Electronic Supplementary Material (ESI) for Chemical Science.

A Highly Diastereoselective "Super Silyl" Governed Aldol Reaction:

Synthesis of α,β-Dioxyaldehydes and 1,2,3-Triols

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— Supporting Information —

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1. General methods.

Chemicals. Anhydrous THF and CH_2Cl_2 were dried with Glass Contour solvent purification system. Dry *t*BuOH, acetone and *n*-hexane were purchased from WAKO chemicals and used as received. $HNTf_2$ was purchased from Aldrich and used in glove box. All aldehydes were freshly distilled before use in aldol reactions. All other chemicals were purchased from their commercial sources and used as received.

Analytics. NMR spectra were recorded on a JEOL JNM LA-400 (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR and 376 MHz for ^{19}F). Chemical shifts were reported in ppm on the δ scale relative to Me_4Si (δ = 0 for ^{1}H NMR), $CDCl_3$ (δ = 77.2 for ^{13}C NMR), α,α,α-trifluorotoluene (δ = -63.72 for ^{19}F NMR) as an internal reference. Multiplicities are indicated as: s (singlet), br. s (broad singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet), dq (doublet of quadruplet) or m (multiplet). Coupling constants (*J*) are reported in Hertz (Hz). X-ray crystallographic analysis was performed with a Rigaku XtaLAB mini diffractomer (graphite monochromator, MoKα radiation, λ = 0.71075 Å), ESI mass spectra were measured on a Bruker Daltonics micrOTOF. Optical rotations were measured on an ATAGO AP-300 polarimeter with a path length of 100 mm at 589 nm. Column chromatography was conducted with silica gel 60 N (KANTO CHEMICAL, spherical, neutral, 40-50 or 63-210 μm). For thin-layer chromatography (TLC) analysis Merck precoated TLC plates (silica gel 60 F254 0.25 mm) were used. Visualization was accomplished by UV light (254 nm), I_2, anisaldehyde and $KMnO_4$.

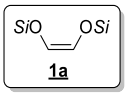
***Si*=Si(TMS)$_3$**

2. Preparation of super silyl enol ethers

GP1. General procedure

To a solution of triflic acid (0.93 mL, 10.5 mmol) in CH_2Cl_2 (20 mL) was added tris(trimethylsilyl)silane (3.08 mL, 10 mmol) at 0 °C. The reaction mixture was stirred at the same temperature for 1h. In a second flask, a mixture of aldehyde[1] (11 mmol) and Et_3N (2.1 mL, 15 mmol) in CH_2Cl_2 (20 mL) was then cooled to –60 °C. The triflic solution was canulated to the reaction vessel at this temperature then cold bath was removed. After being stirred at room temperature until TLC analysis indicated total conversion of starting material, the reaction was quenched by sat. aq. $NaHCO_3$, and extracted with Hexane. The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to give the crude product which was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100/0-85/15) to give the desired pure compound.

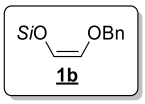
(1a): (*Z*)-1,2-bis(tris(trimethylsilyl)siloxy)-ethene :



1a

(68%, >99:1 *Z/E*); white solid; TLC (hexane:CH_2Cl_2, 90:10) R_f =0.69; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.24 (s, 2H), 0.19 (s, 54H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.2, 128.6 ppm. HRMS (ESI+) calculated for $C_{20}H_{57}O_2Si_8$ ([M+H]$^+$) : 553.2507, found : 553.2497.

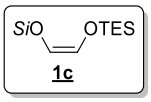
(1b): (*Z*)-1-benzyloxy-2-tris(trimethylsilyl)siloxy-ethene:



1b

(73%, >99:1 *Z/E*); colorless oil; TLC (hexane:CH_2Cl_2, 80:20) R_f =0.33; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.20 (s, 27H), 4.80 (s, 2H), 5.34 (d, *J* = 3.2 Hz, 1H), 5.36 (d, *J* = 3.2 Hz, 1H), 7.27-7.33 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.2, 73.7, 127.4, 127.7, 128.0, 128.4, 130.5, 138.1 ppm. HRMS (ESI+) calculated for $C_{18}H_{36}O_2Si_4Na$ ([M+Na]$^+$) : 419.1685, found : 419.1688.

(1c): (*Z*)-1-triethylsilyloxy-2-tris(trimethylsilyl)siloxy-ethene:

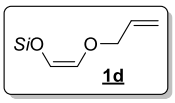


1c

(52%, >99:1 *Z/E*); colorless oil; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.45; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.20 (s, 27H), 0.64 (q, *J* = 8.0 Hz, 6H), 0.96 (t, *J* = 8.2 Hz, 9H), 5.34 (d, *J* = 3.2 Hz, 1H), 5.43 (d, *J* = 3.2 Hz, 1H) ppm. ^{13}C

NMR (100 MHz, $CDCl_3$): δ = 0.1, 4.7, 6.7, 124.3, 129.6 ppm. HRMS (ESI+) calculated for $C_{17}H_{44}O_2Si_5Na$ ($[M+Na]^+$) : 443.2080, found : 443.2084.

(1d): (*Z*)-1-allyloxy-2-tris(trimethylsilyl)siloxy-ethene :



(69%, >99:1 *Z/E*); colorless oil; TLC (hexane:CH_2Cl_2, 80:20) R_f = 0.62 ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.20 (s, 27H), 4.22 (td, *J* = 1.6, 5.5 Hz 2H), 5.17 (ddd, *J* = 1.4, 3.0, 10.6 Hz, 1H), 5.29 (ddd, *J* = 1.6, 3.4, 17.2 Hz, 1H), 5.30 (d, *J* = 3.4 Hz, 1H), 5.35 (d, *J* = 3.4 Hz, 1H), 5.90 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.2, 72.7, 117.0, 127.4, 130.5, 134.4 ppm. HRMS (ESI+) calculated for $C_{14}H_{34}O_2Si_4Na$ ($[M+Na]^+$) : 369.1528, found : 369.1531.

(1e): (*Z*)-1-methoxy-2-tris(trimethylsilyl)siloxy-ethene :

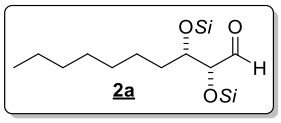
(18%, >99:1 *Z/E*); colorless oil; TLC (hexane:AcOEt, 95:5) R_f = 0.55; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.20 (s, 27H), 3.56 (s, 3H), 5.22 (d, *J* = 3.4 Hz, 1H), 5.31 (d, *J* = 3.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.1, 59.7, 126.9, 132.5 ppm. HRMS (ESI+) calculated for $C_{12}H_{32}O_2Si_4Na$ ($[M+Na]^+$) : 343.1372, found : 343.1370.

3. Mukaiyama aldol reaction : synthesis of protected α,β-dioxyaldehydes

GP2. General procedure

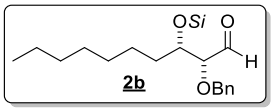
A stirred solution of silyl enol ether (0.2 mmol), aldehyde (0.2 mmol) and iodobenzene (2.3 µL, 0.02 mmol) in anhydrous dichloromethane (2 mL) was cooled to -40 °C. 10 to 20 µL of a fresh solution of triflimide (0.001-0.002 mmol, 0.1 M in CH_2Cl_2) was added dropwise and the solution was stirred at the same temperature for 1 h. After TLC analysis indicated consumption of the starting materials, the reaction was quenched by the addition of saturated aqueous solution of sodium bicarbonate (1 mL). The reaction was allowed to warm to ambient temperature and stirred vigorously for 5 min. The mixture was diluted with 5 mL of hexane and washed with water and brine. The organic layer was dried over sodium sulfate, filtered through cotton and concentrated under reduced pressure. The residue was then purified by flash chromatography on silica gel eluting with Hexane/ CH_2Cl_2 (5% to 40% gradient).

(2a): (2*S*,3*R*)/(2*R*,3*S*)-2,3-bis(tris(trimethylsilyl)siloxy)-decanal :



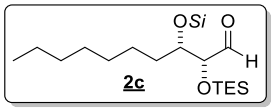
(73%, 95/5 *syn/anti*); white solid; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.51; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.16 (s, 27H), 0.16 (s, 27H), 0.86 (t, *J* = 6.6 Hz, 3H), 1.16-1.32 (m, 10H), 1.32-1.42 (m, 1H), 1.53-1.65 (m, 1H), 3.66 (dt, *J* =4.3, 7.5 Hz, 1H), 3.79 (d, *J* = 4.3 Hz, 1H), 9.72 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.4, 0.5, 14.1, 22.7, 25.8, 29.3, 30.0, 31.8, 33.2, 79.1, 82.6, 205.0 ppm. HRMS (ESI+) calculated for $C_{28}H_{72}O_3Si_8Na$ ($[M+Na]^+$) : 703.3528, found : 703.3522.

(2b): (2*S*,3*R*)/(2*R*,3*S*)-2-benzyloxy-3-tris(trimethylsilyl)siloxy-decanal :



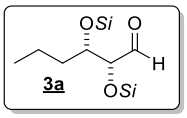
(45%, 96/4 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.45; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.16 (s, 27H), 0.86 (t, *J* = 6.8 Hz, 3H), 1.07-1.40 (m, 10H), 1.70-1.73 (m, 2H), 3.70 (dt, *J* =4.4, 6.1 Hz, 1H), 3.79 (dd, *J* = 1.2, 4.4 Hz, 1H), 4.46 (d, *J* = 12.2 Hz, 1H), 4.76 (d, *J* = 12.1 Hz, 1H), 7.25-7.32 (m, 5H), 9.75 (d, *J* = 0.9 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.4, 14.2, 22.7, 25.6, 29.3, 29.9, 31.8, 77.8, 78.1, 84.4, 127.9, 128.0, 128.4, 128.8, 137.5, 204.3 ppm. HRMS (ESI+) calculated for $C_{26}H_{52}O_3Si_4Na$ ($[M+Na]^+$) : 547.2886, found : 547.2889.

(2c): (2*S*,3*R*)/(2*R*,3*S*)-2-triethylsilyloxy-3-tris(trimethylsilyl)siloxy-decanal :

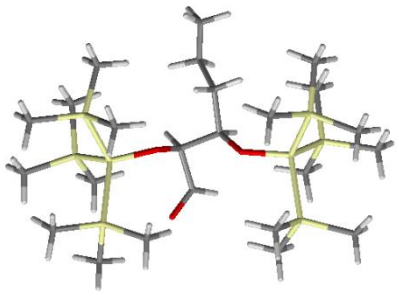


(51%, 98/2 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.27; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.18 (s, 27H), 0.56 (qd, *J* = 3.2, 8.5 Hz, 6H), 0.93 (t, *J* = 5.5 Hz, 9H), 1.20-1.31 (m, 15H), 3.65 (dt, *J* = 4.4, 6.6 Hz, 1H), 4.05 (dd, *J* = 0.7, 4.1 Hz, 1H), 9.70 (d, *J* = 0.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.5, 5.1, 6.8, 14.2, 22.7, 25.9, 29.3, 29.9, 31.8, 33.1, 78.9, 79.4, 204.2 ppm. HRMS (ESI+) calculated for $C_{25}H_{60}O_3Si_5Na$ ([M+Na]$^+$) : 571.3281, found : 571.3256.

(3a): (2*S*,3*R*)/(2*R*,3*S*)-2,3-bis(tris(trimethylsilyl)siloxy)-hexanal :



(78%, 98/2 *syn/anti*); colorless crystals (crystallized from methanol); TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.16 (s, 27H), 0.16 (s, 27H), 0.87 (t, *J* = 7.1 Hz, 3H), 1.16-1.40 (m, 3H), 1.54-1.64 (m, 1H), 3.68 (dt, *J* = 4.3, 7.7 Hz, 1H), 3.78 (d, *J* = 4.1 Hz, 1H), 9.71 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.4, 0.5, 14.3, 19.0, 35.6, 78.5, 82.5, 204.8 ppm. HRMS (ESI+) calculated for $C_{24}H_{64}O_3Si_8Na$ ([M+Na]$^+$) : 647.2902, found : 647.2903



Single crystal X-ray crystallographic analysis for **3a** (CCDC No. 1409680)

Bond precision: C-C = 0.0320 A Wavelength=0.71075

Cell: a=16.614(19) b=18.221(19) c=14.051(16)
alpha=90 beta=105.69(2) gamma=90

Temperature: 173 K

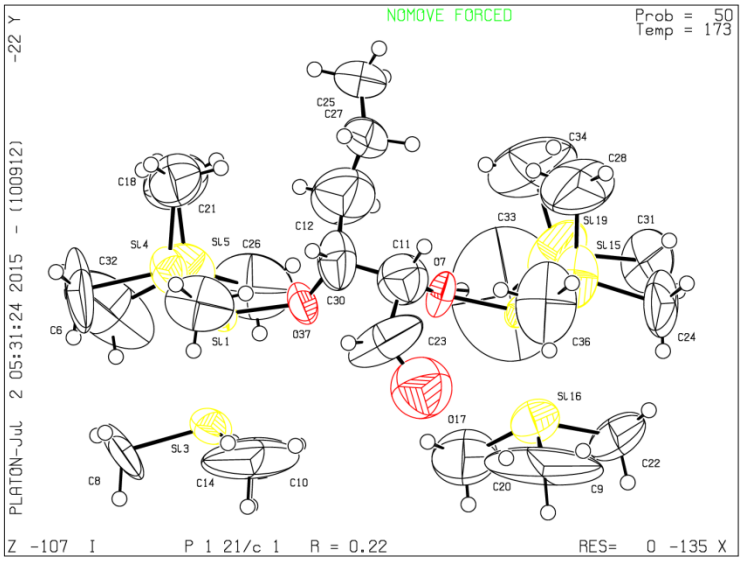
	Calculated	Reported
Volume	4095(8)	4095(8)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C24 H64 O3 Si8	C24 H64 O3 Si8
Sum formula	C24 H64 O3 Si8	C24 H64 O3 Si8
Mr	625.47	625.45
Dx,g cm-3	1.015	1.014
Z	4	4
Mu (mm-1)	0.283	0.282
F000	1376.0	1376.0
F000'	1378.89	
h,k,lmax	21,23,18	21,23,18
Nref	9668	9468
Tmin,Tmax	0.945,0.945	0.714,0.945
Tmin'	0.945	

Correction method= # Reported T Limits: Tmin=0.714 Tmax=0.945
AbsCorr = MULTI-SCAN

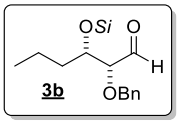
Data completeness= 0.979 Theta(max)= 27.770

R(reflections)= 0.2228(3829) wR2(reflections)= 0.5310(9468)

S = 1.285 Npar= 306

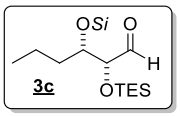


(3b): (2*S*,3*R*)/(2*R*,3*S*)-2-benzyloxy-3-tris(trimethylsilyl)siloxy-hexanal :



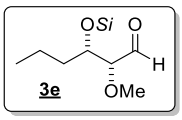
(78%, 97/3 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 80:20) R_f = 0.26; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.16 (s, 27H), 0.86 (t, *J* = 7.3 Hz, 3H), 1.18-1.40 (m, 3H), 1.68-1.71 (m, 1H), 3.73 (dt, *J* = 4.6, 6.2 Hz, 1H), 3.79 (dd, *J* = 0.9, 4.4 Hz, 1H), 4.47 (d, *J* = 12.2 Hz, 1H), 4.76 (d, *J* = 12.2 Hz, 1H), 9.75 (d, *J* = 1.1 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.5, 14.3, 18.9, 35.6, 72.6, 77.7, 84.4, 128.1, 128.2, 128.6, 137.5, 204.1 ppm. HRMS (ESI+) calculated for $C_{22}H_{44}O_3Si_4Na$ ([M+Na]$^+$) : 491.2260, found : 491.2257.

(3c): (2*S*,3*R*)/(2*R*,3*S*)-2-triethylsilyloxy-3-tris(trimethylsilyl)siloxy-hexanal :



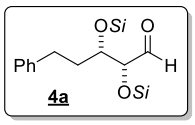
(53%, 97/3 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.19; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.17 (s, 27H), 0.59 (qd, *J* = 2.0, 7.6 Hz, 6H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 8.0 Hz, 9H), 1.22-1.38 (m, 3H), 1.61-1.69 (m, 1H), 3.66 (m, 1H), 4.05 (dd, *J* = 0.5, 4.2 Hz, 1H), 9.71 (d, *J* = 0.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.5, 5.0, 6.8, 14.4, 19.1, 35.3, 78.7, 79.4, 204.2 ppm. HRMS (ESI+) calculated for $C_{21}H_{52}O_3Si_5Na$ ([M+Na]$^+$) : 515.2655, found : 515.2652.

(3e): (2*S*,3*R*)/(2*R*,3*S*)-2-methoxy-3-tris(trimethylsilyl)siloxy-hexanal :



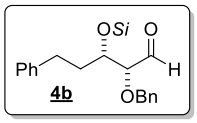
(51%, 94/6 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 60:40) R_f = 0.46; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.18 (s, 27H), 0.89 (t, *J* = 7.1 Hz, 3H), 1.24-1.40 (m, 3H), 1.57-1.67 (m, 1H), 3.42 (s, 3H), 3.59 (dd, *J* = 1.2, 4.6 Hz, 1H), 3.70-3.75 (m, 1H), 9.72 (d, *J* = 1.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.6, 14.3, 18.8, 35.5, 58.9, 77.2, 87.6, 203.7 ppm. HRMS (ESI+) calculated for $C_{16}H_{40}O_3Si_4Na$ ([M+Na]$^+$) : 415.1947, found : 415.1948.

(4a): (2*S*,3*R*)/(2*R*,3*S*)-2,3-bis(tris(trimethylsilyl)siloxy)-5-phenylpentanal :



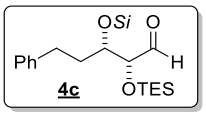
(68%, 91/9 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.56; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.20 (s, 27H), 0.21 (s, 27H), 1.71-1.78 (m, 1H), 1.87-1.97 (m, 1H), 2.45-2.55 (m, 1H), 2.59-2.69 (m, 1H), 3.82 (dt, *J* = 4.8, 7.1 Hz, 1H), 3.97 (d, *J* = 4.8 Hz, 1H), 7.10-7.20 (m, 3H), 7.25-7.30 (m, 2H), 9.83 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.4, 0.5, 31.9, 35.5, 78.4, 82.8, 125.9, 128.9, 128.5, 141.9, 204.0 ppm. HRMS (ESI+) calculated for $C_{29}H_{66}O_3Si_8Na$ ([M+Na]$^+$) : 709.3058, found : 709.3052.

(4b): (2*S*,3*R*)/(2*R*,3*S*)-2-benzyloxy-3-tris(trimethylsilyl)siloxy-5-phenylpentanal



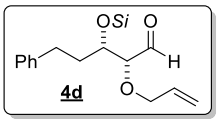
(79%, 97/3 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 80:20) R_f = 0.38; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.20 (s, 27H), 1.70-1.75 (m, 1H), 2.05-2.15 (m, 1H), 2.50-2.55 (m, 1H), 2.60-2.65 (m, 1H), 3.82-3.87 (m, 1H), 3.91 (dd, *J* = 0.8, 4.4 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.81 (d, *J* = 12.0 Hz, 1H), 7.14-7.40 (m, 10H), 9.81 (d, *J* = 0.9 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.6, 32.0, 35.4, 72.6, 84.3, 126.0, 128.2, 128.3, 128.4, 128.5 (2C), 128.7, 137.4, 141.7, 203.7 ppm. HRMS (ESI+) calculated for $C_{27}H_{46}O_3Si_4Na$ ([M+Na]$^+$) : 553.2416, found : 553.2418.

(4c): (2*S*,3*R*)/(2*R*,3*S*)-2-triethylsilyloxy-3-tris(trimethylsilyl)siloxy-5-phenylpentanal



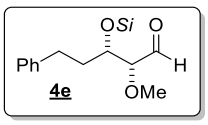
(50%, 98/2 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.24; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.20 (s, 27H), 0.64 (qd, *J* = 2.1, 7.6 Hz, 6H), 0.97 (t, *J* = 8.0 Hz, 9H), 1.60-1.70 (m, 1H), 1.98-2.10 (m, 1H), 2.55-2.71 (m, 2H), 3.77 (dt, *J* = 4.6, 10.6 Hz, 1H), 4.18 (dd, *J* = 0.7, 4.6 Hz, 1H), 7.14-7.20 (m, 3H), 7.25-7.29 (m, 2H), 9.77 (d, *J* = 0.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.5, 5.1, 6.9, 32.3, 35.2, 78.6, 79.5, 126.0, 128.3, 128.5, 141.9, 203.5 ppm. HRMS (ESI+) calculated for $C_{26}H_{54}O_3Si_5Na$ ([M+Na]$^+$) : 577.2811, found : 577.2812.

(4d): (2*S*,3*R*)/(2*R*,3*S*)-2-allyloxy-3-tris(trimethylsilyl)siloxy-5-phenylpentanal



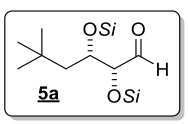
(42%, 98/2 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 60:40) R_f = 0.37; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.20 (s, 27H), 1.61-1.71 (m, 1H), 2.00-2.08 (m, 1H), 2.57 (td, *J* = 5.3, 11.5 Hz, 1H), 2.66 (td, *J* = 5.5, 11.7 Hz, 1H), 3.81 (dt, *J* = 4.6, 10.8, 1H), 3.87 (dd, *J* = 1.2, 4.8 Hz, 1H), 3.98 (tdd, *J* = 1.2, 6.2, 12.8 Hz, 1H), 4.20 (tdd, *J* = 1.4, 5.3, 12.8 Hz, 1H), 5.22 (ddd, *J* = 1.1, 2.6, 10.4 Hz, 1H), 5.26 (ddd, *J* = 1.6, 3.2, 17.2 Hz, 1H), 5.85-5.95 (m, 1H), 7.14-7.18 (m, 3H), 7.24-7.27 (m, 2H), 9.77 (d, *J* = 1.1 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.6, 32.0, 35.4, 72.0, 77.4, 84.6, 118.4, 126.0, 128.4, 128.5, 134.2, 141.7, 203.6 ppm. HRMS (ESI+) calculated for $C_{23}H_{44}O_3Si_4Na$ ([M+Na]$^+$) : 503.2260, found : 503.2251.

(4e): (2*S*,3*R*)/(2*R*,3*S*)-2-methoxy-3-tris(trimethylsilyl)siloxy-5-phenylpentanal



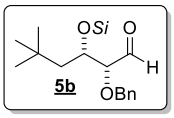
(55%, 97/3 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 80:20) R_f = 0.45; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.20 (s, 27H), 1.60-1.69 (m, 1H), 1.94-2.03 (m, 1H), 2.53-2.70 (m, 2H), 3.43 (s, 3H), 3.68 (dd, *J* = 1.6, 4.8 Hz, 1H), 3.80 (dt, *J* = 4.8, 10.8 Hz, 1H), 7.14-7.20 (m, 3H), 7.24-7.27 (m, 2H), 9.75 (d, *J* = 1.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.6, 31.9, 35.3, 58.9, 75.8, 87.5, 126.0, 128.4, 128.5, 141.7, 203.4 ppm. HRMS (ESI+) calculated for $C_{21}H_{42}O_3Si_4Na$ ([M+Na]$^+$) : 477.2103, found : 477.2105.

(5a): (2*S*,3*R*)/(2*R*,3*S*)-2,3-bis(tris(trimethylsilyl)siloxy)-5,5-dimethylhexanal :



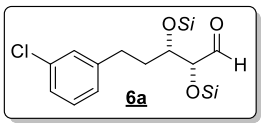
(82%, 98/2 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.54; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.16 (s, 27H), 0.21 (s, 27H), 0.88 (s, 9H), 1.12 (dd, *J* = 6.9, 14.0 Hz, 1H), 1.50 (dd, *J* = 2.8, 14.4 Hz, 1H), 3.70-3.74 (m, 1H), 4.00 (d, *J* = 5.0 Hz, 1H), 9.80 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.5, 1.1, 30.0, 30.4, 46.9, 76.5, 82.0, 203.9 ppm. HRMS (ESI+) calculated for $C_{26}H_{68}O_3Si_8Na$ ([M+Na]$^+$) : 675.3215, found : 675.3217.

(5b): (2*S*,3*R*)/(2*R*,3*S*)-2-benzyloxy-3-tris(trimethylsilyl)siloxy-5,5-dimethylhexanal :



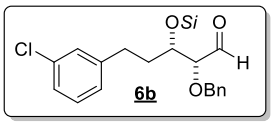
(83%, 98/2 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.49; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.19 (s, 27H), 0.91 (s, 9H), 1.25 (dd, *J* = 6.4, 13.8 Hz, 1H), 1.72 (dd, *J* = 4.4, 14.0 Hz, 1H), 3.90-3.94 (m, 2H), 4.50 (d, *J* = 11.7 Hz, 1H), 4.75 (d, *J* = 11.9 Hz, 1H), 7.26-7.35 (m, 5H), 9.74 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.9, 30.0, 30.3, 46.5, 72.2, 75.3, 84.8, 127.8, 127.9, 128.5, 137.8, 203.9 ppm. HRMS (ESI+) calculated for $C_{24}H_{48}O_3Si_4Na$ ([M+Na]$^+$) : 519.2573, found : 519.2577.

(6a): (2*S*,3*R*)/(2*R*,3*S*)-2,3-bis(tris(trimethylsilyl)siloxy)-5-(3-chlorophenyl) pentanal :



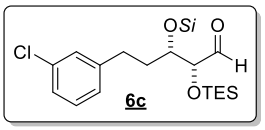
(51%, 94/6 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.42; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.18 (s, 27H), 0.19 (s, 27H), 1.64-1.74 (m, 1H), 1.80-1.89 (m, 1H), 2.44-2.52 (m, 1H), 2.55-2.63 (m, 1H), 3.77 (dt, *J* = 5.0, 6.9 Hz, 1H), 3.95 (d, *J* = 5.0 Hz, 1H), 6.98 (d, *J* = 7.1 Hz, 1H), 7.10-7.20 (m, 3H), 9.80 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.4, 0.5, 35.3, 78.0, 78.4, 82.8, 126.0, 126.8, 128.1, 129.8, 134.3, 144.0, 203.9 ppm. HRMS (ESI+) calculated for $C_{29}H_{65}O_3Si_8ClNa$ ([M+Na]$^+$) : 743.2669, found : 743.2660.

(6b): (2*S*,3*R*)/(2*R*,3*S*)-2-benzyloxy-3-tris(trimethylsilyl)siloxy-5-(3-chlorophenyl) pentanal :



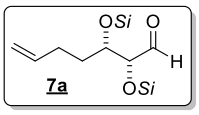
(30%, 94/6 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 80:20) R_f = 0.37; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.18 (s, 27H), 1.59-1.68 (m, 1H), 1.97-2.06 (m, 1H), 2.40-2.49 (m, 1H), 2.53-2.62 (m, 1H), 3.77 (dt, *J* = 4.8, 6.2 Hz, 1H), 3.88 (dd, *J* = 1.2, 4.8 Hz, 1H), 4.45 (d, *J* = 11.9 Hz, 1H), 4.78 (d, *J* = 11.9 Hz, 1H), 7.00-7.18 (m, 4H), 7.30-7.35 (m, 5H), 9.78 (d, *J* = 1.1 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.5, 31.5, 35.1, 72.6, 84.2, 126.2, 126.5, 126.6, 128.3, 128.3, 128.5, 128.7, 129.7, 134.2, 137.2, 143.7, 203.5 ppm. HRMS (ESI+) calculated for $C_{27}H_{45}ClO_3Si_4Na$ ([M+Na]$^+$) : 587.2026, found : 587.2005.

(6c): (2*S*,3*R*)/(2*R*,3*S*)-2-triethylsilyloxy-3-tris(trimethylsilyl)siloxy-5-(3-chlorophenyl) pentanal :



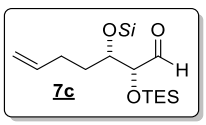
(37%, 94/6 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 80:20) R_f = 0.55; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.19 (s, 27H), 0.62 (qd, *J* = 2.4, 7.7 Hz, 6H), 0.95 (t, *J* = 7.9 Hz, 9H), 1.58-1.67 (m, 1H), 1.93-2.02 (m, 1H), 2.50-2.66 (m, 2H), 3.73 (ddd, *J* = 4.4, 6.0, 10.8 Hz, 1H), 4.17 (d, *J* = 4.4 Hz, 1H), 7.00-7.02 (m, 1H), 7.12-7.20 (m, 3H), 9.76 (d, *J* = 0.5 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.5, 5.1, 6.9, 31.9, 35.0, 78.4, 79.5, 126.2, 126.5, 128.5, 129.8, 134.2, 144.0, 203.3 ppm. HRMS (ESI+) calculated for $C_{26}H_{53}O_3Si_5ClNa$ ([M+Na]$^+$) : 611.2422, found : 611.2417.

(7a): (2*S*,3*R*)/(2*R*,3*S*)-2,3-bis(tris(trimethylsilyl)siloxy)-hept-6-enal :



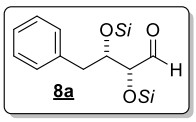
(58%, 98/2 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.24; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.16 (s, 27H), 0.17 (s, 27H), 1.43-1.52 (m, 1H), 1.65-1.74 (m, 1H), 1.89-2.08 (m, 2H), 3.72 (dt, *J* = 4.8, 7.1 Hz, 1H), 3.81 (d, *J* = 4.8 Hz, 1H), 4.92-5.00 (m, 2H), 5.70-5.81 (m, 1H), 9.73 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.3, 0.4, 29.8, 32.5, 78.2, 82.5, 114.9, 137.9, 204.5 ppm. HRMS (ESI+) calculated for $C_{25}H_{64}O_3Si_8Na$ ([M+Na]$^+$) : 659.2902, found : 659.2896.

(7c): (2*S*,3*R*)/(2*R*,3*S*)-2-triethylsilyloxy-3-tris(trimethylsilyl)siloxy- hept-6-enal :



(58%, 97/3 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.19; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.19 (s, 27H), 0.59 (qd, *J* = 2.1, 7.6 Hz, 6H), 0.93 (t, *J* = 8.0 Hz, 9H), 1.40-1.49 (m, 1H), 1.73-1.83 (m, 1H), 2.00-2.05 (m, 2H), 3.68 (dt, *J* = 4.4, 6.4 Hz, 1H), 4.07 (dd, *J* = 0.9, 4.6 Hz, 1H), 4.92-5.01 (m, 2H), 5.71-5.82 (m, 1H), 9.71 (d, *J* = 0.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.5, 5.1, 6.8, 29.9, 32.3, 78.3, 79.3, 114.8, 137.9, 203.9 ppm. HRMS (ESI+) calculated for $C_{22}H_{52}O_3Si_5Na$ ([M+Na]$^+$) : 527.2654, found : 527.2647.

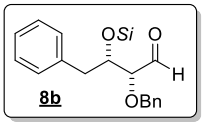
(8a): (2*S*,3*R*)/(2*R*,3*S*)-2,3-bis(tris(trimethylsilyl)siloxy)-4-phenylbutanal :



8a

(45%, 93/7 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.16 (s, 27H), 0.18 (s, 27H), 2.60 (dd, *J* = 5.7, 13.7 Hz, 1H), 2.96 (dd, *J* = 5.5, 13.7 Hz, 1H), 3.81 (d, *J* = 4.8 Hz, 1H), 3.98 (dd, *J* = 5.5, 10.6 Hz, 1H), 7.14-7.25 (m, 5H), 9.53 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.5, 0.6, 38.8, 79.8, 81.6, 126.6, 128.3, 130.2, 138.0, 203.3 ppm. HRMS (ESI+) calculated for $C_{28}H_{64}O_3Si_8Na$ ([M+Na]$^+$) : 695.2902, found : 695.2896.

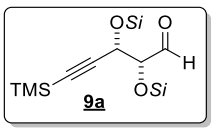
(8b): (2*S*,3*R*)/(2*R*,3*S*)-2-benzyloxy-3-tris(trimethylsilyl)siloxy-4-phenylbutanal :



8b

(80%, >99/1 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 80:20) R_f = 0.35; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.17 (s, 27H), 2.78 (dd, *J* = 6.0, 13.3 Hz, 1H), 3.05 (dd, *J* = 7.8, 13.3 Hz, 1H), 3.59 (dd, *J* = 1.0, 3.8 Hz, 1H), 4.07 (ddd, *J* = 1.6, 3.9, 6.0 Hz, 1H), 4.47 (d, *J* = 11.7 Hz, 1H), 4.66 (d, *J* = 11.7 Hz, 1H), 7.14-7.16 (m, 2H), 7.20-7.27 (m, 3H), 7.28-7.37 (m, 5H), 9.62 (d, *J* = 1.1 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.6, 39.4, 72.7, 78.9, 83.8, 126.7, 128.0, 128.1, 128.5, 128.6, 129.8, 137.6, 137.7, 204.3 ppm. HRMS (ESI+) calculated for $C_{26}H_{44}O_3Si_4Na$ ([M+Na]$^+$) : 539.2260, found : 539.2264.

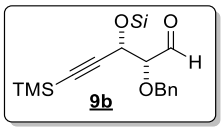
(9a): (2*S*,3*R*)/(2*R*,3*S*)-2,3-bis(tris(trimethylsilyl)siloxy)-5-(trimethylsilyl)pent-4-ynal:



9a

(20%, 68/32 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 80:20) R_f = 0.55; Major : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.12 (s, 9H), 0.17 (s, 27H), 0.18 (s, 27H), 3.78 (dd, *J* = 1.4, 3.4 Hz, 1H), 4.19 (d, *J* = 3.4 Hz, 1H), 9.54 (d, *J* = 1.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.3, 0.4, 0.5, 70.8, 85.9, 92.7, 104.3, 200.3 ppm. Minor : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.15 (s, 9H), 0.17 (s, 27H), 0.19 (s, 27H), 3.60 (dd, *J* = 1.8, 4.8 Hz, 1H), 4.25 (d, *J* = 4.8 Hz, 1H), 9.61 (d, *J* = 1.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = -0.1, 0.3, 0.4, 68.9, 82.0, 92.1, 103.9, 201.6 ppm. HRMS (ESI+) calculated for $C_{26}H_{66}O_3Si_9Na$ ([M+Na]$^+$) : 701.2833, found : 701.2827.

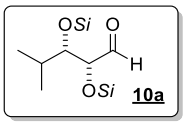
(9b): (2*S*,3*R*)/(2*R*,3*S*)-2-benzyloxy-3-tris(trimethylsilyl)siloxy-5-(trimethylsilyl)pent-4-ynal:



9b

(36%, 57/43 *syn/anti*); colorless oil; TLC (hexane:AcOEt, 95:5) R_f = 0.55; Major : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.16 (s, 9H), 0.18 (s, 27H), 3.84 (dd, *J* = 1.6, 4.6 Hz, 1H), 4.39 (d, *J* = 4.6 Hz, 1H), 4.68 (d, *J* = 12.4 Hz, 1H), 4.77 (d, *J* = 12.4 Hz, 1H), 7.24-7.34 (m, 5H), 9.66 (d, *J* = 1.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = -0.2, 0.4, 67.5, 72.9, 84.8, 93.4, 103.4, 128.0, 128.1, 128.5, 137.4, 200.7 ppm. Minor : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.15 (s, 9H), 0.19 (s, 27H), 3.76 (dd, *J* = 1.8, 5.3 Hz, 1H), 4.34 (d, *J* = 5.3 Hz, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 4.70 (d, *J* = 12.0 Hz, 1H), 7.24-7.34 (m, 5H), 9.63 (d, *J* = 1.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = -0.2, 0.4, 68.3, 73.0, 85.9, 92.6, 103.7, 127.5, 128.1, 128.2, 128.5, 200.0 ppm. HRMS (ESI+) calculated for $C_{24}H_{46}O_3Si_5Na$ ([M+Na]$^+$) : 545.2185, found : 545.2186.

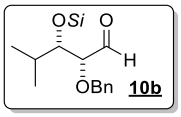
(10a): (2*S*,3*R*)/(2*R*,3*S*)-2,3-bis(tris(trimethylsilyl)siloxy)-4-methylpentanal :



10a

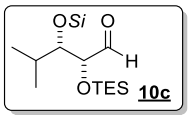
(51%, 39/61 *syn/anti*); Major : colorless oil; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.46; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.16 (s, 27H), 0.17 (s, 27H), 0.90 (d, *J* = 7.1 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 3H), 1.84 (m, 1H), 3.52 (dd, *J* = 2.5, 3.9 Hz, 1H), 3.68 (dd, *J* = 2.0, 2.3 Hz, 1H), 9.45 (d, *J* = 1.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.6, 0.7, 16.3, 19.1, 33.0, 82.4, 86.0, 201.7 ppm. Minor : colorless oil; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.56; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.16 (s, 27H), 0.19 (s, 27H), 0.82 (d, *J* = 7.1 Hz, 3H), 0.86 (d, *J* = 7.1 Hz, 3H), 1.86 (m, 1H), 3.64 (dd, *J* = 3.2, 6.0 Hz, 1H), 3.90 (d, *J* = 6.2 Hz, 1H), 9.88 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.4, 0.7, 18.3, 19.3, 32.1, 82.8, 83.2, 203.9 ppm. HRMS (ESI+) calculated for $C_{24}H_{64}O_3Si_8Na$ ([M+Na]$^+$) : 647.2902, found : 647.2922.

(10b): (2*S*,3*R*)/(2*R*,3*S*)-2-benzyloxy-3-tris(trimethylsilyl)siloxy-4-methylpentanal :



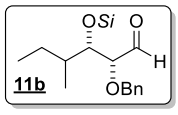
(72%, 96/4 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 80:20) R_f = 0.45; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.18 (s, 27H), 0.85 (d, *J* = 6.9 Hz, 3H), 0.96 (d, *J* = 7.1 Hz, 3H), 1.90-1.97 (m, 1H), 3.62 (dd, *J* = 4.0, 5.2 Hz, 1H), 3.88 (dd, *J* = 0.5, 5.2 Hz, 1H), 4.48 (d, *J* = 11.9 Hz, 1H), 4.77 (d, *J* = 11.9 Hz, 1H), 7.23-7.35 (m, 5H), 9.83 (d, *J* = 0.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.7, 18.2, 19.6, 31.8, 72.7, 81.8, 85.1, 128.0, 128.0, 128.6, 137.6, 203.3 ppm. HRMS (ESI+) calculated for $C_{22}H_{44}O_3Si_4Na$ ([M+Na]$^+$) : 491.2260, found : 491.2262.

(10c): (2*S*,3*R*)/(2*R*,3*S*)-2-triethylsilyloxy-3-tris(trimethylsilyl)siloxy-4-methylpentanal :



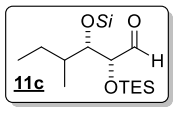
(69%, 97/3 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.21; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.20 (s, 27H), 0.58 (qd, *J* = 3.6, 7.6 Hz, 6H), 0.81 (d, *J* = 6.9 Hz, 3H), 0.91-0.96 (m, 12H), 1.89-1.97 (m, 1H), 3.57 (dd, *J* = 3.9, 5.8 Hz, 1H), 4.15 (d, *J* = 5.5 Hz, 1H), 9.82 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.7, 5.1, 6.8, 18.2, 19.9, 31.4, 80.0, 83.1, 203.1 ppm. HRMS (ESI+) calculated for $C_{21}H_{52}O_3Si_5Na$ ([M+Na]$^+$) : 515.2655, found : 515.2643.

(11B): (2*S*,3*R*)/(2*R*,3*S*)-2-benzyloxy-3-tris(trimethylsilyl)siloxy-4-methylhexanal :



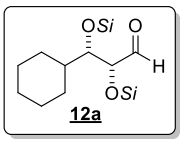
(50%, 81/19 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 60:40) R_f = 0.52; Major : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.16 (s, 27H), 0.80 (d, *J* = 6.9 Hz, 3H), 0.86 (t, *J* = 7.3 Hz, 3H), 1.16-1.21 (m, 1H), 1.47-1.52 (m, 1H), 1.62-1.67 (m, 1H), 3.69 (dd, *J* = 3.2, 5.5 Hz, 1H), 3.85 (dd, *J* = 0.9, 5.7 Hz, 1H), 4.49 (d, *J* = 11.9 Hz, 1H), 4.75 (d, *J* = 11.9 Hz, 1H), 7.26-7.32 (m, 5H), 9.82 (d, *J* = 0.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.7, 12.3, 14.5, 26.5, 38.4, 72.7, 81.2, 85.1, 127.9, 128.0, 128.5, 137.6, 203.1 ppm. HRMS (ESI+) calculated for $C_{23}H_{46}O_3Si_4Na$ ([M+Na]$^+$) : 505.2422, found : 505.2418.

(11c): (2*S*,3*R*)/(2*R*,3*S*)-2-triethylsilyloxy-3-tris(trimethylsilyl)siloxy-4-methylhexanal :



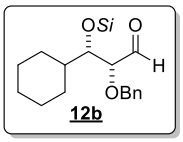
(46%, 79/21 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 80:20) R_f = 0.50; Major : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.20 (s, 27H), 0.55-0.63 (m, 6H), 0.77 (d, *J* = 4.8 Hz, 3H), 0.93 (t, *J* = 7.8 Hz, 9H), 1.09-1.12 (m, 3H), 1.40-1.48 (m, 2H), 1.61-1.69 (m, 1H), 3.65 (dd, *J* = 3.0, 5.8 Hz, 1H), 4.14 (d, *J* = 5.7 Hz, 1H), 9.83 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.7, 5.1, 6.8, 12.4, 14.7, 26.9, 37.8, 80.0, 82.4, 202.9 ppm. HRMS (ESI+) calculated for $C_{22}H_{54}O_3Si_5Na$ ([M+Na]$^+$) : 529.2811, found : 529.2788.

(12a): (2*S*,3*R*)/(2*R*,3*S*)-3-cyclohexyl-2,3-bis(tris(trimethylsilyl)siloxy)propanal



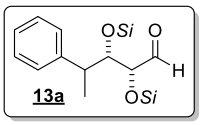
(56%, 71/29 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.40; Major : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.17 (s, 27H), 0.17 (s, 27H), 0.98-1.28 (m, 5H), 1.50-1.57 (m, 2H), 1.68-1.77 (m, 4H), 3.49 (dd, *J* = 2.8,3.4 Hz, 1H), 3.72 (dd, *J* = 2.0, 2.4 Hz, 1H), 9.45 (d, *J* = 1.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.6, 0.6, 26.3, 26.5, 26.8, 27.1, 29.9, 43.5, 83.0, 86.0, 201.7 ppm. HRMS (ESI+) calculated for $C_{27}H_{68}O_3Si_8Na$ ([M+Na]$^+$) : 687.3215, found : 687.3217.

(12b): (2*S*,3*R*)/(2*R*,3*S*)-3-cyclohexyl-2-benzyloxy-3-tris(trimethylsilyl)siloxy-propanal



(76%, 98/2 *syn/anti*); colorless oil; TLC (hexane:AcOEt, 95:5) R_f = 0.46; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.16 (s, 27H), 1.04-1.19 (m, 6H), 1.49-1.77 (m, 5H), 3.58 (dd, *J* = 4.2, 5.5 Hz, 1H), 3.84 (dd, *J* = 0.7, 5.5 Hz, 1H), 4.48 (d, *J* = 12.2 Hz, 1H), 4.76 (d, *J* = 12.2 Hz, 1H), 7.27-7.34 (m, 5H), 9.83 (d, *J* = 0.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.7, 26.4, 26.6, 28.5, 29.7, 41.9, 72.7, 81.6, 84.9, 128.0, 128.5, 137.6, 203.2 ppm. HRMS (ESI+) calculated for $C_{25}H_{48}O_3Si_4Na$ ([M+Na]$^+$) : 531.2572, found : 531.2568.

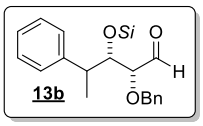
(13a): (2*S*,3*R*)/(2*R*,3*S*)-2,3-bis(tris(trimethylsilyl)siloxy)-4-phenylpentanal :



13a

(30%, 34/66 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.43; Major : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.15 (s, 27H), 0.18 (s, 27H), 1.22 (d, *J* = 7.3 Hz, 3H), 3.11-3.17 (m, 1H), 3.87 (d, *J* = 6.6 Hz, 1H), 3.96 (dd, *J* = 2.0, 6.4 Hz, 1H), 7.16-7.31 (m, 5H), 9.42 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.5, 0.8, 15.0, 41.1, 82.7, 83.5, 126.7, 128.0, 128.9, 143.4, 201.3 ppm. Minor : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.02 (s, 27H), 0.23 (s, 27H), 1.32 (d, *J* = 7.3 Hz, 3H), 3.11-3.17 (m, 1H), 3.58 (d, *J* = 1.8 Hz, 1H), 3.98 (dd, *J* = 1.8, 4.8 Hz, 1H), 7.16-7.31 (m, 5H), 9.28 (d, *J* = 1.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.9, 1.1, 12.4, 43.5, 85.1, 86.7, 128.3, 128.8, 130.2, 141.5, 202.5 ppm. HRMS (ESI+) calculated for $C_{29}H_{66}O_3Si_8Na$ ([M+Na]$^+$) : 709.3058, found : 709.3061.

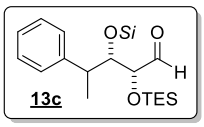
(13b): (2*S*,3*R*)/(2*R*,3*S*)-2-benzyloxy-3-tris(trimethylsilyl)siloxy-4-phenylpentanal :



13b

(71%, >99/1 *syn/anti*); colorless oil; TLC (hexane: AcOEt, 95:5) R_f = 0.52; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.15 (s, 27H), 1.30 (d, *J* = 7.2 Hz, 3H), 3.12-3.19 (m, 1H), 3.80 (d, *J* = 5.6 Hz, 1H), 3.98 (dd, *J* = 4.4, 5.6 Hz, 1H), 4.43 (d, *J* = 12.0 Hz, 1H), 4.70 (d, *J* = 12.0 Hz, 1H), 7.18-7.34 (m, 10H), 9.61 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.8, 16.7, 42.4, 72.8, 82.1, 84.6, 126.7, 127.7, 127.9, 128.3, 128.5, 128.6, 137.7, 143.9, 202.2 ppm. HRMS (ESI+) calculated for $C_{27}H_{46}O_3Si_4Na$ ([M+Na]$^+$) : 553.2416, found : 553.2434.

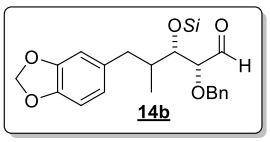
(13c): (2*S*,3*R*)/(2*R*,3*S*)-2-triethylsilyloxy-3-tris(trimethylsilyl)siloxy-4-phenylpentanal :



13c

(59%, 86/14 *syn/anti*); colorless oil; TLC (hexane: CH_2Cl_2, 80:20) R_f = 0.40; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.16 (s, 27H), 0.57 (qd, *J* = 2.0, 7.8 Hz, 6H), 0.92 (t, *J* = 7.8 Hz, 9H), 1.23 (d, *J* = 7.4 Hz, 3H), 3.12 (qd, *J* = 3.2, 7.1 Hz, 1H), 3.90 (dd, *J* = 3.5, 6.0 Hz, 1H), 4.12 (d, *J* = 6.0 Hz, 1H), 7.14-7.18 (m, 3H), 7.21-7.25 (m, 2H), 9.54 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.7, 5.1, 6.9, 16.2, 41.7, 79.6, 83.4, 126.5, 128.1, 128.6, 144.2, 201.5 ppm. HRMS (ESI+) calculated for $C_{26}H_{54}O_3Si_5Na$ ([M+Na]$^+$) : 577.2811, found : 577.2794.

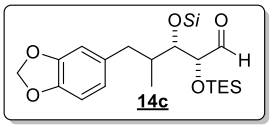
(14b): (2*S*,3*R*)/(2*R*,3*S*)-2-benzyloxy-3-tris(trimethylsilyl)siloxy-4-methyl-5-(3,4-methylenedioxy phenyl)pentanal



14b

(57%, 98/2 *syn/anti*); colorless oil; TLC (hexane:AcOEt, 95:5) R_f = 0.34; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.19 (s, 27H), 0.70 (d, *J* = 6.8 Hz, 3H), 2.00-2.07 (m, 1H), 2.27 (dd, *J* = 11.2, 13.3 Hz, 1H), 2.80 (dd, *J* = 3.6, 13.2 Hz, 1H), 3.77 (dd, *J* = 3.6, 5.6 Hz, 1H), 3.95 (d, *J* = 5.9 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.81 (d, *J* = 12.0 Hz, 1H), 5.90 (s, 2H), 6.55 (dd, *J* = 1.6, 8.0 Hz, 1H), 6.61 (d, *J* = 1.6 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 7.25-7.35 (m, 5H), 9.89 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.8, 14.2, 38.5, 40.0, 72.8, 81.3, 85.0, 100.8, 108.0, 109.6, 122.0, 128.0, 128.1, 128.6, 134.6, 137.5, 145.7, 147.5, 202.6 ppm. HRMS (ESI+) calculated for $C_{29}H_{48}O_5Si_4Na$ ([M+Na]$^+$) : 611.2471, found : 611.2471.

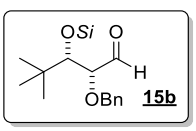
(14c): (2*S*,3*R*)/(2*R*,3*S*)-2-triethylsilyloxy-3-tris(trimethylsilyl)siloxy-4-methyl-5-(3,4-methylene dioxyphenyl)pentanal



14c

(41%, 93/7 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 80:20) R_f = 0.29; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.23 (s, 27H), 0.58-0.68 (m, 9H), 0.95 (t, *J* = 8.0 Hz, 9H), 2.05-2.10 (m, 1H), 2.27 (dd, *J* = 11.2, 13.2 Hz, 1H), 2.73 (dd, *J* = 3.9, 13.1 Hz, 1H), 3.74 (dd, *J* = 3.2, 6.2 Hz, 1H), 4.22 (d, *J* = 6.0 Hz, 1H), 5.90 (s, 2H), 6.54 (dd, *J* = 1.6, 7.8 Hz, 1H), 6.59 (d, *J* = 1.6 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 9.90 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.8, 5.1, 6.9, 14.0, 37.9, 40.6, 79.9, 82.6, 100.8, 108.1, 109.4, 121.9, 134.8, 145.7, 147.5, 202.5 ppm. HRMS (ESI+) calculated for $C_{28}H_{56}O_5Si_5Na$ ([M+Na]$^+$) : 635.2823, found : 635.2830.

(15b): (2*S*,3*R*)/(2*R*,3*S*)-2-benzyloxy-3-tris(trimethylsilyl)siloxy-4,4-dimethylpentanal :

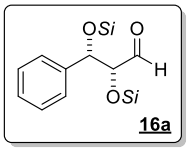


15b

(81%, 98/2 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 80:20) R_f = 0.42; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.19 (s, 27H), 0.92 (s, 9H), 3.56 (d, *J* = 5.1 Hz, 1H), 4.00 (d, *J* = 5.1 Hz, 1H), 4.44 (d, *J* = 11.7 Hz, 1H), 4.80

(d, *J* = 11.7 Hz, 1H), 7.25-7.35 (m, 5H), 9.92 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.9, 27.4, 36.9, 72.9, 85.0, 86.7, 127.5, 127.8, 128.5, 137.9, 202.7 ppm. HRMS (ESI+) calculated for $C_{23}H_{46}O_3Si_4Na$ ([M+Na]$^+$) : 505.2416, found : 505.2417.

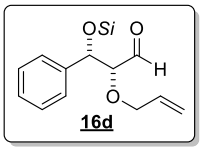
(16a): (2*S*,3*R*)/(2*R*,3*S*)-2,3-bis(tris(trimethylsilyl)siloxy)-3-phenylpropanal :



16a

(78%, 65/35 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.32; Major : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.07 (s, 27H), 0.08 (s, 27H), 3.83 (dd, *J* = 1.4, 4.6 Hz, 1H), 4.61 (d, *J* = 4.4 Hz, 1H), 7.18-7.30 (m, 5H), 9.65 (d, *J* = 1.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.3, 0.4, 80.7, 83.7, 127.4, 127.8, 128.4, 140.0, 204.1 ppm. Minor : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.03 (s, 27H), 0.04 (s, 27H), 3.59 (dd, *J* = 3.0, 6.4 Hz, 1H), 4.37 (d, *J* = 6.2 Hz, 1H), 7.18-7.30 (m, 5H), 9.58 (d, *J* = 3.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.3, 0.5, 81.0, 86.1, 127.7, 127.9, 128.3, 141.5, 201.7 ppm. HRMS (ESI+) calculated for $C_{27}H_{62}O_3Si_8Na$ ([M+Na]$^+$) : 681.2745, found : 681.2734.

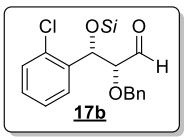
(16d): (2*S*,3*R*)/(2*R*,3*S*)-2-allyloxy-3-tris(trimethylsilyl)siloxy-3-phenylpropanal



16d

(68%, 90/10 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.28; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.09 (s, 27H), 3.82 (dd, *J* = 2.1, 5.5 Hz, 1H), 3.88-3.95 (m, 1H), 4.02-4.07 (m, 1H), 4.65 (d, *J* = 5.3 Hz, 1H), 5.10-5.21 (m, 2H), 5.73-5.82 (m, 1H), 7.23-7.34 (m, 5H), 9.53 (d, *J* = 1.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.4, 72.1, 79.2, 86.7, 117.9, 127.2, 128.2, 128.7, 134.1, 139.7, 202.1 ppm. HRMS (ESI+) calculated for $C_{21}H_{40}O_3Si_4Na$ ([M+Na]$^+$) : 475.1946, found : 475.1928.

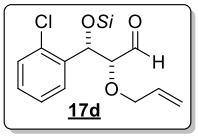
(17b): (2*S*,3*R*)/(2*R*,3*S*)-2-benzyloxy-3-tris(trimethylsilyl)siloxy-3-(2-chlorophenyl)propanal



17b

(50%, 65/35 *syn/anti*); colorless oil; TLC (hexane:AcOEt, 95:5) R_f = 0.48; Major : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.08 (s, 27H), 3.83 (dd, *J* = 1.8, 4.3 Hz, 1H), 4.33 (d, *J* = 12.4 Hz, 1H), 4.47 (d, *J* = 12.4 Hz, 1H), 5.26 (d, *J* = 4.4 Hz, 1H), 7.06-7.08 (m, 2H), 7.20-7.32 (m, 6H), 7.52 (dd, *J* = 2.0, 7.6 Hz, 1H), 9.68 (d, *J* = 1.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.4, 73.1, 75.7, 85.5, 126.9, 127.9, 128.4, 128.4, 129.2, 129.2, 130.1, 132.0, 137.2, 137.7, 202.5 ppm. Minor : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.10 (s, 27H), 3.76 (dd, *J* = 2.0, 2.5 Hz, 1H), 4.52 (d, *J* = 12.2 Hz, 1H), 4.70 (d, *J* = 12.2 Hz, 1H), 5.17 (d, *J* = 2.6 Hz, 1H), 7.18-7.31 (m, 8H), 7.38 (dd, *J* = 2.0, 7.6 Hz, 1H), 9.61 (d, *J* = 2.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.3, 72.6, 77.8, 85.8, 126.9, 128.1, 128.4, 128.7, 129.2, 129.2, 129.4, 132.0, 137.1, 138.1, 201.5 ppm. HRMS (ESI+) calculated for $C_{25}H_{41}O_3Si_4ClNa$ ([M+Na]$^+$) : 559.1719, found : 559.1699.

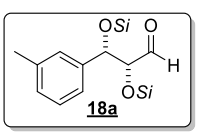
(17d): (2*S*,3*R*)/(2*R*,3*S*)-2-allyloxy-3-tris(trimethylsilyl)siloxy-3-(2-chlorophenyl)propanal



17d

(49%, 60/40 *syn/anti*); white solid; TLC (hexane:AcOEt, 95:5) R_f = 040; Major : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.09 (s, 27H), 3.78 (dd, *J* = 1.8, 4.6 Hz, 1H), 3.80-3.92 (m, 2H), 5.06-5.10 (m, 2H), 5.23 (d, *J* = 4.8 Hz, 1H), 5.58-5.65 (m, 1H), 7.20-7.32 (m, 3H), 7.51 (dd, *J* = 2.0, 7.8 Hz, 1H), 9.66 (d, *J* = 2.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.4, 72.5, 75.5, 86.3, 118.1, 127.0, 129.2, 129.3, 129.9, 132.0, 133.8, 137.8, 202.4 ppm. Minor : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.11 (s, 27H), 3.75 (dd, *J* = 2.3, 5.1 Hz, 1H), 4.01-4.17 (m, 2H), 5.09-5.21 (m, 2H), 5.06 (d, *J* = 5.3 Hz, 1H), 5.80-5.87 (m, 1H), 7.18-7.31 (m, 3H), 7.38 (dd, *J* = 2.0, 7.6 Hz, 1H), 9.61 (d, *J* = 2.3 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.3, 71.8, 77.9, 86.0, 118.3, 128.2, 129.3, 129.3, 129.4, 132.0, 134.0, 138.0, 201.8 ppm. HRMS (ESI+) calculated for $C_{21}H_{39}O_3Si_4ClNa$ ([M+Na]$^+$) : 509.1557, found : 509.1556.

(18a): (2*S*,3*R*)/(2*R*,3*S*)-2,3-bis(tris(trimethylsilyl)siloxy)-3-(3-methylphenyl)propanal

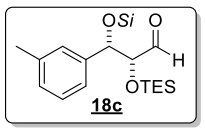


18a

(74%, 63/37 *syn/anti*); yellow solid; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.49; Major : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.07 (s, 27H), 0.08 (s, 27H), 2.30 (s, 3H), 3.81 (dd, *J* = 1.4, 4.4 Hz, 1H), 4.58 (d, *J* = 4.2 Hz, 1H), 6.96-7.20 (m, 4H), 9.63 (d, *J* = 1.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.2, 0.4, 21.5, 80.7, 83.8, 124.4, 127.7, 128.1, 128.6, 137.1, 139.8, 204.3 ppm. Minor : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.03 (s, 27H), 0.04 (s, 27H), 2.31 (s, 3H), 3.57 (dd, *J* = 3.2, 6.6 Hz, 1H), 4.32 (d, *J* = 6.6 Hz, 1H), 6.96-7.20 (m, 4H), 9.56 (d, *J* = 3.0 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.3, 0.4, 21.5, 80.9, 86.1, 124.9, 128.3, 128.4, 129.0, 137.8, 141.4, 201.7 ppm. HRMS (ESI+) calculated for $C_{28}H_{64}O_3Si_8Na$ ([M+Na]$^+$) : 695.2902, found : 695.2892.

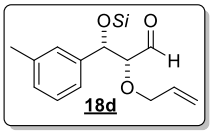
(18c): (2*S*,3*R*)/(2*R*,3*S*)-2-triethylsilyloxy-3-tris(trimethylsilyl)siloxy-3-(3-methylphenyl) propanal



18c

(36%, 57/43 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.35; Major : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.08 (s, 27H), 0.45 (qd, *J* = 3.0, 7.6 Hz, 6H), 0.83 (t, *J* = 8.0 Hz, 9H), 2.30 (s, 3H), 4.01 (dd, *J* = 1.6, 4.1 Hz, 1H), 4.60 (d, *J* = 4.1 Hz, 1H), 7.00-7.18 (m, 4H), 9.58 (d, *J* = 1.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.4, 4.8, 6.7, 21.5, 80.5, 81.0, 124.5, 127.7, 128.2, 128.7, 137.3, 139.9, 203.3 ppm. Minor : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.06 (s, 27H), 0.39 (dq, *J* = 3.0, 7.5 Hz, 6H), 0.77 (t, *J* = 8.0 Hz, 9H), 2.32 (s, 3H), 3.84 (dd, *J* = 2.7, 6.0 Hz, 1H), 4.46 (d, *J* = 6.0 Hz, 1H), 7.00-7.18 (m, 4H), 9.60 (d, *J* = 2.5 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.4, 4.8, 6.7, 21.5, 80.5, 81.0, 124.5, 127.7, 128.2, 128.7, 137.3, 139.9, 203.3 ppm. HRMS (ESI+) calculated for $C_{25}H_{52}O_3Si_5Na$ ([M+Na]$^+$) : 563.2660, found : 563.2657.

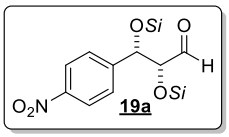
(18d): (2*S*,3*R*)/(2*R*,3*S*)-2-allyloxy-3-tris(trimethylsilyl)siloxy-3-(3-methylphenyl) propanal



18d

(56%, 93/7 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 80:20) R_f = 0.48; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.09 (s, 27H), 2.31 (s, 3H), 3.80 (dd, *J* = 1.8, 5.2 Hz, 1H), 3.92 (tdd, *J* = 1.6, 6.0, 13.1 Hz, 1H), 4.05 (tdd, *J* = 1.6, 5.6, 13.1 Hz, 1H), 4.60 (d, *J* = 5.6 Hz, 1H), 5.14 (ddd, *J* = 1.6, 3.2, 10.8 Hz, 1H), 5.20 (ddd, *J* = 1.6, 3.2, 17.2 Hz, 1H), 5.73-5.84 (m, 1H), 7.02-7.08 (m, 3H), 7.15-7.21 (m, 1H), 9.52 (d, *J* = 1.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.4, 21.5, 72.1, 79.2, 86.9, 117.9, 124.4, 127.9, 128.1, 129.0, 134.2, 137.8, 139.7, 202.1 ppm. HRMS (ESI+) calculated for $C_{22}H_{42}O_3Si_4Na$ ([M+Na]$^+$) : 489.2103, found : 489.2107.

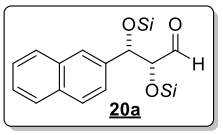
(19a): (2*S*,3*R*)/(2*R*,3*S*)-2,3-bis(tris(trimethylsilyl)siloxy)-3-(4-nitrophenyl)propanal



19a

(63%, 53/47 *syn/anti*); yellow cristals; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.19; Major : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.08 (s, 27H), 0.10 (s, 27H), 3.94 (dd, *J* = 1.1, 5.0 Hz, 1H), 4.71 (d, *J* = 5.0 Hz, 1H), 8.14 (d, *J* = 8.7 Hz, 2H), 8.19 (d, *J* = 8.7 Hz, 2H), 9.63 (d, *J* = 1.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.3, 0.5, 80.1, 83.0, 123.0, 128.2, 147.5, 148.0, 202.6 ppm. Minor : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.03 (s, 27H), 0.06 (s, 27H), 3.65 (dd, *J* = 2.5, 5.8 Hz, 1H), 4.52 (d, *J* = 5.8 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 9.57 (d, *J* = 2.5 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.3, 0.4, 80.4, 85.7, 123.4, 128.4, 147.7, 149.0, 201.7 ppm. HRMS (ESI+) calculated for $C_{27}H_{61}NO_5Si_8Na$ ([M+Na]$^+$) : 726.2596, found : 726.259.

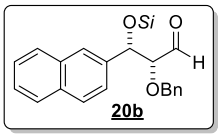
(20a): (2*S*,3*R*)/(2*R*,3*S*)-2,3-bis(tris(trimethylsilyl)siloxy)3-(naphthalen-2-yl)propanal



20a

(55%, 89/11 *syn/anti*); colorless oil; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.47; Major : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.05 (s, 27H), 0.09 (s, 27H), 3.92 (dd, *J* = 1.4, 4.3 Hz, 1H), 4.80 (d, *J* = 4.4 Hz, 1H), 7.32-7.42 (m, 3H), 7.70-7.80 (m, 4H), 9.67 (d, *J* = 1.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.2, 0.4, 80.6, 83.8, 125.9, 126.1, 127.1, 127.7, 128.1, 132.9, 133.3, 137.6, 203.9 ppm. Minor : ^{1}H NMR (400 MHz, $CDCl_3$): δ = -0.01 (s, 27H), 0.04 (s, 27H), 3.70 (dd, *J* = 2.8, 6.2 Hz, 1H), 4.56 (d, *J* = 6.2 Hz, 1H), 7.30-7.47 (m, 3H), 7.70-7.80 (m, 4H), 9.63 (d, *J* = 2.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.5 (2C), 81.3, 86.1, 125.5, 125.7, 126.1, 126.8, 128.3, 133.1, 133.5, 138.5, 201.7 ppm. HRMS (ESI+) calculated for $C_{31}H_{64}O_3Si_8Na$ ([M+Na]$^+$) : 731.2902, found : 731.2905.

(20b): (2*S*,3*R*)/(2*R*,3*S*)-2-benzyloxy-3-tris(trimethylsilyl)siloxy-3-(naphthalen-2-yl) propanal

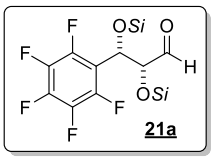


20b

(60%, 98/2 *syn/anti*); colorless oil; TLC (hexane:AcOEt, 95:5) R_f = 0.51; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.07 (s, 27H), 3.97 (dd, *J* = 1.8, 5.0 Hz, 1H), 4.46 (d, *J* = 12.3 Hz, 1H), 4.66 (d, *J* = 12.2 Hz, 1H), 4.90 (d, *J* = 5.0 Hz, 1H), 7.18-7.20 (m, 2H), 7.23-7.26 (m, 3H), 7.41-7.49 (m, 3H), 7.77-7.86 (m, 4H), 9.65 (d, *J* = 1.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.5, 72.8, 79.4, 86.3, 125.3, 126.1, 126.2, 126.2, 127.9,

128.0, 128.2, 128.5, 133.1, 133.4, 137.4, 137.5, 202.3 ppm. HRMS (ESI+) calculated for $C_{29}H_{44}O_3Si_4Na$ ([M+Na]$^+$) : 575.2260, found : 575.2252.

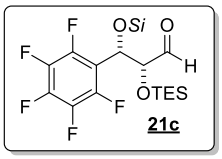
(21a): (2*S*,3*R*)/(2*R*,3*S*)-2,3-bis(tris(trimethylsilyl)siloxy)-3-pentafluorophenylpropanal :



21a

(68%, 82/18 *syn/anti*); white solid; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.30; Major : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.05 (s, 27H), 0.08 (s, 27H), 3.95 (dd, *J* = 2.7, 8.5 Hz, 1H), 4.80 (d, *J* = 8.5 Hz, 1H), 9.65 (d, *J* = 2.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.04, 0.18, 71.8, 82.6, 200.4 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -140.1 (br. s, 2F), -154.2 (t, *J* = 22.9 Hz, 1F), -162.1 (br. s, 2F); Minor : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.09 (s, 27H), 0.13 (s, 27H), 4.10 (d, *J* = 6.4 Hz, 1H), 5.14 (d, *J* = 6.4 Hz, 1H), 9.79 (d, *J* = 3.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.04, 0.18, 73.8, 82.3, 201.0 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -140.1 (br. s, 2F), -154.2 (t, *J* = 22.9 Hz, 1F), -162.1 (br. s, 2F); HRMS (ESI+) calculated for $C_{27}H_{57}O_3Si_8F_5Na$ ([M+Na]$^+$) : 771.2274, found : 771.2259.

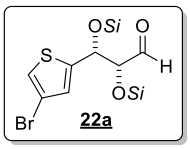
(21c): (2*S*,3*R*)/(2*R*,3*S*)-2-triethylsilyloxy-3-tris(trimethylsilyl)siloxy-3-pentafluorophenylpropanal :



21c

(44%, 95/5 *syn/anti*); colorless oil; TLC (hexane:AcOEt, 95:5) R_f = 0.35; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.09 (s, 27H), 0.33-0.47 (m, 6H), 0.78 (t, *J* = 7.8 Hz, 9H), 4.14 (dd, *J* = 2.5, 7.8 Hz, 1H), 4.93 (d, *J* = 7.6 Hz, 1H), 9.65 (d, *J* = 2.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.2, 4.5, 6.3, 72.1, 79.5, 199.9 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -140.2 (d, *J* = 51.9 Hz, 2F), -153.9 (t, *J* = 23.1 Hz, 1F), -162.2 to -162.0 (m, 2F); HRMS (ESI+) calculated for $C_{24}H_{45}O_3Si_5F_5Na$ ([M+Na]$^+$) : 639.2033, found : 639.2028.

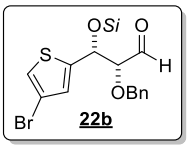
(22a): (2*S*,3*R*)/(2*R*,3*S*)- 2,3-bis(tris(trimethylsilyl)siloxy)-3-(4-bromothiophen-2-yl) propanal



22a

(61%, 81/19 *syn/anti*); yellow solid; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.29; Major : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.13 (s, 27H), 0.14 (s, 27H), 3.86 (dd, *J* = 1.2, 5.0 Hz, 1H), 4.75 (dd, *J* = 0.9, 5.0 Hz, 1H),6.79 (dd, *J* = 0.9, 1.4 Hz, 1H), 7.08 (d, *J* = 1.4 Hz, 1H), 9.58 (d, *J* = 1.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.3, 0.4, 82.3, 85.8, 109.1, 122.3, 127.6, 144.7, 202.3 ppm. Minor : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.09 (s, 27H), 0.09 (s, 27H), 3.64 (dd, *J* = 2.7, 5.9 Hz, 1H), 4.56 (d, *J* = 6.0 Hz, 1H), 6.79 (dd, *J* = 1.6 Hz, 1H), 7.15 (d, *J* = 1.6 Hz, 1H), 9.55 (d, *J* = 2.5 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.4, 0.5, 77.6, 97.9, 109.2, 122.6, 128.1, 146.9, 201.4 ppm. HRMS (ESI+) calculated for $C_{25}H_{59}BrO_3SSi_8Na$ ([M+Na]$^+$) : 765.1420, found : 765.1409.

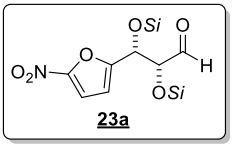
(22b): (2*S*,3*R*)/(2*R*,3*S*)-2-benzyloxy-3-tris(trimethylsilyl)siloxy-3-(4-bromothiophen-2-yl) propanal



22b

(49%, 83/17 *syn/anti*); yellow solid; TLC (hexane:AcOEt, 95:5) R_f = 0.23; Major : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.10 (s, 27H), 3.82 (dd, *J* = 1.8, 5.0 Hz, 1H), 4.50 (d, *J* = 12.1 Hz, 1H), 4.72 (d, *J* = 12.1 Hz, 1H), 4.82 (dd, *J* = 0.9, 5.0 Hz, 1H), 6.89 (dd, *J* = 0.9, 1.4 Hz, 1H), 7.13 (d, *J* = 1.6 Hz, 1H), 7.28-7.33 (m, 5H), 9.58 (d, *J* = 1.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.3, 72.9, 75.3, 84.6, 109.3, 122.7, 127.7, 128.1, 128.2, 128.6, 137.1, 144.9, 201.1 ppm. HRMS (ESI+) calculated for $C_{23}H_{39}O_3BrSSi_4Na$ ([M+Na]$^+$) : 609.0778, found : 609.0777.

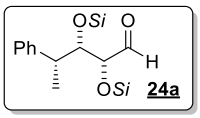
(23a): (2*S*,3*R*)/(2*R*,3*S*)-2,3-bis(tris(trimethylsilyl)siloxy)-3-(5-nitrofuran-2-yl) propanal



23a

(44%, 58/42 *syn/anti*); yellow oil; TLC (hexane:AcOEt, 80:20) R_f = 0.33; Major : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.11 (s, 27H), 0.13 (s, 27 H), 3.96 (dd, *J* = 1.4, 5.5 Hz, 1H), 4.70 (d, *J* = 5.5 Hz, 1H), 6.36 (dd, *J* = 0.5, 3.7 Hz, 1H), 7.23-7.35 (m, 1H), 9.72 (d, *J* = 1.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.2, 0.3, 74.8, 81.8, 111.4, 112.0, 128.3, 157.5, 201.3 ppm. Minor : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.10 (s, 27H), 0.12 (s, 27H), 3.86 (dd, *J* = 2.1, 4.8 Hz, 1H), 4.56 (d, *J* = 5.3 Hz, 1H), 6.46 (dd, *J* = 0.7, 3.7 Hz, 1H), 7.23-7.35 (m, 1H), 9.58 (d, *J* = 2.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.4, 0.5, 75.9, 84.1, 111.6, 112.1, 128.5, 157.7, 201.1 ppm. HRMS (ESI+) calculated for $C_{25}H_{59}O_6NSi_8Na$ ([M+Na]$^+$) : 716.2394, found : 716.2380.

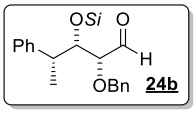
(24a): (2*S*,3*R*,4*R*)/(2*R*,3*S*,4*R*)-2,3-bis(tris(trimethylsilyl)siloxy)-4-phenylpentanal :



24a

(32%, 65/35 *syn/anti*); white solid; TLC (hexane:CH_2Cl_2, 90:10) R_f = 0.51; Major : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.16 (s, 27H), 0.19 (s, 27H), 1.23 (d, *J* = 7.6 Hz, 3H), 3.10-3.17 (m, 1H), 3.87 (d, *J* = 6.5 Hz, 1H), 3.96 (dd, *J* = 1.8, 6.4 Hz, 1H), 7.17-7.30 (m, 5H), 9.43 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.5, 0.8, 15.0, 41.2, 77.4, 83.5, 126.7, 128.1, 128.9, 143.4, 201.3 ppm. Minor : ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.02 (s, 27H), 0.24 (s, 27H), 1.32 (d, *J* = 7.4 Hz, 3H), 3.11-3.17 (m, 1H), 3.59 (dd, *J* = 0.7, 1.8 Hz, 1H), 3.98 (d, *J* = 4.8 Hz, 1H), 7.18-7.31 (m, 5H), 9.29 (d, *J* = 1.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.5, 0.9, 12.4, 43.5, 77.4, 86.7, 127.0, 128.3, 128.9, 141.5, 202.5 ppm. HRMS (ESI+) calculated for $C_{29}H_{66}O_3Si_8Na$ ([M+Na]$^+$) : 709.3058, found : 709.3050. $[\alpha]_D^{26}$ -6.80 (c 1.47, $CHCl_3$).

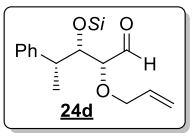
(24b): (2*S*,3*R*,4*R*)/(2*R*,3*S*,4*R*)-2-benzyloxy-3-tris(trimethylsilyl)siloxy-4-phenylpentanal :



24b

(53%, 98/2 *syn/anti*); colorless oil; TLC (hexane:AcOEt, 95:5) R_f = 0.42; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.14 (s, 27H), 1.28 (d, *J* = 7.2 Hz, 3H), 3.15 (dq, *J* = 4.4, 7.4 Hz, 1H), 3.79 (d, *J* = 5.3 Hz, 1H), 3.97 (dd, *J* = 4.6, 5.3 Hz, 1H), 4.42 (d, *J* = 12.1 Hz, 1H), 4.69 (d, *J* = 12.0 Hz, 1H), 7.18-7.31 (m, 10H), 9.60 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.7, 16.7, 42.4, 72.8, 82.1, 84.6, 126.6, 127.7, 127.9, 128.3, 128.5, 128.6, 137.7, 143.8, 202.2 ppm. HRMS (ESI+) calculated for $C_{27}H_{46}O_3Si_4Na$ ([M+Na]$^+$) : 553.2416, found : 553.2415. $[\alpha]_D^{26}$ -15.70 (c 1.02, $CHCl_3$).

(24d): (2*S*,3*R*,4*R*)/(2*R*,3*S*,4*R*)-2-allyloxyoxy-3-tris(trimethylsilyl)siloxy-4-phenylpentanal :



24d

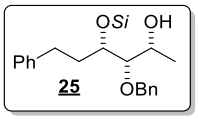
(62%, 98/2 *syn/anti*); colorless oil; TLC (hexane:AcOEt, 95:5) R_f = 0.42 ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.17 (s, 27H), 1.30 (d, *J* = 7.4 Hz, 3H), 3.10 (dq, *J* = 4.4, 7.4 Hz, 1H), 3.73 (d, *J* = 5.3 Hz, 1H), 3.91 (ddt, *J* = 1.6, 5.6, 12.8 Hz, 1H), 3.96 (dd, *J* = 4.2, 5.3 Hz, 1H), 4.10 (ddt, *J* = 1.4, 5.2, 12.8 Hz, 1H), 5.13-5.22 (m, 2H), 5.77-5.85 (m, 1H), 7.16-7.20 (m, 3H), 7.23-7.25 (m, 2H), 9.59 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.8, 16.5, 42.2, 71.9, 82.0, 84.7, 117.7, 126.6, 128.3, 128.5, 134.2, 143.9, 202.2 ppm. HRMS (ESI+) calculated for $C_{23}H_{44}O_3Si_4Na$ ([M+Na]$^+$) : 503.2260, found : 503.2252. $[\alpha]_D^{24}$ -46.00 (c 1, $CHCl_3$).

4. One-pot sequential reaction : synthesis of protected 1,2,3-triols

GP3. General procedure

The aldol reaction was done according to GP2, but instead of quenching the reaction, the following procedure was performed: Reaction was maintained at -40 °C and a solution of nucleophile (1.5 eq.) was added dropwise. After stirring for 1-2h at -40 °C reaction was quenched by the addition of saturated aqueous solution of sodium bicarbonate (2 mL). The reaction was allowed to warm to ambient temperature and stirred vigorously for 20 min. The mixture was diluted with 5 mL of dichloromethane and washed with water and brine. The organic layer was dried over sodium sulfate, filtered through cotton and concentrated under reduced pressure. The residue was then purified by flash chromatography on silica gel eluting with Hexane/ CH_2Cl_2 (20% to 50% gradient).

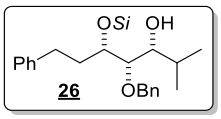
(25): (2*S*,3*S*,4*R*)/(2*R*,3*R*,4*S*)-3-benzyloxy-4-tris(trimethylsilyl)siloxy-6-phenylhexan-2-ol



25

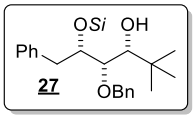
(84%, >99/1/0 *syn/anti*); colorless oil; TLC (hexane:AcOEt, 95:5) R_f = 0.27; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.20 (s, 27H), 1.21 (d, *J* = 6.4 Hz, 3H), 1.73-1.83 (m, 1H), 1.98-2.05 (m, 1H), 2.49 (d, *J* = 4.6 Hz, 1H), 2.67 (dd, *J* = 8.5, 8.7 Hz, 1H), 3.28 (dd, *J* = 3.9, 5.7 Hz, 1H), 3.75 (dt, *J* = 3.9, 6.4 Hz, 1H), 3.96-4.00 (m, 1H), 4.62 (d, *J* = 11.3 Hz, 1H), 4.76 (d, *J* = 11.3 Hz, 1H), 7.14-7.18 (m, 3H), 7.23-7.27 (m, 3H), 7.29-7.36 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.7, 20.5, 32.7, 35.2, 66.5, 73.4, 76.0, 85.4, 125.9, 127.6, 127.9, 128.3, 128.5, 128.6, 138.4, 142.3 ppm. HRMS (ESI+) calculated for $C_{28}H_{50}O_3Si_4Na$ ([M+Na]$^+$) : 569.2729, found : 569.2737.

(26): (3*S*,4*S*,5*R*)/(3*R*,4*R*,5*S*)-4-benzyloxy-5-tris(trimethylsilyl)siloxy-2-methyl-7-phenylheptan-3-ol

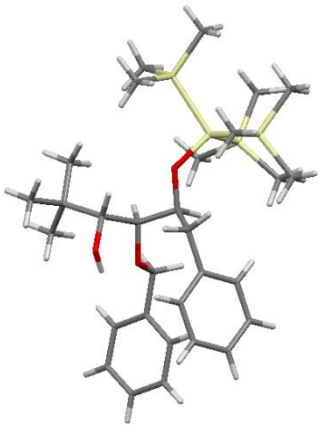


(81%, >99/1/0 *syn/anti*); colorless oil; TLC (hexane: AcOEt, 95:5) R_f = 0.29; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.21 (s, 27H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H), 1.69-1.88 (m, 2H), 2.05-2.16 (m, 1H), 2.41 (d, *J* = 7.6 Hz, 1H), 2.62 (td, *J* = 5.2, 12.0 Hz, 1H), 2.81 (td, *J* = 4.8, 12.8 Hz, 1H), 3.51-3.55 (m, 1H), 3.77-3.81 (m, 1H), 4.64 (d, *J* = 11.5 Hz, 1H), 4.79 (d, *J* = 11.4 Hz, 1H), 7.15-7.22 (m, 2H), 7.24-7.36 (m, 8H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.8, 17.6, 19.9, 31.9, 32.1, 35.7, 73.1, 74.1, 75.8, 80.8, 125.8, 127.8, 127.9, 128.4, 128.5, 128.6, 138.4, 142.4 ppm. HRMS (ESI+) calculated for $C_{30}H_{54}O_3Si_4Na$ ([M+Na]$^+$) : 597.3042, found : 597.3044.

