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Synthesis of Linear Tetraquinane by [3+2] Cycloaddition, Chemoselective Allylation of 7-Ketonorbornene and Ring-Rearrangement Metathesis as Key Steps

Sambasivarao Kotha*[,a]
Arpit Agrawal [a]

[a] Indian Institute of Technology, Bombay, Powai, Mumbai, Maharashtra, India – 400076, Email: srk@chem.iitb.ac.in

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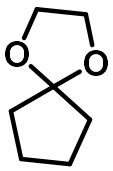
1. EXPERIMENTAL PROCEDURES AND CHARACTERIZATION DATA

General Information

All the reactions were monitored by thin-layer chromatography (TLC) using appropriate solvent systems. Anhydrous tetrahydrofuran (THF) was obtained by distillation from sodium and benzophenone immediately prior to use. Column chromatography was performed by using Acme's silica gel (100–200 mesh) with an appropriate mixture of EtOAc and petroleum ether. Yields refer to samples which are chromatographically isolated. Without further purification, all the commercial grade reagents were used. In general, NMR samples have been analyzed in $CDCl_3$ solvent and chemical changes are recorded as an internal standard in δ values using tetramethylsilane (TMS). The standard abbreviations for singlet, doublet, triplet, quartet, doublet of doublet and multiplet are: s, d, t, q, dd and m. The constants of coupling (*J*) are recorded in Hz. Bruker (AVANCE IIITM) 500 MHz and Bruker (AVANCE IIITM) 400 MHz spectrometers were used to record both ^1H NMR and ^{13}C NMR spectroscopic data. The high-resolution mass measurements were carried out by using an electrospray ionization (ESI) spectrometer. Single-crystal X-ray diffraction data were collected on a diffractometer equipped with graphite monochromated Mo K_α radiation (Bruker instrument). Melting points were recorded on a Veego melting point apparatus.

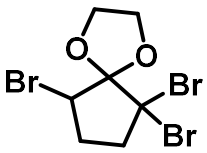
EXPERIMENTAL PROCEDURES

Synthesis of Cyclopentanone ethylene ketal (12)



p-TSA (20 mol%) was added in the solution of cyclopentanone **11** (19 g, 0.23 mmol), ethylene glycol (18.2 g, 0.29 mmol) and benzene (100 ml). The round bottom (RB) flask containing the reaction mixture (RM) was fitted with Dean Stark Apparatus (to collect water produced during the reaction) and refluxed for 25 h. After 25 h the reaction was cooled to room temperature (rt) and benzene was removed carefully under vacuum. The remaining mixture was distilled under vacuum to get pure product **12** (colourless liquid, 23.4 g, 81%).

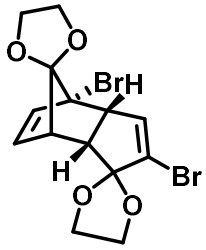
Synthesis of 2,2,5-tribromocyclopentanone ethylene ketal (13)



In a two neck RB flask, compound **12** (15 g, 0.18 mmol) was dissolved in pure dioxane (100 ml) under nitrogen atmosphere and the mixture was cooled to 10 ºC. Keeping the inert atmosphere, Br_2 (58.1 g, 0.36 mmol) was added dropwise with continuous stirring during 1 h at temperature less than 15 ºC. During the reaction there should be continuous flow of nitrogen gas though one neck of the RB flask and a guard tube was placed at the other neck to release the fumes coming out of the reaction. The mixture was stirred for 48 h at room temperature. After 48 h, pour the RM in 5% solution of sodium bicarbonate ($NaHCO_3$) (500 ml) with continuous stirring. Now the RM was extracted three times with ethyl acetate (EtOAc). The organic layer was washed with water, filtered through sodium sulphate (Na_2SO_4) and concentrated to get crude product. The crude product was purified by column chromatography on silica gel, eluting with 100% pet ether (PE) to get pure product **13** (pale green solid, 24.8 g, 58%).

^1H (400 MHz, $CDCl_3$): δ 4.86-4.81 (m, 1H), 4.45-4.34 (m, 4H), 3.07-2.98 (m, 1H), 2.78-2.71 (m, 1H), 2.62-2.51 (m, 1H), 2.14-2.05 (m, 1H). **^{13}C (100 MHz, $CDCl_3$):** δ 114.9, 68.3, 68.2, 68.1, 47.5, 45.2, 30.3. **DEPT135 (100 MHz, $CDCl_3$):** CH, CH_3 (δ 47.5); CH_2 (δ 68.2, 68.1, 45.2, 30.3)

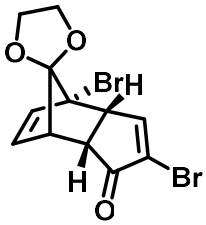
Synthesis of endo-2,4-dibromodicyclopentadiene-1,8-dione bisethylene ketal (14)



NaOH (11 g, 0.27 mmol) was added in a suspension of compound **13** (20 g, 54.7 mmol) and methanol (100 ml). The mixture was refluxed for 3 h. After cooling, the RM was poured into ice and stirred for 1 h. The mixture was kept for sometime and the precipitated solid was filtered, washed with water and dried in a desiccator. The crude product was recrystallized with ethanol to get pure crystals of compound **14** (white solid, 17.5 g, 79%).

^{1}H (400 MHz, $CDCl_3$): δ 6.18-6.16 (m, 1H), 6.05 (s, 1H), 5.83-5.81 (m, 3H), 4.22-4.11 (m, 4H), 4.02-3.86 (m, 4H), 3.50-3.48 (m, 1H), 3.07-3.05 (m, 1H), 2.71 (s, 1H). **^{13}C (100 MHz, $CDCl_3$):** δ 134.7, 133.2, 132.7, 128.2, 126.2, 115.8, 67.9, 66.5, 66.4, 65.5, 65.4, 55.9, 49.7, 47.4. **DEPT135 (100 MHz, $CDCl_3$):** CH, CH_3 (δ 134.7, 133.2, 132.7, 55.9, 49.7, 47.4); CH_2 (δ 66.5, 66.4, 65.5, 65.4)

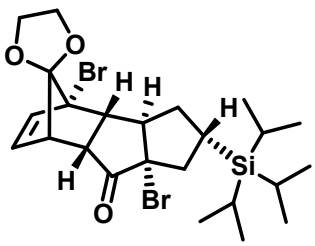
Synthesis of endo-2,4-dibromodicyclopentadiene-1,8-dione 8-ethylene ketal (15)



At rt, conc. HCl (20 ml) was added dropwise to a stirred solution of compound **15** (15g, 36.9 mmol) in THF (100 ml). The mixture was stirred for 18 h and then poured into 10% aqueous solution of $NaHCO_3$ (500 ml). The mixture was kept at rt for some time. The precipitated product was filtered off, dried and recrystallized with toluene to get pure crystals of compound **14** (creamy solid, 11.6 g, 87%).

^{1}H (400 MHz, $CDCl_3$): δ 7.62-7.61 (m, 1H), 6.01-5.98 (m, 1H), 5.93-5.91 (m, 1H), 4.27-4.16 (m, 2H), 4.07-4.02 (m, 1H), 3.97-3.92 (m, 1H), 3.65-3.63 (m, 1H), 3.19 (t, J = 5.35 Hz, 1H), 3.08-3.05 (m, 1H). **^{13}C (100 MHz, $CDCl_3$):** δ 200.0, 158.4, 134.9, 131.1, 130.5, 126.9, 66.6, 66.5, 65.9, 52.1, 48.1, 47.4. **DEPT135 (100 MHz, $CDCl_3$):** CH, CH_3 (δ 158.4, 134.9, 130.5, 52.1, 48.1, 47.4); CH_2 (δ 66.6, 65.9)

Synthesis of (2'S,3a'R,3b'S,4'S,7'S,7a'R,8a'S)-4',8a'-dibromo-2'-(triisopropylsilyl)-2',3',3a',3b',4',7',7a',8a'-octahydrospiro[[1,3]dioxolane-2,9'-[4,7]methanocyclopenta[a]inden]-8'(1'H)-one (16)

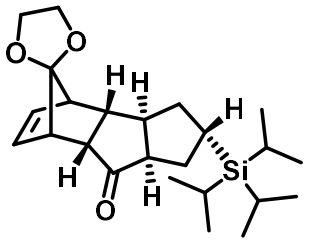


Compound **15** (3 g, 8.2 mmol) was stirred in dry DCM (50 ml). $TiCl_4$ (4.7 g, 24.8 mmol) was added in the RM under inert atmosphere followed by the addition of allyltriisopropylsilane (2.4 g, 12.4 mmol) at rt. The RM was stirred for 12 h and then the reaction was quenched with aqueous solution of ammonium chloride (NH_4Cl). Extract the RM three times with DCM and the organic layer was washed with water, filtered through Na_2SO_4 and concentrated to get the crude product. The crude product was purified by column chromatography on silica gel, eluting with 10% EtOAc in PE to get pure product **16** (white solid, 2.5 g, 54%, mp: 108-110^{o}C).

^{1}H (400 MHz, $CDCl_3$): δ 6.25-6.21 (m, 2H), 4.25-4.15 (m, 2H), 4.03-3.98 (m, 1H), 3.94-3.90 (m, 1H), 3.28-3.25 (m, 1H), 2.99-2.96 (m, 1H), 2.75 (dd, J = 5.51 Hz, 3.87 Hz, 1H), 2.68-2.65 (m, 1H), 2.54-2.49 (m, 1H), 2.36-2.27 (m, 2H), 1.97 (dd, J = 7.73 Hz, 5.15 Hz, 1H), 1.584-1.581 (m, 1H), 1.08-1.05 (m, 21H). **^{13}C (100 MHz, $CDCl_3$):** δ 215.4, 137.5, 134.6, 125.8, 71.4, 69.3, 66.6, 65.8, 54.6, 54.3, 53.3, 47.8, 47.4, 39.2, 24.8, 19.28, 19.25, 11.46. **DEPT135 (100 MHz, $CDCl_3$):** CH, CH_3 (δ 137.5, 134.6, 54.6, 54.3, 53.2, 47.4, 24.8, 19.28, 19.25, 11.4); CH_2 (δ 66.6, 65.8, 47.8, 39.2). **HRMS (ESI)** m/z calcd. for

$C_{24}H_{36}Br_2O_3SiNa$ $[M + Na]^+$: 581.0693; found: 581.0691. **IR** (neat)**:** 2942, 2865, 1745, 1464, 1267, 1027, 760, 675 cm^{-1}.

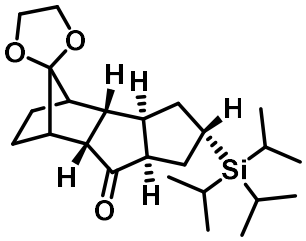
Synthesis of (2'S,3a'R,3b'R,4'R,7'S,7a'S,8a'R)-2'-(triisopropylsilyl)-2',3',3a',3b',4',7',7a',8a'-octahydrospiro[[1,3]dioxolane-2,9'-[4,7]methanocyclopenta[a]inden]-8'(1'H)-one (17)



Dissolve the compound **16** (2 g, 3.5 mmol) in dry toluene followed by the addition of azobisisobutyronitrile (10 mol%). The whole setup was covered with aluminum foil to maintain dark conditions. Now tributyltinhydride (3 g, 10.7 mmol) was added dropwise to the RM. Reflux the reaction mixture at 110 ºC for 4 h. After monitoring via TLC, the reaction mixture was cooled down and solvent was evaporated at reduced pressure to get crude mixture. The crude mixture was purified by column chromatography on silica gel, eluting with 10% EtOAc in PE to get pure product **17** (pale green liquid, 962 mg, 67%).

^{1}H (400 MHz, $CDCl_3$): δ 6.29-6.27 (m, 1H), 6.17-6.14 (m, 1H), 3.94-3.87 (m, 2H), 3.84-3.80 (m, 2H), 3.02-2.99 (m, 1H), 2.96-2.93 (m, 1H), 2.91-2.89 (m, 1H), 2.68-2.64 (m, 1H), 2.36-2.29 (m, 2H), 2.08-2.03 (m, 1H), 1.88-1.85 (m, 2H), 1.71-1.67 (m, 1H), 1.60 (s, 1H), 1.05-1.03 (m, 21H). **^{13}C (100 MHz, $CDCl_3$):** δ 226.1, 133.9, 133.7, 127.0, 65.1, 64.6, 58.6, 55.0, 51.5, 50.0, 47.0, 42.9, 40.5, 36.2, 24.4, 19.3, 11.5. **DEPT135 (100 MHz, $CDCl_3$):** CH, CH_3 (δ 133.9, 133.7, 58.6, 55.0, 51.5, 49.9, 47.0, 42.9, 24.4, 19.3, 11.5); CH_2 (δ 65.1, 64.6, 40.5, 36.2). **HRMS (ESI)** m/z calcd. for $C_{24}H_{39}O_3Si$ $[M + H]^+$: 403.2663; found: 403.2660. **IR** (neat)**:** 2931, 2865, 1727, 1465, 1296, 1100, 757 cm^{-1}.

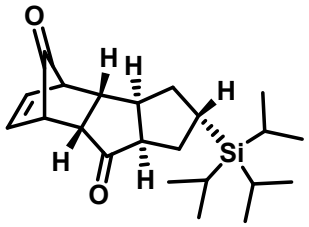
Synthesis of (2'S,3a'R,3b'S,4'R,7'S,7a'S,8a'R)-2'-(triisopropylsilyl)decahydrospiro[[1,3]dioxolane-2,9'-[4,7]methanocyclopenta[a]inden]-8'(1'H)-one (21b)



Compound **17** (100 mg, 0.24 mmol) was dissolved in trietyleneglycol (20 ml) followed by the addition of KOH (17 mg, 0.3 mmol) and hydrazine hydrate (15 mg, 0.3 mol). The RM was refluxed for overnight at 150 ºC. After the completion of the reaction, the RM was cooled to rt and water was added. The mixture was extracted three times with EtOAc. The organic layer was washed with water, filtered through Na_2SO_4 and concentrated to get crude product. The crude mixture was purified by column chromatography on silica gel, eluting with 10% EtOAc in PE to get pure product **21b** (white solid, 95 mg, 95%, mp: 110-112ºC).

^{1}H (400 MHz, $CDCl_3$): δ 3.97-3.90 (m, 4H), 2.74-2.63 (m, 3H), 2.58-2.51 (m, 1H), 2.24-2.19 (m, 1H), 2.07-1.92 (m, 3H), 1.82-1.58 (m, 6H), 1.25-1.24 (m, 1H), 1.04-1.01 (m, 21H). **^{13}C (100 MHz, $CDCl_3$):** δ 227.3, 121.6, 64.89, 64.87, 58.7, 53.6, 47.8, 44.0, 42.6, 40.5, 36.6, 23.7, 22.7, 20.8, 19.3, 11.5. **DEPT135 (100 MHz, $CDCl_3$):** CH, CH_3 (δ 58.7, 53.6, 47.8, 44.0, 42.6, 23.7, 19.3, 11.5); CH_2 (δ 64.89, 64.87, 40.5, 36.6, 22.7, 20.8). **HRMS (ESI)** m/z calcd. for $C_{24}H_{41}O_3Si$ $[M + H]^+$: 405.2819; found: 405.2819. **IR** (neat)**:** 2943, 2865, 1723, 1327, 1096, 882 cm^{-1}.

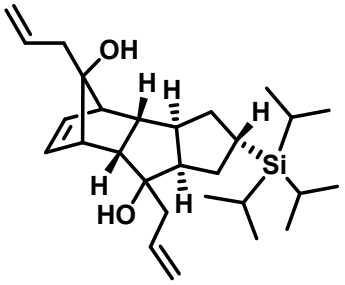
Synthesis of (2S,3aR,3bS,4R,7S,7aS,8aR)-2-(triisopropylsilyl)-2,3,3a,3b,4,7,7a,8a-octahydro-4,7-methanocyclopenta[a]indene-8,9(1H)-dione (18)



Compound **17** (300 mg, 0.75 mmol) was dissolved in 1N HCl (5 ml) and dioxane (20 ml). The RM was refluxed for 16 h. After 16 h, the RM was cooled to rt and water was added to it. The mixture was then extracted three times with EtOAc and the organic layer was washed with water, filtered through Na_2SO_4 and concentrated to get crude product. The crude product was purified by column chromatography on silica gel, eluting with 10% EtOAc in PE to get pure product **18** (yellow liquid, 257 mg, 96%).

^{1}H (400 MHz, $CDCl_3$): δ 6.52-6.41 (m, 2H), 3.29-3.26 (m, 2H), 2.98-2.94 (m, 1H), 2.57-2.53 (m, 1H), 2.46-2.42 (m, 1H), 2.30 (t, J = 9.40 Hz, 1H), 2.13-2.08 (m, 1H), 1.98-1.87 (m, 2H), 1.79-1.69 (m, 1H), 1.05-1.01 (m, 22H). **^{13}C (100 MHz, $CDCl_3$):** δ 223.6, 200.6, 132.2, 131.4, 57.9, 51.9, 50.9, 49.5, 44.2, 43.6, 40.3, 36.2, 24.5, 19.2, 11.4. **DEPT135 (100 MHz, $CDCl_3$):** CH, CH_3 (δ 132.2, 131.4, 57.9, 51.9, 50.9, 49.5, 44.2, 43.6, 24.5, 19.2, 11.4); CH_2 (δ 40.3, 36.2). **HRMS (ESI)** m/z calcd. for $C_{22}H_{34}O_2SiNa$ $[M + Na]^+$: 381.2220; found: 381.2223. **IR** (neat)**:** 2933, 2865, 1779, 1731, 1464, 1175, 883, 667 cm^{-1}.

