Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary Information

Asymmetric Hydrogenation of Quinazolinium Salts Catalysed by Halide-bridged Dinuclear Iridium Complexes bearing Chiral Diphosphine Ligands

Yusuke Kita, Kosuke Higashida, Kenta Yamaji, Atsuhiro Iimuro, and Kazushi Mashima*

Department of Materials Engineering, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

Contents

1. General remarks

All reactions and manipulations involving air- and moisture-sensitive organometallic compounds were operated using the standard Schlenk techniques under argon. [{Ir(H)(chiral diphosphine)}$_2$(μ-Cl)$_3$]Cl, were prepared according to the literatures.[1,2] 1,4-Dioxane was dried and deoxygenated by distillation over sodium benzophenone ketyl under argon, and ethanol was distilled from magnesium ethoxide under argon. ^{i}PrOH was distilled from the calcium hydride. Alternatively, DCM, Et_2O, hexane, THF, toluene were dried and deoxygenated by using Grubbs column (Glass Counter Solvent Dispending System, Nikko Hansen & Co, Ltd.). Other chemicals were purchased and used without further purification. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F NMR (376 MHz) spectra were measured on Bruker Avance III-400 spectrometers. All ^{1}H NMR chemical shifts were recorded in ppm (δ) relative to tetramethylsilane or referenced to the chemical shifts of residual solvent resonances ($CHCl_3$ was used as internal standard, δ 7.26). All ^{13}C NMR chemical shifts were recorded in ppm (δ) relative to carbon resonances in $CDCl_3$ at δ 77.16. All ^{19}F NMR chemical shifts were recorded in ppm (δ) relative to carbon resonances in α,α,α-trifluorotoluene at δ -63.90. HPLC spectra were recorded on a JASCO UV-2075. Optical rotation values were recorded on a JASCO DIP-370 polarimeter at 589 nm (sodium lamp) and are given in 10^{-1} deg cm^2 g^{-1}. Mass spectra were obtained on and JEOL JMS-700. All melting points were recorded on BUCHI Melting Point M-565. Flash column chromatography was performed using silica gel 60 (0.040-0.0663 nm, 230-400 mesh ASTM). Hydrogenation reaction was conducted using TAIATSU stainless autoclave.

2. Preparation of substituted quinazolinium salt

2.1. Synthesis of substituted quinazoline

General procedure for preparation of substituted quinazolines (2a, 2c, 2i, 2j, 2l).[3]

Corresponding 2-aminobenzophenone (9.3 mmol), NIS (0.429 g, 1.9 mmol, 0.2 equiv.), TBHP (70% aq, 36.5 mmol, 3.9 equiv.) and NH_4OAc (1.83 g, 23.8 mmol, 2.6 equiv.) were added to a 200 mL Schlenk in ice bath, followed by addition of DMA (45 mL) as solvent. The mixture was stirred at 100 °C for 8 hours. The solution was cooled to room temperature, added excess amount of $Na_2S_2O_3$ and water and stirred at r.t. overnight. The mixture was extracted with EtOAc, the combined organic layer was dried over Na_2SO_4, filtered and evaporated in vacuo. The residue was purified by flash column chromatography (hexane : EtOAc = 4 : 1) to afford substituted quinazoline in moderate to high yield.

General procedure for preparation of substituted quinazolines (2b, 2d, 2e, 2f, 2g, 2h, 2k).

A mixture of 4-chloroquinazoline (843 mg, 5.0 mmol), Boronic Acid Reagent (7.5 mmol, 1.5 equiv.), PPh_3 (262 mg, 1.0 mmol, 0.2 equiv.), $Pd(OAc)_2$ (112 mg, 0.5 mmol, 0.1 equiv.) and K_2CO_3

(2.07 g, 15.0 mmol, 3.0 equiv.) in toluene (60 mL) and EtOH (4 mL) under argon atmosphere was stirred at the reflux temperature for 12 h. After addition of water a mixture was extracted with EtOAc, and the combined organic layers were concentrated in vacuo. The resulting crude product was purified by flash column chromatography (hexane : EtOAc = 4 : 1) to afford substituted quinazoline in moderate to high yield.

2.2. Synthesis of Substitued quinazolinium salt (2a-HCl, 2l-HCl, 2a-HBr, 2a-HI, 2a-HNO_3)

Typical procedure for preparation of 4-substituted quinazolinium chloride.

To a solution of the 4-phenylquinazoline (3.66 g, 17.8 mmol) in toluene, excess amount of HCl (1.0 M / Et_2O) was added and stirred overnight. HCl and solvent were removed in vacuo and the crude product was washed with cooled Et_2O to afford 4-phenylquinazolinium chloride (4.04 g, 16.7 mmol, 94% yield).

Synthetic procedure for 4-substituted quinazolinium bromide (2a-HBr).

To a solution of the 4-phenylquinazoline (257 mg, 1.25 mmol) in toluene, excess amount of conc. HBr aq was added and stirred overnight. HBr and solvent were removed in vacuo and the crude product was washed with hexane to afford 4-phenylquinazolinium bromide (450 mg, 1.22 mmol, 98% yield).

Synthetic procedure for 4-substituted quinazolinium iodide (2a-HI).

To a solution of the 4-phenylquinazoline (291 mg, 1.41 mmol) in toluene, conc. HI aq (3.0 equiv.) was added and stirred for 15 min. HI and solvent were removed in vacuo and the crude product was washed with EtOAc to afford 4-phenylquinazolinium iodide (184 mg, 0.51 mmol, 36% yield).

Synthetic procedure for 4-substituted quinazolinium nitrate (2a-HNO_3).

To a solution of the 4-phenylquinazoline (248 mg, 1.20 mmol) in toluene, excess amount of conc. HNO_3 aq was added and stirred overnight. HNO_3 and solvent were removed in vacuo and the crude product was washed with hexane to afford 4-phenylquinazolinium nitrate (308 mg, 1.14 mmol, 95% yield).

3.1. General procedure for the Ir-catalyzed asymmetric hydrogenation of quinazolines.

An Iridium dinuclear complex (2.4 μmol, 1.0 mol%) and quinazolinium chloride (0.24 mmol) were added to a glass tube in the autoclave and the tube was charged with argon gas. Dry DCM (3 mL) was added into a glass tube in the autoclave, and charged with H_2 and the pressure was increased to desired pressure. The reaction mixture was stirred for periodic time. After release of

H_2, the mixture was poured into a saturated $NaHCO_3$ and extracted with DCM. The organic layer was dried over Na_2SO_4. After removal of the solvent, the crude product was purified by flash column chromatography (hexane : EtOAc = 4 : 1 to EtOAc) to afford tetrahydroquinazoline. The enantiomeric excesses were determined by HPLC analysis.

3.2. Procedure for Ir-catalysed asymmetric hydrogenation of quinazolium salts.

An iridinium complex (7.2 μmol, 1.0 mol%) and qunazoliumn salt (0.72 mmol, 1 equiv.) were added to a right size of glass tube in the reactor under atmosphere and the tube was charged with argon gas. Dry DCM (9.0 mL) were added into the glass tube in the reactor from the inlet, and charged with H_2 and the pressure was increased to desired pressure. The reaction mixture was stirred at 50 °C for periodic time. After release of H_2, all volatiles were removed under reduced pressure to give a yellow solid. The solid was washed with ether 3 times and all volatiles were removed under reduced pressure to give a corresponding salt as a yellow solid. The product was not stable in column conditions and used for further reaction without any purification.

3.3. Procedure for preparation of 3,4-dihydro-4-phenylquinazoline (4a).

To a solution of the quinazolinium chloride (5.0 mmol) in Dry THF under Ar, PhLi (5.5 mmol, 1.6M / butyl ether) was added at 0 °C and stirred at r.t. for 3h. The mixture was poured into a saturated $NaHCO_3$ and extracted with EtOAc. After removal of the solvent, the crude product was washed with cold EtOH to afford the 3,4-dihydro-4-phenylquinazoline (**4a**) (2.43 mmol, 48% yield).

3.4. Procedure for benzylation of 4-isopropyl-3,4-dihydroquinazoline (4l).

4-Isopropyl-3,4-dihydroquinazolinium chloride **4l-HCl** (114 mg, 0.54 mmol) was dissolved in DCM. A saturated aqueous solution of $NaHCO_3$ was add to the solution and extracted with DCM. The organic layer was dried over Na_2SO_4. After evaporation, the yellow oil was replaced into a 20 mL Schlenk with a magnetic stir bar and charged with argon gas. Dry toluene (10 mL) was added into the Schlenk. Benzylbromide was added dropwise to the solution at 0 °C. The reaction mixture was stirred for 30 min room temperature and for 48 h at 70 °C. A saturated aqueous solution of $NaHCO_3$ was add to the reaction mixture and was washed with ether to remove the excess of benzylbromide 5 times and extracted with DCM 5 times. The organic layer was dried over Na_2SO_4. All volatiles were removed under reduced pressure to give an ash solid.

3.5. Procedure for iridium-NHC complex (6).

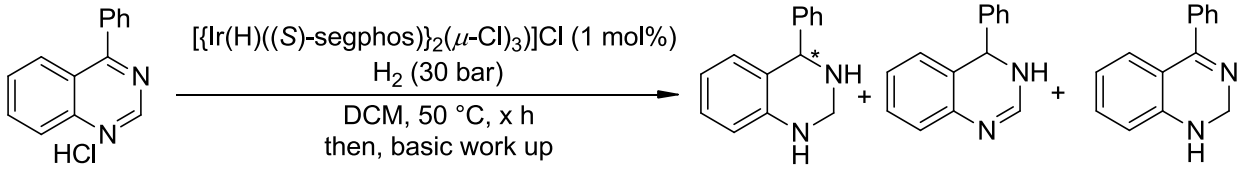
In a glovebox, 20 mL Schlenk equipped with magnetic stir bar and Teflon cap was charged with KO^tBu (1.2 equiv.) and benzylated **4l** (1.0 equiv.) then removed from the glovebox. Dry THF (1 mL per 0.1 mmol) was added. The resulting suspension was stirred at r.t. for 3 h at which time

$[Ir(\mu\text{-Cl})(cod)]_2$ (0.5 equiv.) was added in one shot. After stirring for 24 h, the suspension was filtered through a pad of silica gel with DCM. The filtrate was the concentrated and the residue thus obtained was purified via flash chromatography (hexane : EtOAc = 95 : 5) to yield Iridium-NHC complex **6**.

4. Time-course experiments

(*S*)-**1b** (2.4 μmol, 1.0 mol%) and 4-phenylquinazolinium chloride (**2a-HCl**) (0.24 mmol) were added to a glass tube in the autoclave and the tube was charged with argon gas. Dry DCM (3 mL) was added into a glass tube in the autoclave, and charged with H_2 and the pressure was increased to desired pressure. The reaction mixture was stirred for periodic time. After release of H_2, the mixture was poured into a saturated $NaHCO_3$ and extracted with DCM. The organic layer was dried over Na_2SO_4. After removal of solvent, the yields were determined by ^1H NMR analysis using phenanthrene as an internal standard.

Table S1. Time course experiment.



3a **4a** **5a**

Time	Conv.	Yield of **3a**	Yield of **4a**	Yield of **5a**
0	0	0	0	0
2	31	0	1	30
4	65	0	2	63
6	98	46	10	42
8	99	87	12	0
10	100	89	11	0
16	100	89	11	0
48	100	90	10	0

5. X-ray crystallographic analysis

A crystal of (*S*)-**3i** was synthesized in large scale according to procedure of asymmetric hydrogenation. To a solution of the product (96% ee) in toluene, excess amount of conc. HBr aq was added and stirred for 30 min. The product salt (*S*)-**3i-HBr** was recrystallized from Et_2O/EtOH and obtained brown solid.

Crystal of (*S*)-**3i-HBr** was mounted on the CryoLoop (Hampton Research Corp.) with a layer of

light mineral oil and placed in a nitrogen stream at 113(1) K. Measurements were made on Rigaku AFC7R/Mercury CCD detector with graphite-monochromated Mo Kα (0.71075 Å) radiation. Crystal data and structure refinement parameters are listed in Table S2.

The structure of (*S*)-**3i-HBr** was solved by direact methods (SHELXS-97).[4] The structures were refined on F^2 by full-matrix least-squares method, using SHELXL-97. Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\Sigma w(Fo^2-Fc^2)^2]$ ($w = 1/[\sigma^2(Fo^2)+(aP)^2+bP]$), where $P = (\mathrm{Max}(Fo^2,0)+2Fc^2)/3$ with $\sigma^2(Fo^2)$ from counting statistics. The function *R*1 and *wR*2 were $(\Sigma||Fo|-|Fc||)/(\Sigma|Fo|)$ and $[\Sigma w (Fo^2-Fc^2)^2]]/\{\Sigma w (Fo^4)\}^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecule.[5] The Flack parameter[6] is the recent accepted method to determine the absolute configuration of a chiral structure. For publication quality assignment of chirality, the Flack parameter must be close to 0 with an error (esd) of <0.1 (10%). Based on the value of the Flack parameter for this **3i-HBr** in Table S2, the absolute configuration was determined as S isomer.

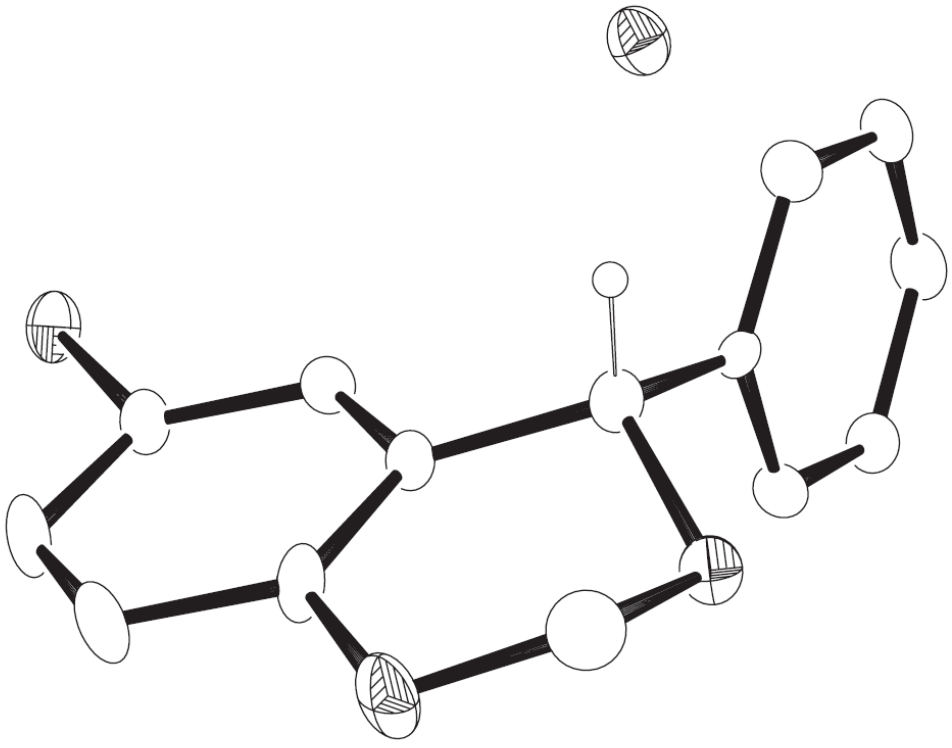


Figure S1. X-ray structure ORTEP plot of **3i**-HBr (thermal ellipsoids drawn at the 30% level).

Table S2. Crystal Data and Data Collection Parameters of **3i-HBr**.

empirical formula	$C_{14}H_{14}Br_2N_2$
formula weight	370.09
crystal system	orthorhombic
space group	*C* 222_1 (#20)
a, Å	7.3088(17)
b, Å	31.966(9)
c, Å	12.460(4)
α, deg.	90.0000
β, deg.	90.0000
γ, deg.	90.0000
V, $Å^3$	2911.0(14)
Z	8
D_{calcd}, g/cm^{-3}	1.689
μ[Mo-*K*α], mm^{-1}	5.570
T, K	113
crystal size, mm	0.31 x 0.25 x 0.25
θ range for data collection (deg.)	3.028 to 26.911
no. of reflections measured	13401
unique data (R_{int})	3143 (0.0871)
data/restraints/parameters	3143 / 163 / 0
*R*1 (*I* > 2.0σ(*I*))	0.0472
*wR*2 (*I* > 2.0σ(*I*))	0.0935
*R*1 (all data)	0.0612
*wR*2 (all data)	0.1014
GOF on F^2	0.999
Flack Parameter	0.033(11)
$\Delta\rho$, e $Å^{-3}$	1.00, -0.78

a) $R1 = (\Sigma||Fo|-|Fc||)/(\Sigma|Fo|)$ b) $wR2 = [\{\Sigma w(Fo^2-Fc^2)^2\}]/(\Sigma w(Fo^4)\}]^{1/2}$
The CCDC number of this complex is 1042856.

The iridium complex **6** was recrystallized from hexane and used for X-ray crystallographic analysis. The crystals were mounted on the CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 113(2) K. Measurements were made on a Rigaku RAXIS-RAPID Imaging Plate area detector with graphite monochromated Mo-Kα (0.71075 Å) radiation. Crystal data and structure refinement parameters were summarized in Table S3.

The structure of **6** was solved by direct methods (SHELXS-97).[4] The structure was refined on F^2 by full-matrix least-squares methods, using SHELXL-97. Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\Sigma w(Fo^2-Fc^2)^2]$ ($w = 1/[\sigma^2(Fo^2)+(aP)^2+bP]$)), where $P = (\mathrm{Max}(Fo^2,0)+2Fc^2)/3$ with $\sigma^2(Fo^2)$ from counting statistics. The function $R1$ and $wR2$ were $(\Sigma||Fo|-|Fc||)/(\Sigma|Fo|)$ and $[\Sigma w (Fo^2-Fc^2)^2]]/\{\Sigma w (Fo^4)\}^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecule.[5] Large solvent accessible voids in the lattice were involved in the crystal packing, but we could not find suitable solvent molecules. The Flack parameter[6] is the recent accepted method to determine the absolute configuration of a chiral structure. For publication quality assignment of chirality, the Flack parameter must be close to 0 with an error (esd) of <0.1 (10%). Based on the value of the Flack parameter for this **6** in Table S3, the absolute configuration was determined as S isomer.

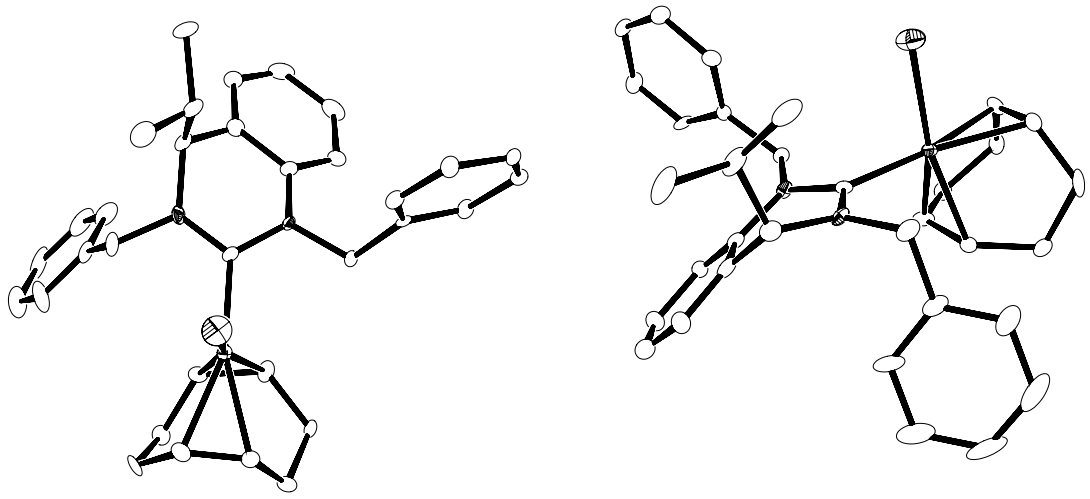


Figure S2. X-ray structure ORTEP plot of **6** (thermal ellipsoids drawn at the 30% level).

Table S3. Crystal Data and Data Collection Parameters of **6**.

empirical formula	$2(C_{33}H_{38}BrIrN_2)\ C_6$
formula weight	1541.67
crystal system	monoclinic
space group	$P2_1$ (#4)
a, Å	14.4388(5)
b, Å	14.3302(5)
c, Å	14.9599(5)
α, deg.	90.0000
β, deg.	94.1029(10)
γ, deg.	90.0000
V, Å^3	3087.43(18)
Z	4
D_{calcd}, g/cm^{-3}	1.658
μ[Mo-*K*α], mm^{-1}	5.646
T, K	113(2)
crystal size, mm	0.17 x 0.12 x 0.10
θ range for data collection (deg.)	3.05 to 27.43
no. of reflections measured	59618
unique data (R_{int})	13297 (0.0774)
data/restraints/parameters	13297 / 695 / 1
*R*1 (*I* > 2.0σ(*I*))	0.0393
*wR*2 (*I* > 2.0σ(*I*))	0.0688
*R*1 (all data)	0.0566
*wR*2 (all data)	0.0716
GOF on F^2	1.003
Flack Parameter	-0.022(4)
$\Delta\rho$, e Å^{-3}	1.364, -1.839

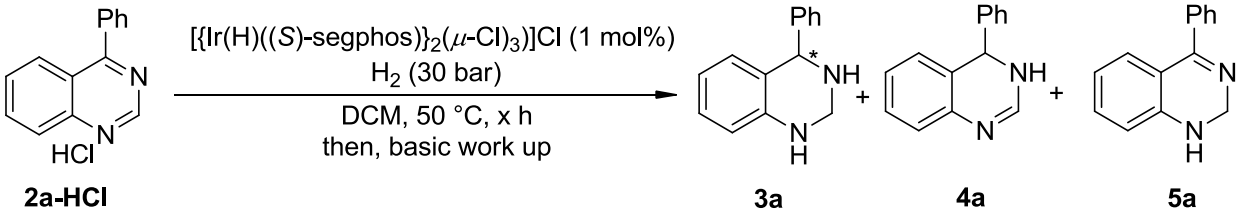
a) $R1 = (\Sigma||Fo|-|Fc||)/(\Sigma|Fo|)$ b) $wR2 = [\{\Sigma w(Fo^2-Fc^2)^2\}]/(\Sigma w(Fo^4))\}]^{1/2}$
The CCDC number of this complex is 1042857.

6. Additional data

6.1. Screening of the reaction temperature

(*S*)-**1b** (2.4 μmol, 1.0 mol%) and 2-phenylquinazolinium chloride (**2a-HCl**) (0.24 mmol) were added to a glass tube in the autoclave and the tube was charged with argon gas. Dry DCM (3 mL) was added into a glass tube in the autoclave, and charged with H_2 and the pressure was increased to desired pressure. The reaction mixture was stirred for periodic time. After release of H_2, the mixture was poured into a saturated $NaHCO_3$ and extracted with DCM. The organic layer was dried over Na_2SO_4. After removal of solvent, the yields were determined by ^1H NMR analysis using phenanthrene as an internal standard.

Table S4. Screening of the reaction temperature.



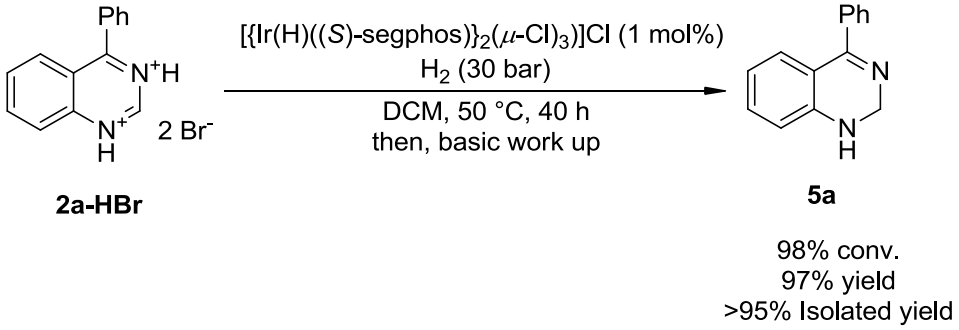
2a-HCl **3a** **4a** **5a**

Temperature [°C]	Conv.	Yield of **3a**	Ee of **3a**	Yield of **4a**	Yield of **5a**
30	86	Trace	Not Determined	Not Detected	86
50	>99	89	99	11	Not Detected
80	>99	66	98	25	Not Detected

6.2. Extension of the reaction time for asymmetric hydrogenation of 4-phenylquinazolinium bromide

(*S*)-**1b** (2.4 μmol, 1.0 mol%) and 2-phenylquinazolinium bromide (**2a-HBr**) (0.24 mmol) were added to a glass tube in the autoclave and the tube was charged with argon gas. Dry DCM (3 mL) was added into a glass tube in the autoclave, and charged with H_2 and the pressure was increased to desired pressure. The reaction mixture was stirred for 40 h. After release of H_2, the mixture was poured into a saturated $NaHCO_3$ and extracted with DCM. The organic layer was dried over Na_2SO_4. After removal of solvent, the yields were determined by ^1H NMR analysis using phenanthrene as an internal standard. The crude product was purified by flash column chromatography (hexane : EtOAc = 4 : 1 to EtOAc) to afford 1,2-dihydro-4-phenylquinazoline (**5a**).

Scheme S1. Extension of the reaction time for asymmetric hydrogenation of **2a-HBr**.



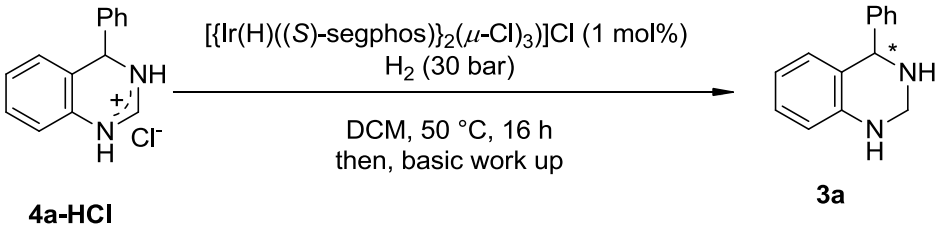
2a-HBr **5a**

98% conv.
97% yield
>95% Isolated yield

6.3. Reactivity of 3,4-dihydro-4-phenylquinazolinium chloride

(*S*)-**1b** (2.4 μmol, 1.0 mol%) and 3,4-dihydro-4-phenylquinazolinium chloride (**4a-HCl**) (0.24 mmol) were added to a glass tube in the autoclave and the tube was charged with argon gas. Dry DCM (3 mL) was added into a glass tube in the autoclave, and charged with H_2 and the pressure was increased to desired pressure. The reaction mixture was stirred for 40 h. After release of H_2, the mixture was poured into a saturated $NaHCO_3$ and extracted with DCM. The organic layer was dried over Na_2SO_4. After removal of solvent, the yields were determined by ^1H NMR analysis using phenanthrene as an internal standard.

Scheme S2. Reactivity of **4a-HCl** under the optimized conditions.

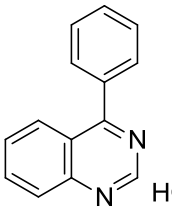


4a-HCl **3a**

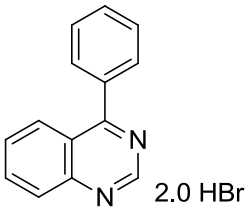
3% conv.
3% yield
Ee was not determined

.

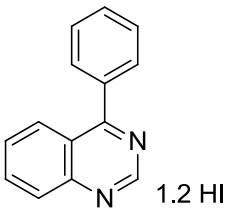
7. Spectral data



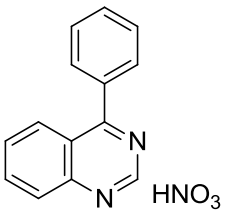
4-Phenylquinazolinium chloride (2a-HCl): White solid. mp: 107 °C (decomp.). IR (KBr, ν /cm^{-1}): 3421 w, 3018 w, 2404 m, 1901 w, 1621 m, 1566 s, 1480 m, 1444 w, 1378 s, 766 m. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 9.53 (s, 1H, NC*H*), 8.82 (d, *J* = 8.5 Hz, 1H, *Ar*), 8.48 (d, *J* = 8.5 Hz, 1H, *Ar*), 8.33 (t, *J* = 7.7 Hz, 1H, *Ar*), 8.05 (t, *J* = 7.8 Hz, 1H, *Ar*), 7.99 (d, *J* = 7.2 Hz, 2H, *Ar*), 7.82-7.68 (m, 3H, *Ar*). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 173.5, 147.6, 143.1, 138.7, 133.5, 133.2, 131.5, 131.2, 129.4, 128.8, 123.3, 122.4. MS (FAB$^+$) m/z calcd. for $C_{14}H_{11}N_2$ 207.0922 found 207.0921.



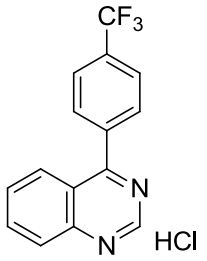
4-Phenylquinazolinium bromide (2a-HBr): Yellow solid. mp: 142 °C (decomp.). IR (KBr, ν /cm^{-1}): 3482 s, 3421 s, 3036 w, 2667 m, 1928 w, 1804 w, 1617 s, 1572 m, 1483 m, 1375 s, 1262 m, 903 m. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 13.23 (s, 1H, N*H*), 9.56 (s, 1H), 8.90 (d, *J* = 8.5 Hz, 1H, *Ar*), 8.49 (d, *J* = 8.3 Hz, 1H, *Ar*), 8.35 (t, *J* = 8.4 Hz, 1H, *Ar*), 8.10-7.95 (m, 3H, *Ar*), 7.84-7.68 (m, 3H, *Ar*). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 173.8, 147.3, 142.9, 139.3, 133.7, 133.3, 131.8, 131.5, 129.6, 129.1, 123.2, 122.5. MS (FAB$^+$) m/z calcd for $C_{14}H_{11}N_2$ 207.0922 found 207.0922.



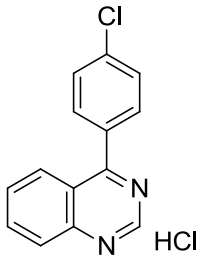
4-Phenylquinazolinium iodide (2a-HI): Yellow solid. mp: 111 °C (decomp.). IR (KBr, ν /cm^{-1}): 3448 w, 3181 w, 3077 w, 3016 w, 2908 w, 2623 s, 1943 w, 1841 w, 1619 s, 1600 m, 1565 s, 1477 m, 1379 s, 1345 m, 1231 m, 764s, 701 s. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 9.57 (s, 1H), 8.87 (d, *J* = 8.6 Hz, 1H, *Ar*), 8.49 (d, *J* = 8.5 Hz, 1H, *Ar*), 8.35 (t, *J* = 7.3 Hz, 1H, *Ar*), 8.10-7.96 (m, 3H, *Ar*), 7.84-7.70 (m, 3H, *Ar*). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 173.1, 147.2, 143.6, 139.4, 133.8, 133.0, 131.9, 131.6, 129.7, 129.2, 123.4, 122.6. MS (FAB$^+$) m/z calcd. for $C_{14}H_{11}N_2$ 207.0922 found 207.0921.



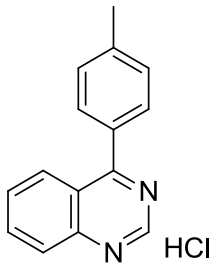
4-Phenylquinazolinium nitrate (2a-HNO_3): Pale yellow solid. mp: 138 °C (decomp.). IR (KBr, ν /cm^{-1}): 3448 w, 3064w, 2478 m, 1988 w, 1891 w, 1624 s, 1578 s, 1491 m, 1385 s, 1304 s, 1035 m, 763 s, 699 s. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 9.61 (s, 1H, *Ar*), 8.40 (d, *J* = 8.4 Hz, 2H, *Ar*), 8.24 (t, *J* = 8.1 Hz, 1H, *Ar*), 8.00-7.85 (m, 3H, *Ar*), 7.80-7.63 (m, 3H, *Ar*). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 172.6, 150.1, 145.4, 138.0, 134.1, 132.8, 140.0, 130.8, 129.5, 128.7, 124.8, 122.8. MS (FAB$^+$) m/z calcd. for $C_{14}H_{11}N_2$ 207.0922 found 207.0922.



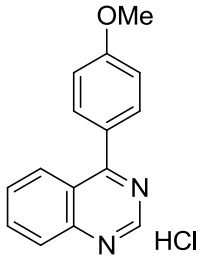
4-(4-Trifluoromethylphenyl)quinazolinium chloride (2b-HCl): White solid. mp: 132 °C (decomp.) IR (KBr, ν /cm^{-1}): 3422 w, 3048 w, 3008 w, 2982 w, 2196 m, 2061 m, 1967 m, 1910 s, 1618 s, 1561 s, 1325 s, 1066 s, 975 m, 772 s. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 9.42 (s, 1H, *Ar*), 8.19 (d, *J* = 8.5 Hz, 1H, *Ar*), 8.06 (dd, *J* = 8.4, 0.7 Hz, 1H, *Ar*), 8.00-7.83 (m, 5H, *Ar*), 7.67 (m, 1H, *Ar*). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 172.0, 149.5, 144.2, 138.3, 138.0, 134.1 (q, *J* = 32.8 Hz), 131.3, 127.8, 126.3 (q, *J* = 3.7 Hz), 124.4, 123.6 (q, *J* = 271.1 Hz), 122.9. ^{19}F NMR (376 MHz, $CDCl_3$, 30 °C): δ –64.2. MS (FAB$^+$) m/z calcd. for $C_{15}H_{10}F_3N_2$ 275.0796 found 275.0804.



