Supporting Information

Catalytic asymmetric construction of 1,5-remote Si- and C-stereocenters via desymmetrizing ene reaction of bis(methallyl)silanes

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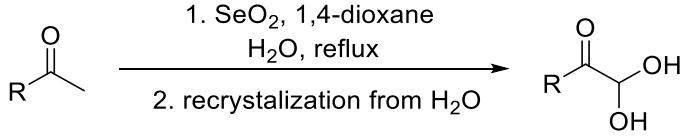
1. General information

Optical rotations were reported as follows: $[\alpha]^{T}_{D}$ = (*c*: g/100 mL, in CH_2Cl_2). ^{1}H NMR spectra were recorded on commercial instruments (400 MHz or 600 MHz). Chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. $^{13}C\{^{1}H\}$ NMR data were collected on commercial instruments (101 MHz or 151 MHz) with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. $^{19}F\{^{1}H\}$ NMR spectra were collected on commercial instruments (376 MHz or 565 MHz) with complete proton decoupling. IR spectra were recorded on BRUKER TENSOR II IR spectrophotometer. Enantiomeric excesses (ee) were determined by HPLC analysis by using the corresponding commercial chiralpak column as stated in the experimental procedures at 25 °C, and SFC at 35 °C with UV detector at 230 nm. HRMS was recorded on a commercial apparatus (FTMS+c ESI). Reagents, solvents and metal salts obtained from commercial sources were used without further purification. Chromatography: Qingdao Haiyang silica gel, HG/T2354-92, H CP.

2. Synthesis of the starting materials.

a) General procedure for the synthesis of glyoxals monohydrates

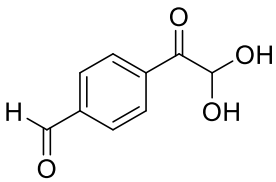
Glyoxal monohydrates were prepared according to the methods reported in the literature.[1]



Sub 1 **A1-A38**

SeO_2 (24 mmol, 1.2 equiv), 1,4-dioxane (30 mL) and water (2 mL) were added to a 100 mL round bottom flask and fitted it with a condenser. The mixture was heated to 50-55 ℃ and stirred until the solid dissolved. It was followed by addition of **Sub 1** (20 mmol, 1.0 equiv) and the reaction was maintained at reflux temperature. After the reaction was complete, as monitored by TLC, the mixture was filtered through a pad of Celite. The filtrate was evaporated to afford a crude product that was purified by distillation under reduced pressure to give a yellow liquid. This liquid was dissolved in hot water (20 mL) and allowed to crystallize to afford glyoxals monohydrates.

A22: 4-(2,2-dihydroxyacetyl)benzaldehyde



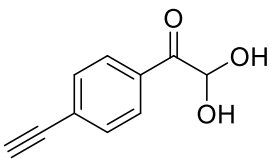
Yellow solid, 37% yield.

^{1}H NMR (400 MHz, DMSO-d6) δ = 10.11 (s, 1H), 8.25 (d, *J* = 8.2 Hz, 2H), 8.04 (d, *J* = 8.3 Hz, 2H), 6.93 (d, *J* = 7.1 Hz, 2H), 5.69 (t, *J* = 7.0 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d6) δ = 196.5, 193.5,139.2, 138.5, 130.4, 129.8, 90.2.

ESI-HRMS Calculated for [$C_9H_8O_4$+Na^+] = 203.0315, found: 203.0315.

A26: 1-(4-ethynylphenyl)-2,2-dihydroxyethan-1-one



Yellow solid, 56% yield.

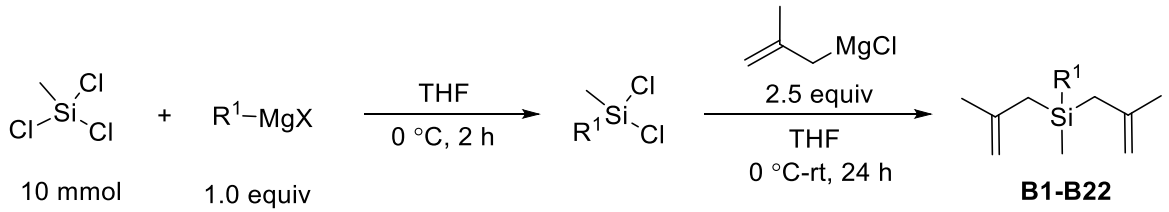
^{1}H NMR (400 MHz, DMSO-d6) δ = 8.07 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 7.1 Hz, 2H), 5.65 (t, *J* = 7.1 Hz, 1H), 4.48 (s, 1H).

^{13}C NMR (101 MHz, DMSO-d6) δ = 196.0, 133.9, 132.2, 130.1, 126.7, 90.0, 84.4, 83.3.

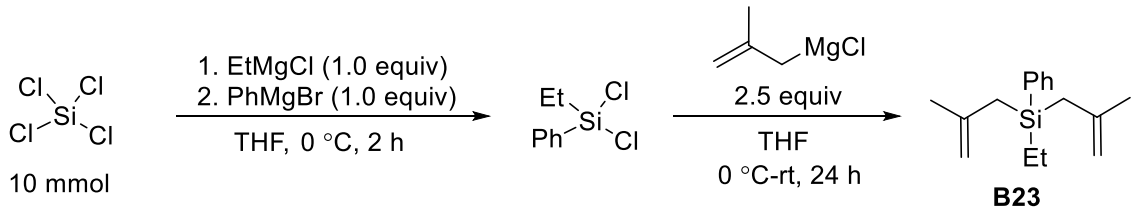
ESI-HRMS Calculated for [$C_{10}H_8O_3$+Na^+] = 199.0366, found: 199.0366.

b) General procedure for the synthesis of the silicon starting materials.

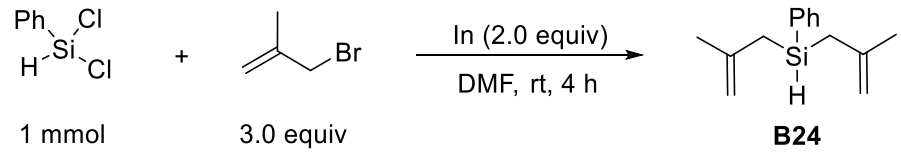
The desired substituted bis(2-methylallyl)silanes were prepared according to reported procedure.[2-3]



Method A: To a solution of methyl trichlorosilane (10.0 mmol) in THF (20 mL), Grignard reagent R^1-MgX (10.0 mmol) was added at 0 ºC under argon atmosphere. After the resulting mixture was stirred at 0 ºC for 2 h, a solution of (2-methylallyl)magnesium chloride (0.5 M in THF, 2.5 equivalent, 25 mmol) was added at 0 °C. The reaction mixture was gradually warmed up to rt and stirred for 24 h. After the completion that was indicated by TLC, the reaction was quenched with sat. aq. NH_4Cl and extracted with petroleum ether. The combined organic phases were dried over Na_2SO_4, filtrated and dried under reduced pressure. Purification of the crude by silica gel chromatography with petroleum ether afforded the desired substituted bis(2-methylallyl)silane **B1-B22**.



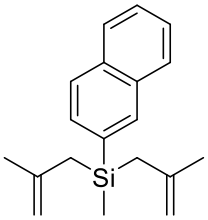
Method B: To a solution of silicon tetrachloride (10.0 mmol) in THF (20 mL), ethyl magnesium chloride (10.0 mmol) was added at 0 ºC under argon, and the resulting mixture was stirred at 0 ºC for 2 h. Phenyl magnesium bromide was then added to the prepared ethyl trichlorosilane via syringe. After 2 h at 0 ºC, a solution of (2-methylallyl)magnesium chloride (0.5 M in THF, 2.5 equivalent, 25 mmol) prepared beforehand was added to the mixture at 0 °C. The reaction mixture was gradually warmed up to room temperature and stirred for 24 h. After the completion that was indicated by TLC, the reaction was quenched with sat. aq. NH_4Cl and extracted with petroleum ether. The combined organic phases were dried over Na_2SO_4, filtrated and dried under reduced pressure. Purification of the crude by silica gel chromatography with petroleum ether afforded the desired product **B23**.



Method C: 3-Bromo-2-methylpropene (3.0 mmol) and indium (2.0 mmol) in dry DMF (2 mL) were added to a round bottom flask with stirring at room temperature under a nitrogen atmosphere. The mixture was stirred for about 1 h. Phenyldichlorosilane (1.0 mmol) was added dropwise. The reaction mixture

was stirred for 4 h and then was quenched with 0.1 M hydrochloric acid (2 mL). The resulting mixture was extracted with diethyl ether (3 × 5 mL), the diethyl ether solution was washed with saturated NaCl (2 × 5 mL) and dried over Na_2SO_4. The solvent was removed by evaporation under reduced pressure. Purification of the crude by silica gel chromatography with petroleum ether afforded the desired product **B24**.

B1: methylbis(2-methylallyl)(naphthalen-2-yl)silane



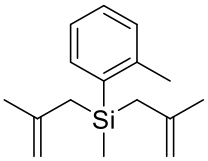
Colorless oil, 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 (s, 1H), 7.89 – 7.74 (m, 3H), 7.61 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.53 – 7.42 (m, 2H), 4.67 – 4.56 (m, 2H), 4.55 – 4.43 (m, 2H), 1.91 (s, 4H), 1.57 (s, 6H), 0.46 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.1, 135.4, 134.8, 133.9, 132.98, 130.4, 128.3, 127.9, 127.0, 126.5, 126.0, 109.6, 26.4, 25.5, -5.0.

ESI-HRMS Calculated for [$C_{19}H_{24}Si+Na^+$] = 303.1539, found: 303.1539.

B3: methylbis(2-methylallyl)(o-tolyl)silane



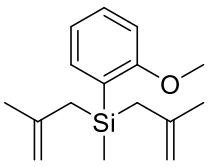
Colorless oil, 23% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.16 – 7.13 (m, 2H), 4.58 (dd, *J* = 2.2, 1.4 Hz, 2H), 4.53 – 4.45 (m, 2H), 2.50 (s, 3H), 1.99 – 1.83 (m, 4H), 1.57 (s, 6H), 0.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.7, 143.4, 136.0, 135.2, 130.1, 129.5, 125.0, 109.6, 26.8,25.3, 23.6, -3.6.

ESI-HRMS Calculated for [$C_{16}H_{24}Si$ +Na^+] = 267.1539, found: 267.1541.

B4: (2-methoxyphenyl)(methyl)bis(2-methylallyl)silane



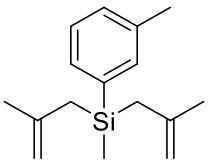
Colorless oil, 40% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 – 7.33 (m, 2H), 6.93 (t, *J* = 7.3 Hz, 1H), 6.81 (d, *J* = 8.5 Hz, 1H), 4.56 – 4.50 (m, 2H), 4.47 – 4.41 (m, 2H), 3.82 (s, 3H), 1.96 – 1.81 (m, 4H), 1.56 (s, 6H), 0.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.3, 144.0, 135.7, 131.2, 125.6, 120.6, 109.4, 108.8, 54.9, 26.2, 25.2, -4.9.

ESI-HRMS Calculated for [$C_{16}H_{24}OSi+Na^+$] = 283.1489, found: 283.1486.

B5: methylbis(2-methylallyl)(m-tolyl)silane



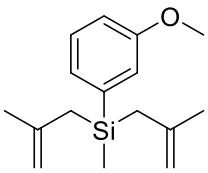
Colorless oil, 67% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 (s, 2H), 7.25 – 7.20 (m, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 4.60 (s, 2H), 4.49 (s, 2H), 2.35 (s, 3H), 1.82 (t, *J* = 13,8 Hz, 4H), 1.58 (s, 6H), 0.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.2, 137.7, 137.1, 134.7, 131.1, 130.0, 127.7, 109.4, 26.3, 25.5, 21.7, -5.0.

ESI-HRMS Calculated for [$C_{16}H_{24}Si + Na^+$] = 267.1539, found: 267.1544.

B6: (3-methoxyphenyl)(methyl)bis(2-methylallyl)silane



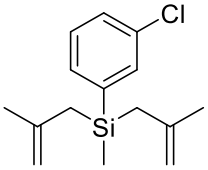
Colorless oil, 43% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 – 7.26 (m, 1H), 7.14 – 7.09 (m, 1H), 7.07 (d, *J* = 2.6 Hz, 1H), 6.91 – 6.88 (m, 1H), 4.63 – 4.56 (m, 2H), 4.54 – 4.44 (m, 2H), 3.81 (s, 3H), 1.82 (s, 4H), 1.58 (s, 6H), 0.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.9, 143.1, 139.5, 129.0, 126.4, 119.7, 114.3, 109.5, 55.2, 26.3, 25.5, -5.0.

ESI-HRMS Calculated for [$C_{16}H_{24}OSi + Na^+$] = 283.1489, found: 283.1489.

B7: (3-chlorophenyl)(methyl)bis(2-methylallyl)silane



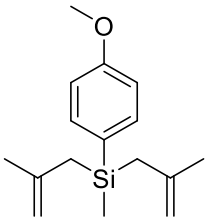
Colorless oil, 42% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (s, 1H), 7.39 (dt, *J* = 7.0, 1.1 Hz, 1H), 7.40 – 7.38 (m, 1H), 7.29 (d, *J* = 7.3 Hz, 1H), 4.65 – 4.56 (m, 2H), 4.52 – 4.44 (m, 2H), 1.82 (s, 4H), 1.58 (s, 6H), 0.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 142.6, 140.6, 134.2, 133.8, 132.1, 129.3, 129.3, 109.9, 26.1, 25.5, -5.1.

ESI-HRMS Calculated for [$C_{15}H_{21}ClSi + NH_4^+$] = 282.1439, 284.1410, found: 282.1437, 284.1409.

B9: (4-methoxyphenyl)(methyl)bis(2-methylallyl)silane



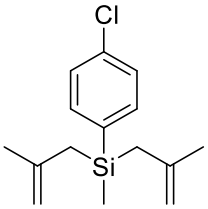
Colorless oil, 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 – 7.37 (m, 2H), 6.97 – 6.81 (m, 2H), 4.59 (dq, *J* = 2.7, 1.3 Hz, 2H), 4.52 – 4.43 (m, 2H), 3.81 (s, 3H), 1.82 – 1.78 (m, 4H), 1.59 – 1.55 (m, 6H), 0.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.6, 143.3, 135.5, 128.5, 113.6, 109.3, 55.1, 26.5, 25.5, -4.9.

ESI-HRMS Calculated for [$C_{16}H_{24}OSi$ +Na^+] = 283.1489, found: 283.1490.

B10: (4-chlorophenyl)(methyl)bis(2-methylallyl)silane



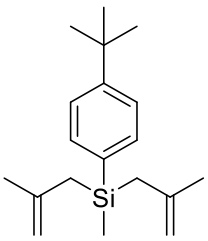
Colorless oil, 35% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 – 7.41 (m, 3H), 7.34 – 7.32 (m, 2H), 4.60 (s, 2H), 4.47 (s, 2H), 1.81 (s, 4H), 1.57 (s, 6H), 0.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 142.6, 135.8, 135.3, 128.2, 128.0, 109.6, 26.1, 25.4, -5.2.

ESI-HRMS Calculated for [$C_{15}H_{21}ClSi$+NH_4^+] = 282.1439, 284.1410, found: 282.1437, 284.1417.

B12: (4-(tert-butyl)phenyl)(methyl)bis(2-methylallyl)silane



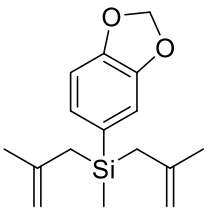
Colorless oil, 33% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 4.65 – 4.56 (m, 2H), 4.50 (s, 2H), 1.82 (d, *J* = 2.9 Hz, 4H), 1.59 (s, 6H), 1.31 (s, 9H), 0.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.2, 143.3, 134.2, 133.9,124.8, 109.4, 34.8, 31.4, 26.3, 25.5, -4.9.

ESI-HRMS Calculated for [$C_{19}H_{30}Si$+Na^+] = 309.2009, found: 309.2012.

B13: benzo[d][1,3]dioxol-5-yl(methyl)bis(2-methylallyl)silane



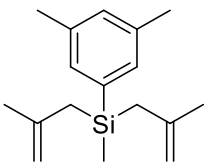
Colorless oil, 61% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.06 – 6.92 (m, 2H), 6.84 (d, *J* =7.6 Hz, 1H), 5.94 (s, 2H), 4.66 – 4.56 (m, 2H), 4.52 – 4.43 (m, 2H), 1.79 (s, 4H), 1.58 (s, 6H), 0.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 148.6, 147.4, 143.1, 130.7,128.3, 113.4, 109.5, 108.6, 100.7, 26.5, 25.5, -4.8.

ESI-HRMS Calculated for [$C_{16}H_{22}O_2Si$+Na^+] = 297.1281, found: 297.1283.

B14: (3,5-dimethylphenyl)(methyl)bis(2-methylallyl)silane



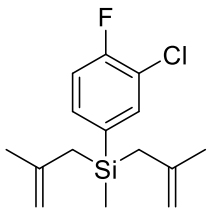
Colorless oil, 26% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.12 (s, 2H), 6.99 (s, 1H), 4.60 (dd, *J* = 2.2, 1.4 Hz, 2H), 4.51 – 4.45 (m, 2H), 2.31 (s, 6H), 1.85 – 1.77 (m, 4H), 1.59 (s, 6H), 0.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.4, 137.6, 137.0, 131.8, 131.0, 109.3, 26.3,25.5, 21.5, -5.0.

ESI-HRMS Calculated for [$C_{17}H_{26}Si+Na^+$] = 281.1696, found: 281.1703.

B15: (3-chloro-4-fluorophenyl)(methyl)bis(2-methylallyl)silane



Colorless oil, 39% yield.

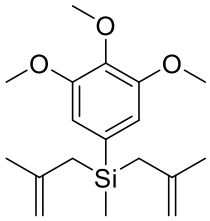
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51 (dd, J = 7.8, 1.4 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.16 – 7.07 (m, 1H), 4.62 (s, 2H), 4.47 (s, 2H), 1.81 (s, 4H), 1.58 (s, 6H), 0.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.0(d, J_{C-F} = 251.2 Hz), 142.4, 136.2, 135.3, 134.0 (d, J_{C-F} = 6.7 Hz), 121.0 (d, J_{C-F} = 16.5 Hz), 116.4 (d, J_{C-F} = 19.7 Hz), 110.0, 26.2, 25.5, -4.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -114.4.

ESI-HRMS Calculated for [$C_{15}H_{20}ClFSi+H^+$] = 283.1080, 285.1050, found: 283.1079, 285.1053.

B16: methylbis(2-methylallyl)(3,4,5-trimethoxyphenyl)silane



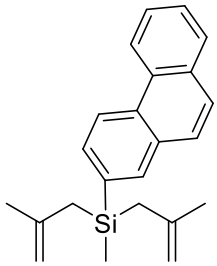
Colorless oil, 27% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.73 (s, 2H), 4.69 – 4.59 (m, 2H), 4.53 (s, 2H), 3.87 (d, J = 2.1 Hz, 9H), 1.83 (s, 4H), 1.61 (s, 6H), 0.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 153.0, 143.2, 139.3, 132.8, 110.9, 109.6, 61.0, 56.3, 26.4, 25.6, -4.6.

ESI-HRMS Calculated for [$C_{18}H_{28}O_3Si+Na^+$] = 343.1700, found: 343.1704.

B17: methylbis(2-methylallyl)(phenanthren-1-yl)silane



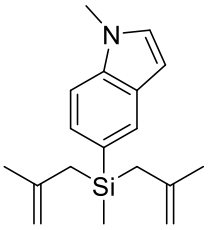
White solid, 54% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.89 (s, 1H), 8.73 (d, J = 8.3 Hz, 1H), 7.90 – 7.85 (m, 2H), 7.77 – 7.71 (m, 3H), 7.70 – 7.64 (m, 1H), 7.64 – 7.55 (m, 1H), 4.66 – 4.61 (m, 2H), 4.55 (s, 2H), 1.97 (t, J = 14.2 Hz, 4H), 1.59 (s, 6H), 0.53 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.2, 136.0, 132.6, 132.3, 131.6, 130.4, 129.5, 128.9, 128.8, 127.7, 127.6, 127.0, 126.8, 126.7, 122.6, 109.7, 26.6, 25.6, -4.7.

ESI-HRMS Calculated for [$C_{23}H_{26}Si+H^+$] = 331.1877, found: 331.1880.

B18: 1-methyl-5-(methylbis(2-methylallyl)silyl)-1H-indole



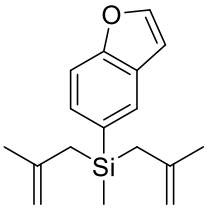
Colorless oil, 37% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81 (s, 1H), 7.42 – 7.30 (m, 2H), 7.03 (d, *J* = 3.1 Hz, 1H), 6.55 – 6.36 (m, 1H), 4.58 (dd, *J* = 2.4, 1.4 Hz, 2H), 4.50 (s, 2H), 3.79 (s, 3H), 1.87 (d, *J* = 0.8 Hz, 4H), 1.57 (s, 6H), 0.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.7, 137.5, 128.8, 128.5, 127.4, 126.9, 126.5, 109.1, 108.9, 101.2, 32.9, 26.9, 25.6, -4.7.

ESI-HRMS Calculated for [$C_{18}H_{25}NSi+Na^+$] = 306.1648, found: 306.1646.

B19: benzofuran-5-yl(methyl)bis(2-methylallyl)silane



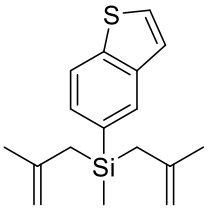
Colorless oil, 30% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 (s, 1H), 7.61 (d, *J* = 2.2 Hz, 1H), 7.55 – 7.41 (m, 2H), 6.77 – 6.76 (m, 1H), 4.59 (dd, *J* = 2.2, 1.4 Hz, 2H), 4.51 – 4.46 (m, 2H), 1.90 – 1.83 (m, 4H), 1.56 (s, 6H), 0.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.9, 144.9, 143.2, 131.3, 130.0, 127.4, 127.3, 111.1, 109.4, 106.6, 26.7, 25.5, -4.7.

ESI-HRMS Calculated for [$C_{17}H_{22}OSi+Na^+$] = 293.1332, found: 293.1332.

B20: benzo[b]thiophen-5-yl(methyl)bis(2-methylallyl)silane



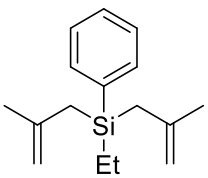
Colorless oil, 31% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.42 (d, *J* = 5.4 Hz, 1H), 7.34 (d, *J* = 5.4 Hz, 1H), 4.63 – 4.57 (m, 2H), 4.50 (s, 2H), 1.88 (s, 4H), 1.57 (s, 6H), 0.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.1, 140.8, 139.3, 133.0, 129.7, 129.4, 126.1, 124.1, 122.0, 109.5, 26.5, 25.6, -4.85.

ESI-HRMS Calculated for [$C_{17}H_{22}SSi+Na^+$] = 309.1104, found: 309.1104.

B23: ethylbis(2-methylallyl)(phenyl)silane



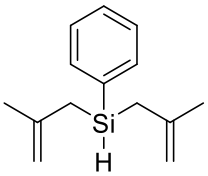
Colorless oil, 63% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56 – 7.48 (m, 2H), 7.39 – 7.30 (m, 3H), 4.64 – 4.58 (m, 2H), 4.53 (s, 2H), 1.86 (s, 4H), 1.58 (s, 6H), 1.03 (t, *J* = 7.5 Hz, 3H), 0.97 – 0.90 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.2, 136.9, 134.4, 129.2, 127.8, 109.7, 25.6, 24.2, 7.5, 3.9.

ESI-HRMS Calculated for [$C_{16}H_{24}Si+Na^+$] = 267.1539, found: 267.1547.

B24: bis(2-methylallyl)(phenyl)silane



Colorless oil, 50% yield.

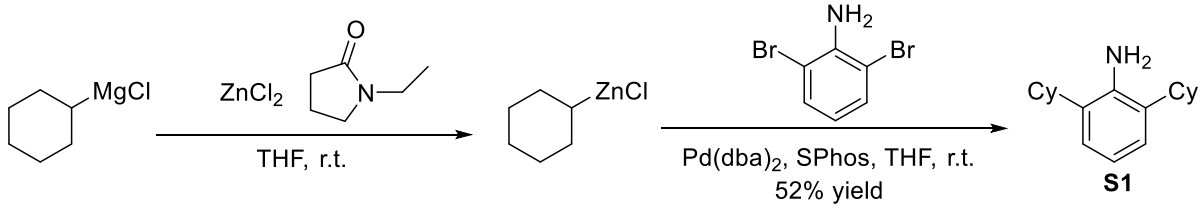
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59 – 7.50 (m, 2H), 7.43 – 7.30 (m, 3H), 4.65 – 4.59 (m, 2H), 4.58 – 4.52 (m, 2H), 4.40 (p, *J* = 3.6 Hz, 1H), 1.92 – 1.83 (m, 4H), 1.68 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 142.8, 135.0, 134.9, 129.7, 128.0, 110.0, 24.9, 23.9.

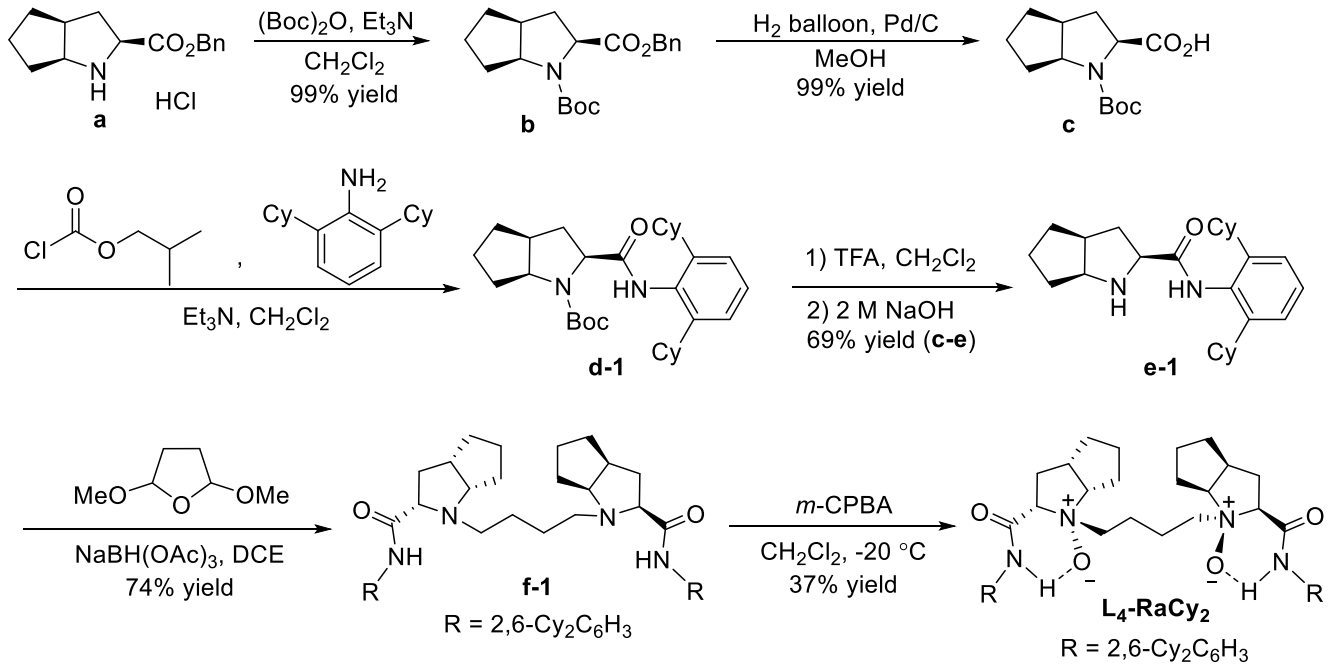
ESI-HRMS Calculated for [$C_{14}H_{20}Si+Na^+$] = 239.1226, found: 239.1227.

3. General procedure for the synthesis of the chiral *N,N'*-dioxide ligands[4-7].

(a) synthesis of 2,6-dicyclohexylaniline



(b) synthesis of *N,N'*-dioxide ligand **L_4-RaCy$_2$**



2,6-dicyclohexylaniline (S1)

Cyclohexylmagnesium chloride (30.8 mL, 40 mmol, 4.0 equiv., 1.3 M in THF) was added dropwise to a 250 mL round bottom flask charged with anhydrouszinc chloride (8.19 g, 60 mmol, 6.0 equiv.) and *N*-ethylpyrrolidinone (6.6 mL) dissolved in THF (30 mL) under Ar over 5 min. The mixture was stirred for another 2 h. Meanwhile, an oven-dried 100 mL round bottom flask was charged with 2,6-dibromoaniline (2.51 g, 10 mmol, 1.0equiv.), $Pd(dba)_2$ (575 mg, 1.0 mmol, 0.1 equiv.) and SPhos (410 mg, 1.0 mmol, 0.1 equiv.), evacuated, and back-filled with Ar (×3). THF (20 mL) was added and the mixture was stirred for 20 min. Then, this solution was added to the solution of organozinc reagent dropwise over 15 min. The reaction was stirred for 14 h at room temperature, then quenched with saturated aqueous NH_4Cl. The mixture was transferred to a separatory funnel with EtOAc. After phase separation, the aqueous layer was extracted with EtOAc. The combined organics were washed with water, brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by silica gel chromatography (Petroleum/EtOAc = 100/1 and 50/1, v/v) to give the product (1.34 g) in approximate 52% yield as a white solid.

Chiral *N,N′*-dioxide ligand L_4-$RaCy_2$

To the solution of *L*-ramipril **a** (8.46 g, 30 mmol) in CH_2Cl_2 (50 mL) was added Et_3N (3.64 g, 36.0 mmol, 1.2 equiv.) at 0 °C (ice bath). After stirring for 30 min, $(Boc)_2O$ (7.86 g, 36.0 mmol, 1.2 equiv.) was added. The reaction mixture was stirred overnight at room temperature. Next, the mixture was washed with 1 M $KHSO_4$ solution, the combined organics were washed with saturated $NaHCO_3$ solution, brine, dried over anhydrous Na_2SO_4, filtered, concentrated in vacuo, and directly used for the next step (10.3 g, 99% yield).

To a 100 mL round bottom flask was added **b** (10.3 g, 30 mmol), 10% Pd/C (0.64 g) and a stir bar. The flask was sealed with a rubber plug, evaluated, charged with two H_2 balloon, and then methanol (40 mL) was added. The reaction mixture was stirred at room temperature and detected by TLC until the reaction was finished. Then, the reaction mixture was filtered, Pd/C was recycled and the filtrate was concentrated in vacuo, and directly used for the next step (7.58 g, 99% yield).

To the solution of **c** (5.10 g, 20 mmol, 1.0 equiv.) in CH_2Cl_2 (30 mL) was added Et_3N (2.23 g, 22 mmol, 1.1 equiv.) and isobutyl carbonochloridate (3.01 g, 22 mmol, 1.1 equiv.) at 0 °C (ice bath) under stirring. After 30 min, 2,6-dicyclohexylaniline **S1** (9.27 g, 36 mmol, 1.2 equiv.) was added. The reaction mixture was stirred at room temperature and detected by TLC. After 4 days, the mixture was washed with 1 M $KHSO_4$ solution, saturated $NaHCO_3$ solution and brine in succession, dried over anhydrousNa_2SO_4, filtered, concentrated in vacuo, and directly used for the next step.

TFA (20 mL) was added to the solution of crude amide **d-1** in CH_2Cl_2 (15 mL) at 0 °C (ice bath), the reaction was warmed to room temperature and stirred until the reaction was finished (30 min). Then, CH_2Cl_2 (20 mL) was added. The pH value of the mixture was brought into the range of 10–12 by the addition of 2 M NaOH solution. The aqueous phase was extracted with CH_2Cl_2. The combined organics were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated, the residue was subjected to flash column chromatography on silica gel and eluted with petroleum ether/EtOAc (9/1 and 4/1 and 2/1, v/v) to give the white solid **e-1** (5.48 g, 69% yield).

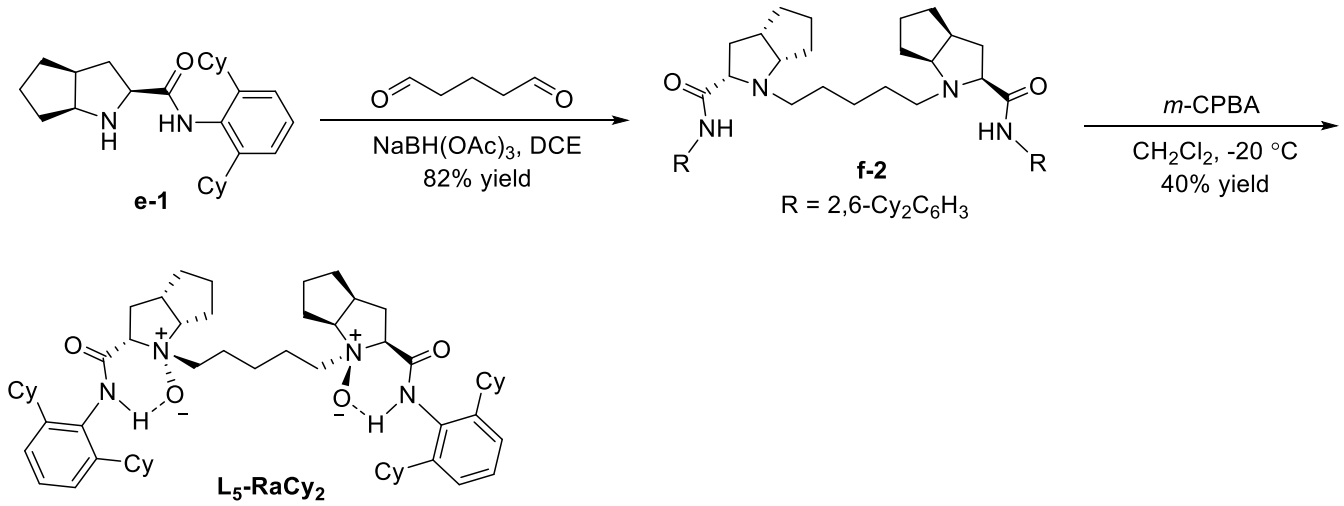
A round-bottom flask was charged with 2,5-dimethoxytetrahydrofuran (0.66 g, 5.0 mmol, 0.5 equiv.) and hydrochloric acid solution (1 M, 5 mL). The mixture was stirred at 60 °C for 45 min. Upon cooling to room temperature, the pH value of the mixture was brought into 7 by the addition of saturated $NaHCO_3$ aqueous solution. Then, a solution of **e-1** (3.94 g, 10.0 mmol, 1.0 equiv.) in DCE (5 mL) was added to the aqueous solution. After stirring for 30 min at room temperature, sodium triacetoxyborohydride (21.2 g, 100.0 mmol, 10.0 equiv.) was added at 0 °C. The reaction mixture was stirred overnight at room temperature. The solution was quenched with the addition of saturated $NaHCO_3$ aqueous solution. The

aqueous phase was extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated, the residue was subjected to flash column chromatography on silica gel and eluted with petroleum ether/EtOAc (9/1 to 2/1, v/v) to give the white solid **f-1**(3.12 g, 74% yield).

Finally, *m*-CPBA (1.35 g, 7.8 mmol, 2.1 equiv.) was added to the solution of compound **f-1** (3.12 g, 3.7 mmol, 1.0 equiv.) in CH_2Cl_2 (10 mL) at −20 °C, the resulting reaction mixture was stirred at−20 °C for 30 min. The solvent was removed in vacuo, and the residue was subjected to flash column chromatography on silica gel and eluted with petroleum ether/EtOAc (4/1 to 1/1, v/v) to provide the desired *N,N′*-dioxide ligand **L_4-RaCy$_2$** as a white solid (1.19 g, 37% yield).

($C_{56}H_{82}N_4O_4$) White solid; $[\alpha]^{25}_D$ = -47.8 (*c* = 0.46 g/100 mL, in CH_2Cl_2).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.65 (s, 2H), 7.26 – 7.19 (m, 2H), 7.13 (d, *J* = 7.6 Hz, 4H), 4.02 – 3.80 (m, 4H), 3.61 (t, *J* = 10.1 Hz, 2H), 3.44 – 3.24 (m, 2H), 2.86 – 2.76 (m, 2H), 2.74 – 2.53 (m, 8H), 2.46 (q, *J* = 12.2 Hz, 2H), 2.31 (d, *J* = 9.0 Hz, 2H), 2.05 (d, *J* = 6.2 Hz, 2H), 1.88 – 1.53 (m, 30H), 1.44 – 1.20 (m, 20H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.6, 131.5, 127.7, 124.0, 82.9, 79.8, 68.1, 53.6, 42.5, 39.8, 35.3 32.5, 27.8, 27.6, 26.8, 26.4, 22.1.
HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{56}H_{82}N_4O_4+Na^+]$ = 897.6228 found 897.6232.
IR (neat):3439, 2926, 2851, 1662, 1589, 1521, 1448, 795, 735, 650 and 549 cm^{-1}.

(c) synthesis of *N,N′*-dioxide ligand **L_5-RaCy$_2$**



Chiral *N,N′*-dioxide ligand L_5-RaCy$_2$

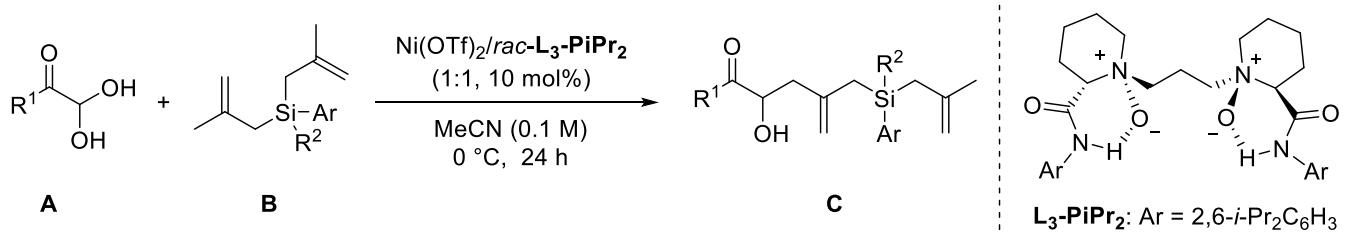
A round-bottom flask was charged with glutaraldehyde (0.40 g, 2.0 mmol, 0.5 equiv.) and DCE (5 mL). Then **e-1** (1.58 g, 4.0 mmol, 1.0 equiv.) was added to the mixture. After stirring for 30 min at room temperature, sodium triacetoxyborohydride (8.48 g, 40 mmol, 10.0 equiv.) was added at 0 °C. The reaction mixture was stirred overnight at room temperature. The solution was quenched with the addition of saturated $NaHCO_3$ aqueous solution. The aqueous phase was extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated, the residue was subjected to flash column chromatography on silica gel and eluted with petroleum ether/EtOAc (9/1 to 2/1, v/v) to give the white solid **f-2**(1.41 g, 82% yield).

Finally, *m*-CPBA (586 mg, 3.4 mmol, 2.1 equiv.) was added to the solution of compound **f-2** (1.41 g, 1.6 mmol, 1.0 equiv.) in CH_2Cl_2 (5 mL) at −20 °C, the resulting reaction mixture was stirred at−20 °C for 30 min. The solvent was removed in vacuo, and the residue was subjected to flash column

chromatography on silica gel and eluted with petroleum ether/EtOAc (4/1 to 1/1, v/v) to provide the desired *N,N'*-dioxide ligand **L_5-RaCy$_2$** as a white solid (583 mg, 40% yield).

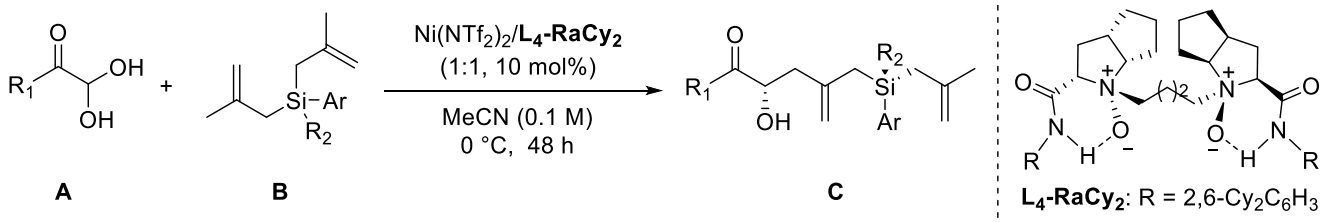
($C_{57}H_{84}N_4O_4$) White solid; $[\alpha]^{25}_D$ = -43.6 (*c* = 0.46 g/100 mL, in CH_2Cl_2).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.72 (s, 2H), 7.25 – 7.20 (m, 2H), 7.13 (m, 4H), 3.97 (m, 2H), 3.89 (m, 2H), 3.58 (td, *J* = 12.1, 3.9 Hz, 2H), 3.25 (td, *J* = 11.8, 4.9 Hz, 2H), 2.86 – 2.77 (m, 2H), 2.66 (m, 8H), 2.44 (m, 2H), 2.31 (m, 2H), 2.08 (m, 2H), 1.85 – 1.63 (m, 30H), 1.32 (m, 22H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.7, 131.6, 127.7, 124.0, 83.3, 80.0, 68.5, 42.5, 39.8, 35.3, 32.5, 27.8, 27.6, 27.4, 27.1, 26.4, 24.9, 24.5.
HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{57}H_{84}N_4O_4+Na^+]$ = 911.6385 found 911.6387.
IR (neat): 3441, 2925, 2851, 1663, 1589, 1522, 1448, 1314, 949, 790, 734, 649, 549 and 495 cm^{-1}.

4. General procedure for the preparation of the racemic products.



A dry reaction tube was charged with Ni(OTf)$_2$/*rac*-**L_3-PiPr$_2$** (1:1, 10 mol%,) and **A** (0.10 mmol). Under N_2 atmosphere, anhydrous MeCN (1.0 mL) was added and the solution was stirred at 35 ºC for 0.5 h. The mixture was cooled to 0 °C for 5 min. Then **B** (0.10 mmol) was added under stirring and the reaction mixture continued stirring at 0 °C for 24 h. The residue was concentrated under reduced pressure and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 7/1, v:v).

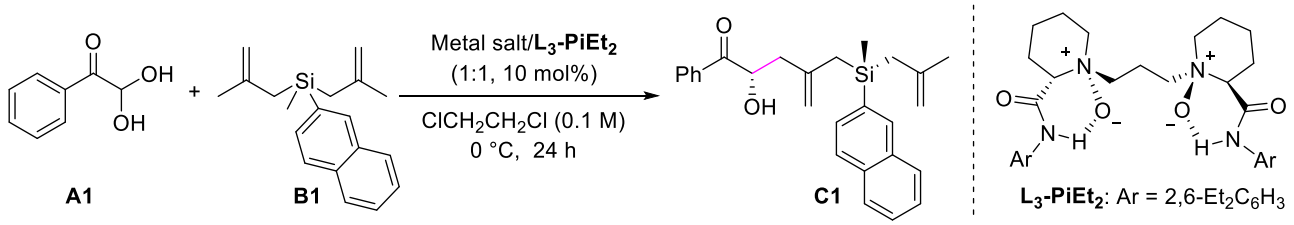
5. General experimental procedure for the catalytic asymmetric reaction.



A dry reaction tube was charged with Ni(NTf$_2$)$_2$/**L_4-RaCy$_2$** (1:1, 10 mol%) and **A** (0.10 mmol). Under N_2 atmosphere, anhydrous MeCN (1.0 mL) was added and the solution was stirred at 35 ºC for 0.5 h. The mixture was cooled to 0 °C for 5 min. Then **B** (0.20 mmol) was added under stirring and the reaction mixture continued stirring at 0 °C for 48 h. The residue was concentrated under reduced pressure and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 7/1, v:v).

6. Optimization of the reaction conditions.

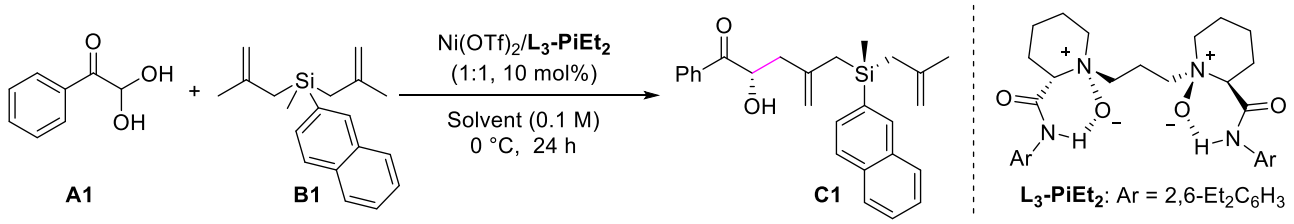
Table S1. The exploration of metal salts[a]



entry	Metal salt	yield (%)[b]	ee (%)[c]	dr[c]
1	$Mg(OTf)_2$	27	96/94	62:38
2	$Co(OTf)_2$	58	99/98	63:37
3	**$Ni(OTf)_2$**	**57**	**99/99**	**64:36**
4	$Cu(OTf)_2$	36	96/97	58:32
5	$Zn(OTf)_2$	68	96/94	63:37
6	$Sc(OTf)_3$	16	16/25	49:51
7	$La(OTf)_3$	36	-27/-6	54:46

[a]The reactions were performed with **A** (0.10 mmol), **B** (0.10 mmol), metal salt/**L_3-PiEt$_2$** (1:1, 10 mol%), in CH_2ClCH_2Cl (1.0 mL) under nitrogen at 0 °C for 24 h. [b]Yield of isolated product. [c]Determined by SFC with chiral chromatography column.

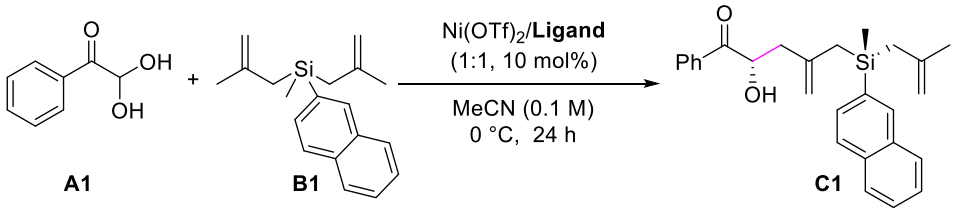
Table S2. The exploration of solvent[a]

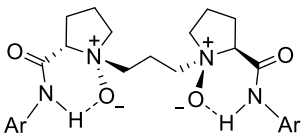


entry	solvent	yield (%)[b]	ee (%)[c]	dr[c]
1	THF	7	99/99	67:33
2	Et_2O	7	99/99	60:40
3	Toluene	trace	--	--
4	EtOAc	33	99/99	69:31
5	$ClCH_2CH_2Cl$	50	99/99	64:36
6	CH_2Cl_2	52	99/99	63:37
7	$CHCl_3$	47	99/99	61:39
8	MeOH	trace	--	--
9	**MeCN**	**47**	**99/99**	**72:28**

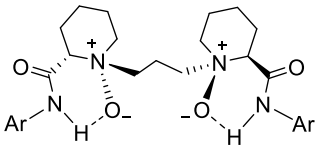
[a]The reactions were performed with **A** (0.10 mmol), **B** (0.10 mmol), $Ni(OTf)_2$/**L_3-PiEt$_2$** (1:1, 10 mol%), in solvent (1.0 mL) under nitrogen at 0 °C for 24 h. [b]Yield of isolated product. [c]Determined by SFC with chiral chromatography column.

Table S3. The exploration of ligand[a]

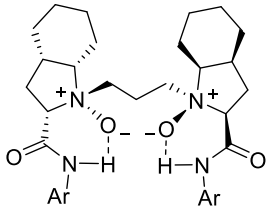




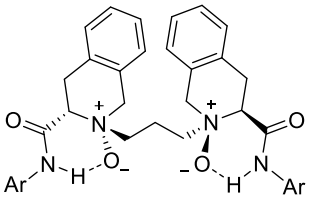
L_3-$PrEt_2$: Ar = 2,6-$Et_2C_6H_3$



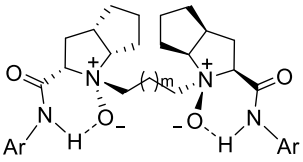
L_3-$PiEt_2$: Ar = 2,6-$Et_2C_6H_3$



L_3-$PeEt_2$: Ar = 2,6-$Et_2C_6H_3$



L_3-$TqEt_2$: Ar = 2,6-$Et_2C_6H_3$

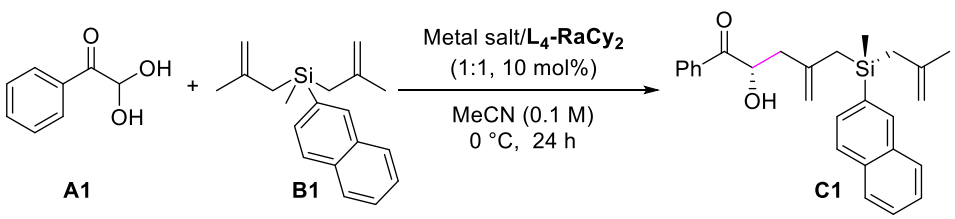


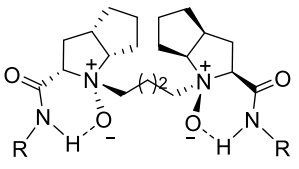
L_3-$RaEt_2$: Ar = 2,6-$Et_2C_6H_3$, m = 1
L_3-$RaMe_2$: Ar = 2,6-$Me_2C_6H_3$, m = 1
L_3-$RaPr_2$: Ar = 2,6-*i*-$Pr_2C_6H_3$, m = 1
L_3-$RaCy_2$: Ar = 2,6-$Cy_2C_6H_3$, m = 1
L_3-$RaPh_2$: Ar = 2,6-$Ph_2C_6H_3$, m = 1
L_3-$RaEt_3$: Ar = 2,4,6-$Et_3C_6H_2$, m = 1
L_4-$RaCy_2$: Ar = 2,6-$Cy_2C_6H_3$, m = 2
L_5-$RaCy_2$: Ar = 2,6-$Cy_2C_6H_3$, m = 3

entry	**ligand**	yield (%)[b]	ee (%)[c]	dr[c]
1	**L_3-$PrEt_2$**	37	99/99	69:31
2	**L_3-$PiEt_2$**	47	99/99	72:28
3	**L_3-$PeEt_2$**	38	84/74	69:31
4	**L_3-$TqEt_2$**	46	99/99	72:28
5	**L_3-$RaEt_2$**	46	99/99	75:25
6	**L_3-$RaMe_2$**	33	95/92	62:38
7	**L_3-$RaPr_2$**	43	97/89	82:18
8	**L_3-$RaCy_2$**	54	99/99	89:11
9	**L_3-$RaPh_2$**	47	99/99	88:12
10	**L_3-$RaEt_3$**	36	99/99	57:43
11	**L_4-$RaCy_2$**	**56**	**99/99**	**90:10**
12	**L_5-$RaCy_2$**	47	99/99	90:10

[a]The reactions were performed with **A** (0.10 mmol), **B** (0.10 mmol), Ni(OTf)2/**ligand** (1:1, 10 mol%), in MeCN (1.0 mL) under nitrogen at 0 °C for 24 h. [b]Yield of isolated product. [c]Determined by SFC with chiral chromatography column.

Table S4. The exploration of the counterions of metal salts[a]





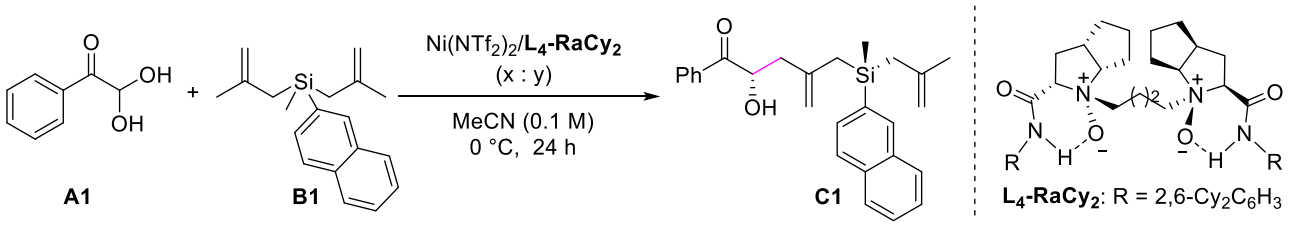
L_4-$RaCy_2$: R = 2,6-$Cy_2C_6H_3$

entry	Metal salt	yield (%)[b]	ee (%)[c]	dr[c]
1	$Ni(BF_4)_2{\cdot}6H_2O$	55	92/73	89:11
2	$Ni(ClO_4)_2{\cdot}6H_2O$	73	93/67	90:10
3	$Ni(acac)_2{\cdot}2H_2O$	trace	--	--
4	$Ni(OAc)_2{\cdot}4H_2O$	trace	--	--
5	**$Ni(NTf_2)_2$**	**67**	**99/99**	**90:10**
6	$Ni(OTf)_2$	56	99/99	90:10

7	NiF_2	trace	--	--
8	$NiCl_2$	60	99/99	89:11
9	$NiBr_2$	57	97/99	90:10

[a]The reactions were performed with **A** (0.10 mmol), **B** (0.10 mmol), Metal salt/**L_4-RaCy$_2$** (1:1, 10 mol%), in MeCN (1.0 mL) under nitrogen at 0 °C for 24 h. [b]Yield of isolated product. [c]Determined by HPLC with chiral chromatography column.

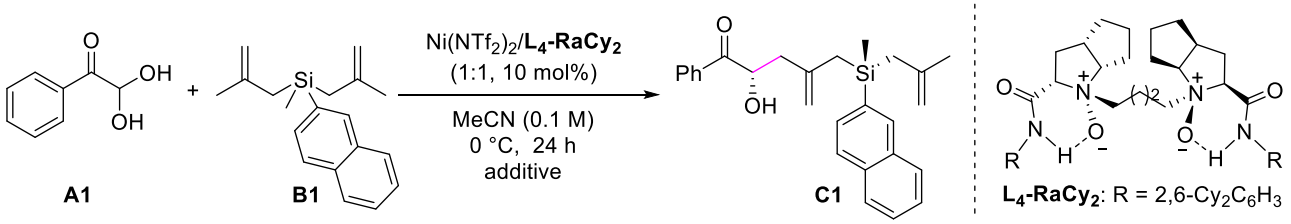
Table S5. The exploration of metal salt/ligand ratio[a]



entry	x : y	yield (%)[b]	ee (%)[c]	dr[c]
1	1.5:1	56	90/70	89:11
2	1.2:1	59	95/87	89:11
3	1.1:1	60	93/93	89:11
4	**1:1**	**67**	**99/99**	**90:10**
5	1:1.1	60	99/99	90:10
6	1:1.2	54	99/99	90:10
7	1:1.5	60	99/99	90:10

[a]The reactions were performed with **A** (0.10 mmol), **B** (0.10 mmol), Ni(NTf$_2$)$_2$/**L_4-RaCy$_2$** (x:y), in MeCN (1.0 mL) under nitrogen at 0 °C for 24 h. [b]Yield of isolated product. [c]Determined by SFC with chiral chromatography column.

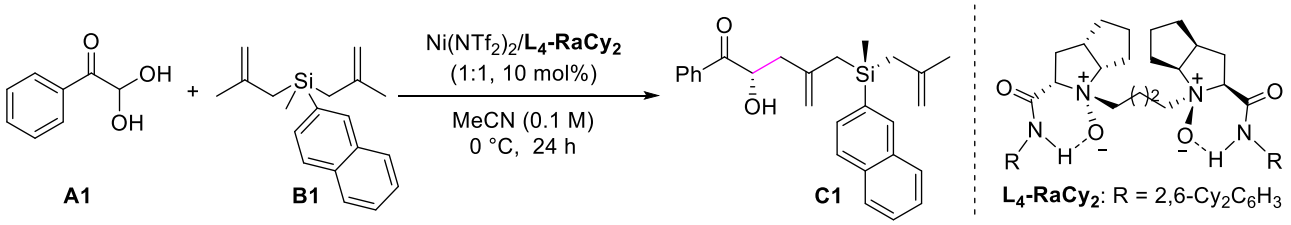
Table S6. The exploration of additive[a]



entry	Additive	yield (%)[b]	ee (%)[c]	dr[c]
1	3Å MS	64	99/99	89:11
2	4 Å MS	64	99/99	89:11
3	5 Å MS	67	99/99	89:11
4	$LiNTf_2$	67	99/99	90:10
5	$NaBAr^F{}_4$	67	99/99	90:10
6	PhCOOH	59	95/80	90:10
7	K_2CO_3	trace	--	--
8	H_2O	59	99/99	90:10
9	**--**	**67**	**99/99**	**90:10**

[a]The reactions were performed with **A** (0.10 mmol), **B** (0.10 mmol), Ni(NTf$_2$)$_2$/**L_4-RaCy$_2$** (1:1, 10 mol%), additive (molecular sieve 20 mg, other additive 20 mol%), in MeCN (1.0 mL) under nitrogen at 0 °C for 24 h. [b]Yield of isolated product. [c]Determined by SFC with chiral chromatography column.

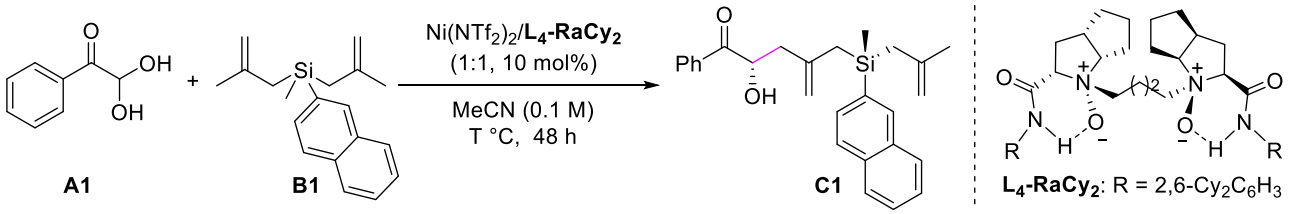
Table S7. The exploration of the ratio of A and B[a]



entry	A:B	yield (%)[b]	ee (%)[c]	dr[c]
1	2:1	67	99/99	93:7
2	1.5:1	68	99/99	92:8
3	1:1	67	99/99	90:10
4	1:1.5	68	99/99	90:10
5	1:2	76	99/99	90:10
6	1:3	76	99/99	90:10
7[d]	**1:2**	**81**	**99/99**	**90:10**
8 [d]	1:3	79	99/99	90:10

[a]The reactions were performed with **A** (x mmol), **B** (y mmol), Ni(NTf$_2$)$_2$/**L$_4$-RaCy$_2$** (1:1, 10 mol%), in MeCN (1.0 mL) under nitrogen at 0 °C for 24 h. [b]Yield of isolated product. [c]Determined by SFC with chiral chromatography column. [d]Performed at 0 °C for 48 h.

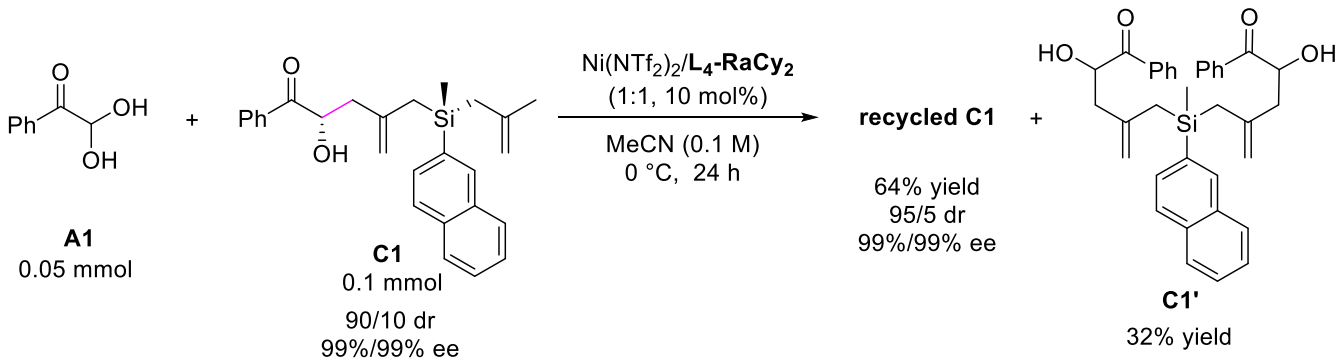
Table S8. The exploration of Temperature[a]



entry	T °C	yield (%)[b]	ee (%)[c]	dr[c]
1	-20	73	99/99	90:10
2	-10	75	99/99	90:10
3	**0**	**81**	**99/99**	**90:10**
4	10	80	99/99	87:13
5	20	91	99/99	86:14

[a]The reactions were performed with **A** (0.1 mmol), **B** (0.2 mmol), Ni(NTf$_2$)$_2$/**L$_4$-RaCy$_2$** (1:1, 10 mol%), in MeCN (1.0 mL) under nitrogen at T °C for 48 h. [b]Yield of isolated product. [c]Determined by SFC with chiral chromatography column.

Figure S1. Control experiment



A dry reaction tube was charged with Ni(NTf$_2$)$_2$/**L$_4$-RaCy$_2$** (1:1, 10 mol%) and **A1** (0.05 mmol). Under N_2 atmosphere, anhydrous MeCN (1.0 mL) was added and the solution was stirred at 35 ºC for 0.5 h. The mixture was cooled to 0 °C for 5 min. Then **C1** (0.10 mmol) was added under stirring and the

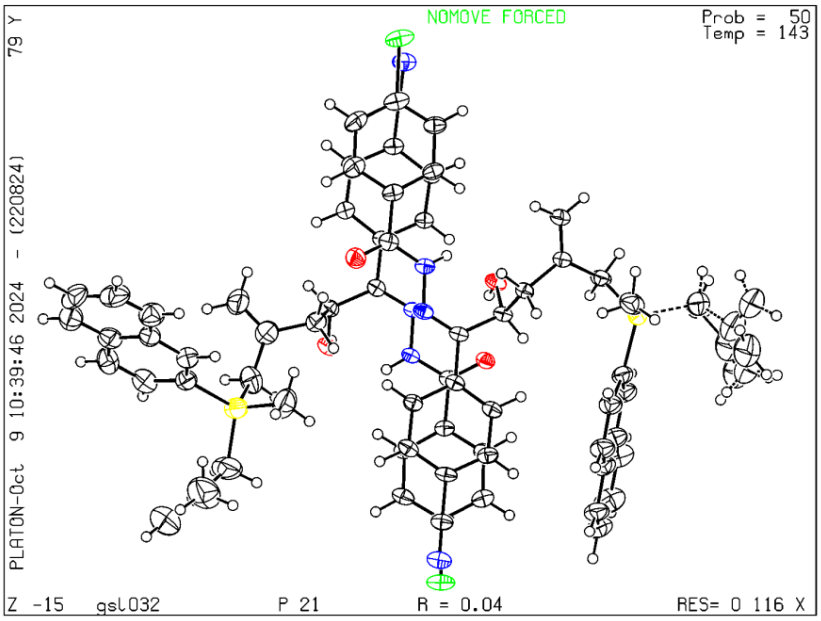
reaction mixture continued stirring at 0 °C for 24 h. The residue was concentrated under reduced pressure and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 7/1, v:v).

7. X-ray crystal data.

7.1 The X-Ray diffraction of compound G.

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **G** in THF and petroleum ether at rt. CCDC 2393874 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

The colourless crystal in rod-shape, with approximate dimensions of 0.140 × 0.142 × 0.652 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 143(2)K equipped with micro-focus Cu radiation source (K_α = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package[8-11]. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested[12].



Crystallographic Data for **G**.

Formula	$C_{70}H_{68}Br_2N_6O_4Si_2$
Formula mass (amu)	1273.30
Space group	$P2_1$ (*No*. 4)
a (Å)	7.1097(2)
b (Å)	31.4596(10)
c (Å)	14.5274(4)
α (deg)	90
β (deg)	97.891(1)
γ (deg)	90
V (Å^3)	3218.55(16)
Z	2

λ (Å)	1.54178
T (K)	143(2)
ρ_{calcd} (g cm^{-3})	1.314
μ (mm^{-1})	2.369
Transmission factors	0.374–0.869
θ_{max} (deg)	68.437
No. of unique data, including $F_o^2 < 0$	11760
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	11527
No. of variables	791
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0428
$R_w(F_o^2)$ [b]	0.1170
Goodness of fit	1.058
Flack Parameter	0.042(5)

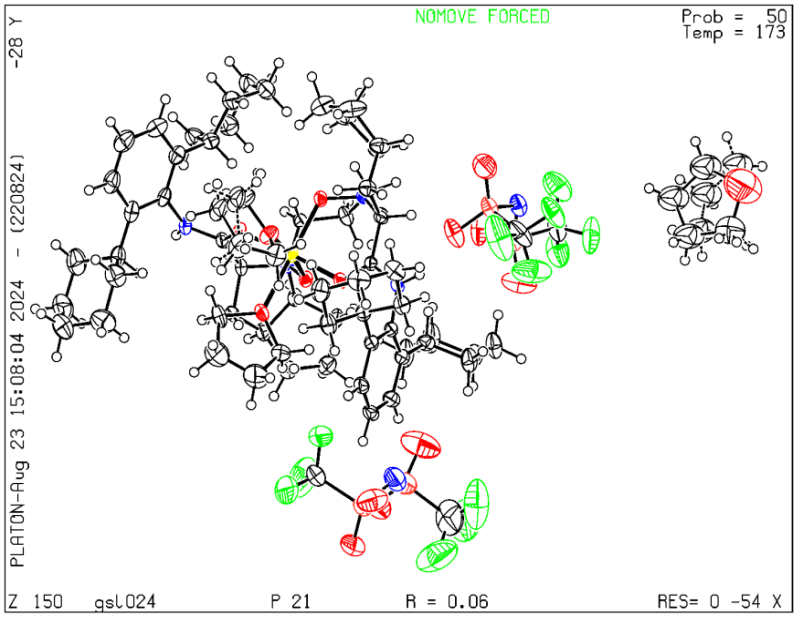
[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

7.2 The X-Ray diffraction of L$_4$-RaCy$_2$/Ni(NTf$_2$)$_2$ complex.

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of **L$_4$-RaCy$_2$**/Ni(NTf$_2$)$_2$ complex in THF and n-hexane at rt. CCDC 2418295 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre via.

The colourless crystal in rod-shape, with approximate dimensions of 0.128 × 0.243 × 0.862 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Cu radiation source (K_α = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package[8-11]. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested[12].



Crystallographic Data for **L_4-RaCy$_2$**/Ni(NTf$_2$)$_2$ complex.

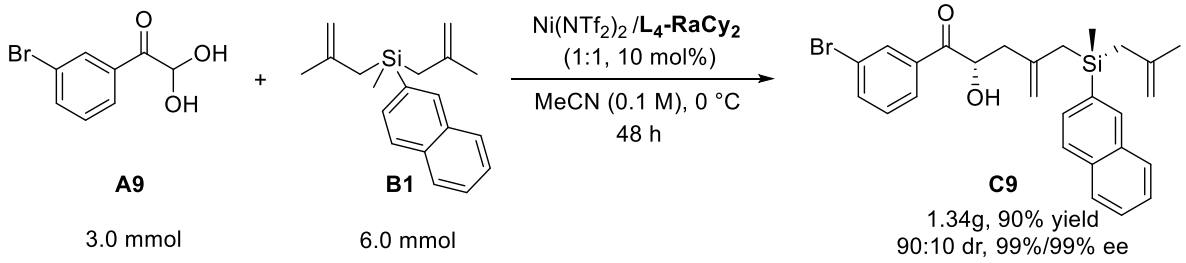
Formula	C72 H106 F12 N6 Ni O15 S4
Formula mass (amu)	1710.57
Space group	P 21
a (Å)	14.5272(5)
b (Å)	18.2708(6)
c (Å)	16.2000(5)
α (deg)	90
β (deg)	111.107(1)
γ (deg)	90
V (Å^3)	4011.4(2)
Z	2
λ (Å)	1.54178
T (K)	173 K
ρ_{calcd} (g cm^{-3})	1.416
μ (mm^{-1})	2.132
Transmission factors	0.544,1.000
θ_{max} (deg)	79.435
No. of unique data, including $F_o^2 < 0$	16319
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	15473
No. of variables	1001
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0611
$R_w(F_o^2)$ [b]	0.1737
Goodness of fit	1.029

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

8. Scale synthesis and transformation of products.

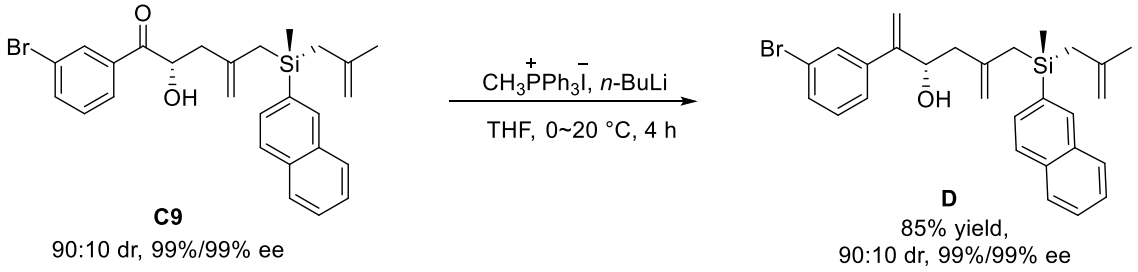
8.1 Experimental procedure for the gram-scale reaction.



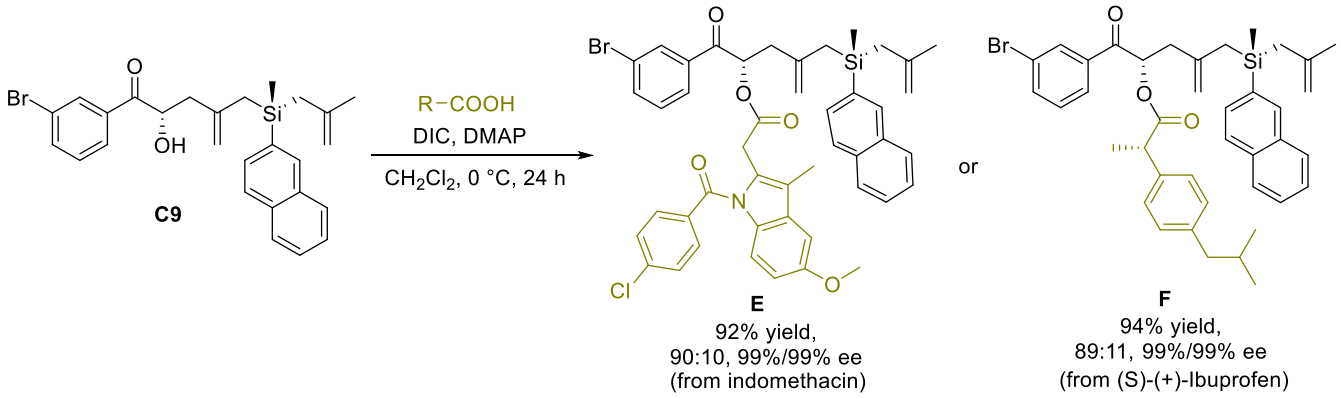
An oven-dried round-bottom flask was charged with **L_4-RaCy$_2$** (0.3 mmol, 10 mol%), Ni(NTf$_2$)$_2$ (0.3 mmol, 10 mol%) and **A9** (3.0 mmol), extract and replace nitrogen three times, and acetonitrile (30 mL) was added under nitrogen atmosphere. The mixture was cooled to 0 °C for 10 min after stirring at

35 °C for 120 min. Next, **B1** (6.0 mmol,) was added into the flask and the reaction mixture was stirred at 0 ºC for 48 h. Then the solvent was removed in vacuum, the residue was subjected to column chromatography (petroleum ether/ethyl acetate = 7:1, v:v) to afford the desired product.

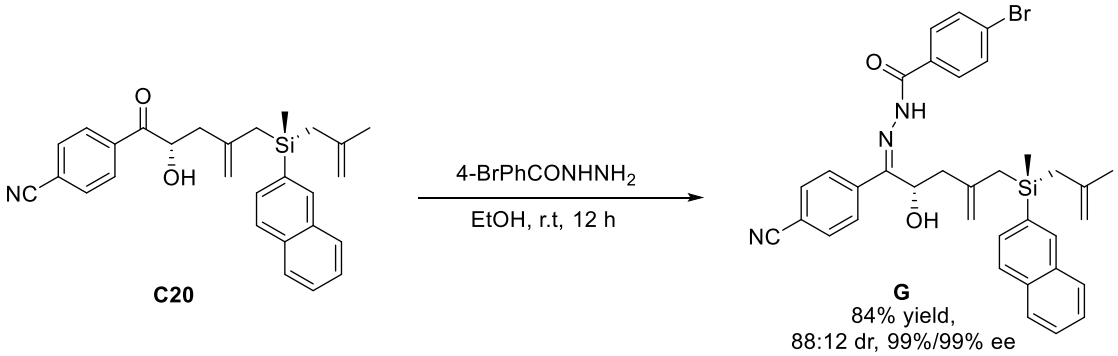
8.2 Experimental procedure for further transformation.



The reaction was carried out with methyltriphenylphosphonium iodide (404 mg, 1.0 mmol) in a dried tube under nitrogen atmosphere. After addition of THF (1.0 mL), the reaction was cooled to 0 °C. *n*-BuLi (333 uL, 0.8 mmol, 2.4 M in THF) was added dropwise to the solution at 0 °C, and the mixture was stirred for 30 min at the same temperature. A solution of **C9** (41.5 mg, 0.10 mmol) in THF (0.5 mL) was charged into the solution at 0 °C. The mixture warmed up to 20 °C and was stirred for 3.0 h. The resulting solution was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 9:1, v:v) to afford the desired product **D** (35.1 mg, 85% yield).



To a solution of **C9** (49.3 mg, 0.1 mmol) and carboxylic acid-based drug (0.12 mmol, 1.2 equiv) in CH_2Cl_2 (1.0 mL) were added DMAP (1.2 mg, 0.01 mmol) and DIC (15.1 mg, 0.12 mmol). The resulting suspension was stirred at 0 °C for 24 h. After adding H_2O, the reaction mixture was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, and concentrated under reduced pressure to give the residue, which was purified by flash column chromatography to afford the drug derivatives (**E**: 76.6 mg, 92% yield; **F**: 64.1 mg, 94% yield).



To an oven-dried reaction tube were added **C20** (45.9 mg, 0.10 mmol), 4-bromobenzhydrazide (36.2 mg, 0.20 mmol) and EtOH (2.0 mL). After the resulting suspension was stirred at room temperature for 12 h, the reaction solvent was removed under the reduced pressure. The obtained residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1, v:v) to afford the desired product (53.4 mg, 84 % yield).

9. Biological activity studies

Cell culture.

Liver cancer cell line HCCLM3 was cultured in DMEM (Hyclone, Utah, USA) supplemented with 10% fetal bovine serum (FBS, Gibco, New York, USA). The cell was purchased from Procell and maintained in a humidified atmosphere with 5% CO_2 at 37 °C. To prevent potential contamination, 1% penicillin-streptomycin (Beyotime, Shanghai, China) was added to culture medium.

CCK-8 in cell assay.

HCCLM3 cells were kept in DMEM supplemented with 10% FBS in 96-well plates in triplicate at 5000 cells per well and treated for 24 h with DMSO or various concentrations of the test compound (0.39 – 50 μM) at 37 °C with 5% CO_2. Then cells were incubated for 1 – 4 h after adding 10% (v/v) CCK-8 reagent (Beyotime, Shanghai, China) to each well. These plates were put into a microplate detector (Thermo Fisher Scientific, USA) to measure their absorbance values at 450 nm. All IC_{50} values were calculated with GraphPad Prism 8.0 software. The IC50 values of **C35** and **C36** towards HCCLM3 were 23.23 μM and 11.69 μM (**Figure S2**.), respectively.

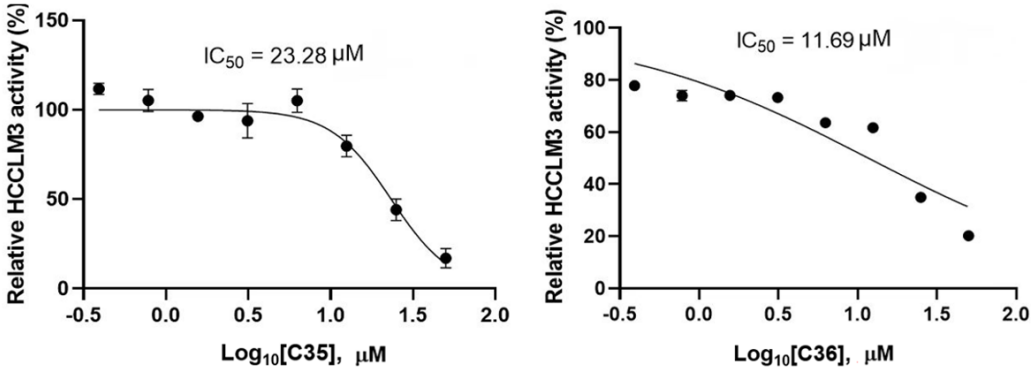


Figure S2. IC_{50} values of **C35** (left) and **C36** (right) towards HCCLM3.

10. Proposed transition states.

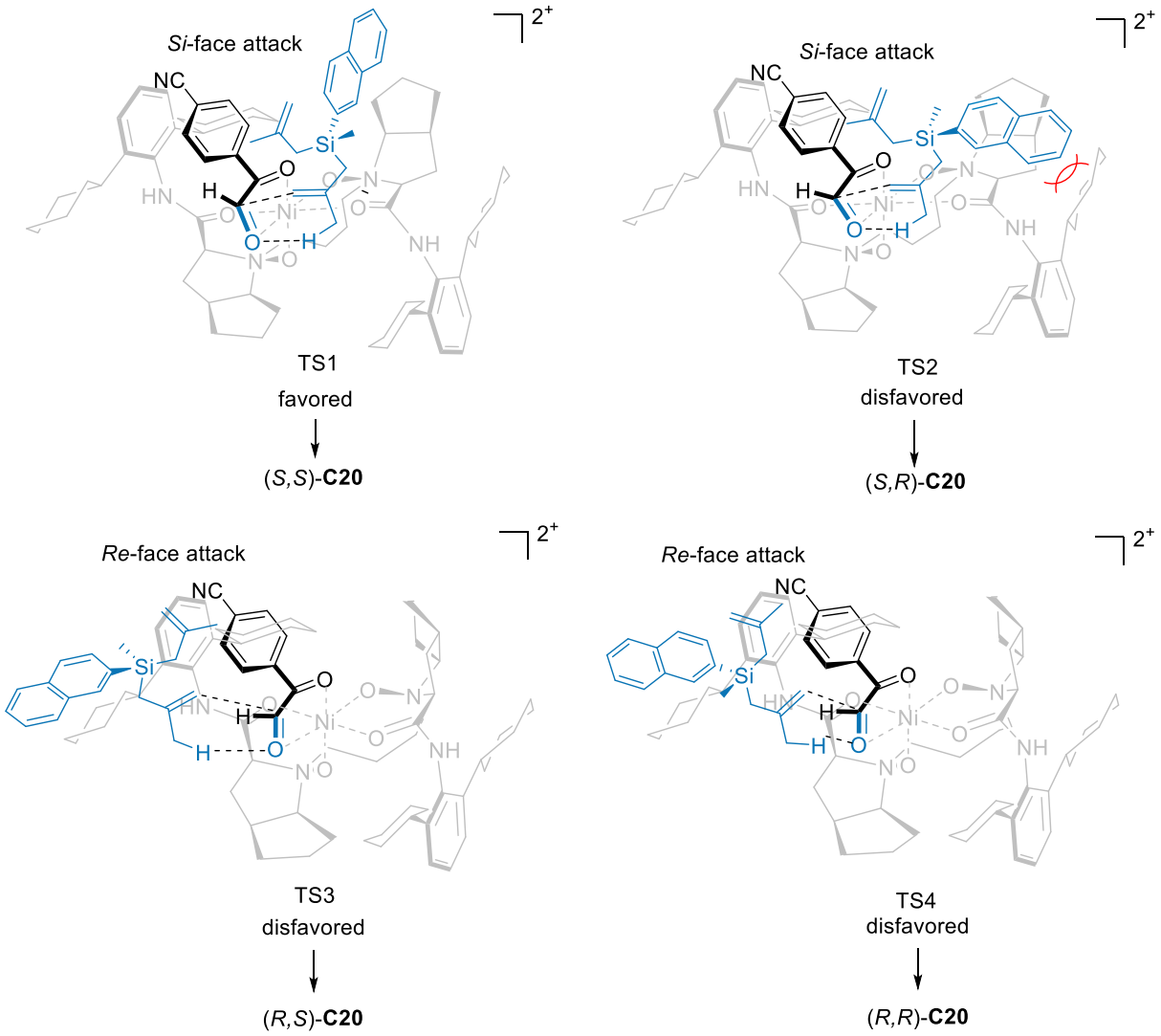
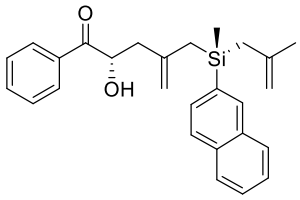


Figure S3. Proposed transition states.

11. Characterization of the products.

C1: (S)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)-1-phenylpent-4-en-1-one



($C_{27}H_{30}O_2Si$) Colorless oil; 33.6 mg, 81% yield, 99/99% ee, 90:10 dr; $[\alpha]_D^{25}$ = +27.7 (c = 0.26 g/100 mL, in CH_2Cl_2).

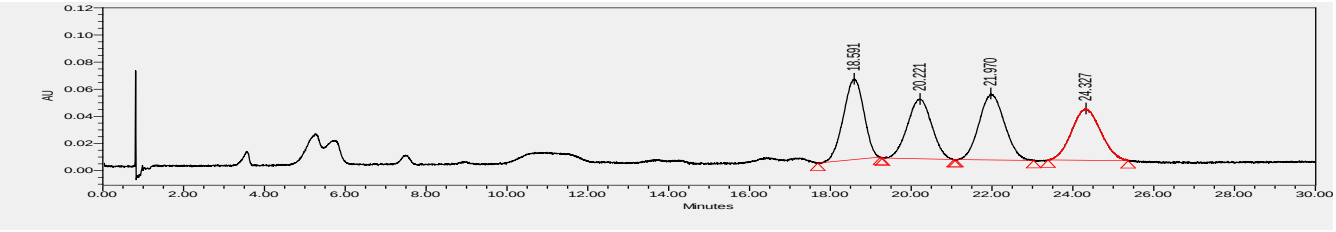
SFC (Daicel Chiralcel IF-3, CO_2/MeOH = 95/5, 1.5 mL/min, λ = 230 nm), t_1 = 19.58 min, t_2 = 21.33 min, t_3 =22.93 min, t_4 = 25.30 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 (s, 1H), 7.88 – 7.75 (m, 3H), 7.59 (t, J = 8.3 Hz, 3H), 7.52 – 7.45 (m, 3H), 7.20 (t, J = 7.7 Hz, 2H), 5.07 (ddd, J = 9.3, 6.6, 3.5 Hz, 1H), 4.72 (d, J = 9.8 Hz, 2H), 4.59 (s, 1H), 4.48 (s, 1H), 3.63 (d, J = 6.6 Hz, 1H), 2.31 (dd, J = 14.6, 3.1 Hz, 1H), 2.08 – 1.96 (m, 3H), 1.88 (s, 2H), 1.55 (s, 3H), 0.42 (s, 3H).

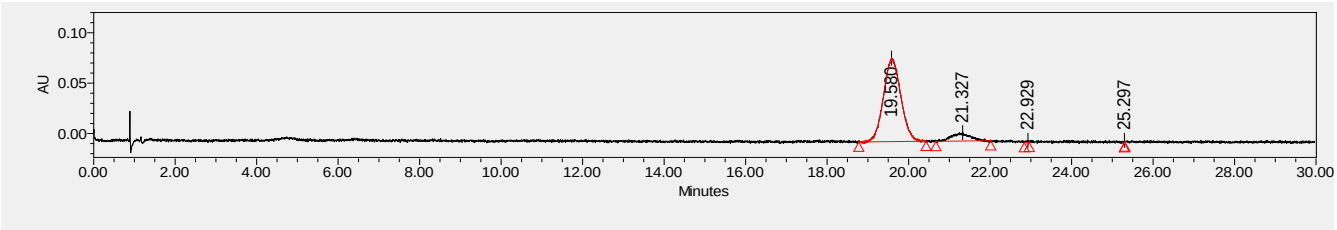
^{13}C NMR (101 MHz, $CDCl_3$) δ = 201.6, 142.8, 142.1, 135.0, 134.9, 133.9, 133.6, 133.0, 130.3, 128.8, 128.6, 128.3, 127.9, 127.2, 126.7, 126.2, 112.4, 109.8, 72.0, 44.2, 26.5, 25.5, 24.5, -5.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{28}H_{32}O_2Si + Na^+]$ = 437.1907 found 437.1908.

IR (neat): 3475, 3053, 2921, 1682, 1635, 1497, 1257, 1162, 1084, 974, 862, 813 and 743 cm^{-1}.

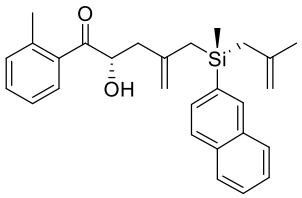


	Retention Time	Area	% Area
1	18.591	2095228	26.32
2	20.221	1845209	23.18
3	21.970	2126377	26.71
4	24.327	1895124	23.80



	Retention Time	Area	% Area
1	19.580	2434786	90.53
2	21.327	247610	9.21
3	22.929	6093	0.23
4	25.297	1085	0.04

C2: (S)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)-1-(o-tolyl)pent-4-en-1-one



($C_{28}H_{32}O_2Si$) Colorless oil; 37.9 mg, 84% yield, 99/99% ee, 87:13 dr; $[\alpha]^{19}_D$ = +43.3 (*c* = 0.36 g/100 mL, in CH_2Cl_2).

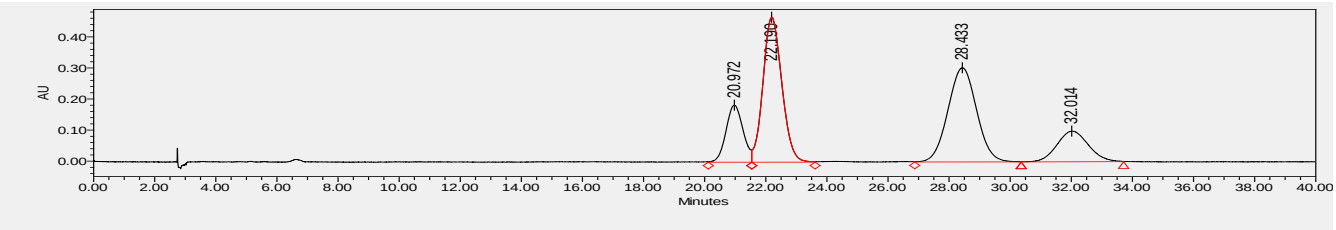
SFC (Daicel Chiralcel AYH, CO_2/EtOH = 90/10, 1.0 mL/min, λ = 230 nm), t_1 = 21.07 min, t_2 = 22.43 min, t_3 =28.94 min, t_4 = 32.18 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (s, 1H), 7.84 – 7.76 (m, 2H), 7.73 (d, J = 8.1 Hz, 1H), 7.50 (dd, J = 6.9, 3.0 Hz, 3H), 7.31 (t, J = 7.4 Hz, 1H), 7.19 (t, J = 6.5 Hz, 2H), 6.94 (t, J = 7.6 Hz, 1H), 4.99 (ddd, J = 9.0, 5.6, 3.4 Hz, 1H), 4.68 (d, J = 9.6 Hz, 2H), 4.57 (s, 1H), 4.47 (s, 1H), 3.70 (d, J = 5.8 Hz, 1H), 2.30 (d, J = 8.5 Hz, 3H), 2.11 (dd, J = 14.6, 2.6 Hz, 1H), 1.99 (d, *J* = 13.8 Hz, 1H), 1.94 (d, *J* = 9.6 Hz, 1H), 1.92 – 1.87 (m, 1H), 1.85 (d, J = 4.6 Hz, 2H), 1.54 (s, 3H), 0.36 (s, 3H).

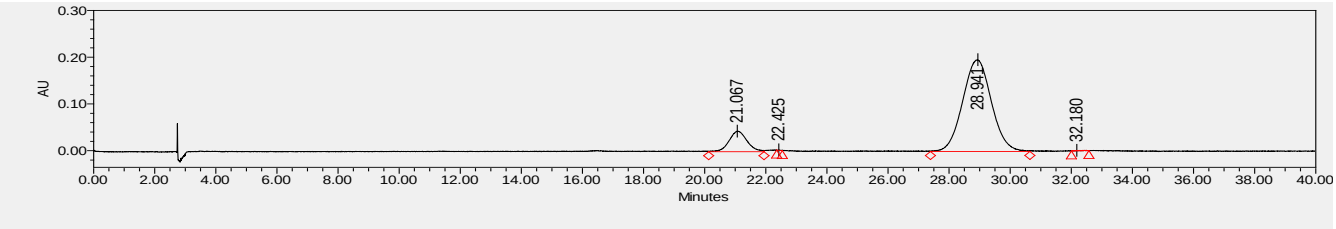
^{13}C NMR (101 MHz, $CDCl_3$) δ = 204.8, 142.8, 142.2, 139.1, 134.9, 134.8, 134.2, 133.9, 132.9, 132.2, 132.1, 130.2, 128.3, 128.2, 127.9, 127.1, 126.1, 125.8, 112.1, 109.7, 77.5, 73.3, 43.1, 26.3, 25.5, 24.5, 21.0, -5.4.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{28}H_{32}O_2Si + Na^+]$ = 451.2064 found 451.2059.

IR (neat): 3462, 3051, 2923, 1683, 1635, 1251, 1160, 1085, 971, 863, 813 and 741 cm^{-1}.

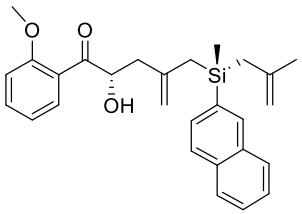


	Retention Time	Area	% Area
1	20.972	7098496	13.17
2	22.190	19977937	37.06
3	28.433	19744856	36.63
4	32.014	7082456	13.14



	Retention Time	Area	% Area
1	21.067	1788456	12.25
2	22.425	4044	0.03
3	28.941	12798808	87.65
4	32.180	10073	0.07

C3:(S)-2-hydroxy-1-(2-methoxyphenyl)-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-en-1-one



($C_{28}H_{32}O_3Si$) Colorless oil; 35.3 mg, 80% yield, 99/95% ee, 85:15 dr; $[\alpha]^{19}_D$ = -42.8 (*c* = 0.44 g/100 mL, in CH_2Cl_2).

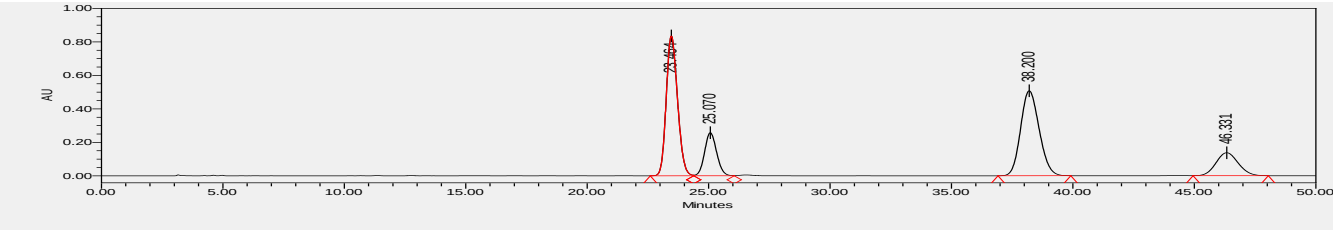
HPLC (Daicel chiralcel OXH, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 230 nm), t_1 = 23.56 min, t_2 = 25.13 min, t_3 =38.29 min, t_4 = 46.39 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93 (s, 1H), 7.78 (q, *J* = 4.8 Hz, 2H), 7.74 – 7.67 (m, 2H), 7.53 – 7.40 (m, 4H), 7.01 – 6.91 (m, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 5.20 (ddd, *J* = 8.8, 6.1, 3.2 Hz, 1H), 4.72 (q, *J* = 7.8, 6.4 Hz, 2H), 4.59 – 4.54 (m, 1H), 4.48 – 4.43 (m, 1H), 3.78 (d, *J* = 6.1 Hz, 1H), 3.70 (s, 3H), 2.29 (dd, *J* = 14.5, 2.6 Hz, 1H), 2.00 – 1.94 (m, 2H), 1.90 (dd, *J* = 14.4, 8.9 Hz, 1H), 1.87 – 1.82 (m, 2H), 1.53 (s, 3H), 0.38 (s, 3H).

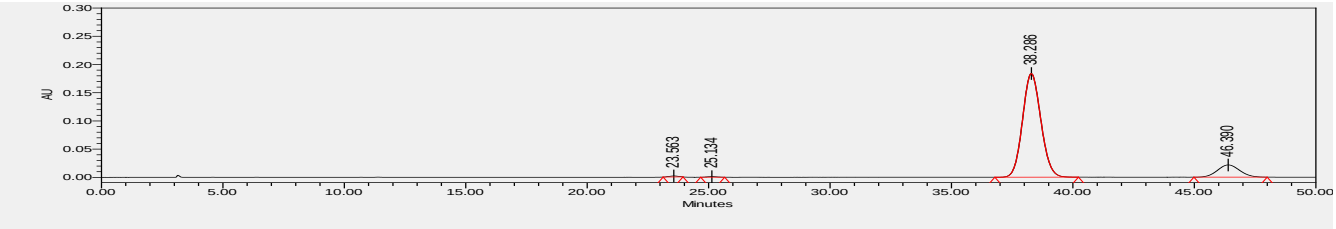
^{13}C NMR (101 MHz, $CDCl_3$) δ = 203.1, 158.5, 142.9, 142.6, 135.1, 134.8, 134.7, 133.8, 132.9, 131.3, 130.3, 128.2, 127.8, 126.9, 126.5, 126.0, 124.4, 121.1, 111.6, 111.6, 109.6, 75.8, 55.6, 43.1, 26.2, 25.5, 24.5, -5.1.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{28}H_{32}O_3Si + Na^+]$ = 467.2013 found 467.2015.

IR (neat): 3473, 3073, 2917, 1663, 1597, 1486, 1291, 1247, 1162, 1085, 1021, 976, 859, 814 and 753 cm^{-1}.

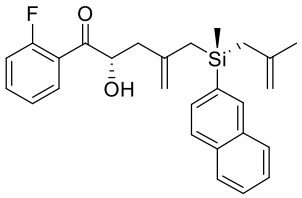


	Retention Time	Area	% Area
1	23.464	26975058	37.69
2	25.070	8894152	12.43
3	38.200	26968970	37.68
4	46.331	8737866	12.21



	Retention Time	Area	% Area
1	23.563	47763	0.43
2	25.134	29401	0.26
3	38.286	9648655	86.91
4	46.390	1376407	12.40

C4: (S)-1-(2-fluorophenyl)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-en-1-one



($C_{27}H_{29}FO_2Si$) Colorless oil; 36.5 mg, 84% yield, 99/93% ee, 89:11 dr (determined by SFC); $[\alpha]_D^{19}$ = +4.9 (*c* = 0.43 g/100 mL, in CH_2Cl_2).

SFC (Daicel Chiralcel IG-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 230 nm), t_1 = 8.27 min, t_2 = 8.98 min, t_3 = 9.64 min, t_4 = 10.40 min.

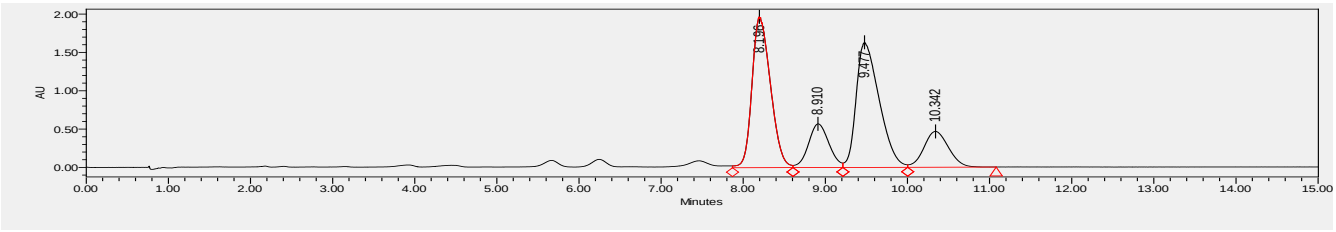
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 (d, *J* = 6.8 Hz, 1H), 7.83 – 7.68 (m, 4H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.51 – 7.43 (m, 3H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.95 (dd, *J* = 11.1, 8.4 Hz, 1H), 5.04 (ddt, *J* = 8.7, 5.7, 2.5 Hz, 1H), 4.72 (s, 2H), 4.58 (s, 1H), 4.49 (s, 1H), 3.61 (d, *J* = 6.3 Hz, 1H), 2.26 (d, *J* = 14.4 Hz, 1H), 2.05 – 1.96 (m, 2H), 1.93 (d, *J* = 3.7 Hz, 1H), 1.90 (d, *J* = 4.4 Hz, 2H), 1.56 (s, 3H), 0.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.1 (d, $J_{C\text{-}F}$ = 4.3 Hz)., 161.4 (d, $J_{C\text{-}F}$ = 255.1 Hz)., 142.9, 141.9, 135.5 (d, $J_{C\text{-}F}$ = 9.3 Hz)., 134.9, 134.9, 133.8, 132.9, 131.1 (d, $J_{C\text{-}F}$ = 2.6 Hz)., 130.3, 128.3, 127.8, 127.0, 126.5, 126.0, 124.9 (d, $J_{C\text{-}F}$ = 3.3 Hz)., 122.5 (d, $J_{C\text{-}F}$ = 13.0 Hz)., 116.7 (d, $J_{C\text{-}F}$ = 23.4 Hz)., 112.4, 109.7, 75.4 (d, $J_{C\text{-}F}$ = 9.0 Hz)., 43.2, 26.1, 25.5, 24.3, -5.2.

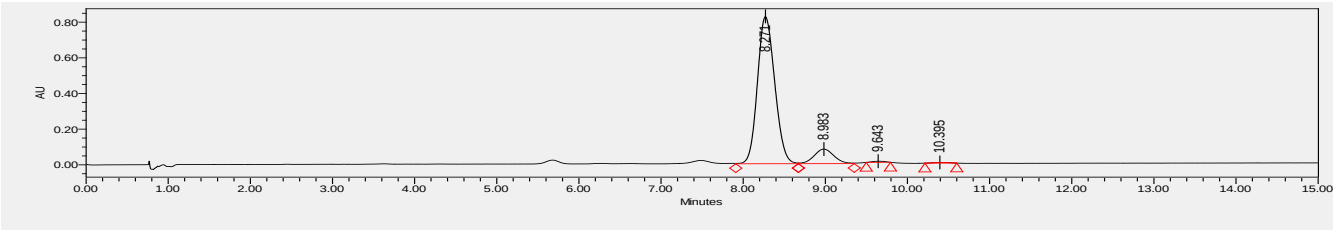
^{19}F NMR (376 MHz, Chloroform-*d*) δ = -108.2.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{27}H_{29}FO_2Si + Na^+]$ = 455.1813 found 455.1808.

IR (neat): 3483, 3050, 2919, 1681, 1610, 1483, 1452, 1281, 1247, 1159, 1086, 976, 865, 813 and 769 cm^{-1}.

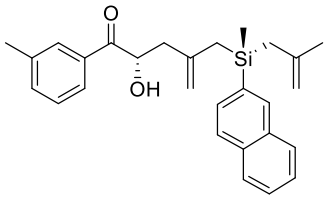


	Retention Time	Area	% Area
1	8.196	30676128	37.45
2	8.910	9843380	12.02
3	9.477	31658755	38.65
4	10.342	9736056	11.89



	Retention Time	Area	% Area
1	8.271	12047112	89.06
2	8.983	1363456	10.08
3	9.643	69821	0.52
4	10.395	46563	0.34

C5: (S)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)-1-(m-tolyl)pent-4-en-1-one



($C_{28}H_{32}O_2Si$) Colorless oil; 37.5 mg, 87% yield, 99/99% ee, 88:12 dr; $[\alpha]^{18}_D$ = +10.5 (*c* = 0.54 g/100 mL, in CH_2Cl_2).

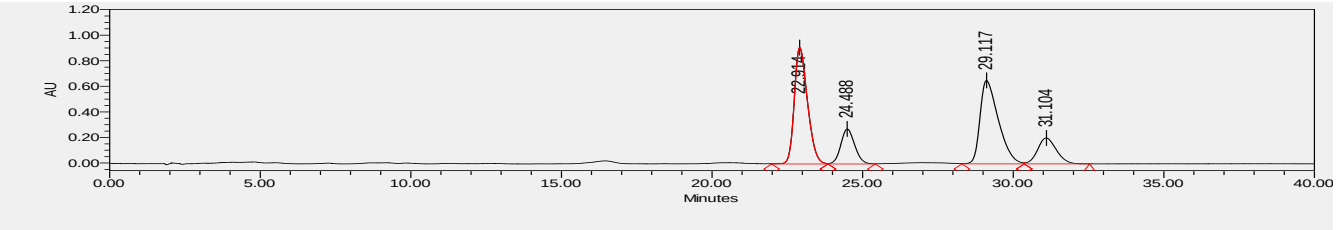
SFC (Daicel Chiralcel IG, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 230 nm), t_1 = 22.93 min, t_2 = 24.63 min, t_3 = 29.13 min, t_4 = 31.24 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 (s, 1H), 7.83 – 7.74 (m, 3H), 7.63 (s, 1H), 7.56 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.06 (t, *J* = 7.7 Hz, 1H), 5.09 (ddd, *J* = 8.7, 6.6, 3.4 Hz, 1H), 4.72 (d, *J* = 3.3 Hz, 2H), 4.60 – 4.57 (m, 1H), 4.50 – 4.46 (m, 1H), 3.64 (dd, *J* = 6.6, 2.3 Hz, 1H), 2.35 (s, 3H), 2.31 (d, *J* = 3.0 Hz, 1H), 2.06 – 2.02 (m, 1H), 1.99 (d, *J* = 4.0 Hz, 1H), 1.99 – 1.93 (m, 1H),, 1.87 (s, 2H), 1.55 (s, 3H), 0.41 (s, 3H).

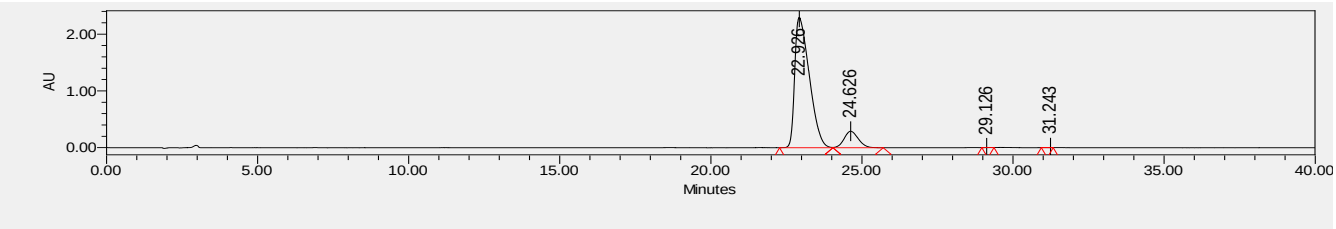
^{13}C NMR (101 MHz, $CDCl_3$) δ = 201.8, 142.8, 142.2, 138.8, 134.9, 134.9, 134.8, 133.9, 133.7, 133.0, 130.2, 129.1, 128.7, 128.3, 127.9, 127.1, 126.6, 126.1, 125.7, 112.3, 109.7, 72.1, 44.3, 26.3, 25.5, 24.6, 21.4, -2.8.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{28}H_{32}O_2Si + Na^+]$ = 451.2064 found 451.2065.

IR (neat): 3471, 3050, 2919, 1680, 1635, 1406, 1275, 1164, 1085, 859, 814 and 745 cm^{-1}.

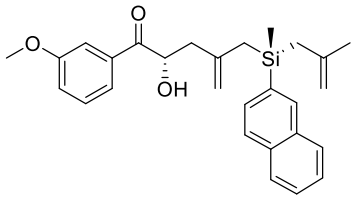


	Retention Time	Area	% Area
1	22.914	27646460	37.95
2	24.488	8761767	12.03
3	29.117	27627215	37.92
4	31.104	8818317	12.10



	Retention Time	Area	% Area
1	22.926	76889940	88.98
2	24.626	9499772	10.99
3	29.126	13445	0.02
4	31.243	6638	0.01

C6: (S)-2-hydroxy-1-(3-methoxyphenyl)-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-en-1-one



($C_{28}H_{32}O_3Si$) Colorless oil; 37.0 mg, 83% yield, 99/99% ee, 87:13 dr; $[\alpha]^{19}_D$ = +20.1 (*c* = 0.58 g/100 mL, in CH_2Cl_2).

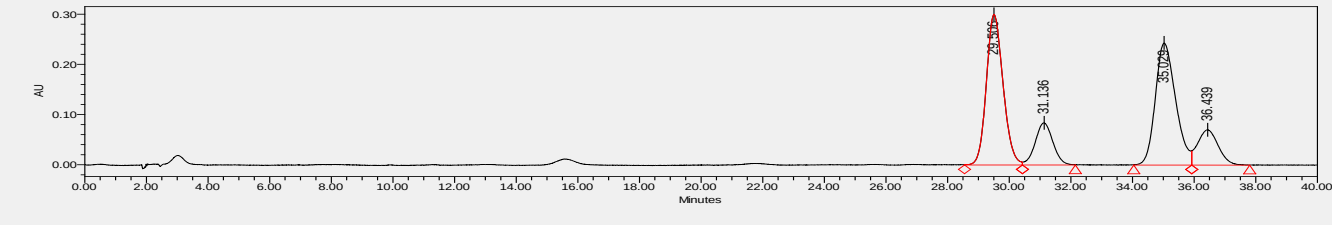
SFC (Daicel Chiralcel IG, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 230 nm), t_1 = 29.27 min, t_2 = 31.01 min, t_3 = 34.98 min, t_4 = 36.38 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 (s, 1H), 7.85 – 7.70 (m, 3H), 7.56 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.35 (d, *J* = 1.9 Hz, 1H), 7.24 – 6.99 (m, 3H), 5.07 (ddd, *J* = 8.7, 6.7, 3.4 Hz, 1H), 4.72 (d, *J* = 4.5 Hz, 2H), 4.61 – 4.53 (m, 1H), 4.48 (s, 1H), 3.79 (s, 3H), 3.60 (d, *J* = 6.7 Hz, 1H), 2.32 (dd, *J* = 14.3, 3.1 Hz, 1H), 2.07 – 2.02 (m, 1H), 2.02 – 1.99 (m, 1H), 1.99 – 1.94 (m, 1H), 1.90 – 1.83 (m, 2H), 1.55 (s, 3H), 0.41 (s, 3H).

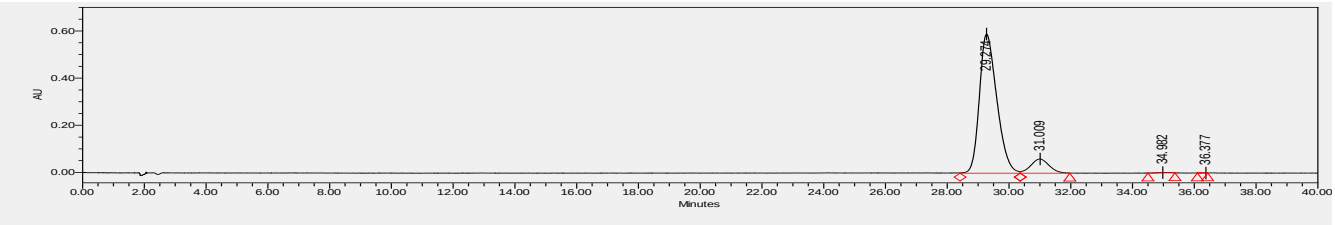
^{13}C NMR (101 MHz, $CDCl_3$) δ = 201.5, 160.0, 142.8, 142.1, 135.0, 134.9, 134.9, 133.9, 133.0, 130.2, 129.8, 128.3, 127.9, 127.1, 126.6, 126.1, 121.0, 120.5, 112.7, 112.4, 109.7, 72.2, 55.5, 44.3, 26.3, 25.5, 24.6, -5.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{28}H_{32}O_3Si + Na^+]$ = 467.2013 found 467.2016.

IR (neat): 3476, 3073, 2917, 1682, 1635, 1590, 1431, 1273, 1165, 1085, 859, 815 and 789 cm^{-1}.

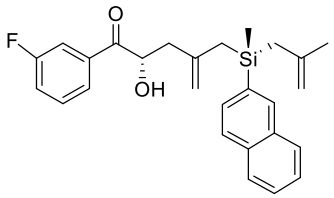


	Retention Time	Area	% Area
1	29.506	11254465	38.77
2	31.136	3340183	11.51
3	35.029	11143920	38.39
4	36.439	3287086	11.32



	Retention Time	Area	% Area
1	29.274	23031440	90.16
2	31.009	2480204	9.71
3	34.982	30736	0.12
4	36.377	3220	0.01

C7: (S)-1-(3-fluorophenyl)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-en-1-one



($C_{27}H_{29}FO_2Si$) Colorless oil; 34.6 mg, 80% yield, 99/99% ee, 85:15 dr; $[\alpha]$ $^{19}_{D}$ = +14.4 (*c* = 0.52 g/100 mL, in CH_2Cl_2).

SFC (Daicel Chiralcel ODH, CO_2/*i*-PrOH = 95/5, 1.0 mL/min), t_1 = 42.41 min, t_2 = 44.11 min, t_3 = 45.71 min, t_4 = 48.79 min.

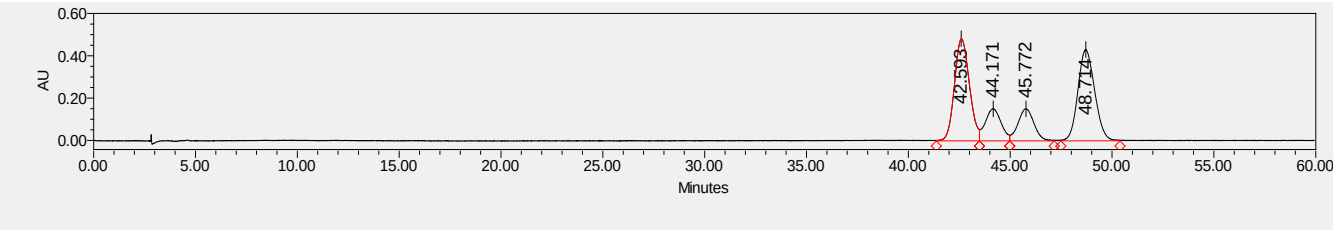
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 (s, 1H), 7.85 – 7.71 (m, 3H), 7.57 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.53 – 7.45 (m, 3H), 7.25 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.22 – 7.15 (m, 1H), 7.06 (td, *J* = 8.0, 5.5 Hz, 1H), 5.02 (ddd, *J* = 8.8, 6.7, 3.6 Hz, 1H), 4.73 (s, 1H), 4.72 – 4.66 (m, 1H), 4.63 – 4.56 (m, 1H), 4.51 – 4.48 (m, 1H), 3.49 (dd, *J* = 6.7, 1.9 Hz, 1H), 2.27 (dd, *J* = 14.2, 3.2 Hz, 1H), 2.07 – 2.02 (m, 1H), 2.00 (d, *J* = 6.3 Hz, 1H), 1.98 – 1.94 (m, 1H), 1.91 – 1.85 (m, 2H), 1.56 (s, 3H), 0.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.6 (d, $J_{C\text{-}F}$ = 2.0 Hz)., 162.9 (d, $J_{C\text{-}F}$ = 248.8 Hz), 142.8, 141.9, 135.8 (d, $J_{C\text{-}F}$ = 6.5 Hz), 134.9, 133.9, 133.0, 130.6 (d, $J_{C\text{-}F}$ = 7.5 Hz)., 130.2, 128.3, 127.9, 127.2, 126.7, 126.2, 124.2 (d, $J_{C\text{-}F}$ = 2.9 Hz)., 121.0 (d, $J_{C\text{-}F}$ = 21.6 Hz)., 115.3 (d, $J_{C\text{-}F}$ = 22.5 Hz), 112.6, 109.8, 72.2, 44.0, 26.3, 25.5, 24.6, -5.3.

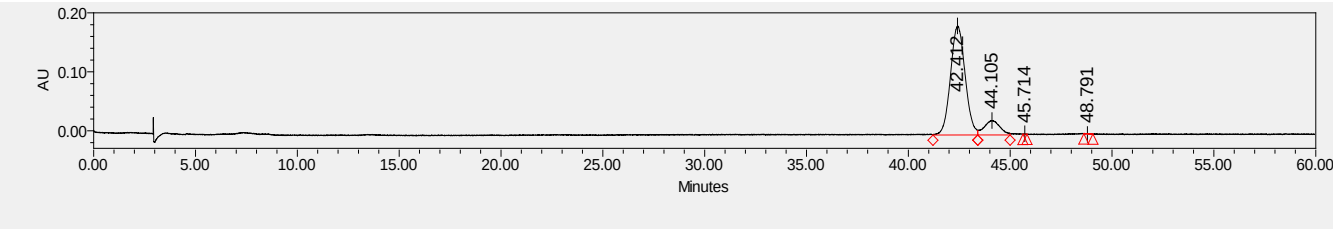
^{19}F NMR (376 MHz, Chloroform-*d*) δ = -110.9.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{27}H_{29}FO_2Si + Na^+]$ = 455.1813 found 455.1817.

IR (neat): 3480, 3071, 2918, 1686, 1635, 1587, 1443, 1267, 1161, 1084, 862, 810 and 744 cm^{-1}.

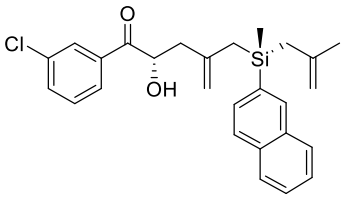


	Retention Time	Area	% Area
1	42.593	24537987	37.31
2	44.171	8248881	12.54
3	45.772	8243394	12.53
4	48.714	24733991	37.61



	Retention Time	Area	% Area
1	42.412	9240395	87.56
2	44.105	1302512	12.34
3	45.714	3031	0.03
4	48.791	7530	0.07

C8: (S)-1-(3-chlorophenyl)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-en-1-one



($C_{27}H_{29}ClO_2Si$) Colorless oil; 36.2 mg, 80% yield, 99/95% ee, 88:12 dr; $[\alpha]^{19}_D$ = +15.8 (*c* = 0.46 g/100 mL, in CH_2Cl_2).

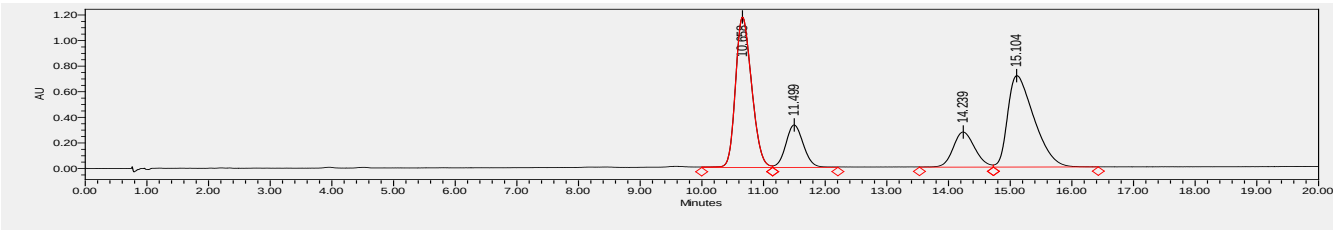
SFC (Daicel Chiralcel IG-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 230 nm), t_1 = 10.61 min, t_2 = 11.46 min, t_3 = 14.11 min, t_4 = 15.29 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 (s, 1H), 7.84 – 7.72 (m, 4H), 7.57 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.02 (t, *J* = 7.9 Hz, 1H), 5.02 (ddd, *J* = 8.8, 6.6, 3.5 Hz, 1H), 4.73 (s, 1H), 4.70 (s, 1H), 4.60 (s, 1H), 4.50 (s, 1H), 3.48 (d, *J* = 6.6 Hz, 1H), 2.26 (dd, *J* = 14.3, 3.1 Hz, 1H), 2.03 (d, *J* = 13.5 Hz, 1H), 1.99 (d, *J* = 8.5 Hz, 1H), 1.97 – 1.92 (m, 1H), 1.88 (d, *J* = 4.9 Hz, 2H), 1.56 (s, 3H), 0.43 (s, 3H).

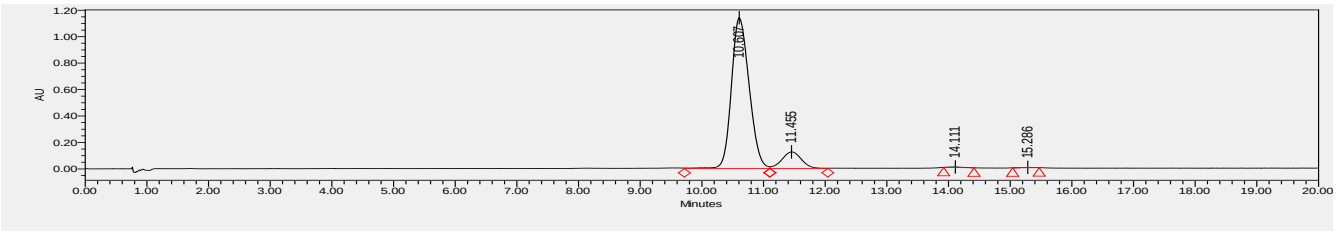
^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.5, 142.8, 141.8, 135.3, 135.3, 134.9, 134.9, 133.9, 133.8, 133.0, 130.2, 130.1, 128.6, 128.3, 127.9, 127.2, 126.7, 126.5, 126.2, 112.6, 109.8, 72.2, 44.0, 26.3, 25.5, 24.6, -5.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{27}H_{29}ClO_2Si + Na^+]$ = 471.1518, 473.1488, found 471.1523, 473.1497.

IR (neat): 3480, 3072, 2918, 1687, 1635, 1570, 1419, 1252, 1160, 1084, 859, 813 and 743 cm^{-1}.

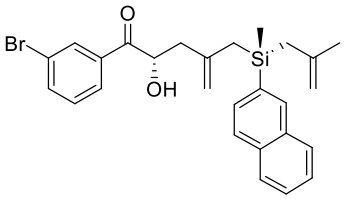


	Retention Time	Area	% Area
1	10.658	21354098	38.23
2	11.499	6560406	11.74
3	14.239	6714360	12.02
4	15.104	21231258	38.01



	Retention Time	Area	% Area
1	10.607	22779994	88.76
2	11.455	2777895	10.82
3	14.111	70360	0.27
4	15.286	37118	0.14

C9: (S)-1-(3-bromophenyl)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-en-1-one



($C_{27}H_{29}BrO_2Si$) Colorless oil; 44.8 mg, 90% yield, 99/99% ee, 90:10 dr; $[\alpha]$ $^{18}_D$ = +14.8 (*c* = 0.59 g/100 mL, in CH_2Cl_2).