Synthesis of (2S,3aR,3bS,4R,7S,7aS,8aR,9S)-8,9-diallyl-2-(triisopropylsilyl)-1,2,3,3a,3b,4,7,7a,8,8a-decahydro-4,7-methanocyclopenta[a]indene-8,9-diol (20) and (2S,3aR,3bS,4R,7S,7aS,8aR,9S)-9-allyl-9-hydroxy-2-(triisopropylsilyl)-2,3,3a,3b,4,7,7a,8a-octahydro-4,7-methanocyclopenta[a]inden-8(1H)-one (19)

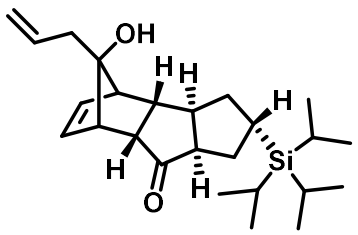


Compound **18** (100 mg, 0.27 mmol) was dissolved in dry THF (20 ml) at -40^{o}C under inert atmosphere followed by the addition of allyl magnesium bromide (161 mg, 1.1 mmol). The reaction was stirred for 6 h at that temperature and after monitoring TLC temperature was raised to rt. Reaction was further stirred for 10h at rt and then quenched with saturated solution of NH_4Cl. The mixture was extracted three times with EtOAc and the organic layer was washed with water, filtered through Na_2SO_4 and concentrated to get crude product. The crude product was purified by column chromatography on silica gel, eluting with 10% EtOAc in PE to get pure products **19** (pale yellow liquid, 33.4 mg, 30%) and **20** (colourless liquid, 55.5 mg, 45%).

Data corresponding to compound **20** is given here. For data of compound **19**, refer to next procedure.

^{1}H (400 MHz, $CDCl_3$): δ 6.37-6.35 (m, 1H), 6.08-6.06 (m, 1H), 5.99-5.89 (m, 1H), 5.79-5.69 (m, 1H), 5.15-5.07 (m, 4H), 3.14-3.10 (m, 1H), 2.86-2.80 (m, 1H), 2.53-2.52 (m, 1H), 2.48-2.45 (m, 3H), 2.36-2.34 (m, 2H), 2.23-2.19 (m, 1H), 2.07-1.99 (m, 2H), 1.88-1.83 (m, 1H), 1.77-1.69 (m, 4H), 1.08-1.02 (m, 22H). **^{13}C (100 MHz, $CDCl_3$):** δ 137.1, 135.5, 135.2, 132.8, 119.2, 117.6, 97.3, 83.3, 63.0, 56.4, 52.1, 50.8, 50.7, 45.9, 44.3, 38.4, 33.5, 29.7, 19.4, 18.8, 11.3. **DEPT135 (100 MHz, $CDCl_3$):** CH, CH_3 (δ 137.1, 135.5, 135.2, 132.8, 63.0, 56.4, 52.1, 50.8, 50.7, 45.9, 19.4, 18.8, 11.3); CH_2 (δ 119.1, 117.6, 44.3, 38.4, 33.5, 29.4). **HRMS (ESI)** m/z calcd. for $C_{28}H_{46}O_2SiNa$ $[M + Na]^+$: 465.3159; found: 465.3159. **IR** (neat)**:** 3423, 2917, 2864, 1650, 1437, 1261, 1016, 953 cm^{-1}.

Synthesis of (2S,3aR,3bS,4R,7S,7aS,8aR,9S)-9-allyl-9-hydroxy-2-(triisopropylsilyl)-2,3,3a,3b,4,7,7a,8a-octahydro-4,7-methanocyclopenta[a]inden-8(1H)-one (19)



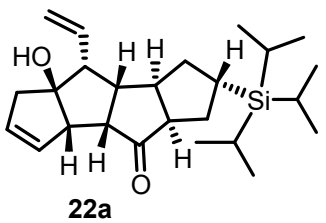
Compound **18** (100 mg, 0.27 mmol) was dissolved in a mixture of THF:H_2O (15 ml : 5 ml) followed by the addition of allyl bromide (267 mg, 2.2 mmol) and In powder (96mg, 0.83 mmol). The RM was stirred at rt for 6 h. After completion of the reaction, the RM was filtered through celite and extracted three times with EtOAc. The organic layer was washed with water, filtered through Na_2SO_4 and concentrated to get crude product. The crude product was purified by column chromatography on silica gel, eluting with 10% EtOAc in PE to get pure product **19** (pale yellow liquid, 104 mg, 93%).

^{1}H (500 MHz, $CDCl_3$): δ 6.16-6.14 (m, 1H), 6.04-6.02 (m, 1H), 5.76-5.67 (m, 1H), 5.16-5.09 (m, 2H), 3.16-3.13 (m, 1H), 2.83-2.78 (m, 3H), 2.46-2.34 (m, 5H), 2.08-2.04 (m, 1H), 1.97 (bs, 1H), 1.86-1.85 (m, 2H), 1.71-1.67 (m, 1H), 1.03 (s, 21H). **^{13}C (125 MHz, $CDCl_3$):** δ 227.6, 134.94, 134.91, 134.7, 119.5, 95.0, 59.1, 56.4, 54.1, 53.5, 48.2, 42.7, 40.6, 37.0, 36.2, 24.4, 19.3, 11.5. **DEPT135 (125 MHz, $CDCl_3$):** CH, CH_3 (δ 134.94, 134.91, 134.7, 59.1, 56.4, 54.1, 53.5, 48.2, 42.7, 24.4, 19.3, 11.5); CH_2 (δ 119.5, 40.6, 37.0, 36.2). **HRMS (ESI)** m/z calcd. for $C_{25}H_{41}O_2Si$ $[M + H]^+$: 401.2877; found: 401.2876. **IR** (neat)**:** 3423, 2925, 2864, 1725, 1464, 1261, 1016, 914, 883, 664 cm^{-1}.

Synthesis of (3aS,3bS,4aR,6S,7aR,7bS,8R,8aS)-8a-hydroxy-6-(triisopropylsilyl)-8-vinyl-3a,3b,4a,5,6,7,7a,7b,8,8a-decahydrodicyclopenta[a,e]pentalen-4(1H)-one (22a) and (3bS,3cR,5S,6aR,7aS)-8a-hydroxy-5-(triisopropylsilyl)-8-vinyl-3a,3b,3c,4,5,6,6a,7a,8, 8a-decahydrodicyclopenta[a,f] pentalen-7(1H)-one (22b)

G-II (10 mol%) was added to a stirred degassed solution of compound **19** (400 mg, 1 mmol) in dry DCM (20 ml) at rt and refluxed it at 50 °C. The RM was stirred for 10 h under ethylene atmosphere. After completion of the reaction, the RM was concentrated and the crude product was purified by column chromatography on silica gel, eluting with 15% EtOAc in PE to get pure product **22a** and **22b.**

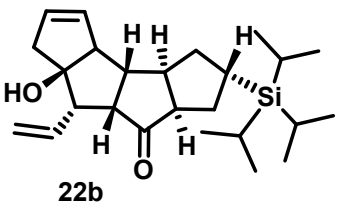
Compound **22a**: pale yellow liquid, 260 mg, 65%



22a

^{1}H (400 MHz, $CDCl_3$): δ 6.01-5.90 (m, 1H), 5.68-5.60 (m, 2H), 5.31-5.22 (m, 2H), 3.30-3.26 (m, 1H), 3.03-2.97 (m, 3H), 2.63 (q, J = 7.69 Hz, 1H), 2.47 (t, J = 9.77 Hz, 1H), 2.37-2.27 (m, 2H), 2.12-2.07 (m, 1H), 1.79-1.64 (m, 5H), 1.07-1.00 (m, 21H). **^{13}C (100 MHz, $CDCl_3$):** δ_C 223.9, 135.0, 130.8, 129.1, 118.8, 92.4, 61.7, 58.2, 57.2, 56.3, 53.0, 45.3, 40.7, 39.0, 34.5, 22.1, 19.3, 11.5. **DEPT135 (100 MHz, $CDCl_3$):** CH, CH_3 (δ 135.0, 130.8, 129.1, 61.7, 58.2, 57.2, 56.3, 53.0, 40.7, 22.1, 19.3, 11.5); CH_2 (δ 118.8, 45.3, 39.0, 34.5). **HRMS (ESI)** m/z calcd. for $C_{25}H_{41}O_2Si$ $[M + H]^+$: 401.2877; found: 401.2877. **IR** (neat)**:** 3423, 2931, 2865, 1731, 1465, 1176, 914, 883, 759 cm^{-1}.

Compound **22b**: white solid, 80 mg, 20%, mp 120-122 °C.



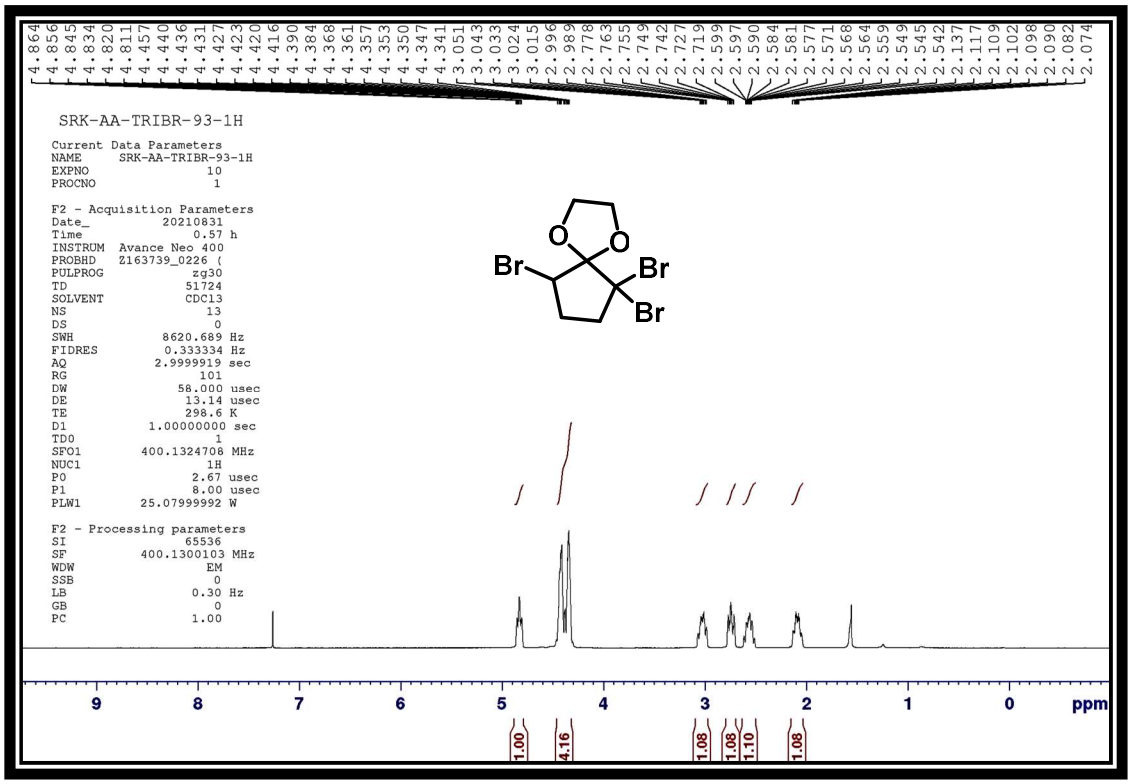
22b

^{1}H (500 MHz, $CDCl_3$): δ 6.32-6.25 (m, 1H), 5.81-5.80 (m, 1H), 5.668-5.660 (m, 1H), 5.24-5.19 (m, 2H), 3.22 (d, J = 11.14 Hz, 1H), 2.90 (t, J = 8.86 Hz, 1H), 2.79 (t, J = 9.37 Hz, 1H), 2.70 (t, J = 8.37 Hz, 1H), 2.57-2.44 (m, 3H), 2.14-2.04 (m, 3H), 1.74-1.69 (m, 4H), 1.03 (s, 21H). **^{13}C (125**

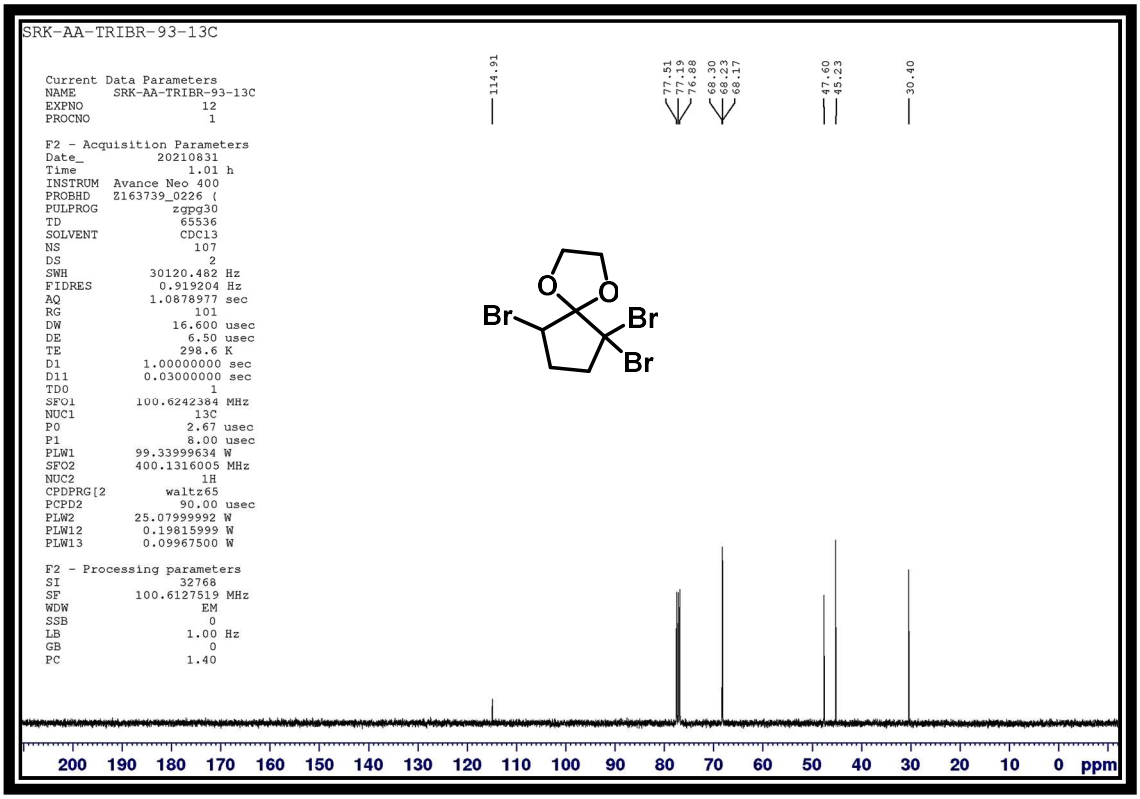
MHz, $CDCl_3$): δ_C 224.9, 134.4, 131.2, 130.0, 118.7, 91.8, 61.3, 58.7, 56.88, 56.80, 49.3, 44.3, 41.8, 38.3, 36.1, 23.2, 19.3, 11.5. **DEPT135 (125 MHz, $CDCl_3$):** CH, CH_3 (δ 134.4, 131.2, 130.0, 61.3, 58.7, 56.88, 56.80, 49.3, 41.8, 23.2, 19.3, 11.5); CH_2 (δ 118.7, 44.3, 38.3, 36.1). **HRMS (ESI)** m/z calcd. for $C_{25}H_{41}O_2Si$ $[M + H]^+$: 401.2877; found: 401.2875. **IR** (neat)**:** 3423, 2942, 2865, 1725, 1465, 1167, 914, 883, 665 cm^{-1}.