4-(4-Chlorophenyl)quinazolinium chloride (2c-HCl): Pale yellow solid. mp: 124 °C (decomp.). IR (KBr, ν /cm^{-1}): 3489 w, 3082 w, 3055 w, 3031 w, 2385 m, 2231 m, 2024 m, 1932 m, 1886 m, 1619 s, 1558 s, 1472 s, 1392 s, 1340 s, 1195 m, 1167 m, 1090 s, 1012 m, 782 s. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 9.40 (s, 1H, *Ar*), 8.27 (d, *J* = 8.5 Hz, 1H, *Ar*), 8.14 (d, *J* = 8.4 Hz, 1H, *Ar*), 8.00 (t, *J* = 8.2 Hz, 1H, *Ar*), 7.78 (d, *J* = 8.5 Hz, 2H, *Ar*), 7.70 (t, *J* = 8.0 Hz, 1H, *Ar*), 7.59 (d, *J* = 8.4 Hz, 2H, *Ar*). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 173.0, 148.5, 143.5, 140.6, 139.1, 132.9, 132.7, 131.9, 130.3, 128.6, 124.0, 122.9. MS (FAB$^+$) m/z calcd. for $C_{14}H_{10}N_2Cl$ 241.0533 found 241.0525.

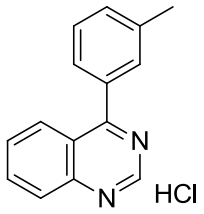


4-(4-Methylphenyl)quinazolinium chloride (2d-HCl): Pale yellow solid. mp: 138 °C (decomp.) IR (KBr, ν /cm^{-1}): 3435 w, 2057 w, 3023 w, 2968 w, 2445 m, 2219 m, 2018 m,1924 m, 1558 s, 1476 m, 1372 s, 924 m, 719 m. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 9.48 (s, 1H, *Ar*), 8.80 (d, *J* = 8.5 Hz, 1H, *Ar*), 8.45 (dd, *J* = 8.6, 0.6 Hz, 1H, *Ar*), 8.26 (m, 1H, *Ar*), 7.96 (m, 1H, *Ar*), 7.92-7.86 (m, 2H, *Ar*), 7.51 (d, *J* = 7.8 Hz, 1H, *Ar*), 2.54 (s, 3H, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 173.0, 147.5, 144.8, 143.6, 138.6, 131.5, 131.3, 130.6, 130.3, 129.0, 123.8, 122.3, 21.8. MS (FAB$^+$) m/z calcd. for $C_{15}H_{13}N_2$ 221.1079 found 221.1077.

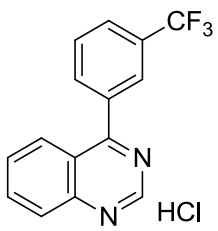


4-(4-Methoxyphenyl)quinazolinium chloride (2e-HCl): Yellow solid. mp: 151 °C (decomp.) IR (KBr, ν /cm^{-1}): 3056 w, 3030 w, 3006 w, 2945 w, 2848 w, 2494 w, 2251 w, 2028 w, 1939 w, 1599 s, 1557 s, 1473 m, 1381 s, 1337 s, 1306 m, 1259 s, 1021 m, 848 s, 781 m. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 9.42 (s, 1H, *Ar*), 8.73 (d, *J* = 8.5 Hz, 1H, *Ar*), 8.45 (d, *J* = 8.5 Hz, 1H, *Ar*), 8.23 (t, *J* = 7.2 Hz, 1H, *Ar*), 8.03 (d, *J* = 8.8 Hz, 1H, *Ar*), 7.95 (t, *J* = 7.4 Hz, 1H, *Ar*), 7.20

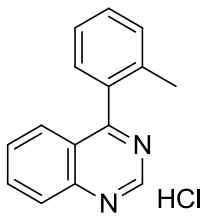
(d, *J* = 8.8 Hz, 1H, *Ar*), 3.98 (s, 3H, O*Me*). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 171.7, 164.4, 147.2, 143.6, 138.4, 133.9, 131.1, 128.9, 125.5, 123.7, 121.9, 115.2, 55.9. MS (FAB^+) m/z calcd. for $C_{15}H_{13}N_2O$ 237.1028 found 237.1025.



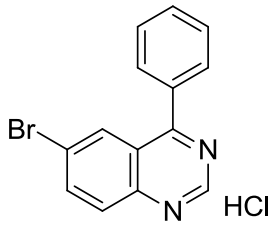
4-(3-Methylphenyl)quinazolinium chloride (2f-HCl): Pale yellow solid. mp: 121 °C (decomp.) IR (KBr, ν /cm^{-1}): 3408 m, 3054 w, 3020 w, 2917 w, 2433 w, 2038 w, 1950 w, 1892 m, 1619 s, 1562 s, 1481 m, 1370 s, 884 m. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 9.47 (s, 1H, *Ar*), 8.65 (d, *J* = 8.5 Hz, 1H, *Ar*), 8.38 (d, *J* = 8.5 Hz, 1H, *Ar*), 8.21 (t, *J* = 8.3 Hz, 1H, *Ar*), 7.92 (t, *J* = 8.1 Hz, 1H, *Ar*), 7.78-7.65 (m, 2H, *Ar*), 7.60-7.50 (m, 2H, *Ar*), 2.53 (s, 3H, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 172.9, 149.7, 145.4, 139.7, 137.8, 134.7, 133.7, 131.7, 130.8, 129.4, 128.9, 128.6, 125.1, 123.1, 21.8. MS (FAB^+) m/z calcd. for $C_{15}H_{13}N_2$ 221.1079 found 221.1082.



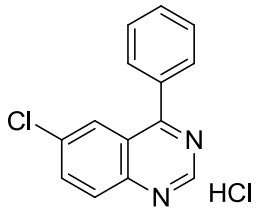
4-(3-Trifluoromethylphenyl)quinazolinium chloride (2g-HCl): White solid. mp: 121 °C (decomp.) IR (KBr, ν /cm^{-1}): 3422 w, 3065 w, 3030 w, 2269 m, 2194 m, 2048 m, 1955 m, 1625 s, 1570 s, 1482 w, 1396 s, 1329 s, 1293 s, 1169 m, 1105 s, 863 m. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 9.51 (s, 1H, *Ar*), 8.60 (d, *J* = 8.5 Hz, 1H, *Ar*), 8.23-8.10 (m, 3H, *Ar*), 8.07 (d, *J* = 7.8 Hz, 1H, *Ar*), 7.94 (d, *J* = 7.8 Hz, 1H, *Ar*), 7.87 (m, 1H, *Ar*), 7.80 (t, *J* = 7.8 Hz, 1H, *Ar*). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 172.7, 148.3, 142.2, 138.6, 134.9, 134.0, 131.8 (q, *J* = 32.8 Hz), 131.6, 129.8, 129.1 (q, *J* = 3.3 Hz), 127.54, 127.49 (q, *J* = 3.8 Hz), 123.1(q, *J* = 270.9 Hz), 122.9, 122.5. ^{19}F NMR (376 MHz, $CDCl_3$, 30 °C): δ -63.9. MS (FAB^+) m/z calcd. for $C_{15}H_{10}F_3N_2$ 275.0796 found 275.0794.



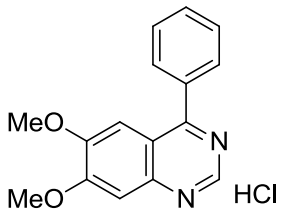
4-(2-Methylphenyl)quinazolinium chloride (2h-HCl): White solid. mp: 118 °C (decomp.) IR (KBr, ν /cm^{-1}): 3449 w, 3059 w, 3023 w, 2989 w, 2369 w, 2045 w, 1936 w, 1625 m, 1568 m, 1381 s, 1349 s, 761 s. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 9.46 (s, 1H, *Ar*), 8.37 (d, *J* = 8.4 Hz, 1H, *Ar*), 8.05 (m, 1H, *Ar*), 7.81 (dd, *J* = 8.3, 0.7 Hz, 1H, *Ar*), 7.69 (m, 1H, *Ar*), 7.52-7.34 (m, 4H, *Ar*), 2.19 (s, 3H, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 171.8, 152.3, 148.3, 136.5, 135.8, 135.2, 131.1, 130.3, 129.7, 129.2, 127.9, 127.2, 126.0, 124.1, 20.0. MS (FAB^+) m/z calcd. for $C_{15}H_{13}N_2$ 221.1079 found 221.1078.



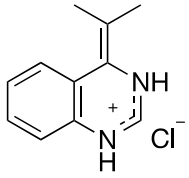
6-Bromo-4-phenylquinazoline (2i-HCl): White solid. mp: 108 °C (decomp.) IR (KBr, ν /cm^{-1}): 3423 w, 3116 w, 3060 m, 3021 w, 2456 m, 2211 m, 1968 w, 1876 w, 1793 w, 1558 s, 1482 m, 1359 s, 1064 m, 918 m. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 9.45 (s, 1H, *Ar*), 8.42-8.30 (m, 2H, *Ar*), 8.13 (dd, *J* = 9.0, 1.8 Hz, 1H, *Ar*), 7.85 (d, *J* = 6.4 Hz, 2H, *Ar*), 7.73-7.60 (m, 3H, *Ar*). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 169.8, 151.9, 146.6, 139.4, 135.1, 131.9, 130.5, 129.9, 129.3, 128.4, 124.0, 123.6. MS (FAB$^+$) m/z calcd. for $C_{14}H_{10}BrN_2$ 285.0027 found 285.0019.



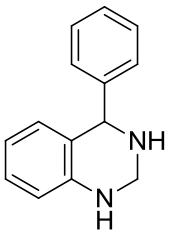
6-Chloro-4-phenylquinazoline (2j-HCl): White solid. mp: 135-137 °C. IR (KBr, ν /cm^{-1}): 3448 w, 3097 w, 3061 w, 2505 w, 2277 w, 2049 w, 1953 m, 1624 m, 1566 s, 1470 s, 1358 s, 979 m, 863 m, 843 s. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 9.38 (s, 1H, *Ar*), 8.15-8.05 (m, 2H, *Ar*), 7.90-7.82 (m, 1H, *Ar*), 7.80-7.74 (m, 2H, *Ar*), 7.64-7.58 (m, 3H, *Ar*). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 167.9, 154.9, 149.7, 136.7, 134.9, 133.7, 130.8, 130.6, 130.0, 129.0, 126.0, 123.9. MS (EI$^+$) m/z calcd. for $C_{14}H_9N_2Cl$ 240.0454 found 240.0445.



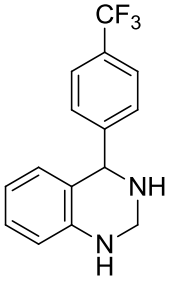
6,7-Dimethoxy-4-phenylquinazolinium chloride (2k-HCl): Pale yellow solid. mp: 155 °C (decomp.) IR (KBr, ν /cm^{-1}): 3323 m, 3220 m, 3043 w, 3015 w, 2946 w, 2489 w, 1995 m, 1915 w, 1623 m, 1579 m, 1498 s, 1375 s, 1262 s, 1157 s. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 9.28 (s, 1H, *Ar*), 8.17 (s, 1H, *Ar*), 7.93-7.88 (m, 2H, *Ar*), 7.75-7.63 (m, 3H, *Ar*), 7.51 (s, 1H, *Ar*), 4.22 (s, 3H, O*Me*), 3.99 (s, 3H, O*Me*). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 168.4, 160.5, 153.4, 145.7, 142.3, 134.5, 132.8, 130.6, 129.7, 119.2, 105.0, 101.9, 58.1, 56.9. MS (FAB$^+$) m/z calcd. for $C_{16}H_{15}N_2O_2$ 267.1134 found 267.1136.



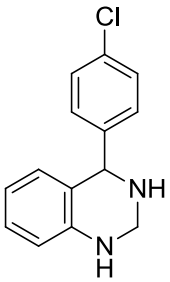
4-(Propan-2-ylidene)-dihydroquinazoline hydrochloride (2l-HCl): Bright yellow solid. This compound was aromatized to 4-isopropylquinazolinium chloride gradually in the chloroform. mp 135 °C (decomp.). IR (KBr, ν /cm^{-1}): 3450 s, 3386 s, 3049 s, 2911 s, 2764 s, 1674 s, 1634 s, 1567 s, 1485 s, 1445 m, 1375 m, 1339 m, 1250 m, 1206 m, 1074 w, 767 s. ^{1}H NMR (400 MHz, $CDCl_3$, 30°C): δ 12.78 (s, 1H, N*H*), 11.64 (s, 1H, N*H*), 8.27 (t, *J* = 5.8, 1H), 7.48-7.38 (m, 2H), 7.30-7.18 (m, 2H), 2.08 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, MeOD-d_4, 30 °C): δ 148.8, 134.2, 131.0, 129.2, 128.7, 122.6, 122.3, 121.1, 118.2, 22.0, 20.3. MS (FAB) m/z calcd. for $C_{11}H_{13}N_2^+$ 173.1073 found 173.1079.



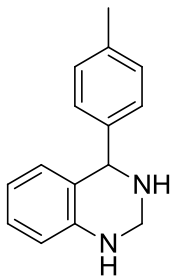
(-)-4-Phenyl-1,2,3,4-tetrahydroquinazoline (3a): Pale yellow solid. mp: 71 °C (decomp.). IR (KBr, ν /cm^{-1}): 3296 m, 3026 m, 2958 m, 2859 m, 1606 s, 1496 s, 1453 s, 1355 m, 1307 s, 1040 s, 887 m. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.35-7.23 (m, 5H, *Ar*), 7.04 (m, 1H, *Ar*), 6.74 (d, *J* = 7.5 Hz, 1H, *Ar*), 6.67-6.55 (m, 2H, *Ar*), 5.15 (s, 1H, ArC*H*), 4.20 (d, *J* = 11.5 Hz, 1H, NCH_2N), 4.10 (d, *J* = 11.5 Hz, 1H, NCH_2N), 2.17 (s, 1H, N*H*). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 144.0, 143.8, 129.1, 128.7, 128.5, 127.7, 127.4, 123.6, 118.0, 115.6, 59.2, 55.3. MS (FAB$^+$) m/z calcd. for $C_{14}H_{14}N_2$ 210.1157 found 210.1160. HPLC (Daicel OJ-H, temperature: 30 °C, hexane : ^{i}PrOH = 90 : 10, detector : 215 nm, flow rate 1.0 mL/min, t_1(-) = 37.4 min, t_2(+) = 55.1 min). $[\alpha]^{30}_{D}$ = -28.4 (c = 0.7, $CHCl_3$) (for an ee of 99%).



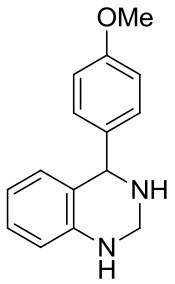
(-)-4-(4-Trifluoromethylphenyl)-1,2,3,4-tetrahydroquinazoline (3b): Pale yellow solid. mp: 92 °C (decomp.) IR (KBr, ν /cm^{-1}): 3427 m, 3259 m, 3023 w, 2932 w, 2866 w, 1934 w, 1606 m, 1504 s, 1330 s, 1155 s, 1116 s, 841 s, 750 s. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.56 (d, *J* = 8.12 Hz, 2H, *Ar*), 7.40 (d, *J* = 8.1 Hz, 2H, *Ar*), 7.08 (t, *J* = 7.7 Hz, 1H, *Ar*), 6.78-6.58 (m, 3H, *Ar*), 5.17 (s, 1H, ArC*H*), 4.18 (d, *J* = 11.6 Hz, 1H, NCH_2N), 4.03 (d, *J* = 11.6 Hz, 1H, NCH_2N) 2.18 (s, 1H, N*H*). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 147.9, 143.7, 129.6 (q, *J* = 34.3 Hz), 129.4, 128.6, 128.1, 125.4 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 270.3 Hz), 122.3, 118.0, 115.8, 58.5, 54.8. ^{19}F NMR (376 MHz, $CDCl_3$, 30 °C): δ -63.6. HPLC (Daicel OJ-H, temperature: 30 °C, hexane : ^{i}PrOH = 90 : 10, detector : 215 nm, flow rate 1.0 mL/min, t_1(-) = 13.5 min, t_2(+) = 18.4 min). $[\alpha]^{30}_{D}$ = -19.4 (c = 1.1, $CHCl_3$) (for an ee of 99%). MS (FAB$^+$) m/z calcd. for $C_{15}H_{13}F_3N_2$ 278.1031 found 278.1034.



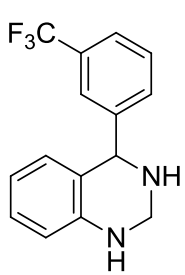
(-)-4-(4-Chlorophenyl)-1,2,3,4-tetrahydroquinazoline (3c): White solid. mp: 86 °C (decomp.) IR (KBr, ν /cm^{-1}): 3268 m, 3051 m, 3020 m, 2966 m, 2927 m, 2862 m, 1605 s, 1493 s, 1364 w, 1093 s, 1015 m, 826 s, 750 s. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.30-7.14 (m, 4H, *Ar*), 7.06 (td, *J* = 7.4, 1.2 Hz, 1H, *Ar*), 6.75-6.55 (m, 3H, *Ar*), 5.10 (s, 1H, ArC*H*), 4.16 (d, *J* = 11.5 Hz, 1H, NCH_2N), 4.03 (d, *J* = 11.5 Hz, 1H, NCH_2N), 2.13 (s, 1H, N*H*). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 143.7, 142.5, 133.2, 130.5, 128.63, 128.61, 128.0, 122.8, 118.0, 115.7, 58.3, 54.9. HPLC (Daicel OJ-H, temperature: 30 °C, hexane : ^{i}PrOH = 90 : 10, detector : 254 nm, flow rate 1.0 mL/min, t_1(-) = 26.3 min, t_2(+) = 30.0 min). $[\alpha]^{31}_{D}$ = -7.2 (c = 1.0, $CHCl_3$) (for an ee of 99%). MS (FAB$^+$) m/z calcd. for $C_{14}H_{13}ClN_2$ 244.0767 found 244.0759.



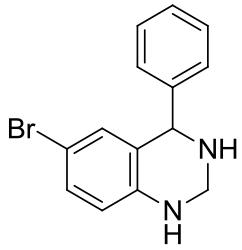
(-)-4-(4-Methylphenyl)-1,2,3,4-tetrahydroquinazoline (3d): Pale yellow solid. mp: 88 °C (decomp.) IR (KBr, ν /cm^{-1}): 3397 w, 3302 w, 3049 w, 3019 w, 2922 w, 2859 w, 1605 m, 1498 s, 1356 w, 1106 w, 811 m, 749 s. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.20-7.09 (m, 4H, *Ar*), 7.04 (t, *J* = 7.0 Hz, 1H, *Ar*), 6.73 (d, *J* = 7.5 Hz, 1H, *Ar*), 6.63 (t, *J* = 7.2 Hz, 1H, *Ar*), 6.58 (d, *J* = 8.0 Hz, 1H, *Ar*), 5.12 (s, 1H, ArC*H*), 4.19 (d, *J* = 11.5 Hz, 1H, NCH_2N), 4.09 (d, *J* = 11.4 Hz, 1H, NCH_2N), 2.32 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 143.8, 141.0, 137.0, 129.2, 128.9, 128.7, 127.6, 123.9, 118.0, 115.6, 58.9, 55.3, 21.2. HPLC (Daicel OJ-H, temperature: 30 °C, hexane : ^{i}PrOH = 90 : 10, detector : 215 nm, flow rate 1.0 mL/min, t_1(+) = 30.5 min, t_2(-) = 50.4 min). $[\alpha]^{27}_{D}$ = -15.0 (c = 0.9, $CHCl_3$) (for an ee of 97%). MS (FAB$^+$) m/z calcd. for $C_{15}H_{16}N_2$ 224.1313 found 224.1304.



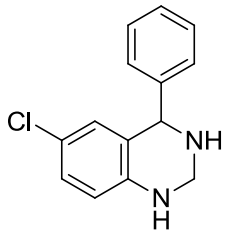
(-)-4-(4-Methoxyphenyl)-1,2,3,4-tetrahydroquinazoline (3e): Pale yellow solid. mp: 68 °C (decomp.) IR (KBr, ν /cm^{-1}): 3397 w, 3309 w, 3000 w, 2955 w, 2930 w, 2836 w, 1608 m, 1509 s, 1249 s, 1175 m, 1036 m, 751 m. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.18 (d, *J* = 8.6 Hz, 2H, *Ar*), 7.04 (t, *J* = 8.1 Hz, 1H, *Ar*), 6.85 (d, *J* = 8.7 Hz, 2H, *Ar*), 6.74 (d, *J* = 7.5 Hz, 1H, *Ar*), 6.64 (t, *J* = 7.4 Hz, 1H, *Ar*), 6.59 (d, *J* = 8.0 Hz, 1H, *Ar*), 5.12 (s, 1H, ArC*H*), 4.20 (d, *J* = 11.4 Hz, 1H, NCH_2N), 4.10 (d, *J* = 11.5 Hz, 1H, NCH_2N), 3.78 (s, 3H, O*Me*). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 158.9, 143.8, 136.2, 130.1, 128.7, 127.7, 123.9, 118.0, 115.6, 113.9, 58.5, 55.4, 55.2. HPLC (Daicel OD-H, temperature: 30 °C, hexane : ^{i}PrOH = 95 : 5, detector : 215 nm, flow rate 1.0 mL/min, t_1(-) = 52.6 min, t_2(+) = 83.9 min). $[\alpha]^{30}_{D}$ = -19.2 (c = 0.8, $CHCl_3$) (for an ee of 98%). MS (FAB$^+$) m/z calcd. for $C_{15}H_{16}N_2O$ 240.1263 found 240.1256.



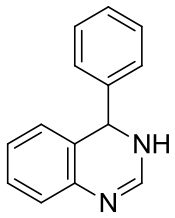
(-)-4-(3-Trifluoromethylphenyl)-1,2,3,4-tetrahydroquinazoline (3g): Pale yellow oil. IR (KBr, ν /cm^{-1}): 3399 w, 3052 w, 3020 w, 2964 w, 2928 w, 2861 w, 1607 m, 1498 m, 1330 s, 1259 w, 1166 m, 1124 s, 1094 m. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.62-7.38 (m, 4H, *Ar*), 7.08 (td, *J* = 8.3, 1.7 Hz, 1H, *Ar*), 6.75-6.58 (m, 3H, *Ar*), 5.20 (s, 1H, ArC*H*), 4.21 (d, *J* = 11.6 Hz, 1H, NCH_2N), 4.05 (d, *J* = 11.6 Hz, 1H, NCH_2N), 2.14 (s, 1H, N*H*). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 145.0, 143.7, 132.5, 131.4, 130.9 (q, *J* = 31.7 Hz), 128.9, 128.6, 128.2, 125.9 (q, *J* = 3.8 Hz), 124.31 (q, *J* = 270.5 Hz), 124.30 (q, *J* = 3.8 Hz), 118.1, 115.8, 58.6, 54.9. ^{19}F NMR (376 MHz, $CDCl_3$, 30 °C): δ -63.6.HPLC (Daicel OD-H, temperature: 30 °C, hexane : ^{i}PrOH = 90 : 10, detector : 215 nm, flow rate 1.0 mL/min, t_1(-) = 16.1 min, t_2(+) = 49.8 min). $[\alpha]^{20}_{D}$ = -28.6 (c = 0.7, $CHCl_3$) (for an ee of 97%). MS (FAB$^+$) m/z calcd. for $C_{15}H_{13}F_3N_2$ 278.1031 found 278.1022.



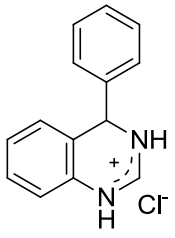
(*S*)-6-Bromo-1,2,3,4-tetrahydro-4-phenylquinazoline (3i): Pale brown solid. mp: 108 °C (decomp.) IR (KBr, ν /cm^{-1}): 3407 m, 3311 w, 3059 w, 3026 w, 2961 w, 2926 w, 2858 w, 1598 m, 1492 s, 1290 m, 810 m, 756 m, 700 m. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.36-7.16 (m, 5H, *Ar*), 7.12 (dd, *J* = 8.6, 2.0 Hz, 1H, *Ar*), 6.85 (d, *J* = 1.6 Hz, 1H, *Ar*), 6.45 (d, *J* = 8.5 Hz, 1H, *Ar*), 5.08 (s, 1H, ArC*H*), 4.16 (d, *J* = 11.6 Hz, 1H, NCH_2N), 4.05 (d, *J* = 11.6 Hz, 1H, NCH_2N), 2.10 (s, 1H, N*H*). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 143.1, 142.7, 131.0, 130.5, 128.9, 128.6, 127.7, 125.2, 117.0, 109.5, 58.9, 54.9. HPLC (Daicel OD-H, temperature: 30 °C, hexane : ^{i}PrOH = 90 : 10, detector : 215 nm, flow rate 1.0 mL/min, t_1(*S*) = 21.3 min, t_2(*R*) = 25.5 min). $[\alpha]^{21}_{D}$ = -103.4 (c = 1.2, $CHCl_3$) (for an ee of 96%). MS (FAB$^+$) m/z calcd. for $C_{14}H_{14}BrN_2$ 289.0340 found 289.0345.



(-)-6-Chloro-1,2,3,4-tetrahydro-4-phenylquinazoline (3j): White solid. mp: 98°C (decomp.) IR (KBr, ν /cm^{-1}): 3407 w, 3302 w, 3026 w, 2926 w, 2858 w, 1604 w, 1493 s, 1292 w, 811 m, 755 m, 700 m. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.38-7.20 (m, 5H, *Ar*), 7.00 (dd, *J* = 8.6, 2.3 Hz, 1H, *Ar*), 6.72 (d, *J* = 2.0 Hz, 1H, *Ar*), 6.51 (d, *J* = 8.6 Hz, 1H, *Ar*), 5.10 (s, 1H, ArC*H*), 4.19 (d, *J* = 11.6 Hz, 1H, NCH_2N), 4.08 (d, *J* = 11.6 Hz, 1H, NCH_2N), 2.06 (s, 1H, N*H*). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 143.1, 142.3, 128.9, 128.7, 128.2, 127.73, 127.69, 124.8, 122.5, 116.7, 59.0, 55.1. HPLC (Daicel OJ-H, temperature: 30 °C, hexane : ^{i}PrOH = 90 : 10, detector : 215 nm, flow rate 1.0 mL/min, t_1(+) = 22.3 min, t_2(-) = 25.6 min). $[\alpha]^{26}_{D}$ = -58.7 (c = 1.1, $CHCl_3$) (for an ee of 97%). MS (FAB$^+$) m/z calcd. for $C_{14}H_{13}N_2Cl$ 244.0767 found 244.0772.

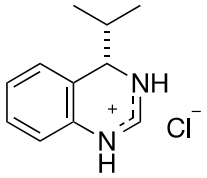


3,4-Dihydro-4-phenylquinazoline (4a): Pale brown solid. mp: 163-166 °C. IR (KBr, ν /cm^{-1}): 3449 w, 3179 w, 3057 w, 2921 m, 2793 m, 1617 s, 1591 s, 1547 s, 1478 s, 1457 s, 1379 s, 1305 m, 1253 m, 754 s. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.40-7.24 (m, 5H, *Ar*), 7.20 (s, 1H, *Ar*), 7.14 (t, *J* = 7.4 Hz, 1H, *Ar*), 7.00 (d, *J* = 7.8 Hz, 1H, *Ar*), 6.93 (t, *J* = 7.5 Hz, 1H, *Ar*), 6.71 (d, *J* = 7.6 Hz, 1H, *Ar*), 5.72 (s, 1H, *Ar*). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 145.9, 145.2, 139.6, 129.0, 128.4, 128.1, 127.6, 127.4, 125.0, 124.4, 122.3, 57.6. MS (FAB$^+$) m/z calcd. for $C_{14}H_{13}N_2$ 209.1079 found 209.1077.

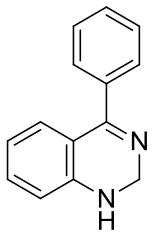


3,4-Dihydro-4-phenylquinazolinium chloride (4a-HCl): Pale pink solid. mp: 187.2 °C (decomp.). IR (KBr, ν /cm^{-1}): 3422 w, 3090 m, 3066 m, 3024 m, 2909 s, 2807 s, 2731 s, 1668 s, 1620 m, 1572 s, 1488 s, 1444 s, 1327 s, 1253 w, 856 m. ^{1}H

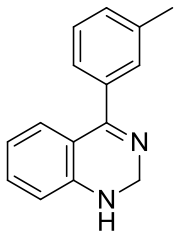
NMR (400 MHz, MeOD, 30 °C): δ 8.32 (s, 1H), 7.50-7.35 (m, 6H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.11 (s, 1H). ^{13}C NMR (100 MHz, MeOD, 30 °C): δ 149.3, 143.3, 130.7, 130.6, 130.4, 130.2, 129.5, 129.0, 128.8, 123.1, 118.2, 57.4. MS (FAB$^+$) m/z calced. for $C_{14}H_{13}N_2$ 209.1079 found 209.1079.



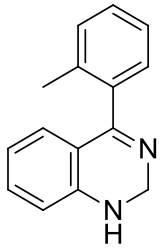
(*S*)-4-Isopropyl-dihydroquinazoline hydrochloride (4l-HCl): Yellow solid. mp 179 °C. (decomp.) IR (KBr, ν /cm^{-1}): 3038 s, 2961 s, 2837 s, 2739 s, 1669 s, 1620 m, 1577 s, 1490 s, 1465 m, 1445 s, 1389 w, 1356 m, 1331 m, 1257 m, 1214 w, 969 w, 848 m. ^{1}H NMR (400 MHz, $CDCl_3$, 30°C): δ 12.22 (brs, N*H*, 1H), 10.80 (brs, N*H*, 1H), 8.53 (s, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.19 (dt, *J* = 25.7, 7.3 Hz, 2H), 6.98 (d, *J* = 7.5 Hz, 1H), 4.76 (d, *J* = 3.2 Hz, 1H), 2.07-1.96 (m, 1H), 1.02 (d, *J* = 6.9 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 30°C): δ 149.3, 131.2, 129.2, 127.3, 127.0, 120.4, 117.7, 58.3, 37.2, 18.1, 16.2. MS (FAB$^+$) m/z calcd. for $C_{11}H_{15}N_2$ 175.1230 found 175.1230. Enantiomeric excess have determined after basic work up..Daicel OD-H, temperature: 30 °C, hexane : ^{i}PrOH = 95 : 5, detector: 215 nm, flow rate: 1.0 mL/min, t(*R*) = 25.6 min, t(*S*) = 46.9 min. $[\alpha]^{23}_D$ = -153.8 (c = 1.1, $CHCl_3$) (for an ee of 94%)



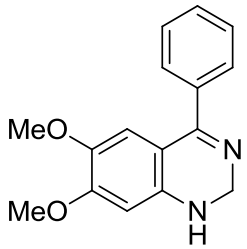
1,2-Dihydro-4-phenylquinazoline (5a): Yellow solid. mp: 161-164 °C. IR (KBr, ν /cm^{-1}): 3449 w, 3263 m, 3177 w, 3058 w, 3034 w, 2992 w, 2838 w, 1626 s, 1336 m, 1318 m, 1263 m, 1149 m, 1071 m, 744 m, 702 m. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.58-7.51 (m, 2H, *Ar*), 7.46-7.38 (m, 3H, *Ar*), 7.24 (m, 1H, *Ar*), 7.14 (d, *J* = 7.8 Hz, 1H, *Ar*), 6.76-6.66 (m, 2H, *Ar*), 5.00 (d, *J* = 1.8 Hz, 2H), 3.97 (s, 1H, N*H*). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 166.6, 148.0, 138.3, 132.6, 129.5, 129.1, 128.9, 128.2, 118.8, 118.4, 114.7, 60.8. MS (FAB$^+$) m/z calcd. for $C_{14}H_{13}N_2$ 209.1079 found 209.1078.



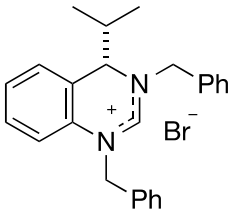
1,2-Dihydro-4-(3-methylphenyl)quinazoline (5f): Yellow solid. mp: 111-113 °C. IR (KBr, ν /cm^{-1}): 3255 m, 3056 w, 3037 w, 2981 w, 2914 w, 2763 m, 1616 s, 1571 m, 1499 m, 1334 m, 1213 w, 1073 m, 978 m, 759 s, 704 m. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.38 (s, 1H, *Ar*), 7.32-7.18 (m, 4H, *Ar*), 7.14 (d, *J* = 7.8 Hz, 1H, *Ar*), 6.71 (t, *J* = 7.4 Hz, 1H, *Ar*), 8.0 (d, *J* = 8.0 Hz, 1H, *Ar*), 4.97 (s, 2H, NC*H*$_2$N), 4.02 (s, 1H, N*H*), 2.38 (s, 3H, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 166.7, 148.0, 138.3, 138.0, 132.5, 130.2, 129.7, 129.0, 128.0, 126.3, 118.9, 118.4, 114.7, 60.8, 21.5. MS (FAB$^+$) m/z calcd. for $C_{15}H_{15}N_2$ 223.1235 found 223.1234.



