Biomimetic Total Synthesis of (±)-Berkeleyamide D

Deokhee Jo[ab] and Sunkyu Han*[ab]

[a] Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea

[b] Center for Catalytic Hydrocarbon Functionalizations, Institute for Basic Science (IBS), Daejeon 34141, Republic of Korea

Supporting Information

General Procedures

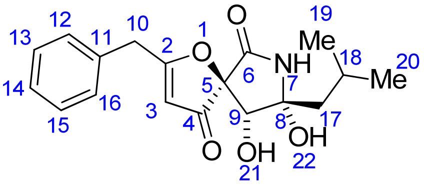
All reactions were performed in oven-dried or flame-dried round-bottomed flasks. Unless otherwise noted, the flasks were fitted with rubber septa and reactions were conducted under a positive pressure of argon. Stainless steel syringes or cannulae were used to transfer air- and moisture-sensitive liquids. Flash column chromatography was performed as described by Still et al. using silica gel (60-Å pore size, 40–63 μm, 4-6% H_2O content, Merck).[1] Analytical thin–layer chromatography (TLC) was performed using glass plates pre-coated with 0.25 mm silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light and/or by exposure to an aqueous solution of ceric ammonium molybdate (CAM).

Materials and Instrumentations

Unless otherwise stated, all commercial reagents and solvents were used without additional purification with the following exceptions: dichloromethane and tetrahydrofuran were purchased from Merck and Daejung Inc., respectively and were purified by the method of Grubbs et al. under positive argon pressure.[2]

Proton and carbon nuclear magnetic resonance spectra were recorded with Bruker Ascend 400 (400 MHz), Varian Inova 600 (600 MHz), or Agilent Technologies DD2 (600 MHz) spectrometers. Proton nuclear magnetic resonance spectra are referenced from the residual protium in the NMR solvent ($CDCl_3$: δ 7.24 ($CHCl_3$)). Data are reported in the following manners: chemical shift in ppm [multiplicity (s = singlet, d = doublet, m = multiplet, app = apparent, br = broad), coupling constant(s) in Hertz, integration]. Carbon-13 nuclear magnetic resonance spectra are referenced from the carbon resonances of the solvent ($CDCl_3$: δ 77.23). Data are reported in the following manners: chemical shift in ppm. High resolution mass spectra were obtained from KAIST Research Analysis Center (Daejeon) by using ESI method.

Positional Numbering System



berkeleyamide D **(3)**

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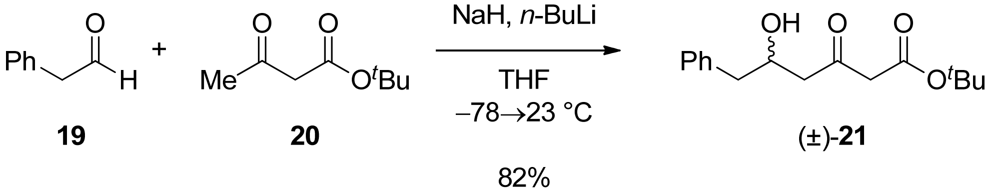
[1] W. C. Still, M. Kahn and A. Mitra, *J. Org. Chem.*, 1978, **43**, 2923.

[2] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518.



tert-Butyl 5-hydroxy-3-oxo-6-phenylhexanoate (21):

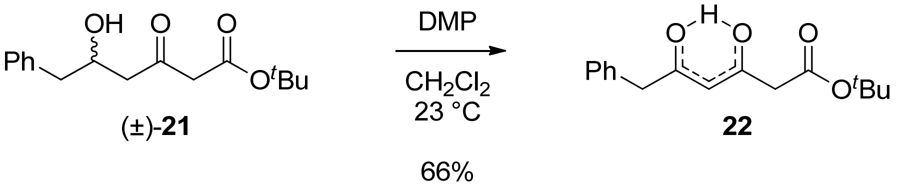
To a suspension of sodium hydride (NaH, 60% dispersion in mineral oil, 704 mg, 17.6 mmol, 1.10 equiv) in THF (40 mL) at 0 °C was added *tert*-butyl acetoacetate (**20**, 2.69 mL, 16.0 mmol, 1 equiv) dropwise under argon. After stirring the reaction mixture at 0 °C for 30 min, a solution of *n*-BuLi (2.45 M in *n*-hexane, 7.18 mL, 17.6 mmol, 1.10 equiv) was added dropwise to the reaction mixture. The reaction mixture was stirred at 0 °C for 30 min. The resulting milky solution was cooled to −78 °C. Subsequently, phenylacetaldehyde (**19**, 1.88 mL, 16.0 mmol, 1.00 equiv) in THF (40 mL) was transferred by cannula to the reaction mixture. The reaction mixture was allowed to warm to 23 °C. After 3 h, saturated aqueous ammonium chloride solution (60 mL) was added to the reaction mixture and the resulting mixture was diluted with ethyl acetate (120 mL), and the layers were separated. The aqueous layer was extracted with ethyl acetate (2 × 120 mL), and the combined organic layers were dried over anhydrous sodium sulfate and were concentrated under reduced pressure. The resulting crude residue was purified by flash column chromatography (silica gel: diam. 5 cm, ht. 13 cm; eluent: ethyl acetate : hexanes = 1 : 4 to 1 : 3) to afford (±)-**21** (3.65 g, 82%) as a yellow oil.

^{1}H NMR (600.0 MHz, $CDCl_3$) δ 7.31−7.17 (m, 5H), 4.32–4.26 (m, 1H), 3.32 (s, 2H), 2.87 (br-s, 1H), 2.82 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.72 (dd, *J* = 13.6, 6.3 Hz, 1H), 2.67 (dd, *J* = 17.5, 3.4 Hz, 1H), 2.61 (dd, *J* = 17.5, 8.6 Hz, 1H), 1.42 (s, 9H).

^{13}C NMR (150.7 MHz, $CDCl_3$) δ 203.6, 166.2, 137.8, 129.4, 128.4, 126.5, 82.0, 68.5, 51.1, 48.6, 42.9, 27.9.

HRMS (ESI): Calculated for $C_{16}H_{22}O_4$ $[M+Na]^+$: 301.1410, found: 301.1412.

TLC (ethyl acetate : hexanes = 1 : 2) R*f*: 0.42 (CAM, UV).



tert-Butyl 3,5-dioxo-6-phenylhexanoate (22):

To a stirred solution of (±)-**21** (668 mg, 2.40 mmol, 1 equiv) in dichloromethane (24 mL) was added Dess–Martin periodinane (DMP, 1.53 g, 3.60 mmol, 1.50 equiv) at 23 °C. After 30 min, a mixture of saturated aqueous sodium thiosulfate solution and saturated aqueous sodium bicarbonate solution (1:1, 35 mL) was added to the reaction mixture, and the layers were separated. The aqueous layer was extracted with dichloromethane (3 × 35 mL), and the combined organic layers were washed with brine (35 mL), were dried over anhydrous sodium sulfate and were concentrated under reduced pressure. The resulting crude residue was purified by flash column chromatography (silica gel: diam. 3 cm, ht. 13 cm; eluent: ethyl acetate : hexanes = 1 : 19 to 1 : 6) to afford **22** (439 mg, 66%) as a yellow oil. **22** was obtained as a mixture of keto/enol tautomers (keto/enol = 1/7).

^{1}H NMR (599.3 MHz, $CDCl_3$, major enol tautomer) δ 7.34–7.16 (m, 5H), 5.50 (s, 1H), 3.59 (s, 2H), 3.19 (s, 2H), 1.40 (s, 9H).

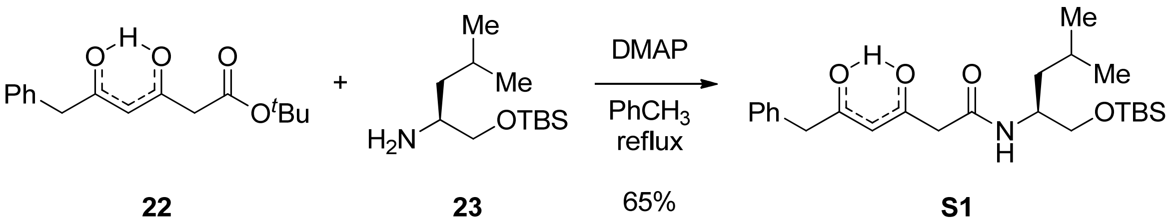
^{1}H NMR (599.3 MHz, $CDCl_3$, minor keto tautomer) δ 7.34–7.16 (m, 5H), 3.78 (s, 2H), 3.69 (s, 2H), 3.38 (s, 2H), 1.43 (s, 9H).

^{13}C NMR (150.7 MHz, $CDCl_3$, major enol tautomer) δ 191.5, 187.9, 166.7, 134.9, 129.5, 128.9, 127.3, 100.1, 82.1, 46.5, 44.8, 28.0.

^{13}C NMR (150.7 MHz, $CDCl_3$, minor keto tautomer) δ 201.7, 197.5, 166.2, 133.3, 129.8, 129.0, 127.5, 82.5, 55.6, 50.8, 50.7, 28.1.

HRMS (ESI): Calculated for $C_{16}H_{20}O_4$ $[M+Na]^+$: 299.1254, found: 299.1255.

TLC (ethyl acetate : hexanes = 1 : 4) R*f*: 0.54 (CAM, UV).



(*S*)-*N*-(1-((*tert*-Butyldimethylsilyl)oxy)-4-methylpentan-2-yl)-3,5-dioxo-6-phenylhexanamide (S1):

To a stirred solution of **22** (735 mg, 2.66 mmol, 1 equiv) and (*S*)-1-((*tert*-butyldimethylsilyl)oxy)-4-methylpentan-2-amine[3,4] (**23**, 727 μL, 2.66 mmol, 1.00 equiv) in toluene (266 mL) was added DMAP (164 mg, 1.33 mmol, 0.50 equiv) at 23 °C and the reaction flask was equipped with a reflux condenser. The resulting reaction mixture was heated to 120 °C. After 3 h, the reaction mixture was cooled to 23 °C and was concentrated under reduced pressure. The resulting crude residue was purified by flash column chromatography (silica gel: diam. 4 cm, ht. 18 cm; eluent: ethyl acetate : hexanes = 1 : 3) to afford **S1** (756 mg, 65%) as a yellow oil. **S1** was obtained as a mixture of keto/enol tautomers (keto/enol = 1/12).

^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.35−7.15 (m, 5H), 6.59 (d, J = 8.9 Hz, 1H), 5.54 (s, 1H), 4.05−3.95 (m, 1H), 3.58 (s, 2H), 3.54 (dd, J = 3.4, 1.9 Hz, 2H), 3.19 (d, J = 3.1 Hz, 2H), 1.60−1.48 (m, 1H), 1.35 (ddd, J = 7.7, 6.3, 3.4 Hz, 2H), 0.89 (d, J = 2.3 Hz, 3H), 0.87 (d, J = 2.6 Hz, 3H), 0.86 (s, 9H), 0.00 (s, 3H), –0.01 (s, 3H).

^{13}C NMR (150.7 MHz, $CDCl_3$) δ 191.2, 190.2, 165.3, 134.7, 129.5, 129.0, 127.5, 100.7, 64.8, 49.2, 47.0, 44.6, 40.6, 26.0, 25.1, 23.2, 22.7, 18.4, –5.4, –5.4.

HRMS (ESI): Calculated for $C_{24}H_{39}NO_4Si$ $[M+Na]^+$: 456.2541, found: 456.2547.

TLC (ethyl acetate : hexanes = 1 : 2) R*f*: 0.49 (CAM, UV).

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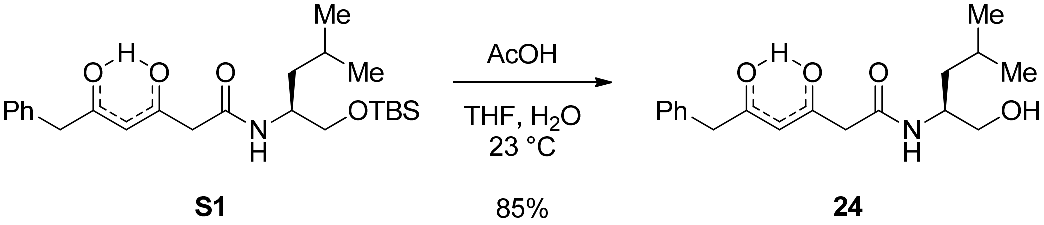
[3] **23** was synthesized using a procedure reported by the Park group: E. Kim, M. Koh, J. Ryu and S. B. Park, *J. Am. Chem. Soc.*, 2008, **130**, 12206.

[4] Spectroscopic data of **23** was consistent with those reported by the TenBrink group: R. E. TenBrink, *J. Org. Chem.*, 1987, **52**, 418.



(*S*)-*N*-(1-Hydroxy-4-methylpentan-2-yl)-3,5-dioxo-6-phenylhexanamide (24):

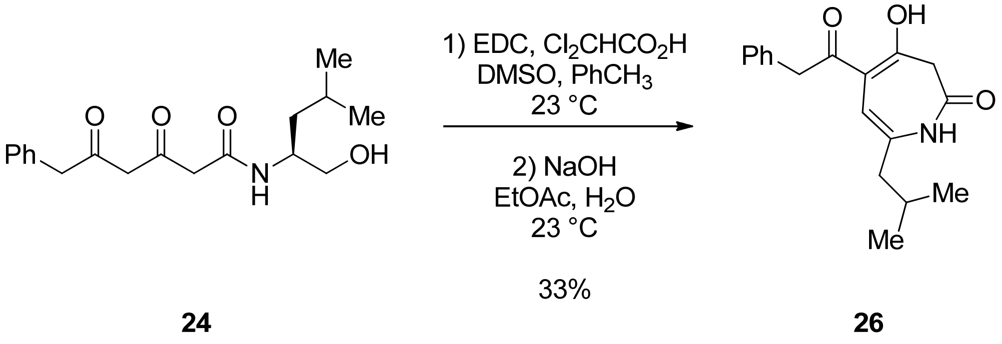
To a stirred solution of **S1** (542 mg, 1.25 mmol, 1 equiv) in a 1:1 mixture of THF/H_2O (14.2 mL) was added glacial acetic acid (10.7 mL) at 23 °C. After 2.5 h, saturated aqueous sodium bicarbonate solution (19 mL) was added to the reaction mixture and the resulting mixture was diluted with ethyl acetate (120 mL), and the layers were separated. The aqueous layer was extracted with ethyl acetate (3 × 75 mL), and the combined organic layers were dried over anhydrous sodium sulfate and were concentrated under reduced pressure. The resulting crude residue was purified by flash column chromatography (silica gel: diam. 3 cm, ht. 18 cm; eluent: methanol : dichloromethane = 1 : 99 to 1 : 15) to afford **24** (338 mg, 85%) as an orange oil. **24** was obtained as a mixture of keto/enol tautomers (keto/enol = 1/9).

^{1}H NMR (599.3 MHz, $CDCl_3$) δ 7.36−7.16 (m, 5H), 6.61 (br-s, 1H), 5.52 (s, 1H), 4.04−3.96 (m, 1H), 3.65 (dd, *J* = 11.1, 3.5 Hz, 1H), 3.59 (s, 2H), 3.50 (dd, *J* = 11.0, 6.1 Hz, 1H), 3.24 (s, 2H), 1.64−1.52 (m, 1H), 1.38 (ddd, *J* = 14.8, 9.2, 5.8 Hz, 1H), 1.31 (ddd, *J* = 14.0, 8.5, 5.5 Hz, 1H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (150.7 MHz, $CDCl_3$) δ 190.8, 190.4, 166.9, 134.7, 129.4, 128.9, 127.4, 100.5, 65.5, 50.3, 46.8, 44.2, 40.1, 24.9, 23.1, 22.2.

HRMS (ESI): Calculated for $C_{18}H_{25}NO_4$ $[M+Na]^+$: 342.1676, found: 342.1683.

TLC (methanol : dichloromethane = 1 : 10) R*f*: 0.49 (CAM, UV).



