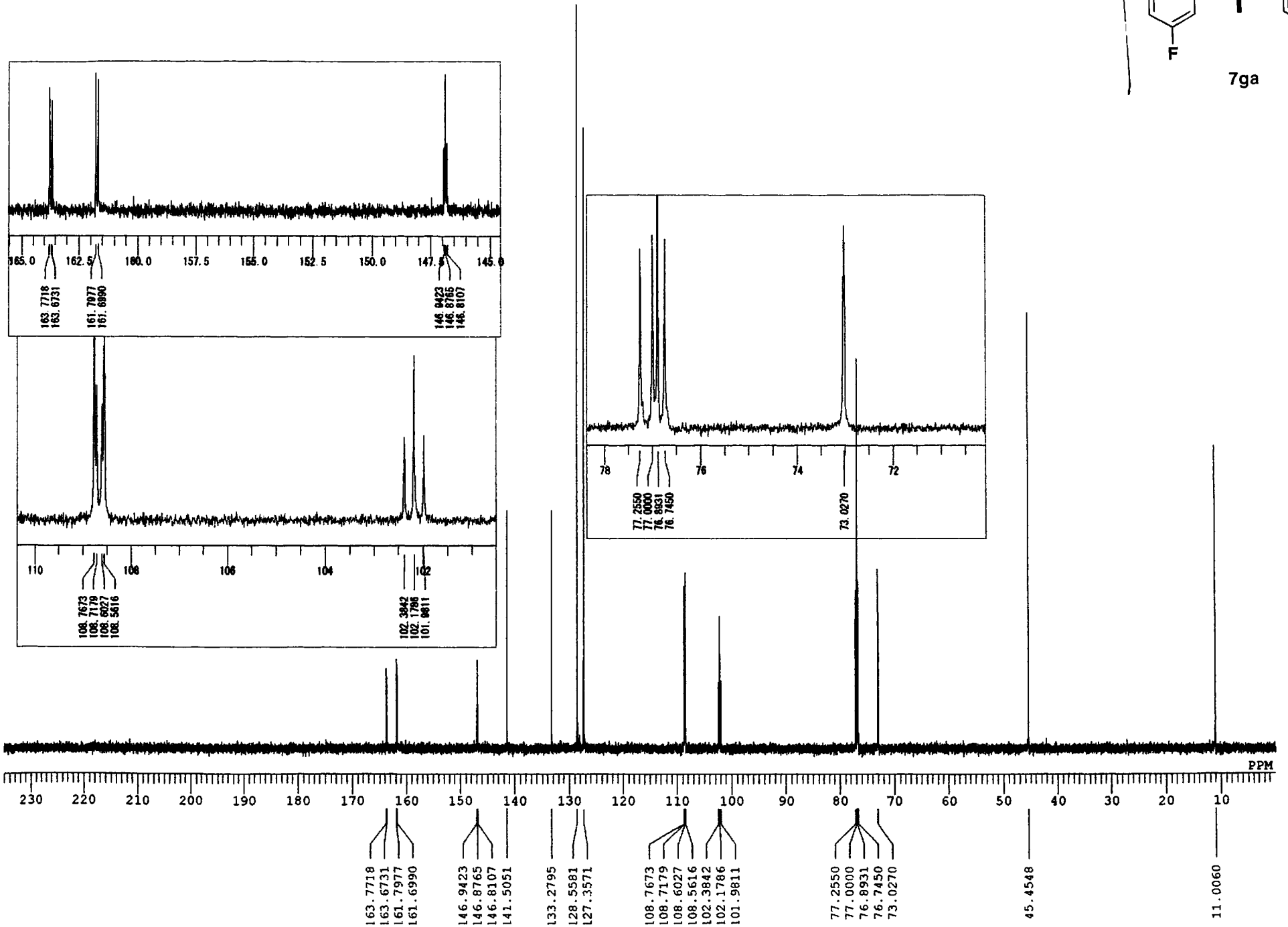
7fa



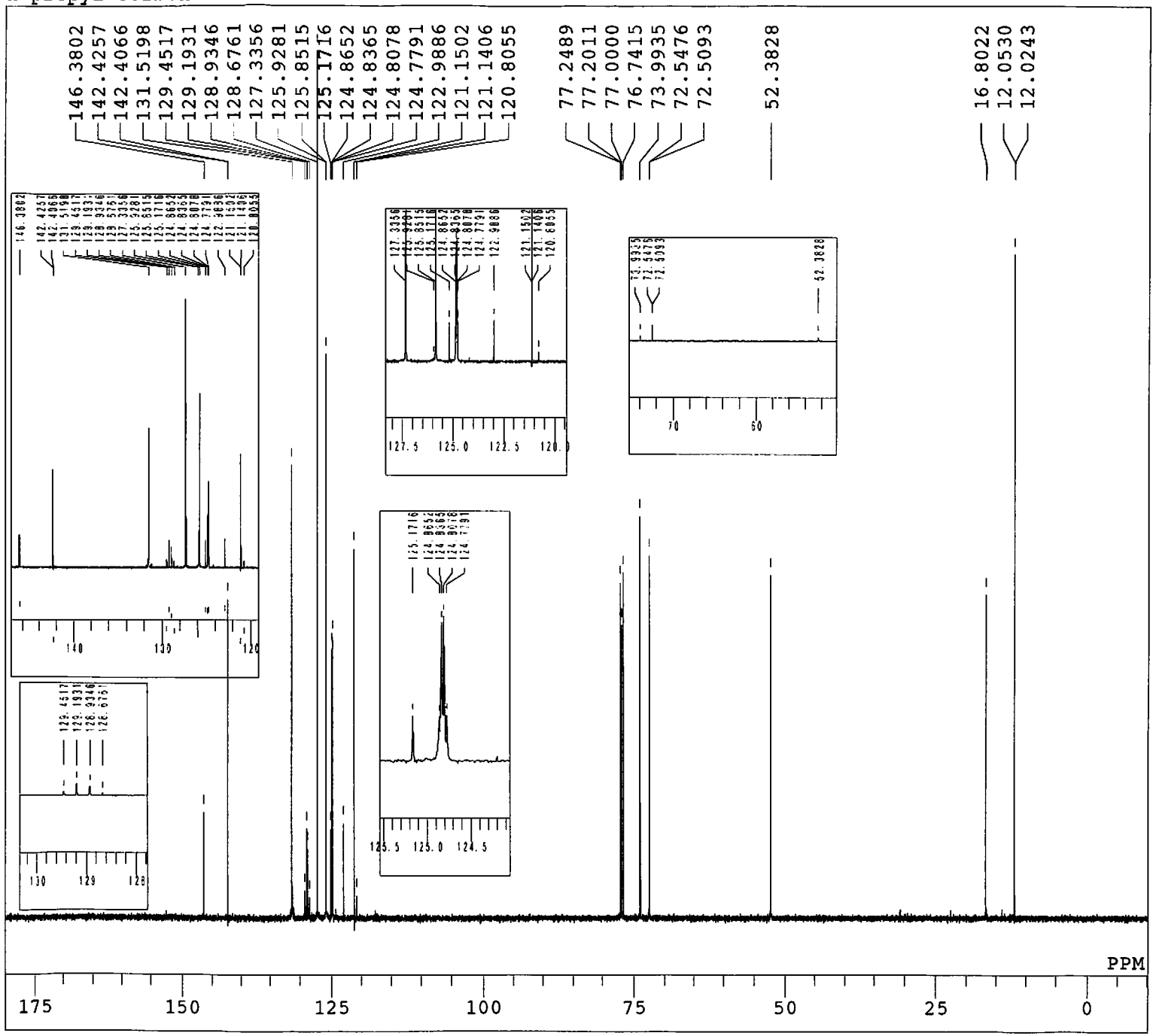
D:\040317 3,5-di F diol C13.als
1H Line



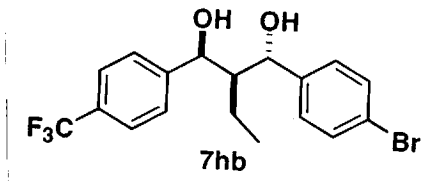
7ga



C:\My Documents\PGousei\vijay\vijay22.1
n-propyl corbon 13 nmr

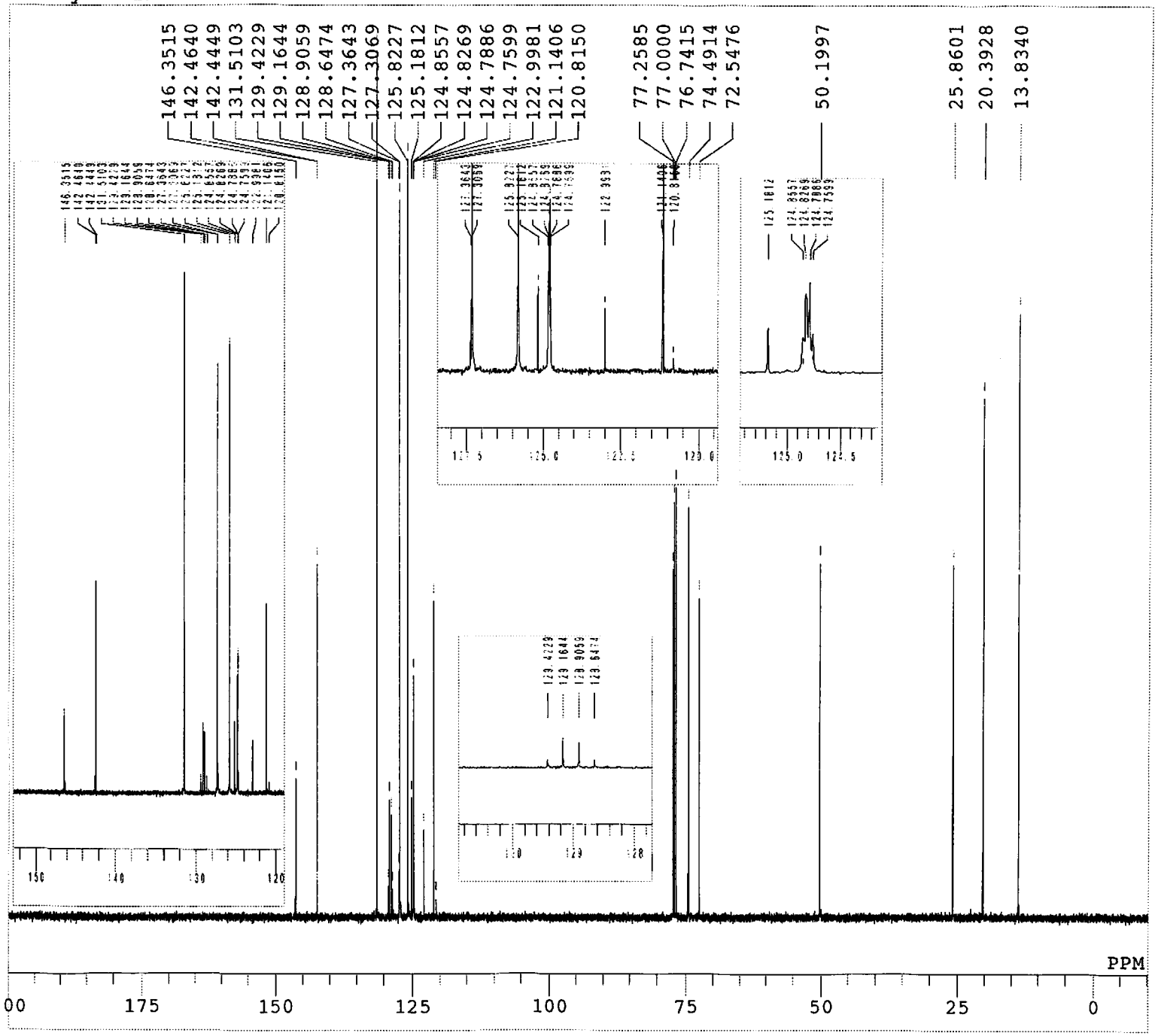


DFILE C:\My Documents\PGousei\vij
COMNT n-propyl corbon 13 nmr
DATIM 26-03-2004 16:45:21
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 124.51 MHz
OBSET 3.45 KHz
OBFIN 6.0 Hz
POINT 32768
FREQU 39062.5 Hz
SCANS 614
ACQTM 0.839 sec
PD 2.000 sec
PW1 3.6 us
IRNUC 1H
CTEMP 21.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 50



7hb

C:\My Documents\PGousei\vijay\vijay20.1
n butyl corbon 13



DFILE	C:\My Documents\PGousei\vij
COMNT	n butyl corbon 13
DATIM	25-03-2004 18:18:20
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	124.51 MHz
OBSET	3.45 KHz
OBFIN	6.0 Hz
POINT	32768
FREQU	39062.5 Hz
SCANS	441
ACQTM	0.839 sec
PD	2.000 sec
PW1	3.6 us
IRNUC	1H
CTEMP	21.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	50