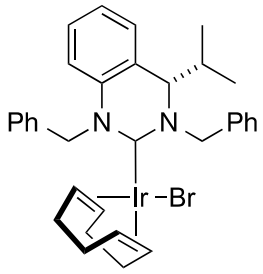
1,2-Dihydro-4-(2-methylphenyl)quinazoline (5h): Yellow solid. mp: 118-120 °C. IR (KBr, ν /cm^{-1}): 3436 w, 3253 m, 3100 w, 3060 w, 2977 w, 2921 w, 1626 s, 1605 m, 1489 m, 1308 m, 1149 m, 1065 m, 761 s. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.31-7.11 (m, 5H, *Ar*), 6.73 (dd, *J* = 7.8, 1.4 Hz, 1H, *Ar*), 6.60-6.55 (m, 2H, *Ar*), 5.02 (s, 2H, C*H*$_2$), 4.22 (s, 1H, N*H*), 2.17 (s, 3H, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 167.5, 147.0, 138.2, 135.8, 132.7, 130.2, 128.55, 128.49, 128.4, 125.7, 119.0, 118.3, 114.2, 60.8, 19.5. MS (FAB$^+$) m/z calcd. for $C_{15}H_{15}N_2$ 223.1235 found 223.1235.



1,2-Dihydro-6,7-dimethoxy-4-phenylquinazoline (5k): Yellow solid. mp: 172-174 °C. IR (KBr, ν /cm^{-1}): 3368 w, 3229 w, 3057 w, 2956 w, 2841 w, 2767 w, 1621 m, 1560 m, 1511 s, 1384 m, 1279 s, 1219 s, 1138 s, 988 w. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.60-7.50 (m, 2H, *Ar*), 7.48-7.38 (m, 3H, *Ar*), 6.69 (s, 1H, *Ar*), 6.27 (s, 1H, *Ar*), 4.85 (s, 2H, NC*H*$_2$N), 3.86 (s, 3H, O*Me*), 3.69 (m, 3H, O*Me*). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 165.9, 153.3, 143.4, 142.1, 138.5, 129.4, 129.1, 128.2, 112.2, 111.5, 98.9, 60.8, 56.7, 56.0. MS (FAB$^+$) m/z calcd. for $C_{16}H_{17}N_2O_2$ 269.1290 found 269.1293.



(*S*)-1,3-Dibenzyl-4-isopropyl-dihydroquinazoline hydrogenbromide: Ash solid. mp 227 ° C (decomp.). IR (KBr, ν /cm^{-1}): 3399 w, 3034 w, 2968 m, 2922 m, 2871 m, 2842 m, 2364 w, 2021 w, 1671 s, 1585 w, 1498 m, 1428 m, 1361 w, 1250 w, 1209 w, 1083 w, 1016 w, 764 s, 742 s, 731 s, 703 s. ^{1}H NMR (400 MHz, $CDCl_3$, 30°C): δ : 11.07 (s, 1H), 7.43-7.12 (m, 14H), 6.84 (dd, *J* = 7.6, 1.3 Hz, 1H), 5.72 (d, *J* = 14.6 Hz, 1H), 5.65 (d, *J* = 15.9 Hz, 1H), 5.25 (d, *J* = 15.9 Hz, 1H), 4.71 (d, *J* = 14.5 Hz, 1H), 4.40 (d, *J* = 3.5 Hz, 1H), 2.22 (septetd, *J* = 6.9, 3.5 Hz, 1H), 0.85 (d, *J* = 7.0 Hz, 3H), 0.69 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 30°C): δ 154.2, 133.3, 132.44, 132.35, 129.8, 129.50, 129.45, 129.2, 129.0, 128.8, 127.78, 127.74, 118.5, 115.6, 61.4, 56.9, 54.1, 32.7, 18.7, 16.1. MS (FAB$^+$) m/z calcd. for $C_{25}H_{27}N_2$ 355.2169 found 355.2176.



[IrBr(cod)(NHC)] (6): Yellow solid. mp 148 °C (decomp.). IR (KBr, ν /cm^{-1}): 3537 w, 3424 w, 3053 w, 3053 w, 3024 w, 2958 m, 2928 m, 2871 m, 2827 m, 2367 w, 2346 w, 2317 w, 1601 m, 1497 s, 1471 s, 1460 s, 1374 s, 1328 m, 1296 m, 1271 m, 1214 s, 961 m, 750 s, 702 s. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.67 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 15.4 Hz, 1H), 7.44 (d, J = 16.5 Hz, 1H), 7.34-7.29 (m, 5H), 7.22 (dd, J = 12.7, 7.4 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 3H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 5.13 (dd, J = 15.0, 11.2

Hz, 1H), 4.89 (dd, *J* = 16.5, 6.6 Hz, 1H), 4.75-4.69 (m, 1H), 4.67-4.56 (m, 1H), 4.01 (d, *J* = 7.8 Hz, 1H), 3.09-3.02 (m, 1H), 2.87-2.81 (m, 1H), 2.29-2.20 (m, 1H), 2.17-2.00 (m, 3H), 1.75-1.66 (m, 1H), 1.64-1.52 (m, 3H), 1.31-1.24 (m, 2H), 1.20 (d, *J* = 6.8 Hz, 3H), 0.69 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 30°C): δ 205.3, 137.3, 136.5, 135.6, 129.06, 129.00, 128.87, 128.6, 128.1, 127.7, 127.45, 127.41, 126.2, 124.2, 123.9, 114.6, 84.2, 83.1, 77.5, 77.2, 76.8, 64.0, 61.1, 56.8, 55.2, 53.7, 34.0, 32.5, 32.1, 30.2, 29.0, 20.6, 18.9. HRMS (FAB) m/z calcd. for $C_{33}H_{38}N_2BrIr$ 734.1848 found 734.1840.

8. Reference

(1) Yamagata, T.; Tadaoka, H.; Nagata, M.; Hirao, T.; Kataoka, Y.; Ratovelomanana-Vidal, V.; Genêt, J.-P.; Mashima, K. *Organometallics* **2006**, *25*, 2505.

(2) Tadaoka, H.; Cartigny, D.; Nagano, T.; Gosavi, T.; Ayad, T.; Genêt, J.-P.; Ohshima, T.; Ratovelomanana-Vidal, V.; Mashima, K. *Chem. Eur. J.* **2009**, *15*, 2100.

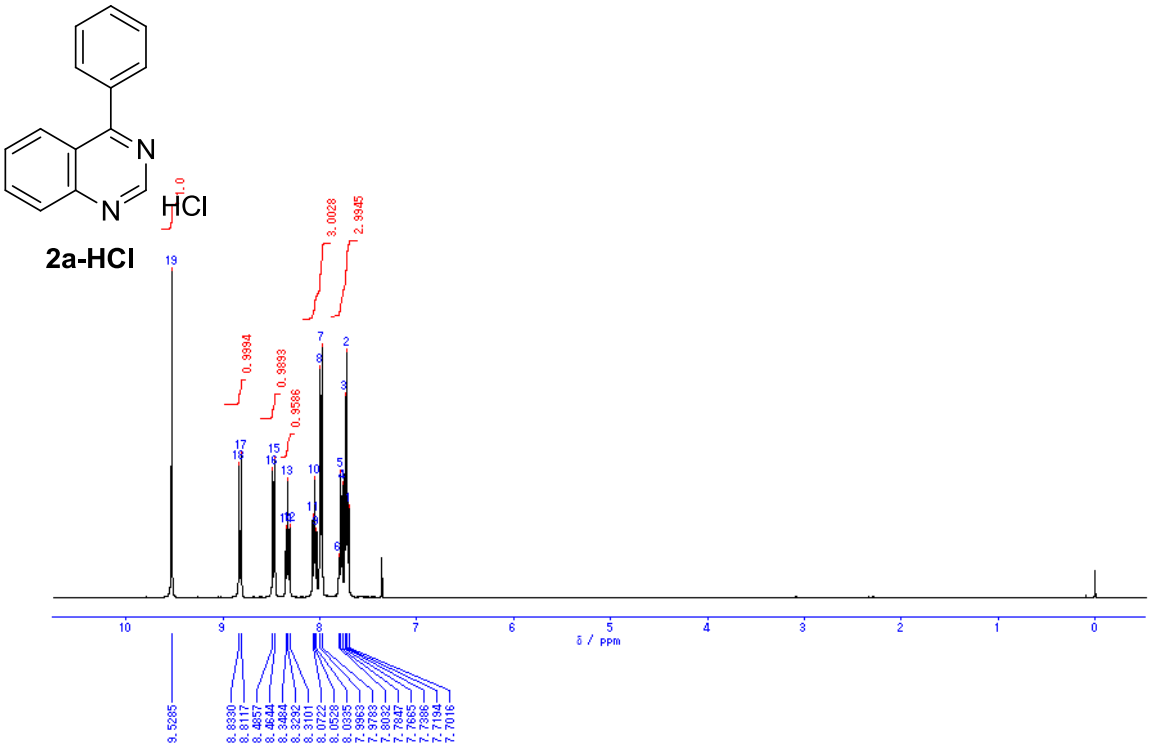
(3) Yan, Y.; Zhang, Y.; Feng, C.; Zha, Z.; Wang, Z. *Angew. Chem., Int. Ed.* **2012**, *51*, 8077.

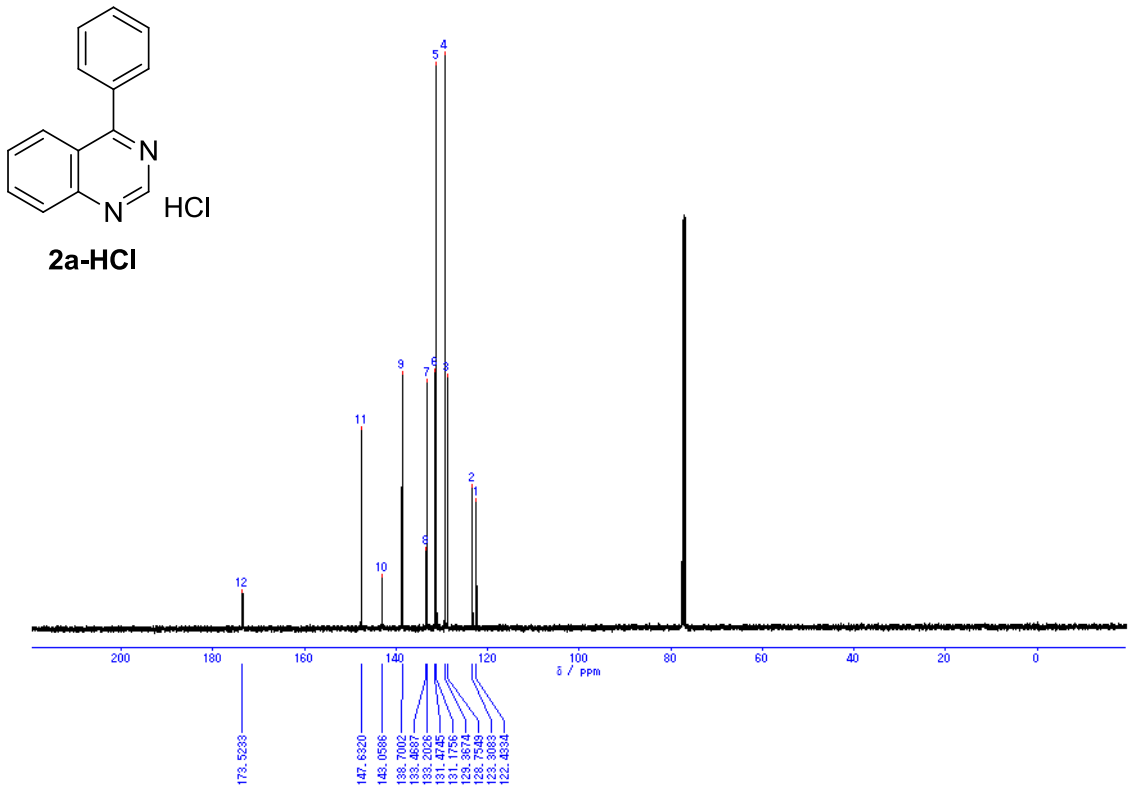
(4) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.

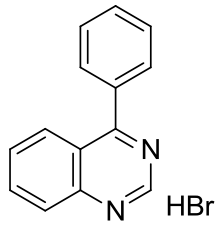
(5) Farrugia, L. J. *Appl. Crystallogr.* **1999**, *32*, 837.

(6) Flack, H. D. (1983), *Acta Cryst.*, **A39**, 876–881

8. ^{1}H and ^{13}C NMR spectra

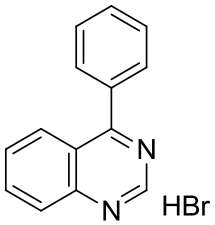





N
N
HBr

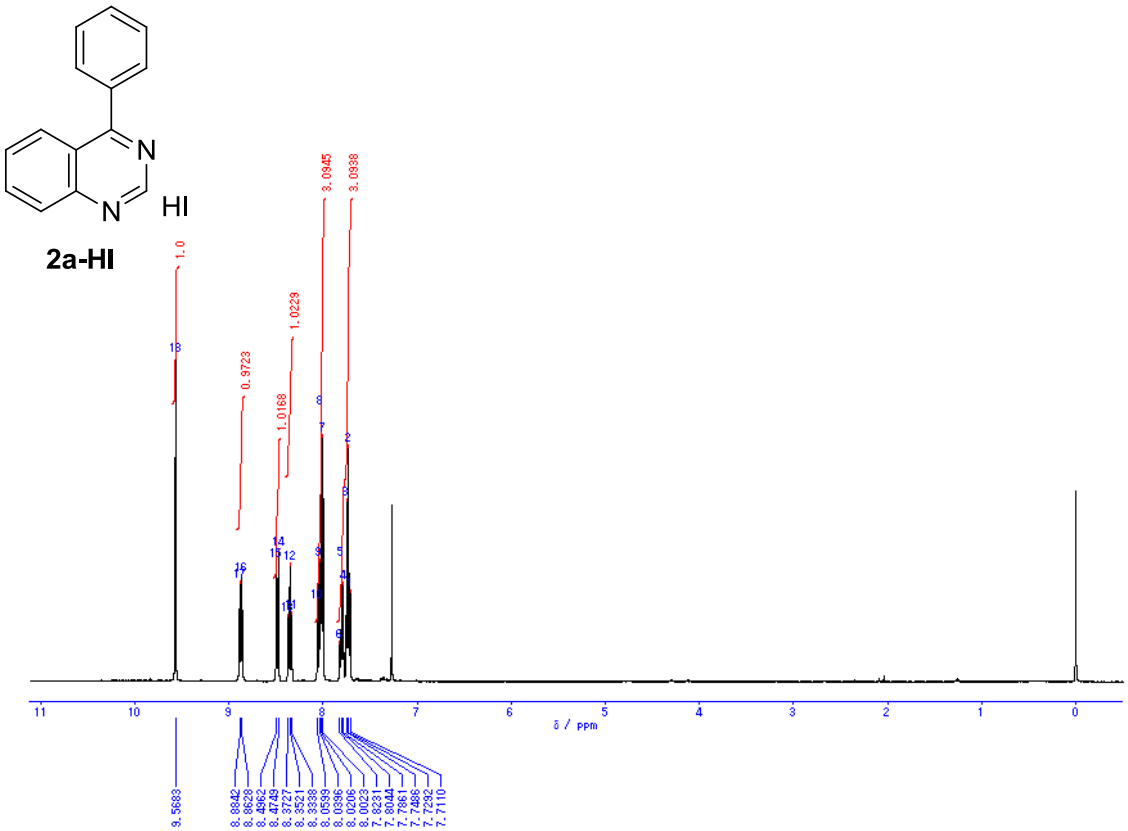
2a-HBr

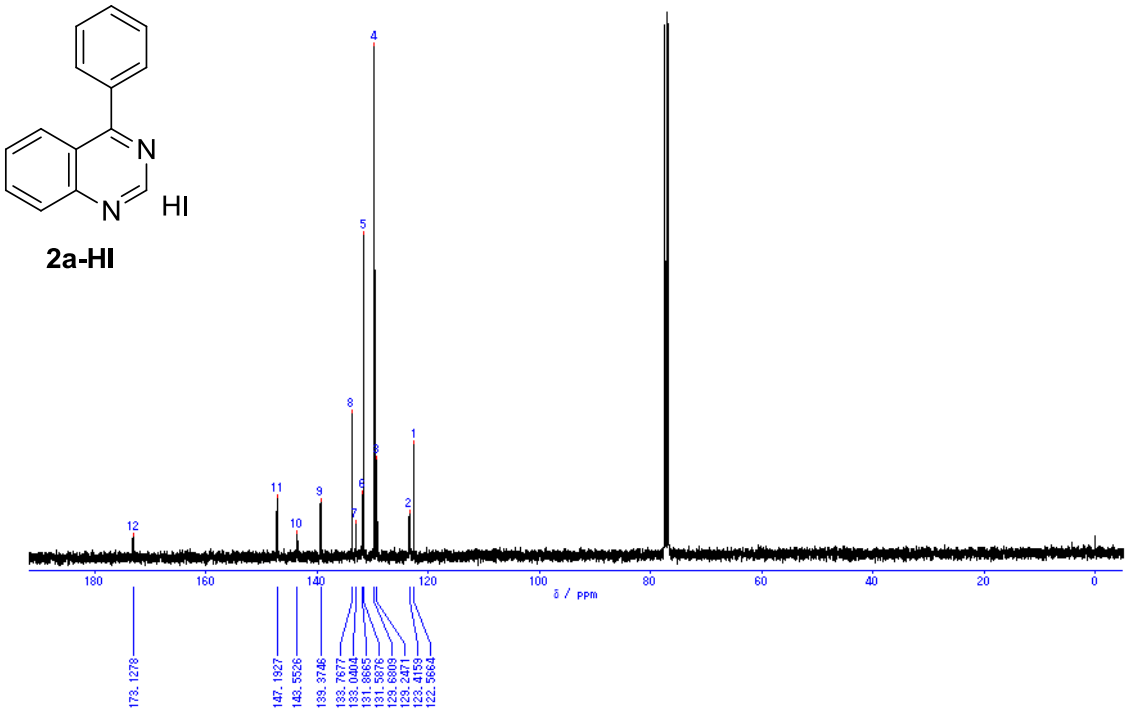
1.0
1.0025
1.0016
1.0117
3.0907
3.1068
1.2789
22
20
23
14
12
10
8
6
4
2
0
δ / ppm
13.2344
9.5570
8.9078
8.8865
8.4573
8.4478
8.3691
8.3661
8.3481
8.3300
8.3270
8.0710
8.0504
8.0319
8.0114
7.9937
7.9902
7.8355
7.8000
7.7815
7.7459
7.7266
7.7088

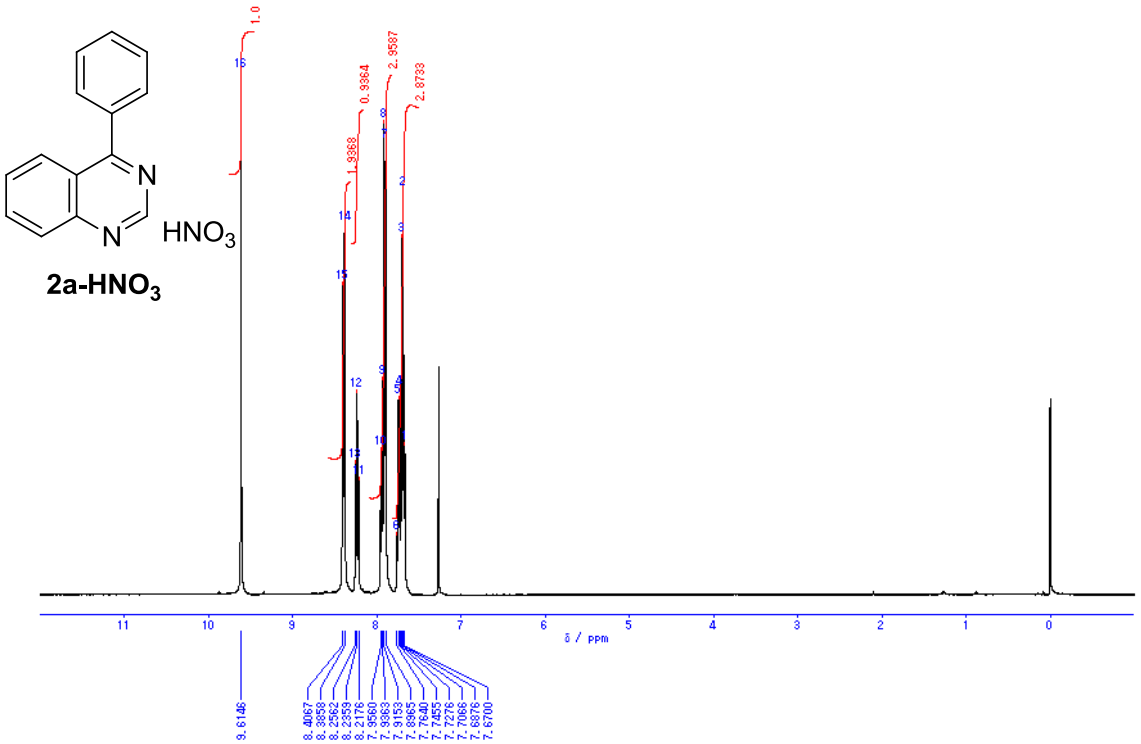

N
N
HBr

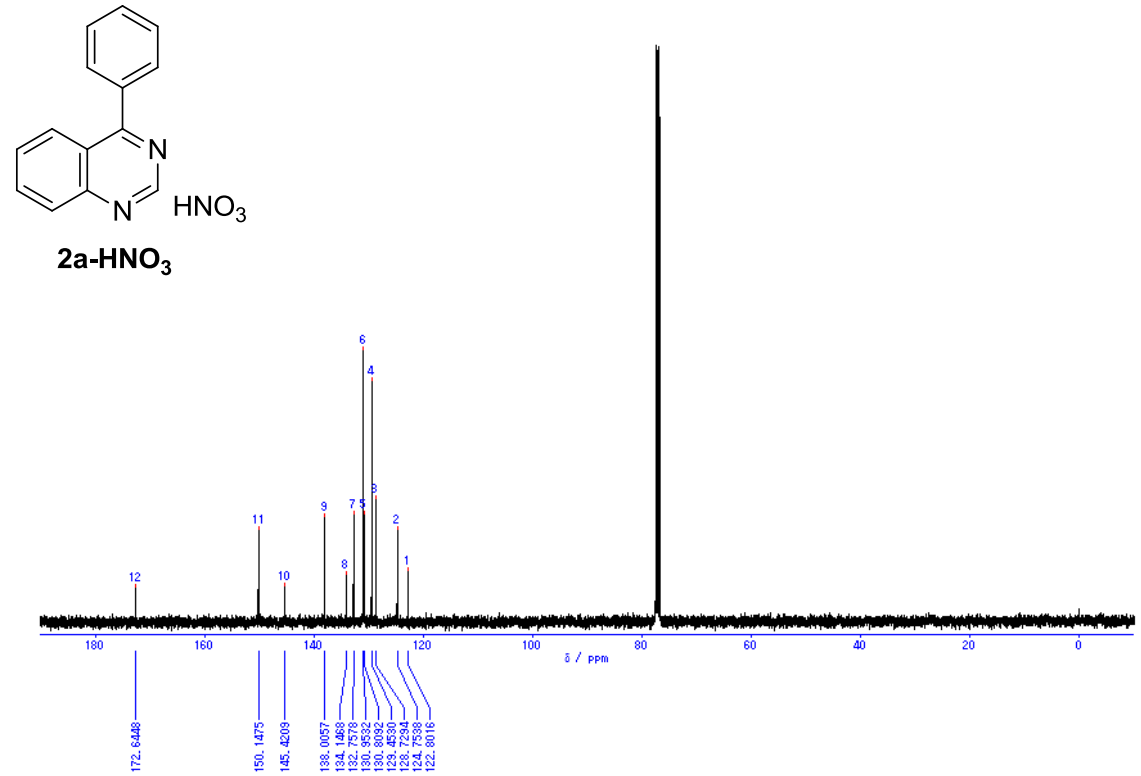
2a-HBr

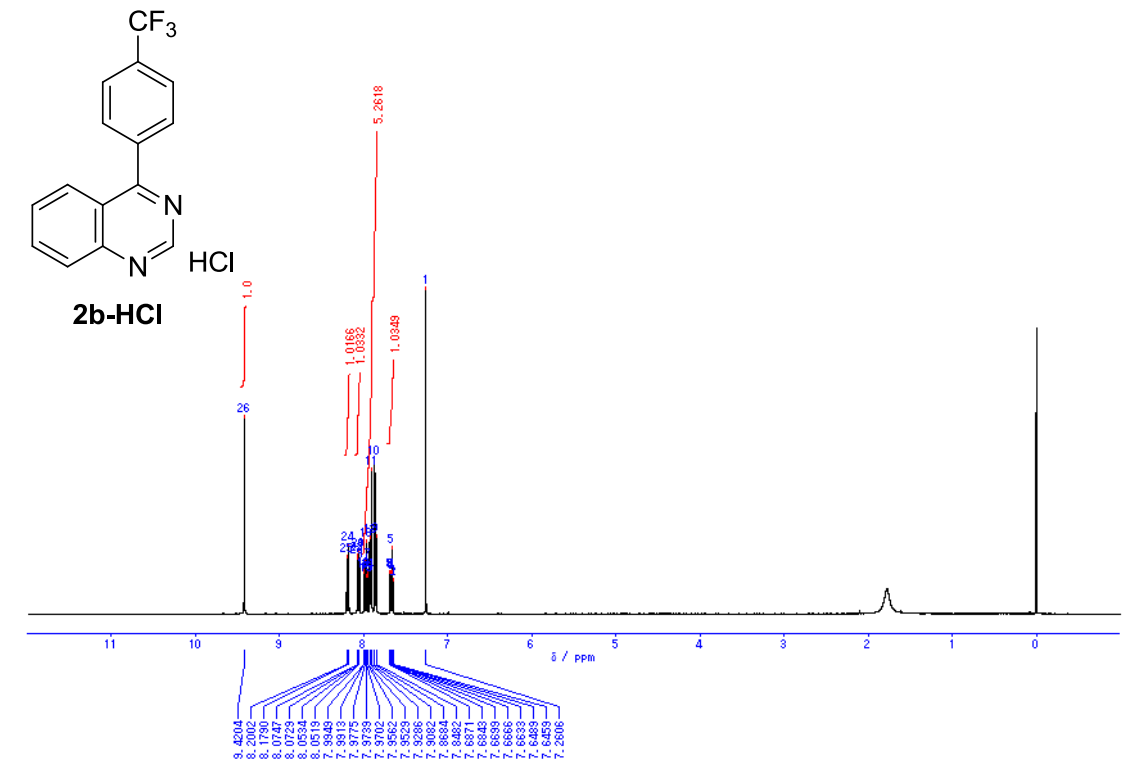
5
4
11
9
8
6
3
2
10
7
1
12
200
180
160
140
120
100
80
60
40
20
0
δ / ppm
173.8332
147.2656
142.9273
139.2853
133.7184
133.2536
131.8300
131.5019
129.6858
129.0695
128.2117
122.5391

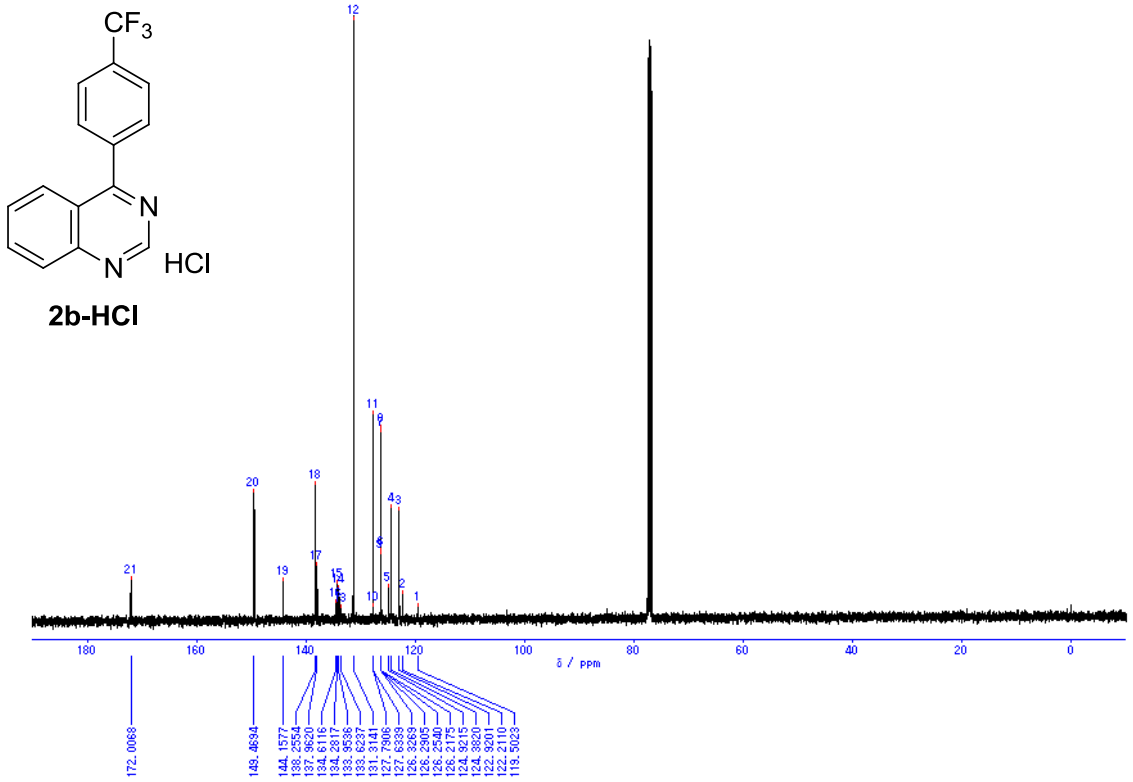

HI
2a-HI
δ / ppm

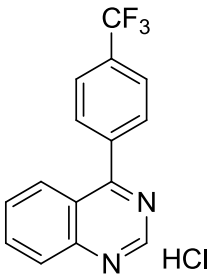

HI
2a-HI
δ / ppm


HNO3
2a-HNO3
δ / ppm


HNO3
2a-HNO3
δ / ppm

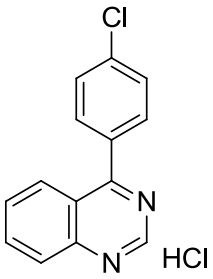

CF3
N
N
HCl
2b-HCl
δ / ppm


CF3
N
N
HCl
2b-HCl
δ / ppm

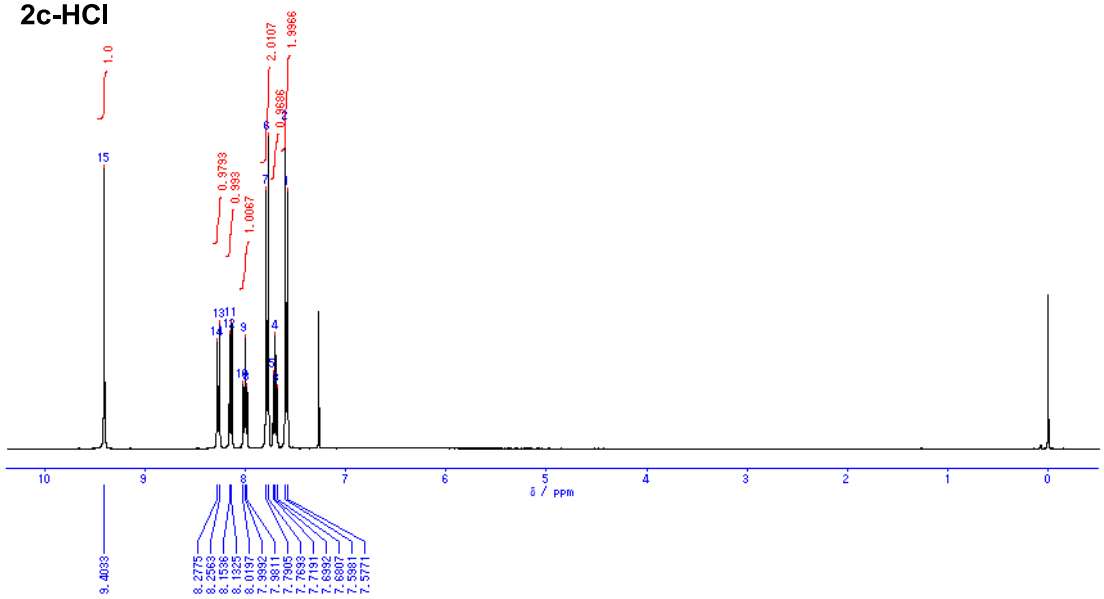

CF3
N
N
HCl

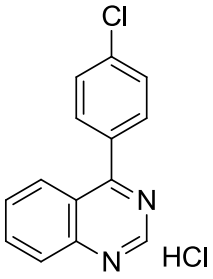
2b-HCl

1
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
δ / ppm
-64.2203


Cl
N
N
HCl

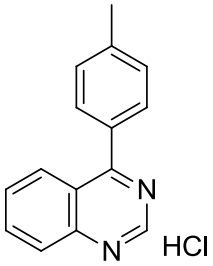
2c-HCl


1.0
2.0107
1.9966
0.9793
0.983
1.0067
15
13
14
9
10
10
9
8
7
6
5
4
3
2
1
0
δ / ppm
9.4033
8.2775
8.2563
8.1536
8.1357
8.0157
7.9932
7.9811
7.7905
7.7693
7.7191
7.6932
7.6807
7.5981
7.5771


