Supporting Information

Diphenylprolinol Silyl Ether as Catalyst of an Asymmetric, Catalytic, and Direct α-Benzoyloxylation of Aldehydes

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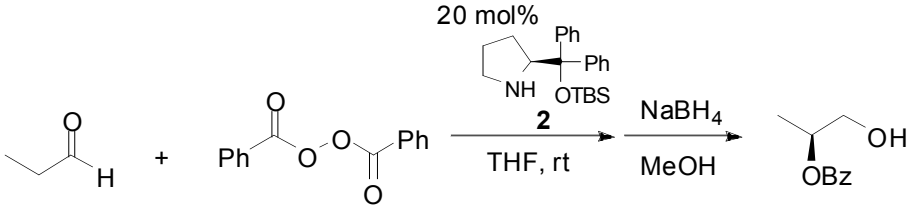
Experimental Section

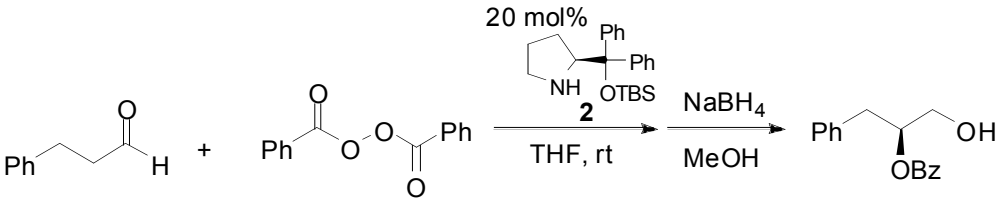
General Remarks: All reactions were carried out under argon atmosphere and monitored by thin-layer chromatography using Merck 60 F_{254} precoated silica gel plates (0.25 mm thickness). FT-IR spectra were recorded on a JASCO FT/IR-410 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Brucker AM400 (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR) instrument. Data for ^{1}H NMR are reported as chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), integration, and assignment. Data for ^{13}C NMR are reported as chemical shift. High-resolution mass spectral analyses (HRMS) were carried out using Bruker ESI-TOF MS. Preparative thin layer chromatography was performed using Wakogel B-5F purchased from Wako Pure Chemical Industries, Tokyo, Japan. Flash chromatography was performed using silica gel 60N of Kanto Chemical Co. Int., Tokyo, Japan. HPLC analysis was performed on a HITACHI Elite LaChrom Series HPLC, UV detection monitered at appropriate wavelength respectively, using Chiralpak AD-H (0.46 cm x 25 cm) or Chiralpak AS-H (0.46 cm x 25 cm).

General procedure: (condition A) Table 2 entry 1



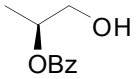
To a solution of benzoyl peroxide (88.0 mg, 0.27 mmol, contains 25% water) and propanal (58.0 μL, 0.81 mmol) in THF (2.7 mL) was added catalyst **2** (9.9 mg, 0.027 mmol, 10 mol%) at the room temperature. After stirring the reaction mixture at room temperature for 4 h, to a reaction mixture was added catalyst **2** (9.9 mg, 0.027 mmol, 10 mol%). After stirring the reaction mixture at room temperature for additional 16 h, MeOH (2.7 mL) and excess amount of $NaBH_4$ were added at 0 °C to the reaction mixture, which was stirred for 5 minutes. The resulting mixture was quenched with saturated aqueous $NaHCO_3$. The organic materials were extracted with AcOEt and dried over anhydrous Na_2SO_4, then concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt:hexane = 1:20 ~ 1:3) to afford (*S*)-1-hydroxypropan-2-yl benzoate (39.3 mg, 78%).

General procedure: (condition B) Table 2 entry 3



To a solution of benzoyl peroxide (130.3 mg, 0.40 mmol, contains 25% water) and 3-phenylpropanal (35.4 μL, 0.27 mmol) in THF (2.7 mL) was added catalyst **2** (9.9 mg, 0.027 mmol, 10 mol%) at the room temperature. After stirring the reaction mixture at room temperature for 4 h, to the reaction mixture was added catalyst **2** (9.9 mg, 0.027 mmol, 10 mol%). After stirring the reaction mixture at room temperature for additional 16 h, MeOH (2.7 mL) and excess amount of $NaBH_4$ were added at 0 °C to the reaction mixture, which was stirred for 5 minutes. The resulting mixture was quenched with saturated aqueous $NaHCO_3$. The organic materials were extracted with AcOEt and dried over anhydrous Na_2SO_4, then concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt:hexane = 1:20 ~ 1:3) to afford (*S*)-1-hydroxy-3-phenylpropan-2-yl benzoate (49.4 mg, 72%).

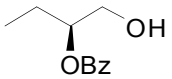
(*S*)-1-Hydroxypropan-2-yl benzoate (Table 2 entry 1)



Prepared according to the general procedure (condition A) with propanal. Spectroscopic data are in agreement with the published data.[S1] $[\alpha]_D^{21}$ −17.7 (*c* 0.6, $CHCl_3$). Lit[S1] $[\alpha]_D^{21}$ −18.6 (*c* 1.0, $CHCl_3$).

Enantiomeric excess was determined by HPLC using a Chiralpak AS-H column (10/1 hexane/*i*-PrOH; flow rate 1.0 mL/min, major enantiomer; t_R = 4.5, minor enantiomer; t_R = 5.3 min.)