2. PLOTS OF ^{1}H NMR, ^{13}C NMR AND DEPT 135 OF ALL COMPOUNDS

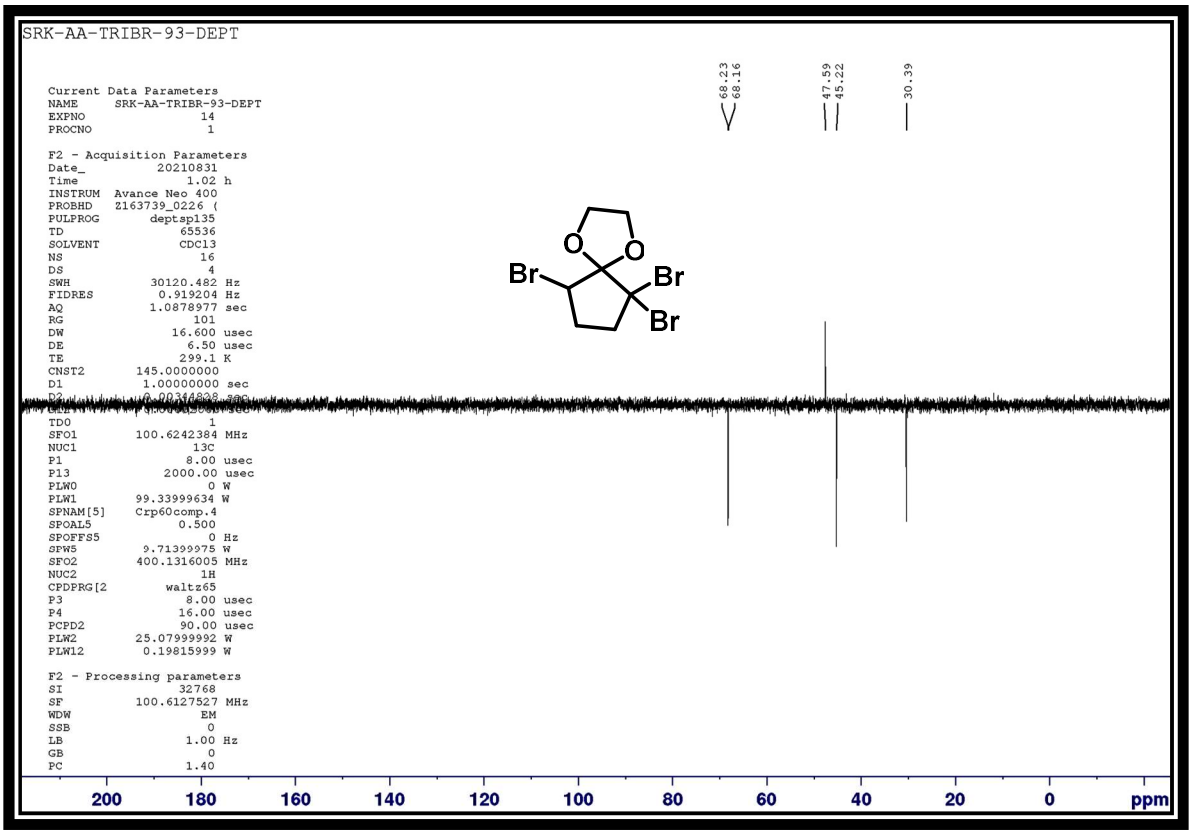
^{1}H NMR (400 MHz, $CDCl_3$) of Compound 13



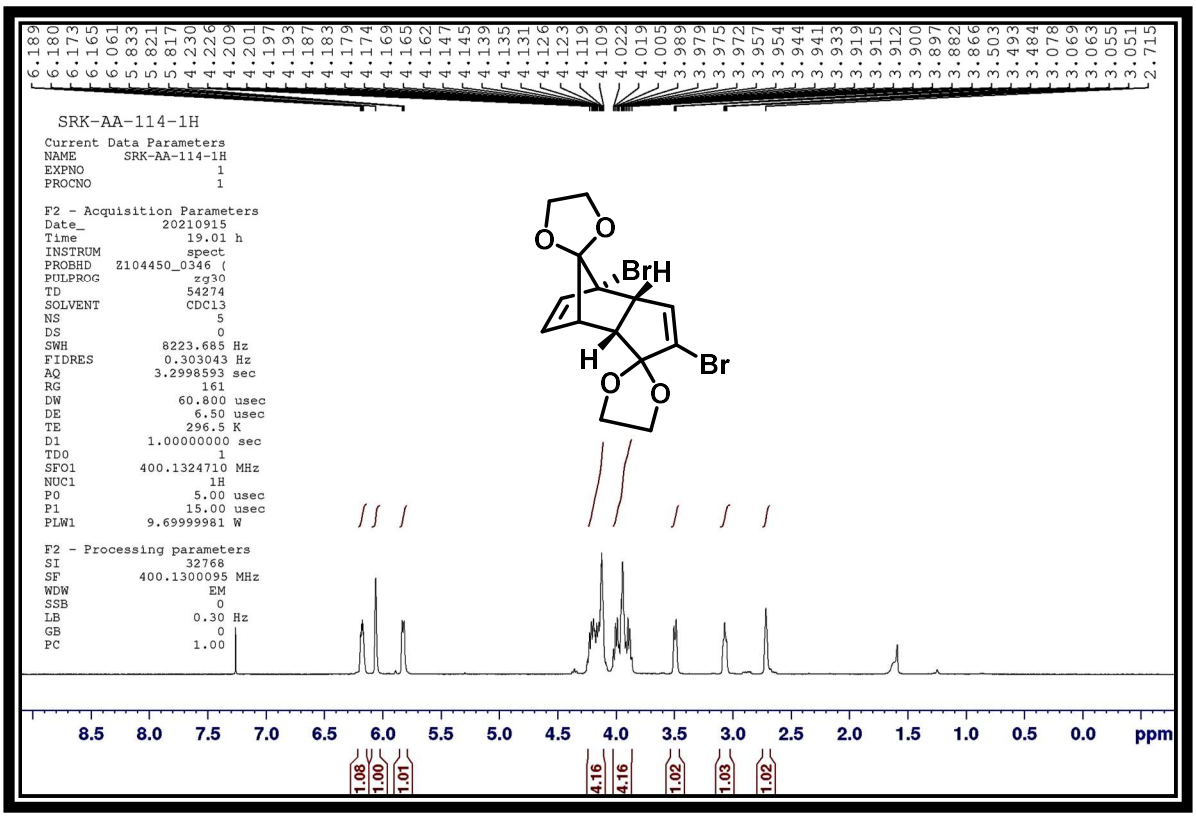
^{13}C NMR (100 MHz, $CDCl_3$) of Compound 13



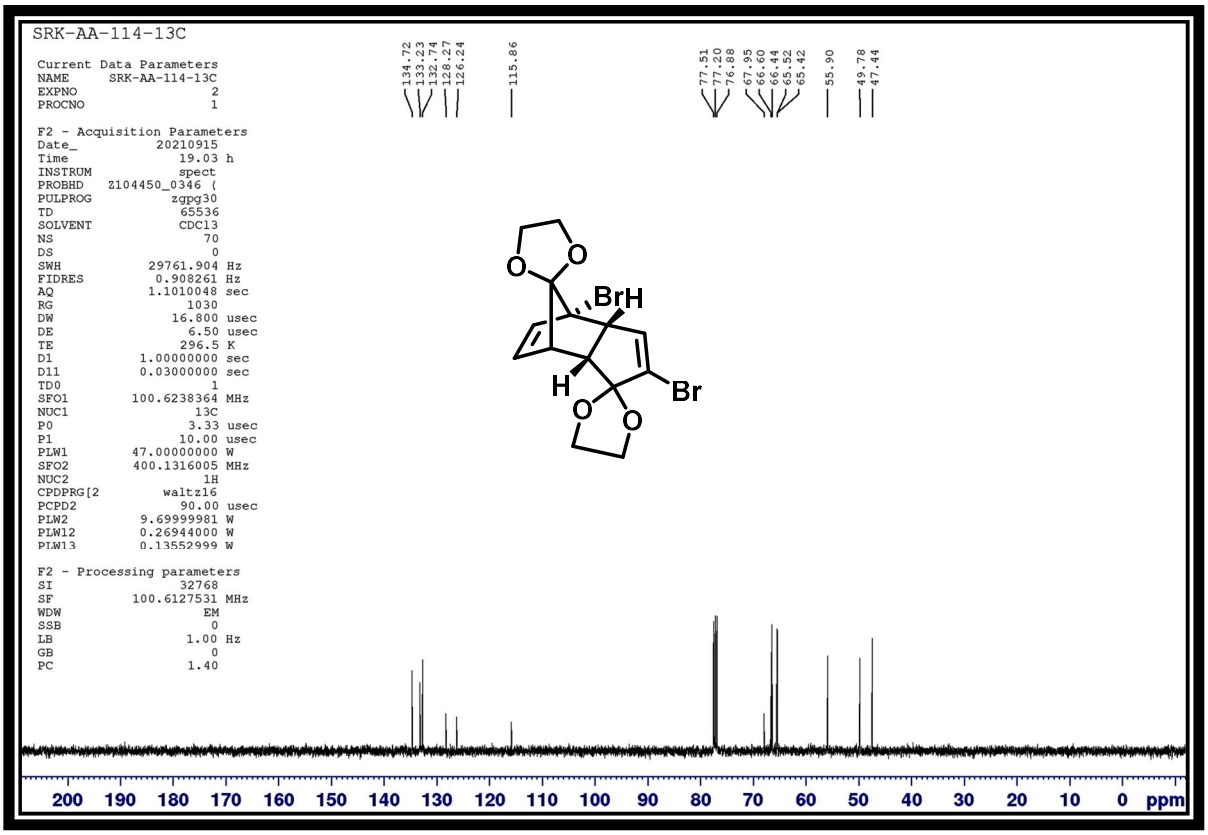
DEPT135 (100 MHz, $CDCl_3$) of Compound 13



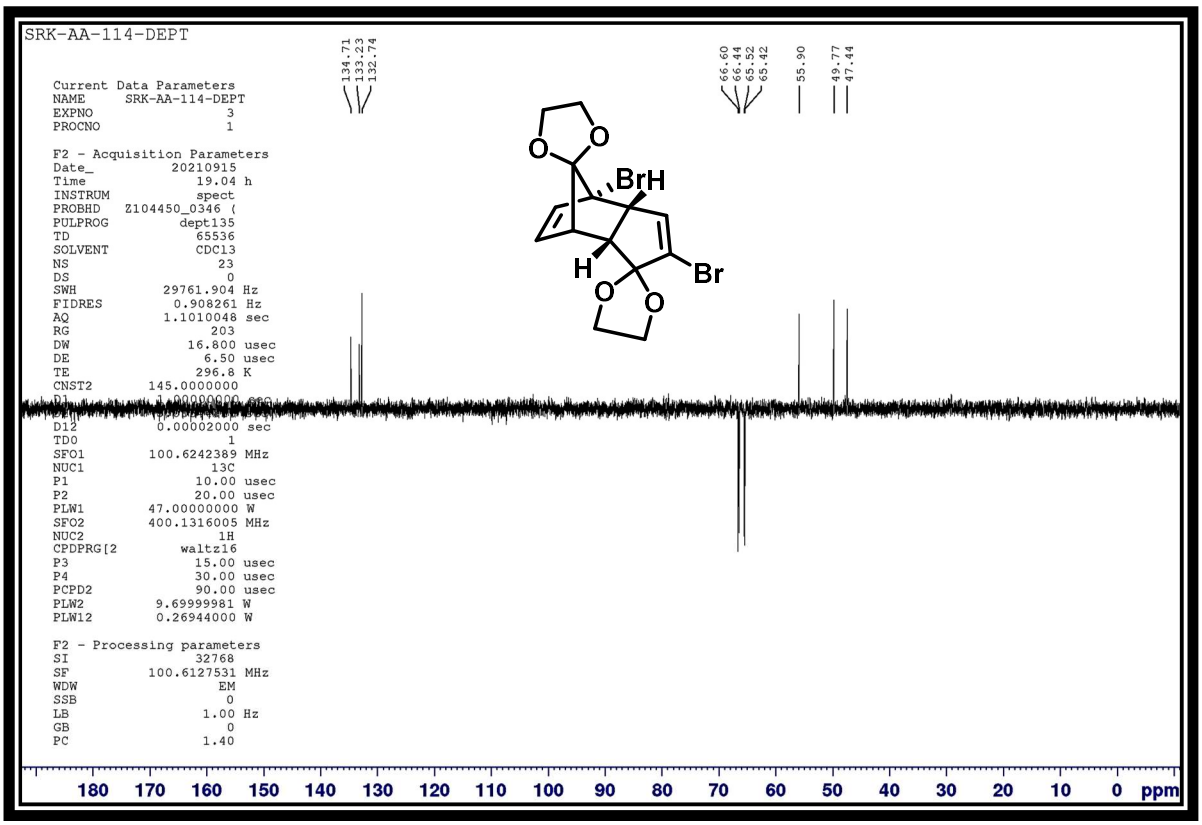
^{1}H NMR (400 MHz, $CDCl_3$) of Compound 14



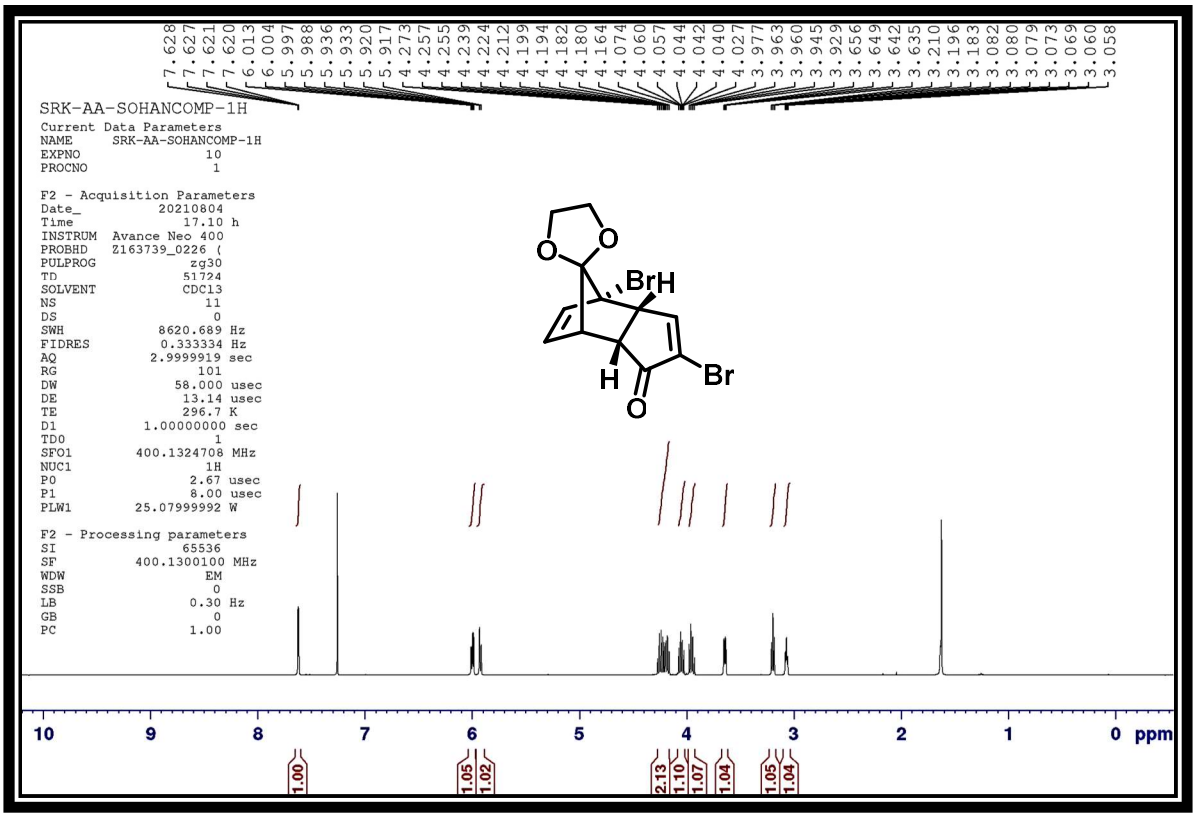
^{13}C NMR (100 MHz, $CDCl_3$) of Compound 14



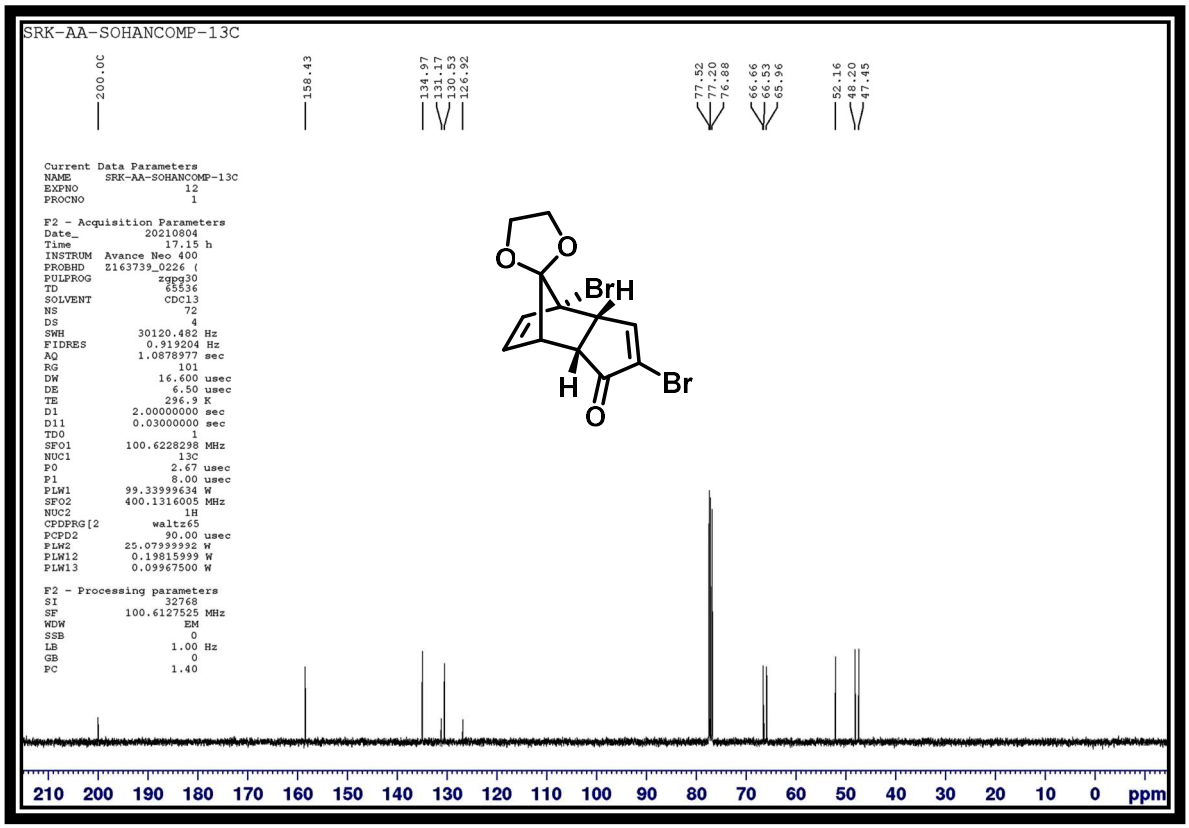
DEPT135 (100 MHz, $CDCl_3$) of Compound 14



