Supporting Information

Asymmetric Formation of *tert*-Alkylamines from Serinols by a Dual Function Catalyst

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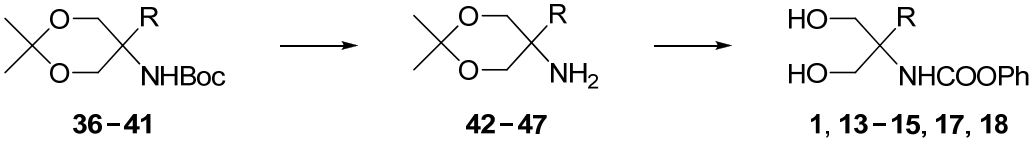
I. General Information

^{1}H and ^{13}C NMR spectra were obtained on Bruker AVANCE 400 spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR) and measured in $CDCl_3$. Chemical shifts were recorded in ppm relative to $SiMe_4$ (δ = 0.00) and referenced internally to the protio impurity of $CDCl_3$ (δ = 7.24) as the internal standard; coupling constants were reported in Hz. The high resolution mass spectra were recorded on Bruker microTOF–Q II spectrometer. The enantioselectivity were determined by HPLC. HPLC measurements were done on a DIONEX model equipped with P580G pump, UV 525 detector (Thermo Science, Waltham, MA) measured at 254 nm, and chiral columns DAICEL AD-H. Eluting solvent was a mixture of 2-propanol and hexane. Optical rotations were measured on a polarimeter (JASCO) in a 10–cm cell. All reactions were carried out in oven-dried glassware under a N_2 atmosphere. All solvents were distilled from the indicated drying reagents right before use: Et_2O, THF and toluene (Na, benzophenone), CH_2Cl_2 (P_2O_5), and MeCN (CaH_2). The normal work-up included extraction, drying over Na_2SO_4 and evaporation of volatile materials *in vacuo*. Purification by column chromatography was performed using Merck (Darmstadt, Germany) silica gel (200-400 mesh).

II. Preparation of the Substrates

1) Diols **1, 13**−**15, 17** and **18**



36–**41** **42**–**47** **1**, **13**–**15**, **17**, **18**

36, **42**, **1**	R = Bn	**39**, **45**, **15**	R = CH_2-cHx
37, **43**, **13**	R = Et	**40**, **46**, **17**	R = $CH_2CH{=}CH_2$
38, **44**, **14**	R = CH_2Bn	**41**, **47**, **18**	R = $CH{=}CH_2$

Diols **1**, **13**−**15, 17** and **18** were obtained by the same procedure starting from the known acetonides **36**−**41**.[12,13] The detailed procedure to prepare **1** from **36** is described as a representative. To **36** (423 mg, 1.32 mmol) dissolved in CH_2Cl_2 (10 mL) were added 2,6-lutidine (0.23 mL, 2.0 mmol) and TMSOTf (0.31 mL, 1.71 mmol) at −78℃ in sequence. After completing the additions, the dry ice/acetone bath was replaced by an ice/water bath.

The reaction mixture was stirred at that temperature for 2 hours, and then quenched with saturated aqueous $NaHCO_3$ (10 mL). The normal work-up with EtOAc (7 mL, four times) and the following purification by column chromatography (EtOAc/hexane = 1/1, then CH_2Cl_2/MeOH = 20/1) afforded **42** (252 mg, 86% yield). **42** (252 mg, 1.14 mmol) was dissolved in CH_2Cl_2 (10 mL), and then Et_3N (0.19 mL, 1.37 mmol) and phenyl chloroformate (0.16 mL, 1.25 mmol) were injected to the substrate in an ice/water bath. After stirring the resulting solution at that temperature for an hour, the reaction mixture was quenched with saturated aqueous NH_4Cl (10 mL). The normal work-up with EtOAc (7 mL, three times) followed by evaporation of all the volatile materials furnished the crude pheny carbamate acetonide. The crude product was heated in a 1:1 mixture of AcOH and H_2O (5 mL) at 80℃ for an hour. Removal of all the volatile materials in vacuo and the subsequent chromatographic separation (EtOAc/hexane = 1/1) gave diol **1** (319 mg, 93% yield). For **1**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 4H), 7.30 – 7.19 (m, 4H), 7.14 – 7.08 (m, 2H), 5.53 (s, 1H), 3.82 (d, *J* = 11.6 Hz, 2H), 3.64 (d, *J* = 11.5 Hz, 2H), 3.51 (s, 2H), 2.96 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.07, 150.67, 135.72, 130.55, 129.51, 128.75, 127.17, 125.81, 121.79, 65.24, 60.15, 37.80. HRMS (ESI) *m/z* calcd for $C_{17}H_{19}NNaO_4$ $[M+Na]^+$, 324.1206 ; found, 324.1211.

From **37** (320 mg, 1.23 mmol) through **43** (158 mg, 1.00 mmol, 81% yield) to **13** (210 mg, 88% yield). For **13**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 7.22 – 7.16 (m, 1H), 7.12 – 7.08 (m, 2H), 5.67 (s, 1H), 3.82 (d, *J* = 11.5 Hz, 2H), 3.61 (d, *J* = 11.5 Hz, 2H), 1.64 (q, *J* = 7.5 Hz, 2H), 0.89 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.02, 150.76, 129.46, 125.67, 121.75, 66.02, 59.90, 25.27, 7.61. HRMS (ESI) *m/z* calcd for $C_{12}H_{17}NNaO_4$ $[M+Na]^+$, 262.1050; found, 262.1055.

From **38** (402 mg, 1.20 mmol) through **44** (248 mg, 1.06 mmol, 86% yield) to **14** (307 mg, 0.98 mmol, 92% yield). For **14**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 2H), 7.30 – 7.25 (m, 2H), 7.23 – 7.15 (m, 4H), 7.14 – 7.08 (m, 2H), 5.64 (s, 1H), 3.95 (d, *J* = 11.5 Hz, 2H), 3.72 (d, *J* = 11.5 Hz, 2H), 2.71 – 2.63 (m, 2H), 2.01 – 1.91 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.96, 150.80, 141.55, 129.54, 128.72, 128.44, 126.30, 125.78, 121.76, 66.59, 59.95, 34.92, 29.78. HRMS (ESI) *m/z* calcd for $C_{18}H_{21}NNaO_4$ $[M+Na]^+$, 338.1363; found, 338.1361.

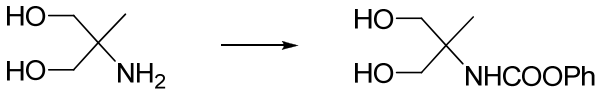
From **39** (407 mg, 1.24 mmol) through **45** (252 mg, 1.10 mmol, 89% yield) to **15** (301 mg, 0.98 mmol, 89% yield). For **15**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 8.5, 7.3 Hz, 2H),

7.23 – 7.17 (m, 1H), 7.12 – 7.07 (m, 2H), 5.56 (s, 1H), 3.91 (d, *J* = 11.5 Hz, 2H), 3.63 (d, *J* = 11.5 Hz, 2H), 3.41 (s, 2H), 1.77 – 1.57 (m, 5H), 1.49 (d, *J* = 5.6 Hz, 2H), 1.40 (dddt, *J* = 14.0, 8.8, 5.9, 2.6 Hz, 1H), 1.30 – 1.06 (m, 3H), 1.05 – 0.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.94, 150.76, 129.50, 125.73, 121.79, 66.97, 60.26, 40.30, 35.22, 33.01, 26.46, 26.18. HRMS (ESI) *m/z* calcd for $C_{17}H_{25}NNaO_4$ $[M+Na]^+$, 330.1676; found, 330.1670.

From **40** (346 mg, 1.27 mmol) through **46** (182 mg, 1.07 mmol, 84% yield) to **17** (228 mg, 0.91 mmol, 85% yield). For **17**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 8.5, 7.3 Hz, 2H), 7.23 – 7.18 (m, 1H), 7.13 – 7.06 (m, 2H), 5.85 (ddt, *J* = 15.3, 10.7, 7.5 Hz, 1H), 5.58 (s, 1H), 5.23 (d, *J* = 1.2 Hz, 1H), 5.22 – 5.17 (m, 1H), 3.88 (d, *J* = 11.7 Hz, 2H), 3.66 (d, *J* = 11.7 Hz, 2H), 3.26 (s, 2H), 2.41 (dd, *J* = 7.4, 1.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.15, 150.73, 132.26, 129.52, 125.82, 121.75, 120.32, 66.07, 59.49, 37.49. HRMS (ESI) *m/z* calcd for $C_{13}H_{17}NNaO_4$ $[M+Na]^+$, 274.1050; found, 274.1051.

From **41** (520 mg, 2.00 mmol) through **47** (252 mg, 1.60 mmol, 80% yield) to **18** (316 mg, 1.33 mmol, 83% yield). For **18**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.23 – 7.18 (m, 1H), 7.12 (dd, *J* = 8.6, 1.2 Hz, 2H), 5.91 – 5.81 (m, 2H), 5.37 – 5.26 (m, 2H), 3.79 (d, *J* = 11.7 Hz, 2H), 3.73 (d, *J* = 11.7 Hz, 2H), 3.14 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.12, 150.73, 136.32, 129.51, 125.81, 121.74, 116.73, 66.19, 62.65. HRMS (ESI) *m/z* calcd for $C_{12}H_{15}NNaO_4$ $[M+Na]^+$, 260.0893; found, 260.0885.

2) Diol **12**

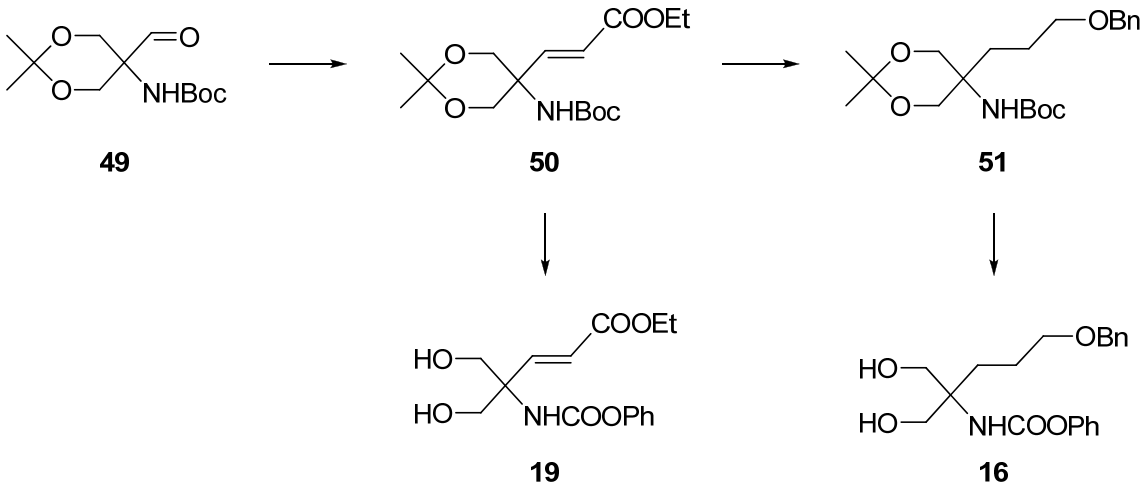


48 **12**

To the commercial amino diol **48** (315 mg, 3.0 mmol) dissolved in CH_2Cl_2 (10 mL) were added $NaHCO_3$ (380 mg, 4.5 mmol) and phenyl chloroformate (0.41 mL, 3.3 mmol) in sequence in an ice/water bath. The reaction mixture was stirred at that temperature for 3 hours and then at room temperature for 8 hours. After quenching the reaction with water (10 mL), the normal work-up with EtOAc (7 mL, three times) and the subsequent chromatographic purification (EtOAc/hexane = 1/1) offered diol **12** (304 mg, 45% yield). For **12**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.9 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.15 – 7.07 (m, 2H), 5.64 (s, 1H), 3.81 (d, *J* = 11.5 Hz, 2H), 3.69 (d, *J* = 11.4 Hz, 2H), 3.07 (s, 2H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.91, 150.78, 129.50, 125.73, 121.79, 67.92, 57.56, 19.97.

HRMS (ESI) *m/z* calcd for $C_{11}H_{15}NNaO_4$ $[M+Na]^+$, 248.0893; found, 248.0897.

3) Diols **16** and **19**

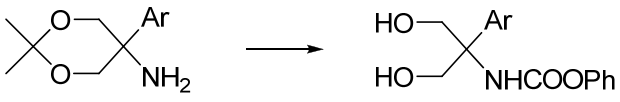


To triethyl phosphonoacetate (0.35 mL, 3.50 mmol) in THF (5 mL) was added NaH (60% dispersion in mineral oil, 140 mg, 3.50 mmol) in an ice/water bath. After stirring the mixture for 30 minutes, the known aldehyde **49**[14] (260 mg, 1.00 mmol) was injected using THF (5 mL), and then the resulting solution was stirred at that temperature for 30 minutes. The reaction was quenched with saturated aqueous NH_4Cl (5mL) and water (5 mL), and the subsequent normal work-up with EtOAc (5 mL, three times), and chromatographic separation (EtOAc/hexane = 1/3) gave rise to the conjugated ester **50** (316 mg, 96% yield). $LiBH_4$ (2.0 M in THF, 0.6 mL, 1.2 mmol) was added to **50** (165 mg, 0.50 mmol) dissolved in THF (5 mL) in an ice/water bath and the mixture was stirred at that temperature for 12 hours. After quenching the reaction with saturated aqueous NH_4Cl (10 mL) in an ice/water bath, the resulting solution was subjected to the normal work-up with EtOAc (5 mL, three times) and column chromatography (EtOAc/hexane = 1/1) to impart the corresponding allylic alcohol (103 mg, 72% yield). To the allylic alcohol (400 mg, 1.39 mmol) in MeOH (5 mL) was added Pd/C (10 wt%, 20 mg) at room temperature, and then the mixture was stirred under a hydrogen atmosphere (1 atm) at room temperature for 12 hours. After filtering the mixture through celite (500 mg) with MeOH (10 mL), the subsequent evaporation of all the volatile materials *in vacuo* and column chromatography (EtOAc/hexane = 1/1) provided the saturated alcohol (367 mg, 91% yield). Benzyl chloride (0.16 mL, 1.36 mmol) and KOH (104 mg, 1.86 mmol) were added sequentially to the saturated alcohol (360 mg, 1.24 mmol) dissolved in

DMF (5 mL) at room temperature, and the resulting mixture was stirred at that temperature for 12 hours. The normal work-up with Et_2O (7 mL, three times) and column chromatography (EtOAc/hexane = 1/10) revealed the benzyl ether **51** (306 mg, 65% yield). **51** (569 mg, 1.50 mmol) was converted to the corresponding amine acetonide (368 mg, 1.32 mmol, 88% yield) and then to diol **16** (409 mg, 1.14 mmol, 86% yield) by the same procedure as disclosed in the synthesis of **1** from **36**. Similarly, **50** (659 mg, 2.00 mmol) was deprotected to the amine acetonide (357 mg, 1.56 mmol, 78% yield), and subsequently formylated and hydrolyzed to diol **19** (437 mg, 1.41 mmol, 89% yield). For **16**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 6H), 7.28 (ddt, *J* = 8.2, 3.6, 1.8 Hz, 1H), 7.19 (ddt, *J* = 7.9, 6.9, 1.1 Hz, 1H), 7.12 – 7.06 (m, 2H), 6.02 (s, 1H), 4.49 (s, 2H), 3.79 (d, *J* = 11.6 Hz, 2H), 3.75 (d, *J* = 6.0 Hz, 2H), 3.58 (d, *J* = 11.6 Hz, 2H), 3.48 (t, *J* = 5.8 Hz, 2H), 1.77 – 1.69 (m, 2H), 1.65 (ddt, *J* = 9.2, 6.1, 3.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.13, 150.74, 137.97, 129.38, 128.52, 127.94, 127.87, 125.59, 121.72, 73.28, 70.48, 65.68, 59.75, 29.34, 23.40. HRMS (ESI) *m/z* calcd for $C_{20}H_{25}NNaO_5$ $[M+Na]^+$, 382.1625 ; found, 382.1606.

For **19**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 2H), 7.23 – 7.17 (m, 1H), 7.14 – 7.07 (m, 2H), 6.92 (d, *J* = 16.0 Hz, 1H), 6.12 (s, 1H), 6.02 (d, *J* = 16.0 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 4H), 3.58 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.34, 154.69, 150.54, 145.97, 129.42, 125.76, 122.59, 121.64, 64.97, 62.04, 60.99, 14.19. HRMS (ESI) *m/z* calcd for $C_{15}H_{19}NNaO_6$ $[M+Na]^+$, 332.1105; found, 332.1101.

4) Diols **20**–**22**



52 – 54 **20 – 22**

52, 20 R = Ph **54, 22** R = 4-MePh
53, 21 R = 4-ClPh

Diols **20**–**22** were supplied starting from the known amino acetonides **52**–**54**[12] by the synthetic process identical to that explained for the preparation of **1** from **42**.

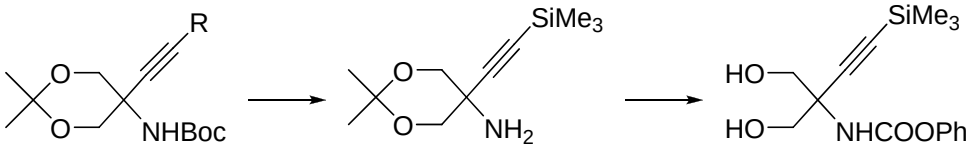
From **52** (517 mg, 2.49 mmol) to **20** (637 mg, 2.21 mmol, 89% yield). For **20**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 6H), 7.32 – 7.26 (m, 1H), 7.23 – 7.11 (m, 3H), 6.21 (s, 1H), 4.04 (d, *J* = 11.7 Hz, 2H), 3.96 (d, *J* = 11.8 Hz, 2H), 3.33 (s, 2H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ 155.20, 150.78, 139.36, 129.50, 129.03, 128.01, 126.03, 125.80, 121.73, 67.79, 64.26. HRMS (ESI) *m/z* calcd for $C_{16}H_{17}NNaO_4$ $[M+Na]^+$, 310.1050; found, 310.1039.

From **53** (297 mg, 1.23 mmol) to **21** (344 mg, 1.07 mmol, 87% yield). For **21**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 6H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.19 (s, 1H), 3.99 (q, *J* = 11.7 Hz, 4H), 3.11 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.11, 150.69, 133.95, 129.55, 129.15, 127.59, 125.90, 121.67, 67.65, 63.78. HRMS (ESI) *m/z* calcd for $C_{16}H_{16}ClNNaO_4$ $[M+Na]^+$, 344.0660; found, 344.0659.

From **54** (313 mg, 1.41 mmol) to **22** (386 mg, 1.28 mmol, 91% yield). For **22**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.25 (m, 2H), 7.22 – 7.07 (m, 5H), 6.18 (s, 1H), 4.06 (d, *J* = 11.7 Hz, 2H), 3.98 (d, *J* = 11.9 Hz, 2H), 3.26 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.17, 150.81, 137.72, 136.31, 129.72, 129.46, 125.92, 125.73, 121.75, 67.83, 64.07, 21.10. HRMS (ESI) *m/z* calcd for $C_{17}H_{19}NNaO_4$ $[M+Na]^+$, 324.1206; found, 324.1207.

5) Diol **23**



55 R = H
56 R = $SiMe_3$

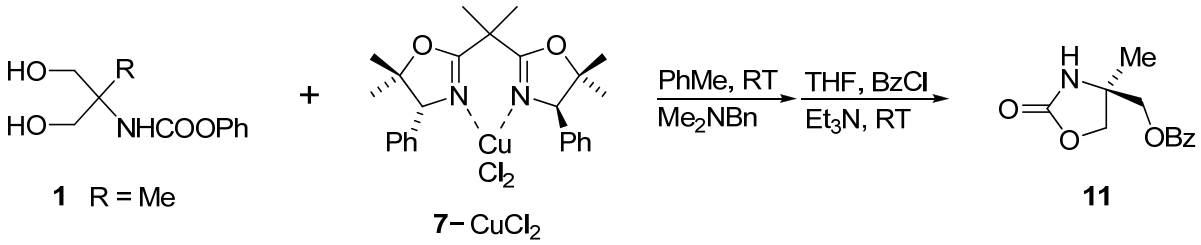
57

23

To the known acetylenic acetonide **55**[15] (511 mg, 2.00 mmol) dissolved in THF (10 mL) was injected n-BuLi (2.5 M in hexane, 1.8 mL, 4.40 mmol) at −78℃, and then the reaction temperature was increased to 0℃ over 30 minutes. After cooling down the resulting solution to −78℃, TMSCl (0.38 mL, 3.00 mmol) was added to the generated acetylide anion, and then the reaction mixture was stirred at that temperature for an hour. The reaction was quenched with saturated aqueous NH_4Cl (5 mL) and water (5 mL), and the following normal work-up with EtOAc (7 mL, three times) and chromatographic separation (EtOAc/hexane = 1/10) delivered the silylated acetylene acetonide **56** (602 mg, 92% yield). **56** was converted to **23** by the same procedure as depicted in the formation of **1** from **36**. From **56** (400 mg, 1.22 mmol) through **57** (225 mg, 0.99 mmol, 81% yield) to **23** (243 mg, 0.79 mmol, 80% yield). For **23**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 7.23 – 7.17 (m, 1H), 7.15 – 7.09

(m, 2H), 5.86 (s, 1H), 3.96 (d, J = 11.6 Hz, 2H), 3.87 (d, J = 11.5 Hz, 2H), 2.97 (s, 2H), 0.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.23, 150.72, 129.50, 125.81, 121.72, 101.77, 91.49, 66.52, 58.15, 0.28, 0.00, –0.18. HRMS (ESI) *m/z* calcd for $C_{15}H_{21}NNaO_4Si$ $[M+Na]^+$, 330.1132; found, 330.1132.

III. General Procedure for the Consecutive Asymmetric Desymmetrization and Kinetic Resolution



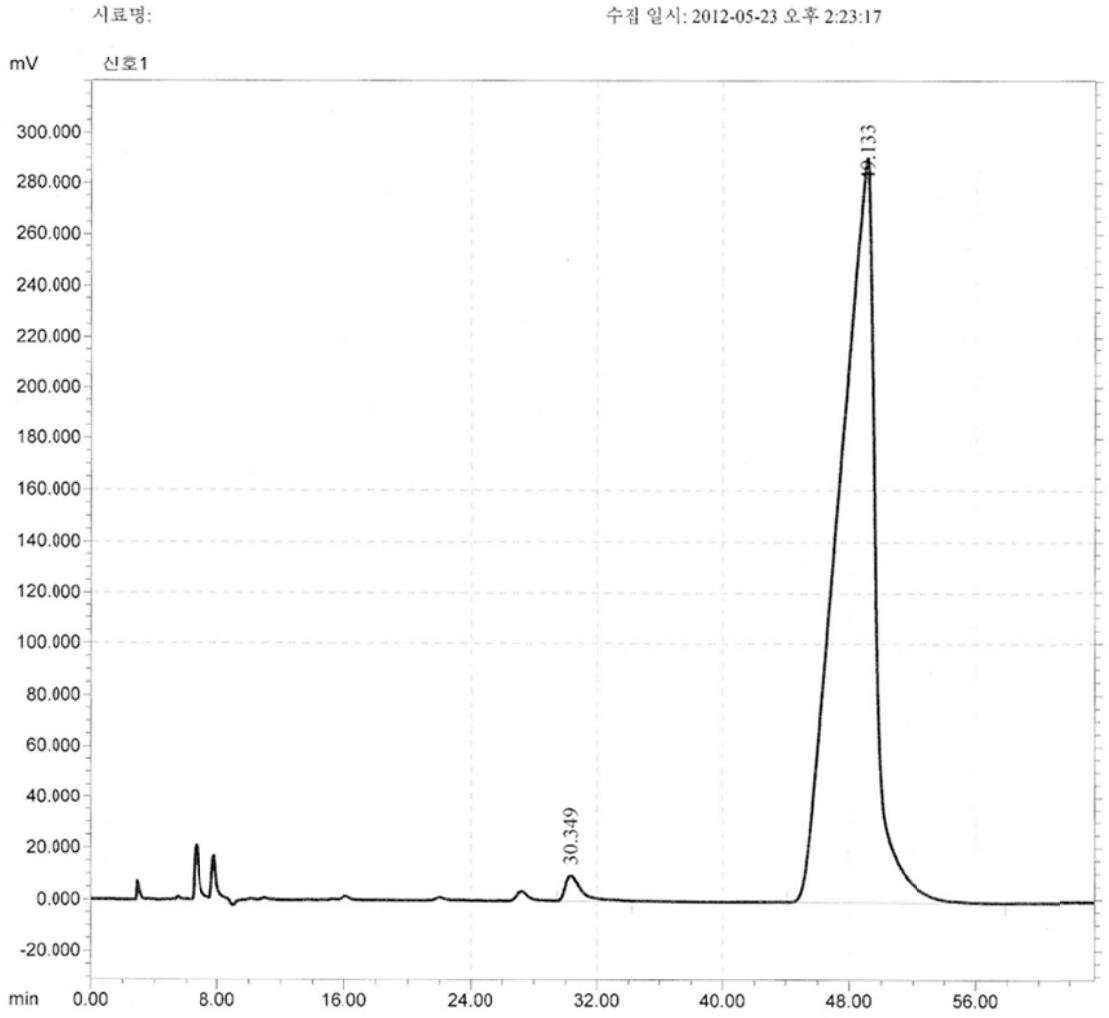
PhMe (10 mL) and N,N-dimethylbenzylamine (45 μL, 0.30 mmol) were added in sequence to a mixture of the substrate **1** (75.3 mg, 0.25 mmol) and the chiral catalyst **7**-$CuCl_2$ (6.6 mg, 0.0125 mmol) at room temperature, and then the mixture was stirred at that temperature for 3 hours. To the resulting solution were injected THF (10 mL), benzoyl chloride (55 μL, 0.48 mmol) and Et_3N (70 μL, 0.50 mmol) sequentially at room temperature. After stirring the reaction mixture at that temperature for 24 hours, the reaction was quenched with saturated NH_4Cl (5 mL) and water (5 mL), and the following normal work-up with EtOAc (7 mL, three times) and chromatographic purification (EtOAc/hexane = 1/3) produced the oxazolidinone benzoate **11** (66.2 mg, 85% yield).

IV. HPLC Analysis Conditions to Determine the % ee Values of the Oxazolidinone Benzoates 11 and 24−35

Prior to the HPLC analysis of all the oxazolidinone benzoates from the consecutive asymmetric desymmetrization and kinetic resolution, the corresponding racemic mixtures were prepared, and then their HPLC analysis conditions were determined. All the oxazolidinone benzoates were analyzed by the identical HPLC analysis conditions using DAICEL AD-H as chiral column, 10% *i*-PrOH in hexane as eluent and 1 mL/min of flow rate.

V. HPLC Chromatograms of the Oxazolidinone Benzoates 11 and 24−35

Prior to the HPLC analysis of the monobenzoates from the asymmetric desymmetrization, the corresponding racemic mixtures were prepared, and then their HPLC analysis conditions were determined. The HPLC analyses were carried out after the first rough purification of the crude benzoate products. Therefore, some chromatograms may contain impurity peaks probably from benzoyl chloride and/or the ligand.



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2	49.133	46226530.91	98.525	BB
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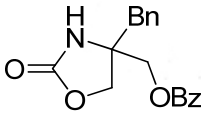
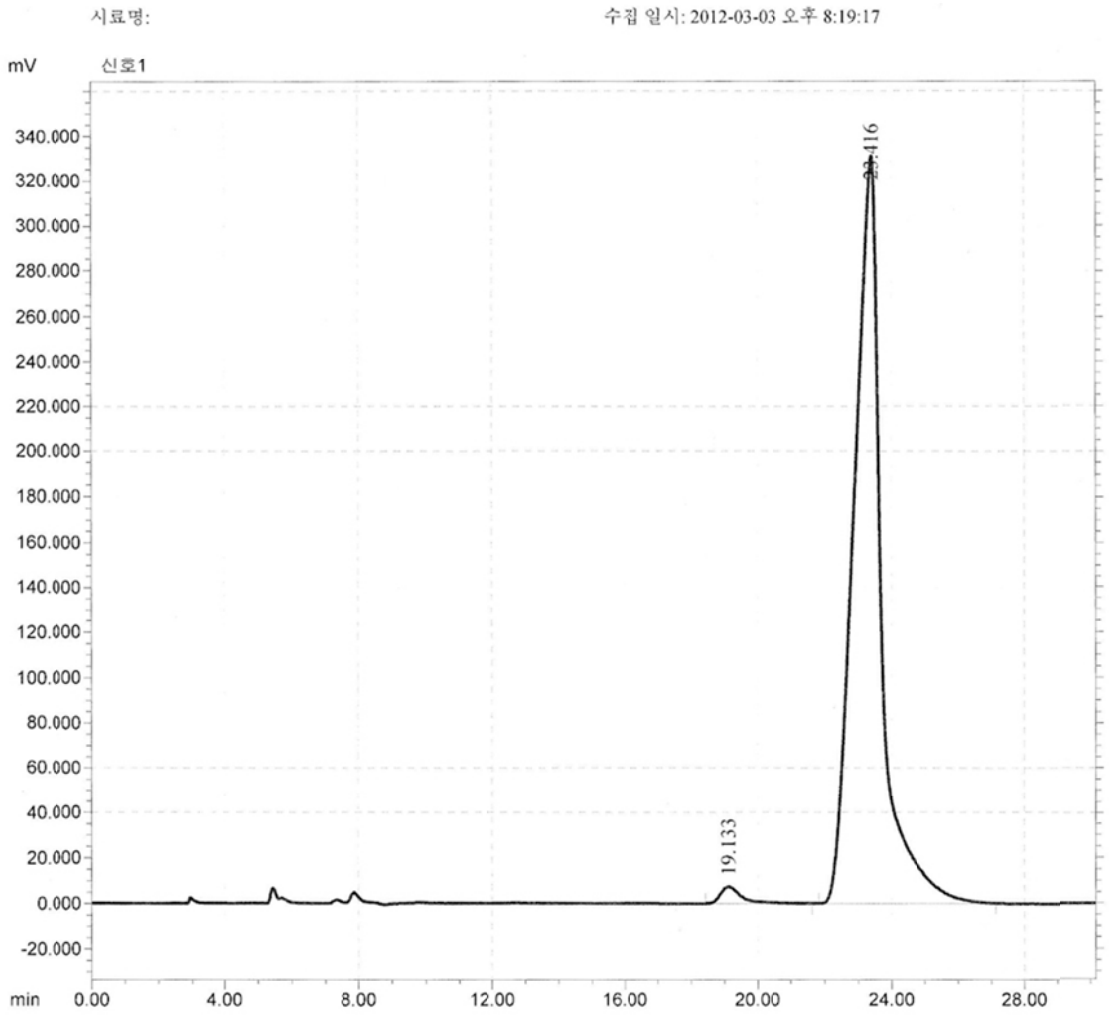


11



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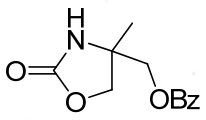
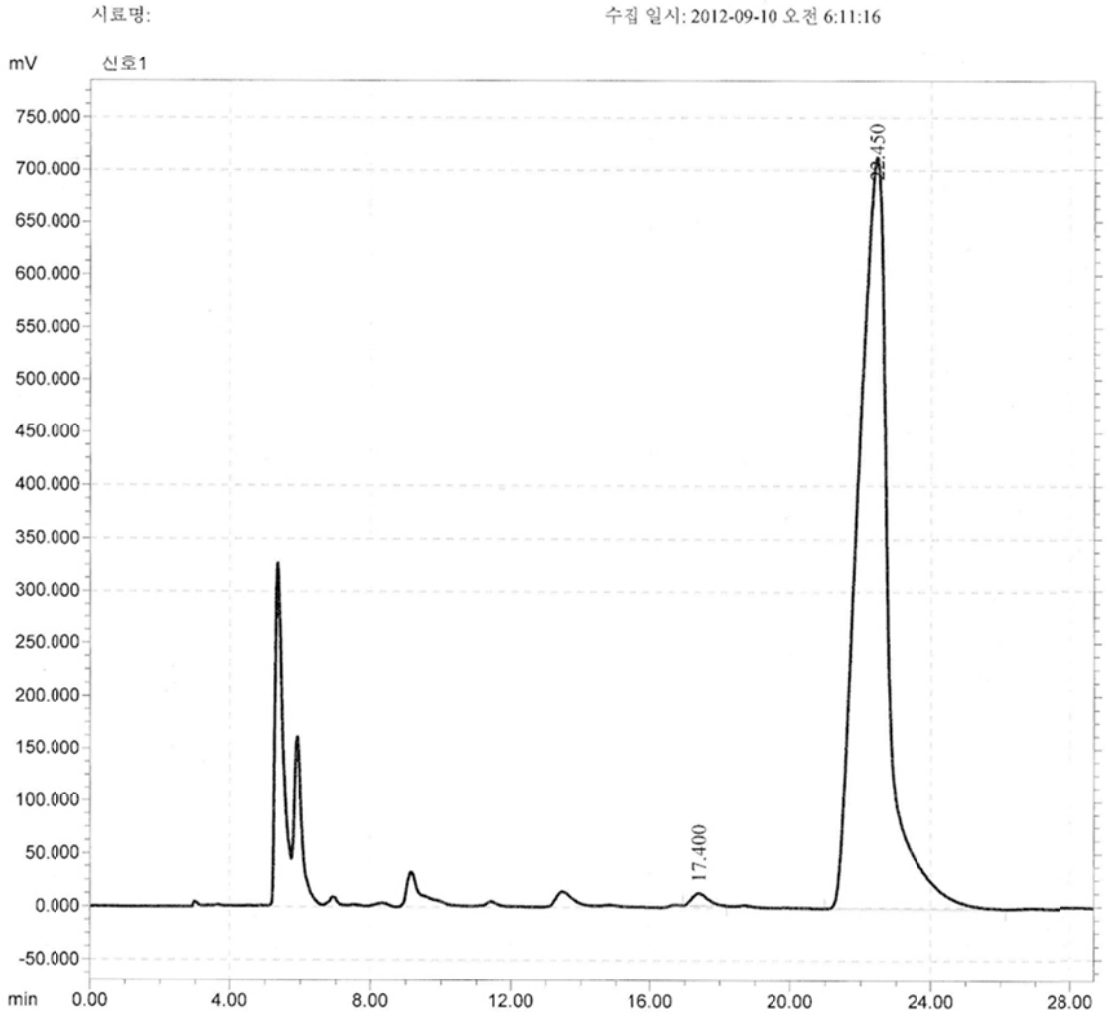
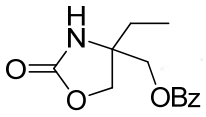


