Supporting Information

Boron-Catalyzed Silylative Reduction of Quinolines: Selective sp^3 C–Si Bond Formation

Narasimhulu Gandhamsetty,[†,‡,#] *Seewon Joung,*[†,‡,#] *Sung-Woo Park,*[†,‡] *Sehoon Park,**[†,‡] *and Sukbok Chang**[†,‡]

[†]*Center for Catalytic Hydrocarbon Functionalizations, Institute for Basic Science (IBS), Daejeon 305-701, South Korea*

[‡]*Department of Chemistry, Korea Advanced Institute of Science & Technology (KAIST), Daejeon 305-701, South Korea*

[*]Email: sehoonp@kaist.ac.kr; sbchang@kaist.ac.kr

[#]These authors equally contributed to this work.

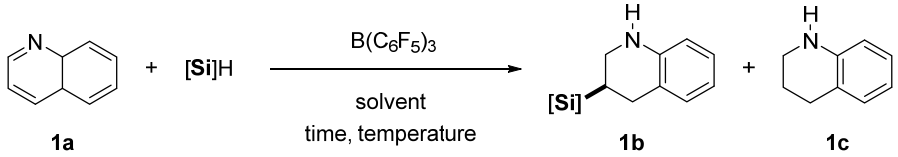
Table of Contents

I. General Considerations

Unless otherwise stated, all catalytic reactions were carried out under argon atmosphere. Chloroform-*d* purchased from Cambridge Isotope Laboratories, Inc. was degassed and used as a solvent without additional purification for optimization and mechanistic studies. Tris(pentafluorophenyl)borane was purchased from TCI and Sigma-Aldrich and lipase A from *Candida antarctica* CLEA was purchased from Sigma. Both were stored at -20 ^{o}C. All other reagents were directly used as purchased without further purification unless otherwise stated.

Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F254 plates. Visualization on TLC was achieved by the use of UV light (254 nm), exposure to treatment with acidic anisaldehyde, phosphomolybdic acid, ninhydrin or ceric ammonium molydate stain followed by heating. Column chromatography was undertaken on silica gel (400-630 mesh) using a proper eluent. ^{1}H NMR was recorded on Bruker Avance (400 MHz) for kinetic and silane scrambling studies, and recorded on Bruker Avance 400 (400 MHz) or Agilent Technologies DD2 (600 MHz). for routine characterization of compounds. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak ($CHCl_3$ in $CDCl_3$: 7.26 ppm; $Cl_2CHCHCl_2$ in $Cl_2CDCDCl_2$: 5.85 ppm). $^{13}C\{^{1}H\}$ NMR was recorded on Agilent Technologies DD2 (150 MHz) and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center of a triplet at 77.0 ppm of $CDCl_3$. $^{29}Si\{^{1}H\}$ NMR was recorded on Bruker Avance 400 (80 MHz) or Agilent Technologies DD2 600 (120 MHz), and the chemical shifts in ppm were referenced to external Et_2SiH_2 or Ph_2SiH_2. High resolution mass spectra were obtained by using EI or FAB method from Korea Basic Science Institute (Daegu) or ESI from KAIST Research Analysis Center (Daejeon). Chiral HPLC analysis was conducted on Agilent Technologies 1260 Infinity Quaternary LC system with a wavelength detector at 254 nm. Optical rotation of $[\alpha]_D$ values of enaniomerically enriched chiral products were measured with Jasco P-1020 Polarimeter.

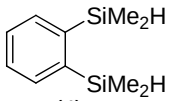
II. Optimization of the $B(C_6F_5)_3$-Catalyzed Silylative Reduction of 1a



1a **1b** **1c**

Silane (2.0 to 4.0 mmol, 4.0 equiv. to 8.0 equiv.) was added to a solution of $B(C_6F_5)_3$ (0.0050 mmol to 0.025 mmol, 1.0 mol% to 5.0 mol%) in deuterated solvent (0.50 mL) in a J. Young NMR tube, and the solution was shaken briefly. Quinoline **1a** (0.50 mmol, 1.0 equiv.) was then added and the reaction mixture was stirred at the indicated temperature during indicated time. Then, it was allowed to cool down to room temperature and filtered through a pad of silica gel with dichloromethane (15 mL) and methanol (2 mL). The filtrate was concentrated under reduced pressure and added 1,1,2,2-tetrachloroethane (TCE, 0.50 mmol, 1.0 equiv.). The resulting residue was subjected to ^{1}H NMR spectroscopy. The crude NMR yields were calculated on the basis of an internal standard of TCE.

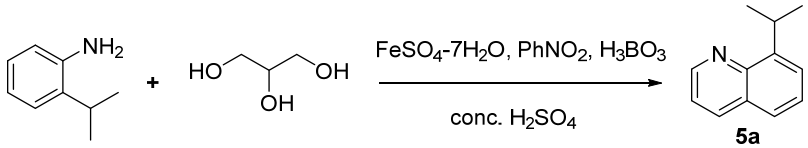
Table S1. Reaction conditions screening.[a]

Entry	Silanes (equiv.)	Solvent (0.5 mL)	*T*, (^{o}C)	Time, (h)	Conversion (%)[b]	Crude NMR yield (%)[b]	
						1b	**1c**
1	Et_2SiH_2 (4)	$CDCl_3$	65	6	100	93	3
2[c]	Et_2SiH_2 (4)	$CDCl_3$	65	6	100	85	15
3	Et_2SiH_2 (8)	$CDCl_3$	65	6	100	97	2
4[d]	Et_2SiH_2 (4)	$CDCl_3$	65	6	100	89	11
5[e]	Et_2SiH_2 (4)	$CDCl_3$	65	6	100	89	7
6	Et_2SiH_2 (4)	$CDCl_3$	r.t.	24	16	0	2
7	Et_2SiH_2 (4)	*neat*	65	6	100	82	6
8	Et_2SiH_2 (4)	CD_2Cl_2	65	6	100	91	8
9	Et_2SiH_2 (4)	benzene-d_6	65	6	100	77	22
10	Et_2SiH_2 (4)	chlorobenzene-d_5	65	12	100	78	21
11	Et_2SiH_2 (4)	toluene-d_8	65	12	100	77	23
12	$PhMeSiH_2$ (4)	$CDCl_3$	65	6	100	97	2
13	Ph_2SiH_2 (4)	$CDCl_3$	65	12	100	89	5
14	$^{t}Bu_2SiH_2$ (4)	$CDCl_3$	65	12	0	0	0
15	TMDS (4)	$CDCl_3$	65	3	100	78	3
16	 (4)	$CDCl_3$	65	6	0	0	0
17	Et_3SiH (4)	$CDCl_3$	65	6	0	0	0
18	Ph_3SiH (4)	$CDCl_3$	65	12	0	0	0
19	Me_2EtSiH (4)	$CDCl_3$	65	6	100	63	7
20	Me_2PhSiH (4)	$CDCl_3$	65	6	100	97	3

[a]Experiments were performed with **1a** (0.50 mmol), Et_2SiH_2 (2.0-4.0 mmol), and $B(C_6F_5)_3$ (0.0050 mmol) in solvent (0.50 mL) for 3-24 hours at r.t. to 65 ^{o}C in a J. Young NMR tube under argon atmosphere. [b]Conversion and yield were determined by ^{1}H NMR spectroscopy using TCE as an internal standard. [c]$B(C_6F_5)_3$ and **1a** were mixed first in $CDCl_3$, followed by adding Et_2SiH_2. [d]Carried out in a reaction vial in $CHCl_3$. [e]5.0 mol% of $B(C_6F_5)_3$ was used as a catalyst.

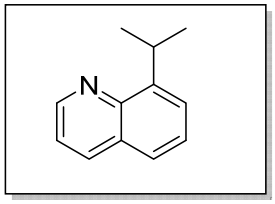
III. $B(C_6F_5)_3$-Catalyzed Silylative Reduction of Quinolines (Table 1)

Preparation of starting materials

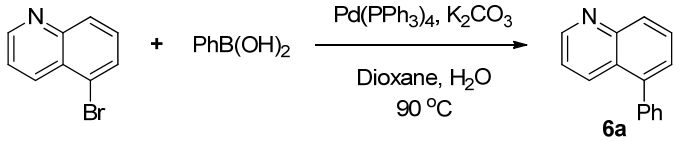


To a mixture of iron(II) sulfate heptahydrate (0.49 mmol, 0.12 equiv.), 2-isopropylaniline (4.1 mmol, 1.0 equiv.), and nitrobenzene was added boric acid (4.1 mmol, 1.0 equiv.) and glycerol (16 mmol, 4.0 equiv.) at room temperature. The resulting mixture was cooled to 0 °C and concentrated sulfuric acid (14 mmol, 3.3 equiv.) was added slowly. The resulting mixture was then heated to 150 °C. After stirring for 12 h, the mixture was cooled to room temperature and quenched with water (2 mL) and saturated sodium bicarbonate solution in water (4 mL). The resulting aqueous layer was extracted with diethyl ether (10 mL x 3) and the combined organic layer was washed with brine (30 mL x 2). The organic mixture was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EA/Hx = 1/20) to give the corresponding 8-isopropylquinoline (**5a**, 527 mg, 75%).[S1]

8-Isopropylquinoline (5a)



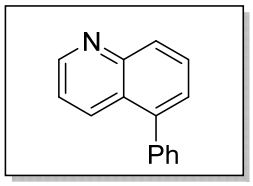
Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.95 (dd, J = 4.2, 1.8 Hz, 1H), 8.12 (dd, J = 8.2, 1.7 Hz, 1H), 7.64 (ddd, J = 12.0, 7.7, 1.4 Hz, 2H), 7.51 (dd, J = 7.6, 7.6 Hz, 1H), 7.37 (dd, J = 8.2, 4.1 Hz, 1H), 4.38 (sep, J = 6.9 Hz, 1H), 1.41 (d, J = 7.0 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.1, 147.3, 146.1, 136.4, 128.3, 126.4, 125.5, 125.1, 120.7, 27.1, 23.5 (2C); **IR** (cm^{-1}) 2959, 2867, 1596, 1496, 1467, 1364, 1324, 1250, 1177, 1133, 1108, 1046, 1016, 828, 791, 755, 687; **HRMS** (EI): Calculated for $C_{12}H_{13}N$ $[M]^+$: 171.1048, Found: 171.1047.



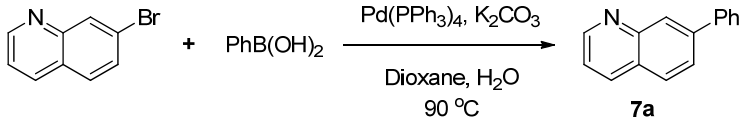
A solution of 5-bromoquinoline (2.0 mmol, 1.0 equiv.), phenylboronic acid (3.0 mmol, 1.5 equiv.), tetrakis(triphenylphosphine)palladium (0.10 mmol, 5.0 mol%), and potassium carbonate (4.0 mmol, 2.0 equiv.) in dioxane (8.0 mL) and water (2.0 mL) was stirred at 90 °C for 14 h. The reaction mixture was then cooled to room temperature and quenched with saturated sodium bicarbonate solution in water (10

mL). The resulting aqueous layer was extracted with ethyl acetate (10 mL x 3) and then, the combined organic layer was washed with brine (20 mL x 2). The resulting mixture was dried over anhydrous $MgSO_4$ and then, filtered. The resulting filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (EA/Hx = 1/10) to give the corresponding 5-phenylquinoline (**6a**, 386 mg, 99%).[S2]

5-Phenylquinoline (6a)

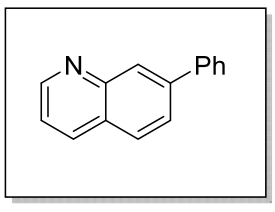


Light yellow solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.93 (dd, J = 4.1, 1.7 Hz, 1H), 8.29 – 8.23 (m, 1H), 8.19 – 8.09 (m, 1H), 7.76 (dd, J = 8.5, 7.0 Hz, 1H), 7.53 – 7.49 (m, 3H), 7.48 – 7.44 (m, 3H), 7.35 (dd, J = 8.6, 4.1 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.2, 148.5, 140.5, 139.4, 134.3, 130.0 (2C), 129.0, 128.9, 128.4 (2C), 127.6, 127.2, 126.7, 121.0.

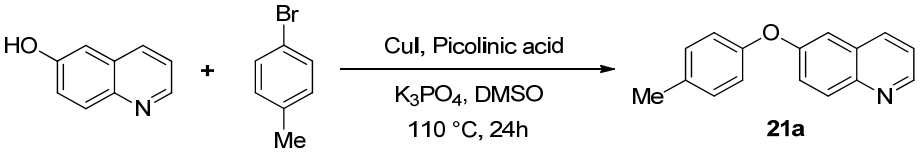


A solution of 7-bromoquinoline (2.0 mmol, 1.0 equiv.), phenylboronic acid (3.0 mmol, 1.5 equiv.), tetrakis(triphenylphosphine)palladium(0) (0.10 mmol 5.0 mol%), and potassium carbonate (4.0 mmol, 2.0 equiv.) in dioxane (8.0 mL) and water (2.0 mL) was stirred at 90 °C with reflux condenser. After 14 h, the reaction mixture was cooled to room temperature and quenched with saturated sodium bicarbonate solution in water (10 mL). The resulting aqueous layer was extracted with ethyl acetate (10 mL x 3) and then, the combined organic layer was washed with brine (20 mL x 2). The resulting mixture was dried over anhydrous $MgSO_4$ and then, filtered. The resulting filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (EA/Hx = 1/10) to give the corresponding 7-phenylquinoline (**7a**, 386 mg, 94%).[S2]

7-Phenylquinoline (7a)



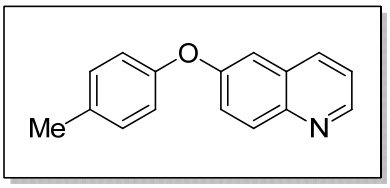
Light yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.95 (dd, J = 4.2, 1.7 Hz, 1H), 8.35 (s, 1H), 8.18 (d, J = 8.3 Hz, 1H), 7.89 (d, J = 8.5 Hz, 1H), 7.83 (dd, J = 8.5, 1.8 Hz, 1H), 7.81 – 7.68 (m, 2H), 7.51 (dd, J = 8.3, 7.1 Hz, 2H), 7.46 – 7.34 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.8, 148.5, 142.3, 140.3, 135.8, 129.0 (2C), 128.2, 127.9, 127.5 (2C), 127.4, 127.1, 126.3, 121.0; **IR** (cm^{-1}) 3035, 1736, 1619, 1488, 1427, 942, 891, 836, 753, 693, 566, 477; **HRMS** (EI): Calculated for $C_{15}H_{11}N$ $[M]^+$: 205.0891, Found: 205.0889.



21a

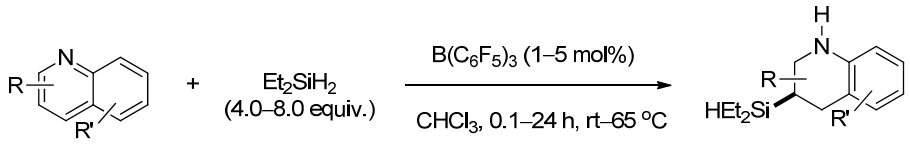
A stirred solution of 6-hydroxyquinoline (1.2 mmol, 1.2 equiv.), picolinic acid (0.20 mmol, 20 mol%), copper(I) iodide (0.10 mmol, 10 mol%), potassium phosphate (2.0 mmol, 2.0 equiv.), and 1-bromo-4-methylbenzene (1.0 mmol, 1.0 equiv.) in dimethylsulfoxide (2.0 mL) was stirred at 110 °C with reflux condenser. After 24 h, the reaction mixture was cooled to room temperature and quenched with water (1 mL). The aqueous layer was extracted with ethyl acetate (2 x 10 mL), and the combined organic layer was washed with saturated ammonium chloride solution (20 mL x 2). The resulting mixture was dried over anhydrous $MgSO_4$, and then filtered. The resulting filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (EA/Hx = 1/4) to give 6-(*p*-tolyloxy)quinoline (**21a**, 202 mg, 86%).[S3]

6-(*p*-Tolyloxy)quinoline (21a)



Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.77 (dd, J = 4.2, 1.7 Hz, 1H), 8.06 (d, J = 9.1 Hz, 1H), 7.96 – 7.84 (m, 1H), 7.45 (dd, J = 9.1, 2.7 Hz, 1H), 7.28 (dd, J = 8.3, 4.2 Hz, 1H), 7.19 – 7.09 (m, 3H), 6.97 (d, J = 8.4 Hz, 2H), 2.33 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.0, 153.8, 148.6, 144.8, 134.9, 133.6, 131.1, 130.3 (2C), 128.9, 122.8, 121.2, 119.6 (2C), 111.9, 20.6; **IR** (cm^{-1}) 3023, 2954, 1595, 1494, 1462, 1374, 1322, 960, 825; **HRMS** (EI): Calculated for $C_{16}H_{13}NO$ $[M]^+$: 235.0997, found: 235.0998.

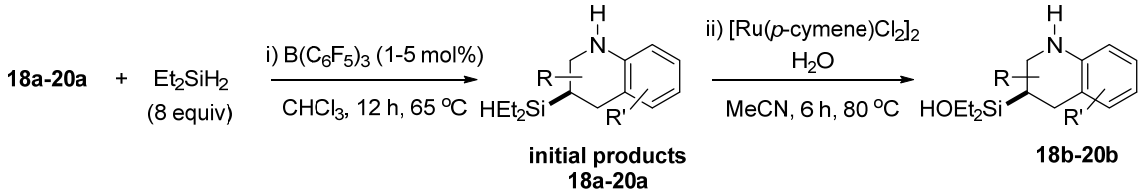
$B(C_6F_5)_3$-Catalyzed Silylative Reduction of Quinolines (Table 1)



1a–17a and 21a–30a **1b–17b and 21b–30b**

In a 2.5 mL reaction vial, $B(C_6F_5)_3$ (0.005 to 0.025 mmol, 1.0 to 5.0 mol%) was dissolved in chloroform (0.50 mL), to which diethylsilane (2.0 to 4.0 mmol, 4.0 to 8.0 equiv.) was added. After shaking briefly, quinoline (0.50 mmol, 1.0 equiv.) was subsequently added to the above solution. The reaction mixture was stirred at room temperature to 65 °C for 0.1 to 24 h, then allowed to cool down to room temperature and filtered through a pad of silica gel with dichloromethane (15 mL) and methanol (2 mL). The filtrate was concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (EA/Hx = 5/95) to give **1b-17b** and **21b-30b**.

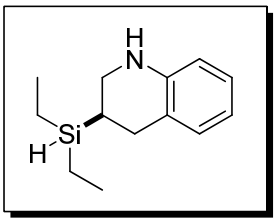
Hydrolytic Oxidation of Silylated Products



In the case of silylative reduction of **18a, 19a** and **20a**, their desired initial products were unable to be isolated by routine silica column chromatography due to the polarity similar to side products in the crude mixture. Thus, the initial products from **18a, 19a** and **20a** were transformed to give **18b, 19b** and **20b**, respectively via hydrolytic oxidation using [Ru(*p*-cymene)Cl_2]$_2$ as a catalyst (*vide infra*), which were then properly obtained in isolated yields of 58% for **18b,** 67% for **19b** and 55% for **20b** for two steps (*steps* i and ii).

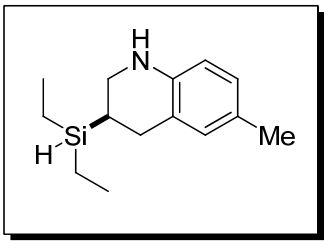
Step *ii*: To a stirred solution of 6-bromo, 7-chloro, or 8-methyl-3-(diethylsilyl)-2-methyl-1,2,3,4-tetrahydro-quinolines (0.50 mmol, 1.0 equiv.) in acetonitrile (3.0 mL) was added [Ru(*p*-cymene)Cl_2]$_2$ (0.025 mmol, 5.0 mol%) and deionized water (10 mmol, 20 equiv.). The reaction mixture was then stirred under air for 6 h at 80 °C, within which complete conversion was observed. Evaporation of solvent and chromatography on silica gel (EA/Hx = 3/7) afforded the corresponding silanols (18b**–**20b**).[8]

3-(Diethylsilyl)-1,2,3,4-tetrahydroquinoline (Table 1, 1b)



Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.11 – 6.87 (m, 2H), 6.61 (ddd, J = 7.6, 1.3, 1.3 Hz, 1H), 6.47 (d, J = 7.9 Hz, 1H), 3.89 (br, 1H), 3.63 (d, J = 3.1 Hz, 1H), 3.39 (ddd, J = 11.6, 3.4, 1.7 Hz, 1H), 3.23 (t, J = 11.4 Hz, 1H), 2.87 – 2.64 (m, 2H), 1.46 (tdd, J = 11.4, 5.7, 2.9 Hz, 1H), 1.04 (td, J = 7.9, 1.4 Hz, 6H), 0.69 (tdd, J = 11.3, 6.3, 3.3 Hz, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.5, 129.0, 126.7, 121.8, 116.9, 114.3, 44.0, 29.1, 17.7, 8.3 (2C), 1.3, 1.2; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.15; **IR** (cm^{-1}) 3403, 2951, 2828, 2093, 1604, 1502, 1262, 1246, 1008, 803, 742; **HRMS** (EI): Calculated for $C_{13}H_{21}NSi$ $[M]^+$: 219.1443, Found: 219.1442.

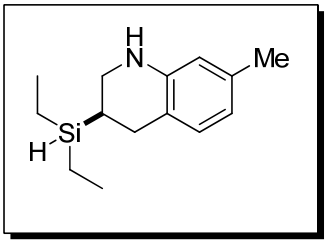
3-(Diethylsilyl)-6-methyl-1,2,3,4-tetrahydroquinoline (Table 1, 2b)



Light yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.94 – 6.88 (m, 2H), 6.51 (d, J = 8.0 Hz, 1H), 3.84 – 3.76 (m, 2H), 3.46 (ddd, J = 11.5, 2.2, 2.2 Hz, 1H), 3.30 (t, J = 11.4 Hz, 1H), 2.88 – 2.83 (m, 2H), 2.35 (s, 3H), 1.58 (dtd, J = 10.9, 6.9, 3.2 Hz, 1H), 1.18 (td, J = 7.9, 1.3 Hz, 6H), 0.82 (qt, J = 8.0,

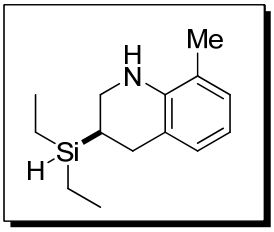
3.3 Hz, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 142.1, 129.4, 127.1, 125.8, 121.7, 114.4, 44.1, 29.0, 20.3, 17.8, 8.3 (2C), 1.2, 1.1; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.43; **IR** (cm^{-1}) 3391, 2951, 2872, 2093, 1618, 1510, 1266, 1249, 1232, 1009, 802; **HRMS** (EI): Calculated for $C_{14}H_{23}NSi$ $[M]^+$: 233.1600, Found: 233.1601.

3-(Diethylsilyl)-7-methyl-1,2,3,4-tetrahydroquinoline (Table 1, 3b)



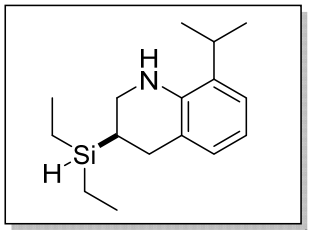
Yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.86 (dd, J = 7.9, 2.0 Hz, 1H), 6.47 (dd, J = 7.7, 1.9 Hz, 1H), 6.33 (s, 1H), 3.60 (br, 1H), 3.71 – 3.58 (m, 1H), 3.45 – 3.29 (m, 1H), 3.28 – 3.14 (m, 1H), 2.84 – 2.67 (m, 2H), 2.25 (s, 3H), 1.47 (ddt, J = 11.4, 5.6, 2.9 Hz, 1H), 1.06 (td, J = 7.9, 2.4 Hz, 6H), 0.82 – 0.57 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.4, 136.3, 128.8, 118.9, 117.8, 114.8, 44.0, 28.7, 21.1, 17.9, 8.3 (2C), 1.4, 1.2; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.37; **IR** (cm^{-1}): 3417, 2952, 2873, 2097, 1600, 1501, 1258, 1228, 806, 752; **HRMS** (EI): Calculated for $C_{14}H_{23}NSi$ $[M]^+$: 233.1600, Found: 233.1601.

3-(Diethylsilyl)-8-methyl-1,2,3,4-tetrahydroquinoline (Table 1, 4b)



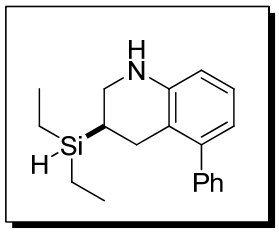
Light yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.10 – 6.80 (m, 2H), 6.68 (dd, J = 7.4, 7.4 Hz, 1H), 3.77 (q, J = 3.1 Hz, 1H), 3.73 (br, 1H) 3.69 – 3.51 (m, 1H), 3.38 (t, J = 11.5 Hz, 1H), 3.06 – 2.67 (m, 2H), 2.19 (s, 3H), 1.76 – 1.38 (m, 1H), 1.16 (t, J = 7.9 Hz, 6H), 0.90 – 0.68 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.4, 127.7, 126.8, 121.20, 121.19, 116.2, 44.3, 29.4, 17.8, 17.0, 8.35, 8.33, 1.3, 1.1; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.43; **IR** (cm^{-1}): 3422, 2951, 2872, 2092, 1598, 1492, 1264, 1247, 1223, 1008, 803, 753; **HRMS** (EI): Calculated for $C_{14}H_{23}NSi$ $[M]^+$: 233.1600, Found: 233.1599.

3-(Diethylsilyl)-8-isopropyl-1,2,3,4-tetrahydroquinoline (Table 1, 5b)



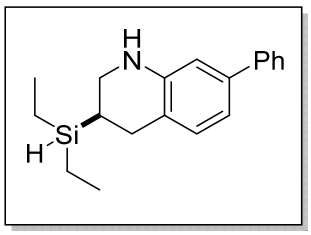
Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.07 – 6.97 (m, 1H), 6.86 (dd, J = 7.5, 1.4 Hz, 1H), 6.66 (d, J = 7.5, 7.5 Hz, 1H), 3.93 (s, 1H), 3.67 (q, J = 3.1 Hz, 1H), 3.56 – 3.50 (m, 1H), 3.30 (t, J = 11.5 Hz, 1H), 2.95 – 2.75 (m, 3H), 1.56 – 1.43 (m, 1H), 1.27 (d, J = 6.8 Hz, 6H), 1.06 (t, J = 7.9 Hz, 6H), 0.77 – 0.64 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 141.2, 131.6, 126.8, 122.7, 121.7, 116.6, 44.5, 29.9, 26.9, 22.5, 22.2, 17.6, 8.40, 8.37, 1.4, 1.2; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.39; **IR** (cm^{-1}) 2954, 2873, 2093, 1596, 1491, 1459, 1349, 1261, 1010, 967, 804, 740; **HRMS** (EI): Calculated for $C_{16}H_{27}NSi$ $[M]^+$: 261.1913, Found: 261.1909.

3-(Diethylsilyl)-5-phenyl-1,2,3,4-tetrahydroquinoline (Table 1, 6b)



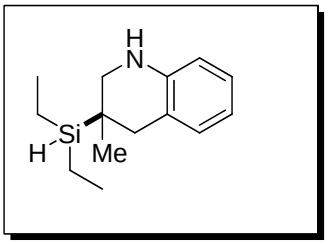
Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 (dd, J = 8.6, 6.7 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.01 (t, J = 7.7 Hz, 1H), 6.60 – 6.53 (m, 1H), 6.48 (dd, J = 8.2, 1.3 Hz, 1H), 3.58 – 3.47 (m, 1H), 3.43 – 3.35 (m, 1H), 3.24 (t, J = 11.3 Hz, 1H), 2.69 – 2.61 (m, 1H), 2.55 (dd, J = 16.5, 11.7 Hz, 1H), 1.31 (d, J = 3.6 Hz, 1H), 0.94 (dtd, J = 14.5, 7.9, 1.2 Hz, 6H), 0.70 – 0.40 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.6, 142.2, 141.8, 129.1 (2C), 127.8 (2C), 126.5, 126.3, 119.3, 118.7, 113.5, 43.9, 27.7, 17.7, 8.31, 8.29, 1.3, 1.2; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.39; **IR** (cm^{-1}): 3405, 2952, 2873, 2096, 1588, 1487, 1459, 1257, 1011, 810, 759; **HRMS** (EI): Calculated $C_{19}H_{25}NSi$ $[M]^+$: 295.1756, Found: 295.1754.

3-(Diethylsilyl)-7-phenyl-1,2,3,4-tetrahydroquinoline (Table 1, 7b)



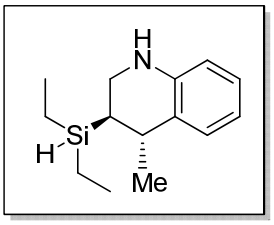
White solid; m.p. 55–57 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.56 (dt, J = 7.8, 1.7 Hz, 2H), 7.41 (td, J = 7.7, 2.2 Hz, 2H), 7.32 (tt, J = 7.7, 1.4 Hz, 1H), 7.02 (dd, J = 7.7, 2.3 Hz, 1H), 6.86 (dt, J = 7.7, 2.1 Hz, 1H), 6.71 (t, J = 2.0 Hz, 1H), 3.71 – 3.63 (m, 1H), 3.51 – 3.38 (m, 1H), 3.28 (td, J = 11.4, 2.3 Hz, 1H), 2.90 – 2.71 (m, 2H), 1.51 (dtd, J = 8.9, 5.9, 3.0 Hz, 1H), 1.14 – 1.00 (m, 6H), 0.72 (dq, J = 8.4, 2.7 Hz, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.8, 141.6, 140.0, 129.4, 128.5 (2C), 126.9 (2C), 126.8, 121.2, 116.0, 112.9, 44.1, 28.9, 17.8, 8.4 (2C), 1.4, 1.2; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.39; **IR** (cm^{-1}) 2951, 2908, 2872, 2090, 1609, 1565, 1484, 1386, 1319, 1288, 1260, 1226, 1008, 804, 757, 695; **HRMS** (EI): Calculated for $C_{19}H_{25}NSi$ $[M]^+$: 295.1756, Found: 295.1754.

3-(Diethylsilyl)-3-methyl-1,2,3,4-tetrahydroquinoline (Table 1, 8b)

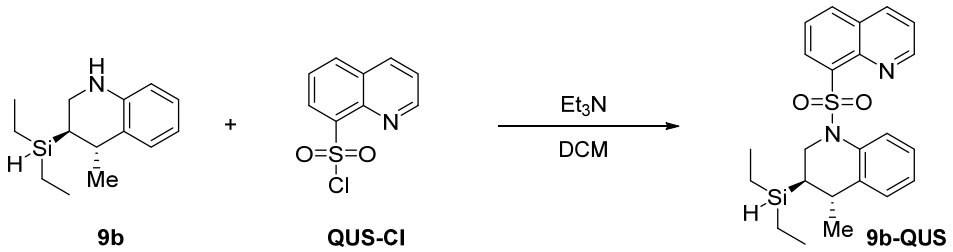


Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.00 (ddd, J = 7.8, 7.0, 1.5 Hz, 1H), 6.96 (dt, J = 7.5, 1.2 Hz, 1H), 6.64 (td, J = 7.4, 1.2 Hz, 1H), 6.49 (dd, J = 8.0, 1.2 Hz, 1H), 3.85 (br, 1H), 3.61 – 3.47 (m, 1H), 3.32 (dd, J = 11.2, 1.1 Hz, 1H), 2.99 (dd, J = 11.3, 1.6 Hz, 1H), 2.91 (d, J = 16.1 Hz, 1H), 2.48 (d, J = 16.1 Hz, 1H), 1.30 – 0.91 (m, 9H), 0.81 – 0.45 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.1, 129.7, 126.5, 120.0, 116.9, 113.7, 49.9, 36.9, 20.9, 19.3, 8.9, 8.8, 0.8, 0.6; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 6.71; **IR** (cm^{-1}) 3397, 2951, 2828, 2092, 1617, 1487, 1261, 1232, 1010, 787; **HRMS** (EI): Calculated for $C_{14}H_{23}NSi$ $[M]^+$: 233.1600, Found: 233.1598.

3-(Diethylsilyl)-4-methyl-1,2,3,4-tetrahydroquinoline (Table 1, 9b)

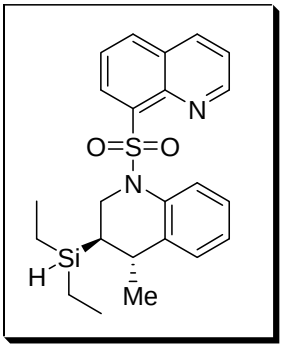


Yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 – 7.06 (m, 1H), 7.00 (dddd, J = 7.9, 7.2, 1.5, 0.6 Hz, 1H), 6.69 (td, J = 7.4, 1.3 Hz, 1H), 6.51 (dd, J = 8.0, 1.3 Hz, 1H), 3.63 (td, J = 3.4, 2.7 Hz, 1H), 3.52 (dd, J = 11.3, 3.6 Hz, 1H), 3.25 (ddd, J = 11.3, 6.0, 0.7 Hz, 1H), 2.96 (dd, J = 7.0, 4.7 Hz, 1H), 1.39 (d, J = 7.0 Hz, 3H), 1.28 – 1.18 (m, 1H), 1.08 – 0.91 (m, 6H), 0.72 – 0.52 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.6, 128.9, 126.8, 126.5, 117.2, 114.4, 40.5, 32.1, 25.2, 25.1, 8.5, 8.4, 1.9, 1.7; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.49; **IR** (cm^{-1}): 3392, 2953, 2872, 2092, 1783, 1606, 1499, 1260, 1228, 1014, 814, 744; **HRMS** (EI): Calculated for $C_{14}H_{23}NSi$ $[M]^+$: 233.1600, Found: 233.1603.

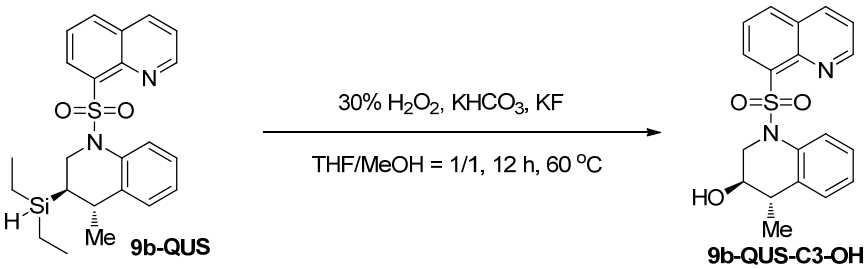


To a solution of **9b** (0.5 mmol, 1 equiv.) in dichloromethane (3 mL) was added triethylamine (1.5 mmol, 3.0 equiv.) at 0 ^{o}C, then stirrer for 10 min. Then, 8-quinolinesulfonyl chloride (**QUS-Cl**, 0.75 mmol, 1.5 equiv.) was added into the above solution at 0 ^{o}C. After stirring for 12 h at room temperature, all volatiles from the reaction mixture were evaporated under reduced pressure, and the crude mixture was subjected to purification by column chromatography on silica gel (EA/Hx = 3/7) to give **9b-QUS** (173 mg, 82%). X-ray quality crystals of **9b-QUS** were grown by slow evaporation from CH_2Cl_2 and MeOH.

8-(3-(Diethylsilyl)-4-methyl-3,4-dihydroquinolin-1(2*H*)-ylsulfonyl)quinolone(Table 1, 9b-QUS)

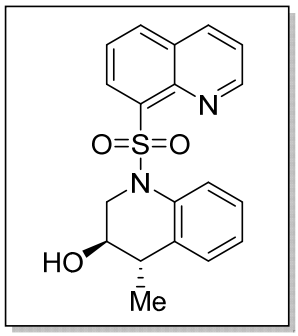


White solid; m.p. 118-119 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (dd, J = 4.2, 1.8 Hz, 1H), 8.46 (dd, J = 7.4, 1.5 Hz, 1H), 8.07 (dd, J = 8.2, 1.8 Hz, 1H), 7.91 (dd, J = 8.3, 1.5 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 7.32 (dd, J = 8.3, 4.2 Hz, 1H), 6.99 (dd, J = 7.5, 1.6 Hz, 1H), 6.94 (td, J = 7.6, 1.7 Hz, 1H), 6.88 (td, J = 7.5, 1.3 Hz, 1H), 4.48 (dd, J = 13.5, 4.1 Hz, 1H), 3.72 – 3.58 (m, 1H), 3.58 – 3.50 (m, 1H), 2.75 (dd, J = 8.9, 6.4 Hz, 1H), 1.01 (ddt, J = 11.6, 7.3, 2.3 Hz, 1H), 0.98 – 0.77 (m, 9H), 0.56 (dd, J = 7.9, 3.5 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.8, 143.8, 138.5, 137.7, 136.2, 134.3, 133.4, 132.3, 128.8, 127.9, 125.7, 125.3, 123.5, 121.9, 121.9, 48.3, 32.8, 27.3, 23.1, 8.4, 8.3, 1.6, 1.3.; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ -0.67; **IR** (cm^{-1}): 2953, 2907, 2871, 2109, 1596, 1560, 1489, 1331, 1221, 1163, 1141, 959, 797; **HRMS** (ESI): Calculated for $C_{23}H_{29}N_2O_2SSi$ $[M+H]^+$: 425.1719, Found: 425.1711.



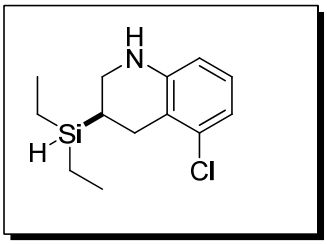
A mixture of **9b-QUS** (0.35 mmol, 1.0 equiv.), potassium fluoride (2.1 mmol, 6.0 equiv.), potassium bicarbontate (2.1 mmol, 6.0 equiv.), and 30% hydrogen peroxide in water (6.3 mmol, 18 equiv.) in tetrahydrofuran (2.5 mL) and methanol (2.5 mL) was stirred at 60 °C for 12 h. The reaction mixture was quenched with 10 % sodium bisulfite solution in water (1 mL) at 0 °C and the aqueous layer was extracted with diethyl ether (5 mL x 3). The combined organic layer was washed with saturated sodium carbonate solution in water (3 mL x 2) and dried over anhydrous $MgSO_4$ and then filtered. The resulting filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (EA/Hx = 1/1) to give **9b-QUS-C3-OH** (106 mg, 85%).[S4]

4-Methyl-1-(quinolin-8-ylsulfonyl)-1,2,3,4-tetrahydroquinolin-3-ol (Table 1, 9b-QUS-C3-OH):



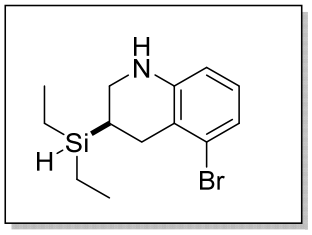
White solid; m.p. 206-207 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.95 (dd, J = 4.3, 1.8 Hz, 1H), 8.78 (dd, J = 7.4, 1.4 Hz, 1H), 8.20 (dd, J = 8.3, 1.8 Hz, 1H), 8.05 (dd, J = 8.2, 1.5 Hz, 1H), 7.70 (t, J = 7.8 Hz, 1H), 7.48 (dd, J = 8.3, 4.3 Hz, 1H), 7.44 (dd, J = 8.4, 1.3 Hz, 1H), 7.13 – 7.05 (m, 1H), 6.94 (td, J = 8.3, 7.8, 1.7 Hz, 1H), 6.88 (td, J = 7.4, 1.3 Hz, 1H), 4.83 (ddd, J = 13.4, 4.6, 1.5 Hz, 1H), 4.67 – 4.45 (m, 1H), 4.08 – 4.02 (m, 1H), 4.01 (d, J = 1.9 Hz, 1H), 2.89 (dd, J = 7.4, 3.1 Hz, 1H), 1.25 (d, J = 7.3 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.4, 143.3, 137.2, 136.9, 135.4, 134.6, 134.3, 130.3, 130.0, 129.1, 126.2, 125.6, 123.1, 122.3, 118.4, 68.8, 47.5, 39.5, 21.9; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ -0.67; **IR** (cm^{-1}): 3521, 2952, 2922, 2849, 1600, 1562, 1487, 1441, 1337, 1277, 1129, 1040, 933, 757; **HRMS** (ESI): Calculated for $C_{19}H_{18}N_2O_3SNa$ $[M+Na]^+$: 377.0936, Found: 377.0943.

5-Chloro-3-(diethylsilyl)-1,2,3,4-tetrahydroquinoline (Table 1, 10b)



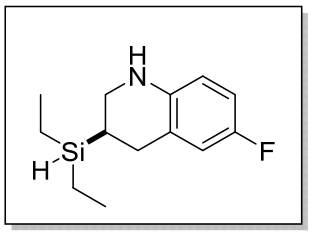
Yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.91 (t, J = 7.9 Hz, 1H), 6.72 (dd, J = 8.0, 1.3 Hz, 1H), 6.38 (d, J = 8.0 Hz, 1H), 4.01 (s, 1H), 3.82 – 3.56 (m, 1H), 3.37 (ddd, J = 11.5, 3.4, 1.9 Hz, 1H), 3.19 (t, J = 11.4 Hz, 1H), 3.03 (ddd, J = 17.1, 5.1, 1.9 Hz, 1H), 2.61 (dd, J = 17.0, 12.0 Hz, 1H), 1.45 (dt, J = 5.8, 3.4 Hz, 1H), 1.10 (tdt, J = 8.0, 2.6, 1.3 Hz, 6H), 0.83 – 0.51 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.1, 134.3, 126.9, 119.3, 117.3, 112.5, 43.3, 26.6, 17.3, 8.3 (2C), 1.3, 1.1; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.52; **IR** (cm^{-1}): 3413, 2952, 2873, 2095, 1596, 1487, 1260, 1233, 1009, 807, 762; **HRMS** (EI): Calculated for $C_{13}H_{20}ClNSi$ $[M]^+$: 253.1054, Found: 253.1051.

5-Bromo-3-(diethylsilyl)-1,2,3,4-tetrahydroquinoline (Table 1, 11b)



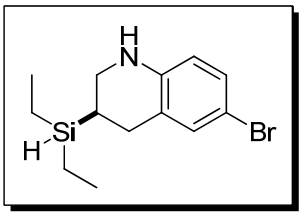
Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.87 (dd, J = 7.8, 1.2 Hz, 1H), 6.82 (t, J = 7.9 Hz, 1H), 6.41 (dd, J = 8.0, 1.2 Hz, 1H), 4.01 (s, 1H), 3.68 (q, J = 3.1 Hz, 1H), 3.35 (ddd, J = 11.5, 3.5, 1.9 Hz, 1H), 3.17 (t, J = 11.4 Hz, 1H), 2.96 (ddd, J = 17.0, 5.0, 1.9 Hz, 1H), 2.69 – 2.49 (m, 1H), 1.50 – 1.35 (m, 1H), 1.06 (td, J = 7.9, 3.6 Hz, 6H), 0.72 (dddd, J = 12.8, 8.0, 7.0, 3.3 Hz, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.3, 127.5, 125.6, 121.0, 120.6, 113.3, 43.5, 29.7, 17.8, 8.4, 8.3, 1.4, 1.2; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.38; **IR** (cm^{-1}) 2952, 2873, 2093, 1593, 1486, 1457, 1344, 1312, 1260, 1230, 1193, 805, 759; **HRMS** (EI): Calculated for $C_{13}H_{20}BrNSi$ $[M]^+$: 297.0548, Found: 297.0551.

3-(Diethylsilyl)-6-fluoro-1,2,3,4-tetrahydroquinoline (Table 1, 12b)



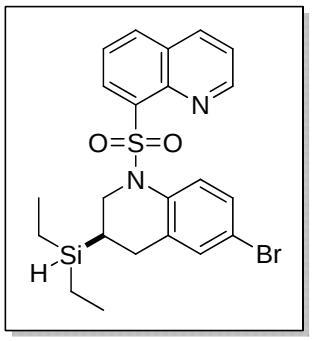
Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.75 – 6.64 (m, 2H), 6.40 (dd, J = 8.4, 4.8 Hz, 1H), 3.65 (q, J = 3.1 Hz, 1H), 3.37 (ddd, J = 11.4, 3.4, 1.6 Hz, 1H), 3.19 (t, J = 11.4 Hz, 1H), 2.81 – 2.63 (m, 2H), 1.47 – 1.34 (m, 1H), 1.05 (td, J = 7.9, 1.4 Hz, 6H), 0.80 – 0.53 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 155.4 (d, J = 234.9 Hz), 140.7 (d, J = 1.8 Hz), 123.1 (d, J = 6.3 Hz), 115.2 (d, J = 21.4 Hz), 115.0 (d, J = 7.5 Hz), 113.2 (d, J = 22.5 Hz), 44.2, 29.2, 17.6, 8.3 (2C), 1.3, 1.2; **^{19}F NMR** (564 MHz, $CDCl_3$) δ -128.1 (td, J = 8.8, 4.9 Hz); **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.39; **IR** (cm^{-1}) 2953, 2910, 2874, 2095, 1503, 1348, 1243, 1221, 1221, 1140, 850, 800; **HRMS** (EI): Calculated for $C_{13}H_{20}FNSi$ $[M]^+$: 237.1349, Found: 237.1349.

6-Bromo-3-(diethylsilyl)-1,2,3,4-tetrahydroquinoline (Table 1, 13b)



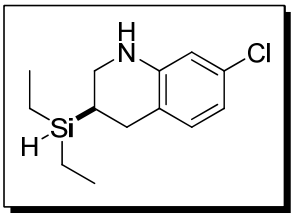
Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.04 (d, J = 9.1 Hz, 2H), 6.33 (dd, J = 8.1, 1.6 Hz, 1H), 3.87 (br, 1H), 3.65 (q, J = 3.2, 2.8 Hz, 1H), 3.49 – 3.28 (m, 1H), 3.20 (td, J = 11.4, 1.6 Hz, 1H), 2.72 (qd, J = 16.3, 8.1 Hz, 2H), 1.40 (td, J = 4.7, 2.2 Hz, 1H), 1.05 (tt, J = 7.9, 1.2 Hz, 6H), 0.70 (dt, J = 7.7, 2.6 Hz, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.4, 131.3, 129.2, 123.7, 115.5, 108.0, 43.8, 29.0, 17.2, 8.3 (2C), 1.3, 1.1; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.32; **IR** (cm^{-1}) 3411, 2950, 2872, 2089, 1598, 1491, 1261, 1243, 1229, 1004, 800, 705; **HRMS** (EI): Calculated for $C_{13}H_{20}BrNSi$ $[M]^+$: 297.0548, Found: 297.0551.

8-{6-Bromo-3-(diethylsilyl)-3,4-dihydroquinolin-1(2*H*)-ylsulfonyl}quinoline (Table 1, 13b-QUS)



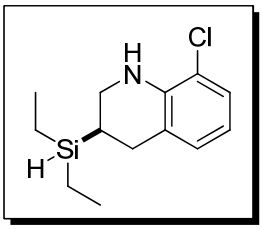
Colorless solid; m.p. 118–120 ^{o}C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.85 (dd, J = 4.1, 1.9 Hz, 1H), 8.55 (dt, J = 7.3, 1.4 Hz, 1H), 8.15 (dt, J = 8.4, 1.8 Hz, 1H), 7.98 (dt, J = 8.2, 1.5 Hz, 1H), 7.66 – 7.54 (m, 1H), 7.50 (d, J = 8.9 Hz, 1H), 7.43 (dd, J = 8.2, 4.2 Hz, 1H), 7.07 (dd, J = 8.9, 2.3 Hz, 1H), 7.01 (d, J = 2.5 Hz, 1H), 4.63 (ddd, J = 12.6, 4.1, 1.7 Hz, 1H), 3.96 (t, J = 12.8 Hz, 1H), 3.68 (q, J = 3.1 Hz, 1H), 2.77 – 2.39 (m, 2H), 1.34 (dd, J = 2.6, 1.4 Hz, 1H), 1.00 (q, J = 8.1 Hz, 6H), 0.78 – 0.59 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.8, 143.7, 137.1, 136.3, 133.8, 133.5, 133.4, 131.6, 130.8, 129.0, 128.8, 125.2, 122.5, 122.0, 115.4, 49.5, 29.7, 18.9, 8.2, 8.19, 1.1, 1.0; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ -0.20; **IR** (cm^{-1}): 2953, 2135, 1478, 1338, 1208, 1166, 1143, 1026, 808, 781, 565; **HRMS** (EI): Calculated for $C_{22}H_{25}BrN_2O_2SSi$ $[M]^+$: 488.0589, Found: 488.0592.

7-Chloro-3-(diethylsilyl)-1,2,3,4-tetrahydroquinoline (Table 1, 14b)



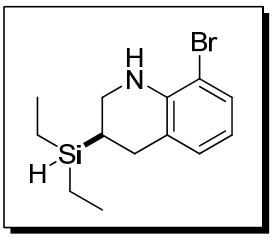
Light yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.81 (d, J = 8.0 Hz, 1H), 6.53 (dd, J = 8.0, 2.1 Hz, 1H), 6.42 (d, J = 2.1 Hz, 1H), 3.89 (br, 1H), 3.62 (q, J = 3.1 Hz, 1H), 3.37 (ddd, J = 11.7, 3.6, 2.0 Hz, 1H), 3.19 (t, J = 11.4 Hz, 1H), 2.86 – 2.47 (m, 2H), 1.39 (dt, J = 4.6, 3.3 Hz, 1H), 1.02 (td, J = 7.9, 1.2 Hz, 6H), 0.67 (dd, J = 7.7, 3.6 Hz, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.4, 131.8, 129.9, 120.0, 116.4, 113.4, 43.7, 28.7, 17.3, 8.3 (2C), 1.3, 1.2; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.36; **IR** (cm^{-1}): 3410, 2953, 2873, 2098, 1600, 1497, 1259, 1238, 1080, 882, 784; **HRMS** (EI): Calculated for $C_{13}H_{20}ClNSi$ $[M]^+$: 253.1054, Found: 253.1053.

8-Chloro-3-(diethylsilyl)-1,2,3,4-tetrahydroquinoline (Table 1, 15b)



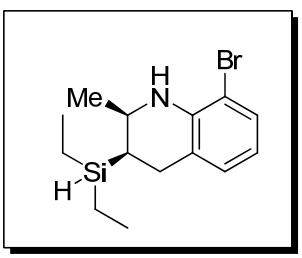
Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.11 – 6.93 (m, 1H), 6.89 – 6.68 (m, 1H), 6.51 (t, J = 7.7 Hz, 1H), 4.49 (br, 1H), 3.64 (q, J = 3.1 Hz, 1H), 3.51 (ddd, J = 11.7, 3.6, 2.0 Hz, 1H), 3.28 (t, J = 11.6 Hz, 1H), 3.04 – 2.56 (m, 2H), 1.47 – 1.36 (m, 1H), 1.09 – 0.93 (m, 6H), 0.74 – 0.64 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 140.5, 127.1, 126.7, 123.1, 118.1, 116.1, 43.8, 29.4, 17.2, 8.3, 1.3, 1.2; **^{29}Si NMR** (80 MHz, $CDCl_3$) δ 0.37; **IR** (cm^{-1}): 3421, 2953, 2092, 1600, 1491, 1332, 1261, 1229, 1051, 801, 784; **HRMS** (EI): Calculated for $C_{13}H_{20}ClNSi$ $[M]^+$: 253.1054, Found: 253.1053.

8-Bromo-3-(diethylsilyl)-1,2,3,4-tetrahydroquinoline (Table 1, 16b)



Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (dt, J = 7.8, 1.3 Hz, 1H), 6.92 (dt, J = 7.4, 1.2 Hz, 1H), 6.49 (dd, J = 8.4, 6.9 Hz, 1H), 4.56 (br, 1H), 3.68 (d, J = 3.0 Hz, 1H), 3.60 – 3.47 (m, 1H), 3.32 (t, J = 11.6 Hz, 1H), 2.91 – 2.59 (m, 2H), 1.45 (dd, J = 3.1, 2.0 Hz, 1H), 1.08 (td, J = 7.8, 1.1 Hz, 6H), 0.77 – 0.61 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.4, 129.9, 127.8, 123.3, 116.7, 108.7, 44.1, 29.6, 17.1, 8.3 (2C), 1.3, 1.1; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.27; **IR** (cm^{-1}): 3413, 2951, 2872, 2094, 1598, 1498, 1284, 1258, 1232, 1064, 803, 749; **HRMS** (EI): Calculated for $C_{13}H_{20}BrNSi$ $[M]^+$: 297.0548, Found: 297.0546.

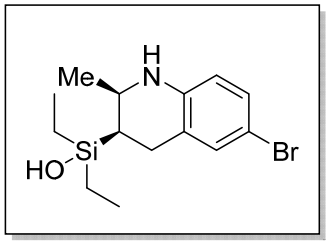
8-Bromo-3-(diethylsilyl)-2-methyl-1,2,3,4-tetrahydroquinoline (Table 1, 17b)



Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 – 7.07 (m, 1H), 6.89 (dt, J = 7.5, 1.5 Hz, 1H), 6.44 (td, J = 7.7, 1.2 Hz, 1H), 4.54 (s, 1H), 3.77 (dt, J = 6.8, 3.4 Hz, 1H), 3.69 (ddd, J = 5.3, 2.3, 1.2 Hz, 1H), 3.03 – 2.43 (m, 2H), 1.47 (ddt, J = 8.6, 5.0, 1.9 Hz, 1H), 1.23 (dd, J = 6.6, 1.5 Hz, 3H), 1.00 (dtt, J

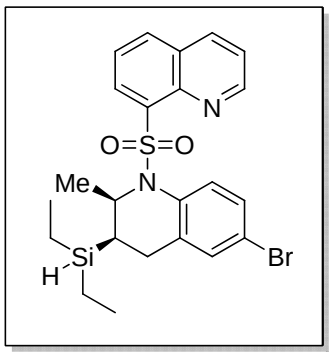
= 18.5, 7.8, 1.3 Hz, 6H), 0.78 – 0.30 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 140.9, 130.0, 127.8, 122.63, 116.5, 108.9, 48.2, 26.5, 22.3, 20.4, 8.4, 8.38, 1.9, 1.7; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ -1.14; **IR** (cm^{-1}): 3423, 2951, 2872, 2094, 1600, 1459, 1284, 1260, 1232, 1009, 918, 752; **HRMS** (ESI): Calculated for $C_{14}H_{23}BrNSi$ $[M+H]^+$: 314.0763, Found: 314.0737.

(6-Bromo-2-methyl-1,2,3,4-tetrahydroquinolin-3-yl)diethylsilanol (Table 1, 18b)



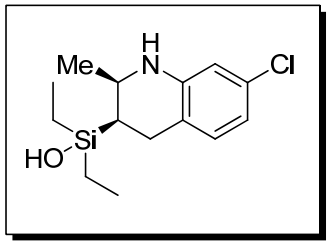
Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.85 (dt, J = 8.1, 1.0 Hz, 1H), 6.56 (dd, J = 8.1, 2.1 Hz, 1H), 6.44 (d, J = 2.1 Hz, 1H), 3.68 (dd, J = 6.6, 3.3 Hz, 1H), 2.77 (d, J = 7.5 Hz, 2H), 1.38 (td, J = 7.5, 3.3 Hz, 1H), 1.25 (d, J = 6.6 Hz, 3H), 0.99 (t, J = 8.0 Hz, 3H), 0.95 (t, J = 8.0 Hz, 3H), 0.74 – 0.56 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.9, 131.9, 130.0, 119.8, 116.9, 114.1, 48.2, 25.2, 24.8, 20.8, 6.6, 6.5, 6.3, 5.7; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 17.04; **IR** (cm^{-1}): 3392, 3351, 2955, 2875, 1599, 1491, 1267, 1239, 1207, 1005, 821, 719; **HRMS** (EI): Calculated for $C_{14}H_{22}BrNOSi$ $[M]^+$: 327.0654, Found: 327.0653.

8-{6-Bromo-3-(diethylsilyl)-2-methyl-3,4-dihydroquinolin-1(2*H*)-ylsulfonyl)}quinoline (Table 1, 18b-QUS)



Colorless solid; m.p. 152–154 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72 (dd, J = 4.1, 1.7 Hz, 1H), 8.55 (dd, J = 7.5, 1.3 Hz, 1H), 8.15 (dd, J = 8.3, 1.6 Hz, 1H), 8.00 (dd, J = 8.2, 1.4 Hz, 1H), 7.69 – 7.55 (m, 2H), 7.46 – 7.36 (m, 1H), 7.19 (dd, J = 9.0, 2.4 Hz, 1H), 7.13 (dd, J = 2.5, 1.2 Hz, 1H), 4.99 (dd, J = 6.9, 3.4 Hz, 1H), 3.56 (dq, J = 3.6, 1.9 Hz, 1H), 2.71 (dd, J = 17.5, 14.0 Hz, 1H), 2.48 (dd, J = 17.6, 5.8 Hz, 1H), 1.19 (d, J = 6.9 Hz, 4H), 0.93 (t, J = 7.9 Hz, 3H), 0.81 (t, J = 7.9 Hz, 3H), 0.68 – 0.49 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.8, 143.8, 137.1, 136.2, 135.1, 133.7, 132.9, 131.23, 129.3, 128.9, 128.8, 125.2, 125.1, 121.9, 115.9, 52.4, 24.9, 20.9, 16.7, 8.0, 7.8, 1.2, 0.9; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ -0.72; **IR** (cm^{-1}): 2954, 2872, 2085, 1477, 1332, 1228, 1162, 1144, 1005, 815, 784, 580; **HRMS** (ESI): Calculated for $C_{23}H_{27}BrNaN_2O_2SSi$ $[M+Na]^+$: 525.0644, Found: 525.0653.

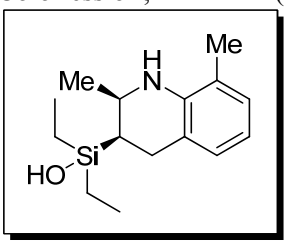
(7-Chloro-2-methyl-1,2,3,4-tetrahydroquinolin-3-yl)diethylsilanol (Table 1, 19b)



Colorless liquid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.07 (dd, J = 2.2, 1.1 Hz, 1H), 7.03 (dd, J = 8.5, 2.3 Hz, 1H), 6.34 (d, J = 8.5 Hz, 1H), 3.67 (qd, J = 6.6, 3.3 Hz, 1H), 2.79 (d, J = 7.4 Hz, 2H), 1.36 (td, J = 7.4, 3.2 Hz, 1H), 1.25 (d, J = 6.6 Hz, 3H), 0.99 (t, J = 8.0 Hz, 3H), 0.94 (t, J = 7.9 Hz, 3H),

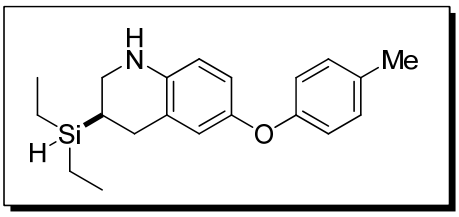
0.74 – 0.55 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 142.9, 131.5, 129.4, 123.6, 116.2, 108.8, 48.5, 25.7, 24.6, 20.8, 6.6, 6.5, 6.3, 5.7; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 17.06; **IR** (cm^{-1}): 3397, 2955, 2914, 2876, 1601, 1579, 1493, 1314, 1268, 1241, 1088, 969, 724; **HRMS** (ESI): Calculated for $C_{14}H_{23}ClNOSi$ $[M+H]^+$: 284.1237, Found: 284.1220.

(2,8-Dimethyl-1,2,3,4-tetrahydroquinolin-3-yl)diethylsilanol (Table 1, 20b)



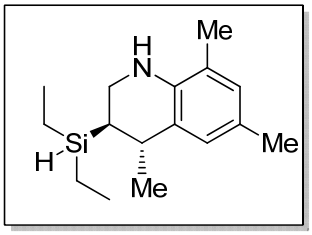
Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.92 (td, J = 6.0, 2.7 Hz, 2H), 6.63 (t, J = 7.4 Hz, 1H), 3.82 (dd, J = 6.7, 3.2 Hz, 1H), 2.92 (dd, J = 12.1, 7.0 Hz, 2H), 2.11 (s, 3H), 1.52 – 1.42 (m, 1H), 1.40 – 1.33 (d, J = 7.9 Hz, 3H), 1.10 – 1.01 (m, 3H), 0.97 (t, J = 7.9 Hz, 3H), 0.80 – 0.55 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.9, 127.9, 127.0, 121.8, 121.2, 117.0, 49.2, 26.7, 24.8, 21.4, 17.2, 6.7, 6.6, 6.5, 5.7; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 17.78; **IR** (cm^{-1}): 3413, 2955, 2874, 1597, 1476, 1265, 1236, 1055, 754; **HRMS** (EI): Calculated for $C_{15}H_{25}NOSi$ $[M]^+$: 263.1705, Found: 263.1704.

3-(Diethylsilyl)-6-(*p*-tolyloxy)-1,2,3,4-tetrahydroquinoline (Table 1, 21b)



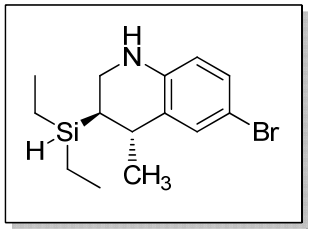
Light yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.12 – 7.05 (m, 2H), 6.89 – 6.83 (m, 2H), 6.72 – 6.64 (m, 2H), 6.46 (d, J = 8.5 Hz, 1H), 3.64 (q, J = 3.1 Hz, 1H), 3.44 – 3.33 (m, 1H), 3.22 (t, J = 11.4 Hz, 1H), 2.73 (d, J = 8.5 Hz, 2H), 2.31 (s, 3H), 1.52 – 1.39 (m, 1H), 1.04 (t, J = 7.9 Hz, 6H), 0.82 – 0.50 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.7, 147.8, 140.81, 131.2, 129.8 (2C), 123.1, 120.3, 118.4, 117.3 (2C), 115.2, 44.2, 29.2, 20.5, 17.7, 8.3 (2C), 1.3, 1.1; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.42; **IR** (cm^{-1}): 3406, 2951, 2872, 2093, 1607, 1495, 1286, 1226, 1011, 805; **HRMS** (EI): Calculated for $C_{20}H_{27}NOSi$ $[M]^+$: 325.1862, Found: 325.1863.

3-(Diethylsilyl)-4,6,8-trimethyl-1,2,3,4-tetrahydroquinoline (Table 1, 22b)



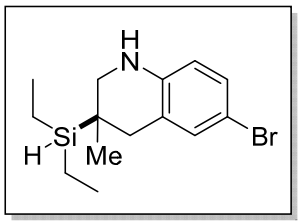
Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.87 – 6.81 (m, 1H), 6.81 – 6.73 (m, 1H), 3.65 (q, J = 3.1 Hz, 1H), 3.56 (dd, J = 11.3, 3.6 Hz, 1H), 3.31 (dd, J = 11.3, 6.3 Hz, 1H), 3.02 – 2.88 (m, 1H), 2.27 (s, 3H), 2.11 (s, 3H), 1.41 (d, J = 6.9 Hz, 3H), 1.24 (dtd, J = 5.1, 2.5, 1.2 Hz, 1H), 1.03 (td, J = 7.9, 3.0 Hz, 6H), 0.65 (dddt, J = 12.6, 8.1, 6.5, 3.0 Hz, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 140.3, 128.5, 127.3, 126.5, 125.6, 121.4, 41.1, 32.3, 25.6, 25.2, 20.5, 17.2, 8.6, 8.5, 2.0, 1.9; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.63; **IR** (cm^{-1}) 2952, 2094, 1495, 1326, 1265, 1248, 1234, 1008, 856, 806; **HRMS** (EI): Calculated for $C_{16}H_{27}NSi$ $[M]^+$: 261.1913, Found: 261.1913.

6-Bromo-3-(diethylsilyl)-4-methyl-1,2,3,4-tetrahydroquinoline (Table 1, 23b)



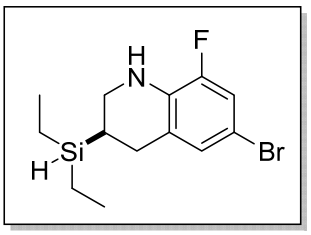
Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.23 – 7.12 (m, 1H), 7.03 (d, J = 8.5 Hz, 1H), 6.34 (d, J = 8.5 Hz, 1H), 3.63 – 3.54 (m, 1H), 3.52 – 3.39 (m, 1H), 3.26 – 3.16 (m, 1H), 2.97 – 2.77 (m, 1H), 1.33 (dd, J = 6.8, 1.5 Hz, 3H), 1.17 (d, J = 2.0 Hz, 1H), 1.03 – 0.94 (m, 6H), 0.61 (dt, J = 7.9, 3.9 Hz, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.6, 131.4, 129.3, 128.8, 115.9, 108.6, 40.3, 32.2, 25.0, 24.7, 8.52, 8.46, 1.9, 1.8; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.06; **IR** (cm^{-1}) 2954, 2872, 2100, 1494, 1465, 1301, 1275, 1260, 1233, 1166, 805; **HRMS** (EI): Calculated for $C_{14}H_{22}BrNSi$ $[M]^+$: 311.0705, Found: 311.0703.

6-Bromo-3-(diethylsilyl)-3-methyl-1,2,3,4-tetrahydroquinoline (Table 1, 24b)



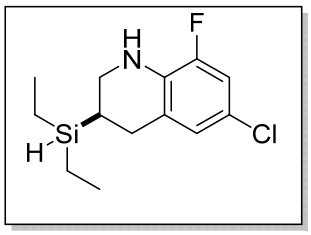
Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.02 (d, J = 2.6 Hz, 2H), 6.32 (d, J = 9.1 Hz, 1H), 3.82 (br, 1H), 3.47 (dd, J = 4.6, 2.4 Hz, 1H), 3.26 (dd, J = 11.4, 1.1 Hz, 1H), 2.94 (dd, J = 11.6, 1.6 Hz, 1H), 2.81 (d, J = 16.3 Hz, 1H), 2.39 (d, J = 16.3 Hz, 1H), 1.14 – 0.82 (m, 9H), 0.63 (ddd, J = 8.2, 6.5, 4.0 Hz, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.01, 132.1, 129.2, 122.0, 115.1, 108.1, 49.7, 36.7, 20.7, 18.9, 8.9, 8.8, 0.8, 0.5.; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 6.59; **IR** (cm^{-1}) 3429, 2953, 2915, 2874, 2098, 1640, 1493, 1460, 1376, 1302, 1276, 1236, 1084, 969, 802; **HRMS** (ESI): Calculated for $C_{14}H_{23}BrNSi$ $[M+H]^+$: 314.0763, Found: 314.0750.

6-Bromo-3-(diethylsilyl)-8-fluoro-1,2,3,4-tetrahydroquinoline (Table 1, 25b)



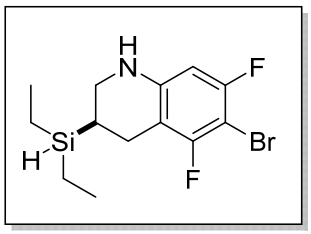
Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.94 (dd, J = 10.5, 2.1 Hz, 1H), 6.86 (dd, J = 2.4, 1.2 Hz, 1H), 4.08 (s, br, 1H), 3.63 (q, J = 3.1 Hz, 1H), 3.45 (ddd, J = 11.6, 3.6, 1.8 Hz, 1H), 3.20 (t, J = 11.5 Hz, 1H), 2.76 (ddd, J = 16.6, 4.8, 1.8 Hz, 1H), 2.68 (dd, J = 16.4, 11.8 Hz, 1H), 1.48 – 1.33 (m, 1H), 1.03 (ddd, J = 8.6, 7.6, 1.2 Hz, 6H), 0.74 – 0.58 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.5 (d, J = 242.1 Hz), 132.2 (d, J = 11.9 Hz), 126.8 (d, J = 3.0 Hz), 125.3 (d, J = 4.4 Hz), 115.6 (d, J = 21.6 Hz), 105.9, 43.2, 28.7 (d, J = 3.0 Hz), 17.1, 8.3 (2C) , 1.3, 1.2; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.28; **^{19}F NMR** (564 MHz, $CDCl_3$) δ -136.8 (d, J = 10.5 Hz); **IR** (cm^{-1}) 2952, 2873, 2831, 2096, 1499, 1306, 1279, 1232, 1207, 991, 842, 806; **HRMS** (EI): Calculated for $C_{13}H_{19}BrFNSi$ $[M]^+$: 315.0454, Found: 315.0451.

6-Chloro-3-(diethylsilyl)-8-fluoro-1,2,3,4-tetrahydroquinoline (Table 1, 26b)



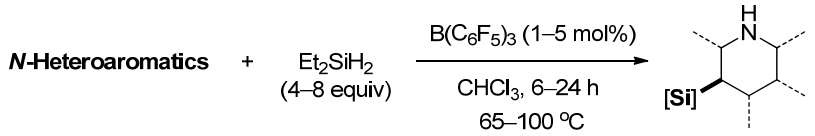
Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.81 (dd, J = 10.8, 2.3 Hz, 1H), 6.73 (dd, J = 2.5, 1.3 Hz, 1H), 4.04 (s, 1H), 3.64 (q, J = 3.1 Hz, 1H), 3.45 (ddd, J = 11.6, 3.5, 1.8 Hz, 1H), 3.21 (t, J = 11.5 Hz, 1H), 2.76 (ddd, J = 16.5, 4.8, 1.8 Hz, 1H), 2.68 (dd, J = 16.4, 11.8 Hz, 1H), 1.50 – 1.31 (m, 1H), 1.04 (td, J = 7.9, 1.4 Hz, 6H), 0.69 (dddd, J = 10.8, 7.9, 4.8, 2.6 Hz, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.3 (d, J = 241.0 Hz), 131.7 (d, J = 12.1 Hz), 124.7 (d, J = 4.7 Hz), 123.9 (d, J = 2.9 Hz), 119.4 (d, J = 10.4 Hz), 112.9 (d, J = 21.9 Hz), 43.2, 28.7 (d, J = 3.1 Hz), 17.1, 8.3 (2C) , 1.3, 1.1; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.34; **^{19}F NMR** (564 MHz, $CDCl_3$) δ -136.9 (d, J = 10.8 Hz); **IR** (cm^{-1}) 2952, 2874, 2095, 1500, 1415, 1308, 1281, 1236, 992, 888, 843, 710; **HRMS** (EI): Calculated for $C_{13}H_{19}ClFNSi$ $[M]^+$: 271.0959, Found: 271.0959.

6-Bromo-3-(diethylsilyl)-5,7-difluoro-1,2,3,4-tetrahydroquinoline (Table 1, 27b)



Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.06 (dd, J = 9.5, 1.1 Hz, 1H), 4.16 (s, br, 1H), 3.62 (q, J = 3.1 Hz, 1H), 3.36 (ddd, J = 11.7, 3.5, 1.9 Hz, 1H), 3.16 (t, J = 11.5 Hz, 1H), 2.86 (ddt, J = 16.5, 2.9, 1.4 Hz, 1H), 2.55 – 2.41 (m, 1H), 1.30 (ddd, J = 11.4, 7.6, 4.1 Hz, 1H), 1.02 (td, J = 7.9, 1.3 Hz, 6H), 0.85 – 0.57 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.6 (dd, J = 130.4, 6.9 Hz), 157.0 (dd, J = 130.1, 7.1 Hz), 145.2 (dd, J = 12.6, 10.5 Hz), 105.7 (dd, J = 22.5, 2.9 Hz), 96.8 (dd, J = 25.8, 2.3 Hz), 82.5 (t, J = 25.3 Hz), 43.4, 21.8 (d, J = 3.0 Hz), 16.2, 8.3 (2C), 1.3, 1.1; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.38; **^{19}F NMR** (564 MHz, $CDCl_3$) δ -111.4 , -111.5; **IR** (cm^{-1}) 2953, 1874, 2098, 1621, 1588, 1492, 1459, 1412, 1347, 1301, 1279, 1262, 1233, 1197, 1080, 1016, 806; **HRMS** (EI): Calculated for $C_{13}H_{18}BrF_2NSi$ $[M]^+$: 333.0360, Found: 333.0361.

IV. $B(C_6F_5)_3$-Catalyzed Silylative Reduction of Other *N*-Heterocycles (Table 1)



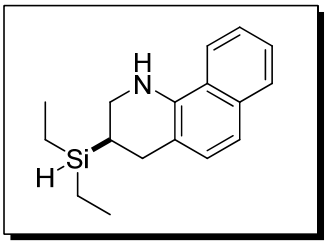
28a–34a **28b–34b**

In a 2.5 mL reaction vial, $B(C_6F_5)_3$ (0.005 to 0.025 mmol, 1.0 to 5.0 mol%) was dissolved in chloroform (0.5 mL), to which diethylsilane (2.0 to 4.0 mmol, 4.0 to 8.0 equiv.) was added. After shaking briefly, *N*-heteroaromatics (0.50 mmol, 1.0 equiv.) was subsequently added to the above catalyst solution. The reaction mixture was stirred at 65 to 100 °C for 6 to 24 h, then allowed to cool down to room temperature and filtered through a pad of silica gel with dichloromethane (15 mL). The filtrate was concentrated under reduced pressure.

For the silylative reduction of **28a**, **29a**, and **30a**, the resulting residue was subjected to purification by column chromatography on silica gel (EA/Hx = 5/95) to afford **28b**, **29b**, and **30b**, respectively. In the case of the reduction of **31a–34a**, the crude mixture was subjected to *N*-sulfonylation using 8-quinolinesulfonyl chloride (QUS-Cl) due to high polarity of the desired silylated products (*vide infra*).

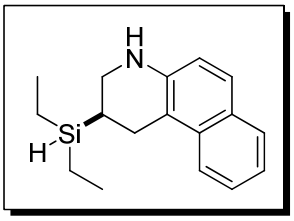
***N*-Sulfonylation: To a crude catalytic reaction mixture in dichloromethane (2 mL) was added 8-quinolinesulfonyl chloride (QUS-Cl, 0.75 mmol, 1.5 equiv.) in the presence of triethylamine (1.5 mmol, 3.0 equiv.) at 0 °C. After stirring for 12 h at room temperature, all volatiles from the reaction mixture were evaporated under reduced pressure, and the crude mixture was subjected to purification by column chromatography on silica gel (EA/Hx = 3/7) to give **31b–34b**. X-ray quality crystals of **31b** were grown by slow evaporation from CH_2Cl_2 and MeOH.

3-(Diethylsilyl)-1,2,3,4-tetrahydrobenzo[*h*]quinoline (Table 1, 28b)



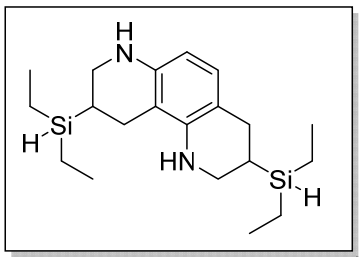
Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 1H), 7.70 (dd, J = 8.1, 1.7 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.19 (d, J = 8.2 Hz, 1H), 7.13 (d, J = 8.3 Hz, 1H), 4.44 (br, 1H), 3.71 (d, J = 3.1 Hz, 1H), 3.66 – 3.58 (m, 1H), 3.37 (t, J = 11.6 Hz, 1H), 3.01 – 2.85 (m, 2H), 1.64 – 1.43 (m, 1H), 1.08 (t, J = 7.9 Hz, 6H), 0.83 – 0.65 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 138.8, 133.0, 128.5, 128.2, 124.8, 124.6, 123.3, 119.3, 116.8, 116.2, 44.5, 29.6, 17.6, 8.4 (2C), 1.4, 1.2; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.34; **IR** (cm^{-1}): 3419, 3050, 2871, 2090, 1574, 1518, 1398, 1266,1233, 1009, 789; **HRMS** (EI): Calculated for $C_{17}H_{23}NSi$ $[M]^+$: 269.1600, Found: 269.1600.

2-(Diethylsilyl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline (Table 1, 29b)



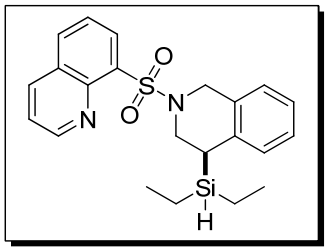
Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, J = 8.3 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.6 Hz, 1H), 7.54 (td, J = 6.6, 3.3 Hz, 1H), 7.33 (dd, J = 8.0, 6.6 Hz, 1H), 6.80 (d, J = 8.7 Hz, 1H), 4.08-3.76 (br, 1H), 3.84 (d, J = 3.1 Hz, 1H), 3.45 (ddd, J = 11.4, 3.4, 1.8 Hz, 1H), 3.30 (t, J = 11.4 Hz, 2H), 2.98 (dd, J = 16.3, 11.7 Hz, 1H), 1.66 (dt, J = 5.6, 3.1 Hz, 1H), 1.18 (dd, J = 7.9, 3.8 Hz, 6H), 0.89 – 0.77 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 141.8, 133.2, 128.3, 127.6, 126.9, 126.1, 121.4, 120.9, 118.3, 111.8, 43.5, 24.7, 17.4, 8.4 (2C), 1.4, 1.2; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.83; **IR** (cm^{-1}): 3399, 2951, 2872, 2092, 1621, 1518, 1259, 1242, 1013, 805, 741; **HRMS** (EI): Calculated for $C_{17}H_{23}NSi$ $[M]^+$: 269.1600, Found: 269.1602.