(27): (3*R*,4*S*,5*R*)/(3*S*,4*R*,5*S*)-4-benzyloxy-2,2-dimethyl-5-tris(trimethylsilyl)siloxy-6-phenylhex-1-en-3-ol



(78%, >99/1/0 *syn/anti*); colorless oil; TLC (hexane:AcOEt, 90:10) R_f = 0.64; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.25 (s, 27H), 0.82 (s, 9H), 2.75 (d, *J* = 9.0 Hz, 1H), 2.90 (dd, *J* = 3.5, 14.0 Hz, 1H), 3.15 (dd, *J* = 10.3, 14.0 Hz, 1H), 3.47-3.49 (m, 2H), 4.09 (dt, *J* = 3.7, 10.3 Hz, 1H), 4.23 (d, *J* = 10.7 Hz, 1H), 4.35 (d, *J* = 10.6 Hz, 1H), 6.72-6.75 (m, 2H), 7.12-7.23 (m, 6H), 7.28-7.30 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.8, 26.4, 35.1, 39.6, 72.1, 75.0, 75.8, 78.6, 125.9, 127.5, 128.0, 128.4, 129.3, 137.6, 138.9 ppm. HRMS (ESI+) calculated for $C_{30}H_{54}O_3Si_4Na$ ([M+Na]$^+$) : 597.3042, found : 597.3041.



Single crystal X-ray crystallographic analysis for **27** (CCDC No. 1409678)

Bond precision: C-C = 0.0087 A Wavelength=0.71075

Cell: a=11.113(3) b=35.197(9) c=9.482(3)
alpha=90 beta=102.084(7) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	3626.7(18)	3626.5(16)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C30 H54 O3 Si4	C30 H54 O3 Si4
Sum formula	C30 H54 O3 Si4	C30 H54 O3 Si4
Mr	575.09	575.10
Dx,g cm-3	1.053	1.580
Z	4	6
Mu (mm-1)	0.189	0.284
F000	1256.0	1884.0

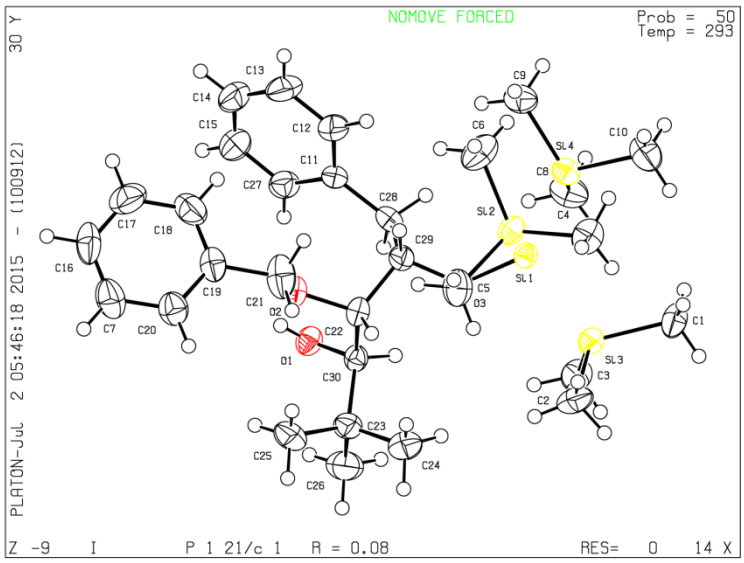
F000'	1257.68	
h,k,lmax	14,45,12	14,45,12
Nref	8322	7577
Tmin,Tmax	0.945,0.945	0.587,0.945
Tmin'	0.945	

Correction method= # Reported T Limits: Tmin=0.587 Tmax=0.945
AbsCorr = MULTI-SCAN

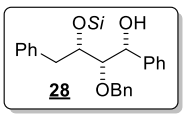
Data completeness= 0.910 Theta(max)= 27.480

R(reflections)= 0.0847(2990) wR2(reflections)= 0.2172(7577)

S = 0.961 Npar= 334

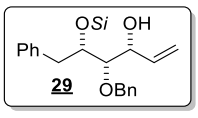


(28): (3*R*,4*S*,5*R*)/(3*S*,4*R*,5*S*)-2-benzyloxy-1,4-diphenyl-3-tris(trimethylsilyl)siloxybutanol



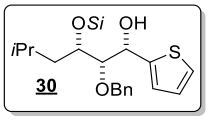
(59%, >99/1/0 *syn/anti*); colorless crystals (crystallized from hexane); TLC (hexane: AcOEt, 95:5) R_f = 0.49; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.18 (s, 27H), 2.94 (dd, *J* = 4.4, 13.7 Hz, 1H), 3.10 (dd, *J* = 8.9, 14.0 Hz, 1H), 3.44 (dd, *J* = 0.9, 3.4 Hz, 1H), 3.98-4.01 (m, 1H), 4.22 (d, *J* = 11.5 Hz, 1H), 4.33 (d, *J* = 11.7 Hz, 1H), 4.9 (d, *J* = 0.9 Hz, 1H), 6.98-6.99 (m, 2H), 7.15-7.32 (m, 13H), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.4, 39.9, 72.4, 73.3, 83.2, 126.2, 126.3, 127.2, 127.4, 127.4, 128.2, 128.3, 128.5, 129.5, 138.2, 138.3, 143.0, 147.2 ppm. HRMS (ESI+) calculated for $C_{32}H_{50}O_3Si_4Na$ ([M+Na]$^+$) : 617.2729, found : 617.2701.

(29): (3*R*,4*S*,5*R*)/(3*S*,4*R*,5*S*)-4-benzyloxy-5-tris(trimethylsilyl)siloxy-6-phenylhex-1-en-3-ol



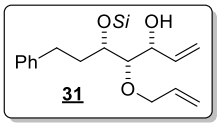
(68%, >99/1/0 *syn/anti*); colorless oil; TLC (hexane: AcOEt, 95:5) R_f = 0.34 ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.18 (s, 27H), 2.62 (d, *J* = 6.2 Hz, 1H), 2.87 (dd, *J* = 6.4, 13.8 Hz, 1H), 3.08 (dd, *J* = 3.9, 13.8 Hz, 1H), 3.30 (t, *J* = 3.9 Hz, 1H), 3.98 (td, *J* = 3.9, 6.5 Hz, 1H), 4.38-4.42 (m, 1H), 4.56 (d, *J* = 11.7 Hz, 1H), 4.61 (d, *J* = 11.7 Hz, 1H), 5.13 (dt, *J* = 1.6, 10.6 Hz, 1H), 5.34 (dt, *J* = 1.6, 17.2 Hz, 1H), 5.83-5.91 (m, 1H), 7.18-7.38 (m, 10H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.8, 39.8, 71.0, 73.1, 77.9, 82.1, 115.4, 126.3, 127.5, 127.7, 128.4, 128.5, 129.7, 138.4, 138.9, 140.0 ppm. HRMS (ESI+) calculated for $C_{28}H_{48}O_3Si_4Na$ ([M+Na]$^+$) : 567.2573, found : 567.2578.

(30): (3*R*,4*S*,5*R*)/(3*S*,4*R*,5*S*)-2-benzyloxy-4-isopropyl-1-(2-thienyl)-3-tris(trimethylsilyl)siloxybutanol



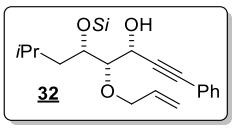
(75%, >99/1/0 *syn/anti*); colorless oil; TLC (hexane: AcOEt, 95:5) R_f = 0.35; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.19 (s, 27H), 0.86-0.90 (m, 6H), 1.40-1.44 (m, 1H), 1.72-1.79 (m, 2H), 3.12 (d, *J* = 6.7 Hz, 1H), 3.68 (dd, *J* = 3.2, 3.4 Hz, 1H), 3.72-3.76 (m, 1H), 4.60 (s, 2H), 5.23 (dd, *J* = 3.2, 6.7 Hz, 1H), 6.96 (dd, *J* = 3.5, 5.0 Hz, 1H), 7.00-7.01 (m, 1H), 7.23 (dd, *J* = 1.1, 5.0 Hz, 1H), 7.26-7.34 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.7, 22.8, 23.9, 24.8, 42.7, 68.4, 73.5, 74.1, 84.0, 124.3, 124.6, 126.6, 127.7, 127.8, 128.5, 138.2, 147.5 ppm. HRMS (ESI+) calculated for $C_{27}H_{50}O_3SSi_4Na$ ([M+Na]$^+$) : 589.2450, found : 589.2461.

(31): (3*R*,4*S*,5*R*)/(3*S*,4*R*,5*S*)-4-allyloxy-5-tris(trimethylsilyl)siloxy-7-phenylhept-1-en-3-ol



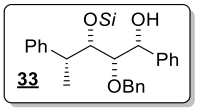
(82%, >99/1/0 *syn/anti*); colorless oil; TLC (hexane:AcOEt, 90:10) R_f = 0.47; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.19 (s, 27H), 1.70-1.85 (m, 1H), 2.00-2.10 (m, 1H), 2.60 (d, *J* = 6.6 Hz, 1H), 2.64-2.69 (m, 1H), 3.32 (t, *J* = 4.1 Hz, 1H), 3.67 (dt, *J* = 4.4, 6.2 Hz, 1H), 4.09-4.20 (m, 2H), 4.30-4.33 (m, 1H), 5.13-5.18 (m, 2H), 5.25-5.37 (m, 2H), 5.84-5.97 (m, 2H), 7.15-7.18 (m, 3H), 7.25-7.28 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.7, 32.4, 35.3, 70.6, 72.6, 76.6, 82.8, 114.9, 117.1, 125.8, 128.4, 128.5, 134.8, 139.2, 142.4 ppm. HRMS (ESI+) calculated for $C_{25}H_{48}O_3Si_4Na$ ([M+Na]$^+$) : 531.2578, found : 531.2564.

(32): (3*R*,4*S*,5*R*)/(3*S*,4*R*,5*S*)-4-allyloxy-7-methyl-5-tris(trimethylsilyl)siloxy-oct-1-yn-3-ol



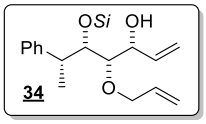
(52%, 88/12/0 *syn/anti*); colorless oil; TLC (hexane: AcOEt, 90:10) R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.20 (s, 27H), 0.89 (d, *J* = 6.6 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 3H), 1.35-1.39 (m, 1H), 1.69-1.75 (m, 1H), 2.84 (d, *J* = 7.1 Hz, 1H), 3.59 (dd, *J* = 3.5, 3.6 Hz, 1H), 3.72 (dt, *J* = 3.7, 6.6 Hz, 1H), 4.21-4.26 (m, 2H), 4.36-4.41 (m, 1H), 4.78 (dd, *J* = 3.4, 7.1 Hz, 1H), 5.16-5.19 (m, 1H), 5.28-5.34 (m, 1H), 5.88-6.00 (m, 1H), 7.27-7.30 (m, 3H), 7.39-7.41 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.7, 23.1, 23.4, 24.7, 42.2, 61.1, 72.6, 75.0, 82.2, 85.0, 89.9, 117.0, 122.9, 128.3, 128.4, 131.7, 134.8 ppm. HRMS (ESI+) calculated for $C_{27}H_{50}O_3Si_4Na$ ([M+Na]$^+$) : 557.2729, found : 557.2714.

(33): (3*R*,4*S*,5*R*)/(3*S*,4*R*,5*S*)-2-benzyloxy-1,4-diphenyl-3-tris(trimethylsilyl)siloxypropanol



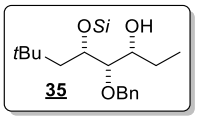
(50%, 83/17/0 *syn/anti*); colorless oil; TLC (hexane: AcOEt, 90:10) R_f = 0.48; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.24 (s, 27H), 1.33 (d, *J* = 7.3 Hz, 3H), 3.05 (d, *J* = 8.7Hz, 1H), 3.33 (t, *J* = 7.1 Hz, 1H), 3.50 (dd, *J* = 2.1, 4.8 Hz, 1H), 3.94 (dd, *J* = 4.8, 7.3 Hz, 1H), 4.00 (d, *J* = 11.2 Hz, 1H), 4.35 (d, *J* = 11.2 Hz, 1H), 4.76 (dd, *J* = 1.8, 8.7 Hz, 1H), 6.74-6.76 (m, 2H), 7.07-7.09 (m, 2H), 7.12-7.30 (m, 11H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 1.18, 20.2, 43.0, 71.4, 73.5, 80.1, 84.2, 126.1, 126.3, 127.2, 127.4, 127.5, 127.9, 128.1, 128.2, 128.4, 128.5, 137.7, 144.7 ppm. HRMS (ESI+) calculated for $C_{33}H_{52}O_3Si_4Na$ ([M+Na]$^+$) : 631.2885, found : 631.2877. $[\alpha]_D^{26}$ -16.13 (c 0.62, $CHCl_3$).

(34): (3*R*,4*S*,5*R*,6*R*)/(3*S*,4*R*,5*S*,6*S*)-4-allyloxy-5-tris(trimethylsilyl)siloxy-6-phenylhept-1-en-3-ol (24) :



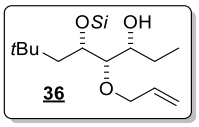
(63%, >99/1/0 *syn/anti*); colorless oil; TLC (hexane:AcOEt, 95:5) R_f = 0.26; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.23 (s, 27H), 1.29 (d, *J* = 7.1 Hz, 3H), 2.48 (d, *J* = 7.8 Hz, 1H), 3.20-3.23 (m, 2H), 3.73 (ddt, *J* = 1.2, 6.0, 12.4 Hz, 1H), 3.83 (dd, *J* = 4.0, 7.6 Hz, 2H), 4.29-4.32 (m, 1H), 4.89-4.98 (m, 2H), 5.10 (dt, *J* = 1.6, 17.2 Hz, 1H), 5.45-5.55 (m, 1H), 5.78-5.85 (m, 1H), 7.12-7.28 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 1.1, 20.2, 42.5, 70.0, 71.8, 79.5, 82.6, 115.1, 116.5, 125.9, 127.8, 128.2, 134.3, 139.2, 145.5 ppm. HRMS (ESI+) calculated for $C_{25}H_{48}O_3Si_4Na$ ([M+Na]$^+$) : 531.2573, found : 531.2569. $[\alpha]_D^{26}$ -16.95 (c 0.59, $CHCl_3$).

(35): (3*R*,4*S*,5*R*)/(3*S*,4*R*,5*S*)-4-benzyloxy-7,7-dimethyl-5-tris(trimethylsilyl)siloxyoct-3-ol



(33%, >99/1/0 *syn/anti*); colorless oil; TLC (hexane:AcOEt, 95:5) R_f = 0.37; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.18 (s, 27H), 0.95 (s, 9H), 1.00 (t, *J* = 7.3 Hz, 3H), 1.42 (dd, *J* = 6.4, 14.2 Hz, 1H), 1.42-1.50 (m, 1H), 1.60-1.65 (m, 1H), 1.77 (dd, *J* = 5.8, 14.4 Hz, 1H), 2.29 (br. s, 1H), 3.34 (dd, *J* = 2.8, 4.6 Hz, 1H), 3.76-3.85 (m, 2H), 4.62 (d, *J* = 11.2 Hz, 1H), 4.71 (d, *J* = 11.2 Hz, 1H), 7.25-7.36 (m, 5H), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = -0.5, 1.0, 10.5, 27.4, 30.8, 46.1, 71.5, 72.2, 73.9, 83.6, 127.5, 127.7, 128.5, 138.6 ppm. HRMS (ESI+) calculated for $C_{26}H_{54}O_3Si_4Na$ ([M+Na]$^+$) : 549.3042, found : 549.3046.

(36): (3*R*,4*S*,5*R*)/(3*S*,4*R*,5*S*)-4-allyloxy-7,7-dimethyl-5-tris(trimethylsilyl)siloxyoct-3-ol



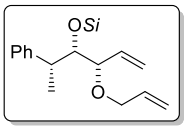
(36%, >99/1/0 *syn/anti*); colorless oil; (hexane:AcOEt, 90:10) R_f = 0.44; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.18 (s, 27H), 0.94 (s, 9H), 1.00 (t, *J* = 7.3 Hz, 3H), 1.38 (dd, *J* = 6.0, 14.2 Hz, 1H), 1.38-1.49 (m, 1H), 1.57-1.65 (m, 1H), 1.72 (dd, *J* = 6.0, 14.2 Hz, 1H), 2.28 (br. s, 1H), 3.19 (dd, *J* = 3.9, 5.3 Hz, 1H), 3.72-3.73 (m, 2H), 4.12 (qd, *J* = 5.5, 12.6 Hz, 2H), 5.14 (d, *J* = 10.6 Hz, 1H), 5.27 (d, *J* = 17.2 Hz, 1H), 5.86-5.93 (m, 1H), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = -0.5, 1.1, 10.5, 27.4, 30.7, 46.1, 71.1, 71.5, 73.9, 83.3, 116.5, 135.0 ppm. HRMS (ESI+) calculated for $C_{22}H_{52}O_3Si_4Na$ ([M+Na]$^+$) : 499.2885, found : 499.2865.

5. Synthesis of the pentose-like scaffold

GP4. Procedure for the Wittig reaction

To a stirring suspension of methyltriphenylphosphium bromide (104 mg, 0.29 mmol) in anhydrous THF (1.8 mL) at 0°C was added *n*-Butyllithium (0.19 mL, 0.30 mmol, 1.6 M in hexane), dropwise. The yellow solution was stirred at this temperature for 1h then cooled to −78°C. In a separate flask, aldehyde **24d** was dissolved in anhydrous THF (0.2 mL) and added to the ylide solution by syringe, drop wise. The reaction was slowly warmed to room temperature and stirred until TLC analysis indicated total conversion of the starting aldehyde. The reaction was then quenched by the addition of 3 mL MeOH/H_2O (3:2 v/v) and 2 mL of saturated aqueous NH_4Cl. 5 mL of hexane was then added. The layers were separated and the organic layer was washed with 5 mL of H_2O and 5 mL of brine. The organic layer was dried over Na_2SO_4, filtered through cotton and evaporated. The crude mixture was purified by flash chromatography with hexane as eluent.

(3*R*,4*S*,5*R*)/(3*S*,4*R*,5*S*)-3-allyloxy-4-tris(trimethylsilyl)siloxy-5-phenylhex-1-ene

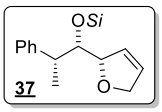


(64%, 98/2 *syn/anti*); colorless oil; TLC (hexane: AcOEt, 95:5) R_f = 0.71; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.18 (s, 27H), 1.22 (d, *J* = 7.1 Hz, 3H), 3.00-3.07 (m, 1H), 3.72-3.80 (m, 3H), 3.91-3.96 (m, 1H), 5.01-5.10 (m, 2H), 5.21-5.26 (m, 2H), 5.72-5.80 (m, 1H), 5.84-5.93 (m, 1H), 7.13-7.19 (m, 3H), 7.22-7.28 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.9, 17.4, 41.1, 69.8, 81.8, 82.4, 115.8, 116.5, 125.8, 128.1, 128.1, 135.1, 135.3, 146.3 ppm. HRMS (ESI+) calculated for $C_{24}H_{46}O_2Si_4Na$ ([M+Na]$^+$) : 501.2467, found : 501.2469. $[\alpha]_D^{26}$ -21.43 (c 1.12, $CHCl_3$).

GP5. Procedure for the RCM reaction

In an oven dried round bottom flask equipped with condenser, 2 mol% of Grubbs catalyst 2nd generation (8 mg, 0.009 mmol) was added to a solution of the olefin (0.47 mmol) in anhydrous dichloromethane (6 mL) and the mixture was then heated at 40 °C for 2h until TLC analysis indicated consumption of starting material. The mixture was then cooled to room temperature and concentrated in vacuum. The crude product was then purified by silica gel flash chromatography using hexane/EtOAc as eluent.

(37): (1*S*,2*S*)/(1*R*,2*R*)-1-((*S*)-2,5-dihydrofuran-2-yl)-1-tris(trimethylsilyl)siloxy-2-phenylpropane



(95%, 98/2 *syn/anti*); colorless oil; TLC (hexane:AcOEt, 95:5) R_f = 0.51; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.17 (s, 27H), 1.22 (d, *J* = 7.1 Hz, 3H), 2.72-2.75 (m, 1H), 3.71 (dd, *J* = 4.8, 5.7 Hz, 1H), 3.92-3.98 (m, 1H), 4.35-4.40 (m, 1H), 4.80-4.83 (m, 1H), 5.78-5.80 (m, 1H), 5.82-5.84 (m, 1H), 7.10-7.15 (m, 3H), 7.21-7.25 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.8, 18.1, 42.2, 75.0, 82.6, 89.6, 125.7, 126.5, 128.0, 128.1, 128.2, 145.7 ppm. HRMS (ESI+) calculated for $C_{22}H_{42}O_2Si_4Na$ ([M+Na]$^+$) : 473.2154, found : 473.2146.

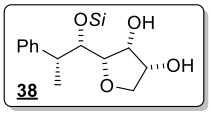
GP6. Optimization of the asymmetric dihydroxylation

37 **38**

entry	conditions	results
1	OsO_4 NMO (2 equiv) *t*-BuOH/H_2O/acetone (17/1/1.3) r.t, 12h	65% yield 62:38 dr 100% conversion
2	AD-mix-α $MeSO_2NH_2$ (3 equiv) *t*-BuOH/H_2O (1:1) 0 °C, 4 days	74% yield 82:18 dr 100% conversion
3	AD-mix-β $MeSO_2NH_2$ (3 equiv) *t*-BuOH/H_2O (1:1) 0 °C, 4 days	73% yield 98:2 dr 100% conversion

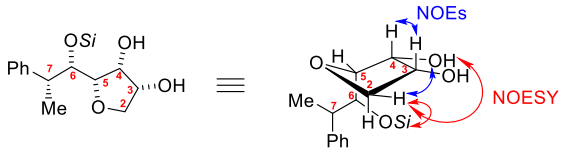
Typical procedure (entry 3): AD-mix-β (124 mg) was dissolved in *t*-BuOH (0.4 mL) and H_2O (0.4 mL). Methanesulfonamide (25 mg, 0.266 mmol) and alkene **37** (40 mg, 0.088 mmol) dissolved in 0.5 mL of *t*-BuOH/H_2O (1:1) were then added at 0 °C and the reaction vigorously stirred for 4 days at same temperature. After complete consumption of the starting material, Na_2SO_3 (122 mg) was then added and the solution stirred for 1h after which the reaction was poured into water (3 mL) and extracted with EtOAc (3 x 5 mL). The combined organics were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to yield the crude diol which was purified by silica gel column chromatography using Hexane/EtOAc (3/2) to yield pure diol **38** (31 mg, 73%) as white solid.

(38): (2*R*,3*S*,4*S*)-2-((1*S*,2*R*)-1-tris(trimethylsilyl)siloxy-2-phenylpropyl)-tetrahydrofuran-3,4-diol



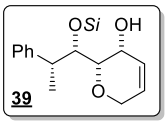
(73%, dr = 98/2, **38**-(*all-syn*)); white solid; TLC (hexane:EtOAc, 60:40) R_f = 0.51, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.09 (s, 27H), 1.26 (d, *J* = 7.1 Hz, 3H), 1.90 (d, *J* = 4.4 Hz, 1H; C3-OH), 2.41 (d, *J* = 7.8 Hz, 1H; C4-OH), 2.98 (dq, *J* = 4.4, 7.1 Hz, 1H; C7-H), 3.50 (d, *J* = 2.8, 8.5 Hz, 1H; C5-H), 3.60 (d, *J* = 6.4, 9.2Hz, 1H; C2a-H), 3.75 (dd, *J* = 2.4, 4.8 Hz, 1H; C4-H), 3.80 (dd, *J* = 7.6, 9.2 Hz, 1H; C3-H), 3.90 (dd, *J* = 4.6, 8.5 Hz, 1H; C6-H), 4.29-4.35 (m, 1H; C5b-H), 7.18-7.21 (m, 1H), 7.23-7.29 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.8, 15.5, 42.7, 71.4, 71.7, 72.4, 80.1, 85.5, 126.5, 128.0, 128.5, 145.2 ppm. HRMS (ESI+) calculated for $C_{22}H_{44}O_4Si_4Na$ ([M+Na]$^+$) : 507.2209, found : 507.2199. $[\alpha]_D^{24}$ -7.69 (c 1.3, $CHCl_3$).

Stereochemistry of compound **38** was assigned *all-syn* by carrying out NOE and NOESY experiments in addition to analysis of coupling constant values of the ^{1}H NMR spectra.



6. Synthesis of the Hexose-like scaffold

(39): (2*S*,3*S*)-2-((1*R*,2*S*)-1-hydroxy-2-phenylpropyl)-3,6-dihydro-2H-pyran-3-ol



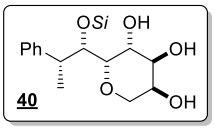
Prepared following **GP5**, (97%, >99/1/0 *syn/anti*); colorless oil; TLC (hexane:AcOEt, 90:10) R_f = 0.33; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.06 (s, 27H), 1.26 (d, *J* = 7.3 Hz, 3H), 3.18 (qd, *J* = 1.6, 7.3 Hz, 1H), 3.24 (dd, *J* = 1.6, 8.5 Hz, 1H), 3.85-3.90 (m, 1H), 4.00 (dd, *J* = 2.1, 8.5 Hz, 1H), 4.00-4.07 (m, 1H), 4.20 (ddd, *J* = 1.6, 3.5, 16.9 Hz, 1H), 5.92 (ddd, *J* = 1.4, 3.4, 10.1, 1H), 5.96-6.16 (m, 1H), 7.14-7.18 (m, 1H), 7.24-7.28 (m, 2H), 7.30-7.33 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.8, 13.0, 40.2, 62.8, 66.4, 81.0, 81.4, 126.1, 126.8, 128.1, 128.3, 130.6, 144.7 ppm. HRMS (ESI+) calculated for $C_{23}H_{44}O_3Si_4Na$ ([M+Na]$^+$) : 503.2260, found : 503.2254. $[\alpha]_D^{26}$ -50.51 (c 0.99, $CHCl_3$).

GP7. Optimization of the asymmetric dihydroxylation

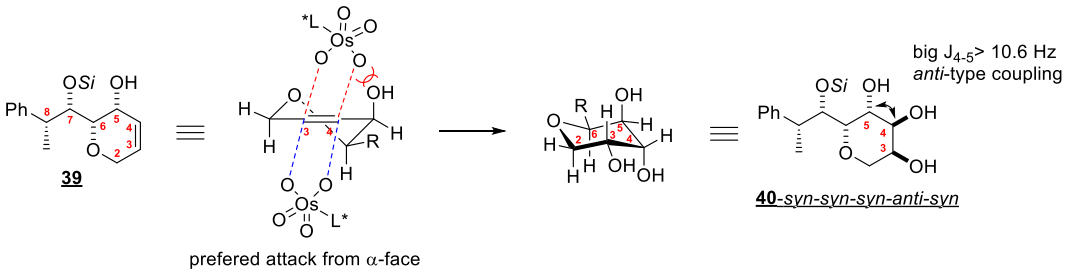
entry	conditions	results
1	OsO_4 NMO (2 equiv) *t*-BuOH/H_2O/acetone (17/1/1.3) r.t, 12h	68% yield >98:2 dr 100% conversion
2	AD-mix-α $MeSO_2NH_2$ (3 equiv) *t*-BuOH/H_2O (1:1) 0 °C, 4 days	62% yield 98:2 dr 54% conversion
3	AD-mix-β $MeSO_2NH_2$ (3 equiv) *t*-BuOH/H_2O (1:1) 0 °C, 4 days	74% yield 96:4 dr 50% conversion

Typical procedure (entry 1): A solution (0.7 mL) of osmium tetroxide in *t*-BuOH (osmium tetroxide/*t*-BuOH = 1/30 w/v) was added to a mixture of **39** (70 mg, 0.145 mmol) and *N*-methylmorpholine *N*-oxide (36 mg, 0.435 mmol) in acetone/water (0.5 mL, 8/1, v/v) and stirred vigorously for overnight at room temperature. After TLC analysis indicated full consumption of starting material, Na_2SO_3 (420 mg) was added to the reaction mixture with ice-cooling and was then vigorously stirred for 30 min at room temperature. The reaction mixture was evaporated under reduced pressure and the crude triol was purified by silica gel chromatography using hexane/methanol (95/5) as eluent.

(40): (2*S*,3*R*,4*S*,5*S*)-2-((1*S*,2*S*)-1-(tris(trimethylsilyl)siloxy)-2-phenylpropyl)tetrahydro-2H-pyran-3,4,5-triol

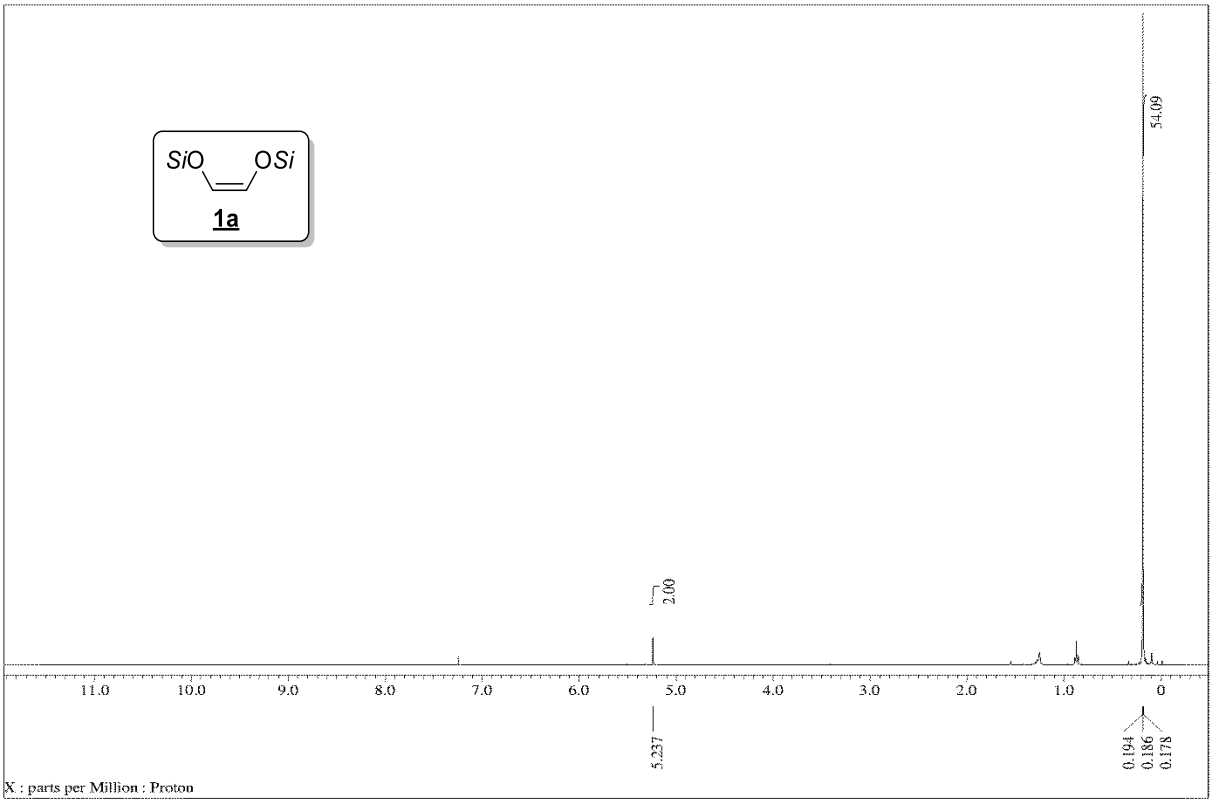


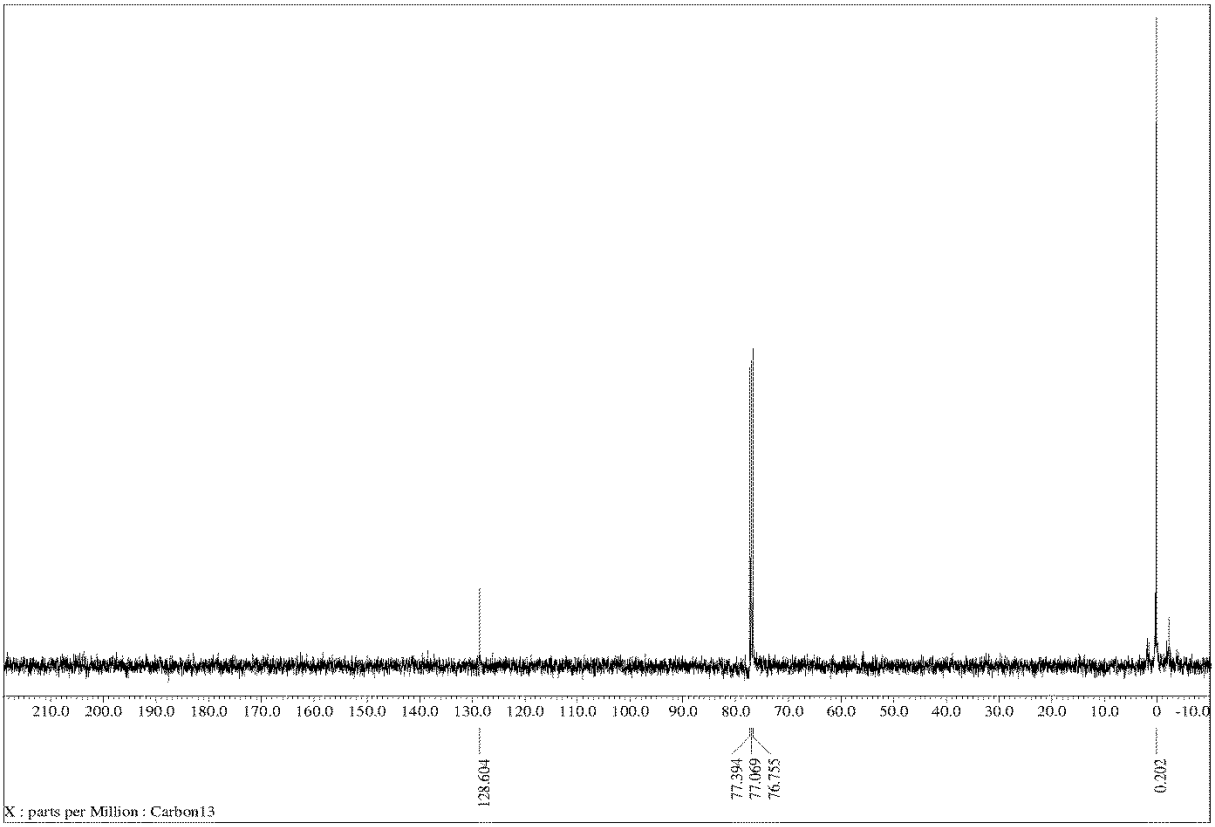
(68%, dr >98/2, **40**-*syn-syn-syn-anti-syn*); white solid; TLC (DCM:MeOH, 90:10) R_f = 0.40; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.08 (s, 27H), 1.26 (d, *J* = 7.4 Hz, 3H), 2.01 (d, *J* = 8.4 Hz, 1H; OH), 2.29 (br. s, 1H, OH), 2.51 (br. s, 1H; OH), 3.02 (qd, *J* = 3.0, 7.1 Hz, 1H; C8-H), 3.31 (t, *J* = 10.8 Hz, 1H; C4-H), 3.50 (d, *J* = 7.8 Hz, 1H; C6-H), 3.72 (dd, *J* = 5.5, 10.6 Hz, 1H; C5-H), 3.78-3.81 (m, 1H; C3-H), 3.85 (dd, *J* = 3.2, 7.8 Hz, 1H; C7-H), 3.94-3.97 (m, 2H; C2-H), 7.14-7.18 (m, 1H), 7.23-7.28 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.9, 14.2, 41.2, 64.5, 66.4, 70.1, 70.3, 77.9, 80.8, 126.3, 128.2, 128.3, 144.4 ppm. HRMS (ESI+) calculated for $C_{23}H_{46}O_5Si_4Na$ ([M+Na]$^+$) : 537.2315, found : 537.2305. $[\alpha]_D^{24}$ -10.75 (c 0.93, $CHCl_3$).

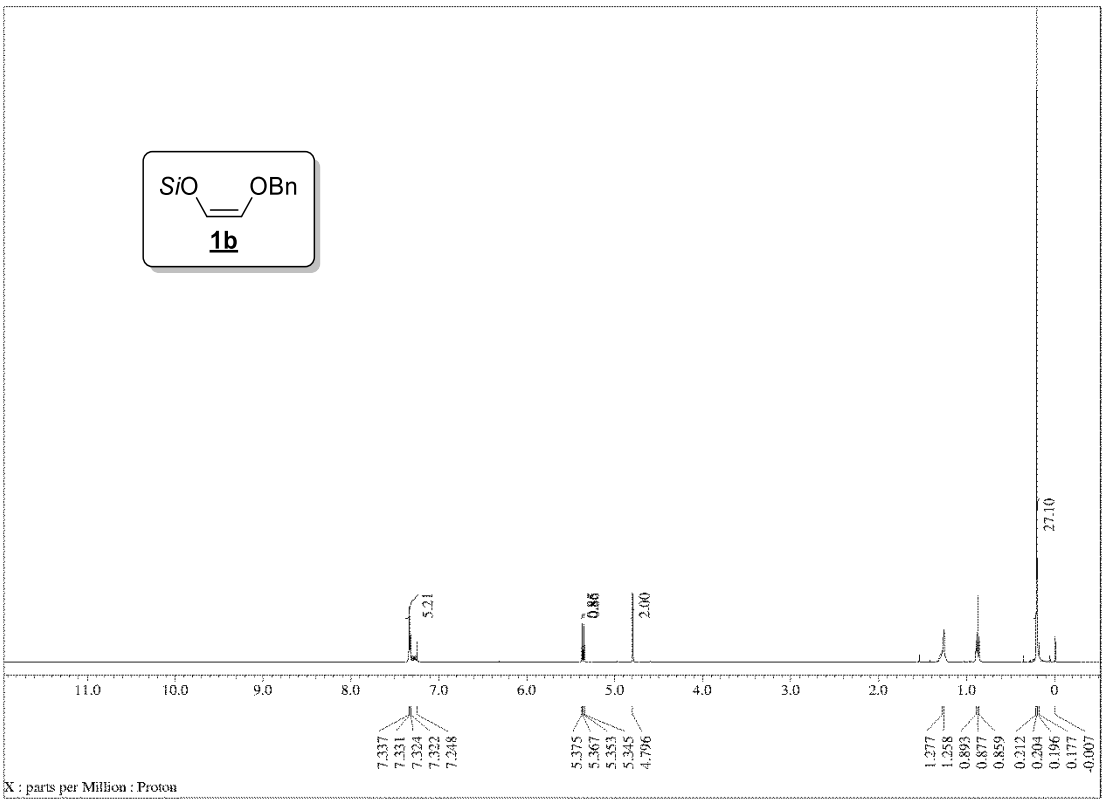


[1] Benzyloxyacetaldehyde was purchased from aldrich and used as received. All other protected β-hydroxyacetaldehydes were prepared according to reported procedure starting from ethyl glycolate : Angle, S. R.; Choi, I.; Tham, F. S. *J. Org. Chem.* 2008, **73**, 6268-6278.

7. ^{1}H, ^{13}C, ^{19}F, NOE and NOESY spectra of compound 1a to 40



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OBn
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2.00
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10.0
9.0
8.0
7.0
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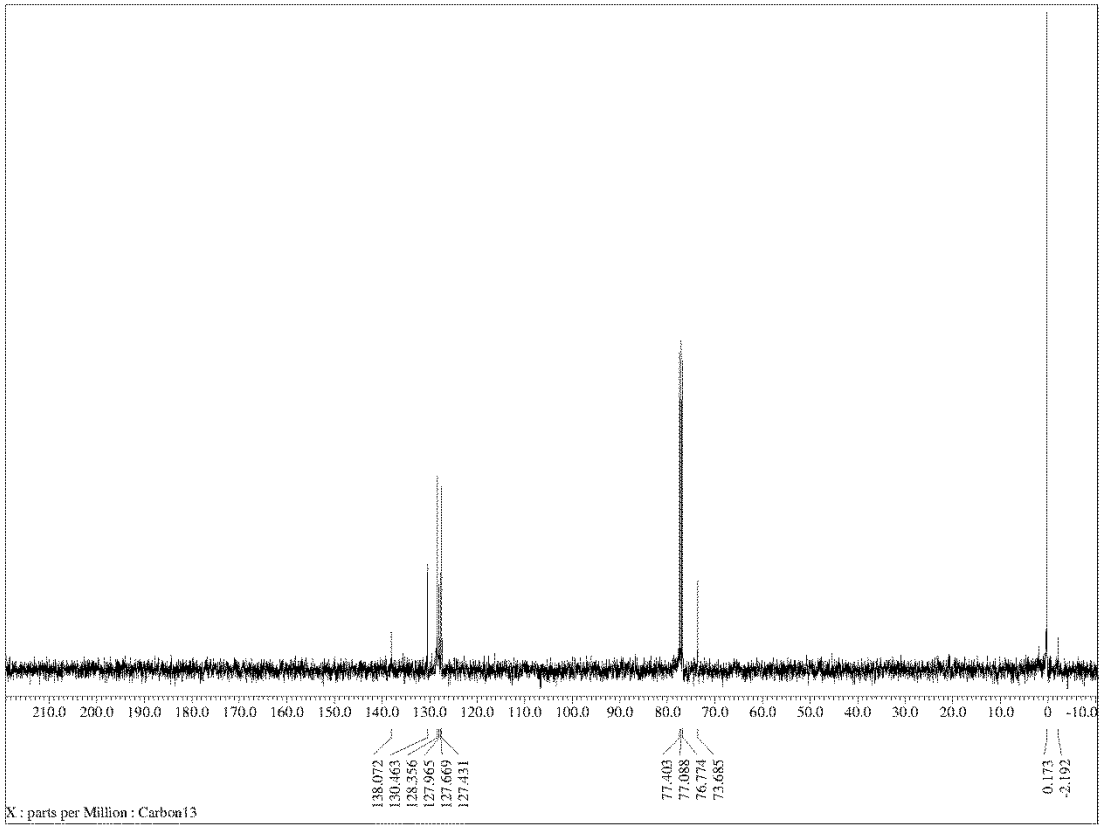
4.0
3.0
2.0
1.0
0
7.337
7.331
7.324
7.322
7.248
5.375
5.367
5.353
5.345
4.796
1.277
1.258
0.893
0.877
0.859
0.212
0.204
0.196
0.177
-0.007
X : parts per Million : Proton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180.0
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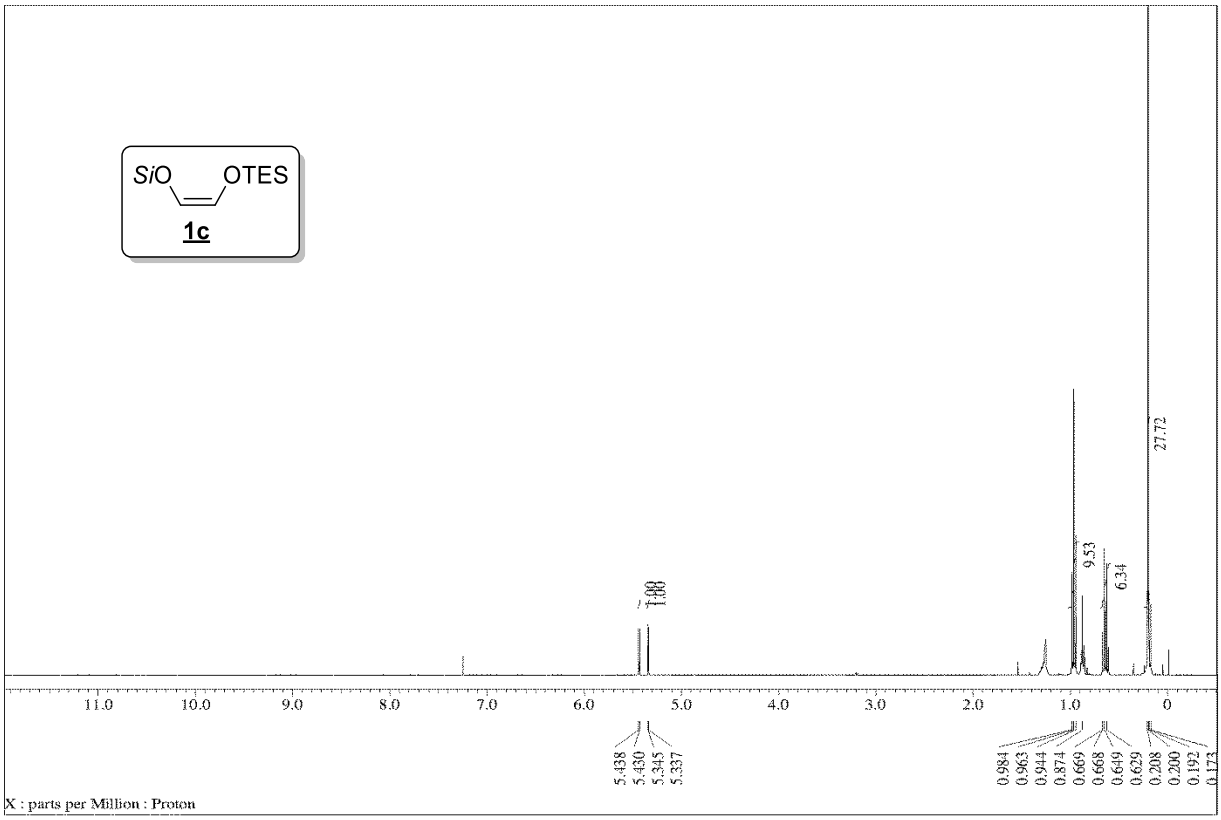
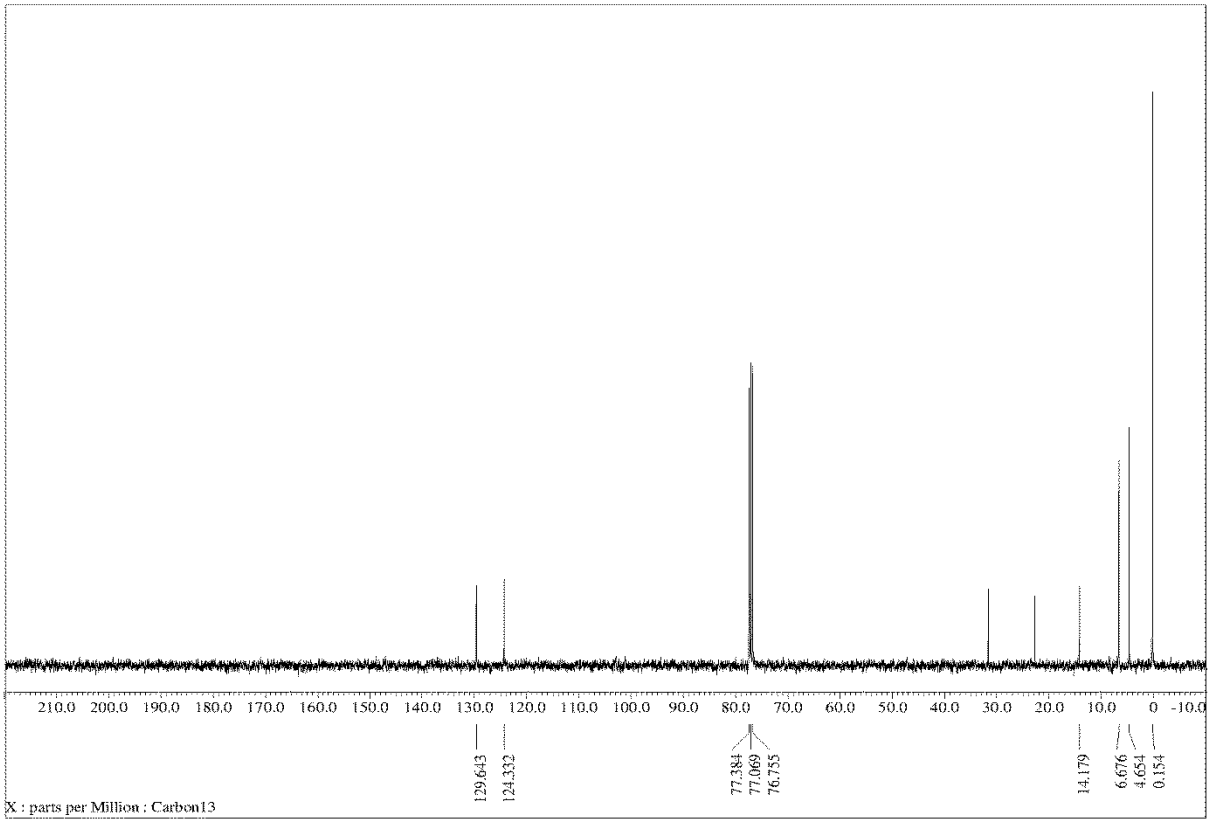
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
138.072
130.463
128.356
127.965
127.669
127.431
77.403
77.088
76.774
73.685
0.173
-2.192
X : parts per Million : Carbon13


SiO
OTES
1c
27.72
9.53
6.34
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
5.438
5.430
5.345
5.337
0.984
0.963
0.944
0.874
0.669
0.668
0.649
0.629
0.208
0.200
0.192
0.173
X : parts per Million : Proton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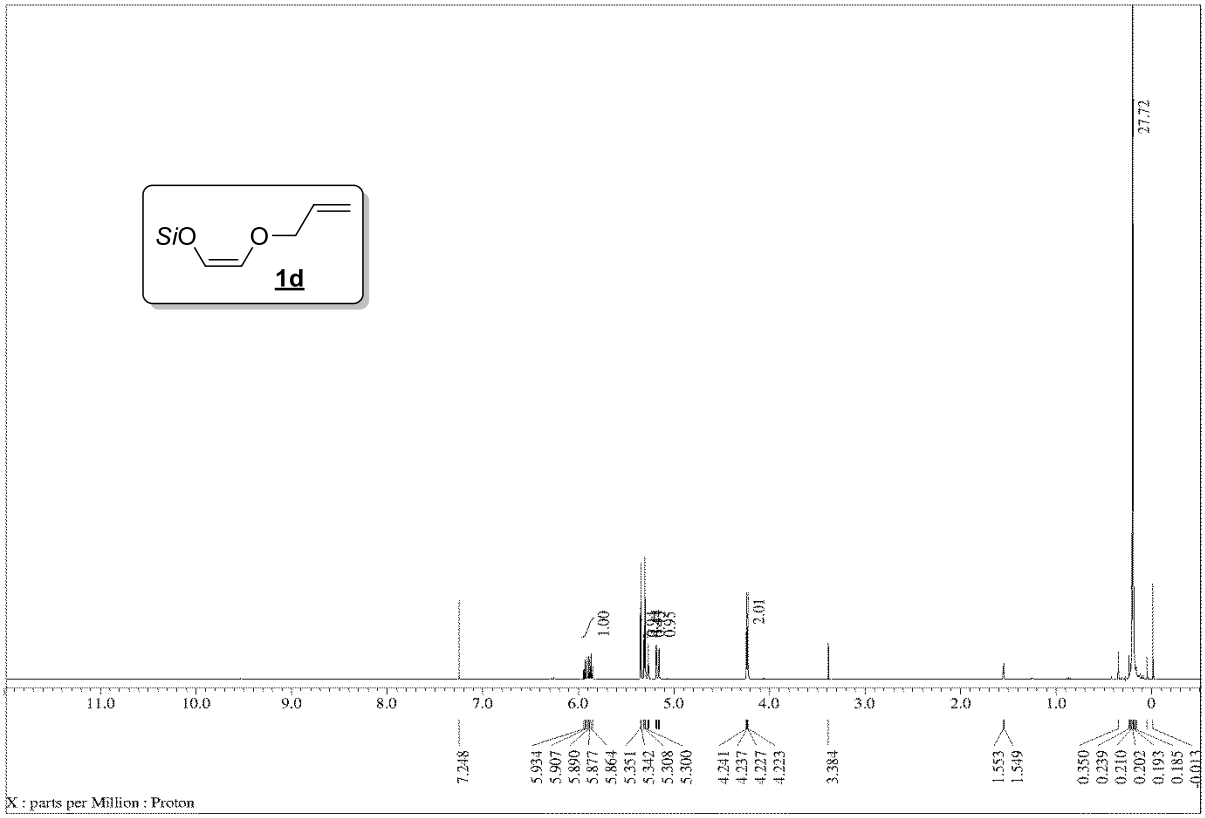
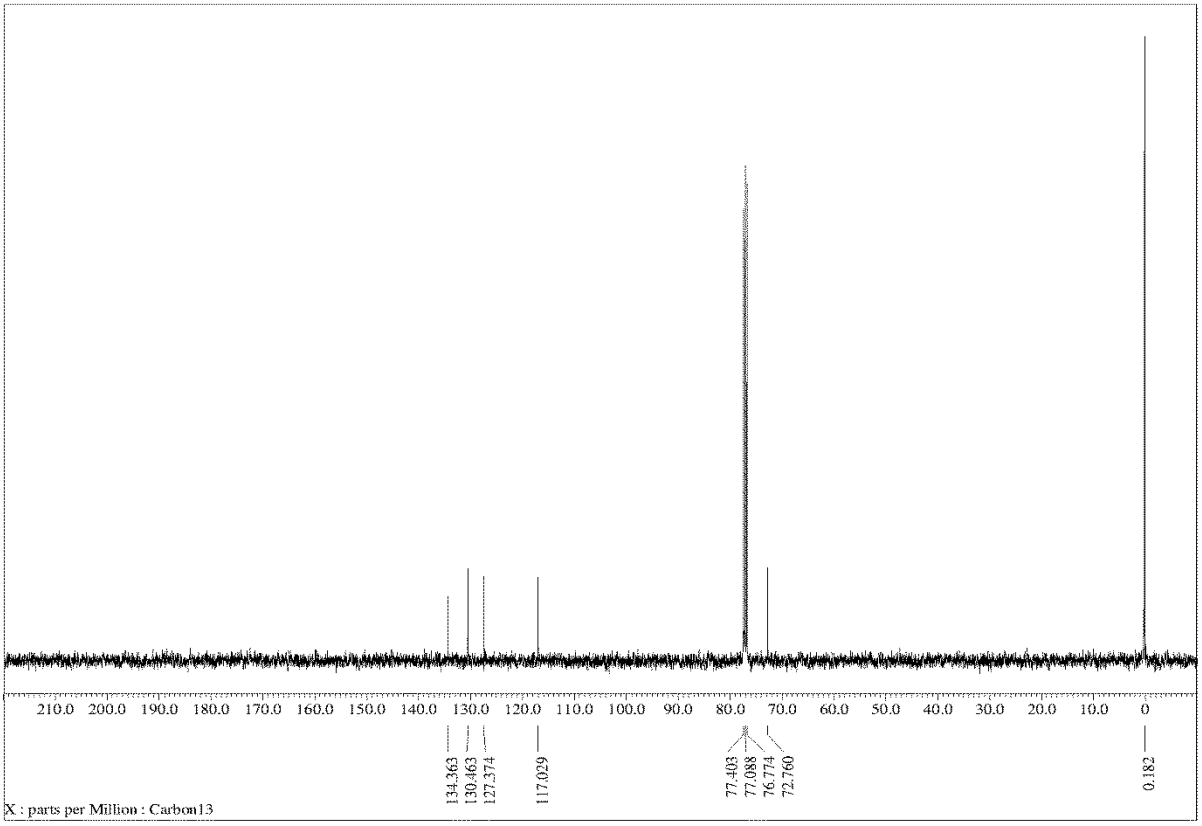
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
129.643
124.332
77.384
77.069
76.755
14.179
6.676
4.654
0.154
X : parts per Million : Carbon13


SiO
O
1d
27.72
1.00
2.01
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.248
5.934
5.907
5.890
5.877
5.864
5.351
5.342
5.308
5.300
4.241
4.237
4.227
4.223
3.384
1.553
1.549
0.350
0.239
0.210
0.202
0.193
0.185
-0.013
X : parts per Million : Proton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180.0
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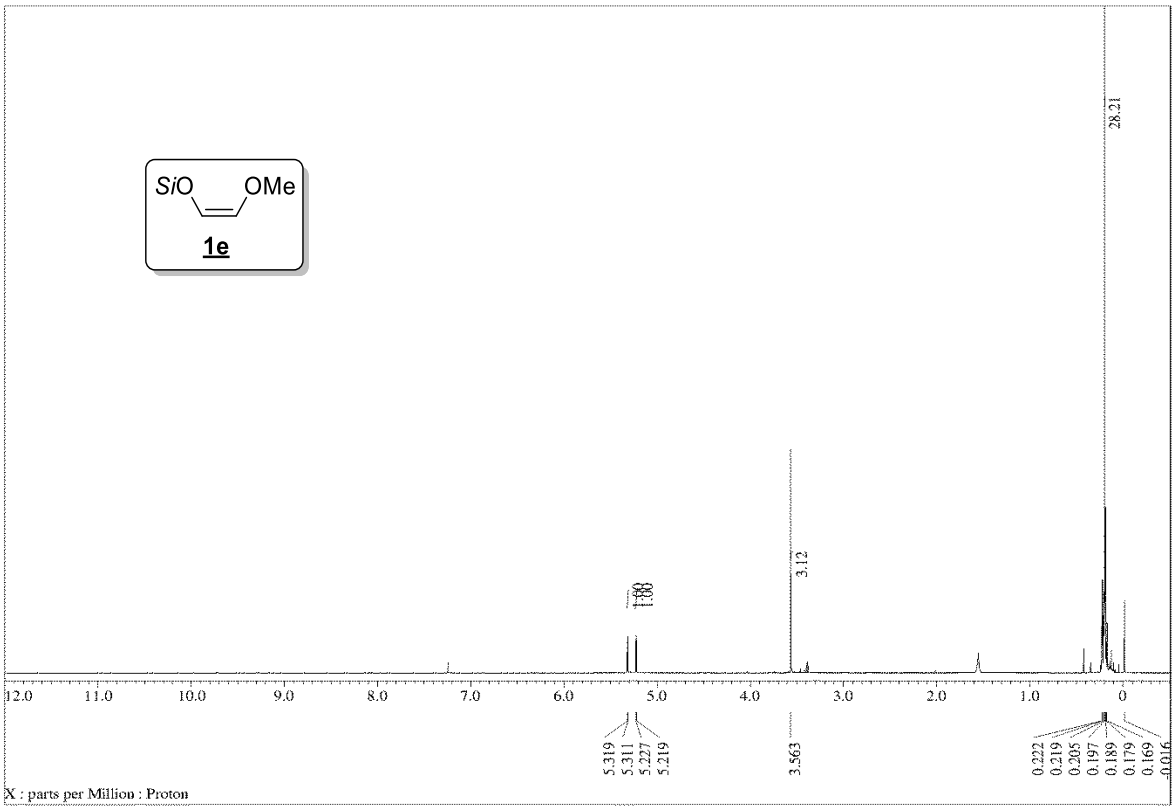
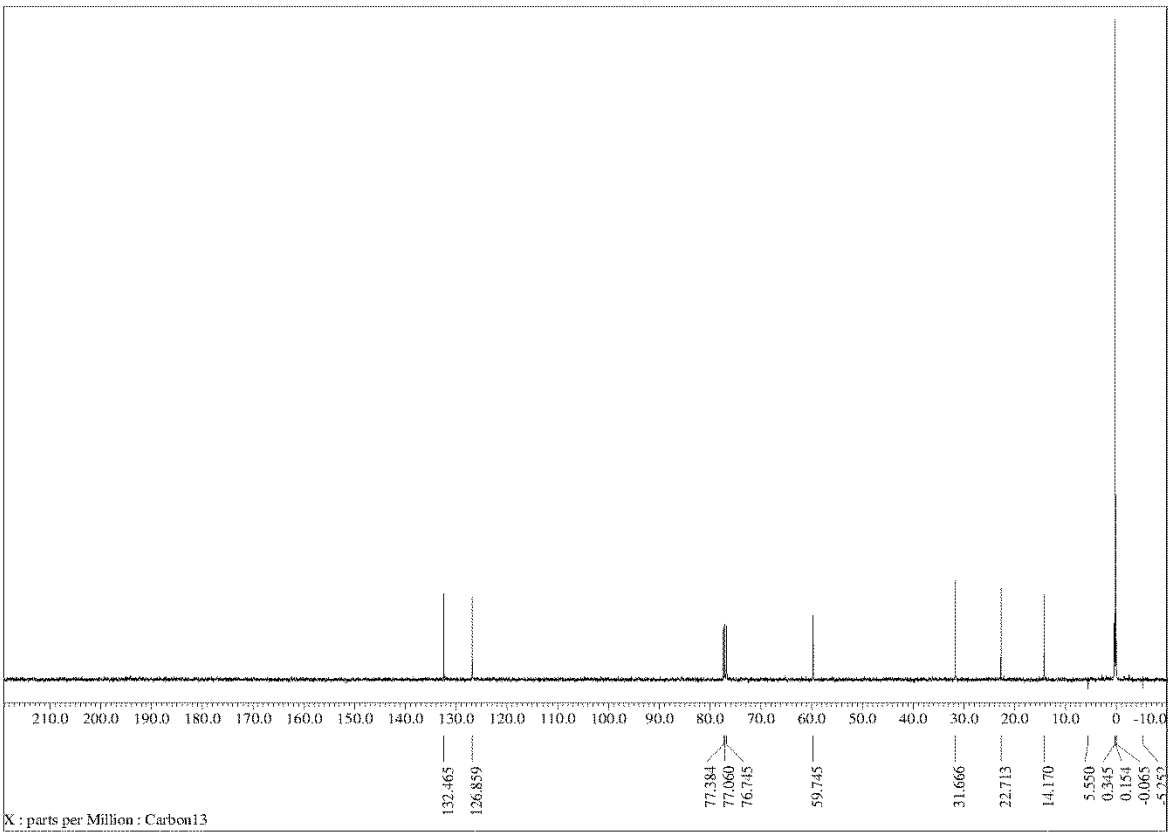
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
134.363
130.463
127.374
117.029
77.403
77.088
76.774
72.760
0.182
X : parts per Million : Carbon13


SiO
OMe
1e
28.21
3.12
5.319
5.311
5.227
5.219
3.563
0.222
0.219
0.205
0.197
0.189
0.179
0.169
-0.016
X : parts per Million : Proton


132.465
126.859
77.384
77.060
76.745
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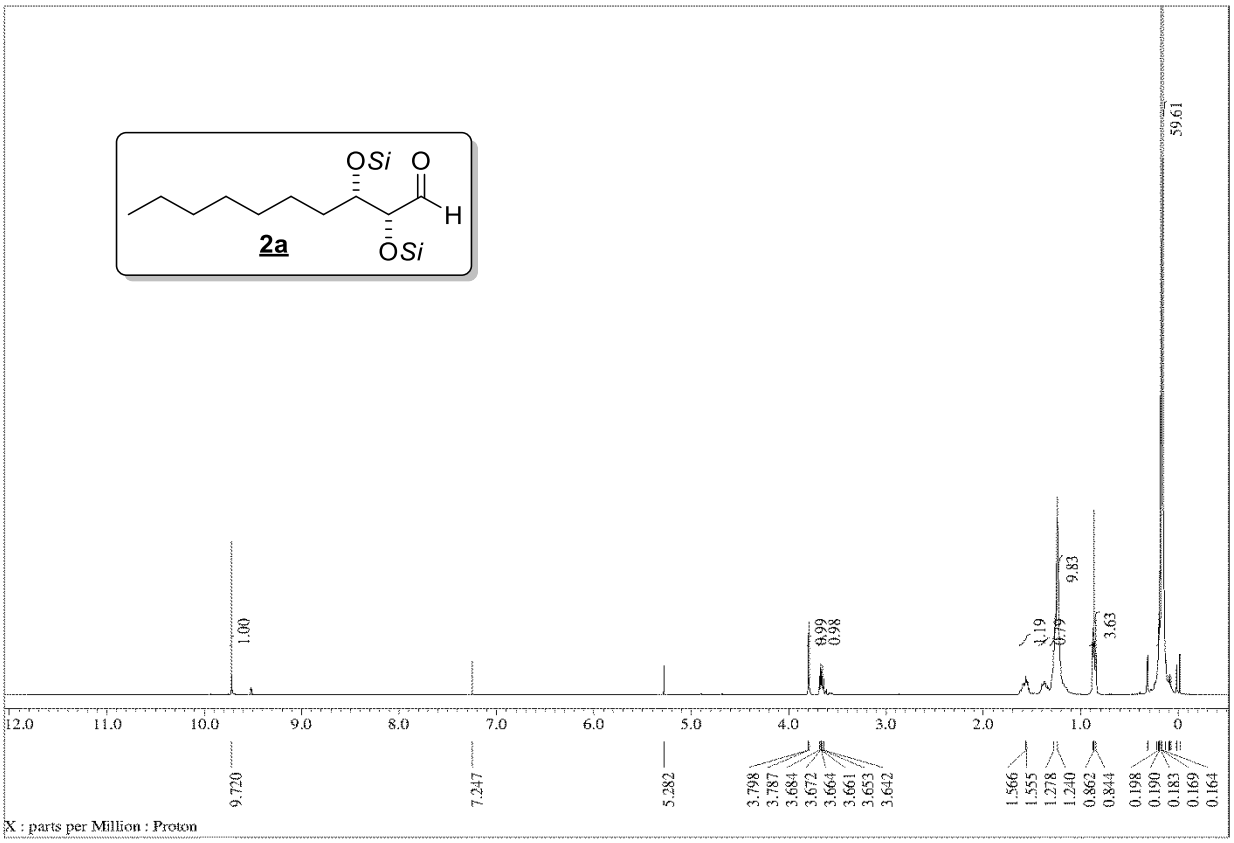
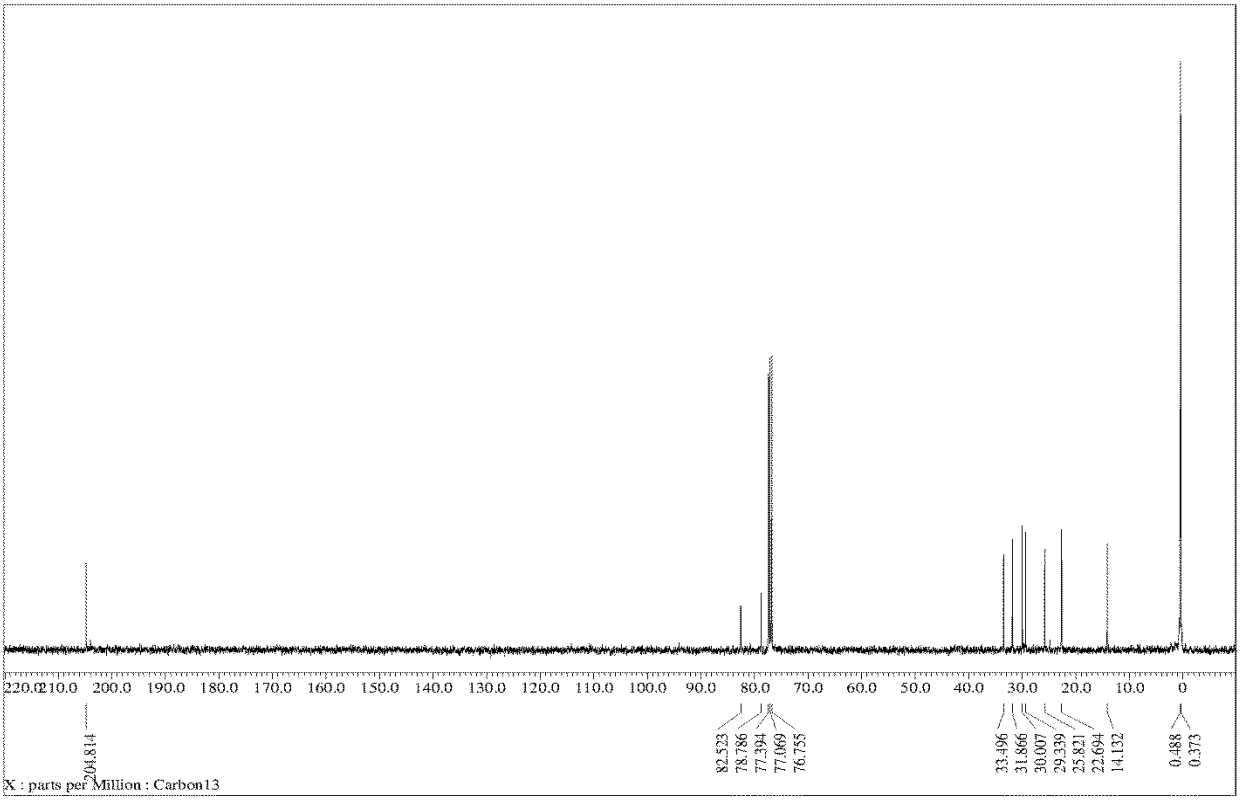
22.713
14.170
5.550
0.345
0.154
-0.065
-5.252
X : parts per Million : Carbon13


OSi
O
H
OSi
2a
59.61
1.00
8.99
0.98
3.19
0.79
9.83
3.63
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.720
7.247
5.282
3.798
3.787
3.684
3.672
3.664
3.661
3.653
3.642
1.566
1.555
1.278
1.240
0.862
0.844
0.198
0.190
0.183
0.169
0.164
X : parts per Million : Proton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190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
204.814
82.523
78.786
77.394
77.069
76.755
33.496
31.866
30.007
29.339
25.821
22.694
14.132
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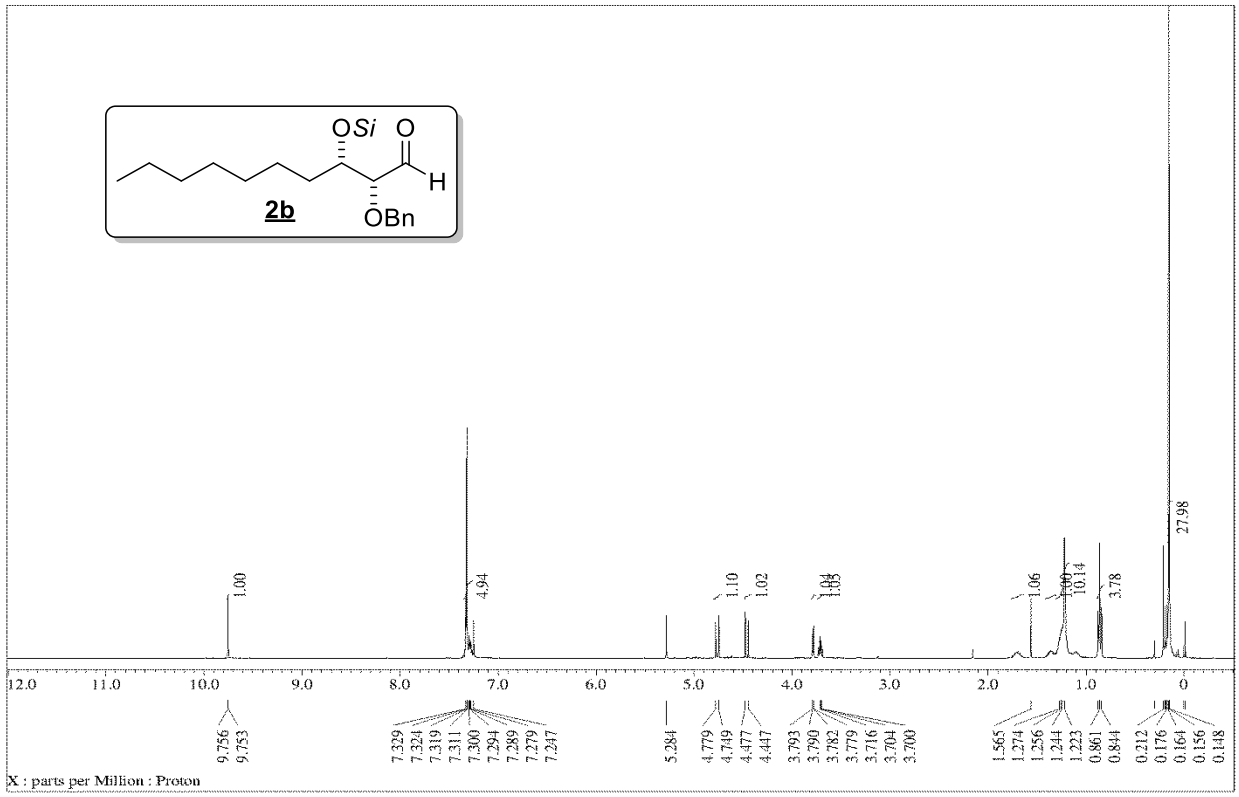
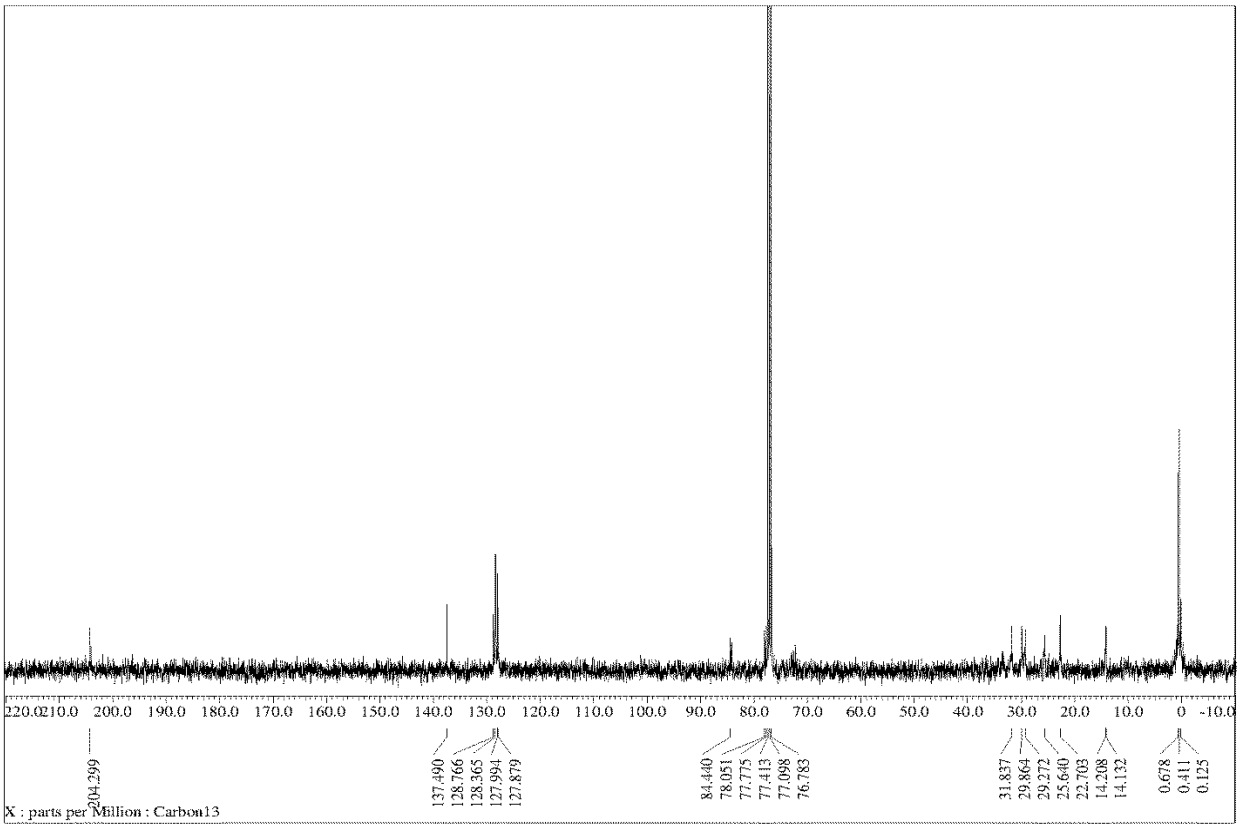
0.373
X : parts per Million : Carbon13


OSi
O
H
OBn
2b
1.00
4.94
1.10
1.02
1.04
1.03
1.06
1.00
10.14
3.78
27.98
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.756
9.753
7.329
7.324
7.319
7.311
7.300
7.294
7.289
7.279
7.247
5.284
4.779
4.749
4.477
4.447
3.793
3.790
3.782
3.779
3.716
3.704
3.700
1.565
1.274
1.256
1.244
1.223
0.861
0.844
0.212
0.176
0.164
0.156
0.148
X : parts per Million : Proton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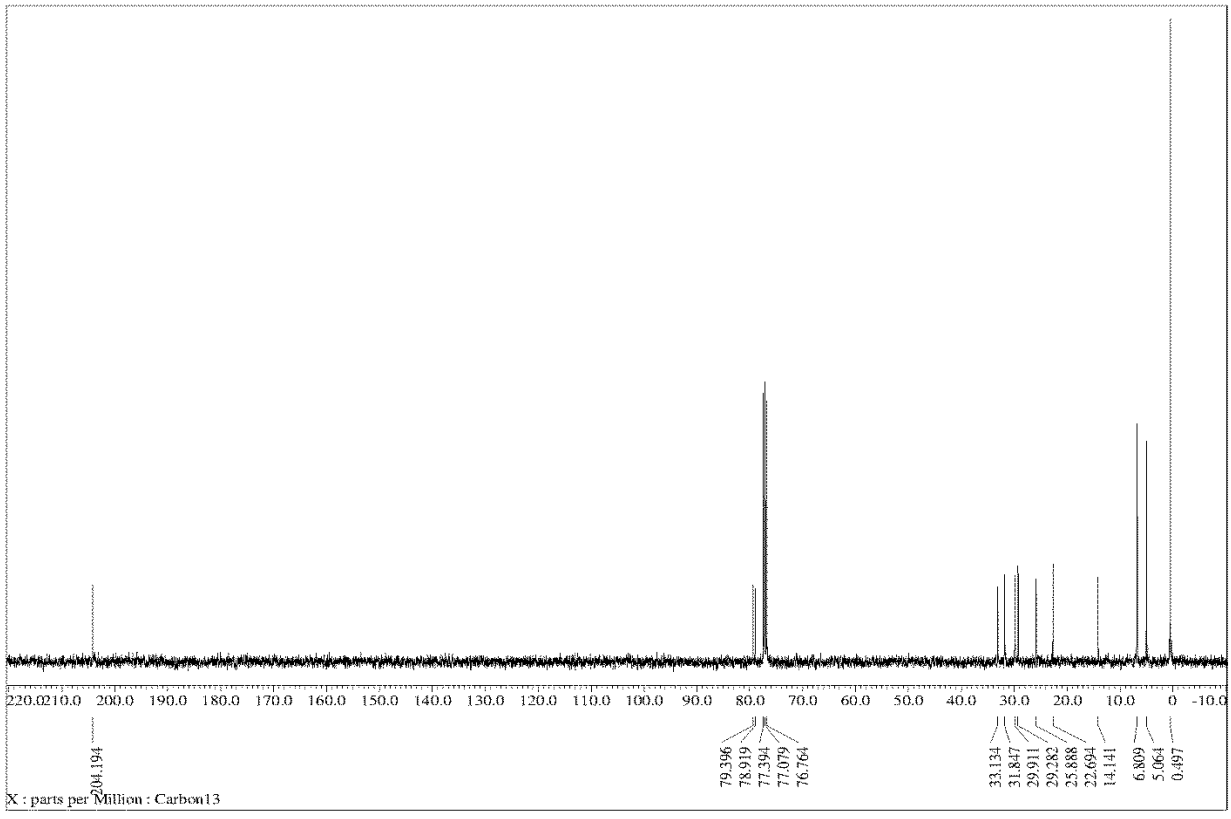
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
204.299
137.490
128.766
128.365
127.994
127.879
84.440
78.051
77.775
77.413
77.098
76.783
31.837
29.864
29.272
25.640
22.703
14.208
14.132
0.678
0.411
0.125
X : parts per Million : Carbon13


