Cu(II)-Based Strategy for Catalytic Enantioselective β-Borylation of α, β-Unsaturated Acceptors

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Electronic Supplementary Information

Table of Contents

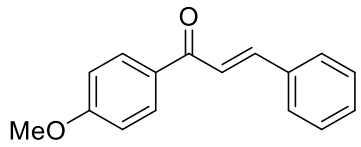
1. General

Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECX-600 or ECX-500 spectrometer, operating at 600 or 500 MHz for ^{1}H and 150 or 125 MHz for ^{13}C NMR in $CDCl_3$ unless otherwise noted. $CDCl_3$ served as the internal standard ($\delta = 7.24$) for ^{1}H NMR and ($\delta = 77.0$) for ^{13}C NMR. Infrared (IR) spectra were obtained using a JASCO FT/IR-4200 spectrometer. Data are represented as frequency of absorption (cm^{-1}). High-performance liquid chromatography was carried out using following apparatuses; SHIMADZU LC-10ATvp (liquid chromatograph), SHIMADZU SPD-10A (UV detector) and SHIMADZU C-R8A (Chromatopac) using Daicel chiralpak® or chiralcel® columns. Preparative thin-layer chromatography (PTLC) was carried out using Wakogel B-5F from Wako Pure Chemical Industries, Ltd. High Resolution Mass Spectra (HRMS) were recorded using a JEOL JMS-T100TD (DART) spectrometer. Optical Rotations were measured on a JASCO P1010 polarimeter using a 2 mL cell with 1 dm path length. Data are reported as follows: $[\alpha]_D^T$ (*c* in g/100 mL, solvent). Deionized water from a MILLIPORE MilliQ machine (Gradient A 10) was used as solvent without further treatment. All organic solvents used were commercially available dry solvents, which were distilled appropriately under an argon atmosphere or were stored over molecular sieves prior to use. All reagents used as additives were either distilled or recrystallized before use.

<Reagents>

Unless stated otherwise, commercially available reagents were used as received with the exception of the following substrates, which were prepared through reported methods. Analytical data for these compounds are in full agreement with reported data.

(*E*)-1-(4'-methoxyphenyl)-3-phenylprop-2-en-1-one (**1c**)[1]

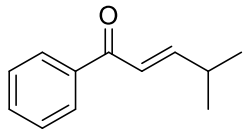


White solid

^{1}H NMR (500 MHz); δ = 8.05-8.03 (t, *J* = 2.3 Hz, 2H), 7.80 (d, *J* = 48.7 Hz, 1H), 7.65-7.56 (m, 2H), 7.48 (d, *J* = 48.7 Hz, 1H), 7.40-7.43 (m, 3H), 6.98 (dd, *J* = 1.7, 5.2 Hz, 2H), 3.90 (s, 3H).

^{13}C NMR (125 MHz); δ = 199.6, 154.0, 153.5, 150.5, 147.3, 141.1, 138.8, 129.9, 38.1, 25.6, 22.7.

(*E*)-4-Methyl-1-phenylpent-2-en-1-one (**1l**)[2]

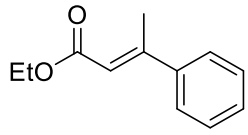


A little bit yellow liquid

^{1}H NMR (500 MHz); δ = 7.89 (d, *J* = 7.6 Hz, 2H), 7.52-7.42 (m, 3H), 7.04 (dd, *J* = 6.4, 9.2 Hz, 1H), 6.79 (dd, *J* = 6.4, 9.2 Hz, 1H), 2.56-2.54 (m, 1H), 1.11 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (125 MHz); δ = 191.3, 156.0, 138.1, 132.5, 128.5, 123.1, 31.5, 21.4.

Ethyl (*E*)-3-phenylbut-2-enoate (**1n**)[3]

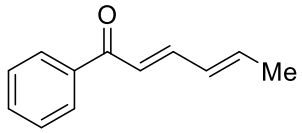


A little bit yellow liquid

^{1}H NMR (500 MHz); δ = 7.38-7.15 (m, 5H), 5.90-5.88 (m, 1H), 4.01-3.96 (m, 2H), 2.16 (s, 3H), 1.06 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (125 MHz); δ = 169.9, 154.3, 138.2, 128.0, 127.5, 126.4, 119.2, 59.5, 26.5, 14.1.

(2*E*,4*E*)-1-phenylhexa-2,4-dien-1-one (**1r**)[4]

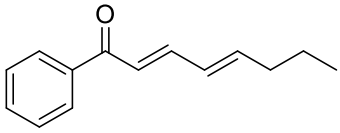


Yellow Solid

^{1}H NMR (500 MHz); δ = 7.96-7.88 (m, 2H), 7.59-7.35 (m, 4H), 6.86 (d, *J* = 14.6 Hz, 1H), 6.38-6.20 (m, 2H), 1.89 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (125 MHz); δ = 193.2, 145.7, 141.1, 138.5, 132.6, 130.7, 128.6, 123.6, 18.9.

(2*E*,4*E*)-1-phenylocta-2,4-dien-1-one (**1s**)[5]

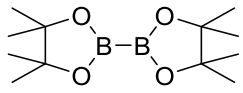


A little bit yellow oil

^{1}H NMR (500 MHz); δ = 7.96-7.88 (m, 2H), 7.59-7.35 (m, 4H), 6.86 (d, *J* = 14.6 Hz, 1H), 6.38-6.20 (m, 2H), 2.22-2.15 (m, 2H), 1.46-1.39 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz); δ = 194.6, 145.5, 141.1, 138.5, 133.2, 131.1, 128.9, 124.1, 36.2, 23.4, 14.0.

Bis(pinacolato)diboron (**2**)[6]



White solid

^{1}H NMR (500 MHz); δ = 1.26 (s, 24H).

^{13}C NMR (125 MHz); δ = 83.5, 25.0.

^{11}B NMR (160 MHz); δ = 30.6 [lit[7] 30.6 ppm].

<Metal Salts>

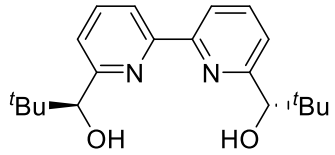
$Cu(OAc)_2$ anhydrous was purchased from Kanto Chemical Co., Inc (95.0% min. purity).

<Preparation of Ligands>

Chiral 2,2'-bipyridine **L7** was synthesized using protocols described in literatures.

All other ligands are commercially available.

(*S*, *S*)-6,6'-bis(1-hydroxy-2,2-dimethylpropyl)-2,2'-bipyridine (**L7**)[8]



White solid

^{1}H NMR (400 MHz); δ = 8.30 (d, *J* = 8.0 Hz, 2H), 7.79 (dd, *J* = 7.6, 8.0 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 2H), 4.50-4.43 (m, 2H), 0.98 (s, 18H).

^{13}C NMR (100 MHz); δ = 159.3, 153.8, 136.6, 123.1, 119.6, 80.2, 36.3, 25.9.

HPLC (Dialcel Chiralcel OD, ^{n}hexane/ ^{i}PrOH = 19/1, flow rate 1.0 mL/min); t_R = 40.2 min (*R*, *R*), t_R = 48.7 min (*S*, *S*), t_R = 19.9 min (*meso* isomer). >99.5% *ee*

2. Typical Experimental Procedure for Chiral $Cu(OAc)_2$-catalyzed Enantioselective β-Borylation to α,β-Unsaturated Carbonyl Compounds in Organic Solvents (Table 2, entry 1):

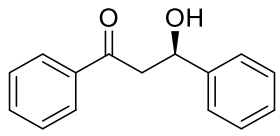
In an oven-dried Schlenk tube, Et_2O (1.5 mL) was added to $Cu(OAc)_2$ (3.6 mg, 5 mol%), chiral 2,2'-bipyridine **L7** (7.9 mg, 6 mol%) and $B_2(pin)_2$ (121.8 mg, 0.48 mmol) under Ar. The reaction mixture was stirred for 1 h at room temperature, followed by successive addition of chalcone **1a** (81.9 mg, 0.4 mmol), MeOH (0.016 mL, 0.4 mmol) and Et_2O (0.5 mL). After stirring for 12 h, the reaction mixture was poured into pyridine aqueous solution and extracted with EtOAc (20 mL) three times. The combined organic layers were concentrated under reduced pressure and the residue was dissolved in THF (3mL) and H_2O (2mL). An excess amount of $NaBO_3 \cdot 4H_2O$ (488 mg) was then added and the mixture was stirred at room

temperature for 4 h. The aqueous layer was extracted with EtOAc (20 mL) three times, and the combined organic layers were dried over anhydrous Na_2SO_4. After concentrated under reduced pressure, the crude mixture was purified by preparative TLC (^{n}hexane/EtOAc = 4/1) to afford the desired product **3a** (85.8 mg, 95% yield) as a white solid.

3. Analytical Data for Oxidized or Substituted Compounds

Almost all products are literature-known; obtained analytical data is in full agreement with reported data. The absolute configurations of the products were determined by comparison of the order of retention time in the chiral HPLC analyses.

(*R*)-3-Hydroxy-1,3-diphenylpropan-1-one (**3a**)[9]



White solid; mp 52-54 °C

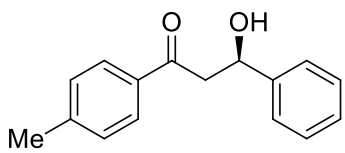
^{1}H NMR (600 MHz); δ = 7.96 (d, *J* = 7.2 Hz, 2H), 7.61-7.58 (m, 1H), 7.51-7.41 (m, 4H), 7.39 (m, 2H), 7.34-7.27 (m, 1H), 5.35 (t, *J* = 5.4 Hz, 1H), 3.63 (s, 1H), 3.38 (d, *J* = 5.4 Hz, 2H).

^{13}C NMR (150 MHz); δ = 200.1, 142.9, 136.5, 133.6, 128.7, 128.5, 128.1, 127.6, 125.7, 70.0, 47.4.

HPLC (Dialcel Chiralcel OD-H, ^{n}hexane/ ^{i}PrOH = 90/10, flow rate 1.0 mL/min); t_R = 16.0 min (*S*, minor), t_R = 17.6 min (*R*, major).

$[\alpha]_D^{27}$ = + 69.3 (*c* = 0.84, $CHCl_3$).

(*R*)-3-Hydroxy-3-phenyl-1-(*p*-tolyl)propan-1-one (**3b**)[10]



White solid; mp 68-72 °C

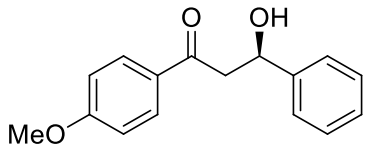
^{1}H NMR (600 MHz); δ = 7.59 (t, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 5.33-5.31 (m, 1H), 3.55 (s, 1H), 3.38-3.36 (m, 2H), 2.36 (s, 3H).

^{13}C NMR (150 MHz); 200.2, 140.0, 137.4, 136.5, 133.6, 129.2, 128.7, 128.1, 125.7, 69.9, 47.4, 21.1.

HPLC (Dialcel Chiralpak AD-H, ^{n}hexane/ ^{i}PrOH = 90/10, flow rate 1.0 mL/min); t_R = 16.0 min (*S*, minor), t_R = 17.7 min (*R*, major).

$[\alpha]_D^{27}$ = +44.0 (*c* = 0.81, $CHCl_3$).

(*R*)-3-Hydroxy-1-(4-methoxyphenyl)-3-phenylpropan-1-one (**3c**)[9]



White solid; mp 71-73 °C

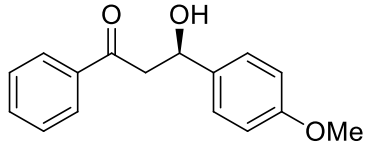
^{1}H NMR (600 MHz); δ = 7.95 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.33-7.24 (m, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 5.34-5.31 (m, 1H), 3.87 (s, 3H), 3.75 (s, 1H), 3.33-3.30 (m, 2H).

^{13}C NMR (150 MHz); δ = 198.7, 163.9, 143.0, 130.5, 129.6, 128.5, 127.6, 125.7, 113.8, 70.1, 55.5, 46.9.

HPLC (Dialcel Chiralpak AD-H, ^{n}hexane/ ^{i}PrOH = 80/20, flow rate 0.5 mL/min); t_R = 22.9 min (*R*, major), minor peak not detected.

$[\alpha]_D^{25}$ = + 37.2 (*c* = 0.80, $CHCl_3$).

(*R*)-3-Hydroxy-3-(4-methoxyphenyl)-1-phenylpropan-1-one (**3d**)[9]



Colorless oil

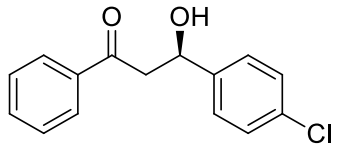
^{1}H NMR (600 MHz); δ = 7.96 (d, *J* = 7.6 Hz, 2H), 7.60-7.56 (m, 1H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.37-7.35 (m, 2H), 6.92-6.90 (m, 2H), 5.29 (m, 1H), 3.81 (s, 3H), 3.54 (s, 1H), 3.37-3.35 (m, 2H).

^{13}C NMR (150 MHz); δ = 200.2, 159.1, 136.6, 135.1, 133.6, 128.7, 128.1, 127.0, 113.9, 69.7, 55.3, 47.3.

HPLC (Dialcel Chiralpak AS-H, ^{n}hexane/ ^{i}PrOH = 80/20, flow rate 1.0 mL/min); t_R = 16.9 min (*S*, minor), t_R = 21.1 min (*R*, major).

$[\alpha]_D^{25}$ = + 46.5 (*c* = 0.92, $CHCl_3$).

(*R*)-3-(4-Chlorophenyl)-3-hydroxy-1-phenylpropan-1-one (**3e**)[9]



Colorless oil

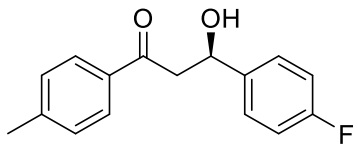
^{1}H NMR (600 MHz); δ = 7.96 (d, *J* = 7.2 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.39-7.34 (m, 4H), 5.33 (m, 1H), 3.65 (s, 1H), 3.35 (t, *J* = 5.8 Hz, 2H).

^{13}C NMR (150 MHz); δ = 199.9, 141.4, 136.4, 133.8, 133.3, 128.72, 128.65, 128.1, 127.1, 69.4, 47.2.

HPLC (Dialcel Chiralcel OD-H, ^{n}hexane/ ^{i}PrOH = 85/15, flow rate 1.0 mL/min); t_R = 15.5 min (*S*, minor), t_R = 18.1 min (*R*, major).

$[\alpha]_D^{26}$ = + 43.3 (*c* = 0.81, $CHCl_3$).

(*R*)-3-(4-Fluorophenyl)-3-hydroxy-1-(*p*-tolyl)propan-1-one (**3f**)



White solid; mp 71-72 °C

^{1}H NMR (600 MHz); δ = 7.85 (d, *J* = 8.2 Hz, 2H), 7.42-7.40 (m, 2H), 7.27-7.26 (m, 2H), 7.06 (t, *J* = 8.7 Hz, 2H), 5.32 (d, *J* = 8.9 Hz, 1H), 3.72 (d, *J* = 2.8 Hz, 1H), 3.36-3.27 (m, 2H), 2.42 (s, 3H).

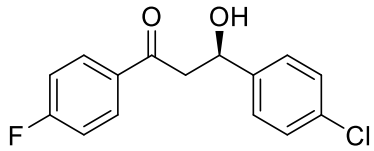
^{13}C NMR (150 MHz); δ = 199.8, 163.0, 161.4, 144.7, 138.74, 138.72, 134.0, 129.4, 128.3, 127.45, 127.40, 115.4, 115.3, 69.5, 47.1, 21.7.

HPLC (Dialcel Chiralcel OD-H, ^{n}hexane/ ^{i}PrOH = 90/10, flow rate 1.0 mL/min); t_R = 14.0 min (*S*, minor), t_R = 14.9 min (*R*, major).

$[\alpha]_D^{27}$ = +52.0 (*c* = 0.83, $CHCl_3$).

HRMS (ESI); Calcd for $C_{16}H_{16}FO_2$ [M+H]: 259.1134, Found: 259.1143.

(*R*)-3-(4-Chlorophenyl)-1-(4-fluorophenyl)-3-hydroxypropan-1-one (**3g**)



White solid; mp 86-90 °C

^{1}H NMR (600 MHz); δ = 7.99-7.96 (m, 2H), 7.38-7.36 (m, 4H), 7.14 (t, *J* = 8.7 Hz, 2H), 5.32 (t, *J* = 6.0 Hz, 1H), 3.59 (br, 1H), 3.31 (d, *J* = 6.8 Hz, 2H).

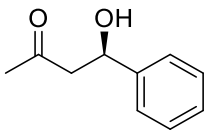
^{13}C NMR (150 MHz); δ = 198.2, 167.1, 165.1, 141.3, 133.4, 132.9, 130.9, 130.8, 128.7, 127.1, 116.0, 115.8, 69.4, 47.2.

HPLC (Dialcel Chiralcel OD-H, ^{n}hexane/ ^{i}PrOH = 85/15, flow rate 1.0 mL/min); t_R = 7.3 min (*S*, minor), t_R = 11.8 min (*R*, major).

$[\alpha]_D^{27}$ = +46.5 (*c* = 0.82, $CHCl_3$).

HRMS (ESI); Calcd for $C_{15}H_{13}ClFO_2$ [M+H]: 279.0588, Found: 279.0588.

(*R*)-4-Hydroxy-4-phenylbutan-2-one (**3h**)[9]



Colorless oil

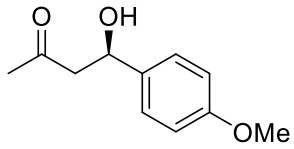
^{1}H NMR (600 MHz); δ = 7.35-7.33 (m, 4H), 7.30-7.26 (m, 1H), 5.17-5.15 (m, 1H), 3.28 (s, 1H), 2.91-2.80 (m, 2H), 2.20 (s, 3H).

^{13}C NMR (150 MHz); δ = 209.1, 142.7, 128.5, 127.7, 125.6, 69.8, 52.0, 30.8.

HPLC (Dialcel Chiralpak AS-H, ^{n}hexane/ ^{i}PrOH = 90/10, flow rate 0.5 mL/min); t_R = 17.2 min (*S*, minor), t_R = 19.0 min (*R*, major).

$[\alpha]_D^{28}$ = + 55.5 (*c* = 1.06, $CHCl_3$).

(*R*)-4-Hydroxy-4-(4-methoxyphenyl)butan-2-one (**3i**)[12]



Colorless oil

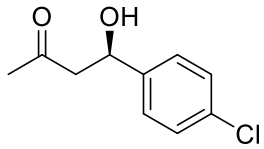
^{1}H NMR (600 MHz); δ = 7.28 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.11-5.09 (m, 1H), 3.79 (s, 3H), 2.90-2.86 (m, 1H), 2.80-2.76 (m, 1H), 2.19 (s, 3H).

^{13}C NMR (150 MHz); δ = 209.2, 159.1, 134.9, 126.9, 113.9, 69.5, 55.3, 51.9, 30.8.

HPLC (Dialcel Chiralcel OD-H, ^{n}hexane/ ^{i}PrOH = 90/10, flow rate 1.0 mL/min); t_R = 16.9 min (*S*, minor), t_R = 21.0 min (*R*, major).

$[\alpha]_D^{25}$= + 45.6 (*c* = 0.80, $CHCl_3$).

(*R*)-4-(4-Chlorophenyl)-4-hydroxybutan-2-one (**3j**)[13]



Colorless oil

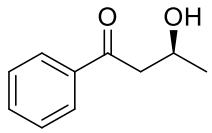
^{1}H NMR (600 MHz); δ = 7.31-7.25 (m, 4H), 5.12-5.10 (m, 1H), 3.40 (s, 1H), 2.82-2.79 (m, 2H), 2.18 (s, 3H).

^{13}C NMR (150 MHz); δ = 208.9, 141.2, 133.3, 128.6, 127.0, 69.1, 51.8, 30.7.

HPLC (Dialcel Chiralcel OD-H, ^{n}hexane/ ^{i}PrOH = 90/10, flow rate 0.5 mL/min); t_R = 17.1 min (*S*, minor), t_R = 19.0 min (*R*, major).

$[\alpha]_D^{25}$= + 53.2 (*c* = 0.86, $CHCl_3$).

(*S*)-3-Hydroxy-1-phenylbutan-1-one (**3k**)[9]



Colorless oil

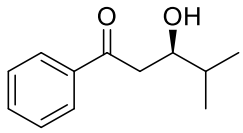
^{1}H NMR (600 MHz); δ = 7.96-7.95 (m, 2H), 7.59-7.57 (m, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 4.41 (t, *J* = 7.2 Hz, 1H), 3.31 (s, 1H), 3.17 (dd, *J* = 14.9, 2.7 Hz), 3.05 (dd, *J* = 17.7, 8.9 Hz), 1.31 (d, *J* = 6.4 Hz).

^{13}C NMR (150 MHz); δ = 200.9, 136.7, 133.5, 128.7, 128.0, 64.0, 46.5, 22.4.

HPLC (Dialcel Chiralcel OD-H, ^{n}hexane/ ^{i}PrOH = 98/2, flow rate 0.8 mL/min); t_R = 14.7 min (*R*, minor), t_R = 16.1 min (*S*, major).

$[\alpha]_D^{29}$ = + 68.2 (*c* = 0.93, $CHCl_3$).

(*R*)-3-Hydroxy-4-methyl-1-phenylpentan-1-one (**3l**)[9]



Colorless oil

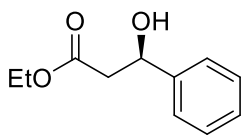
^{1}H NMR (600 MHz); δ = 7.97 (d, *J* = 7.7 Hz, 2H), 7.59-7.57 (m, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 4.06-3.98 (m, 1H), 3.19-3.16 (m, 1H), 3.04 (dd, *J* = 9.6, 7.9 Hz, 1H), 1.84-1.78 (m, 1H), 1.02-0.99 (m, 6H).

^{13}C NMR (150 MHz); δ = 201.3, 136.9, 133.5, 128.7, 128.1, 41.9, 33.1, 18.5, 17.9.