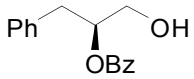
(*S*)-1-Hydroxybutan-2-yl benzoate (Table 2 entry 2)



Prepared according to the general procedure (condition A) with butanal. ^{1}H NMR ($CDCl_3$) δ 1.01 (3H, t, *J* = 7.2 Hz), 1.80 (2H, quint, *J* = 7.2 Hz), 3.78 (1H, dd, *J* = 6.0, 12.0 Hz), 3.84 (1H, dd, *J* = 3.2, 12.0 Hz), 5.10 (1H, dq, J_d = 3.6 Hz, J_q = 6.4 Hz), 7.45 (2H, t, *J* = 8.0 Hz), 7.57 (1H, t, *J* = 7.2 Hz), 8.06 (2H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 9.7, 23.8, 64.7, 77.6, 128.4 (2C), 129.7 (2C), 130.2, 133.1, 167.0 ; IR (neat) ν 3446, 1717, 1276, 1116, 1069, 712 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calculated for $C_{11}H_{14}O_3Na$: 217.0835, found: 217.0845; $[\alpha]_D^{22}$ −19.0 (*c* 0.65, $CHCl_3$).

Enantiomeric excess was determined by HPLC using a Chiralpak AS-H column (100/1 hexane/*i*-PrOH; flow rate 1.0 mL/min, major enantiomer; t_R = 13.0 min, minor enantiomer; t_R = 21.0 min.)

(*S*)-1-Hydroxy-3-phenylpropan-2-yl benzoate (Table2 entry 3)

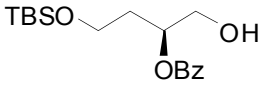


Prepared according to the general procedure (condition B) with 3-phenylpropanal. ^{1}H NMR ($CDCl_3$) δ 3.05 (1H, dd, *J* = 6.8, 14.0 Hz), 3.09 (1H, dd, *J* = 6.8, 14.0 Hz), 3.76 (1H, dd, *J* = 6.0, 12.0 Hz), 3.85 (1H, dd, *J* = 3.6, 12.0 Hz), 5.36 (1H, dq, J_d = 3.2 Hz, J_q = 6.4 Hz), 4.62 (1H, dd, *J* = 7.6, 12.4 Hz), 4.68 (1H, dd, *J* = 7.6, 12.4 Hz), 7.20–7.40 (5H, m), 9.70 (1H, s); ^{13}C NMR ($CDCl_3$) δ 36.9, 63.7, 76.6, 126.7, 128.4 (2C), 128.5 (2C), 129.4 (2C), 129.7 (2C), 130.1, 133.1, 136.8, 166.5; IR (neat) ν 3438, 1715, 1273, 1115, 712 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calculated for $C_{16}H_{16}O_3Na$: 279.0992, found: 279.0991; $[\alpha]_D^{21}$ −63.5 (*c* 1.4, $CHCl_3$).

Enantiomeric excess was determined by HPLC using a Chiralpak AS-H column (20/1

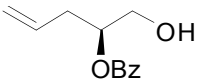
hexane/*i*-PrOH; flow rate 1.0 mL/min, major enantiomer; t_R = 6.7, minor enantiomer; t_R = 9.4 min)

(*S*)-4-(*tert*-Butyldimethylsilyloxy)-1-hydroxybutan-2-yl benzoate (Table 2 entry 4)



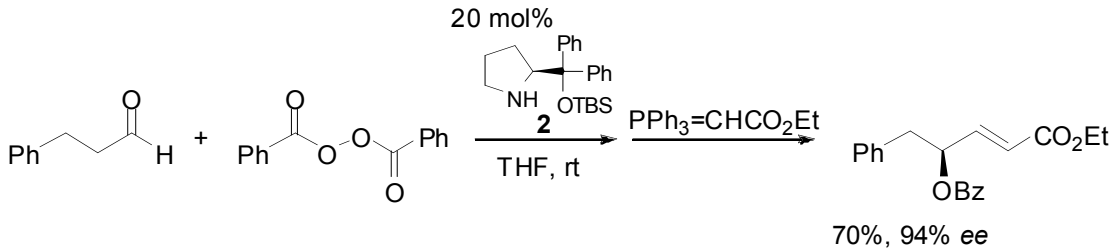
Prepared according to the general procedure (condition B) with 4-(*tert*-butyldimethylsilyloxy)butanal. ^{1}H NMR ($CDCl_3$) δ 0.05 (3H, s), 0.06 (3H, s), 0.90 (9H, s), 1.95–2.06 (2H, m), 3.70–3.91 (4H, m), 5.26 (1H, tt, *J* = 5.6, 5.6 Hz), 7.43 (2H, t, *J* = 7.6 Hz), 7.56 (1H, t, *J* = 7.2 Hz), 8.05 (2H, d, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ –5.5, 18.2, 25.8, 34.0, 59.2, 64.6, 73.9, 128.3, 129.6, 130.2, 133.0, 166.4; IR (neat) ν 3439, 2954, 2929, 1714, 1276, 1093, 837, 777, 713 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calculated for $C_{17}H_{28}O_4SiNa$: 347.1649, found: 347.1651; $[\alpha]_D^{21}$ –18.8 (*c* 2.0, $CHCl_3$).
Enantiomeric excess was determined by HPLC using a Chiralpak AS-H column (10/1 hexane/*i*-PrOH; flow rate 1.0 mL/min, major enantiomer; t_R = 4.8 min, minor enantiomer; t_R = 6.3 min)

(*S*)-1-Hydroxypent-4-en-2-yl benzoate (Table 2 entry 5)



