Supporting Information

Direct Asymmetric Benzoyloxylation of Aldehydes Catalyzed by 2-Tritylpyrrolidine

Taichi Kano, Haruka Mii and Keiji Maruoka*

Department of Chemistry, Graduate School of Science, Kyoto University
Sakyo, Kyoto 606-8502, Japan

General Information. Infrared (IR) spectra were recorded on a Shimadzu IR Prestige-21spectrometer. ^{1}H NMR spectra were measured on a JEOL JNM-FX400 (400 MHz) spectrometer. Data were reported as follows: chemical shifts in ppm from tetramethylsilane (in the case of $CDCl_3$) as an internal standard, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double-doublet, m = multiplet, br = broad), coupling constants (Hz), and assignment. ^{13}C NMR spectra were measured on a JEOL JNM-FX400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard. High performance liquid chromatography (HPLC) was performed on Shimadzu 10A instruments using Daicel Chiralpak AD-H, IA and Chiralcel OD-H 4.6 mm × 25 cm columns. High-resolution mass spectra (HRMS) were performed on a BRUKER microTOF. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm) were used. The products were purified by flash column chromatography on silica gel 60 (Merck 1.09386.9025, 230-400 mesh). In experiments requiring dry solvent, tetrahydrofuran (THF) was purchased from Kanto Chemical Co. Inc. as "Dehydrated". Toluene was dried over sodium metal. 1,4-Dioxane was stored under argon atomosphere. *N*,*N*-Dimethylformamide (DMF) and dichloromethane (CH_2Cl_2) were stored over 4Å molecular sieves. The commercially available aldehydes were distilled and stored under argon atmosphere at –17 °C. Pyrrolidine, benzoyl peroxide (BPO) and hydroquinone were purchased and used without further purification. Cyclohexylacetaldehyde,[1] (*S*)-**1**,[2] nitrone **3**[3] and tris(3,5-dimethylphenyl)methane[4] were synthesized according to literature procedures and used after column chromatography on silica gel. (*S*)-2-(Triarylmethyl)pyrrolidine **2a** and **2b** were synthesized according to the following procedure developed in our laboratory. It should be noted that attempted synthesis of (*S*)-**2a** according to ref 5 gave racemic **2a**.

Synthesis of 2-Tritylpyrrolidine *rac*-2a

To the solution of triphenylmethane (3.13 g, 12.8 mmol) in THF (45 mL) at 0 ℃, a 1.6 M hexane solution of *n*-butyl lithium (8.0 mL, 12.8 mmol) was added. After stirring for 1h, to the mixture at –78 ℃ was added a solution of nitrone **3** (545 mg, 6.4 mmol) in THF (2.0 mL). The mixture was warmed to room temperature and stirred for 2 h and then quenched with saturated NH_4Cl at 0 ℃ keeping pH > 7. After extraction with CH_2Cl_2, the organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The resulting residue was purified by column chromatography on silica gel (ethyl acetate/hexane = 1:20~1:4 as eluent) to give 2-tritylpyrrolidin-1-ol *rac*-**4** (1.14 g, 3.36 mmol, 54% yield).

A mixture of *rac*-**4** (1.46 mg, 4.44 mmol) and 10% Pd/C (400mg) in acetid acid (40 mL) was stirred under an atmosphere of hydrogen at room temperature for 12 h. The mixture was filtered through Celite and the solvent evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 and neutralized with 50 % aqueous NaOH. The organic layer was dried over Na_2SO_4 and concentrated. The resulting residue was purified by column chromatography on silica gel (ethyl acetate/hexane = 1:4 and then ethyl acetate as eluent) to give *rac*-**2** (1.36 g, 3.29 mmol, 98% yield).

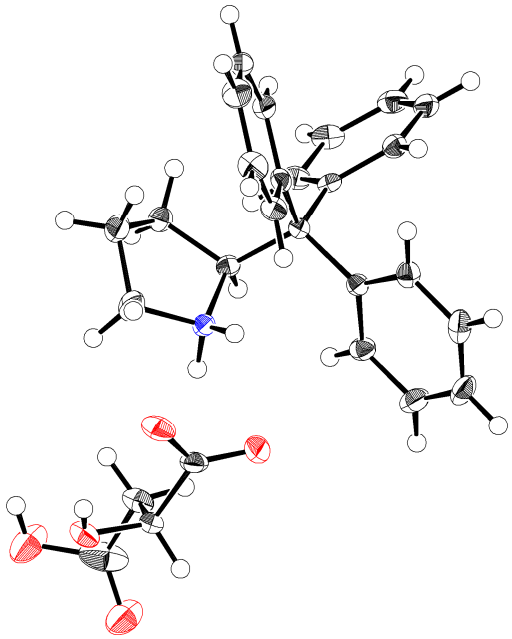
(*S*)-2-Tritylpyrrolidine (*S*)-2a

A mixture of *rac*-**2a** (220 mg, 0.70 mmol) and (*S*)-malic acid (118 mg, 0.88 mmol) in H_2O (0.28 mL) and ethanol (1.1 mL) was heated to 90 ℃ and stirred until the solid was completely dissolved. The solution was then gradually cooled to room temperature. The recrystallized solid was separated by filtrate. The solid (129 mg, 0.29 mmol) and (*S*)-malic acid (7.7 mg, 0.058 mmol, 20 mol%) was again dissolved in H_2O (0.12 mL) and ethanol (0.48 mL) and heated to 90 ℃. After cooled to room temperature, the recrystallized solid was filtered, and dissolved in ethyl acetate. The solution was washed with 1N aqueous NaOH. The organic layer was separated, dried over Na_2SO_4 and concentrated to give enantiopure (*S*)-**2a** (67 mg, 0.21 mmol, 30% yield) : $[\alpha]_D^{23}$ 15.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.33 (6H, m, Ar-H), 7.26-7.23 (6H, m, Ar-H), 7.20-7.16 (3H, m, Ar-H), 4.72 (1H, t, *J* = 8.0 Hz, -NHC**H**-), 2.76-2.67 (2H, m, -NHC**H$_2$**-), 2.09-2.00 (1H, m, -CH**H**CHNH-), 1.63-1.47 (2H, m, -C**H**HCHNH-, -CH_2C**H**HCH_2-), 1.14-1.05 (1H, m, -CH_2CH**H**CH_2-); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 130.2, 127.6, 126.0, 63.9, 61.2, 46.7, 29.1, 25.7; IR (neat) 3055, 1597, 1490, 1035 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{23}H_{24}N$: 314.1903 ([M + H]$^+$), Found: 314.1892 ([M + H]$^+$); HPLC analysis : Daicel Chiralcel OD-H, 230 nm, hexane/2-propanol/diethylamine = 100:1:0.1, flow rate 1.0 mL/min, retention time: 6.0 min (*R*) and 6.4 min (*S*).

Crystal Structure Analysis

Single crystals of (*S*)-**2a**·(*S*)-malic acid salt for X-ray diffraction experiments were obtained from the

optical resolution of *rac*-**2a** described above. The data were collected at –150 °C on a Rigaku R-AXIS RAPID IP diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.5419 Å). The crystal structure was solved by direct methods using SIR97[6] and refined in SHELXL-97[7] by full matrix least-squares using anisotropic thermal displacement parameters for all non-hydrogen atoms. Two carboxylate oxygen atoms were disordered and were refined in two positions with occupancy factors of 0.57 and 0.43, respectively. Crystallographic data for (*S*)-**2a**·(*S*)-malic acid salt: $2(C_{27}H_{19}NO_5)$, colorless prisms, 0.8×0.8×0.5 mm^3, monoclinic, $P2_1$, a = 9.1818(2), b = 9.9425(2), c = 12.9201(2) Å, V = 1149.48(4) Å^3, ρ_{calcd} = 1.293 gcm^{-3}, Z = 2, $2\theta_{max}$ = 68.23°, μ = 0.720 mm^{-1}. A total of 12034 reflections were measured. R = 0.0455, and Rw = 0.1205 for 3939 observed reflections with $I > 2.0\sigma(I)$. CCDC-712617 [(*S*)-**2a**·(*S*)-malic acid salt] contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



ORTEP diagram of (*S*)-**2a**·(*S*)-malic acid

(Minor disordered carboxylate oxygen atoms have been omitted for clarity.)

Synthesis of (*S*)-2-(Tris(3,5-dimethylphenyl)methyl)pyrrolidine (*S*)-2b

rac-**2b** was synthesized following the same procedure with *rac*-**2a** except for using tris(3,5-dimethylphenyl)methane instead of triphenylmethane. After the amine group of *rac*-**2b** was protected with Cbz functionality, optical resolution of the Cbz-protected *rac*-**2b** was performed using a chiral column (Daicel Chiralpak IA, 254 nm, ethyl acetate/hexane = 1:50, flow rate 0.5 mL/min, retention time: 22.1 min (*S*) and 31.4 min (*R*)). Deprotection by hydrogenation reaction gave

enantiopure (*S*)-**2b**: $[\alpha]_D^{24}$ –13.6 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.95 (6H, s, Ar-H), 6.81 (3H, m, Ar-H), 4.66 (1H, t, *J* = 8.0 Hz, -NHC**H**-), 2.74-2.68 (1H, m, -NHC**H**H-), 2.62-2.55 (1H, m, -NHC**H**H-), 2.23 (18H, s, Ar-CH_3), 2.007-1.69 (1H, m, -CH**H**CHNH-), 1.61-1.46 (2H, m, -C**H**HCHNH-, -CH_2C**H**HCH_2-), 1.11-1.04 (1H, m, -CH_2CH**H**CH_2-); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 136.6, 128.0, 127.5, 63.5, 60.9, 46.7, 29.1, 25.7, 21.6; IR (neat) 2916, 2359, 1597, 1462, 1262, 1037, 850.6 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{29}H_{36}N$: 398.2842 ($[M + H]^+$), Found: 398.2833 ($[M + H]^+$).

General Procedure for the Organocatalytic Benzoyloxylation Reaction of Aldehydes with Benzoyl Peroxide (BPO). A mixture of (*S*)-**2** (3.1 mg, 0.01 mmol, 5 mol%), hydroquinone (1.1 mg, 0.01 mmol) and an aldehyde (0.2 mmol) in THF (1.0 mL) was stirred at room temperature. To the mixture was then added BPO (25% hydrate) (71.1 mg, 0.22 mmol). After stirring for 2 h at room temperature, the reaction mixture was poured to 1N HCl and extracted with ethyl acetate. The organic phase was then washed with brine and saturated $NaHCO_3$, and dried over Na_2SO_4. The solvent was removed under reduced pressure following purification by column chromatography on silica gel (ethyl acetate/hexane = 1:20 as eluent) to furnish the corresponding α-benzoyloxyl aldehyde as an oil.

Typical Procedure for Reduction of α-Benzoyloxyl Aldehydes. To a solution of (*S*)-1-oxo-3-phenylpropan-2-yl benzoate (13 mg, 0.05 mmol) in methanol (0.5 mL) and CH_2Cl_2 (0.5 mL) was added $NaBH_4$ (1.9 mg, 0.05 mmol) at 0 ℃. After stirring for 10 min, the mixture was poured into 1N HCl slowly at 0 ℃ and extracted with CH_2Cl_2 three times. The combined organic phases were dried over Na_2SO_4. The solvent was removed under reduced pressure following purification by column chromatography on silica gel (ethyl acetate/hexane = 1:10 as eluent) to furnish (*S*)-1-hydroxy-3-phenylpropan-2-yl benzoate (13 mg, 0.05 mmol, 99% yield).

(*S*)-1-Oxo-3-phenylpropan-2-yl Benzoate 5 (Table 2, entry 4)

The enantiomeric excess was determined by HPLC analysis of the corresponding alcohol.

$[\alpha]_D^{28}$ –93 (*c* 1.3, $CHCl_3$; 94% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 9.66 (1H, s, -CHO), 8.04 (2H, d, *J* = 7.2 Hz, Ar-H), 7.60 (1H, t, *J* = 7.6 Hz, Ar-H), 7.46 (2H, dd, *J* = 8.0, 8.0 Hz, Ar-H), 7.34-7.23 (5H, m, Ar-H), 5.43 (1H, dd, *J* = 8.2, 5.0 Hz, -CH(OBz)-), 3.30 (1H, dd, *J* = 14.8, 4.8 Hz, -C**H**HPh), 3.20 (1H, dd, *J* = 14.8, 8.4 Hz, -CH**H**Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 166.0, 135.4, 133.6, 129.8, 129.4, 129.0, 128.7, 128.5, 127.1, 79.1, 35.4; IR (neat) 3030, 1452, 1717, 1269, 1111 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{16}H_{15}O_3$: 255.1016 ($[M + H]^+$), Found: 255.1011 ($[M + H]^+$).

(*S*)-1-Hydroxy-3-phenylpropan-2-yl Benzoate 7

$[\alpha]_D^{28}$ –37 (*c* 0.1, $CHCl_3$; 94% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 8.04-8.01 (2H, m, Ar-H), 7.59-7.55 (1H, m, Ar-H), 7.46-7.42 (2H, m, Ar-H), 7.30-7.20 (5H, m, Ar-H), 5.39-5.33 (1H, m, -CH(OBz)-), 3.89-3.83 (1H, m, -C**H**HOH), 3.79-3.73 (1H, m, -CH**H**OH), 1.93 (1H, t, *J* = 6.4 Hz), 3.11 (1H, dd, *J* = 13.8, 6.8 Hz, -C**H**HPh), 3.05 (1H, dd, *J* = 14.0, 6.8 Hz, -CH**H**Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 136.8, 133.1, 130.0, 129.6, 129.4, 128.5, 128.3, 126.7, 76.6, 63.7, 36.9; IR (neat) 3500, 1717, 1275, 1219, 1026 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{16}H_{16}NaO_3$: 279.0992 ($[M + Na]^+$), Found: 279.0985 ($[M + Na]^+$); HPLC analysis: Daicel Chiralpak AD-H, 220 nm, hexane/2-propanol = 15:1, flow rate 1.0 mL/min, retention time: 16.5 min (*R*) and 18.5 min (*S*).

(*S*)-1-Oxopropan-2-yl Benzoate (Table 2, entry 1)

The enantiomeric excess was determined by HPLC analysis of the corresponding alcohol.