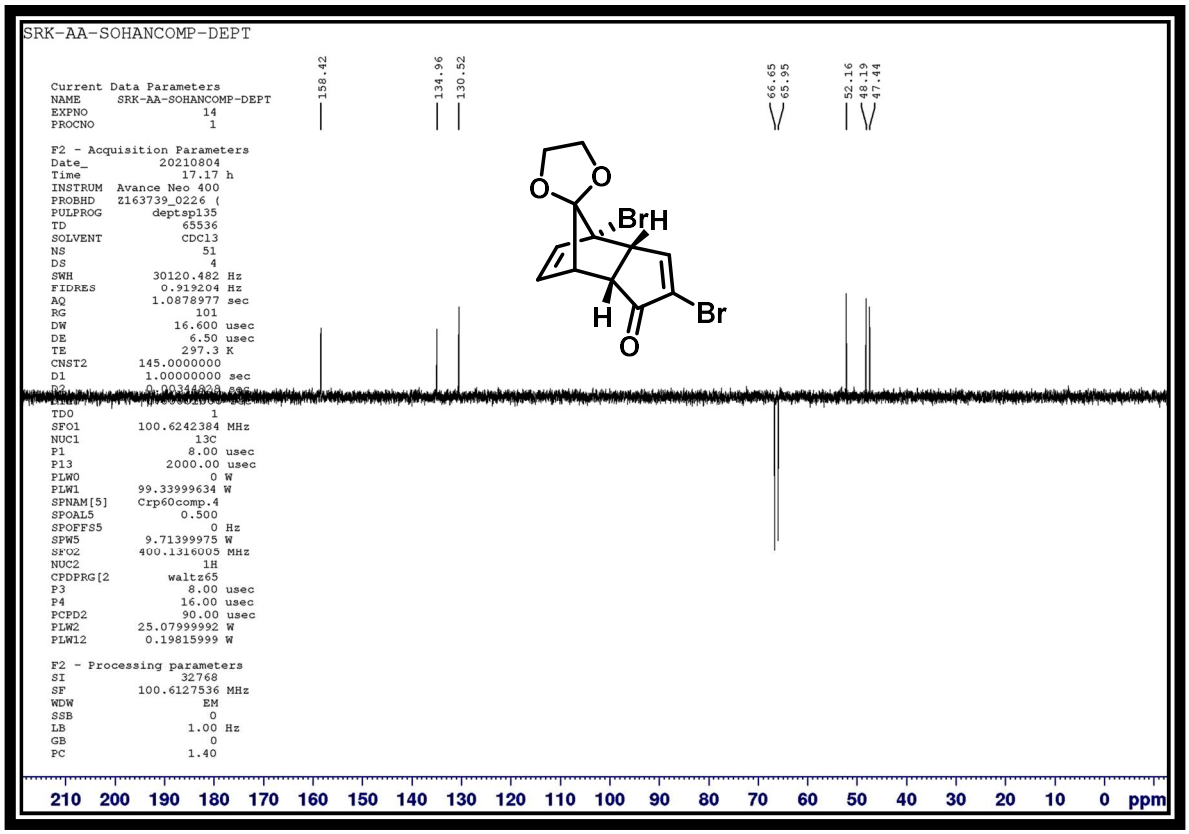
^{1}H NMR (400 MHz, $CDCl_3$) of Compound 15



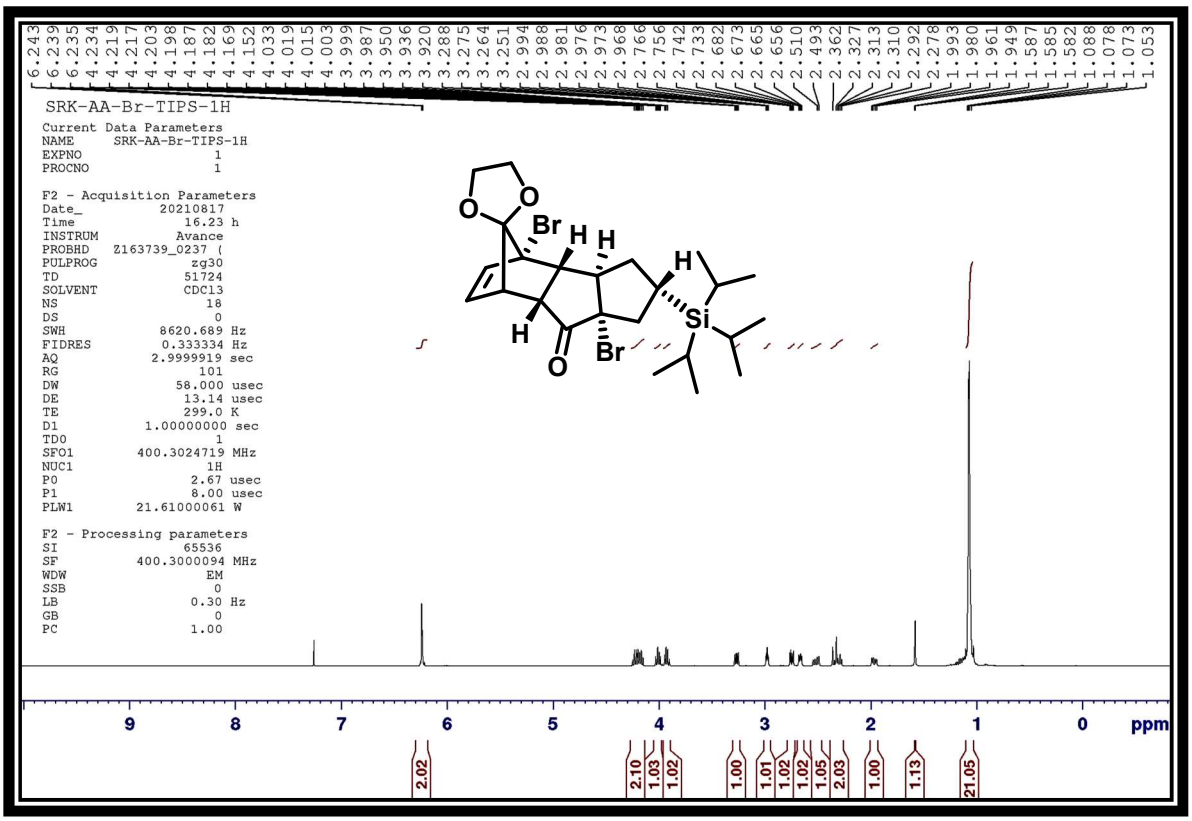
^{13}C NMR (100 MHz, $CDCl_3$) of Compound 15



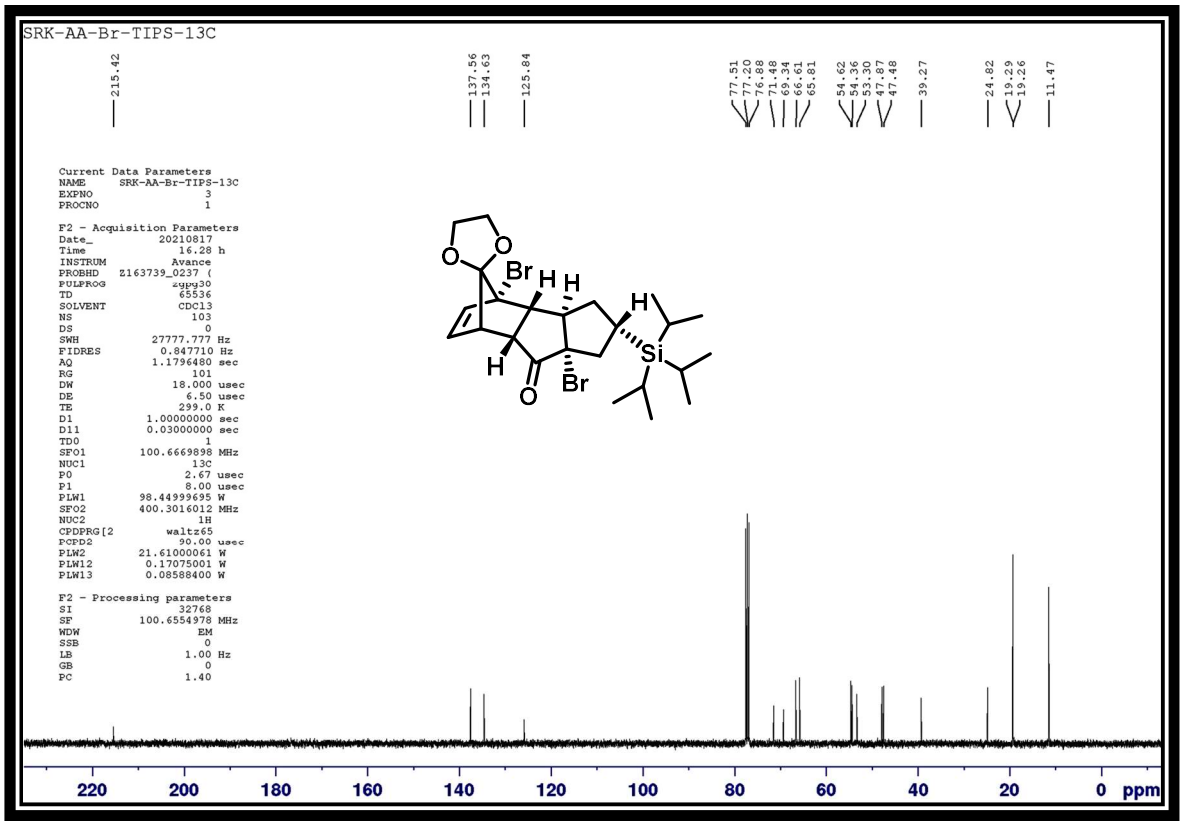
DEPT135 (100 MHz, $CDCl_3$) of Compound 15



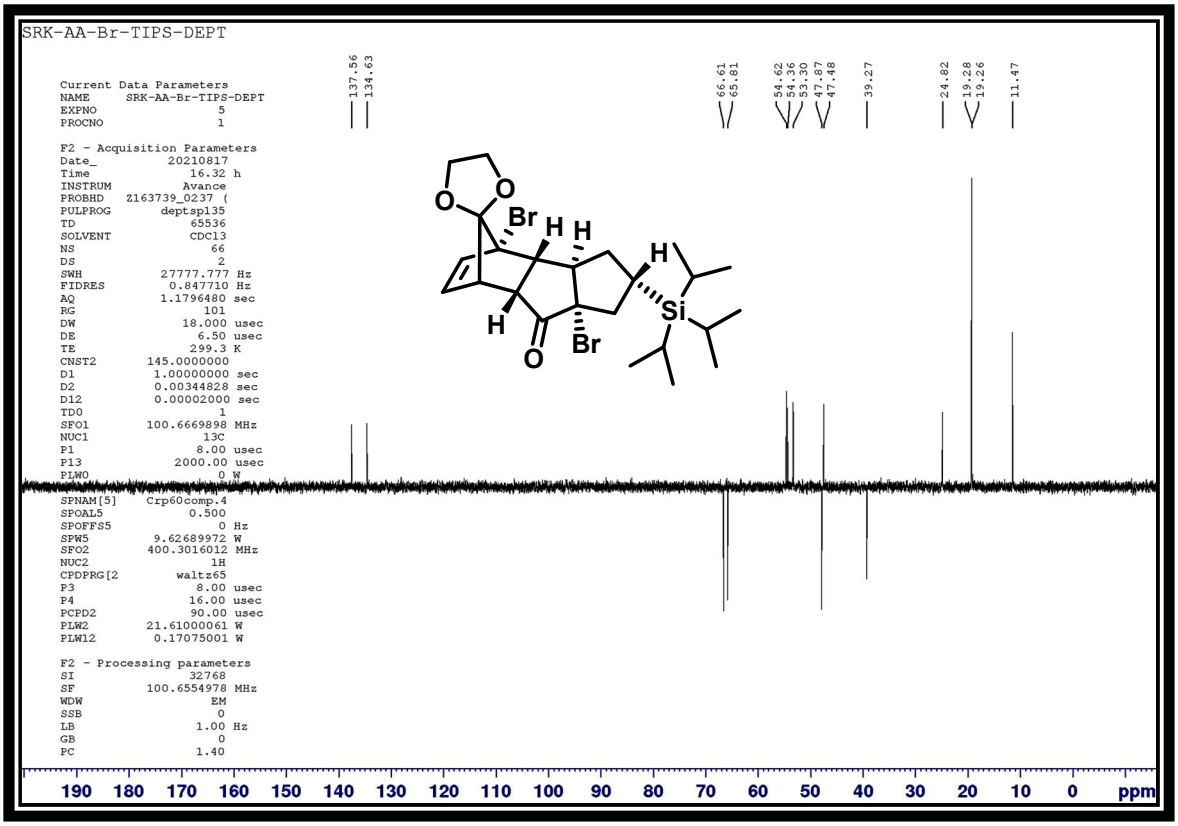
^{1}H NMR (400 MHz, $CDCl_3$) of Compound 16



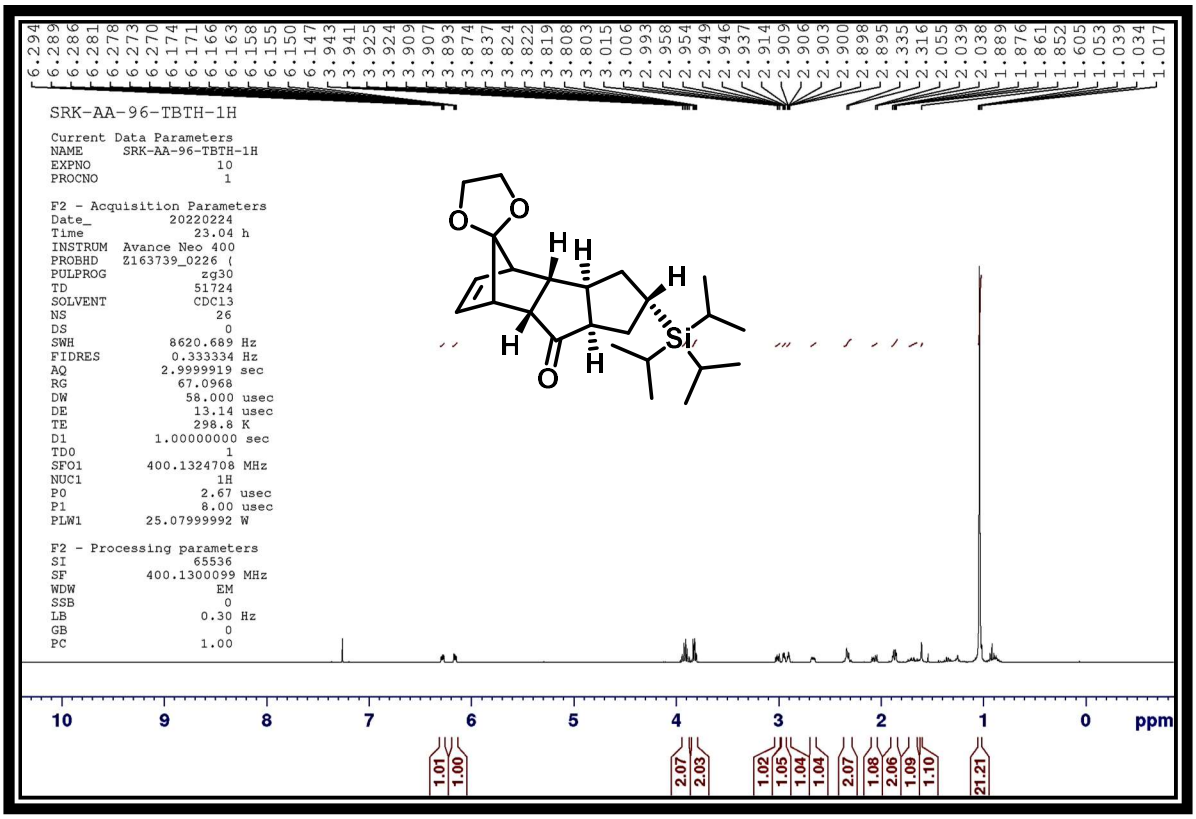
^{13}C NMR (100 MHz, $CDCl_3$) of Compound 16