OSi
O
H
OTES
2c
1.00
1.09
1.12
15.75
9.63
6.80
27.55
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.706
9.704
7.245
4.053
4.051
4.042
4.041
3.657
3.654
3.652
3.641
3.637
3.626
1.658
1.641
1.245
0.930
0.598
0.185
0.176
0.172
0.168
X : parts per Million : Proton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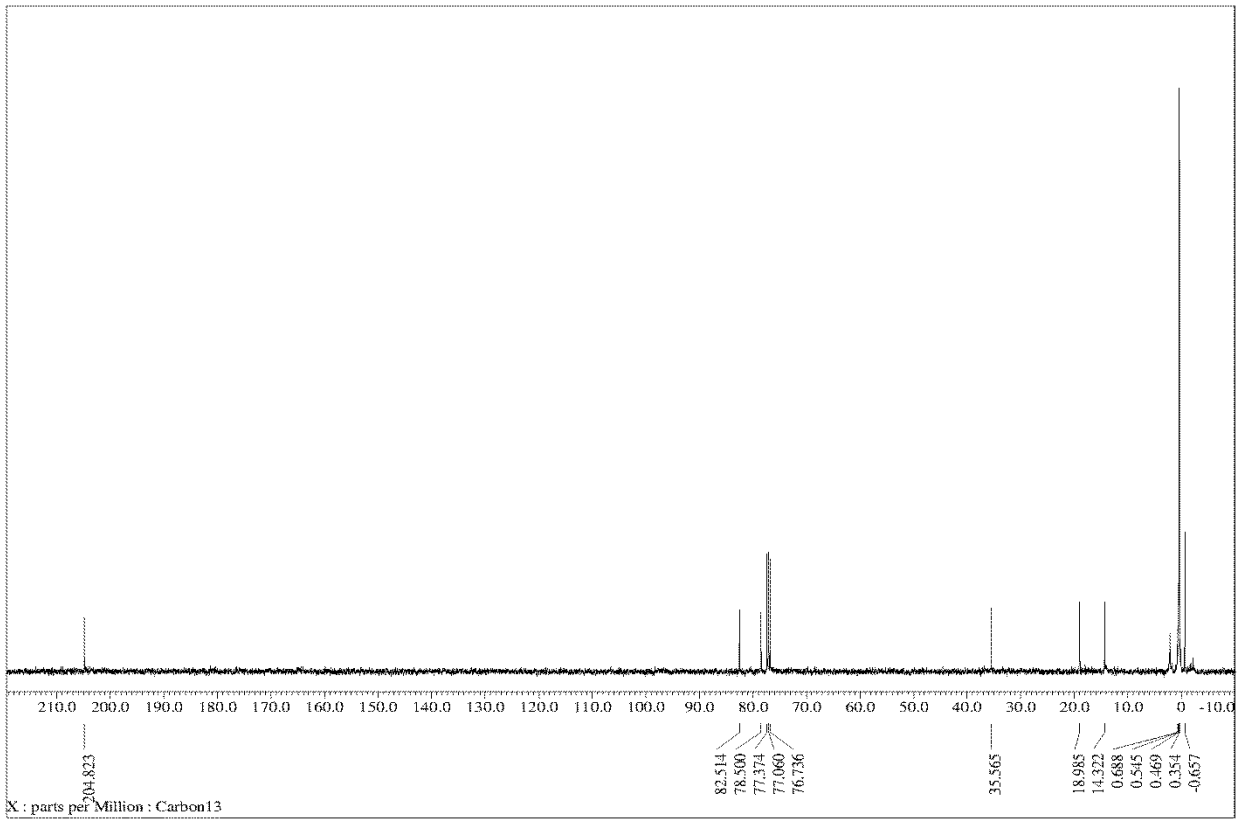
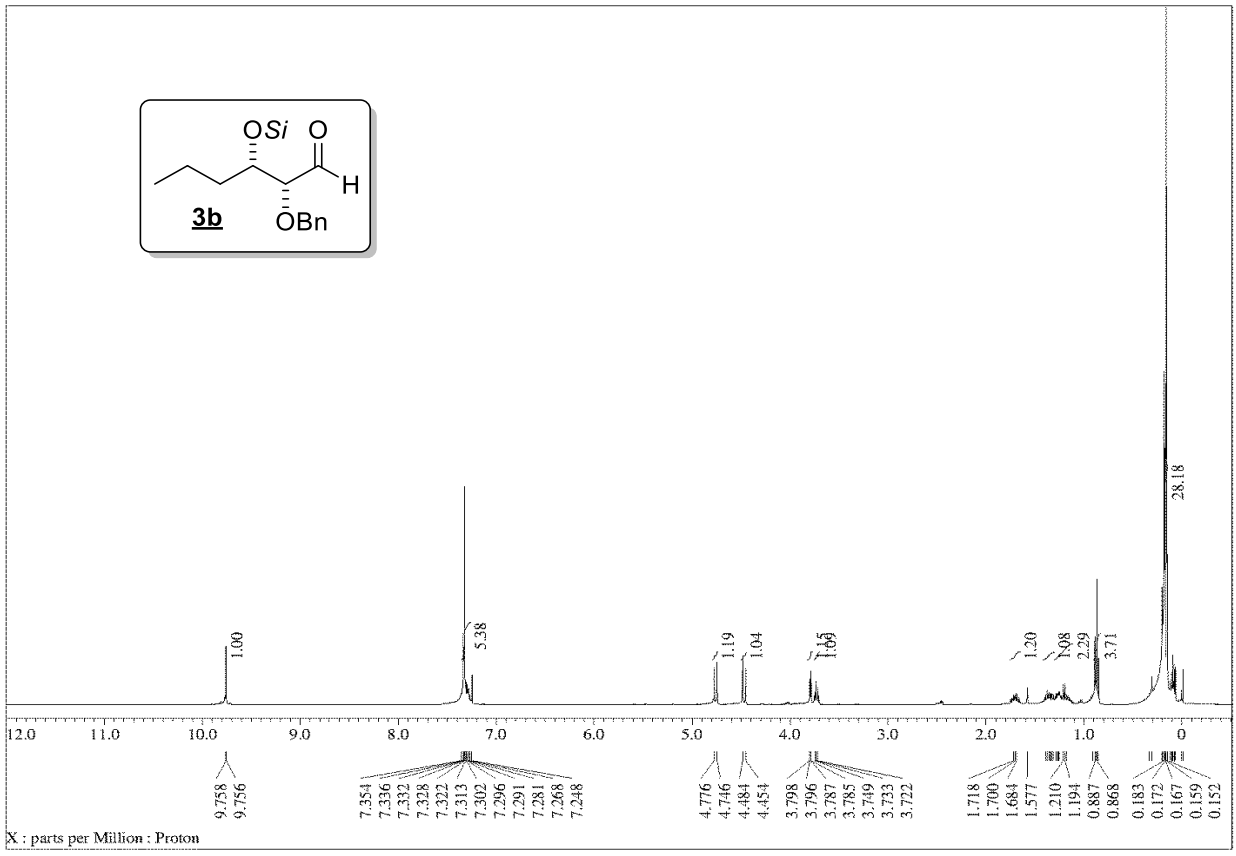
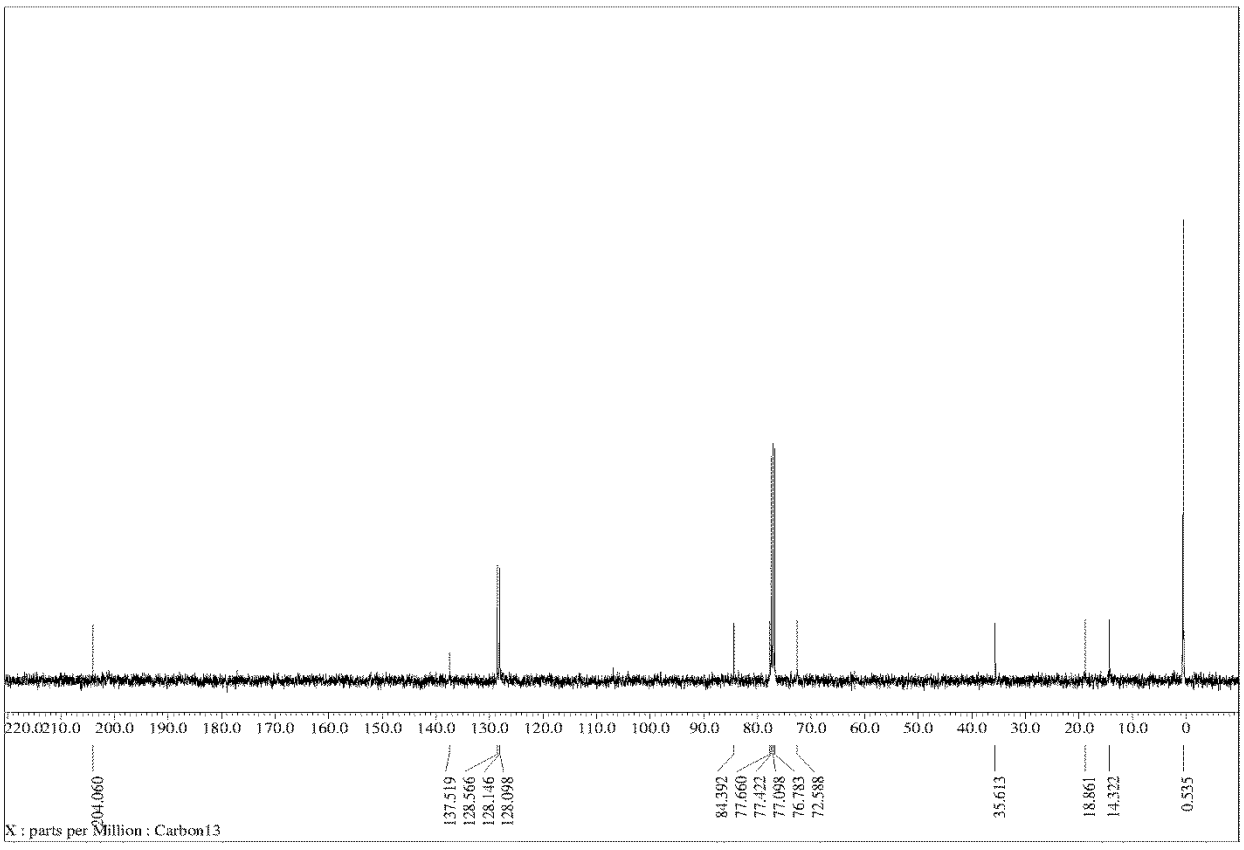
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
204.194
79.396
78.919
77.394
77.079
76.764
33.134
31.847
29.911
29.282
25.888
22.694
14.141
6.809
5.064
0.497
X : parts per Million : Carbon13


OSi
O
H
3a
OSi
55.27
1.00
1.03
1.01
1.11
1.16
2.19
3.19
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.719
7.247
3.793
3.782
3.702
3.691
3.683
3.672
3.661
1.573
1.380
1.367
1.354
1.287
1.257
1.243
0.899
0.880
0.214
0.183
0.172
0.169
0.163
X : parts per Million : Proton


210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
204.823
82.514
78.500
77.374
77.060
76.736
35.565
18.985
14.322
0.688
0.545
0.469
0.354
-0.657
X : parts per Million : Carbon13


OSi
O
H
3b
OBn
1.00
5.38
1.19
1.04
1.15
1.09
1.20
1.08
2.29
3.71
28.18
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.758
9.756
7.354
7.336
7.332
7.328
7.322
7.313
7.302
7.296
7.291
7.281
7.268
7.248
4.776
4.746
4.484
4.454
3.798
3.796
3.787
3.785
3.749
3.733
3.722
1.718
1.700
1.684
1.577
1.210
1.194
0.887
0.868
0.183
0.172
0.167
0.159
0.152
X : parts per Million : Proton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200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
204.060
137.519
128.566
128.146
128.098
84.392
77.660
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77.098
76.783
72.588
35.613
18.861
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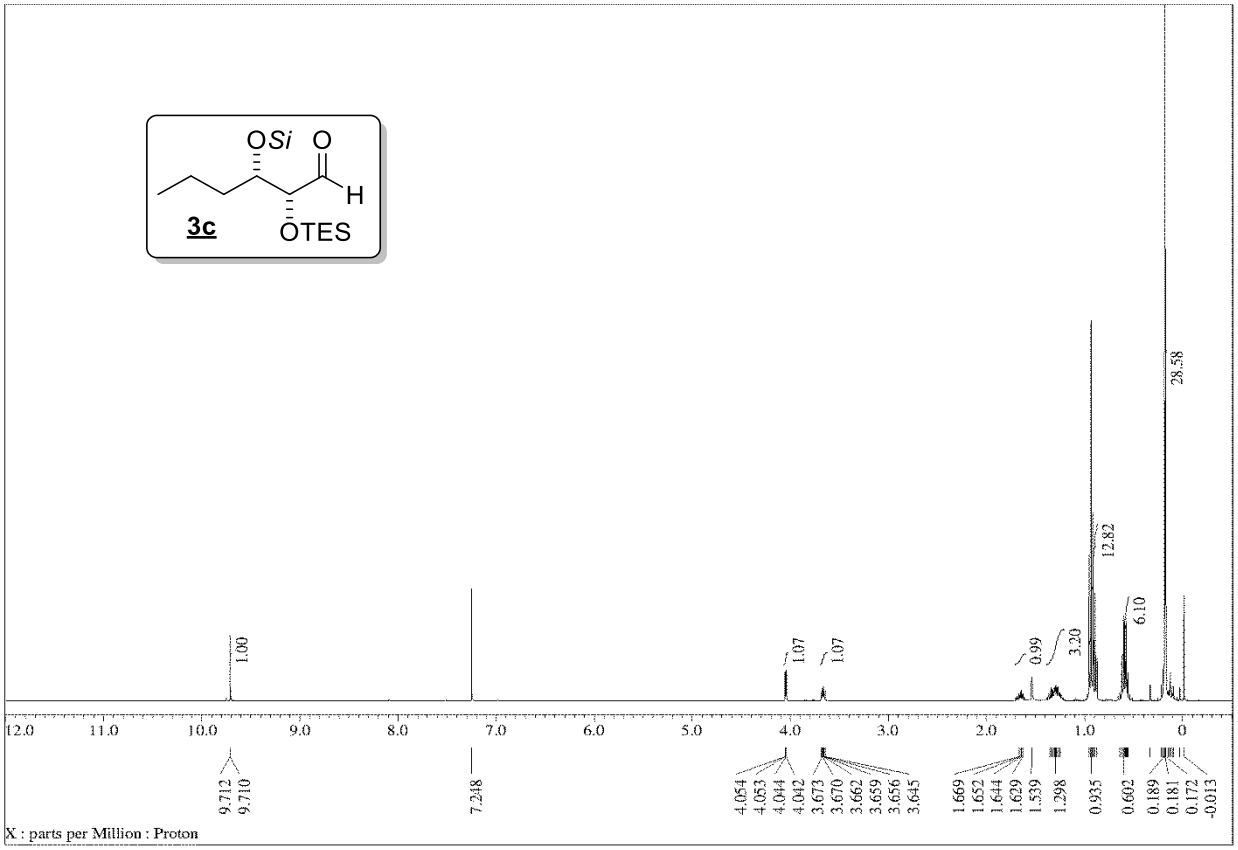
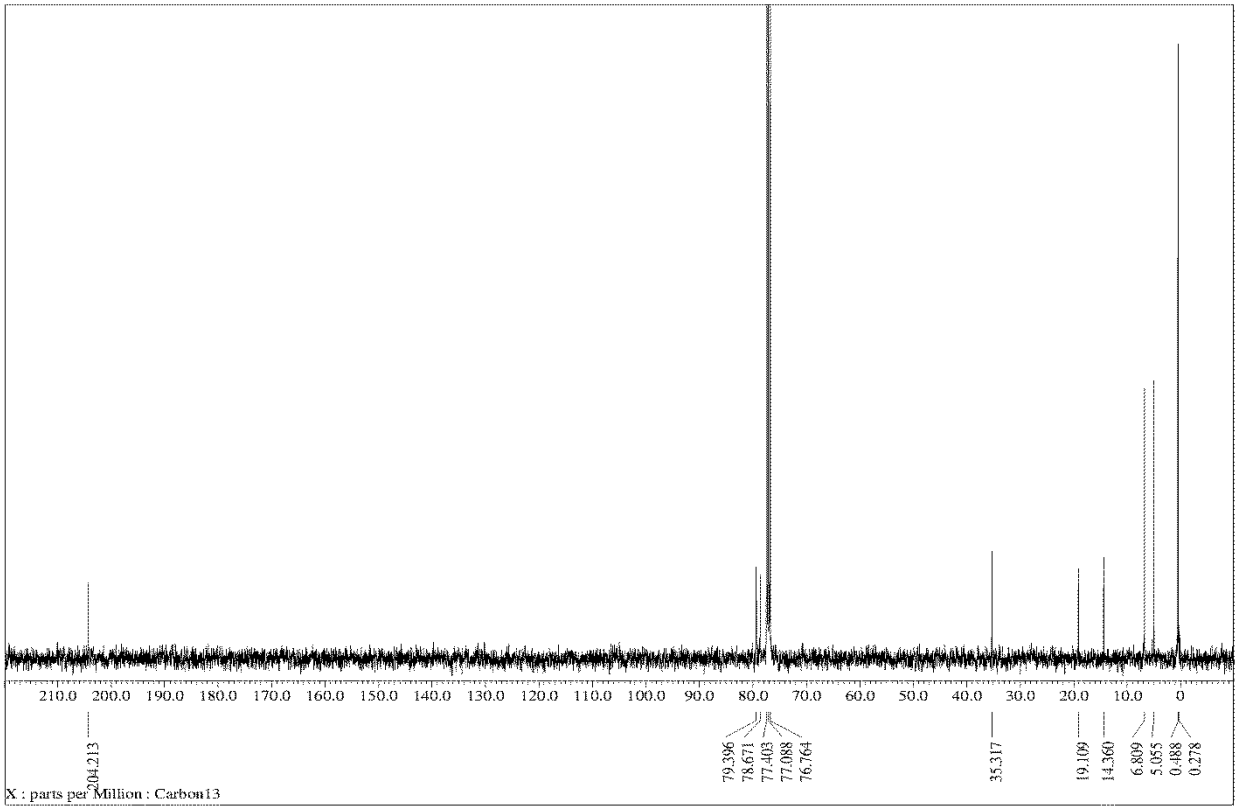

OSi
O
H
OTES
3c
1.00
1.07
1.07
0.99
3.20
12.82
6.10
28.58
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.712
9.710
7.248
4.054
4.053
4.044
4.042
3.673
3.670
3.662
3.659
3.656
3.645
1.669
1.652
1.644
1.629
1.539
1.298
0.935
0.602
0.189
0.181
0.172
-0.013
X : parts per Million : Proton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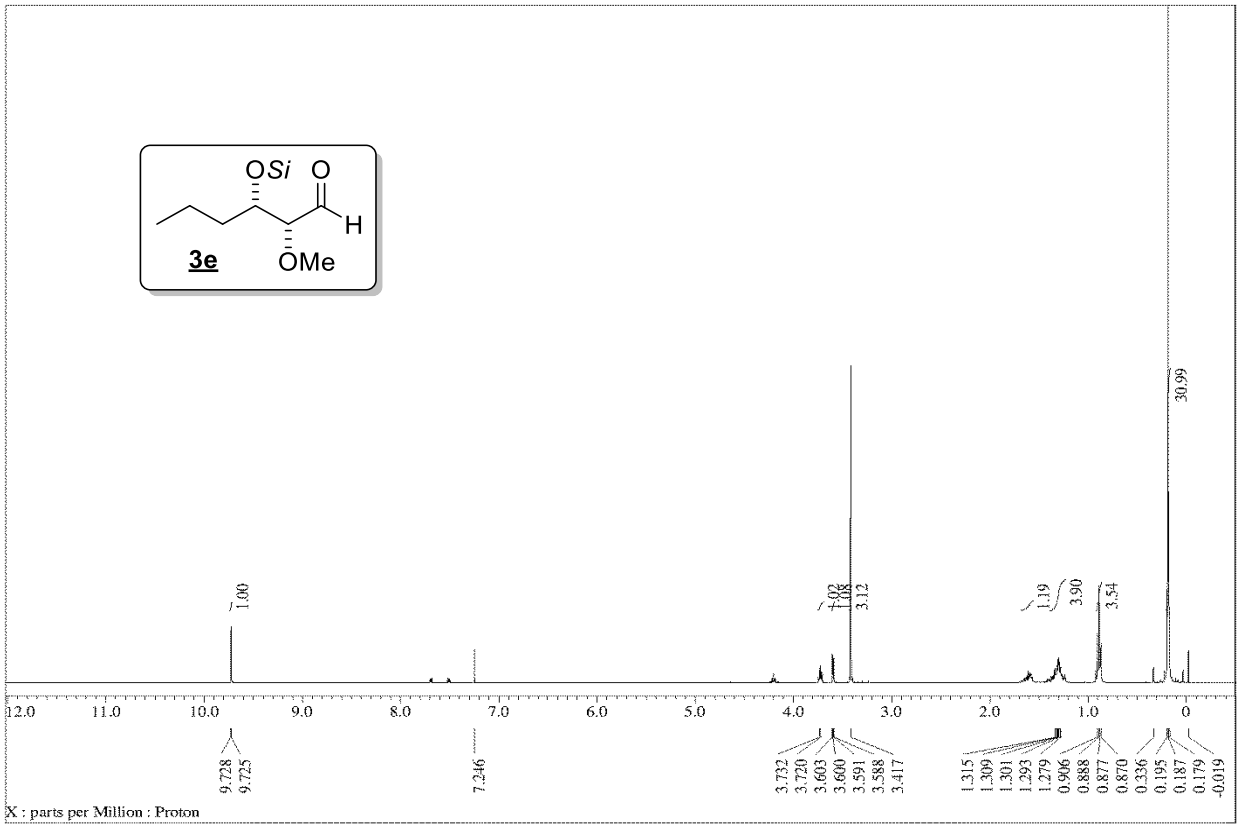
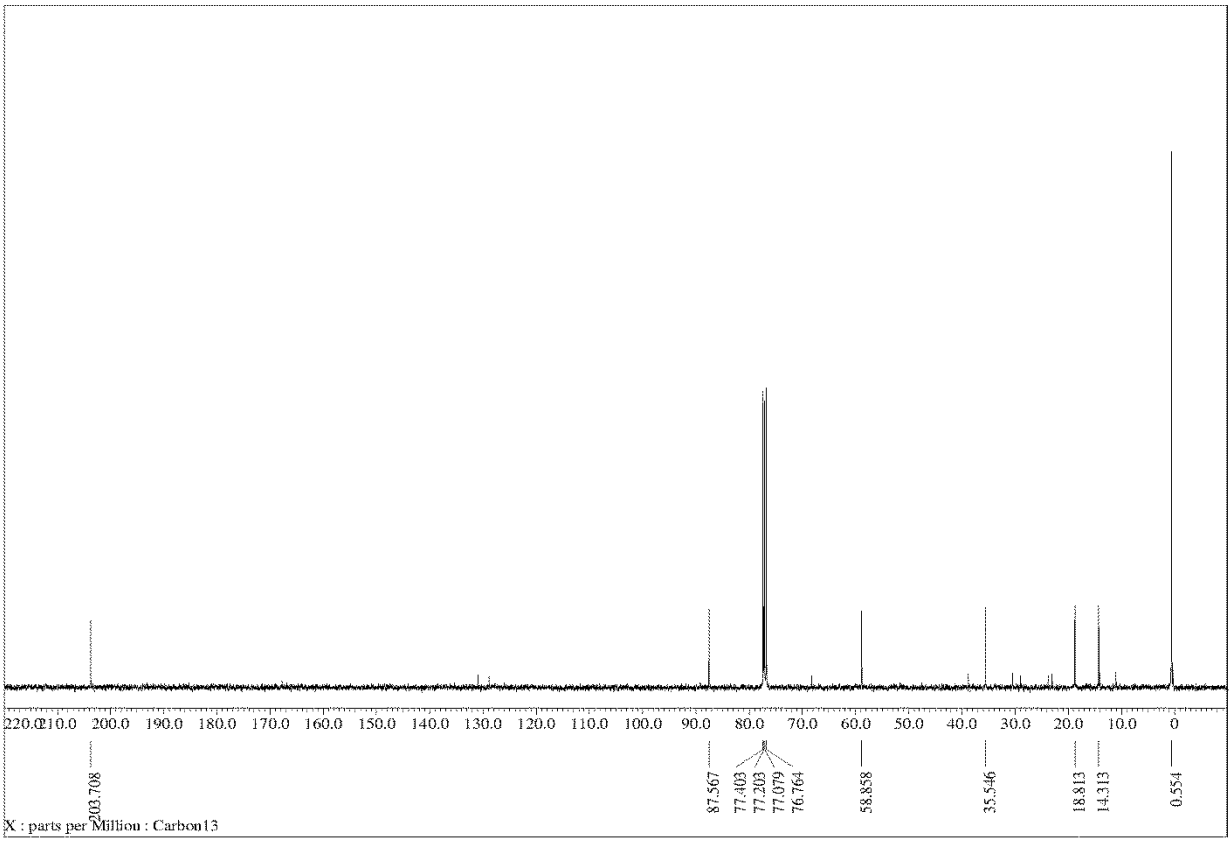
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
204.213
79.396
78.671
77.403
77.088
76.764
35.317
19.109
14.360
6.809
5.055
0.488
0.278
X : parts per Million : Carbon13


OSi
O
H
3e
OMe
1.00
1.02
1.08
3.12
1.19
3.90
3.54
30.99
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.728
9.725
7.246
3.732
3.720
3.603
3.600
3.591
3.588
3.417
1.315
1.309
1.301
1.293
1.279
0.906
0.888
0.877
0.870
0.336
0.195
0.187
0.179
-0.019
X : parts per Million : Proton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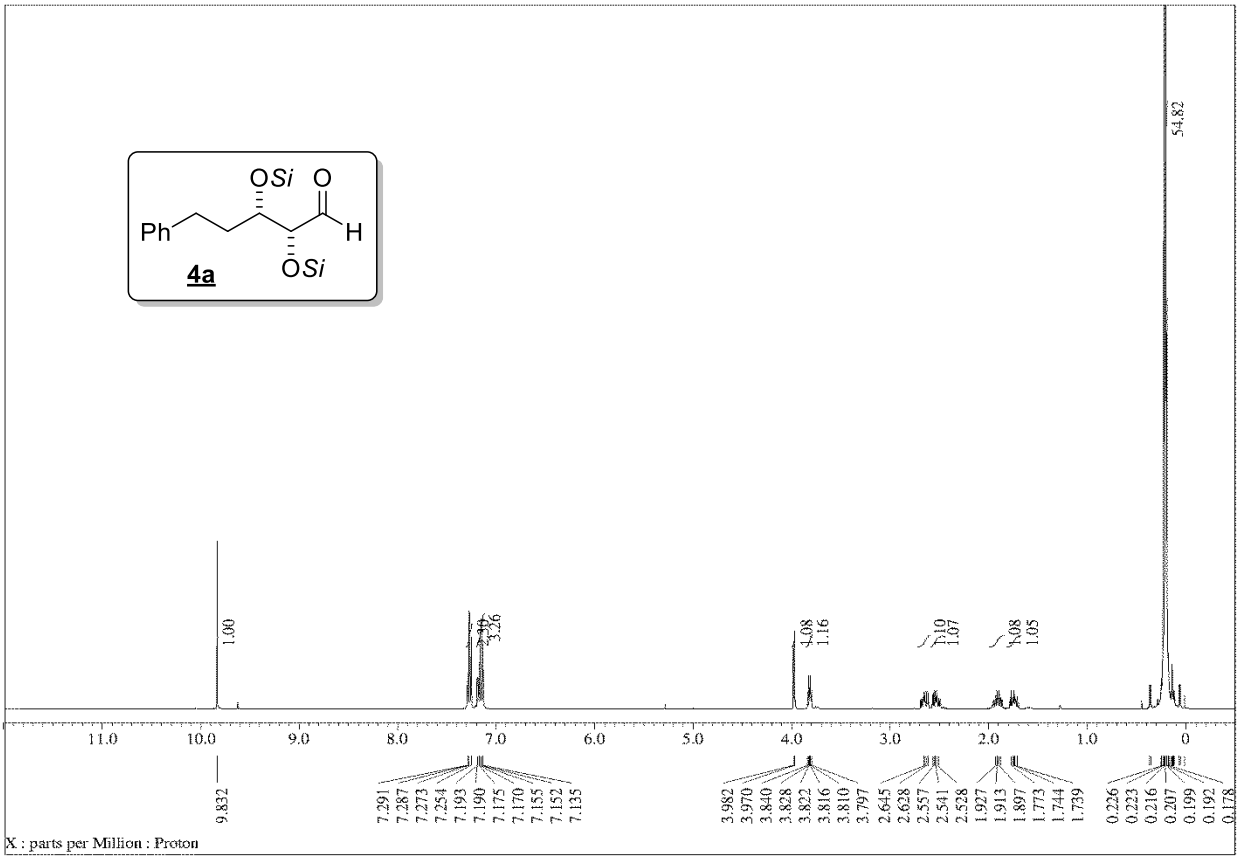
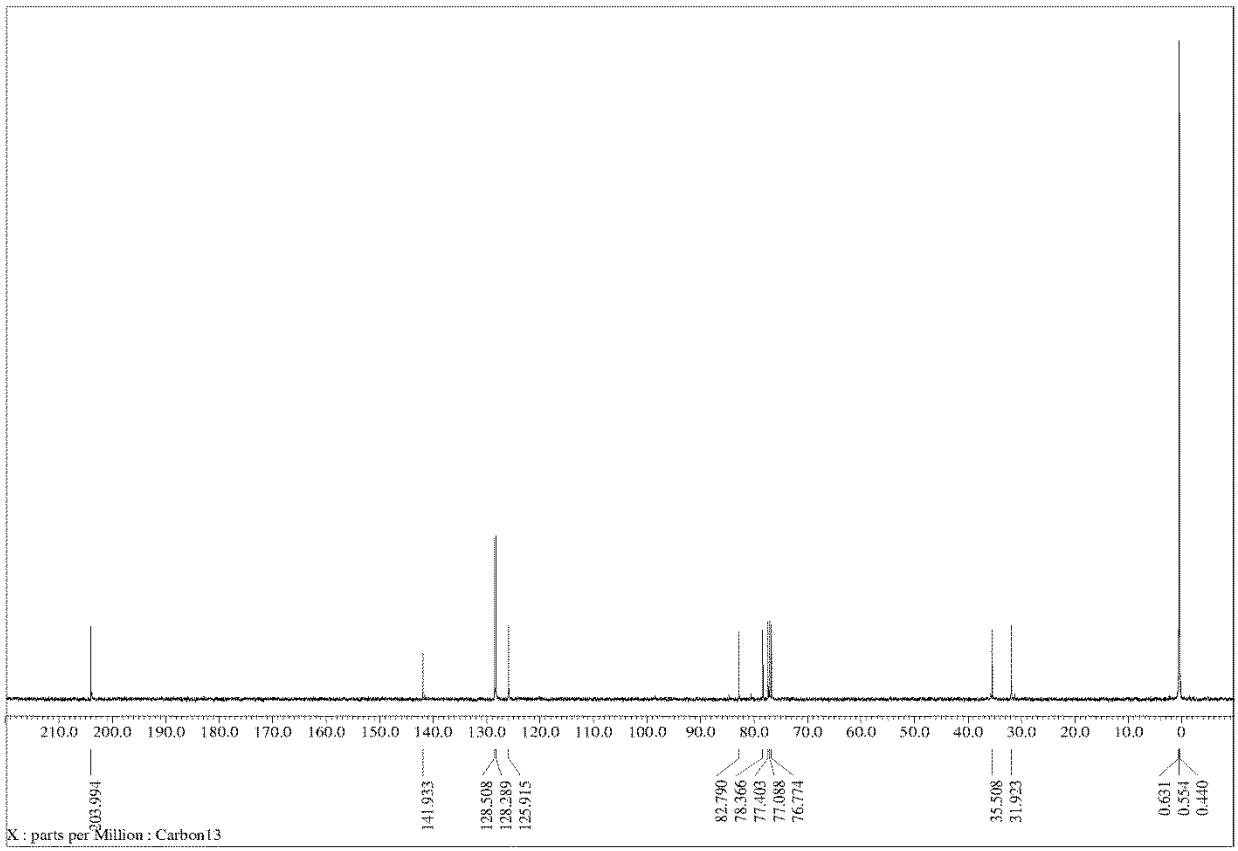
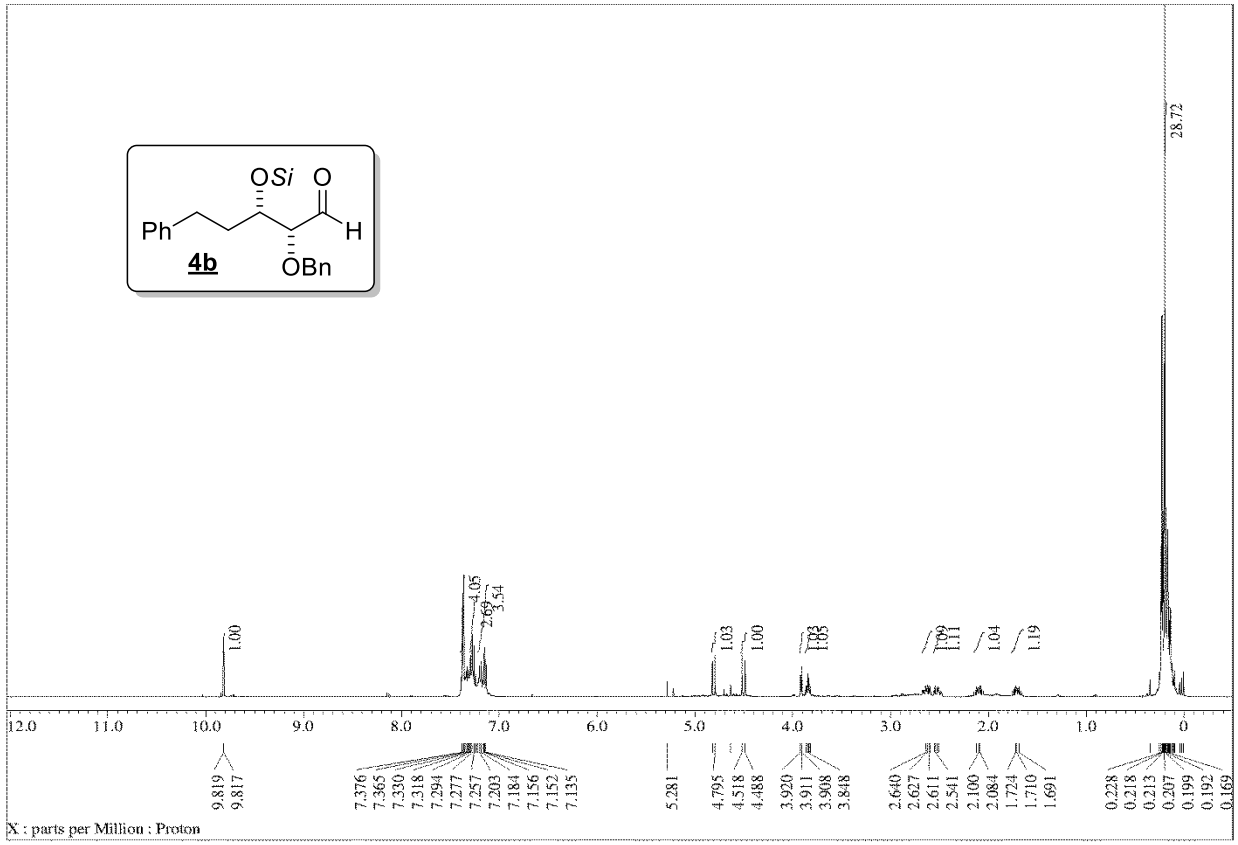
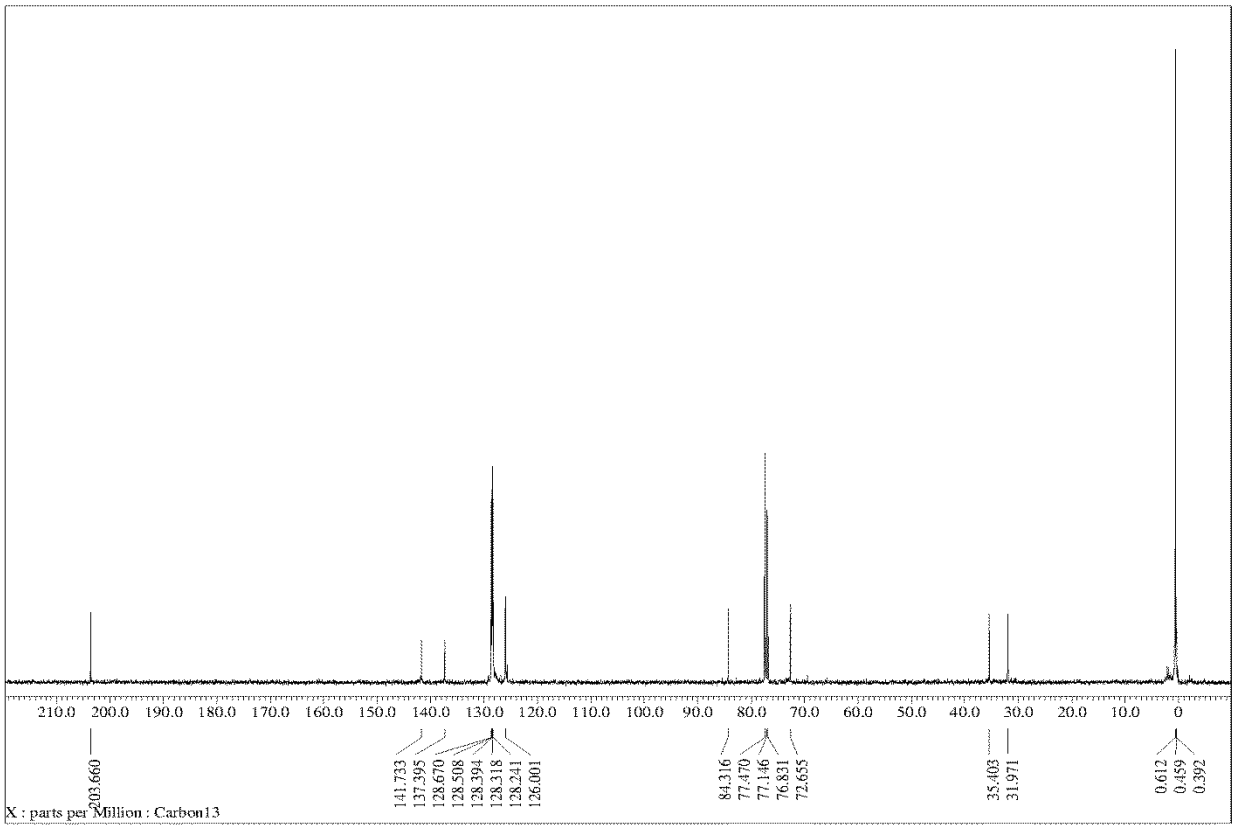
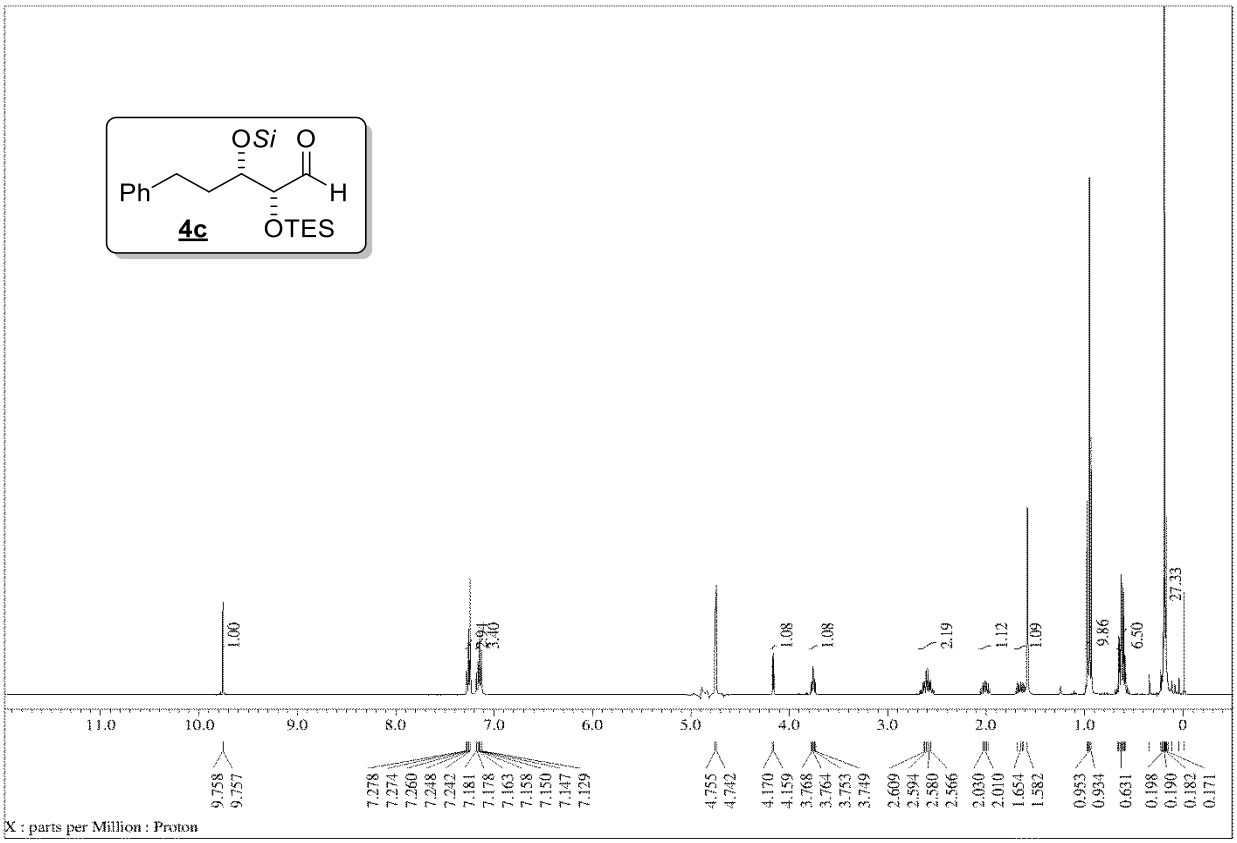
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
203.708
87.567
77.403
77.203
77.079
76.764
58.858
35.546
18.813
14.313
0.554
X : parts per Million : Carbon13

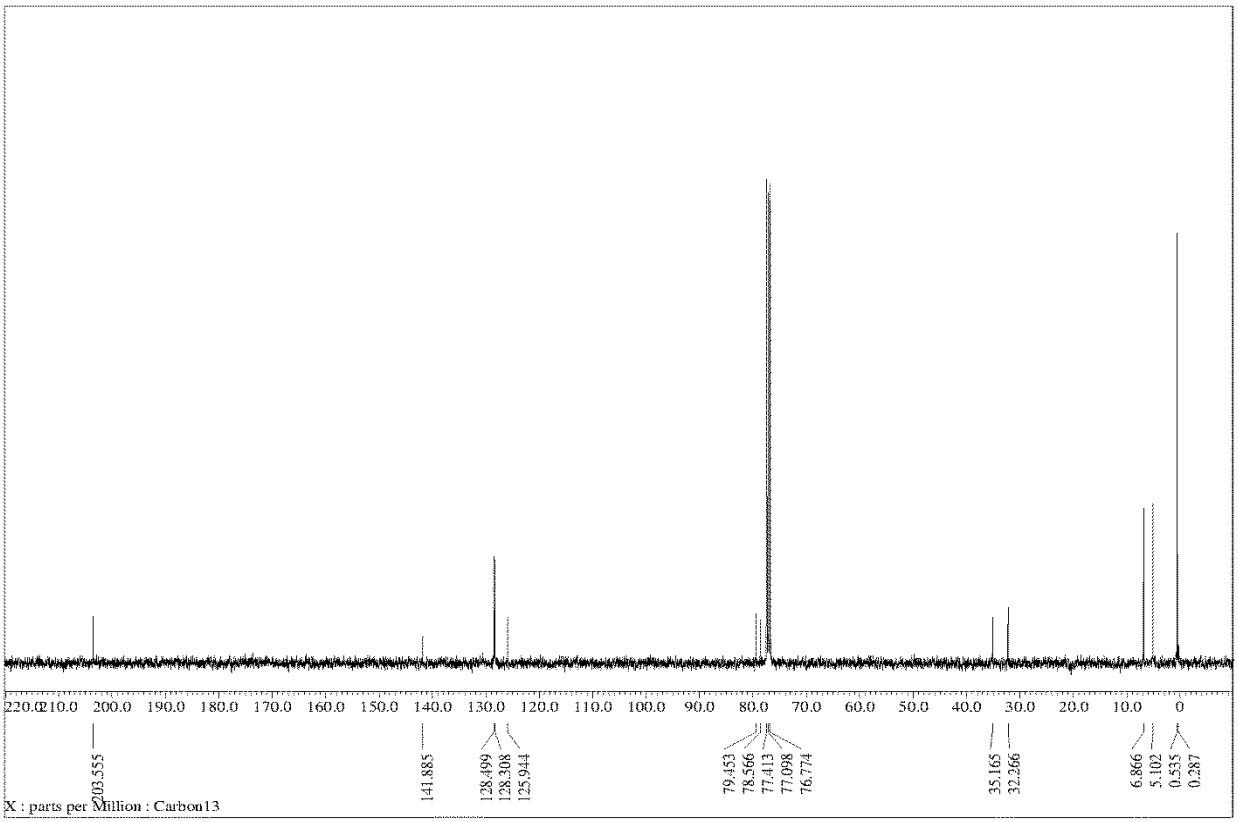

OSi
O
Ph
H
OSi
4a
54.82
1.00
3.08
1.16
3.10
1.07
3.08
1.05
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.832
7.291
7.287
7.273
7.254
7.193
7.190
7.175
7.170
7.155
7.152
7.135
3.982
3.970
3.840
3.828
3.822
3.816
3.810
3.797
2.645
2.628
2.557
2.541
2.528
1.927
1.913
1.897
1.773
1.744
1.739
0.226
0.223
0.216
0.207
0.199
0.192
0.178
X : parts per Million : Proton


210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
203.994
141.933
128.508
128.289
125.915
82.790
78.366
77.403
77.088
76.774
35.508
31.923
0.631
0.554
0.440
X : parts per Million : Carbon13


OSi
O
Ph
H
4b
OBn
X : parts per Million : Proton


X : parts per Million : Carbon13


OSi
O
Ph
H
4c
OTES
1.00
2.94
3.40
1.08
1.08
2.19
1.12
1.09
9.86
6.50
27.33
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.758
9.757
7.278
7.274
7.260
7.248
7.242
7.181
7.178
7.163
7.158
7.150
7.147
7.129
4.755
4.742
4.170
4.159
3.768
3.764
3.753
3.749
2.609
2.594
2.580
2.566
2.030
2.010
1.654
1.582
0.953
0.934
0.631
0.198
0.190
0.182
0.171
X : parts per Million : Proton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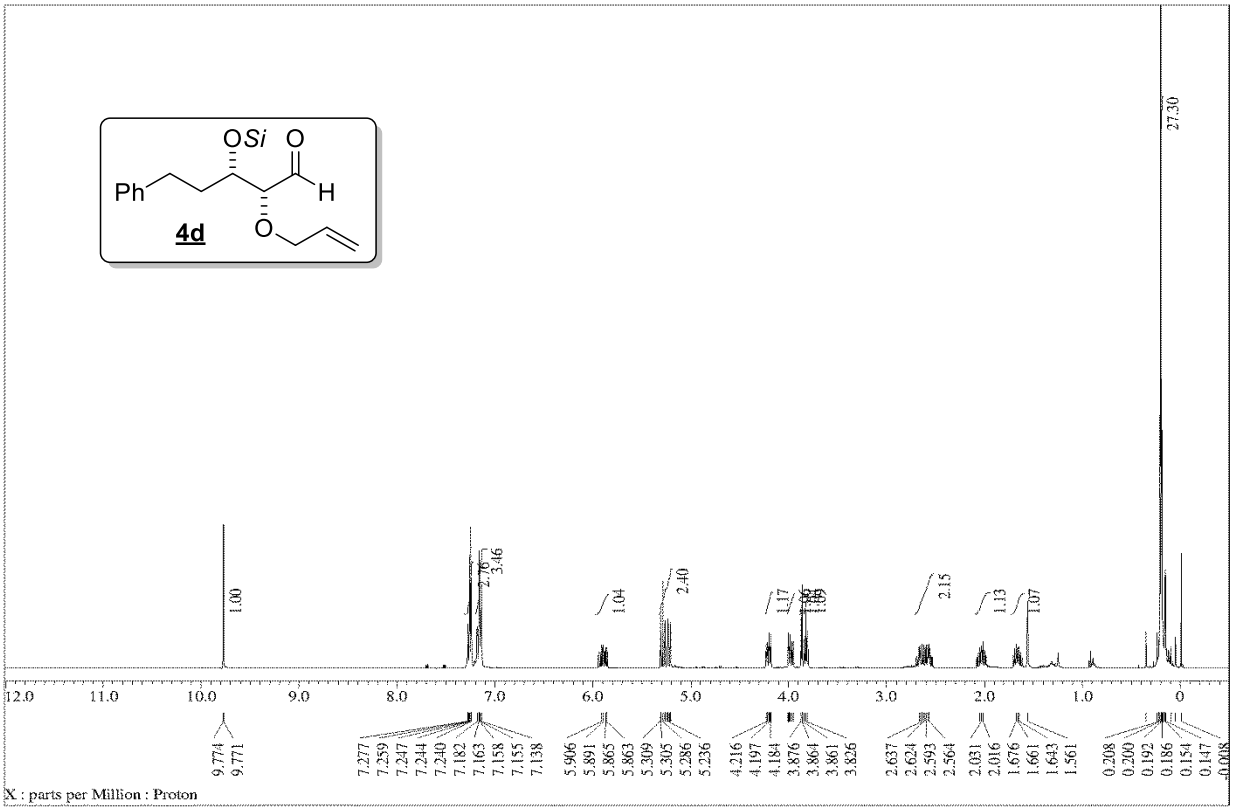
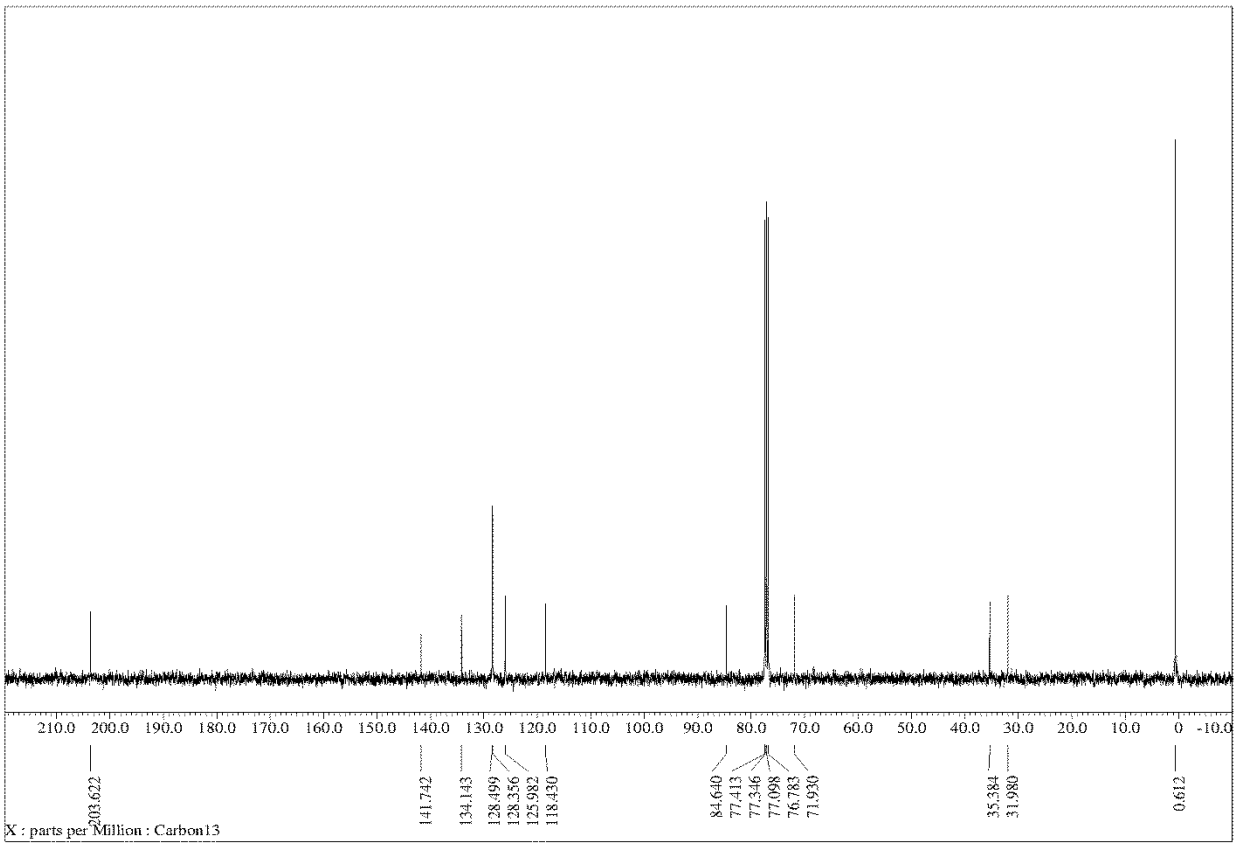
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
203.555
141.885
128.499
128.308
125.944
79.453
78.566
77.413
77.098
76.774
35.165
32.266
6.866
5.102
0.535
0.287
X : parts per Million : Carbon13


OSi
O
Ph
H
O
4d
27.30
1.00
2.76
3.46
1.04
2.40
1.17
2.15
1.13
1.07
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.774
9.771
7.277
7.259
7.247
7.244
7.240
7.182
7.163
7.158
7.155
7.138
5.906
5.891
5.865
5.863
5.309
5.305
5.286
5.236
4.216
4.197
4.184
3.876
3.864
3.861
3.826
2.637
2.624
2.593
2.564
2.031
2.016
1.676
1.661
1.643
1.561
0.208
0.200
0.192
0.186
0.154
0.147
-0.008
X : parts per Million : Proton


210.0
200.0
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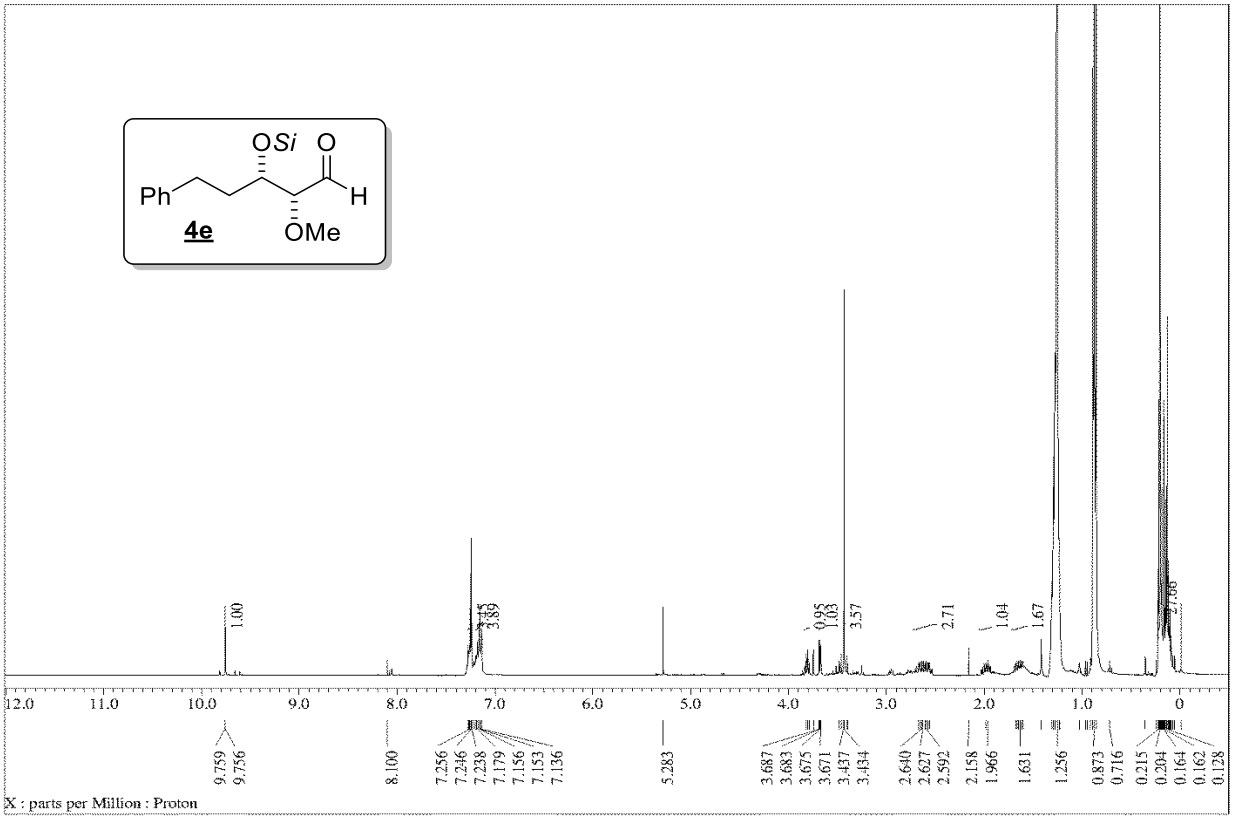
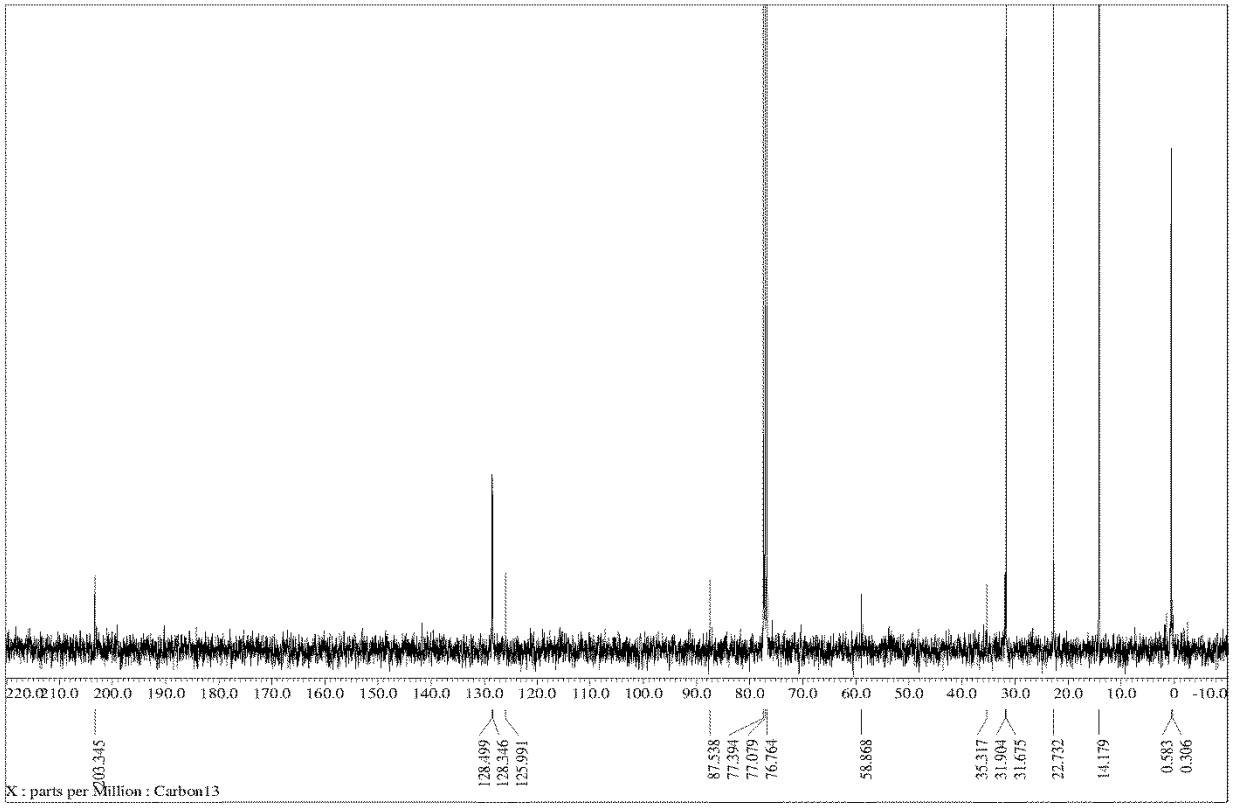
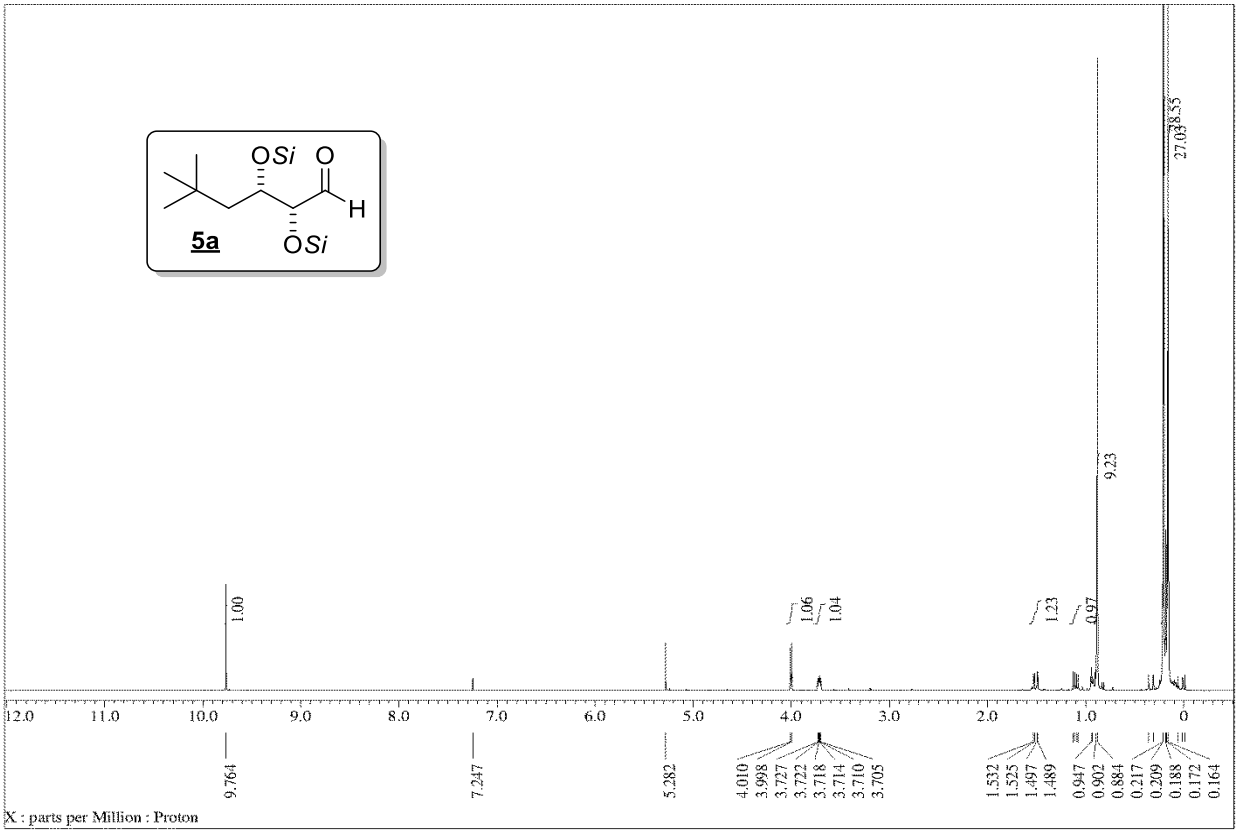
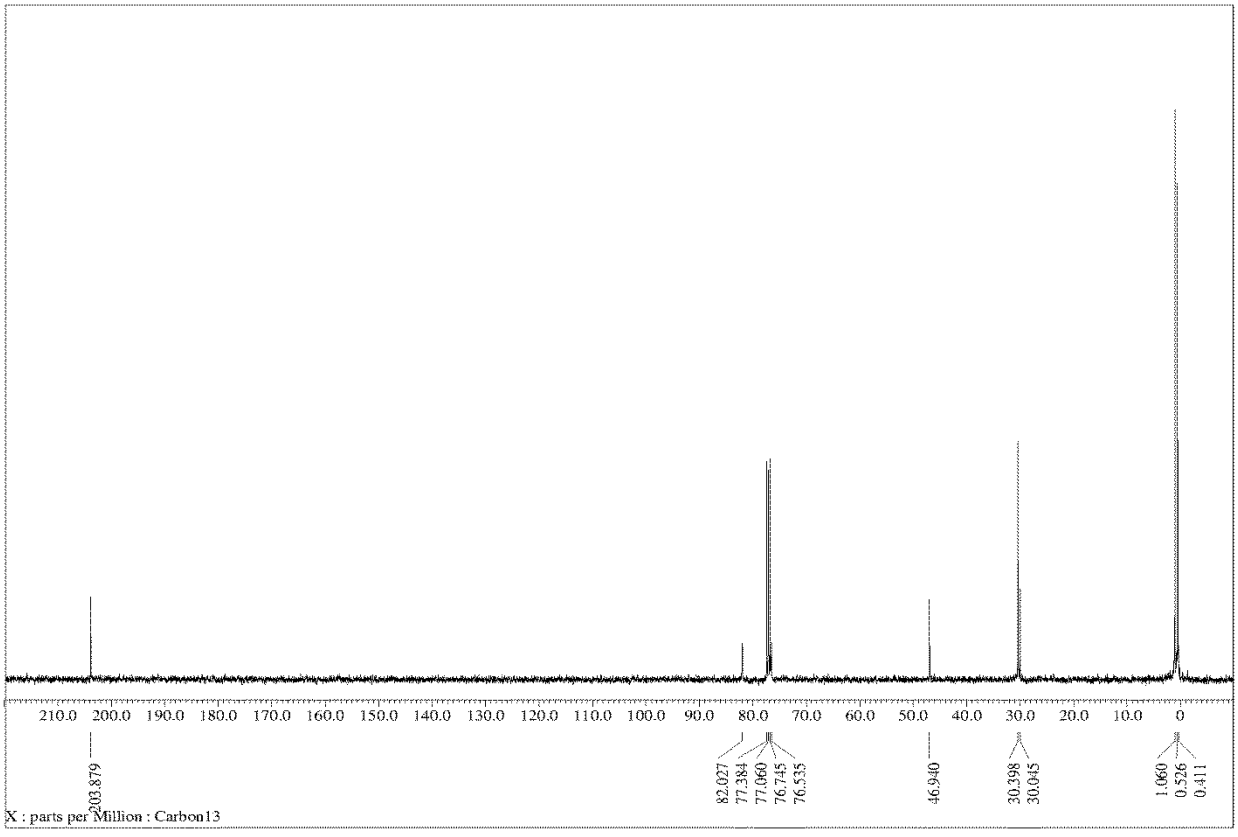
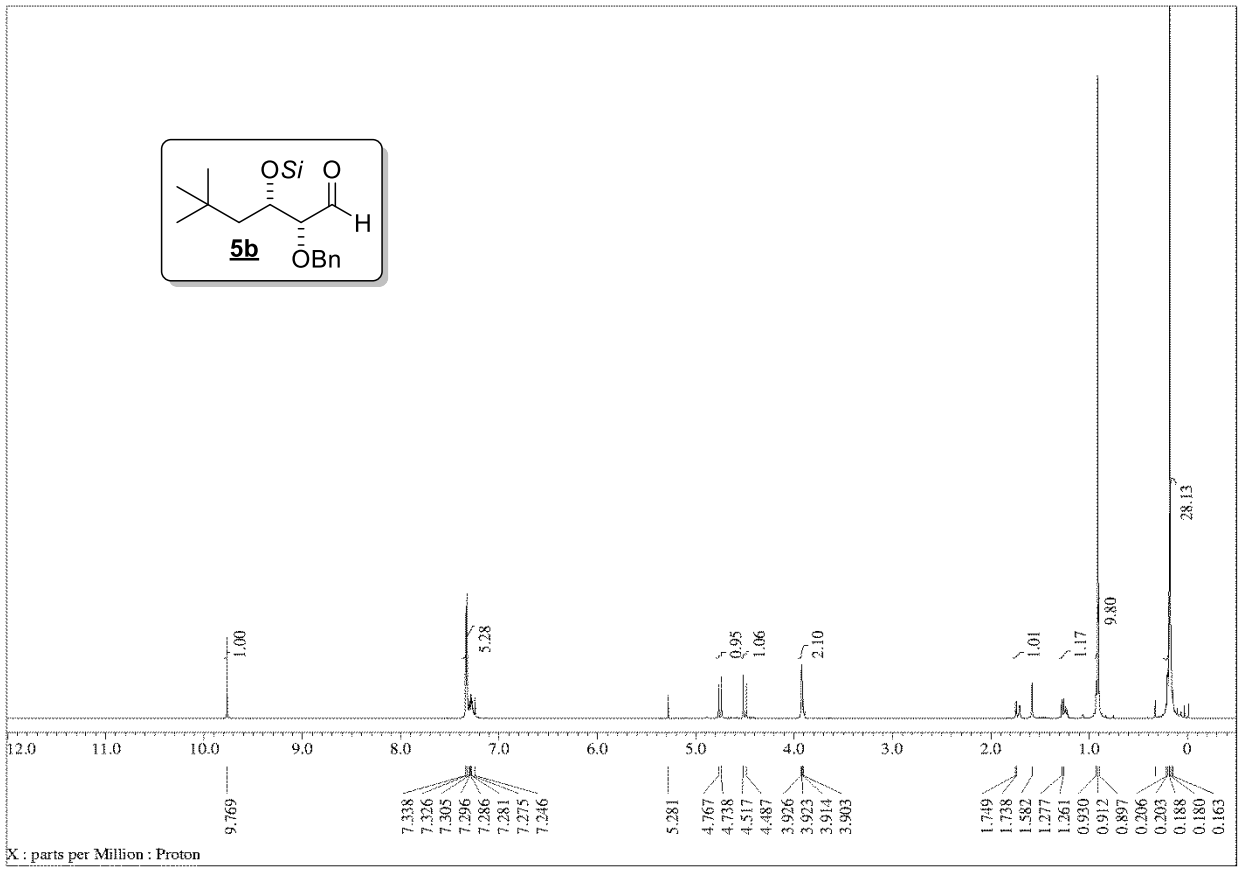
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
203.622
141.742
134.143
128.499
128.356
125.982
118.430
84.640
77.413
77.346
77.098
76.783
71.930
35.384
31.980
0.612
X : parts per Million : Carbon13

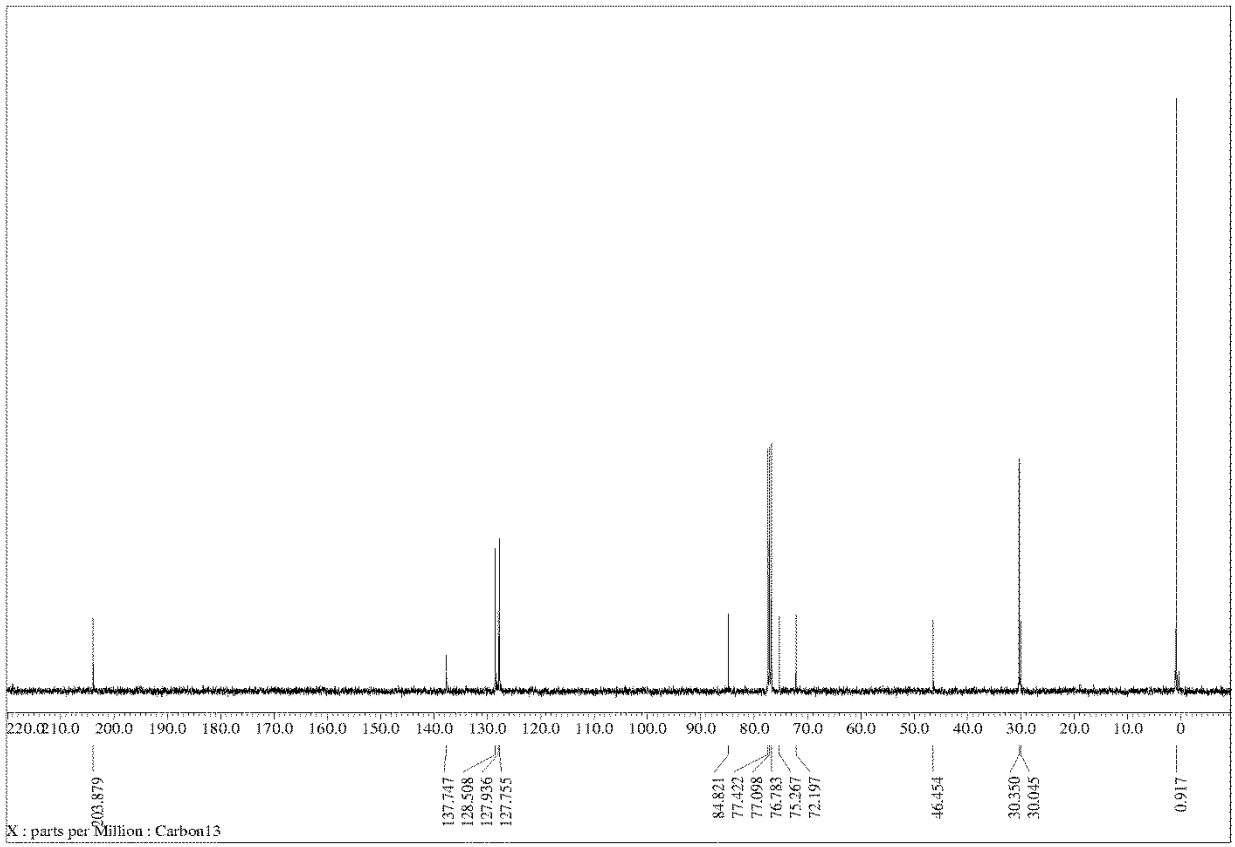

OSi
O
Ph
H
4e
OMe
X : parts per Million : Proton


X : parts per Million : Carbon13

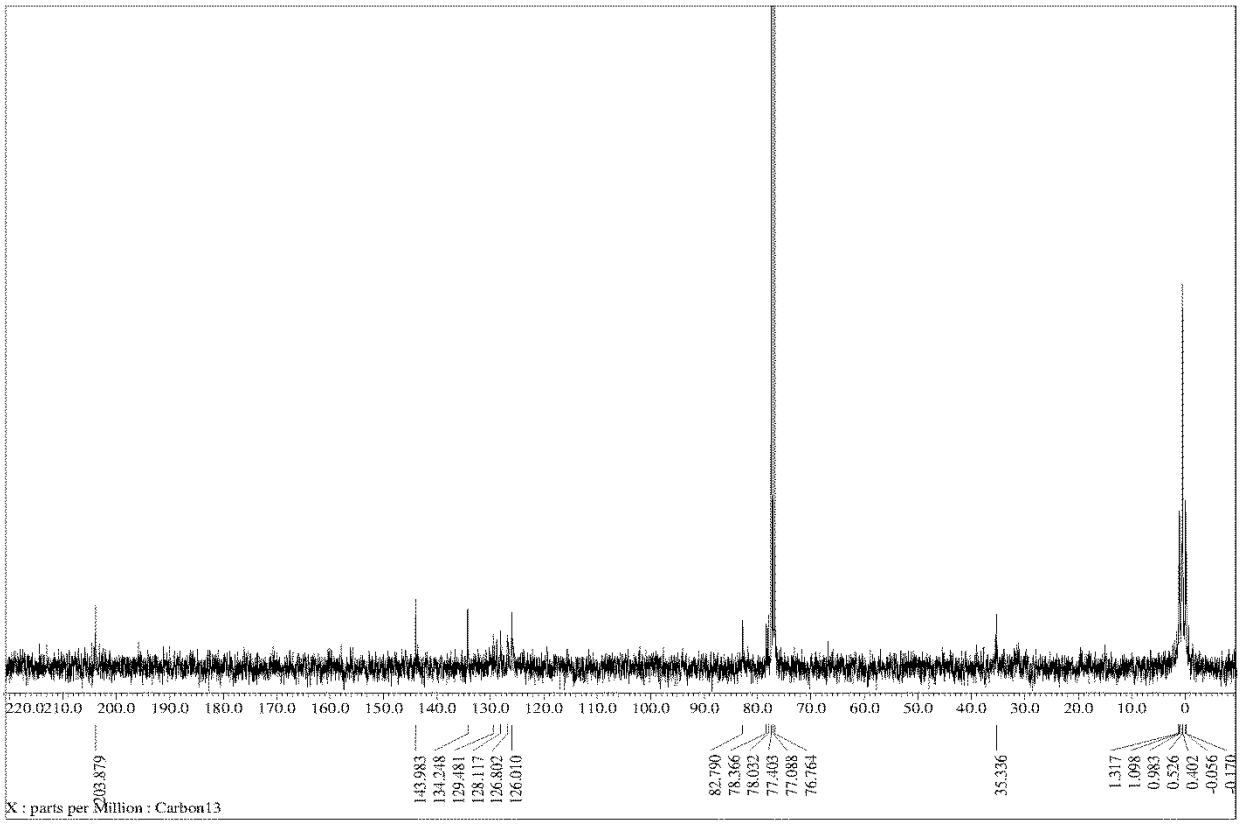

OSi
O
H
5a
OSi
27.038.55
9.23
1.00
1.06
1.04
1.23
0.97
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.764
7.247
5.282
4.010
3.998
3.727
3.722
3.718
3.714
3.710
3.705
1.532
1.525
1.497
1.489
0.947
0.902
0.884
0.217
0.209
0.188
0.172
0.164
X : parts per Million : Proton


210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
203.879
82.027
77.384
77.060
76.745
76.535
46.940
30.398
30.045
1.060
0.526
0.411
X : parts per Million : Carbon13


OSi
O
H
5b
OBn
1.00
5.28
0.95
1.06
2.10
1.01
1.17
9.80
28.13
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.769
7.338
7.326
7.305
7.296
7.286
7.281
7.275
7.246
5.281
4.767
4.738
4.517
4.487
3.926
3.923
3.914
3.903
1.749
1.738
1.582
1.277
1.261
0.930
0.912
0.897
0.206
0.203
0.188
0.180
0.163
X : parts per Million : Proton


220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
203.879
137.747
128.508
127.936
127.755
84.821
77.422
77.098
76.783
75.267
72.197
46.454
30.350
30.045
0.917
X : parts per Million : Carbon13


OSi
O
Cl
H
OSi
6a
56.59
1.00
3.52
1.00
4.04
1.13
3.03
1.02
0.98
1.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.806
7.247
7.199
7.179
7.161
7.152
7.148
7.144
7.127
7.107
7.102
6.995
6.977
5.285
3.958
3.945
3.802
3.789
3.784
3.777
3.772
2.586
2.570
2.503
2.487
2.474
1.845
1.828
1.728
1.699
1.537
0.199
0.187
0.169
0.166
0.161
0.151
0.009
X : parts per Million : Proton