4-Hydroxy-7-isobutyl-5-(2-phenylacetyl)-1*H*-azepin-2(3*H*)-one (26):

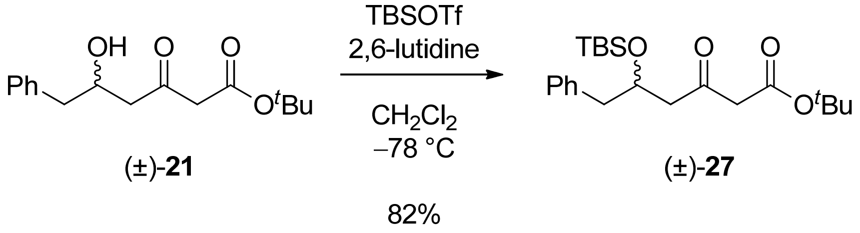
To a stirred solution of **24** (57.9 mg, 0.181 mmol, 1 equiv) in DMSO (1.1 mL) and toluene (1.1 mL) were added EDC (177 mg, 0.906 mmol, 5.00 equiv) and dichloroacetic acid (30.2 μL, 0.363 mmol, 2.00 equiv) at 23 °C. After 18 h, aqueous hydrochloric acid solution (2 M, 2.2 mL) was added to the reaction mixture and the resulting mixture was diluted with ethyl acetate (4 mL), and the layers were separated. The aqueous layer was extracted with ethyl acetate (2 × 4 mL), and the organic layers were combined. Aqueous sodium hydroxide solution (1 M, 15 mL) was added to the combined organic layers and stirred vigorously at 23 °C. After 20 min, the reaction mixture was diluted with diethyl ether (15 mL), and the layers were separated. The aqueous layer was extracted with diethyl ether (3 × 15 mL), and the combined organic layers were dried over anhydrous sodium sulfate and were concentrated under reduced pressure. The resulting crude residue was purified by flash column chromatography (silica gel: diam. 3 cm, ht. 7 cm; eluent: ethyl acetate : hexanes = 1 : 2) to afford **26** (17.8 mg, 33%) as a yellow oil.

^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.41 (br-s, 1H), 7.34−7.17 (m, 5H), 5.84 (s, 1H), 3.84 (s, 2H), 3.23 (s, 2H), 2.10 (d, *J* = 7.5 Hz, 2H), 1.83−1.72 (m, 1H), 0.91 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (150.7 MHz, $CDCl_3$) δ 197.0, 174.9, 165.4, 134.1, 133.6, 129.5, 129.0, 127.4, 108.8, 108.7, 46.1, 45.7, 44.5, 27.2, 22.4.

HRMS (ESI): Calculated for $C_{18}H_{21}NO_3$ $[M+Na]^+$: 322.1414, found: 322.1412.

TLC (ethyl acetate : hexanes = 1 : 2) R*f*: 0.40 (CAM, UV).



***tert*-Butyl 5-((*tert*-butyldimethylsilyl)oxy)-3-oxo-6-phenylhexanoate (27):**

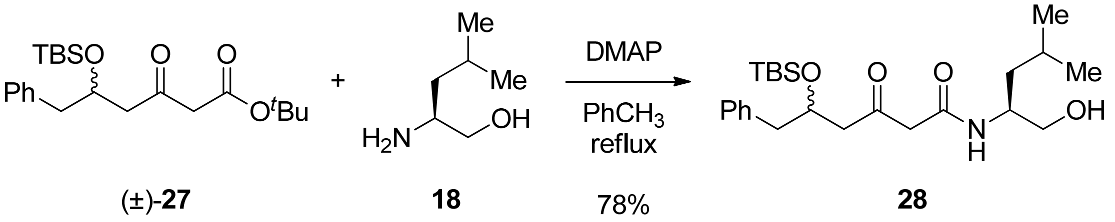
To a stirred solution of (±)-**21** (1.50 g, 5.38 mmol, 1 equiv) and 2,6-lutidine (956 µL, 8.07 mmol, 1.50 equiv) in CH_2Cl_2 (26.9 mL) was added *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBSOTf, 1.39 mL, 5.92 mmol, 1.10 equiv) dropwise at −78 °C. After 1.5 h, saturated aqueous sodium bicarbonate solution (20 mL) was added to the reaction mixture, and the layers were separated. The aqueous layer was extracted with dichloromethane (2 × 30 mL), and the combined organic layers were dried over anhydrous sodium sulfate and were concentrated under reduced pressure. The resulting crude residue was purified by flash column chromatography (silica gel: diam. 4 cm, ht. 12 cm; eluent: ethyl acetate : hexanes = 1 : 40) to afford (±)-**27** (1.72 g, 82%) as a colorless oil.

^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.28−7.13 (m, 5H), 4.39−4.30 (m, 1H), 3.31 (s, 2H), 2.75 (d, *J* = 6.3 Hz, 2H), 2.64 (dd, *J* = 16.1, 6.4 Hz, 1H), 2.55 (dd, *J* = 16.1, 5.5 Hz, 1H), 1.43 (s, 9H), 0.83 (s, 9H), −0.04 (s, 3H), −0.13 (s, 3H).

^{13}C NMR (150.7 MHz, $CDCl_3$) δ 202.3, 166.4, 138.3, 129.9, 128.5, 126.6, 82.0, 70.3, 52.3, 49.8, 44.3, 28.1, 26.0, 18.1, −4.8, −4.8.

HRMS (ESI): Calculated for $C_{22}H_{36}O_4Si$ $[M+Na]^+$: 415.2275, found: 415.2264.

TLC (ethyl acetate : hexanes = 1 : 10) R*f*: 0.44 (CAM, UV).



5-((*tert*-Butyldimethylsilyl)oxy)-*N*-((*S*)-1-hydroxy-4-methylpentan-2-yl)-3-oxo-6-phenylhexanamide (28):

To a stirred solution of (±)-**27** (1.01 g, 2.57 mmol, 1 equiv) and L-leucinol (**18**, 339 μL, 2.57 mmol, 1.00 equiv) in toluene (129 mL) was added DMAP (159 mg, 1.29 mmol, 0.50 equiv) at 23 °C and the reaction flask was equipped with a reflux condenser. The resulting reaction mixture was heated to 140 °C. After 3 h, the reaction mixture was cooled to 23 °C and was concentrated under reduced pressure. The resulting crude residue was purified by flash column chromatography (silica gel: diam. 4 cm, ht. 12 cm; eluent: ethyl acetate : hexanes = 1 : 3 to 1 : 1) to afford **28** (1:1 mixture of diastereomers, 871 mg, 78%) as a pale yellow oil.

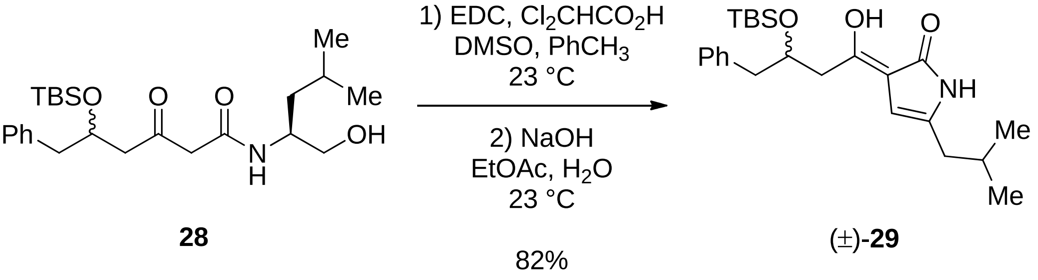
^{1}H NMR and ^{13}C NMR of **28** were taken with sample containing 1:1 mixture of unseparable diastereomers.

^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.31−7.11 (m, 10H), 4.40−4.32 (m, 2H), 4.08−3.96 (m, 2H), 3.63 (dd, *J* =11.1, 3.7 Hz, 2H), 3.49 (ddd, *J* =11.1, 5.8, 1.2 Hz, 2H), 3.37 (s, 2H), 3.36 (d, *J* = 1.5 Hz, 2H), 2.85−2.77 (m, 2H), 2.73 (ddd, *J* =13.4, 6.9, 1.6 Hz, 2H), 2.64 (ddd, *J* =15.8, 6.7, 1.1 Hz, 2H), 2.55 (ddd, *J* =15.8, 8.6, 5.2 Hz, 2H), 1.72−1.54 (m, 2H), 1.46−1.28 (m, 4H), 0.92 (dd, *J* = 6.6, 2.5 Hz, 6H), 0.90 (dd, *J* = 6.6, 1.3 Hz, 6H), 0.85 (s, 9H), 0.85 (s, 9H), −0.01 (s, 3H), −0.02 (s, 3H), −0.08 (s, 3H), −0.08 (s, 3H).

^{13}C NMR (150.7 MHz, $CDCl_3$) δ 206.0, 205.9, 166.4, 166.4, 137.9, 137.9, 129.8, 129.7, 128.5, 128.4, 126.6, 126.6, 70.3, 70.2, 65.7, 65.7, 50.5, 50.4, 50.4, 50.3, 50.3, 50.2, 44.3, 44.2, 40.1, 40.1, 25.9, 25.9, 24.9, 24.9, 23.2, 23.2, 22.2, 22.1, 18.0, 18.0, −4.8, −4.8, −4.8, −4.9.

HRMS (ESI): Calculated for $C_{24}H_{41}NO_4Si$ $[M+Na]^+$: 458.2697, found: 458.2705.

TLC (ethyl acetate : hexanes = 1 : 1) R*f*: 0.26 (CAM, UV).



(*Z*)-3-(3-((*tert*-Butyldimethylsilyl)oxy)-1-hydroxy-4-phenylbutylidene)-5-isobutyl-1*H*-pyrrol-2(3*H*)-one (29):

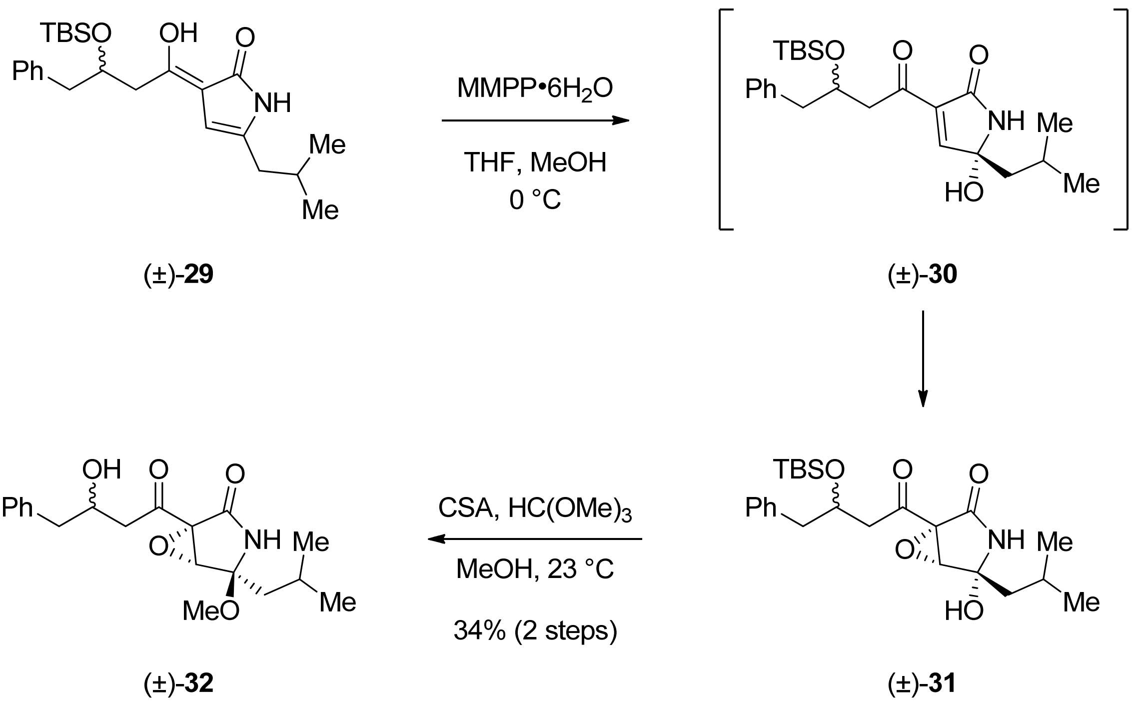
To a stirred solution of **28** (719 mg, 1.65 mmol, 1 equiv) in DMSO (9.7 mL) and toluene (9.7 mL) were added EDC (1.61 g, 8.25 mmol, 5.00 equiv) and dichloroacetic acid (275 μL, 3.30 mmol, 2.00 equiv) at 23 °C. After 18 h, saturated aqueous ammonium chloride solution (20 mL) was added to the reaction mixture and the resulting mixture was diluted with ethyl acetate (33 mL) and water (5 mL), and the layers were separated. The aqueous layer was extracted with ethyl acetate (2 × 33 mL), and the organic layers were combined. Aqueous sodium hydroxide solution (0.3 M, 120 mL) was added to the combined organic layers and stirred vigorously at 23 °C. After 5 h, the layers were separated. The aqueous layer was extracted with ethyl acetate (2 × 100 mL), and the combined organic layers were dried over anhydrous sodium sulfate and were concentrated under reduced pressure. The resulting crude residue was purified by flash column chromatography (silica gel: diam. 4 cm, ht. 7 cm; eluent: ethyl acetate : hexanes = 1 : 6) to afford (±)-**29** (562 mg, 82%) as a blue oil. We observed severe streaking during the flash column chromatography.

^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.29–7.13 (m, 5H), 5.42 (s, 1H), 4.34–4.26 (m, 1H), 2.79 (app-dd, *J* = 6.1, 1.7 Hz, 2H), 2.52 (dd, *J* = 13.6, 7.3 Hz, 1H), 2.46 (dd, *J* = 13.6, 5.5 Hz, 1H), 2.18 (app-s, 2H), 1.78 (app-s, 1H), 0.91 (d, *J* = 5.1 Hz, 6H), 0.78 (s, 9H), –0.12 (s, 3H), –0.23 (s, 3H).

^{13}C NMR (150.7 MHz, $CDCl_3$) δ 171.5, 171.3, 138.5, 133.4, 130.1, 128.5, 126.6, 108.9, 98.6, 71.6, 44.8, 41.2, 37.8, 27.6, 26.0, 22.6, 22.6, 18.1, –4.9, –4.9.

HRMS (ESI): Calculated for $C_{24}H_{37}NO_3Si$ $[M+Na]^+$: 438.2435, found: 438.2431.

TLC (ethyl acetate : hexanes = 1 : 4) R*f*: 0.44 (CAM, UV).



(1*R*,4*S*,5*R*)-1-(3-Hydroxy-4-phenylbutanoyl)-4-isobutyl-4-methoxy-6-oxa-3-azabicyclo[3.1.0]hexan-2-one (32):

To a stirred solution of (±)-**29** (65.2 mg, 0.157 mmol, 1 equiv) in a 1:1 mixture of THF/methanol (7.8 mL) was added magnesium monoperoxyphthalate hexahydrate (MMPP·6H$_2$O, 80%, 107 mg, 0.173 mmol, 1.10 equiv) at 0 °C. After 30 min, a mixture of saturated aqueous sodium thiosulfate solution and saturated aqueous sodium bicarbonate solution (1:1, 6 mL) was added to the reaction mixture and the resulting mixture was diluted with ethyl acetate (5 mL), and the layers were separated. The aqueous layer was extracted with ethyl acetate (2 × 4 mL), and the combined organic layers were washed with brine (2 mL), were dried over anhydrous sodium sulfate and were concentrated under reduced pressure. The resulting crude residue of (±)-**31** was used in the next step without further purification.

To a stirred solution of (±)-**31** in methanol (1.6 mL) were added 10-camphorsulfonic acid (18.4 mg, 0.078 mmol, 0.50 equiv) and trimethyl orthoformate (17.4 μL, 0.157 mmol, 1.00 equiv) at 23 °C. After 4 h, saturated aqueous sodium bicarbonate solution (1 mL) was added to the reaction mixture and the resulting mixture was diluted with ethyl acetate (5 mL) and water (3 mL), and the layers were separated. The aqueous layer was extracted with ethyl acetate (3 × 4 mL), and the combined organic layers were dried over anhydrous sodium sulfate and were concentrated under reduced pressure. The resulting crude residue was purified by flash column chromatography (silica gel: diam. 2.5 cm, ht. 11 cm; eluent: ethyl acetate : hexanes = 1 : 2 to 2 : 3) to afford (±)-**32** (1:1 mixture of diastereomers, 18.3 mg, 34%) as a pale yellow oil.