Prepared according to the general procedure (condition B) with pent-4-enal. ^{1}H NMR ($CDCl_3$) δ 1.76–1.96 (2H, m), 2.13–2.26 (2H, m), 3.78 (1H, dd, *J* = 6.0, 12.0 Hz), 3.85 (1H, dd, *J* = 3.2, 12.0 Hz), 4.99 (1H, dq, J_d = 10.4 Hz, J_q = 1.2 Hz), 5.04 (1H, dq, *J*d = 17.2 Hz, J_q = 1.6 Hz), 5.19 (1H, tt, *J* = 3.6, 8.4 Hz), 5.83 (1H, ddt, J_d = 10.0, 16.8 Hz, J_t = 6.4 Hz), 7.42–7.50 (2H, m), 7.54–7.61 (1H, m), 8.03–8.10 (2H, m); ^{13}C NMR ($CDCl_3$) δ 29.5, 29.9, 64.8, 75.7, 115.4, 128.4 (2C), 129.7 (2C), 130.1, 133.1, 137.4, 166.8; IR (neat) ν 3446, 2929, 1716, 1275, 1116, 712 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calculated for $C_{13}H_{16}O_3Na$: 243.0992, found: 243.0991; $[\alpha]_D^{22}$ –26.3 (*c* 0.64, $CHCl_3$).
Enantiomeric excess was determined by HPLC using a Chiralpak AS-H column (100/1 hexane/*i*-PrOH; flow rate 1.0 mL/min, major enantiomer; t_R = 12.5 min, minor enantiomer; t_R = 19.5 min.)

(*S*)-Ethyl 4-benzoyloxy-5-phenylpent-2-enate (5)



To a solution of benzoyl peroxide (130.3 mg, 0.40 mmol, contains 25% water) and 3-phenylpropanal (35.4 μL, 0.27 mmol) in THF (2.7 mL) was added catalyst **2** (9.9 mg, 0.027 mmol, 10 mol%) at the room temperature. After stirring the reaction mixture at room temperature for 4 h, to a reaction mixture was added catalyst **2** (9.9 mg, 0.027 mmol, 10 mol%). After stiring the reaction mixture at room temperature for additional 16 h, the resulting mixture was add ethyl(triphenylphosphoranylidene)acetate (186.7 mg, 0.536 mmol). After stirring the reaction mixture at room temperature for 7 h, the resulting mixture was quenched with saturated aqueous $Na_2S_2O_3$. The organic materials were extracted with AcOEt and dried over anhydrous Na_2SO_4, then concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt:hexane = 1:20 ~ 1:3) to afford (*S*)-ethyl 4-benzoyloxy-5-phenylpent-2-enate **5** (68.1 mg, 70%).

^{1}H NMR ($CDCl_3$) δ 1.27 (3H, t, *J* = 7.2 Hz), 3.08 (1H, dd, *J* = 6.0, 14.0 Hz), 3.16 (1H, dd, *J* = 7.2, 14.0 Hz), 4.18 (2H, q, *J* = 7.2 Hz), 5.84–5.91 (1H, m), 5.99 (1H, dd, *J* = 1.6, 16 Hz), 6.99 (1H, dd, *J* = 5.2, 15.6 Hz), 7.19–7.32 (5H, m), 7.41–7.49 (2H, m), 7.55–7.61 (1H, m), 8.00–8.06 (2H, m); ^{13}C NMR ($CDCl_3$) δ 14.2, 40.5, 60.6, 73.5, 122.1, 127.0, 128.5 (4C), 129.5 (2C), 129.7 (2C), 129.8, 133.2, 135.9, 144.5, 165.4, 165.9; IR (neat) ν 2981, 1723, 1268, 1110, 712 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calculated for $C_{20}H_{20}O_4Na$: 347.1254, found: 347.1257; $[\alpha]_D^{21}$ –3.0 (*c* 0.35, MeOH).
Enantiomeric excess was determined by HPLC using a Chiralpak AD-H column (100/1 hexane/*i*-PrOH; flow rate 1.0 mL/min, major enantiomer; t_R = 15.6 min, minor enantiomer; t_R = 18.0 min)

References

S1) E. Santaniello, S. Casati, P. Ciuffreda, L. Gamberoni, *Tetrahedron. Asymmetry,* **2005**, *16*, 1705.