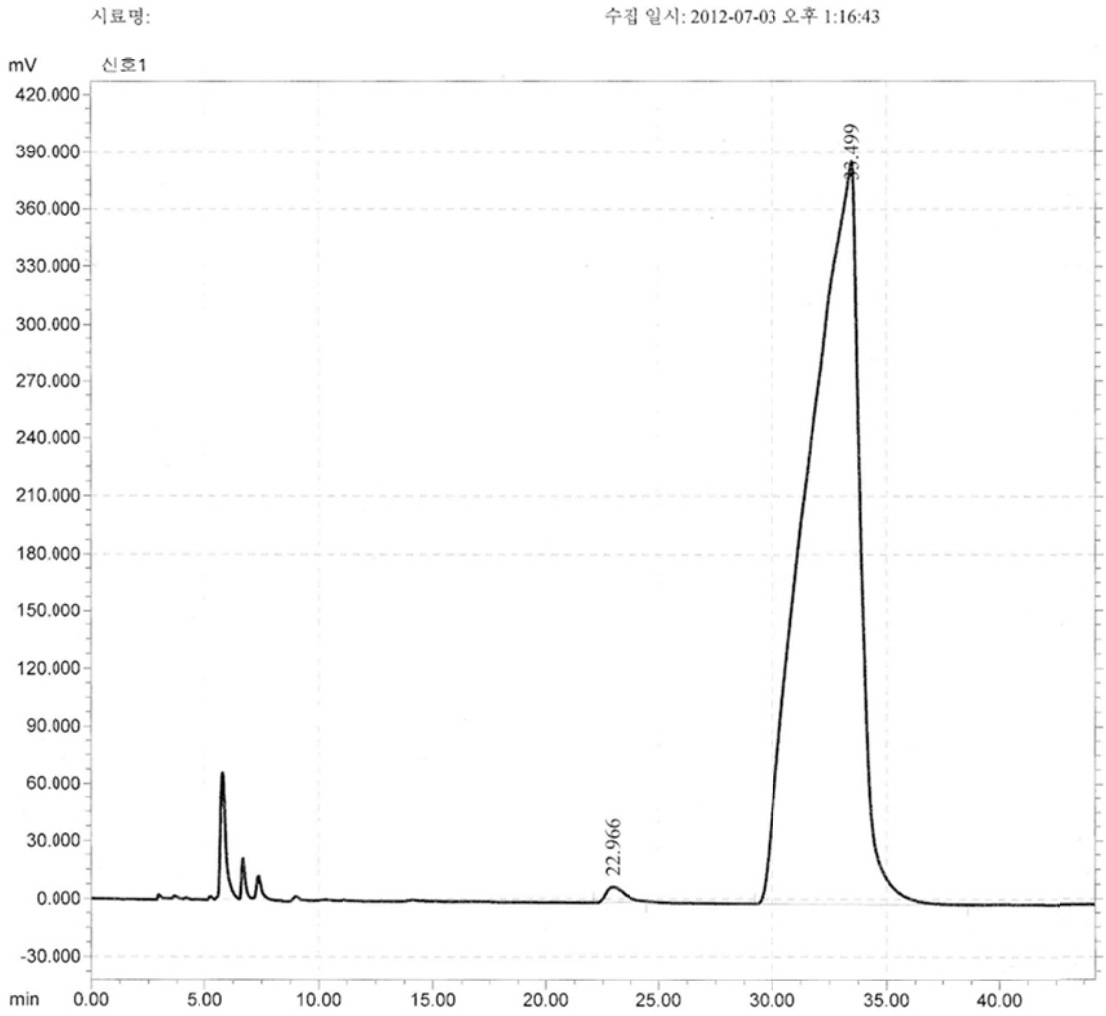
24



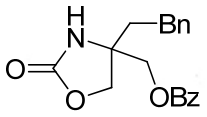
	머무름 시간 [min]	면적 [uV*sec]	면적%	표지
	17.400	371214.15	0.875	BB
	22.450	42041299.05	99.125	BB
Σ		42412513.20	100.000	



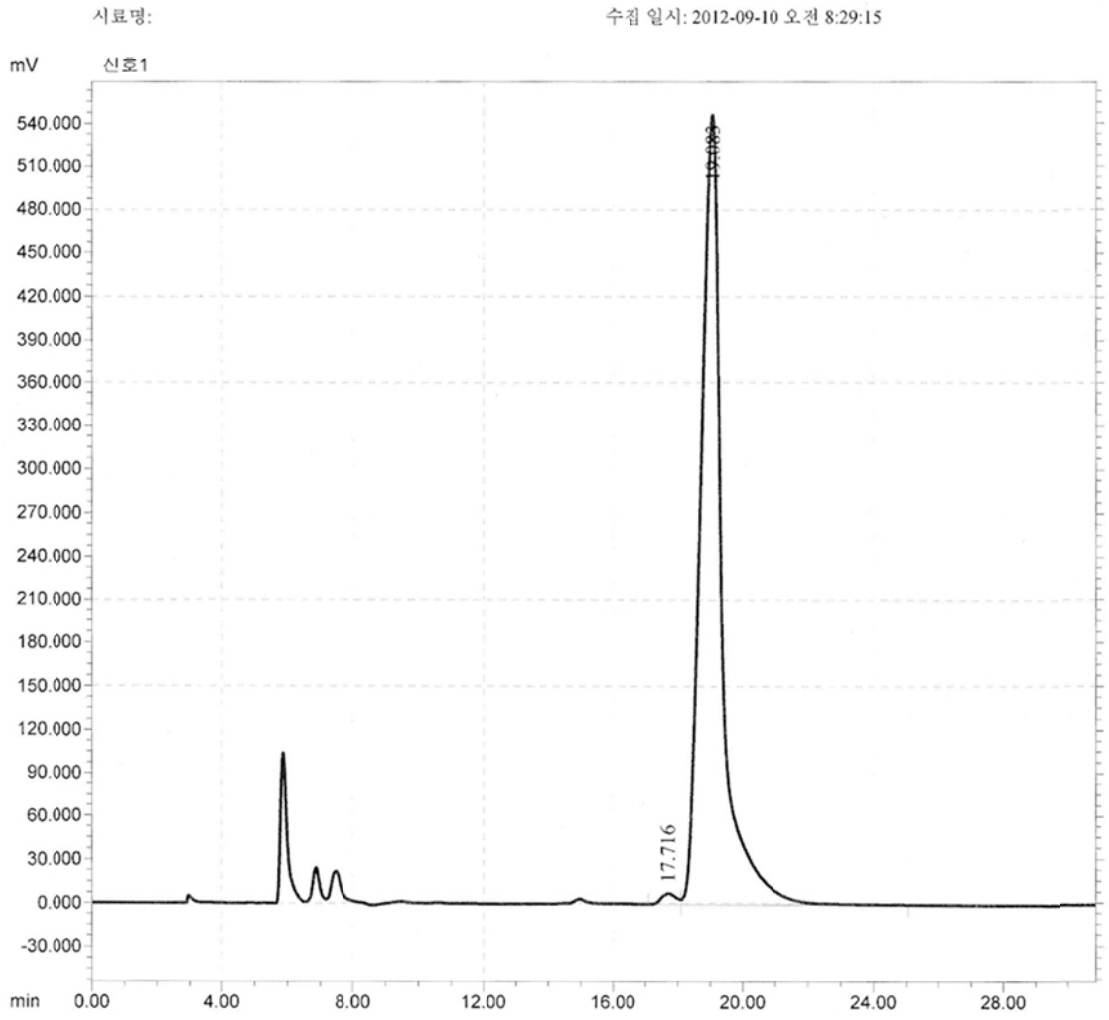
25



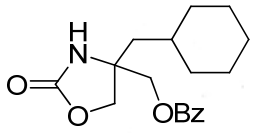
	머무름 시간 [min]	면적 [uV*sec]	면적% [%]	표지
⚠?	22.966	445172.65	0.720	BB
⚠?	33.499	61399006.96	99.280	BB
Σ		61844179.61	100.000	



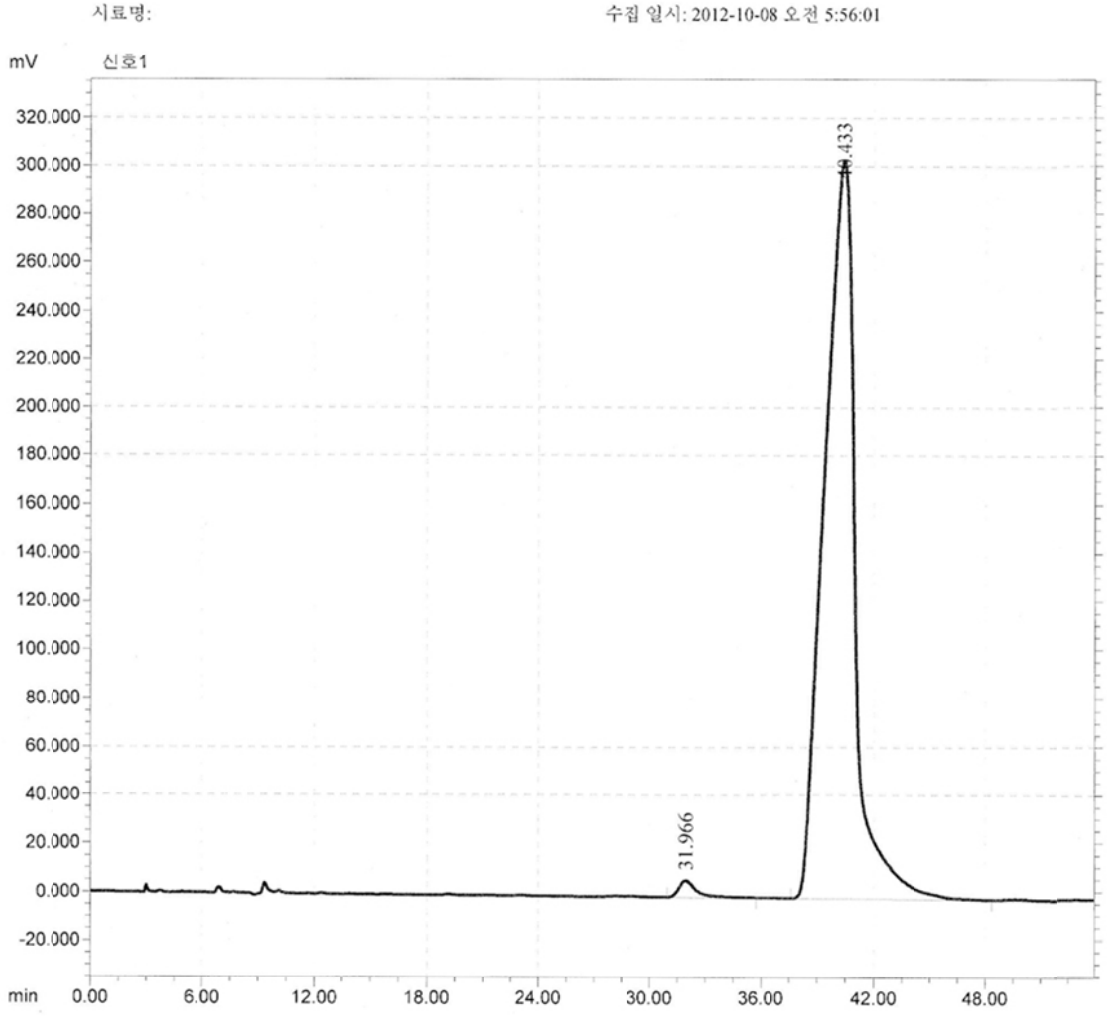
26



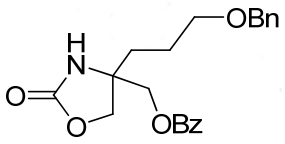
	머무름 시간 [min]	면적 [uV*sec]	면적% [%]	표지
	17.716	234982.79	0.945	BV
	19.083	24625759.72	99.055	VB
Σ		24860742.51	100.000	



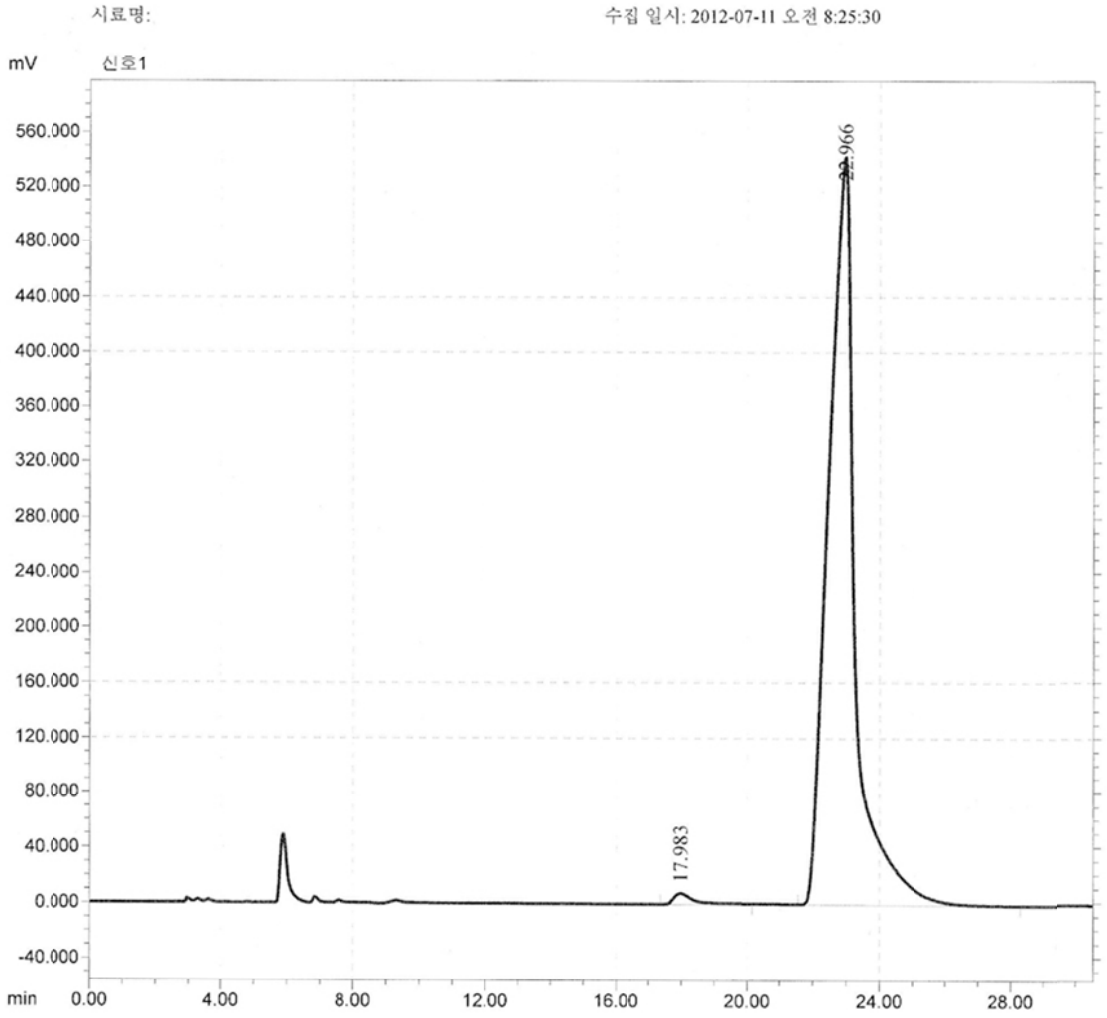
27



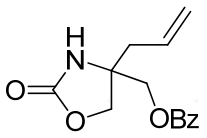
	머무름 시간 [min]	면적 [uV*sec]	면적%	표지
	31.966	439279.23	1.251	BB
	40.433	34661166.82	98.749	BB
Σ		35100446.05	100.000	



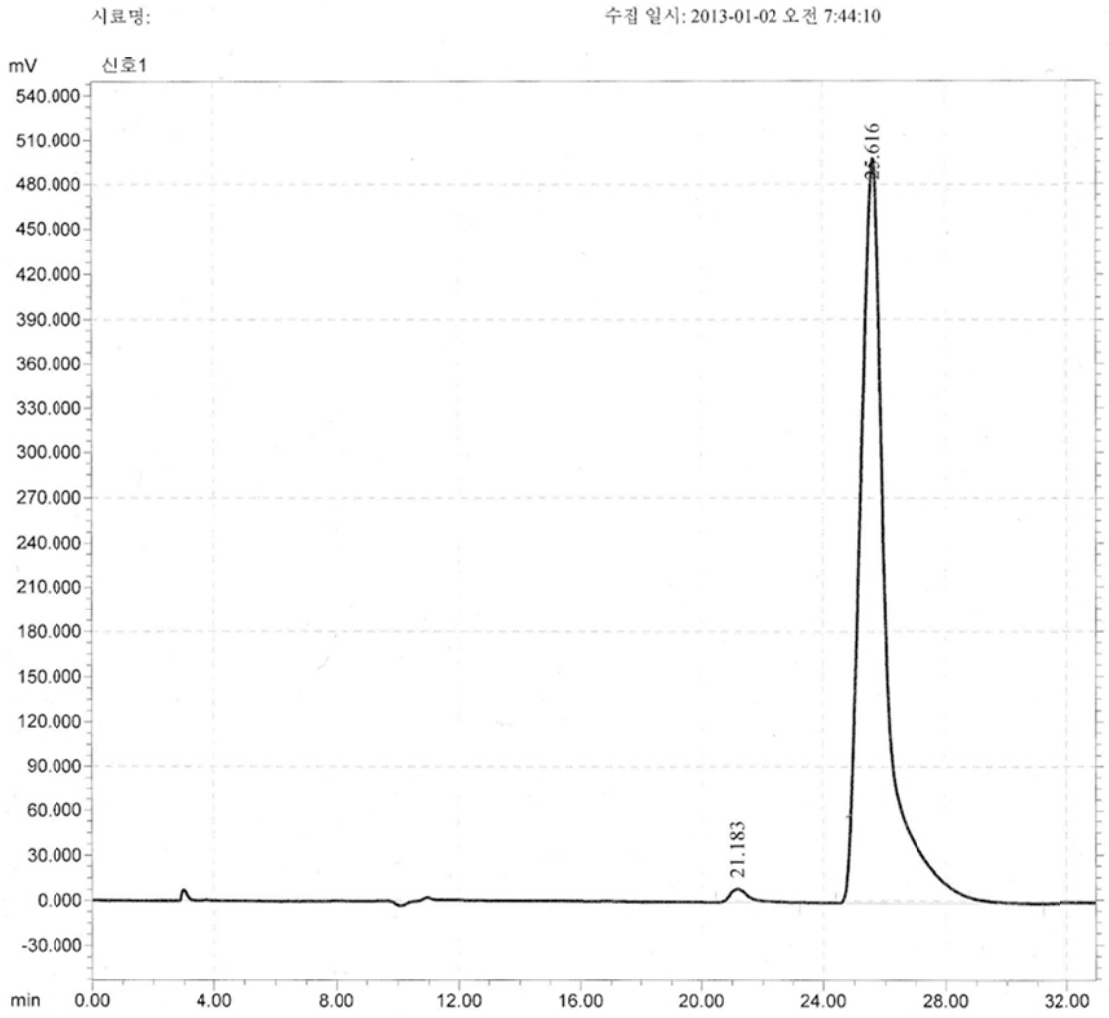
28



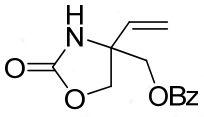
	머무름 시간 [min]	면적 [uV*sec]	면적% [%]	표지
1	17.983	318503.68	1.040	BB
2	22.966	30306135.96	98.960	BB
Σ		30624639.64	100.000	



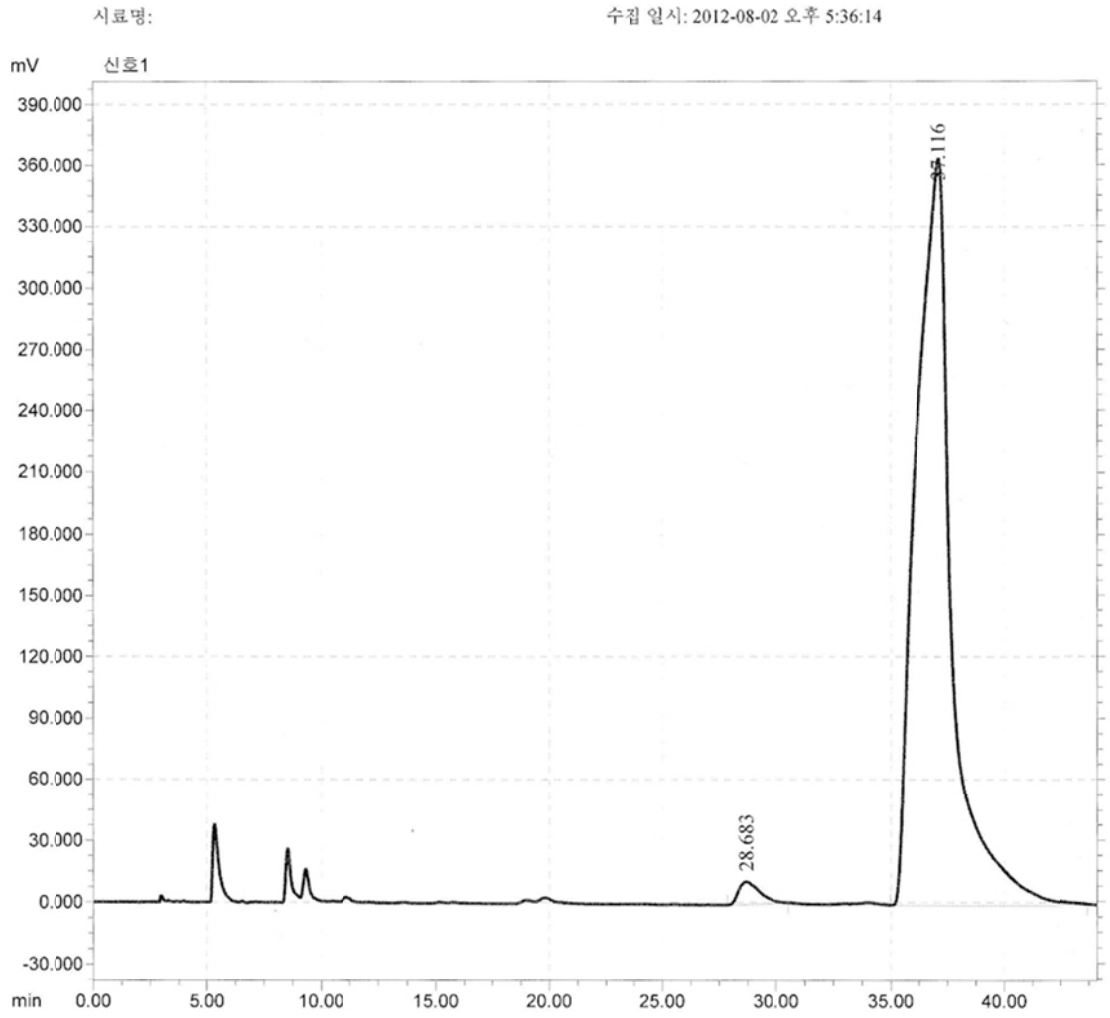
29



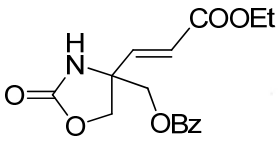
	머무름 시간 [min]	면적 [uV*sec]	면적% [%]	표지
	21.183	385567.90	1.340	BB
	25.616	28377737.94	98.660	BV
Σ		28763305.84	100.000	



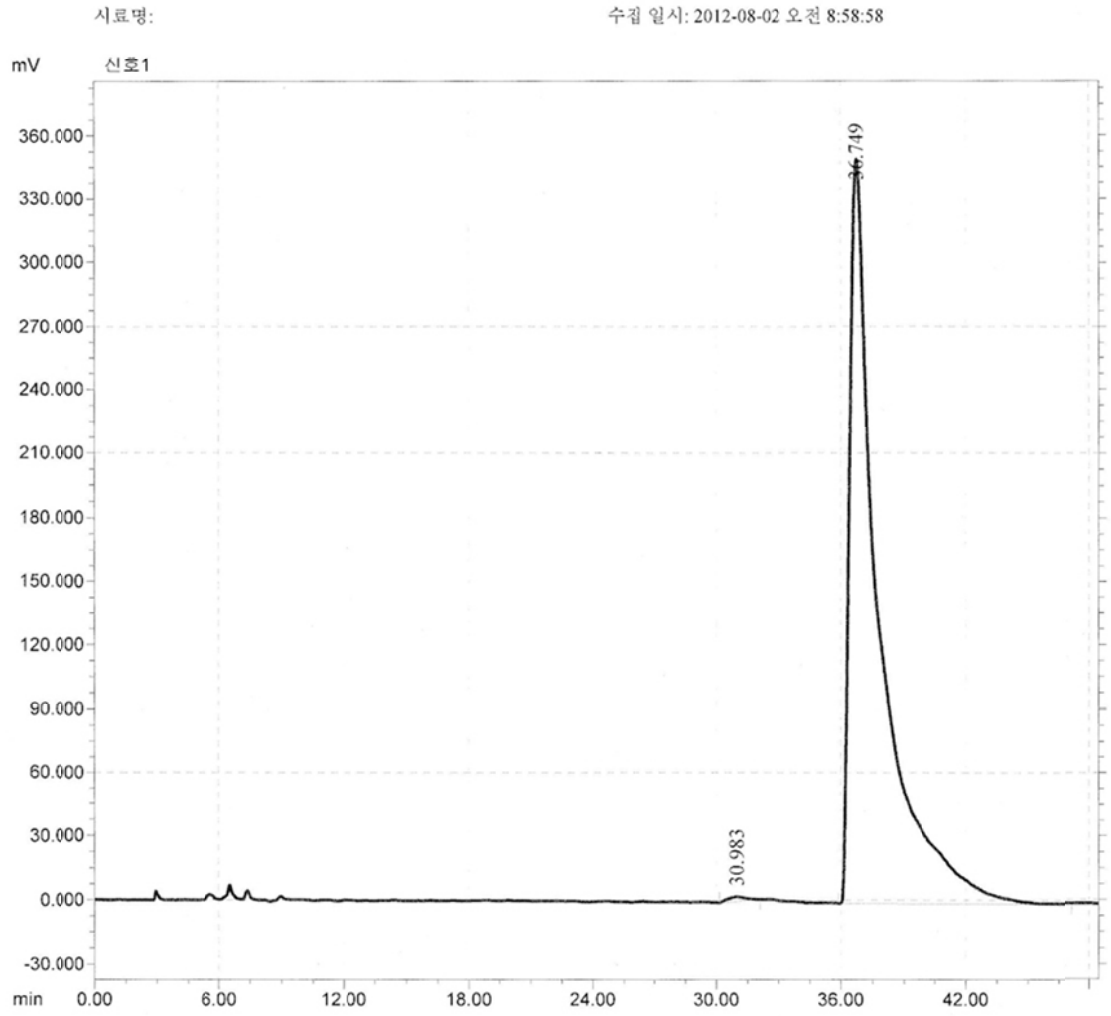
30



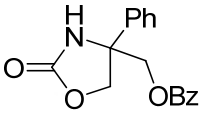
	머무름 시간 [min]	면적 [uV*sec]	면적%	표지
A?	28.683	698479.24	1.722	BB
A?	37.116	39852222.57	98.278	BB
Σ		40550701.81	100.000	



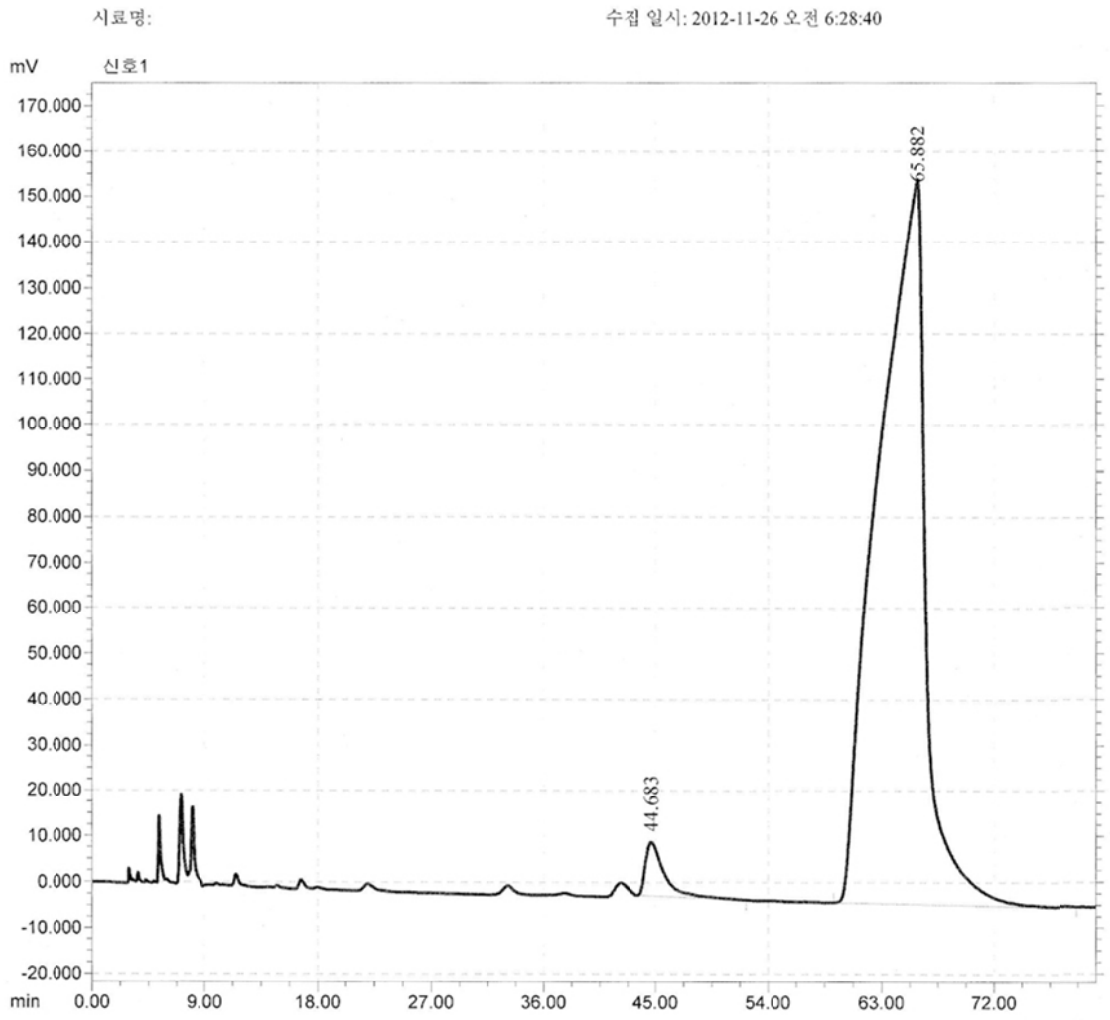
31



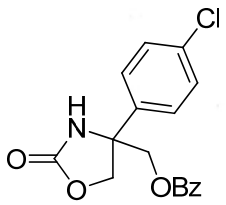
	머무름 시간 [min]	면적 [uV*sec]	면적% [%]	표지
	30.983	129688.25	0.380	BB
	36.749	33983620.58	99.620	BB
Σ		34113308.83	100.000	