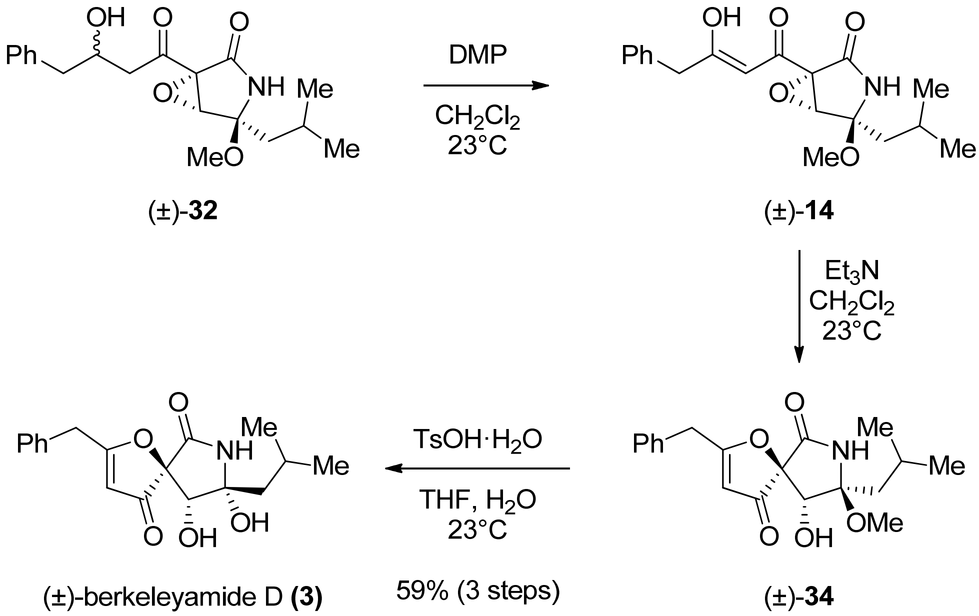
^{1}H NMR and ^{13}C NMR of **32** were taken with sample containing 1:1 mixture of unseparable diastereomers.

^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.32−7.16 (m, 10H), 6.10 (br-s, 2H), 4.41−4.31 (m, 2H), 4.04 (d, J = 2.7 Hz, 1H), 3.95 (d, J = 2.7 Hz, 1H), 3.22 (s, 3H), 3.18 (s, 3H), 2.85−2.50 (m, 10H), 1.96−1.83 (m, 2H), 1.73−1.59 (m, 4H), 1.00 (dd, J = 6.6, 3.1 Hz, 6H), 0.96 (dd, J = 6.7, 1.3 Hz, 6H).

^{13}C NMR (150.7 MHz, $CDCl_3$) δ 200.3, 200.0, 168.7, 168.5, 137.7, 137.6, 129.6, 129.6, 128.9, 128.8, 127.0, 126.9, 89.1, 89.0, 68.8, 68.7, 64.0, 63.4, 61.8, 61.7, 49.9, 49.8, 46.4, 45.5, 43.4, 43.2, 42.7, 42.6, 24.3, 24.3, 24.1, 24.0, 23.8, 23.7.

HRMS (ESI): Calculated for $C_{19}H_{25}NO_5$ $[M+Na]^+$: 370.1625, found: 370.1641.

TLC (ethyl acetate : hexanes = 1 : 1) R*f*: 0.33 (CAM).



(±)-Berkeleyamide D (3):

To a stirred solution of (±)-**32** (39.6 mg, 0.114 mmol, 1 equiv) in dichloromethane (14.2 mL) was added Dess-Martin periodinane (DMP, 121 mg, 0.285 mmol, 2.50 equiv) at 23 °C. After 1.5 h, a mixture of saturated aqueous sodium thiosulfate solution and saturated aqueous sodium bicarbonate solution (1:1, 12 mL) was added to the reaction mixture, and the layers were separated. The aqueous layer was extracted with dichloromethane (3 × 6 mL), and the combined organic layers were dried over anhydrous sodium sulfate and were concentrated under reduced pressure. The resulting crude residue of (±)-**14** was used in the next step without further purification.

To a stirred solution of (±)-**14** in dichloromethane (22 mL) was added triethylamine (257 μL, 1.82 mmol, 16.0 equiv) at 23 °C. After 15 min, the reaction mixture was concentrated under reduced pressure. The resulting crude residue of (±)-**34** was used in the next step without further purification.

A solution of (±)-**34** and *p*-toluenesulfonic acid monohydrate ($TsOH{\cdot}H_2O$, 44.2 mg, 0.228 mmol, 2.00 equiv) in THF (9.2 mL) and H_2O (2.3 mL) was stirred at 23 °C. After 5 h, water (5 mL) was added to the reaction mixture and the resulting mixture was diluted with ethyl acetate (5 mL), and the layers were separated. The aqueous layer was extracted with ethyl acetate (3 × 5 mL), and the combined organic layers were dried over anhydrous sodium sulfate and were concentrated under reduced pressure. The resulting crude residue was purified by flash column chromatography (silica gel: diam. 2.5 cm, ht. 10 cm; eluent: ethyl acetate : hexanes = 1 : 2) to afford (±)-berkeleyamide D (**3**) (22.3 mg, 59%) as a white solid.

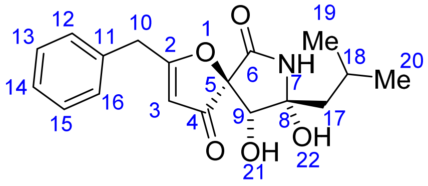
^{1}H NMR (599.3 MHz, $CDCl_3$) δ 7.37−7.27 (m, 5H), 6.64 (br-s, 1H), 5.47 (br-s, 1H), 5.35 (s, 1H), 4.41 (s, 1H), 4.00 (d, J = 17.4 Hz, 1H), 3.94 (d, J = 17.5 Hz, 1H), 2.99 (br-s, 1H), 1.96−1.88 (m, 1H), 1.86 (dd, J = 14.4, 6.0 Hz, 1H), 1.59 (dd, J = 14.3, 6.8 Hz, 1H), 1.01 (d, J = 6.6 Hz, 3H), 0.99 (d, J = 6.6 Hz, 3H).

^{13}C NMR (150.7 MHz, $CDCl_3$) δ 199.6, 198.0, 164.3, 133.5, 129.4, 129.2, 128.0, 104.6, 95.6, 85.1, 75.4, 45.8, 37.7, 24.3, 24.2, 24.0.

HRMS (ESI): Calculated for $C_{18}H_{21}NO_5$ $[M+Na]^+$: 354.1312, found: 354.1313.

TLC (ethyl acetate : hexanes = 1 : 1) R*f*: 0.49 (CAM, UV).

Table S1. Comparison of our data for (±)-berkeleyamide D (3) with literature:



berkeleyamide D (**3**)

Assignment	**Stierle's Report** ^{1}H NMR, 300 MHz, $CDCl_3$	**This Work** ^{1}H NMR, 599.3 MHz, $CDCl_3$
C3	5.35 (br-s, 1H)	5.35 (s, 1H)
N7	6.78 (br-s, 1H)	6.64 (br-s, 1H)
C9	4.41 (d, *J* = 10.0 Hz, 1H)	4.41 (s, 1H)
C10′	3.98 (d, *J* = 17.4 Hz, 1H)	4.00 (d, *J* = 17.4 Hz, 1H)
C10″	3.96 (d, *J* = 17.4 Hz, 1H)	3.94 (d, *J* = 17.5 Hz, 1H)
C12(C16)	7.33 (m, 2H)	7.37−7.27 (m, 2H)
C13(C15)	7.33 (m, 2H)	7.37−7.27 (m, 2H)
C14	7.33 (m, 1H)	7.37−7.27 (m, 1H)
C17′	1.88 (m, 2H)[5]	1.86 (dd, *J* = 14.4, 6.0 Hz, 1H)
C17″		1.59 (dd, *J* = 14.3, 6.8 Hz, 1H)
C18	1.92 (m, 1H)	1.96−1.88 (m, 1H)
C19	1.00 (d, *J* = 5.2 Hz, 3H)	1.01 (d, *J* = 6.6 Hz, 3H)
C20	0.98 (d, *J* = 5.2 Hz, 3H)	0.99 (d, *J* = 6.6 Hz, 3H)
O21	3.04 (d, *J* = 10.0 Hz, 1H)	2.99 (br-s, 1H)
O22	5.48 (br-s, 1H)	5.47 (br-s, 1H)

---

[5] A peak at 1.6 ppm appears in the copy of NMR spectrum of berkeleyamide D attached in the original isolation paper. Proton assignment at C17 requires revision.

Assignment	**Stierle's Report**[6] ^{13}C NMR, 75 MHz, $CDCl_3$	**This Work**[7] ^{13}C NMR, 150.7 MHz, $CDCl_3$
C2	197.8	198.0
C3	104.4	104.6
C4	199.4	199.6
C5	95.3	95.6
C6	164.1	164.3
C8	84.9	85.1
C9	75.1	75.4
C10	37.4	37.7
C11	133.2	133.5
C12(C16)	129.2, 129.0, 127.0	129.4[8]
C13(C15)		129.2[8]
C14		128.0[8]
C17	45.5	45.8
C18	24.0	24.3
C19	23.9	24.2
C20	23.8	24.0

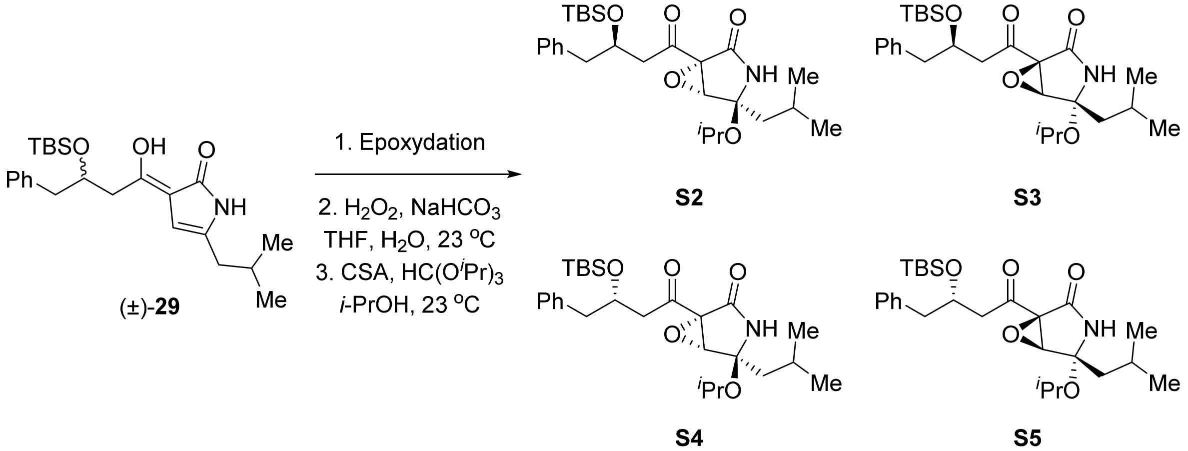
---

[6] The chemical shifts were recorded with respect to the deuterated solvent shift ($CDCl_3$, δ 77.0 for the carbon).

[7] The chemical shifts were recorded with respect to the deuterated solvent shift ($CDCl_3$, δ 77.23 for the carbon).

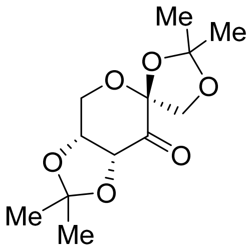
[8] Assignments are based on 2D-NMR experiments including COSY, HSQC and HMBC.

Attempted Asymmetric Epoxidations of (±)-29

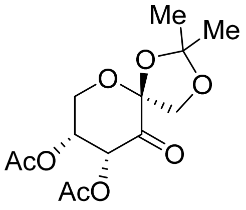


entry	epoxidation conditions	results (% ee)[a]
1	Shi's catalyst 1, Na_2EDTA, Oxone, $NaHCO_3$ MeCN, H_2O, CH_2Cl_2, 0 °C	12% ee, 7% ee
2	Shi's catalyst 2, Na_2EDTA, Oxone, $NaHCO_3$ MeCN, H_2O, CH_2Cl_2, 0 to 23 °C	23% ee, 18% ee
3	(+)-(8,8-Dichlorocamphorylsulfonyl)oxaziridine CH_2Cl_2, 23 °C	17% ee, 17% ee

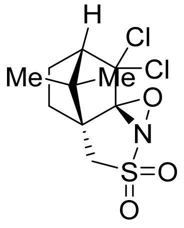
a. Relative stereochemistry of each stereoisomer is not determined. Data are % ee values of two diastereomers.



Shi's catalyst 1



Shi's catalyst 2



(+)-(8,8-Dichlorocamphorylsulfonyl)
oxaziridine

HPLC Traces of Racemic Compounds

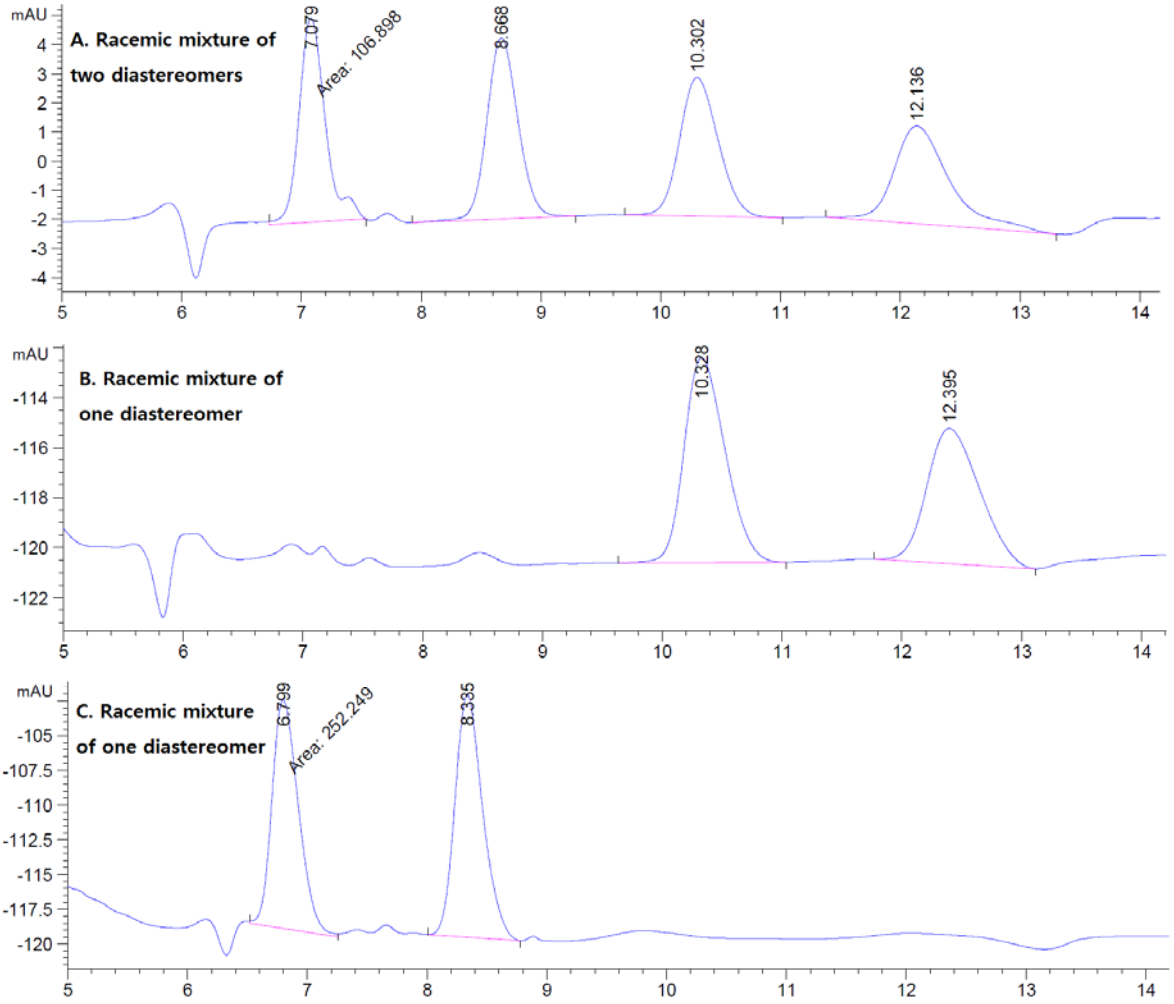
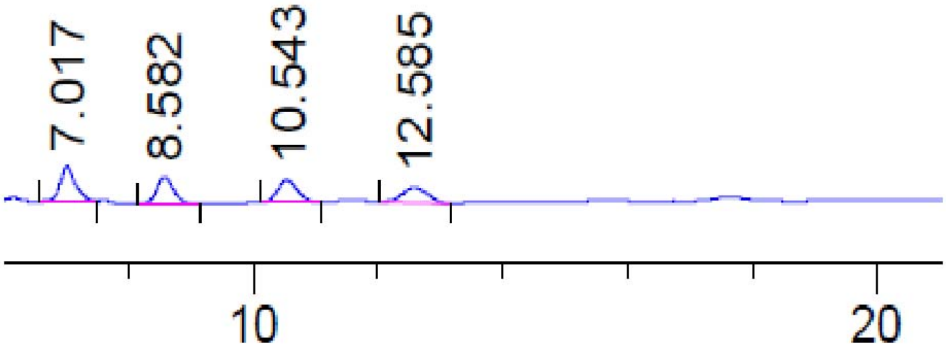


Fig. S1 A. HPLC trace of mixture of **S2–S5**. B. HPLC trace of racemic mixture of one diastereomer (mixture of S2/S5 or S3/S4). C. HPLC trace of racemic mixture of one diastereomer (mixture of S3/S4 or S2/S5). CHIRALPAK IC-3, hexanes : *i*-PrOH = 98 : 2, 1.0 mL/min.