$[\alpha]_D^{24}$ –4.8 (*c* 0.75, $CHCl_3$; 94% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 9.67 (1H, s, -CHO), 8.11 (2H, d, *J* = 8.4 Hz, Ar-H), 7.63-7.59 (1H, m, Ar-H), 7.48 (2H, dd, *J* = 7.2, 7.2 Hz, Ar-H), 5.31 (1H, q, *J* = 7.2 Hz, -CH(OBz)-), 1.54 (3H, d, *J* = 7.2 Hz, $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 166.0, 133.5, 129.8, 129.2, 128.5, 75.1, 14.3; IR (neat) 2993, 1719, 1365, 1267, 1217, 1111 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{10}H_{11}O_3$: 179.0703 ($[M + H]^+$), Found: 179.0705 ($[M + H]^+$).

(*S*)-1-Hydroxypropan-2-yl Benzoate

$[\alpha]_D^{23}$ 21 (*c* 0.8, $CHCl_3$; 92% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (2H, d, *J* = 8.4 Hz, Ar-H), 7.57 (1H, t, *J* = 7.6 Hz, Ar-H), 7.44 (2H, dd, *J* = 7.6, 7.6 Hz, Ar-H), 5.28-5.21 (1H, m, -CH(OBz)-), 3.80-3.73 (2H, m, -C**H$_2$**OH), 2.06 (1H, t, *J* = 6.0 Hz, -OH), 1.38 (3H, d, *J* = 6.8 Hz, $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 133.1, 130.3, 129.7, 128.4, 72.8, 66.2, 16.3; IR (neat) 3433, 2938, 1715, 1275, 1115, 1049 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{10}H_{12}NaO_3$: 203.0679 ($[M + Na]^+$), Found: 203.0686 ($[M + Na]^+$); HPLC analysis: Daicel Chiralpak AD-H, 220 nm, hexane/2-propanol = 15:1, flow rate 1.0 mL/min, retention time: 10.6 min (*S*) and 11.5 min (*R*).

(*S*)-1-Oxobutan-2-yl Benzoate (Table 2, entry 2)

The enantiomeric excess was determined by HPLC analysis of the corresponding alcohol.

$[\alpha]_D^{28}$ –42 (*c* 1.0, $CHCl_3$; 94% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 9.65 (1H, s, -CHO), 8.11 (2H, d, *J* = 7.2 Hz, Ar-H), 7.61 (1H, t, *J* = 7.2 Hz, Ar-H), 7.48 (2H, dd, *J* = 8.0, 8.0 Hz, Ar-H), 5.17 (1H, dd, *J* = 7.6, 5.2 Hz, -CH(OBz)-), 2.08-1.89 (2H, m, $-CH_2Me$), 1.10 (3H, t, *J* = 7.6 Hz, $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 166.2, 133.5, 129.8, 129.2, 128.5, 79.7, 22.4, 9.4; IR (neat) 2974, 2359, 1719, 1452, 1271, 1111 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{11}H_{12}NaO_3$: 215.0679 ($[M + Na]^+$), Found: 215.0680 ($[M + Na]^+$). The absolute configuration was determined to be *S* by comparing the sign of optical rotation of the title compound to (*R*)-1-oxobutan-2-yl benzoate ($[\alpha]_D^{20}$ +41.0 (*c* 1.00,

$CHCl_3$)).[8]

(*S*)-1-Hydroxybutan-2-yl Benzoate

$[\alpha]_D^{28}$ –5.5 (*c* 0.4, $CHCl_3$; 93% ee); ^{1}H NMR (400MHz, $CDCl_3$) δ 8.06 (2H, d, *J* = 8.0 Hz, Ar-H), 7.57 (1H, t, *J* = 7.6 Hz, Ar-H), 7.45 (2H, dd, *J* = 8.0, 8.0 Hz, Ar-H), 5.13-5.08 (1H, m, -CH(OBz)-), 3.85 (1H, dd, *J* = 12.2, 3.2 Hz, -C**H**HOH), 3.78 (1H, dd, *J* = 12.0, 6.4 Hz, -CH**H**OH), 2.33 (1H, br, -OH), 1.78 (2H, dq, *J* = 7.6, 7.6 Hz, -CH_2Me), 1.01 (3H, t, *J* = 7.2 Hz, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 133.1, 130.2, 129.7, 128.4, 77.6, 64.6, 23.8, 9.7; IR (neat) 3470, 2968, 1717, 1273, 1115 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{11}H_{14}NaO_3$: 217.0835 ([M + Na]$^+$), Found: 217.0845 ([M + Na]$^+$); HPLC analysis: Daicel Chiralpak IA, 254 nm, hexane/ethyl acetate = 5:1, flow rate 1.0 mL/min, retention time: 9.7 min (*S*) and 12.0 min (*R*).

(*S*)-1-Oxohexan-2-yl Benzoate (Table 2, entry 3)

The enantiomeric excess was determined by HPLC analysis of the corresponding alcohol.

$[\alpha]_D^{28}$ –42 (*c* 0.8, $CHCl_3$; 94% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (1H, s, -CHO), 8.11 (2H, d, *J* = 8.0 Hz, Ar-H), 7.61 (1H, t, *J* = 7.6 Hz, Ar-H), 7.48 (2H, dd, *J* = 8.0, 8.0 Hz, Ar-H), 5.22 (1H, dd, *J* = 8.4, 4.8 Hz, -CH(OBz)-), 2.01-1.85 (2H, m, -CH_2Pr), 1.54-1.34 (4H, m, -CH_2Et and -CH_2Me), 0.94 (3H, t, *J* = 7.2 Hz, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 166.1, 133.5, 129.8, 129.2, 128.5, 78.8, 28.6, 27.1, 22.4, 13.8; IR (neat) 2968, 2351, 1738, 1366, 1269, 1111 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{13}H_{16}NaO_3$: 243.0992 ([M + Na]$^+$), Found: 243.0991 ([M + Na]$^+$).

(*S*)-1-Hydroxyhexan-2-yl Benzoate

$[\alpha]_D^{23}$ –24 (*c* 0.4, $CHCl_3$; 94% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (2H, d, *J* = 8.0 Hz, Ar-H), 7.58 (1H, t, *J* = 7.2 Hz, Ar-H), 7.45 (2H, dd, *J* = 8.0, 8.0 Hz, Ar-H), 5.20-5.14 (1H, m, -CH(OBz)-), 3.84 (1H, ddd, *J* = 12.2, 6.6, 3.6 Hz, -C**H**HOH), 3.78 (1H, m, -CH**H**OH), 2.00 (1H, t, *J* = 6.4 Hz, -OH), 1.79-1.67 (2H, m, -CH_2Pr), 1.45-1.31 (4H, m, -CH_2Et and -CH_2Me), 0.91 (3H, t, *J* = 6.4 Hz, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 133.1, 130.2, 129.7, 128.4, 76.5, 65.1, 30.4, 27.5, 22.6, 13.9; IR (neat) 3466, 2957, 1719, 1365, 1275, 1114 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{13}H_{18}NaO_3$: 245.1149 ([M + Na]$^+$), Found: 245.1142 ([M + Na]$^+$); HPLC analysis: Daicel Chiralpak AD-H, 220 nm, hexane/2-propanol = 30:1, flow rate 1.0 mL/min, retention time: 16.4 min (*S*) and 18.0 min (*R*).

(*S*)-1-Oxopent-4-en-2-yl Benzoate (Table 2, entry 6)

The enantiomeric excess was determined by HPLC analysis of the corresponding alcohol.

$[\alpha]_D^{31}$ –36 (*c* 0.9, $CHCl_3$; 92% ee); ^{1}H NMR (400MHz, $CDCl_3$) δ 9.66 (1H, s, -CHO), 8.10 (2H, d, *J* = 7.6 Hz, Ar-H), 7.61 (1H, t, *J* = 7.2 Hz, Ar-H), 7.48 (2H, dd, *J* = 7.6, 7.6 Hz, Ar-H), 5.92-5.82 (1H, m, -C**H**=CH_2), 5.30 (1H, dd, *J* = 7.6, 5.2 Hz, -CH(OBz)-), 5.26-5.17 (2H, m, -CH=C**H$_2$**), 2.79-2.63

(2H, m, -C**H**$_2$CH=CH$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 166.0, 133.6, 131.5, 129.9, 129.1, 128.5, 119.3, 77.8, 33.5; IR (neat) 3493, 2916, 2359, 1721, 1273, 1113 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{12}H_{12}NaO_3$: 227.0679 ([M + Na]$^+$), Found: 227.0688 ([M + Na]$^+$).

(*S*)-1-Hydroxypent-4-en-2-yl Benzoate

$[\alpha]_D^{31}$ –9.0 (*c* 1.0, $CHCl_3$; 92% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.04 (2H, m, Ar-H), 7.59-7.55 (1H, m, Ar-H), 7.47-7.43 (2H, m, Ar-H), 5.90-5.79 (1H, m, -C**H**=CH$_2$), 5.24-5.09 (3H, m, -CH(OBz)- and -CH=C**H**$_2$), 3.86 (1H, dd, *J* = 12.4, 3.6 Hz, -C**H**HOH), 3.80 (1H, dd, *J* = 12.0, 6.0 Hz, -CH**H**OH), 2.53 (2H, dd, *J* = 6.8, 6.8 Hz, C**H**$_2$CH=CH$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 133.1, 132.9, 130.1, 129.7, 128.4, 118.4, 75.2, 64.3, 35.3; IR (neat) 3468, 2941, 1717, 1364, 1273, 1114 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{12}H_{14}NaO_3$: 229.0835 ([M + Na]$^+$), Found: 229.0831 ([M + Na]$^+$); HPLC analysis: Daicel Chiralpak AD-H, 220 nm, hexane/2-propanol = 30:1, flow rate 1.0 mL/min, retention time: 24.6 min (*S*) and 26.3 min (*R*).

(*S*)-3-Methyl-1-oxobutan-2-yl Benzoate (Table 2, entry 7)

The enantiomeric excess was determined by HPLC analysis of the corresponding alcohol.

$[\alpha]_D^{30}$ –23 (*c* 1.3, $CHCl_3$; 92% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (1H, d, *J* = 0.8 Hz, -CHO), 8.13-8.10 (2H, m, Ar-H), 7.64-7.59 (1H, m, Ar-H), 7.51-7.46 (2H, m, Ar-H), 5.08 (1H, dd, *J* = 4.6, 0.8 Hz, -CH(OBz)-), 2.47-2.38 (1H, m, -CH(Me)$_2$), 1.42 (3H, d, *J* = 7.2 Hz, -CH$_3$), 1.20 (3H, d, *J* = 6.8 Hz, -CH$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 166.1, 133.5, 129.8, 129.3, 128.5, 82.6, 29.2, 18.8, 17.2; IR (neat) 2968, 1721, 1275, 1111 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{12}H_{15}O_3$: 207.1016 ([M + H]$^+$), Found: 207.1013 ([M + H]$^+$).

(*S*)-3-Methyl-1-hydroxybutan-2-yl Benzoate

$[\alpha]_D^{23}$ –27 (*c* 0.8, $CHCl_3$; 92% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.06 (2H, m, Ar-H), 7.60-7.56 (1H, m, Ar-H), 7.48-7.44 (2H, m, Ar-H), 4.98 (1H, dt, *J* = 6.4, 3.6 Hz, -CH(OBz)-), 3.91-3.79 (2H, m, -C**H**$_2$OH), 2.19-2.07 (2H, m, -CH(Me)$_2$ and -OH), 1.03 (6H, d, *J* = 7.2 Hz, -CH(C**H**$_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 133.1, 130.2, 129.7, 128.4, 81.0, 63.6, 29.4, 18.9, 18.0; IR (neat) 3460, 2967, 1717, 1273, 1115 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{12}H_{17}O_3$: 209.1172 ([M + H]$^+$), Found: 209.1176 ([M + H]$^+$); HPLC analysis: Daicel Chiralpak AD-H, 220 nm, hexane/2-propanol = 30:1, flow rate 1.0 mL/min, retention time: 18.0 min (*S*) and 19.6 min (*R*).

(*S*)-1-Cyclohexyl-2-oxoethyl Benzoate (Table 2, entry 8)

The enantiomeric excess was determined by HPLC analysis of the corresponding alcohol.

$[\alpha]_D^{31}$ –23 (*c* 1.5, $CHCl_3$; 94% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (1H, d, *J* = 1.2 Hz, -CHO), 8.12-8.09 (2H, m, Ar-H), 7.63-7.58 (1H, m, Ar-H), 7.50-7.46 (2H, m, Ar-H), 5.07 (1H, dd, *J* = 4.4,

1.2 Hz, -CH(OBz)-), 2.14-2.06 (1H, m, -CH(OBz)C**H**-), 1.82-1.70 (5H, m, -CH_2-), 1.45-1.15 (5H, m, -CH_2-); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 166.1, 133.4, 129.8, 129.4, 128.5, 82.3, 38.8, 29.2, 27.7, 26.0, 25.9, 25.9; IR (neat) 2927, 1719, 1450, 1273, 1111 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{15}H_{18}NaO_3$: 269.1148 ([M + Na]$^+$), Found: 269.1145 ([M + Na]$^+$).

(*S*)-1-Cyclohexyl-2-hydroxyethyl Benzoate

$[\alpha]_D^{31}$ –23 (*c* 1.2, $CHCl_3$; 94% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (2H, d, *J* = 7.6 Hz, Ar-H), 7.58 (1H, t, *J* = 7.6 Hz, Ar-H), 7.46 (2H, dd, *J* = 8.0, 8.0 Hz, Ar-H), 5.00 (1H, dt, *J* = 6.4, 3.2 Hz, -CH(OBz)-), 3.89-3.81 (2H, m, -C**H**$_2$OH), 1.99 (t, *J* = 6.0 Hz, -OH), 1.84-1.77 (5H, m, -CH**H**-), 1.70-1.67 (1H, m, -CH(OBz)C**H**-), 1.30-1.13 (5H, m, -CH**H**-); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 133.1, 130.2, 129.7, 128.4, 80.3, 63.3, 38.8, 29.2, 28.4, 26.2, 26.0, 25.9; IR (neat) 3460, 2928, 1719, 1450, 1366, 1275, 1115 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{15}H_{20}NaO_3$: 271.1305 ([M + Na]$^+$), Found: 271.1304 ([M + Na]$^+$); HPLC analysis: Daicel Chiralpak AD-H, 220 nm, hexane/2-propanol = 30:1, flow rate 1.0 mL/min, retention time: 20.1 min (*S*) and 22.2 min (*R*).