Cl
N
N
HCl

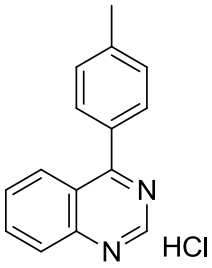
2c-HCl

δ / ppm
173.0166
148.5252
143.4687
140.5504
139.0848
132.9073
132.6776
131.9821
130.3524
128.5327
123.9901
122.8982


N
N
HCl

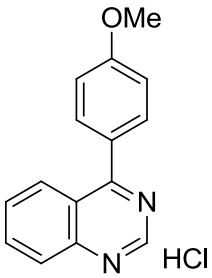
2d-HCl

δ / ppm
1.0
0.9826
1.0199
1.0071
0.952
1.942
2.0333
3.0714
9.4816
8.8134
8.7921
8.4511
8.4397
8.4398
8.4381
8.2817
8.2786
8.2642
8.2606
8.2571
8.2428
8.2394
7.9838
7.9808
7.9661
7.9628
7.9595
7.9448
7.9418
7.9034
7.8991
7.8872
7.8828
7.5192
7.4896
2.5449


N
N
HCl

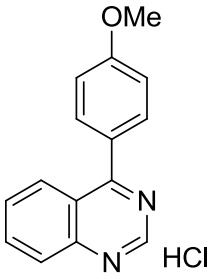
2d-HCl

δ / ppm
173.0038
147.5135
144.8231
143.6054
138.5909
131.5183
131.3778
130.5723
130.3061
128.9645
123.7823
122.3331
21.8137


OMe
N
N
HCl

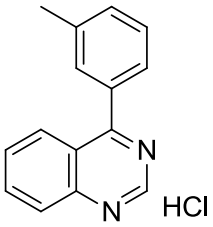
2e-HCl

3.1108
2.0642
1.9787
1.0312
1.0222
0.9932
1.0
δ / ppm
9.4189
8.7376
8.7164
8.4624
8.4412
8.2510
8.2330
8.0372
8.0152
7.9706
7.9520
7.9335
7.2103
7.1882
3.9776


OMe
N
N
HCl

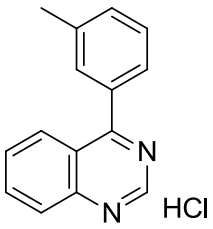
2e-HCl

δ / ppm
171.7260
164.4311
147.1508
143.6109
138.3502
133.8952
131.1391
128.9445
125.4702
123.6638
121.8732
115.2004
55.8640

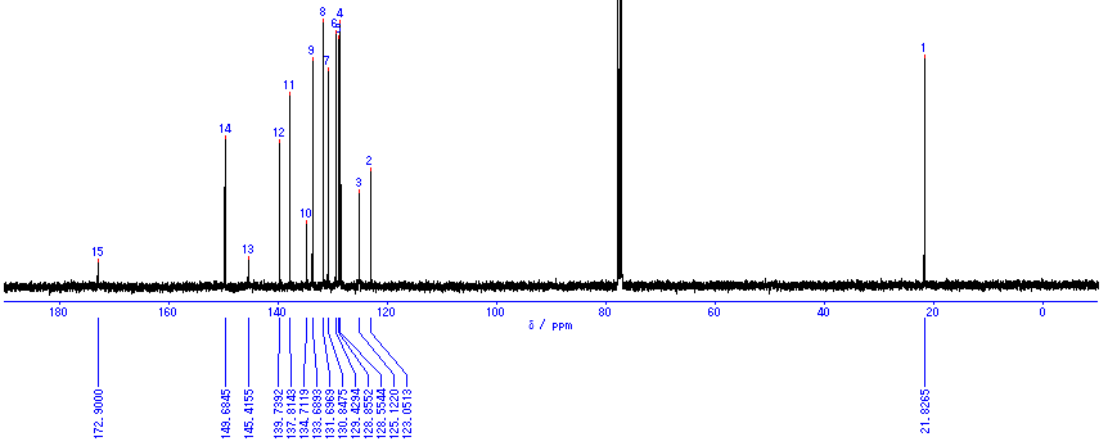

N
N
HCl

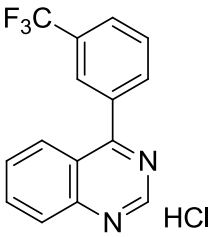
2f-HCl

δ / ppm
9.4748
8.6645
8.6432
8.3948
8.3736
8.2290
8.2082
8.1902
7.9386
7.9183
7.8938
7.7423
7.7033
7.6892
7.5530
7.5407
2.5272

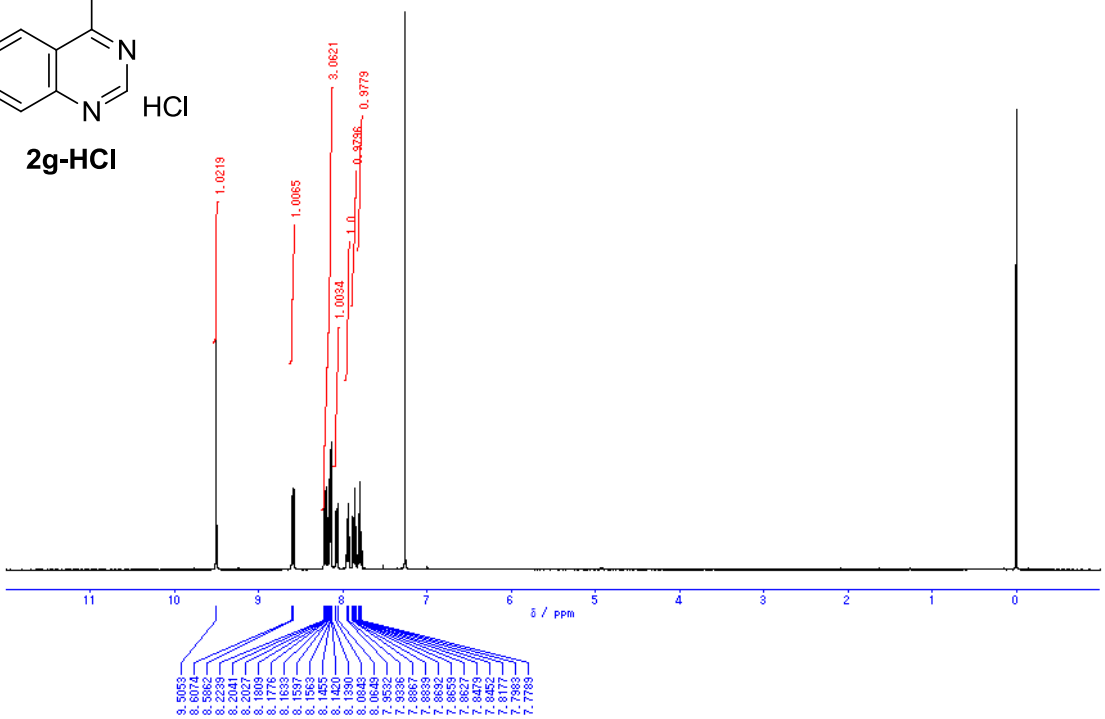

N
N
HCl

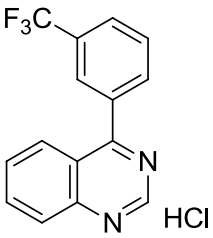
2f-HCl


δ / ppm
172.9000
149.6845
145.4155
139.7332
137.8143
134.7119
133.6893
131.6969
130.8475
129.4294
128.8552
128.5544
125.1220
123.0513
21.8265


F3C
N
N
HCl

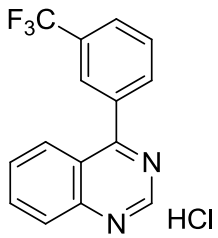
2g-HCl


δ / ppm
1.0219
1.0065
3.0621
0.9779
0.9296
1.0
1.0034

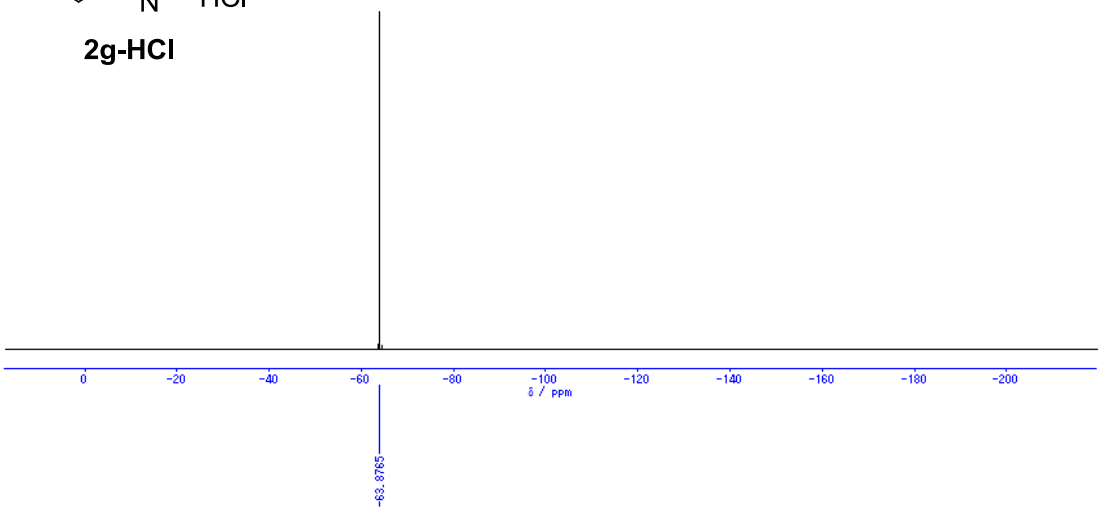

F3C
N
N
HCl

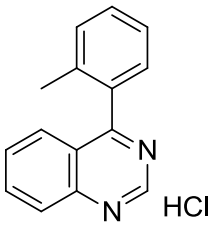
2g-HCl

180
160
140
120
100
80
60
40
20
0
δ / ppm
172.6830
148.2919
142.2456
138.6346
134.8632
133.9700
133.2933
131.9612
131.6113
131.2977
129.8048
129.1468
129.1122
129.0793
129.0447
127.5445
127.5081
127.4638
127.4333
127.2600
124.4695
122.9491
122.5044
121.7808
119.0684


F3C
N
N
HCl

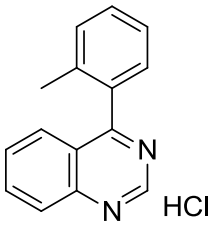
2g-HCl


0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
δ / ppm
-63.8765

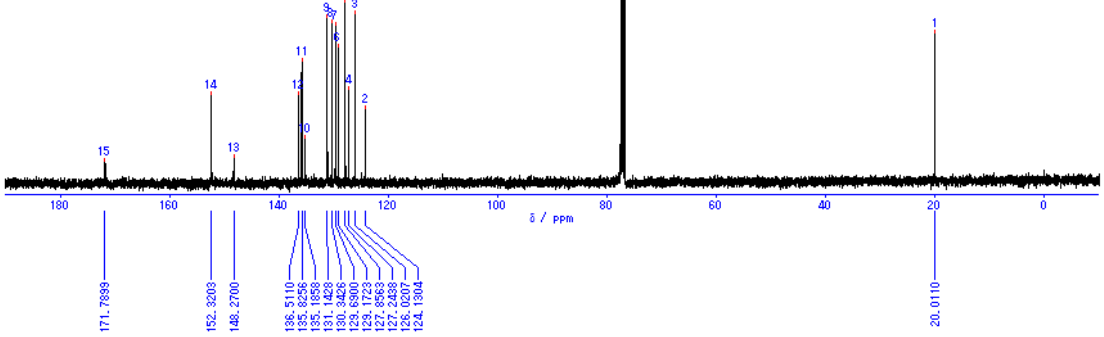

N
N
HCl

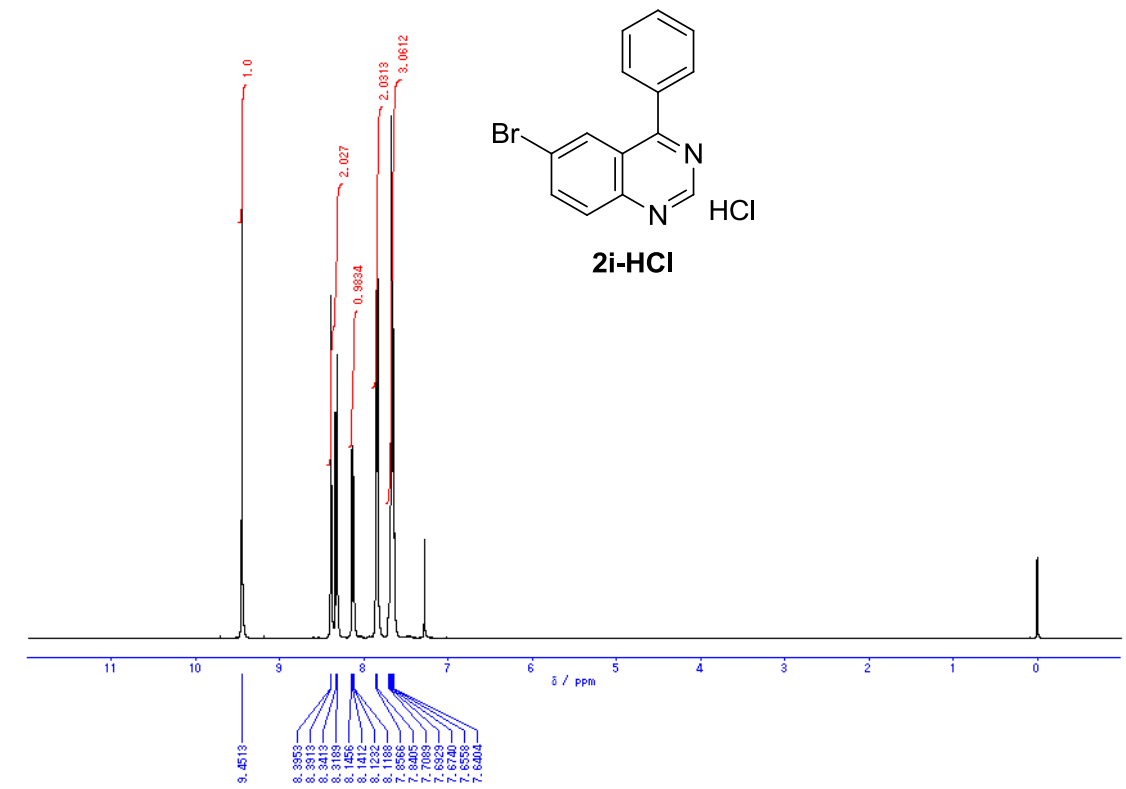
2h-HCl

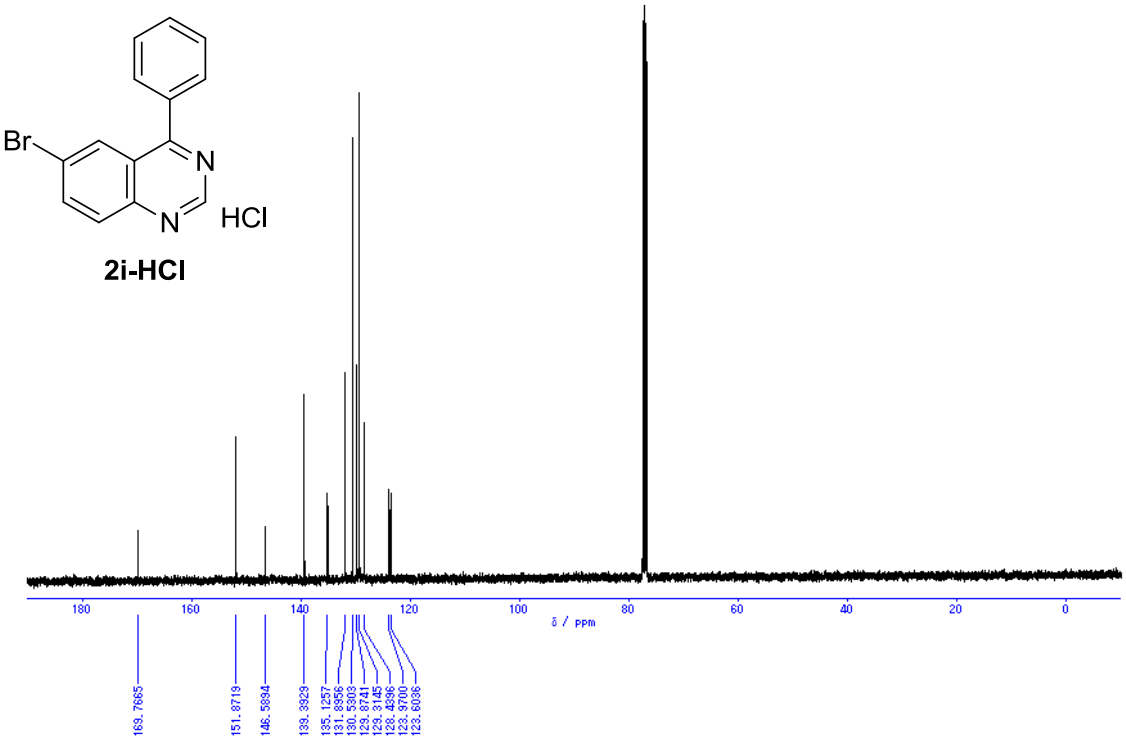
3.1029
4.1137
0.9631
1.0159
1.0244
1.0271
1.0
δ / ppm

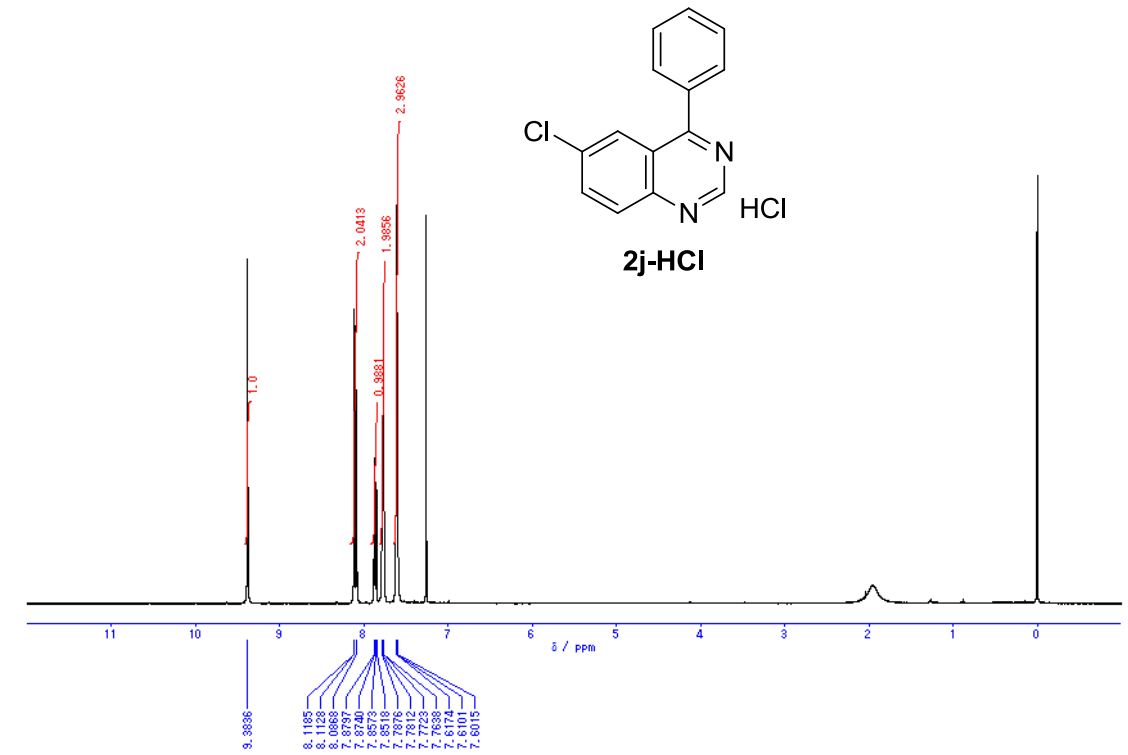

N
N
HCl

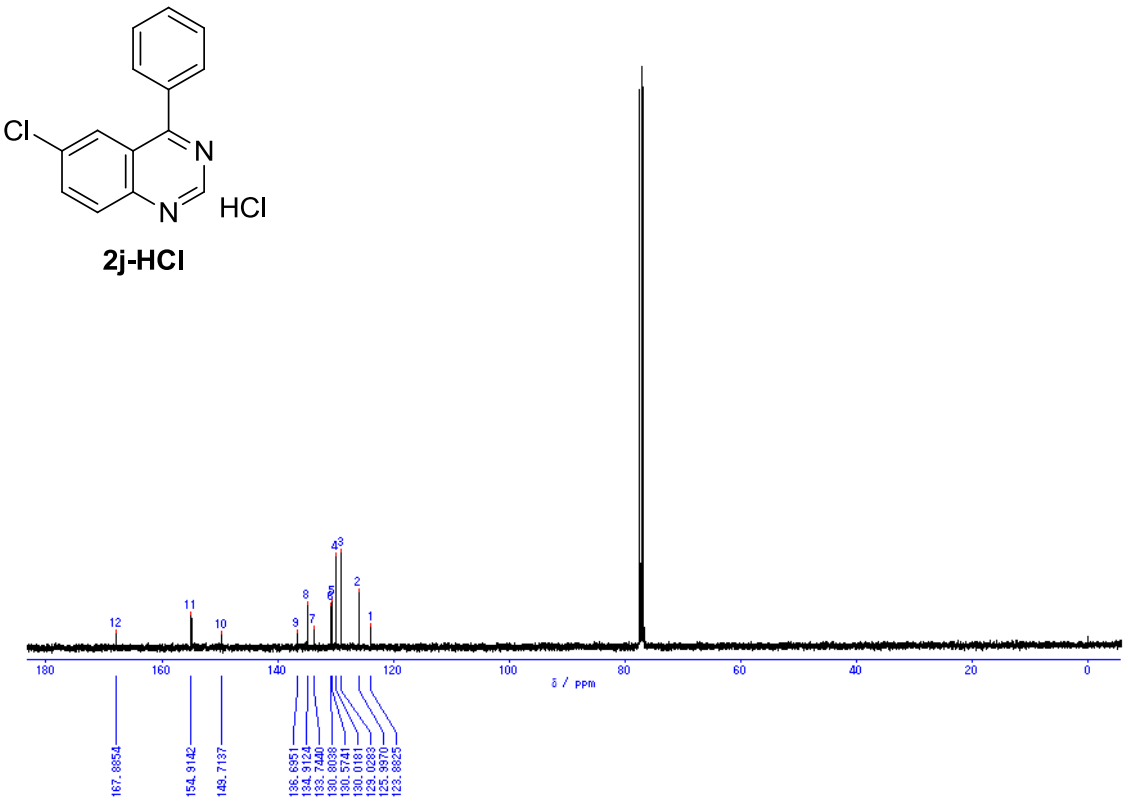
2h-HCl

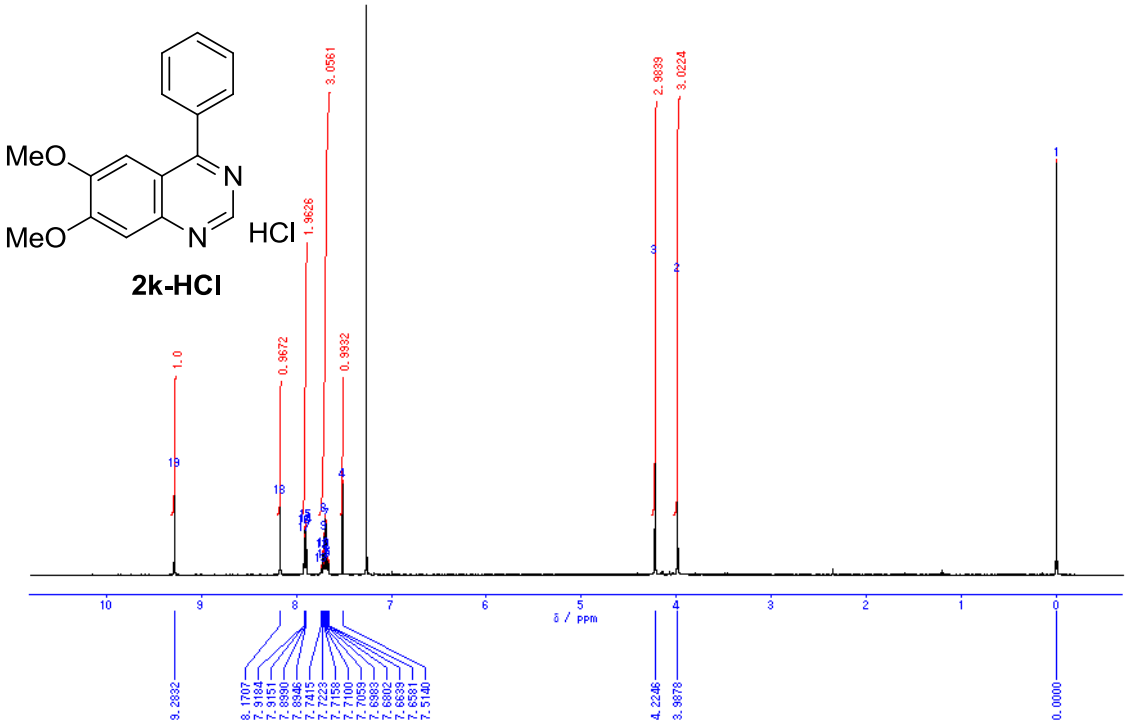

δ / ppm

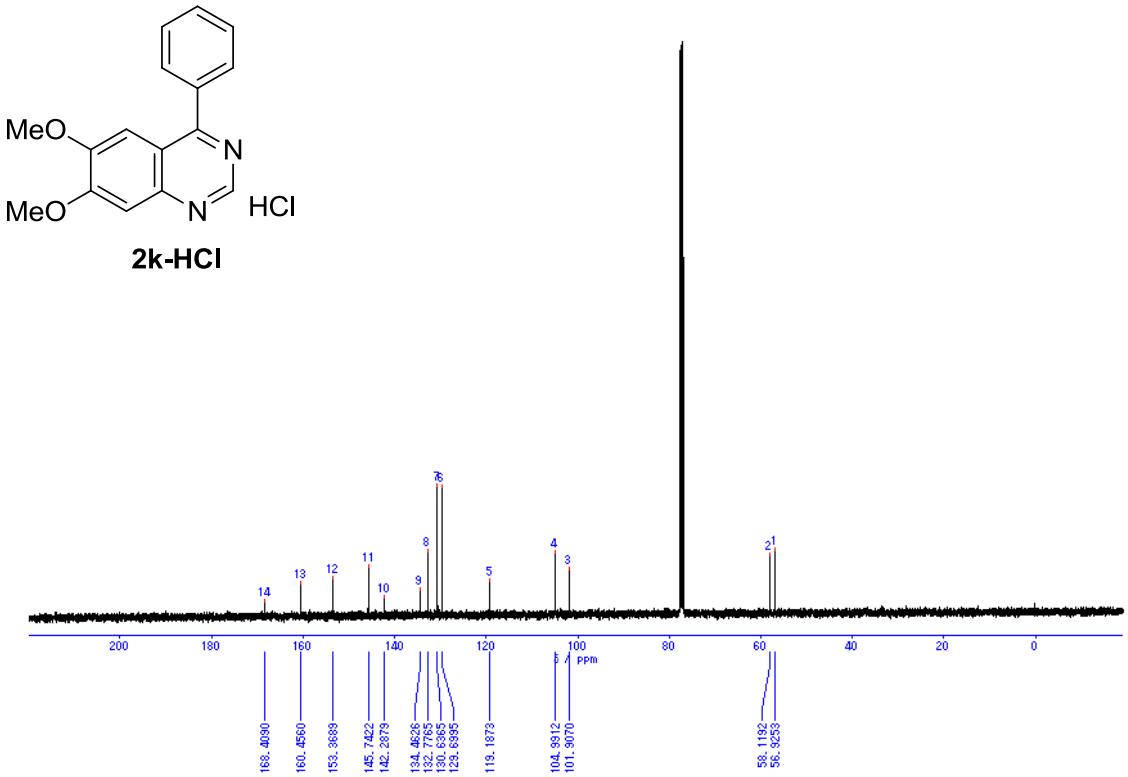

1.0
2.027
0.9834
2.0313
3.0612
Br
N
N
HCl
2i-HCl
11
10
9
8
7
6
5
4
3
2
1
0
δ / ppm
9.4513
8.3953
8.3913
8.3413
8.3189
8.1456
8.1412
8.1252
8.1188
7.8566
7.8405
7.7089
7.6329
7.6740
7.6558
7.6404

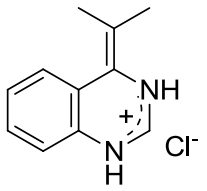

Br
N
N
HCl
2i-HCl
180
160
140
120
100
80
60
40
20
0
δ / ppm
163.7665
151.8719
146.5894
139.3929
135.1257
131.8956
130.5303
123.8741
123.3145
128.4396
123.9700
123.6036


Cl
N
N
HCl
2j-HCl
2.9626
2.0413
1.9856
0.9881
1.0
δ / ppm

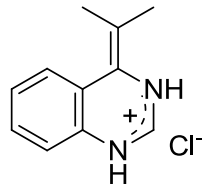

Cl
N
N
HCl
2j-HCl
δ / ppm


MeO
MeO
N
N
HCl
2k-HCl
δ / ppm

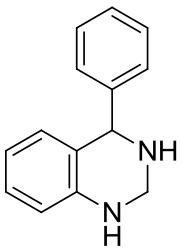

MeO
MeO
N
N
HCl
2k-HCl
δ / ppm



2l-HCl

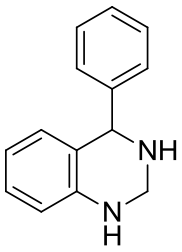


2l-HCl


NH
N
H

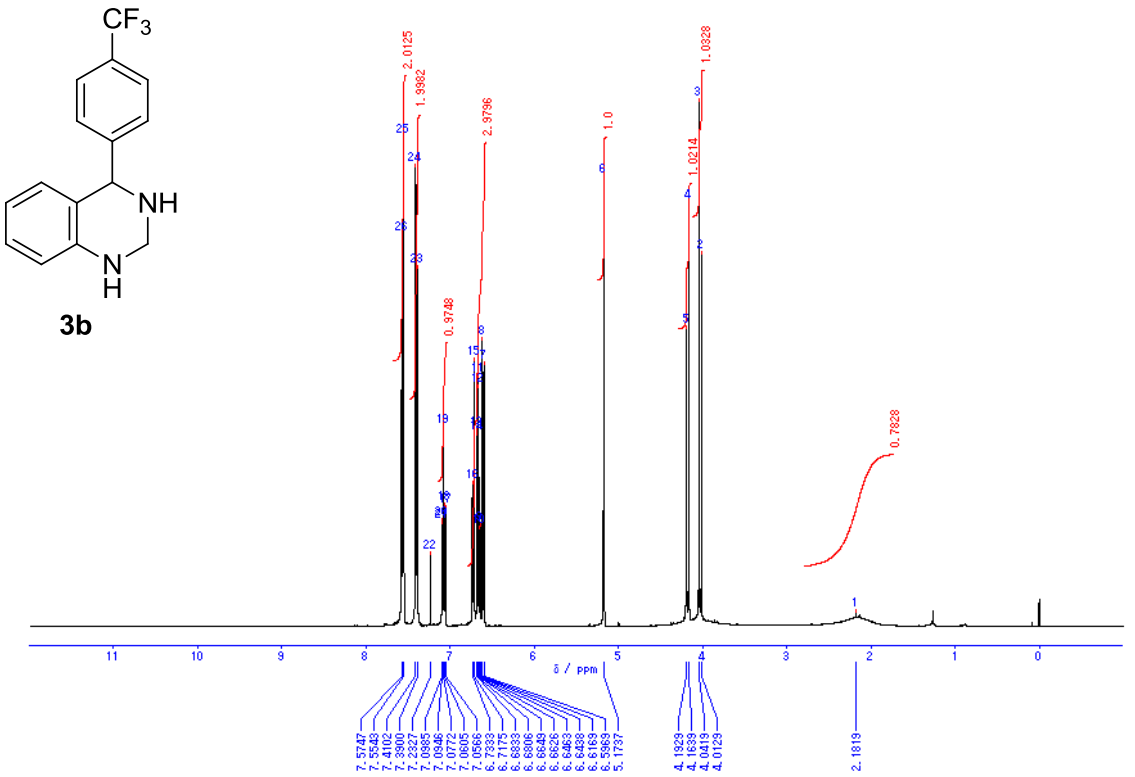
3a

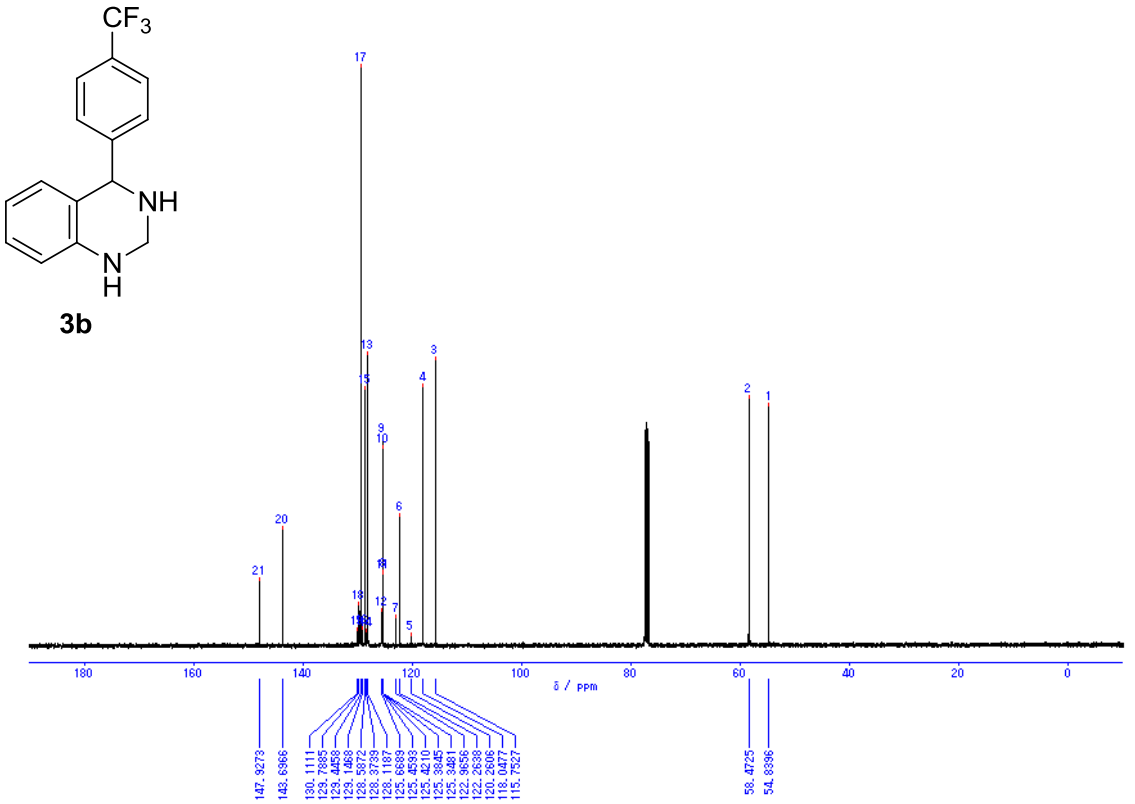
5.1363
1.0062
0.9179
1.8879
1.0
0.9986
0.9074
0.6393
δ / ppm