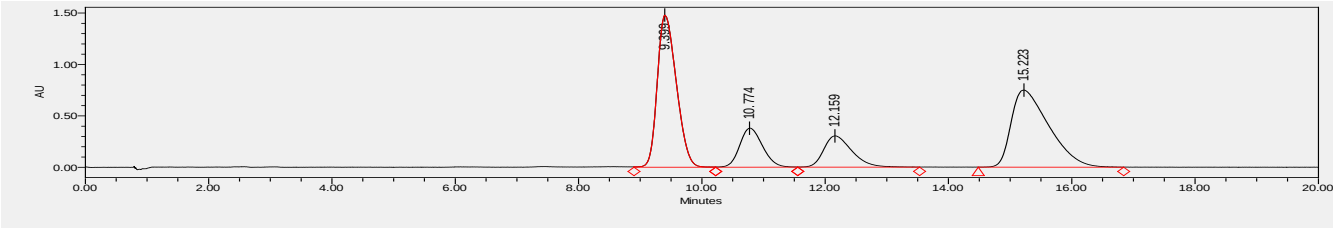
SFC (Daicel Chiralcel AZ-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 230 nm), t_1 = 9.49 min, t_2 = 10.84 min, t_3 = 12.14 min, t_4 = 15.26 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 (dd, *J* = 5.7, 4.0 Hz, 2H), 7.84 – 7.74 (m, 3H), 7.64 – 7.59 (m, 1H), 7.59 – 7.54 (m, 1H), 7.52 – 7.46 (m, 2H), 7.37 (d, *J* = 7.8 Hz, 1H), 6.95 (t, *J* = 7.9 Hz, 1H), 5.01 (ddd, *J* = 8.8, 6.6, 3.5 Hz, 1H), 4.73 (s, 1H), 4.70 (s, 1H), 4.60 (s, 1H), 4.50 (s, 1H), 3.47 (d, *J* = 6.6 Hz, 1H), 2.25 (dd, *J* = 14.3, 3.1 Hz, 1H), 2.03 (d, *J* = 13.4 Hz, 1H), 1.98 (d, *J* = 7.1 Hz, 1H), 1.97 – 1.92 (m, 1H), 1.88 (d, *J* = 4.9 Hz, 2H), 1.57 (s, 3H), 0.43 (s, 3H).

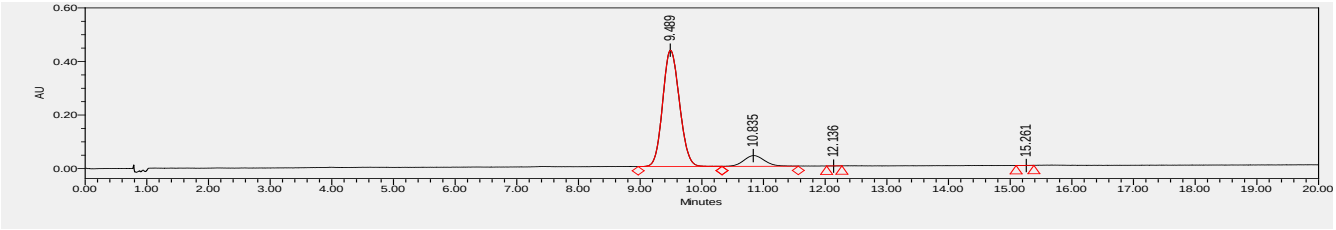
^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.4, 142.8, 141.8, 136.7, 135.5, 134.9, 134.9, 133.9, 133.0, 131.6, 130.3, 130.2, 128.3, 127.9, 127.2, 126.9, 126.7, 126.2, 123.3, 112.7, 109.8, 72.1, 44.0, 26.3, 25.5, 24.6, -5.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{27}H_{29}BrO_2Si + Na^+]$ = 515.1012, 517.0992, found 515.1018, 517.0999.

IR (neat): 3477, 3070, 2918, 1685, 1635, 1415, 1252, 1162, 1084, 980, 860, 813 and 744 cm^{-1}.

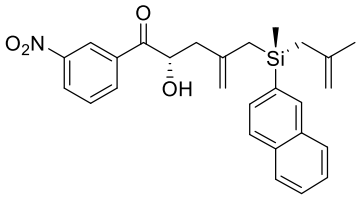


	Retention Time	Area	% Area
1	9.399	31706324	38.17
2	10.774	9768104	11.76
3	12.159	9683074	11.66
4	15.223	31904986	38.41



	Retention Time	Area	% Area
1	9.489	8222578	89.61
2	10.835	948992	10.34
3	12.136	2206	0.02
4	15.261	1987	0.02

C10: (S)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)-1-(3-nitrophenyl)pent-4-en-1-one



($C_{27}H_{29}NO_4Si$) Colorless oil; 34.6 mg, 75% yield, 99/99% ee, 85:15 dr; [α] $^{19}_D$ = +5.7 (*c* = 0.39 g/100 mL, in CH_2Cl_2).

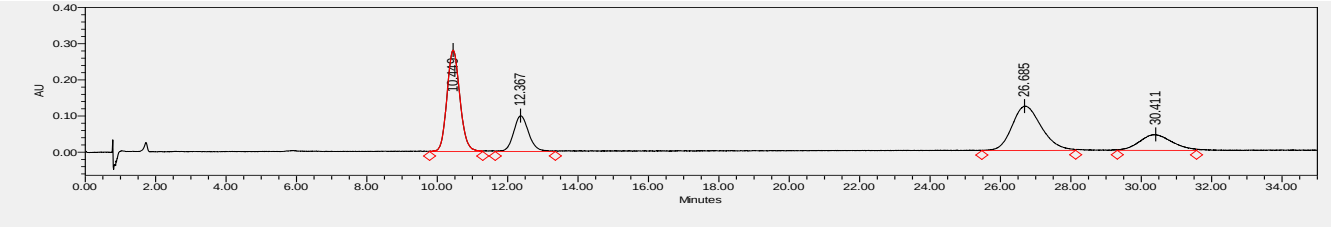
SFC (Daicel Chiralcel OZ-3, CO_2/EtOH = 90/10, 1.5 mL/min, λ = 230 nm), t_1 = 10.51 min, t_2 = 12.44 min, t_3 = 26.71 min, t_4 = 30.46 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.62 (t, *J* = 1.9 Hz, 1H), 8.31 – 8.21 (m, 1H), 7.94 (d, *J* = 21.2 Hz, 1H), 7.82 – 7.66 (m, 4H), 7.56 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 5.04 (ddd, *J* = 8.9, 6.5, 3.7 Hz, 1H), 4.76 (s, 1H), 4.70 (s, 1H), 4.64 – 4.57 (m, 1H), 4.53 – 4.44 (m, 1H), 3.35 (d, *J* = 6.4 Hz, 1H), 2.23 (dd, *J* = 14.3, 3.2 Hz, 1H), 2.07 – 2.02 (m, 1H), 2.01 (d, *J* = 7.3 Hz, 1H), 1.99 – 1.95 (m, 1H), 1.91 (s, 2H), 1.58 (s, 3H), 0.44 (s, 3H).

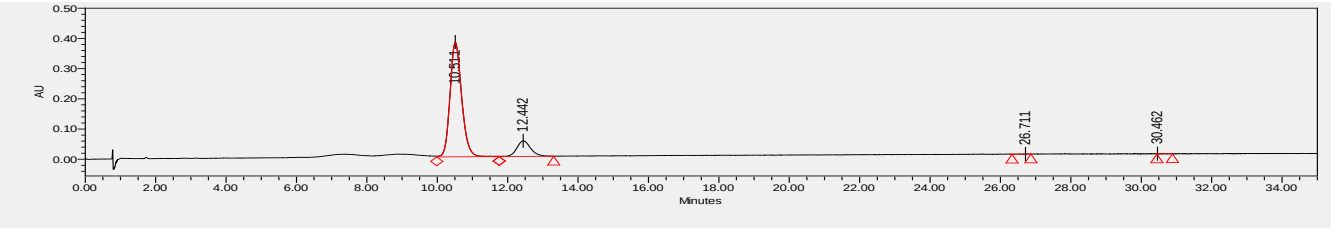
^{13}C NMR (101 MHz, $CDCl_3$) δ = 199.6, 148.4, 142.7, 141.6, 135.2, 134.9, 134.8, 133.9, 133.8, 132.9, 130.2, 130.0, 128.2, 127.9, 127.9, 127.2, 126.8, 126.3, 123.5, 113.0, 109.9, 72.3, 43.8, 26.2, 25.5, 24.6, -5.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{27}H_{29}NO_4Si + Na^+]$ = 482.1758 found 482.1761.

IR (neat): 3484, 3079, 2920, 1692, 1631, 1533, 1349, 1252, 1161, 1084, 863, 814 and 713 cm^{-1}.

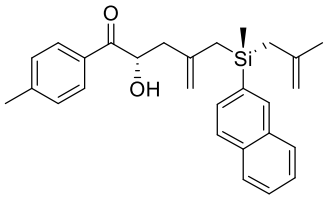


	Retention Time	Area	% Area
1	10.449	7147827	35.67
2	12.367	2959364	14.77
3	26.685	7125059	35.56
4	30.411	2804194	14.00



	Retention Time	Area	% Area
1	10.511	8685365	85.95
2	12.442	1407806	13.93
3	26.711	5453	0.05
4	30.462	6877	0.07

C11:(S)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)-1-(p-tolyl)pent-4-en-1-one



($C_{28}H_{32}O_2Si$) Colorless oil; 36.8 mg, 86% yield, 98/95% ee, 89:11 dr; $[\alpha]^{18}_D$ = +18.8 (*c* = 0.51 g/100 mL, in CH_2Cl_2).

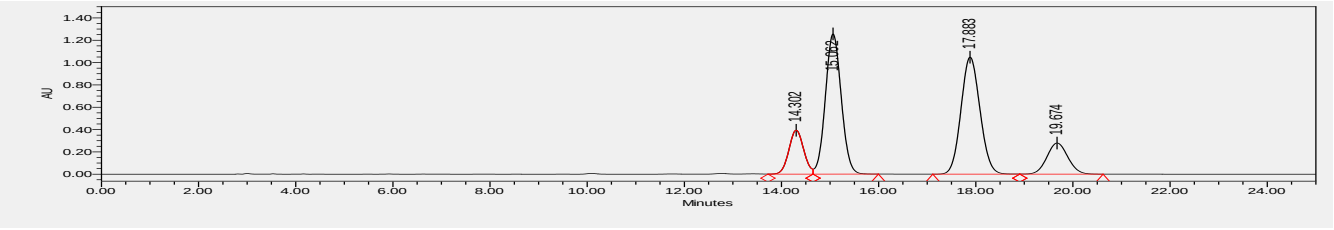
HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 230 nm), t_1 = 14.33 min, t_2 = 15.11 min, t_3 =17.92 min, t_4 = 19.73 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (s, 1H), 7.84 – 7.73 (m, 3H), 7.60 (dt, J = 8.2, 1.7 Hz, 1H), 7.53 – 7.43 (m, 4H), 6.92 (d, J = 8.0 Hz, 2H), 5.04 (ddd, J = 9.7, 6.6, 3.4 Hz, 1H), 4.72 (d, J = 7.9 Hz, 2H), 4.61 – 4.56 (m, 1H), 4.49 (s, 1H), 3.69 – 3.65 (m, 1H), 2.32 (s, 3H), 2.28 (d, J = 4.3 Hz, 1H), 2.09 – 2.08 (d, *J* = 13.9 Hz, 1H), 2.00 (d, *J* = 7.5 Hz, 1H), 1.97 (d, *J* = 8.5 Hz, 1H), 1.90 – 1.86 (m, 2H), 1.56 (s, 3H), 0.42 (s, 3H).

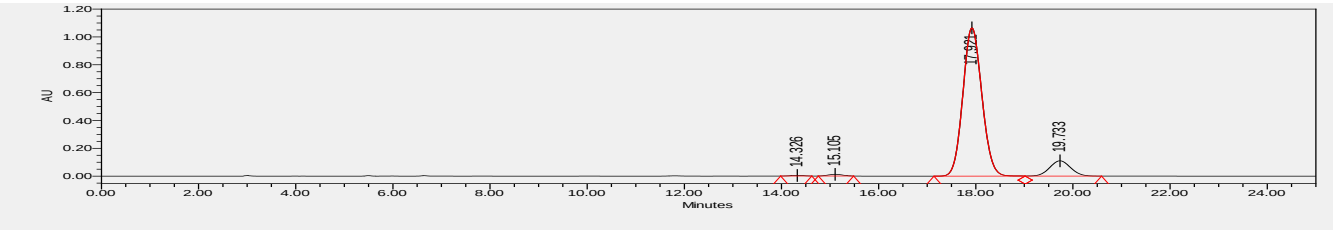
^{13}C NMR (101 MHz, $CDCl_3$) δ = 201.1, 144.9, 142.8, 142.2, 135.1, 134.9, 134.0, 133.0,130.9, 130.3, 129.5, 128.6, 128.3, 127.9, 127.2, 126.7, 126.1, 112.4, 109.7, 71.7, 44.4, 26.5, 25.5, 24.3, 21.8, -5.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{28}H_{32}O_2Si + Na^+]$ = 451.2064 found 451.2064.

IR (neat): 3467, 3049, 2919, 1676, 1635, 1607, 1270, 1175, 1085, 973, 859, 815 and 745 cm^{-1}.

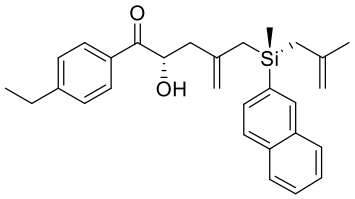


	Retention Time	Area	% Area
1	14.302	8348046	11.32
2	15.062	28492116	38.63
3	17.883	28544137	38.70
4	19.674	8372460	11.35



	Retention Time	Area	% Area
1	14.326	84764	0.26
2	15.105	254623	0.78
3	17.921	28945341	88.82
4	19.733	3304869	10.14

C12: (S)-1-(4-ethylphenyl)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-en-1-one



($C_{29}H_{34}O_2Si$) Colorless oil; 34.9 mg, 79% yield, 99/98% ee, 90:10 dr; $[\alpha]^{21}_D$ = +23.4 (*c* = 0.42 g/100 mL, in CH_2Cl_2).

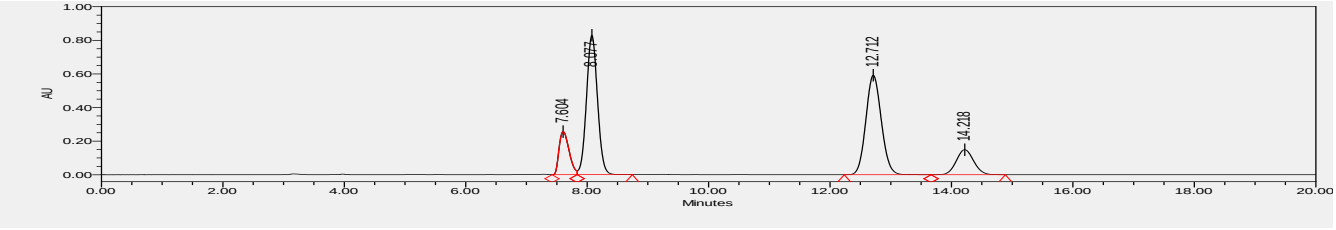
HPLC (Daicel chiralcel OXH, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 230 nm), t_1 = 8.88 min, t_2 = 9.80 min, t_3 =13.91 min, t_4 = 15.71 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (s, 1H), 7.87 – 7.73 (m, 3H), 7.62 (t, *J* = 9.9 Hz, 1H), 7.56 – 7.42 (m, 4H), 6.93 (d, *J* = 8.1 Hz, 2H), 5.04 (ddd, *J* = 9.6, 6.6, 3.4 Hz, 1H), 4.73 (d, *J* = 8.8 Hz, 2H), 4.59 (s, 1H), 4.49 (s, 1H), 3.68 (d, *J* = 6.6 Hz, 1H), 2.60 (q, *J* = 7.6 Hz, 2H), 2.40 – 2.24 (m, 1H), 2.09 (d, *J* = 13.8 Hz, 1H), 2.02 (s, 1H), 1.97 (d, *J* = 12.0 Hz, 1H), 1.88 (s, 2H), 1.56 (s, 3H), 1.19 (t, *J* = 7.6 Hz, 3H), 0.42 (s, 3H).

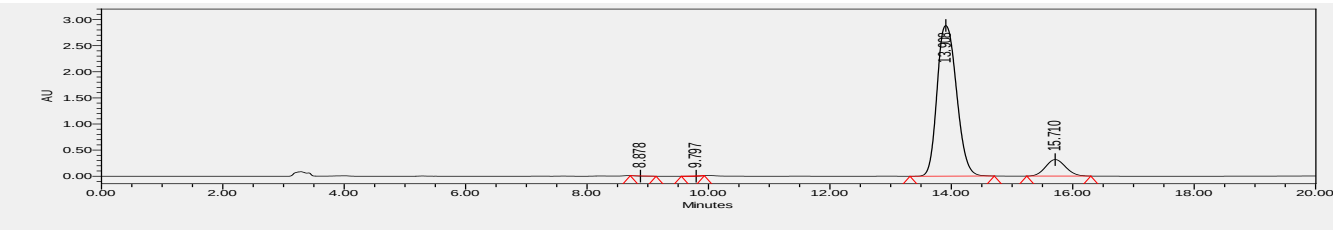
^{13}C NMR (101 MHz, $CDCl_3$) δ = 201.1, 151.1, 142.8, 142.3, 135.1, 134.9, 134.0, 133.0, 131.0, 130.3, 128.8, 128.3, 127.9, 127.2, 126.7, 126.2, 112.4, 109.7, 71.7, 44.4, 29.1, 26.6, 25.5, 24.2, 15.2, -5.4.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{29}H_{34}O_2Si + Na^+]$ = 465.2220 found 465.2223.

IR (neat): 3469, 3050, 2966, 2927, 1677, 1606, 1411, 1265, 1168, 1085, 976, 814 and 744 cm^{-1}.

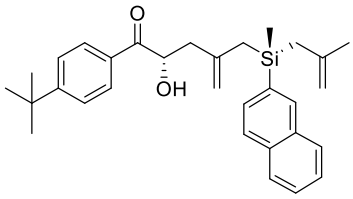


	Retention Time	Area	% Area
1	7.604	2945031	10.96
2	8.077	10464927	38.96
3	12.712	10474137	38.99
4	14.218	2976876	11.08



	Retention Time	Area	% Area
1	8.878	66159	0.09
2	9.797	72845	0.10
3	13.908	64236753	89.64
4	15.710	7284049	10.16

C13: (S)-1-(4-(tert-butyl)phenyl)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-en-1-one



($C_{31}H_{38}O_2Si$) Colorless oil; 37.6 mg, 80% yield, 99/98% ee, 89:11 dr; $[\alpha]^{19}_D$ = +25.7 (*c* = 0.53 g/100 mL, in CH_2Cl_2).

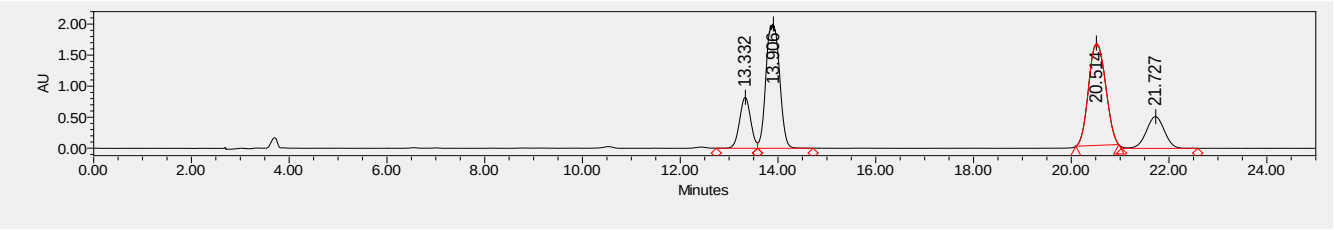
HPLC (Daicel chiralcel OXH, *n*-hexane/MEOH = 80/20, 1.5 mL/min, λ = 230 nm), t_1 = 13.29 min, t_2 = 13.89 min, t_3 = 20.43 min, t_4 = 21.61 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (s, 1H), 7.88 – 7.75 (m, 3H), 7.69 – 7.61 (m, 1H), 7.55 – 7.48 (m, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 5.04 (ddd, *J* = 9.8, 6.6, 3.5 Hz, 1H), 4.74 (s, 1H), 4.72 (s, 1H), 4.59 (t, *J* = 3.7 Hz, 1H), 4.48 (s, 1H), 3.69 (t, *J* = 6.3 Hz, 1H), 2.44 – 2.25 (m, 1H), 2.13 (d, *J* = 13.8 Hz, 1H), 2.07 – 1.93 (m, 2H), 1.87 (s, 2H), 1.56 (s, 3H), 1.26 (s, 9H), 0.42 (s, 3H).

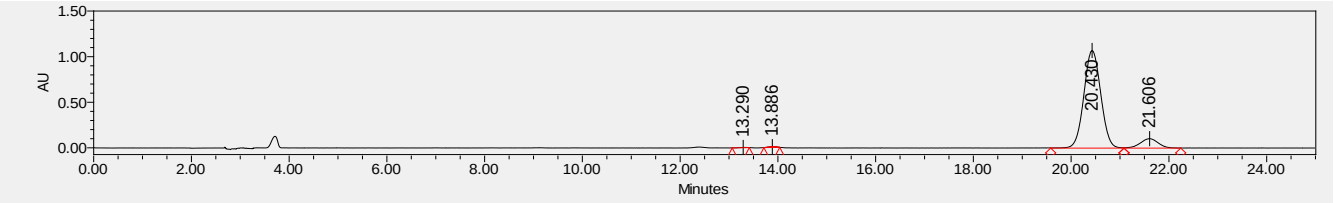
^{13}C NMR (101 MHz, $CDCl_3$) δ = 201.1, 157.9, 142.8, 142.3, 135.2, 134.9, 133.9, 133.0, 130.7, 130.3, 128.6, 128.3, 128.0, 127.3, 126.8, 126.3, 125.8, 112.5, 109.7, 71.6, 44.3, 35.3, 31.1, 26.8, 25.5, 24.1, -5.5.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{31}H_{38}O_2Si + Na^+]$ = 493.2533 found 493.2537.

IR (neat): 3472, 3052, 2962, 1677, 1636, 1604, 1408, 1269, 1162, 1086, 977, 856, 815 and 746 cm^{-1}.

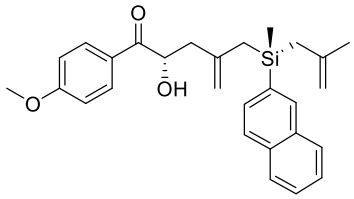


	Retention Time	Area	% Area
1	13.332	12931759	12.37
2	13.906	38757925	37.07
3	20.514	39651791	37.92
4	21.727	13223510	12.65



	Retention Time	Area	% Area
1	13.290	26787	0.09
2	13.886	110467	0.39
3	20.430	25599469	90.30
4	21.606	2613662	9.22

C14: (S)-2-hydroxy-1-(4-methoxyphenyl)-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-en-1-one



($C_{28}H_{32}O_3Si$) Colorless oil; 38.5 mg, 86% yield, 98/93% ee, 89:11 dr; $[\alpha]^{19}_D = +30.6$ ($c = 0.52$ g/100 mL, in CH_2Cl_2).

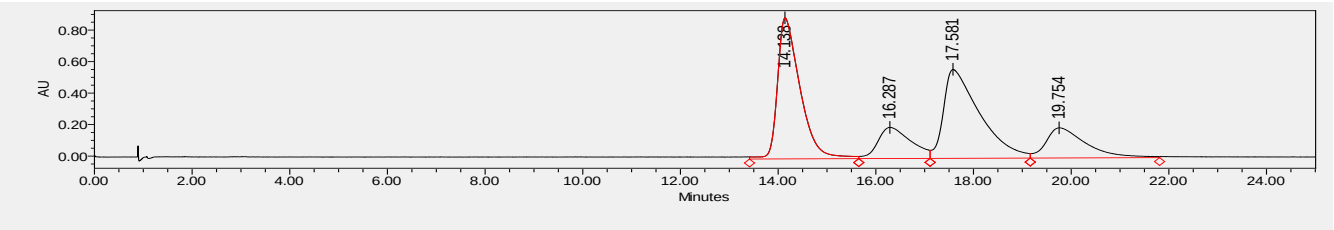
SFC (Daicel Chiralcel IF-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 230 nm), $t_1 = 14.34$ min, $t_2 = 16.63$ min, $t_3 = 18.52$ min, $t_4 = 20.29$ min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (s, 1H), 7.84 (td, J = 8.8, 8.0, 5.5 Hz, 3H), 7.69 – 7.62 (m, 1H), 7.54 – 7.44 (m, 4H), 6.56 – 6.50 (m, 2H), 4.99 (ddd, J = 9.9, 6.7, 3.5 Hz, 1H), 4.74 (s, 1H), 4.72 (s, 1H), 4.61 – 4.57 (m, 1H), 4.51 – 4.47 (m, 1H), 3.79 (d, J = 30.0 Hz, 3H), 3.72 (d, J = 6.7 Hz, 1H), 2.29 (dd, J = 14.4, 3.2 Hz, 1H), 2.12 (d, J = 13.8 Hz, 1H), 2.03 (d, J = 7.2 Hz, 1H), 2.00 – 1.95 (m, 1H), 1.88 (s, 2H), 1.57 (d, J = 6.3 Hz, 3H), 0.43 (s, 3H).

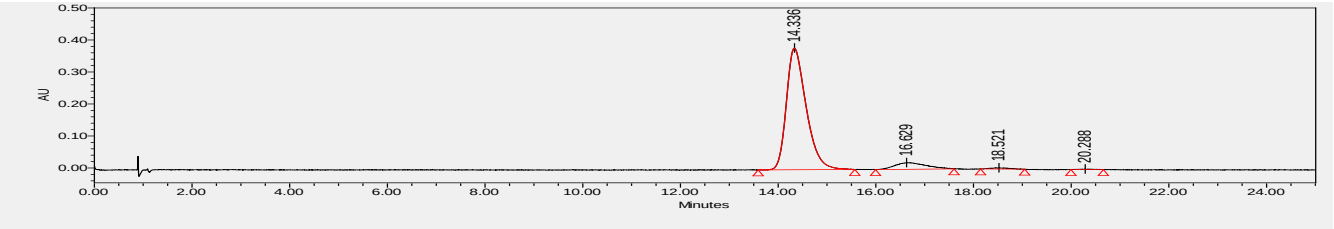
^{13}C NMR (101 MHz, $CDCl_3$) δ = 199.83, 164.09, 142.80, 142.35, 135.27, 134.88, 133.94, 133.03, 130.90, 130.33, 128.35, 127.95, 127.25, 126.69, 126.19, 113.99, 112.41, 109.72, 71.28, 55.66, 44.51, 26.67, 25.49, 24.15, -5.48.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{28}H_{32}O_3Si + Na^+]$ = 467.2013 found 467.2010.

IR (neat): 3462, 3073, 2918, 1670, 1600, 1511, 1258, 1170, 1085, 1026, 975, 876, 814 and 746 cm^{-1}.

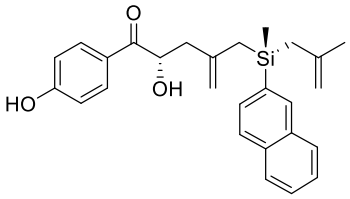


	Retention Time	Area	% Area
1	14.138	28709975	36.86
2	16.287	9301729	11.94
3	17.581	28967395	37.19
4	19.754	10903766	14.00



	Retention Time	Area	% Area
1	14.336	10683443	90.98
2	16.629	927300	7.90
3	18.521	100113	0.85
4	20.288	31585	0.27

C15: (S)-2-hydroxy-1-(4-hydroxyphenyl)-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-en-1-one



($C_{27}H_{30}O_3Si$) Colorless oil; 30.9 mg, 72% yield, 99/99% ee, 90:10 dr; $[\alpha]^{22}_D$ = +38.1 (*c* = 0.39 g/100 mL, in CH_2Cl_2).

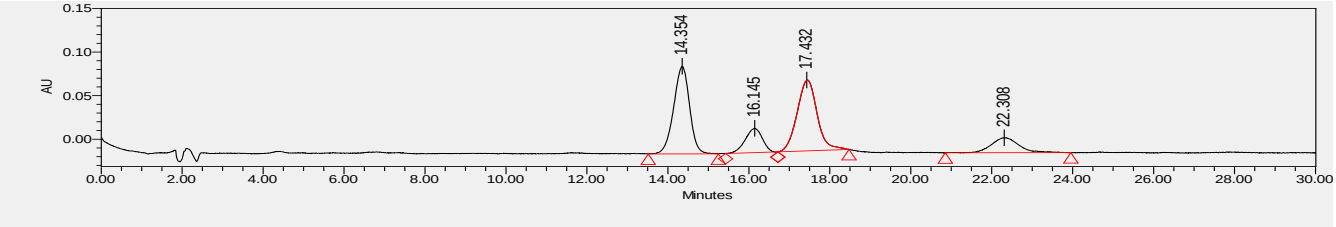
SFC (Daicel Chiralcel IG, CO_2/MeOH = 85/15, 1.5 mL/min), λ = 230 nm, t_1 = 14.31 min, t_2 = 16.15 min, t_3 = 17.44 min, t_4 = 22.28 min..

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (s, 1H), 7.87 – 7.71 (m, 3H), 7.60 (dd, *J* = 16.6, 8.4 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 4H), 6.54 (d, *J* = 8.6 Hz, 2H), 6.35 (s, 1H), 5.01 (td, *J* = 8.2, 6.9, 3.4 Hz, 1H), 4.73 (d, *J* = 4.6 Hz, 2H), 4.59 (s, 1H), 4.48 (s, 1H), 3.84 (d, *J* = 6.6 Hz, 1H), 2.29 (dd, *J* = 14.6, 2.7 Hz, 1H), 2.05 (d, *J* = 13.8 Hz, 1H), 1.98 (dd, *J* = 14.2, 7.1 Hz, 2H), 1.88 (s, 2H), 1.55 (s, 3H), 0.42 (s, 3H).

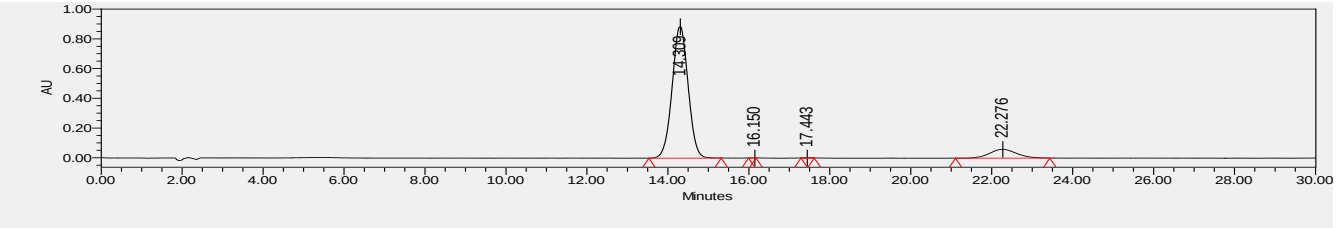
^{13}C NMR (101 MHz, $CDCl_3$) δ = 199.74, 161.09, 142.79, 142.03, 135.08, 134.86, 133.93, 133.01, 131.22, 130.28, 128.34, 127.95, 127.21, 126.67, 126.17, 126.06, 115.70, 112.53, 109.77, 71.40, 44.50, 26.43, 25.50, 24.39, -5.37.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{27}H_{30}O_3Si + Na^+]$ = 453.1856 found 453.1849.

IR (neat): 3297, 3072, 2922, 1667, 1599, 1514, 1443, 1272, 1166, 1084, 976, 814 and 744 cm^{-1}.

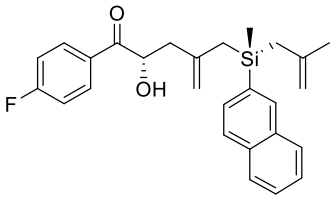


	Retention Time	Area	% Area
1	14.354	2753100	38.36
2	16.145	817426	11.39
3	17.432	2779746	38.73
4	22.308	827015	11.52



	Retention Time	Area	% Area
1	14.309	24310249	89.89
2	16.150	1691	0.01
3	17.443	6116	0.02
4	22.276	2726631	10.08

C16: (S)-1-(4-fluorophenyl)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-en-1-one



($C_{27}H_{29}FO_2Si$) Colorless oil; 35.7 mg, 82% yield, 99/99% ee, 88:12 dr; $[\alpha]$ $^{19}_D$ = -28.9 (*c* = 0.49 g/100 mL, in CH_2Cl_2).

HPLC (Daicel chiralcel OXH, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 230 nm), t_1 = 10.31 min, t_2 = 11.13 min, t_3 = 12.58 min, t_4 = 14.58 min.

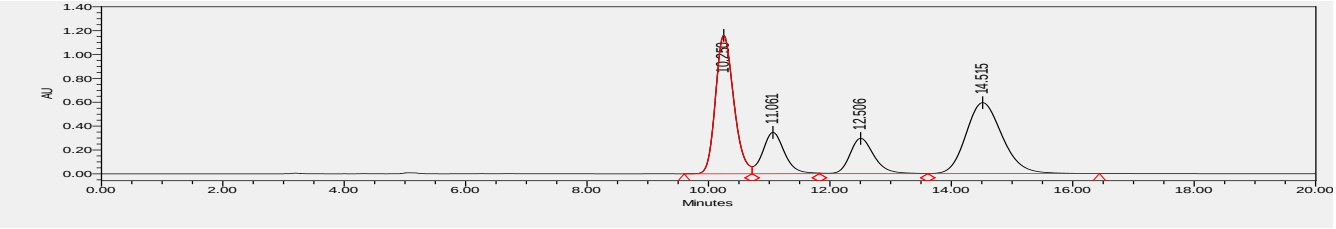
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (s, 1H), 7.87 – 7.71 (m, 3H), 7.69 – 7.58 (m, 1H), 7.52 (tt, *J* = 6.8, 3.7 Hz, 4H), 6.75 (t, *J* = 8.6 Hz, 2H), 4.99 (ddd, *J* = 10.0, 6.7, 3.6 Hz, 1H), 4.75 (s, 1H), 4.70 (s, 1H), 4.64 – 4.55 (m, 1H), 4.50 (s, 1H), 3.57 (d, *J* = 6.6 Hz, 1H), 2.24 (dd, *J* = 14.5, 3.1 Hz, 1H), 2.07 (d, *J* = 13.8 Hz, 1H), 1.99 (d, *J* = 9.2 Hz, 1H), 1.96 (d, *J* = 9.4 Hz, 1H), 1.89 (s, 2H), 1.57 (s, 3H), 0.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.0, 166.1 (d, $J_{C\text{-}F}$ = 256.4 Hz)., 142.8, 142.0, 135.1, 134.9, 133.9, 133.0, 131.2 (d, $J_{C\text{-}F}$ = 9.5 Hz)., 130.2, 129.9 (d, $J_{C\text{-}F}$ = 2.9 Hz)., 128.3, 127.9, 127.3, 126.8, 126.3, 116.0 (d, $J_{C\text{-}F}$ = 22.0 Hz), 112.6, 109.8, 71.6, 44.1, 26.5, 25.5, 24.4, -5.5.

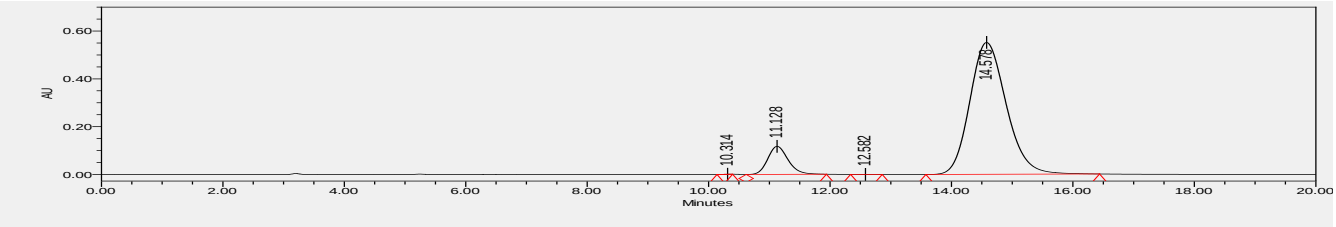
^{19}F NMR (376 MHz, Chloroform-*d*) δ = -103.2.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{27}H_{29}FO_2Si + Na^+]$ = 455.1813 found 455.1816.

IR (neat): 3475, 3073, 2918, 1682, 1635, 1597, 1506, 1408, 1236, 1157, 1085, 976, 847, 814 and 745 cm^{-1}.

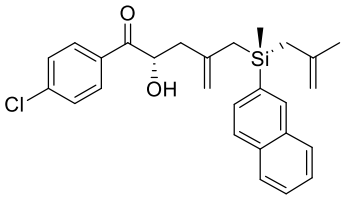


	Retention Time	Area	% Area
1	10.250	24216768	36.84
2	11.061	8628945	13.13
3	12.506	8226510	12.52
4	14.515	24657543	37.51



	Retention Time	Area	% Area
1	10.314	1499	0.01
2	11.128	2709463	10.56
3	12.582	4273	0.02
4	14.578	22951341	89.42

C17: (S)-1-(4-chlorophenyl)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-en-1-one



($C_{27}H_{29}ClO_2Si$) Colorless oil; 40.7 mg, 88% yield, 99/98% ee, 88:12 dr; $[\alpha]^{19}_D$ = +14.4 (*c* = 0.52 g/100 mL, in CH_2Cl_2).

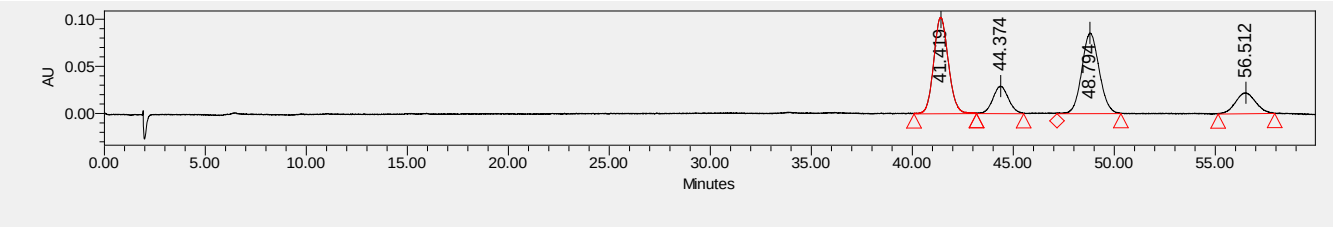
SFC (Daicel Chiralcel IG, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 230 nm), t_1 = 41.50 min, t_2 = 44.53 min, t_3 = 49.02 min, t_4 = 56.69 min

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (s, 1H), 7.87 – 7.73 (m, 3H), 7.61 – 7.49 (m, 3H), 7.49 – 7.34 (m, 2H), 7.07 – 7.00 (m, 2H), 5.03 – 4.92 (m, 1H), 4.75 (s, 1H), 4.70 (s, 1H), 4.63 – 4.56 (m, 1H), 4.54 – 4.44 (m, 1H), 3.53 (d, *J* = 6.6 Hz, 1H), 2.22 (dd, *J* = 14.5, 3.4 Hz, 1H), 2.06 (d, *J* = 13.8 Hz, 1H), 1.99 (s, 1H), 1.97 – 1.93 (m, 1H), 1.89 (s, 2H), 1.57 (s, 3H), 0.42 (s, 3H).

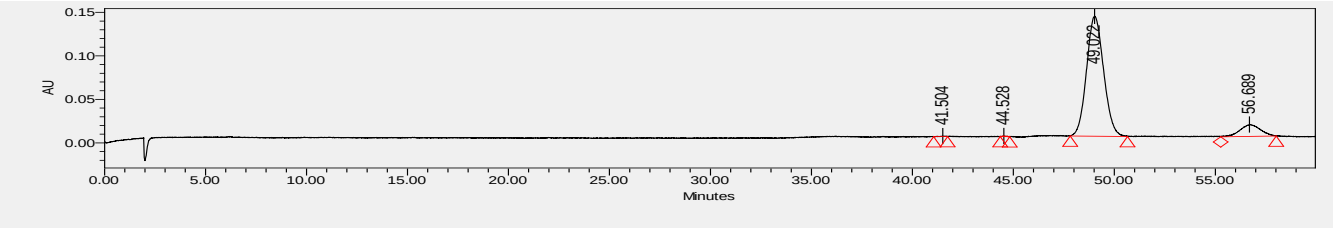
^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.4, 142.7, 141.9, 140.4, 135.0, 134.9, 133.9, 133.0, 131.8, 130.2, 129.8, 129.2, 128.3, 127.9, 127.3, 126.9, 126.3, 112.7, 109.8, 71.7, 44.0, 26.5, 25.5, 24.4, -5.5.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{27}H_{29}ClO_2Si + Na^+]$ = 471.1518, 473.1488, found 471.1519, 473.1493.

IR (neat): 3476, 3072, 2918, 1682, 1634, 1590, 1399, 1257, 1162, 1089, 976, 877, 858, 814 and 744 cm^{-1}.

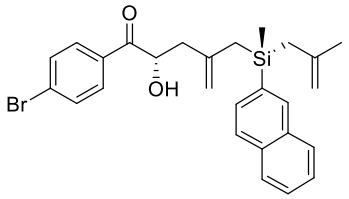


	Retention Time	Area	% Area
1	41.419	5160044	38.47
2	44.374	1570341	11.71
3	48.794	5134889	38.28
4	56.512	1547747	11.54



	Retention Time	Area	% Area
1	41.504	8936	0.10
2	44.528	8273	0.09
3	49.022	8117310	89.27
4	56.689	958370	10.54

C18: (S)-1-(4-bromophenyl)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-en-1-one



($C_{27}H_{29}BrO_2Si$) Colorless oil; 44.9 mg, 90% yield, 99/97% ee, 89:11 dr; $[\alpha]_D^{19}$ = +9.5 (*c* = 0.57 g/100 mL, in CH_2Cl_2).

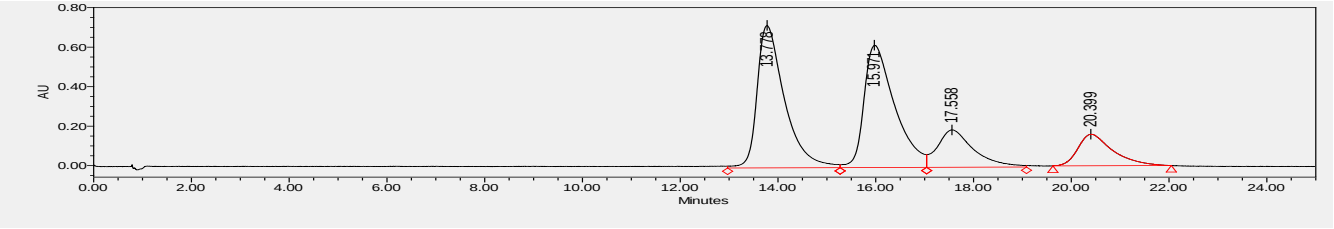
SFC (Daicel Chiralcel OJ-3, CO_2/MeOH = 95/5 , 1.5 mL/min, λ = 230 nm), t_1 = 12.57 min, t_2 = 14.91 min, t_3 = 16.59 min, t_4 = 19.31 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (s, 1H), 7.87 – 7.73 (m, 3H), 7.63 – 7.56 (m, 1H), 7.55 – 7.49 (m, 2H), 7.40 – 7.28 (m, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 4.96 (ddd, *J* = 10.0, 6.7, 3.6 Hz, 1H), 4.75 (s, 1H), 4.70 (s, 1H), 4.60 (s, 1H), 4.50 (s, 1H), 3.53 (d, *J* = 6.6 Hz, 1H), 2.21 (dd, *J* = 14.5, 3.3 Hz, 1H), 2.07 (d, *J* = 13.8 Hz, 1H), 1.99 (d, *J* = 3.5 Hz, 1H), 1.96 – 1.92 (m, 1H), 1.90 (s, 2H), 1.58 (s, 3H), 0.42 (s, 3H).

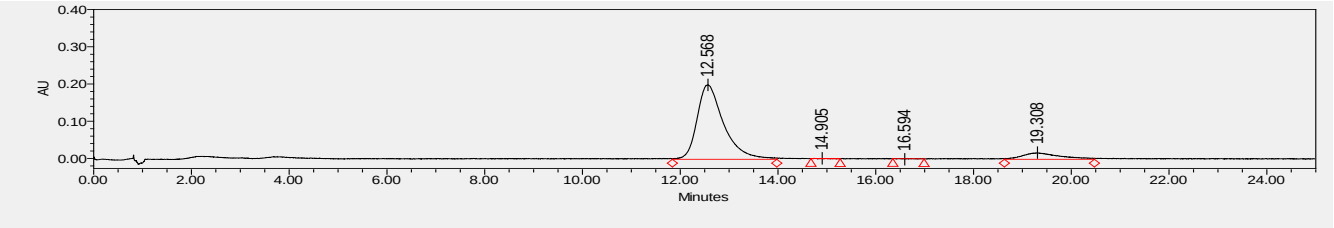
^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.7, 142.7, 141.9, 135.0, 134.9, 133.9, 133.0, 132.2, 132.1, 130.2, 129.9, 129.2, 128.3, 127.9, 127.3, 126.9, 126.4, 112.7, 109.8, 71.7, 44.0, 26.5, 25.5, 24.3, -5.5.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{27}H_{29}BrO_2Si + Na^+]$ = 515.1012, 517.0992, found 515.1022, 517.1001.

IR (neat): 3474, 3070, 2920, 1683, 1635, 1585, 1397, 1258, 1163, 1080, 976, 870, 816 and 744 cm^{-1}.

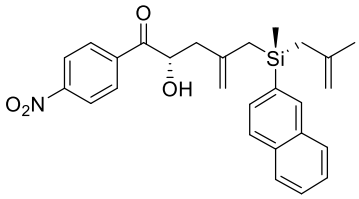


	Retention Time	Area	% Area
1	13.778	28107769	38.61
2	15.971	27077147	37.19
3	17.558	9758717	13.40
4	20.399	7862701	10.80



	Retention Time	Area	% Area
1	12.568	7548421	88.84
2	14.905	9605	0.11
3	16.594	12927	0.15
4	19.308	925821	10.90

C19: (S)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)-1-(4-nitrophenyl)pent-4-en-1-one



($C_{27}H_{29}NO_4Si$) Colorless oil; 36.7 mg, 80% yield, 98/96% ee, 85:15 dr; $[\alpha]_D^{23}$ = +39.7 (*c* = 0.41 g/100 mL, in CH_2Cl_2).

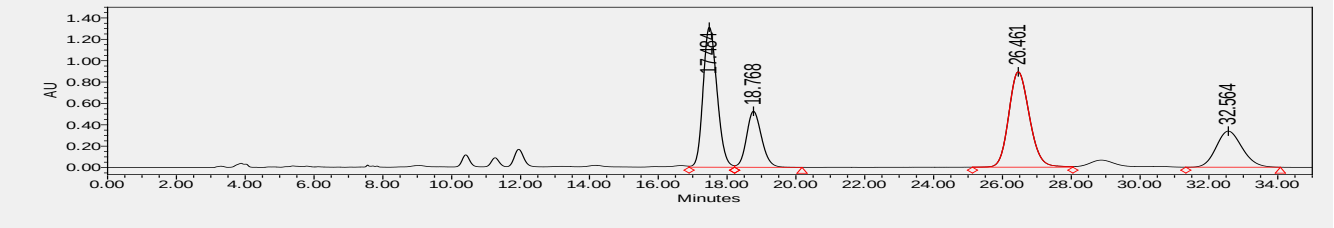
HPLC (Daicel chiralcel OXH, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 230 nm), t_1 = 17.76 min, t_2 = 19.04 min, t_3 = 26.79 min, t_4 = 33.00 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (s, 1H), 7.85 – 7.67 (m, 5H), 7.66 – 7.57 (m, 1H), 7.58 – 7.43 (m, 4H), 4.97 (ddd, *J* = 9.9, 6.4, 3.8 Hz, 1H), 4.78 (s, 1H), 4.70 (s, 1H), 4.65 – 4.58 (m, 1H), 4.52 (s, 1H), 3.38 (d, *J* = 6.4 Hz, 1H), 2.18 (dd, *J* = 14.4, 3.5 Hz, 1H), 2.08 (d, *J* = 13.8 Hz, 1H), 2.00 (d, *J* = 3.6 Hz, 1H), 1.98 – 1.94 (m, 1H), 1.90 (d, *J* = 9.6 Hz, 2H), 1.59 (s, 3H), 0.43 (s, 3H).

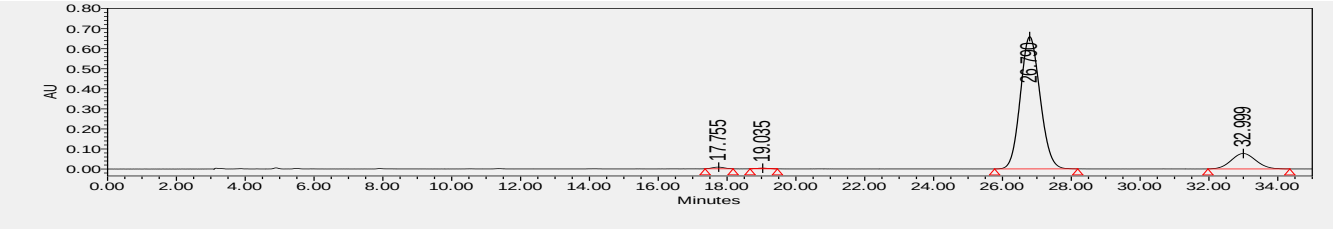
^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.4, 150.5, 142.6, 141.6, 138.2, 135.0, 134.8, 133.9, 133.0, 130.1, 129.4, 128.2, 127.9, 127.4, 127.1, 126.6, 123.9,113.1, 110.0, 72.0, 43.4, 26.4, 25.5, 24.3, -5.6.

HRMS (ESI) m/z: $[M-H]^-$ Calculated for $[C_{27}H_{29}NO_4Si-H^-]$ = 458.1793 found 458.1792.

IR (neat): 3488, 3050, 2921, 1695, 1601, 1526, 1347, 1256, 1088, 979, 855, 815 and 747 cm^{-1}.

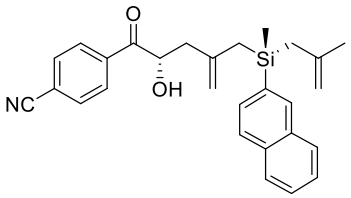


	Retention Time	Area	% Area
1	17.484	36863609	34.22
2	18.768	15886896	14.75
3	26.461	37242960	34.58
4	32.564	17722638	16.45



	Retention Time	Area	% Area
1	17.755	202128	0.66
2	19.035	78848	0.26
3	26.790	26328879	86.49
4	32.999	3830380	12.58

C20: 4-((S)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-enoyl)benzonitrile



($C_{28}H_{29}NO_2Si$) Colorless oil; 28.1 mg, 64% yield, 97/90% ee, 88:12 dr; $[\alpha]_D^{19}$ = +11.6 (*c* = 0.40 g/100 mL, in CH_2Cl_2).

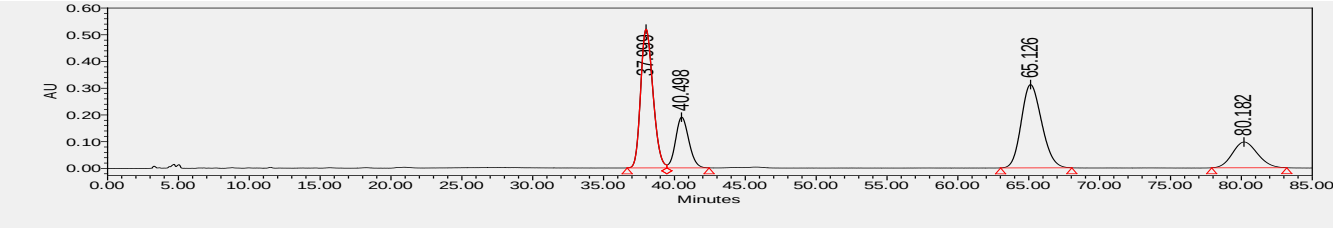
HPLC (Daicel chiralcel OXH, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 230 nm), t_1 = 38.25 min, t_2 = 40.58 min, t_3 = 64.52 min, t_4 = 79.61 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (s, 1H), 7.87 – 7.78 (m, 3H), 7.62 – 7.53 (m, 3H), 7.51 – 7.43 (m, 2H), 7.25 – 7.21 (m, 2H), 4.96 (ddd, *J* = 9.9, 6.4, 3.7 Hz, 1H), 4.77 (s, 1H), 4.72 – 4.68 (m, 1H), 4.62 (dt, *J* = 2.7, 1.4 Hz, 1H), 4.53 – 4.49 (m, 1H), 3.39 (d, *J* = 6.4 Hz, 1H), 2.18 (dd, *J* = 14.4, 3.4 Hz, 1H), 2.06 (d, *J* = 13.8 Hz, 1H), 1.99 (d, *J* = 3.1 Hz, 1H), 1.97 – 1.93 (m, 1H), 1.91 (d, *J* = 0.8 Hz, 2H), 1.62 – 1.58 (m, 3H), 0.44 (s, 3H).

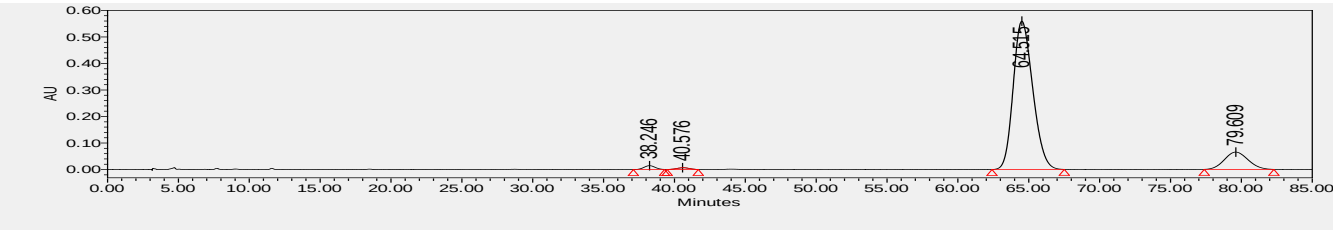
^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.5, 142.6, 141.6, 136.7, 135.1, 134.8, 133.9, 133.0, 132.5, 130.2, 128.7, 128.3, 128.0, 127.3, 126.5, 116.9, 113.0, 109.9, 71.9, 43.5, 26.4, 25.5, 24.3, -5.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{28}H_{29}NO_2Si + Na^+]$ = 462.1860 found 462.1864.

IR (neat): 3479, 3070, 2920, 1690, 1635, 1407, 1255, 1162, 1086, 976, 854, 815 and 747 cm^{-1}.

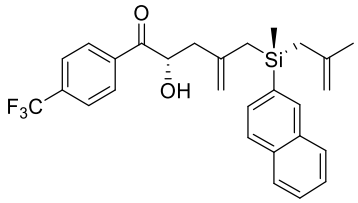


	Retention Time	Area	% Area
1	37.999	31286780	36.06
2	40.498	12322537	14.20
3	65.126	31295190	36.07
4	80.182	11849215	13.66



	Retention Time	Area	% Area
1	38.246	788286	1.26
2	40.576	394949	0.63
3	64.515	53595358	85.94
4	79.609	7586244	12.16

C21: (S)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)-1-(4-(trifluoromethyl)phenyl)pent-4-en-1-one



($C_{28}H_{29}F_3O_2Si$) Colorless oil; 40.1 mg, 83% yield, 99/99% ee, 88:12 dr; $[\alpha]^{19}_D$ = +27.9 (*c* = 0.54 g/100 mL, in CH_2Cl_2).

HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 230 nm), t_1 = 7.22 min, t_2 = 7.83 min, t_3 =9.48 min, t_4 = 10.54 min.

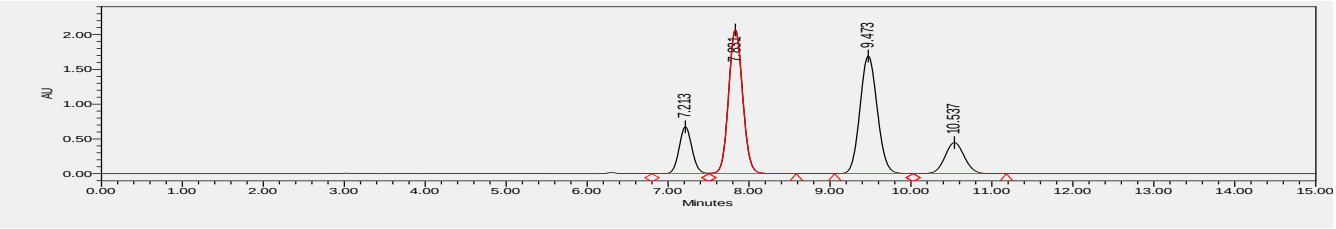
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 (s, 1H), 7.86 – 7.72 (m, 3H), 7.61 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.57 – 7.46 (m, 4H), 7.34 – 7.18 (m, 2H), 5.00 (ddd, *J* = 9.9, 6.5, 3.7 Hz, 1H), 4.76 (s, 1H), 4.71 – 4.67 (m, 1H), 4.64 – 4.57 (m, 1H), 4.54 – 4.46 (m, 1H), 3.54 – 3.40 (m, 1H), 2.31 – 2.16 (m, 1H), 2.09 (d, *J* = 13.6 Hz, 1H), 2.00 (d, *J* = 6.2 Hz, 1H), 1.97 (d, *J* = 6.1 Hz, 1H), 1.90 (s, 2H), 1.58 (s, 3H), 0.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.8, 142.7, 141.8, 136.3, 135.2, 135.0, 134.9, 134.8, 133.9, 133.0, 130.2, 128.8, 128.3, 127.9, 127.3, 127.0, 126.4, 126.0 (q, $J_{C\text{-}F}$= 3.6 Hz), 112.9, 109.8, 71.9, 43.7, 26.6, 25.5, 24.2, -5.6.

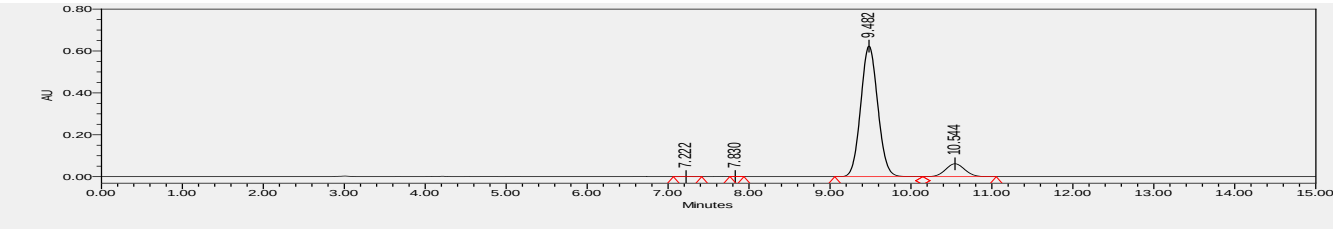
^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.2.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{28}H_{29}F_3O_2Si + Na^+]$ = 505.1781 found 505.1785.

IR (neat): 3482, 3073, 2919, 1690, 1635, 1411, 1324, 1256, 1170, 1132, 1068, 977, 853, 815 and 746 cm^{-1}.

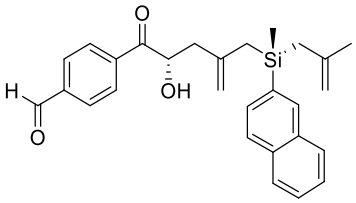


	Retention Time	Area	% Area
1	7.213	7433341	11.44
2	7.831	24992888	38.45
3	9.473	25110551	38.63
4	10.537	7458432	11.48



	Retention Time	Area	% Area
1	7.222	3926	0.04
2	7.830	997	0.01
3	9.482	9122624	89.91
4	10.544	1018969	10.04

C22: 4-((S)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-enoyl)benzaldehyde



($C_{28}H_{30}O_3Si$) Colorless oil; 33.2 mg, 75% yield, 99/99% ee, 90:10 dr; $[\alpha]^{21}_D = +10.0$ ($c = 0.39$ g/100 mL, in CH_2Cl_2).

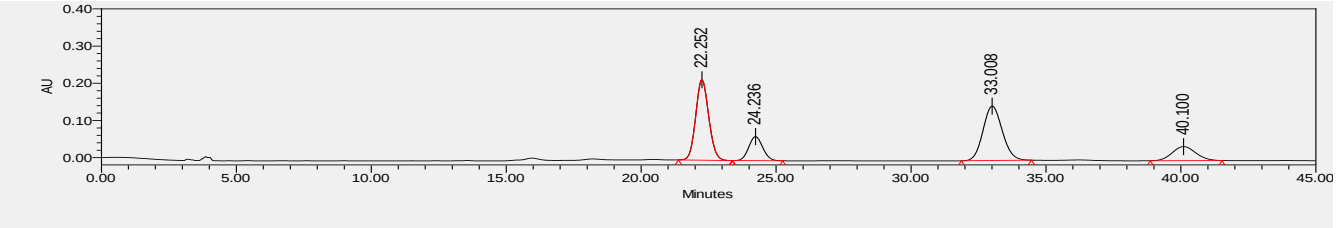
HPLC (Daicel chiralcel OXH, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 230 nm), $t_1 = 22.30$ min, $t_2 = 24.30$ min, $t_3 = 33.03$ min, $t_4 = 40.34$ min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.94 (d, *J* = 15.4 Hz, 1H), 7.99 (s, 1H), 7.85 – 7.75 (m, 3H), 7.74 – 7.58 (m, 3H), 7.57 – 7.44 (m, 4H), 5.03 (ddd, *J* = 9.7, 6.4, 3.6 Hz, 1H), 4.76 (s, 1H), 4.70 (s, 1H), 4.63 – 4.58 (m, 1H), 4.51 (s, 1H), 3.65 – 3.38 (m, 1H), 2.31 – 2.19 (m, 1H), 2.08 (d, *J* = 13.8 Hz, 1H), 2.00 (t, *J* = 4.5 Hz, 1H), 1.99 – 1.94 (m, 1H), 1.89 (d, *J* = 9.1 Hz, 2H), 1.57 (s, 3H), 0.43 (s, 3H).

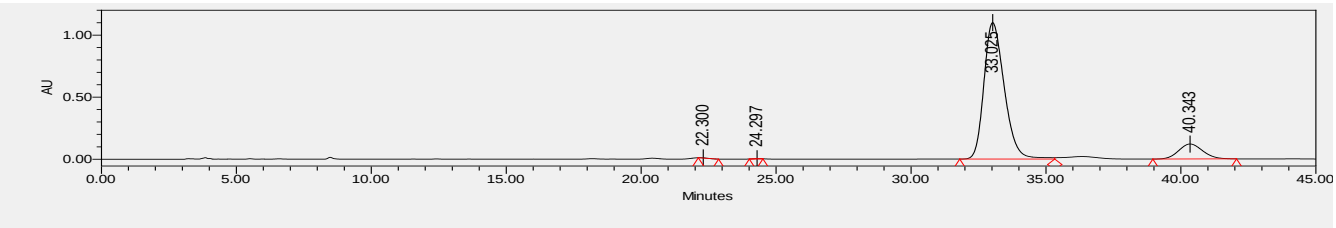
^{13}C NMR (101 MHz, $CDCl_3$) δ = 201.2, 191.4, 142.7, 141.8, 139.4, 137.9, 135.1, 134.9, 133.9, 133.0, 130.2, 129.8, 128.9, 128.3, 128.0, 127.3, 126.9, 126.4, 112.9, 109.9, 72.1, 43.7, 26.4, 25.5, 24.3, -5.5.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{28}H_{30}O_3Si + Na^+]$ = 465.1856 found 465.1847.

IR (neat): 3478, 3073, 2962, 2919, 1702, 1635, 1414, 1255, 1203, 1085, 976, 815 and 745 cm^{-1}.

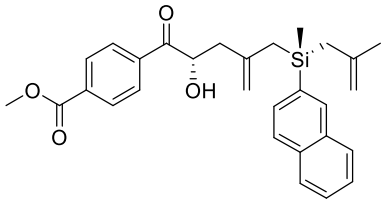


	Retention Time	Area	% Area
1	22.252	7248654	37.85
2	24.236	2342369	12.23
3	33.008	7260697	37.91
4	40.100	2299915	12.01



	Retention Time	Area	% Area
1	22.300	40703	0.06
2	24.297	27428	0.04
3	33.025	57584178	88.40
4	40.343	7487545	11.49

C23: methyl 4-((S)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-enoyl)benzoate



($C_{29}H_{32}O_4Si$) Colorless oil; 40.1 mg, 85% yield, 99/99% ee, 88:12 dr; $[\alpha]^{21}_D$ = +9.1 (*c* = 0.65 g/100 mL, in CH_2Cl_2).

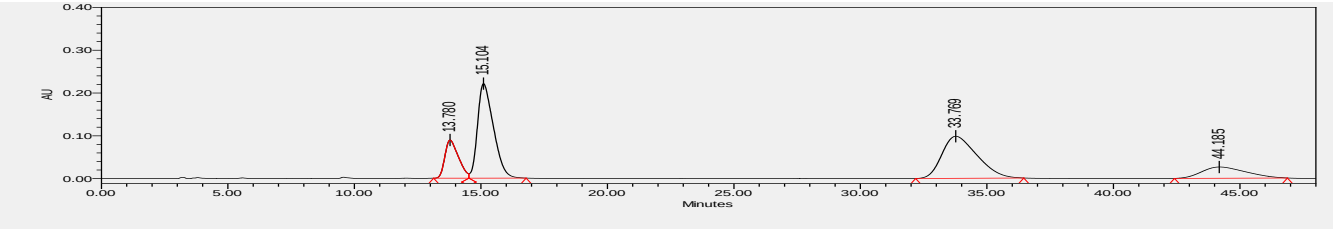
HPLC (Daicel chiralcel OZH, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 230 nm), t_1 = 13.85 min, t_2 = 15.17 min, t_3 = 33.75 min, t_4 = 44.29 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.98 (s, 1H), 7.84 – 7.76 (m, 5H), 7.58 (d, *J* = 8.0 Hz, 3H), 7.50 (h, *J* = 7.1 Hz, 2H), 5.05 (ddd, *J* = 9.6, 6.6, 3.6 Hz, 1H), 4.74 (s, 1H), 4.69 (s, 1H), 4.60 (s, 1H), 4.49 (s, 1H), 3.95 (s, 3H), 3.53 (d, *J* = 6.5 Hz, 1H), 2.25 (dd, *J* = 14.5, 3.1 Hz, 1H), 2.06 (d, *J* = 13.9 Hz, 1H), 1.98 (t, *J* = 13.1 Hz, 2H), 1.89 (s, 2H), 1.57 (s, 3H), 0.42 (s, 3H).

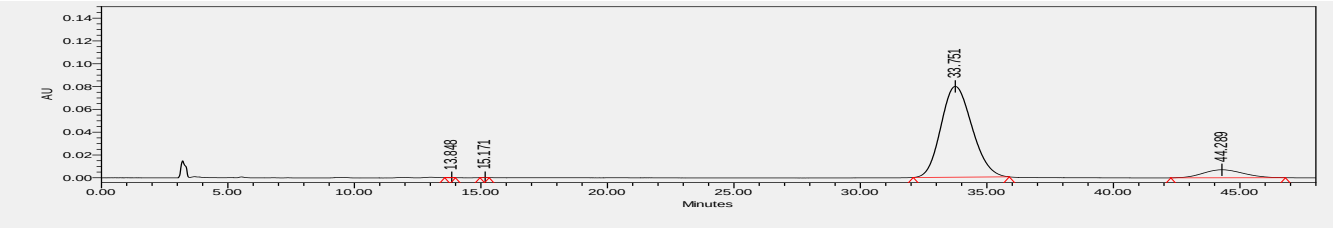
^{13}C NMR (151 MHz, $CDCl_3$) δ = 201.3, 166.0, 142.7, 141.9, 136.9, 134.9, 134.9, 134.5, 133.9, 132.9, 130.2, 130.0, 128.4, 128.2, 127.9, 127.2, 126.8, 126.3, 112.7, 109.8, 72.1, 52.6, 43.8, 26.4, 25.5, 24.4, -5.5.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{29}H_{32}O_4Si + Na^+]$ = 495.1962 found 495.1962.

IR (neat): 3483, 3073, 2917, 1725, 1687, 1635, 1436, 1279, 1109, 975, 858, 814 and 745 cm^{-1}.

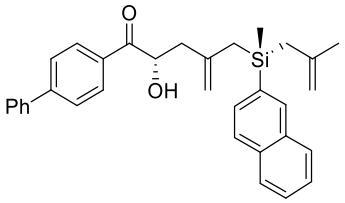


	Retention Time	Area	% Area
1	13.780	3323086	12.95
2	15.104	9638316	37.57
3	33.769	9476320	36.94
4	44.185	3213362	12.53



	Retention Time	Area	% Area
1	13.848	489	0.01
2	15.171	576	0.01
3	33.751	6803229	89.70
4	44.289	780209	10.29

C24: (S)-1-([1,1'-biphenyl]-4-yl)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-en-1-one



($C_{33}H_{34}O_2Si$) Colorless oil; 43.1 mg, 88% yield, 94/81% ee, 90:10 dr; $[\alpha]^{19}_D = +14.4$ ($c = 0.62$ g/100 mL, in CH_2Cl_2).

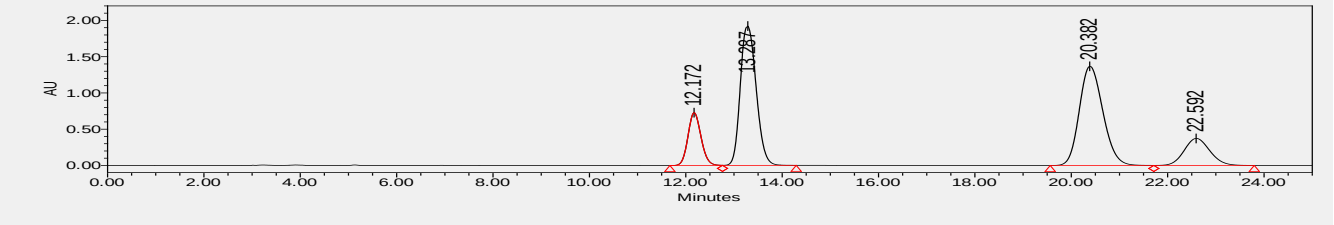
HPLC (Daicel chiralcel OXH, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 230 nm), $t_1 = 12.16$ min, $t_2 = 13.29$ min, $t_3 = 20.37$ min, $t_4 = 22.55$ min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (s, 1H), 7.84 – 7.74 (m, 3H), 7.67 – 7.59 (m, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.53 – 7.39 (m, 7H), 7.32 – 7.23 (m, 2H), 5.07 (ddd, *J* = 9.8, 6.6, 3.5 Hz, 1H), 4.75 (d, *J* = 9.9 Hz, 2H), 4.62 – 4.55 (m, 1H), 4.49 (s, 1H), 3.68 (d, *J* = 6.6 Hz, 1H), 2.41 – 2.29 (m, 1H), 2.13 (d, *J* = 13.8 Hz, 1H), 2.04 (d, *J* = 7.4 Hz, 1H), 2.02 – 1.98 (m, 1H), 1.89 (s, 2H), 1.57 (s, 3H), 0.44 (s, 3H).

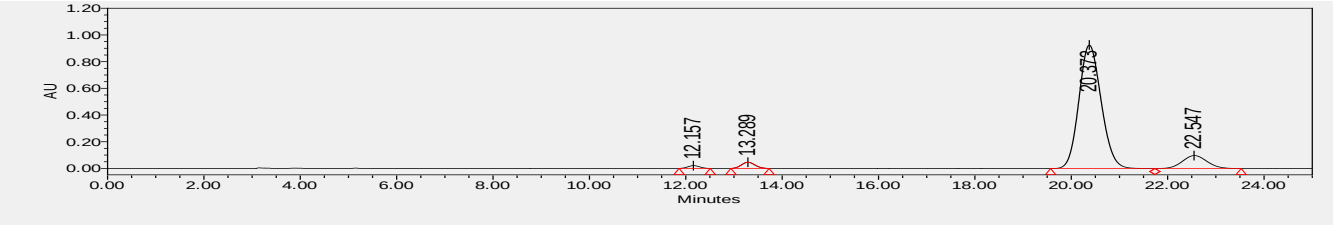
^{13}C NMR (101 MHz, $CDCl_3$) δ = 201.1, 146.5, 142.8, 142.2, 139.5, 135.2, 134.9, 134.0, 133.0, 132.0, 130.3, 129.1, 129.1,128.6, 128.3, 127.9, 127.4, 127.3, 127.3 126.8, 126.3, 112.6, 109.8, 71.7, 44.3, 26.7, 25.5, 24.2, -5.5.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{33}H_{34}O_2Si + Na^+]$ = 513.2220 found 513.2229.

IR (neat): 3467, 3057, 2918, 1677, 1603, 1406, 1264, 1163, 1085, 976, 855, 815 and 744 cm^{-1}.

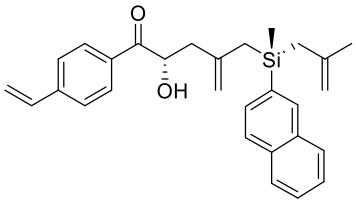


	Retention Time	Area	% Area
1	12.172	13684122	11.61
2	13.287	43938234	37.29
3	20.382	46419028	39.40
4	22.592	13782376	11.70



	Retention Time	Area	% Area
1	12.157	357822	1.04
2	13.289	902513	2.62
3	20.373	29707676	86.32
4	22.547	3448510	10.02

C25: (S)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)-1-(4-vinylphenyl)pent-4-en-1-one



($C_{29}H_{32}O_2Si$) Colorless oil; 25.3 mg, 57% yield, 99/99% ee, 90:10 dr; $[\alpha]^{20}_D$ = +22.3 (*c* = 0.31 g/100 mL, in CH_2Cl_2).

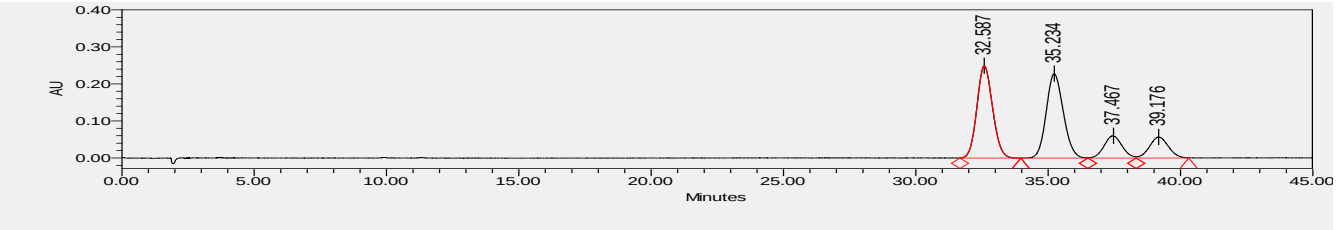
SFC (Daicel Chiralcel IG, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 230 nm), t_1 = 32.41 min, t_2 = 35.27 min, t_3 = 37.47 min, t_4 = 39.13 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (s, 1H), 7.87 – 7.71 (m, 3H), 7.63 (t, *J* = 9.5 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.75 – 6.56 (m, 1H), 5.79 (d, *J* = 17.6 Hz, 1H), 5.40 (d, *J* = 10.9 Hz, 1H), 5.03 (ddd, *J* = 9.7, 6.6, 3.5 Hz, 1H), 4.75 (s, 1H), 4.71 (s, 1H), 4.59 (s, 1H), 4.49 (s, 1H), 3.65 (d, *J* = 6.6 Hz, 1H), 2.38 – 2.23 (m, 1H), 2.10 (d, *J* = 13.8 Hz, 1H), 2.02 (s, 1H), 1.99 – 1.94 (m, 1H), 1.88 (s, 2H), 1.56 (s, 3H), 0.43 (s, 3H).

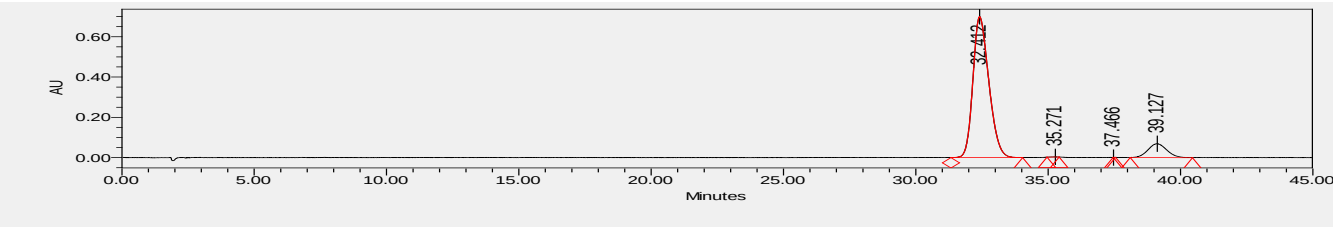
^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.9, 142.9, 142.8, 142.2, 135.8, 135.2, 134.9, 134.0, 133.0, 132.5, 130.3, 128.9, 128.4, 128.0, 127.3, 126.7, 126.5, 126.2, 117.4, 112.5, 109.8, 71.7, 44.2, 26.6, 25.5, 24.2, -5.5.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{29}H_{32}O_2Si + Na^+]$ = 463.2064 found 463.2061.

IR (neat): 3470, 3072, 2918, 1677, 1634, 1603, 1403, 1265, 1175, 1084, 977, 853, 815 and 744 cm^{-1}.

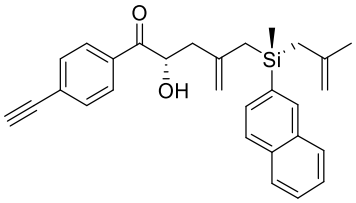


	Retention Time	Area	% Area
1	32.587	10273187	39.30
2	35.234	10237941	39.17
3	37.467	2819267	10.79
4	39.176	2808144	10.74



	Retention Time	Area	% Area
1	32.412	29308713	89.47
2	35.271	13429	0.04
3	37.466	1916	0.01
4	39.127	3433854	10.48

C26: (S)-1-(4-ethynylphenyl)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-en-1-one



($C_{29}H_{30}O_2Si$) Colorless oil; 35.5 mg, 81% yield, 99/99% ee, 90:10 dr; $[\alpha]^{21}_D$ = +8.7 (*c* = 0.43 g/100 mL, in CH_2Cl_2).

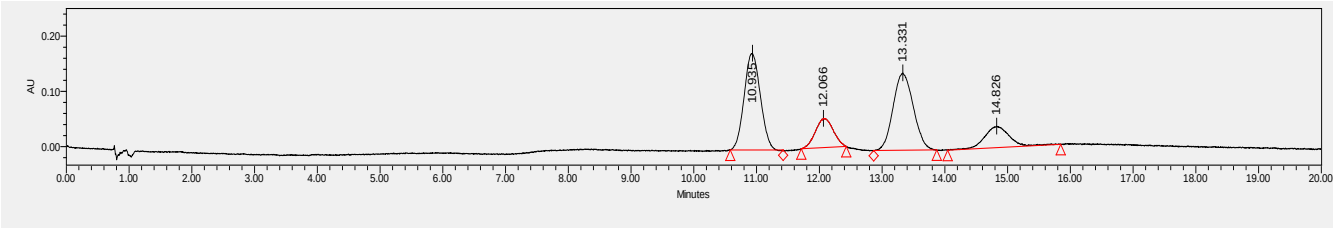
SFC (Daicel Chiralcel IG-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 230 nm), t_1 = 10.76 min, t_2 = 11.93 min, t_3 = 13.19 min, t_4 = 14.73 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 (s, 1H), 7.87 – 7.71 (m, 3H), 7.60 (dd, *J* = 18.6, 8.2 Hz, 1H), 7.56 – 7.43 (m, 4H), 7.24 (d, *J* = 8.5 Hz, 2H), 5.01 (ddd, *J* = 9.9, 6.6, 3.6 Hz, 1H), 4.74 (s, 1H), 4.69 (s, 1H), 4.60 (s, 1H), 4.50 (s, 1H), 3.55 (d, *J* = 6.6 Hz, 1H), 3.29 (s, 1H), 2.24 (dd, *J* = 14.5, 3.1 Hz, 1H), 2.05 (d, *J* = 13.8 Hz, 1H), 1.99 (d, *J* = 7.9 Hz, 1H), 1.96 (d, *J* = 7.1 Hz, 1H), 1.89 (s, 2H), 1.57 (s, 3H), 0.42 (s, 3H).

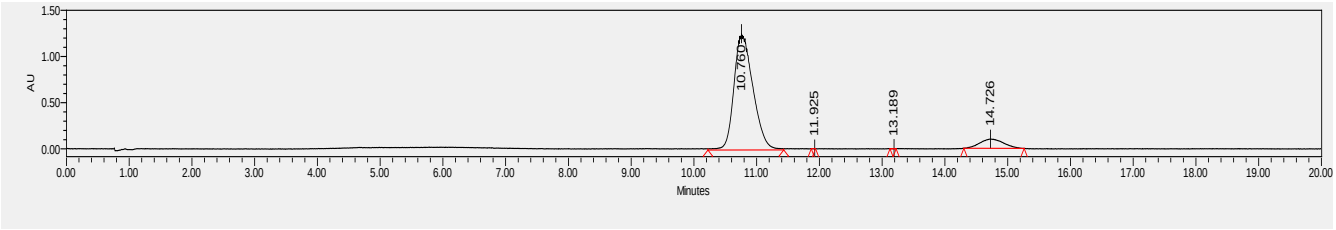
^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.9, 142.8, 141.9, 134.9, 134.9, 133.9, 133.2, 133.0, 132.5, 130.2, 128.3, 128.3, 127.9, 127.7, 127.2, 126.8, 126.3, 112.6, 109.8, 82.6, 81.1, 71.9, 44.0, 26.4, 25.5, 24.5, -0.1.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{29}H_{30}O_2Si + Na^+]$ = 461.1907 found 461.1910.

IR (neat): 3476, 3288, 3073, 2919, 1682, 1635, 1603, 1404, 1257, 1168, 1085, 976, 814 and 745 cm^{-1}.

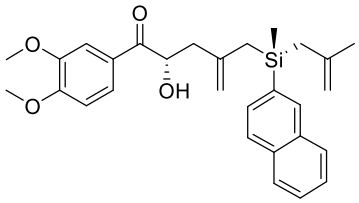


	Retention Time	Area	% Area
1	10.935	3144294	37.67
2	12.066	1043940	12.51
3	13.331	3120640	37.38
4	14.826	1038532	12.44



	Retention Time	Area	% Area
1	10.760	26404608	90.90
2	11.925	4676	0.02
3	13.189	7788	0.03
4	14.726	2629365	9.05

C27: (S)-1-(3,4-dimethoxyphenyl)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-en-1-one



($C_{29}H_{34}O_4Si$) Colorless oil; 35.7 mg, 75% yield, 99/97% ee, 90:10 dr; $[\alpha]^{19}_D$ = +36.4 (*c* = 0.64 g/100 mL, in CH_2Cl_2).

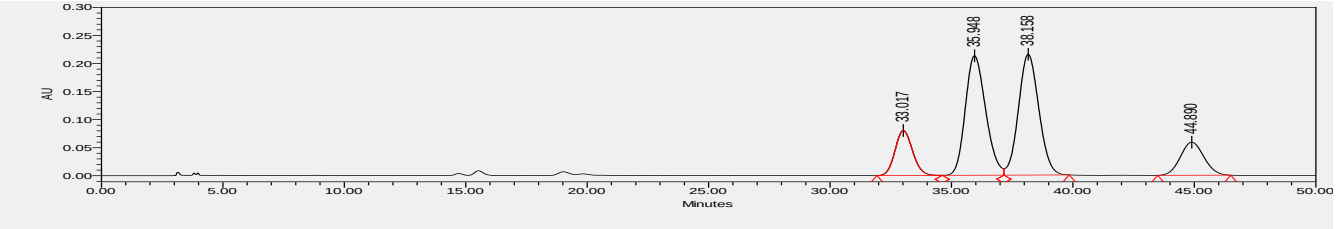
HPLC (Daicel chiralcel OXH, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 230 nm), t_1 = 33.11 min, t_2 = 36.08 min, t_3 =38.16 min, t_4 = 44.95 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (s, 1H), 7.89 – 7.74 (m, 3H), 7.69 – 7.59 (m, 1H), 7.55 – 7.45 (m, 2H), 7.39 (d, *J* = 1.9 Hz, 1H), 6.74 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.12 (d, *J* = 8.4 Hz, 1H), 5.01 (ddd, *J* = 9.9, 6.8, 3.5 Hz, 1H), 4.76 (s, 1H), 4.73 (s, 1H), 4.63 – 4.56 (m, 1H), 4.49 (s, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 3.68 (d, *J* = 6.8 Hz, 1H), 2.30 (dd, *J* = 14.4, 3.2 Hz, 1H), 2.13 (d, *J* = 13.8 Hz, 1H), 2.06 – 2.02 (m, 1H), 2.01 – 1.95 (m, 1H), 1.89 (s, 2H), 1.57 (s, 3H), 0.43 (s, 3H).

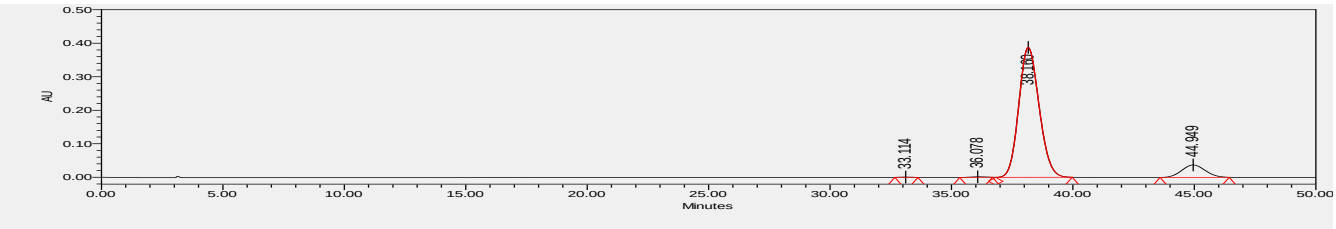
^{13}C NMR (101 MHz, $CDCl_3$) δ = 199.9, 153.9, 149.3, 142.8, 142.4, 135.3, 134.9, 133.9, 133.0, 130.3, 128.4, 128.0, 127.3, 126.7, 126.3, 126.2, 123.2, 112.4, 110.5, 109.9, 109.7, 71.2, 56.3, 56.0, 44.8, 26.7, 25.5, 24.1, -5.5.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{29}H_{34}O_4Si + Na^+]$ = 497.2119 found 497.2123.

IR (neat):3466, 3073, 2931, 1669, 1590, 1515, 1269, 1158, 1085, 1022, 862 and 813 cm^{-1}.

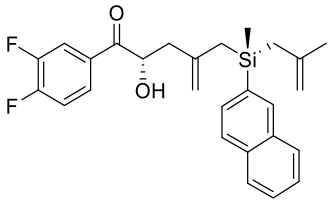


	Retention Time	Area	% Area
1	33.017	4021046	12.19
2	35.948	12409501	37.63
3	38.158	12578941	38.14
4	44.890	3970379	12.04



	Retention Time	Area	% Area
1	33.114	32796	0.13
2	36.078	74277	0.30
3	38.160	22547921	89.69
4	44.949	2484074	9.88

C28: (S)-1-(3,4-difluorophenyl)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-en-1-one



($C_{27}H_{28}F_2O_2Si$) Colorless oil; 40.1 mg, 89% yield, 99/99% ee, 87:13 dr; $[\alpha]^{19}_D$ = +25.7 (*c* = 0.50 g/100 mL, in CH_2Cl_2).

HPLC (Daicel chiralcel AYH, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 230 nm), t_1 = 8.63 min, t_2 = 9.88 min, t_3 =10.89 min, t_4 = 13.10 min.

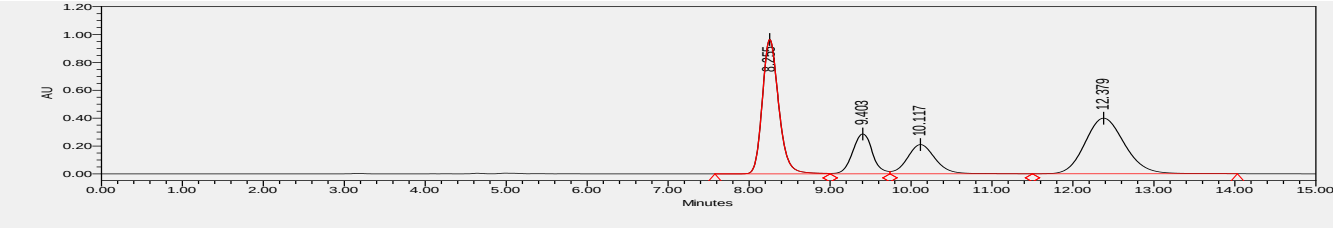
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (s, 1H), 7.86 – 7.72 (m, 3H), 7.68 – 7.55 (m, 2H), 7.54 – 7.47 (m, 2H), 7.10 (ddq, *J* = 7.5, 3.7, 1.6 Hz, 1H), 6.76 – 6.66 (m, 1H), 4.94 (ddt, *J* = 9.2, 6.6, 3.6 Hz, 1H), 4.75 (s, 1H), 4.70 (s, 1H), 4.63 – 4.57 (m, 1H), 4.53 – 4.47 (m, 1H), 3.42 (dd, *J* = 6.6, 4.2 Hz, 1H), 2.21 (dd, *J* = 14.5, 3.2 Hz, 1H), 2.04 (d, *J* = 13.8 Hz, 1H), 1.99 (d, *J* = 7.1 Hz, 1H), 1.97 – 1.93 (m, 1H), 1.92 – 1.87 (m, 2H), 1.58 (s, 3H), 0.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 199.2, 155.2 (d, $J_{C\text{-}F}$ = 12.8 Hz), 152.7 (d, $J_{C\text{-}F}$ = 12.6 Hz)., 151.8 (d, $J_{C\text{-}F}$ = 13.2 Hz), 149.3 (d, $J_{C\text{-}F}$ = 13.1 Hz), 142.7, 141.8, 134.9, 134.9, 133.9, 133.0, 130.7 (t, $J_{C\text{-}F}$ = 4.0 Hz), 130.2, 128.2, 127.9, 127.2, 126.8, 126.3, 125.5 (dd, $J_{C\text{-}F}$= 7.5, 3.7 Hz)., 118.1 – 117.5 (m), 112.7, 109.9, 71.8, 44.0, 26.3, 25.5, -5.4.

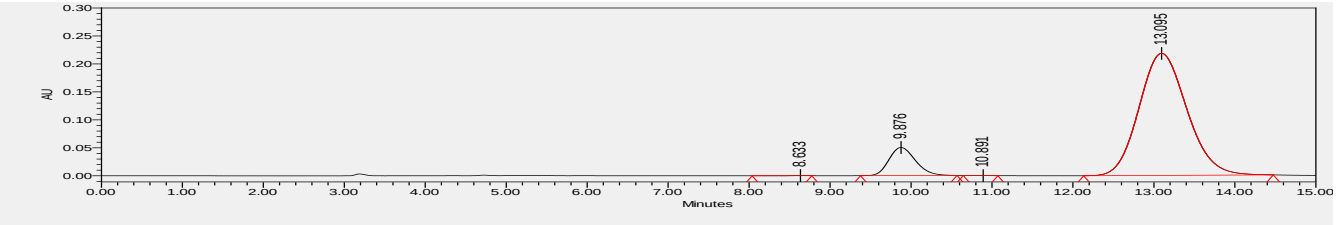
^{19}F NMR (376 MHz, $CDCl_3$) δ = -127.7, -135.0.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{27}H_{28}F_2O_2Si + Na^+]$ = 473.1719found 473.1728.

IR (neat): 3478, 3072, 2919, 1687, 1609, 1516, 1430, 1286, 1162, 1085, 864, 814, 777 and 745 cm^{-1}.

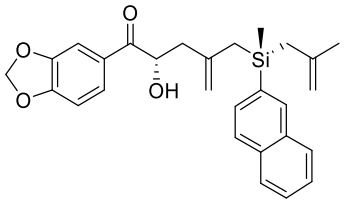


	Retention Time	Area	% Area
1	8.255	13557498	36.65
2	9.403	4877409	13.18
3	10.117	5008314	13.54
4	12.379	13553274	36.63



	Retention Time	Area	% Area
1	8.633	3535	0.03
2	9.876	1138582	11.27
3	10.891	764	0.01
4	13.095	8959107	88.69

C29: (S)-1-(benzo[d][1,3]dioxol-5-yl)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-en-1-one



($C_{28}H_{30}O_4Si$) Colorless oil; 35.2 mg, 76% yield, 99/99% ee, 88:12 dr; $[\alpha]^{19}_D$ = + 21.5 (*c* = 0.48 g/100 mL, in CH_2Cl_2).

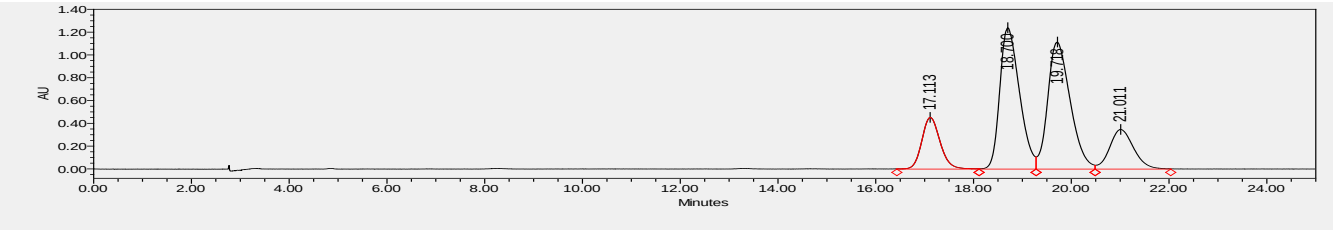
SFC (Daicel Chiralcel OJH, CO_2/MeOH = 90/10, 1.0 mL/min, λ = 230 nm), t_1 = 16.96 min, t_2 = 18.54 min, t_3 =19.59 min, t_4 = 20.83 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (s, 1H), 7.86 – 7.72 (m, 3H), 7.60 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.28 (d, *J* = 1.6 Hz, 1H), 7.01 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.40 (d, *J* = 8.2 Hz, 1H), 6.06 – 5.95 (m, 2H), 4.98 (ddd, *J* = 9.0, 6.9, 3.4 Hz, 1H), 4.72 (d, *J* = 5.8 Hz, 2H), 4.62 – 4.57 (m, 1H), 4.49 (s, 1H), 3.63 (d, *J* = 6.8 Hz, 1H), 2.28 (dd, *J* = 14.6, 3.1 Hz, 1H), 2.06 (d, *J* = 13.9 Hz, 1H), 2.01 (d, *J* = 8.2 Hz, 1H), 1.98 (d, *J* = 6.7 Hz, 1H), 1.89 (s, 2H), 1.56 (s, 3H), 0.43 (s, 3H).

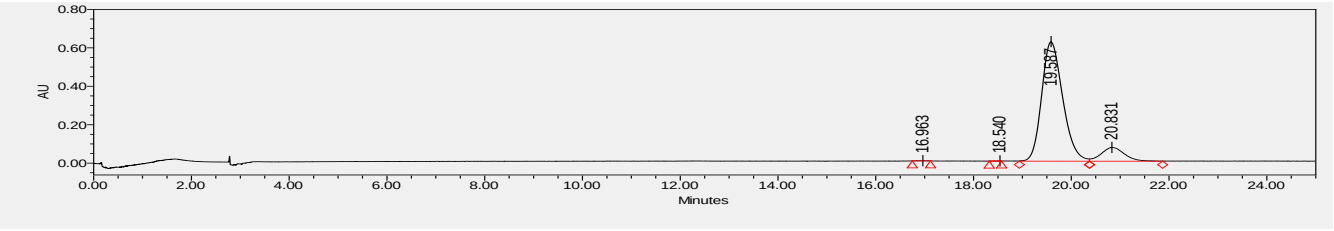
^{13}C NMR (101 MHz, $CDCl_3$) δ = 199.5, 152.5, 148.4, 142.8, 142.2, 135.0, 134.9, 133.9, 133.0, 130.3, 128.3, 128.1, 127.9, 127.2, 126.7, 126.2, 125.0, 112.4, 109.7, 108.3, 108.1, 102.1, 71.6, 44.6, 26.4, 25.5, 24.5, -5.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{28}H_{30}O_4Si + Na^+]$ = 481.1806 found 481.1813.

IR (neat): 3467, 3072, 2914, 1672, 1496, 1445, 1257, 1082, 1038, 869, 812 and 744 cm^{-1}.

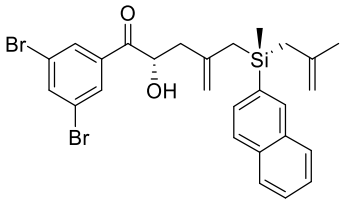


	Retention Time	Area	% Area
1	17.113	11833432	12.58
2	18.700	34721365	36.91
3	19.718	35615496	37.86
4	21.011	11901098	12.65



	Retention Time	Area	% Area
1	16.963	9837	0.05
2	18.540	5047	0.02
3	19.587	18539108	88.57
4	20.831	2377294	11.36

C30: (S)-1-(3,5-dibromophenyl)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-en-1-one



($C_{27}H_{28}Br_2O_2Si$) Colorless oil; 46.2 mg, 80% yield, 99/97% ee, 85:15 dr; $[\alpha]^{19}_D$ = - 5.2 (*c* = 0.59 g/100 mL, in CH_2Cl_2).

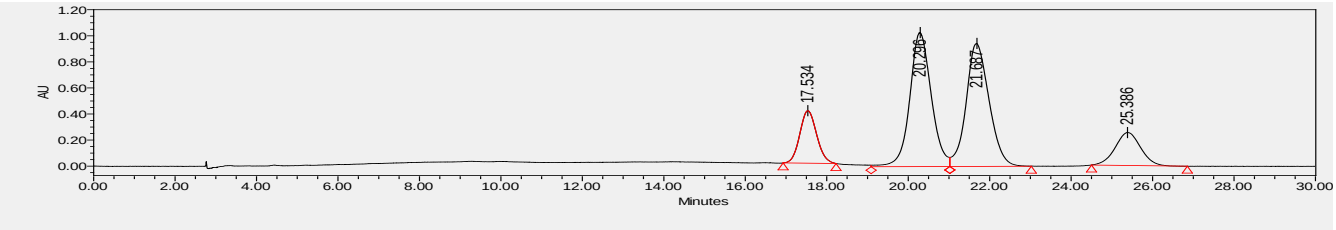
SFC (Daicel Chiralcel OJH, CO_2/MeOH = 90/10, 1.0 mL/min, λ = 230 nm), t_1 = 17.33 min, t_2 = 20.11 min, t_3 =21.58 min, t_4 = 25.09 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 (s, 1H), 7.84 (d, *J* = 1.2 Hz, 3H), 7.80 – 7.77 (m, 2H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.53 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.50 – 7.45 (m, 2H), 4.96 (ddd, *J* = 8.0, 6.7, 3.6 Hz, 1H), 4.73 (s, 1H), 4.71 – 4.67 (m, 1H), 4.62 – 4.59 (m, 1H), 4.53 – 4.48 (m, 1H), 3.30 (d, *J* = 6.6 Hz, 1H), 2.21 (dd, *J* = 14.5, 3.1 Hz, 1H), 2.03 – 1.96 (m, 1H), 1.94 (d, *J* = 3.4 Hz, 2H), 1.89 (d, *J* = 10.9 Hz, 2H), 1.58 (s, 3H), 0.44 (s, 3H).

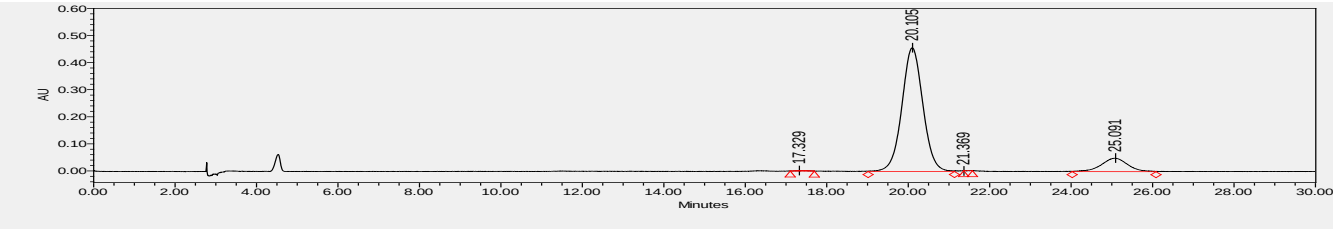
^{13}C NMR (101 MHz, $CDCl_3$) δ = 199.1, 142.8, 141.6, 139.0, 136.9, 134.9, 134.5, 133.8, 132.9, 130.3, 130.1, 128.2, 127.8, 127.1, 126.7, 126.1, 123.7, 112.8, 109.9, 72.5, 43.9, 26.0, 25.5, 24.9, -5.1.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{27}H_{28}Br_2O_2Si + Na^+]$ = 593.0118, 595.0097, 597.0077, found 593.0125, 595.0105, 597.0084.

IR (neat): 3482, 3071, 2917, 1689, 1633, 1552, 1408, 1249,1083, 860, 809 and 738 cm^{-1}.

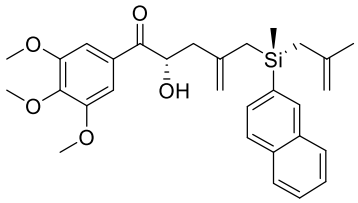


	Retention Time	Area	% Area
1	17.534	11586046	11.93
2	20.296	37670552	38.80
3	21.687	36845177	37.95
4	25.386	10993666	11.32



	Retention Time	Area	% Area
1	17.329	28758	0.15
2	20.105	16394934	87.78
3	21.581	5853	0.03
4	25.091	2247646	12.03

C31: (S)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)-1-(3,4,5-trimethoxyphenyl)pent-4-en-1-one



($C_{30}H_{36}O_5Si$) Colorless oil; 42.8 mg, 85% yield, 99/99% ee, 85:15 dr; $[\alpha]^{18}_D$ = +8.6 (*c* = 0.51 g/100 mL, in CH_2Cl_2).

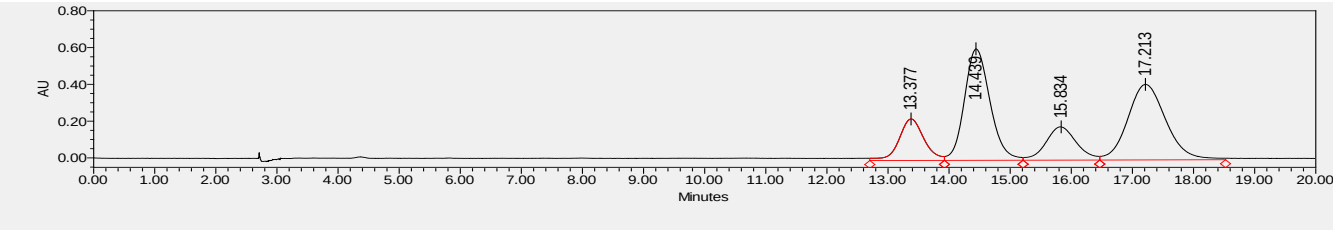
SFC (Daicel Chiralcel AYH, CO_2/EtOH = 80/20, 1,5 mL/min, λ = 230 nm), t_1 = 13.51 min, t_2 = 15.59 min, t_3 = 15.68 min, t_4 = 16.78 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.95 (s, 1H), 7.80 (dd, *J* = 5.7, 3.4 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 1H), 7.48 (dd, *J* = 6.5, 2.7 Hz, 2H), 7.08 (s, 2H), 5.08 (td, *J* = 7.5, 3.3 Hz, 1H), 4.73 (d, *J* = 3.4 Hz, 2H), 4.58 (s, 1H), 4.48 (s, 1H), 3.94 (s, 3H), 3.82 (s, 6H), 3.60 (d, *J* = 6.9 Hz, 1H), 2.36 (dd, *J* = 14.5, 2.9 Hz, 1H), 2.05 (dd, *J* = 14.5, 7.9 Hz, 1H), 1.99 (d, *J* = 3.8 Hz, 2H), 1.88 (s, 2H), 1.54 (s, 3H), 0.42 (s, 3H).

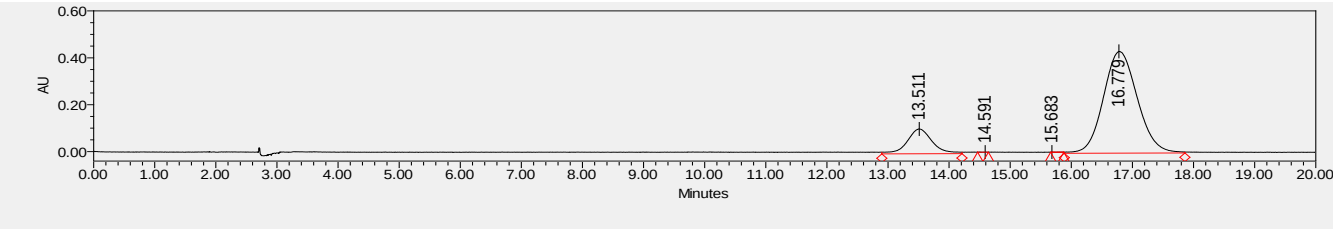
^{13}C NMR (151 MHz, $CDCl_3$) δ = 200.4, 153.3, 143.4, 142.8, 142.4, 134.9, 134.7, 133.8, 132.9, 130.2, 128.8, 128.2, 127.8, 127.0, 126.6, 126.1, 112.2, 109.7, 106.1, 72.5, 61.1, 56.4, 44.8, 26.1, 25.5, 24.9, -5.0.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{30}H_{36}O_5Si + Na^+]$ = 527.2224 found 527.2231.

IR (neat): 3473, 3050, 2937, 1675, 1584, 1503, 1458, 1414, 1330, 1237, 1162, 1128, 1056, 860, 815 and 744 cm^{-1}.

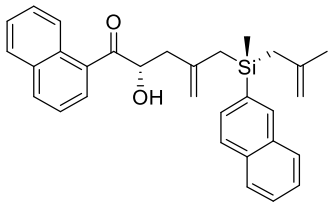


	Retention Time	Area	% Area
1	13.377	6401909	13.30
2	14.439	17584797	36.54
3	15.834	6299550	13.09
4	17.213	17837987	37.07



	Retention Time	Area	% Area
1	13.511	3019719	15.27
2	14.591	2293	0.01
3	15.683	3090	0.02
4	16.779	16749184	84.70

C32: (S)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)-1-(naphthalen-1-yl)pent-4-en-1-one



($C_{31}H_{32}O_2Si$) Colorless oil; 35.7 mg, 77% yield, 99/99% ee, 85:15 dr; $[\alpha]^{19}_D$ = + 18.7 (*c* = 0.57 g/100 mL, in CH_2Cl_2).

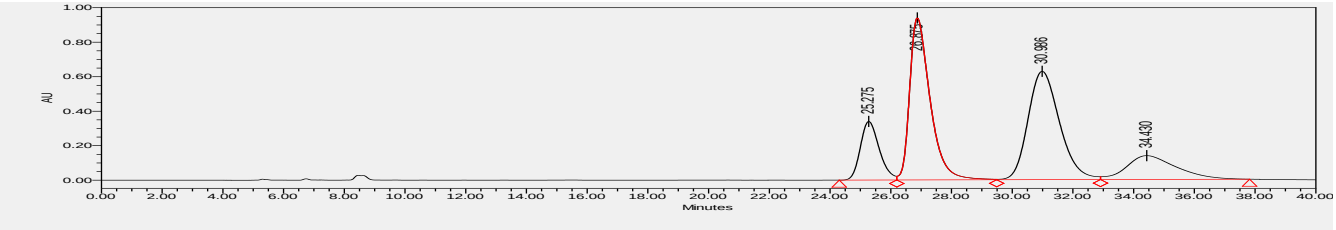
HPLC (Daicel chiralcel AYH, *n*-hexane/*i*-PrOH = 95/5, 0.6 mL/min, λ = 230 nm), t_1 = 25.36 min, t_2 = 27.20 min, t_3 =31.05 min, t_4 = 34.65 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.34 (dq, *J* = 6.8, 3.2 Hz, 1H), 7.92 – 7.82 (m, 3H), 7.78 – 7.72 (m, 2H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.51 – 7.45 (m, 2H), 7.44 – 7.37 (m, 2H), 7.11 (dd, *J* = 8.1, 7.3 Hz, 1H), 5.16 (ddd, *J* = 9.3, 5.9, 3.7 Hz, 1H), 4.66 (d, *J* = 5.6 Hz, 2H), 4.56 – 4.52 (m, 1H), 4.43 – 4.38 (m, 1H), 3.80 (d, *J* = 5.9 Hz, 1H), 2.16 (dd, *J* = 14.5, 3.4 Hz, 1H), 2.00 (dd, *J* = 9.7, 5.0 Hz, 1H), 1.96 (d, *J* = 5.6 Hz, 1H), 1.93 (d, *J* = 14.0 Hz, 1H), 1.81 – 1.75 (m, 2H), 1.50 (s, 3H), 0.31 (s, 3H).

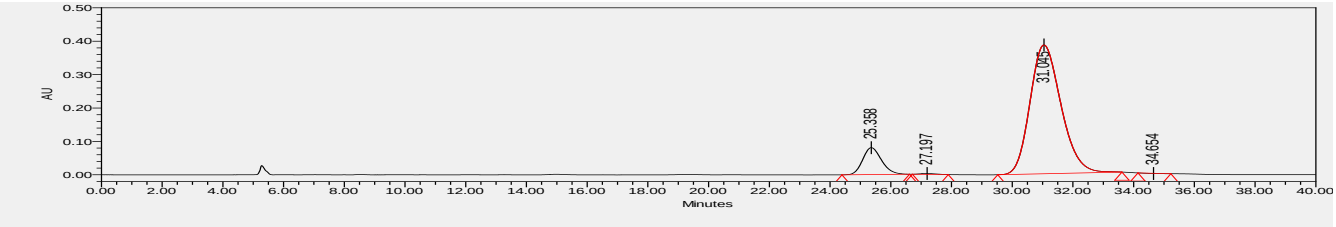
^{13}C NMR (101 MHz, $CDCl_3$) δ = 204.8, 142.8, 142.0, 134.9, 134.9, 134.0, 133.8, 133.5, 132.9, 132.3, 130.5, 130.1, 128.6, 128.3, 128.2, 127.9, 127.6, 127.0, 126.9, 126.6, 126.1, 125.5, 124.2, 112.4, 109.7, 73.5, 43.3, 26.3, 25.4, 24.4, -5.5.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{31}H_{32}O_2Si + Na^+]$ = 487.2064 found 487.2067.

IR (neat): 3466, 3051, 2961, 1678, 1635, 1507, 1278, 1247, 1082, 1065, 857, 812, 780 and 745 cm^{-1}.

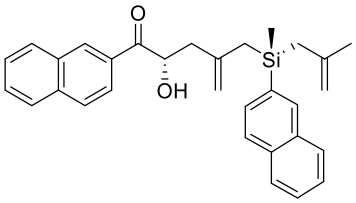


	Retention Time	Area	% Area
1	25.275	14710231	12.31
2	26.875	43837527	36.68
3	30.986	45328878	37.93
4	34.430	15642893	13.09



	Retention Time	Area	% Area
1	25.358	3469043	11.24
2	27.197	93075	0.30
3	31.045	27279452	88.38
4	34.654	24021	0.08

C33: (S)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)-1-(naphthalen-2-yl)pent-4-en-1-one



($C_{31}H_{32}O_2Si$) Colorless oil; 39.7 mg, 85% yield, 99/99% ee, 90:10 dr (determined by HPLC); $[\alpha]_D^{19}$ = -17.9 (*c* = 0.67 g/100 mL, in CH_2Cl_2).

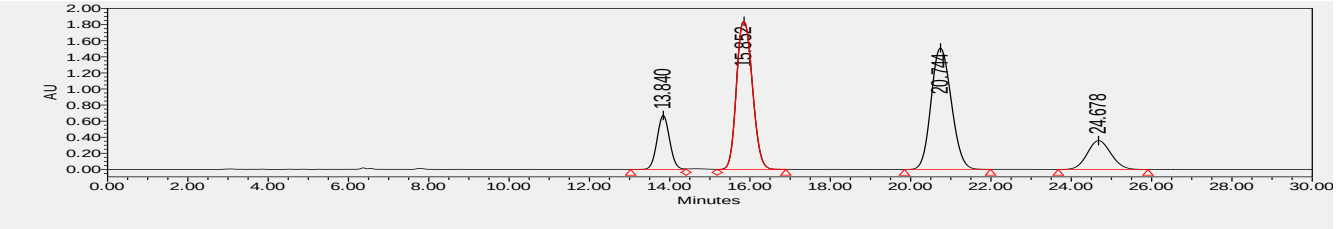
HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 230 nm), t_1 = 13.81 min, t_2 = 15.95 min, t_3 = 20.79 min, t_4 = 24.76 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = δ 8.30 (s, 1H), 7.94 (s, 1H), 7.83 (dt, *J* = 7.8, 4.1 Hz, 2H), 7.78 – 7.71 (m, 2H), 7.69 – 7.57 (m, 4H), 7.56 – 7.49 (m, 2H), 7.46 (dddd, *J* = 10.2, 7.9, 4.5, 2.5 Hz, 2H), 5.25 (ddd, *J* = 8.5, 6.7, 3.5 Hz, 1H), 4.77 – 4.71 (m, 2H), 4.59 – 4.53 (m, 1H), 4.47 (s, 1H), 3.70 (d, *J* = 6.7 Hz, 1H), 2.39 (dd, *J* = 14.5, 3.3 Hz, 1H), 2.12 – 2.07 (m, 1H), 2.05 (q, *J* = 3.5, 2.7 Hz, 1H), 1.99 (d, *J* = 13.7 Hz, 1H), 1.86 (d, *J* = 6.1 Hz, 2H), 1.53 (s, 3H), 0.39 (s, 3H).

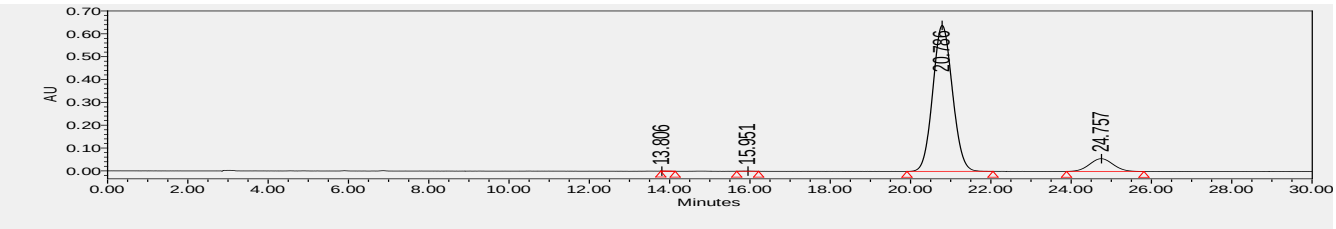
^{13}C NMR (101 MHz, $CDCl_3$) δ = 201.6, 142.8, 142.1, 136.0, 134.9, 134.9, 132.9, 132.5, 131.0, 130.4, 130.2, 130.0, 129.1, 128.9, 128.2, 128.0, 127.9, 127.9, 127.2, 127.1, 126.6, 126.1, 123.9, 112.4, 109.7, 72.2, 44.5, 26.3, 25.5, 24.6, -5.2.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{31}H_{32}O_2Si + Na^+]$ =m 487.2064 found 487.2070.

IR (neat):3470, 3053, 2917, 1677, 1631, 1465, 1278, 1176, 1084, 978, 858, 815 and 748 cm^{-1}.

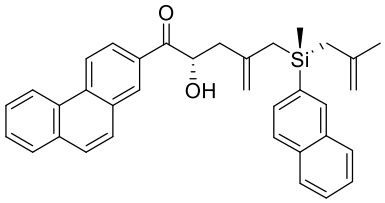


	Retention Time	Area	% Area
1	13.840	14615120	11.00
2	15.852	50678155	38.15
3	20.744	52927410	39.84
4	24.678	14628437	11.01



	Retention Time	Area	% Area
1	13.806	1483	0.01
2	15.951	14245	0.06
3	20.786	21708724	90.50
4	24.757	2262916	9.43

C34: (S)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)-1-(phenanthren-2-yl)pent-4-en-1-one



($C_{35}H_{34}O_2Si$) Colorless oil; 36.3 mg, 70% yield, 99/99% ee, 86:14 dr; $[\alpha]^{21}_D$ = -1.1 (*c* = 0.43 g/100 mL, in CH_2Cl_2).

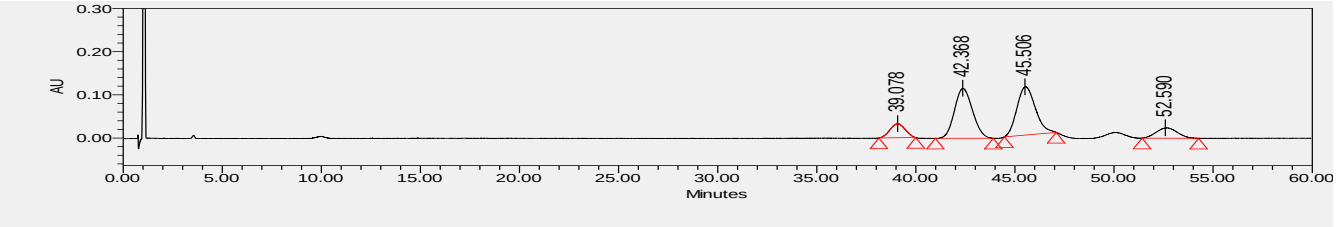
SFC Daicel Chiralcel AD-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 230 nm, t_1 = 38.98 min, t_2 = 42.26 min, t_3 = 45.24 min, t_4 = 52.47 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.19 (s, 1H), 8.67 (m, 1H), 7.93 – 7.80 (m, 3H), 7.76 – 7.60 (m, 7H), 7.57 – 7.34 (m, 4H), 5.31 (ddd, *J* = 8.7, 6.9, 3.4 Hz, 1H), 4.77 (s, 2H), 4.58 (s, 1H), 4.49 (s, 1H), 3.75 (d, *J* = 6.6 Hz, 1H), 2.39 (dd, *J* = 14.5, 3.2 Hz, 1H), 2.13 – 1.99 (m, 3H), 1.89 (d, *J* = 13.9 Hz, 2H), 1.52 (s, 3H), 0.39 (s, 3H).