3,9-Bis(diethylsilyl)-1,2,3,4,7,8,9,10-octahydro-1,7-phenanthroline (Table 1, 30b)



Red oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.68 (d, J = 8.0 Hz, 1H), 5.97 (d, J = 8.0 Hz, 1H), 3.69 (dd, J = 16.1, 3.1 Hz, 2H), 3.63 (br, 2H), 3.51 (ddd, J = 11.8, 3.4, 1.7 Hz, 1H), 3.32 (ddd, J = 11.0, 3.1, 1.5 Hz, 1H), 3.27 (t, J = 11.6 Hz, 1H), 3.15 (t, J = 11.3 Hz, 1H), 2.80 – 2.68 (m, 2H), 2.48 (ddd, J = 16.0, 5.9, 1.6 Hz, 1H), 2.34 (dd, J = 15.9, 11.5 Hz, 1H), 1.56 (dddd, J = 11.4, 8.5, 5.8, 2.9 Hz, 1H), 1.46 (dtd, J = 11.2, 5.7, 3.0 Hz, 1H), 1.16 – 1.01 (m, 12H), 0.73 (ddd, J = 9.1, 4.7, 1.8 Hz, 8H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.5, 141.9, 126.8, 111.2, 106.0, 104.4, 44.4, 43.3, 29.0, 23.3, 18.1, 17.9, 8.36, 8.33, 8.31 (2C), 1.4, 1.3, 1.19, 1.16; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.70, 0.33; **IR** (cm^{-1}) 2952, 2873, 2825, 2093, 1609, 1488, 1336, 1240, 1123, 1012, 808; **HRMS** (EI): Calculated for $C_{20}H_{36}N_2Si_2$ $[M]^+$: 360.2417, Found: 360.2415.

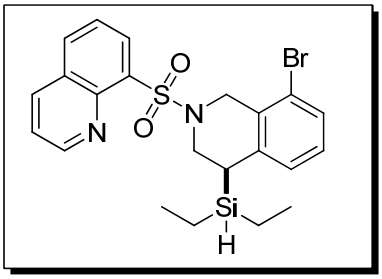
8-{4-(Diethylsilyl)-3,4-dihydroisoquinolin-2(1*H*)-ylsulfonyl}quinoline (Table 1, 31b)



White solid; m.p. 85–87 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.04 (dd, J = 4.2, 1.8 Hz, 1H), 8.58 (dd, J = 7.4, 1.4 Hz, 1H), 8.23 (dd, J = 8.4, 1.9 Hz, 1H), 8.05 (dd, J = 8.1, 1.4 Hz, 1H), 7.66 (t, J = 7.8 Hz, 1H), 7.49 (dd, J = 8.3, 4.2 Hz, 1H), 7.18 – 6.86 (m, 4H), 4.78 (d, J = 15.4 Hz, 1H), 4.40 (d, J = 15.4 Hz, 1H), 4.29 (dd, J = 12.5, 3.1 Hz, 1H), 3.83 (d, J = 3.1 Hz, 1H), 3.51 (dd, J = 12.5, 4.1 Hz, 1H), 2.61 (d, J = 3.2 Hz, 1H), 0.98 (t, J = 7.8 Hz, 3H), 0.91 (t, J = 7.8 Hz, 3H), 0.77 (td, J = 7.5, 4.0 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.1, 144.2, 136.7, 136.3, 136.3, 133.5, 133.4, 131.2, 128.8, 127.7, 126.3, 126.2, 125.4, 124.8, 121.9, 47.3, 46.3, 27.9, 8.3, 8.1, 1.89, 1.82; **^{29}Si NMR** (120 MHz, $CDCl_3$): δ 2.61; **IR** (cm^{-1}): 2951, 2872, 2097, 1610, 1560, 1371,

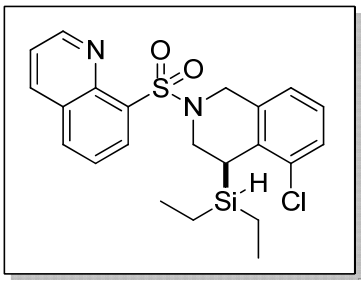
1330, 1284, 1237, 1211, 1162, 1143, 1052, 868, 790; **HRMS** (FAB): Calculated for $C_{22}H_{27}N_2O_2SSi$ $[M+H]^+$: 411.1563, Found: 411.1560.

8-{8-Bromo-4-(diethylsilyl)-3,4-dihydroisoquinolin-2(1*H*)-ylsulfonyl}quinoline (Table 1, 32b)



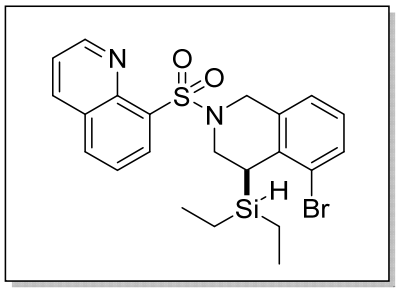
White solid; m.p. 99–101 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.00 (dd, J = 4.1, 2.0 Hz, 1H), 8.64 – 8.46 (m, 1H), 8.19 (dd, J = 8.4, 1.9 Hz, 1H), 8.08 – 7.90 (m, 1H), 7.61 (td, J = 7.9, 3.0 Hz, 1H), 7.50 – 7.37 (m, 1H), 7.24 (d, J = 7.7 Hz, 1H), 7.02 – 6.77 (m, 2H), 4.73 (d, J = 16.4 Hz, 1H), 4.41 – 4.20 (m, 2H), 3.80 (q, J = 3.2 Hz, 1H), 3.42 (dd, J = 12.6, 3.9 Hz, 1H), 2.56 (t, J = 3.4 Hz, 1H), 0.94 (dd, J = 8.8, 7.1 Hz, 3H), 0.87 (t, J = 7.9 Hz, 3H), 0.80 - 0.60 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.0, 144.1, 139.7, 136.3 (2C), 133.53, 133.47, 130.5, 128.8, 128.9, 127.3, 126.9, 125.4, 122.5, 121.9, 48.5, 45.9, 28.4, 8.3, 8.1, 1.8, 1.7; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 3.12; **IR** (cm^{-1}): 2952, 2871, 2101, 1559, 1457, 1274, 1238, 1211, 1160, 953, 875, 787; **HRMS** (FAB): Calculated for $C_{22}H_{26}BrN_2O_2SSi$ $[M+H]^+$: 489.0668, Found: 489.0666.

8-[{5-Chloro-4-(diethylsilyl)-3,4-dihydroisoquinolin-2(1*H*)-yl}sulfonyl]quinoline (Table 1, 33b)



White solid; m.p. 129–131 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.02 (dd, J = 4.2, 1.8 Hz, 1H), 8.56 (dd, J = 7.4, 1.4 Hz, 1H), 8.21 (dd, J = 8.3, 1.8 Hz, 1H), 8.03 (dd, J = 8.2, 1.4 Hz, 1H), 7.65 (dd, J = 8.2, 7.4 Hz, 1H), 7.48 (dd, J = 8.3, 4.2 Hz, 1H), 7.21 – 7.11 (m, 1H), 6.97 (t, J = 7.8 Hz, 1H), 6.94 – 6.85 (m, 1H), 4.82 (d, J = 15.6 Hz, 1H), 4.48 – 4.33 (m, 2H), 3.81 (d, J = 3.3 Hz, 1H), 3.31 (dd, J = 12.1, 3.5 Hz, 1H), 3.04 – 2.95 (m, 1H), 0.94 (t, J = 7.8 Hz, 3H), 0.87 (t, J = 7.9 Hz, 3H), 0.81 (ddd, J = 7.9, 7.0, 4.0 Hz, 1H), 0.76 – 0.68 (m, 1H), 0.65 (ddt, J = 14.9, 8.1, 3.7 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.2, 144.3, 136.4, 136.3, 136.2, 133.9, 133.54, 133.52, 132.4, 129.0, 127.4, 125.6, 125.5, 125.0, 122.0, 47.0, 46.6, 26.5, 8.4, 8.2, 2.9, 2.3; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 1.30; **IR** (cm^{-1}) 2952, 2872, 2117, 1332, 1256, 1238, 1212, 1163, 833, 790, 586; **HRMS** (EI): Calculated for $C_{22}H_{25}ClN_2O_2SSi$ $[M]^+$: 444.1095, Found: 444.1092.

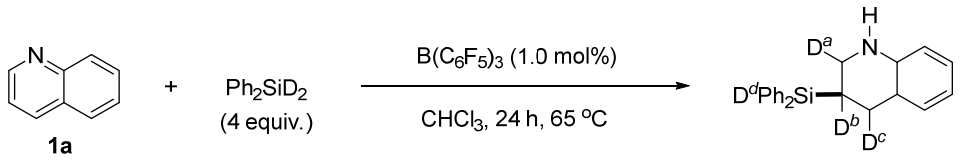
8-[{5-Bromo-4-(diethylsilyl)-3,4-dihydroisoquinolin-2(1*H*)-yl}sulfonyl]quinoline (Table 1, 34b)



Semisolid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.01 (dd, J = 4.2, 1.8 Hz, 1H), 8.55 (dd, J = 7.3, 1.5 Hz, 1H), 8.20 (dd, J = 8.4, 1.8 Hz, 1H), 8.02 (dd, J = 8.3, 1.5 Hz, 1H), 7.64 (t, J = 7.8 Hz, 1H), 7.47 (dd, J = 8.3, 4.2 Hz, 1H), 7.33 (dd, J = 7.8, 1.3 Hz, 1H), 6.94 (dd, J = 7.8, 1.4 Hz, 1H), 6.88 (t, J = 7.8 Hz, 1H), 4.81 (d, J = 15.6 Hz, 1H), 4.42 (d, J = 15.6 Hz, 1H), 4.37 (dd, J = 12.0, 2.0 Hz, 1H), 3.84 (d, J = 3.3 Hz, 1H), 3.31 (dd, J = 12.0, 3.5 Hz, 1H), 2.99 (d, J = 2.7 Hz, 1H), 0.93 (t, J = 7.8 Hz, 3H), 0.88 (t, J = 7.9 Hz, 3H), 0.86 – 0.60 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.1, 144.2, 137.8, 136.4, 136.2, 133.8, 133.7, 133.5, 130.8, 128.9, 126.0, 125.7, 125.5, 123.4, 122.0, 47.0, 46.6, 29.1, 8.4, 8.2, 2.9, 2.3; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 1.07; **IR** (cm^{-1}) 2871, 2118, 1561, 1493, 1437, 1332, 1239, 1221, 1191, 1162, 1147, 1070, 1052, 832, 789, 586; **HRMS** (EI): Calculated for $C_{22}H_{25}ClN_2O_2SSi$ $[M]^+$: 488.0589, Found: 488.0588.

V. Preliminary Mechanistic Studies (Scheme 2)

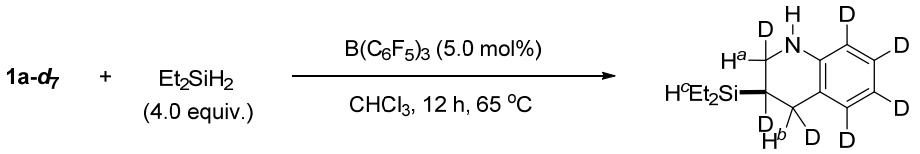
D-Labeling Study Using Diphenylsilane-d_2 or Quinoline-d_7 (Scheme 2A)



1b-d_3 (89% yield)

(D^a:D^b:D^c:D^d = 1.0:0:1.0:0.8)

In a 2.5 mL reaction vial, $B(C_6F_5)_3$ (0.0050 mmol, 1.0 mol%) was dissolved in chloroform (0.50 mL), to which diphenylsilane-d_2 (2.0 mmol, 4.0 equiv.) was added. After shaking briefly, quinoline (0.50 mmol, 1.0 equiv.) was subsequently added to the above catalyst solution. The reaction mixture was stirred at 65 °C for 24 h, then allowed to cool down to room temperature and filtered through a pad of silica gel with dichloromethane (15 mL) and methanol (2 mL). The filtrate was concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (EA/Hx = 5/95) to give **1b-d_3** as colorless oil (142 mg, 89%). The relative ratio of deuterium incorporated in product **1b-d_3** was determined by a ^{2}H NMR analysis.

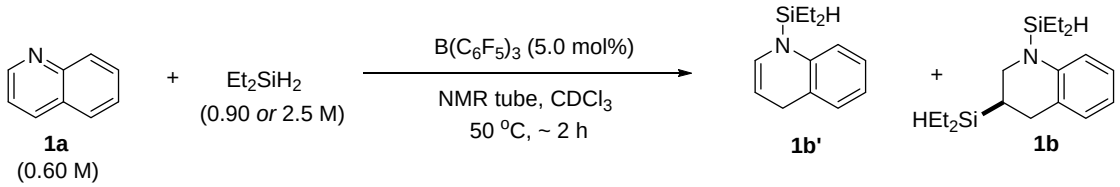


1b-d_7 (91% yield)

(H^a:H^b:H^c = 0.8:1.0:0.9)

In a 2.5 mL reaction vial, $B(C_6F_5)_3$ (0.025 mmol, 5.0 mol%) was dissolved in chloroform (0.50 mL), to which diethylsilane (2.0 mmol, 4.0 equiv.) was added. After shaking briefly, quinoline-d_7 (0.50 mmol, 1.0 equiv.) was subsequently added to the above catalyst solution. The reaction mixture was stirred at 65 °C for 12 h, then allowed to cool down to room temperature and filtered through a pad of silica gel with dichloromethane (15 mL) and methanol (2 mL). The filtrate was concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (EA/Hx = 5/95) to give **1b-d_7** as colorless oil (103.0 mg, 91%). The relative ratio of proton incorporated in product **1b-d_7** was determined by a ^{1}H NMR analysis.

Kinetic Study with Two Different Initial Concentrations of Et_2SiH_2 (0.9 or 2.5 M) (Scheme 2B)



Diethylsilane (0.75 mmol, 0.90 M, 1.5 equiv; 2.2 mmol, 2.5 M, 4.3 equiv.) was added to a solution of $B(C_6F_5)_3$ (0.025 mmol, 5.0 mol%) and TCE (0.074 mmol, 0.20 equiv.) as an internal standard in chloroform-*d* in a J. Young NMR tube, and the solution was well shaken. The NMR tube was placed in a bath of -10 °C to cool down the solution, and then quinoline **1a** (0.50 mmol, 0.60 M, 1 equiv.) was gently added at -10 °C on the top of the solution to bring the total volume of the reaction mixture to 0.85 mL. After briefly shaking, the NMR tube was quickly placed in the NMR probe warmed to 50 °C, where the silylative reduction of **1a** leading to **1b** was monitored with respect to time by ^{1}H NMR. The initial rates (v_i) of a conversion of **1a** to **1b'** was obtained from the linear portion of the concentration (**1b'**) versus time curve in the early stage of the reaction.[S5]

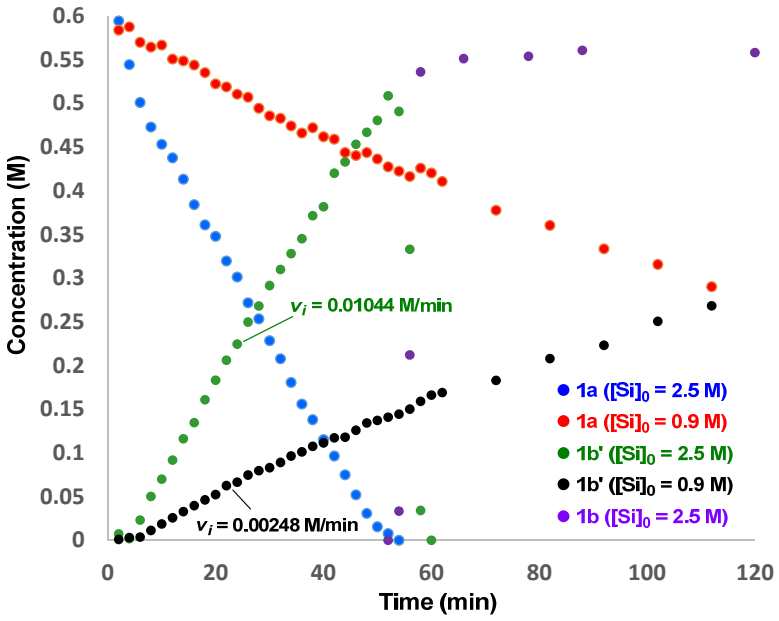
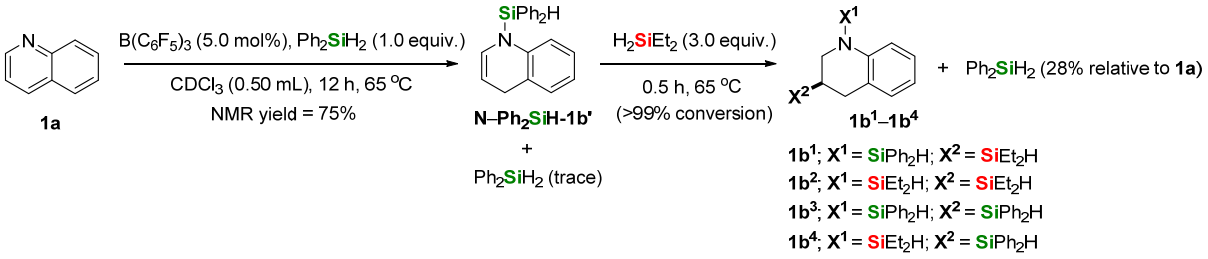
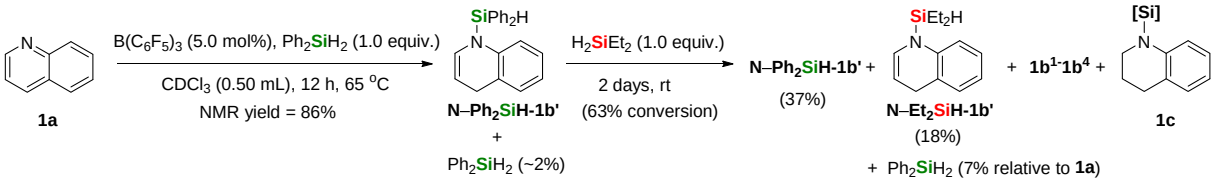


Figure. S1. Concentration versus time curve for the silylative reduction of **1a** with two different initial concentrations of Et_2SiH_2 catalyzed by $B(C_6F_5)_3$ at 50 °C in $CDCl_3$.

Silane Scrambling Experiment



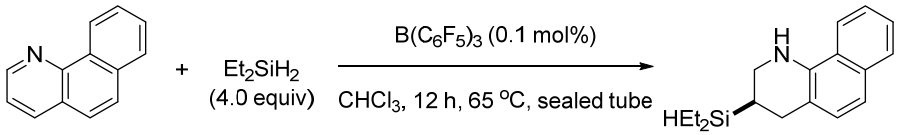
Diphenylsilane (0.50 mmol, 1.0 eqiuv.) was added to a solution of $B(C_6F_5)_3$ (0.025 mmol, 5.0 mol%) and TCE or toluene (0.10 mmol, 0.20 equiv.) as an internal standard in chloroform-*d* (0.50 mL) in a J. Young NMR tube. After shaking briefly, quinoline, **1a** (0.50 mmol, 1.0 equiv.) was subsequently added to the above catalyst solution. The reaction mixture was then heated at 65 °C for 12 h to allow for the formation of **N–Ph$_2$SiH-1b'** in 75% NMR yield, to which diethylsilane (1.5 mmol, 3.0 equiv.) was subsequently added, followed by heating at 65 °C for 0.5 h. It gave rise to a quantitative conversion of **N–Ph$_2$SiH-1b'** to a mixture of silane scrambling products, **1b^1–1b^4**. The characteristic signals of **1b^1–1b^4** were confirmed by NMR spectroscopy.



Diphenylsilane (0.50 mmol, 1.0 equiv.) was added to a solution of $B(C_6F_5)_3$ (0.025 mmol, 5.0 mol%) and toluene (0.10 mmol, 0.20 equiv.) as an internal standard in chloroform-*d* (0.50 mL) in a J. Young NMR tube. After shaking briefly, quinoline, **1a** (0.50 mmol, 1.0 equiv.) was subsequently added to the above catalyst solution. The reaction mixture was then heated at 65 °C for 12 h to allow for the formation of **N–Ph$_2$SiH-1b'** in 86% NMR yield, to which diethylsilane (0.50 mmol, 1.0 equiv.) was subsequently added, followed by standing at room temperature for 2 days. After 2 days, the resulting crude mixture was subjected to NMR analysis, confirming that **N–Ph$_2$SiH-1b'** is convertible to **N–Et$_2$SiH-1b'** with Et_2SiH_2 during the silylative reduction.

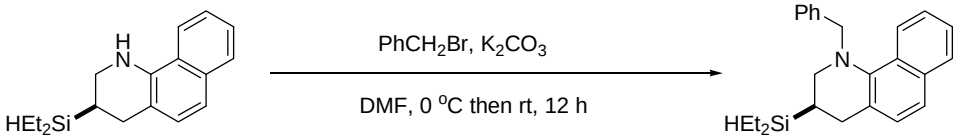
VI. Synthetic Applications (Scheme 3)

Gram-Scale Silylative Reduction and Transformations (Scheme 3A)



28a (1.4 g) **28b** (2.0 g, 95%)

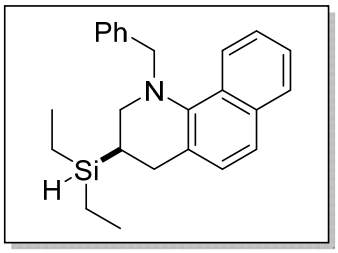
In a 15 ml sealed tube, $B(C_6F_5)_3$ (0.0080 mmol, 0.10 mol%) was dissolved in chloroform (3.0 mL), to which diethylsilane (32 mmol, 4.0 equiv.) was added. After shaking briefly, a solution of **28a** (8.0 mmol, 1.0 equiv.) in chloroform (5.0 mL) was transferred to the above solution. The reaction mixture was stirred at 65 °C for 12 h, then allowed to cool down to room temperature and filtered through a pad of silica gel with dichloromethane (50 mL) and methanol (5 mL). The filtrate was concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (EA/Hx = 5/95) to give **28b** as colorless oil (2.0 g, 95%). This procedure is applied to gram-scale silylative reductions of substrates **1a** and **10a** (with 4.0 equiv. of Et_2SiH_2), and **8a** and **9a** (with 8.0 equiv. of Et_2SiH_2) as shown in Scheme 3A.



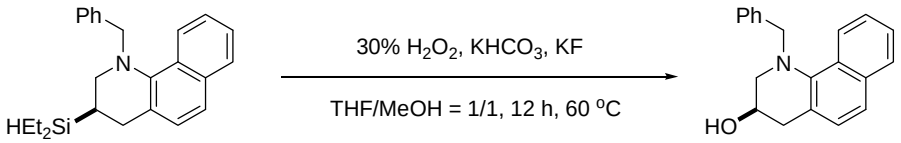
28b (2.0 g) **35** (2.5 g, 95%)

To a stirred solution of **28b** (7.4 mmol, 1.0 equiv.) in *N*,*N*-dimethylformamide (21 mL) was added potassium carbonate (22 mmol, 3.0 equiv.) and then benzyl bromide (8.9 mmol, 1.2 equiv.) dropwisely over 10 min at 0 °C. The reaction mixture was then stirred at room temperature for 12 h, and quenched with water (20 mL). The aqueous layer was extracted with diethyl ether (20 mL x 2). The combined organic layer was washed with saturated ammonium chloride solution (40 mL), dried over anhydrous $MgSO_4$, and then filtered. The resulting filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (EA/Hx = 1/10) to give **35** (2.5 g, 95%).

1-Benzyl-3-(diethylsilyl)-1,2,3,4-tetrahydrobenzo[*h*]quinoline (Scheme 3A, 35)



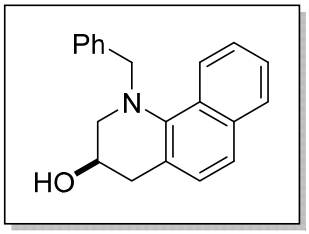
Brown oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.34 – 8.29 (m, 1H), 7.90 – 7.85 (m, 1H), 7.76 – 7.71 (m, 2H), 7.58 – 7.51 (m, 3H), 7.51 – 7.43 (m, 3H), 7.27 (d, J = 8.4 Hz, 1H), 4.68 (d, J = 16.1 Hz, 1H), 4.18 (d, J = 16.0 Hz, 1H), 3.77 (q, J = 3.1 Hz, 1H), 3.38 (ddd, J = 13.7, 2.7, 1.5 Hz, 1H), 3.14 (ddd, J = 13.8, 12.5, 1.5 Hz, 1H), 3.07 – 2.99 (m, 2H), 1.80 (dt, J = 5.6, 2.7 Hz, 1H), 1.13 (dt, J = 19.4, 7.9 Hz, 6H), 0.79 (dd, J = 7.9, 3.2 Hz, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.1, 139.5, 133.4, 128.9, 128.6 (2C), 128.3, 127.8, 127.4 (2C), 127.0, 125.7, 125.2, 124.9, 122.8, 122.0, 58.9, 49.0, 30.1, 11.2, 8.4, 8.3, 1.2, 1.1; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 0.16; **IR** (cm^{-1}): 3047, 2950, 2871, 2090, 1601, 1569, 1451, 1395, 1359, 1028, 801; **HRMS** (EI): Calculated for $C_{24}H_{29}NSi$ $[M]^+$: 359.2069, Found: 359.2067.



35 (2.5 g, 7.0 mmol) **36** (1.8 g, 91%)

A mixture of **35** (7.0 mmol, 1.0 equiv.), potassium fluoride (42 mmol, 6.0 equiv.), potassium bicarbontate (42 mmol, 6.0 equiv.), and 30% hydrogen peroxide in water (130 mmol, 18 equiv.) in tetrahydrofuran (59 mL) and methanol (59 mL) was stirred at 60 °C for 12 h. The reaction mixture was quenched with 10 % sodium bisulfite solution in water (20 mL) at 0 °C and the aqueous layer was extracted with diethyl ether (60 mL x 3). The combined organic layer was washed with saturated sodium carbonate solution in water (60 mL x 2) and dried over anhydrous $MgSO_4$ and then filtered. The resulting filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (EA/Hx = 1/1) to give **36** (1.8 g, 91%).[S4]

1-Benzyl-1,2,3,4-tetrahydrobenzo[*h*]quinolin-3-ol (Scheme 3A, 36)

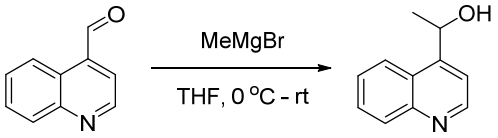


Colorless solid; m.p. 62–64 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.14 – 8.04 (m, 1H), 7.81 (d, J = 7.7 Hz, 1H), 7.60 (d, J = 7.6 Hz, 2H), 7.53 – 7.44 (m, 3H), 7.38 (d, J = 8.0 Hz, 3H), 7.18 (d, J = 8.4 Hz, 1H), 4.69 (d, J = 16.3 Hz, 1H), 4.36 – 4.27 (m, 1H), 4.24 (d, J = 16.3 Hz, 1H), 3.42 – 3.22 (m, 2H), 2.99 (dd, J = 13.1, 9.8 Hz, 1H), 2.92 – 2.76 (m, 1H), 1.93 – 1.58 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 142.7, 139.2, 133.7, 128.7 (2C), 128.4, 128.0, 127.8, 127.2 (2C), 127.1, 125.4, 125.2, 123.1, 122.6, 122.5, 61.1, 60.0, 53.3, 37.6; **IR** (cm^{-1}): 3337, 3050, 2922, 2836, 1569, 1463,

1452, 1397, 1052, 804, 733; **HRMS** (EI): Calculated for $C_{20}H_{19}NO$ $[M]^+$: 289.1467, Found: 289.1464.

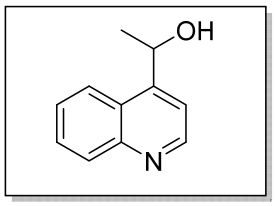
Asymmetric Silylative Reduction of (*S*)-37a and Determination of Absolute Stereochemistry in 39 (Scheme 3B)

Preparation of Chiral Starting Materials and Asymmetric Silylative Reduction

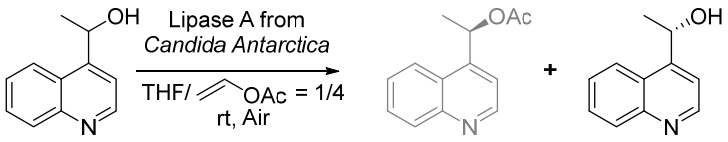


To a stirred solution of 4-quinolinecarboxaldehyde (12 mmol, 1.0 equiv.) in tetrahydrofuran (60 mL) at 0 °C was added 3.0 M methylmagnesium bromide solution in diethyl ether (13 mmol, 1.1 equiv.) dropwisely at that temperature. The resulting mixture was stirred for 12 h at room temperature and quenched with saturated ammonium chloride solution in water (20 mL). The reaction mixture was diluted with water (40 mL) and ethyl acetate (30 mL). The resulting aqueous layer was extracted with ethyl acetate (60 mL x 2). The combined organic layer was dried over anhydrous $MgSO_4$ and then, filtered. The resulting filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (EA/Hx = 1/1) to give the corresponding alcohol (1.8 g, 87%).

1-(Quinolin-4-yl)ethan-1-ol



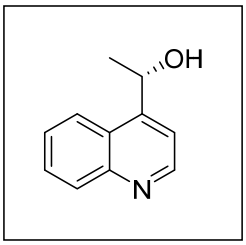
White solid; m.p. 119–121 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.05 (d, J = 8.5 Hz, 1H), 7.98 (d, J = 8.5 Hz, 1H), 7.64 (t, J = 7.9 Hz, 1H), 7.55 (s, 1H), 7.50 (t, J = 7.8 Hz, 1H), 5.63 (d, J = 7.8 Hz, 1H), 1.62 (d, J = 6.5 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.9, 150.2, 147.8, 129.9, 129.0, 126.5, 125.3, 123.0, 116.7, 65.8, 24.6; **IR** (cm^{-1}) 3349, 2976, 2928, 1666, 1592, 1510, 1239, 1168, 1121, 1073, 1017, 856, 763; **HRMS** (EI): Calculated for $C_{11}H_{11}NO$ $[M]^+$: 173.0841, Found: 173.0841.



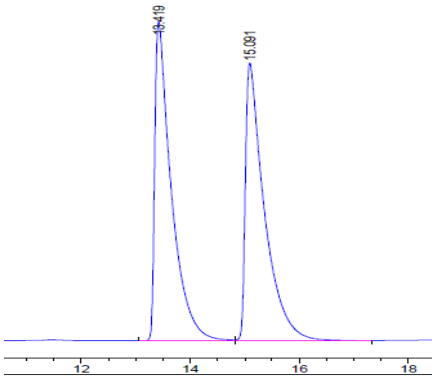
To a stirred solution of racemic alcohol as starting materials (10 mmol, 1.0 equiv.) in tetrahydrofuran (10 mL) and vinyl acetate (40 mL) was added Lipase A from *Candida Antarctica*, CLEA (≥1U / mg, Sigma, 560 mg) at room temperature. And, the resulting mixture was stirred for 8 h in open flask

condition and filtered. The filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (EA/Hx = 1/1) to give the corresponding chiral alcohol (560 mg, 31%, *ee* = 98% based on HPLC).[S6]

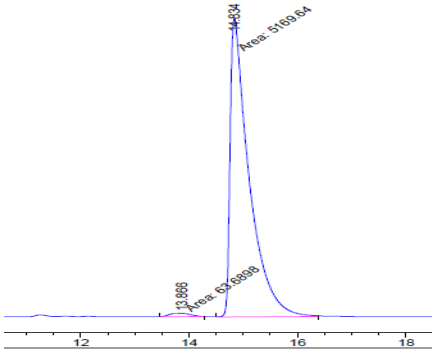
(*S*)-1-(Quinolin-4-yl)ethan-1-ol



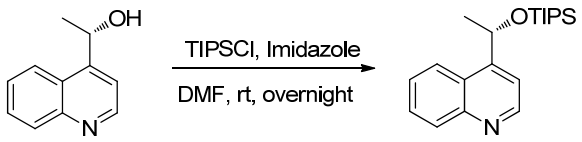
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.58 (d, J = 4.6 Hz, 1H), 7.96 (dd, J = 8.4, 1.3 Hz, 1H), 7.91 (dd, J = 8.6, 1.4 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.46 – 7.38 (m, 1H), 5.58 (q, J = 6.5 Hz, 1H), 1.58 (d, J = 6.6 Hz, 3H); *ee* determination condition : Chiralcel IF, Hexane:EtOH = 90:10, Flow = 1.0 ml/min; $[\alpha]_D^{25}$ - 87.2 (c = 1.19, $CHCl_3$).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.419	BV	0.2951	2822.38599	134.33594	50.0565
2	15.091	VB	0.3387	2816.01123	116.63793	49.9435



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.866	MM	0.4356	63.68975	2.43694	1.2170
2	14.834	MM	0.4041	5169.64063	213.22462	98.7830

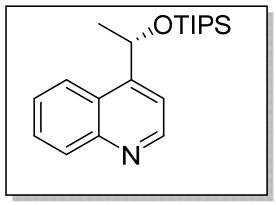


(*S*)-37a
(>98% *ee*)

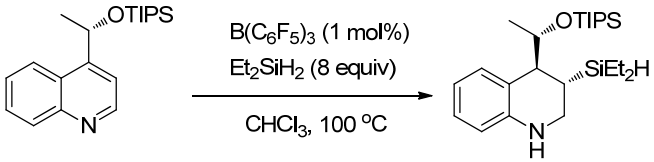
To a solution of alcohol as starting materials (2.3 mmol, 1.0 equiv.) in *N*,*N*-dimethylformamide (6.0 mL) were added imidazole (5.8 mmol, 2.5 equiv.) and triisopropylsilyl chloride (3.5 mmol, 1.5 equiv.) at

room temperature. The resulting mixture was stirred overnight at room temperature, quenched with water (6 mL), and the resulting aqueous layer was extracted with diethyl ether (10 mL x 3). The combined organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EA/Hx = 1/10) to give the corresponding silyl ether [**(S)-37a** (>98% *ee*), 586 mg, 77%].

(*S*)-4-[1-{(Triisopropylsilyl)oxy}ethyl]quinoline (Scheme 3B, (*S*)-37a)



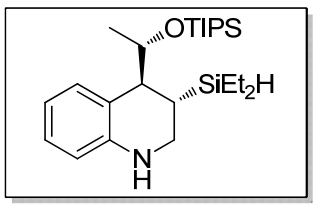
Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.91 (d, J = 4.3 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.76 – 7.60 (m, 2H), 7.53 (t, J = 7.7 Hz, 1H), 5.68 (d, J = 6.3 Hz, 1H), 1.58 (d, J = 6.1 Hz, 3H), 1.14 (d, J = 7.7 Hz, 3H), 1.06 (dd, J = 7.3, 3.2 Hz, 9H), 1.05 – 0.95 (m, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 152.5, 150.5, 148.2, 130.3, 128.8, 126.2, 125.0, 122.9, 117.3, 67.3, 26.7, 18.0 (6C), 12.2 (3C); **IR** (cm-1) 2942, 2865, 1592, 1509, 1462, 1369, 1297, 1239, 1208, 1168, 1121, 1091, 1038, 947, 881, 845, 758, 724, 678, 559, 451; **HRMS** (FAB): Calculated for $C_{20}H_{32}NOSi$ $[M+H]^+$: 330.2253, Found: 330.2251.



(*S*)-37a **37b**

To a solution of $B(C_6F_5)_3$ (0.0055 mmol, 1.0 mol%) in a 2.5 mL reaction vial in chloroform (0.25 mL) was added diethylsilane (4.4 mmol, 8.0 equiv.) and shaken briefly. The quinoline, **(*S*)-37a** (0.55 mmol, 1.0 equiv.) in chloroform (0.30 mL) was transferred to the above solution and heated at 100 °C for 12 h. The reaction mixture was poured on a silica pad filter and washed with dichloromethane (15 mL) and methanol (2 mL). The resulting filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (EA/Hx = 1/20) to give the corresponding reduction product (**37b**, 159 mg, 69%).

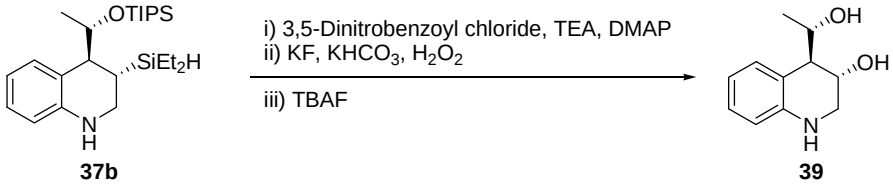
(3*S*,4*S*)-3-(Diethylsilyl)-4-[(*S*)-1-{(triisopropylsilyl)oxy}ethyl]-1,2,3,4-tetrahydroquinoline (Scheme 3B, 37b)



Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.09 (dd, J = 7.6, 1.5 Hz, 1H), 7.03 – 6.90 (m, 1H), 6.58 (td, J = 7.4, 1.2 Hz, 1H), 6.43 (dd, J = 8.0, 1.2 Hz, 1H), 4.14 (t, J = 6.2 Hz, 1H), 3.86 (s, br, 1H), 3.66 (dd, J = 11.3, 4.5 Hz,

1H), 3.48 (q, J = 3.1 Hz, 1H), 3.22 (dd, J = 11.4, 3.0 Hz, 1H), 2.67 (dd, J = 6.4, 2.3 Hz, 1H), 1.85 (dd, J = 4.6, 2.6 Hz, 1H), 1.22 (d, J = 6.1 Hz, 3H), 1.04 (d, J = 5.8 Hz, 21H), 0.99 – 0.89 (m, 6H), 0.66 – 0.46 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.3, 131.3, 127.1, 121.2, 116.3, 113.9, 72.4, 46.0, 40.3, 22.0, 18.24 (3C), 18.22 (3C), 17.3, 12.9 (3C), 8.42, 8.38, 1.8, 1.7; **^{29}Si NMR** (120 MHz, $CDCl_3$) δ 10.07, 1.44; **IR** (cm^{-1}) 2943, 2866, 2089, 1607, 1501, 1462, 1371, 1351, 1315, 1274, 1258, 1236, 1121, 1058, 1002, 920, 882, 806, 744, 673, 495; **HRMS** (EI): Calculated for $C_{24}H_{45}NOSi_2$ $[M]^+$: 419.3040, Found: 419.3036; $[\alpha]_D^{25}$ – 18.9 (c = 1.0, $CHCl_3$).

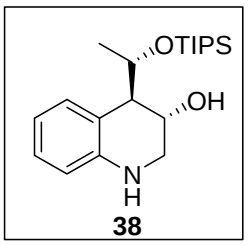
Determination of Absolute Stereochemistry in 39



37b **39**

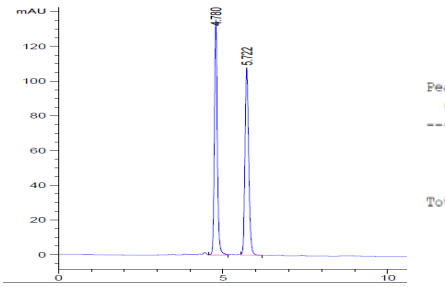
To a solution of **37b** (0.35 mmol, 1.0 equiv.) in dichloromethane (3.0 mL) were added triethylamine (0.88 mmol, 2.5 equiv.), 3,5-dinitrobenzoyl chloride (0.53 mmol, 1.5 equiv.), and 4-(dimethylamino)-pyridine (0.18 mmol, 0.50 equiv.) at room temperature. The resulting mixture was stirred for 2 h at room temperature and quenched with saturated sodium bicarbonate solution in water (4 mL). The aqueous layer was extracted with ethyl acetate (4 mL x 3). The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. The resulting mixture was then concentrated under reduced pressure and purified by column chromatography on silica gel (EA/Hx = 1/10) to give the corresponding amide product. (*step i*)

To a solution of alkyl silane starting materials (0.29 mmol, 1.0 equiv.) in tetrahydrofuran (1.5 mL) and methanol (1.5 mL) were added potassium fluoride (0.87 mmol, 3.0 equiv.), potassium hydrogen carbonate (0.87 mmol, 3.0 equiv.), and 30% hydrogen peroxide in water (2.6 mmol, 9.0 equiv.) at room temperature. The resulting mixture was stirred to 60 ^oC for 8 h and quenched with saturated sodium sulfite solution in water solution (5 mL). The aqueous layer was extracted with ethyl acetate (5 mL x 3). The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (EA/Hx = 1/1) to give the corresponding secondary alcohol product **38** (98% *ee* based on HPLC) as white solid. (*step ii*)

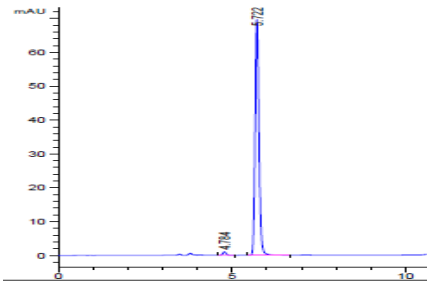


38

ee determination condition : Chiralcel ID, Hexane:IPA = 80:20, Flow = 1.0 ml/min.



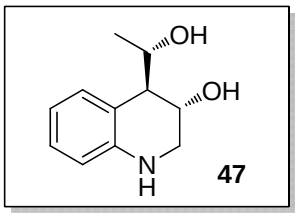
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.780	BV	0.0959	860.79706	135.84378	50.3873
2	5.722	VB	0.1213	847.56421	108.27971	49.6127
Totals :				1708.36127	244.12349	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.784	BB	0.0980	6.56162	1.03462	1.1892
2	5.722	BB	0.1212	545.21564	69.72378	98.8108
Totals :				551.77726	70.75840	

To a solution of **38** as starting materials (0.092 mmol, 1.0 equiv.) in tetrahydrofuran (1.0 mL) was added 1.0 M tetrabutylammonium fluoride solution in tetrahydrofuran (0.14 mmol, 1.5 equiv.) at room temperature. The resulting mixture was then stirred for 16 h at room temperature and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel (EA) to give the corresponding diol product (**39**, 6.2 mg, 35% in 3 steps) (*step iii*). X-ray quality crystals of **39** were grown by slow evaporation from THF and pentane.

(3*S*,4*S*)-4-((*S*)-1-Hydroxyethyl)-1,2,3,4-tetrahydroquinolin-3-ol (Scheme 3B, 39)



47

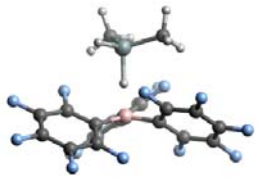
White solid; m.p. 143-145 °C; **^{1}H NMR** (600 MHz, CD_3OD) δ 7.00 (dd, J = 7.6, 1.5 Hz, 1H), 6.98 – 6.90 (m, 1H), 6.57 – 6.46 (m, 2H), 4.35 (d, J = 3.2 Hz, 1H), 3.69 (dd, J = 8.2, 6.3 Hz, 1H), 3.44 (dd, J = 12.6, 2.7 Hz, 1H), 3.26 – 3.18 (m, 1H), 2.65 (ddd, J = 8.3, 3.4, 1.6 Hz, 1H), 1.18 (d, J = 6.3 Hz, 3H); **^{13}C NMR** (100 MHz, CD_3OD) δ 145.9, 133.0, 128.5, 120.0, 117.2, 115.0, 71.3, 64.5, 53.51, 45.5, 22.1; **IR** (cm^{-1}) 3302, 1603, 1580, 1500, 1370, 1319, 1284, 1253, 1225, 1127, 1105, 1056, 1020, 929, 875, 784, 744, 723, 655, 510; **HRMS** (ESI): Calculated for $C_{11}H_{16}NO_2$ $[M+H]^+$: 194.1176, Found: 194.1153.

VII. Computational Studies and Coordinates of Transition State Structures (Scheme 2)

The calculations of energetics for the steps of the conversion of **1b'** to **1b** was carried out by employing the DFT (M11/6-31G**) method[S7] in the Gaussian09 package.[S8] Stationary structures were found by ascertaining that all of the harmonic frequencies were real. The transition states were optimized, where only one of the harmonic frequencies was imaginary. Energetics were calculated under standard conditions (1 atm and 298.15 K) and reported as relative free energies in kcal mol^{-1} with the notation of ΔG. Solvent effects were accounted at the PCM formalism in chloroform (ε=4.7) as the experiments were carried out in the same solvent, $CHCl_3$.

Optimized Structures and Geometries of Stationary and Transition States on the Energy Profile for the Steps of the Conversion of 1b' to 1b (Scheme 2D).

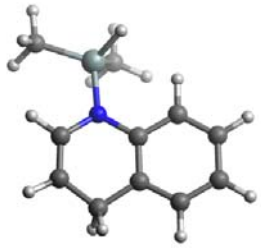
$B(C_6F_5)_3$–$SiMe_2H_2$ (A)



B	-1.12078	1.33328	0.62879
C	0.44806	1.22040	0.32368
C	1.33308	0.95833	1.36426
C	1.03521	1.41396	-0.92018
C	2.70583	0.88451	1.20955
C	2.40835	1.34105	-1.12524
C	3.24709	1.07528	-0.05504
C	-2.02591	2.15759	-0.40357
C	-3.22361	1.71282	-0.95008
C	-1.63902	3.43886	-0.78373
C	-3.98658	2.48232	-1.82059
C	-2.37420	4.24690	-1.63339
C	-3.55905	3.75477	-2.16421
C	-1.81283	0.15216	1.46058
C	-1.28119	-1.11932	1.64118
C	-3.01338	0.38872	2.12274
C	-1.89533	-2.09047	2.42379
C	-3.65326	-0.54087	2.92308
C	-3.08704	-1.80030	3.06833
F	3.50559	0.63639	2.25249
F	0.84344	0.78203	2.61310
F	4.56758	1.00354	-0.23555
F	2.92151	1.52922	-2.34640
F	0.28387	1.67919	-2.00302
F	-0.12428	-1.47531	1.05671
F	-1.34058	-3.29998	2.55906
F	-3.68162	-2.72008	3.83020
F	-4.79279	-0.23454	3.55323
F	-3.58571	1.61227	2.03237

F	-0.49700	3.95706	-0.27811
F	-1.95816	5.48054	-1.94095
F	-4.28384	4.50452	-2.99670
F	-5.12895	2.00443	-2.32704
F	-3.70413	0.49199	-0.65579
Si	-1.04821	3.31241	2.83746
H	-1.03895	2.31496	1.65465
C	-2.23550	4.64166	2.31032
H	-2.46659	5.29896	3.15925
H	-1.82062	5.25364	1.50097
H	-3.17481	4.18666	1.96720
C	-1.54186	2.30897	4.32291
H	-2.62490	2.13297	4.33443
H	-1.02321	1.34116	4.32688
H	-1.27018	2.84382	5.24268
H	0.38239	3.72184	2.83707

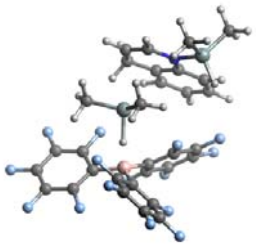
1b’



C	2.14463	-2.04849	-0.37626
C	0.86661	-1.50572	-0.41535
C	0.64804	-0.14410	-0.15288
C	1.75184	0.67652	0.14130
C	3.02734	0.11234	0.15693
C	3.24034	-1.23925	-0.09010
H	2.28058	-3.11045	-0.58485
H	0.03003	-2.15294	-0.68147
C	1.58225	2.15094	0.45354
H	3.87557	0.76543	0.37797
H	4.24826	-1.65362	-0.06379
C	0.22127	2.63420	0.03656
C	-0.77527	1.78993	-0.23217
H	1.73751	2.32390	1.53369
H	0.03174	3.70482	-0.02805
H	-1.76303	2.16484	-0.49982
N	-0.65756	0.39009	-0.22141
Si	-2.10003	-0.64564	-0.24549
C	-3.62042	0.43397	-0.36224
H	-3.70372	1.11899	0.49238
H	-3.65058	1.02481	-1.28678
C	-2.15252	-1.70778	1.29466
H	-2.97965	-2.42881	1.23873
H	-2.31246	-1.07889	2.18120
H	2.37336	2.72573	-0.05361
H	-1.22229	-2.26972	1.44637
H	-4.50902	-0.21240	-0.35519

H	-2.03767	-1.52864	-1.45401

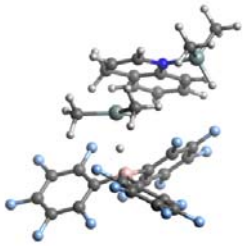
C



B	-2.23499	2.68340	3.63418
C	-1.30871	2.10288	4.81573
C	-1.66321	2.32451	6.14346
C	-0.10098	1.43776	4.63854
C	-0.89565	1.94105	7.22854
C	0.69826	1.02122	5.69830
C	0.30066	1.27438	7.00008
C	-1.60258	2.72106	2.15598
C	-2.14915	2.11146	1.03510
C	-0.43014	3.43466	1.93352
C	-1.57070	2.19904	-0.22658
C	0.17580	3.55805	0.69586
C	-0.40346	2.92548	-0.39667
C	-3.81955	2.44406	3.72550
C	-4.44505	1.47142	4.49373
C	-4.67729	3.26852	3.00345
C	-5.82650	1.32702	4.55151
C	-6.05574	3.15355	3.01813
C	-6.63443	2.16895	3.80638
F	-1.29028	2.21293	8.47819
F	-2.80699	2.99553	6.41750
F	1.06231	0.88640	8.02552
F	1.84988	0.38081	5.46412
F	0.36580	1.15398	3.40968
F	-3.72570	0.60925	5.23689
F	-6.37825	0.37950	5.32098
F	-7.96467	2.05378	3.86791
F	-6.82563	3.97762	2.29739
F	-4.15241	4.26960	2.25766
F	0.16418	4.05856	2.97885
F	1.30171	4.26590	0.54419
F	0.16428	3.01473	-1.60251
F	-2.13180	1.58340	-1.27460
F	-3.27929	1.38716	1.12576
C	-7.96594	4.91516	4.94738
C	-7.17760	5.97436	4.51663
C	-6.07006	6.40635	5.26053
C	-5.75697	5.73868	6.45902
C	-6.55632	4.67046	6.86579
C	-7.65934	4.25054	6.13053
H	-8.80481	4.58898	4.33107
H	-7.41969	6.44026	3.56226

C	-4.55180	6.11340	7.30178
H	-6.29041	4.15375	7.79146
H	-8.25952	3.40335	6.46447
C	-3.80093	7.27092	6.70418
C	-4.18234	7.86595	5.56597
H	-4.87501	6.35677	8.32742
H	-2.93417	7.66908	7.23147
H	-3.62493	8.72116	5.18100
N	-5.27801	7.48338	4.78927
Si	-5.72040	8.39506	3.32263
C	-4.40092	9.66658	2.95637
H	-4.32233	10.41778	3.75407
H	-3.40849	9.23463	2.78077
C	-7.36292	9.26417	3.54548
H	-7.68828	9.70906	2.59492
H	-7.25366	10.07874	4.27489
H	-3.89247	5.23116	7.40144
H	-8.16150	8.60234	3.90137
H	-4.69252	10.19818	2.03963
H	-5.79877	7.40803	2.20027
Si	-2.42645	5.40226	4.55958
H	-2.09917	4.03015	3.86300
H	-3.81988	5.10556	4.94039
C	-2.16017	6.57646	3.13951
H	-3.02030	6.59437	2.45879
H	-1.97845	7.58867	3.52502
H	-1.26933	6.27543	2.57136
C	-1.10323	5.48514	5.86913
H	-0.76187	6.52179	5.98508
H	-1.45185	5.12008	6.84300
H	-0.24161	4.87821	5.55409

TS-I

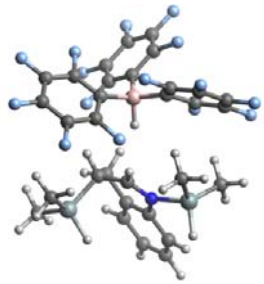


B	-2.22750	2.85587	3.68510
C	-1.36701	2.08994	4.82610
C	-1.73753	2.23764	6.15942
C	-0.21199	1.34460	4.62800
C	-1.03169	1.71715	7.22934
C	0.52731	0.79252	5.67002
C	0.11791	0.98065	6.97874
C	-1.53022	2.97670	2.23099
C	-2.07630	2.58597	1.01638
C	-0.28139	3.58232	2.14277
C	-1.43268	2.77746	-0.20248
C	0.39728	3.79685	0.95563
C	-0.18906	3.38487	-0.23329

C	-3.82098	2.57891	3.69466
C	-4.47103	1.57194	4.39550
C	-4.66753	3.45427	3.02075
C	-5.85576	1.44786	4.44750
C	-6.04820	3.36521	3.03261
C	-6.64958	2.35033	3.76258
F	-1.44091	1.92167	8.48963
F	-2.84596	2.95669	6.46113
F	0.82387	0.46485	7.99094
F	1.63468	0.08218	5.41379
F	0.26471	1.11124	3.38911
F	-3.77805	0.64493	5.08675
F	-6.42159	0.45957	5.15496
F	-7.98382	2.25417	3.80926
F	-6.80642	4.24800	2.36392
F	-4.13012	4.48137	2.31928
F	0.31899	4.01570	3.27750
F	1.59807	4.39253	0.94159
F	0.44156	3.57659	-1.39743
F	-2.00823	2.37783	-1.34521
F	-3.28209	1.98765	0.95794
C	-7.97271	4.88879	5.51753
C	-7.26077	5.86041	4.82287
C	-6.07997	6.39280	5.34766
C	-5.60731	5.94327	6.58973
C	-6.33505	4.96827	7.26797
C	-7.51161	4.43694	6.74921
H	-8.87860	4.47240	5.07676
H	-7.61961	6.16301	3.84041
C	-4.30682	6.44553	7.18772
H	-5.95169	4.61018	8.22613
H	-8.05669	3.66900	7.29814
C	-3.53138	7.28258	6.19399
C	-4.15540	7.78931	5.08504
H	-4.51439	7.04171	8.09099
H	-2.64211	7.81204	6.53731
H	-3.64963	8.55124	4.48938
N	-5.35044	7.37230	4.59885
Si	-5.99113	8.05430	3.05068
C	-4.71571	9.22673	2.35508
H	-4.55638	10.09449	3.01033
H	-3.74519	8.76043	2.14490
C	-7.58147	8.97081	3.39203
H	-8.32227	8.37320	3.93603
H	-8.03590	9.29691	2.44652
H	-3.71566	5.57788	7.52570
H	-7.37052	9.86935	3.98803
H	-5.10370	9.61164	1.40161
H	-6.20012	6.89235	2.14116
Si	-2.51957	5.59615	4.83120
H	-2.11950	4.09102	4.07935
H	-3.86587	5.00398	4.97026
C	-2.03671	6.54404	3.29048
H	-2.88166	6.63011	2.59552
H	-1.66135	7.54650	3.53694
H	-1.23095	6.00589	2.77470

C	-1.13904	5.42265	6.08522
H	-0.61989	6.38293	6.20024
H	-1.49444	5.09571	7.06996
H	-0.41115	4.68626	5.71668

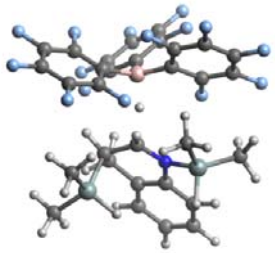
D



B	-5.32753	10.98496	6.54512
C	-3.80882	11.46961	6.15488
C	-3.35100	11.32372	4.84866
C	-2.83412	11.93690	7.03111
C	-2.05917	11.58194	4.42215
C	-1.52085	12.20924	6.65685
C	-1.12346	12.02505	5.34415
C	-5.59963	10.90158	8.15176
C	-6.59998	11.54510	8.86571
C	-4.81372	10.04584	8.91635
C	-6.81522	11.35767	10.22827
C	-4.98428	9.82451	10.27203
C	-6.00287	10.49171	10.93846
C	-6.52048	11.70144	5.69085
C	-6.40776	12.74060	4.77775
C	-7.78455	11.11819	5.73894
C	-7.44961	13.14941	3.94744
C	-8.84980	11.48356	4.93444
C	-8.67747	12.51490	4.02025
F	-1.70804	11.38544	3.14128
F	-4.20894	10.89969	3.87680
F	0.13730	12.27482	4.96915
F	-0.63585	12.64338	7.56593
F	-3.10946	12.16295	8.33198
F	-5.24926	13.41815	4.63310
F	-7.26981	14.15447	3.07723
F	-9.68760	12.89212	3.22527
F	-10.02955	10.84684	5.01827
F	-8.00636	10.09634	6.60120
F	-3.78786	9.38055	8.32438
F	-4.17999	8.98319	10.94209
F	-6.19235	10.30236	12.25179
F	-7.80387	12.01295	10.85626
F	-7.44162	12.41015	8.25943
C	-6.92376	3.72832	5.00558
C	-6.83544	4.98193	4.40810
C	-6.05127	5.96919	4.99951
C	-5.34339	5.72005	6.18166
C	-5.43827	4.45723	6.75810

C	-6.22586	3.46445	6.18008
H	-7.53627	2.95527	4.54233
H	-7.36143	5.17000	3.47229
C	-4.52616	6.83746	6.77910
H	-4.88549	4.25648	7.67784
H	-6.29026	2.48149	6.64682
C	-3.89549	7.65048	5.64508
C	-4.91159	8.02087	4.66534
H	-5.17860	7.50055	7.37066
H	-3.42982	8.57281	6.02268
H	-4.81502	8.95740	4.11379
N	-5.93428	7.26574	4.37347
Si	-7.26043	7.90210	3.23365
C	-6.71496	9.58046	2.65785
H	-6.55101	10.27775	3.49043
H	-5.80124	9.54380	2.05021
C	-8.82408	7.88764	4.23356
H	-9.14078	6.87033	4.49518
H	-9.63448	8.36452	3.66549
H	-3.76082	6.44225	7.45855
H	-8.69203	8.45761	5.16249
H	-7.51357	9.99702	2.02701
H	-7.27896	6.92960	2.10888
Si	-2.48270	6.74848	4.65808
H	-5.39766	9.80864	6.17390
H	-3.15170	5.87591	3.64290
C	-1.49279	8.10096	3.82494
H	-2.13582	8.78396	3.25047
H	-0.96174	8.70013	4.57880
H	-0.74428	7.68893	3.13636
C	-1.50614	5.72933	5.88220
H	-1.13854	6.35566	6.70664
H	-2.12114	4.92395	6.30657
H	-0.63732	5.26862	5.39437

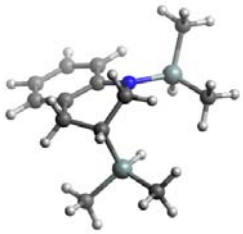
TS-II



B	-5.26441	10.78211	6.48698
C	-3.76815	11.33188	6.13756
C	-3.28066	11.31011	4.83174
C	-2.84562	11.82909	7.05801
C	-1.99277	11.65273	4.45529
C	-1.54415	12.19679	6.73024
C	-1.10347	12.09381	5.42230
C	-5.60693	10.61969	8.06707
C	-6.74698	11.09015	8.71087
C	-4.73667	9.91679	8.89711
C	-7.01294	10.87117	10.05941
C	-4.95660	9.67196	10.24096
C	-6.11582	10.15528	10.83130
C	-6.45634	11.39310	5.58026
C	-6.38136	12.52540	4.77843
C	-7.68876	10.74434	5.56083
C	-7.44236	12.98086	4.00126
C	-8.78378	11.18312	4.83508
C	-8.65136	12.30679	4.03010
F	-1.61160	11.55156	3.17505
F	-4.09824	10.95137	3.80507
F	0.14735	12.42934	5.09459
F	-0.71647	12.65220	7.67944
F	-3.17069	12.01059	8.35151
F	-5.25643	13.26378	4.71793
F	-7.30531	14.07539	3.24213
F	-9.68785	12.74518	3.30919
F	-9.96171	10.54532	4.89714
F	-7.85663	9.63375	6.31492
F	-3.57658	9.43452	8.38912
F	-4.06575	8.98499	10.96971
F	-6.35714	9.93807	12.12821
F	-8.13184	11.35697	10.61427
F	-7.67385	11.82101	8.05961
C	-7.31743	4.23104	5.72003
C	-7.17509	5.47149	5.10801
C	-6.14995	6.34032	5.49360
C	-5.26820	5.95648	6.51410
C	-5.42078	4.70625	7.10868
C	-6.43664	3.83841	6.72144
H	-8.12358	3.56979	5.40228
H	-7.87996	5.74124	4.32479
C	-4.20870	6.92095	6.97856
H	-4.72274	4.41786	7.89759
H	-6.53942	2.86458	7.20008
C	-3.74073	7.78882	5.81083

C	-4.90469	8.36085	5.08174
H	-4.63471	7.55878	7.76595
H	-3.10456	8.61415	6.16287
H	-4.69658	9.11645	4.32616
N	-5.97893	7.59369	4.81249
Si	-6.96228	7.91704	3.30328
C	-6.31795	9.44863	2.46501
H	-6.39797	10.35132	3.08338
H	-5.27658	9.35078	2.13123
C	-8.78341	8.02208	3.70739
H	-9.32784	7.12996	3.37257
H	-9.23041	8.88796	3.20212
H	-3.36688	6.37953	7.43067
H	-8.95067	8.14324	4.78522
H	-6.93496	9.60260	1.56777
H	-6.67055	6.72093	2.46002
Si	-2.69903	6.87554	4.46924
H	-5.26538	9.50947	6.09097
H	-3.65950	6.12454	3.59780
C	-1.83664	8.21614	3.47799
H	-2.54153	8.97818	3.11267
H	-1.09040	8.73033	4.10143
H	-1.31482	7.80317	2.60534
C	-1.51981	5.69887	5.32059
H	-0.90664	6.22617	6.06448
H	-2.06873	4.89714	5.83343
H	-0.84223	5.23092	4.59460

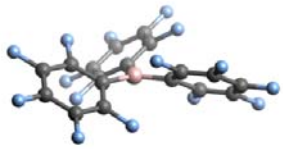
1b



C	-7.21655	2.81275	4.80457
C	-6.90345	3.97418	4.11073
C	-5.93271	4.87596	4.58595
C	-5.25347	4.55192	5.78097
C	-5.58505	3.37810	6.45702
C	-6.56496	2.50643	5.99601
H	-7.97780	2.14219	4.40267
H	-7.41873	4.17328	3.17062
C	-4.14249	5.43267	6.31603
H	-5.03994	3.14546	7.37580
H	-6.80411	1.59721	6.54754
C	-3.56873	6.31095	5.19680
C	-4.74788	7.01706	4.52390
H	-4.53066	6.07219	7.12699
H	-2.91315	7.08055	5.63568
H	-4.38406	7.72412	3.76695
N	-5.63735	6.04849	3.86786

Si	-6.63229	6.59231	2.51321
C	-5.90702	8.16548	1.80062
H	-5.96768	8.99856	2.51462
H	-4.86068	8.05792	1.48624
C	-8.40438	6.91631	3.03916
H	-9.02532	7.17612	2.17059
H	-8.44011	7.76233	3.74005
H	-3.36706	4.79514	6.76986
H	-8.86102	6.05193	3.53749
H	-6.49134	8.45086	0.91472
H	-6.61929	5.52492	1.46227
Si	-2.52386	5.31730	3.95928
H	-5.30512	7.60366	5.28052
H	-3.16056	3.97894	3.73650
C	-2.42006	6.23016	2.31853
H	-3.39761	6.21796	1.81660
H	-2.12022	7.27868	2.46096
H	-1.69197	5.76114	1.64365
C	-0.81526	5.05056	4.70301
H	-0.30319	6.00982	4.86274
H	-0.88150	4.54135	5.67459
H	-0.18290	4.43690	4.04784

$B(C_6F_5)_3$



B	-2.24299	2.26293	3.53323
C	-1.32392	1.92765	4.76100
C	-1.68836	2.23362	6.07454
C	-0.08081	1.30693	4.61590
C	-0.88339	1.95781	7.16811
C	0.74479	1.00275	5.68595
C	0.34025	1.33495	6.97062
C	-1.59914	2.61390	2.14448
C	-2.20709	2.27955	0.93214
C	-0.37598	3.27893	2.03655
C	-1.64459	2.56650	-0.30129
C	0.21034	3.59591	0.82199
C	-0.42842	3.23203	-0.35428
C	-3.80455	2.24851	3.68898
C	-4.46236	1.37508	4.55773
C	-4.63157	3.11205	2.96733
C	-5.84011	1.34563	4.70192
C	-6.01086	3.12335	3.09729
C	-6.61735	2.22998	3.96757
F	-1.27778	2.28064	8.40358
F	-2.85703	2.83895	6.33452
F	1.12511	1.05960	8.00939
F	1.92074	0.39889	5.48979
F	0.37009	0.96049	3.40077
F	-3.76464	0.49778	5.29500

F	-6.42168	0.48119	5.53911
F	-7.94170	2.22229	4.09754
F	-6.75682	3.98134	2.39463
F	-4.10545	3.99911	2.10922
F	0.28905	3.66057	3.13720
F	1.38129	4.23875	0.77683
F	0.12182	3.52215	-1.53081
F	-2.25971	2.20931	-1.43283
F	-3.38565	1.63862	0.91611

Fukui Functions (Scheme 2C)

Yang and Mortier proposed the condensed Fukui functions in a *finite difference approximation* as shown below.[16]

$$f_i^- = -[q_i(\mathrm{N}) - q_i(\mathrm{N}-1)]$$

where q_i is the partial charge of the i^{th} atom, which is extracted by a Hirshfeld population analysis using the B3LYP/6-311++G** basis set.[S9]

Table S2. The Fukui functions f_i^- of each atom in 1,4-addition adduct 1b' calculated by the finite difference approximation.

Atom	Finite difference
N1	0.112
C2	0.065
C3	0.123
C4	0.032
C5	0.032
C6	0.069
C7	0.041
C8	0.041

VIII. References

S1. Lu, B.; Li, C.; Zhang, L. *J. Am. Chem*. *Soc.* **2010,** *132*, 14070.

S2. Xu, L.; Li, B.-J.; Wu, Z.-H.; Lu, X.-Y.; Guan, B.-T.; Wang, B.-Q.; Zhao, K.-Q.; Shi, Z.-J. *Org. Lett.* **2010,** *12*, 884.

S3. Maiti, D.; Buchwald, S. L. *J. Org. Chem*. **2010,** *75*, 1791.

S4. Chan, T. H.; Nwe, K. T. *J. Org. Chem.* **1992,** *57*, 6107.

S5. Lee, S.-H.; Gutsulyak, D. V.; Nikonov, G. I. *Organometallics* **2013,** *32*, 4457.

S6. Nishikawa, T. *et al., Tetrahedron* **1995,** *51*, 9339.

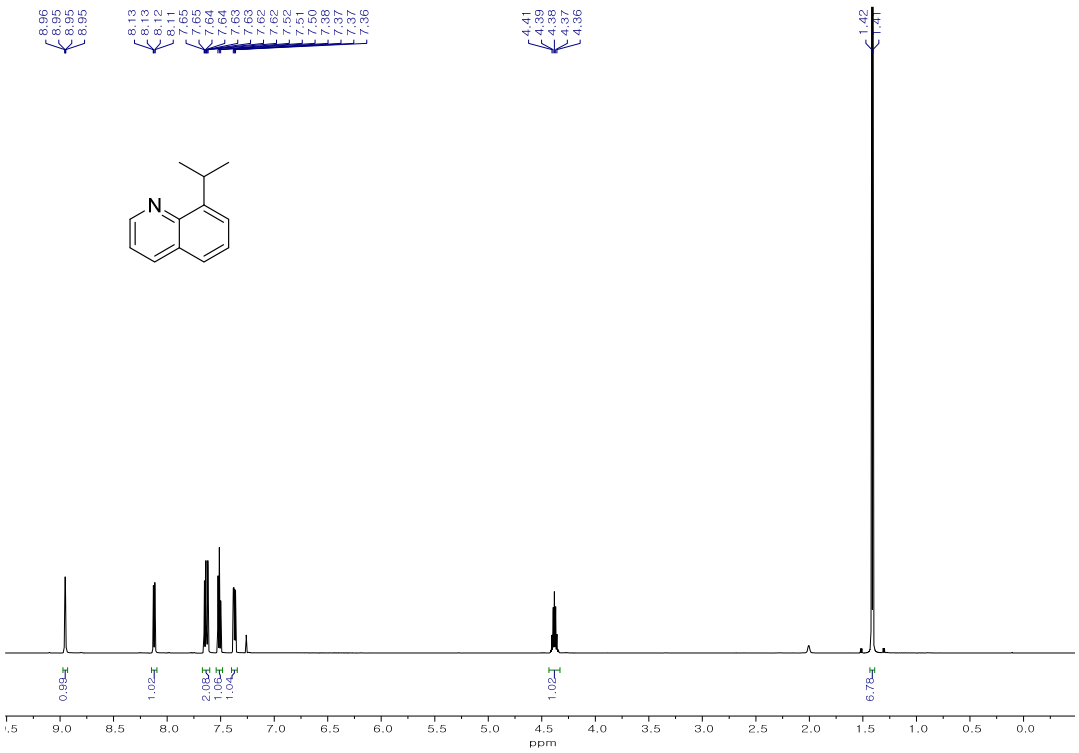
S7. Peverati, R.; Truhlar, D. G. *J. Phys. Chem. Lett.* **2011,** *2*, 2810.

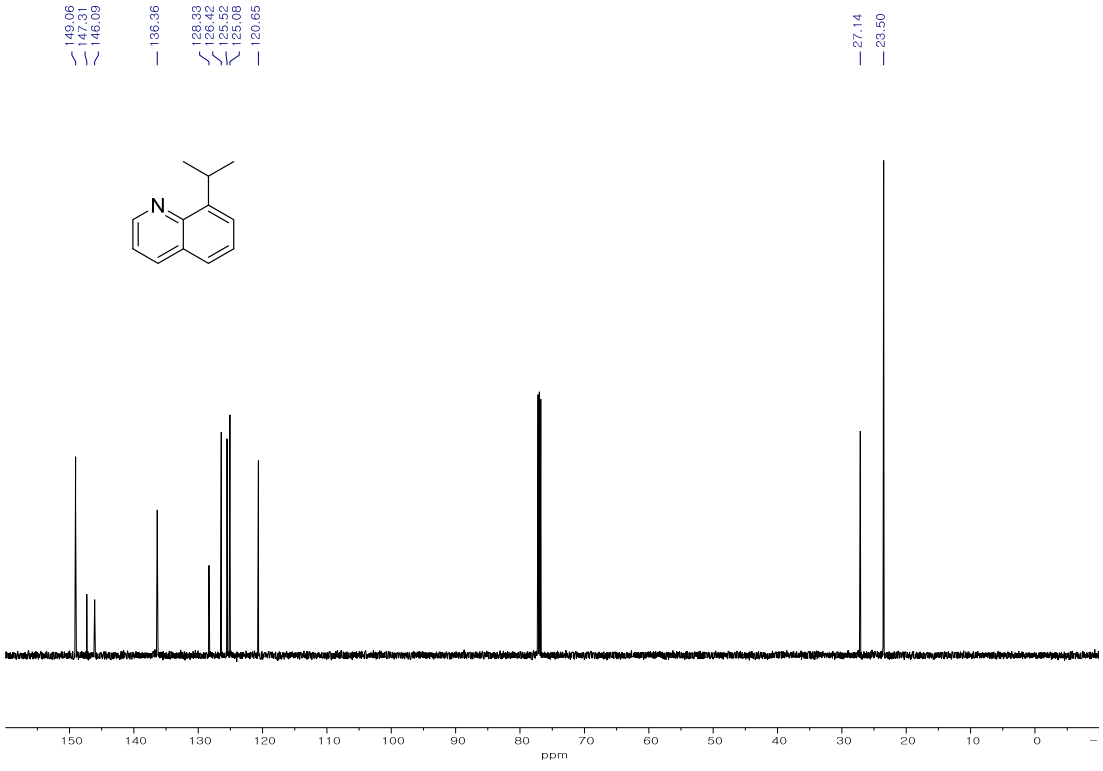
S8. Frisch, M. J. *et al.,* Gaussian 09, Revision **D.01** (Gaussian, Inc., Wallingford CT, 2009).

S9. Hirshfeld, F. L. *Theor. Chem. Acc.*, **1977,** *44*, 129.