220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
203.879
143.983
134.248
129.481
128.117
126.802
126.010
82.790
78.366
78.032
77.403
77.088
76.764
35.336
1.317
1.098
0.983
0.526
0.402
-0.056
-0.170
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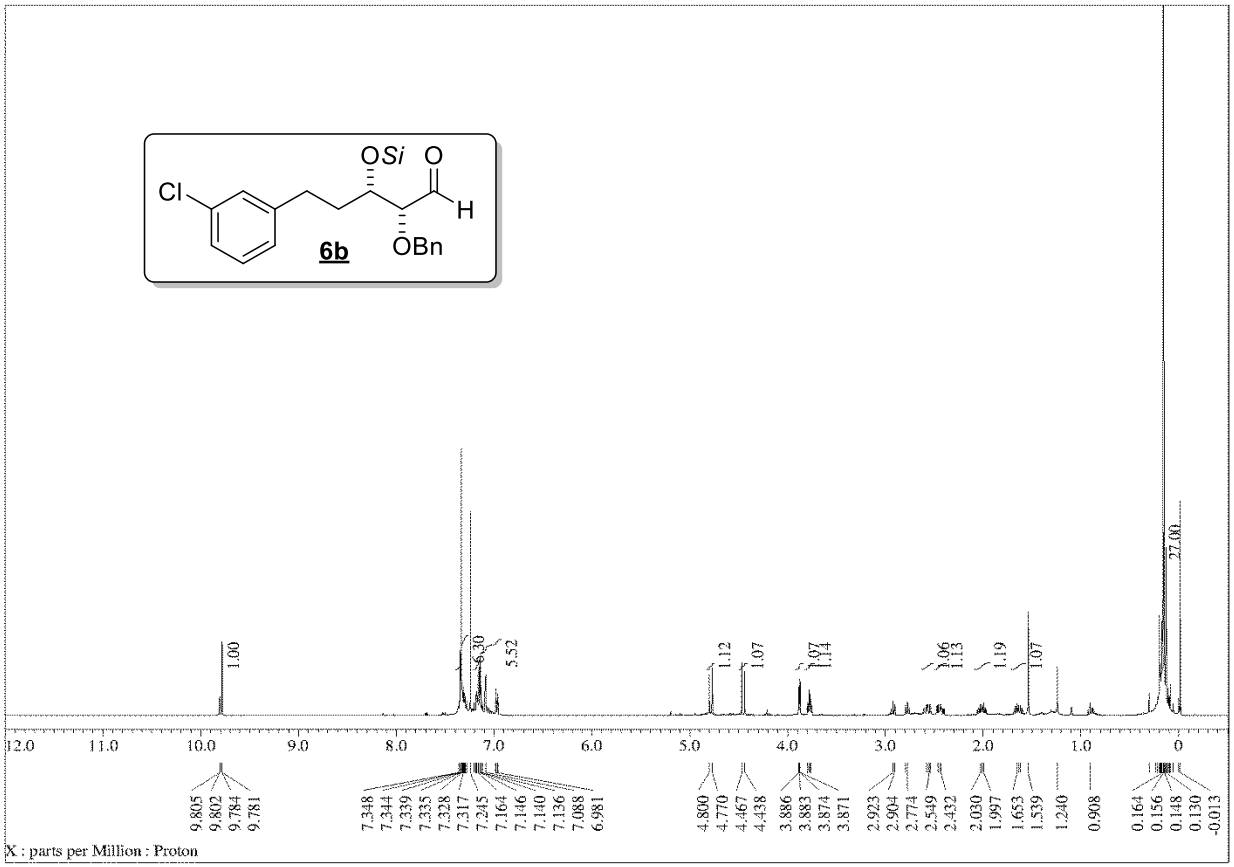
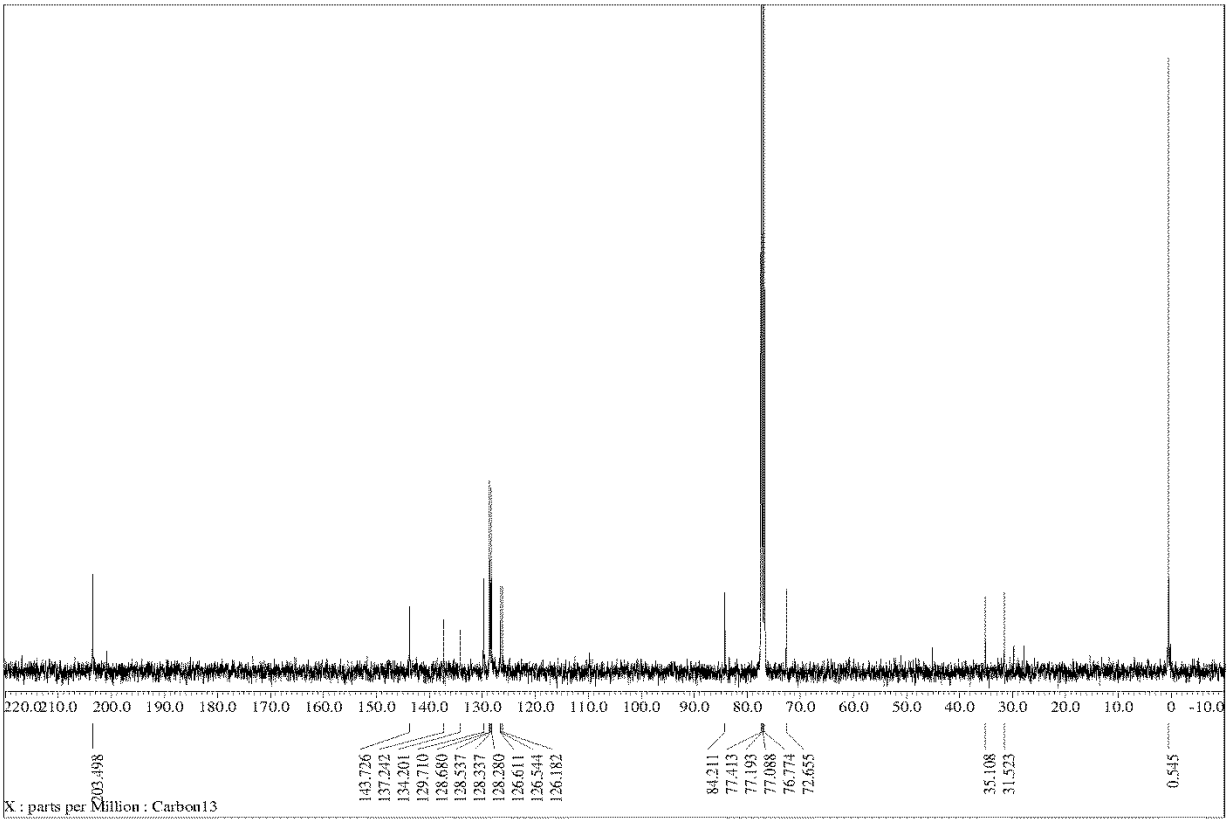
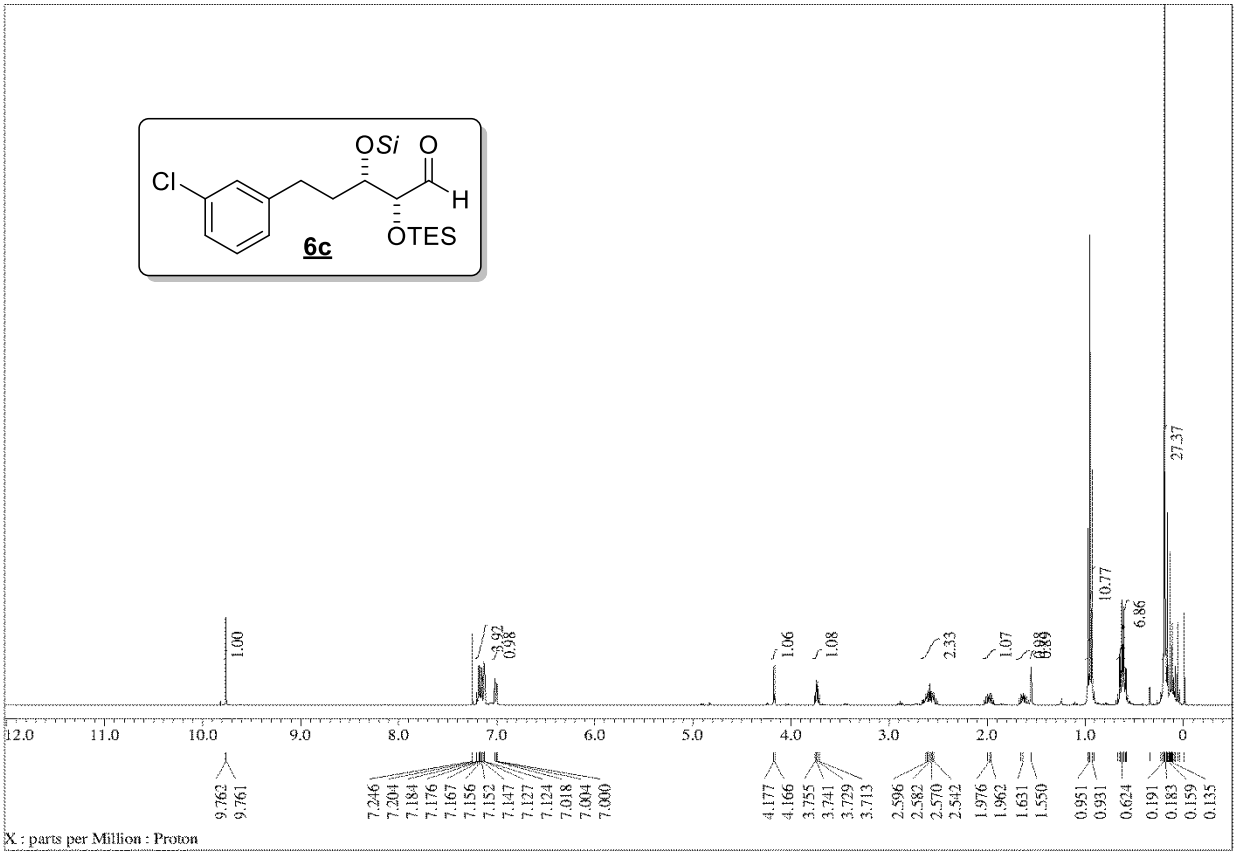
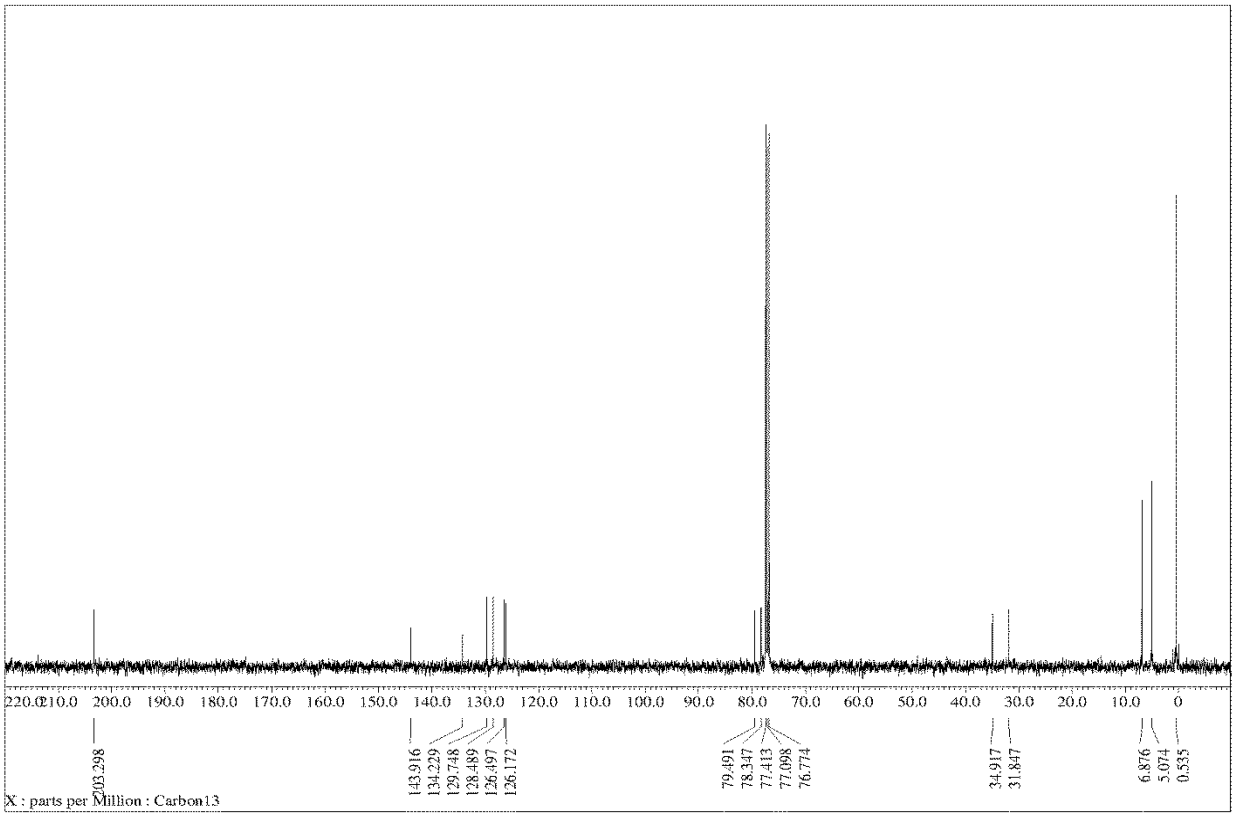
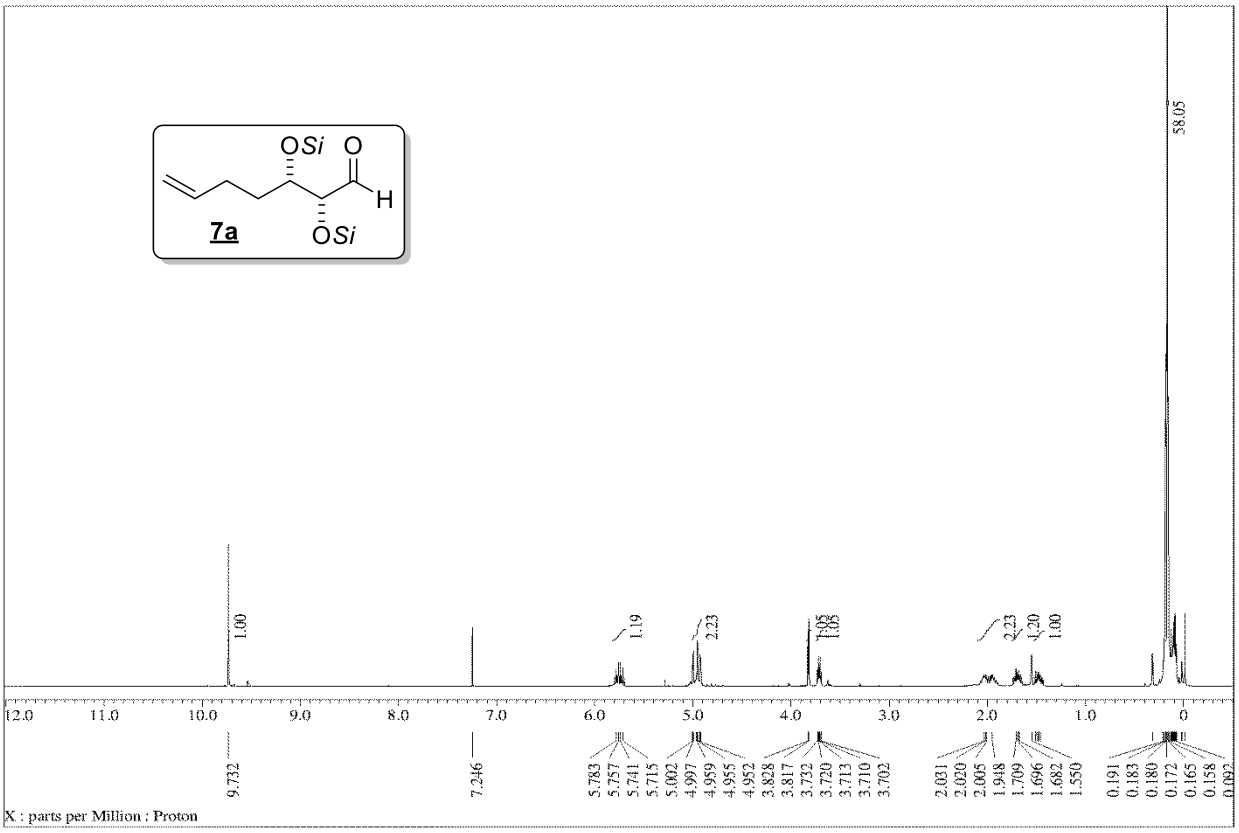
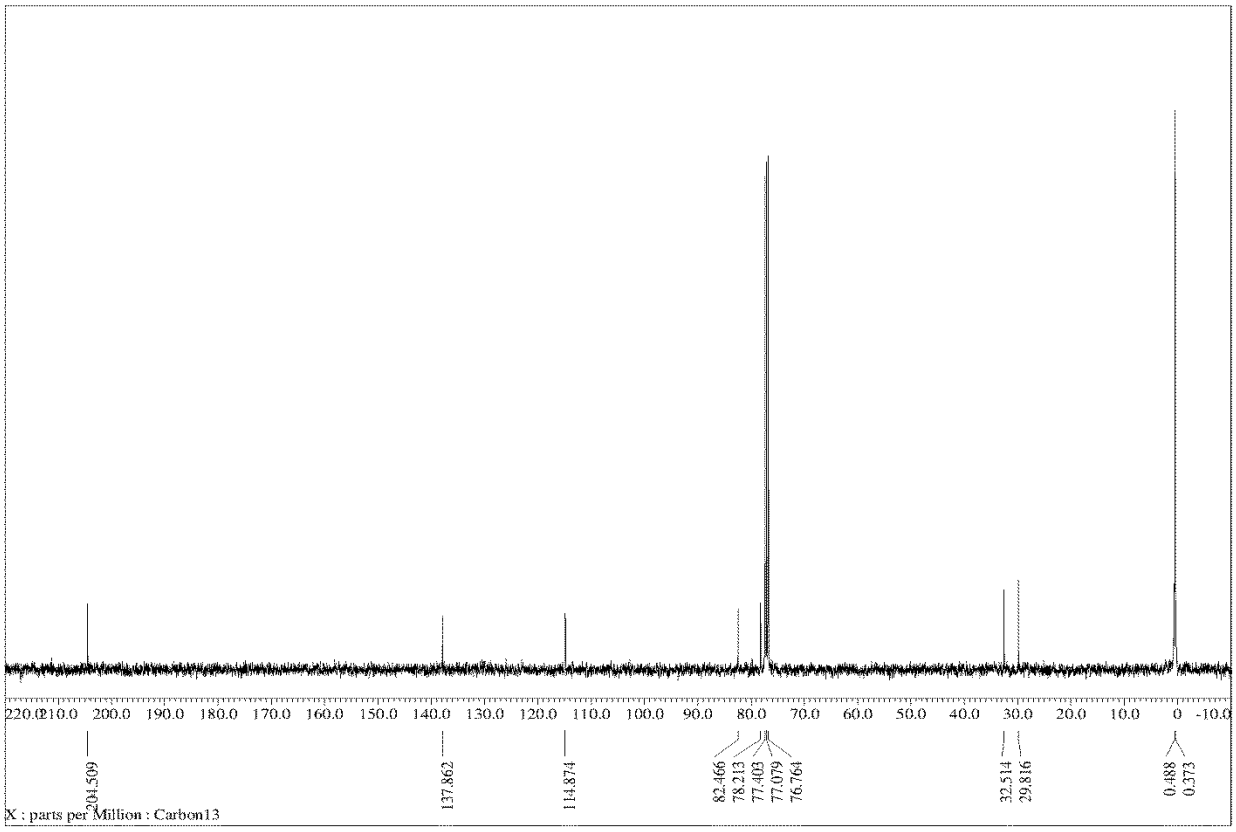

OSi
O
Cl
H
OBn
6b
X : parts per Million : Proton

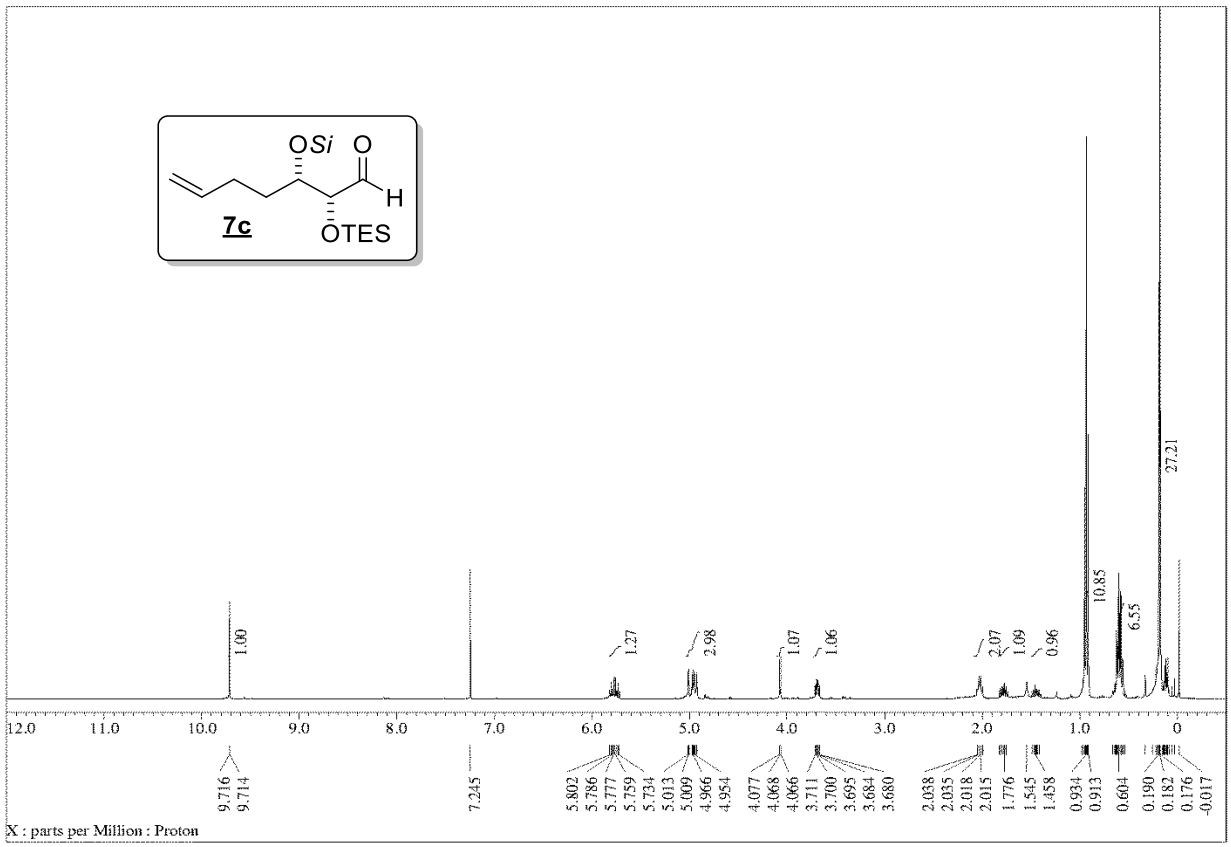

X : parts per Million : Carbon13

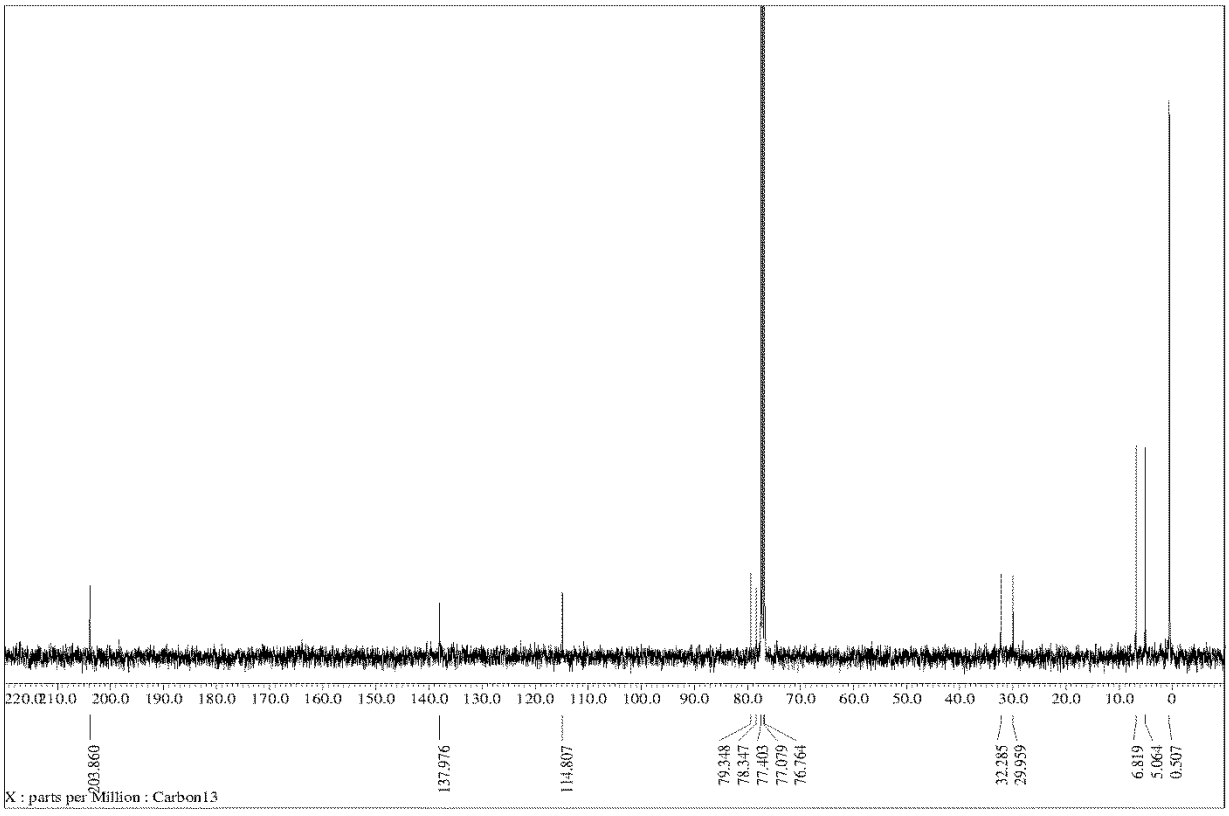

OSi
O
Cl
H
OTES
6c
1.00
3.92
0.98
1.06
1.08
2.33
1.07
10.77
6.86
27.37
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.762
9.761
7.246
7.204
7.184
7.176
7.167
7.156
7.152
7.147
7.127
7.124
7.018
7.004
7.000
4.177
4.166
3.755
3.741
3.729
3.713
2.596
2.582
2.570
2.542
1.976
1.962
1.631
1.550
0.951
0.931
0.624
0.191
0.183
0.159
0.135
X : parts per Million : Proton


220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
203.298
143.916
134.229
129.748
128.489
126.497
126.172
79.491
78.347
77.413
77.098
76.774
34.917
31.847
6.876
5.074
0.535
X : parts per Million : Carbon13

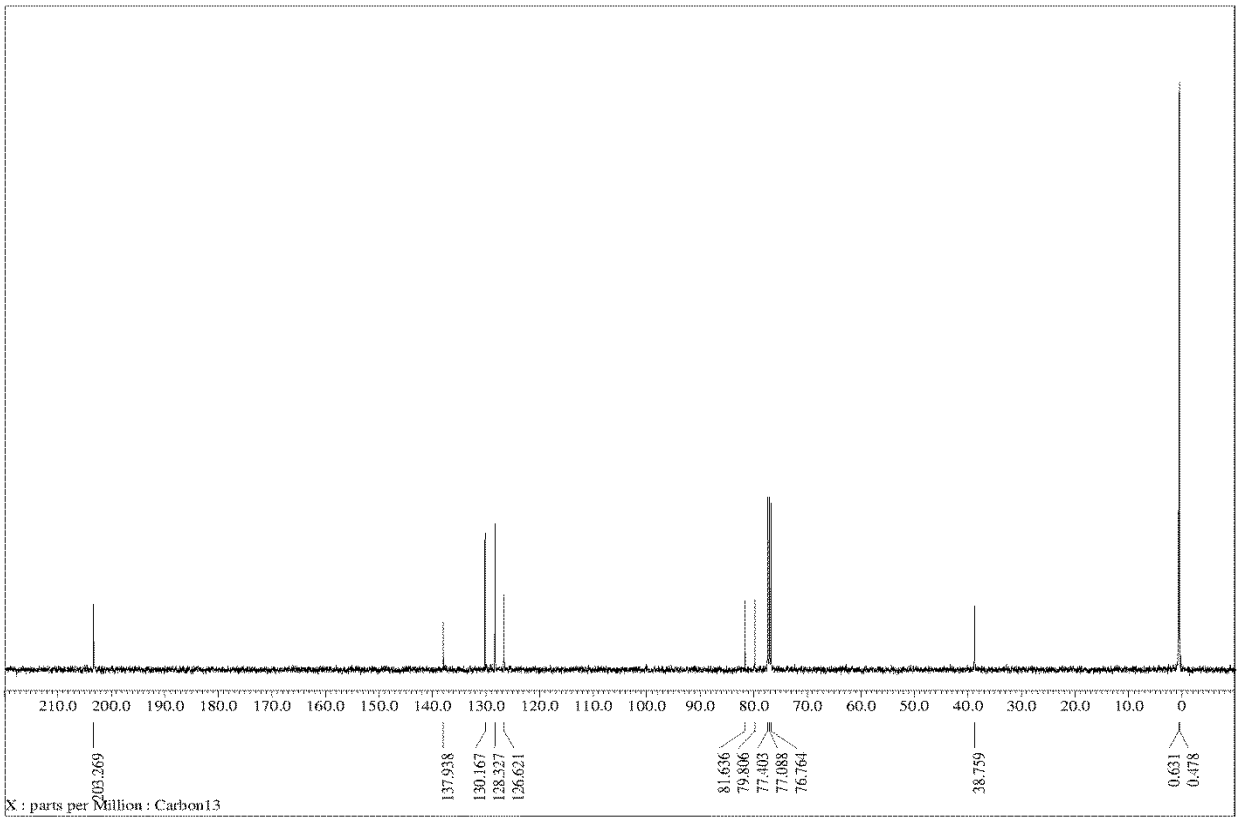

OSi
O
H
OSi
7a
58.05
1.00
1.19
2.23
1.05
1.03
2.23
1.20
1.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.732
7.246
5.783
5.757
5.741
5.715
5.002
4.997
4.959
4.955
4.952
3.828
3.817
3.732
3.720
3.713
3.710
3.702
2.031
2.020
2.005
1.948
1.709
1.696
1.682
1.550
0.191
0.183
0.180
0.172
0.165
0.158
0.092
X : parts per Million : Proton

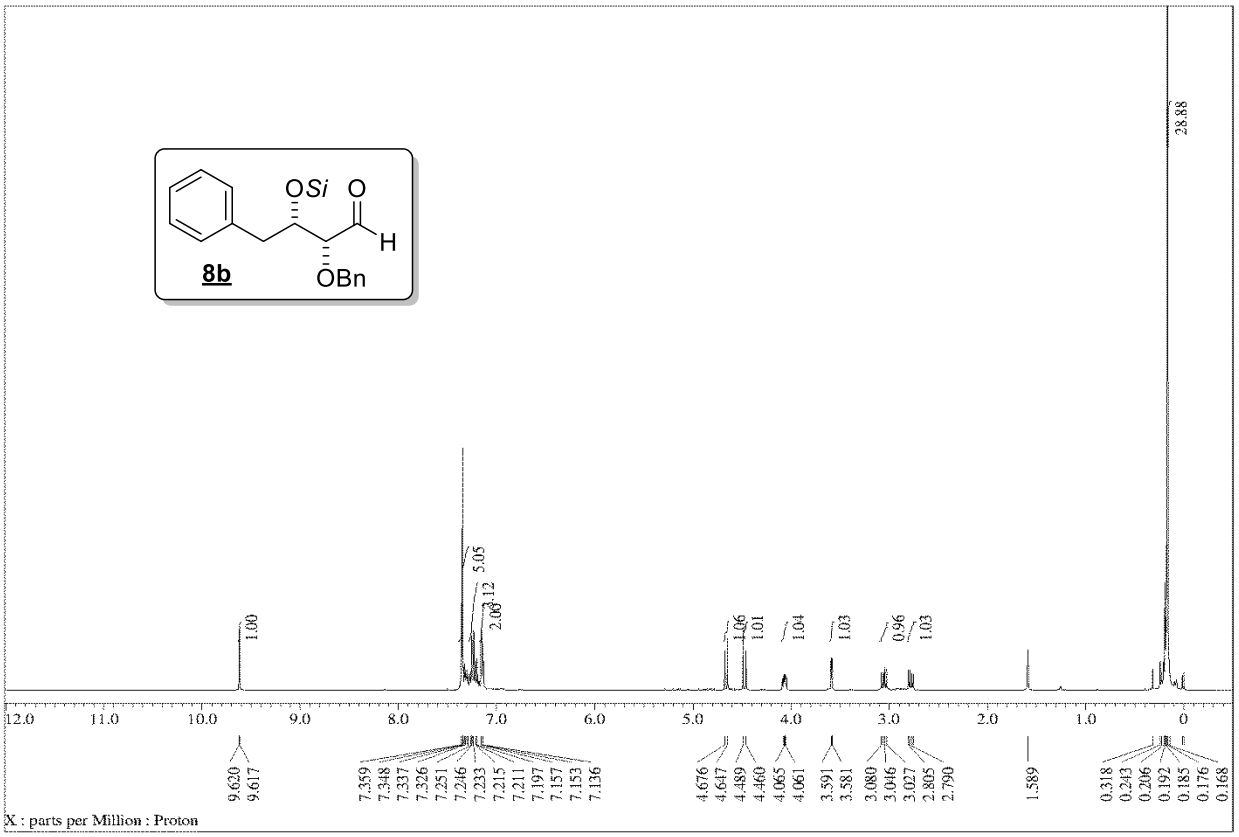

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
204.509
137.862
114.874
82.466
78.213
77.403
77.079
76.764
32.514
29.816
0.488
0.373
X : parts per Million : Carbon13

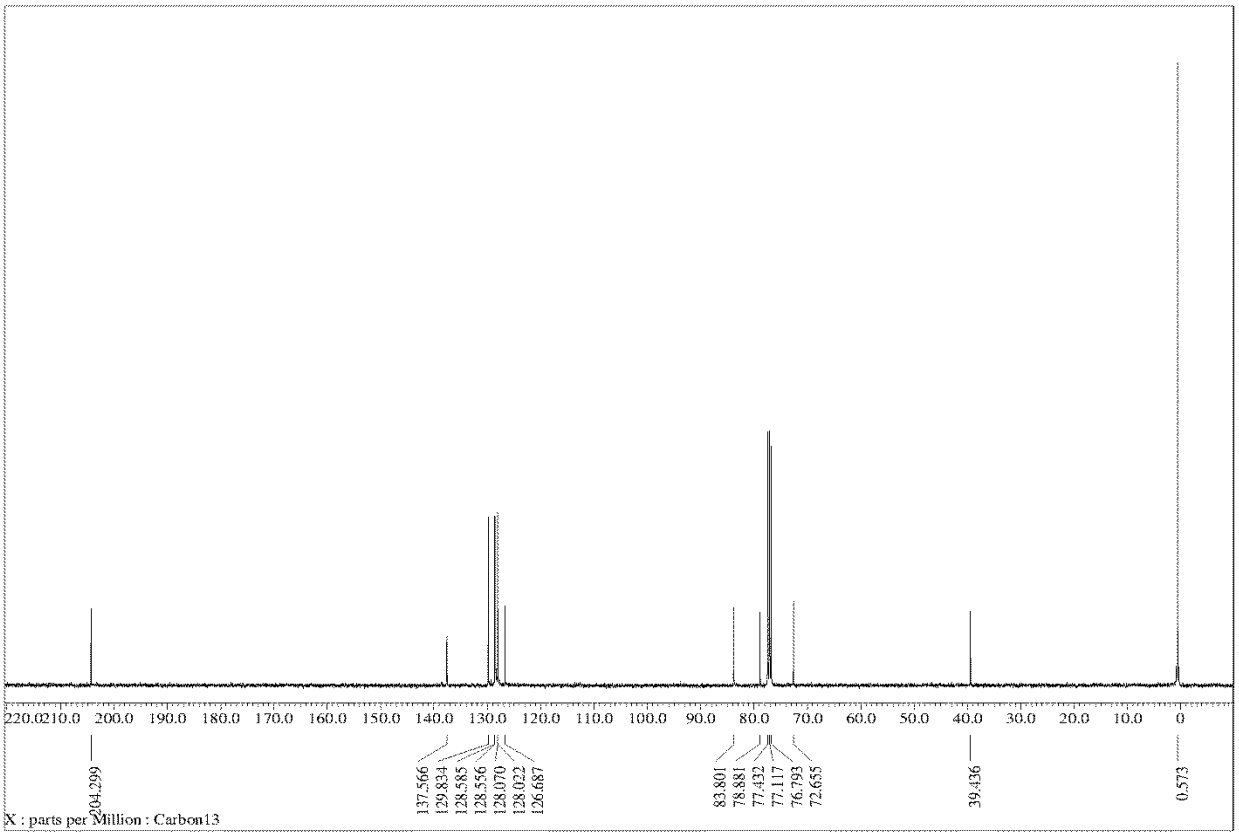

OSi
O
H
OTES
7c
1.00
1.27
2.98
1.07
1.06
2.07
1.09
0.96
10.85
6.55
27.21
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.716
9.714
7.245
5.802
5.786
5.777
5.759
5.734
5.013
5.009
4.966
4.954
4.077
4.068
4.066
3.711
3.700
3.695
3.684
3.680
2.038
2.035
2.018
2.015
1.776
1.545
1.458
0.934
0.913
0.604
0.190
0.182
0.176
-0.017
X : parts per Million : Proton

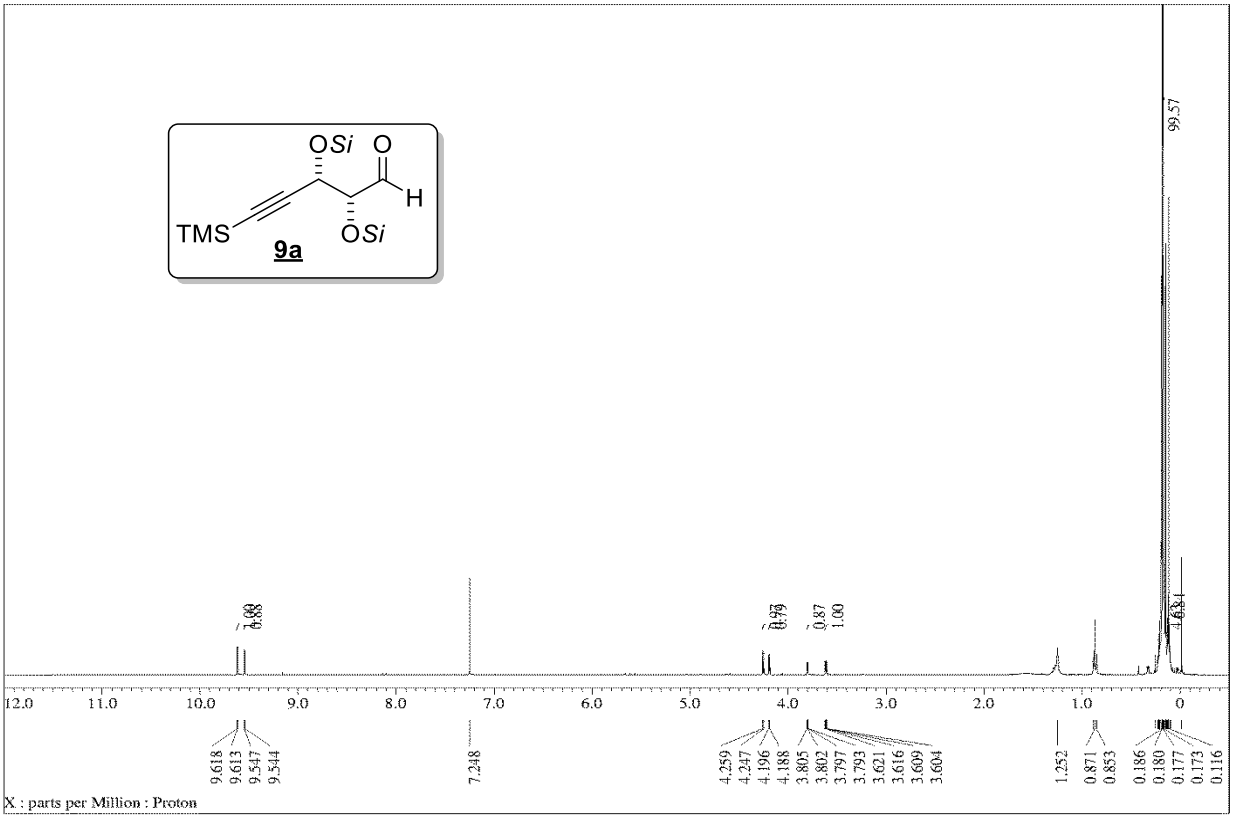

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
203.860
137.976
114.807
79.348
78.347
77.403
77.079
76.764
32.285
29.959
6.819
5.064
0.507
X : parts per Million : Carbon13

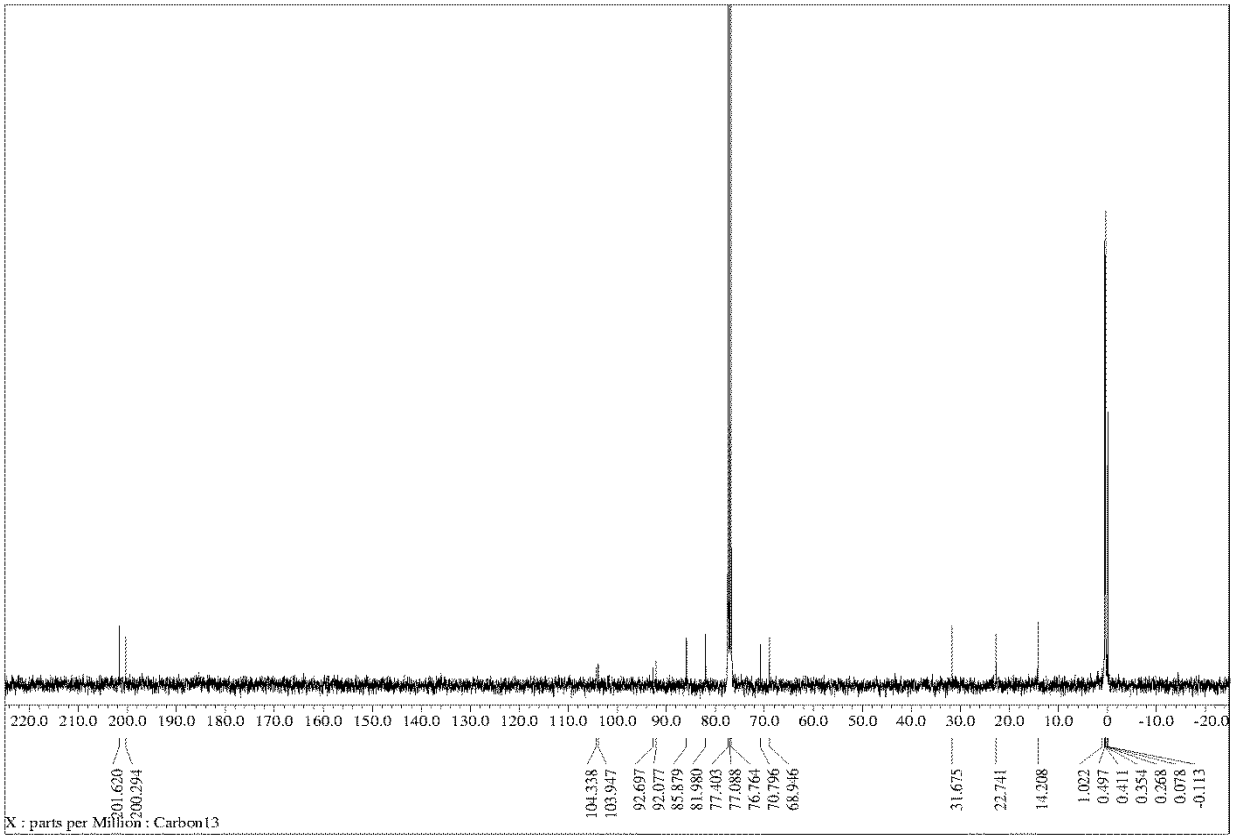

OSi
O
H
OSi
8a
53.73
1.00
5.27
1.02
1.01
0.98
1.02
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.534
7.247
7.232
7.228
7.214
7.196
7.193
7.179
7.160
7.156
7.140
3.984
3.971
3.825
3.813
2.982
2.968
2.947
2.934
2.624
2.609
2.589
2.575
0.326
0.232
0.202
0.196
0.186
0.177
0.164
0.156
0.145
0.033
X : parts per Million : Proton

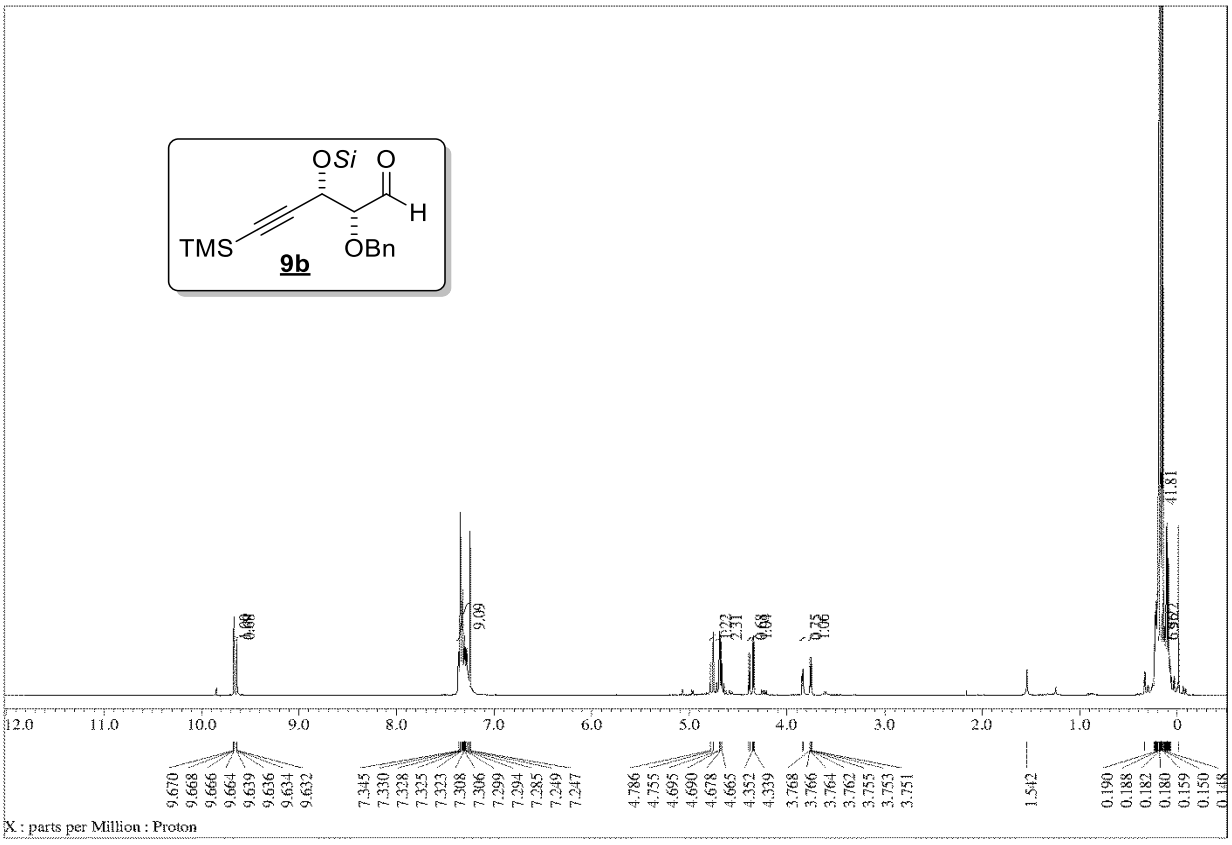

210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
203.269
137.938
130.167
128.327
126.621
81.636
79.806
77.403
77.088
76.764
38.759
0.631
0.478
X : parts per Million : Carbon13

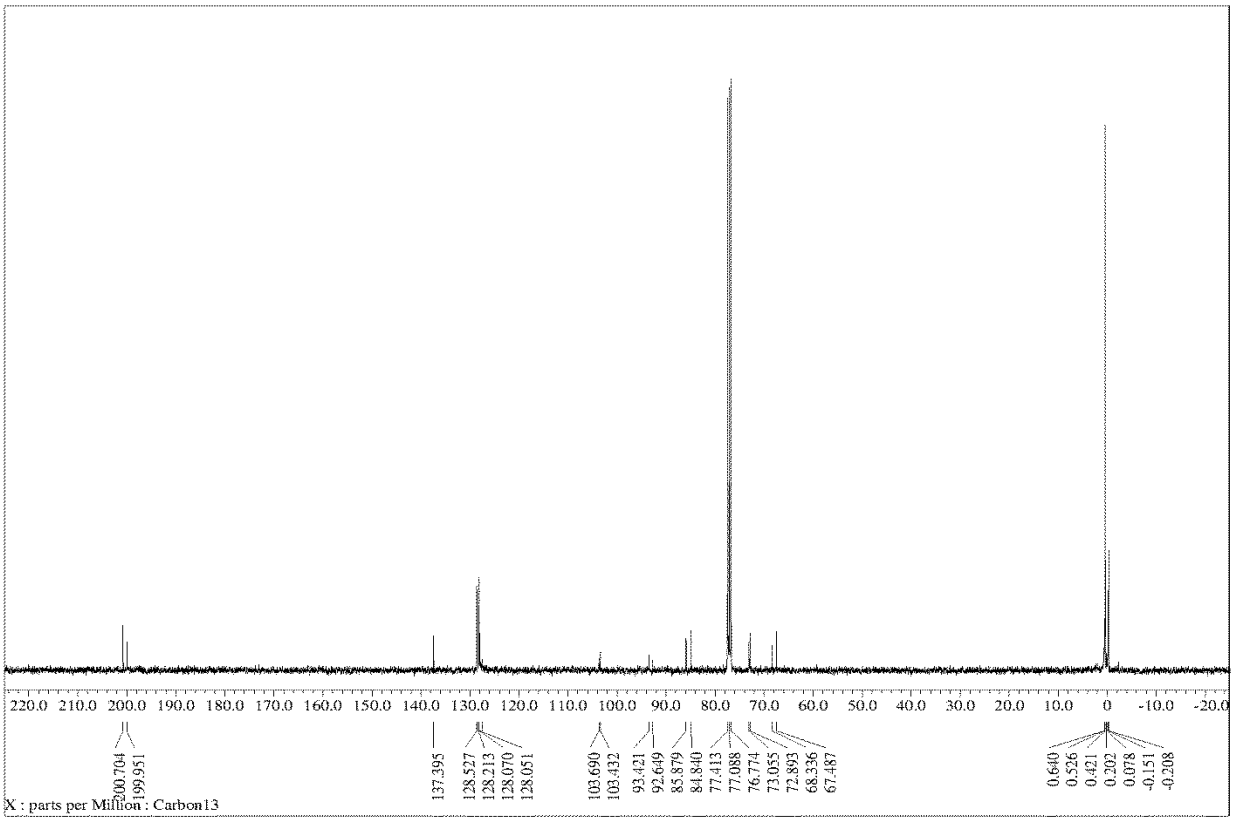

OSi
O
H
OBn
8b
28.88
1.00
5.05
2.12
2.08
1.06
1.01
1.04
1.03
0.96
1.03
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.620
9.617
7.359
7.348
7.337
7.326
7.251
7.246
7.233
7.215
7.211
7.197
7.157
7.153
7.136
4.676
4.647
4.489
4.460
4.065
4.061
3.591
3.581
3.080
3.046
3.027
2.805
2.790
1.589
0.318
0.243
0.206
0.192
0.185
0.176
0.168
X : parts per Million : Proton

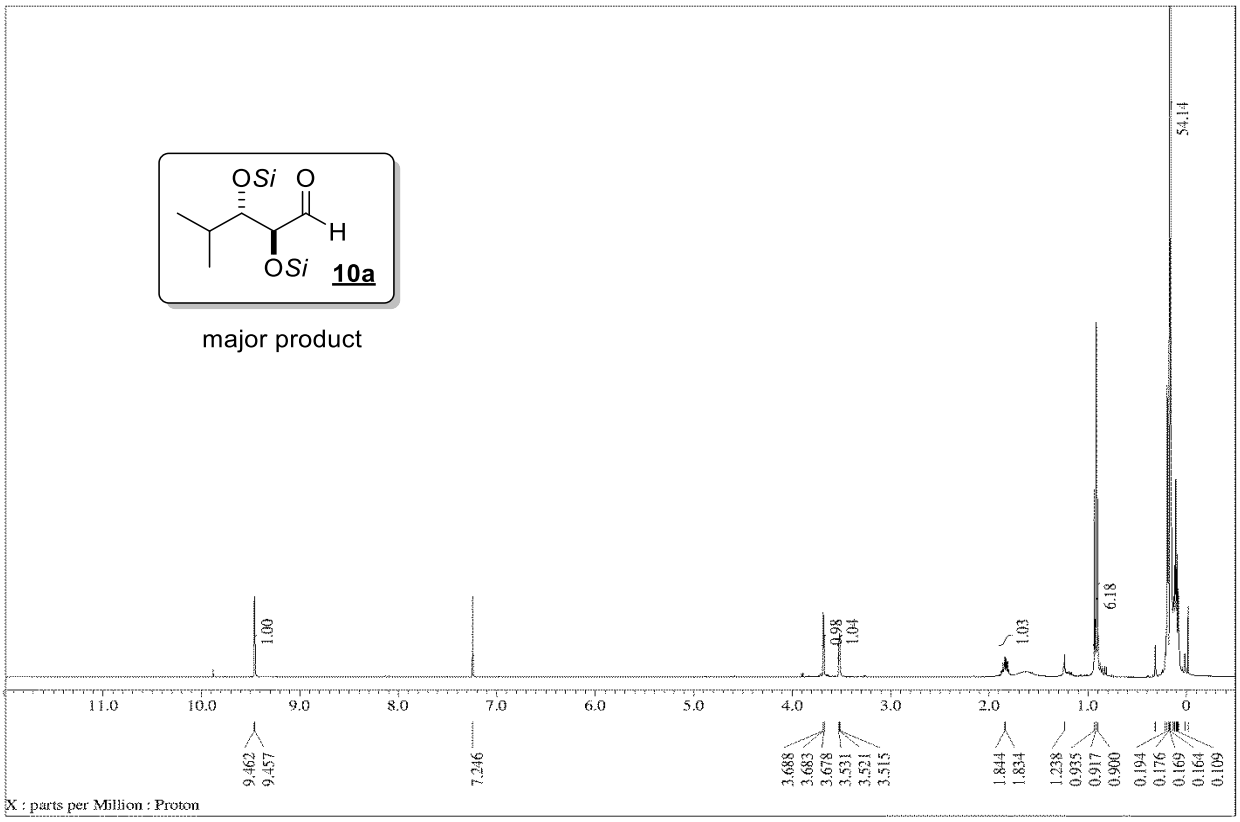

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
204.299
137.566
129.834
128.585
128.556
128.070
128.022
126.687
83.801
78.881
77.432
77.117
76.793
72.655
39.436
0.573
X : parts per Million : Carbon13

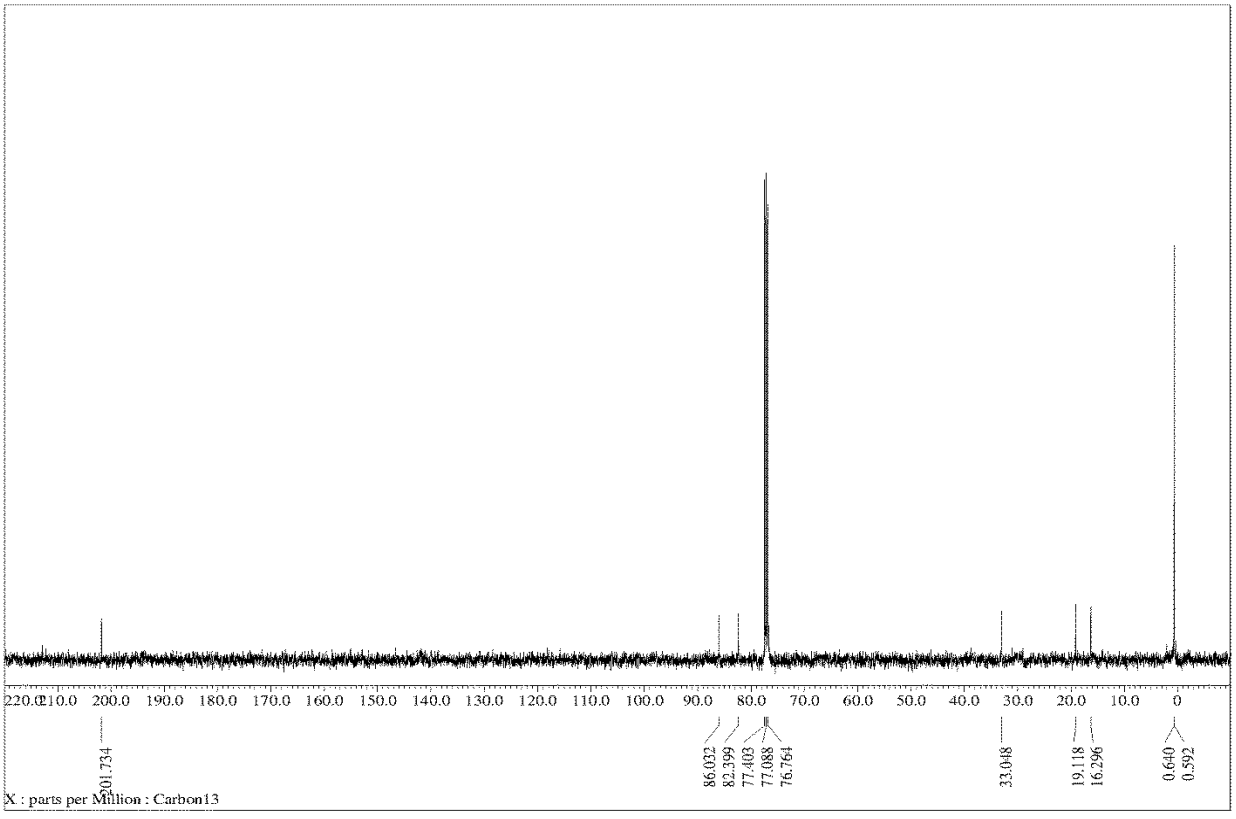

OSi
O
H
TMS
OSi
9a
99.57
X : parts per Million : Proton

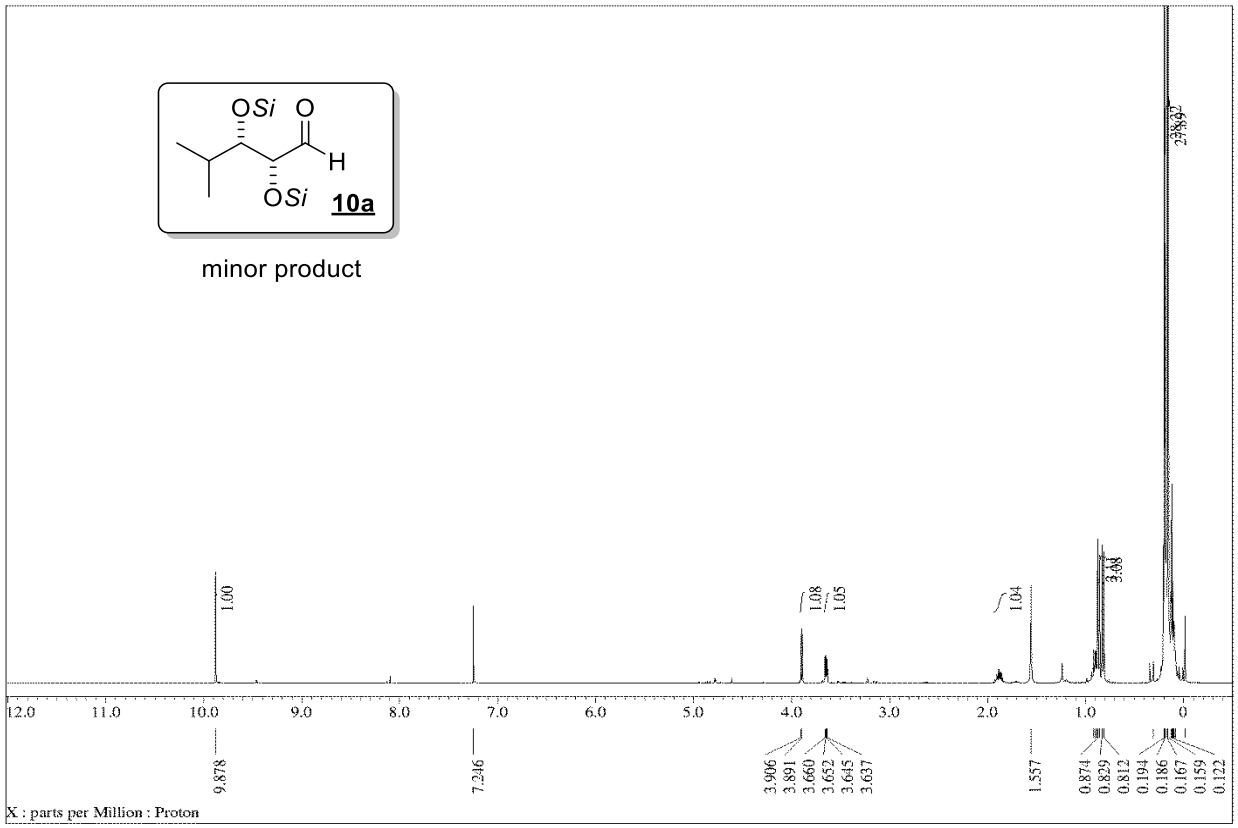

X : parts per Million : Carbon13

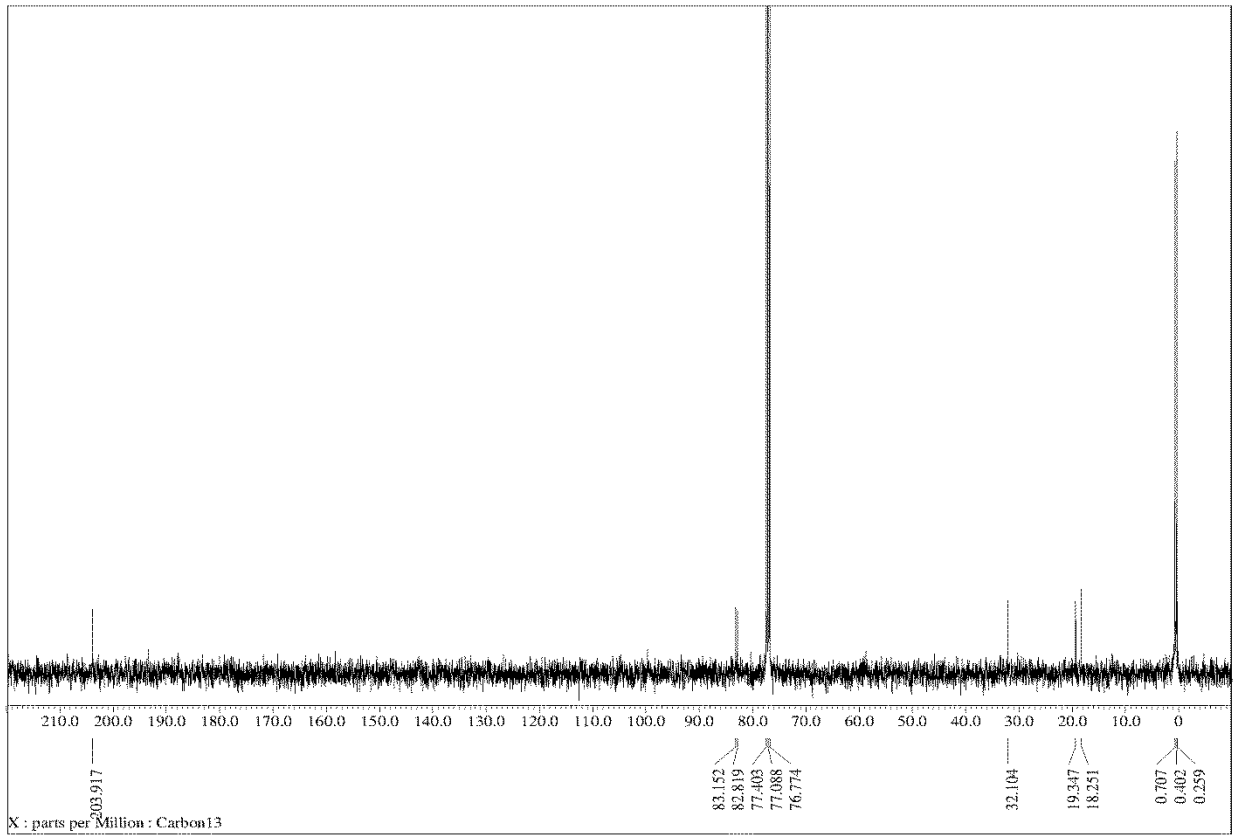

OSi
O
H
TMS
OBn
9b
X : parts per Million : Proton

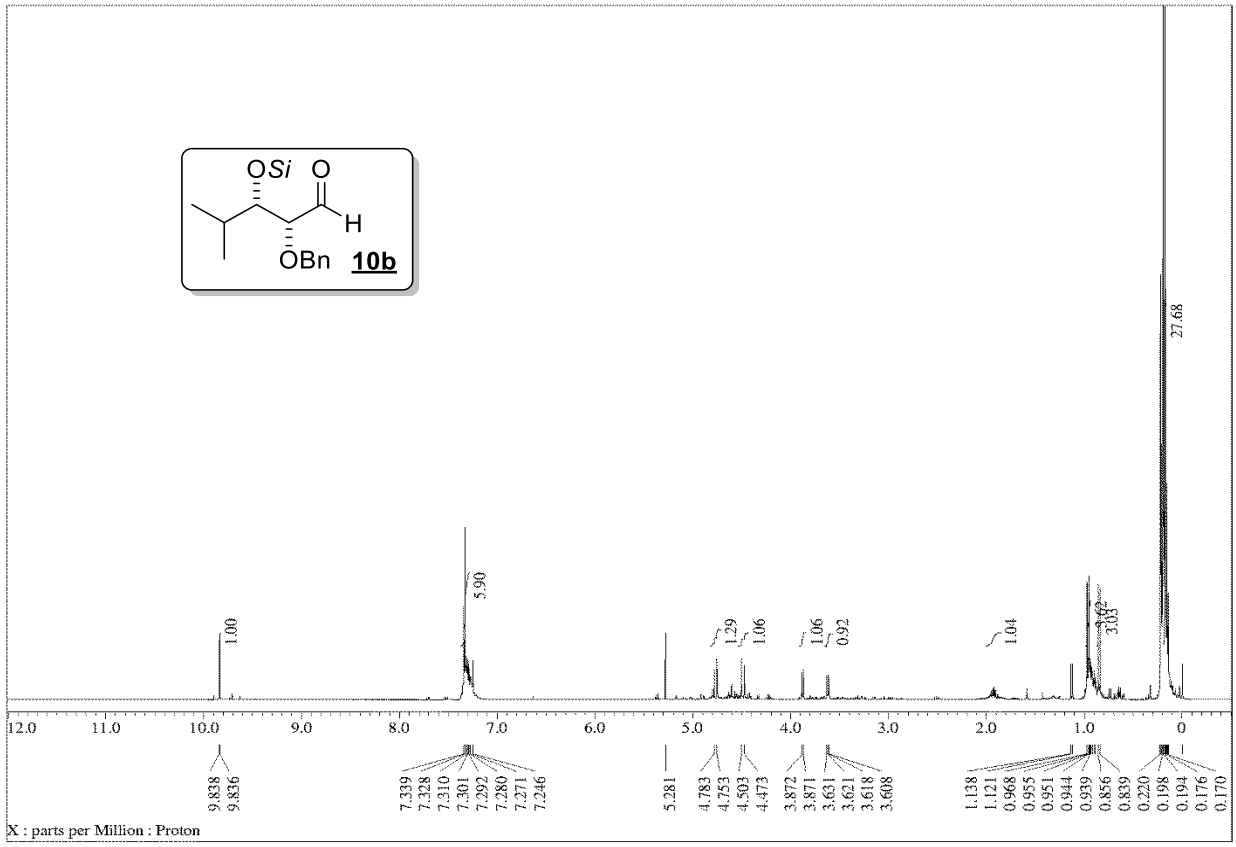

X : parts per Million : Carbon13

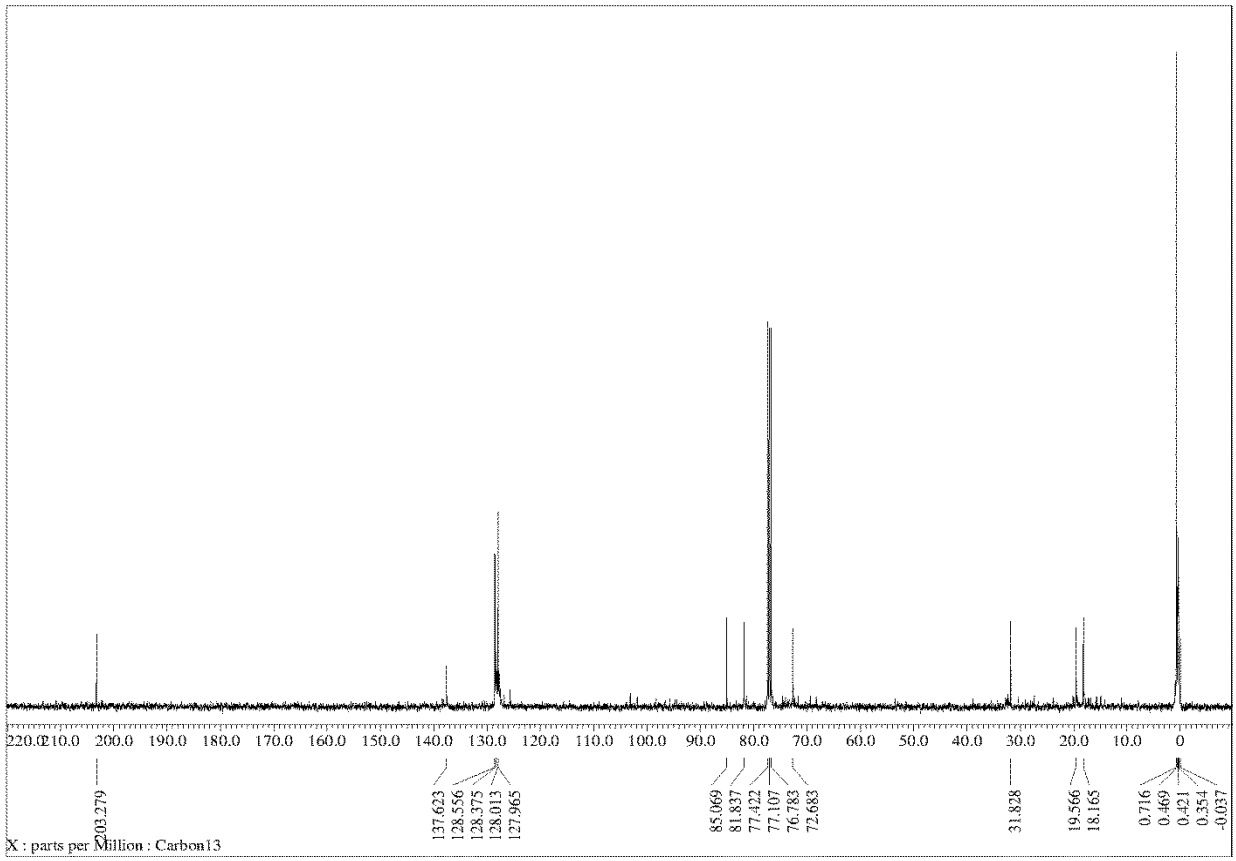

OSi
O
H
OSi
10a
major product
54.14
6.18
1.00
0.98
1.04
1.03
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.462
9.457
7.246
3.688
3.683
3.678
3.531
3.521
3.515
1.844
1.834
1.238
0.935
0.917
0.900
0.194
0.176
0.169
0.164
0.109
X : parts per Million : Proton

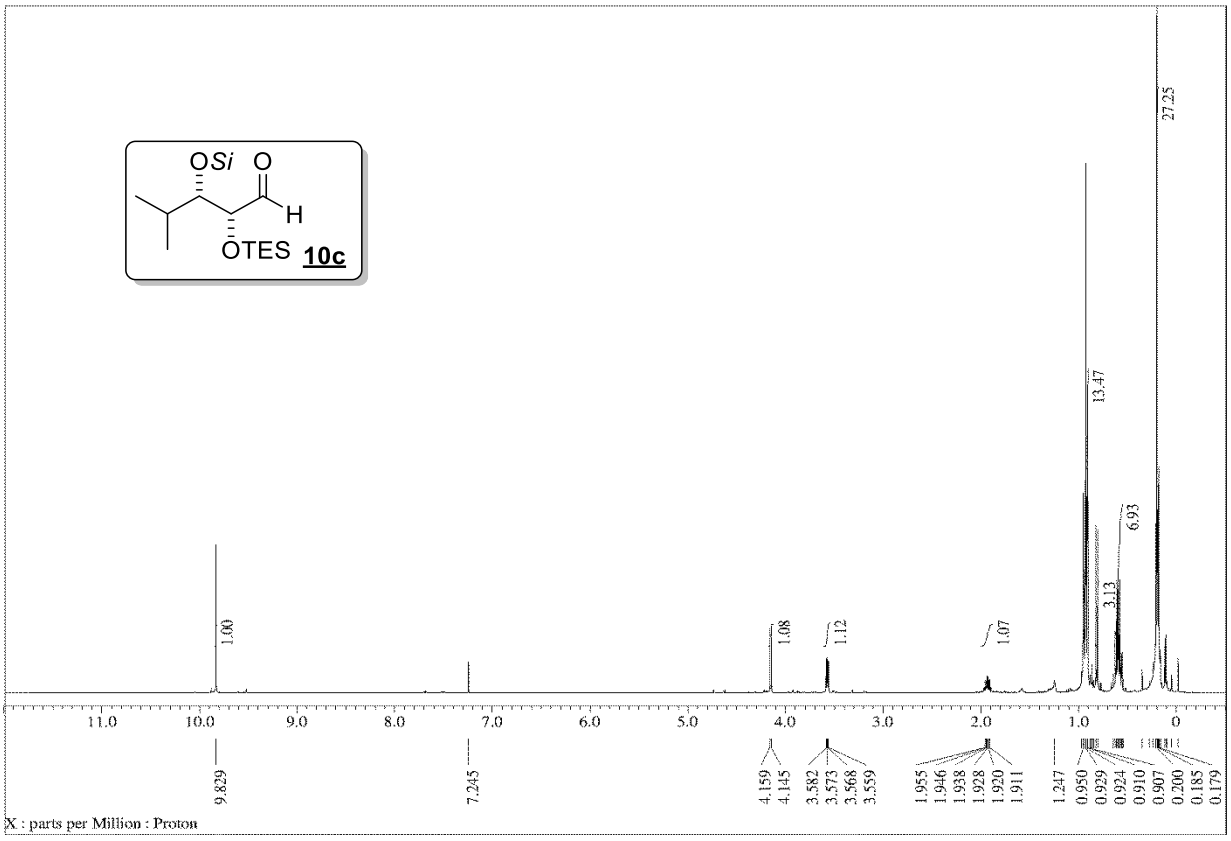

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
201.734
86.032
82.399
77.403
77.088
76.764
33.048
19.118
16.296
0.640
0.592
X : parts per Million : Carbon13

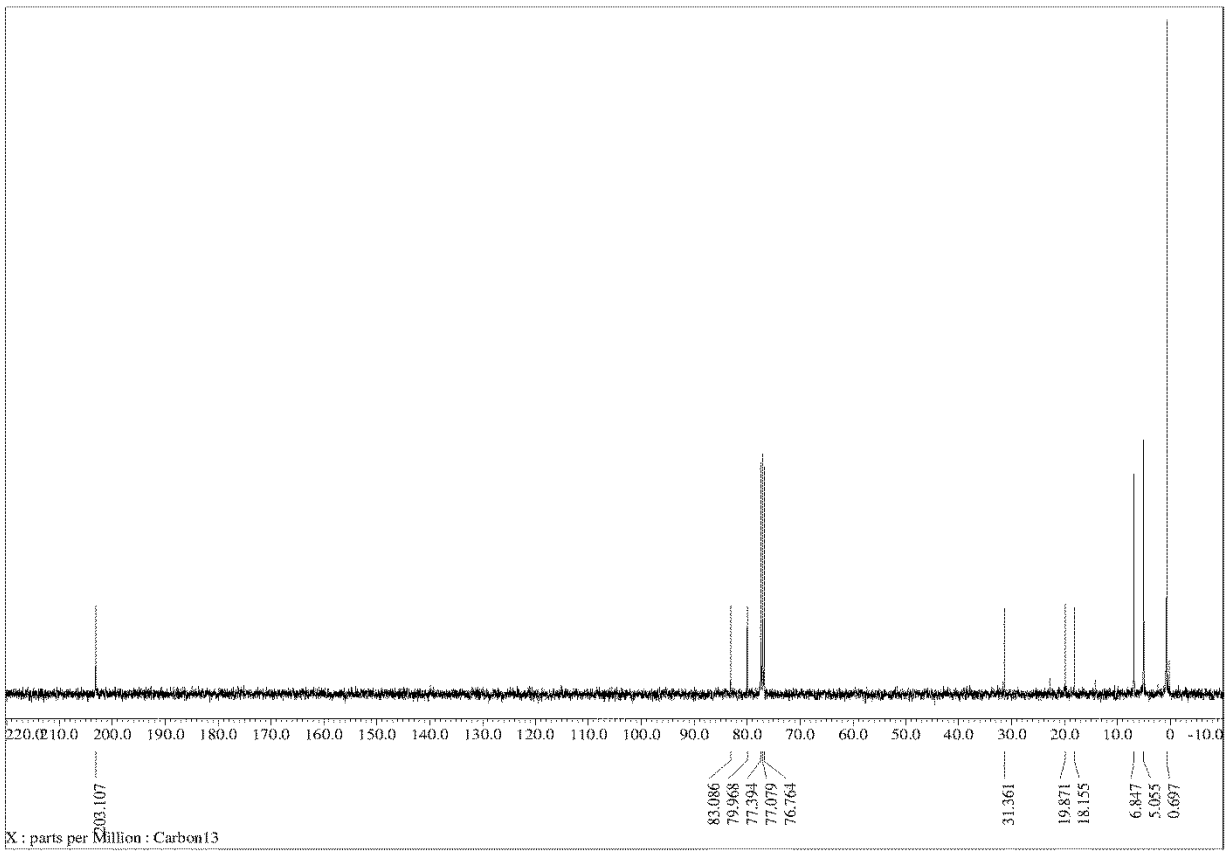

OSi
O
H
OSi
10a
minor product
1.00
1.08
1.05
1.04
3.08
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.878
7.246
3.906
3.891
3.660
3.652
3.645
3.637
1.557
0.874
0.829
0.812
0.194
0.186
0.167
0.159
0.122
X : parts per Million : Proton

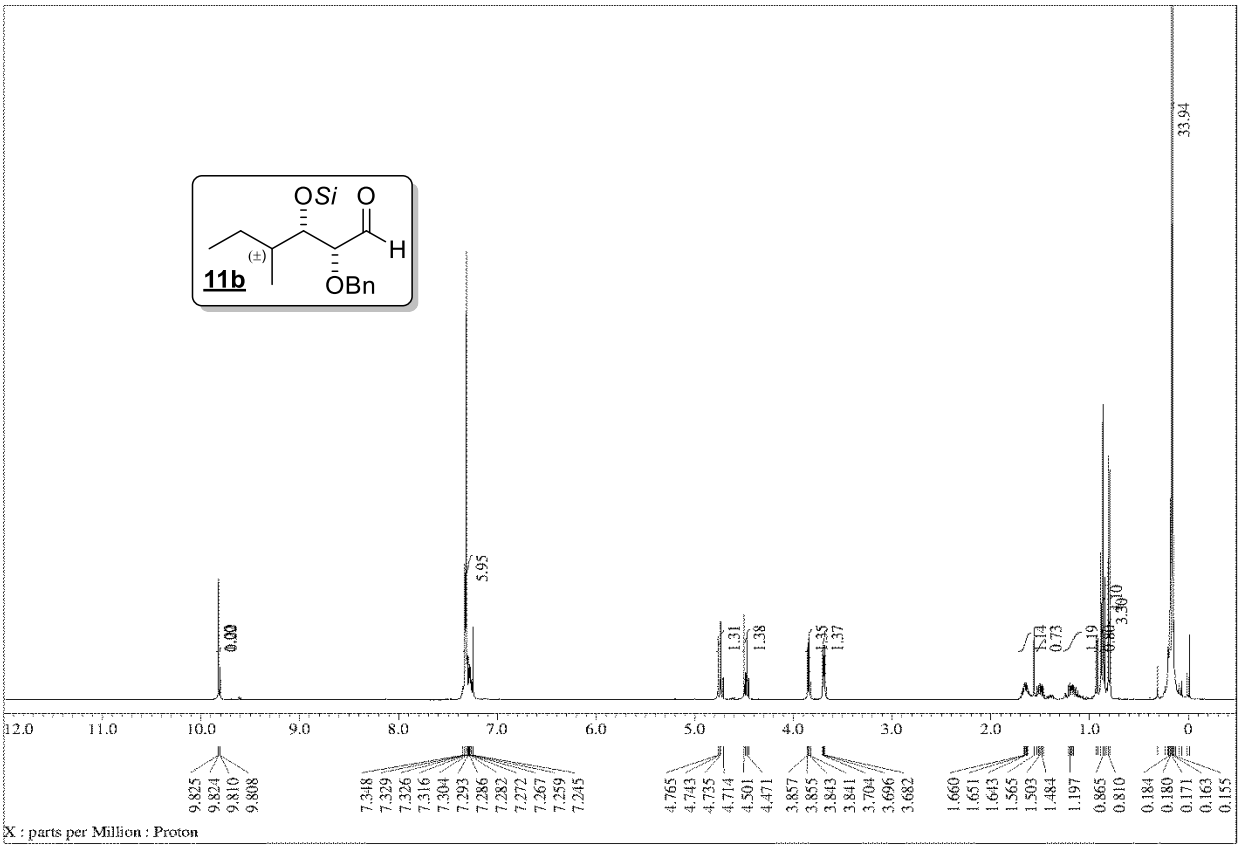

210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
203.917
83.152
82.819
77.403
77.088
76.774
32.104
19.347
18.251
0.707
0.402
0.259
X : parts per Million : Carbon13