Synthesis of (*S*)-3-Phenylpropane-1,2-diol 6

To a solution of (*S*)-1-oxo-3-phenylpropan-2-yl benzoate (15 mg, 0.06 mmol) in methanol (0.5 mL) was added $NaBH_4$ (6.8 mg, 0.18 mmol) at 0 ℃. After stirring for 10 min at 0 ℃, the mixture was heated to 50 ℃ and stirred for 18 h. The reaction mixture was then poured into saturated $NaHCO_3$ and extracted with CH_2Cl_2 three times. The combined organic phase was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane = 1:2~2:1 as eluent) to furnish the title compound (8.3 mg, 0.055 mmol, 94% yield). A literature data[9] was referenced for the spectral data of the title compound.

Synthesis of (*S*)-2-Hydroxy-3-phenylpropyl Benzoate 8

To a solution of (*S*)-1-hydroxy-3-phenylpropan-2-yl benzoate (11 mg, 0.043 mmol) in CH_2Cl_2 (0.5 mL) was added DBU (26 μl, 0.16 mmol). After stirring for 12 h at room temperature, the reaction mixture was poured into 1N HCl and extracted with ethyl acetate three times. The combined organic phase was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane = 1:10 as eluent) to furnish the title compound (7.9 mg, 0.031 mmol, 72% yield): $[\alpha]_D^{29}$ 12 (*c* 1.1, $CHCl_3$; 94% ee); ^{1}H NMR (400MHz, $CDCl_3$) δ 8.06 (2H, d, *J* = 8.4 Hz, Ar-H), 7.58 (1H, t, *J* = 7.2 Hz, Ar-H), 7.46 (2H, dd, *J* = 8.0, 8.0 Hz, Ar-H), 7.35-7.23 (5H, m, Ar-H), 4.42 (1H, dd, *J* = 11.2, 3.6 Hz, -C**H**HOBz), 4.29 (1H, dd, *J* = 11.2, 6.4 Hz, -CH**H**OBz), 4.25 (1H, br, -C**H**OH), 2.95 (1H, dd, *J* = 13.6, 6.0 Hz, -C**H**HPh), 2.89 (1H, dd, *J* = 13.6, 7.2 Hz, -CH**H**Ph), 2.20 (1H, br, -OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 137.2, 133.2, 129.8, 129.7, 129.4, 128.7, 128.4, 126.8, 70.9, 68.1, 40.1; IR (neat) 3460, 3028, 1717, 1452, 1273, 1123

cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{16}H_{16}NaO_3$: 279.0992 ($[M + Na]^+$), Found: 279.0996 ($[M + Na]^+$); HPLC analysis: Daicel Chiralpak AD-H, 220 nm, hexane/2-propanol = 15:1, flow rate 1.0 mL/min, retention time: 17.3 min (*R*) and 20.8 min (*S*).

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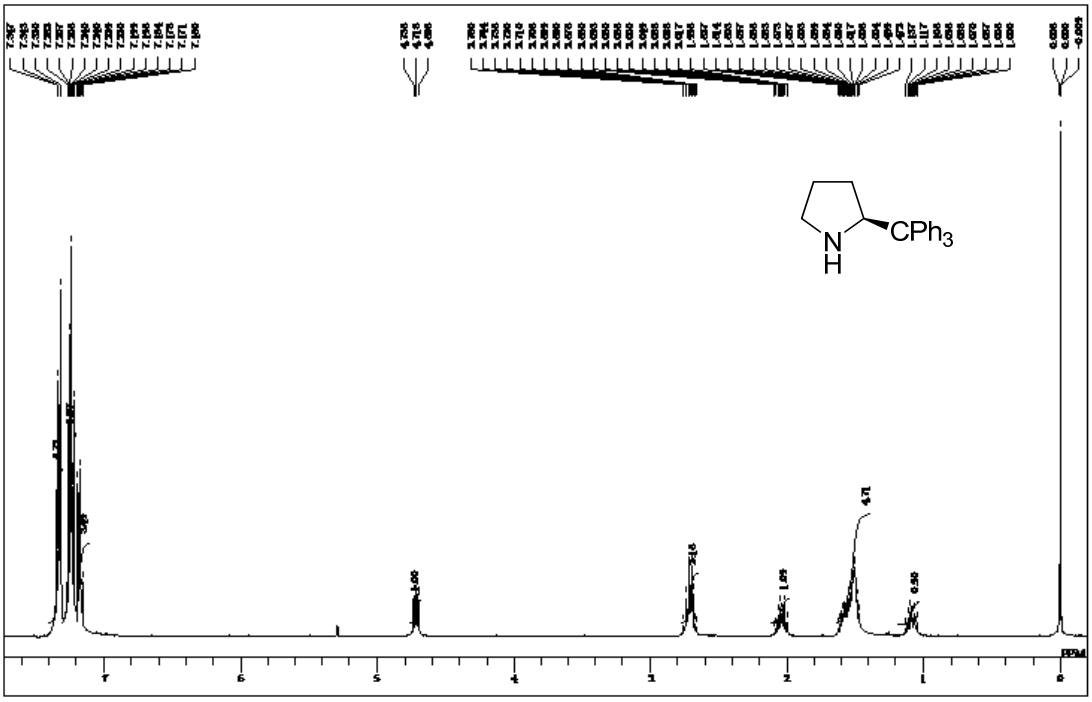
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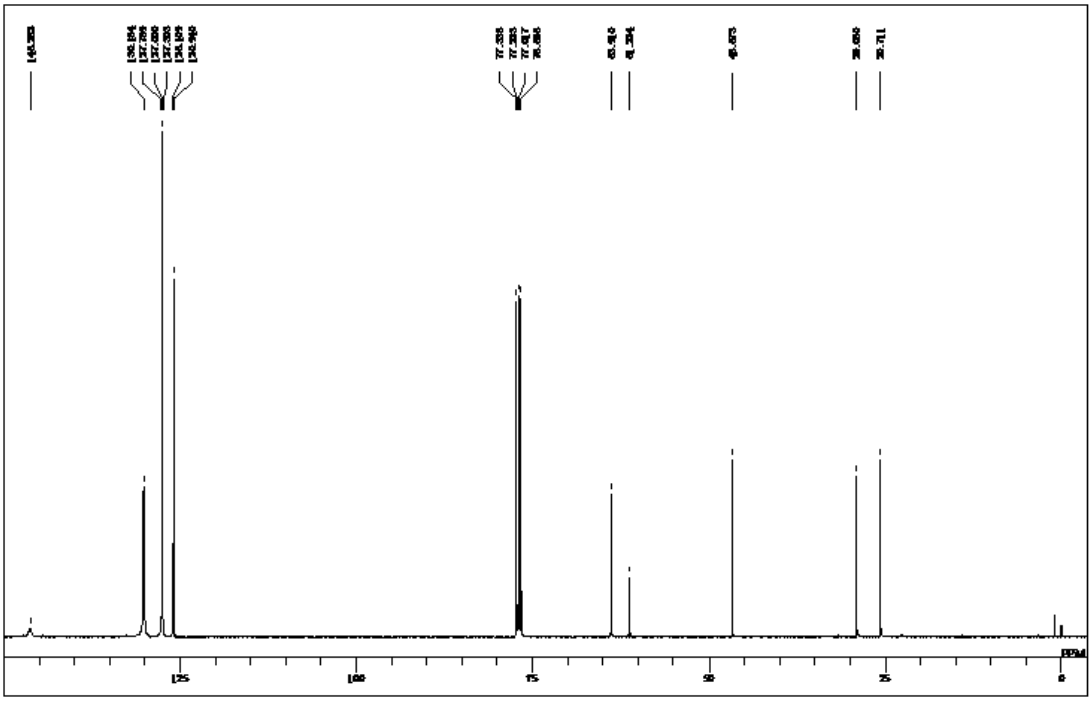

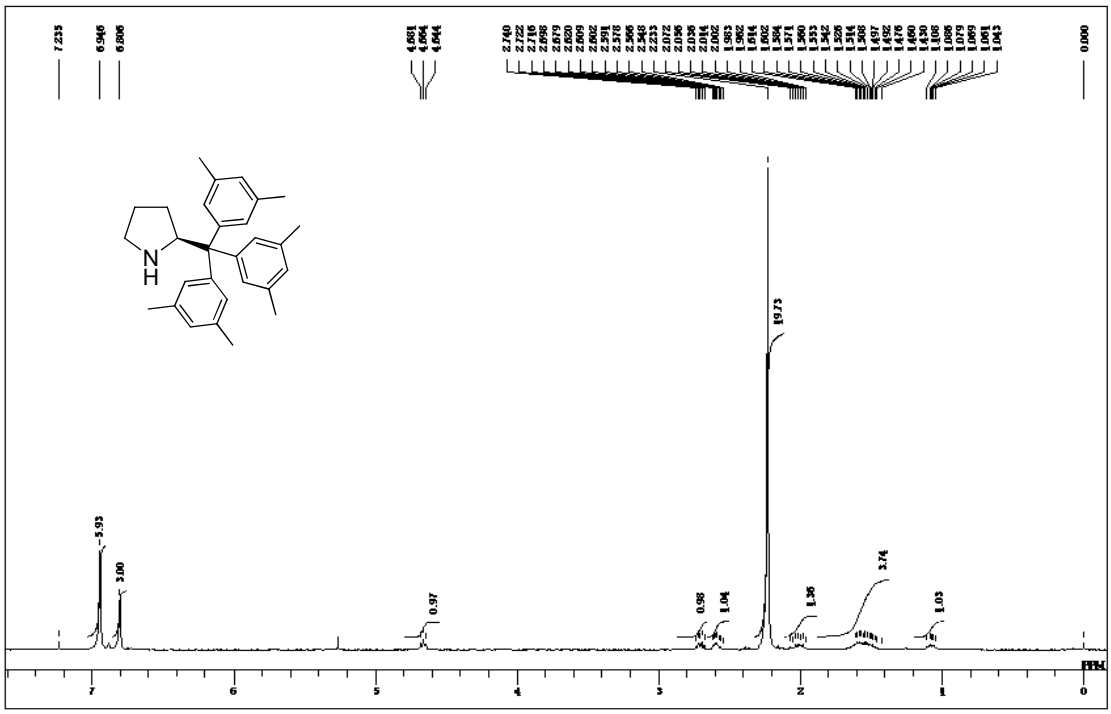
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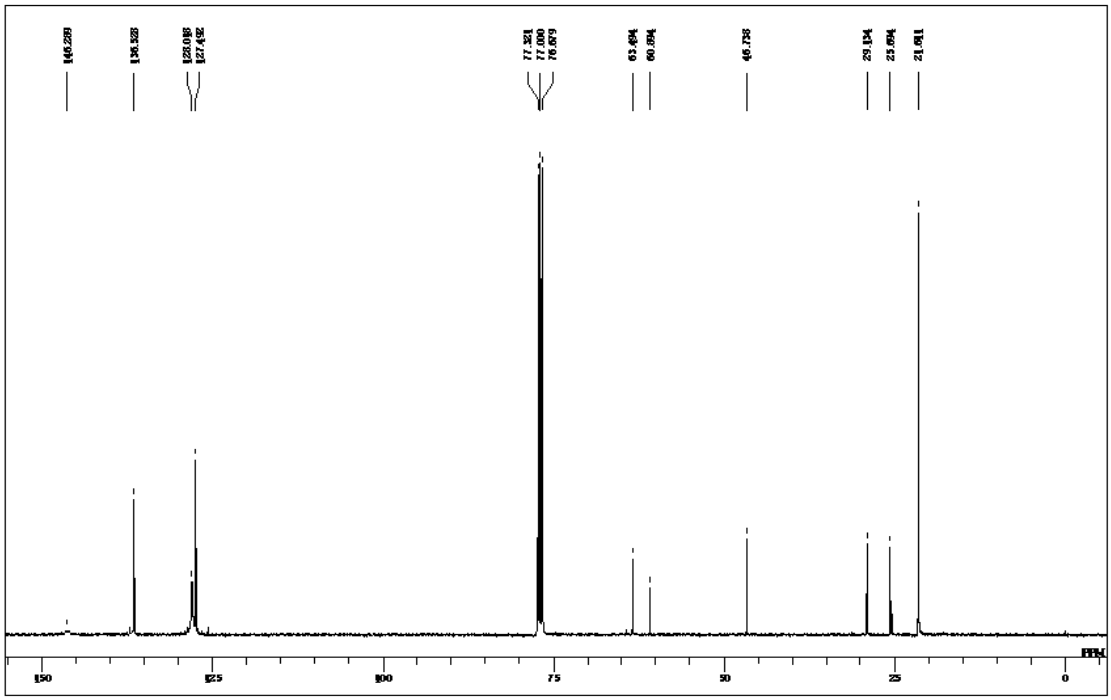
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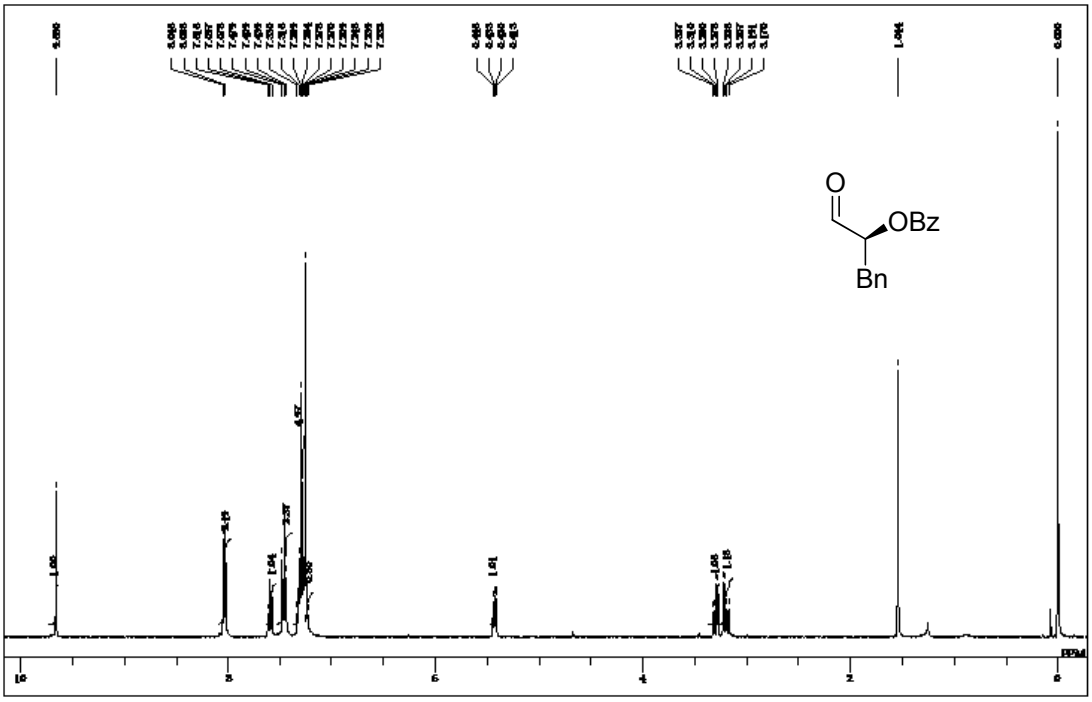
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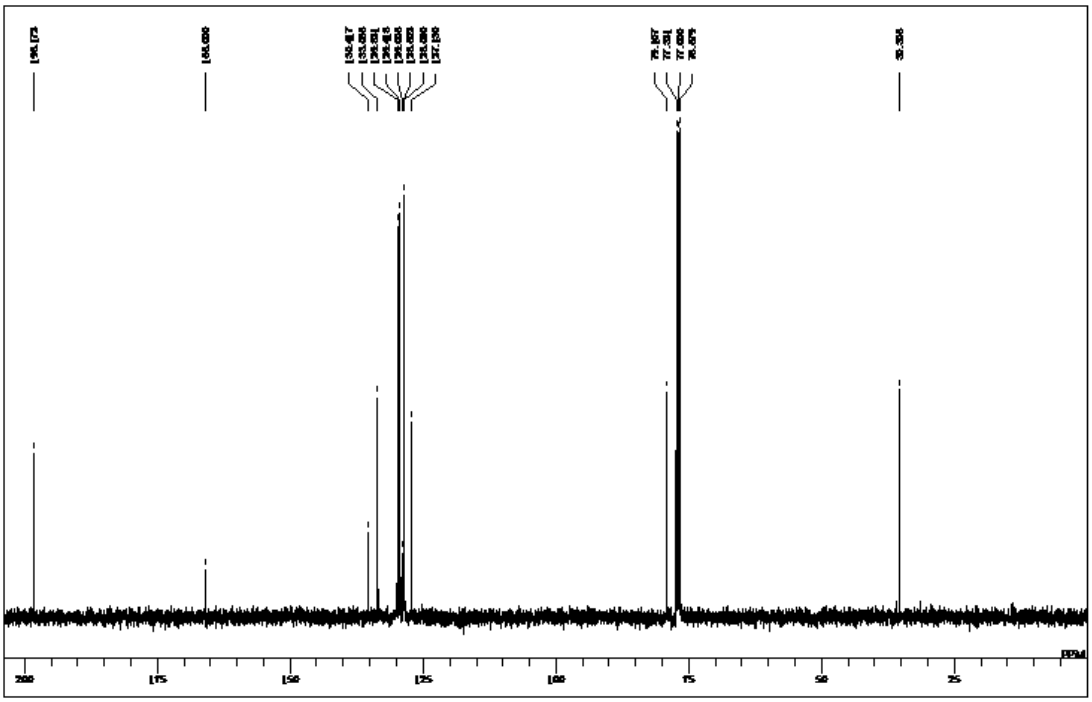