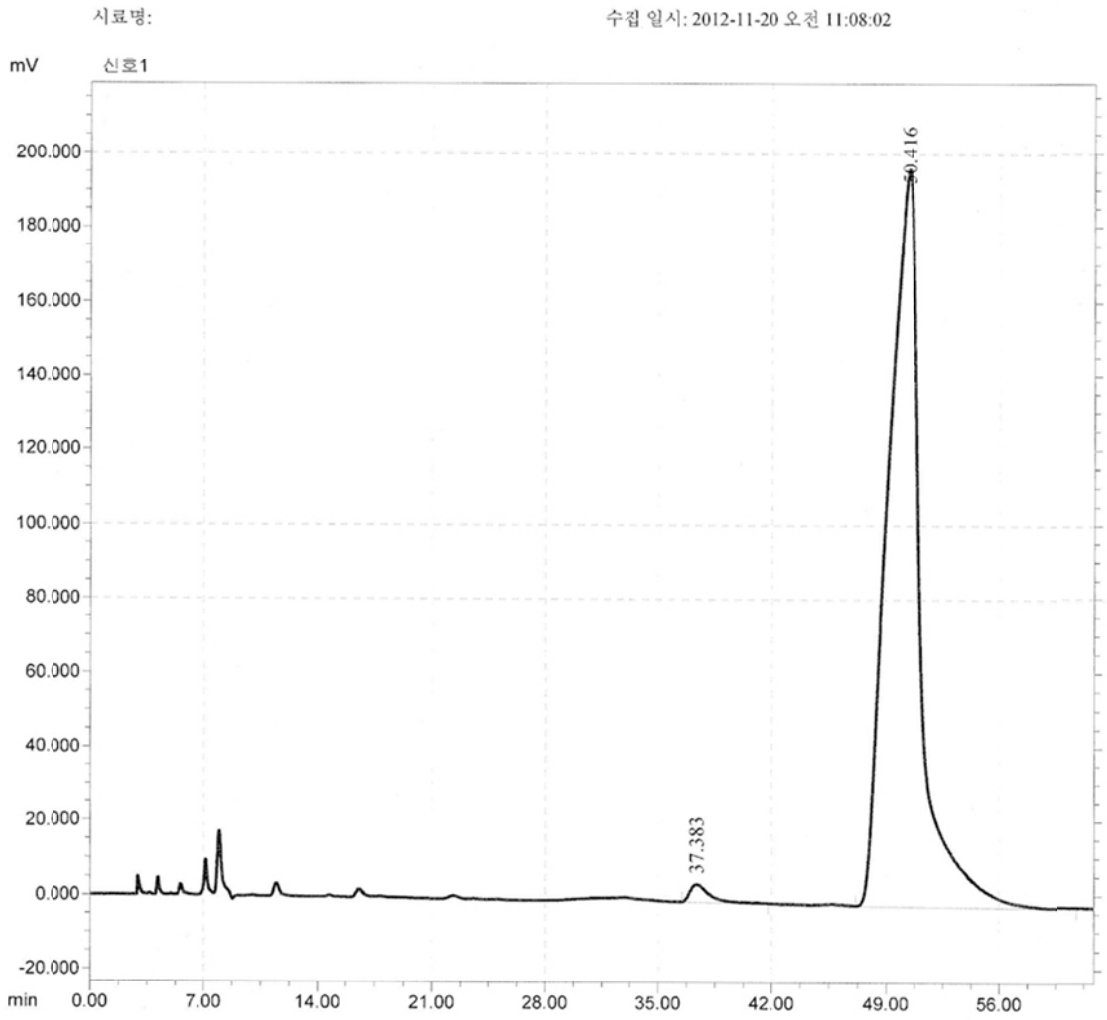
32



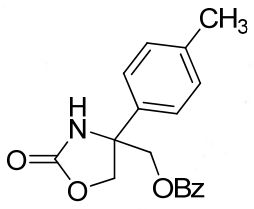
	머무름 시간 [min]	면적 [uV*sec]	면적%	표지
	44.683	1183391.15	2.756	BB
	65.882	41756436.82	97.244	BB
Σ		42939827.98	100.000	



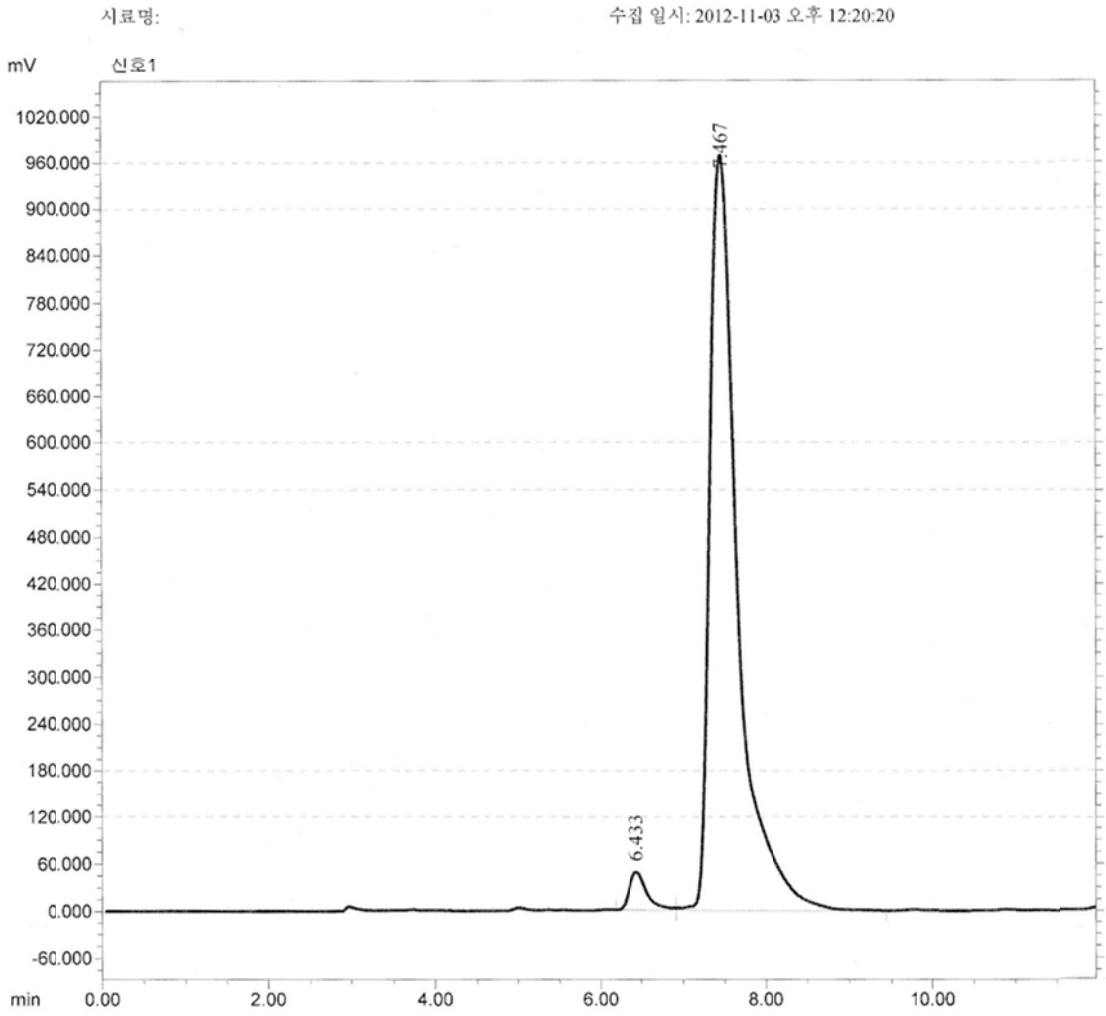
33



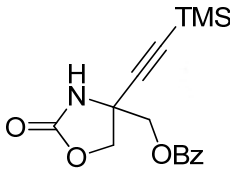
	머무름 시간 [min]	면적 [uV*sec]	면적%	표지
BA?	37.383	394799.98	1.387	BB
BA?	50.416	28074606.75	98.613	BB
Σ		28469406.72	100.000	



34



	머무름 시간 [min]	면적 [uV*sec]	면적%	표지
	6.433	706855.40	3.066	BV
	7.467	22347072.97	96.934	VB
Σ		23053928.38	100.000	



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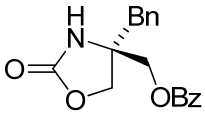
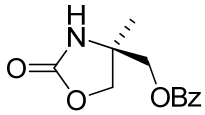
VI. Spectral Data of the Oxazolidinone Benzoates 11 and 24−35 Prepared from the Consecutive Asymmetric Desymmetrization and Kinetic Resolution



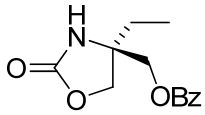
11

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 2H), 7.57 – 7.50 (m, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.34 – 7.23 (m, 3H), 7.22 – 7.15 (m, 2H), 6.52 (s, 1H), 4.32 – 4.26 (m, 3H), 4.19 (d, *J* = 11.4 Hz, 1H), 3.05 (d, *J* = 13.9 Hz, 1H), 2.96 (d, *J* = 13.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.13, 159.01, 134.06, 133.61, 130.24, 129.79, 129.15, 129.00, 128.67, 127.68, 71.27, 67.43, 60.35, 41.92. $[\alpha]_D^{14}$ = +15.6 (0.048 M in $CHCl_3$, 97.0% ee). HRMS (ESI) *m/z* calcd for $C_{18}H_{17}NNaO_4$ $[M+Na]^+$, 334.1050; found, 334.1065.



24

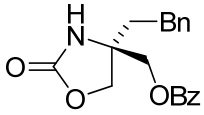
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 2H), 7.54 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 6.23 (s, 1H), 4.36 (d, *J* = 8.7 Hz, 1H), 4.31 (d, *J* = 11.4 Hz, 1H), 4.17 (d, *J* = 11.5 Hz, 1H), 4.12 (d, *J* = 8.8 Hz, 1H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.27, 159.00, 133.65, 129.86, 129.27, 128.72, 73.26, 68.89, 57.42, 23.11. $[\alpha]_D^{14}$ = +6.9 (0.042 M in $CHCl_3$, 96.5% ee). HRMS (ESI) *m/z* calcd for $C_{12}H_{13}NNaO_4$ $[M+Na]^+$, 258.0737; found, 258.0735.



25

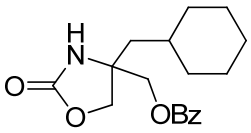
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (ddd, *J* = 8.6, 1.6, 0.8 Hz, 2H), 7.58 – 7.51 (m, 1H), 7.42 (ddt, *J* = 8.6, 6.9, 0.8 Hz, 2H), 6.16 (s, 1H), 4.37 – 4.29 (m, 2H), 4.23 – 4.15 (m, 2H), 1.82 –

1.64 (m, 2H), 1.01 (td, *J* = 7.6, 0.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.30, 159.24, 133.66, 129.85, 129.26, 128.72, 71.33, 67.68, 60.39, 28.73, 7.67. $[\alpha]_D^{14}$ = +2.4 (0.060 M in $CHCl_3$, 98.3% ee). HRMS (ESI) *m/z* calcd for $C_{13}H_{15}NNaO_4$ $[M+Na]^+$, 272.0893; found, 272.0891.



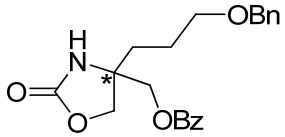
26

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H), 7.57 – 7.50 (m, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.31 – 7.23 (m, 2H), 7.22 – 7.13 (m, 3H), 6.77 (s, 1H), 4.39 (d, *J* = 11.5 Hz, 1H), 4.33 (d, *J* = 9.0 Hz, 1H), 4.26 (d, *J* = 11.5 Hz, 1H), 4.21 (d, *J* = 9.0 Hz, 1H), 2.73 (dd, *J* = 9.4, 7.5 Hz, 2H), 2.11 – 1.91 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.24, 159.46, 140.35, 133.63, 129.82, 129.17, 128.80, 128.69, 128.35, 126.54, 71.73, 67.81, 60.06, 37.74, 29.77. $[\alpha]_D^{13}$ = +11.2 (0.068 M in $CHCl_3$, 98.5% ee). HRMS (ESI) *m/z* calcd for $C_{19}H_{19}NNaO_4$ $[M+Na]^+$, 348.1206 ; found, 348.1212.



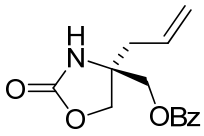
27

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.53 (ddt, *J* = 8.1, 7.0, 1.4 Hz, 1H), 7.40 (dd, *J* = 8.3, 7.1 Hz, 2H), 6.14 (s, 1H), 4.35 – 4.28 (m, 2H), 4.22 – 4.15 (m, 2H), 1.77 – 1.50 (m, 7H), 1.44 (ddq, *J* = 11.1, 5.9, 3.2, 2.7 Hz, 1H), 1.23 (dddd, *J* = 16.3, 7.0, 4.2, 1.5 Hz, 2H), 1.17 – 0.93 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.34, 159.16, 133.60, 129.83, 129.26, 128.71, 72.57, 68.21, 60.07, 43.76, 34.82, 34.62, 33.55, 26.24, 26.20, 26.02. $[\alpha]_D^{14}$ = +5.8 (0.063 M in $CHCl_3$, 98.1% ee). HRMS (ESI) *m/z* calcd for $C_{18}H_{23}NNaO_4$ $[M+Na]^+$, 340.1519; found, 340.1528.



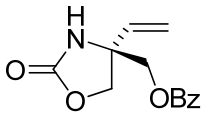
28

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 2H), 7.55 (ddt, *J* = 8.0, 7.0, 1.3 Hz, 1H), 7.45 – 7.36 (m, 2H), 7.36 – 7.22 (m, 5H), 6.26 (s, 1H), 4.48 (s, 2H), 4.34 (d, *J* = 9.7 Hz, 1H), 4.32 (d, *J* = 7.3 Hz, 1H), 4.21 (d, *J* = 11.5 Hz, 1H), 4.16 (d, *J* = 8.9 Hz, 1H), 3.50 (td, *J* = 5.9, 2.1 Hz, 2H), 1.92 – 1.62 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.12, 158.74, 137.93, 133.50, 129.70, 129.11, 128.58, 128.46, 127.76, 127.69, 73.12, 71.75, 69.55, 67.62, 59.58, 33.11, 23.80. $[\alpha]_D^{21}$ = +13.6 (0.041 M in $CHCl_3$, 97.5% ee). HRMS (ESI) *m/z* calcd for $C_{21}H_{23}NNaO_5$ $[M+Na]^+$, 392.1468; found, 392.1465.



29

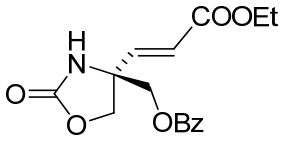
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (ddt, *J* = 7.5, 1.3, 0.7 Hz, 2H), 7.61 – 7.53 (m, 1H), 7.47 – 7.40 (m, 2H), 5.85 – 5.72 (m, 1H), 5.67 (s, 1H), 5.31 – 5.20 (m, 2H), 4.38 (dd, *J* = 11.7, 0.7 Hz, 1H), 4.32 (dd, *J* = 8.9, 0.7 Hz, 1H), 4.24 (dd, *J* = 3.1, 0.7 Hz, 1H), 4.22 (dd, *J* = 5.7, 0.7 Hz, 1H), 2.55 – 2.39 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.24, 158.61, 133.76, 130.15, 129.87, 129.18, 128.78, 121.75, 71.34, 67.54, 59.69, 40.63. $[\alpha]_D^{29}$ = −2.5 (0.076 M in $CHCl_3$, 97.9% ee). HRMS (ESI) *m/z* calcd for $C_{14}H_{15}NNaO_4$ $[M+Na]^+$, 284.0893; found, 284.0881.



30

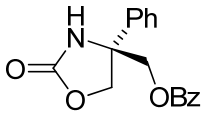
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H), 7.53 (ddt, *J* = 8.0, 7.0, 1.4 Hz, 1H), 7.43 – 7.36 (m, 2H), 6.63 (s, 1H), 5.91 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.47 (d, *J* = 17.3 Hz, 1H), 5.36 (d, *J* = 10.7 Hz, 1H), 4.44 – 4.37 (m, 2H), 4.29 (d, *J* = 11.5 Hz, 1H), 4.20 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.22, 159.26, 135.67, 133.65, 129.86, 129.15, 128.69, 117.74,

72.46, 67.52, 61.53. $[\alpha]_D^{24}$ = −46.8 (0.044 M in $CHCl_3$, 97.1% ee). HRMS (EI) calcd for $C_{13}H_{13}NNaO_4$ $[M+Na]^+$, 270.0737; found, 270.0733.



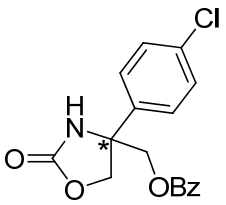
31

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 2H), 7.55 (ddt, *J* = 7.9, 6.9, 1.3 Hz, 1H), 7.41 (dd, *J* = 8.4, 7.1 Hz, 2H), 6.94 (d, *J* = 15.8 Hz, 1H), 6.61 (s, 1H), 6.20 (d, *J* = 15.8 Hz, 1H), 4.47 (d, *J* = 2.7 Hz, 1H), 4.44 (s, 1H), 4.34 (d, *J* = 11.6 Hz, 1H), 4.24 (d, *J* = 9.0 Hz, 1H), 4.20 (q, *J* = 6.8 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.07, 165.43, 158.66, 143.61, 133.84, 129.91, 128.88, 128.76, 123.88, 71.75, 67.13, 61.29, 61.12, 14.28. $[\alpha]_D^{15}$ = −45.7 (0.063 M in $CHCl_3$, 96.5% ee). HRMS (ESI) *m/z* calcd for $C_{16}H_{17}NNaO_6$ $[M+Na]^+$, 342.0948; found, 342.0946.



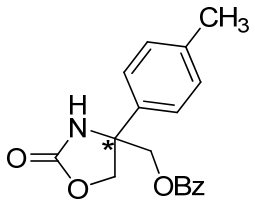
32

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 2H), 7.54 – 7.48 (m, 1H), 7.45 – 7.32 (m, 8H), 7.09 (s, 1H), 4.72 (d, *J* = 8.7 Hz, 1H), 4.59 (d, *J* = 11.7 Hz, 1H), 4.52 (d, *J* = 11.7 Hz, 1H), 4.44 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.15, 159.36, 139.25, 133.48, 129.72, 129.27, 128.95, 128.65, 128.53, 124.87, 73.83, 69.18, 63.16. $[\alpha]_D^{13}$ = −57.3 (0.067 M in $CHCl_3$, 99.2% ee). HRMS (ESI) *m/z* calcd for $C_{17}H_{15}NNaO_4$ $[M+Na]^+$, 320.0893; found, 320.0899.



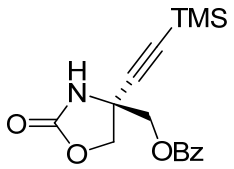
33

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.90 (m, 2H), 7.52 (ddt, *J* = 7.9, 7.0, 1.2 Hz, 1H), 7.41 – 7.33 (m, 4H), 7.32 – 7.26 (m, 2H), 7.20 (d, *J* = 2.1 Hz, 1H), 4.69 (dd, *J* = 8.7, 0.9 Hz, 1H), 4.53 (t, *J* = 1.1 Hz, 2H), 4.39 (dd, *J* = 8.7, 0.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.21, 159.38, 137.97, 134.89, 133.75, 129.86, 129.62, 128.94, 128.72, 128.23, 127.55, 127.46, 126.56, 73.82, 68.98, 63.05. $[\alpha]_D^{26}$ = −32.0 (0.090 M in $CHCl_3$, 94.5% ee). HRMS (ESI) *m/z* calcd for $C_{17}H_{14}ClNNaO_4$ $[M+Na]^+$, 354.0504; found, 354.0507.



34

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.91 (m, 2H), 7.51 (ddt, *J* = 7.6, 6.9, 1.4 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 2.6 Hz, 4H), 7.11 (s, 1H), 4.69 (d, *J* = 8.6 Hz, 1H), 4.57 (d, *J* = 11.7 Hz, 1H), 4.48 (d, *J* = 11.7 Hz, 1H), 4.41 (d, *J* = 8.7 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.30, 159.56, 138.63, 136.40, 133.58, 130.02, 129.86, 129.14, 128.65, 124.91, 74.08, 69.33, 63.10, 21.18. $[\alpha]_D^{28}$ = −35.9 (0.077 M in $CHCl_3$, 97.2% ee). HRMS (ESI) *m/z* calcd for $C_{18}H_{17}NNaO_4$ $[M+Na]^+$, 334.1050; found, 334.1052.

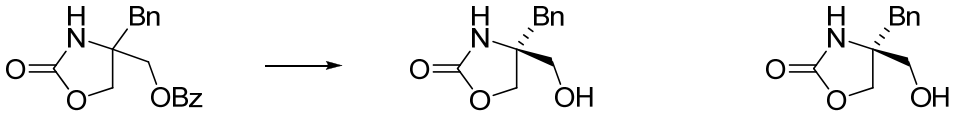


35

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 2H), 7.56 (ddt, *J* = 8.0, 7.0, 1.3 Hz, 1H), 7.46 – 7.39 (m, 2H), 5.77 (s, 1H), 4.54 – 4.49 (m, 2H), 4.46 (d, *J* = 8.7 Hz, 1H), 4.33 (d, *J* = 11.5 Hz, 1H), 0.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.00, 157.80, 133.78, 129.94, 129.06, 128.73, 100.42, 93.11, 72.64, 67.61, 55.19, –0.32. $[\alpha]_D^{27}$ = +25.5 (0.063 M in $CHCl_3$, 93.9% ee). HRMS (ESI) *m/z* calcd for $C_{16}H_{19}NNaO_4Si$ $[M+Na]^+$, 340.0976; found, 340.0968.

VII. Determination of the Absolute Configuration of the Oxazolidinone Benzoates 11 and 24-35

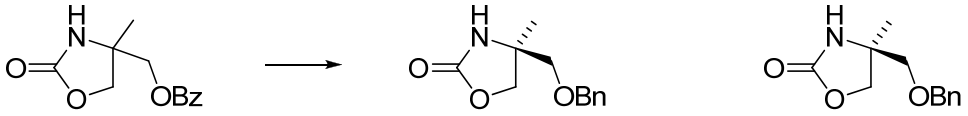
1) The oxazolidinone benzoate **11**



11 **10** (prepared) **(S)-10** (known)

To **11** (31 mg, 0.10 mmol) in MeOH (1 mL) was added K_2CO_3 (5 mg) at −20°C and the mixture was stirred at that temperature for a day. The resulting solution was directly loaded on a silica gel column, and eluted with EtOAc/hexane (1/3) and then 5% MeOH in CH_2Cl_2 to afford the alcohol **10** (19 mg, 91% yield). $[\alpha]_D^{22}$ of **10** = −23.0 (*c* 0.4, $CHCl_3$, measured, 95.5% ee) vs $[\alpha]_D^{26}$ of (*S*)-**10** = −24.3 (*c* 0.4, $CHCl_3$, known, >99% ee).[16] It was determined that the major enantiomers of our synthetic **10** and **11** have (*S*)-configurations, respectively.

2) The oxazolidinone benzoate **24**

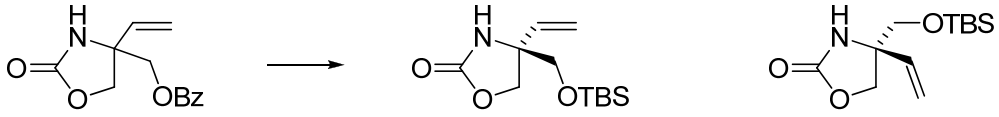


24 **58** (prepared) **(S)-58** (known)

To **24** (12 mg, 0.051 mmol) in MeOH (1 mL) was added K_2CO_3 (5 mg) at −20°C and the mixture was stirred at that temperature for a day. The resulting solution was directly loaded on a silica gel column, and eluted with EtOAc/hexane (1/3) and then 5% MeOH in CH_2Cl_2 to furnish the corresponding alcohol (6.3 mg, 94% yield). The alcohol (6.3 mg, 0.048 mmol) was dissolved in a mixture of THF (2 mL) and DMF (0.5 mL), and then tetra-*n*-butylammonium iodide (1 mg), benzyl chloride (9 μL, 0.070 mmol) and NaH (60% dispersion in mineral oil, 4 mg, 0.10 mmol) were added sequentially in an ice-water bath. The mixture was stirred at that temperature for 2 hours and then at room temperature for 10 hours. After quenching the reaction with saturated aqueous NH_4Cl (1 mL), the normal work-up with EtOAc (2 mL, three times) and column chromatography (EtOAc/hexane = 1/3, then 1/1) gave the benzyl ether **58** (4.5 mg, 42% yield, 95% ee). The HPLC retention time of the major enantiomer of **58** (6.2 minutes, measured) was identical with that of (*S*)-**58** (6.2 minutes,

known) using a chiral column DAICEL OD with 30% *i*-PrOH in hexane as an eluent and a flow rate of 1.0 mL/min.[17] That of the minor enantiomer was found to be 9.0 minutes, which is the reported value of (*R*)-**58**. It was determined that the major enantiomers of our synthetic **58** and **24** have (*S*)-configurations, respectively.

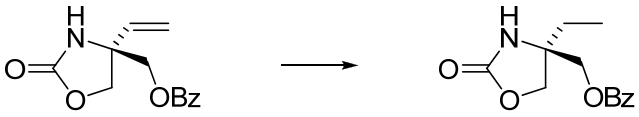
3) The oxazolidinone benzoate **30**



30 **59** (prepared) **(S)-59** (known)

To **30** (48.4 mg, 0.20 mmol) in MeOH (1 mL) was added K_2CO_3 (5 mg) at −20°C and the mixture was stirred at that temperature for a day. The resulting solution was directly loaded on a silica gel column, and eluted with EtOAc/hexane (1/3) and then 5% MeOH in CH_2Cl_2 to afford the corresponding alcohol (27.5 mg, 96% yield). Imidazole (38.8 mg, 0.57 mmol) and TBSCl (57.3 mg, 0.38 mmol) were added to the alcohol (27.5 mg, 0.19 mmol) in an ice-water bath in sequence, and subsequently the resulting solution was stirred at that temperature for an hour and then at room temperature for a day. After quenching the reaction with saturated aqueous NH_4Cl (1 mL), the normal work-up with EtOAc (2 mL, three times) and chromatographic purification (EtOAc/hexane = 1/10, then 1/5) delivered the silyl ether **59** (39.6 mg, 81% yield). $[\alpha]_D^{23}$ of **59** = −69.3 (*c* 0.48, $CHCl_3$, measured) vs $[\alpha]_D^{20}$ of (*S*)-**59** = +66.6 (*c* 0.36, $CHCl_3$, known, >99% ee).[18] It was determined that the major enantiomers of our synthetic **59** and **30** have (*R*)- and (*S*)-configuration, respectively.

4) The oxazolidinone benzoate **25**

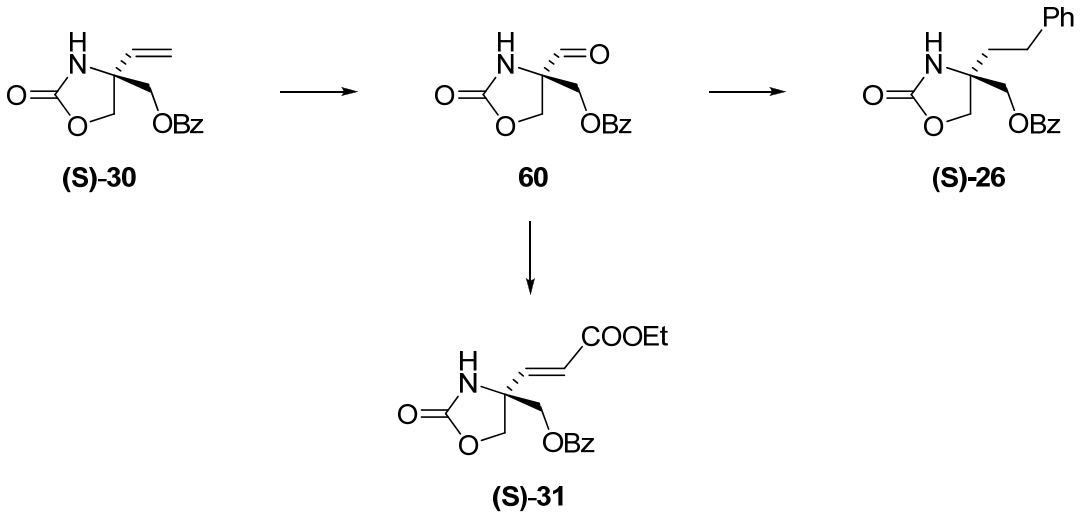


(S)-30 **(S)-25**

To **30** (10 mg, 0.04 mmol) in EtOAc (1 mL) was added 10% Pd/C (3 mg) and the mixture was stirred under an atmospheric hydrogen balloon at room temperature for 4 hours. The resulting solution was filtered through celite (1.5 g) with EtOAc (6 mL) and evaporated in vacuo. The residue was separated chromatographically (EtOAc/hexane = 1/3, then 1/1) to

give rise to **25** (9.9 mg, 99% yield, 98% ee). Since its chiral HPLC chromatogram was identical with that of **25** prepared from **13** by consecutive desymmetrization and kinetic resolution, the major enantiomer of **25** was determined to have (*S*)-configuration.

5) The oxazolidinone benzoates **26** and **31**

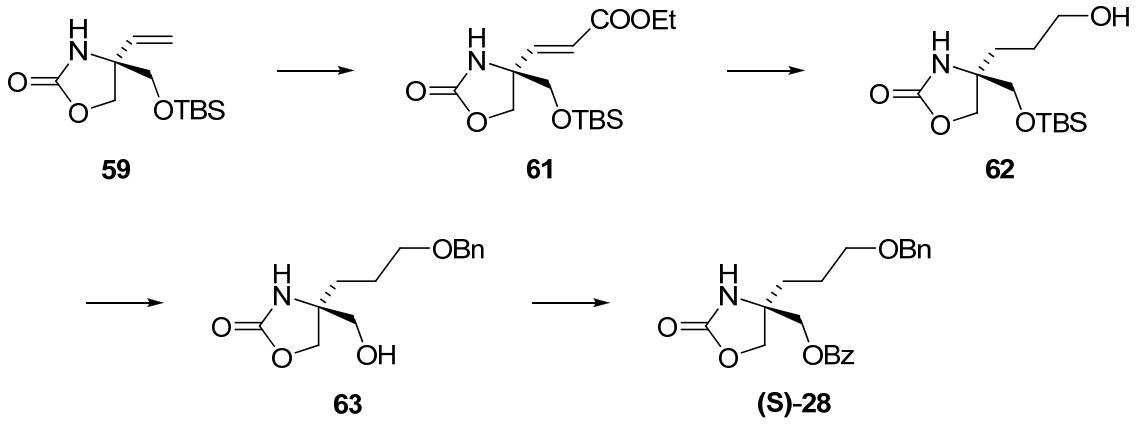


To (*S*)-**30** (20 mg, 0.081 mmol) in a 4 to 1 mixture of THF and water (2.5 mL) were added $NaIO_4$ (173 mg, 0.81 mmol) and OsO_4 (3 mg) in an ice-water bath, and the mixture was stirred at room temperature for 12 hours. After quenching the reaction with saturated aqueous Na_2SO_3 (1 mL), the normal work-up with EtOAc (3 mL, three times) and chromatographic purification (EtOAc/hexane =1/1, then 5% MeOH in CH_2Cl_2) produced the aldehyde **60** (19.3 mg, 96% yield). To benzyltriphenylphosphonium chloride (94 mg, 0.24 mmol) in THF (2 mL) was injected KHMDS (0.5 M in toluene, 0.48 mL, 0.24 mmol) at 0°C, the mixture was stirred at that temperature for 30 minutes, and cooled down to −78°C. The aldehyde **60** (20 mg, 0.08 mmol) was added to the cooled ylid and stirred at that temperature for 2 hours. The reaction was quenched with saturated aqueous NH_4Cl (1 mL), and the following normal work-up with EtOAc (2 mL, three times) and chromatographic separation (EtOAc/hexane = 1/3) provided the corresponding alkenes (23.8 mg, 92% yield). To the alkenes (23.8 mg, 0.074 mmol) in EtOAc (1 mL) was added 10% Pd/C (2 mg) and the mixture was stirred under an atmospheric hydrogen balloon at room temperature for 4 hours. The resulting solution was filtered through celite (1.5 g) with EtOAc (6 mL) and evaporated in vacuo. The residue was separated chromatographically (EtOAc/hexane = 1/3, then 1/1) to procure (*S*)-**26** (23.4 mg, 97% yield, 97% ee). Since its chiral HPLC chromatogram was identical with that of **26** prepared from **14**

by consecutive desymmetrization and kinetic resolution, the major enantiomer of **26** was determined to have (*S*)-configuration.