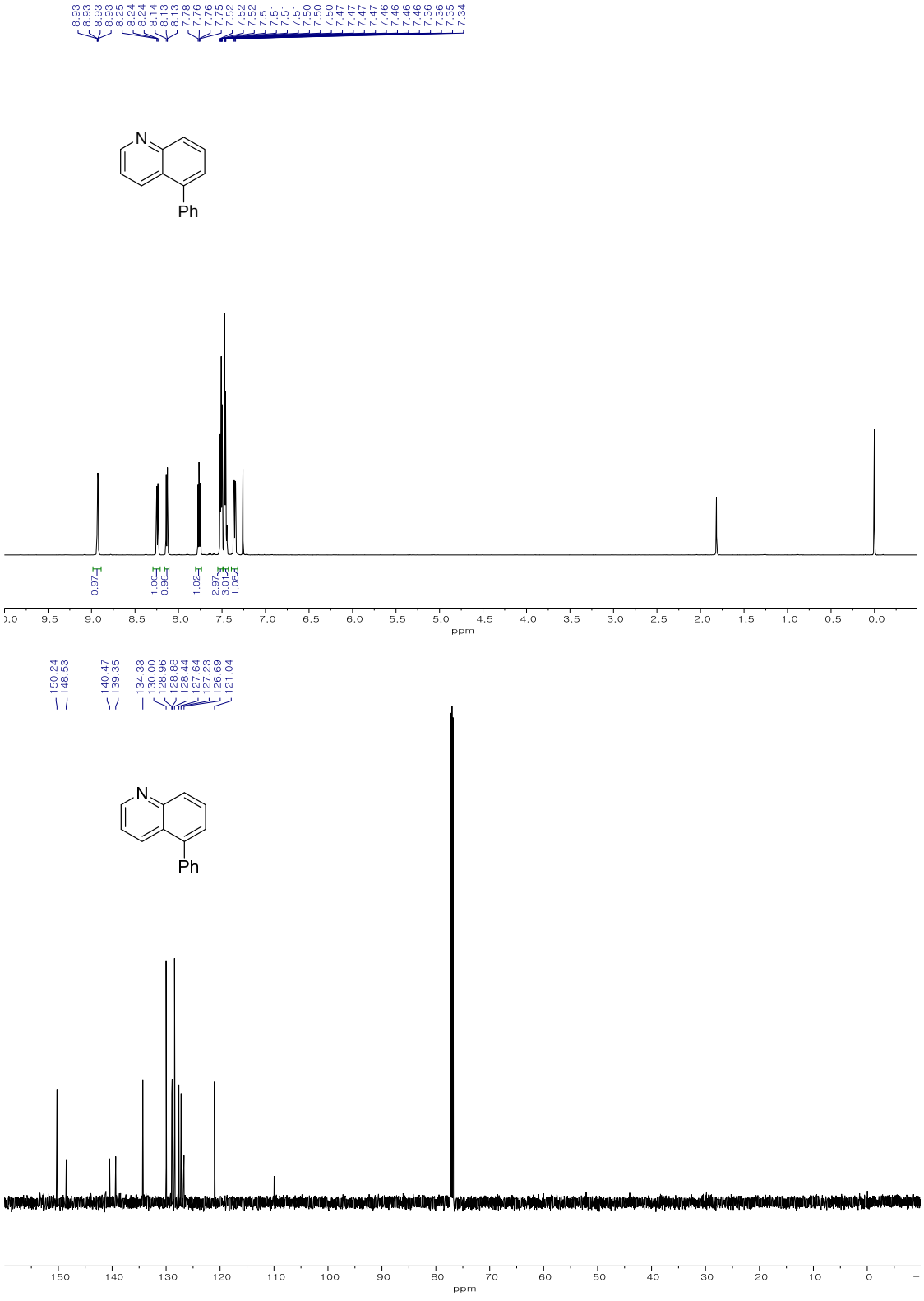
IX. Copies of Spectroscopic Data

8-Isopropylquinoline (5a)

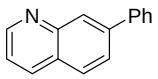


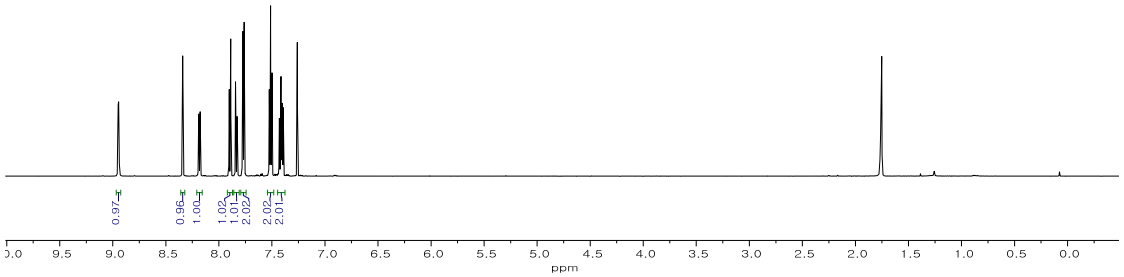


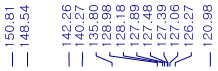
5-Phenylquinoline (6a)

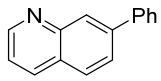


7-Phenylquinoline (7a)

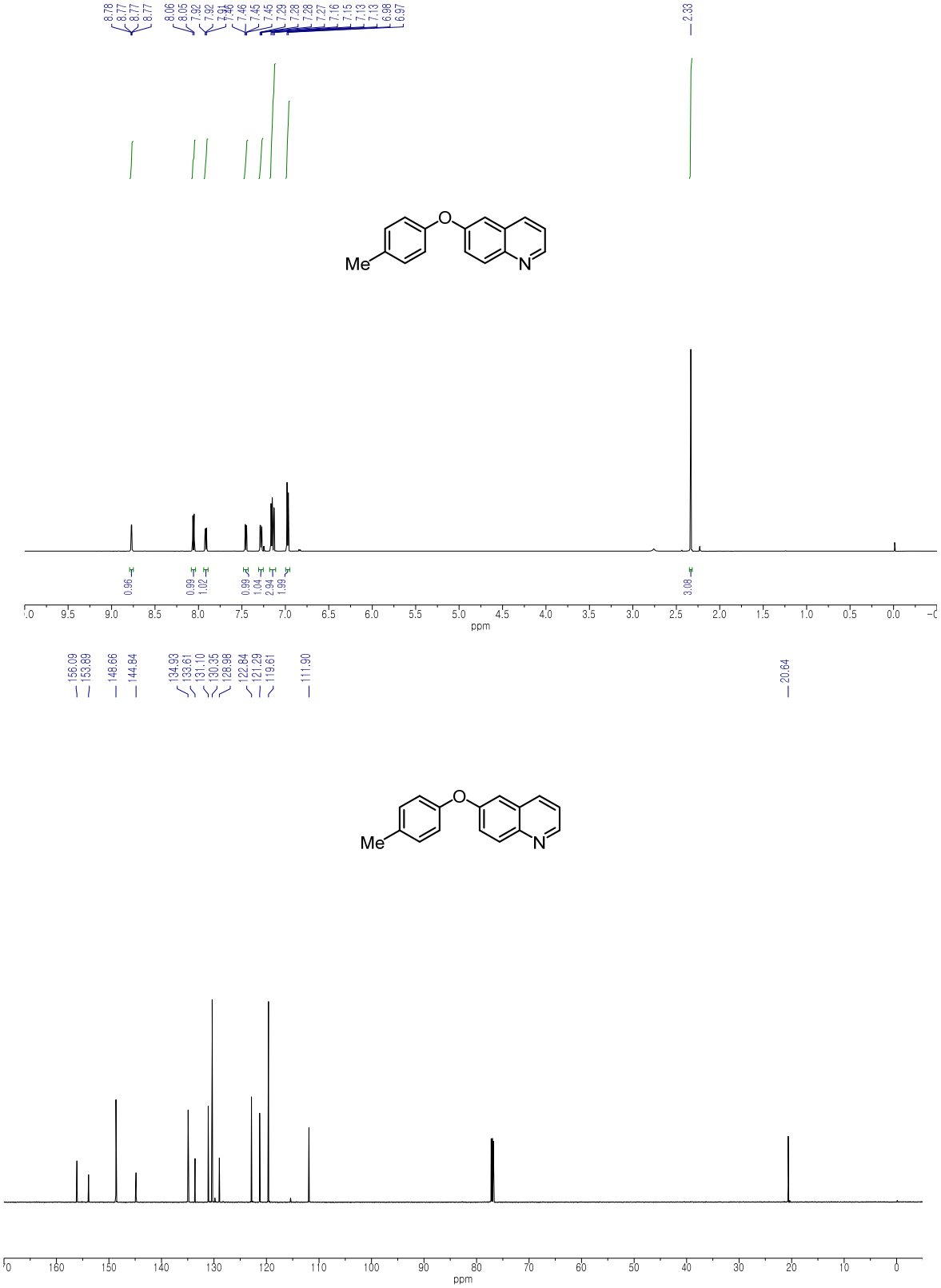




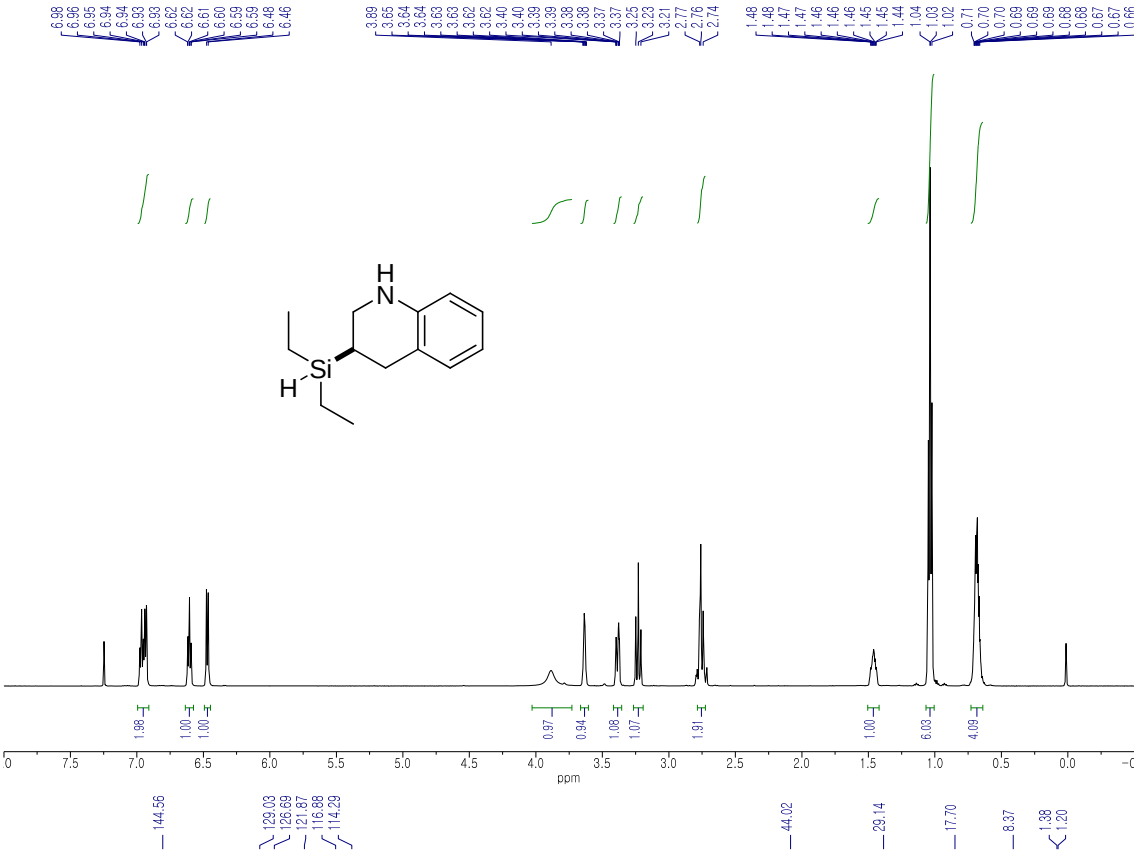


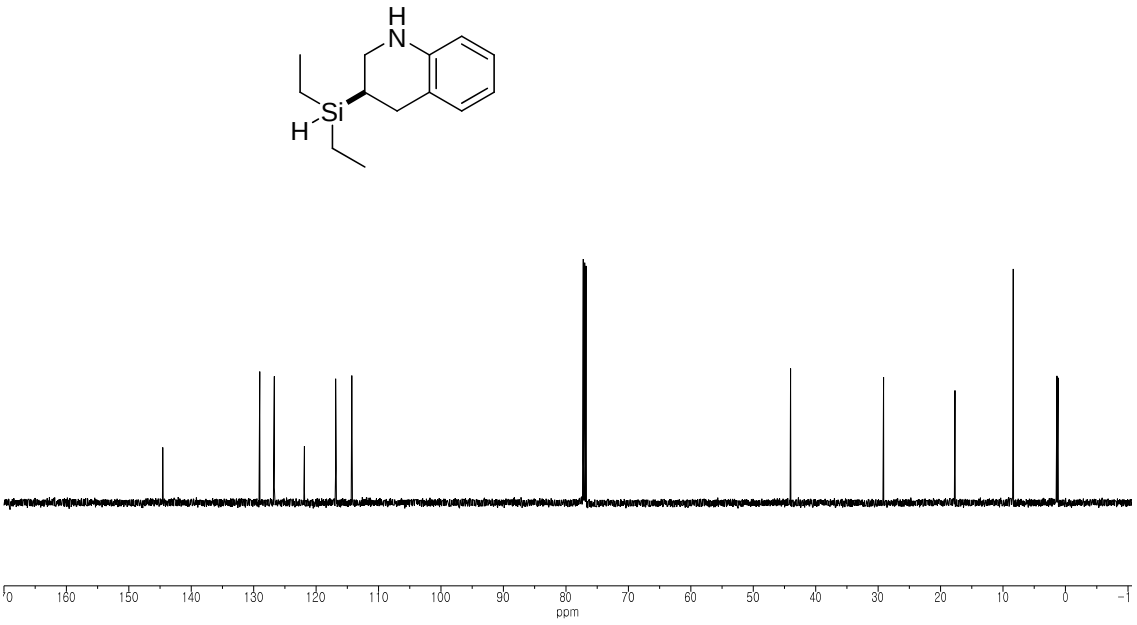


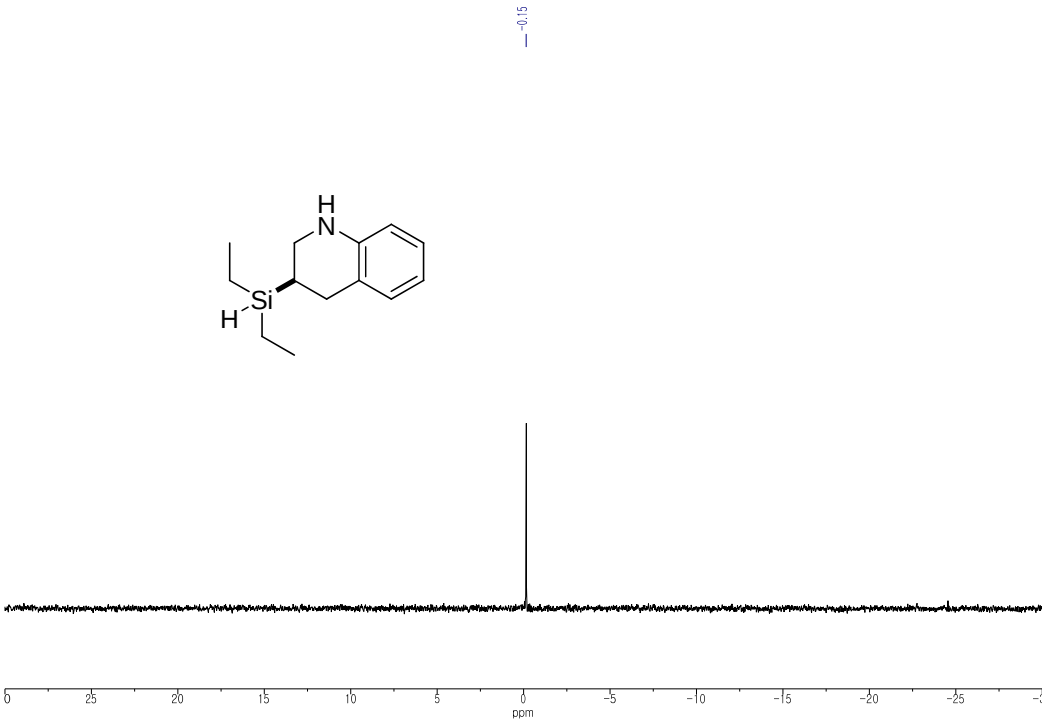
6-(*p*-Tolyloxy)quinoline (21a)



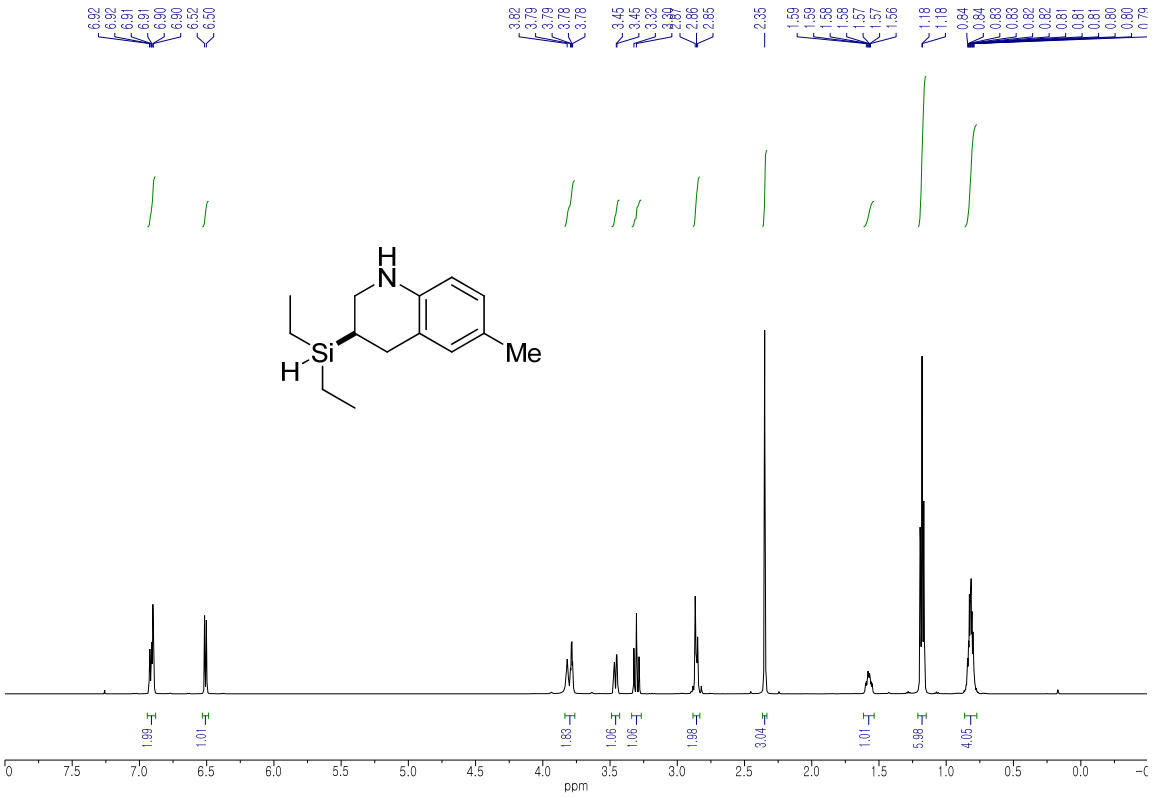
3-(Diethylsilyl)-1,2,3,4-tetrahydroquinoline (Table 1, 1b)

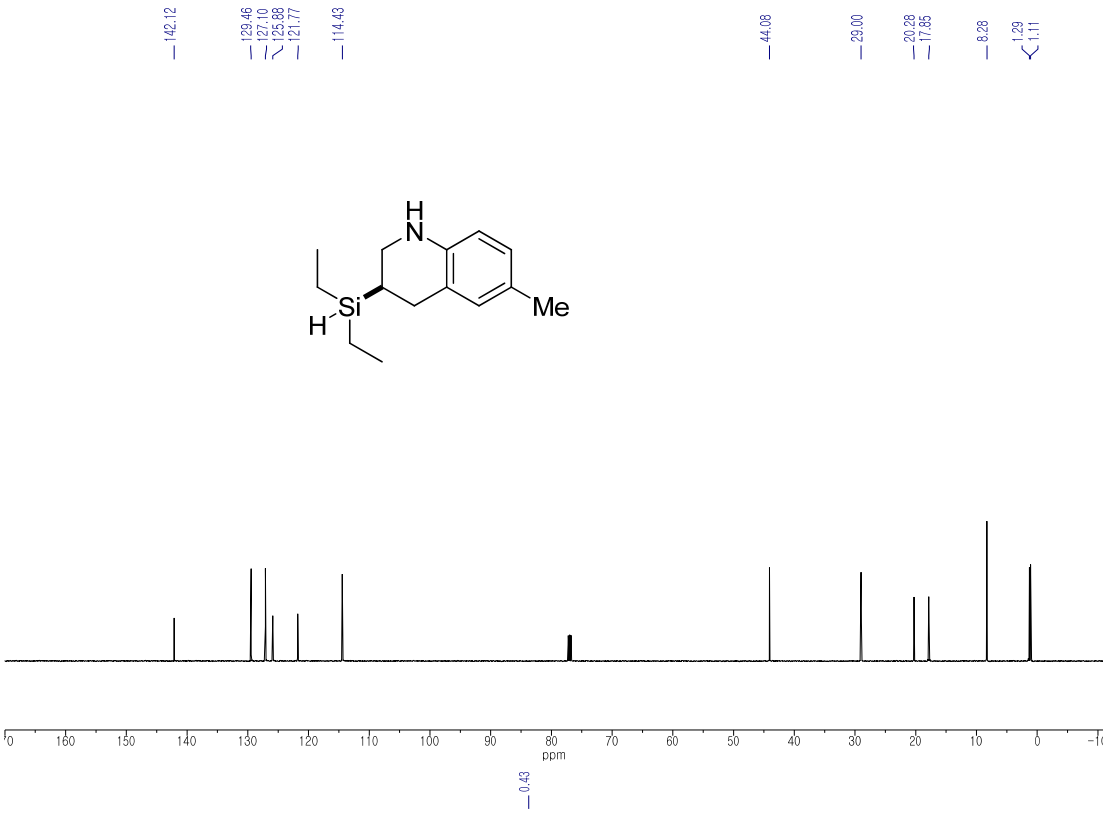


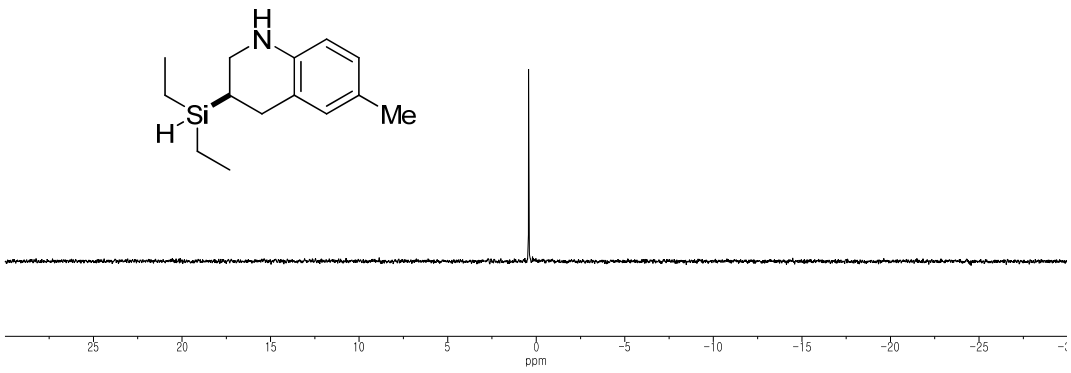




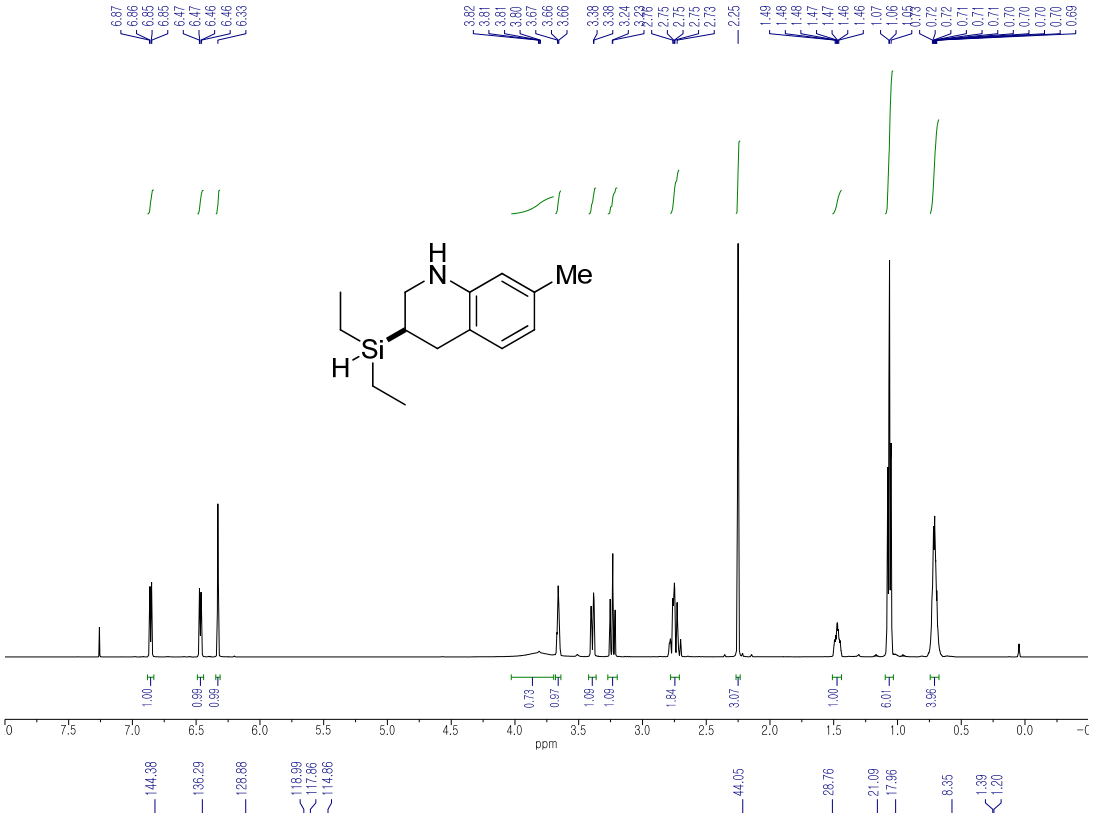
3-(Diethylsilyl)-6-methyl-1,2,3,4-tetrahydroquinoline (Table 1, 2b)

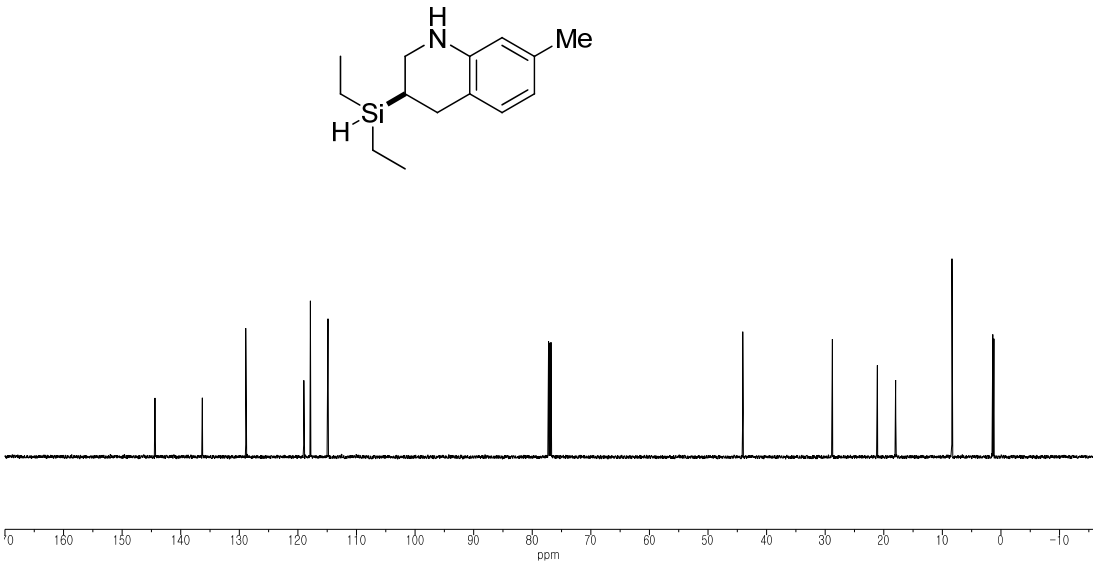


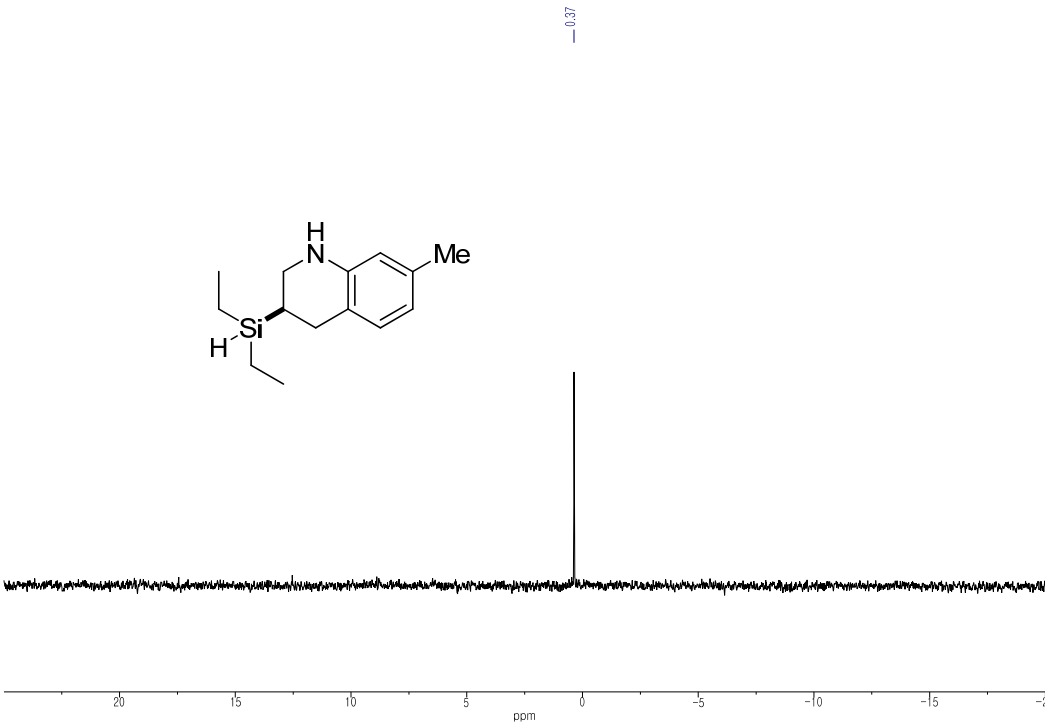

142.12
129.46
127.10
125.88
121.77
114.43
44.08
29.00
20.28
17.85
8.28
1.29
1.11
H
N
Si
H
Me
ppm
0.43


H
N
Si
H
Me
ppm

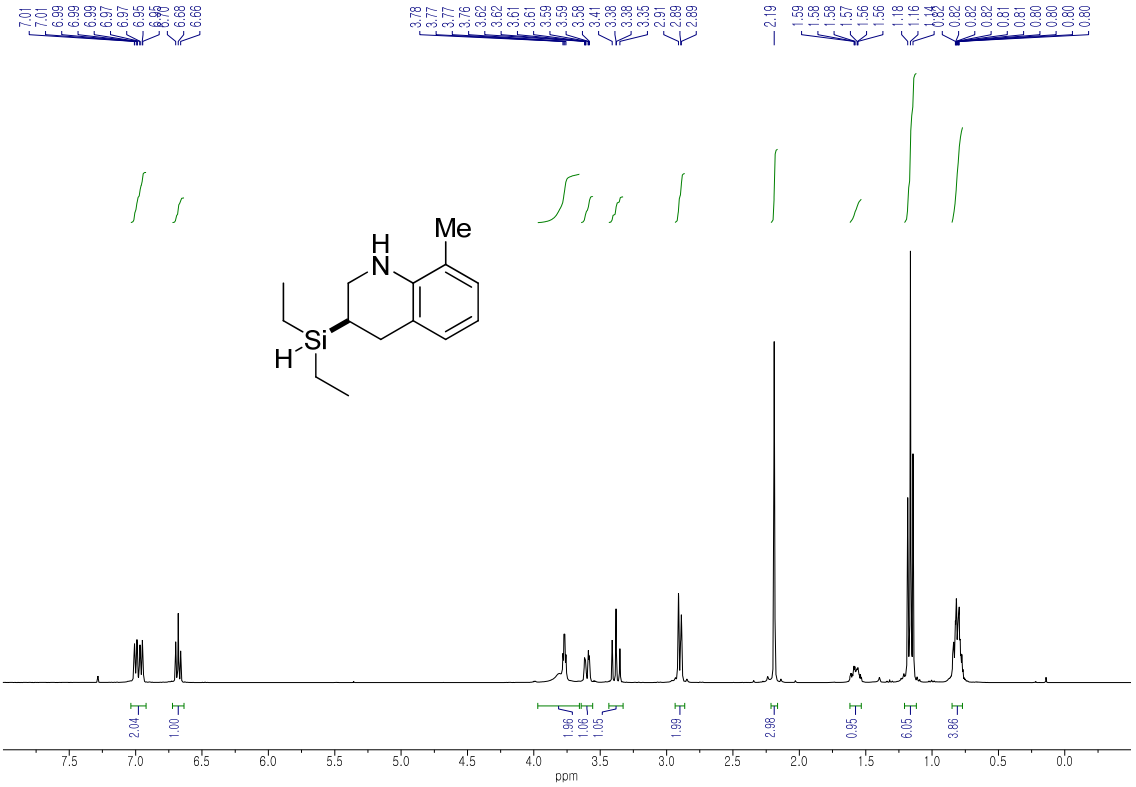
3-(Diethylsilyl)-7-methyl-1,2,3,4-tetrahydroquinoline (Table 1, 3b)

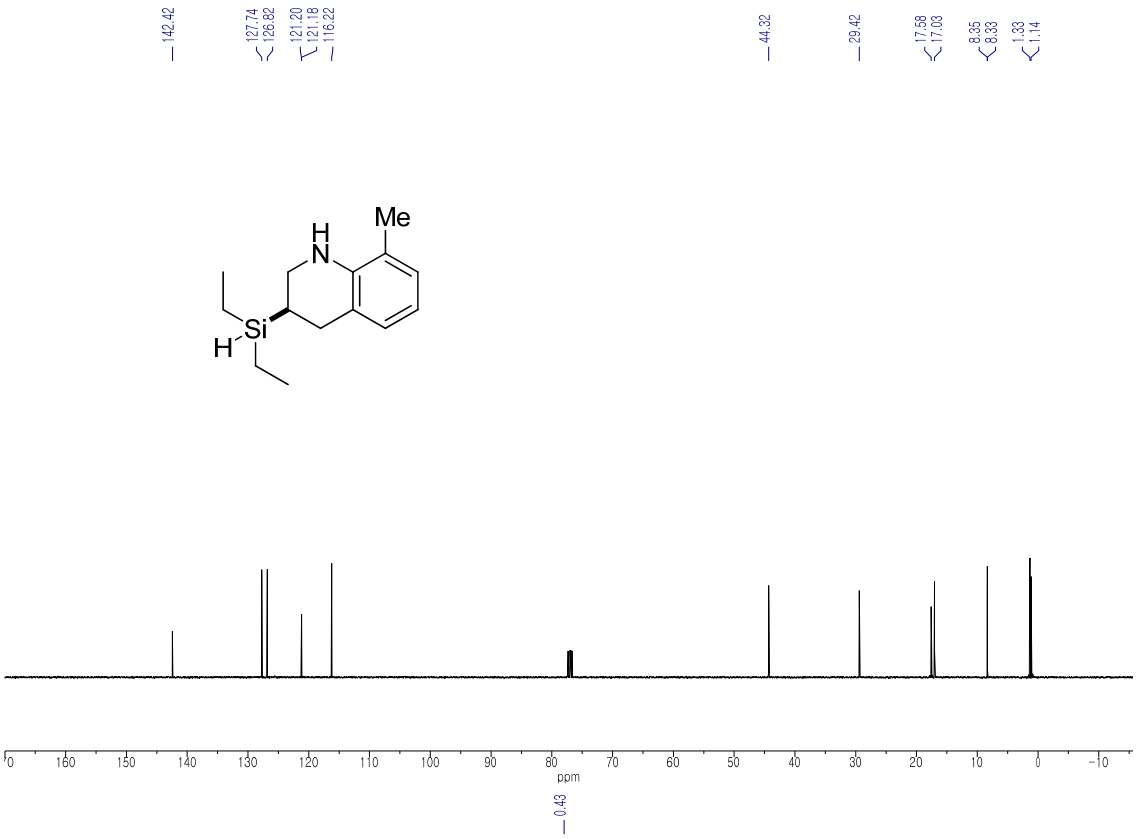


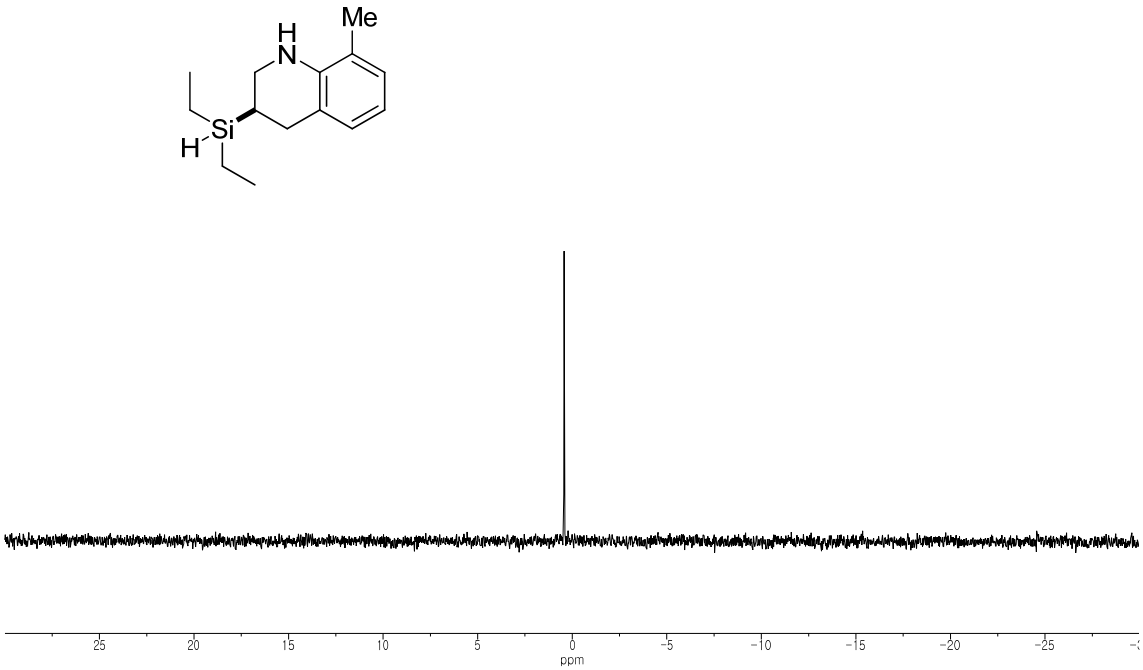




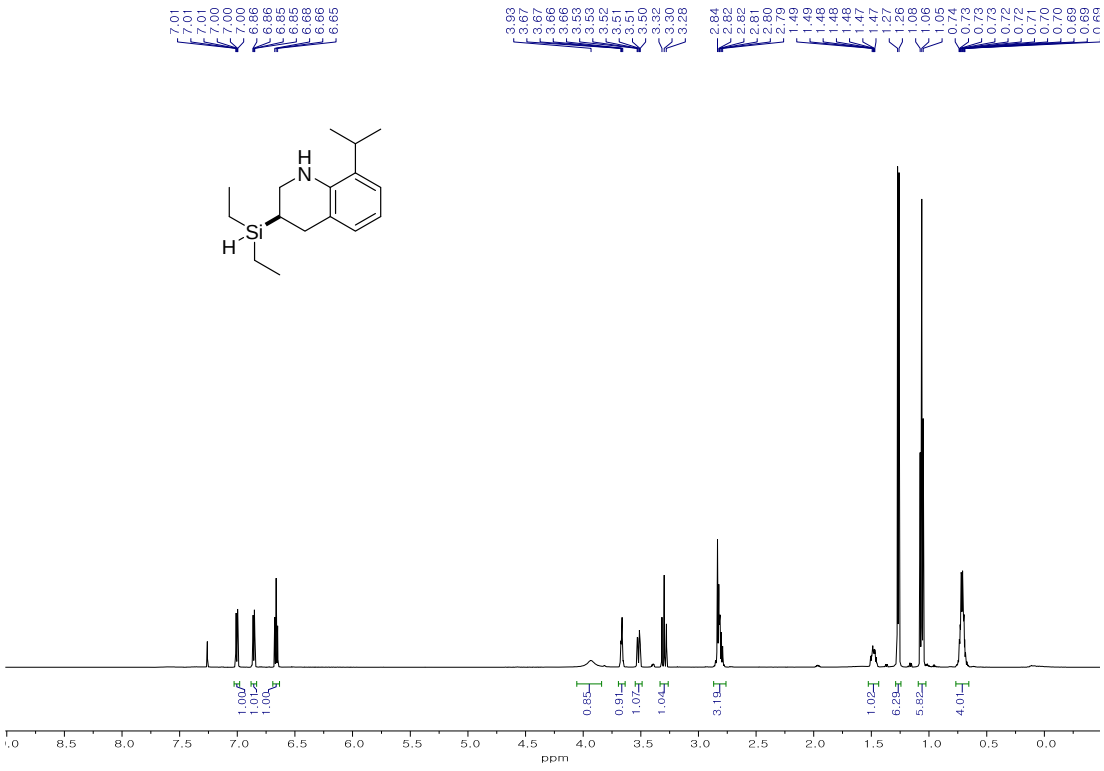
3-(Diethylsilyl)-8-methyl-1,2,3,4-tetrahydroquinoline (Table 1, 4b)

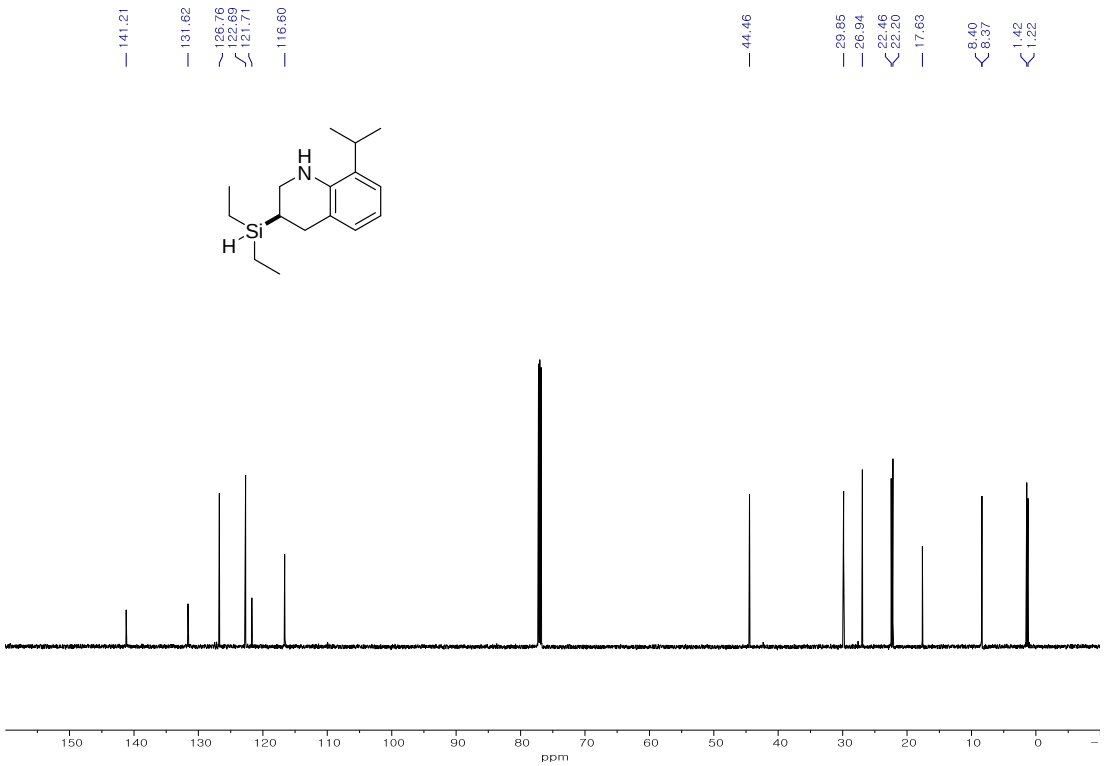


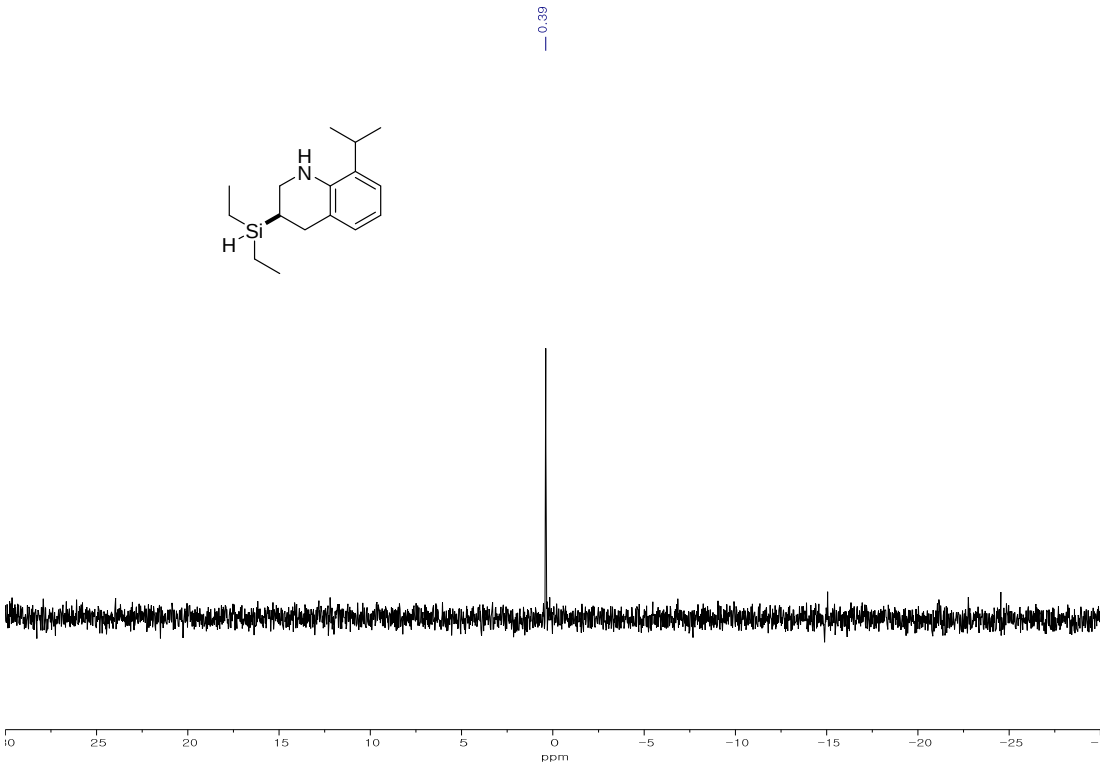

142.42
127.74
126.82
121.20
121.18
116.22
44.32
29.42
17.58
17.03
8.35
8.33
1.33
1.14
Me
H
N
Si
H
ppm


0.43
Me
H
N
Si
H
ppm

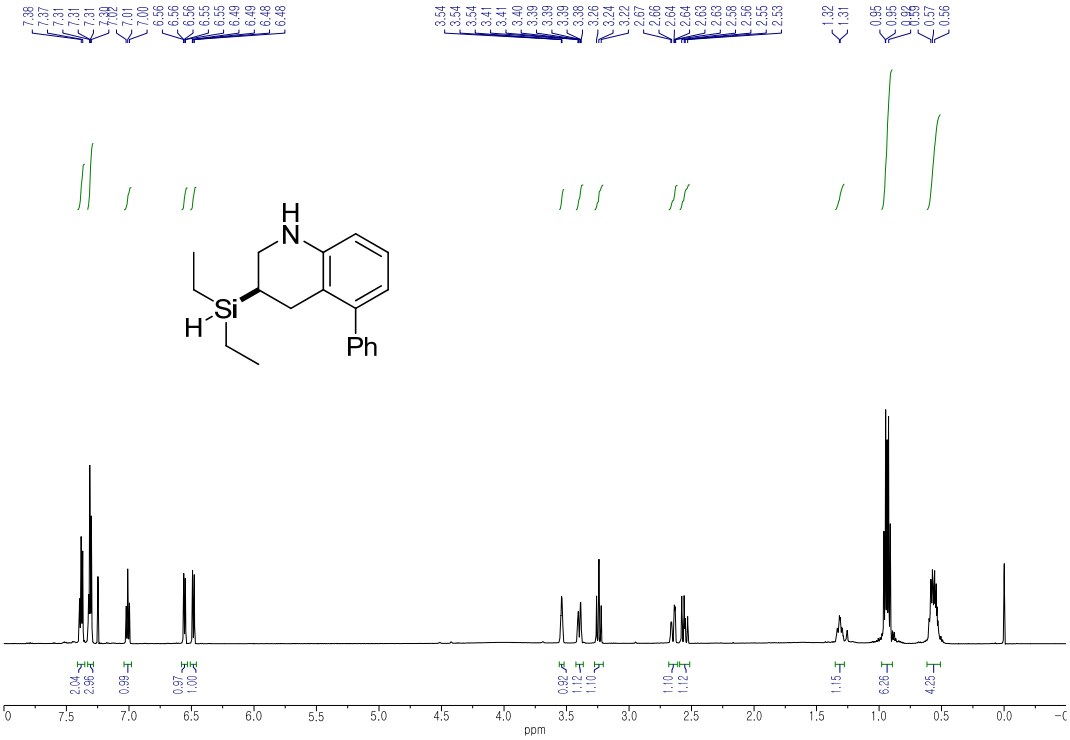
3-(Diethylsilyl)-8-isopropyl-1,2,3,4-tetrahydroquinoline (Table 1, 5b)

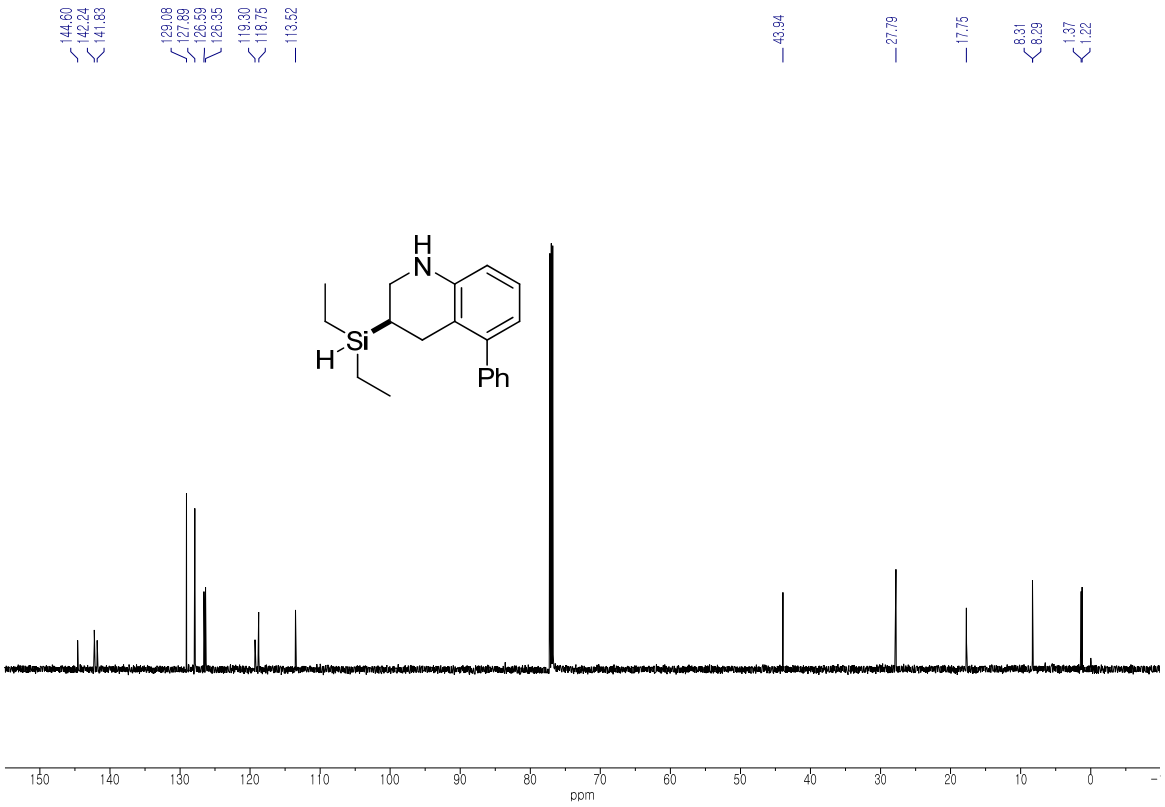


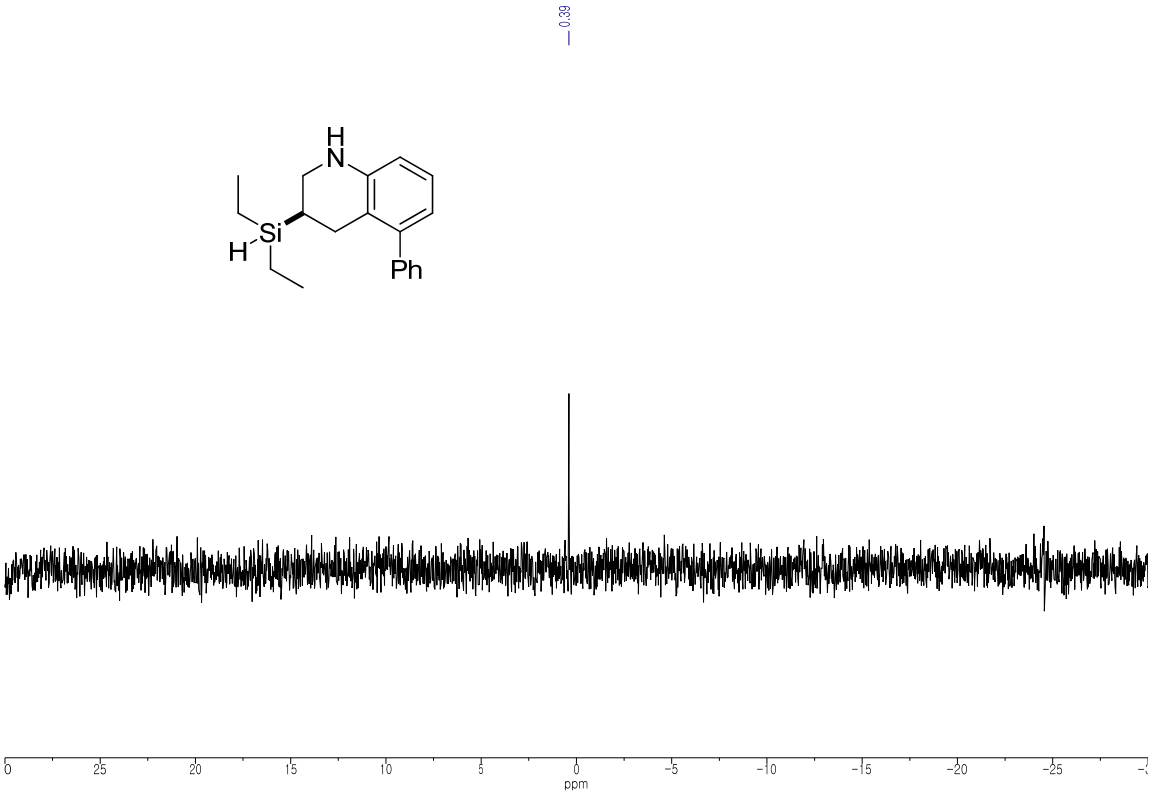




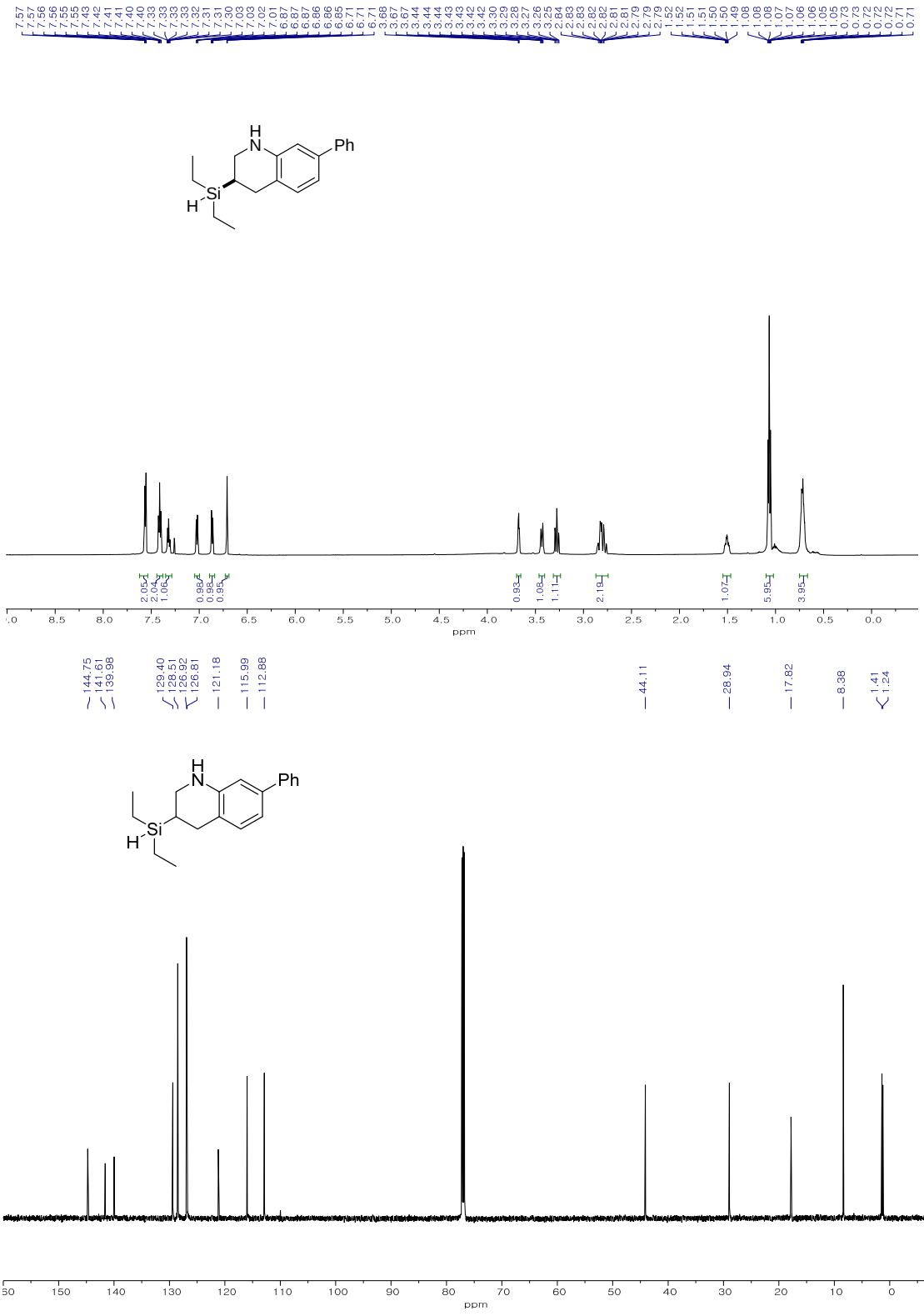
3-(Diethylsilyl)-5-phenyl-1,2,3,4-tetrahydroquinoline (Table 1, 6b)

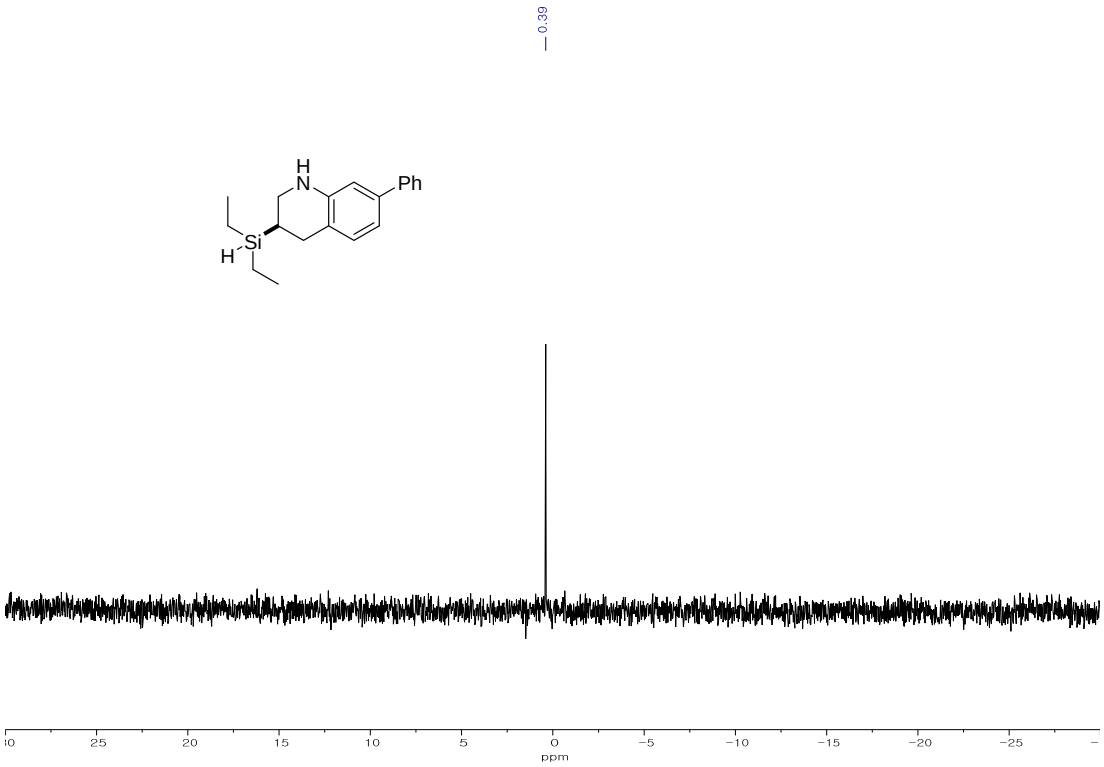



144.60
142.24
141.83
129.08
127.89
126.59
126.35
119.30
118.75
113.52
43.94
27.79
17.75
8.31
8.29
1.37
1.22
H
N
Si
H
Ph
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

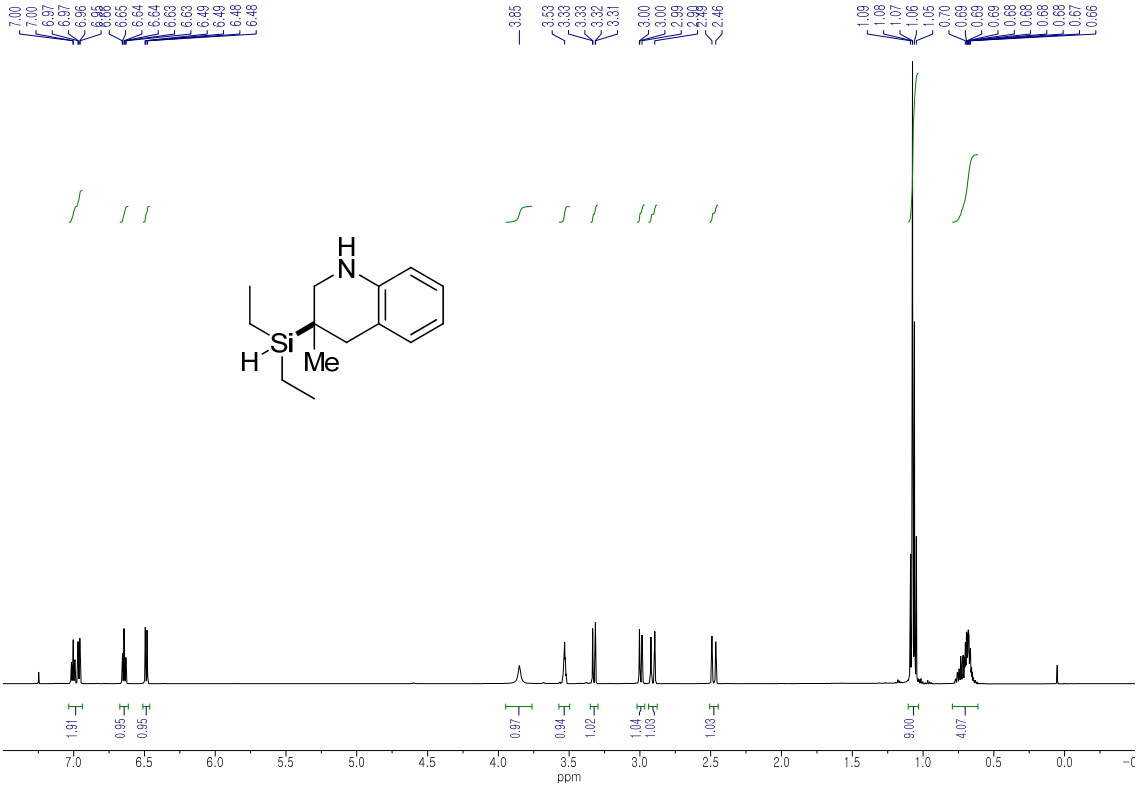

0.39
H
N
Si
H
Ph
0
25
20
15
10
5
0
−5
−10
−15
−20
−25
ppm

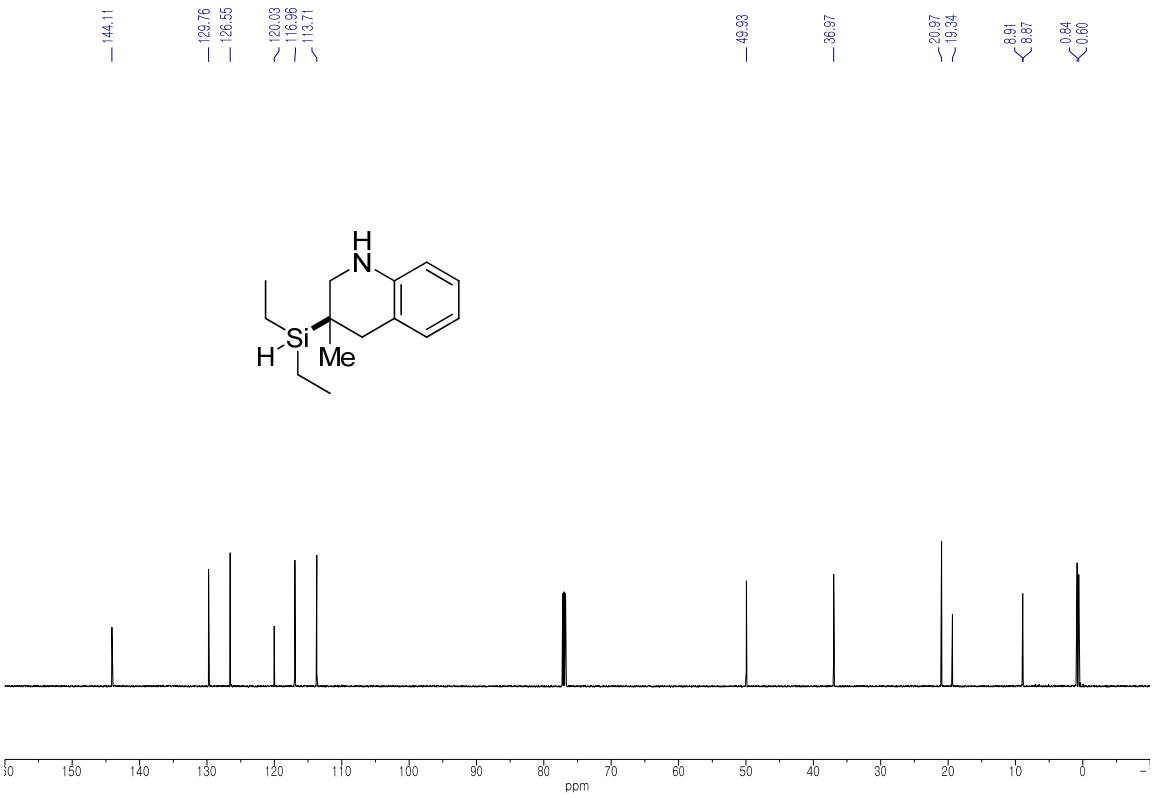
3-(Diethylsilyl)-7-phenyl-1,2,3,4-tetrahydroquinoline (Table 1, 7b)

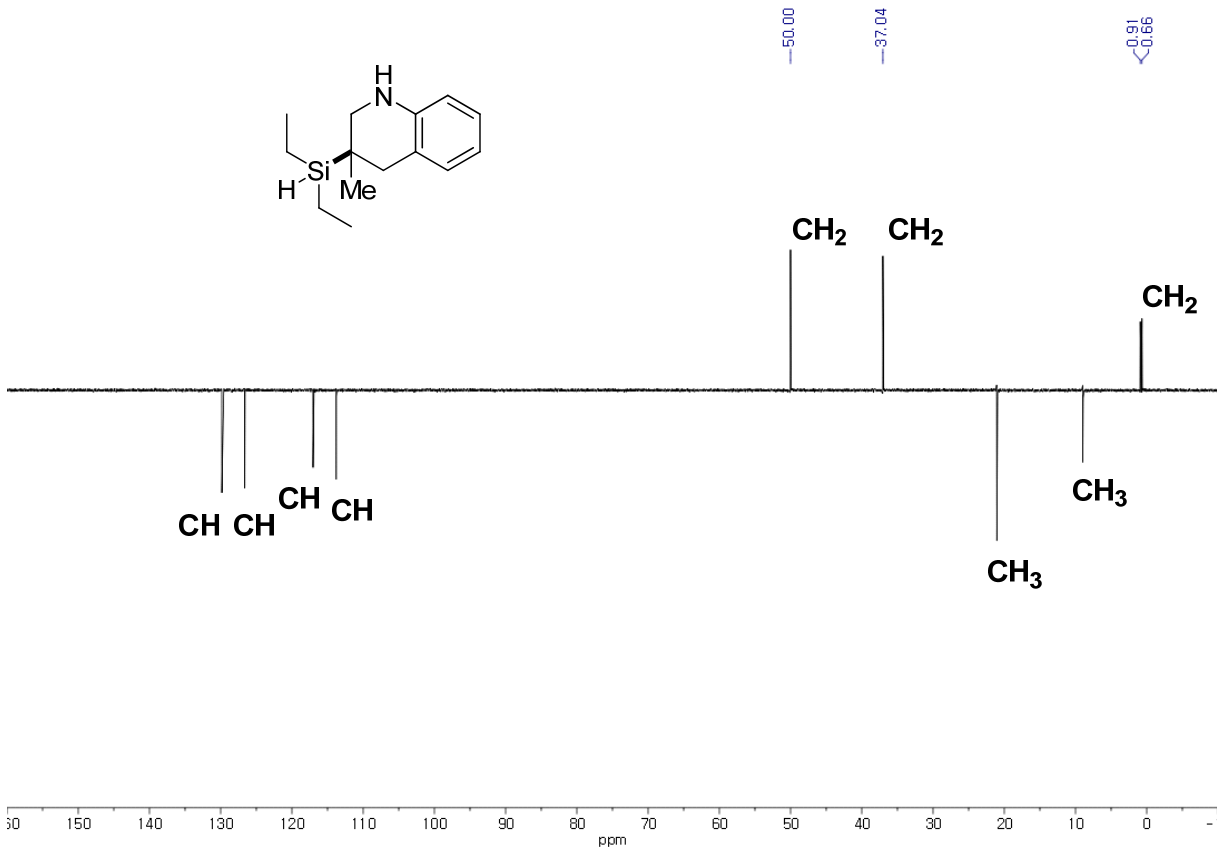


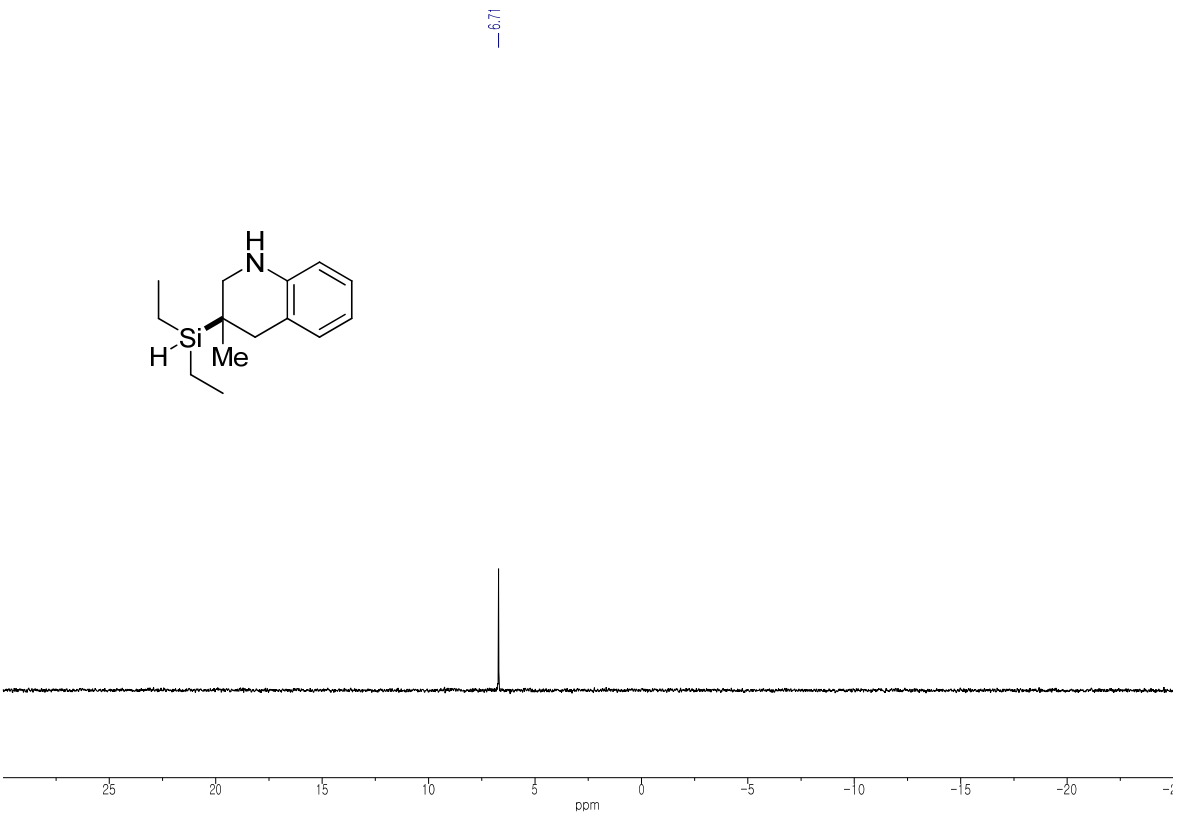


3-(Diethylsilyl)-3-methyl-1,2,3,4-tetrahydroquinoline (Table 1, 8b)

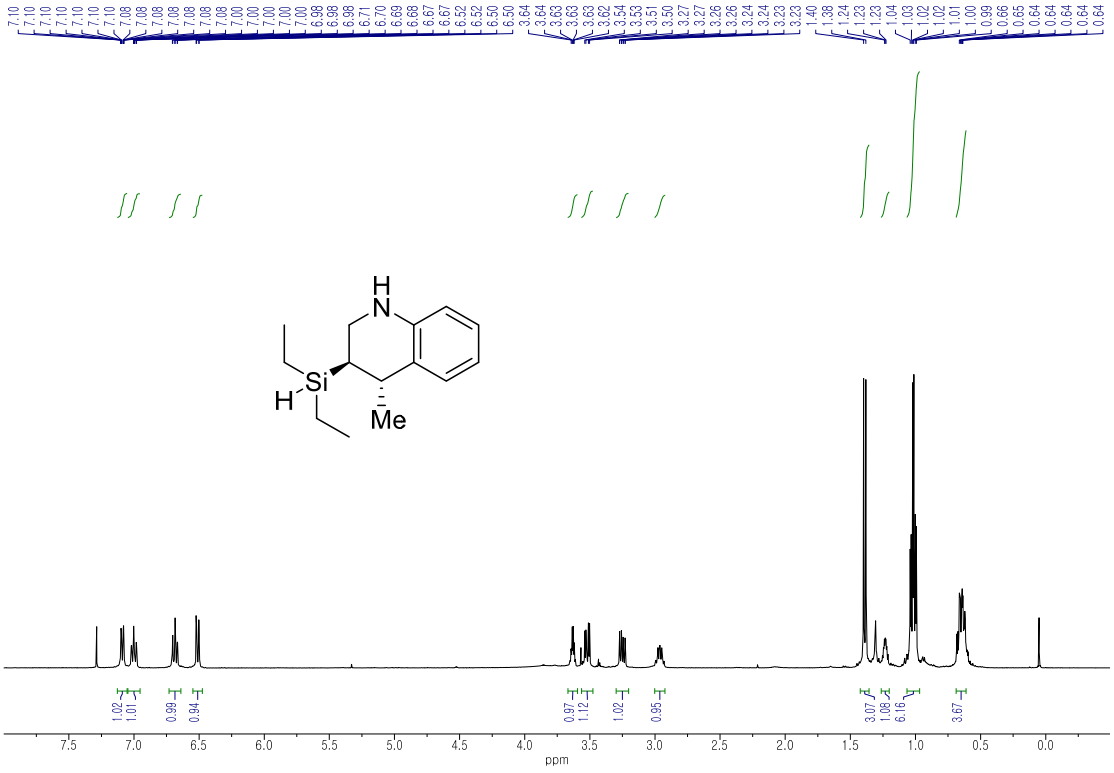



144.11
129.76
126.55
120.03
116.96
113.71
49.93
36.97
20.97
19.34
8.91
8.87
0.84
0.60
H
N
Si
H
Me
ppm

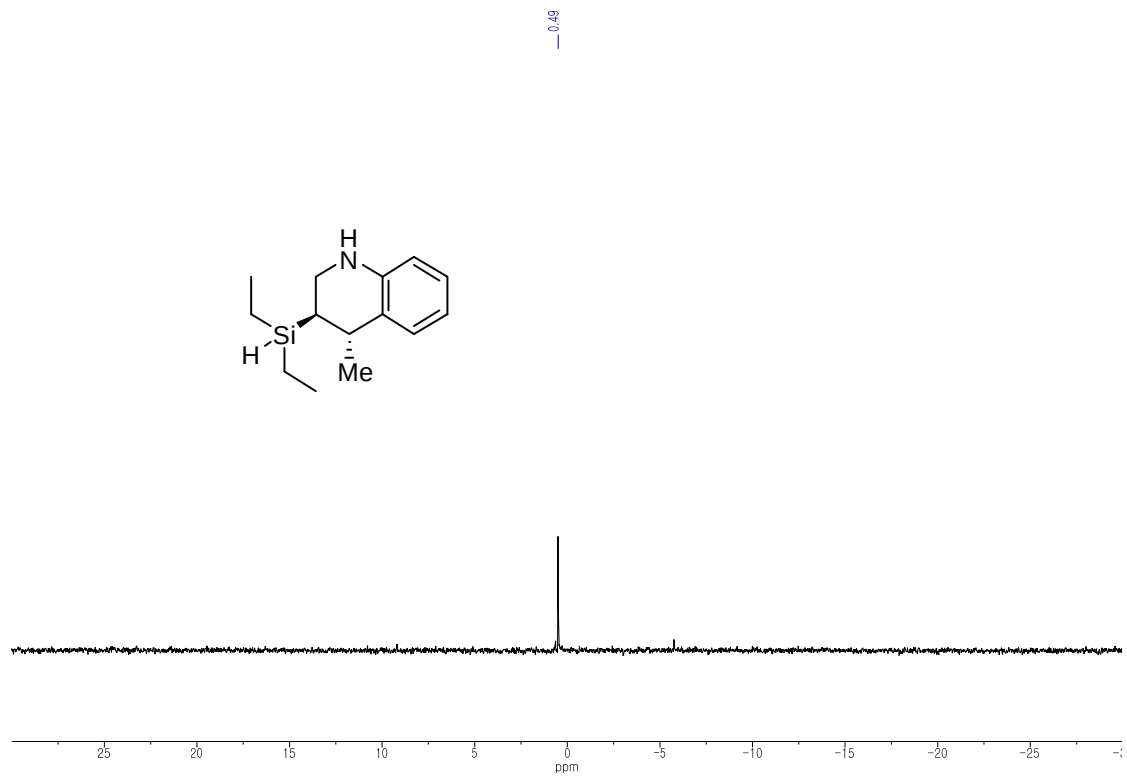

50.00
37.04
0.91
0.66
H
N
Si
H
Me
CH2
CH2
CH2
CH
CH
CH
CH
CH3
CH3
ppm



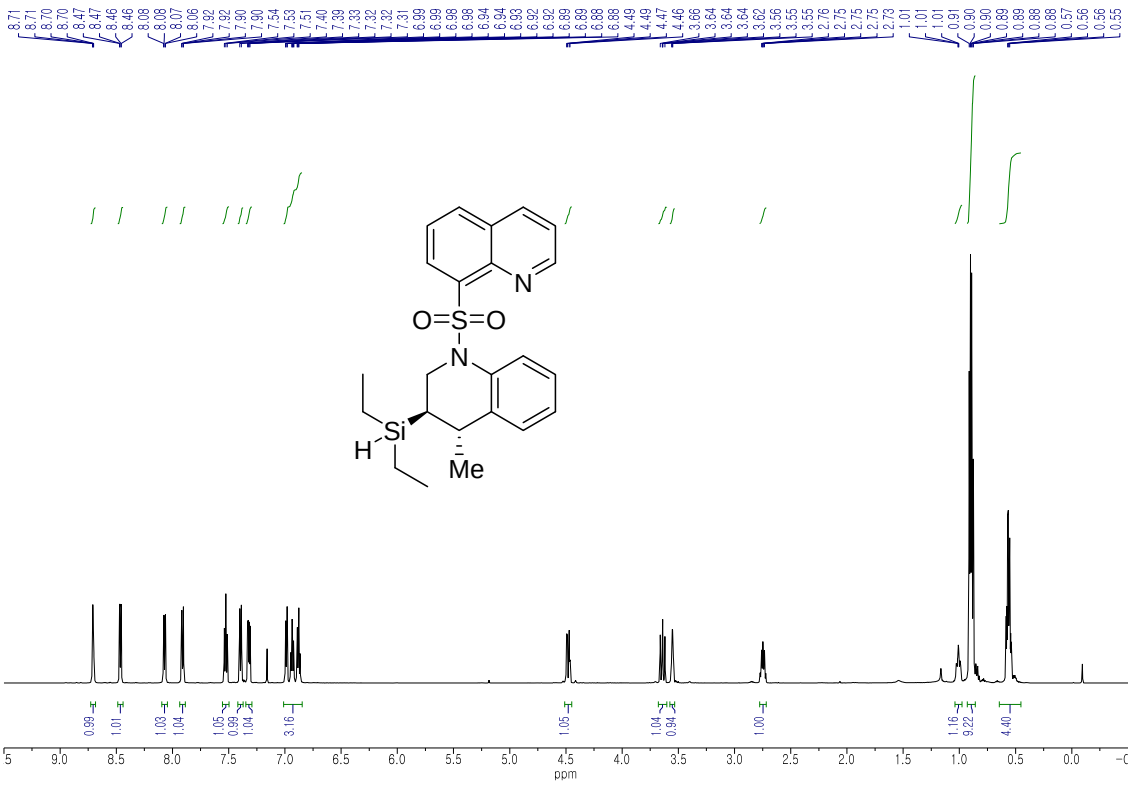
3-(Diethylsilyl)-4-methyl-1,2,3,4-tetrahydroquinoline (Table 1, 9b)