HPLC Traces of Asymmetric Epoxidation Products Derivatives



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                         Area Percent Report
======================================================================

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Dilution              :      1.0000
Sample Amount:               :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

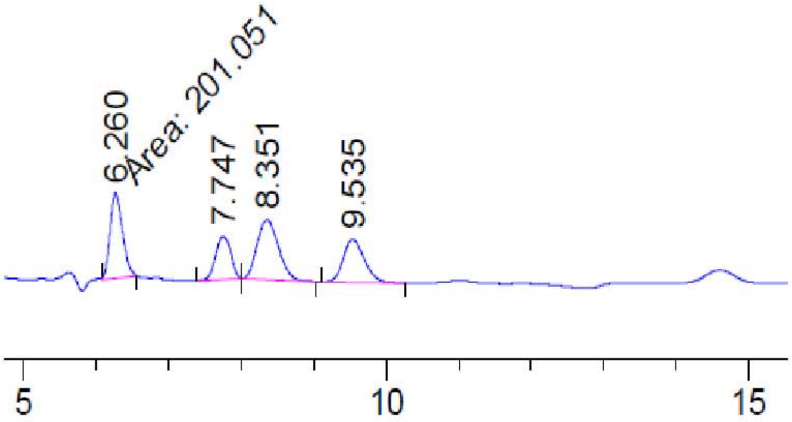

Signal 1: MSD1 TIC, MS File


Signal 2: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   7.017 BB    0.2576   97.18094    5.56915  29.9045
   2   8.582 BB    0.2898   76.85334    4.11753  23.6493
   3  10.543 BB    0.3489   80.39052    3.56807  24.7377
   4  12.585 BB    0.4473   70.54657    2.44742  21.7085

Totals :                  324.97137   15.70218
```

Fig. S2 HPLC trace of **S2–S5** after asymmetric epoxidation of **29** using Shi's catalyst 1 (CHIRALPAK IC-3, hexanes : *i*-PrOH = 98 : 2, 1.0 mL/min).



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                         Area Percent Report
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Dilution              :      1.0000
Sample Amount:               :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

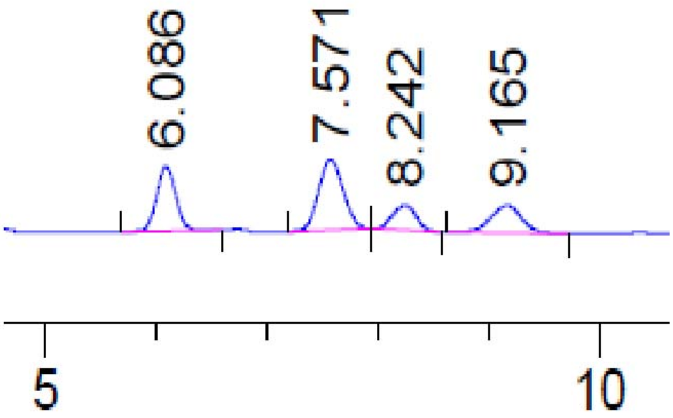

Signal 1: MSD1 TIC, MS File


Signal 2: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   6.260 MM    0.1978  201.05051   16.94238  27.1860
   2   7.747 BB    0.2358  124.62485    8.61391  16.8517
   3   8.351 BB    0.3256  244.27902   11.89501  33.0313
   4   9.535 BB    0.3087  169.58270    8.53759  22.9309

Totals :                   739.53708   45.98889
```

Fig. S3 HPLC trace of **S2–S5** after asymmetric epoxidation of **29** using Shi's catalyst 2 (CHIRALPAK IC-3, hexanes : *i*-PrOH = 98 : 2, 1.0 mL/min).



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                    Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount:               :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MSD1 TIC, MS File

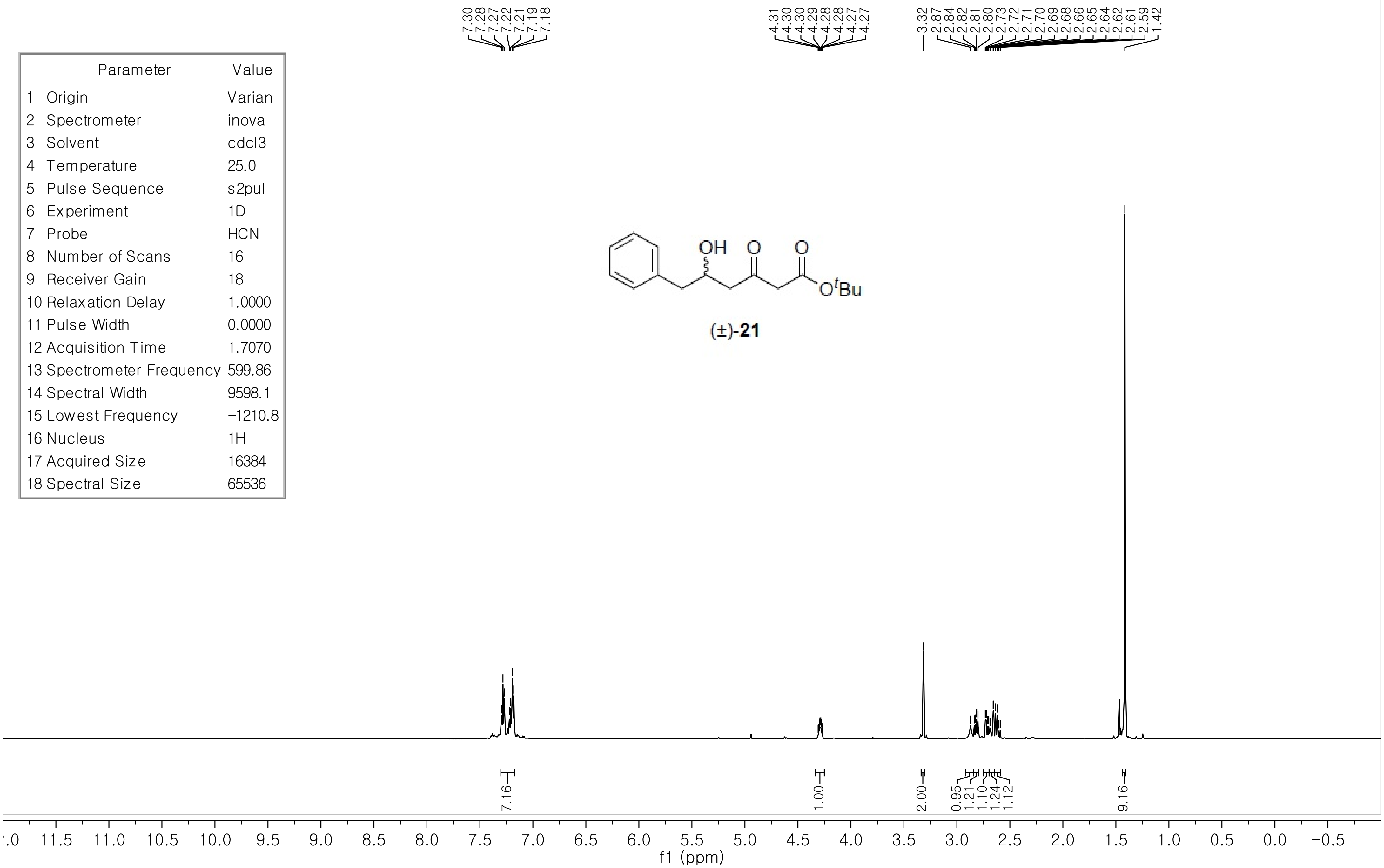

Signal 2: VWD1 A, Wavelength=210 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   6.086 BB    0.1900 3092.11523  254.00690  28.1361
   2   7.571 BB    0.2417 4322.21045  278.99039  39.3292
   3   8.242 BB    0.2436 1492.82080   98.06298  13.5837
   4   9.165 BB    0.3016 2082.68555  107.23061  18.9510