HPLC (Dialcel Chiralcel OD-H, ^{n}hexane/ ^{i}PrOH = 90/10, flow rate 1.0 mL/min); t_R = 7.5 min (*S*, minor), t_R = 9.5 min (*R*, major).

$[\alpha]_D^{28}$ = + 69.9 (*c* = 0.98, $CHCl_3$).

(*R*)-Ethyl-3-hydroxy-3-phenylpropanoate (**3m**)[9]



Colorless oil

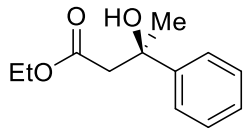
^{1}H NMR (600 MHz); δ = 1.25 (t, *J* = 7.2 Hz, 3H), 2.68-2.77 (m, 2H), 3.23 (d, *J* = 3.4 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 5.11-5.14 (m, 1H), 7.25-7.38 (m, 5H).

^{13}C NMR (150 MHz); δ = 14.1, 43.3, 60.9, 70.3, 125.7, 127.8, 128.6, 142.5, 172.4.

HPLC (Dialcel Chiralcel OD-H, ^{n}hexane/ ^{i}PrOH = 90/10, flow rate 0.8 mL/min); t_R = 17.0 min (*S*, minor), t_R = 19.4 min (*R*, major).

$[\alpha]_D^{28}$ = + 48.9 (*c* = 0.84, $CHCl_3$).

Ethyl (*R*)-3-hydroxy-3-phenylbutanoate (**3n**)[14]



Yellow oil

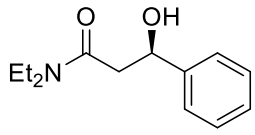
^{1}H NMR (600 MHz); δ =1.22 (t, *J* = 7.1 Hz, 3H), 1.64 (s, 3H), 2.82 (d, *J* = 16.0 Hz, 1H), 3.00 (d, *J* = 15.0 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 7.21-7.36 (m, 5H).

^{13}C NMR (150 MHz); δ = 14.1, 29.4, 45.5, 60.8, 72.6, 124.4, 126.7, 128.5, 146.8, 172.5.

HPLC (Dialcel Chiralcel OD-H, ^{n}hexane/ ^{i}PrOH = 95/5, flow rate 0.5 mL/min); t_R = 15.1 min (*S*, minor), t_R = 18.0 min (*R*, major).

$[\alpha]_D^{21}$ = + 27.9 (*c* = 0.82, $CHCl_3$).

(*R*)-3-Hydroxy-*N,N*-diethyl-3-phenylpropanamide (**3o**)[9]



A little bit yellow oil

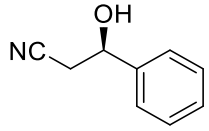
^{1}H NMR (600 MHz); δ = 1.07-1.12 (m, 6H), 2.55-2.67 (m, 2H), 3.16-3.22 (m, 2H), 3.33-3.40 (m, 2H), 4.99 (s, 1H), 5.11 (d, *J* = 11.3 Hz, 1H), 7.23-7.38 (m, 5H).

^{13}C NMR (150 MHz); δ = 12.9, 13.9, 40.1, 41.4, 41.8, 70.5, 125.6, 127.3, 128.3, 143.1, 171.3.

HPLC (Dialcel Chiralpak AD-H, ^{n}hexane/ ^{i}PrOH = 95/5, flow rate 0.8 mL/min); t_R = 23.7 min (*S*, minor), t_R = 28.8 min (*R*, major).

$[\alpha]_D^{27}$ = + 89.9 (*c* = 0.73, $CHCl_3$).

(*R*)-3-Hydroxy-3-phenylpropanenitrile (**3p**)[9]



Pale yellow oil

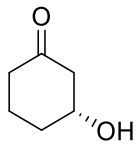
^{1}H NMR (600 MHz); δ = 2.33 (br, 1H), 2.73-2.80 (m, 2H), 5.04 (t, *J* = 6.2 Hz, 1H), 7.34-7.39 (m, 5H).

^{13}C NMR (150 MHz); δ = 27.9, 70.2, 117.2, 125.5, 128.8, 128.9, 141.0.

HPLC (Dialcel Chiralcel OJ-H, ^{n}hexane/ ^{i}PrOH = 80/20, flow rate 1.0 mL/min); t_R = 15.7 min (*S*, minor), t_R = 17.0 min (*R*, major).

$[\alpha]_D^{26}$ = + 55.3 (*c* = 0.84, $CHCl_3$).

(*R*)-3-Hydroxycyclohexanone (**3q**)[9]



Colorless oil

^{1}H NMR (600 MHz); δ = 1.66-1.76 (m, 3H), 1.98-2.08 (m, 2H), 2.23-2.31 (m, 2H), 2.30 (dd, *J* = 7.6, 7.6 Hz, 1H), 2.65 (dd, *J* = 4.2, 14.0 Hz, 1H), 4.16-4.19 (m, 1H).

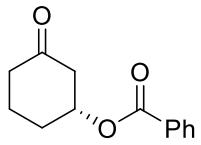
^{13}C NMR (150 MHz); δ = 20.6, 32.9, 40.8, 50.4, 69.8, 209.5.

The ee value was determined as a benzoylated compound;

Pyridine (31.6 mg, 0.4 mmol) and benzoyl chloride (140.6 mg, 1.0 mmol) were added to the oxidized product (ca. 0.2 mmol) in dichloromethane (2 mL). The mixture was stirred for 1 h at 0 °C. The resulting mixture was quenched with water. The obtained organic layer was washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by preparative TLC

(^{n}hexane/AcOEt = 3/1) to afford the benzoylated product (41.9 mg, 96% yield in 3 steps) as a colorless oil.

(*R*)-3-Oxocyclohexyl benzoate[9]



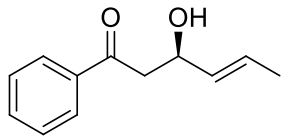
Colorless oil

^{1}H NMR (600 MHz); δ = 1.69-1.79 (m, 2H), 1.99-2.07 (m, 2H), 2.28-2.32 (m, 2H), 2.37-2.42 (m 1H), 2.60-2.66 (m, 1H), 4.83-4.87 (m, 1H), 7.45-7.48 (m, 2H), 7.56-7.59 (m, 1H), 7.96-7.99 (m, 2H).

^{13}C NMR (150 MHz); δ = 21.2, 32.4, 40.8, 50.2, 68.4, 128.0, 128.7, 133.6, 136.9, 207.3, 212.2.

HPLC (Dialcel Chiralcel OD-H, ^{n}hexane/ ^{i}PrOH = 90/10, flow rate 0.5 mL/min); t_R = 14.6 min (*S*, minor), t_R = 17.9 min (*R*, major).

(*R*,*E*)-3-Hydroxy-1-phenylhex-4-en-1-one (**3r**)[11]



Colorless oil

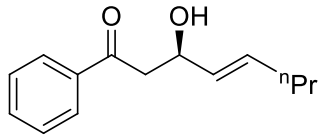
^{1}H NMR (600 MHz); δ = 7.96 (d, *J* = 7.1 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 5.81-5.77 (m, 1H), 5.62-5.58 (m, 1H), 4.70-4.69 (m, 1H), 3.24-3.14 (m, 3H), 1.72 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (150 MHz); δ = 200.3, 136.7, 133.5, 132.0, 128.7, 128.1, 127.2, 68.7, 45.2, 17.7.

HPLC (Dialcel Chiralpak AS-H, ^{n}hexane/ ^{i}PrOH = 85/15, flow rate 1.0 mL/min); t_R = 15.5 min (*S*, minor), t_R = 17.1 min (*R*, major).

$[\alpha]_D^{29}$ = + 27.2 (*c* = 0.54, $CHCl_3$).

(*R*,*E*)-3-Hydroxy-1-phenyloct-4-en-1-one (**3s**)[11]



Colorless oil

^{1}H NMR (600 MHz); δ = 7.96 (d, *J* = 7.1 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 5.78-5.76 (m, 1H), 5.70-5.59 (m, 1H), 4.73-4.70 (m, 1H), 3.22-3.15 (m, 3H), 2.05-2.01 (m, 2H), 1.43-1.39 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (150 MHz); δ = 200.4, 136.7, 133.5, 132.3, 130.8, 128.7, 128.1, 68.8, 45.3, 34.3, 22.2, 13.7.

HPLC (Dialcel Chiralpak AS-H + Chiralcel OD-H, ^{n}hexane/ ^{i}PrOH = 90/10, flow rate 0.8 mL/min); t_R = 12.7 min (*S*, minor), t_R = 14.2 min (*R*, major).

$[\alpha]_D^{30}$ = +28.6 (*c* = 0.91, $CHCl_3$).

4. Procedure for Filtration Experiment

In an oven-dried Schlenk tube, Et_2O (1.5 mL) was added to $Cu(OAc)_2$ (3.6 mg, 5 mol%), chiral 2,2'-bipyridine **L7** (7.9 mg, 6 mol%) and $B_2(pin)_2$ (121.8 mg, 0.48 mmol) under Ar. The reaction mixture was stirred for 1 h at room temperature, followed by successive addition of chalcone **1a** (81.9 mg, 0.4 mmol), MeOH (0.016 mL, 0.4 mmol) and Et_2O (0.5 mL). After stirring for 2 h, the reaction mixture was filtrated through a membrane filter (pore size: 0.2 μm). To the filterate was added benzalacetone **1h** (58.5 mg, 0.4 mmol), $B_2(pin)_2$ (121.8 mg, 0.48 mmol) and MeOH (0.016 mL, 0.4 mmol). After stirring for further 12 h, the reaction mixture was poured into a pyridine aqueous solution and extracted with EtOAc (20 mL) three times. The combined organic layers were concentrated under reduced pressure and the residue was dissolved in THF (6 mL) and H_2O (4 mL). An excess amount of $NaBO_3 \cdot 4H_2O$ (976 mg) was then added and the mixture was stirred at room temperature for 4 h. The aqueous layer was extracted with EtOAc (20 mL) three times, and the combined organic layers were dried over anhydrous Na_2SO_4. After concentrated under reduced pressure, the crude mixture was purified by preparative

TLC (^{n}hexane/EtOAc = 4/1) to afford the desired product **3a** (83.3 mg, 92% yield, 91% ee) and product **3h** (46.0 mg, 70% yield, 86% ee).

5. Typical Procedure for Turnover Frequency Study

In an oven-dried Schlenk tube, Et_2O (1.5 mL) was added to $Cu(OAc)_2$ (0.0036 mg, 0.005 mol%), chiral 2,2'-bipyridine **L7** (0.0079 mg, 0.006 mol%) and $B_2(pin)_2$ (121.8 mg, 0.48 mmol) under Ar. The reaction mixture was stirred for 1 h at room temperature, followed by successive addition of chalcone **1a** (81.9 mg, 0.4 mmol), MeOH (0.016 mL, 0.4 mmol) and Et_2O (0.5 mL). After stirring for 15 min, the reaction mixture was poured into a pyridine aqueous solution and extracted with EtOAc (20 mL) three times. The combined organic layers were concentrated under reduced pressure and the residue was dissolved in THF (3 mL) and H_2O (2 mL). An excess amount of $NaBO_3 \cdot 4H_2O$ (488 mg) was then added and the mixture was stirred at room temperature for 4 h. The aqueous layer was extracted with EtOAc (20 mL) three times, and the combined organic layers were dried over anhydrous Na_2SO_4. After concentrated under reduced pressure, the crude mixture was purified by preparative TLC (^{n}hexane/AcOEt = 4/1) to afford the desired product **3a** (35.2 mg, 39% yield) as a white solid with 82% ee.

6. References

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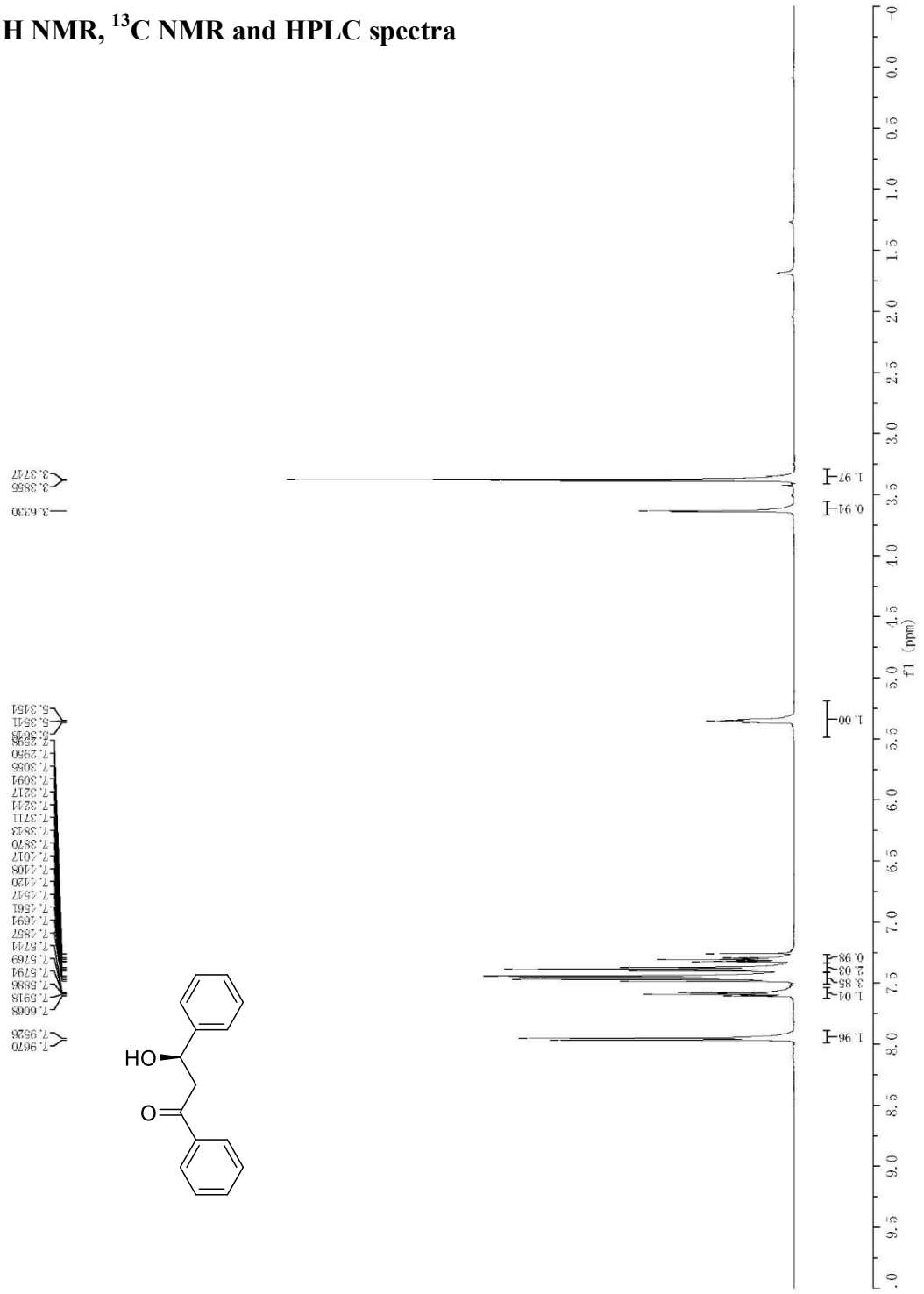
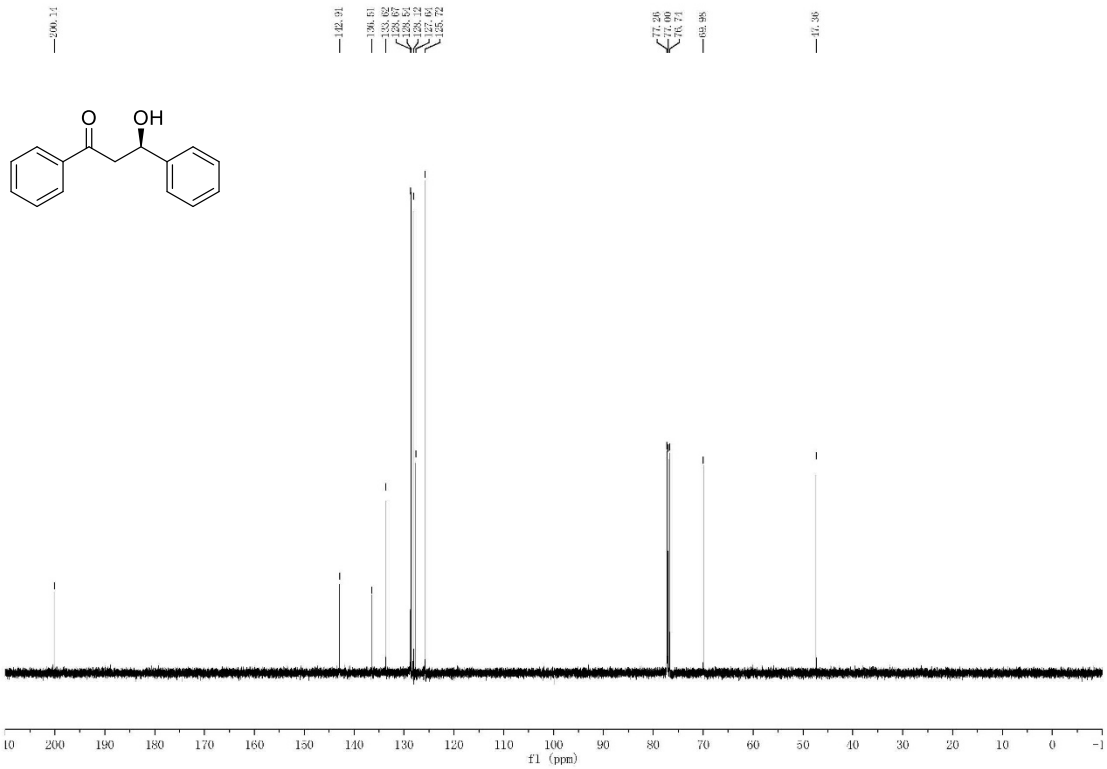
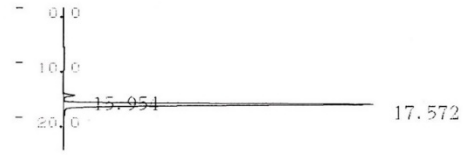
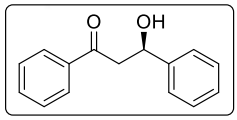
7. ^{1}H NMR, ^{13}C NMR and HPLC spectra









** CALCULATION REPORT **

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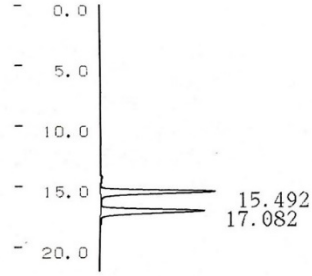
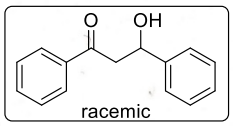
		TOTAL	1493385	52293			100	





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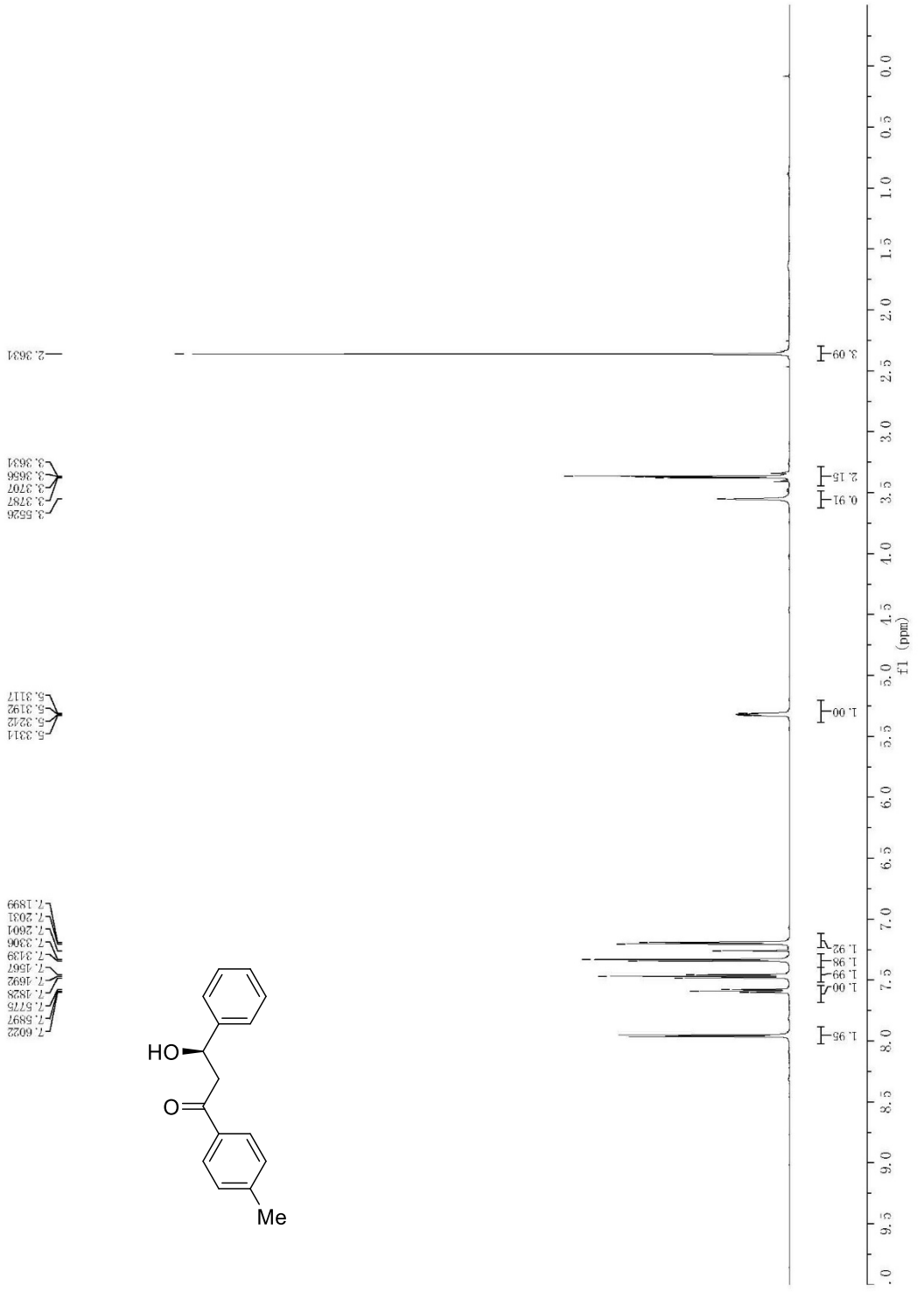
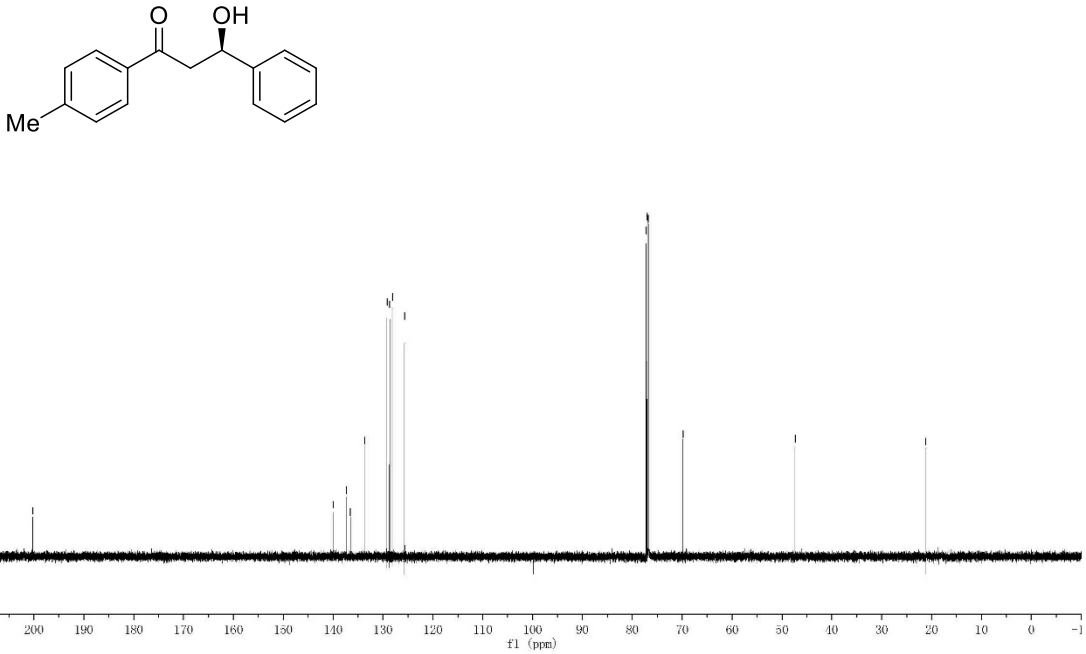
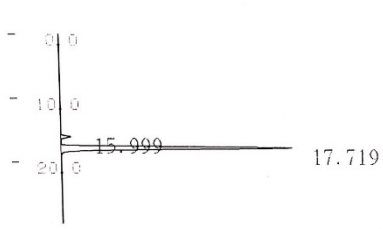
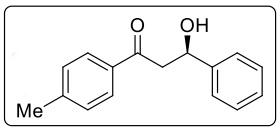