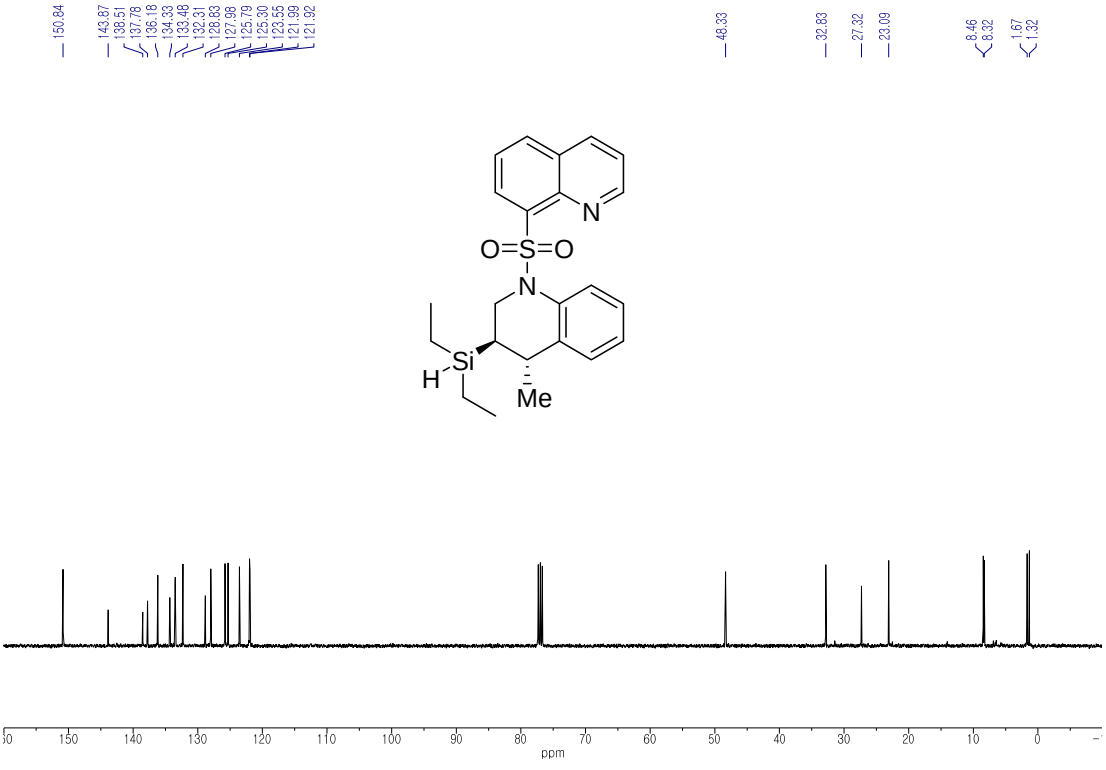


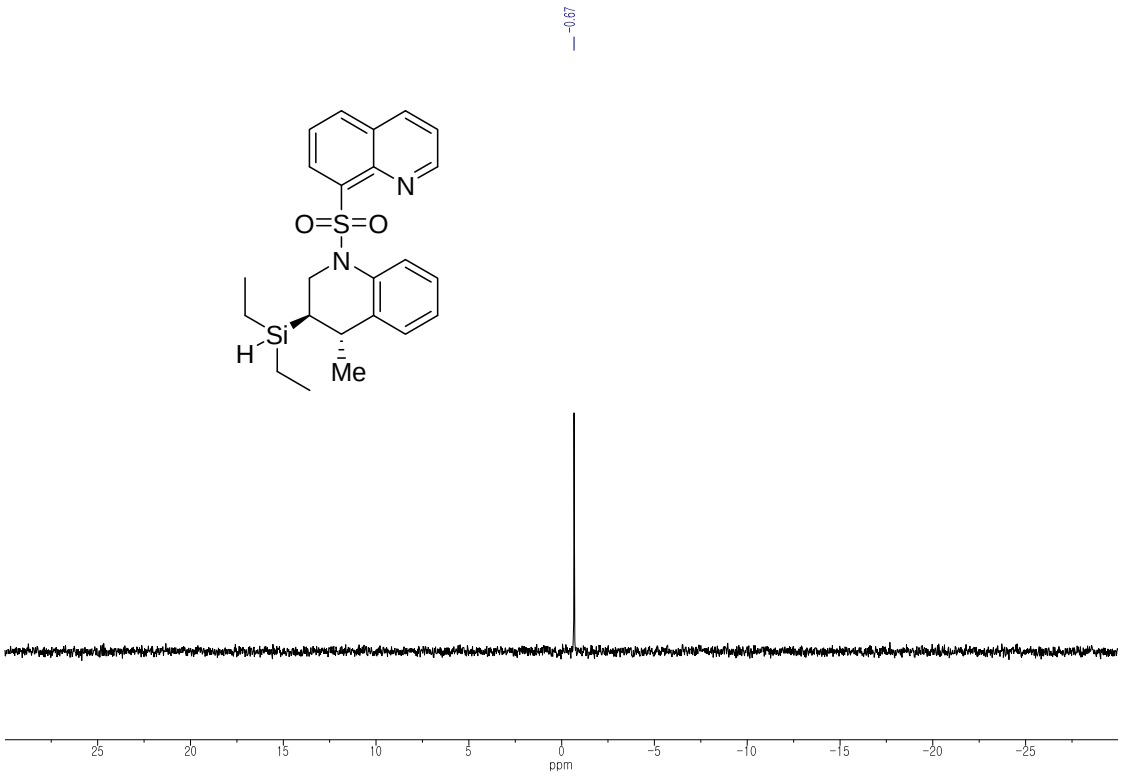

144.64
128.99
126.88
126.51
117.23
114.46
40.53
32.10
25.24
25.08
8.54
8.47
1.92
1.78
H
N
Si
H
Me
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


0.49
H
N
Si
H
Me
25
20
15
10
5
0
-5
-10
-15
-20
-25
ppm

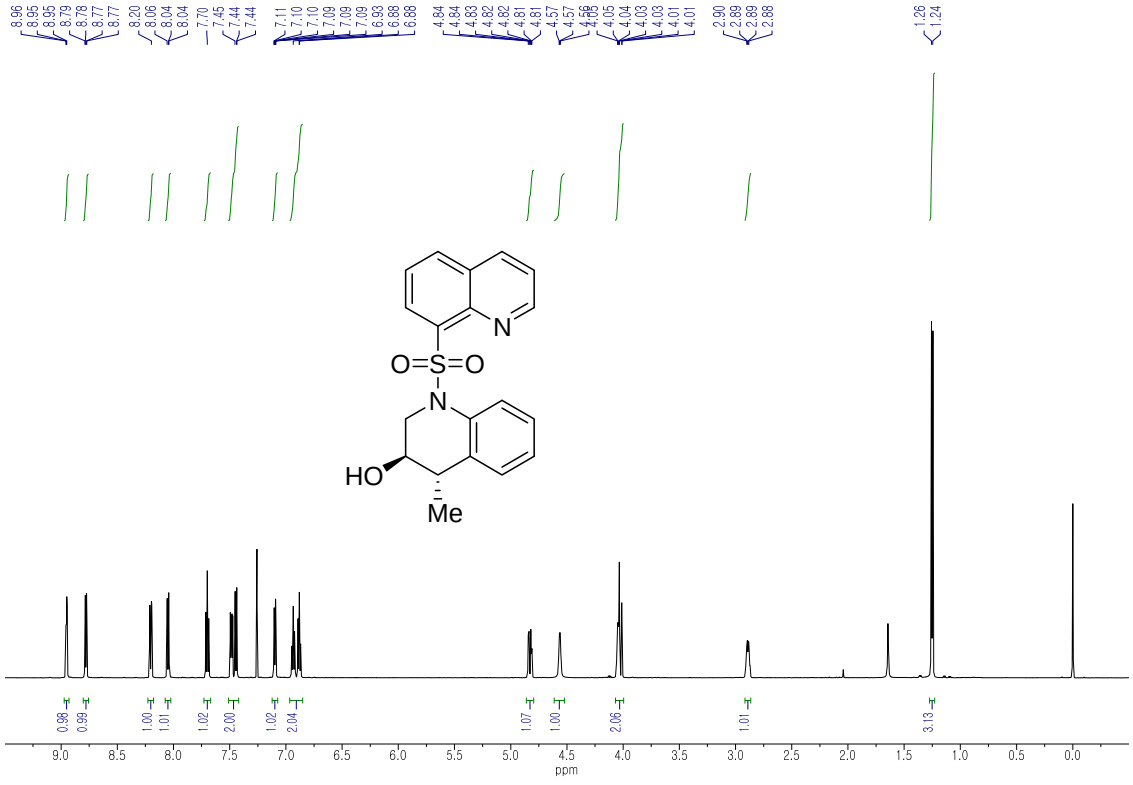
8-(3-(Diethylsilyl)-4-methyl-3,4-dihydroquinolin-1(2*H*)-ylsulfonyl)quinolone(Table 1, 9b-QUS)

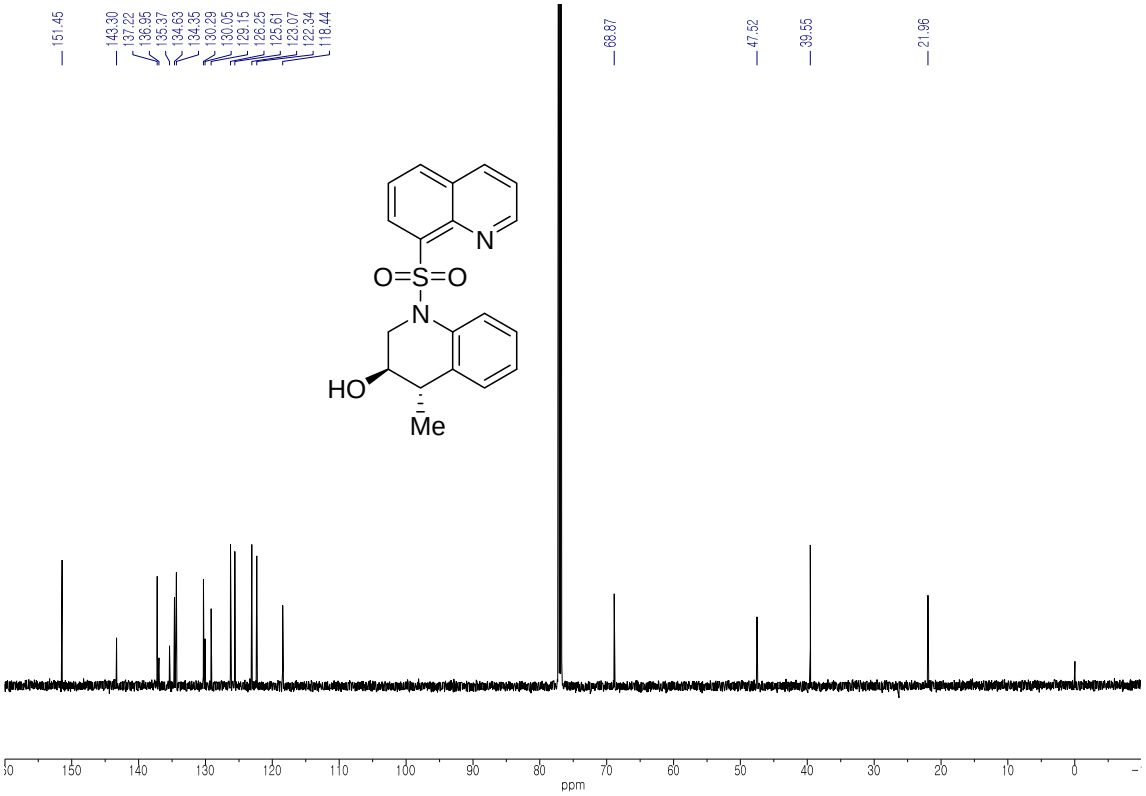




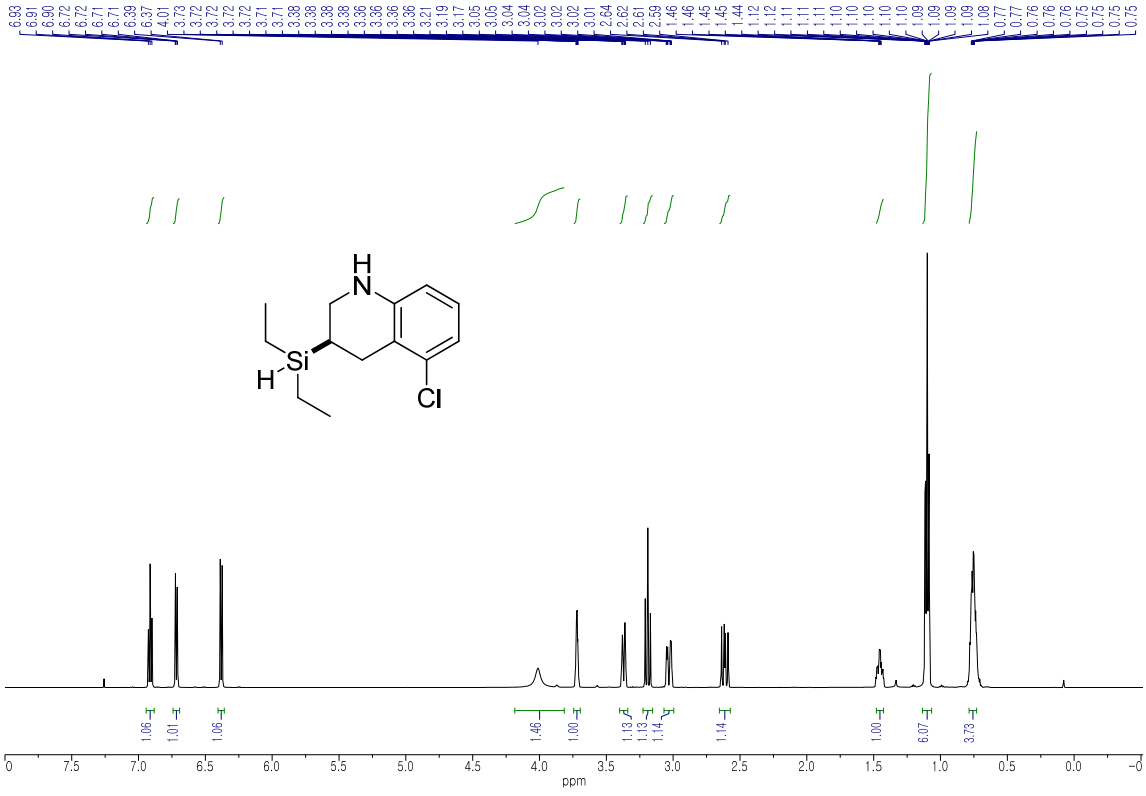


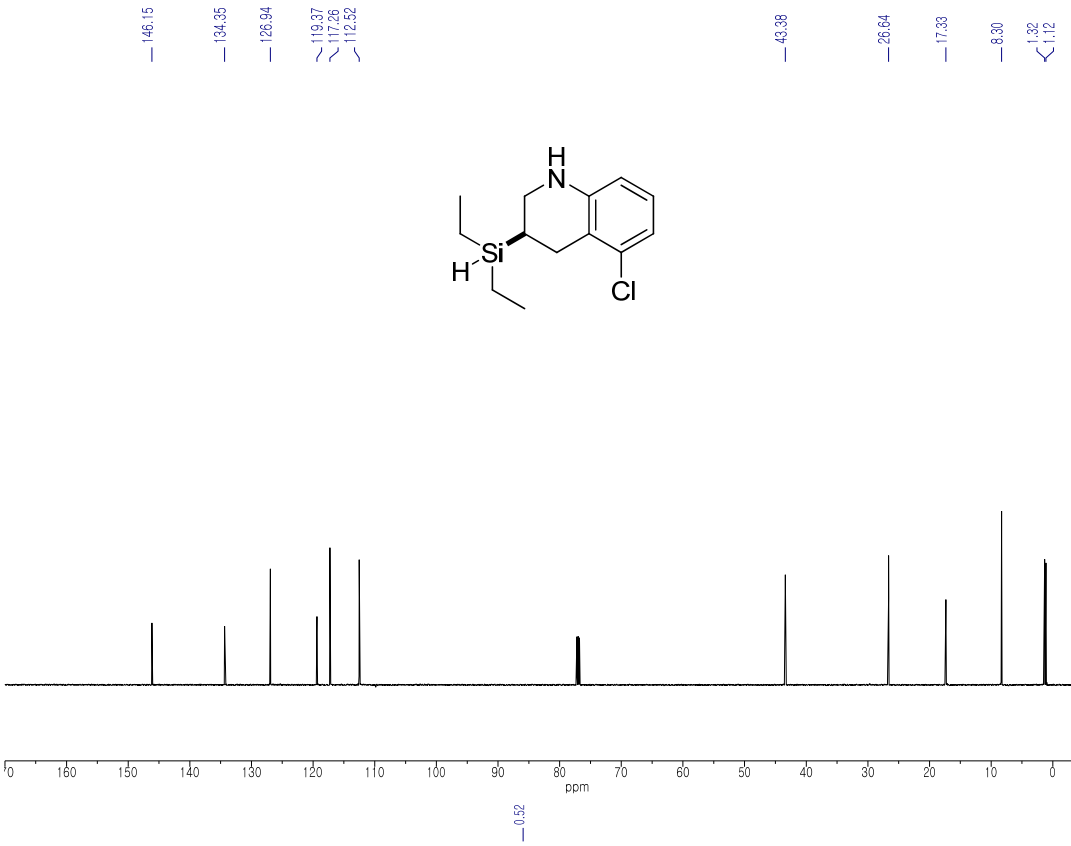
4-Methyl-1-(quinolin-8-ylsulfonyl)-1,2,3,4-tetrahydroquinolin-3-ol (Table 1, 9b-QUS-C3-OH)



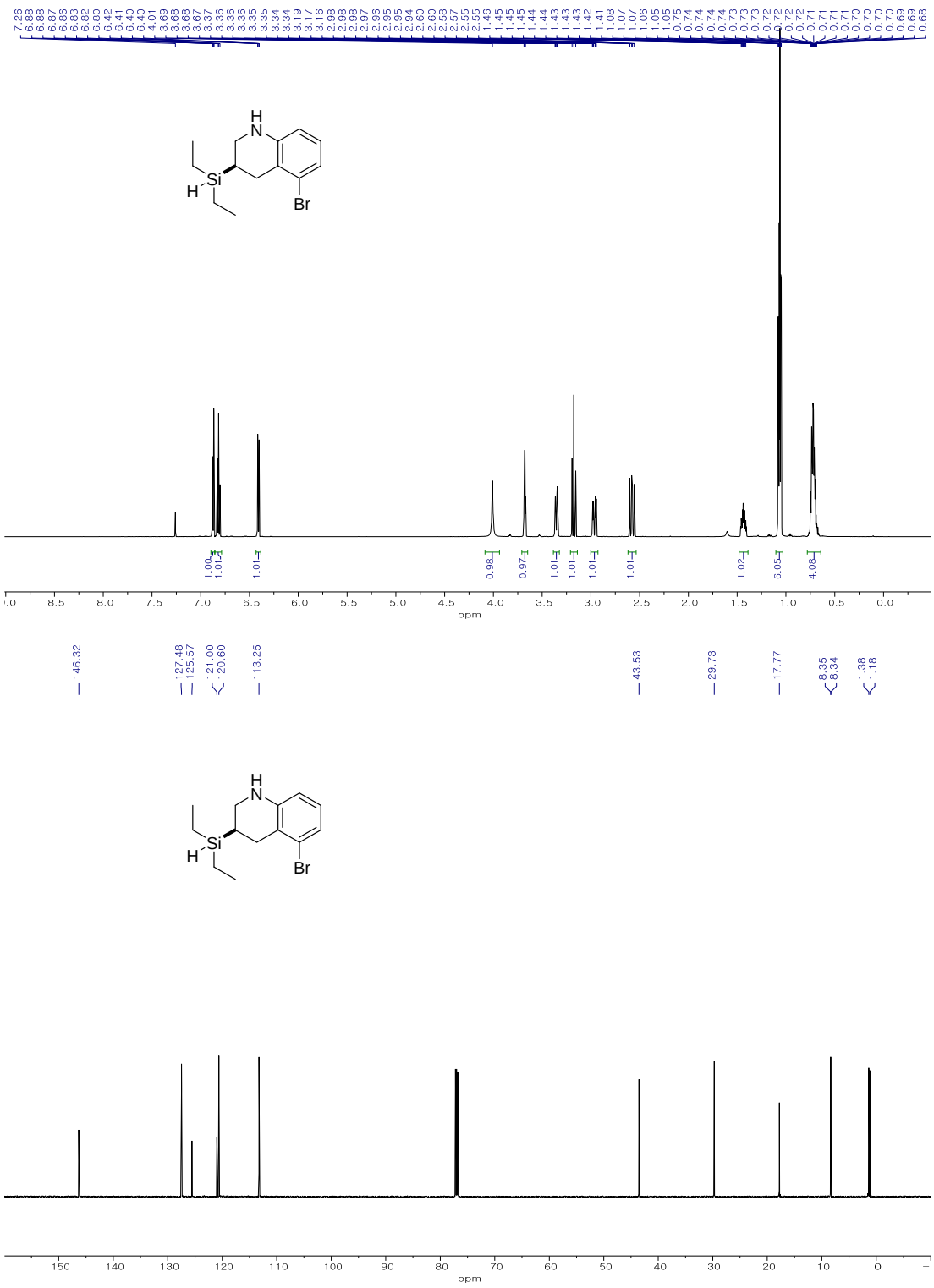


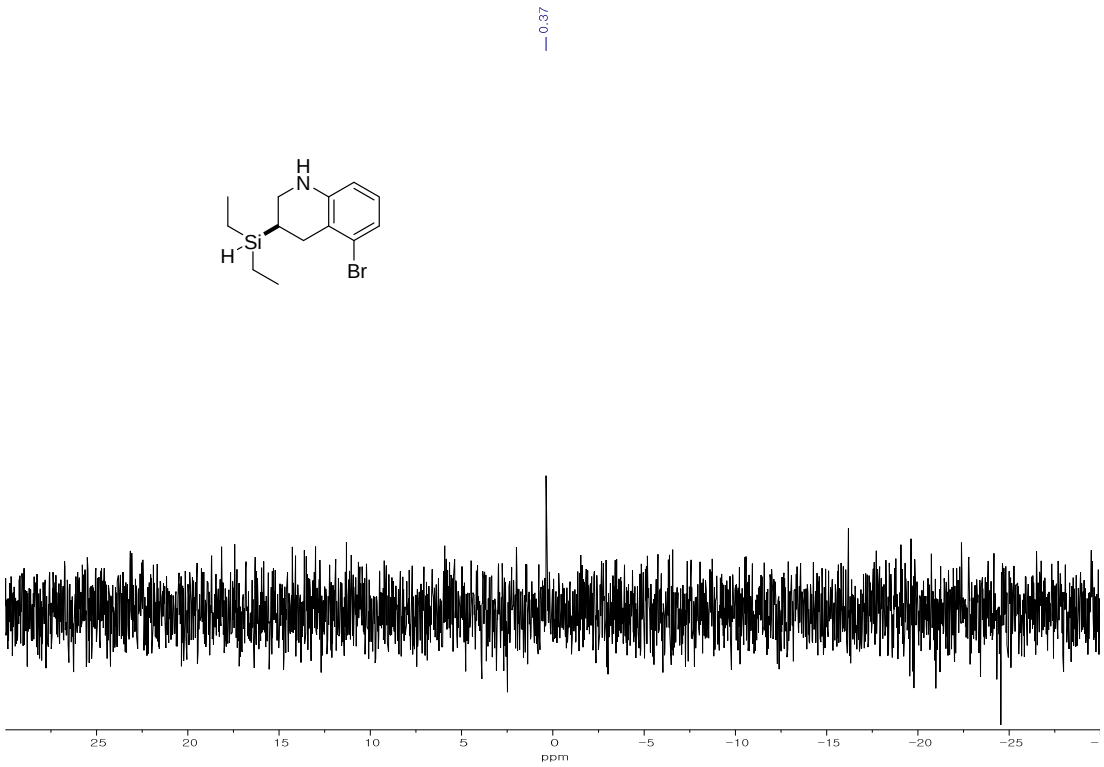
5-Chloro-3-(diethylsilyl)-1,2,3,4-tetrahydroquinoline (Table 1, 10b)



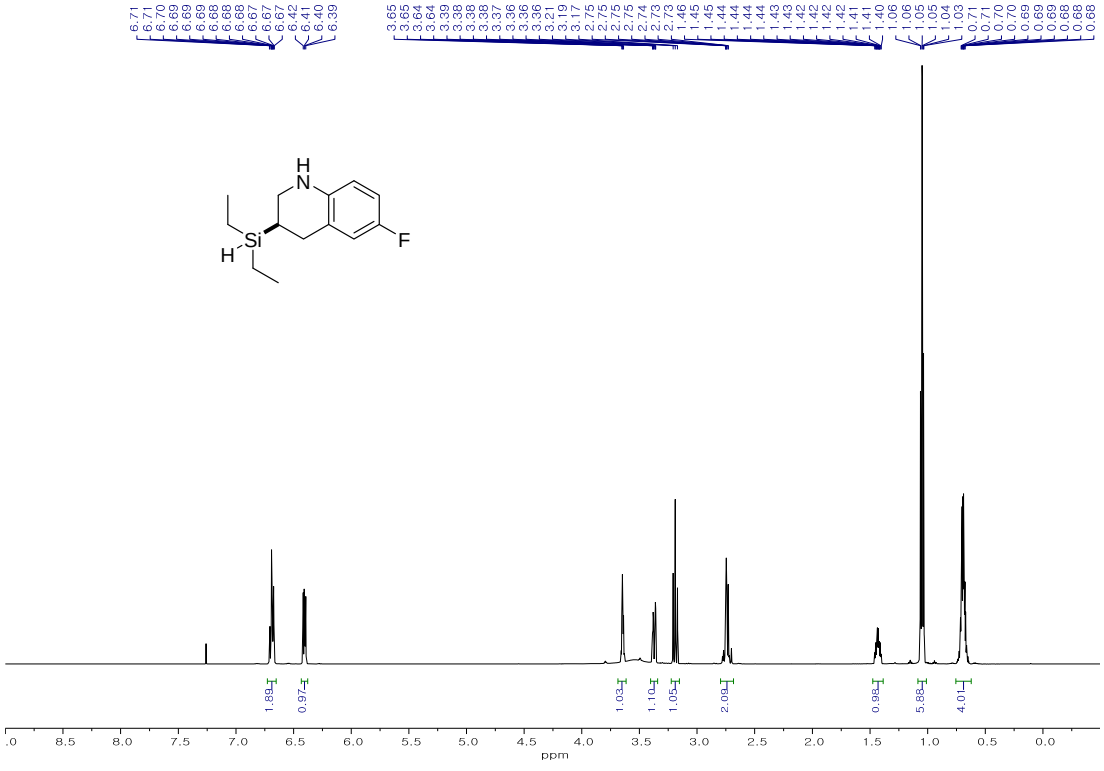

146.15
134.35
126.94
119.37
117.26
112.52
43.38
26.64
17.33
8.30
1.32
1.12
H
N
Si
H
Cl
ppm
0.52
H
N
Si
H
Cl
ppm

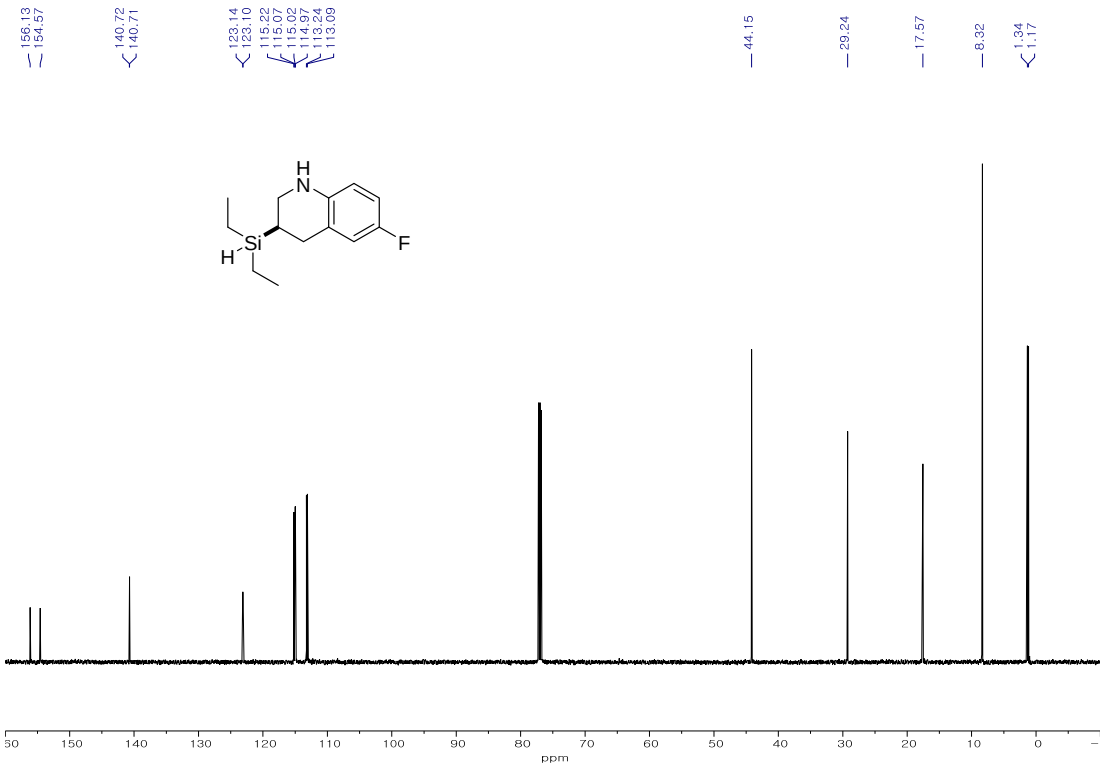
5-Bromo-3-(diethylsilyl)-1,2,3,4-tetrahydroquinoline (Table 1, 11b)

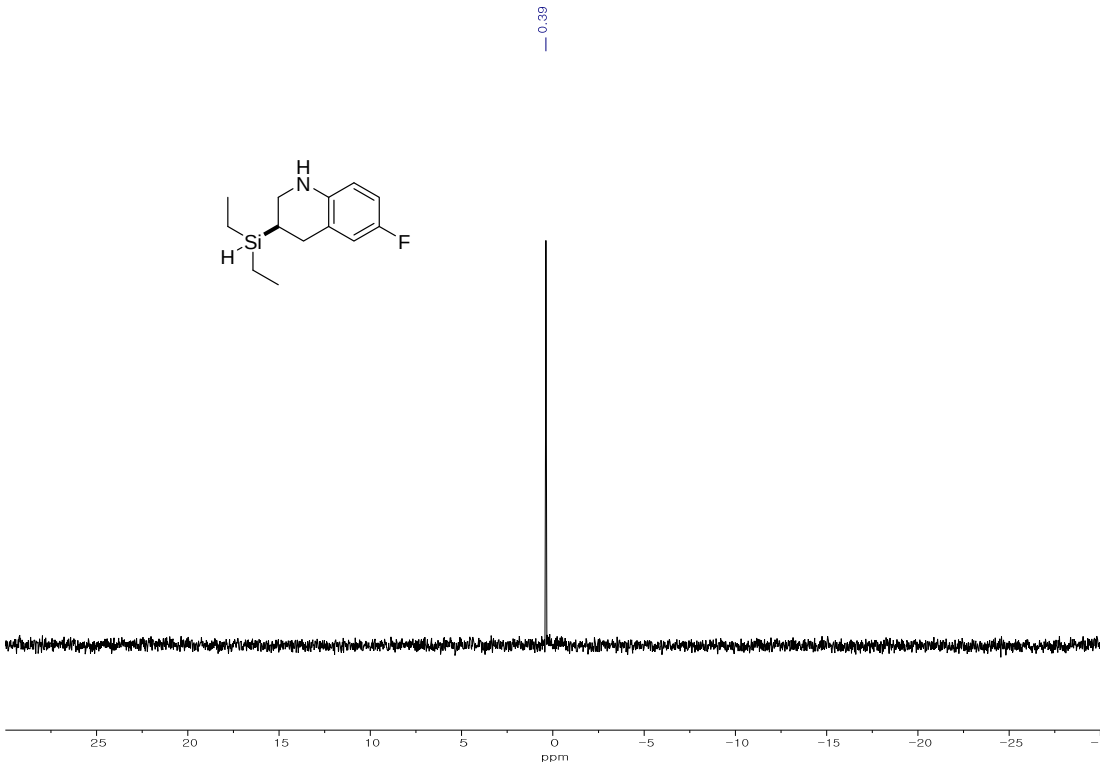




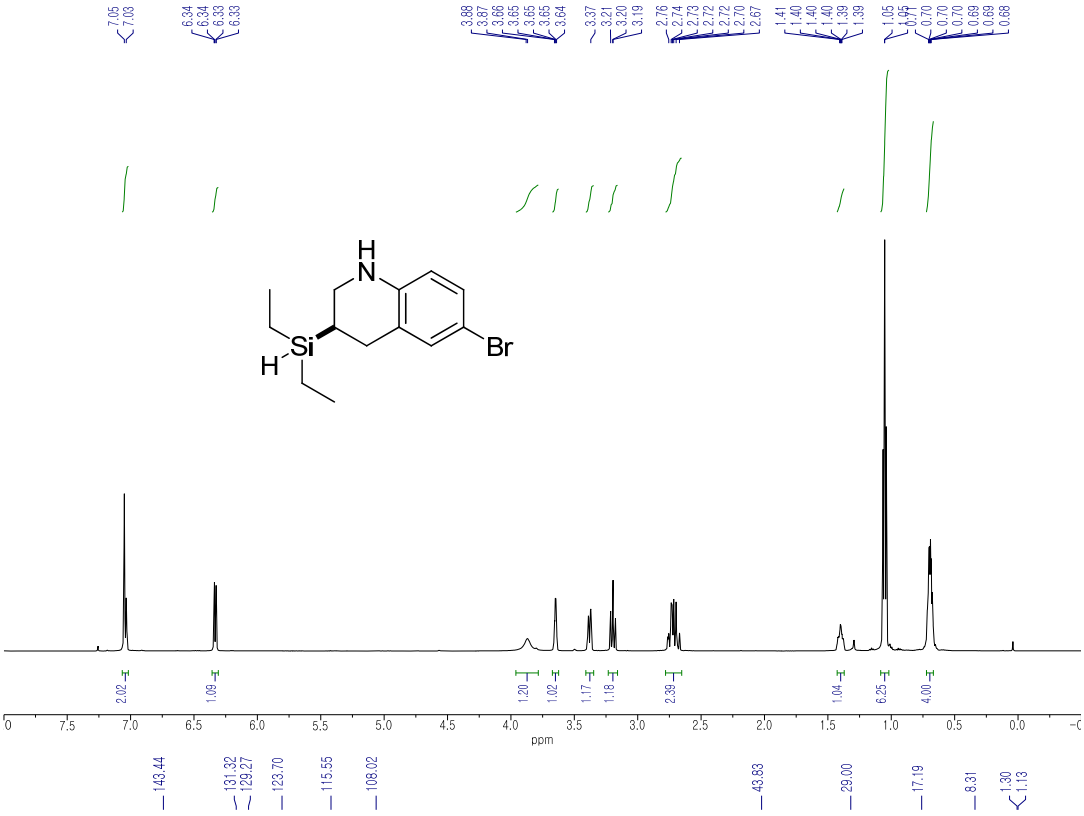
3-(Diethylsilyl)-6-fluoro-1,2,3,4-tetrahydroquinoline (Table 1, 12b)

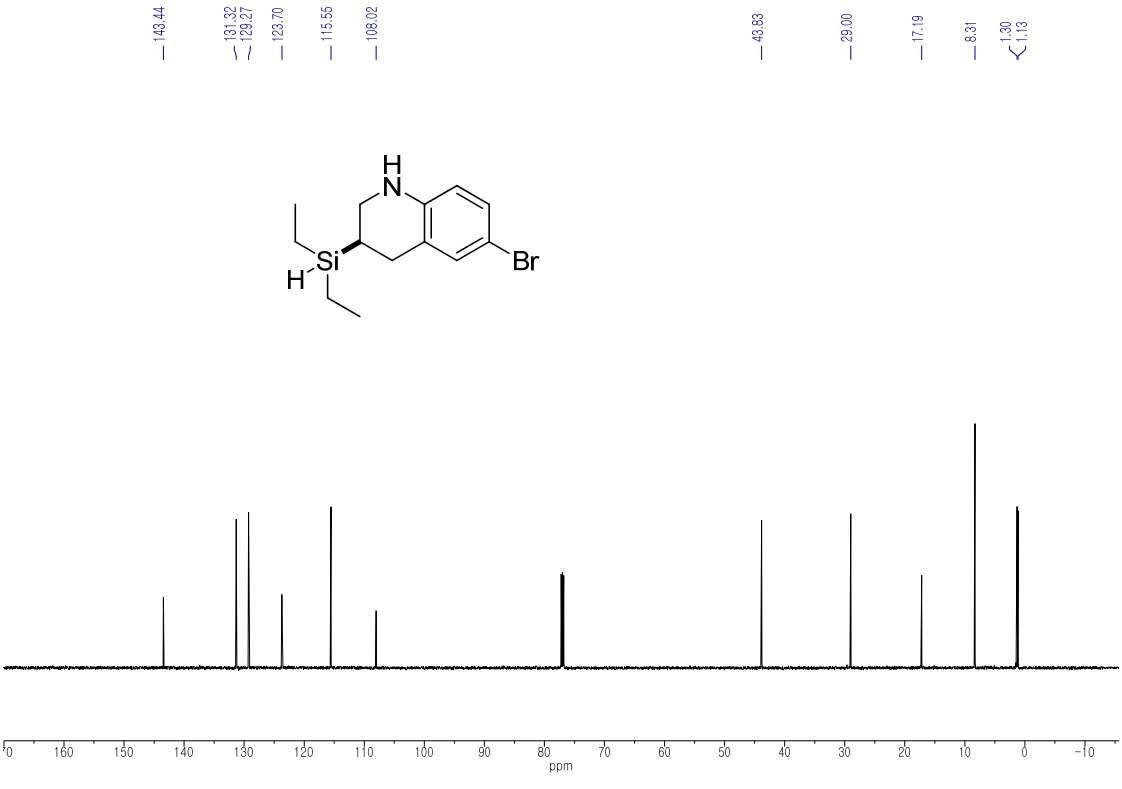


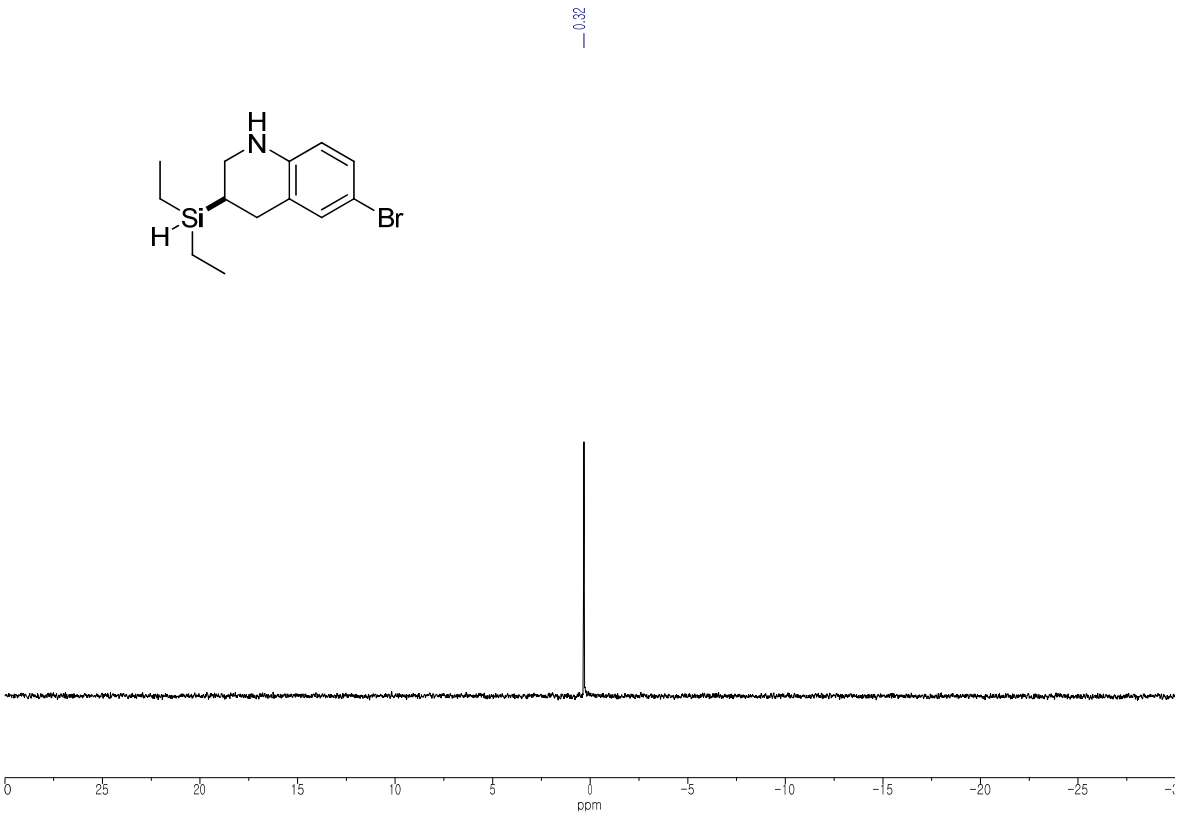

156.13
154.57
140.72
140.71
123.14
123.10
115.22
115.07
115.02
114.97
114.24
113.99
44.15
29.24
17.57
8.32
1.34
1.17
H
N
Si
H
F
ppm


0.39
H
N
Si
H
F
ppm

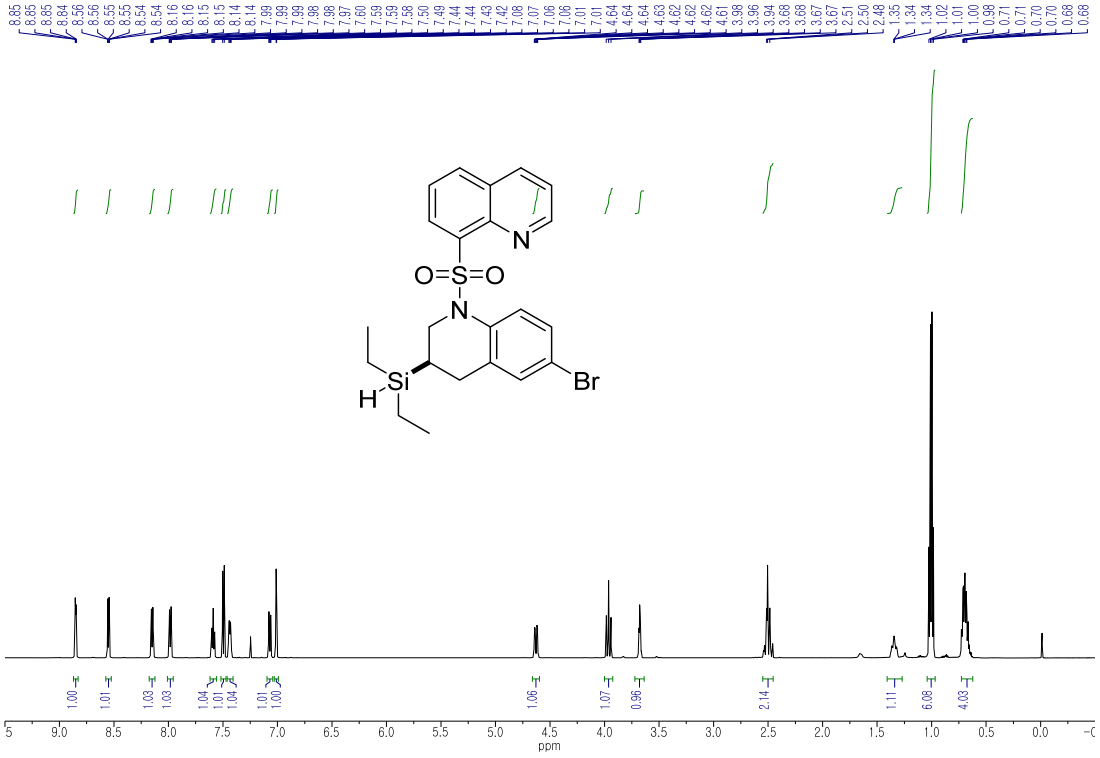
6-Bromo-3-(diethylsilyl)-1,2,3,4-tetrahydroquinoline (Table 1, 13b)

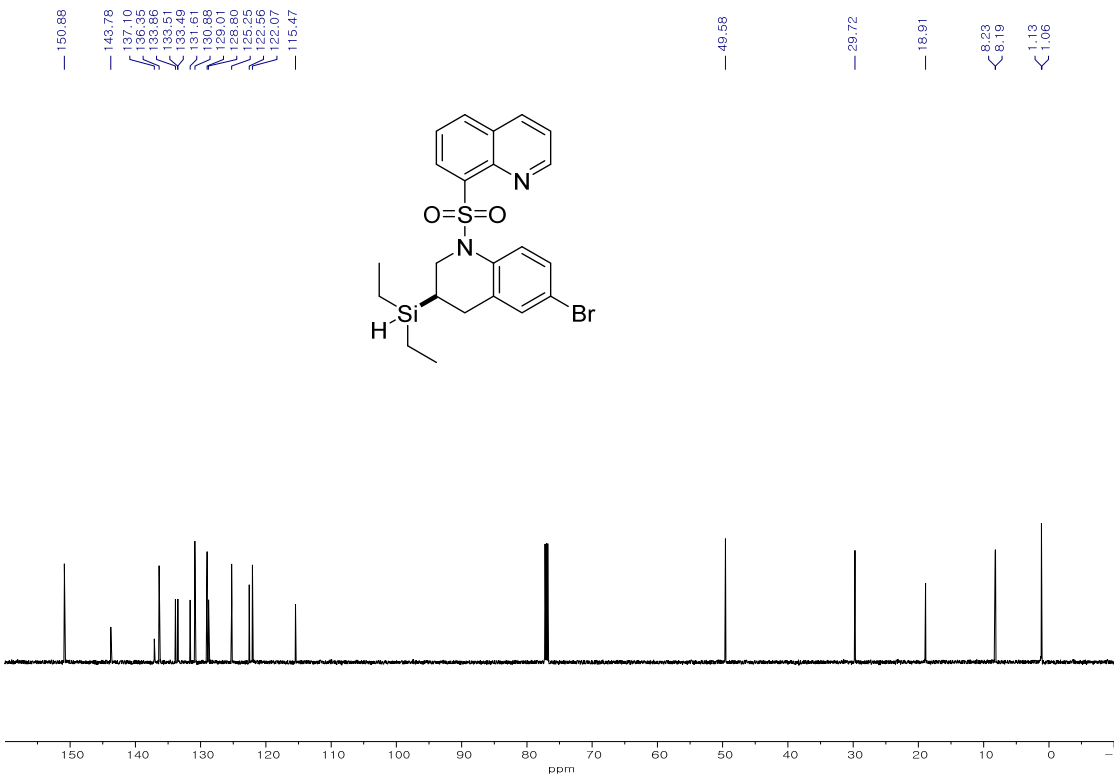


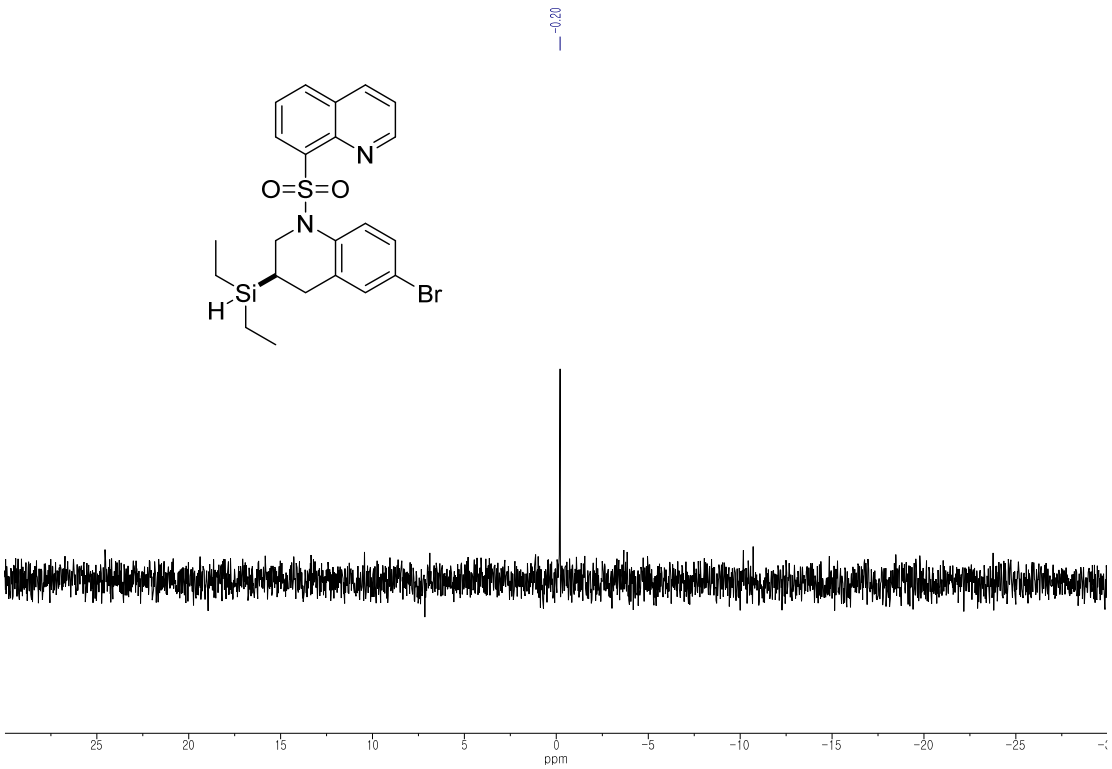




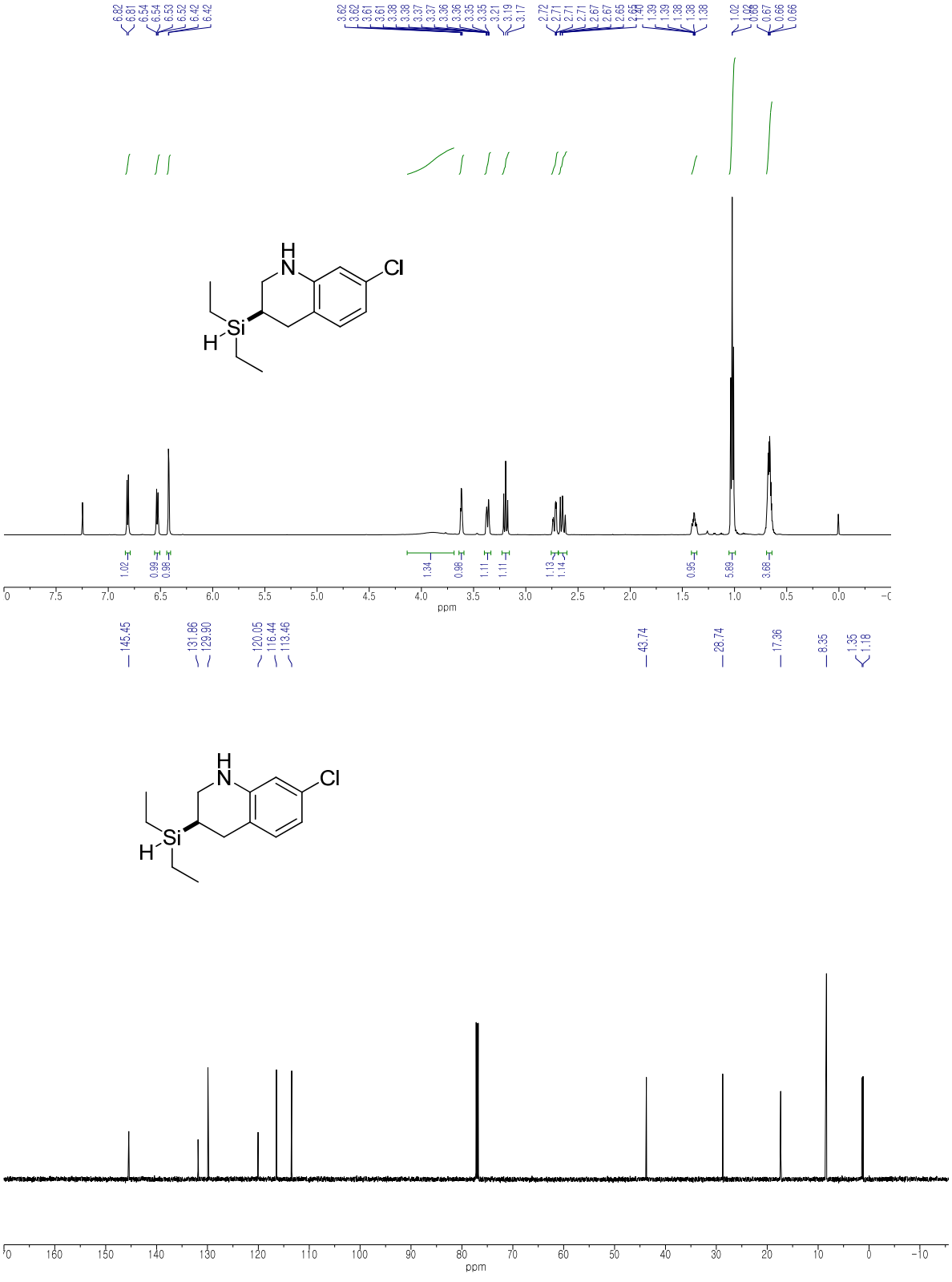
8-{6-Bromo-3-(diethylsilyl)-3,4-dihydroquinolin-1(2*H*)-ylsulfonyl}quinoline (Table 1, 13b-QUS)

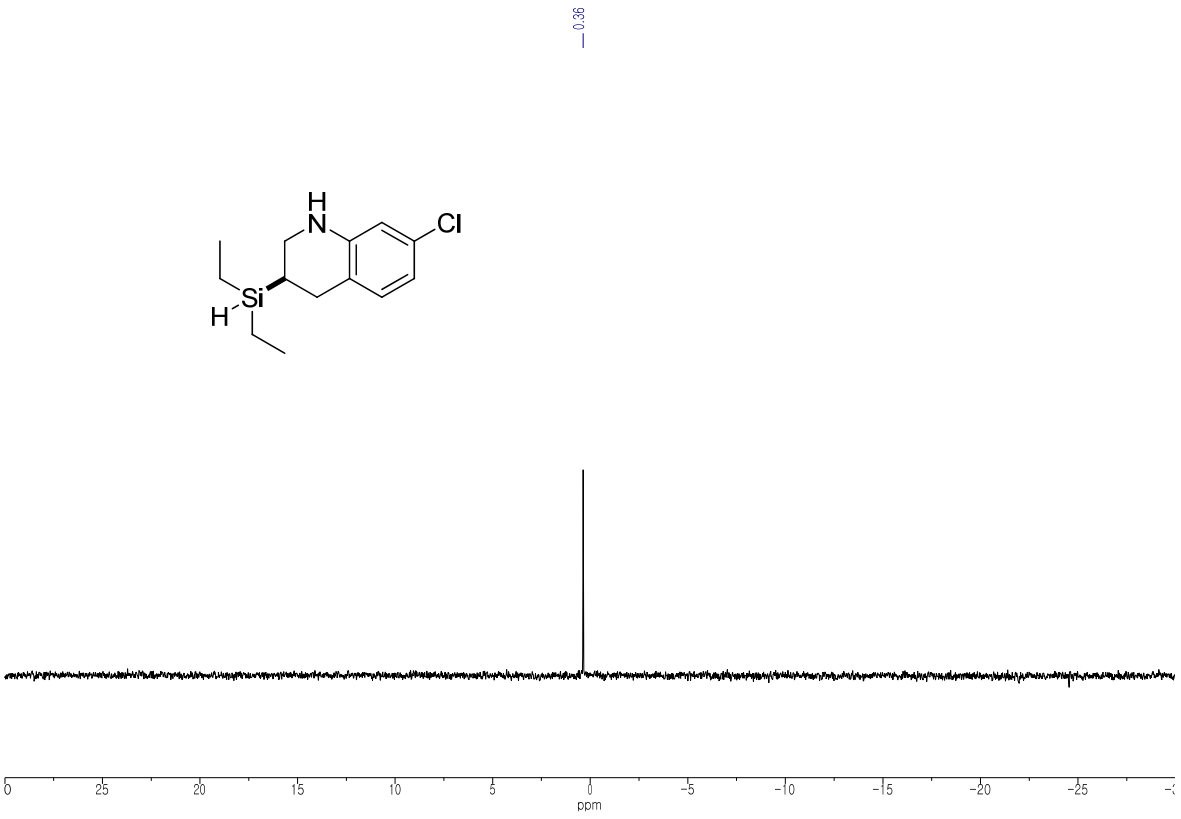



150.88
143.78
137.10
136.35
133.86
133.51
133.49
131.61
130.88
129.01
128.80
125.25
122.56
122.07
115.47
49.58
29.72
18.91
8.23
8.19
1.13
1.06
O=S=O
N
Si
H
Br
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

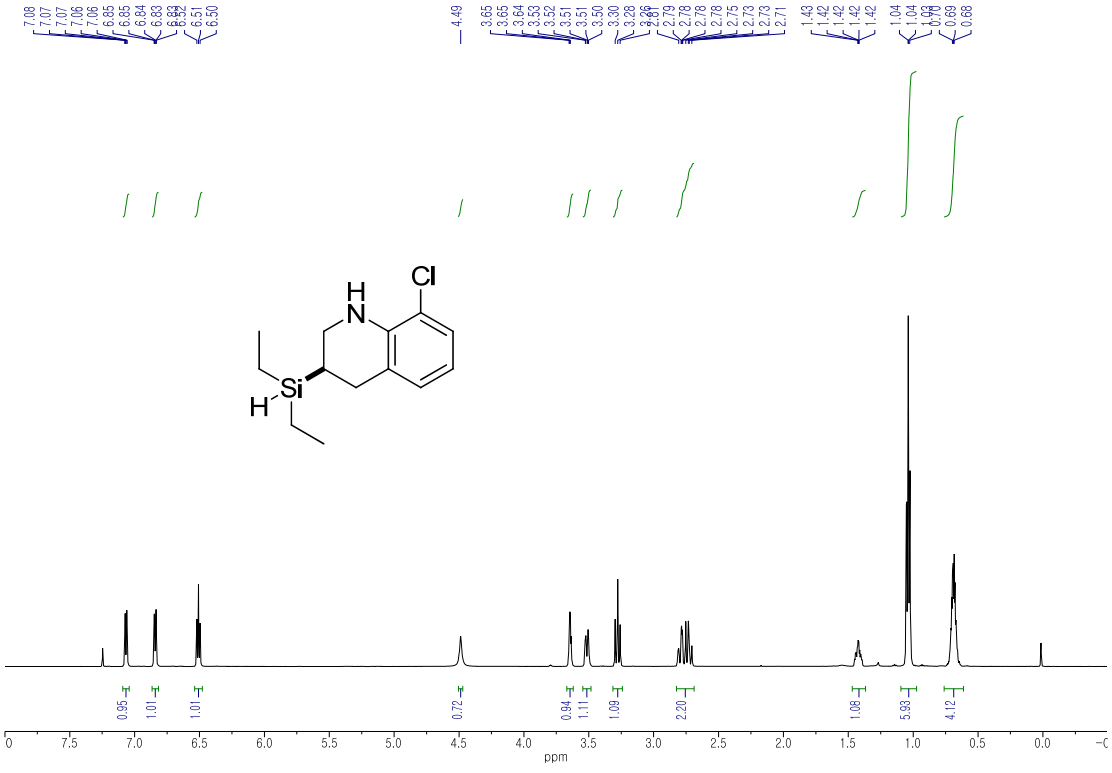

-0.20
O=S=O
N
Si
H
Br
25
20
15
10
5
0
-5
-10
-15
-20
-25
ppm

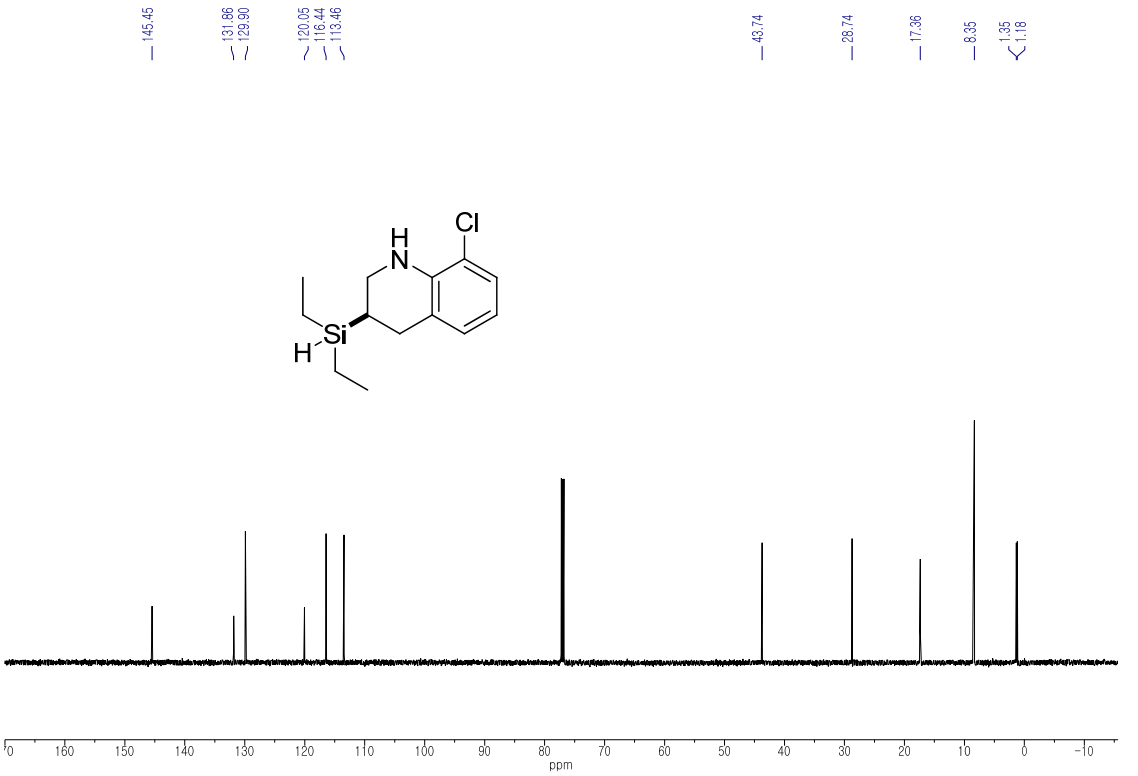
7-Chloro-3-(diethylsilyl)-1,2,3,4-tetrahydroquinoline (Table 1, 14b)

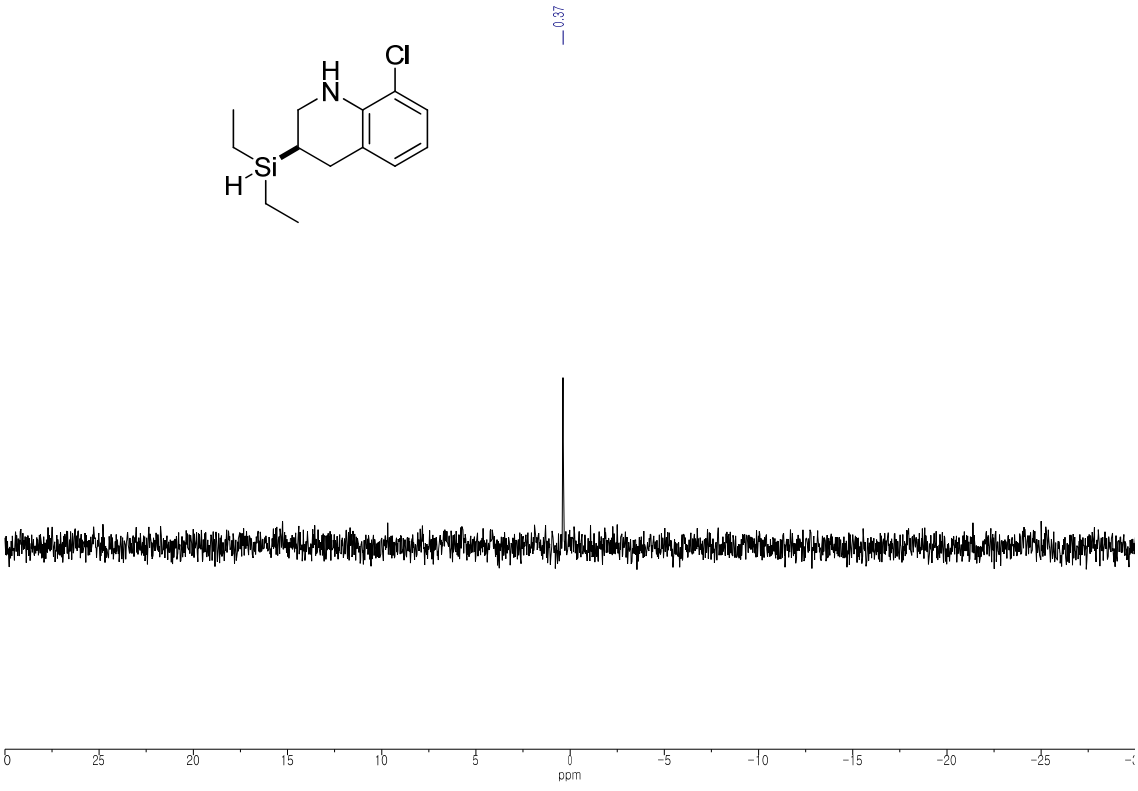




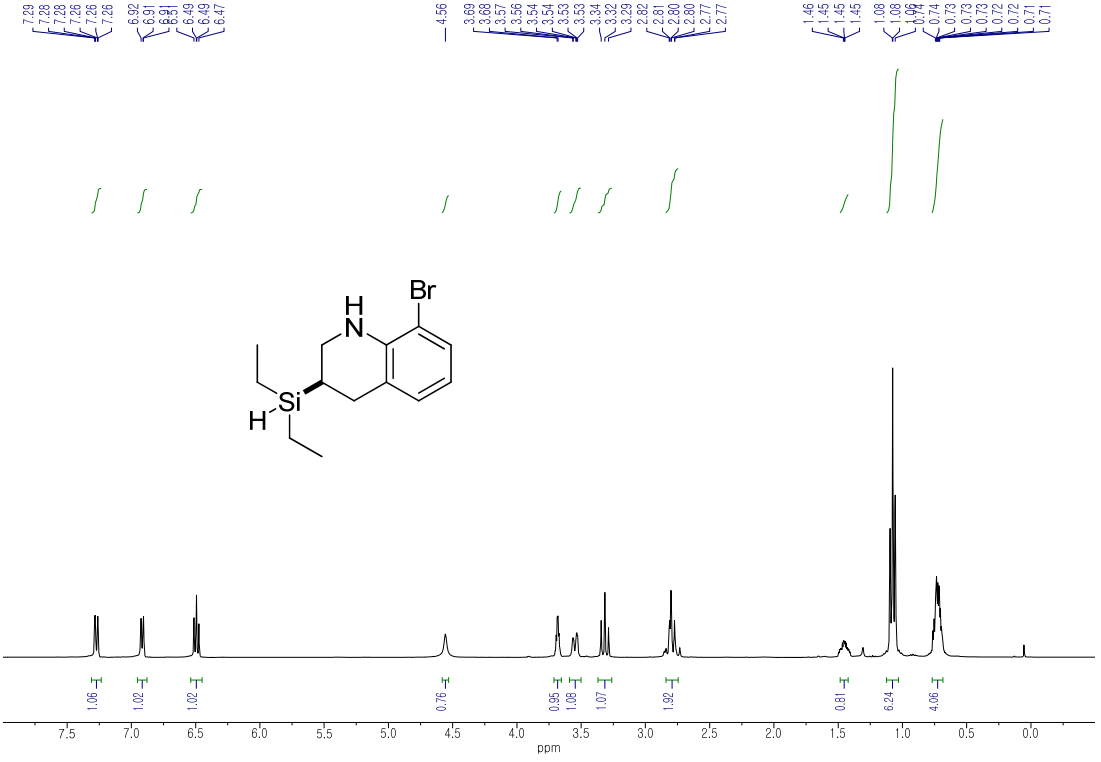
8-Chloro-3-(diethylsilyl)-1,2,3,4-tetrahydroquinoline (Table 1, 15b)

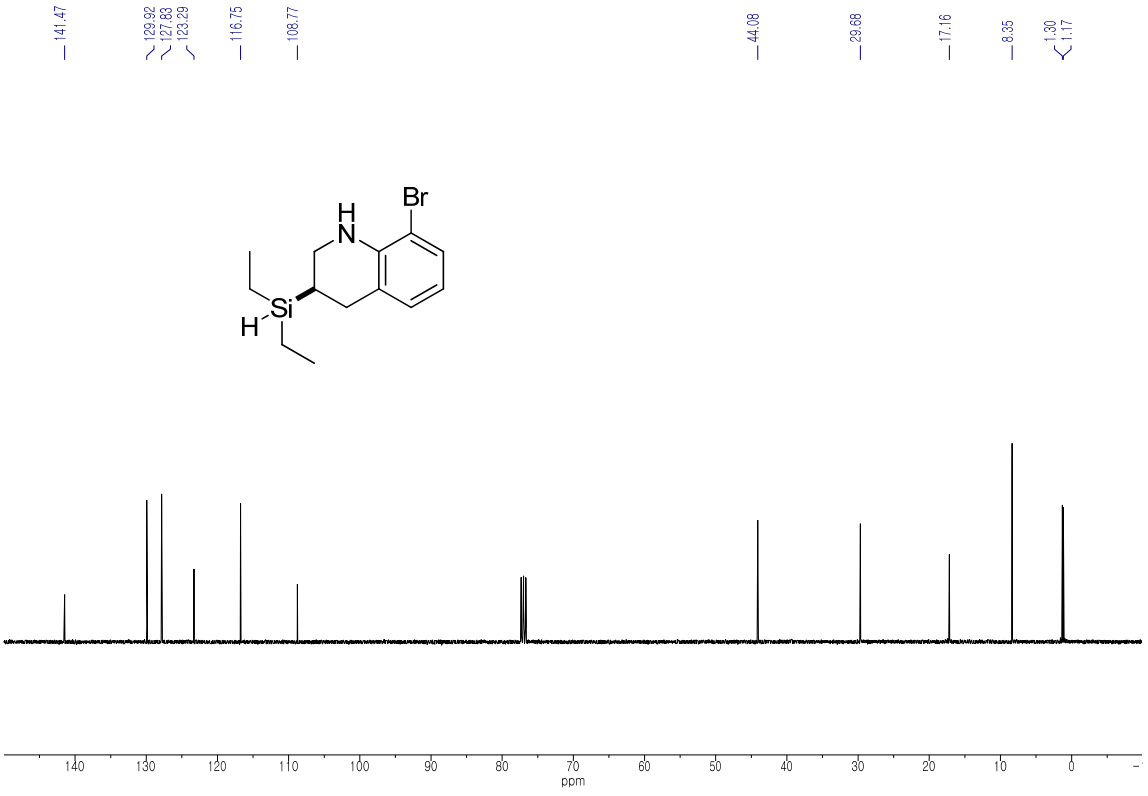


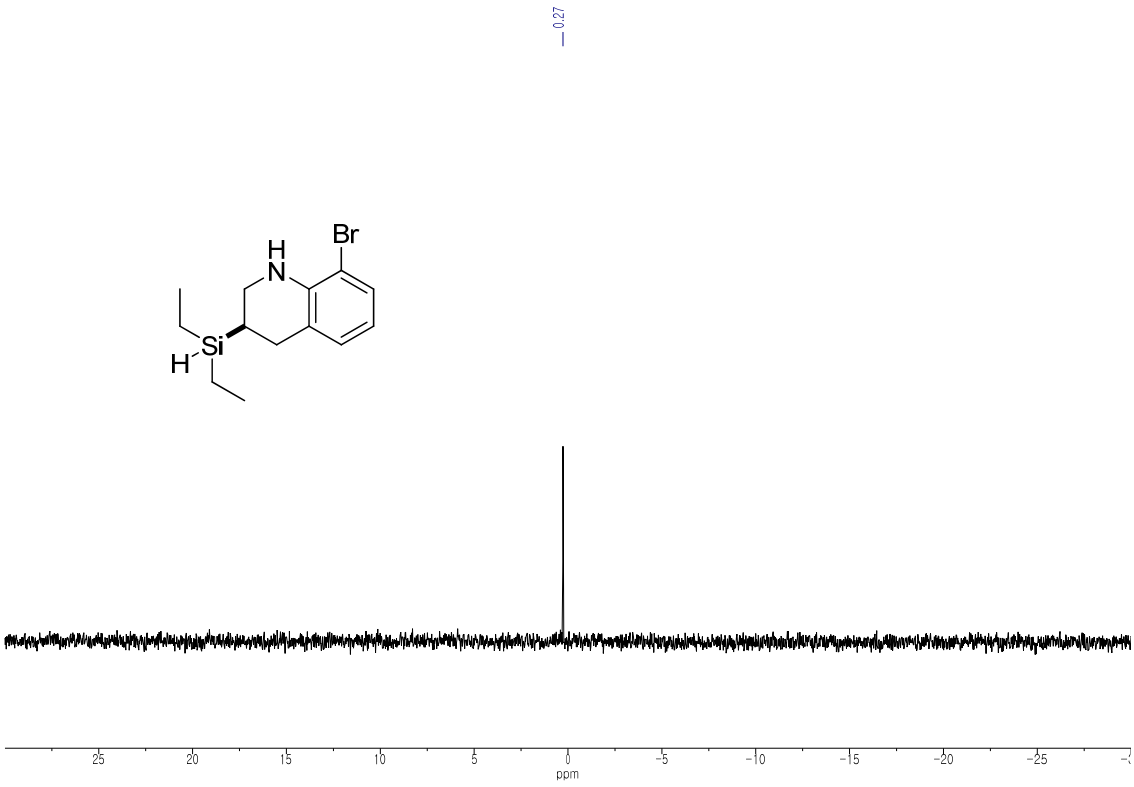

145.45
131.86
129.90
120.05
116.44
113.46
43.74
28.74
17.36
8.35
1.35
1.18
Cl
H
N
Si
H
ppm