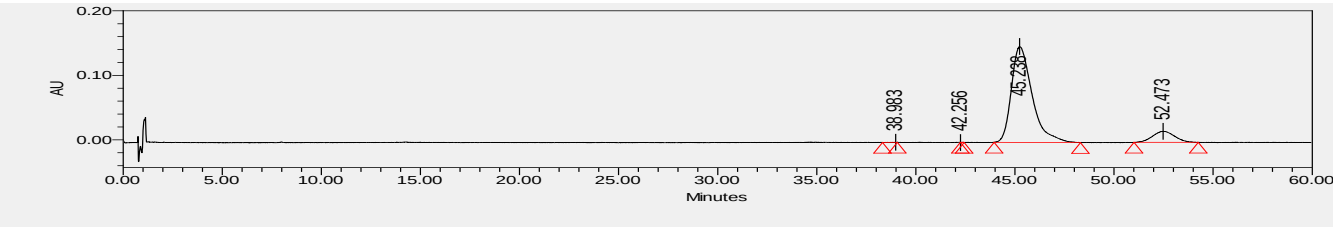
^{13}C NMR (101 MHz, $CDCl_3$) δ = 201.7, 142.8, 142.2, 135.5, 134.8, 133.8, 132.9, 132.3, 131.2, 130.6, 130.4, 130.2, 130.0, 129.2, 129.0, 128.2, 127.8, 127.6, 127.6, 127.1, 126.6, 126.3, 126.1, 125.2, 124.4, 122.8, 112.5, 109.7, 72.3, 44.6, 26.3, 25.5, 24.7, -5.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{35}H_{34}O_2Si + Na^+]$ = 537.2220 found 537.2227.

IR (neat): 3472, 3052, 2918, 1677, 1635, 1401, 1249, 1161, 1085, 980, 852, 813 and 745 cm^{-1}.

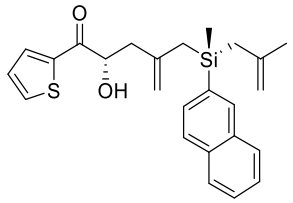


	Retention Time	Area	% Area
1	39.078	1720095	9.53
2	42.368	7315628	40.54
3	45.506	7240887	40.12
4	52.590	1770854	9.81



	Retention Time	Area	% Area
1	38.983	3733	0.03
2	42.256	1339	0.01
3	45.238	10846181	89.30
4	52.473	1294812	10.66

C35: (S)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)-1-(thiophen-2-yl)pent-4-en-1-one



($C_{25}H_{28}O_2SSi$) Colorless oil; 32.3 mg, 77% yield, 99/99% ee, 90:10 dr; $[\alpha]\ ^{19}_D$ = +44.9 (*c* = 0.48 g/100 mL, in CH_2Cl_2).

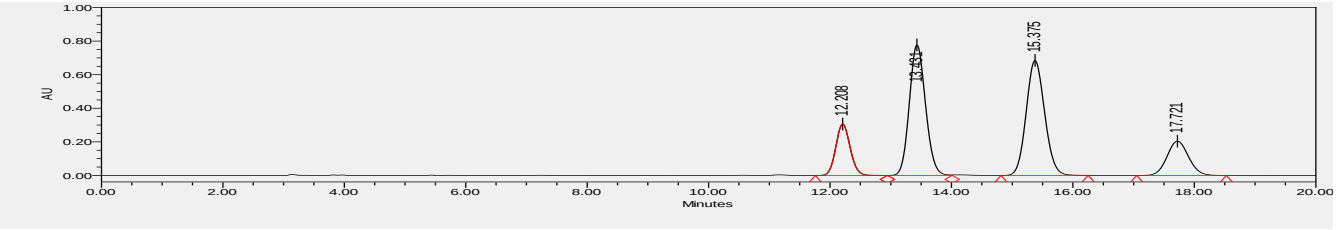
HPLC (Daicel chiralcel OXH, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 230 nm), t_1 = 12.21 min, t_2 = 14.45 min, t_3 =15.37 min, t_4 = 17.72 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (s, 1H), 7.87 – 7.76 (m, 3H), 7.66 – 7.57 (m, 1H), 7.55 – 7.46 (m, 3H), 6.97 – 6.91 (m, 1H), 6.53 (dd, *J* = 4.8, 4.0 Hz, 1H), 4.82 (ddd, *J* = 9.9, 6.8, 3.6 Hz, 1H), 4.76 (d, *J* = 7.4 Hz, 2H), 4.63 – 4.58 (m, 1H), 4.51 (s, 1H), 3.39 (d, *J* = 6.7 Hz, 1H), 2.43 – 2.29 (m, 1H), 2.14 – 2.09 (m, 1H), 2.06 (s, 1H), 2.03 – 1.98 (m, 1H), 1.91 (s, 2H), 1.58 (s, 3H), 0.45 (s, 3H).

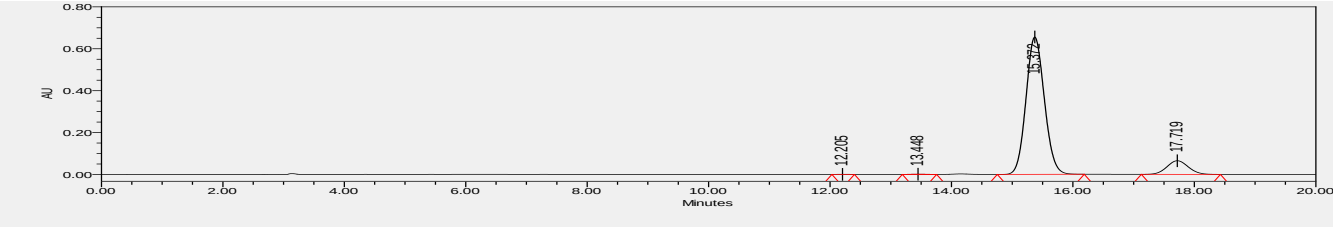
^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.0, 142.8, 142.0, 139.7, 135.2, 134.9, 134.7, 134.0, 133.1, 133.0, 130.3, 128.3, 128.3, 127.9, 127.3, 126.8, 126.3, 112.9, 109.8, 72.5, 45.1, 26.5, 25.5, 24.2, -5.5.

HRMS (ESI) m/z: $[M-H]^-$ Calculated for $[C_{25}H_{28}O_2SSi-H^-]$ = 419.1507 found 419.1507.

IR (neat): 3472, 2962, 2916, 1659, 1411, 1353, 1274, 1253, 1159, 1083, 1056, 875, 856, 815, 744 and 726 cm^{-1}.

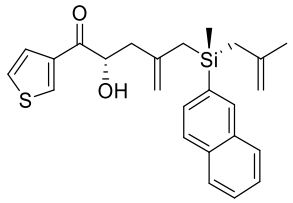


	Retention Time	Area	% Area
1	12.208	5023161	12.94
2	13.431	14380567	37.03
3	15.375	14416616	37.13
4	17.721	5011401	12.91



	Retention Time	Area	% Area
1	12.205	5203	0.03
2	13.448	17014	0.11
3	15.372	13771519	89.54
4	17.719	1586800	10.32

C36: (S)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)-1-(thiophen-3-yl)pent-4-en-1-one



($C_{25}H_{28}O_2SSi$) Colorless oil; 33.6 mg, 80% yield, 98/95% ee, 90:10 dr; $[\alpha]\ ^{18}_D$ = +32.3 (*c* = 0.46 g/100 mL, in CH_2Cl_2).

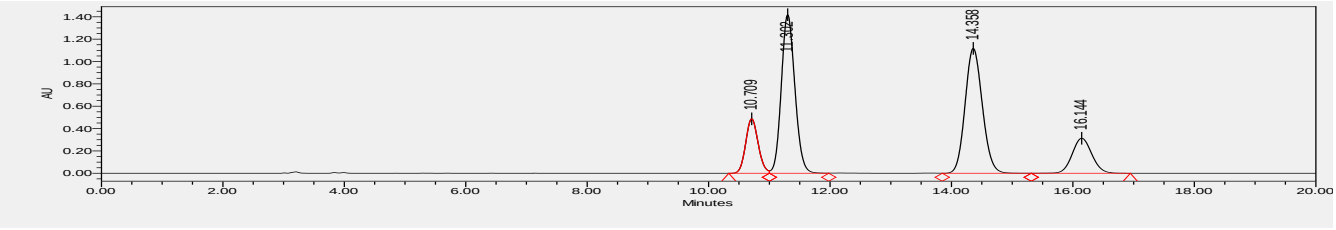
HPLC (Daicel chiralcel OXH, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 230 nm), t_1 = 10,71 min, t_2 = 11.31 min, t_3 =14.36 min, t_4 = 16.13 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (s, 1H), 7.84 (dt, *J* = 8.2, 4.2 Hz, 3H), 7.64 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.52 (tq, *J* = 9.8, 4.8 Hz, 2H), 7.35 – 7.29 (m, 1H), 7.19 – 7.10 (m, 1H), 6.99 (dd, *J* = 5.1, 2.9 Hz, 1H), 4.77 (q, *J* = 6.4, 4.9 Hz, 2H), 4.74 (s, 1H), 4.63 – 4.58 (m, 1H), 4.54 – 4.47 (m, 1H), 3.50 (t, *J* = 6.5 Hz, 1H), 2.37 – 2.23 (m, 1H), 2.10 (d, *J* = 13.8 Hz, 1H), 2.03 (t, *J* = 4.8 Hz, 1H), 1.99 (dd, *J* = 8.1, 4.1 Hz, 1H), 1.90 (s, 2H), 1.58 (s, 3H), 0.45 (s, 3H).

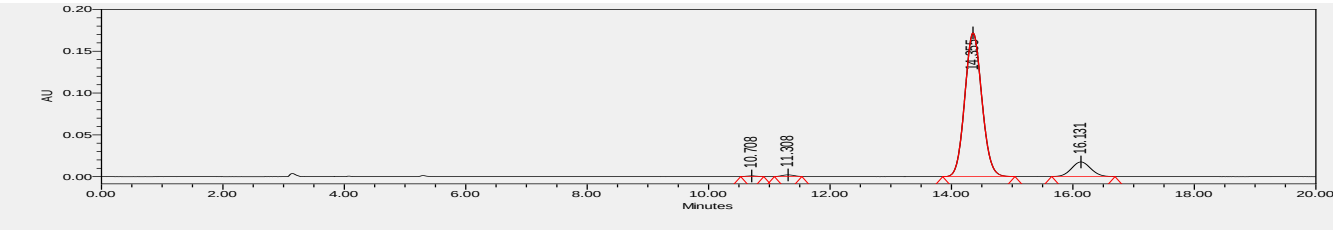
^{13}C NMR (101 MHz, $CDCl_3$) δ = 195.4, 142.7, 142.1, 137.8, 135.2, 134.9, 134.0, 133.4, 133.1, 130.3, 128.3, 128.0, 127.5, 126.9, 126.7, 126.4, 112.7, 109.8, 72.5, 44.5, 26.7, 25.5, 24.1, -5.6.

HRMS (ESI) m/z: $[M-H]^-$ Calculated for $[C_{25}H_{28}O_2SSi-H^-]$ = 419.1507 found 419.1507.

IR (neat): 3474, 3075, 2917, 1671, 1635, 1509, 1379, 1255, 1162, 1082, 860, 812 and 746 cm^{-1}.

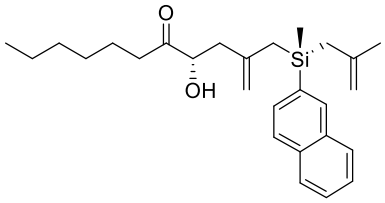


	Retention Time	Area	% Area
1	10.709	6967889	11.99
2	11.302	22024341	37.89
3	14.358	22094138	38.01
4	16.144	7041964	12.11



	Retention Time	Area	% Area
1	10.708	9450	0.25
2	11.308	26881	0.71
3	14.355	3354684	88.94
4	16.131	380919	10.10

C37: (S)-4-hydroxy-2-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)undec-1-en-5-one



($C_{27}H_{38}O_2Si$) Yellow oil; 17.7 mg, 42% yield, 91/82% ee, 84:16 dr; $[\alpha]_D^{22}$ = +51.1(*c* = 0.17 g/100 mL, in CH_2Cl_2).

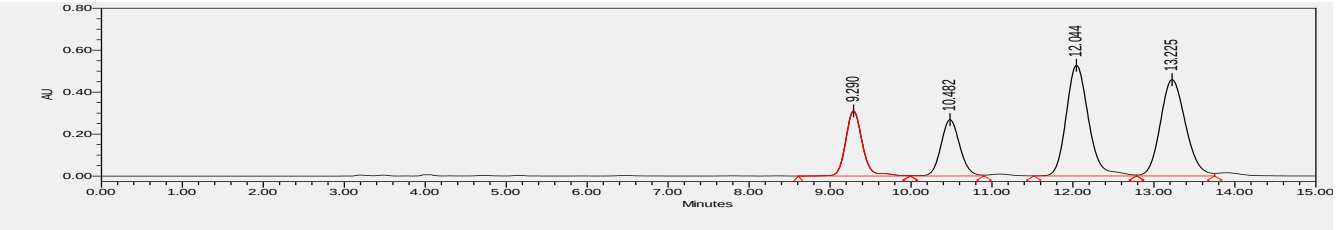
HPLC (Daicel chiralcel OXH, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 230 nm), t_1 = 9,23 min, t_2 = 10.44 min, t_3 = 11.95 min, t_4 = 13.10 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (d, *J* = 6.0 Hz, 1H), 7.89 – 7.76 (m, 3H), 7.67 – 7.59 (m, 1H), 7.50 (dtd, *J* = 7.9, 4.1, 1.8 Hz, 2H), 4.75 (d, *J* = 13.3 Hz, 2H), 4.66 – 4.58 (m, 1H), 4.54 – 4.49 (m, 1H), 4.14 – 3.95 (m, 1H), 3.27 (d, *J* = 4.9 Hz, 1H), 2.11 – 2.05 (m, 1H), 2.00 (dd, *J* = 17.7, 4.4 Hz, 2H), 1.95 – 1.90 (m, 2H), 1.89 – 1.77 (m, 2H), 1.71 (dt, *J* = 17.2, 7.3 Hz, 1H), 1.63 – 1.58 (m, 3H), 1.29 – 1.18 (m, 4H), 1.15 – 1.04 (m, 2H), 0.96 – 0.77 (m, 5H), 0.49 (s, 3H).

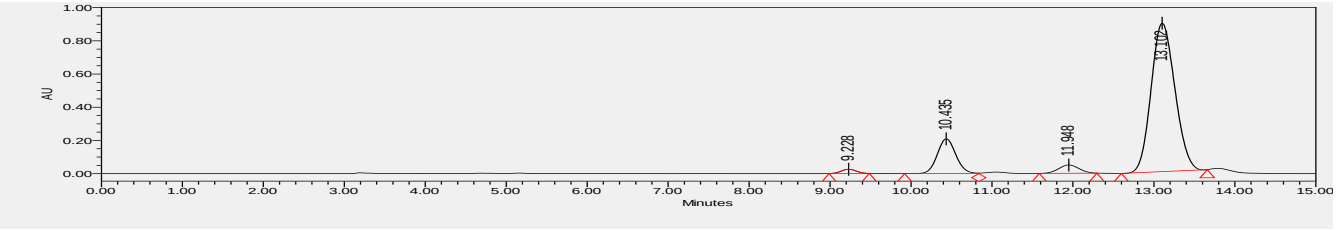
^{13}C NMR (101 MHz, $CDCl_3$) δ = 212.1, 142.8, 142.2, 135.2, 134.9, 133.9, 133.1, 130.2, 128.2, 127.9, 127.3, 126.8, 126.3, 112.6, 109.8, 74.6, 42.3, 37.6, 31.6, 28.7, 26.5, 25.5, 24.0, 23.3, 22.6, 14.2, -5.7.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{27}H_{38}O_2Si + Na^+]$ = 445.2533 found 445.2538.

IR (neat): 3474, 3050, 2927, 1711, 1636, 1499, 1252, 1085, 858, 815 and 744 cm^{-1}.

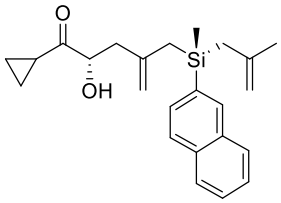


	Retention Time	Area	% Area
1	9.290	4452121	15.44
2	10.482	4340289	15.05
3	12.044	10136423	35.16
4	13.225	9900819	34.34



	Retention Time	Area	% Area
1	9.228	328584	1.44
2	10.435	3337830	14.65
3	11.948	868022	3.81
4	13.102	18251079	80.10

C38: (S)-1-cyclopropyl-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-en-1-one



($C_{24}H_{30}O_2Si$) Colorless oil; 33.7 mg, 89% yield, 99/99% ee, 84:16 dr; $[\alpha]^{25}_D$ = +97.4 (*c* = 0.43 g/100 mL, in CH_2Cl_2).

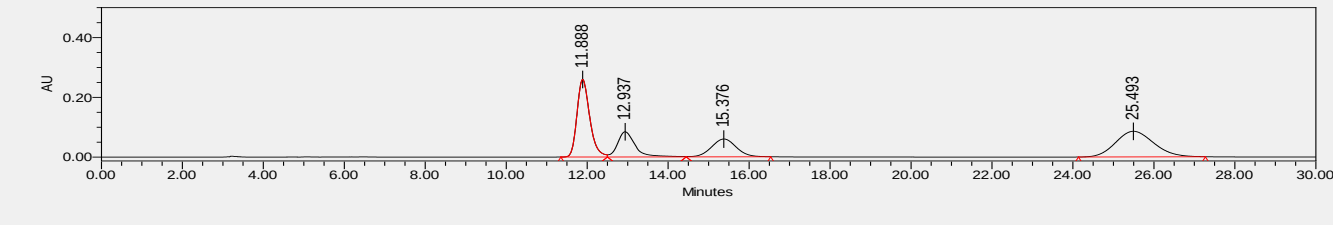
HPLC (Daicel chiralcel AYH, *n*-hexane/*i*-PrOH = 97/3, 1.0 mL/min, λ = 230 nm), t_1 = 11.88 min, t_2 = 12.93 min, t_3 = 15.34 min, t_4 = 25.16 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.07 (s, 1H), 7.81 (ddd, *J* = 22.2, 5.9, 3.2 Hz, 3H), 7.65 (ddd, *J* = 14.8, 8.2, 1.0 Hz, 1H), 7.48 (dt, *J* = 6.2, 3.2 Hz, 2H), 4.83 – 4.74 (m, 2H), 4.66 – 4.61 (m, 1H), 4.56 – 4.52 (m, 1H), 4.22 (ddd, *J* = 10.0, 5.1, 3.0 Hz, 1H), 3.34 (dd, *J* = 27.6, 5.1 Hz, 1H), 2.17 (d, *J* = 14.2 Hz, 1H), 2.12 – 1.98 (m, 2H), 1.95 (s, 2H), 1.87 (ddd, *J* = 37.5, 14.6, 9.8 Hz, 1H), 1.62 (s, 3H), 0.85 – 0.77 (m, 1H), 0.70 (qd, *J* = 6.1, 5.4, 3.3 Hz, 2H), 0.50 (s, 3H), 0.35 (dtd, *J* = 9.1, 7.5, 3.3 Hz, 1H), 0.28 – 0.21 (m, 1H).

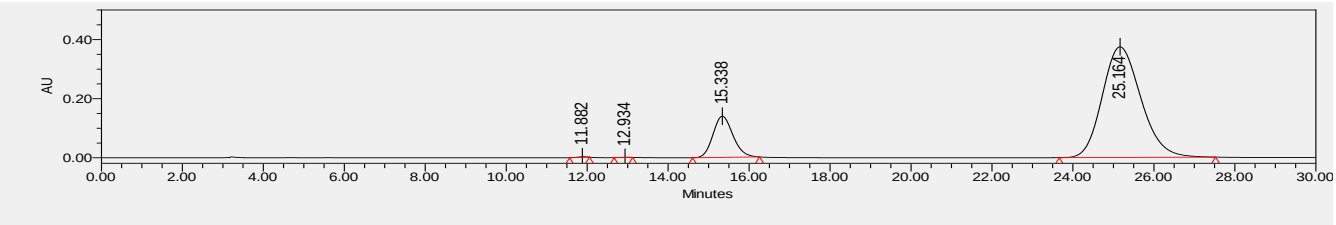
^{13}C NMR (151 MHz, $CDCl_3$) δ = 211.9, 142.7, 142.2, 135.5, 134.9, 133.8, 133.0, 130.3, 128.1, 127.7, 127.3, 126.8, 126.3, 112.6, 109.9, 75.0, 42.3, 26.4, 25.5, 24.1, 16.7, 11.8, -6.0.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{24}H_{30}O_2Si + Na^+]$ = 401.1907 found 401.1907.

IR (neat): 3469, 3051, 2917, 1694, 1635, 1373, 1251, 1373, 1251, 1159, 1082, 1059, 1012, 873, 856, 813 and 745 cm^{-1}.

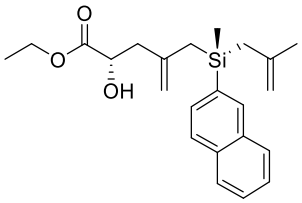


	Retention Time	Area	% Area
1	11.888	5681137	34.65
2	12.937	2555067	15.58
3	15.376	2537493	15.48
4	25.493	5623309	34.29



	Retention Time	Area	% Area
1	11.882	27716	0.09
2	12.934	8772	0.03
3	15.338	4767968	16.11
4	25.164	24797262	83.77

C39: ethyl (S)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-enoate



($C_{23}H_{30}O_3Si$) Colorless oil; 10.3 mg, 27% yield, 99/99% ee, 78:22 dr; $[\alpha]^{24}_D = +19.2$ ($c = 0.17$ g/100 mL, in CH_2Cl_2).

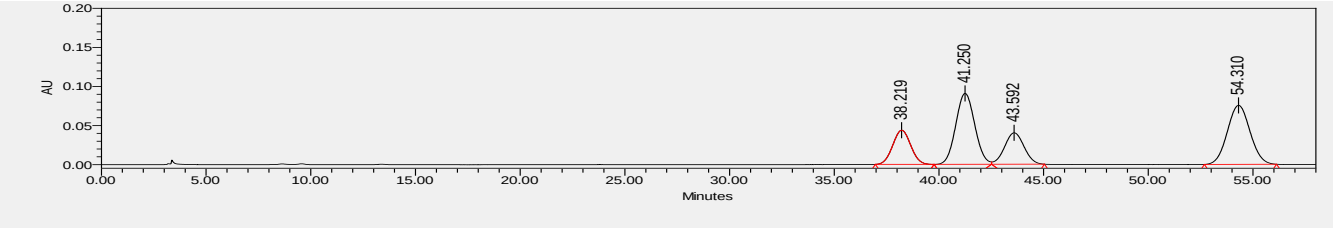
HPLC (Daicel chiralcel OXH, *n*-hexane/*i*-PrOH = 99/1, 1.0 mL/min, λ = 230 nm), $t_1 = 38.52$ min, $t_2 = 41.73$ min, $t_3 = 43.92$ min, $t_4 = 54.66$ min.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.01 (s, 1H), 7.83 (dd, *J* = 10.4, 6.2 Hz, 3H), 7.60 (dd, *J* = 8.0, 3.8 Hz, 1H), 7.55 – 7.44 (m, 2H), 4.74 (d, *J* = 5.7 Hz, 2H), 4.61 (s, 1H), 4.52 (s, 1H), 4.20 (ddt, *J* = 13.7, 9.0, 4.8 Hz, 1H), 4.13 – 4.00 (m, 2H), 2.64 (dd, *J* = 11.7, 5.8 Hz, 1H), 2.22 (dd, *J* = 14.2, 3.4 Hz, 1H), 2.11 (td, *J* = 15.5, 14.2, 8.6 Hz, 1H), 2.00 (d, *J* = 13.8 Hz, 1H), 1.95 (d, *J* = 5.5 Hz, 1H), 1.92 (d, *J* = 5.2 Hz, 2H), 1.58 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 1H), 1.10 (t, *J* = 7.1 Hz, 2H), 0.47 (s, 3H).

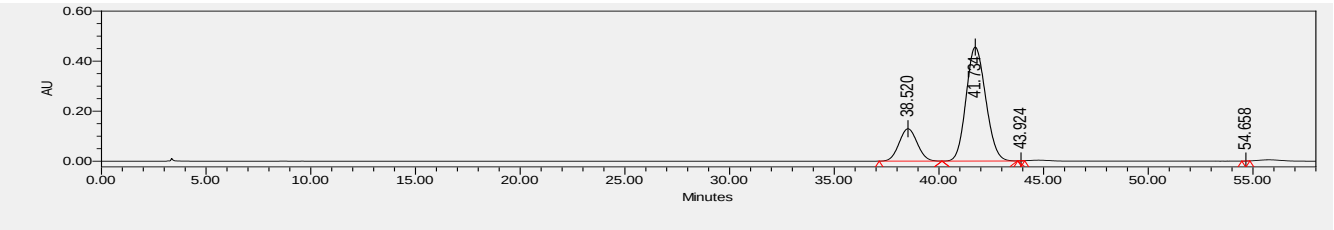
^{13}C NMR (151 MHz, $CDCl_3$) δ = 174.7, 142.9, 142.0, 134.9, 133.9, 133.0, 130.3, 128.3, 127.8, 127.1, 126.6, 126.1, 112.6, 109.7, 69.1, 61.6, 43.1, 26.3, 25.5, 24.3, 14.1, -5.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{23}H_{30}O_3Si + Na^+]$ = 405.1856 found 405.1859.

IR (neat): 3471, 3048, 2922, 1730, 1634, 1372, 1252, 1200, 1160, 1085, 1028, 860, 810 and 743 cm^{-1}.

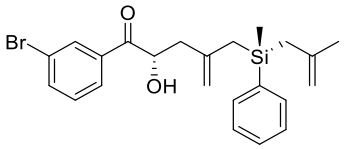


	Retention Time	Area	% Area
1	38.219	2610182	15.69
2	41.250	5727556	34.43
3	43.592	2603494	15.65
4	54.310	5691975	34.22



	Retention Time	Area	% Area
1	38.520	7800691	20.82
2	41.734	29661865	79.17
3	43.924	2009	0.01
4	54.658	2166	0.01

C40: (S)-1-(3-bromophenyl)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(phenyl)silyl)methyl)pent-4-en-1-one



($C_{23}H_{27}BrO_2Si$) Colorless oil; 37.3 mg, 84% yield, 99/99% ee, 85:15 dr (determined by SFC); $[\alpha]_D^{22}$ = -4.1 (*c* = 0.54 g/100 mL, in CH_2Cl_2).

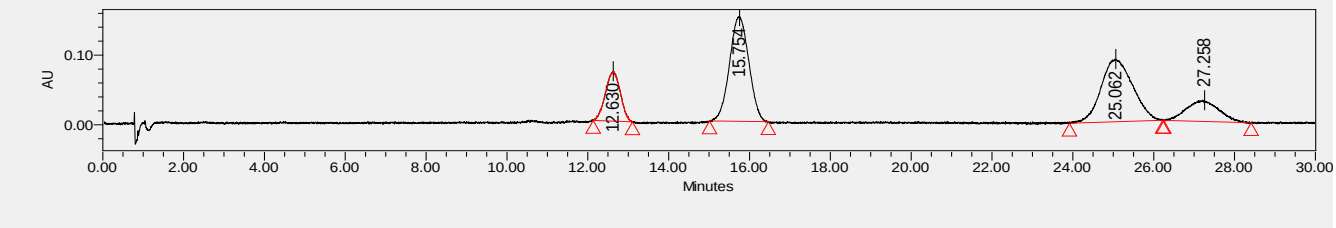
SFC (Daicel Chiralcel IG-3, CO_2/MeOH = 95/5, 1.5 mL/min, λ = 230 nm), t_1 = 12.70 min, t_2 = 15.75 min, t_3 = 25.11 min, t_4 = 27.24 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 (d, *J* = 5.2 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.35 – 7.26 (m, 4H), 5.03 (tt, *J* = 6.7, 3.5 Hz, 1H), 4.71 (d, *J* = 6.3 Hz, 2H), 4.62 – 4.56 (m, 1H), 4.47 (s, 1H), 3.45 (d, *J* = 6.7 Hz, 1H), 2.25 (td, *J* = 14.4, 13.9, 2.9 Hz, 1H), 2.00 – 1.93 (m, 1H), 1.88 (dd, *J* = 13.7, 3.6 Hz, 2H), 1.81 (s, 2H), 1.56 (s, 3H), 0.33 (s, 3H).

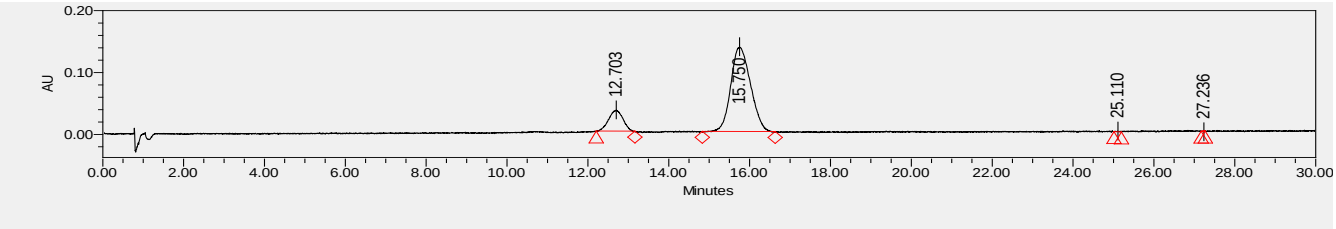
^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.4, 142.8, 141.8, 137.2, 136.8, 135.6, 134.0, 131.7, 130.6, 129.4, 127.9, 127.1, 123.3, 112.5, 109.7, 72.2, 44.0, 26.1, 25.5, 24.6, -5.4.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{23}H_{27}BrO_2Si + Na^+]$ = 465.0856, 467.0835, found 465.0862, 467.0840.

IR (neat): 3479, 3071, 2921, 1687, 1635, 1565, 1424, 1252, 1112, 980, 876, 815 and 706 cm^{-1}.

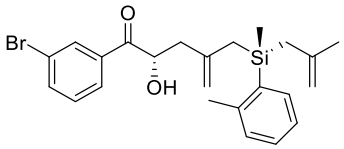


	Retention Time	Area	% Area
1	12.630	1812140	13.58
2	15.754	4976531	37.30
3	25.062	4886437	36.62
4	27.258	1668464	12.50



	Retention Time	Area	% Area
1	12.703	822930	15.15
2	15.750	4600387	84.72
3	25.110	4791	0.09
4	27.236	2079	0.04

C41: (S)-1-(3-bromophenyl)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(o-tolyl)silyl)methyl)pent-4-en-1-one



($C_{24}H_{29}BrO_2Si$) Colorless oil; 33.7 mg, 74% yield, 99/99% ee, 75:25 dr; $[\alpha]^{22}_D$ = -7.5 (*c* = 0.46 g/100 mL, in CH_2Cl_2).

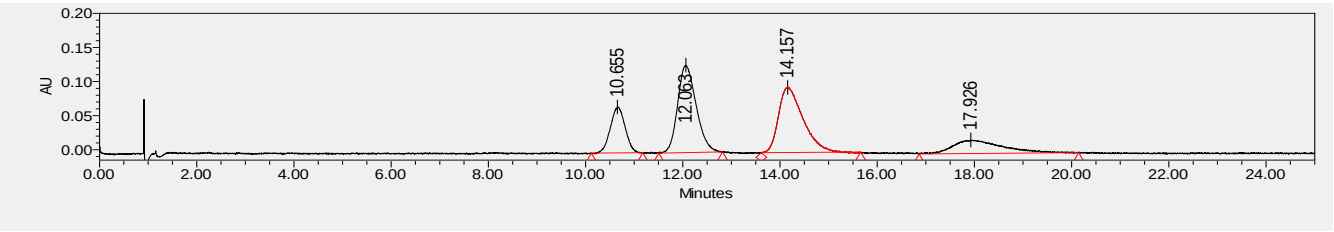
SFC (Daicel Chiralcel IF-3 , CO_2/MeOH = 95/5, 1.5 mL/min, λ = 230 nm), t_1 = 10.62 min, t_2 = 11.90 min, t_3 = 14.16 min, t_4 = 18.07 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.99 (dt, *J* = 14.3, 1.7 Hz, 1H), 7.72 (dtd, *J* = 7.9, 2.3, 1.9, 1.0 Hz, 1H), 7.62 – 7.59 (m, 1H), 7.41 – 7.35 (m, 1H), 7.34 – 7.28 (m, 1H), 7.26 – 7.20 (m, 1H), 7.15 – 7.06 (m, 2H), 5.08 – 5.01 (m, 1H), 4.70 (dd, *J* = 12.6, 8.7 Hz, 2H), 4.58 – 4.56 (m, 1H), 4.46 (s, 1H), 3.46 (d, *J* = 6.6 Hz, 1H), 2.44 (s, 3H), 2.30 (ddd, *J* = 14.2, 10.5, 2.8 Hz, 1H), 2.05 – 2.00 (m, 1H), 1.99 – 1.90 (m, 2H), 1.89 – 1.82 (m, 2H), 1.56 (s, 3H), 0.38 (3, 3H).

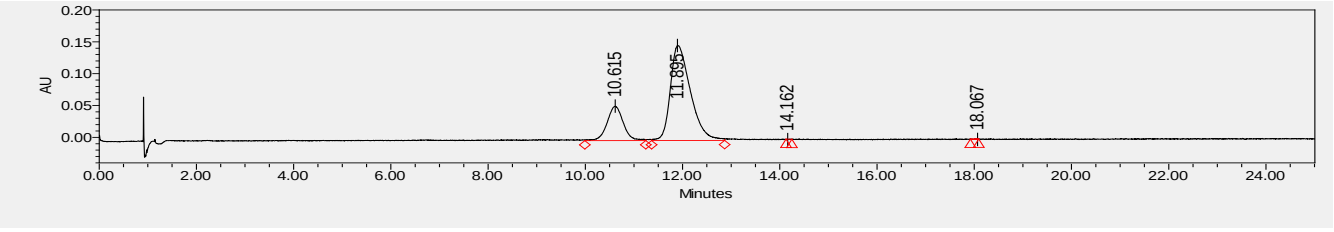
^{13}C NMR (151 MHz, $CDCl_3$) δ = 200.4, 143.6, 143.1, 142.1, 136.8, 135.7, 135.5, 135.2, 131.7, 130.6, 130.2, 129.70 127.1, 125.2, 123.4, 112.6, 109.8, 72.3, 43.9, 26.7, 25.3, 25.0, 23.6, -3.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{24}H_{29}BrO_2Si + Na^+]$ = 479.1012, 481.0992, found 479.1019, 481.0996.

IR (neat): 3479, 3072, 2924, 1686, 1634, 1565, 1417, 1282, 1252, 1080, 980, 876, 817 and 745 cm^{-1}.

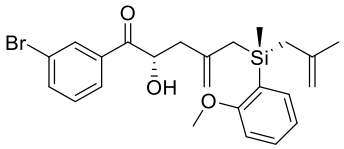


	Retention Time	Area	% Area
1	10.655	1419263	14.86
2	12.063	3399882	35.61
3	14.157	3347235	35.06
4	17.926	1381602	14.47



	Retention Time	Area	% Area
1	10.615	1246976	22.58
2	11.895	4271327	77.34
3	14.162	1680	0.03
4	18.067	2717	0.05

C42: (S)-1-(3-bromophenyl)-2-hydroxy-4-(((S)-(2-methoxyphenyl)(methyl)(2-methylallyl)silyl)methyl)pent-4-en-1-one



($C_{24}H_{29}BrO_3Si$) Colorless oil; 38.4 mg, 81% yield, 99/99% ee, 80:20 dr; $[\alpha]^{21}_D$ = +17.7 (*c* = 0.43 g/100 mL, in CH_2Cl_2).

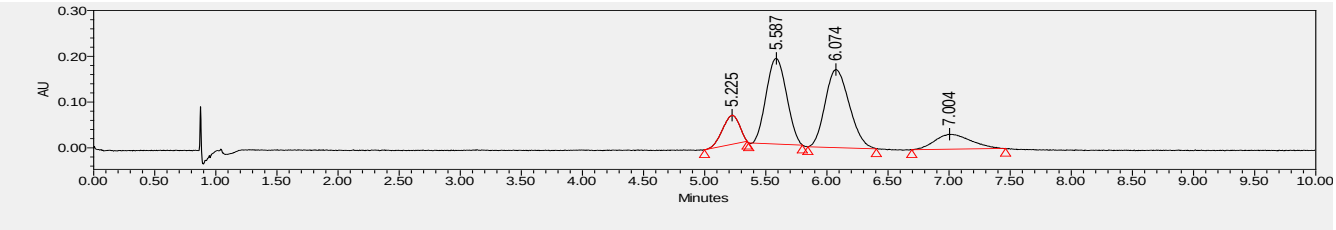
SFC (Daicel Chiralcel IF-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 230 nm), t_1 = 5.32 min, t_2 = 5.71 min, t_3 = 6.20 min, t_4 = 7.16 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 (dt, *J* = 12.1, 1.7 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.60 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.38 – 7.32 (m, 1H), 7.32 – 7.26 (m, 2H), 6.93 (td, *J* = 7.3, 0.8 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 5.04 (ddd, *J* = 8.9, 6.6, 3.6 Hz, 1H), 4.67 (d, *J* = 4.7 Hz, 2H), 4.53 (ddd, *J* = 5.1, 2.4, 1.2 Hz, 1H), 4.45 – 4.39 (m, 1H), 3.78 (s, 3H), 3.38 (d, *J* = 6.6 Hz, 1H), 2.32 (dd, *J* = 14.6, 3.4 Hz, 1H), 2.08 – 1.96 (m, 2H), 1.93 – 1.89 (m, 1H), 1.89 – 1.86 (m, 1H), 1.82 (dd, *J* = 13.3, 0.8 Hz, 1H), 1.57 – 1.50 (m, 3H), 0.30 (s, 3H).

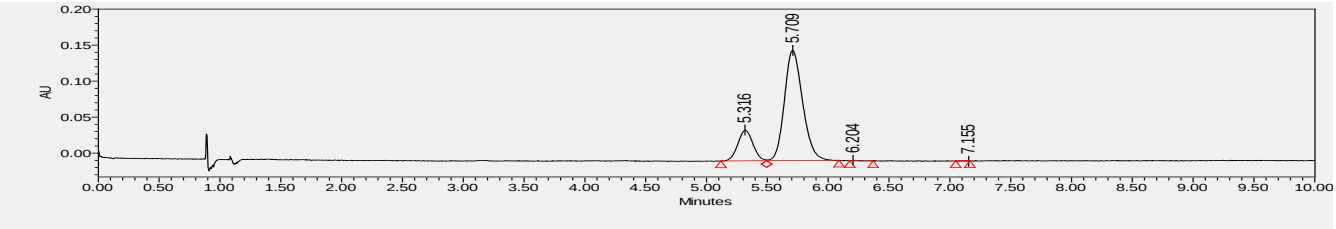
^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.5, 164.2, 143.6, 142.5, 136.7, 135.8, 135.8, 131.7, 131.4, 130.5, 127.1, 125.0, 123.3, 120.7, 111.8, 109.5, 109.0, 72.2, 55.0, 43.9, 26.1, 25.2, 24.3, -5.0.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{24}H_{29}BrO_3Si + Na^+]$ = 495.0962, 497.0941, found 495.097, 497.0947.

IR (neat): 3483, 3070, 2938, 1690, 1568, 1466, 1426, 1240, 1085, 985, 877, 819 and 760 cm^{-1}.

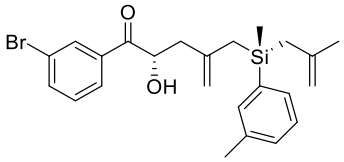


	Retention Time	Area	% Area
1	5.225	606342	10.47
2	5.587	2170559	37.49
3	6.074	2344837	40.50
4	7.004	667701	11.53



	Retention Time	Area	% Area
1	5.316	366085	18.68
2	5.709	1589837	81.12
3	6.204	1813	0.09
4	7.155	2103	0.11

C43: (S)-1-(3-bromophenyl)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(m-tolyl)silyl)methyl)pent-4-en-1-one



($C_{24}H_{29}BrO_2Si$) Colorless oil; 40.4 mg, 88% yield, 99/99% ee, 84:16 dr; $[\alpha]^{20}_D$ = -2.6 (*c* = 0.58 g/100 mL, in CH_2Cl_2).

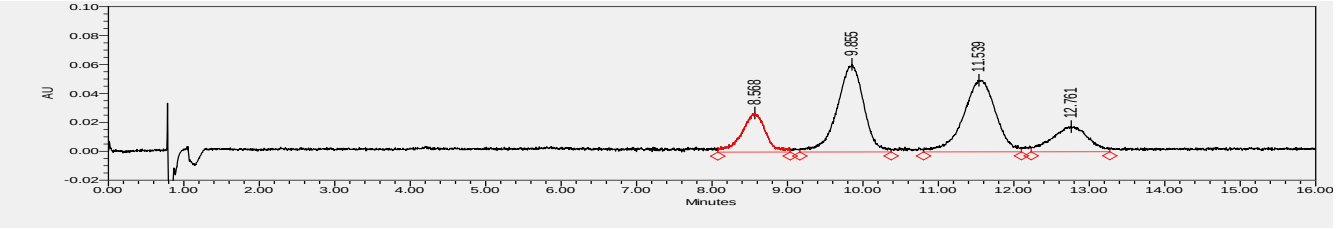
SFC (Daicel Chiralcel IG-3, CO_2/MeOH = 95/5, 1.5 mL/min, λ = 230 nm), t_1 = 8.58 min, t_2 = 9.84 min, t_3 = 11.50 min, t_4 = 12.72 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.37 – 7.26 (m, 3H), 7.20 (p, *J* = 6.4 Hz, 1H), 7.17 – 7.11 (m, 1H), 5.10 – 5.00 (m, 1H), 4.70 (d, *J* = 3.2 Hz, 2H), 4.59 (s, 1H), 4.47 (s, 1H), 3.45 (d, *J* = 6.6 Hz, 1H), 2.31 (s, 3H), 2.27 (dd, *J* = 14.7, 3.0 Hz, 1H), 2.00 (dd, *J* = 14.6, 8.6 Hz, 1H), 1.92 – 1.86 (m, 2H), 1.80 (d, *J* = 5.5 Hz, 2H), 1.57 (s, 3H), 0.32 (s, 3H).

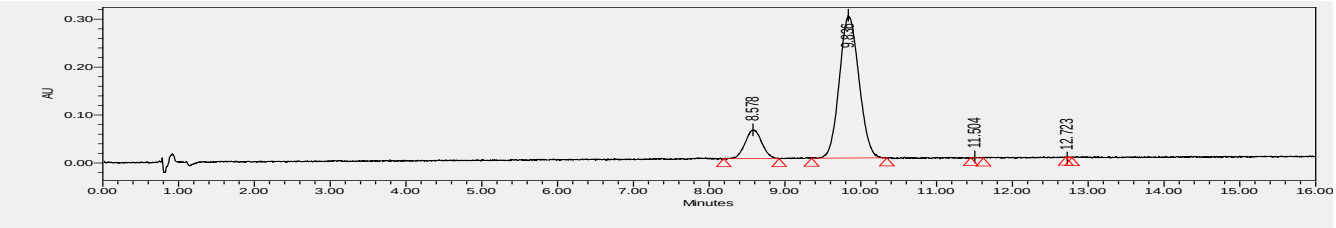
^{13}C NMR (151 MHz, $CDCl_3$) δ = 200.4, 142.9, 141.9, 137.2, 137.1, 136.8, 135.6, 134.7, 131.7, 131.1, 130.5, 130.2, 127.8, 127.1, 123.3, 112.4, 109.6, 72.2, 44.0, 26.2, 25.5, 24.6, 21.7, -5.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{24}H_{29}BrO_2Si + Na^+]$ = 479.1012, 481.0992, found 479.1016, 481.0996.

IR (neat): 3481, 3073, 2921, 1687, 1635, 1566, 1408, 1251, 1117, 1084, 983, 872, 780 and 715 cm^{-1}.

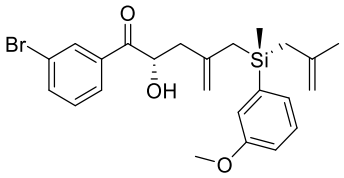


	Retention Time	Area	% Area
1	8.568	587110	14.20
2	9.855	1486270	35.95
3	11.539	1479275	35.79
4	12.761	581125	14.06



	Retention Time	Area	% Area
1	8.578	916701	14.68
2	9.836	5319366	85.19
3	11.504	5633	0.09
4	12.723	2650	0.04

C44: (S)-1-(3-bromophenyl)-2-hydroxy-4-(((S)-(3-methoxyphenyl)(methyl)(2-methylallyl)silyl)methyl)pent-4-en-1-one



($C_{24}H_{29}BrO_3Si$) Colorless oil; 37.8 mg, 80% yield, 99/99% ee, 84:16 dr; $[\alpha]^{22}_D$ = -4.8 (*c* = 0.50 g/100 mL, in CH_2Cl_2).

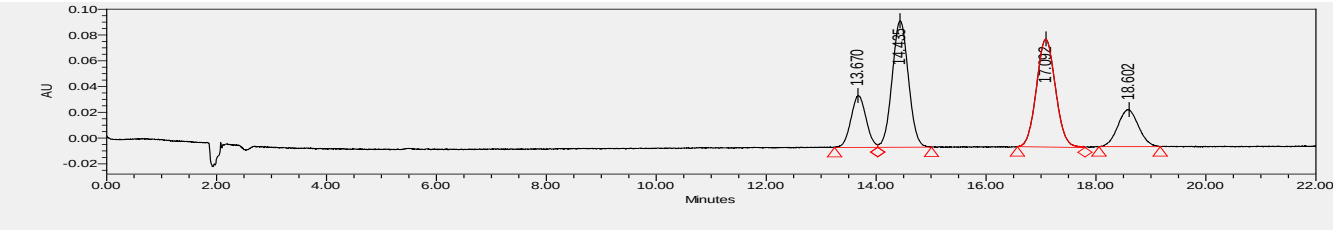
SFC (Daicel Chiralcel IG, CO_2/MeOH = 90/10 , 1.5 mL/min, λ = 230 nm), t_1 = 13.38 min, t_2 = 14.09 min, t_3 = 16.57 min, t_4 = 18.30 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (s, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.10 – 6.98 (m, 2H), 6.87 (dt, *J* = 9.7, 5.0 Hz, 1H), 5.10 – 4.97 (m, 1H), 4.75 – 4.67 (m, 2H), 4.60 (s, 1H), 4.48 (s, 1H), 3.79 (s, 3H), 3.46 (d, *J* = 6.6 Hz, 1H), 2.33 – 2.21 (m, 1H), 2.00 (dd, *J* = 14.6, 8.7 Hz, 1H), 1.88 (dd, *J* = 13.0, 4.7 Hz, 2H), 1.80 (s, 2H), 1.57 (s, 3H), 0.32 (s, 3H).

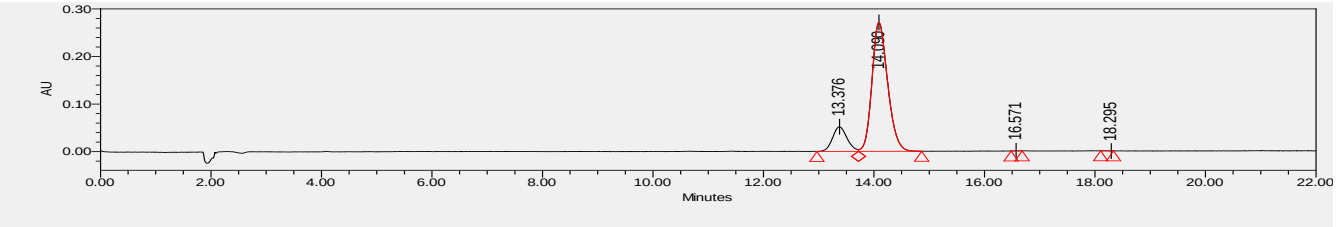
^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.4, 159.0, 142.8,.141.8, 139.0, 136.8, 135.6, 131.7, 130.5, 129.2, 127.1, 126.3, 123.4, 119.7, 114.5, 112.5, 109.8, 72.3, 55.2, 44.0, 26.1, 25.5, 24.6, -5.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{24}H_{29}BrO_3Si + Na^+]$ = 495.0962, 497.0941, found 495.0965, 497.0945.

IR (neat): 3477, 3071, 2919, 1687, 1635, 1569, 1407, 1282, 1246, 982, 876, 785 and 718 cm^{-1}.

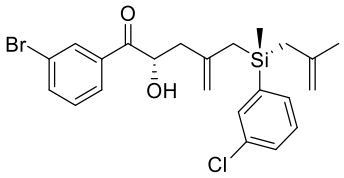


	Retention Time	Area	% Area
1	13.670	766720	13.82
2	14.435	2014721	36.32
3	17.092	2009377	36.23
4	18.602	755867	13.63



	Retention Time	Area	% Area
1	13.376	939102	14.96
2	14.090	5337623	85.00
3	16.571	887	0.01
4	18.295	1872	0.03

C45: (S)-1-(3-bromophenyl)-4-(((S)-(3-chlorophenyl)(methyl)(2-methylallyl)silyl)methyl)-2-hydroxypent-4-en-1-one



($C_{23}H_{26}BrClO_2Si$) Colorless oil; 37.3 mg, 78% yield, 99/99% ee, 84:16 dr; $[\alpha]^{22}_D$ = -7.7 (*c* = 0.56 g/100 mL, in CH_2Cl_2).

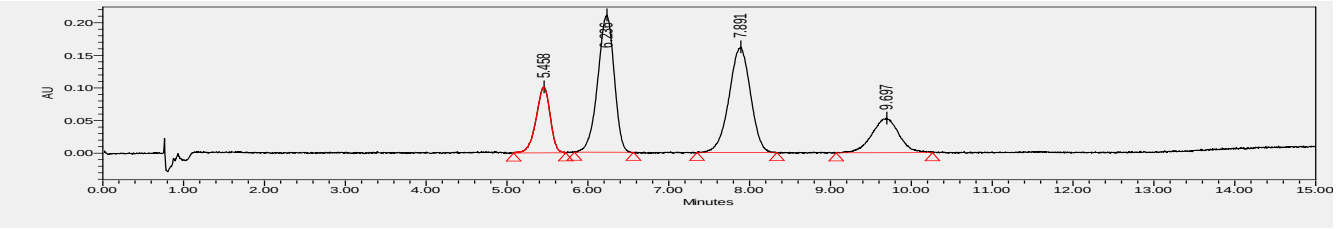
SFC (Daicel Chiralcel IG-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 230 nm), t_1 = 5.47 min, t_2 = 6.24 min, t_3 = 7.84 min, t_4 = 9.70 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.00 (m, 1H), 7.74 (ddd, *J* = 8.0, 1.9, 0.9 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.38 – 7.33 (m, 2H), 7.32 – 7.28 (m, 1H), 7.26 – 7.20 (m, 1H), 5.06 (ddd, *J* = 8.4, 6.6, 3.5 Hz, 1H), 4.75 – 4.67 (m, 2H), 4.63 – 4.58 (m, 1H), 4.46 (s, 1H), 3.50 (d, *J* = 6.6 Hz, 1H), 2.29 (td, *J* = 14.7, 2.9 Hz, 1H), 2.00 (td, *J* = 14.1, 13.6, 7.6 Hz, 1H), 1.91 – 1.85 (m, 2H), 1.82 – 1.75 (m, 2H), 1.56 (s, 3H), 0.34 (s, 3H).

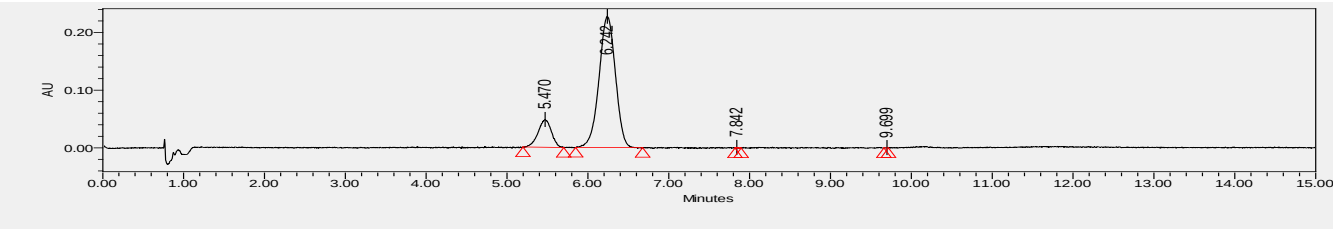
^{13}C NMR (151 MHz, $CDCl_3$) δ = 200.3, 142.3, 141.4, 140.1, 136.9, 135.6, 134.3, 133.8, 132.0, 131.7, 130.6, 129.5, 129.4, 127.0, 123.4, 112.8, 110.1, 72.4, 44.1, 25.9, 25.5, 24.5, -5.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{23}H_{26}BrClO_2Si + Na^+]$ = 499.0466, 501.0446, 503. 0416, found 499.0468, 501.0446, 503.0425.

IR (neat): 3479, 3073, 2918, 1687, 1636, 1561, 1390, 1252, 1163, 1122, 1091, 980, 878, 832 and 784 cm^{-1}.

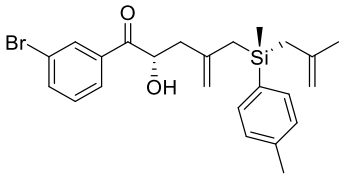


	Retention Time	Area	% Area
1	5.458	1220368	14.56
2	6.236	2960135	35.32
3	7.891	2962492	35.35
4	9.697	1236813	14.76



	Retention Time	Area	% Area
1	5.470	547269	14.60
2	6.242	3197173	85.32
3	7.842	1945	0.05
4	9.699	911	0.02

C46: (S)-1-(3-bromophenyl)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(p-tolyl)silyl)methyl)pent-4-en-1-one



($C_{24}H_{29}BrO_2Si$) Colorless oil; 40.4 mg, 88% yield, 99/97% ee, 85:15 dr; $[\alpha]^{21}_D$ = +7.3 (*c* = 0.35 g/100 mL, in CH_2Cl_2).

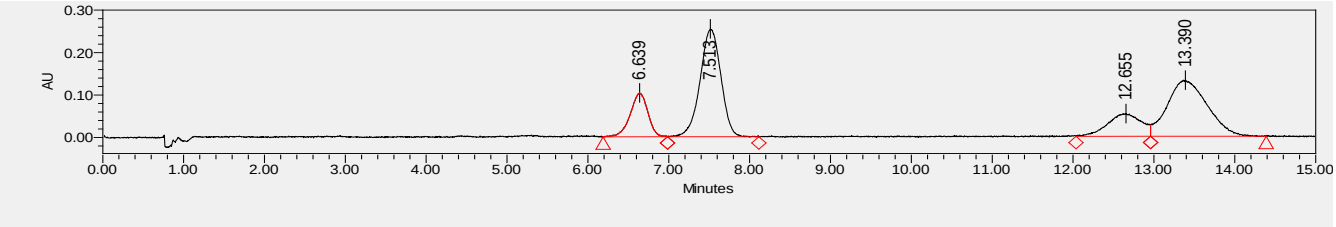
SFC (Daicel Chiralcel IG-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 230 nm), t_1 = 6.68 min, t_2 = 7.58 min, t_3 = 12.69 min, t_4 = 13.41 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ = δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.76 – 7.71 (m, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.33 – 7.29 (m, 1H), 7.10 (dd, *J* = 13.4, 7.6 Hz, 2H), 5.03 (ddd, *J* = 8.7, 6.8, 3.5 Hz, 1H), 4.70 (d, *J* = 4.1 Hz, 2H), 4.58 (s, 1H), 4.47 (s, 1H), 3.44 (d, *J* = 6.6 Hz, 1H), 2.31 (d, *J* = 6.7 Hz, 3H), 2.23 (dd, *J* = 14.6, 2.9 Hz, 1H), 1.98 (dd, *J* = 14.4, 8.7 Hz, 1H), 1.92 – 1.83 (m, 2H), 1.83 – 1.76 (m, 2H), 1.56 (s, 3H), 0.31 (d, *J* = 8.9 Hz, 3H).

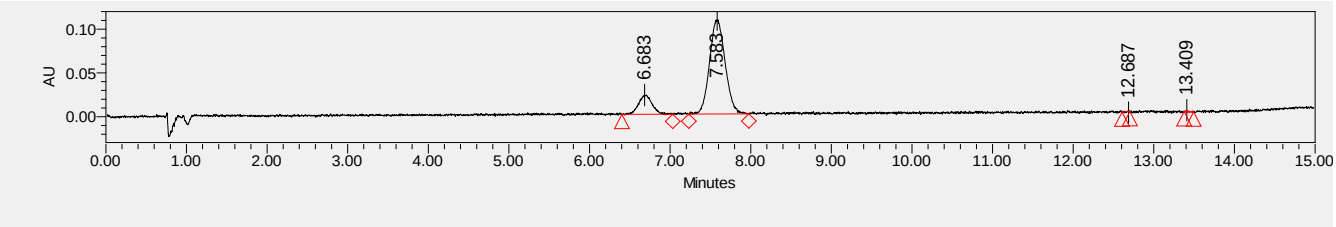
^{13}C NMR (151 MHz, $CDCl_3$) δ = 200.4, 143.0, 141.9, 139.2, 136.8, 135.7, 134.1, 133.5, 131.7, 130.5, 128.8, 127,1, 123.3, 112.4, 109.6, 72.2, 44.0, 26.1, 25.5, 24.7, 21.6, -5.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{24}H_{29}BrO_2Si + Na^+]$ = 479.1012, 481.0992, found 479.1014, 481.0993.

IR (neat): 3482, 3071, 2921, 1688, 1635, 1565, 1416, 1252, 1107, 980, 876, 827, 793 and 722 cm^{-1}.

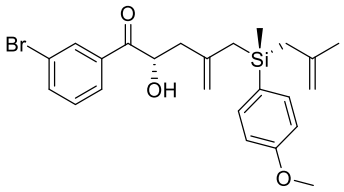


	Retention Time	Area	% Area
1	6.639	1557443	12.80
2	7.513	4535375	37.28
3	12.655	1556795	12.80
4	13.390	4514976	37.12



	Retention Time	Area	% Area
1	6.683	254316	14.91
2	7.583	1446291	84.77
3	12.687	2716	0.16
4	13.409	2787	0.16

C47: (S)-1-(3-bromophenyl)-2-hydroxy-4-(((S)-(4-methoxyphenyl)(methyl)(2-methylallyl)silyl)methyl)pent-4-en-1-one



($C_{24}H_{29}BrO_3Si$) Colorless oil; 41.0 mg, 86% yield, 97/92% ee, 86:14 dr; $[\alpha]^{21}_D$ = +7.1 (*c* = 0.48 g/100 mL, in CH_2Cl_2).

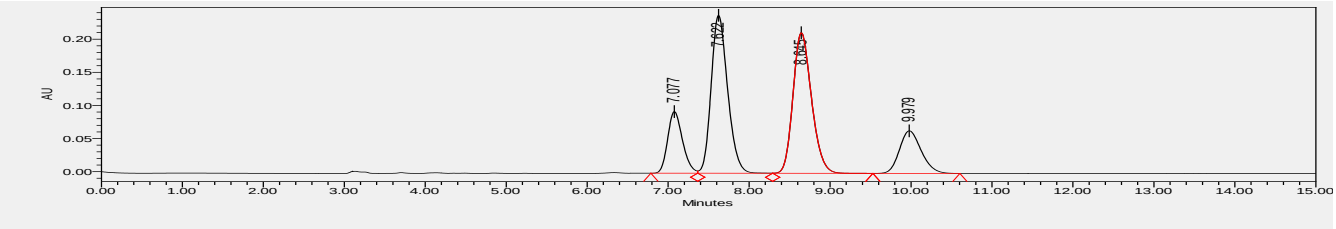
HPLC (Daicel chiralcel OZH, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 230 nm), t_1 = 6.81 min, t_2 = 7.30 min, t_3 = 8.21 min, t_4 = 9.43 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 – 7.95 (m, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 9.4 Hz, 2H), 7.32 (t, *J* = 7.9 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 2H), 5.03 (ddd, *J* = 9.8, 6.6, 3.4 Hz, 1H), 4.70 (d, *J* = 9.1 Hz, 2H), 4.58 (s, 1H), 4.46 (s, 1H), 3.79 (s, 3H), 3.45 (d, *J* = 6.6 Hz, 1H), 2.26 (td, *J* = 14.5, 3.2 Hz, 1H), 1.97 (dd, *J* = 14.6, 8.5 Hz, 1H), 1.85 (dd, *J* = 14.4, 3.8 Hz, 2H), 1.78 (d, *J* = 5.1 Hz, 2H), 1.56 (s, 3H), 0.31 (s, 3H).

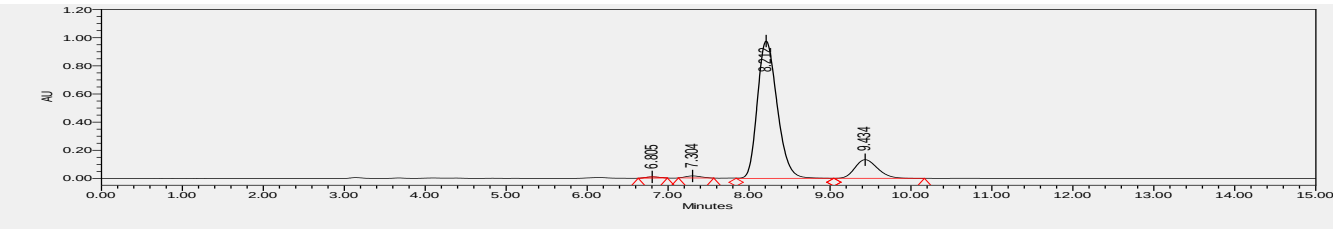
^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.4, 160.7, 143.0, 142.0, 136.8, 135.6, 135.5, 131.7, 130.5, 127.9, 127.1, 123.3, 113.7, 112.4, 109.6, 72.2, 55.1, 44.0, 26.4, 25.5, 24.8, -5.17.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{24}H_{29}BrO_3Si + Na^+]$ = 495.0962, 497.0941, found 495.0968, 497.0946.

IR (neat): 3478, 3073, 2919, 1688, 1594, 1503, 1279, 1249, 1182, 1111, 877, 818 and 721 cm^{-1}.

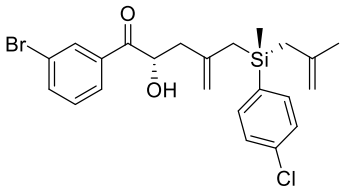


	Retention Time	Area	% Area
1	7.077	1184025	12.96
2	7.622	3381190	37.01
3	8.645	3371265	36.91
4	9.979	1198363	13.12



	Retention Time	Area	% Area
1	6.805	100168	0.52
2	7.304	193896	1.00
3	8.212	16519674	85.19
4	9.434	2576854	13.29

C48: (S)-1-(3-bromophenyl)-4-(((S)-(4-chlorophenyl)(methyl)(2-methylallyl)silyl)methyl)-2-hydroxypent-4-en-1-one



($C_{23}H_{26}BrClO_2Si$) Colorless oil; 37.3 mg, 78% yield, 99/99% ee, 86:14 dr; $[\alpha]\ ^{24}_{405}$ = +20.1 (*c* = 0.32 g/100mL, in CH_2Cl_2).

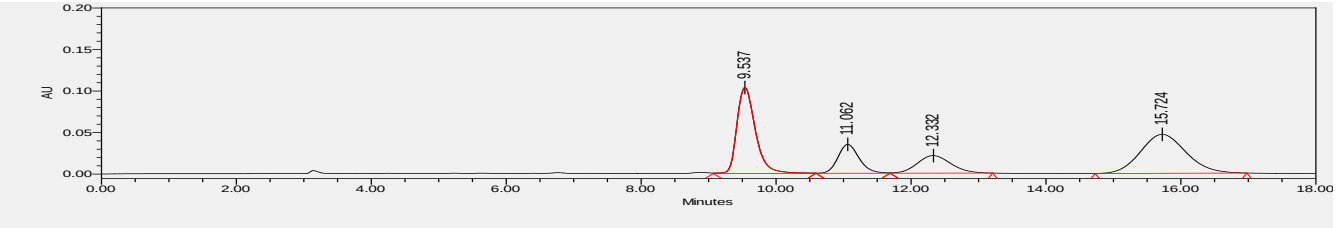
HPLC (Daicel chiralcel AYH, *n*-hexane/*i*-PrOH= 95/5, 1.0 mL/min, λ = 230 nm), t_1 = 9.09 min, t_2 = 10.65 min, t_3 = 11.88 min, t_4 = 15.23 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.98 (d, *J* = 8.9 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.34 (m, 3H), 7.27 (d, *J* = 7.6 Hz, 2H), 5.08 – 4.99 (m, 1H), 4.74 – 4.68 (m, 2H), 4.59 (s, 1H), 4.45 (s, 1H), 3.55 – 3.47 (m, 1H), 2.31 – 2.19 (m, 1H), 1.99 (dd, *J* = 14.6, 8.4 Hz, 1H), 1.92 – 1.84 (m, 2H), 1.78 (d, *J* = 7.6 Hz, 2H), 1.55 (s, 3H), 0.32 (s, 3H).

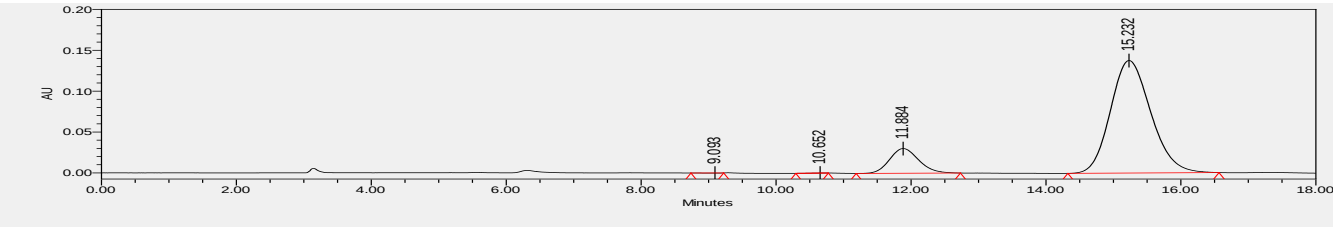
^{13}C NMR (151 MHz, $CDCl_3$) δ = 200.4, 142.4, 141.5, 136.9, 135.9, 135.8, 135.6, 135.4, 131.6, 130.6, 128.2, 127.0, 123.4, 112.7, 110.0, 72.3, 44.0, 26.0, 25.5, 24.6, -5.2.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{23}H_{26}BrClO_2Si + Na^+]$ = 499.0466, 501.0446, 503. 0416, found 499.0472, 501.0448, 503.0421.

IR (neat): 3479, 3074, 2921, 1687, 1636, 1570, 1413, 1252, 1162, 1084, 981, 878, 808 and 735 cm^{-1}.

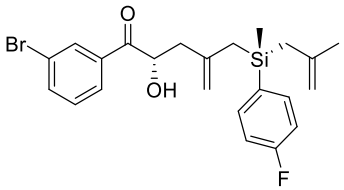


	Retention Time	Area	% Area
1	9.537	1970002	34.74
2	11.062	762827	13.45
3	12.332	735325	12.97
4	15.724	2203267	38.85



	Retention Time	Area	% Area
1	9.093	3389	0.05
2	10.652	721	0.01
3	11.884	902970	13.62
4	15.232	5723174	86.32

C49: (S)-1-(3-bromophenyl)-4-(((S)-(4-fluorophenyl)(methyl)(2-methylallyl)silyl)methyl)-2-hydroxypent-4-en-1-one



($C_{23}H_{26}BrFO_2Si$) Colorless oil; 39.6 mg, 86% yield, 99/98% ee, 83:17 dr; $[\alpha]^{22}_D$ = -10.2 (c = 0.27 g/100 mL, in CH_2Cl_2).

SFC (Daicel Chiralcel IG-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 230 nm), t_1 = 4.84min, t_2 = 5.99 min, t_3 = 7.43 min, t_4 = 8.91 min.

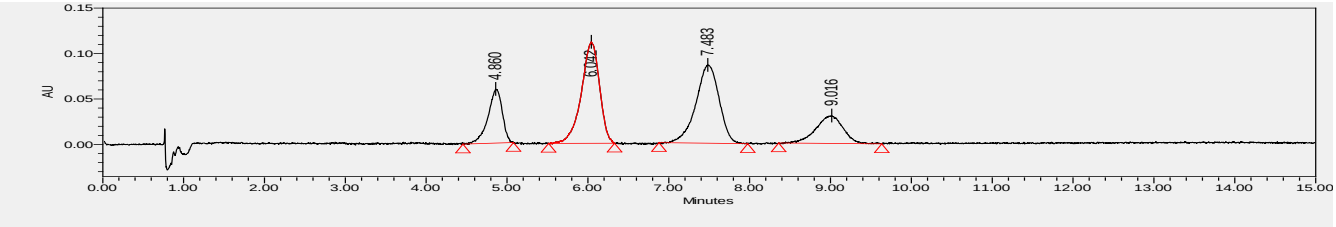
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.98 (s, 1H), 7.74 (d, J = 7.9 Hz, 1H), 7.65 (d, J = 7.7 Hz, 1H), 7.43 (dt, J = 25.0, 7.1 Hz, 2H), 7.34 (t, J = 7.9 Hz, 1H), 7.07 – 6.92 (m, 2H), 5.04 (td, J = 8.5, 3.6 Hz, 1H), 4.69 (d, J = 4.6 Hz, 2H), 4.59 (s, 1H), 4.46 (s, 1H), 3.49 (d, J = 6.6 Hz, 1H), 2.29 – 2.22 (m, 1H), 1.97 (td, J = 13.9, 13.3, 7.4 Hz, 1H), 1.90 – 1.84 (m, 2H), 1.82 – 1.76 (m, 2H), 1.55 (s, 3H), 0.33 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 200.4, 163.9 (d, J_{C-F} = 248.6 Hz)., 142.6, 141.6, 136.9, 136.0 (d, J_{C-F} = 7.5 Hz), 135.6, 132.7 (d, J_{C-F} = 3.7 Hz)., 131.7, 130.6, 127.1, 123.4, 115.1 (d, J_{C-F} = 19.6 Hz)., 112.6, 109.9, 72.3, 44.0, 26.2, 25.5, 24.8, -5.1.

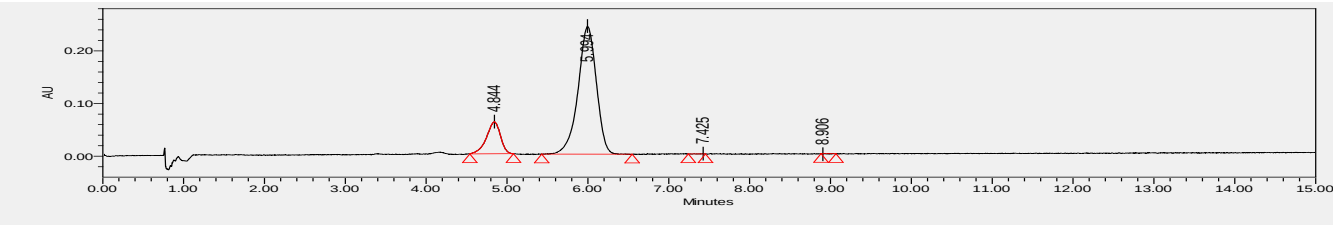
^{19}F NMR (565 MHz, $CDCl_3$) δ = -111.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{23}H_{26}BrFO_2Si + Na^+]$ = 483.0762, 485.0741, found 483.0766, 485.0743.

IR (neat): 3480, 3073, 2922, 1687, 1636, 1588, 1450, 1413, 1231, 1161, 1103, 980, 877, 826 and 722 cm^{-1}.

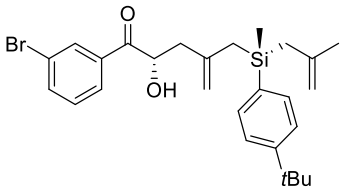


	Retention Time	Area	% Area
1	4.860	729085	14.87
2	6.042	1738257	35.46
3	7.483	1718887	35.07
4	9.016	715489	14.60



	Retention Time	Area	% Area
1	4.844	725251	15.94
2	5.994	3818043	83.90
3	7.425	2860	0.06
4	8.906	4488	0.10

C50: (S)-1-(3-bromophenyl)-4-(((S)-(4-(tert-butyl)phenyl)(methyl)(2-methylallyl)silyl)methyl)-2-hydroxypent-4-en-1-one



($C_{27}H_{35}BrO_2Si$) Colorless oil; 42.9 mg, 86% yield, 99/99% ee, 81:19 dr (determined by SFC); $[\alpha]^{20}_D$ = +10.5 (c = 0.49 g/100 mL, in CH_2Cl_2).

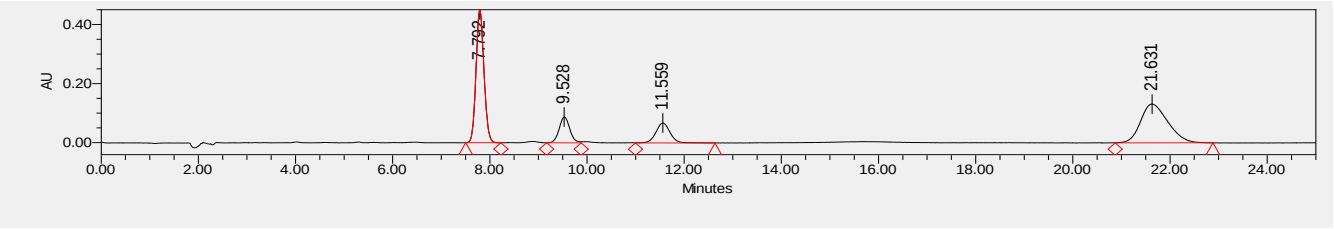
SFC (Daicel Chiralcel IG, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 230 nm), t_1 = 7.73min, t_2 = 9.46 min, t_3 = 11.55 min, t_4 = 21.54 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (s, 1H), 7.78 – 7.71 (m, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.39 (dd, J = 13.6, 8.1 Hz, 2H), 7.32 (td, J = 9.3, 8.1, 3.8 Hz, 3H), 5.04 (ddd, J = 9.3, 6.8, 3.3 Hz, 1H), 4.72 (s, 2H), 4.60 (s, 1H), 4.48 (s, 1H), 3.42 (t, J = 5.5 Hz, 1H), 2.32 – 2.15 (m, 1H), 1.99 – 1.91 (m, 1H), 1.87 (d, J = 7.9 Hz, 2H), 1.81 (d, J = 5.1 Hz, 2H), 1.58 (s, 3H), 1.27 (s, 9H), 0.32 (s, 3H).

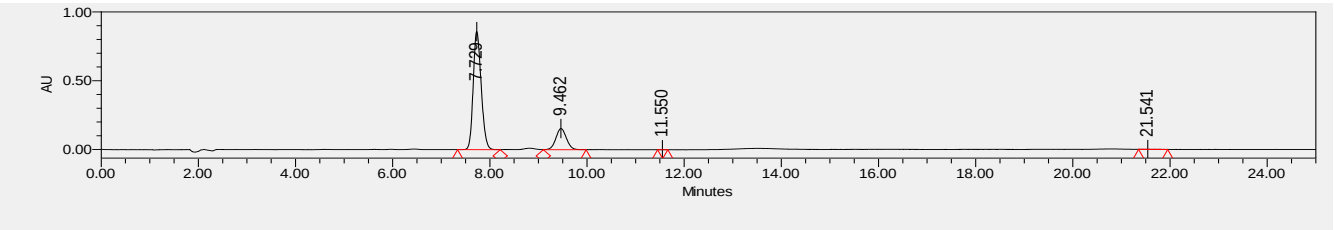
^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.4, 152.4, 143.0, 141.9, 136.8, 135.6, 133.9, 133.6, 131.7, 130.5, 127.1, 124.9, 123.3, 112.4, 109.6, 72.1, 44.1, 34.7, 31.3, 26.1, 25.5, 24.6, -5.2.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{27}H_{35}BrO_2Si + Na^+]$ = 521.1482, 523.1461, found 521.1478, 523.1457.

IR (neat): 3483, 3072, 2961, 1688, 1635, 1565, 1392, 1253, 1086, 981, 876, 816 and 719 cm^{-1}.

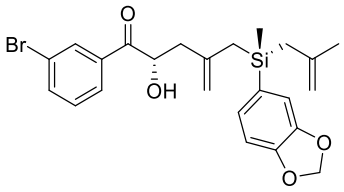


	Retention Time	Area	% Area
1	7.792	5112643	39.52
2	9.528	1328896	10.27
3	11.559	1374078	10.62
4	21.631	5120932	39.58



	Retention Time	Area	% Area
1	7.729	9799836	80.90
2	9.462	2308103	19.05
3	11.550	2159	0.02
4	21.541	3104	0.03

C51: (S)-4-(((S)-benzo[d][1,3]dioxol-5-yl(methyl)(2-methylallyl)silyl)methyl)-1-(3-bromophenyl)-2-hydroxypent-4-en-1-one



($C_{24}H_{27}BrO_4Si$) Colorless oil; 39.9 mg, 82% yield, 99/99% ee, 84:16 dr; $[\alpha]^{22}_D$ = -2.1 (*c* = 0.52 g/100 mL, in CH_2Cl_2).

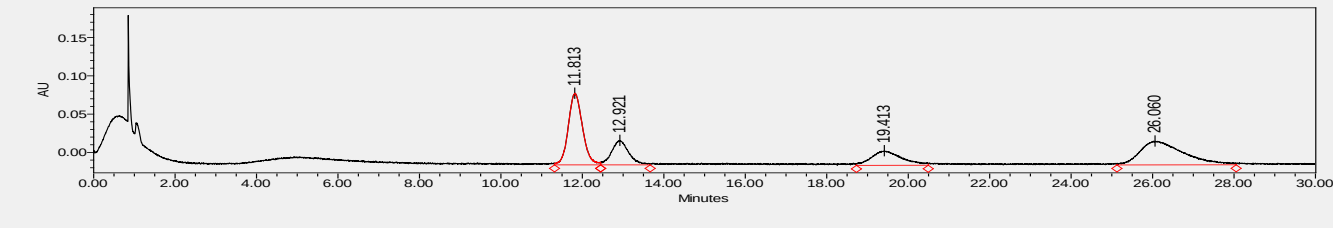
SFC (Daicel Chiralcel ODH, CO_2/MeOH = 90/10, 1.0 mL/min, λ = 230 nm), t_1 = 11.79 min, t_2 = 13.01 min, t_3 = 19.44 min, t_4 = 26.08 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 6.5 Hz, 1H), 7.76 – 7.72 (m, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 6.98 – 6.93 (m, 1H), 6.92 (s, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 5.94 – 5.90 (m, 2H), 5.05 (ddd, *J* = 8.7, 6.8, 3.5 Hz, 1H), 4.70 (s, 2H), 4.59 (s, 1H), 4.47 (s, 1H), 3.47 (dd, *J* = 6.4, 3.6 Hz, 1H), 2.28 (td, *J* = 15.2, 14.8, 3.0 Hz, 1H), 2.00 (dd, *J* = 14.7, 8.5 Hz, 1H), 1.88 – 1.82 (m, 2H), 1.80 – 1.73 (m, 2H), 1.57 (s, 3H), 0.30 (s, 3H).

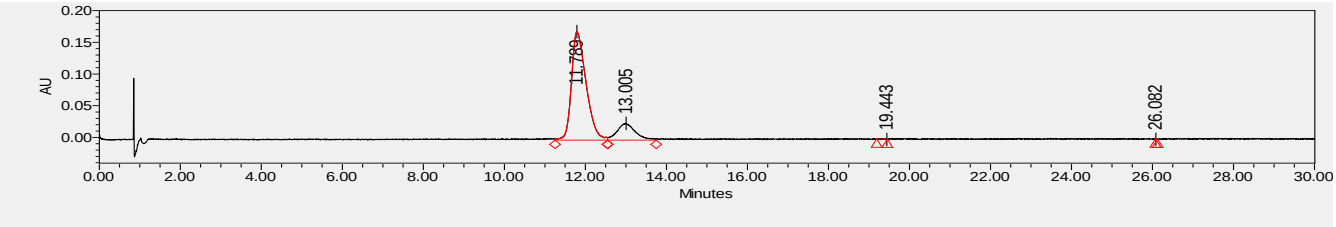
^{13}C NMR (151 MHz, $CDCl_3$) δ = 200.4, 148.7, 147.5, 142.8, 141.8, 136.9, 135.6, 131.7, 130.5, 130.1, 128.2, 127.1, 123.4, 113.3, 112.5, 109.7, 108.7, 100.7, 72.3, 44.0, 26.3, 25.5, 249, -5.1.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{24}H_{27}BrO_4Si + Na^+]$ = 509.0754, 511.0734, found 509.0759, 511.0739.

IR (neat): 3480, 3072, 2911, 1687, 1635, 1566, 1481, 1415, 1235, 1040, 935, 886, 804 and 719 cm^{-1}.

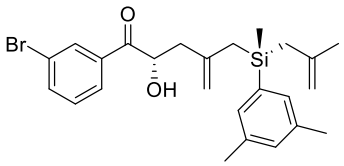


	Retention Time	Area	% Area
1	11.813	2261260	34.97
2	12.921	929903	14.38
3	19.413	965074	14.93
4	26.060	2309774	35.72



	Retention Time	Area	% Area
1	11.789	4272806	83.75
2	13.005	823771	16.15
3	19.443	4913	0.10
4	26.082	523	0.01

C52: (S)-1-(3-bromophenyl)-4-(((S)-(3,5-dimethylphenyl)(methyl)(2-methylallyl)silyl)methyl)-2-hydroxypent-4-en-1-one



($C_{25}H_{31}BrO_2Si$) Colorless oil; 42.1 mg, 89% yield, 99/99% ee, 86:14 dr; $[\alpha]_D^{23}$ = +9.3 (*c* = 0.60 g/100 mL, in CH_2Cl_2).

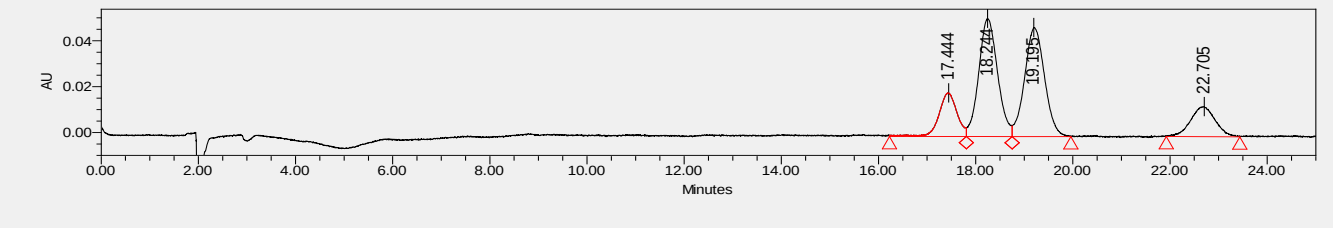
SFC (Daicel Chiralcel IG, CO_2/MeOH = 95/5, 1.5 mL/min, λ = 230 nm), t_1 = 17.04 min, t_2 = 18.03 min, t_3 = 19.02 min, t_4 = 22.46 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (q, *J* = 3.5, 2.5 Hz, 1H), 7.75 – 7.69 (m, 1H), 7.69 – 7.55 (m, 1H), 7.31 (dt, *J* = 15.8, 7.9 Hz, 1H), 7.09 (s, 2H), 6.98 (s, 1H), 5.04 (ddd, *J* = 8.8, 6.7, 3.5 Hz, 1H), 4.74 – 4.67 (m, 2H), 4.59 (s, 1H), 4.47 (s, 1H), 3.45 (d, *J* = 6.6 Hz, 1H), 2.32 (d, *J* = 3.6 Hz, 1H), 2.27 (d, *J* = 4.2 Hz, 6H), 2.02 (dd, *J* = 14.6, 8.7 Hz, 1H), 1.88 (d, *J* = 5.9 Hz, 2H), 1.79 (d, *J* = 4.2 Hz, 2H), 1.58 (s, 3H), 0.31 (s, 3H).

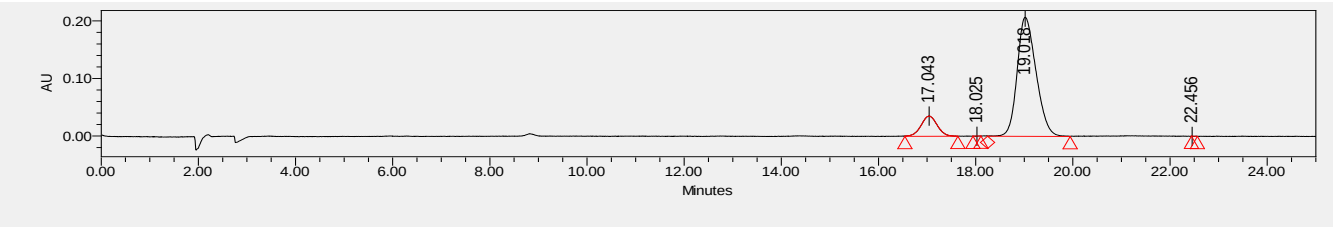
^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.4, 143.0, 142.0, 137.1, 137.1, 136.8, 135.6, 131.8, 131.7, 131.2, 130.5, 127.1, 123.3, 112.4, 109.6, 72.2, 44.1, 26.2, 25.5, 24.6, 21.5, -5.2.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{25}H_{31}BrO_2Si + Na^+]$ = 493.1169, 495.1148, found 493.1169, 495.1148,.

IR (neat): 3480, 3073, 2918, 1687, 1635, 1565, 1405, 1251, 1143, 1086, 980, 867, 788 and 719 cm^{-1}.

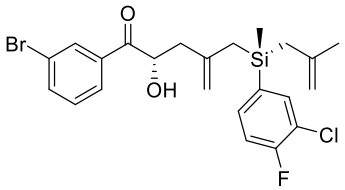


	Retention Time	Area	% Area
1	17.444	495126	13.38
2	18.244	1385258	37.45
3	19.195	1356825	36.68
4	22.705	462156	12.49



	Retention Time	Area	% Area
1	17.043	811383	12.68
2	18.025	1069	0.02
3	19.018	5583204	87.28
4	22.456	999	0.02

C53: (S)-1-(3-bromophenyl)-4-(((S)-(3-chloro-4-fluorophenyl)(methyl)(2-methylallyl)silyl)methyl)-2-hydroxypent-4-en-1-one



($C_{23}H_{25}BrClFO_2Si$) Colorless oil; 38.2 mg, 77% yield, 99/99% ee, 82:18 dr; $[\alpha]^{20}_D$ = -6.2 (c = 0.35 g/100 mL, in CH_2Cl_2).

SFC (Daicel Chiralcel IG-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 230 nm), t_1 = 4.79 min, t_2 = 5.37 min, t_3 = 5.99 min, t_4 = 7.11 min.

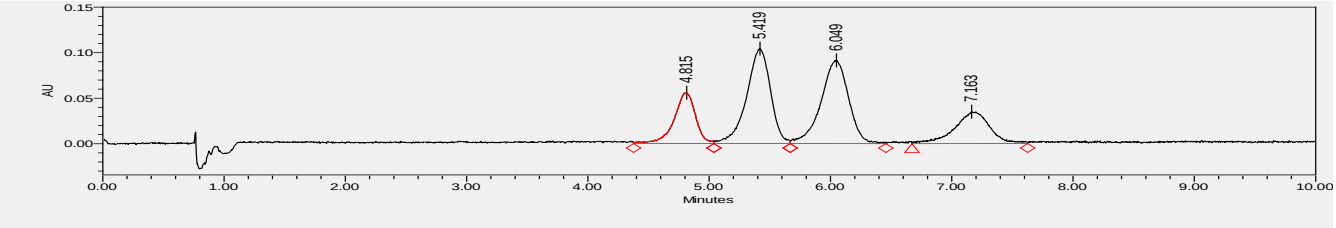
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.00 (d, J = 6.6 Hz, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.68 (d, J = 7.7 Hz, 1H), 7.45 (dd, J = 12.9, 7.9 Hz, 1H), 7.39 – 7.27 (m, 2H), 7.08 (dt, J = 13.1, 8.7 Hz, 1H), 5.11 – 5.02 (m, 1H), 4.71 (s, 1H), 4.68 (s, 1H), 4.61 (s, 1H), 4.45 (s, 1H), 3.53 (d, J = 6.5 Hz, 1H), 2.30 (td, J = 14.6, 3.1 Hz, 1H), 2.01 (td, J = 16.6, 15.6, 7.4 Hz, 1H), 1.87 (d, J = 7.4 Hz, 2H), 1.82 – 1.75 (m, 2H), 1.56 (s, 3H), 0.33 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 200.2, 158.9 (d, J_{C-F} = 251.8 Hz), 142.0, 141.2, 136.9, 136.1, 135.5, 134.7 (d, J_{C-F} = 4.7 Hz), 133.9 (d, J_{C-F} = 6.7 Hz), 131.6, 130.5, 126.9, 123.3, 121.0 (d, J_{C-F} = 16.3 Hz), 116.4 (d, J_{C-F} = 19.7 Hz), 112.8, 110.1, 72.4, 43.9, 25.8, 25.4, 24.5, -5.2.

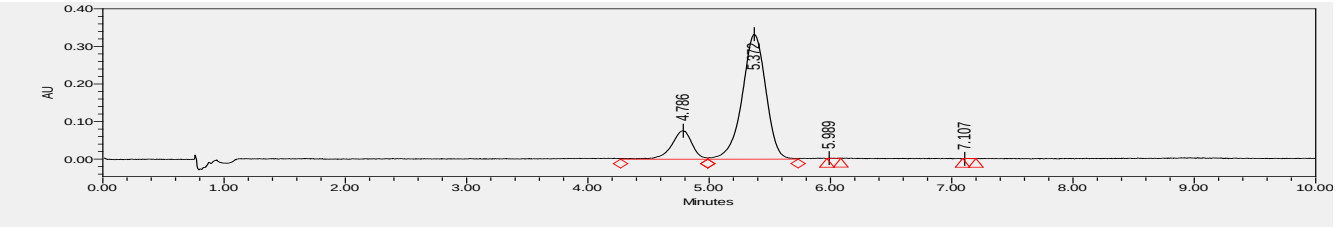
^{19}F NMR (565 MHz, $CDCl_3$) δ = -113.8.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for [$C_{23}H_{25}BrClFO_2Si$ +Na^+] = 517.0372, 519.0351, 521.0322, found 517.0380, 519.0358, 521.0331.

IR (neat): 3476, 3074, 2923, 1687, 1636, 1576, 1490, 1253, 1153, 1103, 981, 866, 813, 708 cm^{-1}.

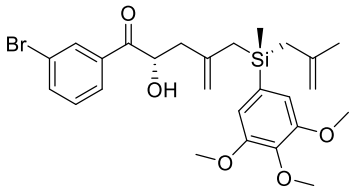


	Retention Time	Area	% Area
1	4.815	688591	16.10
2	5.419	1431754	33.48
3	6.049	1449447	33.89
4	7.163	706499	16.52



	Retention Time	Area	% Area
1	4.786	898609	16.62
2	5.372	4501894	83.29
3	5.989	2064	0.04
4	7.107	2816	0.05

C54: (S)-1-(3-bromophenyl)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(3,4,5-trimethoxyphenyl)silyl)methyl)pent-4-en-1-one



($C_{26}H_{33}BrO_5Si$) Colorless oil; 42.6 mg, 80% yield, 99/99% ee, 82:18 dr; $[\alpha]^{20}_D$ = +6.9 (*c* = 0.65 g/100 mL, in CH_2Cl_2).

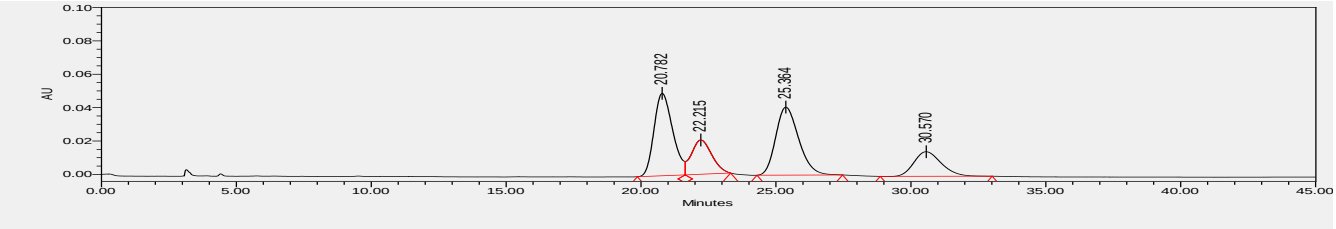
HPLC (Daicel chiralcel OZH, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 230 nm), t_1 = 21.04 min, t_2 = 22.72 min, t_3 = 25.63 min, t_4 = 30.82 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.02 (s, 1H), 7.75 – 7.71 (m, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.9 Hz, 1H), 6.69 (d, *J* = 14.7 Hz, 2H), 5.11 – 5.01 (m, 1H), 4.72 (s, 1H), 4.70 (s, 1H), 4.63 (d, *J* = 9.0 Hz, 1H), 4.50 (s, 1H), 3.85 (t, *J* = 3.8 Hz, 9H), 3.52 (d, *J* = 6.5 Hz, 1H), 2.36 (td, *J* = 14.7, 13.7, 3.2 Hz, 1H), 2.05 (td, *J* = 15.0, 8.4 Hz, 1H), 1.91 (q, *J* = 13.8 Hz, 2H), 1.81 (d, *J* = 6.7 Hz, 2H), 1.60 (s, 3H), 0.33 (s, 3H).

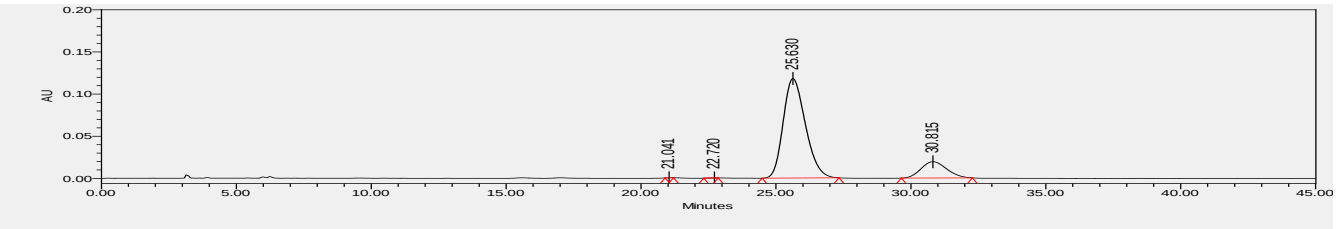
^{13}C NMR (151 MHz, $CDCl_3$) δ = 200.3, 153.0, 142.8, 142.0, 139.4, 136.9, 135.5, 132.3, 131.6, 130.5, 127.1, 123.4, 112.5, 110.8, 109.8, 72.4, 61.0, 56.3, 44.0, 26.4, 25.5, 24.7, -4.9.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{26}H_{33}BrO_5Si + Na^+]$ = 555.1173, 557.1152, found 555.1176, 557.1157.

IR (neat): 3479, 3073, 2933, 1687, 1569, 1502, 1395, 1305, 1247, 1123, 1005, 881, 811 and 722 cm^{-1}.

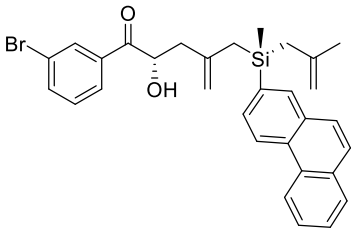


	Retention Time	Area	% Area
1	20.782	2382800	34.45
2	22.215	1079531	15.61
3	25.364	2413598	34.89
4	30.570	1040888	15.05



	Retention Time	Area	% Area
1	21.041	879	0.01
2	22.720	1995	0.02
3	25.630	6750252	84.05
4	30.815	1277863	15.91

C55: (S)-1-(3-bromophenyl)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(phenanthren-2-yl)silyl)methyl)pent-4-en-1-one



($C_{31}H_{31}BrO_2Si$) Colorless oil; 44.9 mg, 82% yield, 99/99% ee, 88:12 dr; $[\alpha]\ ^{22}_D$ = +3.6 (*c* = 0.72 g/100 mL, in CH_2Cl_2).

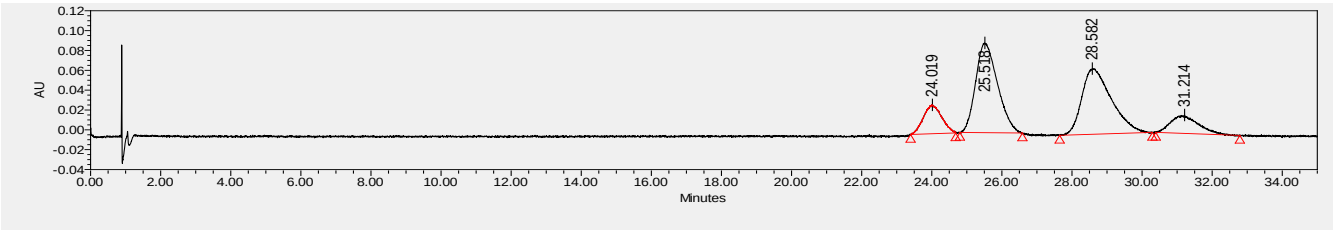
SFC (Daicel Chiralcel IF-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 230 nm), t_1 = 23.56 min, t_2 = 24.90 min, t_3 = 28.02 min, t_4 = 31.78 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.84 (s, 1H), 8.70 (d, *J* = 8.3 Hz, 1H), 7.94 – 7.87 (m, 2H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.78 – 7.74 (m, 1H), 7.72 – 7.64 (m, 3H), 7.61 (t, *J* = 7.1 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 6.90 (t, *J* = 7.9 Hz, 1H), 5.01 (ddd, *J* = 9.8, 6.6, 3.5 Hz, 1H), 4.77 (s, 1H), 4.72 (s, 1H), 4.63 (s, 1H), 4.54 (s, 1H), 3.50 (d, *J* = 6.6 Hz, 1H), 2.25 (dd, *J* = 14.5, 3.2 Hz, 1H), 2.08 (d, *J* = 13.8 Hz, 1H), 2.04 – 1.97 (m, 2H), 1.95 (d, *J* = 4.9 Hz, 2H), 1.59 (s, 3H), 0.50 (s, 3H).

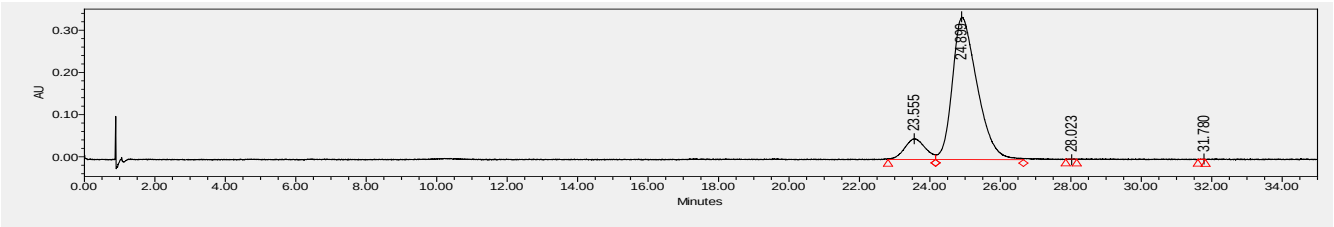
^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.4, 142.8, 141.8, 136.7, 135.4, 132.7, 132.3, 131.5, 131.4, 130.3, 130.3, 129.5, 128.8, 128.8, 127.9, 127.8, 126.9, 126.8, 126.8, 123.2, 122.6, 112.7, 109.9, 72.2, 44.0, 26.4, 25.6, 24.9, -5.0.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{31}H_{31}BrO_2Si + Na^+]$ = 565.1169, 567.1148, found 565.1178, 567.1155.

IR (neat): 3478, 3071, 2919, 1685, 1635, 1565, 1418, 1248, 1088, 980, 870, 837 and 746 cm^{-1}.

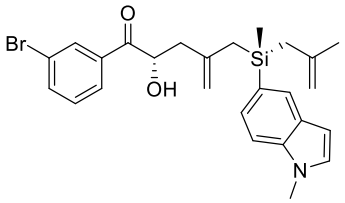


	Retention Time	Area	% Area
1	24.019	1051871	10.70
2	25.518	3921392	39.88
3	28.582	3861039	39.27
4	31.214	998710	10.16



	Retention Time	Area	% Area
1	23.555	1989312	10.77
2	24.899	16459193	89.15
3	28.023	9208	0.05
4	31.780	5539	0.03

C56: (S)-1-(3-bromophenyl)-2-hydroxy-4-(((S)-methyl(1-methyl-1H-indol-5-yl)(2-methylallyl)silyl)methyl)pent-4-en-1-one



($C_{26}H_{30}BrNO_2Si$) Yellow oil; 43.6 mg, 88% yield, 99/99% ee, 90:10 dr; $[\alpha]_D^{23}$ = +20.2 (*c* = 0.54 g/100 mL, in CH_2Cl_2).

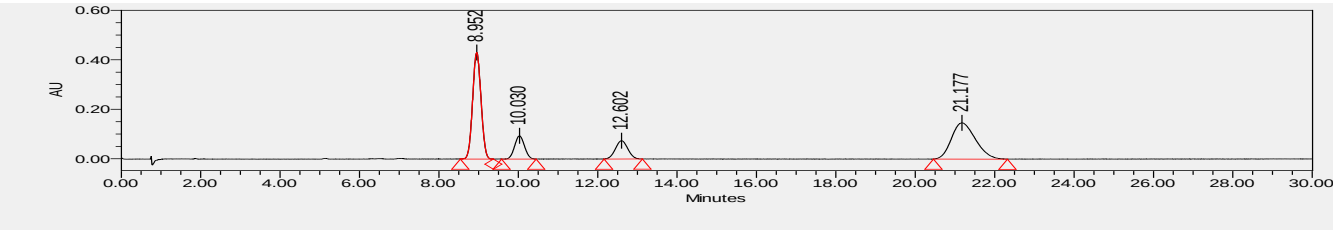
SFC (Daicel Chiralcel AD-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 230 nm), t_1 = 8.92 min, t_2 = 10.12 min, t_3 = 12.60 min, t_4 = 21.23 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 (s, 1H), 7.77 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.32 (t, *J* = 6.7 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.04 (dd, *J* = 6.1, 3.2 Hz, 1H), 6.97 (t, *J* = 7.9 Hz, 1H), 6.46 (dd, *J* = 6.7, 3.1 Hz, 1H), 5.00 (ddd, *J* = 9.6, 6.6, 3.5 Hz, 1H), 4.73 (s, 1H), 4.68 (s, 1H), 4.58 (s, 1H), 4.49 (s, 1H), 3.77 (s, 3H), 3.42 (d, *J* = 6.6 Hz, 1H), 2.24 (dd, *J* = 14.4, 3.2 Hz, 1H), 2.01 – 1.97 (m, 1H), 1.93 (dd, *J* = 14.2, 8.4 Hz, 2H), 1.85 (s, 2H), 1.56 (s, 3H), 0.37 (s, 3H).

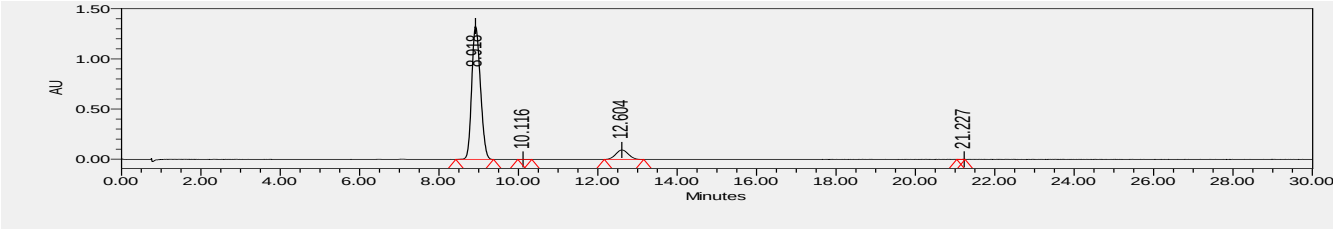
^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.5, 143.4, 142.3, 137.5, 136.6, 135.5, 131.6, 130.3, 128.9, 128.5, 127.4, 127.1, 126.8, 125.9, 123.2, 112.3, 109.3, 109.1, 101.3, 72.0, 44.0, 32.9, 26.9, 25.5, 24.9, -5.1.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{26}H_{30}BrNO_2Si + Na^+]$ = 518.1121, 520.1101, found 518.1127, 520.1102.

IR (neat): 3482, 3072, 2916, 1685, 1634, 1565,1425, 1323, 1278, 1248, 1158, 1073, 979, 874, 794 and 722 cm^{-1}.

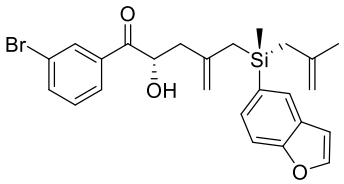


	Retention Time	Area	% Area
1	8.952	6346705	40.33
2	10.030	1628115	10.35
3	12.602	1608669	10.22
4	21.177	6154563	39.11



	Retention Time	Area	% Area
1	8.918	20178576	90.76
2	10.116	2699	0.01
3	12.604	2050871	9.22
4	21.227	1898	0.01

C57: (S)-4-(((S)-benzofuran-5-yl(methyl)(2-methylallyl)silyl)methyl)-1-(3-bromophenyl)-2-hydroxypent-4-en-1-one



($C_{25}H_{27}BrO_3Si$) Colorless oil; 43.4 mg, 90% yield, 99/99% ee, 88:12 dr; $[\alpha]^{21}_D$ = +3.2 (*c* = 0.71 g/100 mL, in CH_2Cl_2).

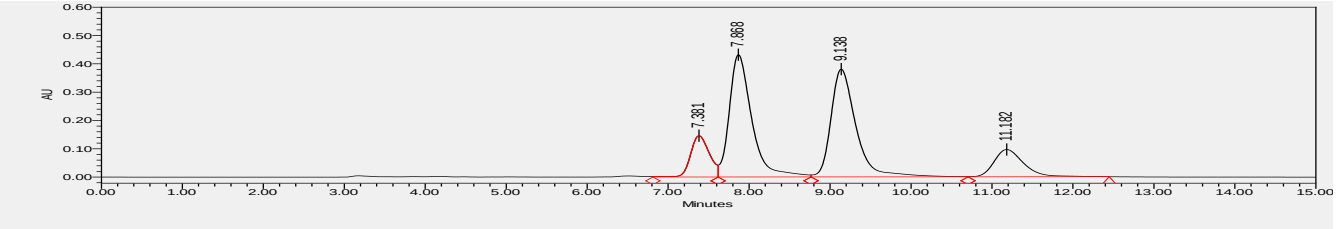
HPLC (Daicel chiralcel OZH, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 230 nm), t_1 = 7.38 min, t_2 = 7.87 min, t_3 = 9.16 min, t_4 = 11.23 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.99 – 7.94 (m, 1H), 7.74 (s, 1H), 7.71 – 7.67 (m, 1H), 7.60 (dd, *J* = 7.0, 2.2 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.42 – 7.39 (m, 1H), 7.16 (t, *J* = 7.9 Hz, 1H), 6.77 – 6.69 (m, 1H), 5.02 (ddt, *J* = 8.9, 6.6, 3.5 Hz, 1H), 4.70 (d, *J* = 11.7 Hz, 2H), 4.59 (s, 1H), 4.48 (s, 1H), 3.47 (d, *J* = 6.6 Hz, 1H), 2.29 – 2.20 (m, 1H), 2.00 – 1.96 (m, 1H), 1.95 (s, 1H), 1.92 (d, *J* = 14.0 Hz, 1H), 1.89 – 1.81 (m, 2H), 1.55 (s, 3H), 0.38 (s, 3H).

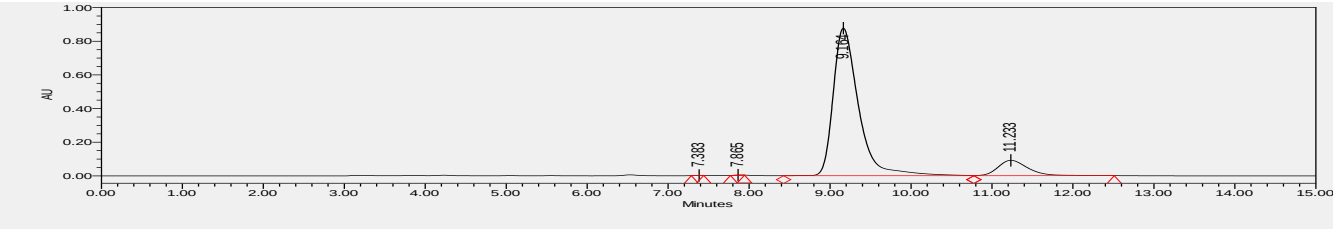
^{13}C NMR (151 MHz, $CDCl_3$) δ = 200.4, 155.9, 145.0, 142.9, 141.9, 136.8, 135.5, 131.6, 130.8, 130.4, 129.8, 127.4, 127.0, 123.3, 112.5, 111.3, 109.7, 106.6, 72.2, 44.0, 26.5, 25.5, 24.9, -5.0.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{25}H_{27}BrO_3Si + Na^+]$ = 505.0805, 507.0785, found 505.0805, 507.0776.

IR (neat): 3479, 3073, 2919, 1686, 1635,1566, 1416, 1250, 1111, 1075, 981, 877, 804 and 739 cm^{-1}.

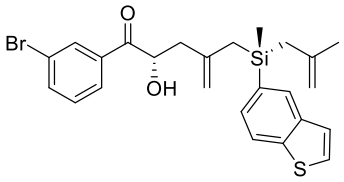


	Retention Time	Area	% Area
1	7.381	2348269	11.05
2	7.868	8323771	39.18
3	9.138	8138379	38.31
4	11.182	2434808	11.46



	Retention Time	Area	% Area
1	7.383	1124	0.01
2	7.865	6080	0.03
3	9.164	19052387	88.94
4	11.233	2361034	11.02

C58: (S)-4-(((S)-benzo[b]thiophen-5-yl(methyl)(2-methylallyl)silyl)methyl)-1-(3-bromophenyl)-2-hydroxypent-4-en-1-one



($C_{25}H_{27}BrO_2SSi$) Colorless oil; 41.4 mg, 83% yield, 99/99% ee, 86:14 dr; $[\alpha]^{22}_D$ = +21.5 (*c* = 0.47 g/100 mL in CH_2Cl_2).

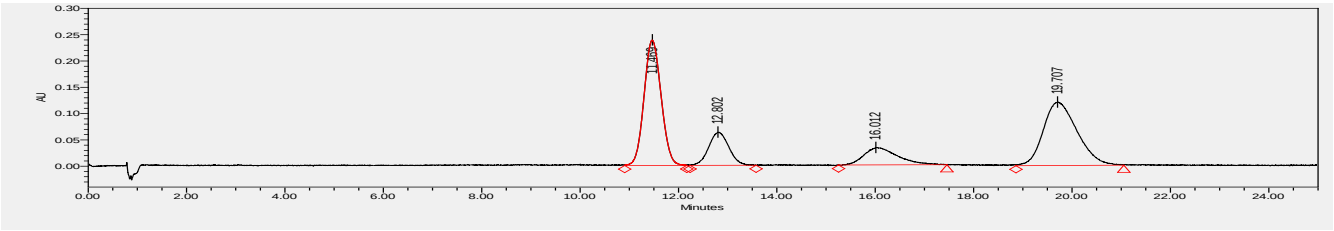
SFC (Daicel Chiralcel AZ-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 230 nm), t_1 = 11.39 min, t_2 = 12.84 min, t_3 = 16.14 min, t_4 = 19.74 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 (t, *J* = 1.7 Hz, 1H), 7.93 (d, *J* = 14.7 Hz, 1H), 7.83 (t, *J* = 7.0 Hz, 1H), 7.66 (ddd, *J* = 8.0, 1.9, 0.9 Hz, 1H), 7.59 – 7.35 (m, 3H), 7.34 – 7.28 (m, 1H), 7.08 (t, *J* = 7.9 Hz, 1H), 5.02 (ddd, *J* = 8.7, 6.6, 3.5 Hz, 1H), 4.71 (d, *J* = 10.0 Hz, 2H), 4.63 – 4.55 (m, 1H), 4.52 – 4.42 (m, 1H), 3.48 (d, *J* = 6.6 Hz, 1H), 2.25 (dd, *J* = 14.5, 3.1 Hz, 1H), 2.04 – 1.95 (m, 2H), 1.92 (d, *J* = 1.8 Hz, 1H), 1.86 (d, *J* = 4.3 Hz, 2H), 1.56 (s, 3H), 0.40 (s, 3H)

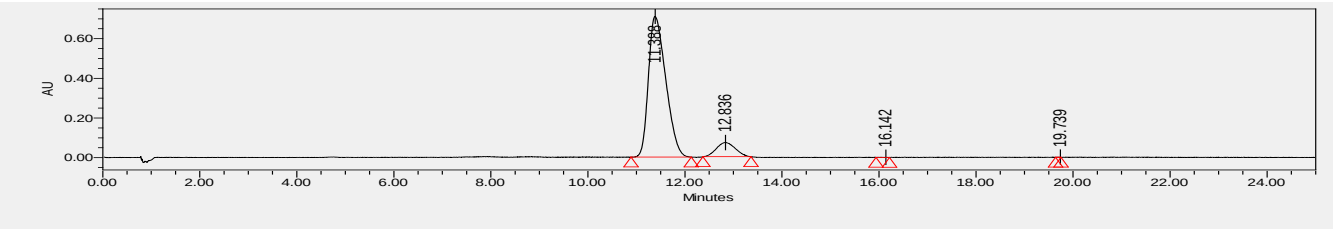
^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.4, 142.8, 141.8, 141.0, 139.4, 136.8, 135.5, 132.5, 131.6, 130.4, 129.7, 129.2, 127.0, 126.3, 124.0, 123.3, 122.1, 112.6, 109.8, 72.1, 44.0, 26.4, 25.5, 24.7, -5.1.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{25}H_{27}BrO_2SSi + Na^+]$ = 521.0577, 523.0556, found 521.0580, 523.0559.

IR (neat): 3478, 3072, 2919, 1686, 1635, 1566, 1402, 1283, 1251, 1160, 1088, 1042, 981, 876, 799 and 701 cm^{-1}.

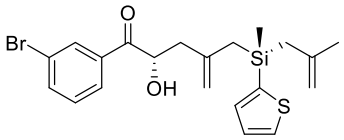


	Retention Time	Area	% Area
1	11.469	5737827	38.68
2	12.802	1777327	11.98
3	16.012	1567315	10.57
4	19.707	5750924	38.77



	Retention Time	Area	% Area
1	11.388	17570383	89.98
2	12.836	1947036	9.97
3	16.142	7058	0.04
4	19.739	1942	0.01

C59: (S)-1-(3-bromophenyl)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(thiophen-2-yl)silyl)methyl)pent-4-en-1-one



($C_{21}H_{25}BrO_2SSi$) Colorless oil; 34.2 mg, 76% yield, 99/99% ee, 75:25 dr; $[\alpha]^{21}_D$ = -13.1 (c = 0.56 g/100 mL, in CH_2Cl_2).

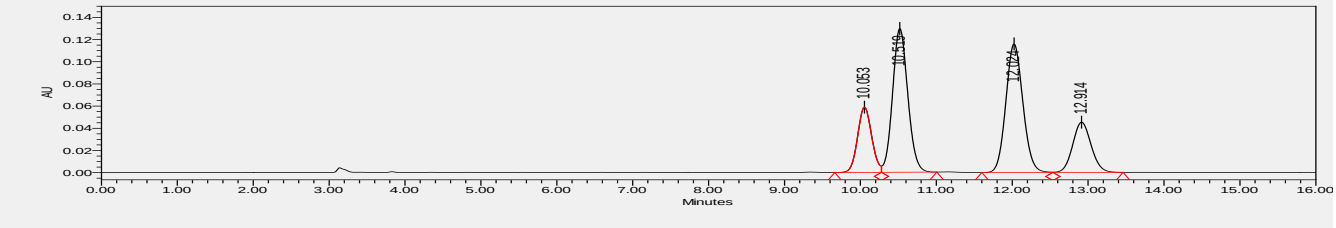
HPLC (Daicel chiralcel OXH, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 230 nm), t_1 = 9.21 min, t_2 = 9.83 min, t_3 = 11.42 min, t_4 = 12.24 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.99 (d, J = 5.8 Hz, 1H), 7.76 – 7.72 (m, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.57 (dd, J = 10.4, 4.6 Hz, 1H), 7.38 – 7.30 (m, 1H), 7.26 (d, J = 2.4 Hz, 1H), 7.16 – 7.13 (m, 1H), 5.06 (tt, J = 6.7, 3.4 Hz, 1H), 4.75 (d, J = 9.2 Hz, 2H), 4.63 (s, 1H), 4.51 (s, 1H), 3.47 (d, J = 6.6 Hz, 1H), 2.34 – 2.23 (m, 1H), 2.00 (dd, J = 14.7, 8.5 Hz, 1H), 1.90 (dd, J = 18.4, 5.3 Hz, 2H), 1.87 – 1.80 (m, 2H), 1.60 (s, 3H), 0.37 (s, 3H).

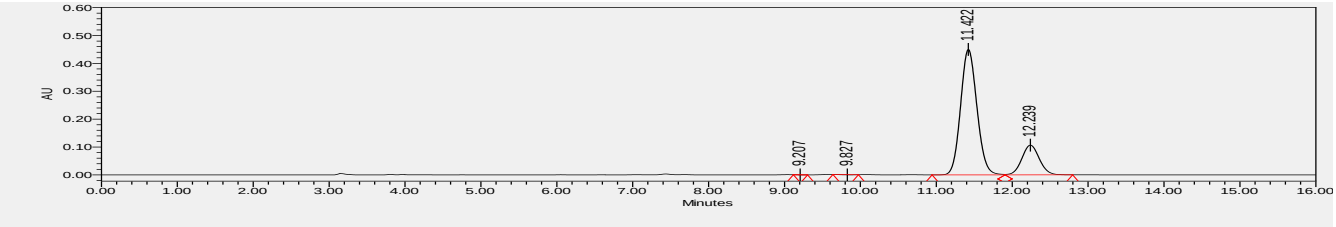
^{13}C NMR (151 MHz, $CDCl_3$) δ = 200.4, 142.4, 141.5, 136.8, 136.5, 135.6, 135.4, 131.7, 131.3, 130.6, 128.4, 127.2, 123.4, 112.8, 110.1, 72.2, 43.9, 27.1, 25.4, 25.4, -3.9.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{21}H_{25}BrO_2SSi + Na^+]$ = 471.0420, 473.0400, found 471.0427, 473. 0405.

IR (neat): 3478, 3073, 2920, 1686, 1636, 1565, 1407, 1251, 1214, 1163, 1084, 990, 878, 810 and 713 cm^{-1}.