To the aldehyde **60** (19.3 mg, 0.077 mmol) in CH_2Cl_2 (1 mL) was added (carbethoxy-methylene)triphenylphosphorane (53.5 mg, 0.154 mmol) and the mixture was stirred at room temperature for 4 hours. The subsequent normal work-up with EtOAc (2 mL, three times) and chromatographic purification (EtOAc/hexane = 1/3, then 1/1) rendered (*S*)-**31** (22.2 mg, 91% yield, 93.5% ee). Since its chiral HPLC chromatogram was identical with that of **31** prepared from **19** by consecutive desymmetrization and kinetic resolution, the major enantiomer of **31** was determined to have (*S*)-configuration.

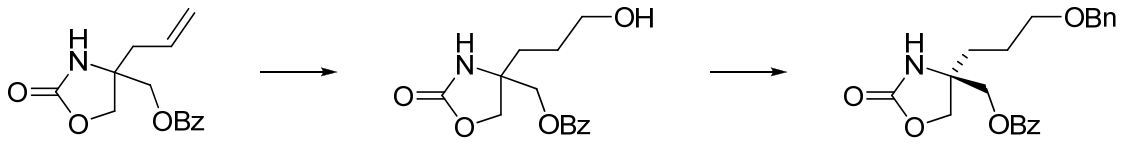
6) The oxazolidinone benzoate **28**



To **59** (20 mg, 0.081 mmol) in a 4 to 1 mixture of THF and water (2.5 mL) were $NaIO_4$ (173 mg, 0.809 mmol) and OsO_4 (3 mg) in an ice-water bath, and the mixture was stirred at room temperature for 12 hours. After quenching the reaction with saturated aqueous Na_2SO_3 (1 mL), the normal work-up with EtOAc (3 mL, three times) and chromatographic purification (EtOAc/hexane =1/1, then 5% MeOH in CH_2Cl_2) revealed the corresponding aldehyde (20 mg, 99% yield). To the aldehyde (20 mg, 0.080 mmol) in CH_2Cl_2 (1 mL) was added (carbethoxymethylene)triphenylphosphorane (56 mg, 0.160 mmol) and the mixture was stirred at room temperature for 3 hours. The subsequent normal work-up with EtOAc (2 mL, three times) and chromatographic purification (EtOAc/hexane = 1/5, then 1/3) afforded **61** (25.1 mg, 97% yield). To **61** (25.1 mg, 0.078 mmol) in EtOAc (1 mL) was added 10% Pd/C (2 mg) and the mixture was stirred under an atmospheric hydrogen balloon at room temperature for 8 hours. The resulting solution was filtered through celite (1.5 g) with EtOAc

(6 mL) and evaporated in vacuo. The residue was separated chromatographically (EtOAc/hexane = 1/5, then 1/3) to furnish the corresponding saturated ester (25 mg, 99% yield). To the saturated ester (25 mg, 0.078 mmol) in THF (1.5 mL) was injected diisobutylaluminum hydride (1.0 M in THF, 0.18 mL, 0.18 mmol) at −78°C and the mixture was stirred at that temperature for 8 hours. After quenching the reaction with saturated aqueous NH_4Cl (1 mL), the normal work-up with EtOAc (2 mL, three times) followed by the chromatographic separation (EtOAc/hexane = 1/3, then 1/1) to yield the alcohol **62** (19.8 mg, 89% yield). **62** (19.8 mg, 0.069 mmol) was dissolved in a mixture of THF (2 mL) and DMF (0.5 mL), and then tetra-*n*-butylammonium iodide (1 mg), benzyl chloride (16 μL, 0.138 mmol) and NaH (60% dispersion in mineral oil, 4.2 mg, 0.104 mmol) were added sequentially in an ice-water bath. The mixture was stirred at that temperature for 2 hours and then at room temperature for 10 hours. After quenching the reaction with saturated aqueous NH_4Cl (2 mL), the normal work-up with Et_2O (2 mL, three times) and column chromatography (EtOAc/hexane = 1/7, then 1/3) gave the corresponding benzyl ether (18.2 mg, 69% yield). To the benzyl ether (18.2 mg, 0.047 mmol) in CH_2Cl_2 (1 mL) was added TBAF (75 wt%, 0.1 mL) in an ice-water bath and the mixture was stirred at that temperature for an hour. After adding saturated aqueous NH_4Cl (1 mL), the normal work-up with EtOAc (2 mL, three times) and chromatographic purification (EtOAc/hexane = 1/1, then 5% MeOH in CH_2Cl_2) gave the alcohol **63** (9.3 mg, 74% yield). To **63** (9.3 mg, 0.035 mmol) in CH_2Cl_2 (1 mL) were added imidazole (9.5 mg, 0.14 mmol) and benzoyl chloride (8 μL, 0.070 mmol) at room temperature, and the mixture was stirred at that temperature for 12 hours. After quenching the reaction with saturated aqueous NH_4Cl (1 mL), the normal work-up with EtOAc (2 mL, three times) followed by chromatographic separation (EtOAc/hexane = 1/3, then 1/1) to deliver (*S*)-**28** (11.5 mg, 89% yield, 96.8% ee). Since its chiral HPLC chromatogram was identical with that of **28** prepared from **16** by consecutive desymmetrization and kinetic resolution, the major enantiomer of **28** was determined to have (*S*)-configuration.

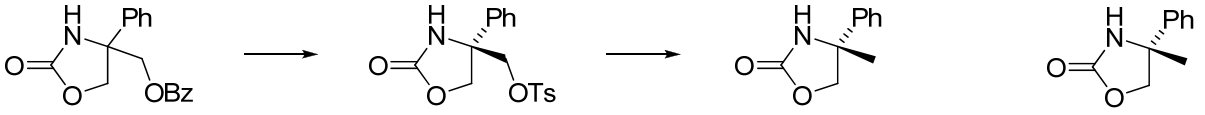
7) The oxazolidinone benzoate **29**



29 **64** **28**

To **29** (13 mg, 0.05 mmol) in THF (1 mL) was injected 9-BBN (0.5 M in THF, 0.05 mL, 0.25 mmol) in an ice-water bath and the mixture was stirred at room temperature for 8 hours. The reaction was quenched with aqueous $NaBO_3$ solution (41 mg in 2 mL of water) in an ice-water bath and the resulting solution was stirred at that temperature for 12 hours. After adding saturated aqueous NH_4Cl (1 mL) to the solution, all the volatile materials were evaporated in vacuo and the residue was purified chromatographically (EtOAc/hexane =1/1, then 5% MeOH in CH_2Cl_2) to give the corresponding alcohol (12.8 mg, 92% yield). The alcohol (12.8 mg, 0.046 mmol) was dissolved in a mixture of THF (2 mL) and DMF (0.5 mL), and then tetra-*n*-butylammonium iodide (1 mg), benzyl chloride (11 μL, 0.092 mmol) and NaH (60% dispersion in mineral oil, 2.8 mg, 0.070 mmol) were added sequentially in an ice-water bath. The mixture was stirred at that temperature for 2 hours and then at room temperature for 10 hours. After quenching the reaction with saturated aqueous NH_4Cl (2 mL), the normal work-up with Et_2O (2 mL, three times) and column chromatography (EtOAc/hexane = 1/3, then 1/1) gave rise to the benzyl ether **28** (10.5 mg, 62% yield, 97.8% ee). Since its chiral HPLC chromatogram was identical with that of (*S*)-**28** prepared from **59** or **16** by consecutive desymmetrization and kinetic resolution, the major enantiomer of **29** was determined to have (*S*)-configuration.

8) The oxazolidinone benzoate **32**

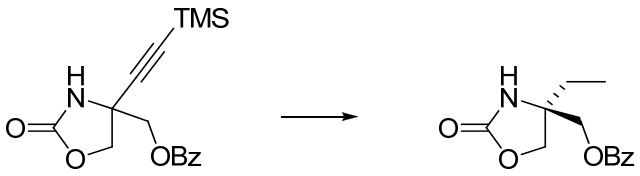


32 **65** **66** (prepared) **(S)-66** (known)

To **32** (15 mg, 0.05 mmol) in MeOH (1 mL) was added K_2CO_3 (5 mg) at −20°C and the mixture was stirred at that temperature for a day. The resulting solution was directly loaded

on a silica gel column, and eluted with EtOAc/hexane (1/3) and then 5% MeOH in CH_2Cl_2 to produce the corresponding alcohol (9.1 mg, 94% yield). To the alcohol (9.1 mg, 0.047 mmol) in CH_2Cl_2 (1 mL) were added Et_3N (20 μL, 0.141 mmol) and *p*-TsCl (27 mg, 0.141 mmol) in an ice-water bath, and the mixture was stirred at room temperature for 12 hours. After quenching the reaction with saturated aqueous NH_4Cl (1 mL), the normal work-up with EtOAc (2 mL, three times) and the subsequent chromatographic separation (EtOAc/hexane = 1/5, then 1/1) provided the tosylate **65** (14.8 mg, 91% yield). To **65** (14.8 mg, 0.043 mmol) in acetone (1 mL) were added KI (35.7 mg, 0.215 mmol) and 18-crown-6 (1 mg) at room temperature, and the mixture was heated at reflux (80°C) for 12 hours. After adding 1 mL of water, the normal work-up with EtOAc (2 mL, three times) followed by chromatographic purification (EtOAc/hexane = 1/5, then 1/1) procured the corresponding iodide (9.4 mg, 72% yield). To the iodide (9.4 mg, 0.031 mmol) in *t*-BuOH (1 mL) and H_2O (0.5 mL) was added Zn (20 mg, 0.31 mmol), and the mixture was heated at reflux (100°C) for 12 hours. After adding water (2 mL) to the solution at room temperature, the normal work-up with EtOAc (2 mL, three times) and chromatographic separation (EtOAc/hexane = 1/5, then 1/3) revealed **66** (4.1 mg, 75% yield). $[\alpha]_D^{22}$ of **66** = −105.6 (*c* 0.2, EeOH, measured) vs $[\alpha]_D^{25}$ of (*S*)-**66** = +107.2 (*c* 3, EtOH, known, >99% ee).[19] It was determined that the major enantiomers of our synthetic **66** and **32** have (*R*)- and (*S*)-configuration, respectively.

9) The Oxazolidinone benzoate **35**



35 **25**

To **35** (14 mg, 0.044 mmol) in CH_2Cl_2 (1 mL) was added TBAF (75 wt%, 0.1 mL) in an ice-water bath and the mixture was stirred at that temperature for 30 minutes. After adding saturated aqueous NH_4Cl (1 mL), the normal work-up with EtOAc (2 mL, three times) and chromatographic purification (EtOAc/hexane = 1/5, then 1/3) yielded the corresponding acetylene (10.5 mg, 97% yield). To the acetylene (10.5 mg, 0.043 mmol) in EtOAc (1 mL) was added 10% Pd/C (3 mg) and the mixture was stirred under an atmospheric hydrogen balloon at room temperature for 12 hours. The resulting solution was filtered through celite

(1.5 g) with EtOAc (6 mL) and evaporated in vacuo. The residue was separated chromatographically (EtOAc/hexane = 1/3, then 1/1) to supply **25** (10.5 mg, 98% yield, 95% ee). Since its chiral HPLC chromatogram was identical with that of (*S*)-**25** prepared from **13** by consecutive desymmetrization and kinetic resolution, the major enantiomer of **35** was determined to have (*S*)-configuration.

VIII. References

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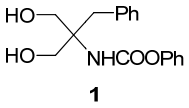
17 Y. Iio, M. Yamaoka, M. Jin, Y. Nakamura, T. Nishi, *Tetrahedron: Asymmetry* 2011, **22**, 323.

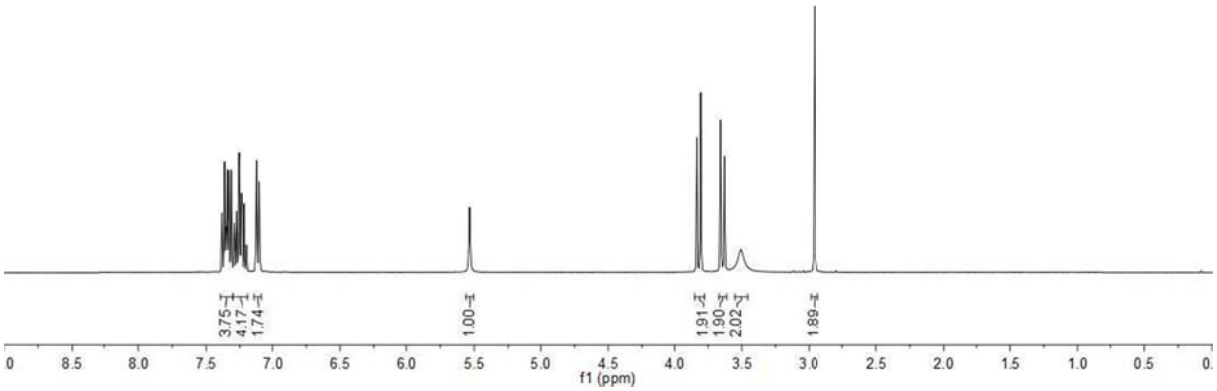
18 M. Martinkova, J. Gonda, J. Raschmanova, A. Uhrikova, *Tetrahedron: Asymmetry* 2008, **19**, 1879..

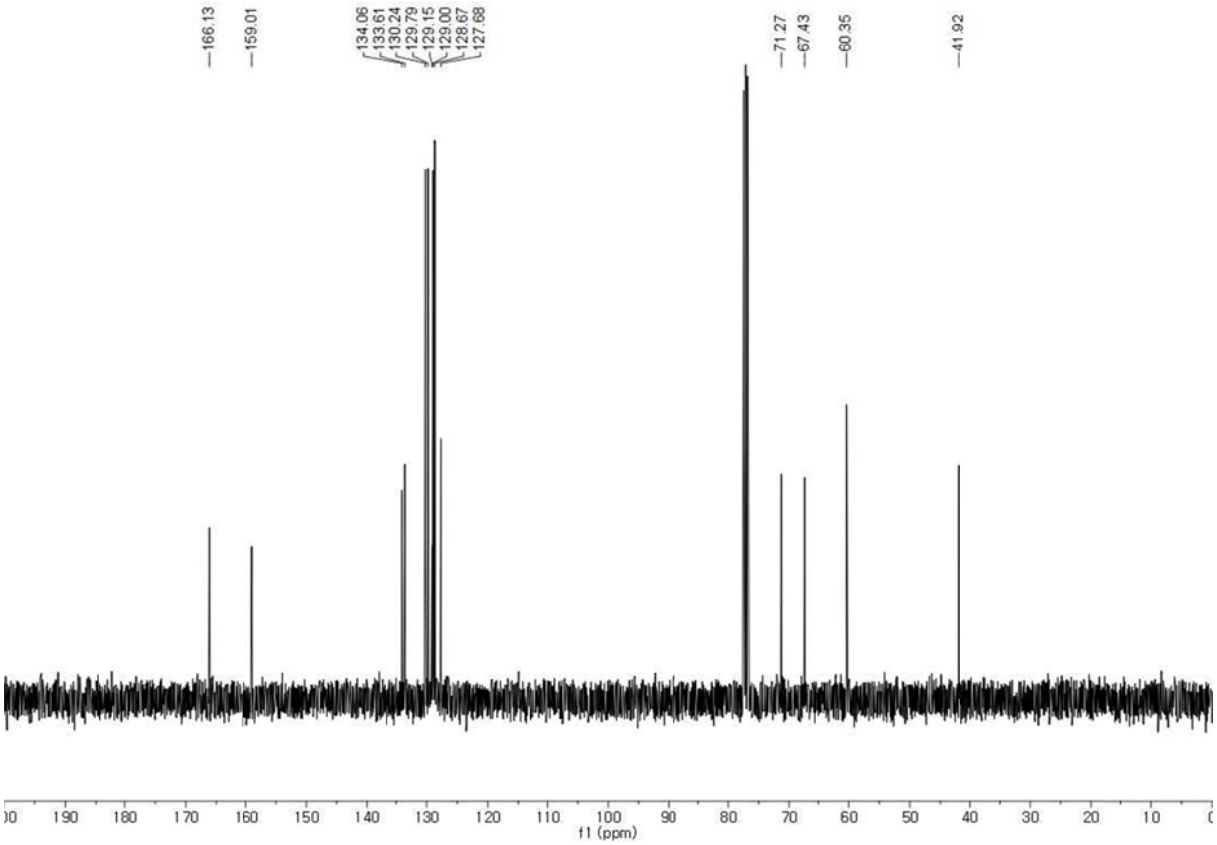
19 H. Pietsch, *Tetrahedron Lett.* 1972, **27**, 2789.

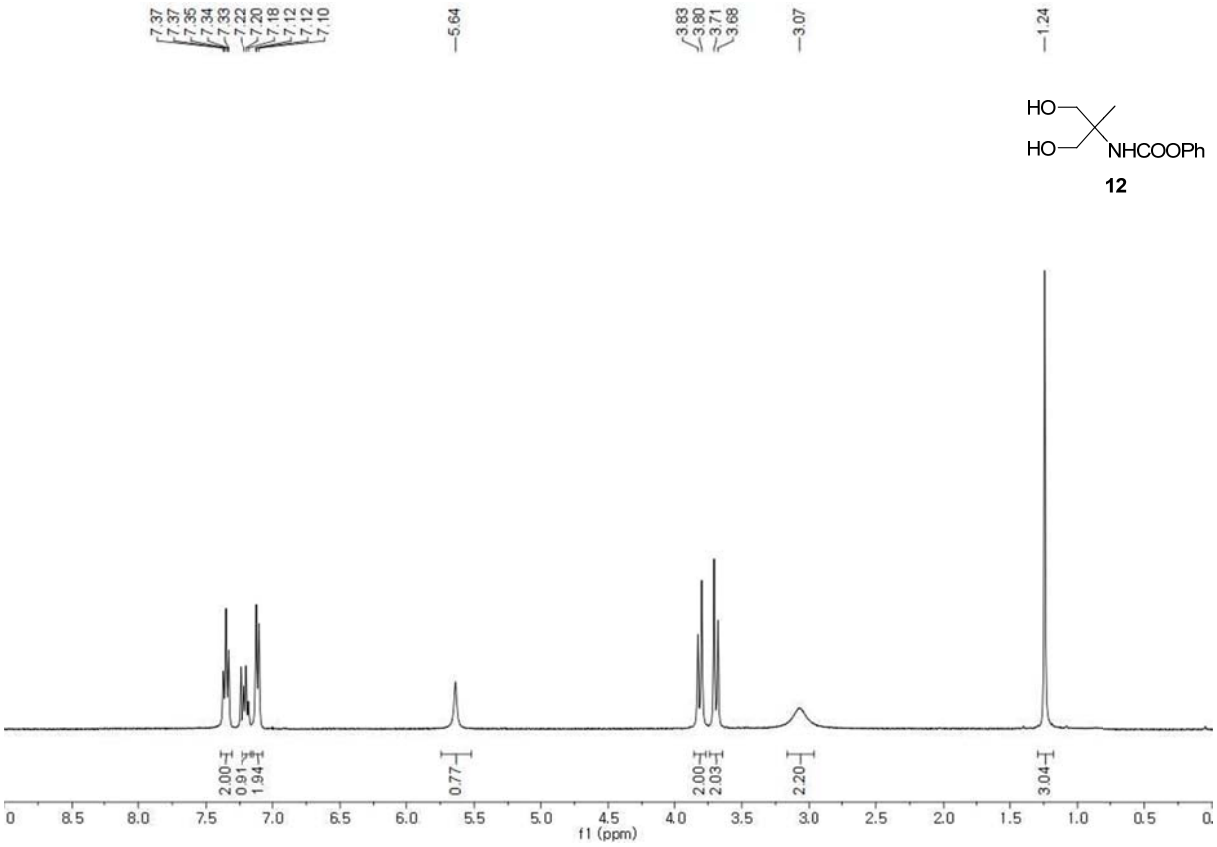
IX. Selected NMR Spectral Charts



1



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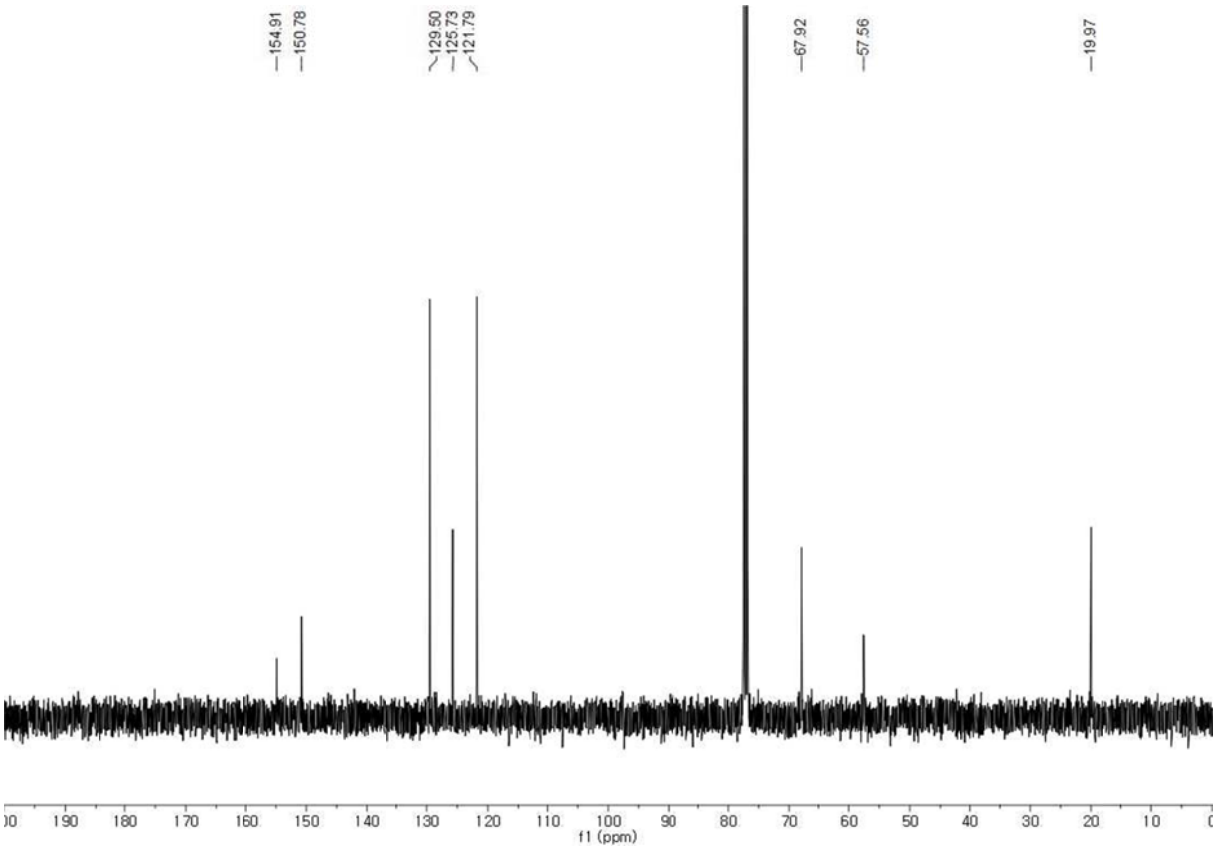
7.37
7.35
7.34
7.33
7.22
7.20
7.18
7.12
7.12
7.10
5.64
3.83
3.80
3.71
3.68
3.07
1.24
HO
HO
NHCOOPh
12
2.00
0.91
1.94
0.77
2.00
2.03
2.20
3.04
f1 (ppm)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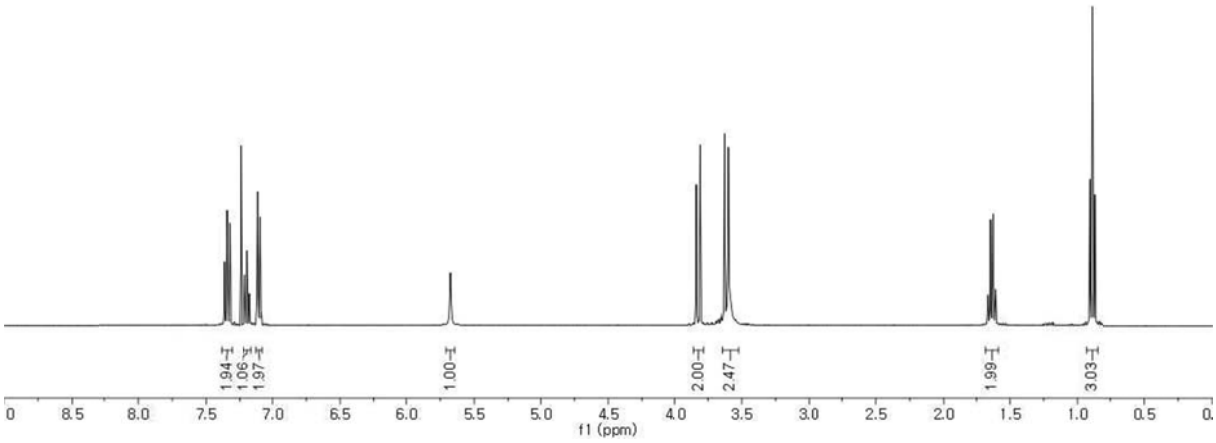
150.78
129.50
125.73
121.79
67.92
57.56
19.97
f1 (ppm)


7.36
7.36
7.35
7.34
7.34
7.34
7.33
7.33
7.32
7.21
7.21
7.21
7.19
7.19
7.19
7.18
7.17
7.12
7.11
7.11
7.11
7.10
7.10
7.09
7.09
5.87
3.84
3.81
3.63
3.60
1.66
1.65
1.63
1.61
0.91
0.89
0.87
HO
HO
NHCOOPh

13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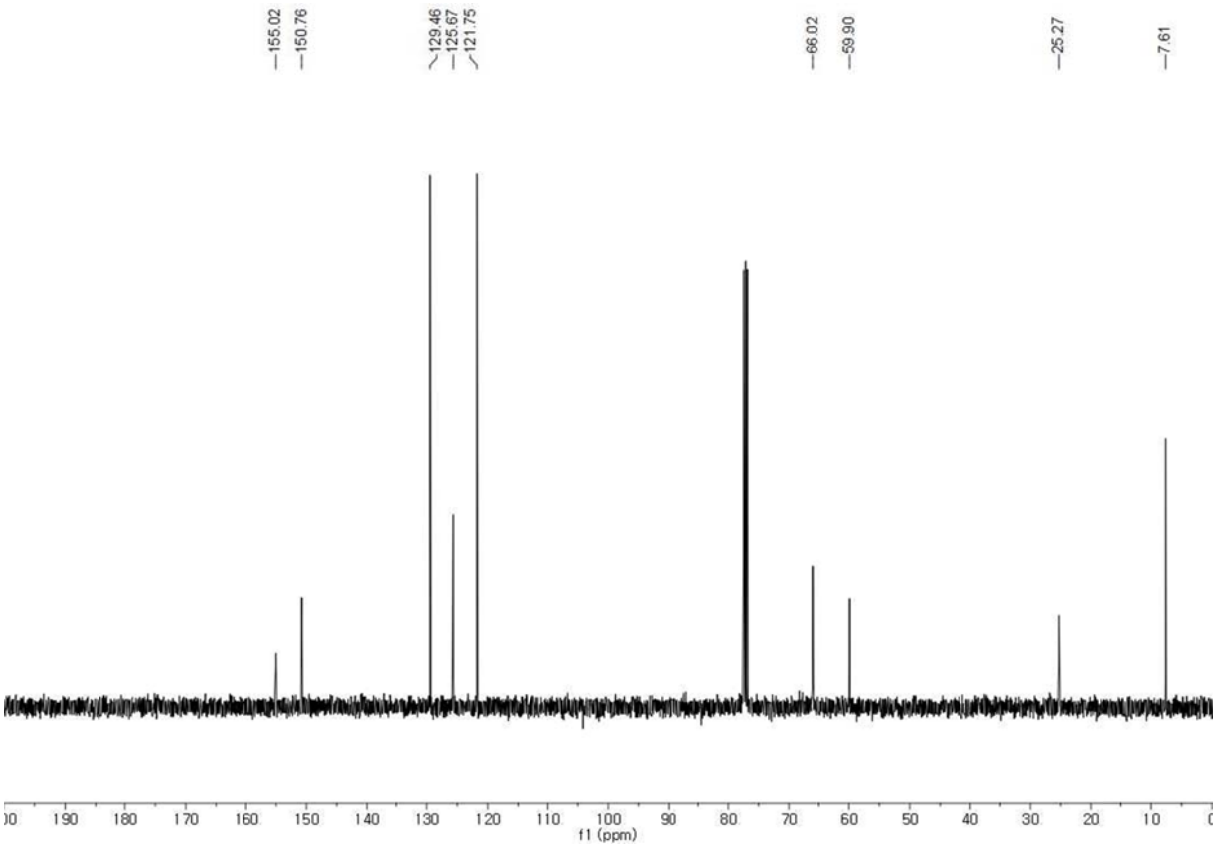
1.06
1.97
1.00
2.00
2.47
1.99
3.03
f1 (ppm)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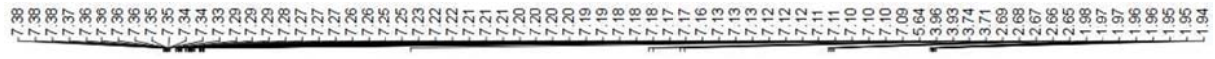
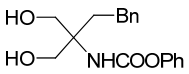
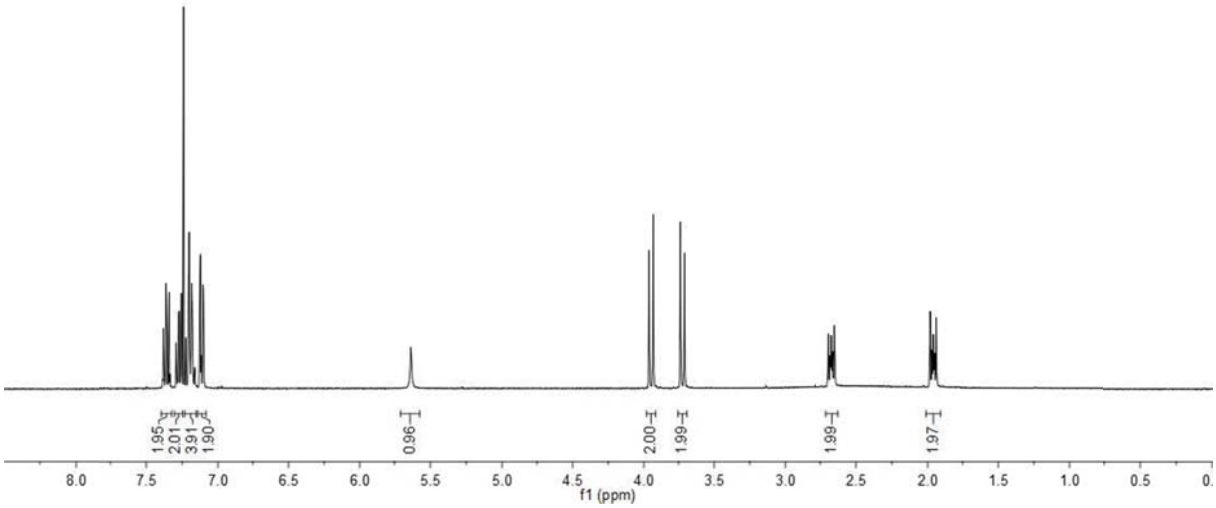
150.76
129.46
125.67
121.75
66.02
59.90
25.27
7.61
f1 (ppm)