0.37
Cl
H
N
Si
H
ppm

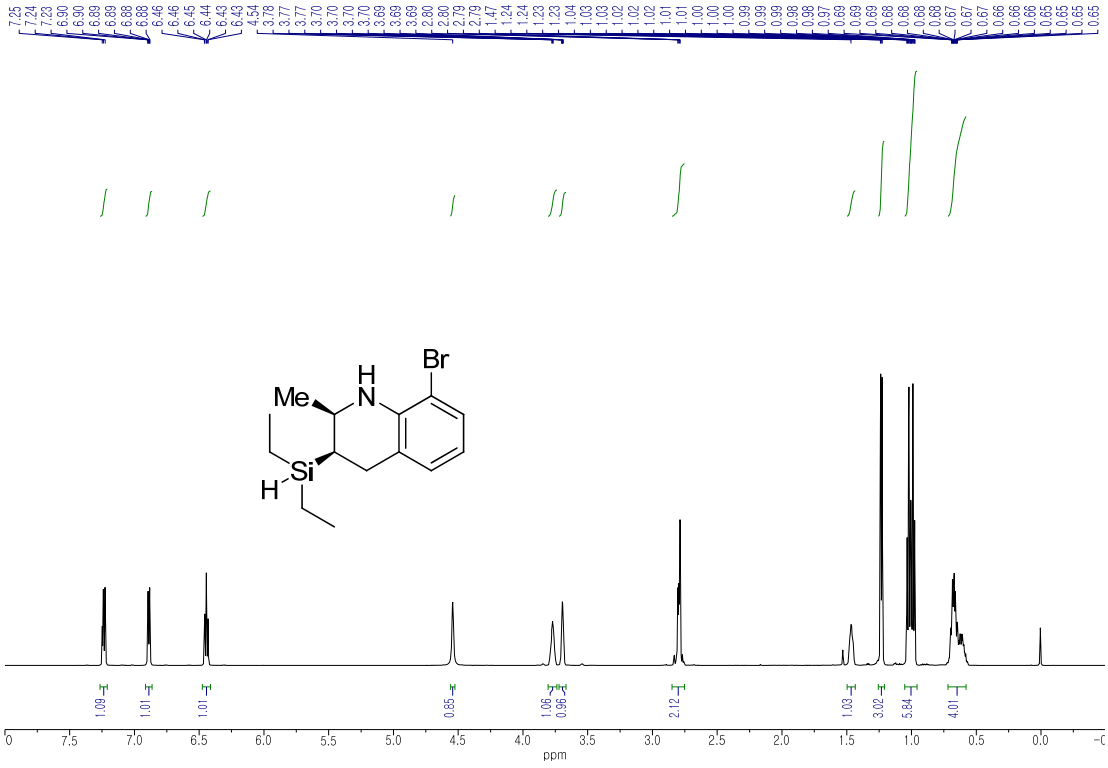
8-Bromo-3-(diethylsilyl)-1,2,3,4-tetrahydroquinoline (Table 1, 16b)

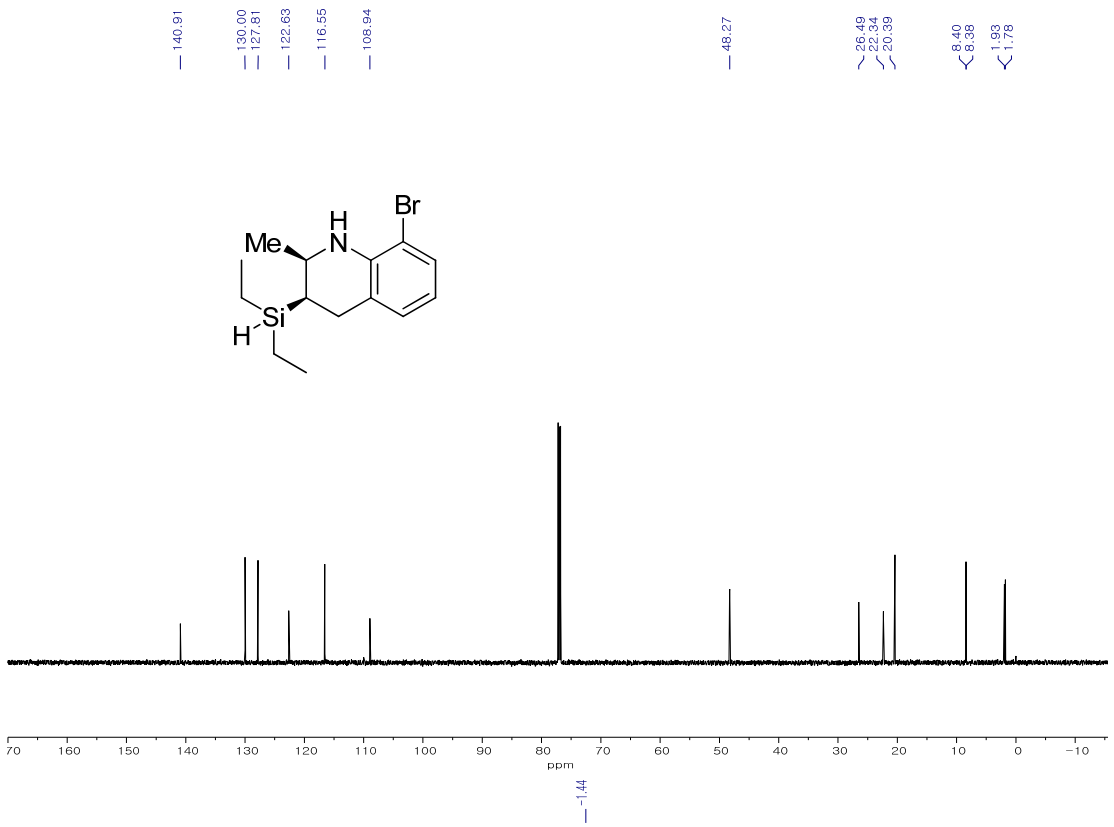


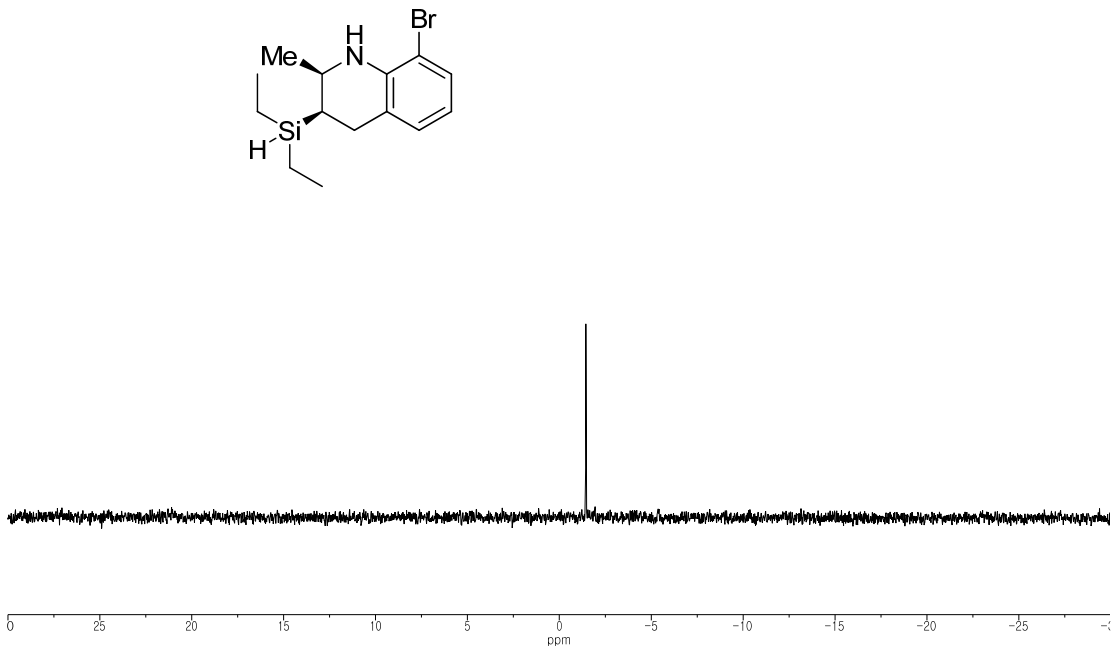




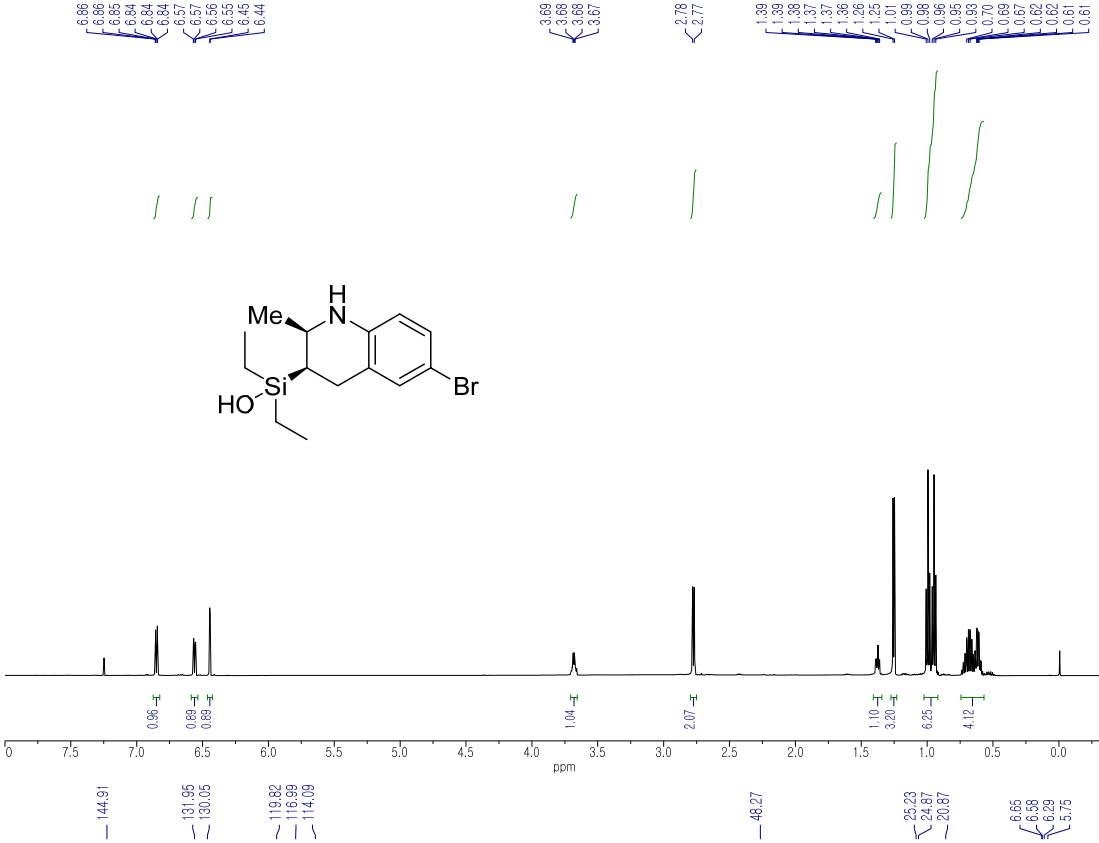
8-Bromo-3-(diethylsilyl)-2-methyl-1,2,3,4-tetrahydroquinoline (Table 1, 17b)

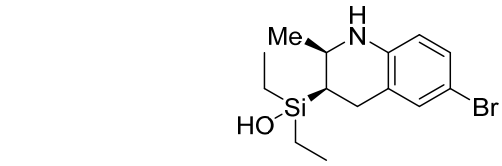


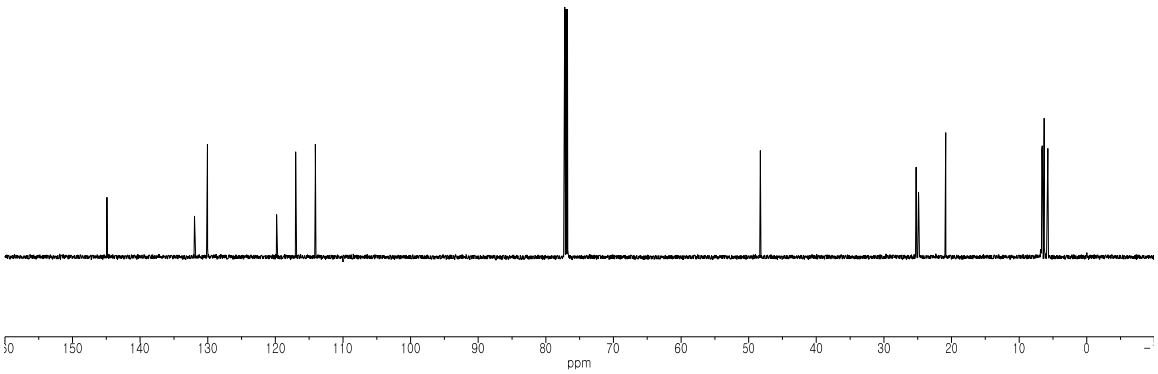

140.91
130.00
127.81
122.63
116.55
108.94
48.27
26.49
22.34
20.39
8.40
8.38
1.93
1.78
Br
H
N
Me
Si
H
ppm

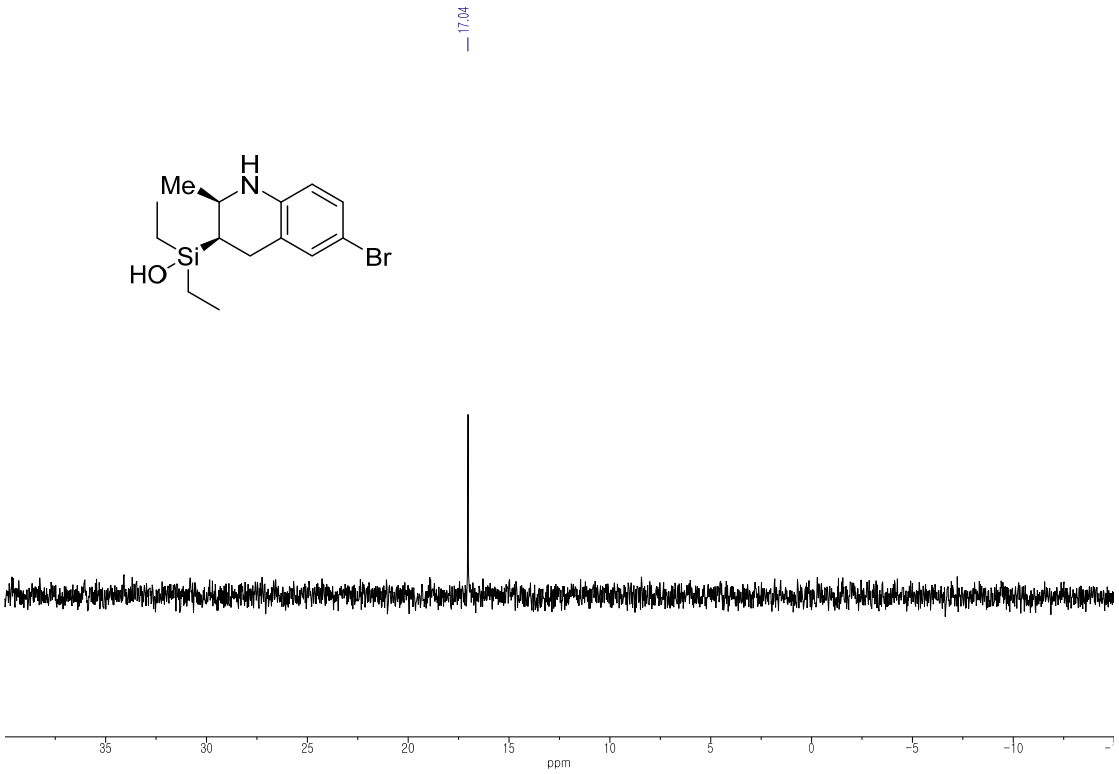

-1.44
Br
H
N
Me
Si
H
ppm

6-Bromo-2-methyl-1,2,3,4-tetrahydroquinolin-3-yl)diethylsilanol (Table 1, 18b)

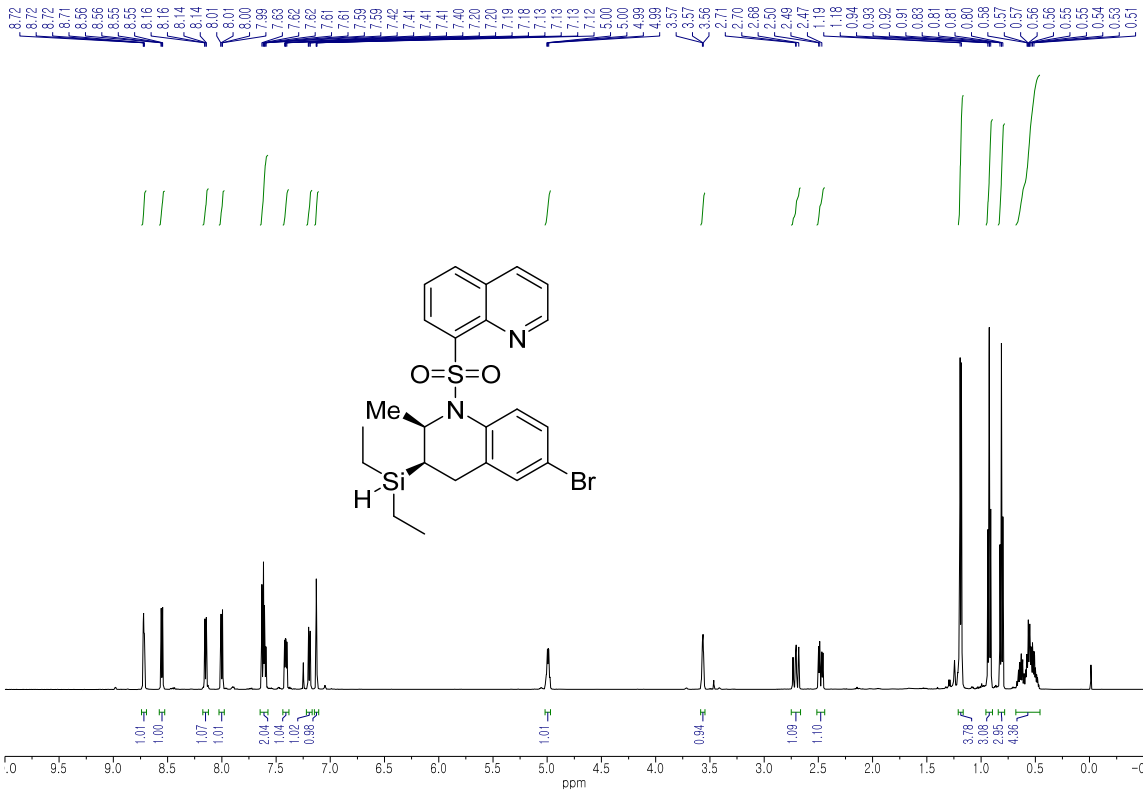


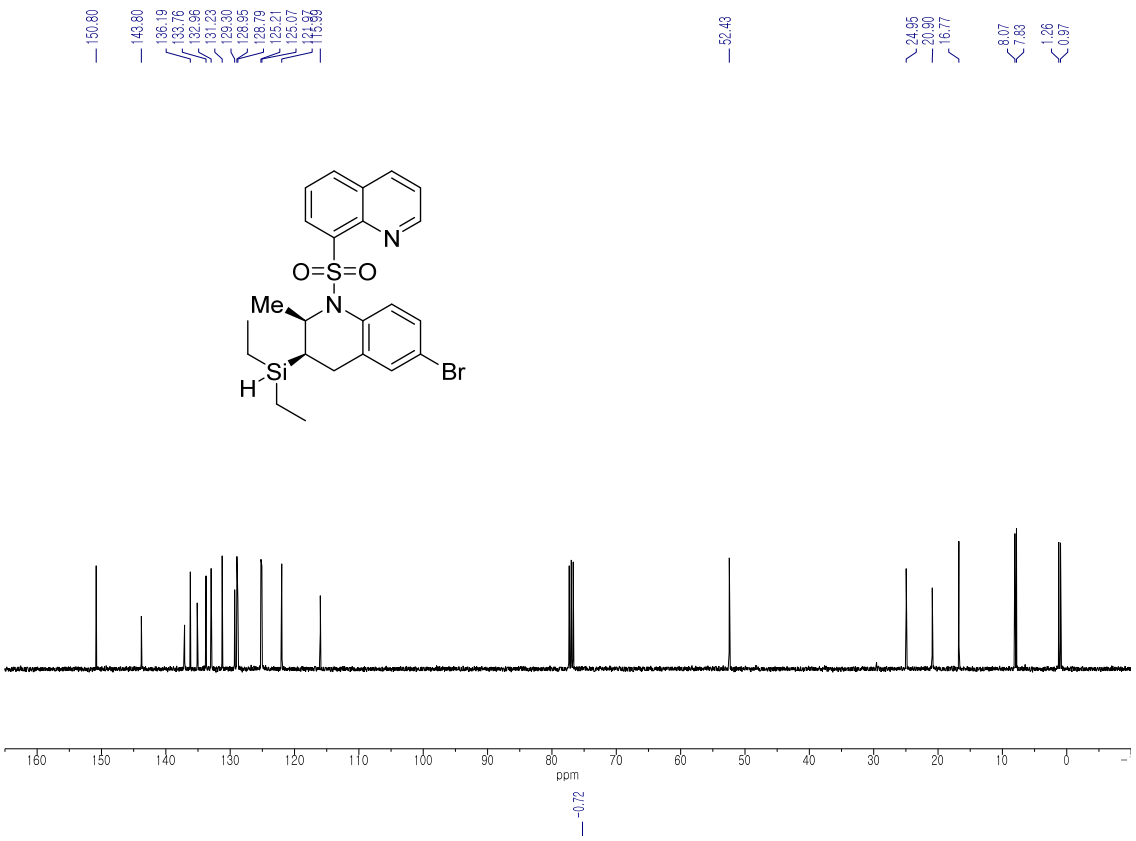


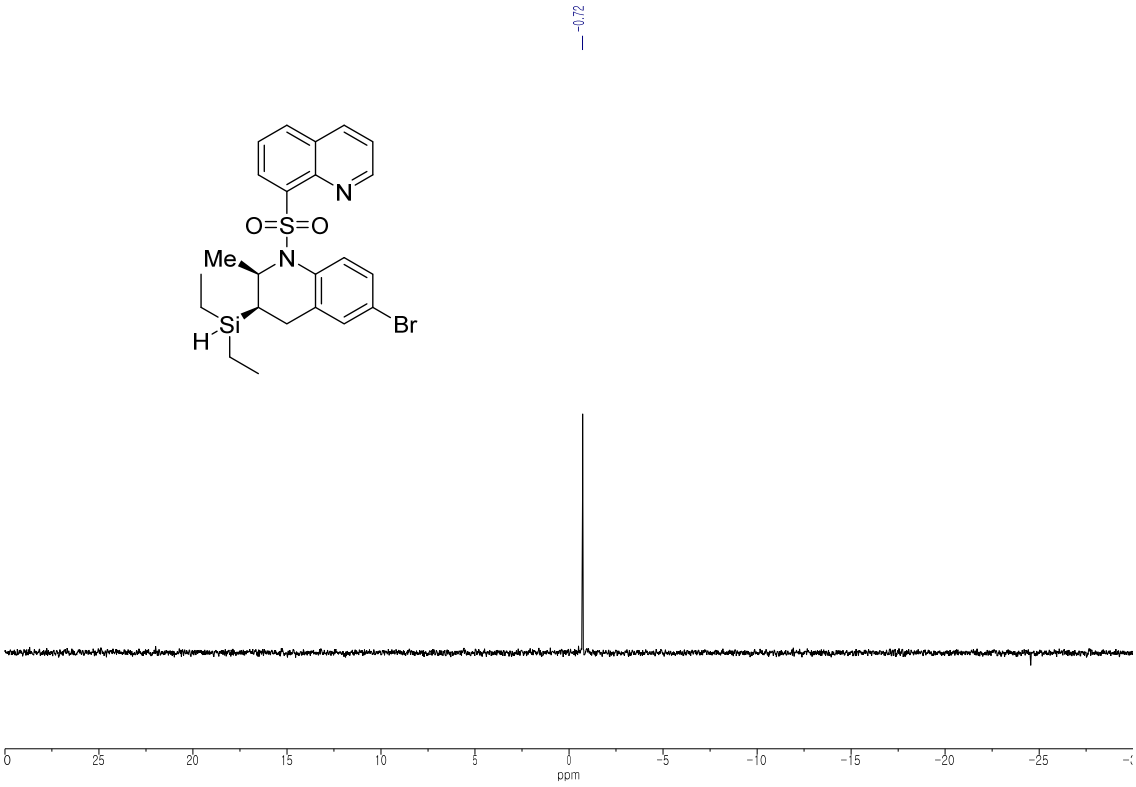




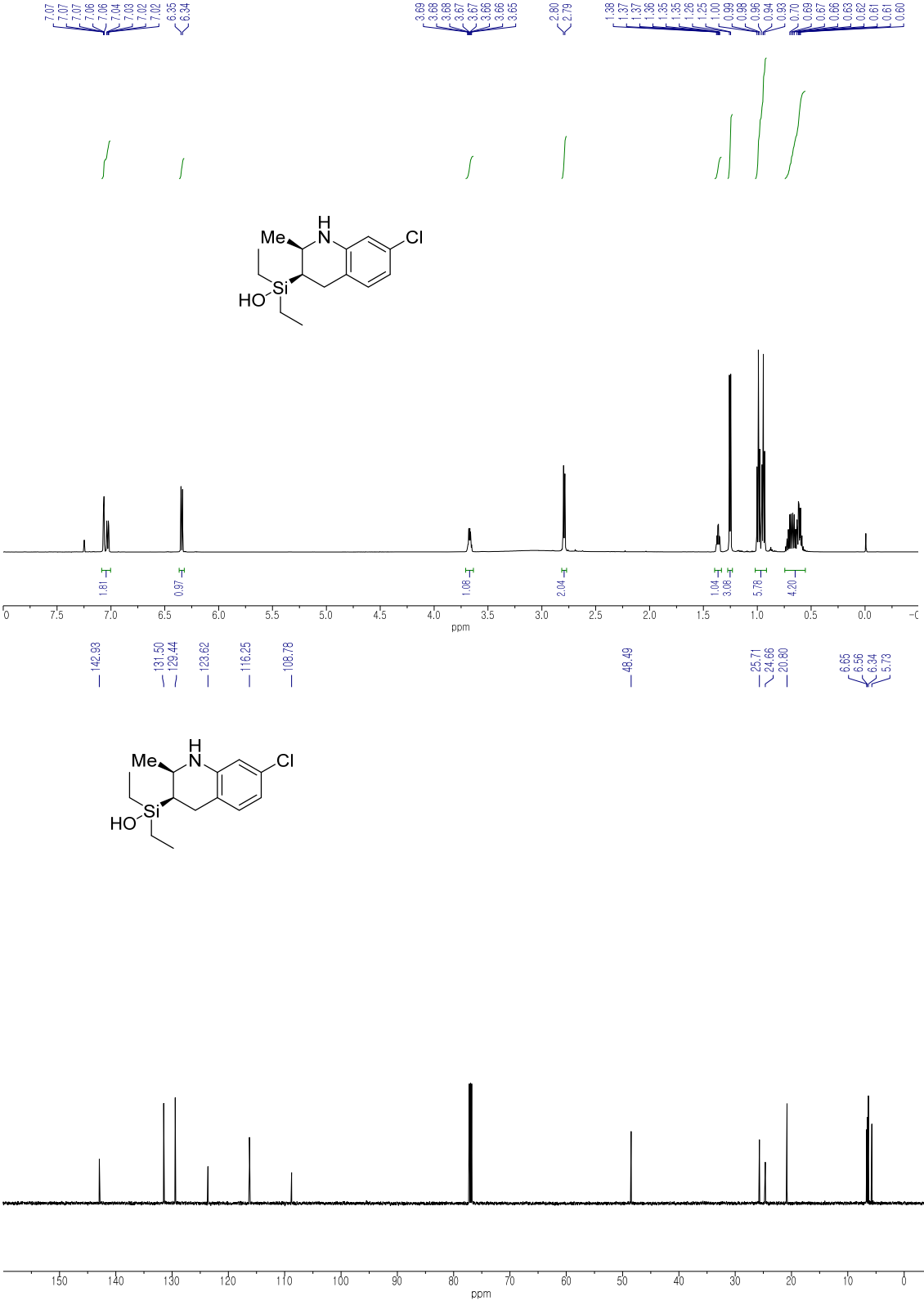
8-{6-Bromo-3-(diethylsilyl)-2-methyl-3,4-dihydroquinolin-1(2*H*)-ylsulfonyl}quinoline (Table 1, 18b-QUS)

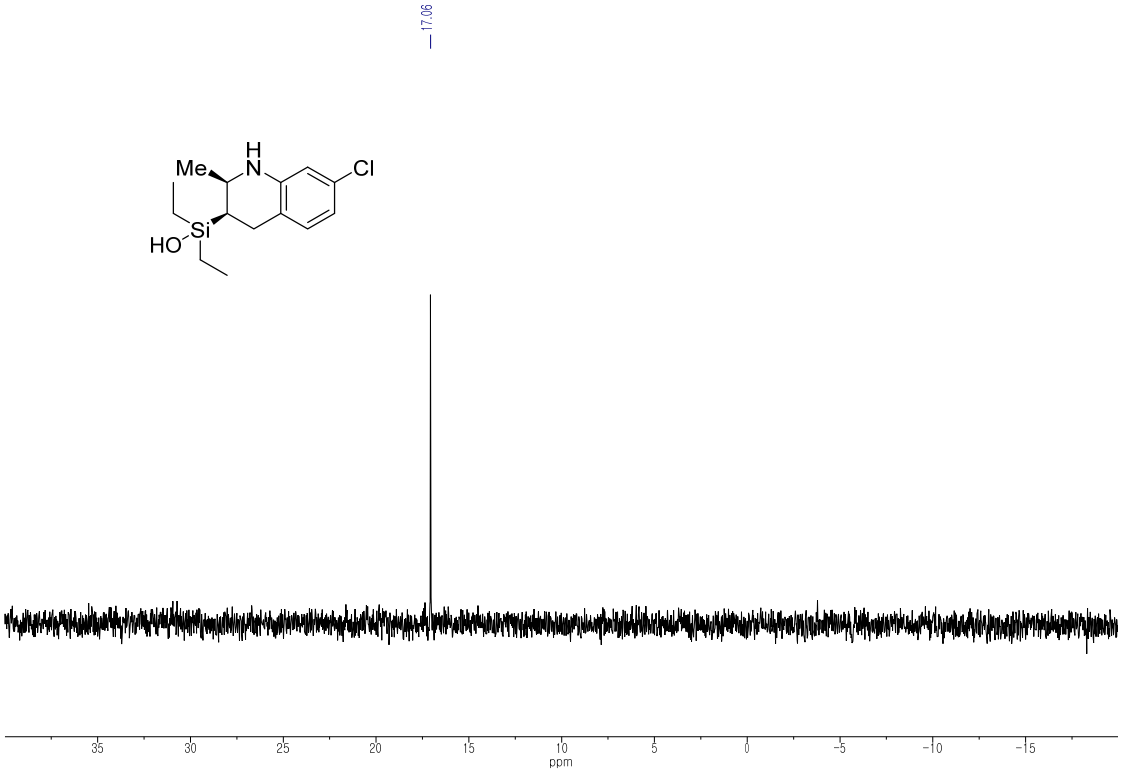



150.80
143.80
138.19
133.76
132.96
131.23
129.30
128.95
128.79
125.21
125.07
121.97
115.99
52.43
24.95
20.90
16.77
8.07
7.83
1.26
0.97
N
O=S=O
Me
N
Si
H
Br
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

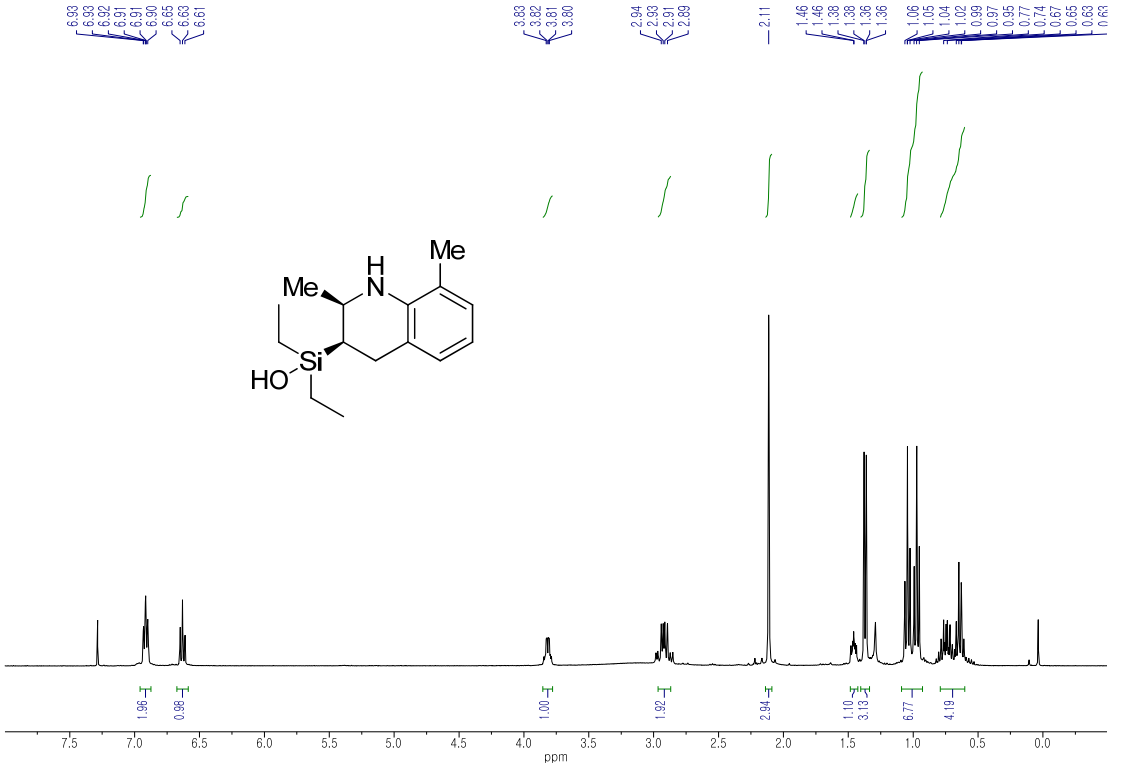

-0.72
N
O=S=O
Me
N
Si
H
Br
0
25
20
15
10
5
0
-5
-10
-15
-20
-25
ppm

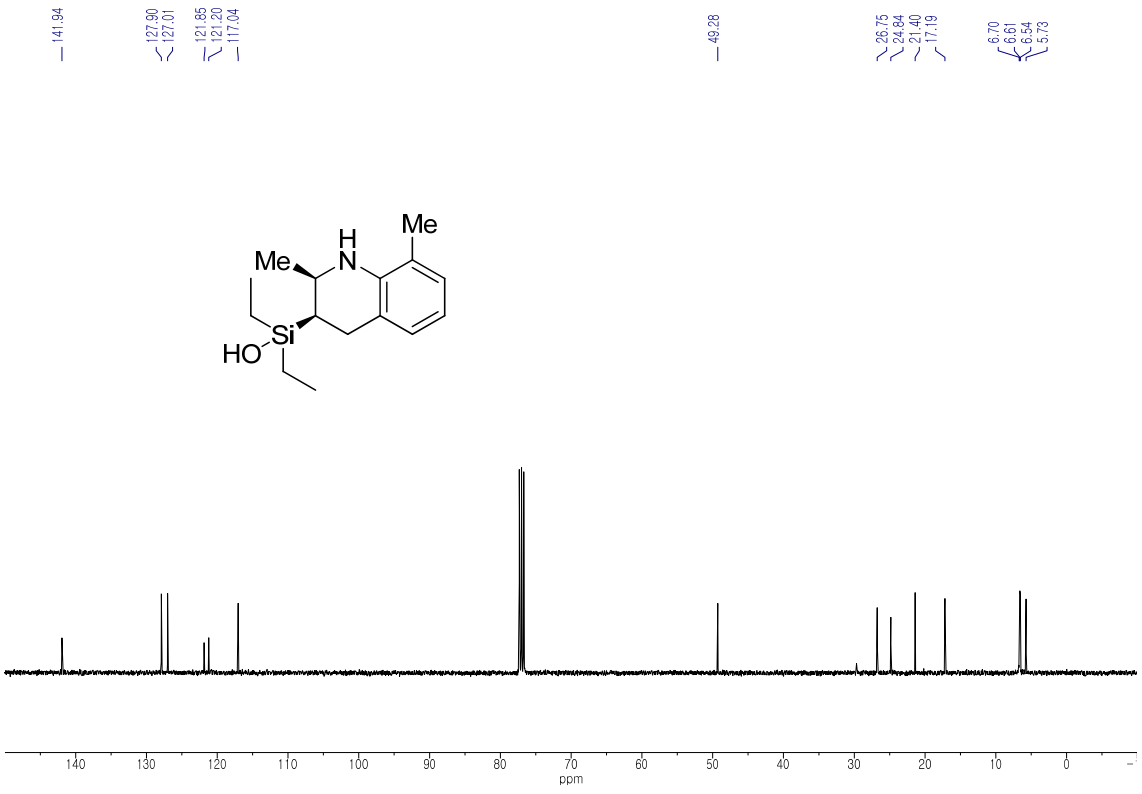
(7-Chloro-2-methyl-1,2,3,4-tetrahydroquinolin-3-yl)diethylsilanol (Table 1, 19b)

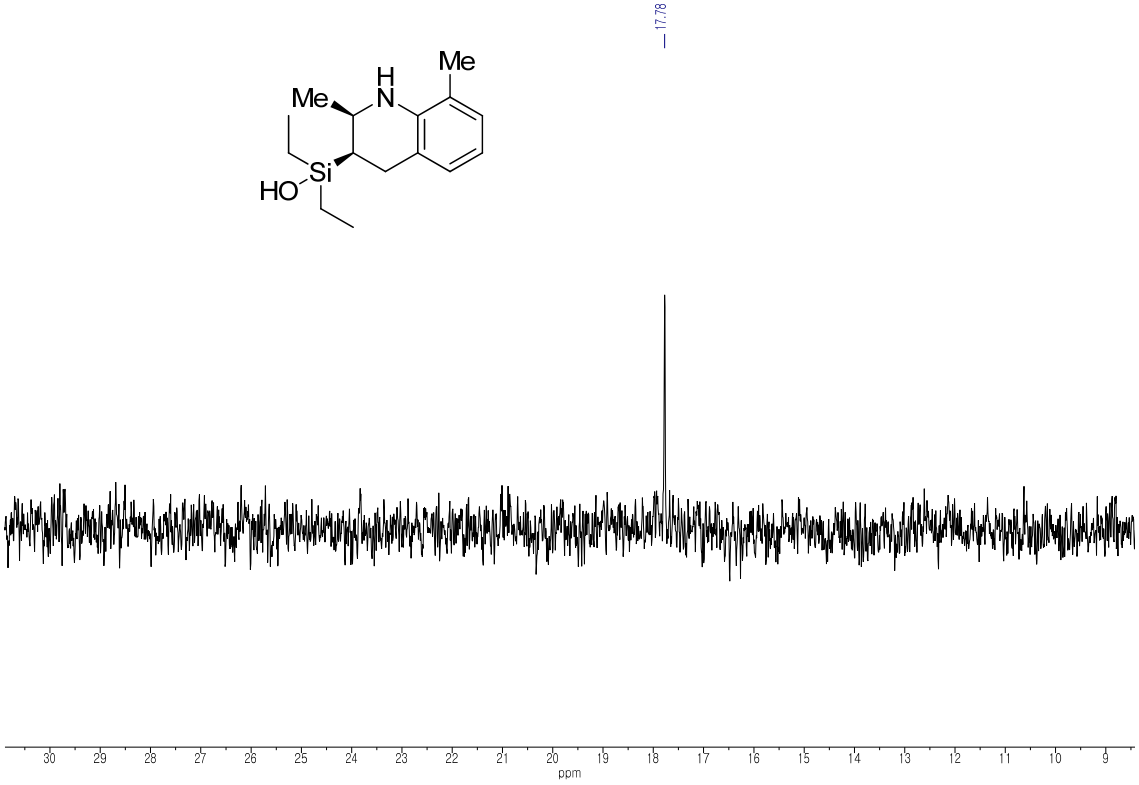




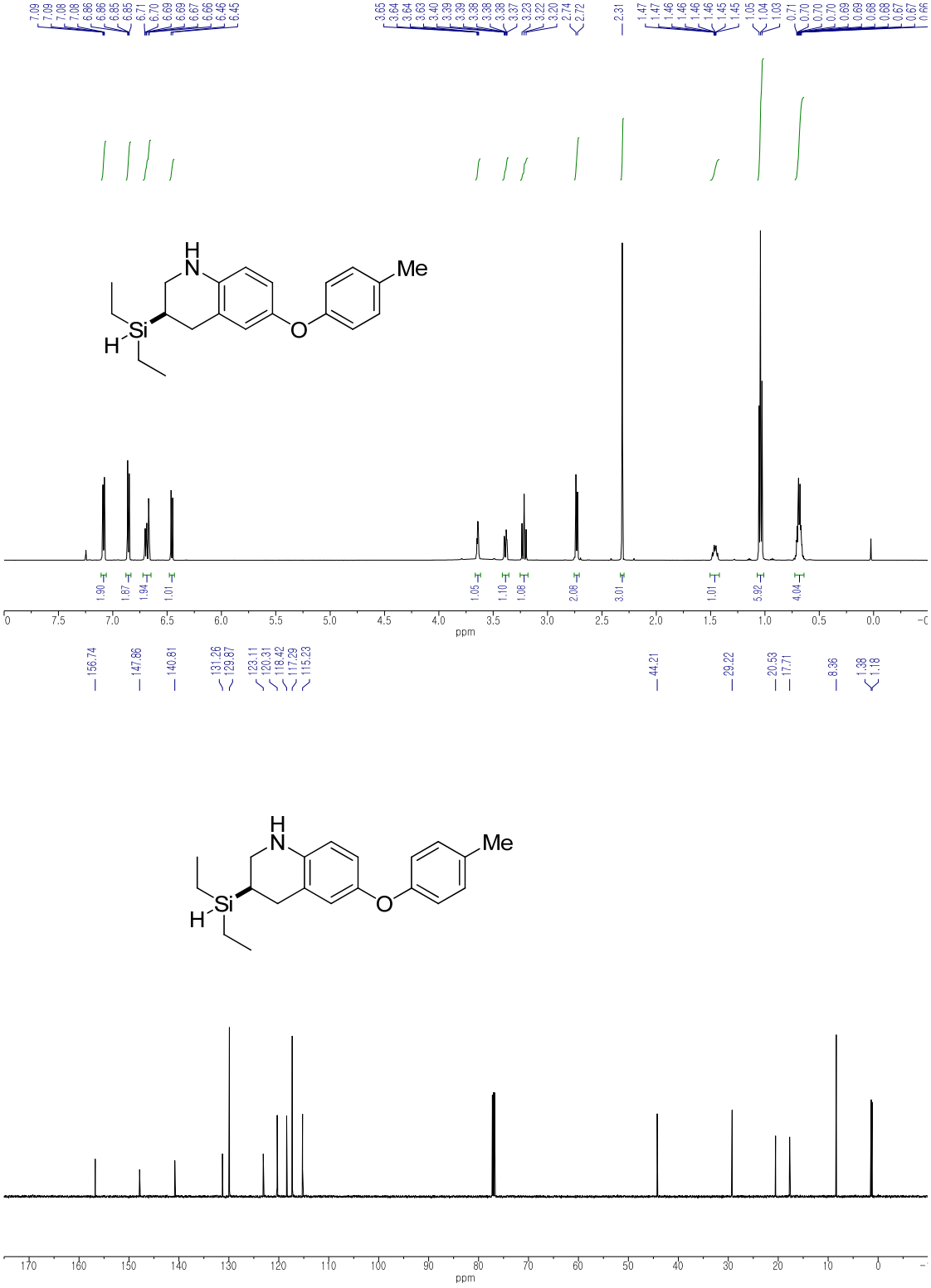
(2,8-Dimethyl-1,2,3,4-tetrahydroquinolin-3-yl)diethylsilanol (Table 1, 20b)

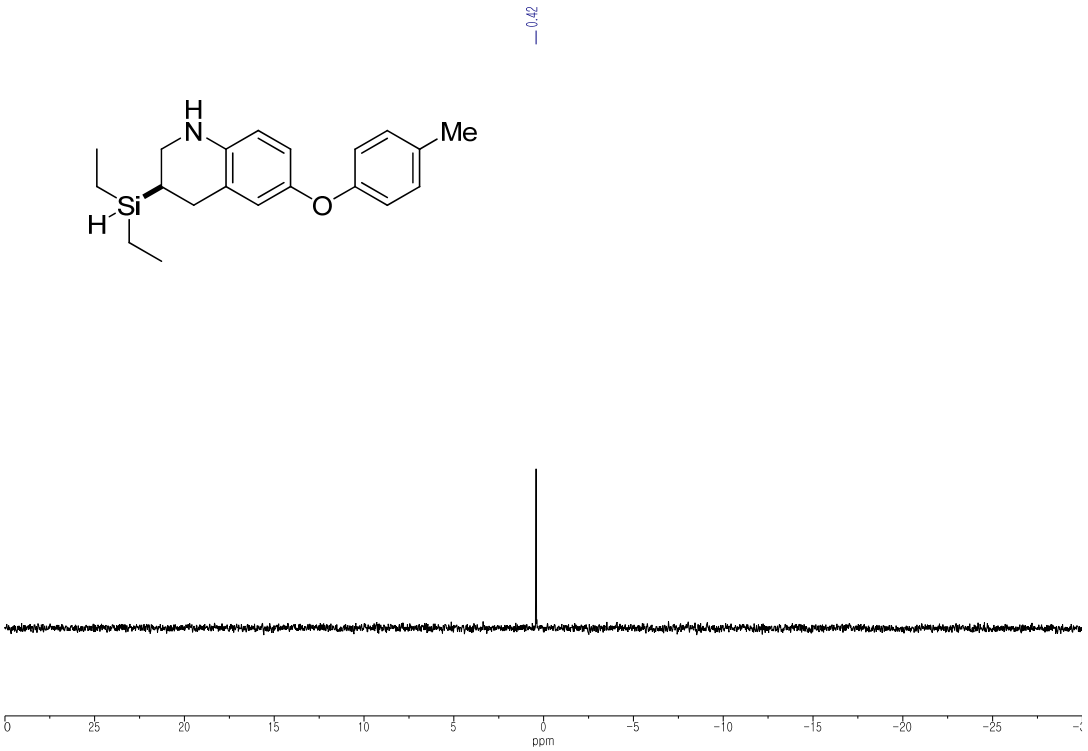



141.94
127.90
127.01
121.85
121.20
117.04
49.28
26.75
24.84
21.40
17.19
6.70
6.61
6.54
5.73
Me
H
N
Me
Si
HO
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

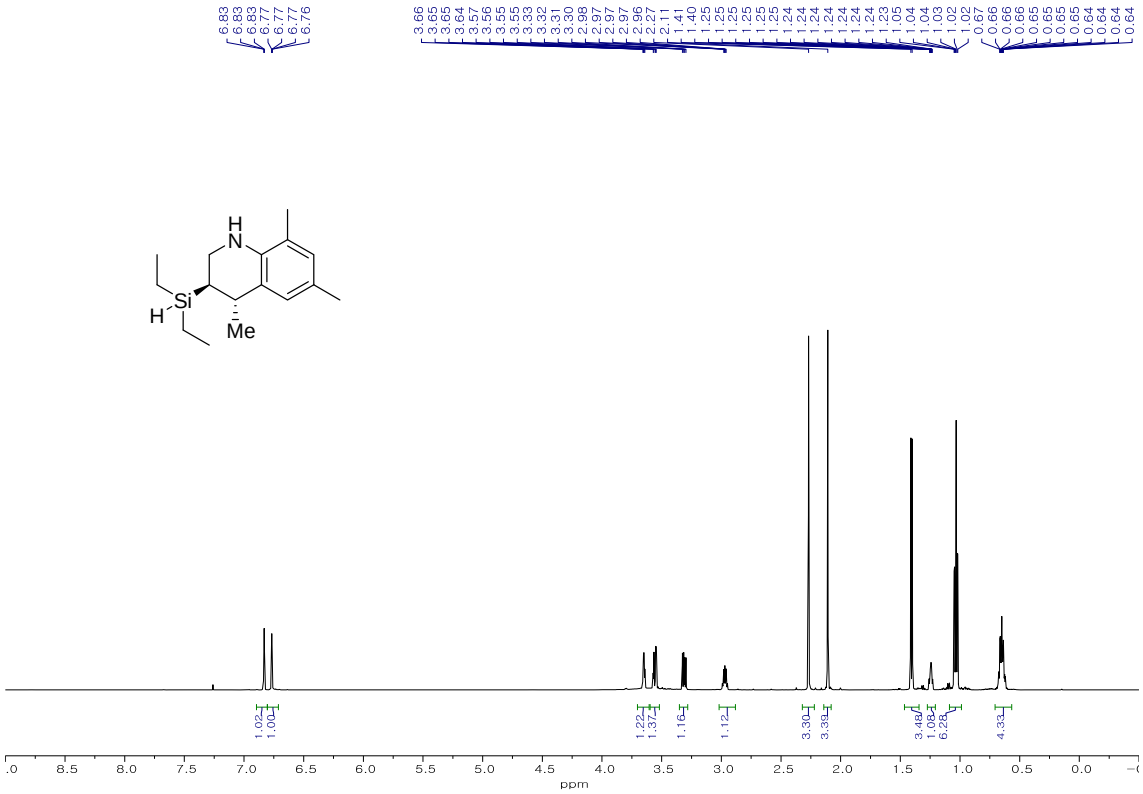

17.78
Me
H
N
Me
Si
HO
30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
ppm

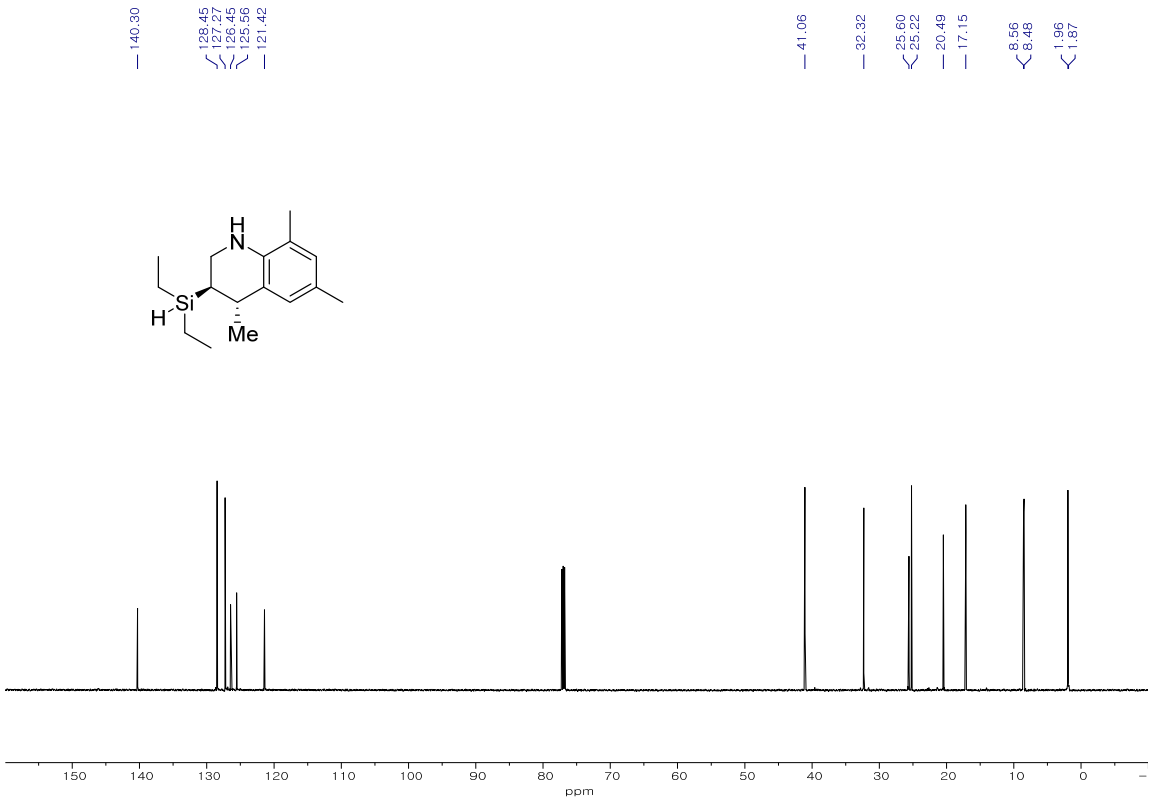
3-(Diethylsilyl)-6-(*p*-tolyloxy)-1,2,3,4-tetrahydroquinoline (Table 1, 21b)

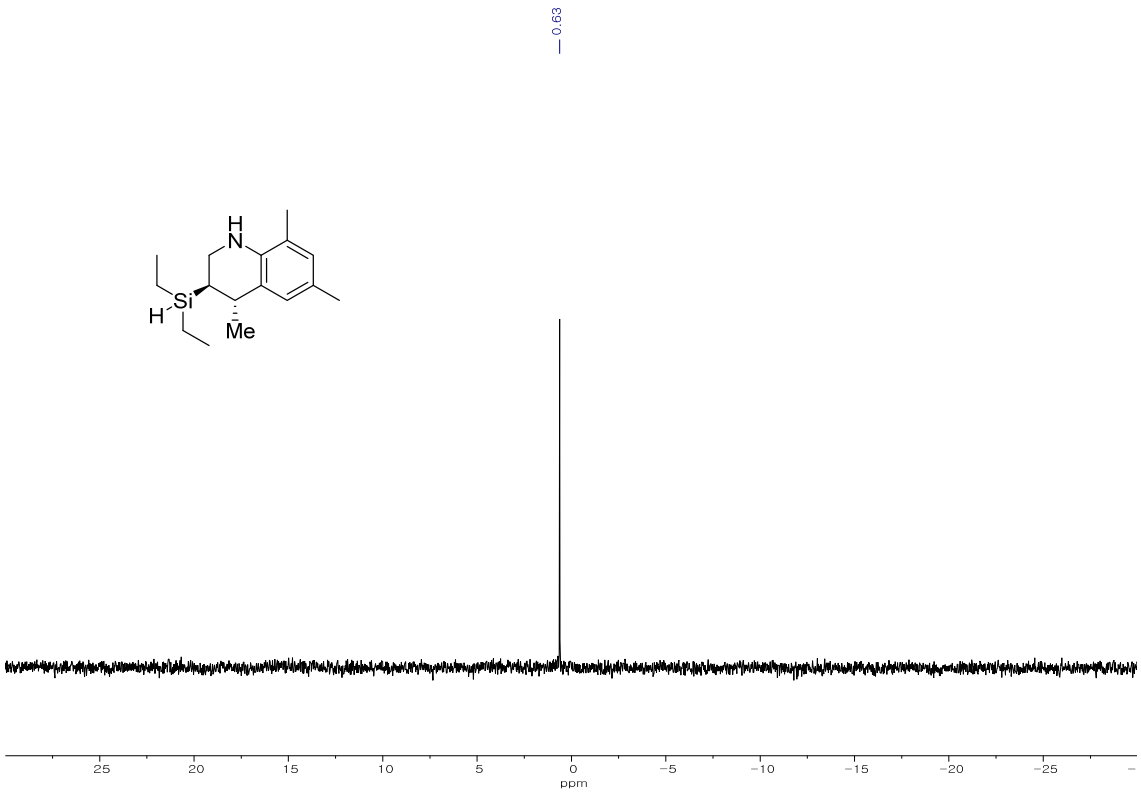




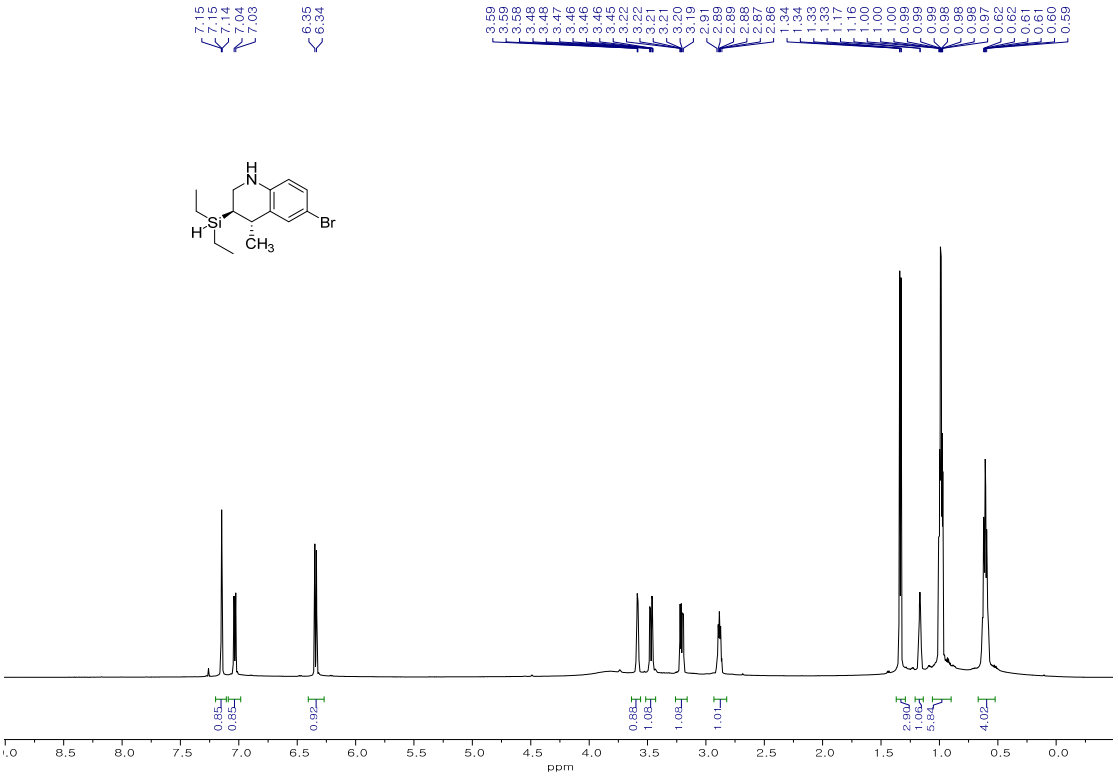
3-(Diethylsilyl)-4,6,8-trimethyl-1,2,3,4-tetrahydroquinoline (Table 1, 22b)

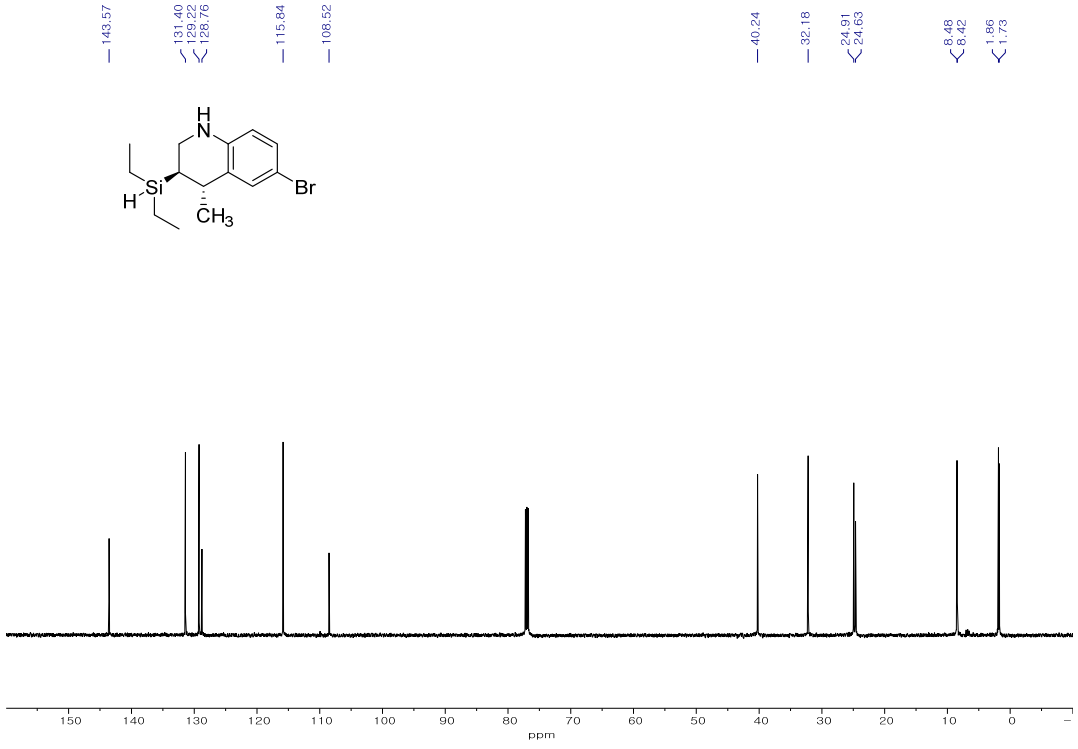


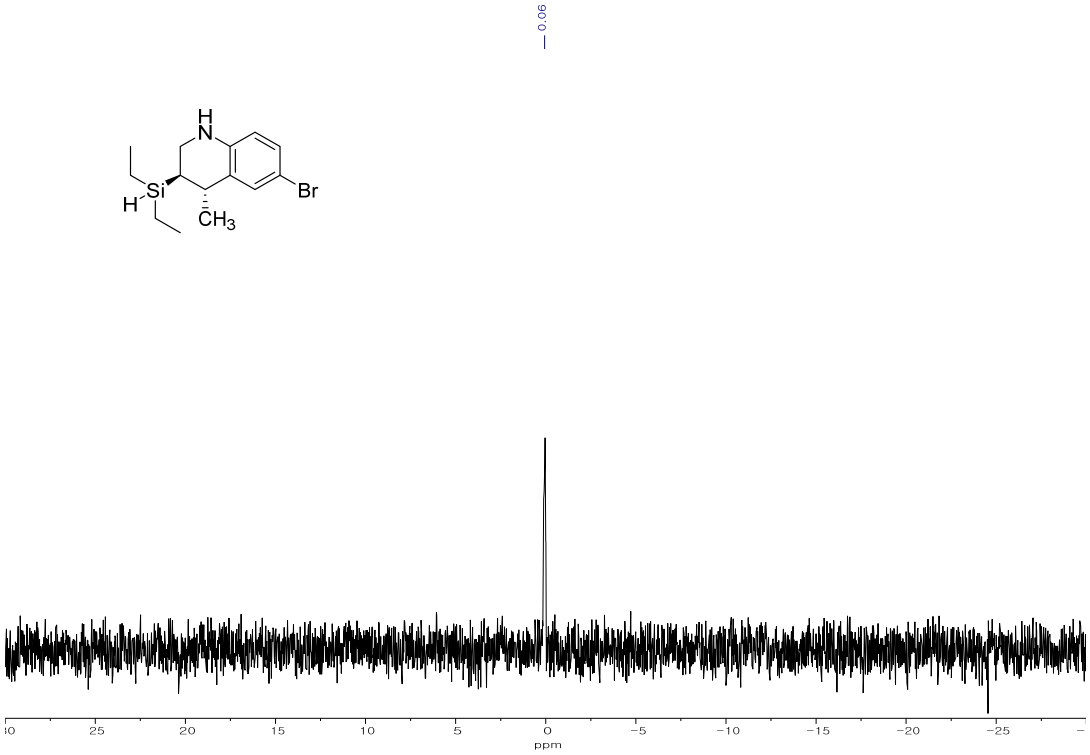

140.30
128.45
127.27
126.45
125.56
121.42
41.06
32.32
25.60
25.22
20.49
17.15
8.56
8.48
1.96
1.87
H
N
Si
H
Me
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


0.63
H
N
Si
H
Me
25
20
15
10
5
0
−5
−10
−15
−20
−25
ppm

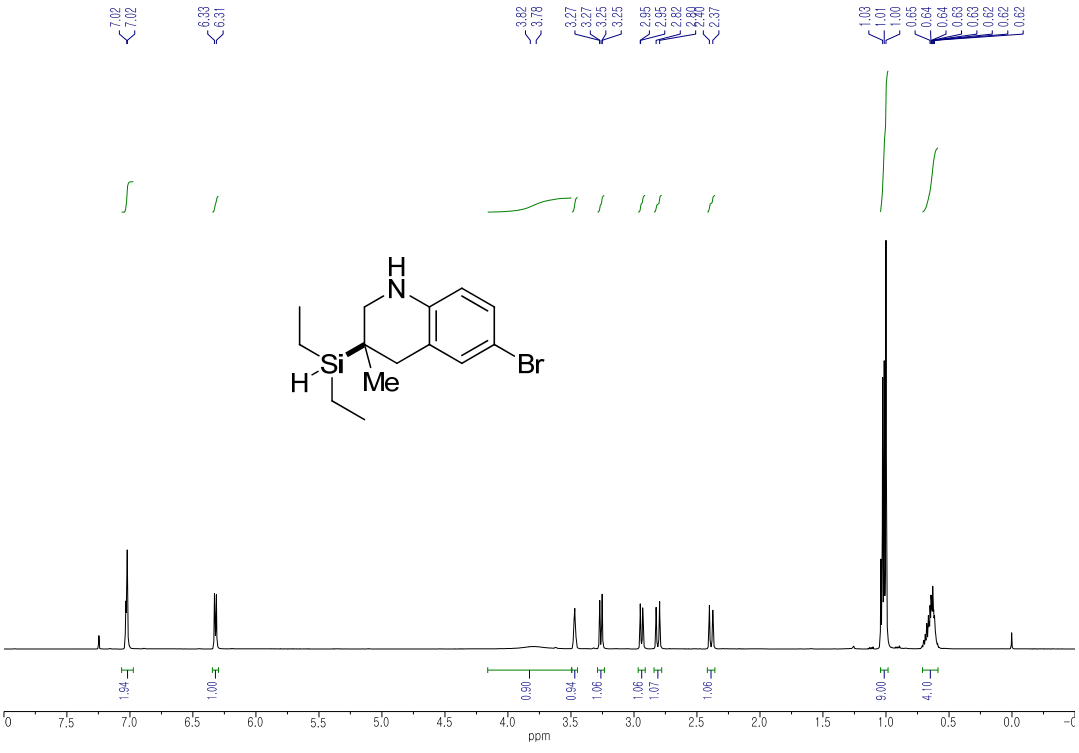
6-Bromo-3-(diethylsilyl)-4-methyl-1,2,3,4-tetrahydroquinoline (Table 1, 23b)

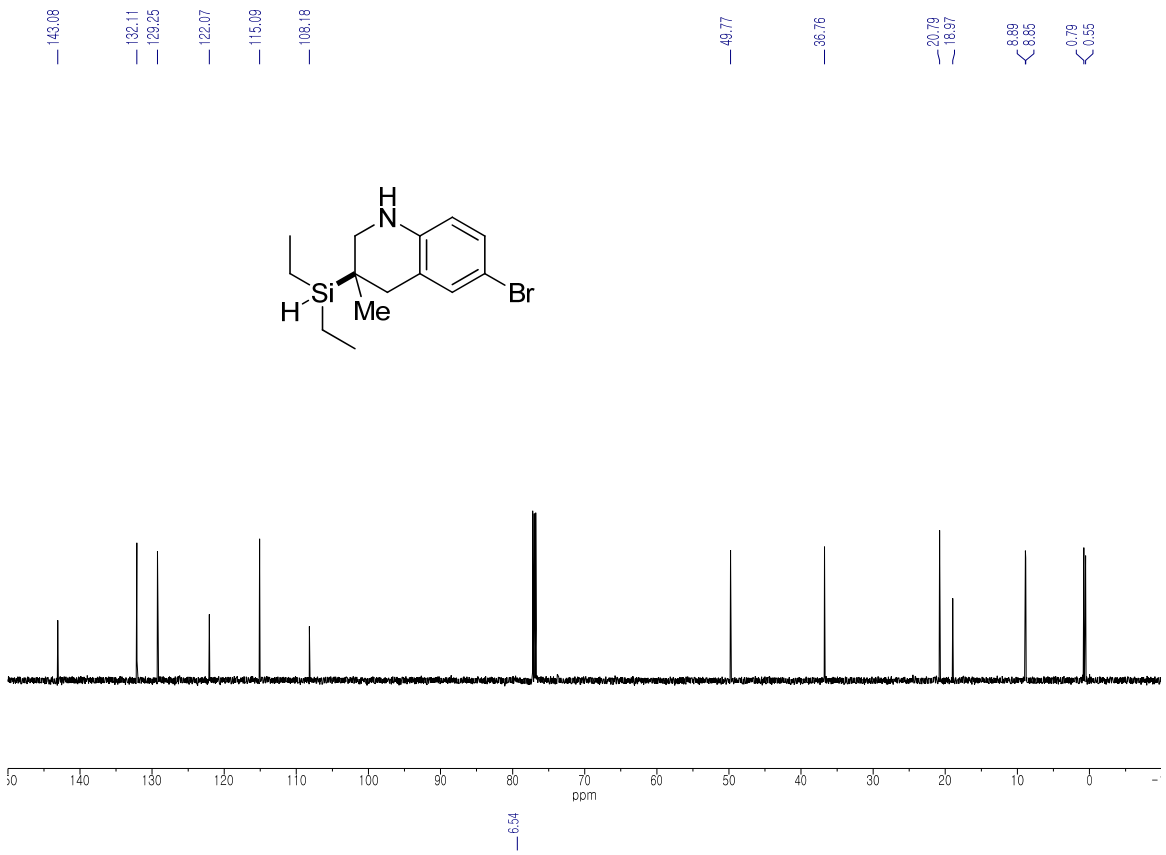


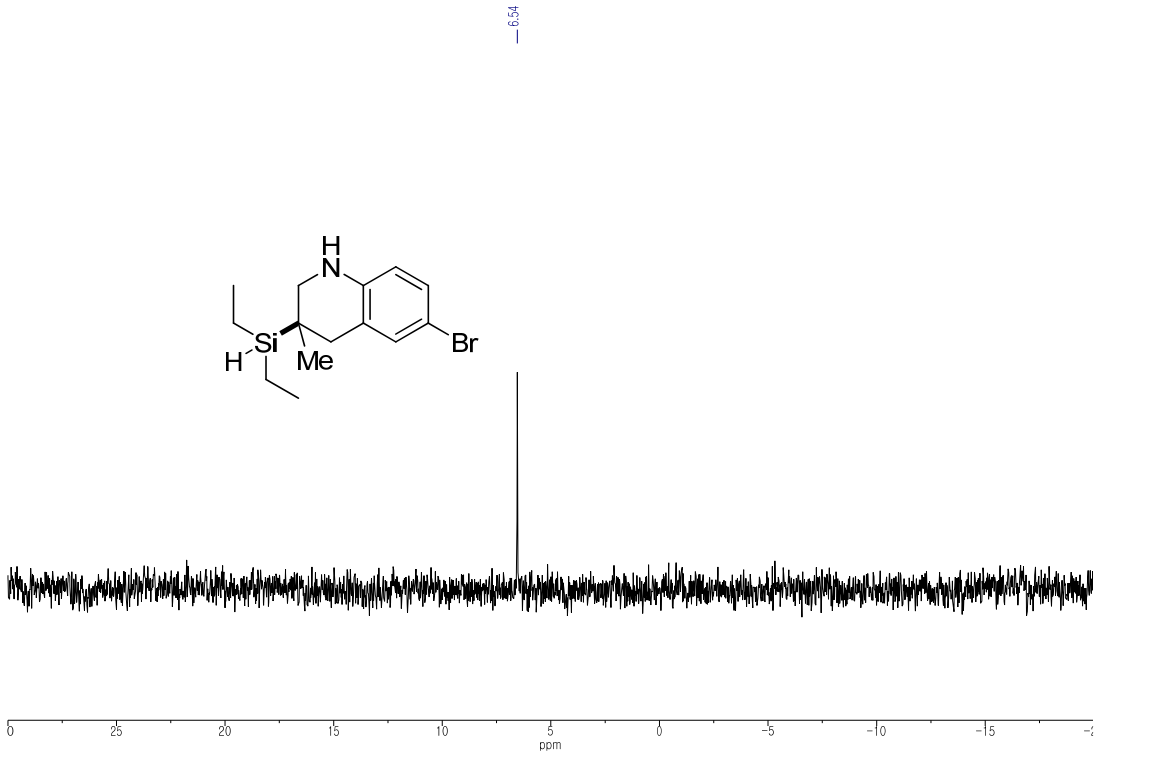




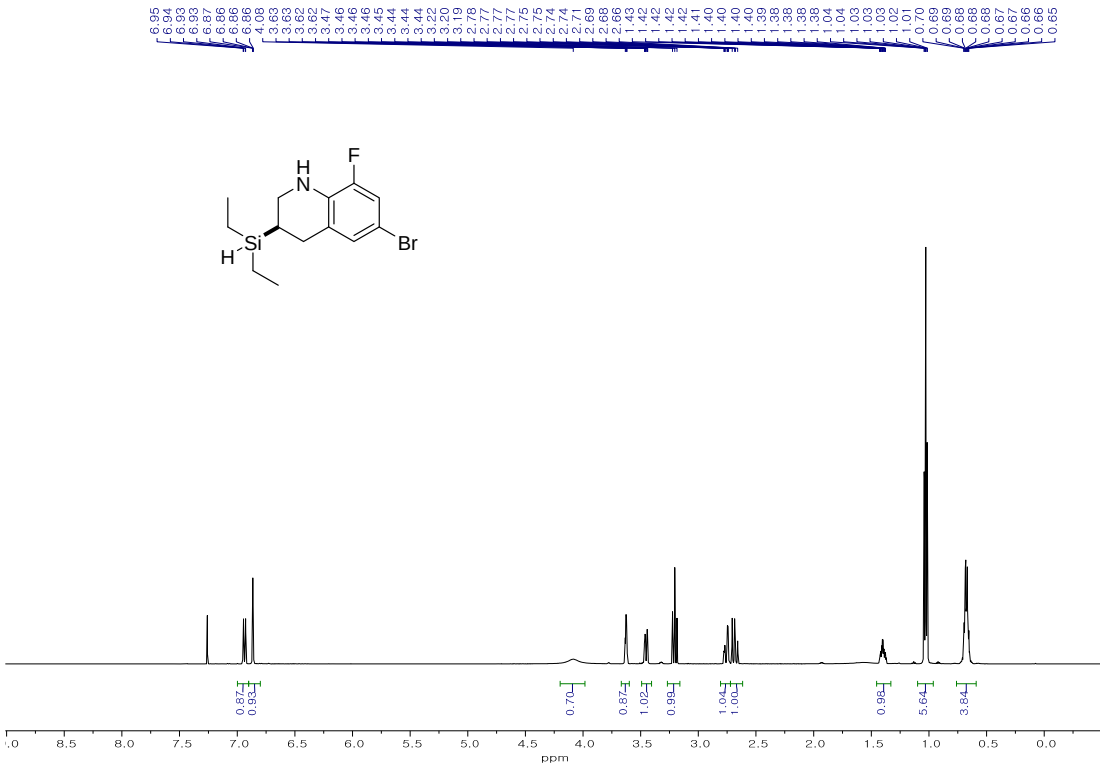
6-Bromo-3-(diethylsilyl)-3-methyl-1,2,3,4-tetrahydroquinoline (Table 1, 24b)