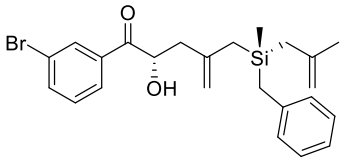


	Retention Time	Area	% Area
1	10.053	759401	14.78
2	10.519	1807019	35.17
3	12.024	1808483	35.20
4	12.914	762952	14.85



	Retention Time	Area	% Area
1	9.207	1126	0.01
2	9.827	9227	0.11
3	11.422	6729074	79.70
4	12.239	1703668	20.18

C60: (S)-4-(((S)-benzyl(methyl)(2-methylallyl)silyl)methyl)-1-(3-bromophenyl)-2-hydroxypent-4-en-1-one



($C_{24}H_{29}BrO_2Si$) Colorless oil; 32.2 mg, 70% yield, 99/99% ee, 48:52 dr (determined by SFC); $[\alpha]_D^{22}$ = +6.2 (c = 0.51 g/100 mL, in CH_2Cl_2).

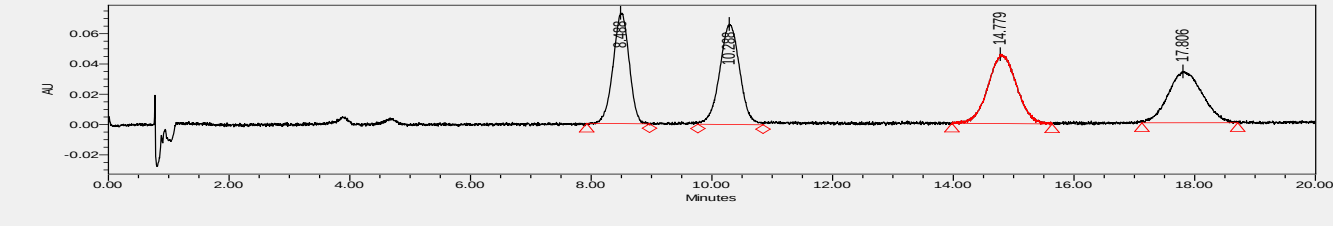
SFC (Daicel Chiralcel IG-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 230 nm), t_1 = 8.46 min, t_2 = 10.32 min, t_3 = 14.74 min, t_4 = 17.81 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 – 8.00 (m, 1H), 7.85 – 7.69 (m, 2H), 7.41 – 7.32 (m, 1H), 7.20 (q, J = 7.7 Hz, 2H), 7.07 (q, J = 7.1 Hz, 1H), 6.99 (t, J = 7.5 Hz, 2H), 5.10 (ddd, J = 10.2, 8.5, 5.0 Hz, 1H), 4.76 (d, J = 13.8 Hz, 2H), 4.65 – 4.60 (m, 1H), 4.48 (d, J = 7.1 Hz, 1H), 3.52 (d, J = 6.5 Hz, 1H), 2.47 – 2.36 (m, 1H), 2.20 – 2.04 (m, 3H), 1.70 – 1.65 (m, 4H), 1.65 – 1.55 (m, 3H), -0.02 (d, J = 5.2 Hz, 3H).

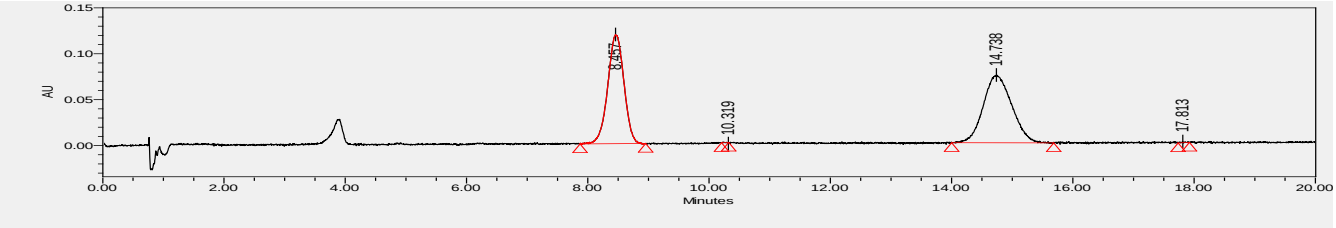
^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.4, 143.0, 142.1, 139.4, 137.0, 135.6, 131.7, 130.6, 128.5, 128.4, 127.2, 124.4, 123.4, 112.3, 109.7, 72.5, 44.4, 25.6, 25.3, 24.2, 23.5, -4.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{24}H_{29}BrO_2Si + Na^+]$ = 479.1012, 481.0992, found 479.1013, 481.0991.

IR (neat): 3478, 3073, 2920, 1686, 1635, 1565, 1412, 1250, 1208, 1162, 1087, 979, 875, 819, 7634 and 701 cm^{-1}.

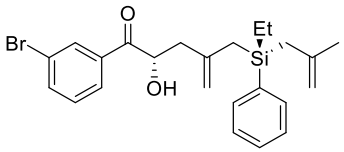


	Retention Time	Area	% Area
1	8.488	1351682	23.67
2	10.288	1520985	26.64
3	14.779	1500231	26.28
4	17.806	1336535	23.41



	Retention Time	Area	% Area
1	8.457	2198800	47.76
2	10.319	2693	0.06
3	14.738	2397135	52.07
4	17.813	5021	0.11

C61: (S)-1-(3-bromophenyl)-4-(((S)-ethyl(2-methylallyl)(phenyl)silyl)methyl)-2-hydroxypent-4-en-1-one



($C_{24}H_{29}BrO_2Si$) Colorless oil; 30.4 mg, 66% yield, 99/99% ee, 69:31 dr; $[\alpha]^{20}_D$ = -4.7 (*c* = 0.49 g/100 mL, in CH_2Cl_2).

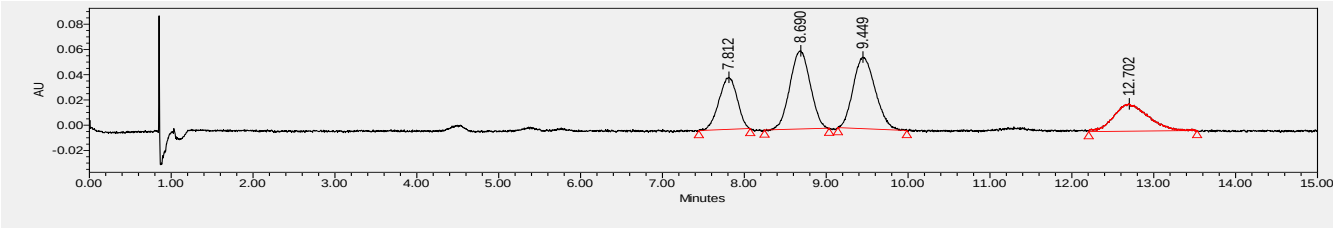
SFC (Daicel Chiralcel ODH, CO_2/MeOH = 90/10, 1.0 mL/min, λ = 230 nm), t_1 = 7.80 min, t_2 = 8.63 min, t_3 = 9.45 min, t_4 = 12.77 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 (q, *J* = 2.7, 2.2 Hz, 1H), 7.78 – 7.71 (m, 1H), 7.65 – 7.59 (m, 1H), 7.45 (ddd, *J* = 11.1, 7.7, 1.7 Hz, 2H), 7.37 – 7.26 (m, 4H), 5.04 (ddd, *J* = 8.4, 6.7, 3.5 Hz, 1H), 4.72 (d, *J* = 6.3 Hz, 2H), 4.65 – 4.56 (m, 1H), 4.54 – 4.47 (m, 1H), 3.44 (dd, *J* = 6.7, 1.7 Hz, 1H), 2.24 (ddd, *J* = 14.1, 10.9, 3.3 Hz, 1H), 2.01 – 1.92 (m, 1H), 1.88 (d, *J* = 6.1 Hz, 2H), 1.84 (d, *J* = 5.3 Hz, 2H), 1.58 (s, 3H), 1.05 – 0.95 (m, 3H), 0.91 (dddd, *J* = 12.7, 9.6, 4.7, 2.9 Hz, 2H).

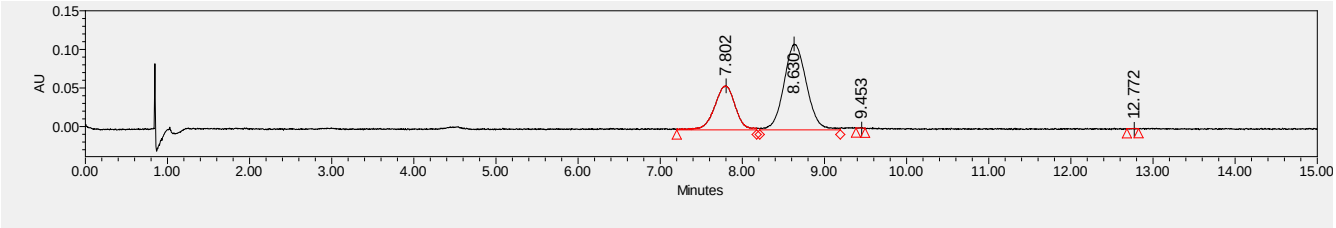
^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.4, 142.9, 141.9, 136.8, 136.3, 135.7, 134.3, 131.7, 130.5, 129.3, 127.9, 127.1, 123.3, 112.6, 110.0, 72.3, 44.1, 25.6, 23.8, 22.8, 7.4, 3.5.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{24}H_{29}BrO_2Si + Na^+]$ = 479.1012, 481.0992, found 479.1009, 481.0984.

IR (neat): 3480, 3072, 2919, 1688, 1636, 1565, 1423, 1250, 1111, 980, 877, 792 and 703 cm^{-1}.

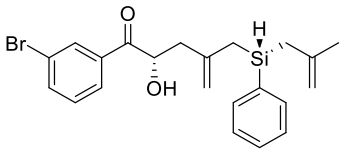


	Retention Time	Area	% Area
1	7.812	637414	18.72
2	8.690	1073762	31.54
3	9.449	1062224	31.20
4	12.702	631174	18.54



	Retention Time	Area	% Area
1	7.802	1001717	32.05
2	8.630	2119666	67.81
3	9.453	1984	0.06
4	12.772	2462	0.08

C62: (S)-1-(3-bromophenyl)-2-hydroxy-4-(((S)-(2-methylallyl)(phenyl)silyl)methyl)pent-4-en-1-one



($C_{22}H_{25}BrO_2Si$) Colorless oil; 28.6 mg, 66% yield, 99/99% ee, 78:22 dr; $[\alpha]^{22}_D$ = +3.4 (*c* = 0.41 g/100 mL, in CH_2Cl_2).

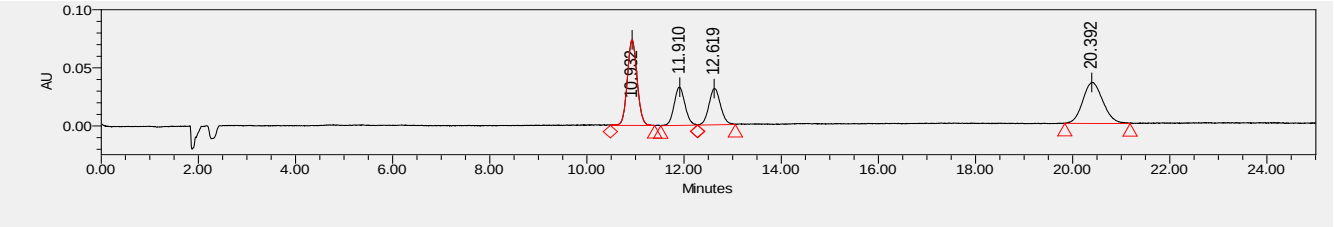
SFC (Daicel Chiralcel ADH, CO_2/MeOH = 90/10 , 1.5 mL/min, λ = 230 nm), t_1 = 10.76 min, t_2 = 11,74 min, t_3 = 12.39 min, t_4 = 20.19 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (s, 1H), 7.78 – 7.66 (m, 2H), 7.56 – 7.45 (m, 2H), 7.41 – 7.28 (m, 4H), 5.09 (td, *J* = 9.1, 8.0, 3.4 Hz, 1H), 4.78 (d, *J* = 5.8 Hz, 1H), 4.75 (s, 1H), 4.61 (s, 1H), 4.53 (s, 1H), 4.38 (dp, *J* = 7.1, 3.6 Hz, 1H), 3.49 (dd, *J* = 6.5, 3.6 Hz, 1H), 2.45 (dd, *J* = 14.7, 2.8 Hz, 1H), 2.17 – 2.07 (m, 1H), 1.96 (dd, *J* = 8.4, 4.1 Hz, 2H), 1.91 – 1.80 (m, *J* = 4.2, 3.8 Hz, 2H), 1.69 (s, 1H), 1.65 (s, 2H).

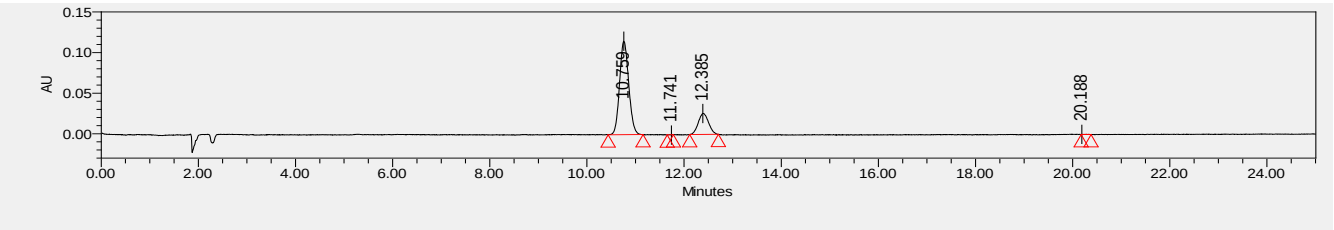
^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.4, 142.5, 141.6, 136.9, 135.6, 134.8, 134.4, 131.7, 130.6, 129.9, 128.1, 127.2, 123.4, 113.1, 110.2, 72.3, 43.8, 24.9, 23.8, 22.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{22}H_{25}BrO_2Si + Na^+]$ = 451.0699, 453.0697, found 451.0701, 453.0681.

IR (neat): 3476, 3071, 2921, 2123, 1685, 1636, 1565, 1424, 1249, 1161, 1112, 979, 837, 791 and 703 cm^{-1}.

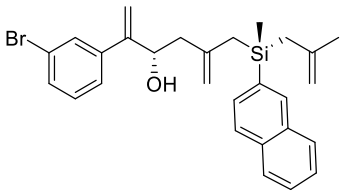


	Retention Time	Area	% Area
1	10.932	1031349	33.43
2	11.910	512778	16.62
3	12.619	520570	16.88
4	20.392	1020046	33.07



	Retention Time	Area	% Area
1	10.759	1502550	79.66
2	11.741	722	0.04
3	12.385	382097	20.26
4	20.188	916	0.05

D: (S)-2-(3-bromophenyl)-5-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)hexa-1,5-dien-3-ol



($C_{28}H_{31}BrOSi$) Colorless oil; 41.8 mg, 85% yield, 99/99% ee, 90:10 dr; $[\alpha]^{21}_D$ = +24.1 (*c* = 0.33 g/100 mL, in CH_2Cl_2).

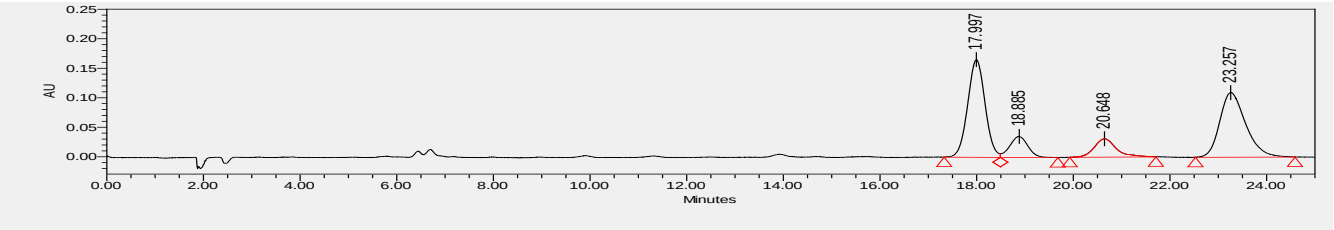
SFC (Daicel Chiralcel IG, CO_2/MeOH = 90/10, 1.0 mL/min, λ = 230 nm), t_1 = 17.89 min, t_2 = 18.76 min, t_3 = 20.58 min, t_4 = 23.21 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (s, 1H), 7.82 – 7.76 (m, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.50 – 7.44 (m, 3H), 7.41 (t, *J* = 1.6 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 7.02 (t, *J* = 7.8 Hz, 1H), 5.29 (s, 1H), 5.17 (s, 1H), 4.75 (d, *J* = 4.7 Hz, 2H), 4.61 – 4.58 (m, 1H), 4.55 (d, *J* = 9.3 Hz, 1H), 4.49 (s, 1H), 2.07 (s, 1H), 2.00 – 1.92 (m, 2H), 1.89 – 1.81 (m, 4H), 1.56 (s, 3H), 0.38 (s, 3H).

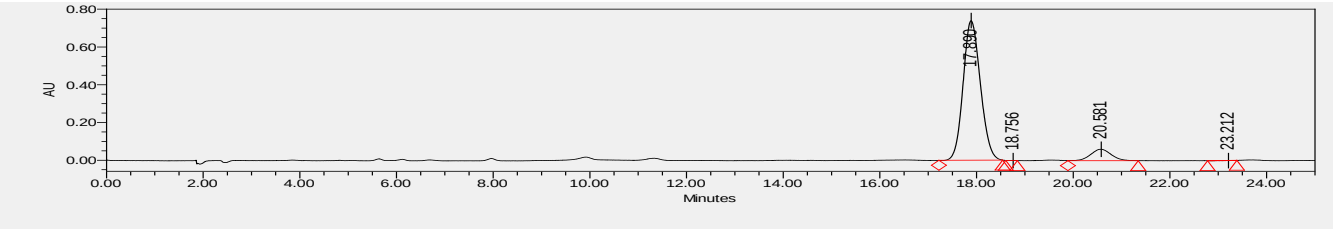
^{13}C NMR (101 MHz, $CDCl_3$) δ = 149.7, 143.6, 142.8, 142.1, 134.8, 134.6, 133.9, 132.9, 130.6, 130.1, 130.0, 129.9, 128.2, 127.9, 127.1, 126.6, 126.1, 125.5, 122.6, 114.0, 112.6, 109.8, 70.4, 45.7, 26.2, 25.5, 24.3, -5.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{28}H_{31}BrOSi + Na^+]$ = 513.1220, 515.1199, found 513.1221, 515.1193.

IR (neat): 3448, 3055, 2921, 1633, 1557, 1407, 1254, 1159, 1082, 863, 813 and 743 cm^{-1}.

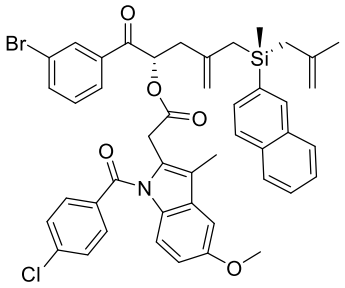


	Retention Time	Area	% Area
1	17.997	4127053	40.73
2	18.885	929237	9.17
3	20.648	990068	9.77
4	23.257	4087214	40.33



	Retention Time	Area	% Area
1	17.890	18299973	91.05
2	18.756	2039	0.01
3	20.581	1780645	8.86
4	23.212	16756	0.08

E: (S)-1-(3-bromophenyl)-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)-1-oxopent-4-en-2-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-3-methyl-1H-indol-2-yl)acetate



($C_{46}H_{43}BrClNO_5Si$) Colorless oil; 76.6 mg, 92% yield, 99/99% ee, 90:10 dr; $[\alpha]^{26}_D$ = -3.7 (*c* = 0.63 g/100 mL, in CH_2Cl_2).

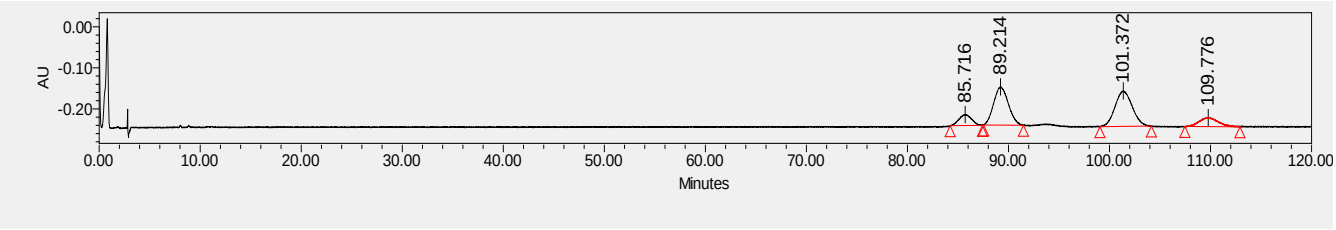
SFC (Daicel Chiralcel ODH, CO_2/*i*-PrOH = 85/15, 1.0 mL/min, λ = 230 nm), t_1 = 85.76 min, t_2 = 89.25 min, t_3 = 101.32 min, t_4 = 109.99 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.95 (s, 1H), 7.89 (s, 1H), 7.81 – 7.75 (m, 2H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.42 (m, 6H), 7.00 (t, *J* = 7.9 Hz, 1H), 6.92 (d, *J* = 2.4 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 1H), 6.67 (dd, *J* = 9.0, 2.4 Hz, 1H), 5.82 (dd, *J* = 8.9, 4.3 Hz, 1H), 4.64 (s, 2H), 4.61 (s, 1H), 4.50 (s, 1H), 3.82 (s, 3H), 3.71 (d, *J* = 2.3 Hz, 2H), 2.32 (s, 3H), 2.29 – 2.18 (m, 2H), 1.87 (d, *J* = 2.5 Hz, 4H), 1.57 (s, 3H), 0.42 (s, 3H).

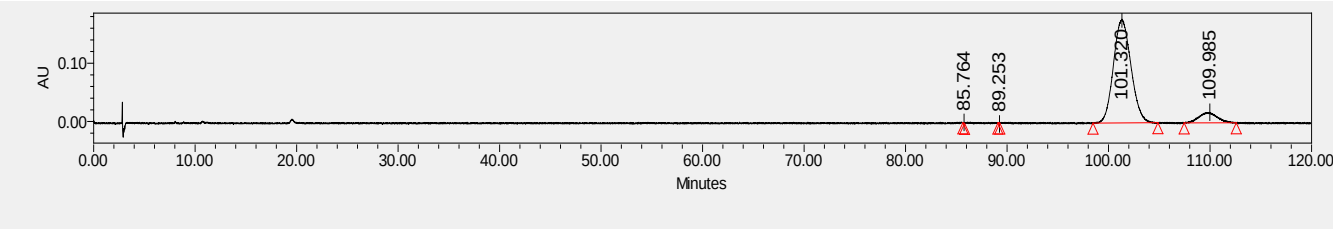
^{13}C NMR (101 MHz, $CDCl_3$) δ = 195.0, 170.4, 168.4, 156.2, 142.7, 140.8, 139.4, 136.4, 136.1, 134.8, 134.5, 134.0, 133.9, 132.9, 131.4, 131.3, 130.9, 130.6, 130.2, 130.0, 129.2, 128.2, 127.9, 127.2, 126.7, 126.2, 123.1, 115.1, 112.8, 112.1, 112.0, 109.9, 101.3, 74.0, 55.8, 39.5, 30.0, 26.2, 25.5, 24.3, 13.5, -5.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{46}H_{43}BrClNO_5Si + Na^+]$ = 854.1675, 856.1654, 858.1625, found 854.1678, 856.1663, 858.1624.

IR (neat): 3058, 2924, 1738, 1684, 1594, 1475, 1360, 1317, 1223, 1157, 1079, 809,734 and 478 cm^{-1}.

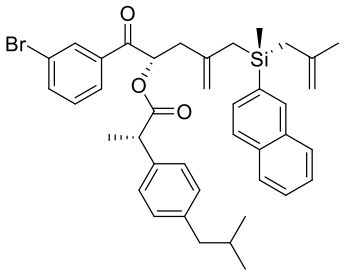


	Retention Time	Area	% Area
1	85.716	2308713	9.33
2	89.214	9420331	38.06
3	101.372	10195181	41.19
4	109.776	2828948	11.43



	Retention Time	Area	% Area
1	85.764	4132	0.02
2	89.253	4329	0.02
3	101.320	21348046	90.62
4	109.985	2201122	9.34

F: (S)-1-(3-bromophenyl)-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)-1-oxopent-4-en-2-yl (S)-2-(4-isobutylphenyl)propanoate



($C_{40}H_{45}BrO_3Si$) Colorless oil; 64.1 mg, 94% yield, 99/99% ee, 89:11 dr (determined by SFC); $[\alpha]^{24}_D$ = +28.2 (*c* = 0.60 g/100 mL, in CH_2Cl_2).

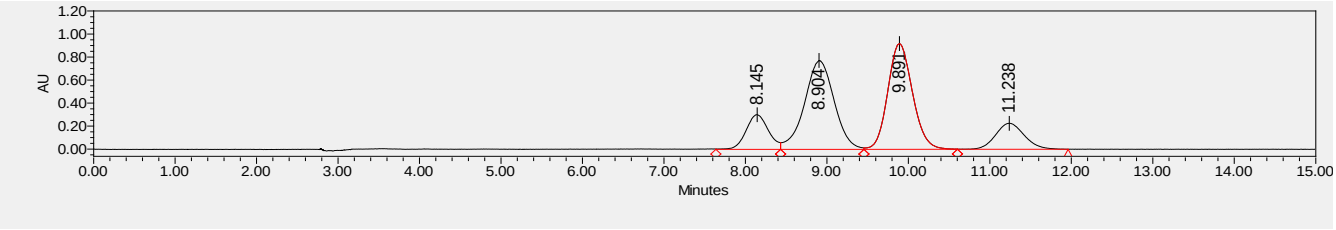
SFC (Daicel Chiralcel OJH, CO_2/MeOH = 80/20, 1.0 mL/min, λ = 230 nm), t_1 = 8.17 min, t_2 = 8.91 min, t_3 = 9.92 min, t_4 = 11.29 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 (s, 1H), 7.87 (s, 1H), 7.81 – 7.75 (m, 2H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.46 (dd, *J* = 8.6, 4.1 Hz, 3H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.04 – 6.97 (m, 3H), 5.76 (dd, *J* = 8.7, 4.5 Hz, 1H), 4.65 (s, 1H), 4.62 (d, *J* = 8.8 Hz, 2H), 4.51 (s, 1H), 3.69 (q, *J* = 7.2 Hz, 1H), 2.41 (d, *J* = 7.2 Hz, 2H), 2.31 – 2.20 (m, 2H), 1.89 (d, *J* = 5.8 Hz, 4H), 1.84 – 1.76 (m, 1H), 1.57 (s, 3H), 1.47 (d, *J* = 7.2 Hz, 3H), 0.88 (s, 3H), 0.87 (s, 3H), 0.43 (s, 3H).

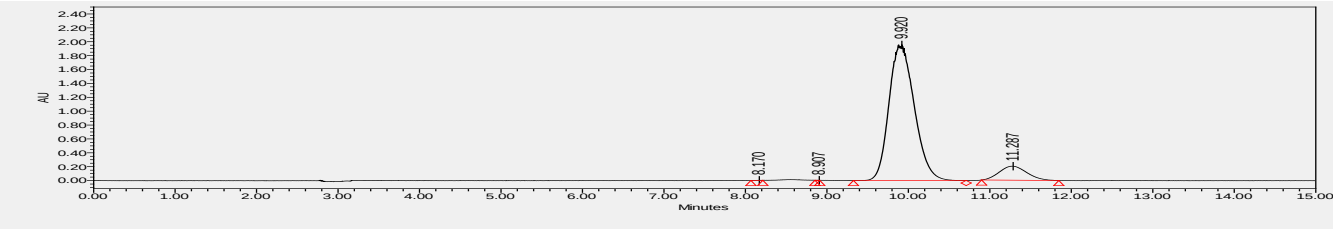
^{13}C NMR (101 MHz, $CDCl_3$) δ = 195.0, 174.1, 142.8, 140.9, 140.7, 136.9, 136.5, 136.1, 134.9, 134.7, 133.9, 132.9, 131.4, 130.1, 130.1, 129.4, 128.2, 127.9, 127.4, 127.2, 126.8, 126.7, 126.2, 123.0, 112.8, 109.8, 73.8, 45.2, 45.0, 39.4, 30.3, 26.2, 25.5, 24.4, 22.5, 18.5, -5.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{40}H_{45}BrO_3Si + Na^+]$ = 703.2214, 705.2193, found 703.2217, 705.2200.

IR (neat): 3051, 2956, 1736, 1701, 1636, 1419, 1157, 1080, 856, 810 and 742 cm^{-1}.

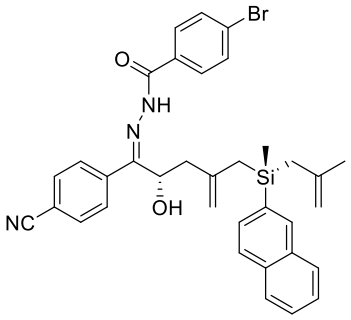


	Retention Time	Area	% Area
1	8.145	5713183	11.41
2	8.904	19476816	38.90
3	9.891	19308361	38.56
4	11.238	5575987	11.14



	Retention Time	Area	% Area
1	8.170	3443	0.01
2	8.907	1591	0.00
3	9.920	42173542	89.91
4	11.287	4727932	10.08

G: 4-bromo-N'-((S,Z)-1-(4-cyanophenyl)-2-hydroxy-4-(((S)-methyl(2-methylallyl)(naphthalen-2-yl)silyl)methyl)pent-4-en-1-ylidene)benzohydrazide



($C_{35}H_{34}BrN_3O_2Si$) White solid; 53.4 mg, 84% yield, 99/99% ee, 88:12 dr (determined by SFC); m.p. 133-135 °C, $[\alpha]_D^{23}$ = -87.0 (*c* = 0.55 g/100 mL, in CH_2Cl_2).

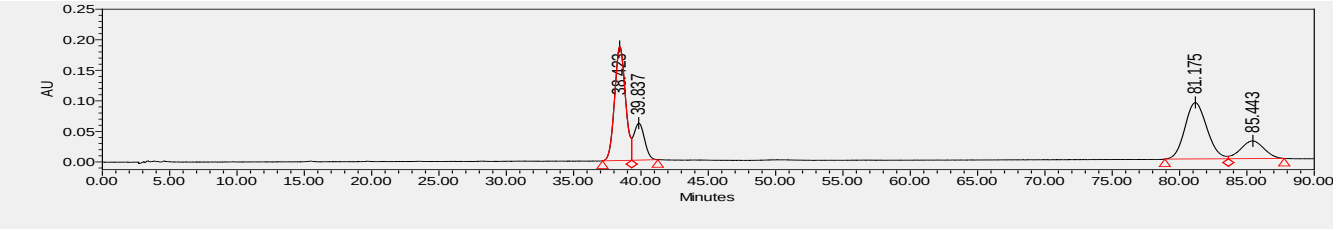
SFC (Daicel Chiralcel OXH, CO_2/MeOH = 80/20, 1.0 mL/min, λ = 230 nm), t_1 = 38.49 min, t_2 = 39.85 min, t_3 = 81.14 min, t_4 = 85.44 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.27 (s, 1H), 7.89 (d, *J* = 8.7 Hz, 1H), 7.74 (t, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.47 (m, 6H), 7.47 – 7.35 (m, 3H), 7.22 (d, *J* = 7.9 Hz, 2H), 5.17 – 4.90 (m, 1H), 4.81 (d, *J* = 20.9 Hz, 2H), 4.61 (s, 1H), 4.49 (s, 1H), 4.05 (s, 1H), 2.40 – 2.17 (m, 1H), 2.00 – 1.78 (m, 5H), 1.57 (s, 3H), 0.40 (s, 3H).

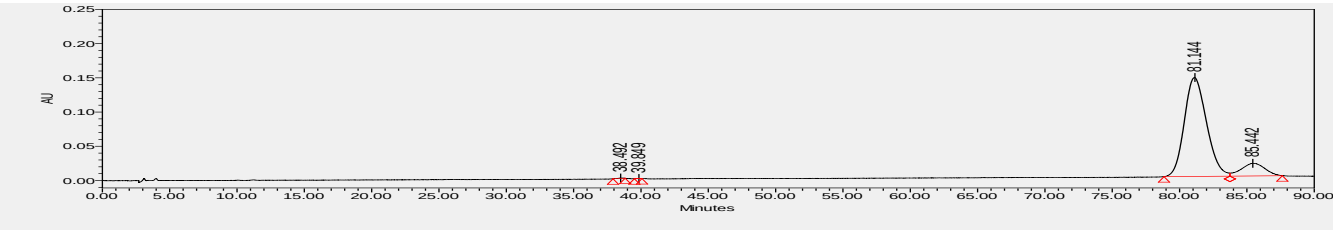
^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.4, 142.3, 141.5, 139.8, 134.6, 134.1, 133.7, 133.1, 132.7, 132.1, 132.0, 131.4, 129.5, 128.6, 128.0, 127.8, 127.2, 127.0, 127.0, 126.4, 118.3, 113.9, 112.7, 110.0, 109.8, 70.8, 41.5, 26.0, 25.4, 24.5, -5.7.

HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $[C_{35}H_{34}BrN_3O_2Si + Na^+]$ = 658.1496, 660.1475, found 658.1489, 660.1472.

IR (neat): 3231, 3070, 2920, 2229, 1667, 1589, 1479, 1272, 1156, 1077, 1012, 863, 814 and 746 cm^{-1}.

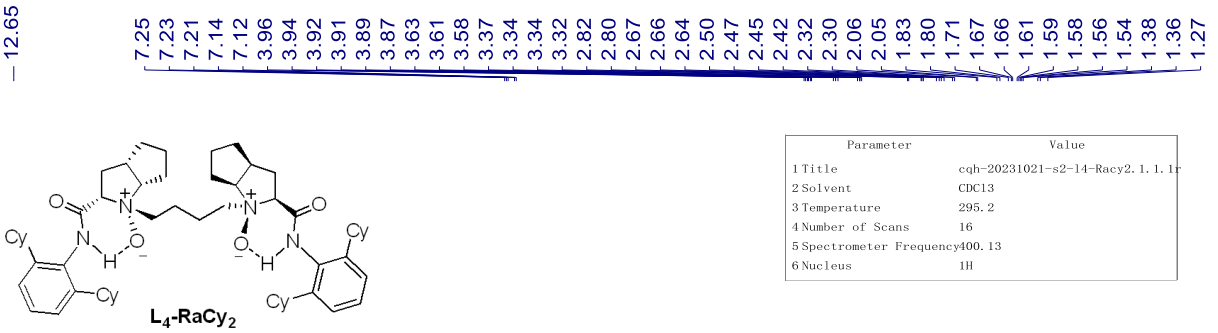


	Retention Time	Area	% Area
1	38.423	10474312	37.71
2	39.837	3368263	12.13
3	81.175	10475947	37.71
4	85.443	3459881	12.46

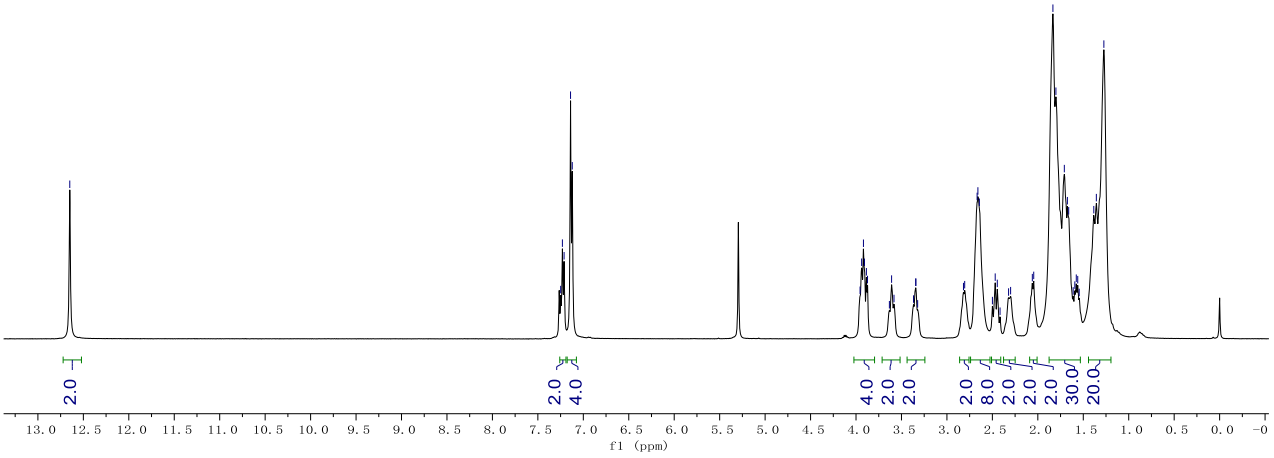


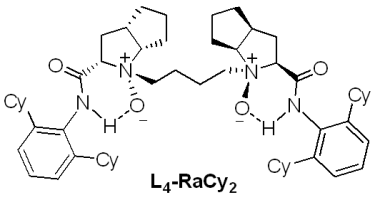
	Retention Time	Area	% Area
1	38.492	16728	0.09
2	39.849	2970	0.02
3	81.144	16587202	87.93
4	85.442	2256136	11.96

12. Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra of the products.

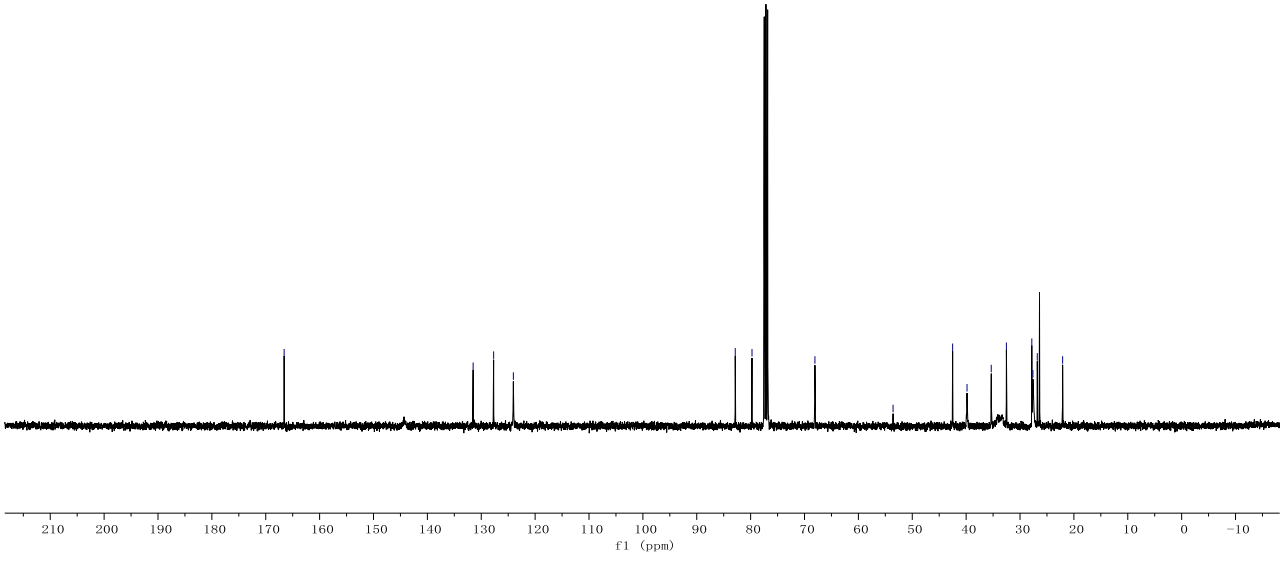


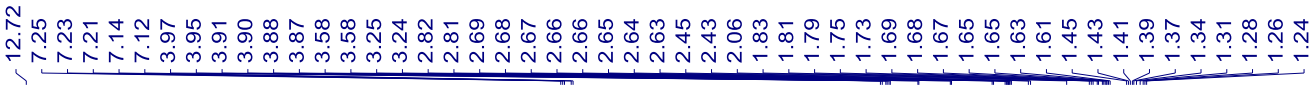
Parameter	Value
1 Title	cqh-20231021-s2-14-Racy2.1.1.1r
2 Solvent	CDCl3
3 Temperature	295.2
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H

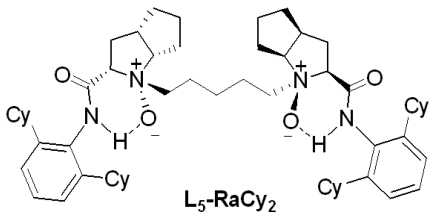




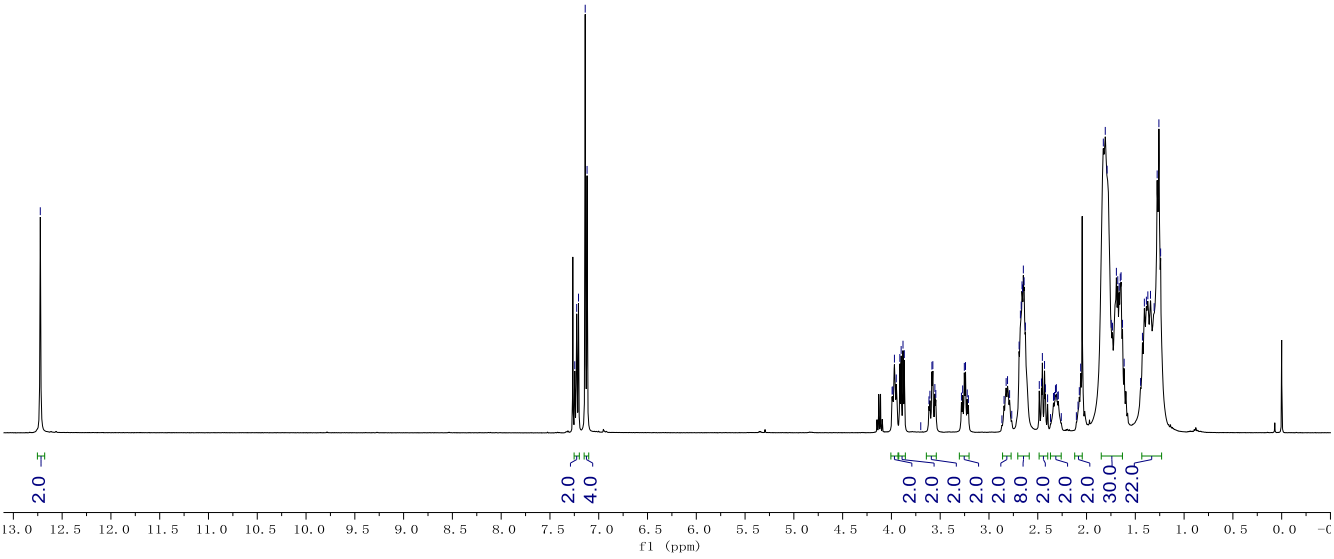
Parameter	Value
1 Title	cqh-20231021-s2-14-Racy2.2.1.1r
2 Solvent	CDCl3
3 Temperature	296.0
4 Number of Scans	256
5 Spectrometer Frequency	100.61
6 Nucleus	13C



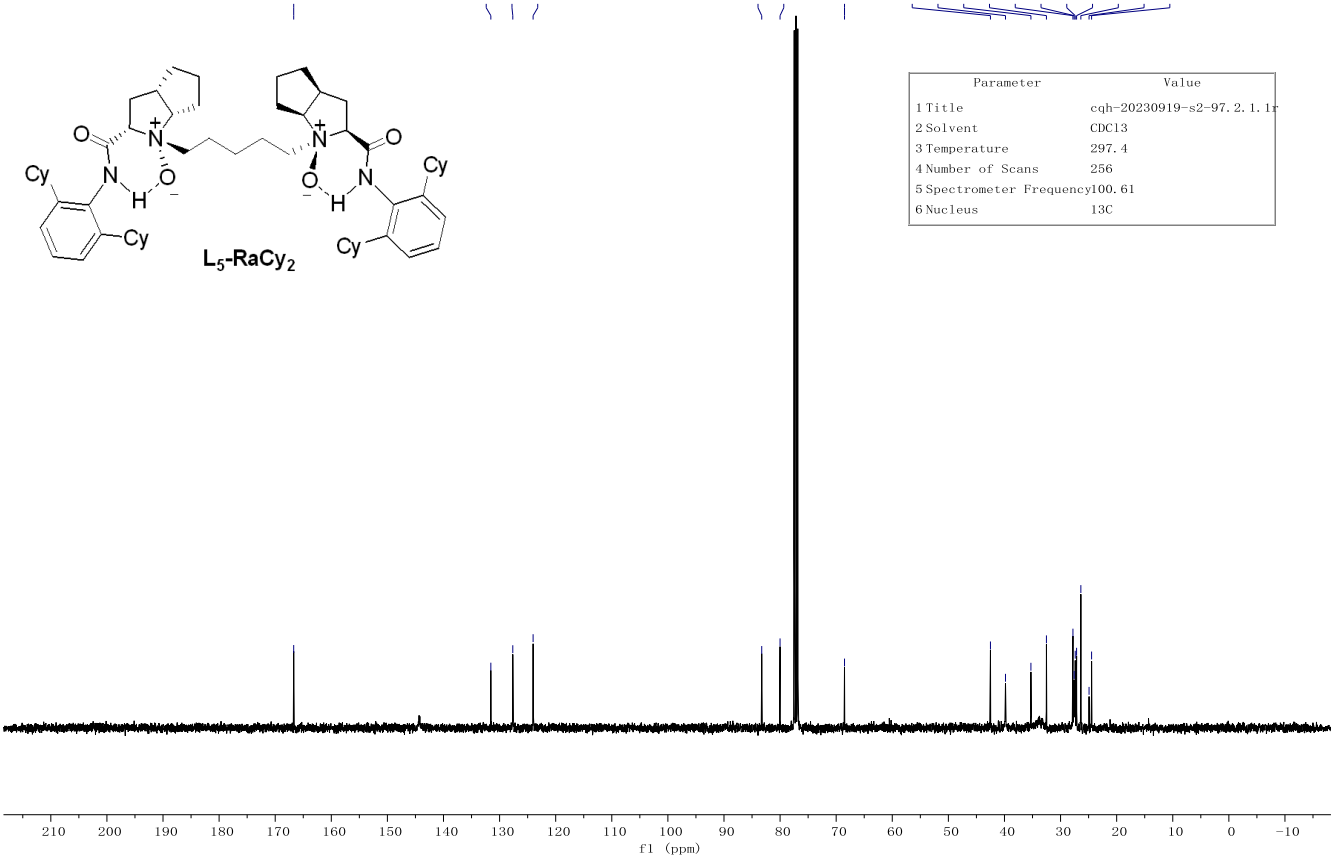




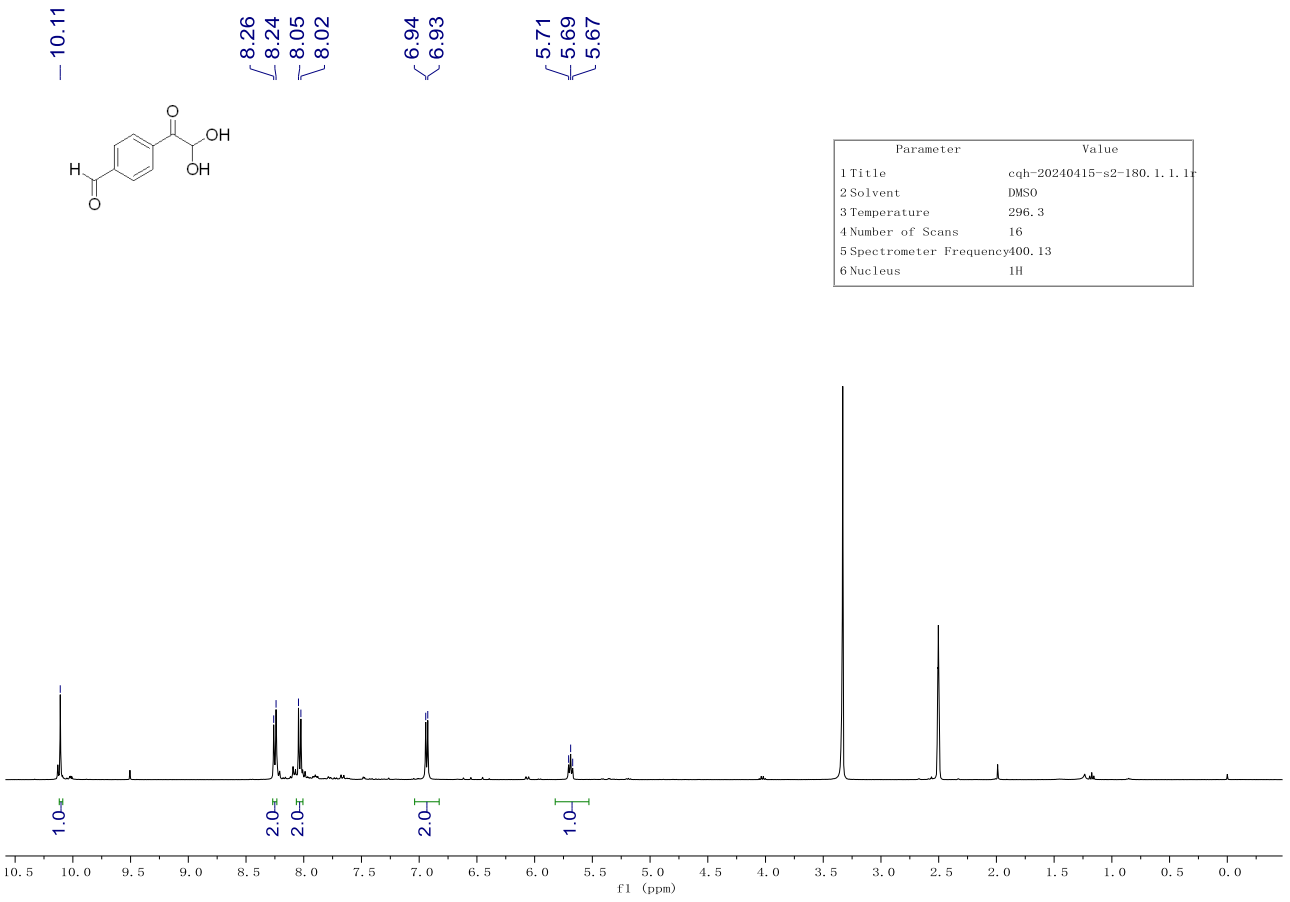
Parameter	Value
1 Title	cqh-20230919-s2-97.1.1.1r
2 Solvent	CDCl3
3 Temperature	296.6
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H

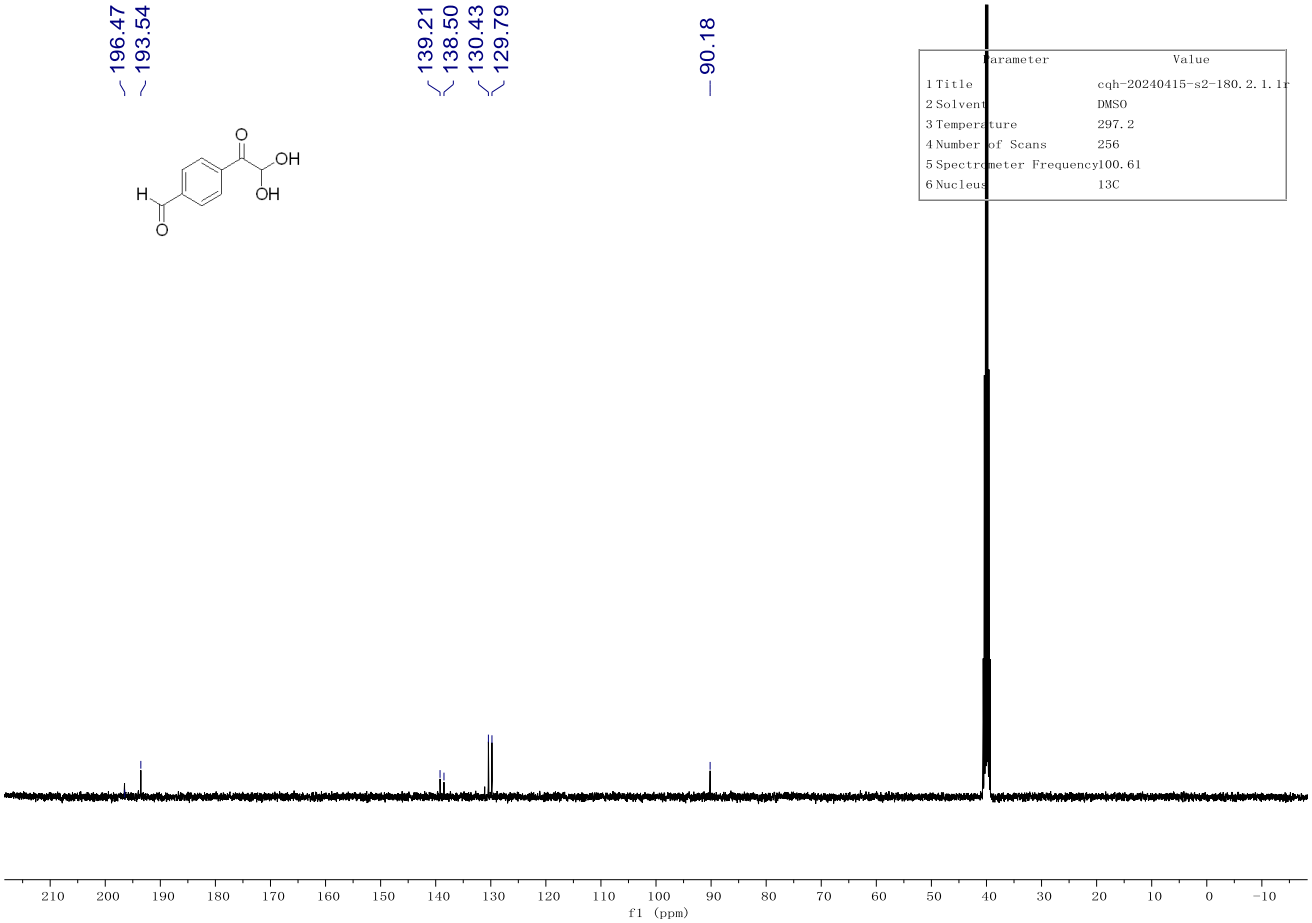


Parameter	Value
1 Title	cqh-20230919-s2-97.2.1.1r
2 Solvent	CDCl3
3 Temperature	297.4
4 Number of Scans	256
5 Spectrometer Frequency	100.61
6 Nucleus	13C

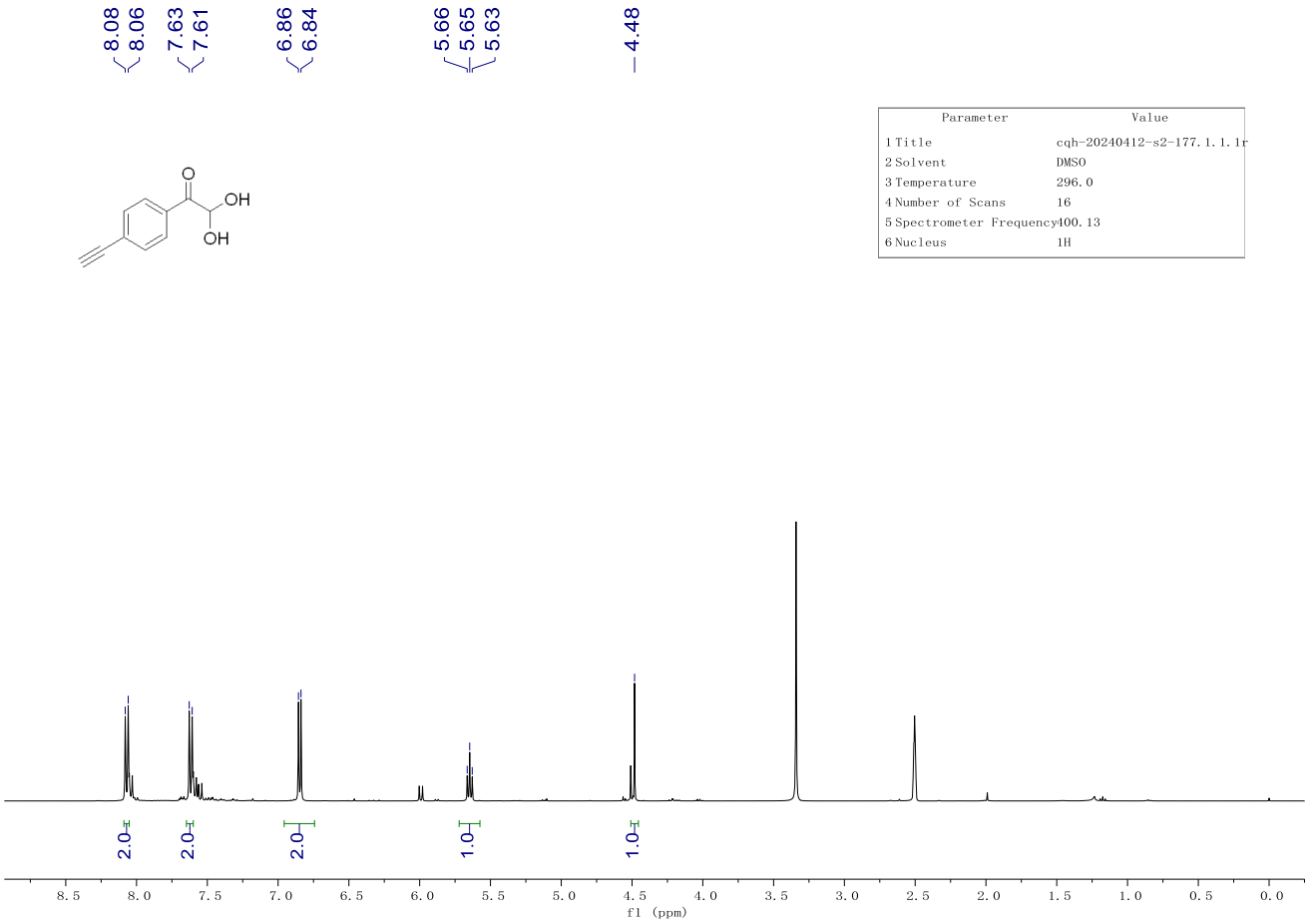


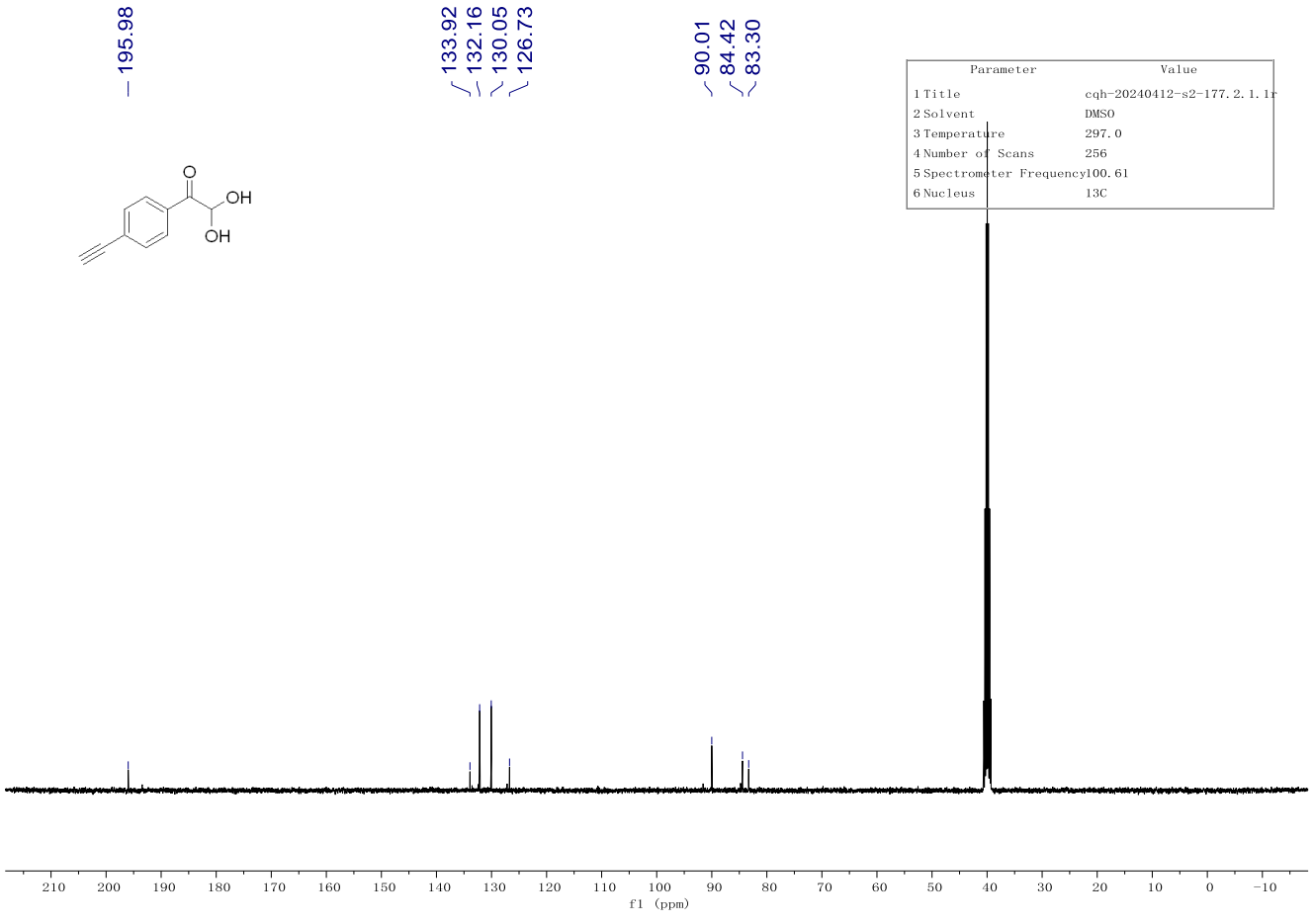
A22


10.11
8.26
8.24
8.05
8.02
6.94
6.93
5.71
5.69
5.67
OH
OH
H
O
O
Parameter Value
1 Title cqh-20240415-s2-180.1.1.1r
2 Solvent DMSO
3 Temperature 296.3
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
1.0
2.0
2.0
2.0
1.0
f1 (ppm)

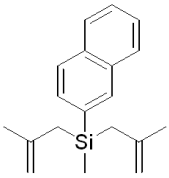

196.47
193.54
139.21
138.50
130.43
129.79
90.18
OH
OH
H
O
O
Parameter Value
1 Title cqh-20240415-s2-180.2.1.1r
2 Solvent DMSO
3 Temperature 297.2
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)

A26

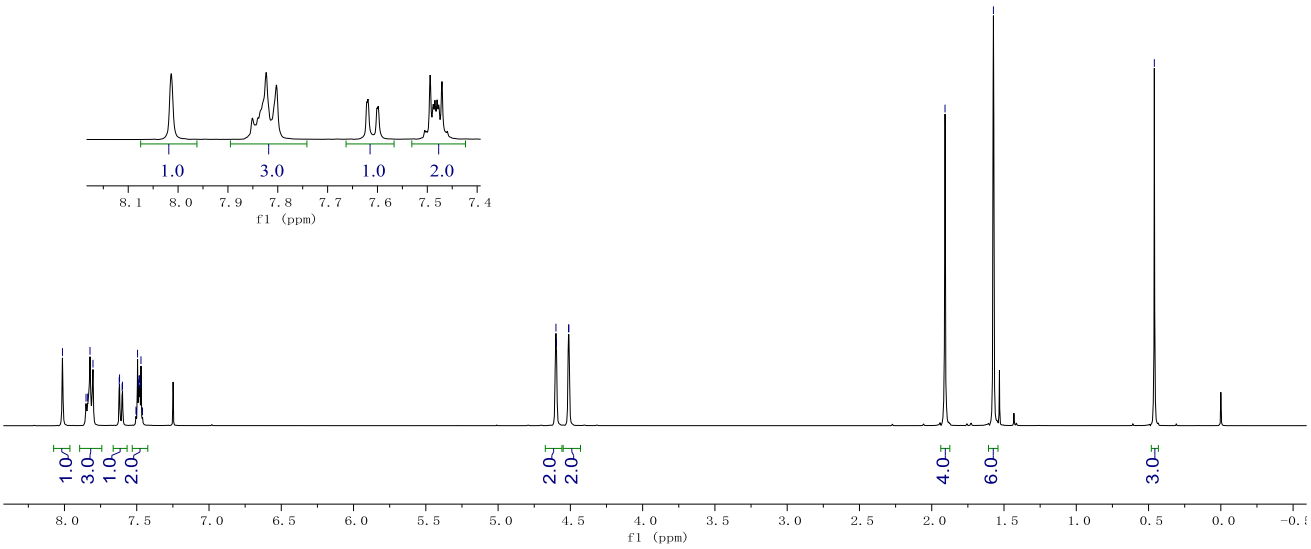

8.08
8.06
7.63
7.61
6.86
6.84
5.66
5.65
5.63
4.48
OH
OH
Parameter Value
1 Title cqh-20240412-s2-177.1.1.1r
2 Solvent DMSO
3 Temperature 296.0
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
2.0
2.0
2.0
1.0
1.0
f1 (ppm)

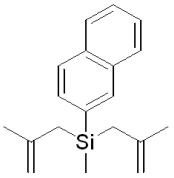

195.98
133.92
132.16
130.05
126.73
90.01
84.42
83.30
OH
OH
Parameter Value
1 Title cqh-20240412-s2-177.2.1.1r
2 Solvent DMSO
3 Temperature 297.0
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)

B1

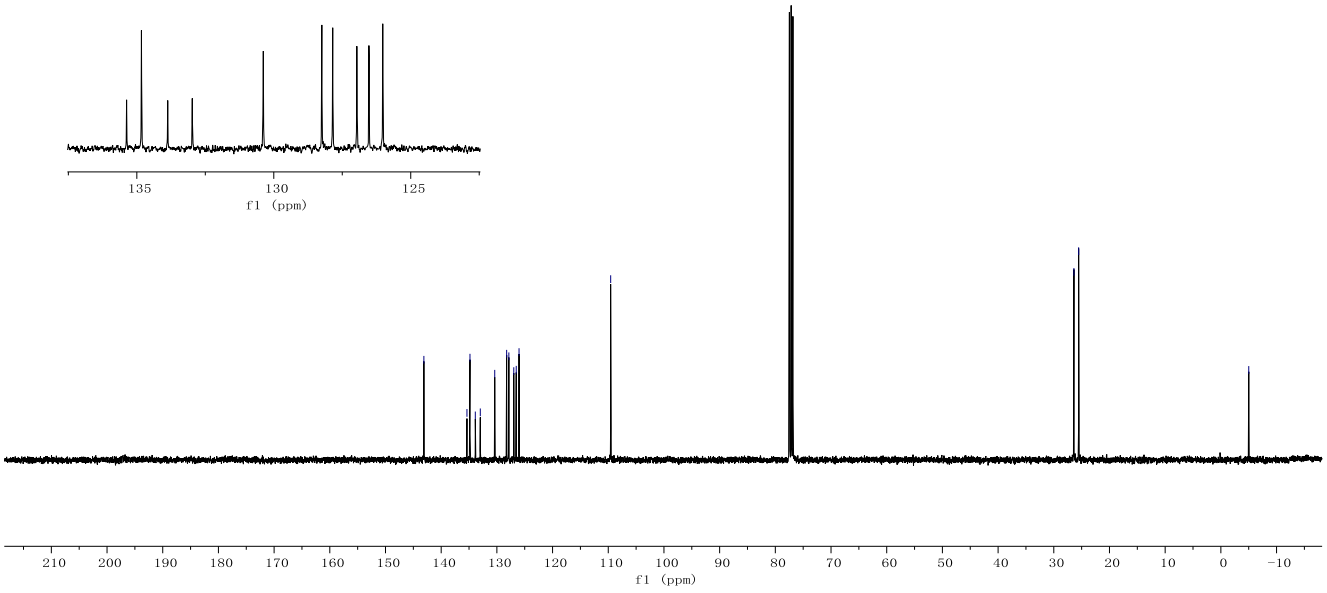


Parameter	Value
1 Title	cqh-20231026-s2-122.1.1.1r
2 Solvent	CDCl3
3 Temperature	295.5
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H

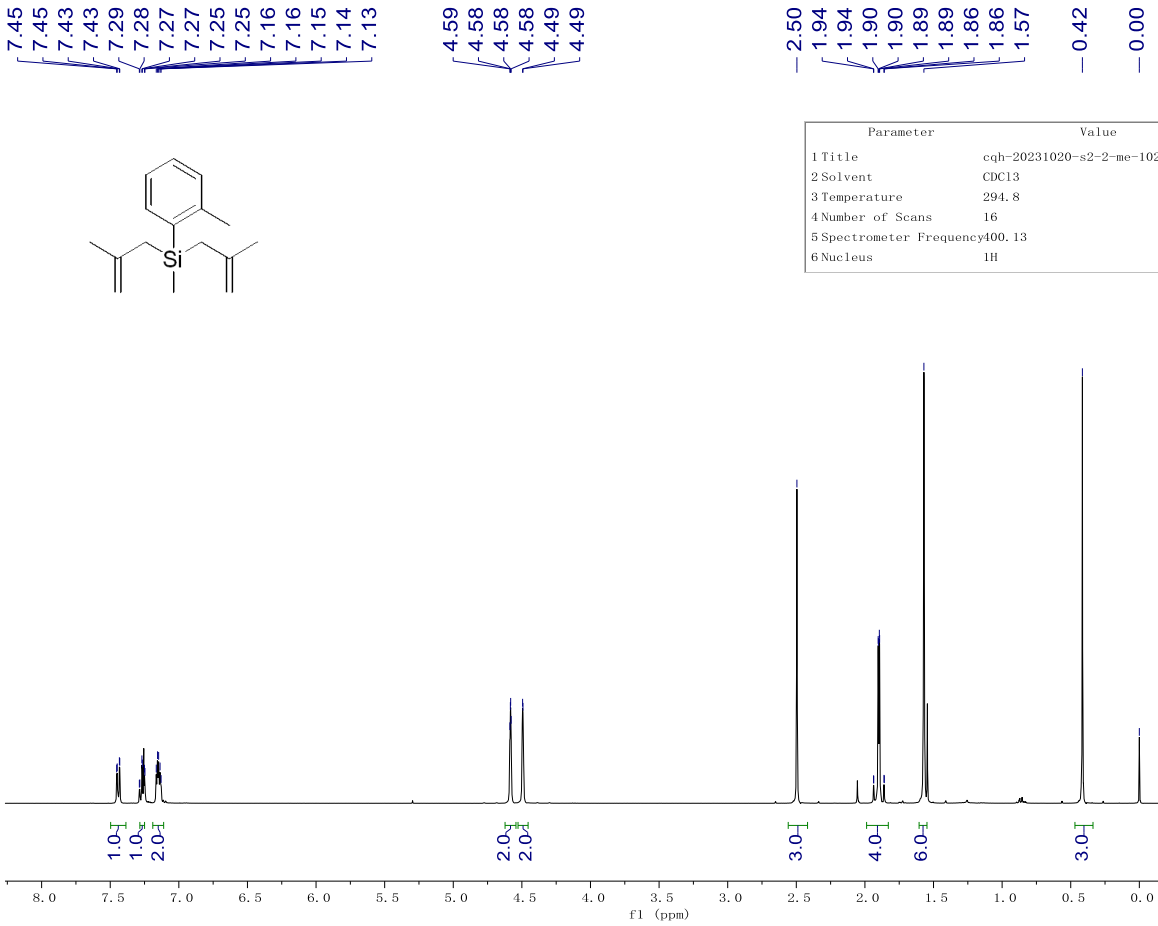


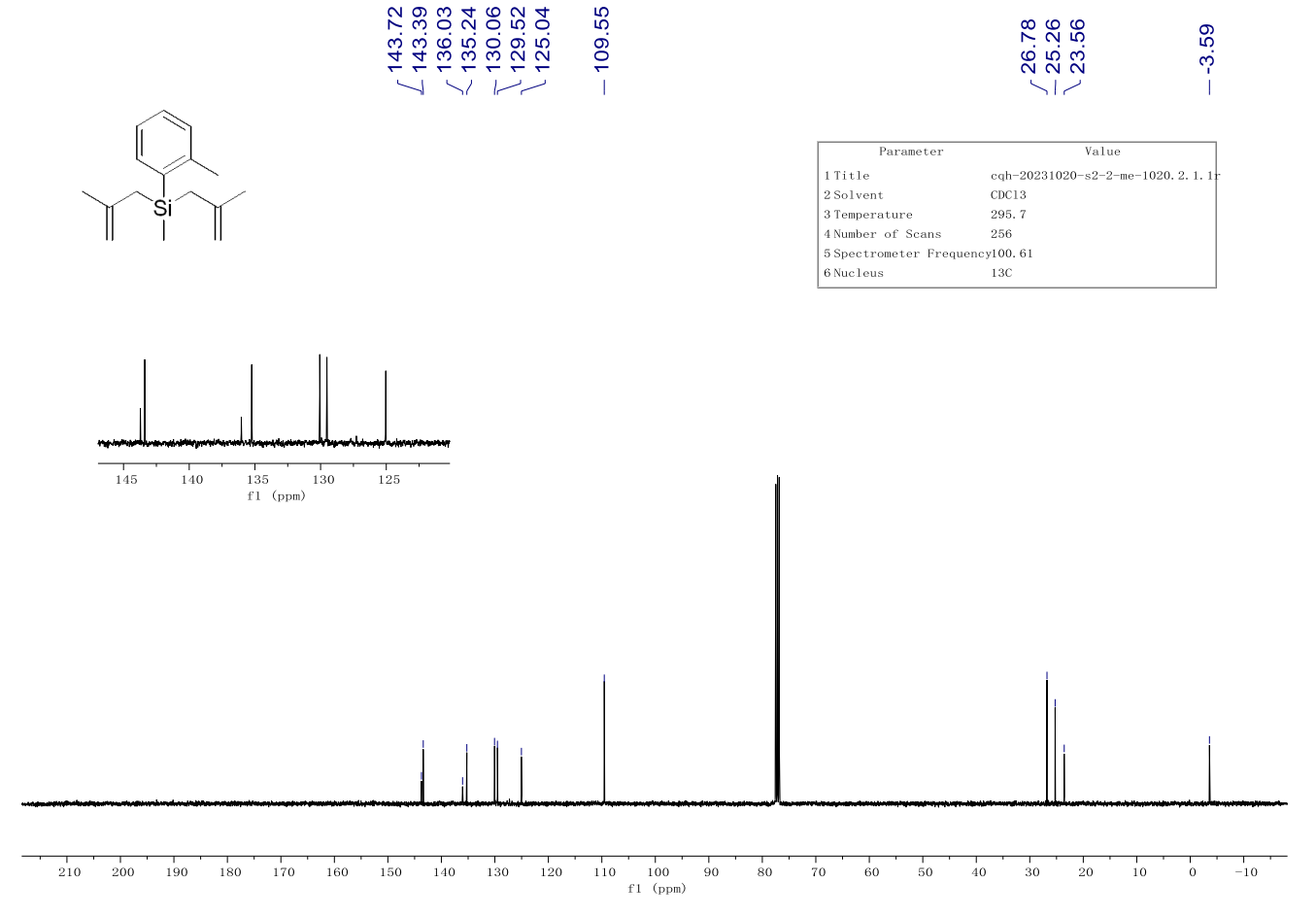


Parameter	Value
1 Title	cqh-20231026-s2-122.2.1.1r
2 Solvent	CDCl3
3 Temperature	296.2
4 Number of Scans	256
5 Spectrometer Frequency	100.61
6 Nucleus	13C

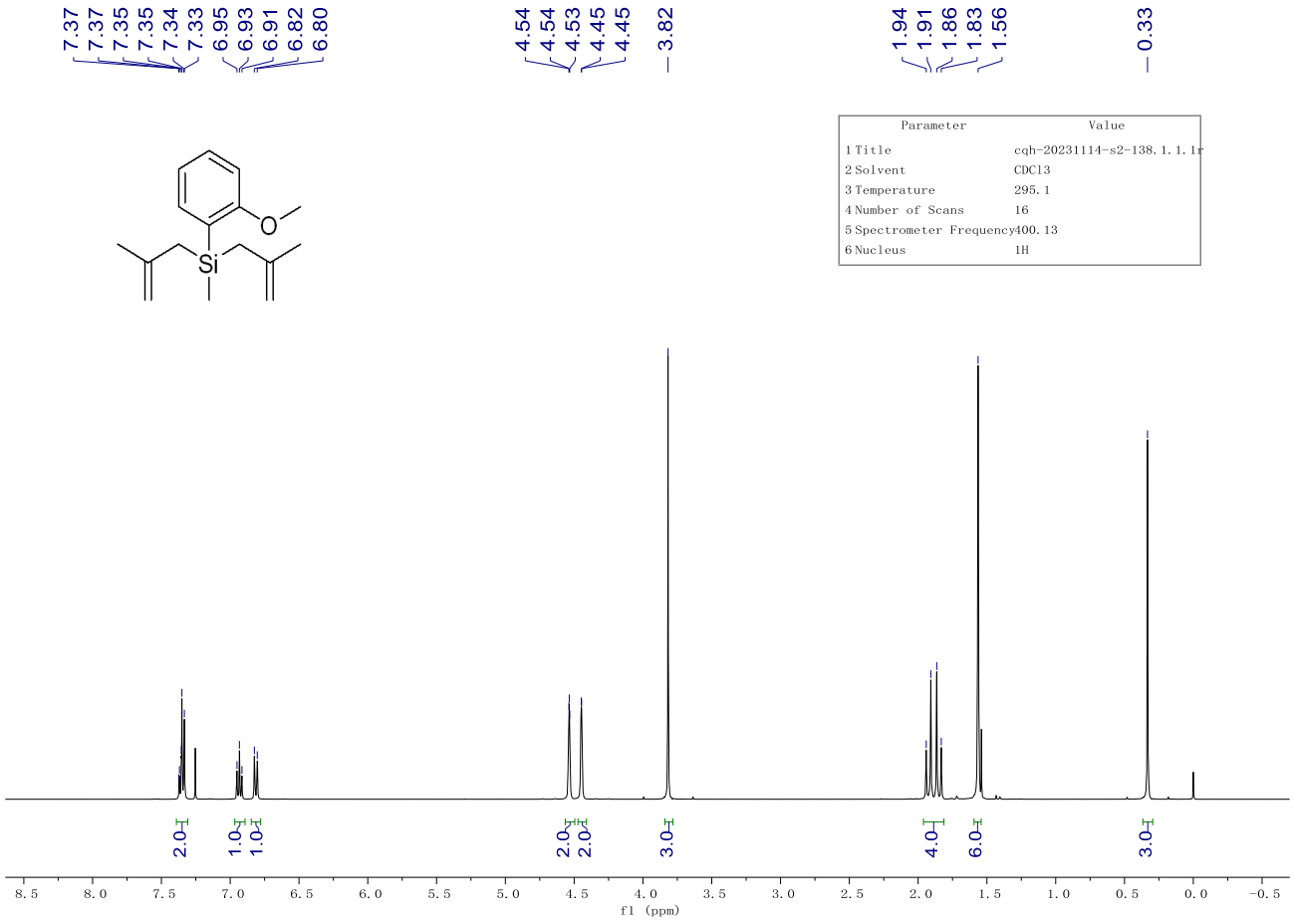


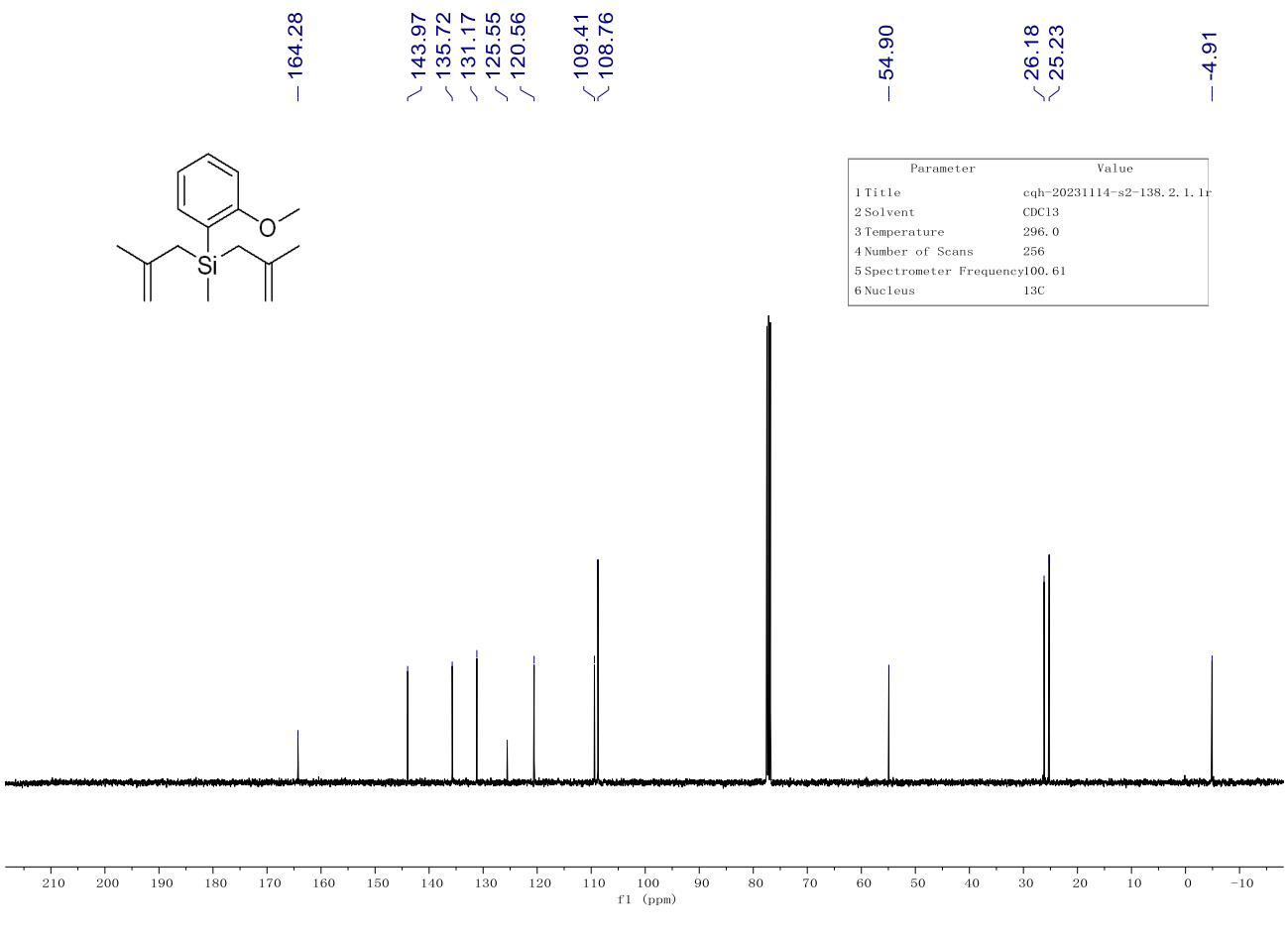
B3


7.45 7.45 7.43 7.43 7.29 7.28 7.27 7.27 7.25 7.25 7.16 7.16 7.15 7.14 7.13
4.59 4.58 4.58 4.58 4.49 4.49
2.50 1.94 1.94 1.90 1.90 1.89 1.89 1.86 1.86 1.57
0.42
0.00
Si
Parameter Value
1 Title cqh-20231020-s2-2-me-1020.1.1.1r
2 Solvent CDCl3
3 Temperature 294.8
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
1.0 1.0 2.0 2.0 2.0 3.0 4.0 6.0 3.0
f1 (ppm)


143.72 143.39 136.03 135.24 130.06 129.52 125.04 109.55
26.78 25.26 23.56
-3.59
Si
Parameter Value
1 Title cqh-20231020-s2-2-me-1020.2.1.1r
2 Solvent CDCl3
3 Temperature 295.7
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)
f1 (ppm)

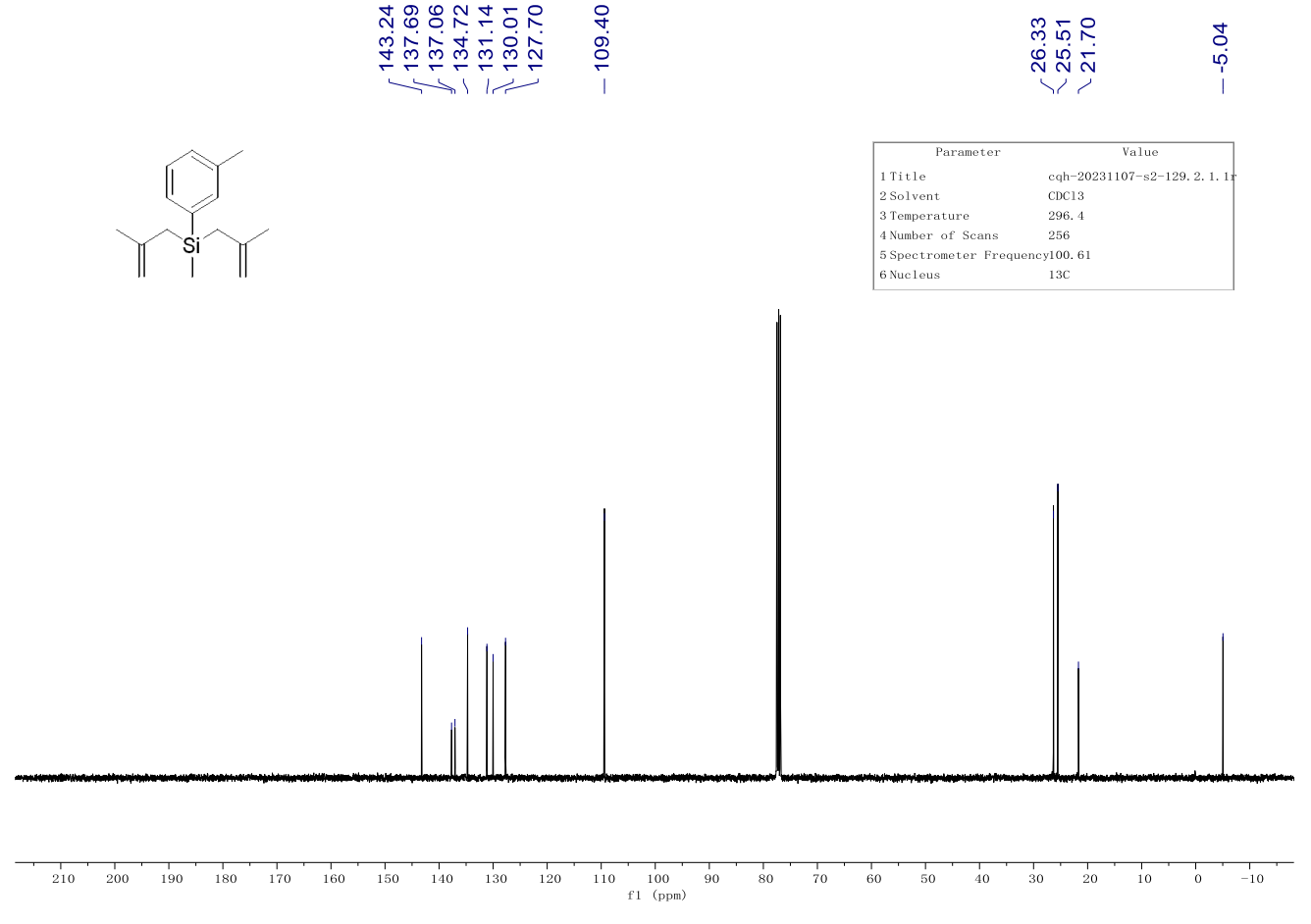
B4


7.37
7.37
7.35
7.35
7.34
7.33
6.95
6.93
6.91
6.82
6.80
4.54
4.54
4.53
4.45
4.45
3.82
1.94
1.91
1.86
1.83
1.56
0.33
Parameter Value
1 Title cqh-20231114-s2-138.1.1.1r
2 Solvent CDCl3
3 Temperature 295.1
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
O
Si
2.0
1.0
1.0
2.0
2.0
3.0
4.0
6.0
3.0
f1 (ppm)

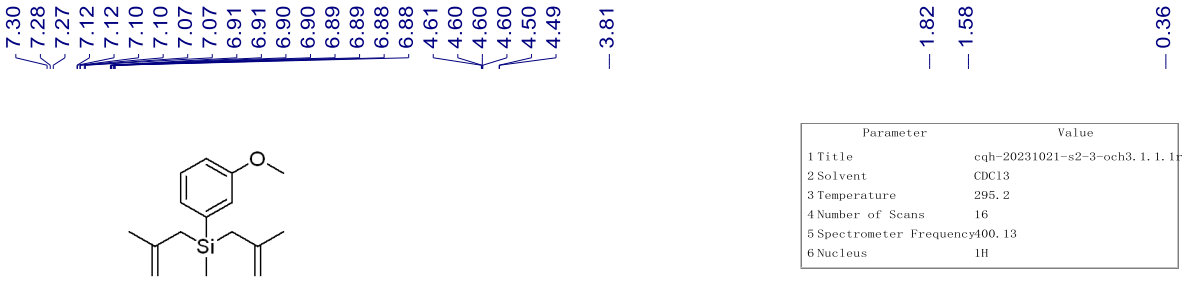

164.28
143.97
135.72
131.17
125.55
120.56
109.41
108.76
54.90
26.18
25.23
-4.91
Parameter Value
1 Title cqh-20231114-s2-138.2.1.1r
2 Solvent CDCl3
3 Temperature 296.0
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
O
Si
f1 (ppm)

B5

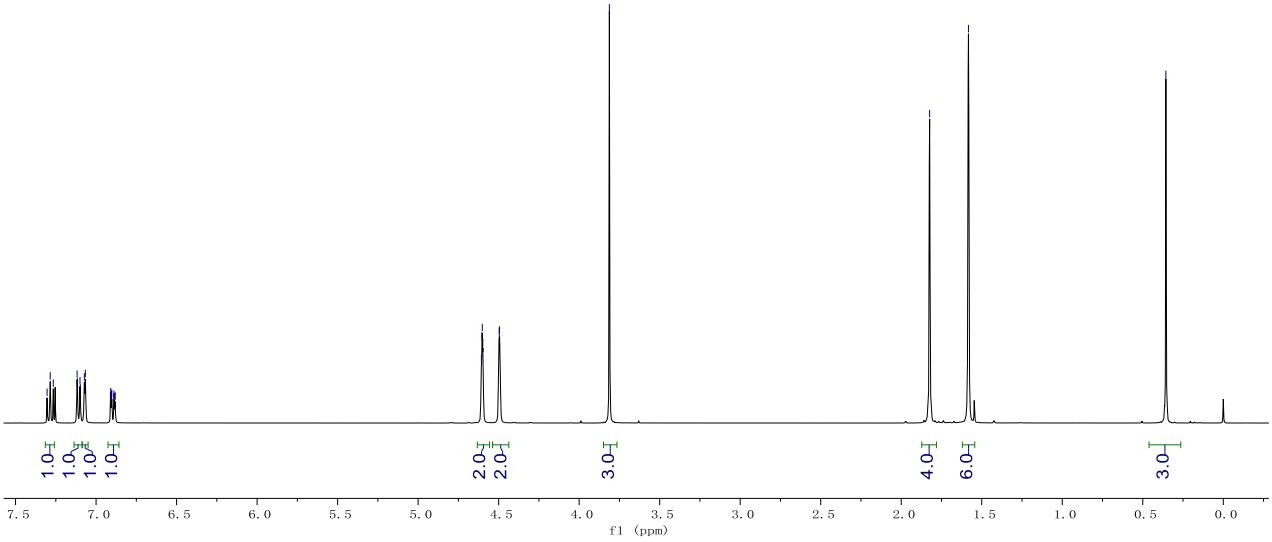

7.32
7.25
7.24
7.22
7.18
7.16
4.60
4.49
2.35
1.86
1.82
1.79
1.58
0.35
Si
Parameter Value
1 Title cqh-20231107-s2-129.1.1.1r
2 Solvent CDCl3
3 Temperature 295.6
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
2.0 1.0 1.0
f1 (ppm)
2.0 1.0 1.0 2.0 2.0 3.0 4.0 6.0 3.0
f1 (ppm)

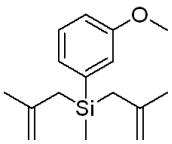

143.24
137.69
137.06
134.72
131.14
130.01
127.70
109.40
26.33
25.51
21.70
-5.04
Si
Parameter Value
1 Title cqh-20231107-s2-129.2.1.1r
2 Solvent CDCl3
3 Temperature 296.4
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)

B6

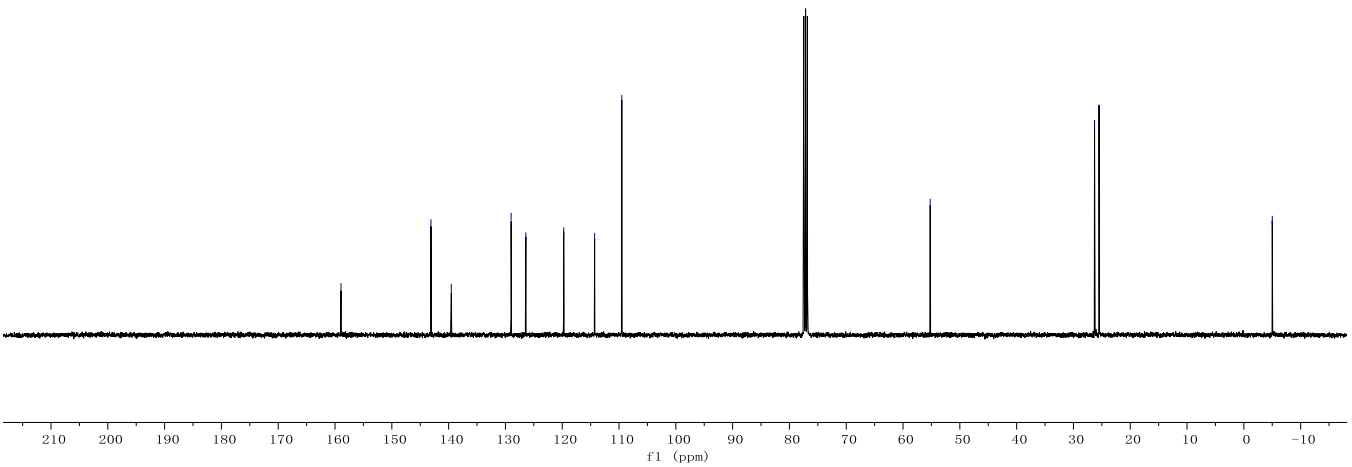


Parameter	Value
1 Title	cqh-20231021-s2-3-och3.1.1.1r
2 Solvent	CDCl3
3 Temperature	295.2
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H

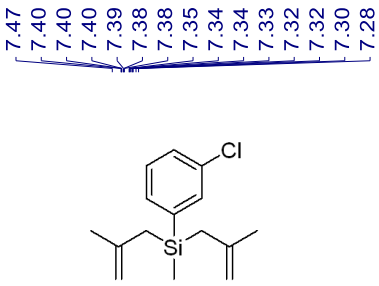




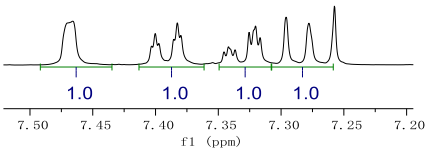
Parameter	Value
1 Title	cqh-20231021-s2-3-och3.2.1.1r
2 Solvent	CDCl3
3 Temperature	296.0
4 Number of Scans	256
5 Spectrometer Frequency	100.61
6 Nucleus	13C

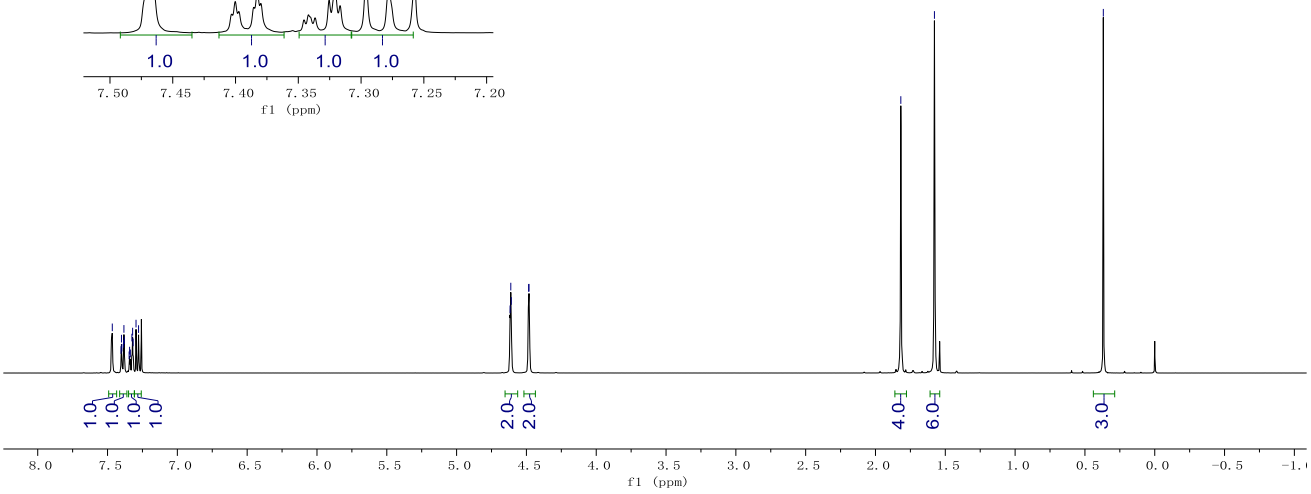


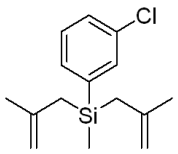
B7



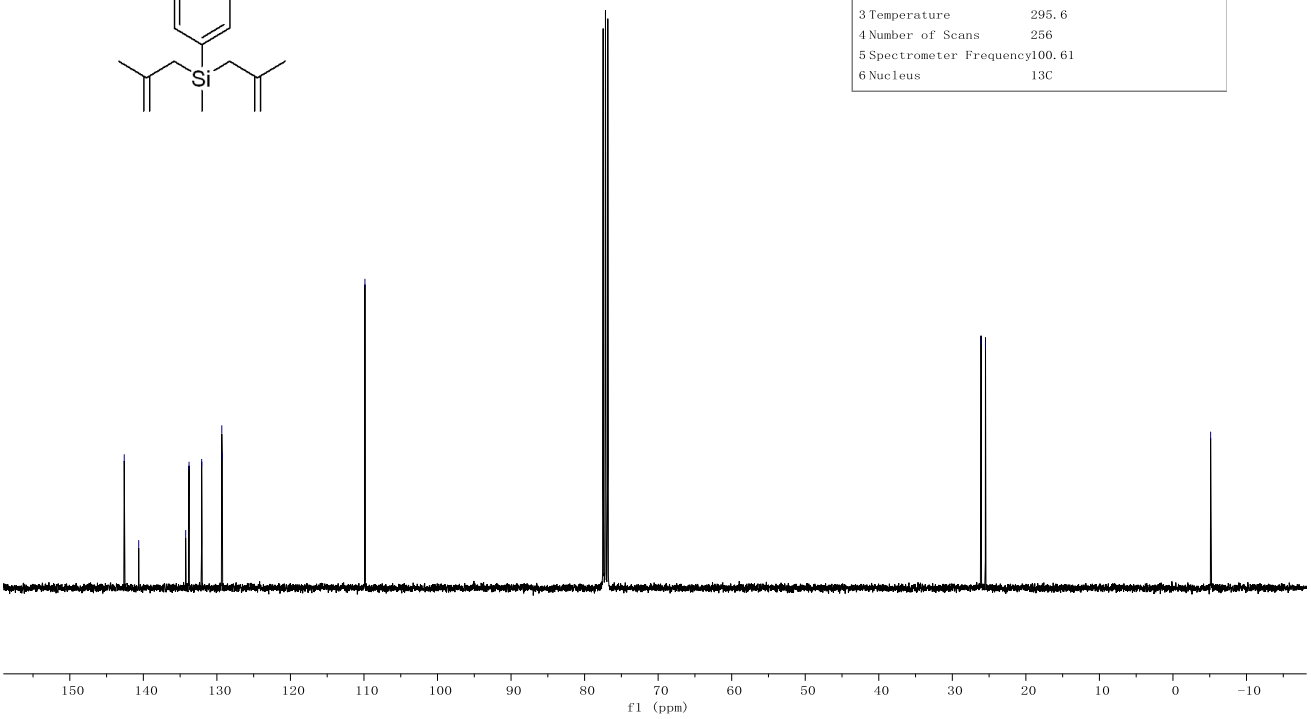
Parameter	Value
1 Title	cqh-20231020-s2-3-cl.1.1.1r
2 Solvent	CDCl3
3 Temperature	294.9
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H



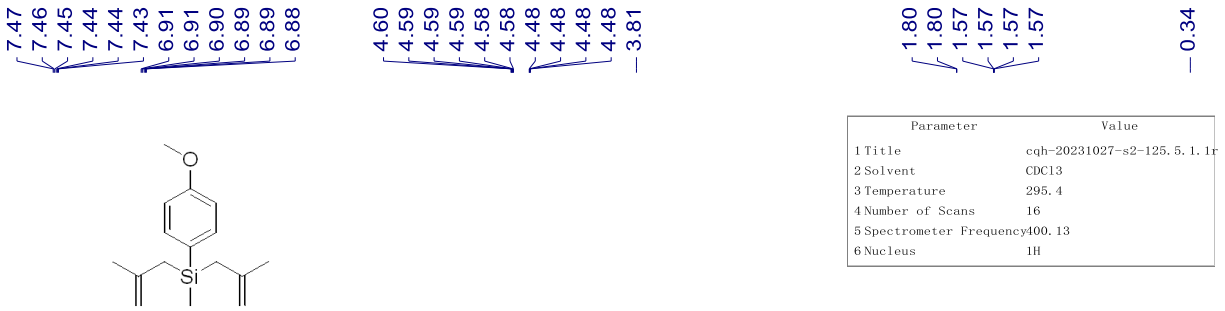




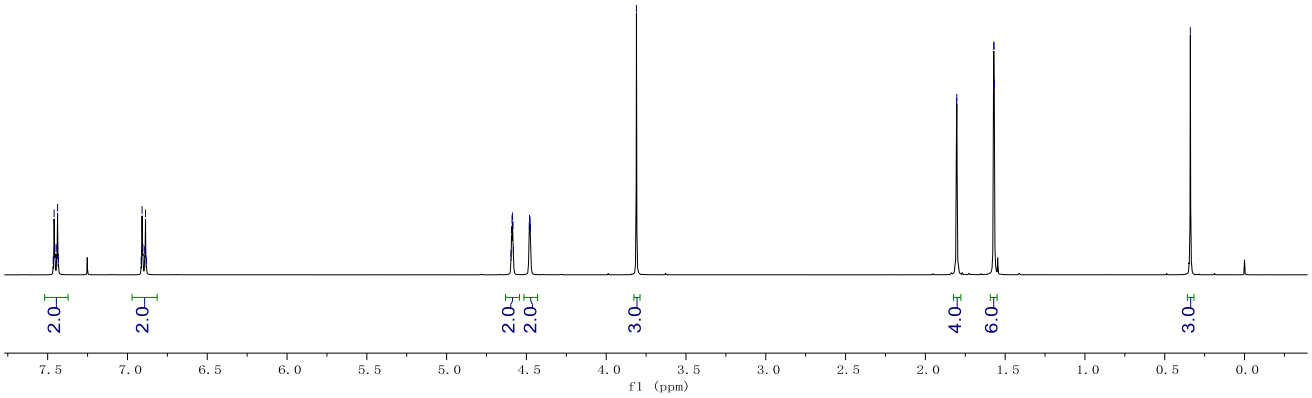
Parameter	Value
1 Title	cqh-20231020-s2-3-cl.2.1.1r
2 Solvent	CDCl3
3 Temperature	295.6
4 Number of Scans	256
5 Spectrometer Frequency	100.61
6 Nucleus	13C

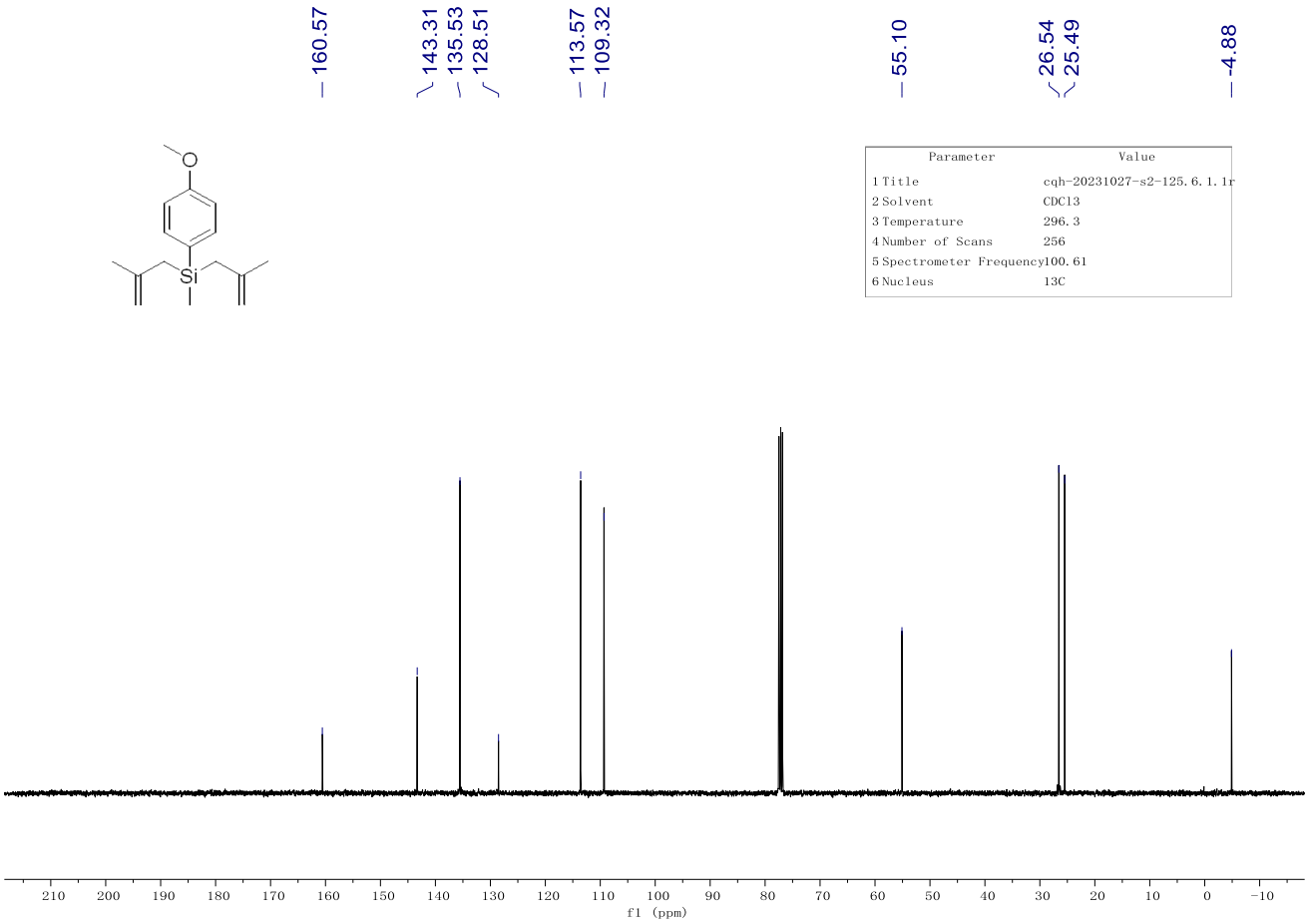


B9



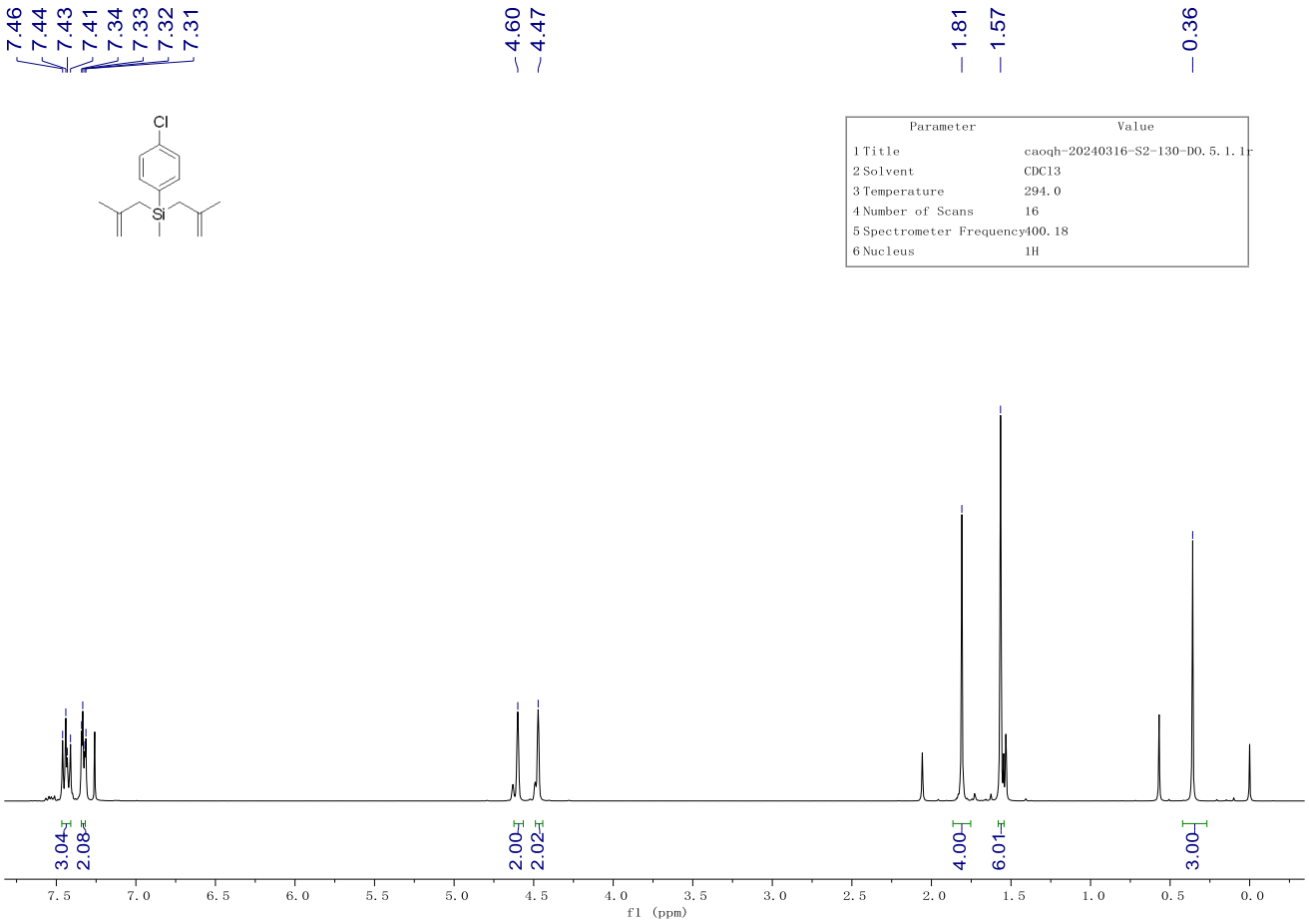
Parameter	Value
1 Title	cqh-20231027-s2-125.5.1.1r
2 Solvent	CDCl3
3 Temperature	295.4
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H

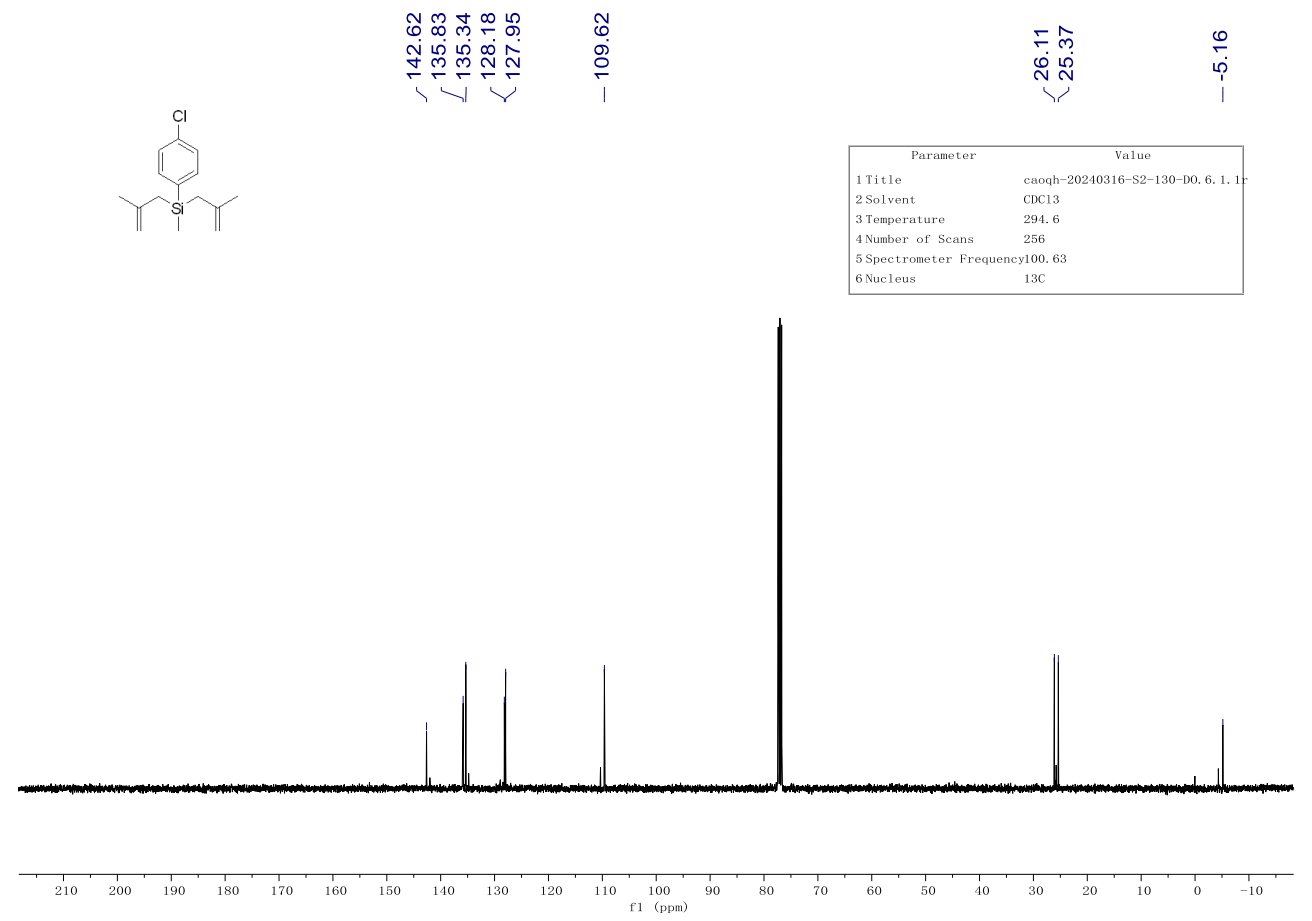




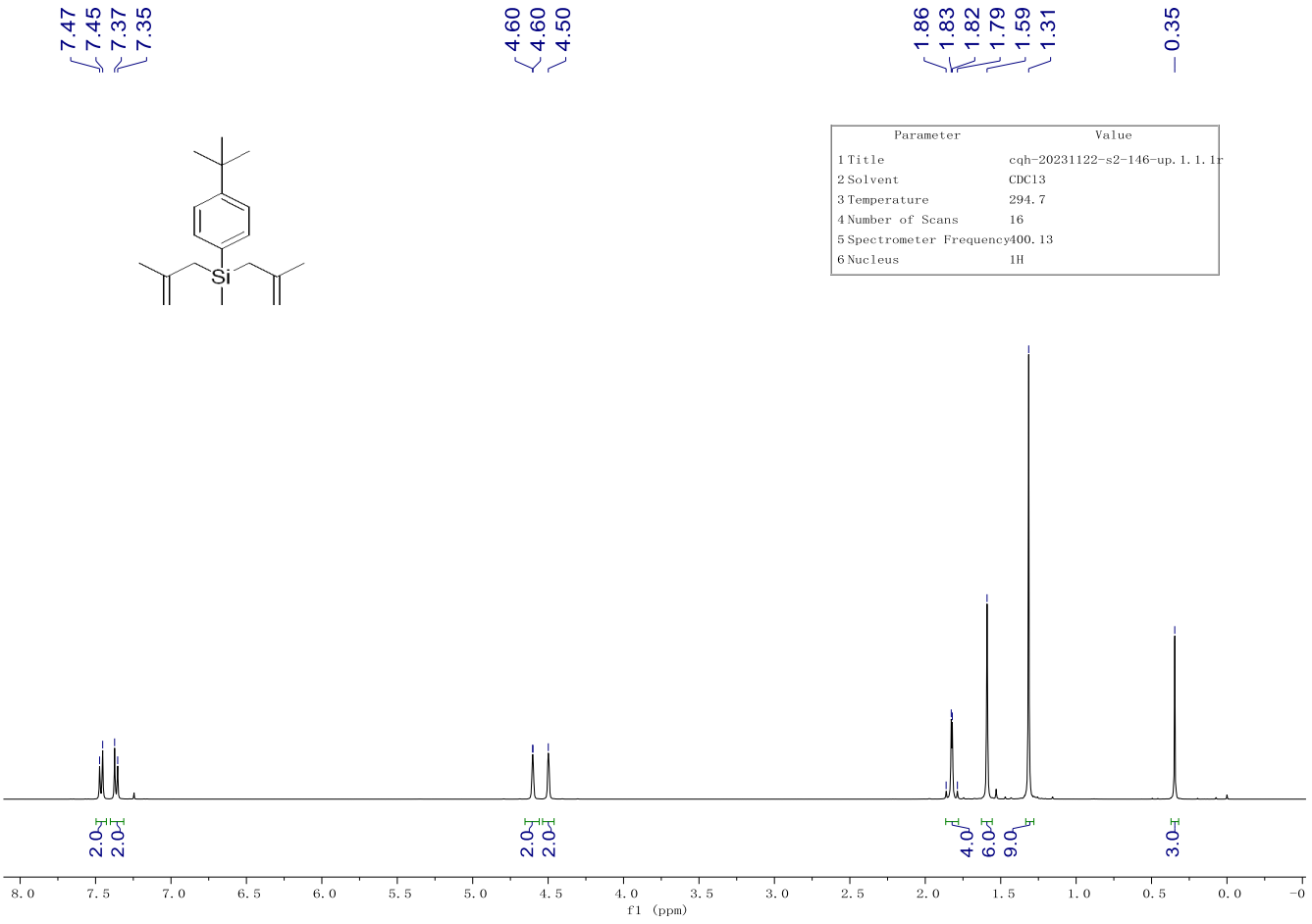
Parameter	Value
1 Title	cqh-20231027-s2-125.6.1.1r
2 Solvent	CDCl3
3 Temperature	296.3
4 Number of Scans	256
5 Spectrometer Frequency	100.61
6 Nucleus	13C