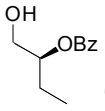
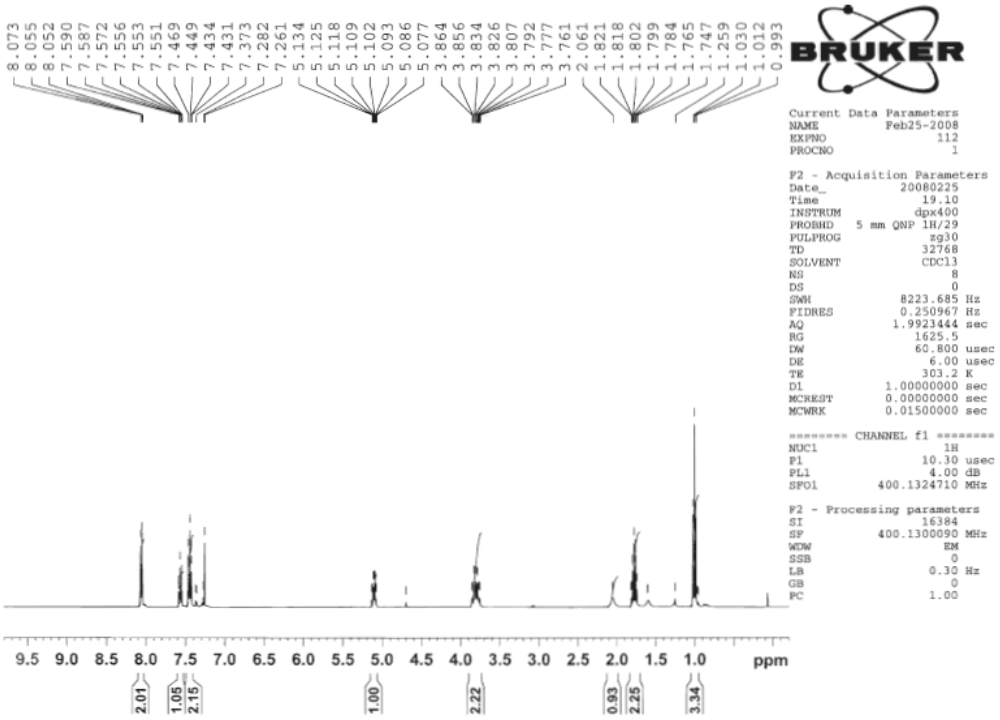
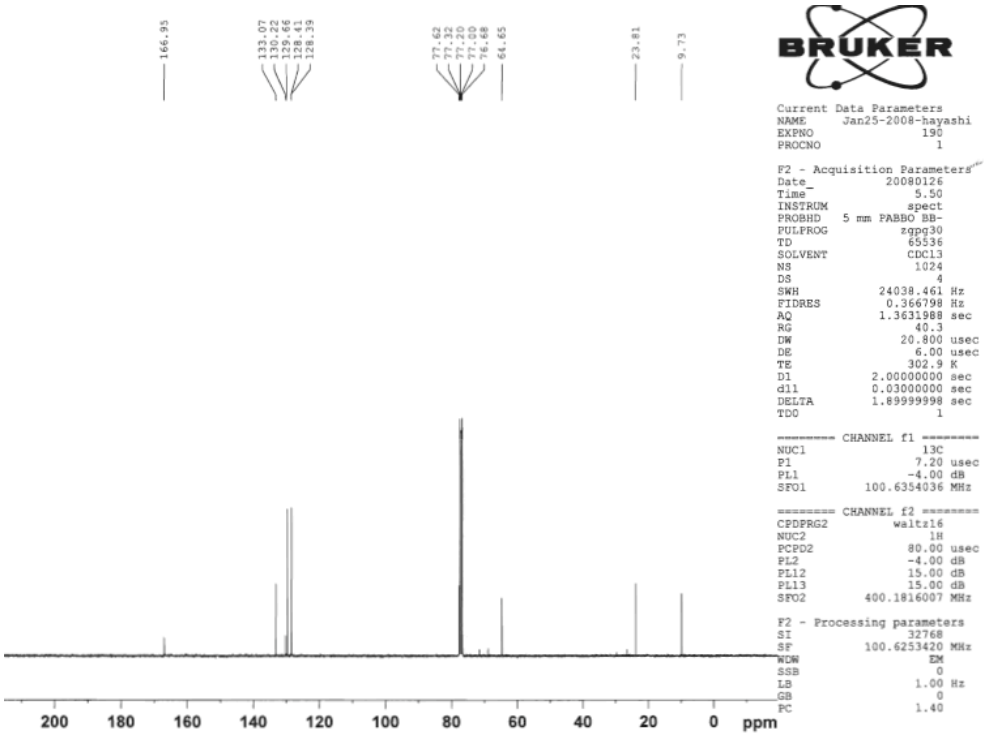
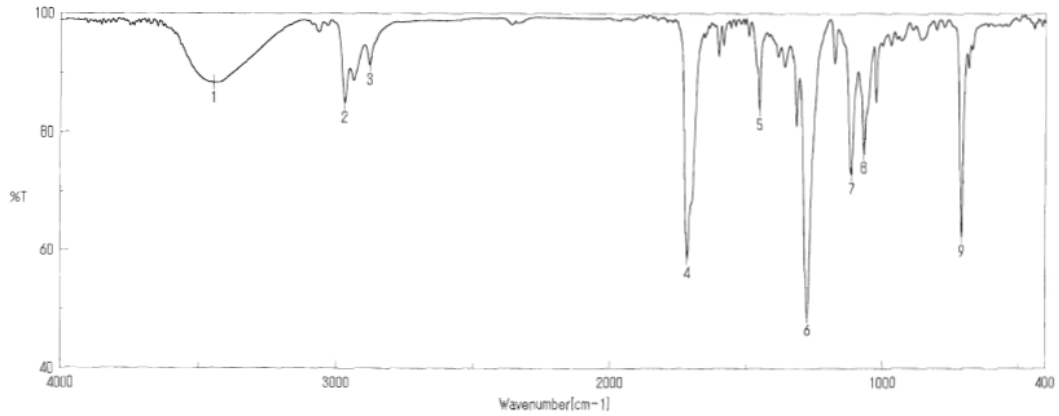


Table 2 entry 2







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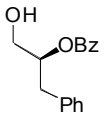

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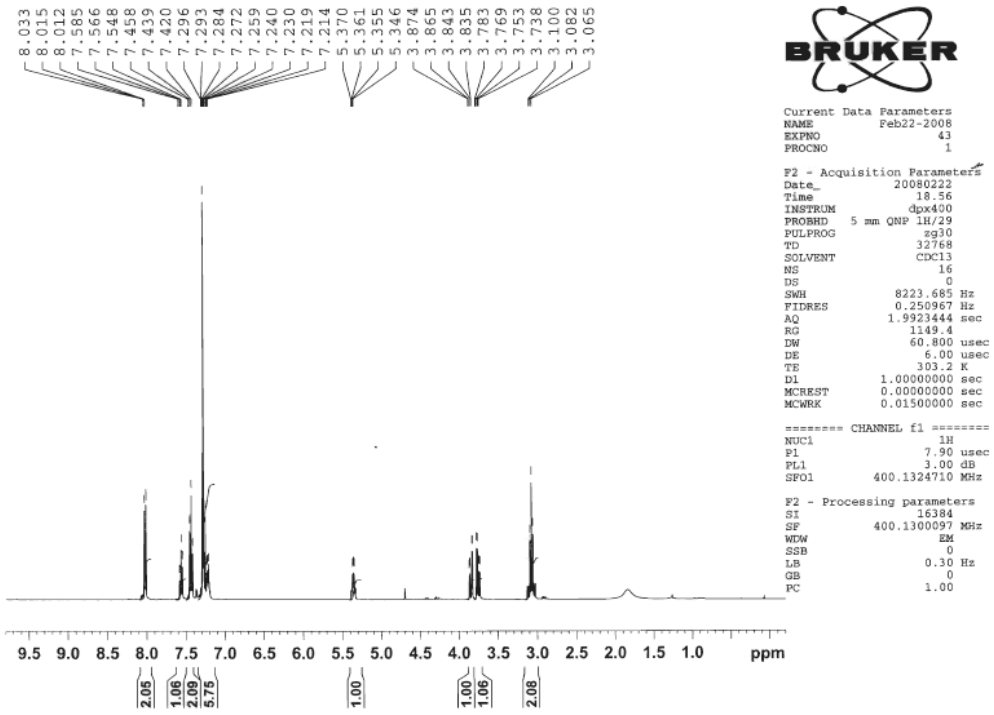