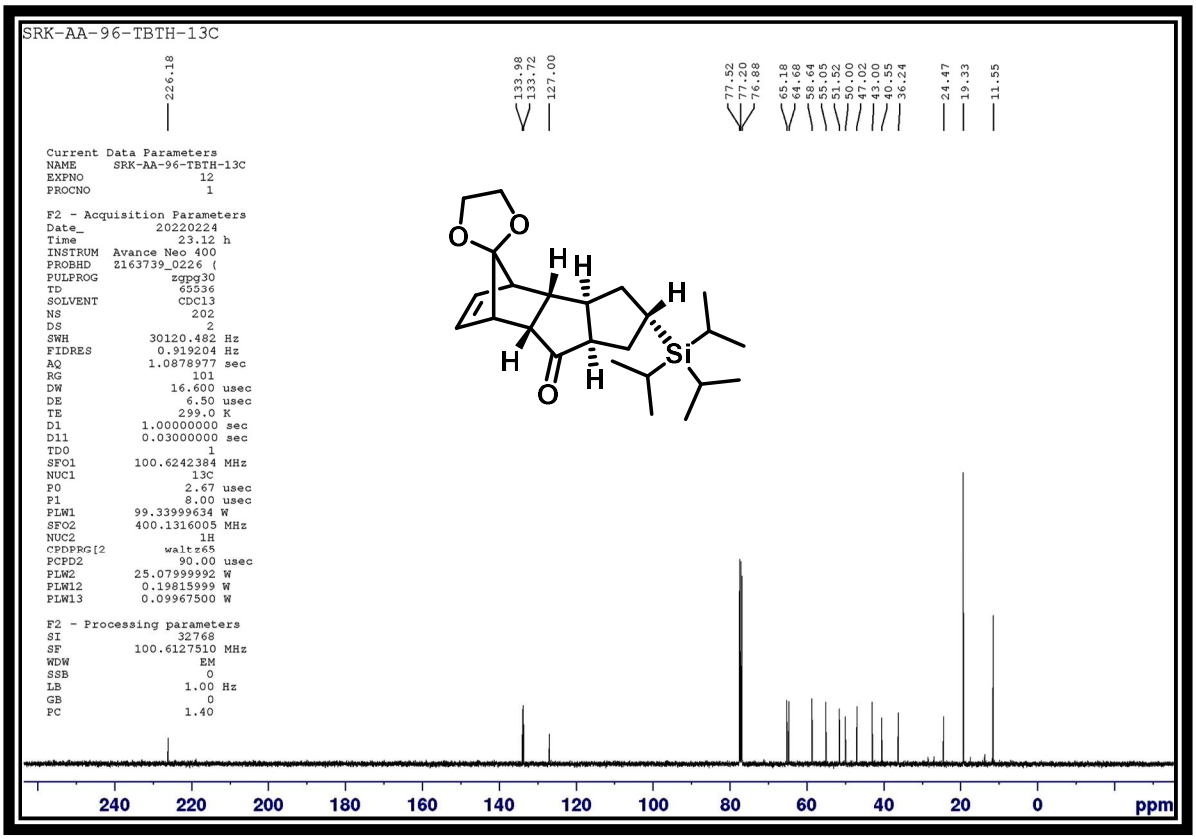
DEPT135 (100 MHz, $CDCl_3$) of Compound 16



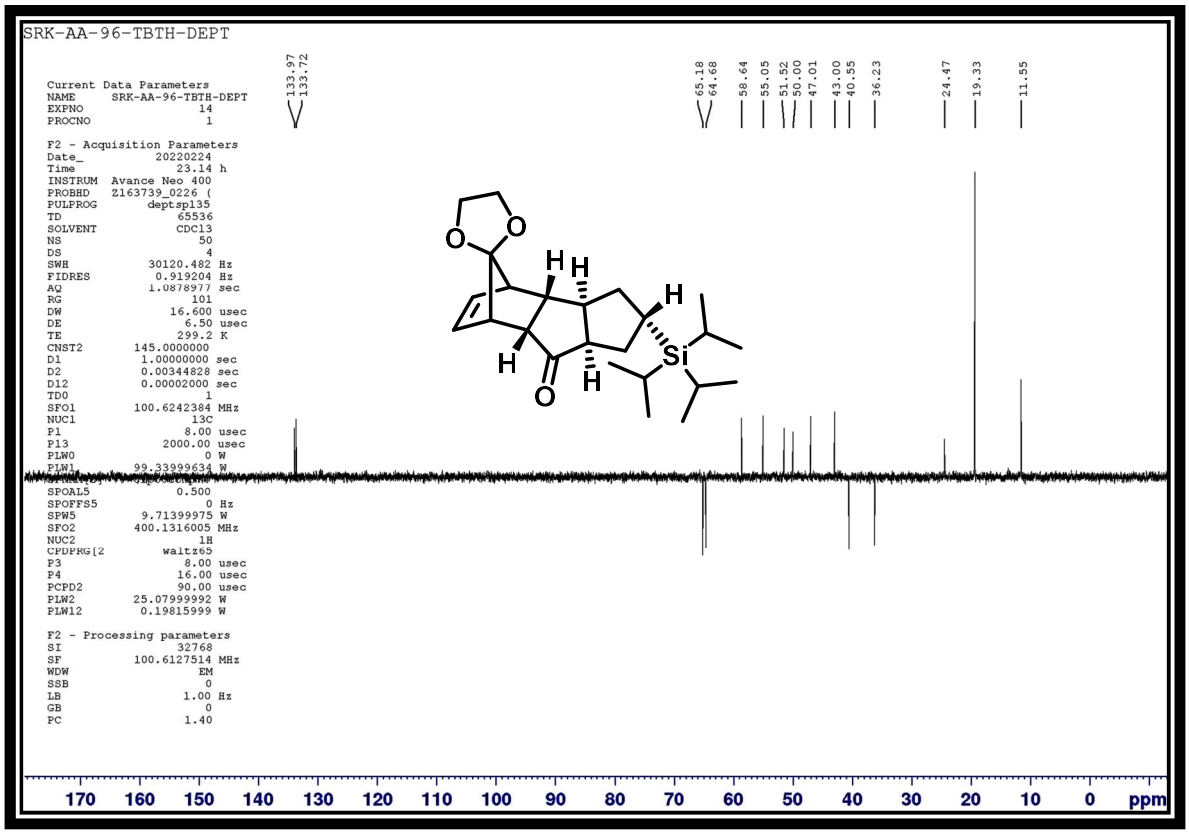
^{1}H NMR (400 MHz, $CDCl_3$) of Compound 17



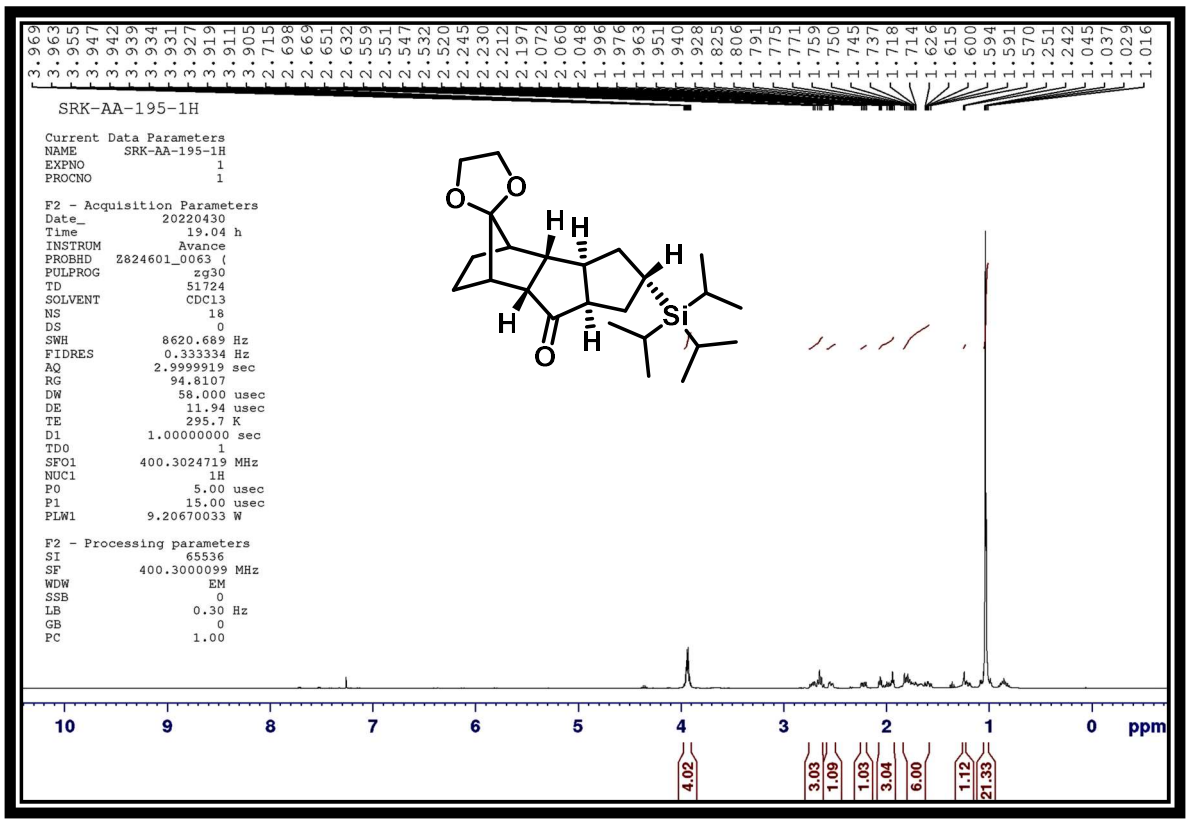
^{13}C NMR (100 MHz, $CDCl_3$) of Compound 17



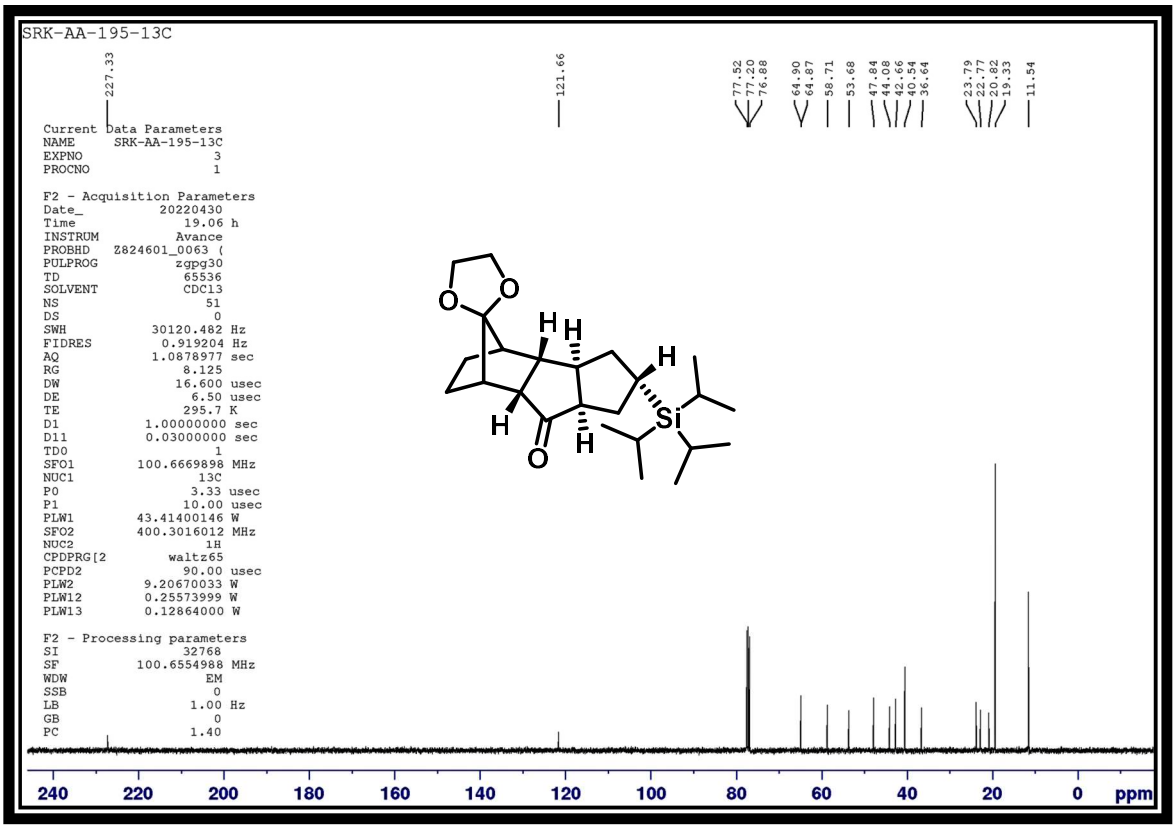
DEPT135 (100 MHz, $CDCl_3$) of Compound 17



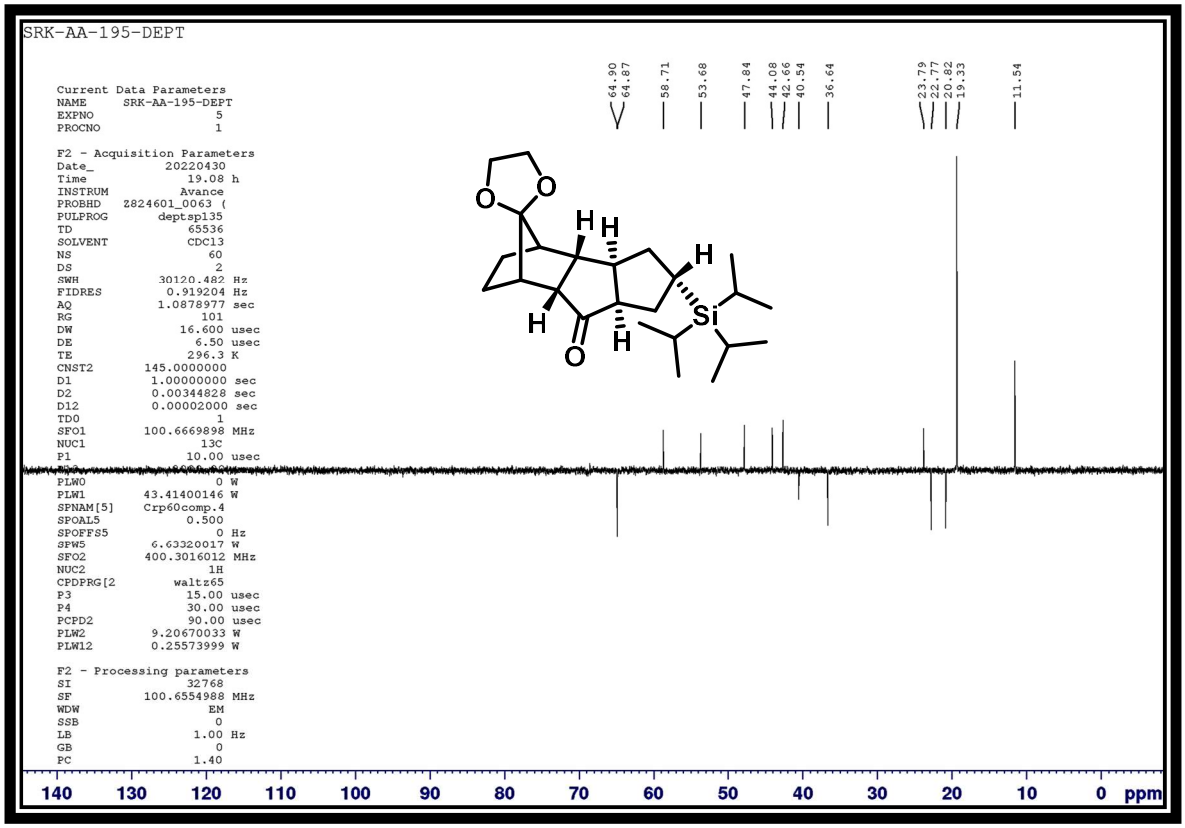
^{1}H NMR (400 MHz, $CDCl_3$) of Compound 21b



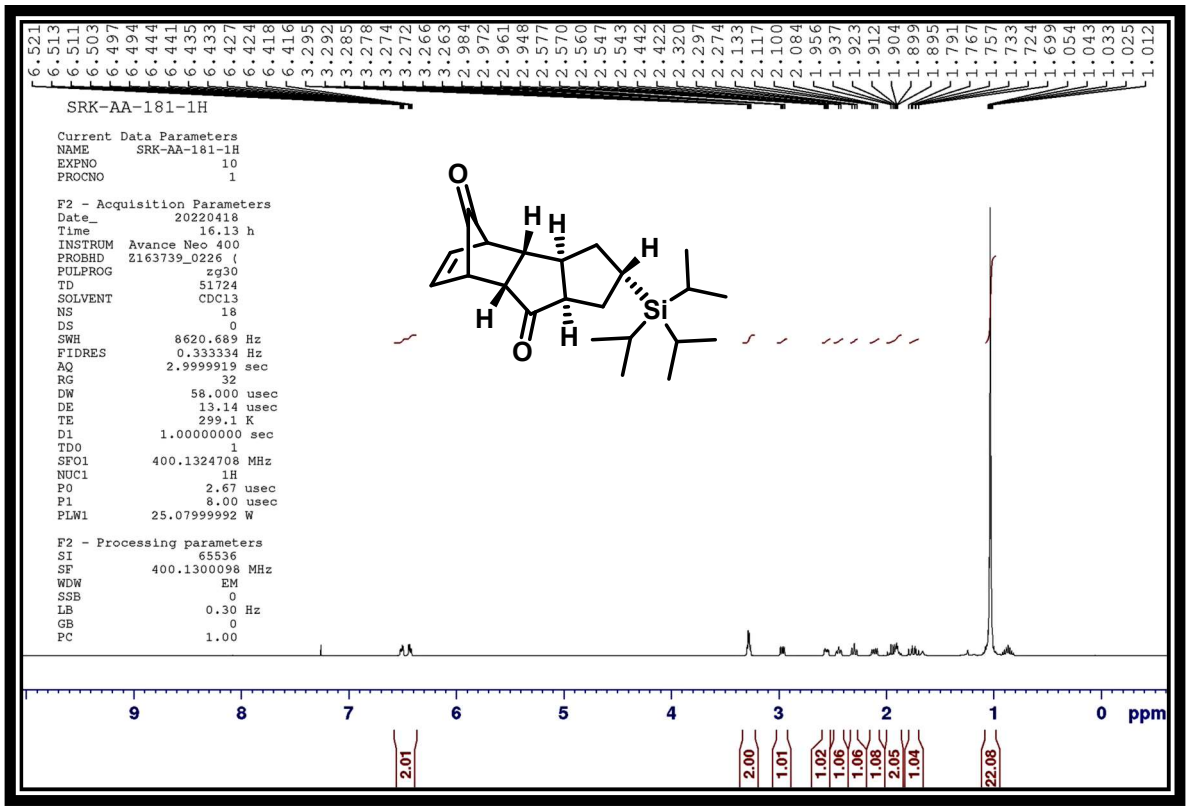
^{13}C NMR (100 MHz, $CDCl_3$) of Compound 21b