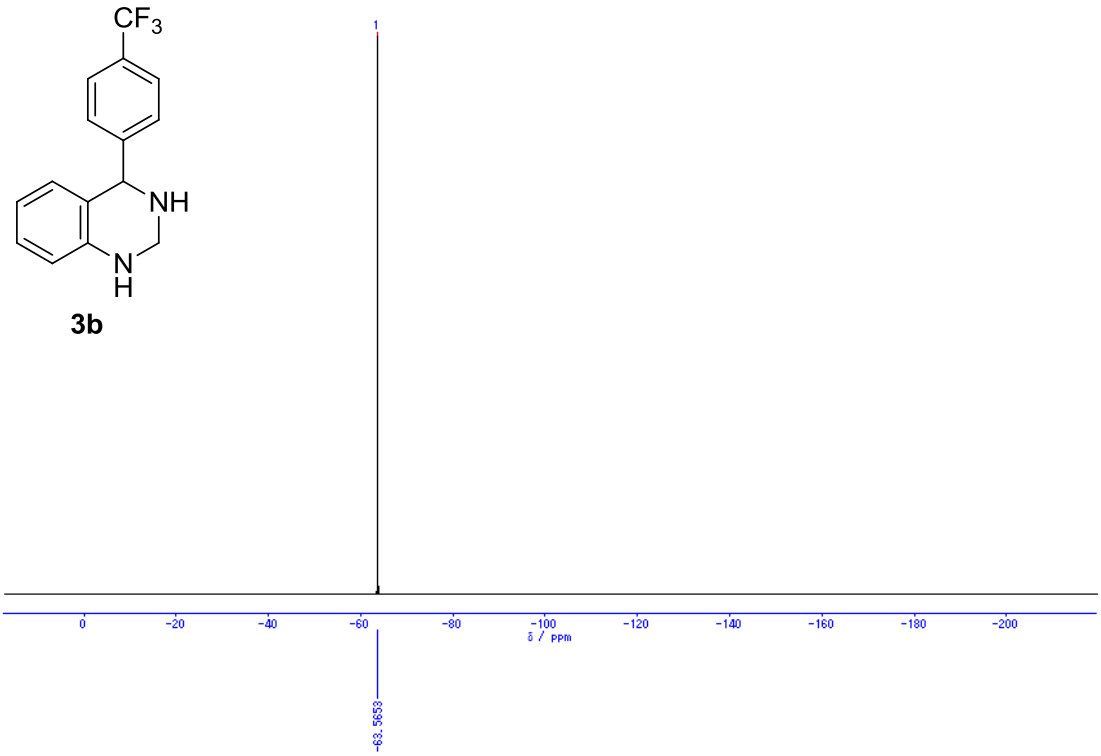

NH
N
H

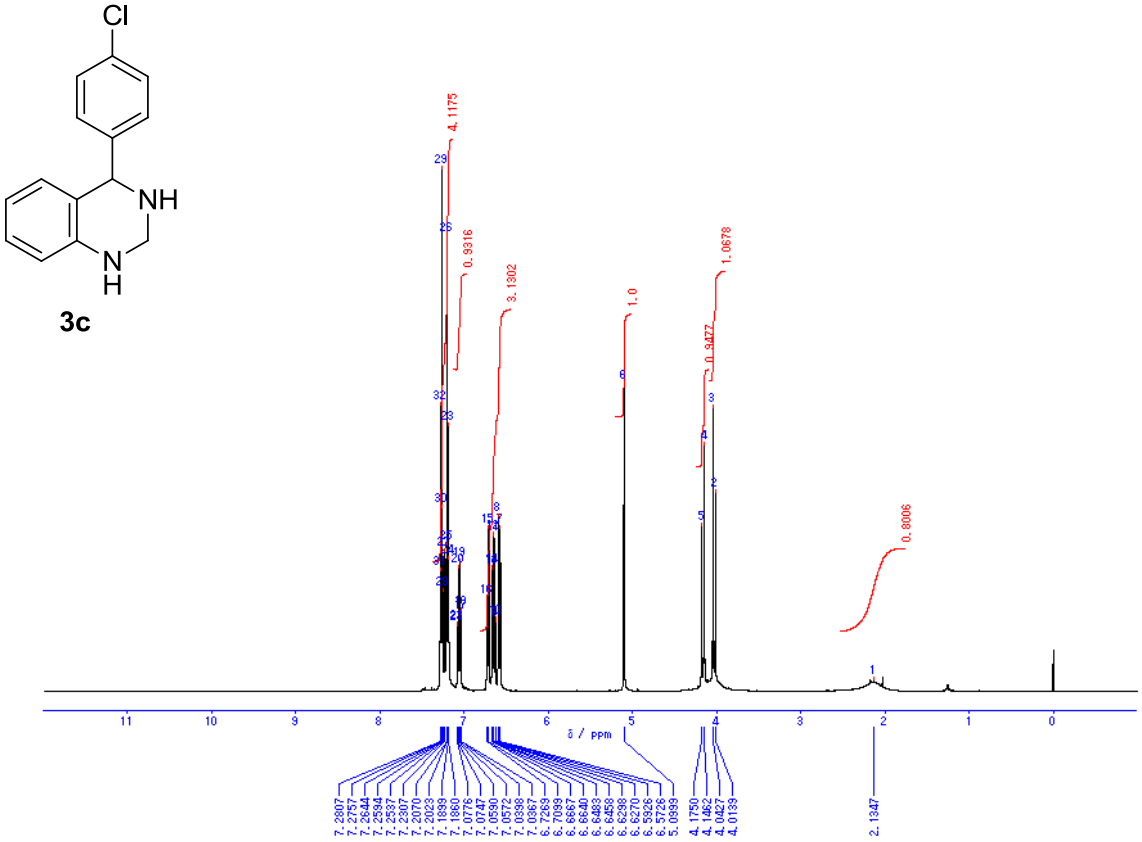
3a

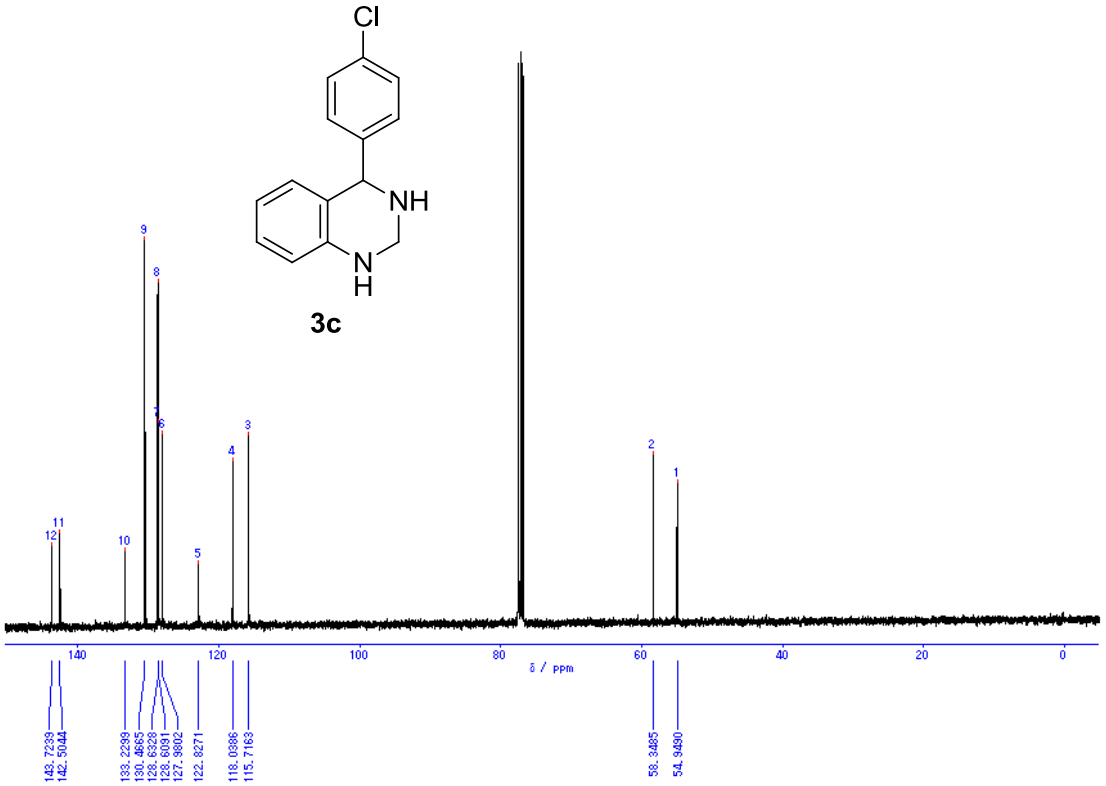
δ / ppm

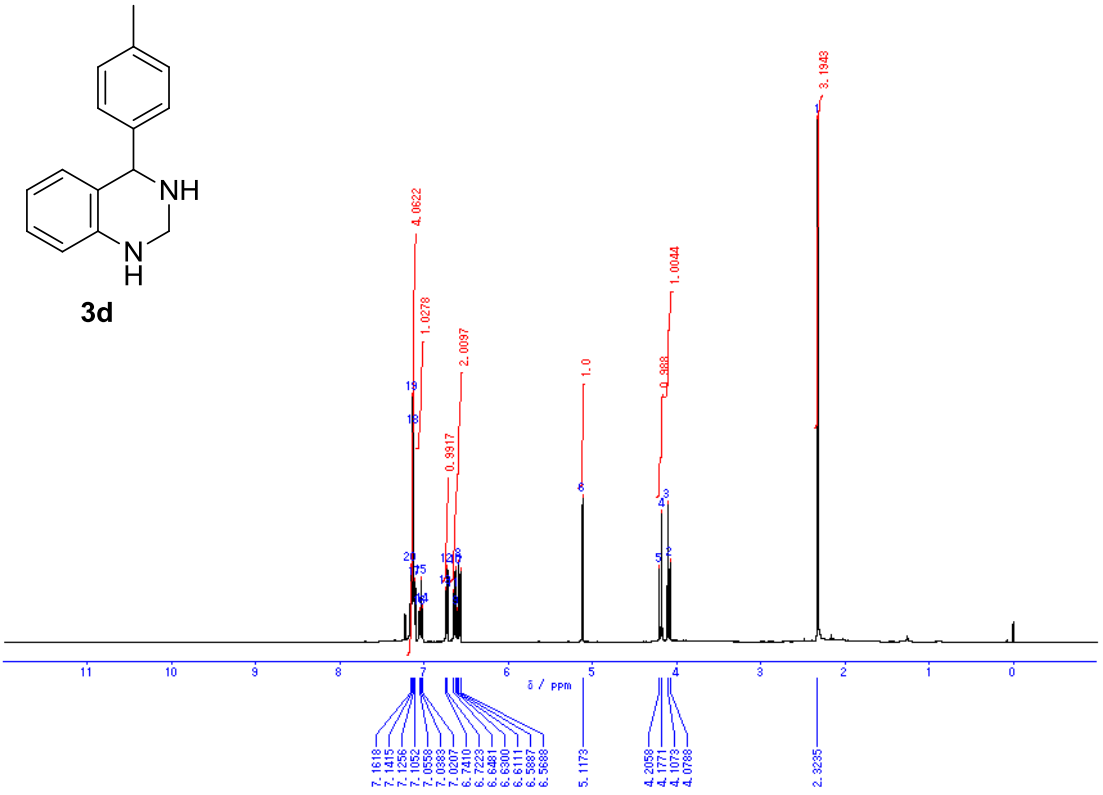

CF3
NH
N
H
3b
2.0125
1.9982
2.9796
1.0
1.0328
1.0214
0.9748
0.7828
δ / ppm

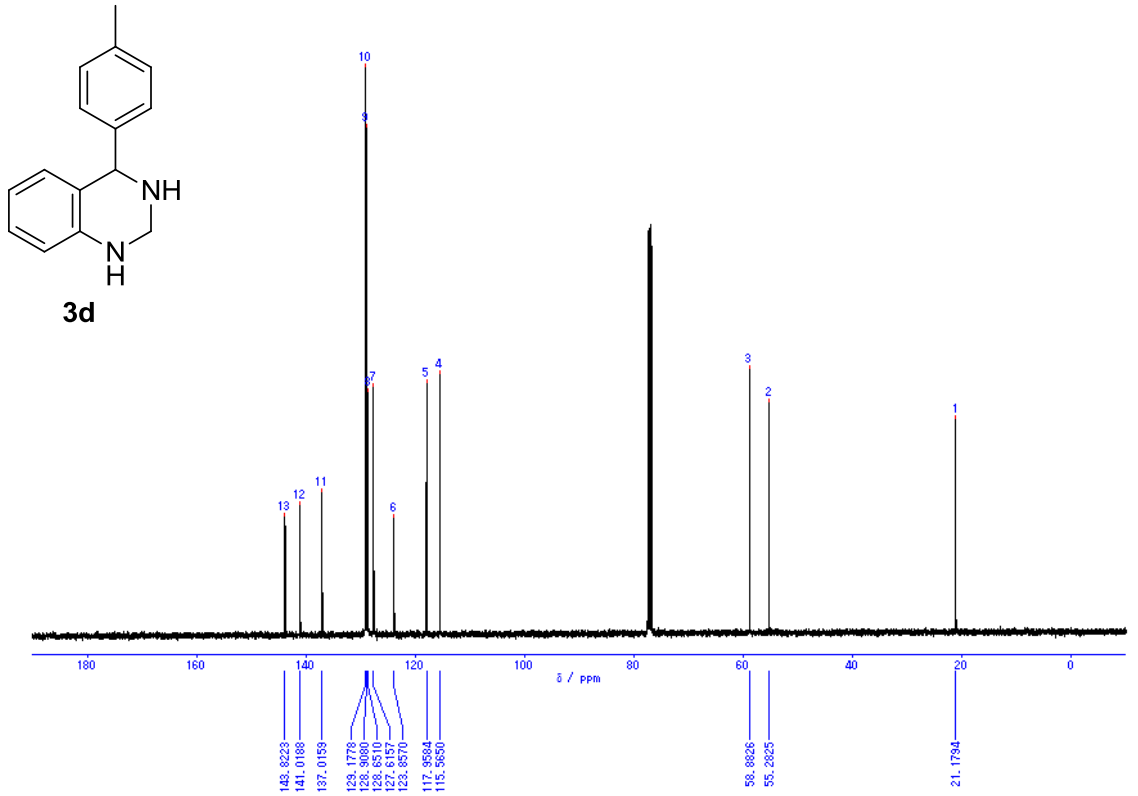

CF3
NH
N
H
3b
δ / ppm


CF3
NH
N
H
3b
δ / ppm
-63.5653

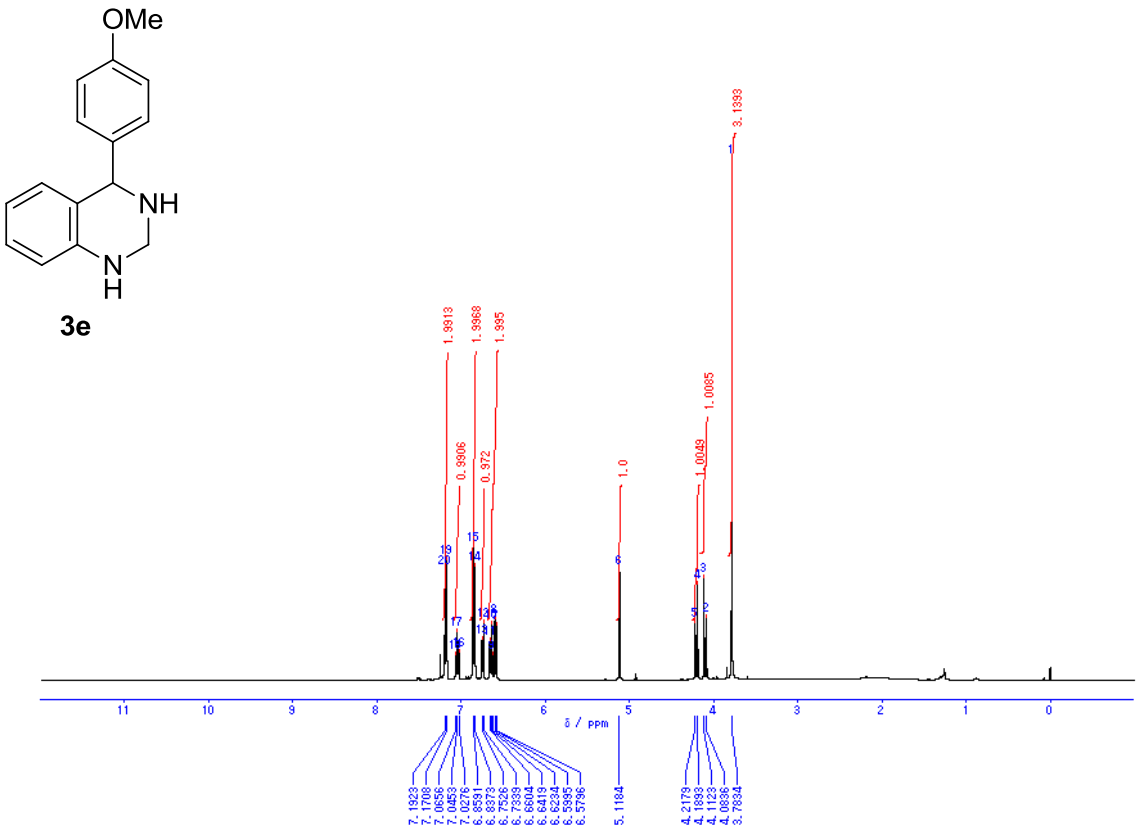

Cl
NH
N
H
3c
δ / ppm


Cl
NH
N
H
3c
δ / ppm

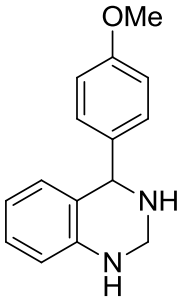

NH
N
H
3d
δ / ppm



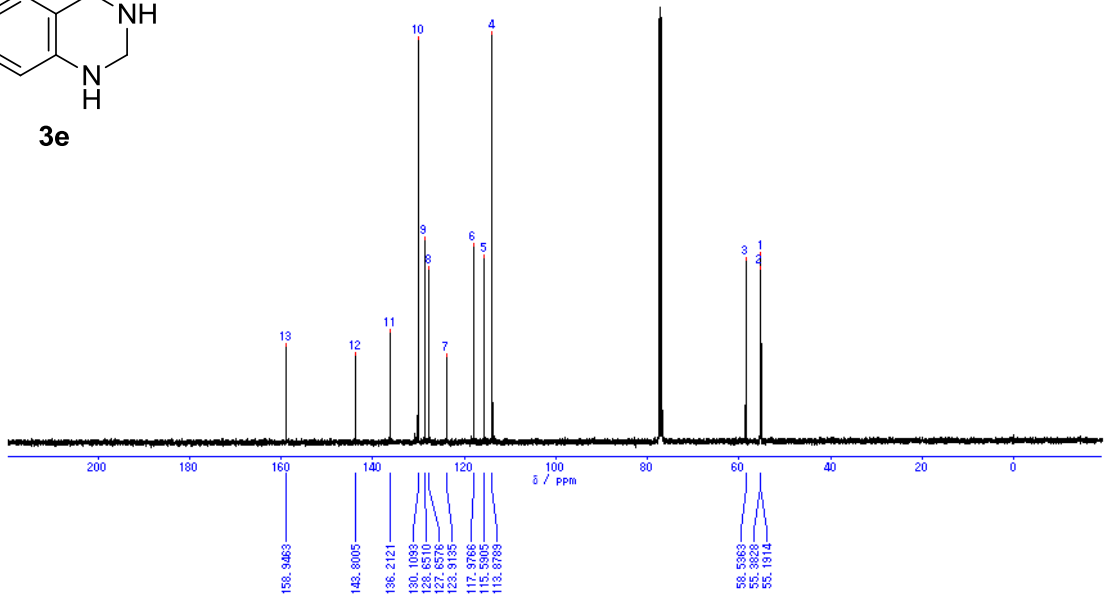
3d

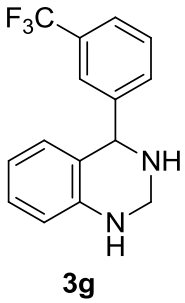


3e

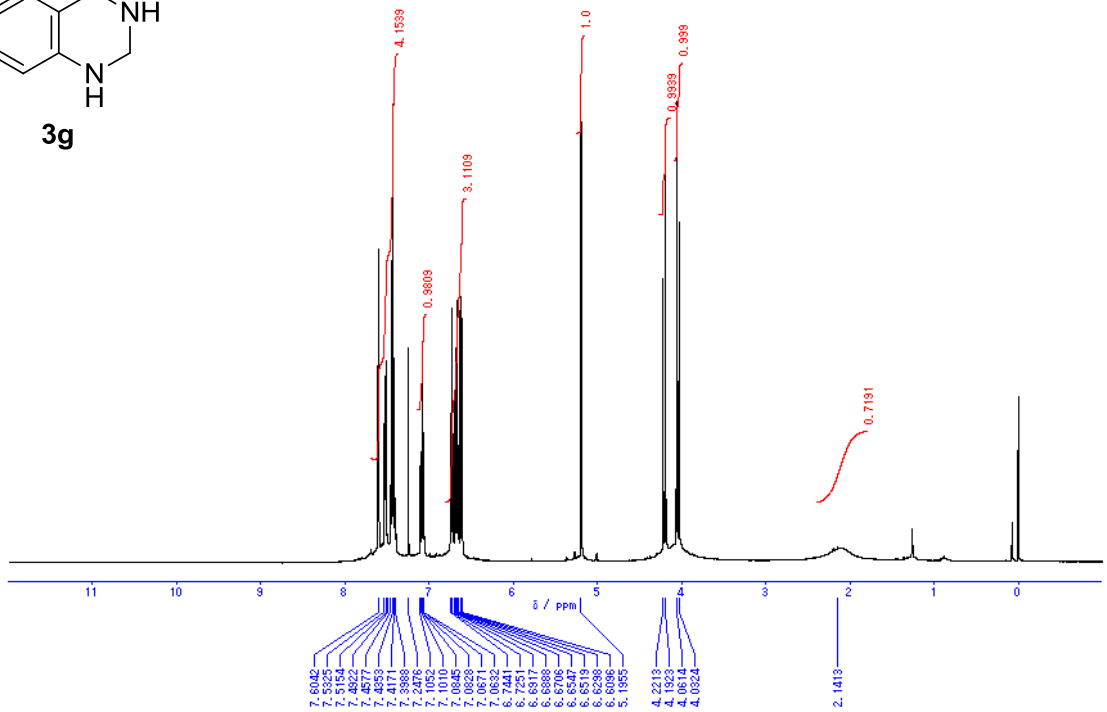

OMe
NH
N
H

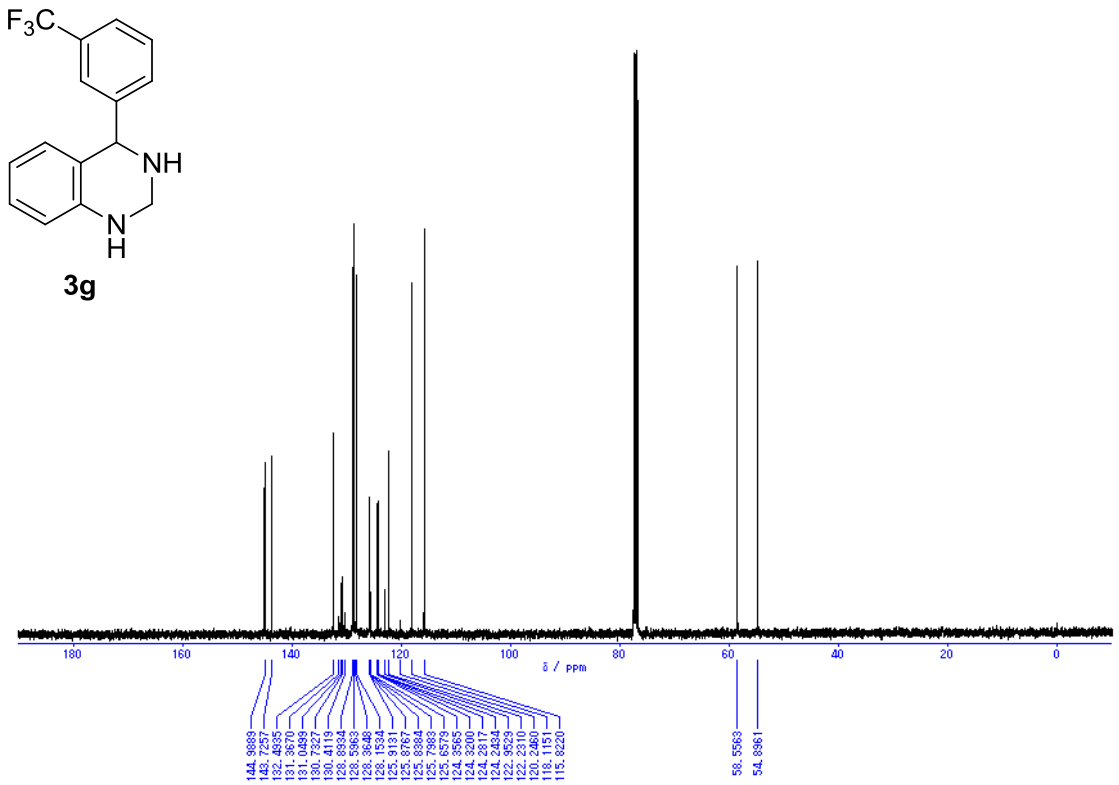
3e

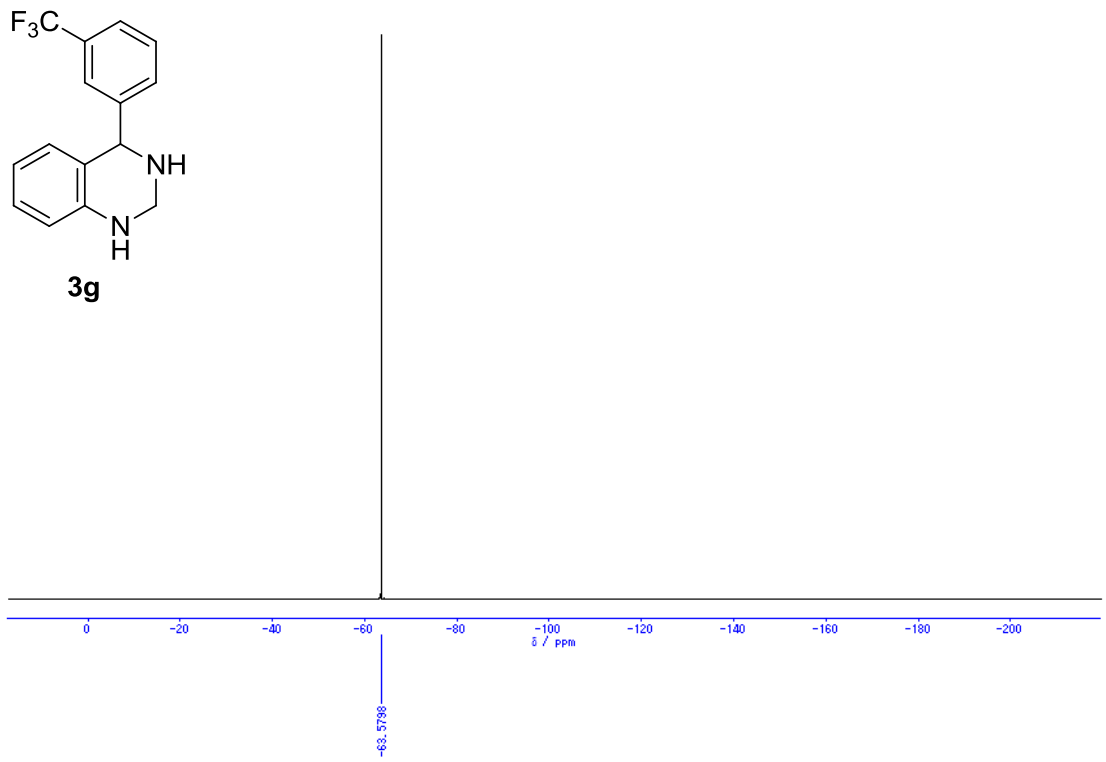

δ / ppm
158.9463
142.8005
136.2121
130.1033
128.8510
127.6578
123.9135
117.9766
115.5905
113.8789
58.5363
55.3828
55.1914

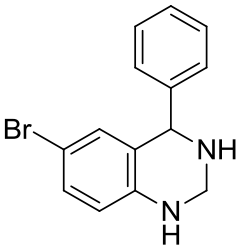

F3C
NH
N
H

3g


δ / ppm
4.1539
0.9809
3.1109
1.0
0.9939
0.999
0.7191
2.1413

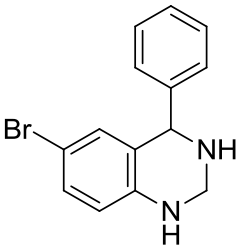

F3C
NH
N
H
3g
180
160
140
120
100
80
60
40
20
0
δ / ppm
144.9889
142.7257
132.4835
131.3670
131.0499
130.7327
130.4119
128.8934
128.5963
128.3648
128.1534
125.9181
125.8787
125.8394
125.7983
125.6579
124.3565
124.3200
124.2817
124.2434
122.9529
122.2310
120.2460
118.1151
115.8220
58.5563
54.8961


F3C
NH
N
H
3g
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
δ / ppm
-63.5798