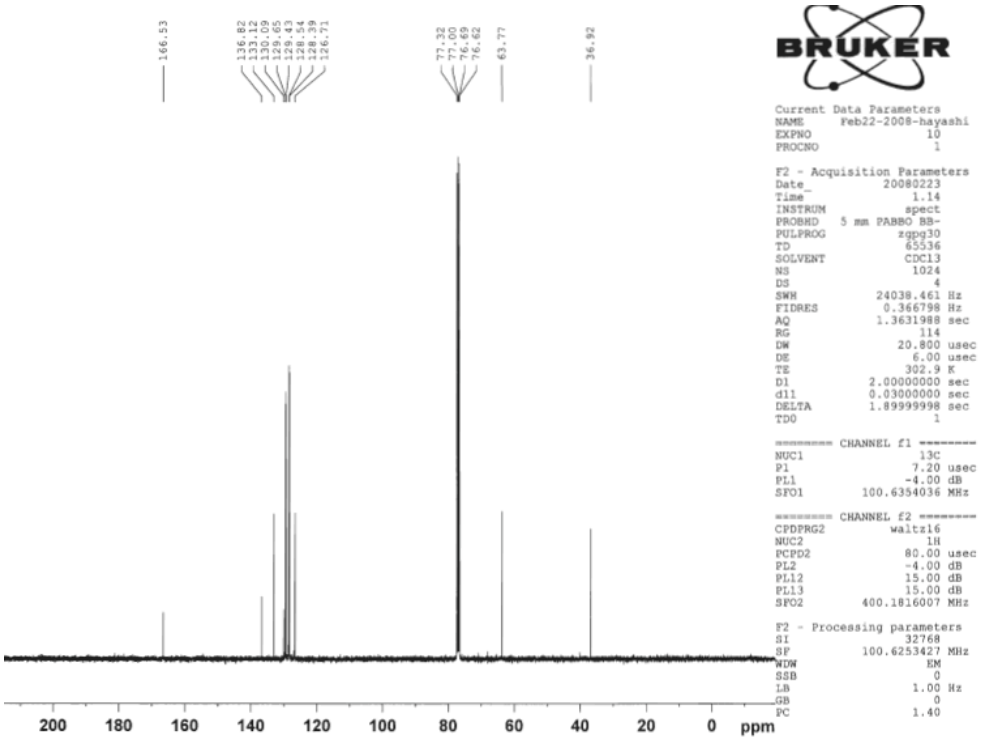

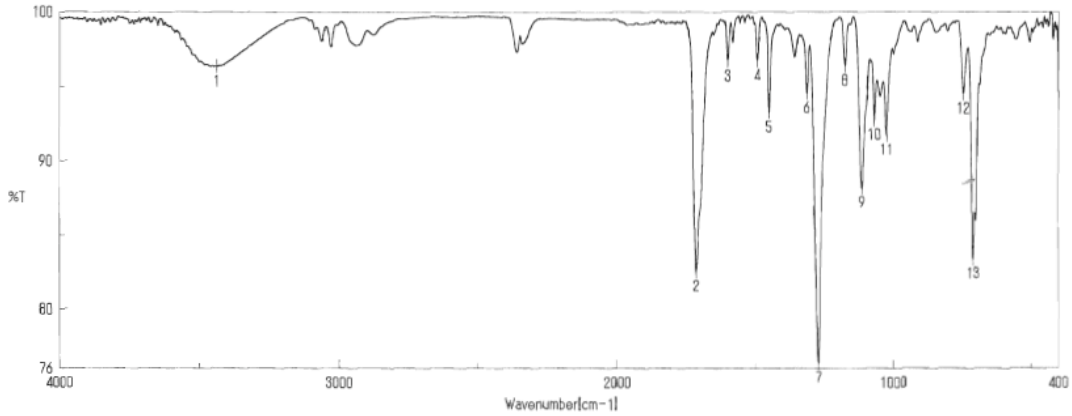

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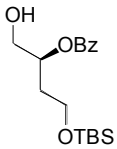