HO
Bn
HO
NHCOOPh

14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2.01
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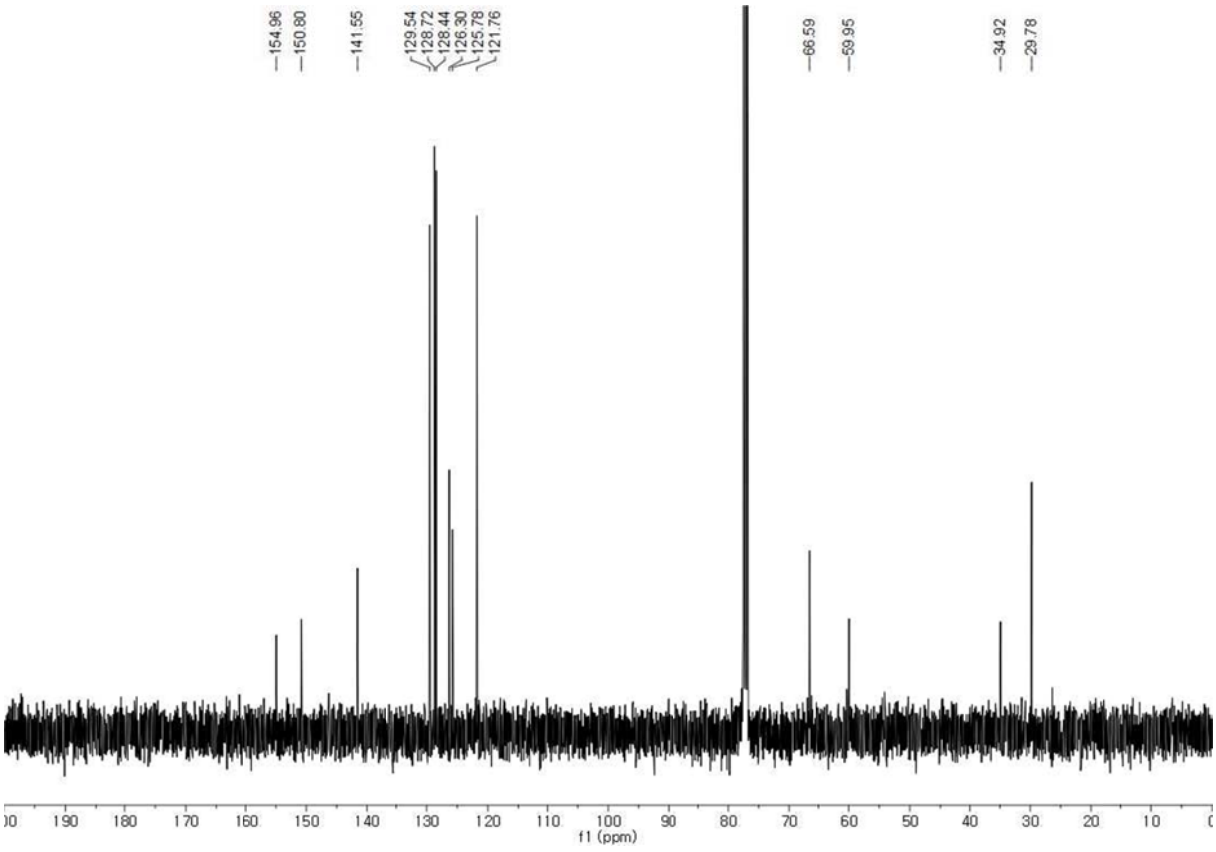
1.90
0.96
2.00
1.99
1.99
1.97
f1 (ppm)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150.80
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128.72
128.44
126.30
125.78
121.76
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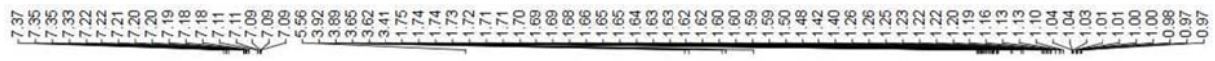
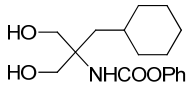
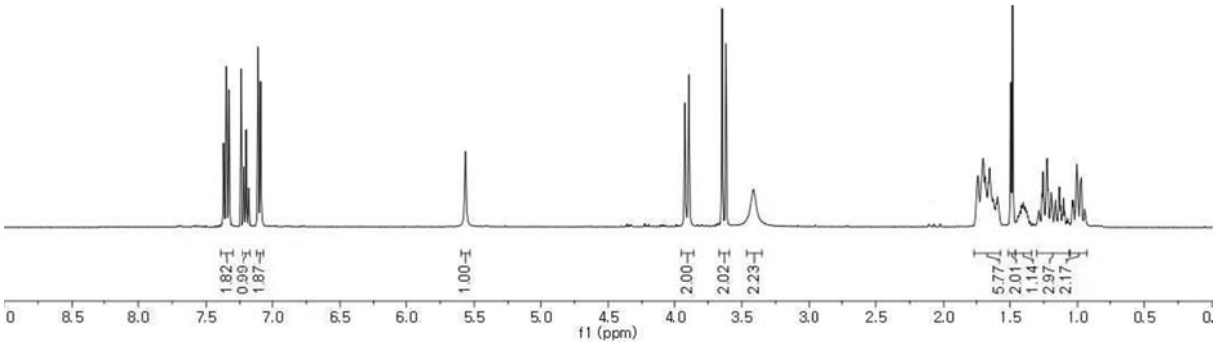
59.95
34.92
29.78
f1 (ppm)




HO
HO
NHCOOPh

15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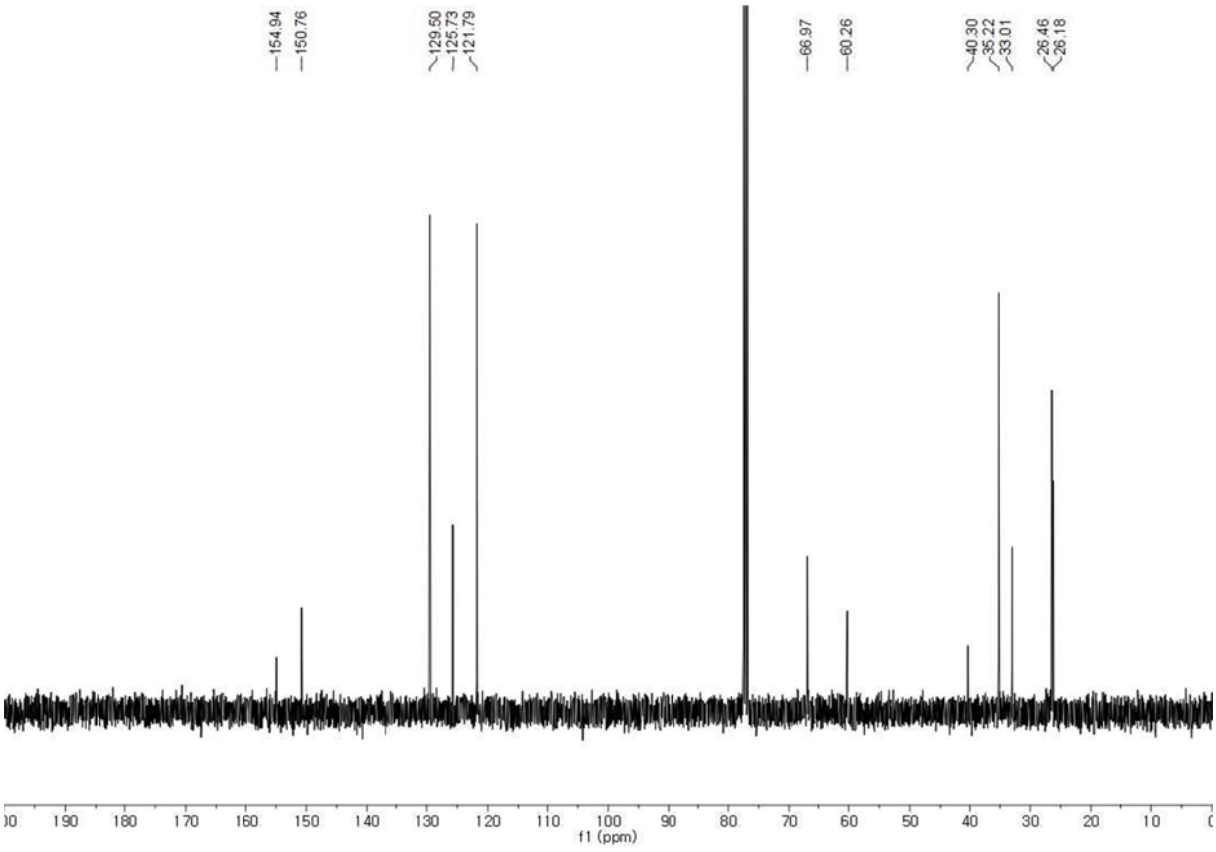
0.99
1.87
1.00
2.00
2.02
2.23
5.77
2.01
1.14
2.97
2.17
f1 (ppm)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129.50
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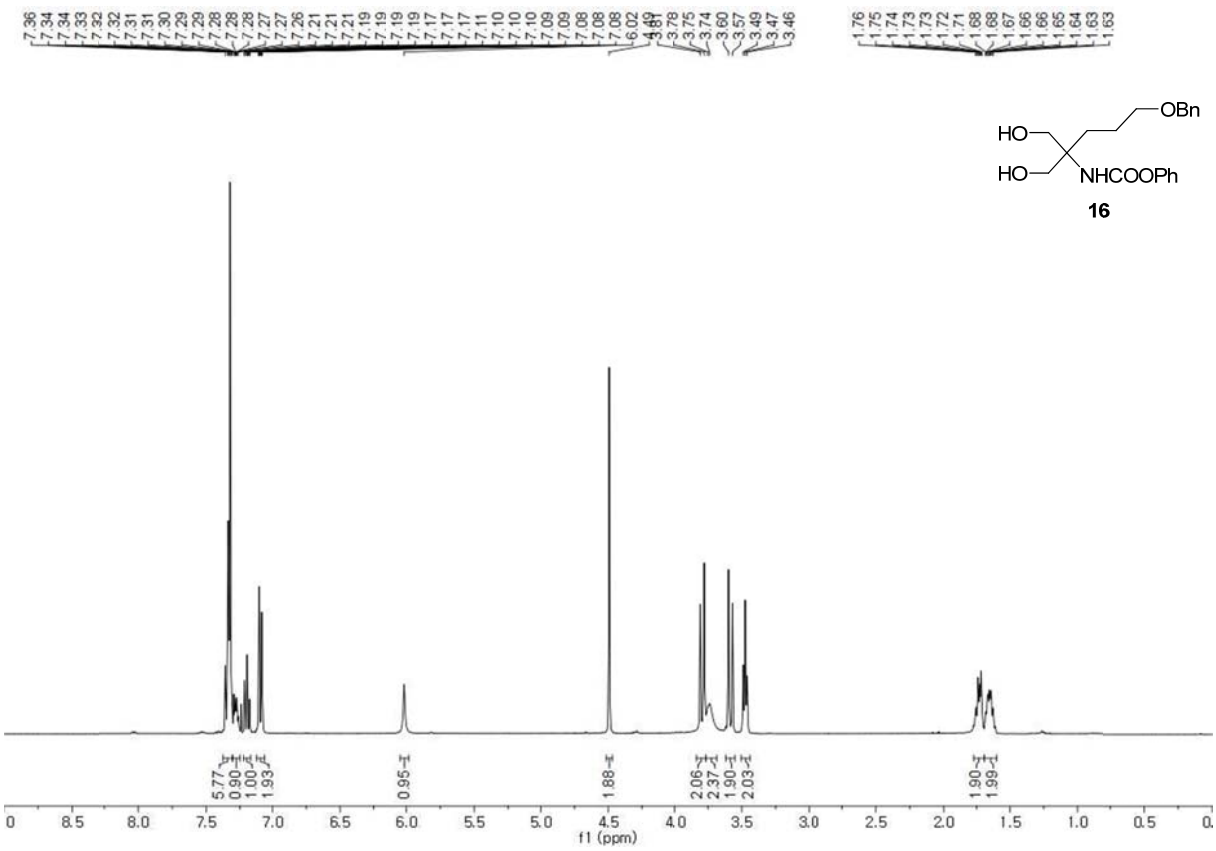
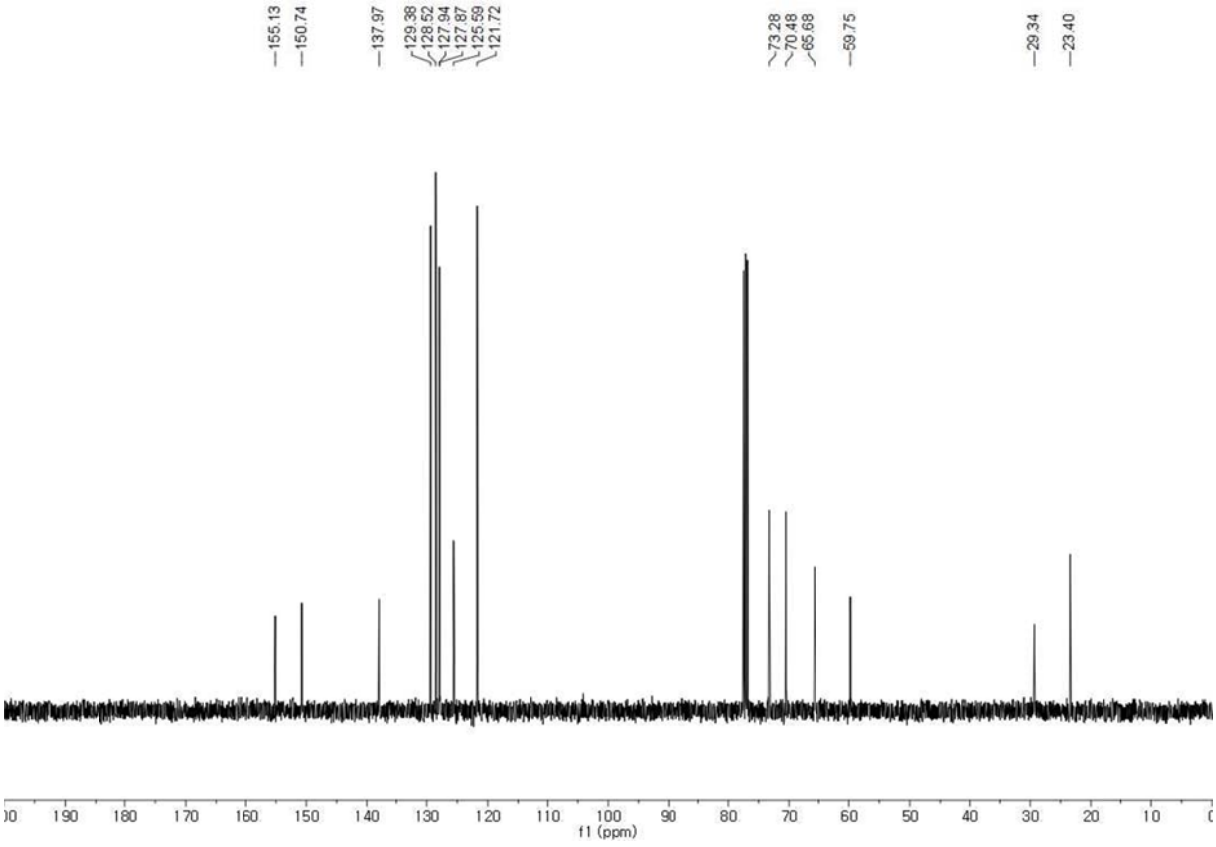
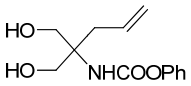
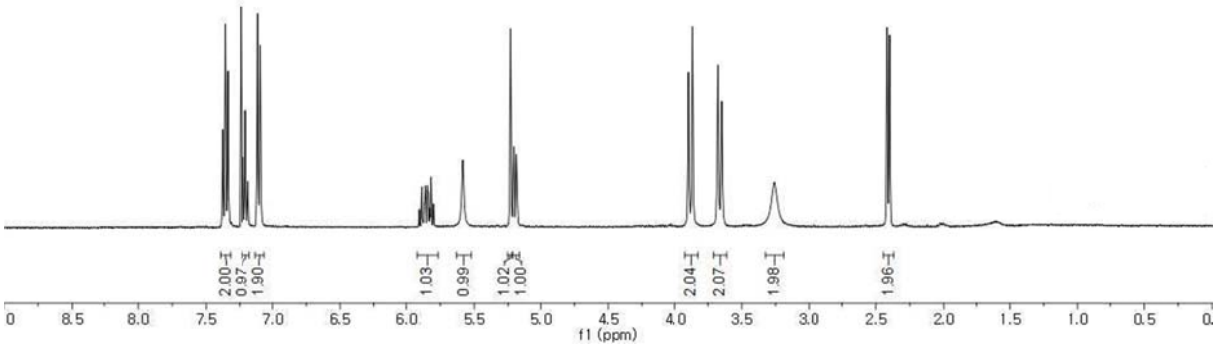
121.79
66.97
60.26
40.30
35.22
33.01
26.46
26.18
f1 (ppm)


OBn
HO
HO
NHCOOPh
16
f1 (ppm)


f1 (ppm)


HO
HO
NHCOOPh

17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0.97
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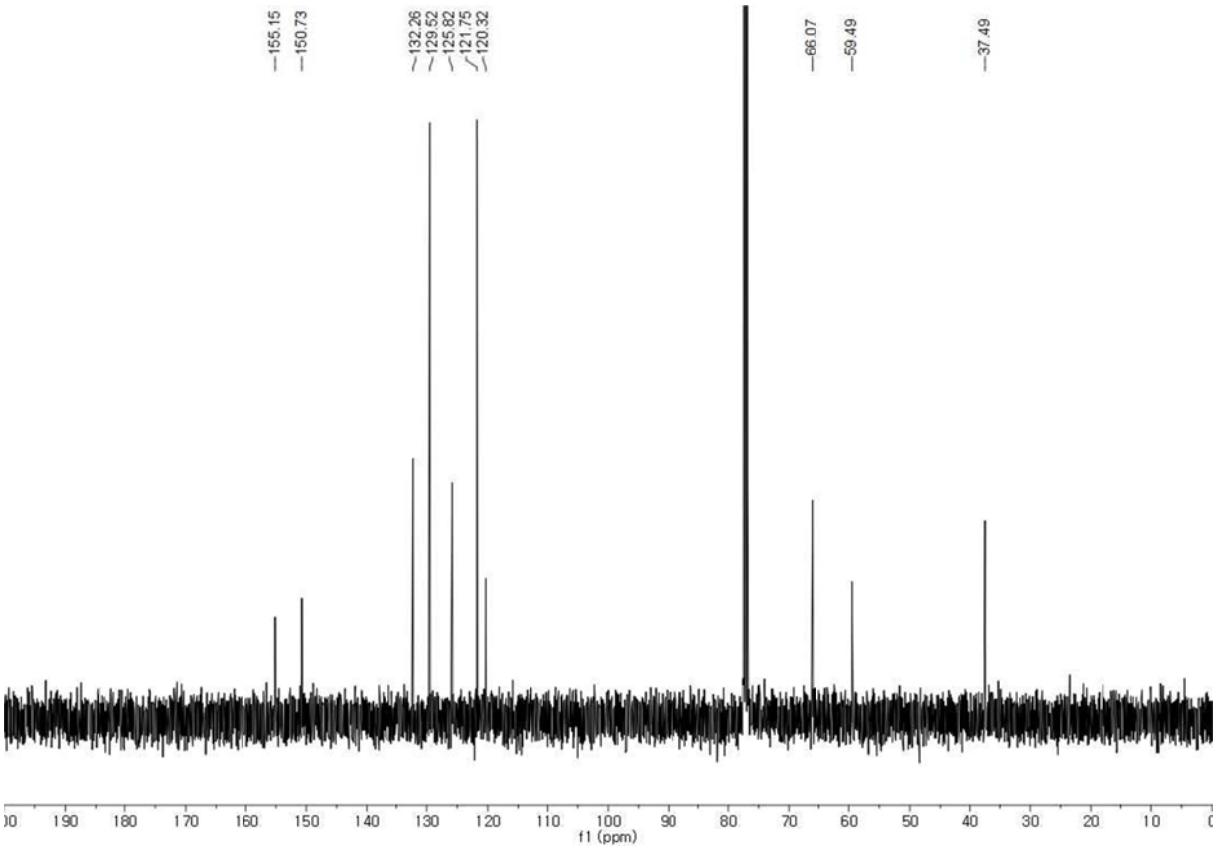
1.02
1.00
2.04
2.07
1.98
1.96
f1 (ppm)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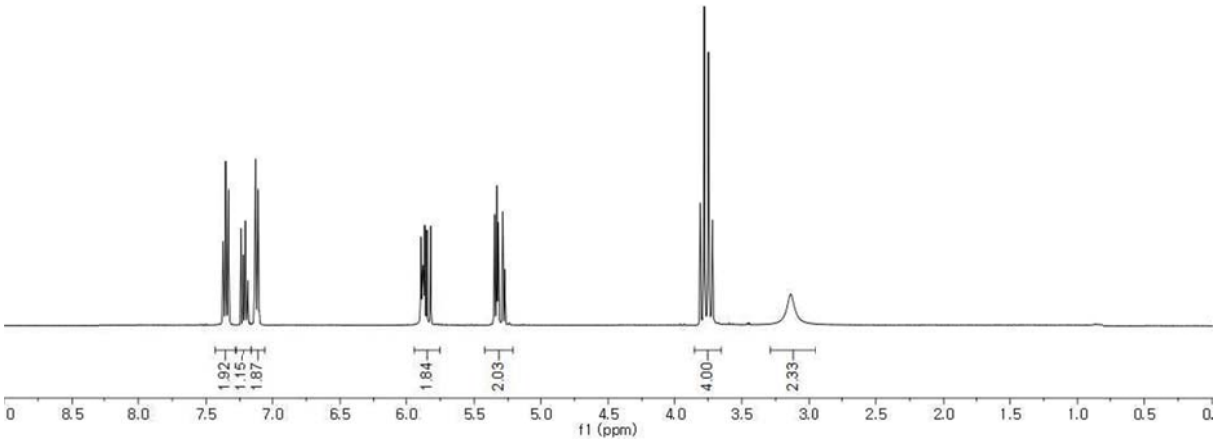
132.26
129.52
125.82
121.75
120.32
66.07
59.49
37.49
f1 (ppm)


7.37
7.36
7.36
7.35
7.34
7.33
7.24
7.22
7.22
7.22
7.21
7.20
7.18
7.13
7.13
7.13
7.12
7.11
7.11
7.11
7.11
5.89
5.88
5.88
5.86
5.85
5.33
5.32
5.29
5.27
3.81
3.78
3.75
3.72
3.14

HO
HO
NHCOOPh

18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1.15
1.87
1.84
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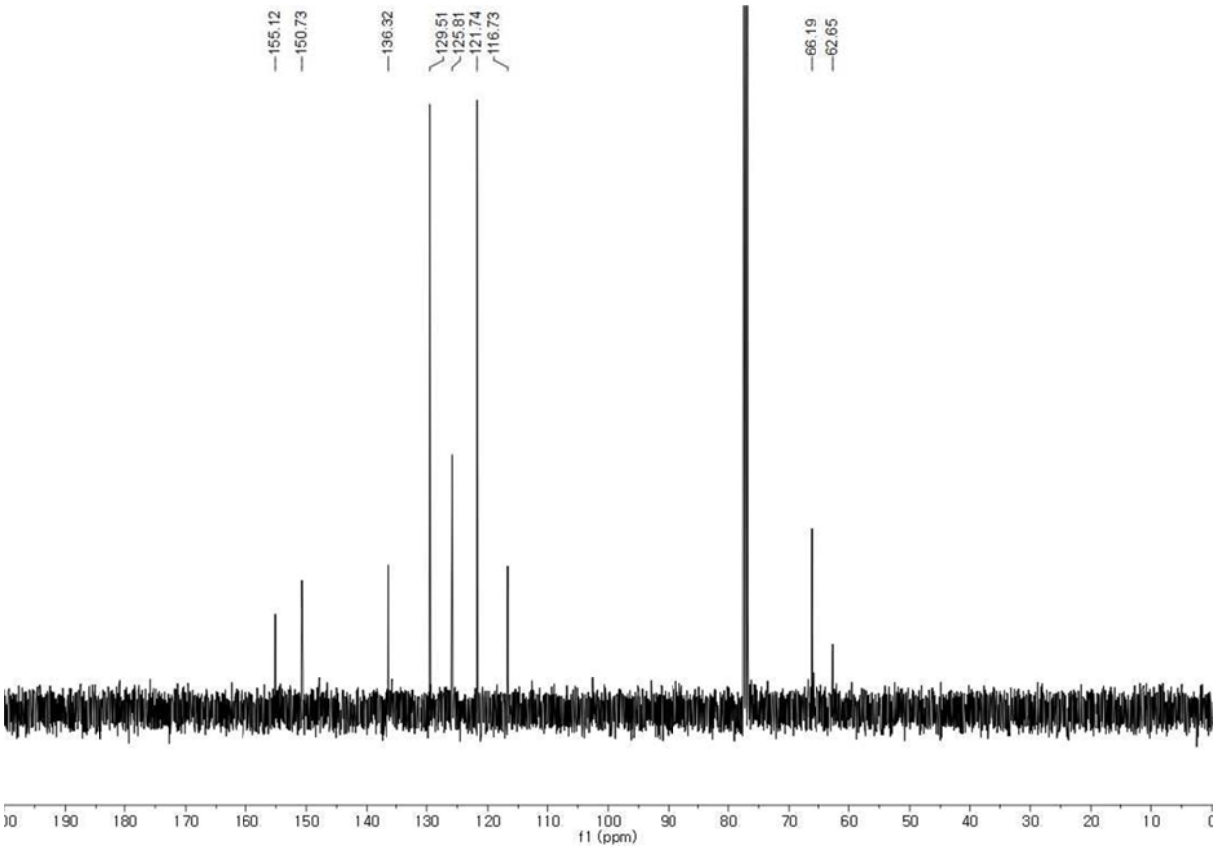
4.00
2.33
f1 (ppm)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125.81
121.74
116.73
66.19
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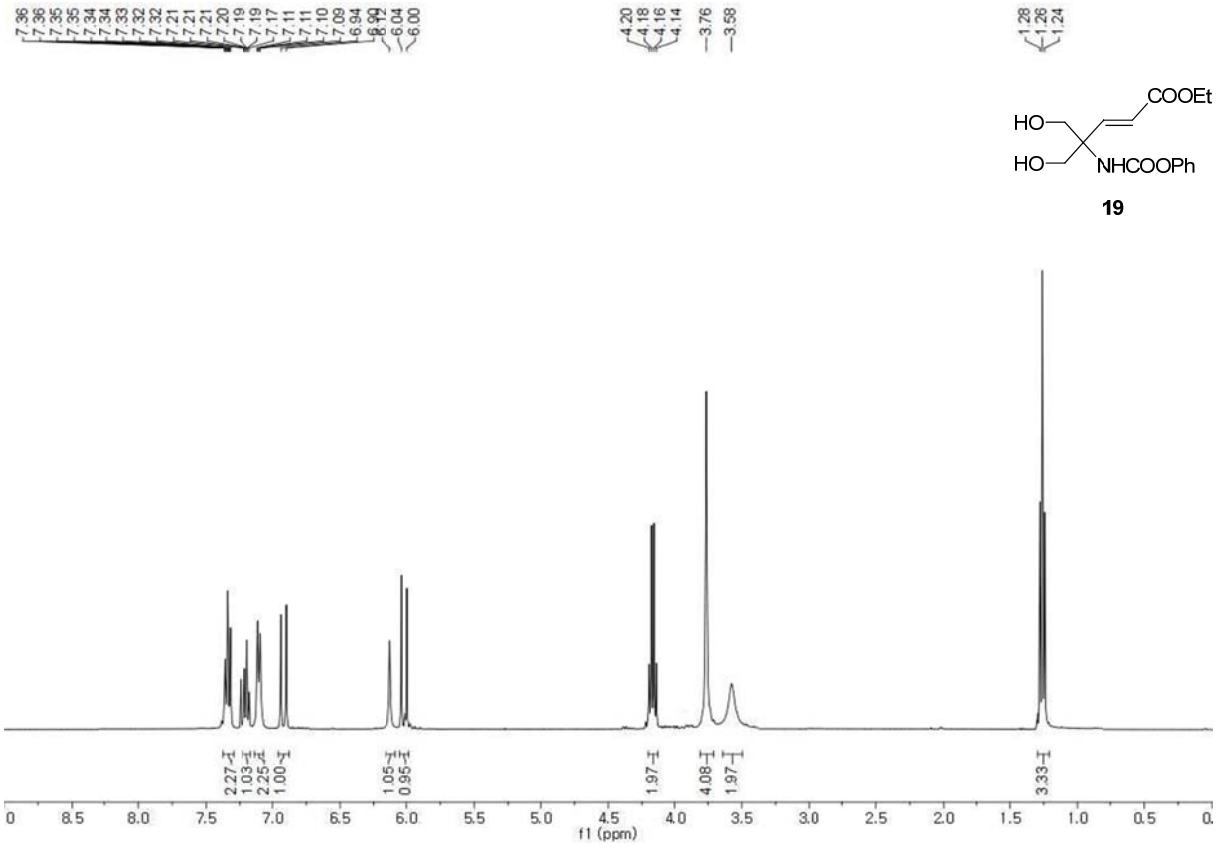
f1 (ppm)