Br
NH
N
H

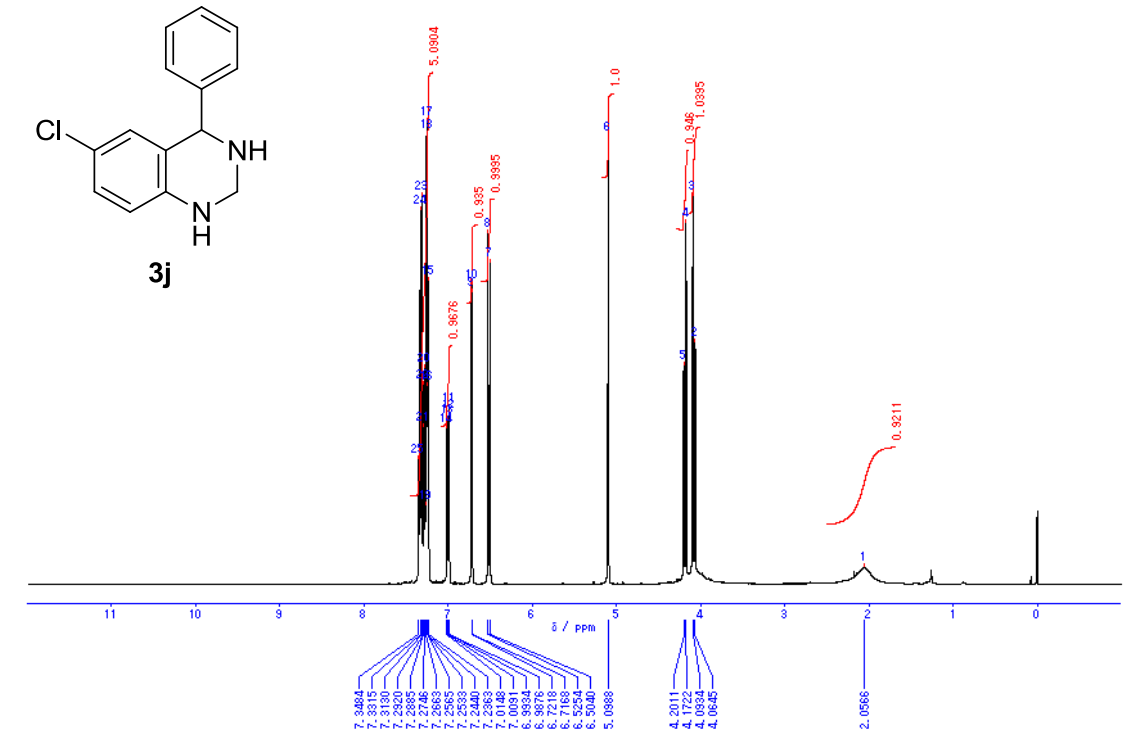
3i

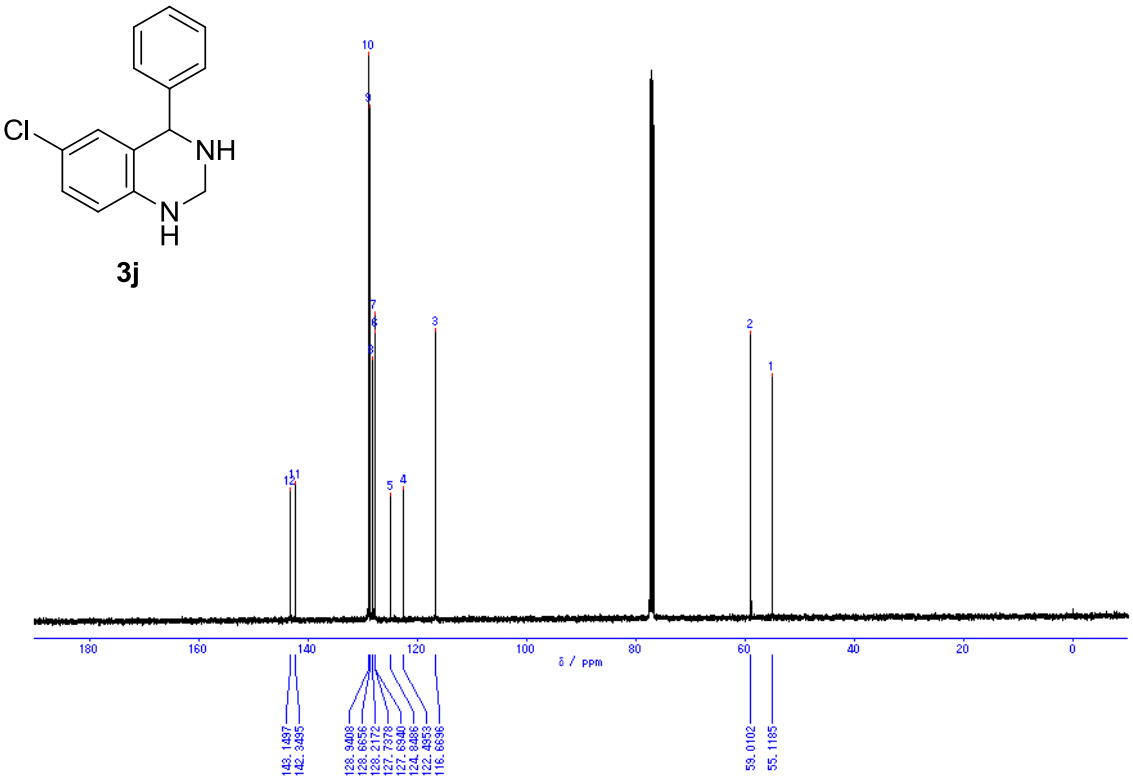
6.087
0.9466
0.9817
1.0
0.9441
0.9106
0.7754
11
10
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.3411
7.3238
7.3052
7.2851
7.2677
7.2482
7.2365
7.2257
7.1978
7.1877
7.1745
7.1113
6.8517
6.8478
6.4622
6.4409
5.0826
4.1744
4.1454
4.0658
4.0367
2.0977

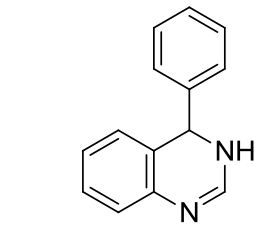

Br
NH
N
H

3i

180
160
140
120
100
80
60
40
20
0
δ / ppm
143.0804
142.7450
131.0061
130.5322
128.9208
128.6364
127.6867
125.2168
116.9341
109.4804
58.8516
54.9307

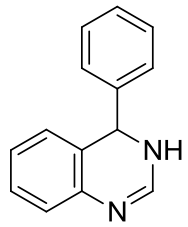

Cl
NH
N
H
3j
δ / ppm


Cl
NH
N
H
3j
δ / ppm

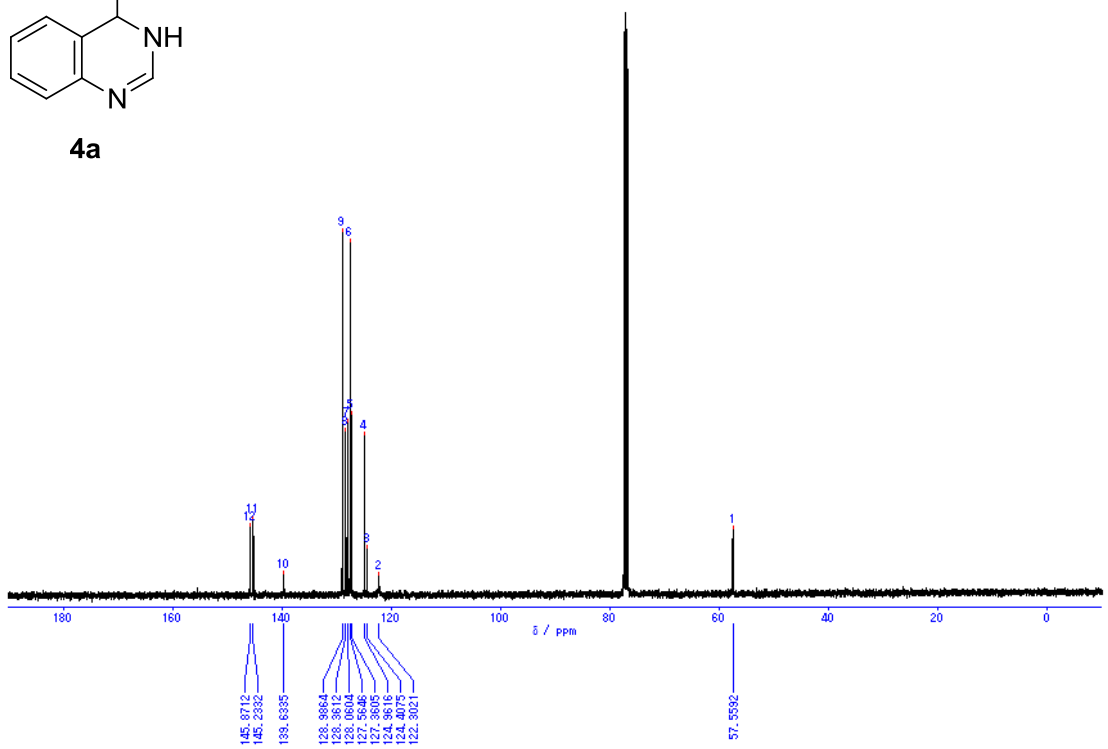

NH
N

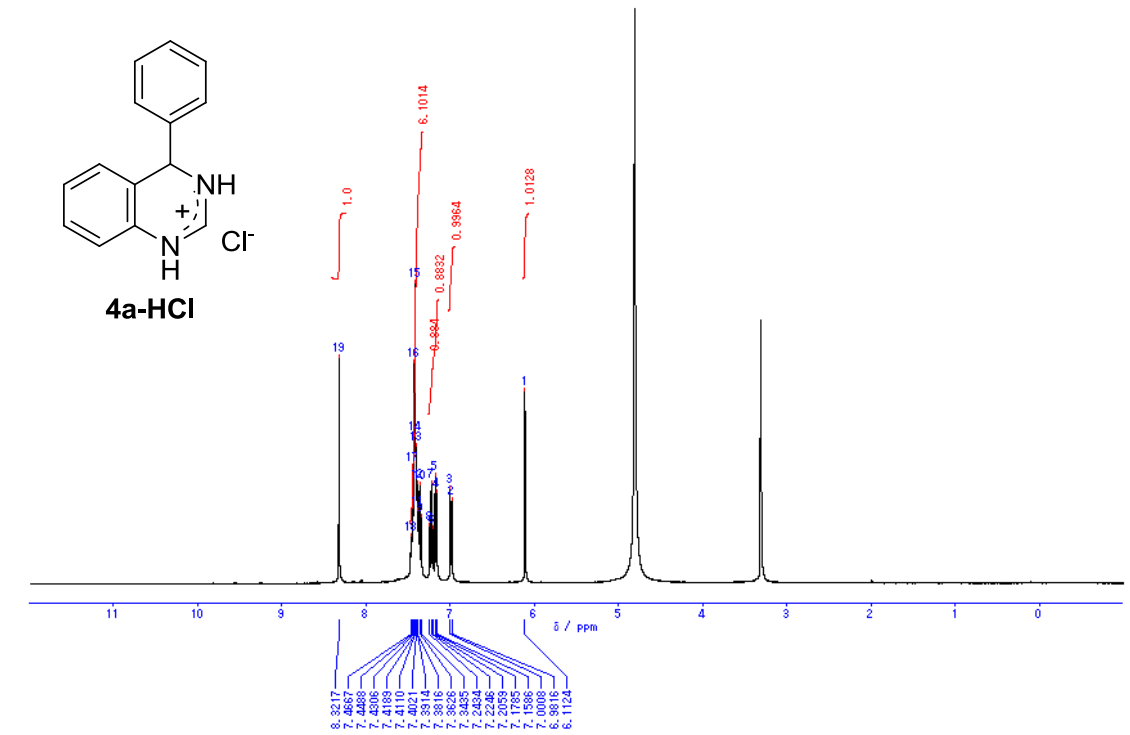
4a

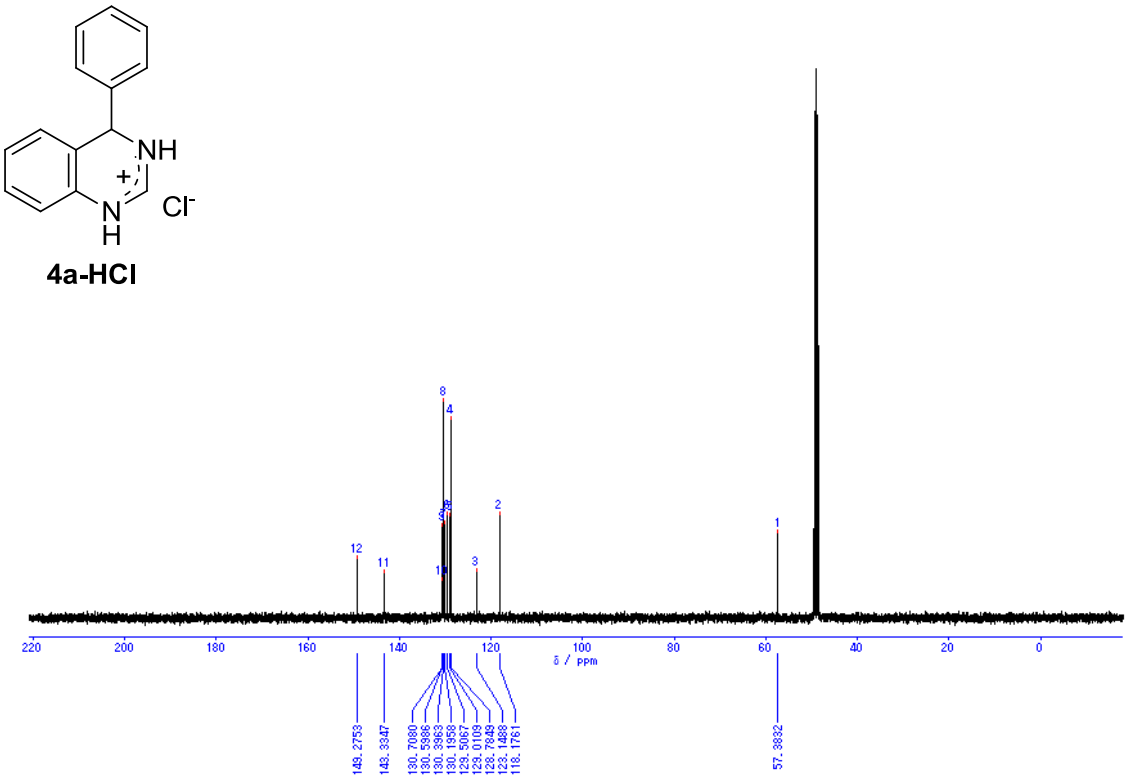
18
1.0676
5.1782
0.9816
0.9825
0.9964
1.0
19
0.8493
1
12
13
8
5
3
11
10
9
7
6
4
2
11 10 9 8 7 6 5 4 3 2 1 0
δ / ppm
7.3404
7.3301
7.2950
7.2845
7.2740
7.2613
7.2533
7.2046
7.1565
7.1378
7.1193
7.0088
6.9884
6.9504
6.9313
6.9128
6.7244
6.7055
5.7171

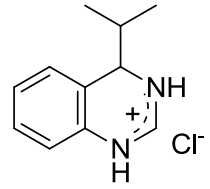

NH
N

4a

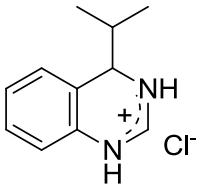

9
6
5
4
11
12
10
3
2
1
180 160 140 120 100 80 60 40 20 0
δ / ppm
145.8712
145.2332
139.6335
128.9864
126.3612
126.0604
125.5846
124.9615
124.4075
122.3021
57.5592


NH
Cl-
4a-HCl
δ / ppm

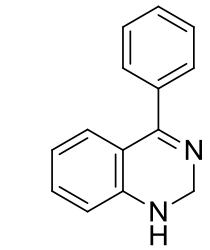

NH
Cl-
4a-HCl
δ / ppm



4l-HCl

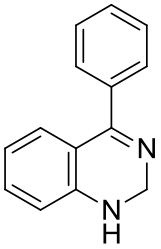


4l-HCl



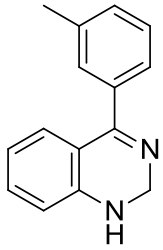
5a

1.9294
3.0000
1.9997
2.0564
2.0834
1.0
0.823
δ / ppm

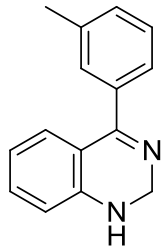


5a

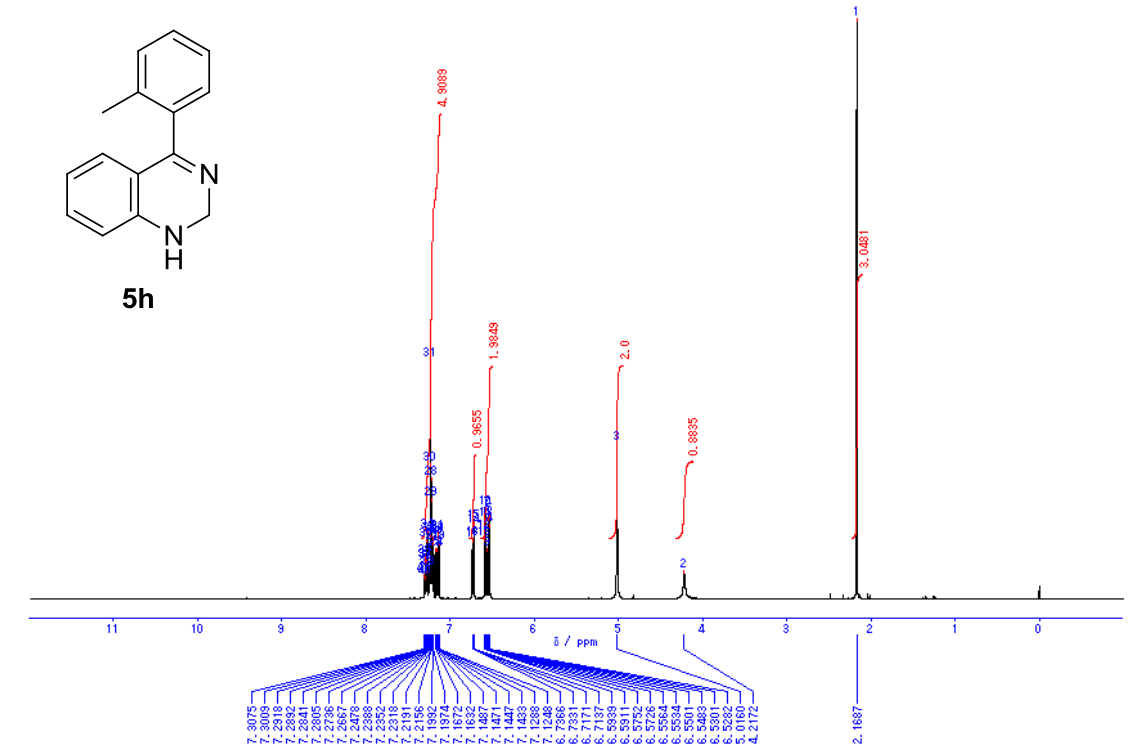
δ / ppm
166.5784
148.0312
138.3101
132.5719
129.4884
128.9158
128.3117
128.2263
118.7932
118.4396
114.6937
60.7874

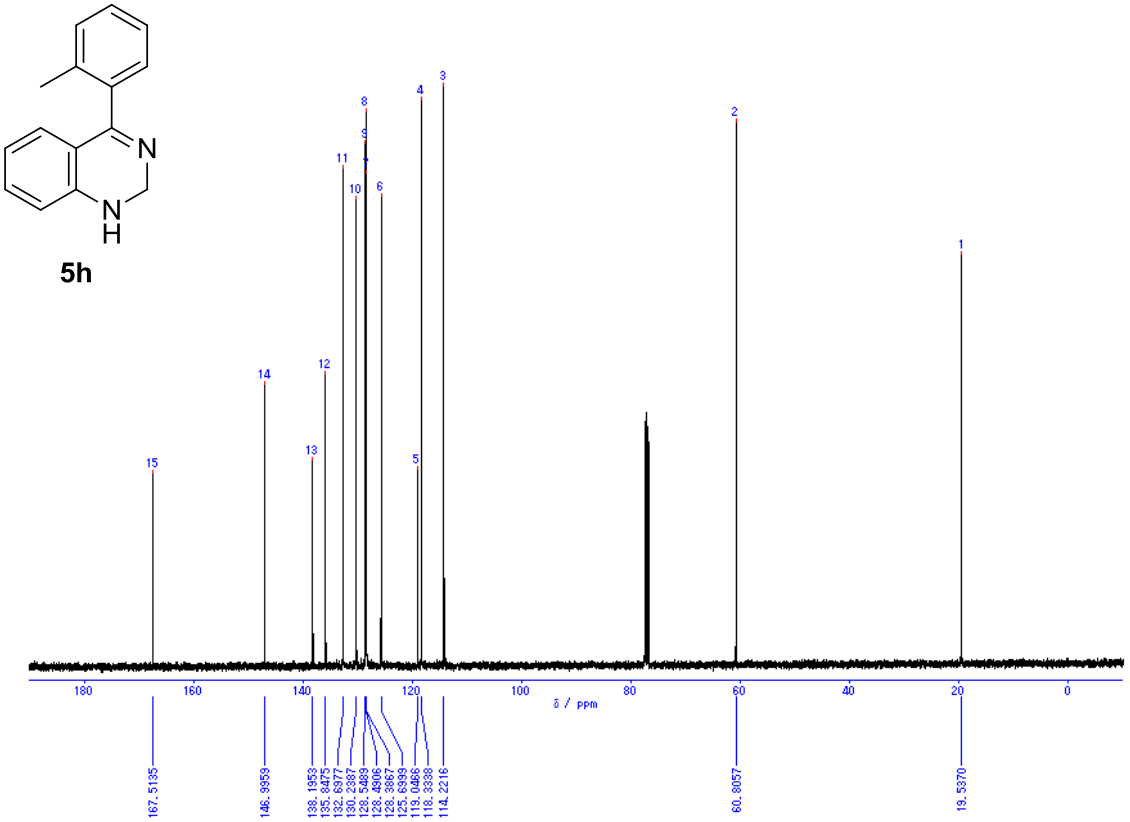


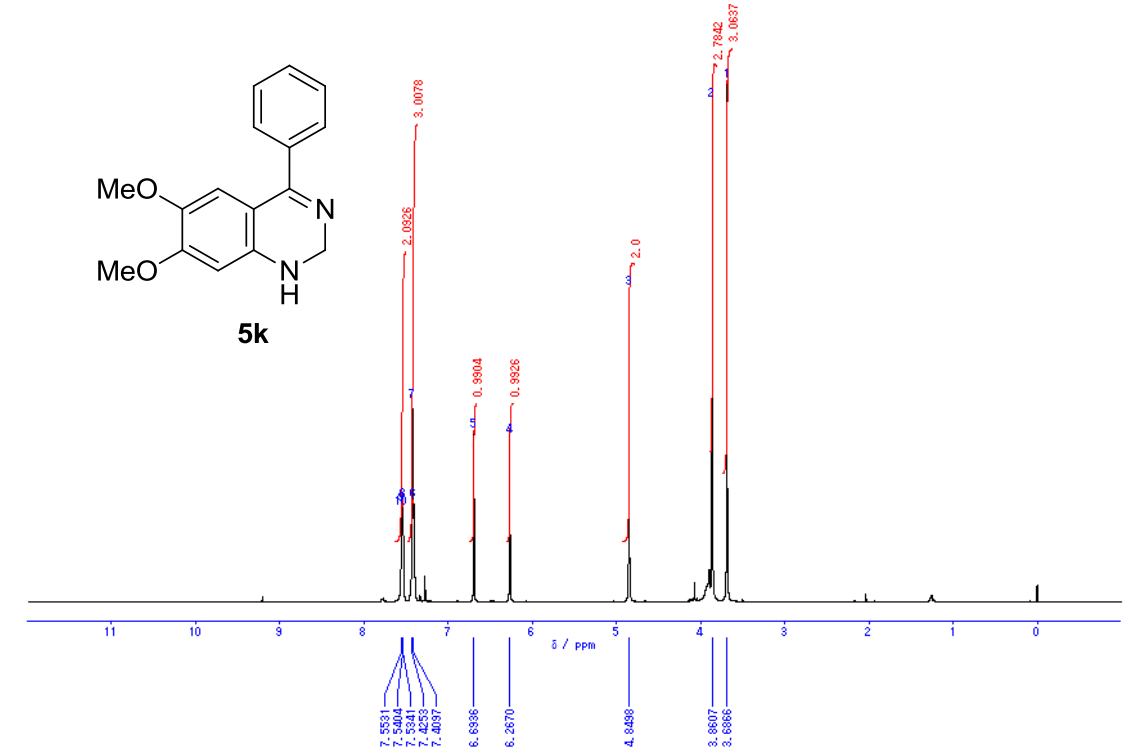
5f

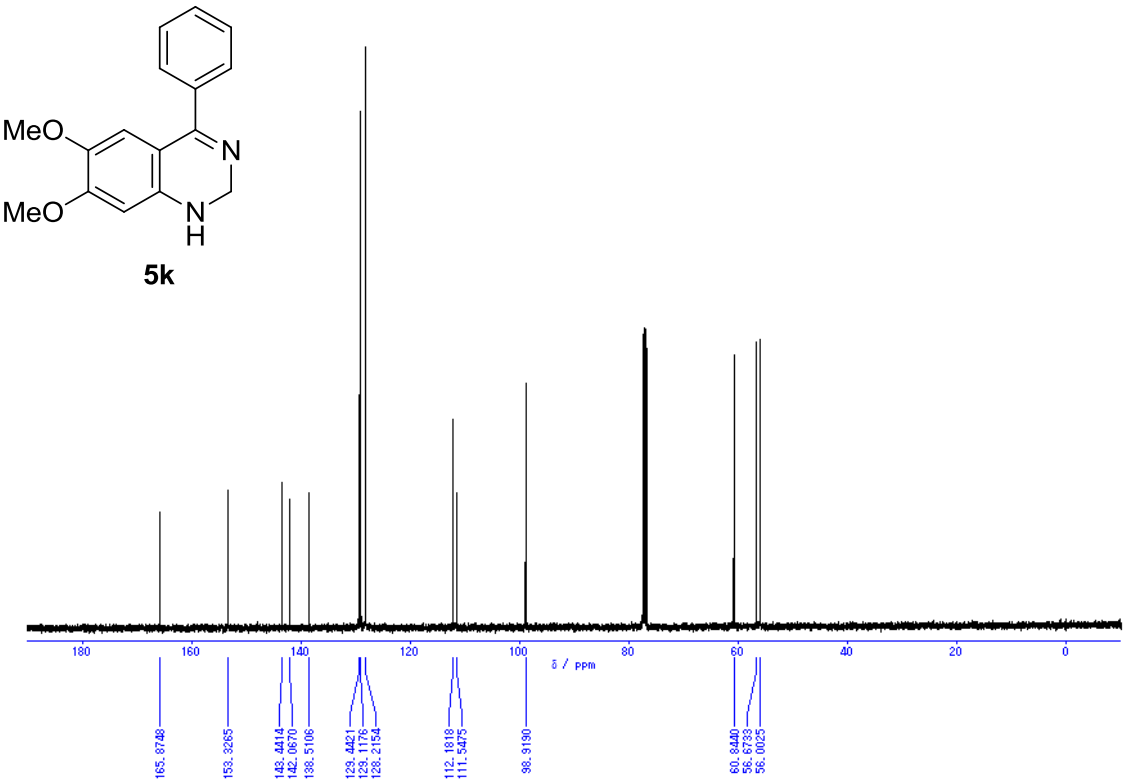


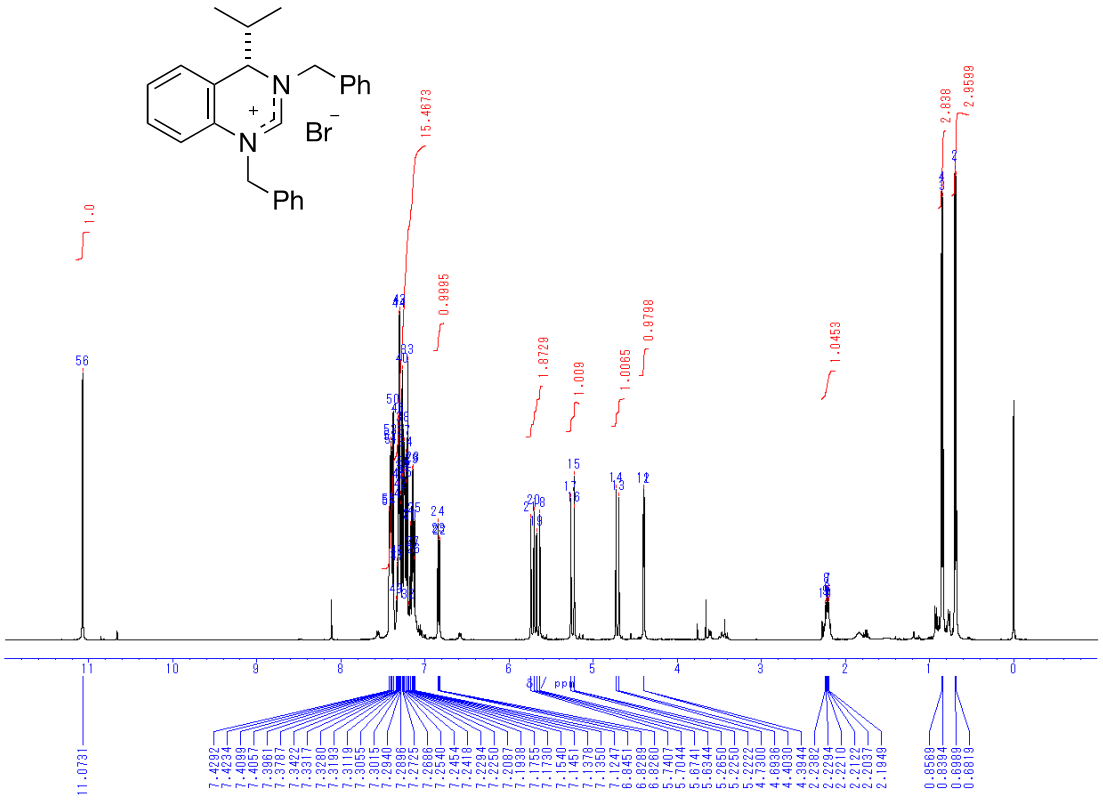
5f

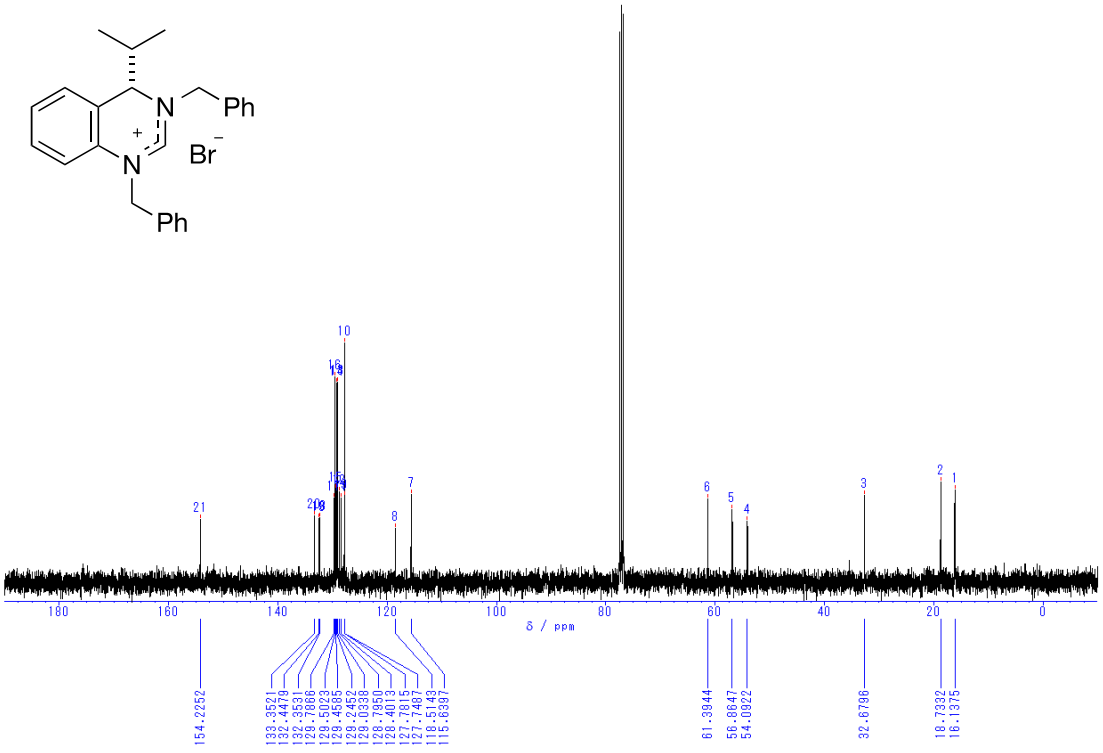

5h
4.9089
1.9849
0.9655
2.0
0.8835
3.0481
δ / ppm
2.1687

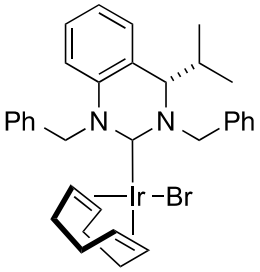

5h
δ / ppm
167.5135
146.9959
138.1953
135.8475
132.6977
130.2387
128.5489
128.4806
128.3867
125.6898
119.9495
118.3338
114.2216
60.8057
19.5370


MeO
MeO
N
N
H
5k
3.0078
2.0926
0.9904
0.9926
2.0
2.7842
3.0637
11
10
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.5531
7.5404
7.5341
7.4253
7.4097
6.6986
6.2670
4.8498
3.8607
3.6866