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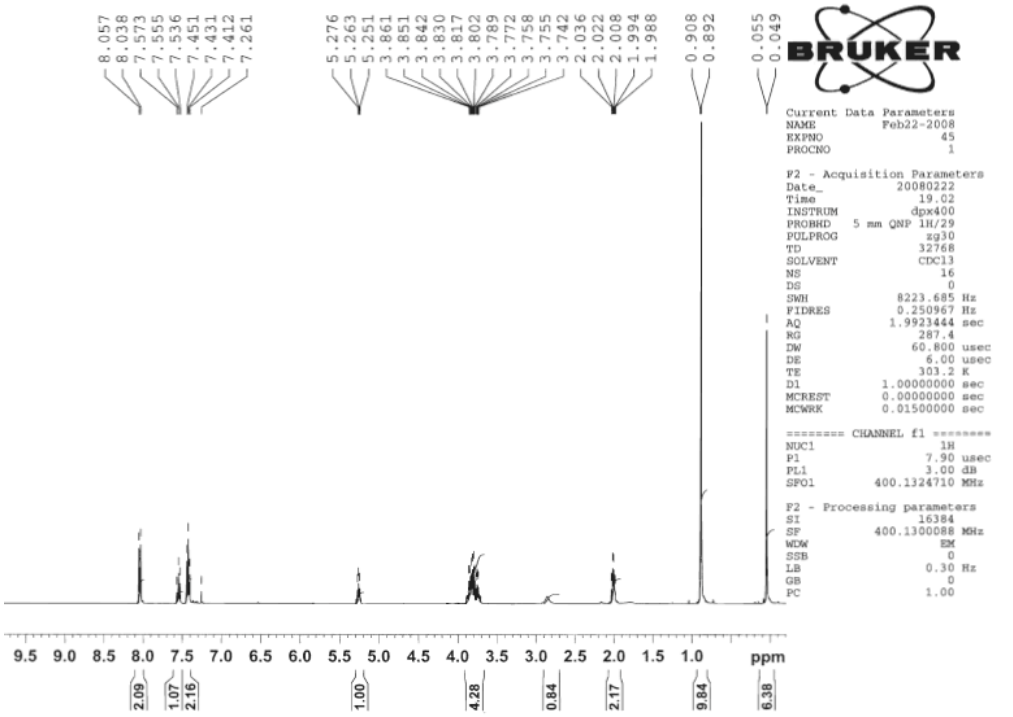

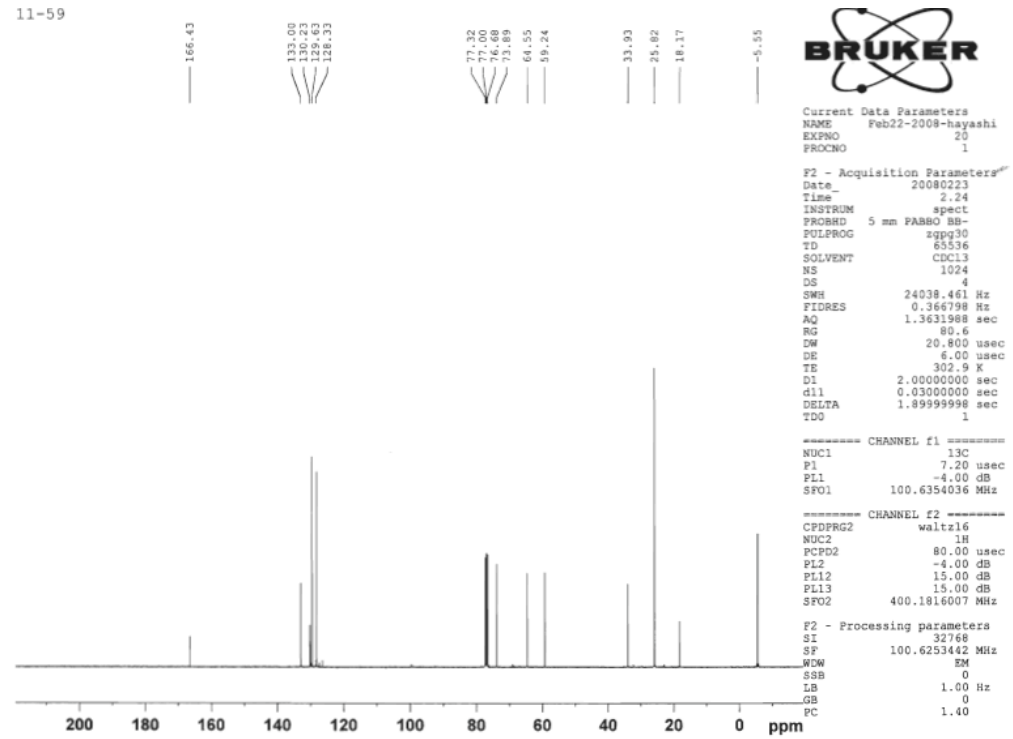

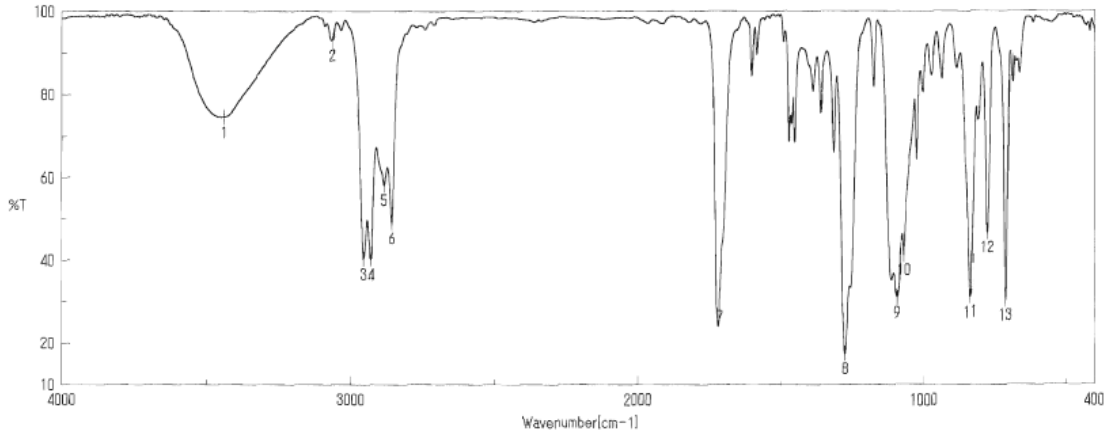

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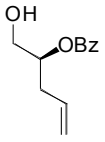