HO
O
Me
f1 (ppm)







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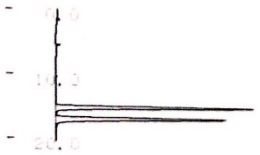
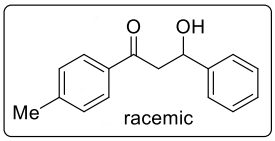
		TOTAL	2269574	76967			100	





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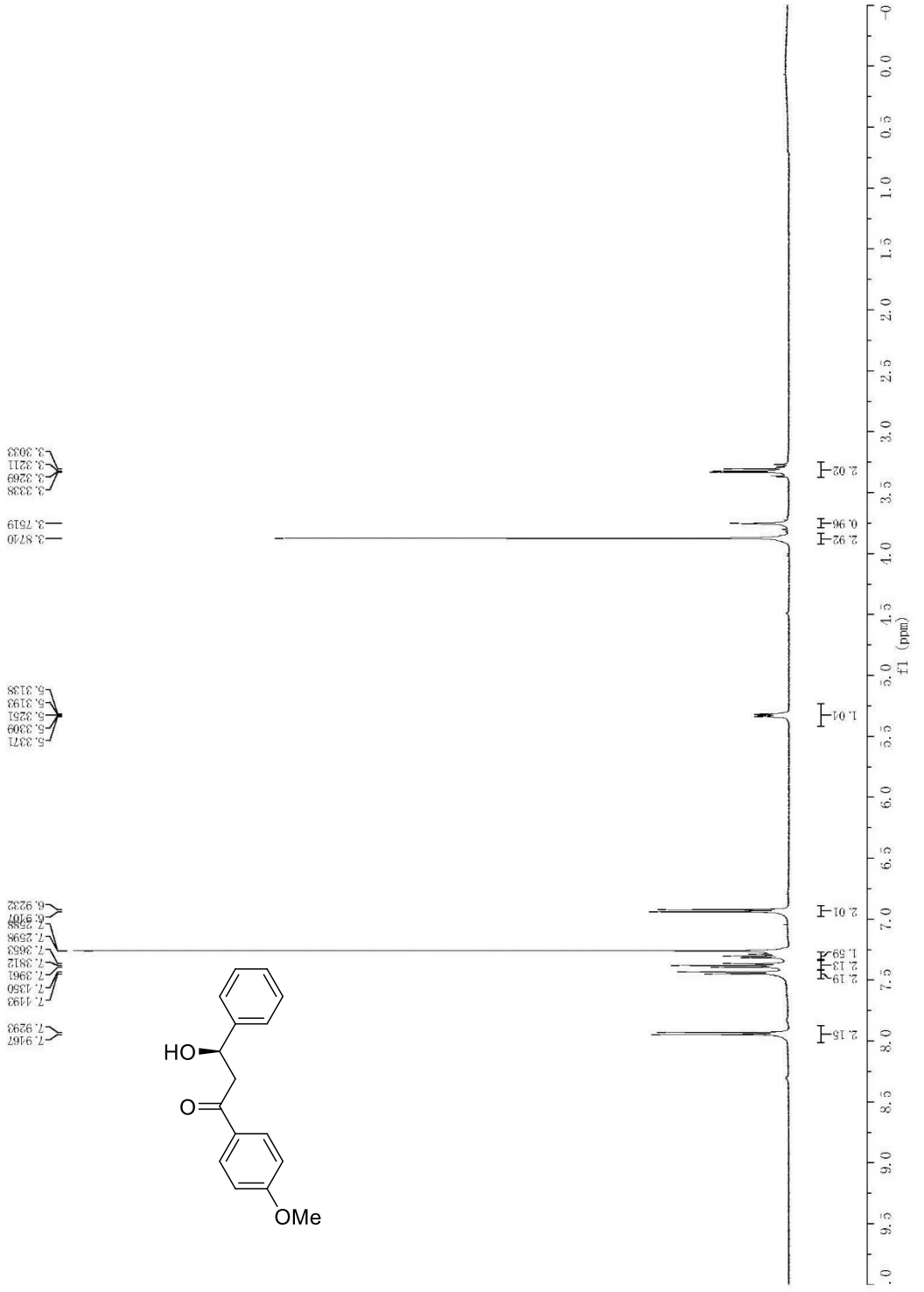
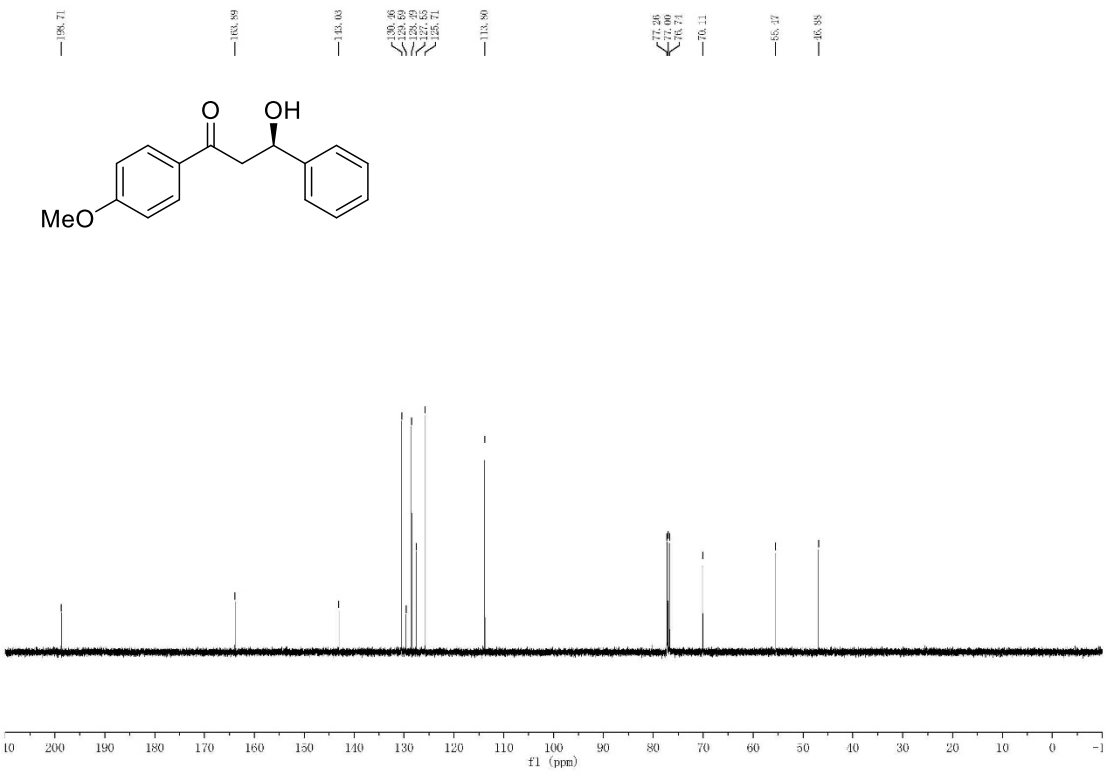
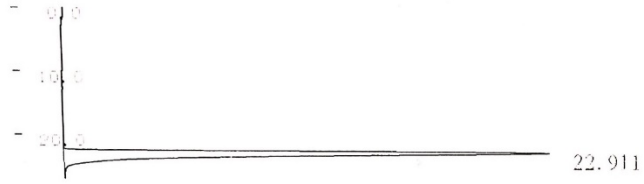
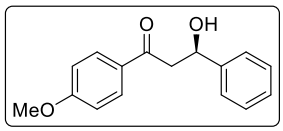

HO
O
OMe
f1 (ppm)

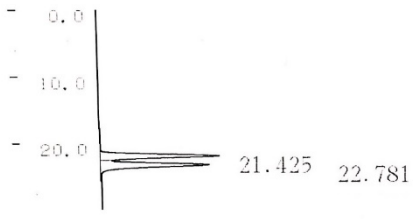


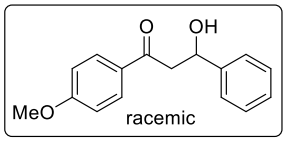




** CALCULATION REPORT **

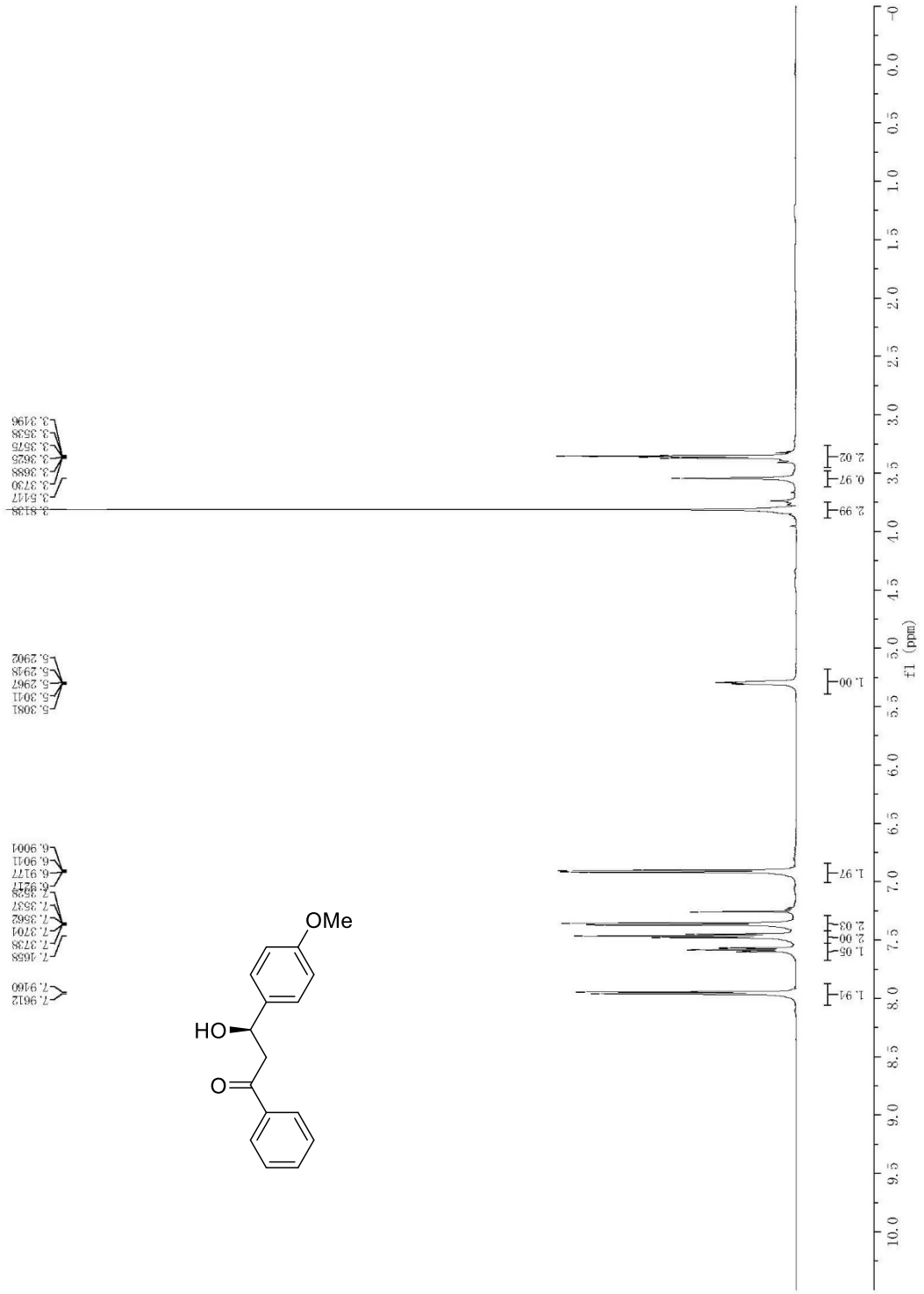
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	18	22.911	4073454	75040			100	
		TOTAL	4073454	75040			100	

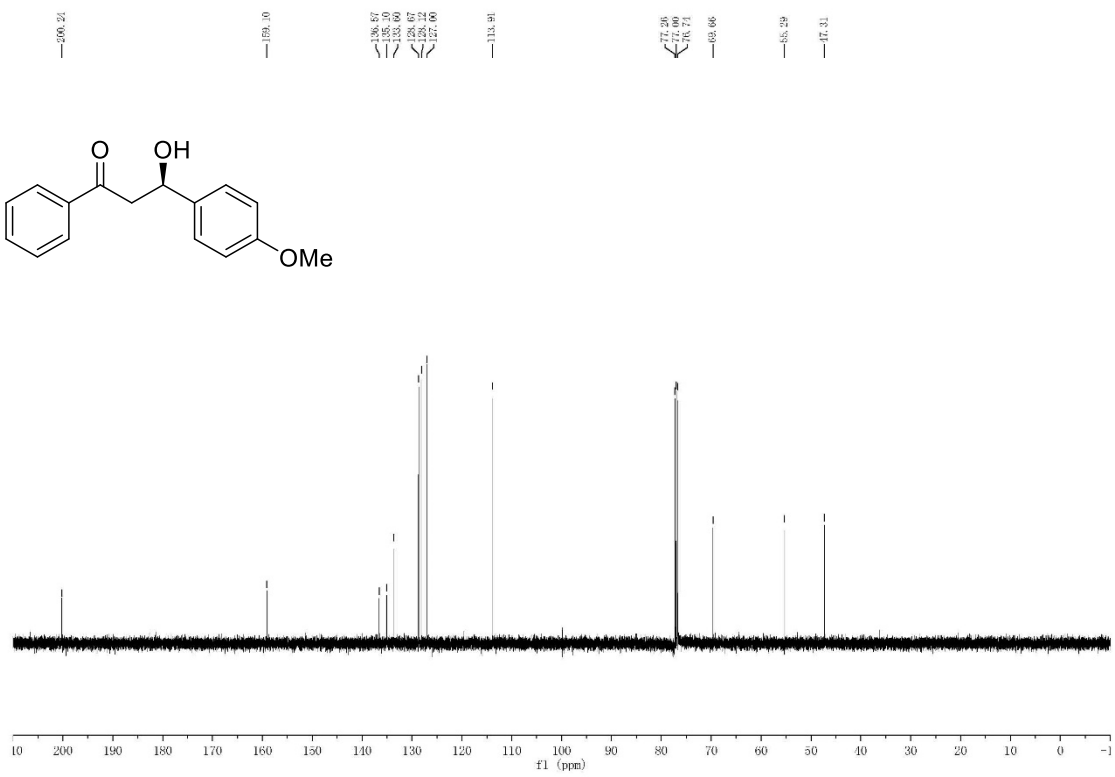




** CALCULATION REPORT **

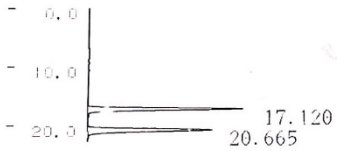
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	39	21.425	1414320	34342	V		49.672	
	40	22.781	1432999	31890	V		50.328	
		TOTAL	2847319	66232			100	


OMe
HO
O
f1 (ppm)



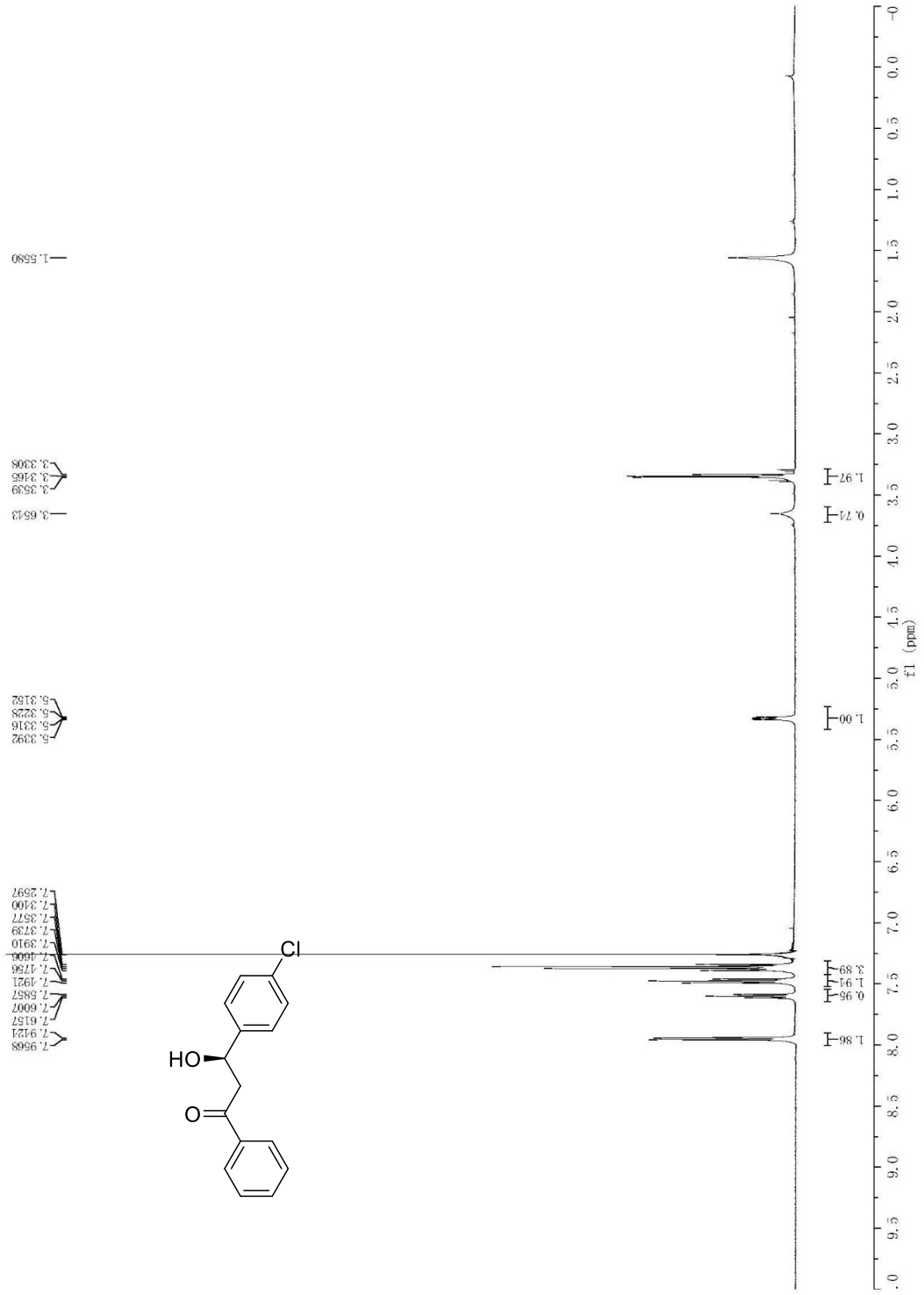
** CALCULATION REPORT **

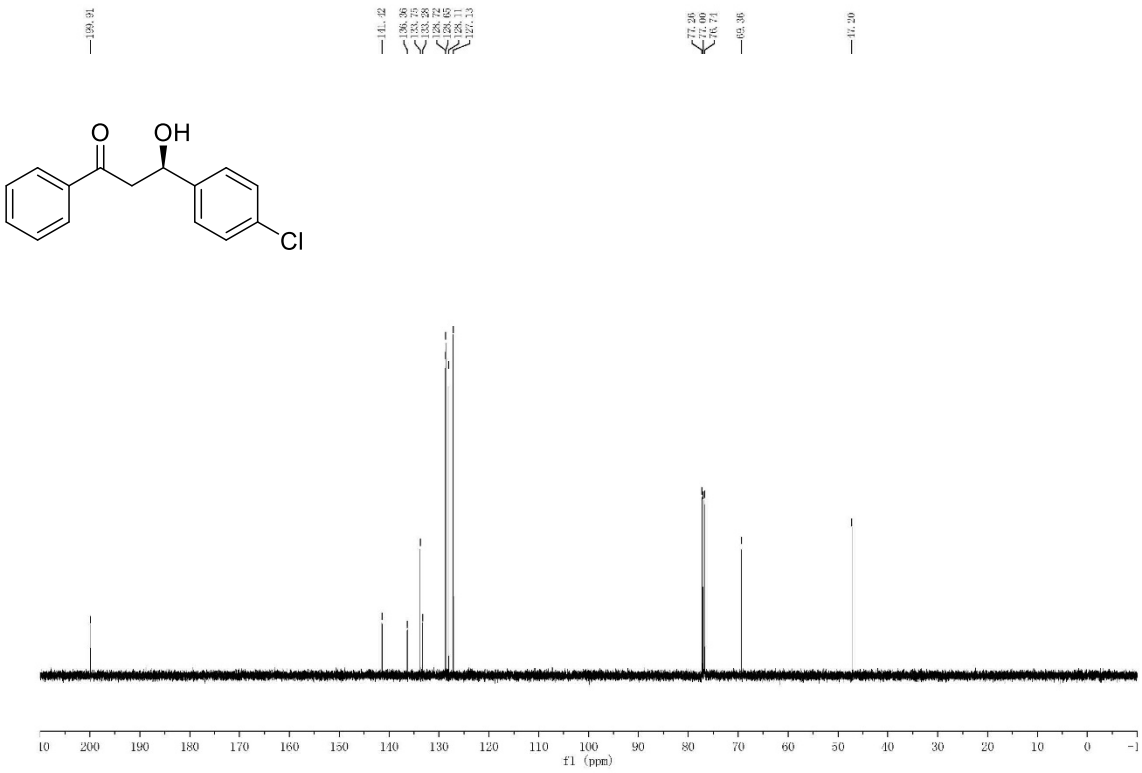
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	20	16.946	92520	2604	V		2.2542	
	21	21.106	4011899	85120			97.7458	
		TOTAL	4104419	87725			100	