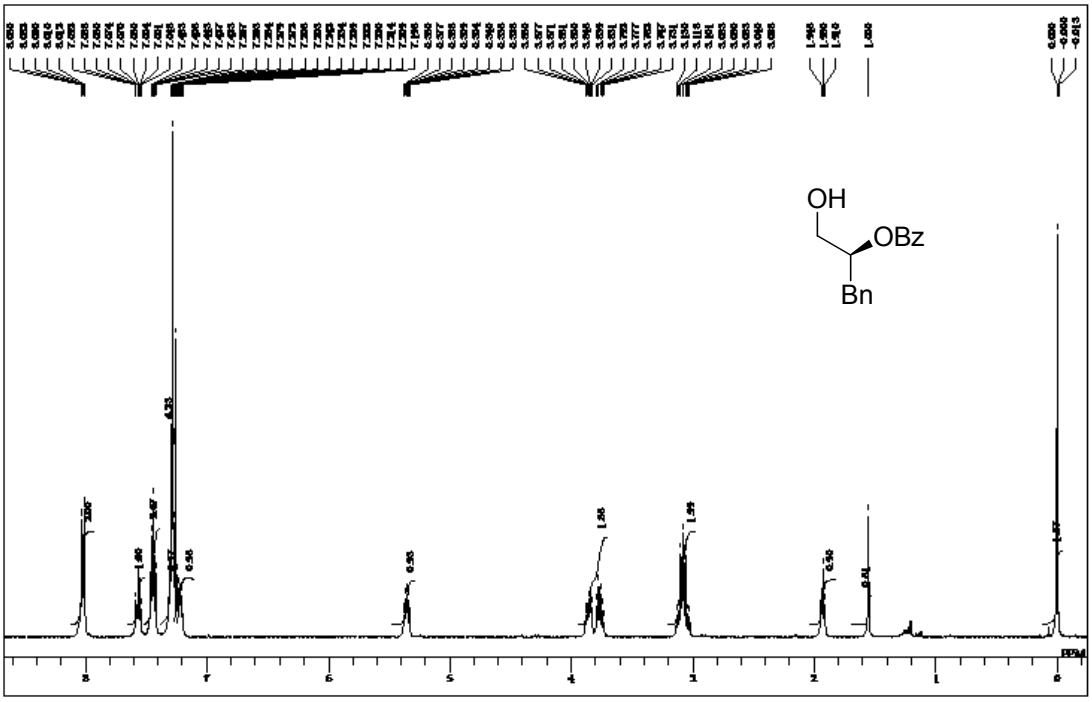
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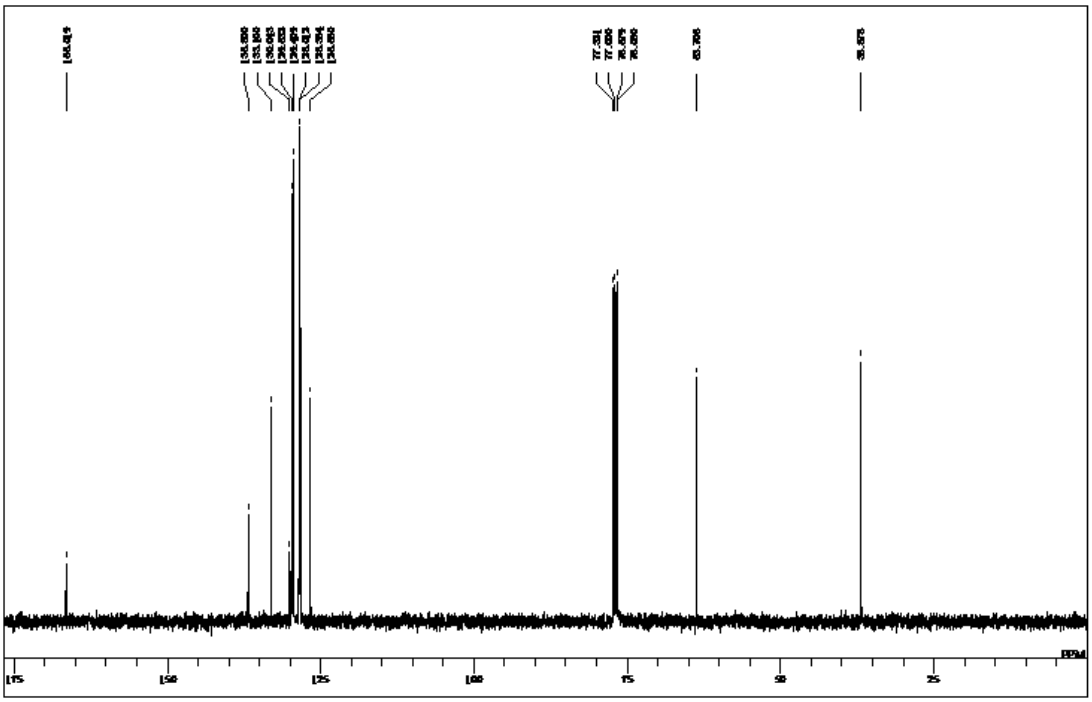

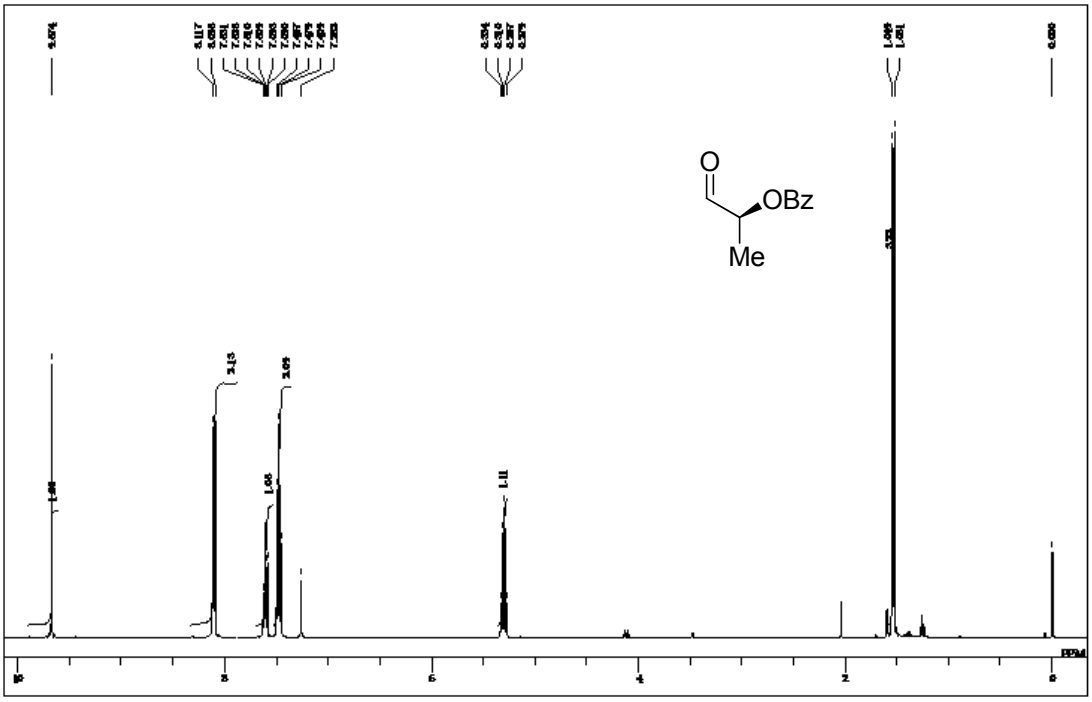
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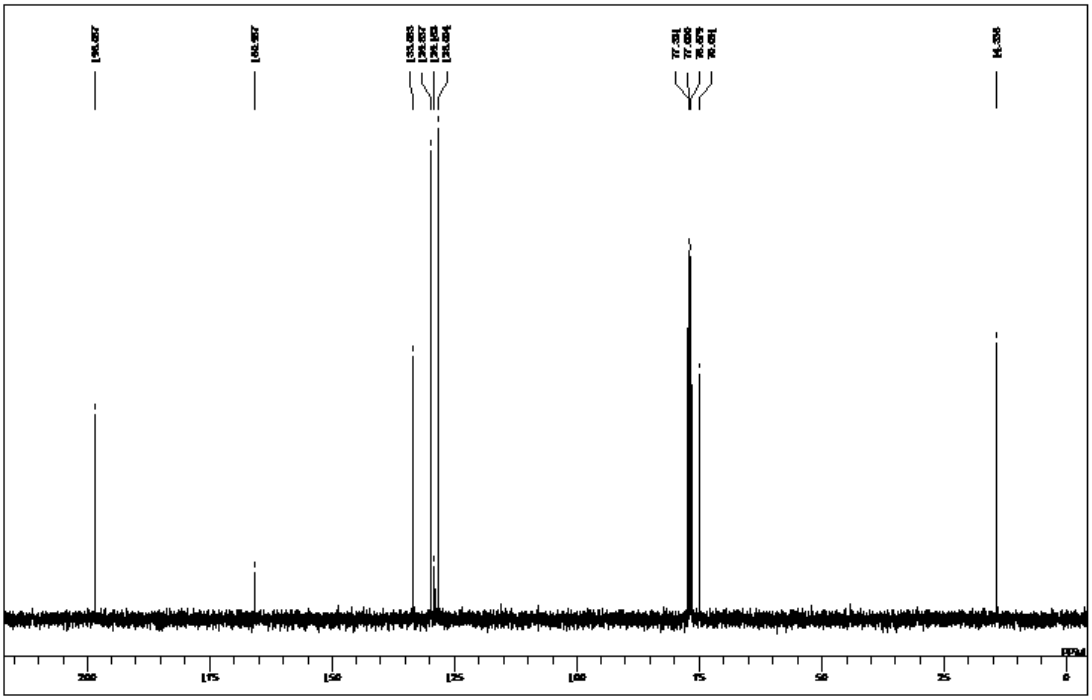