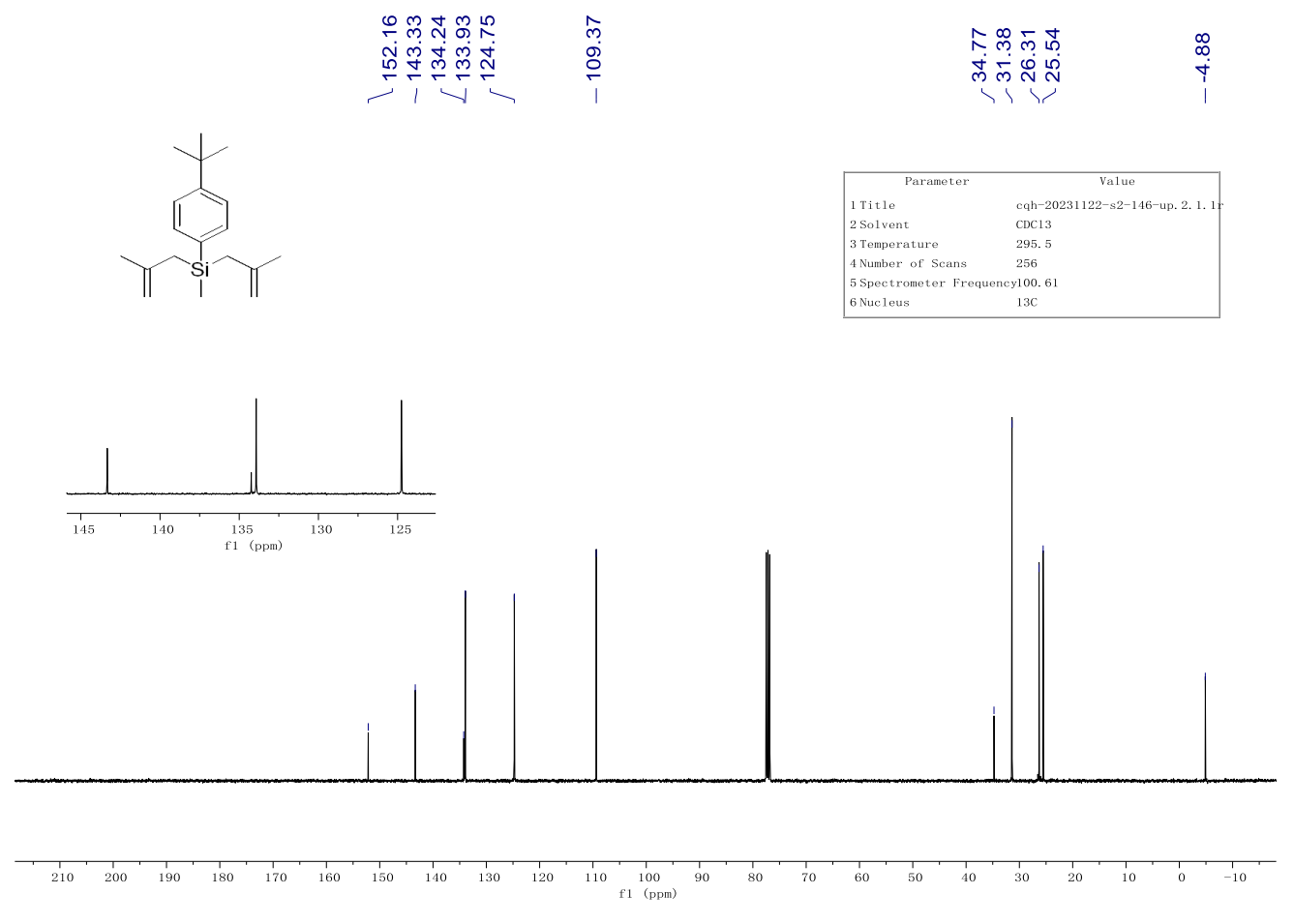
B10


7.46
7.44
7.43
7.41
7.34
7.33
7.32
7.31
4.60
4.47
1.81
1.57
0.36
Cl
Si
Parameter Value
1 Title caoqh-20240316-S2-130-D0.5.1.1r
2 Solvent CDCl3
3 Temperature 294.0
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
3.04
2.08
2.00
2.02
4.00
6.01
3.00
f1 (ppm)

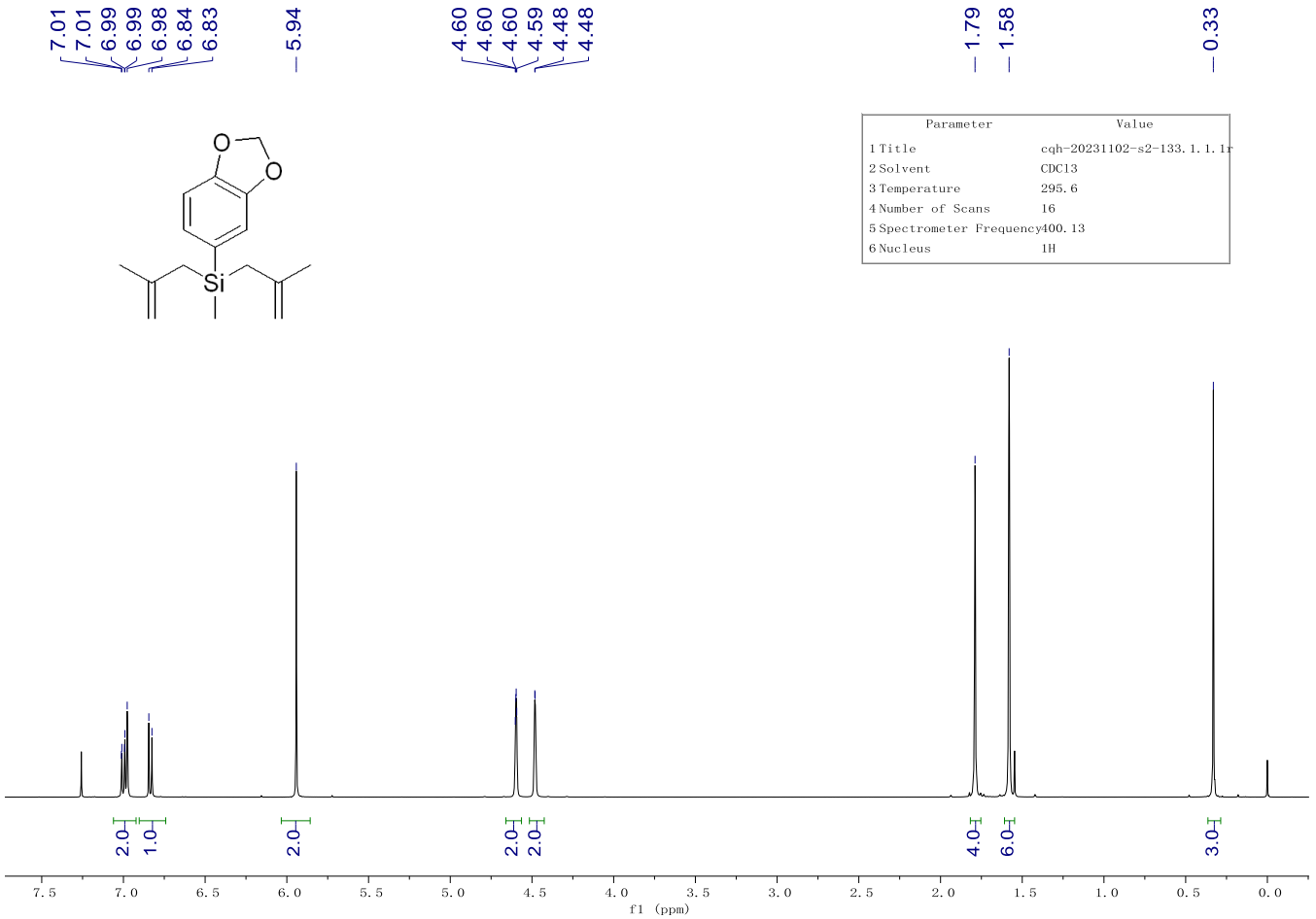

142.62
135.83
135.34
128.18
127.95
109.62
26.11
25.37
-5.16
Cl
Si
Parameter Value
1 Title caoqh-20240316-S2-130-D0.6.1.1r
2 Solvent CDCl3
3 Temperature 294.6
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
f1 (ppm)

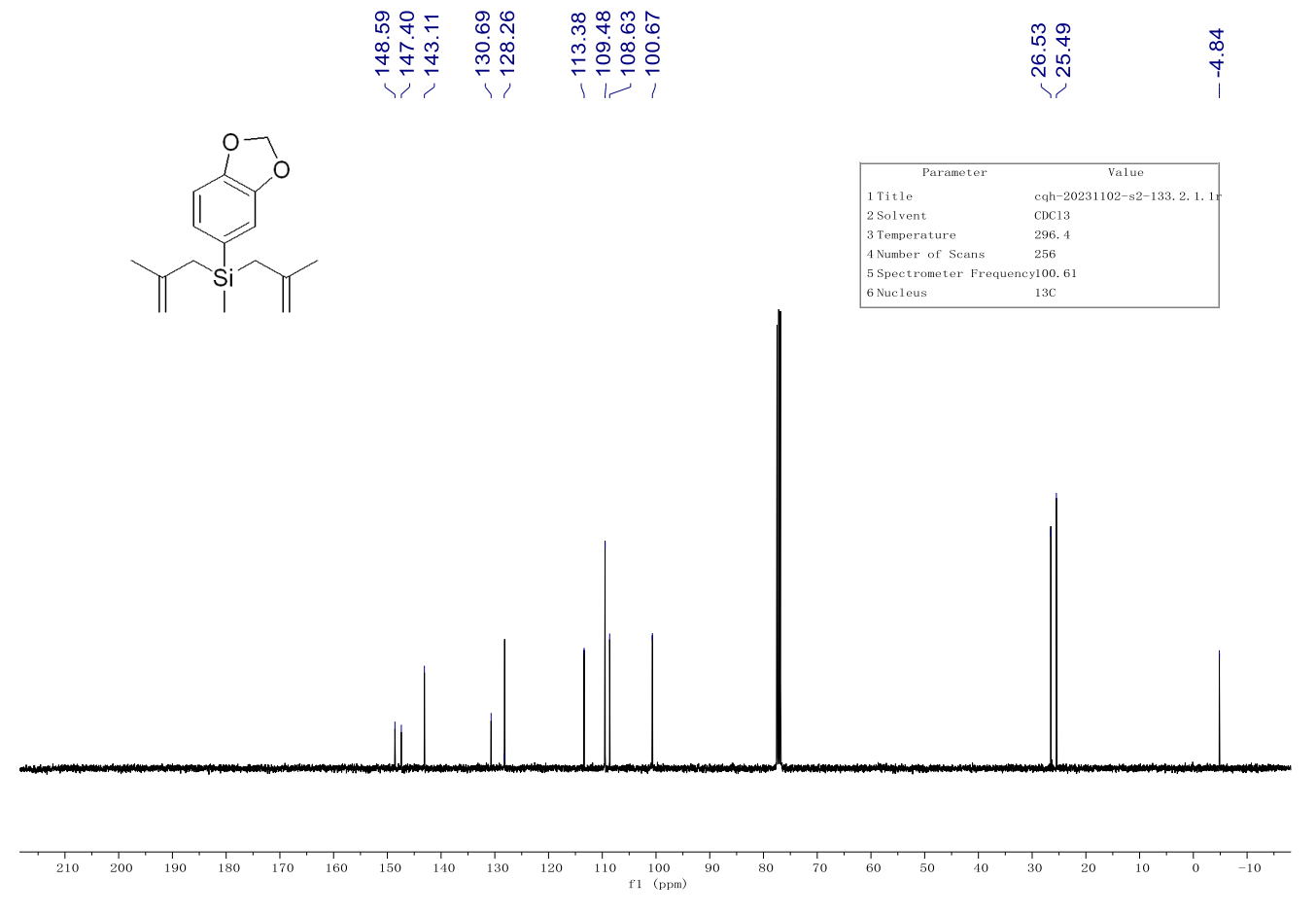
B12


7.47
7.45
7.37
7.35
4.60
4.60
4.50
1.86
1.83
1.82
1.79
1.59
1.31
0.35
Si
Parameter Value
1 Title cqh-20231122-s2-146-up.1.1.1r
2 Solvent CDCl3
3 Temperature 294.7
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
2.0
2.0
2.0
2.0
4.0
6.0
9.0
3.0
f1 (ppm)

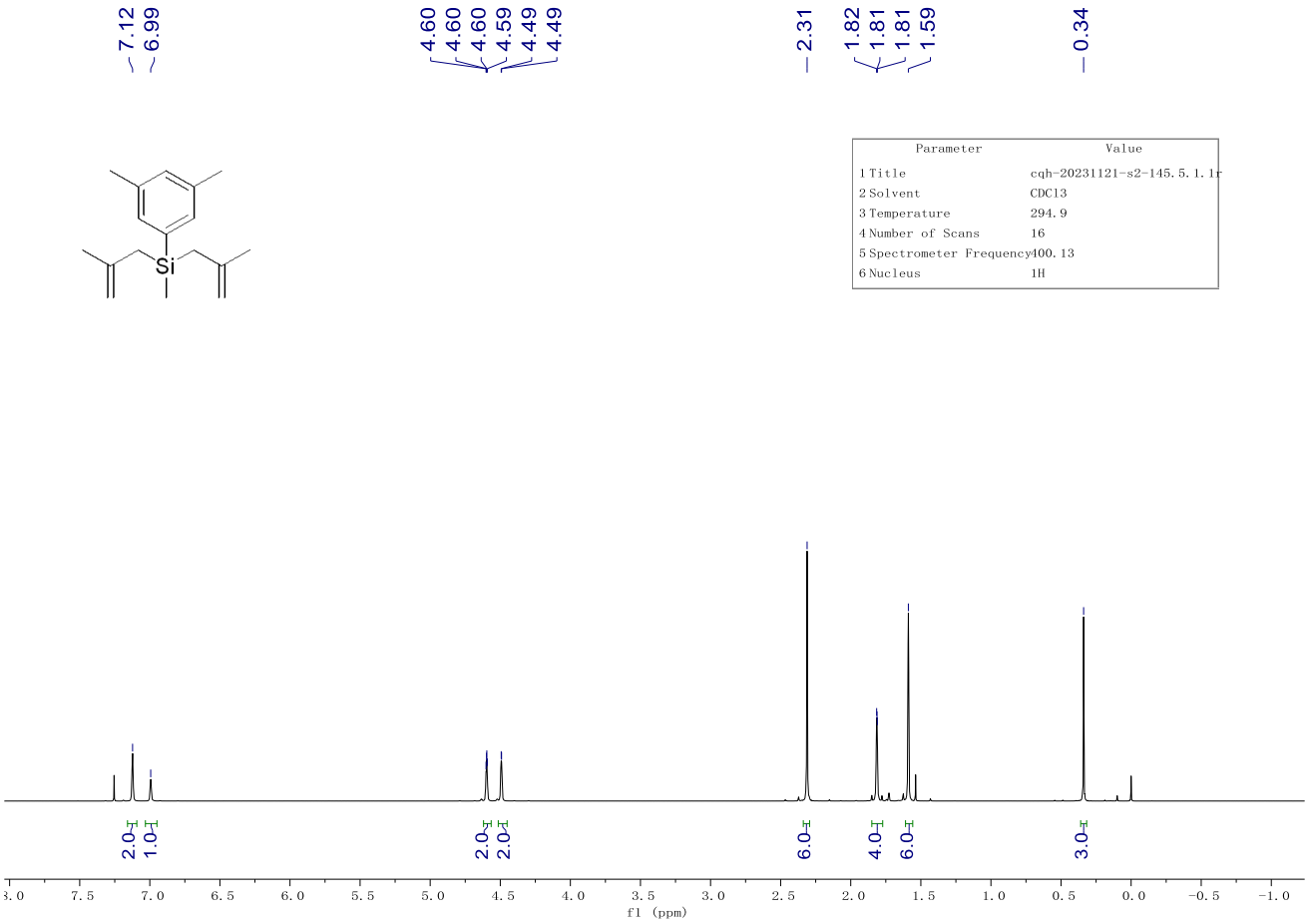

152.16
143.33
134.24
133.93
124.75
109.37
34.77
31.38
26.31
25.54
-4.88
Si
Parameter Value
1 Title cqh-20231122-s2-146-up.2.1.1r
2 Solvent CDCl3
3 Temperature 295.5
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)
f1 (ppm)

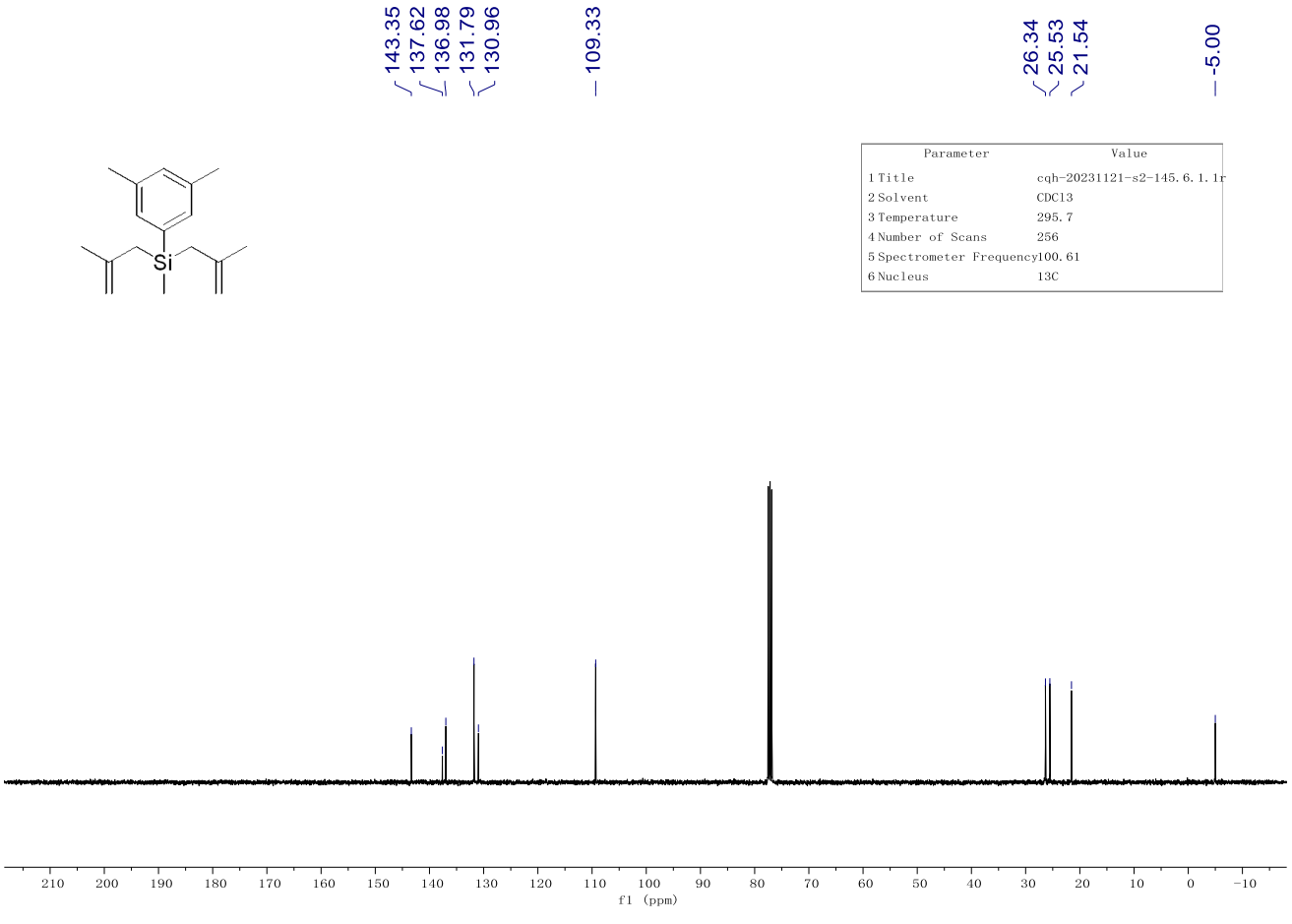
B13


7.01
7.01
6.99
6.99
6.98
6.84
6.83
5.94
4.60
4.60
4.60
4.59
4.48
4.48
1.79
1.58
0.33
O
O
Si
Parameter Value
1 Title cqh-20231102-s2-133.1.1.1r
2 Solvent CDCl3
3 Temperature 295.6
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
2.0
1.0
2.0
2.0
2.0
4.0
6.0
3.0
f1 (ppm)

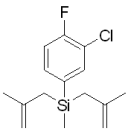

148.59
147.40
143.11
130.69
128.26
113.38
109.48
108.63
100.67
26.53
25.49
-4.84
O
O
Si
Parameter Value
1 Title cqh-20231102-s2-133.2.1.1r
2 Solvent CDCl3
3 Temperature 296.4
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)

B14

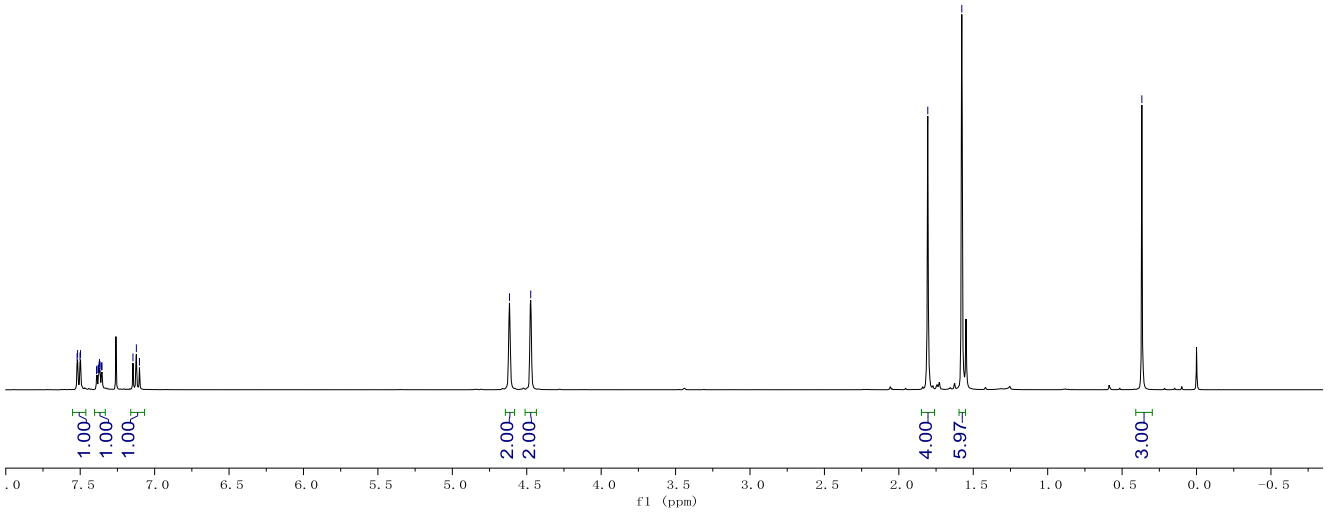

7.12
6.99
4.60
4.60
4.60
4.59
4.49
4.49
2.31
1.82
1.81
1.81
1.59
0.34
Si
Parameter Value
1 Title cqh-20231121-s2-145.5.1.1r
2 Solvent CDCl3
3 Temperature 294.9
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
2.0
1.0
2.0
2.0
6.0
4.0
6.0
3.0
f1 (ppm)

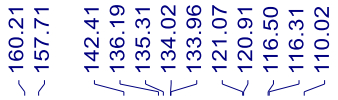

143.35
137.62
136.98
131.79
130.96
109.33
26.34
25.53
21.54
-5.00
Si
Parameter Value
1 Title cqh-20231121-s2-145.6.1.1r
2 Solvent CDCl3
3 Temperature 295.7
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)

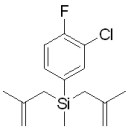
B15



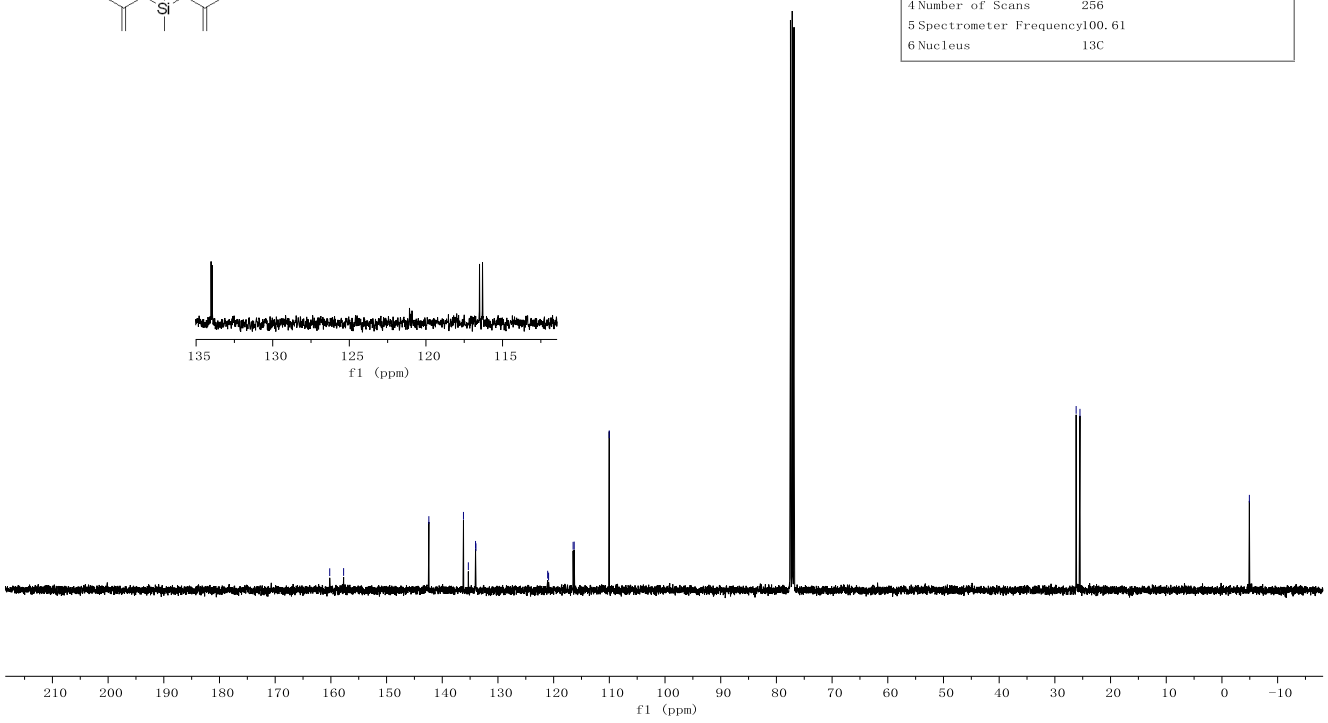
Parameter	Value
1 Title	as-20240730-cqh-c2-b11.1.1.1r
2 Solvent	CDCl3
3 Temperature	297.0
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H

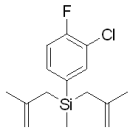






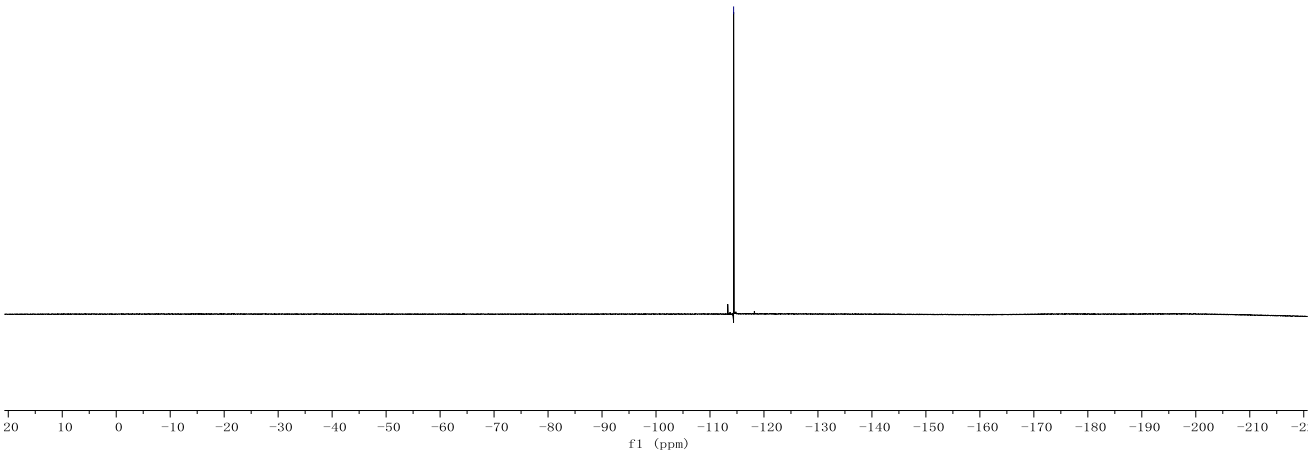
Parameter	Value
1 Title	as-20240730-cqh-c2-b11.2.1.1r
2 Solvent	CDCl3
3 Temperature	297.6
4 Number of Scans	256
5 Spectrometer Frequency	100.61
6 Nucleus	13C



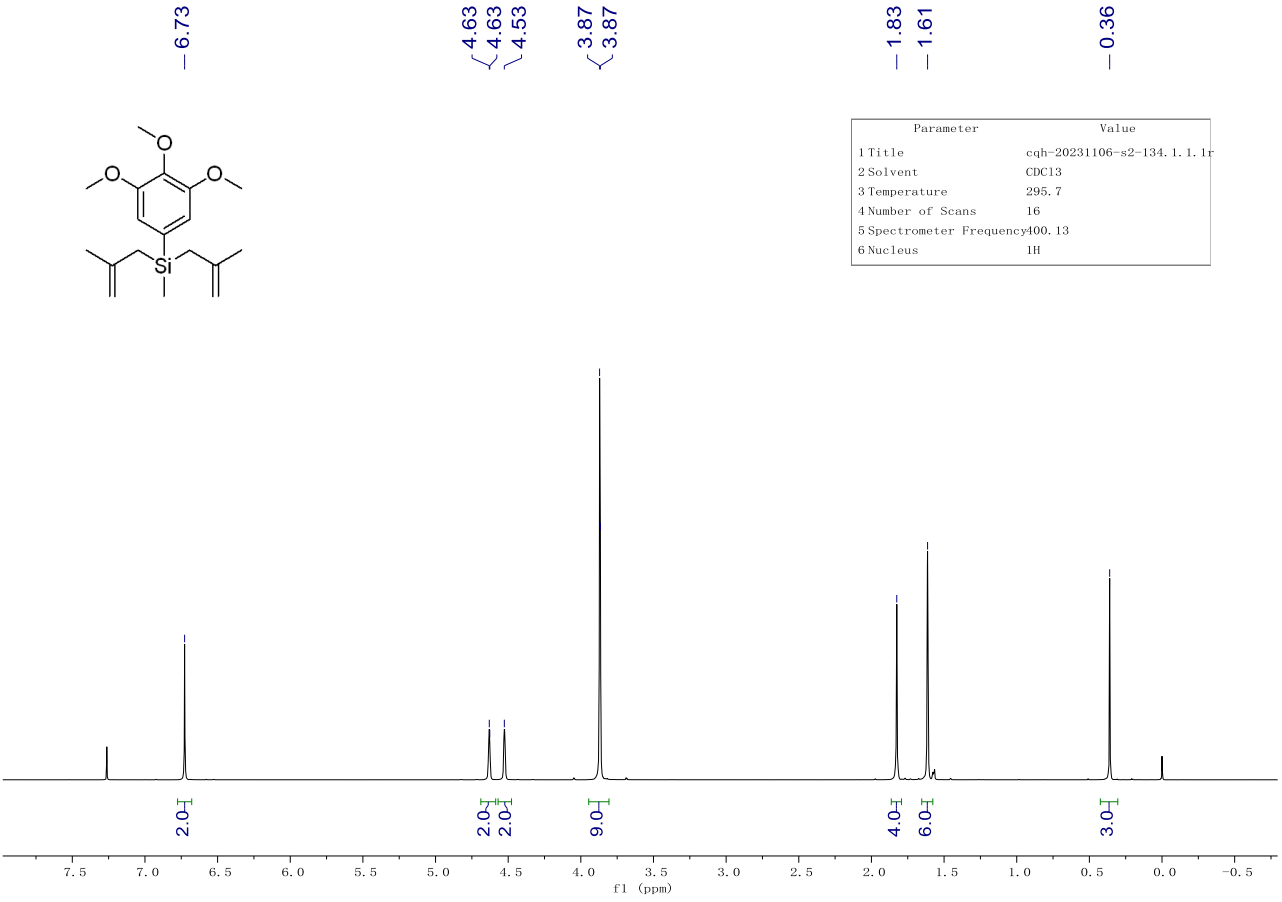


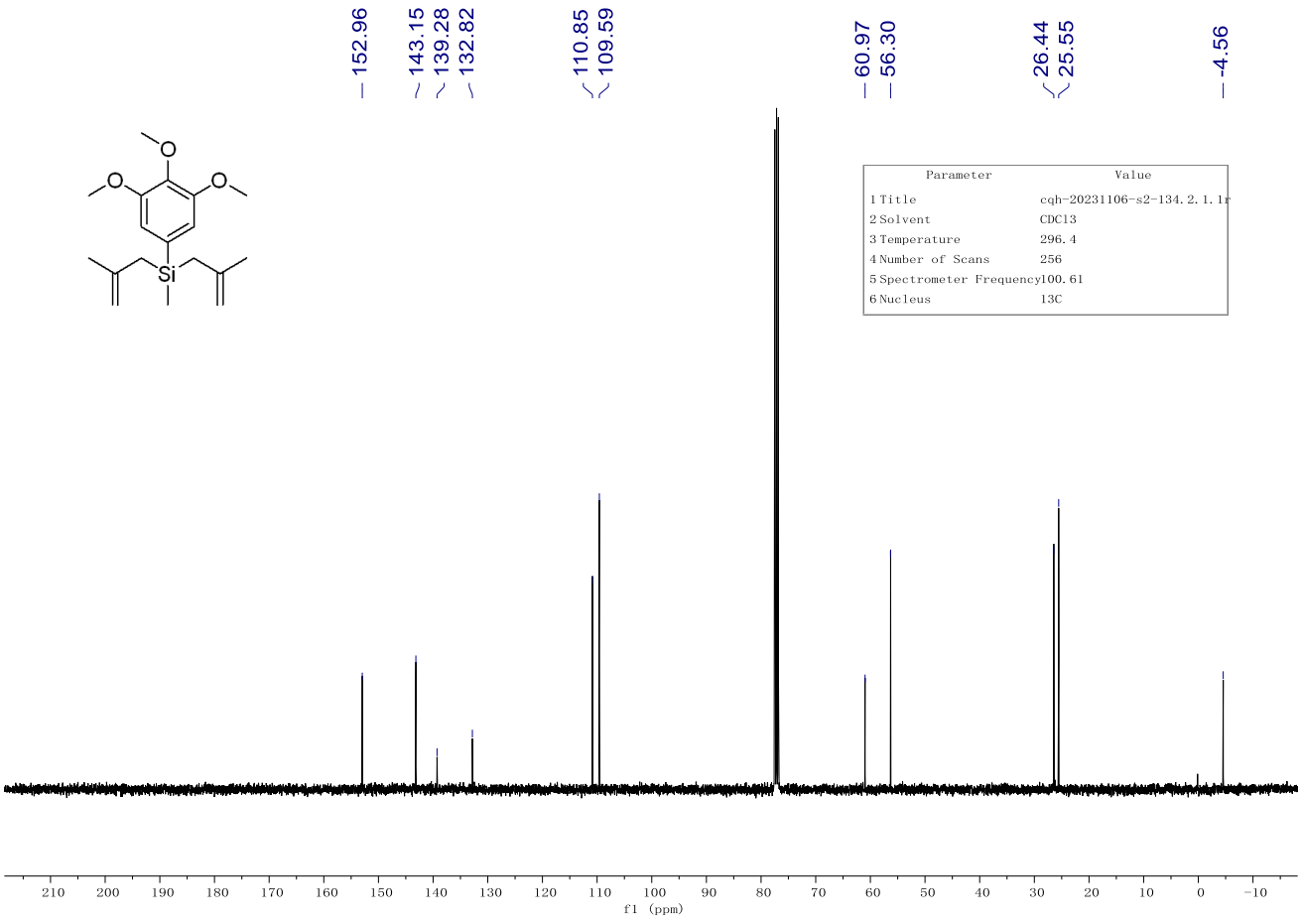
-114.38

Parameter	Value
1 Title	as-20240730-cqh-c2-b11.3.1.1r
2 Solvent	CDCl3
3 Temperature	297.2
4 Number of Scans	16
5 Spectrometer Frequency	376.50
6 Nucleus	19F

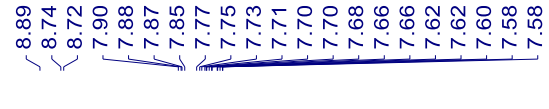


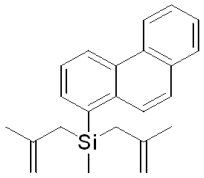
B16


6.73
4.63
4.63
4.53
3.87
3.87
1.83
1.61
0.36
Parameter Value
1 Title cqh-20231106-s2-134.1.1.1r
2 Solvent CDCl3
3 Temperature 295.7
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
2.0
2.0
2.0
9.0
4.0
6.0
3.0
f1 (ppm)

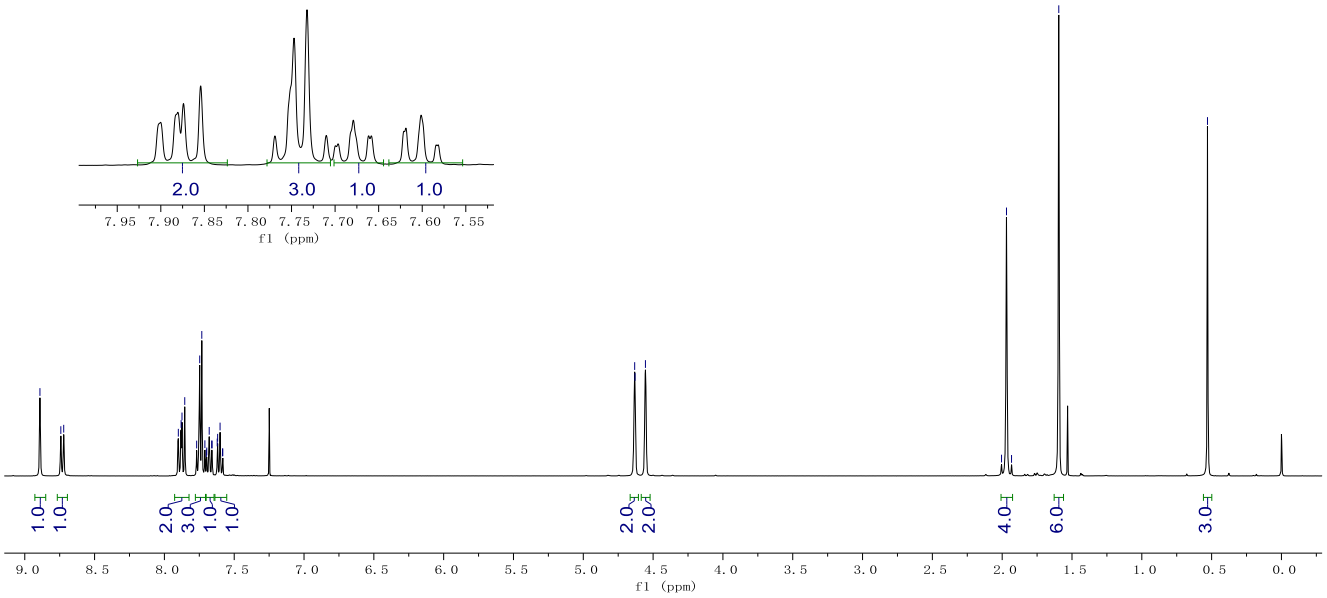

152.96
143.15
139.28
132.82
110.85
109.59
60.97
56.30
26.44
25.55
-4.56
Parameter Value
1 Title cqh-20231106-s2-134.2.1.1r
2 Solvent CDCl3
3 Temperature 296.4
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)

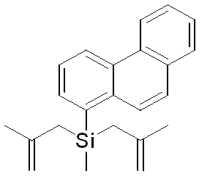
B17



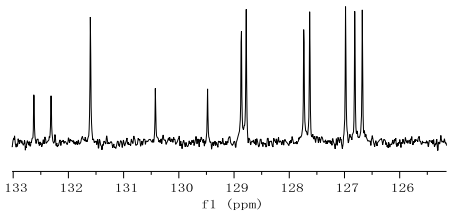


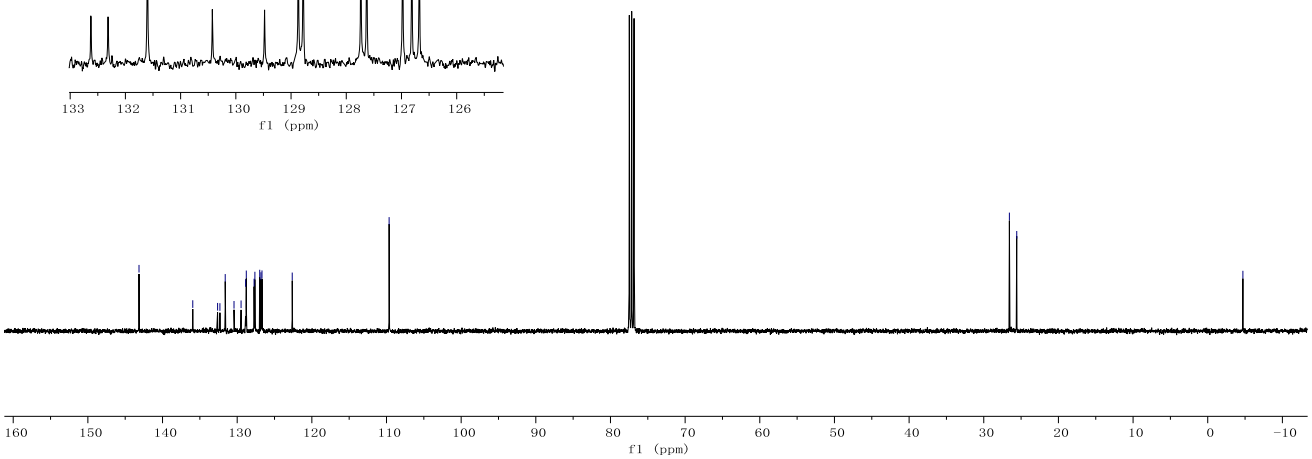
Parameter	Value
1 Title	cqh-20231121-s2-147.1.1.1r
2 Solvent	CDCl3
3 Temperature	295.0
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H



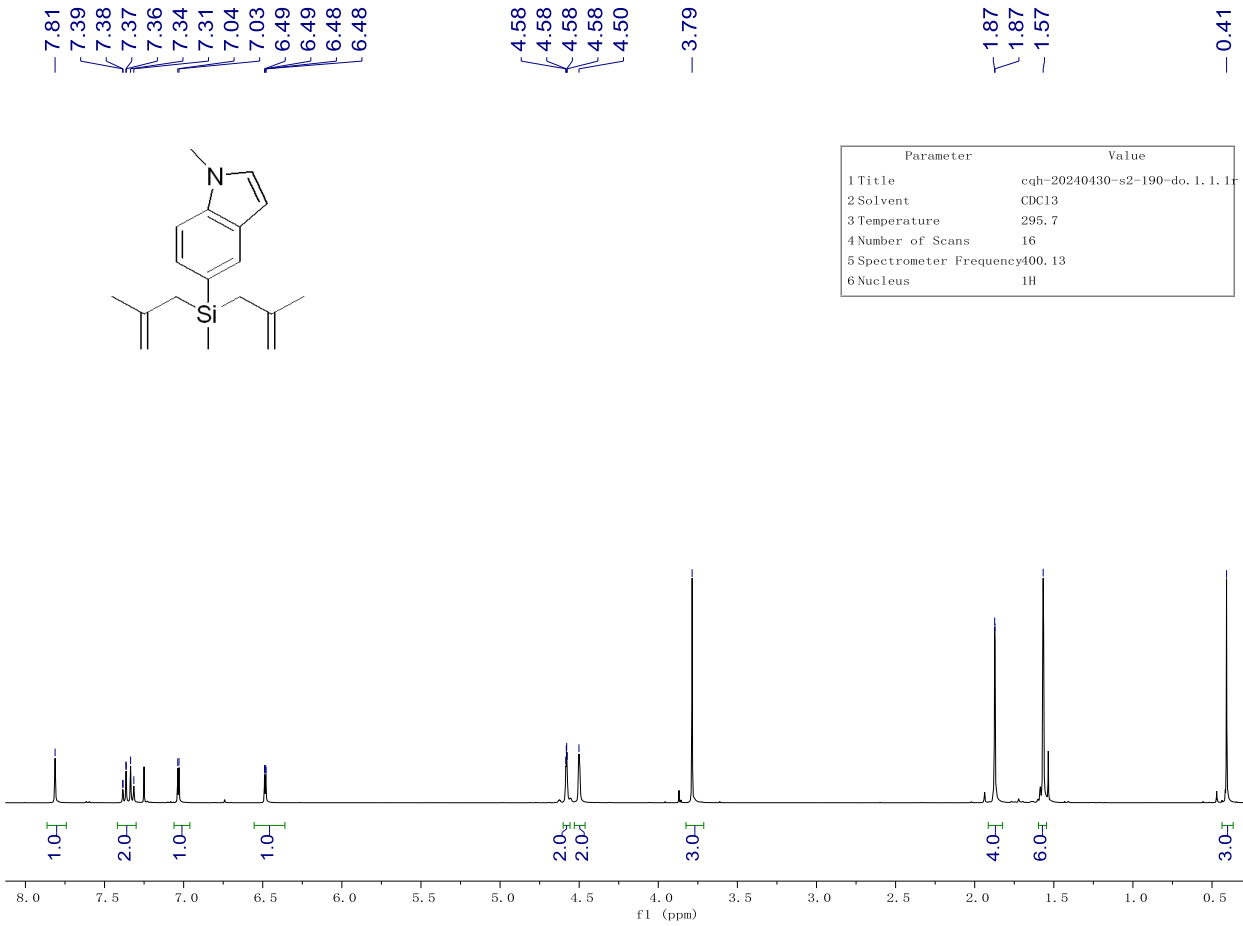


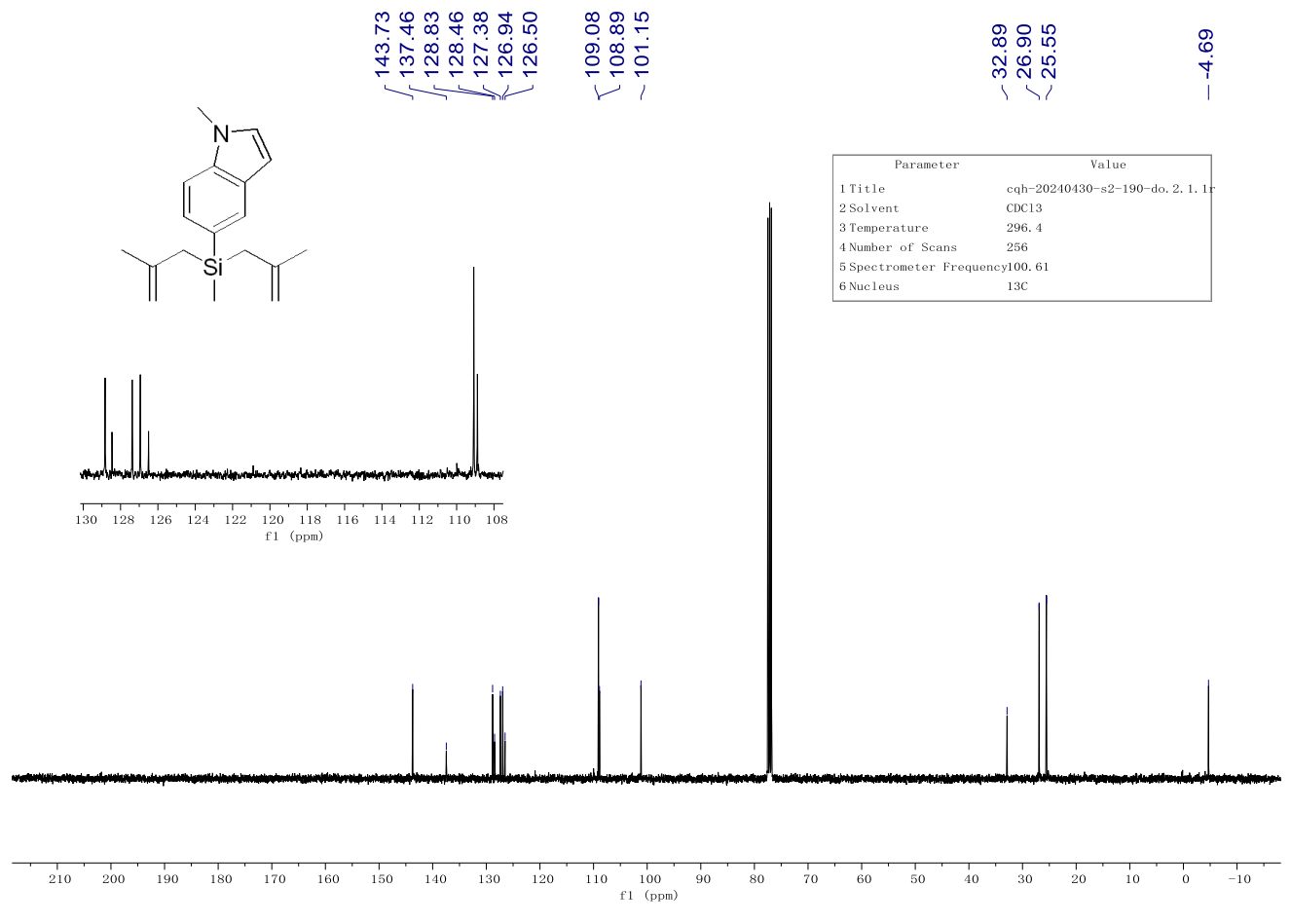
Parameter	Value
1 Title	cqh-20231121-s2-147.2.1.1r
2 Solvent	CDCl3
3 Temperature	295.8
4 Number of Scans	256
5 Spectrometer Frequency	100.61
6 Nucleus	13C



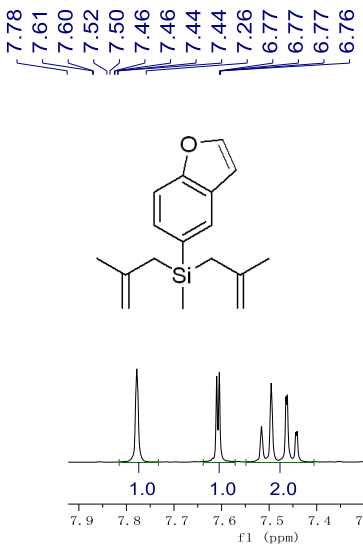


B18

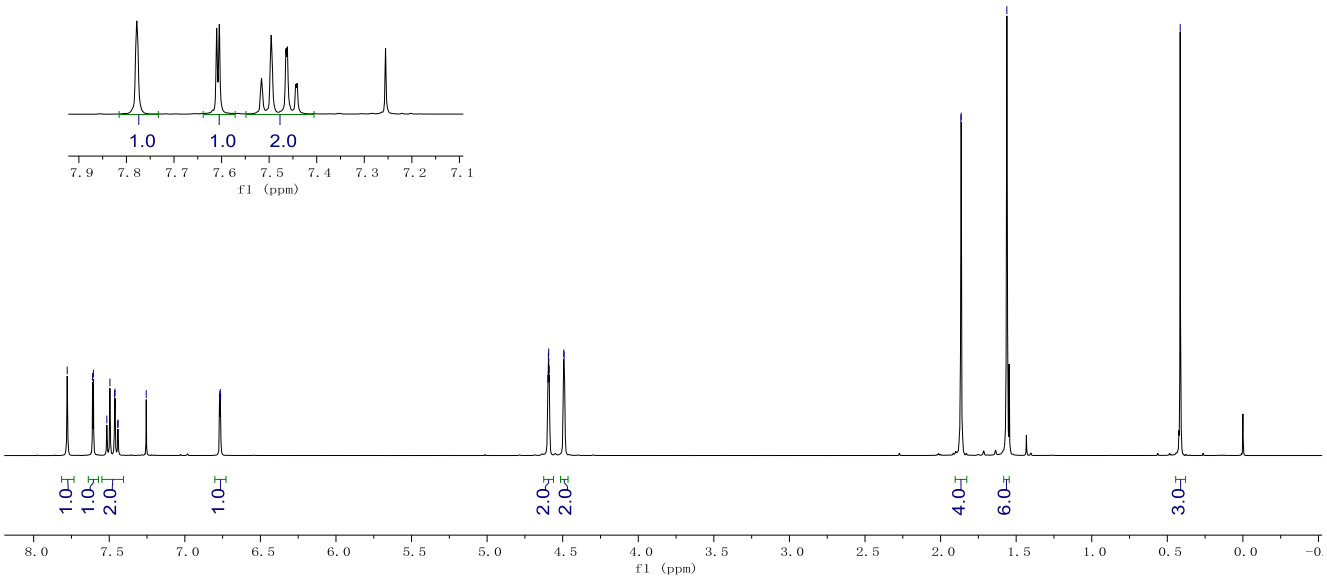

7.81
7.39
7.38
7.37
7.36
7.34
7.31
7.04
7.03
6.49
6.49
6.48
6.48
4.58
4.58
4.58
4.58
4.50
3.79
1.87
1.87
1.57
0.41
N
Si
Parameter Value
1 Title cqh-20240430-s2-190-do.1.1.1r
2 Solvent CDCl3
3 Temperature 295.7
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
1.0
2.0
1.0
1.0
2.0
2.0
3.0
4.0
6.0
3.0
f1 (ppm)

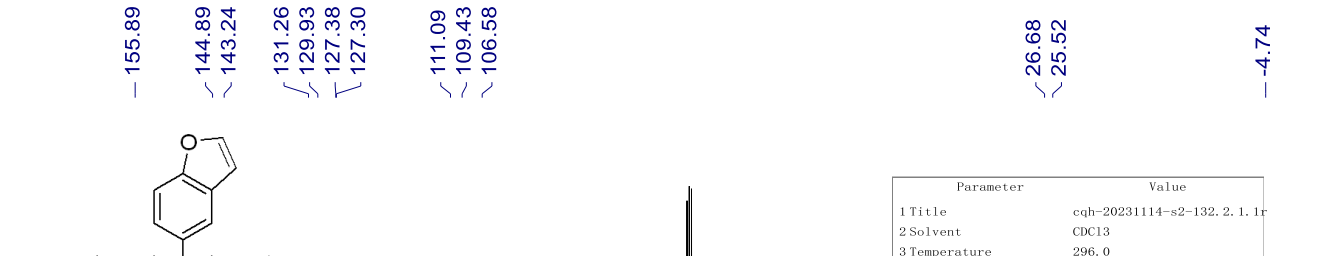

143.73
137.46
128.83
128.46
127.38
126.94
126.50
109.08
108.89
101.15
32.89
26.90
25.55
-4.69
N
Si
Parameter Value
1 Title cqh-20240430-s2-190-do.2.1.1r
2 Solvent CDCl3
3 Temperature 296.4
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)
f1 (ppm)

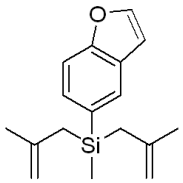
B19



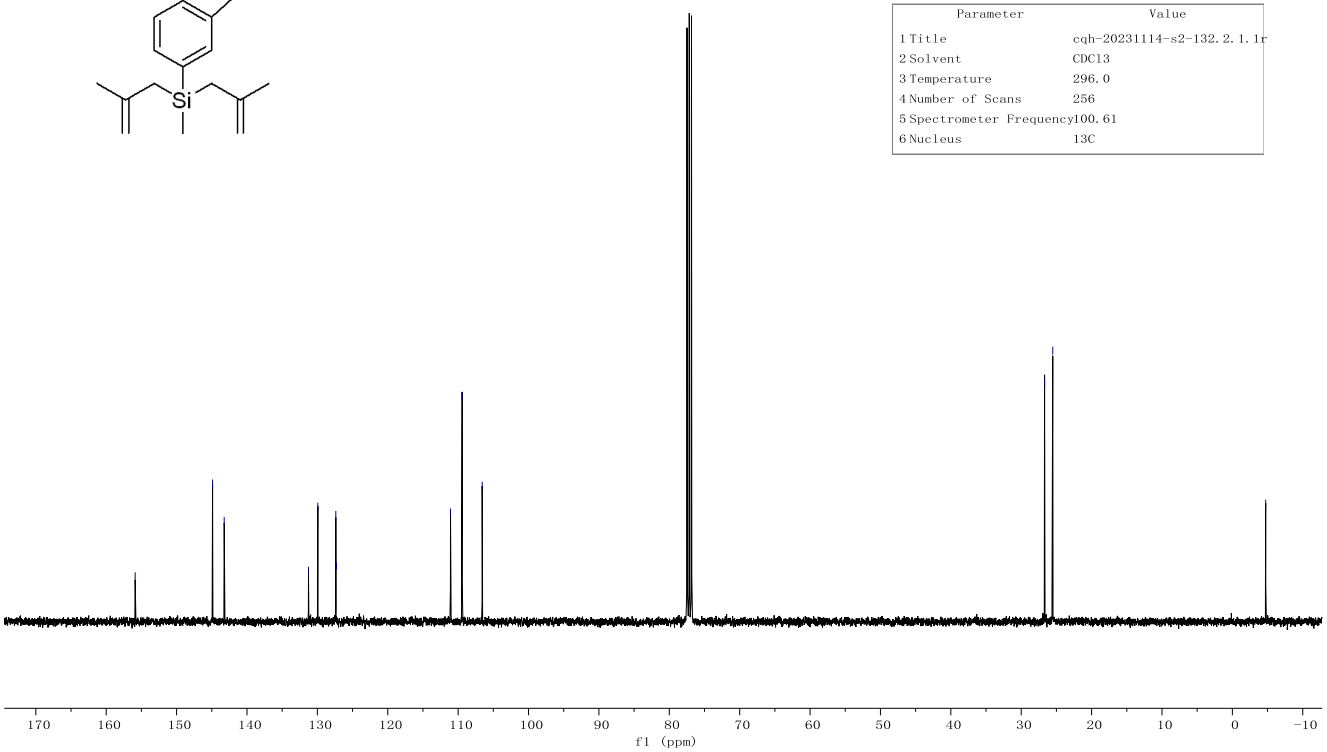
Parameter	Value
1 Title	cqh-20231114-s2-132.1.1.1r
2 Solvent	CDCl3
3 Temperature	295.1
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H



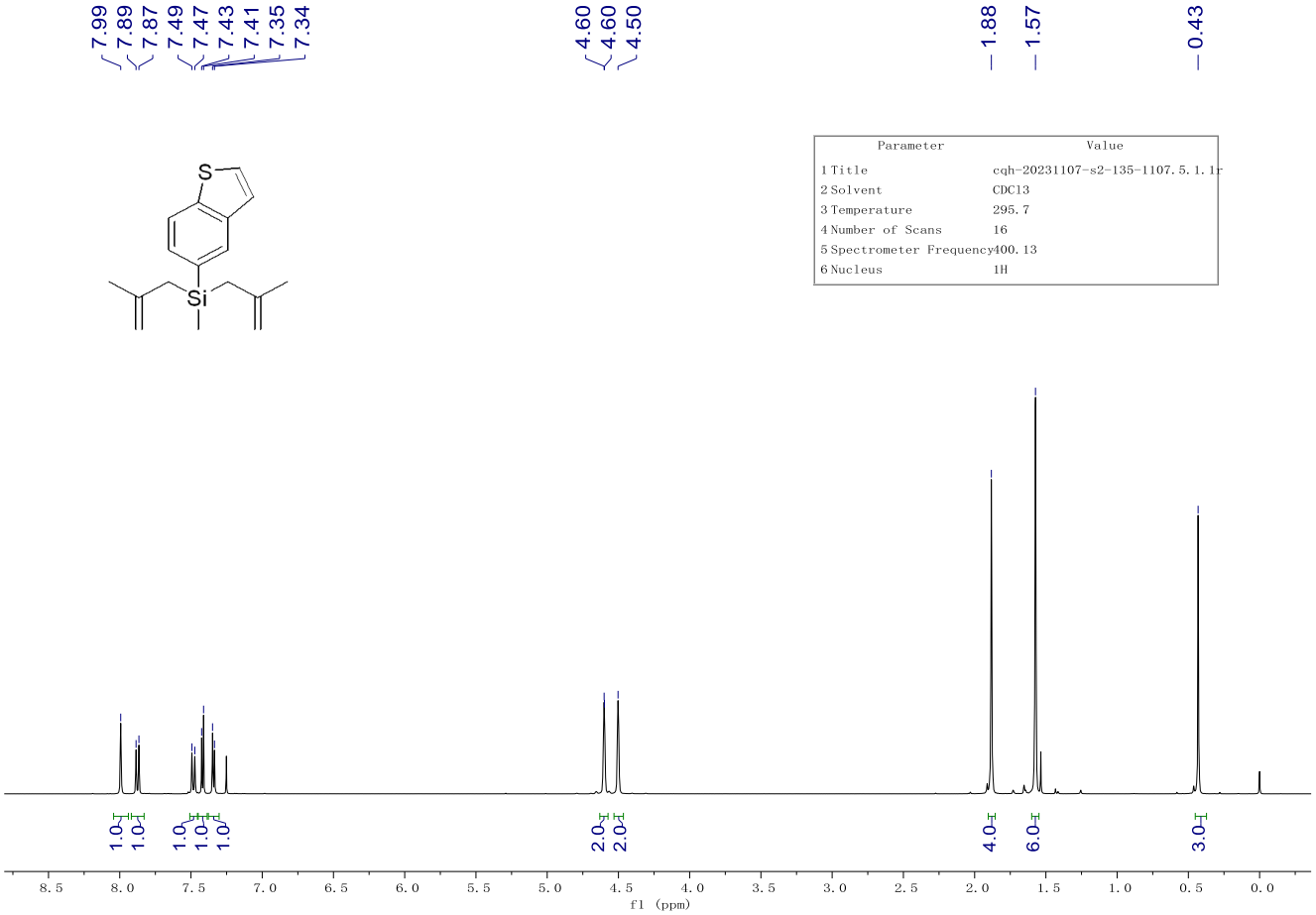


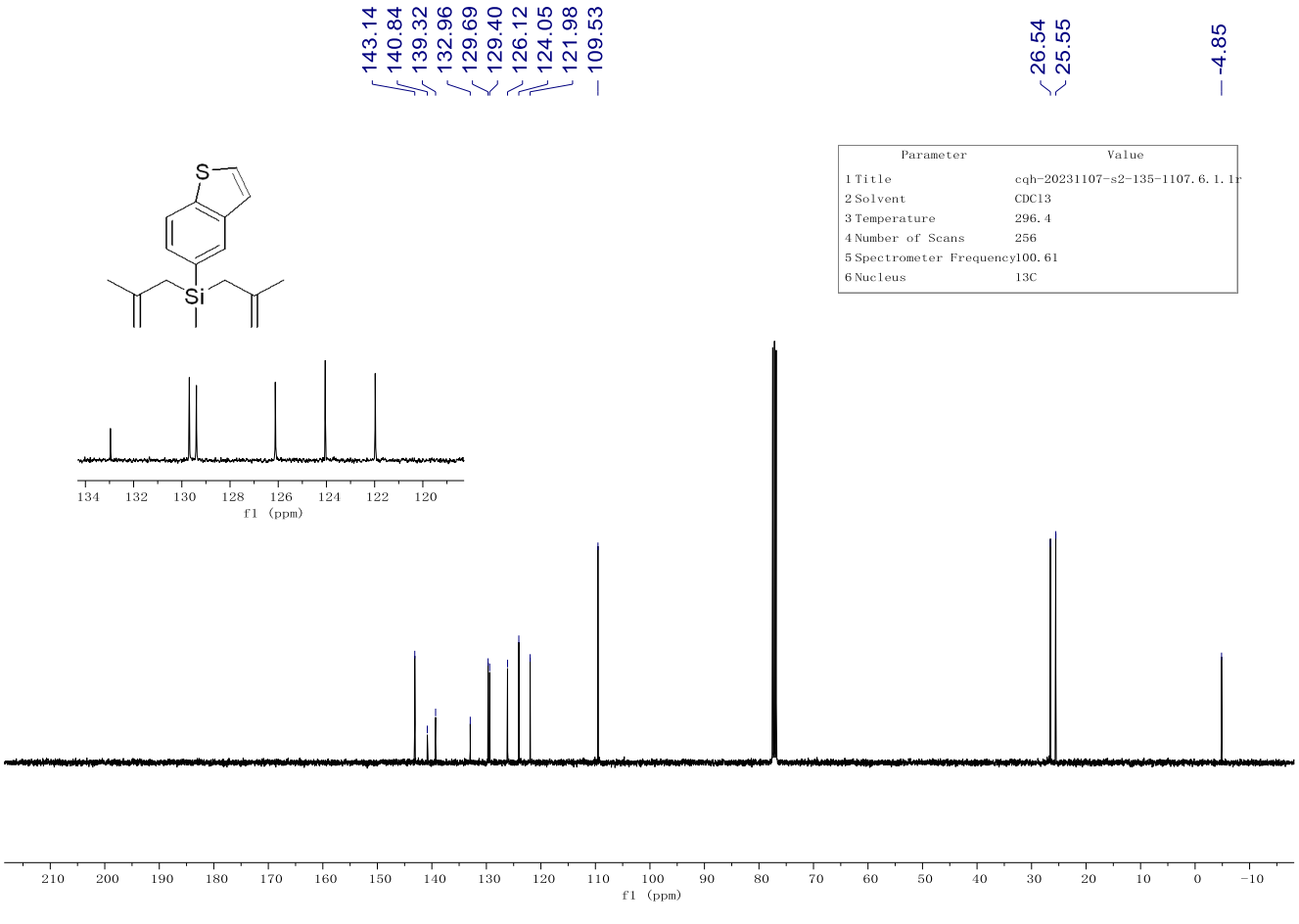


Parameter	Value
1 Title	cqh-20231114-s2-132.2.1.1r
2 Solvent	CDCl3
3 Temperature	296.0
4 Number of Scans	256
5 Spectrometer Frequency	100.61
6 Nucleus	13C

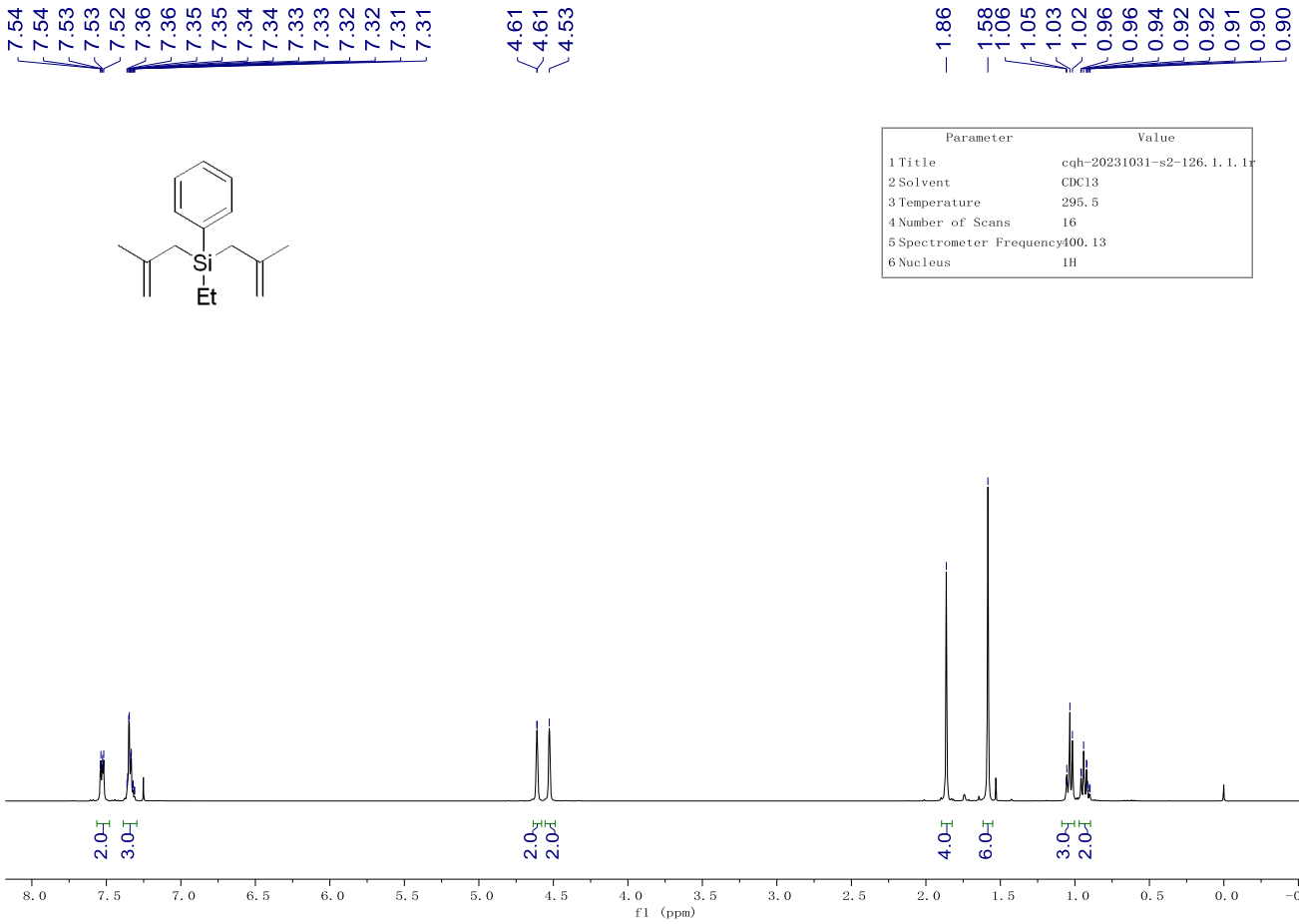


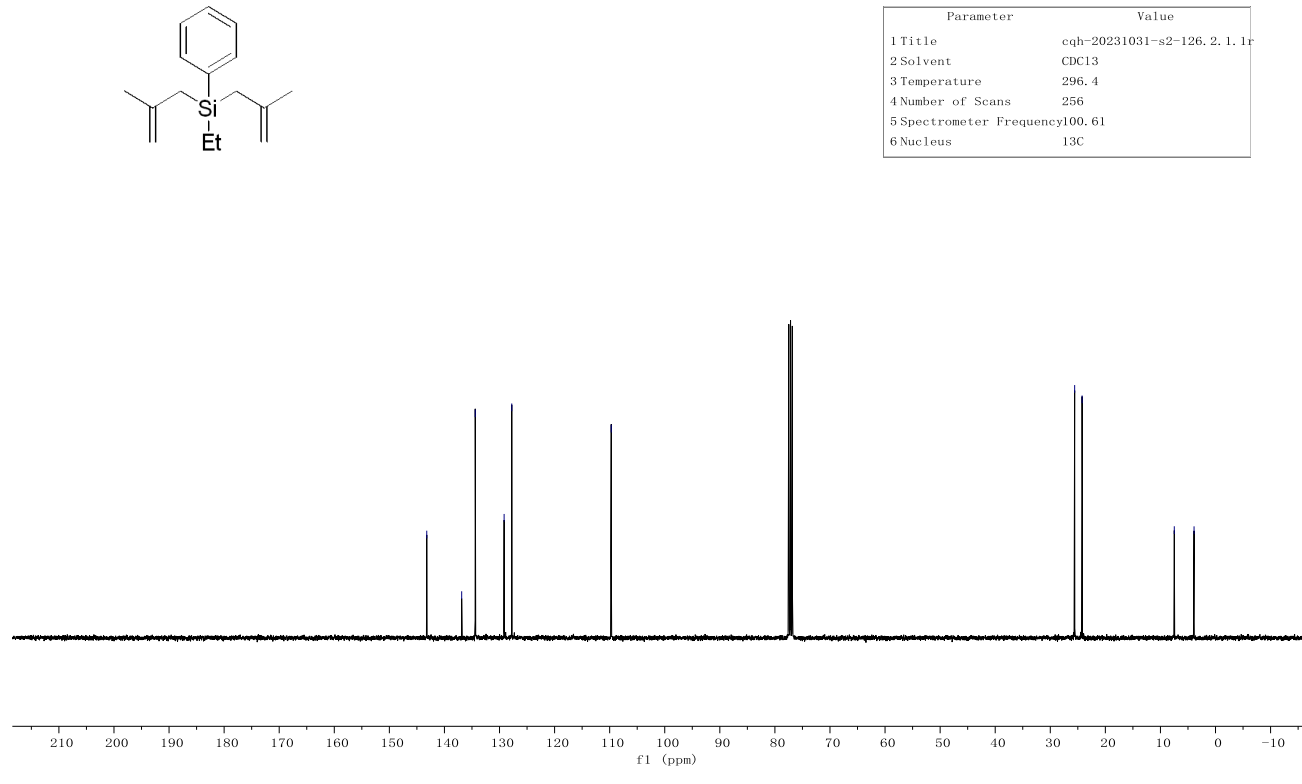
B20


7.99
7.89
7.87
7.49
7.47
7.43
7.41
7.35
7.34
4.60
4.60
4.50
1.88
1.57
0.43
S
Si
Parameter Value
1 Title cqh-20231107-s2-135-1107.5.1.1r
2 Solvent CDCl3
3 Temperature 295.7
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
1.0
1.0
1.0
1.0
1.0
2.0
2.0
4.0
6.0
3.0
f1 (ppm)

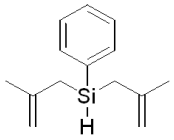

143.14
140.84
139.32
132.96
129.69
129.40
126.12
124.05
121.98
109.53
26.54
25.55
-4.85
S
Si
Parameter Value
1 Title cqh-20231107-s2-135-1107.6.1.1r
2 Solvent CDCl3
3 Temperature 296.4
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)
f1 (ppm)

B23

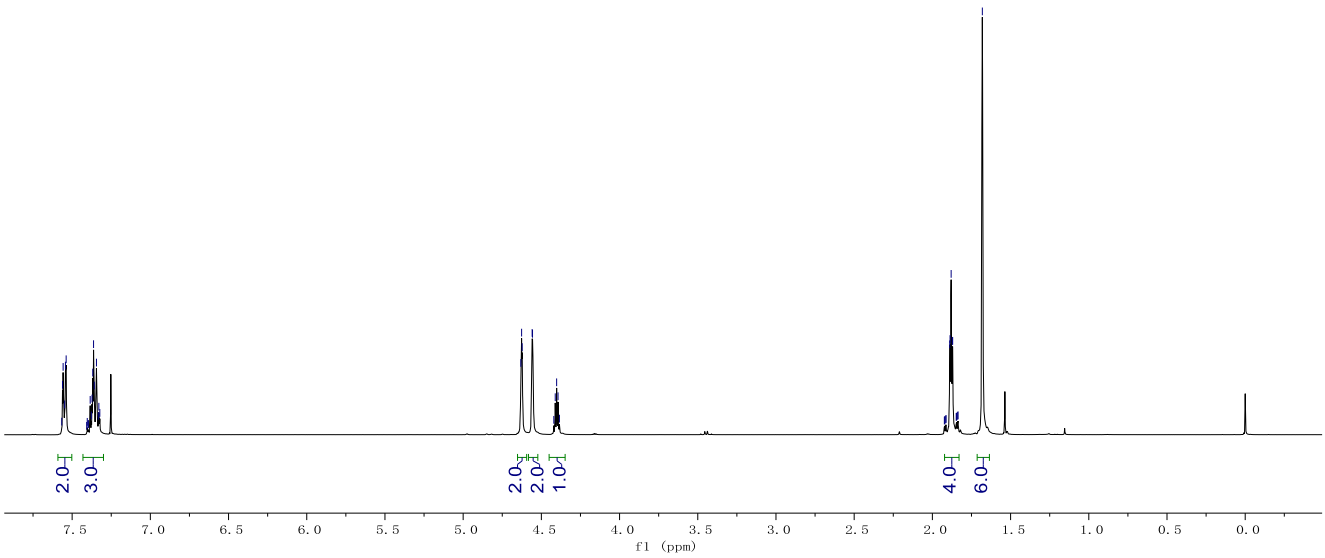

7.54 7.54 7.53 7.53 7.52 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31
4.61 4.61 4.53
1.86 1.58 1.06 1.05 1.03 1.02 0.96 0.96 0.94 0.92 0.92 0.91 0.90 0.90
Si
Et
Parameter Value
1 Title cqh-20231031-s2-126.1.1.1r
2 Solvent CDCl3
3 Temperature 295.5
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
2.0 3.0 2.0 2.0 4.0 6.0 3.0 2.0
f1 (ppm)

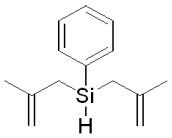

143.21 136.87 134.41 129.16 127.78
109.72
25.57 24.22
7.49 3.90
Si
Et
Parameter Value
1 Title cqh-20231031-s2-126.2.1.1r
2 Solvent CDCl3
3 Temperature 296.4
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)

B24

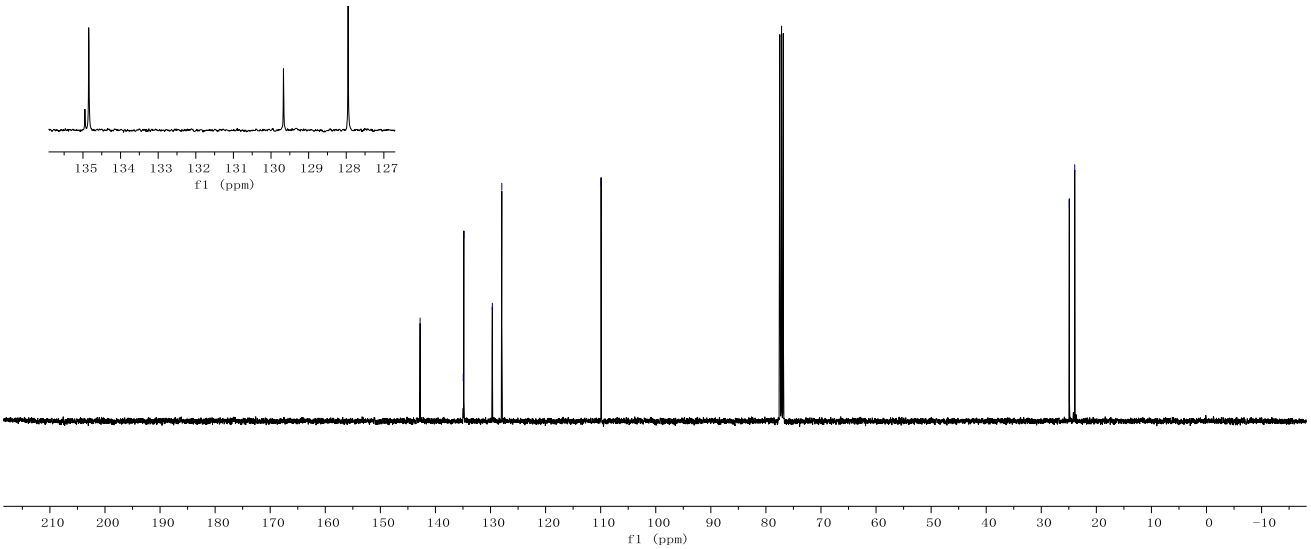


Parameter	Value
1 Title	cqh-20240313-s2-77.1.1.1r
2 Solvent	CDCl3
3 Temperature	294.8
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H

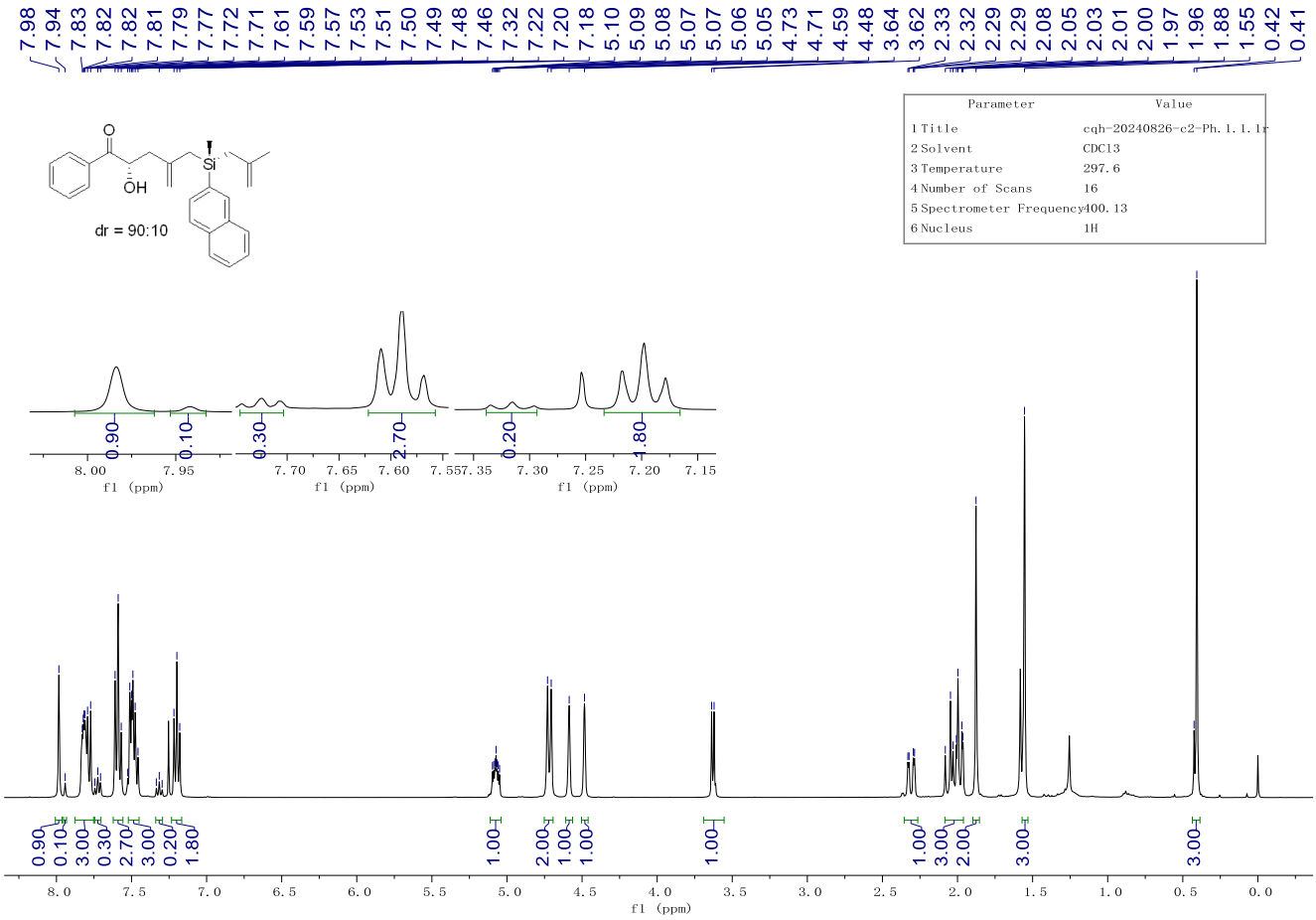


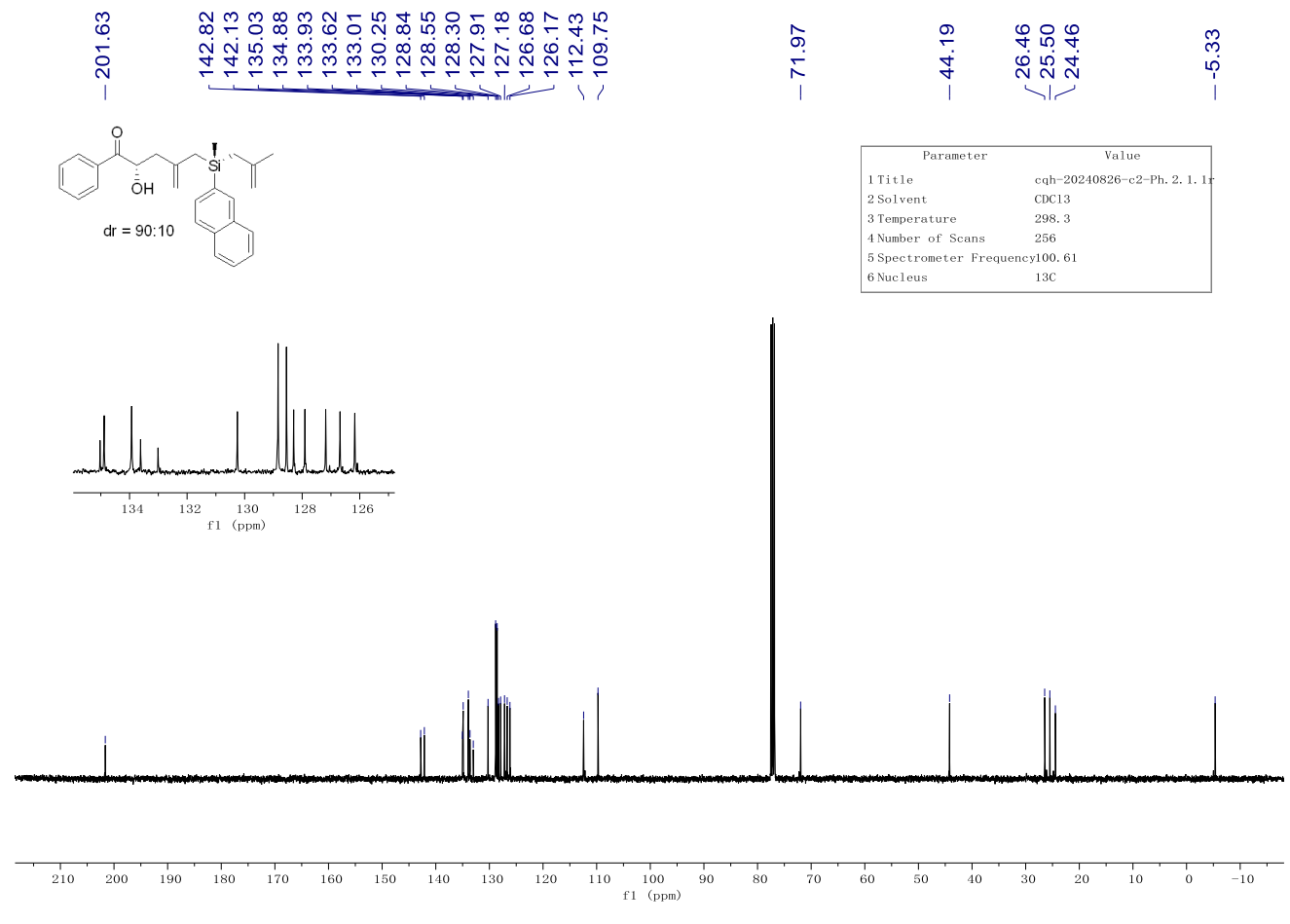


Parameter	Value
1 Title	cqh-20240314-s2-77.1.1.1r
2 Solvent	CDCl3
3 Temperature	295.9
4 Number of Scans	256
5 Spectrometer Frequency	100.61
6 Nucleus	13C

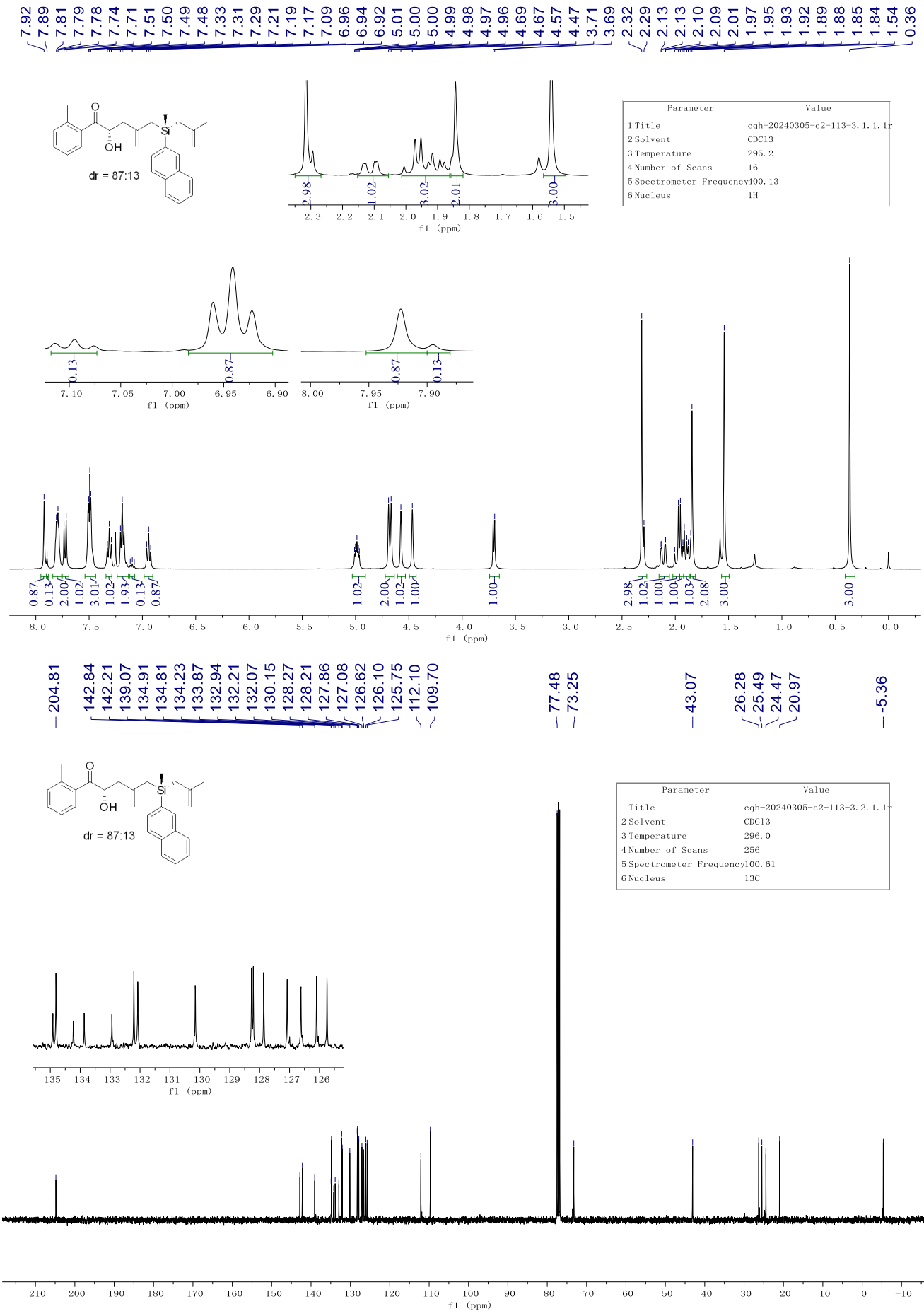


C1

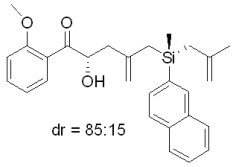

7.98 7.94 7.83 7.82 7.82 7.81 7.79 7.77 7.72 7.71 7.61 7.59 7.57 7.53 7.51 7.50 7.49 7.48 7.46 7.32 7.22 7.20 7.18 5.10 5.09 5.08 5.07 5.07 5.06 5.05 4.73 4.71 4.59 4.48 3.64 3.62 2.33 2.32 2.29 2.29 2.08 2.05 2.03 2.01 2.00 1.97 1.96 1.88 1.55 0.42 0.41
O
OH
Si
dr = 90:10
Parameter Value
1 Title cqh-20240826-c2-Ph.1.1.1r
2 Solvent CDCl3
3 Temperature 297.6
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
0.90 0.10 0.30 2.70 0.20 1.80
f1 (ppm)
0.90 0.10 3.00 0.30 2.70 3.00 0.20 1.80 1.00 2.00 1.00 1.00 1.00 1.00 3.00 3.00
f1 (ppm)

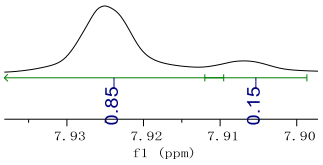

201.63
142.82 142.13 135.03 134.88 133.93 133.62 133.01 130.25 128.84 128.55 128.30 127.91 127.18 126.68 126.17 112.43 109.75
71.97
44.19
26.46 25.50 24.46
-5.33
O
OH
Si
dr = 90:10
Parameter Value
1 Title cqh-20240826-c2-Ph.2.1.1r
2 Solvent CDCl3
3 Temperature 298.3
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)
f1 (ppm)

C2

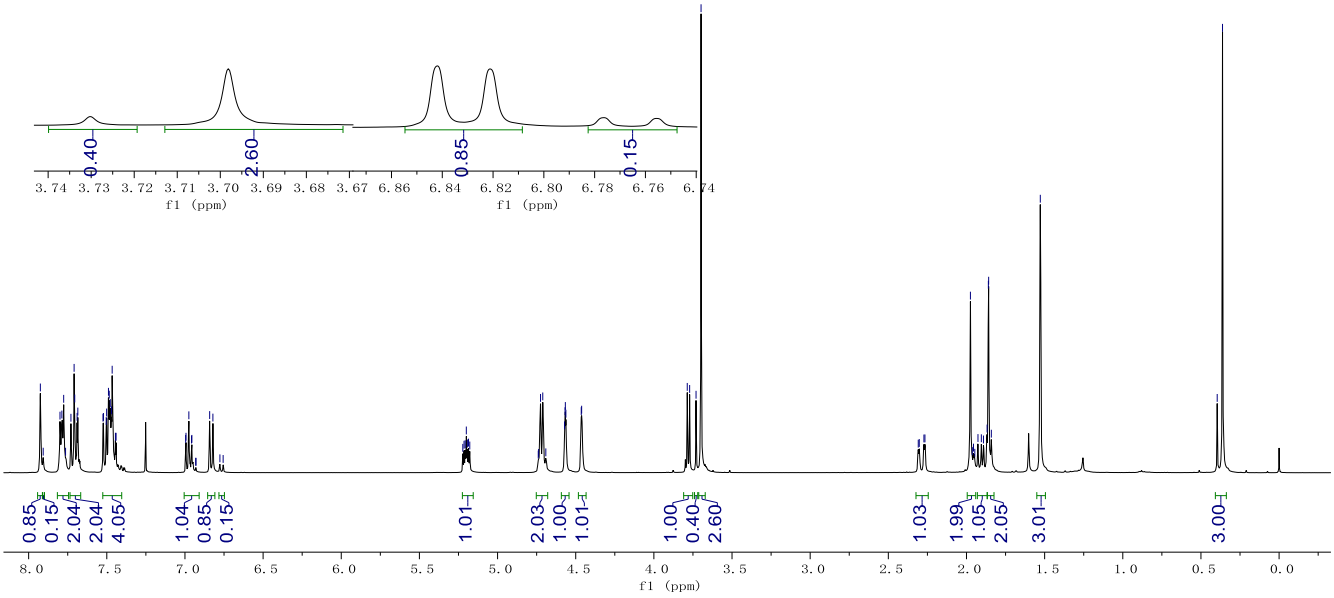

7.92 7.89 7.81 7.79 7.78 7.74 7.71 7.51 7.50 7.49 7.48 7.33 7.31 7.29 7.21 7.19 7.17 7.09 6.96 6.94 6.92 5.01 5.00 5.00 4.99 4.98 4.97 4.96 4.69 4.67 4.57 4.47 3.71 3.69 2.32 2.29 2.13 2.13 2.10 2.09 2.01 1.97 1.95 1.93 1.92 1.89 1.88 1.85 1.84 1.54 0.36
dr = 87:13
Parameter Value
1 Title cqh-20240305-c2-113-3.1.1.1r
2 Solvent CDCl3
3 Temperature 295.2
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
f1 (ppm)
204.81 142.84 142.21 139.07 134.91 134.81 134.23 133.87 132.94 132.21 132.07 130.15 128.27 128.21 127.86 127.08 126.62 126.10 125.75 112.10 109.70 77.48 73.25 43.07 26.28 25.49 24.47 20.97 -5.36
dr = 87:13
Parameter Value
1 Title cqh-20240305-c2-113-3.2.1.1r
2 Solvent CDCl3
3 Temperature 296.0
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)

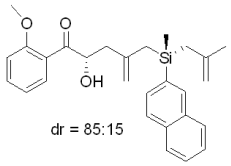
C3



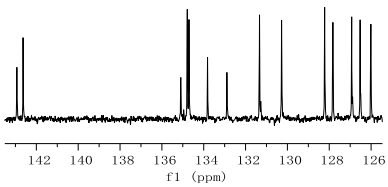


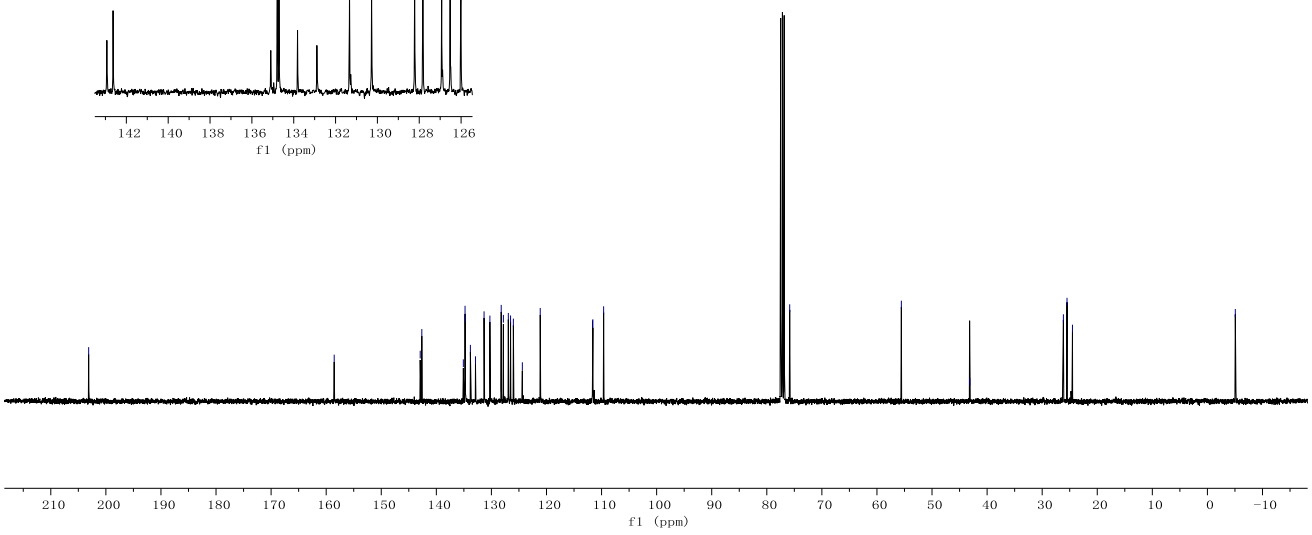
Parameter	Value
1 Title	cqh-20240227-c2-110-4.7.1.1r
2 Solvent	CDCl3
3 Temperature	295.8
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H



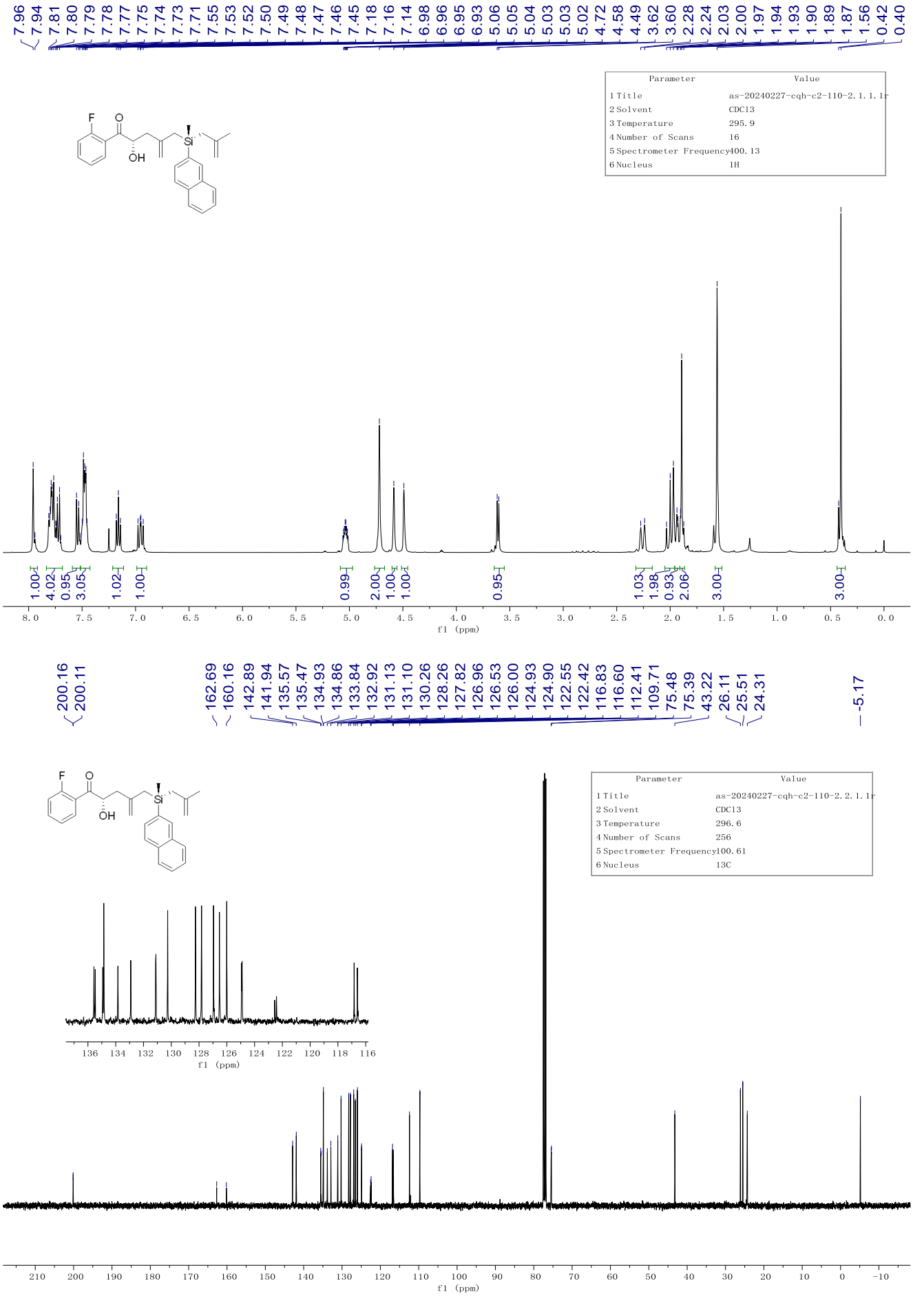


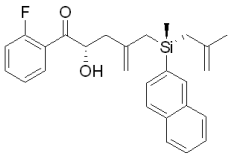
Parameter	Value
1 Title	cqh-20240227-c2-110-4.8.1.1r
2 Solvent	CDCl3
3 Temperature	296.8
4 Number of Scans	256
5 Spectrometer Frequency	100.61
6 Nucleus	13C





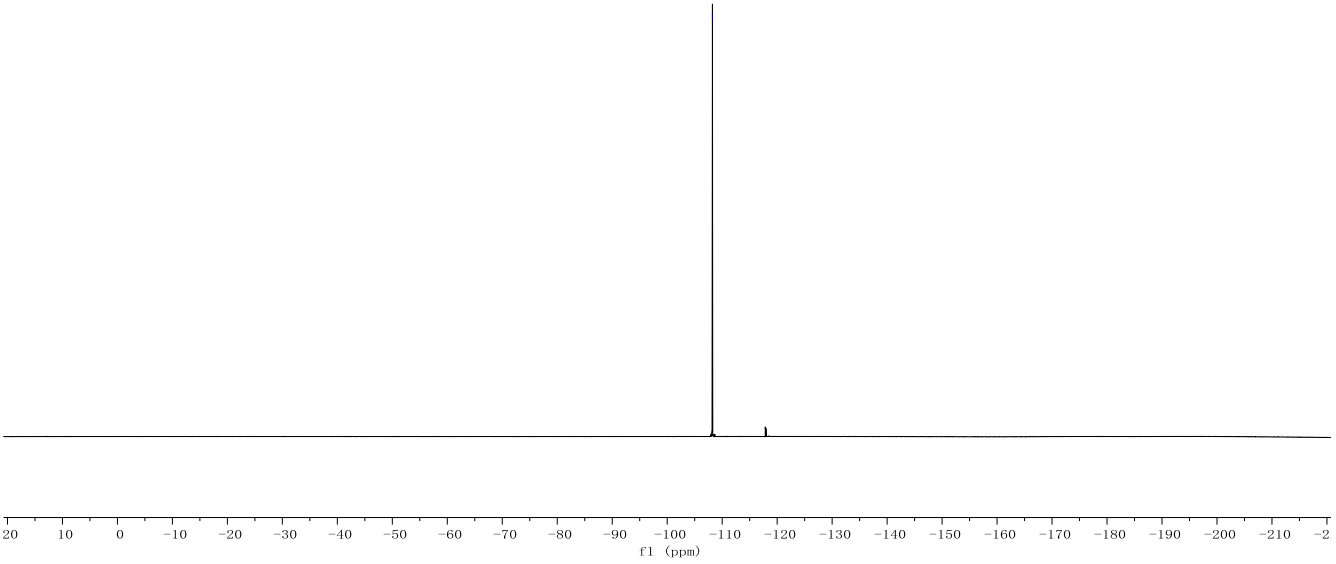
C4


7.96 7.94 7.81 7.80 7.79 7.78 7.77 7.75 7.74 7.73 7.71 7.55 7.53 7.52 7.50 7.49 7.48 7.47 7.46 7.45 7.18 7.16 7.14 6.98 6.96 6.95 6.93 5.06 5.05 5.04 5.03 5.03 5.02 4.72 4.58 4.49 3.62 3.60 2.28 2.24 2.03 2.00 1.97 1.94 1.93 1.90 1.89 1.87 1.56 0.42 0.40
Parameter Value
1 Title as-20240227-cqh-c2-110-2.1.1.1r
2 Solvent CDCl3
3 Temperature 295.9
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
F O OH Si
1.00 4.02 0.95 3.05 1.02 1.00 0.99 2.00 1.00 1.00 0.95 1.03 1.98 0.93 2.06 3.00 3.00
f1 (ppm)
200.16 200.11 162.69 160.16 142.89 141.94 135.57 135.47 134.93 134.86 133.84 132.92 131.13 131.10 130.26 128.26 127.82 126.96 126.53 126.00 124.93 124.90 122.55 122.42 116.83 116.60 112.41 109.71 75.48 75.39 43.22 26.11 25.51 24.31 -5.17
Parameter Value
1 Title as-20240227-cqh-c2-110-2.2.1.1r
2 Solvent CDCl3
3 Temperature 296.6
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)
f1 (ppm)

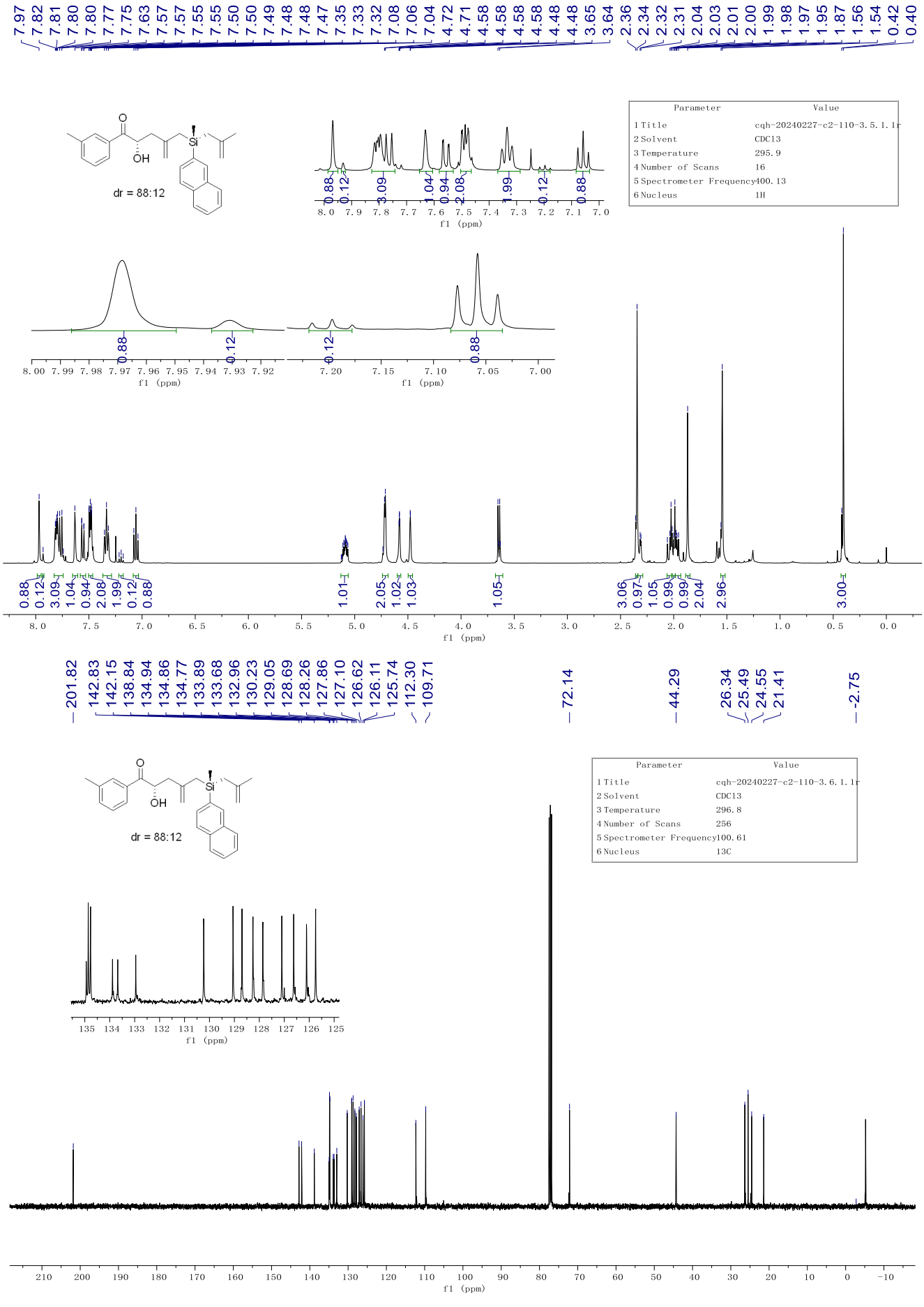


-108.23

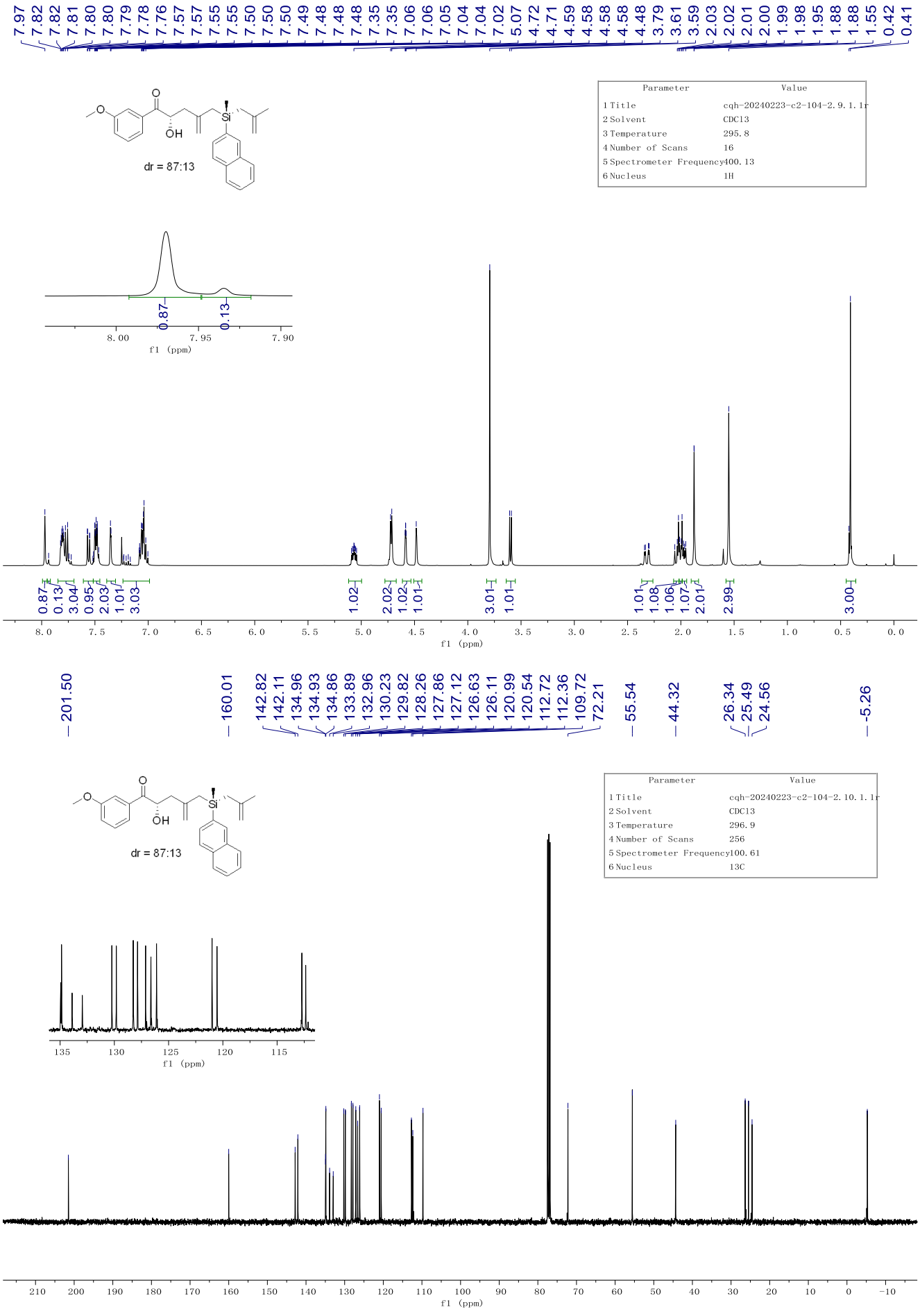
Parameter	Value
1 Title	as-20240227-cqh-c2-110-2.3.1.1r
2 Solvent	CDCl3
3 Temperature	296.3
4 Number of Scans	16
5 Spectrometer Frequency	376.50
6 Nucleus	19F



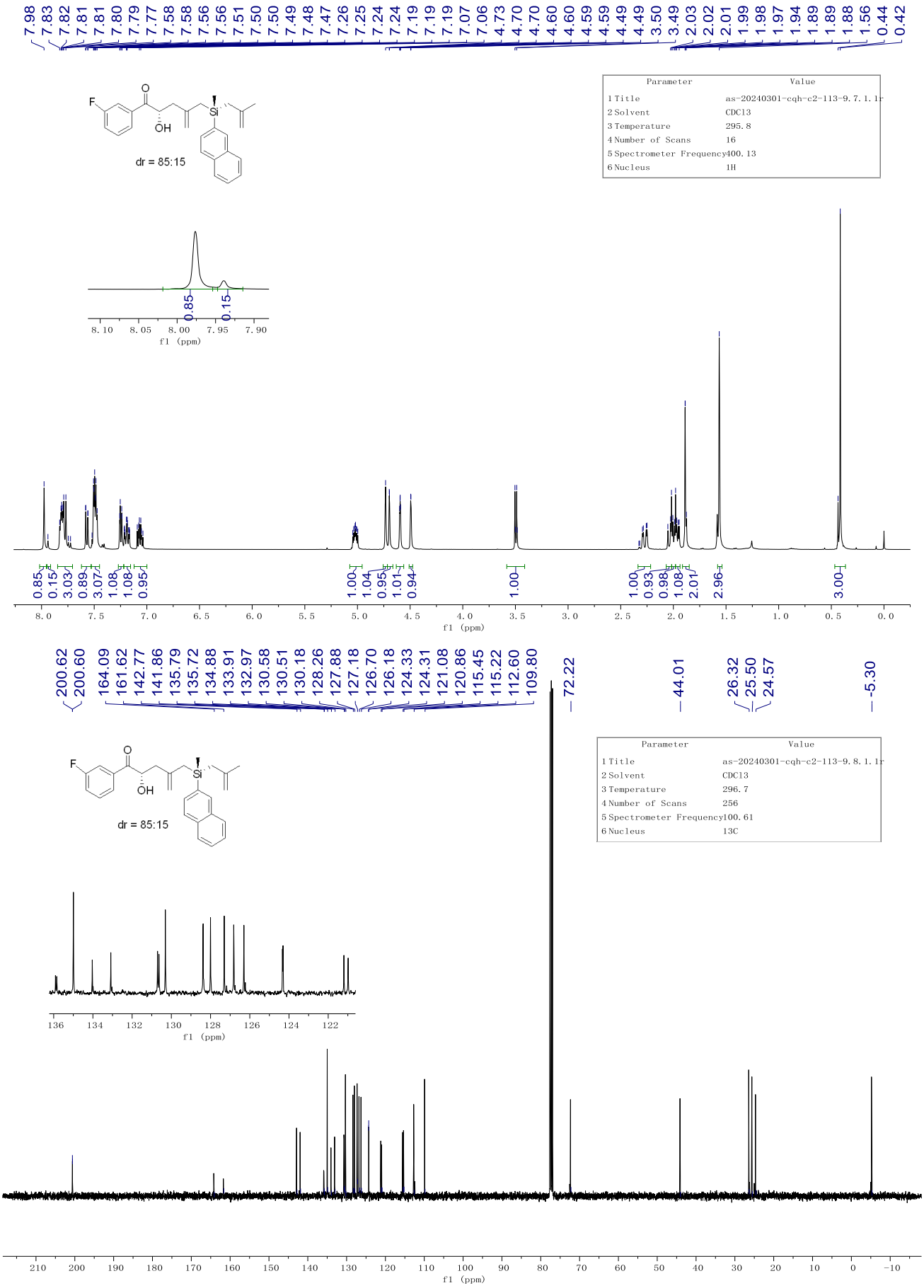
C5

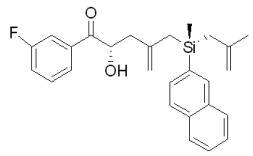

dr = 88:12
Parameter Value
1 Title cqh-20240227-c2-110-3.5.1.1r
2 Solvent CDCl3
3 Temperature 295.9
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
f1 (ppm)
dr = 88:12
Parameter Value
1 Title cqh-20240227-c2-110-3.6.1.1r
2 Solvent CDCl3
3 Temperature 296.8
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)