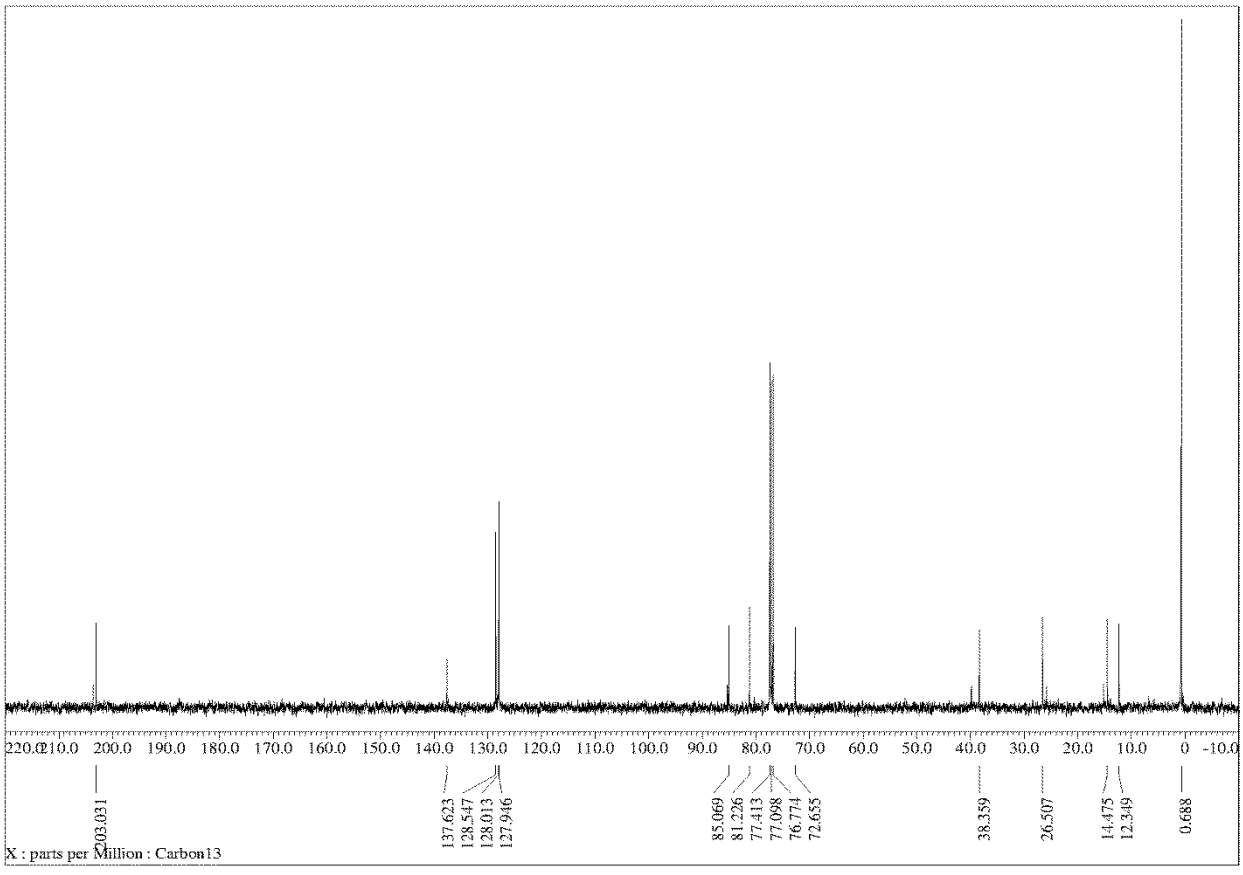

OSi
O
H
OBn
10b
X : parts per Million : Proton

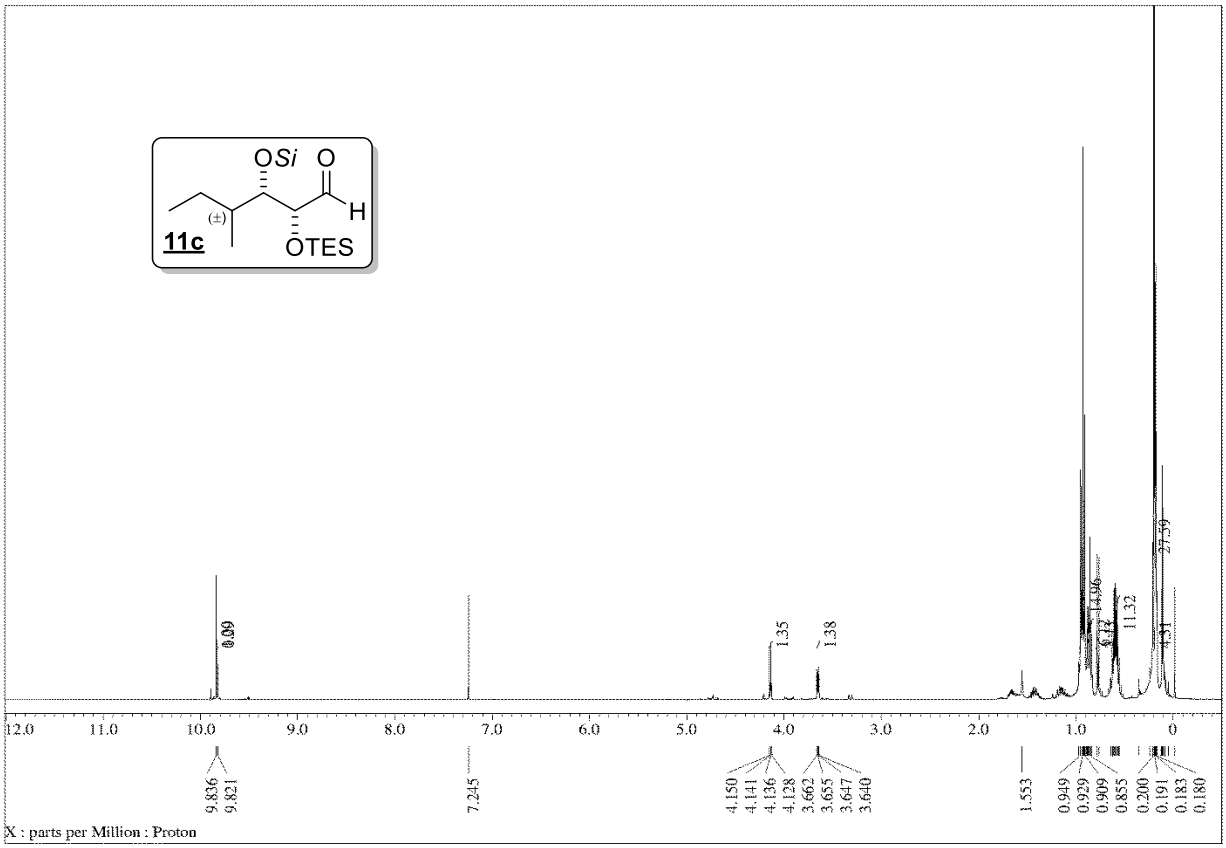

X : parts per Million : Carbon13

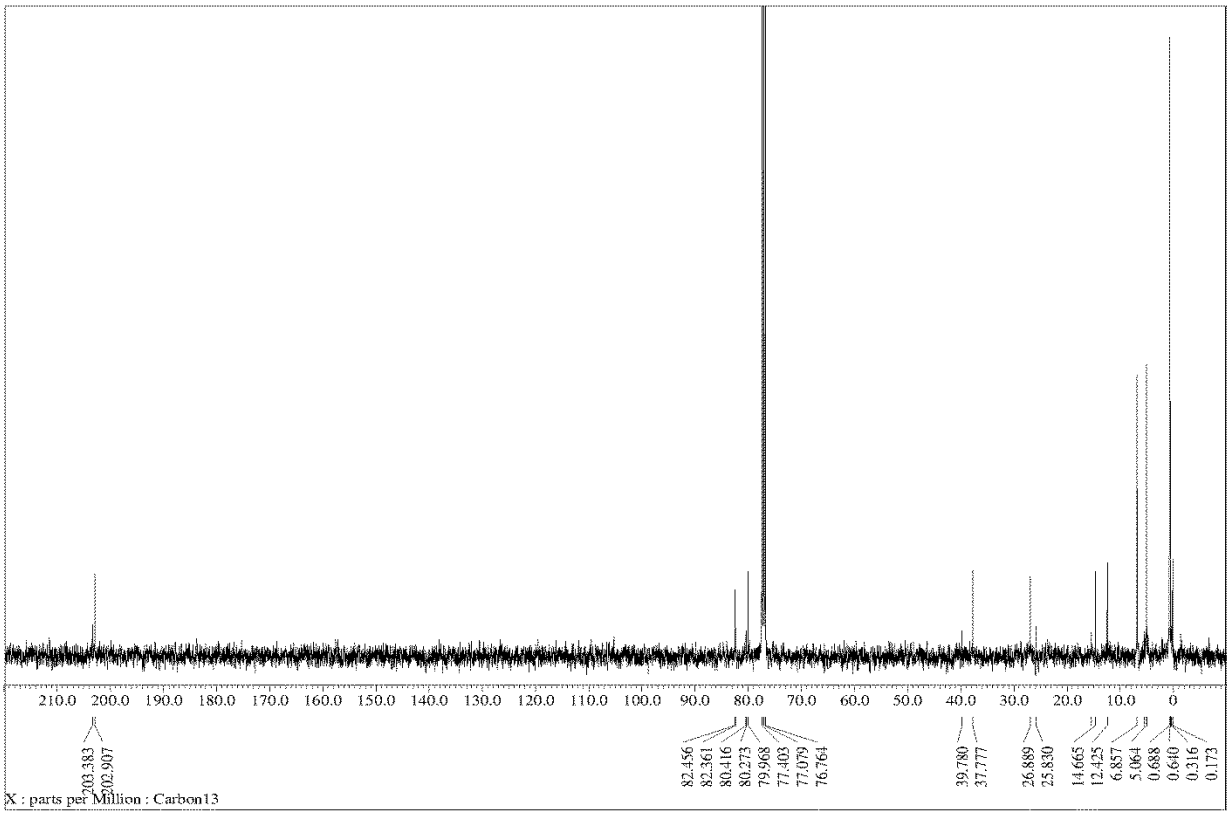

OSi O
H
OTES
10c
27.25
13.47
6.93
3.13
1.00
1.08
1.12
1.07
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
9.829
7.245
4.159
4.145
3.582
3.573
3.568
3.559
1.955
1.946
1.938
1.928
1.920
1.911
1.247
0.950
0.929
0.924
0.910
0.907
0.200
0.185
0.179
X : parts per Million : Proton

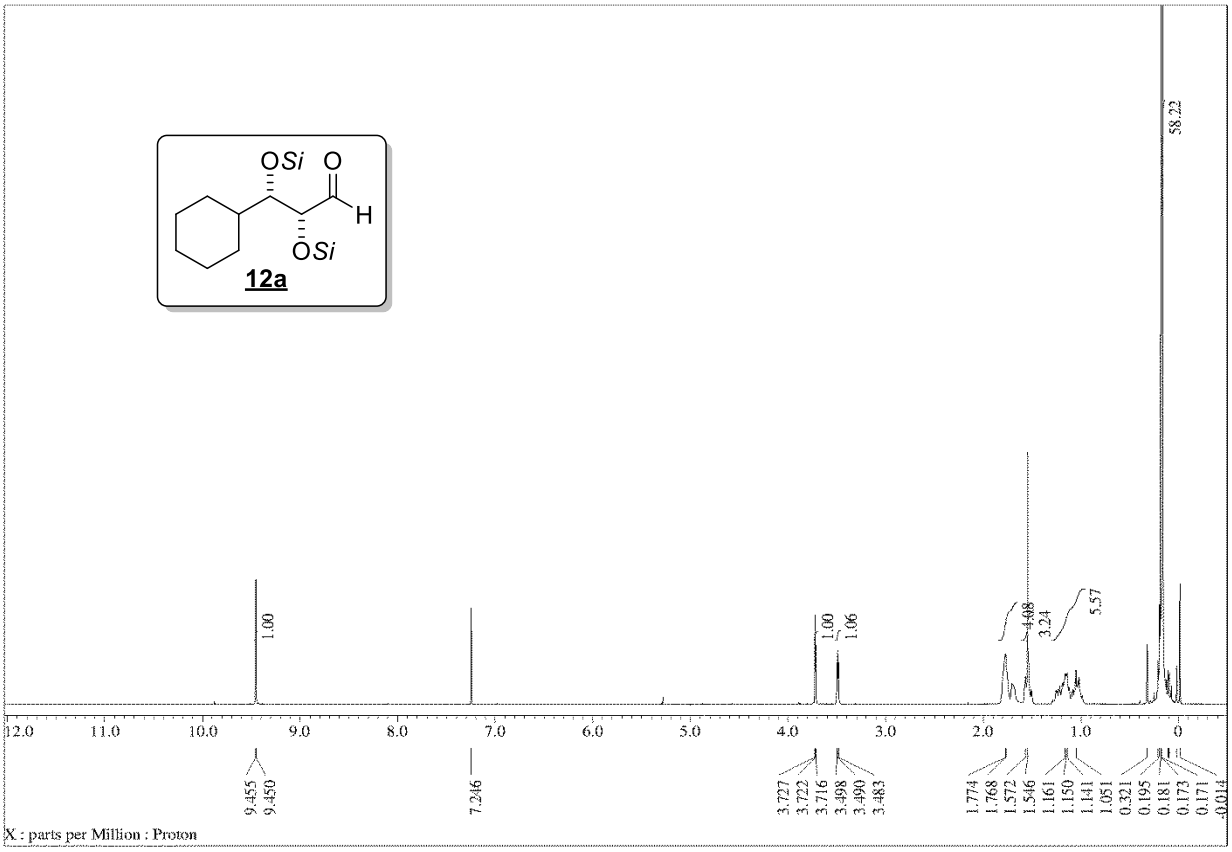

220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
203.107
83.086
79.968
77.394
77.079
76.764
31.361
19.871
18.155
6.847
5.055
0.697
X : parts per Million : Carbon13

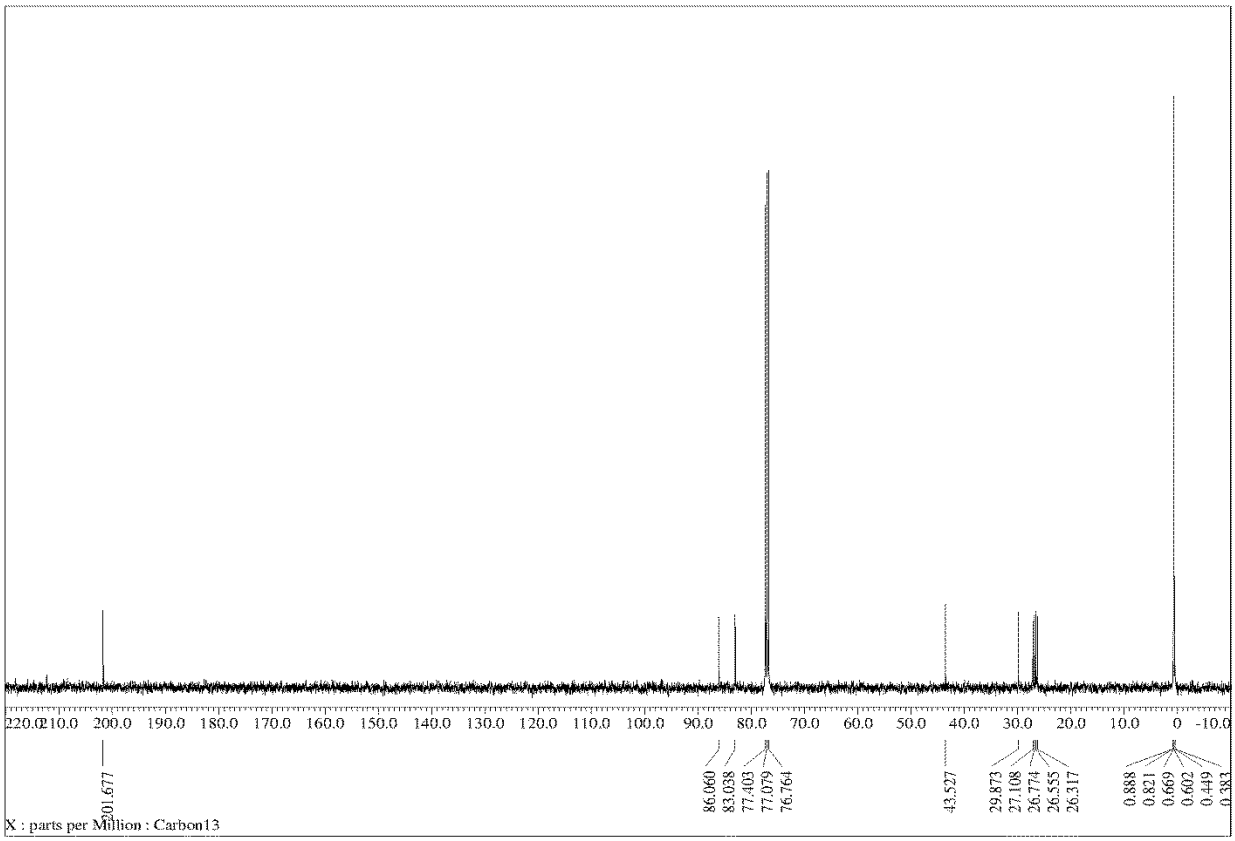

OSi
O
H
(±)
11b
OBn
33.94
5.95
1.31
1.38
1.35
1.37
3.30
3.10
X : parts per Million : Proton

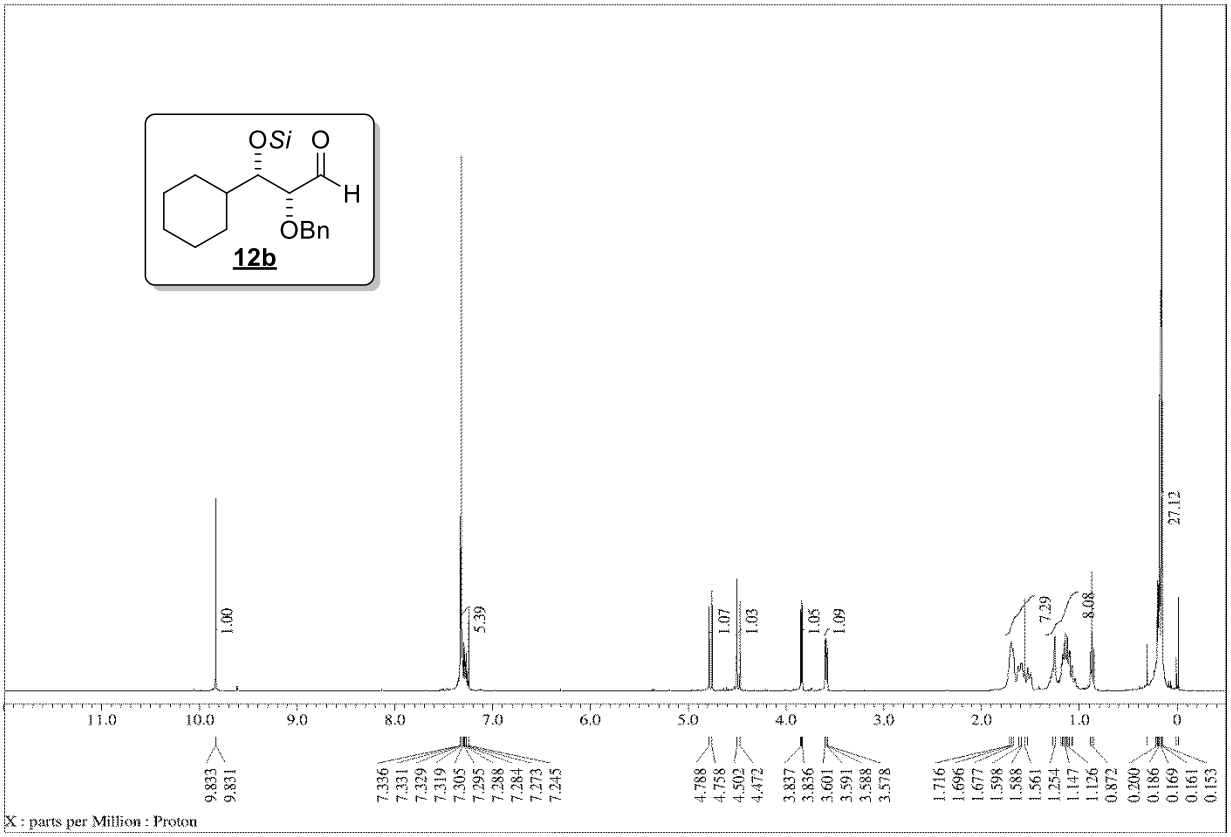

203.031
137.623
128.547
128.013
127.946
85.069
81.226
77.413
77.098
76.774
72.655
38.359
26.507
14.475
12.349
0.688
X : parts per Million : Carbon13

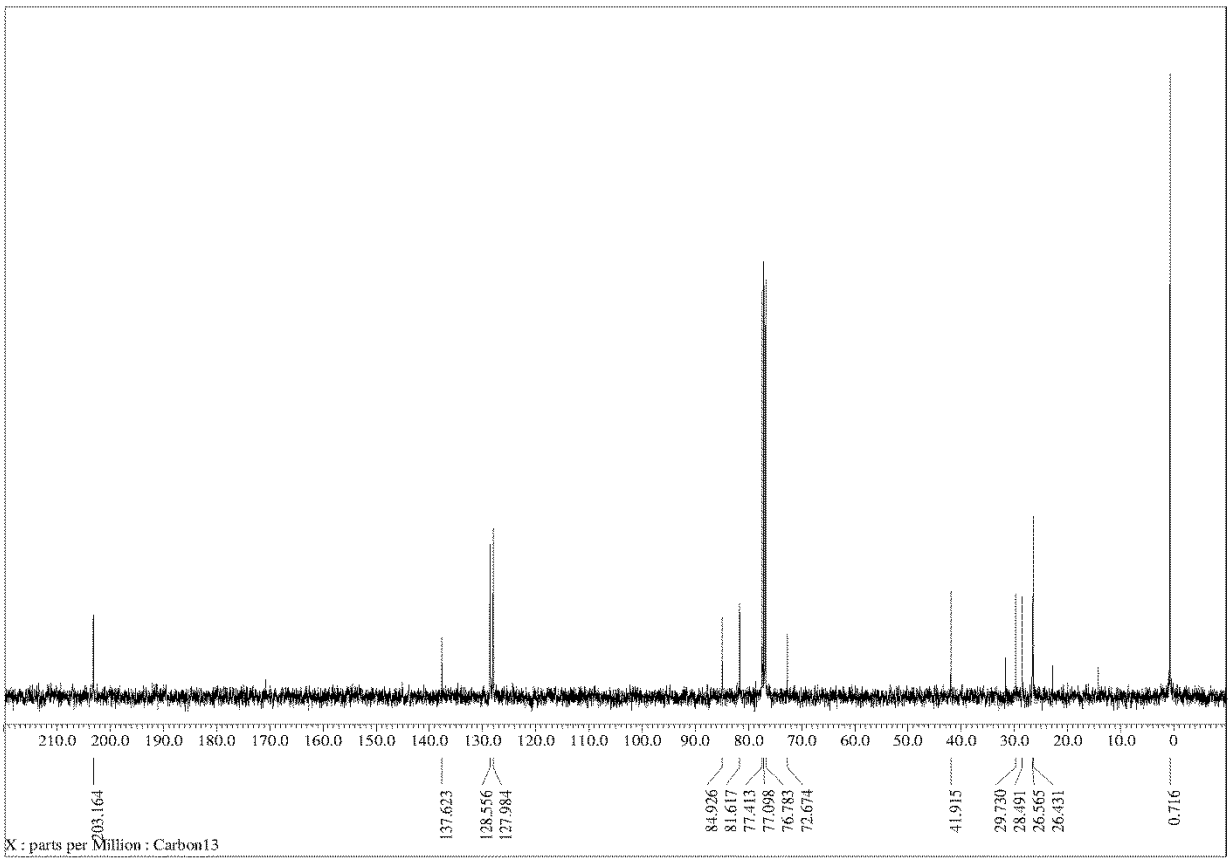

OSi
O
H
(±)
11c
OTES
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.836
9.821
7.245
4.150
4.141
4.136
4.128
3.662
3.655
3.647
3.640
1.553
0.949
0.929
0.909
0.855
0.200
0.191
0.183
0.180
1.35
1.38
11.32
27.59
X : parts per Million : Proton

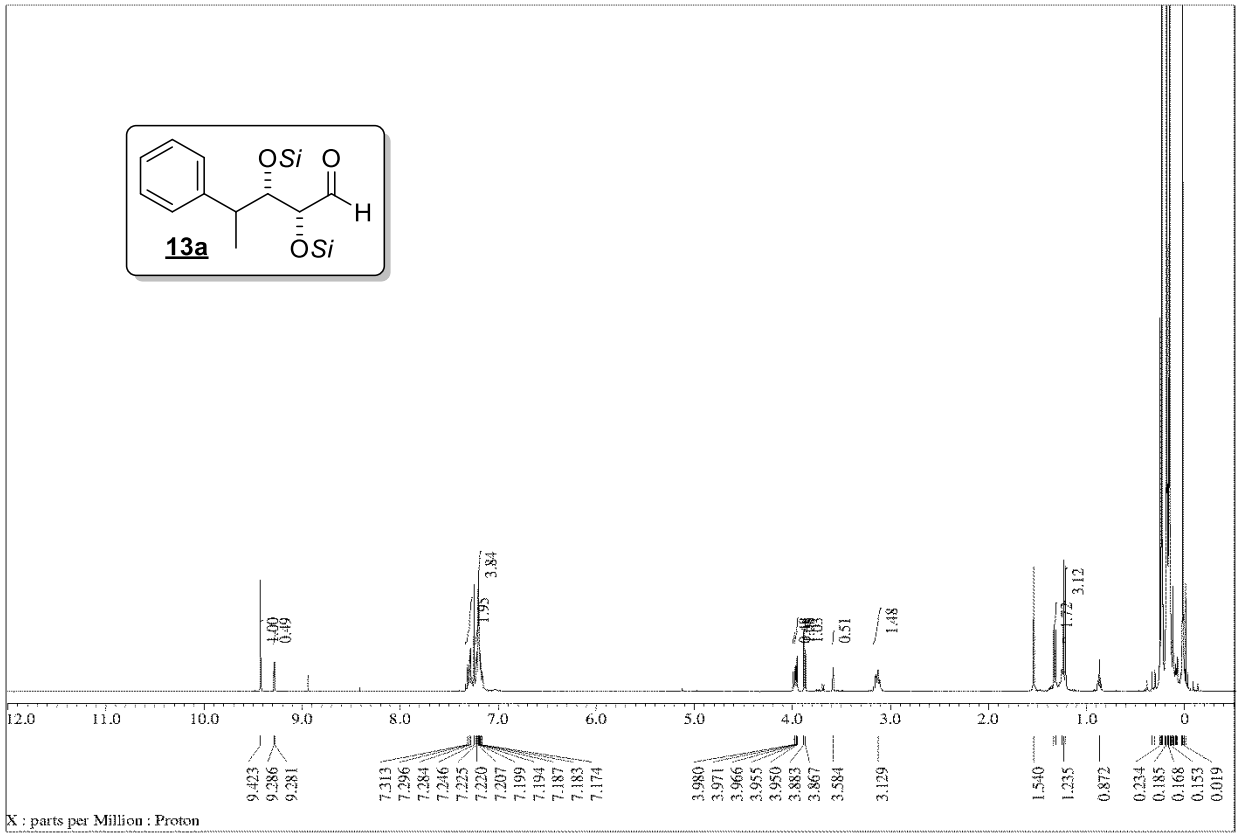

210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
203.383
202.907
82.456
82.361
80.416
80.273
79.968
77.403
77.079
76.764
39.780
37.777
26.889
25.830
14.665
12.425
6.857
5.064
0.688
0.640
0.316
0.173
X : parts per Million : Carbon13

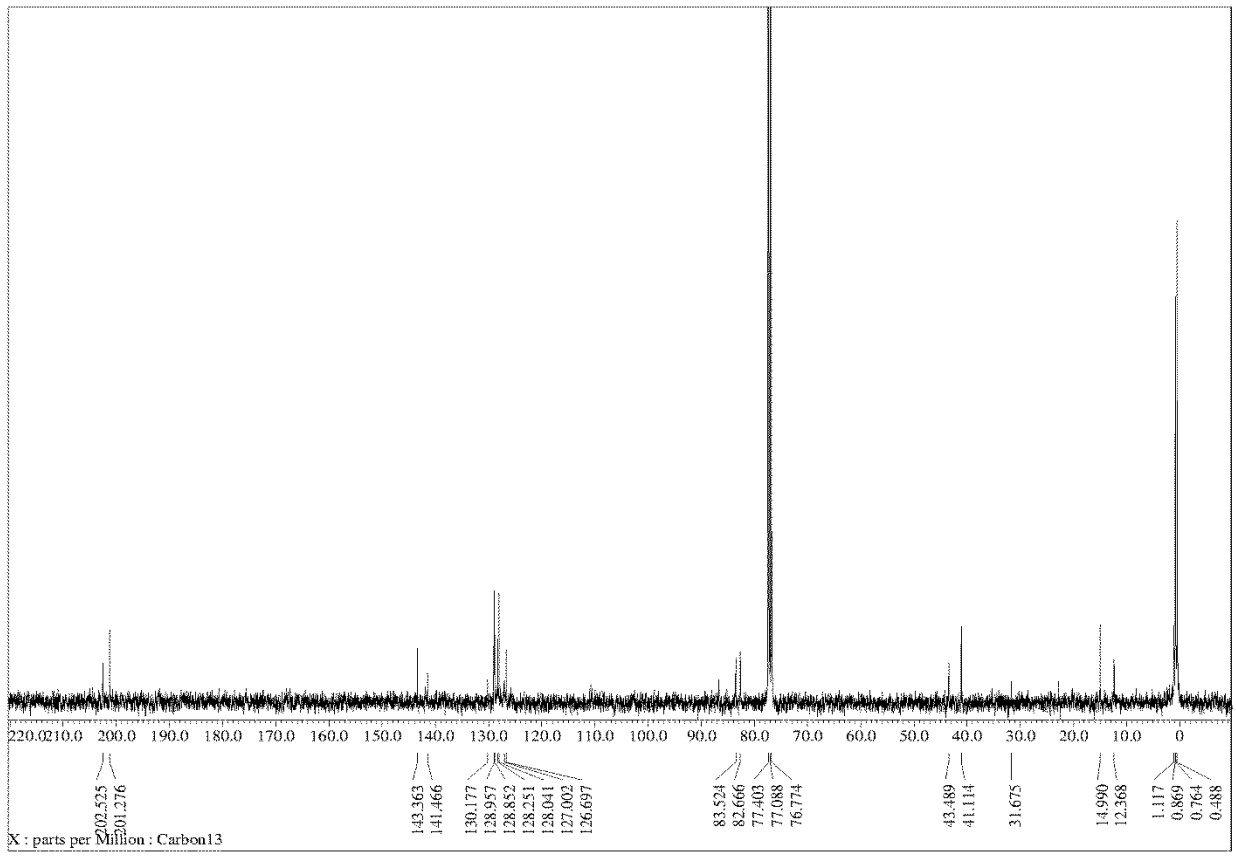

OSi
O
H
OSi
12a
58.22
1.00
1.00
1.06
4.48
3.24
5.57
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.455
9.450
7.246
3.727
3.722
3.716
3.498
3.490
3.483
1.774
1.768
1.572
1.546
1.161
1.150
1.141
1.051
0.321
0.195
0.181
0.173
0.171
-0.014
X : parts per Million : Proton

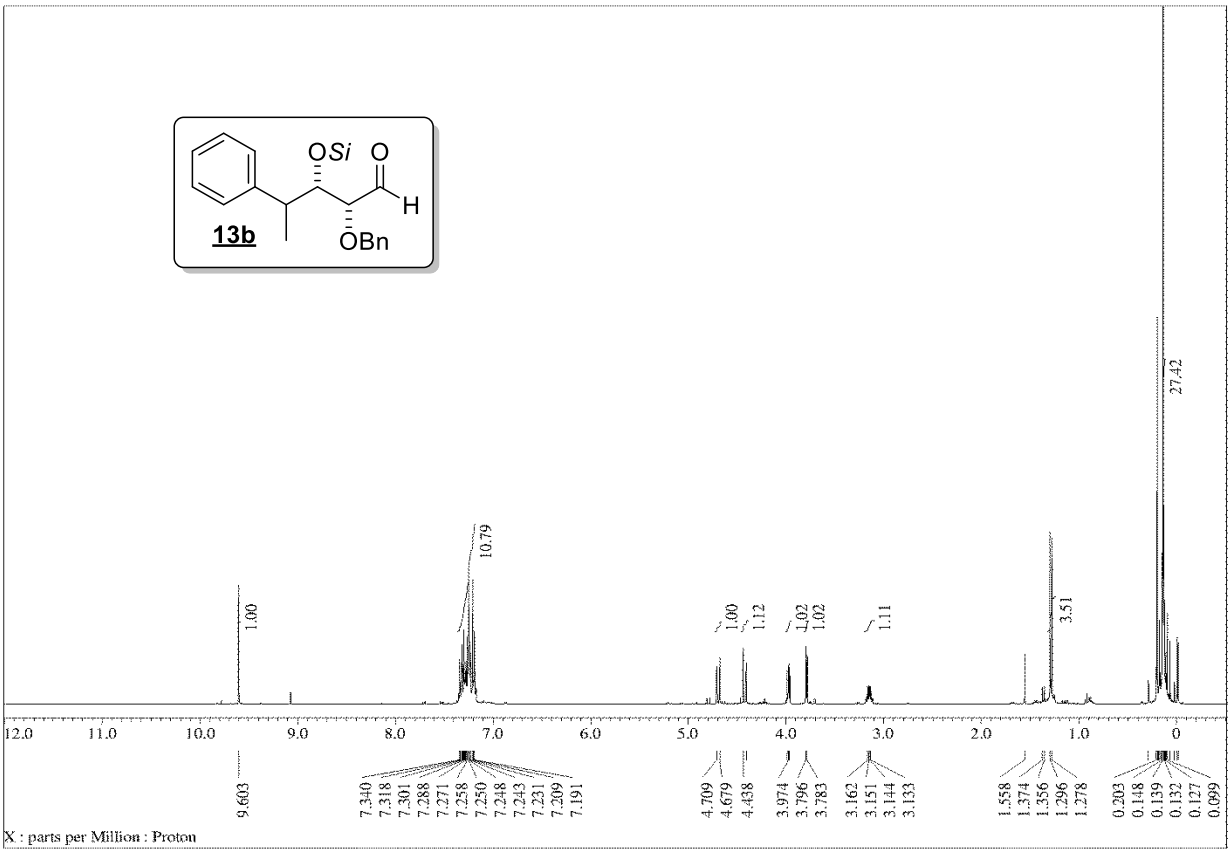

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
201.677
86.060
83.038
77.403
77.079
76.764
43.527
29.873
27.108
26.774
26.555
26.317
0.888
0.821
0.669
0.602
0.449
0.383
X : parts per Million : Carbon13

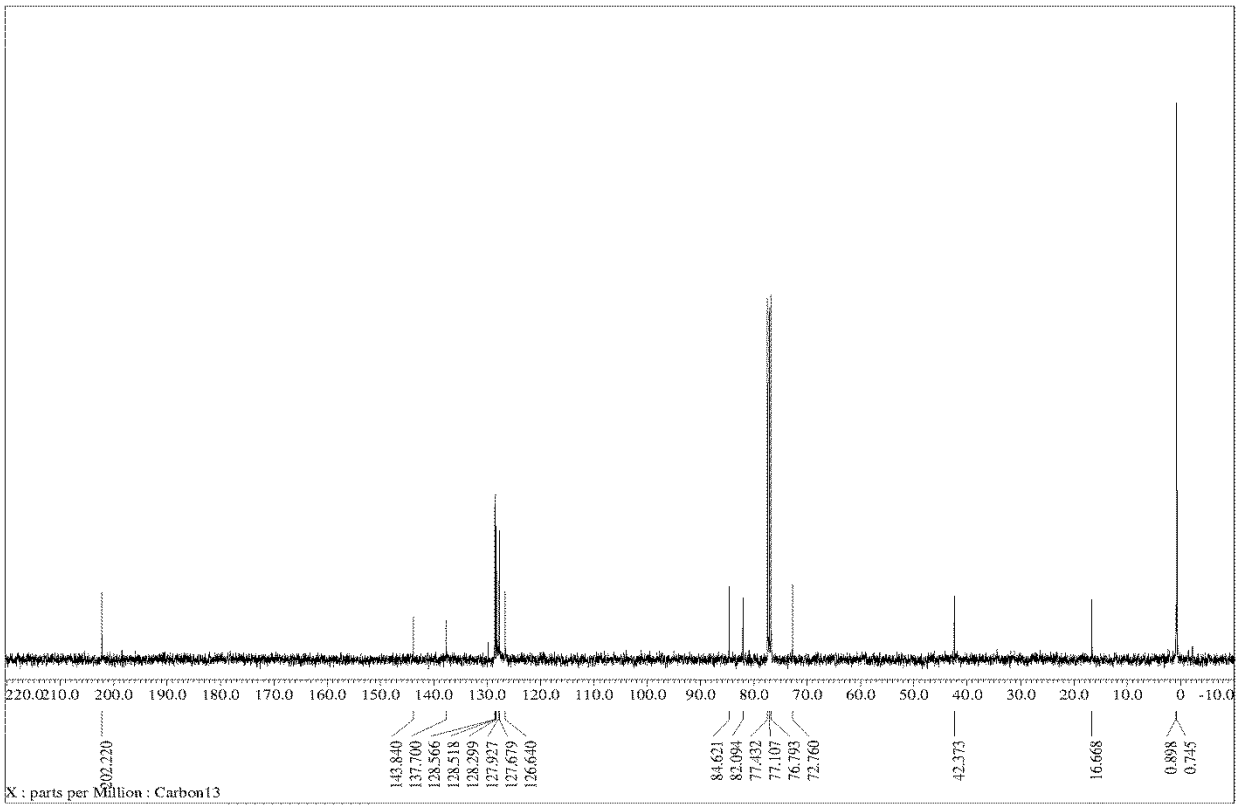

OSi
O
H
OBn
12b
1.00
5.39
1.07
1.03
1.05
1.09
7.29
8.08
27.12
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.833
9.831
7.336
7.331
7.329
7.319
7.305
7.295
7.288
7.284
7.273
7.245
4.788
4.758
4.502
4.472
3.837
3.836
3.601
3.591
3.588
3.578
1.716
1.696
1.677
1.598
1.588
1.561
1.254
1.147
1.126
0.872
0.200
0.186
0.169
0.161
0.153
X : parts per Million : Proton

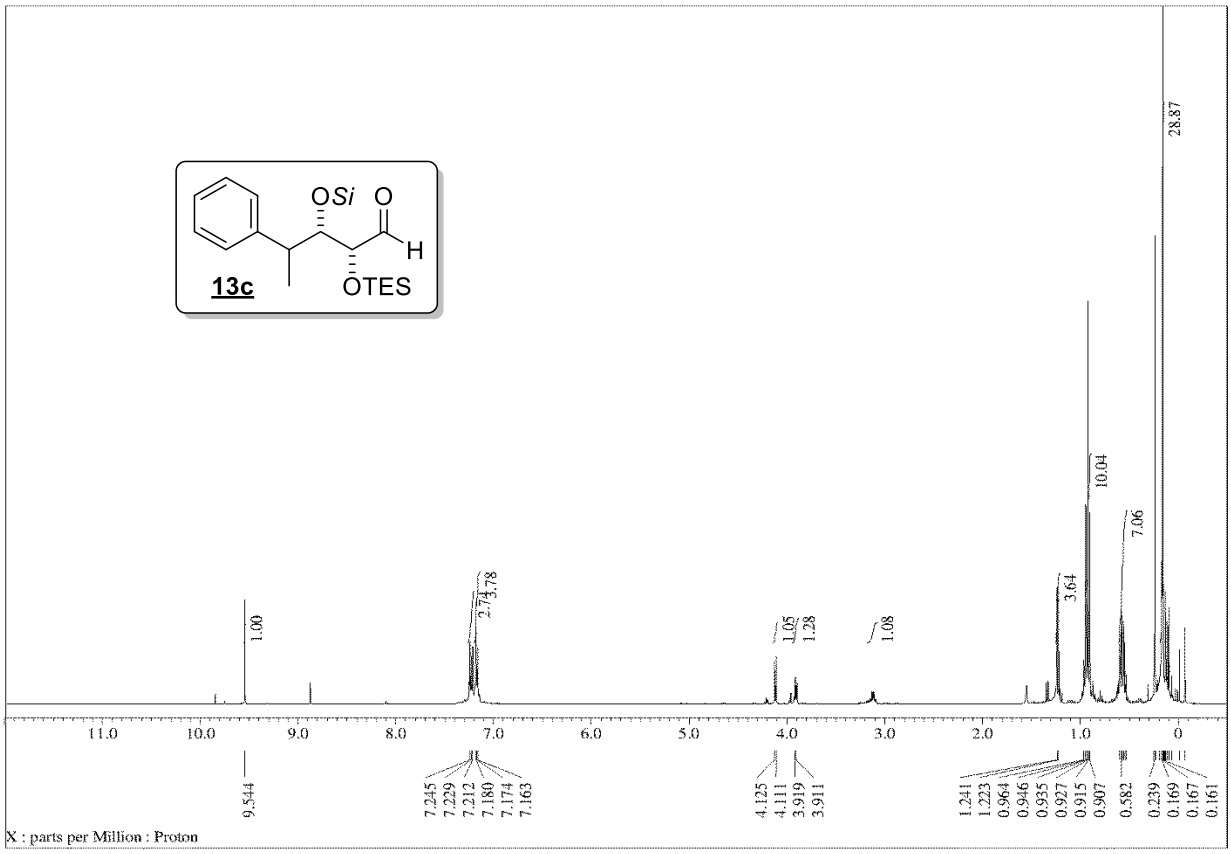

210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
203.164
137.623
128.556
127.984
84.926
81.617
77.413
77.098
76.783
72.674
41.915
29.730
28.491
26.565
26.431
0.716
X : parts per Million : Carbon13

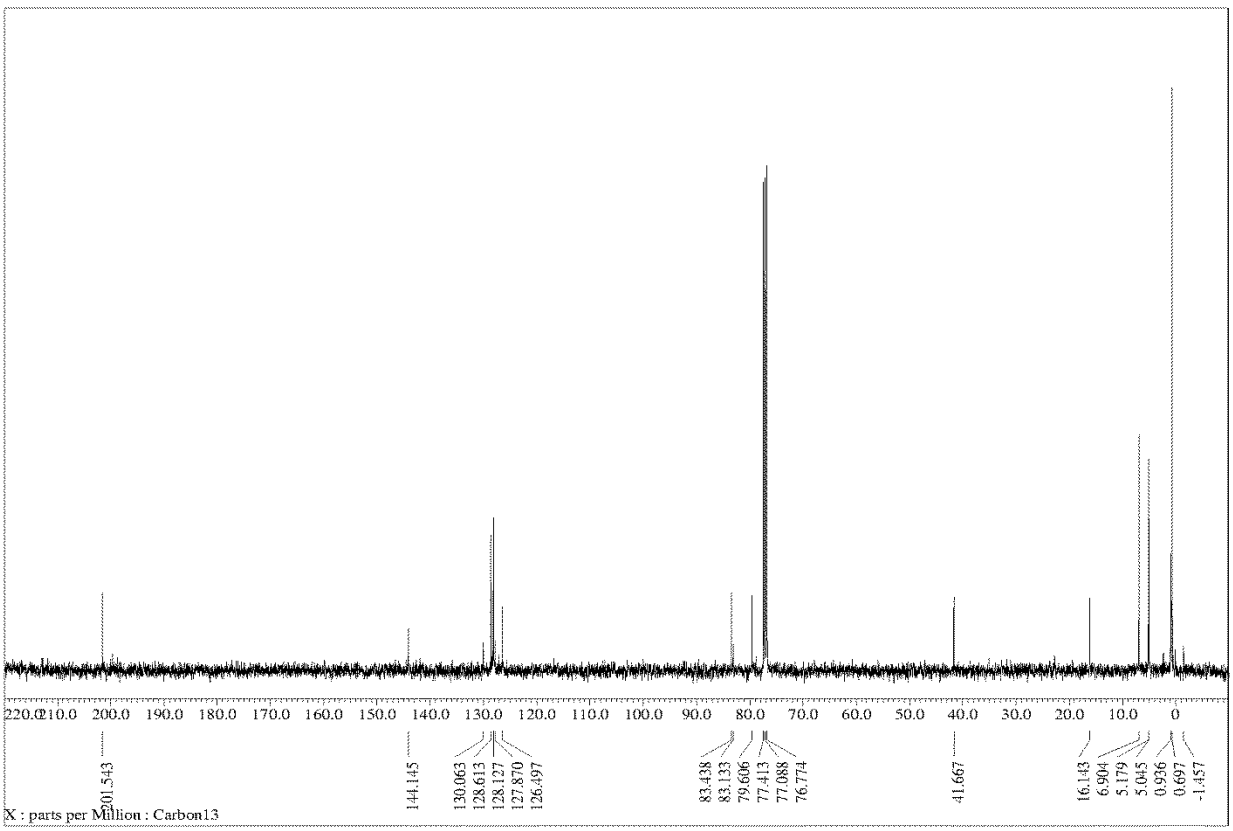

OSi
O
H
OSi
13a
X : parts per Million : Proton

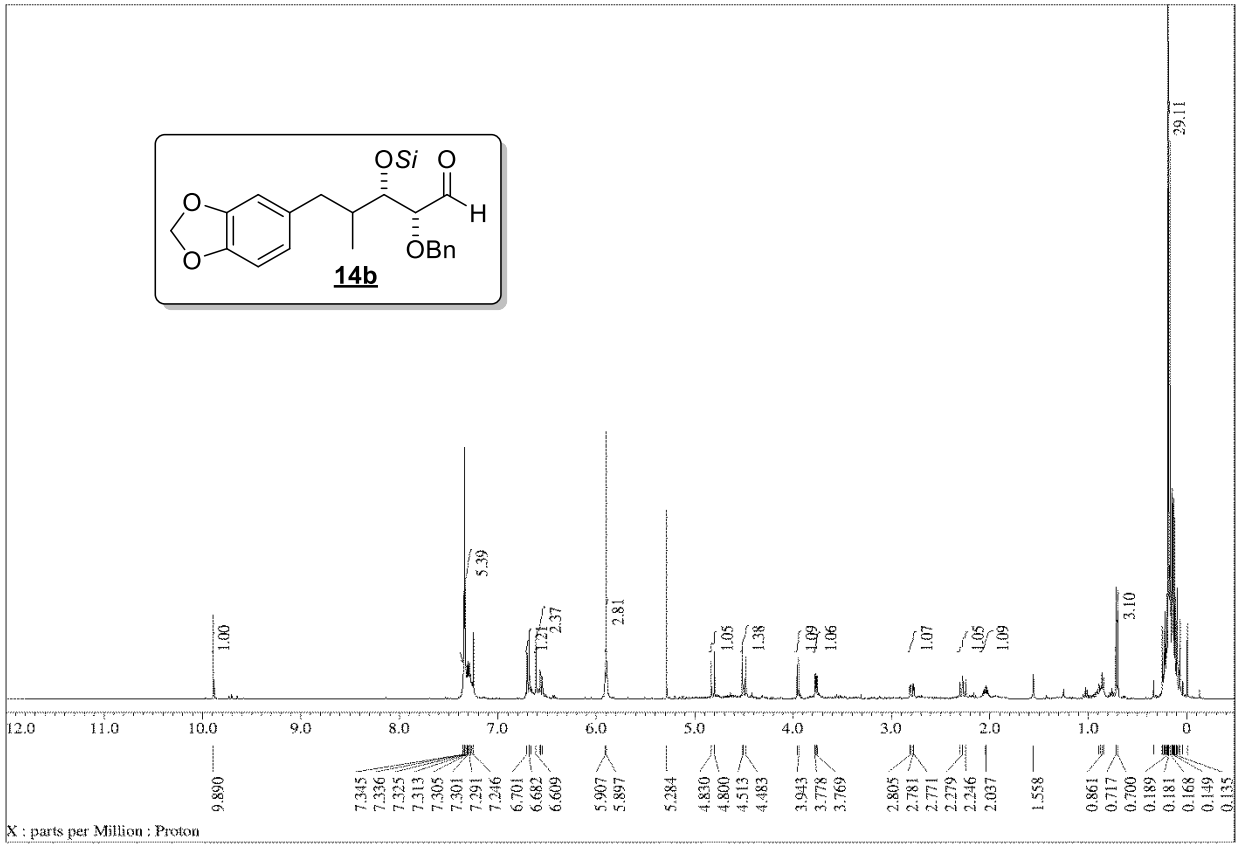

X : parts per Million : Carbon13

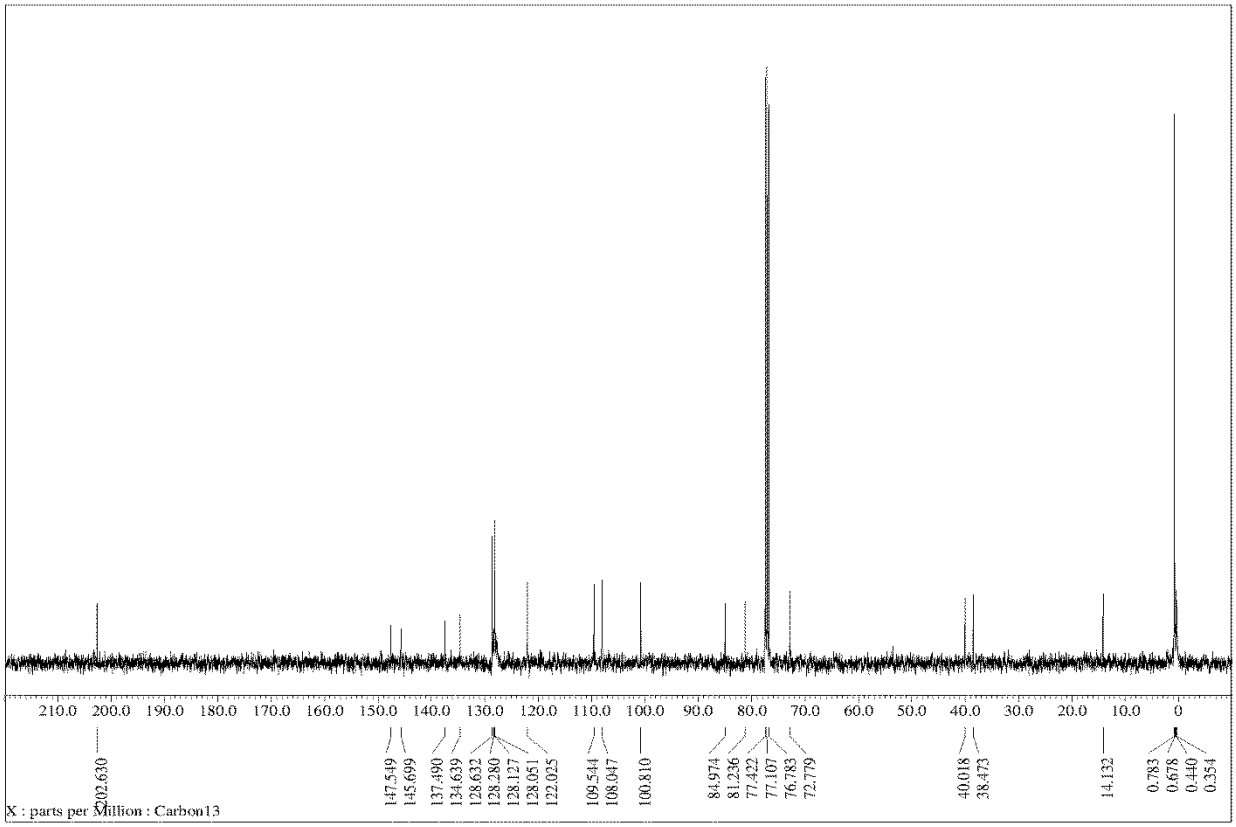

OSi
O
H
OBn
13b
1.00
10.79
1.00
1.12
1.02
1.02
1.11
3.51
27.42
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.603
7.340
7.318
7.301
7.288
7.271
7.258
7.250
7.248
7.243
7.231
7.209
7.191
4.709
4.679
4.438
3.974
3.796
3.783
3.162
3.151
3.144
3.133
1.558
1.374
1.356
1.296
1.278
0.203
0.148
0.139
0.132
0.127
0.099
X : parts per Million : Proton

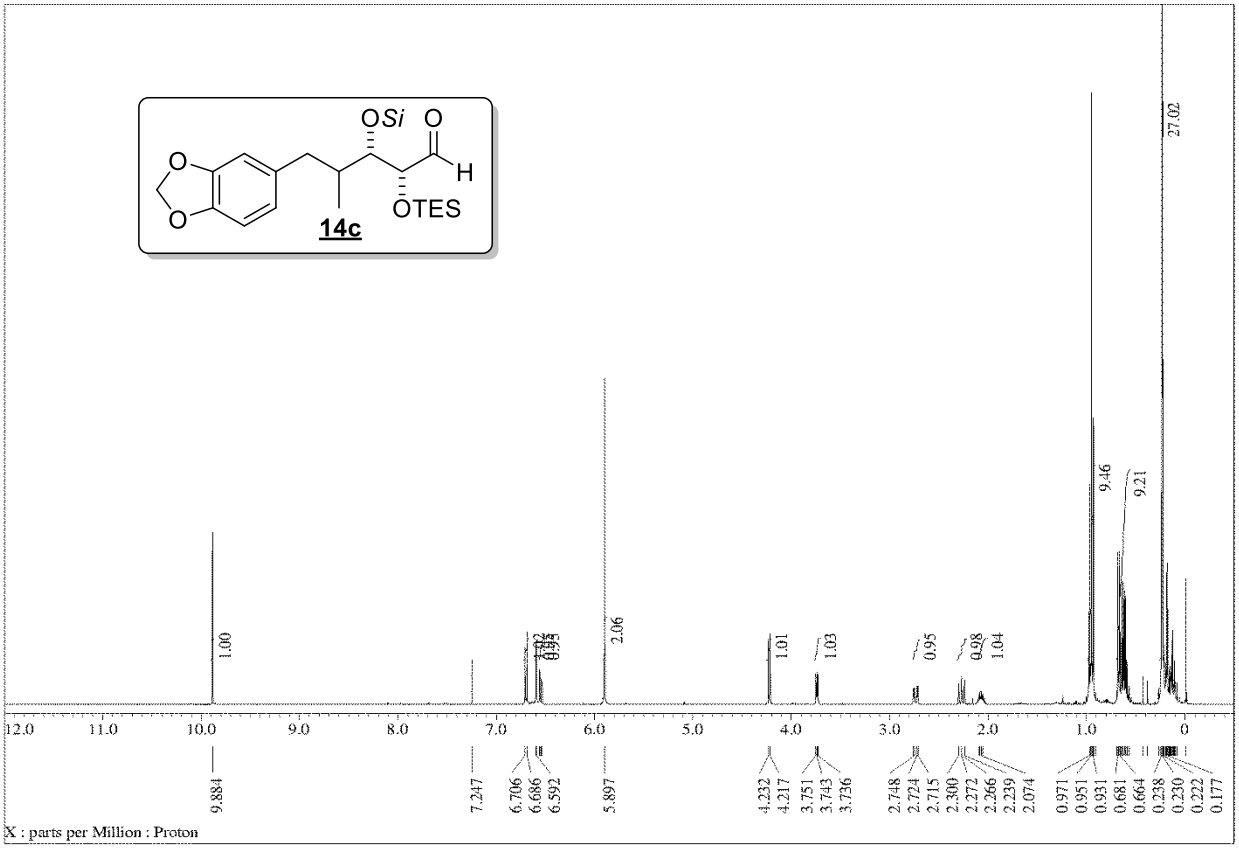

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
202.220
143.840
137.700
128.566
128.518
128.299
127.927
127.679
126.640
84.621
82.094
77.432
77.107
76.793
72.760
42.373
16.668
0.898
0.745
X : parts per Million : Carbon13

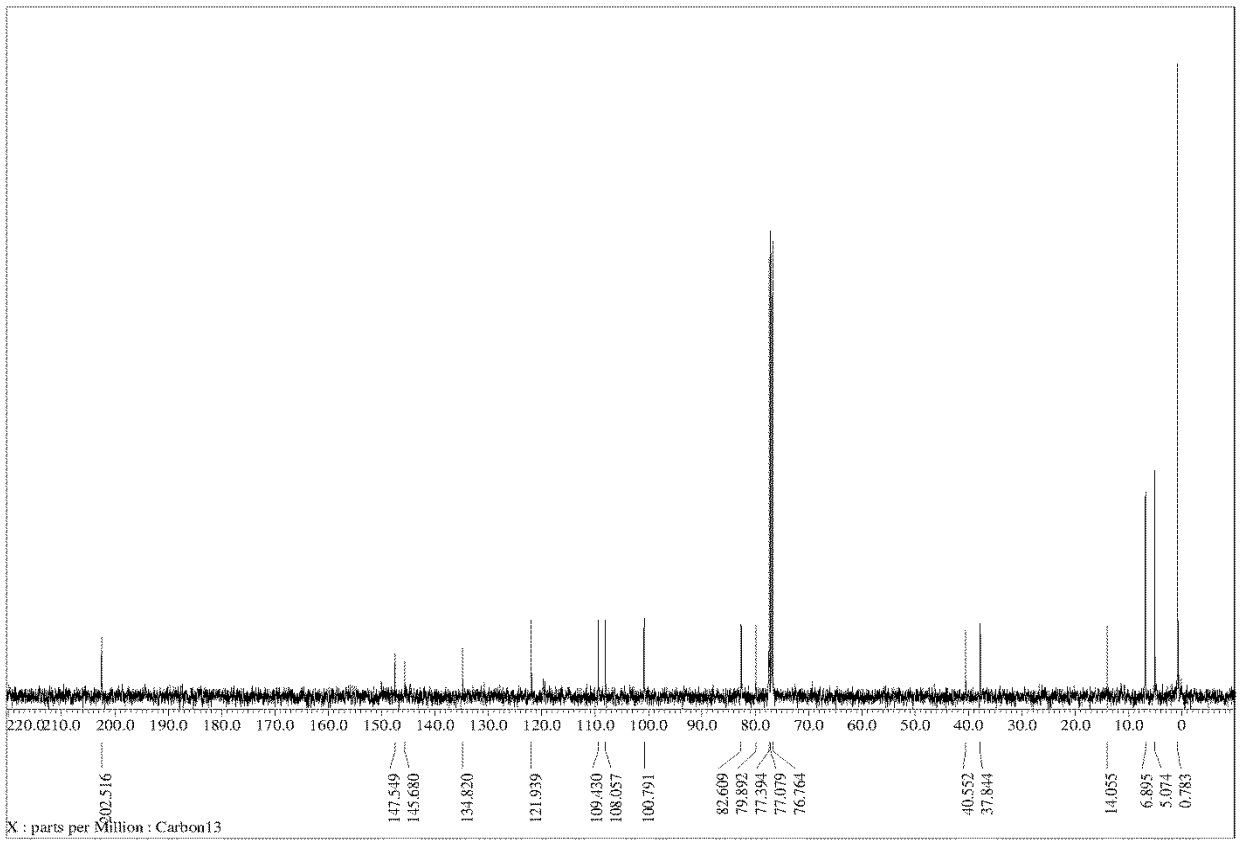

OSi
O
H
OTES
13c
X : parts per Million : Proton

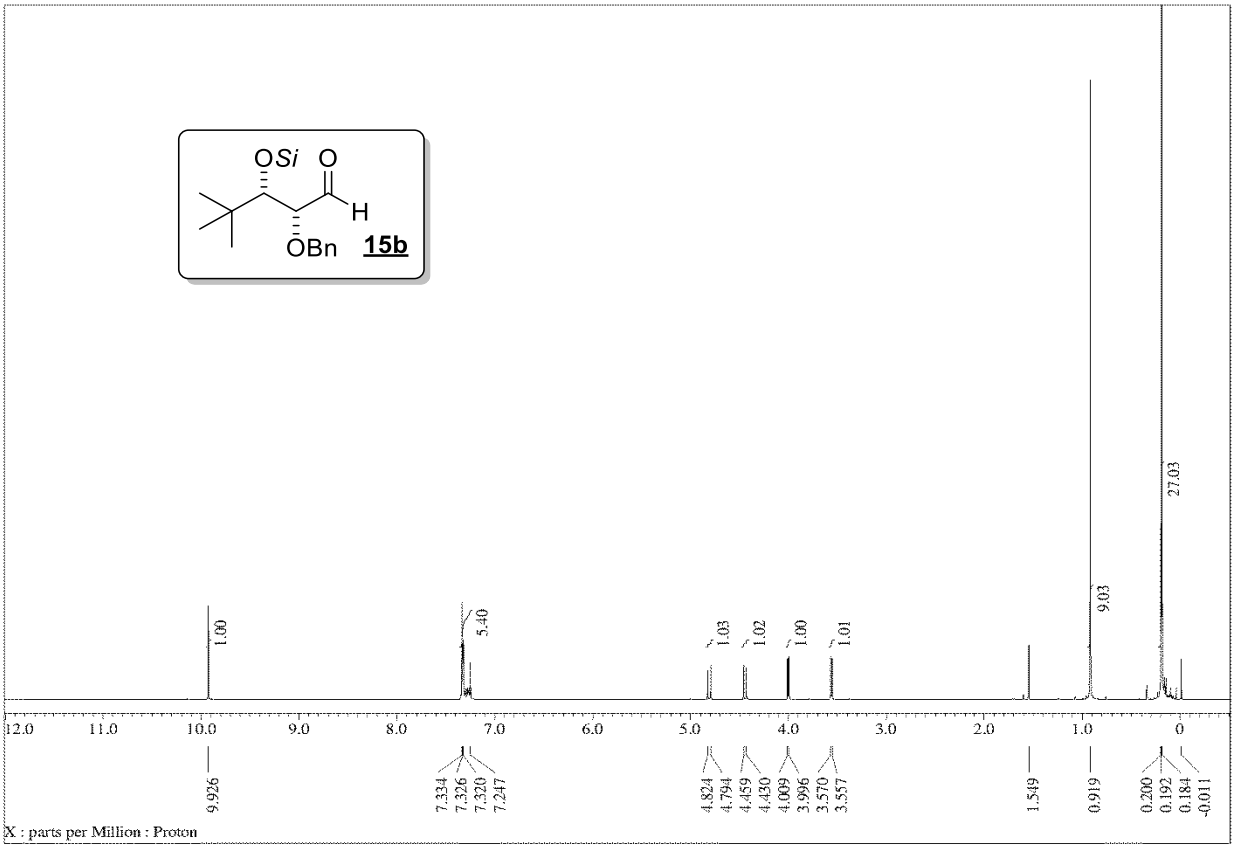

X : parts per Million : Carbon13

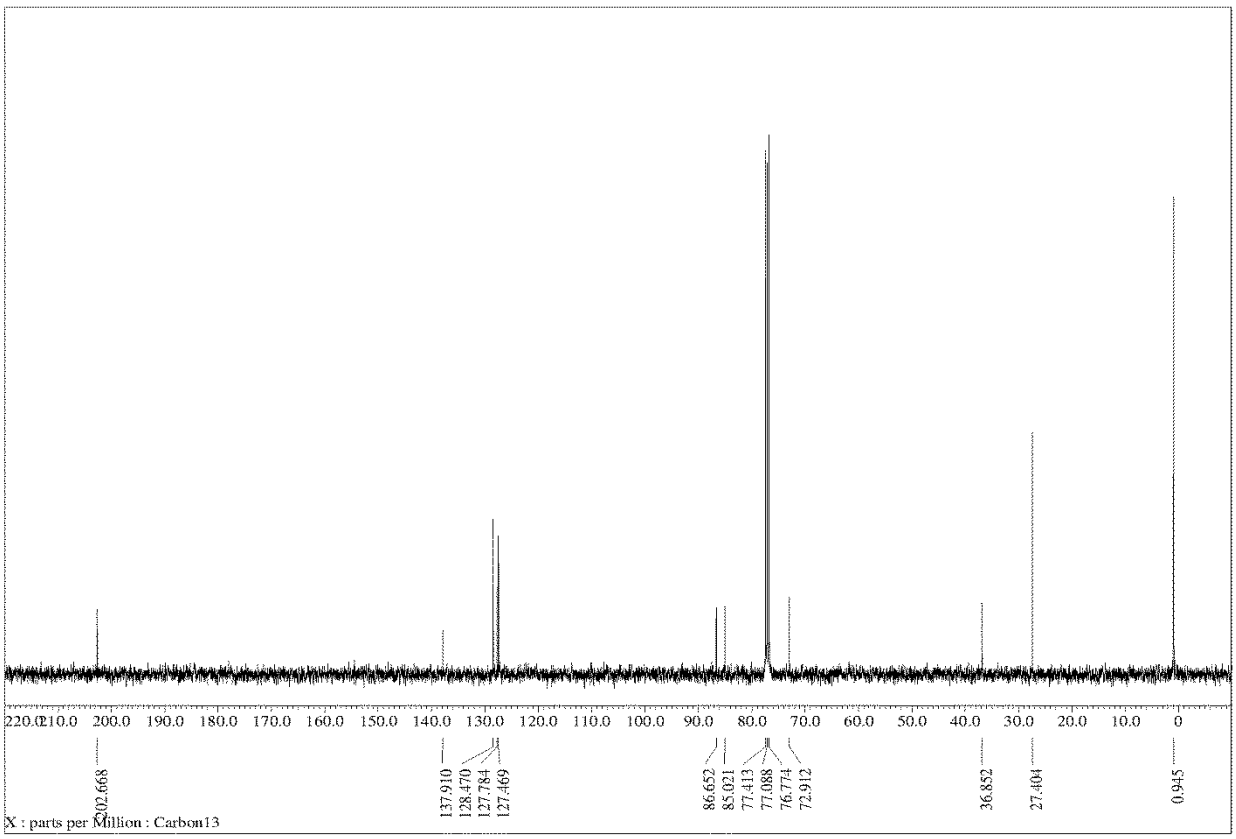

OSi
O
H
OBn
O
O
14b
29.11
5.39
3.10
2.81
2.37
1.21
1.00
1.05
1.38
1.09
1.06
1.07
1.05
1.09
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
9.890
7.345 7.336 7.325 7.313 7.305 7.301 7.291 7.246
6.701 6.682 6.609
5.907 5.897
5.284
4.830 4.800 4.513 4.483
3.943 3.778 3.769
2.805 2.781 2.771 2.279 2.246 2.037
1.558
0.861 0.717 0.700 0.189 0.181 0.168 0.149 0.135
X : parts per Million : Proton

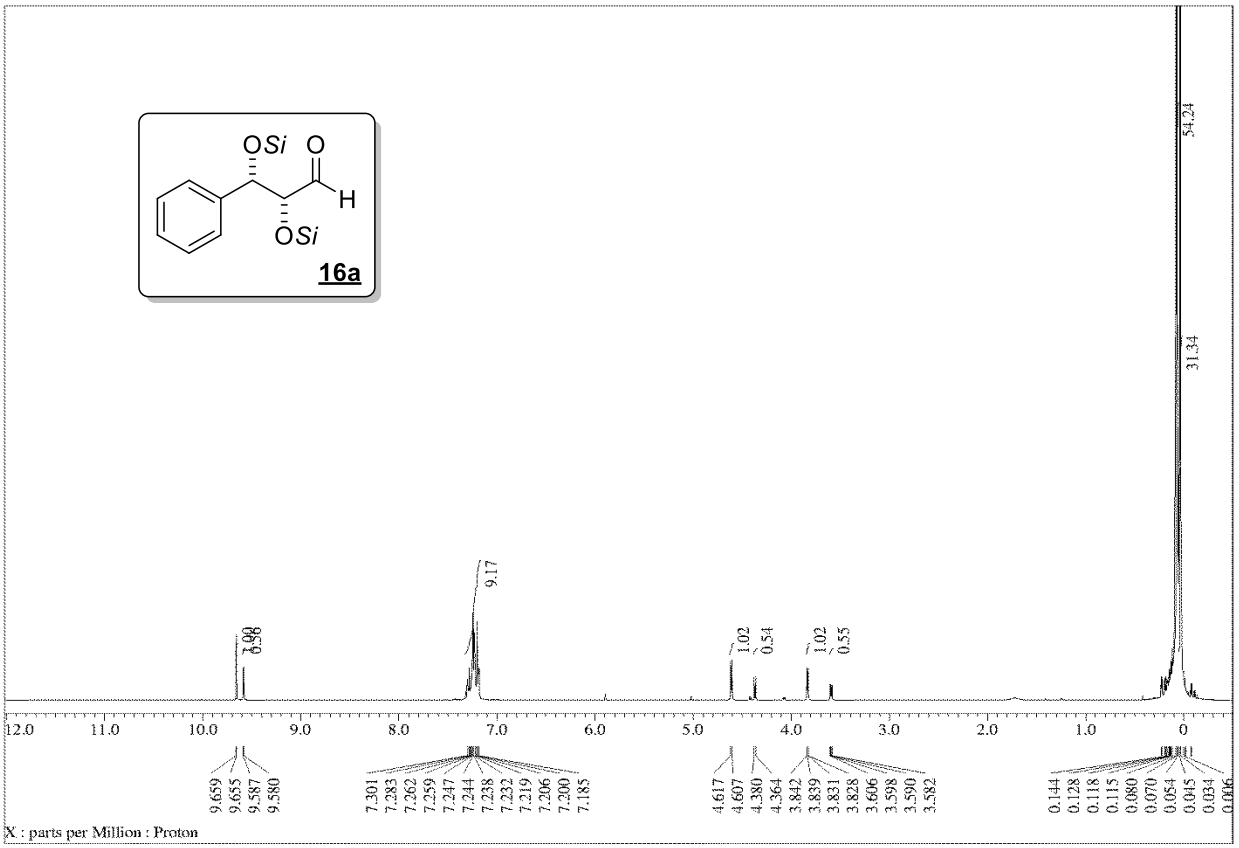

210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
202.630
147.549 145.699 137.490 134.639 128.632 128.280 128.127 128.051 122.025
109.544 108.047
100.810
84.974 81.236 77.422 77.107 76.783 72.779
40.018 38.473
14.132
0.783 0.678 0.440 0.354
X : parts per Million : Carbon13

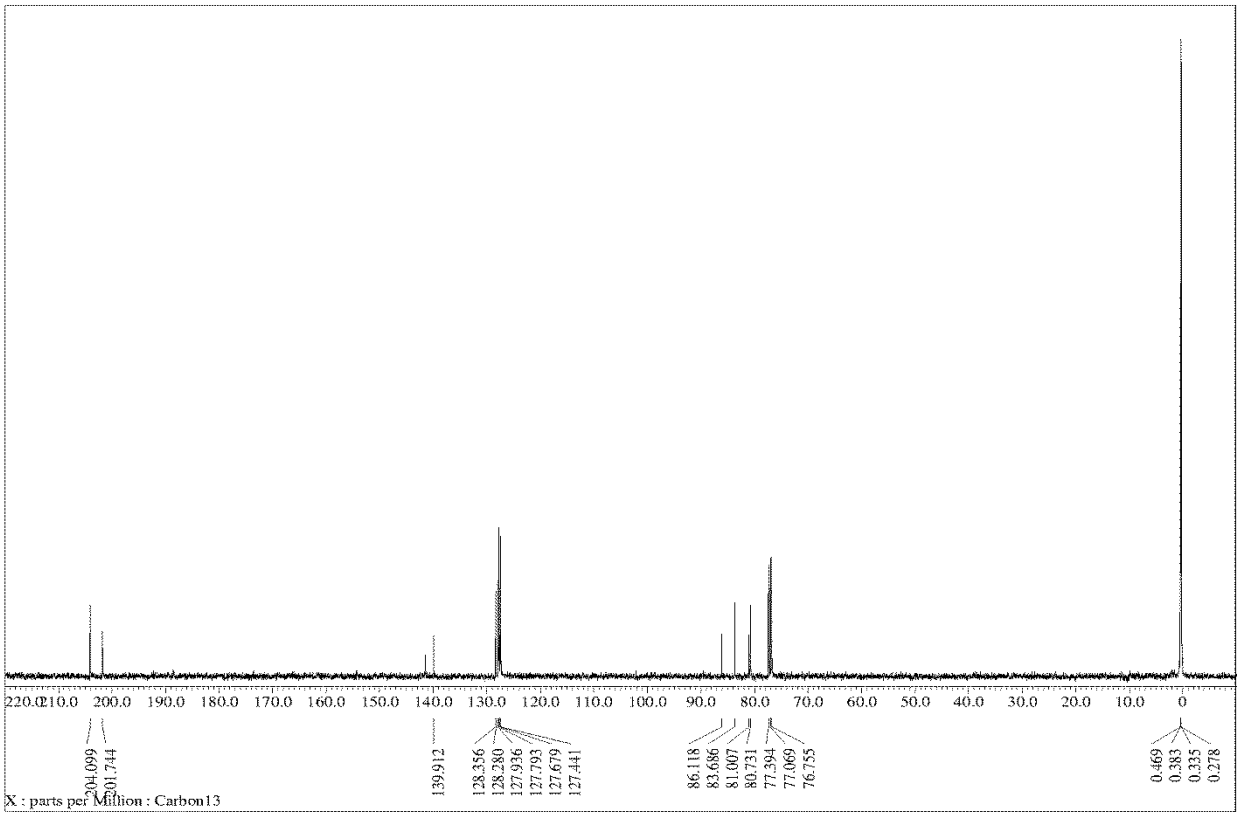

OSi
O
H
OTES
O
O
14c
27.02
9.46
9.21
2.06
1.00
1.01
1.03
0.95
1.04
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.884
7.247
6.706
6.686
6.592
5.897
4.232
4.217
3.751
3.743
3.736
2.748
2.724
2.715
2.300
2.272
2.266
2.239
2.074
0.971
0.951
0.931
0.681
0.664
0.238
0.230
0.222
0.177
X : parts per Million : Proton

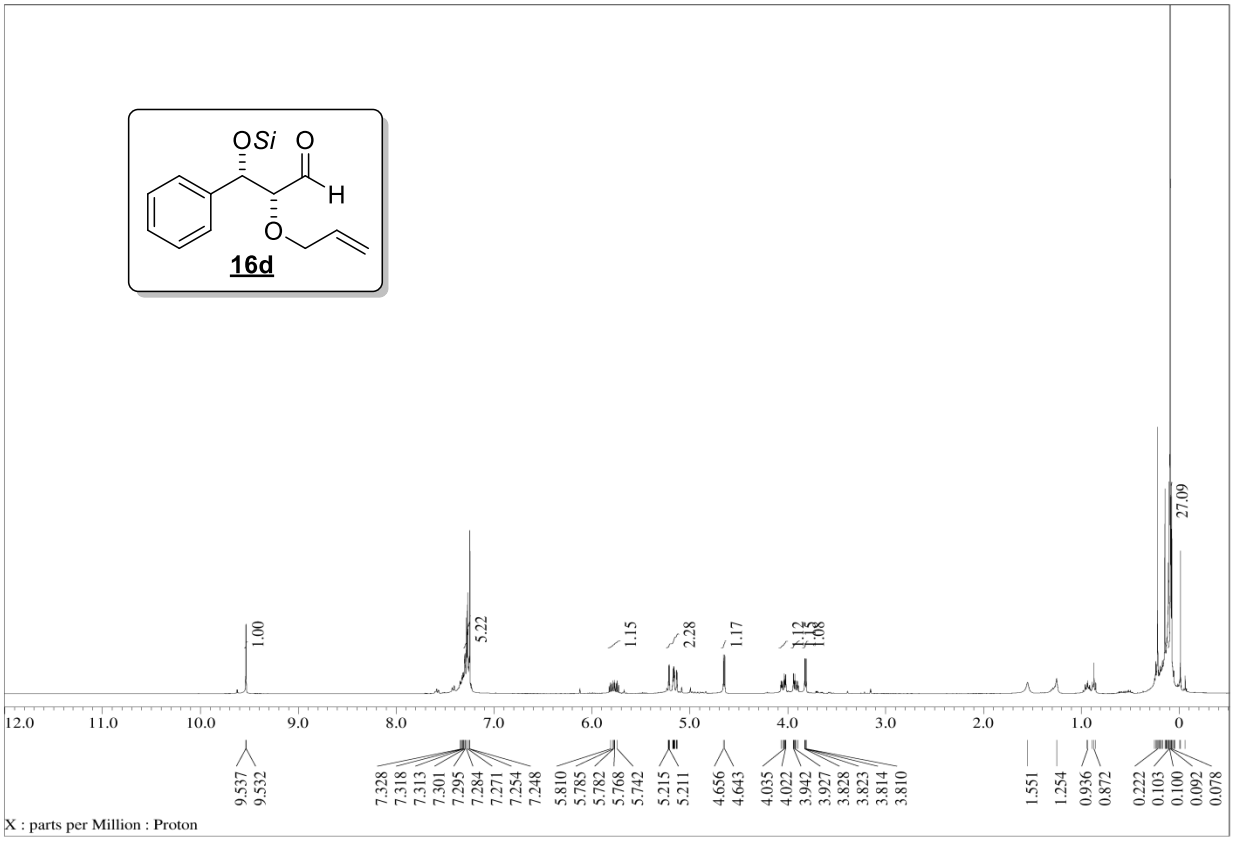

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
202.516
147.549
145.680
134.820
121.939
109.430
108.057
100.791
82.609
79.892
77.394
77.079
76.764
40.552
37.844
14.055
6.895
5.074
0.783
X : parts per Million : Carbon13

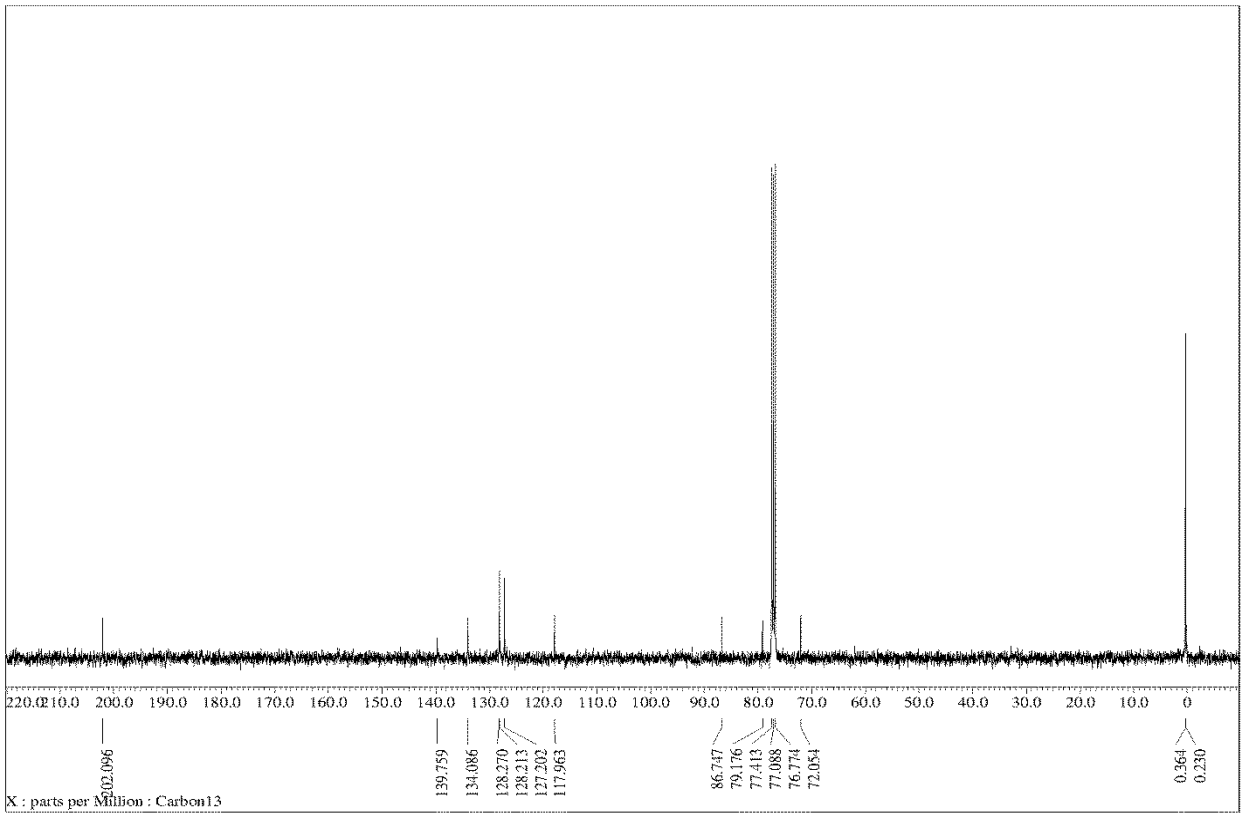

OSi
O
H
OBn
15b
1.00
5.40
1.03
1.02
1.00
1.01
9.03
27.03
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.926
7.334
7.326
7.320
7.247
4.824
4.794
4.459
4.430
4.009
3.996
3.570
3.557
1.549
0.919
0.200
0.192
0.184
-0.011
X : parts per Million : Proton

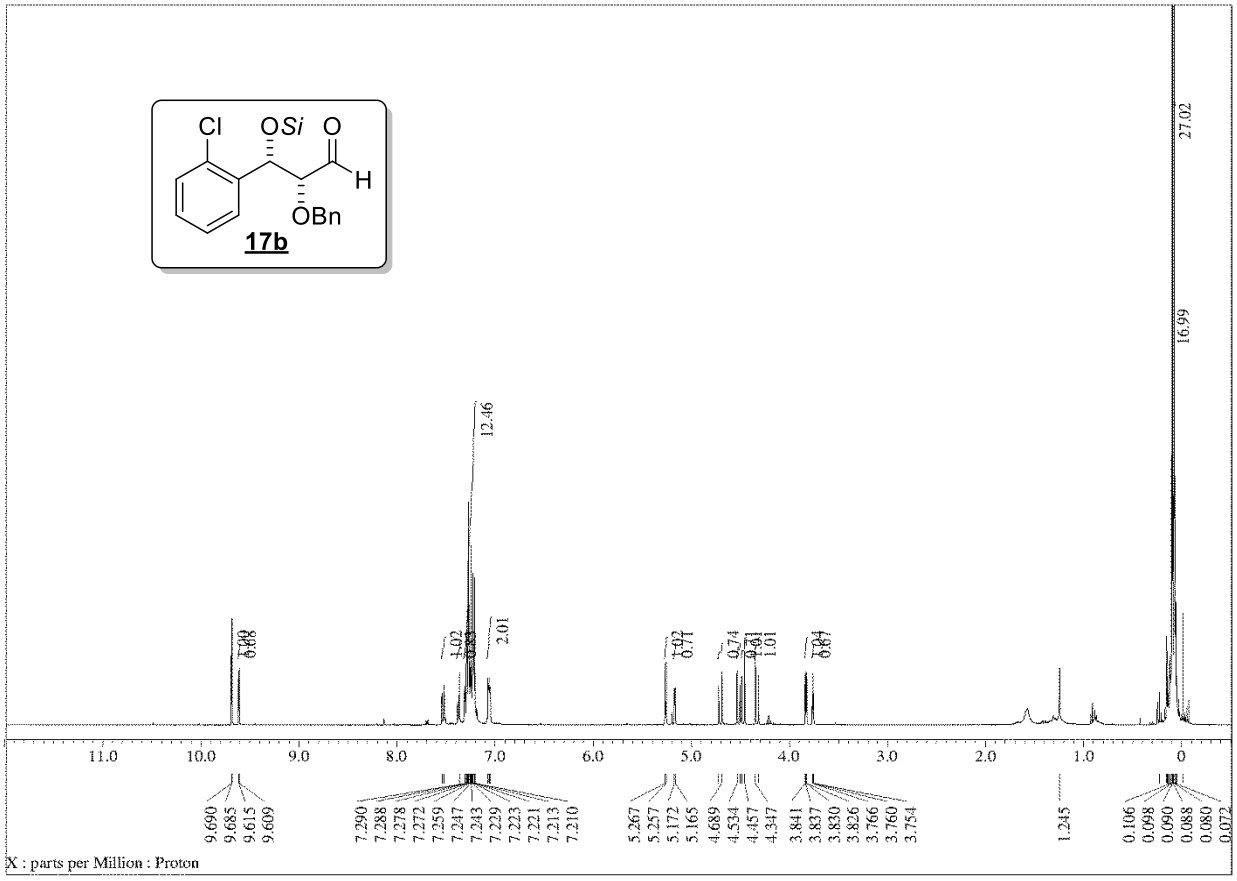

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
202.668
137.910
128.470
127.784
127.469
86.652
85.021
77.413
77.088
76.774
72.912
36.852
27.404
0.945
X : parts per Million : Carbon13