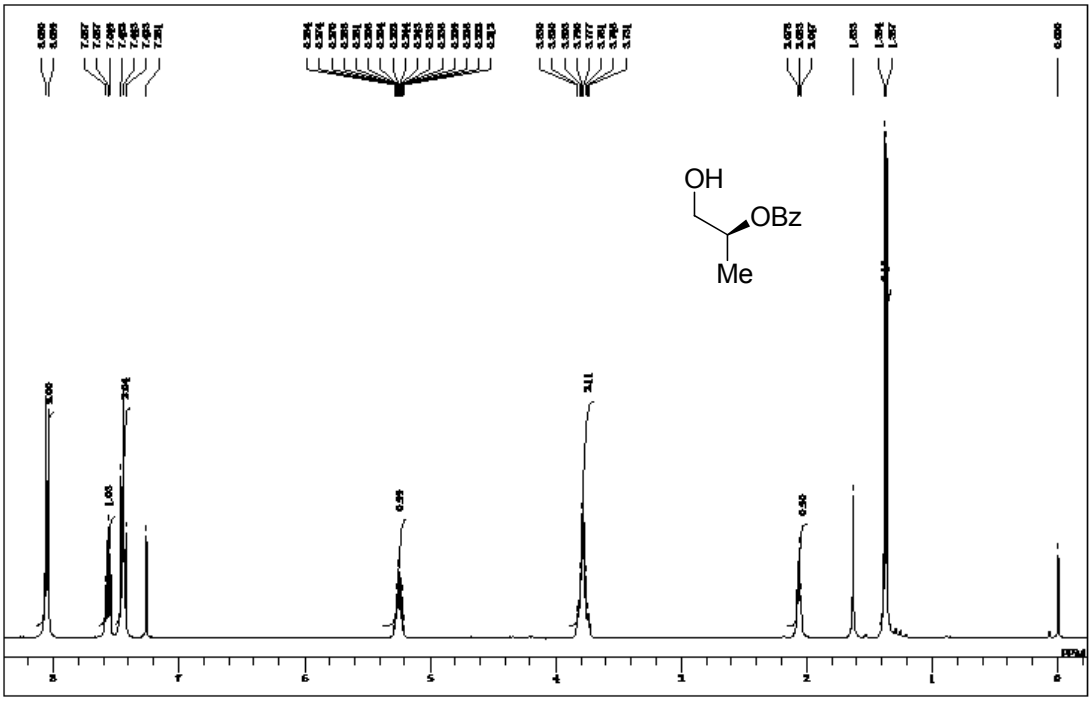
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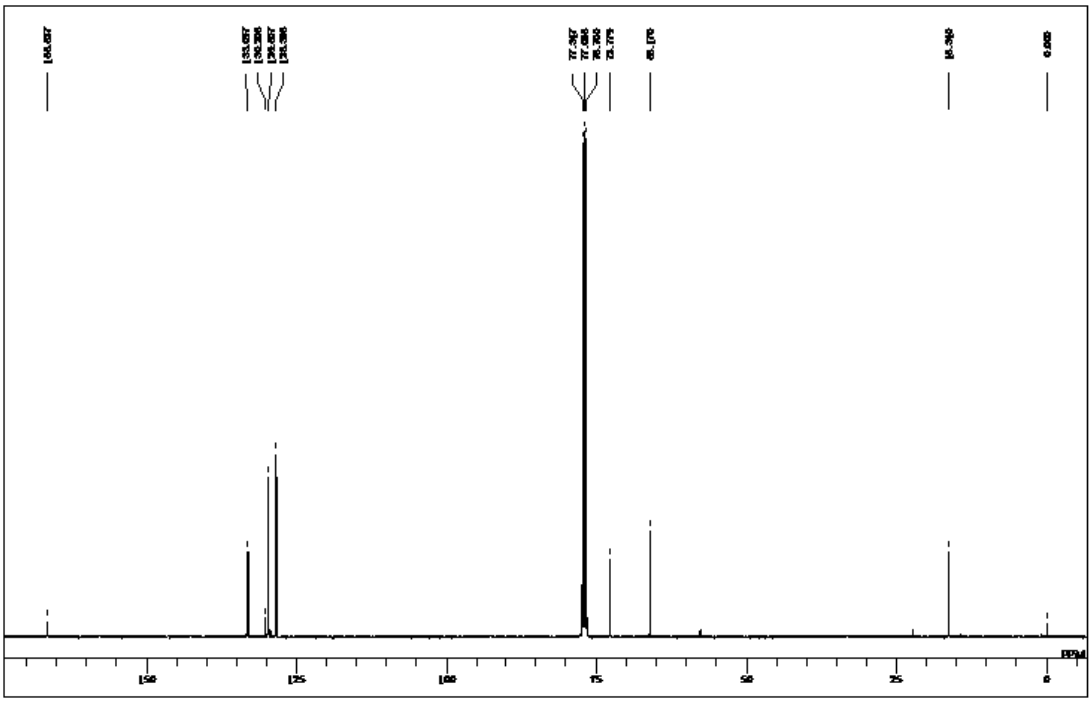

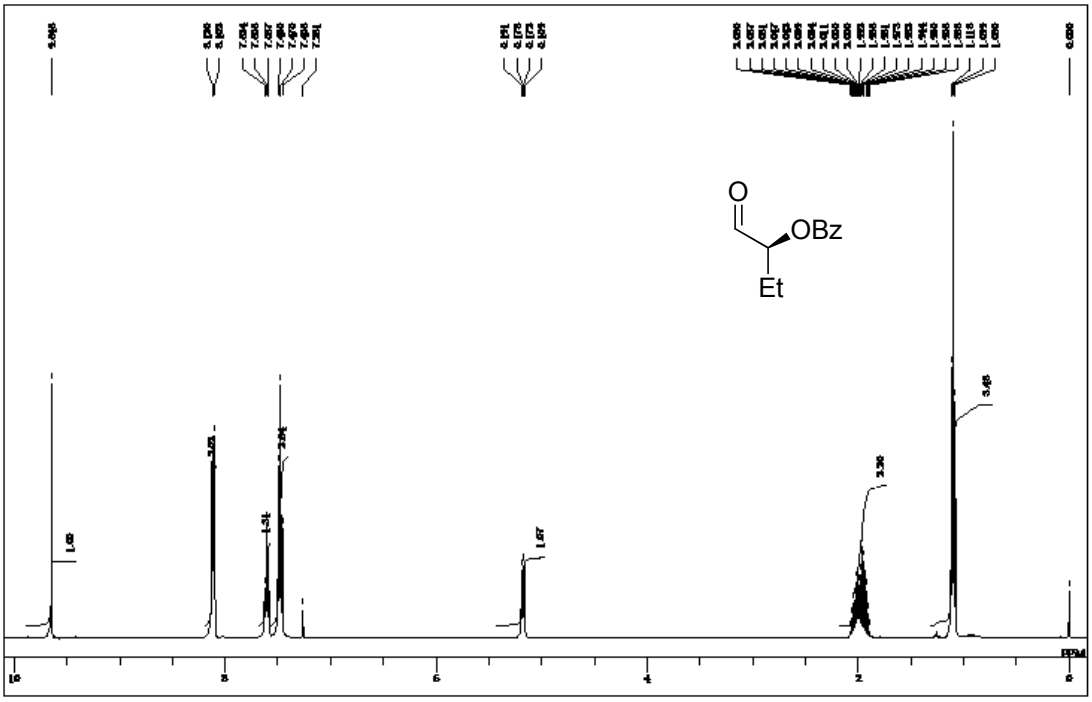
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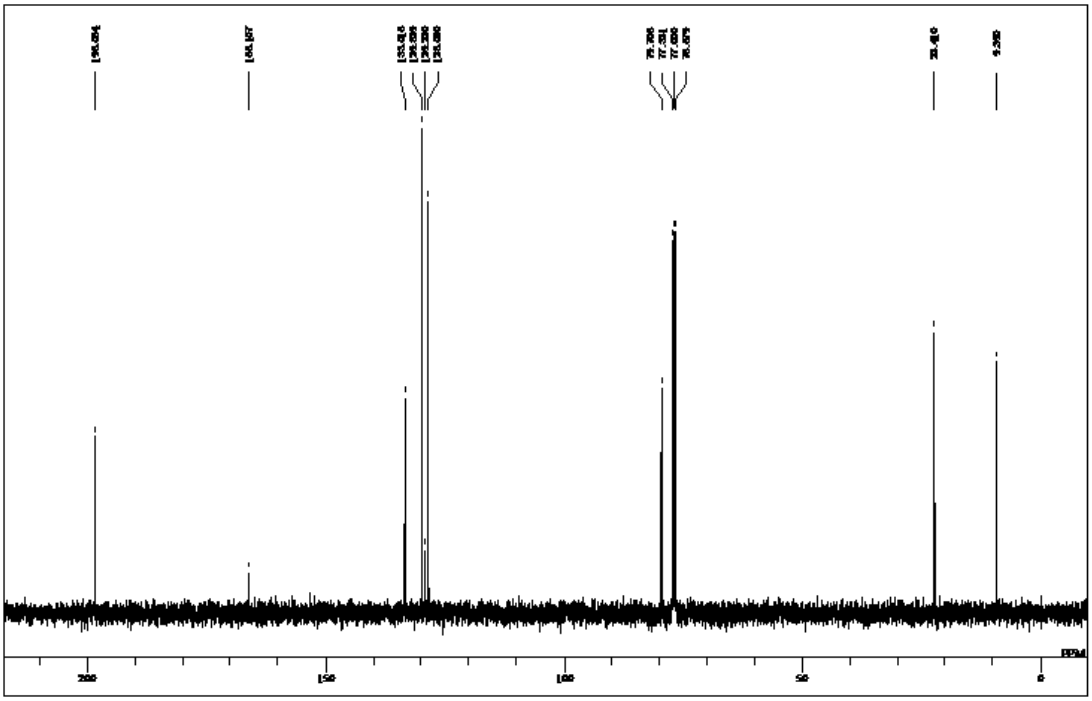

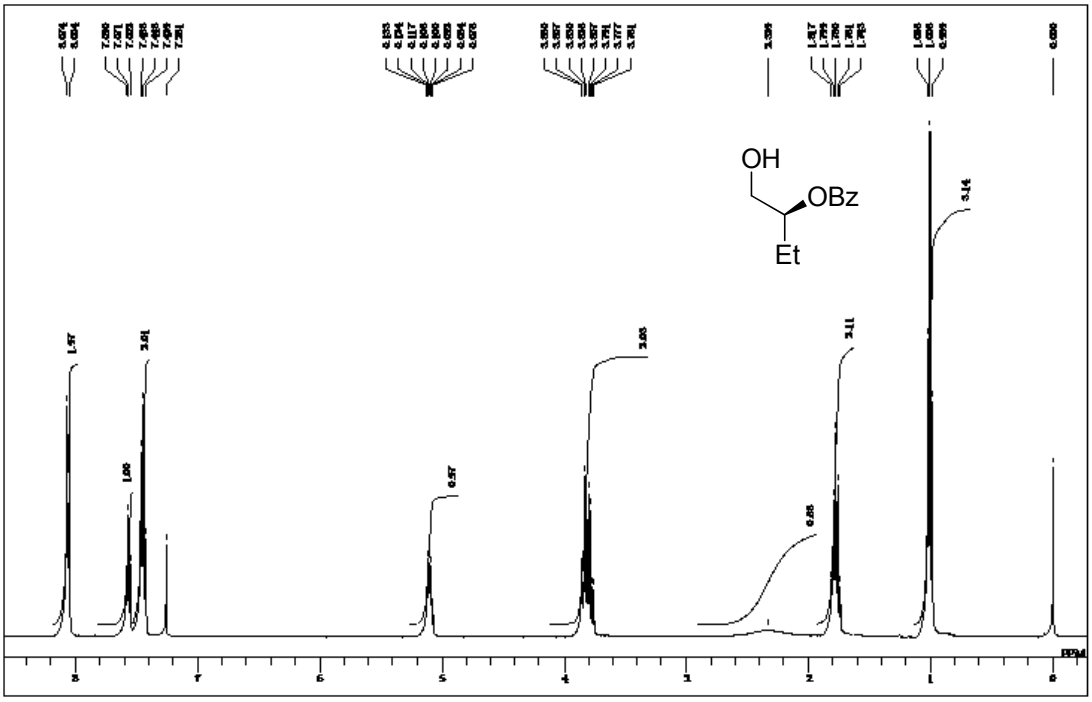
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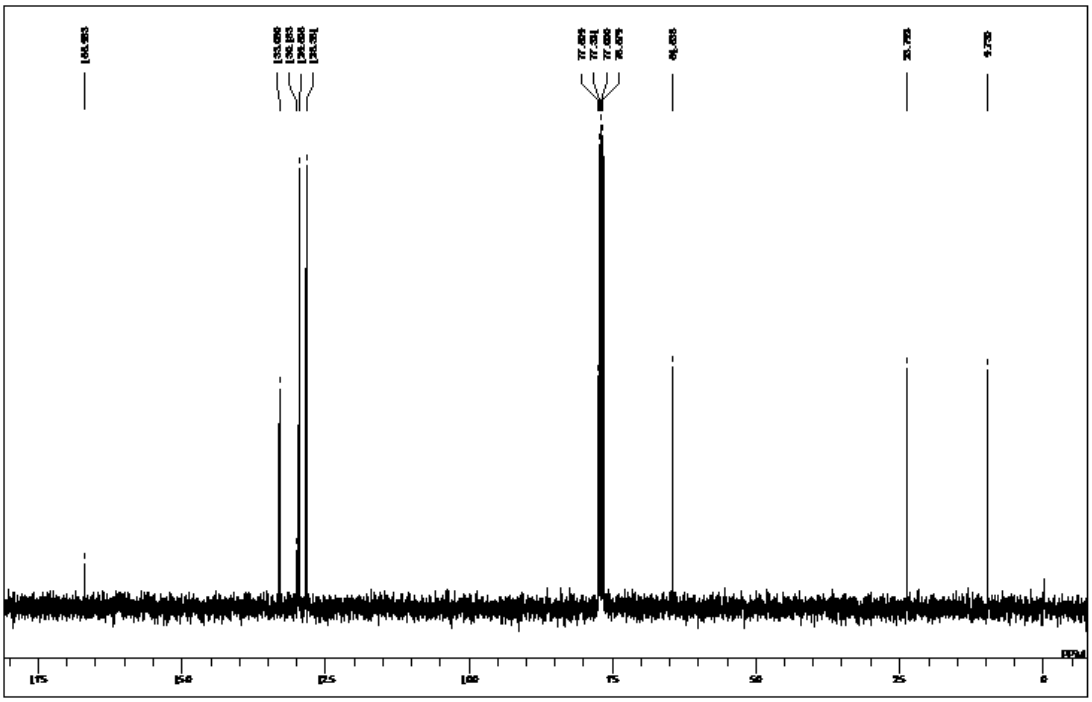