7.36
7.36
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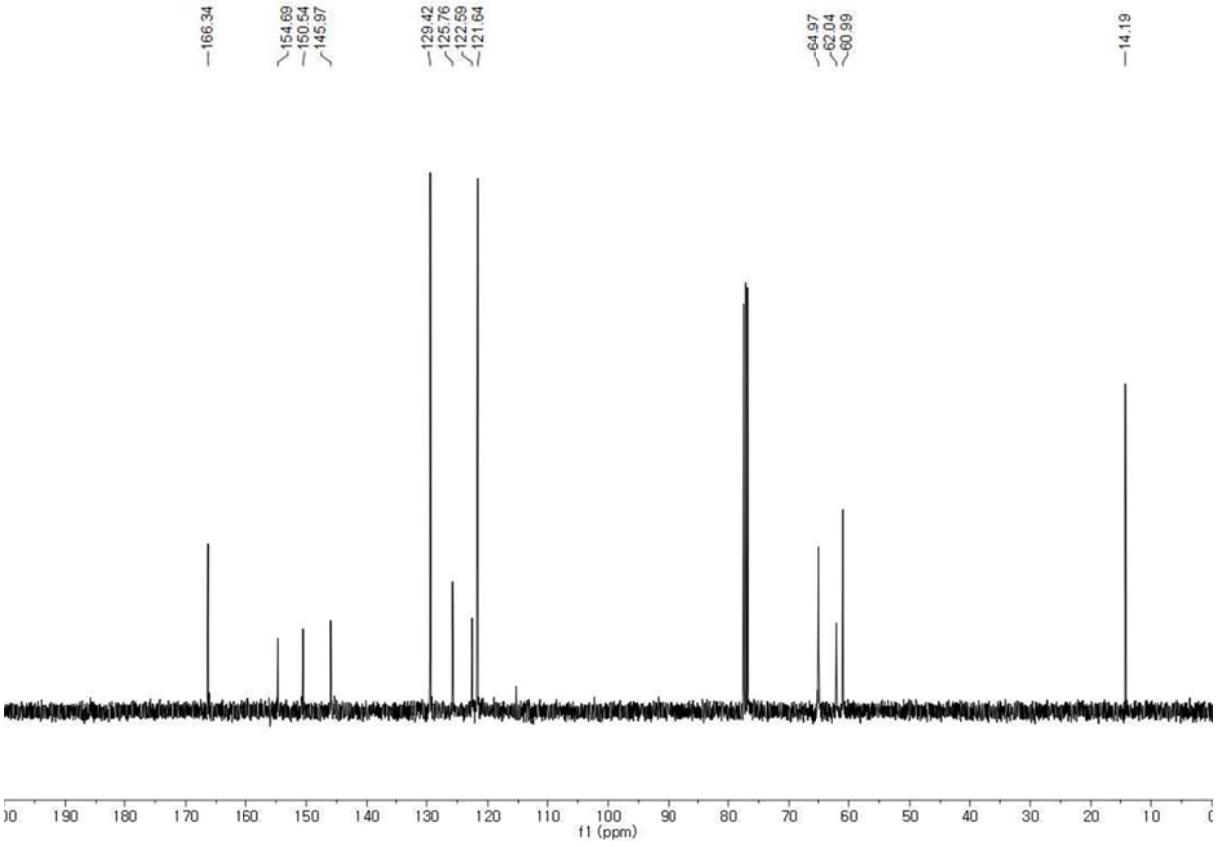
7.33
7.32
7.21
7.21
7.20
7.19
7.19
7.17
7.11
7.11
7.10
7.09
6.94
6.92
6.04
6.00
4.20
4.18
4.16
4.14
3.76
3.58
1.28
1.26
1.24
COOEt
HO
HO
NHCOOPh
19
2.27
1.03
2.25
1.00
1.05
0.95
1.97
4.08
1.97
3.33
f1 (ppm)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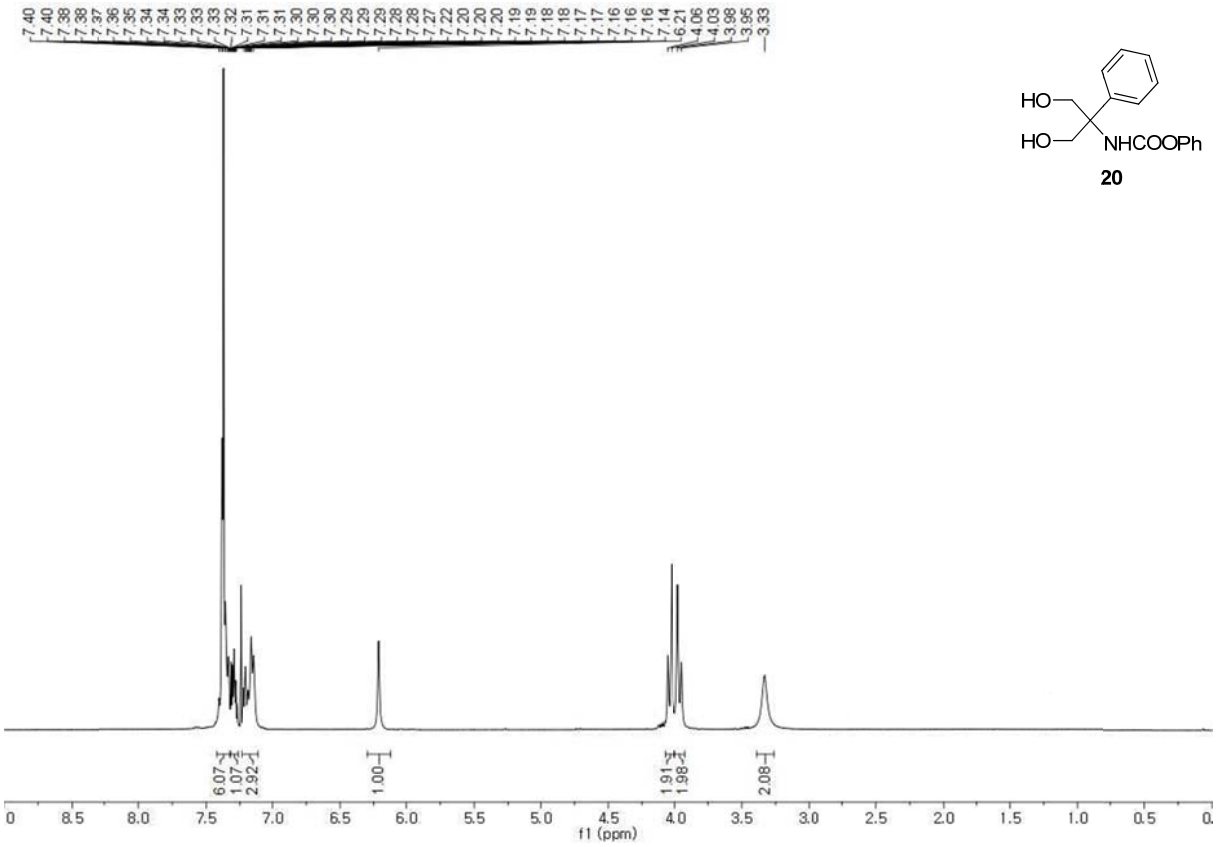
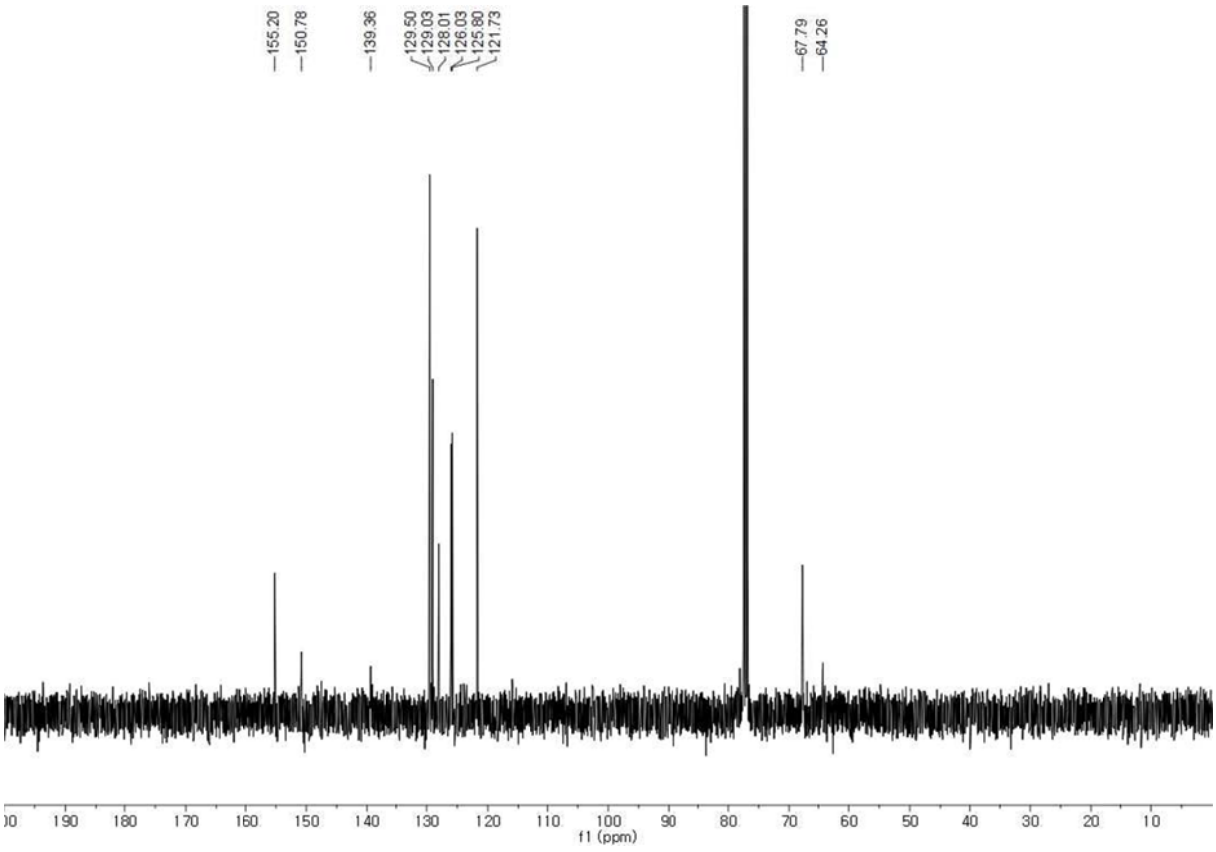
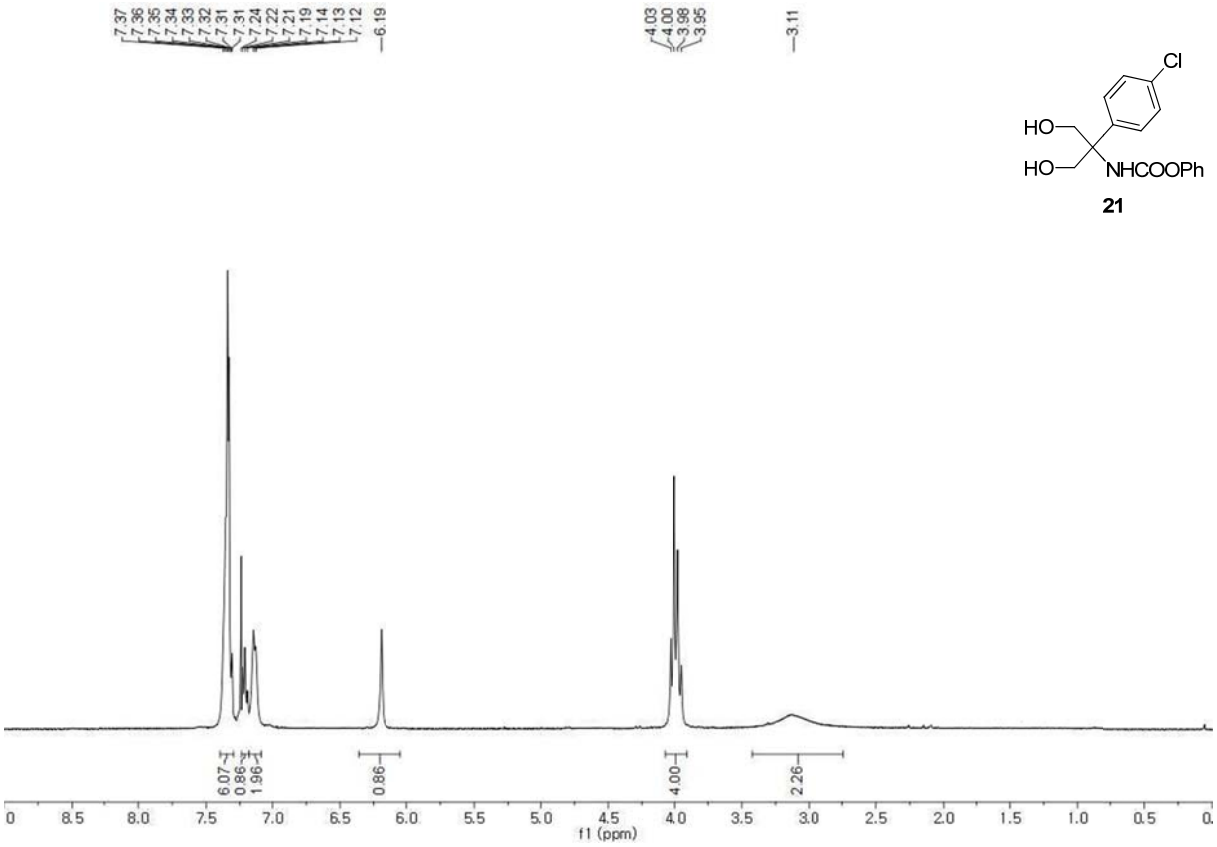
122.59
121.64
64.97
62.04
60.99
14.19
f1 (ppm)


HO
HO
NHCOOPh
20
f1 (ppm)


f1 (ppm)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7.31
7.31
7.24
7.22
7.21
7.19
7.14
7.13
7.12
6.19
4.03
4.00
3.98
3.95
3.11
Cl
HO
HO
NHCOOPh
21
6.07
0.86
1.96
0.86
4.00
2.26
f1 (ppm)
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133.95
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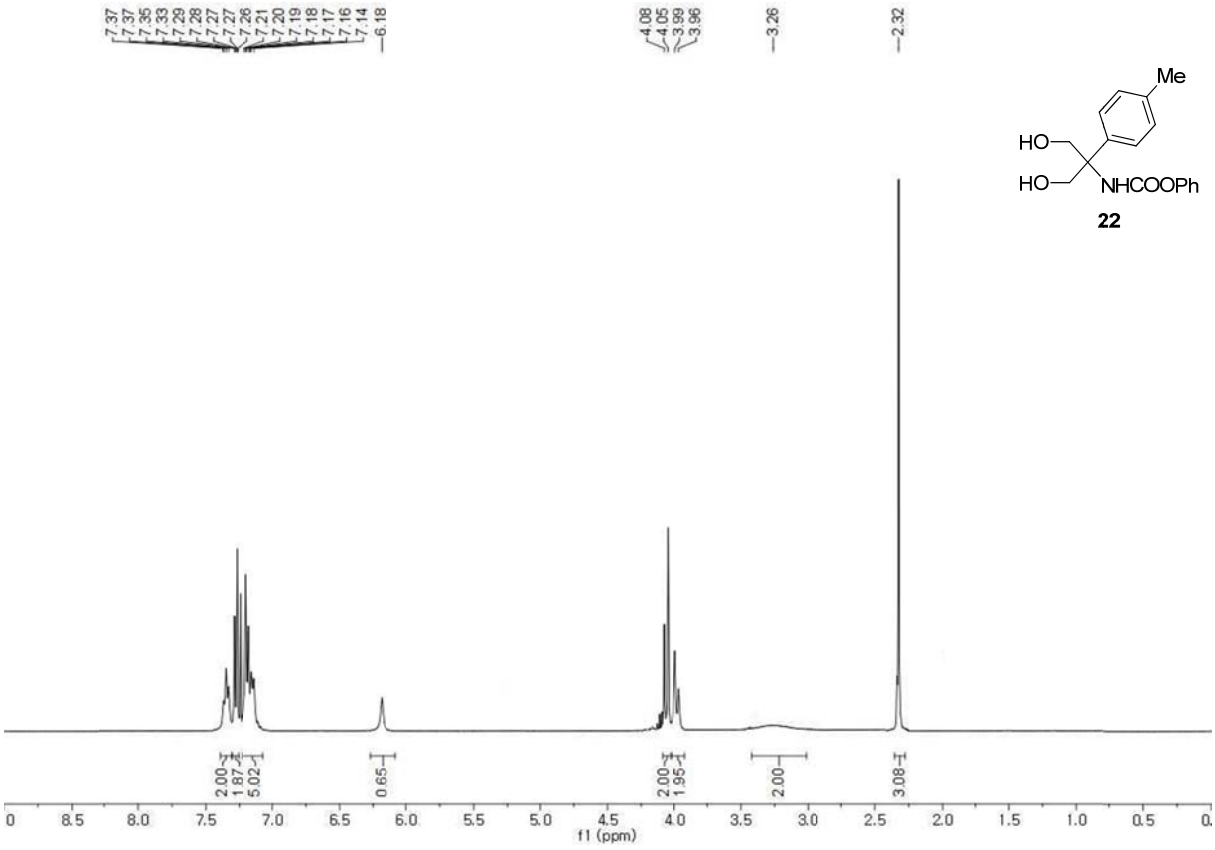
129.15
127.59
125.90
121.67
67.65
63.78
f1 (ppm)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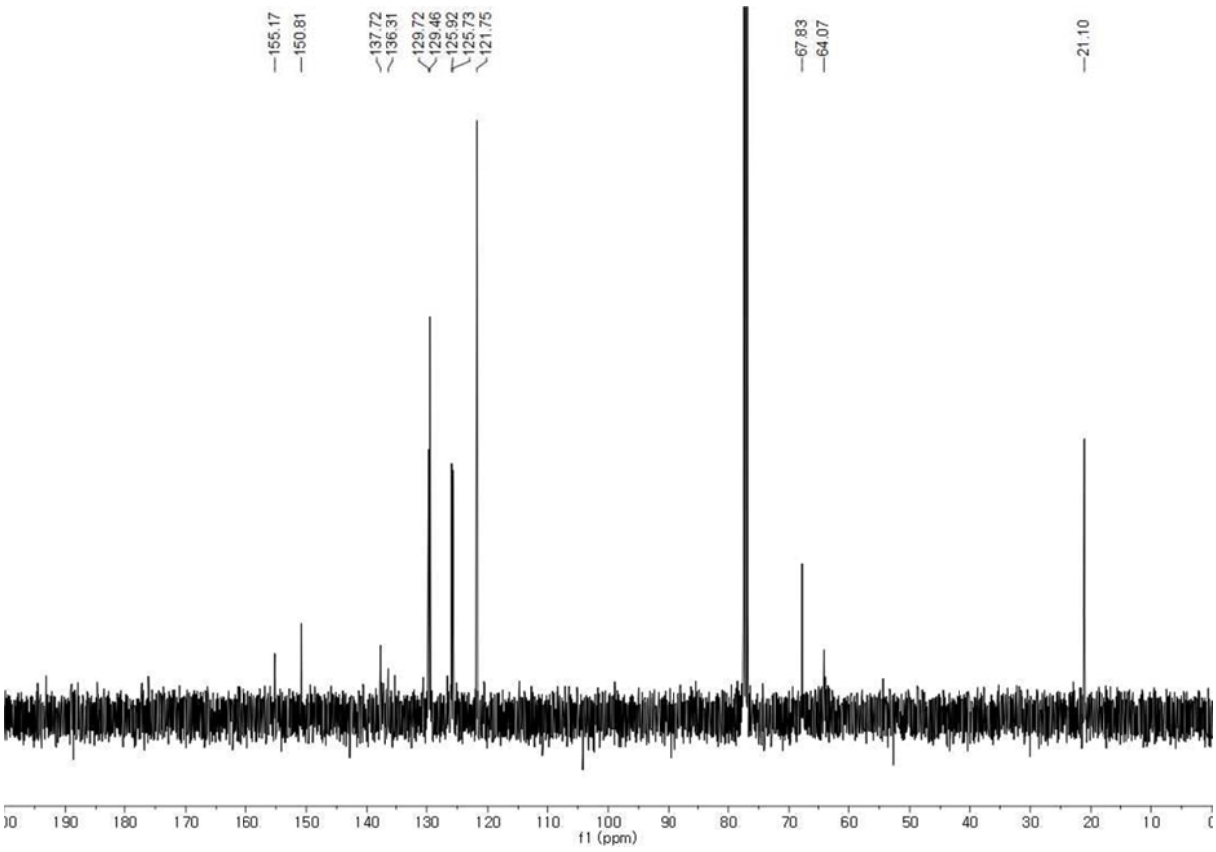
7.21
7.20
7.19
7.18
7.17
7.16
7.14
6.18
4.08
4.05
3.99
3.96
3.26
2.32
2.00
1.87
5.02
0.65
2.00
1.95
2.00
3.08
f1 (ppm)

Me
HO
HO
NHCOOPh

22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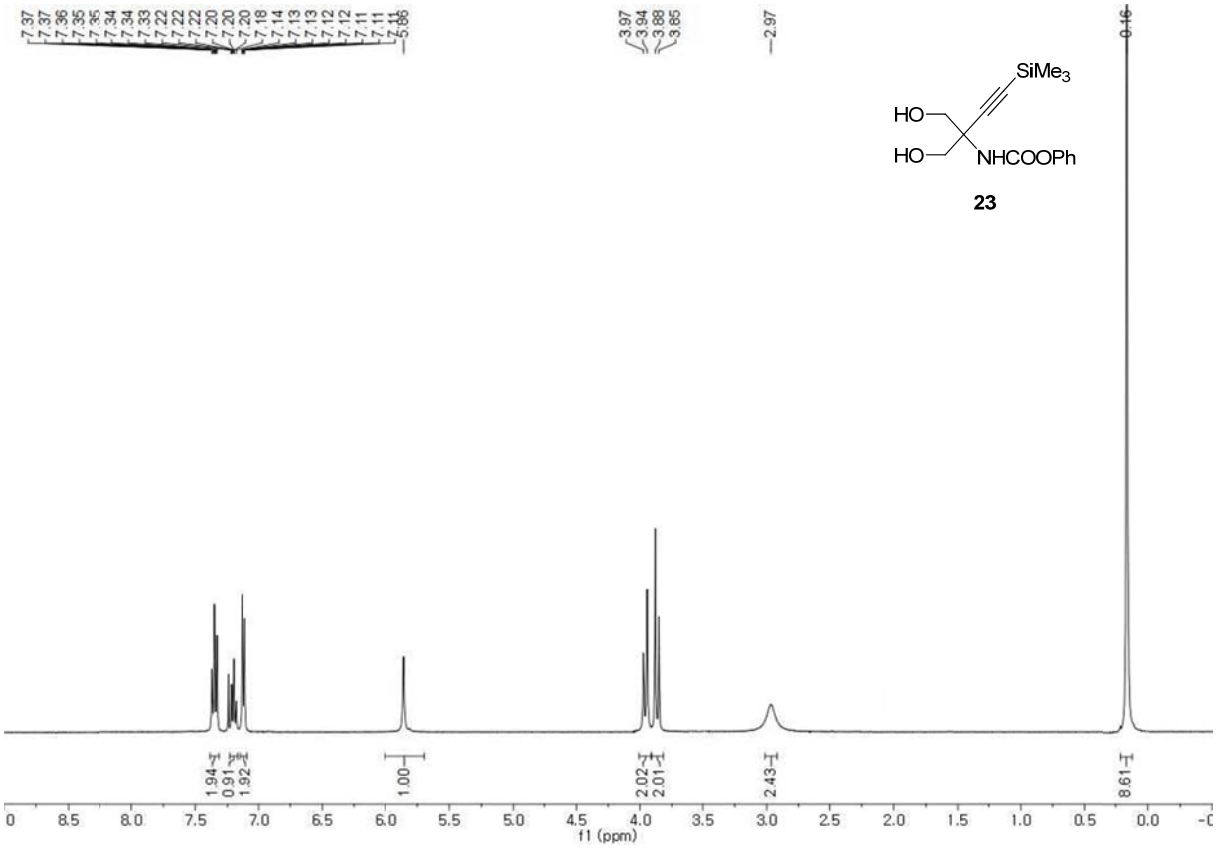
125.73
121.75
67.83
64.07
21.10
f1 (ppm)



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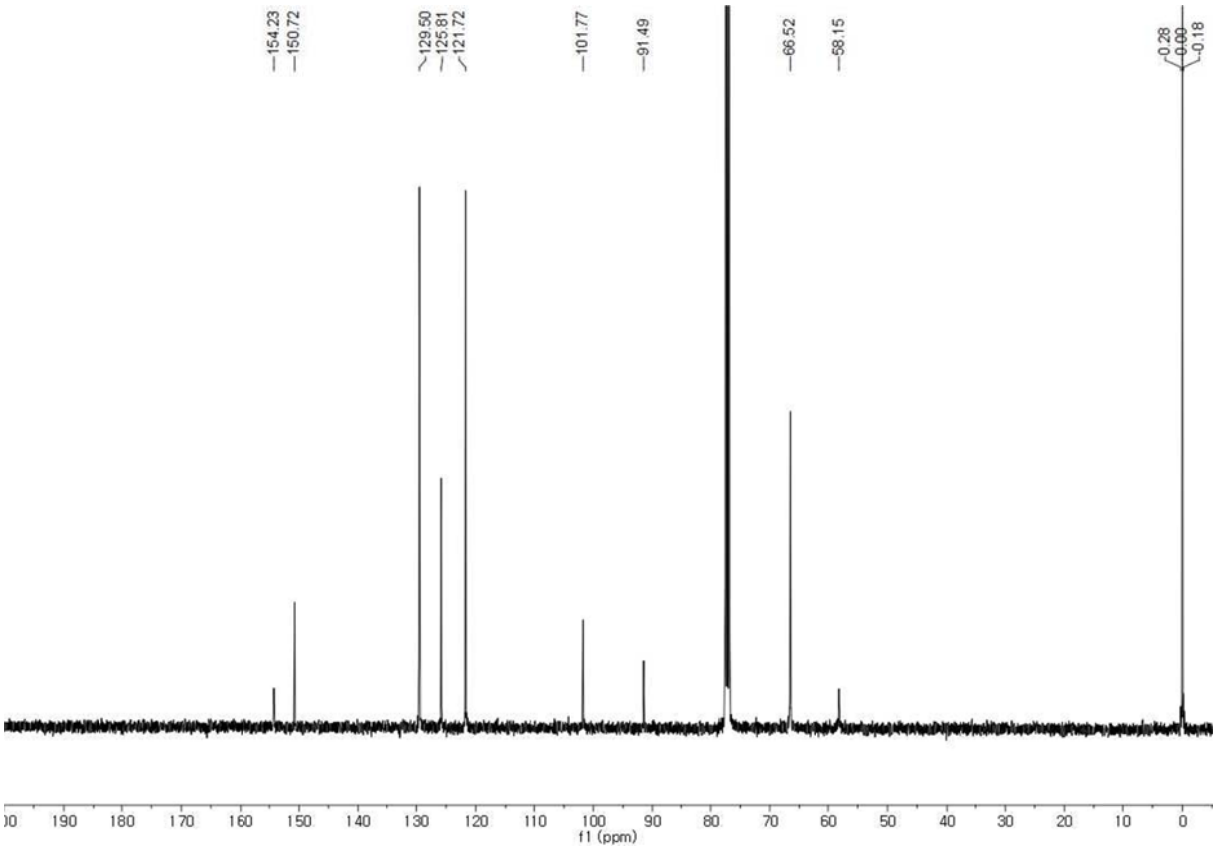


8.00
8.00
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7.98
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7.53
7.52
7.52
7.52
7.42
7.42
7.40
7.39
7.38
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7.33
7.32
7.32
7.31
7.31
7.30
7.29
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7.26
7.25
7.25
7.24
7.20
7.20
7.19
7.18
7.18
6.52
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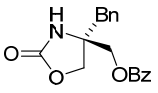
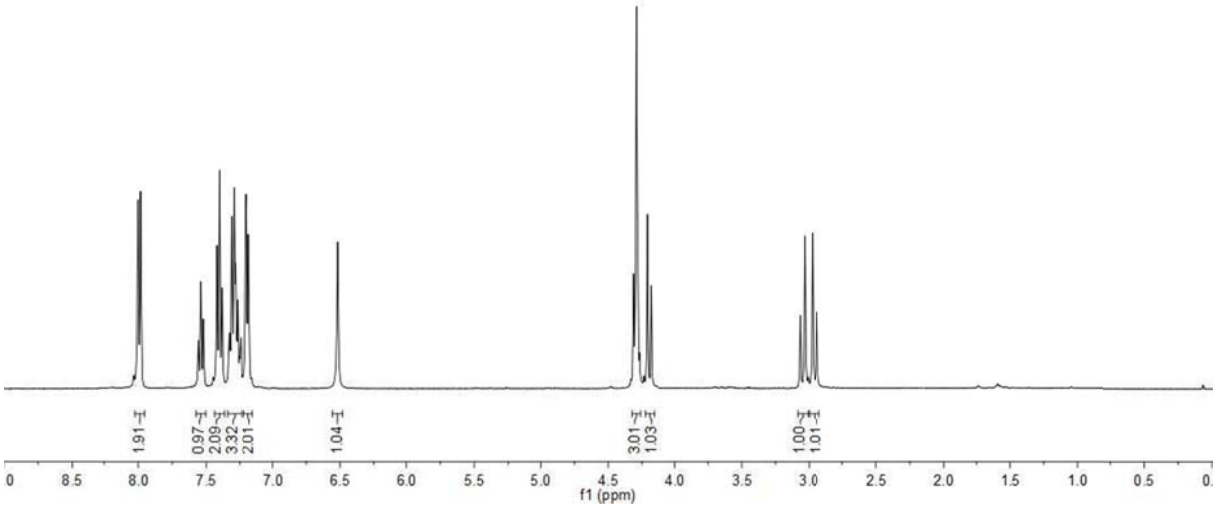
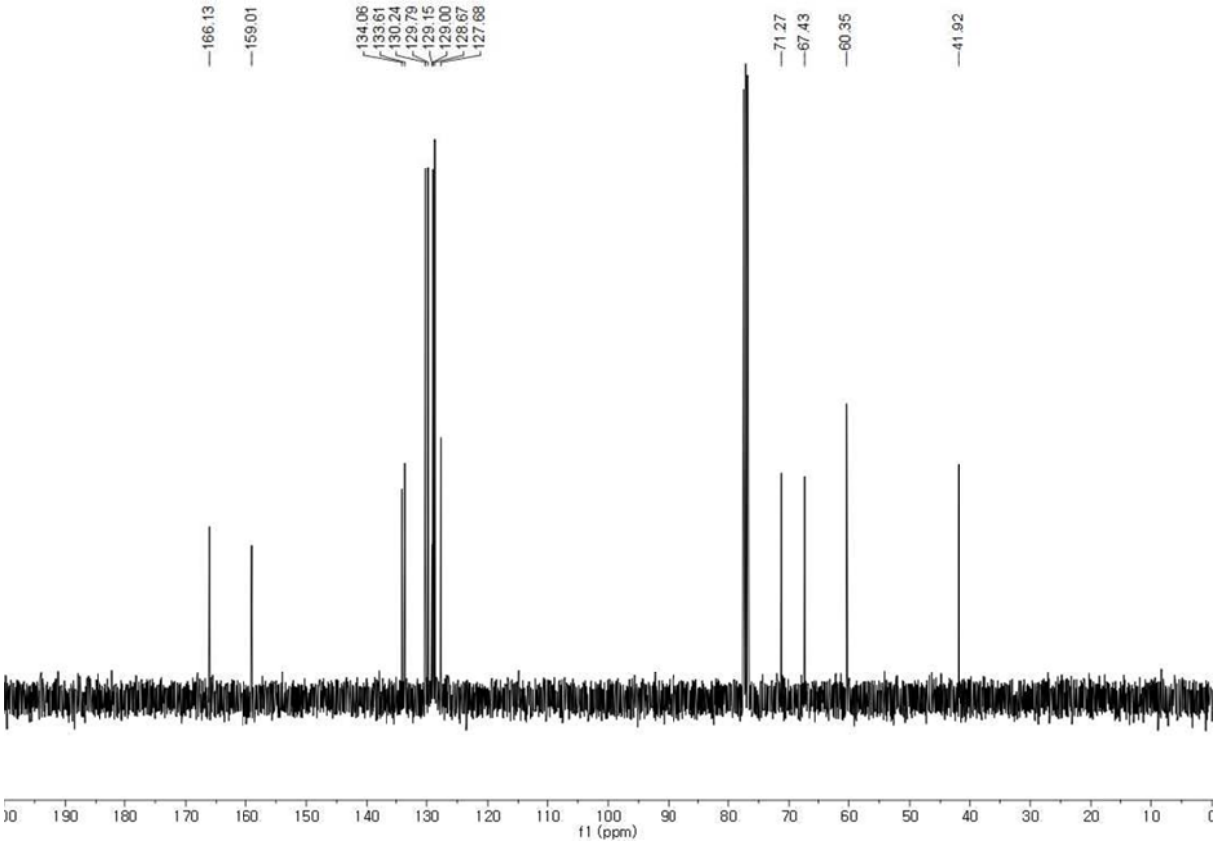
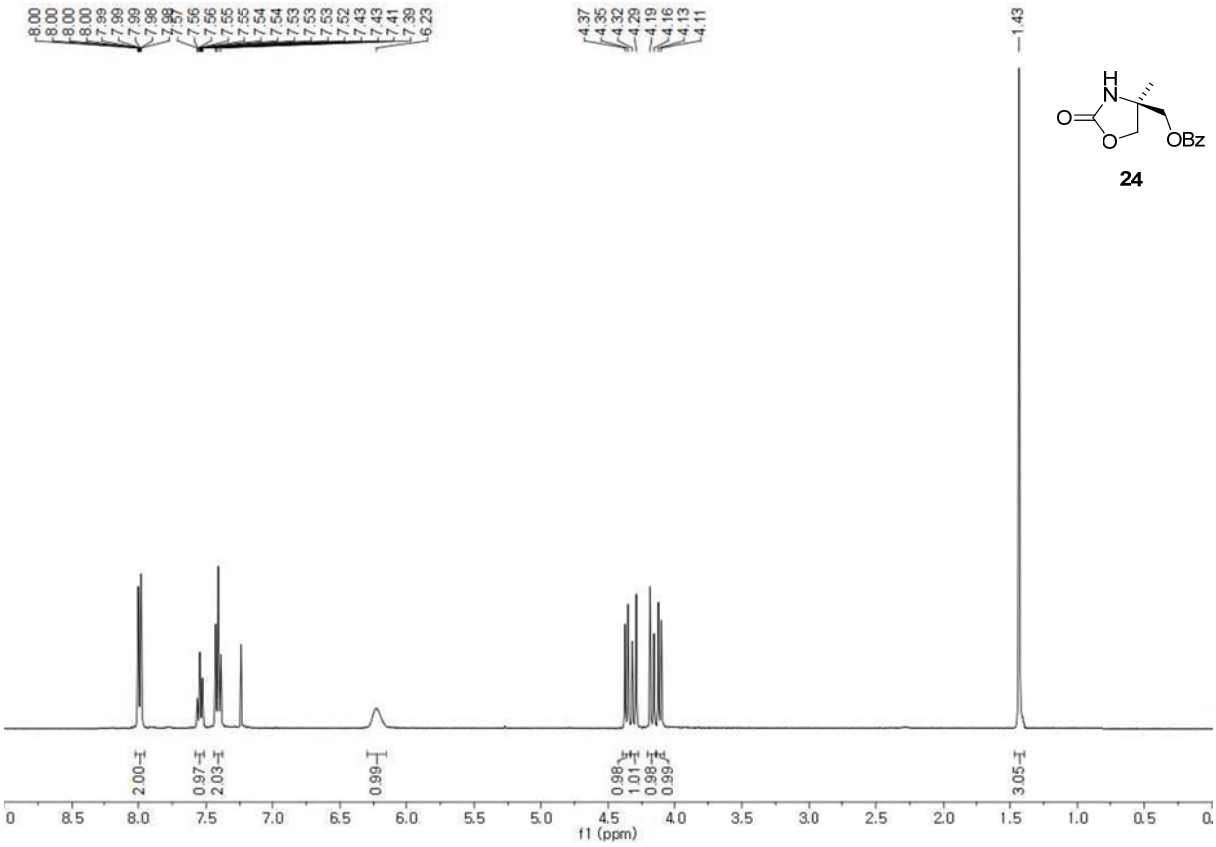
4.31
4.29
4.29
4.28
4.21
4.18
3.07
3.03
2.97
2.94


H
N
Bn
O
O
OBz

11


1.91
0.97
2.09
3.32
2.01
1.04
3.01
1.03
1.00
1.01
f1 (ppm)


166.13
159.01
134.06
133.61
130.24
129.79
129.15
129.00
128.67
127.68
71.27
67.43
60.35
41.92
f1 (ppm)