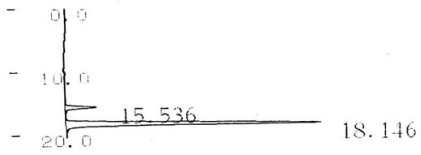


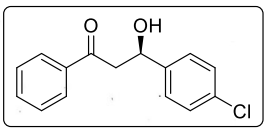
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	41	17.12	2761568	94675			50.1769	
	42	20.665	2742092	74248			49.8231	
		TOTAL	5503660	168923			100	


Cl
HO
O
f1 (ppm)

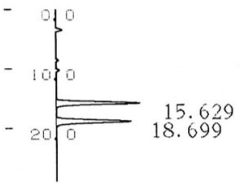


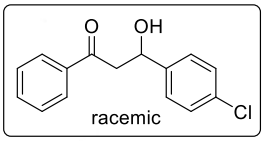




** CALCULATION REPORT **

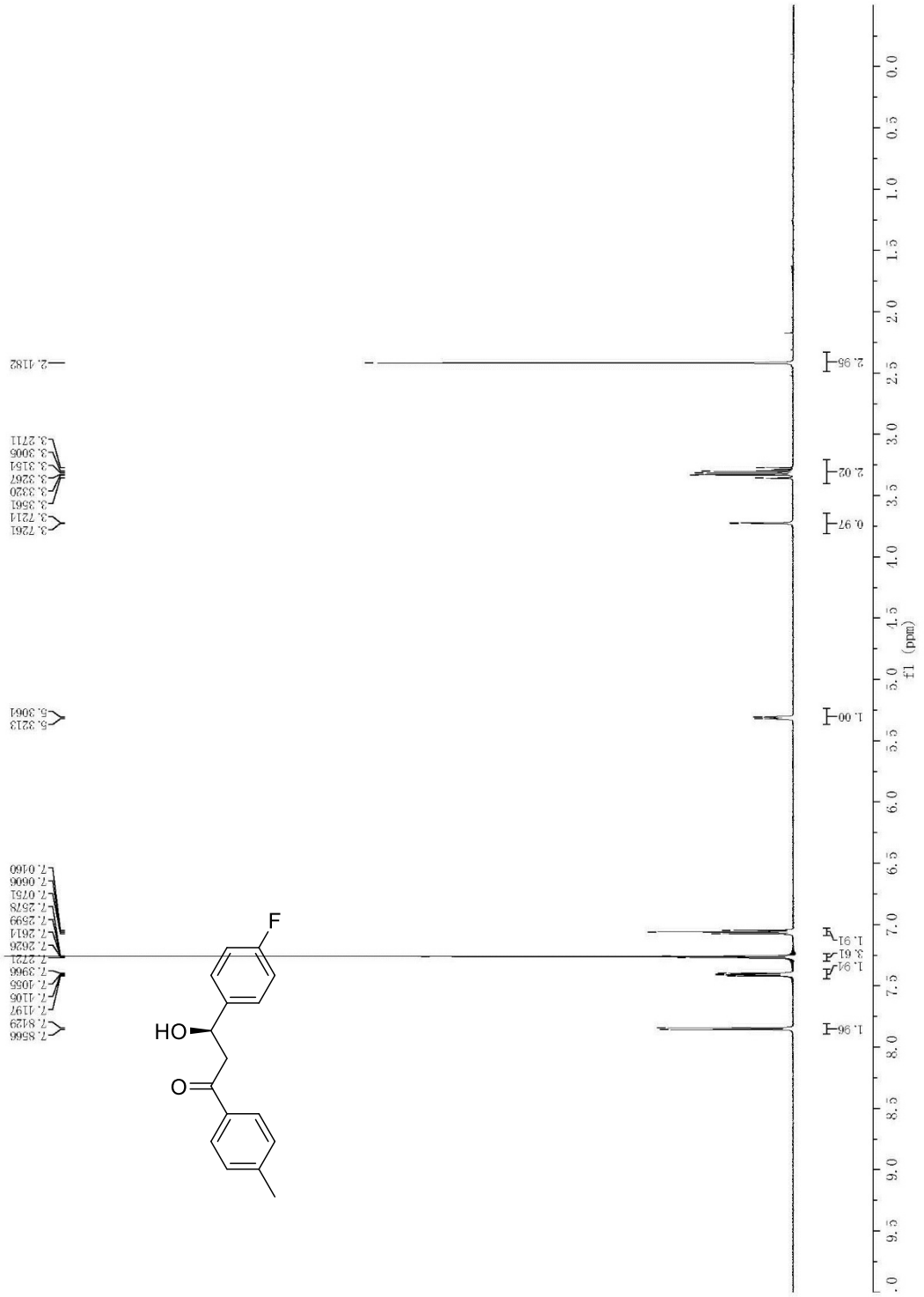
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	12	15.536	114248	4322			9.3373	
	13	18.146	1109317	35340			90.6627	
		TOTAL	1223565	39663			100	

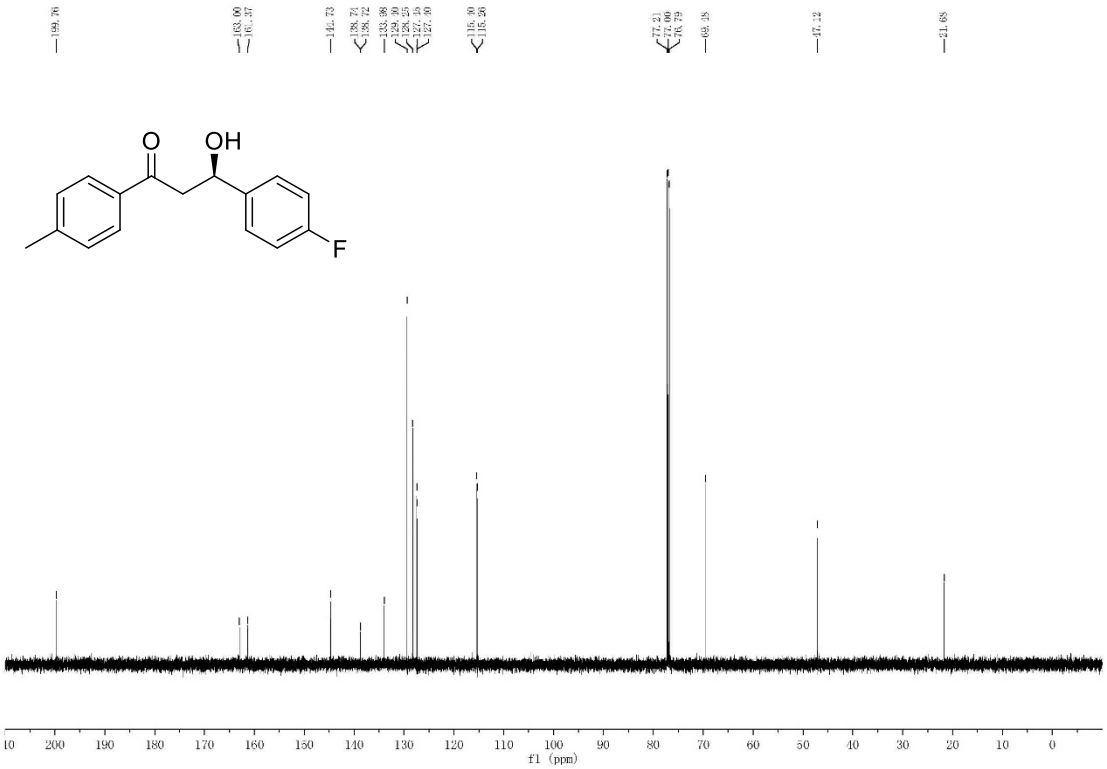


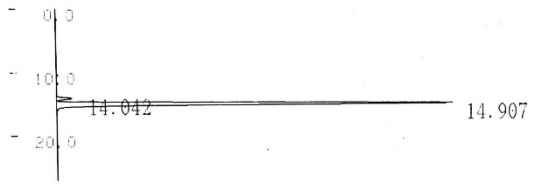


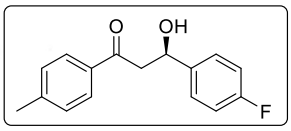
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	158	15.629	417959	12643	SV		50.0192	
	191	18.699	417638	11329	SV		49.9808	
		TOTAL	835598	23971			100	


F
HO
O
f1 (ppm)

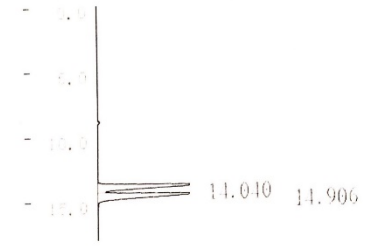


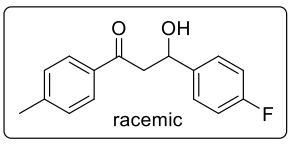




** CALCULATION REPORT **

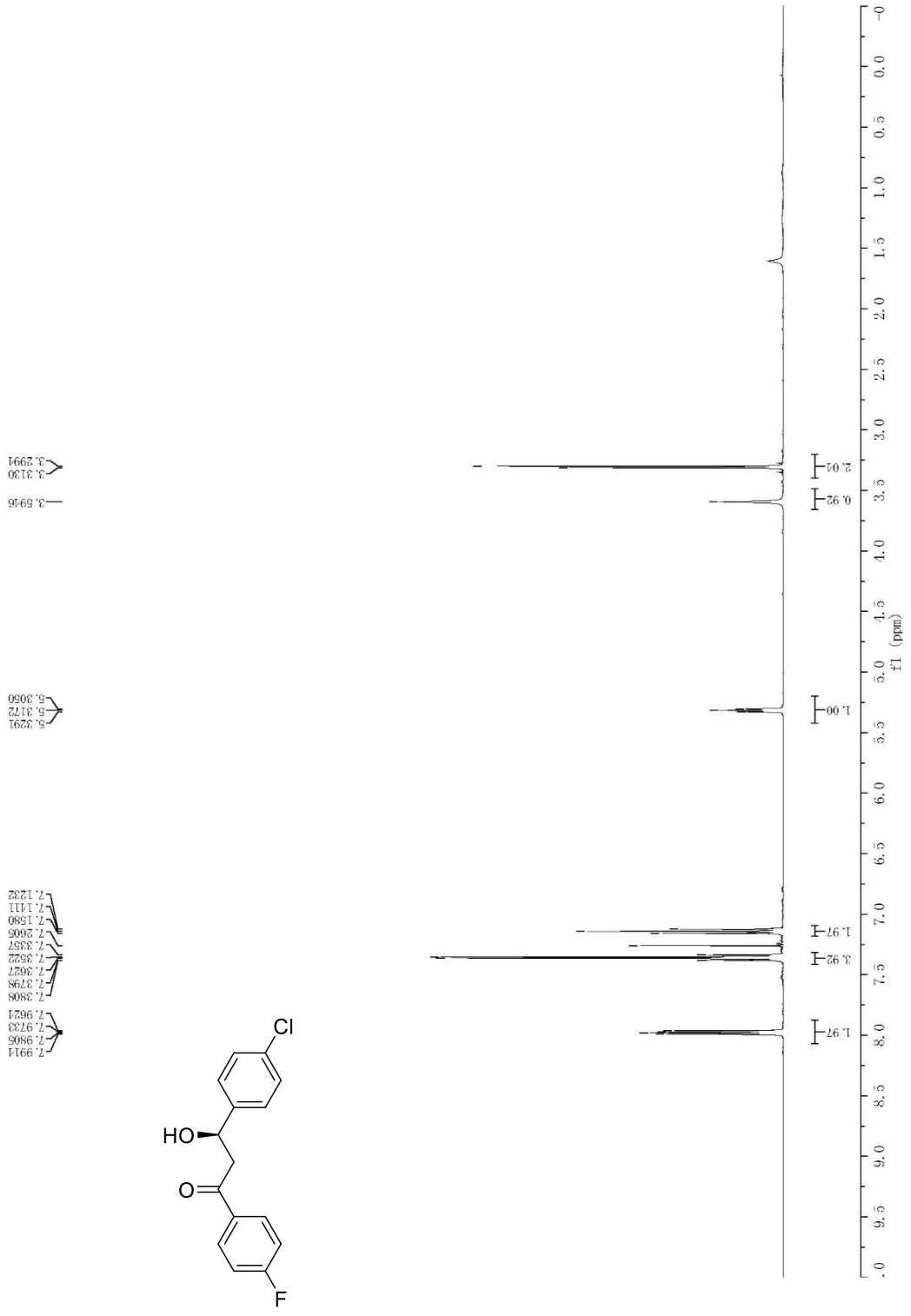
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	11	14.042	248336	10655			3.4811	
	12	14.907	6885444	273073	V		96.5189	
		TOTAL	7133780	283728			100	

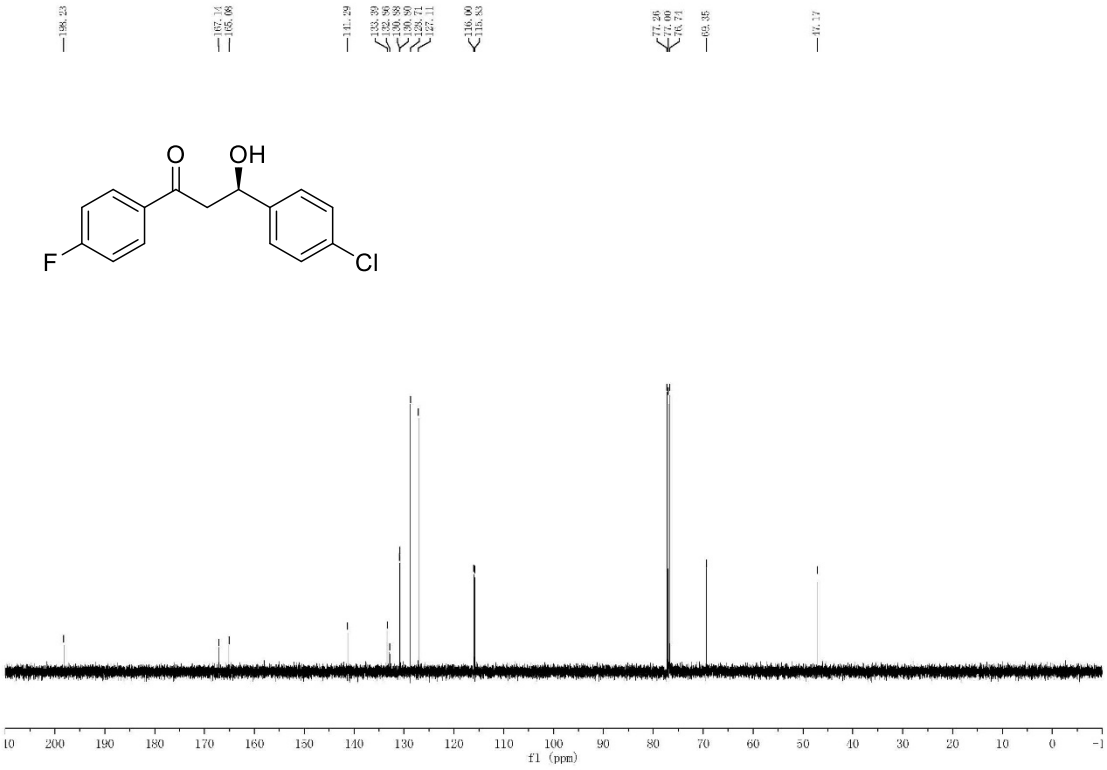


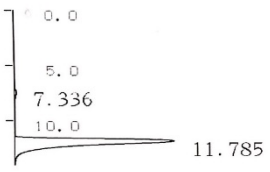


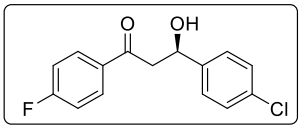
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	26	14.040	22077384	998614	VE		49.986	
	27	14.906	22089758	988220	SVE		50.014	
		TOTAL	44167140	1986834			100	


7.9914
7.9806
7.9733
7.9621
7.3808
7.3798
7.3627
7.3522
7.3357
7.2605
7.1580
7.1411
7.1242
5.3291
5.3172
5.3050
3.5946
3.3130
3.2991
Cl
HO
O
F
1.97
3.92
1.97
1.00
0.92
2.01
f1 (ppm)

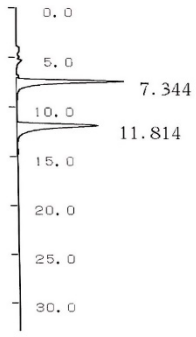


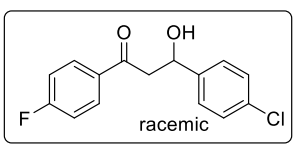




** CALCULATION REPORT **

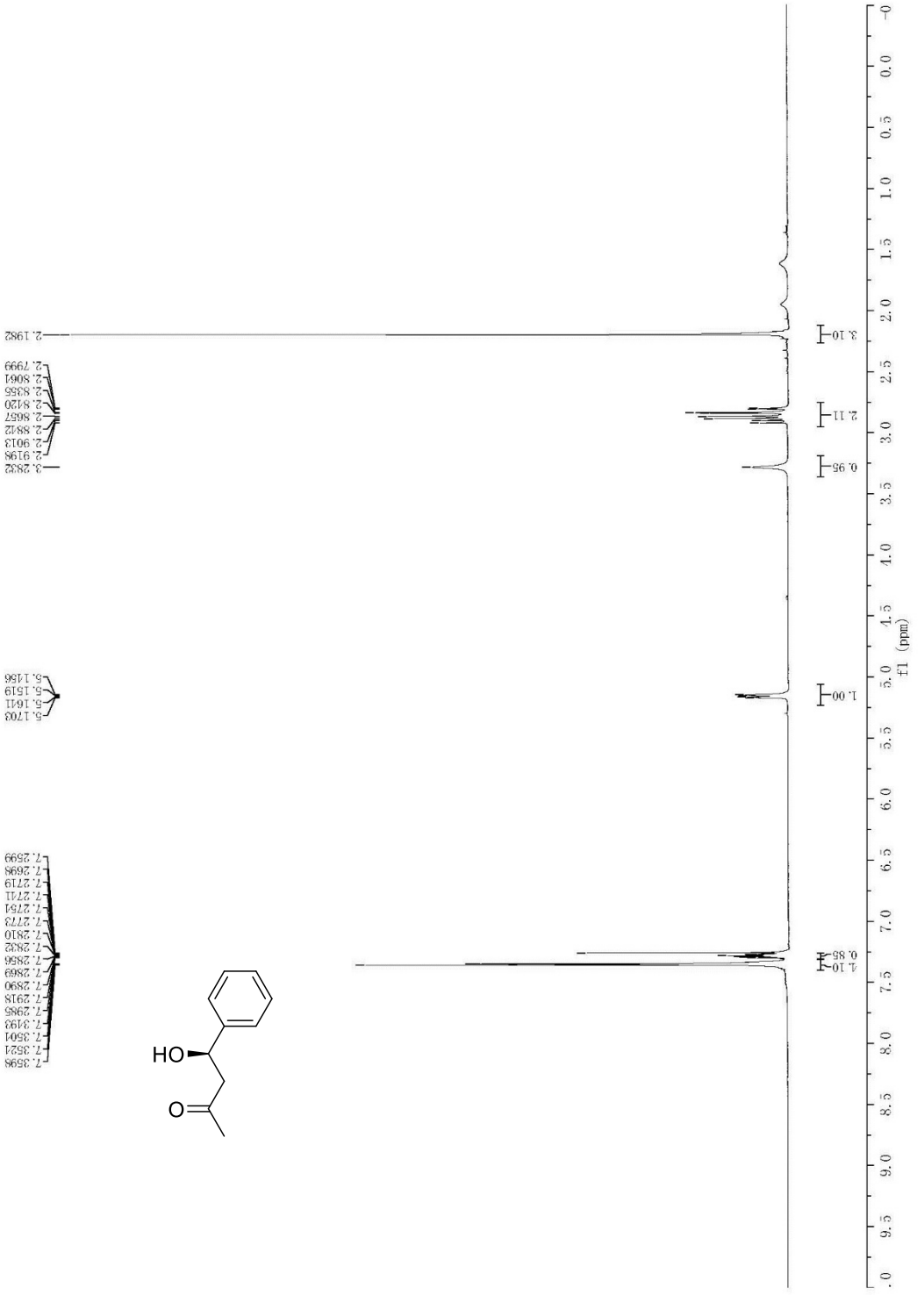
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	4	7.336	394933	11451	V		1.2486	
	6	11.785	31235224	767989	V		98.7514	
		TOTAL	31630156	779441			100	