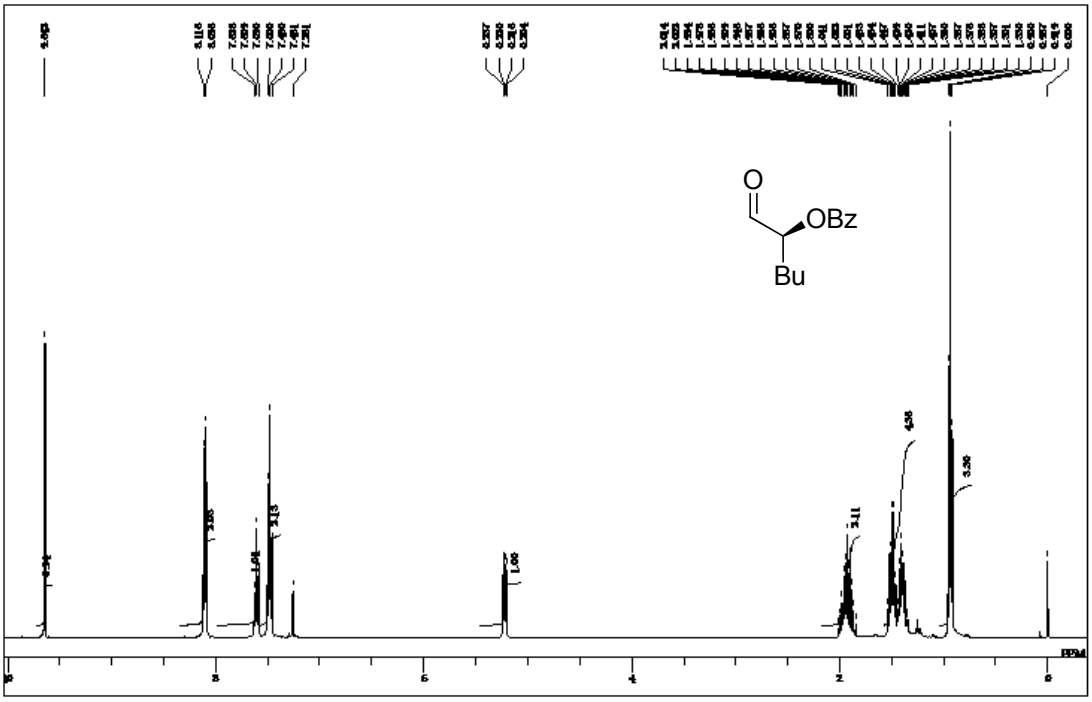
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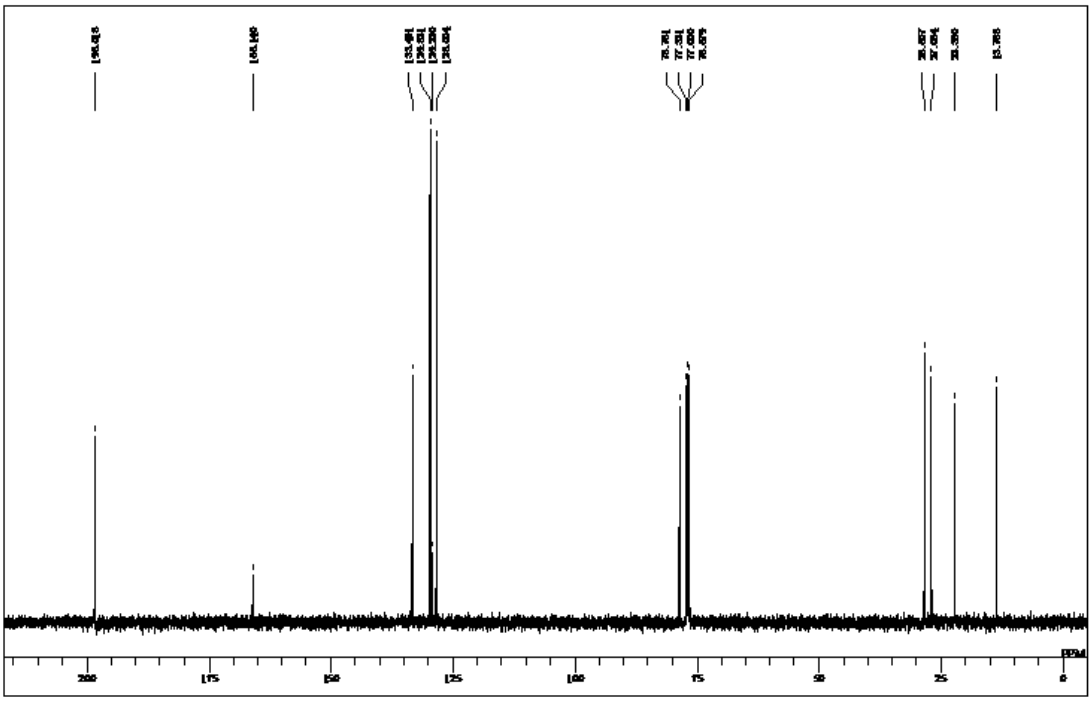

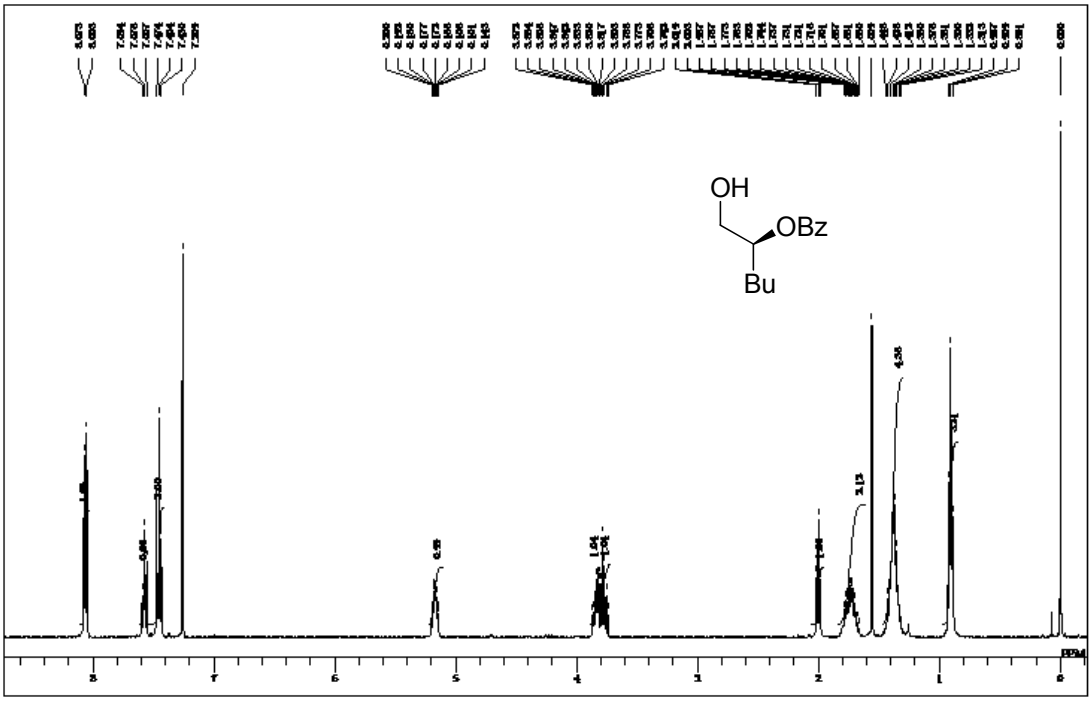
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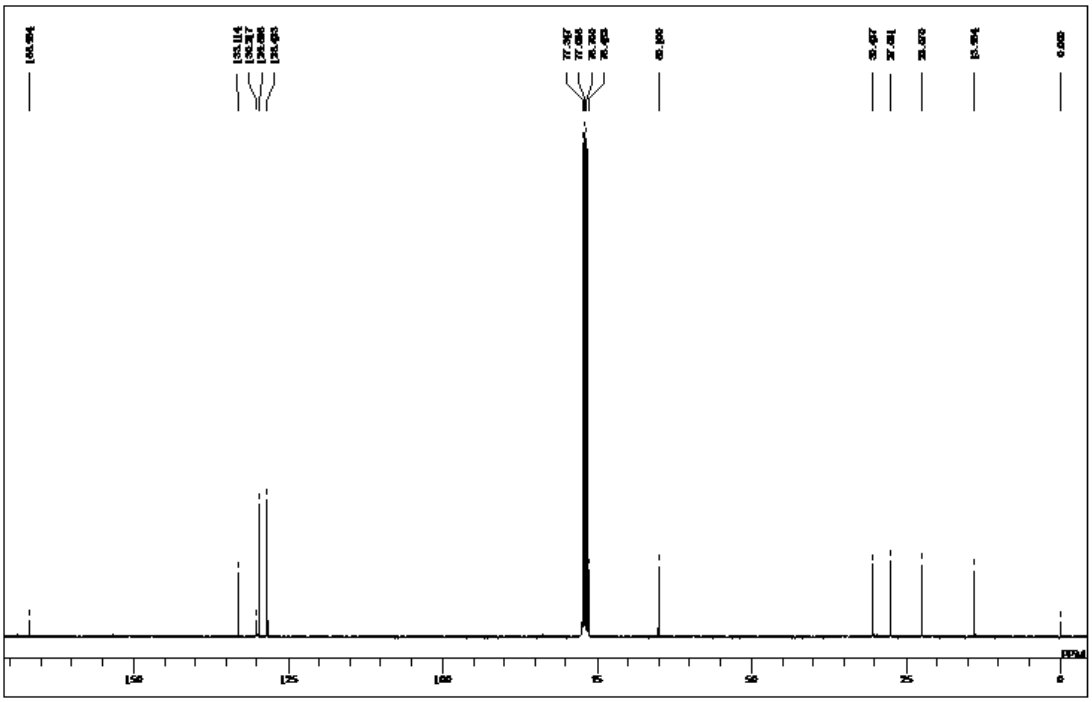

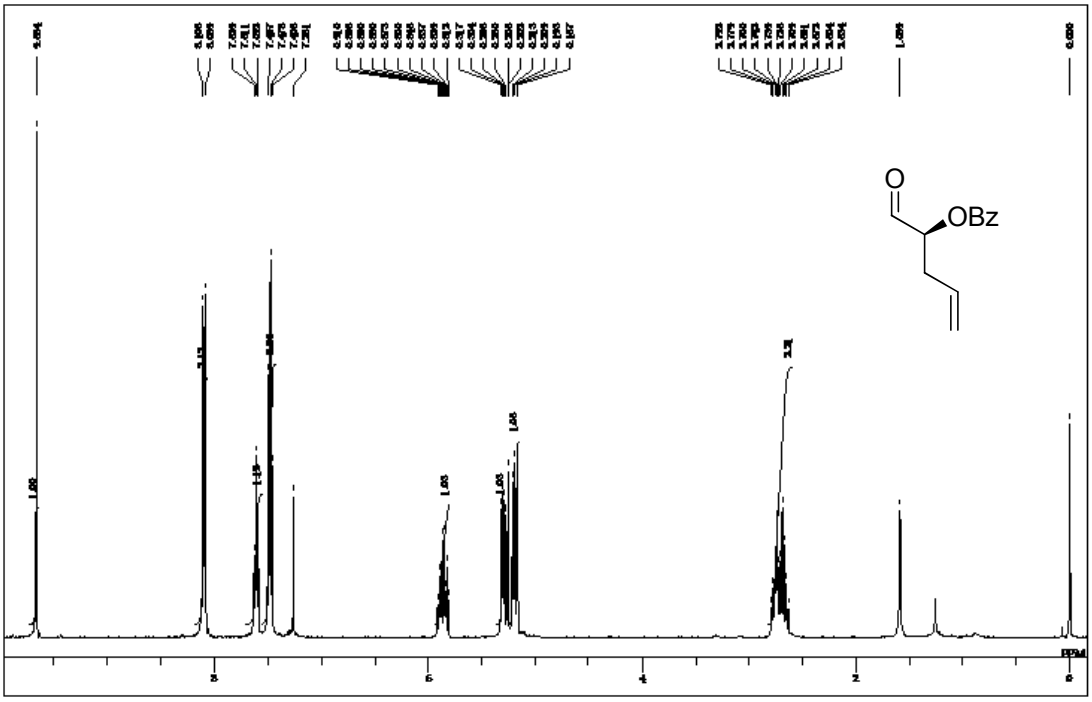
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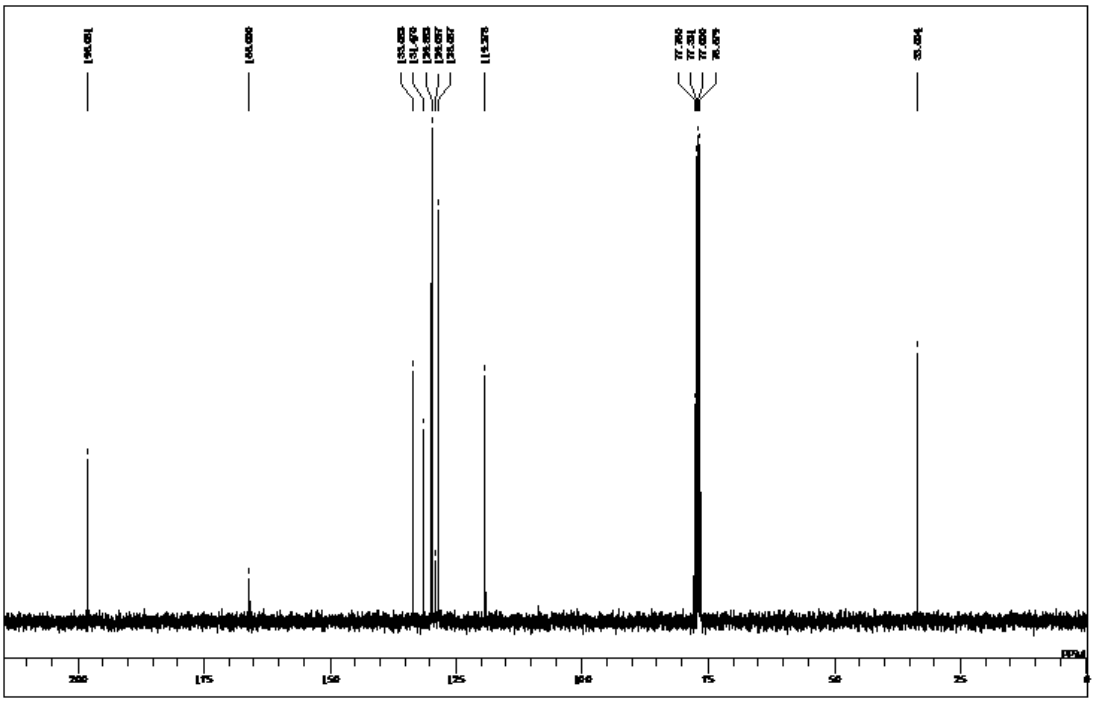