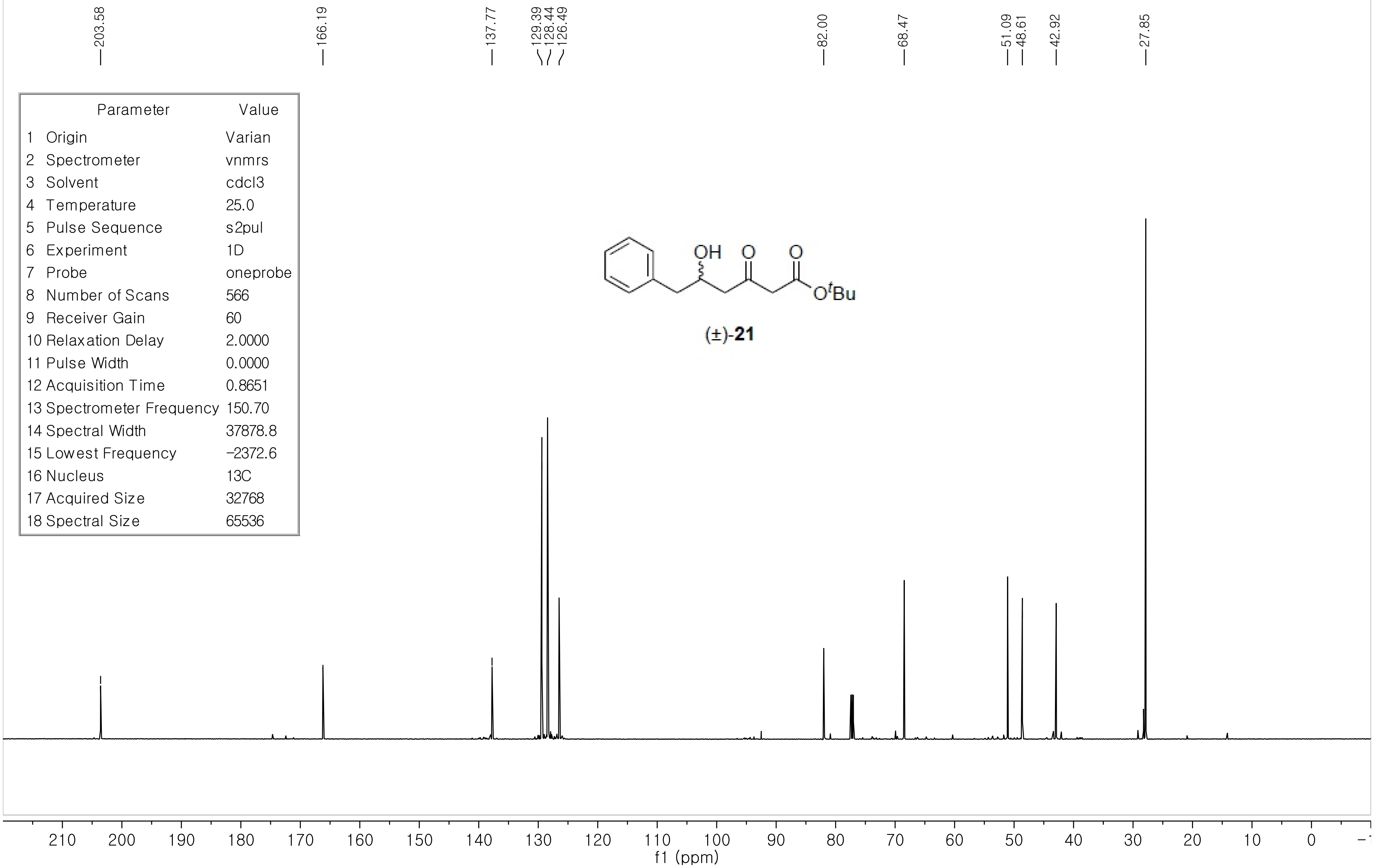
Totals :                  1.09898e4   738.29087
```

Fig. S4 HPLC trace of **S2**–**S5** after asymmetric epoxidation of **29** using (+)-(8,8-dichlorocamphorylsulfonyl)oxaziridine (CHIRALPAK IC-3, hexanes : *i*-PrOH = 98 : 2, 1.0 mL/min).

	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	HCN
8	Number of Scans	16
9	Receiver Gain	18
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	1.7070
13	Spectrometer Frequency	599.86
14	Spectral Width	9598.1
15	Lowest Frequency	−1210.8
16	Nucleus	1H
17	Acquired Size	16384
18	Spectral Size	65536



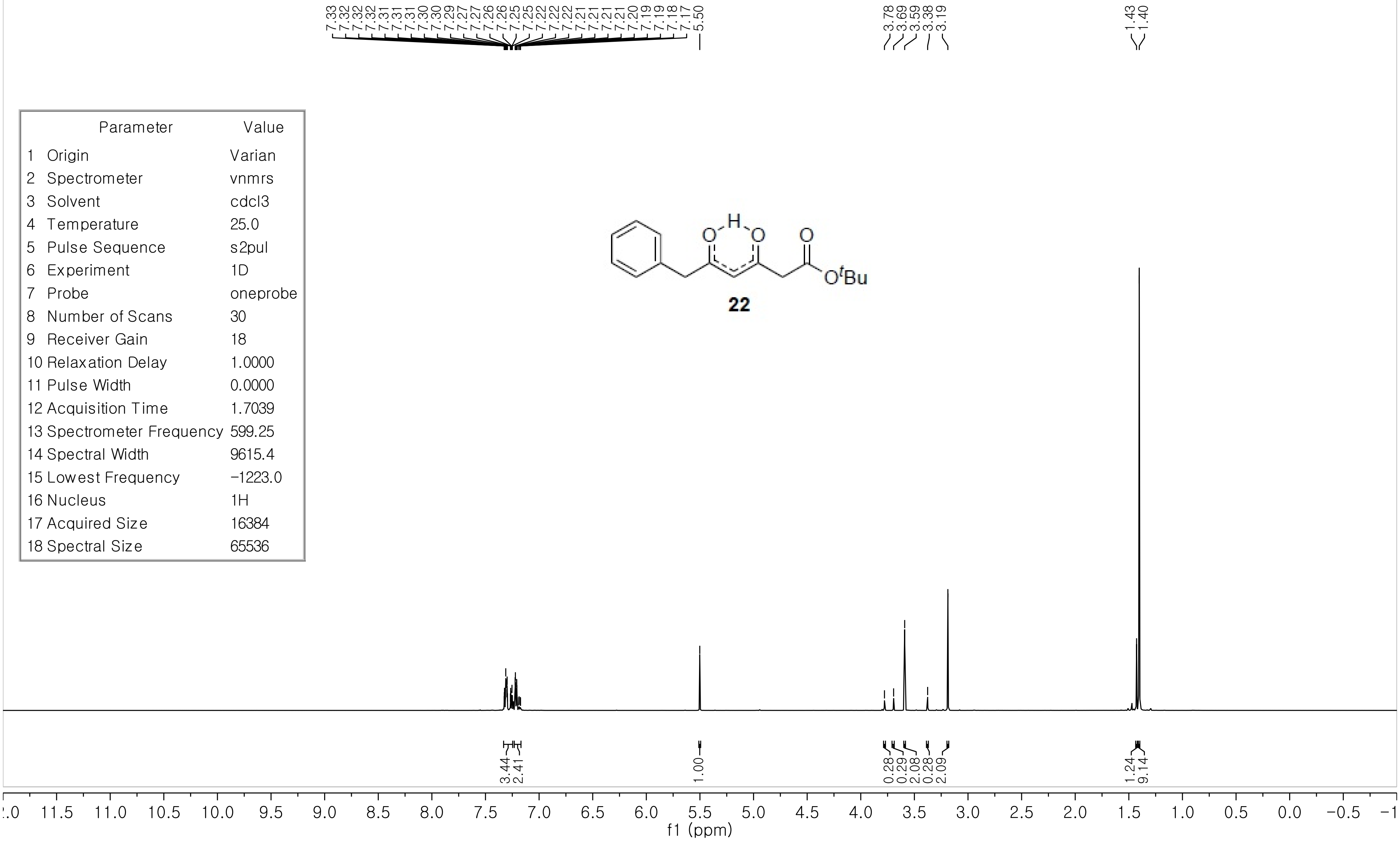
(±)-**21**



(±)-**21**

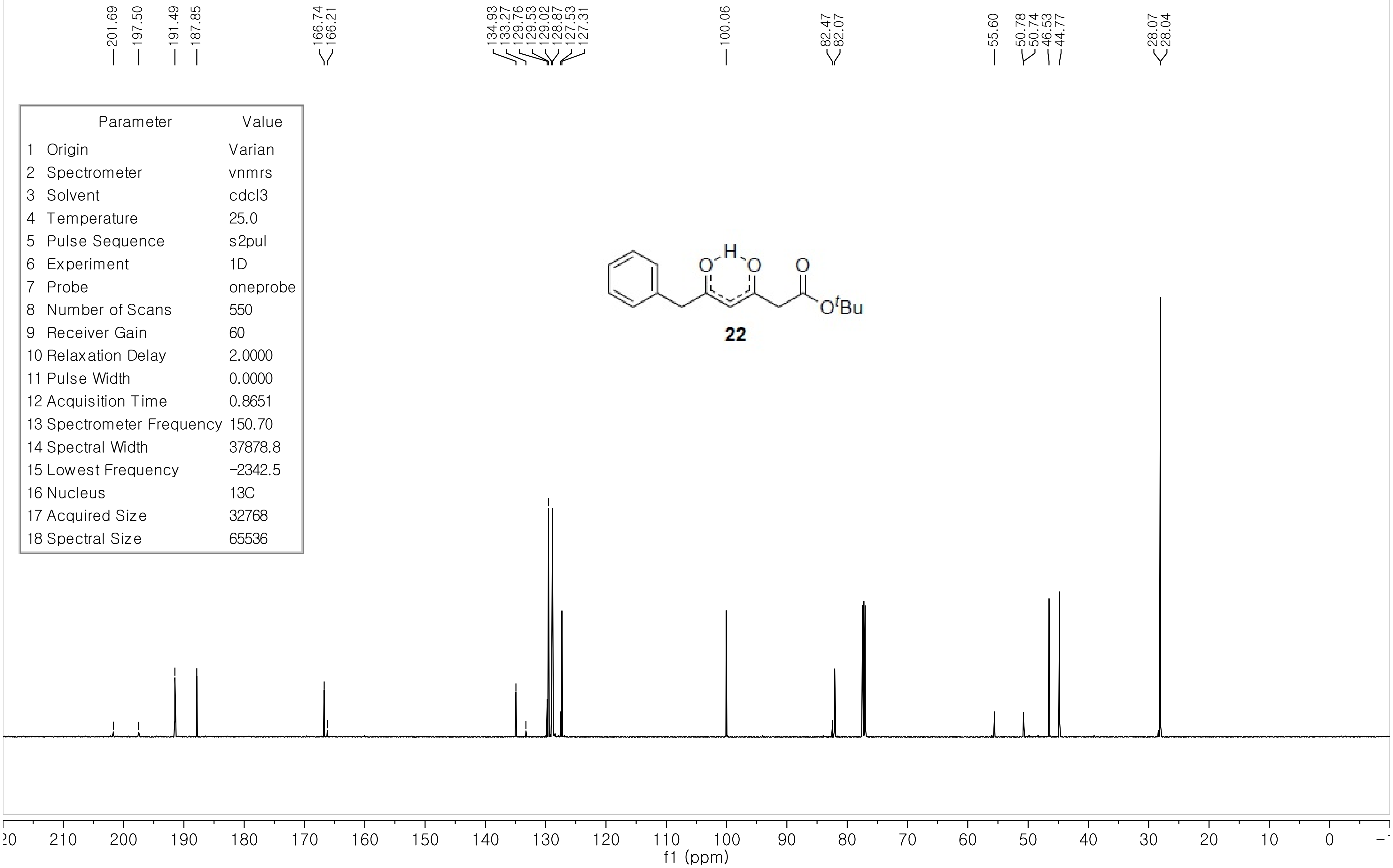
	Parameter	Value
1	Origin	Varian
2	Spectrometer	vnmrs
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	oneprobe
8	Number of Scans	566
9	Receiver Gain	60
10	Relaxation Delay	2.0000
11	Pulse Width	0.0000
12	Acquisition Time	0.8651
13	Spectrometer Frequency	150.70
14	Spectral Width	37878.8
15	Lowest Frequency	−2372.6
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

	Parameter	Value
1	Origin	Varian
2	Spectrometer	vnmrs
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	oneprobe
8	Number of Scans	30
9	Receiver Gain	18
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	1.7039
13	Spectrometer Frequency	599.25
14	Spectral Width	9615.4
15	Lowest Frequency	−1223.0
16	Nucleus	1H
17	Acquired Size	16384
18	Spectral Size	65536



22

	Parameter	Value
1	Origin	Varian
2	Spectrometer	vnmrs
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	oneprobe
8	Number of Scans	550
9	Receiver Gain	60
10	Relaxation Delay	2.0000
11	Pulse Width	0.0000
12	Acquisition Time	0.8651
13	Spectrometer Frequency	150.70
14	Spectral Width	37878.8
15	Lowest Frequency	-2342.5
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536



22

	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.0
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0389
8	Number of Scans	36
9	Receiver Gain	50
10	Relaxation Delay	0.2000
11	Pulse Width	15.0000
12	Acquisition Time	4.5438
13	Spectrometer Frequency	400.13
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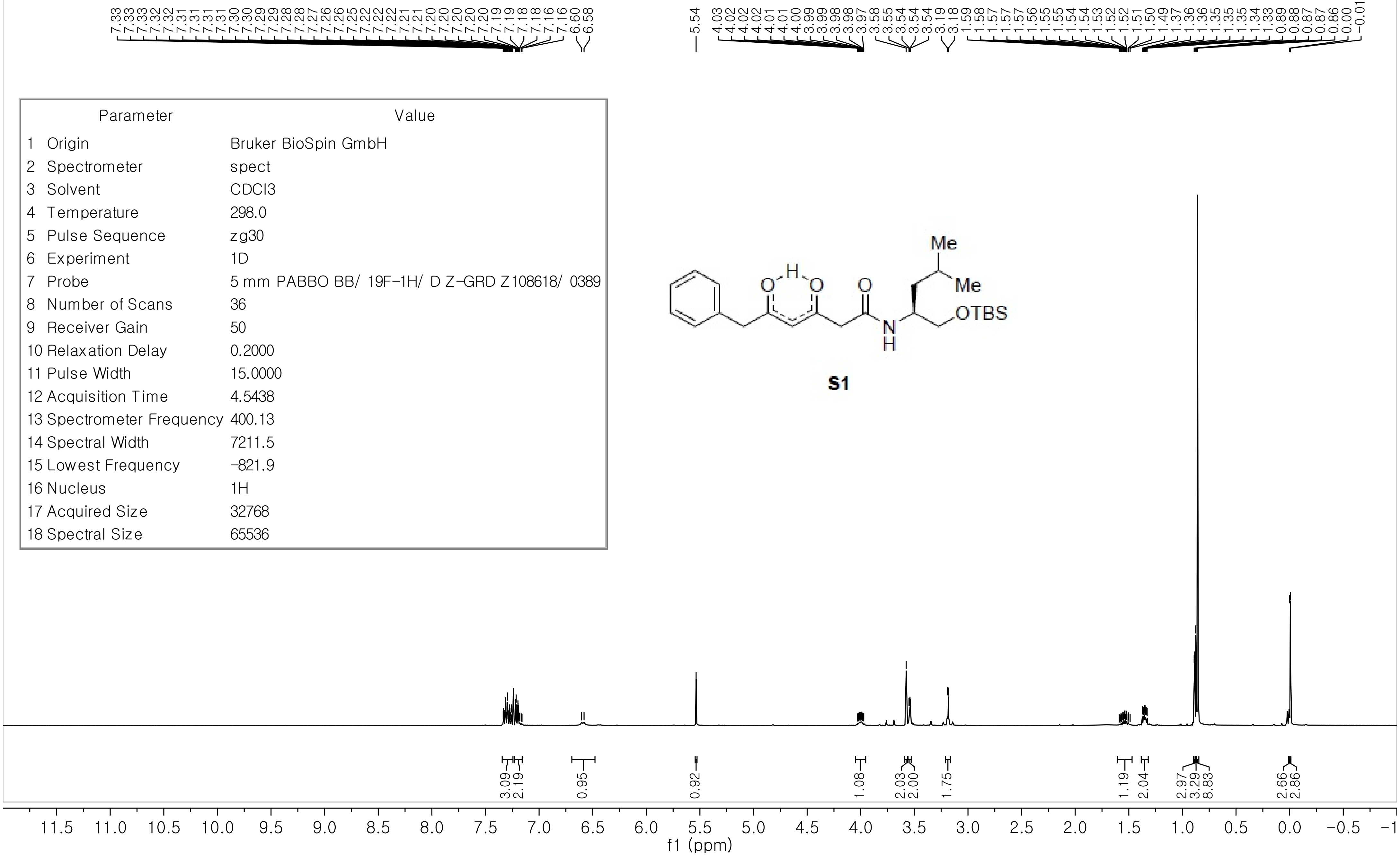