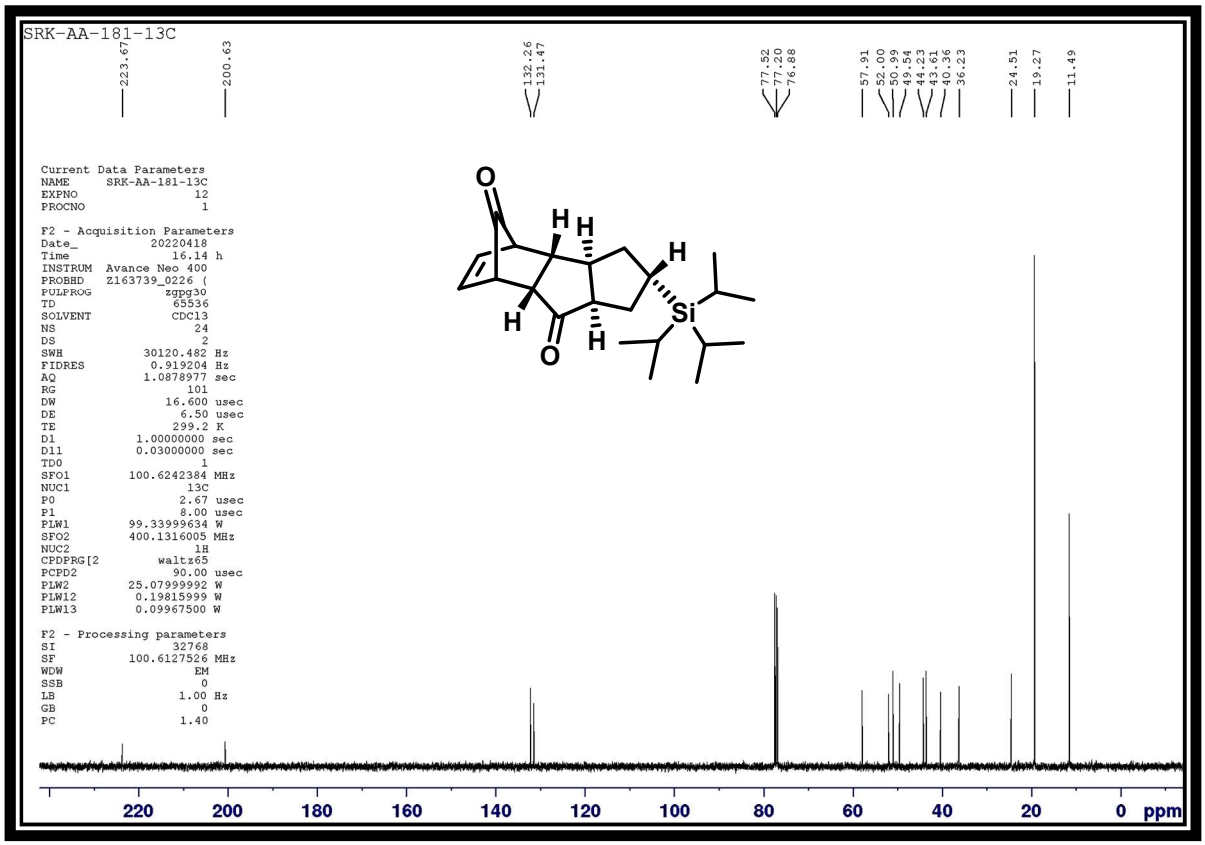
DEPT135 (100 MHz, $CDCl_3$) of Compound 21b



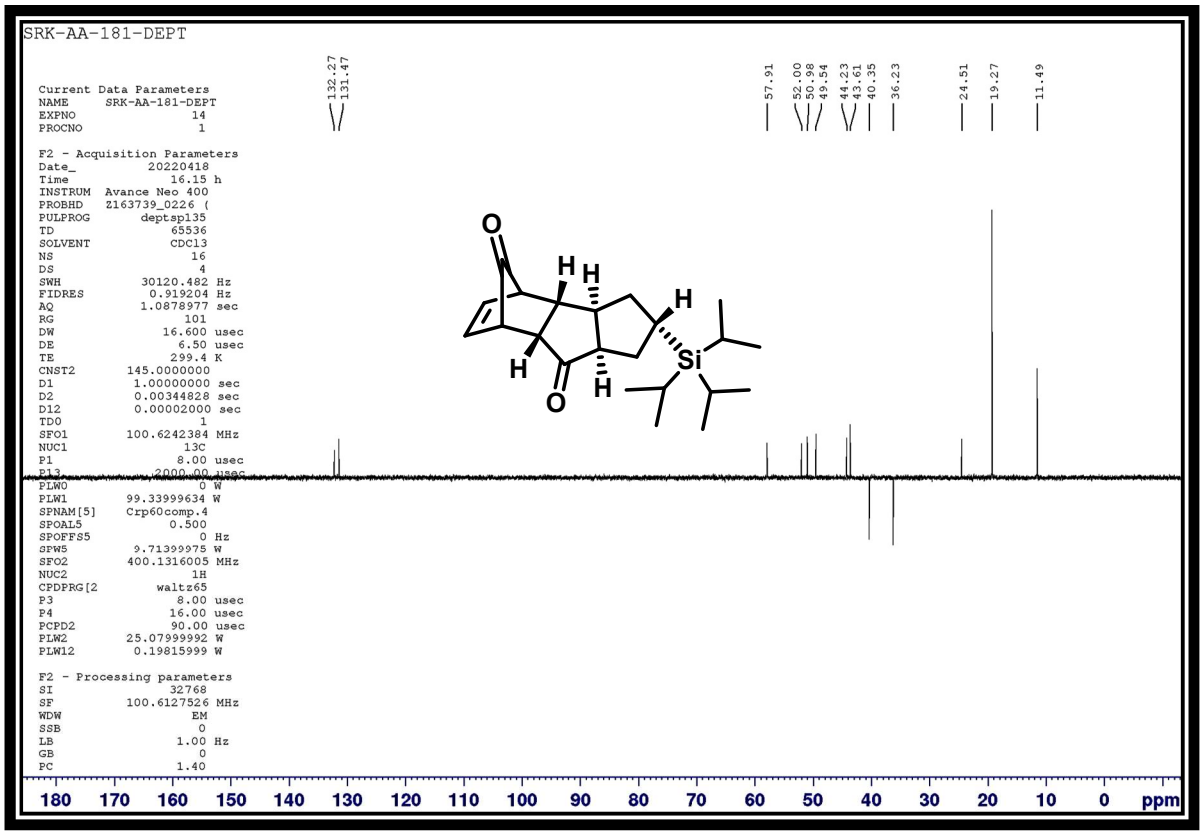
^{1}H NMR (400 MHz, $CDCl_3$) of Compound 18



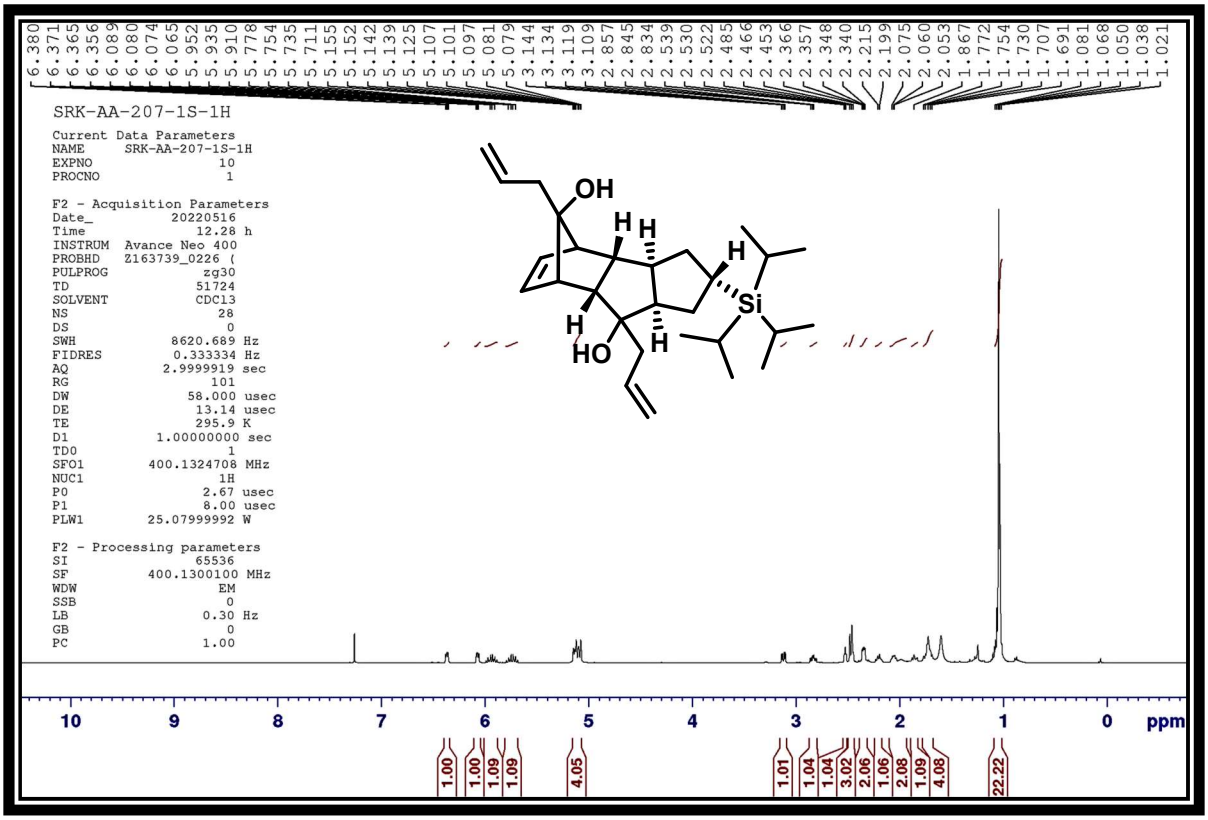
^{13}C NMR (100 MHz, $CDCl_3$) of Compound 18



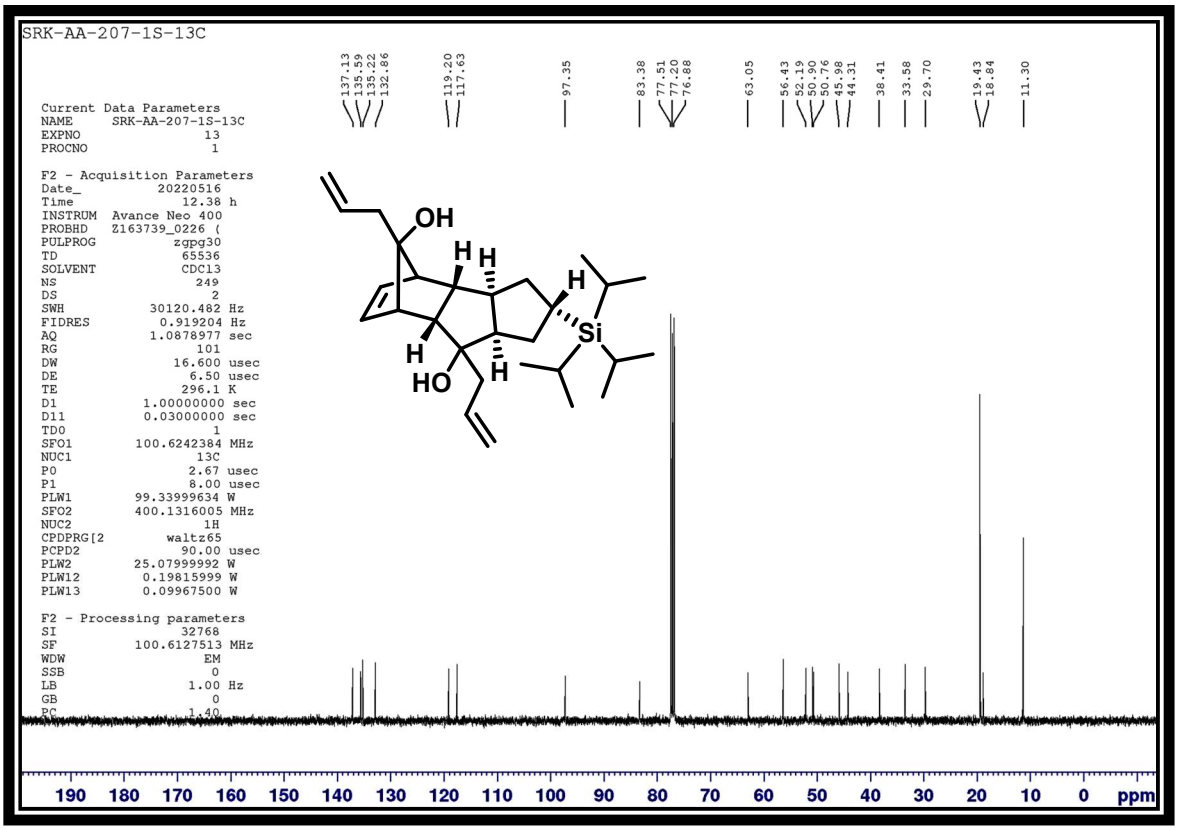
DEPT135 (100 MHz, $CDCl_3$) of Compound 18



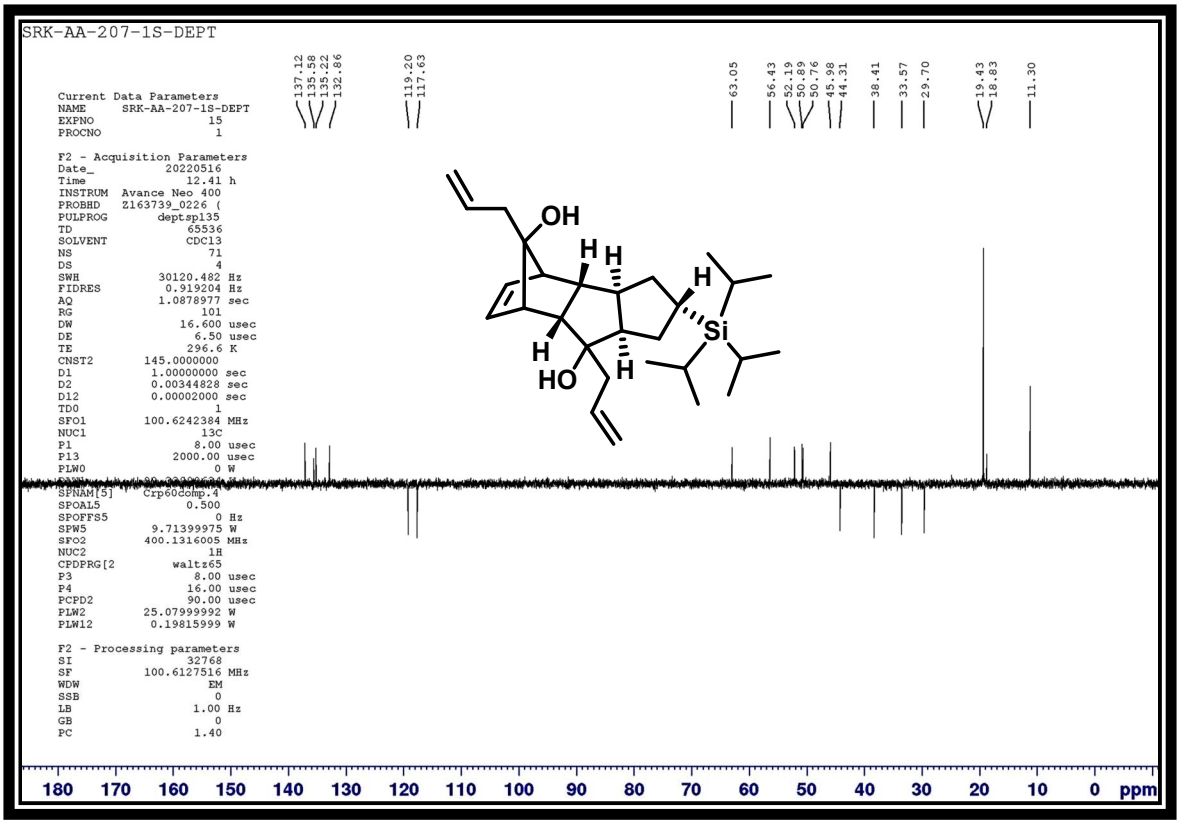
^{1}H NMR (400 MHz, $CDCl_3$) of Compound 20