8.00
8.00
8.00
8.00
7.99
7.99
7.99
7.98
7.98
7.97
7.56
7.56
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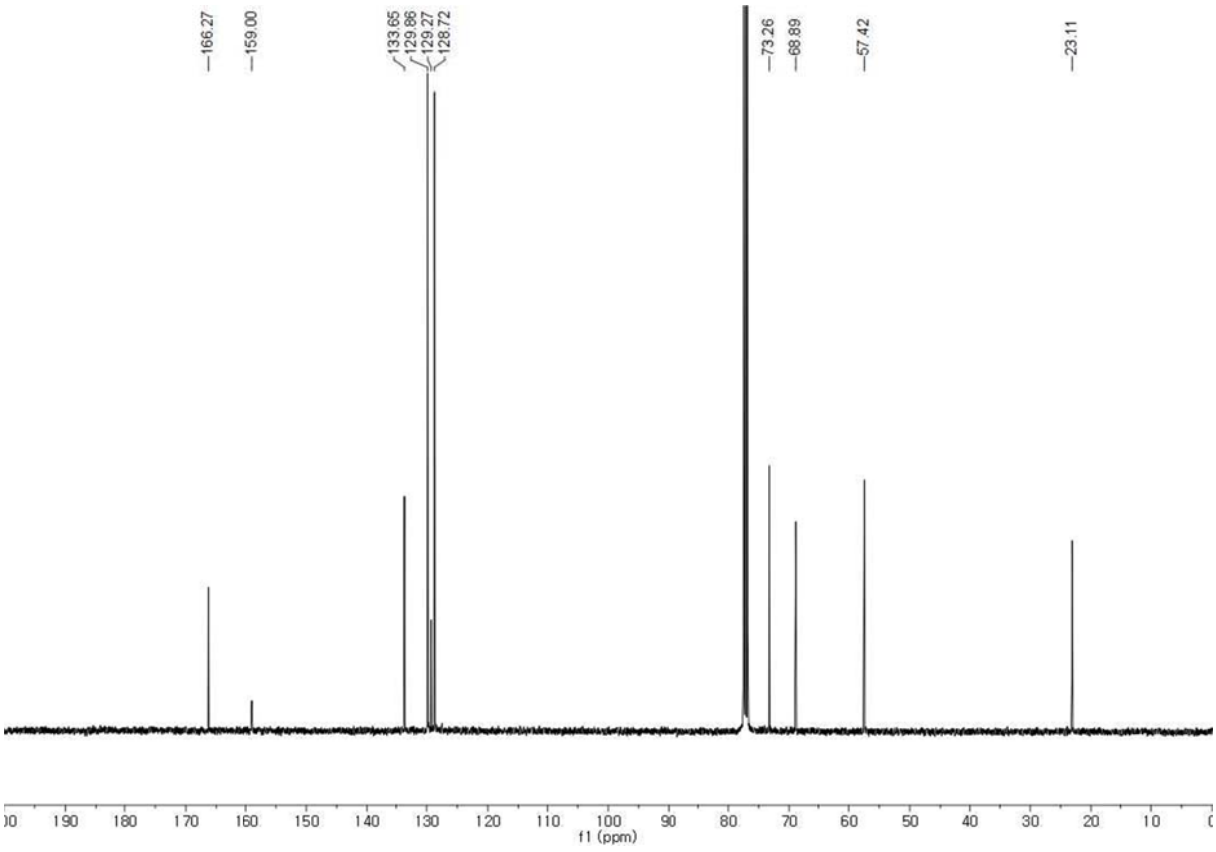
7.55
7.54
7.54
7.53
7.53
7.52
7.43
7.43
7.41
7.39
6.23
4.37
4.35
4.32
4.29
4.19
4.16
4.13
4.11
1.43
2.00
0.97
2.03
0.99
0.98
1.01
0.98
0.99
3.05
f1 (ppm)

H
N
O
O
OBz

24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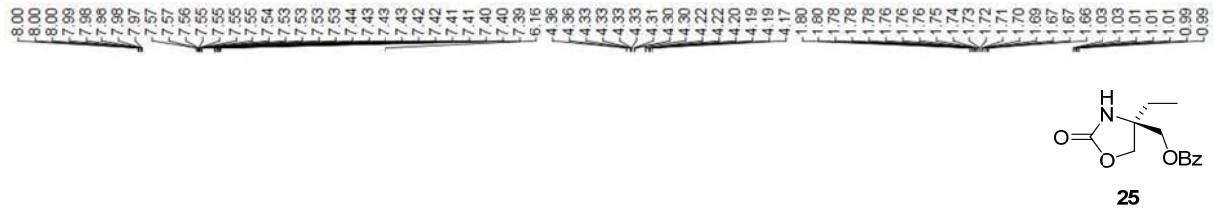
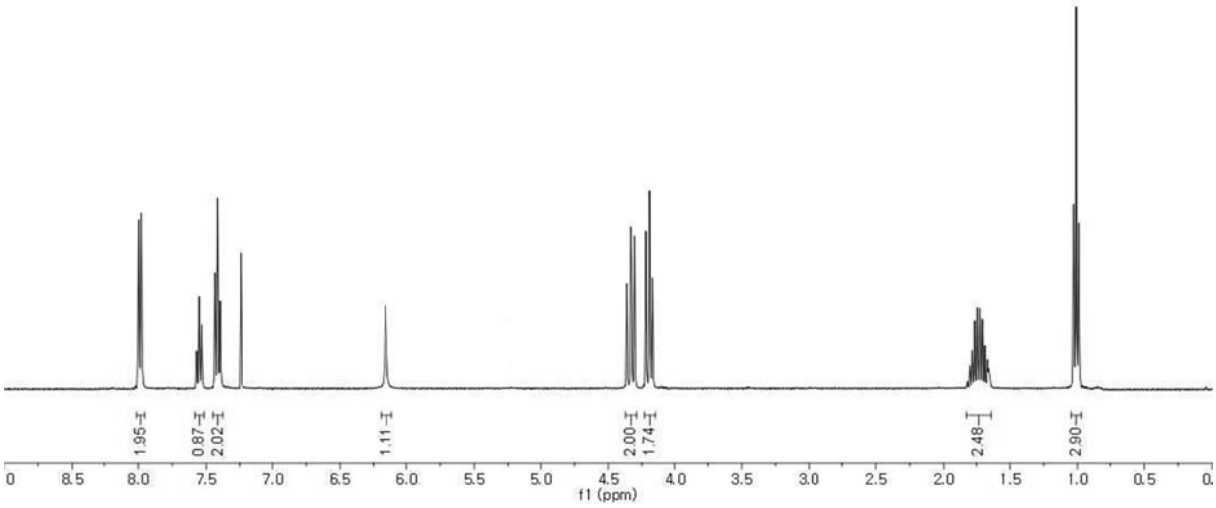
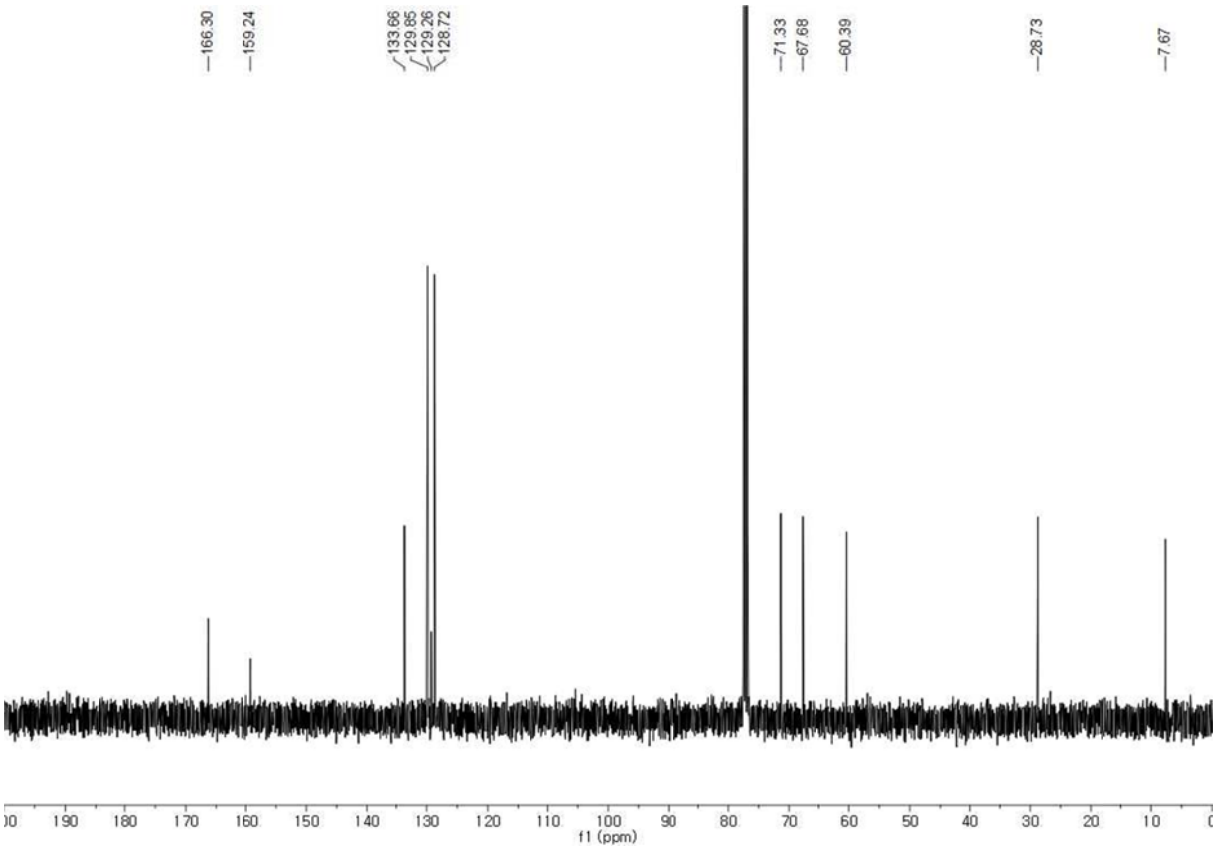
128.72
73.26
68.89
57.42
23.11
f1 (ppm)

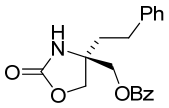


H
N
O
O
OBz

25


1.95
0.87
2.02
1.11
2.00
1.74
2.48
2.90
f1 (ppm)


166.30
159.24
133.66
129.85
129.26
128.72
71.33
67.68
60.39
28.73
7.67
f1 (ppm)


Ph
H
N
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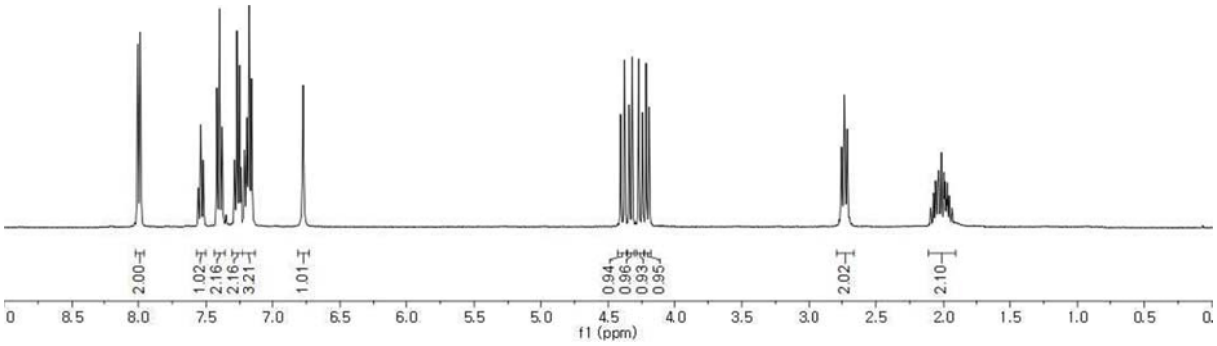
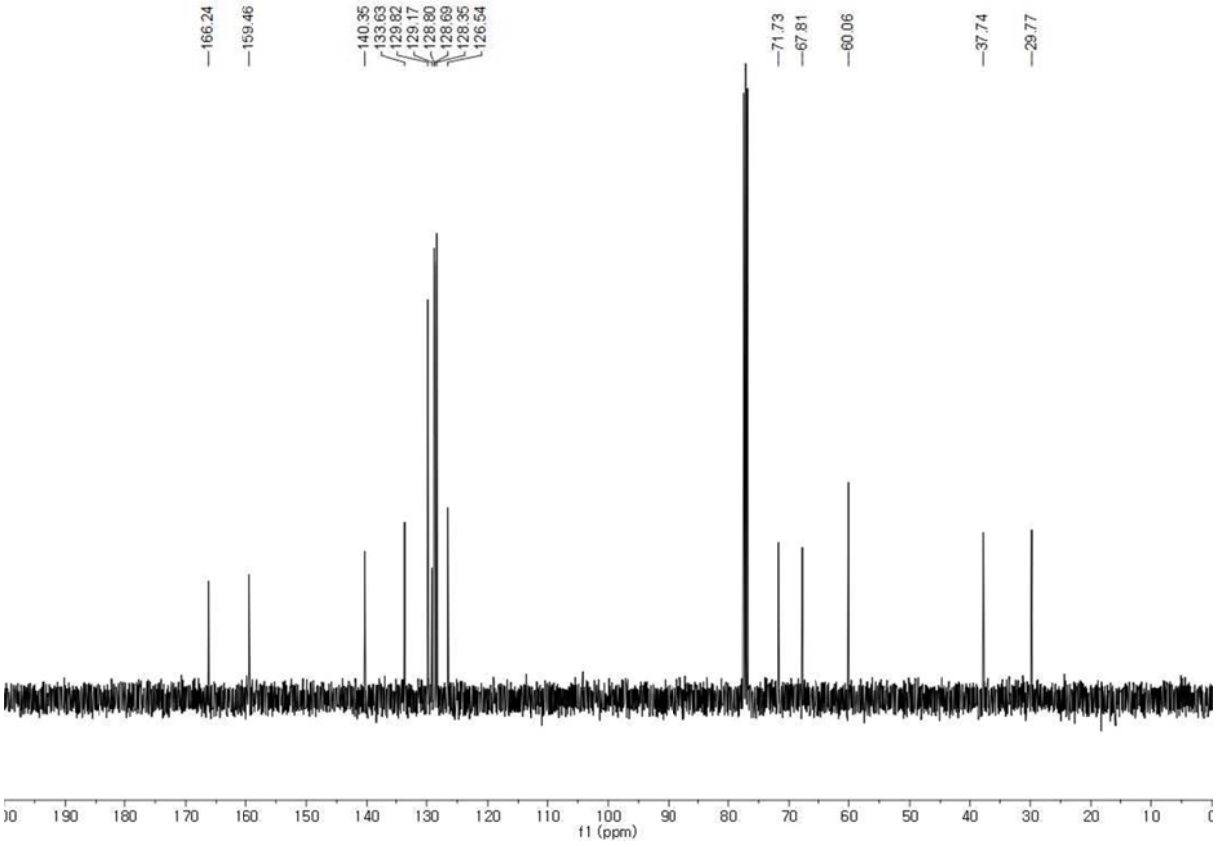
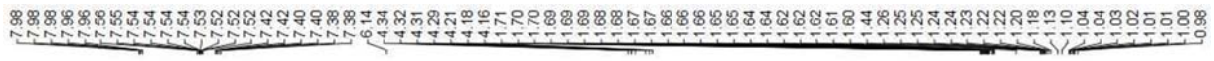
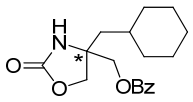
OBz

26


2.00
1.02
2.16
2.16
3.21
1.01
0.94
0.96
0.93
0.95
2.02
2.10
f1 (ppm)


166.24
159.46
140.35
133.63
129.82
129.17
128.80
128.69
128.35
126.54
71.73
67.81
60.06
37.74
29.77
f1 (ppm)




H
N
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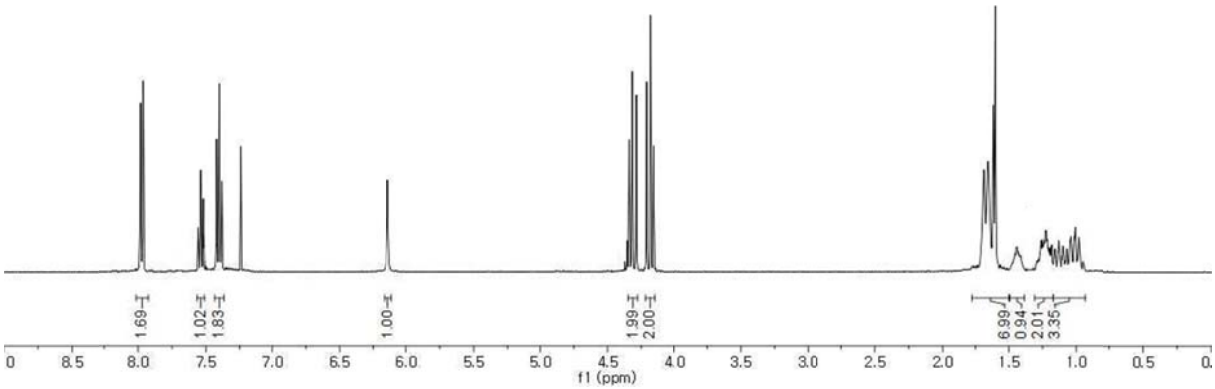
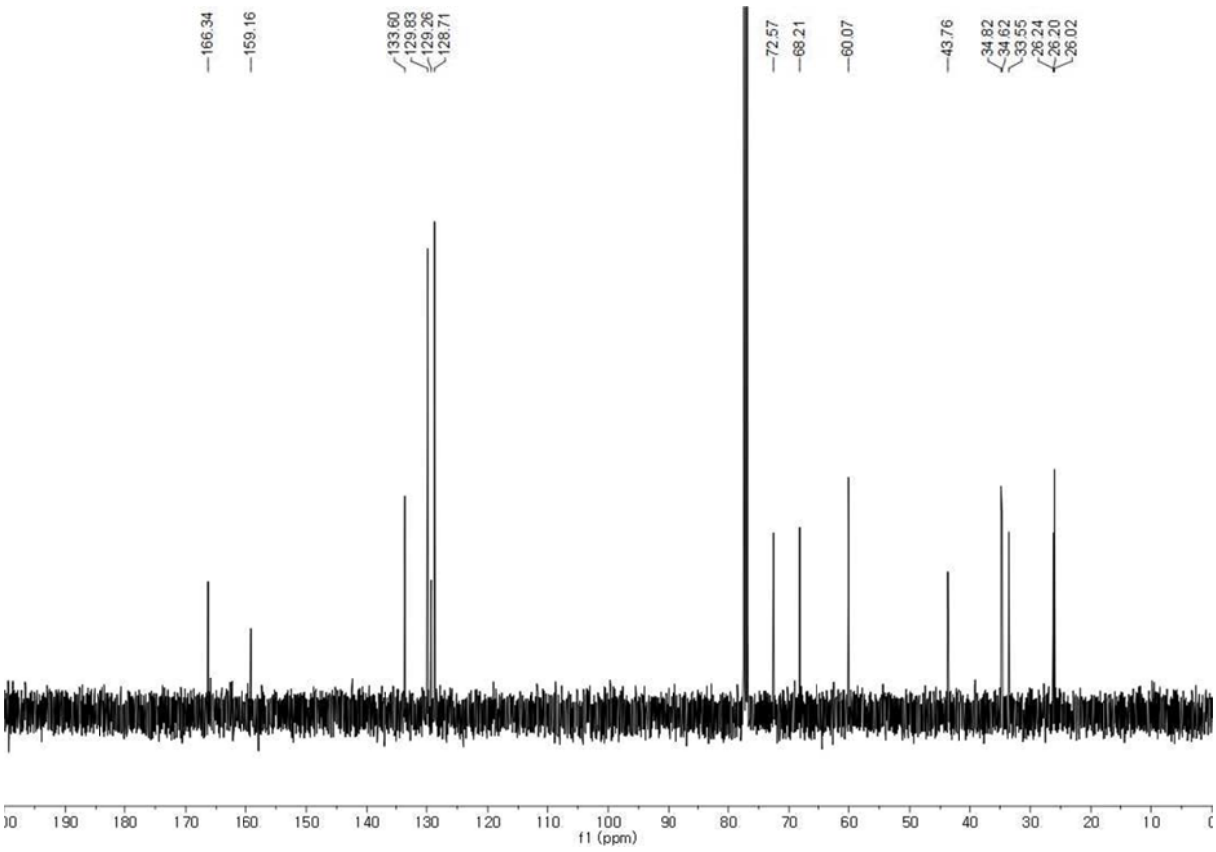
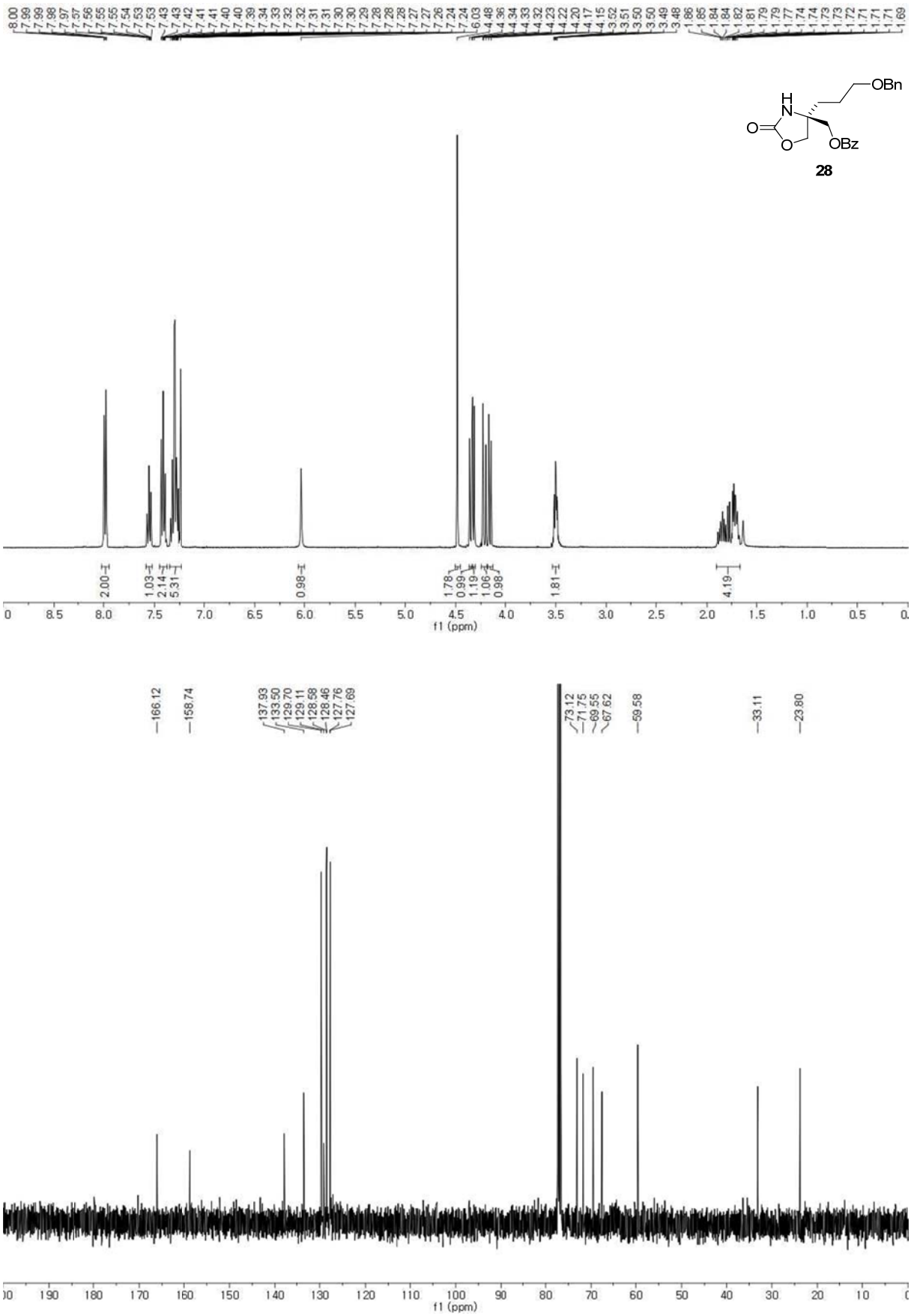
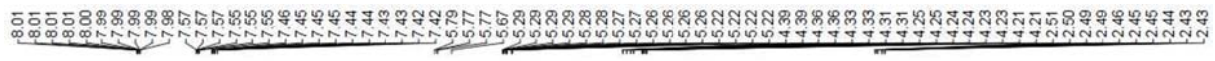
OBz

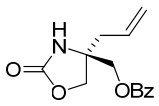
27


1.69
1.02
1.83
1.00
1.99
2.00
6.99
0.94
2.01
3.35
f1 (ppm)

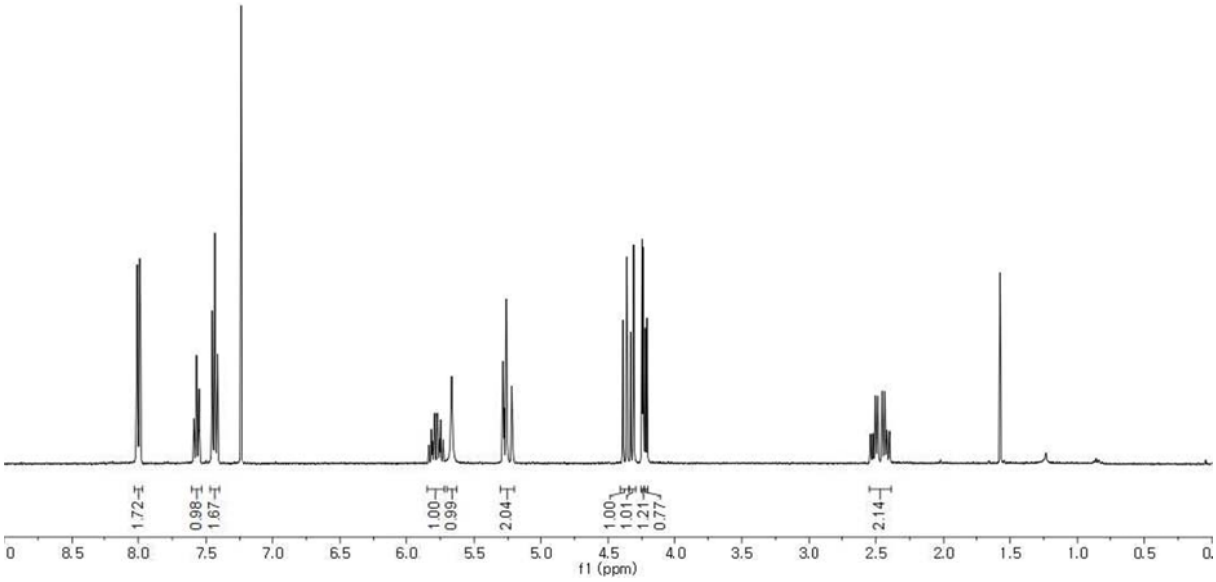

166.34
159.16
133.60
129.83
129.26
128.71
72.57
68.21
60.07
43.76
34.82
34.62
33.55
26.24
26.20
26.02
f1 (ppm)

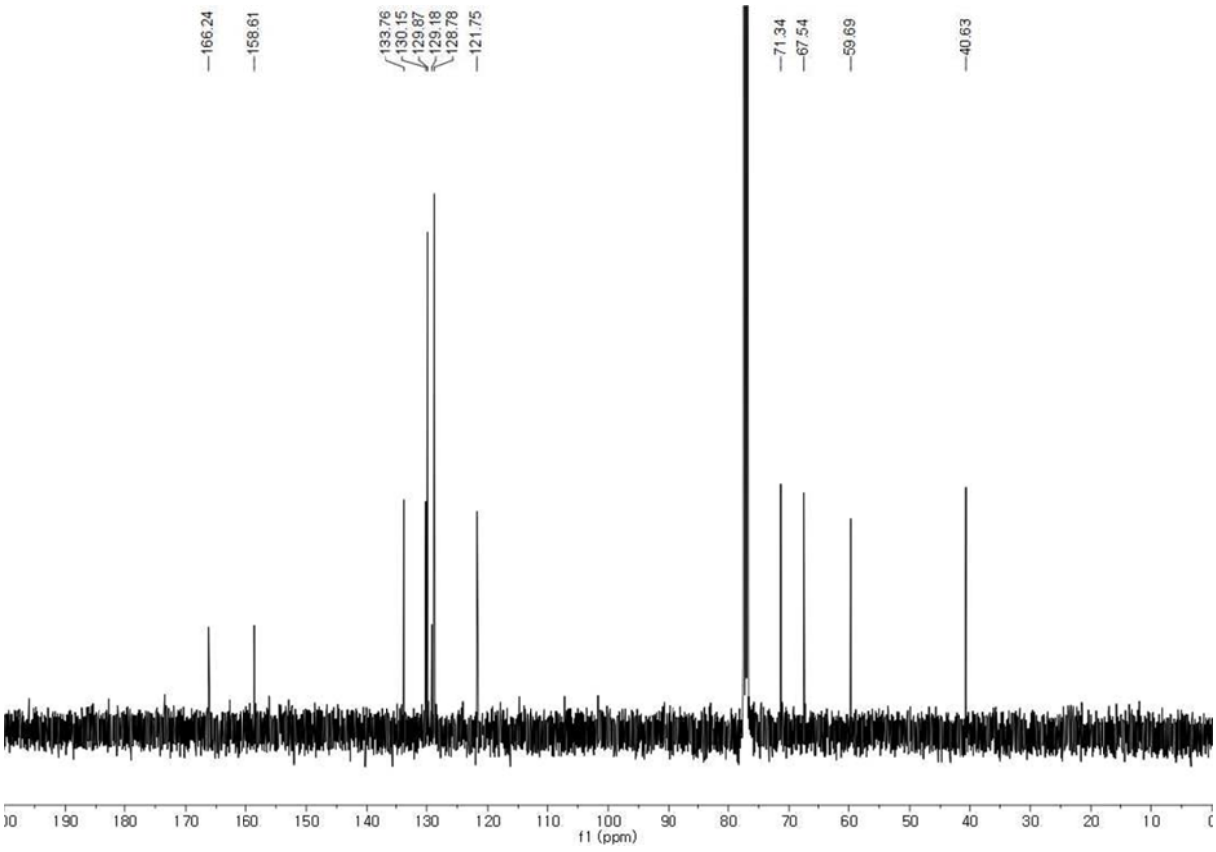

OBn
H
N
O
O
OBz
28
f1 (ppm)
f1 (ppm)




H
N
O
O
OBz

29


1.72
0.98
1.67
1.00
0.99
2.04
1.00
1.01
1.21
0.77
2.14
f1 (ppm)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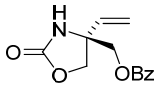
158.61
133.76
130.15
129.87
129.18
128.78
121.75
71.34
67.54
59.69
40.63
f1 (ppm)


H
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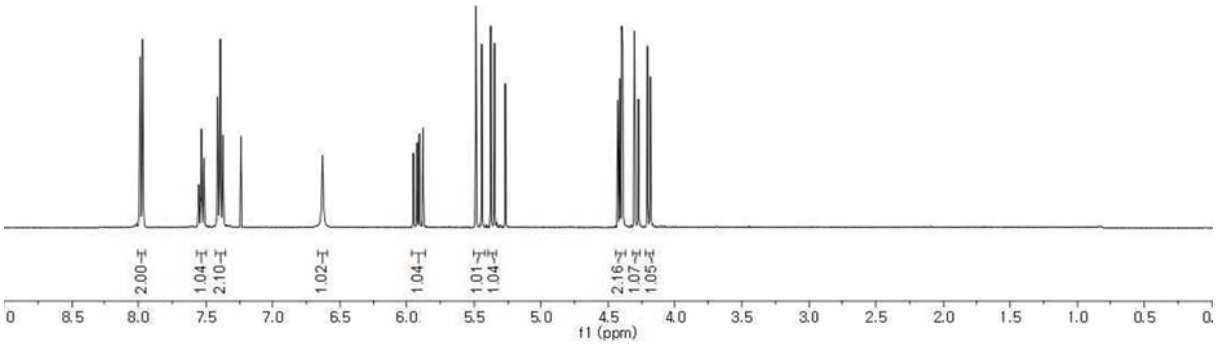
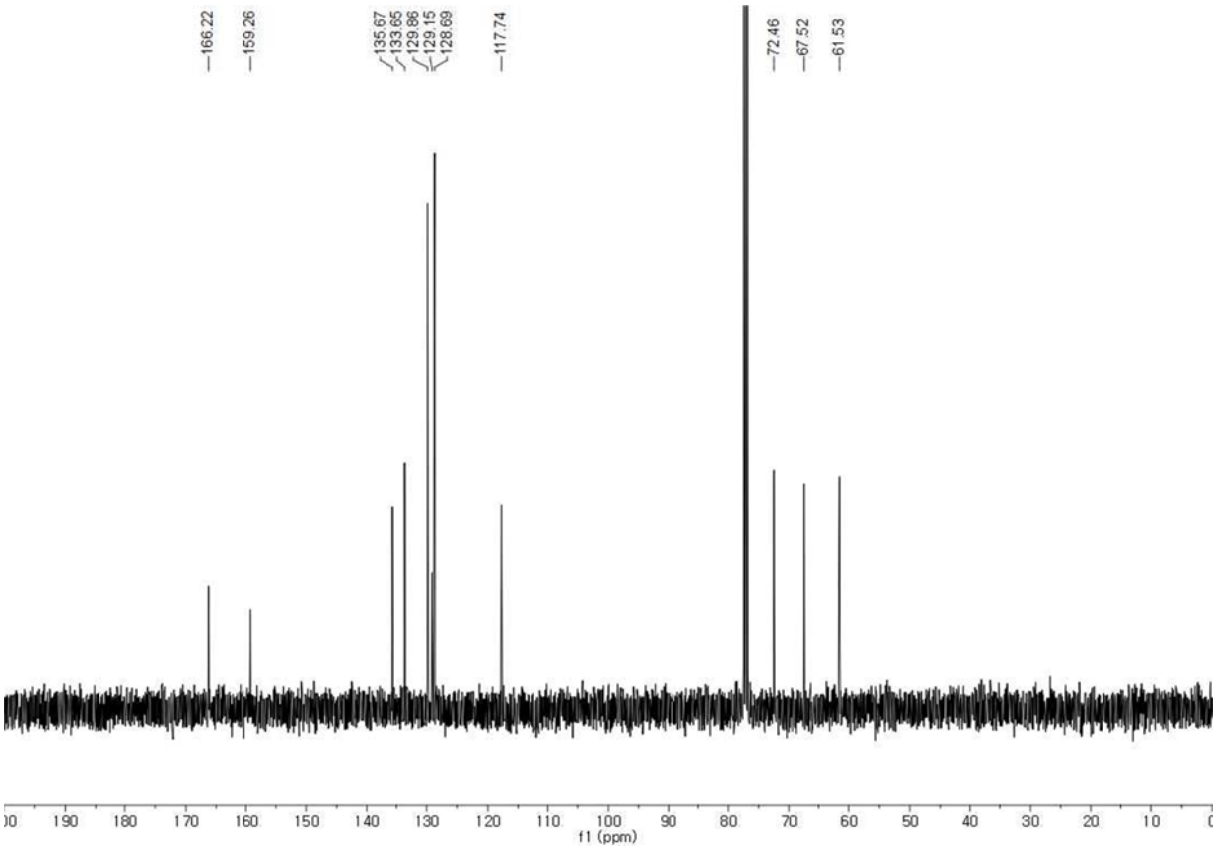
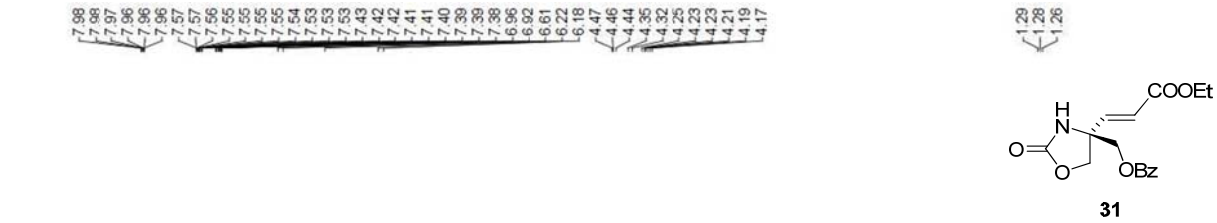
30