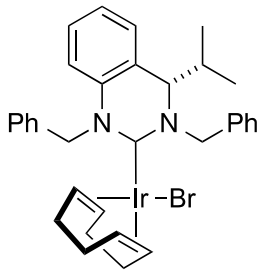

MeO
MeO
N
N
H
5k
180
160
140
120
100
80
60
40
20
0
δ / ppm
165.8748
153.3265
143.4414
142.0670
138.5106
129.4421
129.1176
128.2154
112.1818
111.5475
98.9190
60.8440
56.6733
56.0025


Ph
N
Br
N
Ph
1.0
15.4673
0.9995
1.8729
1.009
1.0085
0.9798
1.0453
2.838
2.9598
δ / ppm


Ph
N
Br
N
Ph
δ / ppm

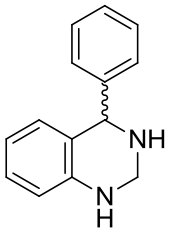


6

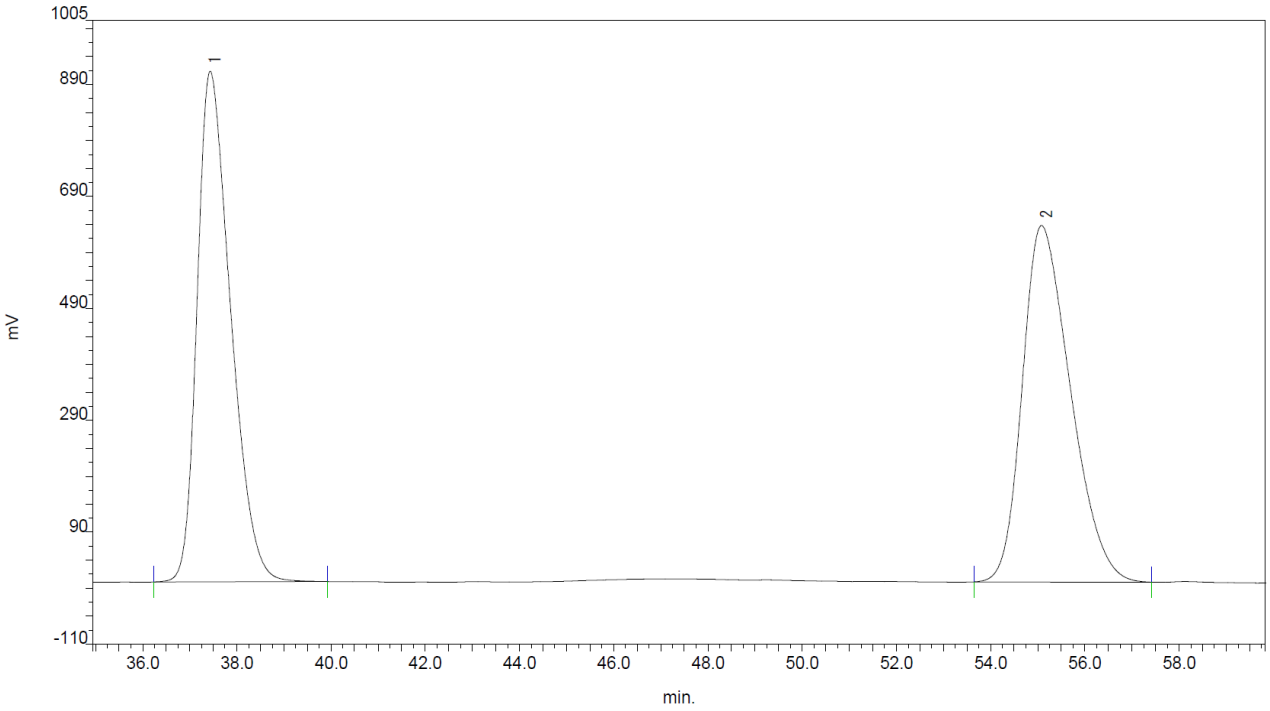


6

Sample Name	: 4-Phenyl-1,2,3,4-tetrahydroquinazoline_racemic
Data File Name	: 4-Phenyl-1,2,3,4-tetrahydroquinazoline_racemic.ch1
Analysis Time	: 60.0 min
Conditions	: OJ-H, Hexane/IPA= 90/10, WL : 215 nm, Flow: 1.0 mL/min, 30 °C

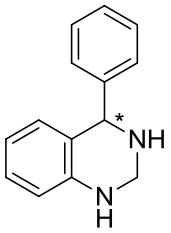


racemic-**3a**

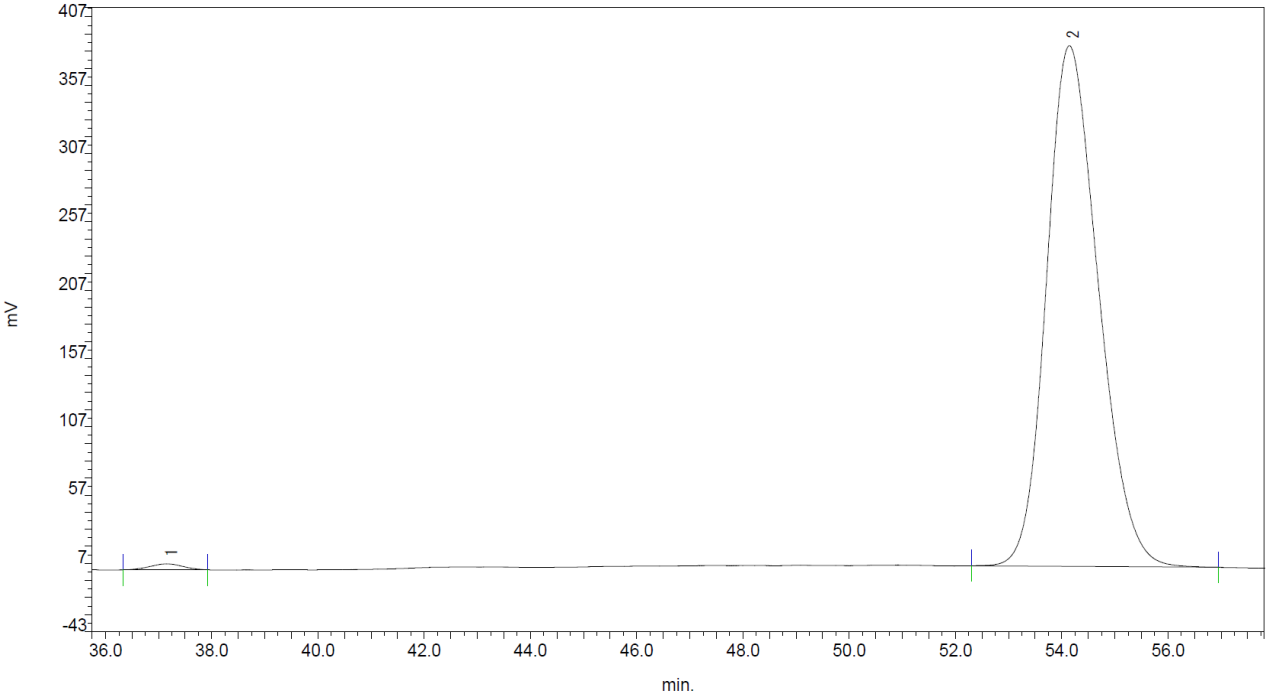


Peak	Rt (min)	Area	Area (%)	Height
1	37.43	45024172.400	49.8833	912290
2	55.08	45234820.200	50.1167	637023
	Total	90258992.600	100.0000	1549313

Sample Name	: 4-Phenyl-1,2,3,4-tetrahydroquinazoline
Data File Name	: 4-Phenyl-1,2,3,4-tetrahydroquinazoline_racemi.ch1
Analysis Time	: 60.0 min
Conditions	: OJ-H, Hexane/IPA= 90/10, WL : 215 nm, Flow: 1.0 mL/min, 30 °C

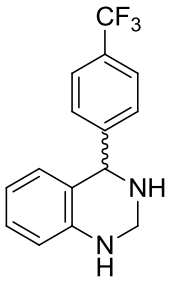


(-)-3a

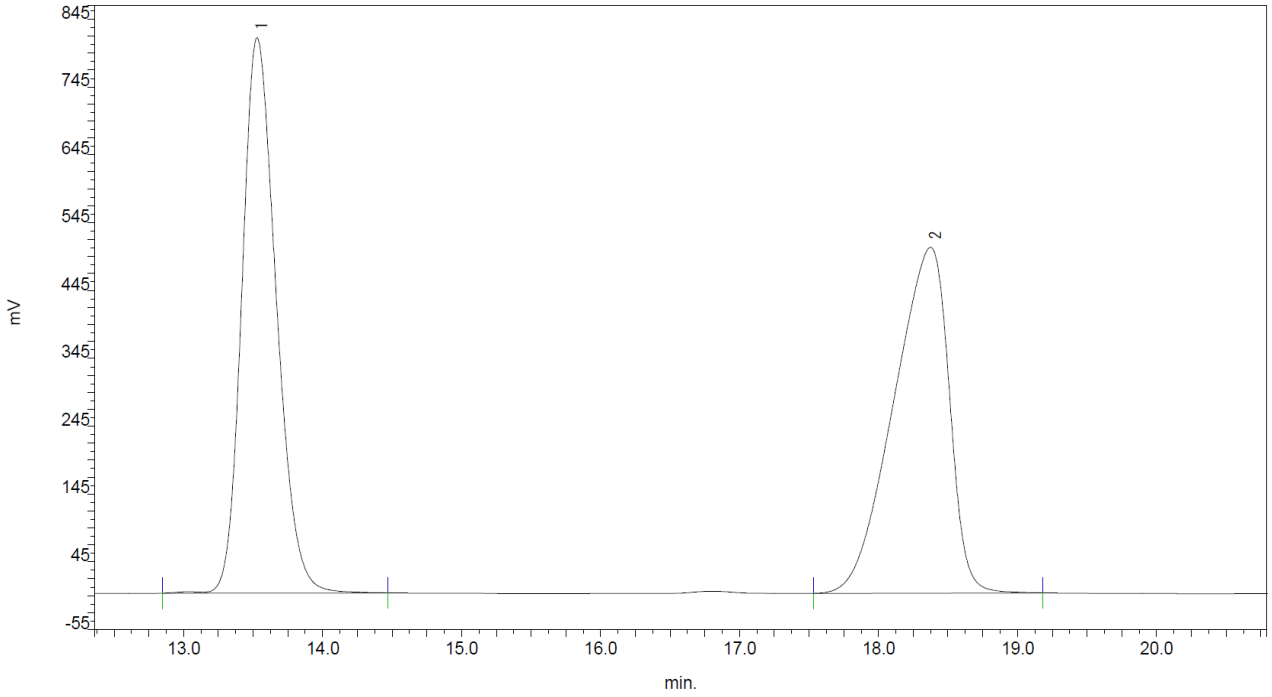


Peak	Rt (min)	Area	Area (%)	Height
1	37.15	185710.000	0.7124	4347
2	54.13	25882413.600	99.2876	381229
	Total	26068123.600	100.0000	385576

Sample Name	: 1,2,3,4-tetrahydro-(4-Triflurorомethylphenyl)quinazoline_racemic
Data File Name	: 1,2,3,4-tetrahydro-(4-Triflurorомethylphenyl)quinazoline_racemic.ch1
Analysis Time	: 60.0 min
Conditions	: OJ-H, Hexane/IPA= 90/10, WL : 215 nm, Flow: 1.0 mL/min, 30 °C

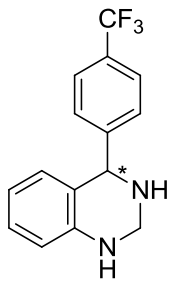


racemic-**3b**

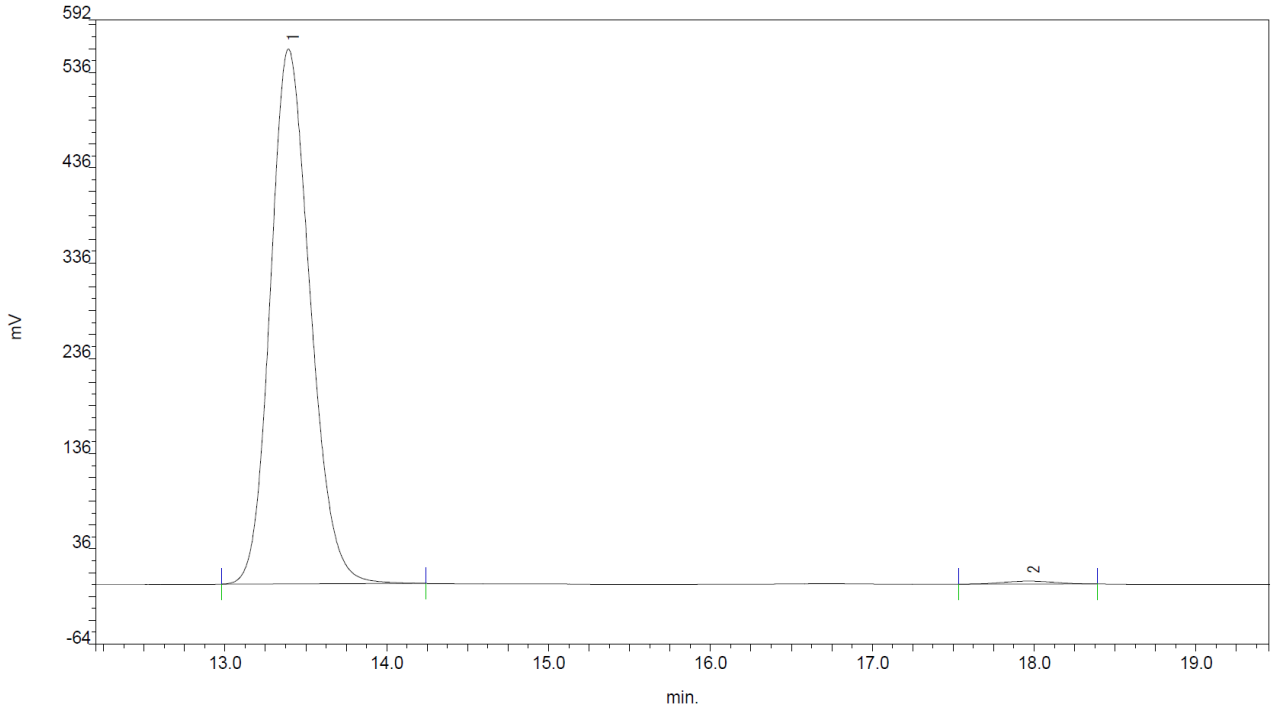


Peak	Rt (min)	Area	Area (%)	Height
1	13.53	14044847.800	49.8319	818779
2	18.37	14139599.400	50.1681	509917
	Total	28184447.200	100.0000	1328696

Sample Name	: 1,2,3,4-tetrahydro-(4-Triflurorомethylphenyl)quinazoline
Data File Name	: 1,2,3,4-tetrahydro-(4-Triflurorомethylphenyl)quinazoline.ch1
Analysis Time	: 60.0 min
Conditions	: OJ-H, Hexane/IPA= 90/10, WL : 215 nm, Flow: 1.0 mL/min, 30 °C

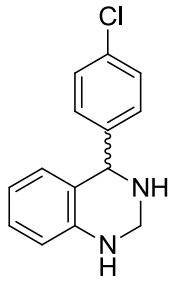


(-)-3b

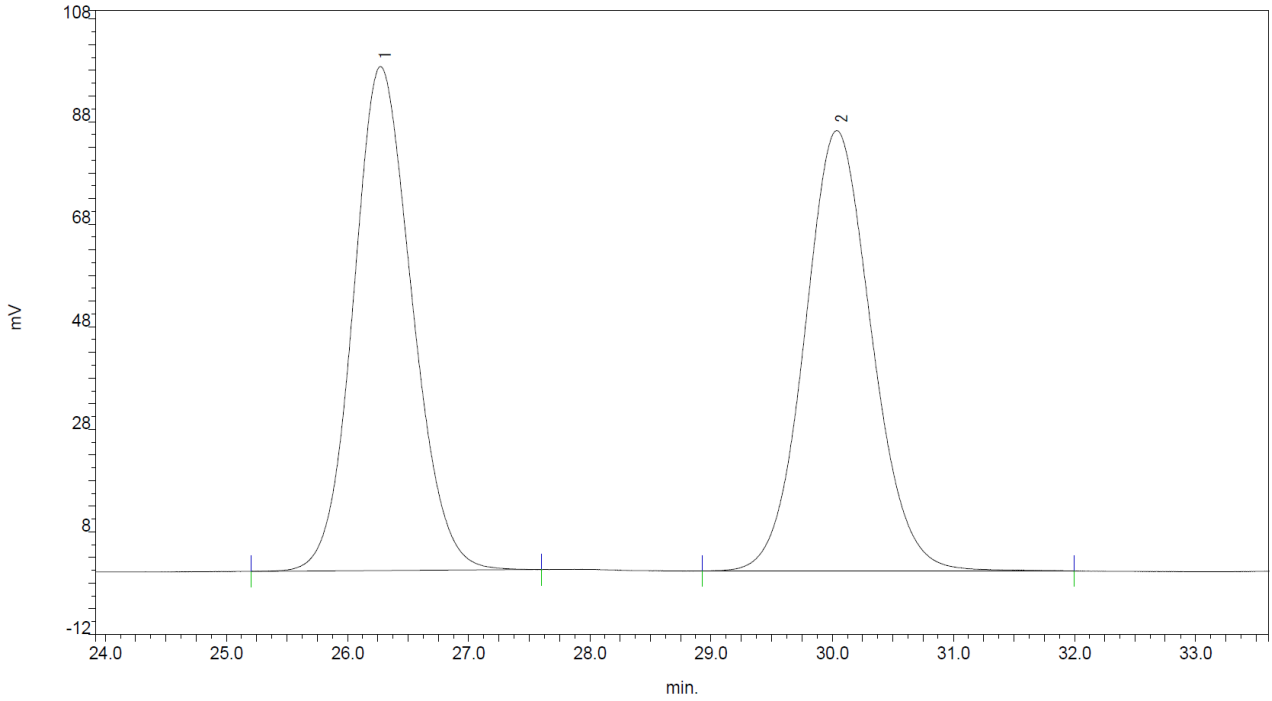


Peak	Rt (min)	Area	Area (%)	Height
1	13.39	9622101.800	99.2810	561452
2	17.97	69686.800	0.7190	3096
	Total	9691788.800	100.0000	564548

Sample Name	: 4-(4-Chlorophenyl)-1,2,3,4-tetrahydroquinazoline_racemic
Data File Name	: 4-(4-Chlorophenyl)-1,2,3,4-tetrahydroquinazoline_racemic.ch1
Analysis Time	: 60.0 min
Conditions	: OJ-H, Hexane/IPA= 90/10, WL : 254 nm, Flow: 1.0 mL/min, 30 °C

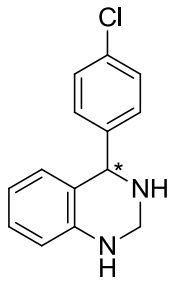


racemic-**3c**

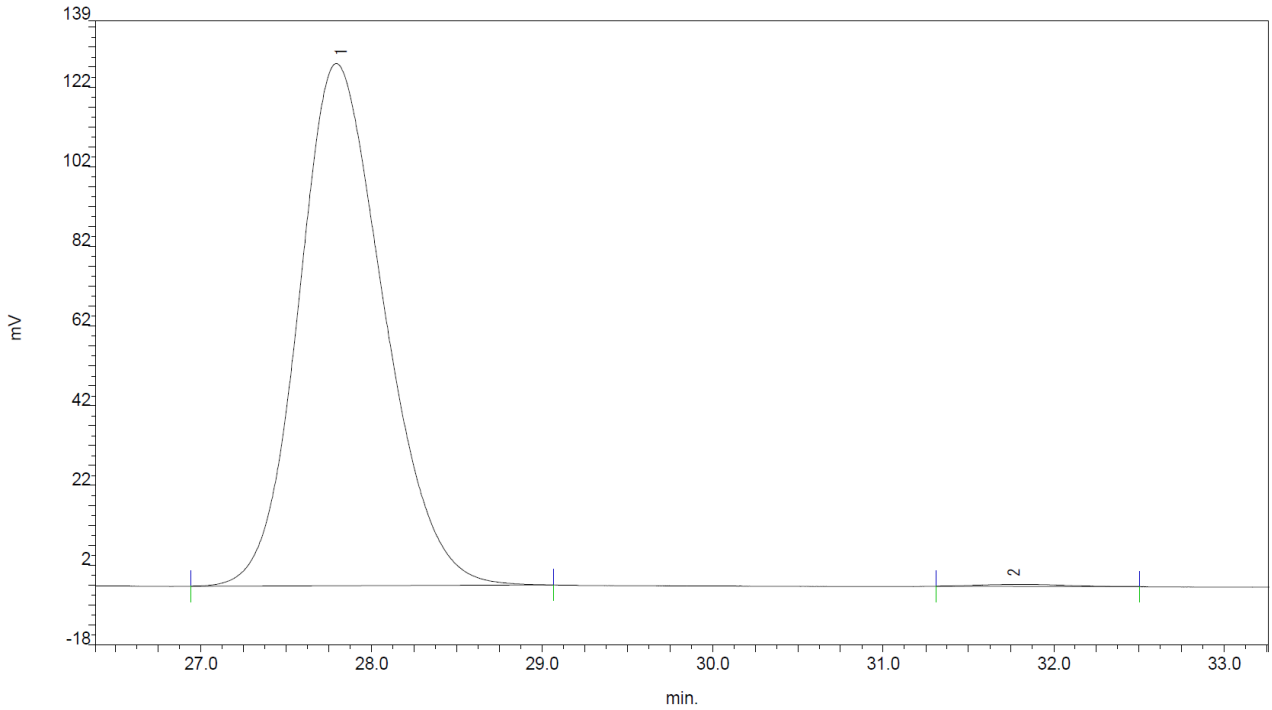


Peak	Rt (min)	Area	Area (%)	Height
1	26.27	3301454.800	49.9774	98299
2	30.04	3304441.800	50.0226	85897
	Total	6605896.600	100.0000	184196

Sample Name	: 4-(4-Chlorophenyl)-1,2,3,4-tetrahydroquinazoline
Data File Name	: 4-(4-Chlorophenyl)-1,2,3,4-tetrahydroquinazoline.ch1
Analysis Time	: 60.0 min
Conditions	: OJ-H, Hexane/IPA= 90/10, WL : 254 nm, Flow: 1.0 mL/min, 30 °C

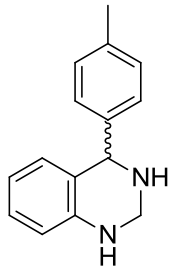


(-)-3c

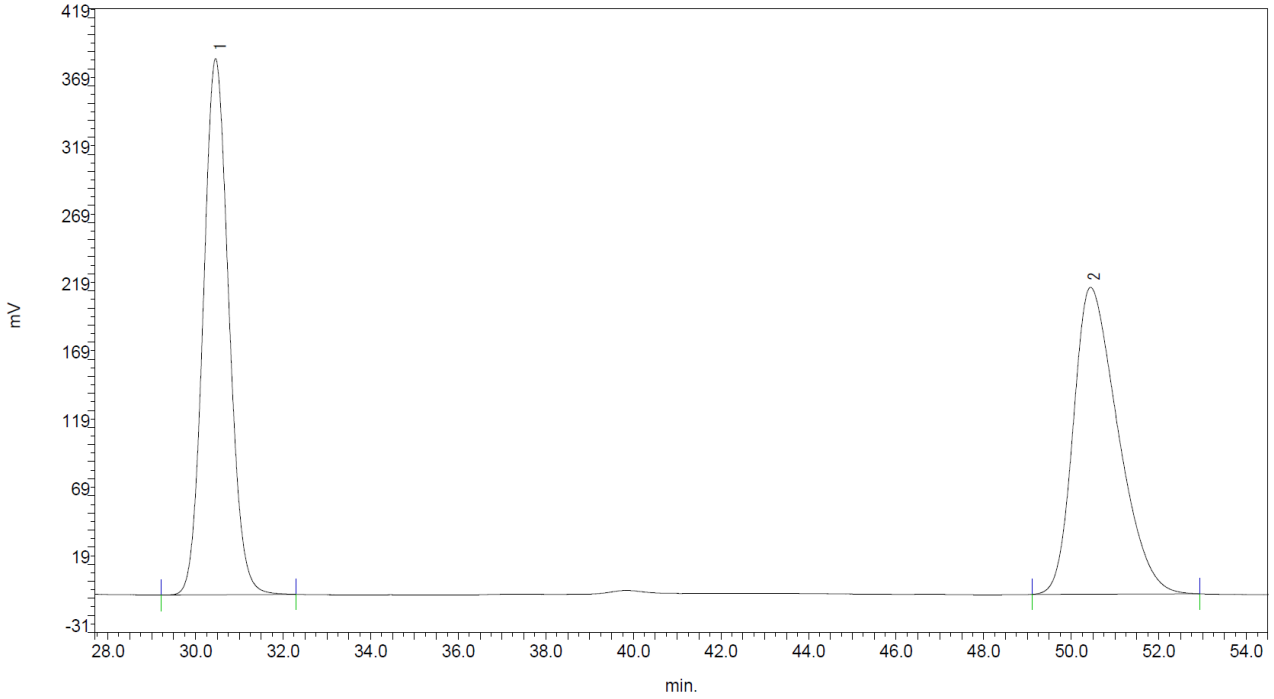


Peak	Rt (min)	Area	Area (%)	Height
1	27.80	4543499.800	99.5904	131062
2	31.74	186686.000	0.4096	552
	Total	4562185.800	100.0000	131614

Sample Name	: 4-(4-Methylphenyl)-1,2,3,4-tetrahydroquinazoline_racemic
Data File Name	: 4-(4-Methylphenyl)-1,2,3,4-tetrahydroquinazoline_racemic.ch1
Analysis Time	: 60.0 min
Conditions	: OJ-H, Hexane/IPA= 90/10, WL : 215 nm, Flow: 1.0 mL/min, 30 °C

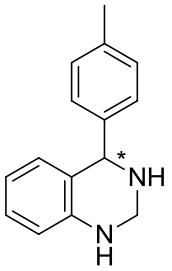


racemic-**3d**

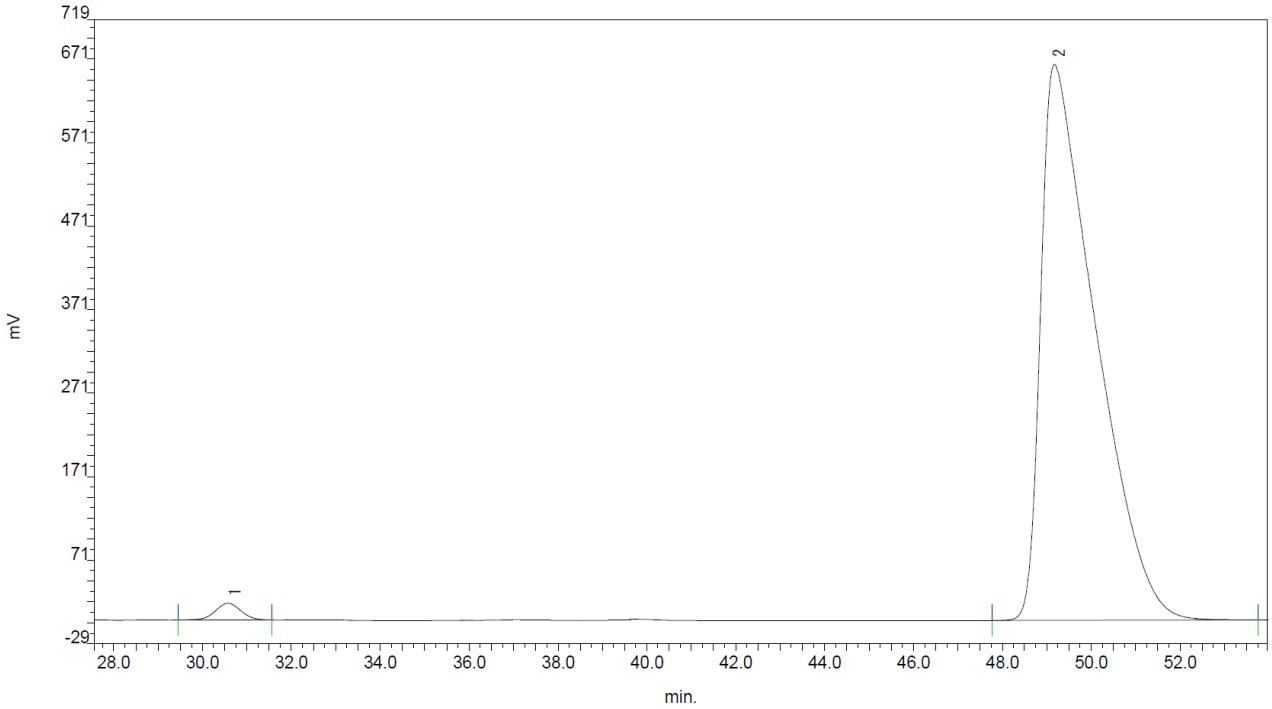


Peak	Rt (min)	Area	Area (%)	Height
1	30.46	15880468.200	50.0034	392384
2	50.41	15878291.800	49.9966	224594
	Total	31758760.000	100.0000	616978

Sample Name	: 4-(4-Methylphenyl)-1,2,3,4-tetrahydroquinazoline
Data File Name	: 4-(4-Methylphenyl)-1,2,3,4-tetrahydroquinazoline.ch1
Analysis Time	: 60.0 min
Conditions	: OJ-H, Hexane/IPA= 90/10, WL : 215 nm, Flow: 1.0 mL/min, 30 °C

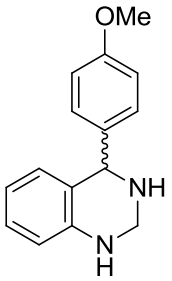


(-)-3d

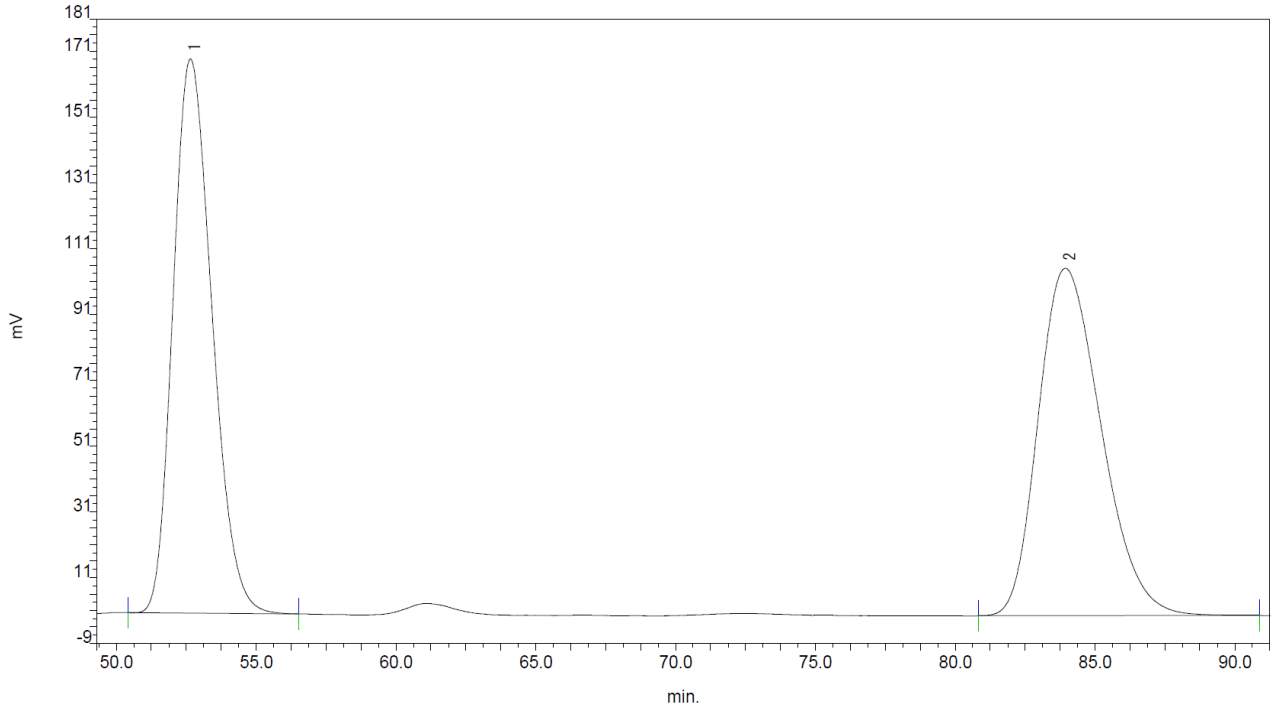


Peak	Rt (min)	Area	Area (%)	Height
1	30.63	800919.600	1.3932	20088
2	49.17	56687596.800	98.6068	665600
	Total	57488516.400	100.0000	685688

Sample Name	: 4-(4-Metoxyphenyl)-1,2,3,4-tetrahydroquinazoline_racemic
Data File Name	: 4-(4-Metoxyphenyl)-1,2,3,4-tetrahydroquinazoline_racemic.ch1
Analysis Time	: 120.0 min
Conditions	: OD-H, Hexane/IPA= 95/5, WL : 215 nm, Flow: 1.0 mL/min, 30 °C