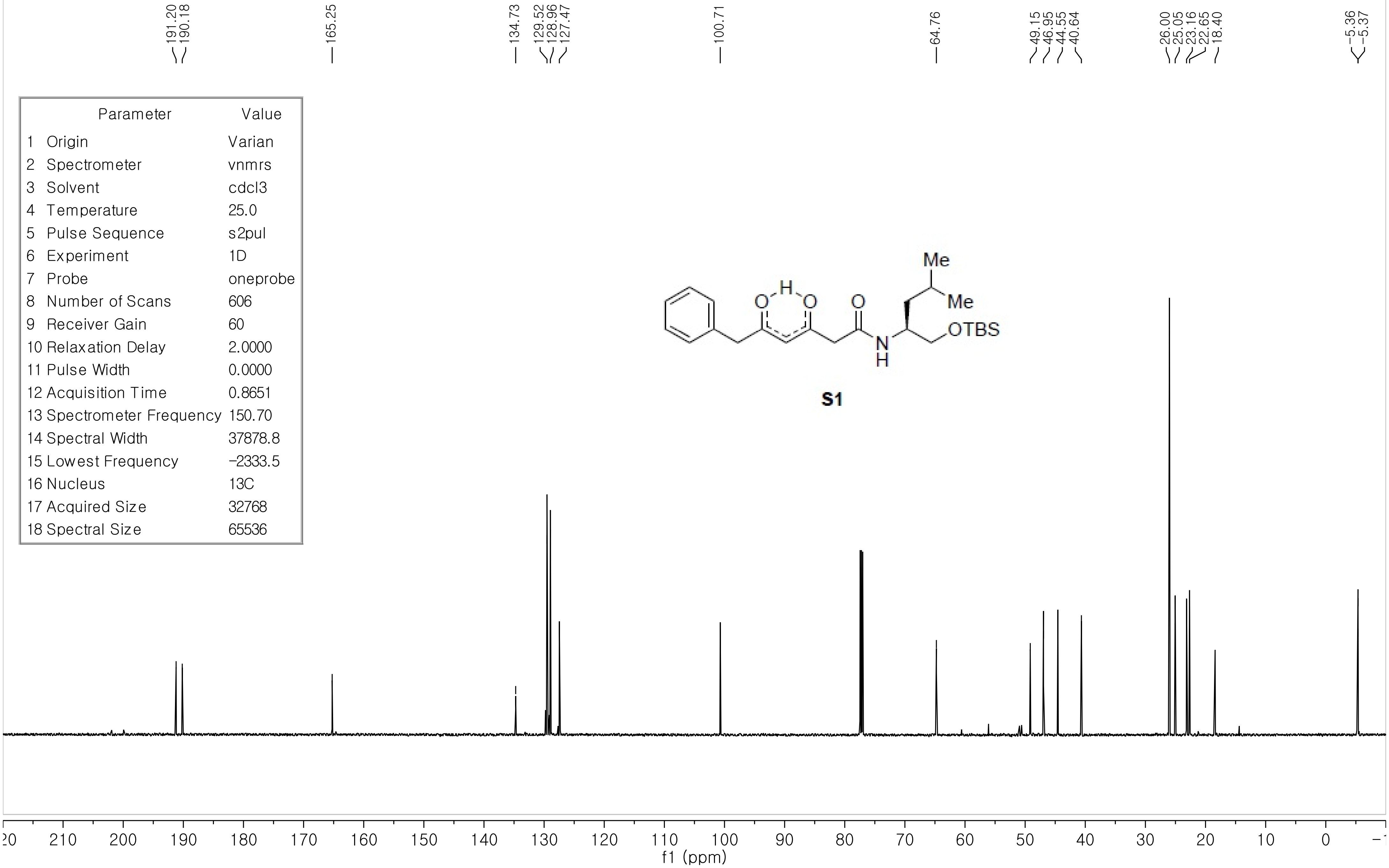
15	Lowest Frequency	-821.9
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



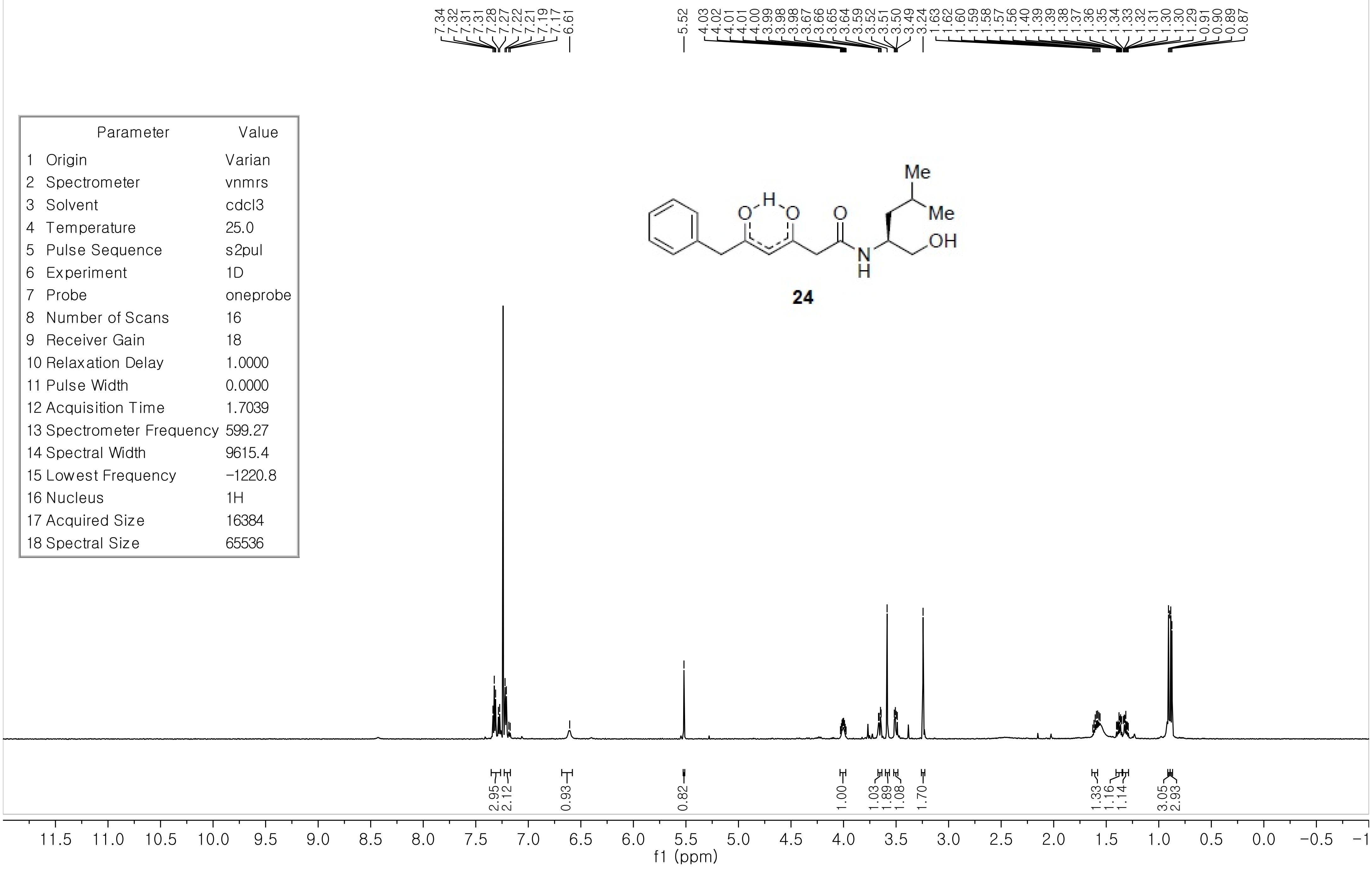
S1

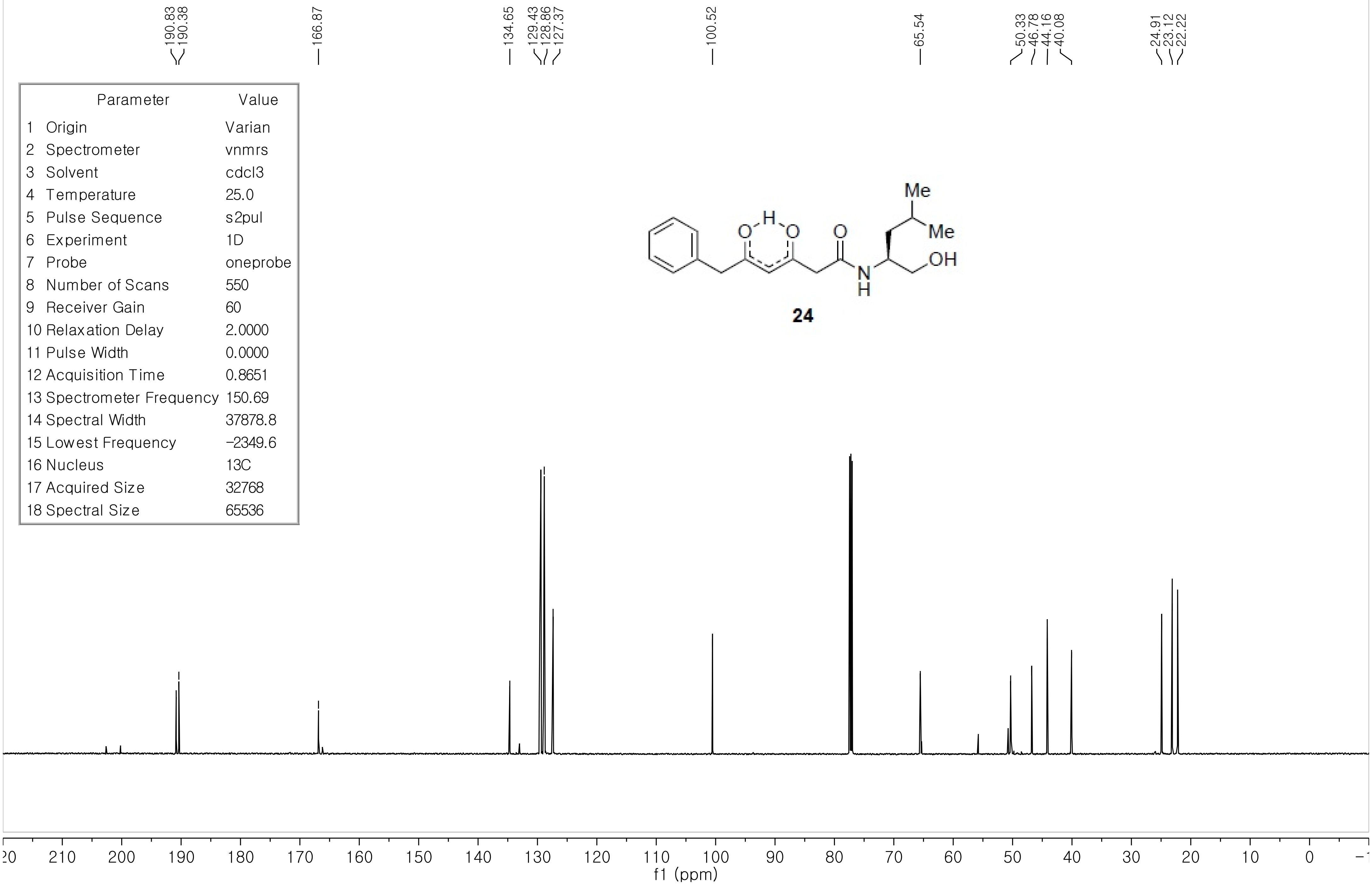


	Parameter	Value
1	Origin	Varian
2	Spectrometer	vnmrs
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	oneprobe
8	Number of Scans	606
9	Receiver Gain	60
10	Relaxation Delay	2.0000
11	Pulse Width	0.0000
12	Acquisition Time	0.8651
13	Spectrometer Frequency	150.70
14	Spectral Width	37878.8
15	Lowest Frequency	−2333.5
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

S1

	Parameter	Value
1	Origin	Varian
2	Spectrometer	vnmrs
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	oneprobe
8	Number of Scans	16
9	Receiver Gain	18
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	1.7039
13	Spectrometer Frequency	599.27
14	Spectral Width	9615.4
15	Lowest Frequency	−1220.8
16	Nucleus	1H
17	Acquired Size	16384
18	Spectral Size	65536

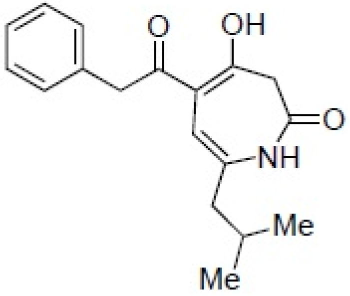




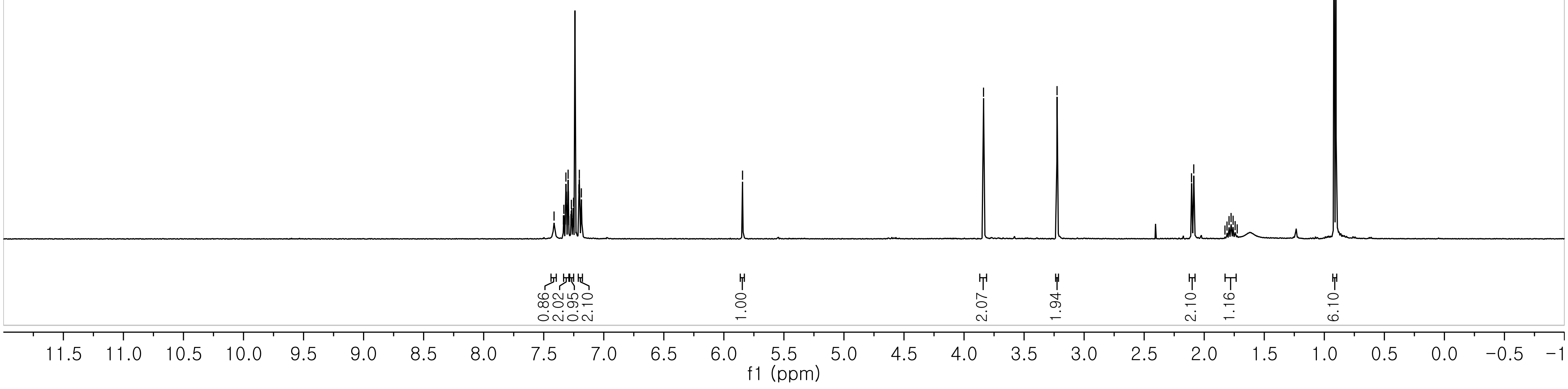
24

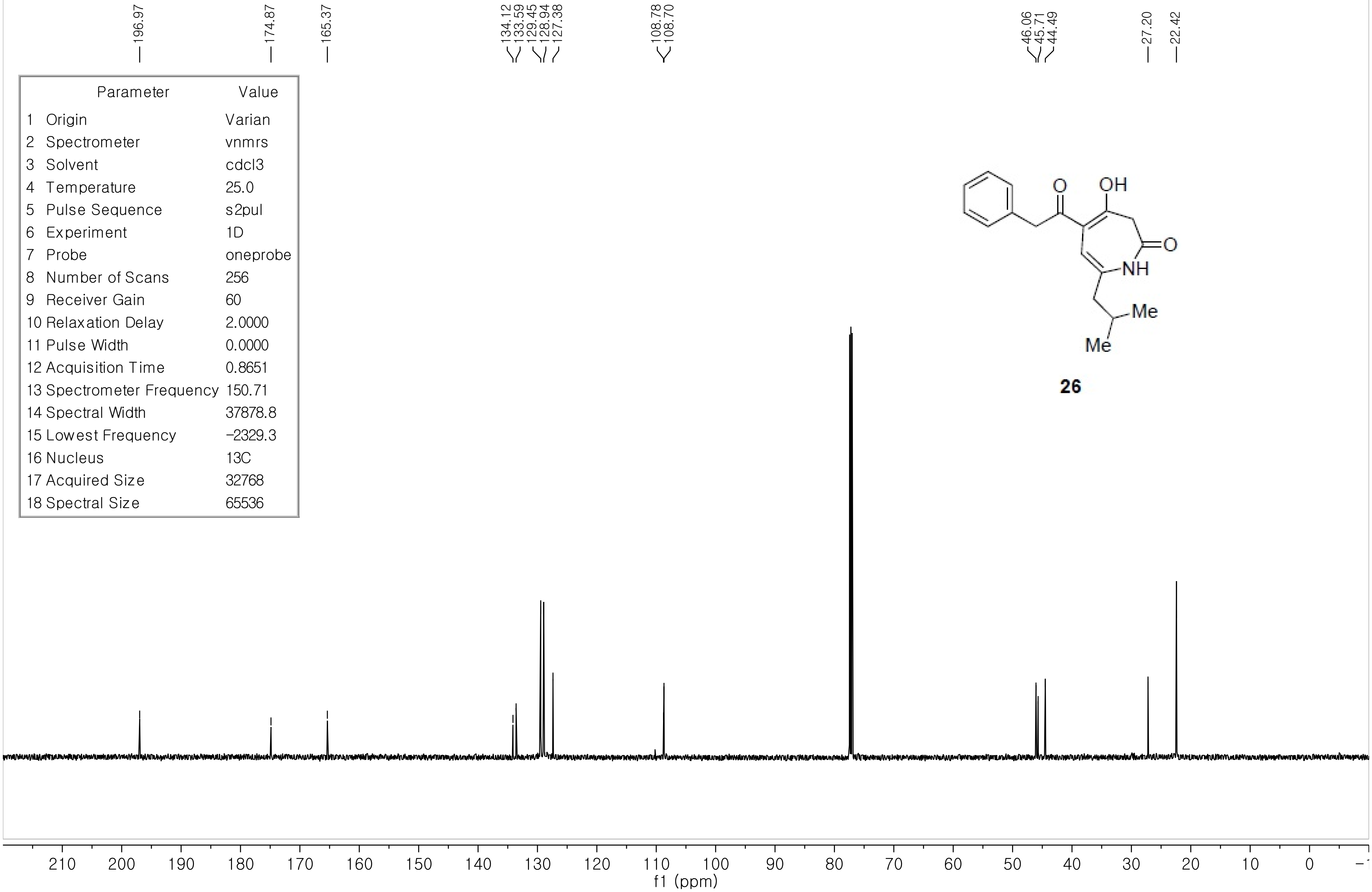
	Parameter	Value
1	Origin	Varian
2	Spectrometer	vnmrs
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	oneprobe
8	Number of Scans	550
9	Receiver Gain	60
10	Relaxation Delay	2.0000
11	Pulse Width	0.0000
12	Acquisition Time	0.8651
13	Spectrometer Frequency	150.69
14	Spectral Width	37878.8
15	Lowest Frequency	−2349.6
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.0
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0389
8	Number of Scans	11
9	Receiver Gain	202
10	Relaxation Delay	0.2000
11	Pulse Width	15.0000
12	Acquisition Time	4.5438
13	Spectrometer Frequency	400.13
14	Spectral Width	7211.5
15	Lowest Frequency	-822.5
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



26





	Parameter	Value
1	Origin	Varian
2	Spectrometer	vnmrs
3	Solvent	cdcl3
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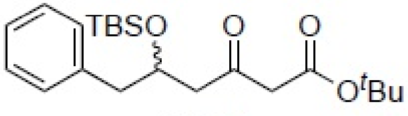
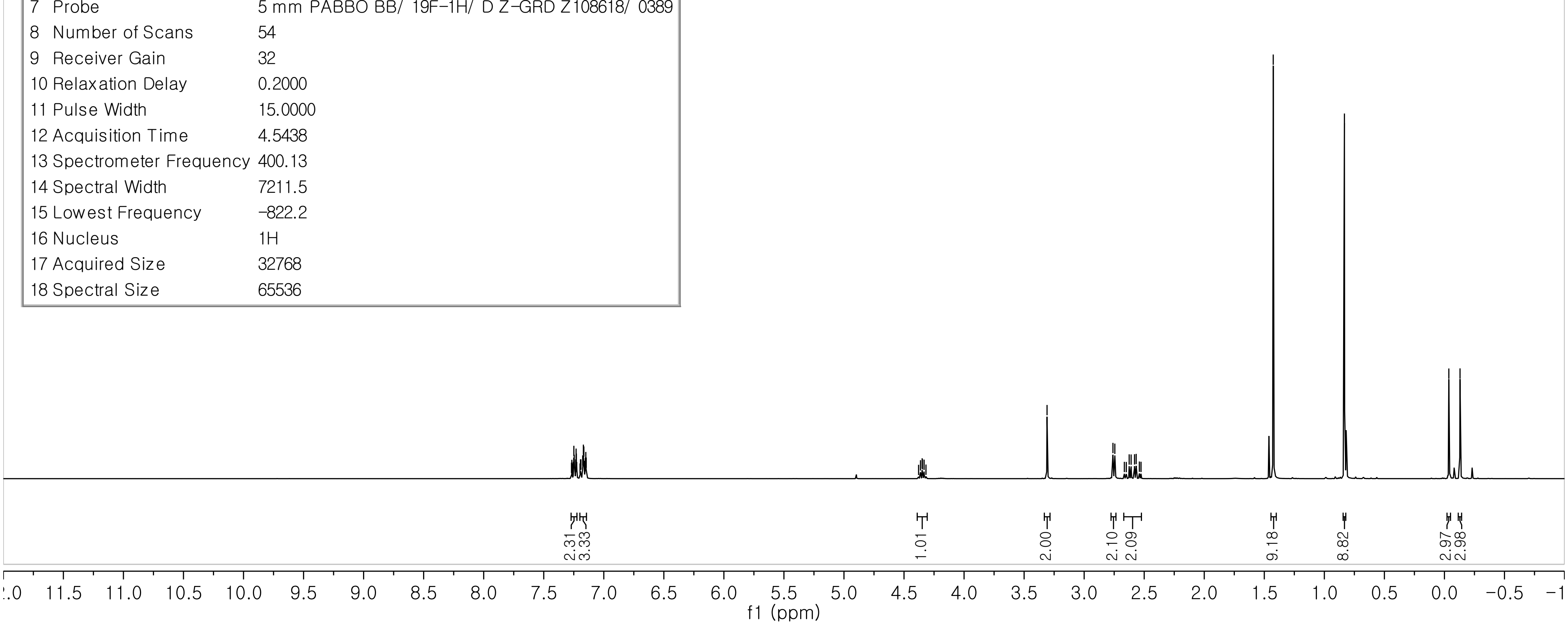
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	oneprobe
8	Number of Scans	256
9	Receiver Gain	60
10	Relaxation Delay	2.0000
11	Pulse Width	0.0000
12	Acquisition Time	0.8651
13	Spectrometer Frequency	150.71