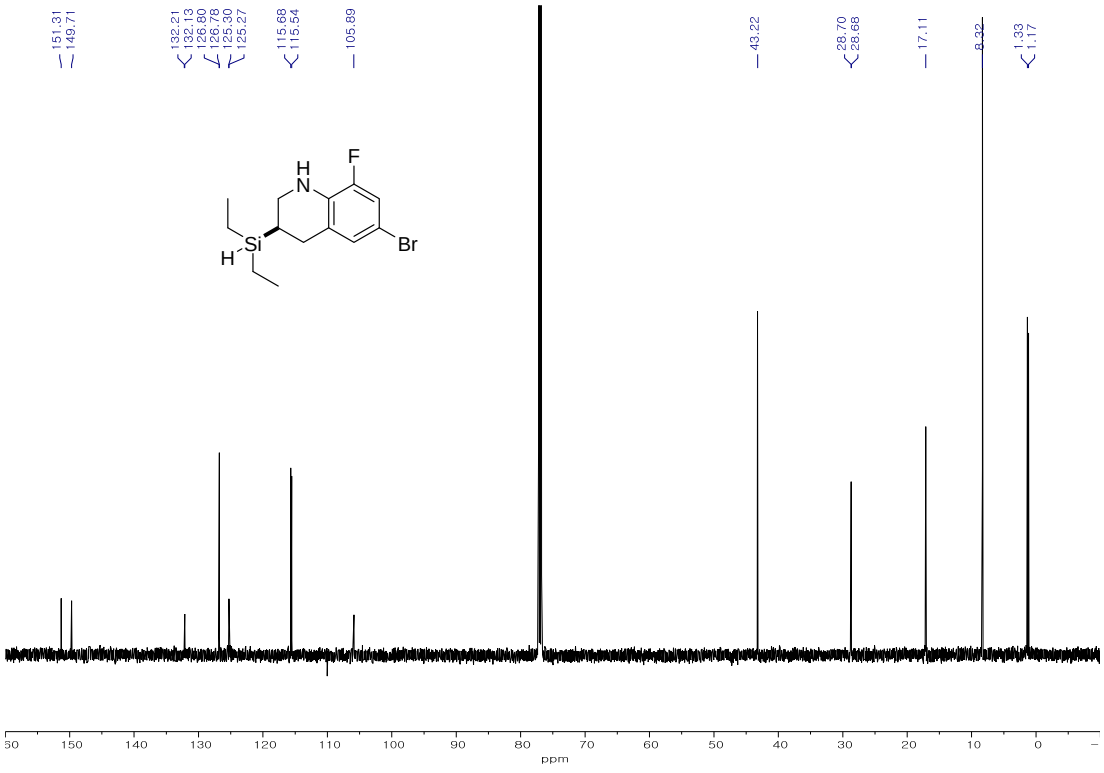


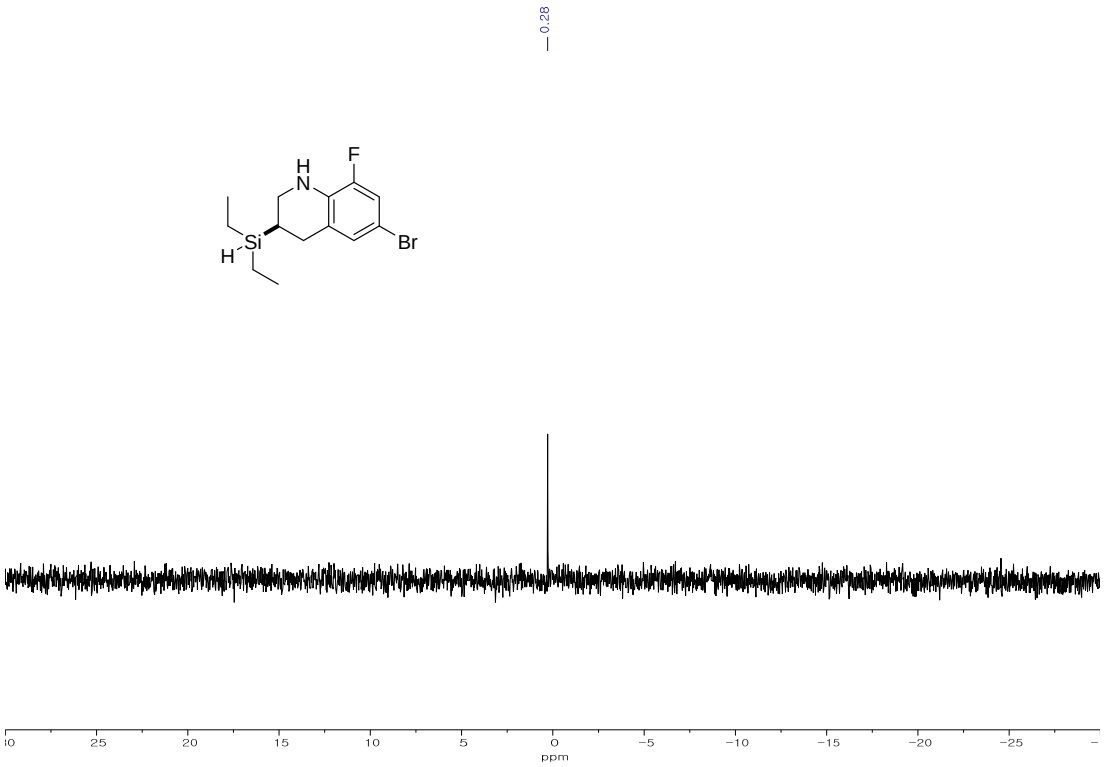

143.08
132.11
129.25
122.07
115.09
108.18
49.77
36.76
20.79
18.97
8.89
8.85
0.79
0.55
H
N
Si
H
Me
Br
ppm


6.54
H
N
Si
H
Me
Br
ppm

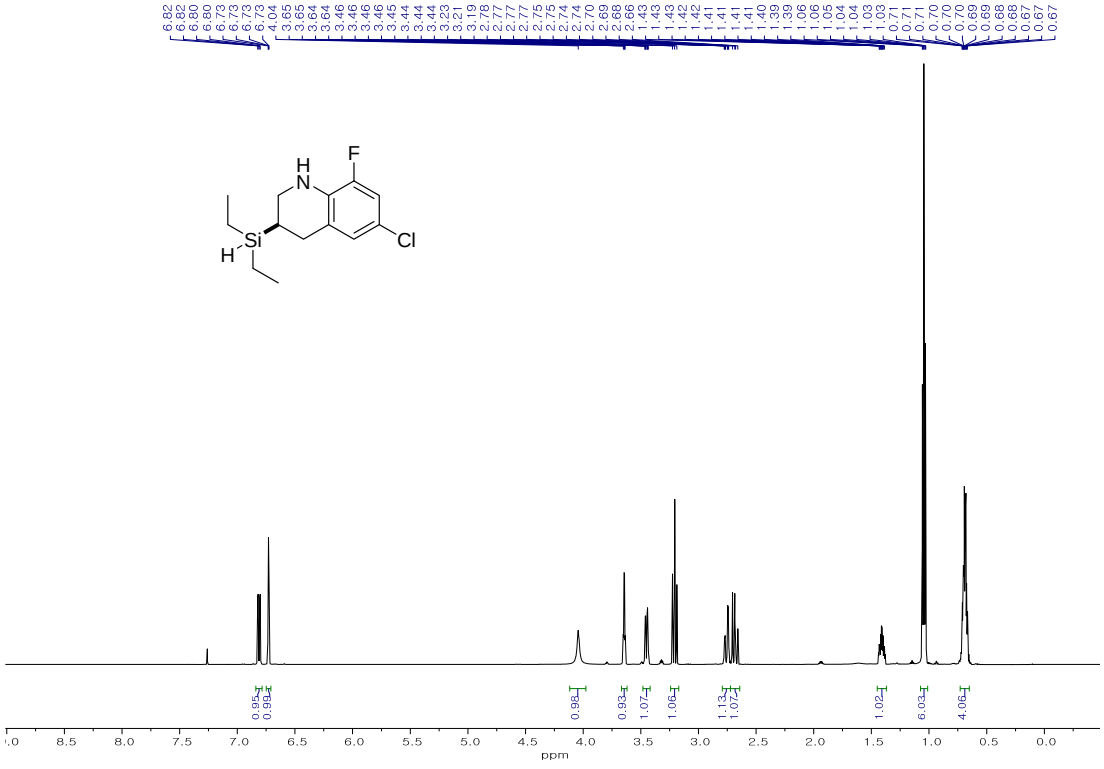
6-Bromo-3-(diethylsilyl)-8-fluoro-1,2,3,4-tetrahydroquinoline (Table 1, 25b)

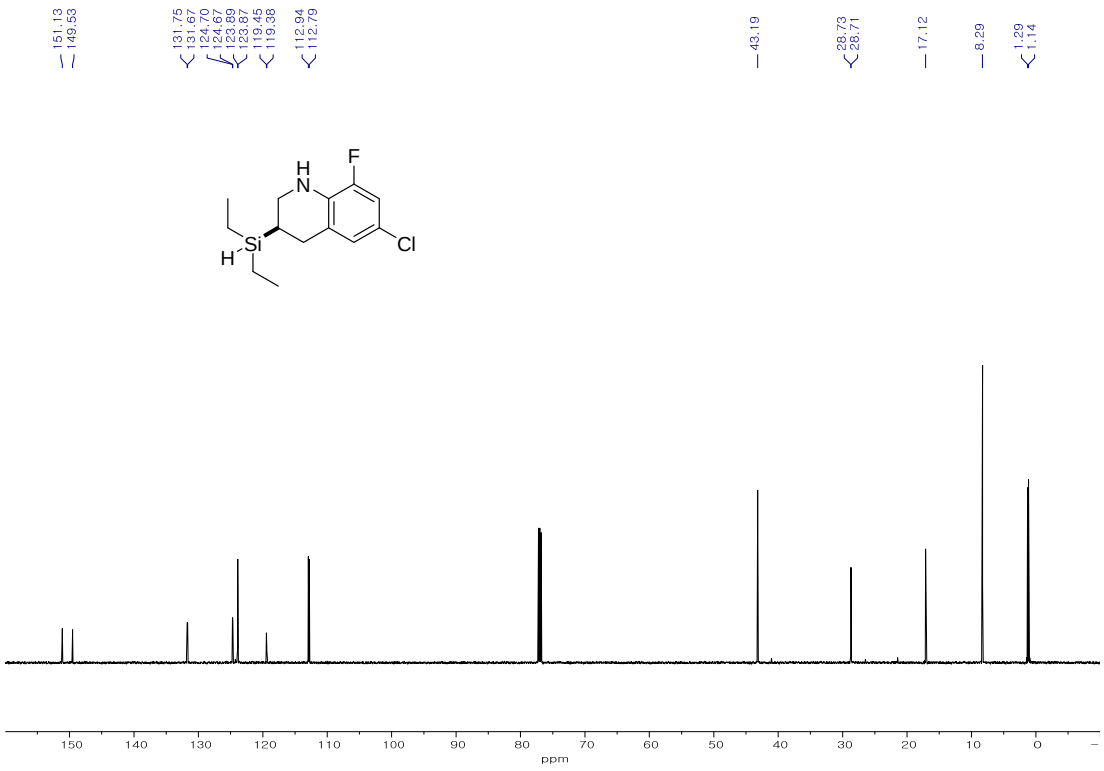


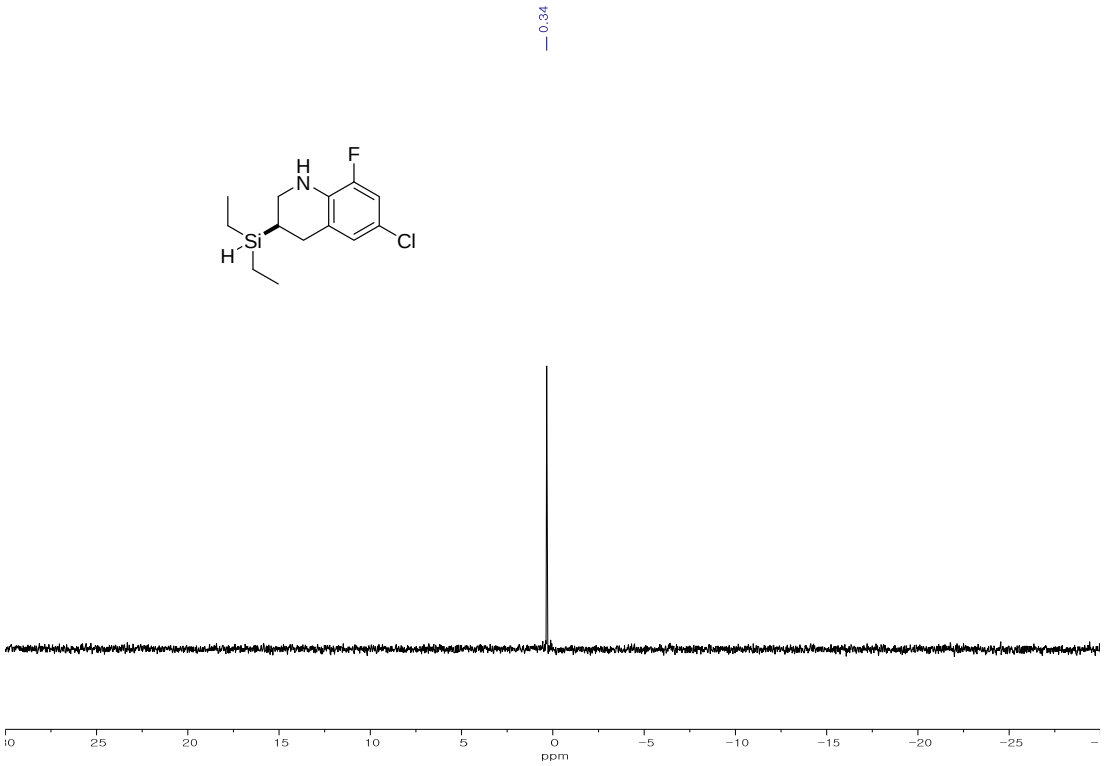




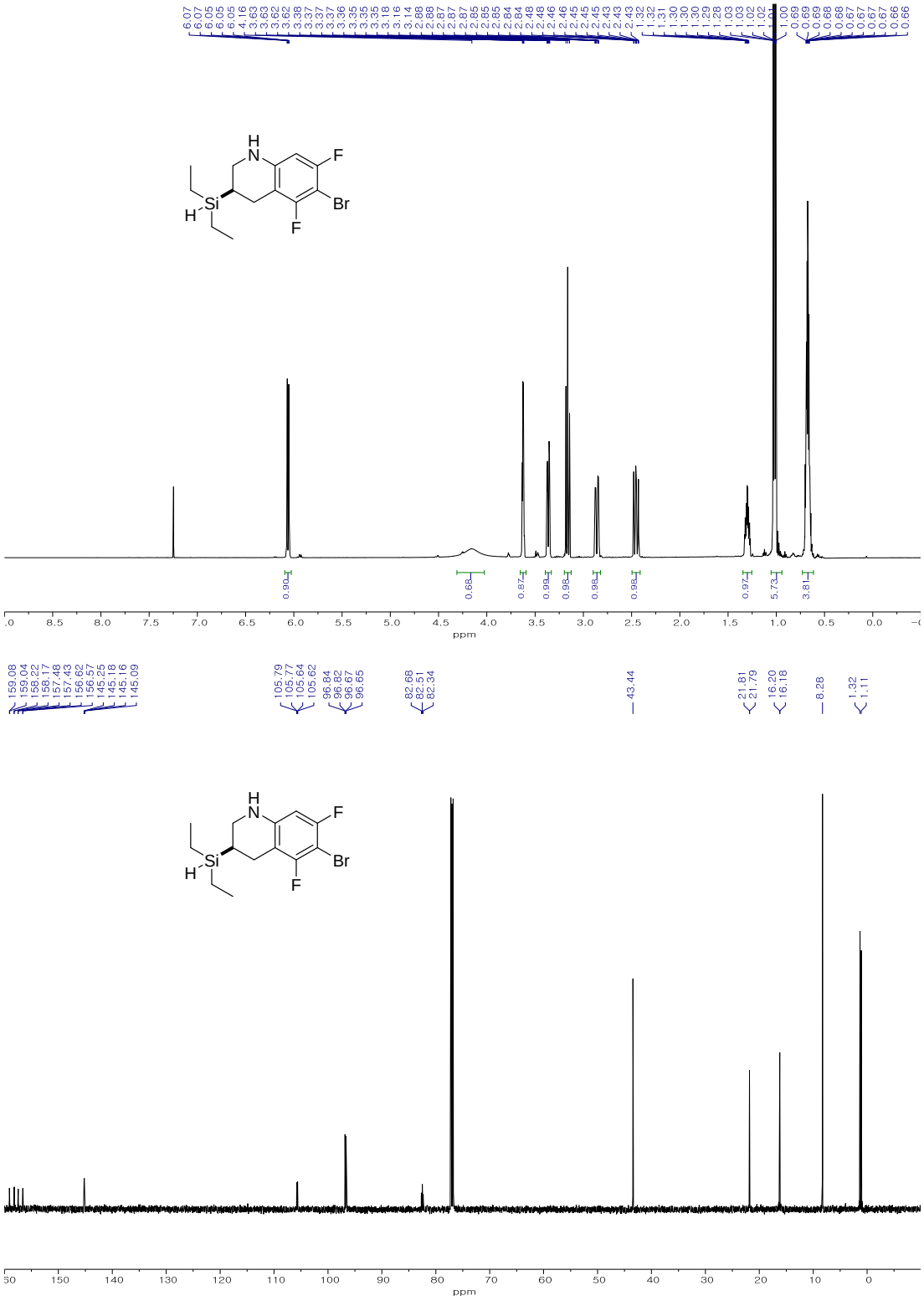
6-Chloro-3-(diethylsilyl)-8-fluoro-1,2,3,4-tetrahydroquinoline (Table 1, 26b)

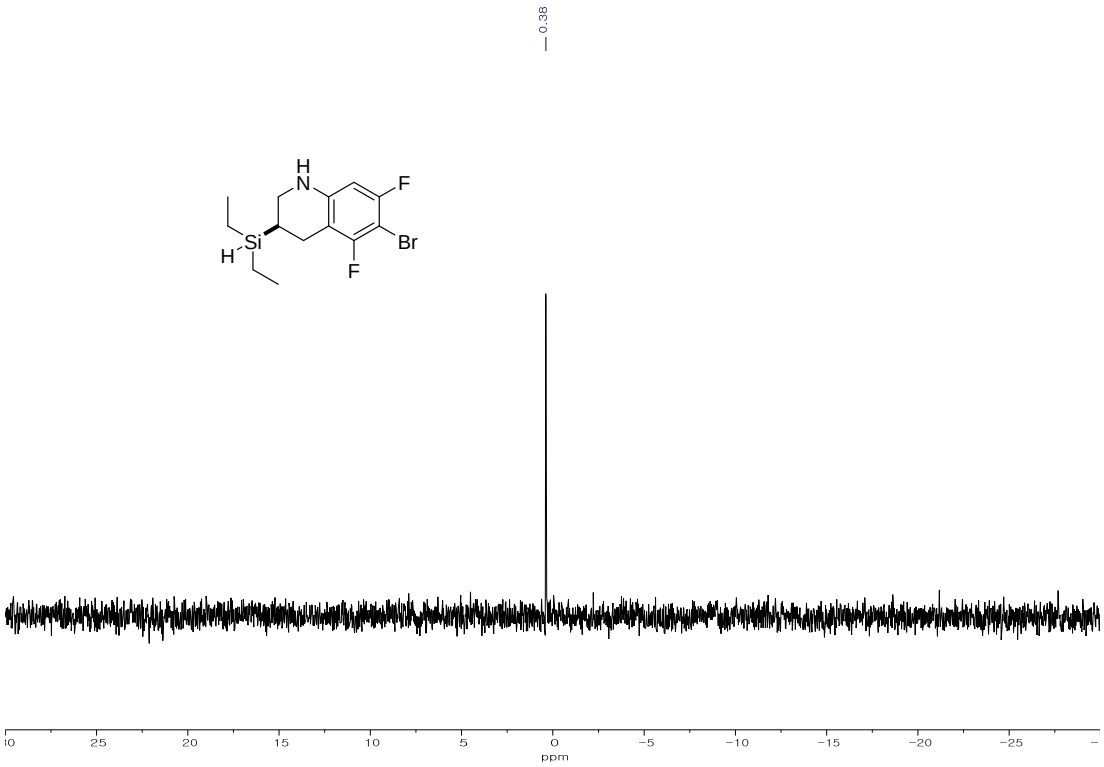



151.13
149.53
131.75
131.67
124.70
124.67
123.89
123.87
119.45
119.38
112.94
112.79
43.19
28.73
28.71
17.12
8.29
1.29
1.14
H
N
F
Si
H
Cl
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

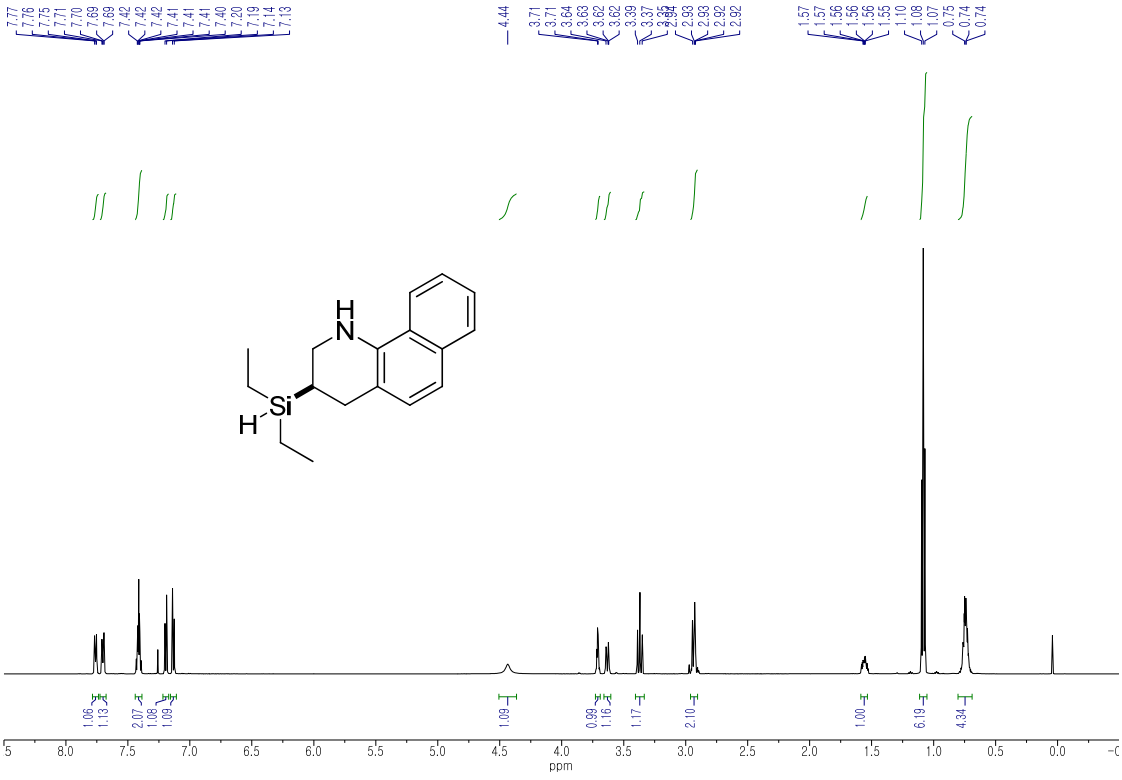

0.34
H
N
F
Si
H
Cl
25
20
15
10
5
0
−5
−10
−15
−20
−25
ppm

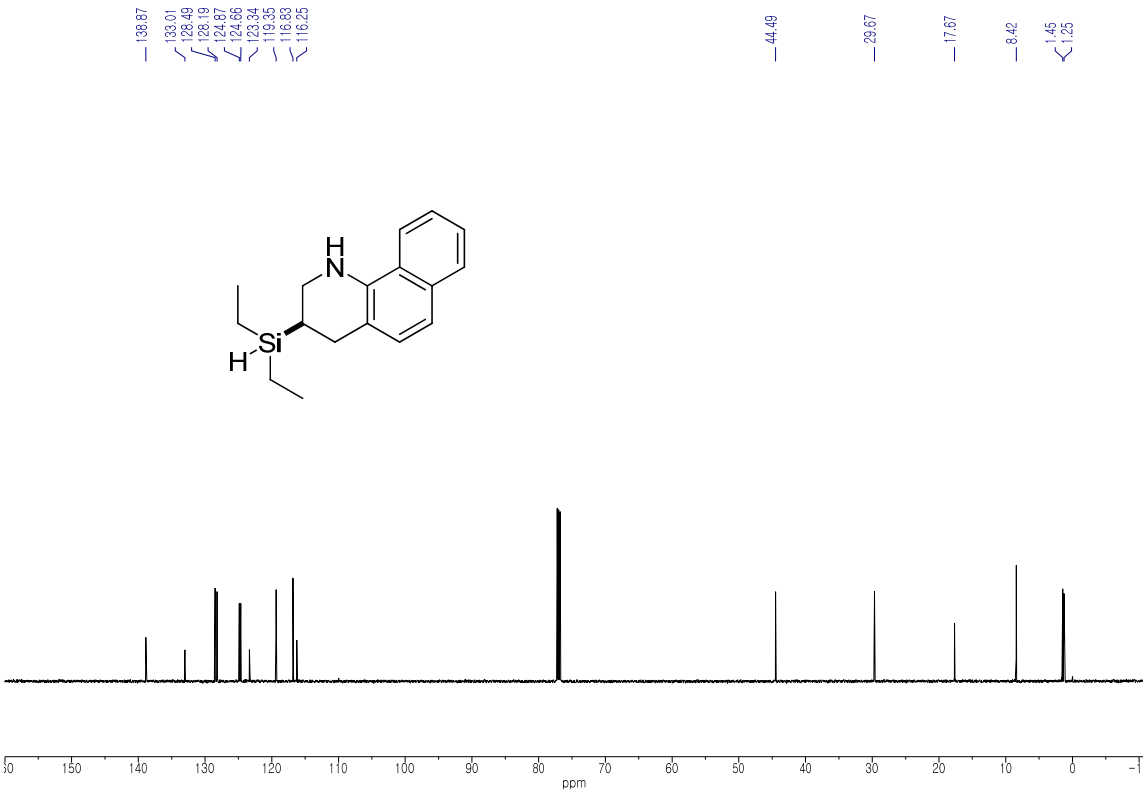
6-Bromo-3-(diethylsilyl)-5,7-difluoro-1,2,3,4-tetrahydroquinoline (Table 1, 27b)

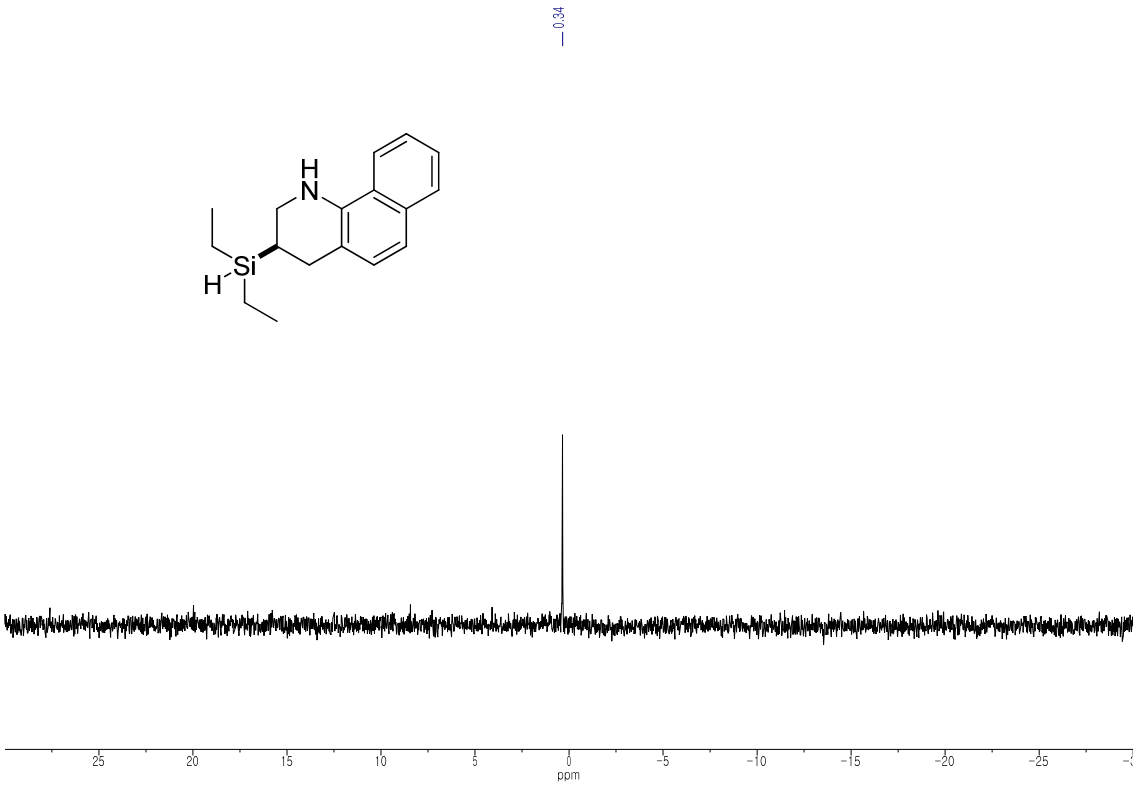




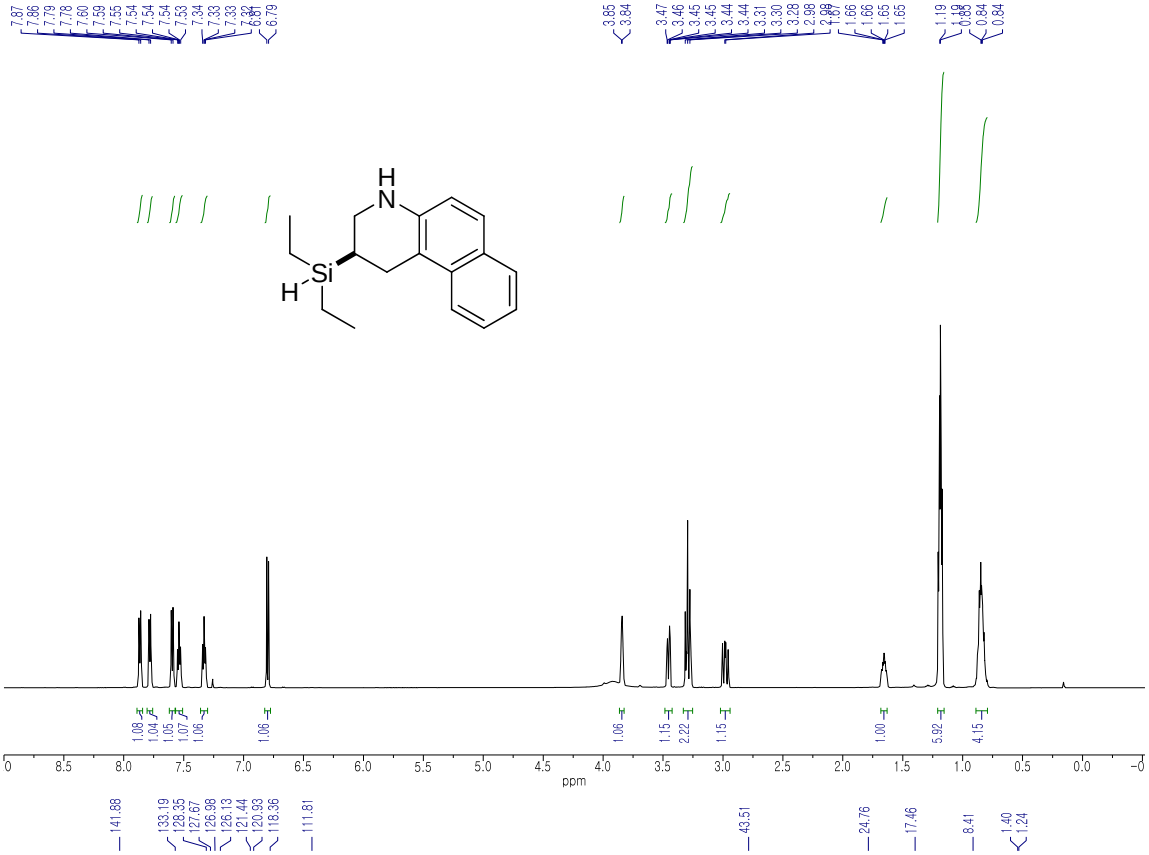
3-(Diethylsilyl)-1,2,3,4-tetrahydrobenzo[*h*]quinoline (Table 1, 28b)

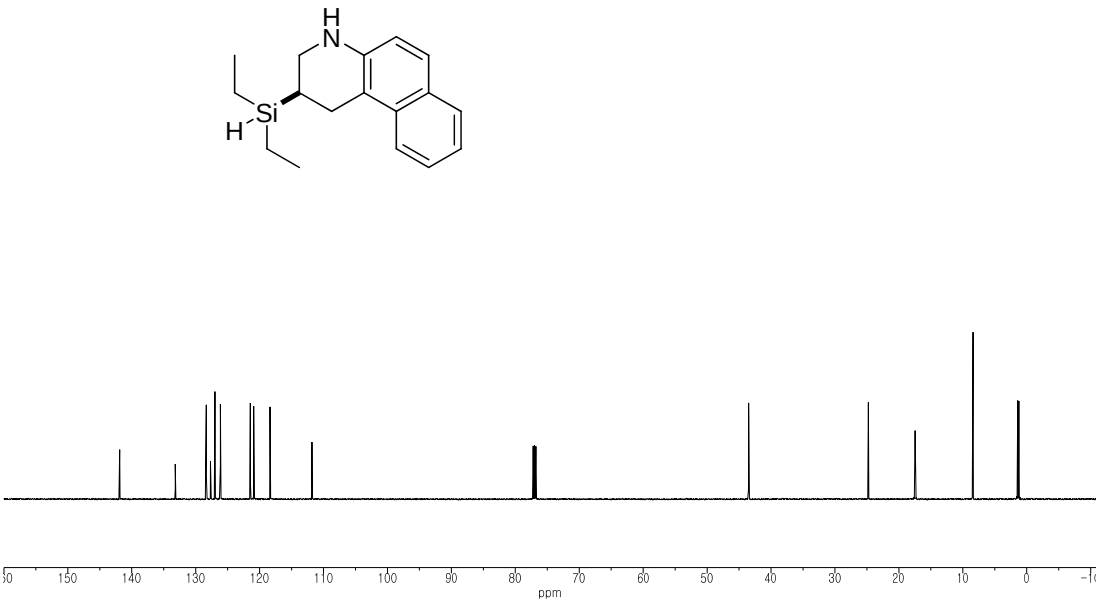



138.87
133.01
128.49
128.19
124.87
124.66
123.34
119.35
116.83
116.25
44.49
29.67
17.67
8.42
1.45
1.25
H
N
Si
H
ppm

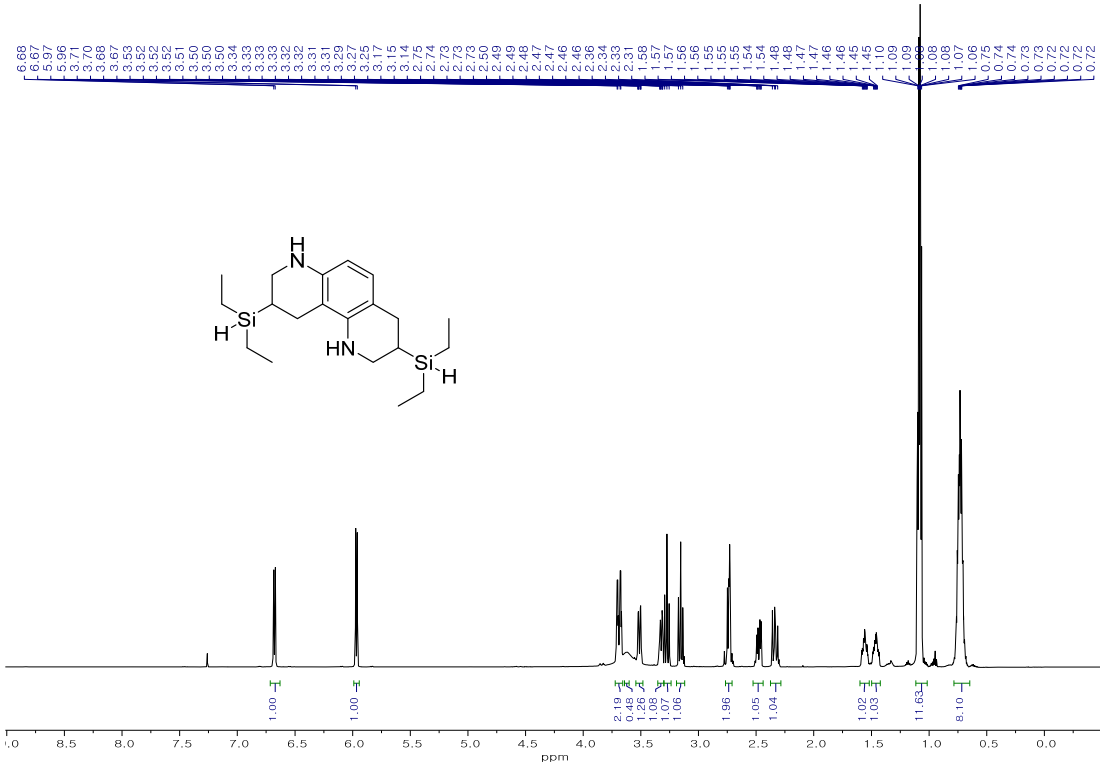

0.34
H
N
Si
H
ppm

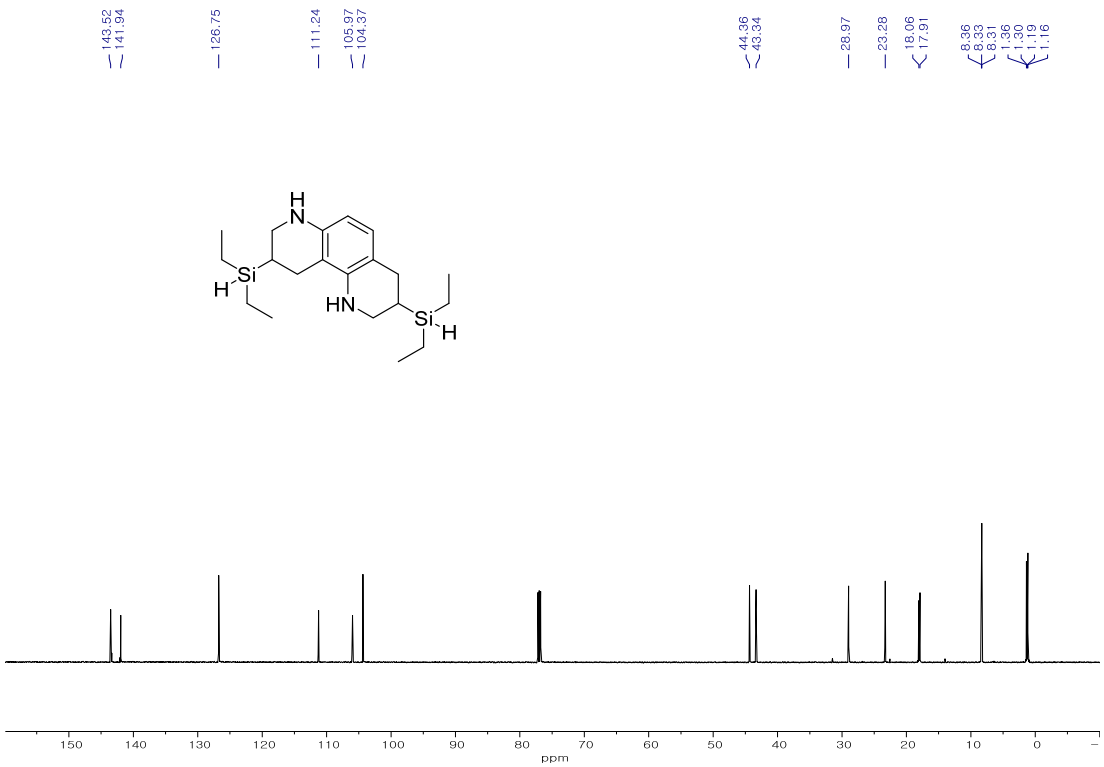
2-(Diethylsilyl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline (Table 1, 29b)

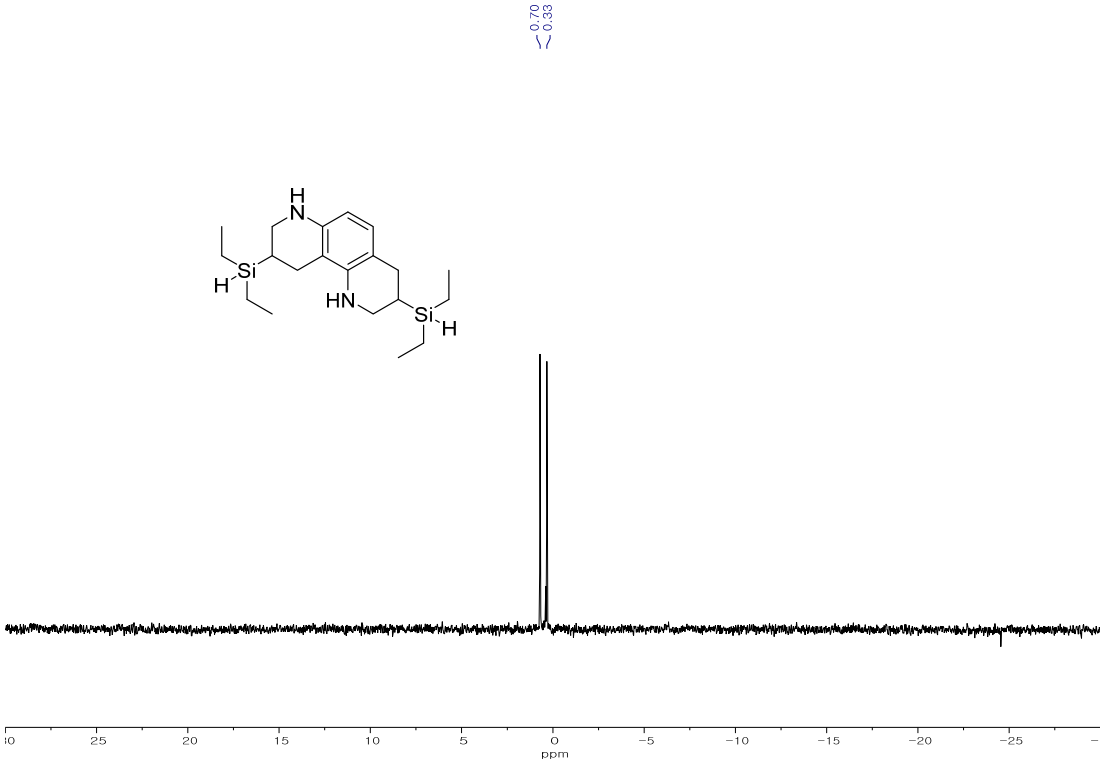




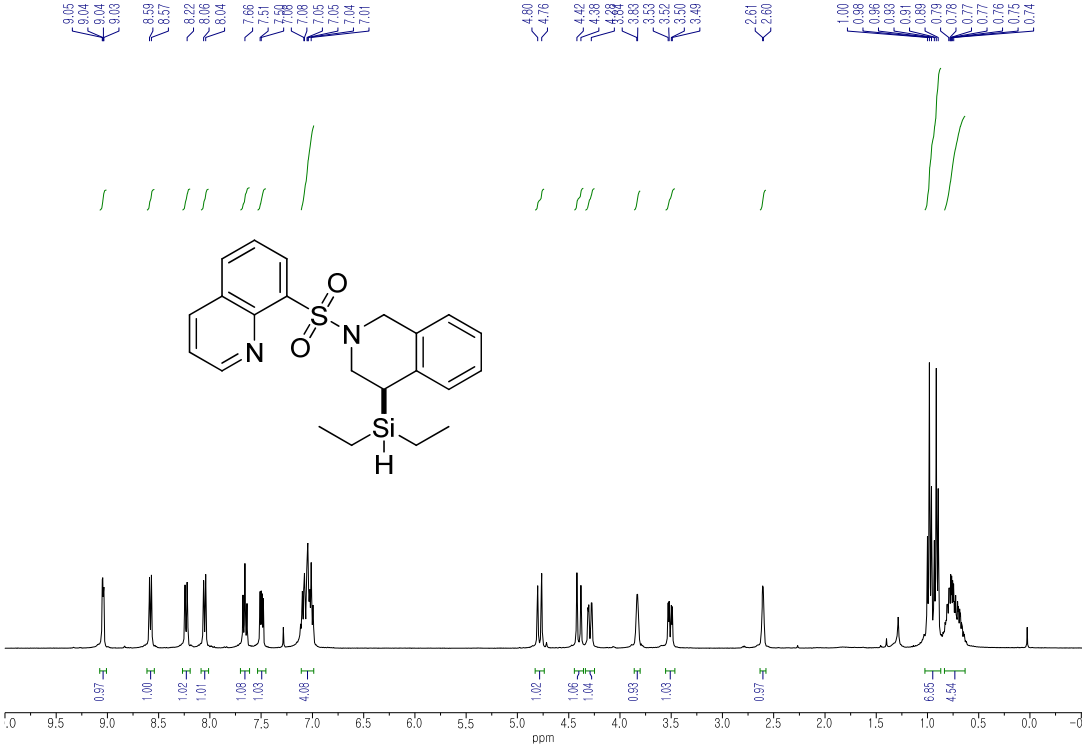
3,9-Bis(diethylsilyl)-1,2,3,4,7,8,9,10-octahydro-1,7-phenanthroline (Table 1, 30b)

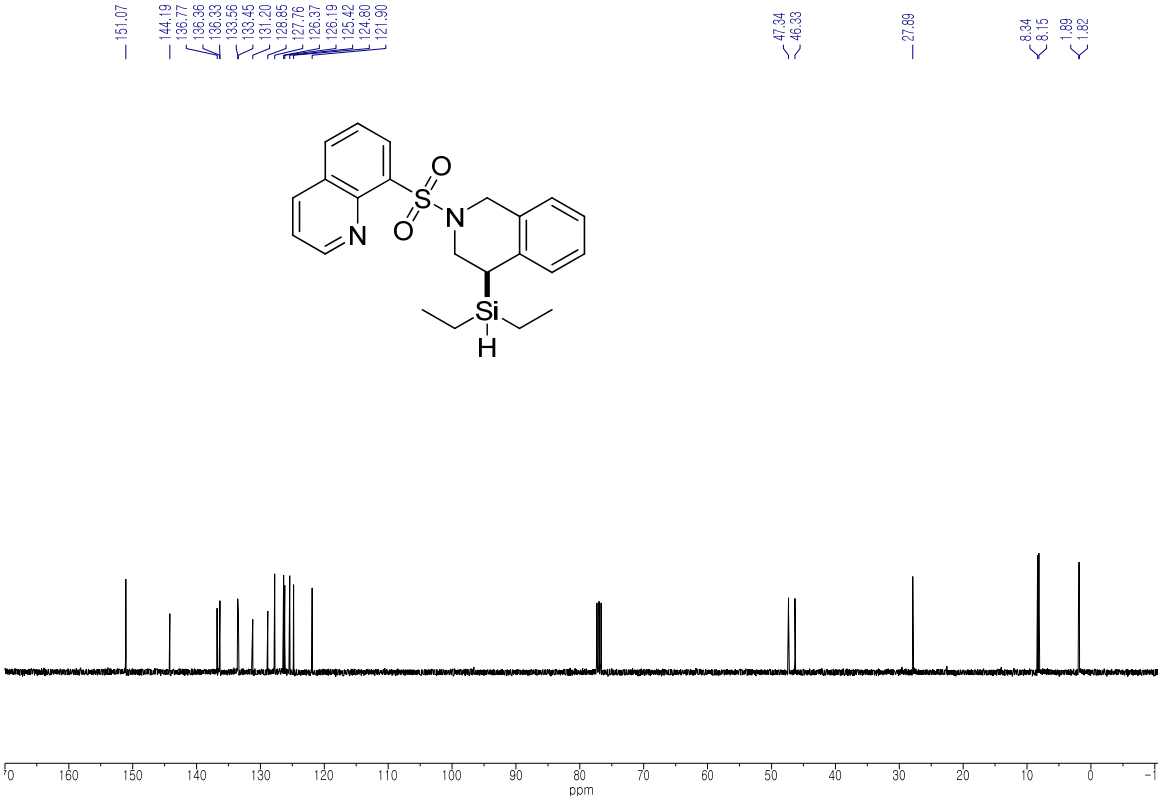


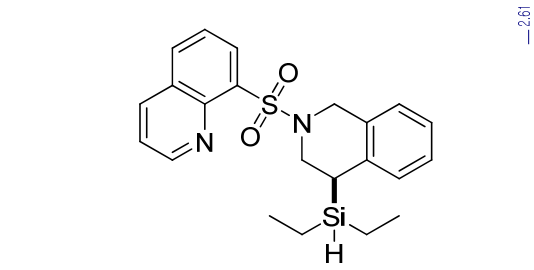

143.52
141.94
126.75
111.24
105.97
104.37
44.36
43.34
29.97
23.28
18.06
17.91
8.36
8.33
8.31
1.36
1.30
1.19
1.16
H
N
Si
H
HN
Si
H
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

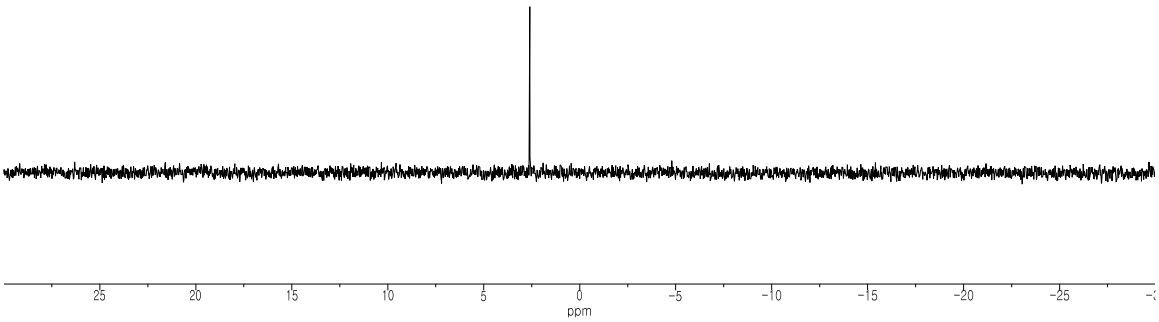

0.70
0.33
H
N
Si
H
HN
Si
H
10
25
20
15
10
5
0
-5
-10
-15
-20
-25
ppm

8-{4-(Diethylsilyl)-3,4-dihydroisoquinolin-2(1*H*)-ylsulfonyl}quinoline (Table 1, 31b)

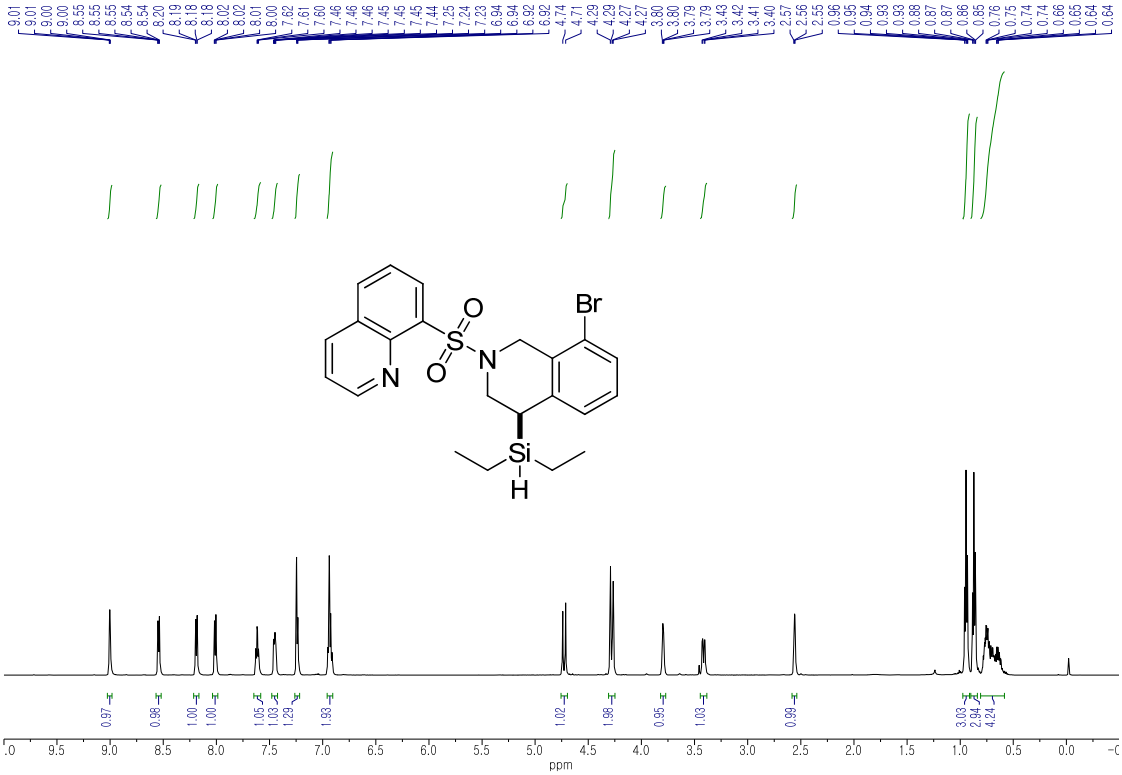


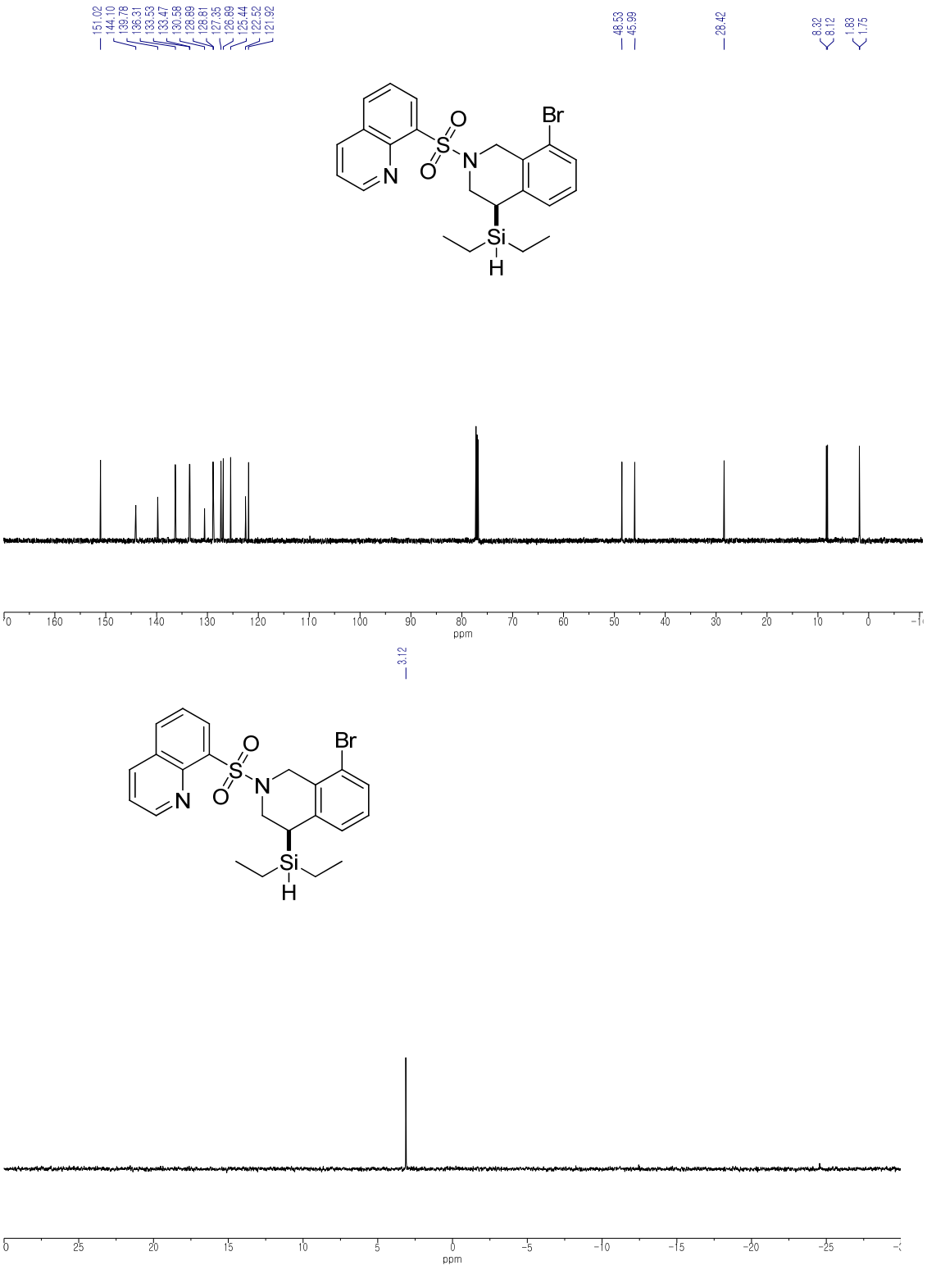




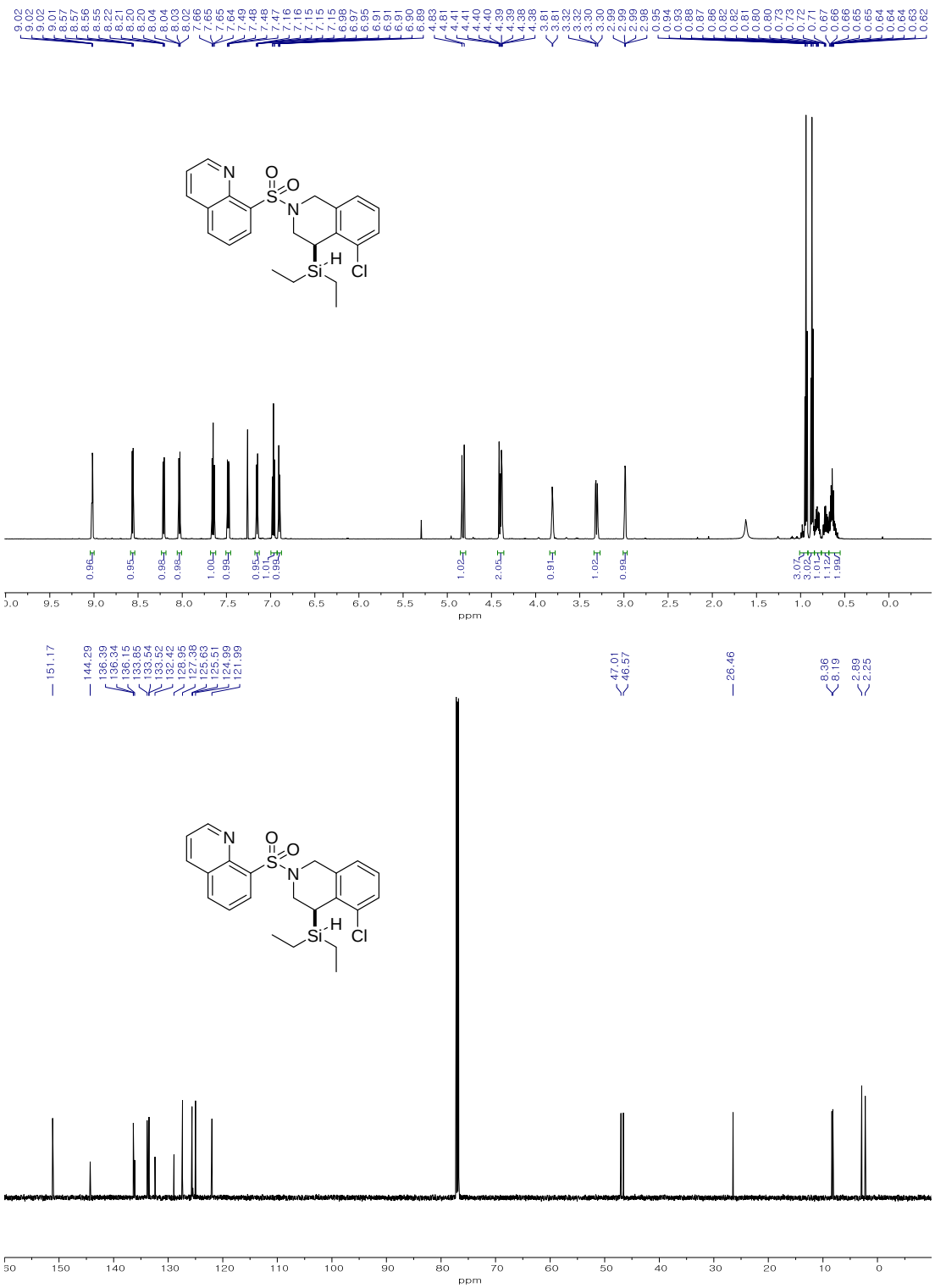


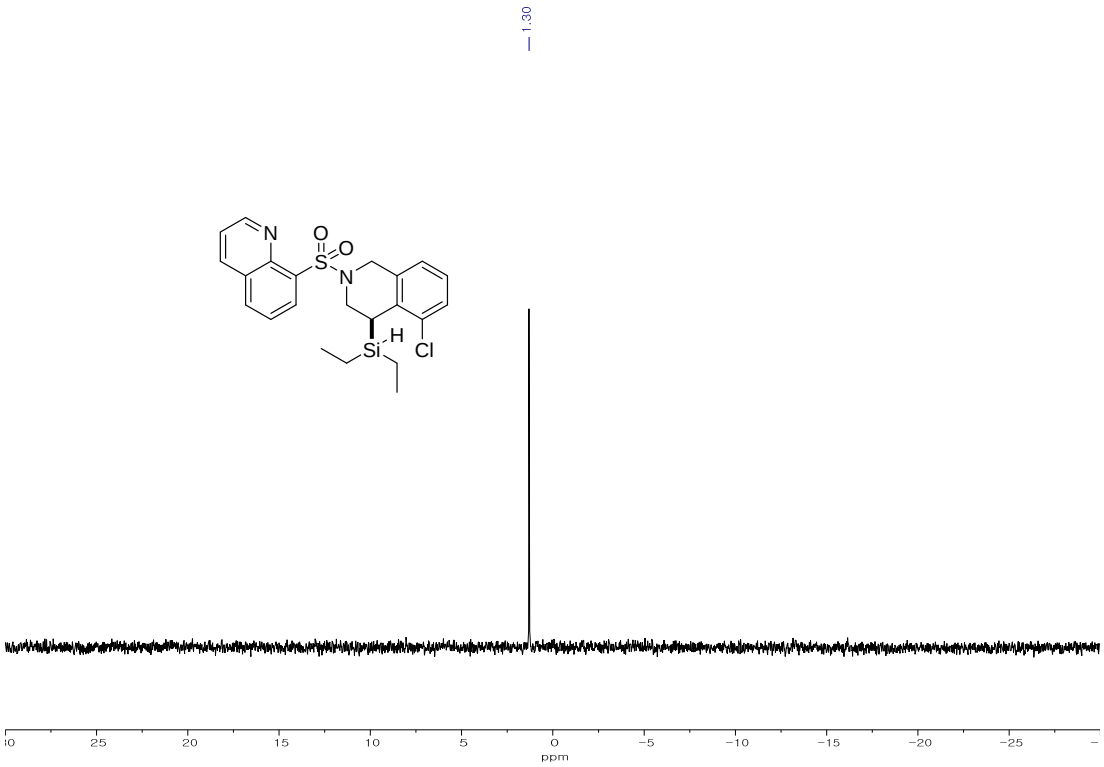
8-{8-Bromo-4-(diethylsilyl)-3,4-dihydroisoquinolin-2(1*H*)-ylsulfonyl}quinoline (Table 1, 32b)



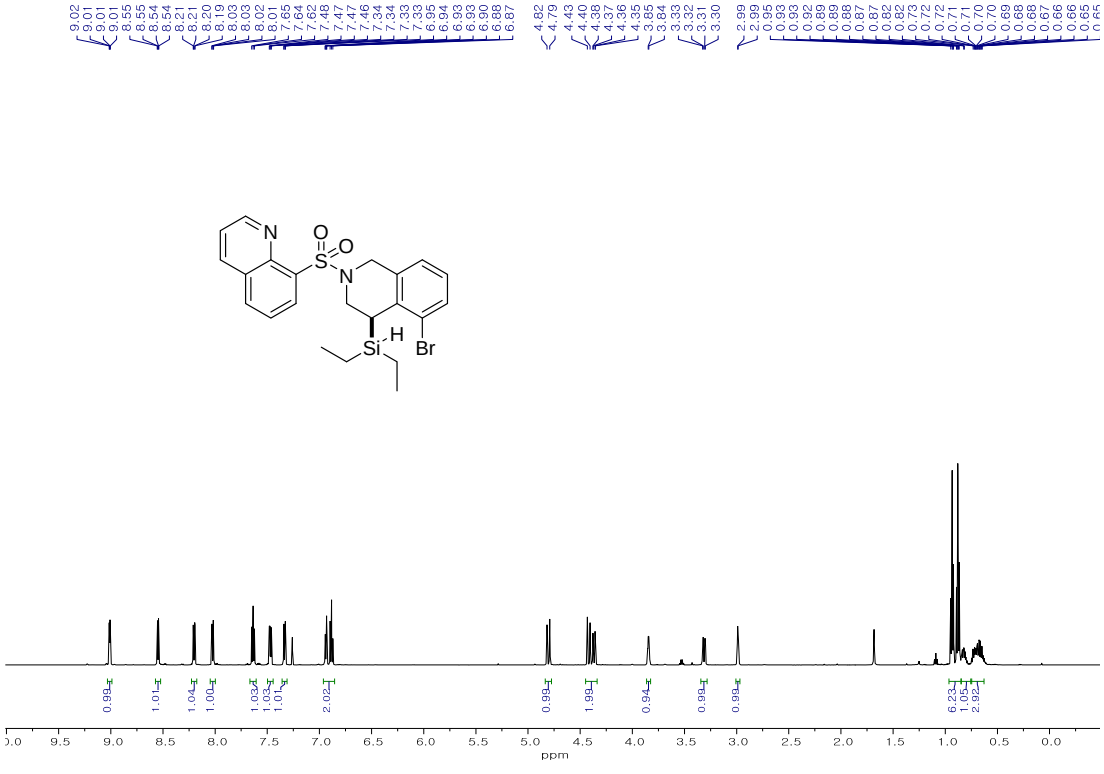

151.02
144.10
139.78
136.31
133.53
133.47
130.58
128.89
128.81
127.35
126.89
125.44
122.52
121.92
48.53
45.99
28.42
8.32
8.12
1.83
1.75
Br
O
S
O
N
N
Si
H
ppm
3.12
Br
O
S
O
N
N
Si
H
ppm

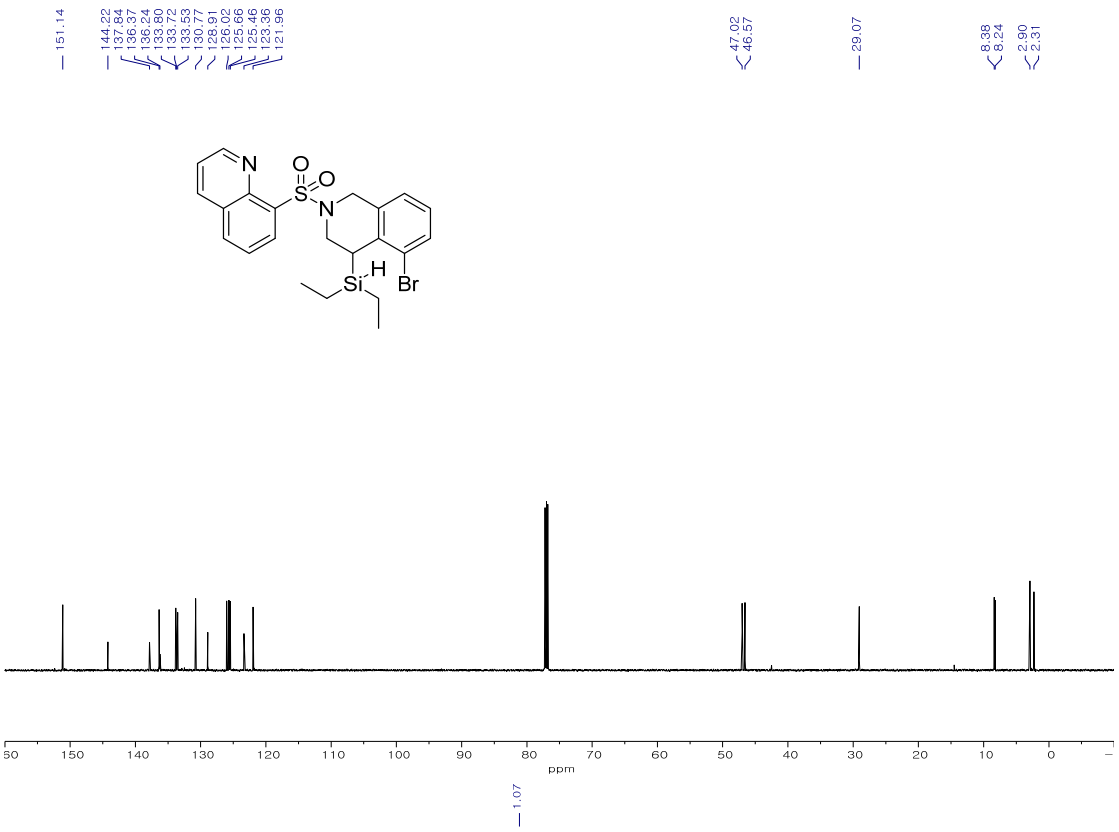
8-[{5-Chloro-4-(diethylsilyl)-3,4-dihydroisoquinolin-2(1H)-yl}sulfonyl]quinoline (Table 1, 33b)

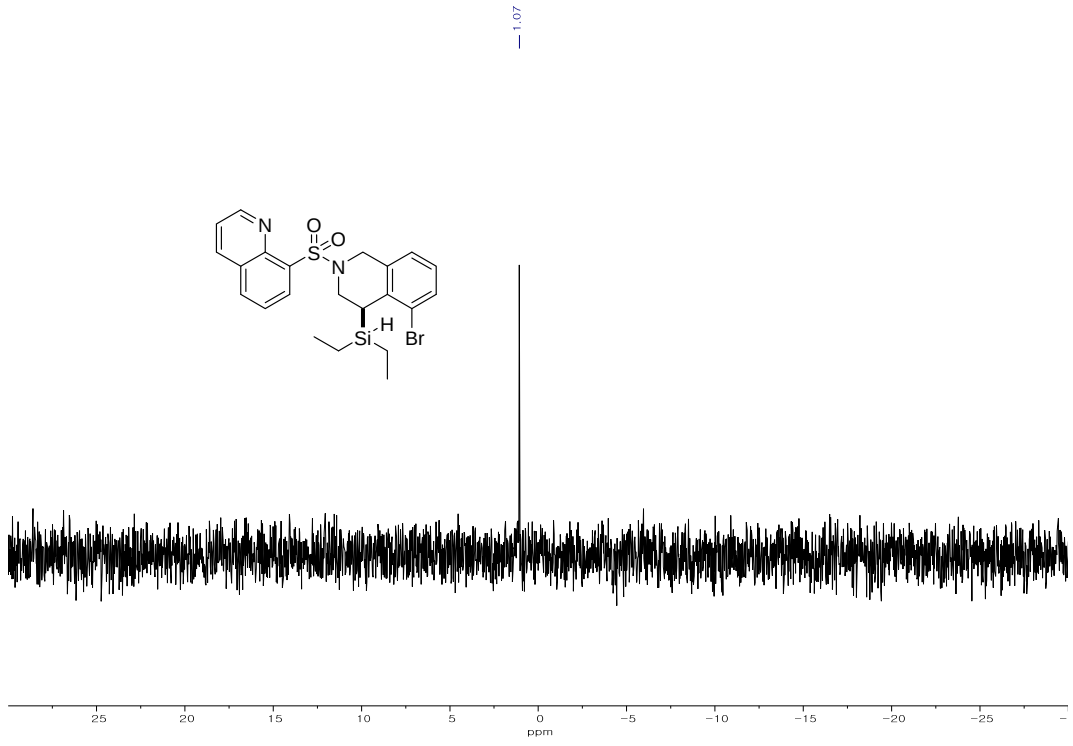


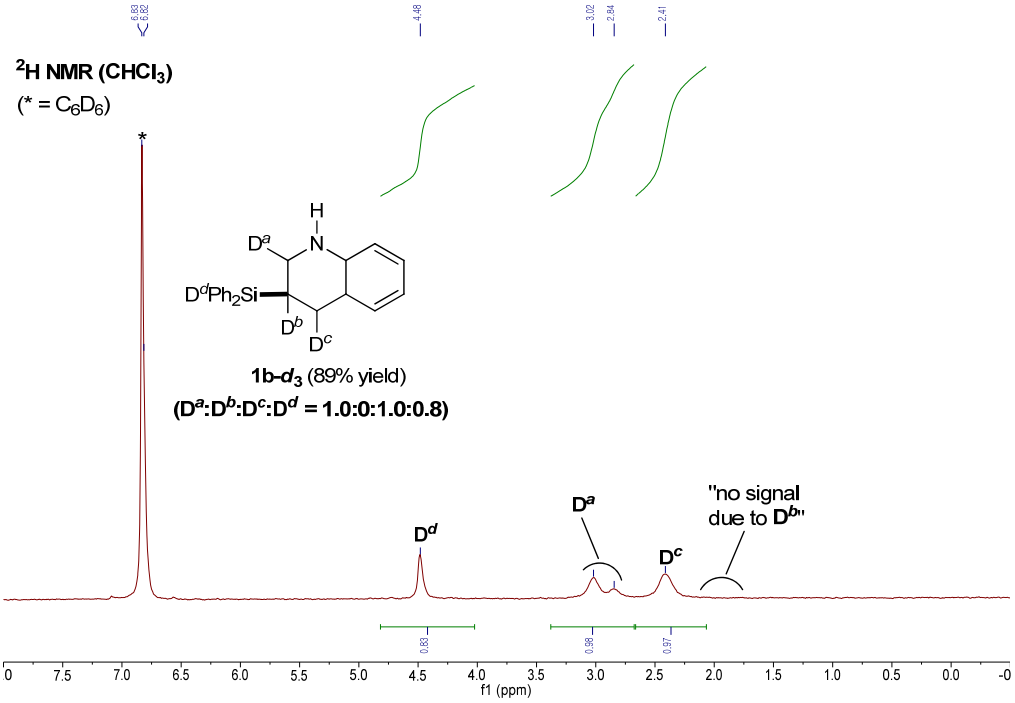


8-[{5-Bromo-4-(diethylsilyl)-3,4-dihydroisoquinolin-2(1*H*)-yl}sulfonyl]quinoline (Table 1, 34b)

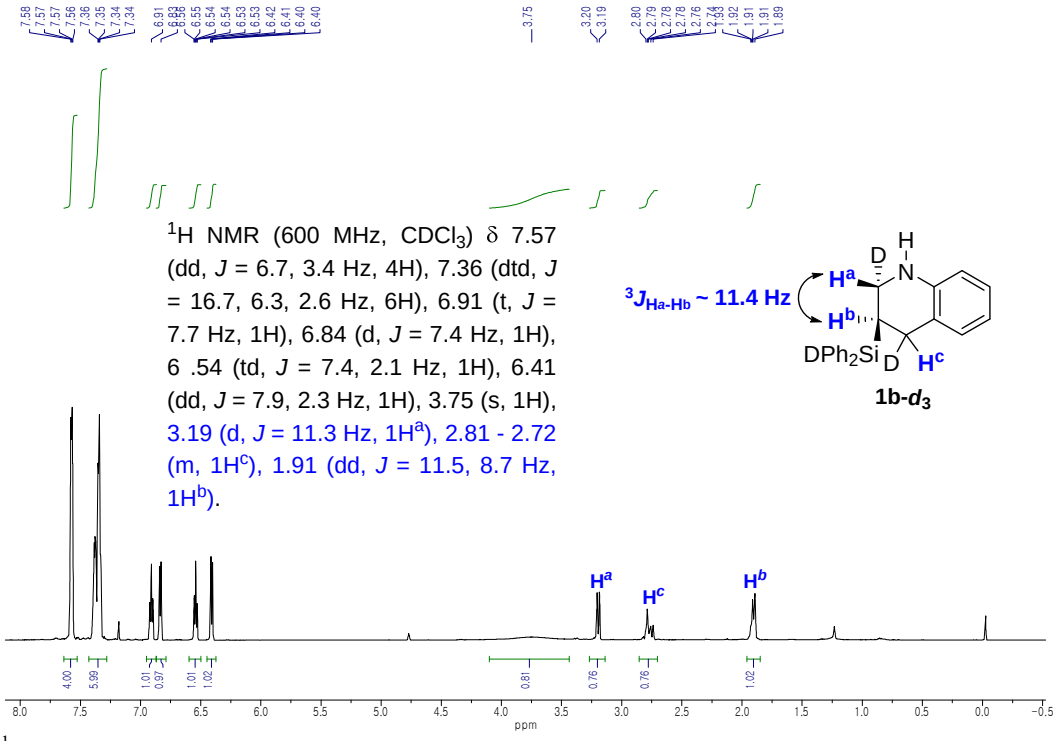



151.14
144.22
137.84
136.37
136.24
133.80
133.72
133.53
130.77
128.91
126.02
125.66
125.46
123.36
121.96
47.02
46.57
29.07
8.38
8.24
2.90
2.31
N
O
O
S
N
H
Si
Br
50
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

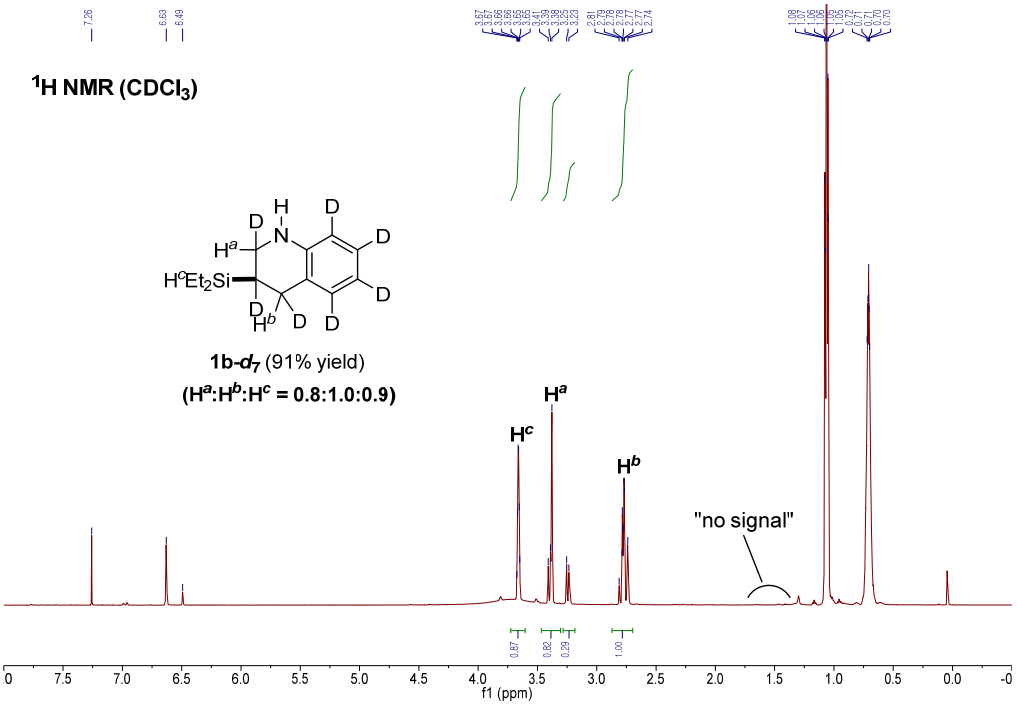

1.07
N
O
O
S
N
H
Si
Br
25
20
15
10
5
0
−5
−10
−15
−20
−25
ppm



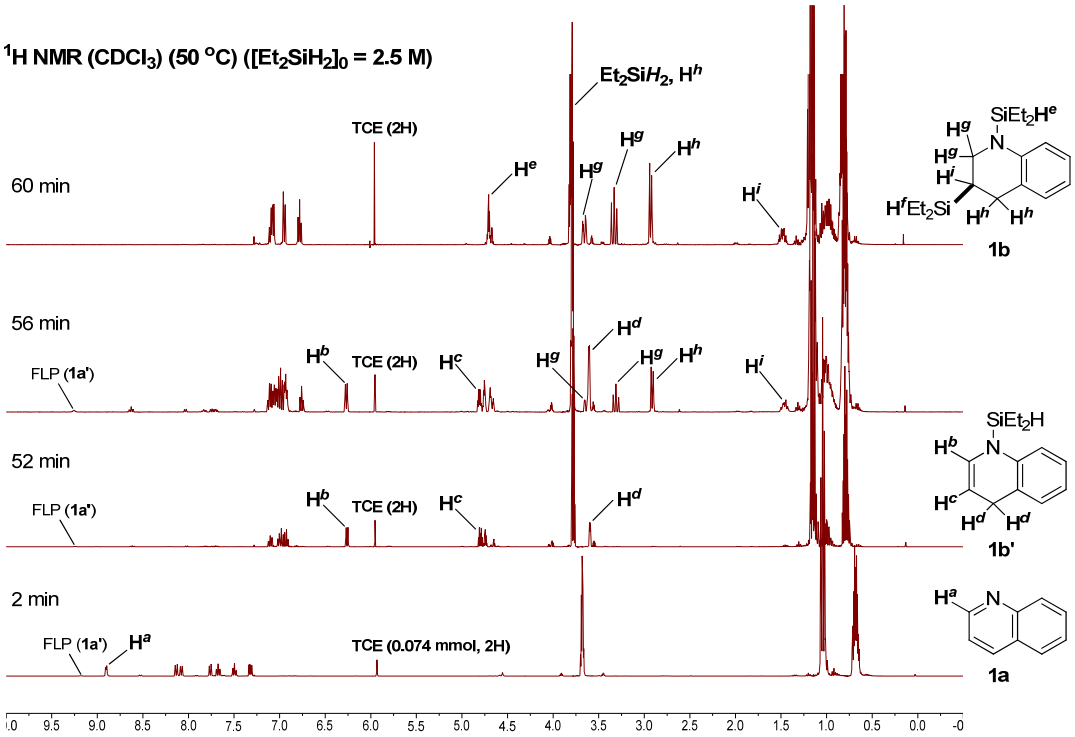
^{2}H NMR spectrum of the silylated product, **1b-d_3** obtained by using Ph_2SiD_2 as a reducing agent (Scheme 2A).