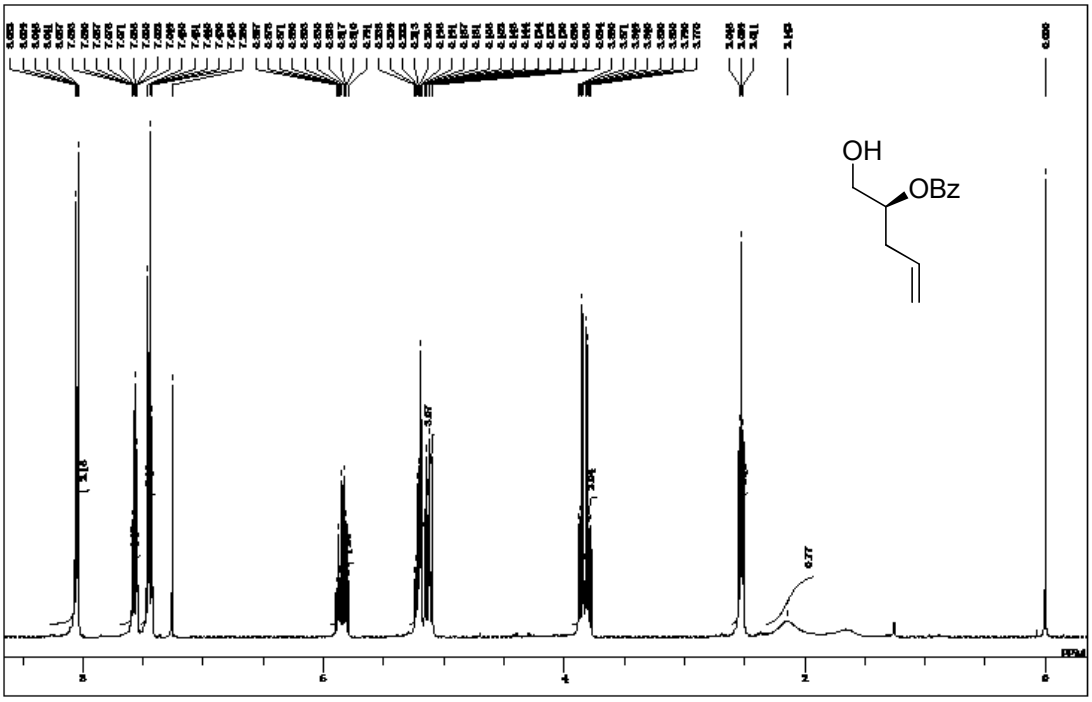
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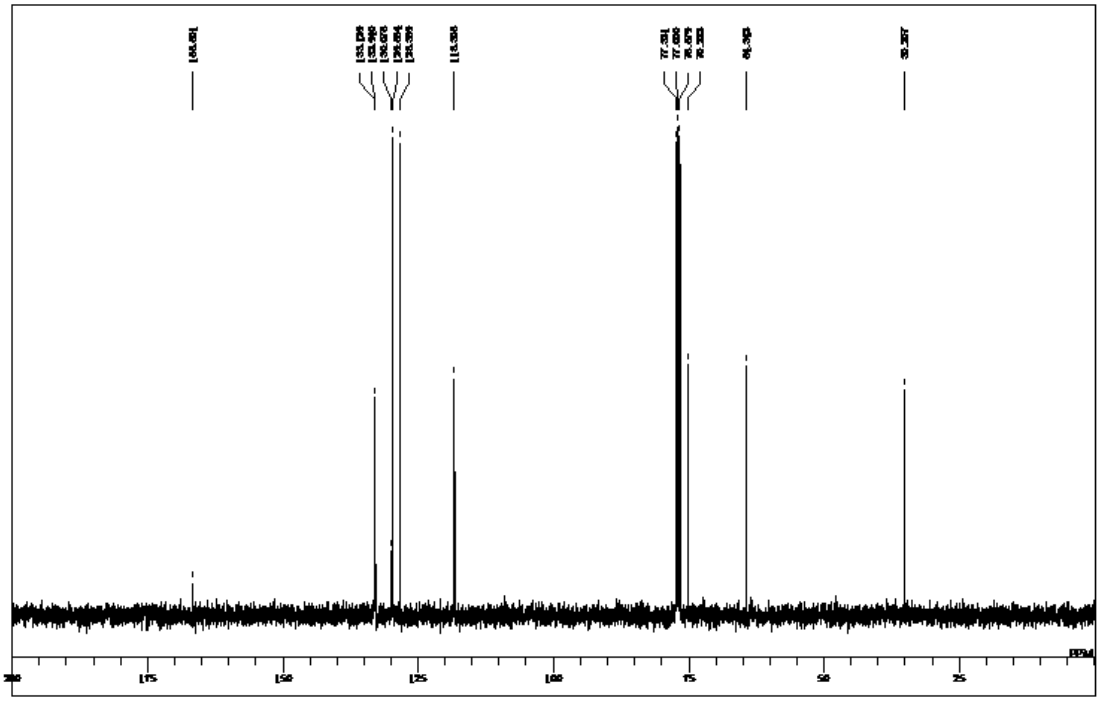

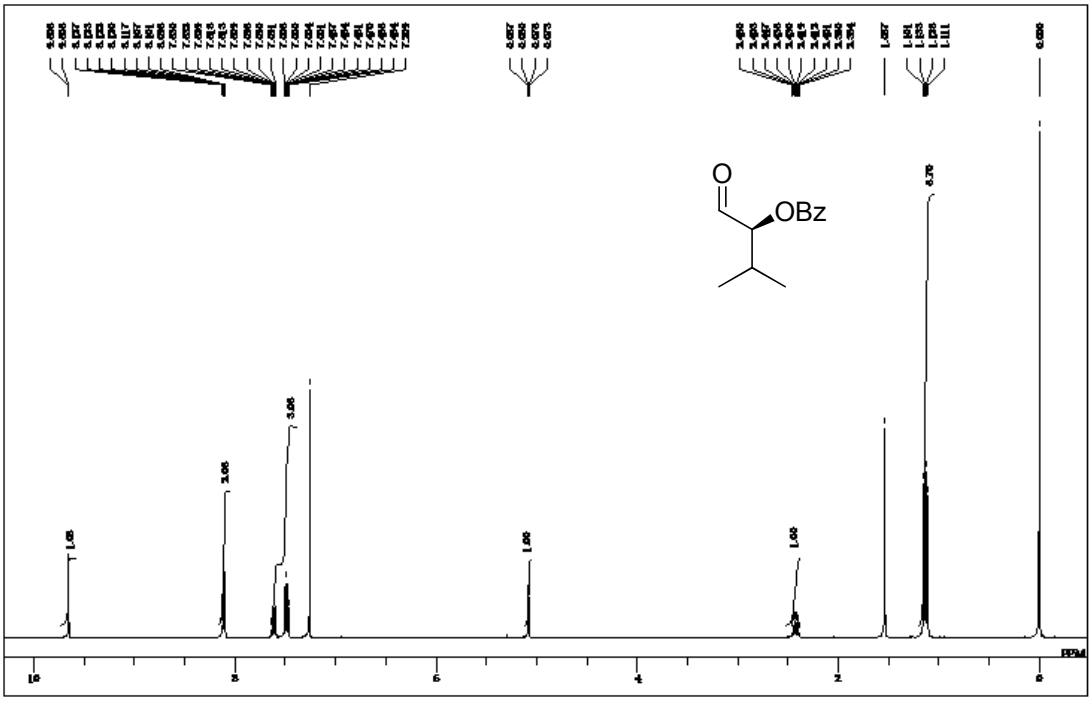
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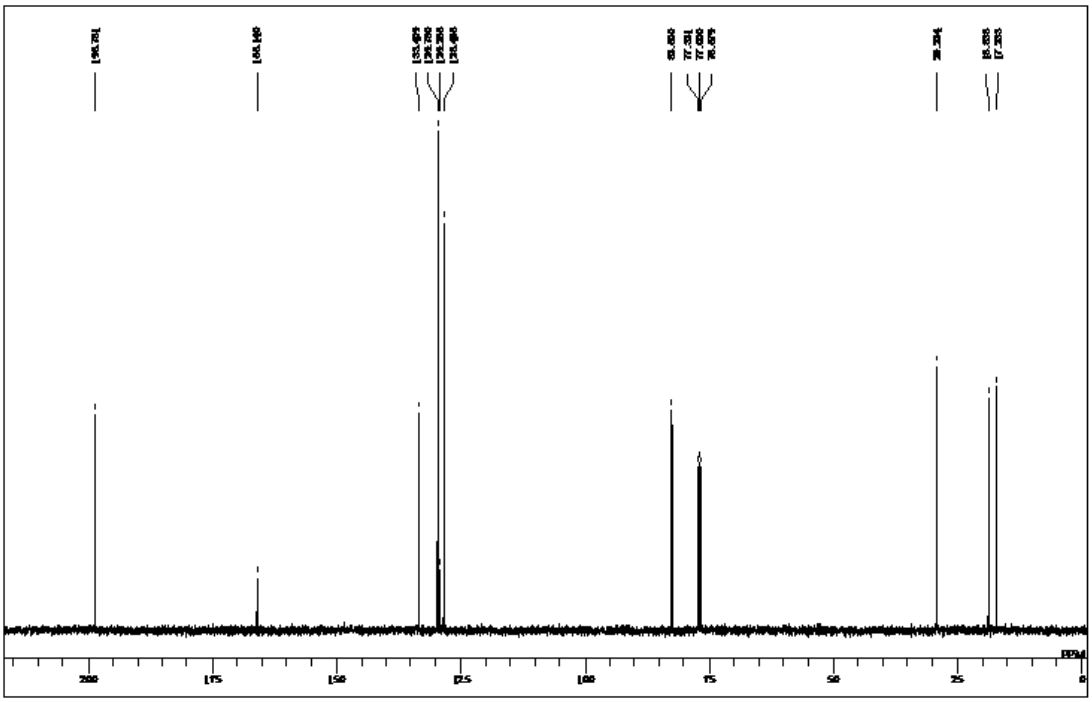

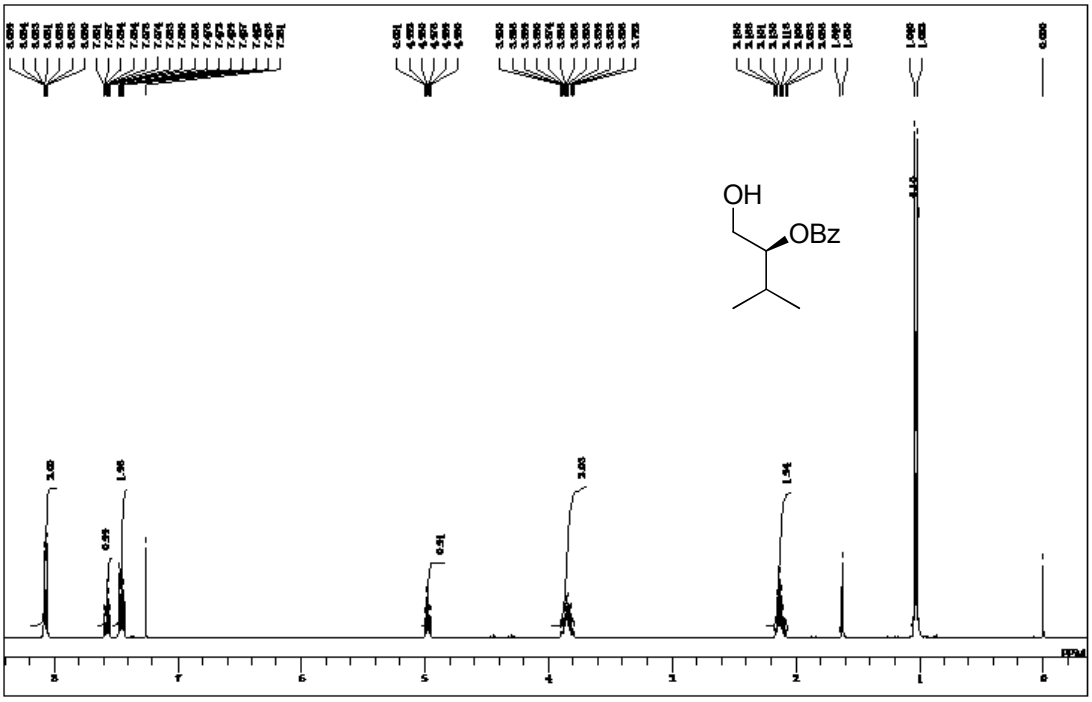
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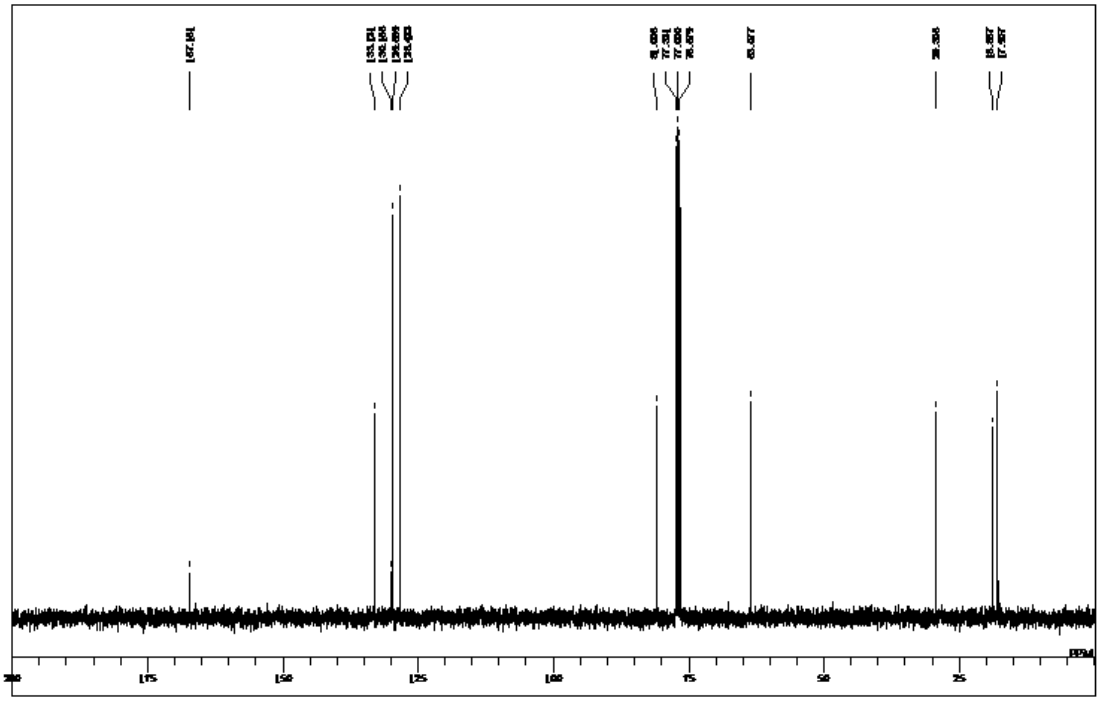