C6


7.97 7.82 7.82 7.81 7.80 7.80 7.79 7.78 7.76 7.57 7.57 7.55 7.55 7.50 7.50 7.50 7.49 7.48 7.48 7.48 7.35 7.35 7.06 7.06 7.05 7.04 7.04 7.02 5.07 4.72 4.71 4.59 4.58 4.58 4.58 4.48 3.79 3.61 3.59 2.03 2.02 2.01 2.00 1.99 1.98 1.95 1.88 1.88 1.55 0.42 0.41
dr = 87:13
Parameter Value
1 Title cqh-20240223-c2-104-2.9.1.1r
2 Solvent CDCl3
3 Temperature 295.8
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
0.87 0.13
f1 (ppm)
0.87 0.13 3.04 0.95 2.03 1.01 3.03 1.02 2.02 1.02 1.01 3.01 1.01 1.01 1.08 1.06 1.07 2.01 2.99 3.00
f1 (ppm)
201.50 160.01 142.82 142.11 134.96 134.93 134.86 133.89 132.96 130.23 129.82 128.26 127.86 127.12 126.63 126.11 120.99 120.54 112.72 112.36 109.72 72.21 55.54 44.32 26.34 25.49 24.56 -5.26
dr = 87:13
Parameter Value
1 Title cqh-20240223-c2-104-2.10.1.1r
2 Solvent CDCl3
3 Temperature 296.9
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)
f1 (ppm)

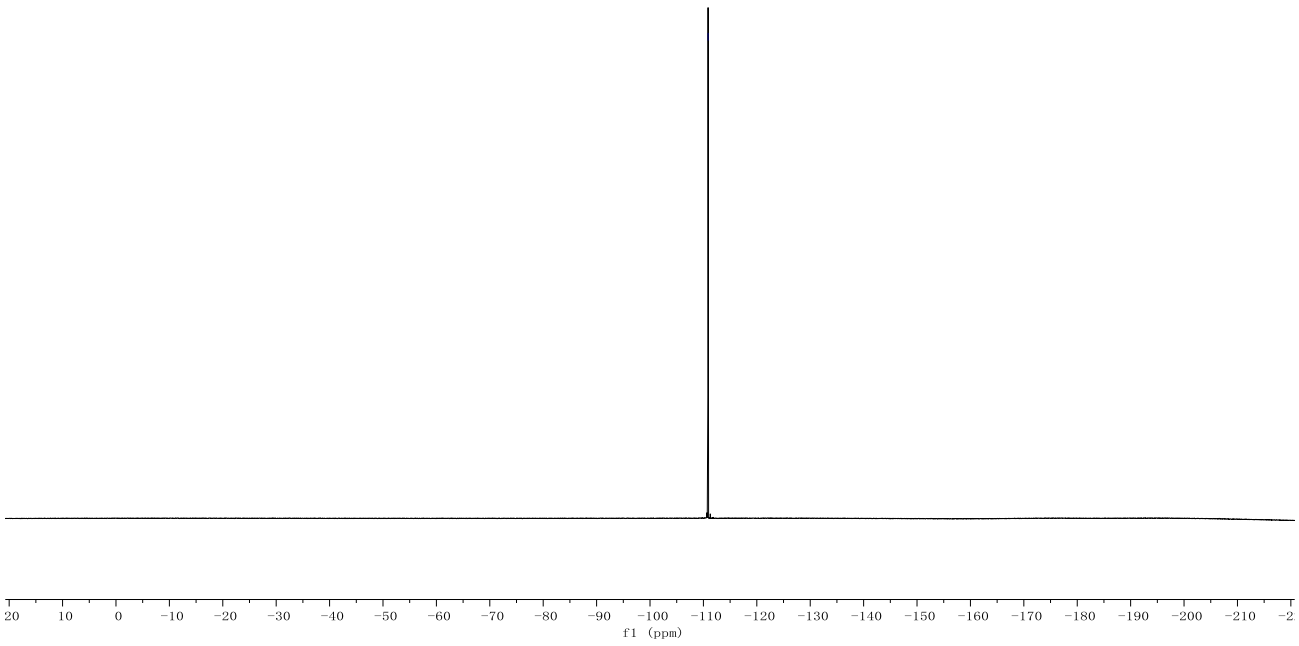
C7


7.98 7.83 7.82 7.81 7.81 7.80 7.79 7.77 7.58 7.58 7.56 7.56 7.51 7.50 7.50 7.49 7.48 7.47 7.26 7.25 7.24 7.24 7.19 7.19 7.19 7.07 7.06 4.73 4.70 4.70 4.60 4.60 4.59 4.59 4.49 4.49 3.50 3.49 2.03 2.02 2.01 1.99 1.98 1.97 1.94 1.89 1.89 1.88 1.56 0.44 0.42
F
O
OH
Si
dr = 85:15
Parameter Value
1 Title as-20240301-cqh-c2-113-9.7.1.1r
2 Solvent CDCl3
3 Temperature 295.8
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
0.85 0.15
8.10 8.05 8.00 7.95 7.90
f1 (ppm)
0.85 0.15 3.03 0.89 3.07 1.08 1.08 0.95 1.00 1.04 0.95 1.01 0.94 1.00 1.00 0.93 0.98 1.08 2.01 2.96 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
200.62 200.60 164.09 161.62 142.77 141.86 135.79 135.72 134.88 133.91 132.97 130.58 130.51 130.18 128.26 127.88 127.18 126.70 126.18 124.33 124.31 121.08 120.86 115.45 115.22 112.60 109.80 72.22 44.01 26.32 25.50 24.57 -5.30
F
O
OH
Si
dr = 85:15
Parameter Value
1 Title as-20240301-cqh-c2-113-9.8.1.1r
2 Solvent CDCl3
3 Temperature 296.7
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
136 134 132 130 128 126 124 122
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

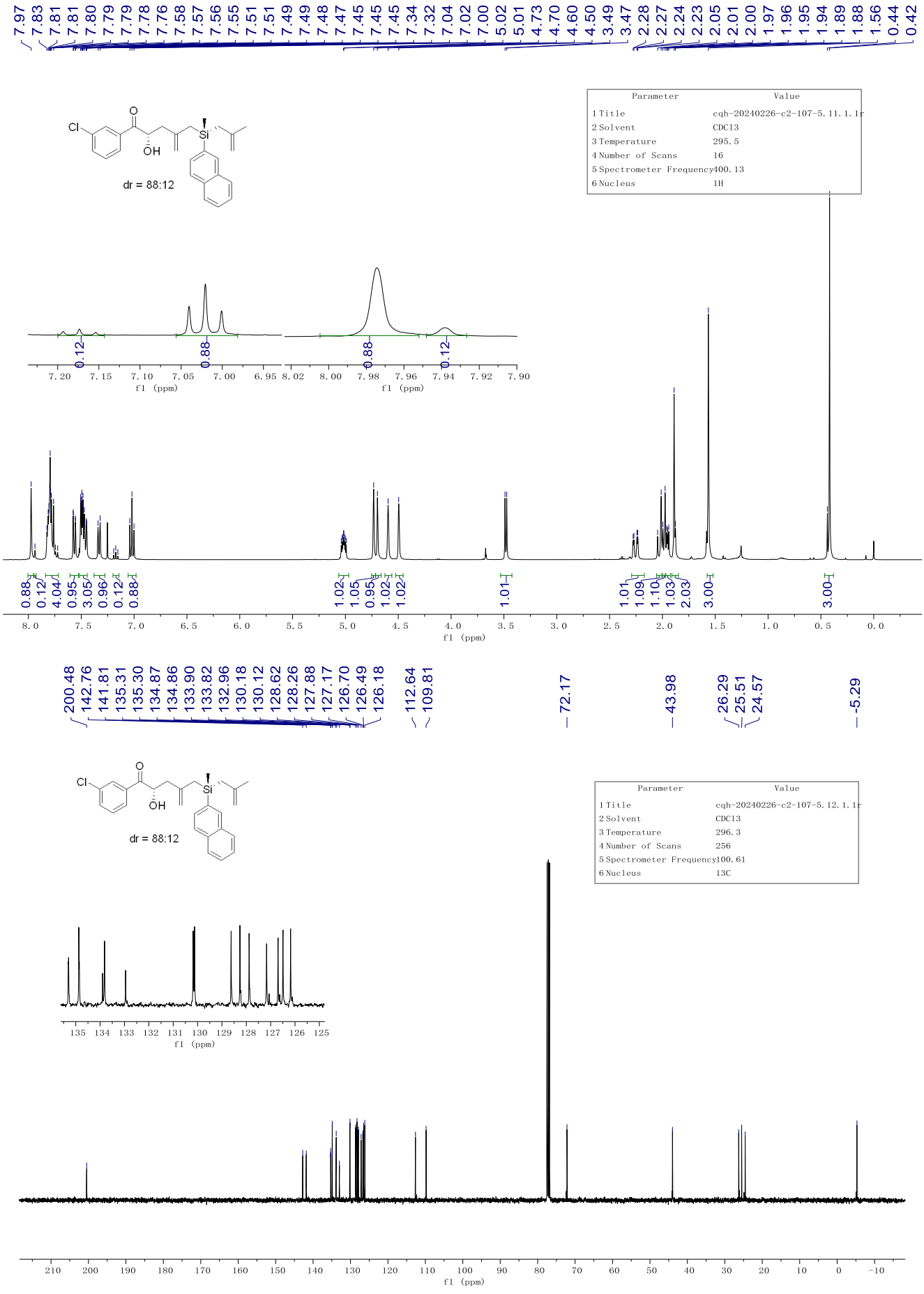


-110.88

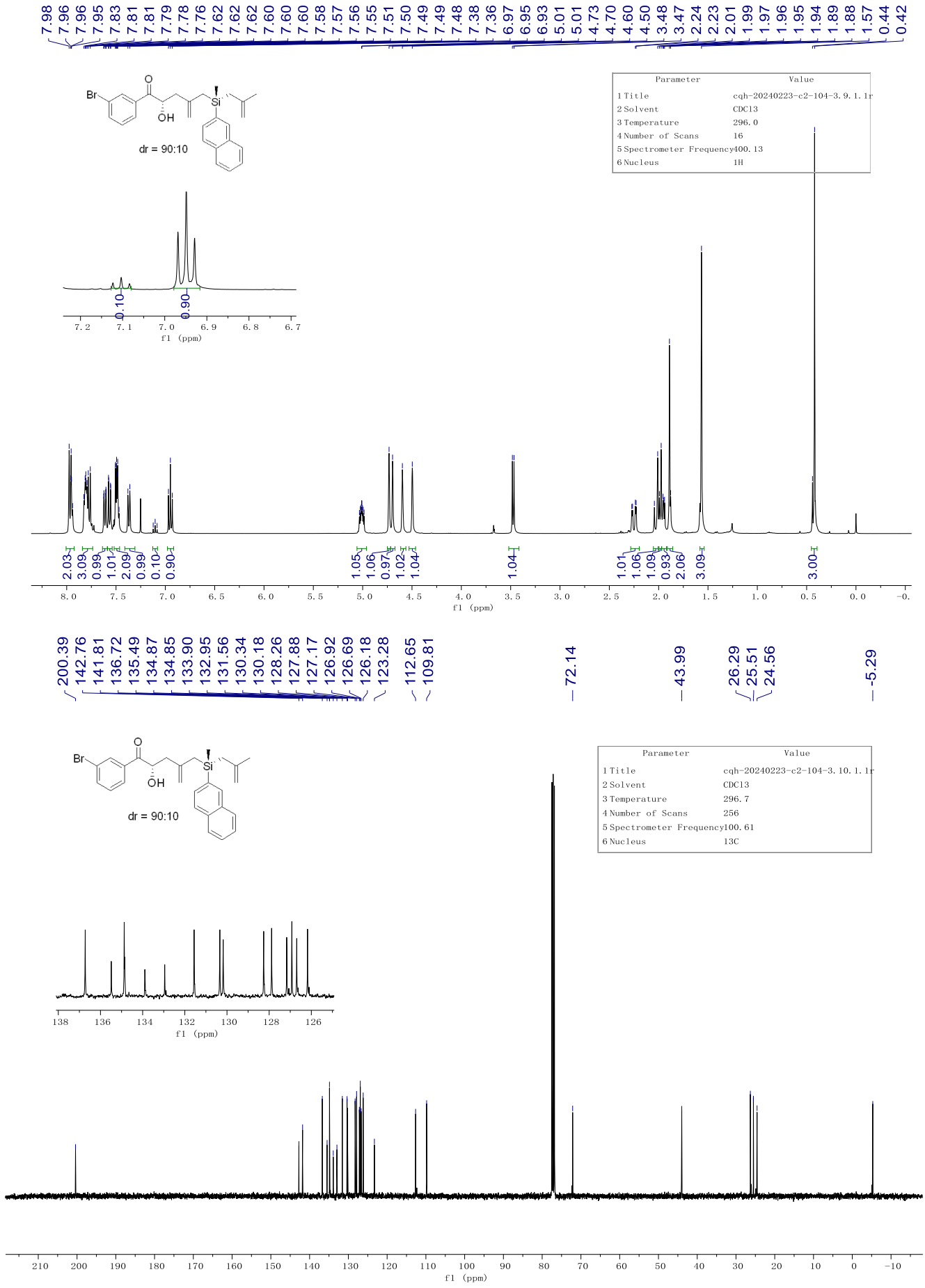
Parameter	Value
1 Title	as-20240301-cqh-c2-113-9.9.1.1r
2 Solvent	CDCl3
3 Temperature	296.2
4 Number of Scans	16
5 Spectrometer Frequency	376.50
6 Nucleus	19F



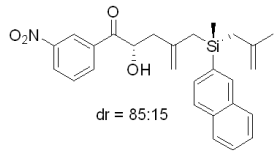
C8


dr = 88:12
Parameter Value
1 Title cqh-20240226-c2-107-5.11.1.1r
2 Solvent CDCl3
3 Temperature 295.5
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
f1 (ppm)
dr = 88:12
Parameter Value
1 Title cqh-20240226-c2-107-5.12.1.1r
2 Solvent CDCl3
3 Temperature 296.3
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)

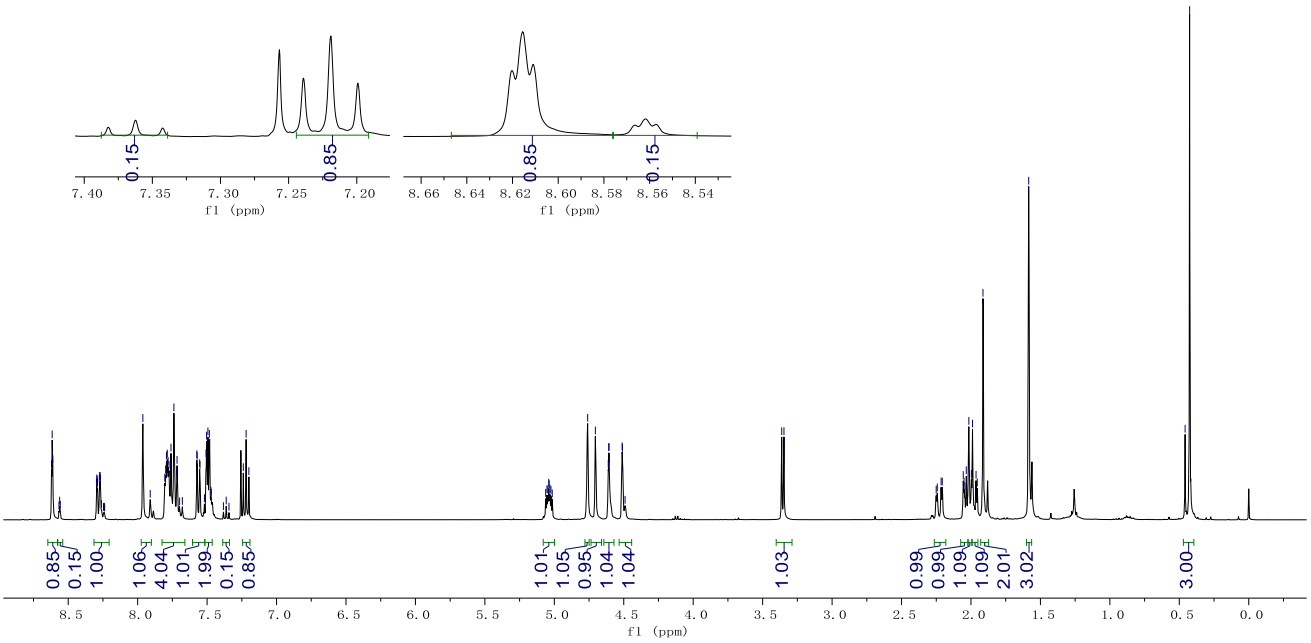
C9

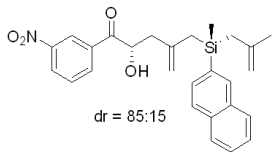

dr = 90:10
Parameter Value
1 Title cqh-20240223-c2-104-3.9.1.1r
2 Solvent CDCl3
3 Temperature 296.0
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
f1 (ppm)
dr = 90:10
Parameter Value
1 Title cqh-20240223-c2-104-3.10.1.1r
2 Solvent CDCl3
3 Temperature 296.7
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)

C10

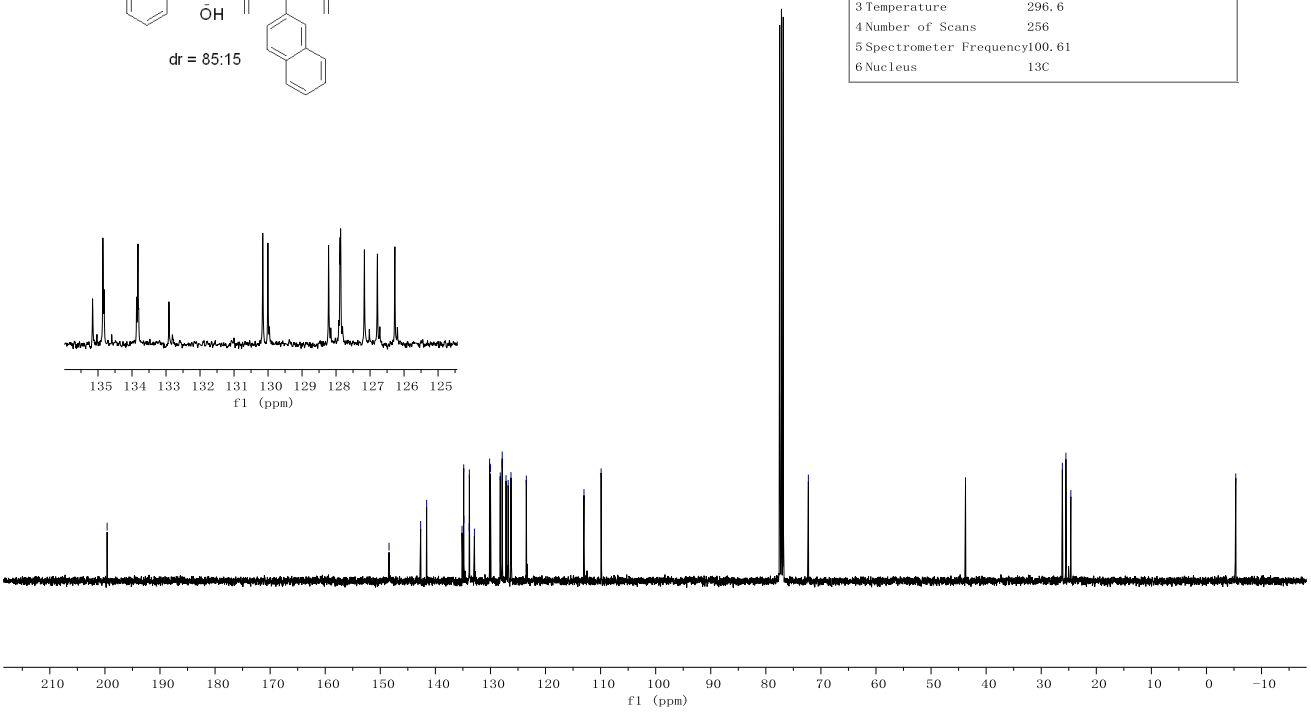


Parameter	Value
1 Title	cqh-20240227-c2-110-5.9.1.1r
2 Solvent	CDCl3
3 Temperature	295.7
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H

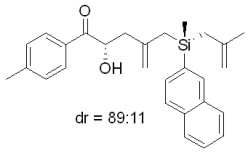




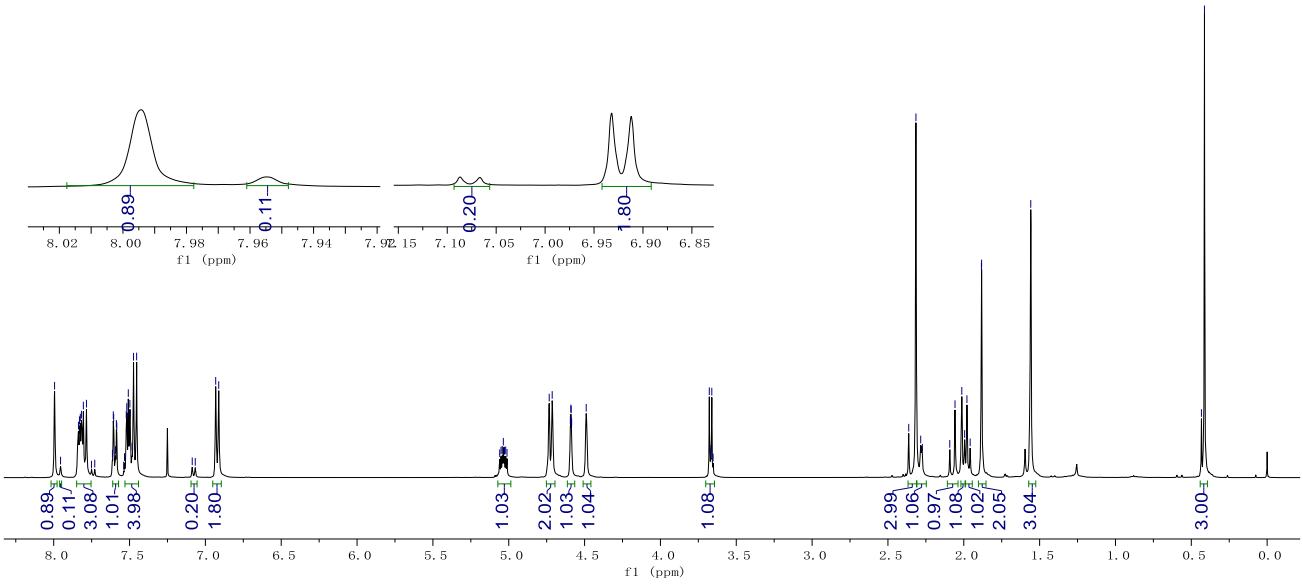
Parameter	Value
1 Title	cqh-20240227-c2-110-5.10.1.1r
2 Solvent	CDCl3
3 Temperature	296.6
4 Number of Scans	256
5 Spectrometer Frequency	100.61
6 Nucleus	13C



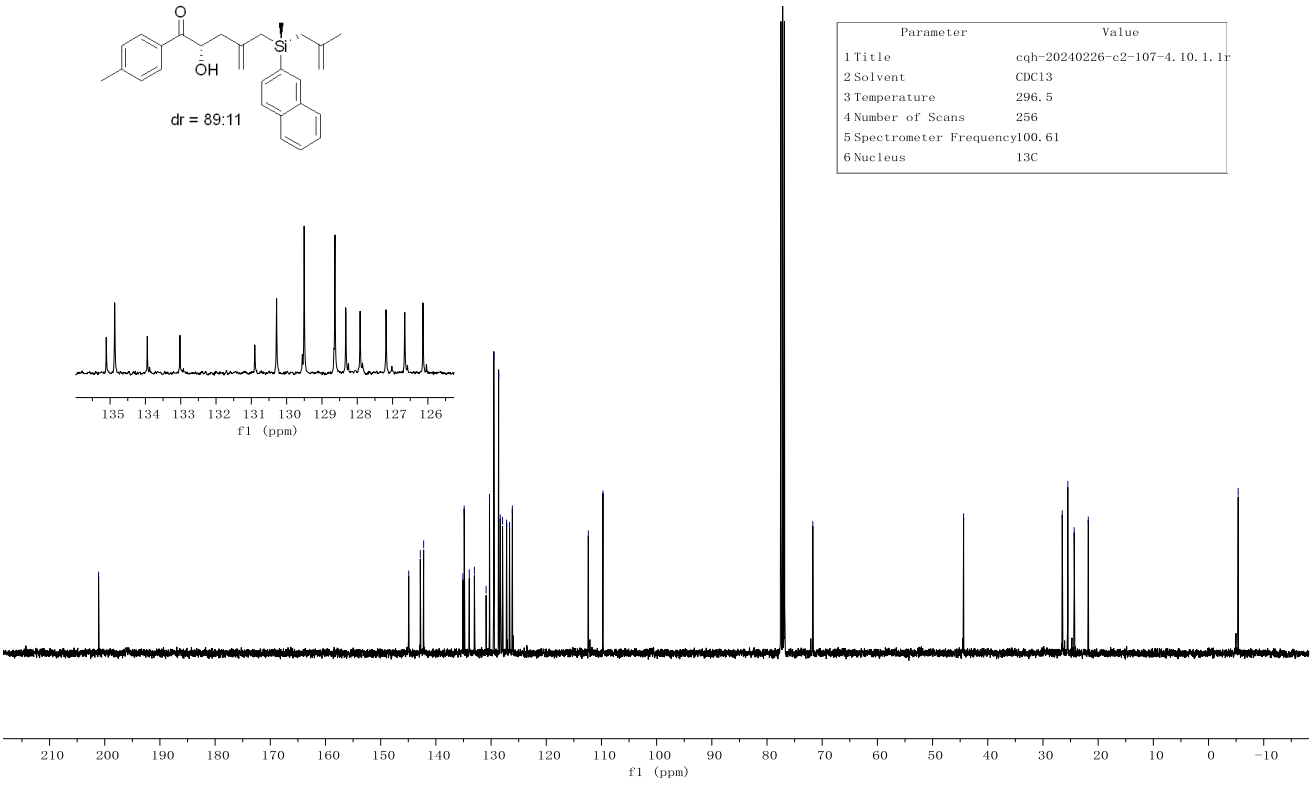
C11



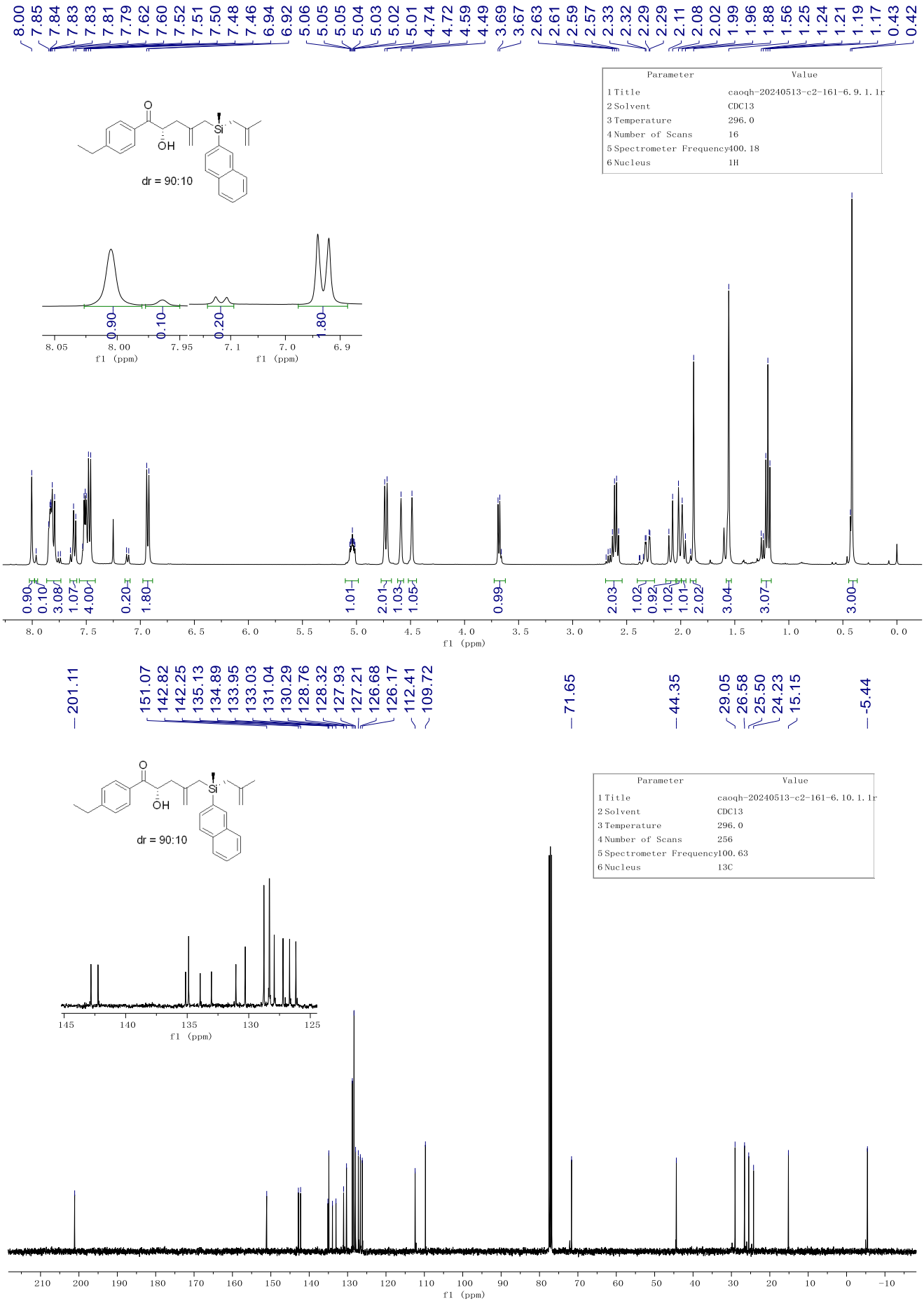
Parameter	Value
1 Title	cqh-20240226-c2-107-4.9.1.1r
2 Solvent	CDCl3
3 Temperature	295.5
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H



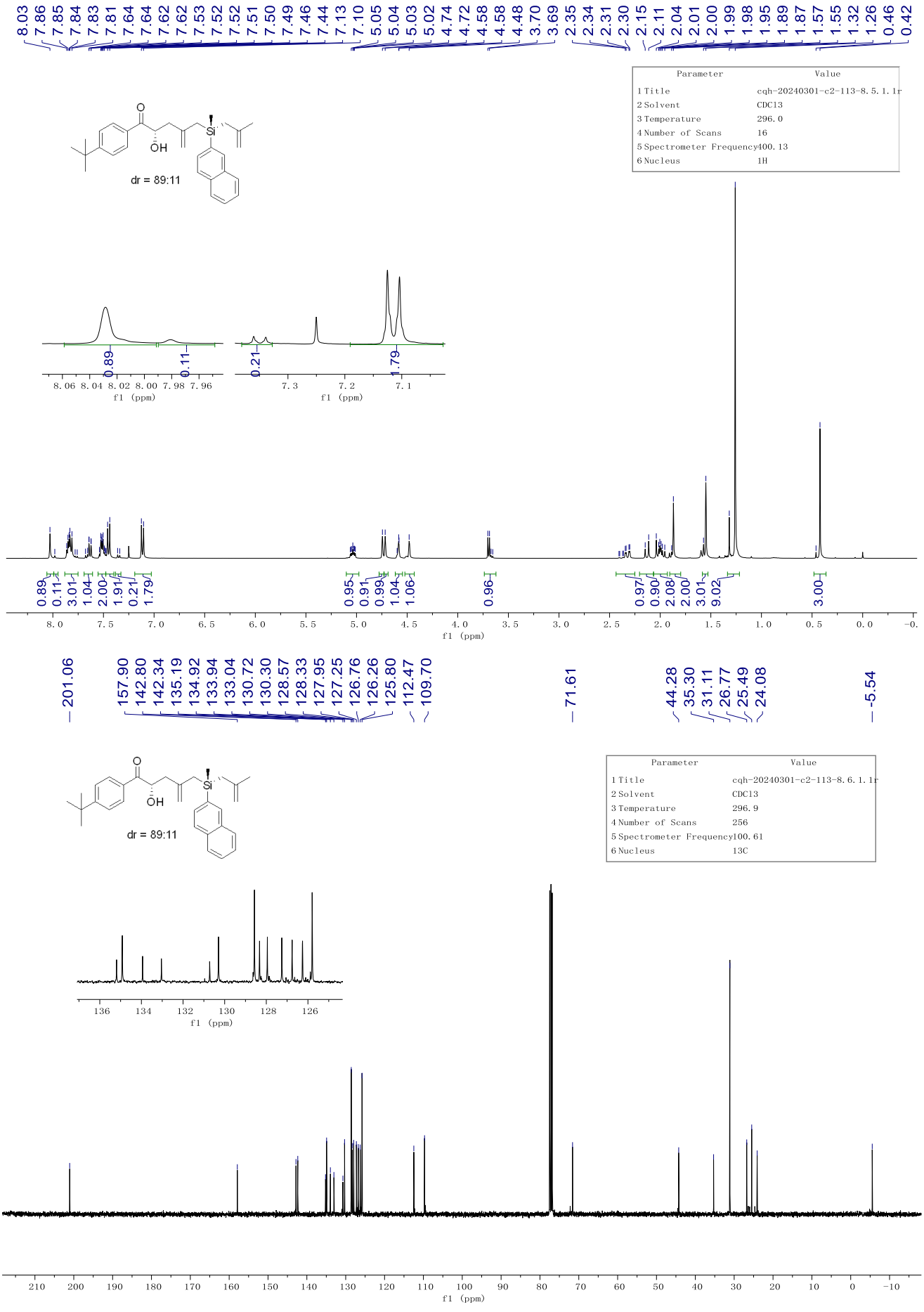
Parameter	Value
1 Title	cqh-20240226-c2-107-4.10.1.1r
2 Solvent	CDCl3
3 Temperature	296.5
4 Number of Scans	256
5 Spectrometer Frequency	100.61
6 Nucleus	13C



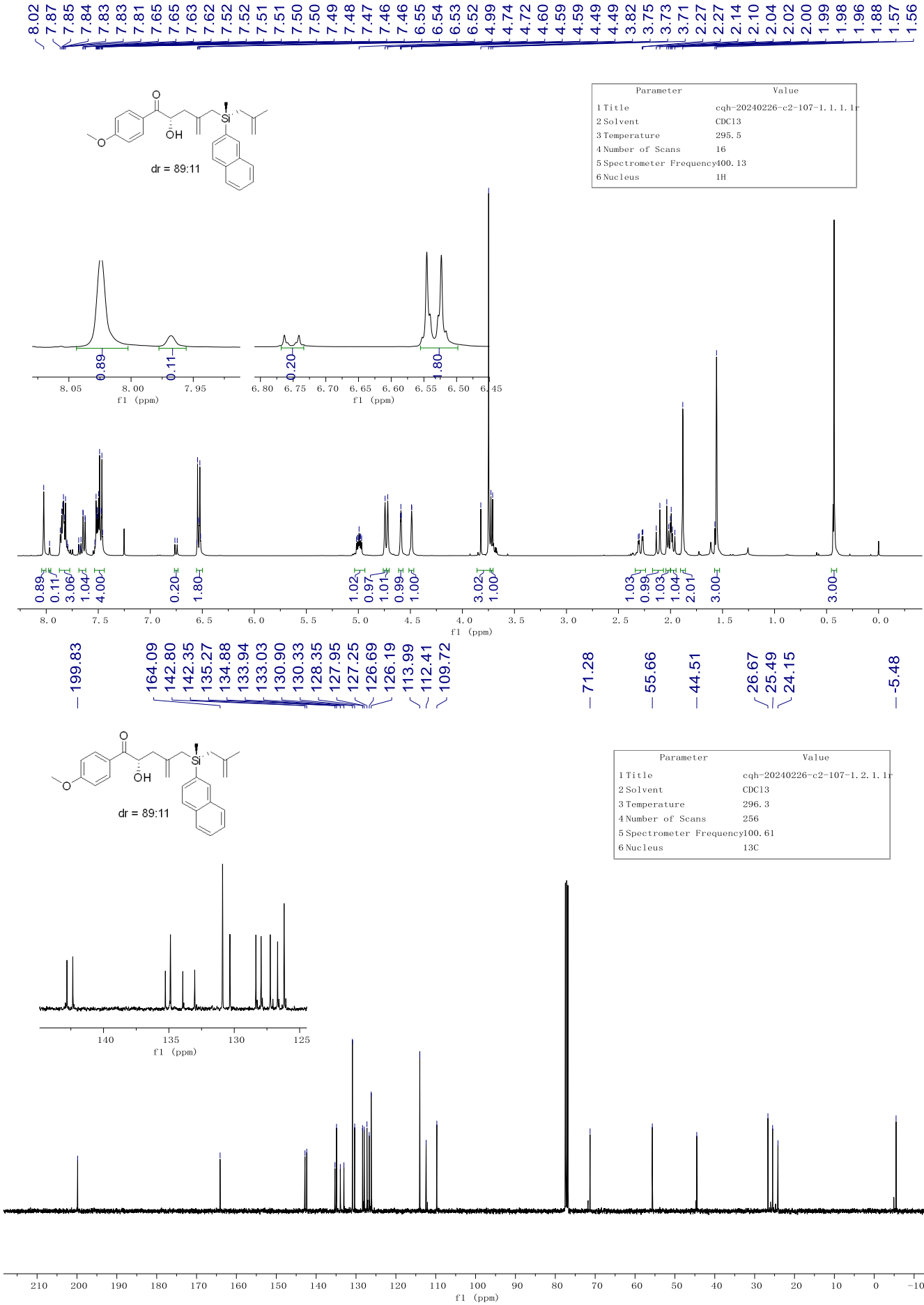
C12


8.00 7.85 7.84 7.83 7.83 7.81 7.79 7.62 7.60 7.52 7.51 7.50 7.48 7.46 6.94 6.92 5.06 5.05 5.05 5.04 5.03 5.02 5.01 4.74 4.72 4.59 4.49 3.69 3.67 2.63 2.61 2.59 2.57 2.33 2.32 2.29 2.29 2.11 2.08 2.02 1.99 1.96 1.88 1.56 1.25 1.24 1.21 1.19 1.17 0.43 0.42
Parameter Value
1 Title caoqh-20240513-c2-161-6.9.1.1r
2 Solvent CDCl3
3 Temperature 296.0
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
O
OH
Si
dr = 90:10
0.90 0.10 0.20 1.80
8.05 8.00 7.95 7.1 7.0 6.9
f1 (ppm)
0.90 0.10 3.08 1.07 4.00 0.20 1.80 1.01 2.01 1.03 1.05 0.99 2.03 1.02 0.92 1.02 1.01 2.02 3.04 3.07 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
201.11 151.07 142.82 142.25 135.13 134.89 133.95 133.03 131.04 130.29 128.76 128.32 127.93 127.21 126.68 126.17 112.41 109.72 71.65 44.35 29.05 26.58 25.50 24.23 15.15 -5.44
Parameter Value
1 Title caoqh-20240513-c2-161-6.10.1.1r
2 Solvent CDCl3
3 Temperature 296.0
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
O
OH
Si
dr = 90:10
145 140 135 130 125
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

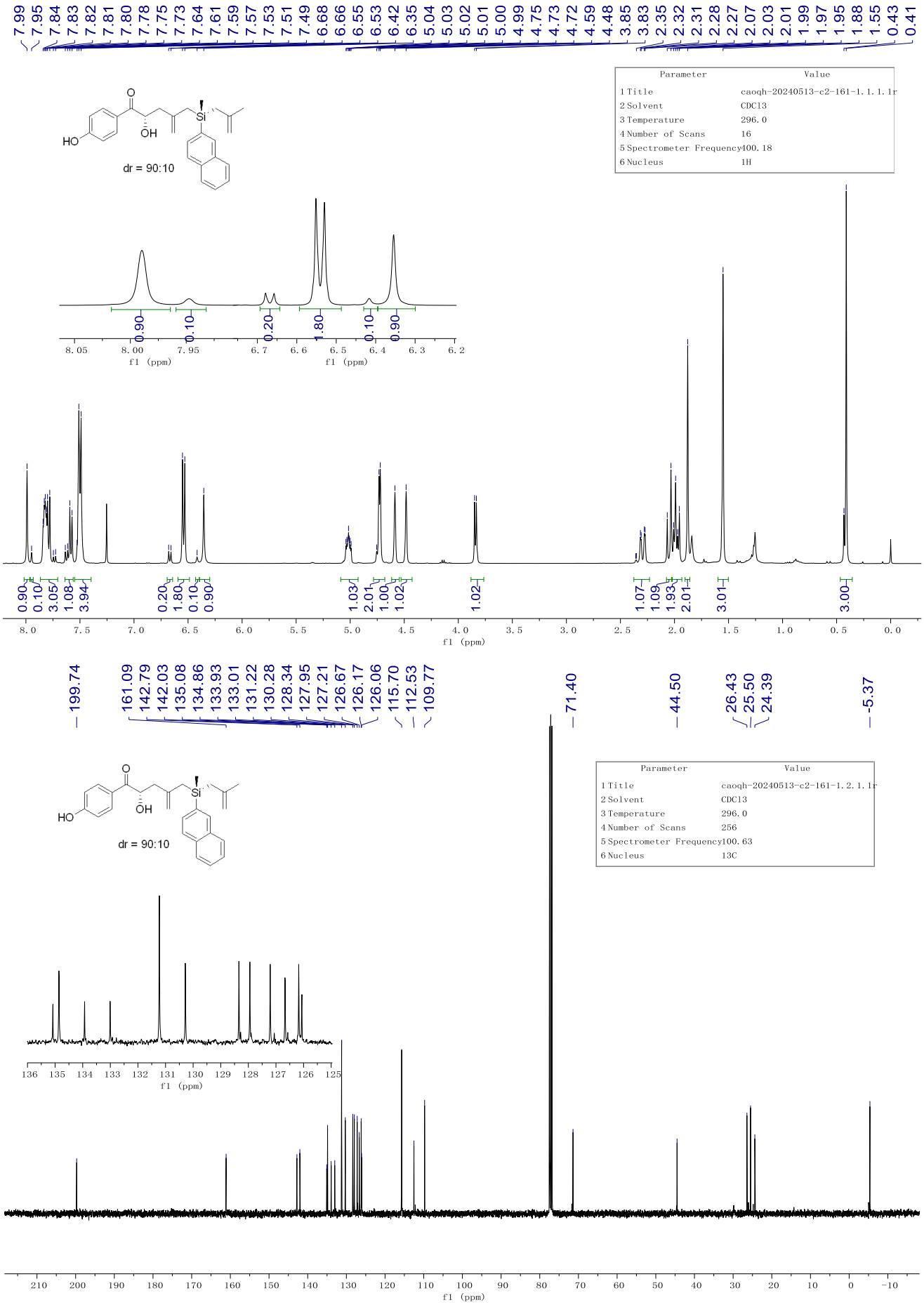
C13


8.03 7.86 7.85 7.84 7.83 7.81 7.64 7.64 7.62 7.62 7.53 7.52 7.52 7.51 7.50 7.49 7.46 7.44 7.13 7.10 5.05 5.04 5.03 5.02 4.74 4.72 4.58 4.58 4.48 3.70 3.69 2.35 2.34 2.31 2.30 2.15 2.11 2.04 2.01 2.00 1.99 1.98 1.95 1.89 1.87 1.57 1.55 1.32 1.26 0.46 0.42
Parameter Value
1 Title cqh-20240301-c2-113-8.5.1.1r
2 Solvent CDCl3
3 Temperature 296.0
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
O
OH
Si
dr = 89:11
0.89 0.11 0.21 1.79
f1 (ppm)
0.89 0.11 3.01 1.04 2.00 1.91 0.21 1.79 0.95 0.91 0.99 1.04 1.06 0.96 0.97 0.90 2.08 2.00 3.01 9.02 3.00
f1 (ppm)
201.06 157.90 142.80 142.34 135.19 134.92 133.94 133.04 130.72 130.30 128.57 128.33 127.95 127.25 126.76 126.26 125.80 112.47 109.70 71.61 44.28 35.30 31.11 26.77 25.49 24.08 -5.54
Parameter Value
1 Title cqh-20240301-c2-113-8.6.1.1r
2 Solvent CDCl3
3 Temperature 296.9
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
O
OH
Si
dr = 89:11
f1 (ppm)
f1 (ppm)

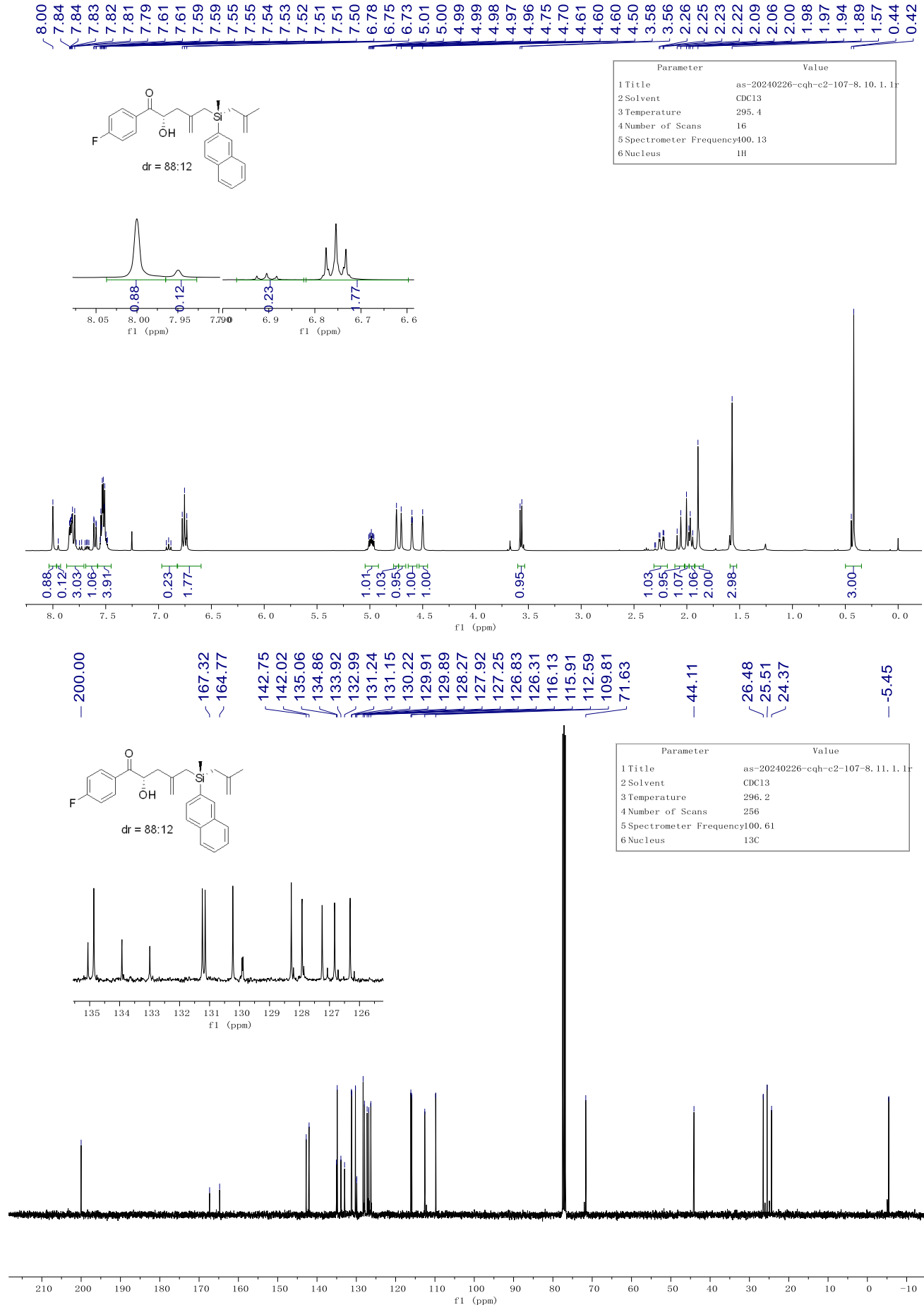
C14


dr = 89:11
Parameter Value
1 Title cqh-20240226-c2-107-1.1.1.1r
2 Solvent CDCl3
3 Temperature 295.5
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
f1 (ppm)
dr = 89:11
Parameter Value
1 Title cqh-20240226-c2-107-1.2.1.1r
2 Solvent CDCl3
3 Temperature 296.3
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)

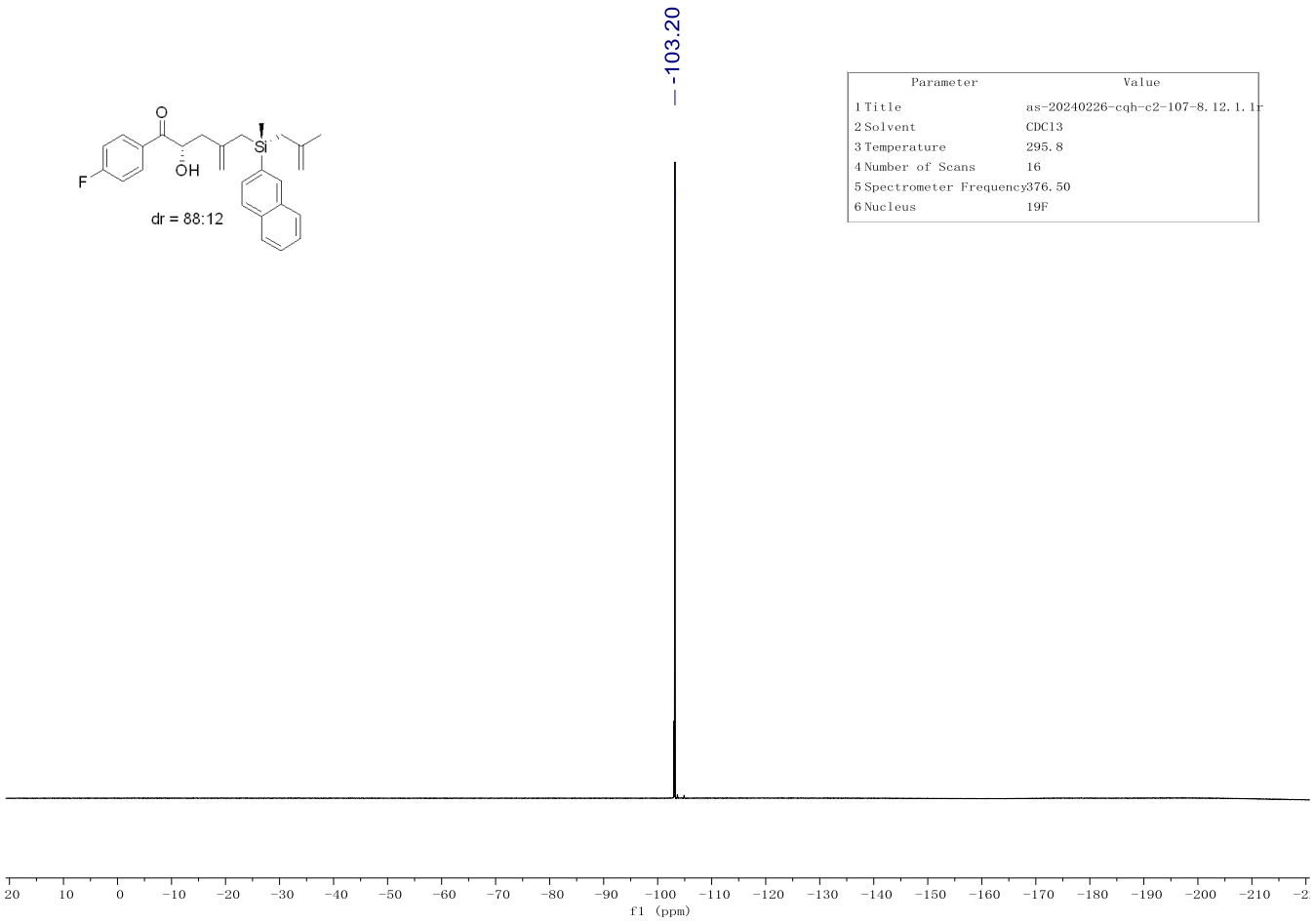
C15


7.99 7.95 7.84 7.83 7.82 7.81 7.80 7.78 7.75 7.73 7.64 7.61 7.59 7.57 7.53 7.51 7.49 6.68 6.66 6.55 6.53 6.42 6.35 5.04 5.03 5.02 5.01 5.00 4.99 4.75 4.73 4.72 4.59 4.48 3.85 3.83 2.35 2.32 2.31 2.28 2.27 2.07 2.03 2.01 1.99 1.97 1.95 1.88 1.55 0.43 0.41
Parameter Value
1 Title caoqh-20240513-c2-161-1.1.1.1r
2 Solvent CDCl3
3 Temperature 296.0
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
HO
O
OH
Si
dr = 90:10
0.90 0.10 0.20 1.80 0.10 0.90
f1 (ppm)
0.90 0.10 3.05 1.08 3.94 0.20 1.80 0.10 0.90 1.03 2.01 1.00 1.02 1.02 1.07 1.09 1.93 2.01 3.01 3.00
f1 (ppm)
199.74 161.09 142.79 142.03 135.08 134.86 133.93 133.01 131.22 130.28 128.34 127.95 127.21 126.67 126.17 126.06 115.70 112.53 109.77 71.40 44.50 26.43 25.50 24.39 -5.37
Parameter Value
1 Title caoqh-20240513-c2-161-1.2.1.1r
2 Solvent CDCl3
3 Temperature 296.0
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
HO
O
OH
Si
dr = 90:10
f1 (ppm)
f1 (ppm)

C16

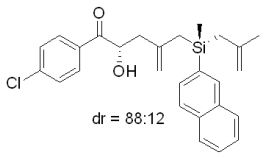

8.00 7.84 7.84 7.83 7.82 7.81 7.79 7.61 7.61 7.59 7.59 7.55 7.55 7.54 7.53 7.52 7.51 7.51 7.50 6.78 6.75 6.73 5.01 5.00 4.99 4.99 4.98 4.97 4.96 4.75 4.70 4.61 4.60 4.60 4.50 3.58 3.56 2.26 2.25 2.23 2.22 2.09 2.06 2.00 1.98 1.97 1.94 1.89 1.57 0.44 0.42
Parameter Value
1 Title as-20240226-cqh-c2-107-8.10.1.1r
2 Solvent CDC13
3 Temperature 295.4
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
O
OH
Si
F
dr = 88:12
0.88 0.12 0.23 1.77
f1 (ppm)
0.88 0.12 3.03 1.06 3.91 0.23 1.77 1.01 1.03 0.95 1.00 1.00 0.95 1.03 0.95 1.07 1.06 2.00 2.98 3.00
f1 (ppm)
200.00 167.32 164.77 142.75 142.02 135.06 134.86 133.92 132.99 131.24 131.15 130.22 129.91 129.89 128.27 127.92 127.25 126.83 126.31 116.13 115.91 112.59 109.81 71.63 44.11 26.48 25.51 24.37 -5.45
Parameter Value
1 Title as-20240226-cqh-c2-107-8.11.1.1r
2 Solvent CDC13
3 Temperature 296.2
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
O
OH
Si
F
dr = 88:12
f1 (ppm)
f1 (ppm)

dr = 88:12

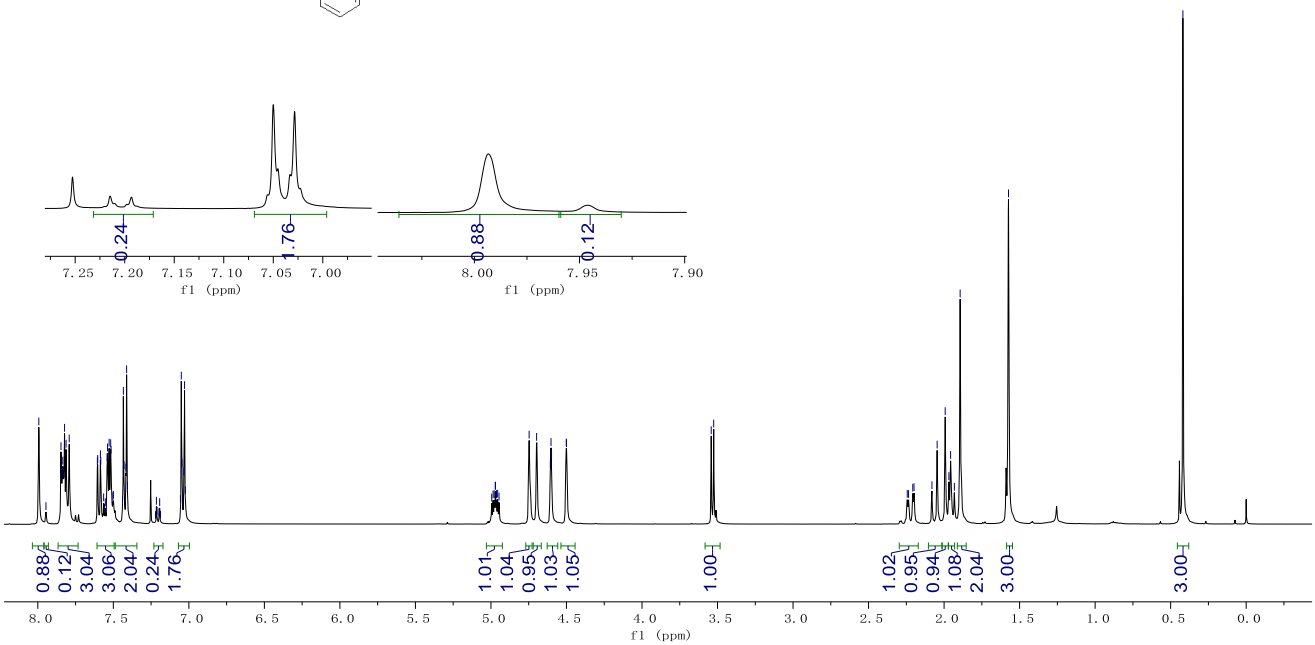


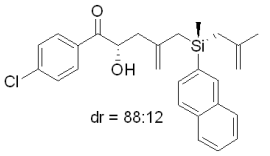
Parameter	Value
1 Title	as-20240226-cqh-c2-107-8.12.1.1r
2 Solvent	CDCl3
3 Temperature	295.8
4 Number of Scans	16
5 Spectrometer Frequency	376.50
6 Nucleus	19F

C17

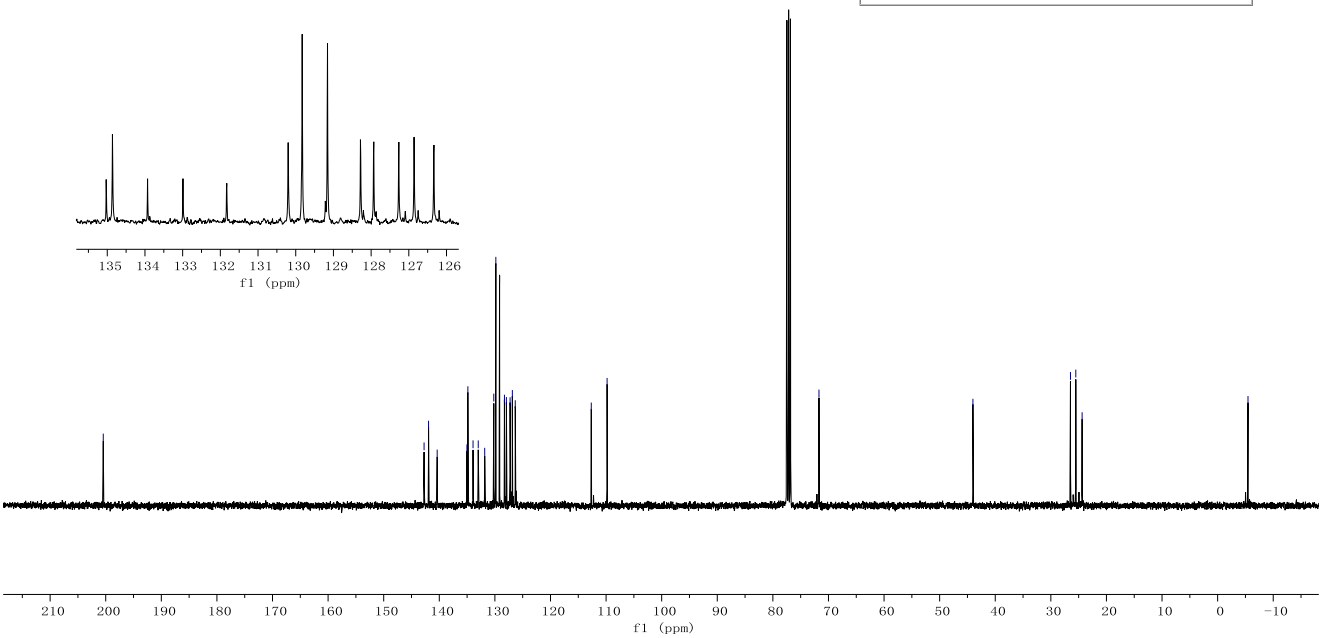


Parameter	Value
1 Title	cqh-20240301-c2-113-10.7.1.1r
2 Solvent	CDCl3
3 Temperature	295.8
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H

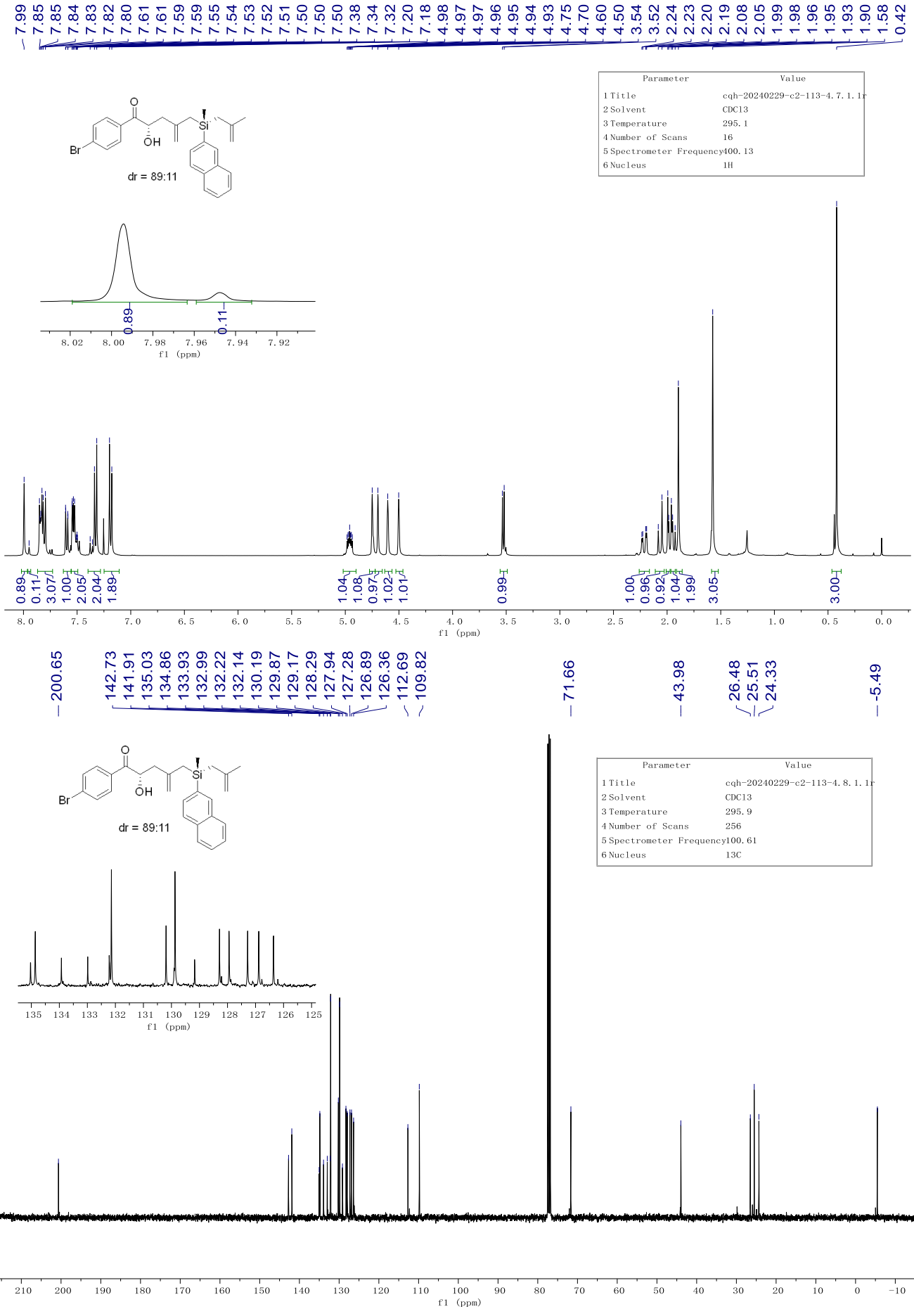




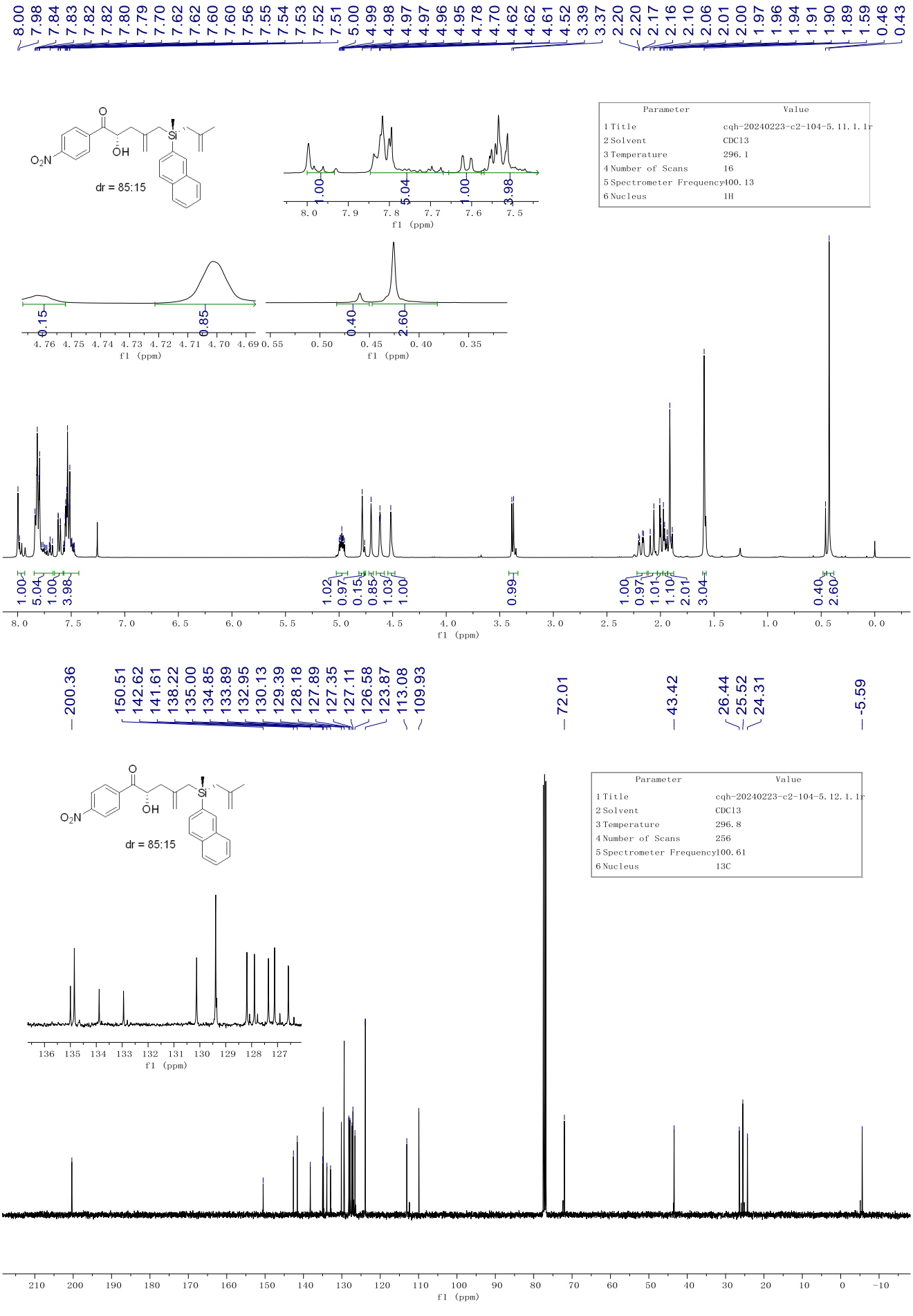
Parameter	Value
1 Title	cqh-20240301-c2-113-10.8.1.1r
2 Solvent	CDCl3
3 Temperature	296.6
4 Number of Scans	256
5 Spectrometer Frequency	100.61
6 Nucleus	13C



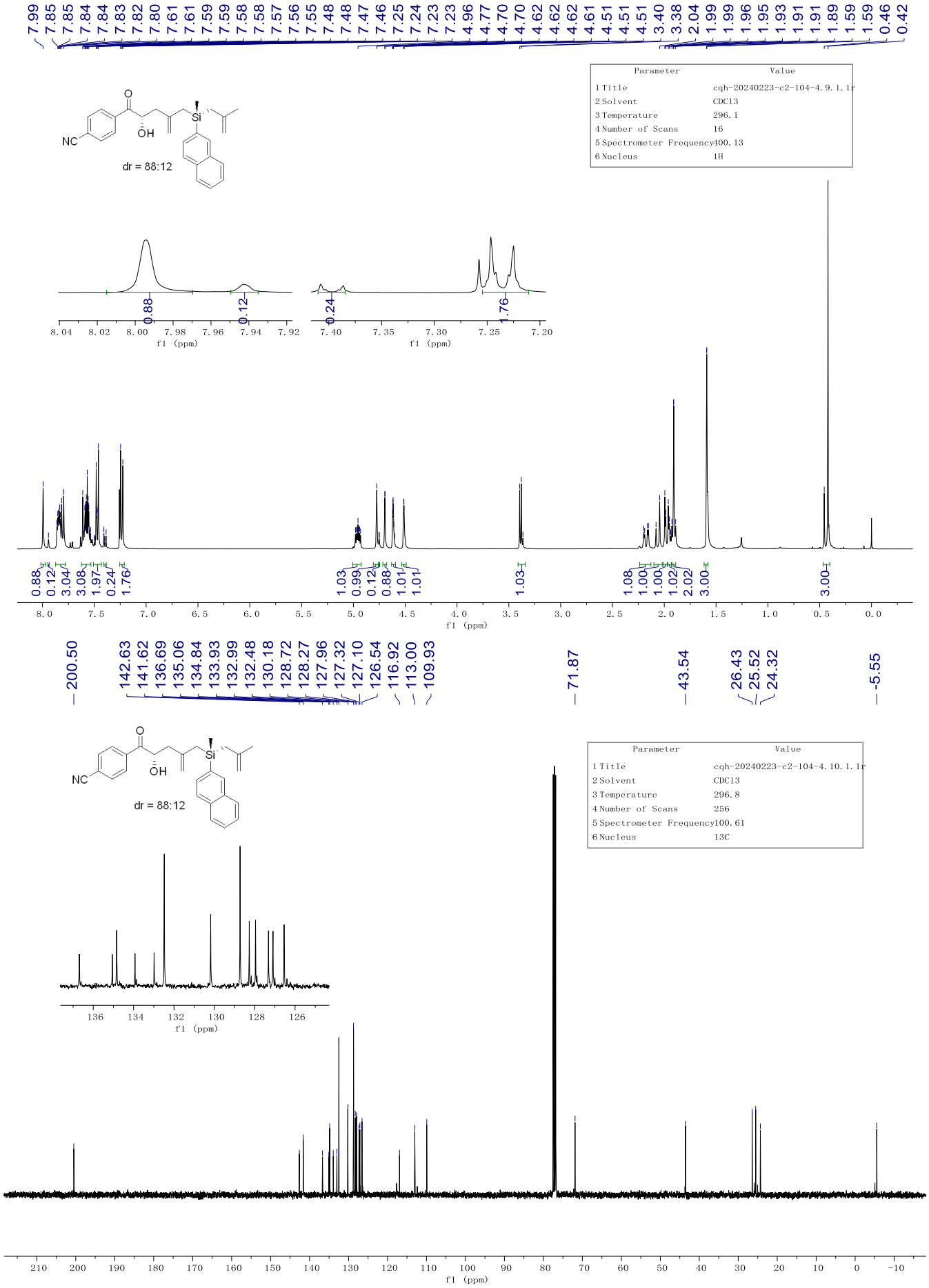
C18


7.99 7.85 7.85 7.84 7.83 7.82 7.80 7.61 7.61 7.59 7.59 7.55 7.54 7.53 7.52 7.51 7.50 7.50 7.50 7.38 7.34 7.32 7.20 7.18 4.98 4.97 4.97 4.96 4.95 4.94 4.93 4.75 4.70 4.60 4.50 3.54 3.52 2.24 2.23 2.20 2.19 2.08 2.05 1.99 1.98 1.96 1.95 1.93 1.90 1.58 0.42
Parameter Value
1 Title cqh-20240229-c2-113-4.7.1.1r
2 Solvent CDCl3
3 Temperature 295.1
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
O
OH
Si
Br
dr = 89:11
0.89
0.11
8.02 8.00 7.98 7.96 7.94 7.92
f1 (ppm)
0.89 0.11 3.07 1.00 2.05 2.04 1.89 1.04 1.08 0.97 1.02 1.01 0.99 1.00 0.96 0.92 1.04 1.99 3.05 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
200.65 142.73 141.91 135.03 134.86 133.93 132.99 132.22 132.14 130.19 129.87 129.17 128.29 127.94 127.28 126.89 126.36 112.69 109.82 71.66 43.98 26.48 25.51 24.33 -5.49
Parameter Value
1 Title cqh-20240229-c2-113-4.8.1.1r
2 Solvent CDCl3
3 Temperature 295.9
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
O
OH
Si
Br
dr = 89:11
135 134 133 132 131 130 129 128 127 126 125
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

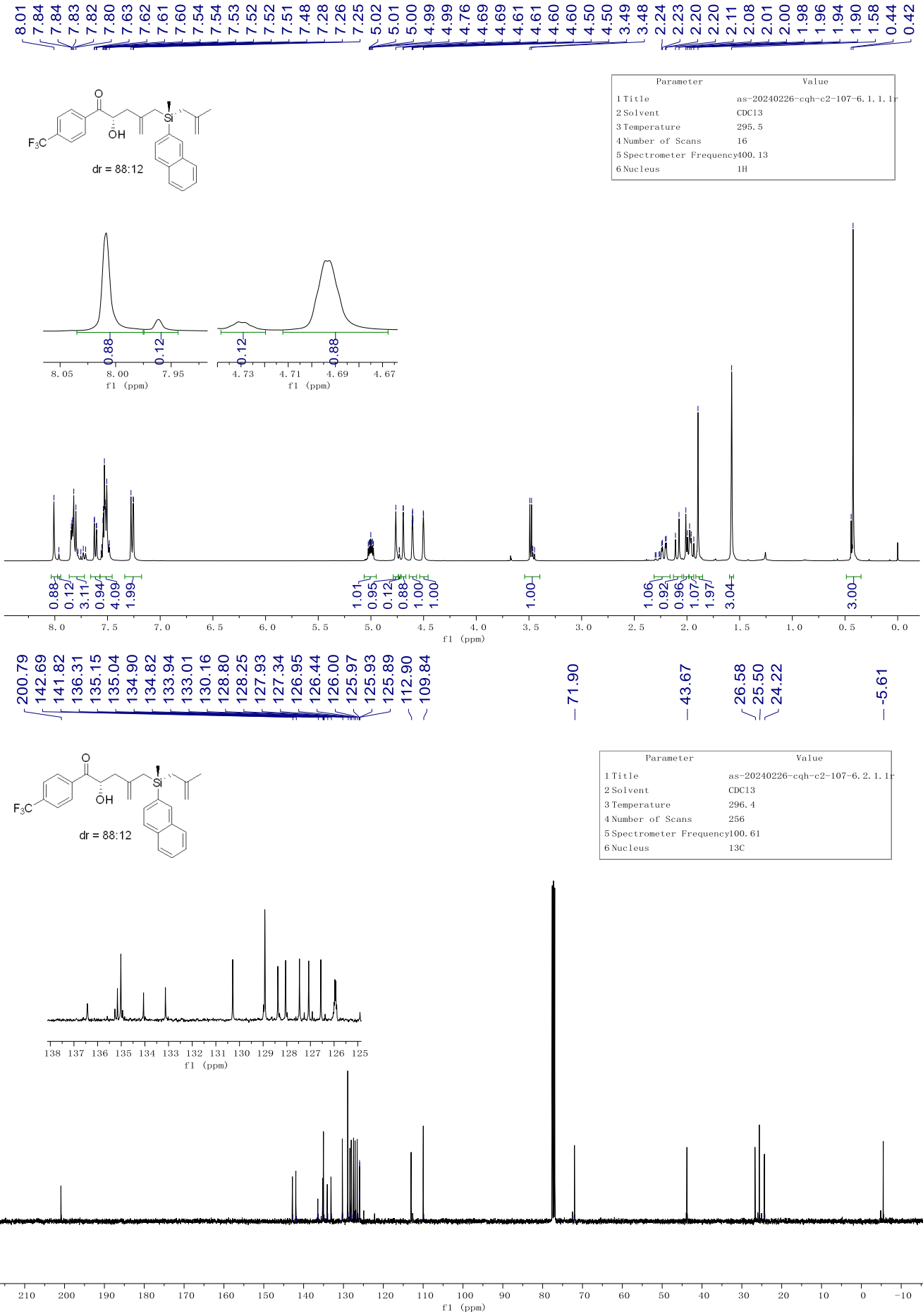
C19

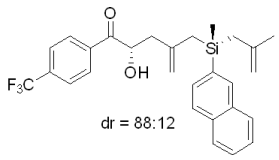

8.00 7.98 7.84 7.83 7.82 7.82 7.80 7.79 7.70 7.62 7.62 7.60 7.60 7.56 7.55 7.54 7.53 7.52 7.51 5.00 4.99 4.98 4.97 4.97 4.96 4.95 4.78 4.70 4.62 4.62 4.61 4.52 3.39 3.37 2.20 2.20 2.17 2.16 2.10 2.06 2.01 2.00 1.97 1.96 1.94 1.91 1.90 1.89 1.59 0.46 0.43
dr = 85:15
Parameter Value
1 Title cqh-20240223-c2-104-5.11.1.1r
2 Solvent CDCl3
3 Temperature 296.1
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
f1 (ppm)
200.36 150.51 142.62 141.61 138.22 135.00 134.85 133.89 132.95 130.13 129.39 128.18 127.89 127.35 127.11 126.58 123.87 113.08 109.93 72.01 43.42 26.44 25.52 24.31 -5.59
dr = 85:15
Parameter Value
1 Title cqh-20240223-c2-104-5.12.1.1r
2 Solvent CDCl3
3 Temperature 296.8
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)

C20


7.99 7.85 7.85 7.84 7.84 7.83 7.82 7.80 7.61 7.61 7.59 7.59 7.58 7.58 7.57 7.56 7.55 7.48 7.48 7.47 7.46 7.25 7.24 7.23 7.23 4.96 4.77 4.70 4.70 4.62 4.62 4.62 4.61 4.51 4.51 4.51 3.40 3.38 2.04 1.99 1.99 1.96 1.95 1.93 1.91 1.91 1.89 1.59 1.59 0.46 0.42
Parameter Value
1 Title cqh-20240223-c2-104-4.9.1.1r
2 Solvent CDCl3
3 Temperature 296.1
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
dr = 88:12
0.88 0.12 0.24 1.76
f1 (ppm)
0.88 0.12 3.04 3.08 1.97 0.24 1.76 1.03 0.99 0.12 0.88 1.01 1.01 1.03 1.08 1.00 1.00 1.02 2.02 3.00 3.00
f1 (ppm)
200.50 142.63 141.62 136.69 135.06 134.84 133.93 132.99 132.48 130.18 128.72 128.27 127.96 127.32 127.10 126.54 116.92 113.00 109.93 71.87 43.54 26.43 25.52 24.32 -5.55
dr = 88:12
Parameter Value
1 Title cqh-20240223-c2-104-4.10.1.1r
2 Solvent CDCl3
3 Temperature 296.8
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)
f1 (ppm)

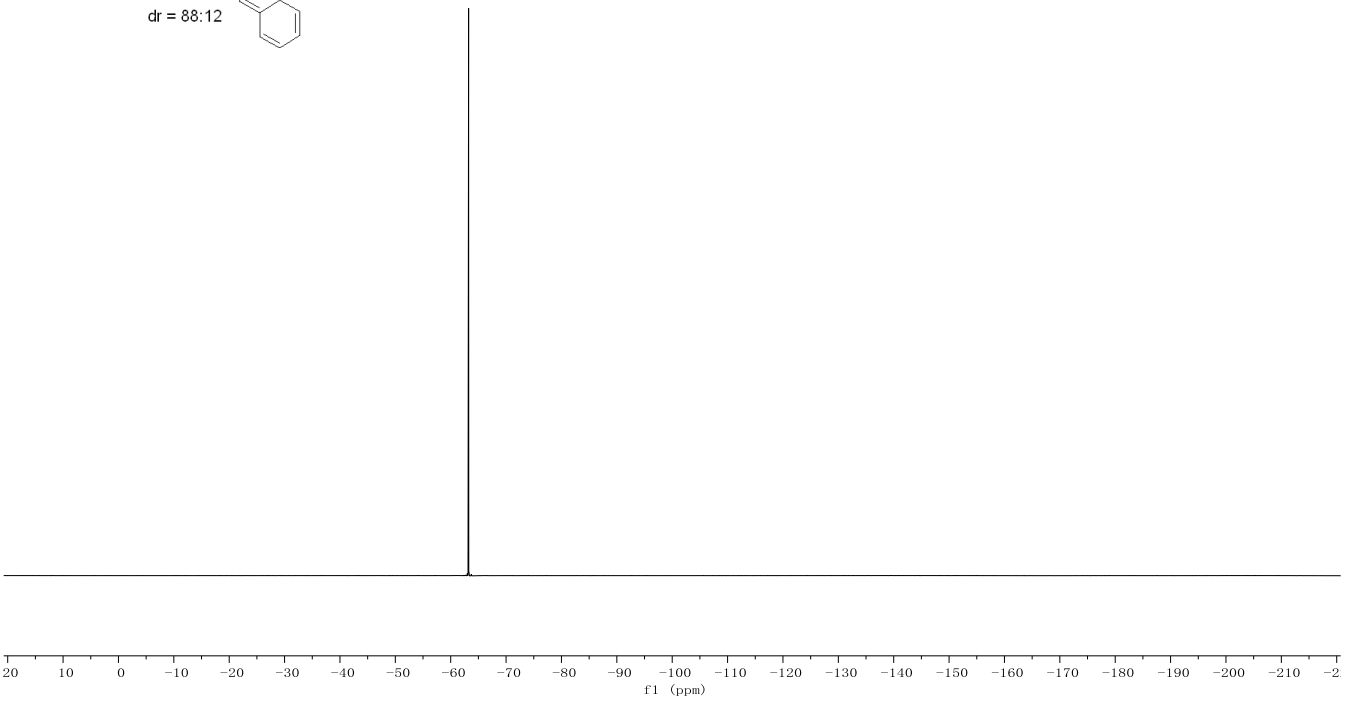
C21


8.01 7.84 7.84 7.83 7.82 7.80 7.63 7.62 7.61 7.60 7.54 7.54 7.53 7.52 7.52 7.51 7.48 7.28 7.26 7.25 5.02 5.01 5.00 4.99 4.99 4.76 4.69 4.69 4.61 4.61 4.60 4.60 4.50 4.50 3.49 3.48 2.24 2.23 2.20 2.20 2.11 2.08 2.01 2.00 1.98 1.96 1.94 1.90 1.58 0.44 0.42
dr = 88:12
Parameter Value
1 Title as-20240226-cqh-c2-107-6.1.1.1r
2 Solvent CDCl3
3 Temperature 295.5
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
0.88 0.12 3.11 0.94 4.09 1.99
1.01 0.95 0.12 0.88 1.00 1.00
1.00
1.06 0.92 0.96 1.07 1.97 3.04
3.00
f1 (ppm)
200.79 142.69 141.82 136.31 135.15 135.04 134.90 134.82 133.94 133.01 130.16 128.80 128.25 127.93 127.34 126.95 126.44 126.00 125.97 125.93 125.89 112.90 109.84
71.90
43.67
26.58 25.50 24.22
-5.61
dr = 88:12
Parameter Value
1 Title as-20240226-cqh-c2-107-6.2.1.1r
2 Solvent CDCl3
3 Temperature 296.4
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)

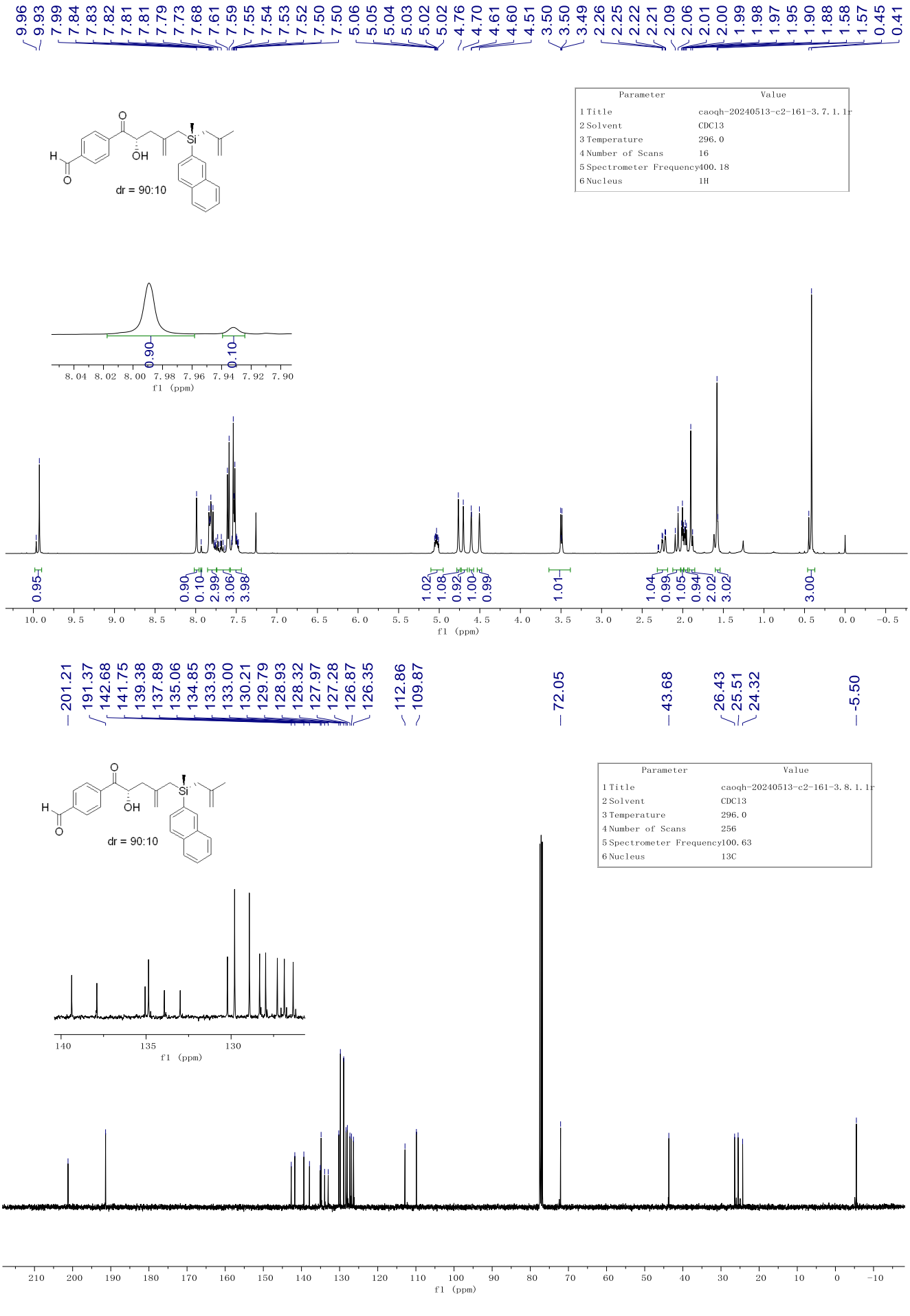


dr = 88:12

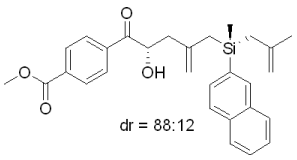
Parameter	Value
1 Title	as-20240226-cqh-c2-107-6.3.1.1r
2 Solvent	CDCl3
3 Temperature	296.0
4 Number of Scans	16
5 Spectrometer Frequency	376.50
6 Nucleus	19F



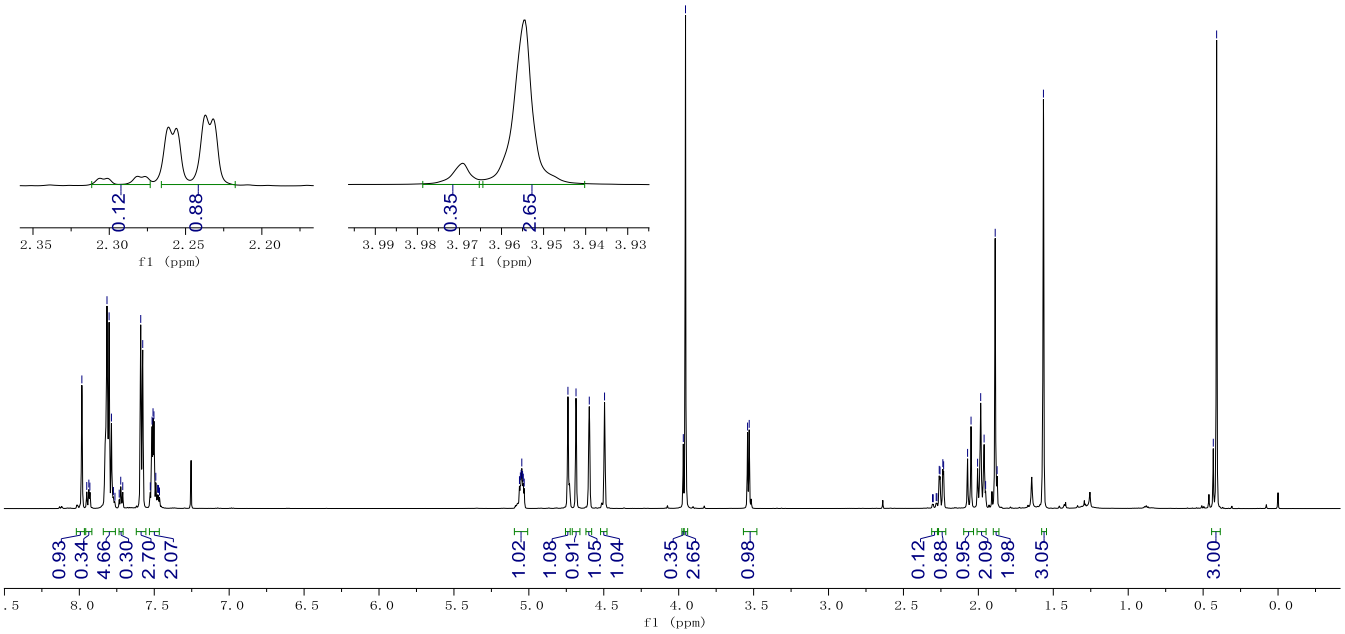
C22

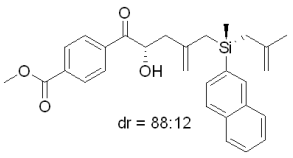

9.96 9.93 7.99 7.84 7.83 7.82 7.81 7.81 7.79 7.73 7.68 7.61 7.59 7.55 7.54 7.53 7.52 7.50 7.50 5.06 5.05 5.04 5.03 5.02 5.02 4.76 4.70 4.61 4.60 4.51 3.50 3.50 3.49 2.26 2.25 2.22 2.21 2.09 2.06 2.01 2.00 1.99 1.98 1.97 1.95 1.90 1.88 1.58 1.57 0.45 0.41
dr = 90:10
Parameter Value
1 Title caoqh-20240513-c2-161-3.7.1.1r
2 Solvent CDCl3
3 Temperature 296.0
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
0.90 0.10
f1 (ppm)
0.95 0.90 0.10 2.99 3.06 3.98 1.02 1.08 0.92 1.00 0.99 1.01 1.04 0.99 1.05 0.94 2.02 3.02 3.00
f1 (ppm)
201.21 191.37 142.68 141.75 139.38 137.89 135.06 134.85 133.93 133.00 130.21 129.79 128.93 128.32 127.97 127.28 126.87 126.35 112.86 109.87 72.05 43.68 26.43 25.51 24.32 -5.50
dr = 90:10
Parameter Value
1 Title caoqh-20240513-c2-161-3.8.1.1r
2 Solvent CDCl3
3 Temperature 296.0
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
f1 (ppm)
f1 (ppm)

C23

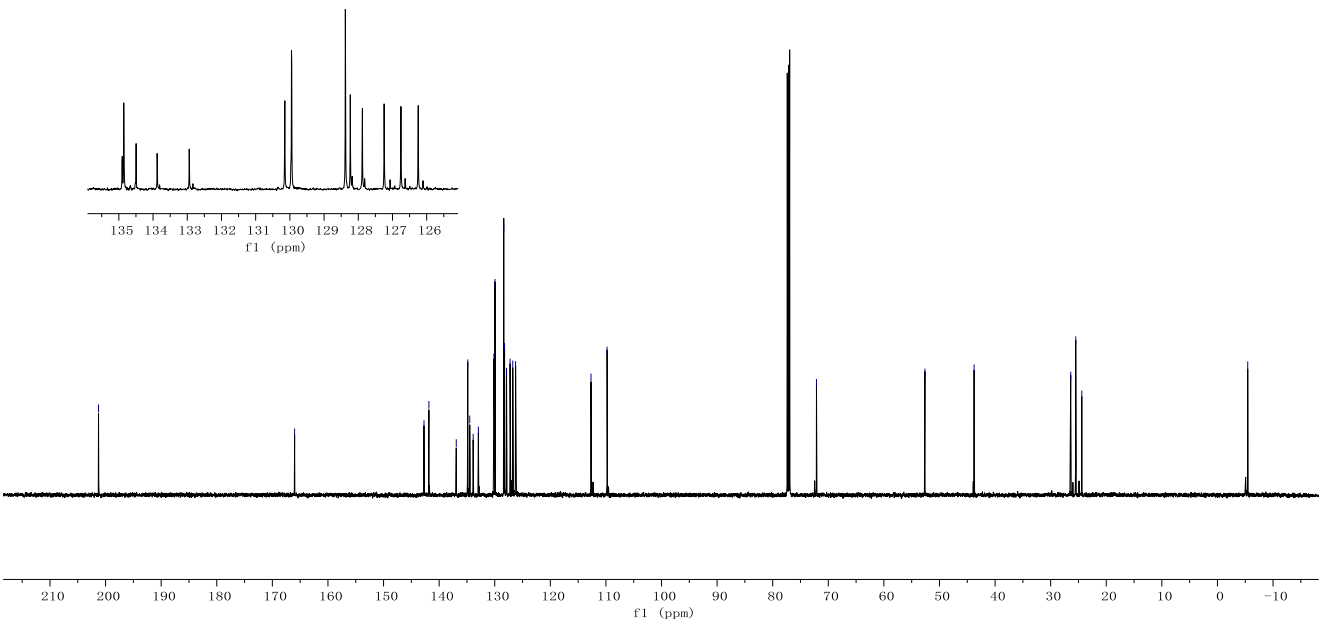


Parameter	Value
1 Title	caoqh-20240513-C2-161-5.1.1.1r
2 Solvent	CDCl3
3 Temperature	295.0
4 Number of Scans	16
5 Spectrometer Frequency	600.17
6 Nucleus	1H

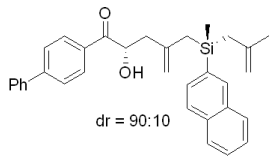




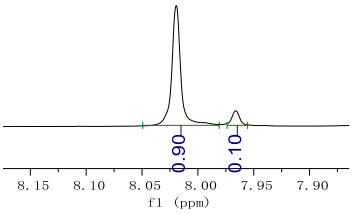
Parameter	Value
1 Title	caoqh-20240513-C2-161-5.2.1.1r
2 Solvent	CDCl3
3 Temperature	295.2
4 Number of Scans	256
5 Spectrometer Frequency	150.91
6 Nucleus	13C

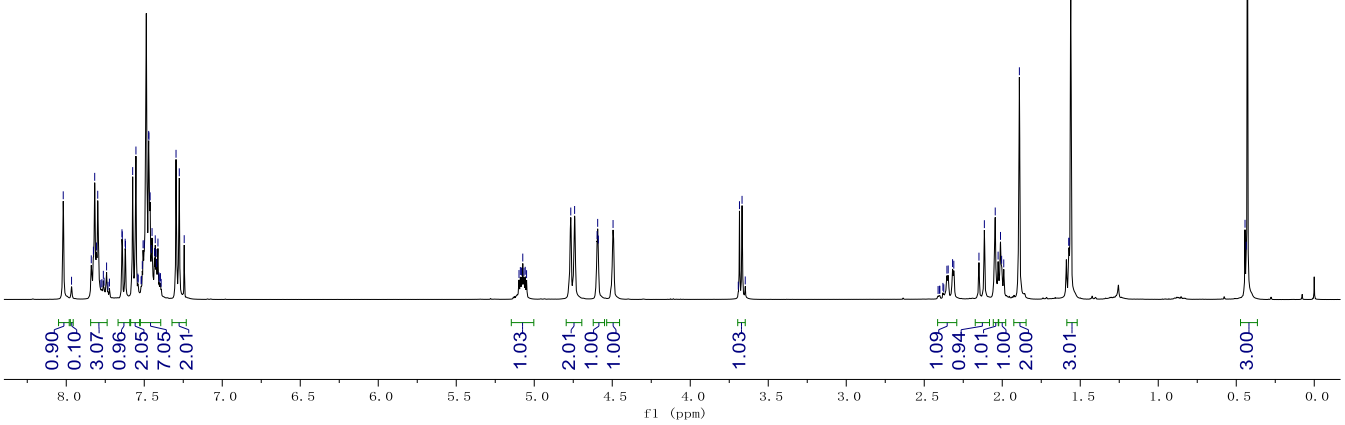


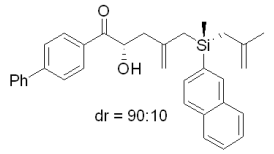
C24



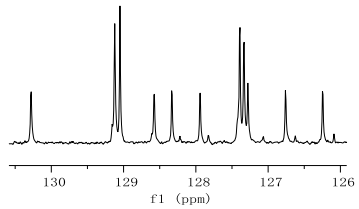
Parameter	Value
1 Title	cqh-20240223-c2-104-6.13.1.1r
2 Solvent	CDCl3
3 Temperature	296.1
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H

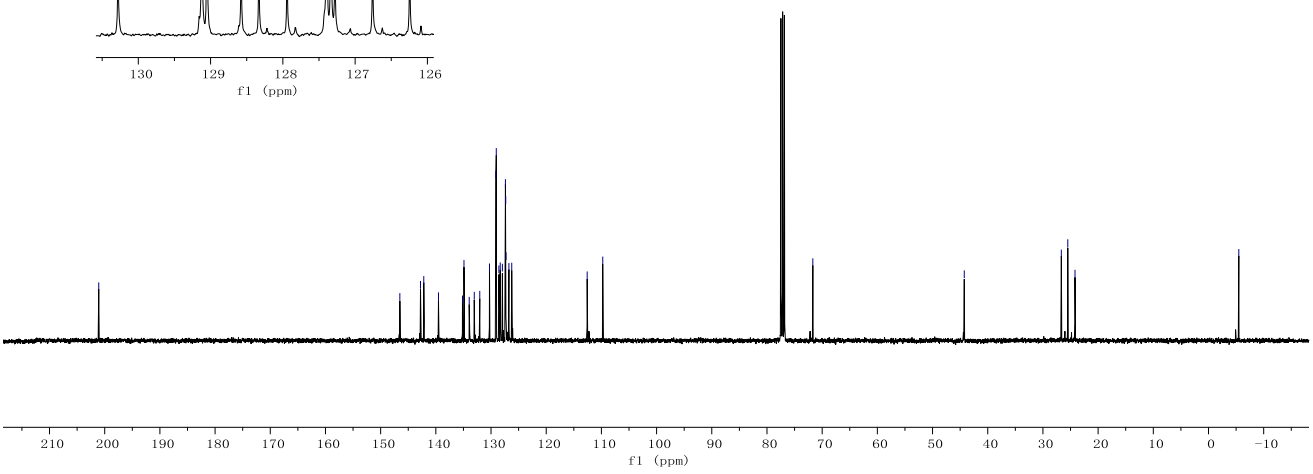




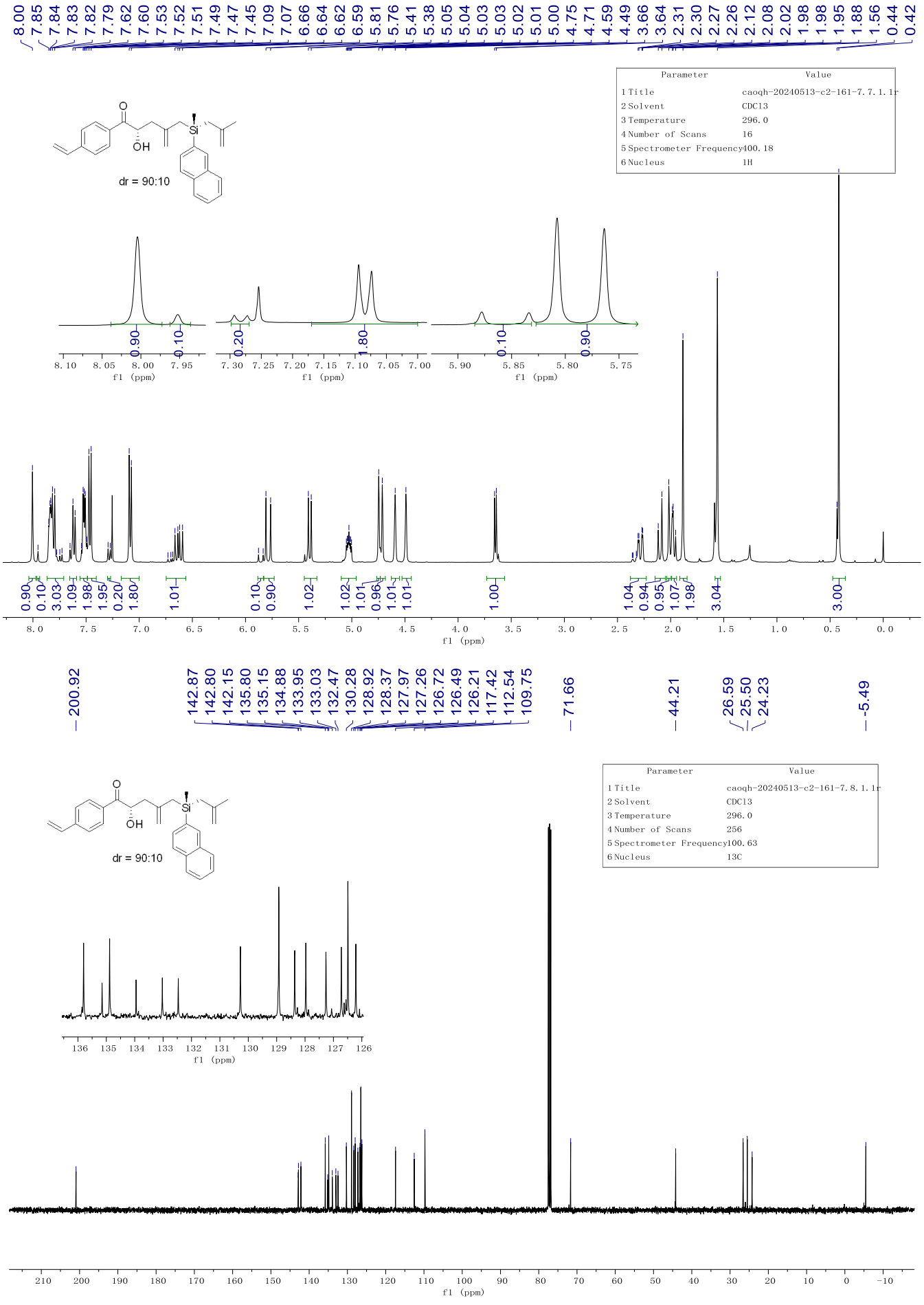


Parameter	Value
1 Title	cqh-20240223-c2-104-6.14.1.1r
2 Solvent	CDCl3
3 Temperature	296.9
4 Number of Scans	256
5 Spectrometer Frequency	100.61
6 Nucleus	13C

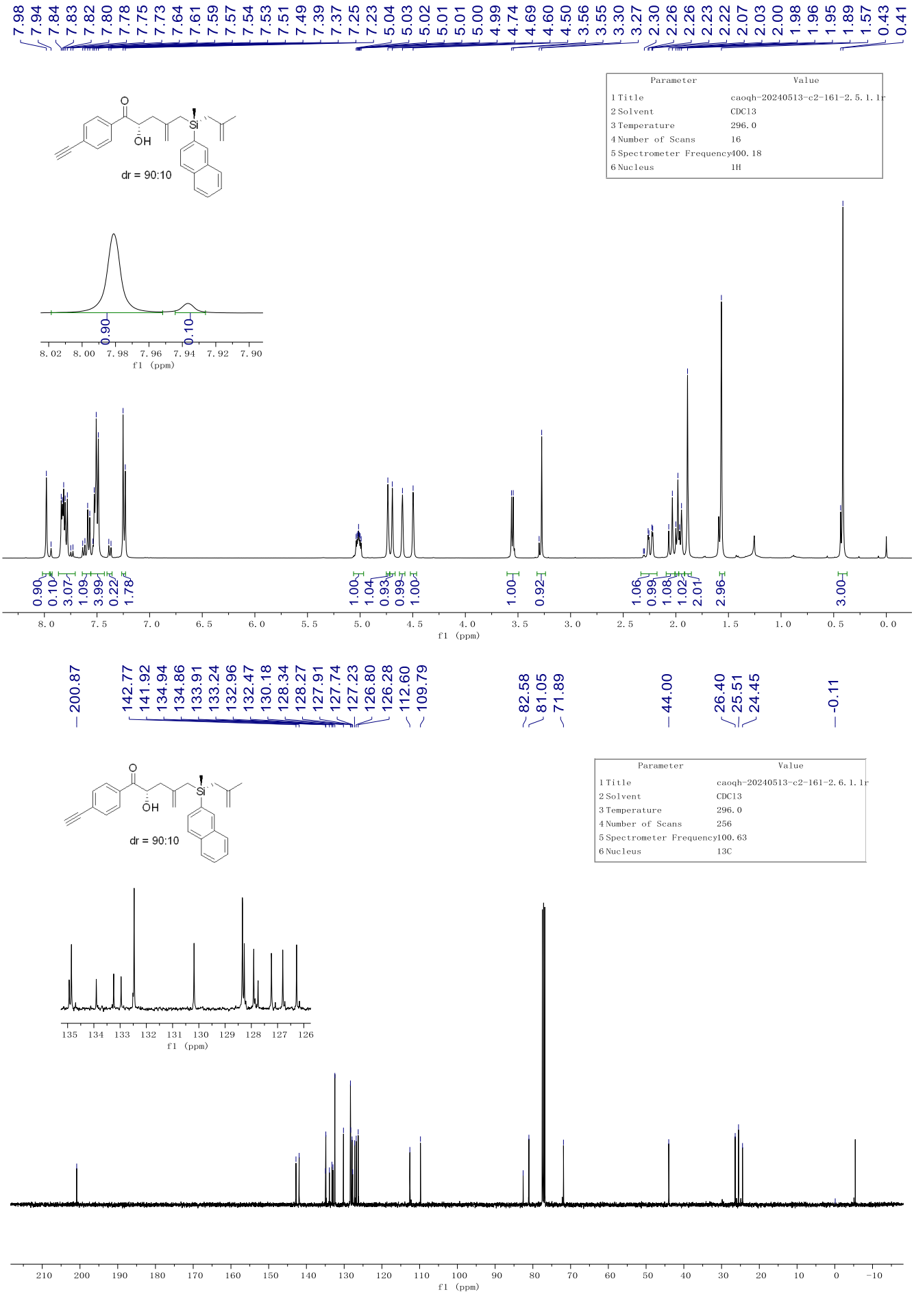




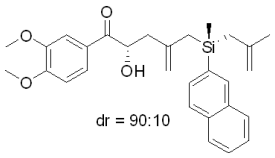
C25


8.00 7.85 7.84 7.83 7.82 7.79 7.62 7.60 7.53 7.52 7.51 7.49 7.47 7.45 7.09 7.07 6.66 6.64 6.62 6.59 5.81 5.76 5.41 5.38 5.05 5.04 5.03 5.03 5.02 5.01 5.00 4.75 4.71 4.59 4.49 3.66 3.64 2.31 2.30 2.27 2.26 2.12 2.08 2.02 1.98 1.98 1.95 1.88 1.56 0.44 0.42
Parameter Value
1 Title caoqh-20240513-c2-161-7.7.1.1r
2 Solvent CDCl3
3 Temperature 296.0
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
dr = 90:10
0.90 0.10 0.20 1.80 0.10 0.90
f1 (ppm)
0.90 0.10 3.03 1.09 1.98 1.95 0.20 1.80 1.01 0.10 0.90 1.02 1.02 1.01 0.96 1.01 1.01 1.00 1.04 0.94 0.95 1.07 1.98 3.04 3.00
f1 (ppm)
200.92 142.87 142.80 142.15 135.80 135.15 134.88 133.95 133.03 132.47 130.28 128.92 128.37 127.97 127.26 126.72 126.49 126.21 117.42 112.54 109.75 71.66 44.21 26.59 25.50 24.23 -5.49
Parameter Value
1 Title caoqh-20240513-c2-161-7.8.1.1r
2 Solvent CDCl3
3 Temperature 296.0
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
dr = 90:10
f1 (ppm)
f1 (ppm)

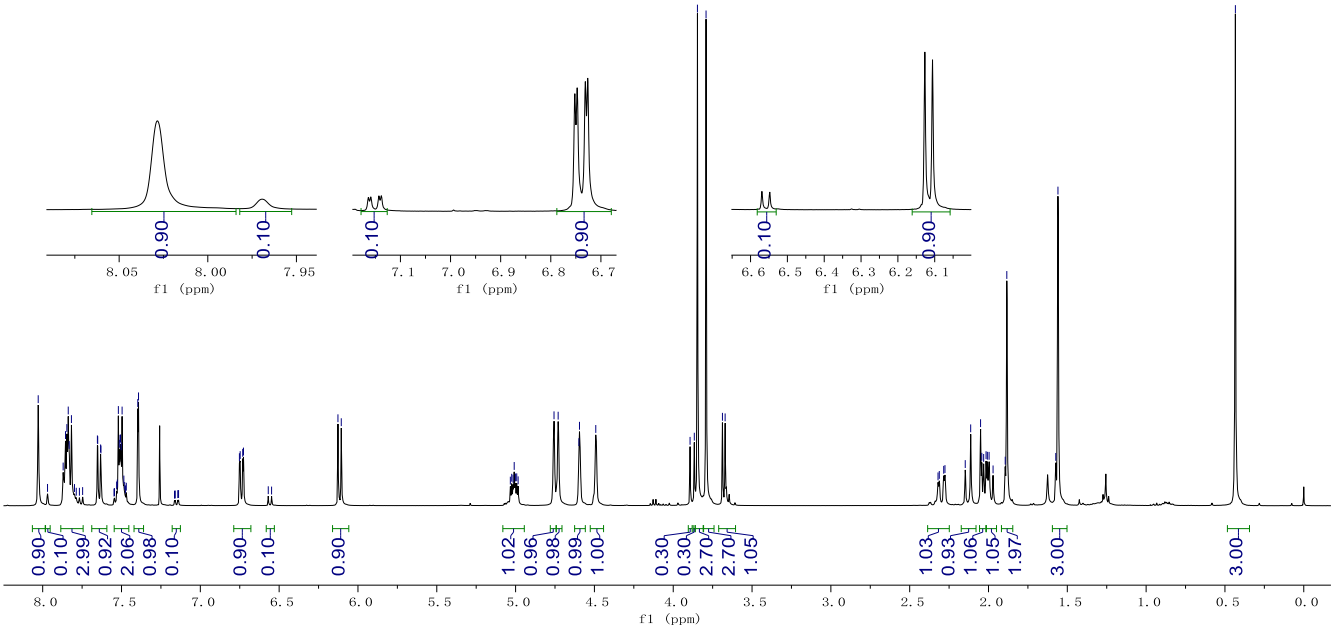
C26


7.98 7.94 7.84 7.83 7.82 7.80 7.78 7.75 7.73 7.64 7.61 7.59 7.57 7.54 7.53 7.51 7.49 7.39 7.37 7.25 7.23 5.04 5.03 5.02 5.01 5.01 5.00 4.99 4.74 4.69 4.60 4.50 3.56 3.55 3.30 3.27 2.30 2.26 2.26 2.23 2.22 2.07 2.03 2.00 1.98 1.96 1.95 1.89 1.57 0.43 0.41
Parameter Value
1 Title caoqh-20240513-c2-161-2.5.1.1r
2 Solvent CDCl3
3 Temperature 296.0
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
OH
Si
dr = 90:10
0.90
0.10
8.02 8.00 7.98 7.96 7.94 7.92 7.90
f1 (ppm)
0.90 0.10 3.07 1.09 3.99 0.22 1.78 1.00 1.04 0.93 0.99 1.00 1.00 0.92 1.06 0.99 1.08 1.02 2.01 2.96 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
200.87
142.77 141.92 134.94 134.86 133.91 133.24 132.96 132.47 130.18 128.34 128.27 127.91 127.74 127.23 126.80 126.28 112.60 109.79
82.58 81.05 71.89
44.00
26.40 25.51 24.45
-0.11
Parameter Value
1 Title caoqh-20240513-c2-161-2.6.1.1r
2 Solvent CDCl3
3 Temperature 296.0
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
OH
Si
dr = 90:10
135 134 133 132 131 130 129 128 127 126
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

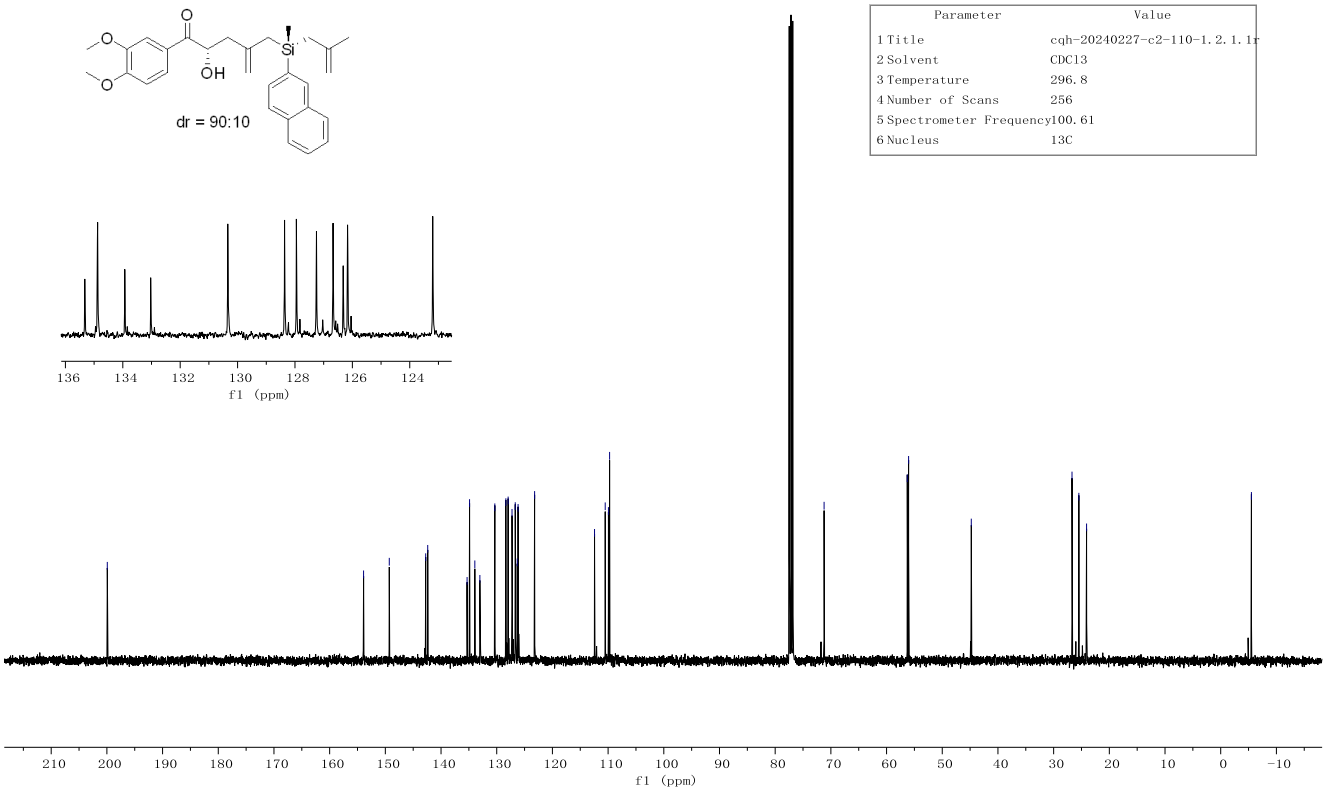
C27



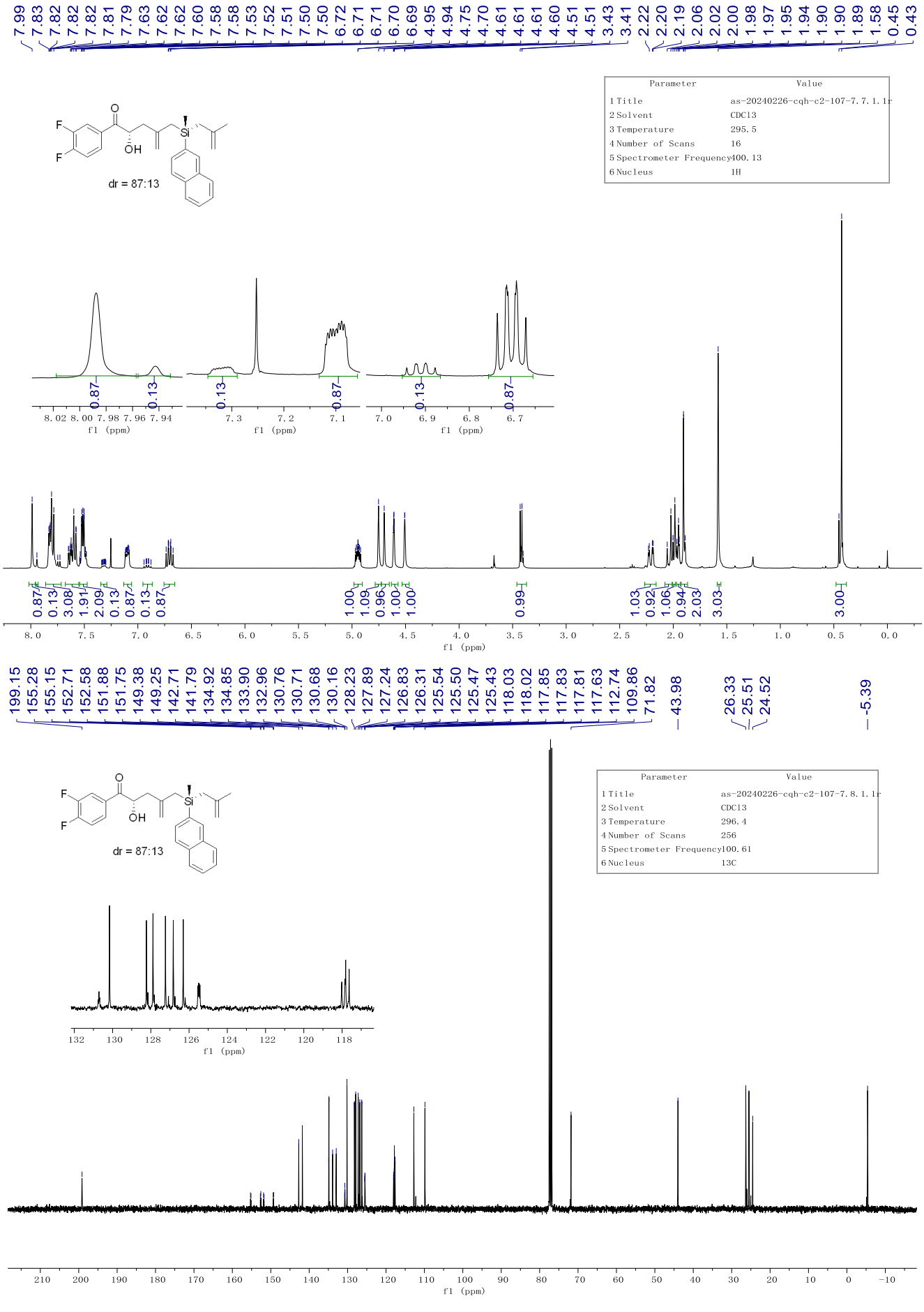
Parameter	Value
1 Title	cqh-20240227-c2-110-1.1.1.1r
2 Solvent	CDCl3
3 Temperature	295.9
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H