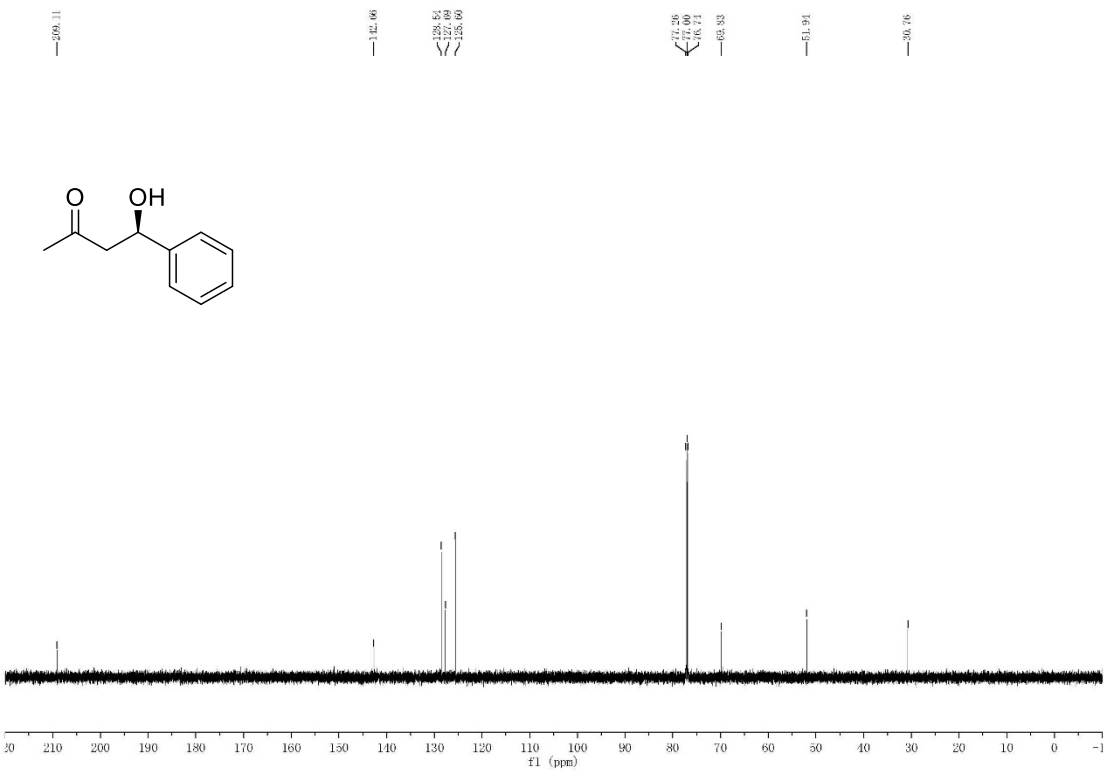


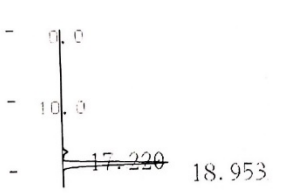


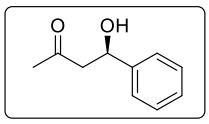
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	6	7.344	7430066	291416	SV		50.4653	
	9	11.814	7293055	220229	SV		49.5347	
		TOTAL	14723121	511645			100	


HO
O
f1 (ppm)

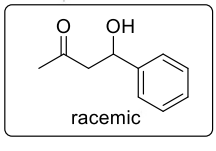






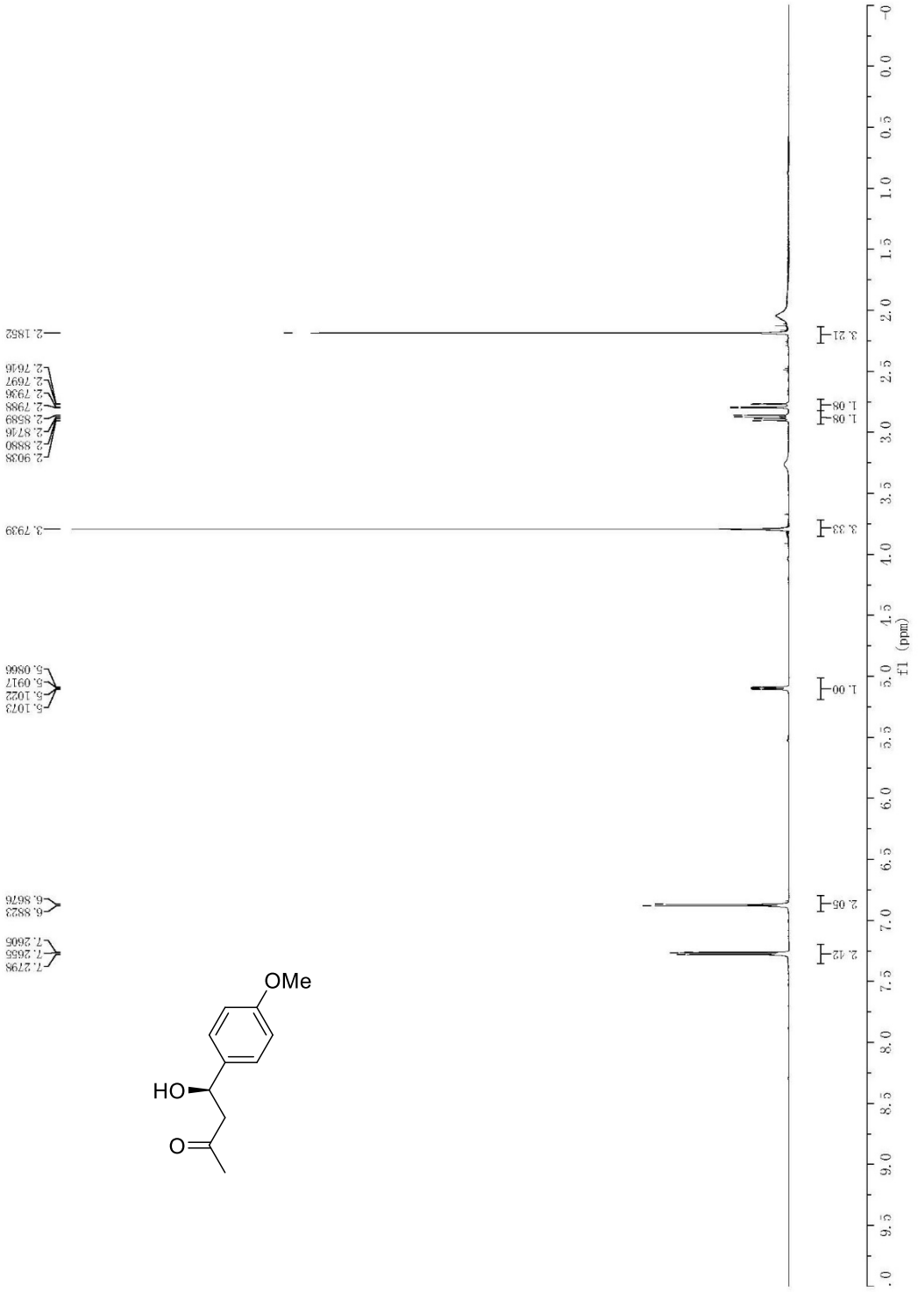
** CALCULATION REPORT **

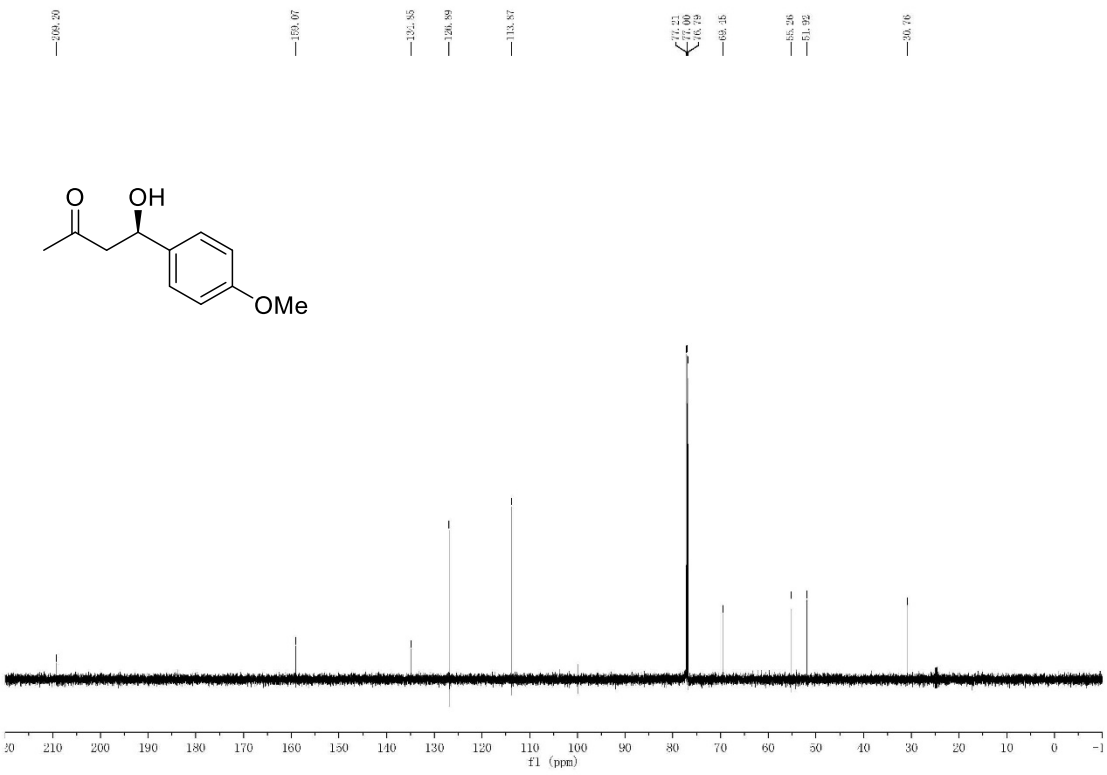
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	26	17.22	82442	1600			7.8173	
	27	18.953	972169	30536	V		92.1827	
		TOTAL	1054612	32136			100	



** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	17	17.036	1238017	51826			49.1207	
	18	18.772	1282339	46156	S		50.8793	
		TOTAL	2520356	97982			100	


2.1862
2.7636
2.7697
2.7936
2.7988
2.8589
2.8746
2.8880
2.9038
3.7939
5.0866
5.0917
5.1022
5.1073
6.8676
6.8823
7.2606
7.2655
7.2798
3.21
1.08
1.08
3.33
1.00
2.05
2.42
f1 (ppm)
OMe
HO
O

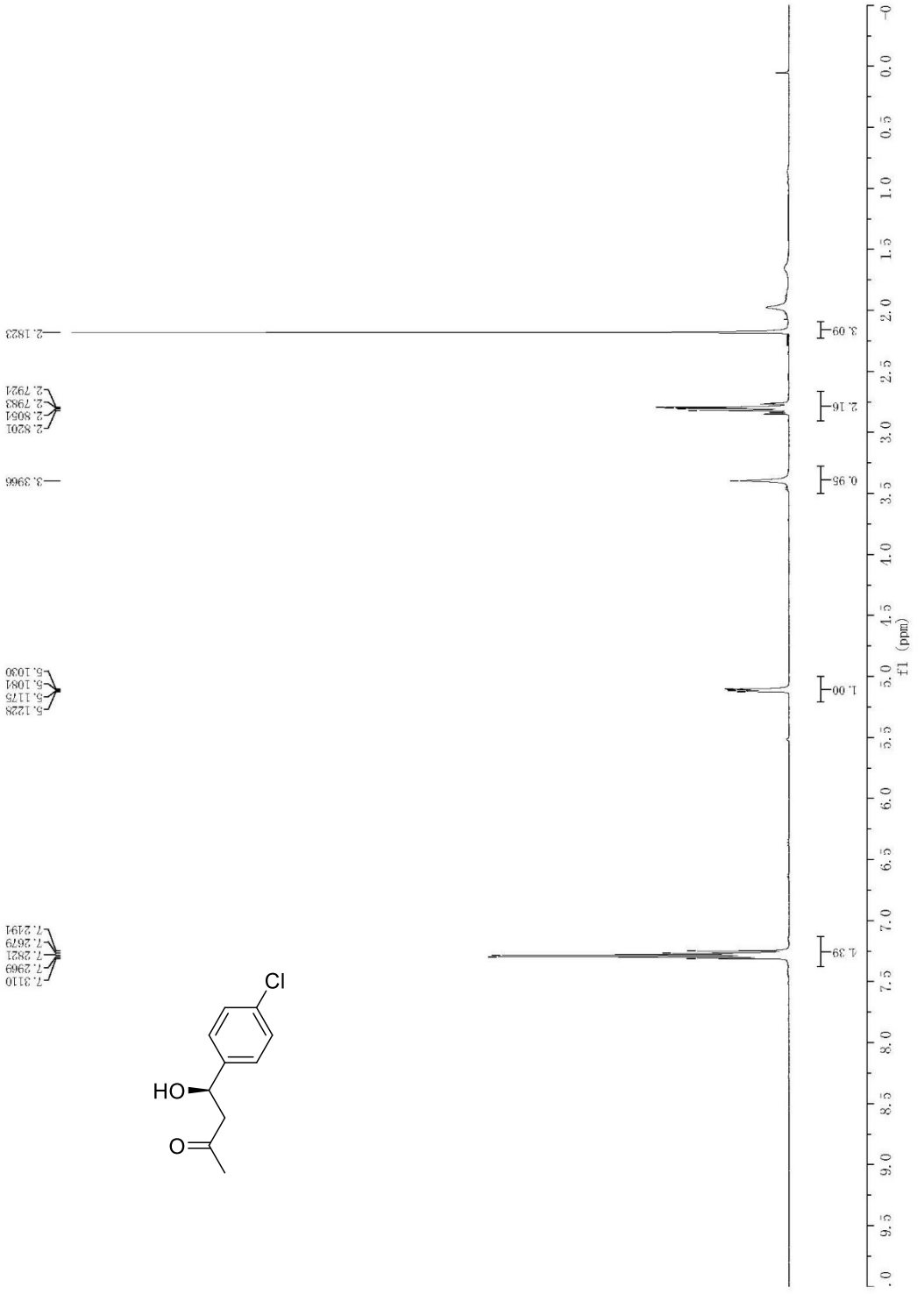


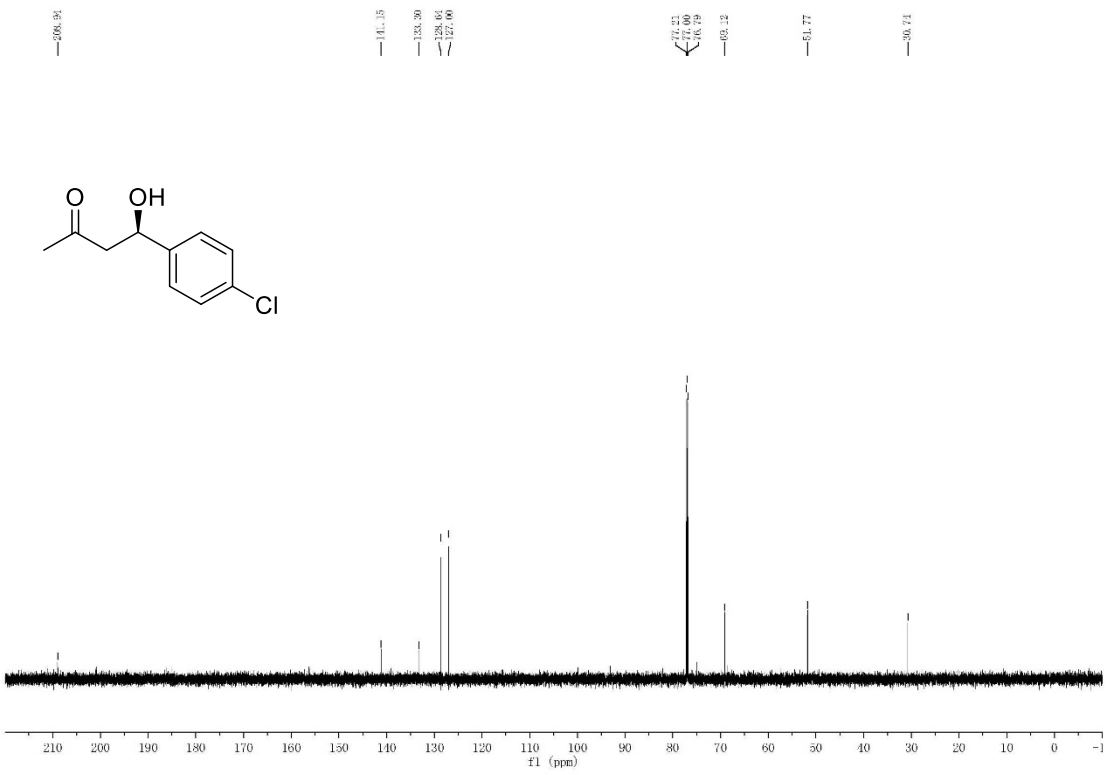
** CALCULATION REPORT **

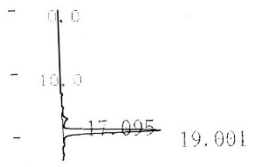
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	16	16.94	139878	4012	V		2.2239	
	17	20.994	6149867	127318			97.7761	
		TOTAL	6289744	131330			100	

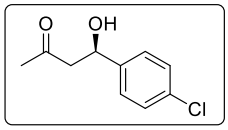
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	19	16.751	818336	16335			49.3961	
	21	20.783	838347	12678			50.6039	
		TOTAL	1656682	29013			100	


2.1823
2.7924
2.7983
2.8054
2.8201
3.3966
5.1228
5.1175
5.1084
5.1030
7.3110
7.2969
7.2821
7.2679
7.2494
3.09
2.16
0.95
1.00
4.39
f1 (ppm)
Cl
HO
O

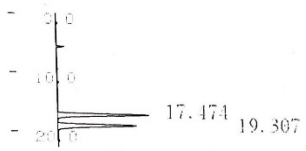


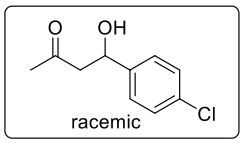




** CALCULATION REPORT **

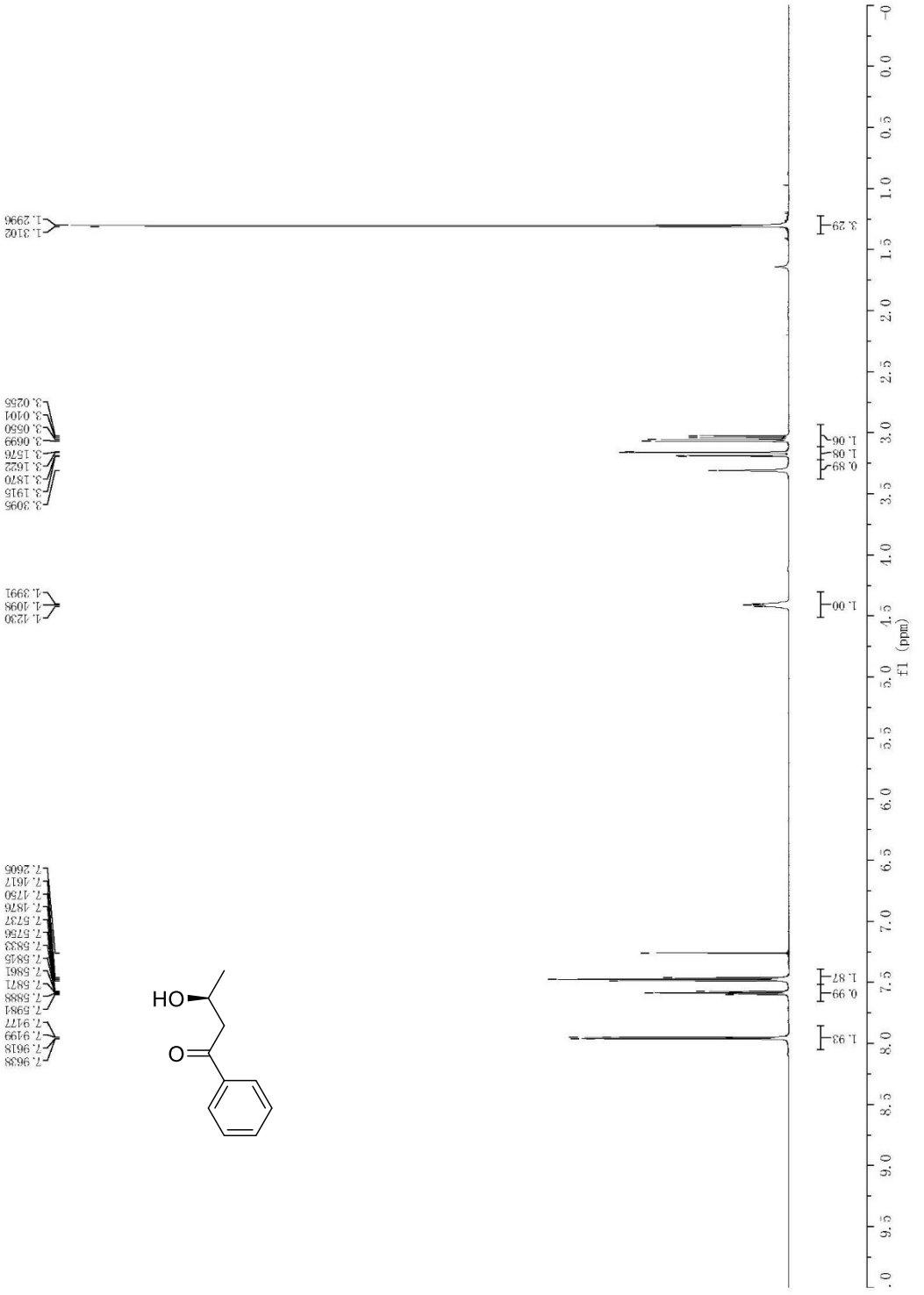
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	10	17.095	44407	784	V		7.353	
	11	19.001	559521	15370	V		92.647	
		TOTAL	603928	16154			100	