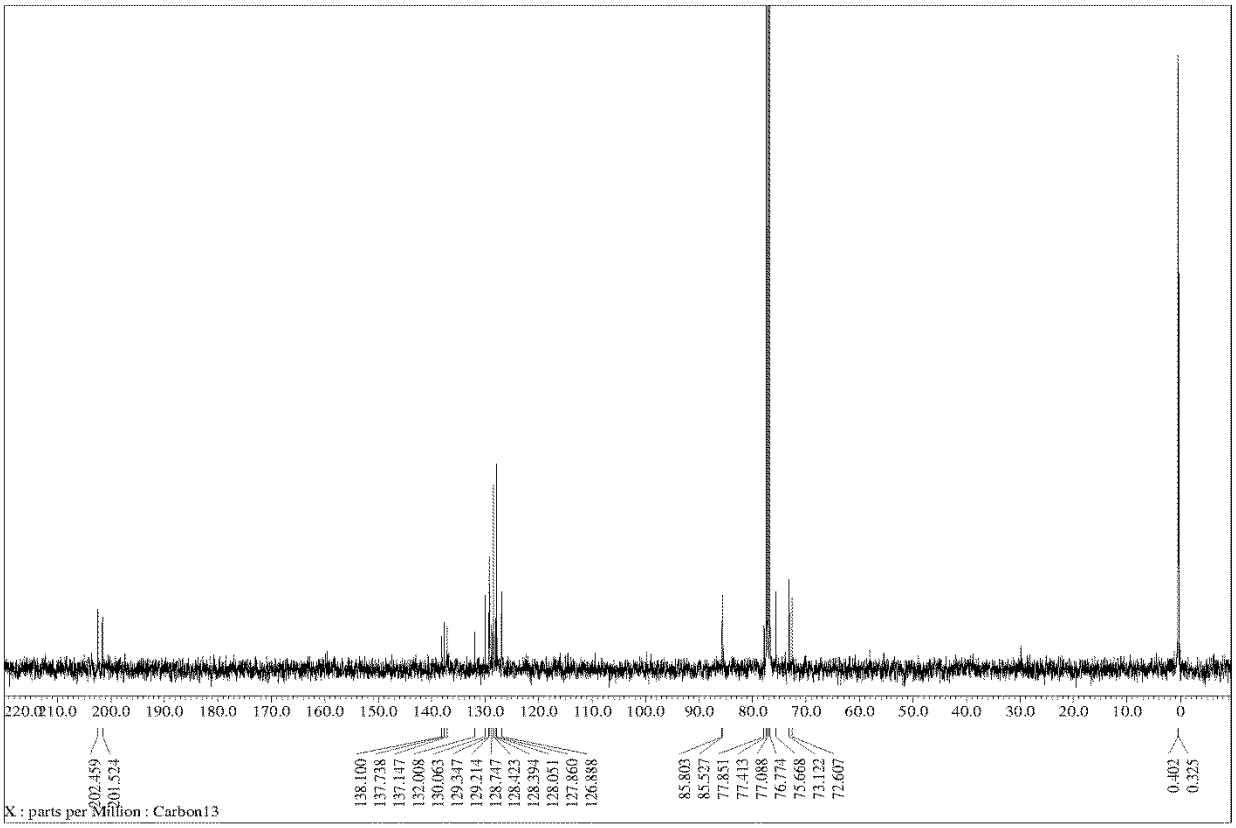

OSi
O
H
OSi
16a
54.24
31.34
9.17
1.02
0.54
1.02
0.55
X : parts per Million : Proton

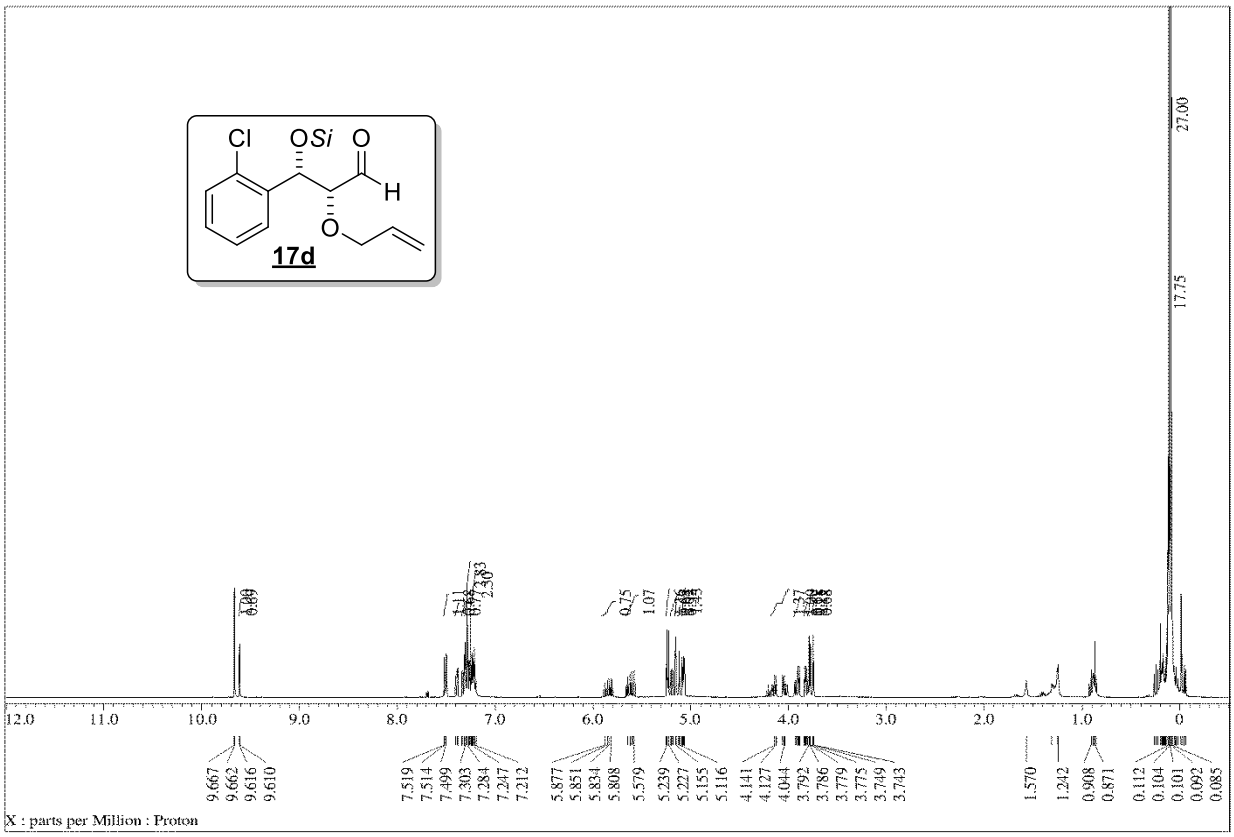

X : parts per Million : Carbon13

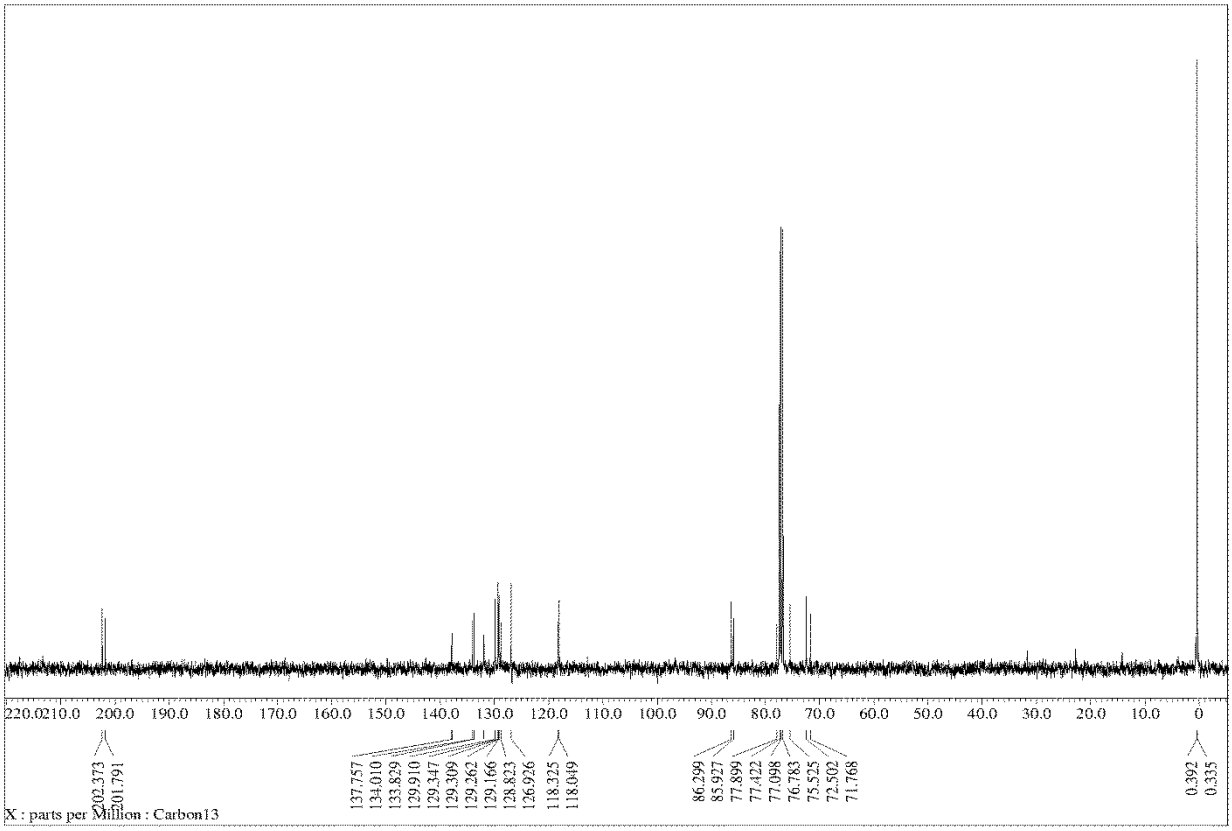

OSi
O
H
O
16d
1.00
5.22
1.15
2.28
1.17
1.12
1.15
1.08
27.09
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.537
9.532
7.328
7.318
7.313
7.301
7.295
7.284
7.271
7.254
7.248
5.810
5.785
5.782
5.768
5.742
5.215
5.211
4.656
4.643
4.035
4.022
3.942
3.927
3.828
3.823
3.814
3.810
1.551
1.254
0.936
0.872
0.222
0.103
0.100
0.092
0.078
X : parts per Million : Proton

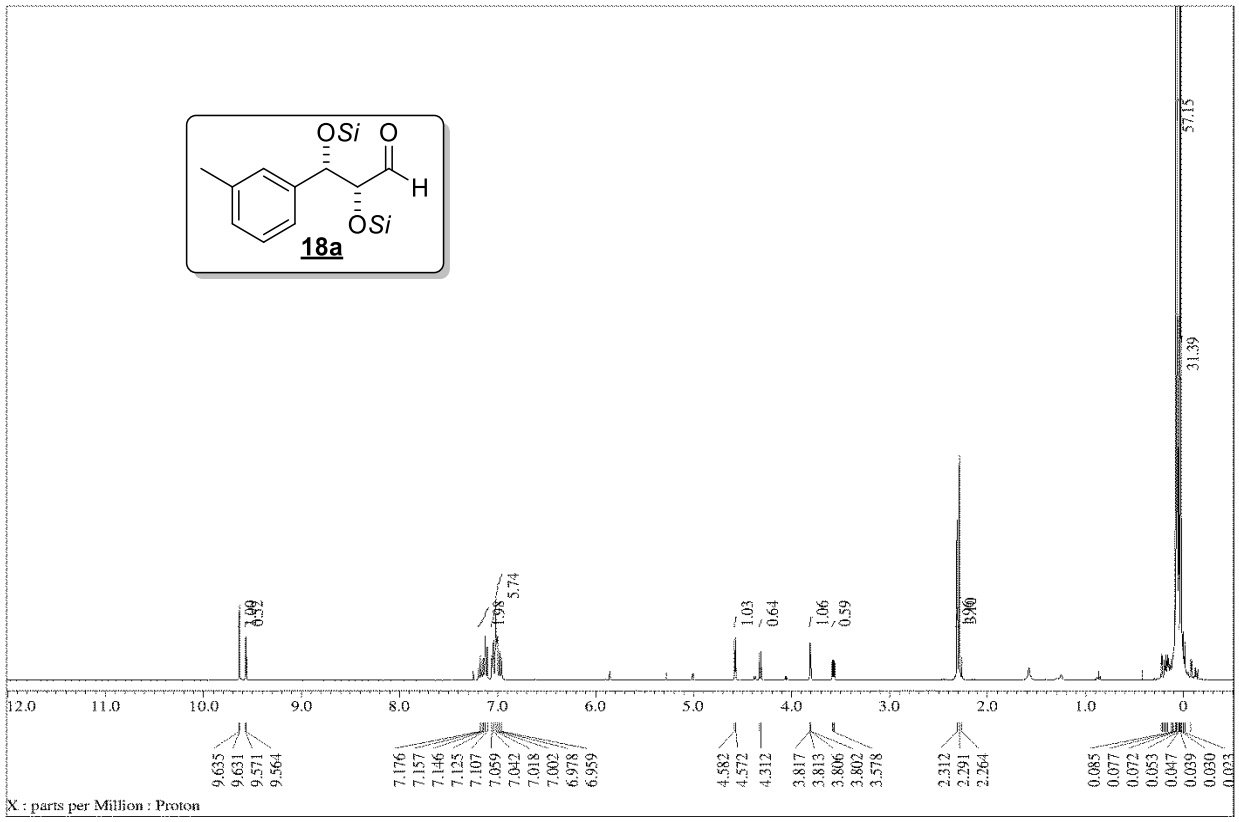

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
202.096
139.759
134.086
128.270
128.213
127.202
117.963
86.747
79.176
77.413
77.088
76.774
72.054
0.364
0.230
X : parts per Million : Carbon13

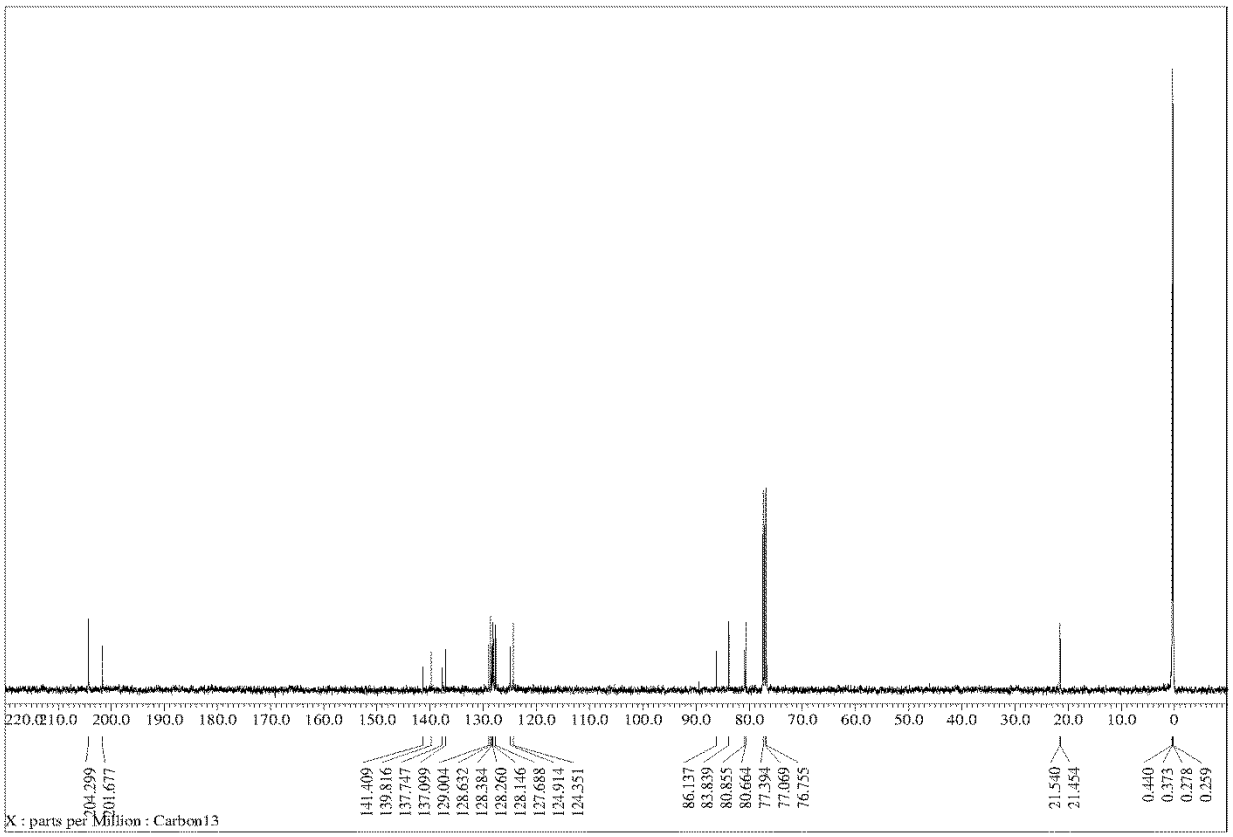

Cl
OSi
O
H
OBn
17b
27.02
16.99
12.46
2.01
1.01
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.690
9.685
9.615
9.609
7.290
7.288
7.278
7.272
7.259
7.247
7.243
7.229
7.223
7.221
7.213
7.210
5.267
5.257
5.172
5.165
4.689
4.534
4.457
4.347
3.841
3.837
3.830
3.826
3.766
3.760
3.754
1.245
0.106
0.098
0.090
0.088
0.080
0.072
X : parts per Million : Proton


220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
202.459
201.524
138.160
137.738
137.147
132.008
130.063
129.347
129.214
128.747
128.423
128.394
128.051
127.860
126.888
85.803
85.527
77.851
77.413
77.088
76.774
75.668
73.122
72.607
0.402
0.325
X : parts per Million : Carbon13


Cl
OSi
O
H
O
17d
27.00
17.75
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
9.667 9.662 9.616 9.610
7.519 7.514 7.499 7.303 7.284 7.247 7.212
5.877 5.851 5.834 5.808 5.579 5.239 5.227 5.155 5.116
4.141 4.127 4.044 3.792 3.786 3.779 3.775 3.749 3.743
1.570 1.242 0.908 0.871
0.112 0.104 0.101 0.092 0.085
X : parts per Million : Proton


220.0210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
202.373
201.791
137.757
134.010
133.829
129.910
129.347
129.309
129.262
129.166
128.823
126.926
118.325
118.049
86.299
85.927
77.899
77.422
77.098
76.783
75.525
72.502
71.768
0.392
0.335
X : parts per Million : Carbon13


OSi
O
H
OSi
18a
57.15
31.39
5.74
1.98
1.03
0.64
1.06
0.59
9.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.635
9.631
9.571
9.564
7.176
7.157
7.146
7.125
7.107
7.059
7.042
7.018
7.002
6.978
6.959
4.582
4.572
4.312
3.817
3.813
3.806
3.802
3.578
2.312
2.291
2.264
0.085
0.077
0.072
0.053
0.047
0.039
0.030
0.023
X : parts per Million : Proton


220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
204.299
201.677
141.409
139.816
137.747
137.099
129.004
128.632
128.384
128.260
128.146
127.688
124.914
124.351
86.137
83.839
80.855
80.664
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77.069
76.755
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21.454
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0.373
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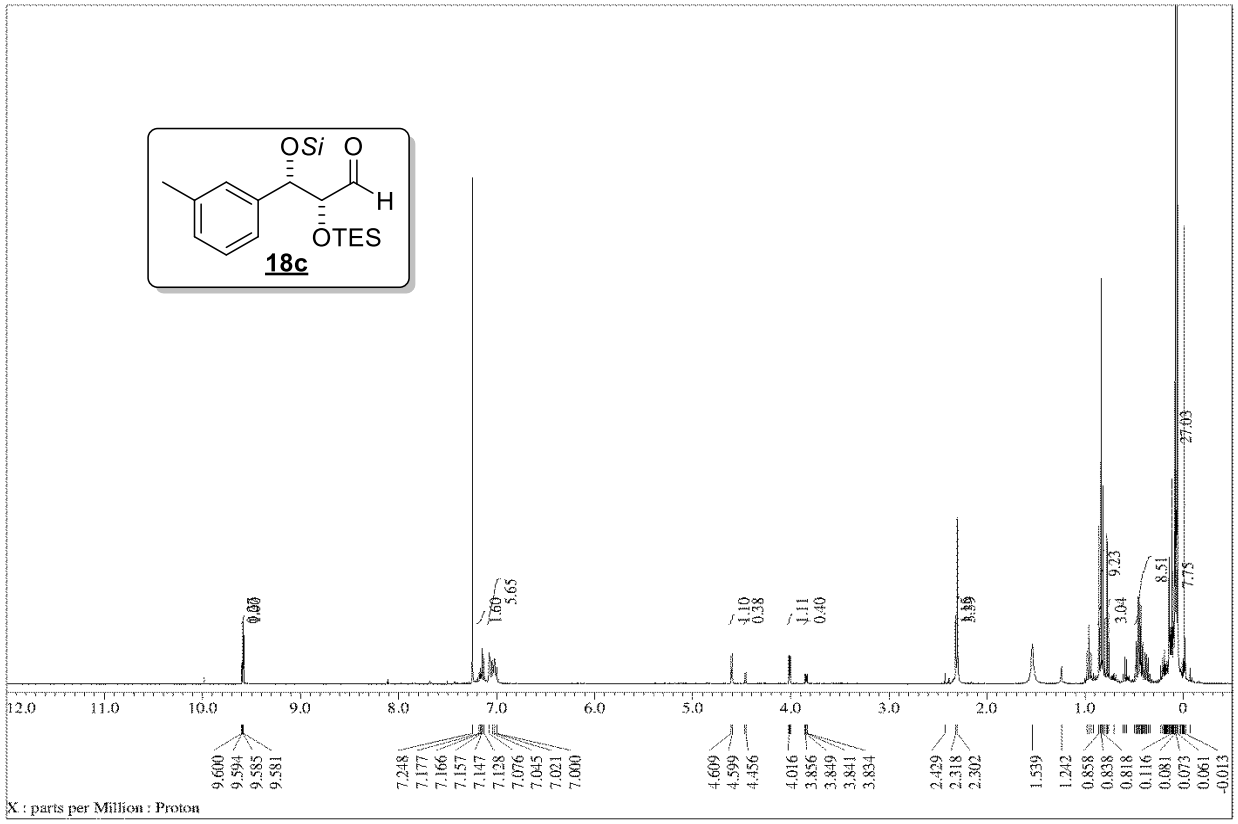
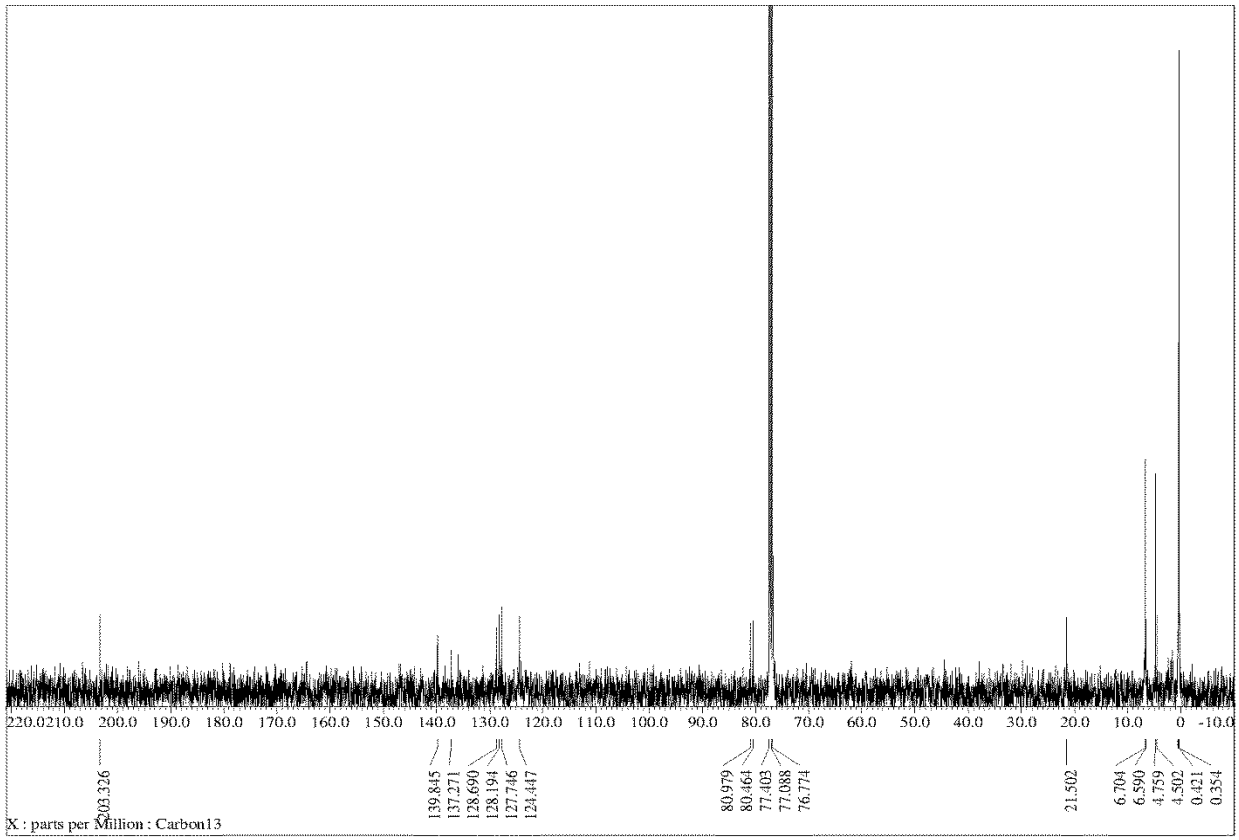
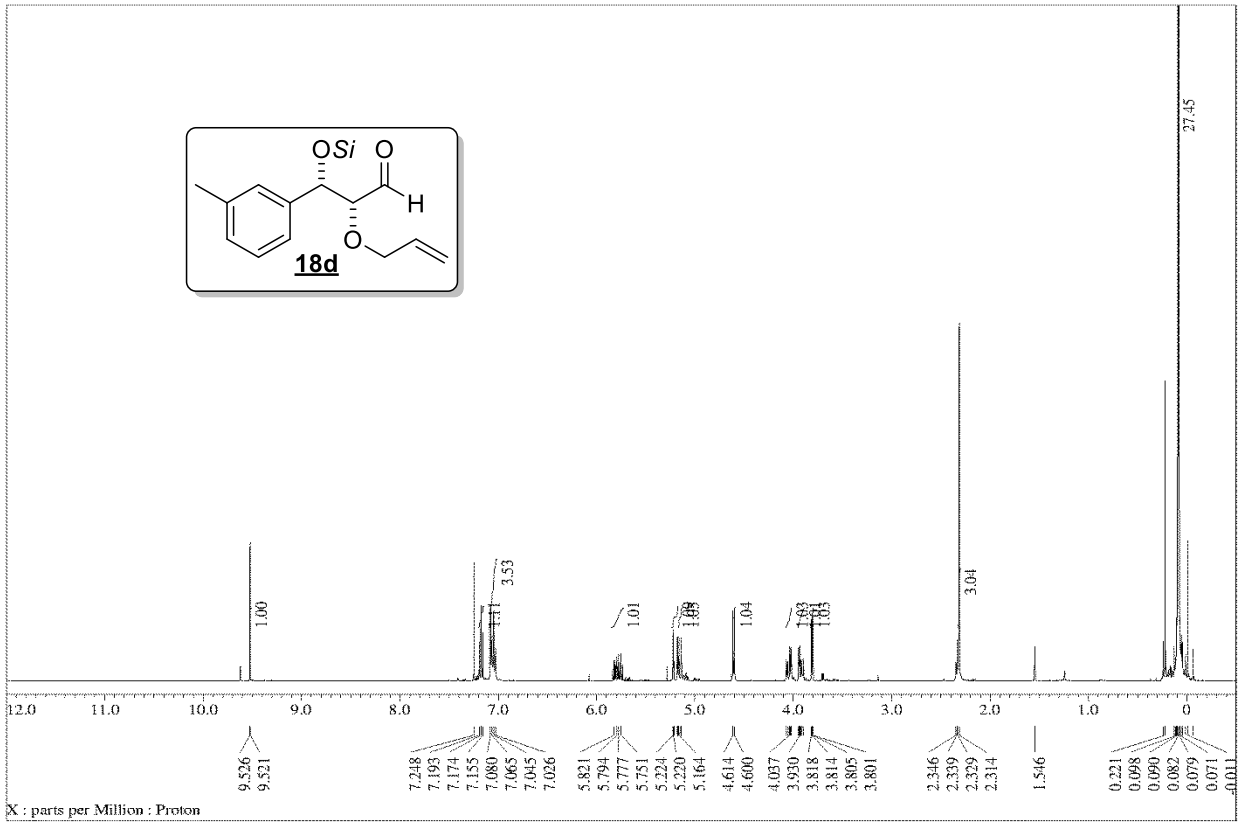
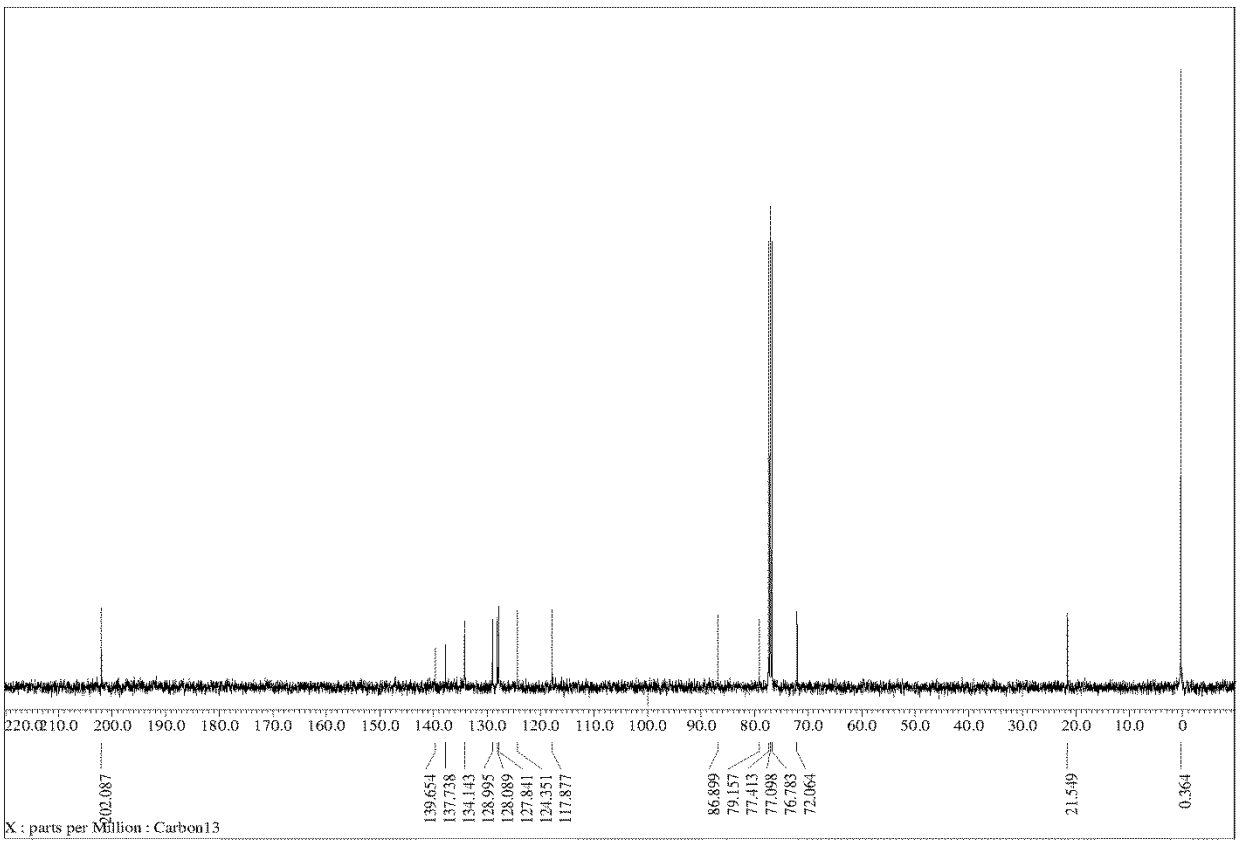
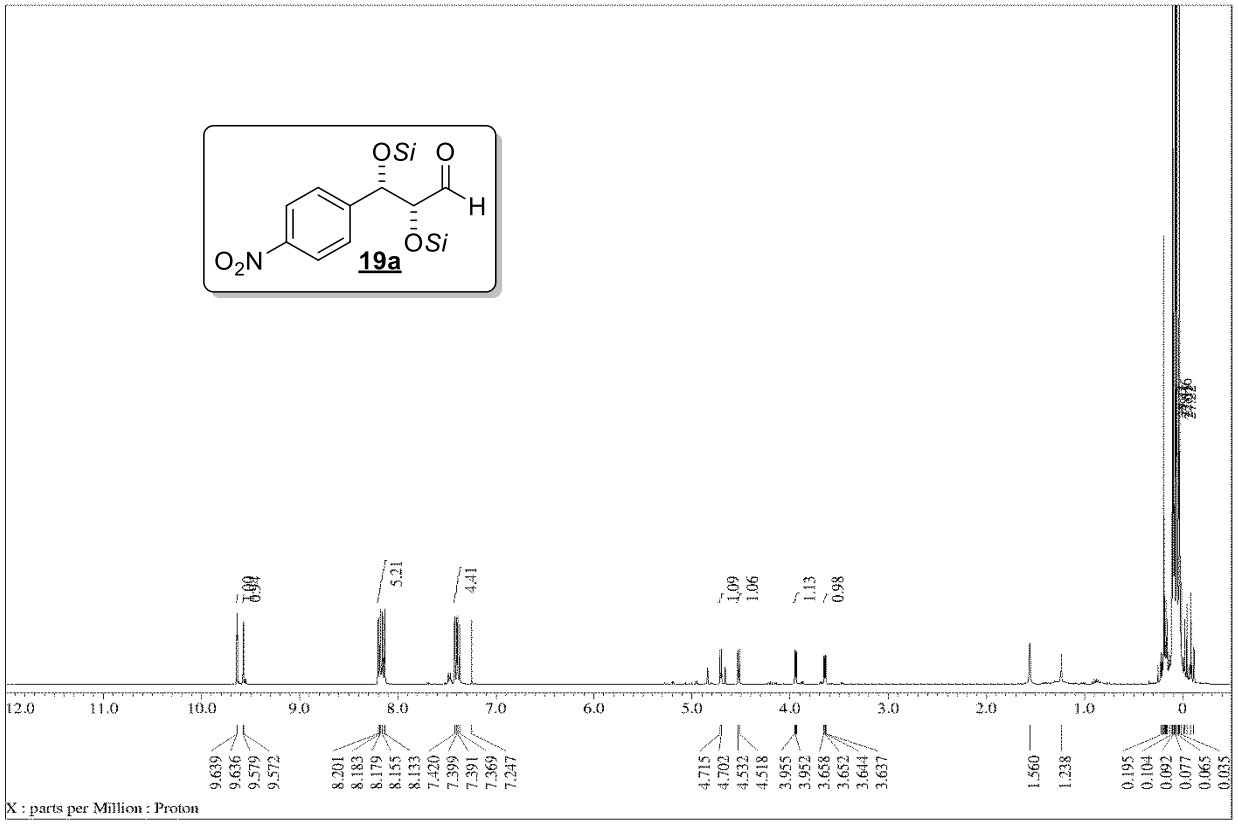
0.259
X : parts per Million : Carbon13

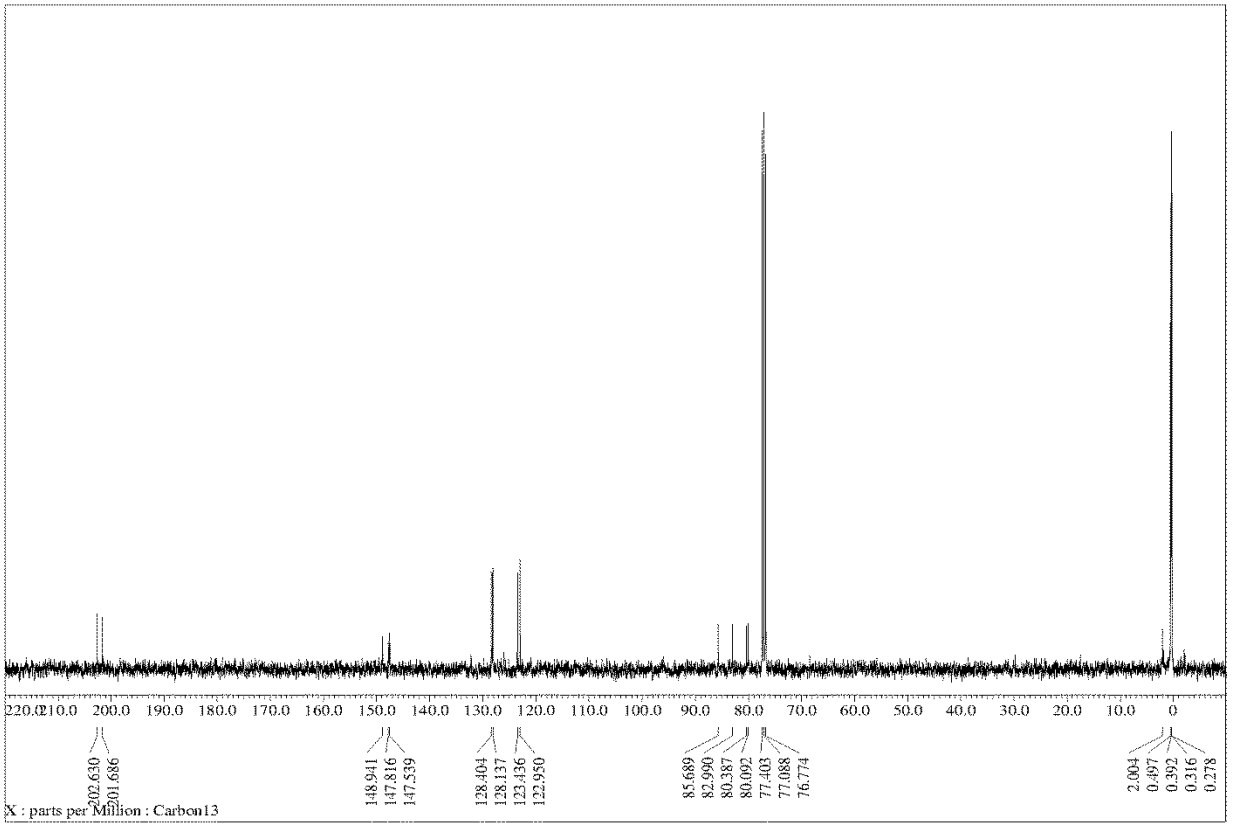

OSi
O
H
OTES
18c
X : parts per Million : Proton


X : parts per Million : Carbon13

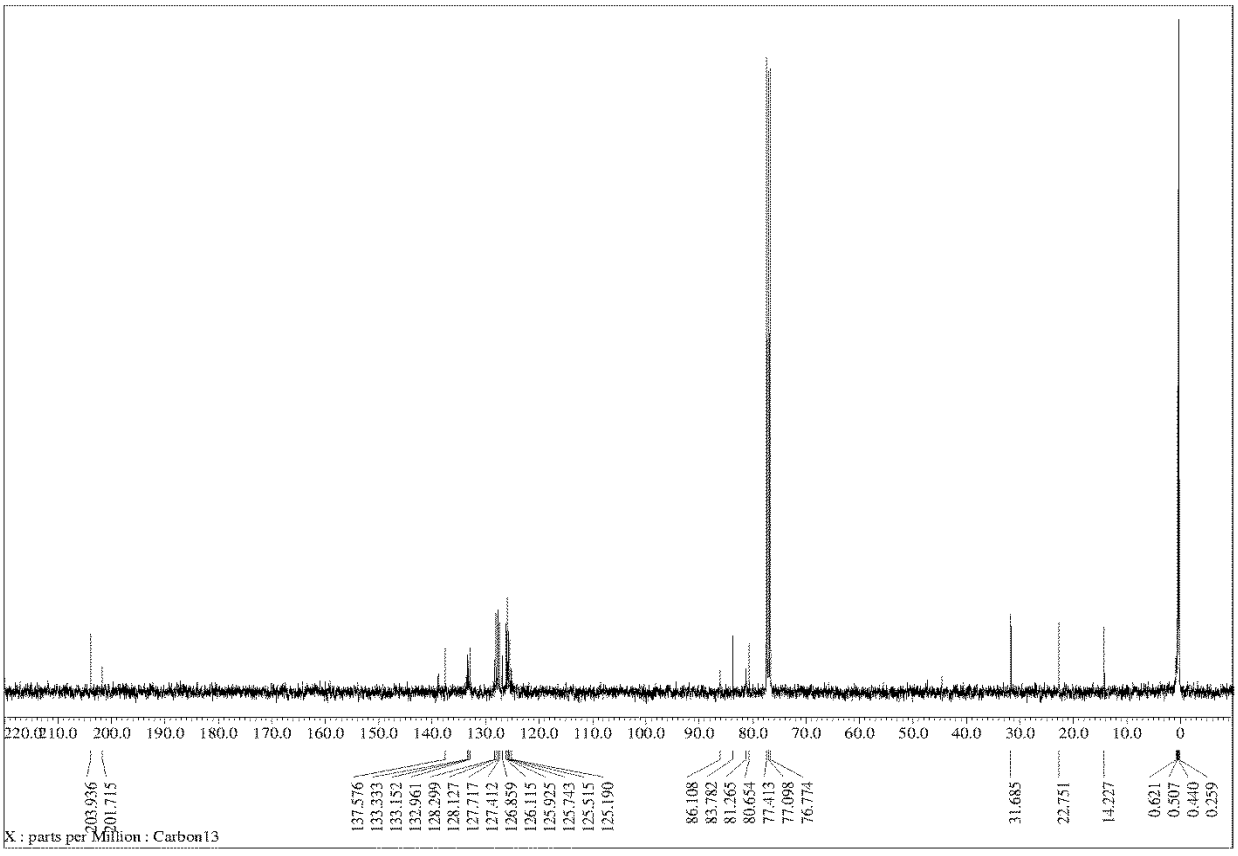

OSi
O
H
O
18d
27.45
1.00
3.53
1.01
1.04
3.04
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.526
9.521
7.248
7.193
7.174
7.155
7.080
7.065
7.045
7.026
5.821
5.794
5.777
5.751
5.224
5.220
5.164
4.614
4.600
4.037
3.930
3.818
3.814
3.805
3.801
2.346
2.339
2.329
2.314
1.546
0.221
0.098
0.090
0.082
0.079
0.071
0.011
X : parts per Million : Proton

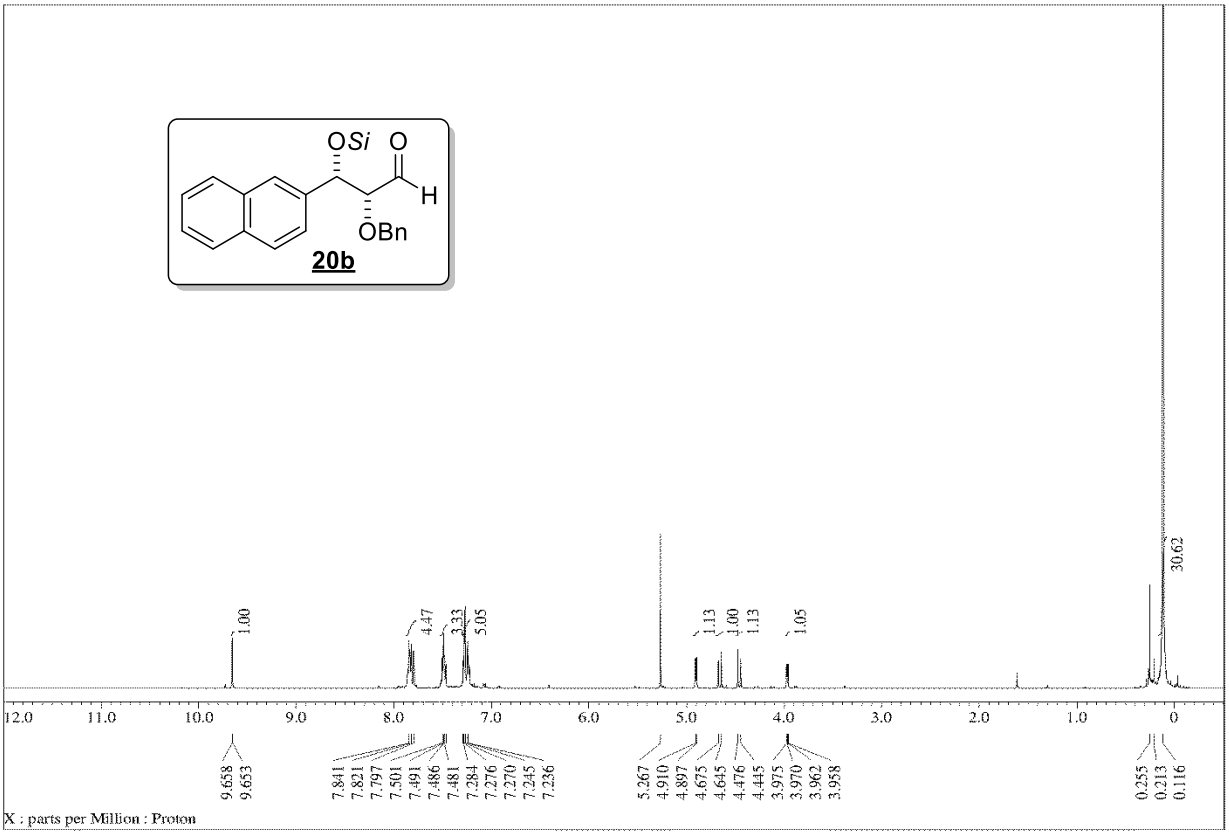

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
202.087
139.654
137.738
134.143
128.995
128.089
127.841
124.351
117.877
86.899
79.157
77.413
77.098
76.783
72.064
21.549
0.364
X : parts per Million : Carbon13

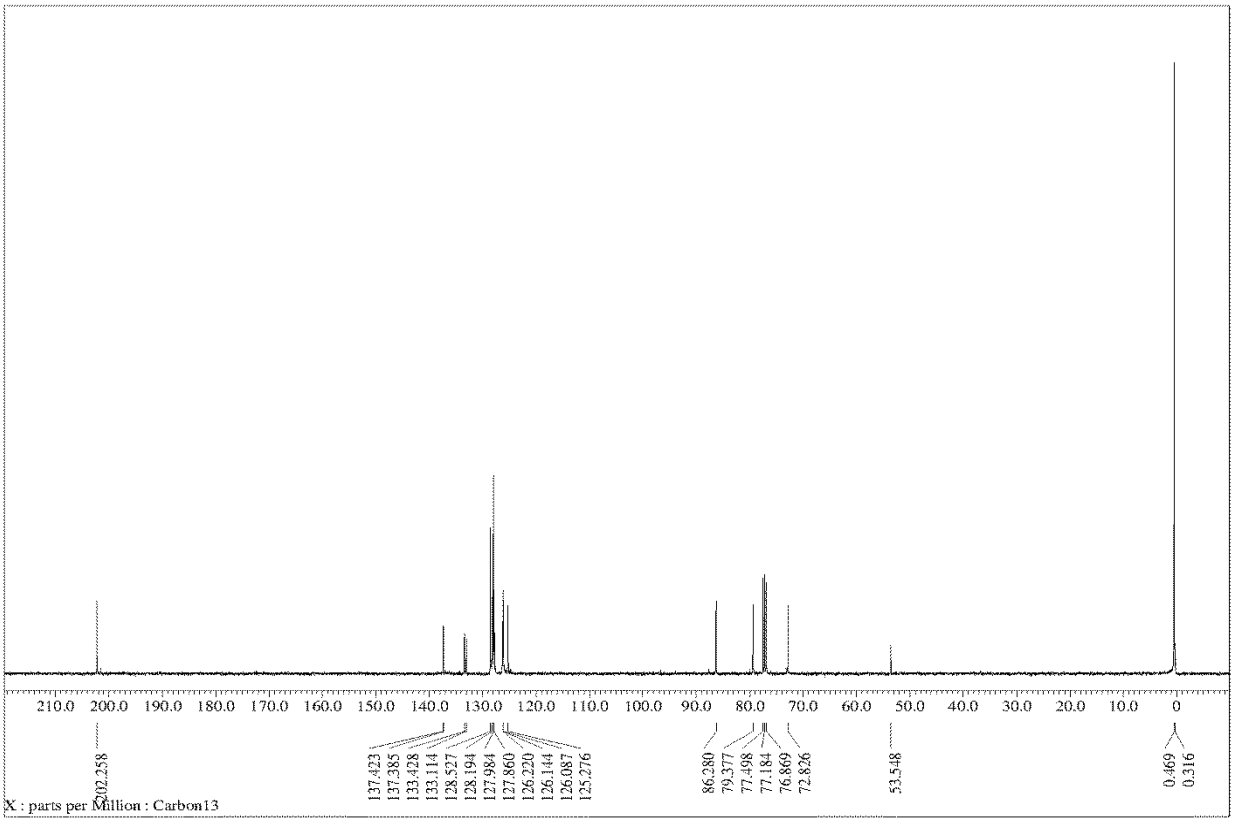

OSi
O
H
OSi
O2N
19a
5.21
4.41
1.09
1.06
1.13
0.98
9.639
9.636
9.579
9.572
8.201
8.183
8.179
8.155
8.133
7.420
7.399
7.391
7.369
7.247
4.715
4.702
4.532
4.518
3.955
3.952
3.658
3.652
3.644
3.637
1.560
1.238
0.195
0.104
0.092
0.077
0.065
0.035
X : parts per Million : Proton

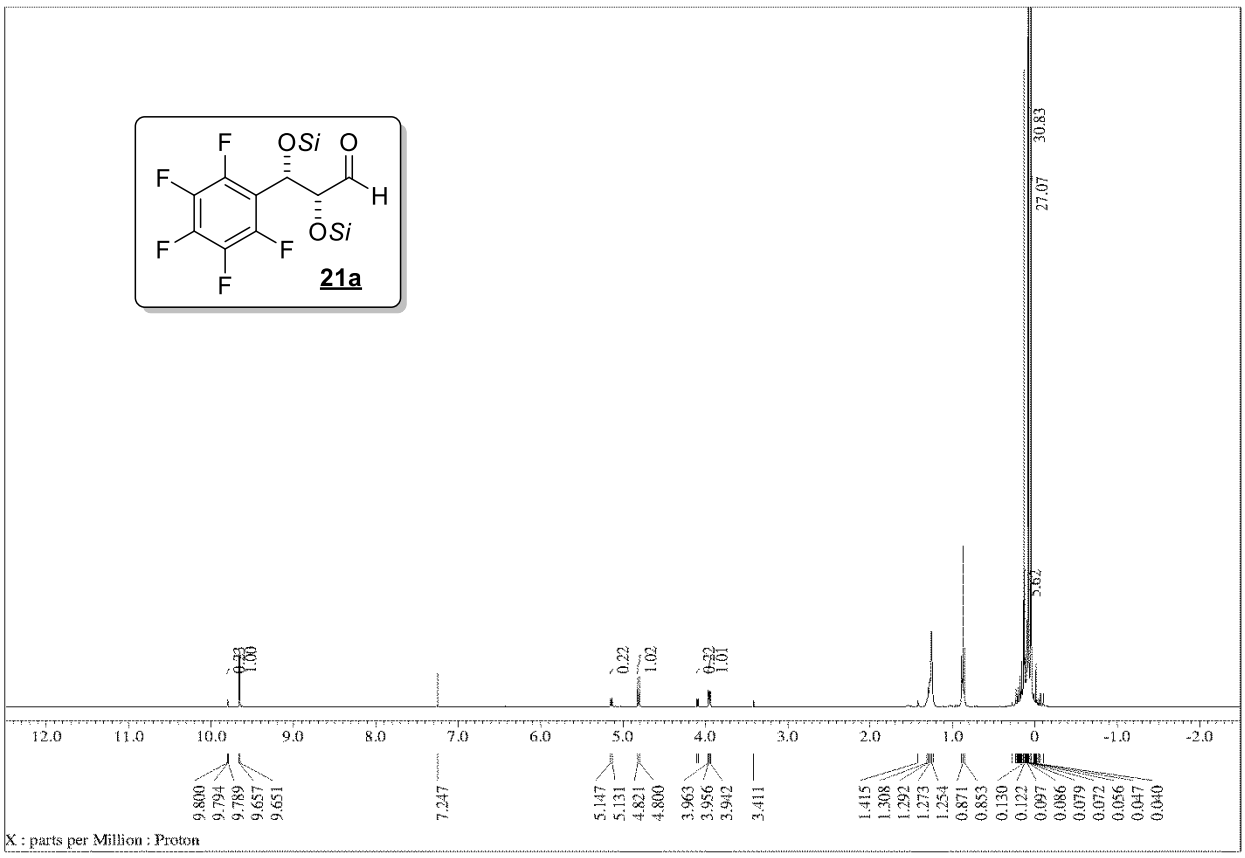

202.630
201.686
148.941
147.816
147.539
128.404
128.137
123.436
122.950
85.689
82.990
80.387
80.092
77.403
77.088
76.774
2.004
0.497
0.392
0.316
0.278
X : parts per Million : Carbon13

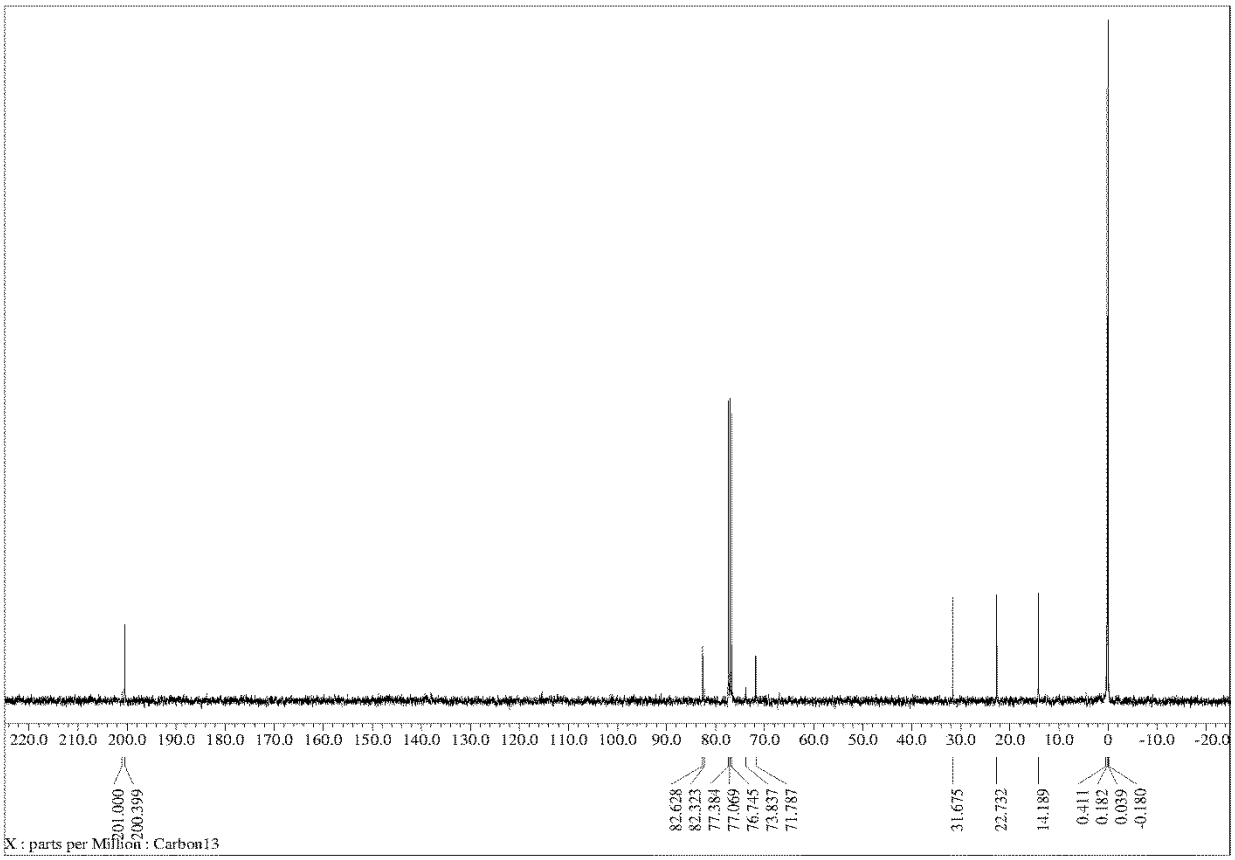

OSi
O
H
OSi
20a
12.59
40.83
X : parts per Million : Proton

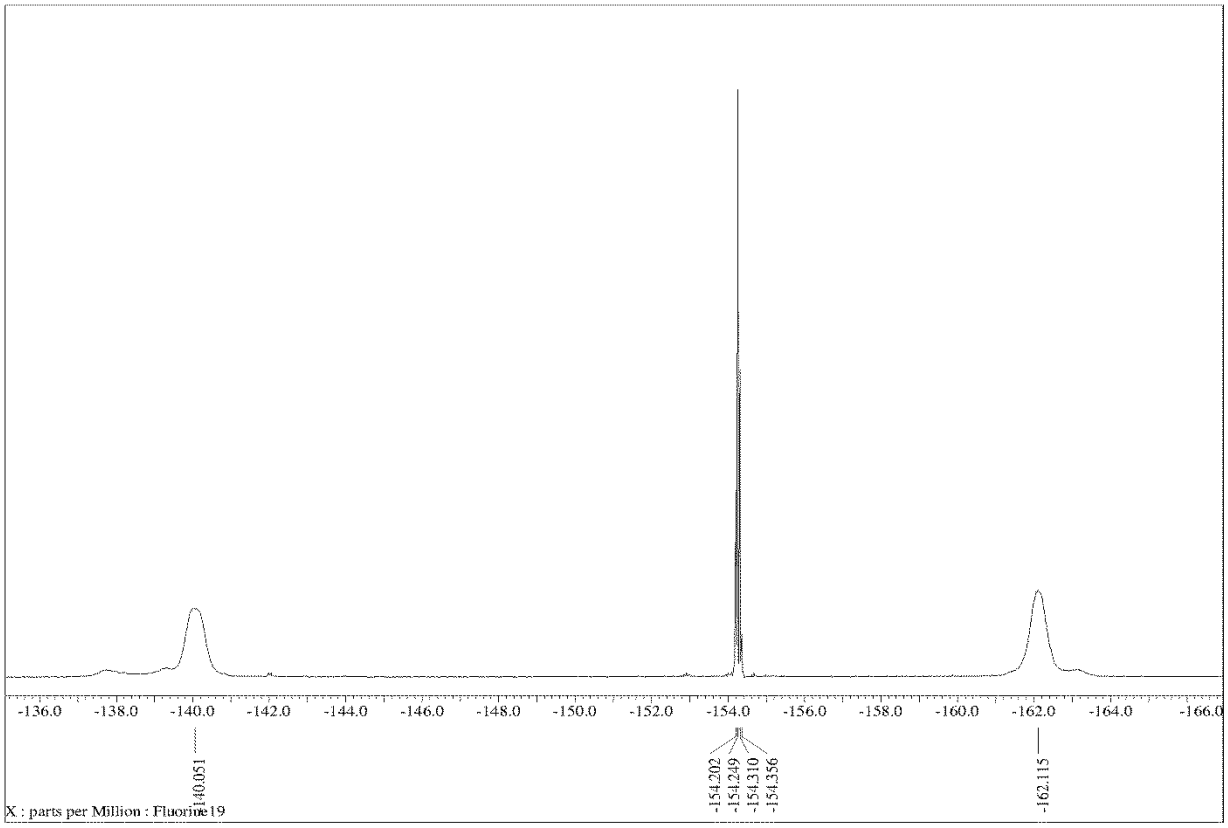

X : parts per Million : Carbon13


OSi
O
H
OBn
20b
1.00
4.47
2.33
5.05
1.13
1.00
1.13
1.05
30.62
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.658
9.653
7.841
7.821
7.797
7.501
7.491
7.486
7.481
7.284
7.276
7.270
7.245
7.236
5.267
4.910
4.897
4.675
4.645
4.476
4.445
3.975
3.970
3.962
3.958
0.255
0.213
0.116
X : parts per Million : Proton

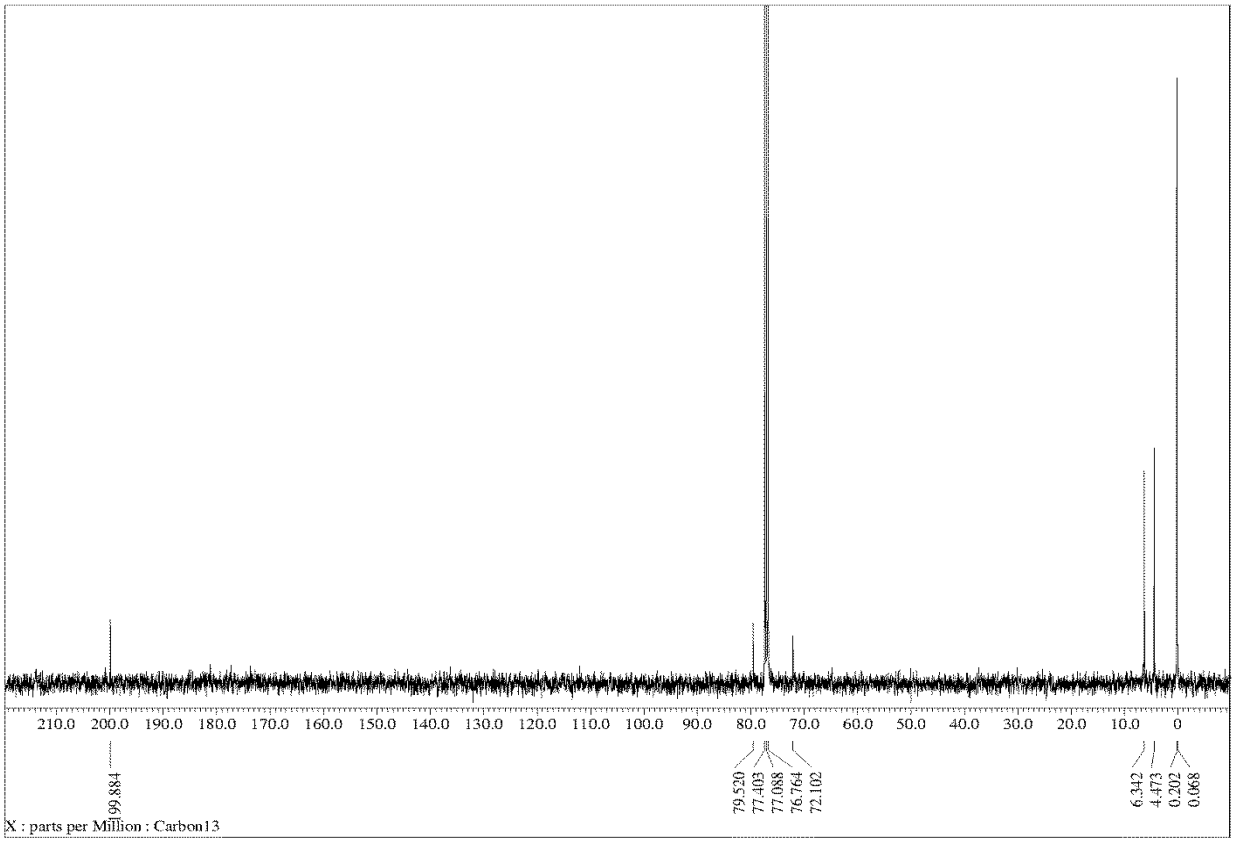

210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
202.258
137.423
137.385
133.428
133.114
128.527
128.194
127.984
127.860
126.220
126.144
126.087
125.276
86.280
79.377
77.498
77.184
76.869
72.826
53.548
0.469
0.316
X : parts per Million : Carbon13

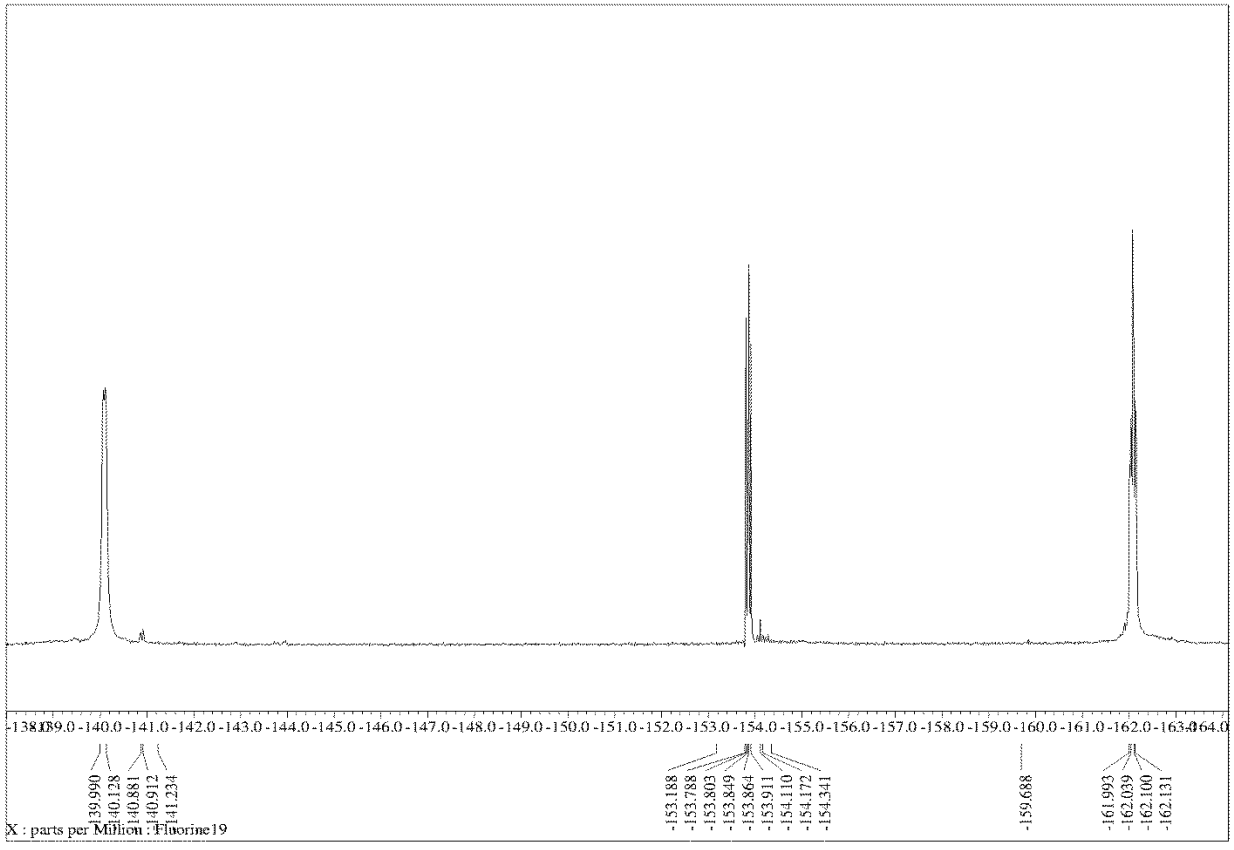

F
OSi
O
H
F
F
F
F
OSi
21a
30.83
27.07
5.62
0.23
1.00
0.22
1.02
0.32
1.01
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
9.800 9.794 9.789 9.657 9.651
7.247
5.147 5.131 4.821 4.800
3.963 3.956 3.942
3.411
1.415 1.308 1.292 1.273 1.254
0.871 0.853
0.130 0.122 0.097 0.086 0.079 0.072 0.056 0.047 0.040
X : parts per Million : Proton

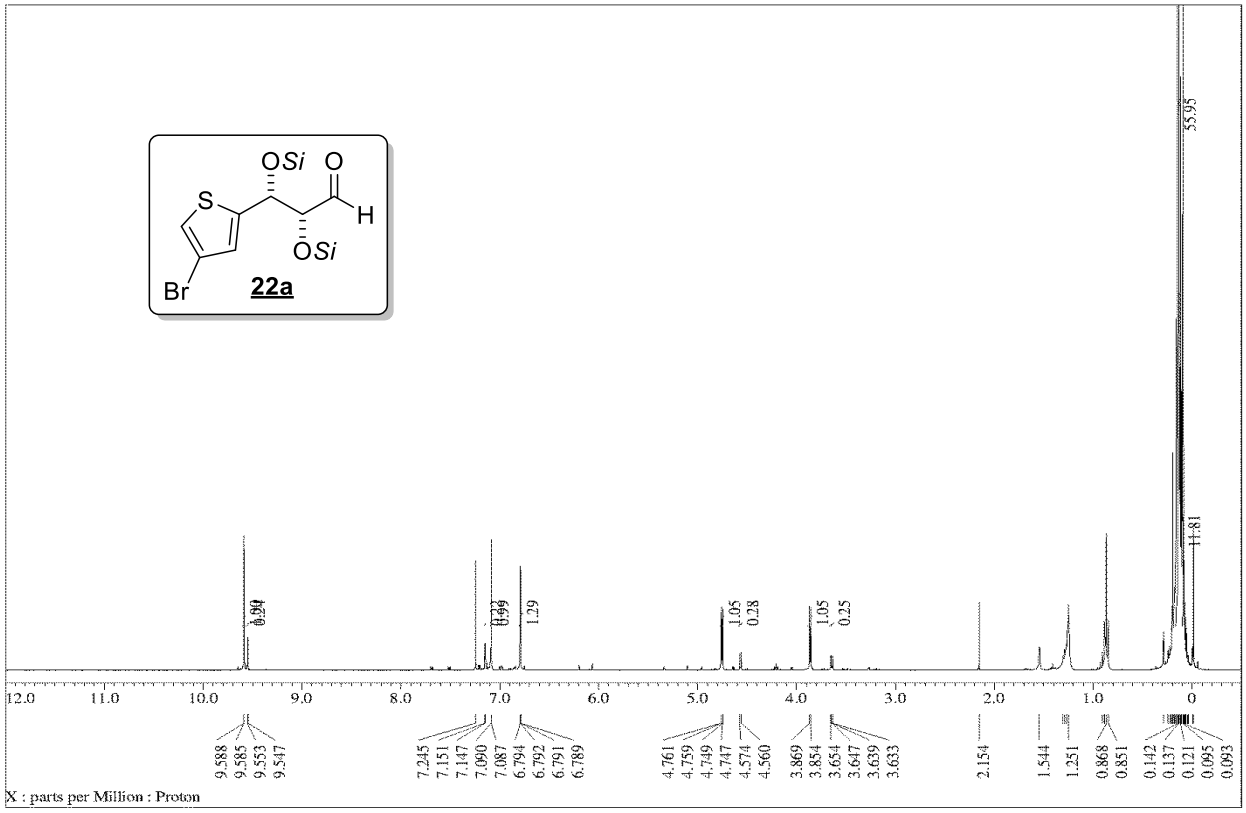

220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
201.000
200.399
82.628
82.323
77.384
77.069
76.745
73.837
71.787
31.675
22.732
14.189
0.411
0.182
0.039
-0.180
X : parts per Million : Carbon13

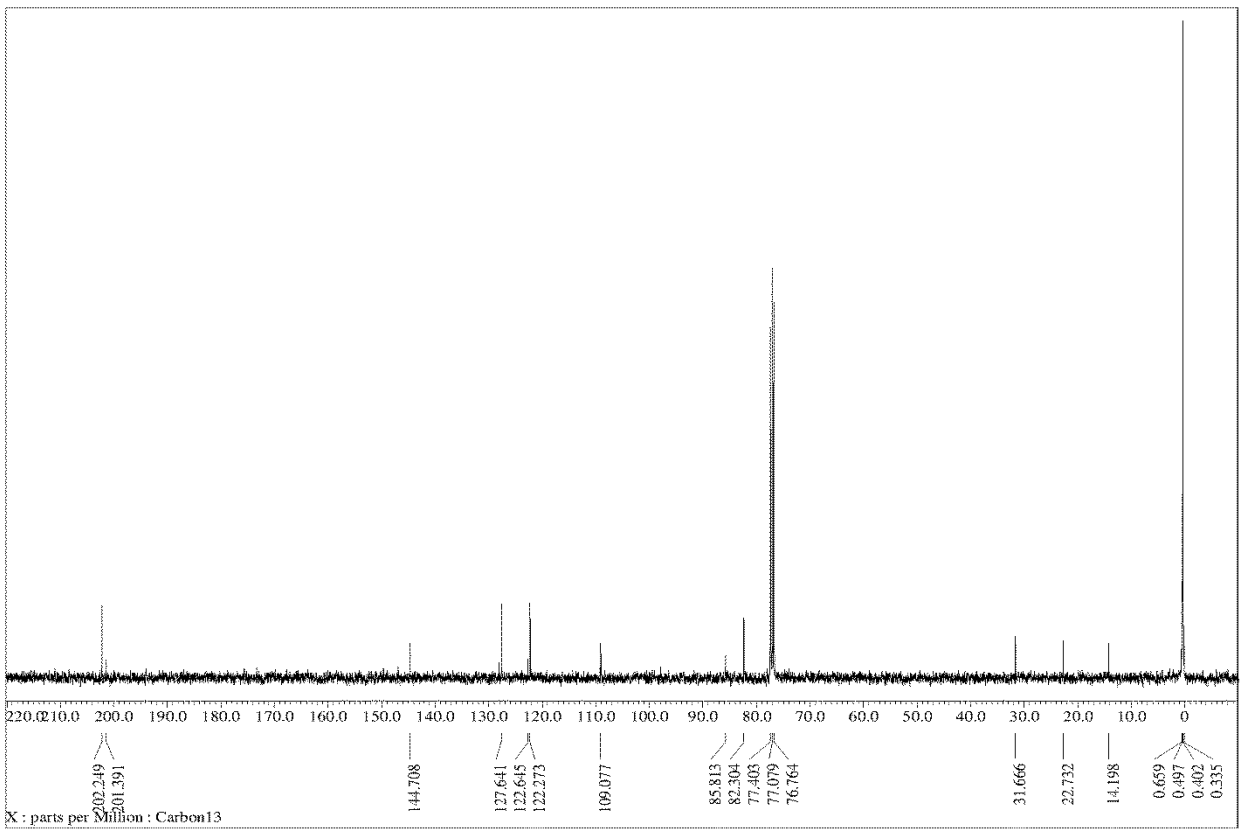

-136.0
-138.0
-140.0
-142.0
-144.0
-146.0
-148.0
-150.0
-152.0
-154.0
-156.0
-158.0
-160.0
-162.0
-164.0
-166.0
-140.051
-154.202
-154.249
-154.310
-154.356
-162.115
X : parts per Million : Fluorine19

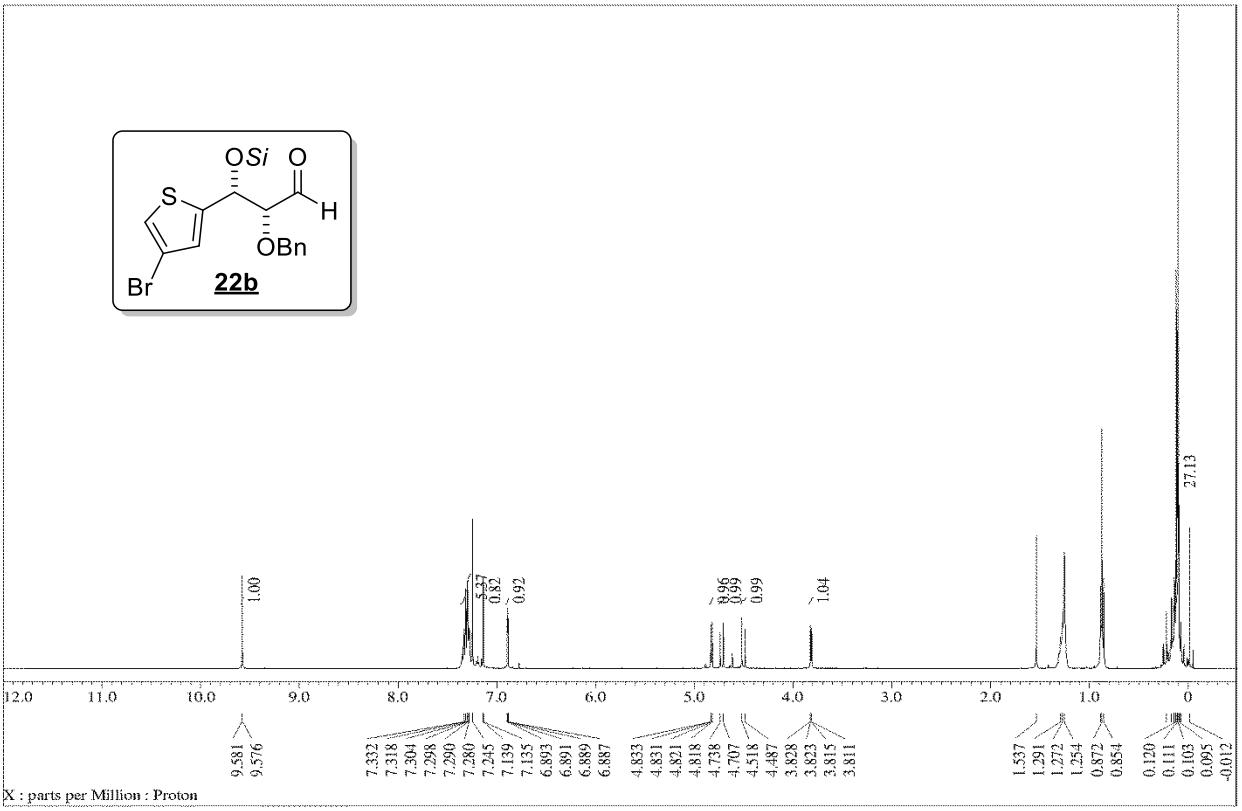

F
OSi
O
H
F
F
F
OTES
21c
1.00
1.03
1.04
9.41
6.20
27.38
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.659
9.652
7.248
4.946
4.927
4.151
4.144
4.131
4.125
1.530
0.800
0.781
0.761
0.128
0.101
0.093
0.085
-0.013
X : parts per Million : Proton

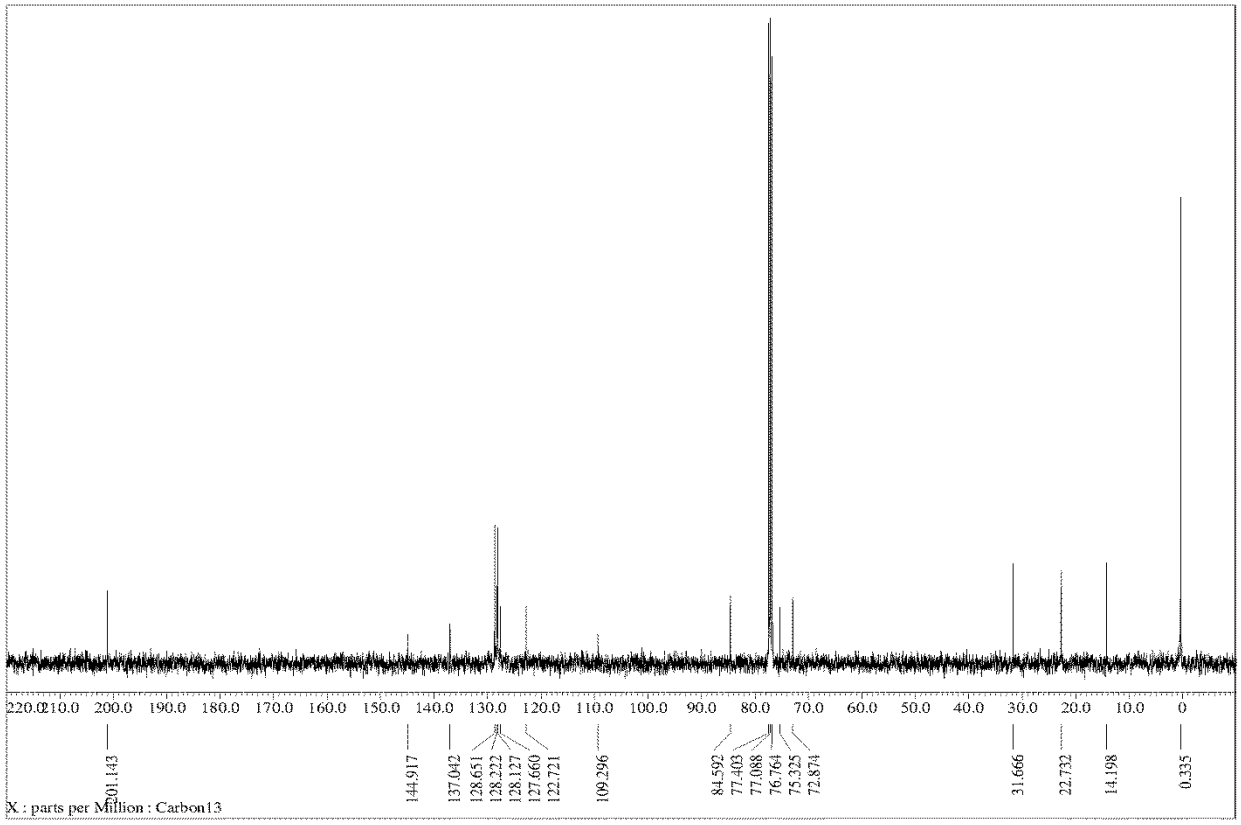

210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
199.884
79.520
77.403
77.088
76.764
72.102
6.342
4.473
0.202
0.068
X : parts per Million : Carbon13