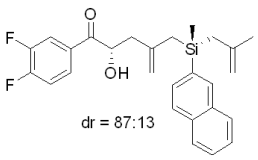


Parameter	Value
1 Title	cqh-20240227-c2-110-1.2.1.1r
2 Solvent	CDCl3
3 Temperature	296.8
4 Number of Scans	256
5 Spectrometer Frequency	100.61
6 Nucleus	13C



C28

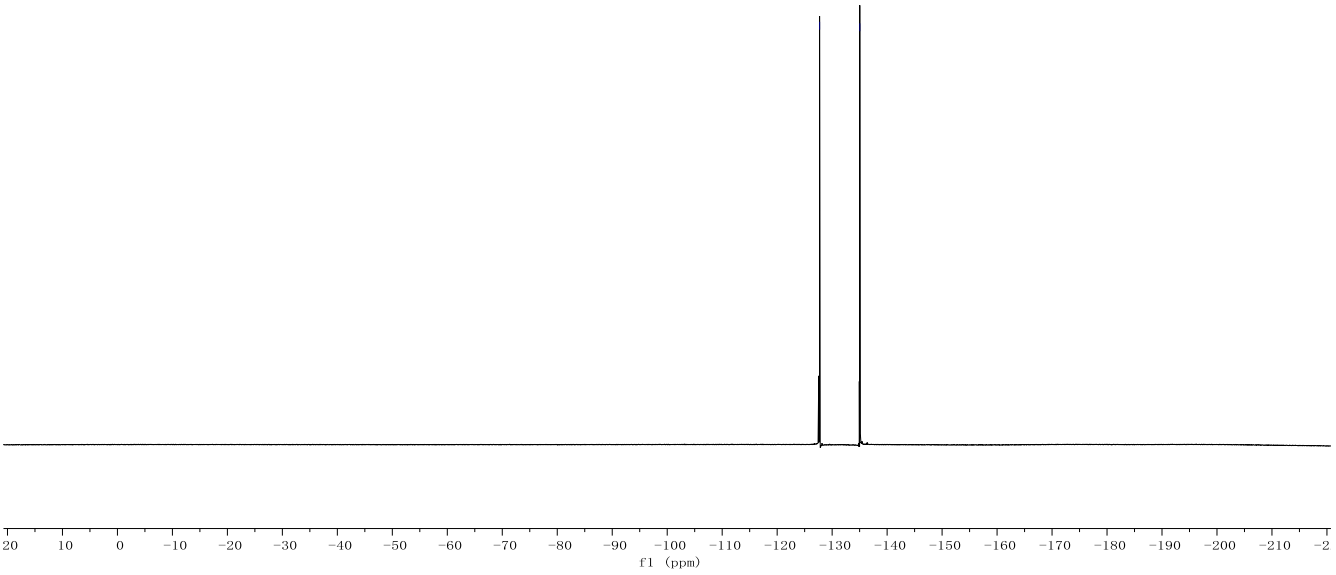

7.99 7.83 7.82 7.82 7.82 7.81 7.79 7.63 7.62 7.62 7.60 7.58 7.58 7.53 7.52 7.51 7.50 7.50 6.72 6.71 6.71 6.70 6.69 4.95 4.94 4.75 4.70 4.61 4.61 4.61 4.60 4.51 4.51 3.43 3.41 2.22 2.20 2.19 2.06 2.02 2.00 1.98 1.97 1.95 1.94 1.90 1.90 1.89 1.58 0.45 0.43
F
F
O
OH
Si
dr = 87:13
Parameter Value
1 Title as-20240226-cqh-c2-107-7.7.1.1r
2 Solvent CDCl3
3 Temperature 295.5
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
0.87 0.13
8.02 8.00 7.98 7.96 7.94
f1 (ppm)
0.13 0.87
7.3 7.2 7.1
f1 (ppm)
0.13 0.87
7.0 6.9 6.8 6.7
f1 (ppm)
0.87 0.13 3.08 1.91 2.09 0.13 0.87 0.13 0.87 1.00 1.09 0.96 1.00 1.00 0.99 1.03 0.92 1.06 0.94 2.03 3.03 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
199.15 155.28 155.15 152.71 152.58 151.88 151.75 149.38 149.25 142.71 141.79 134.92 134.85 133.90 132.96 130.76 130.71 130.68 130.16 128.23 127.89 127.24 126.83 126.31 125.54 125.50 125.47 125.43 118.03 118.02 117.85 117.83 117.81 117.63 112.74 109.86 71.82 43.98 26.33 25.51 24.52 -5.39
F
F
O
OH
Si
dr = 87:13
Parameter Value
1 Title as-20240226-cqh-c2-107-7.8.1.1r
2 Solvent CDCl3
3 Temperature 296.4
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
132 130 128 126 124 122 120 118
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



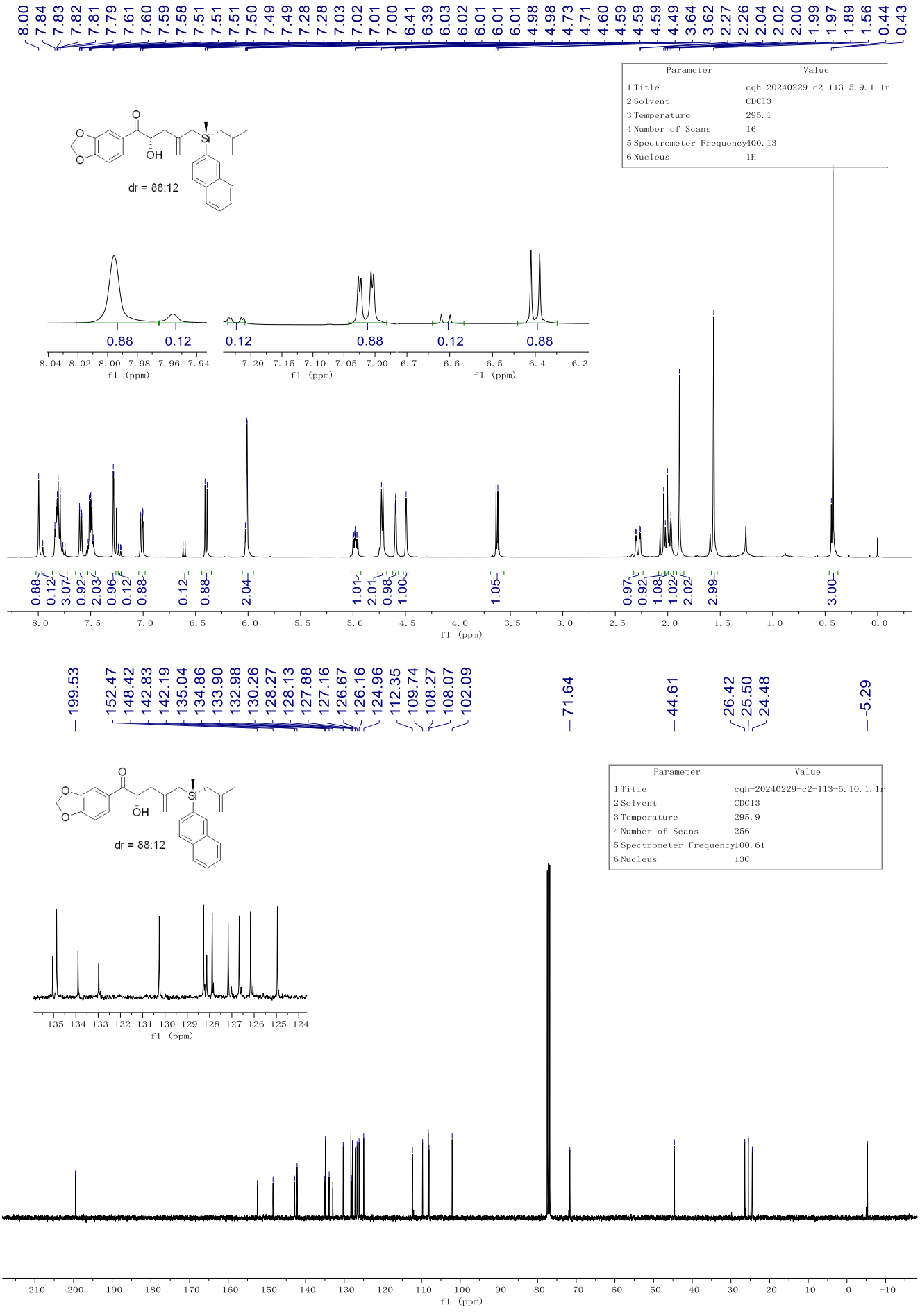
dr = 87:13

-127.72
-135.03

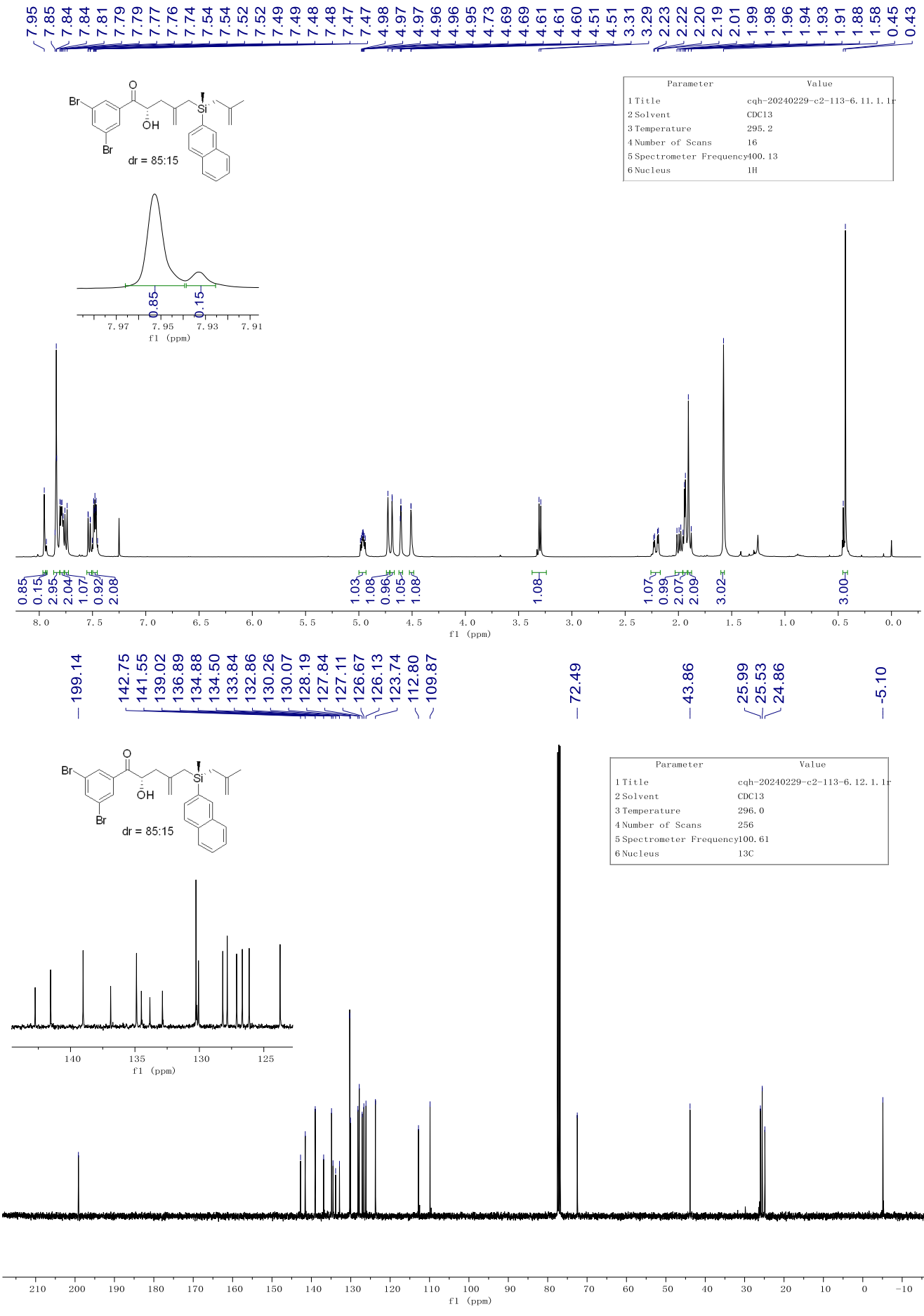
Parameter	Value
1 Title	as-20240226-cqh-c2-107-7.9.1.1r
2 Solvent	CDCl3
3 Temperature	296.0
4 Number of Scans	16
5 Spectrometer Frequency	376.50
6 Nucleus	19F



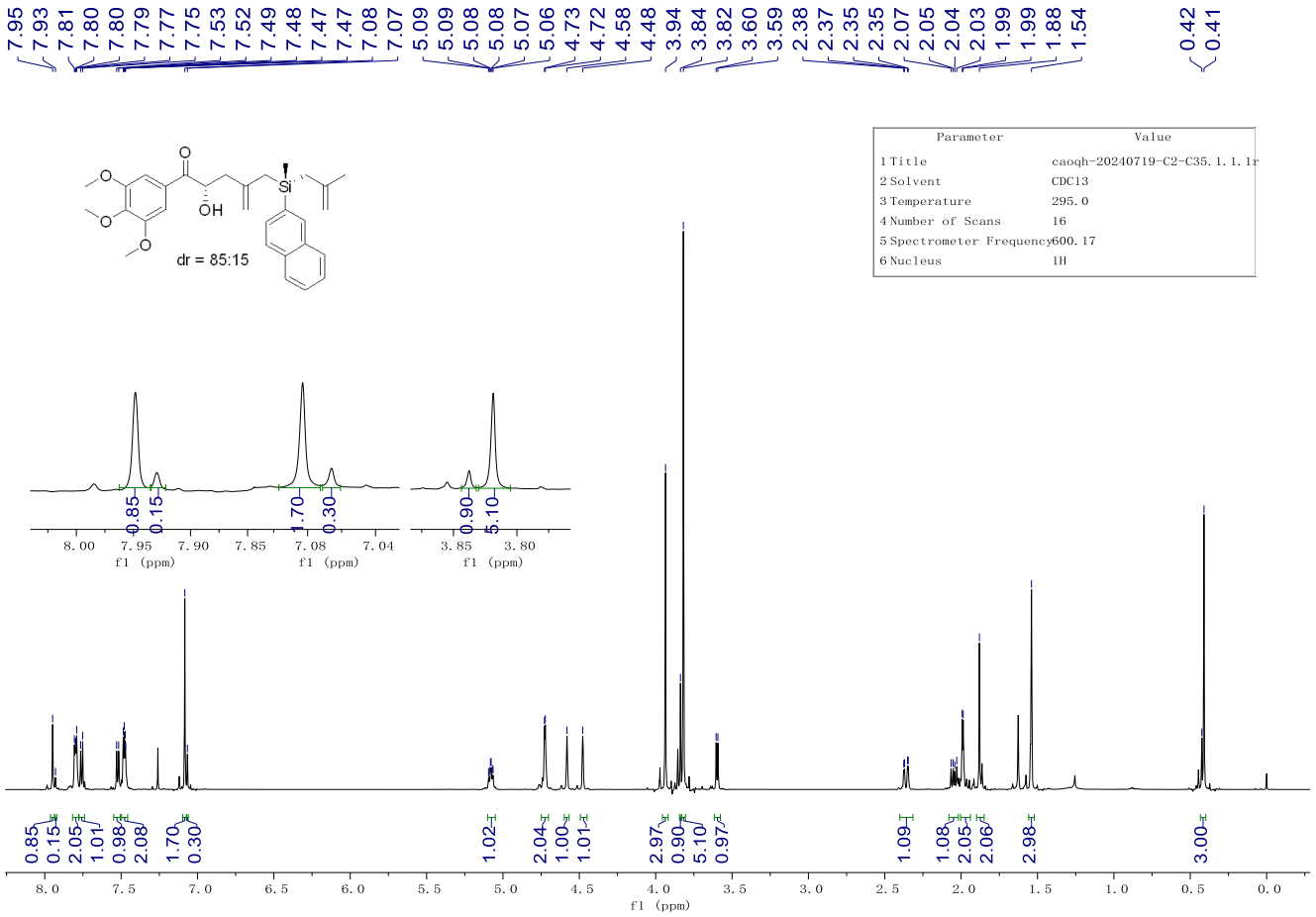
C29

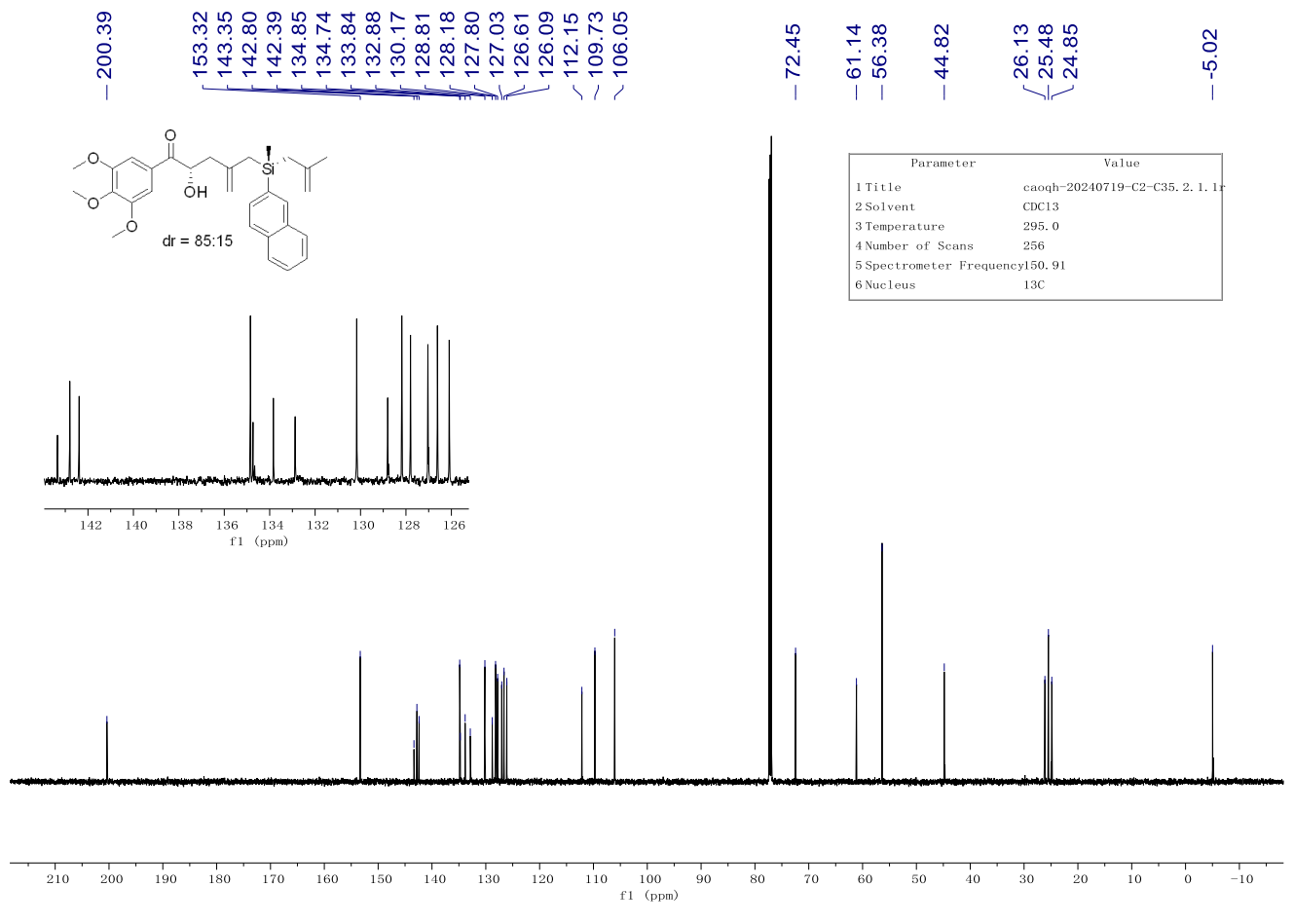

8.00 7.84 7.83 7.82 7.81 7.79 7.61 7.60 7.59 7.58 7.51 7.51 7.51 7.50 7.49 7.49 7.28 7.28 7.03 7.02 7.01 7.00 6.41 6.39 6.03 6.02 6.01 6.01 6.01 4.98 4.98 4.73 4.71 4.60 4.59 4.59 4.59 4.49 3.64 3.62 2.27 2.26 2.04 2.02 2.00 1.99 1.97 1.89 1.56 0.44 0.43
Parameter Value
1 Title cqh-20240229-c2-113-5.9.1.1r
2 Solvent CDCl3
3 Temperature 295.1
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
O
OH
Si
dr = 88:12
0.88 0.12
0.12 0.88 0.12 0.88
f1 (ppm)
0.88 0.12 3.07 0.92 2.03 0.96 0.12 0.88 0.12 0.88 2.04 1.01 2.01 0.98 1.00 1.05 0.97 0.92 1.08 1.02 2.02 2.99 3.00
f1 (ppm)
199.53 152.47 148.42 142.83 142.19 135.04 134.86 133.90 132.98 130.26 128.27 128.13 127.88 127.16 126.67 126.16 124.96 112.35 109.74 108.27 108.07 102.09 71.64 44.61 26.42 25.50 24.48 -5.29
Parameter Value
1 Title cqh-20240229-c2-113-5.10.1.1r
2 Solvent CDCl3
3 Temperature 295.9
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
O
OH
Si
dr = 88:12
135 134 133 132 131 130 129 128 127 126 125 124
f1 (ppm)
f1 (ppm)

C30

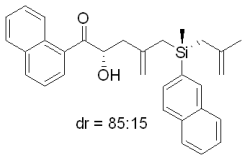

7.95 7.85 7.84 7.84 7.81 7.79 7.79 7.77 7.76 7.74 7.54 7.54 7.52 7.52 7.49 7.49 7.48 7.48 7.47 7.47 4.98 4.97 4.97 4.96 4.96 4.95 4.73 4.69 4.69 4.61 4.61 4.60 4.51 4.51 3.31 3.29 2.23 2.22 2.20 2.19 2.01 1.99 1.98 1.96 1.94 1.93 1.91 1.88 1.58 0.45 0.43
Br
O
OH
Si
Br
dr = 85:15
Parameter Value
1 Title cqh-20240229-c2-113-6.11.1.1r
2 Solvent CDCl3
3 Temperature 295.2
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
0.85
0.15
7.97 7.95 7.93 7.91
f1 (ppm)
0.85 0.15 2.95 2.04 1.07 0.92 2.08 1.03 1.08 0.96 1.05 1.08 1.08 1.07 0.99 2.07 2.09 3.02 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
199.14 142.75 141.55 139.02 136.89 134.88 134.50 133.84 132.86 130.26 130.07 128.19 127.84 127.11 126.67 126.13 123.74 112.80 109.87 72.49 43.86 25.99 25.53 24.86 -5.10
Br
O
OH
Si
Br
dr = 85:15
Parameter Value
1 Title cqh-20240229-c2-113-6.12.1.1r
2 Solvent CDCl3
3 Temperature 296.0
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
140 135 130 125
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

C31

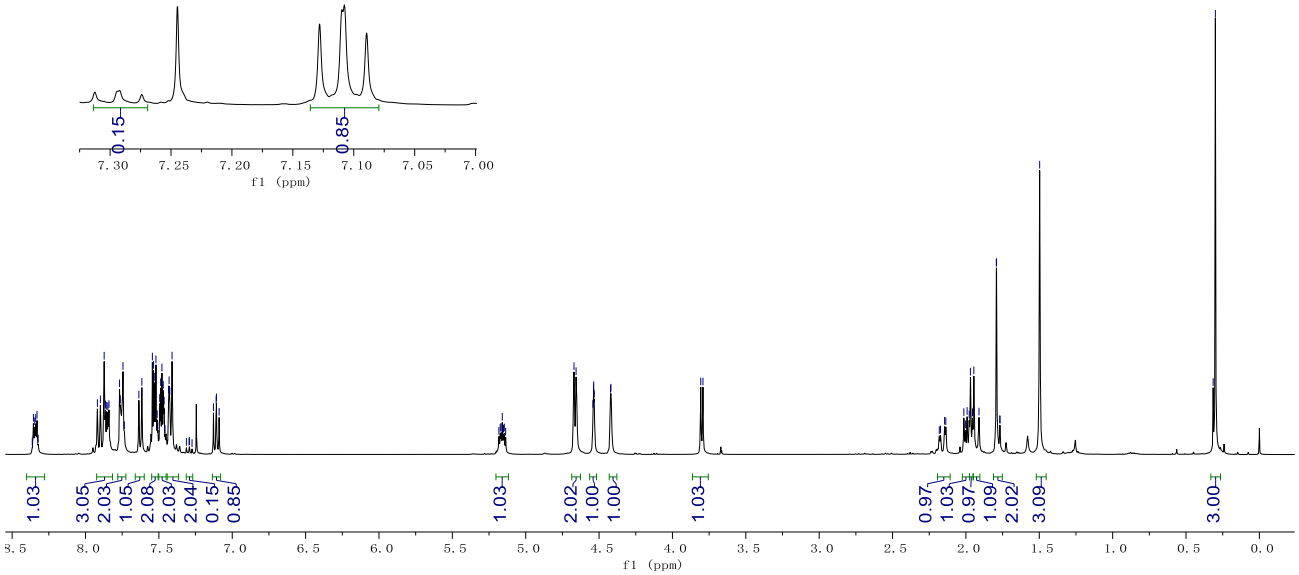

7.95 7.93 7.81 7.80 7.80 7.80 7.79 7.77 7.75 7.53 7.52 7.49 7.48 7.47 7.47 7.08 7.07
5.09 5.09 5.08 5.08 5.07 5.06 4.73 4.72 4.58 4.48
3.94 3.84 3.82 3.60 3.59
2.38 2.37 2.35 2.35 2.07 2.05 2.04 2.03 1.99 1.99 1.88 1.54
0.42 0.41
dr = 85:15
Parameter Value
1 Title caoqh-20240719-C2-C35.1.1.1r
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 600.17
6 Nucleus 1H
0.85 0.15 1.70 0.30
0.90 5.10
f1 (ppm)
0.85 0.15 2.05 1.01 0.98 2.08 1.70 0.30 1.02 2.04 1.00 1.01 2.97 0.90 5.10 0.97 1.09 1.08 2.05 2.06 2.98 3.00
f1 (ppm)

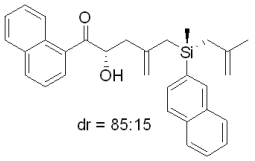

200.39
153.32 143.35 142.80 142.39 134.85 134.74 133.84 132.88 130.17 128.81 128.18 127.80 127.03 126.61 126.09 112.15 109.73 106.05
72.45 61.14 56.38 44.82 26.13 25.48 24.85 -5.02
dr = 85:15
Parameter Value
1 Title caoqh-20240719-C2-C35.2.1.1r
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
f1 (ppm)
f1 (ppm)

C32

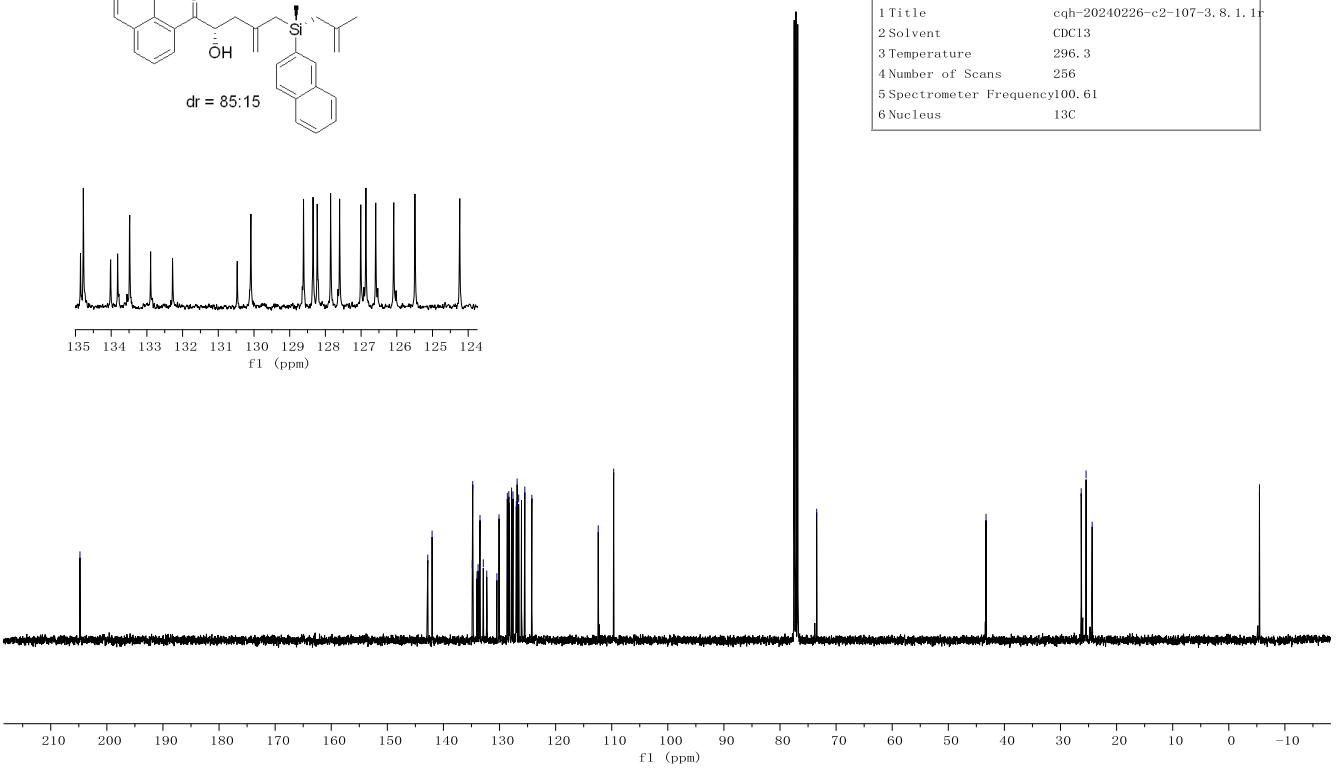


Parameter	Value
1 Title	cqh-20240226-c2-107-3.7.1.1r
2 Solvent	CDCl3
3 Temperature	295.7
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H

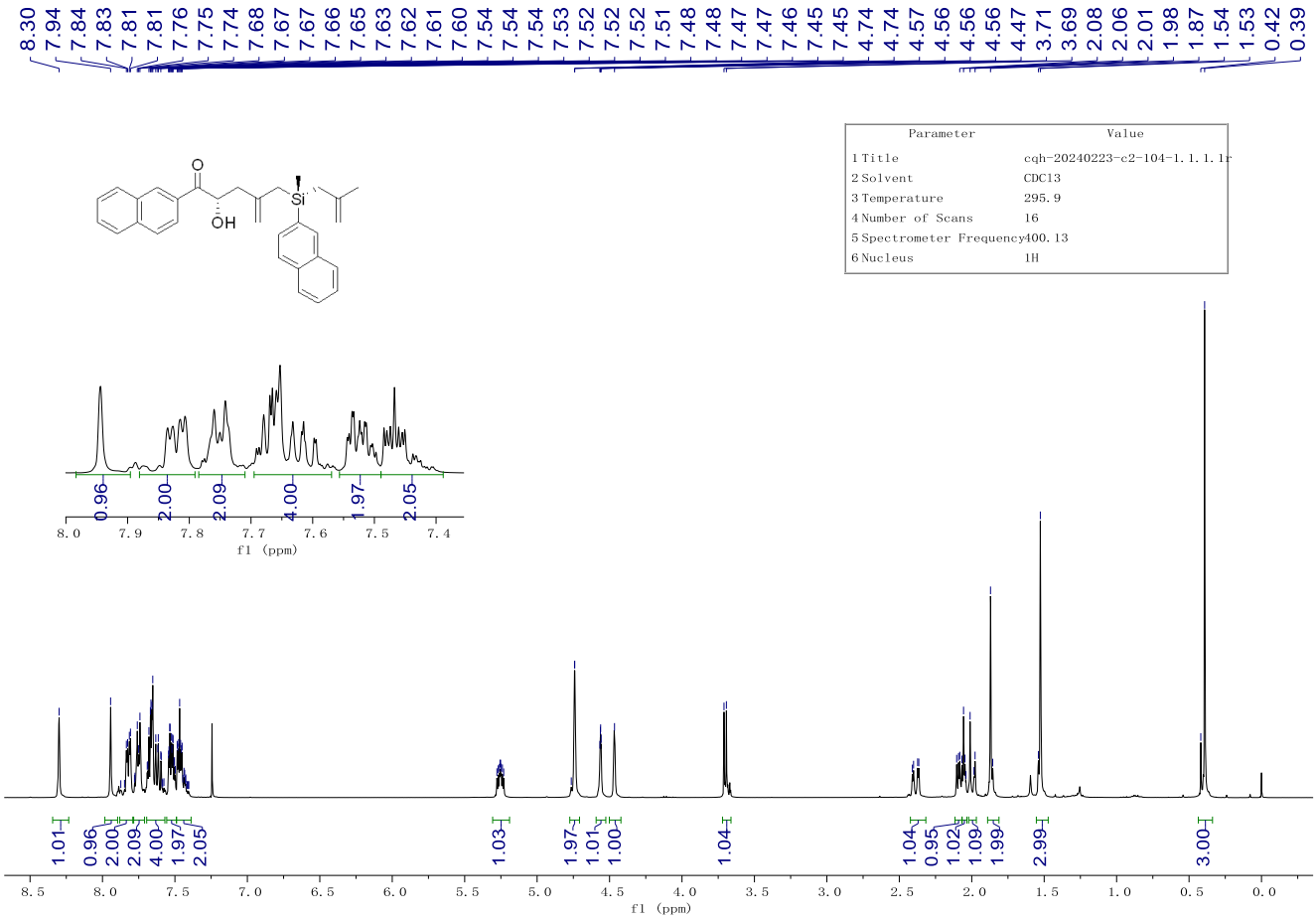


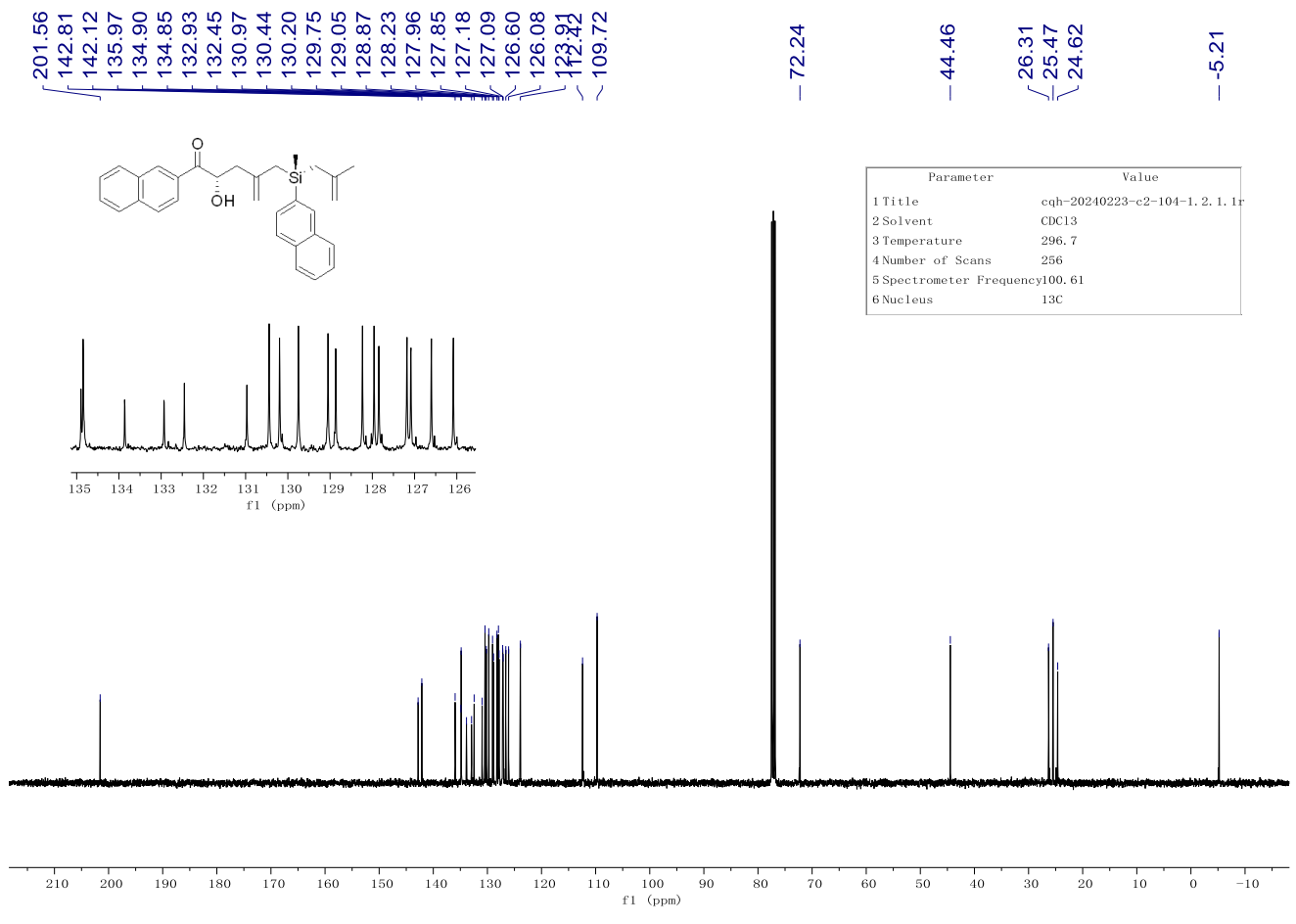


Parameter	Value
1 Title	cqh-20240226-c2-107-3.8.1.1r
2 Solvent	CDCl3
3 Temperature	296.3
4 Number of Scans	256
5 Spectrometer Frequency	100.61
6 Nucleus	13C

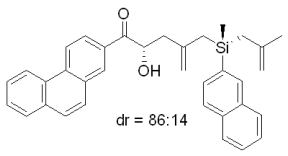


C33

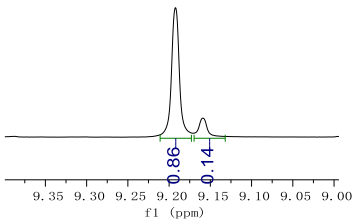

8.30 7.94 7.84 7.83 7.81 7.81 7.76 7.75 7.74 7.68 7.67 7.67 7.66 7.65 7.63 7.62 7.61 7.60 7.54 7.54 7.54 7.53 7.52 7.52 7.52 7.51 7.48 7.48 7.47 7.47 7.46 7.45 7.45 4.74 4.74 4.57 4.56 4.56 4.56 4.47 3.71 3.69 2.08 2.06 2.01 1.98 1.87 1.54 1.53 0.42 0.39
O
OH
Si
Parameter Value
1 Title cqh-20240223-c2-104-1.1.1.1r
2 Solvent CDCl3
3 Temperature 295.9
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
0.96 2.00 2.09 4.00 1.97 2.05
f1 (ppm)
1.01 0.96 2.00 2.09 4.00 1.97 2.05 1.03 1.97 1.01 1.00 1.04 1.04 0.95 1.02 1.09 1.99 2.99 3.00
f1 (ppm)

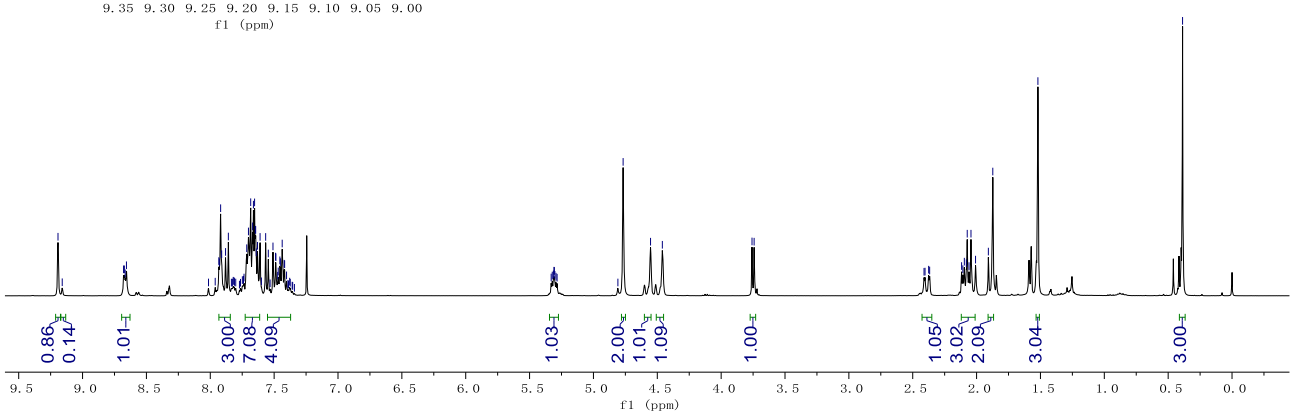

201.56 142.81 142.12 135.97 134.90 134.85 132.93 132.45 130.97 130.44 130.20 129.75 129.05 128.87 128.23 127.96 127.85 127.18 127.09 126.60 126.08 123.91 112.42 109.72
72.24
44.46
26.31 25.47 24.62
-5.21
O
OH
Si
Parameter Value
1 Title cqh-20240223-c2-104-1.2.1.1r
2 Solvent CDCl3
3 Temperature 296.7
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)
f1 (ppm)

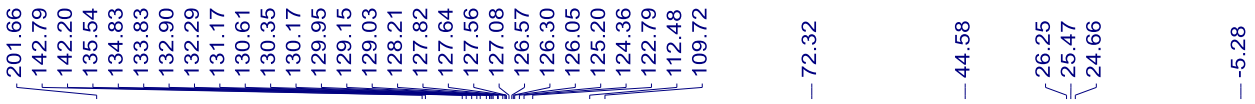
C34

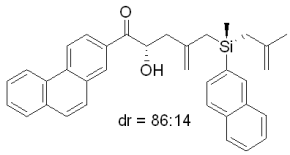


Parameter	Value
1 Title	caoqh-20240513-c2-161-4.9.1.1r
2 Solvent	CDCl3
3 Temperature	296.0
4 Number of Scans	16
5 Spectrometer Frequency	400.18
6 Nucleus	1H

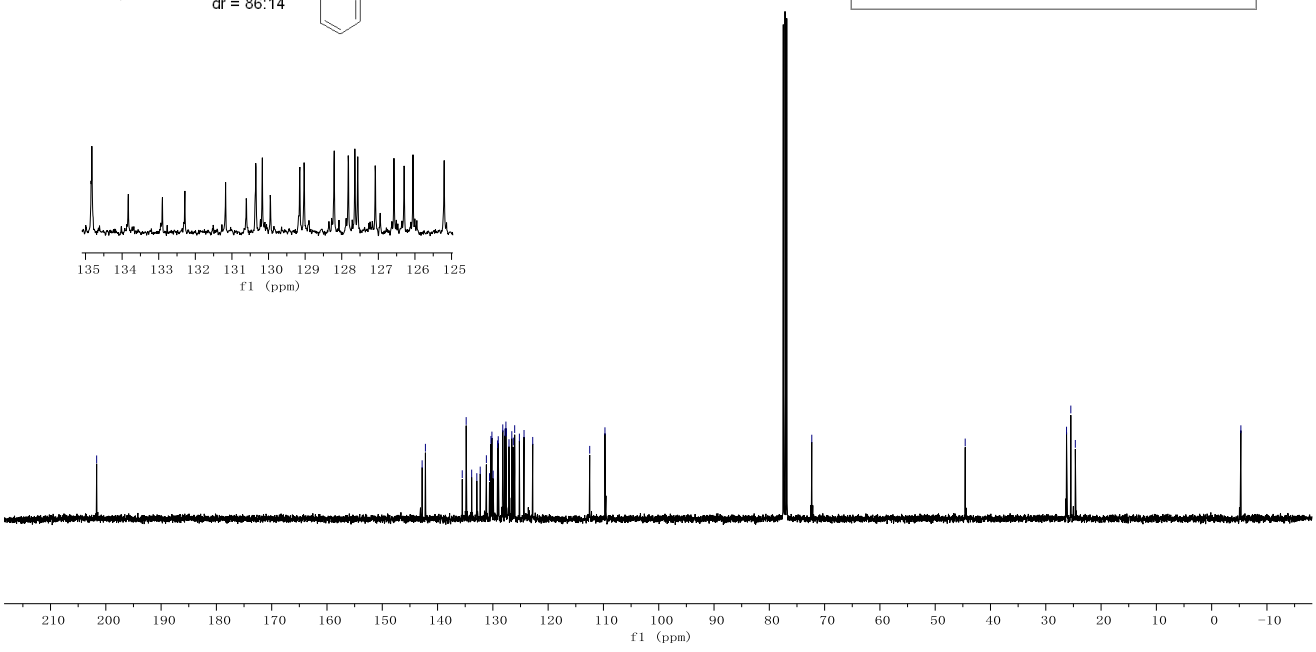




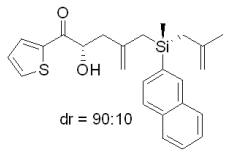




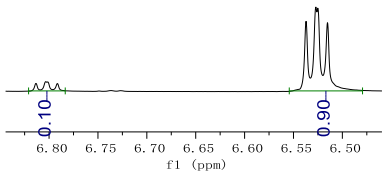
Parameter	Value
1 Title	caoqh-20240513-c2-161-4.10.1.1r
2 Solvent	CDCl3
3 Temperature	296.0
4 Number of Scans	256
5 Spectrometer Frequency	100.63
6 Nucleus	13C

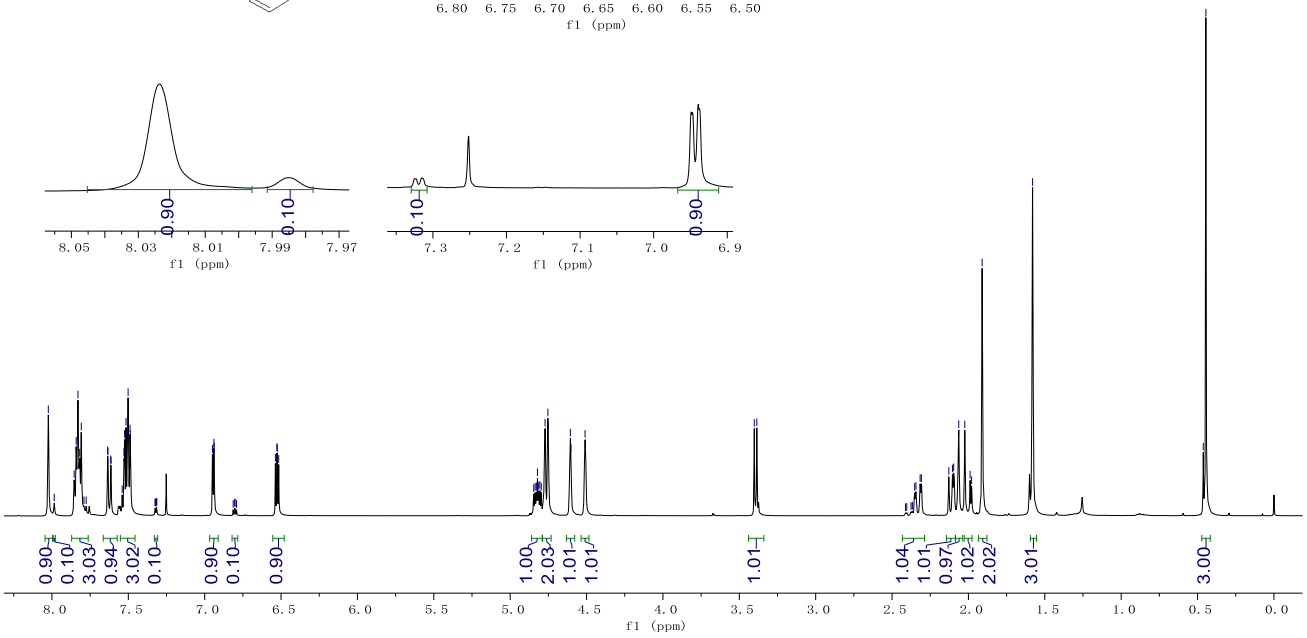


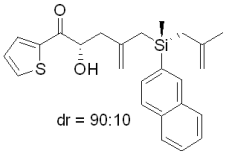
C35



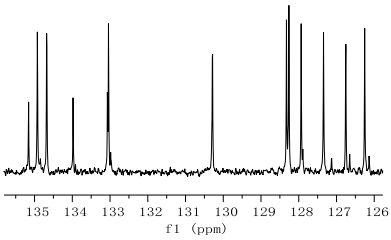
Parameter	Value
1 Title	cqh-20240227-c2-110-6.11.1.1r
2 Solvent	CDCl3
3 Temperature	295.8
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H

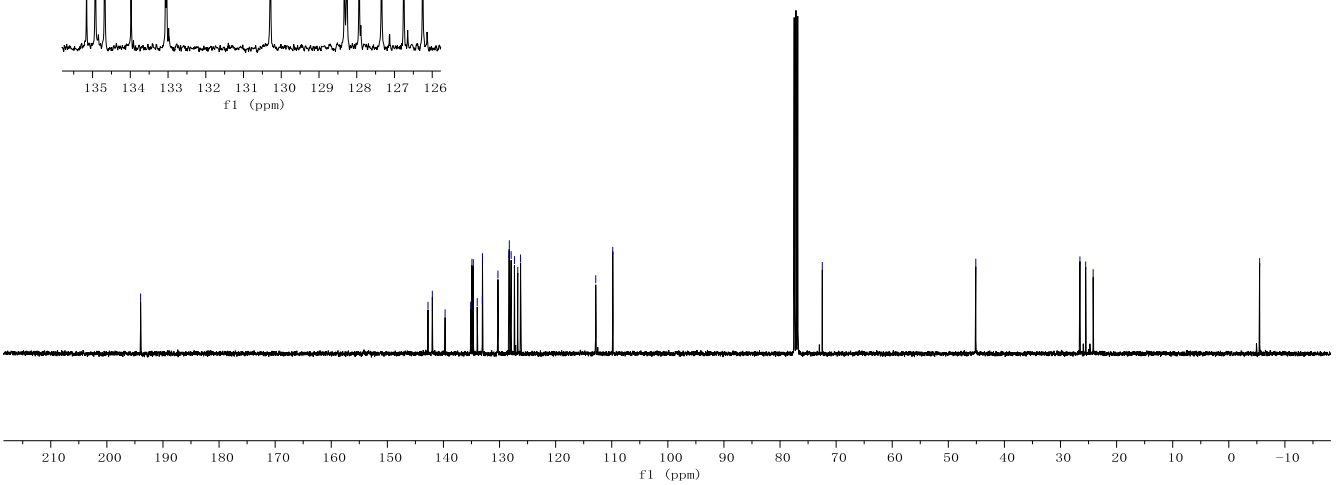




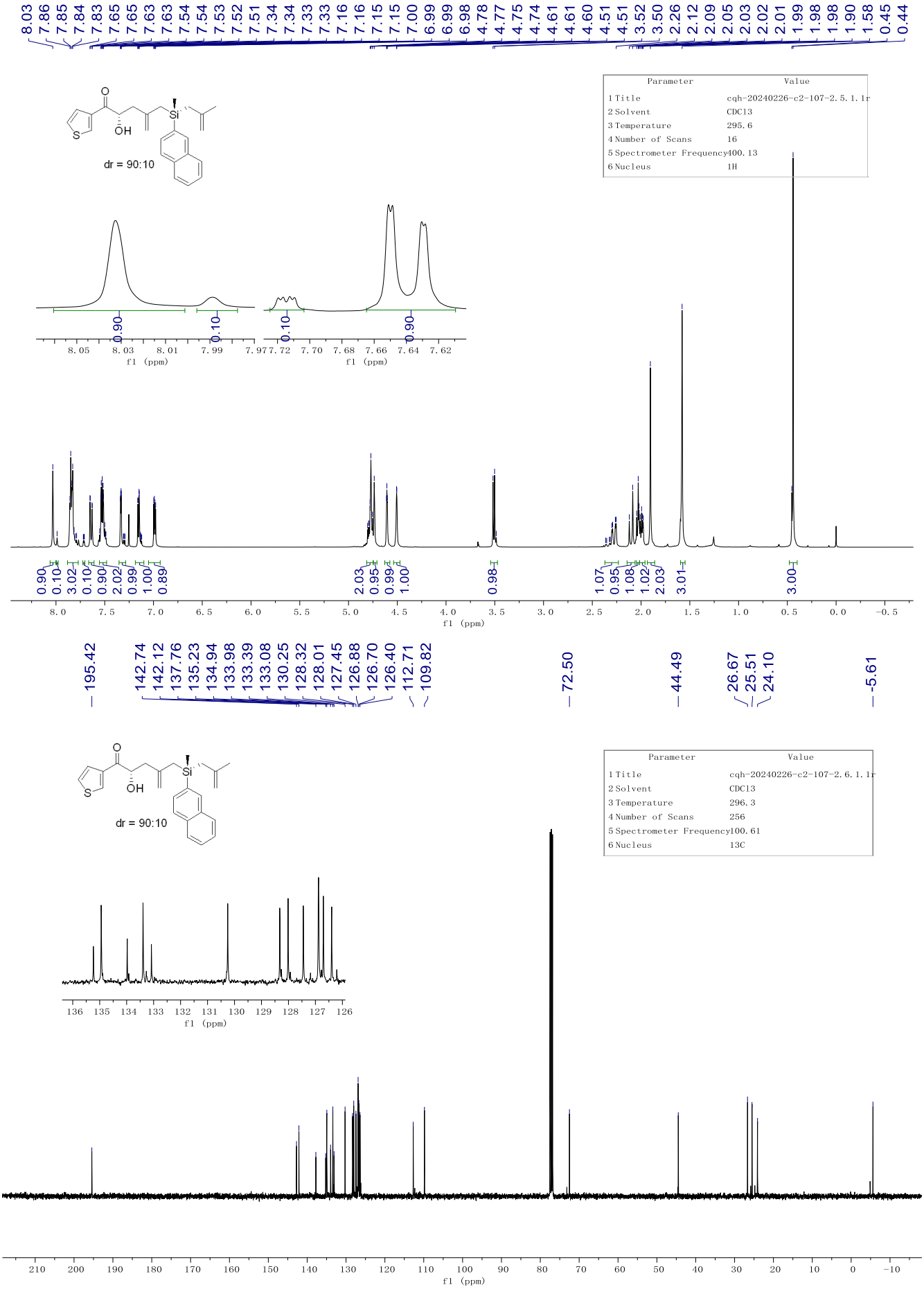


Parameter	Value
1 Title	cqh-20240227-c2-110-6.12.1.1r
2 Solvent	CDCl3
3 Temperature	296.5
4 Number of Scans	256
5 Spectrometer Frequency	100.61
6 Nucleus	13C

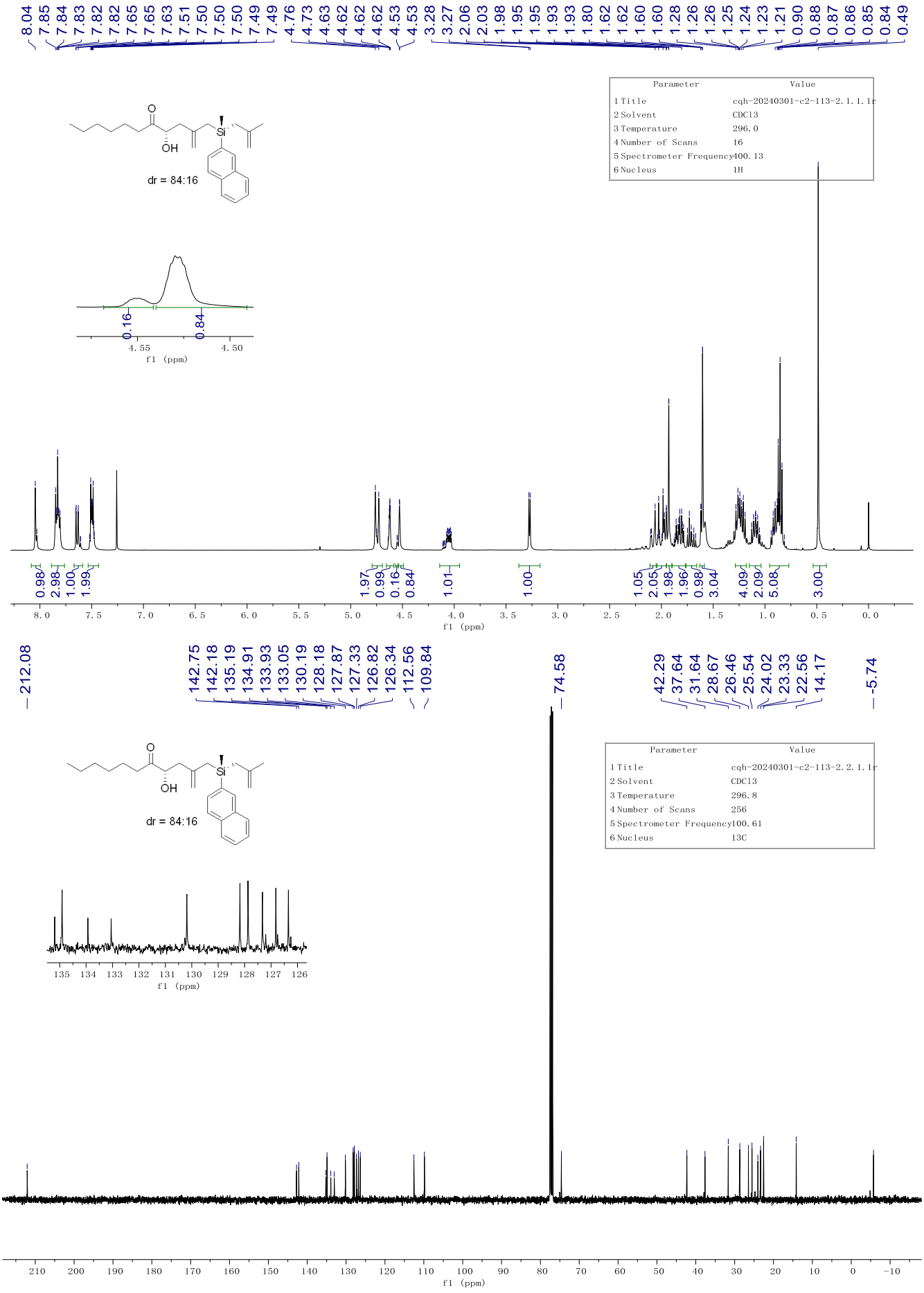




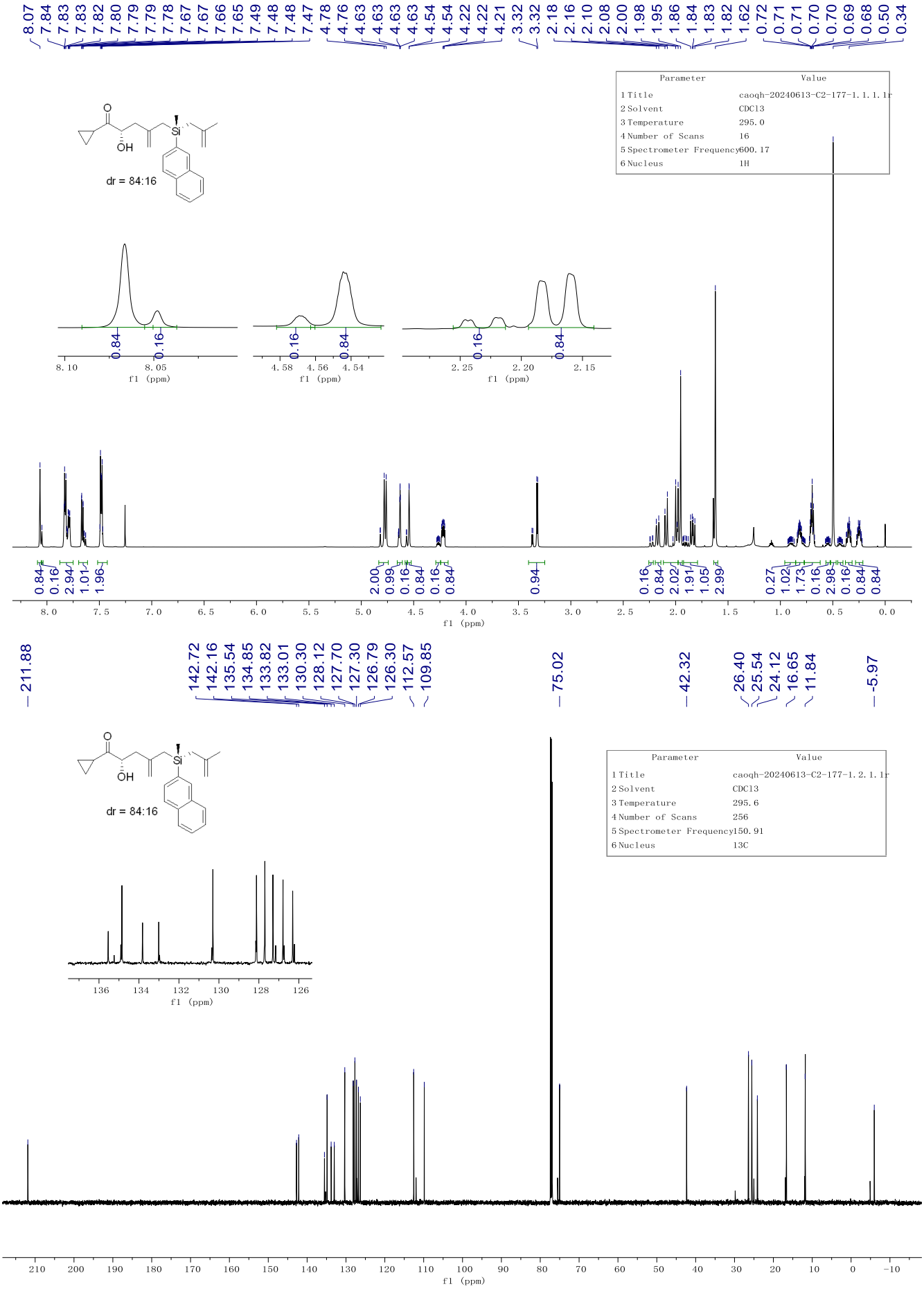
C36


dr = 90:10
Parameter Value
1 Title cqh-20240226-c2-107-2.5.1.1r
2 Solvent CDCl3
3 Temperature 295.6
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
f1 (ppm)
dr = 90:10
Parameter Value
1 Title cqh-20240226-c2-107-2.6.1.1r
2 Solvent CDCl3
3 Temperature 296.3
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)

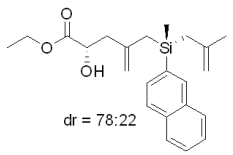
C37


8.04 7.85 7.84 7.83 7.82 7.82 7.65 7.65 7.63 7.51 7.50 7.50 7.50 7.49 7.49 4.76 4.73 4.63 4.62 4.62 4.62 4.53 4.53 3.28 3.27 2.06 2.03 1.98 1.95 1.95 1.93 1.93 1.80 1.62 1.62 1.60 1.60 1.28 1.26 1.26 1.25 1.24 1.23 1.21 0.90 0.88 0.87 0.86 0.85 0.84 0.49
O
OH
Si
dr = 84:16
0.16
0.84
4.55
4.50
f1 (ppm)
Parameter Value
1 Title cqh-20240301-c2-113-2.1.1.1r
2 Solvent CDCl3
3 Temperature 296.0
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
0.98 2.98 1.00 1.99 1.97 0.99 0.16 0.84 1.01 1.00 1.05 2.05 1.98 1.96 0.98 3.04 4.09 2.09 5.08 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
212.08
142.75 142.18 135.19 134.91 133.93 133.05 130.19 128.18 127.87 127.33 126.82 126.34 112.56 109.84
74.58
42.29 37.64 31.64 28.67 26.46 25.54 24.02 23.33 22.56 14.17
-5.74
O
OH
Si
dr = 84:16
135 134 133 132 131 130 129 128 127 126
f1 (ppm)
Parameter Value
1 Title cqh-20240301-c2-113-2.2.1.1r
2 Solvent CDCl3
3 Temperature 296.8
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

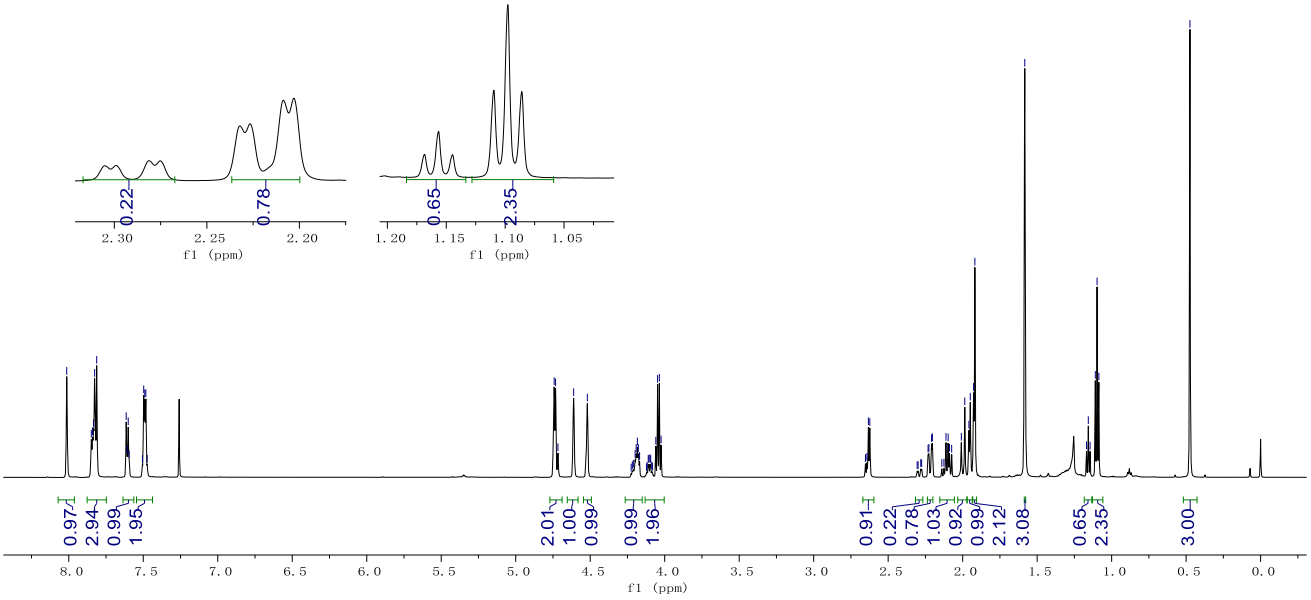
C38

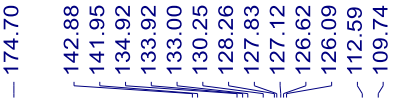

8.07 7.84 7.83 7.83 7.82 7.80 7.79 7.79 7.78 7.67 7.67 7.66 7.65 7.49 7.48 7.48 7.47 4.78 4.76 4.63 4.63 4.63 4.63 4.54 4.54 4.22 4.22 4.21 3.32 3.32 2.18 2.16 2.10 2.08 2.00 1.98 1.95 1.86 1.84 1.83 1.82 1.62 0.72 0.71 0.71 0.70 0.70 0.69 0.68 0.50 0.34
Parameter Value
1 Title caoqh-20240613-C2-177-1.1.1.1r
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 600.17
6 Nucleus 1H
dr = 84:16
0.84 0.16
0.16 0.84
0.16 0.84
f1 (ppm)
0.84 0.16 2.94 1.01 1.96 2.00 0.99 0.16 0.84 0.16 0.84 0.94 0.16 0.84 2.02 1.91 1.05 2.99 0.27 1.02 1.73 0.16 2.98 0.16 0.84 0.84
f1 (ppm)
211.88 142.72 142.16 135.54 134.85 133.82 133.01 130.30 128.12 127.70 127.30 126.79 126.30 112.57 109.85 75.02 42.32 26.40 25.54 24.12 16.65 11.84 -5.97
Parameter Value
1 Title caoqh-20240613-C2-177-1.2.1.1r
2 Solvent CDCl3
3 Temperature 295.6
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
dr = 84:16
f1 (ppm)
f1 (ppm)

C39

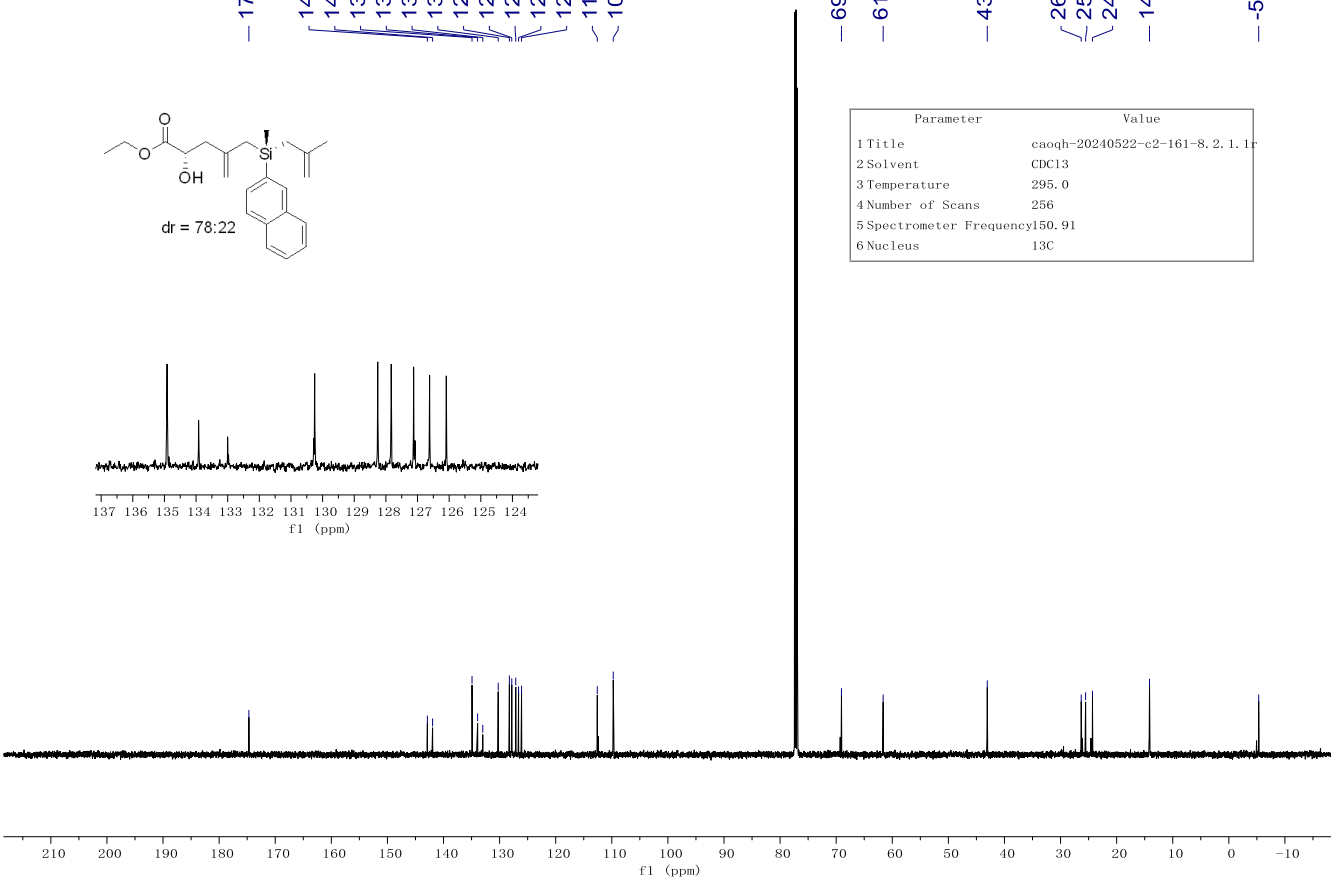


Parameter	Value
1 Title	caoqh-20240522-c2-161-8.1.1.1r
2 Solvent	CDCl3
3 Temperature	295.0
4 Number of Scans	16
5 Spectrometer Frequency	600.17
6 Nucleus	1H

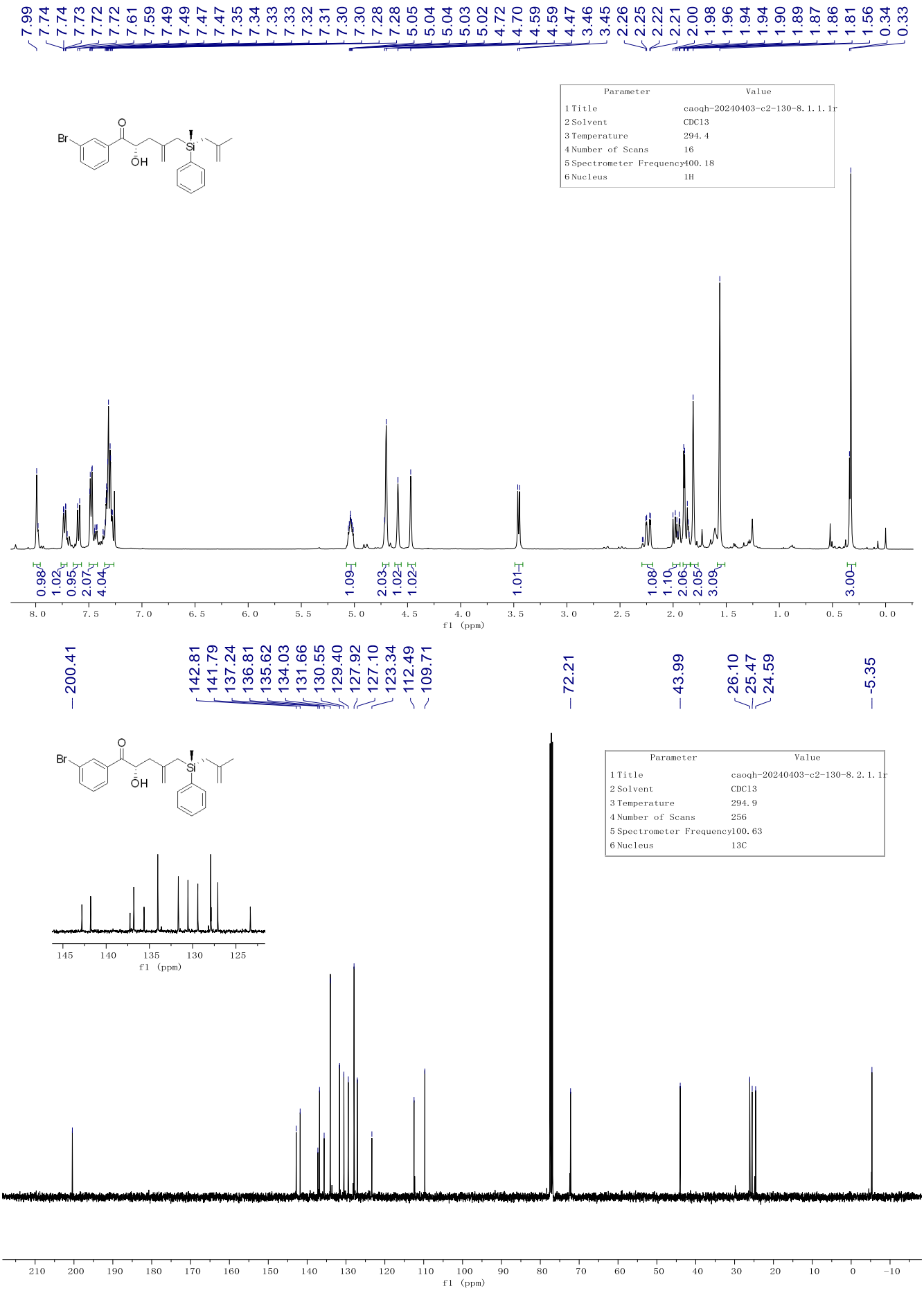




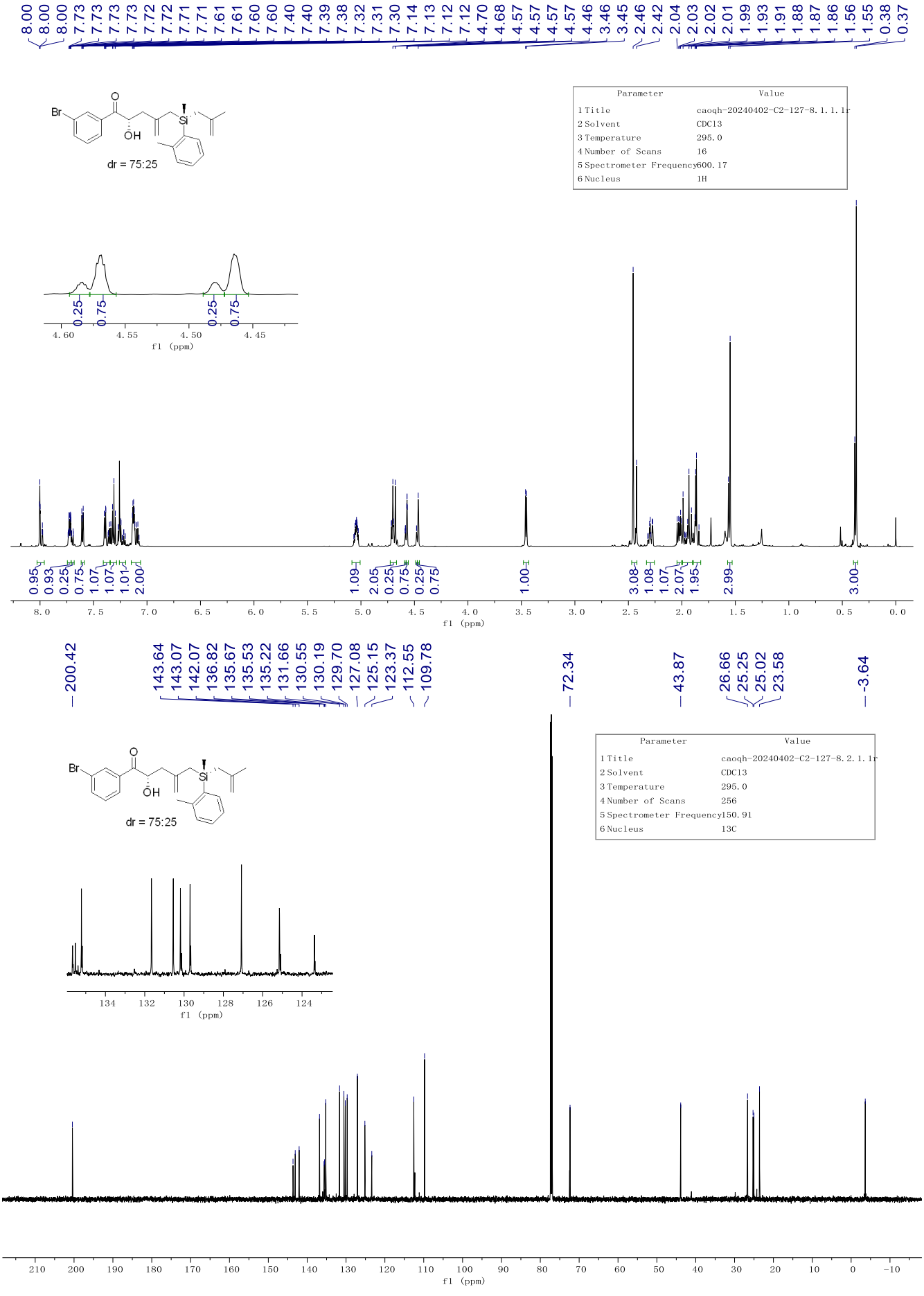
Parameter	Value
1 Title	caoqh-20240522-c2-161-8.2.1.1r
2 Solvent	CDCl3
3 Temperature	295.0
4 Number of Scans	256
5 Spectrometer Frequency	150.91
6 Nucleus	13C



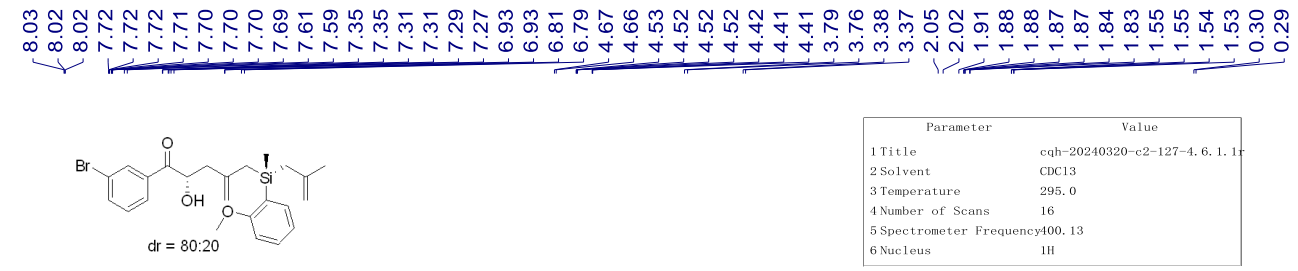
C40


7.99 7.74 7.74 7.73 7.72 7.72 7.61 7.59 7.49 7.49 7.47 7.47 7.35 7.34 7.33 7.33 7.32 7.31 7.30 7.30 7.28 7.28 5.05 5.04 5.04 5.03 5.02 4.72 4.70 4.59 4.59 4.47 3.46 3.45 2.26 2.25 2.22 2.21 2.00 1.98 1.96 1.94 1.94 1.90 1.89 1.87 1.86 1.81 1.56 0.34 0.33
Br
O
OH
Si
Parameter Value
1 Title caoqh-20240403-c2-130-8.1.1.1r
2 Solvent CDCl3
3 Temperature 294.4
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
0.98 1.02 0.95 2.07 4.04 1.09 2.03 1.02 1.02 1.01 1.08 1.10 2.06 2.05 3.09 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
200.41 142.81 141.79 137.24 136.81 135.62 134.03 131.66 130.55 129.40 127.92 127.10 123.34 112.49 109.71 72.21 43.99 26.10 25.47 24.59 -5.35
Br
O
OH
Si
Parameter Value
1 Title caoqh-20240403-c2-130-8.2.1.1r
2 Solvent CDCl3
3 Temperature 294.9
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
145 140 135 130 125
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

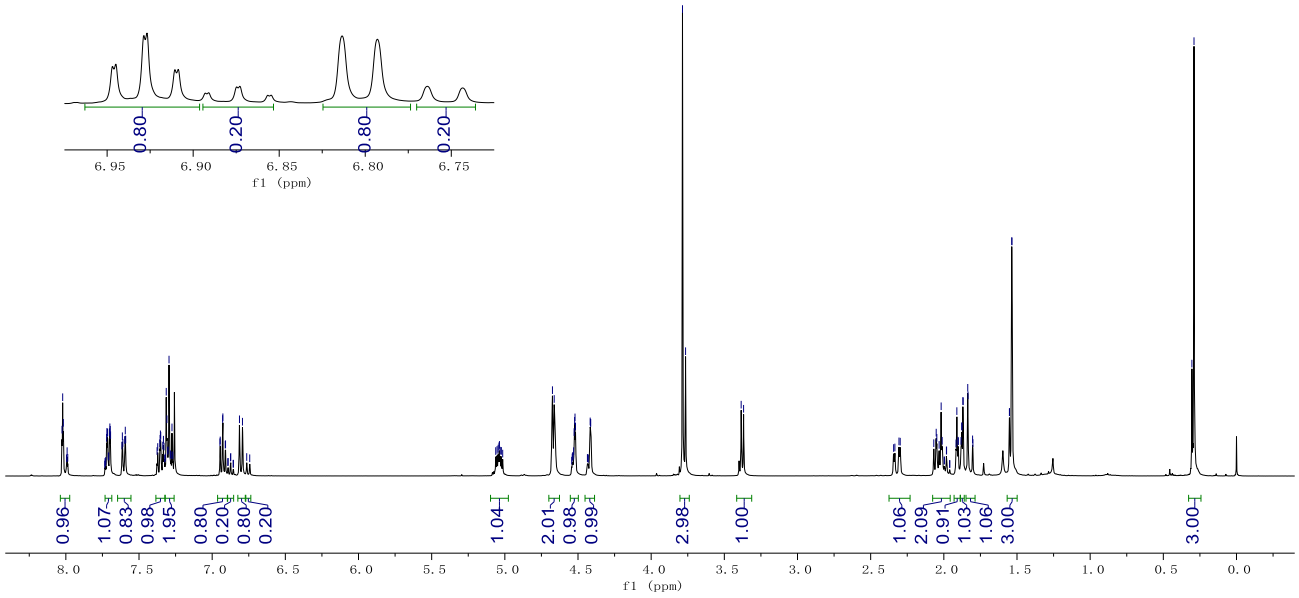
C41

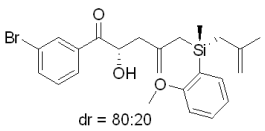

8.00 8.00 8.00 7.73 7.73 7.73 7.73 7.72 7.72 7.71 7.71 7.61 7.61 7.60 7.60 7.40 7.40 7.39 7.38 7.32 7.31 7.30 7.14 7.13 7.12 7.12 4.70 4.68 4.57 4.57 4.57 4.46 3.46 3.45 2.46 2.42 2.04 2.03 2.02 2.01 1.99 1.93 1.91 1.88 1.87 1.86 1.56 1.55 0.38 0.37
Br
O
OH
Si
dr = 75:25
Parameter Value
1 Title caoqh-20240402-C2-127-8.1.1.1r
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 600.17
6 Nucleus 1H
0.25 0.75 0.25 0.75
4.60 4.55 4.50 4.45
f1 (ppm)
0.95 0.93 0.25 0.75 1.07 1.07 1.01 2.00 1.09 2.05 0.25 0.75 0.25 0.75 1.00 3.08 1.08 1.07 2.07 1.95 2.99 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
200.42 143.64 143.07 142.07 136.82 135.67 135.53 135.22 131.66 130.55 130.19 129.70 127.08 125.15 123.37 112.55 109.78 72.34 43.87 26.66 25.25 25.02 23.58 -3.64
Br
O
OH
Si
dr = 75:25
Parameter Value
1 Title caoqh-20240402-C2-127-8.2.1.1r
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
134 132 130 128 126 124
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

C42

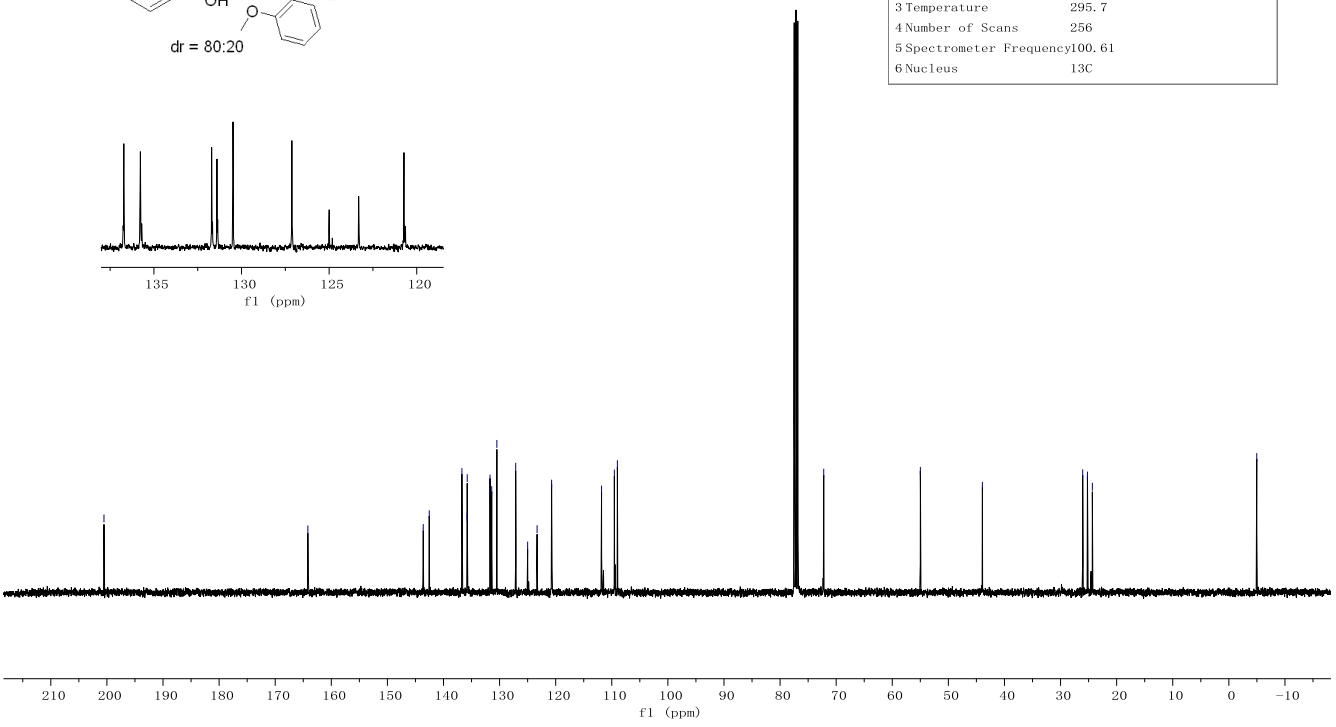


Parameter	Value
1 Title	cqh-20240320-c2-127-4.6.1.1r
2 Solvent	CDCl3
3 Temperature	295.0
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H

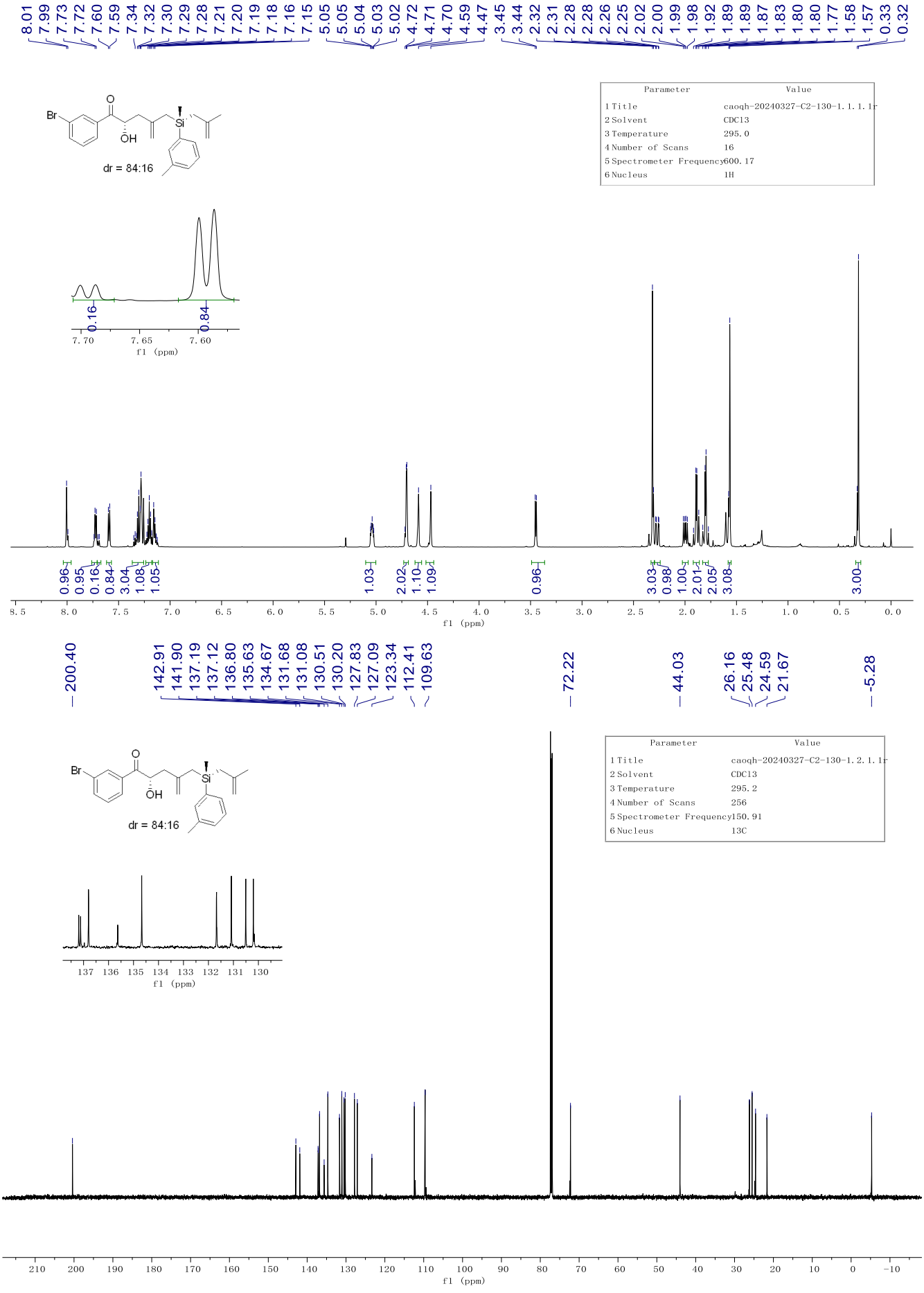




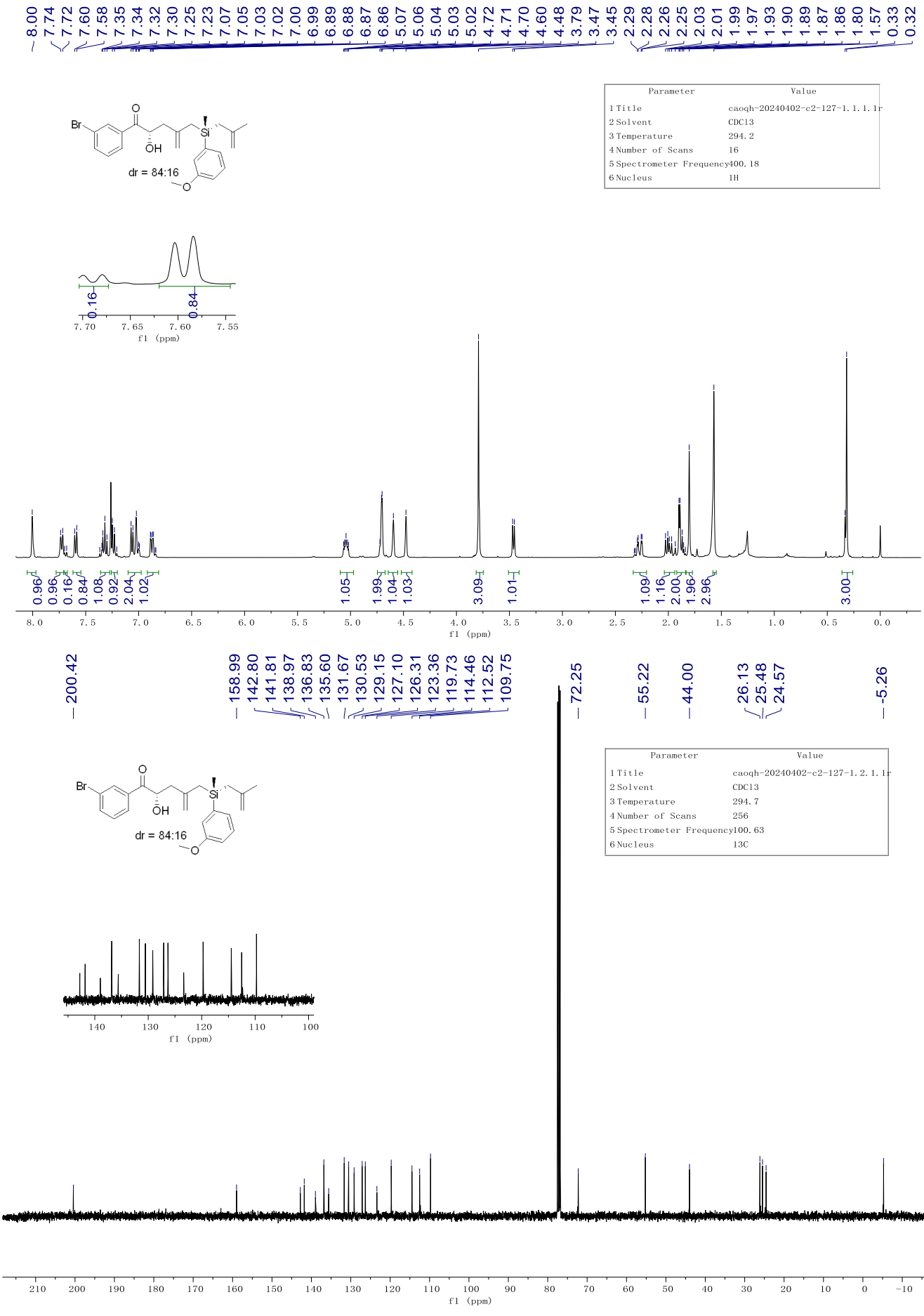
Parameter	Value
1 Title	cqh-20240320-c2-127-4.7.1.1r
2 Solvent	CDCl3
3 Temperature	295.7
4 Number of Scans	256
5 Spectrometer Frequency	100.61
6 Nucleus	13C



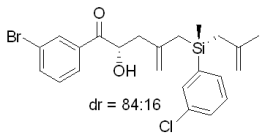
C43


8.01 7.99 7.73 7.72 7.60 7.59 7.34 7.32 7.30 7.29 7.28 7.21 7.20 7.19 7.18 7.16 7.15 5.05 5.05 5.04 5.03 5.02 4.72 4.71 4.70 4.59 4.47 3.45 3.44 2.32 2.31 2.28 2.28 2.26 2.25 2.02 2.00 1.99 1.98 1.92 1.89 1.89 1.87 1.83 1.80 1.80 1.77 1.58 1.57 0.33 0.32
Br
O
OH
Si
dr = 84:16
Parameter Value
1 Title caoqh-20240327-C2-130-1.1.1.1r
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 600.17
6 Nucleus 1H
0.16
0.84
7.70 7.65 7.60
f1 (ppm)
0.96 0.95 0.16 0.84 3.04 1.08 1.05 1.03 2.02 1.10 1.09 0.96 3.03 0.98 1.00 2.01 2.05 3.08 3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
200.40
142.91 141.90 137.19 137.12 136.80 135.63 134.67 131.68 131.08 130.51 130.20 127.83 127.09 123.34 112.41 109.63
72.22
44.03
26.16 25.48 24.59 21.67
-5.28
Br
O
OH
Si
dr = 84:16
Parameter Value
1 Title caoqh-20240327-C2-130-1.2.1.1r
2 Solvent CDCl3
3 Temperature 295.2
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
137 136 135 134 133 132 131 130
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

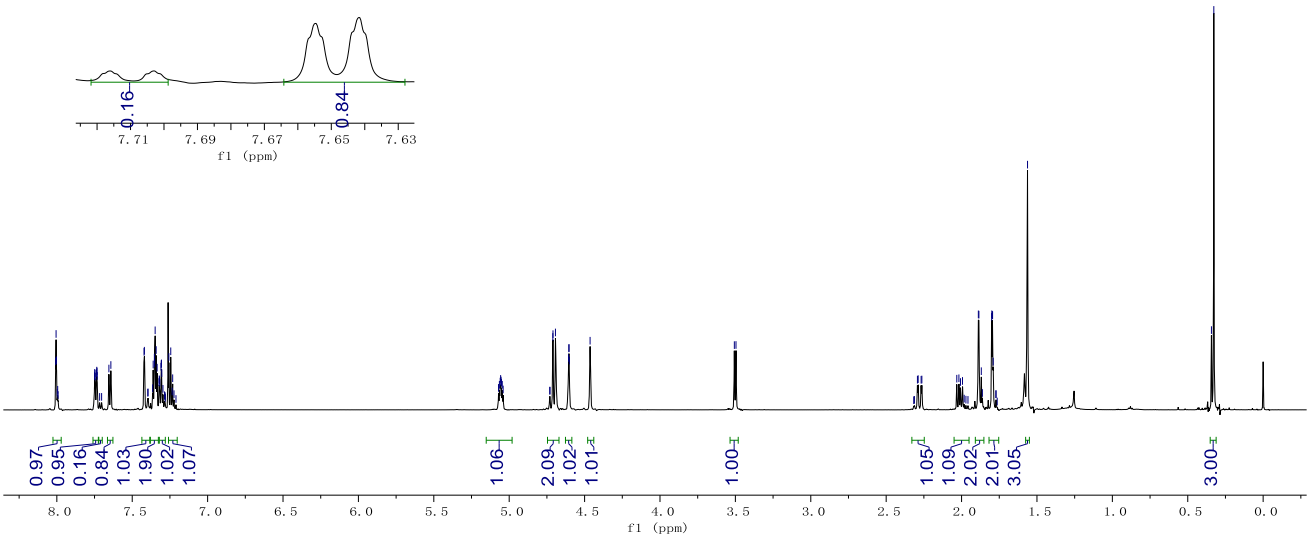
C44

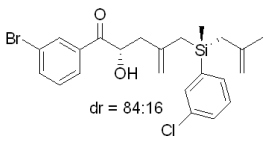

8.00 7.74 7.72 7.60 7.58 7.35 7.34 7.32 7.30 7.25 7.23 7.07 7.05 7.03 7.02 7.00 6.99 6.89 6.88 6.87 6.86 5.07 5.06 5.04 5.03 5.02 4.72 4.71 4.70 4.60 4.48 3.79 3.47 3.45 2.29 2.28 2.26 2.25 2.03 2.01 1.99 1.97 1.93 1.90 1.89 1.87 1.86 1.80 1.57 0.33 0.32
Br
O
OH
Si
O
dr = 84:16
Parameter Value
1 Title caoqh-20240402-c2-127-1.1.1.1r
2 Solvent CDCl3
3 Temperature 294.2
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
0.16
0.84
7.70 7.65 7.60 7.55
f1 (ppm)
0.96 0.96 0.16 0.84 1.08 0.92 2.04 1.02 1.05 1.99 1.04 1.03 3.09 1.01 1.09 1.16 2.00 1.96 2.96 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
200.42 158.99 142.80 141.81 138.97 136.83 135.60 131.67 130.53 129.15 127.10 126.31 123.36 119.73 114.46 112.52 109.75 72.25 55.22 44.00 26.13 25.48 24.57 -5.26
Br
O
OH
Si
O
dr = 84:16
Parameter Value
1 Title caoqh-20240402-c2-127-1.2.1.1r
2 Solvent CDCl3
3 Temperature 294.7
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
140 130 120 110 100
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

C45

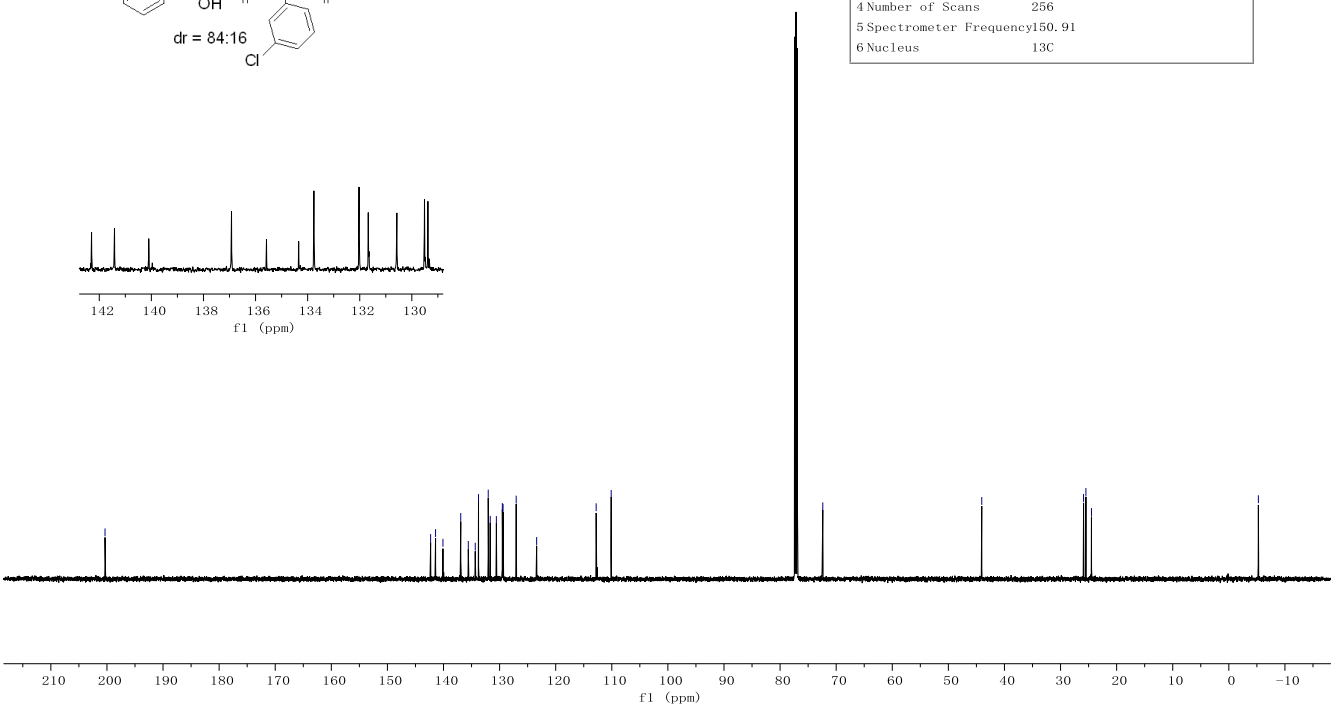


Parameter	Value
1 Title	caoqh-20240402-C2-127-2.5.1.1r
2 Solvent	CDCl3
3 Temperature	295.0
4 Number of Scans	16
5 Spectrometer Frequency	600.17
6 Nucleus	1H

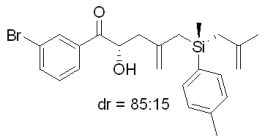




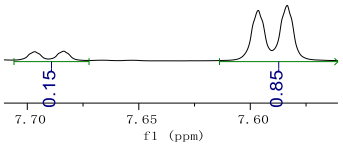
Parameter	Value
1 Title	caoqh-20240402-C2-127-2.6.1.1r
2 Solvent	CDCl3
3 Temperature	295.1
4 Number of Scans	256
5 Spectrometer Frequency	150.91
6 Nucleus	13C

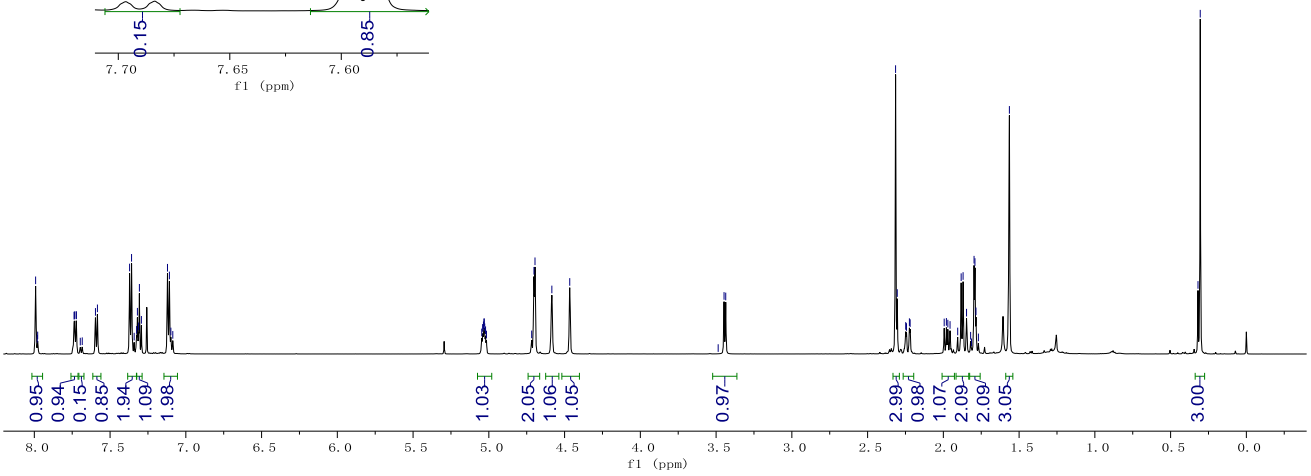


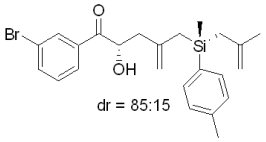
C46



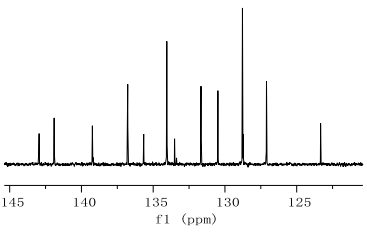
Parameter	Value
1 Title	caoqh-20240327-C2-130-2.5.1.1r
2 Solvent	CDCl3
3 Temperature	295.0
4 Number of Scans	16
5 Spectrometer Frequency	600.17
6 Nucleus	1H

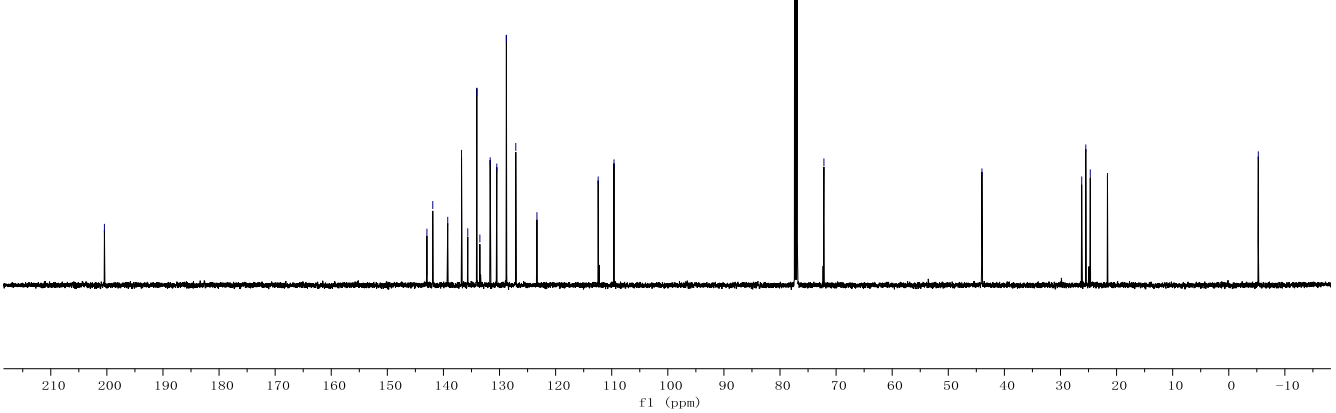




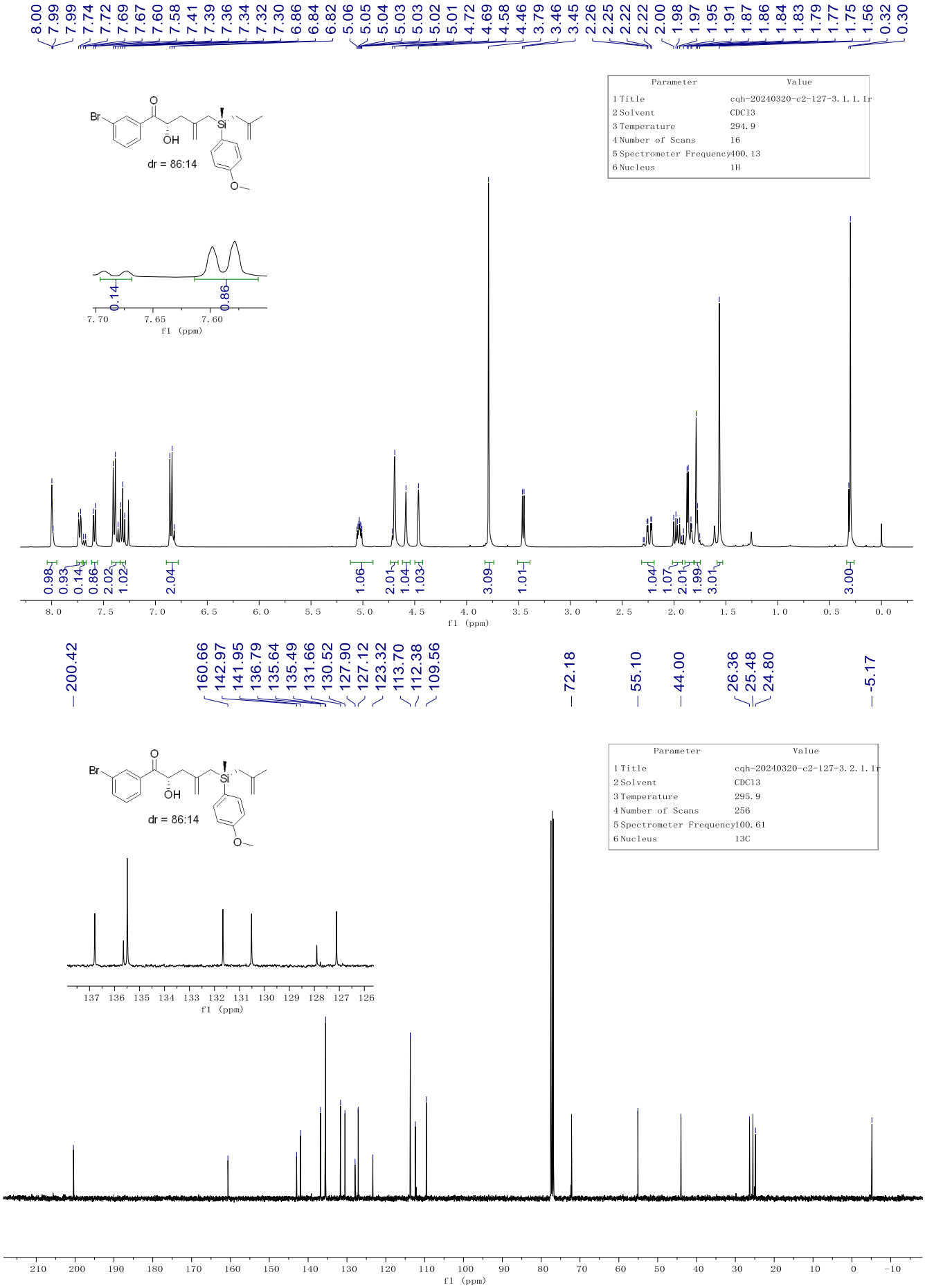


Parameter	Value
1 Title	caoqh-20240327-C2-130-2.6.1.1r
2 Solvent	CDCl3
3 Temperature	295.0
4 Number of Scans	256
5 Spectrometer Frequency	150.91
6 Nucleus	13C