2.00
1.04
2.10
1.02
1.04
1.01
1.04
2.16
1.07
1.05
f1 (ppm)


166.22
159.26
135.67
133.65
129.86
129.15
128.69
117.74
72.46
67.52
61.53
f1 (ppm)


7.98
7.98
7.97
7.96
7.96
7.96
7.57
7.57
7.56
7.55
7.55
7.55
7.55
7.54
7.53
7.53
7.53
7.43
7.42
7.42
7.41
7.41
7.40
7.39
7.39
7.38
6.96
6.92
6.61
6.22
6.18
4.47
4.46
4.44
4.35
4.32
4.25
4.23
4.23
4.21
4.19
4.17
1.29
1.28
1.26

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N
O
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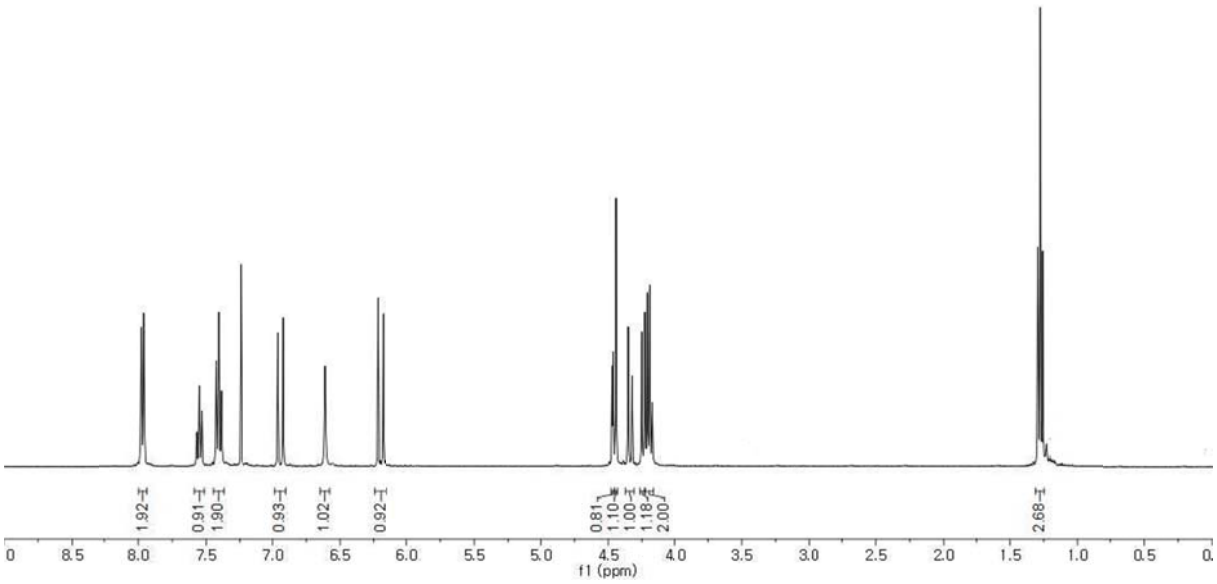
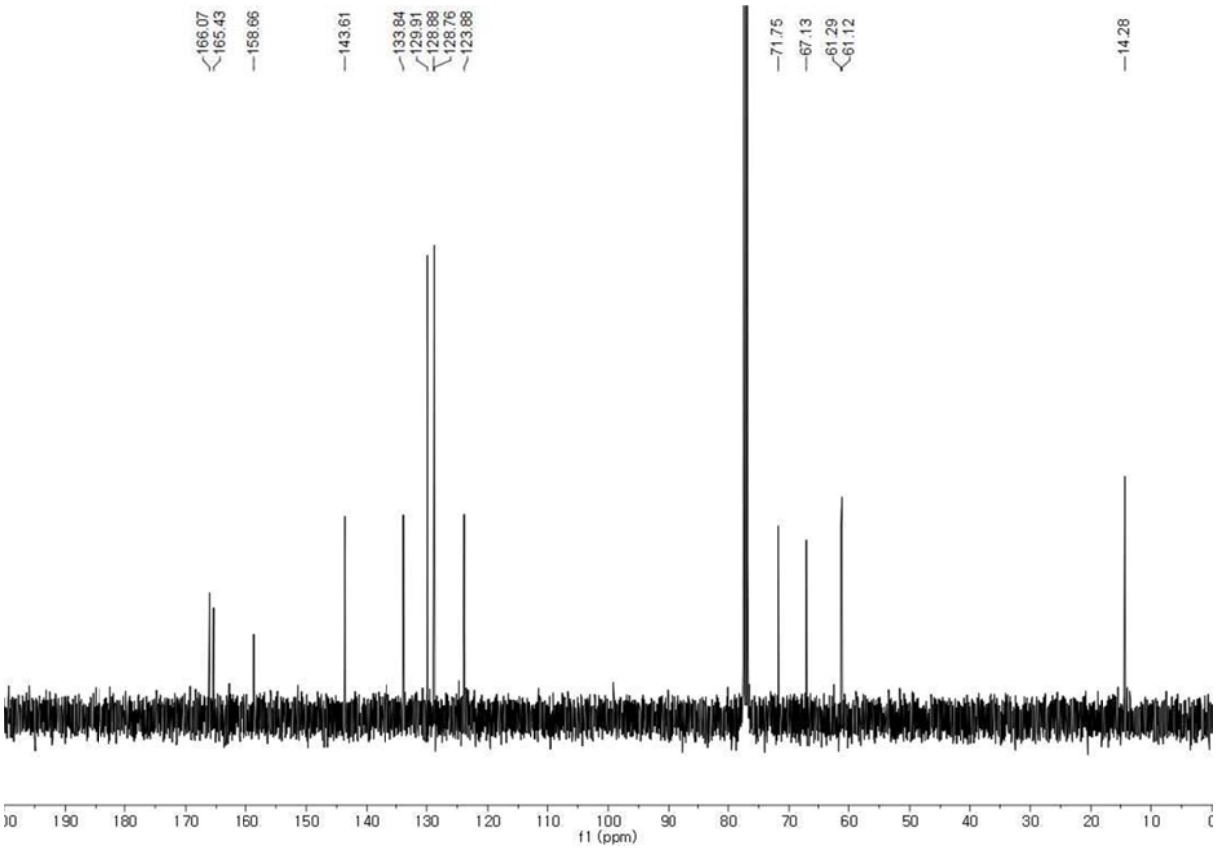
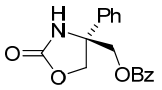
OBz

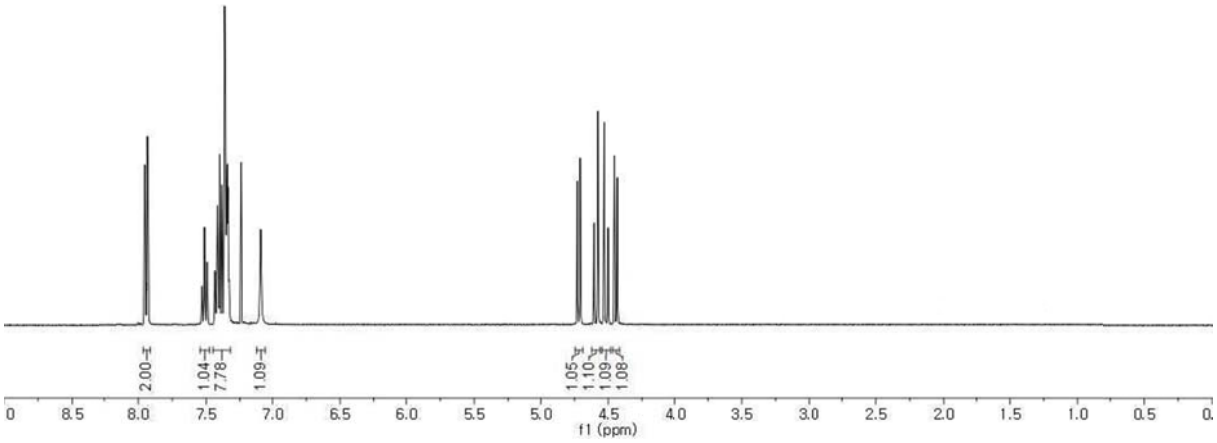
31

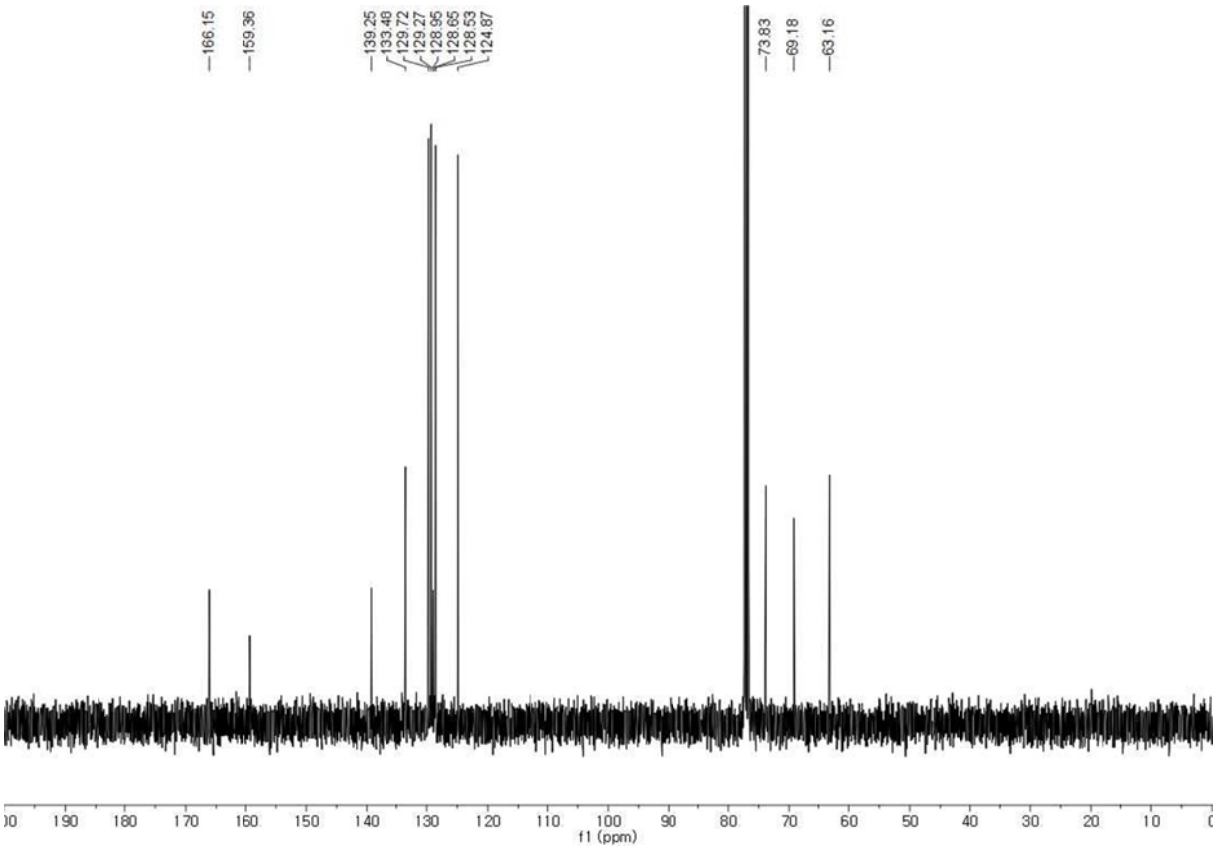

1.92
0.91
1.90
0.93
1.02
0.92
0.81
1.10
1.00
1.18
2.00
2.68
f1 (ppm)


166.07
165.43
158.66
143.61
133.84
129.91
128.88
128.76
123.88
71.75
67.13
61.29
61.12
14.28
f1 (ppm)


H
N
Ph
O
O
OBz

32


2.00
1.04
7.78
1.09
1.05
1.10
1.09
1.08
f1 (ppm)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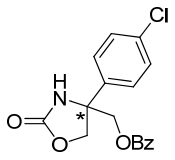
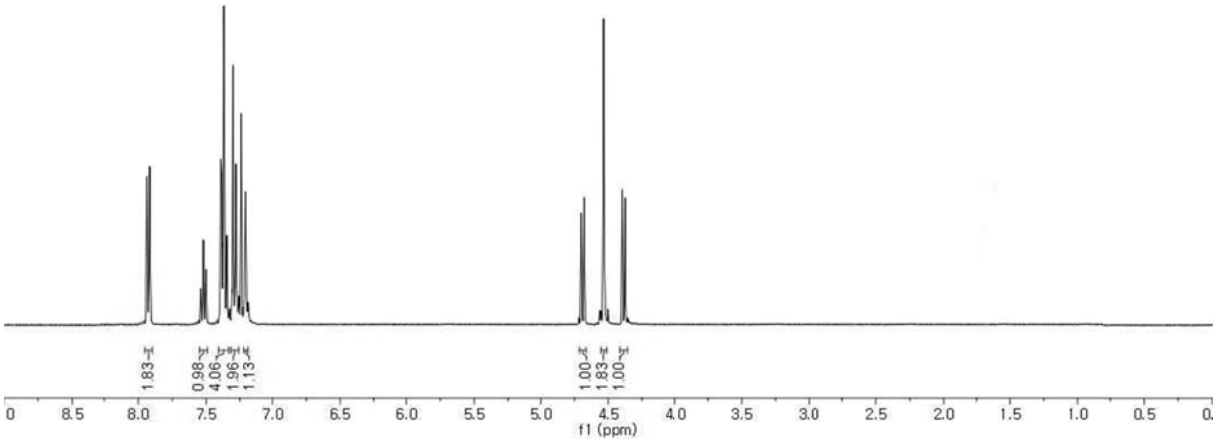
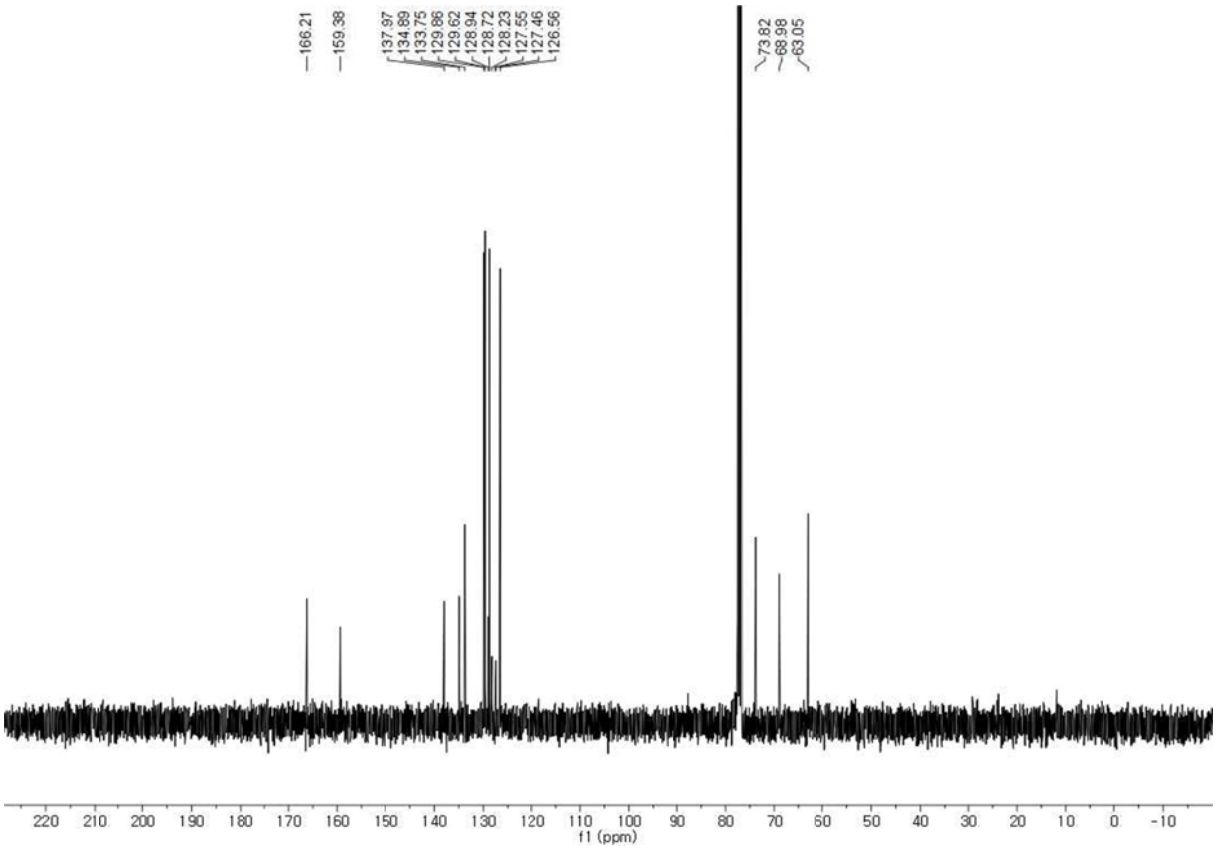
159.36
139.25
133.48
129.72
129.27
128.95
128.65
128.53
124.87
73.83
69.18
63.16
f1 (ppm)


Cl
H
N
O
O
*
OBz

33


1.83
0.98
4.06
1.96
1.13
1.00
1.83
1.00
f1 (ppm)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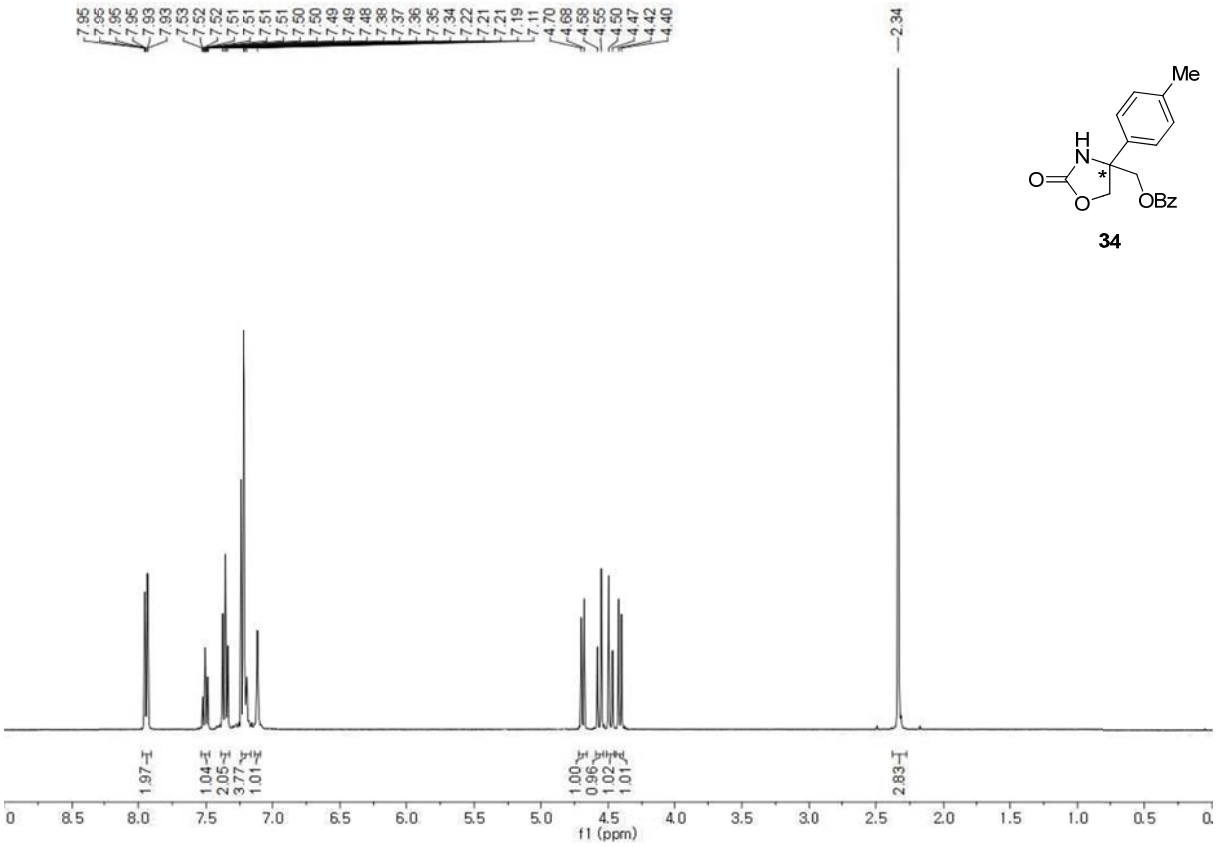
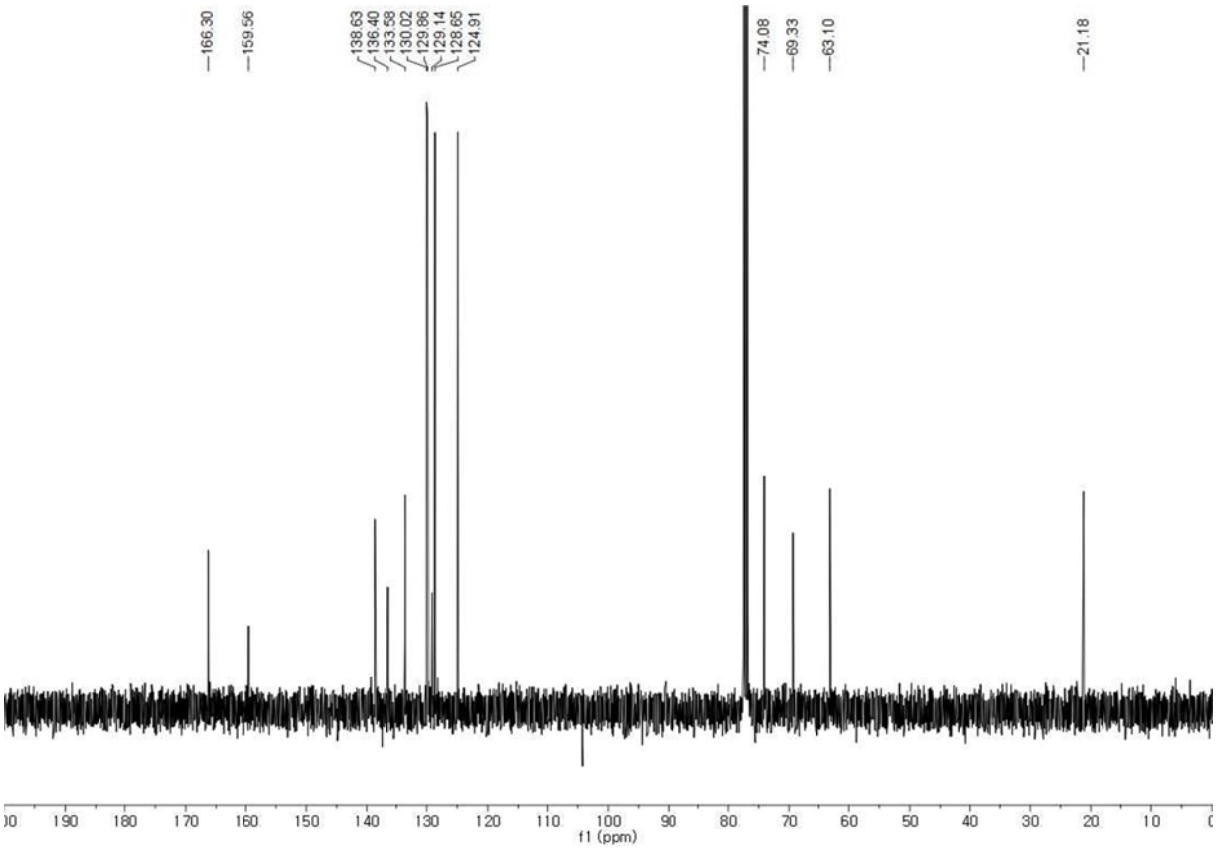
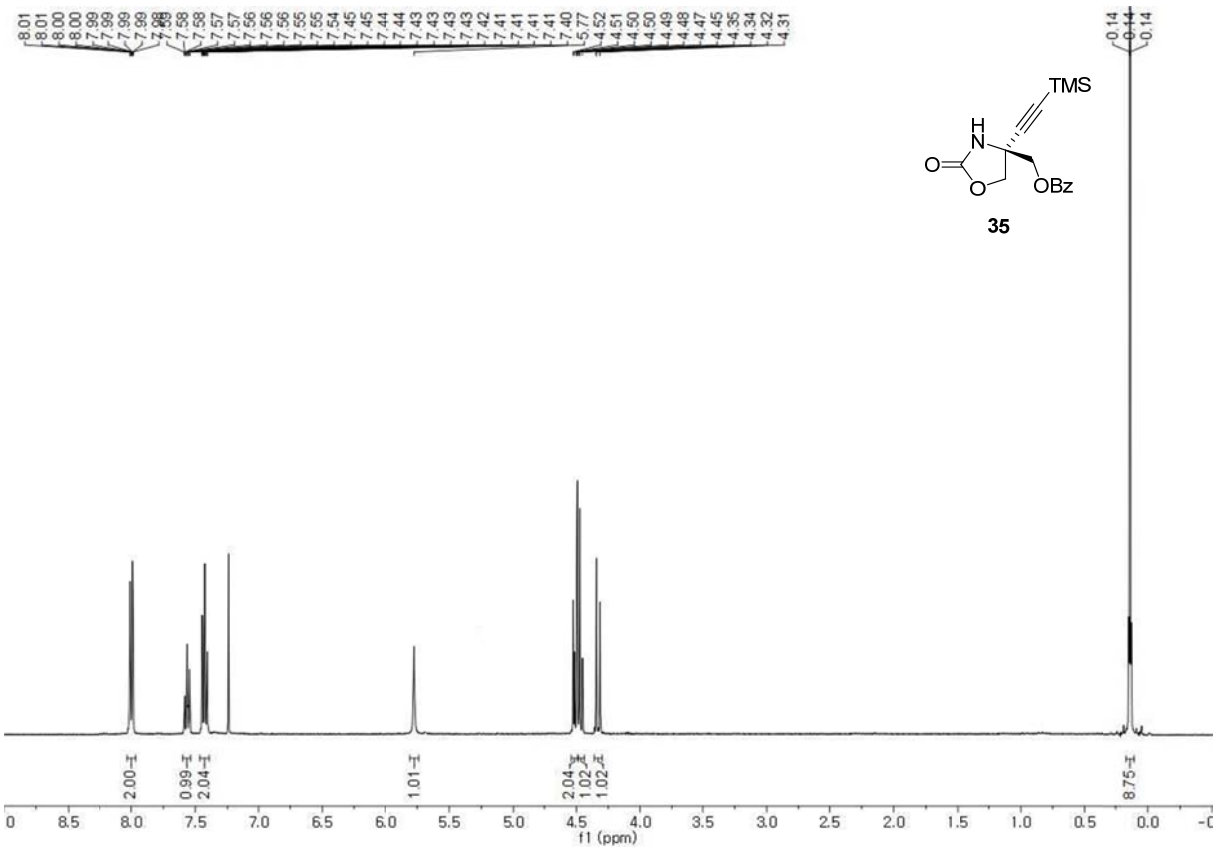
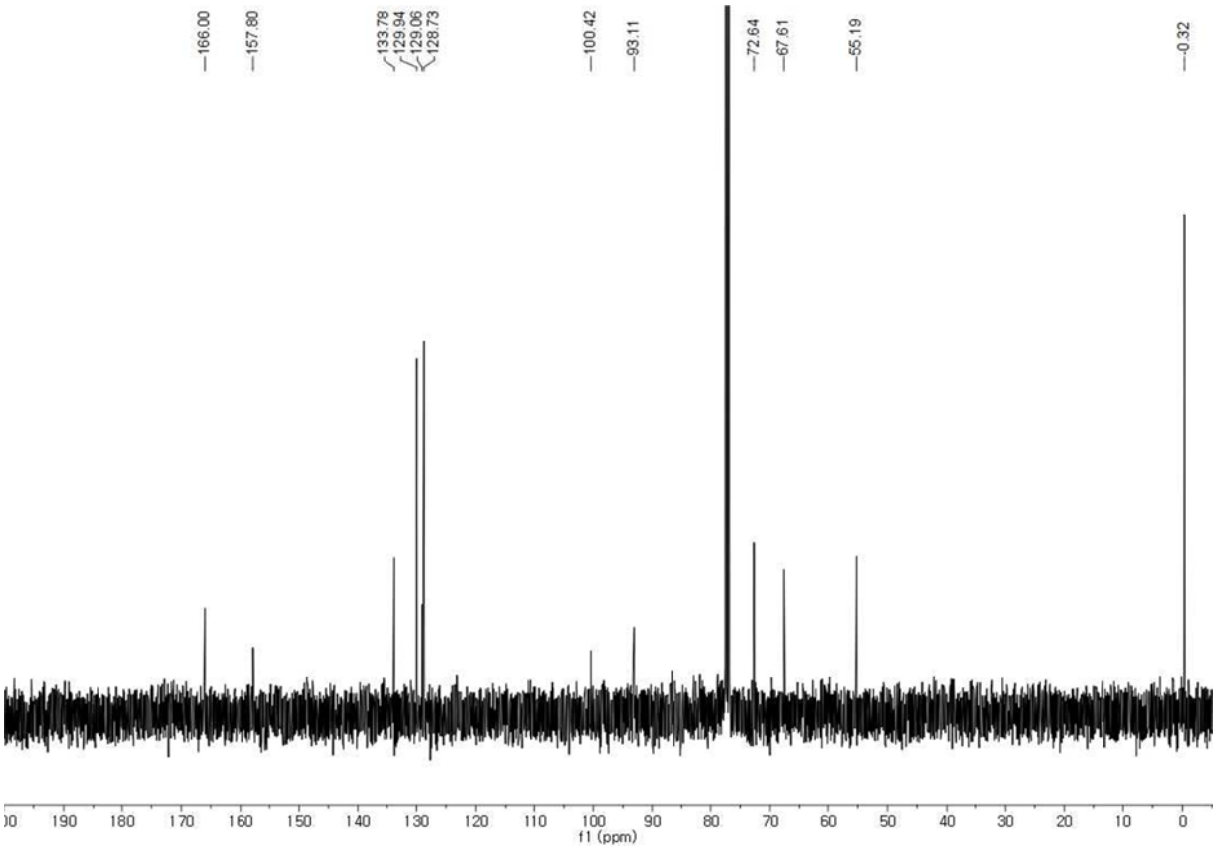
159.38
137.97
134.89
133.75
129.86
129.62
128.94
128.72
128.23
127.55
127.46
126.56
73.82
68.98
63.05
f1 (ppm)


Me
H
N
O
O
*
OBz
34
f1 (ppm)


f1 (ppm)


TMS
H
N
O
O
OBz
35
f1 (ppm)


166.00
157.80
133.78
129.94
129.06
128.73
100.42
93.11
72.64
67.61
55.19
0.32
f1 (ppm)