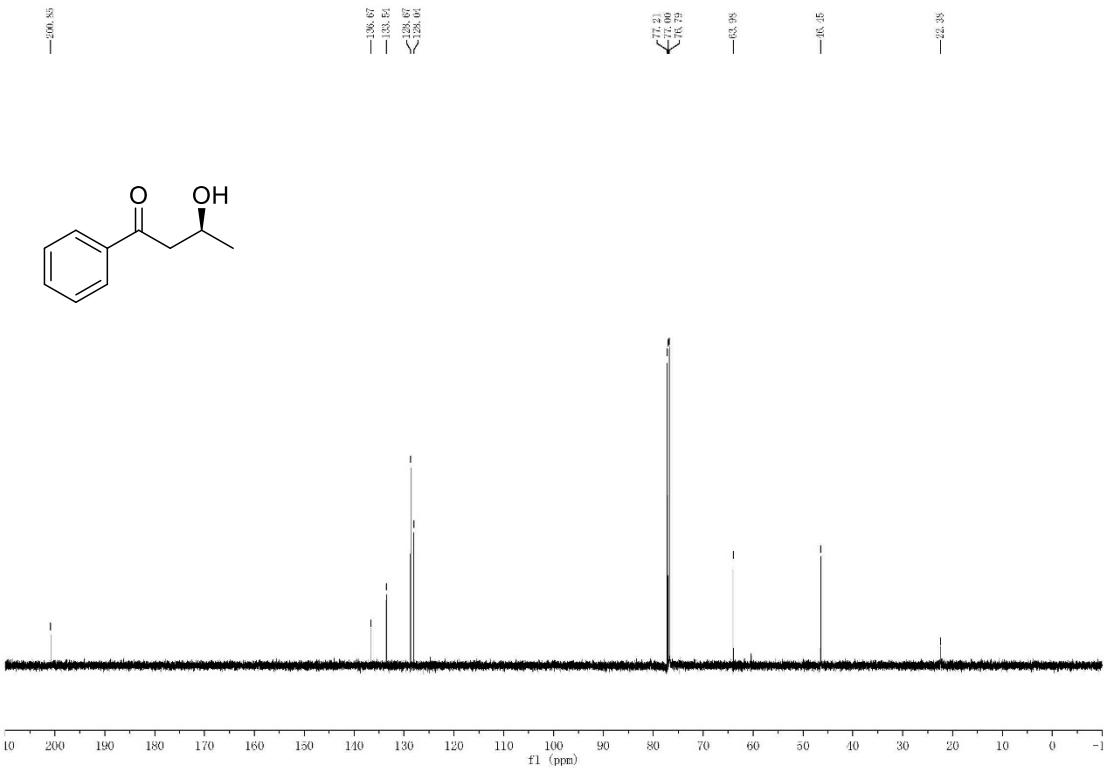


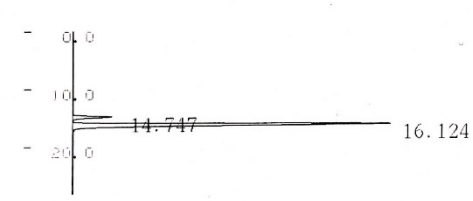


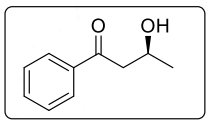
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	16	17.474	837347	30872			50.0354	
	17	19.307	836161	26453			49.9646	
		TOTAL	1673508	57325			100	


HO
O
f1 (ppm)

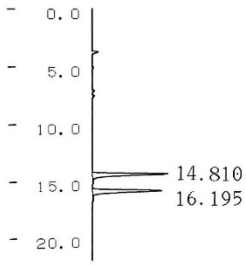


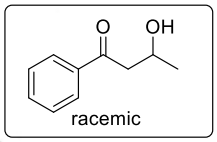




** CALCULATION REPORT **

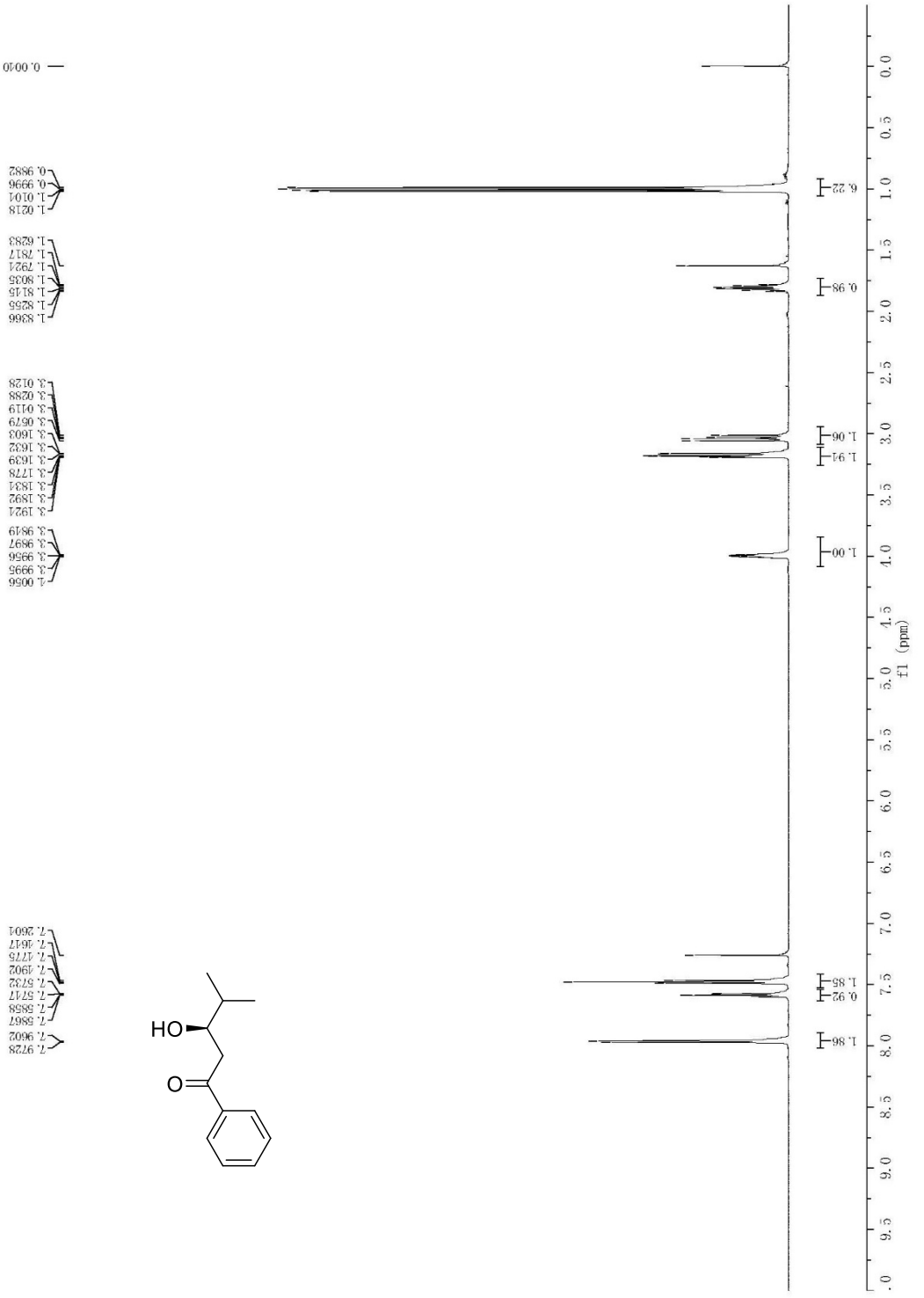
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	14	14.747	293126	12528			9.5575	
	15	16.124	2773836	102299			90.4425	
		TOTAL	3066962	114827			100	

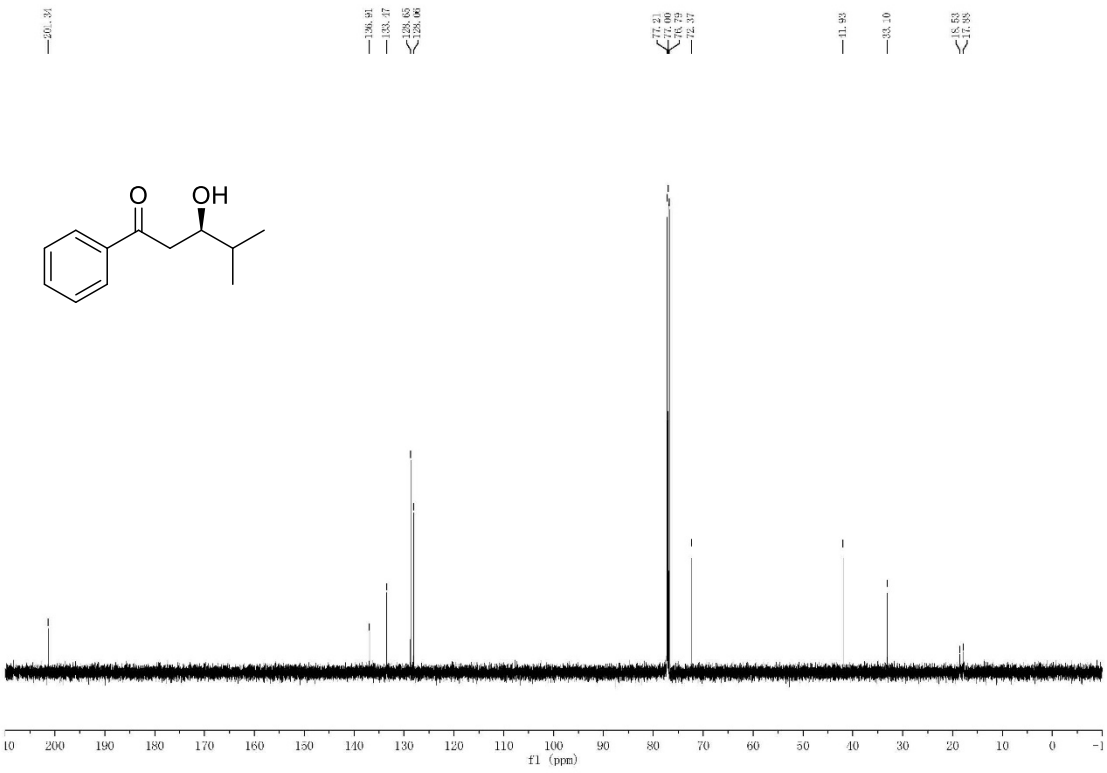


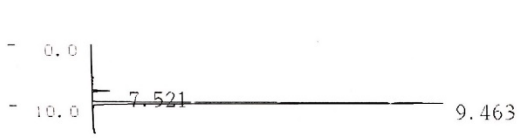


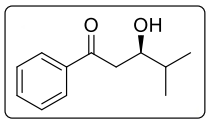
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	20	14.81	1333150	95435			49.6214	
	22	16.195	1353493	88195			50.3786	
		TOTAL	2686642	183630			100	


HO
O
f1 (ppm)

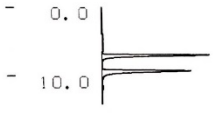


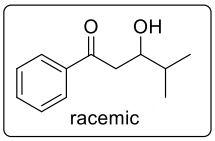




** CALCULATION REPORT **

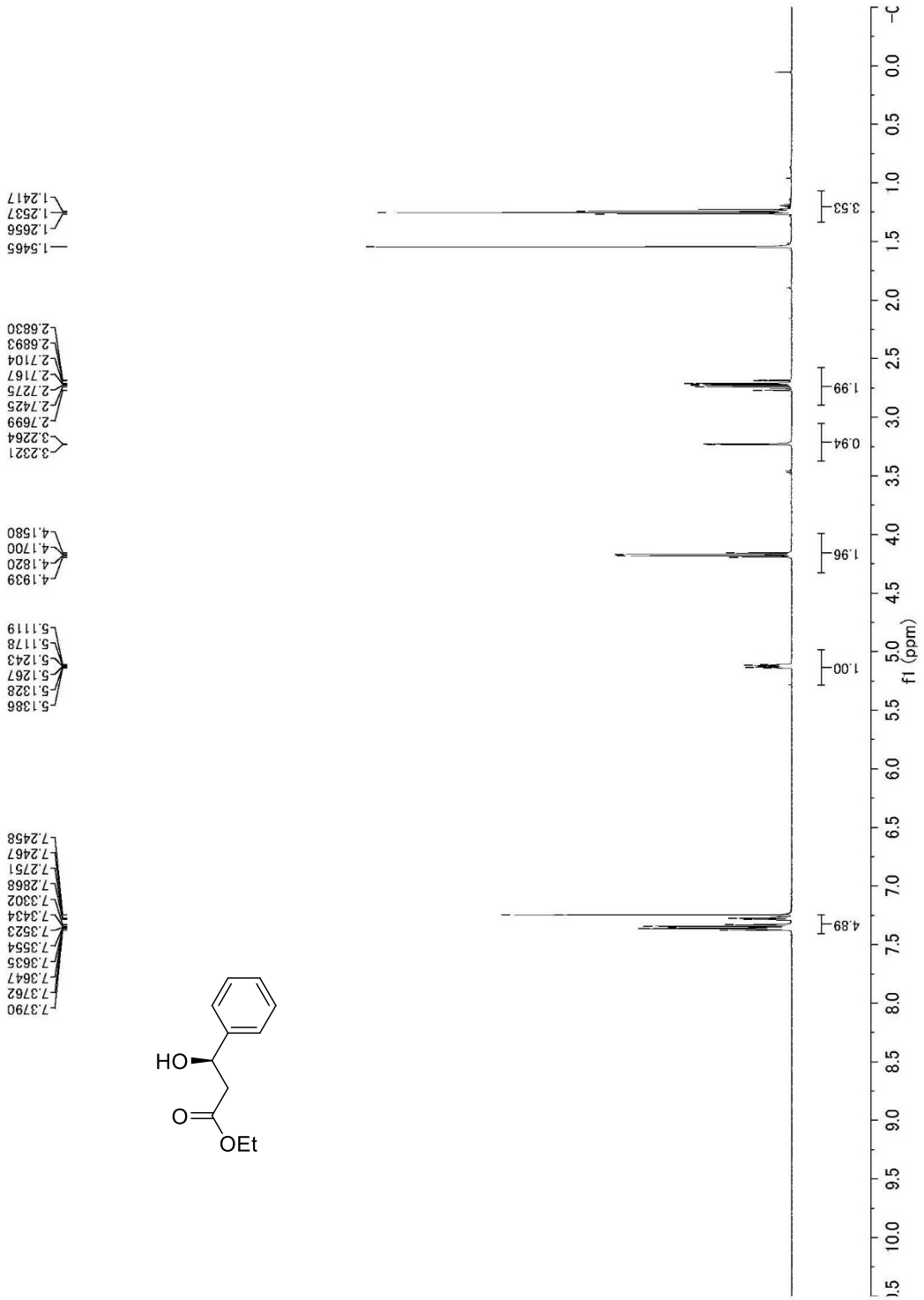
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	17	7.521	421031	42608			3.5983	
	20	9.463	11279902	847678			96.4017	
		TOTAL	11700932	890286			100	

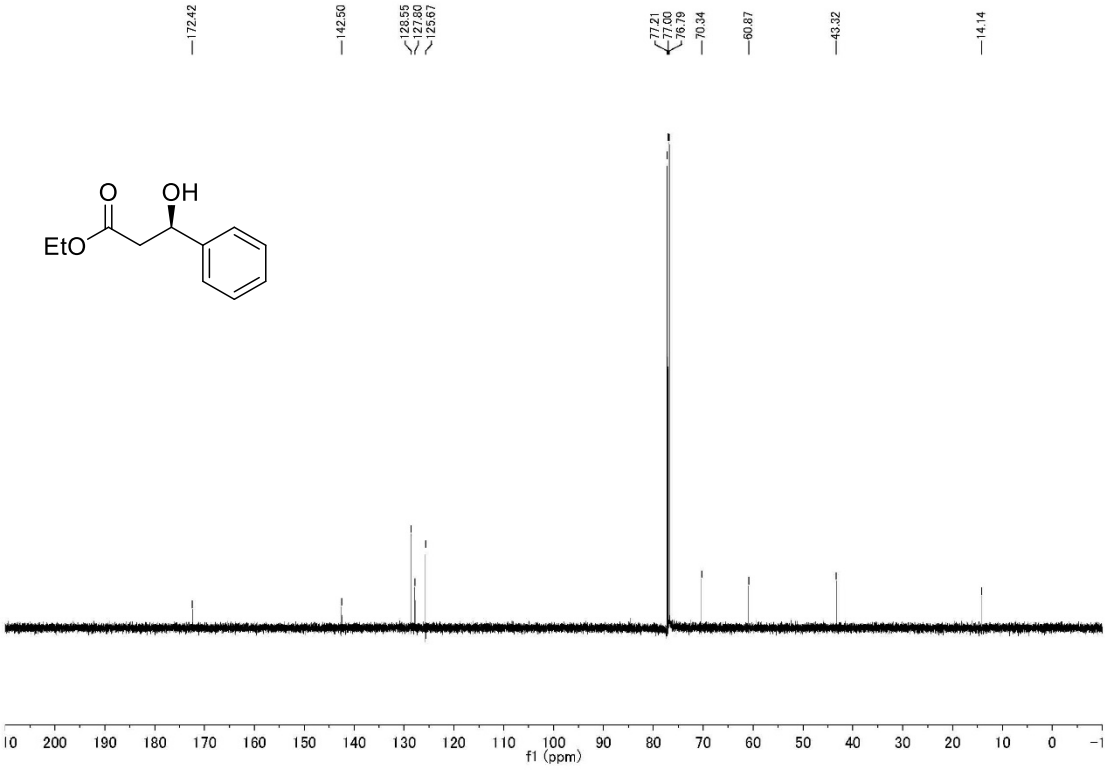


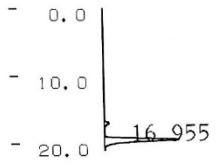


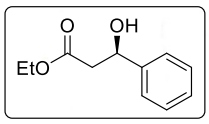
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	6	7.344	2144903	116865	V		49.8085	
	7	9.287	2161399	96224	SV		50.1915	
		TOTAL	4306302	213089			100	


1.2417
1.2537
1.2656
1.5465
2.6830
2.6893
2.7104
2.7167
2.7275
2.7425
2.7699
3.2264
3.2321
4.1580
4.1700
4.1820
4.1939
5.1119
5.1178
5.1243
5.1267
5.1328
5.1386
7.2458
7.2467
7.2751
7.2868
7.3302
7.3434
7.3523
7.3554
7.3635
7.3647
7.3762
7.3790
HO
O
OEt
3.53
1.99
0.94
1.96
1.00
4.89
f1 (ppm)

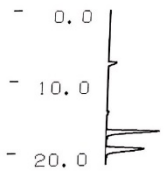


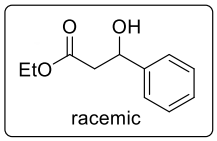




** CALCULATION REPORT **

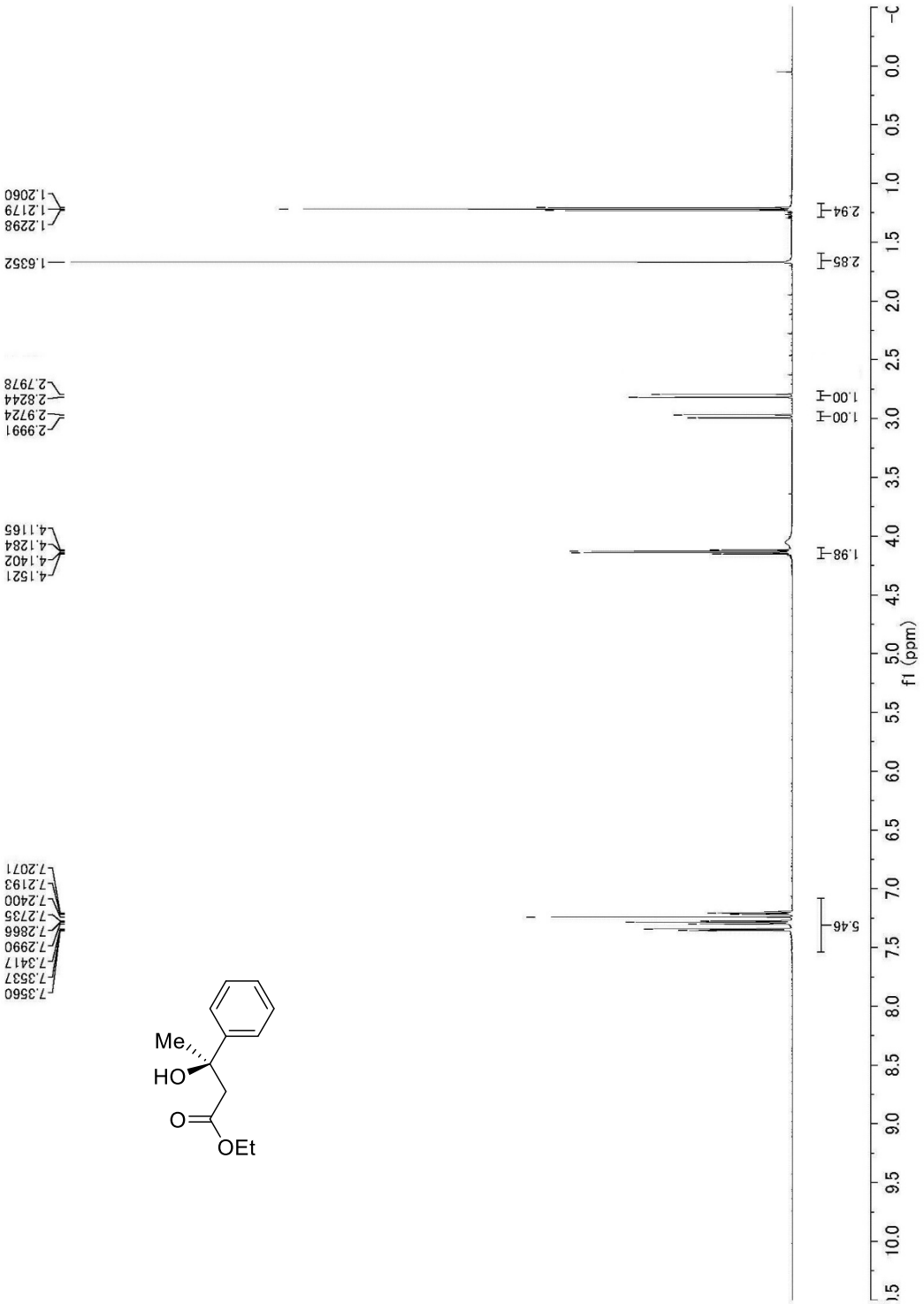
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	40	16.955	165122	5382			5.5964	
	41	19.428	2785373	81942			94.4036	
		TOTAL	2950495	87323			100	