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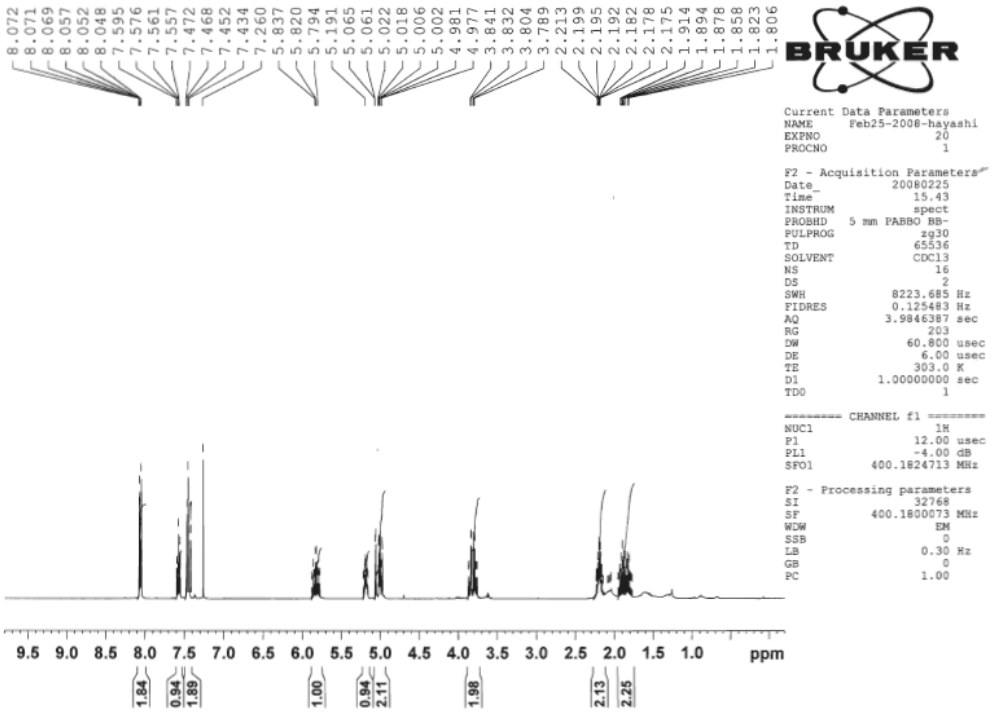