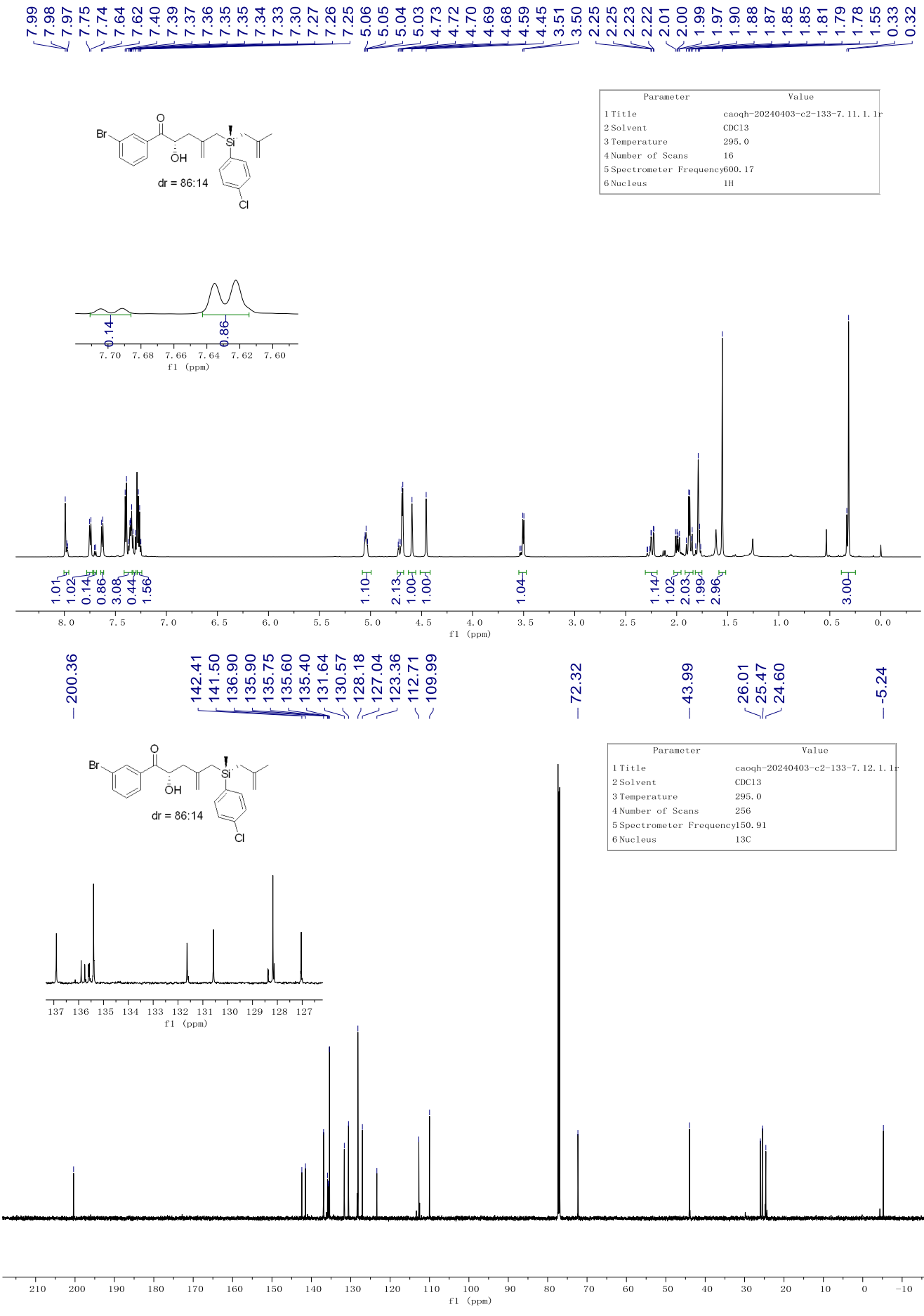




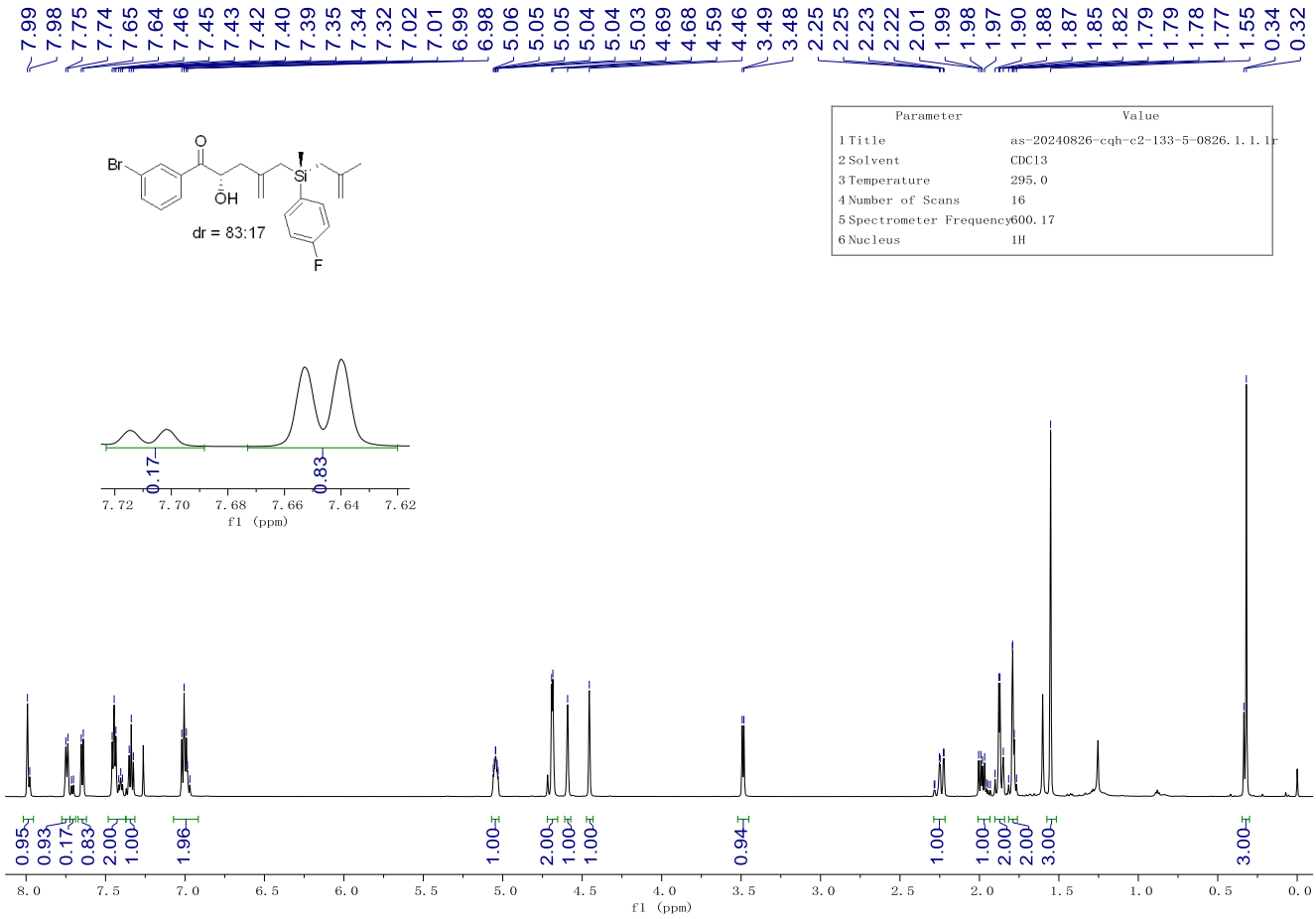
C47

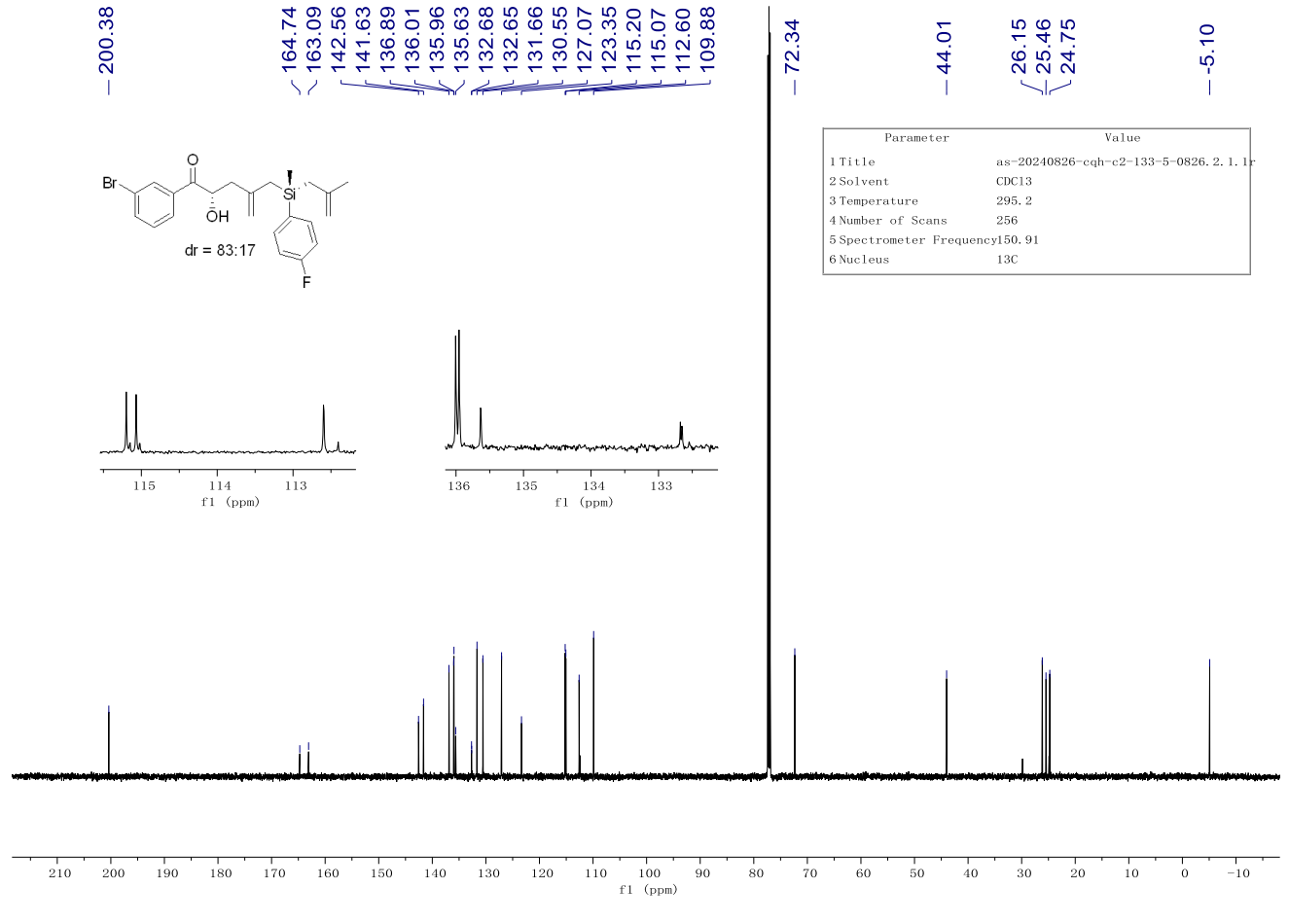

8.00 7.99 7.99 7.74 7.72 7.69 7.67 7.60 7.58 7.41 7.39 7.36 7.34 7.32 7.30 6.86 6.84 6.82 5.06 5.05 5.04 5.03 5.03 5.02 5.01 4.72 4.69 4.58 4.46 3.79 3.46 3.45 2.26 2.25 2.22 2.22 2.00 1.98 1.97 1.95 1.91 1.87 1.86 1.84 1.83 1.79 1.77 1.75 1.56 0.32 0.30
Parameter Value
1 Title cqh-20240320-c2-127-3.1.1.1r
2 Solvent CDCl3
3 Temperature 294.9
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
Br
O
OH
Si
O
dr = 86:14
0.14
0.86
7.70 7.65 7.60
f1 (ppm)
0.98 0.93 0.14 0.86 2.02 1.02 2.04 1.06 2.01 1.04 1.03 3.09 1.01 1.04 1.07 2.01 1.99 3.01 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
200.42
160.66 142.97 141.95 136.79 135.64 135.49 131.66 130.52 127.90 127.12 123.32 113.70 112.38 109.56
72.18
55.10
44.00
26.36 25.48 24.80
-5.17
Parameter Value
1 Title cqh-20240320-c2-127-3.2.1.1r
2 Solvent CDCl3
3 Temperature 295.9
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
Br
O
OH
Si
O
dr = 86:14
137 136 135 134 133 132 131 130 129 128 127 126
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

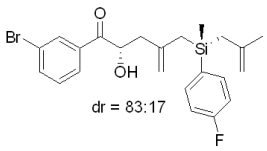
C48


7.99 7.98 7.97 7.75 7.74 7.64 7.62 7.40 7.39 7.37 7.36 7.35 7.35 7.34 7.33 7.30 7.27 7.26 7.25 5.06 5.05 5.04 5.03 4.73 4.72 4.70 4.69 4.68 4.59 4.45 3.51 3.50 2.25 2.25 2.23 2.22 2.01 2.00 1.99 1.97 1.90 1.88 1.87 1.85 1.85 1.81 1.79 1.78 1.55 0.33 0.32
Br
O
OH
Si
Cl
dr = 86:14
Parameter Value
1 Title caoqh-20240403-c2-133-7.11.1.1r
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 600.17
6 Nucleus 1H
0.14
0.86
7.70 7.68 7.66 7.64 7.62 7.60
f1 (ppm)
1.01 1.02 0.14 0.86 3.08 0.44 1.56 1.10 2.13 1.00 1.00 1.04 1.14 1.02 2.03 1.99 2.96 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
200.36
142.41 141.50 136.90 135.90 135.75 135.60 135.40 131.64 130.57 128.18 127.04 123.36 112.71 109.99
72.32
43.99
26.01 25.47 24.60
-5.24
Br
O
OH
Si
Cl
dr = 86:14
Parameter Value
1 Title caoqh-20240403-c2-133-7.12.1.1r
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
137 136 135 134 133 132 131 130 129 128 127
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

C49


7.99 7.98 7.75 7.74 7.65 7.64 7.46 7.45 7.43 7.42 7.40 7.39 7.35 7.34 7.32 7.02 7.01 6.99 6.98 5.06 5.05 5.05 5.04 5.04 5.03 4.69 4.68 4.59 4.46 3.49 3.48 2.25 2.25 2.23 2.22 2.01 1.99 1.98 1.97 1.90 1.88 1.87 1.85 1.82 1.79 1.79 1.78 1.77 1.55 0.34 0.32
Br
O
OH
Si
F
dr = 83:17
Parameter Value
1 Title as-20240826-cqh-c2-133-5-0826.1.1.1r
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 600.17
6 Nucleus 1H
0.17
0.83
7.72 7.70 7.68 7.66 7.64 7.62
f1 (ppm)
0.95 0.93 0.17 0.83 2.00 1.00 1.96 1.00 2.00 1.00 1.00 0.94 1.00 1.00 2.00 2.00 3.00 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

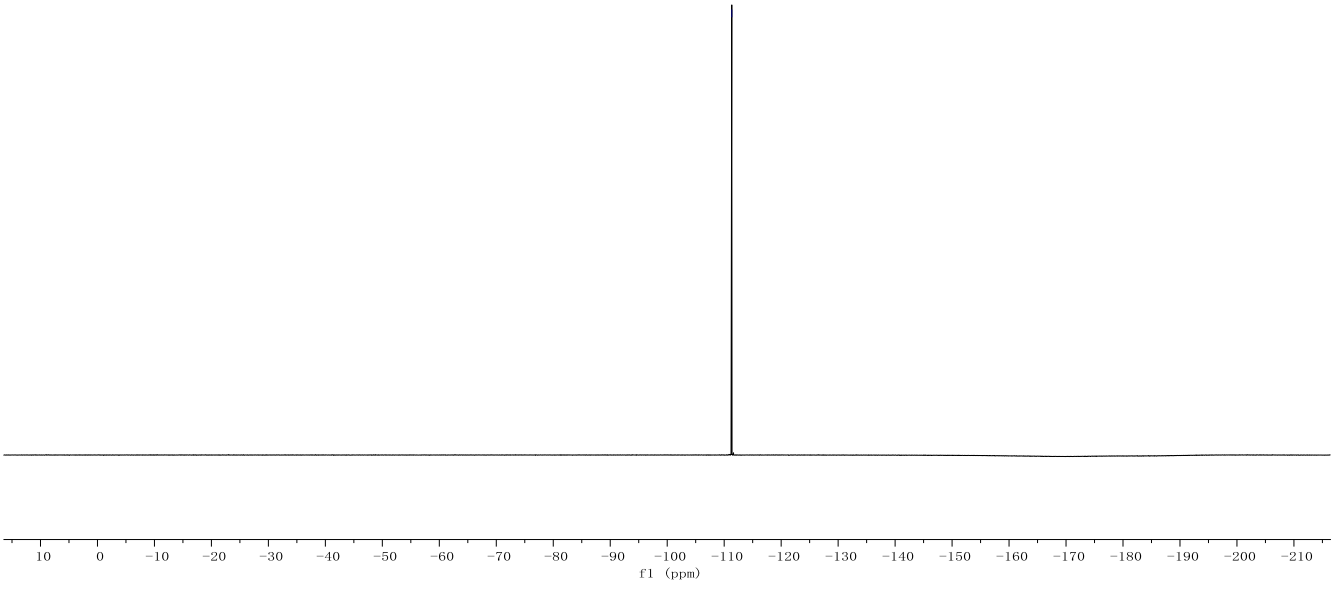

200.38
164.74 163.09 142.56 141.63 136.89 136.01 135.96 135.63 132.68 132.65 131.66 130.55 127.07 123.35 115.20 115.07 112.60 109.88
72.34
44.01
26.15 25.46 24.75
-5.10
Br
O
OH
Si
F
dr = 83:17
Parameter Value
1 Title as-20240826-cqh-c2-133-5-0826.2.1.1r
2 Solvent CDCl3
3 Temperature 295.2
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
115 114 113
f1 (ppm)
136 135 134 133
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



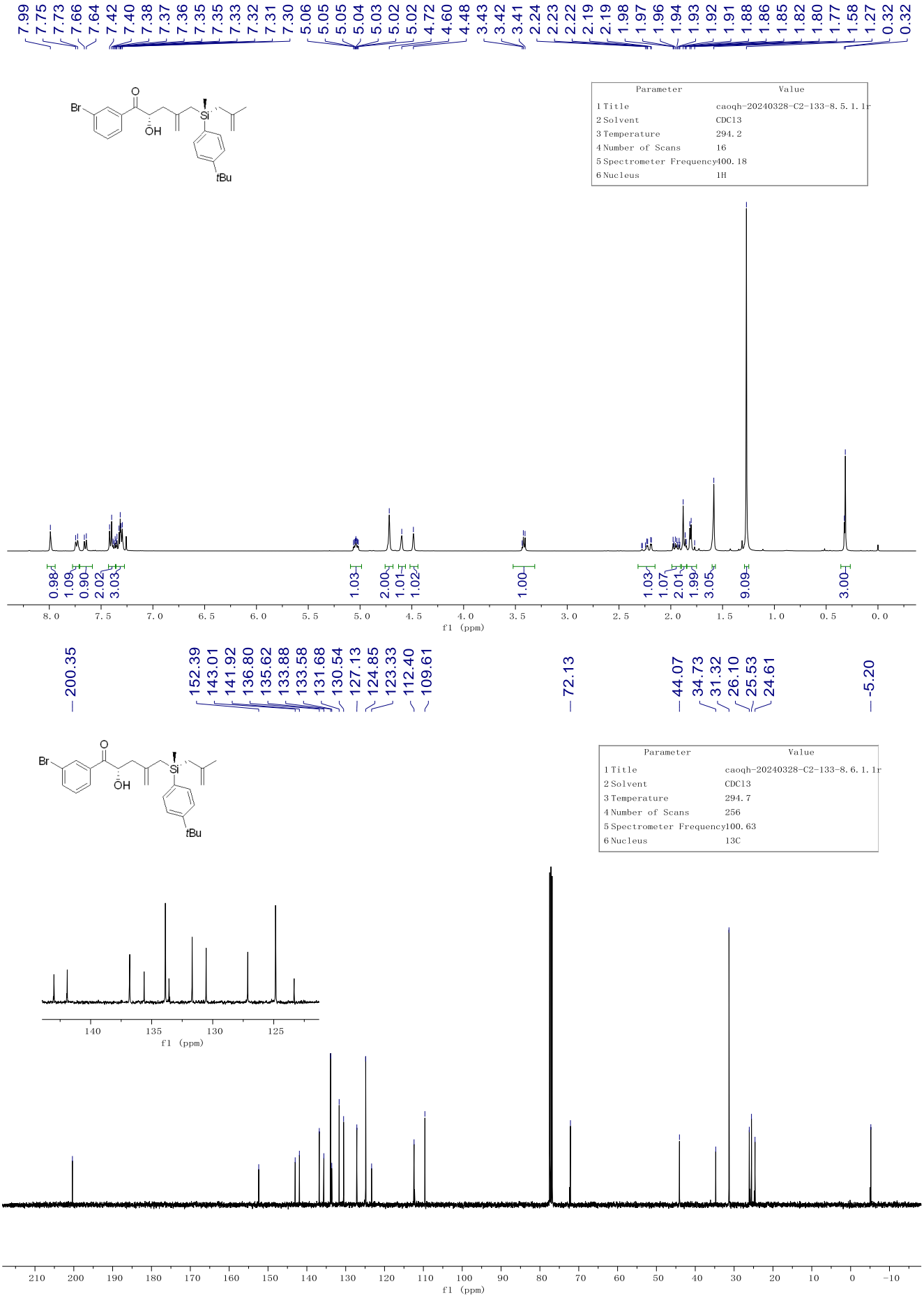
dr = 83:17

-111.33

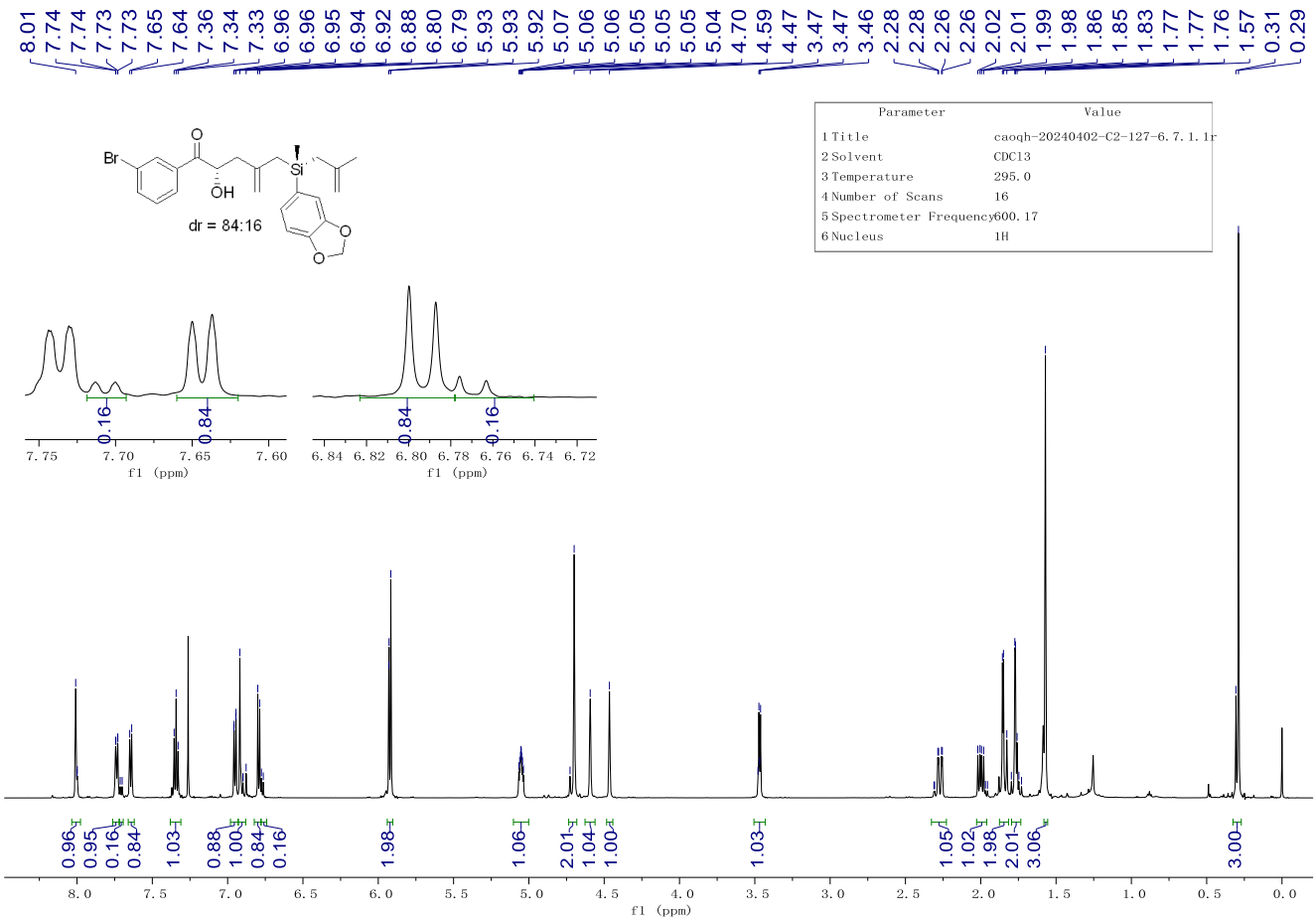
Parameter	Value
1 Title	as-20240826-cqh-c2-133-5-0826.3.1.1r
2 Solvent	CDCl3
3 Temperature	295.1
4 Number of Scans	16
5 Spectrometer Frequency	564.72
6 Nucleus	19F

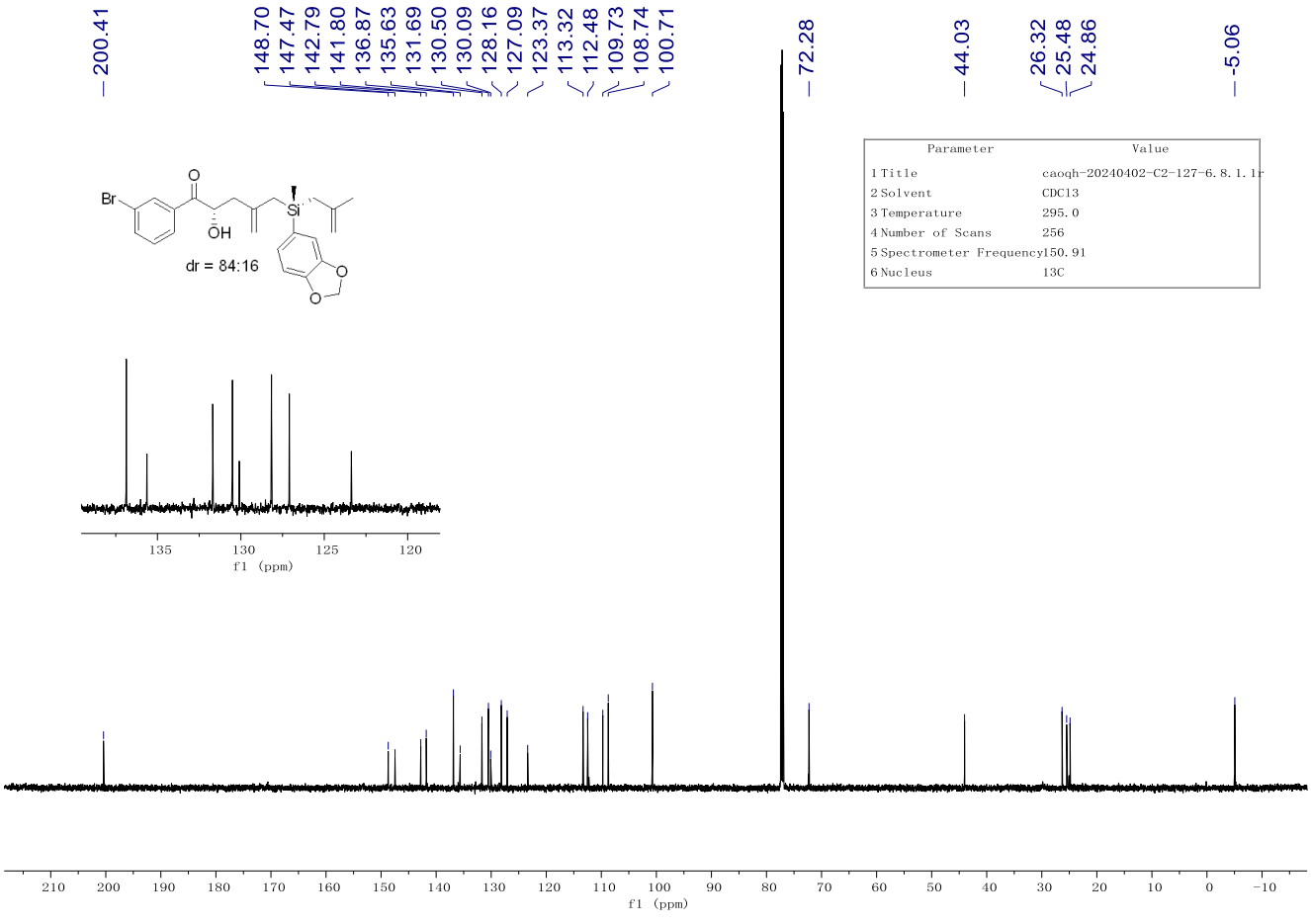


C50

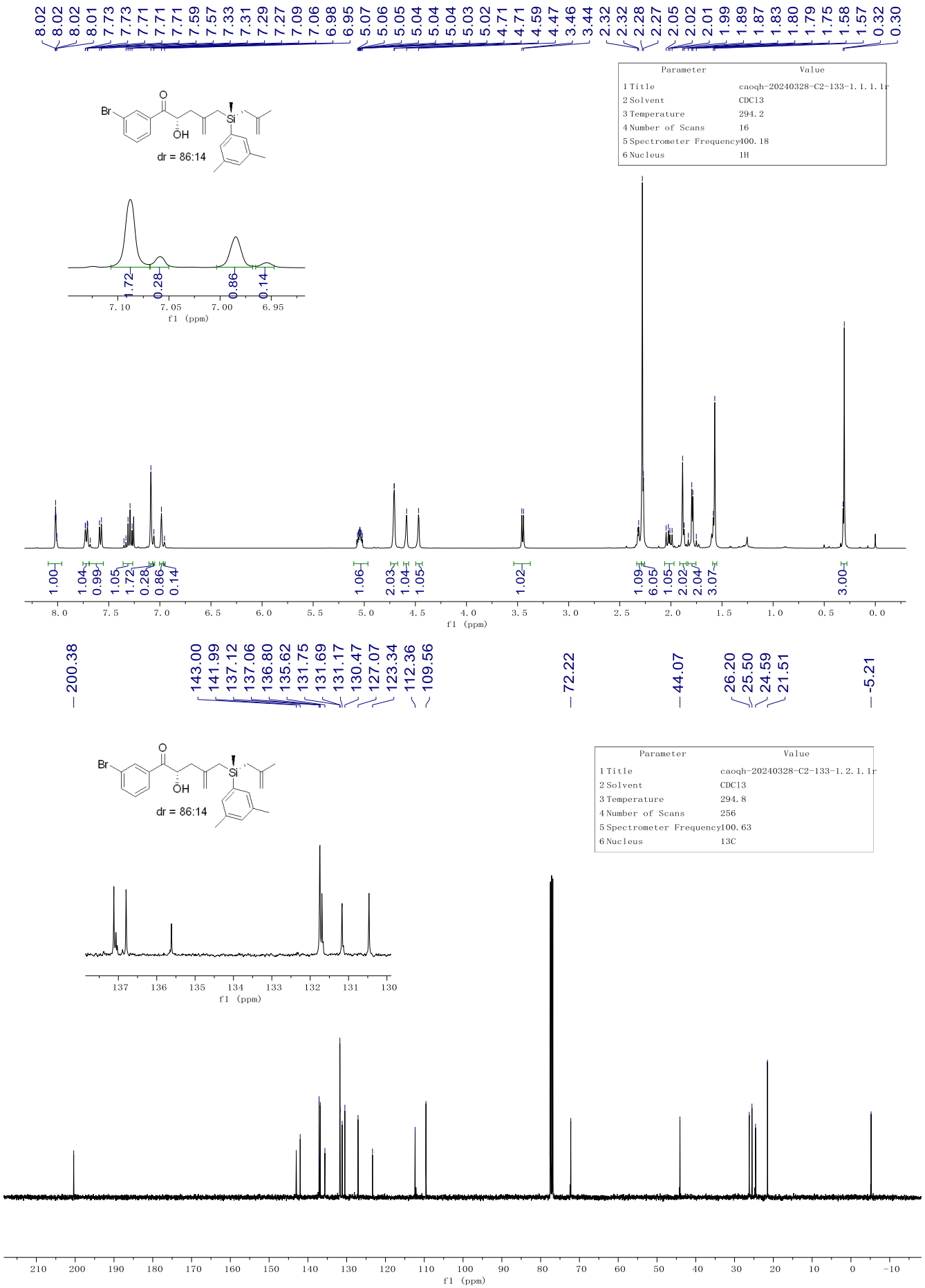

7.99 7.75 7.73 7.66 7.64 7.42 7.40 7.38 7.37 7.36 7.35 7.35 7.33 7.32 7.31 7.30 5.06 5.05 5.05 5.04 5.03 5.02 5.02 4.72 4.60 4.48 3.43 3.42 3.41 2.24 2.23 2.22 2.19 2.19 1.98 1.97 1.96 1.94 1.93 1.92 1.91 1.88 1.86 1.85 1.82 1.80 1.77 1.58 1.27 0.32 0.32
Br
O
OH
Si
tBu
Parameter Value
1 Title caoqh-20240328-C2-133-8.5.1.1r
2 Solvent CDCl3
3 Temperature 294.2
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
0.98 1.09 0.90 2.02 3.03 1.03 2.00 1.01 1.02 1.00 1.03 1.07 2.01 1.99 3.05 9.09 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
200.35 152.39 143.01 141.92 136.80 135.62 133.88 133.58 131.68 130.54 127.13 124.85 123.33 112.40 109.61 72.13 44.07 34.73 31.32 26.10 25.53 24.61 -5.20
Br
O
OH
Si
tBu
Parameter Value
1 Title caoqh-20240328-C2-133-8.6.1.1r
2 Solvent CDCl3
3 Temperature 294.7
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
140 135 130 125
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

C51

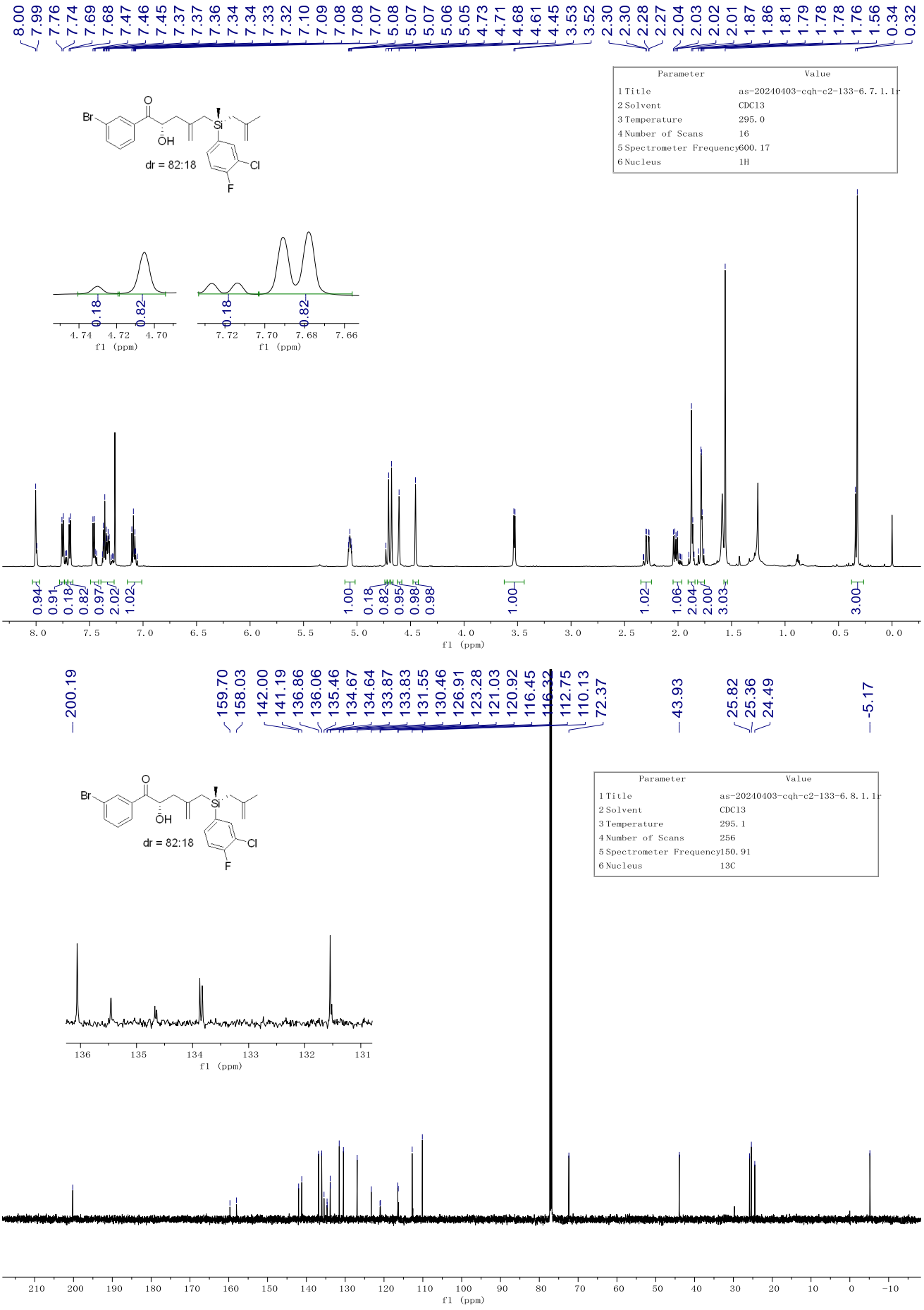

8.01 7.74 7.74 7.73 7.73 7.65 7.64 7.36 7.34 7.33 6.96 6.96 6.95 6.94 6.92 6.88 6.80 6.79 5.93 5.93 5.92 5.07 5.06 5.06 5.05 5.05 5.05 5.04 4.70 4.59 4.47 3.47 3.47 3.46 2.28 2.28 2.26 2.26 2.02 2.01 1.99 1.98 1.86 1.85 1.83 1.77 1.77 1.76 1.57 0.31 0.29
Parameter Value
1 Title caoqh-20240402-C2-127-6.7.1.1r
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 600.17
6 Nucleus 1H
Br
O
OH
Si
O
O
dr = 84:16
0.16 0.84
0.84 0.16
f1 (ppm)
0.96 0.95 0.16 0.84 1.03 0.88 1.00 0.84 0.16 1.98 1.06 2.01 1.04 1.00 1.03 1.05 1.02 1.98 2.01 3.06 3.00
f1 (ppm)


200.41
148.70 147.47 142.79 141.80 136.87 135.63 131.69 130.50 130.09 128.16 127.09 123.37 113.32 112.48 109.73 108.74 100.71
72.28
44.03
26.32 25.48 24.86
-5.06
Parameter Value
1 Title caoqh-20240402-C2-127-6.8.1.1r
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
Br
O
OH
Si
O
O
dr = 84:16
f1 (ppm)
f1 (ppm)

C52

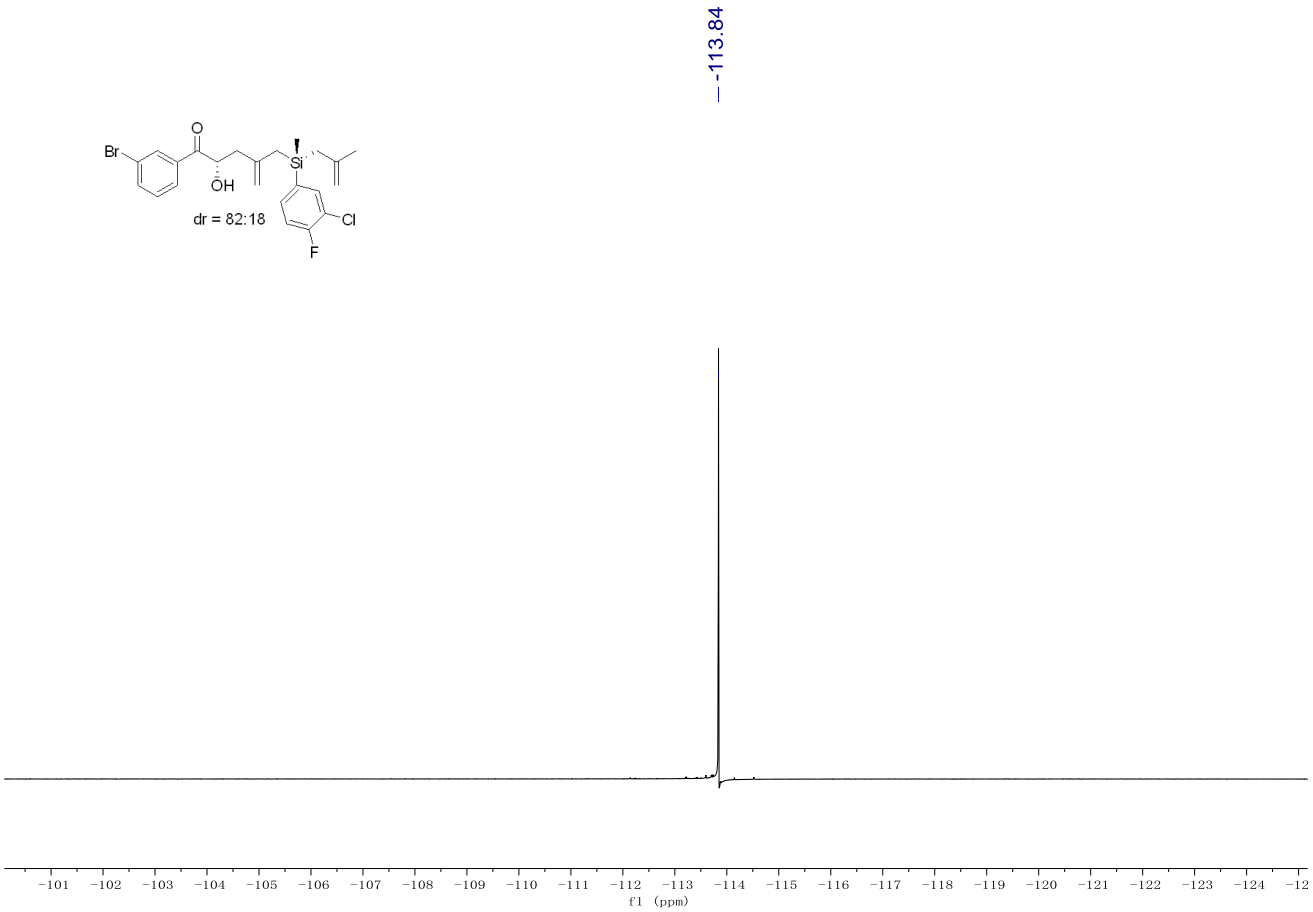

8.02 8.02 8.02 8.01 7.73 7.73 7.71 7.71 7.71 7.59 7.57 7.33 7.31 7.29 7.27 7.09 7.06 6.98 6.95 5.07 5.06 5.05 5.04 5.04 5.04 5.03 5.02 4.71 4.71 4.59 4.47 3.46 3.44 2.32 2.32 2.28 2.27 2.05 2.02 2.01 1.99 1.89 1.87 1.83 1.80 1.79 1.75 1.58 1.57 0.32 0.30
Parameter Value
1 Title caoqh-20240328-C2-133-1.1.1.1r
2 Solvent CDCl3
3 Temperature 294.2
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
Br
O
OH
Si
dr = 86:14
1.72 0.28 0.86 0.14
7.10 7.05 7.00 6.95
f1 (ppm)
1.00 1.04 0.99 1.05 1.72 0.28 0.86 0.14 1.06 2.03 1.04 1.05 1.02 1.09 6.05 1.05 2.02 2.04 3.07 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
200.38
143.00 141.99 137.12 137.06 136.80 135.62 131.75 131.69 131.17 130.47 127.07 123.34 112.36 109.56
72.22
44.07
26.20 25.50 24.59 21.51
-5.21
Parameter Value
1 Title caoqh-20240328-C2-133-1.2.1.1r
2 Solvent CDCl3
3 Temperature 294.8
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
Br
O
OH
Si
dr = 86:14
137 136 135 134 133 132 131 130
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

C53

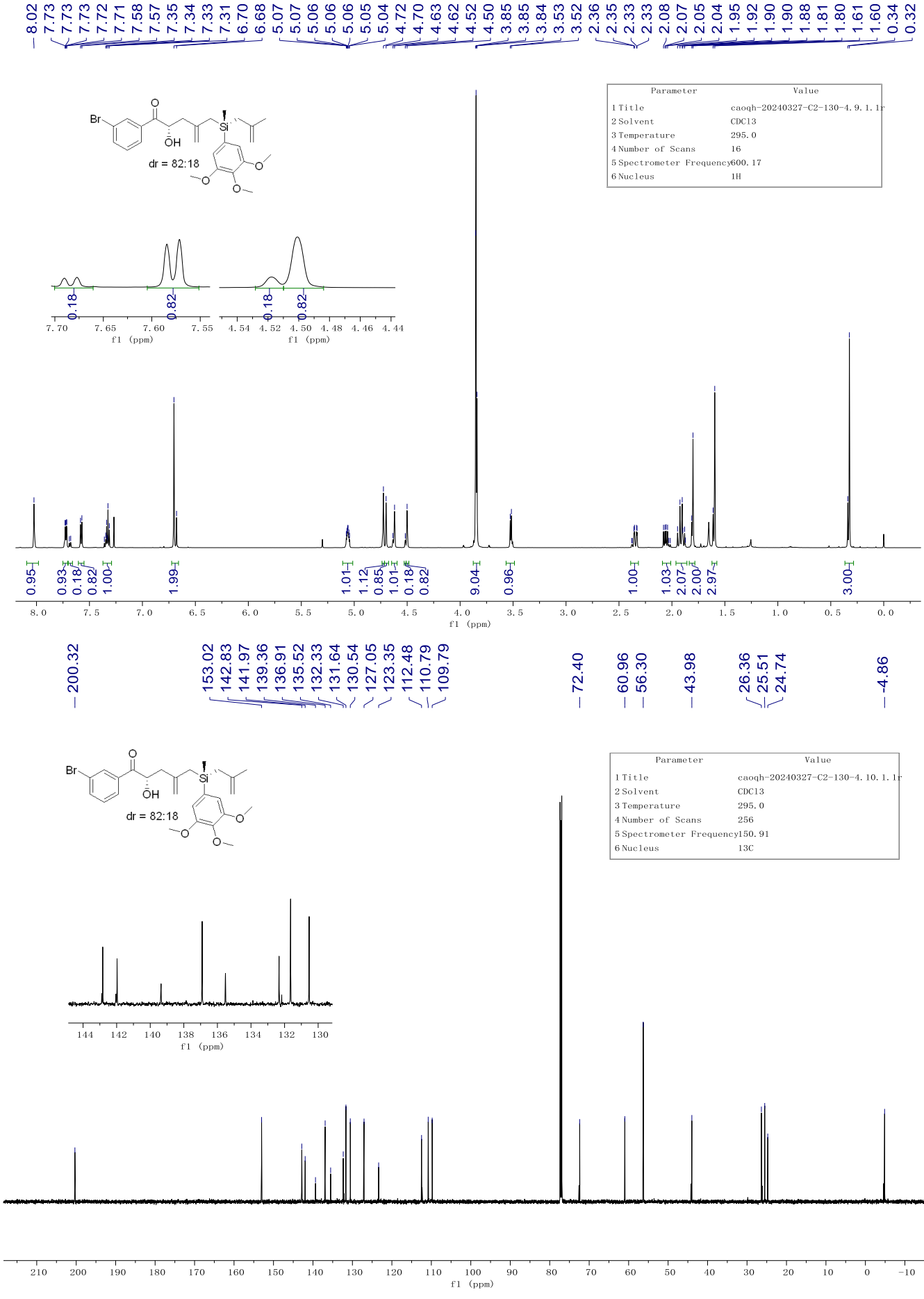

8.00 7.99 7.76 7.74 7.69 7.68 7.47 7.46 7.45 7.37 7.37 7.36 7.34 7.34 7.33 7.32 7.10 7.09 7.08 7.08 7.07 5.08 5.07 5.07 5.06 5.05 4.73 4.71 4.68 4.61 4.45 3.53 3.52 2.30 2.30 2.28 2.27 2.04 2.03 2.02 2.01 1.87 1.86 1.81 1.79 1.78 1.78 1.76 1.56 0.34 0.32
Parameter Value
1 Title as-20240403-cqh-c2-133-6.7.1.1r
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 600.17
6 Nucleus 1H
dr = 82:18
0.18 0.82
f1 (ppm)
0.94 0.91 0.18 0.82 0.97 2.02 1.02 1.00 0.18 0.82 0.95 0.98 0.98 1.00 1.02 1.06 2.04 2.00 3.03 3.00
f1 (ppm)
200.19 159.70 158.03 142.00 141.19 136.86 136.06 135.46 134.67 134.64 133.87 133.83 131.55 130.46 126.91 123.28 121.03 120.92 116.45 116.32 112.75 110.13 72.37 43.93 25.82 25.36 24.49 -5.17
Parameter Value
1 Title as-20240403-cqh-c2-133-6.8.1.1r
2 Solvent CDCl3
3 Temperature 295.1
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
dr = 82:18
f1 (ppm)
f1 (ppm)

O
Br
OH
Si
Cl
F

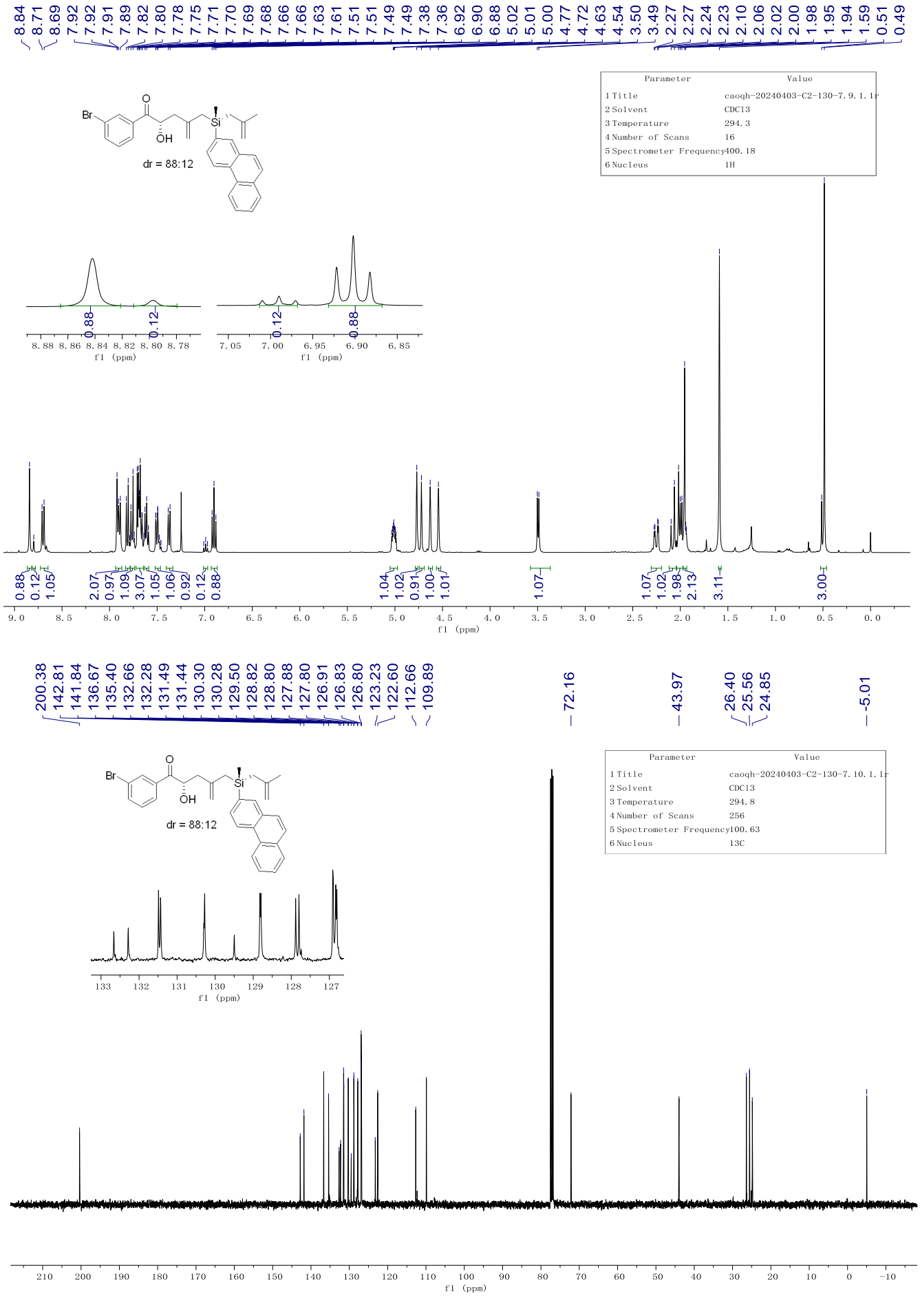
dr = 82:18


-113.84
−101 −102 −103 −104 −105 −106 −107 −108 −109 −110 −111 −112 −113 −114 −115 −116 −117 −118 −119 −120 −121 −122 −123 −124 −12
f1 (ppm)

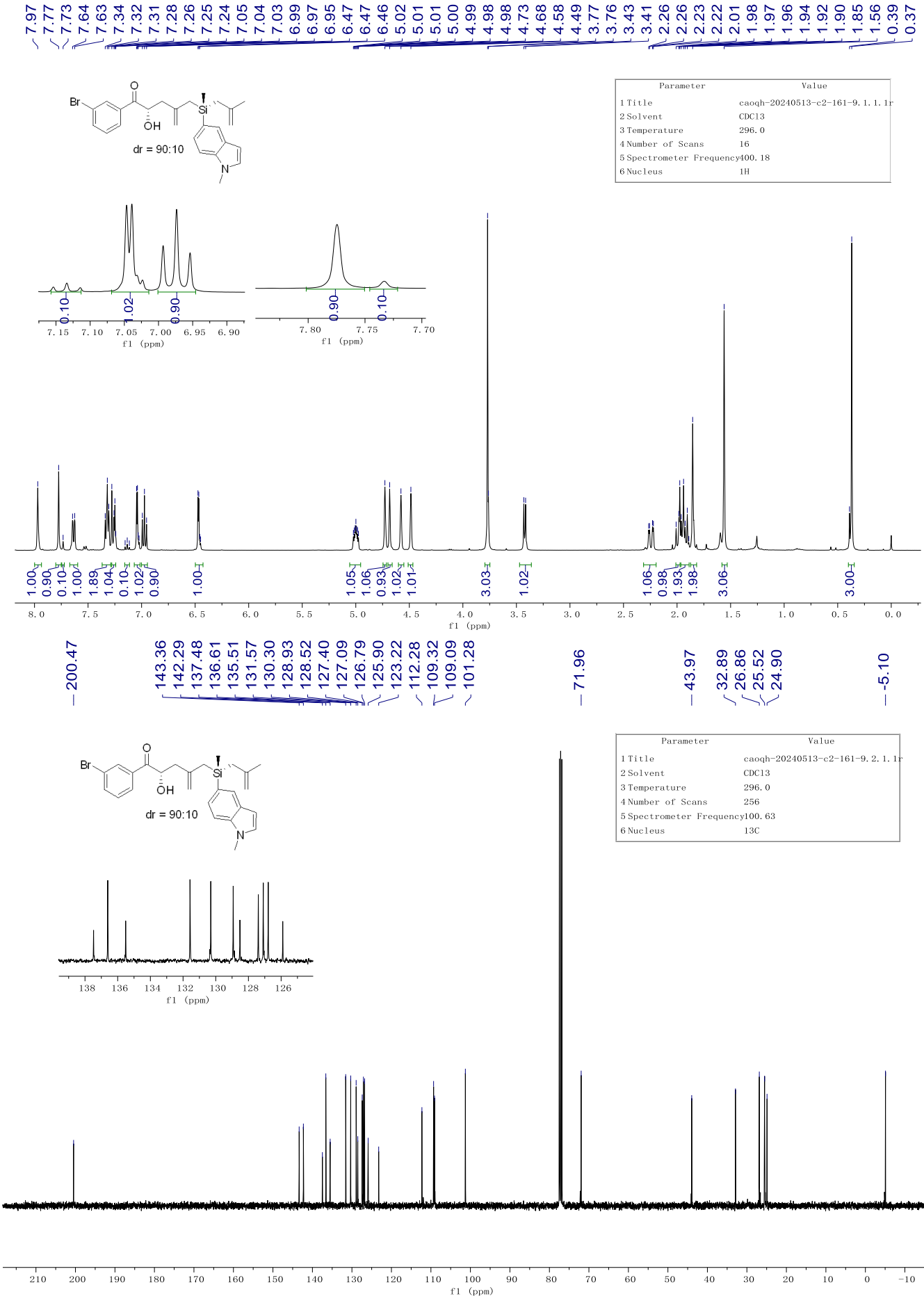
C54


8.02 7.73 7.73 7.73 7.72 7.71 7.58 7.57 7.35 7.34 7.33 7.31 6.70 6.68 5.07 5.07 5.06 5.06 5.06 5.05 5.04 4.72 4.70 4.63 4.62 4.52 4.50 3.85 3.84 3.53 3.52 2.36 2.35 2.33 2.33 2.08 2.07 2.05 2.04 1.95 1.92 1.90 1.90 1.88 1.81 1.80 1.61 1.60 0.34 0.32
Br
O
OH
Si
O
O
O
dr = 82:18
Parameter Value
1 Title caoqh-20240327-C2-130-4.9.1.1r
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 600.17
6 Nucleus 1H
0.18 0.82
7.70 7.65 7.60 7.55
f1 (ppm)
0.18 0.82
4.54 4.52 4.50 4.48 4.46 4.44
f1 (ppm)
0.95 0.93 0.18 0.82 1.00 1.99 1.01 1.12 0.85 1.01 0.18 0.82 9.04 0.96 1.00 1.03 2.07 2.00 2.97 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
200.32 153.02 142.83 141.97 139.36 136.91 135.52 132.33 131.64 130.54 127.05 123.35 112.48 110.79 109.79 72.40 60.96 56.30 43.98 26.36 25.51 24.74 -4.86
Br
O
OH
Si
O
O
O
dr = 82:18
Parameter Value
1 Title caoqh-20240327-C2-130-4.10.1.1r
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
144 142 140 138 136 134 132 130
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

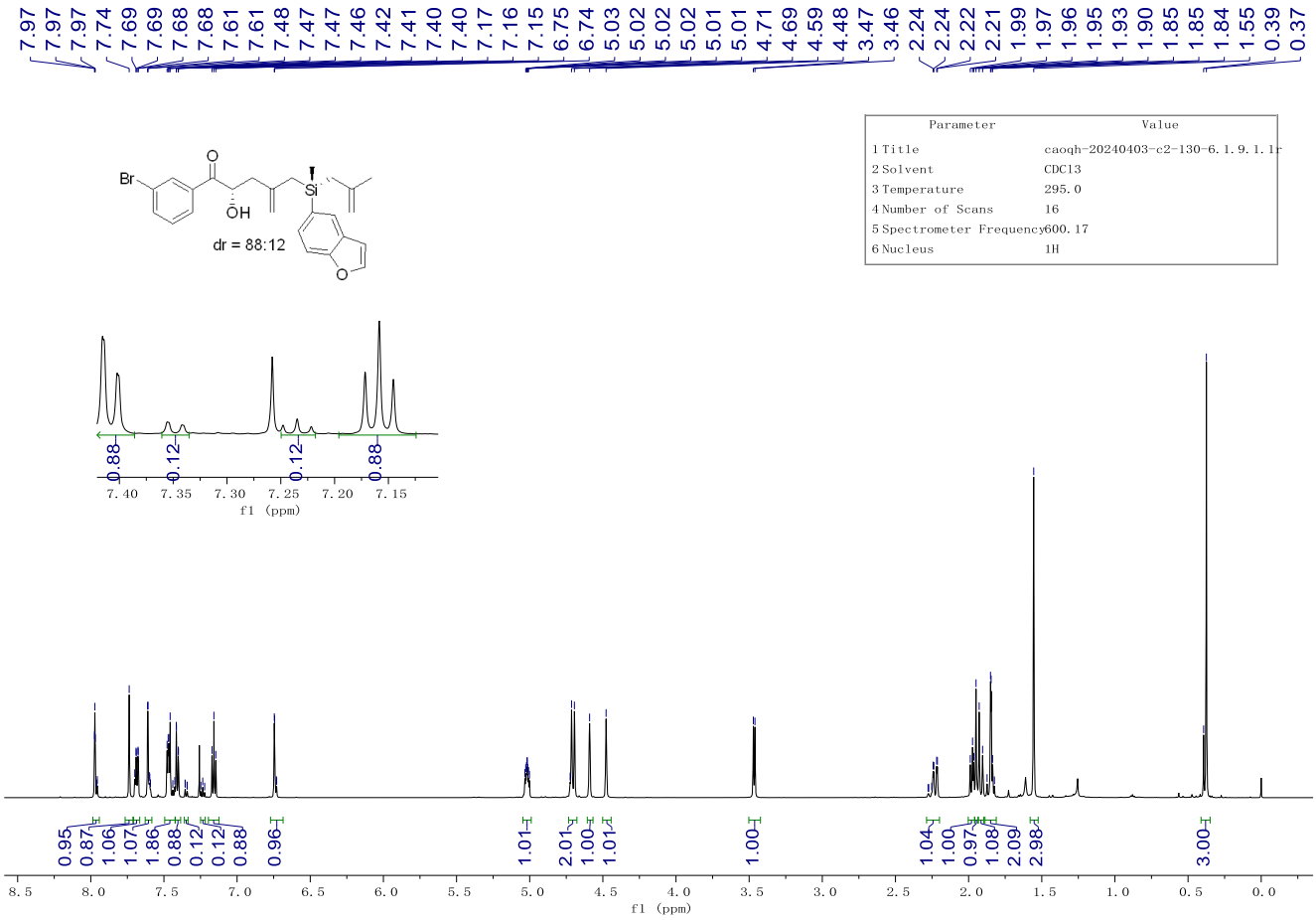
C55

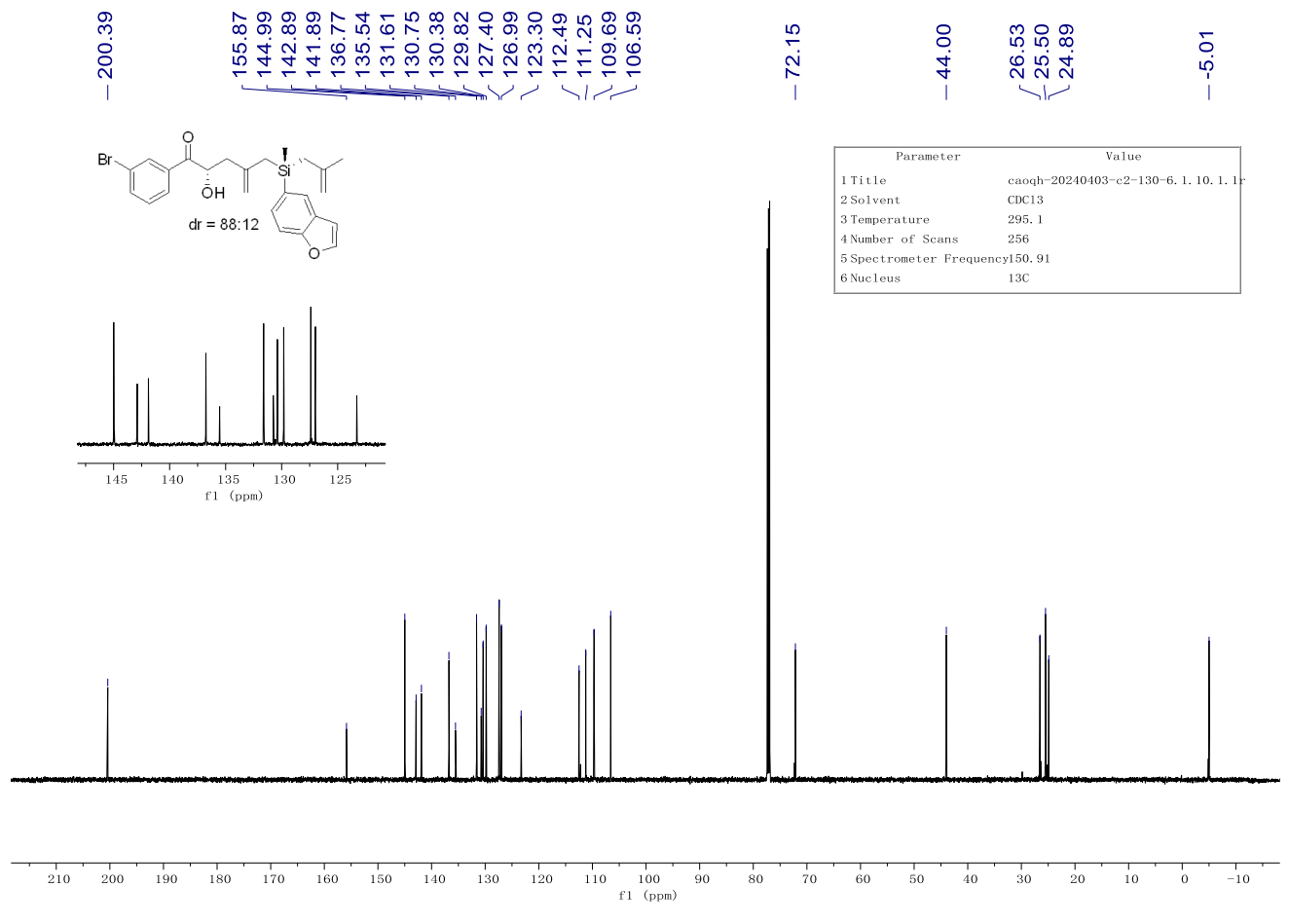

8.84 8.71 8.69 7.92 7.92 7.91 7.89 7.82 7.80 7.78 7.75 7.71 7.70 7.69 7.68 7.66 7.66 7.63 7.61 7.51 7.51 7.49 7.49 7.38 7.36 6.92 6.90 6.88 5.02 5.01 5.00 4.77 4.72 4.63 4.54 3.50 3.49 2.27 2.27 2.24 2.23 2.10 2.06 2.02 2.00 1.98 1.95 1.94 1.59 0.51 0.49
Br
O
OH
Si
dr = 88:12
Parameter Value
1 Title caoqh-20240403-C2-130-7.9.1.1r
2 Solvent CDCl3
3 Temperature 294.3
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
0.88 0.12
8.88 8.86 8.84 8.82 8.80 8.78
f1 (ppm)
0.12 0.88
7.05 7.00 6.95 6.90 6.85
f1 (ppm)
0.88 0.12 1.05 2.07 0.97 1.09 3.07 1.05 1.06 0.92 0.12 0.88 1.04 1.02 0.91 1.00 1.01 1.07 1.07 1.02 1.98 2.13 3.11 3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
200.38 142.81 141.84 136.67 135.40 132.66 132.28 131.49 131.44 130.30 130.28 129.50 128.82 128.80 127.88 127.80 126.91 126.83 126.80 123.23 122.60 112.66 109.89
72.16
43.97
26.40 25.56 24.85
-5.01
Br
O
OH
Si
dr = 88:12
Parameter Value
1 Title caoqh-20240403-C2-130-7.10.1.1r
2 Solvent CDCl3
3 Temperature 294.8
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
133 132 131 130 129 128 127
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

C56

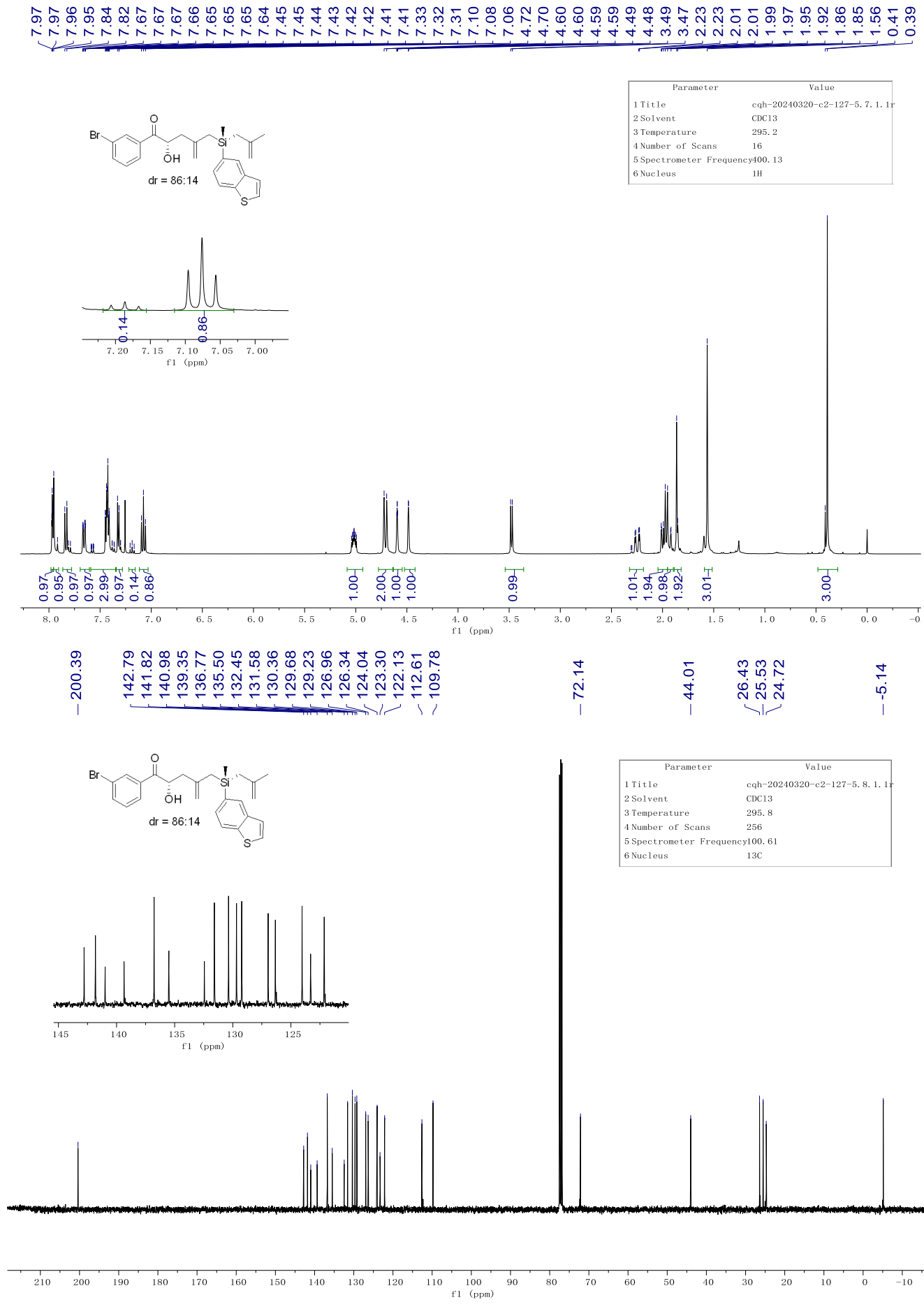

dr = 90:10
Parameter Value
1 Title caoqh-20240513-c2-161-9.1.1.1r
2 Solvent CDCl3
3 Temperature 296.0
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
f1 (ppm)
dr = 90:10
Parameter Value
1 Title caoqh-20240513-c2-161-9.2.1.1r
2 Solvent CDCl3
3 Temperature 296.0
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
f1 (ppm)

C57

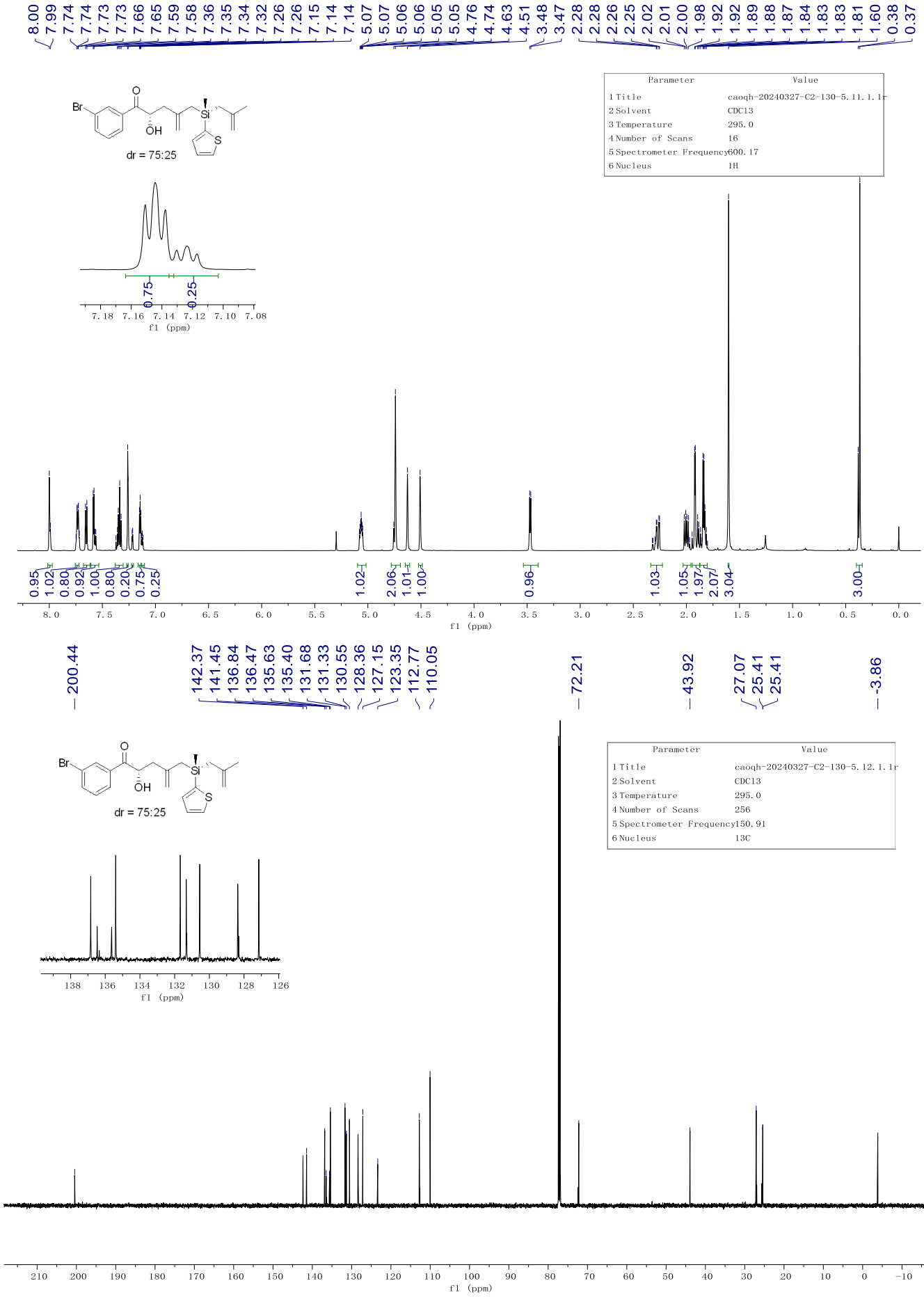

7.97 7.97 7.97 7.74 7.69 7.69 7.68 7.68 7.61 7.61 7.48 7.47 7.47 7.46 7.42 7.41 7.40 7.40 7.17 7.16 7.15 6.75 6.74 5.03 5.02 5.02 5.02 5.01 5.01 4.71 4.69 4.59 4.48 3.47 3.46 2.24 2.24 2.22 2.21 1.99 1.97 1.96 1.95 1.93 1.90 1.85 1.85 1.84 1.55 0.39 0.37
Br
O
OH
Si
O
dr = 88:12
Parameter Value
1 Title caoqh-20240403-c2-130-6.1.9.1.1r
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 600.17
6 Nucleus 1H
0.88 0.12 0.12 0.88
7.40 7.35 7.30 7.25 7.20 7.15
f1 (ppm)
0.95 0.87 1.06 1.07 1.86 0.88 0.12 0.12 0.88 0.96 1.01 2.01 1.00 1.01 1.00 1.04 1.00 0.97 1.08 2.09 2.98 3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


200.39
155.87 144.99 142.89 141.89 136.77 135.54 131.61 130.75 130.38 129.82 127.40 126.99 123.30 112.49 111.25 109.69 106.59
72.15
44.00
26.53 25.50 24.89
-5.01
Br
O
OH
Si
O
dr = 88:12
Parameter Value
1 Title caoqh-20240403-c2-130-6.1.10.1.1r
2 Solvent CDCl3
3 Temperature 295.1
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
145 140 135 130 125
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

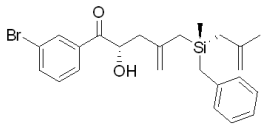
C58


7.97 7.97 7.96 7.95 7.84 7.82 7.67 7.67 7.67 7.66 7.65 7.65 7.65 7.64 7.45 7.45 7.44 7.43 7.42 7.42 7.41 7.41 7.33 7.32 7.31 7.10 7.08 7.06 4.72 4.70 4.60 4.60 4.59 4.59 4.49 4.48 3.49 3.47 2.23 2.23 2.01 2.01 1.99 1.97 1.95 1.92 1.86 1.85 1.56 0.41 0.39
Parameter Value
1 Title cqh-20240320-c2-127-5.7.1.1r
2 Solvent CDCl3
3 Temperature 295.2
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
Br
O
OH
Si
S
dr = 86:14
0.14
0.86
7.20 7.15 7.10 7.05 7.00
f1 (ppm)
0.97 0.95 0.97 0.97 2.99 0.97 0.14 0.86 1.00 2.00 1.00 1.00 0.99 1.01 1.94 0.98 1.92 3.01 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
200.39
142.79 141.82 140.98 139.35 136.77 135.50 132.45 131.58 130.36 129.68 129.23 126.96 126.34 124.04 123.30 122.13 112.61 109.78
72.14
44.01
26.43 25.53 24.72
-5.14
Parameter Value
1 Title cqh-20240320-c2-127-5.8.1.1r
2 Solvent CDCl3
3 Temperature 295.8
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
145 140 135 130 125
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

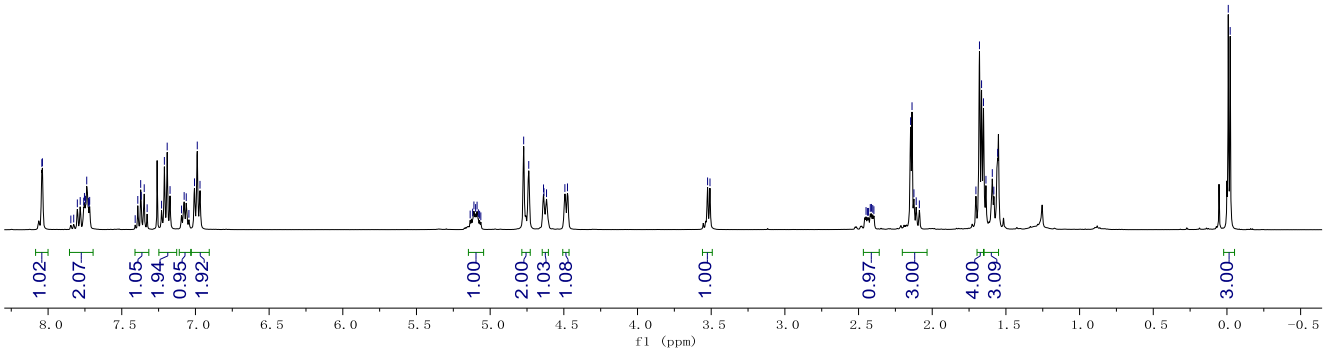
C59

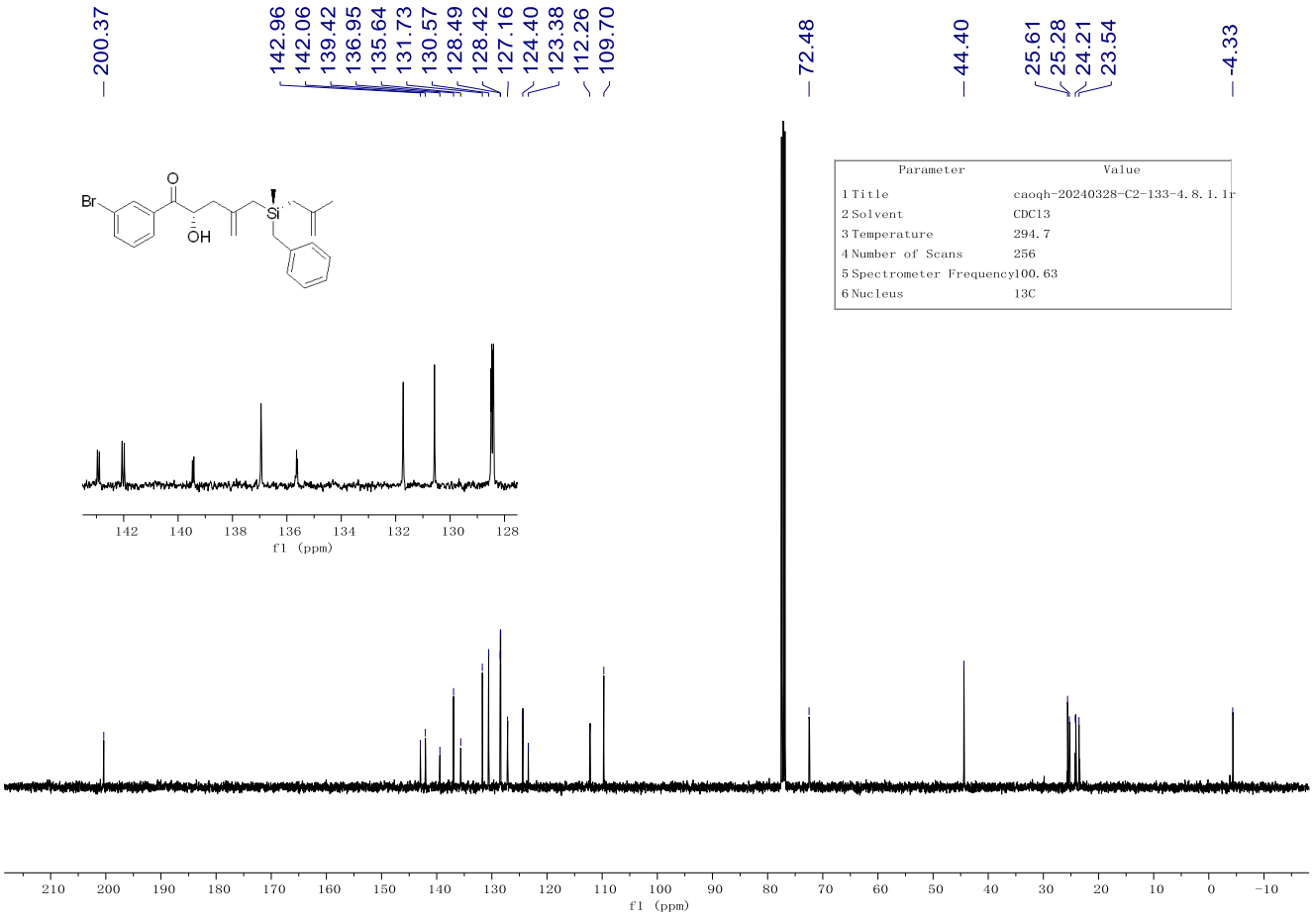

8.00 7.99 7.74 7.74 7.73 7.73 7.66 7.65 7.59 7.58 7.36 7.35 7.34 7.32 7.26 7.26 7.15 7.14 7.14 5.07 5.07 5.06 5.06 5.05 5.05 4.76 4.74 4.63 4.51 3.48 3.47 2.28 2.28 2.26 2.25 2.02 2.01 2.00 1.98 1.92 1.92 1.89 1.88 1.87 1.84 1.83 1.83 1.81 1.60 0.38 0.37
Br
O
OH
Si
S
dr = 75:25
Parameter Value
1 Title caoqh-20240327-C2-130-5.11.1.1r
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 600.17
6 Nucleus 1H
0.75
0.25
7.18 7.16 7.14 7.12 7.10 7.08
f1 (ppm)
0.95 1.02 0.80 0.92 1.00 0.80 0.20 0.75 0.25 1.02 2.06 1.01 1.00 0.96 1.03 1.05 1.97 2.07 3.04 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
200.44
142.37 141.45 136.84 136.47 135.63 135.40 131.68 131.33 130.55 128.36 127.15 123.35 112.77 110.05
72.21
43.92
27.07 25.41 25.41
-3.86
Br
O
OH
Si
S
dr = 75:25
Parameter Value
1 Title caoqh-20240327-C2-130-5.12.1.1r
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
138 136 134 132 130 128 126
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

C60



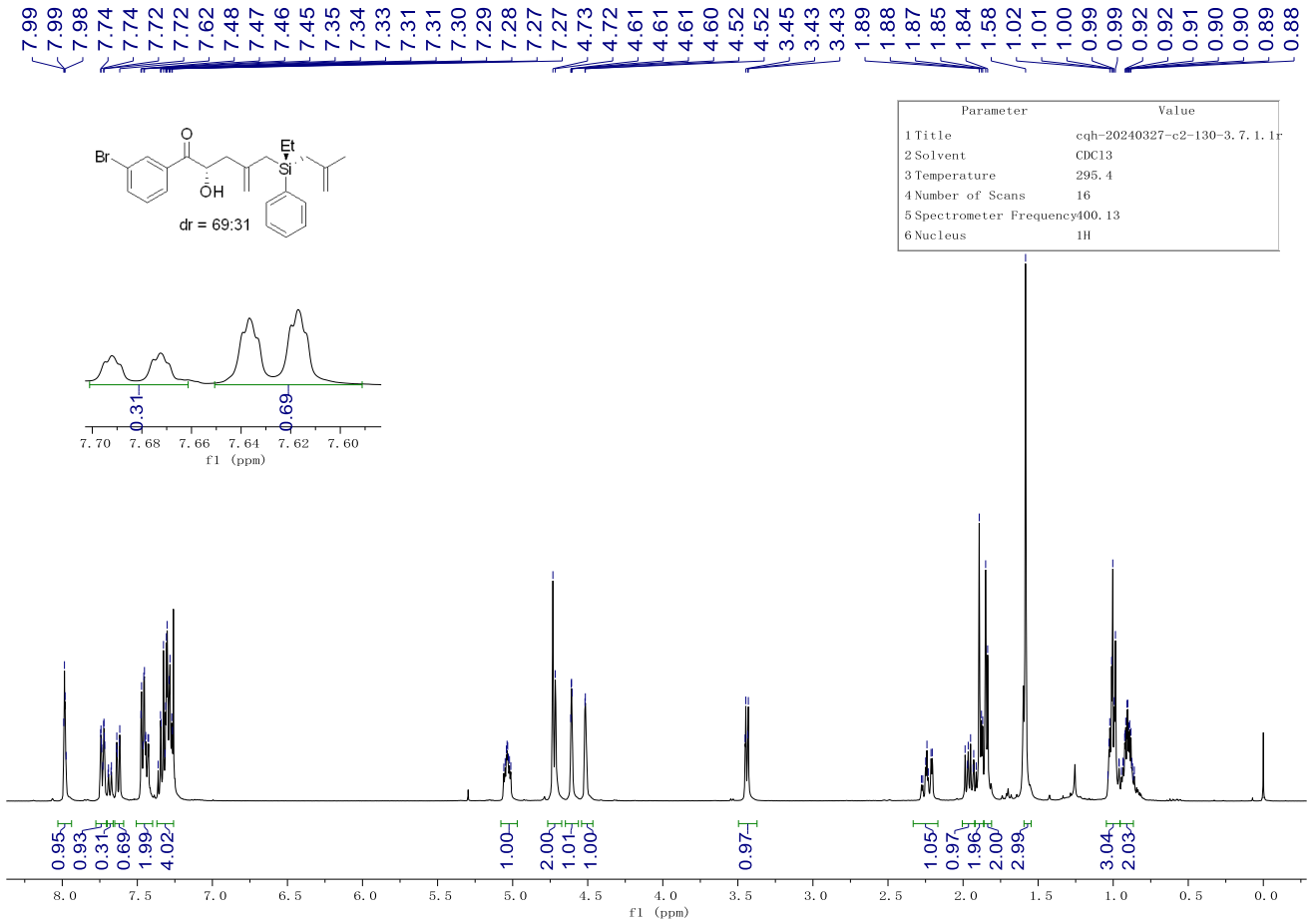
Parameter	Value
1 Title	caoqh-20240328-C2-133-4.7.1.1r
2 Solvent	CDCl3
3 Temperature	294.3
4 Number of Scans	16
5 Spectrometer Frequency	400.18
6 Nucleus	1H

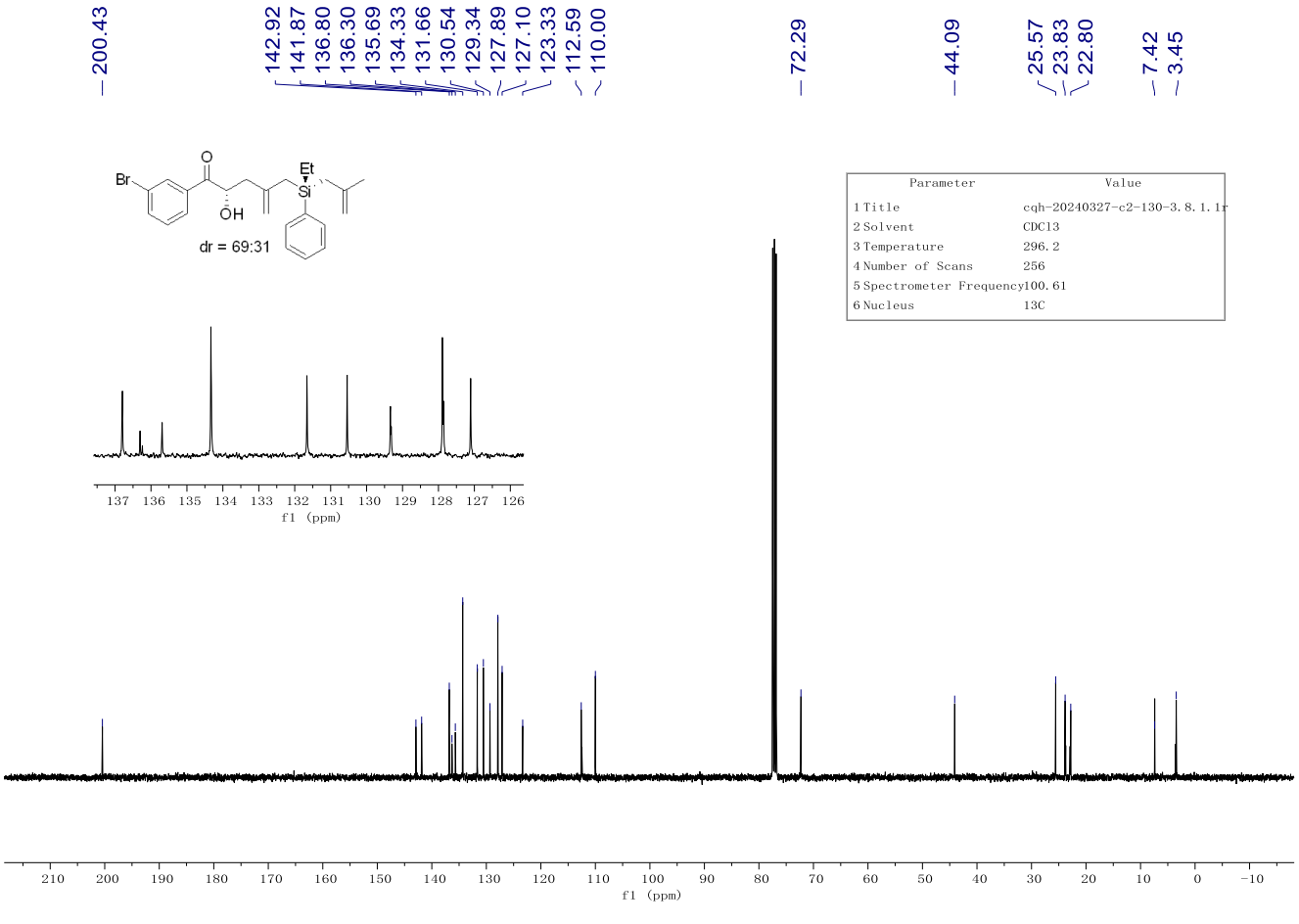




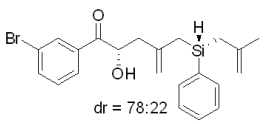
Parameter	Value
1 Title	caoqh-20240328-C2-133-4.8.1.1r
2 Solvent	CDCl3
3 Temperature	294.7
4 Number of Scans	256
5 Spectrometer Frequency	100.63
6 Nucleus	13C

C61

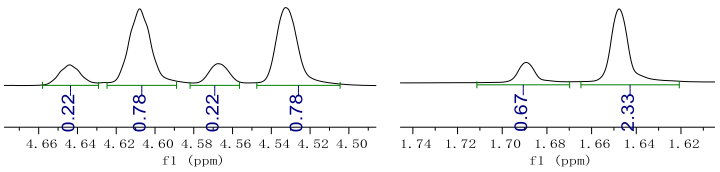

7.99 7.99 7.98 7.74 7.74 7.72 7.72 7.62 7.48 7.47 7.46 7.45 7.35 7.34 7.33 7.31 7.31 7.30 7.29 7.28 7.27 7.27 4.73 4.72 4.61 4.61 4.61 4.60 4.52 4.52 3.45 3.43 3.43 1.89 1.88 1.87 1.85 1.84 1.58 1.02 1.01 1.00 0.99 0.99 0.92 0.92 0.91 0.90 0.90 0.89 0.88
Br
O
Et
Si
OH
dr = 69:31
Parameter Value
1 Title cqh-20240327-c2-130-3.7.1.1r
2 Solvent CDCl3
3 Temperature 295.4
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
0.31
0.69
7.70 7.68 7.66 7.64 7.62 7.60
f1 (ppm)
0.95 0.93 0.31 0.69 1.99 4.02 1.00 2.00 1.01 1.00 0.97 1.05 0.97 1.96 2.00 2.99 3.04 2.03
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

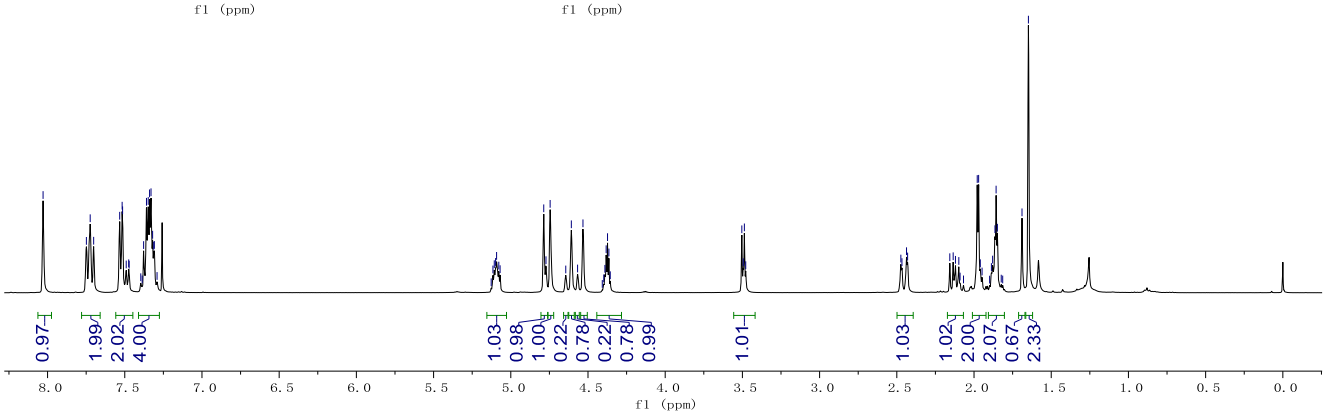

200.43
142.92 141.87 136.80 136.30 135.69 134.33 131.66 130.54 129.34 127.89 127.10 123.33 112.59 110.00
72.29
44.09
25.57 23.83 22.80
7.42 3.45
Br
O
Et
Si
OH
dr = 69:31
Parameter Value
1 Title cqh-20240327-c2-130-3.8.1.1r
2 Solvent CDCl3
3 Temperature 296.2
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
137 136 135 134 133 132 131 130 129 128 127 126
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

C62

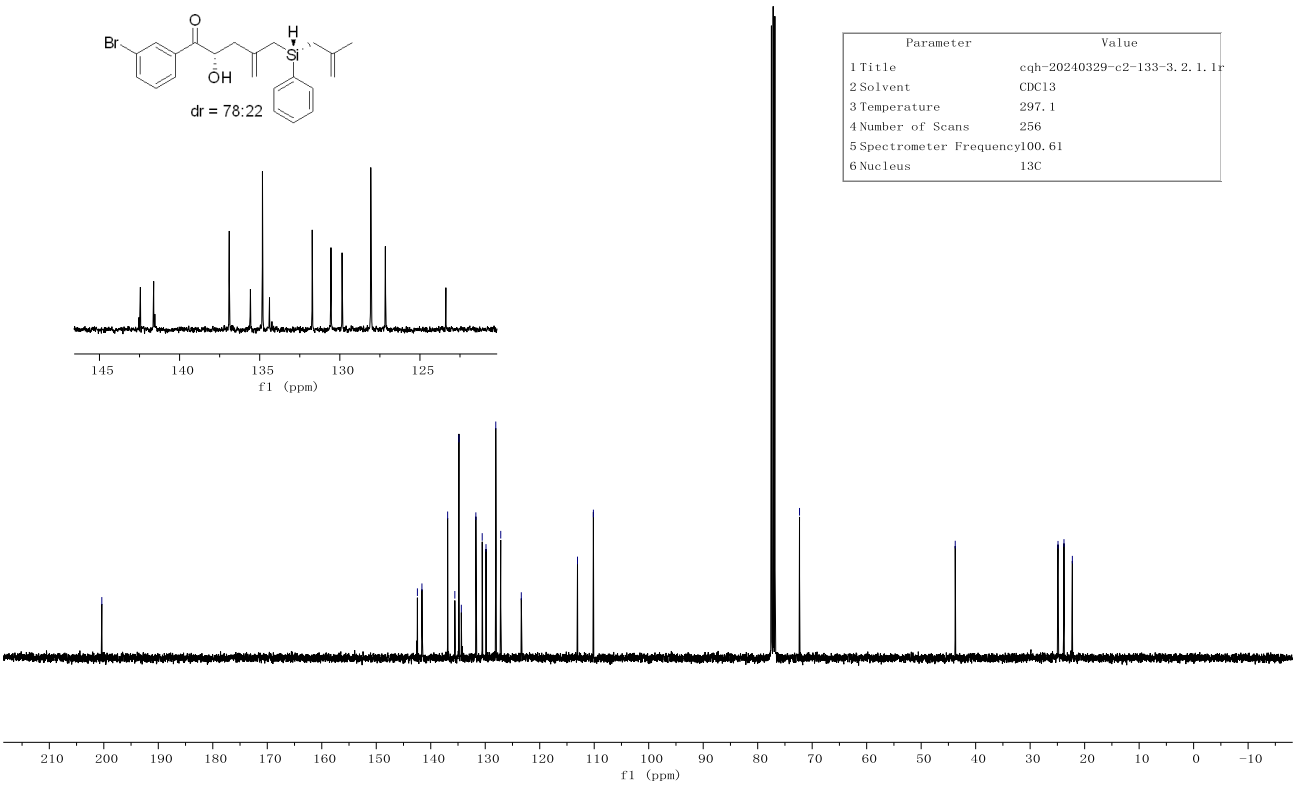


Parameter	Value
1 Title	cqh-20240329-c2-133-3.1.1.1r
2 Solvent	CDCl3
3 Temperature	296.3
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H

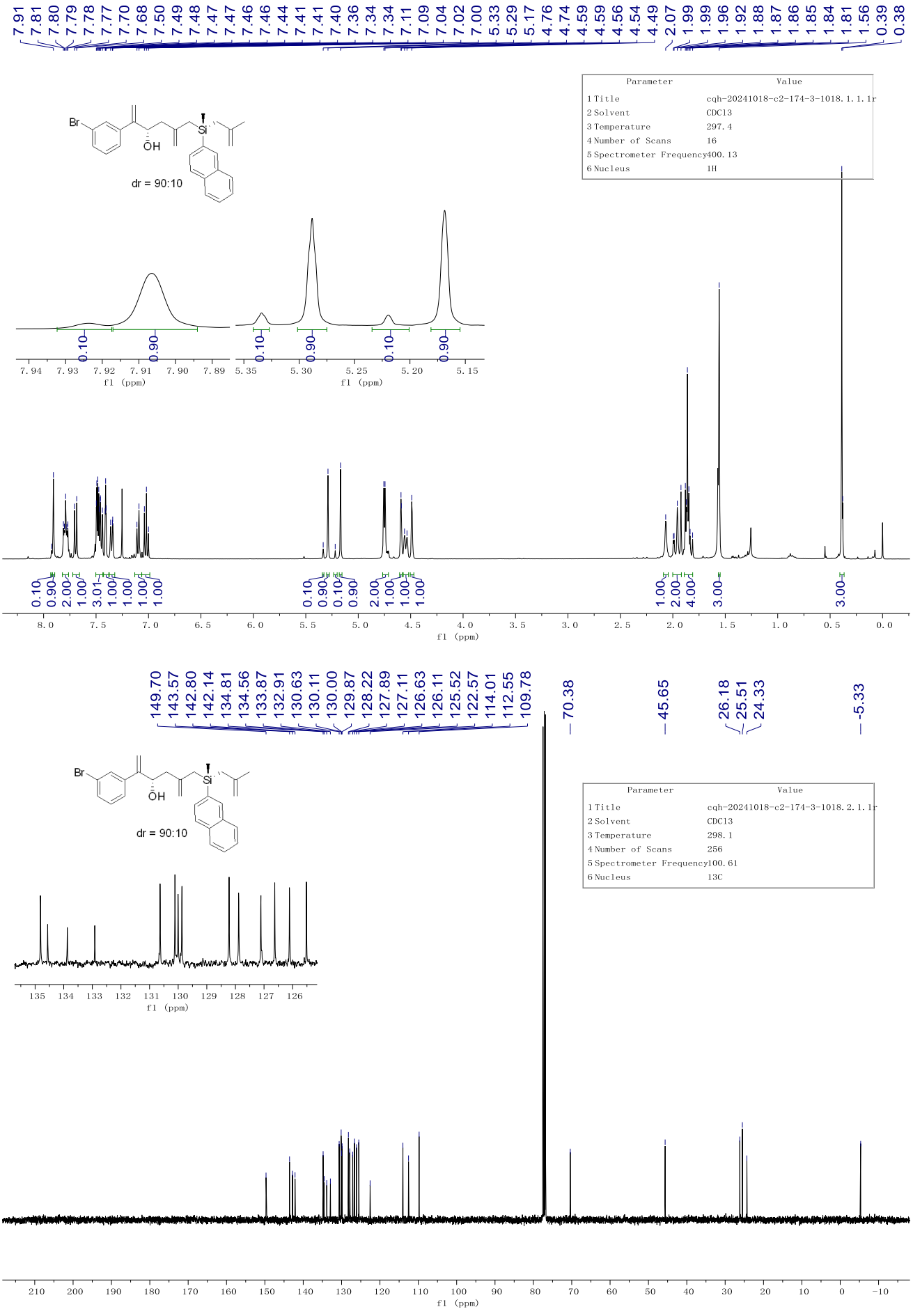




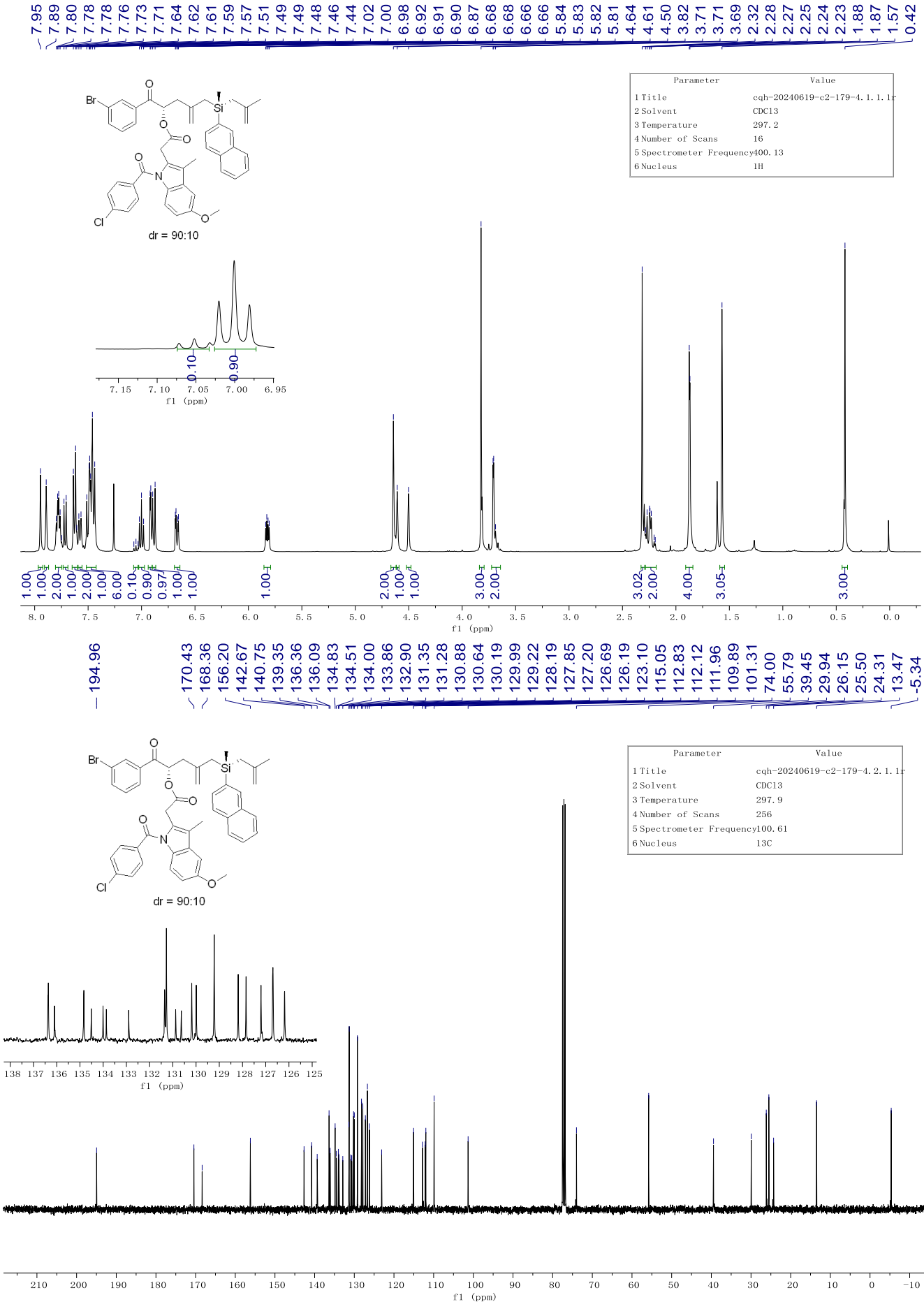
Parameter	Value
1 Title	cqh-20240329-c2-133-3.2.1.1r
2 Solvent	CDCl3
3 Temperature	297.1
4 Number of Scans	256
5 Spectrometer Frequency	100.61
6 Nucleus	13C



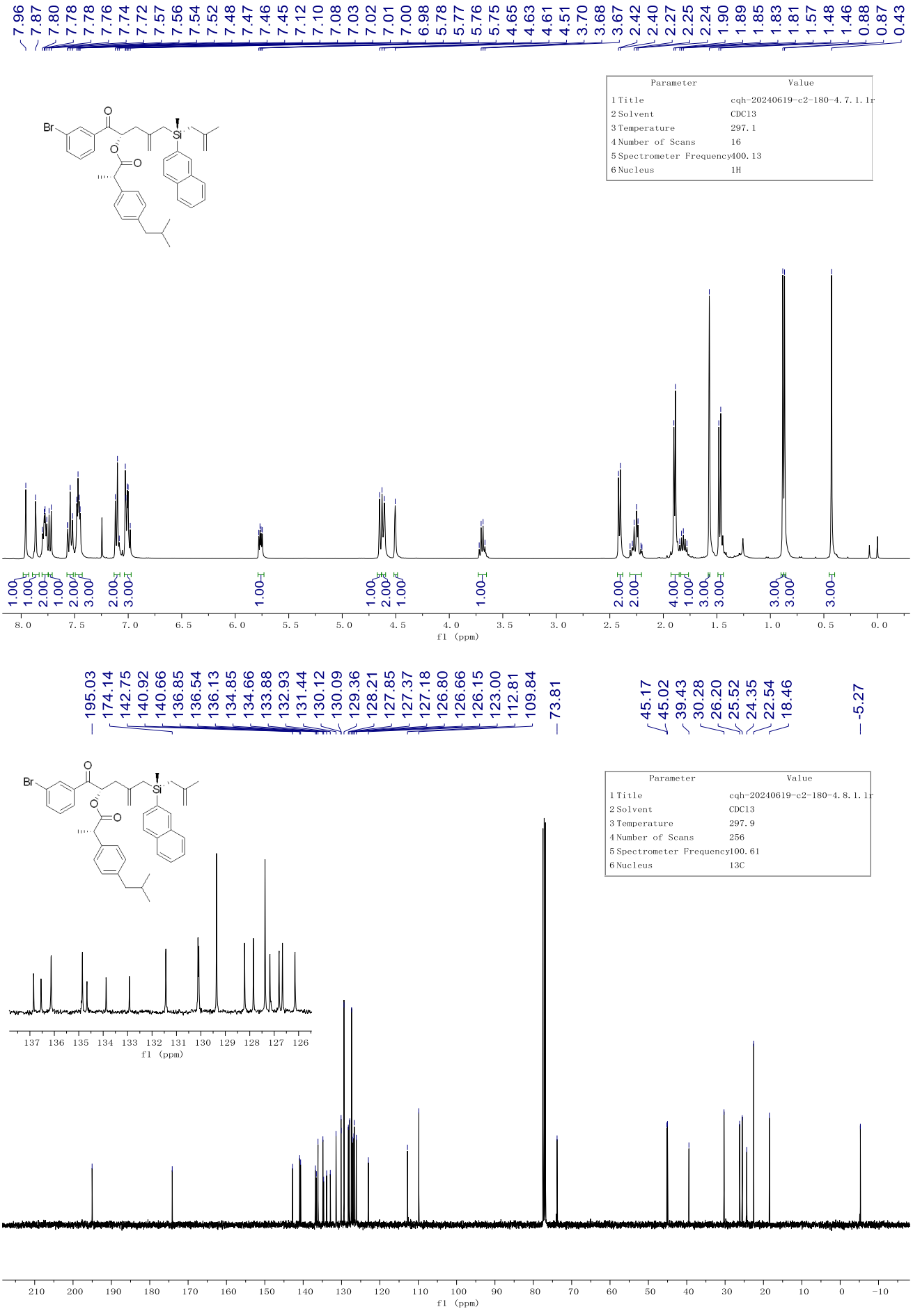
D


7.91 7.81 7.80 7.79 7.78 7.77 7.70 7.68 7.50 7.49 7.48 7.47 7.47 7.46 7.46 7.44 7.41 7.41 7.40 7.36 7.34 7.34 7.11 7.09 7.04 7.02 7.00 5.33 5.29 5.17 4.76 4.74 4.59 4.59 4.56 4.54 4.49 2.07 1.99 1.99 1.96 1.92 1.88 1.87 1.86 1.85 1.84 1.81 1.56 0.39 0.38
Br
OH
Si
dr = 90:10
Parameter Value
1 Title cqh-20241018-c2-174-3-1018.1.1.1r
2 Solvent CDCl3
3 Temperature 297.4
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
f1 (ppm)
149.70 143.57 142.80 142.14 134.81 134.56 133.87 132.91 130.63 130.11 130.00 129.87 128.22 127.89 127.11 126.63 126.11 125.52 122.57 114.01 112.55 109.78 70.38 45.65 26.18 25.51 24.33 -5.33
Parameter Value
1 Title cqh-20241018-c2-174-3-1018.2.1.1r
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C

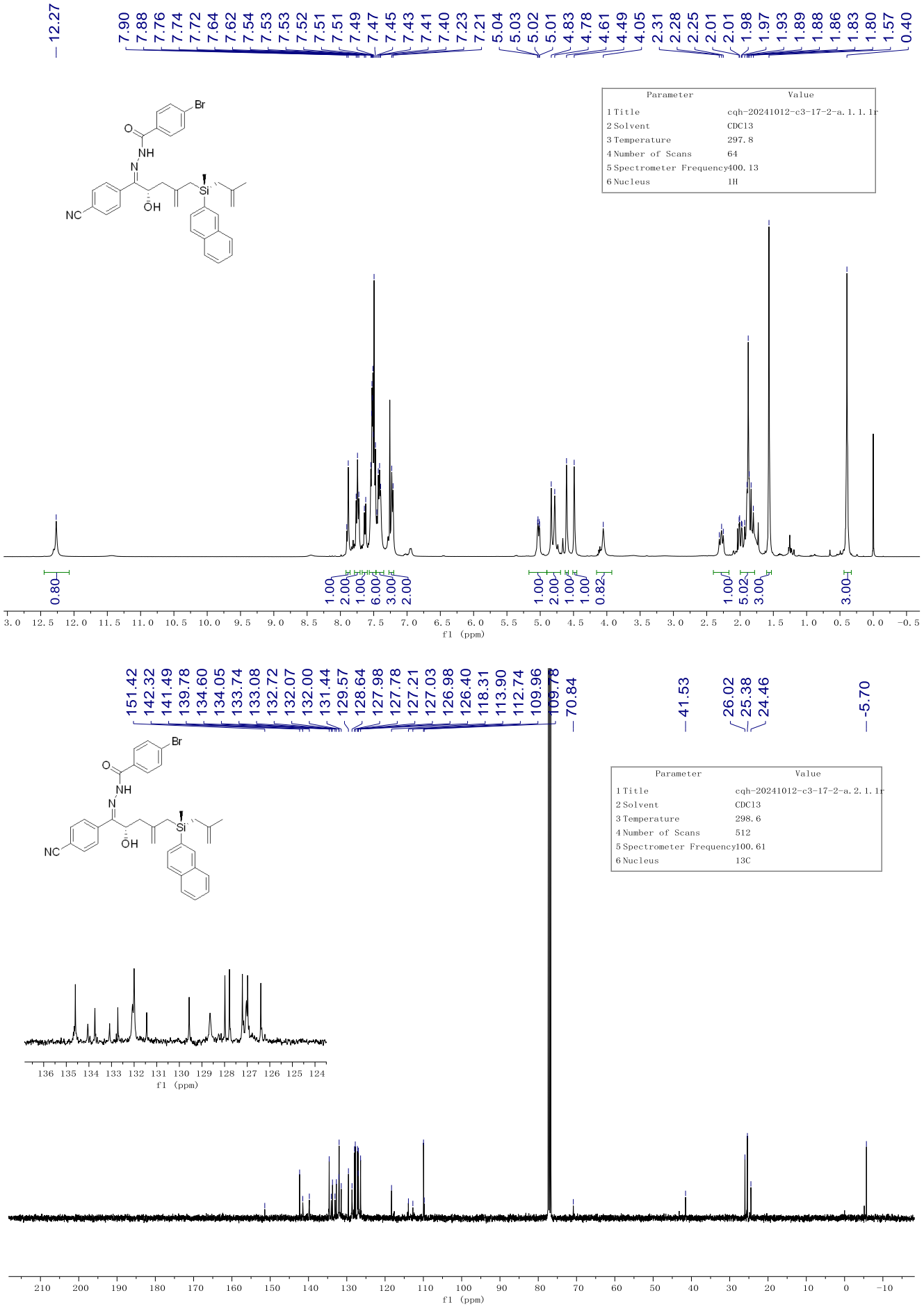
E


7.95 7.89 7.80 7.78 7.78 7.76 7.73 7.71 7.64 7.62 7.61 7.59 7.57 7.51 7.49 7.49 7.48 7.46 7.44 7.02 7.00 6.98 6.92 6.91 6.90 6.87 6.68 6.68 6.66 6.66 5.84 5.83 5.82 5.81 4.64 4.61 4.50 3.82 3.71 3.71 3.69 2.32 2.28 2.27 2.25 2.24 2.23 1.88 1.87 1.57 0.42
Br
Si
O
N
Cl
dr = 90:10
0.10
0.90
7.15 7.10 7.05 7.00 6.95
f1 (ppm)
Parameter Value
1 Title cqh-20240619-c2-179-4.1.1.1r
2 Solvent CDCl3
3 Temperature 297.2
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
1.00 1.00 2.00 1.00 2.00 1.00 6.00 0.10 0.90 0.97 1.00 1.00 1.00 2.00 1.00 1.00 3.00 2.00 3.02 2.00 4.00 3.05 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
194.96 170.43 168.36 156.20 142.67 140.75 139.35 136.36 136.09 134.83 134.51 134.00 133.86 132.90 131.35 131.28 130.88 130.64 130.19 129.99 129.22 128.19 127.85 127.20 126.69 126.19 123.10 115.05 112.83 112.12 111.96 109.89 101.31 74.00 55.79 39.45 29.94 26.15 25.50 24.31 13.47 -5.34
Parameter Value
1 Title cqh-20240619-c2-179-4.2.1.1r
2 Solvent CDCl3
3 Temperature 297.9
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
138 137 136 135 134 133 132 131 130 129 128 127 126 125
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

F


7.96 7.87 7.80 7.78 7.78 7.76 7.74 7.72 7.57 7.56 7.54 7.52 7.48 7.47 7.46 7.45 7.12 7.10 7.08 7.03 7.02 7.01 7.00 6.98 5.78 5.77 5.76 5.75 4.65 4.63 4.61 4.51 3.70 3.68 3.67 2.42 2.40 2.27 2.25 2.24 1.90 1.89 1.85 1.83 1.81 1.57 1.48 1.46 0.88 0.87 0.43
Parameter Value
1 Title cqh-20240619-c2-180-4.7.1.1r
2 Solvent CDCl3
3 Temperature 297.1
4 Number of Scans 16
5 Spectrometer Frequency 400.13
6 Nucleus 1H
Br
O
Si
1.00 1.00 2.00 1.00 2.00 3.00 2.00 3.00 1.00 1.00 2.00 1.00 1.00 2.00 2.00 4.00 1.00 3.00 3.00 3.00 3.00 3.00
f1 (ppm)
195.03 174.14 142.75 140.92 140.66 136.85 136.54 136.13 134.85 134.66 133.88 132.93 131.44 130.12 130.09 129.36 128.21 127.85 127.37 127.18 126.80 126.66 126.15 123.00 112.81 109.84 73.81 45.17 45.02 39.43 30.28 26.20 25.52 24.35 22.54 18.46 -5.27
Parameter Value
1 Title cqh-20240619-c2-180-4.8.1.1r
2 Solvent CDCl3
3 Temperature 297.9
4 Number of Scans 256
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)

G


12.27
7.90 7.88 7.76 7.74 7.72 7.64 7.62 7.54 7.53 7.53 7.52 7.51 7.51 7.49 7.47 7.45 7.43 7.41 7.40 7.23 7.21
5.04 5.03 5.02 5.01 4.83 4.78 4.61 4.49 4.05
2.31 2.28 2.25 2.01 2.01 1.98 1.97 1.93 1.89 1.88 1.86 1.83 1.80 1.57 0.40
Parameter Value
1 Title cqh-20241012-c3-17-2-a.1.1.1r
2 Solvent CDCl3
3 Temperature 297.8
4 Number of Scans 64
5 Spectrometer Frequency 400.13
6 Nucleus 1H
Br
O
NH
N
OH
Si
NC
0.80 1.00 2.00 1.00 6.00 3.00 2.00 1.00 2.00 1.00 1.00 0.82 1.00 5.02 3.00 3.00
f1 (ppm)
151.42 142.32 141.49 139.78 134.60 134.05 133.74 133.08 132.72 132.07 132.00 131.44 129.57 128.64 127.98 127.78 127.21 127.03 126.98 126.40 118.31 113.90 112.74 109.96 109.78 70.84
41.53 26.02 25.38 24.46 -5.70
Parameter Value
1 Title cqh-20241012-c3-17-2-a.2.1.1r
2 Solvent CDCl3
3 Temperature 298.6
4 Number of Scans 512
5 Spectrometer Frequency 100.61
6 Nucleus 13C
f1 (ppm)

13. Reference.

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