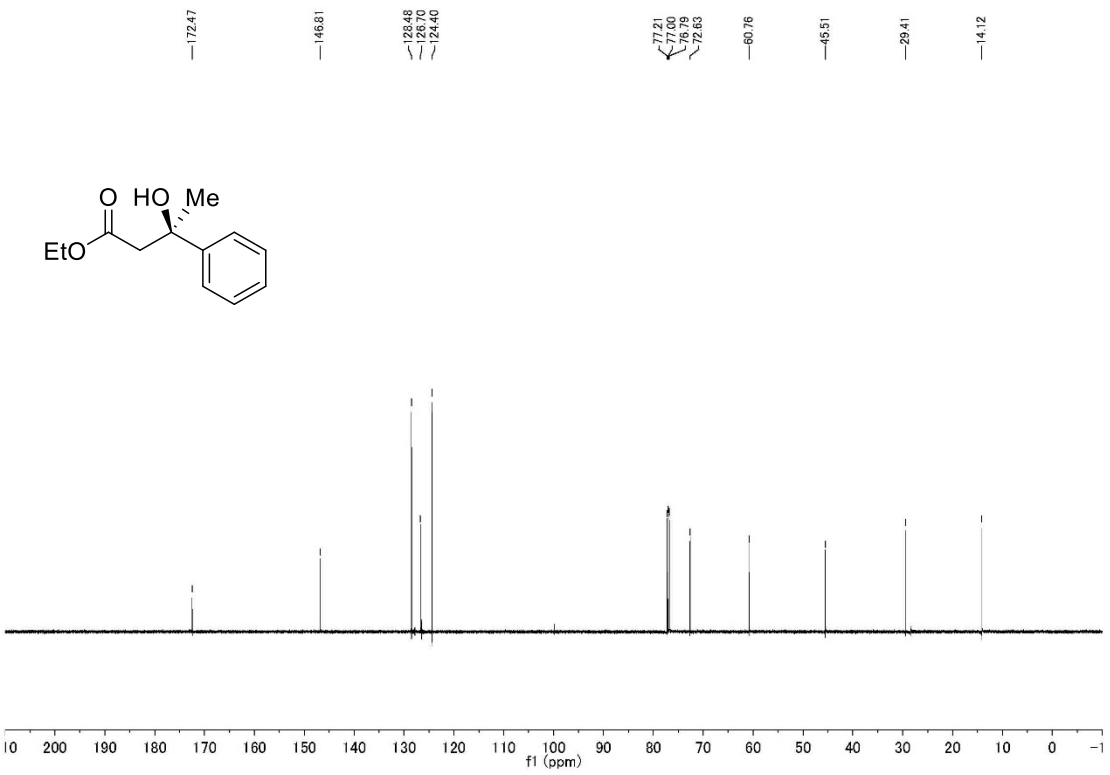


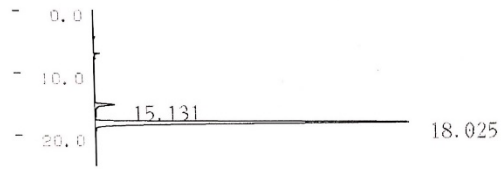


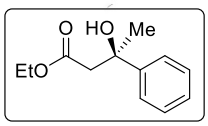
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	23	17.088	1431915	54783			50.4657	
	24	19.522	1405489	39840			49.5343	
		TOTAL	2837404	94623			100	


1.2060
1.2179
1.2298
1.6352
2.7978
2.8244
2.9724
2.9991
4.1165
4.1284
4.1402
4.1521
7.3560
7.3537
7.3417
7.2990
7.2866
7.2735
7.2400
7.2193
7.2071
2.94
2.85
1.00
1.00
1.98
5.46
Me
HO
O
OEt
f1 (ppm)

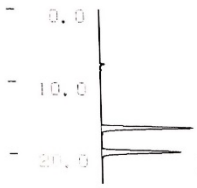


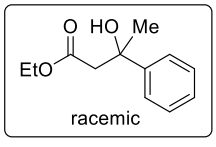




** CALCULATION REPORT **

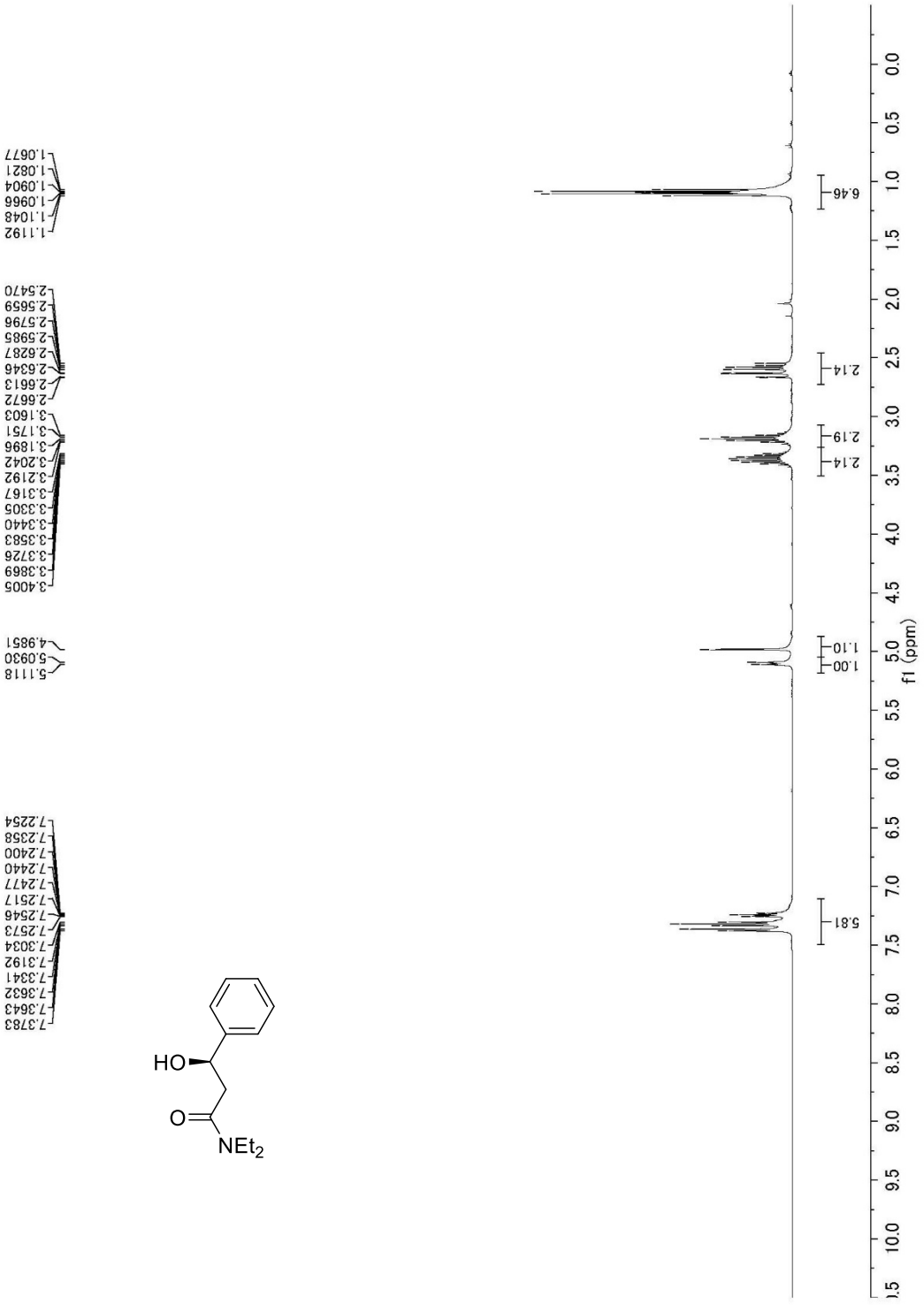
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	38	15.131	1308674	49807	V		5.718	
	39	18.025	21578362	781240	SV		94.282	
		TOTAL	22887036	831047			100	





** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	39	16.22	20439058	777634	S		50.1377	
	41	19.605	20326774	677672	SV		49.8623	
		TOTAL	40765832	1455307			100	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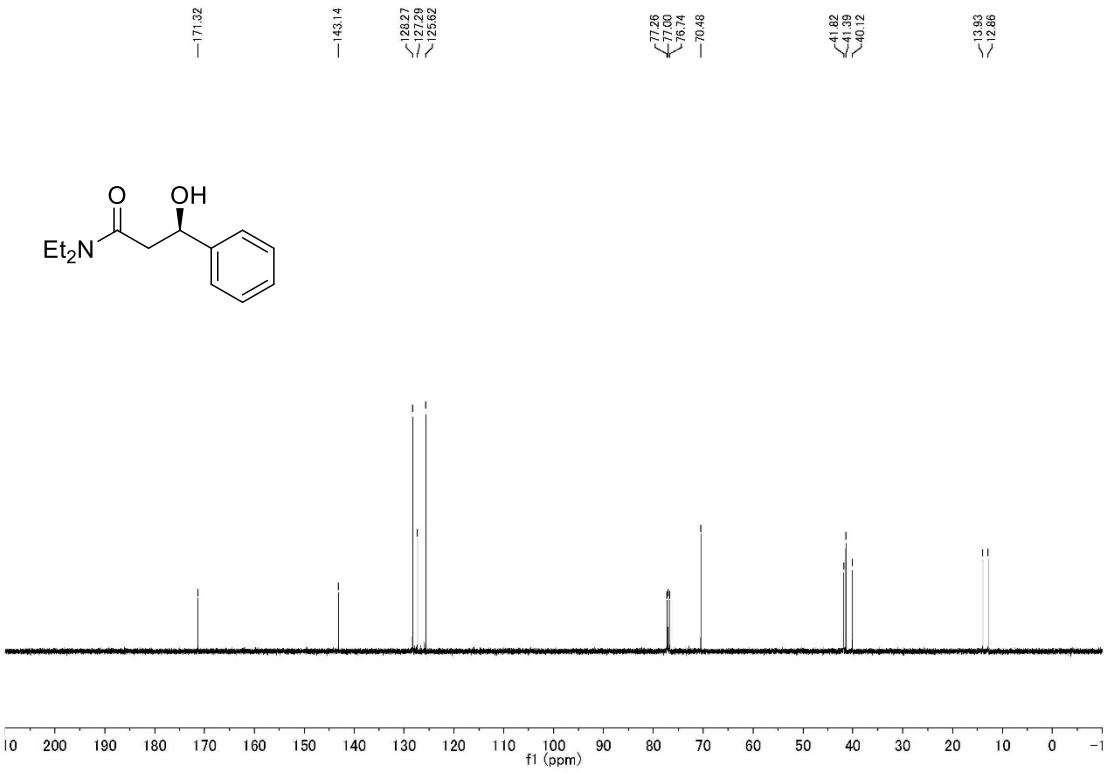
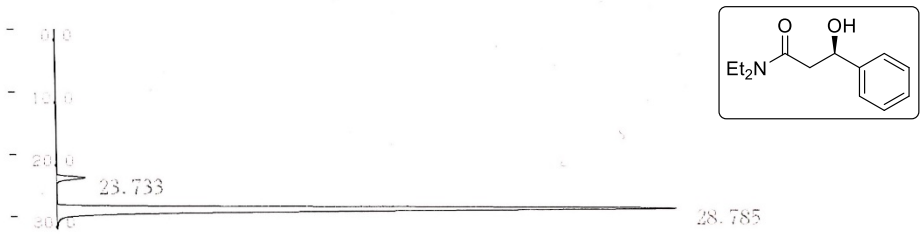
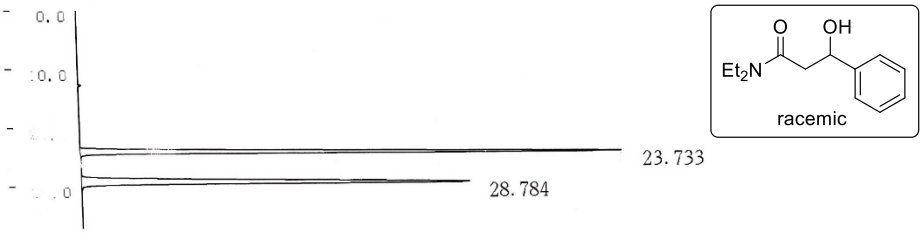
1.0821
1.0904
1.0966
1.1048
1.1192
2.5470
2.5659
2.5796
2.5985
2.6287
2.6346
2.6613
2.6672
3.1603
3.1751
3.1896
3.2042
3.2192
3.3167
3.3305
3.3440
3.3583
3.3726
3.3869
3.4005
4.9851
5.0930
5.1118
7.2254
7.2358
7.2400
7.2440
7.2477
7.2517
7.2546
7.2573
7.3034
7.3192
7.3341
7.3532
7.3643
7.3783
HO
O
NEt2
6.46
2.14
2.19
2.14
1.10
1.00
5.81
f1 (ppm)





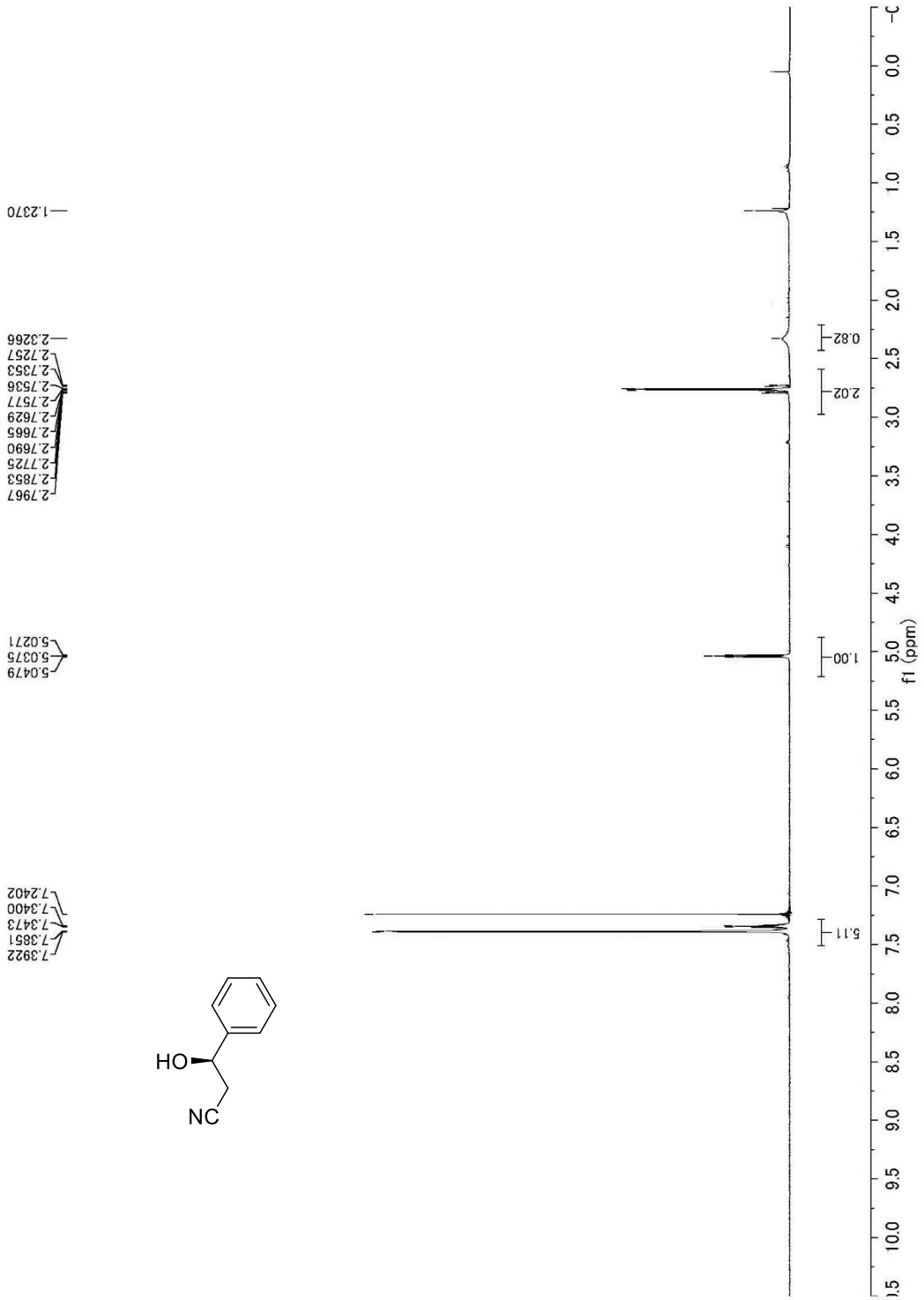
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	17	23.733	191670	4807			3.6233	
	18	28.785	5098273	104404			96.3767	
		TOTAL	5289942	109210			100	



** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	39	23.733	5940188	194438			49.6628	
	44	28.784	6020857	140001			50.3372	
		TOTAL	11961044	334438			100	


HO
NC
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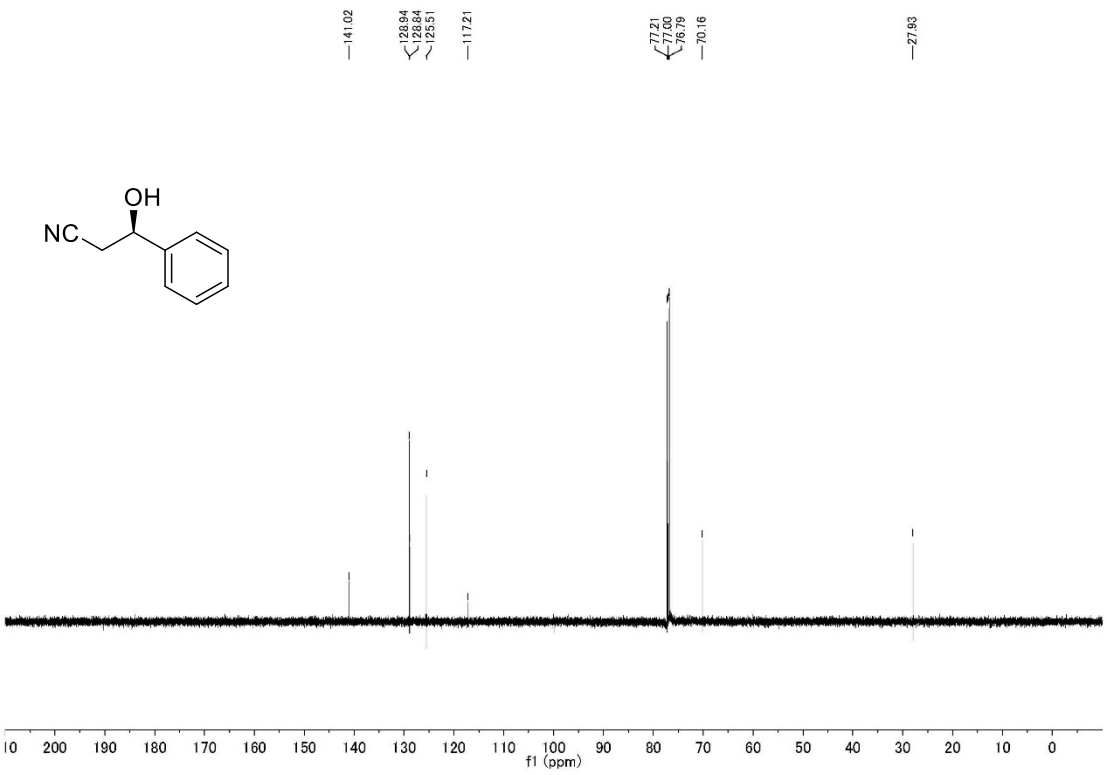
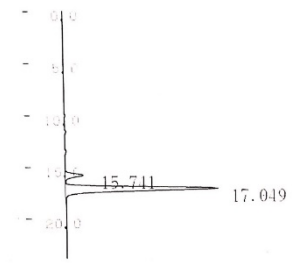
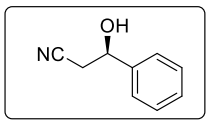
7.3473
7.3400
7.2402
5.0479
5.0375
5.0271
2.7967
2.7853
2.7725
2.7690
2.7665
2.7629
2.7577
2.7536
2.7353
2.7257
2.3266
1.2370
5.11
1.00
2.02
0.82
f1 (ppm)