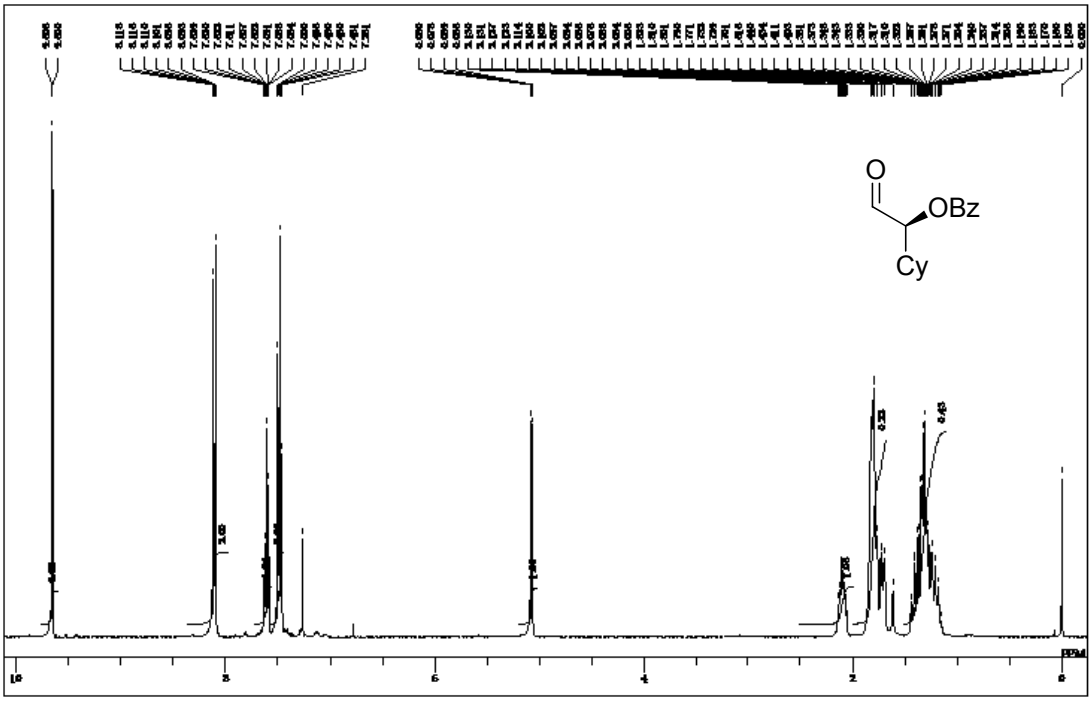
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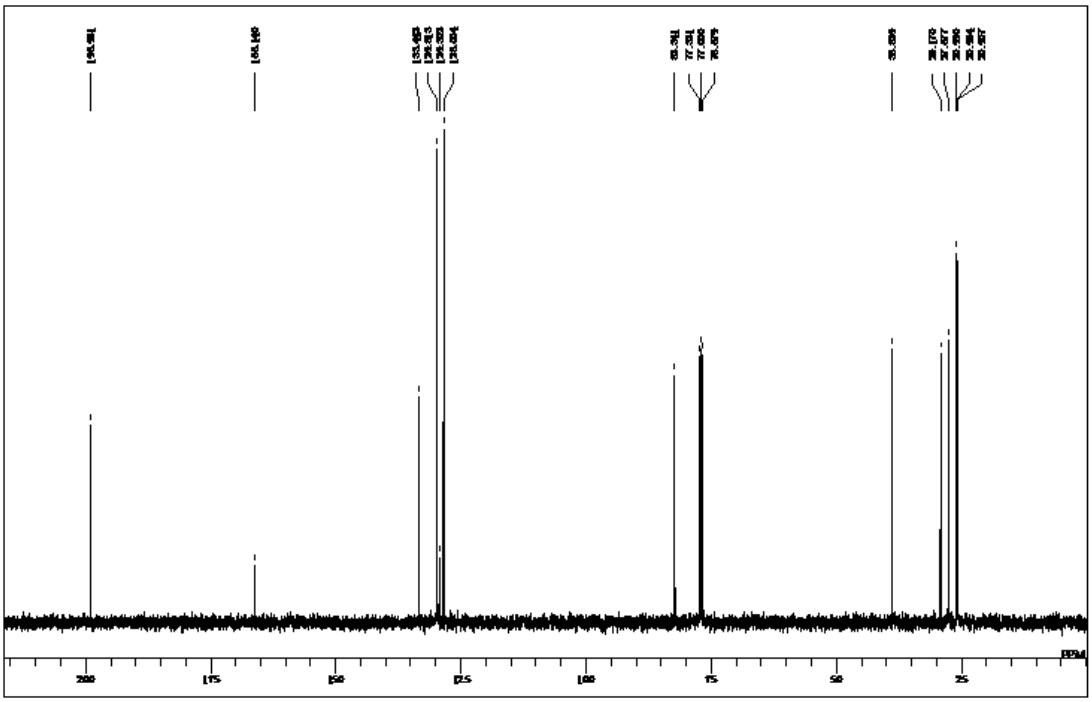

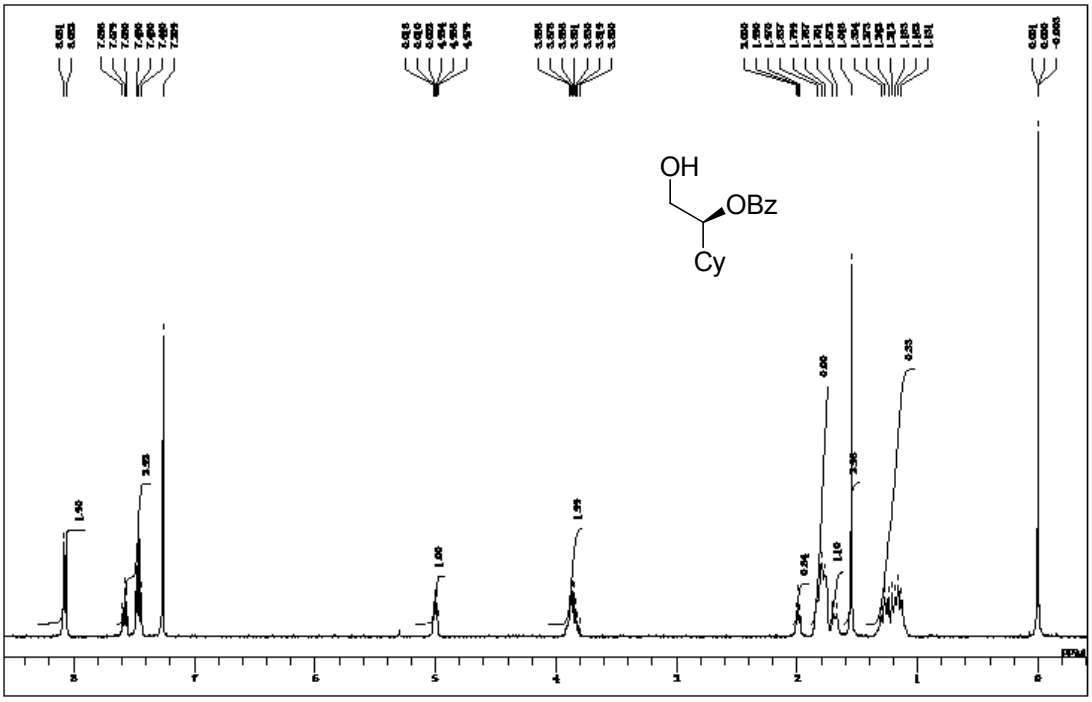
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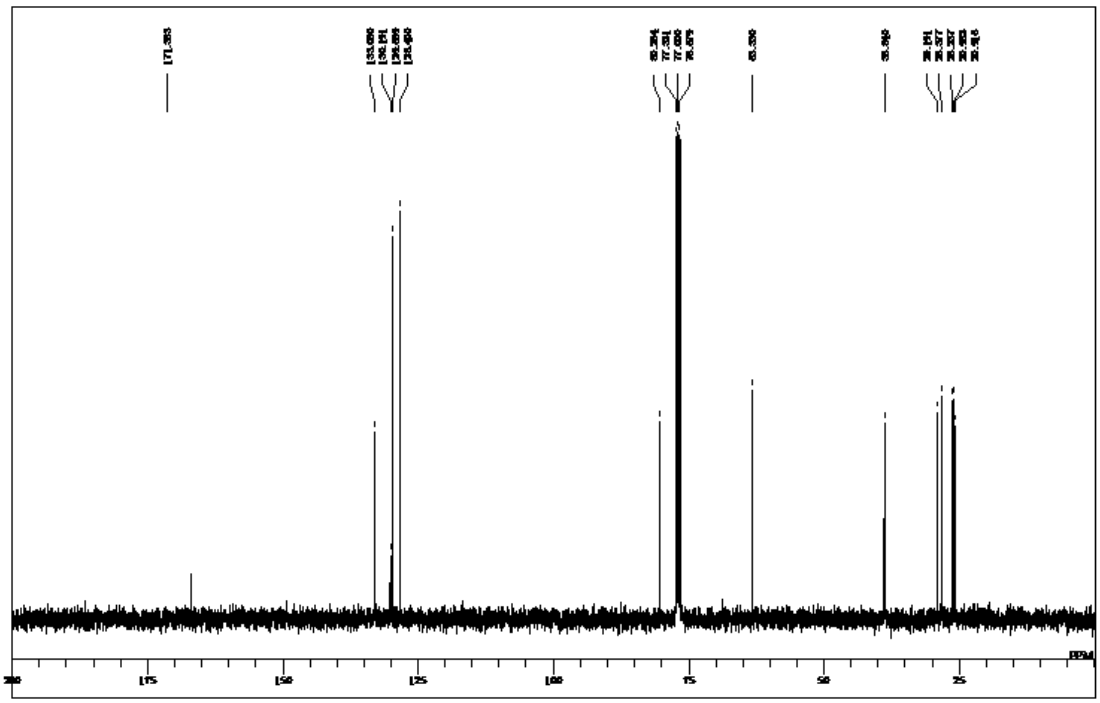

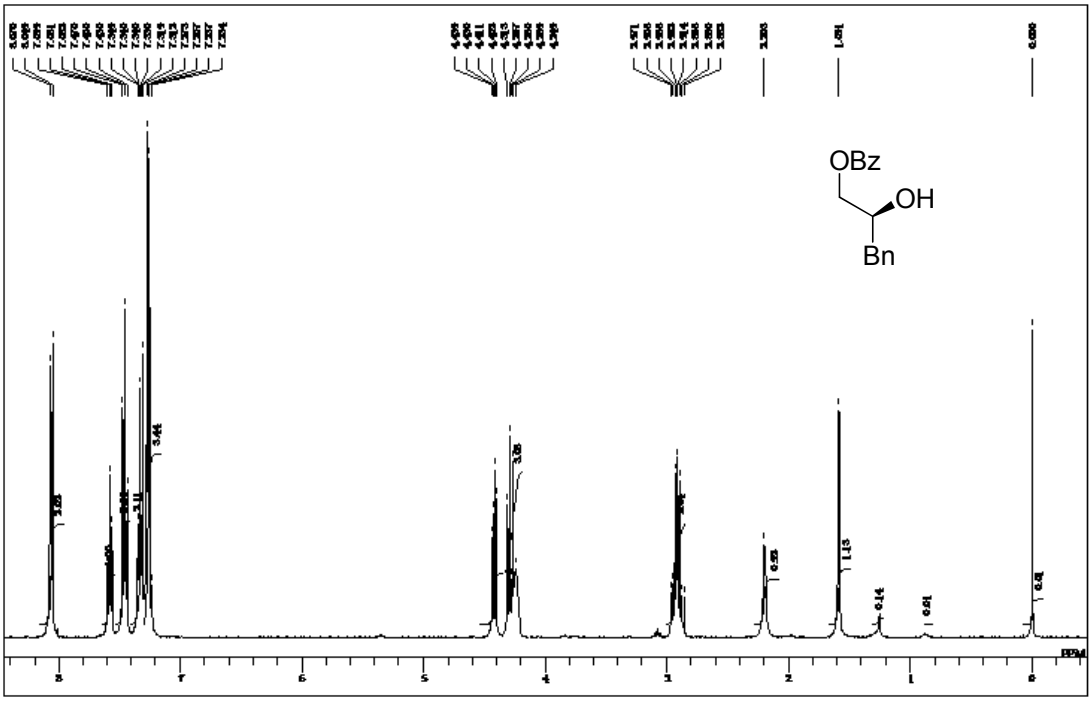
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