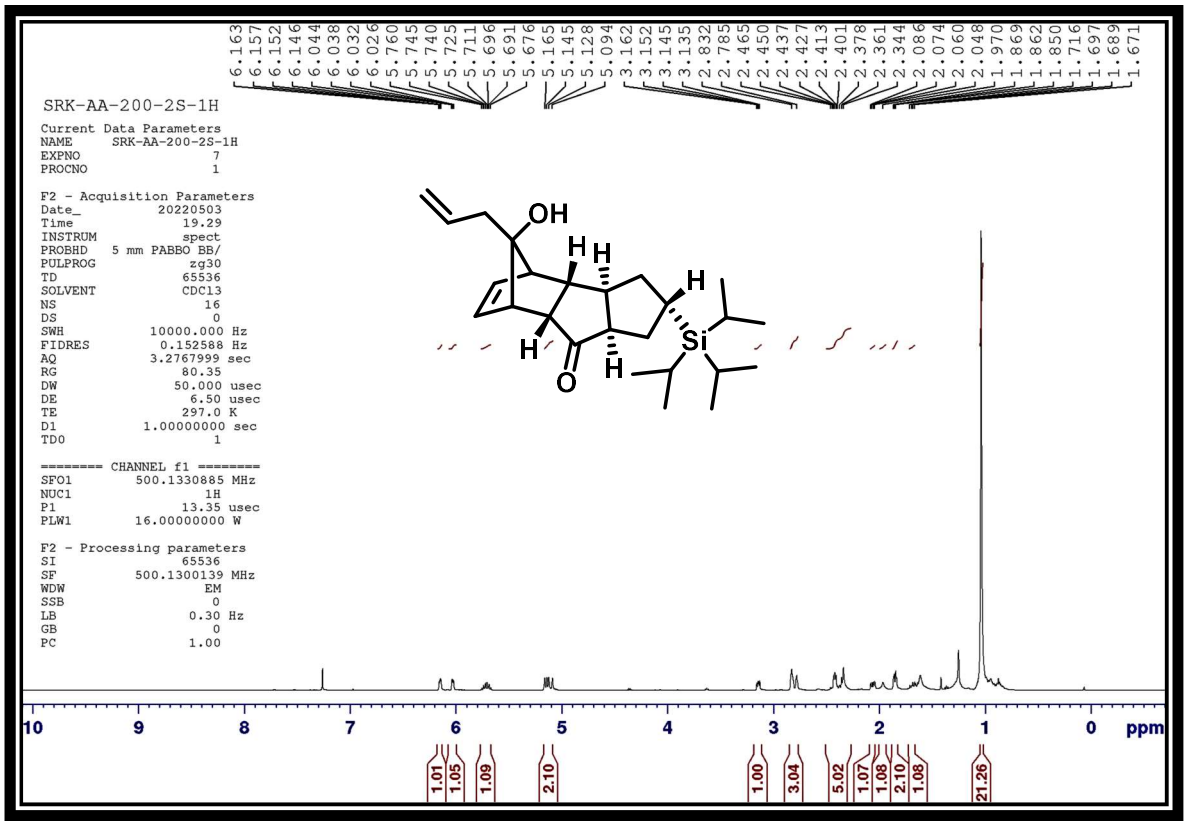
^{13}C NMR (100 MHz, $CDCl_3$) of Compound 20



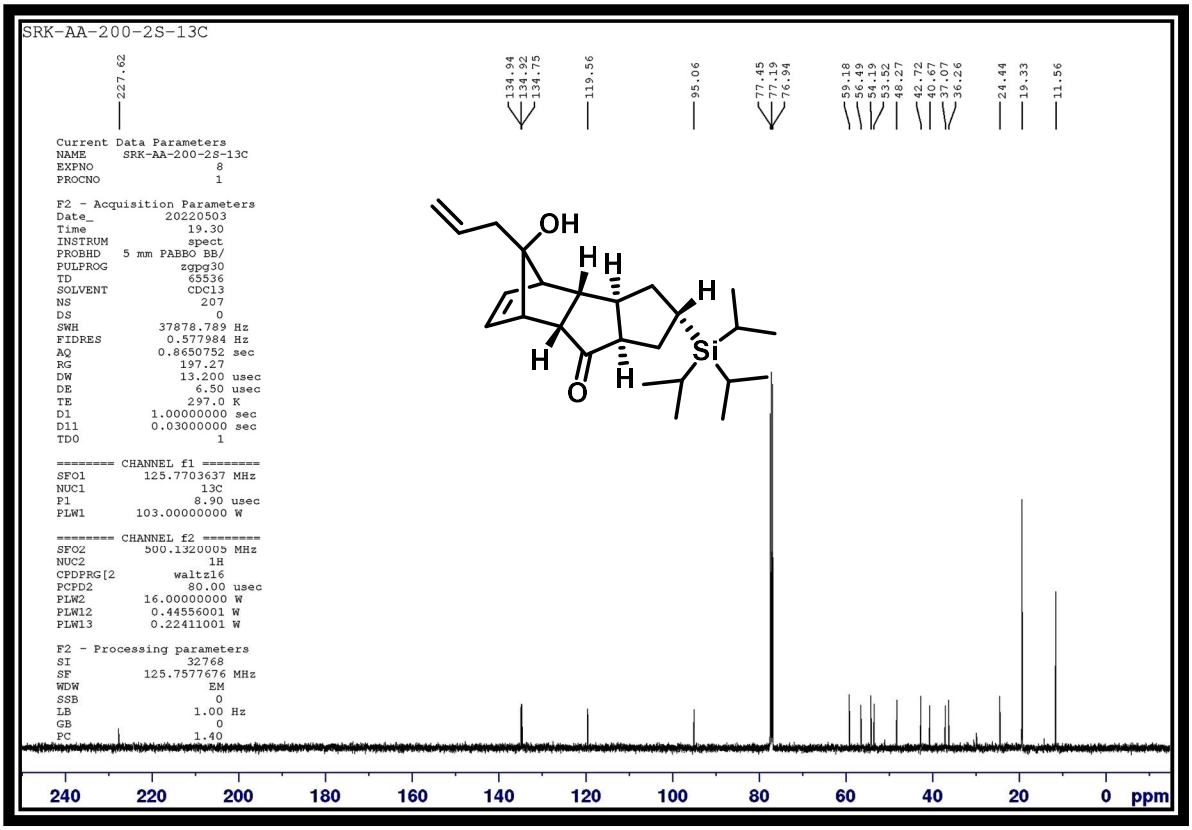
DEPT135 (100 MHz, $CDCl_3$) of Compound 20



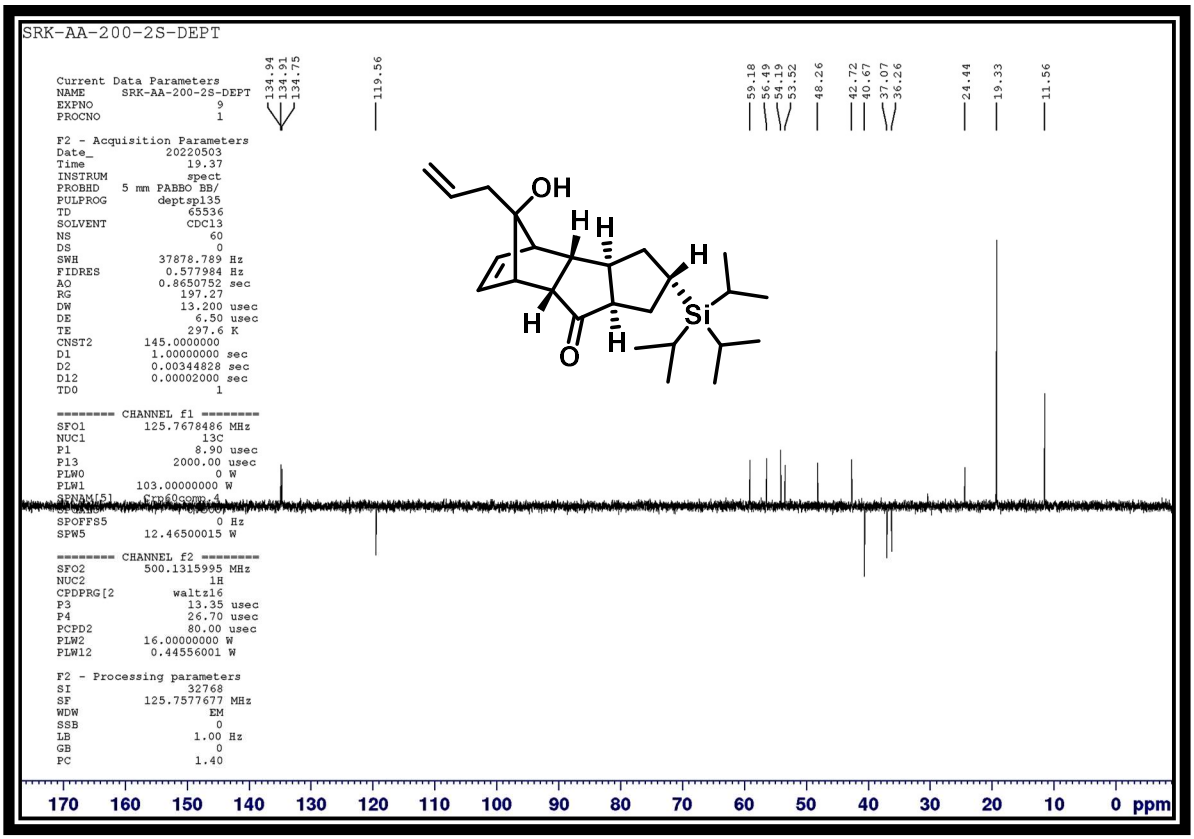
^{1}H NMR (500 MHz, $CDCl_3$) of Compound 19



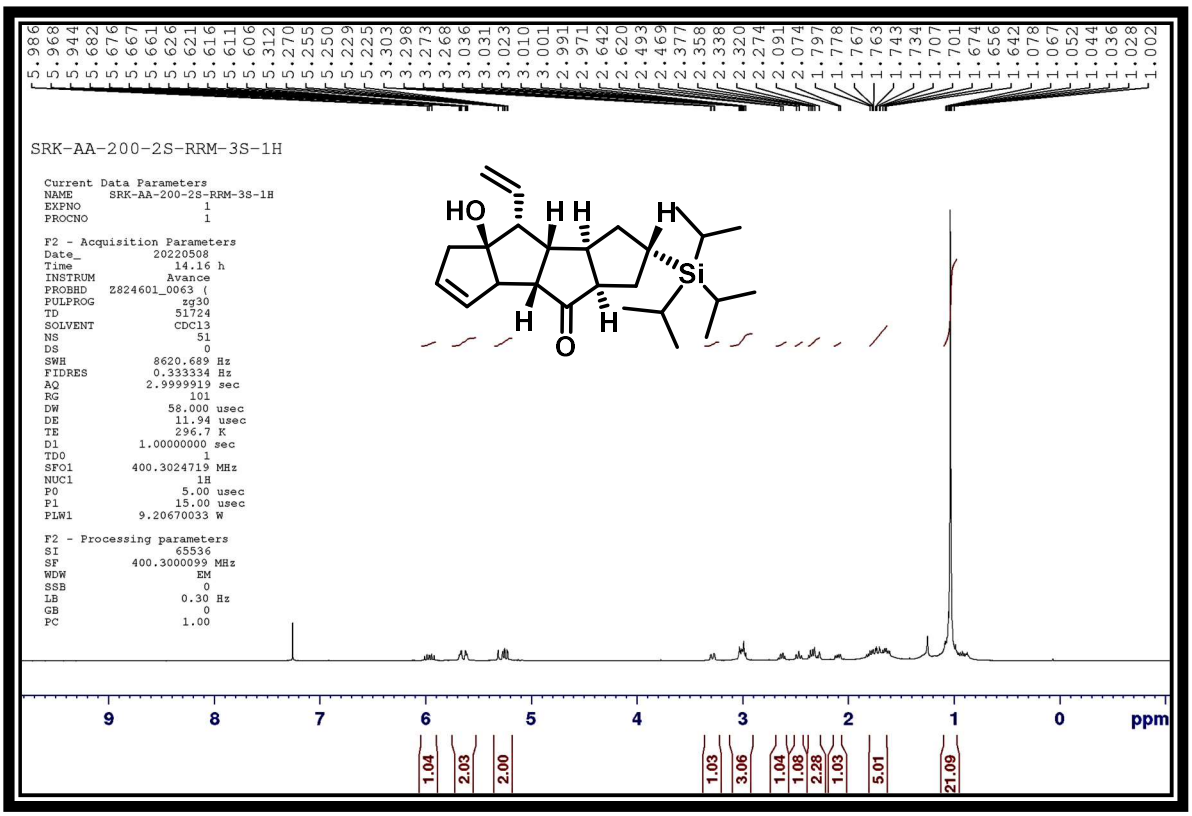
^{13}C NMR (125 MHz, $CDCl_3$) of Compound 19



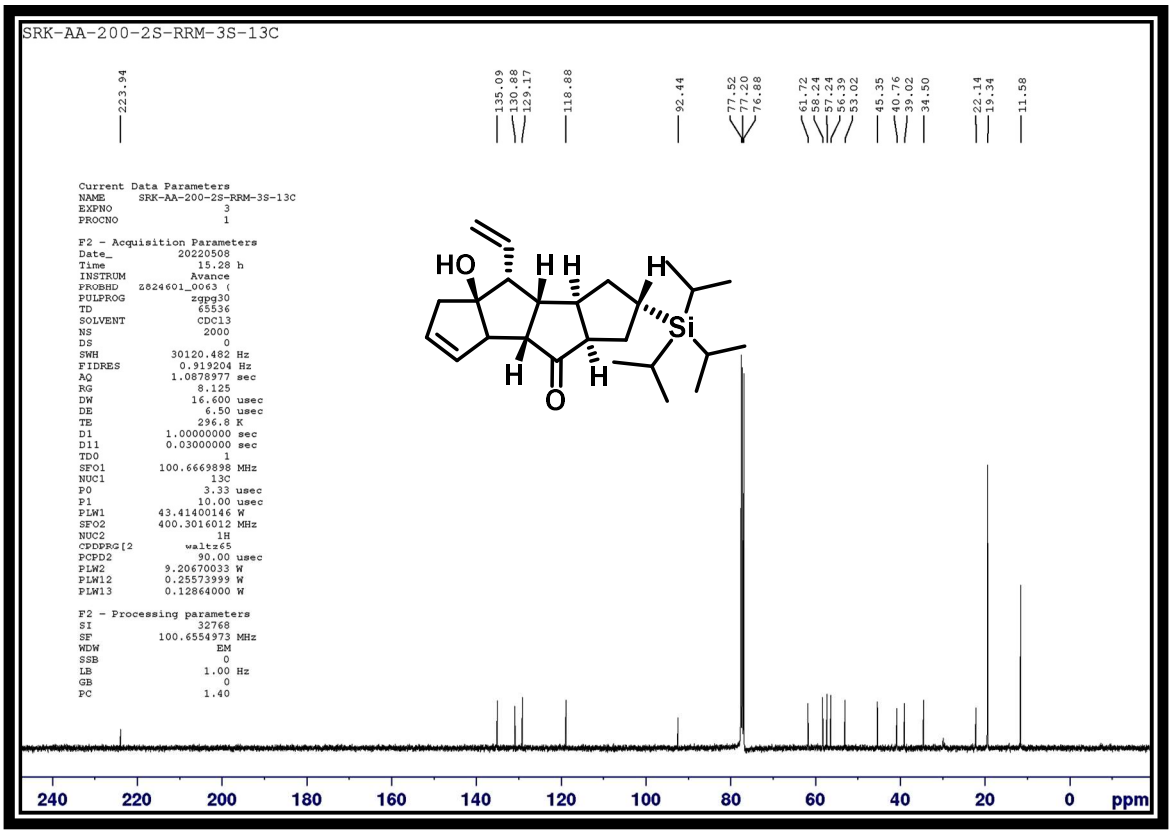
DEPT135 (125 MHz, $CDCl_3$) of Compound 19



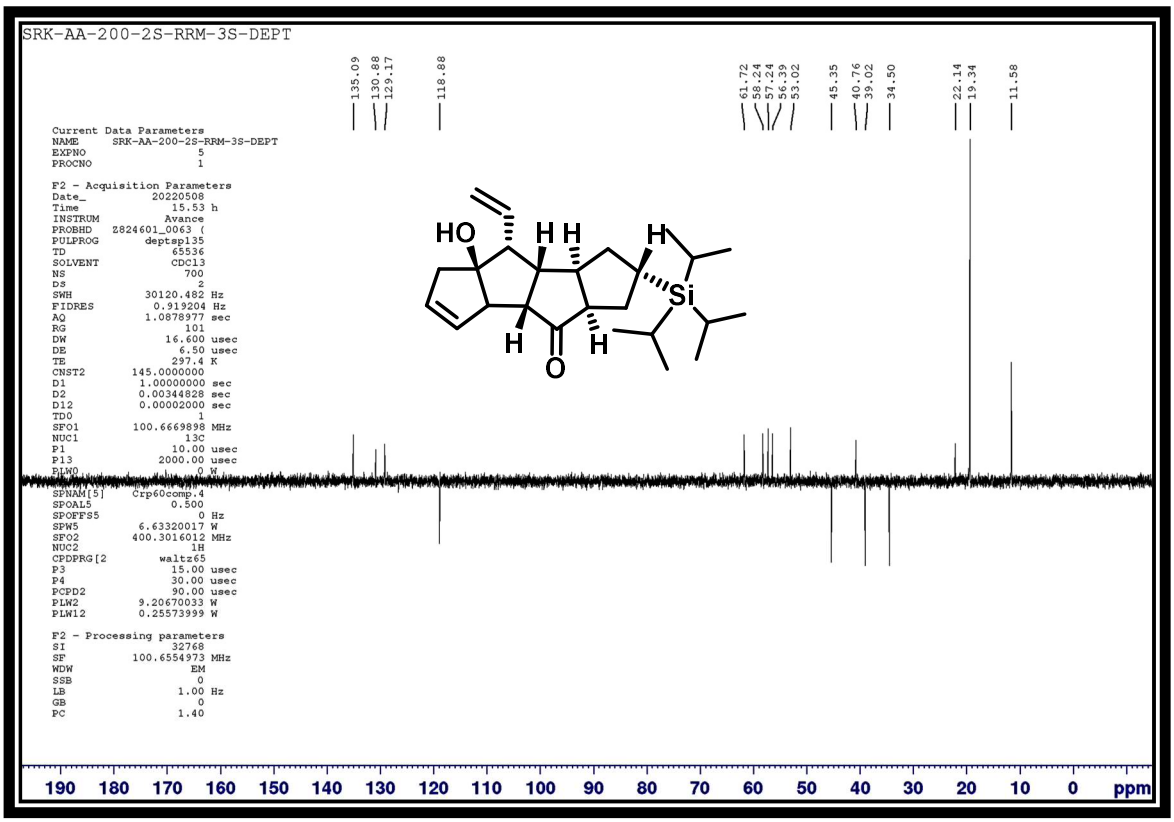
^{1}H NMR (400 MHz, $CDCl_3$) of Compound 22a