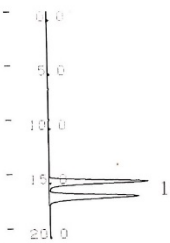


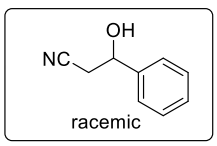




** CALCULATION REPORT **

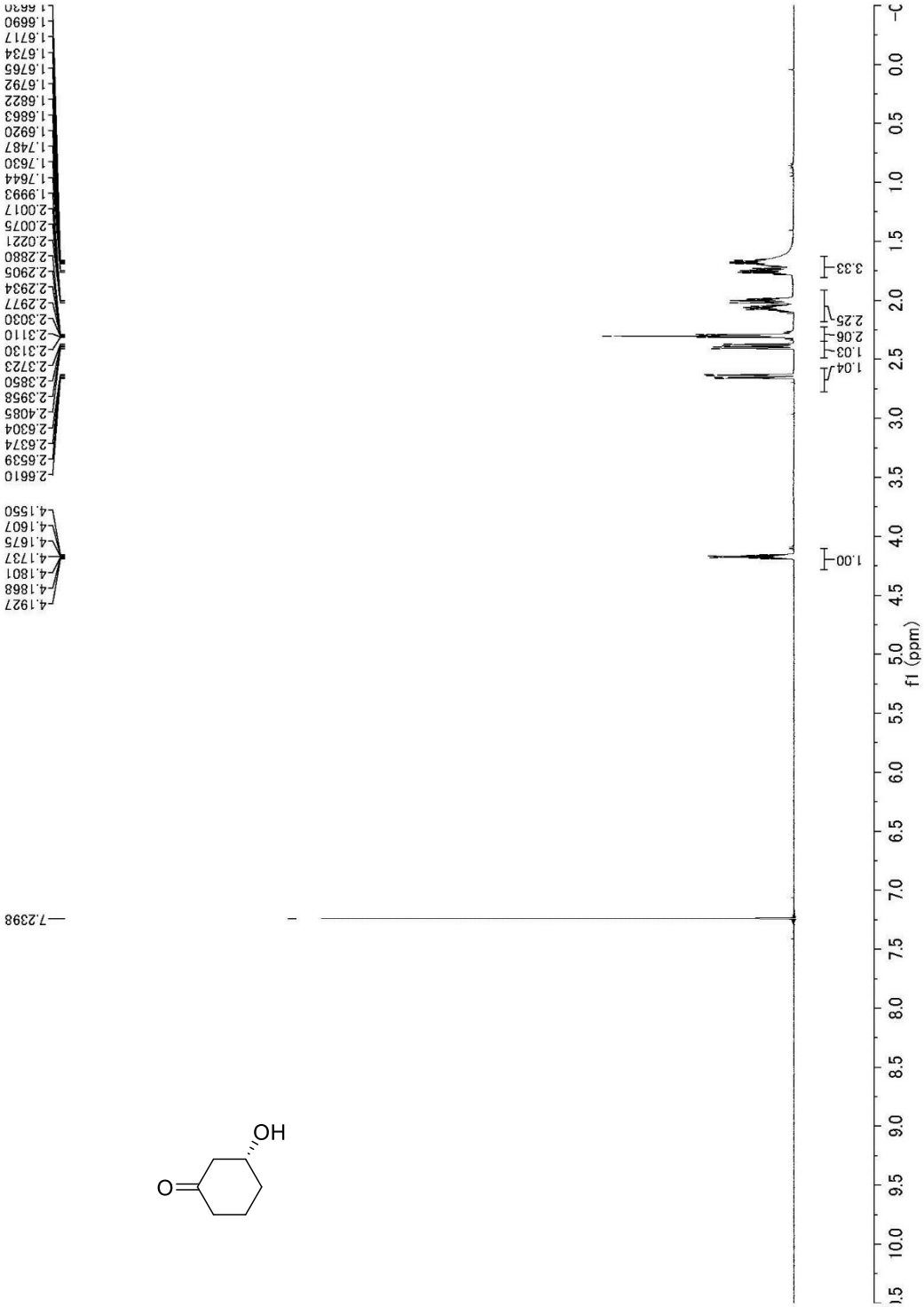
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	17	15.741	172512	6955			9.3806	
	18	17.049	1666514	60070	V		90.6194	
		TOTAL	1839025	67025			100	





** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	18	15.713	891639	35615			49.8501	
	19	17.059	897000	32008	V		50.1498	
		TOTAL	1788638	67623			100	


OH
O
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4.1927
4.1868
4.1801
4.1737
4.1675
4.1607
4.1550
2.6610
2.6539
2.6374
2.6304
2.4085
2.3958
2.3850
2.3723
2.3130
2.3110
2.3030
2.2977
2.2934
2.2905
2.2880
2.0221
2.0075
2.0017
1.9993
1.7644
1.7630
1.7487
1.6920
1.6863
1.6822
1.6792
1.6765
1.6734
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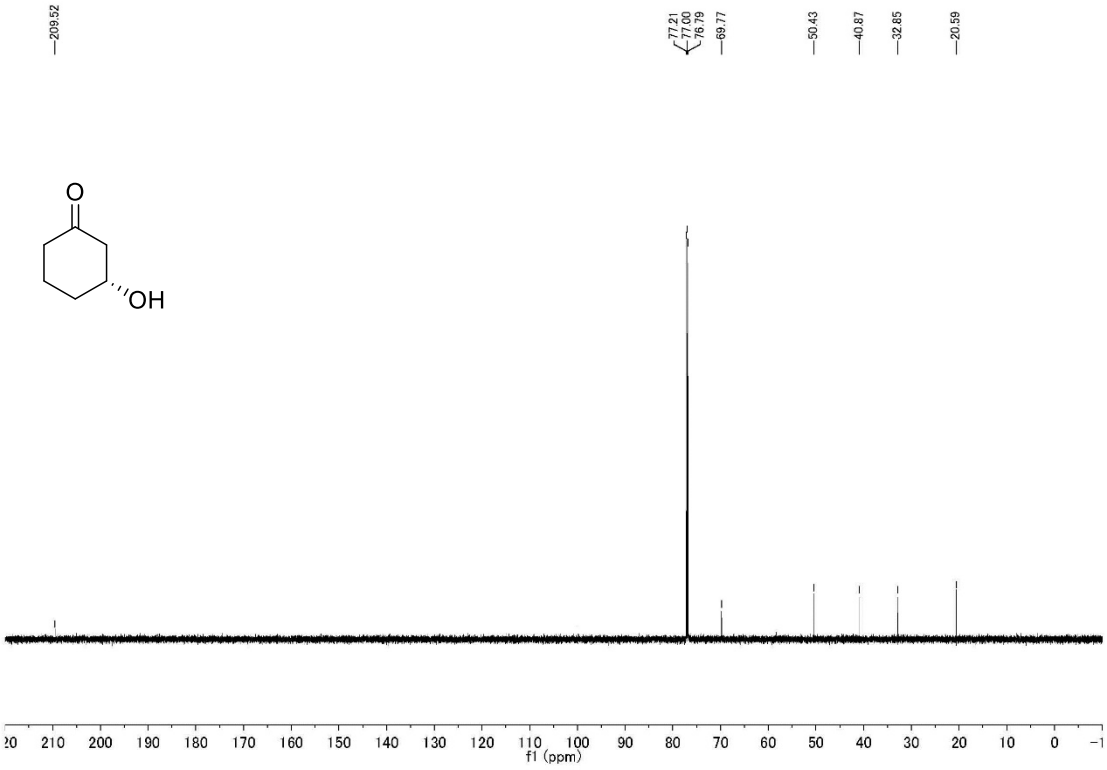
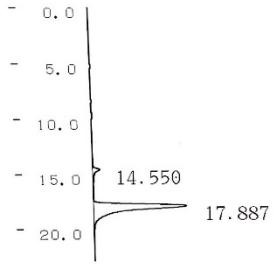
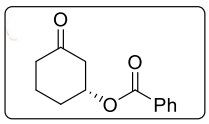
1.6630
1.00
1.04
1.03
2.06
2.25
3.33
f1 (ppm)

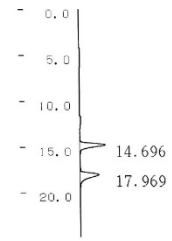


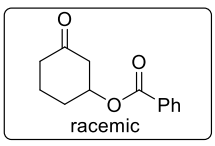




** CALCULATION REPORT **

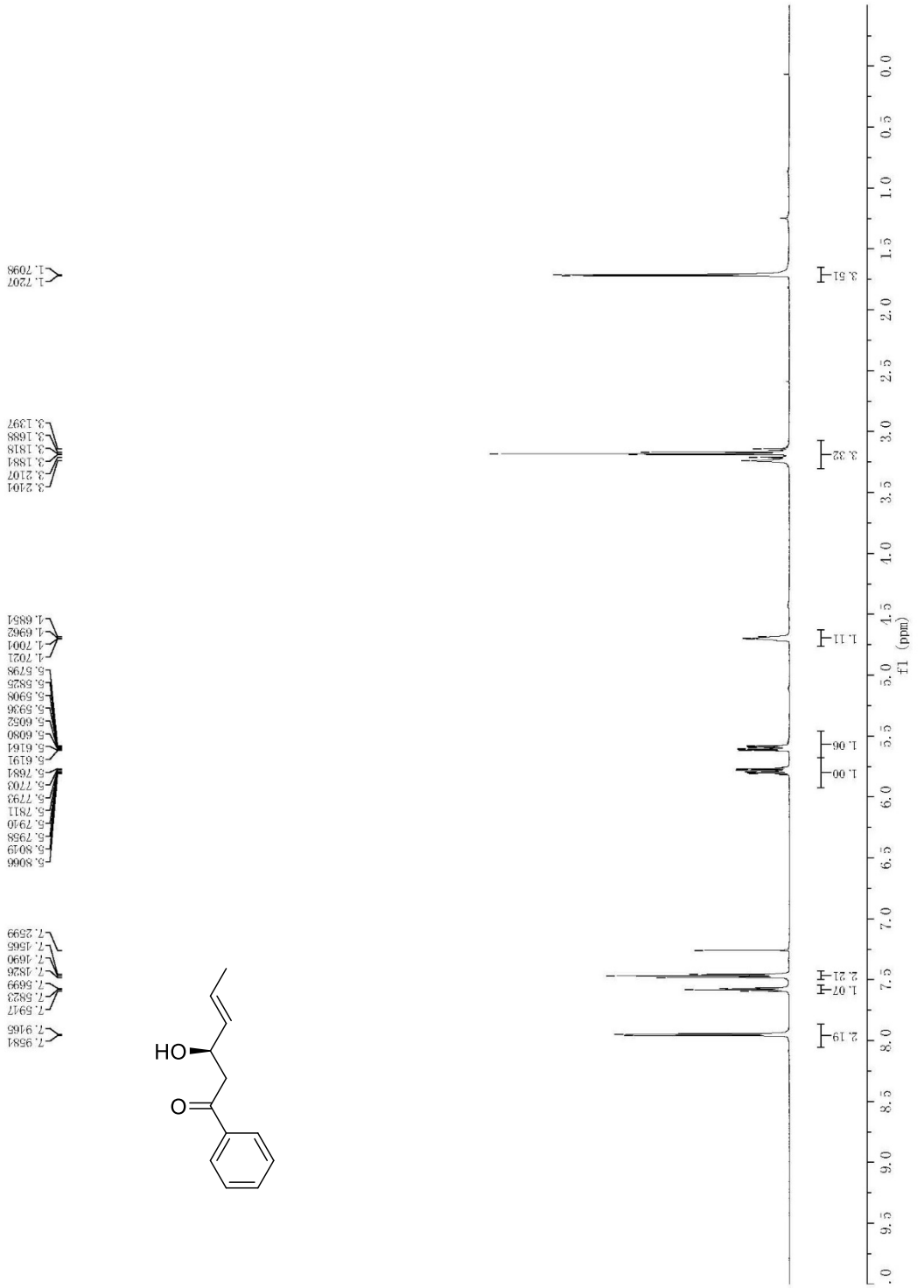
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	18	14.55	1932734	71199			4.8009	
	19	17.887	38324592	977158			95.199	
		TOTAL	40257324	1048357			100	

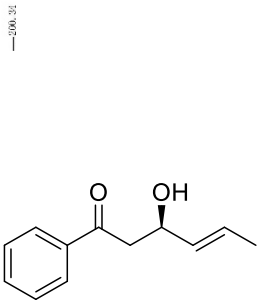


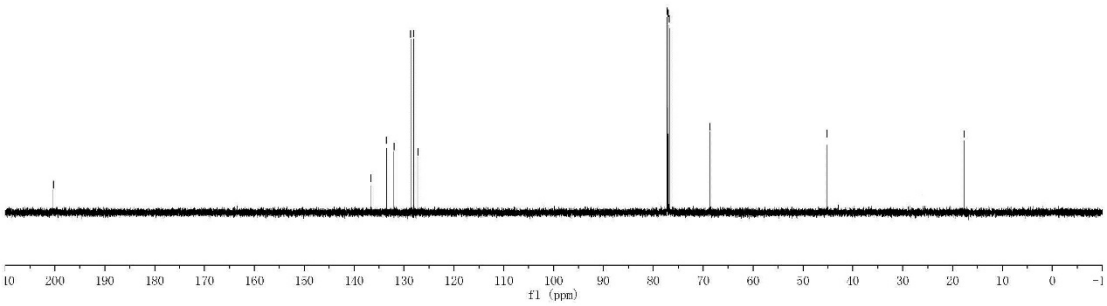


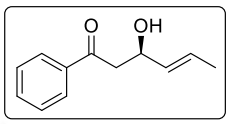
** CALCULATION REPORT **

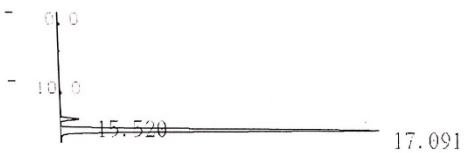
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	20	14.696	5019695	173858			50.1397	
	21	17.969	4991725	128539			49.8603	
		TOTAL	10011419	302396			100	


HO
O
f1 (ppm)



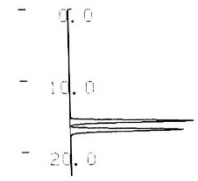


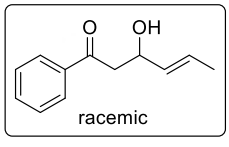




** CALCULATION REPORT **

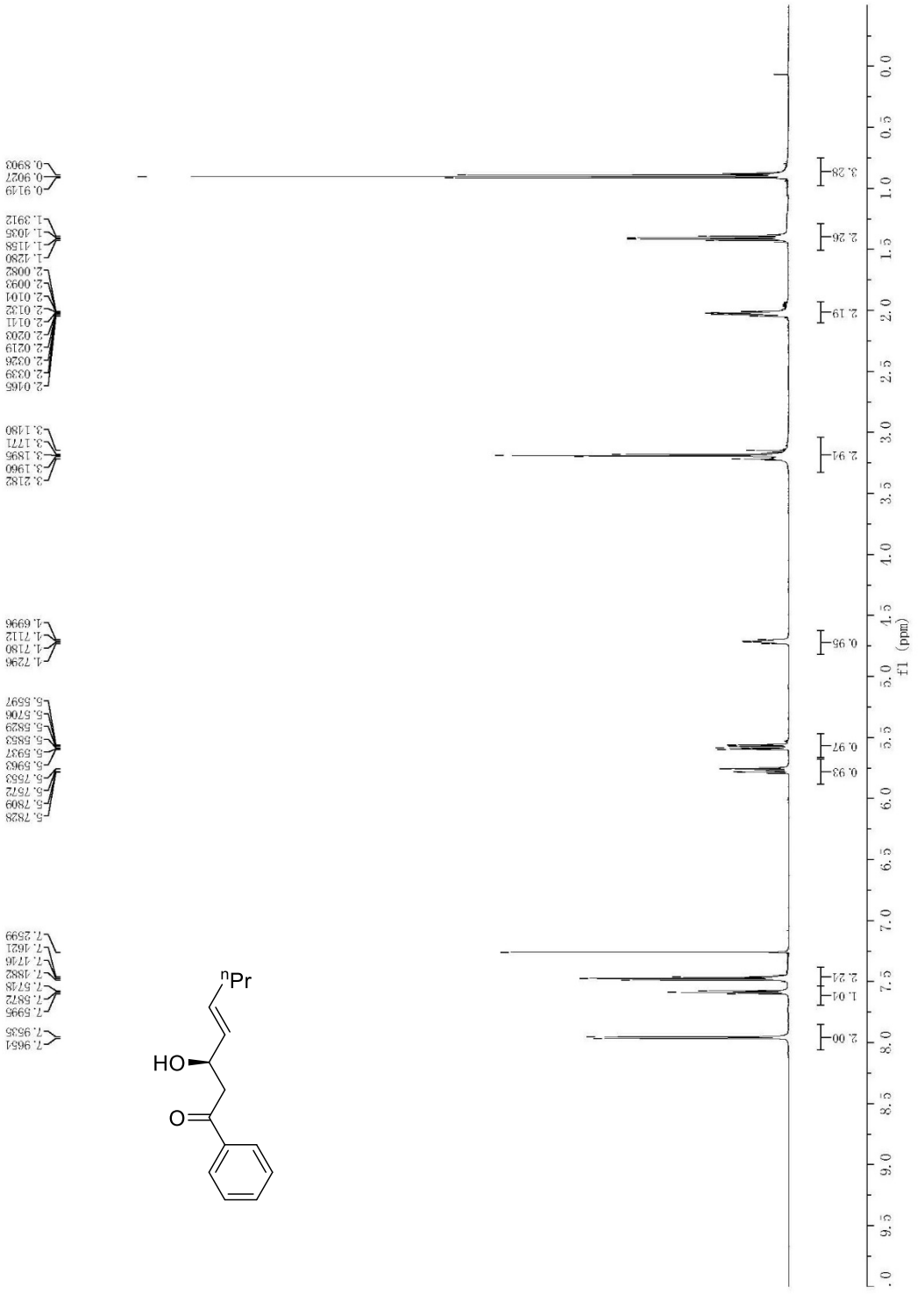
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	18	15.52	71410	2877			4.8371	
	19	17.091	1404884	49044			95.1629	
		TOTAL	1476294	51921			100	

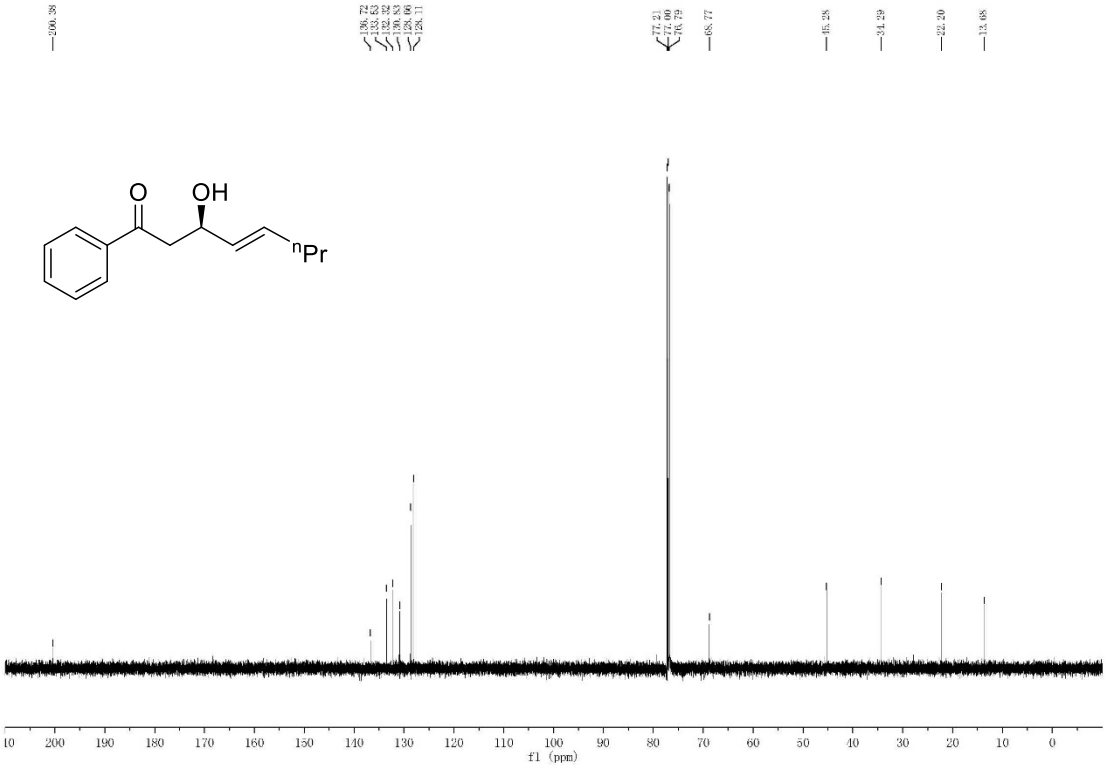


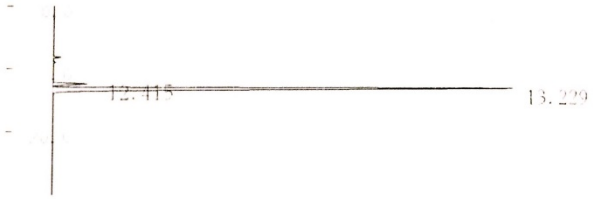


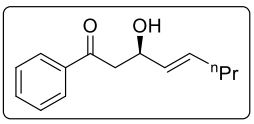
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	19	15.627	884469	36150			49.756	
	20	16.849	893145	33076	V		50.244	
		TOTAL	1777614	69227			100	


HO
O
nPr
f1 (ppm)

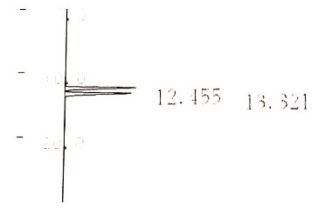


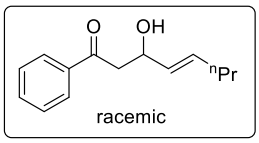




** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	16	12.415	214298	11218	V		6.1126	
	17	13.229	3291542	156184	SV		93.8874	
		TOTAL	3505839	167402			100	





** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	23	12.455	446929	23190			49.6996	
	24	13.321	452331	21599	SV		50.3004	
		TOTAL	899260	44789			100	