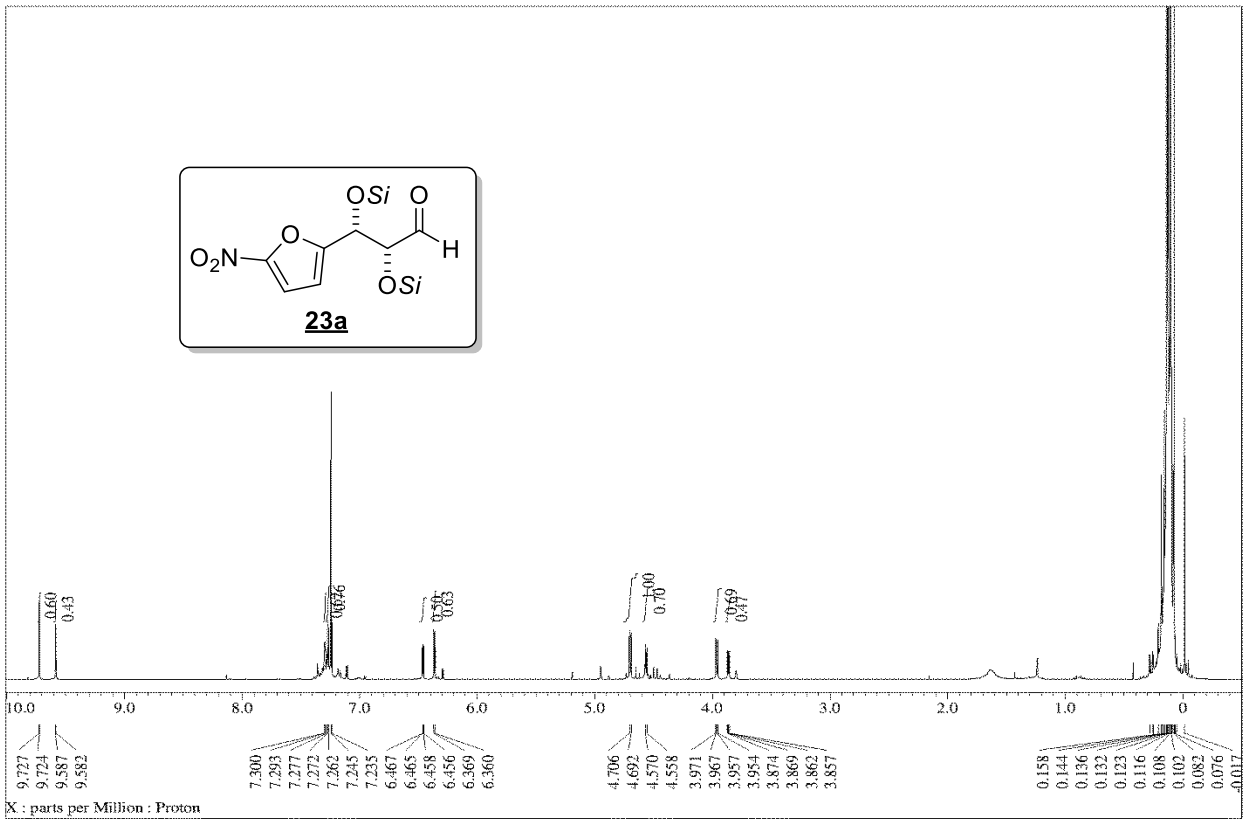

-139.990
-140.128
-140.881
-140.912
-141.234
-153.188
-153.788
-153.803
-153.849
-153.864
-153.911
-154.110
-154.172
-154.341
-159.688
-161.993
-162.039
-162.100
-162.131
X : parts per Million : Fluorine19

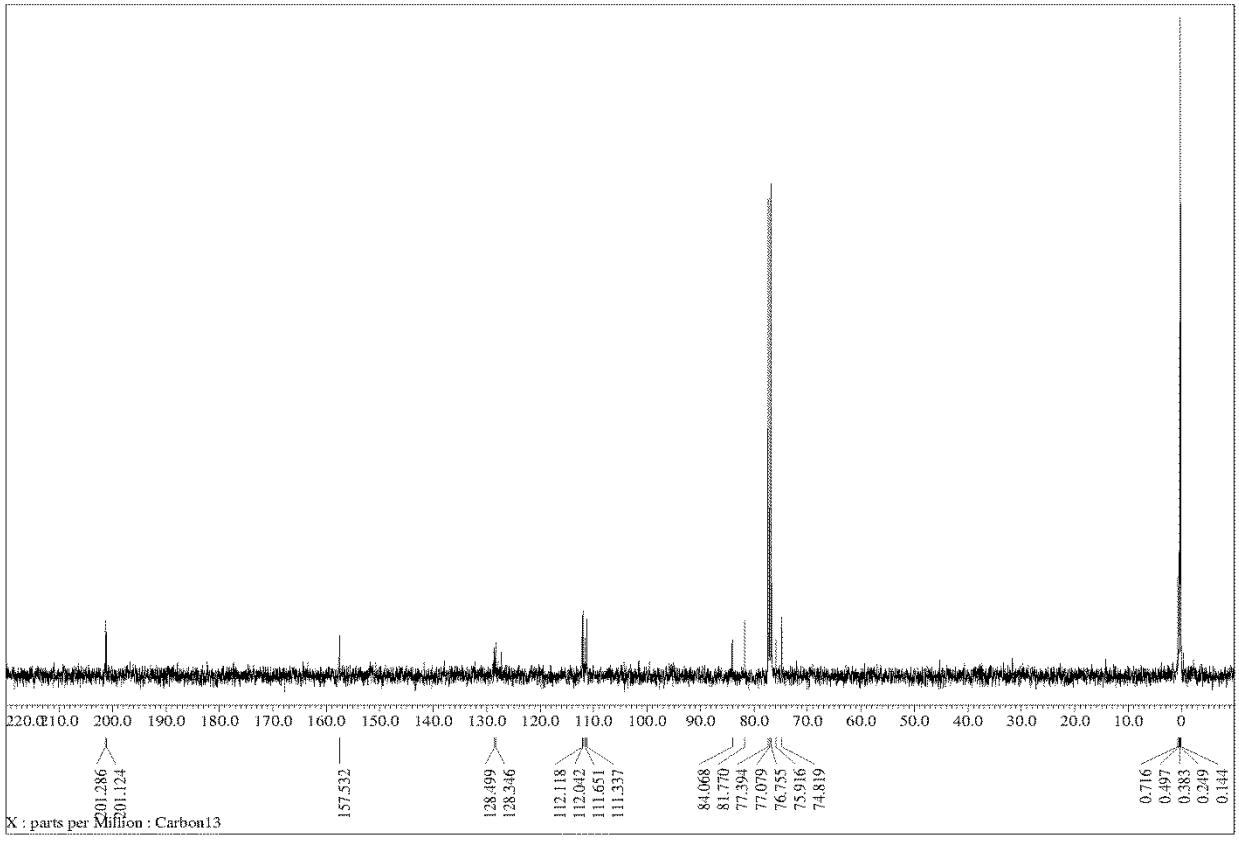

OSi
O
S
H
OSi
Br
22a
55.95
11.81
1.29
1.05
0.28
1.05
0.25
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.588
9.585
9.553
9.547
7.245
7.151
7.147
7.090
7.087
6.794
6.792
6.791
6.789
4.761
4.759
4.749
4.747
4.574
4.560
3.869
3.854
3.654
3.647
3.639
3.633
2.154
1.544
1.251
0.868
0.851
0.142
0.137
0.121
0.095
0.093
X : parts per Million : Proton

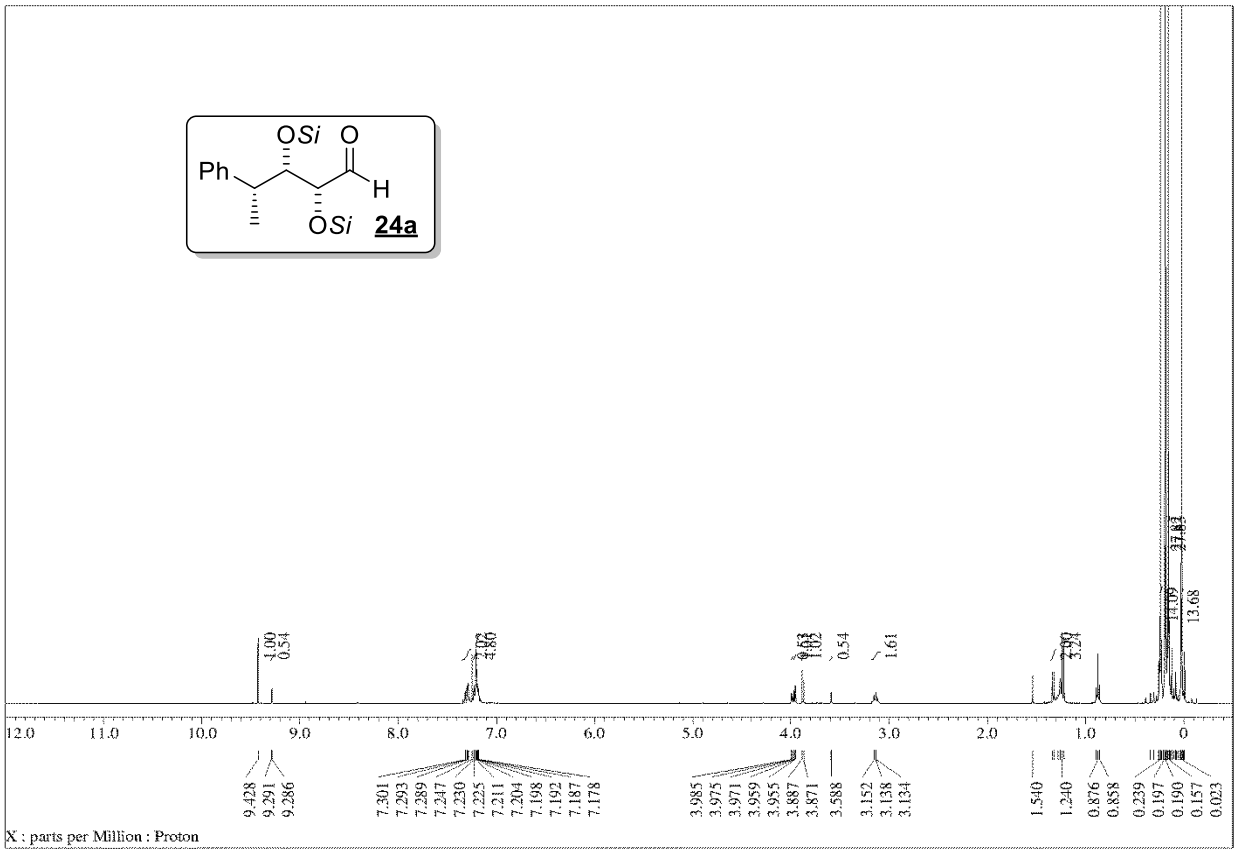

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
202.249
201.391
144.708
127.641
122.645
122.273
109.077
85.813
82.304
77.403
77.079
76.764
31.666
22.732
14.198
0.659
0.497
0.402
0.335
X : parts per Million : Carbon13

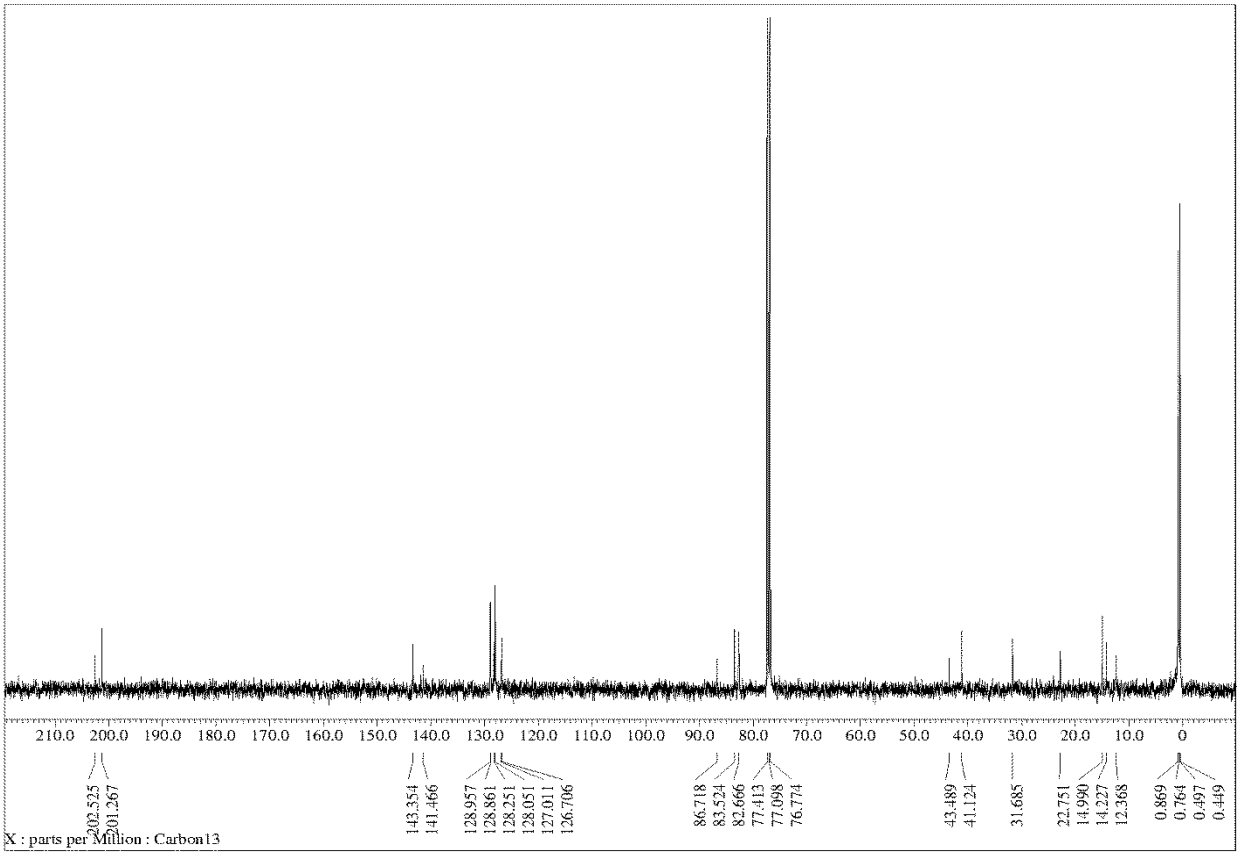

OSi
O
S
H
OBn
Br
22b
1.00
5.37
0.82
0.92
0.96
0.98
0.99
0.99
1.04
27.13
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.581
9.576
7.332
7.318
7.304
7.298
7.290
7.280
7.245
7.139
7.135
6.893
6.891
6.889
6.887
4.833
4.831
4.821
4.818
4.738
4.707
4.518
4.487
3.828
3.823
3.815
3.811
1.537
1.291
1.272
1.254
0.872
0.854
0.120
0.111
0.103
0.095
-0.012
X : parts per Million : Proton

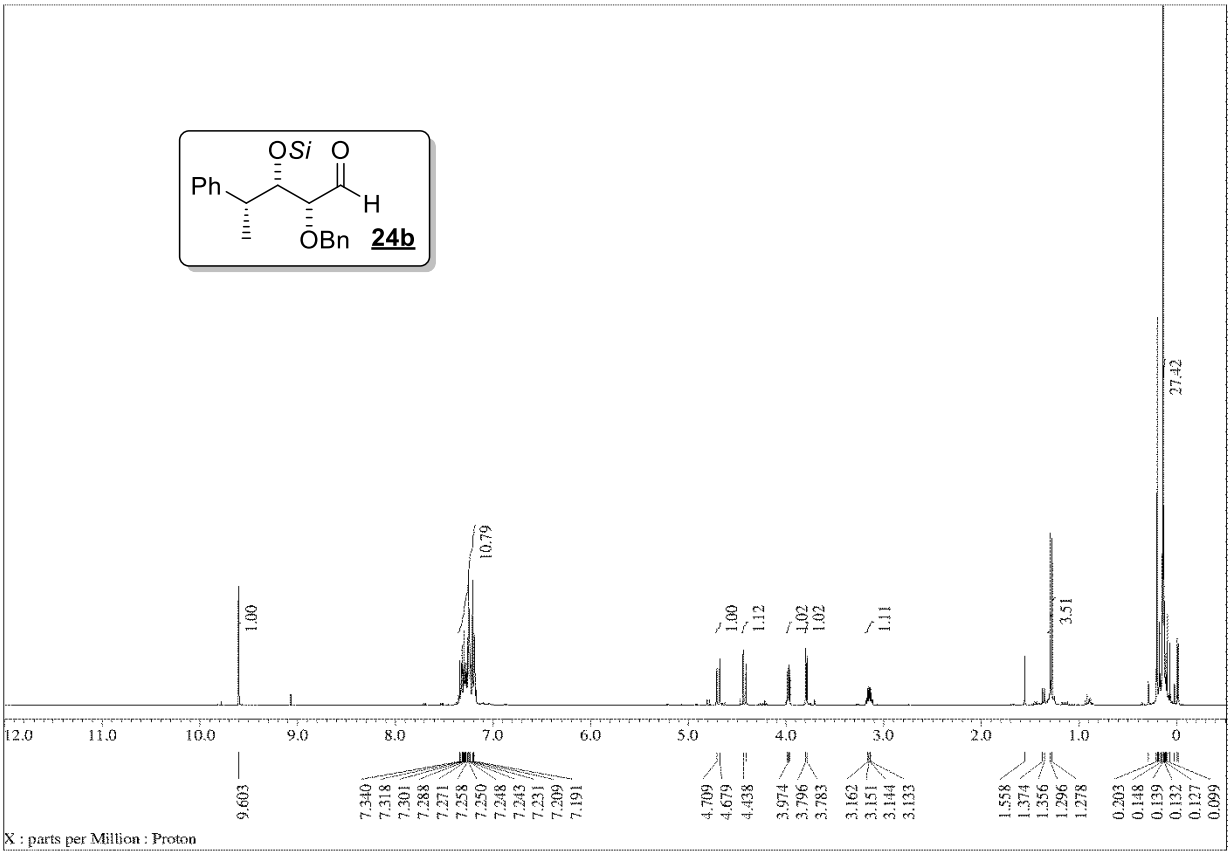

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
201.143
144.917
137.042
128.651
128.222
128.127
127.660
122.721
109.296
84.592
77.403
77.088
76.764
75.325
72.874
31.666
22.732
14.198
0.335
X : parts per Million : Carbon13

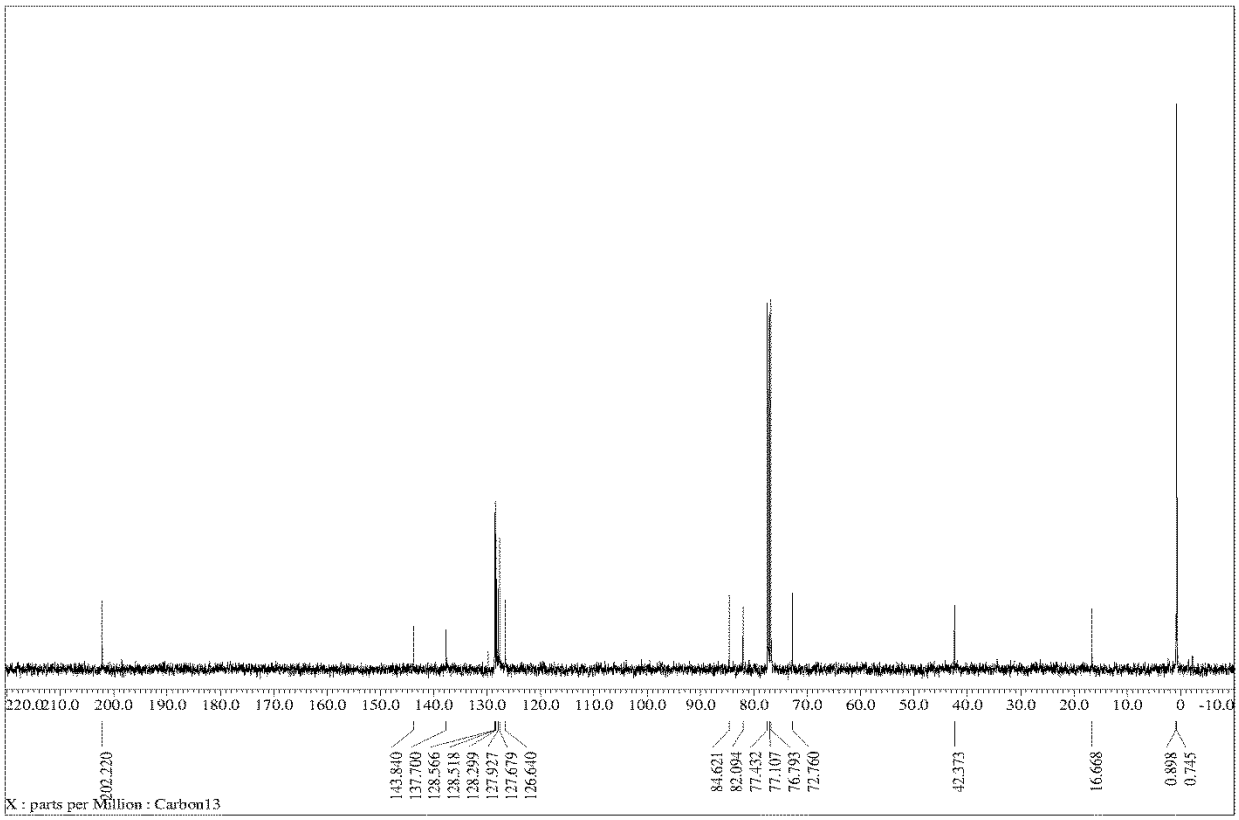

OSi
O
O2N
O
H
OSi
23a
0.60
0.43
0.70
0.69
0.47
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.727
9.724
9.587
9.582
7.300
7.293
7.277
7.272
7.262
7.245
7.235
6.467
6.465
6.458
6.456
6.369
6.360
4.706
4.692
4.570
4.558
3.971
3.967
3.957
3.954
3.874
3.869
3.862
3.857
0.158
0.144
0.136
0.132
0.123
0.116
0.108
0.102
0.082
0.076
0.017
X : parts per Million : Proton


220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
201.286
201.124
157.532
128.499
128.346
112.118
112.042
111.651
111.337
84.068
81.770
77.394
77.079
76.755
75.916
74.819
0.716
0.497
0.383
0.249
0.144
X : parts per Million : Carbon13

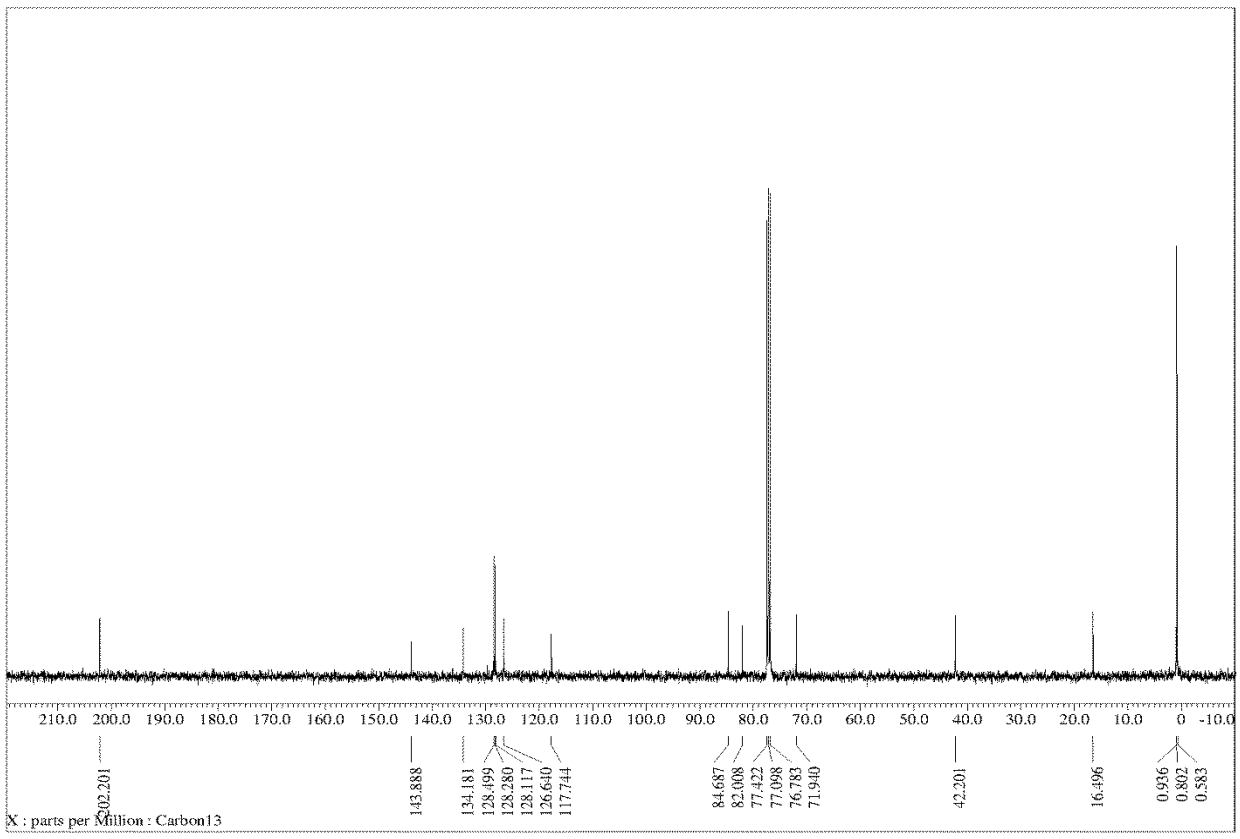

OSi
O
Ph
H
OSi
24a
X : parts per Million : Proton

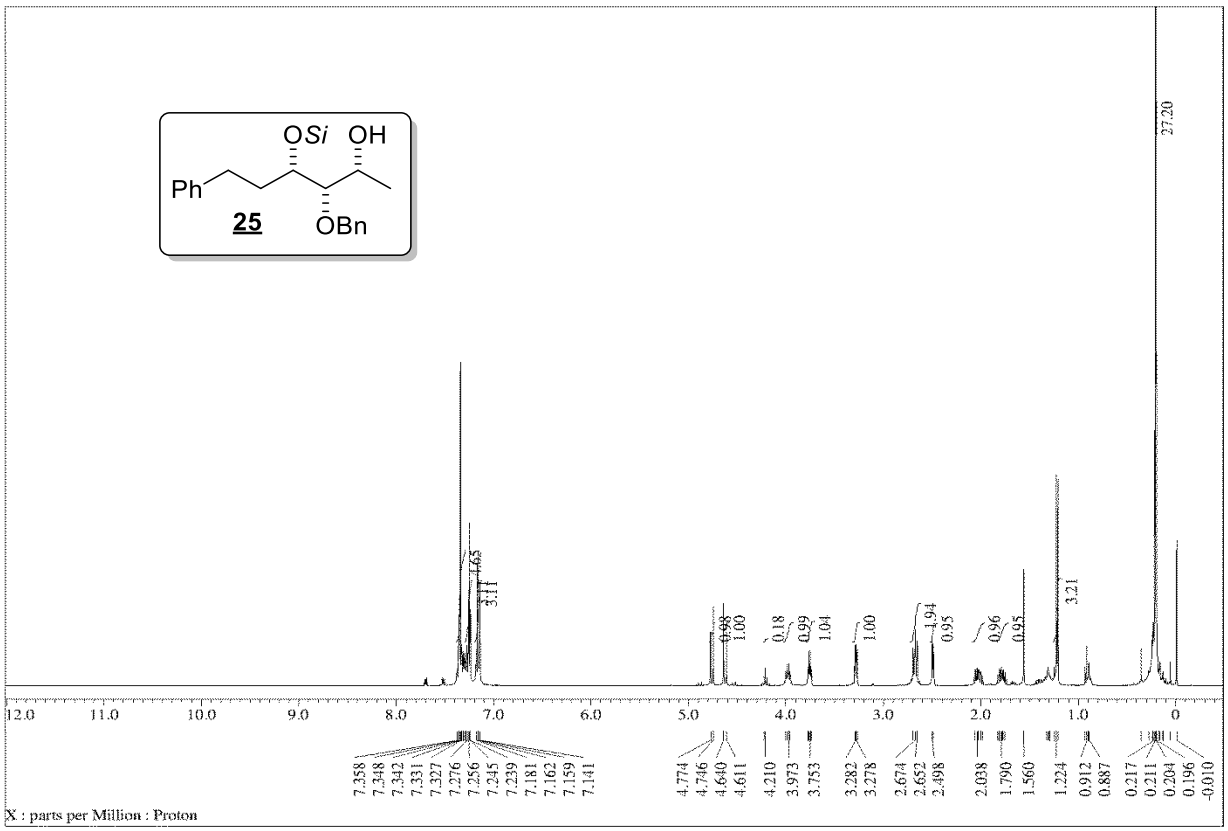

X : parts per Million : Carbon13

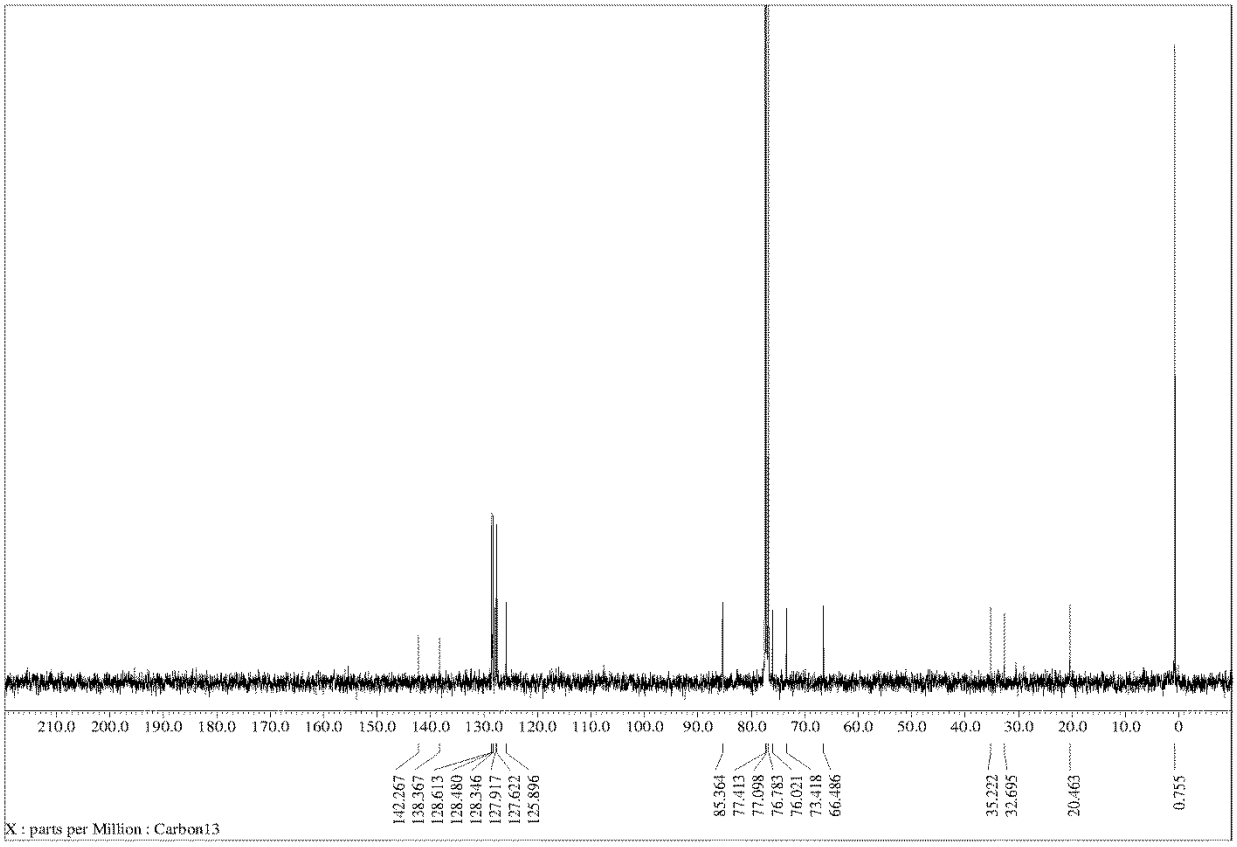

OSi
O
Ph
H
OBn
24b
27.42
10.79
1.00
1.00
1.12
1.02
1.02
1.11
3.51
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.603
7.340
7.318
7.301
7.288
7.271
7.258
7.250
7.248
7.243
7.231
7.209
7.191
4.709
4.679
4.438
3.974
3.796
3.783
3.162
3.151
3.144
3.133
1.558
1.374
1.356
1.296
1.278
0.203
0.148
0.139
0.132
0.127
0.099
X : parts per Million : Proton

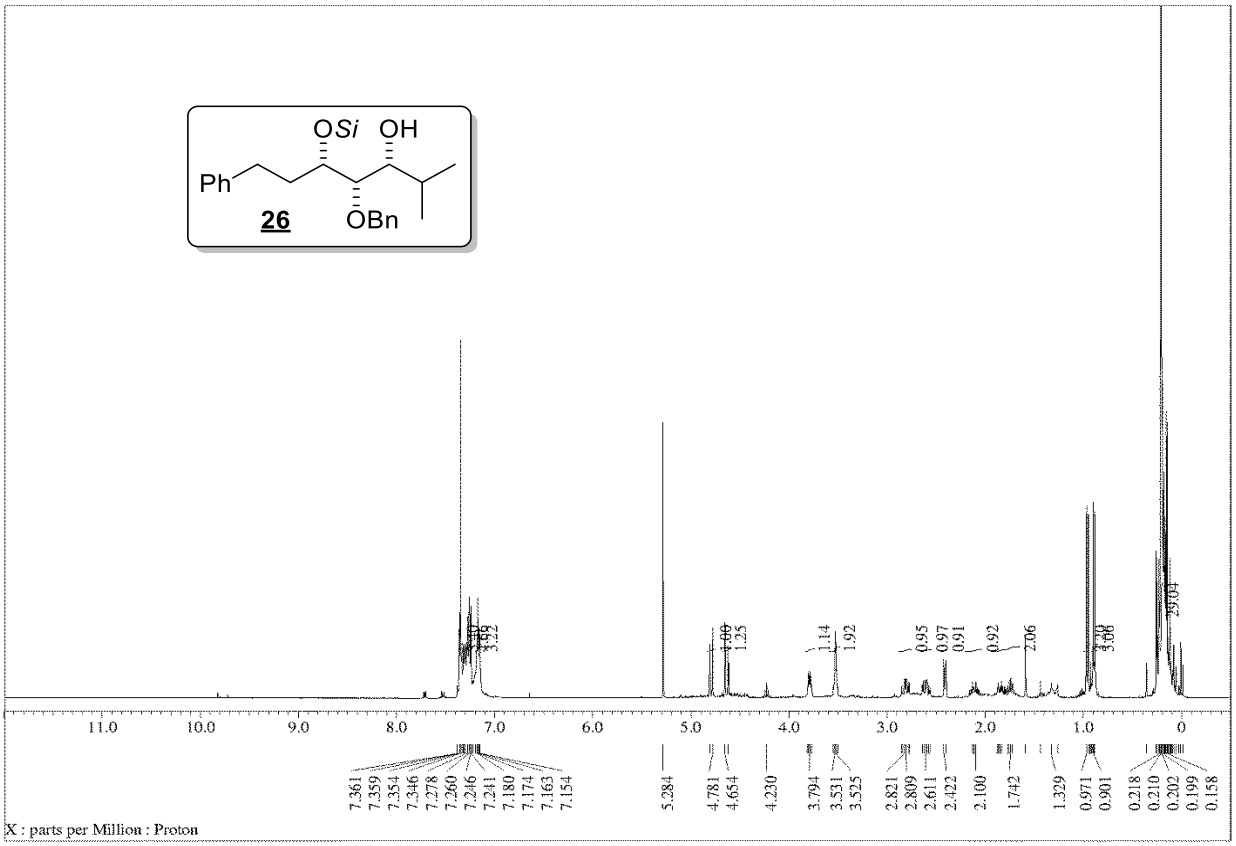

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
202.220
143.840
137.700
128.566
128.518
128.299
127.927
127.679
126.640
84.621
82.094
77.452
77.107
76.793
72.760
42.373
16.668
0.898
0.745
X : parts per Million : Carbon13

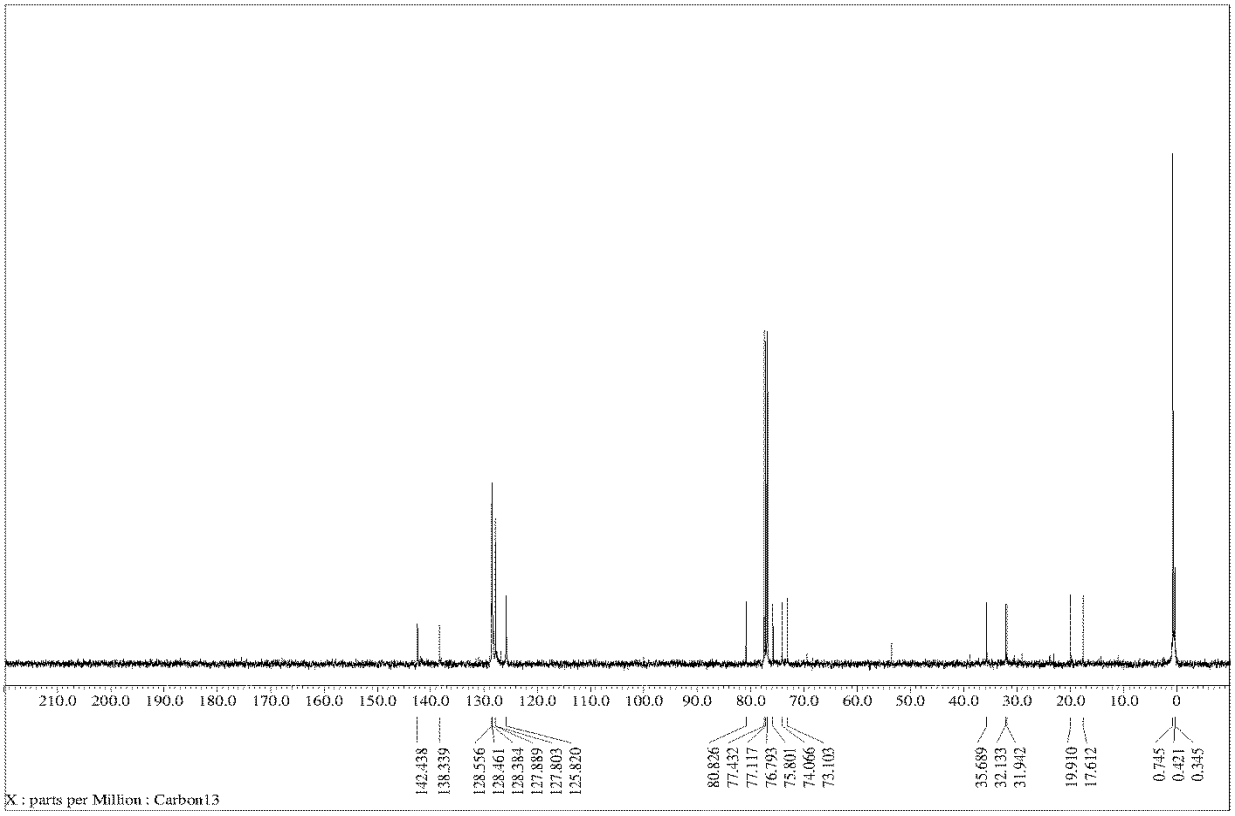

OSi
O
Ph
H
O
24d
1.00
2.02
3.41
1.06
2.45
1.04
1.02
1.16
1.13
3.39
27.72
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.593
7.273
7.254
7.251
7.248
7.242
7.237
7.202
7.184
7.180
5.856
5.830
5.813
5.800
5.788
5.221
5.216
5.174
5.163
3.975
3.964
3.962
3.951
3.741
3.124
3.113
3.106
3.096
1.553
1.371
1.266
1.248
0.235
0.222
0.182
0.174
0.167
-0.010
X : parts per Million : Proton

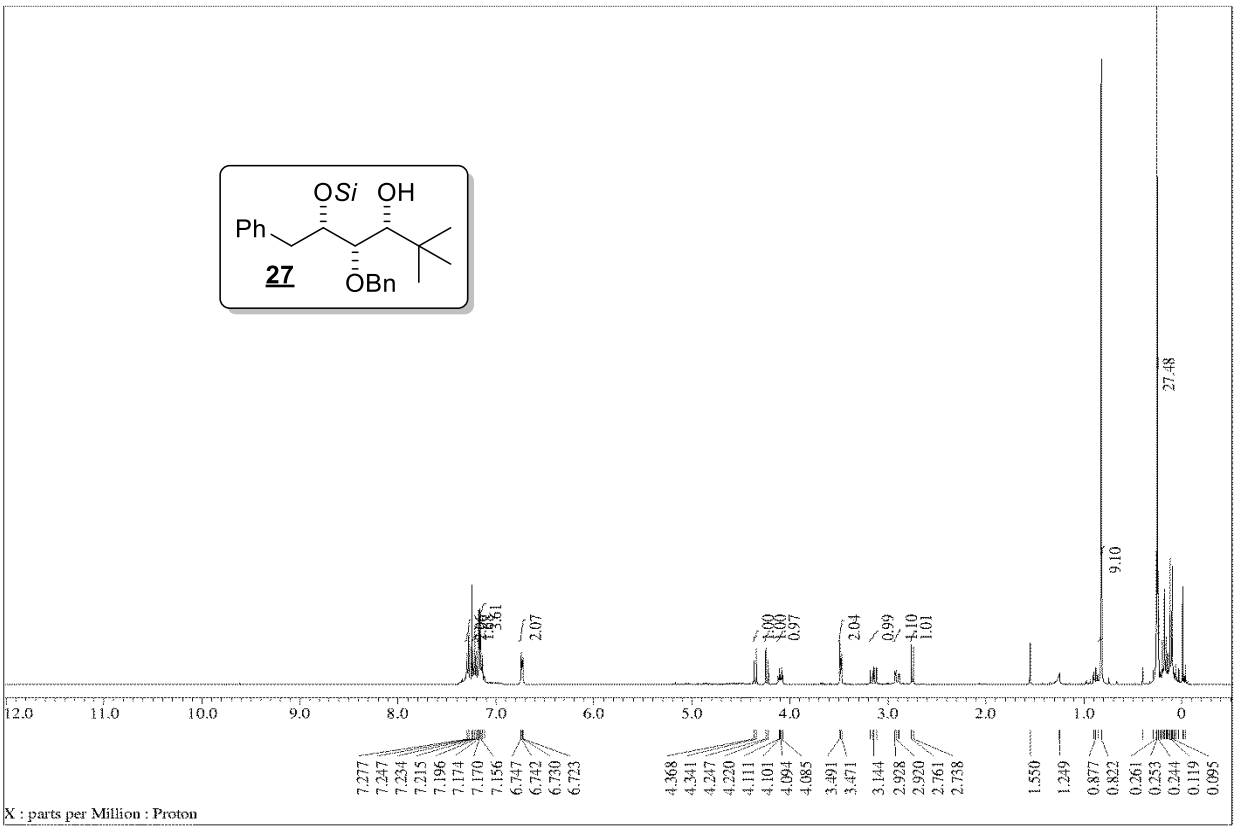

210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
202.201
143.888
134.181
128.499
128.280
128.117
126.640
117.744
84.687
82.008
77.422
77.098
76.783
71.940
42.201
16.496
0.936
0.802
0.583
X : parts per Million : Carbon13

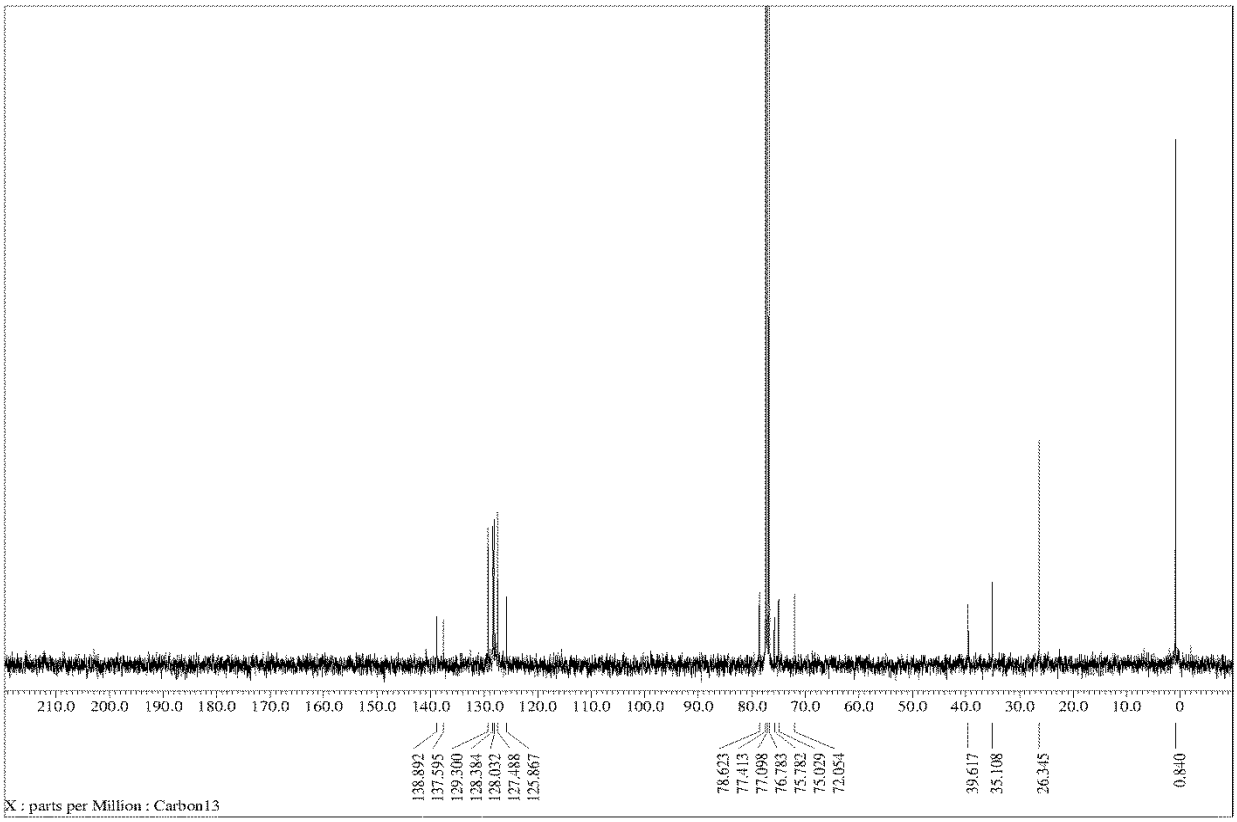

OSi
OH
Ph
25
OBn
27.20
3.21
X : parts per Million : Proton

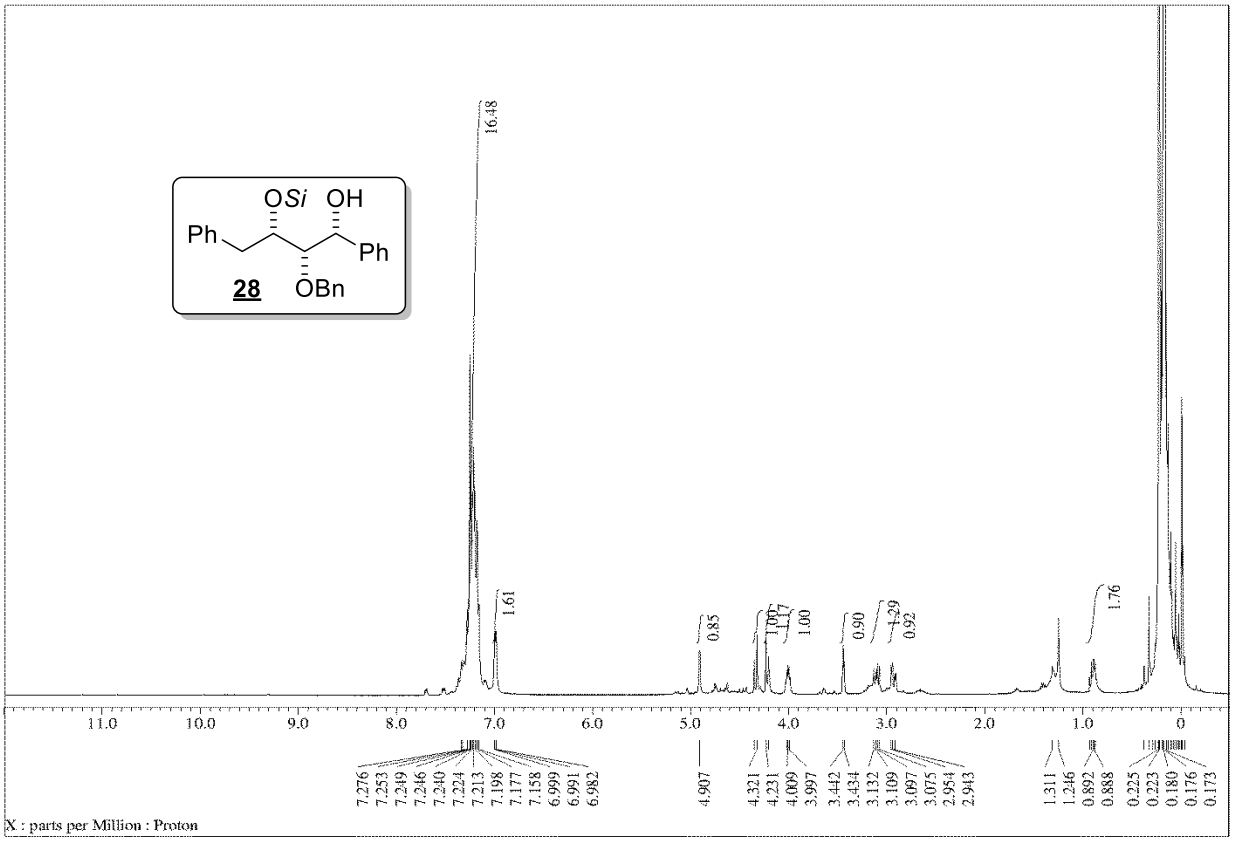

X : parts per Million : Carbon13

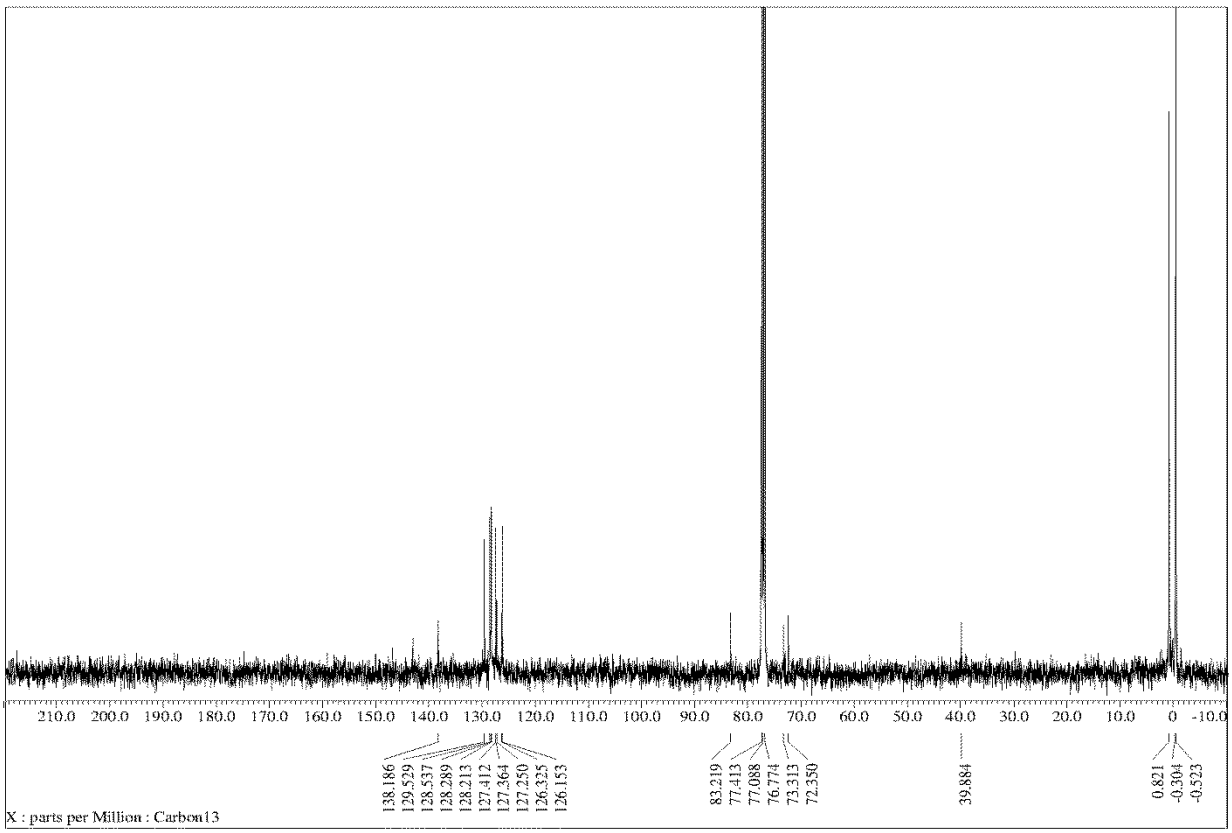

OSi
OH
Ph
OBn
26
X : parts per Million : Proton

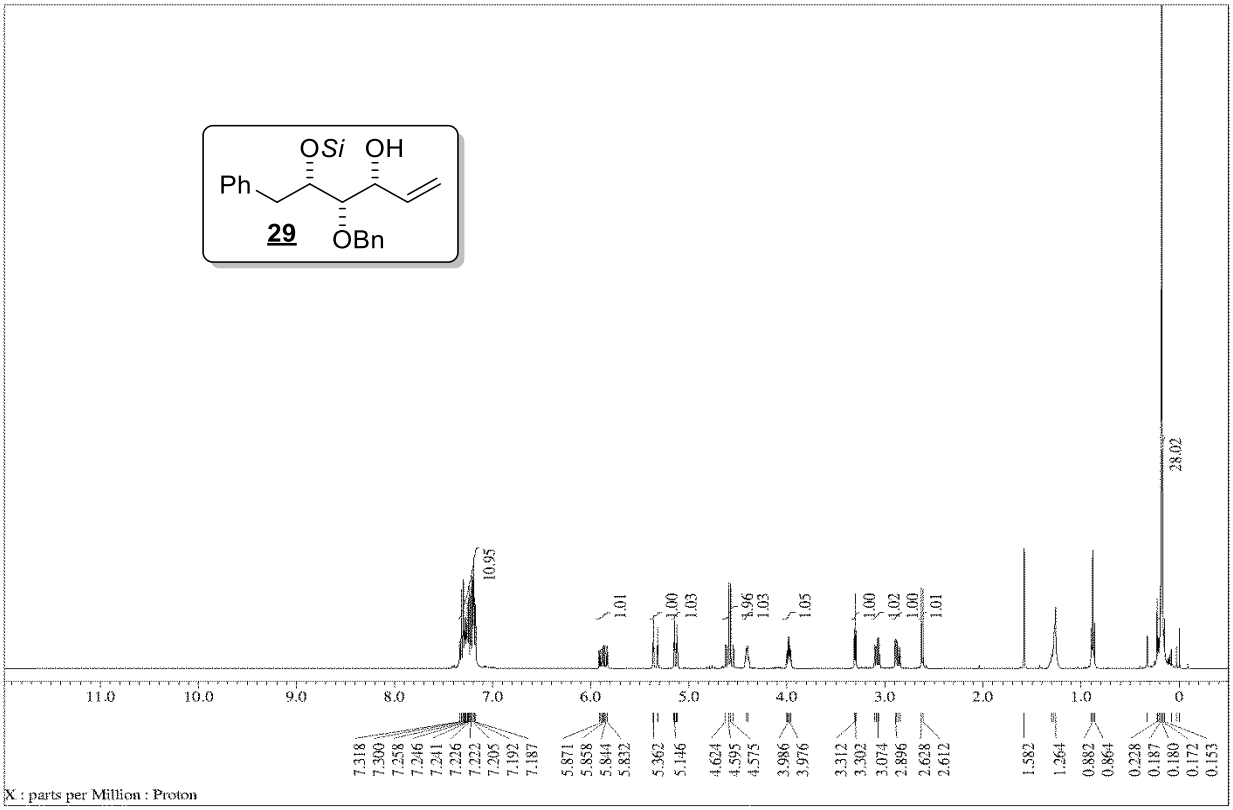

X : parts per Million : Carbon13

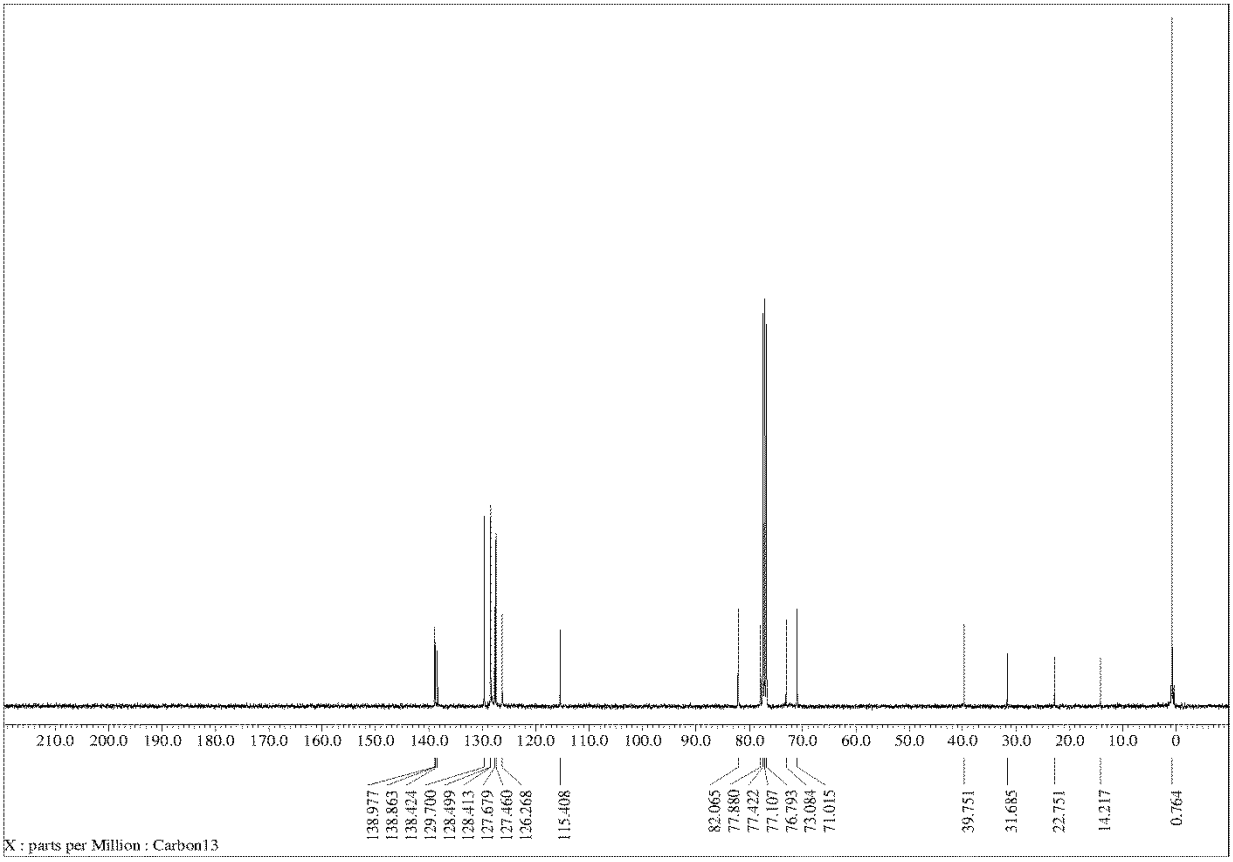

OSi
OH
Ph
27
OBn
27.48
9.10
2.07
2.04
1.01
1.00
0.99
0.97
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.277
7.247
7.234
7.215
7.196
7.174
7.170
7.156
6.747
6.742
6.730
6.723
4.368
4.341
4.247
4.220
4.111
4.101
4.094
4.085
3.491
3.471
3.144
2.928
2.920
2.761
2.738
1.550
1.249
0.877
0.822
0.261
0.253
0.244
0.119
0.095
X : parts per Million : Proton

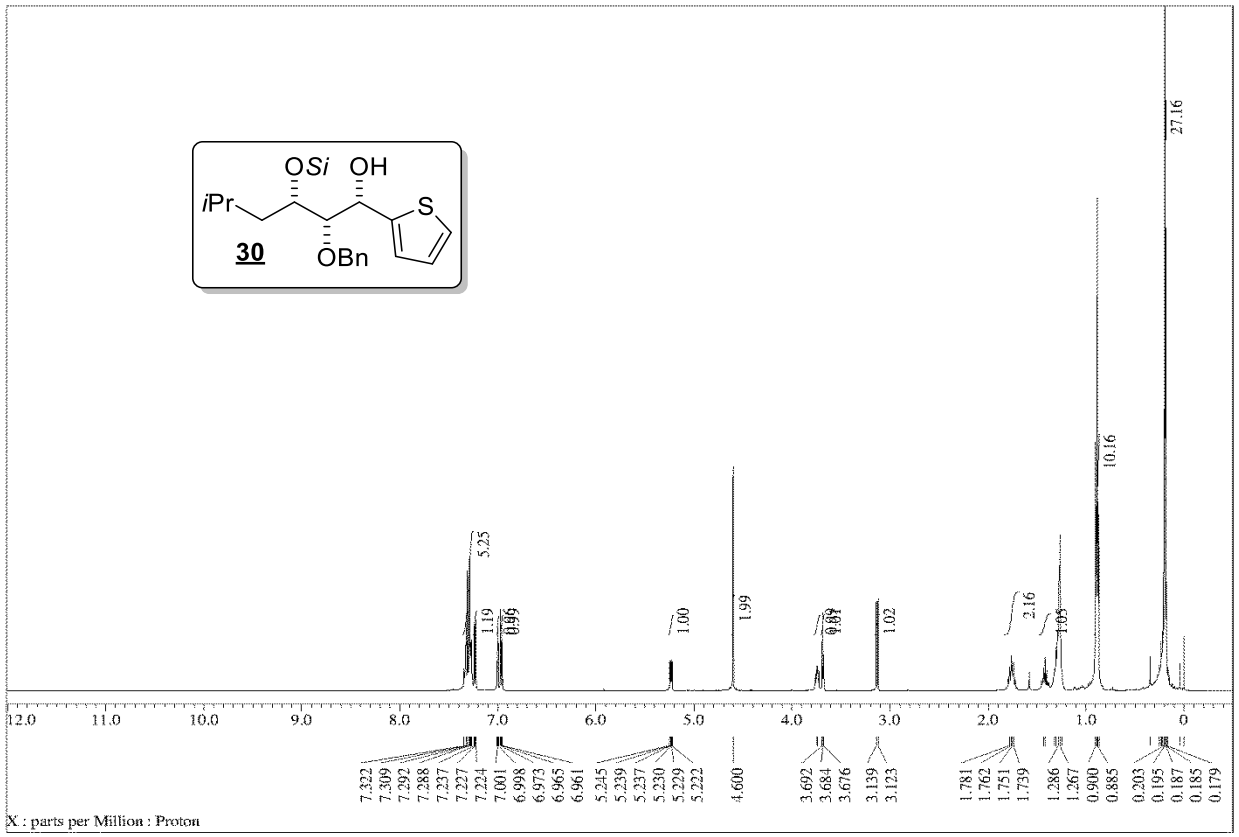

210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
138.892
137.595
129.300
128.384
128.032
127.488
125.867
78.623
77.413
77.098
76.783
75.782
75.029
72.054
39.617
35.108
26.345
0.840
X : parts per Million : Carbon13

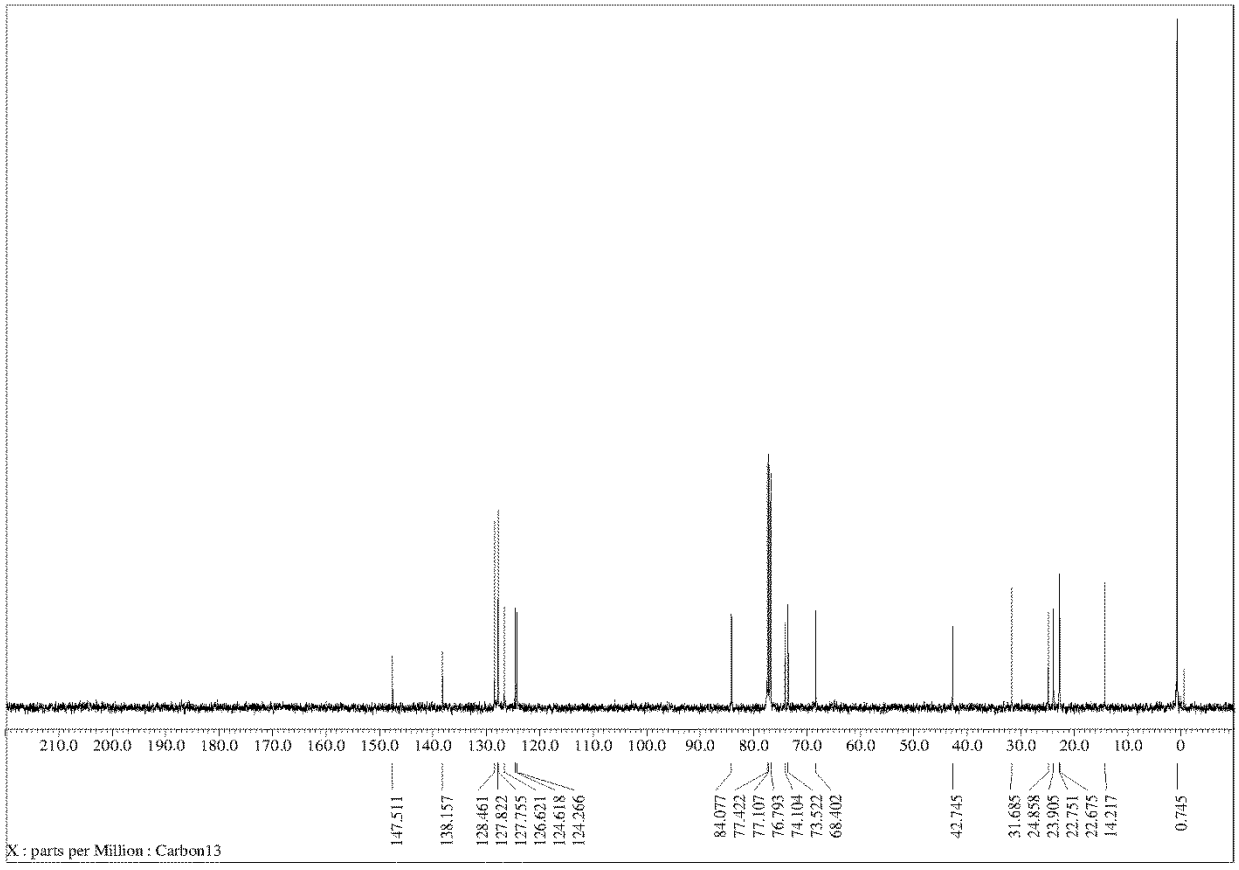

OSi
OH
Ph
Ph
28
OBn
16.48
1.61
0.85
1.05
1.17
1.00
0.90
1.29
0.92
1.76
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.276
7.253
7.249
7.246
7.240
7.224
7.213
7.198
7.177
7.158
6.999
6.991
6.982
4.907
4.321
4.231
4.009
3.997
3.442
3.434
3.132
3.109
3.097
3.075
2.954
2.943
1.311
1.246
0.892
0.888
0.225
0.223
0.180
0.176
0.173
X : parts per Million : Proton

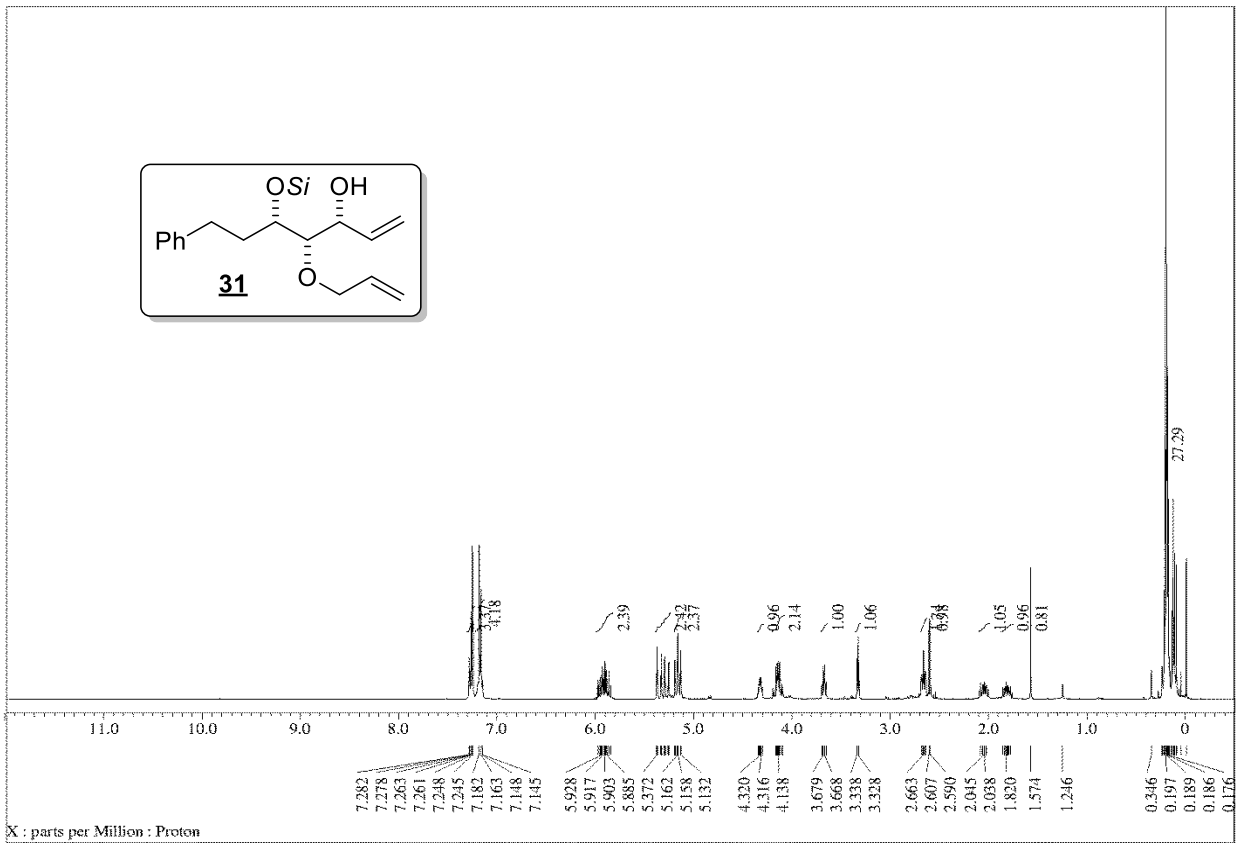

210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
138.186
129.529
128.537
128.289
128.213
127.412
127.364
127.250
126.325
126.153
83.219
77.413
77.088
76.774
73.313
72.350
39.884
0.821
-0.304
-0.523
X : parts per Million : Carbon13

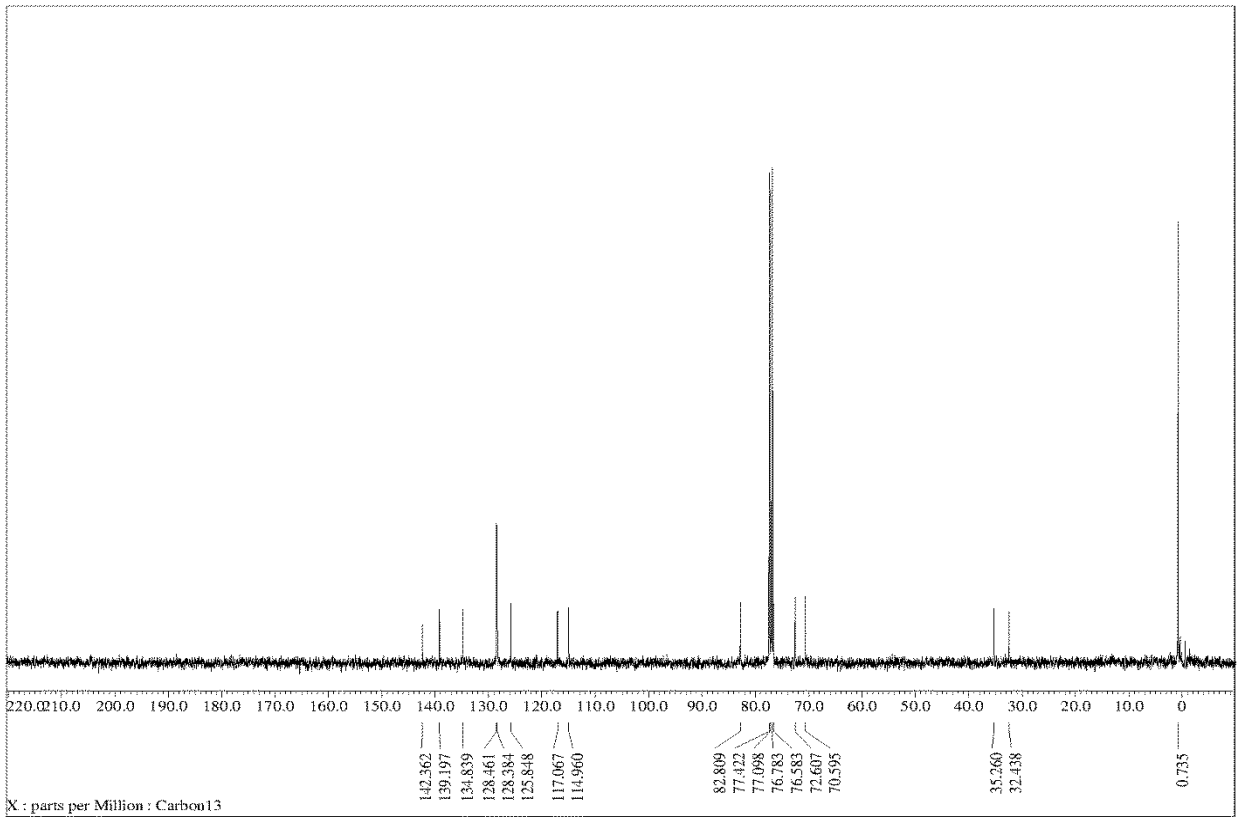

OSi
OH
Ph
29
OBn
28.02
10.95
1.01
1.00
1.03
3.96
1.03
1.05
1.00
1.02
1.00
1.01
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.318
7.300
7.258
7.246
7.241
7.226
7.222
7.205
7.192
7.187
5.871
5.858
5.844
5.832
5.362
5.146
4.624
4.595
4.575
3.986
3.976
3.312
3.302
3.074
2.896
2.628
2.612
1.582
1.264
0.882
0.864
0.228
0.187
0.180
0.172
0.153
X : parts per Million : Proton


210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
138.977
138.863
138.424
129.700
128.499
128.413
127.679
127.460
126.268
115.408
82.065
77.880
77.422
77.107
76.793
73.084
71.015
39.751
31.685
22.751
14.217
0.764
X : parts per Million : Carbon13


OSi
OH
iPr
S
30
OBn
27.16
10.16
5.25
2.16
1.03
1.99
1.00
1.02
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.322 7.309 7.292 7.288 7.237 7.227 7.224 7.001 6.998 6.973 6.965 6.961
5.245 5.239 5.237 5.230 5.229 5.222
4.600
3.692 3.684 3.676
3.139 3.123
1.781 1.762 1.751 1.739
1.286 1.267
0.900 0.885
0.203 0.195 0.187 0.185 0.179
X : parts per Million : Proton


210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
147.511
138.157
128.461 127.822 127.755 126.621 124.618 124.266
84.077 77.422 77.107 76.793 74.104 73.522 68.402
42.745
31.685 24.858 23.905 22.751 22.675 14.217
0.745
X : parts per Million : Carbon13