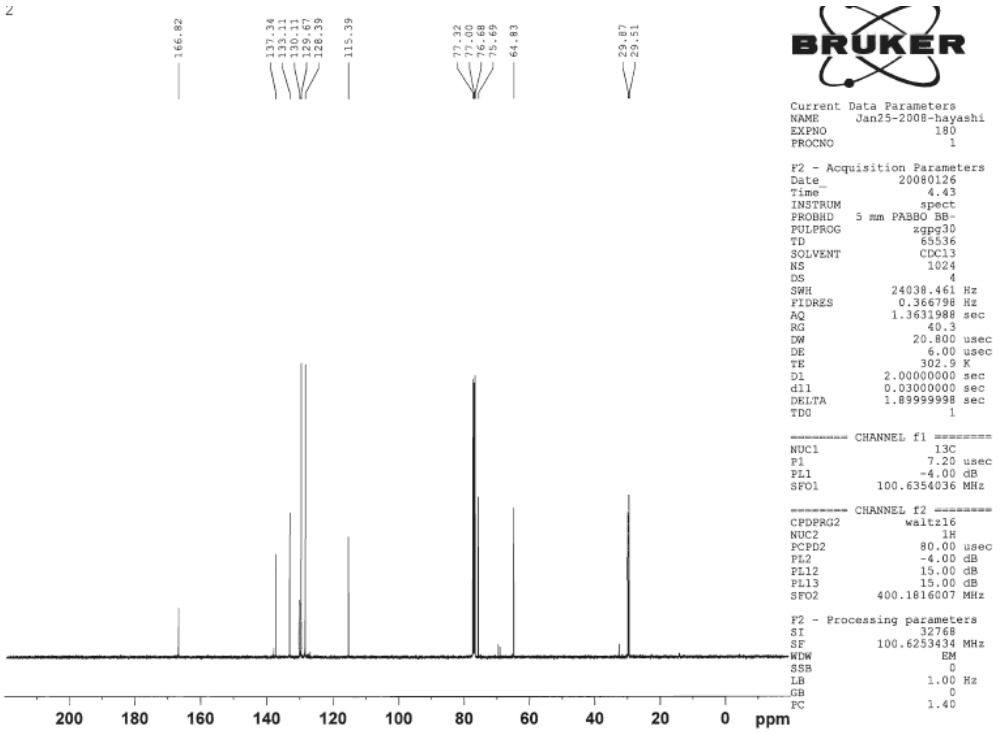

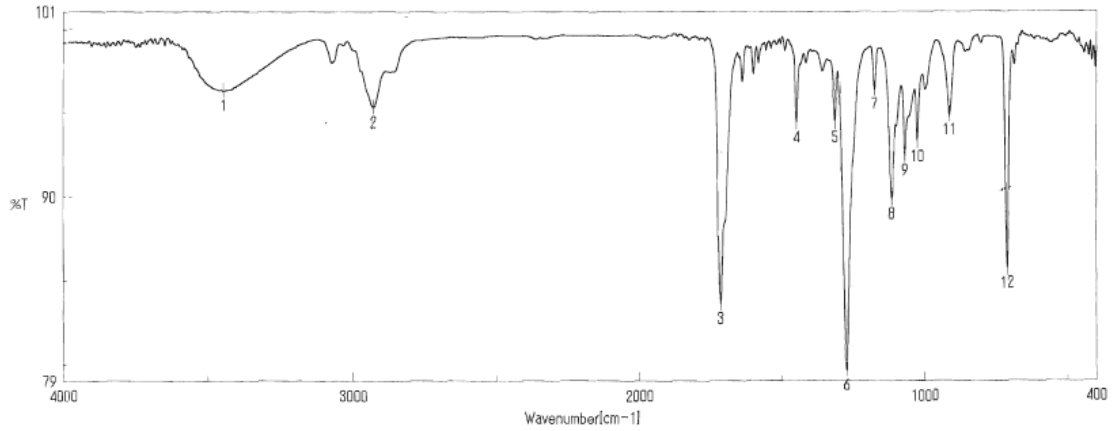

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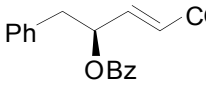
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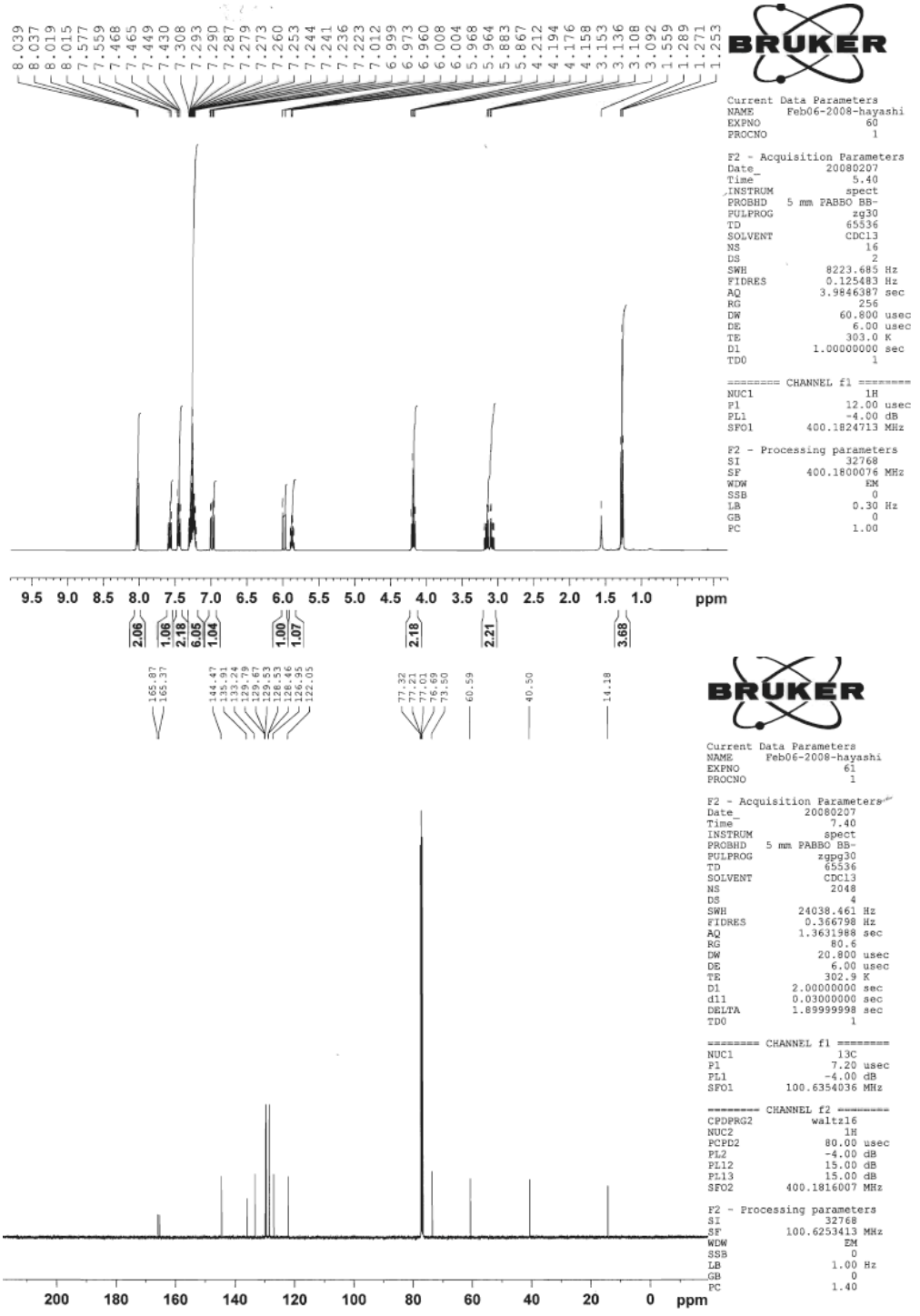
CO2Et
OBz

Compound **5**


8.039
8.037
8.019
8.015
7.577
7.559
7.468
7.465
7.449
7.430
7.308
7.293
7.290
7.287
7.279
7.273
7.260
7.253
7.244
7.241
7.236
7.223
7.012
6.999
6.973
6.960
6.008
6.004
5.968
5.964
5.883
5.867
4.212
4.194
4.176
4.158
3.153
3.136
3.108
3.092
1.559
1.289
1.271
1.253
BRUKER
Current Data Parameters
NAME Feb06-2008-hayashi
EXPNO 60
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080207
Time 5.40
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 256
DW 60.800 usec
DE 6.00 usec
TE 303.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -4.00 dB
SFO1 400.1824713 MHz
F2 - Processing parameters
SI 32768
SF 400.1800076 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.06
1.06
2.18
6.05
1.04
1.00
1.07
2.18
2.21
3.68
165.87
165.37
144.47
135.91
133.24
129.79
129.67
128.53
128.53
128.46
126.95
122.05
77.32
77.21
77.01
76.69
73.50
60.59
40.50
14.18
BRUKER
Current Data Parameters
NAME Feb06-2008-hayashi
EXPNO 61
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080207
Time 7.40
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 80.6
DW 20.800 usec
DE 6.00 usec
TE 302.9 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.20 usec
PL1 -4.00 dB
SFO1 100.6354036 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.1816007 MHz
F2 - Processing parameters
SI 32768
SF 100.6253413 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm