# Supporting Information

# Enantioselective Organocatalytic Oxidative Enamine Catalysis/1,5-Hydride Transfer/Cyclization Sequences: Asymmetric Synthesis of Tetrahydroquinolines

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**Contents**

### 1.1 General

All commercial reagents and solvents were used without purification. TLC analyses were carried out on pre-coated silica gel plates with $F_{254}$ indicator. Visualization was accomplished by UV light (254 nm), $I_2$, *p*-anisaldehyde, ninhydrin, and phosphomolybdic acid solution as an indicator. Purification of reaction products was carried out by flash chromatography using E. Merck silica gel 60 (230-400 mesh). $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker 400 MHz NMR (400 MHz for $^1$H, 100 MHz for $^{13}$C). Chemical shift values (δ) are reported in ppm relative to $Me_4Si$ (δ 0.0 ppm). Optical rotations were measured on a JASCO-DIP-1000 digital polarimeter with a sodium lamp. The enantiomeric excesses (ee's) were determined by HPLC. HPLC analysis was performed on Younglin M930 Series and Younglin M720 Series, measured at 254 nm using the indicated chiral column.

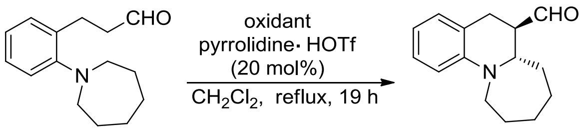
### 1.2 Preparation of starting materials

(3-(2-(Dialkylamino)aryl)propanal derivatives were prepared in accordance with literature methods.[1]

### 2.1 Optimization of the nonchiral reaction conditions

In an attempt to validate the feasibility of the proposed organocatalytic oxidative enamine catalysis and intramolecular redox reactions, 3-(2-(azepan-1-yl)phenyl)propanal (**1a**) was reacted in the presence of oxidant and nonchiral secondary amine as an organocatalyst in dichloromethane. The results of a representative selection of oxidative enamine catalysis and intramolecular redox reactions are summarized in Table SI-1. We started the study on the effect of various oxidants for the oxidative coupling reaction of 3-(2-(azepan-1-yl)phenyl)propanal (**1a**) in the presence of pyrrolidinium trifluoromethanesulfonate (20 mol %) as a catalyst in dichloromethane. The reaction gave a moderate yield (55%) when using a 1.0 equiv. of 2,3-dichloro-5,6-dicyanoquinone (DDQ) (Table SI-1, entry 1). Other oxidants including organic and metal oxidants were also used to improve the activity of this reaction. The organic oxidant, such as Dess-Martin periodinane (DMP) and *o*-iodoxybenzoic acid (IBX), could give the desired product in moderate yields (Table SI-1, entries 2-3). However, the reaction of **1a** with metal oxidant such as ceric ammonium nitrate (CAN), $Pd(OAc)_2/O_2$, CuBr/TBHP, and $(bpy)_2RuCl_2$/CFL, did not occur and the starting **1a** was recoverd (Table SI-1, entries 4-7).

**Table SI-1.** Optimization of the reaction conditions.[a]




**1a** → **2a**

| Entry | Oxidant | Yield (%)[b] | dr (%)[c] |
|---|---|---|---|
| 1 | DDQ | 55 | 1.5:1 |
| 2 | DMP | 45 | 1.5:1 |
| 3 | IBX | 38 | 1.5:1 |
| 4[d] | CAN | n.r. | |
| 5[e] | $Pd(OAc)_2/O_2$ | n.r. | |
| 6[f] | CuBr/TBHP | n.r. | |
| 7[g] | $(bpy)_3RuCl_2$/23 W CFL | n.r. | |

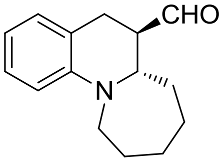
[a] Reactions were carried out with **1a** (0.2 mmol), catalyst (20 mol%), oxidant (1.0 equiv.) in $CH_2Cl_2$ (0.1 M). [b] Combined yield of both diastereomers. [c] Diastereomeric ratio is determined by $^1$H NMR spectroscopic analysis. [d] CAN (2.0 equiv.) was used. [e] $Pd(OAc)_2$ (20 mol%) and $O_2$ (1 atm) were used. [f] CuBr (20 mol%)/TBHP (1.5 eq, 5.0-6.0 M in decane) was used. [g] $(bpy)_3RuCl_2$ (20 mol%) was used. n.r.: no reaction, CFL: compact fluorescent light.

### 2.2 General procedure for the catalytic enantioselective 1,5-hydride transfer/ring closure of 1.

To a stirred solution of starting material **1** (0.1 mmol) in $CHCl_3$ (1.0 mL) was added catalyst **I** (11.9 mg, 0.02 mmol) and DNBS (4.9 mg, 0.02 mmol). After the mixture was stirred for 1 min, IBX (56.0 mg, 0.2 mmol) was added into reaction mixture at room temperature. Reaction mixture was stirred for indicated time, diluted with saturated $NaHCO_3$ solution (10 mL) and extracted with ethyl acetate (2×10 mL). The combined organic layers were dried over $MgSO_4$, filtered, concentrated, and purified by flash chromatography (EtOAc/hexane = 1:10) to afford analytically pure **2**

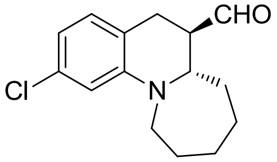
## 3. Product data

(6*R*,6a*S*)-5,6,6a,7,8,9,10,11-Octahydroazepino[1,2-a]quinoline-6-carbaldehyde (**2a**)



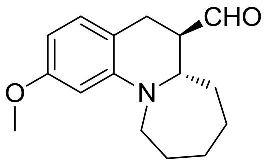

Major diastereomer. $[\alpha]^{28}_{D}$ = -42.2 (c = 0.9, $CH_2Cl_2$)$^1$H NMR (400 MHz, $CDCl_3$) δ = 9.55 (s, 1H), 7.06-7.01 (m, 2H), 6.52-6.54 (m, 1H), 6.40-6.48 (m, 1H), 3.85 (dd, *J* = 6.0 Hz, 3.0 Hz, 1H), 3.82-3.79 (m, 1H), 3.22-3.09 (m, 2H), 3.02 (dd, *J* = 8.0 Hz, 6.5 Hz, 1 H), 2.54-2.52 (m, 1H), 1.81-1.95 (m, 1H), 1.67-1.57 (m, 6H), 1.37-1.34 (m, 1H) ; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 203.17, 144.90, 129.50, 127.53, 117.15, 115.67, 110.39, 58.26, 49.58, 47.95, 35.02, 26.63, 26.13, 25.94, 23.80; EI-MS : m/z=230.1 $[M+H]^+$; ESI-HRMS : m/z calcd for $C_{15}H_{20}NO$ $[M+H]^+$ : 230.1545; found 230.1541; HPLC (95 : 5, *n*-hexane : *i*-PrOH, 254 nm, 0.5 mL/min) Chiralpak IC column, $t_R$ = 22.2 (major), $t_R$ = 23.8 (minor), 93% ee.

(6*R*,6a*S*)-2-Chloro-5,6,6a,7,8,9,10,11-octahydroazepino[1,2-a]quinoline-6-carbaldehyde (**2b**)



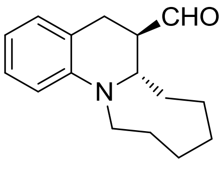

Major diastereomer. $[\alpha]^{28}_{D}$ = -52.2 (c = 1.0, $CH_2Cl_2$) $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.52 (s, 1H), 6.95-6.93 (m, 1H), 6.54 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 6.51-6.50 (m, 1H), 3.85-3.76 (m, 2H), 3.21-2.90 (m, 2H), 2.97 (dd, *J* = 17.2 Hz, 6.4 Hz, 1H), 2.58-2.53 (m, 1H), 2.15-2.04 (m, 1H), 1.80-1.50 (m, 6H), 1.45-1.32 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 202.41, 144, 76, 133.06, 130.37, 119.85, 115.50, 110.11, 57.90, 49.76, 47.73, 35.10, 26.21, 26.04, 25.84, 23.16; EI-MS : m/z=264.1 $[M+H]^+$; HPLC (95 : 5, *n*-hexane : *i*-PrOH, 254 nm, 1.0 mL/min) Chiralpak OJ-H column, $t_R$ = 10.1 (minor), $t_R$ = 11.0 (major), 91% ee.

(6*R*,6a*S*)-2-Methoxy-5,6,6a,7,8,9,10,11-octahydroazepino[1,2-a]quinoline-6-carbaldehyde (**2c**)



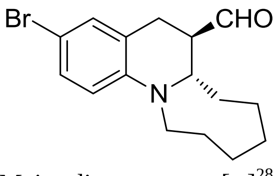

Major diastereomer. $[\alpha]^{28}_{D}$ = -95.3 (c = 1.4, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.54 (s, 1H), 6.96-6.94 (m, 1H), 6.18 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.12-6.11 (m, 1H), 3.85-3.79 (m, 2H), 3.79 (s, 3H), 3.20-3.06 (m, 2H), 2.98 (dd, *J* = 16.1 Hz, 6.0 Hz, 1H), 2.54-2.51 (m, 1H), 2.14-2.04 (m, 1H), 1.74-1.60 (m, 6H), 1.40-1.36 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 203.31, 159.50, 144.87, 129.98, 110.03, 100.24, 97.02, 58.14, 55.10, 49.68, 48.03, 35.08, 26.50, 26.10, 25.91, 23.14; EI-MS : m/z=260.1 $[M+H]^+$; HPLC (95 : 5, *n*-hexane : *i*-PrOH, 254 nm, 1.0 mL/min) Chiralpak IC column, $t_R$ = 17.6 (minor), $t_R$ = 22.4 (major), 81% ee.

(6*R*,6a*R*)-6,6a,7,8,9,10,11,12-Octahydro-5H-azocino[1,2-a]quinoline-6-carbaldehyde (**2d**)




Major diastereomer. $[\alpha]^{28}_{D}$ = 45.2 (c = 1.3, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.51 (d, *J* = 0.8 Hz, 1H), 7.09-7.04 (m, 2H) 6.62-6.55 (m, 2H), 3.85-3.80 (m, 2H), 3.25-3.21 (m, 1H), 3.21-3.10 (m, 2H), 2.55-2.52 (m, 1H), 1.71-1.32 (m, 10H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 203.32, 143.98, 129.52, 127.54, 117.37, 115.53, 111.33, 55.45, 53.15, 48.65, 33.90, 27.82, 26.91, 26.26, 26.09, 24.17; EI-MS : m/z=244.1 $[M+H]^+$;ESI-HRMS : m/z calcd for $C_{16}H_{22}NO$ $[M+H]^+$ : 244.1701; found 244.1697; HPLC (90 : 10, *n*-hexane : *i*-PrOH, 254 nm, 1.0 mL/min) Chiralpak AS-H column, $t_R$ = 16.6 (major), $t_R$ = 27.7 (minor), 98% ee.

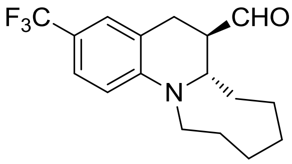
(6*R*,6a*R*)-3-Bromo-6,6a,7,8,9,10,11,12-octahydro-5H-azocino[1,2-a]quinoline-6-carbaldehyde (**2e**)




Major diastereomer. $[\alpha]^{28}_{D}$ = 33.4 (c = 1.0, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.47 (s, 1H), 7.14-7.10 (m, 2H), 6.62-6.39 (m, 1H), 3.85-3.80 (m, 1H), 3.74 (dt, *J* = 15.2 Hz, 4.4 Hz, 1H), 3.23-3.16 (m, 1H), 3.10-3.06 (m, 1H), 3.02 (dd, *J* = 16.8

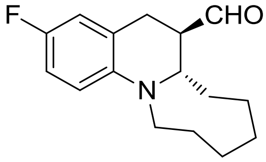
Hz, 6.0 Hz, 1H), 2.54-2.51 (m, 1H), 1.95-1.35 (m, 10H) ; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 202.44, 142.88, 131.84, 130.16, 119.57, 112.90, 107.20, 58.35, 53.21, 48.47, 33.82, 27.79, 26.59, 26.08, 26.05, 23.75; EI-MS : m/z=322.0 $[M+H]^+$; ESI-HRMS : m/z calcd for $C_{16}H_{21}BrNO$ $[M+H]^+$ : 322.0807; found 322.0807; HPLC (90 : 10, *n*-hexane : *i*-PrOH, 254 nm, 0.5 mL/min) Chiralpak AS-H column, $t_R$ = 16.6 (major), $t_R$ = 22.6 (minor), 99% ee.

(6*R*,6a*R*)-3-(Trifluoromethyl)-6,6a,7,8,9,10,11,12-octahydro-5H-azocino[1,2-a]quinoline-6-carbaldehyde (**2f**)



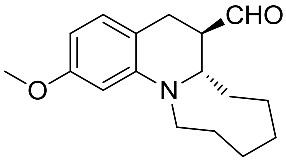

Major diastereomer. $[\alpha]^{28}_D$ = 27.6 (c = 0.9, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.49 (s, 1H), 7.25-7.20 (m, 2H), 6.56-6.54 (m, 1H), 3.89-3.80 (m, 2H), 3.25 (ddd, *J* = 14.4 Hz, 10.8 Hz, 3.6 Hz, 1H), 3.17-3.13 (m, 1H), 3.06 (dd, *J* = 16.8 Hz, 6.4 Hz, 1H), 2.58 (dt, *J* = 6.4 Hz, 2.4 Hz, 1H), 2.00-1.30 (m, 10H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 202.18, 146.32, 126.50 (q, *J* = 3.5 Hz), 124.74 (q, *J* = 3.8 Hz), 123.86 (q, *J* = 265.5 Hz), 117.19, 116.99 (q, *J* = 32.2 Hz), 110.71, 58.62, 53.25, 48.40, 34.08, 27.75, 26.42, 26.01, 25.81, 23.83; EI-MS : m/z=312.1 $[M+H]^+$; ESI-HRMS : m/z calcd for $C_{17}H_{21}F_3NO$ $[M+H]^+$ : 312.1575; found 312.1571; HPLC (98 : 2, *n*-hexane : *i*-PrOH, 254 nm, 1.0 mL/min) Chiralpak AS-H column, $t_R$ = 10.0 (major), $t_R$ = 12.7 (minor), 96% ee.

(6*R*,6a*R*)-3-Fluoro-6,6a,7,8,9,10,11,12-octahydro-5H-azocino[1,2-a]quinoline-6-carbaldehyde (**2g**)



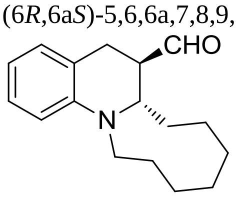

Major diastereomer. $[\alpha]^{28}_D$ = 36.5 (c = 0.5, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.51 (s, 1H), 6.79-6.75 (m, 2H), 6.46-6.43 (m, 1H), 3.84 (dt, *J* = 6.4 Hz, 2.4 Hz, 1H), 3.74 (dt, *J* = 14.8 Hz, 4.4 Hz, 1H), 3.24-3.20 (m, 1H), 3.12-3.08 (m, 1H), 3.01 (dd, *J* = 16.8 Hz, 6.0 Hz, 1H), 2.56-2.53 (m, 1H)1.95-1.40 (m, 10H) ; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 201.67, 153.44 (d, *J* = 232.7 Hz), 139.21, 114.61 (d, *J* = 6.7 Hz), 112.97 (d, *J* = 21.8 Hz), 110.70 (d, *J* = 21.7 Hz), 57.09, 52.42, 47.65, 32.59, 26.76, 25.83, 25.36, 22.03, 23.00; EI-MS : m/z=262.1 $[M+H]^+$; HPLC (95 : 5, *n*-hexane : *i*-PrOH, 254 nm, 1.0 mL/min) Chiralpak AS-H column, $t_R$ = 10.5 (major), $t_R$ = 13.9 (minor), 97% ee.

(6*R*,6a*R*)-2-Methoxy-6,6a,7,8,9,10,11,12-octahydro-5H-azocino[1,2-a]quinoline-6-carbaldehyde (**2h**)



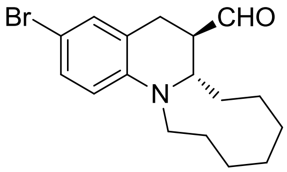

Major diastereomer. $[\alpha]^{28}_D$ = 36.0 (c = 1.8, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.48 (s, 1H), 7.05-7 (m, 1H), 6.15-5.90 (m, 2H), 3.80-3.75 (m, 5H), 3.28-3.21 (m, 1H), 3.02 (dd, *J* = 16.4 Hz, 2.4 Hz, 1H), 2.99 (dd, *J* = 6.0 Hz, 0.8 Hz, 1H), 2.53-2.51 (m, 1H), 2.00-1.30 (m, 10H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 203.44, 159.48, 144.96, 129.99, 110.31, 100.26, 97.84, 58.45, 55.09, 53.20, 48.81, 33.97, 27.83, 26.77, 26.18, 26.09, 23.51; EI-MS : m/z=274.1 $[M+H]^+$; HPLC (90 : 10, *n*-hexane : *i*-PrOH, 254 nm, 1.0 mL/min) Chiralpak IC column, $t_R$ = 10.0 (major), $t_R$ = 13.9 (minor), 95% ee.

(6*R*,6a*S*)-5,6,6a,7,8,9,10,11,12,13-Decahydroazonino[1,2-a]quinoline-6-carbaldehyde (**2i**)



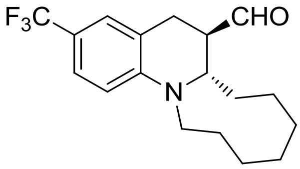

Major diastereomer. $[\alpha]^{28}_D$ = -145.8 (c = 1.0, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.83 (d, *J* = 0.8 Hz, 1H), 7.14-7.07 (m, 2H), 6.80-6.77 (m, 1H), 6.70 (td, J = 7.2 Hz, 1.2 Hz, 1H), 3.76 (dt, *J* = 10.8 Hz, 2.4 Hz, 1H), 3.67 (ddd, *J* = 14.8 Hz, 8.0 Hz, 3.6 Hz, 1H), 3.22 (ddd, *J* = 14.8 Hz, 6.8 Hz, 3.6 Hz, 1H), 3.05-2.98 (m, 1H), 2.87 (dd, *J* = 16.8 Hz, 5.6 Hz, 1H), 2.70-2.65 (m, 1H), 1.84-1.10 (m, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 203.24, 144.98, 129.78, 127.36, 120.32, 117.05, 115.26, 58.89, 56.80, 48.00, 28.88, 27.62, 27.26, 25.45, 25.11, 24.75, 23.33; EI-MS : m/z=258.1 $[M+H]^+$; ESI-HRMS : m/z calcd for $C_{17}H_{24}NO$ $[M+H]^+$ : 258.1861; found 258.1858; HPLC (97 : 3, *n*-hexane : *i*-PrOH, 254 nm, 1.0 mL/min) Chiralpak AS-H column, $t_R$ = 6.41 (major), $t_R$ = 7.21 (minor), 98% ee.

(6*R*,6a*S*)-3-Bromo-5,6,6a,7,8,9,10,11,12,13-decahydroazonino[1,2-a]quinoline-6-carbaldehyde (**2j**)



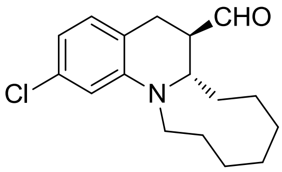
Major diastereomer. $[\alpha]^{28}_{D}$ = -51.8 (c = 1.0, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.81 (d, *J* = 0.8 Hz,1H), 7.19-7.17 (m, 2H), 6.65-6.62 (m, 1H), 3.76 (dt, *J* = 10.4 Hz, 2.8 Hz, 1H), 3.61 (ddd, *J* = 14.8 Hz, 7.6 Hz, 3.2 Hz, 1H), 3.21 (ddd, *J* = 14.8 Hz, 6.8 Hz, 3.2 Hz, 1H), 3.01 (dd, *J* = 16.8 Hz, 13.6 Hz, 1H), 2.82 (dd, *J* = 17.2 Hz, 5.6 Hz, 1H), 2.67-2.61 (m, 1H), 1.90-1.10 (m, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 202.46, 143.95, 132.07, 130.11, 122.40, 116.58, 108.80, 58.92, 56.75, 47.82, 28.81, 27.46, 27.10, 25.51, 25.16, 24.74, 23.15; EI-MS : m/z=336.0 $[M+H]^+$; HPLC (95 : 5, *n*-hexane : *i*-PrOH, 254 nm, 1.0 mL/min) Chiralpak AS-H column, $t_R$ = 8.41 (major), $t_R$ = 9.71 (minor), 91% ee.

(6*R*,6a*S*)-3-(Trifluoromethyl)-5,6,6a,7,8,9,10,11,12,13-decahydroazonino[1,2-a]quinoline-6-carbaldehyde (**2k**)



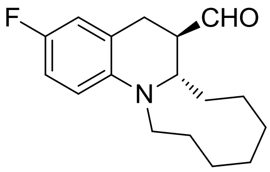
Major diastereomer. $[\alpha]^{28}_{D}$ = -41.5 (c = 1.2, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.50 (s, 1H), 7.30-7.28 (m, 2H), 6.66-6.64 (m, 1H), 3.92-3.88 (m, 1H), 3.72 (ddd, *J* = 12.4 Hz, 6.4 Hz, 3.2 Hz, 1H), 3.27 (ddd, *J* = 15.2 Hz, 7.6 Hz, 3.2 Hz, 1H), 3.18-3.14 (m, 1H), 3.12-3.10 (m, 1H), 2.61 (dt, *J* = 6.4 Hz, 2.4 Hz, 1H), 1.90-1.30 (m, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 202.31, 147.19, 126.57 (q, *J* = 3.6 Hz), 124.60 (q, *J* = 4.1 Hz), 123.81 (q, *J* = 265.2), 117.19, 116.99 (q, *J* = 32.2 Hz), 110.71,59.84, 56.65, 48.75, 33.22, 30.92, 27.69, 26.57, 26.39, 25.35, 23.75; EI-MS : m/z=326.1 $[M+H]^+$;HPLC (97 : 3, *n*-hexane : *i*-PrOH, 254 nm, 1.0 mL/min) Chiralpak IB column, $t_R$ = 8.51 (minor), $t_R$ = 8.91 (major), 95% ee.

(6*R*,6a*S*)-2-Chloro-5,6,6a,7,8,9,10,11,12,13-decahydroazonino[1,2-a]quinoline-6-carbaldehyde (**2l**)



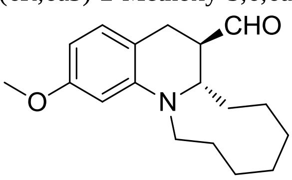
Major diastereomer. $[\alpha]^{28}_{D}$ = -129.4 (c = 0.8, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.81 (d, *J* = 0.4 Hz, 1H), 6.98-6.96 (m, 1H), 6.72-6.70 (m, 1H), 6.64 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 3.77 (dt, *J* = 10.8 Hz, 2.4 Hz, 1H), 3.64 (ddd, *J* = 15.2 Hz, 7.2 Hz, 3.6 Hz, 1H), 3.22 (ddd, *J* = 14.8 Hz, 7.2 Hz, 3.6 Hz, 1H), 3.02-2.94 (m, 1H), 2.82 (dd, *J* = 17.2 Hz, 5.6 Hz, 1H), 2.64 (ddd, *J* = 13.6 Hz, 5.2 Hz, 4 Hz, 1H), 1.90-1.10 (m, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 202.53, 145.92, 132.75, 130.66, 118.62, 116.85, 114.40, 58.98, 56.75, 48.11, 29.06, 27.40, 17.10, 25.60, 25.24, 24.77, 22.87; EI-MS : m/z=292.1 $[M+H]^+$;HPLC (97 : 3, *n*-hexane : *i*-PrOH, 254 nm, 1.0 mL/min) Chiralpak AS-H column, $t_R$ = 7.80 (major), $t_R$ = 8.76 (minor), 98% ee.

(6*R*,6a*S*)-3-Fluoro-5,6,6a,7,8,9,10,11,12,13-decahydroazonino[1,2-a]quinoline-6-carbaldehyde (**2m**)



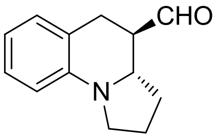
Major diastereomer. $[\alpha]^{28}_{D}$ = -85.4 (c = 1.0, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ =9.82 (d, *J* = 0.4 Hz, 1H), 6.86-6.77 (m, 2H), 6.71 (dd, *J* = 8.8 Hz, 4.8 Hz, 1H), 3.75 (dt, *J* = 11.2 Hz, 2.8 Hz, 1H), 3.54 (ddd, *J* = 14.8 Hz, 8.4 Hz, 3.6 Hz, 1H), 3.21 (ddd, *J* = 14.8 Hz, 6.4 Hz, 3.2 Hz, 1H), 3.03 (dd, *J* = 16.4 Hz, 13.6 Hz, 1H), 2.82 (dd, *J* = 16.8 Hz, 5.2 Hz, 1H), 2.70-2.64 (m, 1H), 1.90-1.25 (m, 11H), 1.15-1.05 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 202.77, 155.38 (d, *J* = 234.7 Hz), 141.38, 121.78 (d, *J* = 7.1 Hz), 116.55 (d, *J* = 8.4 Hz), 115.62 (d, *J* = 21.7 Hz), 114.08 (d, *J* = 22.0 Hz), 58.20, 57.21, 47.47, 28.52, 27.53, 27.44, 24.89, 24.55, 24.31, 23.38; EI-MS : m/z=276.1 $[M+H]^+$; HPLC (97 : 3, *n*-hexane : *i*-PrOH, 254 nm, 1.0 mL/min) Chiralpak AS-H column, $t_R$ = 7.43 (major), $t_R$ = 8.91 (minor), 96% ee.

(6*R*,6a*S*)-2-Methoxy-5,6,6a,7,8,9,10,11,12,13-decahydroazonino[1,2-a]quinoline-6-carbaldehyde (**2n**)



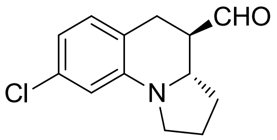
Major diastereomer. $[\alpha]^{28}_{D}$ = -108.6 (c = 1.4, $CH_2Cl_2$); $^{1}H$ NMR (400 MHz, $CDCl_3$) δ = 9.81 (d, *J* = 0.8 Hz, 1H), 7.00-6.98 (m, 1H), 6.31-6.29 (m, 2H), 3.78 (s, 3H), 3.73-3.64 (m, 2H), 3.22 (ddd, *J* = 15.2 Hz, 7.2 Hz, 3.6 Hz, 1H), 3.00-2.94 (m, 2H), 2.82 (dd, *J* = 16.0 Hz, 5.2 Hz, 2.68-2.63 (m, 1H), 1.90-1.10 (m, 12H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 203.38, 159.33, 146.03, 130.37, 113.17, 102.23, 101.07, 59.31, 56.92, 55.20, 48.64, 29.14 27.76, 26.78, 25.75, 25.36, 24.98, 22.81; EI-MS : m/z=288.1 $[M+H]^+$; HPLC (95 : 5, *n*-hexane : *i*-PrOH, 254 nm, 1.0 mL/min) Chiralpak AS-H column, $t_R$ = 7.40 (major), $t_R$ = 8.43 (minor), 98% ee.

(3a*S*,4*R*)-1,2,3,3a,4,5-Hexahydropyrrolo[1,2-a]quinoline-4-carbaldehyde (**2o**)



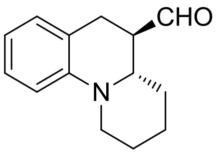

Major diastereoisomer. $[\alpha]^{25}_{D}$ = -14 (c = 1.0, $CHCl_3$); $^{1}H$ NMR (400 MHz, $CDCl_3$) δ = 9.91 (d, *J* = 2.0 Hz, 1H), 7.13-7.05 (m, 1H), 7.10 (d, *J* = 1.6 Hz. 1H), 6.60-6.60 (m, 1H), 6.46 (d, *J* = 8.0 Hz, 1H) 3.50 (ddd, *J* = 10.4 Hz, 10.1 Hz, 4.9 Hz, 1H), 3.32 (ddd, *J* = 11.1 Hz, 8.9 Hz, 2.1 Hz, 1H), 3.23-3.20 (m, 1H), 2.93-2.91 (m, 2H), 2.50-2.44 (m, 1H), 2.33-2.31 (m, 1H), 2.16-2.10 (m, 1H), 1.99-1.97 (m, 1H), 1.58-1.57 (m, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 202.99, 143.89, 128.70, 127.76, 119.06, 115.48, 110.45, 57.75, 50.35, 46.64, 31.62, 28.59, 24.02; EI-MS : m/z=202.1 $[M+H]^+$; ESI-HRMS : m/z calcd for $C_{13}H_{16}NO$ $[M+H]^+$ : 202.1232; found 202.1238; HPLC (98 : 2, *n*-hexane : *i*-PrOH, 254 nm, 1.0 mL/min) Chiralpak IC column, $t_R$ = 10.3 (minor), $t_R$ = 10.8 (major), 87% ee.

(3a*S*,4*R*)-8-chloro-1,2,3,3a,4,5-Hexahydropyrrolo[1,2-a]quinoline-4-carbaldehyde (**2p**)



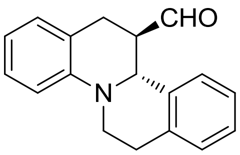

Major diastereoisomer. $[\alpha]^{25}_{D}$ = -19 (c = 1.0, $CHCl_3$) $^{1}H$ NMR (400 MHz, $CDCl_3$) δ = 9.91 (d, *J* = 2.0 Hz, 1H), 6.95-6.93 (m, 1H), 6.55 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 6.41-6.40 (m, 1H), 3.48 (ddd, *J* = 15.2 Hz, 10.8 Hz, 5.2 Hz, 1H), 3.36 (ddd, *J* = 10.8 Hz, 8.8 Hz, 1.6 Hz, 1H), 3.18 (ddd, *J* = 16.8 Hz, 9.2 Hz, 7.2 Hz, 1H), 2.95-2.81 (m, 2H), 2.44-2.32 (m, 2H), 2.19-2.12 (m, 1H), 2.05-1.92 (m, 1H), 1.62-1.55 (m, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 202.60, 150.04, 133.34, 129.60, 121.51, 115.19, 110.15, 57.81, 50.44, 46.78, 31.76, 28.29, 24.14; EI-MS : m/z=236.0 $[M+H]^+$; HPLC (97 : 3, *n*-hexane : *i*-PrOH, 254 nm, 1.0 mL/min) Chiralpak IC column, $t_R$ = 11.1 (minor), $t_R$ = 11.4 (major), 90% ee.]

(4a*S*,5*R*)-2,3,4,4a,5,6-Hexahydro-1H-pyrido[1,2-a]quinoline-5-carbaldehyde (**2q**)



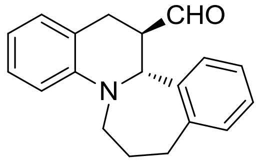

Major diastereomer. $[\alpha]^{28}_{D}$ = -50.6 (c = 0.5, $CH_2Cl_2$); $^{1}H$ NMR (400 MHz, $CDCl_3$) δ = 9.63 (d, *J* = 1.6 Hz, 1H), 7.10 (td, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.03-7.01 (m, 1H), 6.78-6.76 (m, 1H), 6.67 (td, *J* = 7.2 Hz, 0.8 Hz, 1H), 3.95-3.91 (m, 1H), 3.45 (ddd, *J* = 10.8 Hz, 5.2 Hz, 2.0 Hz, 1H), 2.99 (dd, *J* = 15.2 Hz, 6.4 Hz, 1H), 2.90-2.84 (m, 2H), 2.63-2.58 (m, 1H), 1.90-1.50 (m, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 202.72, 145.73, 128.89, 127.65, 122.10, 117.62, 112.60, 56.53, 52.01, 48.39, 31.26, 25.99, 24.98, 24.06; EI-MS : m/z=216.1 $[M+H]^+$; HPLC (90 : 10, *n*-hexane : *i*-PrOH, 254 nm, 0.5 mL/min) Chiralpak AS-H column, $t_R$ = 21.3 (major), $t_R$ = 27.9 (minor), 80% ee.

(11b*R*,12*R*)-7,11b,12,13-Tetrahydro-6H-isoquinolino[2,1-a]quinoline-12-carbaldehyde (**2r**)



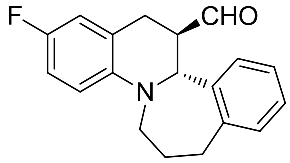

Major diastereomer. $^{1}H$ NMR (400 MHz, $CDCl_3$) δ = 9.40 (s, 1H), 7.35-7.20 (m, 2H), 7.25-7.20 (m, 2H), 7.14-7.11 (m, 2H), 6.86-6.80 (m, 1H), 6.79 (td, J = 7.2 Hz, 0.8 Hz, 1H), 4.66-4.67 (m, 1H), 4.02-3.99 (m, 1H), 3.42 (d, *J* = 15.6 Hz, 1H), 3.29 (dt, *J* = 7.2 Hz, 1.6 Hz, 1H), 3.17 (dd, *J* = 16.4 Hz, 6.8 Hz, 1H), 3.08-3.04 (m, 1H), 3.02-2.99 (m, 1H), 2.93-2.89 (m, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 202.02, 146.38, 135.36, 134.98, 129.86, 128.81, 126.95, 126.83, 126.24, 121.32, 118.87, 112.11 (one aromatic carbon missing), 57.61, 51.21, 42.06, 29.89, 27.67; EI-MS : m/z=264.1 $[M+H]^+$;

(12b*R*,13*R*)-6,7,8,12b,13,14-Hexahydrobenzo[3,4]azepino[1,2-a]quinoline-13-carbaldehyde (**2s**)



Major diastereomer. $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 9.64 (d, *J* = 1.6 HZ, 1H), 7.18-7.02 (m, 6H), 6.67-6.58 (m, 2H), 5.05 (d, *J* = 6.4 Hz, 1H), 2.99-2.90 (m, 2H), 2.65 (dt, *J* = 14 Hz, 4.8 Hz, 1H), 2.27-2.19 (m, 1H), 1.68-1.61 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 203.02, 143.42, 139.63, 139.28, 130.80, 129.28, 127.86, 127.65, 127.16, 126.54, 119.34, 116.07, 110.66, 63.26, 49.49, 46.33, 31.88, 26.72, 24.73; EI-MS : m/z=278.1 $[M+H]^+$.

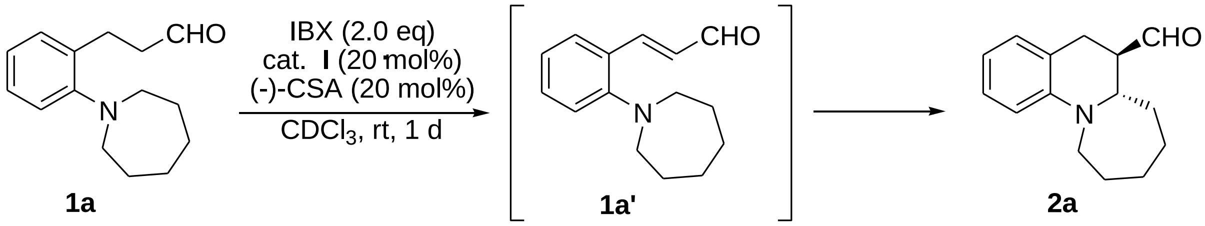
(12b*R*,13*R*)-2-Fluoro-6,7,8,12b,13,14-hexahydrobenzo[3,4]azepino[1,2-a]quinoline-13-carbaldehyde (**2t**)



Major diastereomer. $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 9.65 (d, *J* = 0.8 Hz, 1H), 7.17-7.11 (m, 4H), 6.78-6.72 (m, 2H), 6.55-6.52 (m, 1H), 5.07 (d, *J* = 5.6 Hz, 1H), 3.85 (ddd, *J* = 15.2 Hz, 5.2 Hz, 1.6 Hz, 1H), 3.32 (ddd, *J* = 16.8 Hz, 12.0 Hz, 5.2 Hz, 1H), 3.23-3.13 (m, 2H), 3.00-2.87 (m, 2H), 2.72 (ddd, *J* = 14.4 Hz, 6.0 Hz, 4.0 Hz, 1H), 2.22-2.12 (m, 1H), 1.71-1.63 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 202.42, 154.82 (d, *J* = 233.5 Hz), 140.03, 139.84, 139.42, 130.84, 127.83, 126.89, 126.51, 120.88 (d, *J* = 7.0 Hz), 115.66 (d, *J* = 22.0 Hz), 113.74 (d, *J* = 21.5 Hz), 111.42 (d, *J* = 7.4 Hz), 62.34, 49.38, 47.70, 32.59, 25.99, 24.55; EI-MS : m/z=296.1 $[M+H]^+$.

## 4. Mechanistic studies

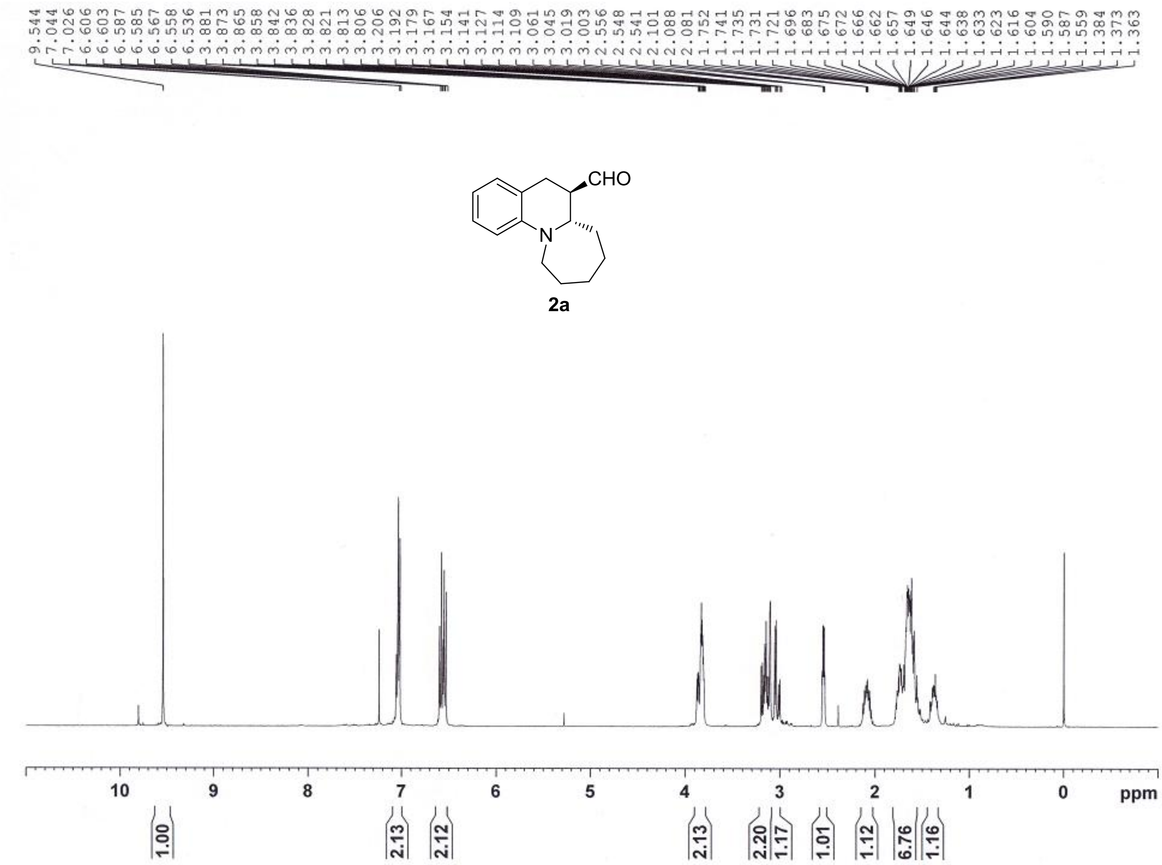
To obtain information on the reaction pathway, we investigated the reaction of 3-(2-(azepan-1-yl)phenyl)propanal (**1a**) in the presence of catalyst **I** (20 mol %) and (-)-camphorsulfonic acid (CSA) in $CDCl_3$. After 1 d, $^{1}$H NMR analysis of the reaction mixture revealed the formation of 3-(2-(azepan-1-yl)phenyl)propenal (**1a'**) as reaction intermediate. This result indicate that the saturated aldehyde **1a** is converted *in situ* into the corresponding α,β-unsaturated aldehyde **1a'** through oxidative enamine catalysis. Based on this experimental result, we proposed the reaction mechanism that the saturated aldehyde is converted *in situ* into the corresponding α,β-unsaturated aldehyde which can then be manipulated with 1,5-hydride transfer/cyclization towards the asymmetric synthesis of tetrahydroquinolines as shown in Scheme 1.

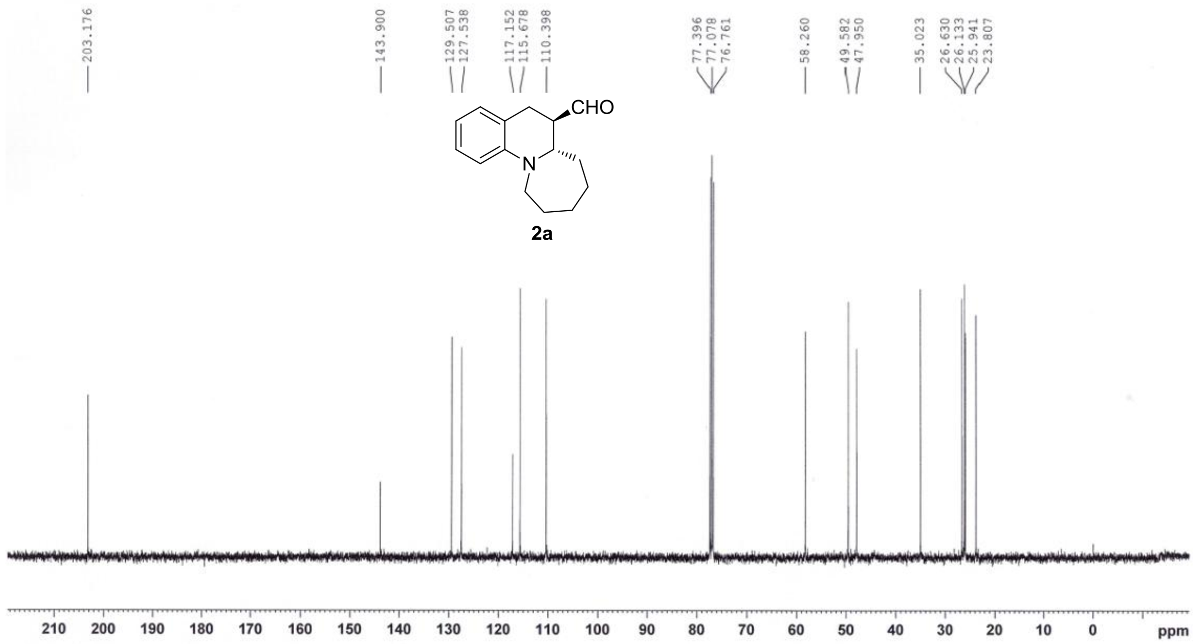


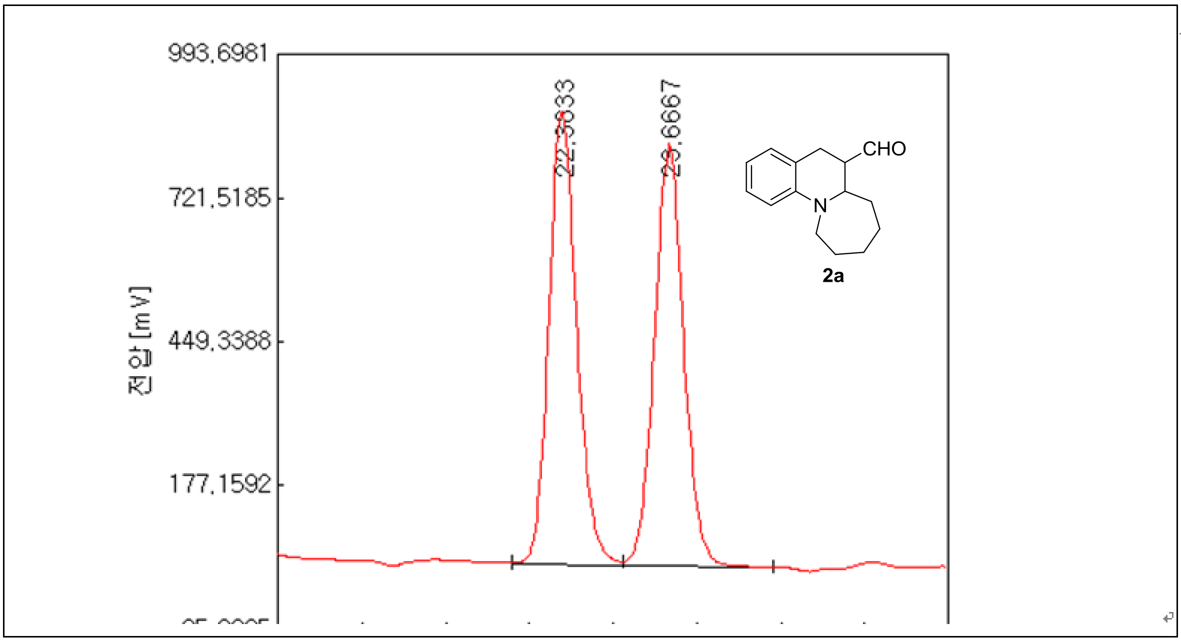

## 5. References

1.(a) Murarka, S.; Zhang, C.; Konieczynska, M. D.; Seidel, D. *Org. Lett*. **2009**, *11*, 129. (b) Murarka, S.; Deb, I.; Zhang, C.; Seidel. D. *J. Am. Chem. Soc*. **2009**, *131*, 13226. (c) Kohler, E. P.; Chadwell, H, M. *Org. Synth*. **1941**, *1*, 78. (d) Brown, H, C.; Hess, H. M. *J. Org. Chem*. **1969**, *34*, 2206.

## 6. NMR spectra and HPLC chromatogram






분석 결과

| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
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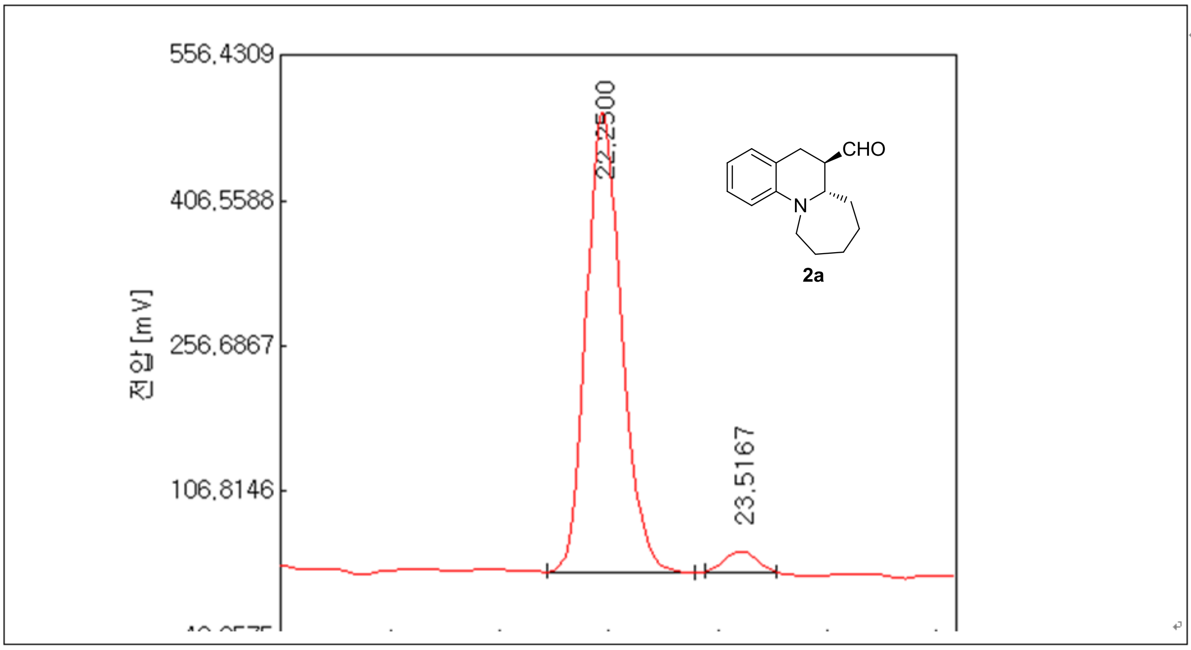
| 2 | 23.6667 | 20113.1251 | VV | 108.0000 | 49.4137 |




분석 결과

| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
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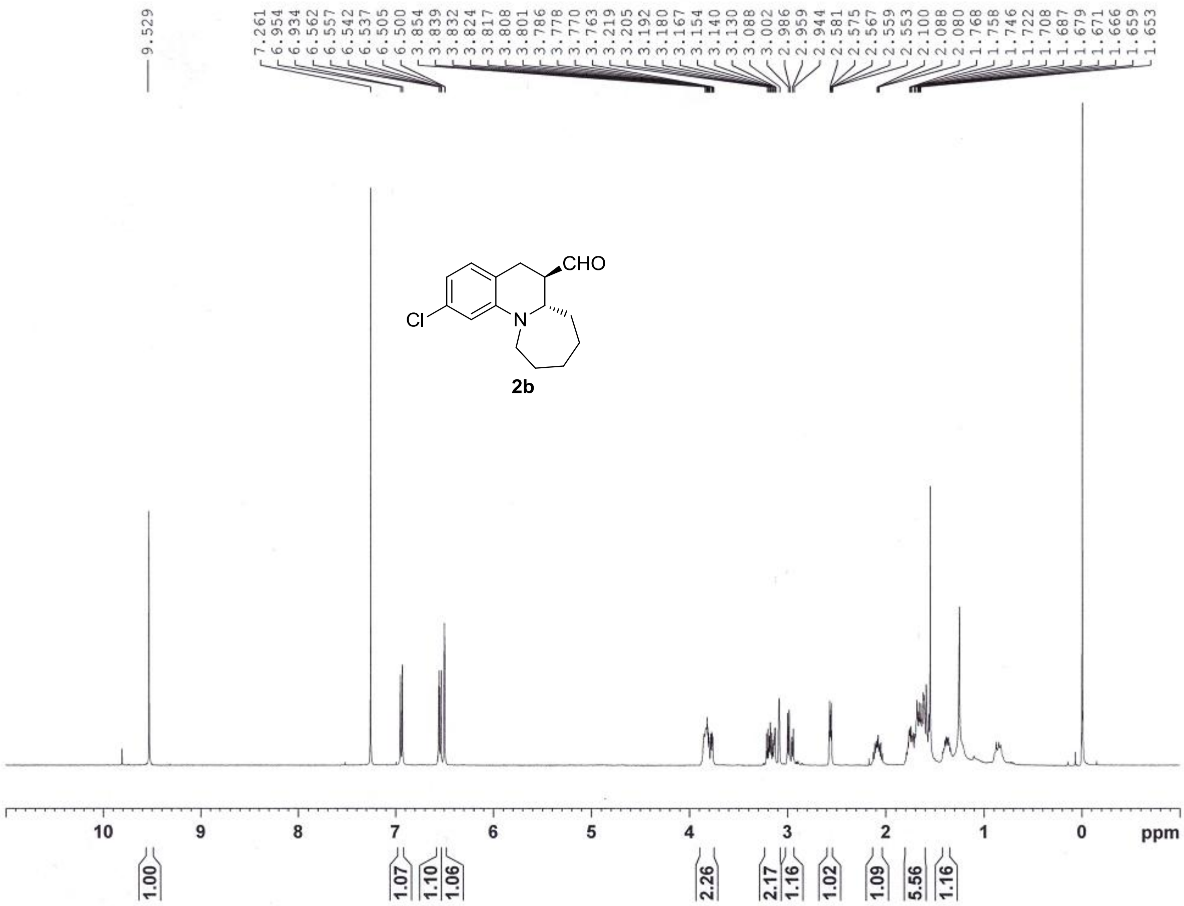
| 2 | 23.5167 | 448.7142 | FF | 39.0000 | 3.8805 |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6.934
6.562
6.557
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6.505
6.500
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3.824
3.817
3.808
3.801
3.786
3.778
3.770
3.763
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1.666
1.659
1.653
CHO
Cl
N
2b
10
9
8
7
6
5
4
3
2
1
0
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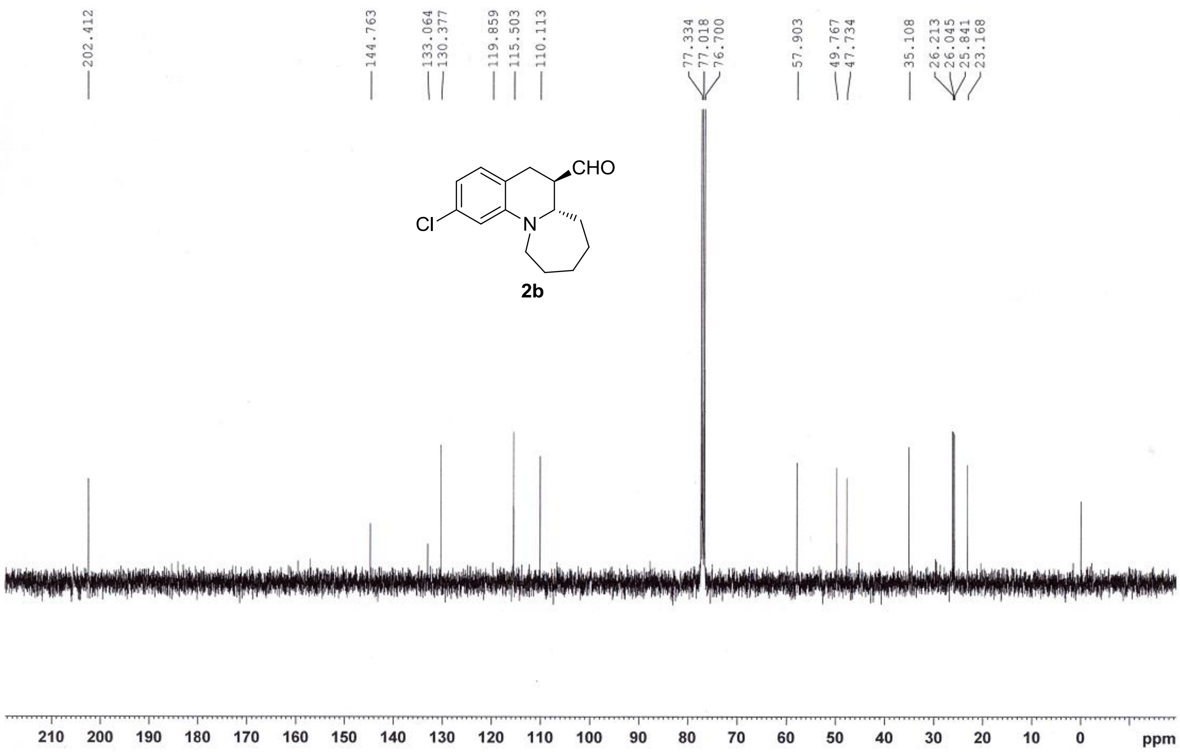
1.07
1.10
1.06
2.26
2.17
1.16
1.02
1.09
5.56
1.16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144.763
133.064
130.377
119.859
115.503
110.113
77.334
77.018
76.700
57.903
49.767
47.734
35.108
26.213
26.045
25.841
23.168
CHO
Cl
N
2b
210
200
190
180
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140
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120
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100
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80
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60
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20
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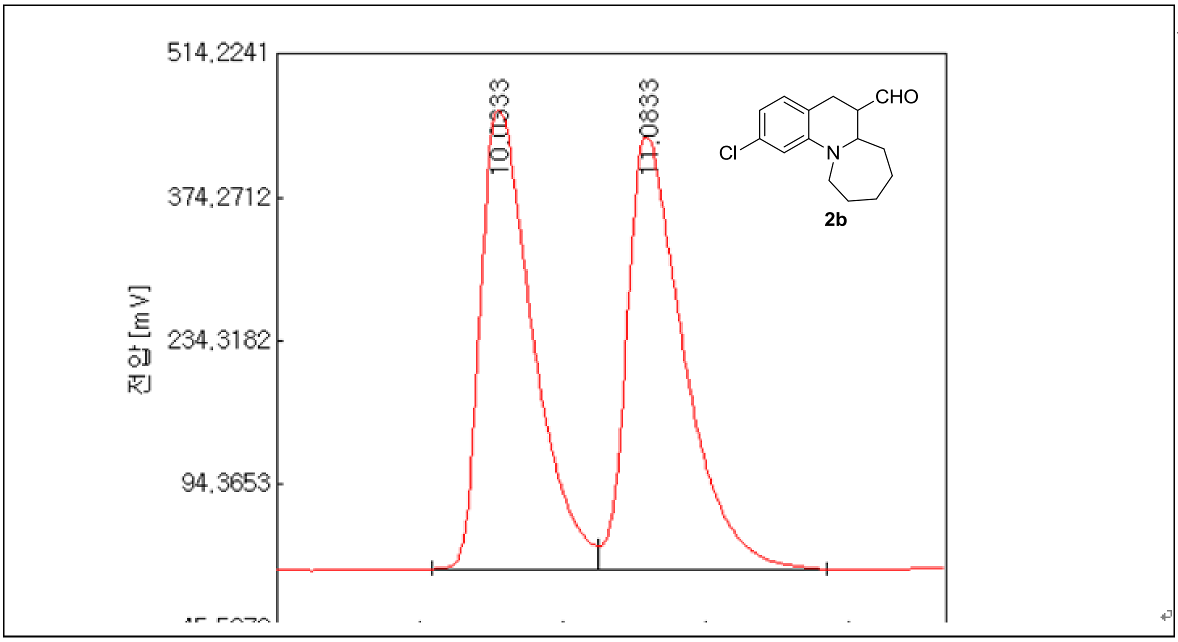
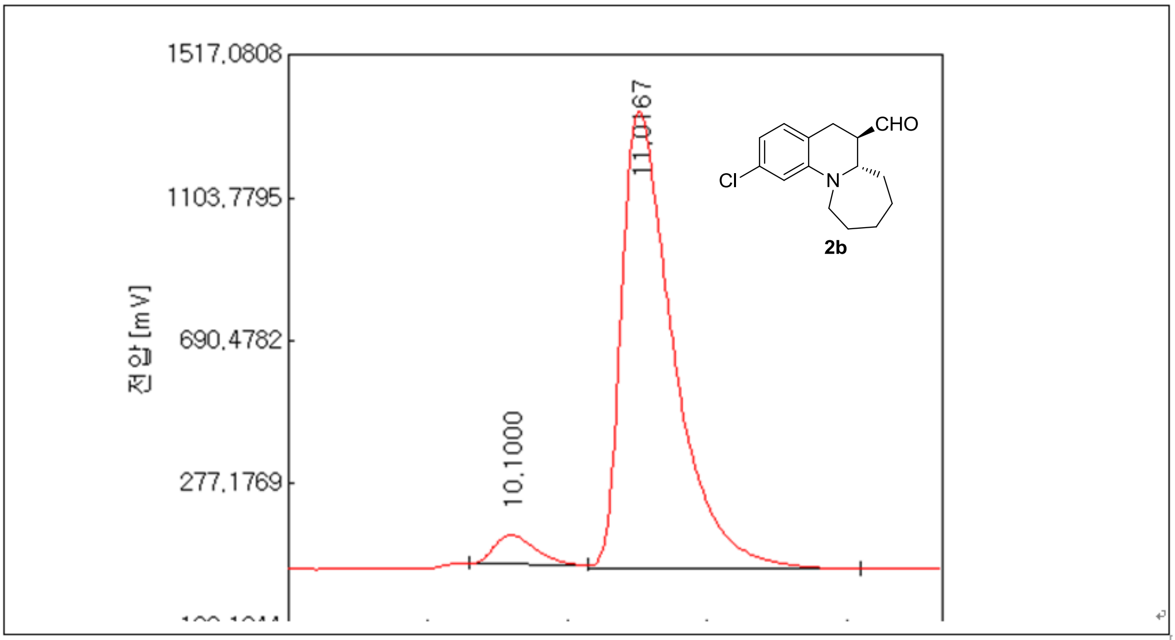
0
ppm




분석 결과

| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 10.0333 | 11828.1328 | BV | 70.0000 | 49.4871 |
| 2 | 11.0833 | 12073.3301 | VV | 96.0000 | 50.5129 |




분석 결과

| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
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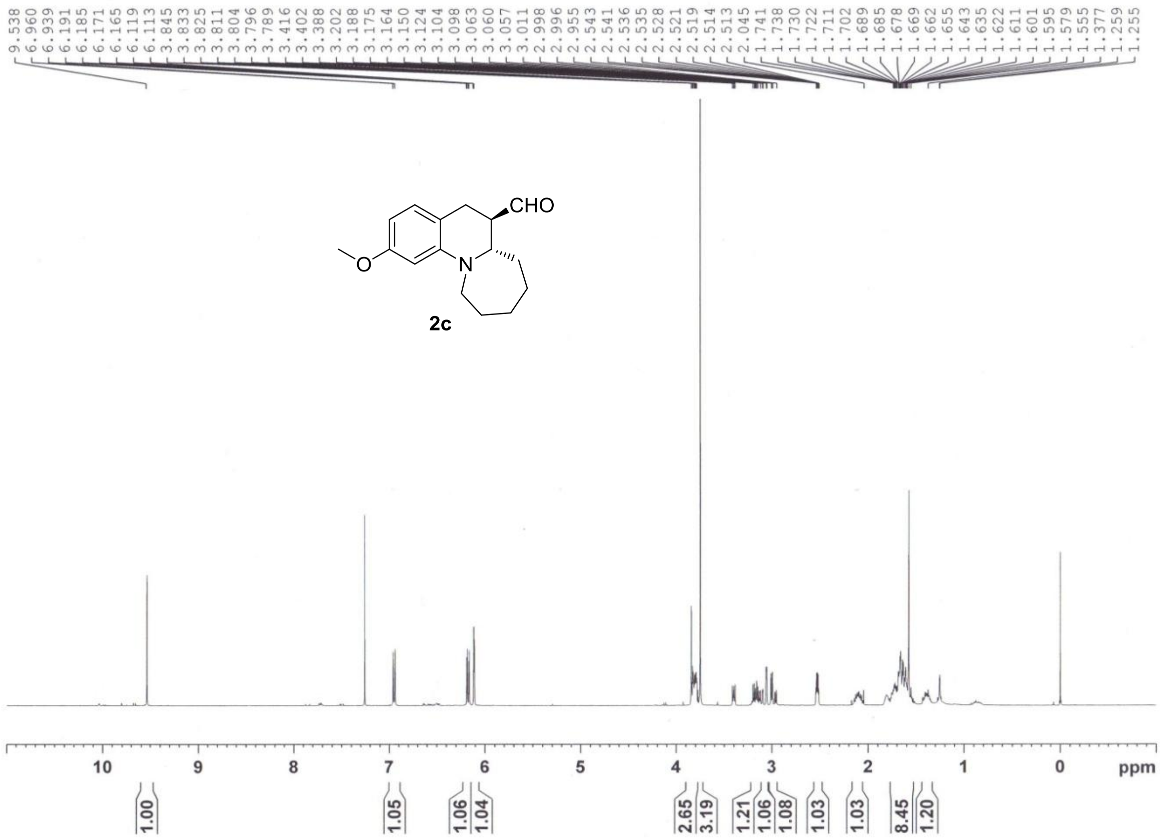
| 2 | 11.0167 | 35411.9142 | BB | 117.0000 | 95.1639 |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9
8
7
6
5
4
3
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1.00
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1.08
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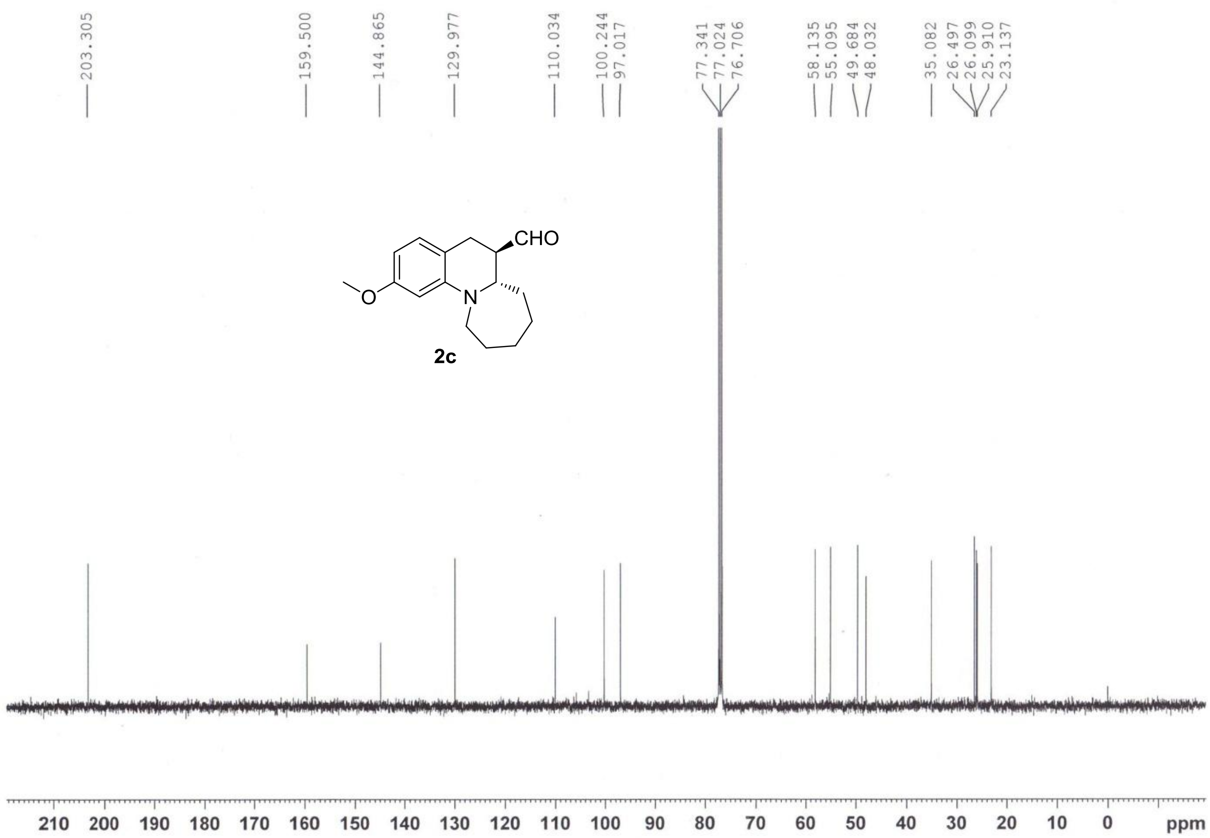
8.45
1.20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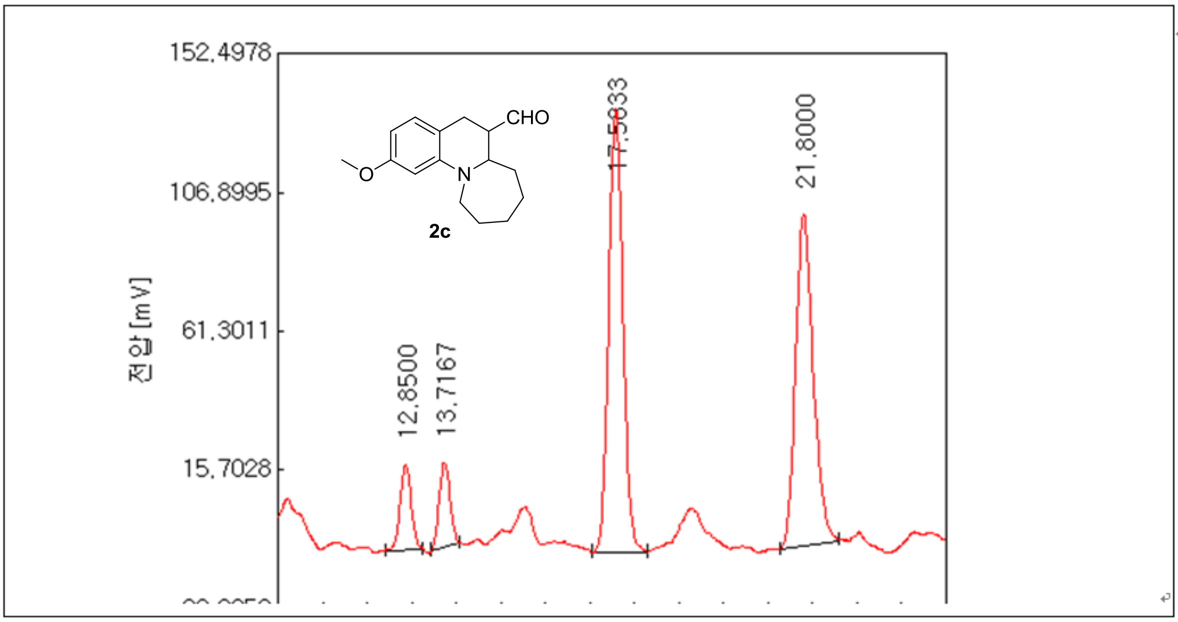
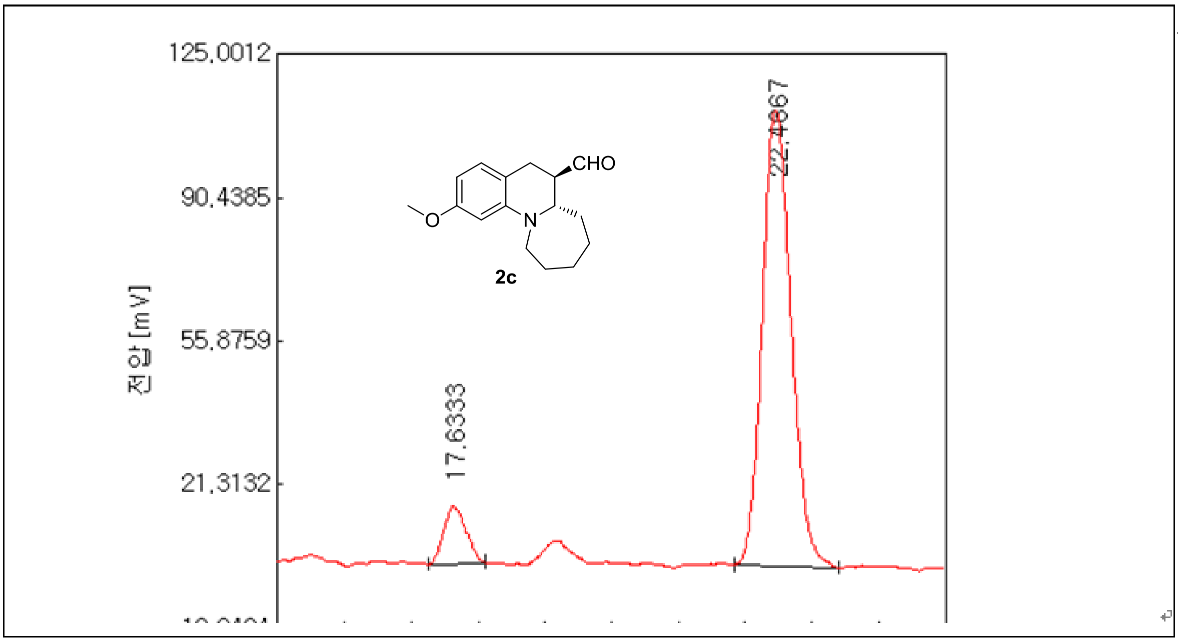
144.865
129.977
110.034
100.244
97.017
77.341
77.024
76.706
58.135
55.095
49.684
48.032
35.082
26.497
26.099
25.910
23.137
CHO
O
N
2c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



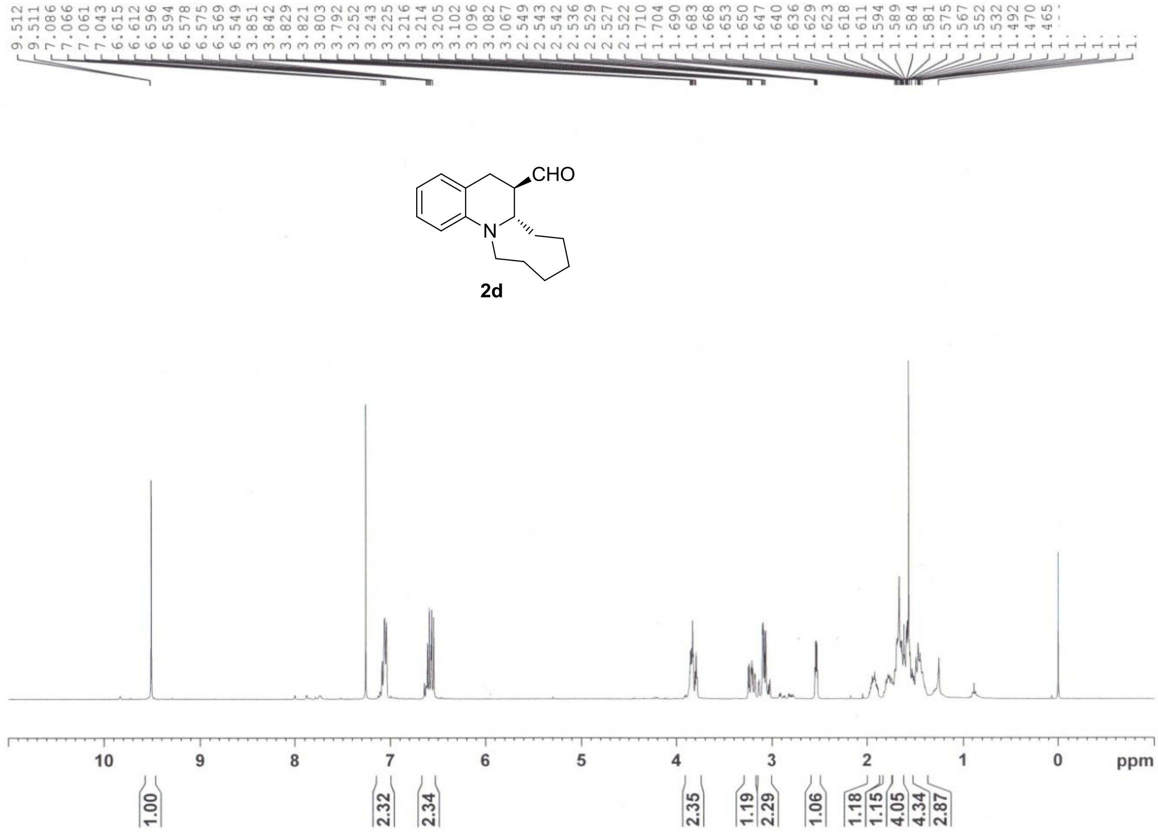

분석 결과

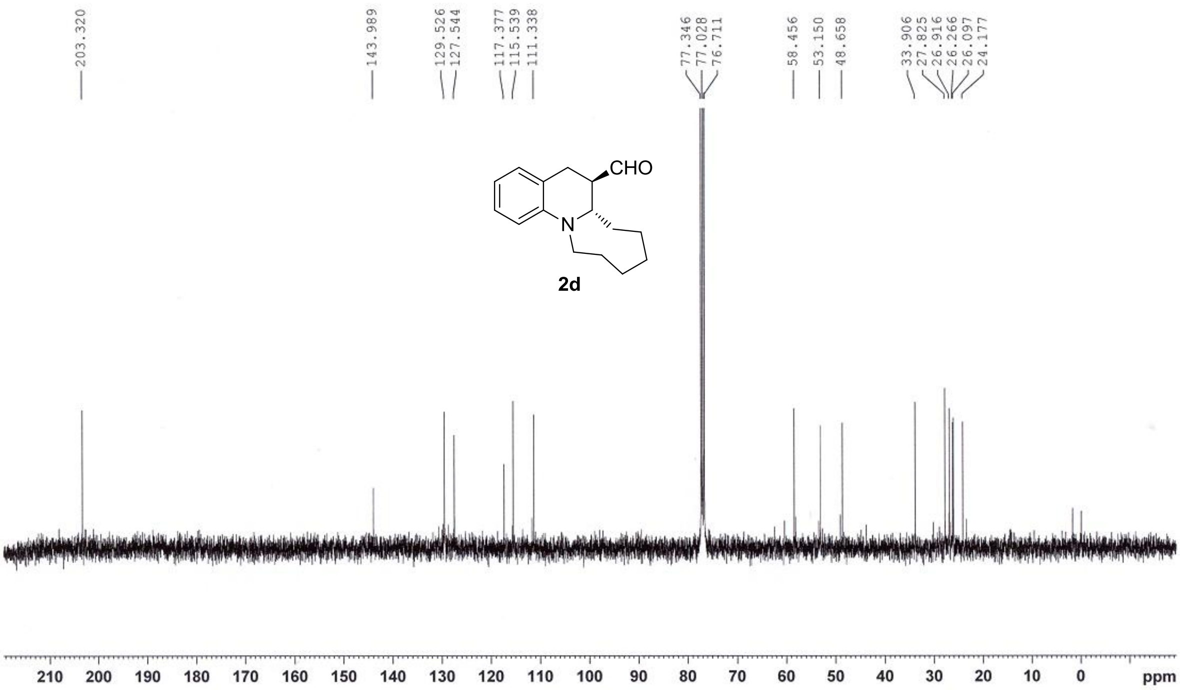
| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 12.8500 | 506.5475 | FF | 51.0000 | 6.7606 |
| 2 | 13.7167 | 489.8605 | FF | 38.0000 | 6.5379 |
| 3 | 17.5833 | 3350.4979 | BP | 74.0000 | 44.7169 |
| 4 | 21.8000 | 3145.7770 | BV | 79.0000 | 41.9847 |

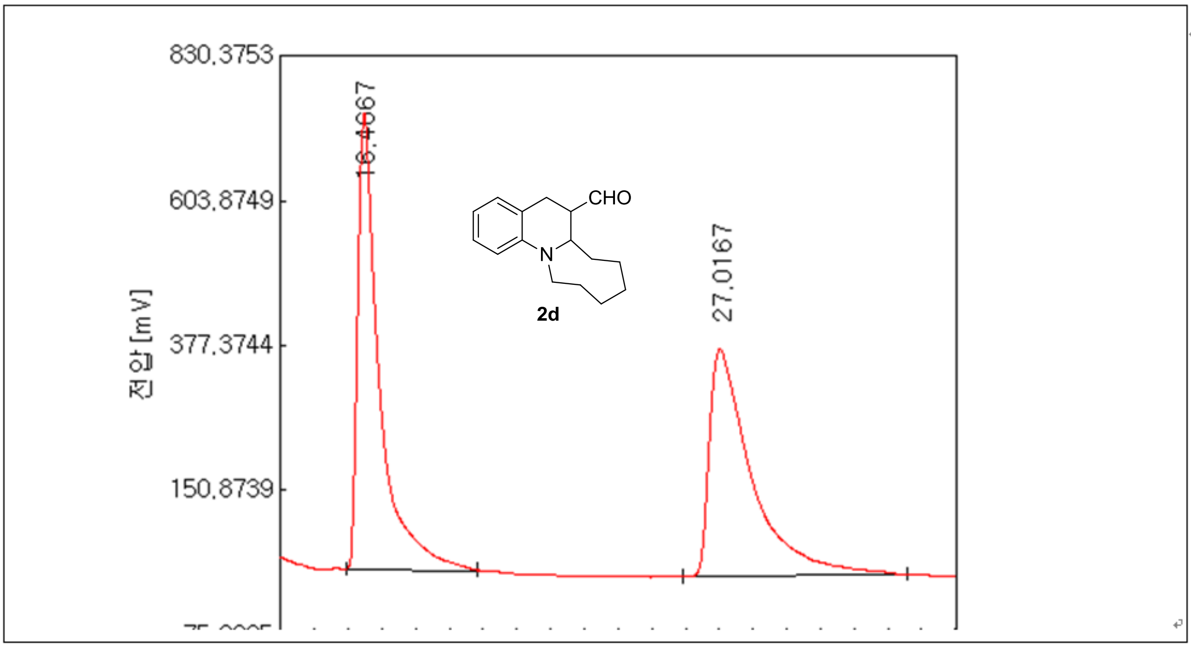



분석 결과

| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 17.6333 | 337.2080 | BV | 52.0000 | 8.9995 |
| 2 | 22.4667 | 3409.7427 | BB | 94.0000 | 91.0005 |

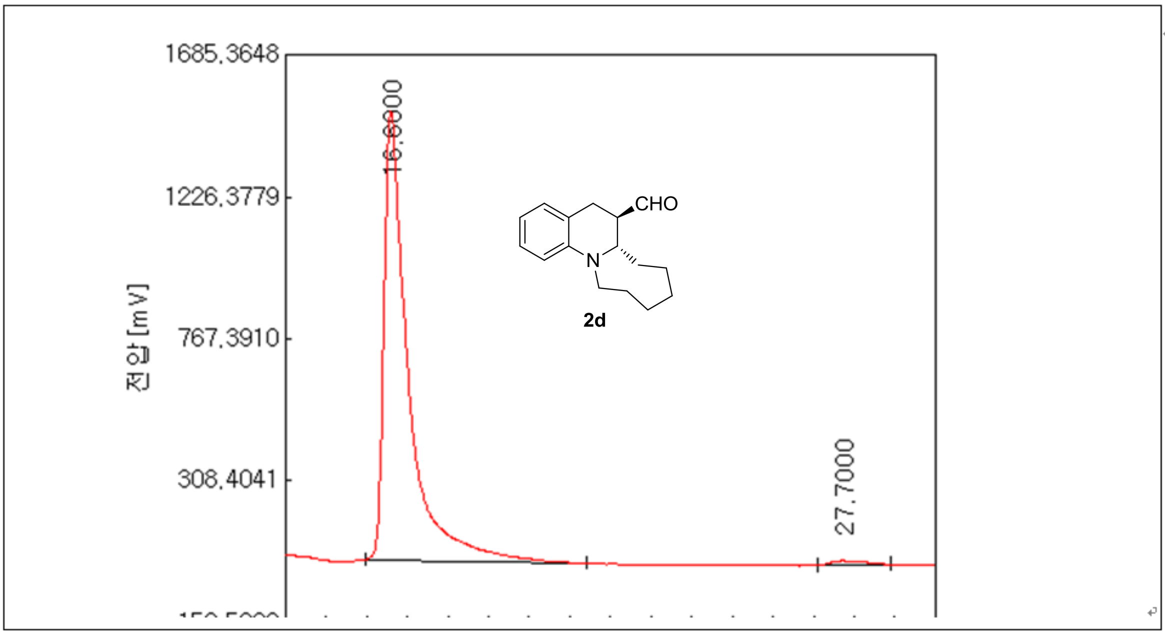

9.512
9.511
7.086
7.066
7.061
7.043
6.615
6.612
6.596
6.594
6.578
6.575
6.569
6.549
3.851
3.842
3.829
3.821
3.803
3.792
3.252
3.243
3.225
3.216
3.214
3.205
3.102
3.096
3.082
3.067
2.549
2.543
2.542
2.536
2.529
2.527
2.522
1.710
1.704
1.690
1.683
1.668
1.653
1.650
1.647
1.640
1.636
1.629
1.623
1.618
1.611
1.594
1.589
1.584
1.581
1.575
1.567
1.552
1.532
1.492
1.470
1.465
CHO
N
2d
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.32
2.34
2.35
1.19
2.29
1.06
1.18
1.15
4.05
4.34
2.87


203.320
143.989
129.526
127.544
117.377
115.539
111.338
77.346
77.028
76.711
58.456
53.150
48.658
33.906
27.825
26.916
26.266
26.097
24.177
CHO
N
2d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



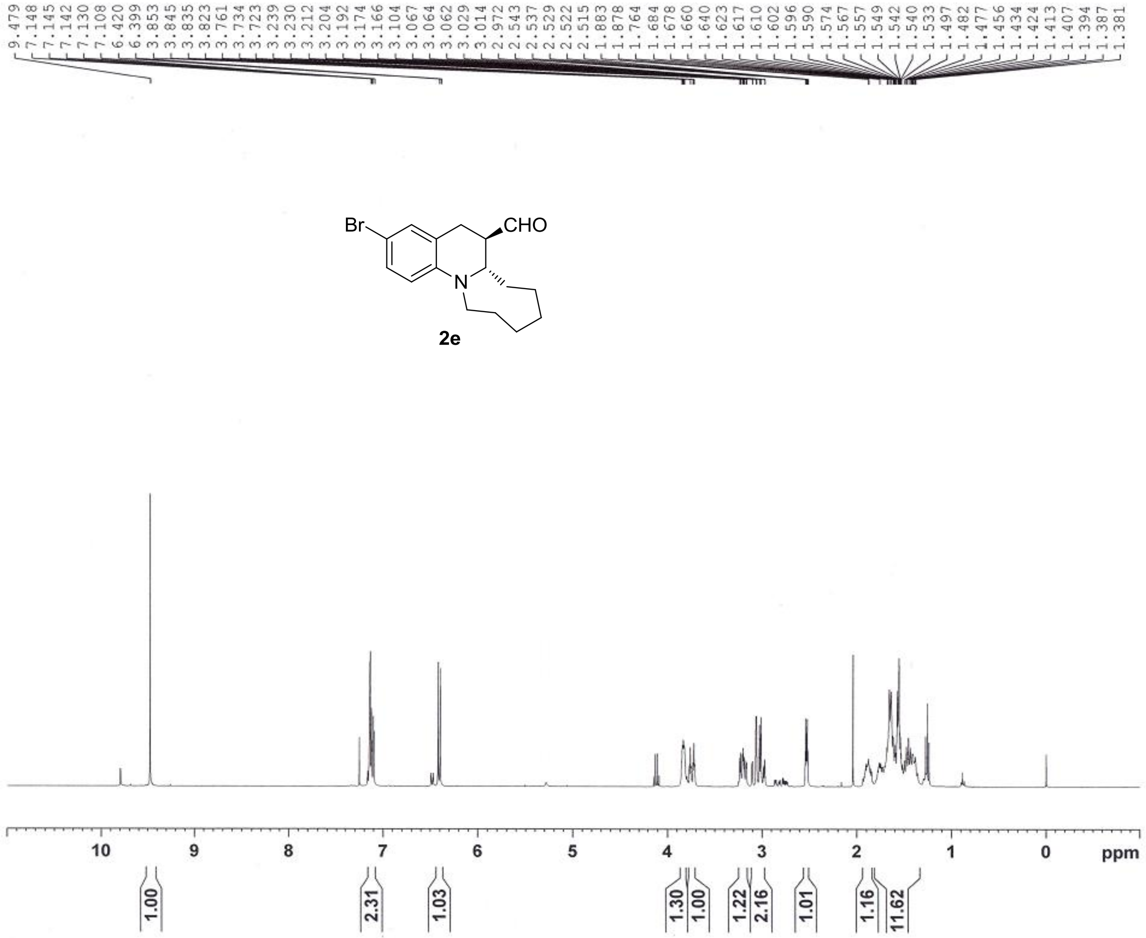

분석 결과

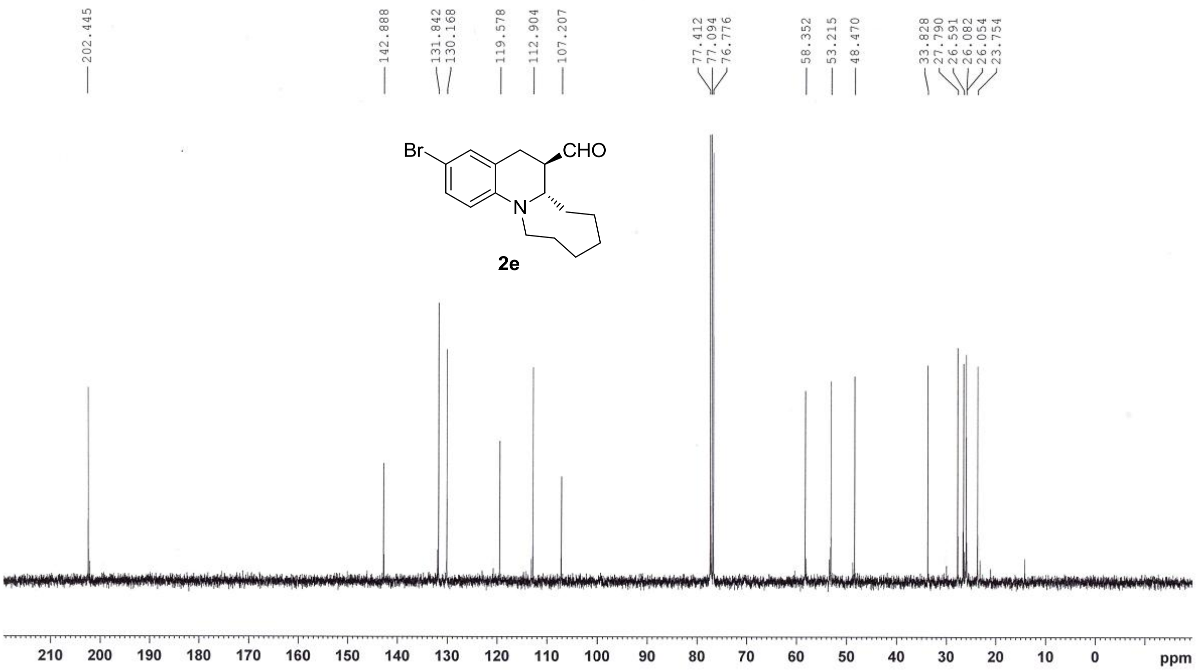
| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 16.4667 | 33022.6145 | BB | 234.0000 | 50.5595 |
| 2 | 27.0167 | 32291.6838 | FF | 397.0000 | 49.4405 |

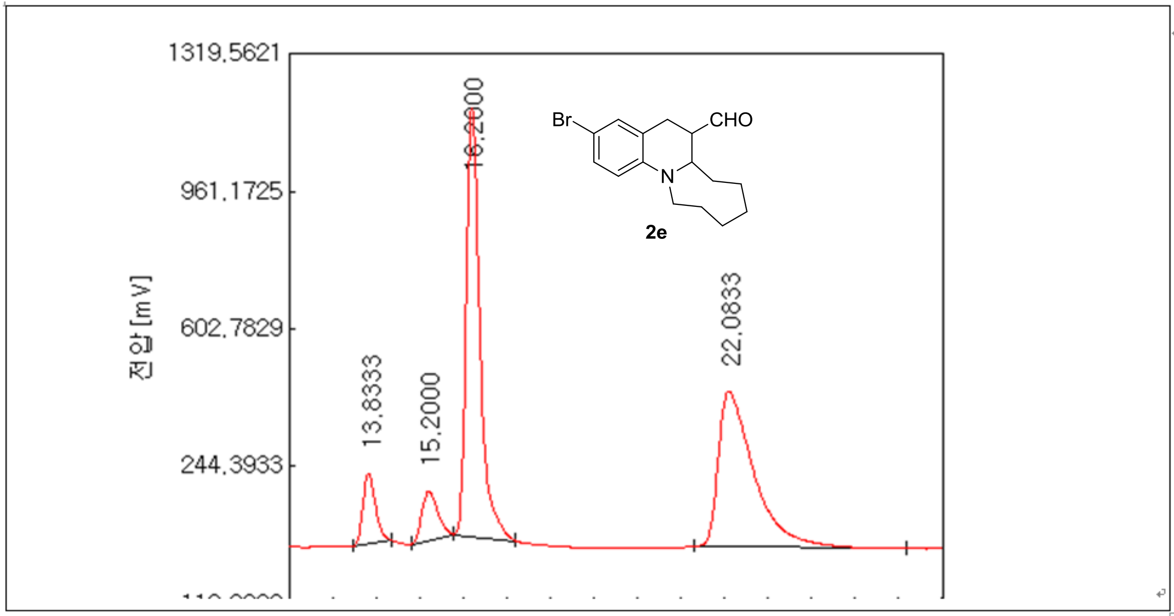



분석 결과

| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 16.6000 | 62643.3399 | FF | 327.0000 | 98.6958 |
| 2 | 27.7000 | 827.7694 | FF | 108.0000 | 1.3042 |

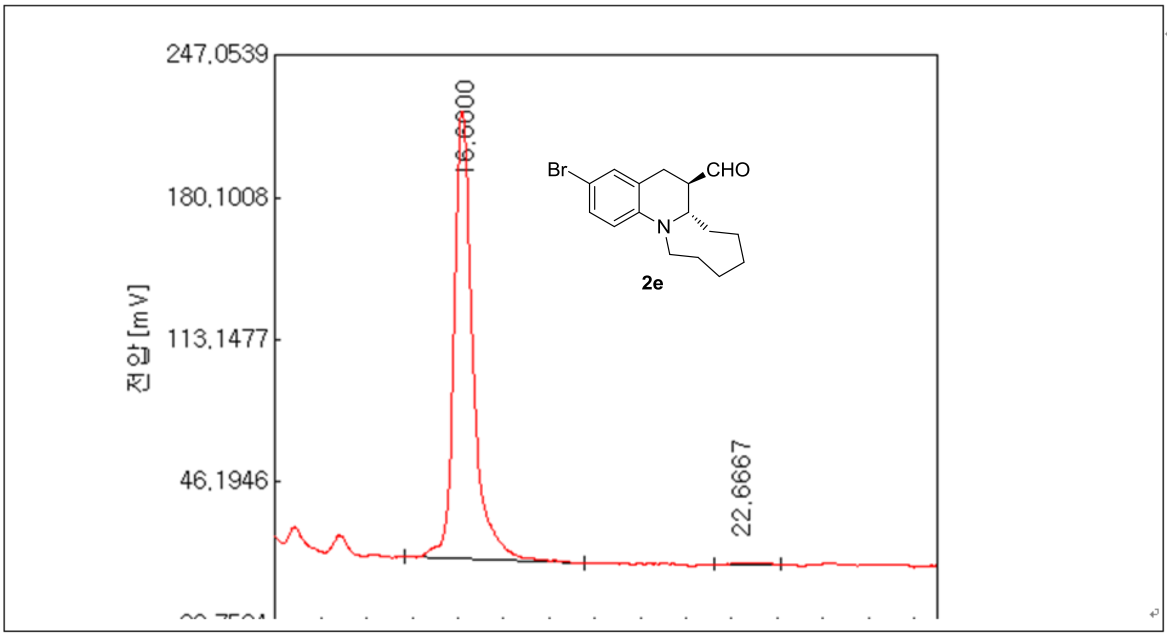

9.479
7.148
7.145
7.142
7.130
7.108
6.420
6.399
3.853
3.845
3.835
3.823
3.761
3.734
3.723
3.239
3.230
3.212
3.204
3.192
3.174
3.166
3.104
3.067
3.064
3.062
3.029
3.014
2.972
2.543
2.537
2.529
2.522
2.515
1.883
1.878
1.764
1.684
1.678
1.660
1.640
1.623
1.617
1.610
1.602
1.596
1.590
1.574
1.567
1.557
1.549
1.542
1.540
1.533
1.497
1.482
1.477
1.456
1.434
1.424
1.413
1.407
1.394
1.387
1.381
Br
CHO
N
2e
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
2.31
1.03
1.30
1.00
1.22
2.16
1.01
1.16
11.62


202.445
142.888
131.842
130.168
119.578
112.904
107.207
77.412
77.094
76.776
58.352
53.215
48.470
33.828
27.790
26.591
26.082
26.054
23.754
Br
CHO
N
2e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



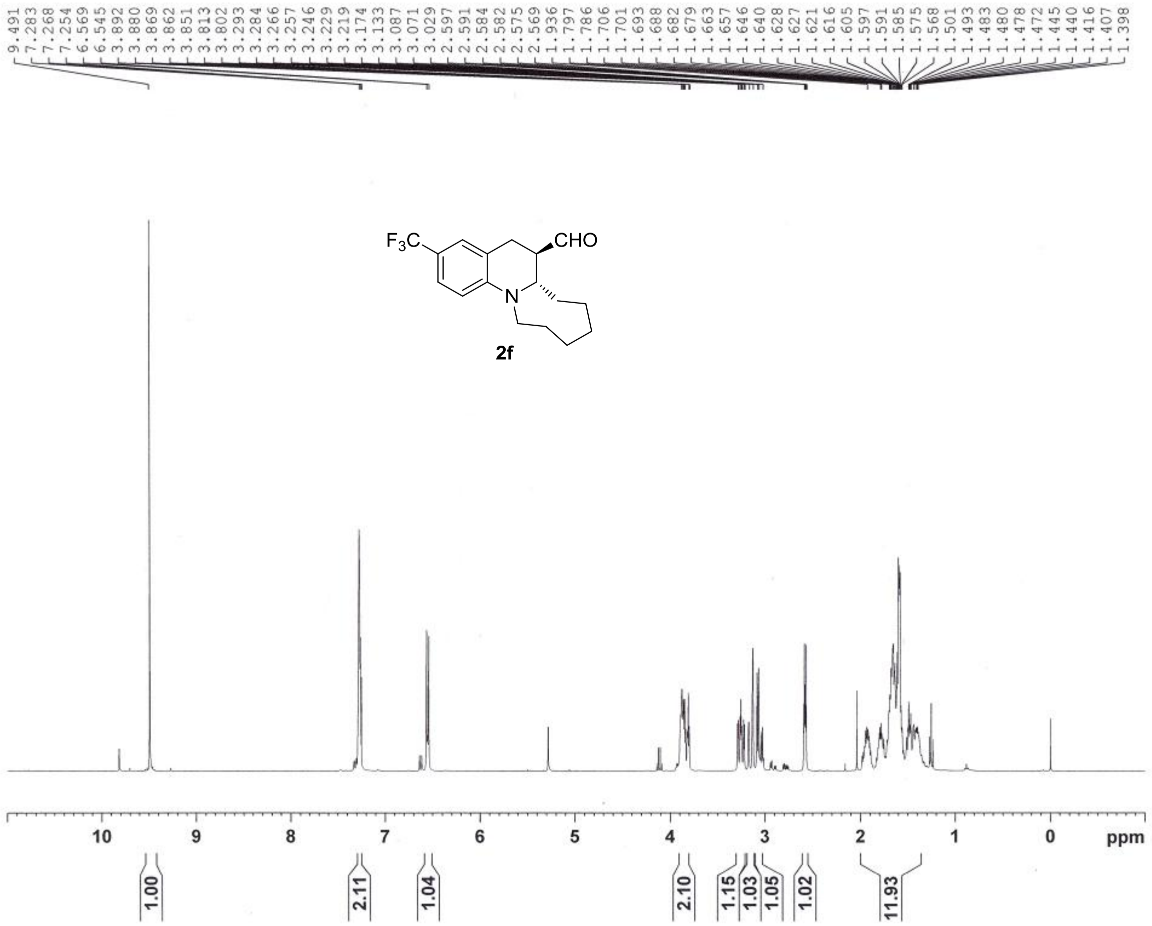

분석 결과

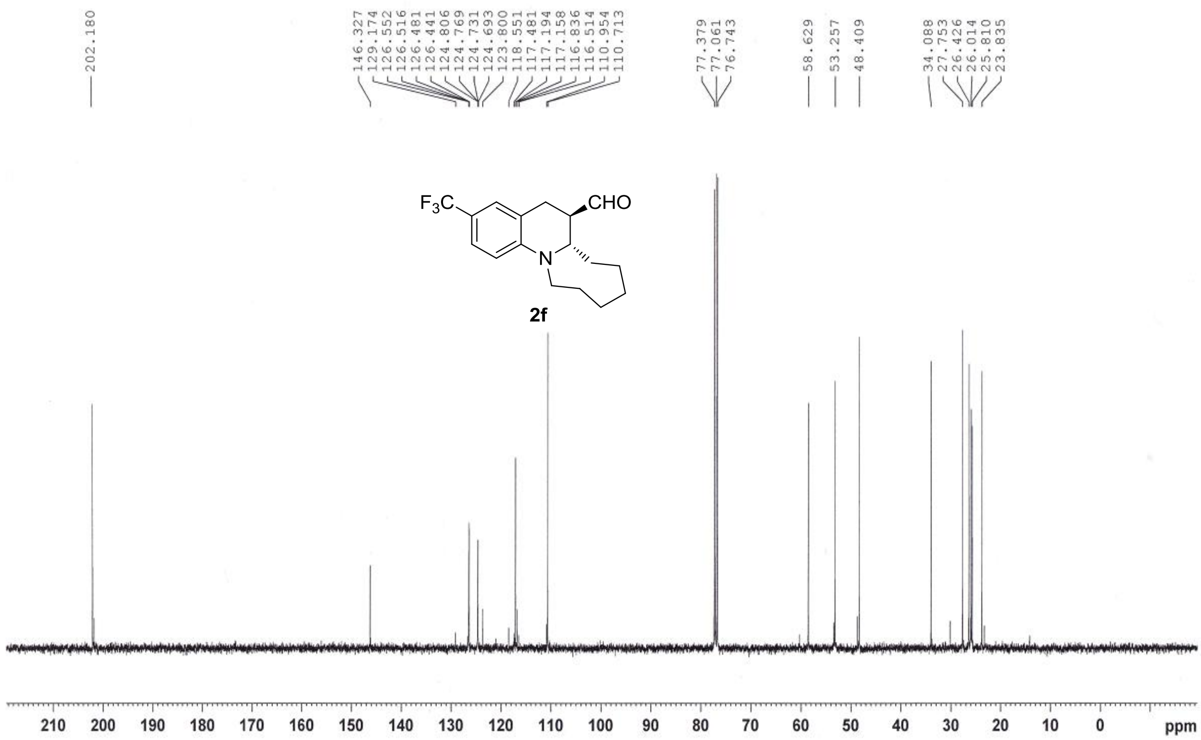
| 번호 | RT[분] | 면적 [mV*s] | 형태 | 폭 [초] | 면적% |
|---|---|---|---|---|---|
| 1 | 13.8333 | 3805.0891 | BB | 53.0000 | 6.7656 |
| 2 | 15.2000 | 3325.1969 | BB | 58.0000 | 5.9123 |
| 3 | 16.2000 | 25229.7620 | BB | 85.0000 | 44.8595 |
| 4 | 22.0833 | 23881.7241 | FF | 292.0000 | 42.4626 |

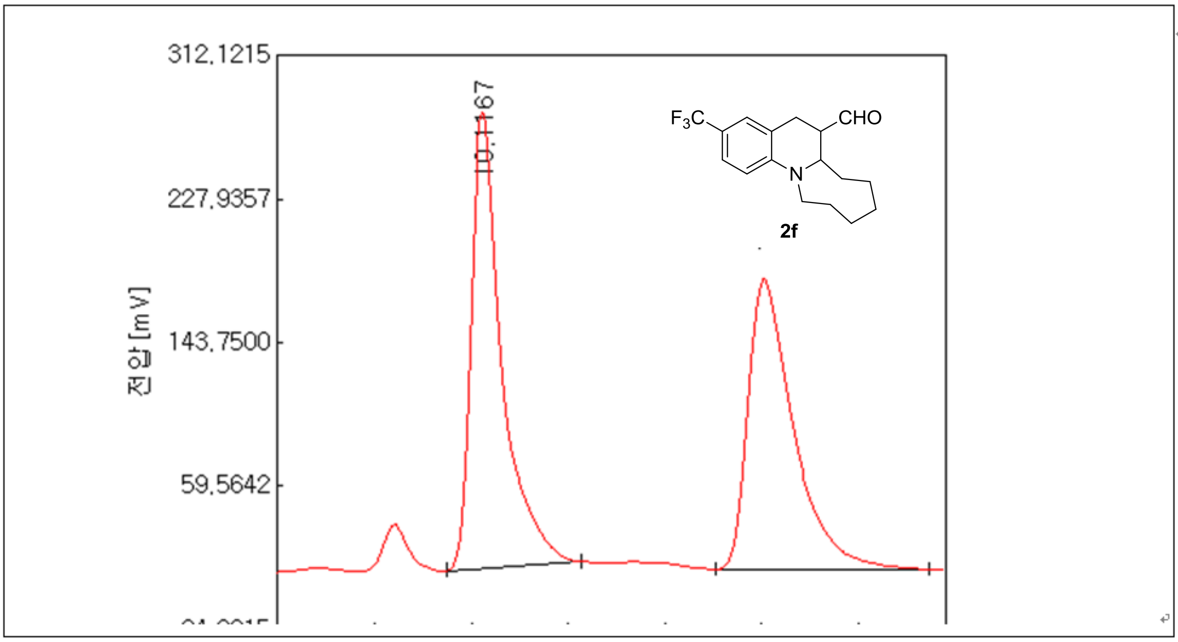



분석 결과

| 번호 | RT[분] | 면적 [mV*s] | 형태 | 폭 [초] | 면적% |
|---|---|---|---|---|---|
| 1 | 16.6000 | 6389.8638 | FF | 237.0000 | 99.4916 |
| 2 | 22.6667 | 32.6539 | FF | 87.0000 | 0.5084 |

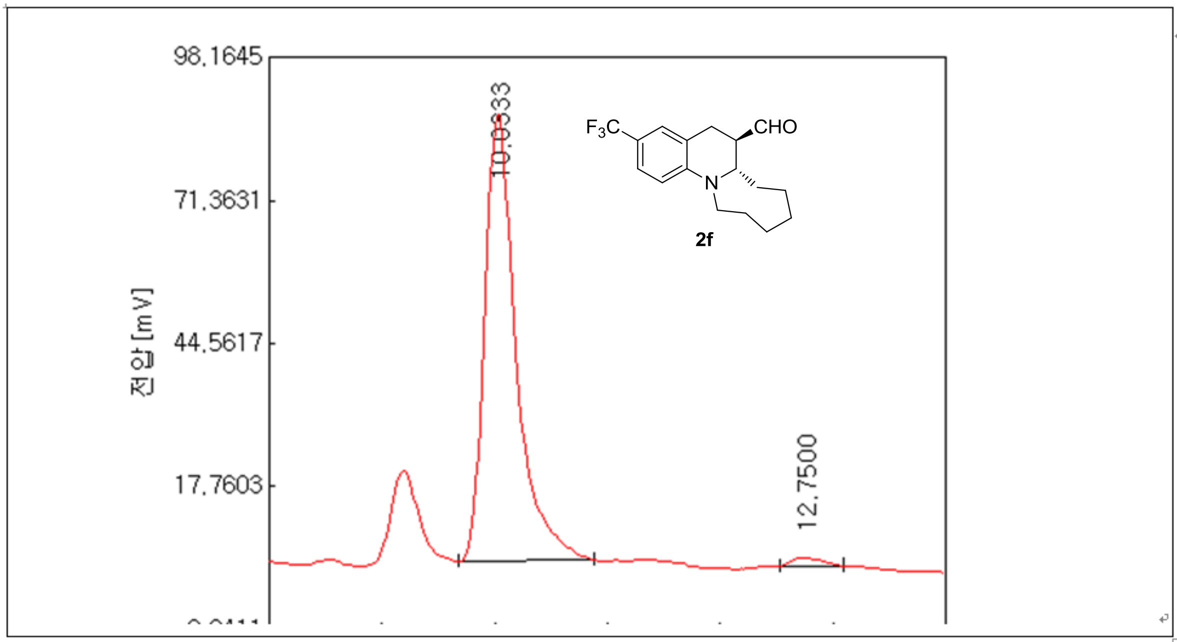

F3C
CHO
N
2f
ppm


F3C
CHO
N
2f
ppm



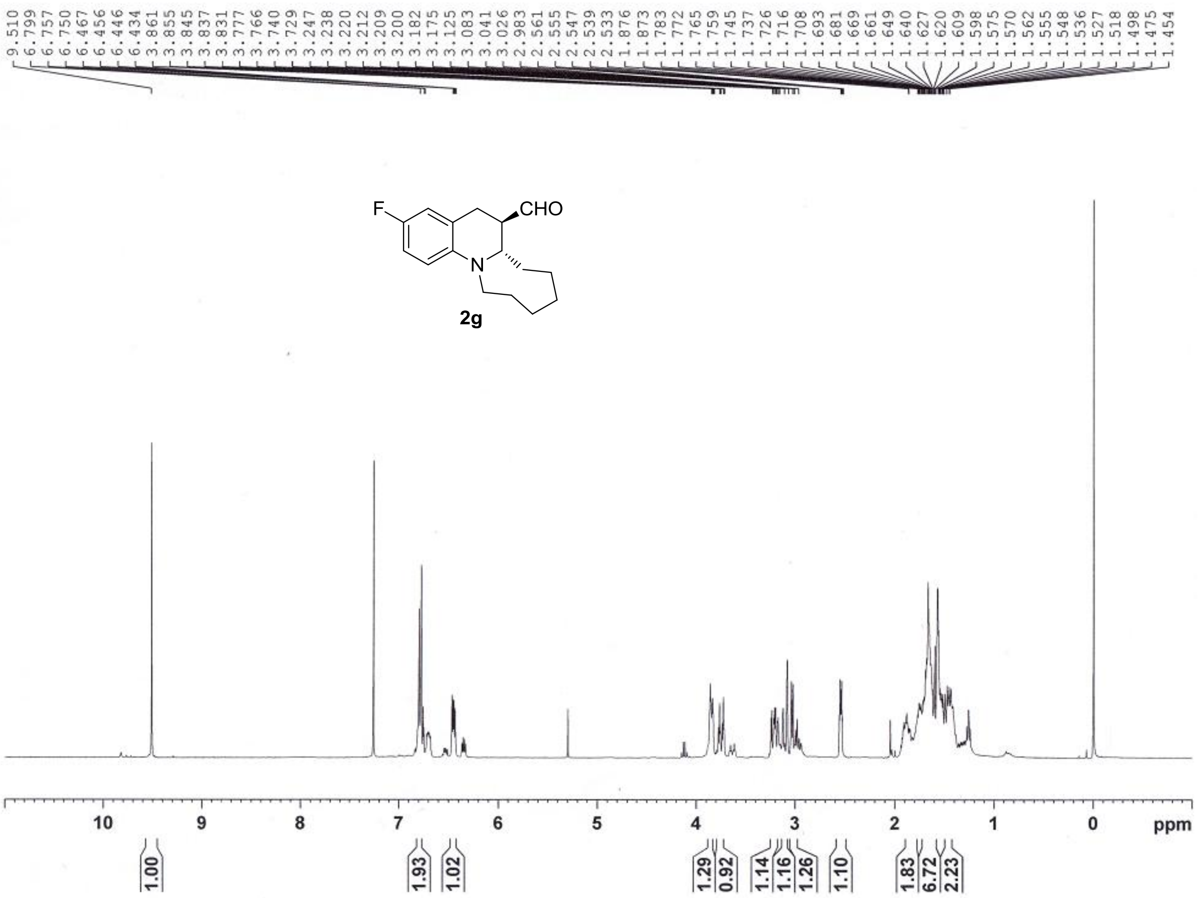

분석 결과

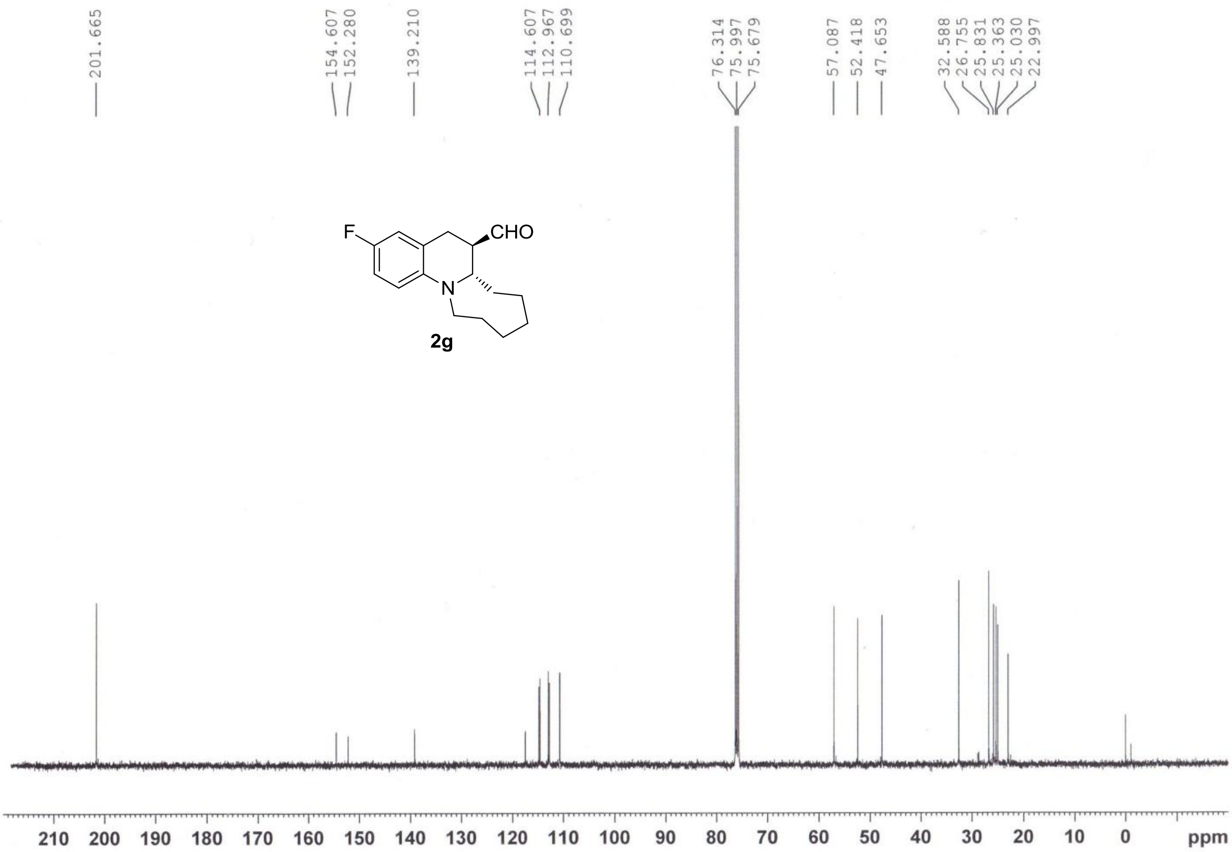
| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 10.1167 | 6125.9363 | BB | 83.0000 | 51.4649 |
| 2 | 13.0167 | 5777.2055 | FF | 133.0000 | 48.5351 |

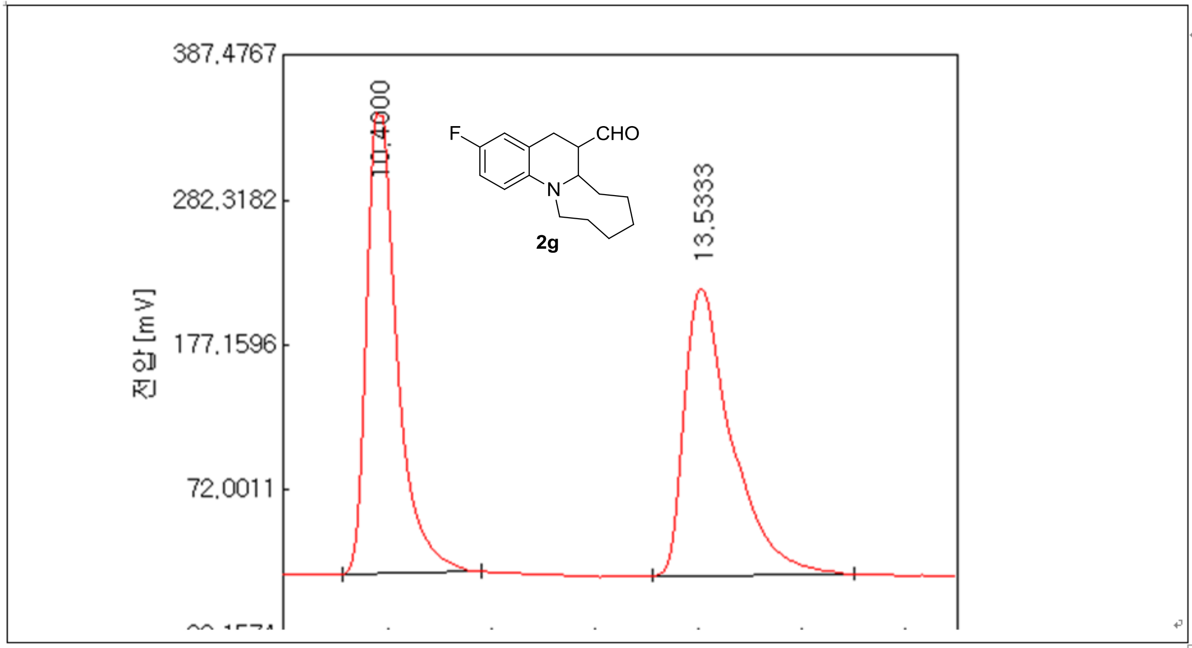



분석 결과

| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 10.0333 | 1688.9008 | BB | 72.0000 | 98.2012 |
| 2 | 12.7500 | 30.9373 | FF | 34.0000 | 1.7988 |

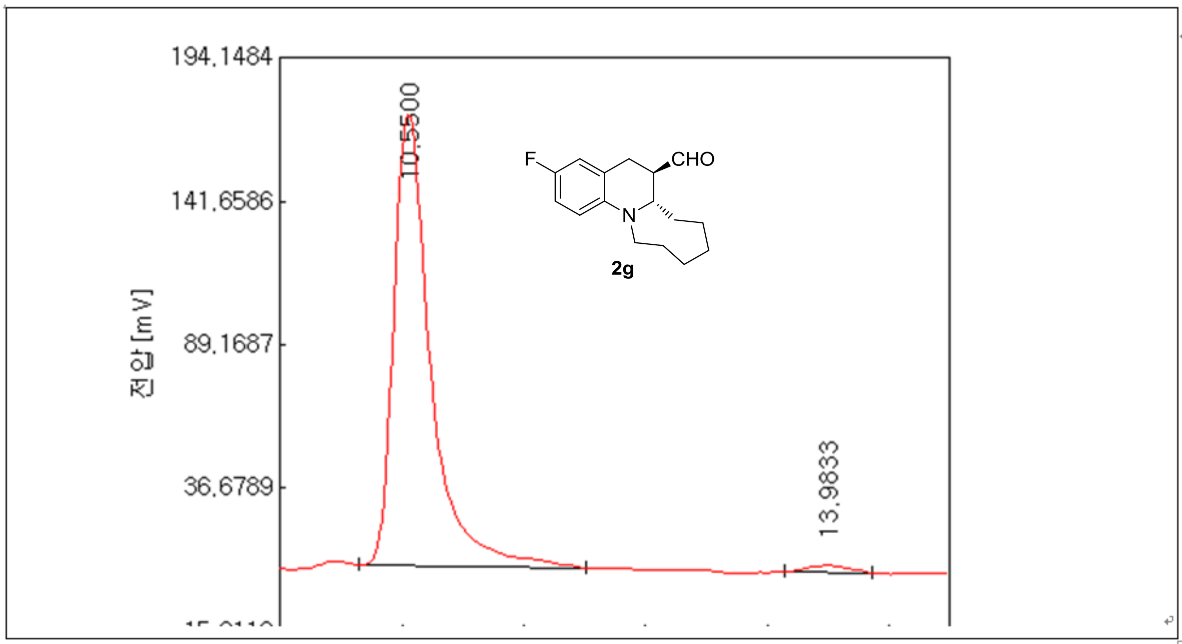

9.510
6.799
6.757
6.750
6.467
6.456
6.446
6.434
3.861
3.855
3.845
3.837
3.831
3.777
3.766
3.740
3.729
3.247
3.238
3.220
3.212
3.209
3.200
3.182
3.175
3.125
3.083
3.041
3.026
2.983
2.561
2.555
2.547
2.539
2.533
1.876
1.873
1.783
1.772
1.765
1.759
1.745
1.737
1.726
1.716
1.708
1.693
1.681
1.669
1.661
1.649
1.640
1.627
1.620
1.609
1.598
1.575
1.570
1.562
1.555
1.548
1.536
1.527
1.518
1.498
1.475
1.454
F
CHO
N
2g
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.93
1.02
1.29
0.92
1.14
1.16
1.26
1.10
1.83
6.72
2.23


201.665
154.607
152.280
139.210
114.607
112.967
110.699
76.314
75.997
75.679
57.087
52.418
47.653
32.588
26.755
25.831
25.363
25.030
22.997
F
CHO
N
2g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



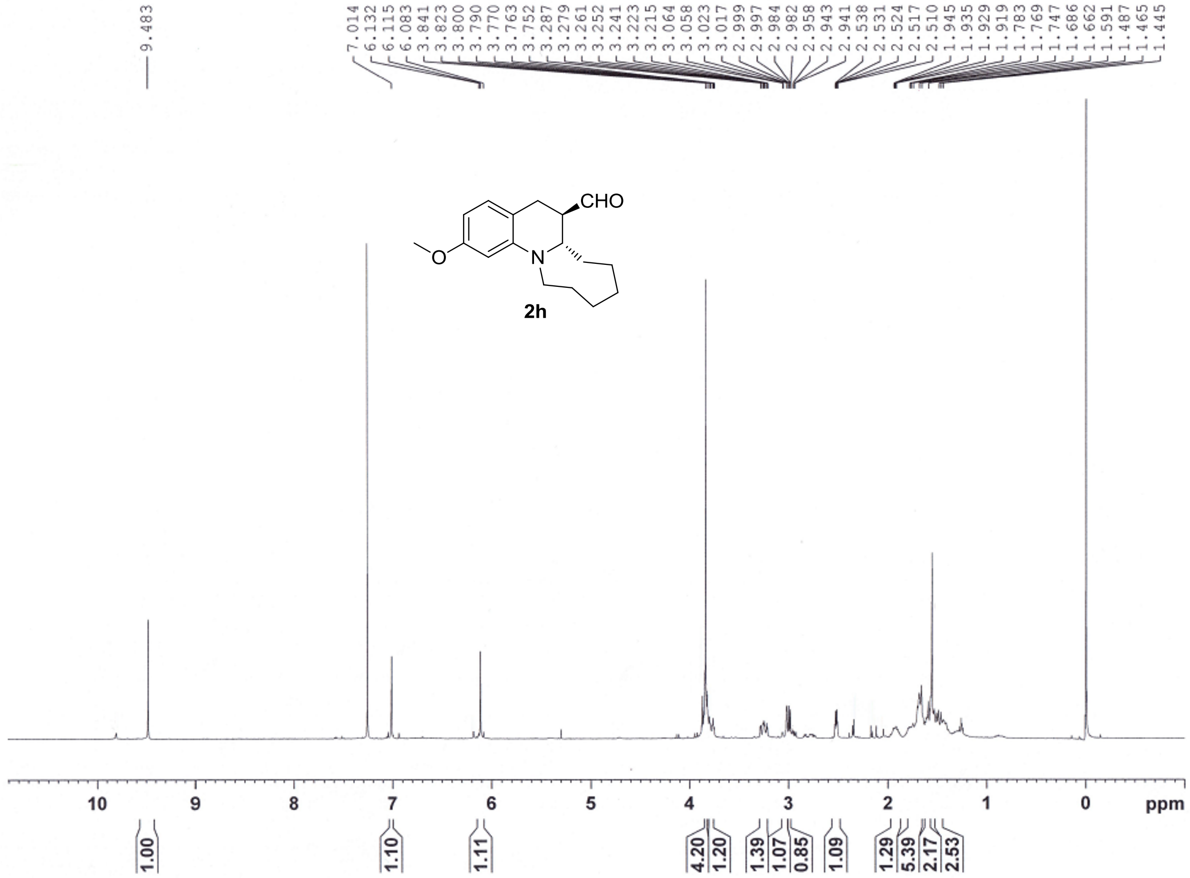

분석 결과

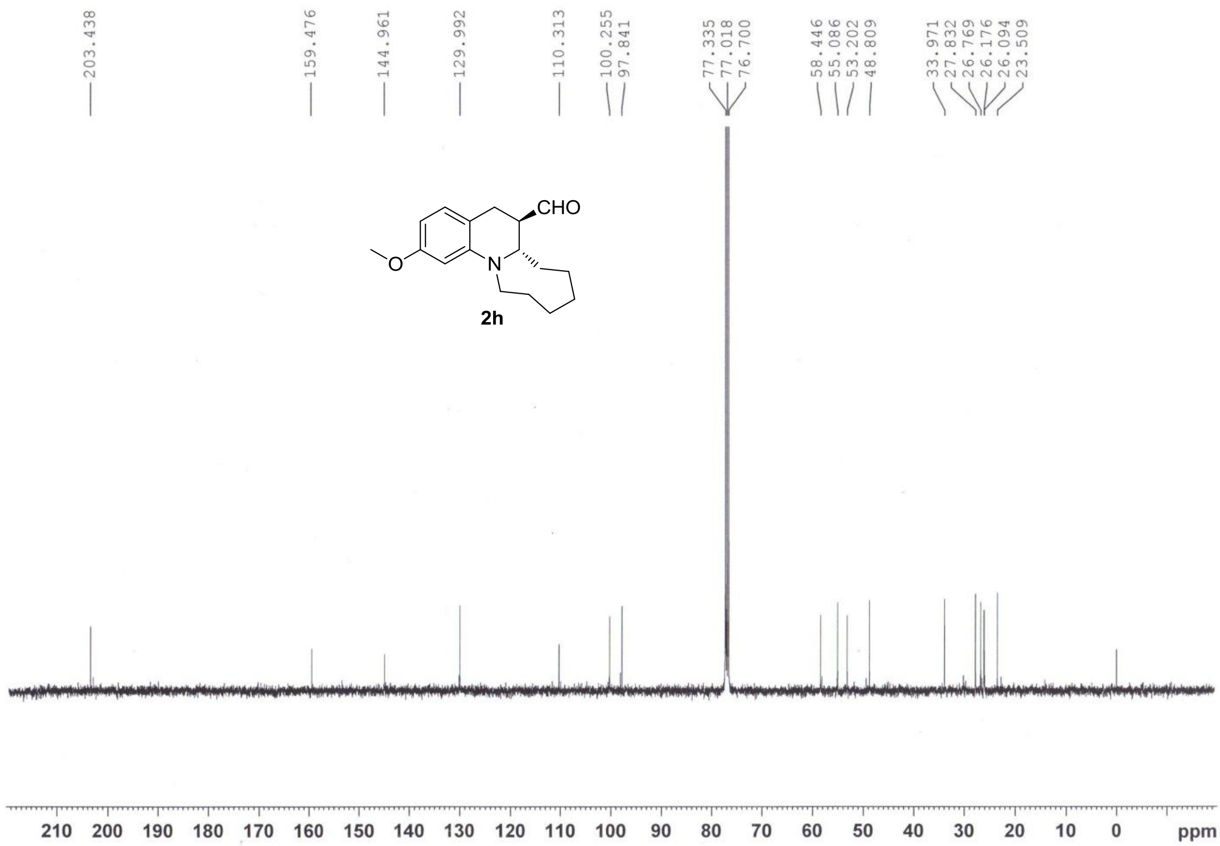
| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 10.4000 | 6958.4383 | BB | 80.0000 | 50.2231 |
| 2 | 13.5333 | 6896.6210 | BB | 117.0000 | 49.7769 |

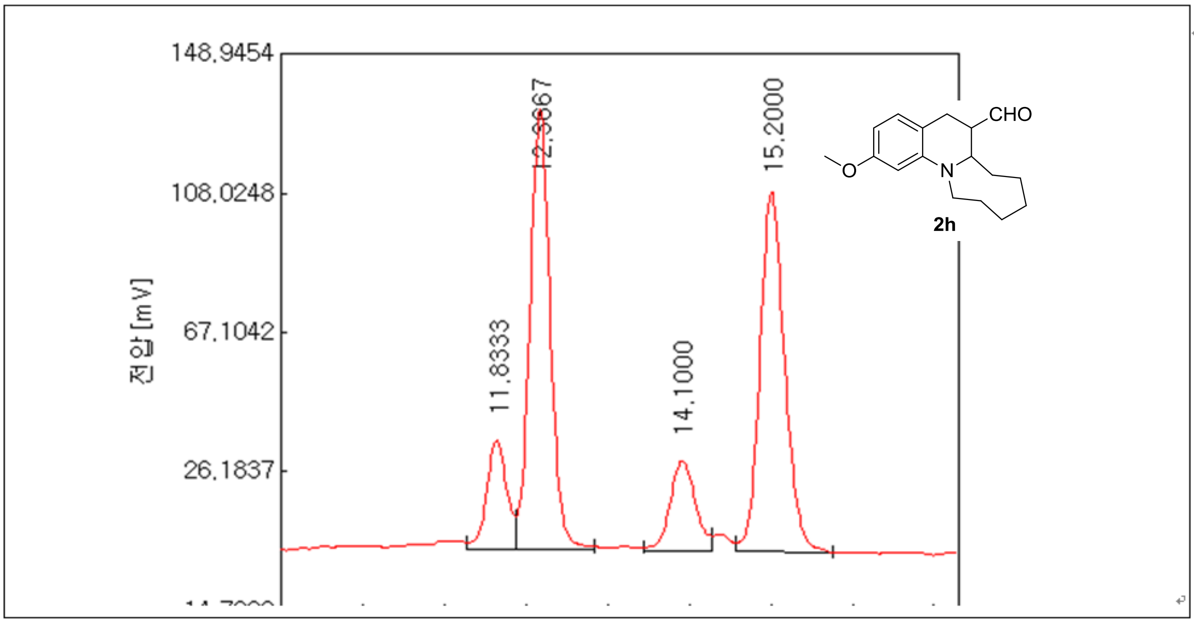



분석 결과

| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 10.5500 | 3615.2193 | FF | 112.0000 | 98.2663 |
| 2 | 13.9833 | 63.7819 | FF | 43.0000 | 1.7337 |

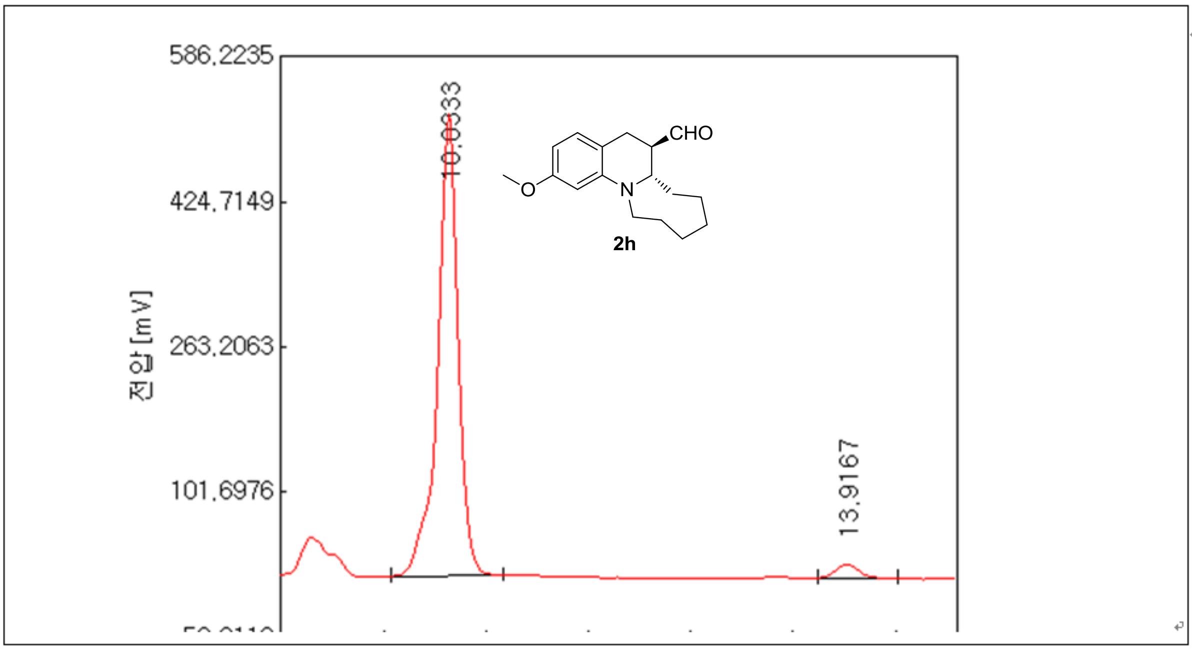

9.483
7.014
6.132
6.115
6.083
3.841
3.823
3.800
3.790
3.770
3.763
3.752
3.287
3.279
3.261
3.252
3.241
3.223
3.215
3.064
3.058
3.023
3.017
2.999
2.997
2.984
2.982
2.958
2.943
2.941
2.538
2.531
2.524
2.517
2.510
1.945
1.935
1.929
1.919
1.783
1.769
1.747
1.686
1.662
1.591
1.487
1.465
1.445
CHO
O
N
2h
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.10
1.11
4.20
1.20
1.39
1.07
0.85
1.09
1.29
5.39
2.17
2.53


203.438
159.476
144.961
129.992
110.313
100.255
97.841
77.335
77.018
76.700
58.446
55.086
53.202
48.809
33.971
27.832
26.769
26.176
26.094
23.509
CHO
O
N
2h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



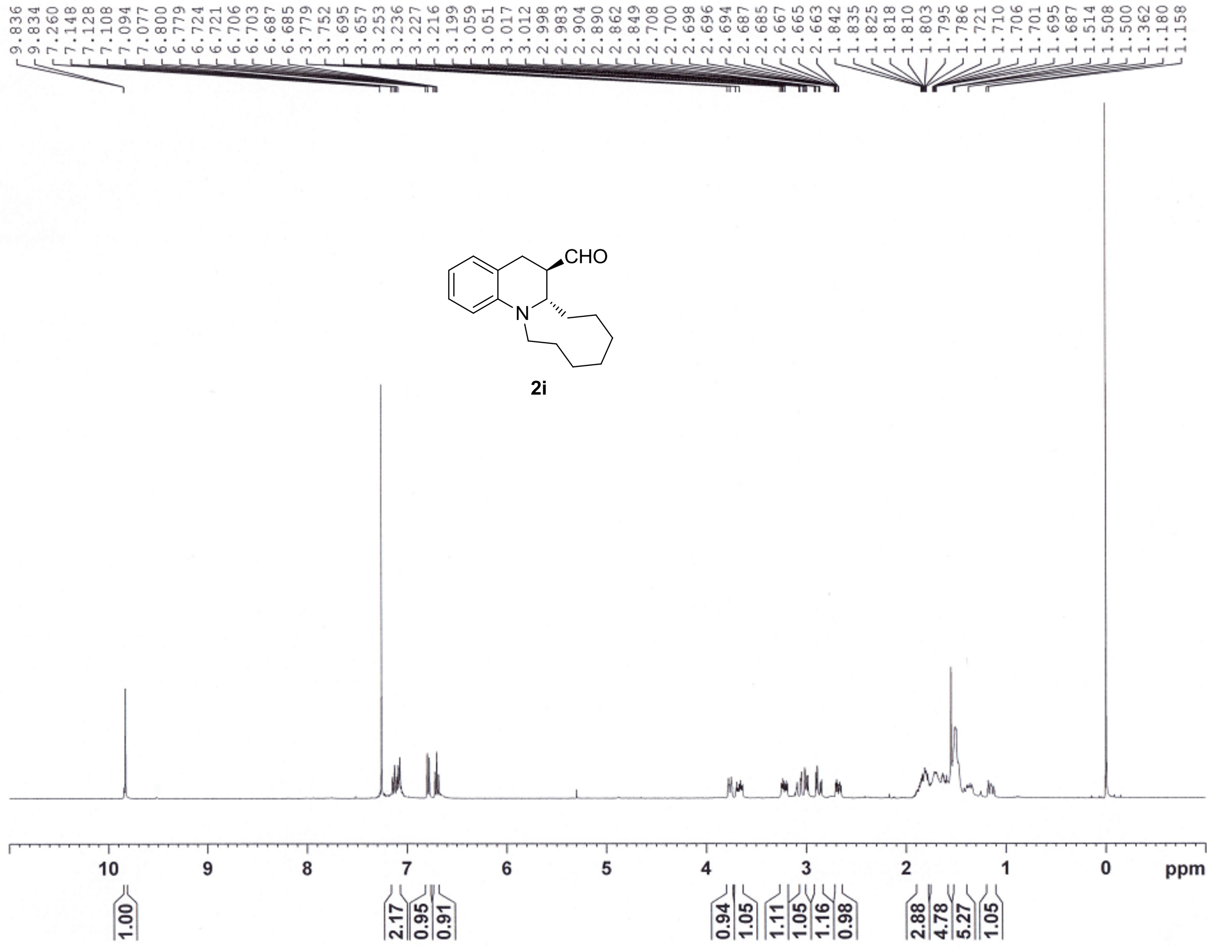

분석 결과

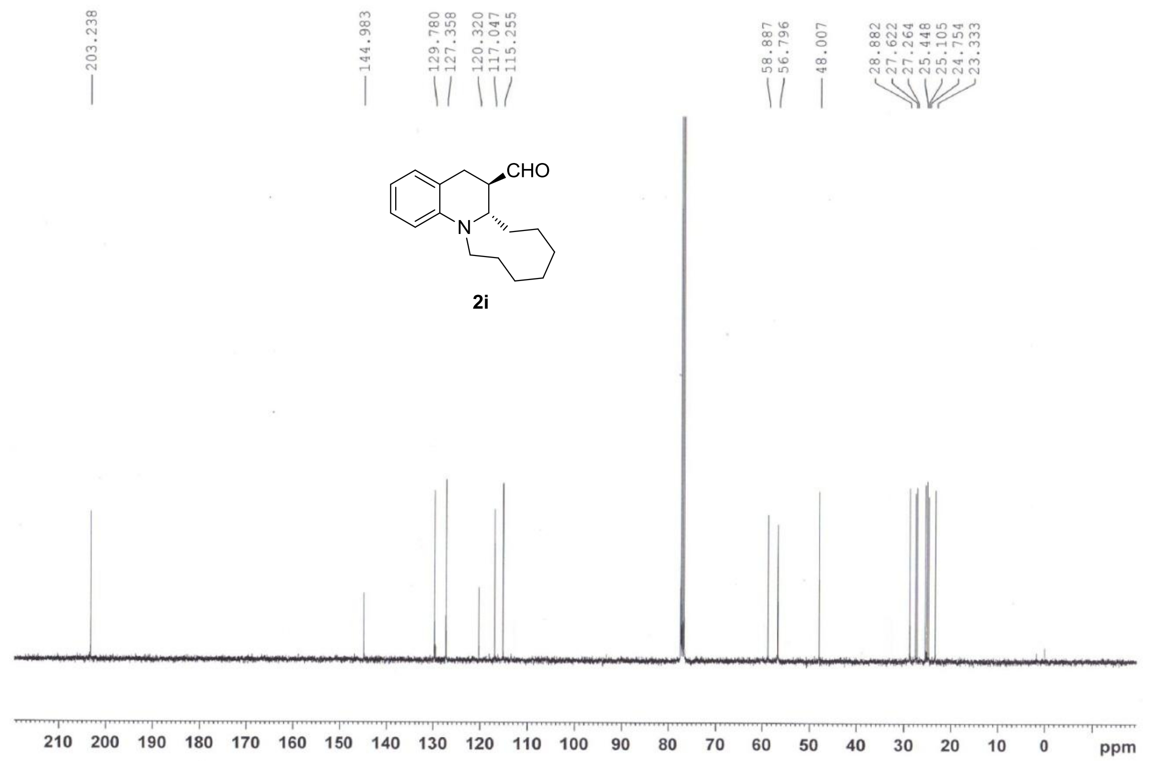
| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 11.8333 | 565.0889 | BB | 36.0000 | 9.7173 |
| 2 | 12.3667 | 2358.0405 | BB | 58.0000 | 40.5490 |
| 3 | 14.1000 | 593.8637 | BV | 51.0000 | 10.2121 |
| 4 | 15.2000 | 2298.2975 | BB | 71.0000 | 39.5216 |

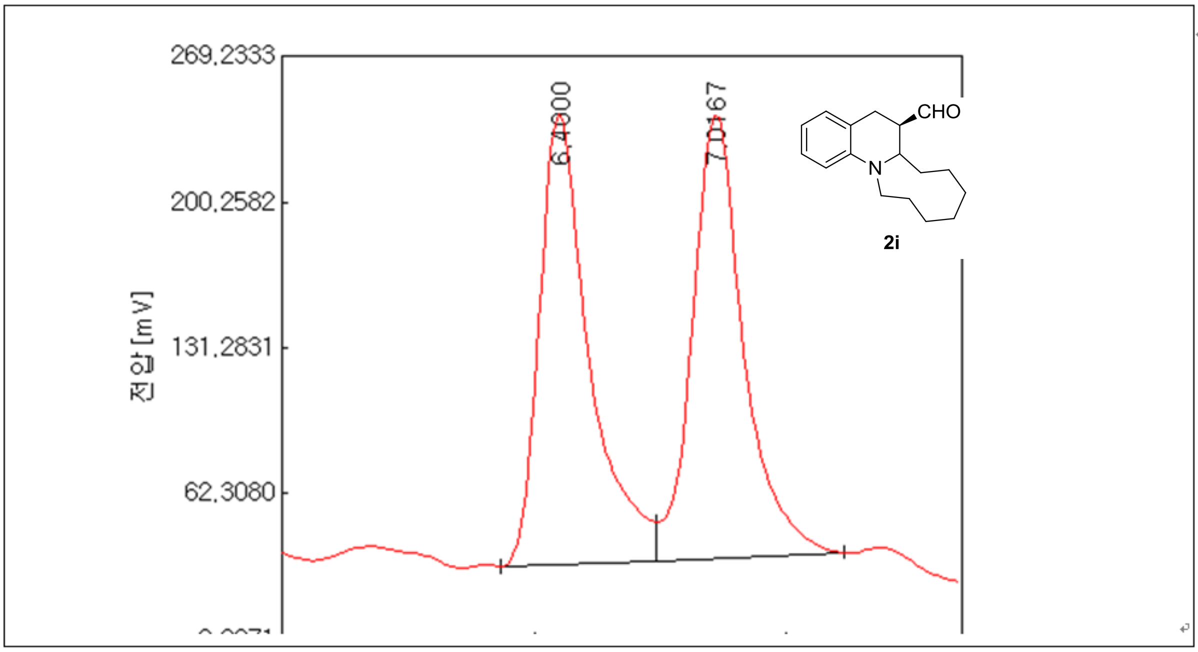



분석 결과

| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 10.0333 | 7366.8692 | BB | 66.0000 | 96.7923 |
| 2 | 13.9167 | 244.1411 | FF | 47.0000 | 3.2077 |

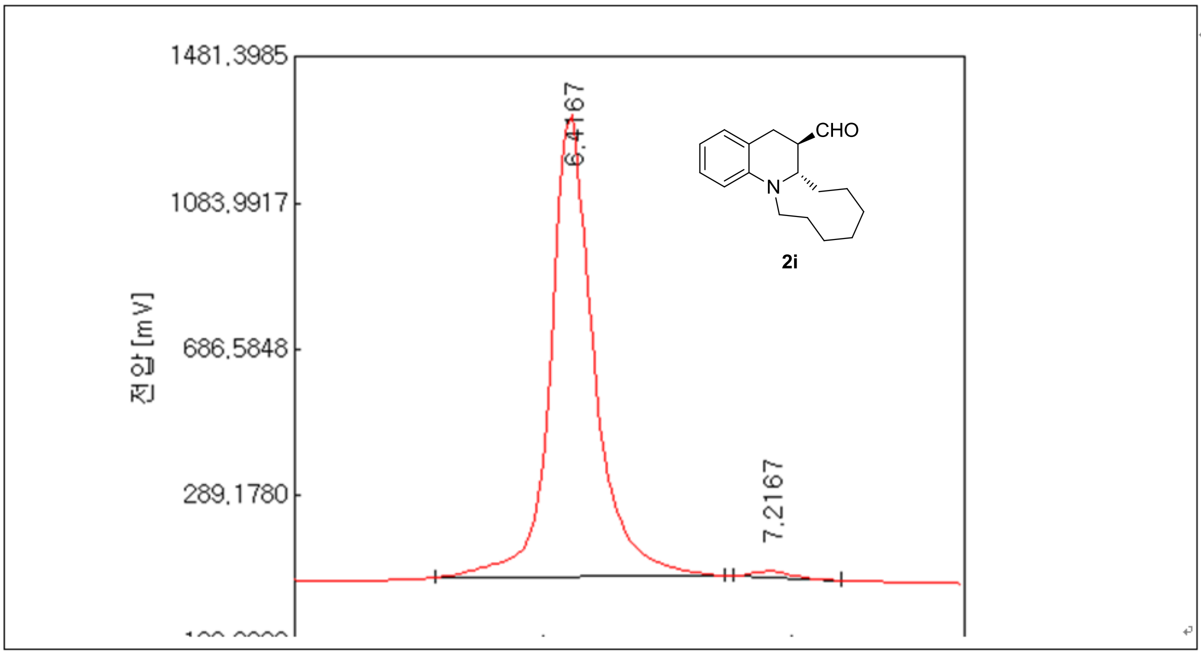






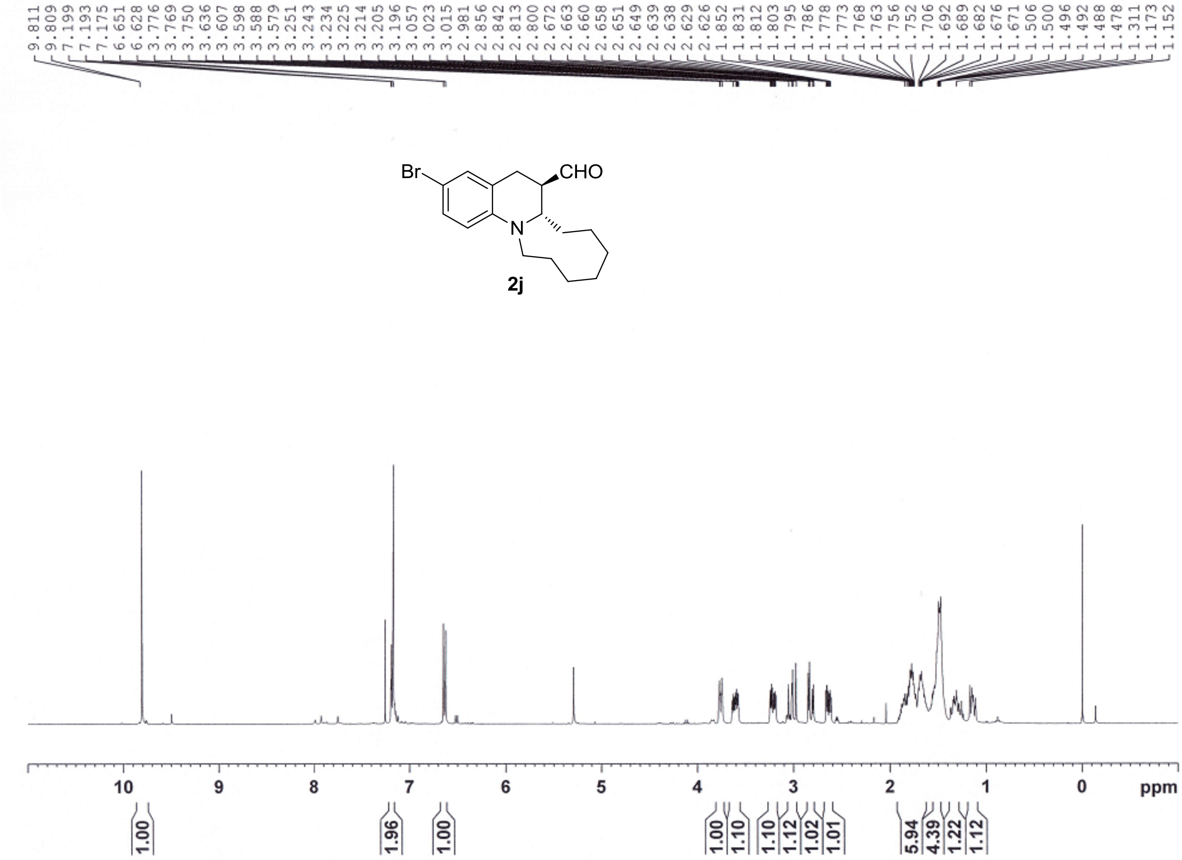

분석 결과

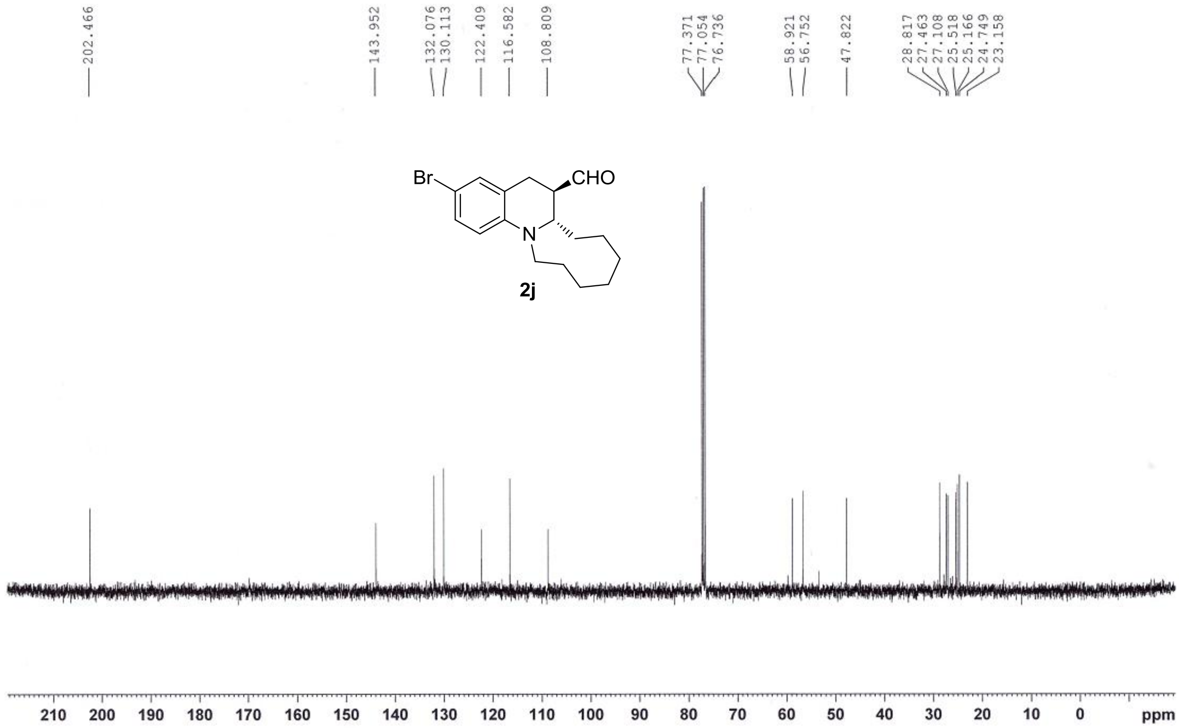
| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 6.4000 | 3039.9738 | BB | 37.0000 | 49.5289 |
| 2 | 7.0167 | 3097.8071 | BB | 45.0000 | 50.4711 |

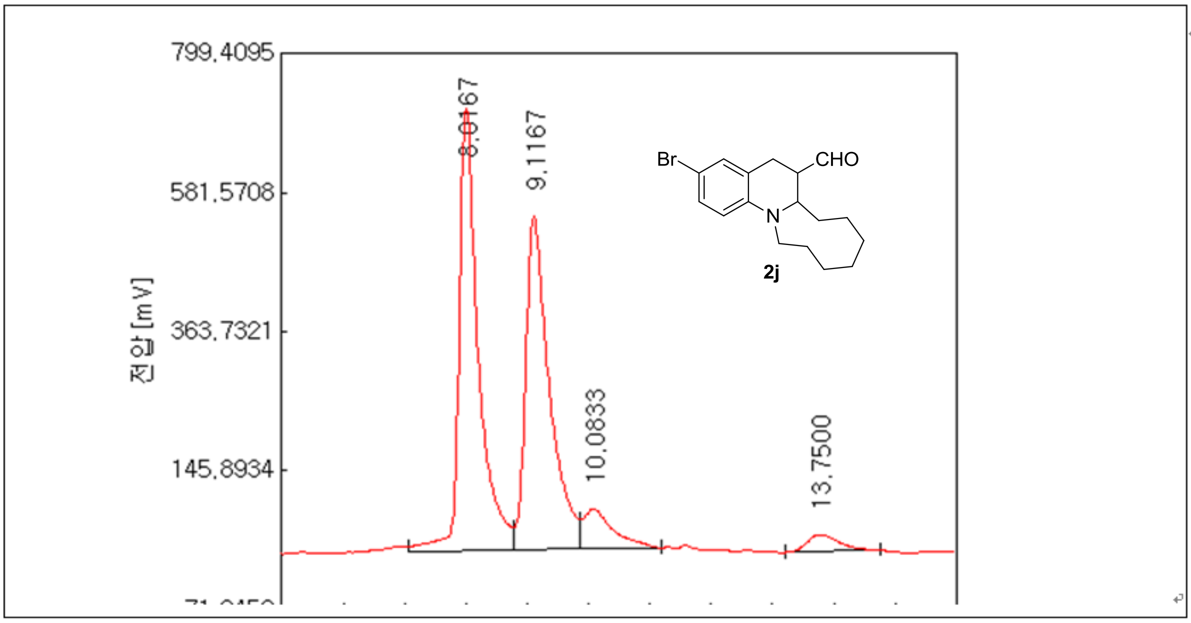



분석 결과

| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 6.4167 | 16029.2550 | FF | 70.0000 | 98.8728 |
| 2 | 7.2167 | 182.7363 | FF | 26.0000 | 1.1272 |

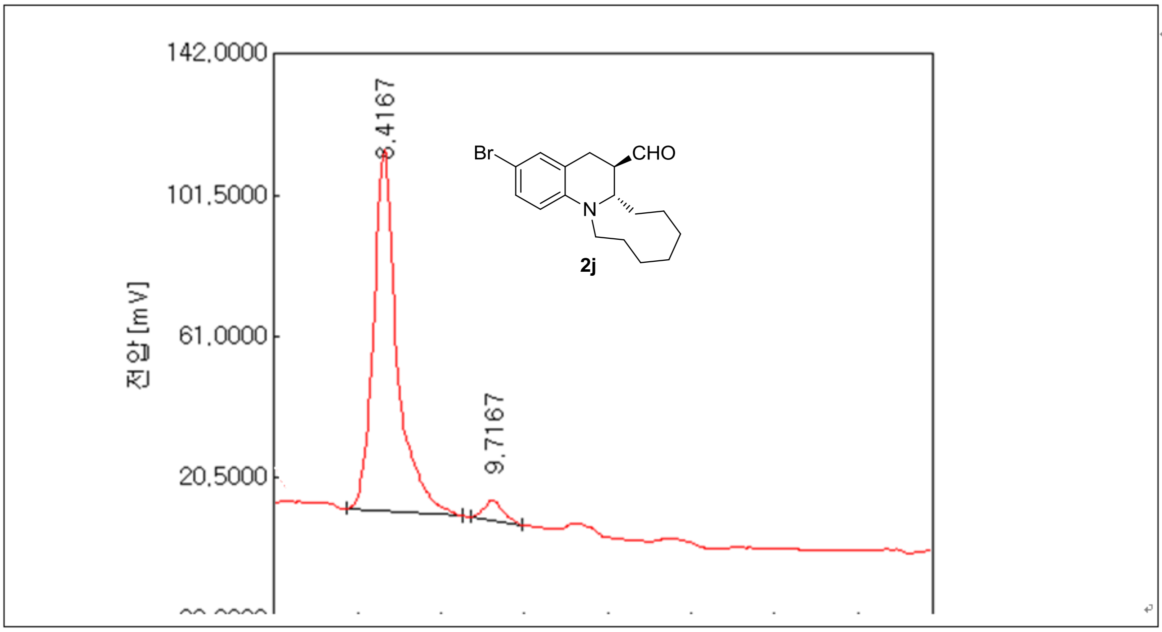






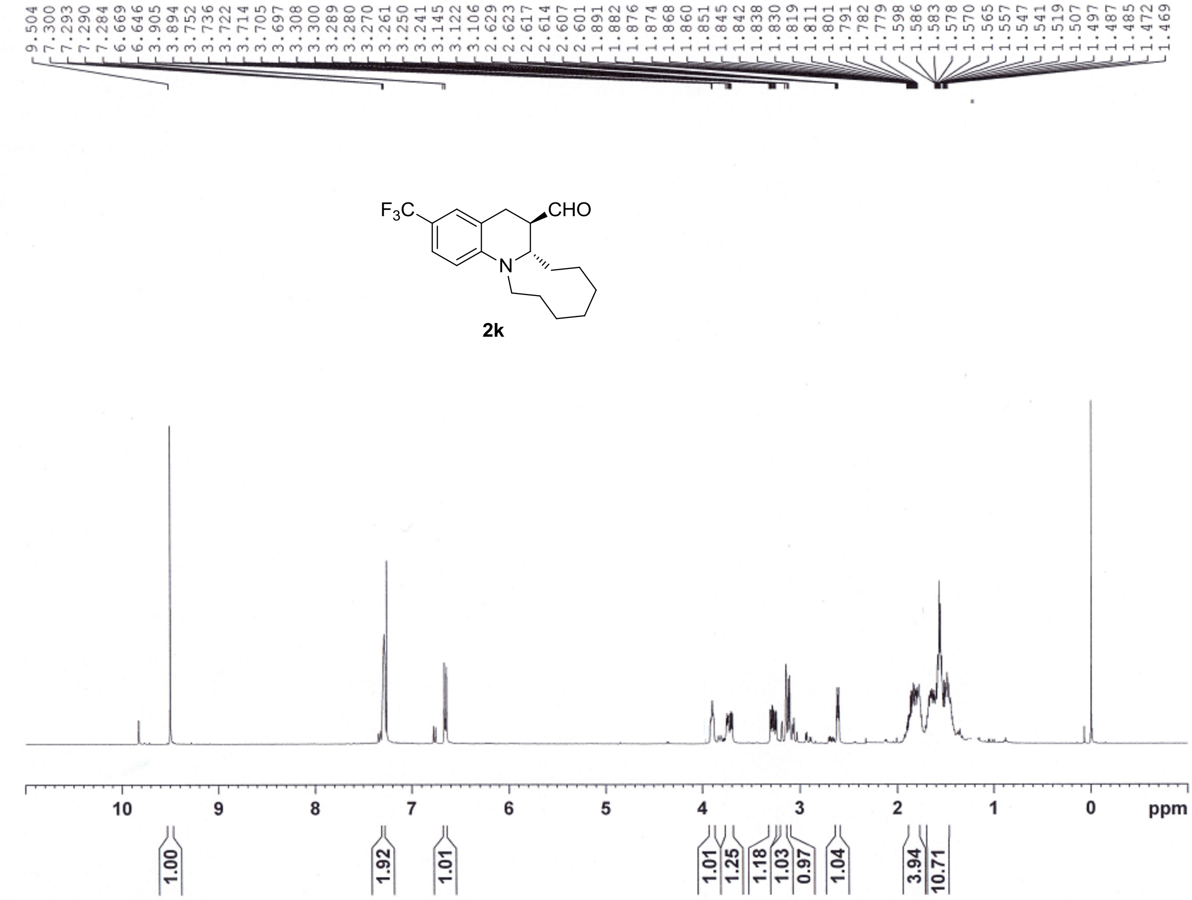

분석 결과

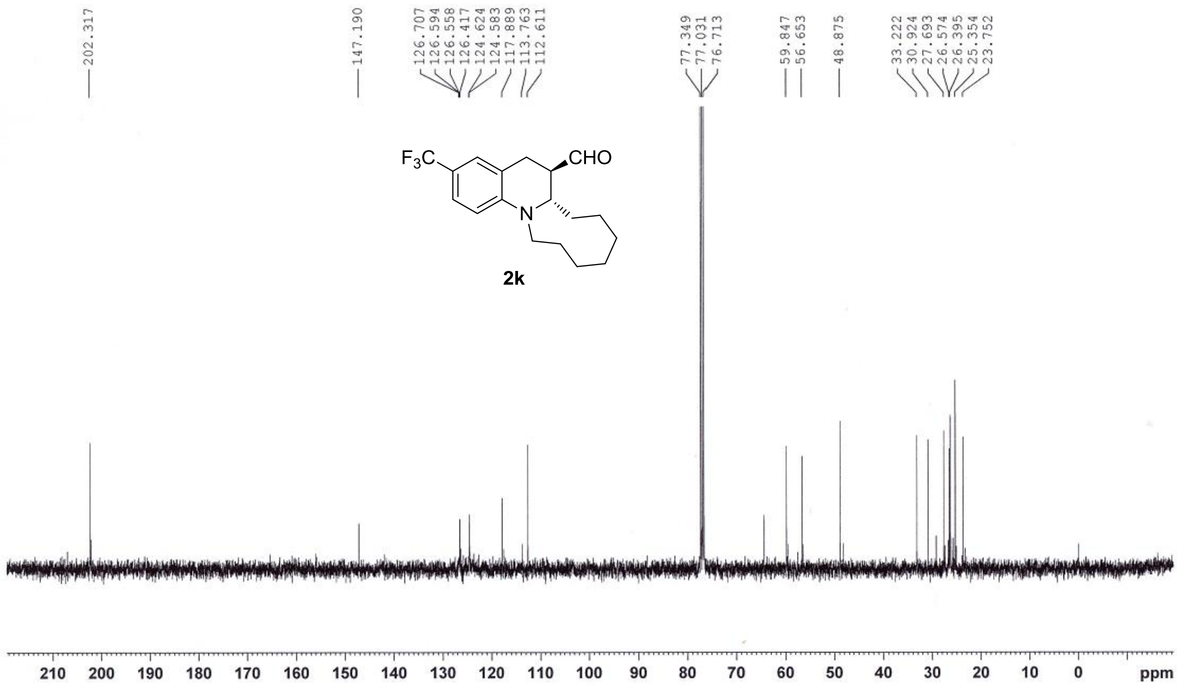
| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 8.0167 | 15825.9074 | VB | 102.0000 | 46.9534 |
| 2 | 9.1167 | 14655.6514 | BB | 66.0000 | 43.4814 |
| 3 | 10.0833 | 2209.9942 | BB | 79.0000 | 6.5568 |
| 4 | 13.7500 | 1014.0415 | FF | 92.0000 | 3.0085 |

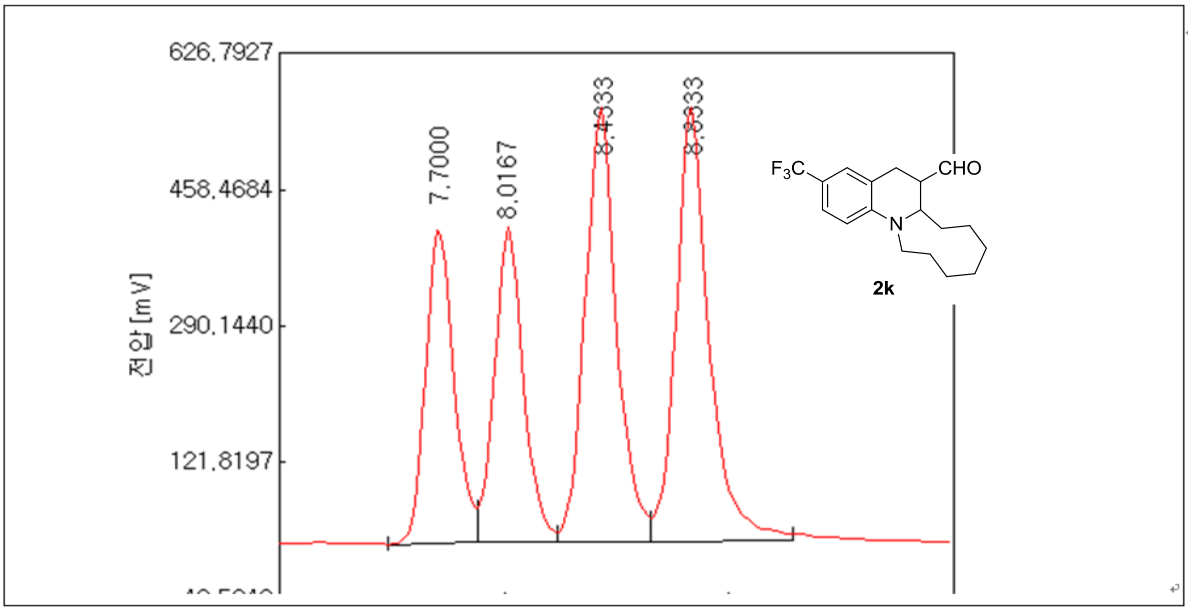



분석 결과

| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 8.4167 | 2039.3506 | BB | 84.0000 | 95.5407 |
| 2 | 9.7167 | 95.1864 | FF | 37.0000 | 4.4593 |

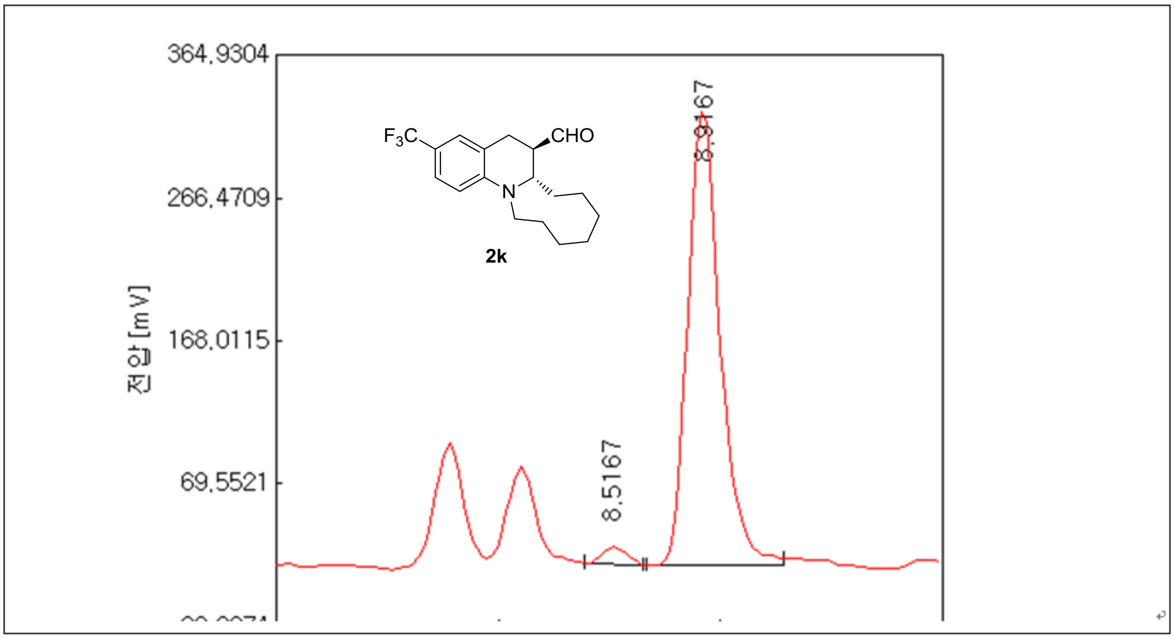

9.504
7.300
7.293
7.290
7.284
6.669
6.646
3.905
3.894
3.752
3.736
3.722
3.714
3.705
3.697
3.308
3.300
3.289
3.280
3.270
3.261
3.250
3.241
3.145
3.122
3.106
2.629
2.623
2.617
2.614
2.607
2.601
1.891
1.882
1.876
1.874
1.868
1.860
1.851
1.845
1.842
1.838
1.830
1.819
1.811
1.801
1.791
1.782
1.779
1.598
1.586
1.583
1.578
1.570
1.565
1.557
1.547
1.541
1.519
1.507
1.497
1.487
1.485
1.472
1.469
F3C
CHO
N
2k
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.92
1.01
1.01
1.25
1.18
1.03
0.97
1.04
3.94
10.71


202.317
147.190
126.707
126.594
126.558
126.417
124.624
124.583
117.889
113.763
112.611
77.349
77.031
76.713
59.847
56.653
48.875
33.222
30.924
27.693
26.574
26.395
25.354
23.752
F3C
CHO
N
2k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



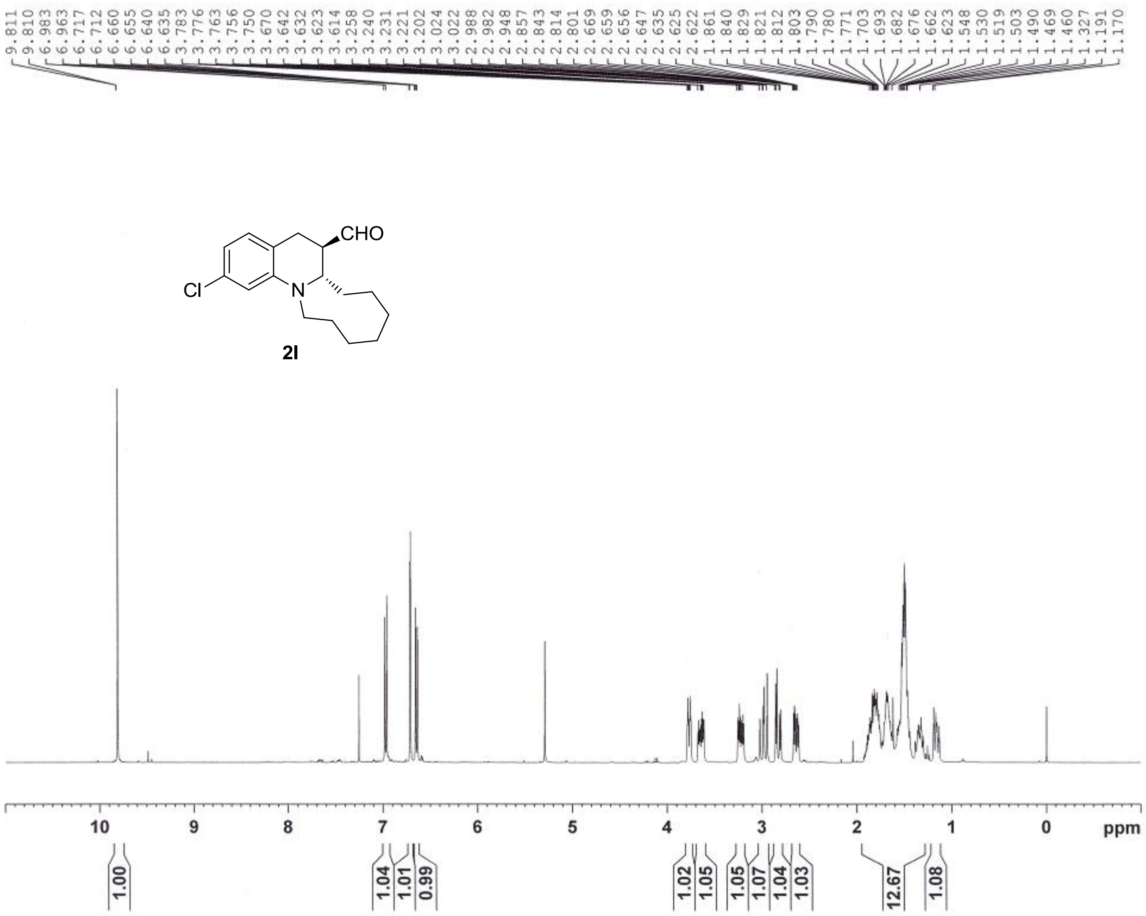

분석 결과

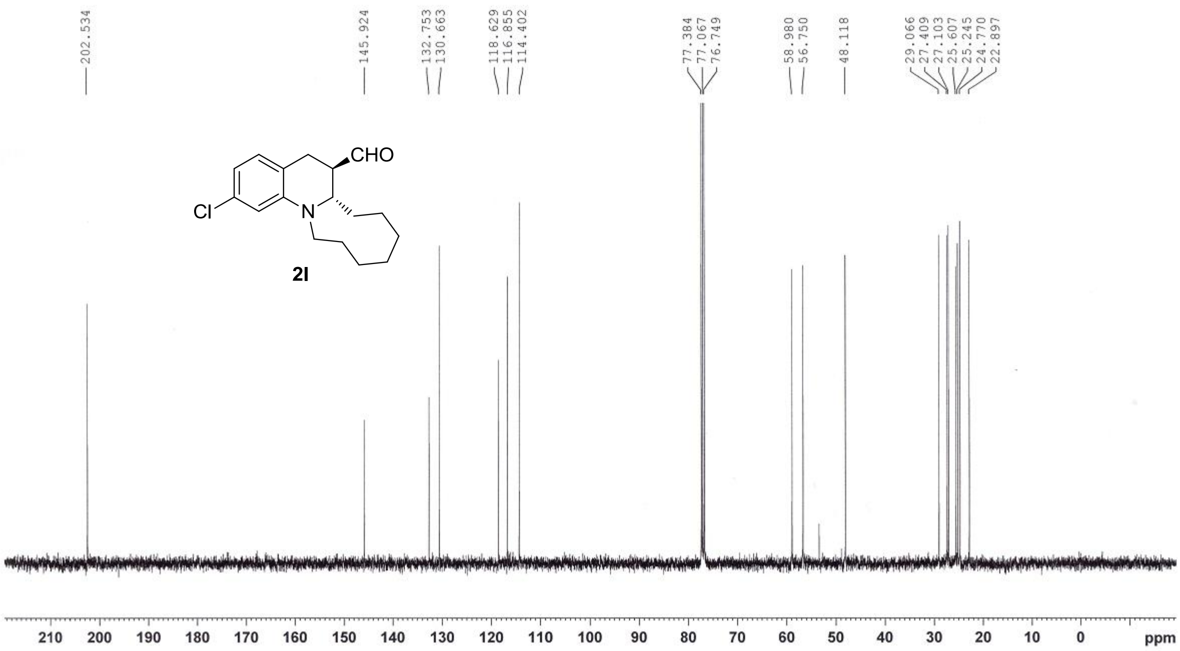
| 번호 | RT[분] | 면적 [mV*s] | 형태 | 폭 [초] | 면적% |
|---|---|---|---|---|---|
| 1 | 7.7000 | 3539.2566 | BV | 24.0000 | 19.3692 |
| 2 | 8.0167 | 3596.4558 | BV | 21.0000 | 19.6822 |
| 3 | 8.4333 | 5412.4912 | BB | 25.0000 | 29.6208 |
| 4 | 8.8333 | 5724.4267 | BV | 38.0000 | 31.3279 |

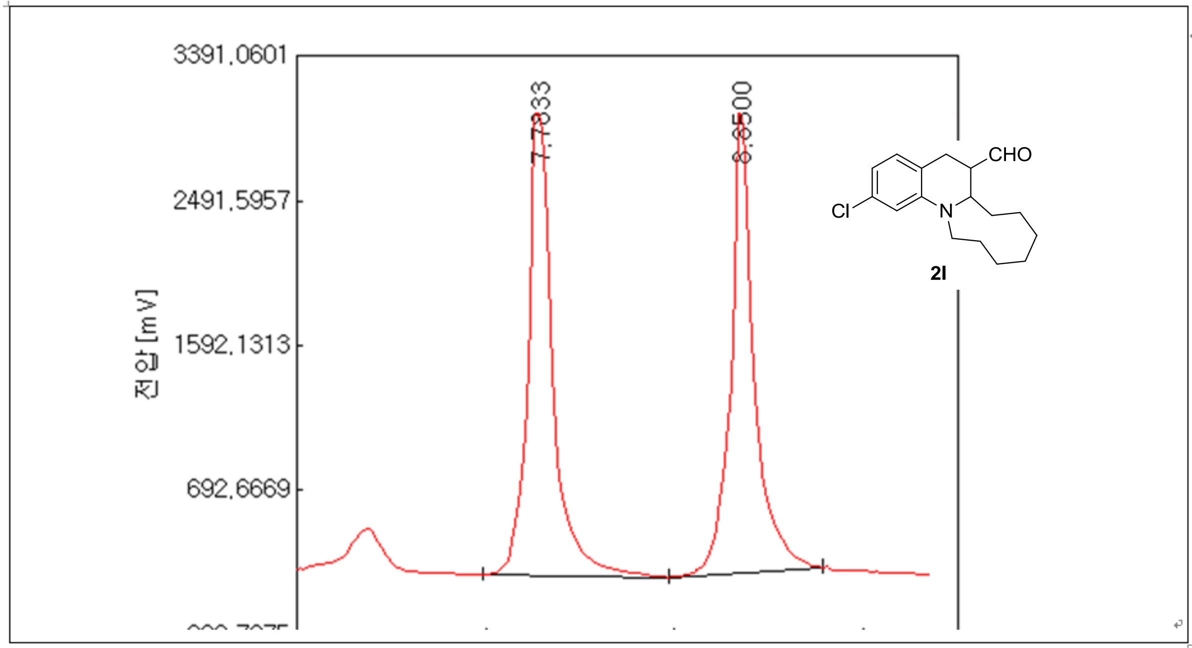



분석 결과

| 번호 | RT[분] | 면적 [mV*s] | 형태 | 폭 [초] | 면적% |
|---|---|---|---|---|---|
| 1 | 8.5167 | 95.3366 | FF | 16.0000 | 2.7954 |
| 2 | 8.9167 | 3315.1881 | BV | 37.0000 | 97.2046 |

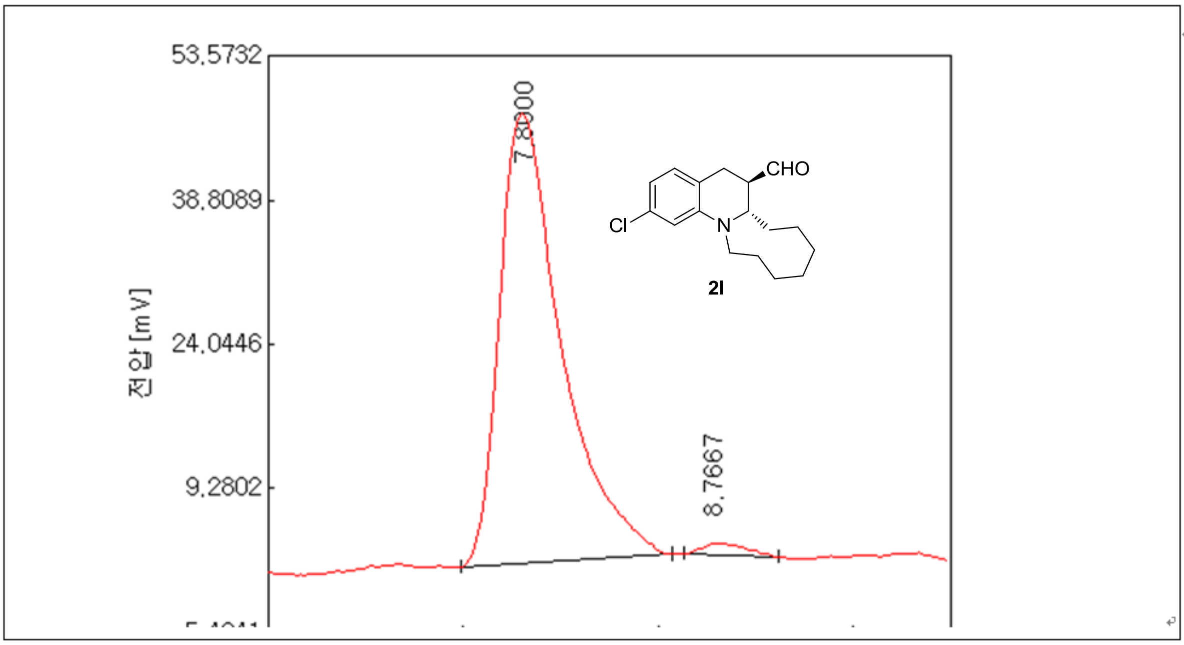

9.811
9.810
6.983
6.963
6.717
6.712
6.660
6.655
6.640
6.635
3.783
3.776
3.763
3.756
3.750
3.670
3.642
3.632
3.623
3.614
3.258
3.240
3.231
3.221
3.202
3.024
3.022
2.988
2.982
2.948
2.857
2.843
2.814
2.801
2.669
2.659
2.656
2.647
2.635
2.625
2.622
1.861
1.840
1.829
1.821
1.812
1.803
1.790
1.780
1.771
1.703
1.693
1.682
1.676
1.662
1.623
1.548
1.530
1.519
1.503
1.490
1.469
1.460
1.327
1.191
1.170
CHO
Cl
N
2l
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.04
1.01
0.99
1.02
1.05
1.05
1.07
1.04
1.03
12.67
1.08


202.534
145.924
132.753
130.663
118.629
116.855
114.402
77.384
77.067
76.749
58.980
56.750
48.118
29.066
27.409
27.103
25.607
25.245
24.770
22.897
CHO
Cl
N
2l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



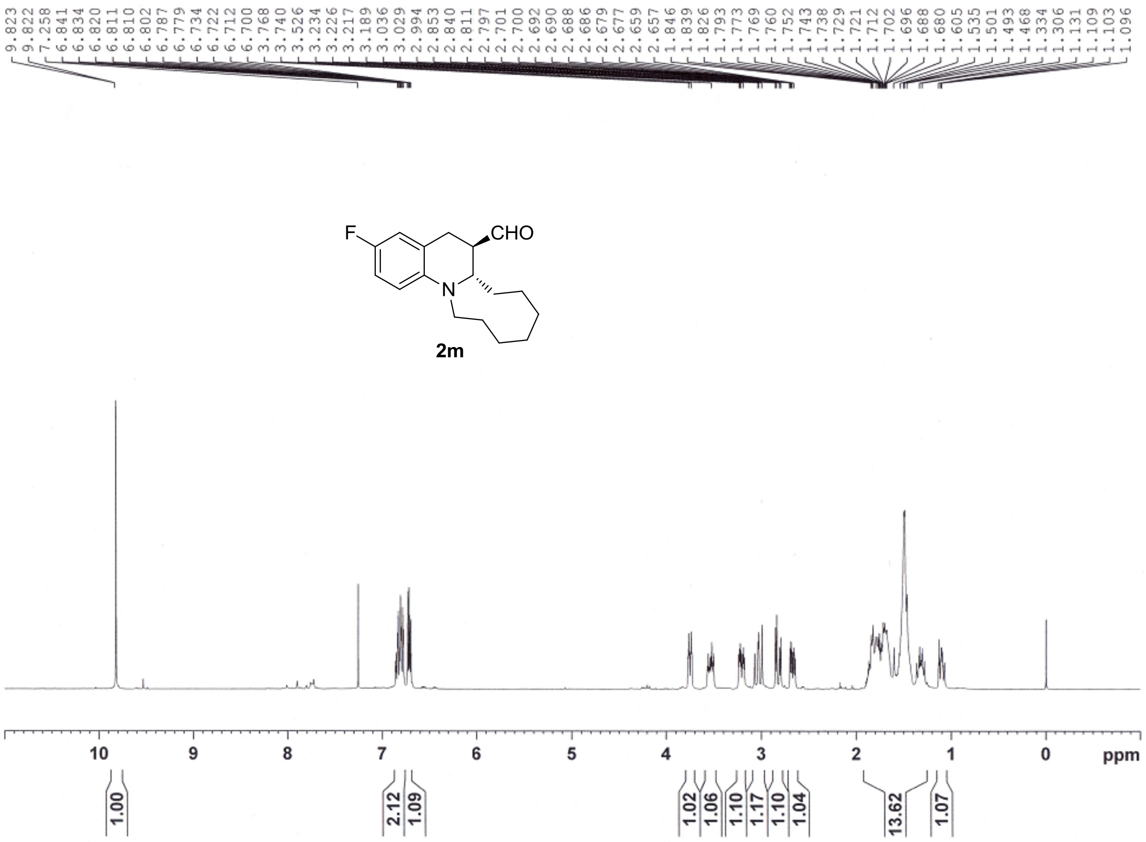

분석 결과

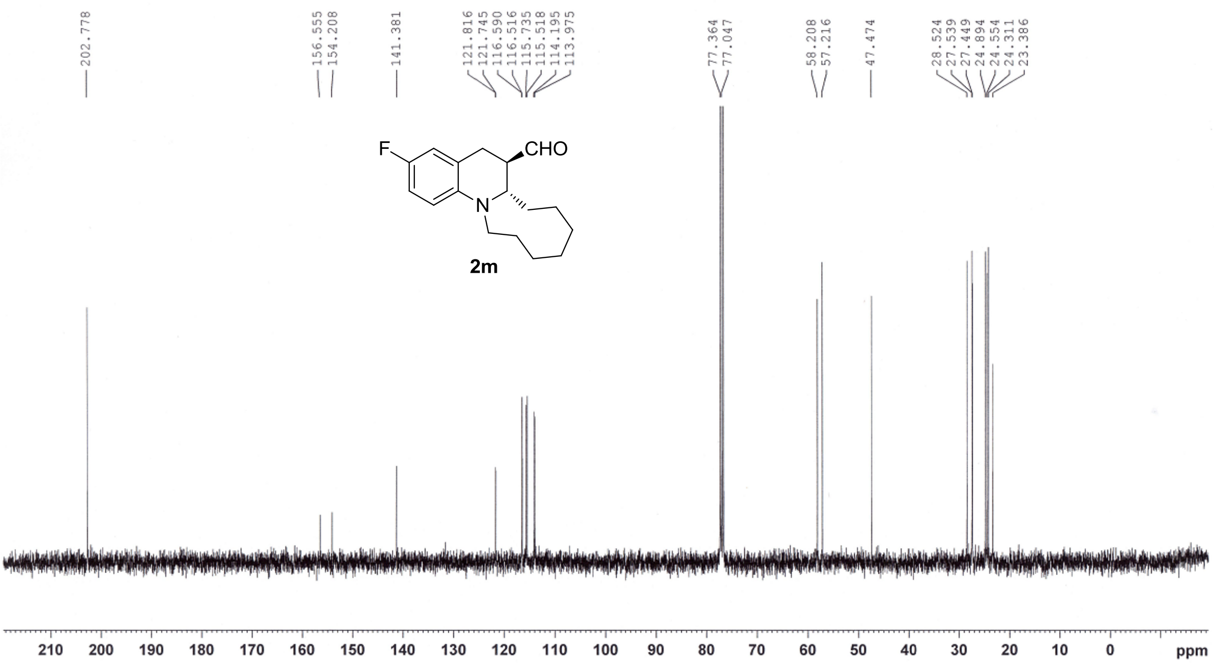
| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 7.7833 | 27936.2758 | VV | 59.0000 | 51.8857 |
| 2 | 8.8500 | 25905.6347 | VV | 49.0000 | 48.1143 |

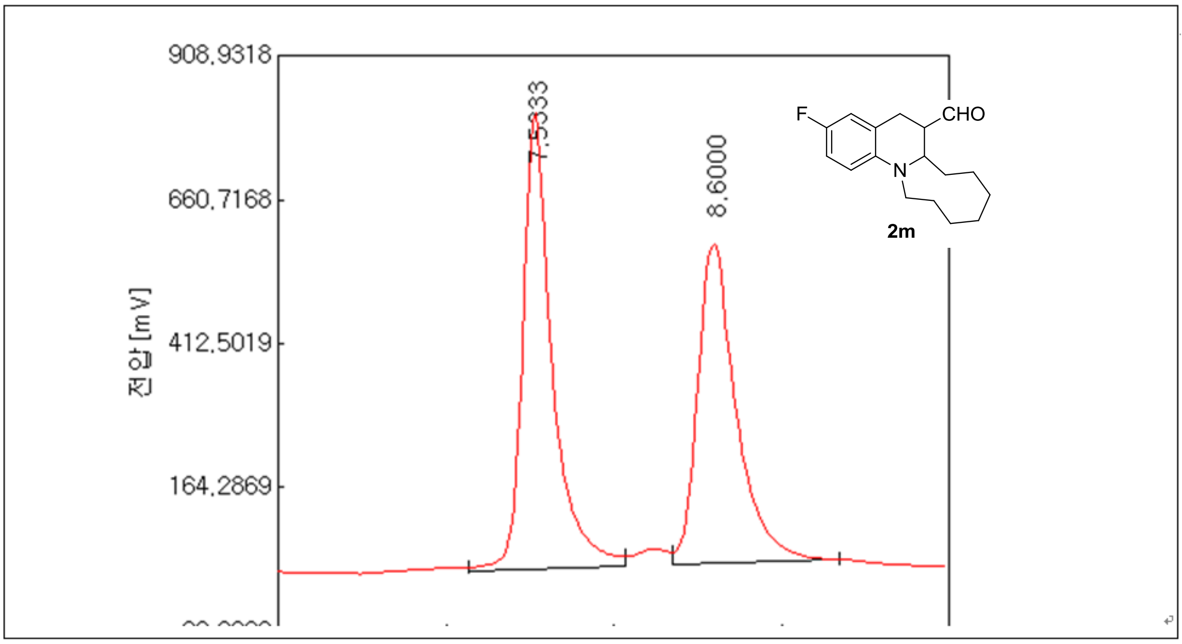



분석 결과

| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 7.8000 | 1057.7961 | BB | 65.0000 | 98.2131 |
| 2 | 8.7667 | 19.2452 | FF | 29.0000 | 1.7869 |

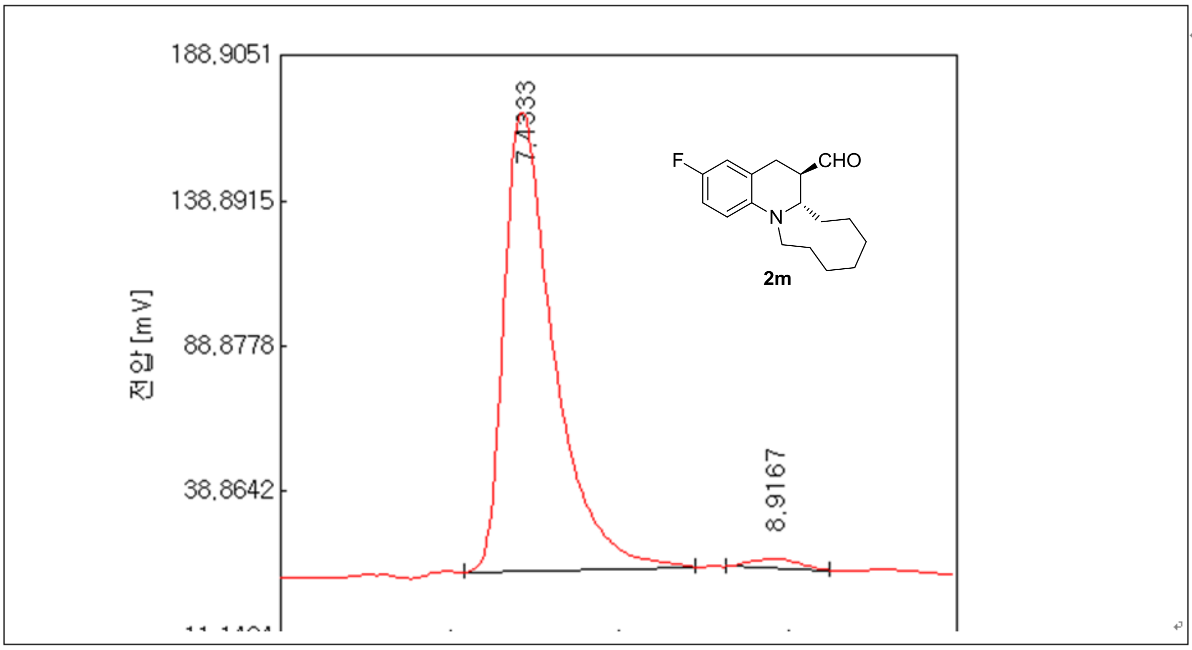






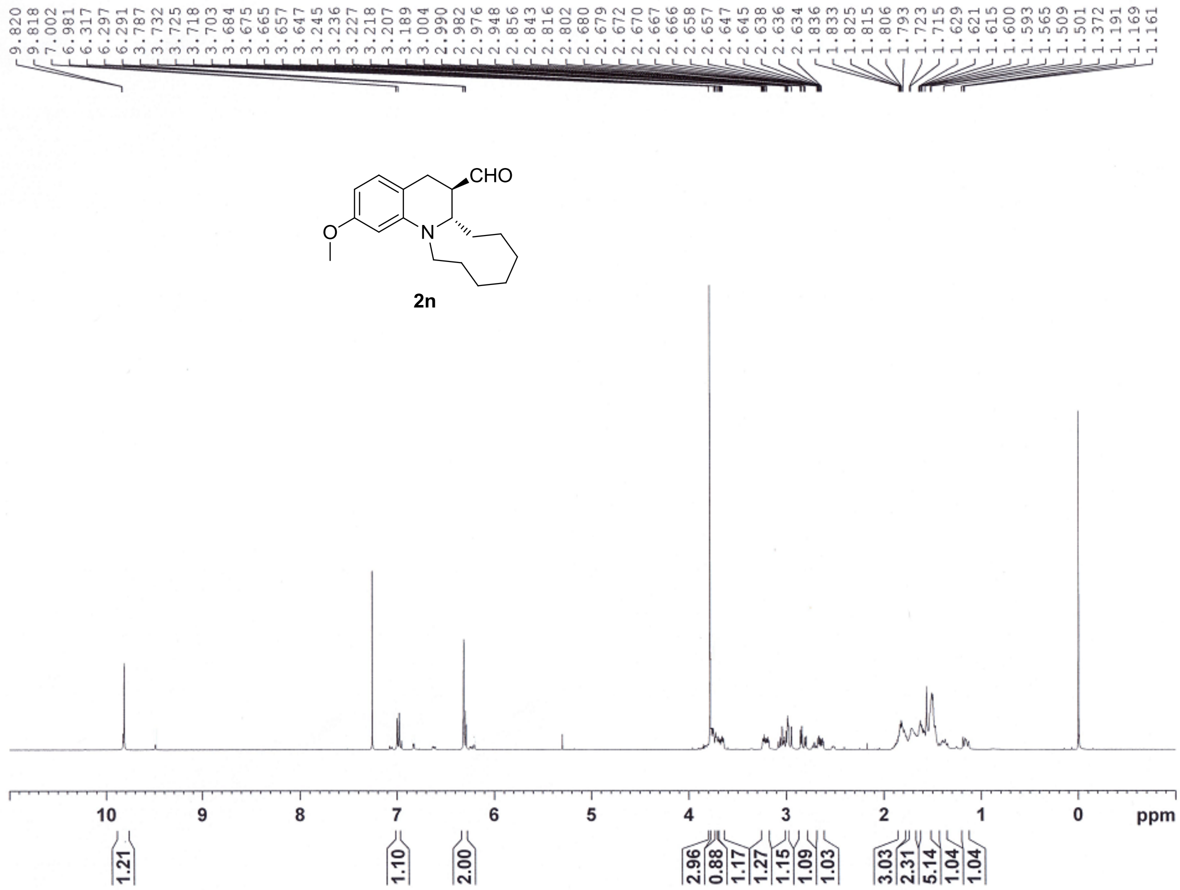

분석 결과

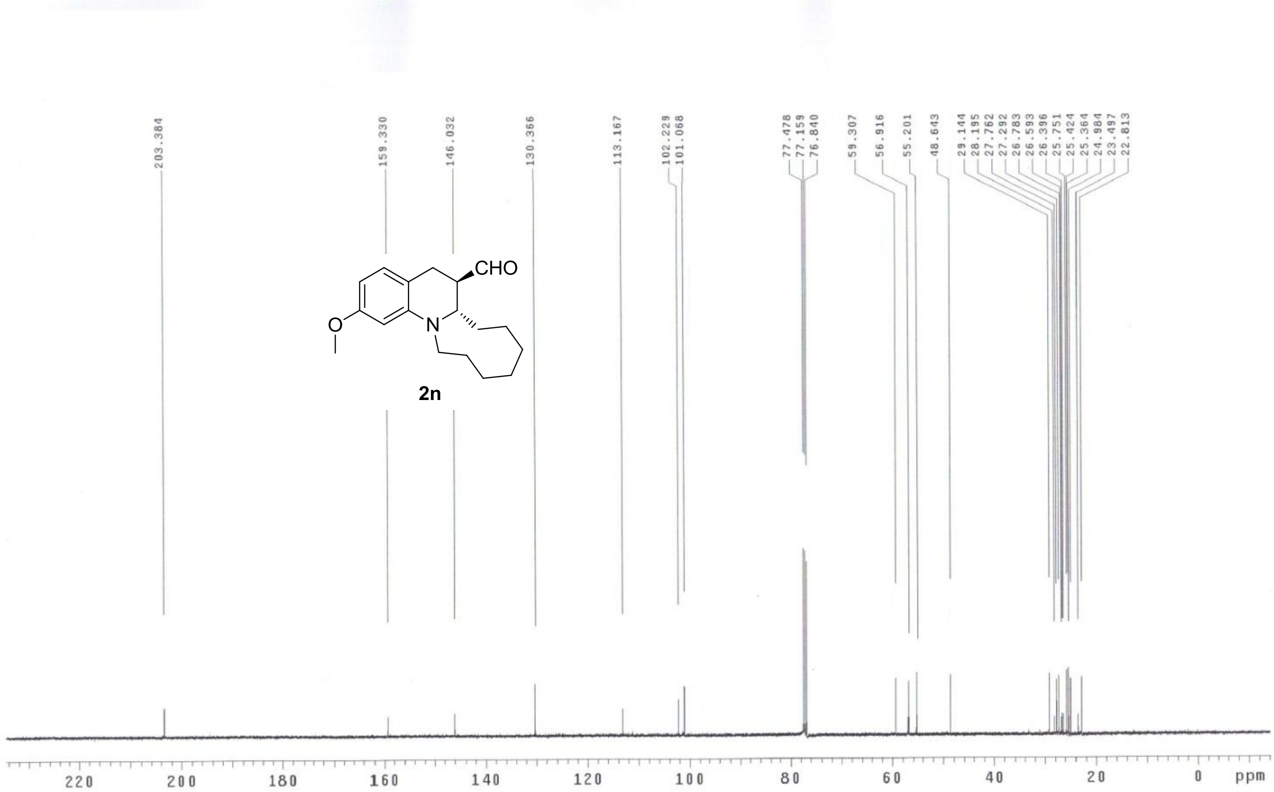
| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 7.5333 | 10059.5523 | VV | 56.0000 | 52.2806 |
| 2 | 8.6000 | 9181.8961 | VB | 60.0000 | 47.7194 |

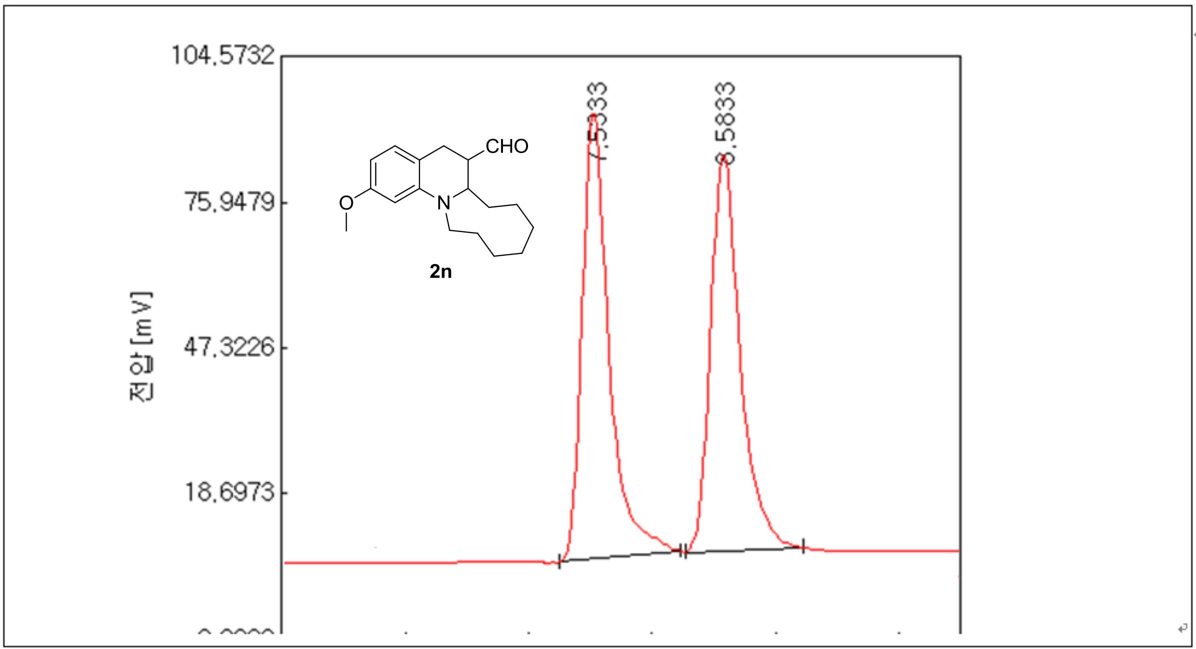



분석 결과

| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 7.4333 | 3375.2458 | BV | 82.0000 | 97.9657 |
| 2 | 8.9167 | 70.0880 | FF | 37.0000 | 2.0343 |

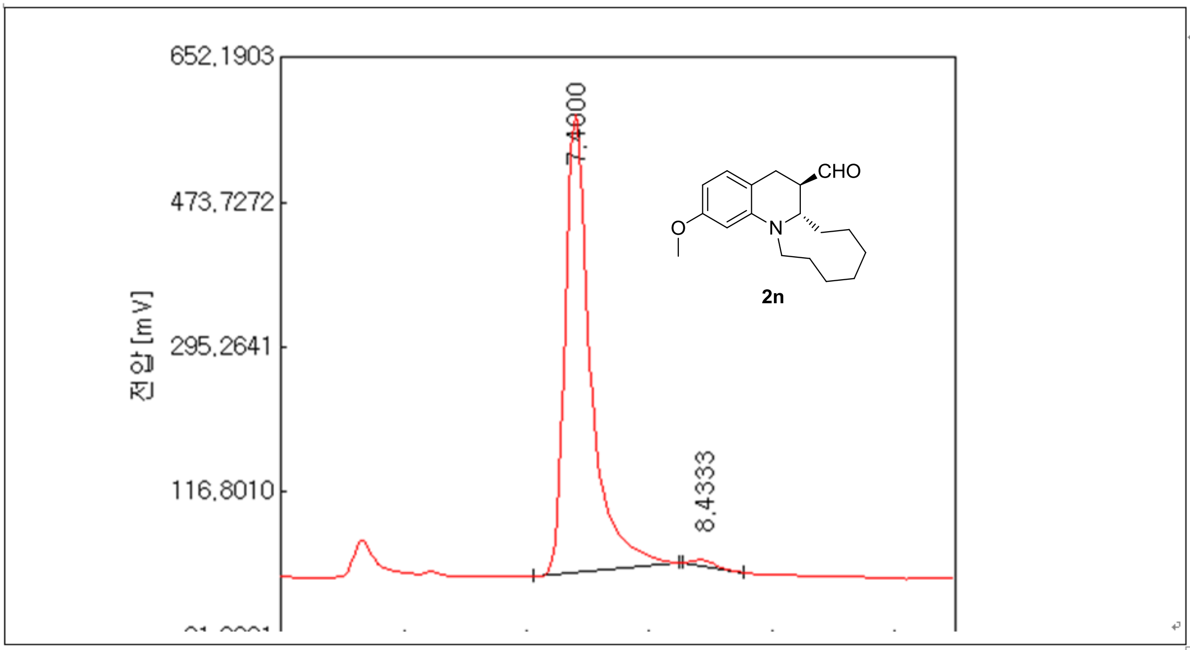






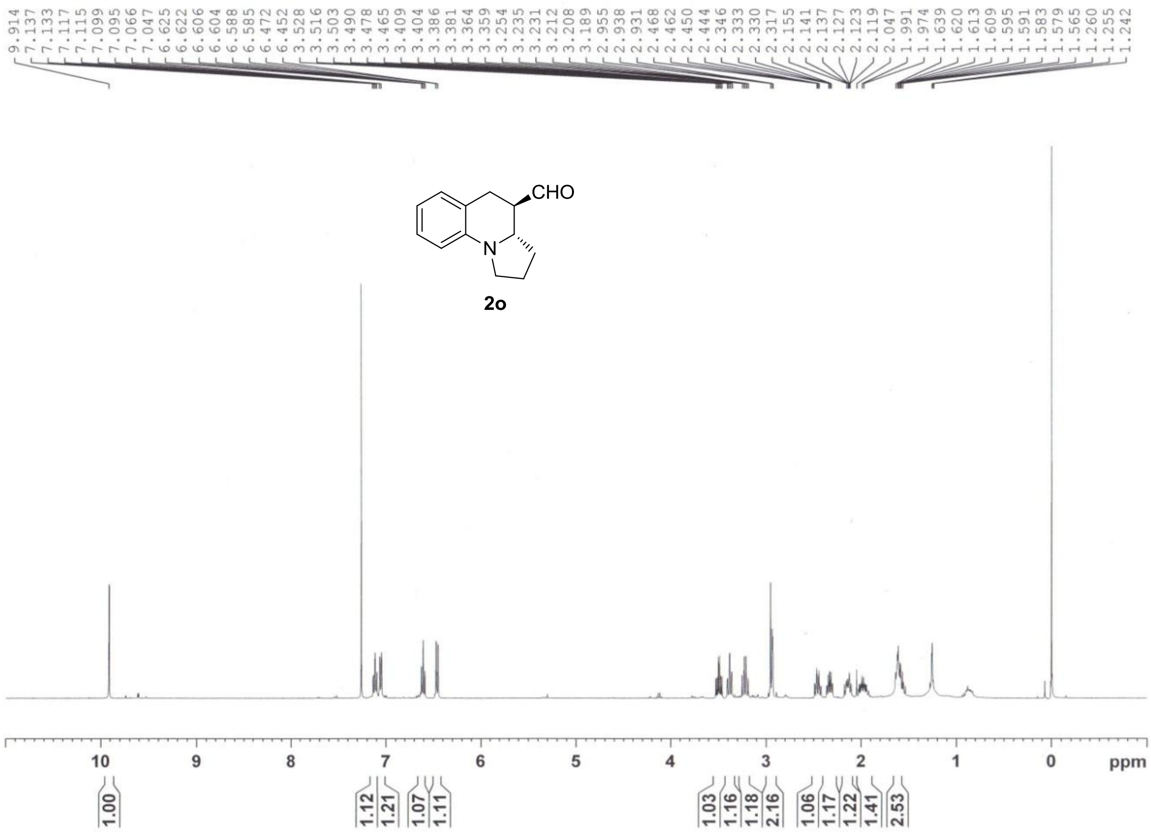

분석 결과

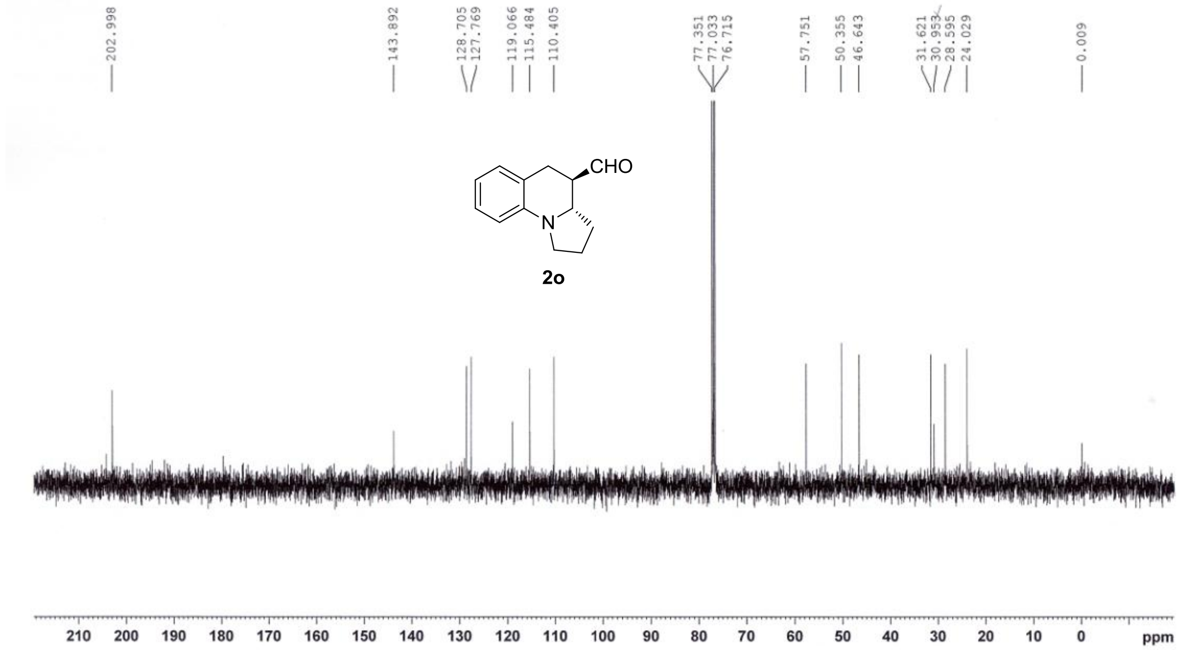
| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 7.5333 | 1379.0729 | BB | 59.0000 | 50.5353 |
| 2 | 8.5833 | 1349.8594 | BB | 58.0000 | 49.4647 |

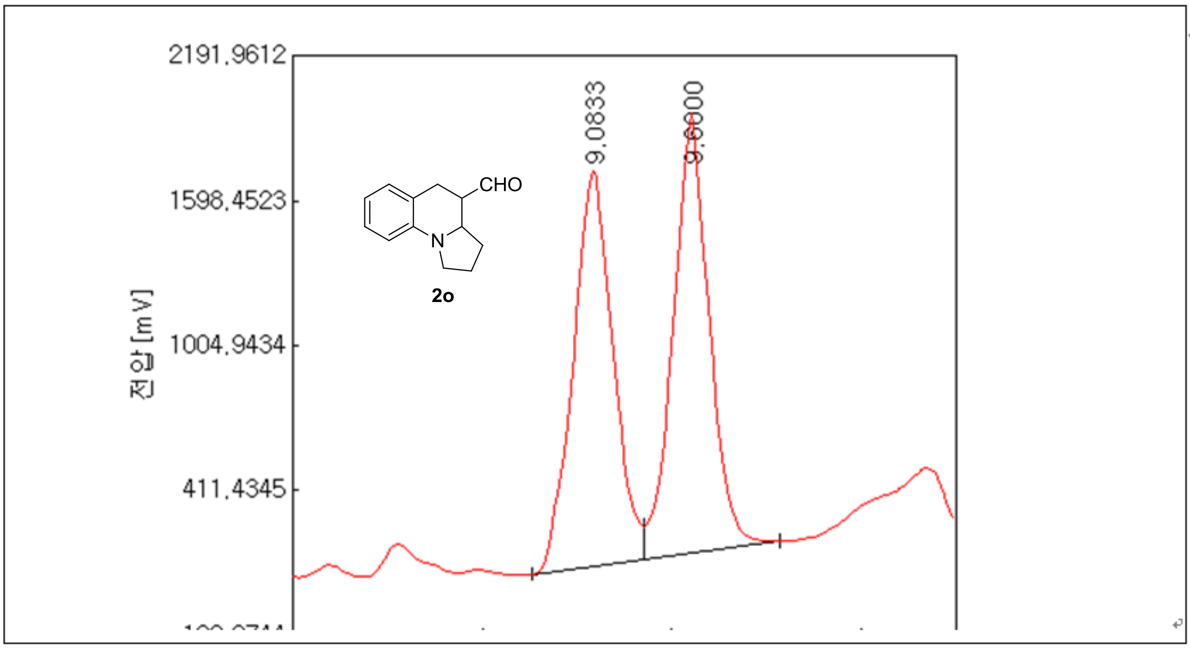



분석 결과

| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 7.4000 | 8465.1441 | FF | 72.0000 | 98.8195 |
| 2 | 8.4333 | 101.1278 | FF | 30.0000 | 1.1805 |

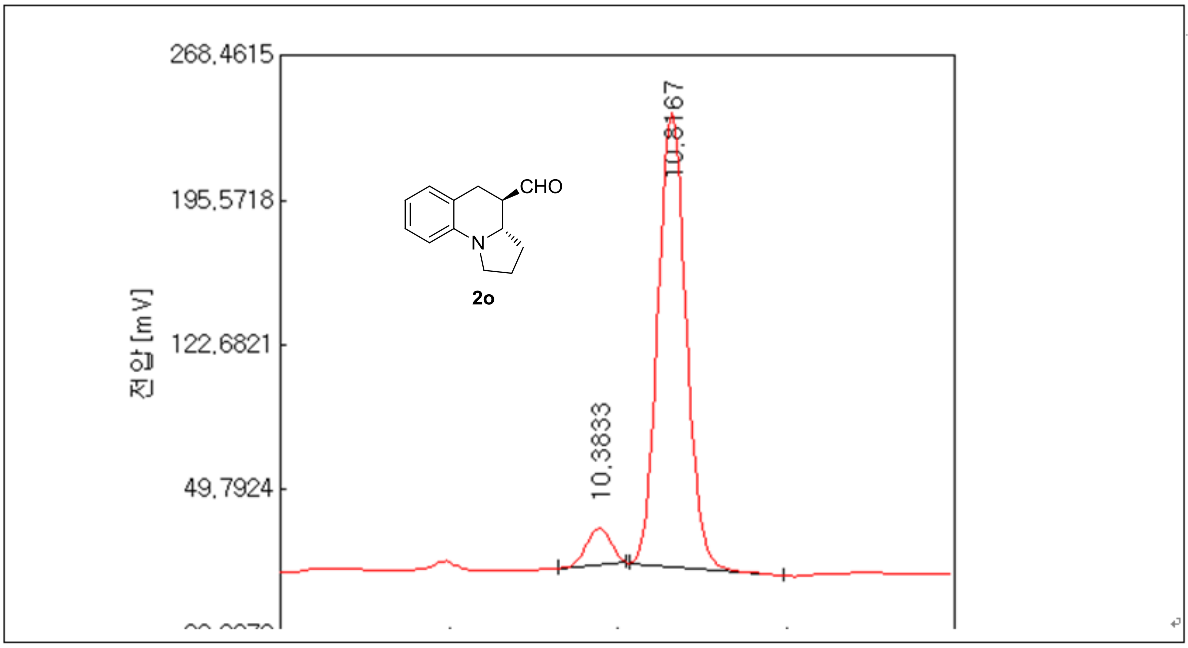

9.914
7.137
7.133
7.117
7.115
7.099
7.095
7.066
7.047
6.625
6.622
6.606
6.604
6.588
6.585
6.472
6.452
3.528
3.516
3.503
3.490
3.478
3.465
3.409
3.404
3.386
3.381
3.364
3.359
3.254
3.235
3.231
3.212
3.208
3.189
2.955
2.938
2.931
2.468
2.462
2.450
2.444
2.346
2.333
2.330
2.317
2.155
2.141
2.137
2.127
2.123
2.119
2.047
1.991
1.974
1.639
1.620
1.613
1.609
1.595
1.591
1.583
1.579
1.565
1.260
1.255
1.242
CHO
N
2o
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.12
1.21
1.07
1.11
1.03
1.16
1.18
2.16
1.06
1.17
1.22
1.41
2.53


202.998
143.892
128.705
127.769
119.066
115.484
110.405
77.351
77.033
76.715
57.751
50.355
46.643
31.621
30.953
28.595
24.029
0.009
CHO
N
2o
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



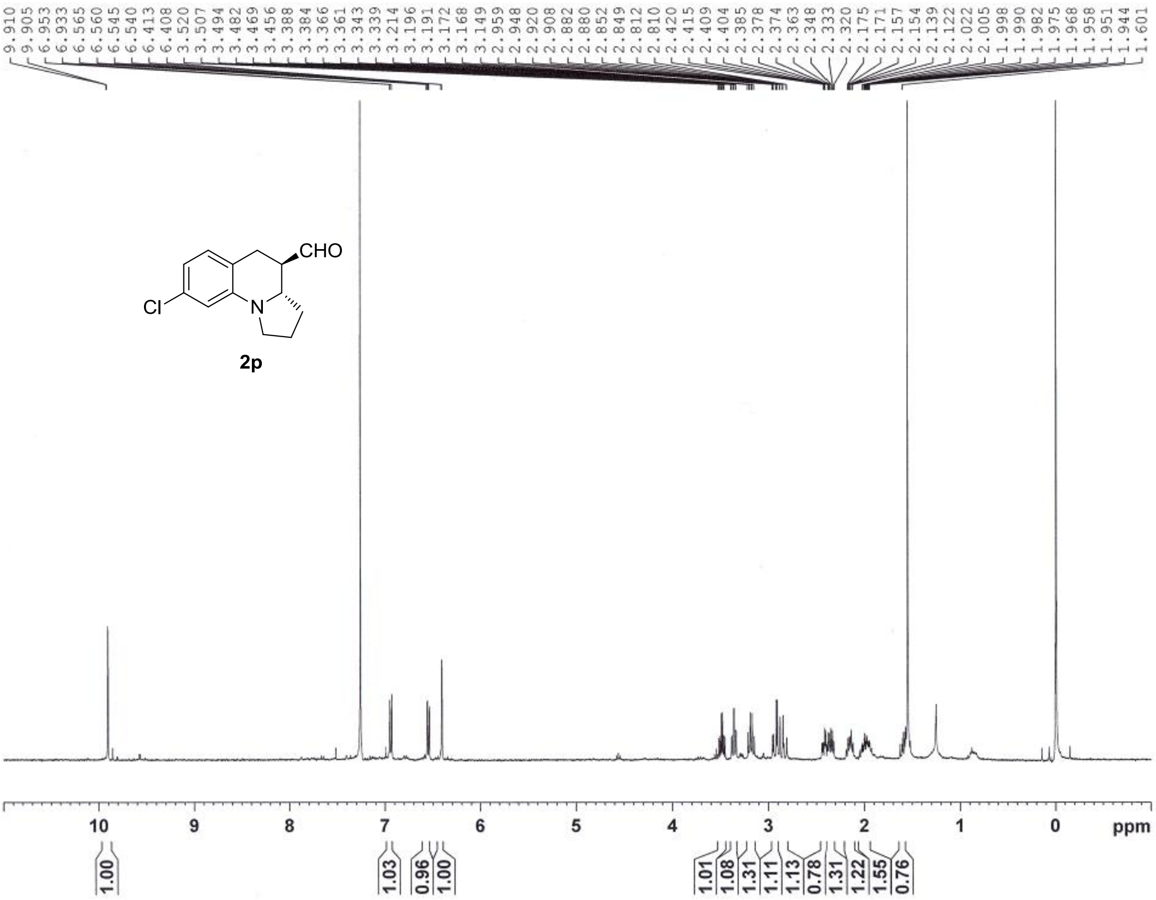

분석 결과

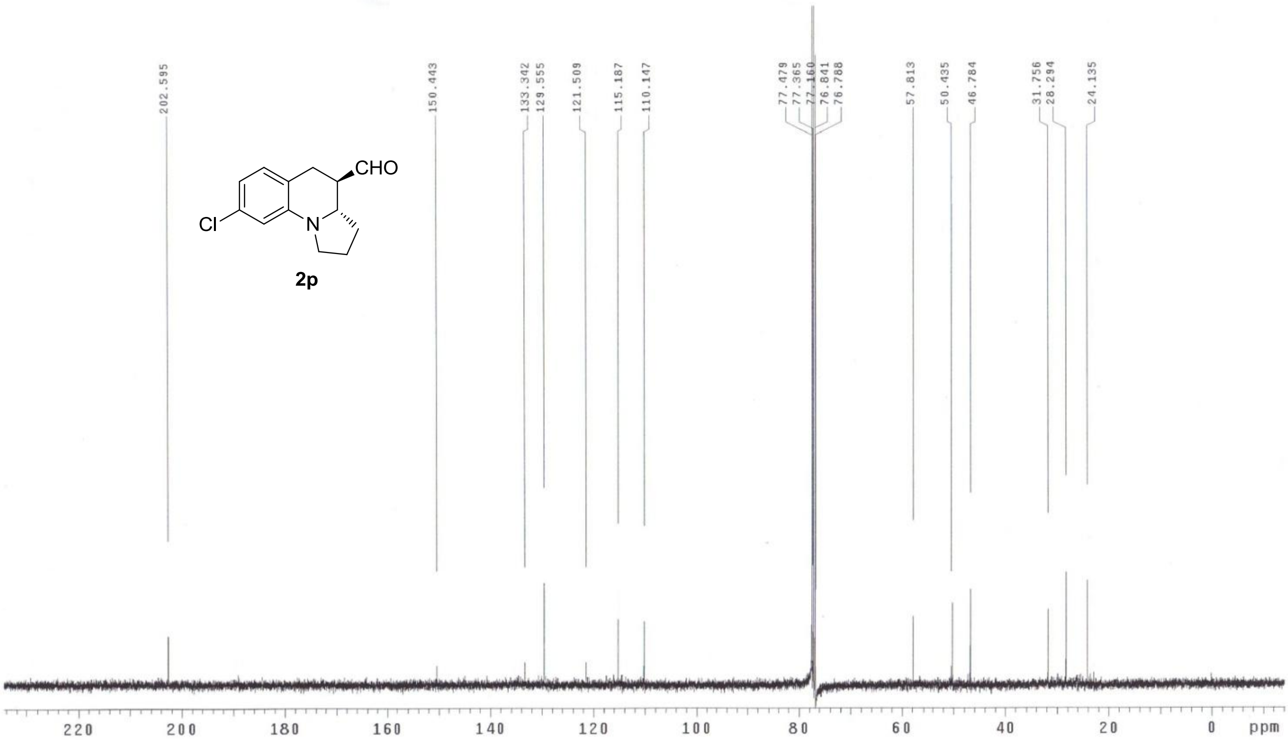
| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 9.0833 | 24313.7227 | BV | 35.0000 | 49.7426 |
| 2 | 9.6000 | 24565.3788 | VB | 43.0000 | 50.2574 |

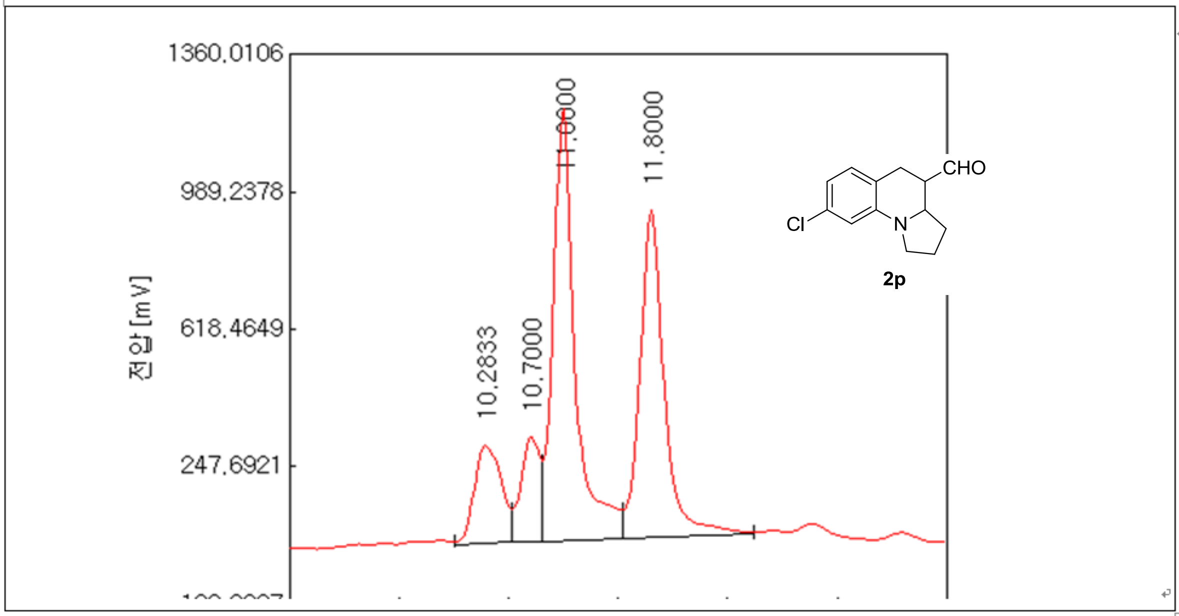



분석 결과

| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 10.3833 | 190.7781 | FF | 24.0000 | 6.4630 |
| 2 | 10.8167 | 2761.0712 | FF | 55.0000 | 93.5370 |

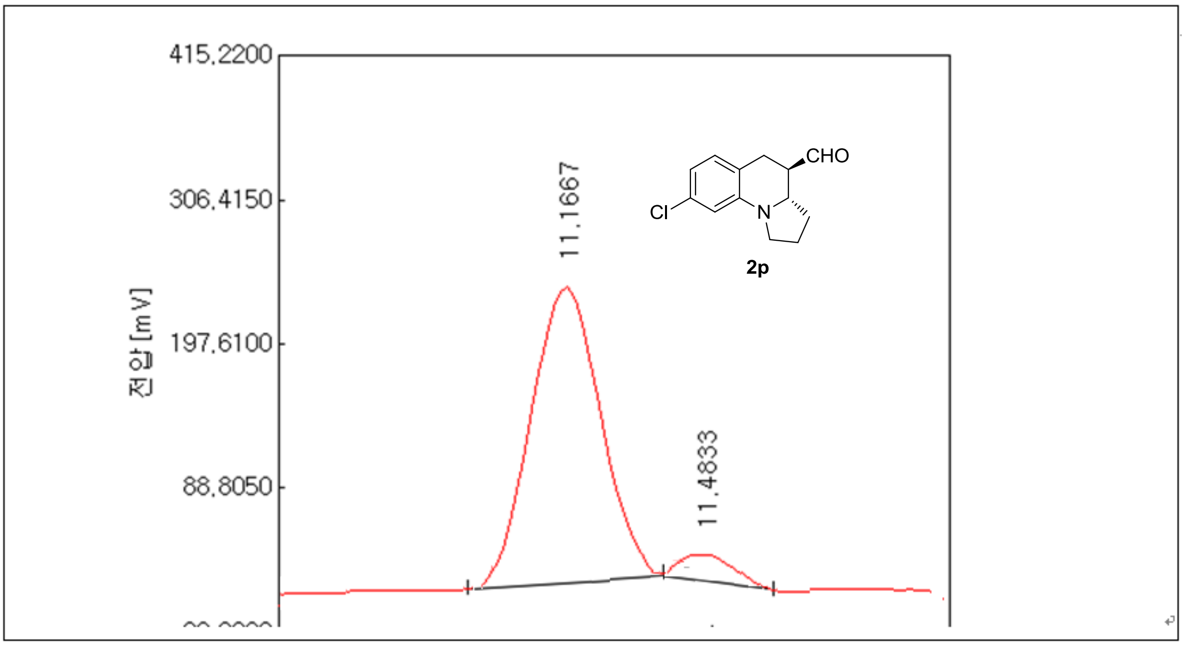

9.910
9.905
6.953
6.933
6.565
6.560
6.545
6.540
6.413
6.408
3.520
3.507
3.494
3.482
3.469
3.456
3.388
3.384
3.366
3.361
3.343
3.339
3.214
3.196
3.191
3.172
3.168
3.149
2.959
2.948
2.920
2.908
2.882
2.880
2.852
2.849
2.812
2.810
2.420
2.415
2.409
2.404
2.385
2.378
2.374
2.363
2.348
2.333
2.320
2.175
2.171
2.157
2.154
2.139
2.122
2.022
2.005
1.998
1.990
1.982
1.975
1.968
1.958
1.951
1.944
1.601
CHO
Cl
N
2p
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.03
0.96
1.00
1.01
1.08
1.31
1.11
1.13
0.78
1.31
1.22
1.55
0.76


202.595
150.443
133.342
129.555
121.509
115.187
110.147
77.479
77.365
77.160
76.841
76.788
57.813
50.435
46.784
31.756
28.294
24.135
CHO
Cl
N
2p
220
200
180
160
140
120
100
80
60
40
20
0
ppm



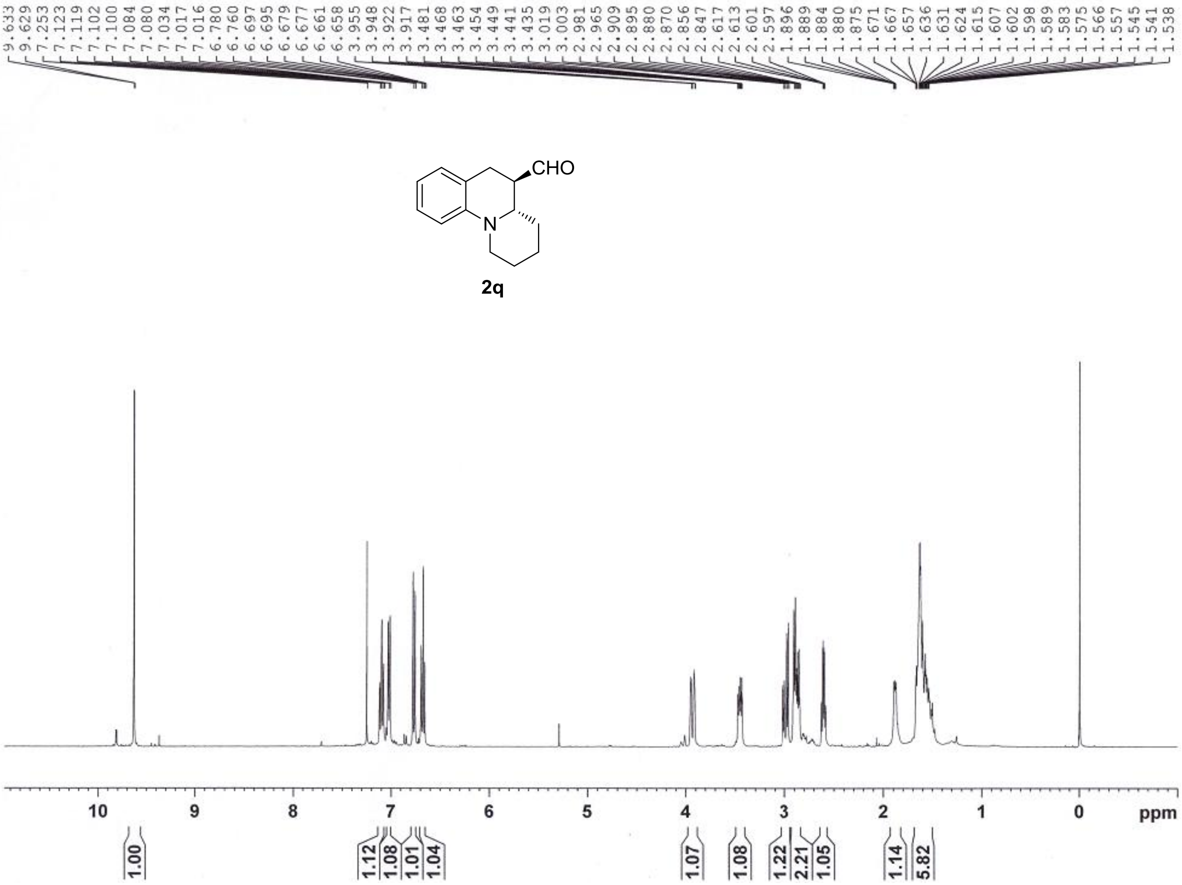

분석 결과

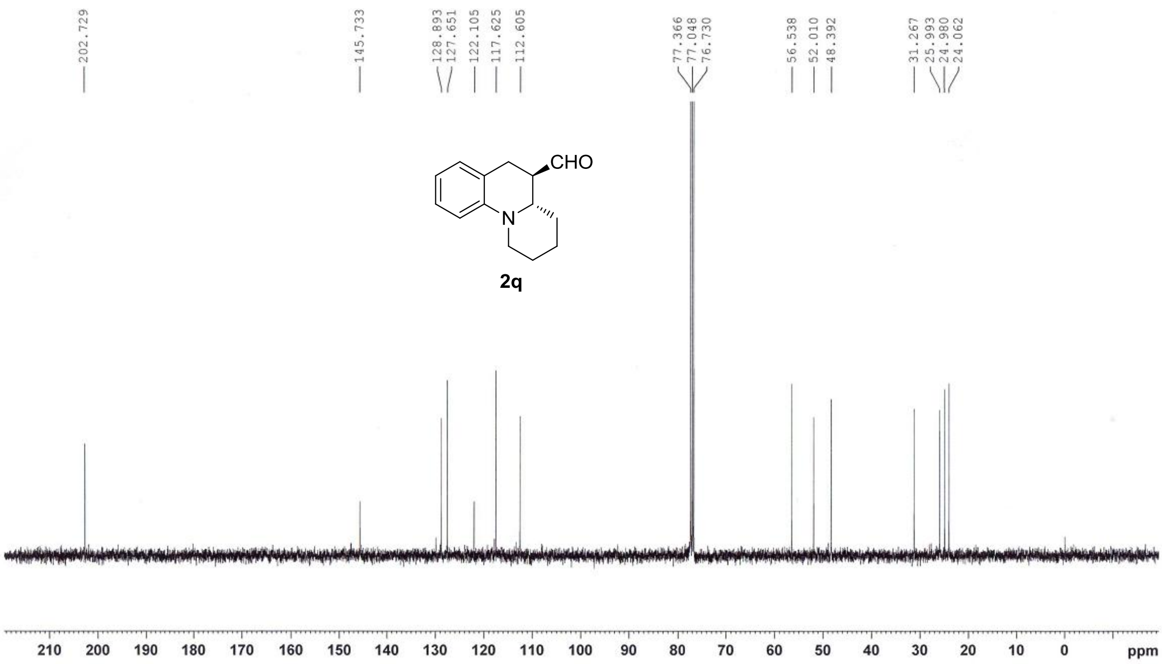
| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 10.2833 | 4670.7695 | VV | 32.0000 | 11.8348 |
| 2 | 10.7000 | 3381.9621 | VV | 16.0000 | 8.5692 |
| 3 | 11.0000 | 17186.2143 | VV | 44.0000 | 43.5466 |
| 4 | 11.8000 | 14227.3483 | VV | 72.0000 | 36.0494 |

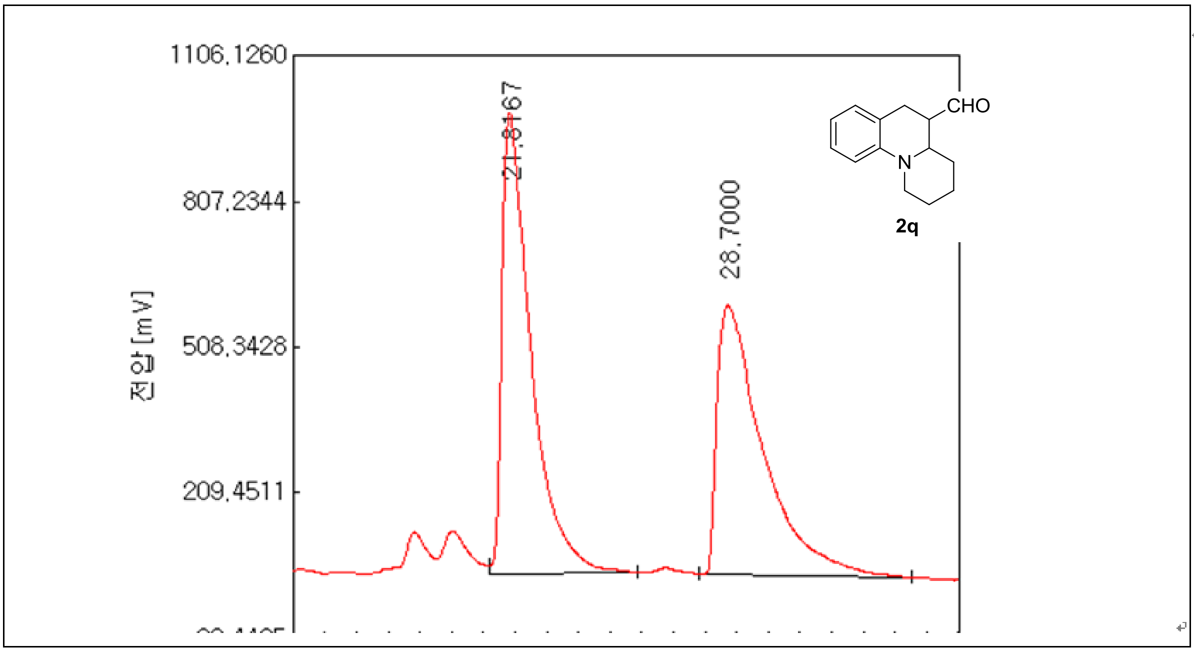



분석 결과

| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 11.1667 | 2363.7984 | FF | 28.0000 | 95.0924 |
| 2 | 11.4833 | 121.9919 | FF | 16.0000 | 4.9076 |

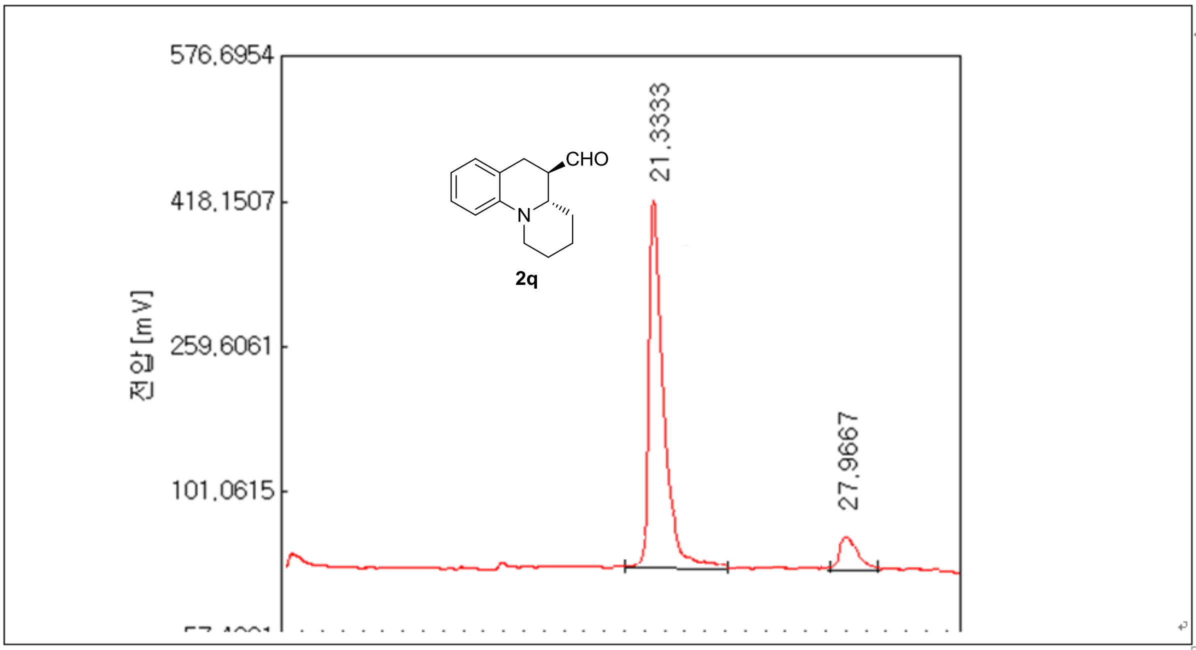

CHO
N
2q
ppm


CHO
N
2q
ppm



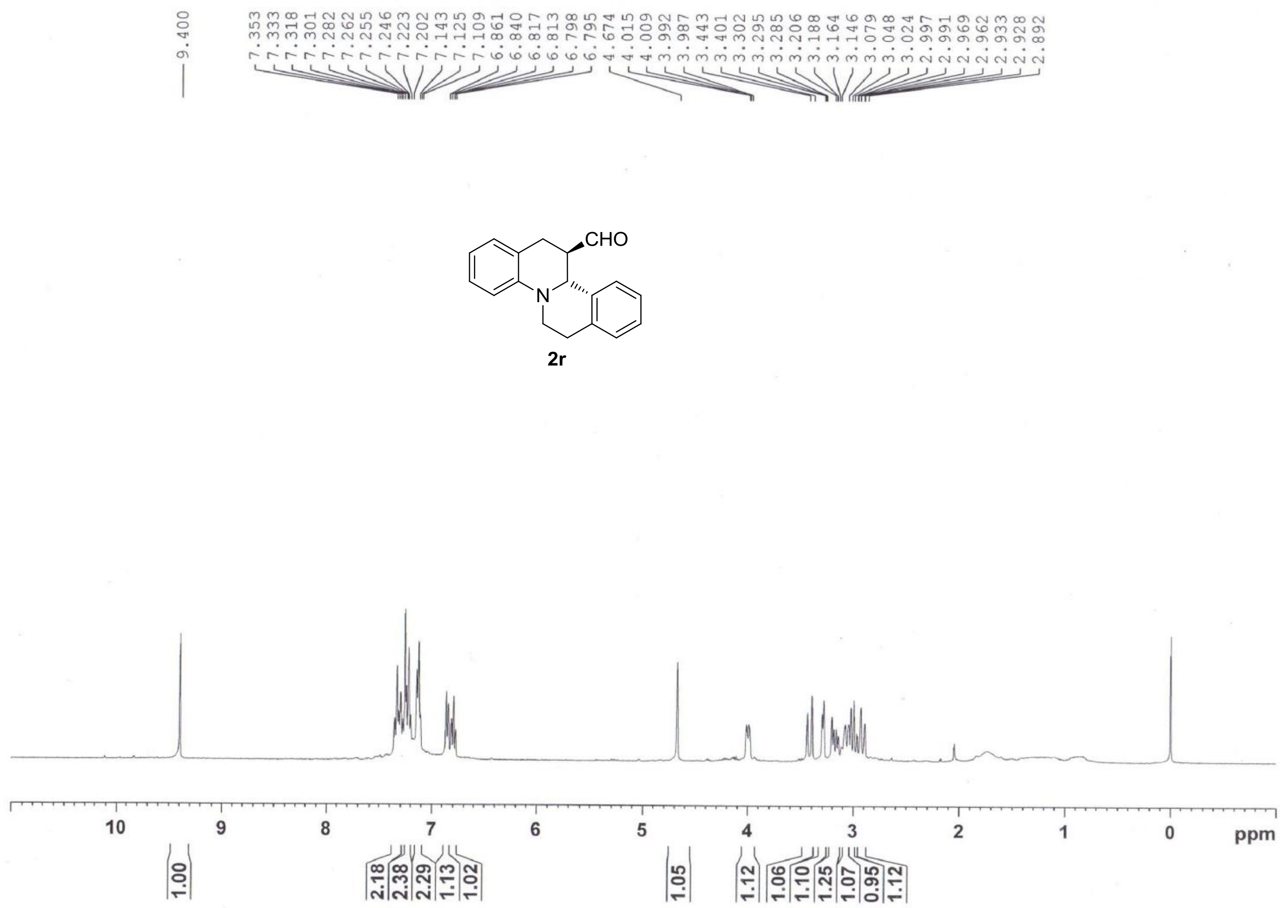

분석 결과

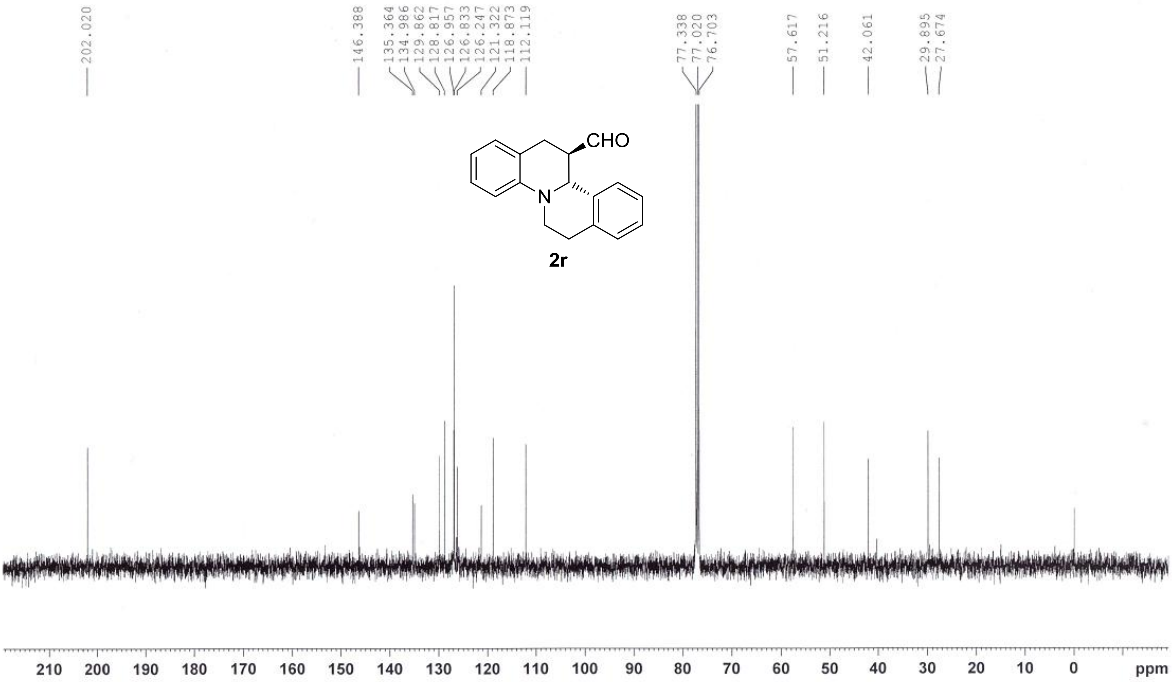
| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 21.8167 | 62411.8779 | BB | 281.0000 | 51.9628 |
| 2 | 28.7000 | 57696.8101 | FF | 402.0000 | 48.0372 |

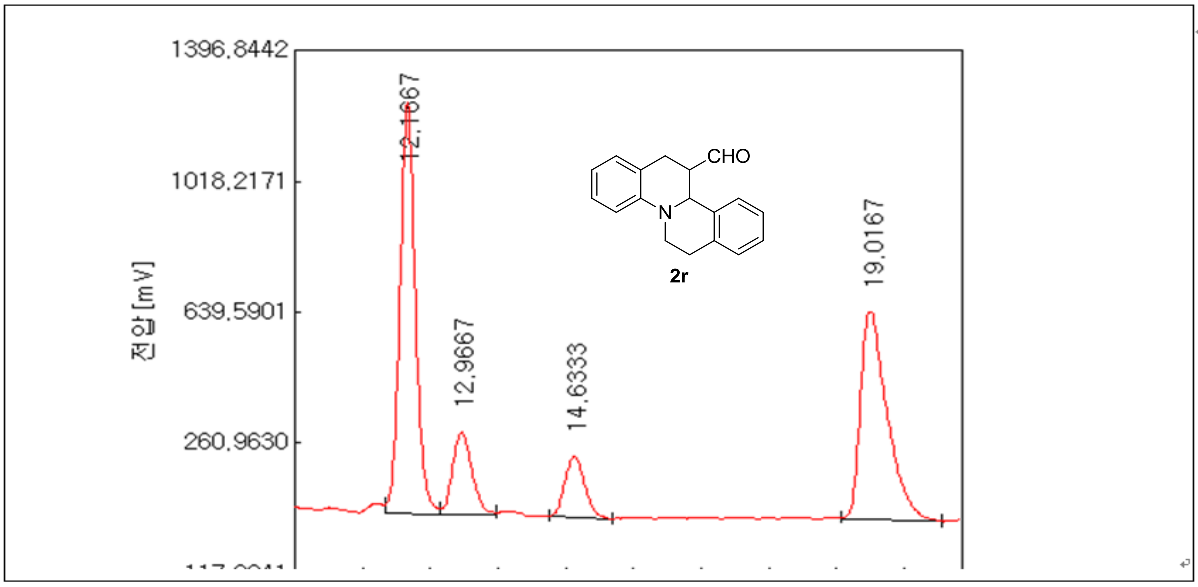



분석 결과

| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 21.3333 | 10743.1187 | PB | 170.0000 | 89.7214 |
| 2 | 27.9667 | 1230.7429 | FF | 110.0000 | 10.2786 |

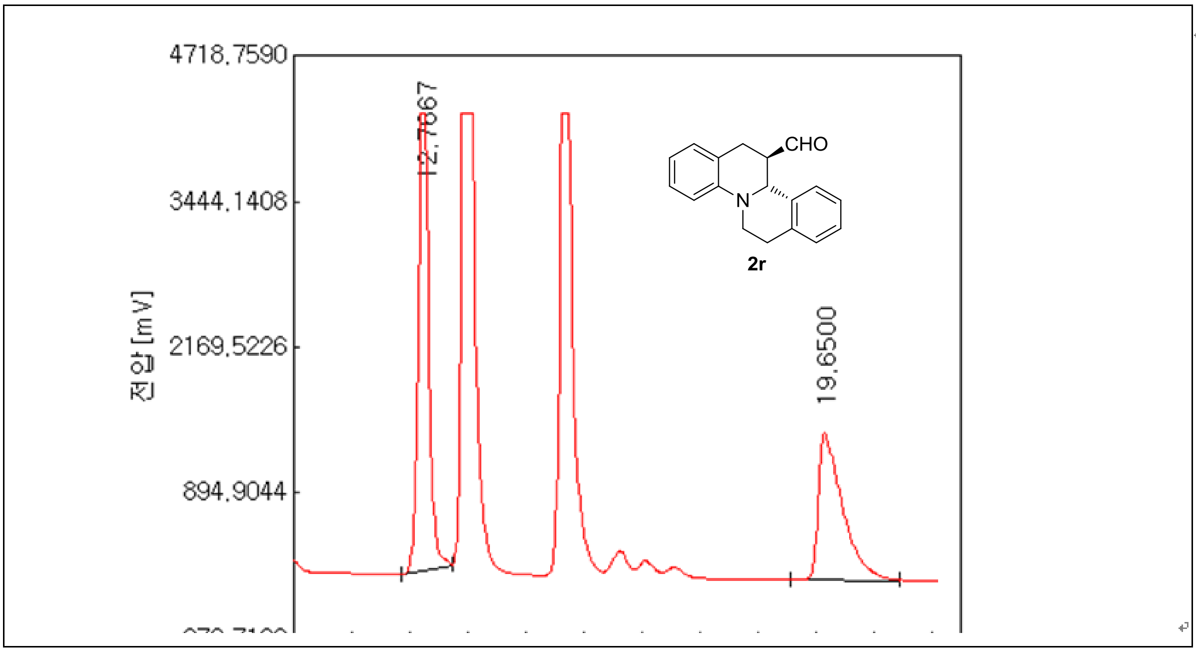

9.400
7.353
7.333
7.318
7.301
7.282
7.262
7.255
7.246
7.223
7.202
7.143
7.125
7.109
6.861
6.840
6.817
6.813
6.798
6.795
4.674
4.015
4.009
3.992
3.987
3.443
3.401
3.302
3.295
3.285
3.206
3.188
3.164
3.146
3.079
3.048
3.024
2.997
2.991
2.969
2.962
2.933
2.928
2.892
CHO
N
2r
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
2.18
2.38
2.29
1.13
1.02
1.05
1.12
1.06
1.10
1.25
1.07
0.95
1.12


202.020
146.388
135.364
134.986
129.862
128.817
126.957
126.833
126.247
121.322
118.873
112.119
77.338
77.020
76.703
57.617
51.216
42.061
29.895
27.674
CHO
N
2r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



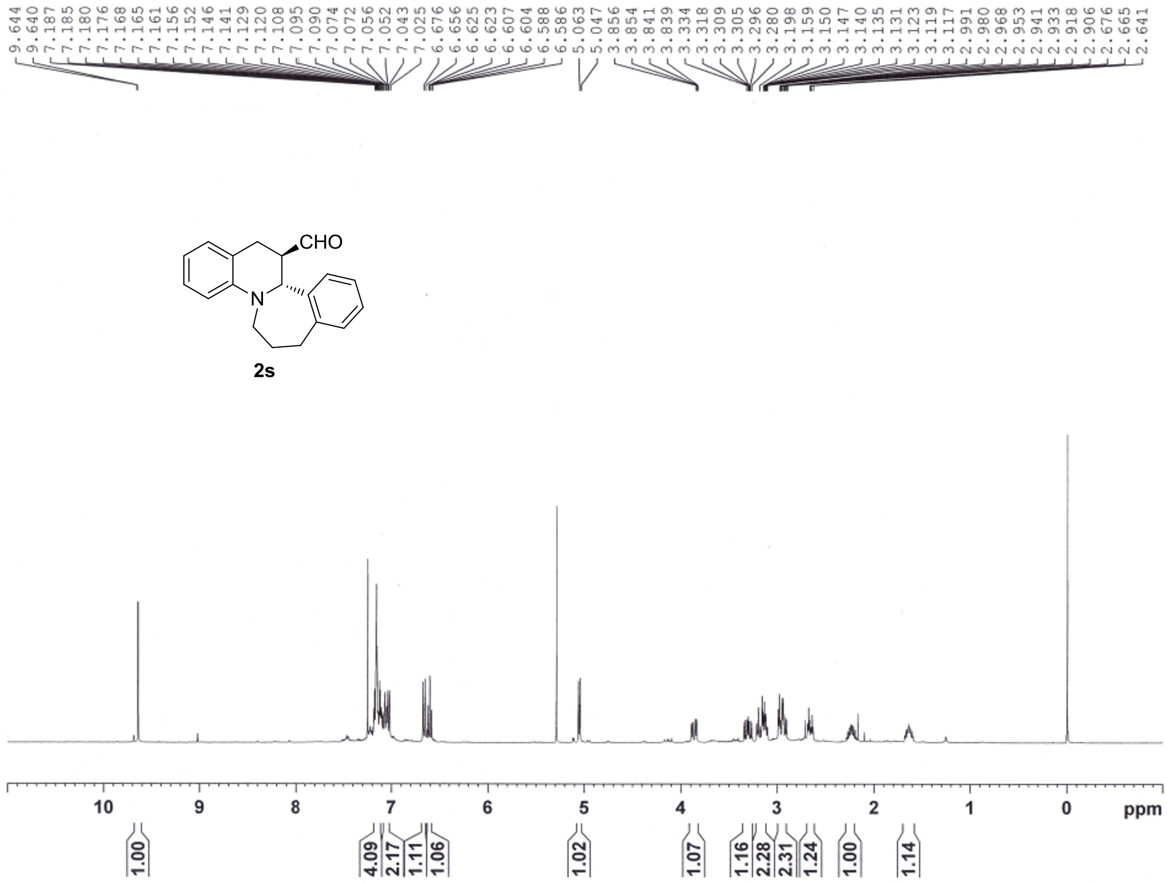

분석 결과

| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 12.1667 | 19434.4534 | BV | 49.0000 | 43.0987 |
| 2 | 12.9667 | 4934.6017 | BV | 50.0000 | 10.9432 |
| 3 | 14.6333 | 3667.6977 | BV | 55.0000 | 8.1337 |
| 4 | 19.0167 | 17056.1186 | BB | 89.0000 | 37.8244 |

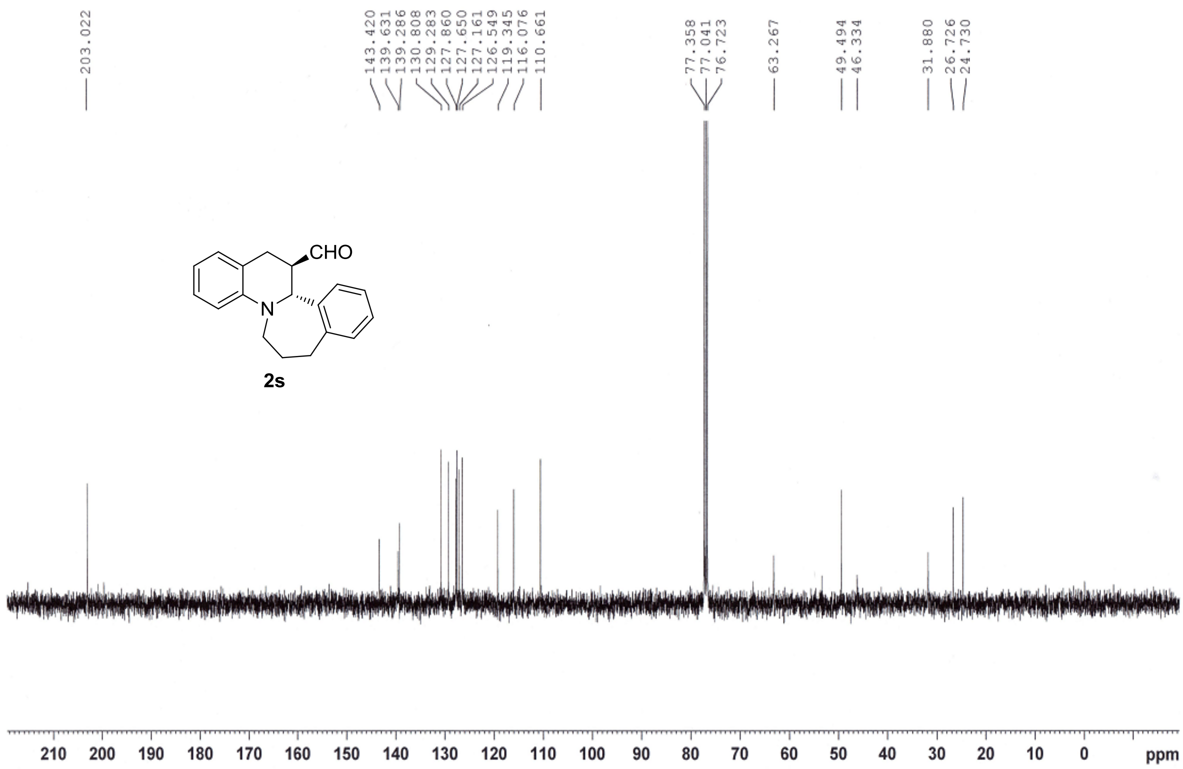



분석 결과

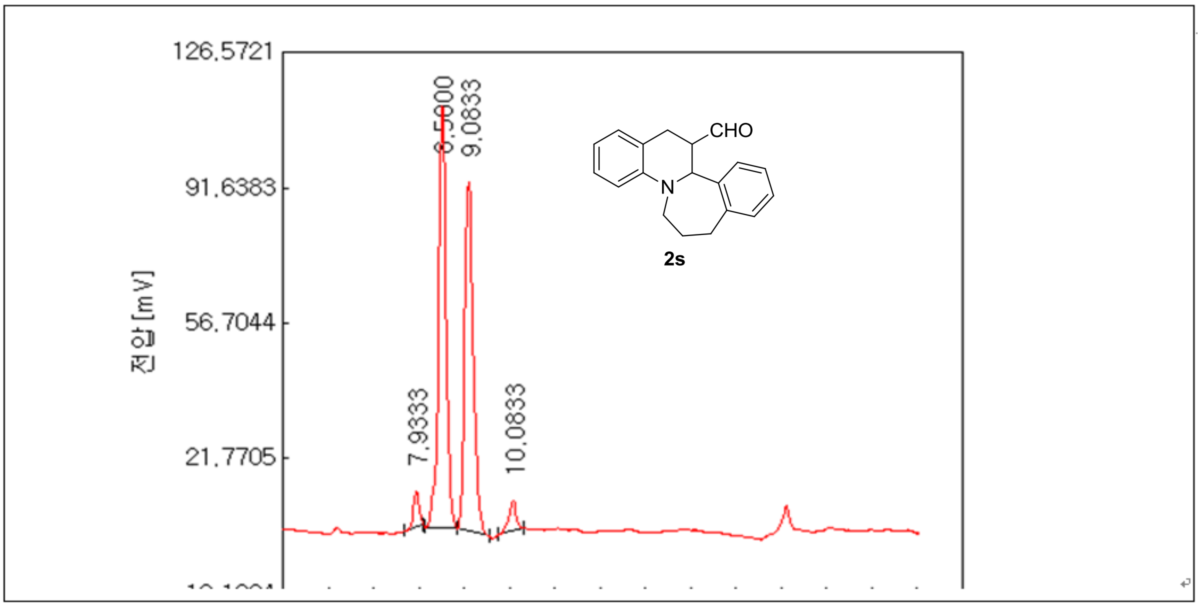
| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 12.7667 | 54708.6472 | BB | 52.0000 | 58.7746 |
| 2 | 19.6500 | 38373.4720 | BB | 113.0000 | 41.2254 |


9.644
9.640
7.187
7.185
7.180
7.176
7.168
7.165
7.161
7.156
7.152
7.146
7.141
7.129
7.120
7.108
7.095
7.090
7.074
7.072
7.056
7.052
7.043
7.025
6.676
6.656
6.625
6.623
6.607
6.604
6.588
6.586
5.063
5.047
3.856
3.854
3.841
3.839
3.334
3.318
3.309
3.305
3.296
3.280
3.198
3.159
3.150
3.147
3.140
3.135
3.131
3.123
3.119
3.117
2.991
2.980
2.968
2.953
2.941
2.933
2.918
2.906
2.676
2.665
2.641
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
4.09
2.17
1.11
1.06
1.02
1.07
1.16
2.28
2.31
1.24
1.00
1.14

**2s**

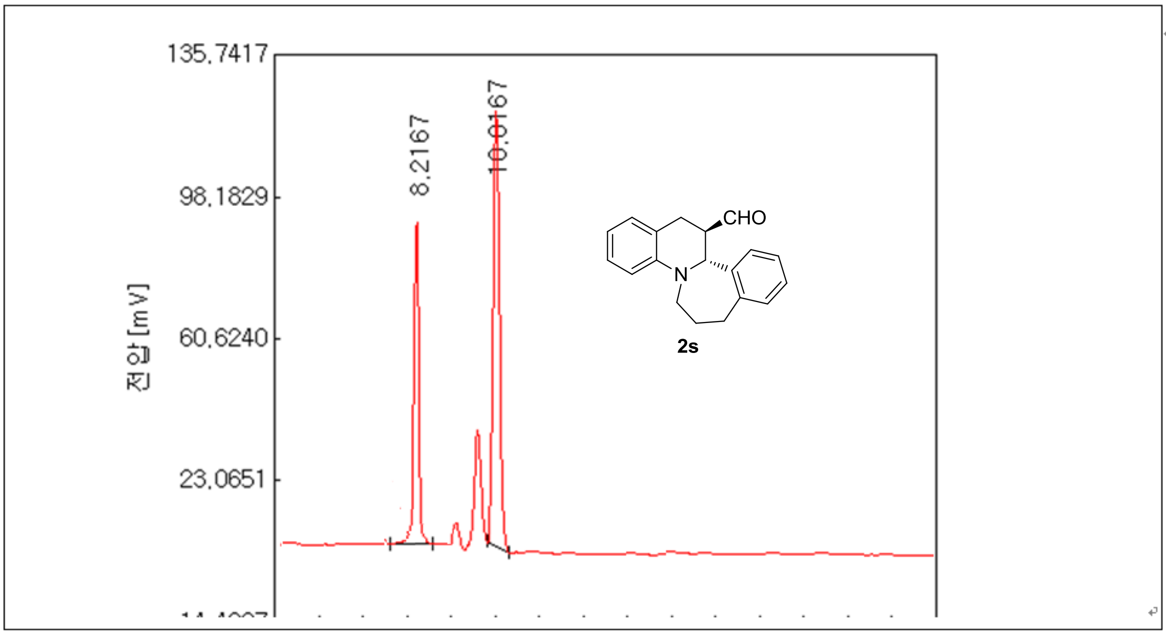

203.022
143.420
139.631
139.286
130.808
129.283
127.860
127.650
127.161
126.549
119.345
116.076
110.661
77.358
77.041
76.723
63.267
49.494
46.334
31.880
26.726
24.730
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

**2s**



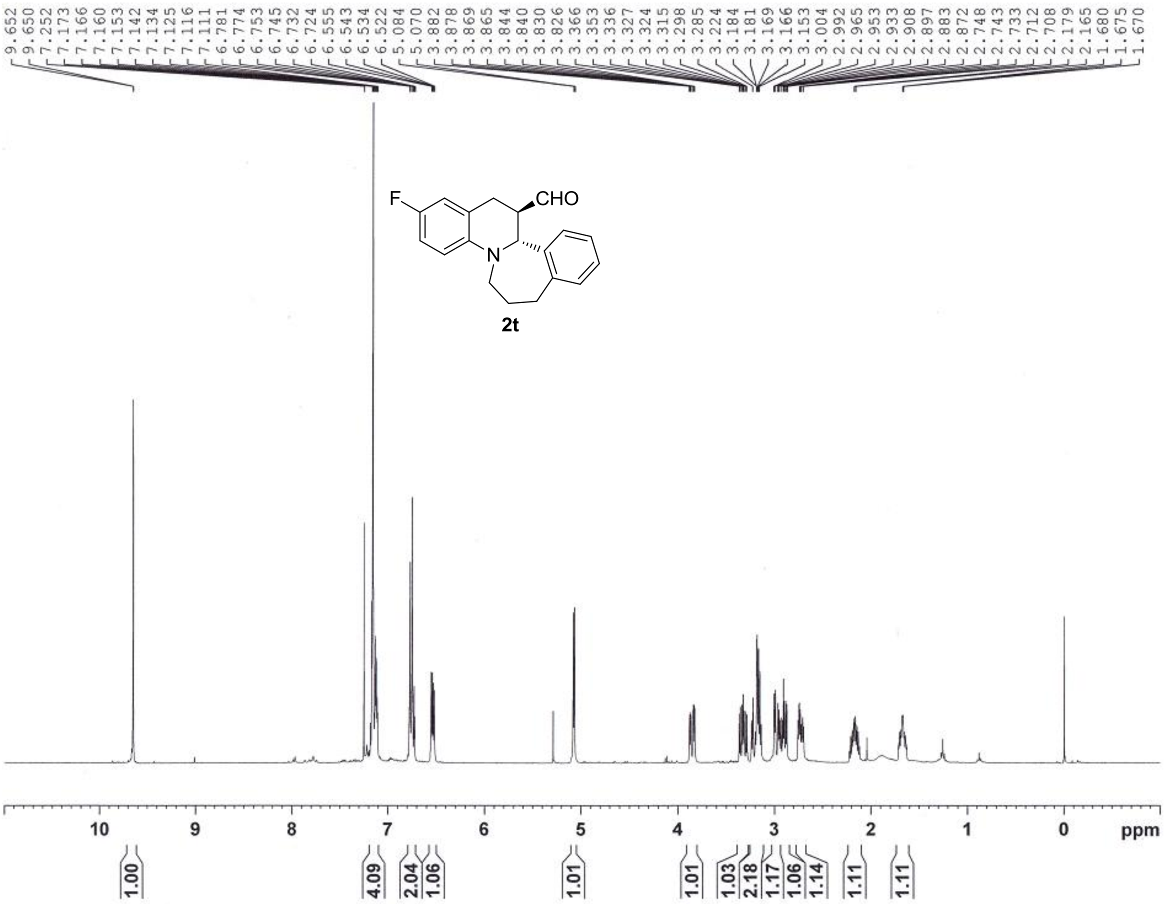

분석 결과

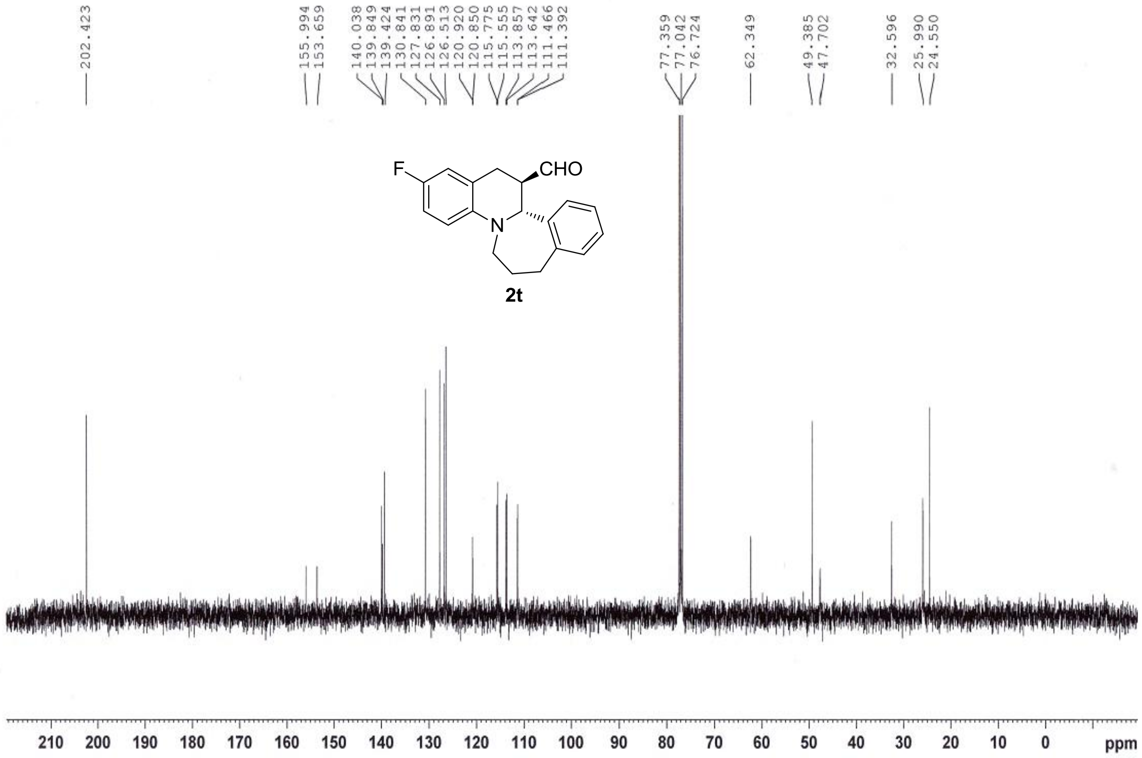
| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 7.9333 | 85.6473 | FF | 25.0000 | 3.1472 |
| 2 | 8.5000 | 1313.3456 | FF | 42.0000 | 48.2605 |
| 3 | 9.0833 | 1232.2616 | FF | 43.0000 | 45.2810 |
| 4 | 10.0833 | 90.1105 | FF | 34.0000 | 3.3112 |

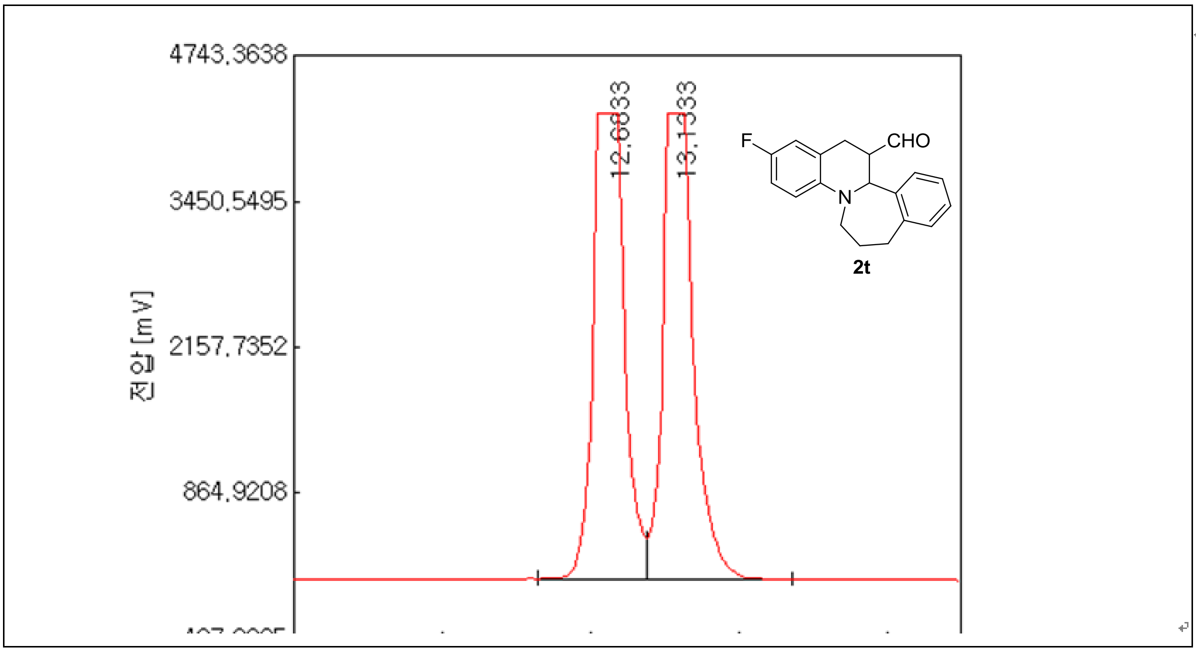



분석 결과

| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 8.2167 | 620.1112 | BB | 20.0000 | 33.9485 |
| 2 | 10.0167 | 1206.5124 | BB | 31.0000 | 66.0515 |

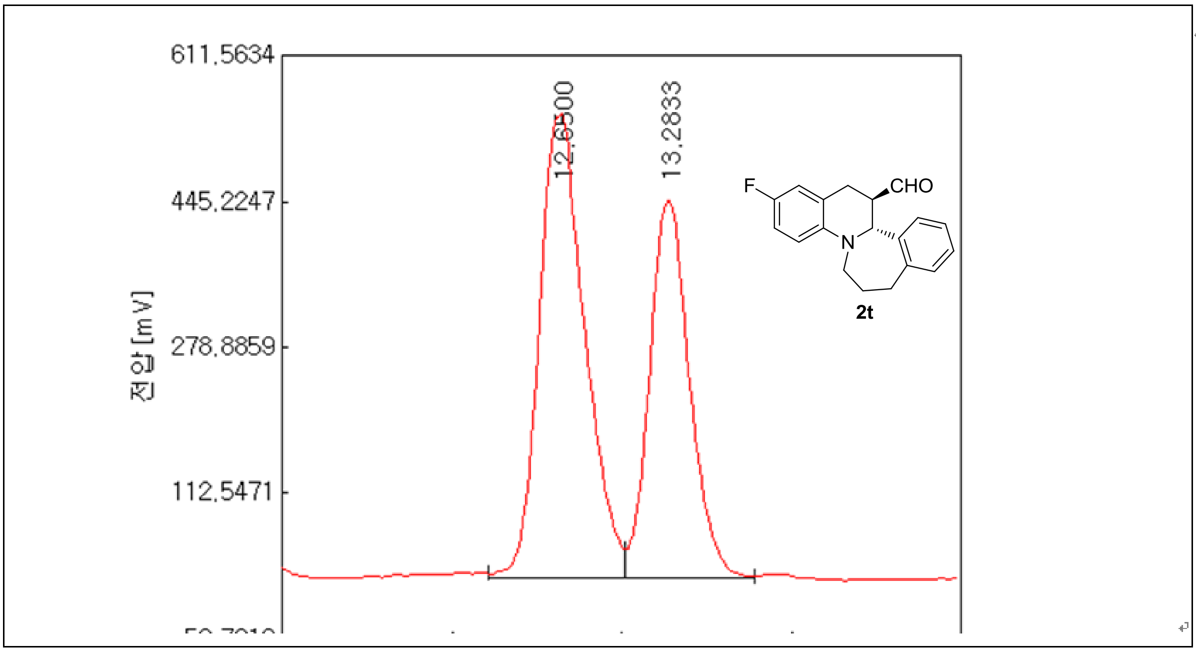

9.652
9.650
7.252
7.173
7.166
7.160
7.153
7.142
7.134
7.125
7.116
7.111
6.781
6.774
6.753
6.745
6.732
6.724
6.555
6.543
6.534
6.522
5.084
5.070
3.882
3.878
3.869
3.865
3.844
3.840
3.830
3.826
3.366
3.353
3.336
3.327
3.324
3.315
3.298
3.285
3.224
3.184
3.181
3.169
3.166
3.153
3.004
2.992
2.965
2.953
2.933
2.908
2.897
2.883
2.872
2.748
2.743
2.733
2.712
2.708
2.179
2.165
1.680
1.675
1.670
F
CHO
N
2t
ppm
1.00
4.09
2.04
1.06
1.01
1.01
1.03
2.18
1.17
1.06
1.14
1.11
1.11


202.423
155.994
153.659
140.038
139.849
139.424
130.841
127.831
126.891
126.513
120.920
120.850
115.775
115.555
113.857
113.642
111.466
111.392
77.359
77.042
76.724
62.349
49.385
47.702
32.596
25.990
24.550
F
CHO
N
2t
ppm




분석 결과

| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 12.6833 | 64276.9990 | BV | 44.0000 | 50.3703 |
| 2 | 13.1333 | 63331.8893 | BB | 59.0000 | 49.6297 |




분석 결과

| 번호 | RT[분] | 면적[mV*s] | 형태 | 폭[초] | 면적% |
|---|---|---|---|---|---|
| 1 | 12.6500 | 10223.3796 | BV | 48.0000 | 58.2676 |
| 2 | 13.2833 | 7322.1752 | VB | 46.0000 | 41.7324 |