OSi
OH
Ph
O
31
27.29
2.39
7.42
7.37
4.18
0.96
2.14
1.00
1.06
1.05
0.96
0.81
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.282
7.278
7.263
7.261
7.248
7.245
7.182
7.163
7.148
7.145
5.928
5.917
5.903
5.885
5.372
5.162
5.158
5.132
4.320
4.316
4.138
3.679
3.668
3.338
3.328
2.663
2.607
2.590
2.045
2.038
1.820
1.574
1.246
0.346
0.197
0.189
0.186
0.176
X : parts per Million : Proton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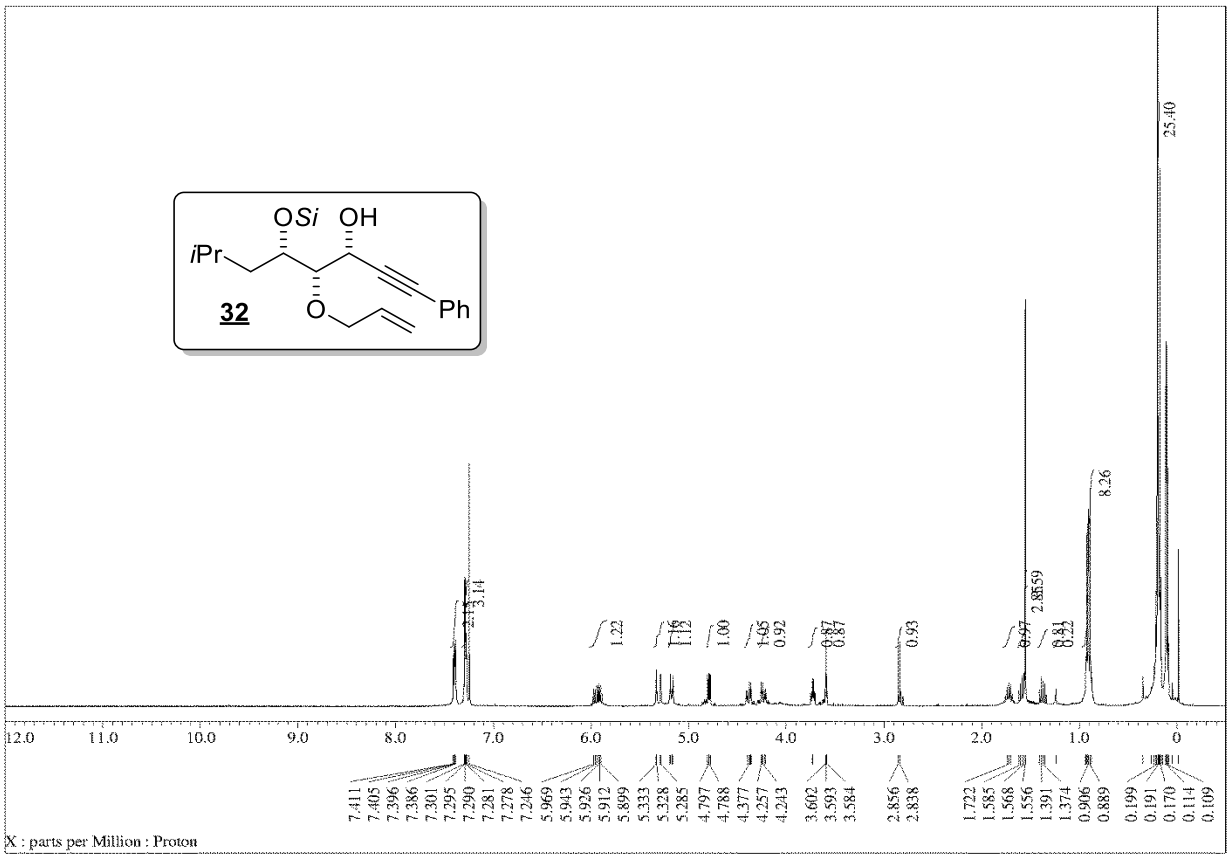
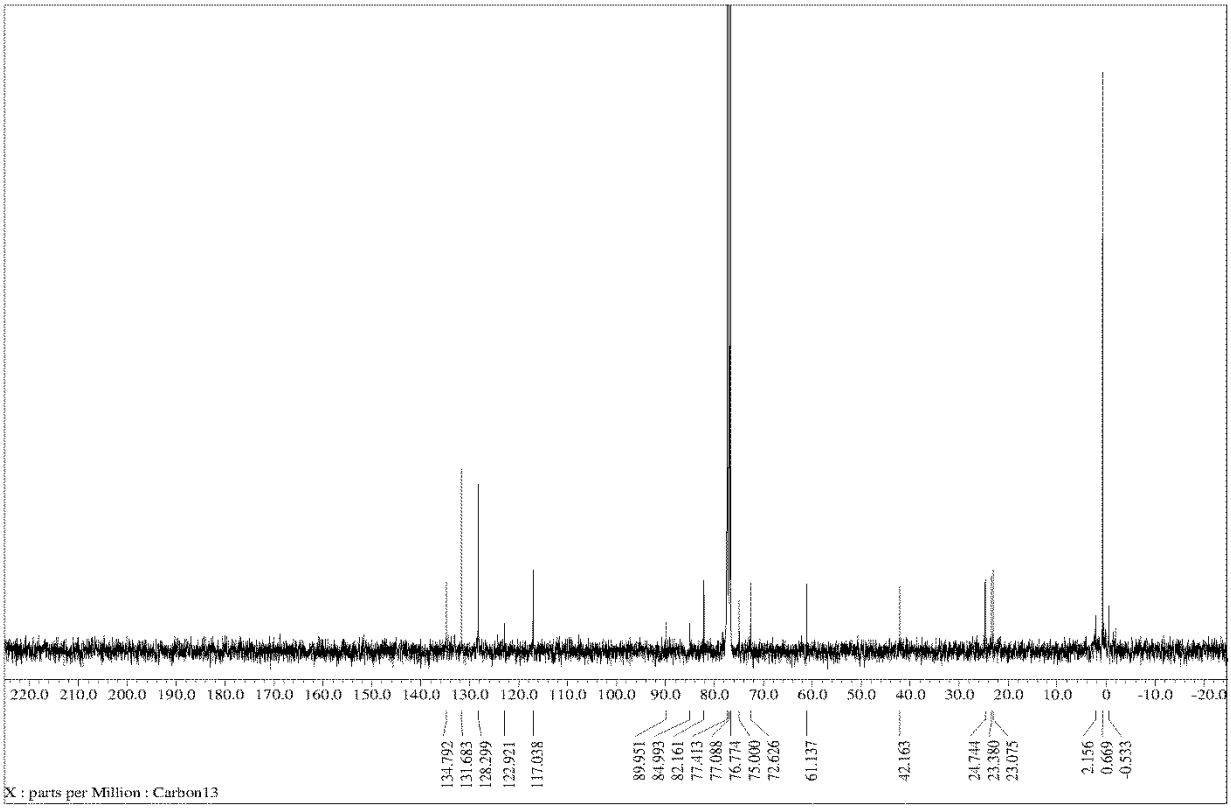
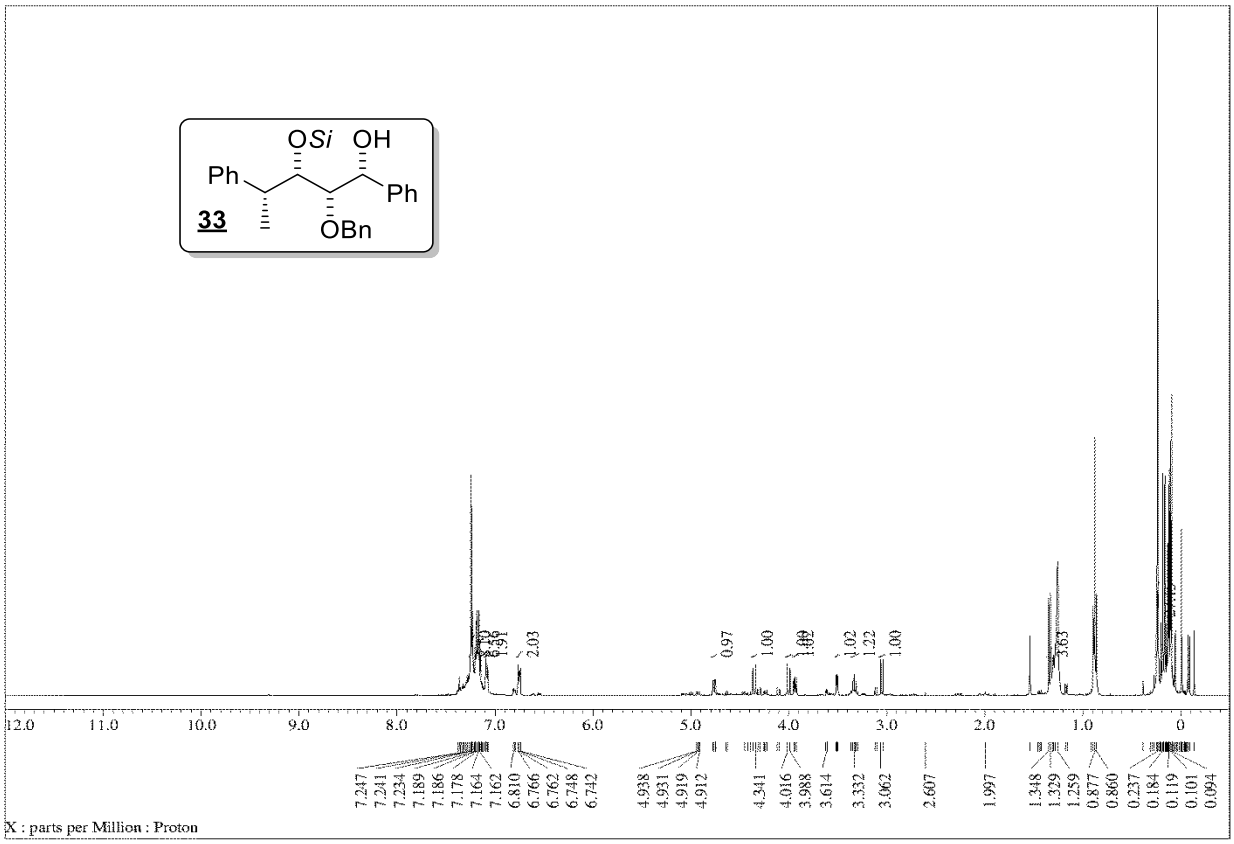
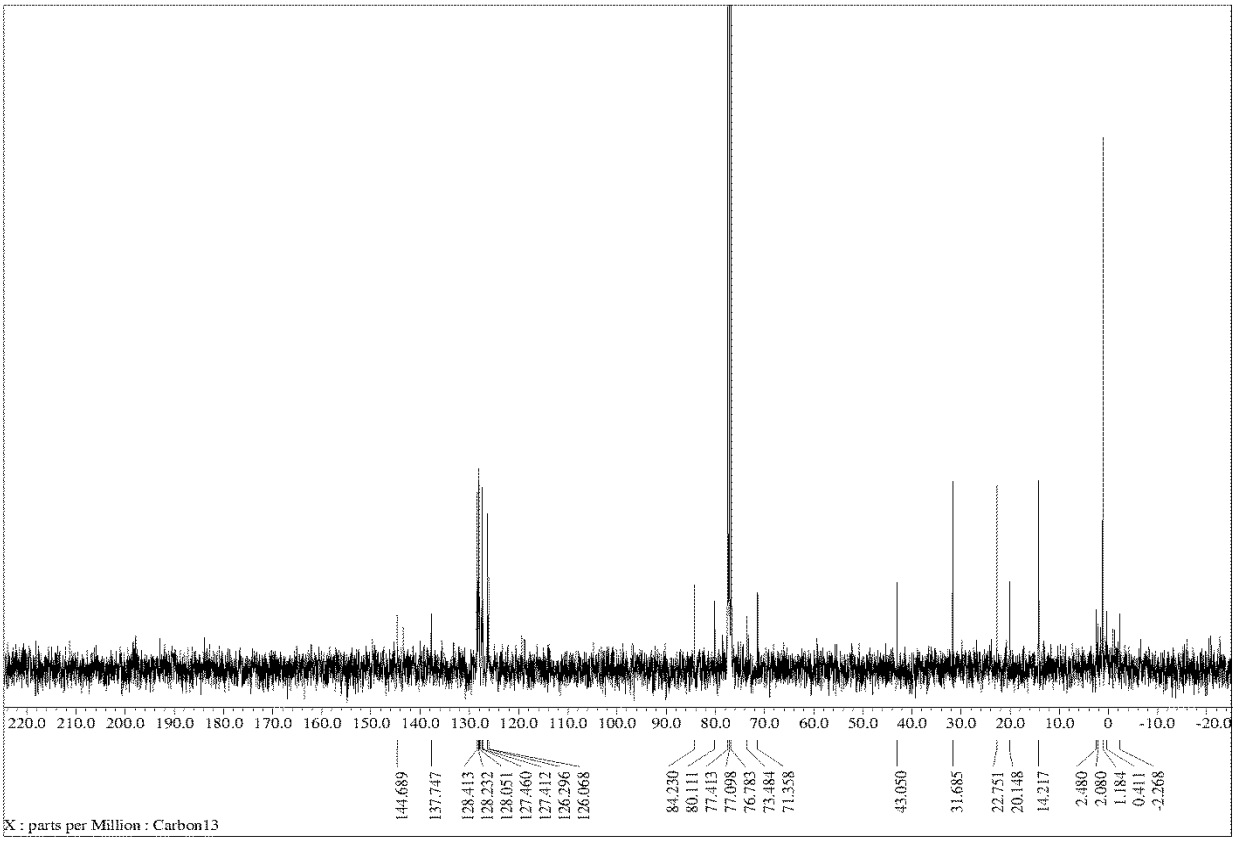
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
142.362
139.197
134.839
128.461
128.384
125.848
117.067
114.960
82.809
77.422
77.098
76.783
76.583
72.607
70.595
35.260
32.438
0.735
X : parts per Million : Carbon13


OSi
OH
iPr
32
O
Ph
25.40
8.26
1.22
1.00
0.92
0.93
3.14
X : parts per Million : Proton


134.792
131.683
128.299
122.921
117.038
89.951
84.993
82.161
77.413
77.088
76.774
75.000
72.626
61.137
42.163
24.744
23.380
23.075
2.156
0.669
-0.533
X : parts per Million : Carbon13


OSi
OH
Ph
Ph
33
OBn
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.247 7.241 7.234 7.189 7.186 7.178 7.164 7.162 6.810 6.766 6.762 6.748 6.742
4.938 4.931 4.919 4.912
4.341 4.016 3.988 3.614 3.332 3.062 2.607 1.997 1.348 1.329 1.259 0.877 0.860 0.237 0.184 0.119 0.101 0.094
2.03 0.97 1.00 1.02 1.22 1.00 3.63
X : parts per Million : Proton


220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
144.689 137.747 128.413 128.232 128.051 127.460 127.412 126.296 126.068
84.230 80.111 77.413 77.098 76.783 73.484 71.358
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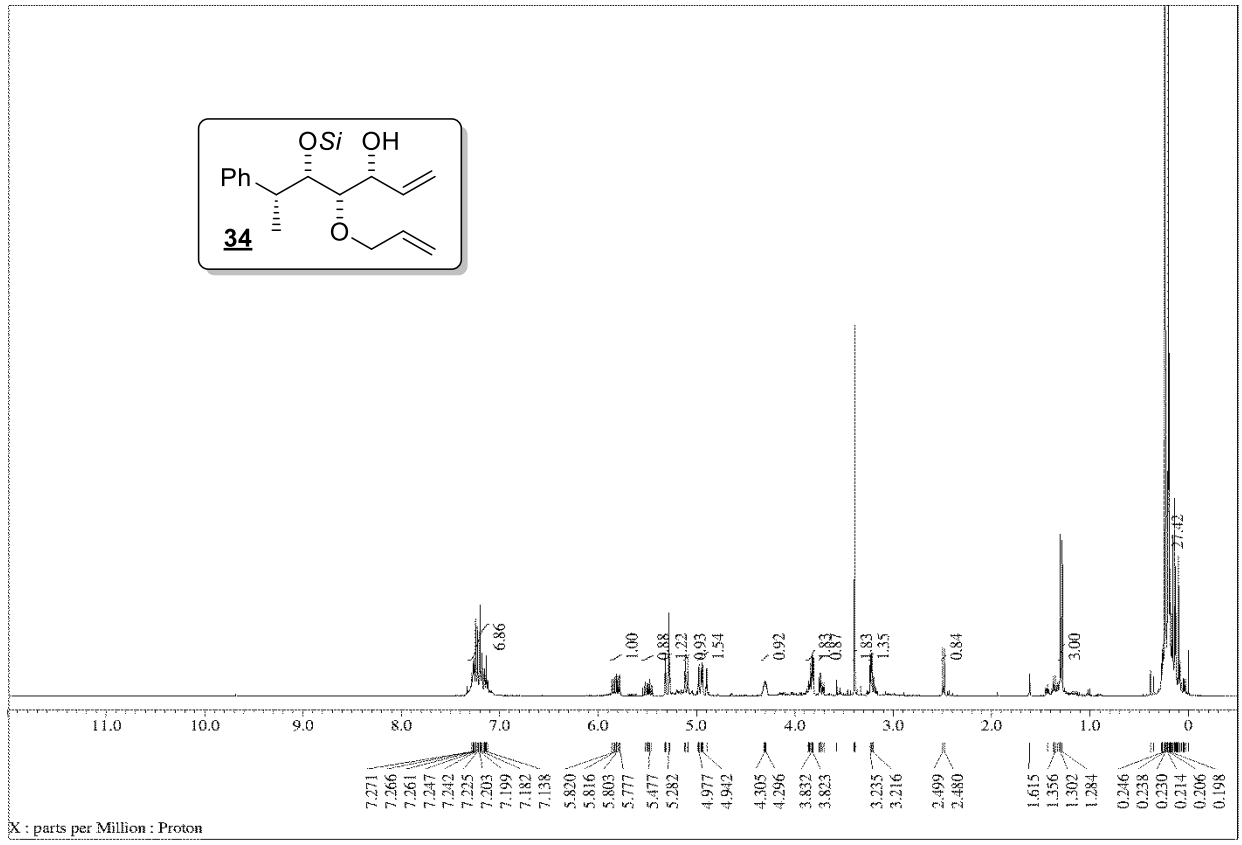
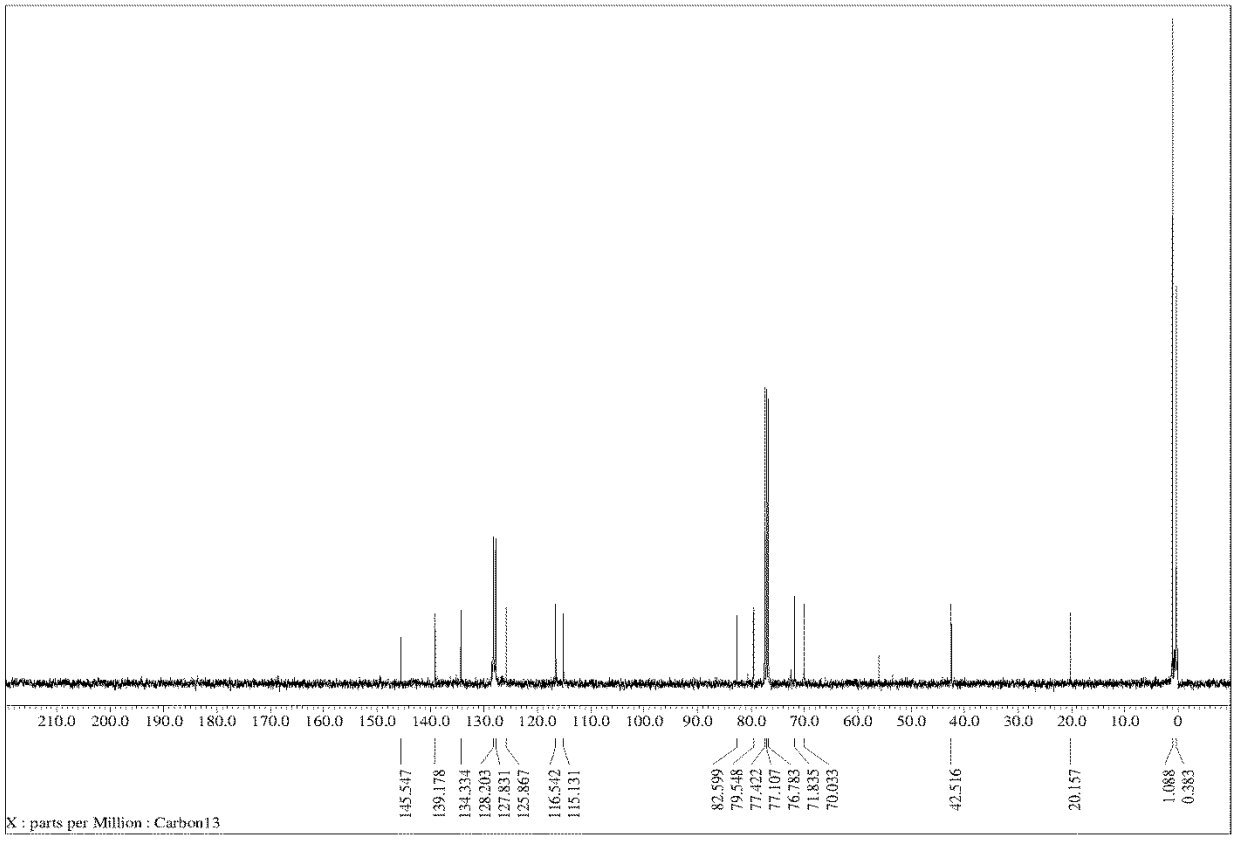
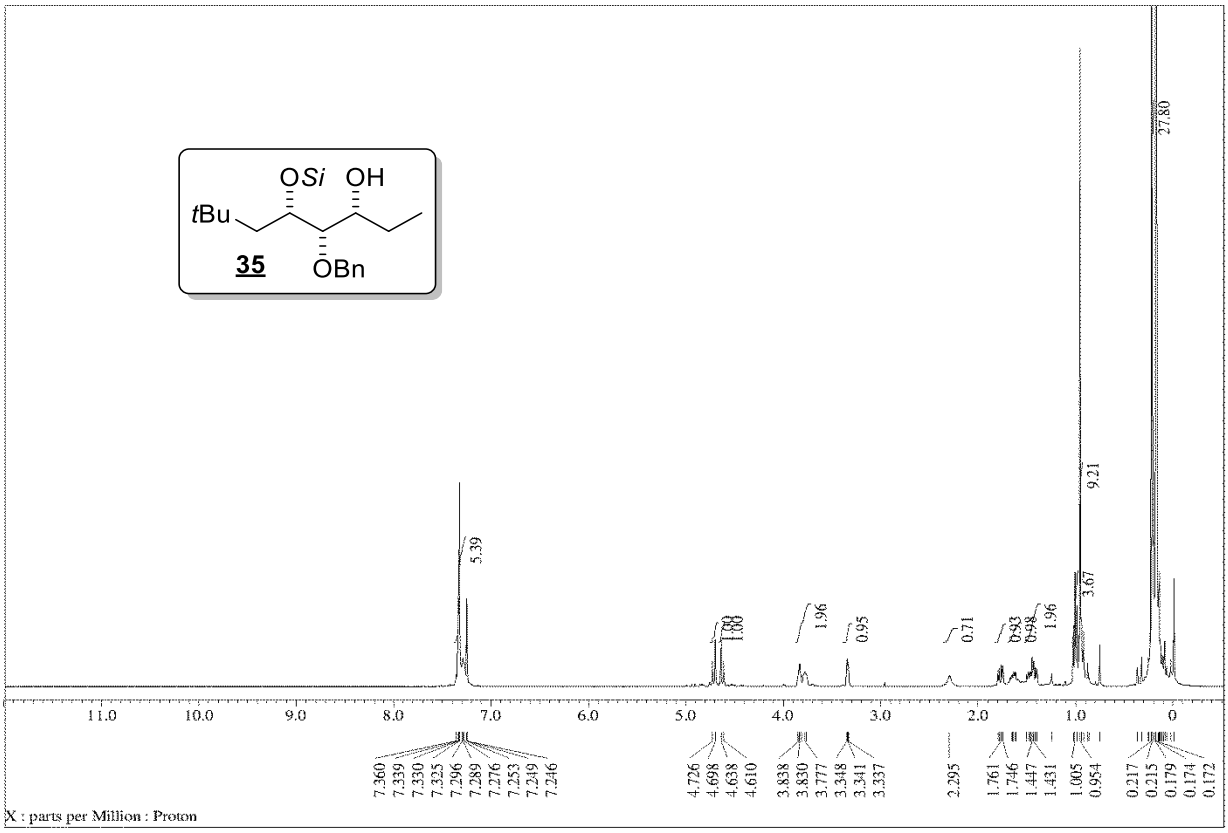
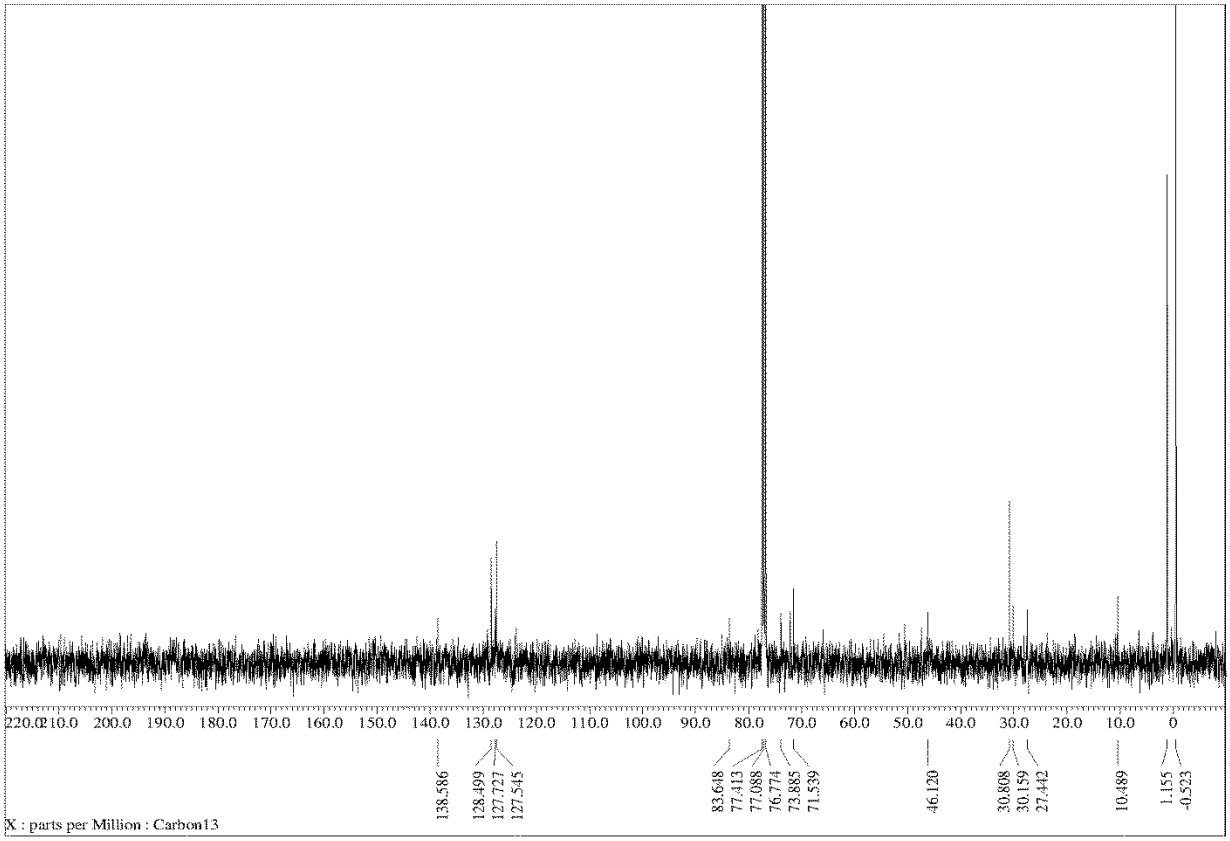
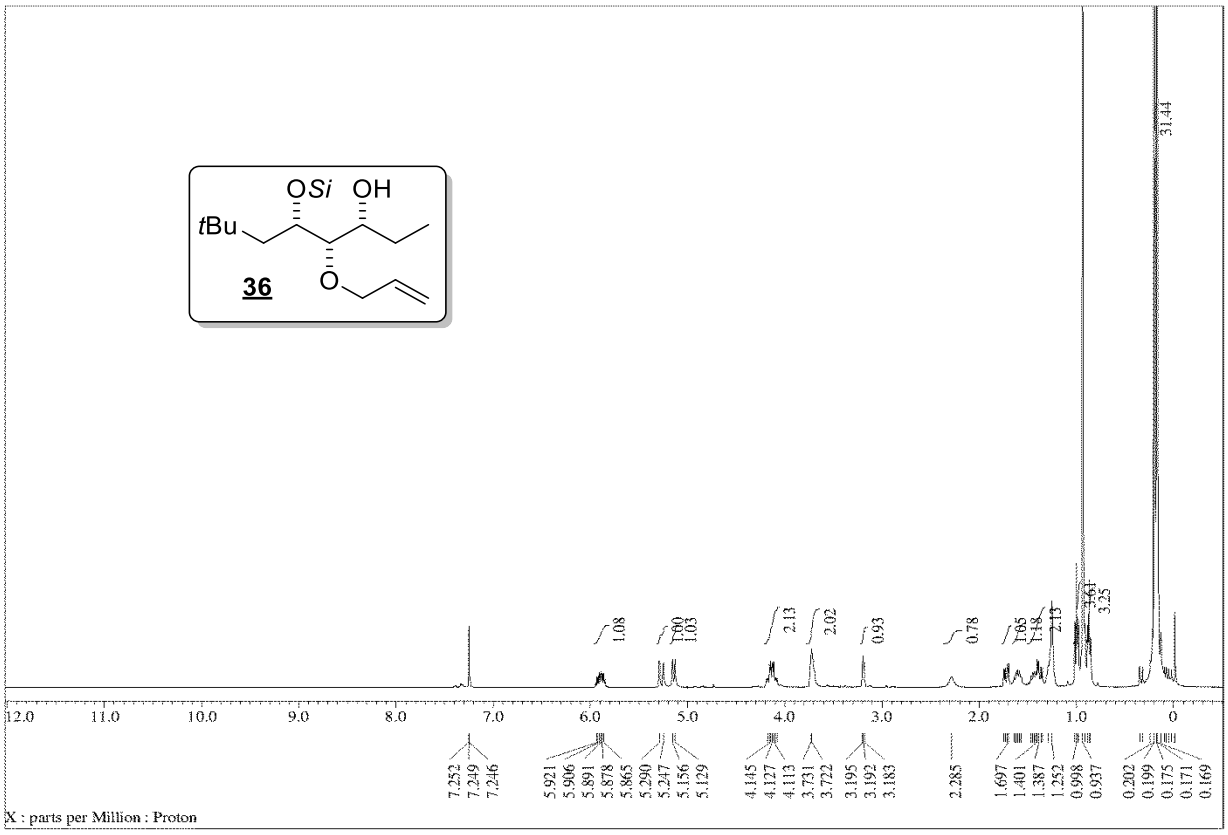
X : parts per Million : Carbon13

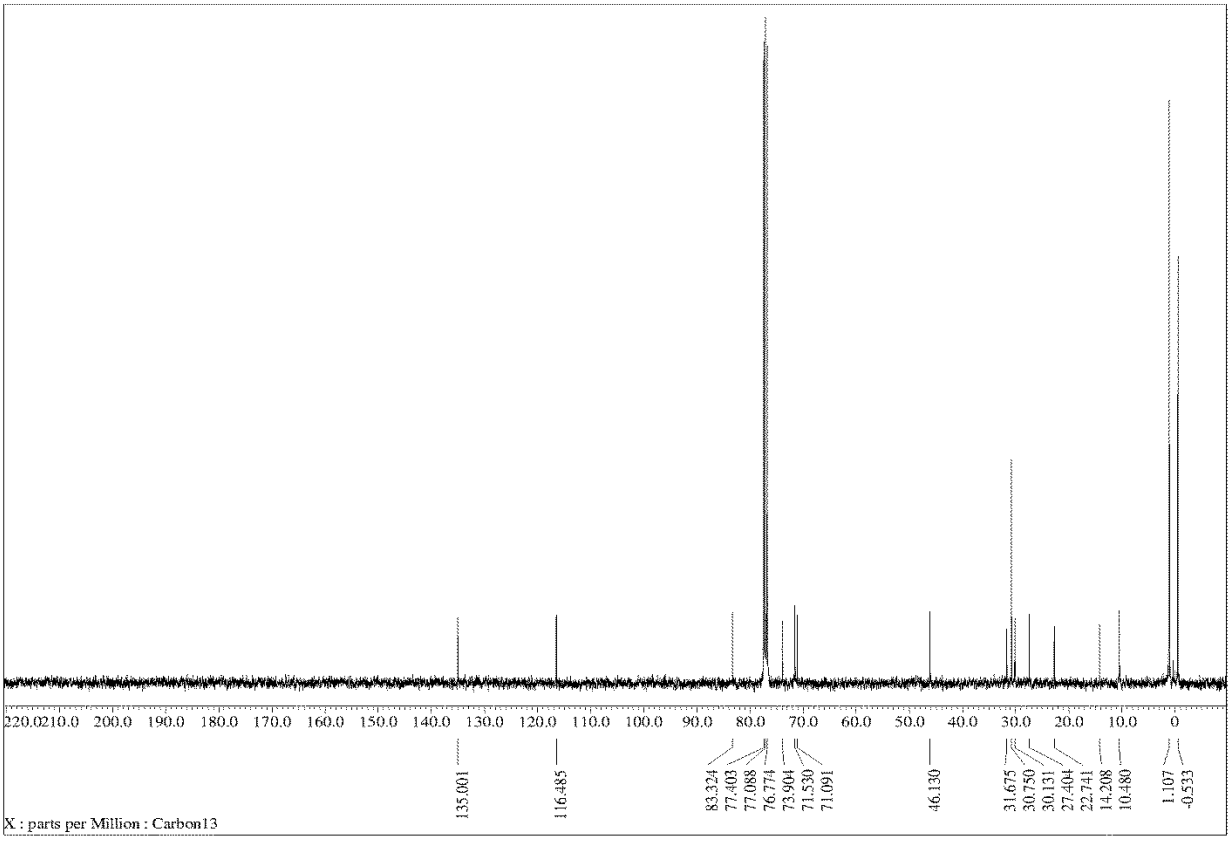

OSi
OH
Ph
O
34
6.86
1.00
0.88
1.22
0.93
1.54
0.92
1.83
0.87
1.83
1.35
0.84
3.00
27.42
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.271
7.266
7.261
7.247
7.242
7.225
7.203
7.199
7.182
7.138
5.820
5.816
5.803
5.777
5.477
5.282
4.977
4.942
4.305
4.296
3.832
3.823
3.235
3.216
2.499
2.480
1.615
1.356
1.302
1.284
0.246
0.238
0.230
0.214
0.206
0.198
X : parts per Million : Proton

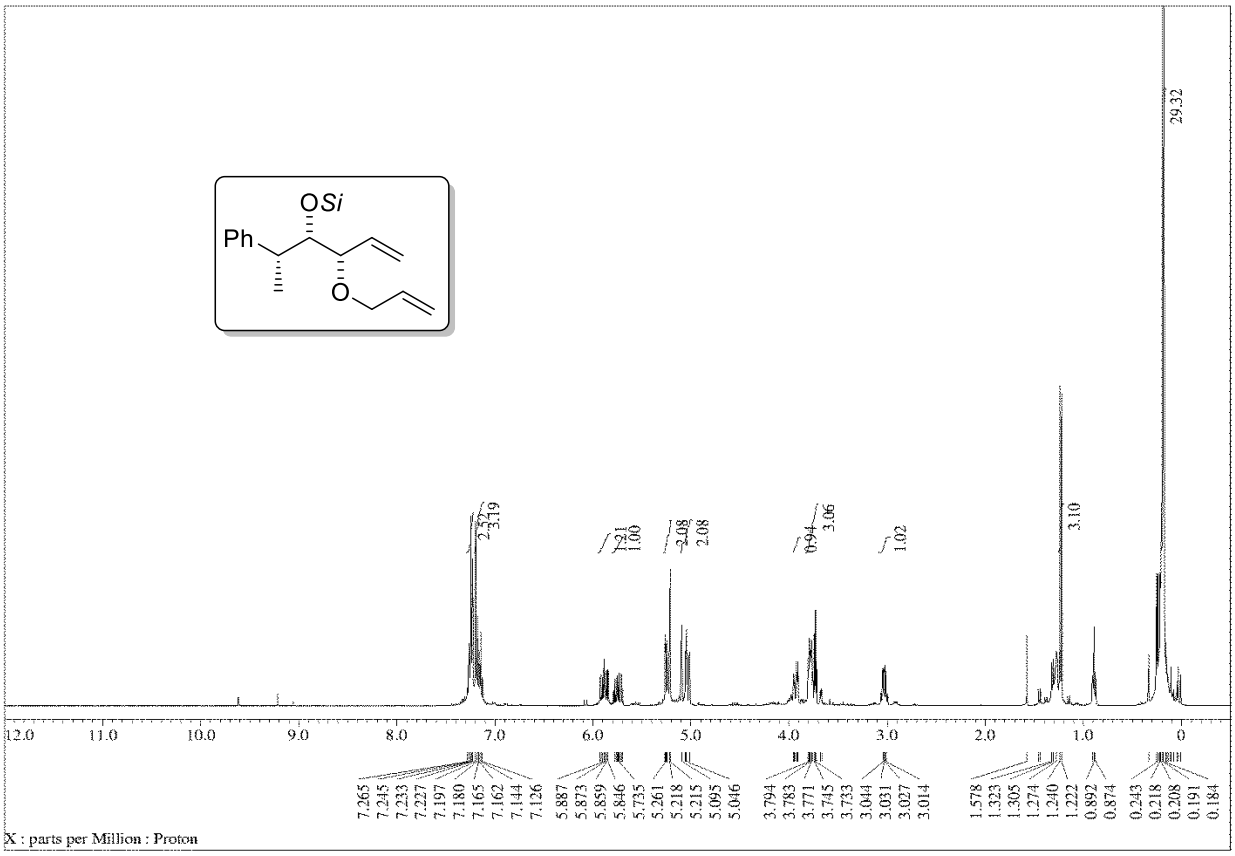

210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
145.547
139.178
134.334
128.203
127.831
125.867
116.542
115.131
82.599
79.548
77.422
77.107
76.783
71.835
70.033
42.516
20.157
1.088
0.383
X : parts per Million : Carbon13

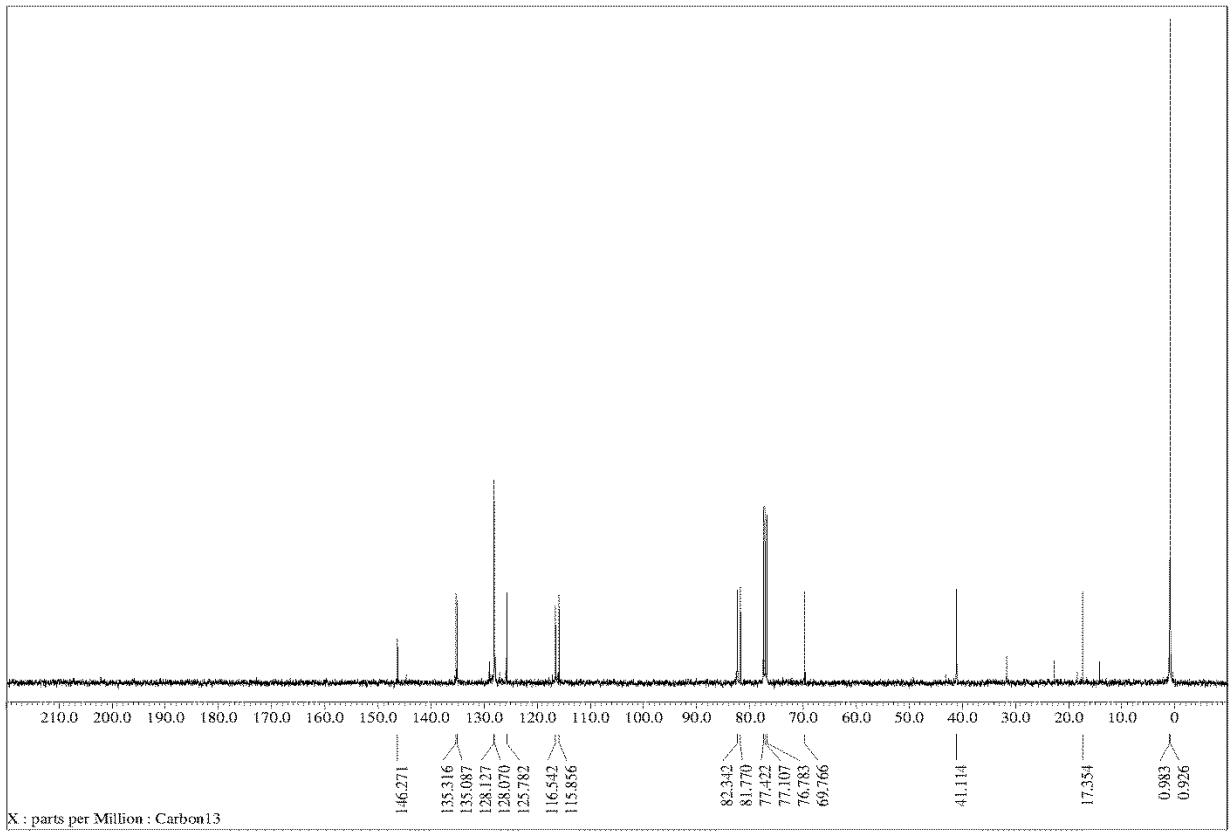

OSi
OH
tBu
35
OBn
X : parts per Million : Proton

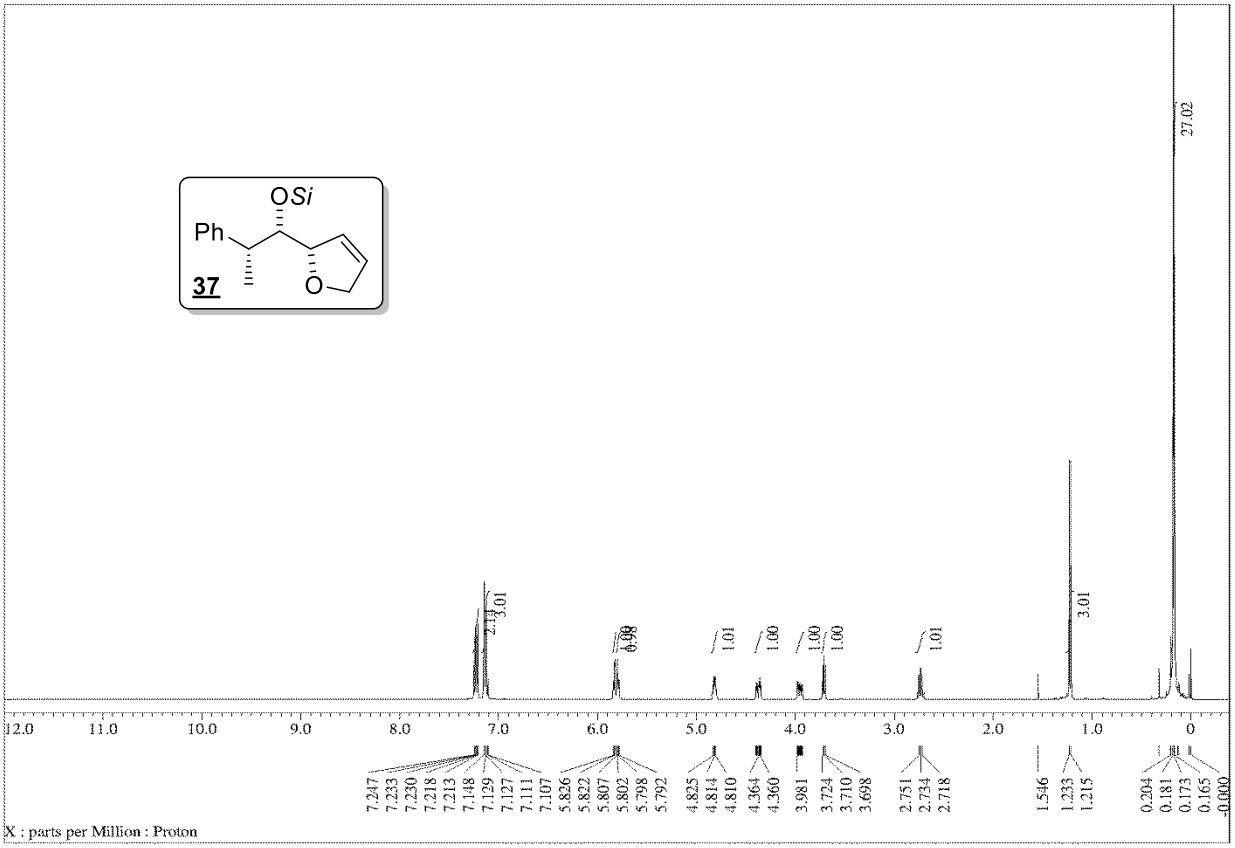

X : parts per Million : Carbon13

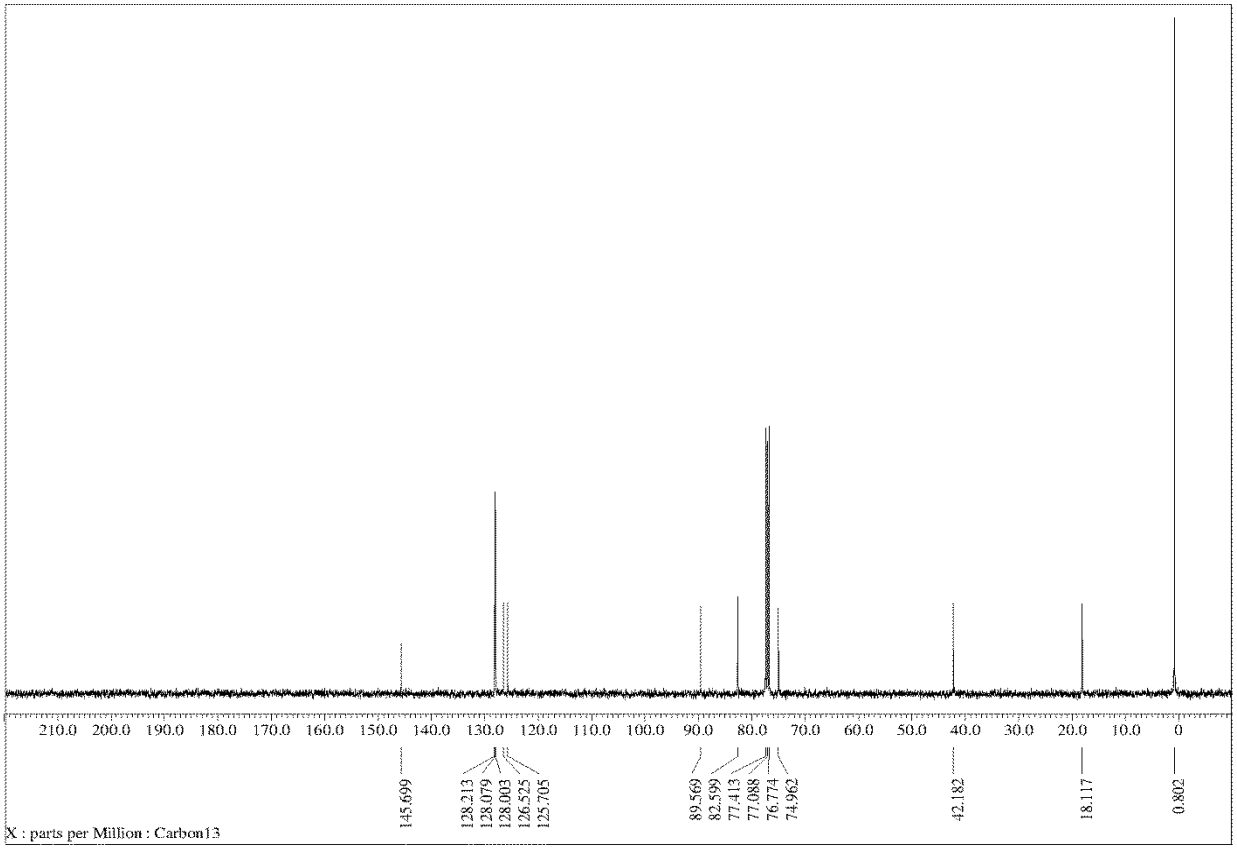

OSi
OH
tBu
O
36
31.44
1.08
1.00
1.03
2.13
2.02
0.93
0.78
1.66
1.18
2.13
3.61
3.25
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.252
7.249
7.246
5.921
5.906
5.891
5.878
5.865
5.290
5.247
5.156
5.129
4.145
4.127
4.113
3.731
3.722
3.195
3.192
3.183
2.285
1.697
1.401
1.387
1.252
0.998
0.937
0.202
0.199
0.175
0.171
0.169
X : parts per Million : Proton

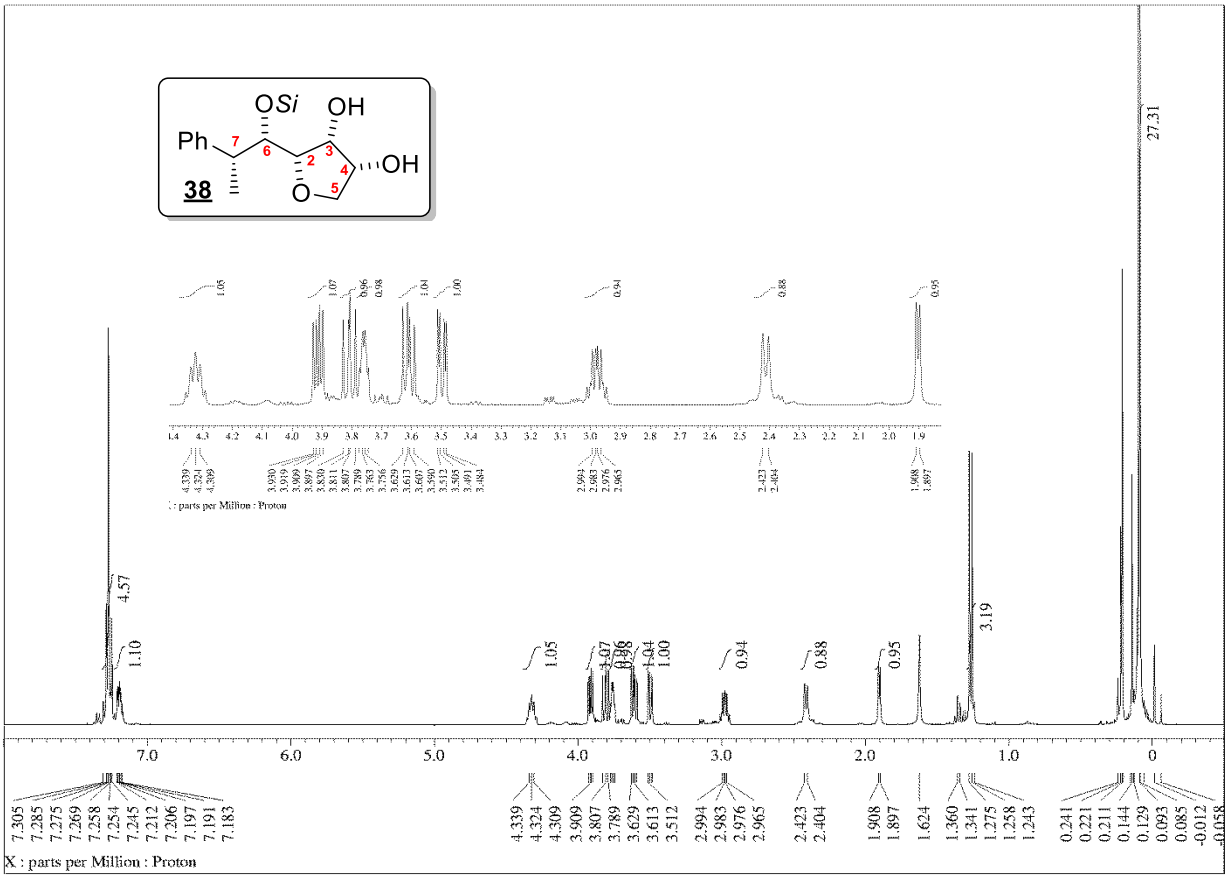

220.0210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
135.001
116.485
83.324
77.403
77.088
76.774
73.904
71.530
71.091
46.130
31.675
30.750
30.131
27.404
22.741
14.208
10.480
1.107
-0.533
X : parts per Million : Carbon13

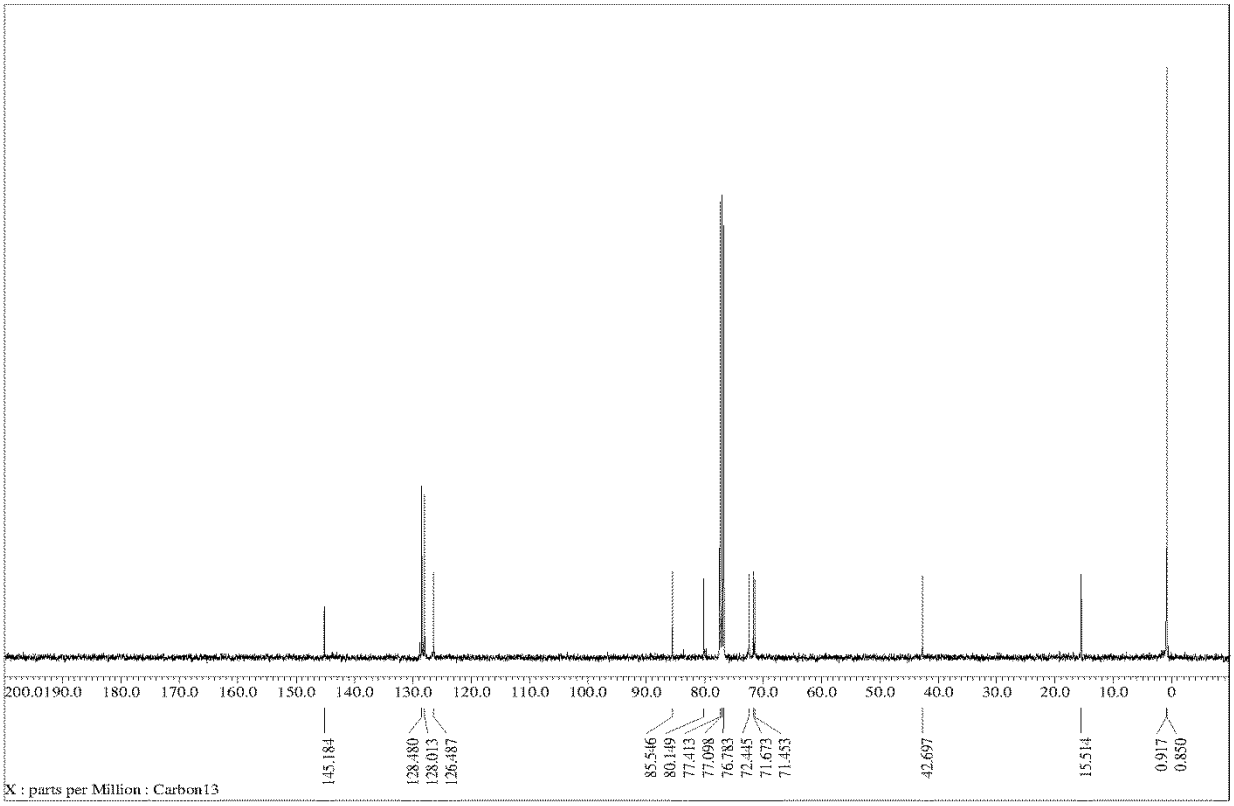

OSi
Ph
O
29.32
3.10
3.06
2.37
3.19
2.08
2.08
1.21
1.00
1.02
0.94
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.265
7.245
7.233
7.227
7.197
7.180
7.165
7.162
7.144
7.126
5.887
5.873
5.859
5.846
5.735
5.261
5.218
5.215
5.095
5.046
3.794
3.783
3.771
3.745
3.733
3.044
3.031
3.027
3.014
1.578
1.323
1.305
1.274
1.240
1.222
0.892
0.874
0.243
0.218
0.208
0.191
0.184
X : parts per Million : Proton


210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
146.271
135.316
135.087
128.127
128.070
125.782
116.542
115.856
82.342
81.770
77.422
77.107
76.783
69.766
41.114
17.354
0.983
0.926
X : parts per Million : Carbon13

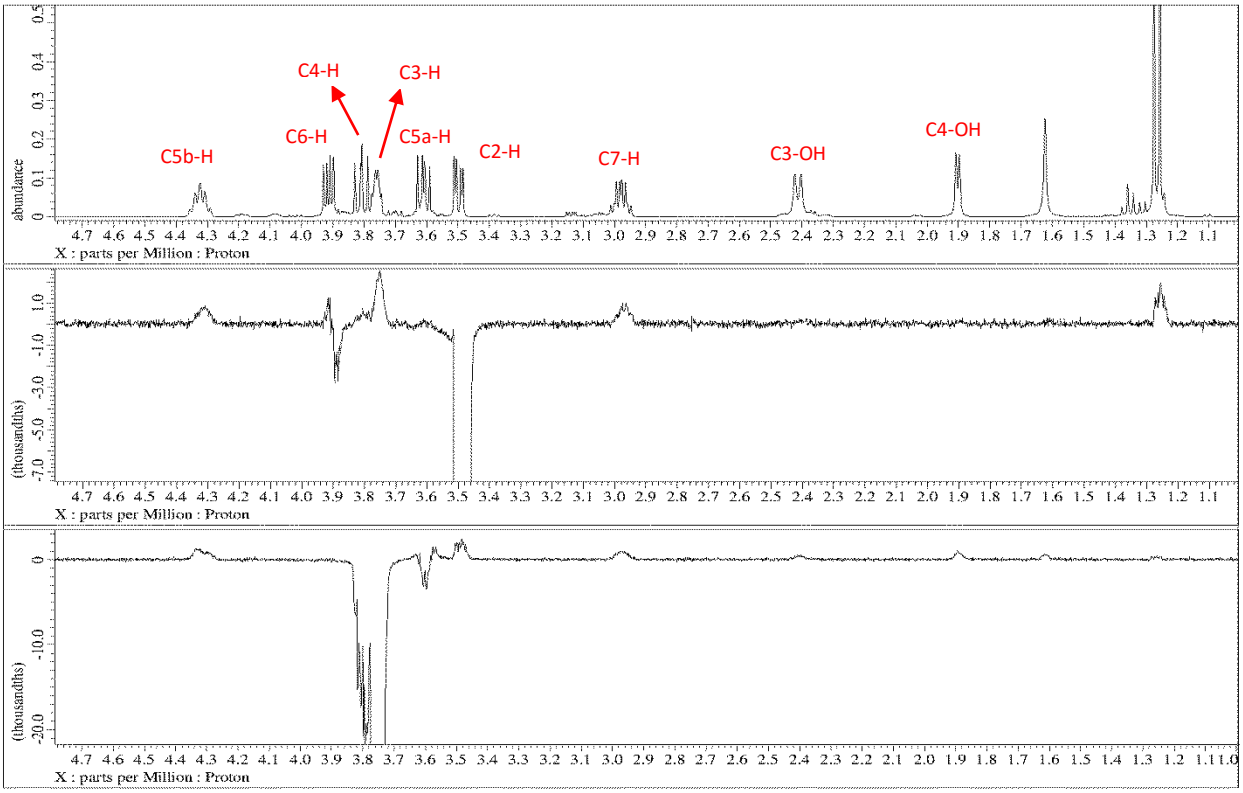

OSi
Ph
37
O
27.02
3.01
2.13
3.01
0.98
0.98
1.01
1.00
1.00
1.00
1.01
3.01
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.247
7.233
7.230
7.218
7.213
7.148
7.129
7.127
7.111
7.107
5.826
5.822
5.807
5.802
5.798
5.792
4.825
4.814
4.810
4.364
4.360
3.981
3.724
3.710
3.698
2.751
2.734
2.718
1.546
1.233
1.215
0.204
0.181
0.173
0.165
-0.000
X : parts per Million : Proton


210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
145.699
128.213
128.079
128.003
126.525
125.705
89.569
82.599
77.413
77.088
76.774
74.962
42.182
18.117
0.802
X : parts per Million : Carbon13

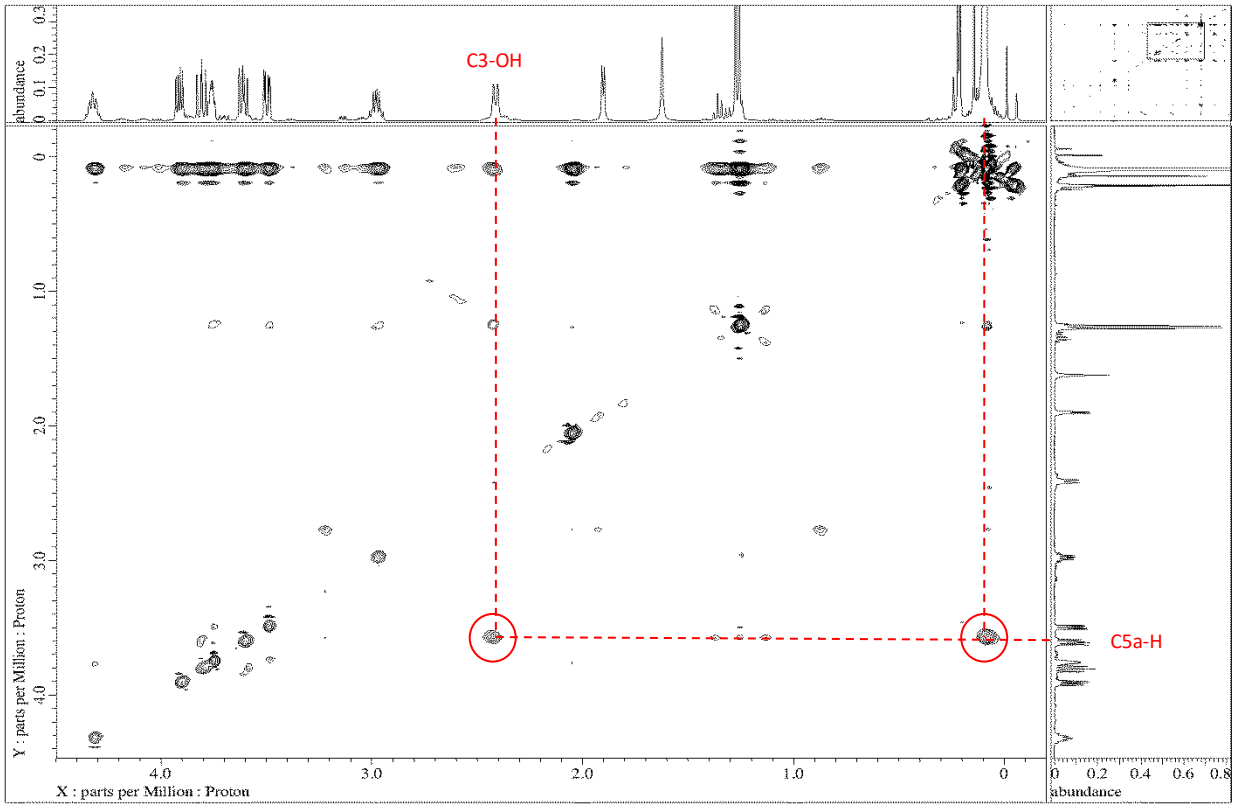

OSi
OH
Ph
OH
O
38
X : parts per Million : Proton

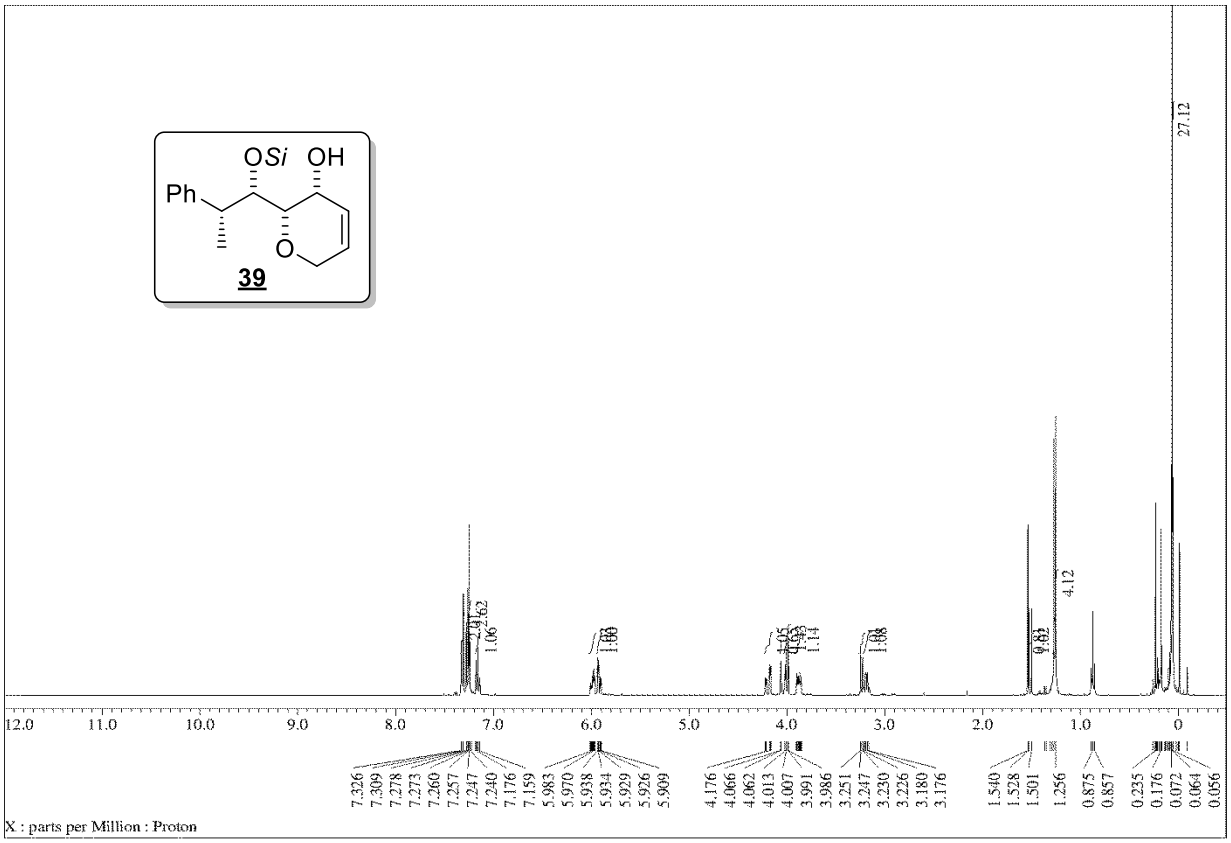

X : parts per Million : Carbon13

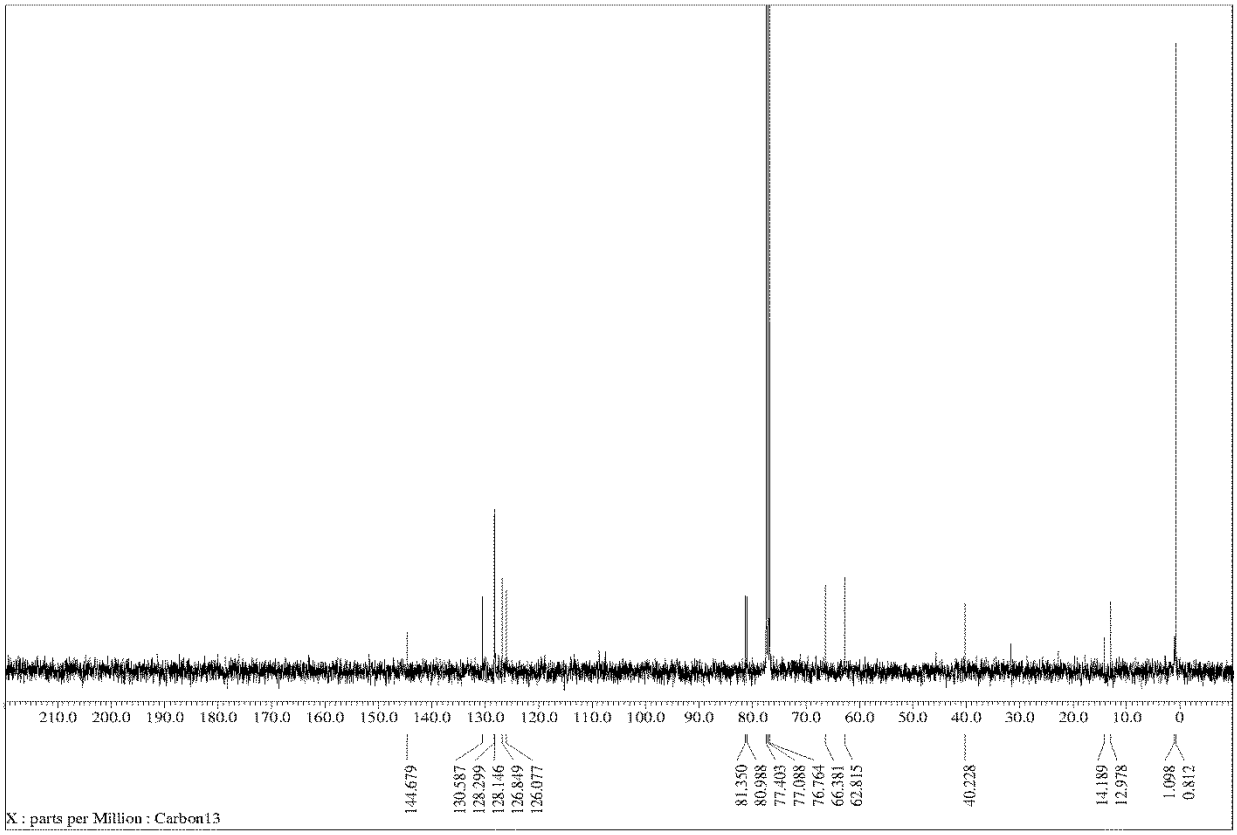
NOE Experiment :

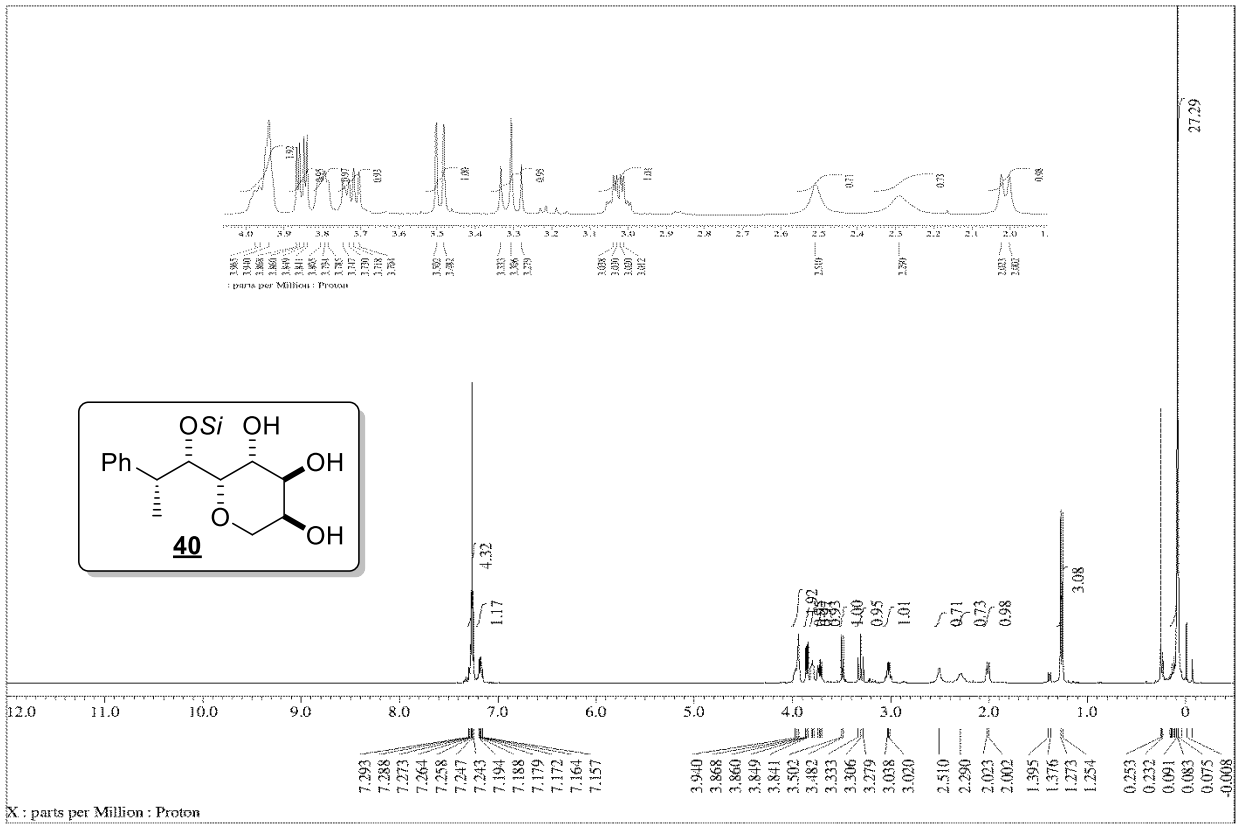


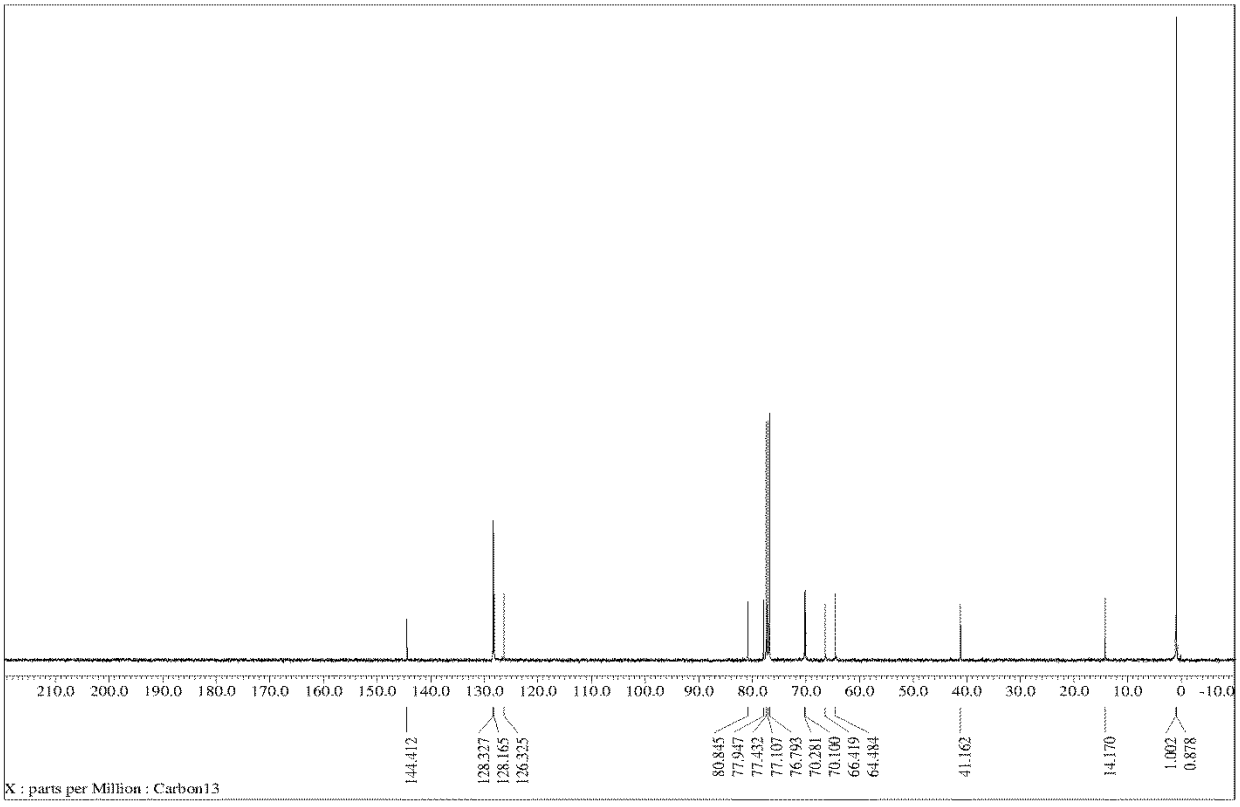
NOESY Experiment :



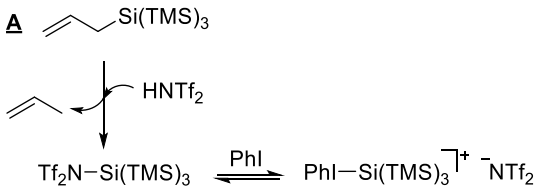

OSi
OH
Ph
O
39
27.12
4.12
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.326 7.309 7.278 7.273 7.260 7.257 7.247 7.240 7.176 7.159
5.983 5.970 5.938 5.934 5.929 5.926 5.909
4.176 4.066 4.062 4.013 4.007 3.991 3.986
3.251 3.247 3.230 3.226 3.180 3.176
1.540 1.528 1.501 1.256 0.875 0.857
0.235 0.176 0.072 0.064 0.056
X : parts per Million : Proton


210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
144.679
130.587 128.299 128.146 126.849 126.077
81.350 80.988 77.403 77.088 76.764 66.381 62.815
40.228
14.189 12.978
1.098 0.812
X : parts per Million : Carbon13

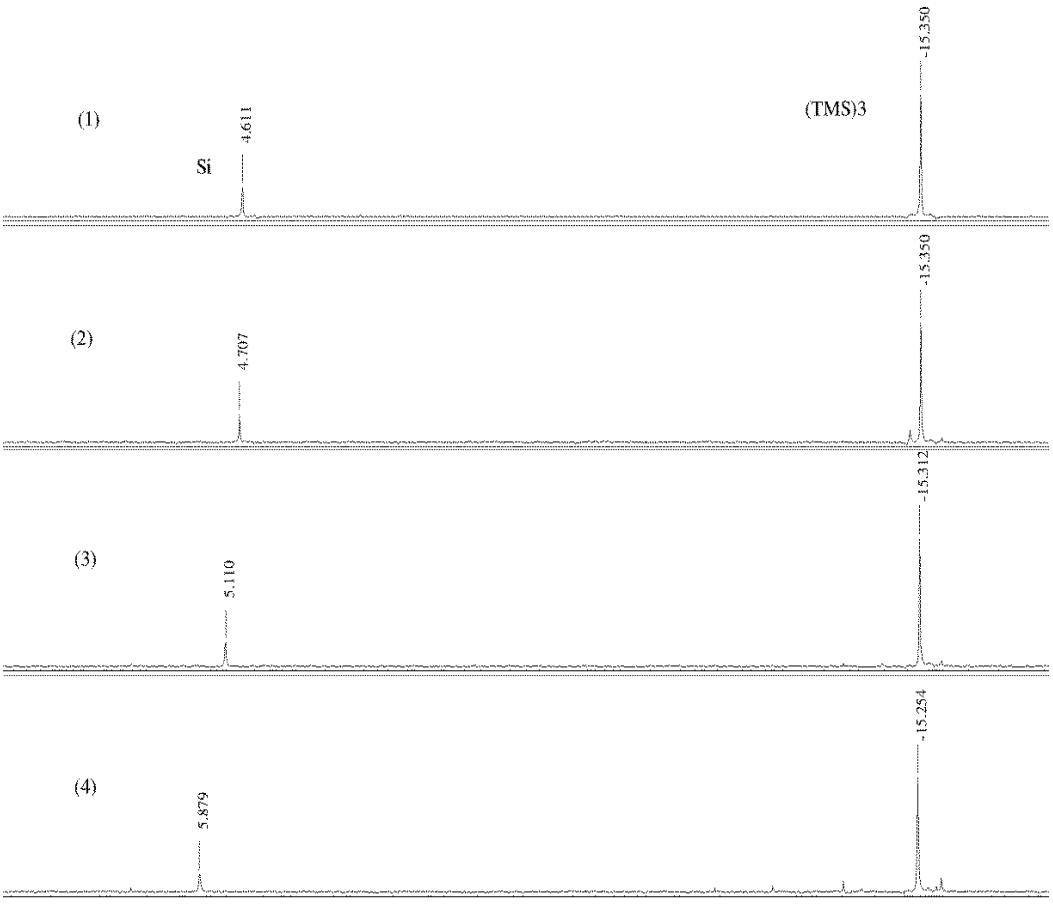

OSi
OH
Ph
OH
O
OH
40
X : parts per Million : Proton


X : parts per Million : Carbon13

8. ^{29}Si NMR study on the influence of iodobenzene



Influence of stoicheometrie



spectra (1) : reference ^{29}Si NMR spectra of substrate test in presence of triflimide

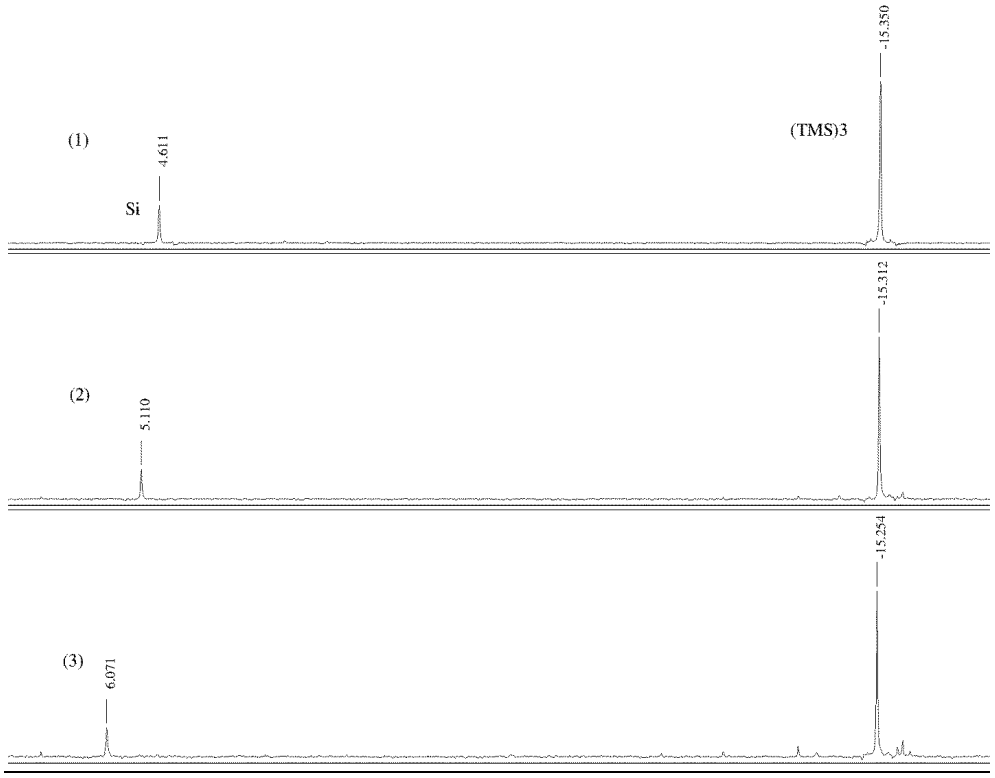
spectra (2) : 1 mmol of substrate **A**, 0.1 equiv. of iodobenzene and 1 mol% of $HNTf_2$ were successively added to NMR test tube.

spectra (3) : 1 mmol of substrate **A**, 1 equiv. of iodobenzene and 1 mol% of $HNTf_2$ were successively added to NMR test tube.

spectra (4) : 1 mmol of substrate **A**, 1.5 equiv. of iodobenzene and 1 mol% of $HNTf_2$ were successively added to NMR test tube.

All ^{29}Si NMR were performed in CD_2Cl_2 at room temperature and under nitrogen atmosphere.

Influence of reaction time



spectra (1) : reference ^{29}Si NMR spectra of substrate test in presence of triflimide

spectra (2) : 1 mmol of substrate **A**, 1 equiv. of iodobenzene and of $HNTf_2$ were successively added to NMR test tube. Spectra registered After 1 min of addition of $HNTf_2$.

spectra (3) : 1 mmol of substrate **A**, 1 equiv. of iodobenzene and of $HNTf_2$ were successively added to NMR test tube. Spectra registered After 45 min of addition of $HNTf_2$.

All ^{29}Si NMR were performed in CD_2Cl_2 at room temperature and under nitrogen atmosphere. 1 mol% of $HNTf_2$ was used.