14	Spectral Width	37878.8
15	Lowest Frequency	−2329.3
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

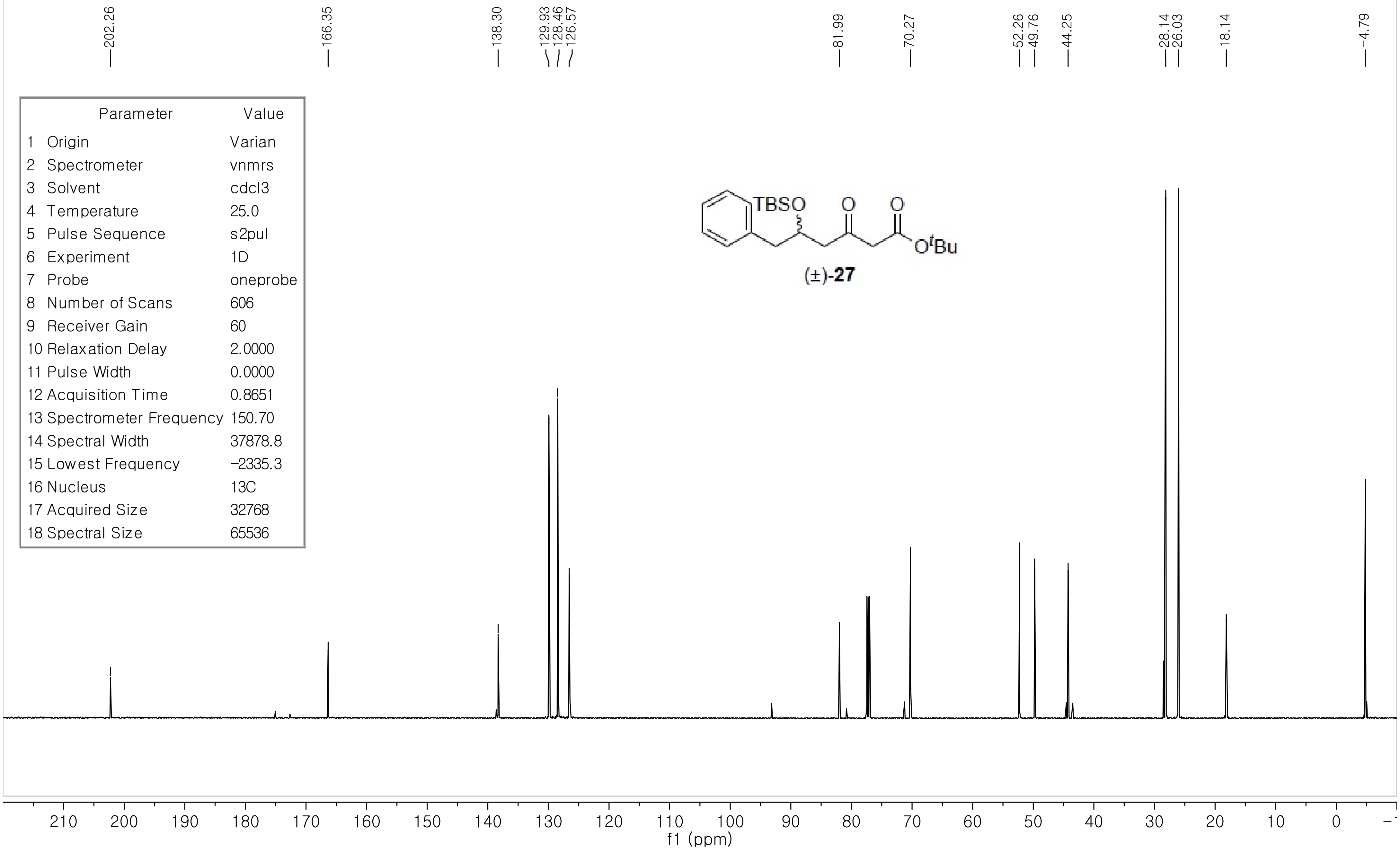
26

	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.0
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0389
8	Number of Scans	54
9	Receiver Gain	32
10	Relaxation Delay	0.2000
11	Pulse Width	15.0000
12	Acquisition Time	4.5438
13	Spectrometer Frequency	400.13
14	Spectral Width	7211.5
15	Lowest Frequency	-822.2
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



(±)-**27**

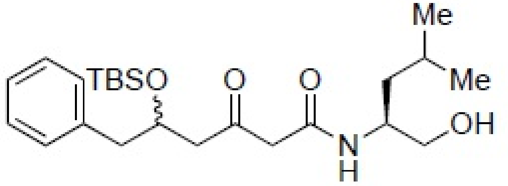




(±)-**27**

	Parameter	Value
1	Origin	Varian
2	Spectrometer	vnmrs
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	oneprobe
8	Number of Scans	606
9	Receiver Gain	60
10	Relaxation Delay	2.0000
11	Pulse Width	0.0000
12	Acquisition Time	0.8651
13	Spectrometer Frequency	150.70
14	Spectral Width	37878.8
15	Lowest Frequency	−2335.3
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.0
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0389
8	Number of Scans	27
9	Receiver Gain	32
10	Relaxation Delay	0.2000
11	Pulse Width	15.0000
12	Acquisition Time	4.5438
13	Spectrometer Frequency	400.13
14	Spectral Width	7211.5
15	Lowest Frequency	-809.1
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



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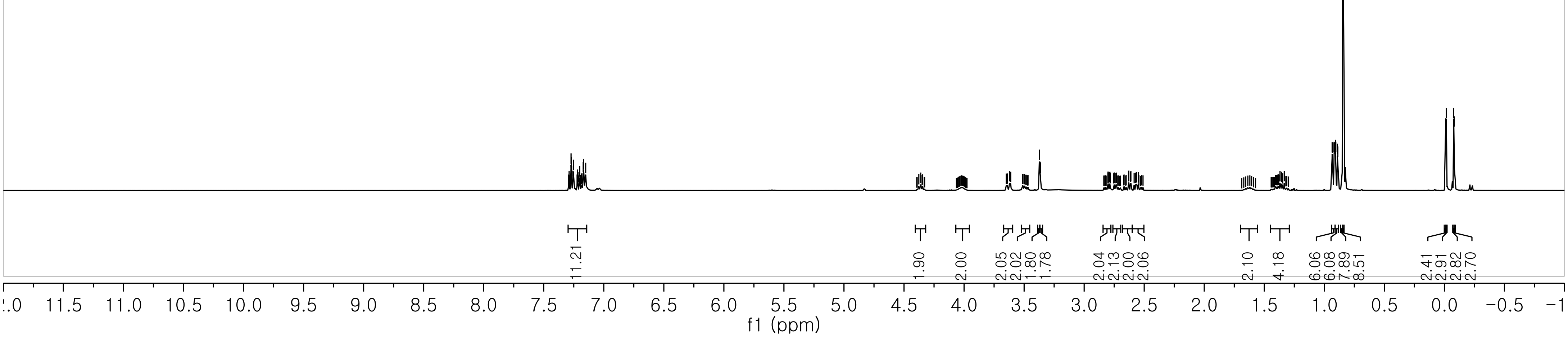
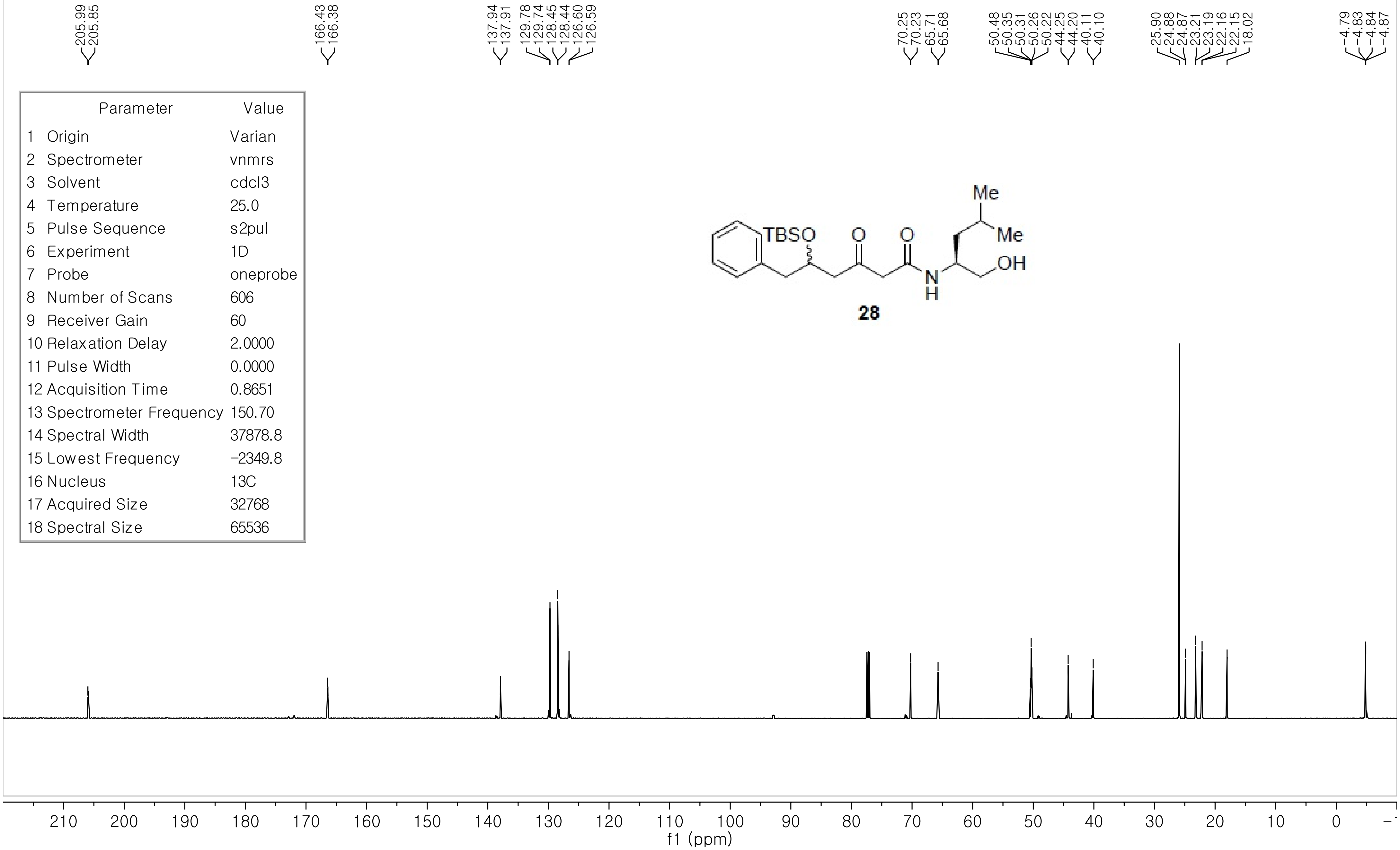
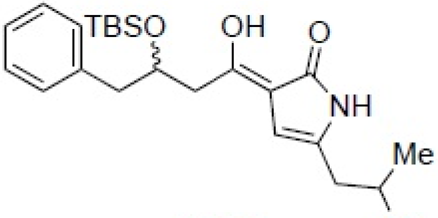


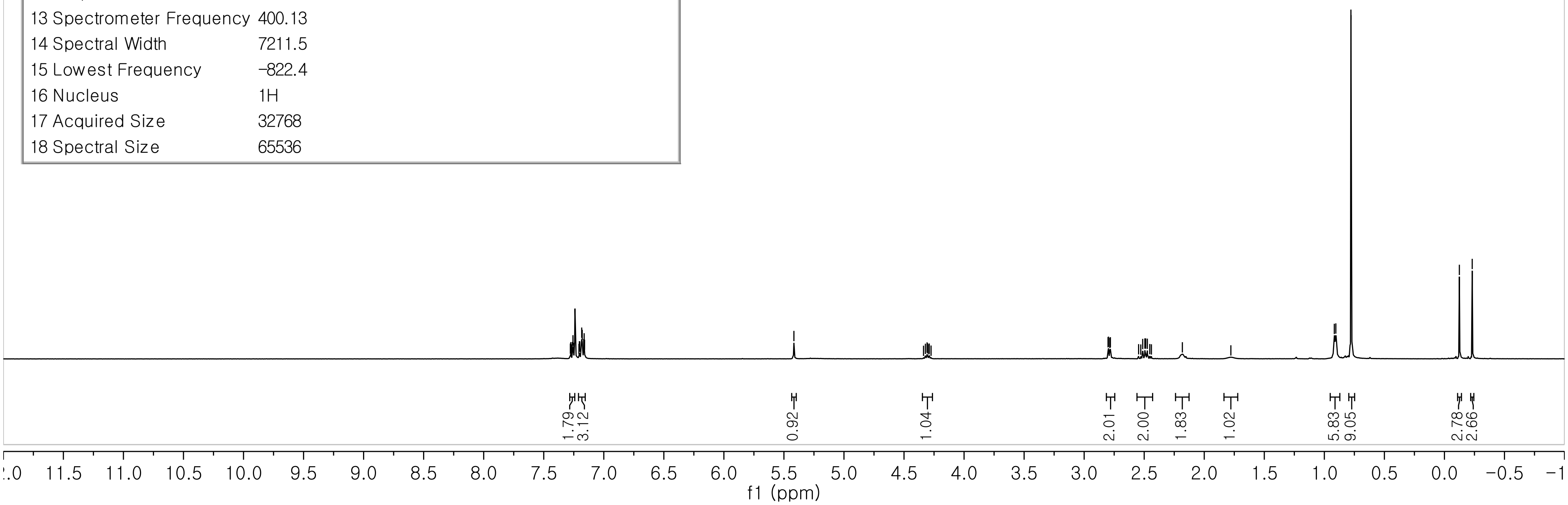


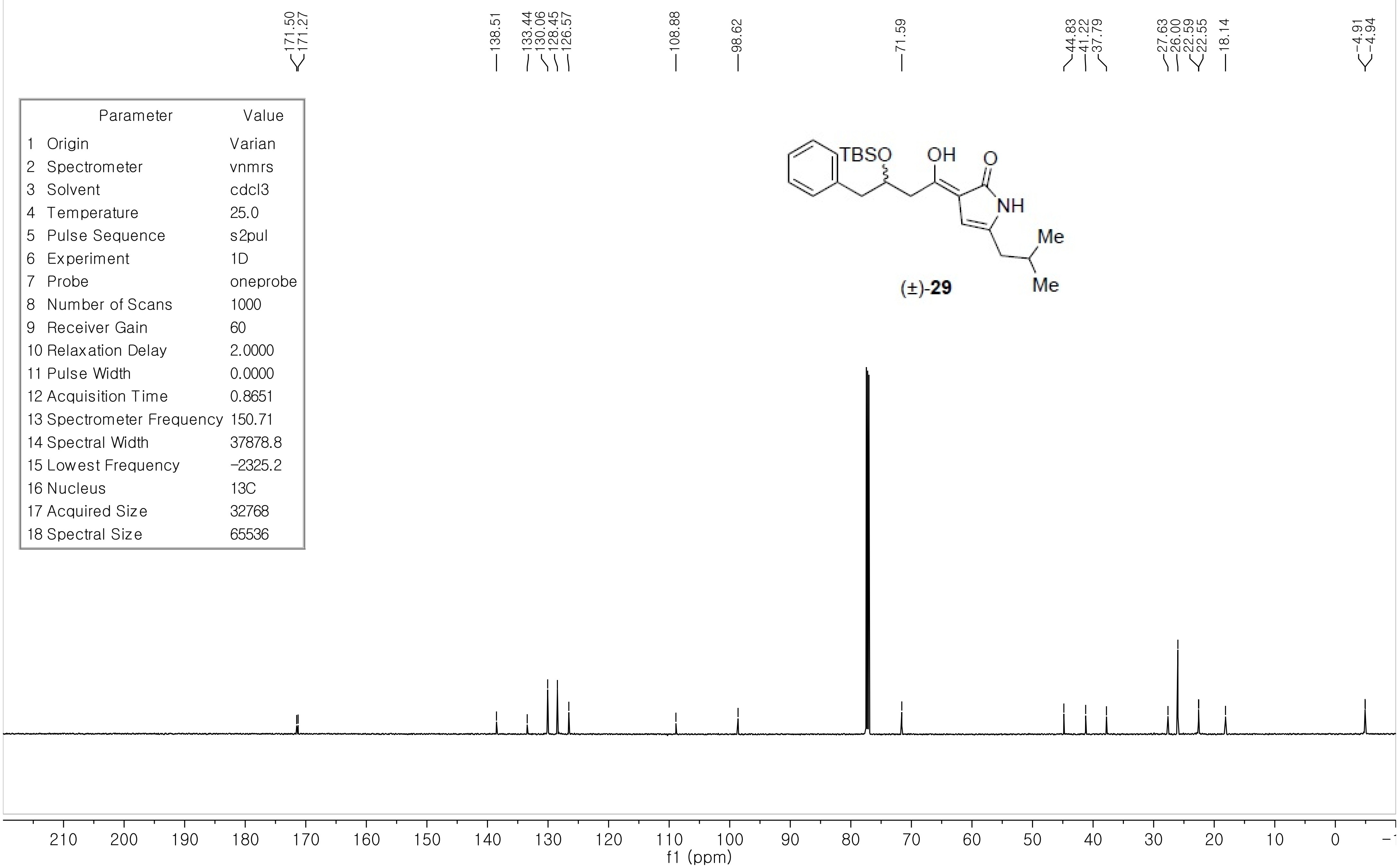
	Parameter	Value
1	Origin	Varian
2	Spectrometer	vnmrs
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	oneprobe
8	Number of Scans	606
9	Receiver Gain	60
10	Relaxation Delay	2.0000
11	Pulse Width	0.0000
12	Acquisition Time	0.8651
13	Spectrometer Frequency	150.70
14	Spectral Width	37878.8
15	Lowest Frequency	−2349.8
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.0
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0389
8	Number of Scans	57
9	Receiver Gain	202
10	Relaxation Delay	0.2000
11	Pulse Width	15.0000
12	Acquisition Time	4.5438
13	Spectrometer Frequency	400.13
14	Spectral Width	7211.5
15	Lowest Frequency	-822.4