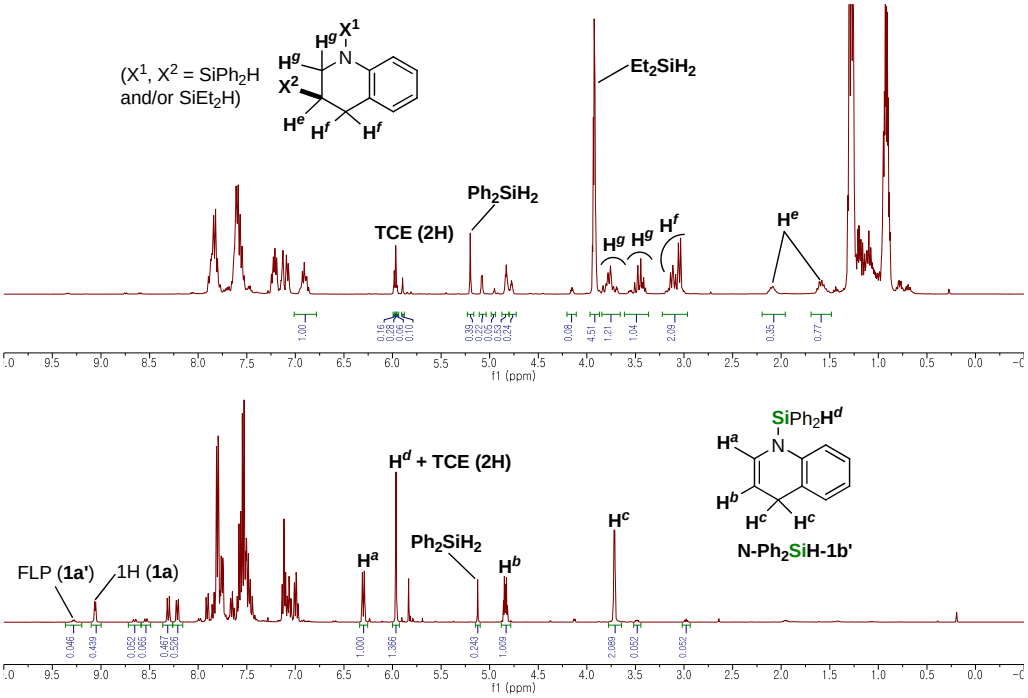
^{1}H NMR spectrum of the silylated product, **1b-d_3** obtained by using Ph_2SiD_2 as a reducing agent (Scheme 2A).



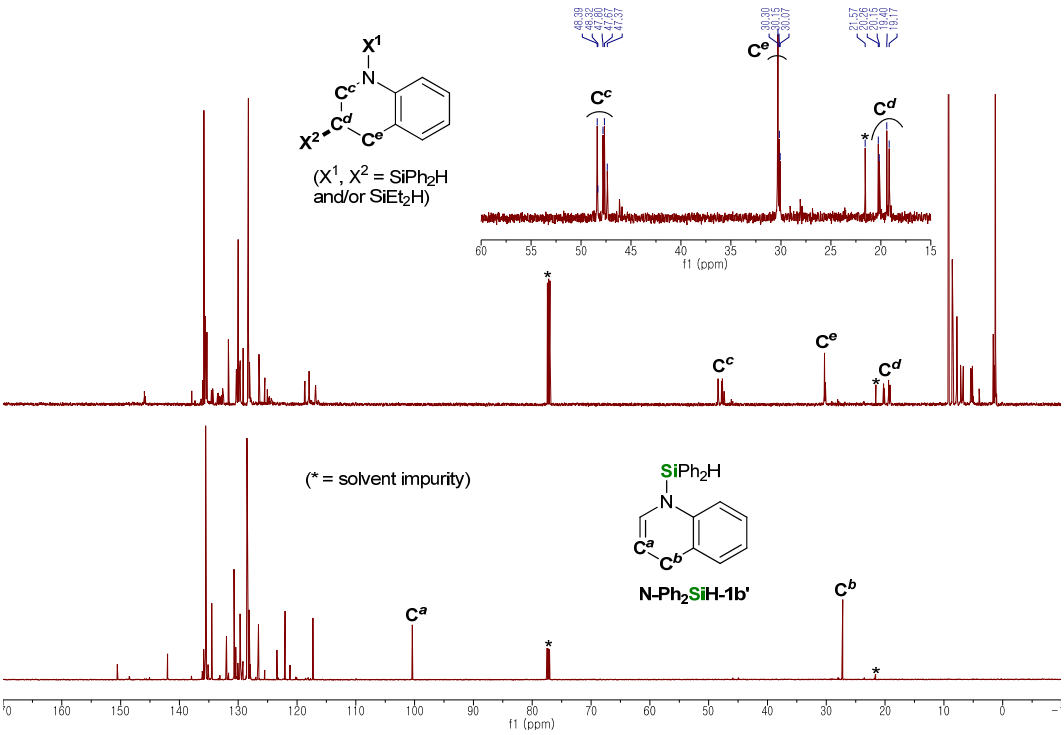
^{1}H NMR spectrum of the silylated product, **1b**-d_7 obtained in the catalytic reaction of **1a**-d_7 with Et_2SiH_2 as a reducing agent.



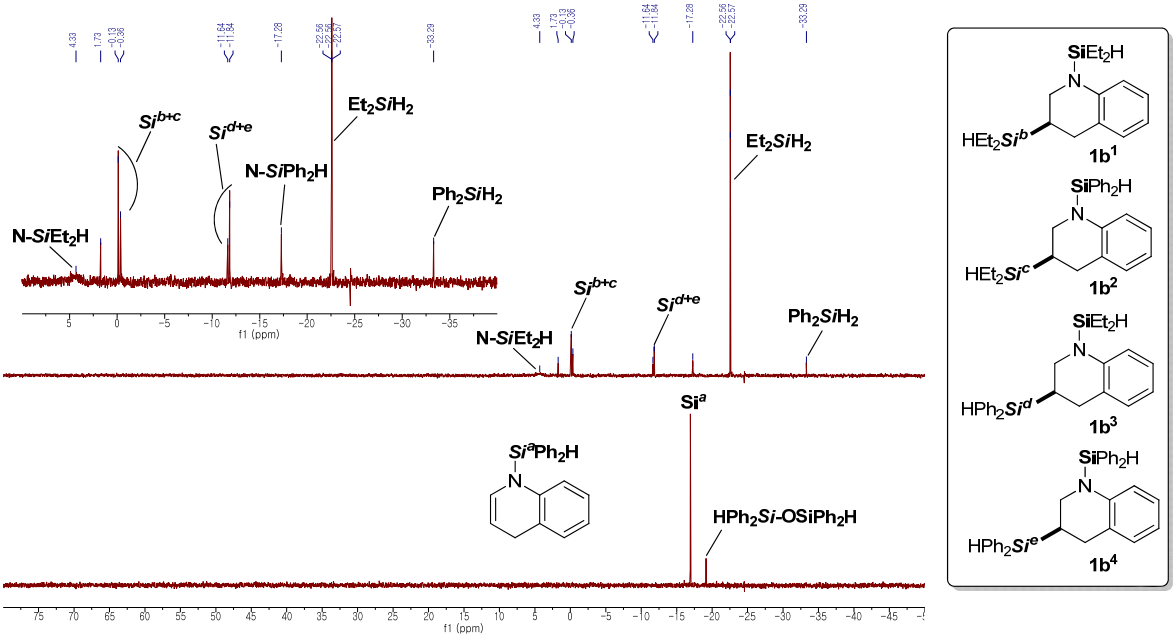
^{1}H NMR spectra of the silylative reduction of **1a** at 50 °C over ~ 1 h with [Et_2SiH_2]$_0$ = 2.5 M in $CDCl_3$ (Scheme 2B).



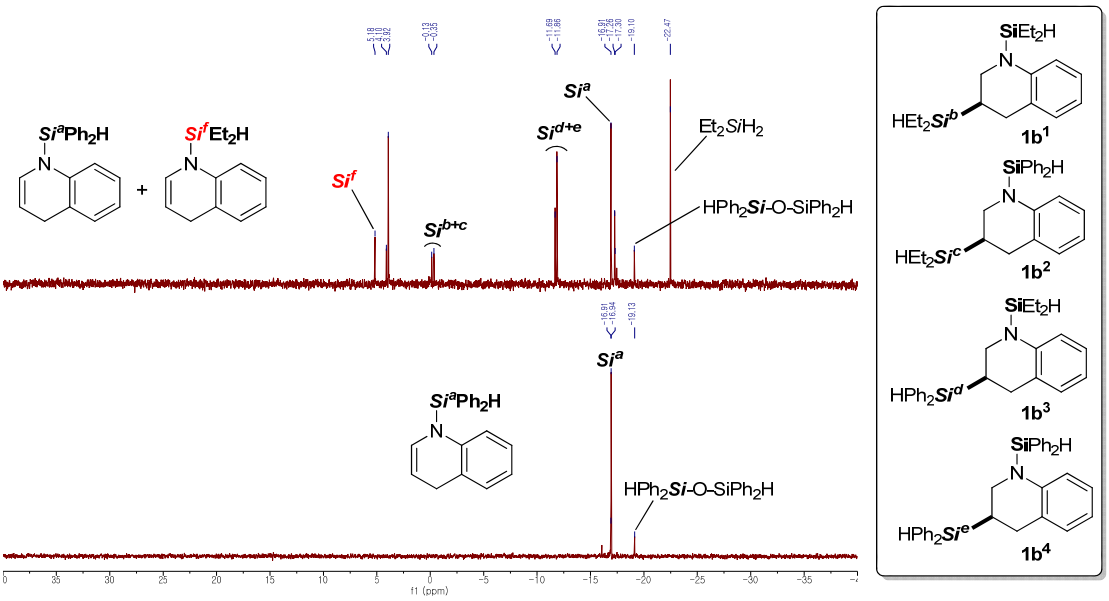
^{1}H NMR spectra of the silylative reduction of **1a** with Ph_2SiH_2 (1 equiv.) at 65 ^{o}C for 12 h (*below*) and of a crude mixture (*above*) formed at 65 ^{o}C in 0.5 h after adding Et_2SiH_2 (3 equiv.) into the mixture in $CDCl_3$.



^{13}C{^{1}H} NMR spectra of the silylative reduction of **1a** with Ph_2SiH_2 (1 equiv.) at 65 ^{o}C for 12 h (*below*) and of a crude mixture (*above*) formed at 65 ^{o}C in 0.5 h after adding Et_2SiH_2 (3 equiv.) into the mixture in $CDCl_3$.

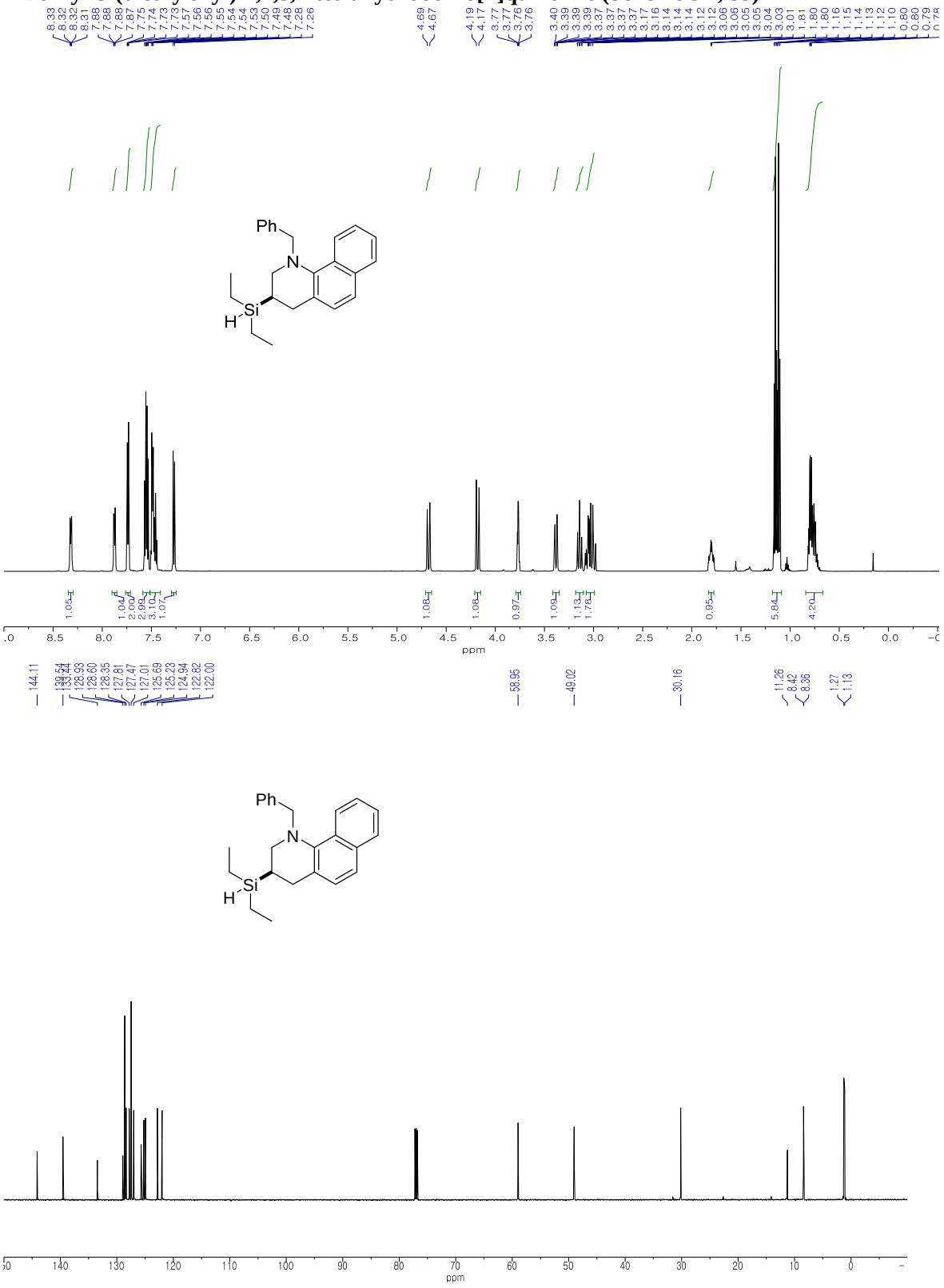


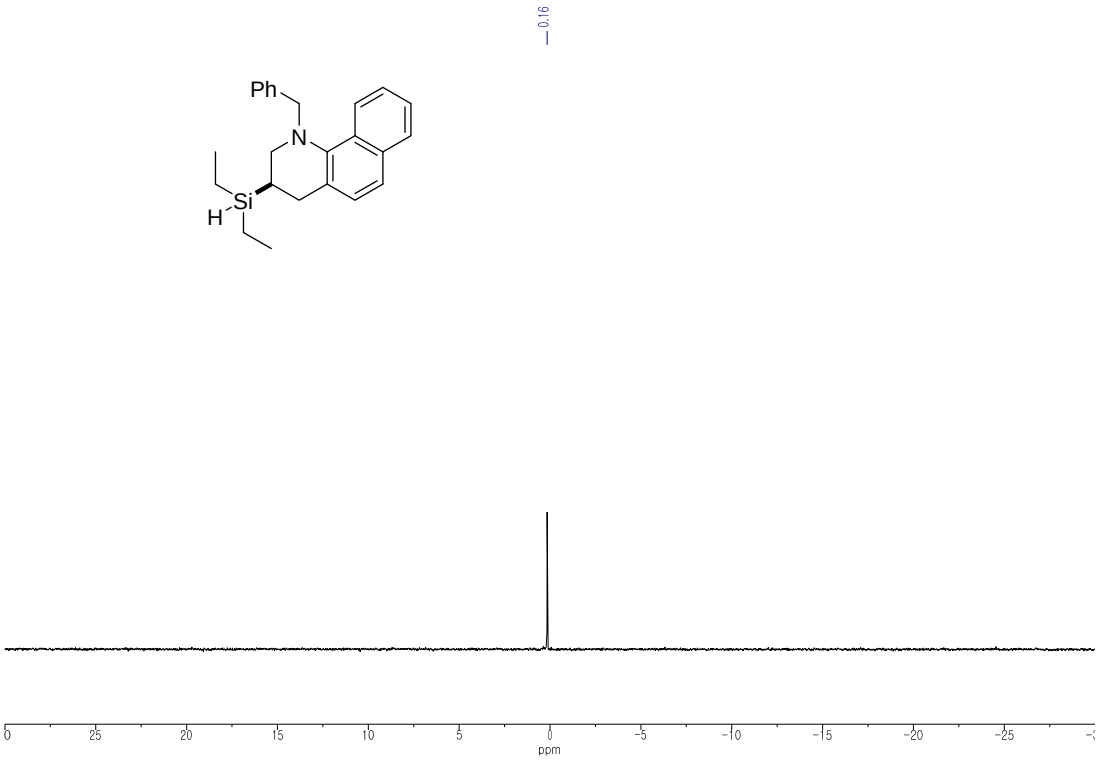
$^{29}Si\{^{1}H\}$ NMR spectra of the silylative reduction of **1a** with Ph_2SiH_2 (1 equiv.) at 65 °C for 12 h (*below*) and of a crude mixture (*above*) formed at 65 °C in 0.5 h after adding Et_2SiH_2 (3 equiv.) into the mixture in $CDCl_3$.



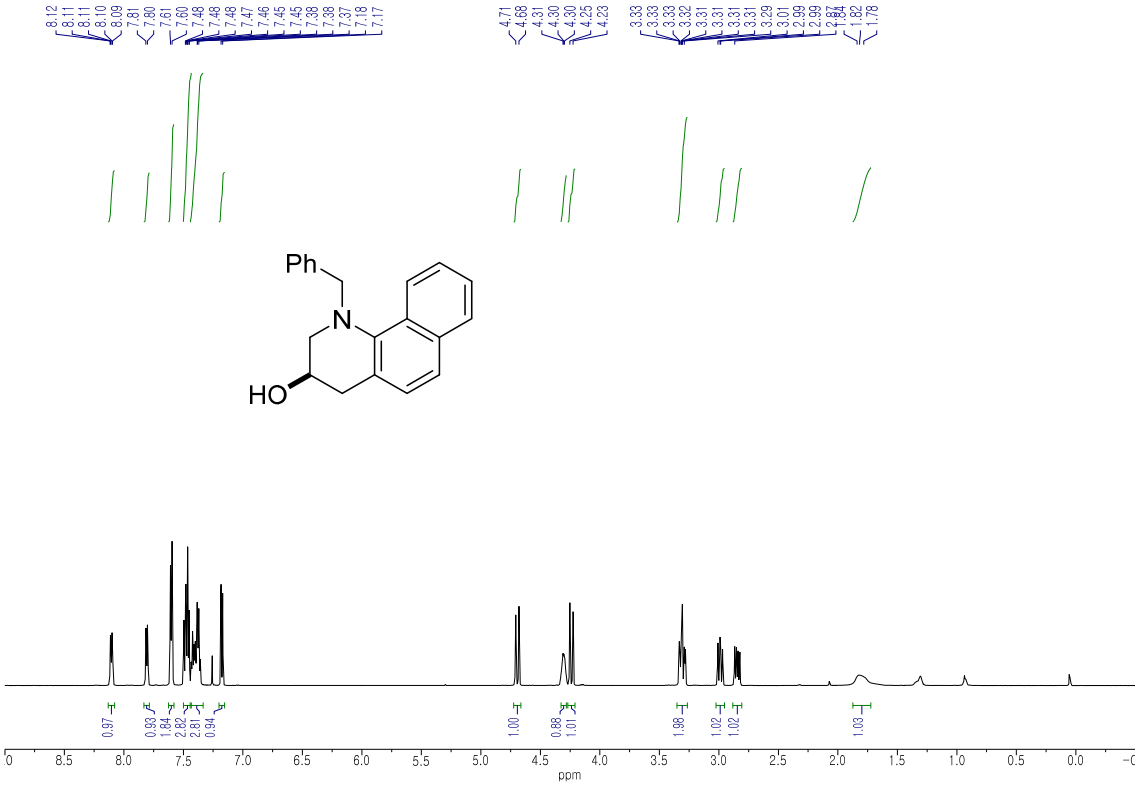
$^{29}Si\{^{1}H\}$ NMR ($CDCl_3$) spectra of the silylative reduction of **1a** with Ph_2SiH_2 (1 equiv.) at 65 °C for 12 h (*below*) and of a crude mixture (*above*) formed at room temperature over ~ 2 days after adding Et_2SiH_2 (1 equiv.) into the mixture.

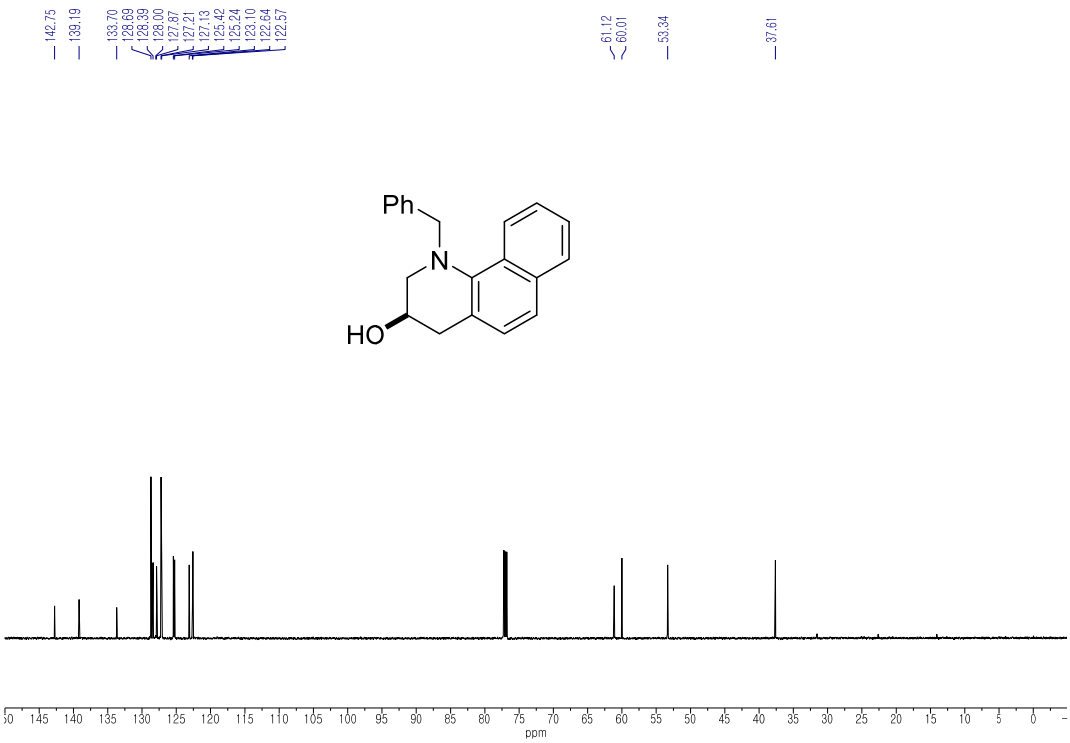
1-Benzyl-3-(diethylsilyl)-1,2,3,4-tetrahydrobenzo[*h*]quinoline (Scheme 3A, 35)



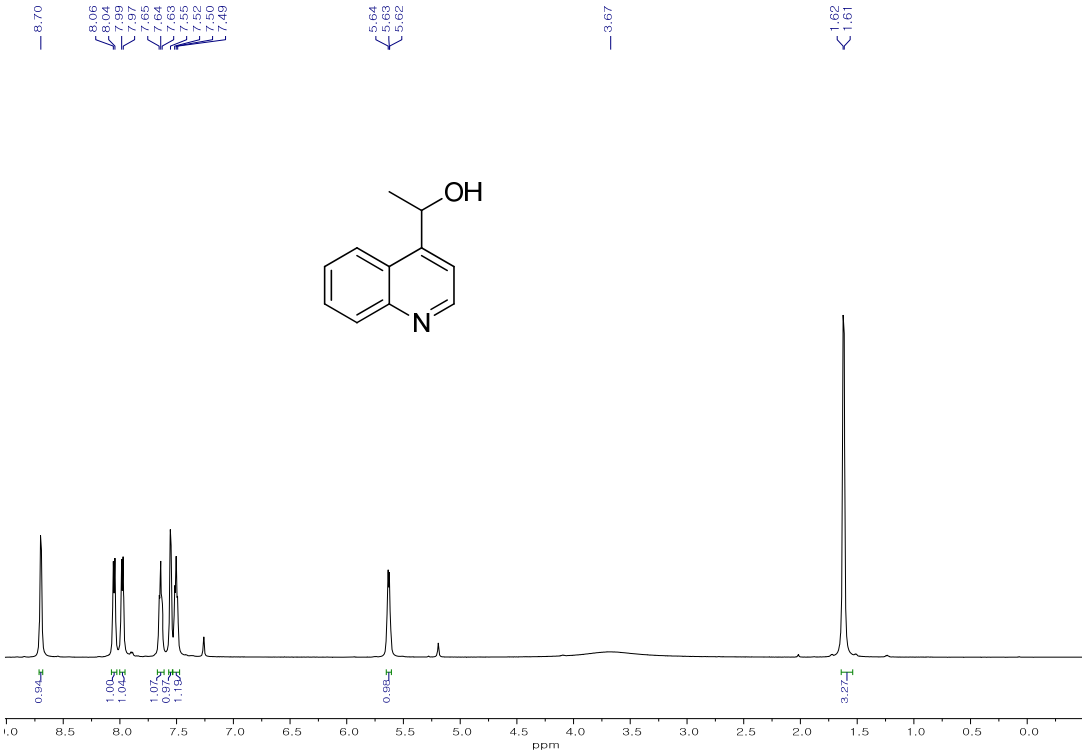


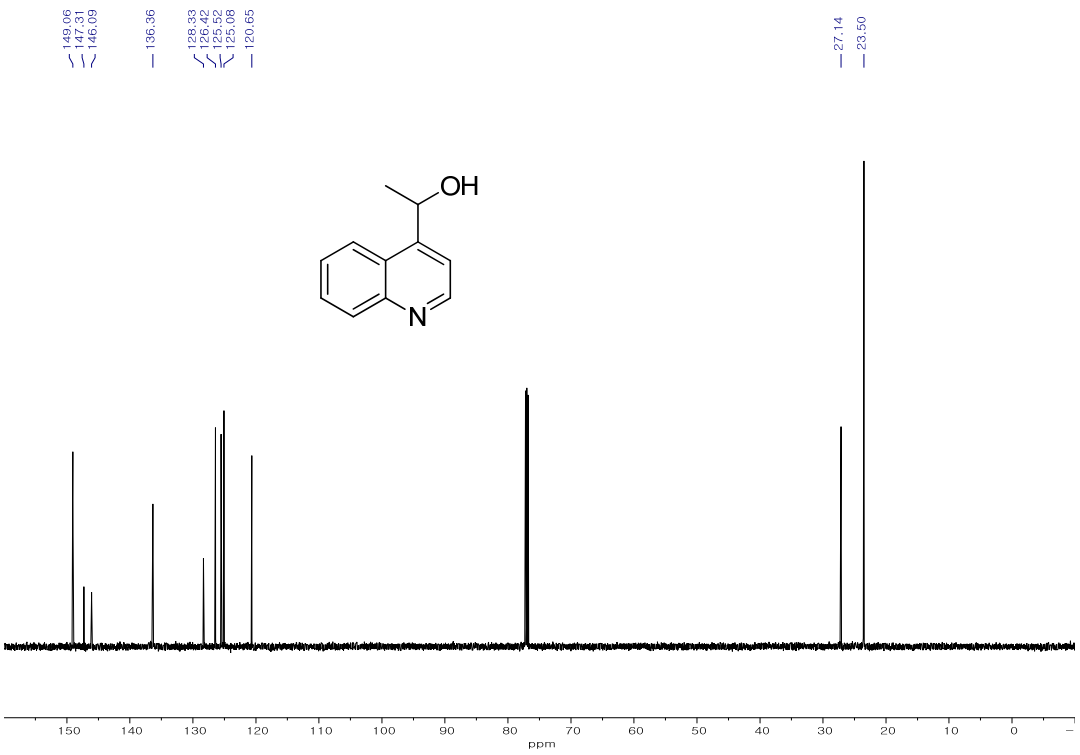
1-Benzyl-1,2,3,4-tetrahydrobenzo[*h*]quinolin-3-ol (Scheme 3A, 36)



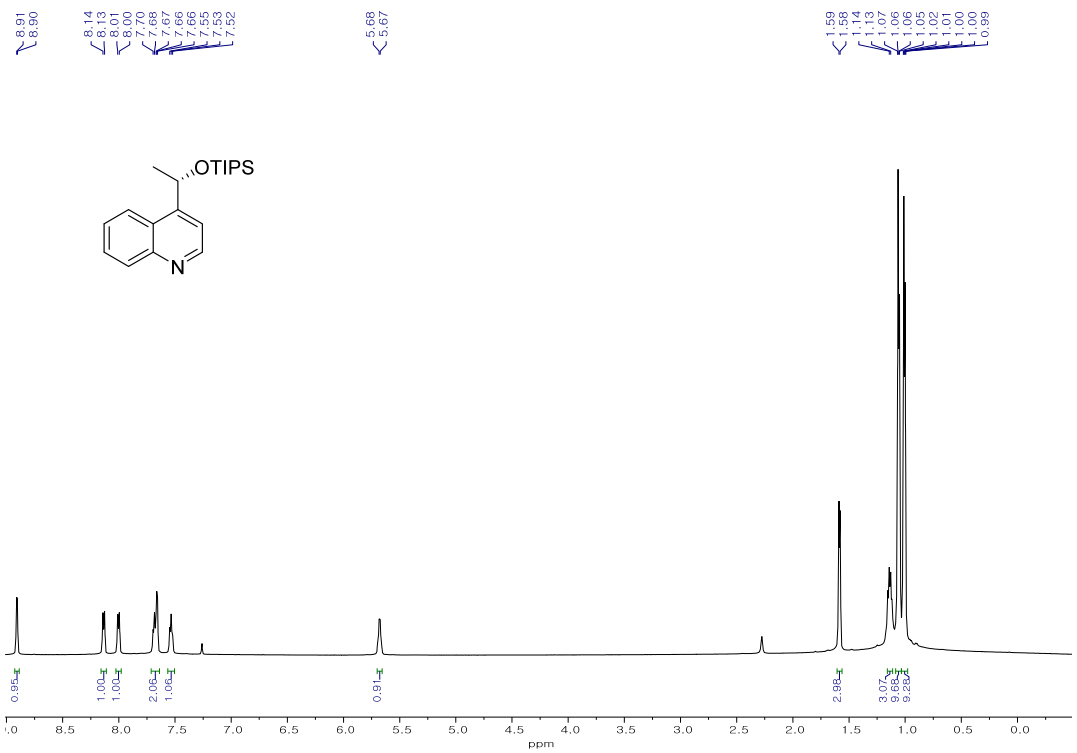


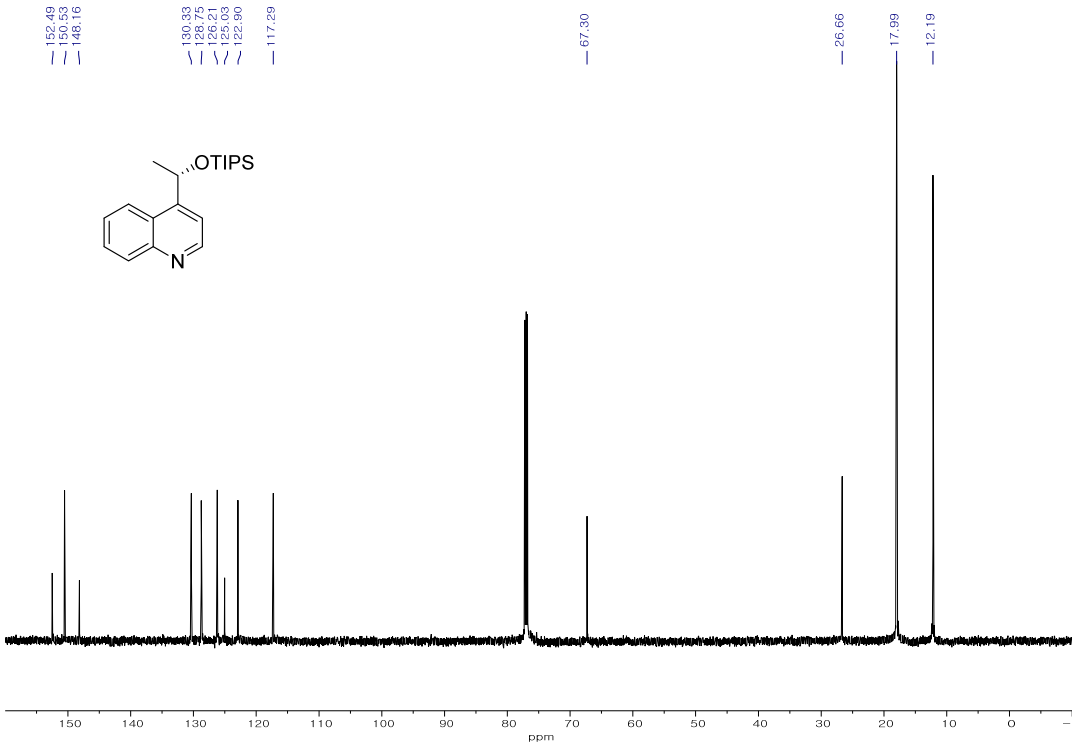
1-(quinolin-4-yl)ethan-1-ol



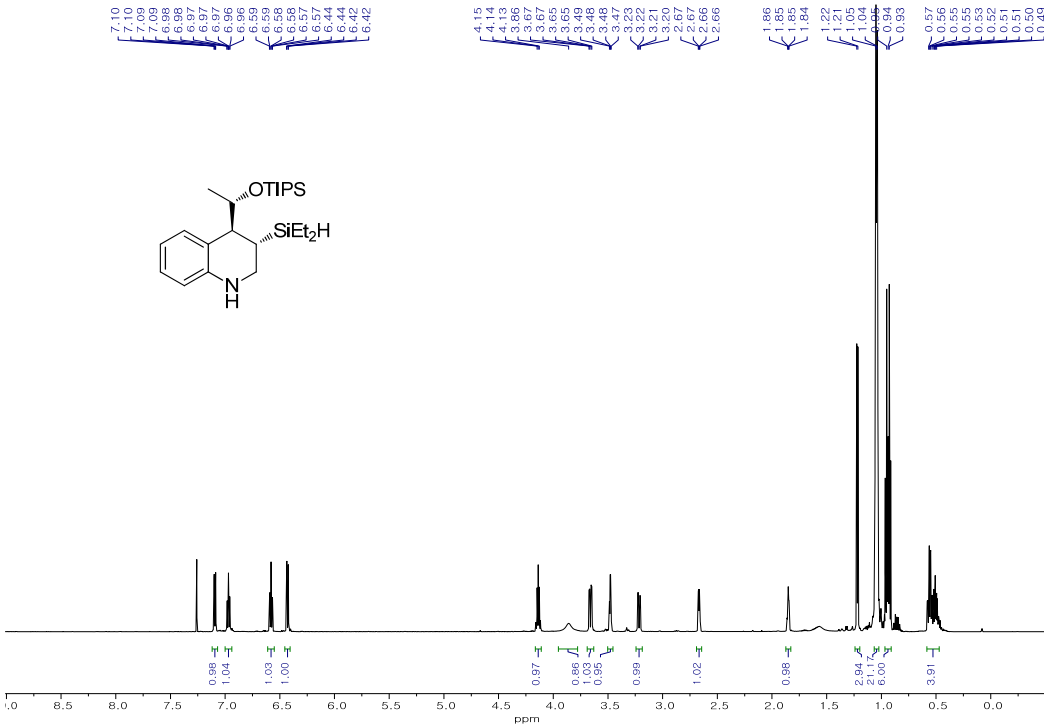


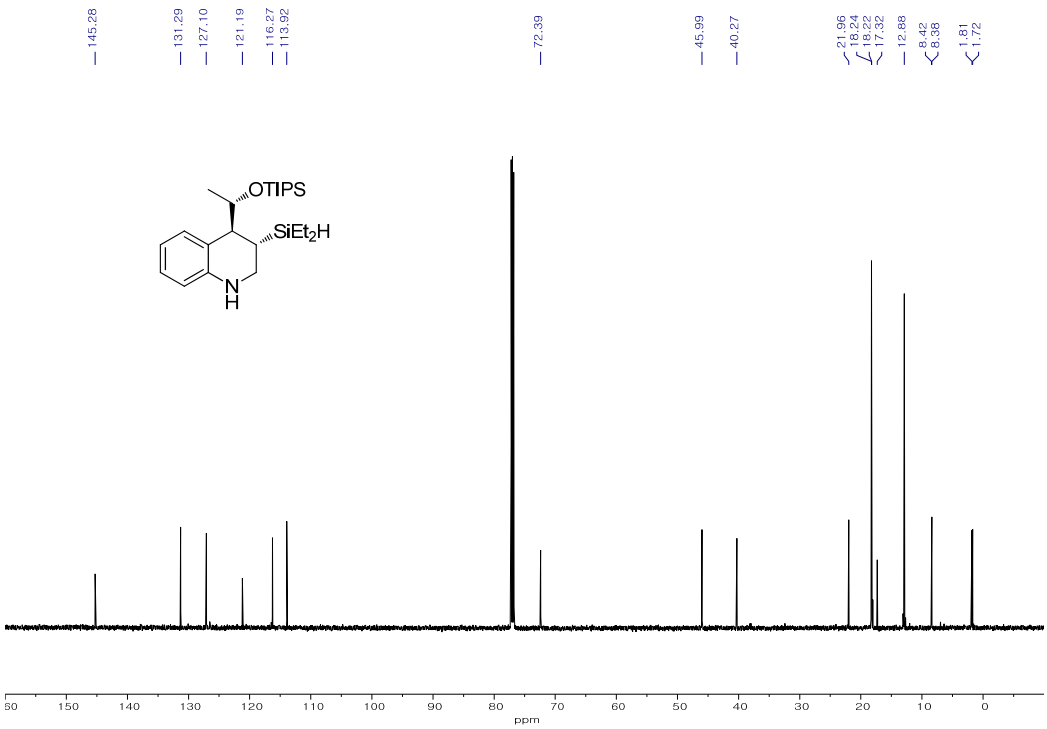
(*S*)-4-[1-{(triisopropylsilyl)oxy}ethyl]quinoline (Scheme 3B, (*S*)-37a)

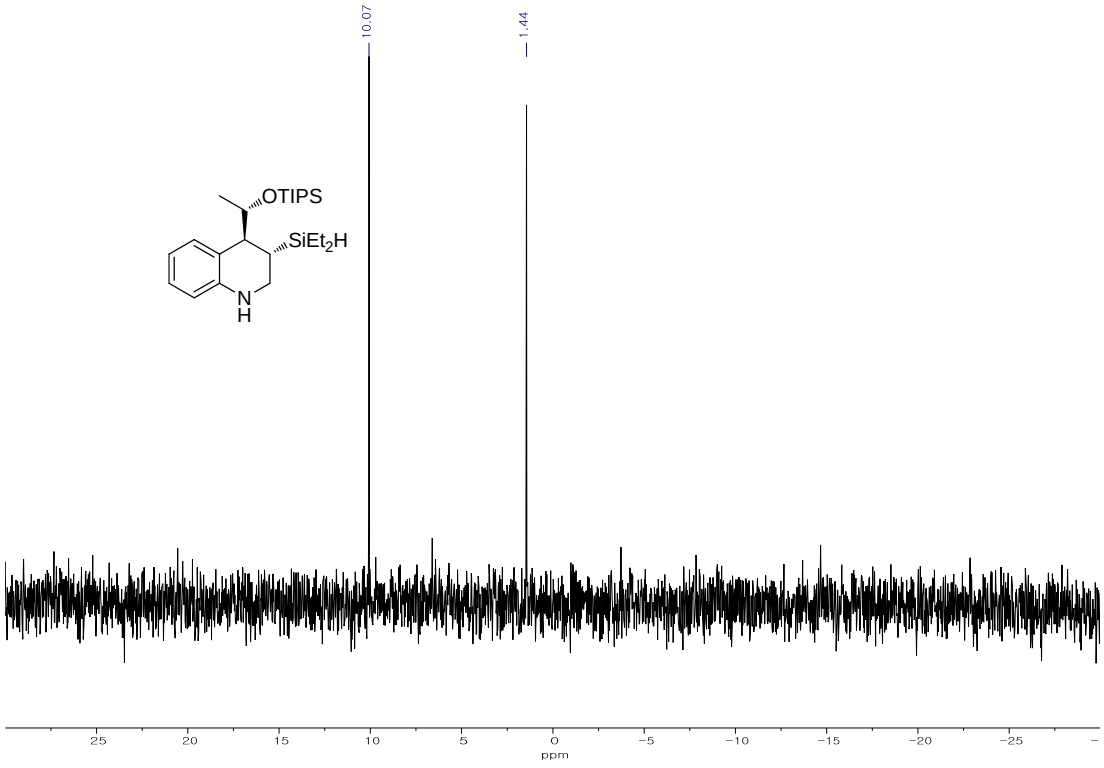




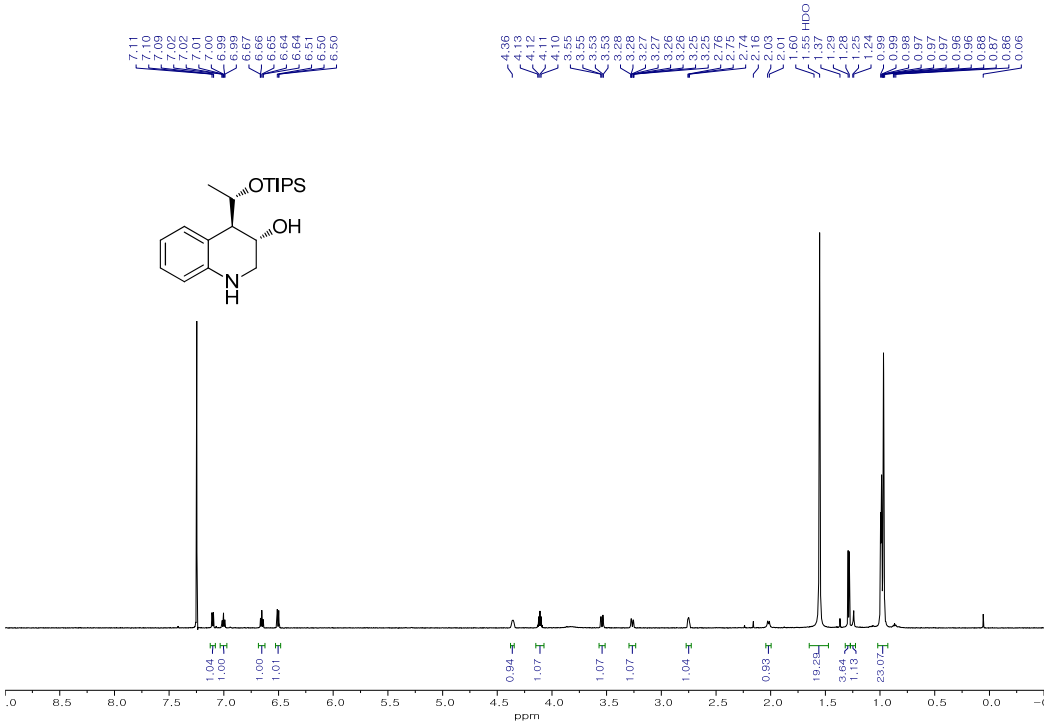
(3*S*,4*S*)-3-(Diethylsilyl)-4-[(*S*)-1-{(triisopropylsilyl)oxy}ethyl]-1,2,3,4-tetrahydroquinoline (Scheme 3B, 37b)



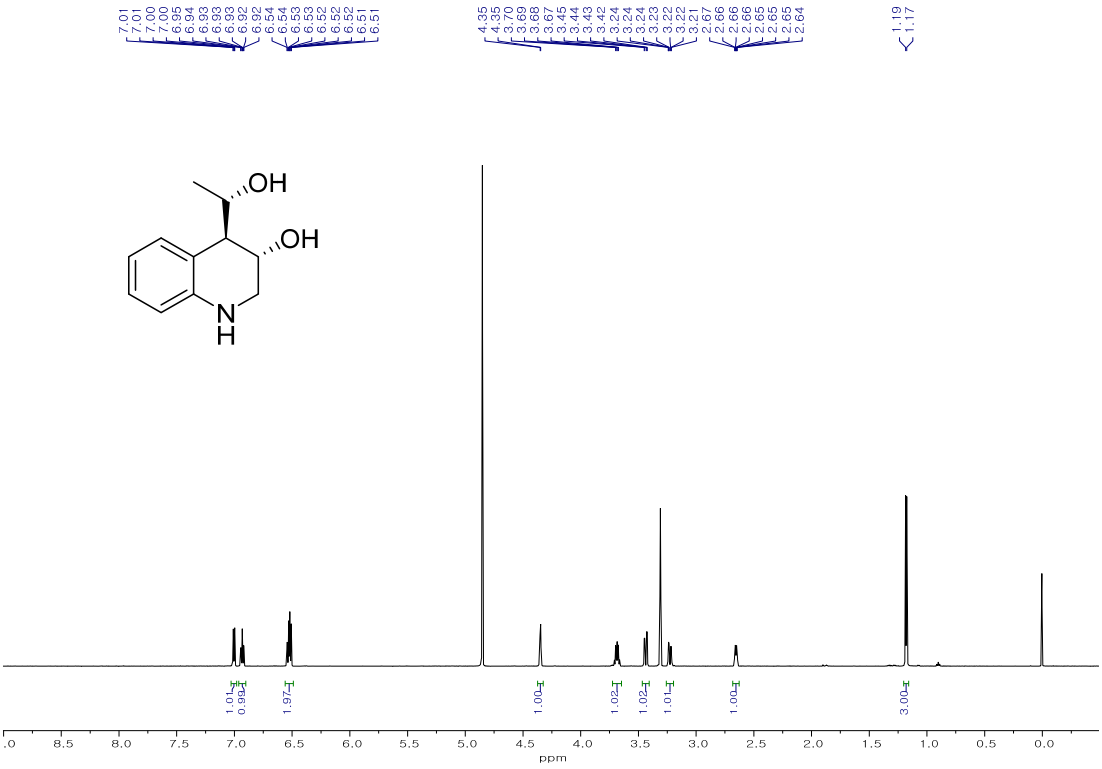

145.28
131.29
127.10
121.19
116.27
113.92
72.39
45.99
40.27
21.96
18.24
18.22
17.32
12.88
8.42
8.38
1.81
1.72
OTIPS
SiEt2H
N
H
ppm

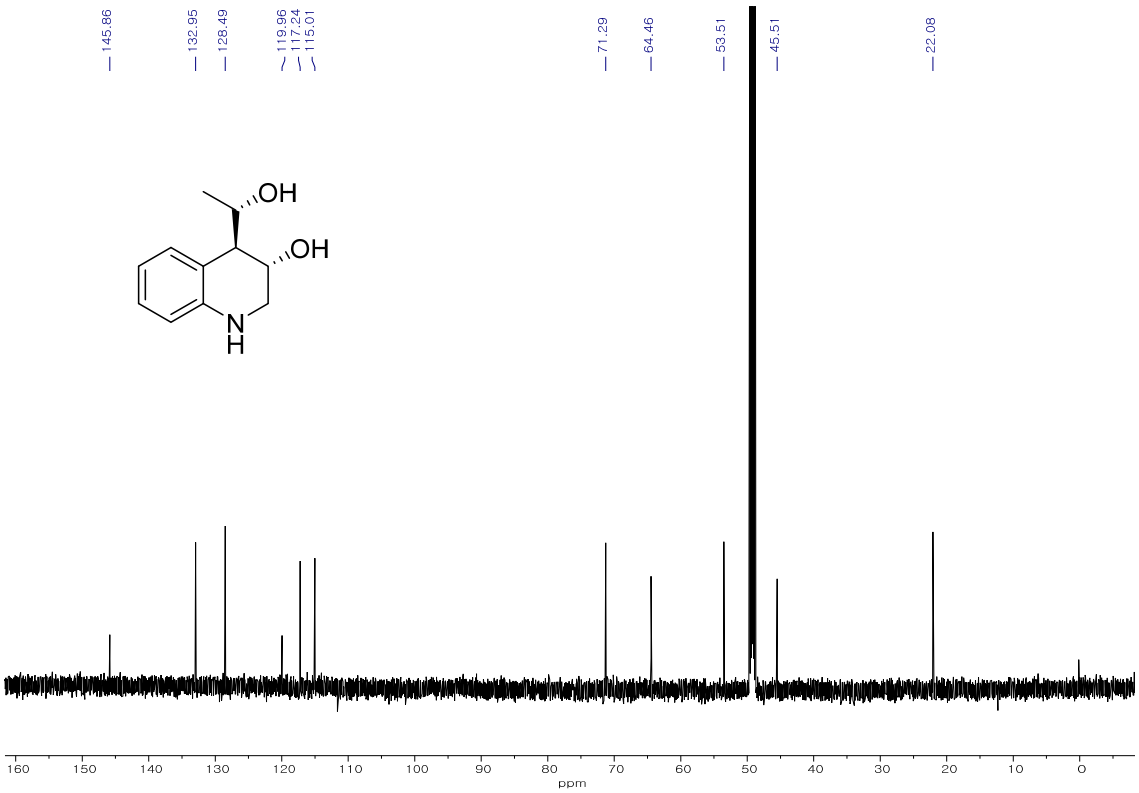

10.07
1.44
OTIPS
SiEt2H
N
H
ppm

(3*S*,4*S*)-4-[(*S*)-1-{(triisopropylsilyl)oxy}ethyl]-1,2,3,4-tetrahydroquinolin-3-ol (Scheme 3B, 38)



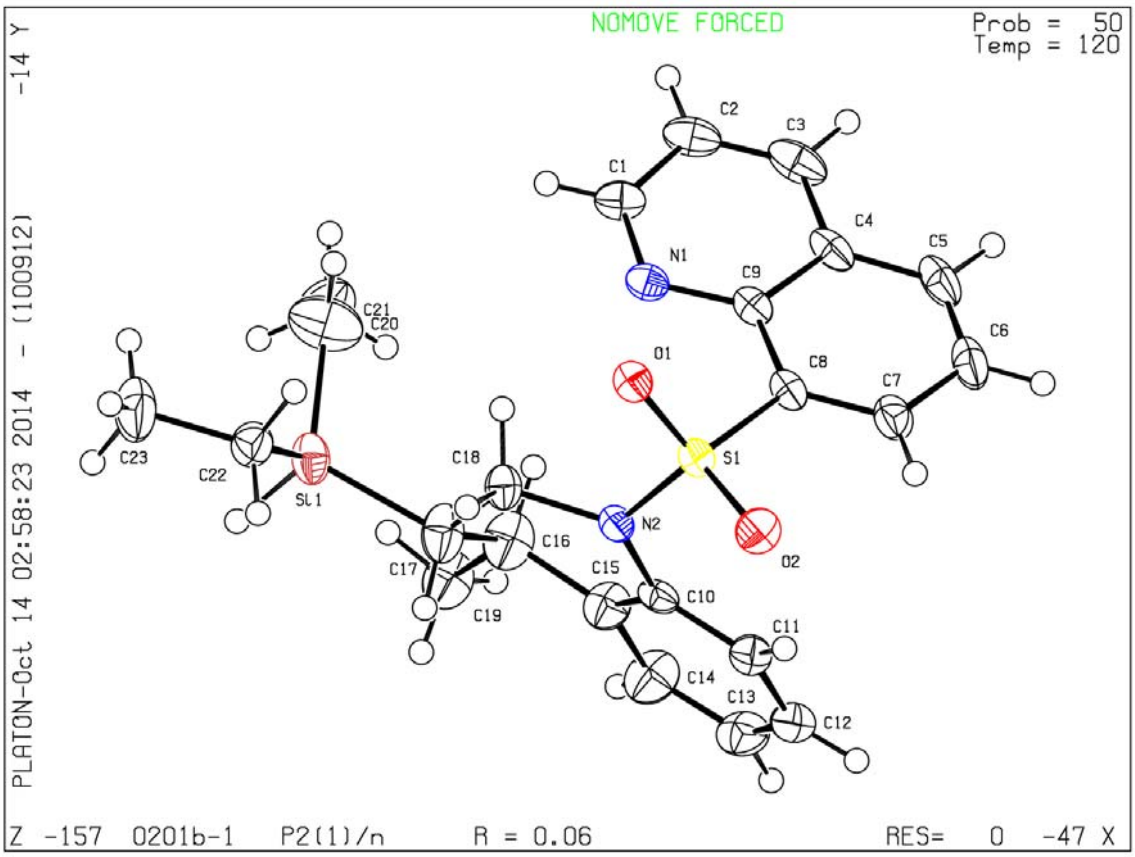
(3*S*,4*S*)-4-((*S*)-1-hydroxyethyl)-1,2,3,4-tetrahydroquinolin-3-ol (Scheme 3B, 39)




145.86
132.95
128.49
119.96
117.24
115.01
71.29
64.46
53.51
45.51
22.08
OH
OH
N
H
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

X. Crystallographic Data

3-(Diethylsilyl)-4-methyl-1,2,3,4-tetrahydroquinoline (Table 1, 9b-QUS)



Crystal data and structure refinement for **9b-QUS**.

Identification code	**9b-QUS (CCDC1029108)**	
Empirical formula	C_{23} H_{27} N_2 O_2 S Si	
Formula weight	423.62	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.0102(5) Å	α= 90°.
	b = 8.7962(4) Å	β= 96.328(2)°.
	c = 22.3342(9) Å	γ = 90°.
Volume	2149.84(16) Å^3	
Z	4	
Density (calculated)	1.309 Mg/m^3	
Absorption coefficient	0.228 mm^{-1}	
F(000)	900	
Crystal size	0.26 x 0.15 x 0.15 mm^3	
Theta range for data collection	1.83 to 28.00°.	
Index ranges	-14<=h<=14, -11<=k<=11, -29<=l<=29	
Reflections collected	41711	
Independent reflections	5210 [R(int) = 0.0796]	
Completeness to theta = 28.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9665 and 0.9430	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5210 / 0 / 263	
Goodness-of-fit on F^2	1.089	
Final R indices [I>2sigma(I)]	R1 = 0.0641, wR2 = 0.1759	
R indices (all data)	R1 = 0.0850, wR2 = 0.1959	
Largest diff. peak and hole	1.297 and -0.580 e.Å^{-3}	

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **9b-QUS**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	-533(1)	3214(1)	1815(1)	22(1)
O(1)	391(2)	3574(2)	2300(1)	24(1)
O(2)	-1657(2)	4054(2)	1784(1)	31(1)
Si(1)	3711(1)	3690(1)	836(1)	33(1)
N(1)	1190(2)	504(3)	1927(1)	26(1)
N(2)	87(2)	3426(3)	1184(1)	22(1)
C(1)	2008(3)	-582(4)	2029(1)	30(1)
C(2)	1730(4)	-2120(4)	2134(2)	36(1)
C(3)	532(4)	-2535(4)	2113(2)	39(1)
C(4)	-393(3)	-1420(3)	2002(1)	29(1)
C(5)	-1658(3)	-1758(4)	1972(1)	36(1)
C(6)	-2512(3)	-639(4)	1890(2)	37(1)
C(7)	-2147(3)	889(4)	1834(1)	31(1)
C(8)	-939(3)	1252(3)	1851(1)	24(1)
C(9)	-8(3)	112(3)	1925(1)	23(1)
C(10)	-563(3)	2970(3)	623(1)	24(1)
C(11)	-1835(3)	3085(4)	522(1)	31(1)
C(12)	-2461(3)	2585(4)	-16(2)	36(1)
C(13)	-1826(3)	2002(4)	-460(2)	39(1)
C(14)	-574(4)	1903(5)	-364(2)	43(1)
C(15)	97(3)	2363(4)	179(1)	35(1)
C(16)	1474(3)	2210(5)	296(2)	44(1)
C(17)	1975(3)	3580(5)	656(2)	40(1)
C(18)	1422(3)	3776(3)	1236(1)	27(1)
C(19)	2071(3)	1910(5)	-275(2)	43(1)
C(20)	4381(5)	1928(5)	1198(2)	61(1)
C(21)	4700(4)	601(5)	809(2)	59(1)
C(22)	4105(3)	5325(4)	1363(2)	33(1)
C(23)	5458(4)	5765(5)	1424(2)	52(1)

Bond lengths [Å] and angles [°] for **9b-QUS**.

S(1)-O(2)	1.437(2)
S(1)-O(1)	1.437(2)
S(1)-N(2)	1.641(2)
S(1)-C(8)	1.787(3)
Si(1)-C(20)	1.863(4)
Si(1)-C(22)	1.878(3)
Si(1)-C(17)	1.912(4)
N(1)-C(1)	1.315(4)
N(1)-C(9)	1.363(4)
N(2)-C(10)	1.430(4)
N(2)-C(18)	1.495(4)
C(1)-C(2)	1.412(5)
C(2)-C(3)	1.364(5)
C(3)-C(4)	1.416(5)
C(4)-C(5)	1.419(5)
C(4)-C(9)	1.429(4)
C(5)-C(6)	1.359(5)
C(6)-C(7)	1.412(5)
C(7)-C(8)	1.364(4)
C(8)-C(9)	1.430(4)
C(10)-C(11)	1.397(4)
C(10)-C(15)	1.399(4)
C(11)-C(12)	1.390(5)
C(12)-C(13)	1.372(5)
C(13)-C(14)	1.374(5)
C(14)-C(15)	1.408(5)
C(15)-C(16)	1.516(5)
C(16)-C(17)	1.518(5)
C(16)-C(19)	1.521(5)
C(17)-C(18)	1.500(4)
C(20)-C(21)	1.518(6)
C(22)-C(23)	1.531(5)
O(2)-S(1)-O(1)	117.23(13)
O(2)-S(1)-N(2)	109.73(13)

O(1)-S(1)-N(2)	107.15(12)
O(2)-S(1)-C(8)	106.27(14)
O(1)-S(1)-C(8)	109.81(13)
N(2)-S(1)-C(8)	106.15(13)
C(20)-Si(1)-C(22)	108.19(18)
C(20)-Si(1)-C(17)	112.8(2)
C(22)-Si(1)-C(17)	109.10(15)
C(1)-N(1)-C(9)	117.4(3)
C(10)-N(2)-C(18)	121.2(2)
C(10)-N(2)-S(1)	120.32(19)
C(18)-N(2)-S(1)	117.14(18)
N(1)-C(1)-C(2)	124.6(3)
C(3)-C(2)-C(1)	118.5(3)
C(2)-C(3)-C(4)	119.6(3)
C(3)-C(4)-C(5)	123.2(3)
C(3)-C(4)-C(9)	117.2(3)
C(5)-C(4)-C(9)	119.6(3)
C(6)-C(5)-C(4)	121.0(3)
C(5)-C(6)-C(7)	120.1(3)
C(8)-C(7)-C(6)	120.4(3)
C(7)-C(8)-C(9)	121.5(3)
C(7)-C(8)-S(1)	118.2(2)
C(9)-C(8)-S(1)	120.2(2)
N(1)-C(9)-C(4)	122.5(3)
N(1)-C(9)-C(8)	120.2(3)
C(4)-C(9)-C(8)	117.2(3)
C(11)-C(10)-C(15)	120.2(3)
C(11)-C(10)-N(2)	121.2(3)
C(15)-C(10)-N(2)	118.7(3)
C(12)-C(11)-C(10)	120.6(3)
C(13)-C(12)-C(11)	119.9(3)
C(12)-C(13)-C(14)	119.5(3)
C(13)-C(14)-C(15)	122.6(3)
C(10)-C(15)-C(14)	117.1(3)
C(10)-C(15)-C(16)	120.0(3)
C(14)-C(15)-C(16)	122.9(3)

C(15)-C(16)-C(17)	108.6(3)
C(15)-C(16)-C(19)	112.8(3)
C(17)-C(16)-C(19)	114.6(3)
C(18)-C(17)-C(16)	113.0(3)
C(18)-C(17)-Si(1)	107.7(2)
C(16)-C(17)-Si(1)	116.6(3)
N(2)-C(18)-C(17)	113.6(2)
C(21)-C(20)-Si(1)	119.8(3)
C(23)-C(22)-Si(1)	113.9(3)

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **9b-QUS**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	24(1)	19(1)	23(1)	-1(1)	5(1)	0(1)
O(1)	29(1)	22(1)	23(1)	-4(1)	4(1)	-3(1)
O(2)	30(1)	30(1)	36(1)	-3(1)	9(1)	8(1)
Si(1)	30(1)	38(1)	32(1)	-5(1)	11(1)	-7(1)
N(1)	31(1)	19(1)	26(1)	1(1)	3(1)	2(1)
N(2)	24(1)	21(1)	20(1)	1(1)	4(1)	-3(1)
C(1)	38(2)	27(2)	26(2)	-1(1)	3(1)	9(1)
C(2)	54(2)	24(2)	30(2)	2(1)	4(2)	10(2)
C(3)	70(3)	17(1)	29(2)	-1(1)	9(2)	-1(2)
C(4)	46(2)	21(1)	22(1)	1(1)	7(1)	-9(1)
C(5)	51(2)	31(2)	28(2)	-1(1)	7(2)	-22(2)
C(6)	38(2)	43(2)	30(2)	0(1)	6(1)	-22(2)
C(7)	32(2)	35(2)	27(2)	2(1)	7(1)	-6(1)
C(8)	30(2)	22(1)	21(1)	0(1)	6(1)	-6(1)
C(9)	33(2)	19(1)	17(1)	-2(1)	4(1)	-5(1)
C(10)	32(2)	16(1)	22(1)	3(1)	2(1)	-2(1)
C(11)	31(2)	36(2)	26(2)	4(1)	1(1)	-3(1)
C(12)	36(2)	37(2)	34(2)	10(1)	-3(1)	-4(1)
C(13)	47(2)	35(2)	33(2)	-2(1)	-7(2)	-4(2)
C(14)	44(2)	55(2)	30(2)	-14(2)	1(2)	1(2)
C(15)	36(2)	39(2)	29(2)	-6(1)	2(1)	-1(1)
C(16)	41(2)	51(2)	41(2)	-13(2)	9(2)	0(2)
C(17)	34(2)	52(2)	35(2)	-15(2)	12(1)	-9(2)
C(18)	26(2)	26(1)	29(2)	-4(1)	5(1)	-5(1)
C(19)	40(2)	59(2)	33(2)	-15(2)	10(2)	1(2)
C(20)	92(4)	41(2)	50(2)	0(2)	10(2)	14(2)
C(21)	48(2)	49(2)	79(3)	-13(2)	-4(2)	7(2)
C(22)	30(2)	36(2)	32(2)	-1(1)	2(1)	-4(1)
C(23)	41(2)	64(3)	52(2)	-7(2)	7(2)	-24(2)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **9b-QUS**.

	x	y	z	U(eq)
H(1)	4262	3961	270	39
H(1A)	2844	-312	2032	36
H(2A)	2363	-2848	2218	43
H(3A)	320	-3567	2172	46
H(5A)	-1913	-2781	2011	44
H(6A)	-3355	-886	1870	44
H(7A)	-2747	1669	1784	37
H(11A)	-2276	3510	824	38
H(12A)	-3327	2645	-77	44
H(13A)	-2249	1670	-830	47
H(14A)	-145	1509	-676	52
H(16A)	1642	1301	561	53
H(17A)	1728	4494	405	48
H(18A)	1855	3104	1544	32
H(18B)	1550	4839	1375	32
H(19A)	1710	1000	-475	65
H(19B)	2951	1752	-171	65
H(19C)	1939	2784	-546	65
H(20A)	4523	1860	1624	73
H(21A)	3955	213	580	89
H(21B)	5080	-209	1067	89
H(21C)	5272	941	530	89
H(22A)	3612	6219	1217	39
H(22B)	3876	5056	1766	39
H(23A)	5597	6620	1704	78
H(23B)	5689	6061	1029	78
H(23C)	5954	4895	1578	78

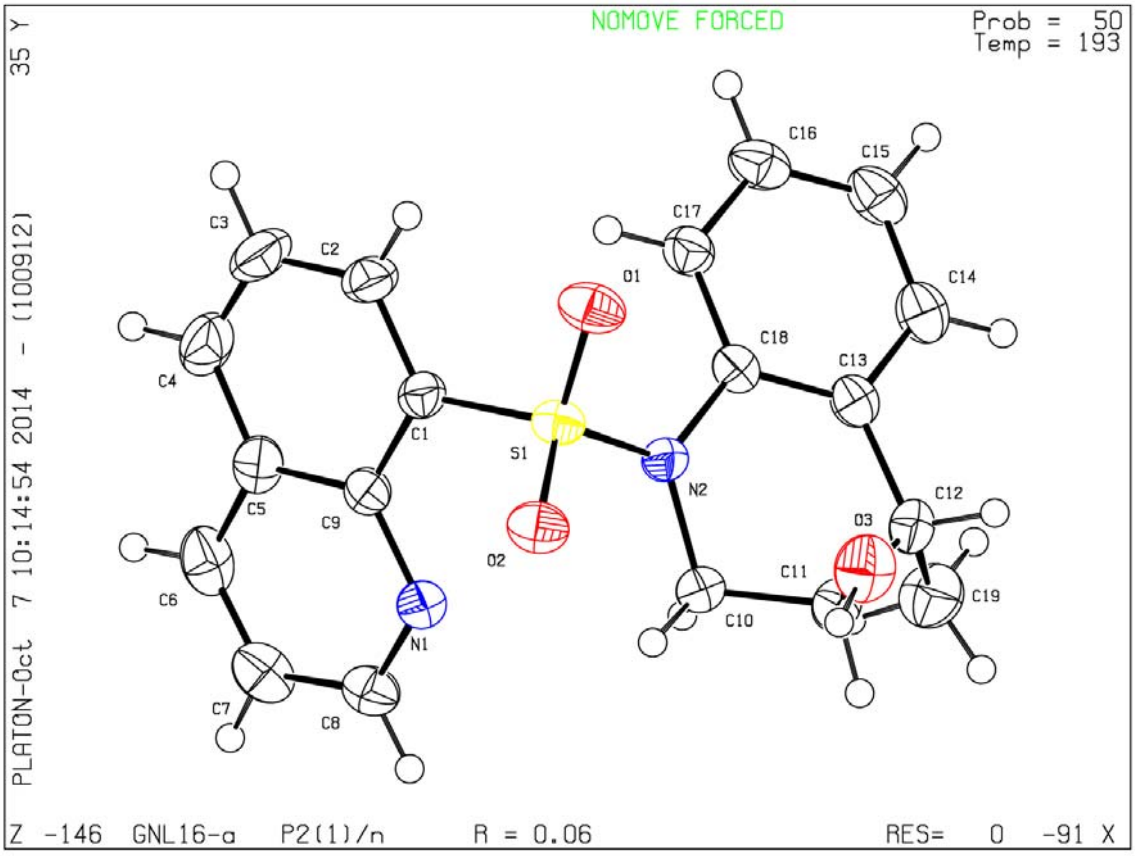
Torsion angles [°] for **9b-QUS**.

O(2)-S(1)-N(2)-C(10)	-59.4(2)
O(1)-S(1)-N(2)-C(10)	172.3(2)
C(8)-S(1)-N(2)-C(10)	55.0(2)
O(2)-S(1)-N(2)-C(18)	133.7(2)
O(1)-S(1)-N(2)-C(18)	5.5(2)
C(8)-S(1)-N(2)-C(18)	-111.8(2)
C(9)-N(1)-C(1)-C(2)	0.3(4)
N(1)-C(1)-C(2)-C(3)	2.0(5)
C(1)-C(2)-C(3)-C(4)	-1.6(5)
C(2)-C(3)-C(4)-C(5)	180.0(3)
C(2)-C(3)-C(4)-C(9)	-0.9(5)
C(3)-C(4)-C(5)-C(6)	177.2(3)
C(9)-C(4)-C(5)-C(6)	-1.9(5)
C(4)-C(5)-C(6)-C(7)	-0.2(5)
C(5)-C(6)-C(7)-C(8)	1.2(5)
C(6)-C(7)-C(8)-C(9)	0.0(4)
C(6)-C(7)-C(8)-S(1)	-177.0(2)
O(2)-S(1)-C(8)-C(7)	1.1(3)
O(1)-S(1)-C(8)-C(7)	128.8(2)
N(2)-S(1)-C(8)-C(7)	-115.7(2)
O(2)-S(1)-C(8)-C(9)	-175.9(2)
O(1)-S(1)-C(8)-C(9)	-48.2(3)
N(2)-S(1)-C(8)-C(9)	67.3(2)
C(1)-N(1)-C(9)-C(4)	-3.0(4)
C(1)-N(1)-C(9)-C(8)	176.5(3)
C(3)-C(4)-C(9)-N(1)	3.3(4)
C(5)-C(4)-C(9)-N(1)	-177.5(3)
C(3)-C(4)-C(9)-C(8)	-176.2(3)
C(5)-C(4)-C(9)-C(8)	3.0(4)
C(7)-C(8)-C(9)-N(1)	178.5(3)
S(1)-C(8)-C(9)-N(1)	-4.6(4)
C(7)-C(8)-C(9)-C(4)	-2.1(4)
S(1)-C(8)-C(9)-C(4)	174.8(2)
C(18)-N(2)-C(10)-C(11)	-160.4(3)

S(1)-N(2)-C(10)-C(11)	33.3(4)
C(18)-N(2)-C(10)-C(15)	21.3(4)
S(1)-N(2)-C(10)-C(15)	-145.0(2)
C(15)-C(10)-C(11)-C(12)	0.7(5)
N(2)-C(10)-C(11)-C(12)	-177.5(3)
C(10)-C(11)-C(12)-C(13)	-1.5(5)
C(11)-C(12)-C(13)-C(14)	0.8(5)
C(12)-C(13)-C(14)-C(15)	0.7(6)
C(11)-C(10)-C(15)-C(14)	0.7(5)
N(2)-C(10)-C(15)-C(14)	179.0(3)
C(11)-C(10)-C(15)-C(16)	-178.7(3)
N(2)-C(10)-C(15)-C(16)	-0.4(5)
C(13)-C(14)-C(15)-C(10)	-1.4(6)
C(13)-C(14)-C(15)-C(16)	178.0(4)
C(10)-C(15)-C(16)-C(17)	-37.6(5)
C(14)-C(15)-C(16)-C(17)	143.1(4)
C(10)-C(15)-C(16)-C(19)	-165.7(3)
C(14)-C(15)-C(16)-C(19)	14.9(5)
C(15)-C(16)-C(17)-C(18)	56.7(4)
C(19)-C(16)-C(17)-C(18)	-176.1(3)
C(15)-C(16)-C(17)-Si(1)	-177.7(3)
C(19)-C(16)-C(17)-Si(1)	-50.6(4)
C(20)-Si(1)-C(17)-C(18)	75.6(3)
C(22)-Si(1)-C(17)-C(18)	-44.6(3)
C(20)-Si(1)-C(17)-C(16)	-52.5(4)
C(22)-Si(1)-C(17)-C(16)	-172.8(3)
C(10)-N(2)-C(18)-C(17)	-0.7(4)
S(1)-N(2)-C(18)-C(17)	166.0(2)
C(16)-C(17)-C(18)-N(2)	-38.9(4)
Si(1)-C(17)-C(18)-N(2)	-169.1(2)
C(22)-Si(1)-C(20)-C(21)	-153.7(4)
C(17)-Si(1)-C(20)-C(21)	85.5(4)
C(20)-Si(1)-C(22)-C(23)	70.5(3)
C(17)-Si(1)-C(22)-C(23)	-166.4(3)

Symmetry transformations used to generate equivalent atoms:

4-Methyl-1-(quinolin-8-ylsulfonyl)-1,2,3,4-tetrahydroquinolin-3-ol (Table 1, 9b-QUS-C3-OH)



Crystal data and structure refinement for **9b-QUS-C3-OH**.