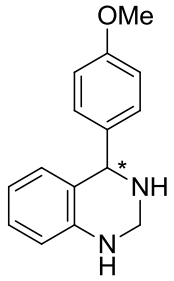


racemic-**3e**

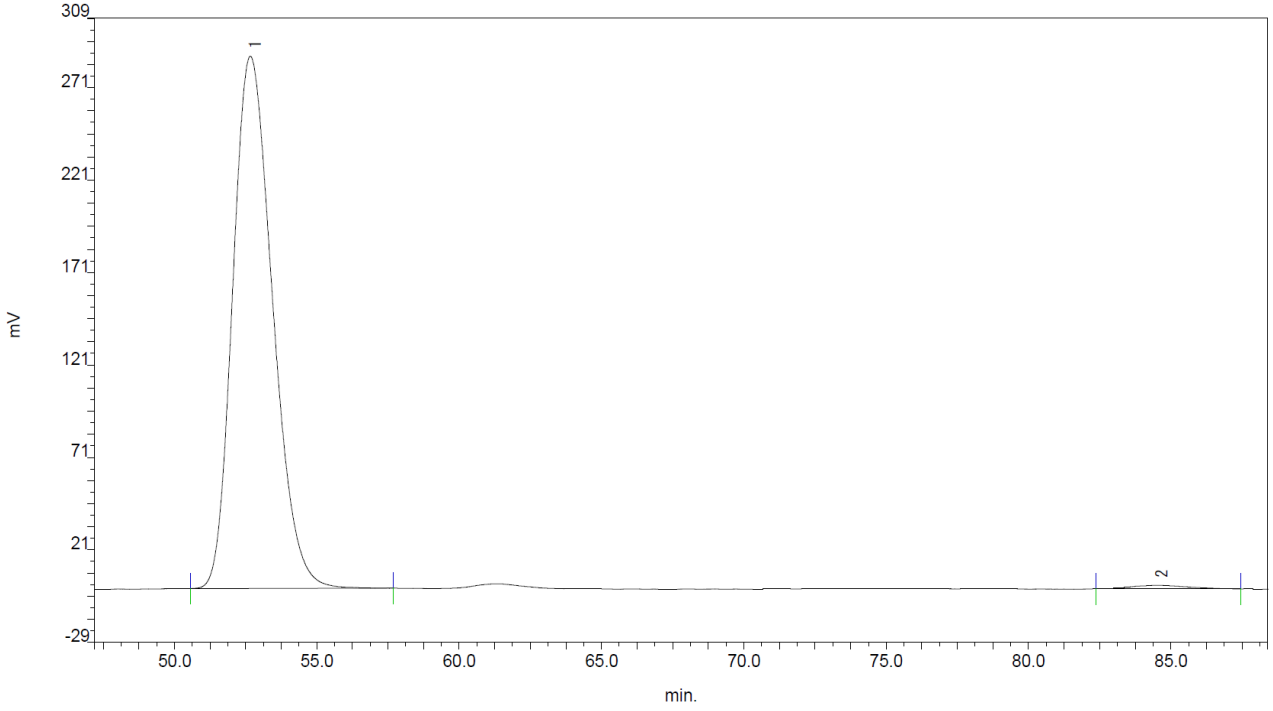


Peak	Rt (min)	Area	Area (%)	Height
1	52.63	16314690.400	49.7029	168464
2	83.92	16509752.600	50.2971	105602
	Total	32824443.000	100.0000	274066

Sample Name	: 4-(4-Metoxyphenyl)-1,2,3,4-tetrahydroquinazoline
Data File Name	: 4-(4-Metoxyphenyl)-1,2,3,4-tetrahydroquinazoline.ch1
Analysis Time	: 120.0 min
Conditions	: OD-H, Hexane/IPA= 95/5, WL : 215 nm, Flow: 1.0 mL/min, 30 °C

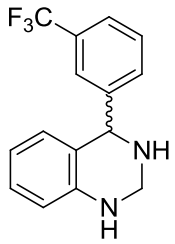


(-)-3e

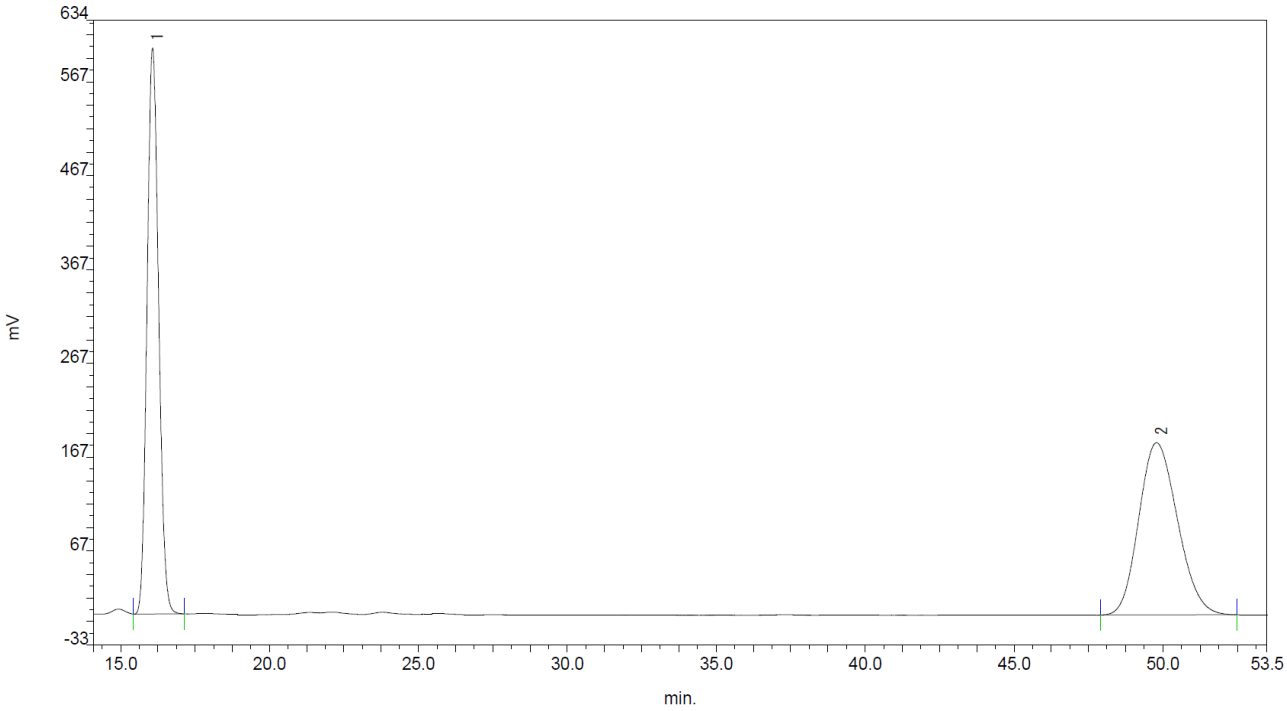


Peak	Rt (min)	Area	Area (%)	Height
1	52.66	27970920.200	99.0440	288028
2	84.51	269976.400	0.9560	1906
	Total	28240896.600	100.0000	289934

Sample Name	: 1,2,3,4-tetrahydro-4-(3-trifluoromethylphenyl)-quinazoline_racemic
Data File Name	: 1,2,3,4-tetrahydro-4-(3-trifluoromethylphenyl)-quinazoline_racemic.ch1
Analysis Time	: 60.0 min
Conditions	: OD-H, Hexane/IPA= 90/10, WL : 215 nm, Flow: 1.0 mL/min, 30 °C

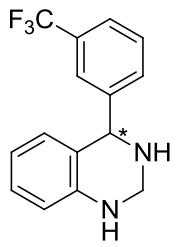


racemic-**3g**

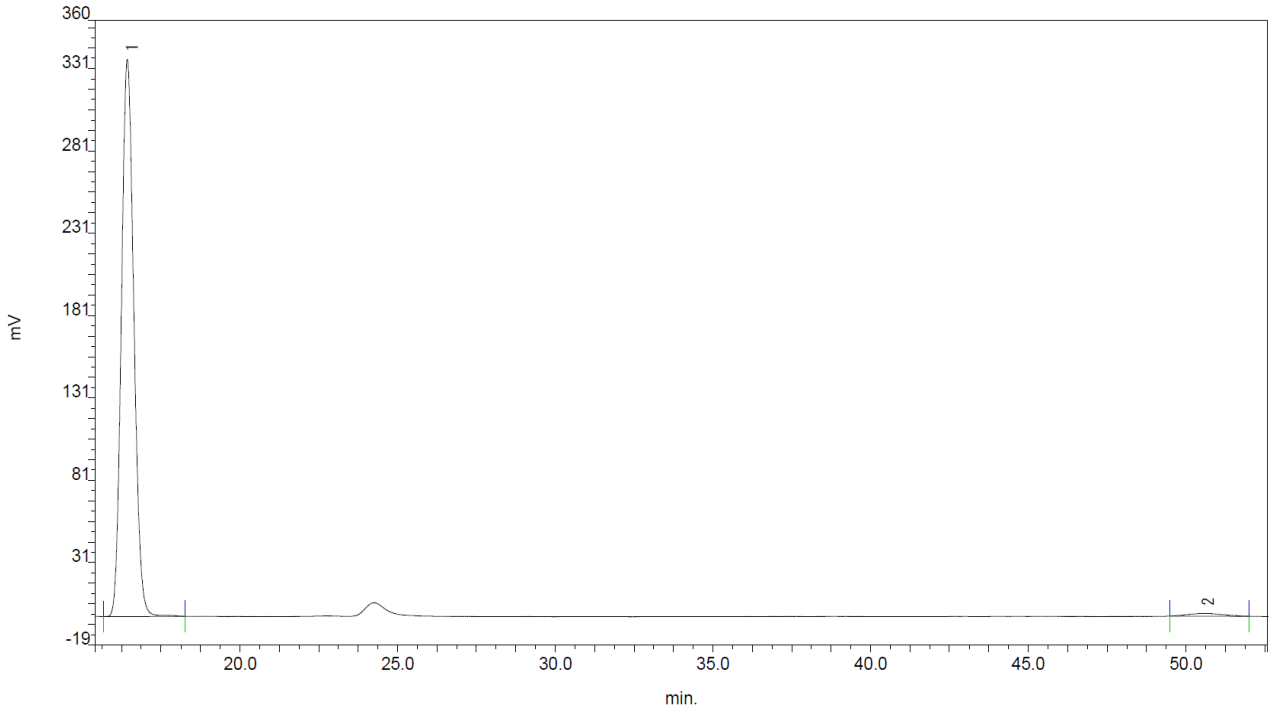


Peak	Rt (min)	Area	Area (%)	Height
1	16.08	16257271.000	49.5029	603190
2	49.79	16583759.800	50.4971	183568
	Total	32841030.800	100.0000	789758

Sample Name	: 1,2,3,4-tetrahydro-4-(3-trifluoromethylphenyl)-quinazoline
Data File Name	: 1,2,3,4-tetrahydro-4-(3-trifluoromethylphenyl)-quinazoline.ch1
Analysis Time	: 60.0 min
Conditions	: OD-H, Hexane/IPA= 90/10, WL : 215 nm, Flow: 1.0 mL/min, 30 °C

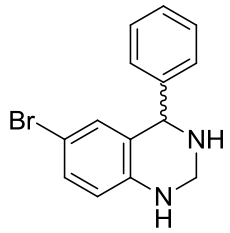


(-)-3g

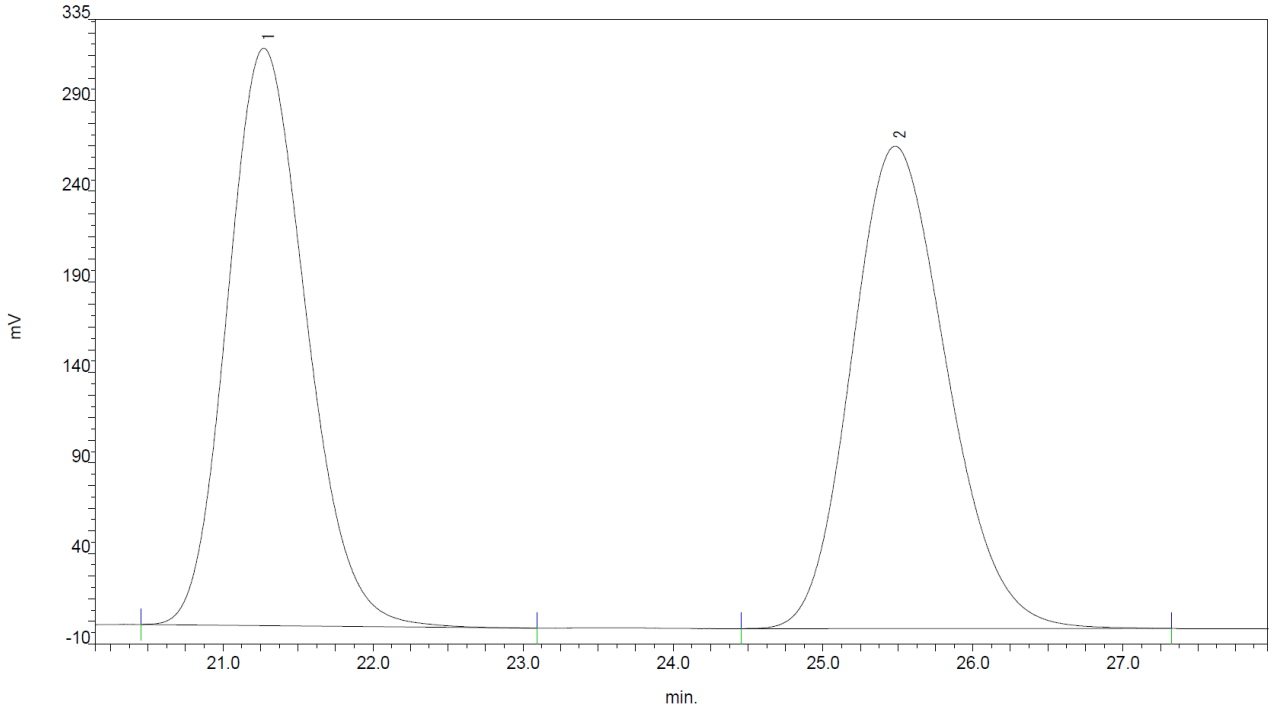


Peak	Rt (min)	Area	Area (%)	Height
1	16.43	9283937.200	98.6555	338376
2	50.55	126520.600	1.3445	1599
	Total	9410457.800	100.0000	339975

Sample Name	: 6-Bromo-4-phenyl-1,2,3,4-tetrahydroquinazoline_racemic
Data File Name	: 6-Bromo-4-phenyl-1,2,3,4-tetrahydroquinazoline_racemic.ch1
Analysis Time	: 60.0 min
Conditions	: OD-H, Hexane/IPA= 90/10, WL : 215 nm, Flow: 1.0 mL/min, 30 °C

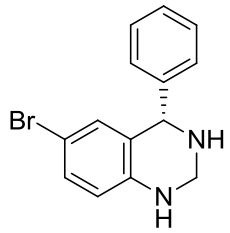


racemic-**3i**

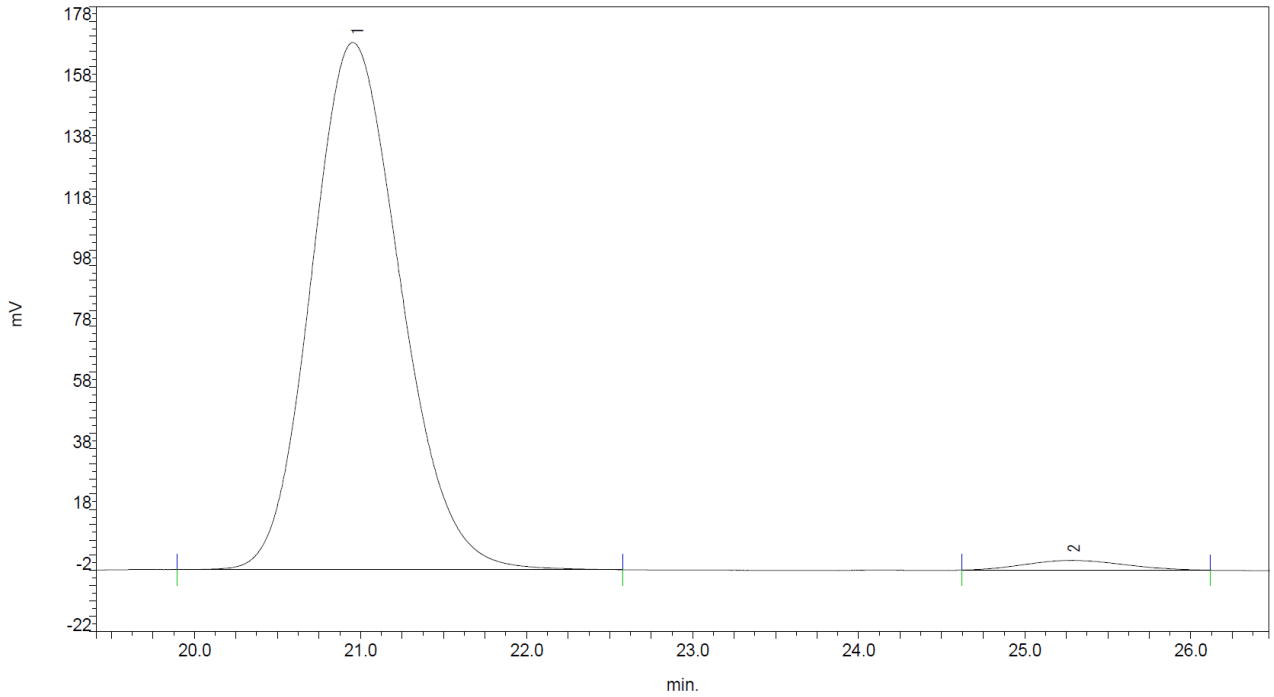


Peak	Rt (min)	Area	Area (%)	Height
1	21.27	11612470.000	49.6883	318777
2	25.48	11758176.400	50.3117	266373
	Total	23370646.400	100.0000	585150

Sample Name	: 6-Bromo-4-phenyl-1,2,3,4-tetrahydroquinazoline
Data File Name	: 6-Bromo-4-phenyl-1,2,3,4-tetrahydroquinazoline.ch1
Analysis Time	: 60.0 min
Conditions	: OD-H, Hexane/IPA= 90/10, WL : 215 nm, Flow: 1.0 mL/min, 30 °C

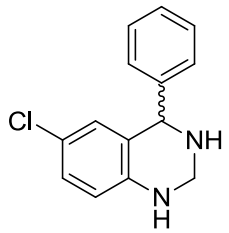


(*S*)-**3i**

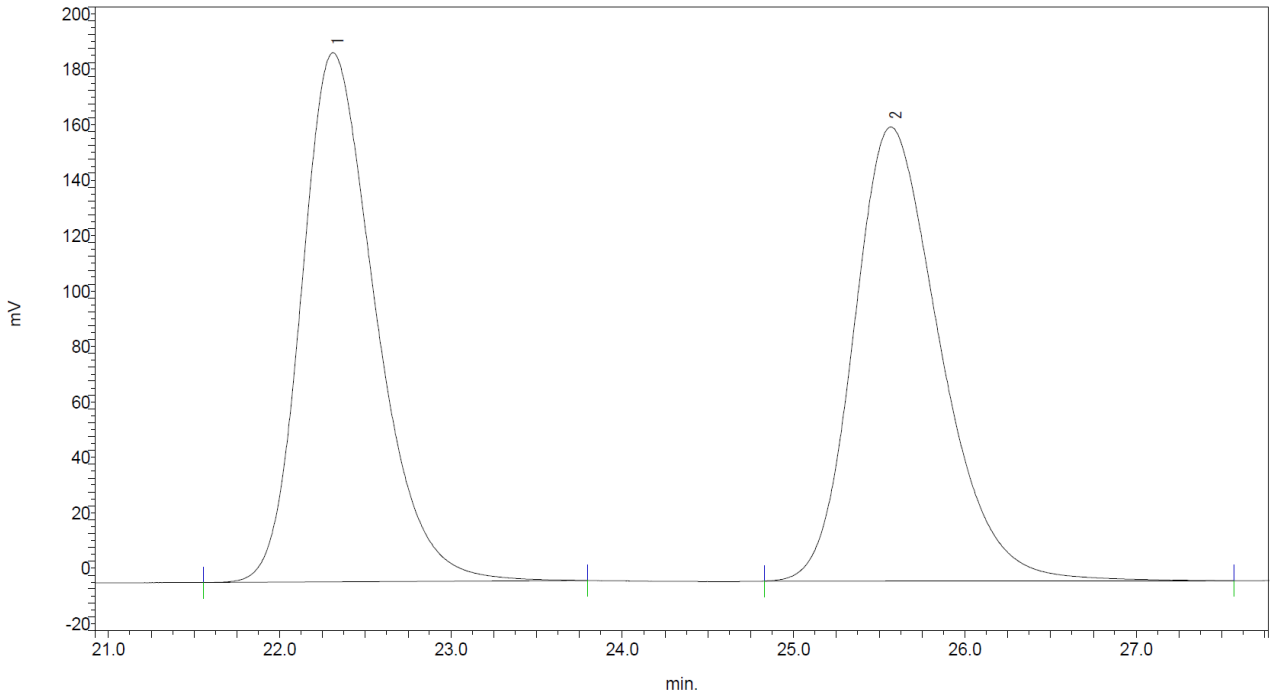


Peak	Rt (min)	Area	Area (%)	Height
1	20.95	6453449.600	97.9928	172731
2	25.27	132190.200	2.0072	3178
	Total	6585639.800	100.0000	175909

Sample Name	: 6-Chloro-4-phenyl-1,2,3,4-tetrahydroquinazoline_racemic
Data File Name	: 6-Chloro-4-phenyl-1,2,3,4-tetrahydroquinazoline_racemic.ch1
Analysis Time	: 60.0 min
Conditions	: OJ-H, Hexane/IPA= 90/10, WL : 215 nm, Flow: 1.0 mL/min, 30 °C

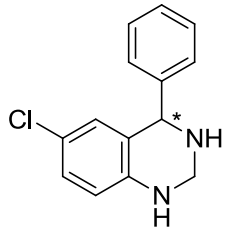


racemic-**3j**

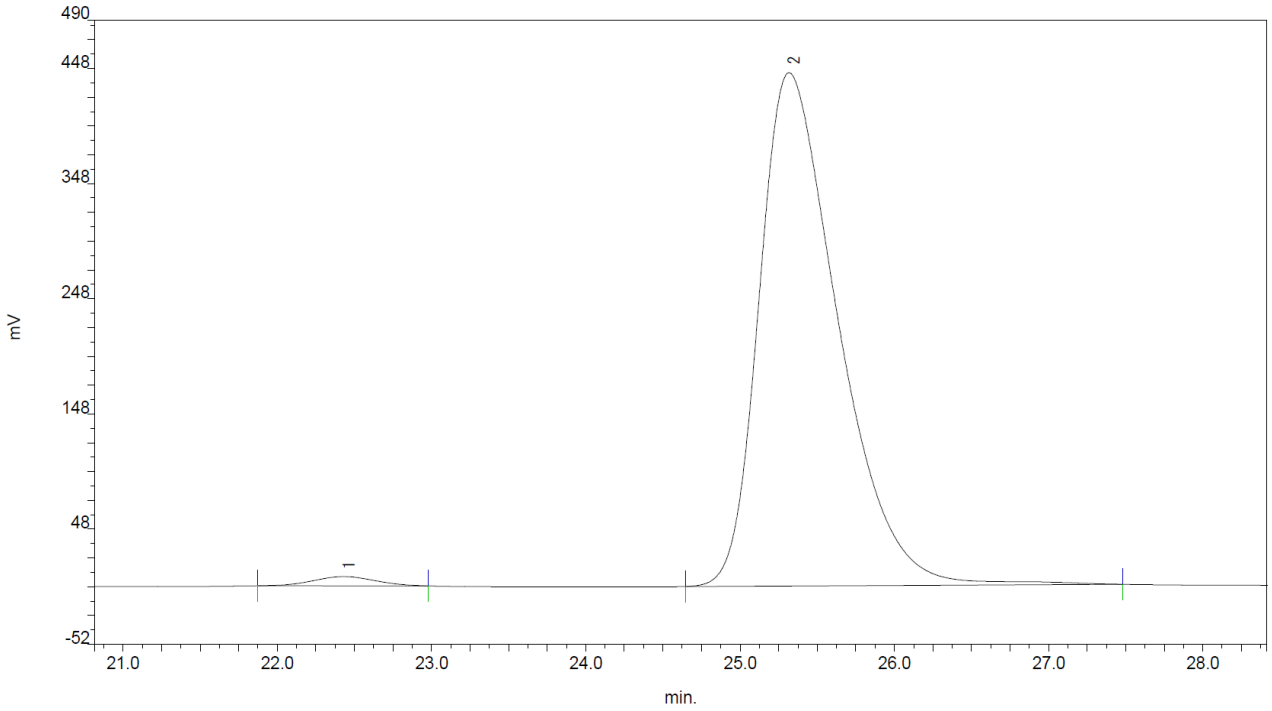


Peak	Rt (min)	Area	Area (%)	Height
1	22.31	5714084.000	49.9389	190926
2	25.57	5728070.400	50.0611	163820
	Total	11442154.400	100.0000	354746

Sample Name	: 1,2-dihydro-4-isopropylquinazoline_racemic
Data File Name	: 1,2-dihydro-4-isopropylquinazoline_racemic.ch1
Analysis Time	: 60.0 min
Conditions	: OD-H, Hexane/IPA= 95/5, WL : 215 nm, Flow: 1.0 mL/min, 30 °C

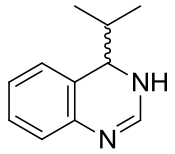


(-)-3j

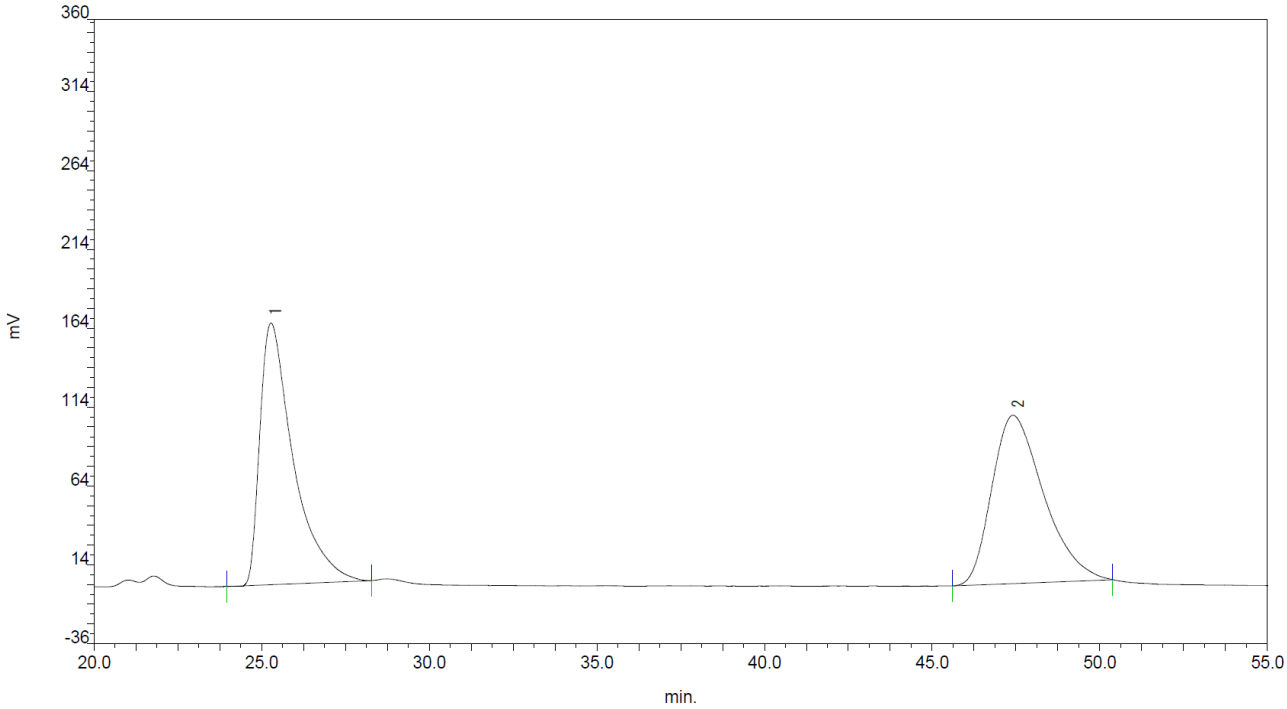


Peak	Rt (min)	Area	Area (%)	Height
1	22.43	226699.800	1.4111	8075
2	25.32	15839256.400	98.5889	445742
	Total	16065956.200	100.0000	453817

Sample Name	: 6-Chloro-4-phenyl-1,2,3,4-tetrahydroquinazoline_racemic
Data File Name	: 6-Chloro-4-phenyl-1,2,3,4-tetrahydroquinazoline_racemic.ch1
Analysis Time	: 60.0 min
Conditions	: OJ-H, Hexane/IPA= 90/10, WL : 215 nm, Flow: 1.0 mL/min, 30 °C

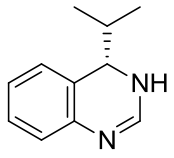


racemic-**3l**

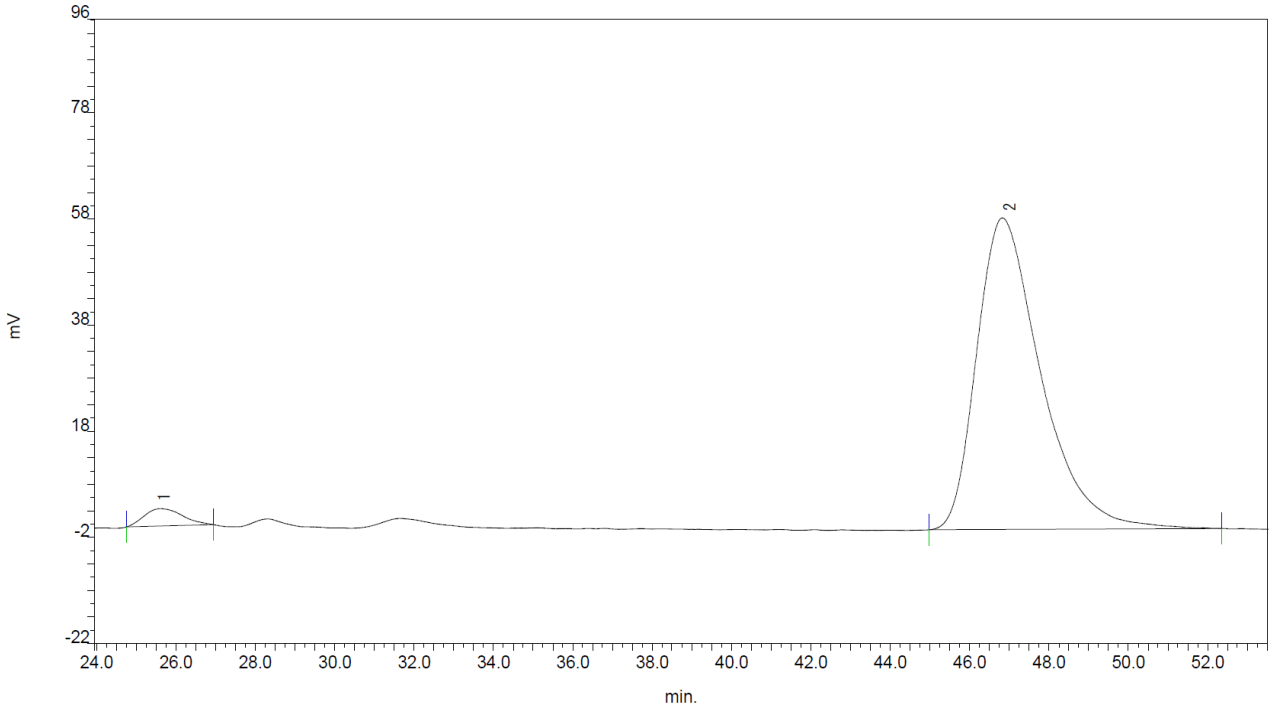


Peak	Rt (min)	Area	Area (%)	Height
1	25.28	11470844.600	50.0629	165969
2	47.42	11442017.600	49.9371	106721
	Total	22912862.200	100.0000	272690

Sample Name	: 6-Chloro-4-phenyl-1,2,3,4-tetrahydroquinazoline
Data File Name	: 6-Chloro-4-phenyl-1,2,3,4-tetrahydroquinazoline.ch1
Analysis Time	: 60.0 min
Conditions	: OJ-H, Hexane/IPA= 90/10, WL : 215 nm, Flow: 1.0 mL/min, 30 °C



(*S*)-**3l**



Peak	Rt (min)	Area	Area (%)	Height
1	25.59	219823.200	3.2336	3298
2	46.89	6578227.800	96.7664	58731
	Total	6798051.000	100.0000	62029