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



(±)-**29**

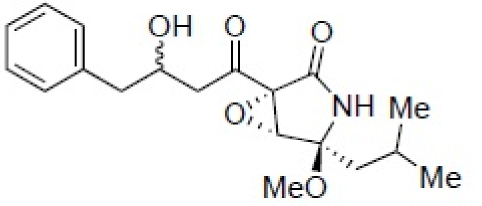




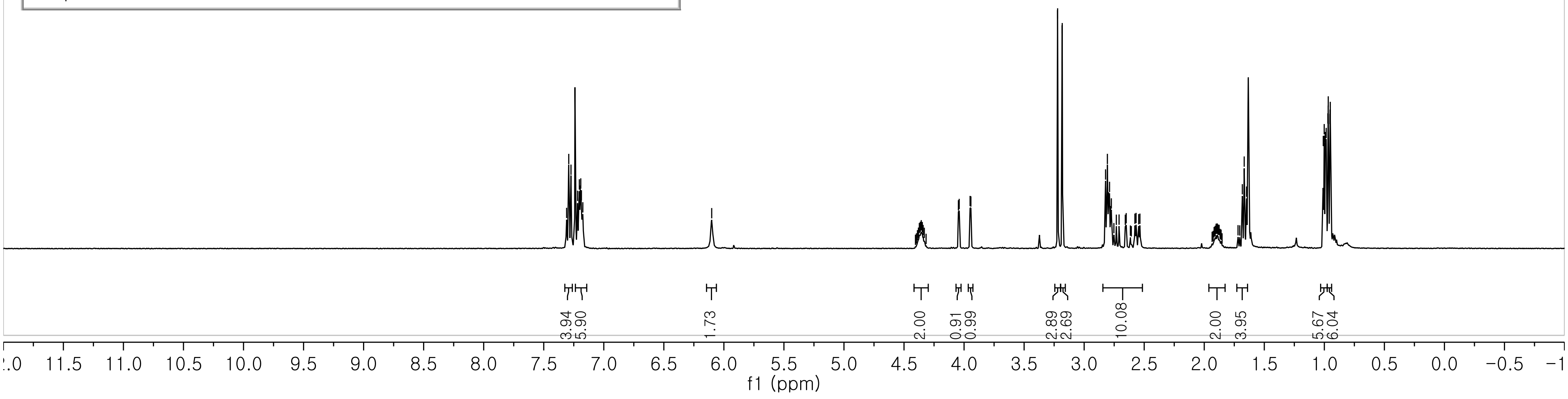
(±)-**29**

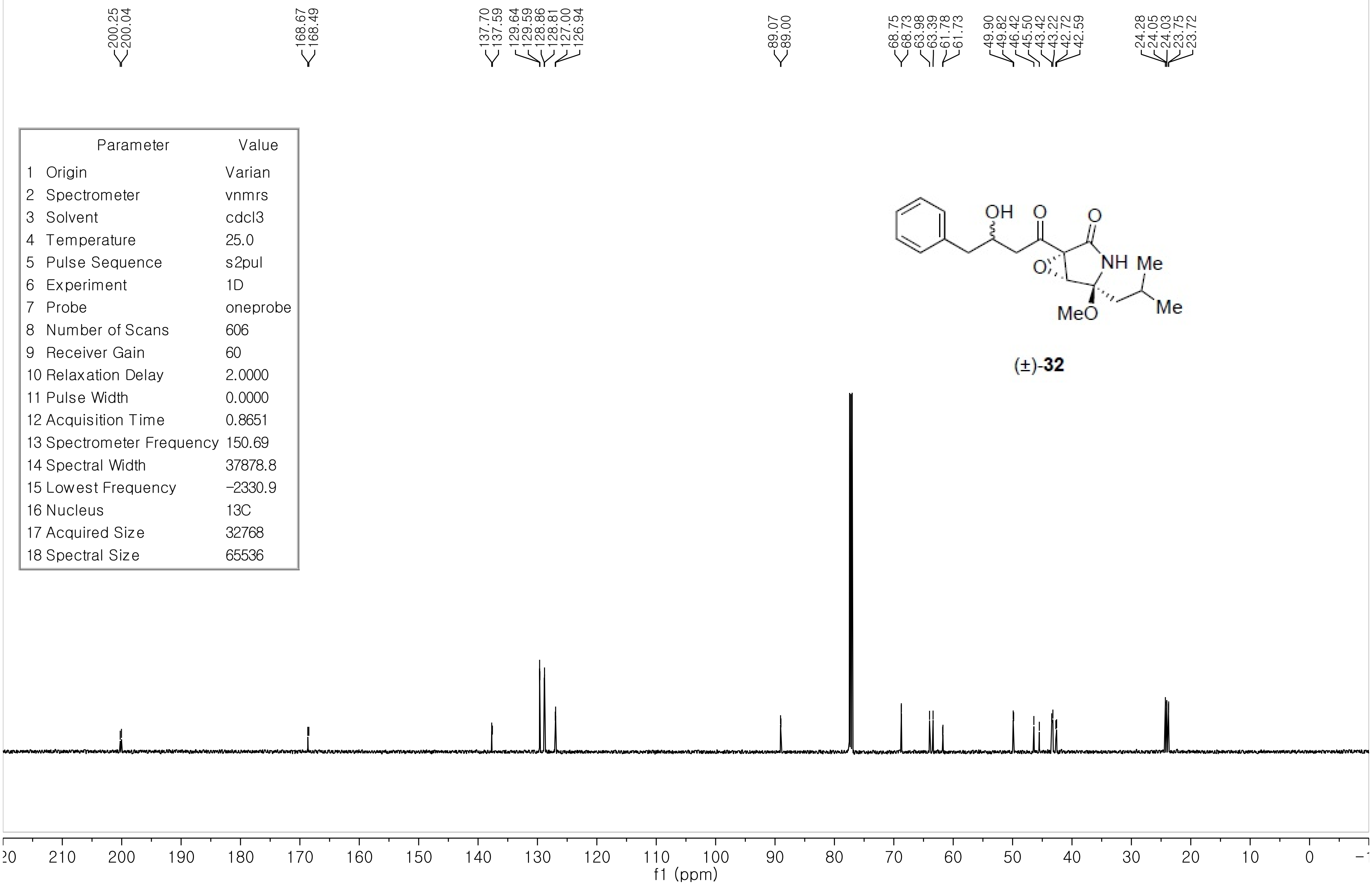
	Parameter	Value
1	Origin	Varian
2	Spectrometer	vnmrs
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	oneprobe
8	Number of Scans	1000
9	Receiver Gain	60
10	Relaxation Delay	2.0000
11	Pulse Width	0.0000
12	Acquisition Time	0.8651
13	Spectrometer Frequency	150.71
14	Spectral Width	37878.8
15	Lowest Frequency	−2325.2
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.0
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0389
8	Number of Scans	22
9	Receiver Gain	158
10	Relaxation Delay	0.2000
11	Pulse Width	15.0000
12	Acquisition Time	4.5438
13	Spectrometer Frequency	400.13
14	Spectral Width	7211.5
15	Lowest Frequency	-822.4
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



(±)-**32**

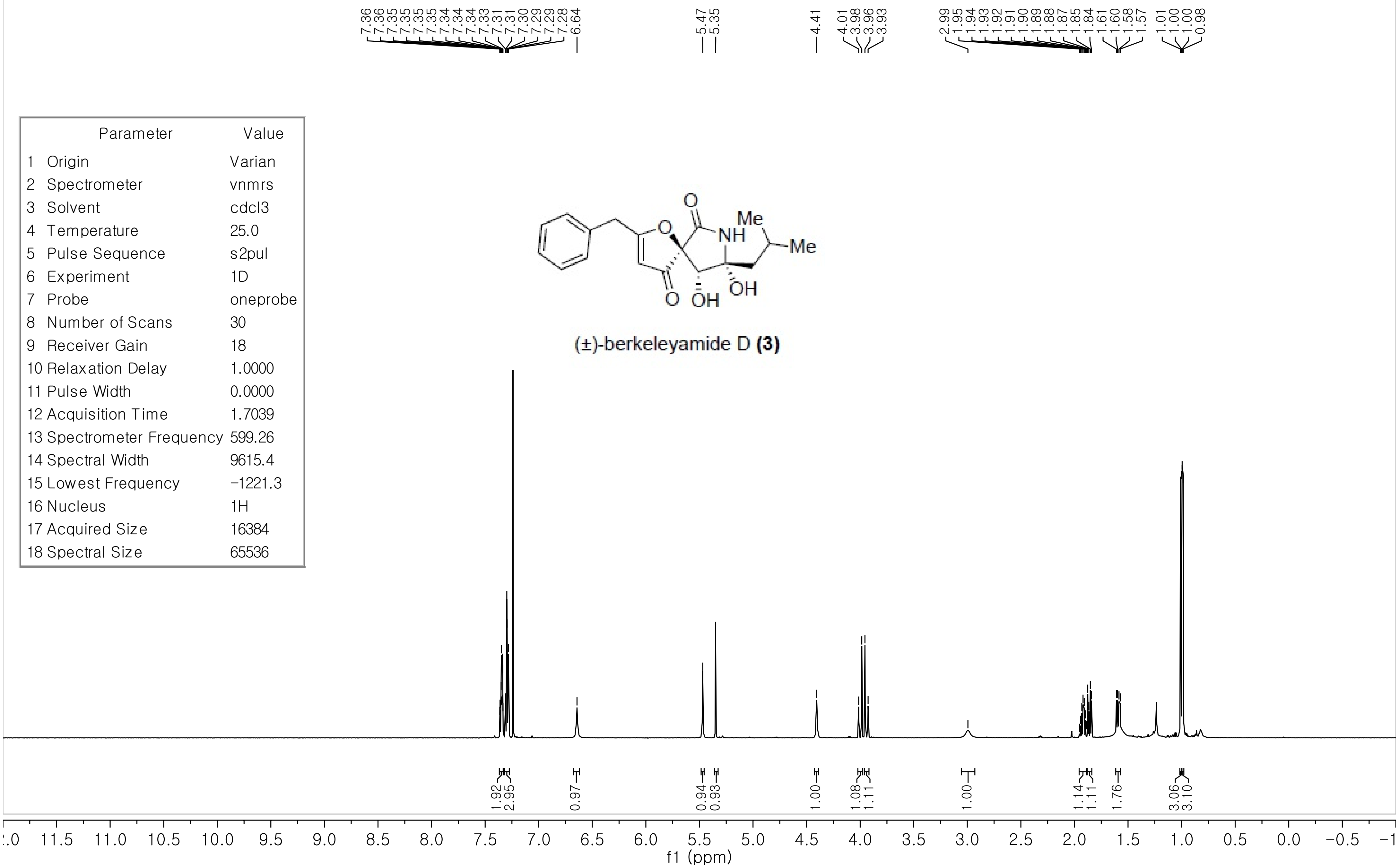




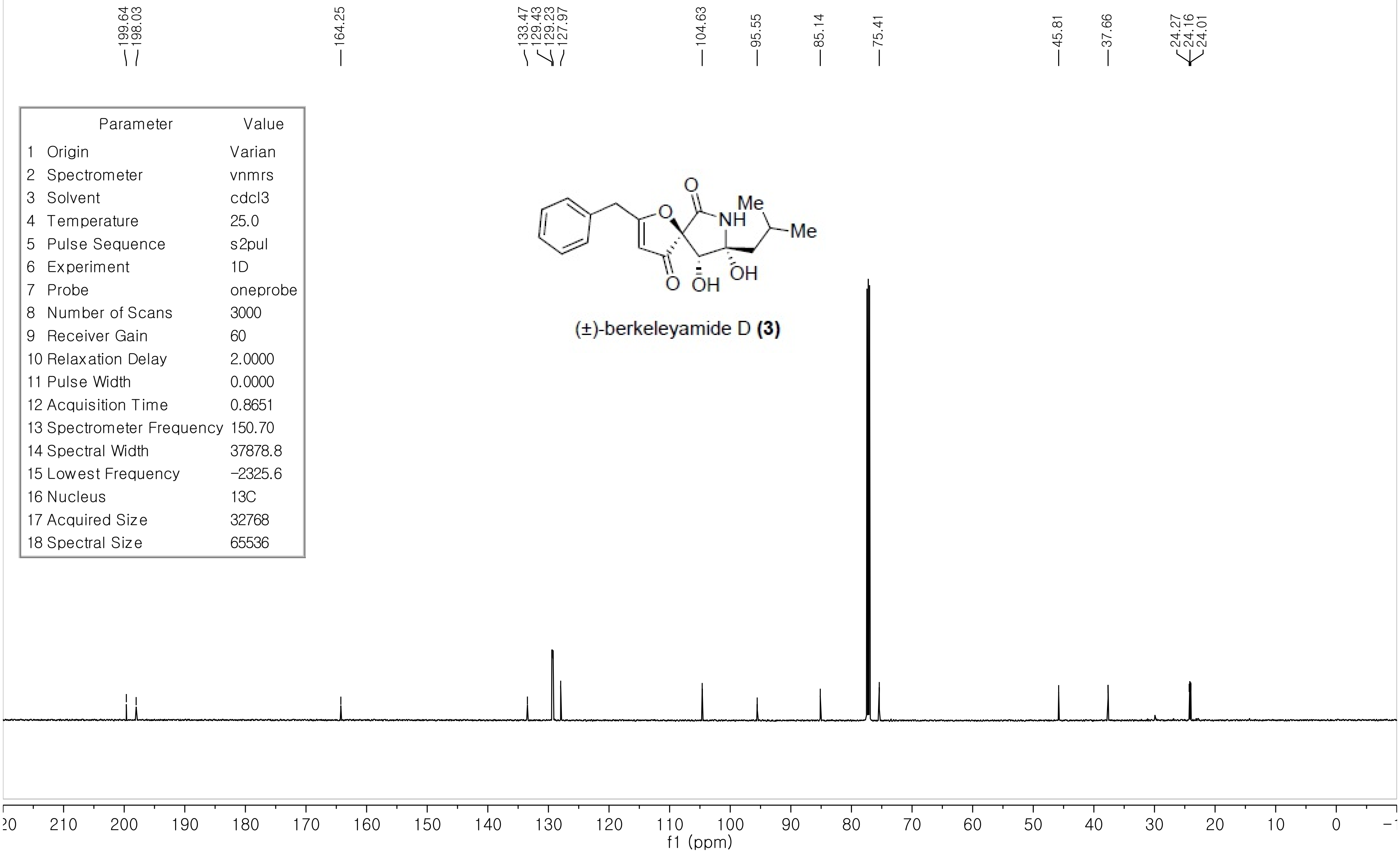
(±)-**32**

	Parameter	Value
1	Origin	Varian
2	Spectrometer	vnmrs
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	oneprobe
8	Number of Scans	606
9	Receiver Gain	60
10	Relaxation Delay	2.0000
11	Pulse Width	0.0000
12	Acquisition Time	0.8651
13	Spectrometer Frequency	150.69
14	Spectral Width	37878.8
15	Lowest Frequency	−2330.9
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

	Parameter	Value
1	Origin	Varian
2	Spectrometer	vnmrs
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	oneprobe
8	Number of Scans	30
9	Receiver Gain	18
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	1.7039
13	Spectrometer Frequency	599.26
14	Spectral Width	9615.4
15	Lowest Frequency	−1221.3
16	Nucleus	1H
17	Acquired Size	16384
18	Spectral Size	65536



(±)-berkeleyamide D **(3)**



(±)-berkeleyamide D **(3)**

	Parameter	Value
1	Origin	Varian
2	Spectrometer	vnmrs
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	oneprobe
8	Number of Scans	3000
9	Receiver Gain	60
10	Relaxation Delay	2.0000
11	Pulse Width	0.0000
12	Acquisition Time	0.8651
13	Spectrometer Frequency	150.70
14	Spectral Width	37878.8
15	Lowest Frequency	-2325.6
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536