Identification code	**9b-QUS-C3-OH (CCDC1029110)**	
Empirical formula	$C_{19}\ H_{18}\ N_2\ O_3\ S$	
Formula weight	354.41	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.9207(6) Å	α= 90°.
	b = 11.1361(7) Å	β= 100.731(2)°.
	c = 15.2656(9) Å	γ = 90°.
Volume	1657.02(17) $Å^3$	
Z	4	
Density (calculated)	1.421 Mg/m^3	
Absorption coefficient	0.217 mm^{-1}	
F(000)	744	
Crystal size	0.22 x 0.14 x 0.09 mm^3	
Theta range for data collection	2.27 to 28.41°.	
Index ranges	-13<=h<=13, -14<=k<=14, -20<=l<=20	
Reflections collected	55410	
Independent reflections	4124 [R(int) = 0.0579]	
Completeness to theta = 28.41°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9807 and 0.9538	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4124 / 0 / 228	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2sigma(I)]	R1 = 0.0566, wR2 = 0.1470	
R indices (all data)	R1 = 0.0668, wR2 = 0.1580	
Largest diff. peak and hole	0.716 and -0.362 $e.Å^{-3}$	

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **9b-QUS-C3-OH**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	6853(1)	8428(1)	1271(1)	29(1)
N(2)	5303(2)	8254(2)	1478(1)	29(1)
O(3)	4161(2)	10587(2)	1608(1)	46(1)
C(1)	7349(2)	7018(2)	898(1)	29(1)
O(1)	7766(2)	8684(2)	2094(1)	41(1)
N(1)	5492(2)	7081(2)	-364(1)	31(1)
C(9)	6601(2)	6492(2)	105(1)	27(1)
O(2)	6773(2)	9270(2)	552(1)	37(1)
C(8)	4793(3)	6548(2)	-1080(2)	36(1)
C(5)	7033(3)	5351(2)	-165(2)	35(1)
C(13)	3848(2)	8150(2)	2593(1)	30(1)
C(16)	5719(3)	6595(2)	3644(2)	38(1)
C(18)	5060(2)	7805(2)	2315(1)	27(1)
C(12)	2799(2)	8990(2)	2061(2)	32(1)
C(17)	5985(2)	7021(2)	2838(1)	33(1)
C(2)	8468(2)	6439(2)	1390(2)	38(1)
C(11)	3313(2)	9581(2)	1285(2)	36(1)
C(6)	6261(3)	4841(2)	-945(2)	43(1)
C(10)	4103(2)	8686(2)	835(1)	32(1)
C(19)	1444(3)	8330(3)	1729(2)	50(1)
C(7)	5144(3)	5427(2)	-1397(2)	41(1)
C(14)	3610(3)	7694(2)	3402(2)	38(1)
C(3)	8889(3)	5315(3)	1105(2)	51(1)
C(15)	4526(3)	6937(2)	3928(2)	42(1)
C(4)	8206(3)	4795(3)	356(2)	49(1)

Bond lengths [Å] and angles [°] for **9b-QUS-C3-OH.**

S(1)-O(1)	1.4334(16)
S(1)-O(2)	1.4349(16)
S(1)-N(2)	1.6375(19)
S(1)-C(1)	1.771(2)
N(2)-C(18)	1.433(3)
N(2)-C(10)	1.475(3)
O(3)-C(11)	1.432(3)
O(3)-H(3)	0.8400
C(1)-C(2)	1.379(3)
C(1)-C(9)	1.423(3)
N(1)-C(8)	1.321(3)
N(1)-C(9)	1.364(3)
C(9)-C(5)	1.426(3)
C(8)-C(7)	1.406(4)
C(8)-H(8)	0.9500
C(5)-C(6)	1.410(4)
C(5)-C(4)	1.423(4)
C(13)-C(14)	1.395(3)
C(13)-C(18)	1.402(3)
C(13)-C(12)	1.518(3)
C(16)-C(15)	1.387(4)
C(16)-C(17)	1.389(3)
C(16)-H(16)	0.9500
C(18)-C(17)	1.403(3)
C(12)-C(11)	1.524(3)
C(12)-C(19)	1.533(3)
C(12)-H(12)	1.0000
C(17)-H(17)	0.9500
C(2)-C(3)	1.413(4)
C(2)-H(2)	0.9500
C(11)-C(10)	1.509(3)
C(11)-H(11)	1.0000
C(6)-C(7)	1.359(4)
C(6)-H(6)	0.9500

C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(7)-H(7)	0.9500
C(14)-C(15)	1.382(4)
C(14)-H(14)	0.9500
C(3)-C(4)	1.347(4)
C(3)-H(3A)	0.9500
C(15)-H(15)	0.9500
C(4)-H(4)	0.9500
O(1)-S(1)-O(2)	118.47(10)
O(1)-S(1)-N(2)	108.47(10)
O(2)-S(1)-N(2)	107.76(10)
O(1)-S(1)-C(1)	106.81(11)
O(2)-S(1)-C(1)	108.24(10)
N(2)-S(1)-C(1)	106.49(10)
C(18)-N(2)-C(10)	117.24(17)
C(18)-N(2)-S(1)	122.22(14)
C(10)-N(2)-S(1)	120.21(14)
C(11)-O(3)-H(3)	109.5
C(2)-C(1)-C(9)	120.7(2)
C(2)-C(1)-S(1)	118.92(18)
C(9)-C(1)-S(1)	120.40(16)
C(8)-N(1)-C(9)	117.7(2)
N(1)-C(9)-C(1)	119.38(19)
N(1)-C(9)-C(5)	122.2(2)
C(1)-C(9)-C(5)	118.4(2)
N(1)-C(8)-C(7)	124.0(2)
N(1)-C(8)-H(8)	118.0
C(7)-C(8)-H(8)	118.0
C(6)-C(5)-C(4)	123.8(2)
C(6)-C(5)-C(9)	117.2(2)
C(4)-C(5)-C(9)	119.0(2)
C(14)-C(13)-C(18)	117.7(2)

C(14)-C(13)-C(12)	119.1(2)
C(18)-C(13)-C(12)	123.23(19)
C(15)-C(16)-C(17)	119.7(2)
C(15)-C(16)-H(16)	120.1
C(17)-C(16)-H(16)	120.1
C(13)-C(18)-C(17)	120.29(19)
C(13)-C(18)-N(2)	118.09(18)
C(17)-C(18)-N(2)	121.61(19)
C(13)-C(12)-C(11)	112.77(18)
C(13)-C(12)-C(19)	110.7(2)
C(11)-C(12)-C(19)	110.4(2)
C(13)-C(12)-H(12)	107.6
C(11)-C(12)-H(12)	107.6
C(19)-C(12)-H(12)	107.6
C(16)-C(17)-C(18)	120.3(2)
C(16)-C(17)-H(17)	119.8
C(18)-C(17)-H(17)	119.8
C(1)-C(2)-C(3)	120.1(2)
C(1)-C(2)-H(2)	120.0
C(3)-C(2)-H(2)	120.0
O(3)-C(11)-C(10)	110.56(19)
O(3)-C(11)-C(12)	109.27(19)
C(10)-C(11)-C(12)	110.22(19)
O(3)-C(11)-H(11)	108.9
C(10)-C(11)-H(11)	108.9
C(12)-C(11)-H(11)	108.9
C(7)-C(6)-C(5)	119.9(2)
C(7)-C(6)-H(6)	120.0
C(5)-C(6)-H(6)	120.0
N(2)-C(10)-C(11)	109.65(18)
N(2)-C(10)-H(10A)	109.7
C(11)-C(10)-H(10A)	109.7
N(2)-C(10)-H(10B)	109.7
C(11)-C(10)-H(10B)	109.7
H(10A)-C(10)-H(10B)	108.2
C(12)-C(19)-H(19A)	109.5

C(12)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(12)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(6)-C(7)-C(8)	118.8(2)
C(6)-C(7)-H(7)	120.6
C(8)-C(7)-H(7)	120.6
C(15)-C(14)-C(13)	122.3(2)
C(15)-C(14)-H(14)	118.8
C(13)-C(14)-H(14)	118.8
C(4)-C(3)-C(2)	120.7(2)
C(4)-C(3)-H(3A)	119.6
C(2)-C(3)-H(3A)	119.6
C(14)-C(15)-C(16)	119.6(2)
C(14)-C(15)-H(15)	120.2
C(16)-C(15)-H(15)	120.2
C(3)-C(4)-C(5)	121.2(2)
C(3)-C(4)-H(4)	119.4
C(5)-C(4)-H(4)	119.4

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **9b-QUS-C3-OH**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	29(1)	31(1)	27(1)	3(1)	2(1)	-3(1)
N(2)	28(1)	34(1)	26(1)	5(1)	6(1)	7(1)
O(3)	53(1)	30(1)	56(1)	0(1)	15(1)	-3(1)
C(1)	25(1)	34(1)	29(1)	6(1)	8(1)	3(1)
O(1)	39(1)	48(1)	32(1)	1(1)	-3(1)	-12(1)
N(1)	29(1)	34(1)	30(1)	0(1)	5(1)	2(1)
C(9)	29(1)	28(1)	26(1)	6(1)	9(1)	0(1)
O(2)	40(1)	34(1)	35(1)	8(1)	6(1)	-6(1)
C(8)	36(1)	40(1)	30(1)	0(1)	2(1)	-5(1)
C(5)	43(1)	28(1)	39(1)	8(1)	18(1)	4(1)
C(13)	33(1)	27(1)	29(1)	-4(1)	6(1)	-4(1)
C(16)	50(1)	32(1)	30(1)	4(1)	2(1)	-3(1)
C(18)	32(1)	24(1)	25(1)	-1(1)	7(1)	-3(1)
C(12)	29(1)	33(1)	36(1)	-3(1)	10(1)	2(1)
C(17)	40(1)	31(1)	28(1)	1(1)	6(1)	3(1)
C(2)	27(1)	53(1)	35(1)	12(1)	5(1)	8(1)
C(11)	33(1)	37(1)	38(1)	1(1)	8(1)	5(1)
C(6)	66(2)	24(1)	45(1)	-2(1)	24(1)	-2(1)
C(10)	30(1)	37(1)	29(1)	3(1)	4(1)	6(1)
C(19)	33(1)	60(2)	56(2)	2(1)	9(1)	-6(1)
C(7)	52(2)	37(1)	36(1)	-3(1)	8(1)	-12(1)
C(14)	42(1)	38(1)	37(1)	-2(1)	15(1)	-6(1)
C(3)	41(1)	58(2)	53(2)	21(1)	10(1)	24(1)
C(15)	55(2)	40(1)	32(1)	6(1)	15(1)	-6(1)
C(4)	58(2)	38(1)	53(2)	12(1)	21(1)	20(1)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3)
for **9b-QUS-C3-OH**.

	x	y	z	U(eq)
H(3)	4273	11019	1176	69
H(8)	4006	6946	-1399	43
H(16)	6352	6071	4000	46
H(12)	2611	9643	2472	39
H(17)	6796	6780	2640	40
H(2)	8957	6796	1920	46
H(11)	2507	9872	842	43
H(6)	6520	4087	-1153	52
H(10A)	3503	8000	610	38
H(10B)	4411	9070	322	38
H(19A)	1567	7754	1265	75
H(19B)	734	8913	1482	75
H(19C)	1165	7902	2227	75
H(7)	4610	5086	-1919	50
H(14)	2789	7912	3598	46
H(3A)	9663	4922	1446	61
H(15)	4341	6653	4480	50
H(4)	8513	4044	172	58

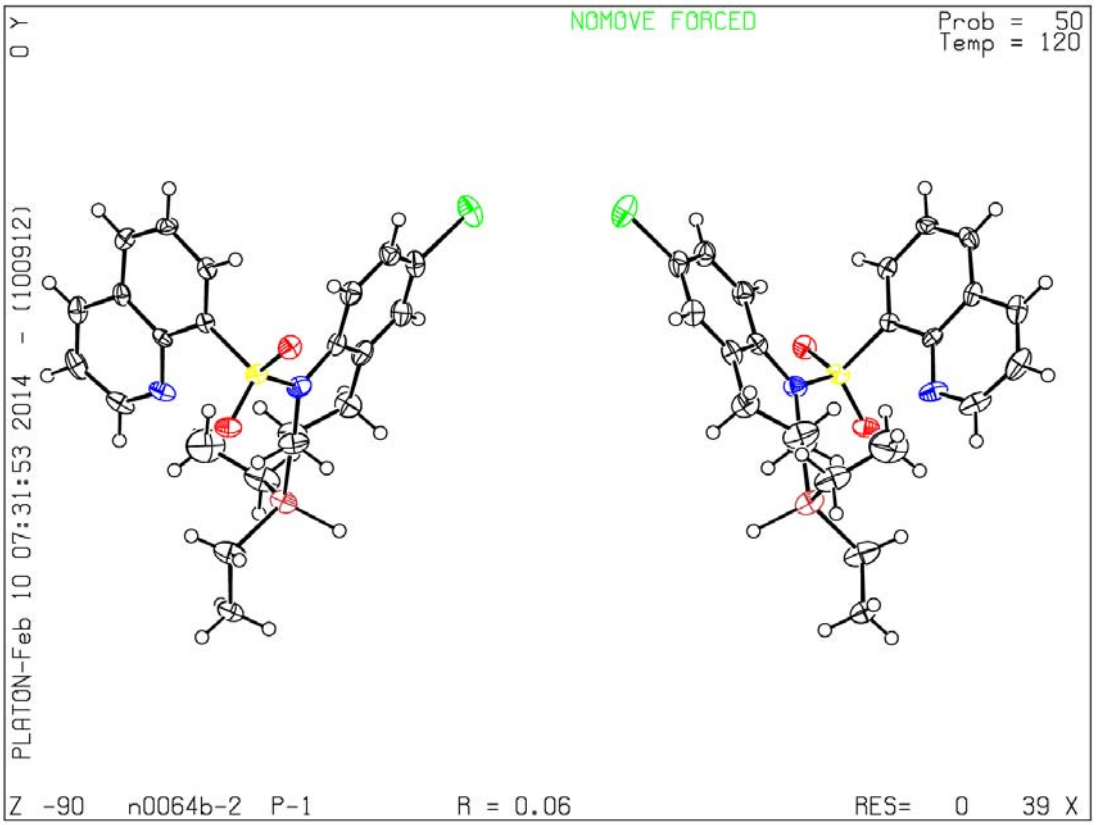
Torsion angles [°] for **9b-QUS-C3-OH**.

O(1)-S(1)-N(2)-C(18)	-29.7(2)
O(2)-S(1)-N(2)-C(18)	-159.15(16)
C(1)-S(1)-N(2)-C(18)	84.90(18)
O(1)-S(1)-N(2)-C(10)	143.45(17)
O(2)-S(1)-N(2)-C(10)	14.0(2)
C(1)-S(1)-N(2)-C(10)	-101.90(18)
O(1)-S(1)-C(1)-C(2)	-2.1(2)
O(2)-S(1)-C(1)-C(2)	126.51(18)
N(2)-S(1)-C(1)-C(2)	-117.86(18)
O(1)-S(1)-C(1)-C(9)	177.82(16)
O(2)-S(1)-C(1)-C(9)	-53.58(19)
N(2)-S(1)-C(1)-C(9)	62.06(18)
C(8)-N(1)-C(9)-C(1)	-177.72(19)
C(8)-N(1)-C(9)-C(5)	1.4(3)
C(2)-C(1)-C(9)-N(1)	179.5(2)
S(1)-C(1)-C(9)-N(1)	-0.4(3)
C(2)-C(1)-C(9)-C(5)	0.4(3)
S(1)-C(1)-C(9)-C(5)	-179.55(15)
C(9)-N(1)-C(8)-C(7)	-1.6(3)
N(1)-C(9)-C(5)-C(6)	-0.2(3)
C(1)-C(9)-C(5)-C(6)	179.0(2)
N(1)-C(9)-C(5)-C(4)	179.6(2)
C(1)-C(9)-C(5)-C(4)	-1.3(3)
C(14)-C(13)-C(18)-C(17)	0.4(3)
C(12)-C(13)-C(18)-C(17)	-179.8(2)
C(14)-C(13)-C(18)-N(2)	179.07(19)
C(12)-C(13)-C(18)-N(2)	-1.1(3)
C(10)-N(2)-C(18)-C(13)	-20.5(3)
S(1)-N(2)-C(18)-C(13)	152.89(17)
C(10)-N(2)-C(18)-C(17)	158.1(2)
S(1)-N(2)-C(18)-C(17)	-28.5(3)
C(14)-C(13)-C(12)-C(11)	169.9(2)
C(18)-C(13)-C(12)-C(11)	-9.9(3)
C(14)-C(13)-C(12)-C(19)	-65.8(3)

C(18)-C(13)-C(12)-C(19)	114.4(2)
C(15)-C(16)-C(17)-C(18)	0.7(4)
C(13)-C(18)-C(17)-C(16)	-1.1(3)
N(2)-C(18)-C(17)-C(16)	-179.7(2)
C(9)-C(1)-C(2)-C(3)	0.4(3)
S(1)-C(1)-C(2)-C(3)	-179.72(19)
C(13)-C(12)-C(11)-O(3)	-81.4(2)
C(19)-C(12)-C(11)-O(3)	154.2(2)
C(13)-C(12)-C(11)-C(10)	40.3(3)
C(19)-C(12)-C(11)-C(10)	-84.1(2)
C(4)-C(5)-C(6)-C(7)	179.3(2)
C(9)-C(5)-C(6)-C(7)	-1.0(3)
C(18)-N(2)-C(10)-C(11)	52.0(3)
S(1)-N(2)-C(10)-C(11)	-121.58(18)
O(3)-C(11)-C(10)-N(2)	59.9(2)
C(12)-C(11)-C(10)-N(2)	-61.0(2)
C(5)-C(6)-C(7)-C(8)	0.8(4)
N(1)-C(8)-C(7)-C(6)	0.5(4)
C(18)-C(13)-C(14)-C(15)	0.6(3)
C(12)-C(13)-C(14)-C(15)	-179.2(2)
C(1)-C(2)-C(3)-C(4)	-0.1(4)
C(13)-C(14)-C(15)-C(16)	-1.1(4)
C(17)-C(16)-C(15)-C(14)	0.4(4)
C(2)-C(3)-C(4)-C(5)	-0.8(4)
C(6)-C(5)-C(4)-C(3)	-178.7(3)
C(9)-C(5)-C(4)-C(3)	1.5(4)

Symmetry transformations used to generate equivalent atoms:

8-{6-Bromo-3-(diethylsilyl)-3,4-dihydroquinolin-1(2*H*)-ylsulfonyl}quinoline (Table 1, 13b-QUS)



Crystal data and structure refinement for **13b-QUS**.

Identification code	**13b-QUS (CCDC1022515)**	
Empirical formula	C_{22} H_{25} Br N_2 O_2 S Si	
Formula weight	489.50	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.6277(3) Å	α= 71.5700(10)°.
	b = 16.5219(6) Å	β= 78.1050(10)°.
	c = 18.3654(7) Å	γ = 89.9540(10)°.
Volume	2143.46(14) Å^3	
Z	4	
Density (calculated)	1.517 Mg/m^3	
Absorption coefficient	2.093 mm^{-1}	
F(000)	1008	
Crystal size	0.20 x 0.13 x 0.08 mm^3	
Theta range for data collection	2.74 to 29.96°.	
Index ranges	-10<=h<=10, -23<=k<=21, -25<=l<=25	
Reflections collected	55874	
Independent reflections	11976 [R(int) = 0.0591]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8504 and 0.6796	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7540 / 0 / 523	
Goodness-of-fit on F^2	1.184	
Final R indices [I>2sigma(I)]	R1 = 0.0599, wR2 = 0.1616	
R indices (all data)	R1 = 0.0802, wR2 = 0.1840	
Largest diff. peak and hole	2.339 and -0.570 e.Å^{-3}	

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **13b-QUS**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	11372(1)	3453(1)	5372(1)	45(1)
Br(2)	11753(1)	1550(1)	4628(1)	45(1)
S(2)	8520(2)	1766(1)	1174(1)	21(1)
S(1)	4690(2)	3228(1)	8826(1)	21(1)
Si(1)	1954(2)	5458(1)	6513(1)	29(1)
Si(2)	3462(2)	-447(1)	3490(1)	32(1)
O(1)	5411(5)	2404(2)	9019(2)	26(1)
O(2)	2878(4)	3281(2)	9214(2)	27(1)
O(4)	7094(5)	1713(2)	789(2)	28(1)
O(3)	9426(5)	2590(2)	985(2)	26(1)
N(1)	4776(6)	3584(3)	7872(3)	26(1)
N(2)	4232(5)	5095(3)	8681(3)	26(1)
N(3)	7660(6)	1412(3)	2128(3)	26(1)
N(4)	7930(6)	-98(3)	1300(3)	29(1)
C(39)	13331(6)	849(3)	593(3)	24(1)
C(16)	7692(7)	3618(3)	9254(3)	21(1)
C(15)	6166(6)	3933(3)	9011(3)	18(1)
C(14)	5744(6)	4797(3)	8931(3)	18(1)
C(19)	6955(6)	5308(3)	9122(3)	20(1)
C(18)	8535(7)	4975(3)	9351(3)	25(1)
C(17)	8895(6)	4149(3)	9416(3)	23(1)
C(38)	11960(6)	1377(3)	752(3)	21(1)
C(40)	12921(7)	29(3)	652(3)	25(1)
C(3)	9303(7)	3058(3)	6933(3)	28(1)
C(36)	9696(6)	200(3)	1061(3)	19(1)
C(4)	9372(8)	3506(4)	6163(3)	31(1)
C(41)	11105(7)	-312(3)	878(3)	22(1)
C(42)	10617(8)	-1156(3)	921(3)	31(1)
C(24)	10306(7)	1915(4)	2498(3)	28(1)
C(2)	7803(7)	3085(3)	7503(3)	27(1)
C(25)	11235(7)	1944(4)	3066(3)	29(1)

C(27)	8951(8)	997(4)	4049(3)	31(1)
C(1)	6366(7)	3573(3)	7304(3)	23(1)
C(37)	10191(6)	1061(3)	987(3)	18(1)
C(35)	344(7)	-908(4)	3059(3)	32(1)
C(26)	10533(8)	1496(4)	3840(3)	32(1)
C(23)	8681(7)	1426(3)	2697(3)	25(1)
C(29)	6297(8)	382(4)	3765(3)	35(1)
C(20)	6504(7)	6150(3)	9077(3)	28(1)
C(22)	3886(7)	5885(3)	8651(3)	31(1)
C(21)	4966(8)	6441(4)	8846(3)	34(1)
C(13)	-1593(7)	5909(4)	6939(3)	31(1)
C(10)	2954(8)	6559(4)	5906(4)	43(2)
C(28)	8009(7)	952(3)	3491(3)	27(1)
C(5)	7989(8)	4011(4)	5948(3)	31(1)
C(6)	6485(7)	4046(3)	6511(3)	26(1)
C(12)	0(7)	5501(4)	7292(4)	39(2)
C(7)	5040(8)	4621(4)	6238(3)	34(1)
C(8)	3812(7)	4826(4)	6913(3)	33(1)
C(44)	7555(8)	-891(4)	1334(4)	36(1)
C(9)	3213(7)	4013(4)	7588(4)	35(1)
C(43)	8852(9)	-1442(4)	1144(3)	38(1)
C(34)	2281(8)	-479(5)	2712(4)	45(2)
C(32)	3889(9)	-1548(4)	4075(4)	44(2)
C(31)	5819(8)	987(4)	2406(4)	43(2)
C(30)	5719(9)	186(4)	3084(4)	47(2)
C(11)	3723(11)	7036(5)	6366(6)	67(2)
C(33)	5114(11)	-2017(5)	3617(6)	71(2)

Bond lengths [Å] and angles [°] for **13b-QUS**.

Br(1)-C(4)	1.901(6)
Br(2)-C(26)	1.899(6)
S(2)-O(4)	1.431(4)
S(2)-O(3)	1.434(4)
S(2)-N(3)	1.649(4)
S(2)-C(37)	1.780(5)
S(1)-O(1)	1.434(4)
S(1)-O(2)	1.435(4)
S(1)-N(1)	1.651(4)
S(1)-C(15)	1.774(5)
Si(1)-C(12)	1.860(6)
Si(1)-C(10)	1.871(6)
Si(1)-C(8)	1.892(6)
Si(2)-C(34)	1.853(6)
Si(2)-C(32)	1.865(6)
Si(2)-C(30)	1.896(6)
N(1)-C(1)	1.431(7)
N(1)-C(9)	1.488(7)
N(2)-C(22)	1.318(7)
N(2)-C(14)	1.362(6)
N(3)-C(23)	1.431(7)
N(3)-C(31)	1.485(7)
N(4)-C(44)	1.321(7)
N(4)-C(36)	1.367(6)
C(39)-C(40)	1.355(8)
C(39)-C(38)	1.405(7)
C(16)-C(15)	1.375(7)
C(16)-C(17)	1.407(7)
C(15)-C(14)	1.433(7)
C(14)-C(19)	1.417(7)
C(19)-C(18)	1.412(7)
C(19)-C(20)	1.415(7)
C(18)-C(17)	1.365(8)
C(38)-C(37)	1.378(7)

C(40)-C(41)	1.424(7)
C(3)-C(4)	1.363(8)
C(3)-C(2)	1.394(8)
C(36)-C(41)	1.419(7)
C(36)-C(37)	1.429(7)
C(4)-C(5)	1.388(8)
C(41)-C(42)	1.417(7)
C(42)-C(43)	1.363(9)
C(24)-C(25)	1.388(8)
C(24)-C(23)	1.397(8)
C(2)-C(1)	1.401(7)
C(25)-C(26)	1.371(8)
C(27)-C(26)	1.376(8)
C(27)-C(28)	1.387(8)
C(1)-C(6)	1.403(7)
C(35)-C(34)	1.555(8)
C(23)-C(28)	1.404(7)
C(29)-C(28)	1.509(8)
C(29)-C(30)	1.532(9)
C(20)-C(21)	1.365(8)
C(22)-C(21)	1.407(9)
C(13)-C(12)	1.548(8)
C(10)-C(11)	1.520(11)
C(5)-C(6)	1.392(8)
C(6)-C(7)	1.515(8)
C(7)-C(8)	1.521(8)
C(8)-C(9)	1.506(8)
C(44)-C(43)	1.410(9)
C(32)-C(33)	1.505(11)
C(31)-C(30)	1.492(9)

O(4)-S(2)-O(3)	117.4(2)
O(4)-S(2)-N(3)	107.0(2)
O(3)-S(2)-N(3)	108.4(2)
O(4)-S(2)-C(37)	110.2(2)
O(3)-S(2)-C(37)	107.0(2)

N(3)-S(2)-C(37)	106.5(2)
O(1)-S(1)-O(2)	117.2(2)
O(1)-S(1)-N(1)	108.7(2)
O(2)-S(1)-N(1)	107.1(2)
O(1)-S(1)-C(15)	106.9(2)
O(2)-S(1)-C(15)	110.1(2)
N(1)-S(1)-C(15)	106.3(2)
C(12)-Si(1)-C(10)	110.9(3)
C(12)-Si(1)-C(8)	113.4(3)
C(10)-Si(1)-C(8)	107.3(3)
C(34)-Si(2)-C(32)	110.7(3)
C(34)-Si(2)-C(30)	112.9(3)
C(32)-Si(2)-C(30)	106.9(3)
C(1)-N(1)-C(9)	118.6(4)
C(1)-N(1)-S(1)	122.3(3)
C(9)-N(1)-S(1)	118.8(4)
C(22)-N(2)-C(14)	116.9(5)
C(23)-N(3)-C(31)	118.8(4)
C(23)-N(3)-S(2)	122.4(3)
C(31)-N(3)-S(2)	118.5(4)
C(44)-N(4)-C(36)	117.1(5)
C(40)-C(39)-C(38)	120.3(5)
C(15)-C(16)-C(17)	120.3(5)
C(16)-C(15)-C(14)	121.2(4)
C(16)-C(15)-S(1)	118.1(4)
C(14)-C(15)-S(1)	120.6(4)
N(2)-C(14)-C(19)	122.9(4)
N(2)-C(14)-C(15)	120.0(4)
C(19)-C(14)-C(15)	117.1(4)
C(18)-C(19)-C(20)	122.1(5)
C(18)-C(19)-C(14)	120.5(5)
C(20)-C(19)-C(14)	117.3(5)
C(17)-C(18)-C(19)	120.6(5)
C(18)-C(17)-C(16)	120.3(5)
C(37)-C(38)-C(39)	120.3(5)
C(39)-C(40)-C(41)	120.8(5)

C(4)-C(3)-C(2)	119.6(5)
N(4)-C(36)-C(41)	122.9(4)
N(4)-C(36)-C(37)	120.0(4)
C(41)-C(36)-C(37)	117.1(4)
C(3)-C(4)-C(5)	120.4(5)
C(3)-C(4)-Br(1)	120.4(4)
C(5)-C(4)-Br(1)	119.2(4)
C(42)-C(41)-C(36)	117.3(5)
C(42)-C(41)-C(40)	122.5(5)
C(36)-C(41)-C(40)	120.1(5)
C(43)-C(42)-C(41)	119.4(5)
C(25)-C(24)-C(23)	121.4(5)
C(3)-C(2)-C(1)	121.4(5)
C(26)-C(25)-C(24)	119.5(5)
C(26)-C(27)-C(28)	121.3(5)
C(6)-C(1)-C(2)	118.0(5)
C(6)-C(1)-N(1)	119.3(5)
C(2)-C(1)-N(1)	122.7(5)
C(38)-C(37)-C(36)	121.4(4)
C(38)-C(37)-S(2)	118.0(4)
C(36)-C(37)-S(2)	120.6(4)
C(25)-C(26)-C(27)	120.1(5)
C(25)-C(26)-Br(2)	120.2(4)
C(27)-C(26)-Br(2)	119.7(4)
C(24)-C(23)-C(28)	118.2(5)
C(24)-C(23)-N(3)	122.5(5)
C(28)-C(23)-N(3)	119.2(5)
C(28)-C(29)-C(30)	111.9(5)
C(21)-C(20)-C(19)	119.6(5)
N(2)-C(22)-C(21)	125.0(5)
C(20)-C(21)-C(22)	118.2(5)
C(11)-C(10)-Si(1)	113.8(5)
C(27)-C(28)-C(23)	119.4(5)
C(27)-C(28)-C(29)	118.2(5)
C(23)-C(28)-C(29)	122.5(5)
C(4)-C(5)-C(6)	120.6(5)

C(5)-C(6)-C(1)	119.9(5)
C(5)-C(6)-C(7)	117.9(5)
C(1)-C(6)-C(7)	122.2(5)
C(13)-C(12)-Si(1)	111.6(4)
C(6)-C(7)-C(8)	112.0(5)
C(9)-C(8)-C(7)	109.4(5)
C(9)-C(8)-Si(1)	115.7(4)
C(7)-C(8)-Si(1)	107.8(4)
N(4)-C(44)-C(43)	124.3(5)
N(1)-C(9)-C(8)	111.2(5)
C(42)-C(43)-C(44)	118.9(5)
C(35)-C(34)-Si(2)	112.1(4)
C(33)-C(32)-Si(2)	114.9(5)
N(3)-C(31)-C(30)	111.6(5)
C(31)-C(30)-C(29)	110.2(6)
C(31)-C(30)-Si(2)	116.6(5)
C(29)-C(30)-Si(2)	107.6(4)

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **13b-QUS**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	48(1)	47(1)	37(1)	-18(1)	4(1)	9(1)
Br(2)	60(1)	47(1)	37(1)	-18(1)	-21(1)	-2(1)
S(2)	20(1)	19(1)	21(1)	-1(1)	-4(1)	2(1)
S(1)	21(1)	17(1)	20(1)	-1(1)	-4(1)	-2(1)
Si(1)	27(1)	29(1)	25(1)	1(1)	-3(1)	4(1)
Si(2)	34(1)	30(1)	27(1)	3(1)	-10(1)	-8(1)
O(1)	32(2)	14(2)	29(2)	-2(2)	-7(2)	-1(1)
O(2)	20(2)	25(2)	28(2)	1(2)	-2(2)	-4(1)
O(4)	23(2)	30(2)	28(2)	-2(2)	-9(2)	6(2)
O(3)	31(2)	15(2)	30(2)	-3(2)	-5(2)	1(1)
N(1)	27(2)	26(2)	24(2)	-2(2)	-12(2)	2(2)
N(2)	18(2)	22(2)	29(2)	1(2)	-1(2)	4(2)
N(3)	22(2)	29(2)	23(2)	-6(2)	0(2)	-2(2)
N(4)	24(2)	24(2)	33(3)	2(2)	-13(2)	-4(2)
C(39)	16(2)	30(3)	22(3)	-7(2)	-1(2)	-2(2)
C(16)	26(3)	21(3)	16(2)	-4(2)	-5(2)	5(2)
C(15)	20(2)	14(2)	14(2)	-1(2)	1(2)	-2(2)
C(14)	16(2)	20(3)	13(2)	-2(2)	2(2)	4(2)
C(19)	25(3)	19(3)	14(2)	-5(2)	3(2)	-2(2)
C(18)	28(3)	26(3)	22(3)	-8(2)	-8(2)	-2(2)
C(17)	19(2)	30(3)	21(3)	-7(2)	-8(2)	4(2)
C(38)	26(3)	19(3)	15(2)	-3(2)	-4(2)	-3(2)
C(40)	27(3)	29(3)	18(3)	-8(2)	-2(2)	8(2)
C(3)	32(3)	23(3)	30(3)	-10(2)	-9(2)	5(2)
C(36)	22(2)	17(2)	18(2)	-2(2)	-9(2)	-2(2)
C(4)	38(3)	27(3)	30(3)	-15(2)	-3(2)	2(2)
C(41)	34(3)	19(3)	14(2)	-3(2)	-8(2)	0(2)
C(42)	50(4)	21(3)	25(3)	-7(2)	-14(2)	8(2)
C(24)	31(3)	28(3)	24(3)	-8(2)	0(2)	-1(2)
C(2)	34(3)	25(3)	24(3)	-7(2)	-11(2)	4(2)
C(25)	33(3)	27(3)	29(3)	-11(2)	-4(2)	-2(2)

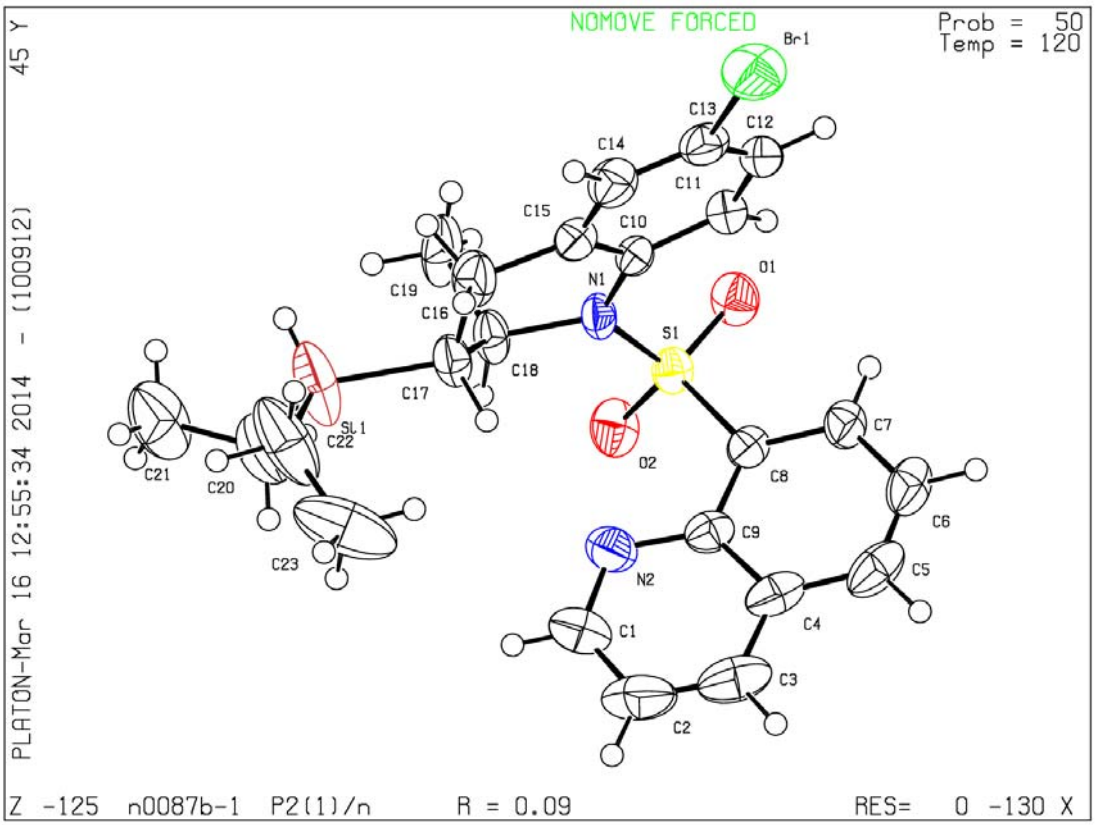
C(27)	37(3)	27(3)	27(3)	-7(2)	-6(2)	2(2)
C(1)	30(3)	19(3)	21(3)	-7(2)	-7(2)	-2(2)
C(37)	19(2)	17(2)	16(2)	-2(2)	-4(2)	1(2)
C(35)	29(3)	31(3)	35(3)	-8(3)	-11(2)	-2(2)
C(26)	40(3)	24(3)	35(3)	-15(3)	-9(3)	6(2)
C(23)	24(3)	23(3)	26(3)	-9(2)	-2(2)	4(2)
C(29)	34(3)	38(3)	25(3)	-2(3)	-2(2)	-8(3)
C(20)	38(3)	20(3)	22(3)	-7(2)	1(2)	-4(2)
C(22)	22(3)	25(3)	33(3)	0(2)	3(2)	7(2)
C(21)	45(3)	20(3)	31(3)	-7(2)	4(3)	9(2)
C(13)	21(3)	30(3)	38(3)	-9(3)	-3(2)	5(2)
C(10)	32(3)	34(3)	42(4)	10(3)	1(3)	1(3)
C(28)	32(3)	22(3)	23(3)	-6(2)	0(2)	4(2)
C(5)	40(3)	33(3)	21(3)	-10(2)	-6(2)	2(2)
C(6)	36(3)	20(3)	24(3)	-5(2)	-11(2)	-3(2)
C(12)	27(3)	42(4)	31(3)	5(3)	1(2)	5(3)
C(7)	37(3)	37(3)	23(3)	-2(2)	-9(2)	7(3)
C(8)	30(3)	26(3)	35(3)	2(2)	-7(2)	2(2)
C(44)	35(3)	27(3)	41(3)	4(3)	-22(3)	-8(2)
C(9)	28(3)	38(3)	36(3)	-2(3)	-12(2)	0(2)
C(43)	60(4)	18(3)	33(3)	-1(2)	-20(3)	-11(3)
C(34)	38(3)	51(4)	32(3)	8(3)	-14(3)	-13(3)
C(32)	43(4)	32(3)	48(4)	9(3)	-24(3)	-6(3)
C(31)	28(3)	53(4)	39(4)	-6(3)	0(3)	-9(3)
C(30)	42(4)	43(4)	41(4)	7(3)	-11(3)	-14(3)
C(11)	64(5)	32(4)	102(7)	-12(4)	-24(5)	3(3)
C(33)	58(5)	41(4)	107(7)	-18(5)	-15(5)	-5(4)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **13b-QUS**.

	x	y	z	U(eq)
H(1)	1329	5059	5999	35
H(2)	2333	-58	4015	39
H(39A)	14550	1067	443	28
H(16A)	7935	3039	9313	26
H(18A)	9355	5330	9462	30
H(17A)	9962	3932	9571	28
H(38A)	12254	1955	697	25
H(40A)	13858	-322	542	30
H(3A)	10272	2729	7080	33
H(42A)	11514	-1519	795	38
H(24A)	10784	2235	1963	34
H(2A)	7755	2766	8038	33
H(25A)	12350	2271	2918	35
H(27A)	8496	676	4586	37
H(35A)	-228	-915	2630	48
H(35B)	-356	-584	3368	48
H(35C)	397	-1496	3399	48
H(29A)	5328	665	4021	42
H(29B)	6476	-161	4161	42
H(20A)	7267	6512	9208	33
H(22A)	2826	6096	8484	37
H(21A)	4633	7002	8817	41
H(13A)	-2595	5923	7364	46
H(13B)	-1977	5569	6641	46
H(13C)	-1215	6493	6587	46
H(10A)	3920	6517	5470	51
H(10B)	2017	6894	5670	51
H(5A)	8069	4336	5412	38
H(12A)	-391	4914	7652	46
H(12B)	367	5838	7602	46

H(7A)	4313	4337	5988	41
H(7B)	5612	5161	5838	41
H(8A)	4526	5203	7094	40
H(44A)	6332	-1103	1496	43
H(9A)	2400	4145	8024	42
H(9B)	2536	3621	7417	42
H(43A)	8500	-2005	1171	45
H(34A)	2222	112	2364	54
H(34B)	2974	-799	2389	54
H(32A)	4419	-1512	4513	53
H(32B)	2724	-1888	4307	53
H(31A)	5453	850	1970	52
H(31B)	4970	1385	2567	52
H(30A)	6603	-197	2906	56
H(11A)	4221	7605	6014	101
H(11B)	4674	6717	6591	101
H(11C)	2769	7095	6791	101
H(33A)	5267	-2587	3968	106
H(33B)	6286	-1696	3395	106
H(33C)	4588	-2074	3191	106

8-{6-Bromo-3-(diethylsilyl)-2-methyl-3,4-dihydroquinolin-1(2*H*)-ylsulfonyl}quinoline (Table 1, 18b-QUS)



Crystal data and structure refinement for **18b-QUS**.

Identification code	**18b-QUS** (**CCDC1022516**)	
Empirical formula	C_{23} H_{27} Br N_2 O_2 S Si	
Formula weight	503.53	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 17.1983(12) Å	α= 90°.
	b = 8.0849(6) Å	β= 111.473(2)°.
	c = 17.9476(14) Å	γ = 90°.
Volume	2322.3(3) Å^3	
Z	4	
Density (calculated)	1.440 Mg/m^3	
Absorption coefficient	1.934 mm^{-1}	
F(000)	1040	
Crystal size	0.48 x 0.29 x 0.25 mm^3	
Theta range for data collection	3.25 to 26.00°.	
Index ranges	-21<=h<=21, -9<=k<=9, -22<=l<=22	
Reflections collected	50154	
Independent reflections	4551 [R(int) = 0.0392]	
Completeness to theta = 26.00°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6435 and 0.4571	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4551 / 82 / 271	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0882, wR2 = 0.2242	
R indices (all data)	R1 = 0.1036, wR2 = 0.2375	
Largest diff. peak and hole	2.974 and -2.597 e.Å^{-3}	

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **18b-QUS**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	10614(1)	6690(1)	6976(1)	72(1)
S(1)	6900(1)	2092(2)	6309(1)	36(1)
Si(1)	8291(2)	-1283(3)	4461(2)	81(1)
O(2)	6339(3)	745(5)	5996(3)	50(1)
O(1)	7106(3)	2490(6)	7136(3)	48(1)
N(1)	7765(3)	1688(5)	6155(3)	35(1)
N(2)	6203(4)	2474(7)	4516(3)	50(1)
C(8)	6490(3)	3922(7)	5759(4)	34(1)
C(11)	8553(4)	4040(7)	6962(3)	39(1)
C(12)	9200(4)	5167(8)	7147(4)	43(1)
C(9)	6147(3)	3888(7)	4909(4)	39(1)
C(10)	8445(3)	2825(7)	6377(3)	33(1)
C(13)	9744(4)	5078(8)	6754(4)	45(1)
C(15)	9028(4)	2719(8)	5999(4)	41(1)
C(7)	6480(4)	5327(7)	6179(4)	43(1)
C(18)	7818(4)	144(7)	5713(4)	42(1)
C(14)	9674(4)	3878(9)	6200(4)	49(2)
C(17)	8150(4)	552(7)	5053(3)	43(1)
C(4)	5772(4)	5362(9)	4506(4)	50(2)
C(6)	6119(4)	6793(8)	5764(5)	54(2)
C(5)	5763(4)	6800(8)	4959(5)	58(2)
C(16)	8990(5)	1408(9)	5396(4)	54(2)
C(19)	8340(7)	-1120(9)	6320(5)	72(3)
C(3)	5414(5)	5274(13)	3661(5)	73(2)
C(1)	5849(5)	2506(12)	3726(4)	69(2)
C(2)	5448(5)	3874(14)	3278(5)	81(2)
C(20)	7510(6)	-2863(11)	4259(6)	78(2)
C(22)	8435(9)	-551(13)	3543(5)	101(4)
C(21)	7844(8)	-4594(10)	4203(6)	97(4)
C(23)	7803(7)	638(18)	3048(6)	117(4)

Bond lengths [Å] and angles [°] for **18b-QUS**.

Br(1)-C(13)	1.914(6)
S(1)-O(2)	1.426(4)
S(1)-O(1)	1.431(4)
S(1)-N(1)	1.643(5)
S(1)-C(8)	1.775(6)
Si(1)-C(20)	1.792(9)
Si(1)-C(22)	1.852(8)
Si(1)-C(17)	1.891(6)
N(1)-C(10)	1.424(7)
N(1)-C(18)	1.499(7)
N(2)-C(1)	1.322(9)
N(2)-C(9)	1.365(8)
C(8)-C(7)	1.367(8)
C(8)-C(9)	1.421(8)
C(11)-C(12)	1.381(9)
C(11)-C(10)	1.400(8)
C(12)-C(13)	1.365(9)
C(9)-C(4)	1.420(9)
C(10)-C(15)	1.405(8)
C(13)-C(14)	1.362(10)
C(15)-C(14)	1.396(9)
C(15)-C(16)	1.498(9)
C(7)-C(6)	1.416(9)
C(18)-C(19)	1.523(9)
C(18)-C(17)	1.527(8)
C(17)-C(16)	1.515(10)
C(4)-C(3)	1.414(11)
C(4)-C(5)	1.422(11)
C(6)-C(5)	1.346(11)
C(3)-C(2)	1.337(14)
C(1)-C(2)	1.392(13)
C(20)-C(21)	1.530(13)
C(22)-C(23)	1.479(17)

O(2)-S(1)-O(1)	117.0(3)
O(2)-S(1)-N(1)	107.8(3)
O(1)-S(1)-N(1)	108.9(3)
O(2)-S(1)-C(8)	110.1(3)
O(1)-S(1)-C(8)	106.6(3)
N(1)-S(1)-C(8)	105.8(2)
C(20)-Si(1)-C(22)	112.5(5)
C(20)-Si(1)-C(17)	115.6(4)
C(22)-Si(1)-C(17)	109.6(4)
C(10)-N(1)-C(18)	118.9(5)
C(10)-N(1)-S(1)	121.7(4)
C(18)-N(1)-S(1)	119.2(4)
C(1)-N(2)-C(9)	116.4(6)
C(7)-C(8)-C(9)	121.6(5)
C(7)-C(8)-S(1)	118.0(5)
C(9)-C(8)-S(1)	120.4(4)
C(12)-C(11)-C(10)	121.2(6)
C(13)-C(12)-C(11)	119.0(6)
N(2)-C(9)-C(4)	123.0(6)
N(2)-C(9)-C(8)	119.4(5)
C(4)-C(9)-C(8)	117.6(6)
C(11)-C(10)-C(15)	118.9(5)
C(11)-C(10)-N(1)	122.2(5)
C(15)-C(10)-N(1)	118.9(5)
C(14)-C(13)-C(12)	121.4(6)
C(14)-C(13)-Br(1)	119.4(5)
C(12)-C(13)-Br(1)	119.2(5)
C(14)-C(15)-C(10)	118.3(6)
C(14)-C(15)-C(16)	118.9(6)
C(10)-C(15)-C(16)	122.8(6)
C(8)-C(7)-C(6)	119.8(6)
N(1)-C(18)-C(19)	108.4(5)
N(1)-C(18)-C(17)	110.0(5)
C(19)-C(18)-C(17)	114.1(6)
C(13)-C(14)-C(15)	121.1(6)
C(16)-C(17)-C(18)	110.8(5)

C(16)-C(17)-Si(1)	106.7(4)
C(18)-C(17)-Si(1)	115.3(4)
C(3)-C(4)-C(9)	116.2(7)
C(3)-C(4)-C(5)	124.3(7)
C(9)-C(4)-C(5)	119.5(6)
C(5)-C(6)-C(7)	120.5(6)
C(6)-C(5)-C(4)	120.9(6)
C(15)-C(16)-C(17)	113.5(5)
C(2)-C(3)-C(4)	120.7(8)
N(2)-C(1)-C(2)	124.8(9)
C(3)-C(2)-C(1)	118.8(8)
C(21)-C(20)-Si(1)	113.2(8)
C(23)-C(22)-Si(1)	115.7(9)

Symmetry transformations used to generate equivalent atoms:

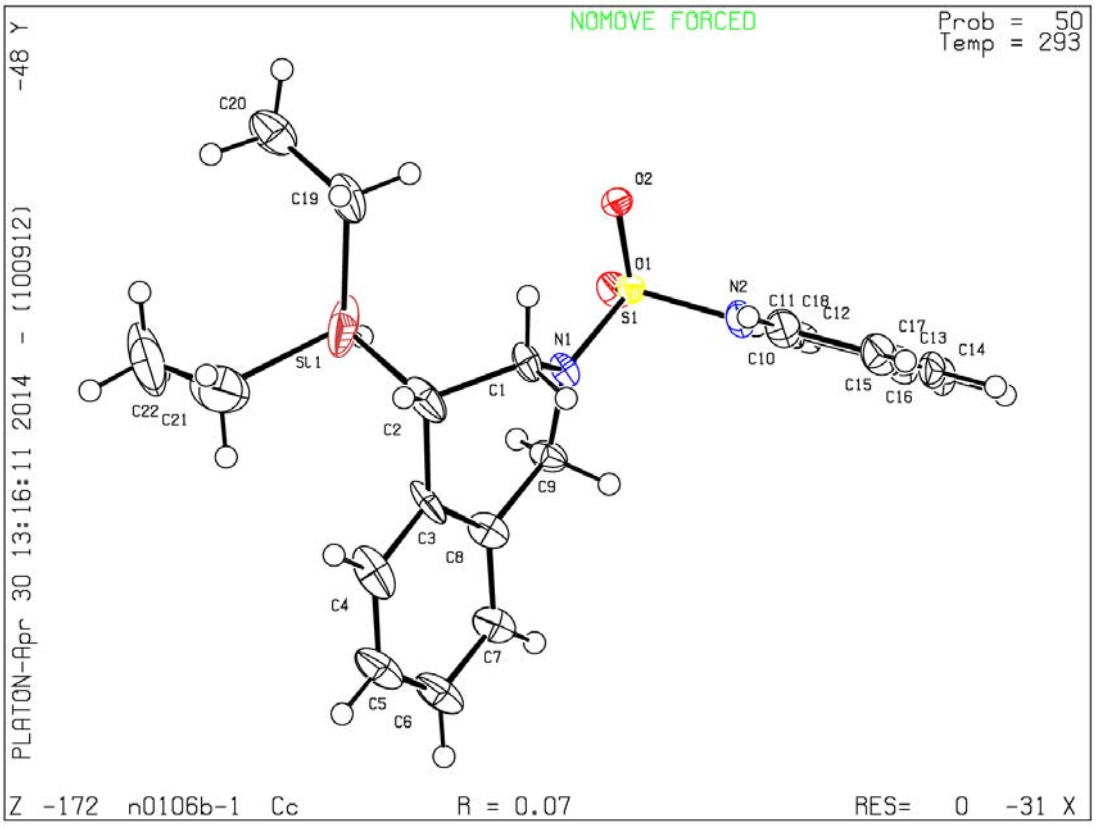
Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **18b-QUS**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	45(1)	66(1)	95(1)	-6(1)	14(1)	-17(1)
S(1)	43(1)	26(1)	40(1)	2(1)	18(1)	-2(1)
Si(1)	164(3)	40(1)	64(1)	-13(1)	72(2)	-16(1)
O(2)	60(3)	28(2)	68(3)	1(2)	28(2)	-11(2)
O(1)	61(3)	51(3)	40(2)	2(2)	27(2)	4(2)
N(1)	46(3)	24(2)	36(2)	-3(2)	16(2)	2(2)
N(2)	49(3)	49(3)	43(3)	-3(2)	8(2)	-4(3)
C(8)	28(3)	25(2)	47(3)	1(2)	11(2)	-5(2)
C(11)	40(3)	36(3)	39(3)	-4(2)	12(2)	2(2)
C(12)	41(3)	37(3)	42(3)	-4(3)	4(2)	4(2)
C(9)	29(3)	39(3)	46(3)	6(2)	11(2)	-4(2)
C(10)	37(3)	25(2)	33(3)	3(2)	9(2)	5(2)
C(13)	32(3)	41(3)	55(4)	2(3)	6(3)	0(2)
C(15)	38(3)	42(3)	39(3)	0(2)	12(2)	8(2)
C(7)	36(3)	30(3)	61(4)	-8(2)	15(3)	-6(2)
C(18)	70(4)	22(3)	38(3)	0(2)	26(3)	2(2)
C(14)	40(3)	51(4)	57(4)	1(3)	20(3)	3(3)
C(17)	70(4)	28(3)	33(3)	0(2)	22(3)	4(3)
C(4)	32(3)	51(3)	63(4)	20(3)	11(3)	2(3)
C(6)	44(4)	27(3)	93(5)	-4(3)	27(4)	-5(3)
C(5)	43(4)	36(3)	94(5)	23(3)	24(4)	6(3)
C(16)	57(4)	57(4)	57(4)	-12(3)	30(3)	6(3)
C(19)	142(8)	34(4)	53(4)	17(3)	50(5)	34(4)
C(3)	57(5)	85(5)	64(4)	34(4)	6(4)	9(4)
C(1)	64(5)	83(5)	44(4)	-6(4)	2(3)	-2(4)
C(2)	59(5)	118(7)	50(4)	15(4)	2(4)	10(5)
C(20)	94(7)	69(5)	82(6)	-20(5)	43(5)	-23(4)
C(22)	193(11)	74(6)	57(5)	-21(4)	72(6)	-45(6)
C(21)	165(11)	40(4)	81(6)	-1(4)	39(7)	-20(5)
C(23)	115(8)	172(12)	50(5)	9(6)	16(5)	-74(8)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3)
for **18b-QUS**.

	x	y	z	U(eq)
H(1)	8831	-1813	4798	97
H(11A)	8175	4090	7237	47
H(12A)	9265	5992	7543	52
H(7A)	6716	5321	6747	52
H(18A)	7240	-311	5455	50
H(14A)	10071	3830	5947	59
H(17A)	7748	1332	4671	52
H(6A)	6128	7778	6055	65
H(5A)	5502	7779	4691	70
H(16A)	9426	570	5652	65
H(16B)	9118	1916	4952	65
H(19A)	8088	-1322	6721	109
H(19B)	8908	-695	6584	109
H(19C)	8359	-2157	6044	109
H(3A)	5147	6220	3363	88
H(1A)	5870	1524	3444	82
H(2A)	5204	3813	2711	97
H(20A)	7278	-2857	4689	94
H(20B)	7049	-2605	3748	94
H(22A)	8992	-26	3700	121
H(22B)	8434	-1525	3208	121
H(21A)	7390	-5401	4088	145
H(21B)	8290	-4873	4712	145
H(21C)	8067	-4617	3772	145
H(23A)	7934	952	2580	175
H(23B)	7806	1625	3366	175
H(23C)	7248	123	2871	175

8-{4-(Diethylsilyl)-3,4-dihydroisoquinolin-2(1*H*)-ylsulfonyl}quinolone (Table.1, 31b)



Crystal data and structure refinement for **31b**.

Identification code	**31b (CCDC1022519)**	
Empirical formula	C_{22} H_{26} N_2 O_2 S Si	
Formula weight	410.60	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 18.662(15) Å	α= 90°.
	b = 10.727(9) Å	β= 119.34(5)°.
	c = 11.793(10) Å	γ = 90°.
Volume	2058(3) $Å^3$	
Z	4	
Density (calculated)	1.325 Mg/m^3	
Absorption coefficient	0.236 mm^{-1}	
F(000)	872	
Crystal size	0.20 x 0.10 x 0.07 mm^3	
Theta range for data collection	2.58 to 26.99°.	
Index ranges	-23<=h<=23, -13<=k<=13, -15<=l<=15	
Reflections collected	9147	
Independent reflections	4102 [R(int) = 0.0546]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9837 and 0.9543	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4102 / 78 / 247	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0743, wR2 = 0.1586	
R indices (all data)	R1 = 0.0994, wR2 = 0.1717	
Absolute structure parameter	0.00(15)	
Largest diff. peak and hole	1.394 and -1.375 $e.Å^{-3}$	

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **31b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	586(1)	-1272(1)	3824(1)	18(1)
O(2)	815(2)	-1849(3)	5054(3)	22(1)
O(1)	1018(2)	-1609(3)	3160(4)	24(1)
N(2)	-889(3)	-838(4)	4173(4)	24(1)
N(1)	666(3)	228(3)	4032(4)	18(1)
Si(1)	2360(1)	1353(3)	6295(2)	63(1)
C(10)	-1079(3)	-1385(4)	3015(5)	18(1)
C(11)	-456(3)	-1646(4)	2715(5)	21(1)
C(8)	719(3)	2392(5)	3261(5)	25(1)
C(6)	487(4)	4509(5)	2448(7)	38(1)
C(7)	451(4)	3220(5)	2234(6)	29(1)
C(12)	-635(3)	-2212(4)	1565(5)	23(1)
C(15)	-1901(3)	-1740(4)	2072(5)	23(1)
C(9)	684(3)	977(5)	2997(5)	23(1)
C(16)	-2519(3)	-1501(5)	2399(6)	28(1)
C(14)	-2060(3)	-2306(5)	886(5)	31(1)
C(3)	1027(4)	2822(5)	4521(6)	30(1)
C(18)	-1495(3)	-645(5)	4415(6)	28(1)
C(1)	663(3)	840(5)	5151(5)	22(1)
C(4)	1053(4)	4129(5)	4722(7)	40(1)
C(5)	788(4)	4972(5)	3674(7)	38(1)
C(17)	-2317(3)	-959(5)	3542(6)	33(1)
C(13)	-1453(4)	-2541(5)	638(6)	34(1)
C(2)	1285(4)	1907(5)	5625(6)	38(1)
C(19)	2629(4)	164(5)	7622(6)	37(1)
C(20)	3532(4)	-239(5)	8381(7)	44(2)
C(21)	2953(6)	2988(7)	7013(9)	66(2)
C(22)	3755(7)	2915(9)	7393(9)	94(4)

Bond lengths [Å] and angles [°] for **31b**.

S(1)-O(1)	1.420(4)
S(1)-O(2)	1.436(4)
S(1)-N(1)	1.624(4)
S(1)-C(11)	1.777(5)
N(2)-C(18)	1.311(7)
N(2)-C(10)	1.363(6)
N(1)-C(9)	1.475(6)
N(1)-C(1)	1.476(7)
Si(1)-C(2)	1.857(8)
Si(1)-C(19)	1.886(7)
Si(1)-C(21)	2.025(9)
C(10)-C(11)	1.401(7)
C(10)-C(15)	1.436(6)
C(11)-C(12)	1.370(7)
C(8)-C(7)	1.383(8)
C(8)-C(3)	1.383(8)
C(8)-C(9)	1.544(7)
C(6)-C(5)	1.363(10)
C(6)-C(7)	1.401(8)
C(12)-C(13)	1.420(7)
C(15)-C(16)	1.406(8)
C(15)-C(14)	1.416(8)
C(16)-C(17)	1.341(9)
C(14)-C(13)	1.325(9)
C(3)-C(4)	1.419(8)
C(3)-C(2)	1.510(8)
C(18)-C(17)	1.407(8)
C(1)-C(2)	1.527(7)
C(4)-C(5)	1.410(9)
C(19)-C(20)	1.533(9)
C(21)-C(22)	1.337(14)
O(1)-S(1)-O(2)	118.7(2)
O(1)-S(1)-N(1)	107.5(2)
O(2)-S(1)-N(1)	108.3(2)

O(1)-S(1)-C(11)	104.4(2)
O(2)-S(1)-C(11)	108.8(2)
N(1)-S(1)-C(11)	108.8(2)
C(18)-N(2)-C(10)	117.2(4)
C(9)-N(1)-C(1)	120.6(4)
C(9)-N(1)-S(1)	116.9(3)
C(1)-N(1)-S(1)	122.4(3)
C(2)-Si(1)-C(19)	111.2(3)
C(2)-Si(1)-C(21)	99.0(3)
C(19)-Si(1)-C(21)	111.7(3)
N(2)-C(10)-C(11)	119.9(4)
N(2)-C(10)-C(15)	123.0(5)
C(11)-C(10)-C(15)	117.1(4)
C(12)-C(11)-C(10)	120.6(4)
C(12)-C(11)-S(1)	118.5(4)
C(10)-C(11)-S(1)	120.9(4)
C(7)-C(8)-C(3)	120.5(5)
C(7)-C(8)-C(9)	119.6(5)
C(3)-C(8)-C(9)	119.9(5)
C(5)-C(6)-C(7)	120.6(6)
C(8)-C(7)-C(6)	120.7(6)
C(11)-C(12)-C(13)	121.4(5)
C(16)-C(15)-C(14)	123.1(5)
C(16)-C(15)-C(10)	116.5(5)
C(14)-C(15)-C(10)	120.4(5)
N(1)-C(9)-C(8)	112.6(4)
C(17)-C(16)-C(15)	119.4(5)
C(13)-C(14)-C(15)	120.8(5)
C(8)-C(3)-C(4)	118.1(5)
C(8)-C(3)-C(2)	119.9(5)
C(4)-C(3)-C(2)	121.9(5)
N(2)-C(18)-C(17)	123.3(5)
N(1)-C(1)-C(2)	109.0(4)
C(5)-C(4)-C(3)	121.2(6)
C(6)-C(5)-C(4)	118.7(5)
C(16)-C(17)-C(18)	120.5(5)

C(14)-C(13)-C(12)	119.7(5)
C(3)-C(2)-C(1)	107.9(5)
C(3)-C(2)-Si(1)	113.3(4)
C(1)-C(2)-Si(1)	112.6(4)
C(20)-C(19)-Si(1)	116.4(5)
C(22)-C(21)-Si(1)	112.5(7)

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **31b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	15(1)	17(1)	22(1)	2(1)	8(1)	-1(1)
O(2)	17(2)	22(2)	24(2)	7(1)	7(1)	0(1)
O(1)	26(2)	20(2)	35(2)	-2(2)	21(2)	2(1)
N(2)	19(2)	21(2)	31(2)	-4(2)	11(2)	-4(2)
N(1)	22(2)	15(2)	23(2)	-4(2)	15(2)	-4(2)
Si(1)	35(1)	115(2)	26(1)	10(1)	4(1)	-44(1)
C(10)	17(2)	9(2)	22(2)	-3(2)	6(2)	-4(2)
C(11)	22(2)	11(2)	26(2)	2(2)	7(2)	-2(2)
C(8)	35(3)	23(2)	30(3)	0(2)	25(2)	1(2)
C(6)	49(3)	18(2)	66(3)	2(2)	43(3)	1(2)
C(7)	34(3)	24(2)	39(3)	4(2)	26(3)	4(2)
C(12)	29(3)	15(2)	27(3)	0(2)	16(2)	-3(2)
C(15)	16(2)	12(2)	29(3)	2(2)	2(2)	0(2)
C(9)	35(3)	16(2)	23(3)	-1(2)	16(2)	0(2)
C(16)	13(2)	21(3)	43(3)	0(2)	7(2)	-2(2)
C(14)	25(3)	31(3)	25(3)	0(2)	3(2)	-12(2)
C(3)	49(3)	19(2)	36(3)	-9(2)	31(3)	-20(2)
C(18)	24(3)	24(3)	37(3)	-3(2)	15(2)	0(2)
C(1)	29(3)	20(2)	24(3)	-10(2)	17(2)	-10(2)
C(4)	55(4)	32(3)	53(4)	-16(3)	41(3)	-17(3)
C(5)	49(3)	18(2)	66(3)	2(2)	43(3)	1(2)
C(17)	22(3)	26(3)	54(4)	-1(3)	21(3)	1(2)
C(13)	41(3)	26(3)	26(3)	-3(2)	10(2)	-13(2)
C(2)	67(4)	28(3)	25(3)	-11(2)	29(3)	-24(3)
C(19)	45(3)	31(3)	40(3)	-15(2)	26(3)	-16(3)
C(20)	56(4)	22(3)	59(4)	-6(3)	33(3)	-2(3)
C(21)	83(5)	49(4)	63(5)	9(4)	34(5)	0(4)
C(22)	102(6)	99(7)	64(6)	-16(5)	26(5)	-79(6)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **31b**.

	x	y	z	U(eq)
H(1)	2511	865	5258	76
H(6A)	303	5054	1746	46
H(7A)	246	2918	1392	35
H(12A)	-211	-2385	1387	27
H(9A)	197	794	2175	28
H(9B)	1160	739	2920	28
H(16A)	-3062	-1715	1827	34
H(14A)	-2596	-2514	275	37
H(18A)	-1375	-282	5205	34
H(1A)	807	241	5846	27
H(1B)	119	1161	4893	27
H(4A)	1248	4436	5560	48
H(5A)	818	5828	3818	46
H(17A)	-2724	-790	3758	40
H(13A)	-1563	-2920	-140	41
H(2A)	1246	2333	6328	45
H(19A)	2475	501	8236	44
H(19B)	2296	-572	7236	44
H(20A)	3598	-852	9019	66
H(20B)	3869	472	8808	66
H(20C)	3693	-590	7791	66
H(21A)	2704	3627	6350	79
H(21B)	2887	3236	7747	79
H(22A)	4010	3707	7731	142
H(22B)	3824	2694	6664	142
H(22C)	4006	2291	8058	142

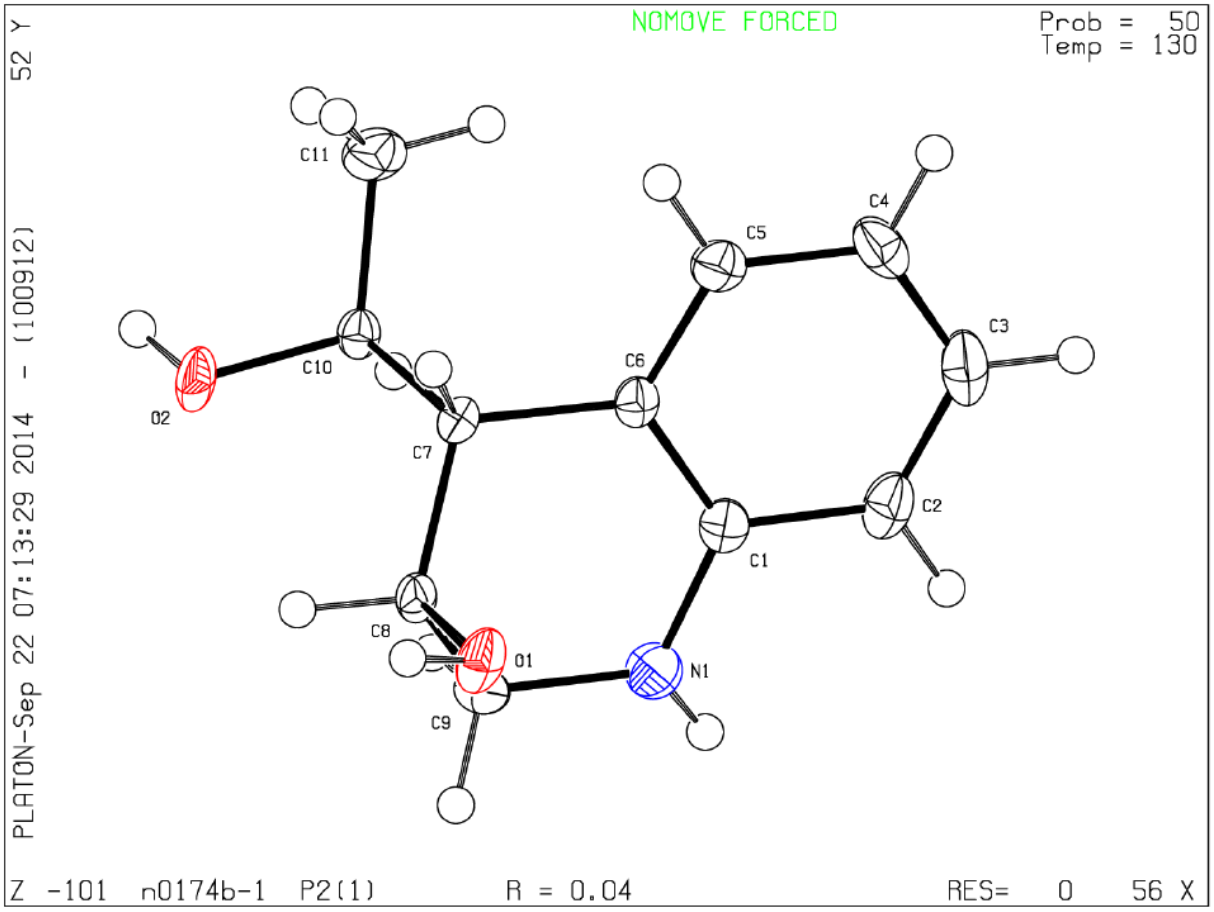
Torsion angles [°] for **31b**.

O(1)-S(1)-N(1)-C(9)	34.2(4)
O(2)-S(1)-N(1)-C(9)	163.6(3)
C(11)-S(1)-N(1)-C(9)	-78.2(4)
O(1)-S(1)-N(1)-C(1)	-150.1(4)
O(2)-S(1)-N(1)-C(1)	-20.7(5)
C(11)-S(1)-N(1)-C(1)	97.5(4)
C(18)-N(2)-C(10)-C(11)	-178.3(4)
C(18)-N(2)-C(10)-C(15)	0.4(7)
N(2)-C(10)-C(11)-C(12)	179.0(4)
C(15)-C(10)-C(11)-C(12)	0.2(6)
N(2)-C(10)-C(11)-S(1)	-0.1(6)
C(15)-C(10)-C(11)-S(1)	-178.9(3)
O(1)-S(1)-C(11)-C(12)	3.9(4)
O(2)-S(1)-C(11)-C(12)	-123.8(4)
N(1)-S(1)-C(11)-C(12)	118.3(4)
O(1)-S(1)-C(11)-C(10)	-177.0(4)
O(2)-S(1)-C(11)-C(10)	55.3(4)
N(1)-S(1)-C(11)-C(10)	-62.5(4)
C(3)-C(8)-C(7)-C(6)	0.0(9)
C(9)-C(8)-C(7)-C(6)	-179.2(5)
C(5)-C(6)-C(7)-C(8)	0.2(9)
C(10)-C(11)-C(12)-C(13)	0.6(7)
S(1)-C(11)-C(12)-C(13)	179.7(4)
N(2)-C(10)-C(15)-C(16)	-0.2(7)
C(11)-C(10)-C(15)-C(16)	178.5(4)
N(2)-C(10)-C(15)-C(14)	-180.0(5)
C(11)-C(10)-C(15)-C(14)	-1.2(6)
C(1)-N(1)-C(9)-C(8)	1.4(7)
S(1)-N(1)-C(9)-C(8)	177.2(4)
C(7)-C(8)-C(9)-N(1)	-157.1(5)
C(3)-C(8)-C(9)-N(1)	23.6(7)
C(14)-C(15)-C(16)-C(17)	-179.9(5)
C(10)-C(15)-C(16)-C(17)	0.4(7)
C(16)-C(15)-C(14)-C(13)	-178.3(5)

C(10)-C(15)-C(14)-C(13)	1.5(8)
C(7)-C(8)-C(3)-C(4)	0.4(8)
C(9)-C(8)-C(3)-C(4)	179.7(5)
C(7)-C(8)-C(3)-C(2)	177.5(6)
C(9)-C(8)-C(3)-C(2)	-3.3(8)
C(10)-N(2)-C(18)-C(17)	-0.7(8)
C(9)-N(1)-C(1)-C(2)	-43.4(6)
S(1)-N(1)-C(1)-C(2)	141.1(4)
C(8)-C(3)-C(4)-C(5)	-1.1(9)
C(2)-C(3)-C(4)-C(5)	-178.1(6)
C(7)-C(6)-C(5)-C(4)	-0.9(9)
C(3)-C(4)-C(5)-C(6)	1.4(10)
C(15)-C(16)-C(17)-C(18)	-0.7(8)
N(2)-C(18)-C(17)-C(16)	0.9(9)
C(15)-C(14)-C(13)-C(12)	-0.6(8)
C(11)-C(12)-C(13)-C(14)	-0.4(8)
C(8)-C(3)-C(2)-C(1)	-39.3(7)
C(4)-C(3)-C(2)-C(1)	137.6(6)
C(8)-C(3)-C(2)-Si(1)	86.1(6)
C(4)-C(3)-C(2)-Si(1)	-96.9(6)
N(1)-C(1)-C(2)-C(3)	60.5(6)
N(1)-C(1)-C(2)-Si(1)	-65.4(5)
C(19)-Si(1)-C(2)-C(3)	-177.6(4)
C(21)-Si(1)-C(2)-C(3)	64.7(5)
C(19)-Si(1)-C(2)-C(1)	-54.8(5)
C(21)-Si(1)-C(2)-C(1)	-172.4(4)
C(2)-Si(1)-C(19)-C(20)	-172.1(4)
C(21)-Si(1)-C(19)-C(20)	-62.5(6)
C(2)-Si(1)-C(21)-C(22)	-170.3(7)
C(19)-Si(1)-C(21)-C(22)	72.4(8)

Symmetry transformations used to generate equivalent atoms:

(3*S*,4*S*)-4-((*S*)-1-Hydroxyethyl)-1,2,3,4-tetrahydroquinolin-3-ol (Table 1, 39)



Crystal data and structure refinement for **39**.

Identification code	**39 (CCDC1025810)**	
Empirical formula	C_{11} H_{15} N O_2	
Formula weight	193.24	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 5.8577(3) Å	α= 90°.
	b = 6.6735(3) Å	β= 98.084(3)°.
	c = 12.7807(6) Å	γ = 90°.
Volume	494.65(4) $Å^3$	
Z	2	
Density (calculated)	1.297 Mg/m^3	
Absorption coefficient	0.089 mm^{-1}	
F(000)	208	
Crystal size	0.06 x 0.04 x 0.02 mm^3	
Theta range for data collection	3.22 to 29.90°.	
Index ranges	-8<=h<=8, -9<=k<=9, -17<=l<=17	
Reflections collected	17353	
Independent reflections	2853 [R(int) = 0.0633]	
Completeness to theta = 29.90°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9982 and 0.9947	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2853 / 1 / 136	
Goodness-of-fit on F^2	1.081	
Final R indices [I>2sigma(I)]	R1 = 0.0432, wR2 = 0.0941	
R indices (all data)	R1 = 0.0635, wR2 = 0.1015	
Largest diff. peak and hole	0.334 and -0.242 $e.Å^{-3}$	

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **39**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	3303(2)	-677(2)	9388(1)	23(1)
O(2)	3195(2)	5296(2)	9054(1)	23(1)
N(1)	-822(2)	-318(2)	7915(1)	28(1)
C(1)	449(3)	-168(2)	7087(1)	19(1)
C(2)	-250(3)	-1240(2)	6155(1)	26(1)
C(3)	1081(3)	-1264(3)	5350(1)	29(1)
C(4)	3157(3)	-244(2)	5460(1)	26(1)
C(5)	3853(3)	836(2)	6376(1)	21(1)
C(6)	2521(2)	929(2)	7193(1)	16(1)
C(7)	3279(2)	2140(2)	8188(1)	14(1)
C(8)	2249(3)	1223(2)	9118(1)	17(1)
C(9)	-317(3)	946(2)	8841(1)	22(1)
C(10)	2719(2)	4381(2)	8033(1)	16(1)
C(11)	4120(3)	5389(3)	7276(1)	28(1)

Bond lengths [Å] and angles [°] for **39**.

O(1)-C(8)	1.4313(17)
O(2)-C(10)	1.4317(17)
N(1)-C(1)	1.380(2)
N(1)-C(9)	1.449(2)
C(1)-C(2)	1.401(2)
C(1)-C(6)	1.407(2)
C(2)-C(3)	1.375(3)
C(3)-C(4)	1.383(3)
C(4)-C(5)	1.386(2)
C(5)-C(6)	1.390(2)
C(6)-C(7)	1.5198(19)
C(7)-C(8)	1.534(2)
C(7)-C(10)	1.537(2)
C(8)-C(9)	1.507(2)
C(10)-C(11)	1.512(2)
C(1)-N(1)-C(9)	120.93(13)
N(1)-C(1)-C(2)	119.38(14)
N(1)-C(1)-C(6)	120.99(13)
C(2)-C(1)-C(6)	119.48(14)
C(3)-C(2)-C(1)	120.89(16)
C(2)-C(3)-C(4)	120.07(15)
C(3)-C(4)-C(5)	119.45(15)
C(4)-C(5)-C(6)	121.85(15)
C(5)-C(6)-C(1)	118.20(13)
C(5)-C(6)-C(7)	121.57(13)
C(1)-C(6)-C(7)	120.23(12)
C(6)-C(7)-C(8)	109.62(11)
C(6)-C(7)-C(10)	112.19(12)
C(8)-C(7)-C(10)	112.81(12)
O(1)-C(8)-C(9)	109.27(12)
O(1)-C(8)-C(7)	109.74(12)
C(9)-C(8)-C(7)	110.82(12)
N(1)-C(9)-C(8)	110.19(12)

O(2)-C(10)-C(11)	109.85(13)
O(2)-C(10)-C(7)	106.69(12)
C(11)-C(10)-C(7)	112.95(13)

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **39**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	33(1)	12(1)	22(1)	2(1)	-7(1)	1(1)
O(2)	39(1)	9(1)	19(1)	-2(1)	-4(1)	0(1)
N(1)	20(1)	38(1)	24(1)	-5(1)	2(1)	-12(1)
C(1)	21(1)	16(1)	18(1)	1(1)	-1(1)	2(1)
C(2)	28(1)	21(1)	25(1)	-2(1)	-6(1)	-2(1)
C(3)	44(1)	21(1)	20(1)	-4(1)	-6(1)	5(1)
C(4)	41(1)	22(1)	18(1)	0(1)	9(1)	9(1)
C(5)	24(1)	16(1)	24(1)	2(1)	6(1)	3(1)
C(6)	19(1)	12(1)	16(1)	0(1)	0(1)	2(1)
C(7)	12(1)	12(1)	17(1)	-2(1)	1(1)	0(1)
C(8)	26(1)	10(1)	14(1)	0(1)	1(1)	1(1)
C(9)	24(1)	22(1)	20(1)	2(1)	7(1)	-2(1)
C(10)	17(1)	14(1)	15(1)	-1(1)	0(1)	1(1)
C(11)	37(1)	16(1)	33(1)	4(1)	13(1)	1(1)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **39**.

	x	y	z	U(eq)
H(2B)	-1664	-1959	6077	31
H(3A)	575	-1982	4718	35
H(4A)	4098	-284	4913	32
H(5A)	5281	1533	6447	25
H(7A)	4993	2016	8352	17
H(8A)	2559	2140	9740	20
H(9A)	-944	323	9444	26
H(9B)	-1067	2267	8701	26
H(10A)	1042	4536	7762	19
H(11A)	3692	6807	7206	42
H(11B)	3812	4738	6583	42
H(11C)	5765	5275	7548	42
H(1A)	4420(30)	-510(40)	9901(15)	33
H(2A)	3010(40)	6530(40)	8993(16)	33
H(1B)	-2150(40)	-780(40)	7769(15)	33

Hydrogen bonds for **39** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2A)...O(1)#1	0.83(2)	1.93(2)	2.7207(16)	158(2)
O(1)-H(1A)...O(2)#2	0.86(2)	1.87(2)	2.7288(16)	171(2)

Symmetry transformations used to generate equivalent atoms:

#1 x,y+1,z #2 -x+1,y-1/2,-z+2