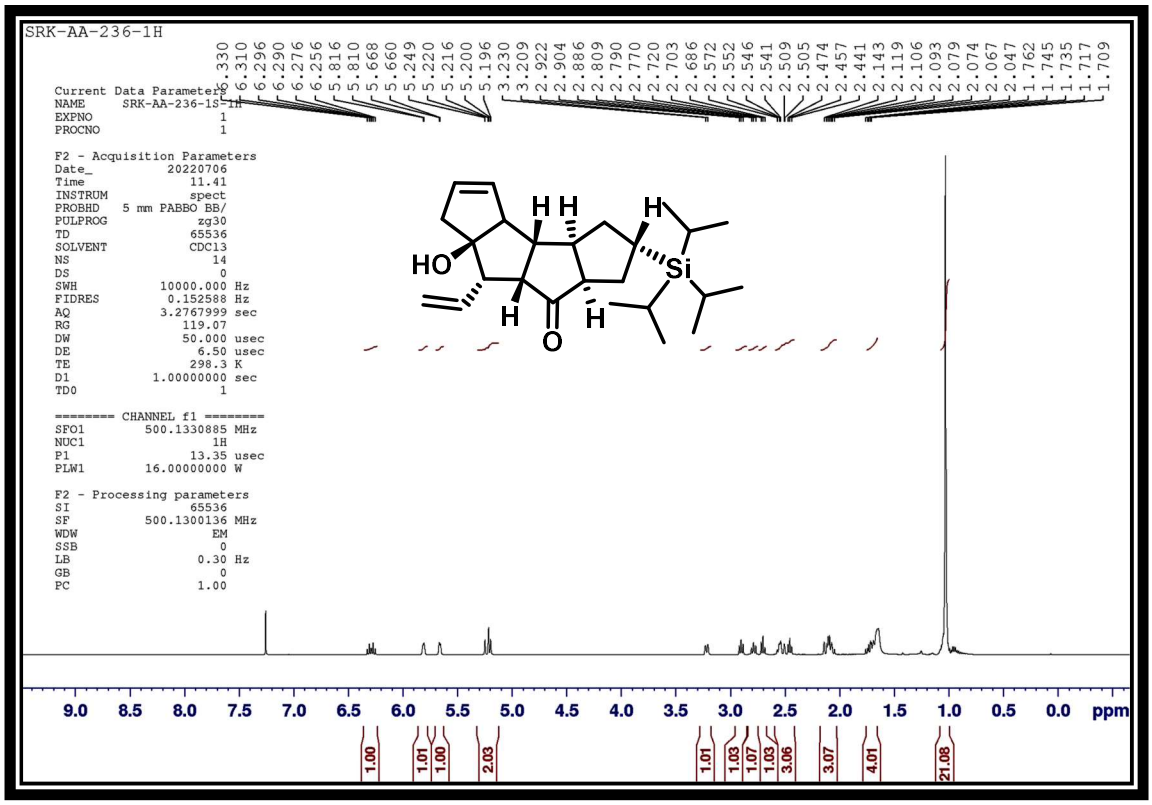
^{13}C NMR (100 MHz, $CDCl_3$) of Compound 22a



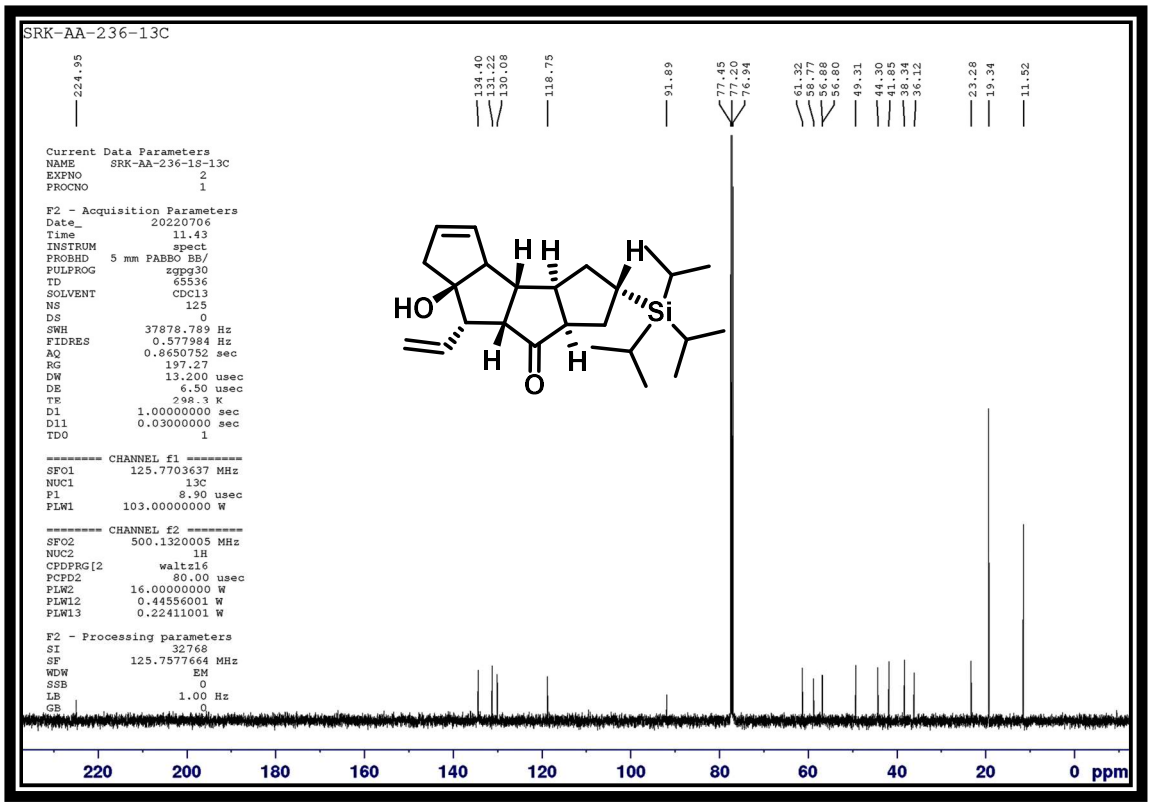
DEPT135 (100 MHz, $CDCl_3$) of Compound 22a



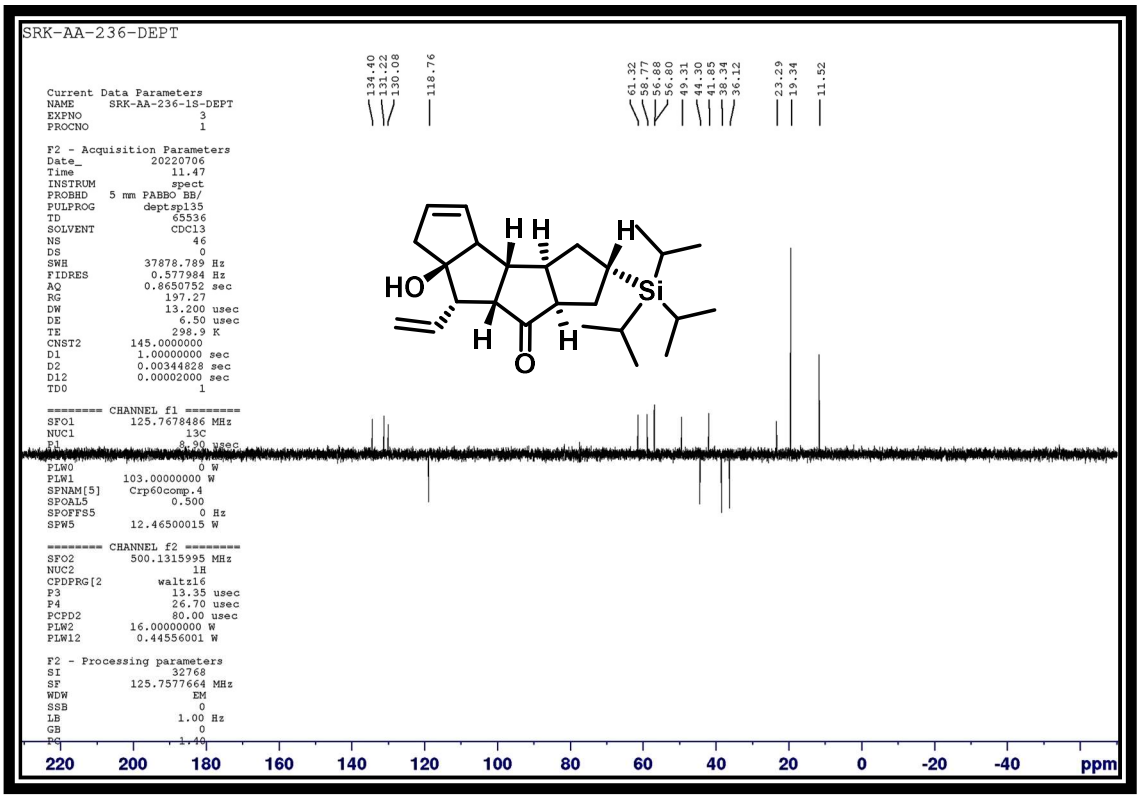
^{1}H NMR (500 MHz, $CDCl_3$) of Compound 22b



^{13}C NMR (125 MHz, $CDCl_3$) of Compound 22b



DEPT135 (125 MHz, $CDCl_3$) of Compound 22b

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Current Data Parameters
NAME      SRK-AA-236-1S-DEPT
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220706
Time              11.47
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG       deptsp135
TD              65536
SOLVENT           CDCl3
NS                   46
DS                    0
SWH           37878.789 Hz
FIDRES         0.577984 Hz
AQ             0.8650752 sec
RG                197.27
DW              13.200 usec
DE               6.50 usec
TE               298.9 K
CNST2       145.0000000
D1           1.00000000 sec
D2           0.00344828 sec
D12          0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        125.7678486 MHz
NUC1               13C
P1               8.90 usec
PLW0                 0 W
PLW1       103.00000000 W
SPNAM[5]    Crp60comp.4
SPOAL5             0.500
SPOFFS5                0 Hz
SPW5        12.46500015 W

======== CHANNEL f2 ========
SFO2        500.1315995 MHz
NUC2               1H
CPDPRG[2         waltz16
P3               13.35 usec
P4               26.70 usec
PCPD2            80.00 usec
PLW2        16.00000000 W
PLW12        0.44556001 W

F2 - Processing parameters
SI                 32768
SF          125.7577664 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

3. X-RAY DATA AND REFINEMENT PARAMETERS FOR TARGET COMPOUNDS

(2'S,3a'R,3b'S,4'S,7'S,7a'R,8a'S)-4',8a'-dibromo-2'-(triisopropylsilyl)-2',3',3a',3b',4',7',7a',8a'-octahydrospiro[[1,3]dioxolane-2,9'-[4,7]methanocyclopenta[a]inden]-8'(1'H)-one (16)

CCDC Number = 2176916

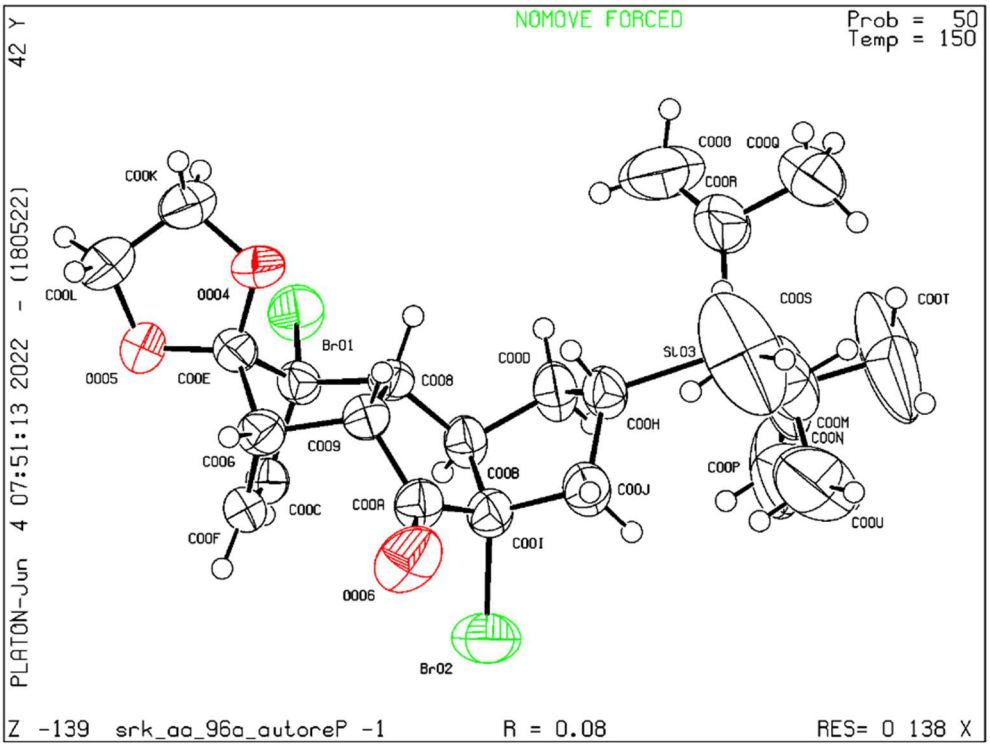

Table 1 Crystal data and structure refinement for SRK_AA_96A_autored.

Identification code	SRK_AA_96A_autored
Empirical formula	$C_{24}H_{35}Br_2O_3Si$
Formula weight	559.436
Temperature/K	150.15
Crystal system	triclinic
Space group	P-1
a/Å	7.8488(4)
b/Å	7.8922(3)
c/Å	23.1234(11)
α/°	96.478(4)
β/°	92.274(4)
γ/°	115.567(4)
Volume/Å^3	1277.60(11)
Z	2
ρ_{calc}g/cm^3	1.454
μ/mm^{-1}	3.241
F(000)	573.6
Crystal size/mm^3	0.28 × 0.25 × 0.17

Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.56 to 50
Index ranges	$-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-34 \leq l \leq 37$
Reflections collected	62528
Independent reflections	4491 [R_{int} = 0.1633, R_{sigma} = 0.1869]
Data/restraints/parameters	4491/0/277
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0801, wR_2 = 0.1988
Final R indexes [all data]	R_1 = 0.1160, wR_2 = 0.2257
Largest diff. peak/hole / e $Å^{-3}$	1.61/-1.13

(2'S,3a'R,3b'S,4'R,7'S,7a'S,8a'R)-2'-(triisopropylsilyl)decahydrospiro[[1,3]dioxolane-2,9'-[4,7]methanocyclopenta[a]inden]-8'(1'H)-one (21b)

CCDC Number = 2176327

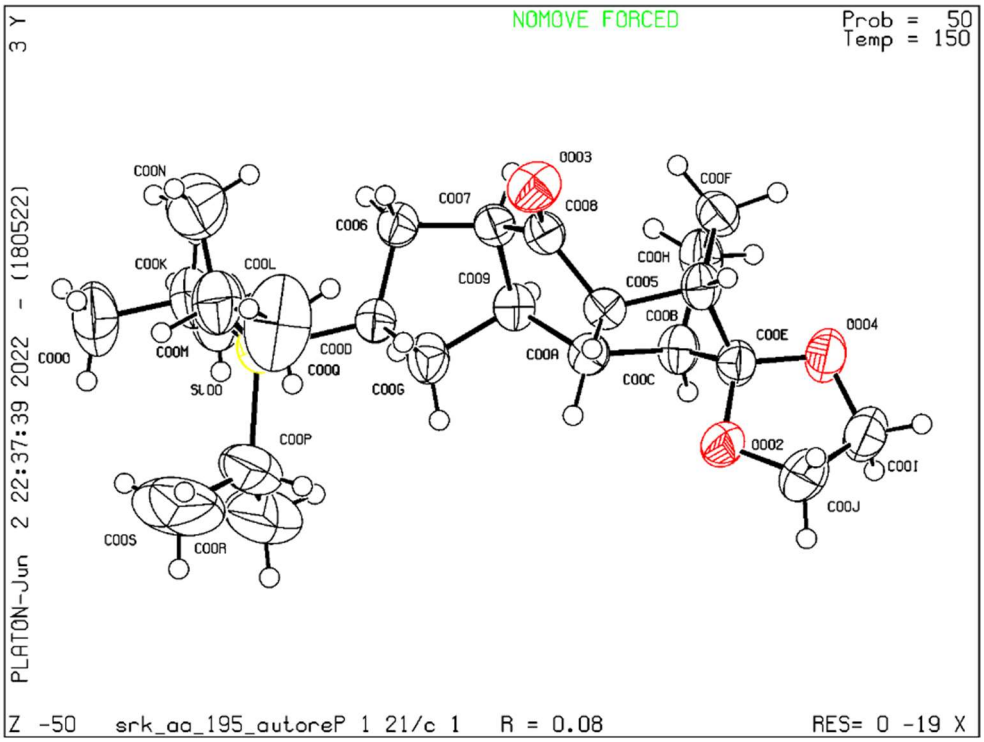

Table 1 Crystal data and structure refinement for SRK_AA_195_autored.

Identification code	SRK_AA_195_autored
Empirical formula	$C_{24}H_{40}O_3Si$
Formula weight	404.65
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	19.494(2)
b/Å	10.5294(12)
c/Å	11.4423(13)
α/°	90
β/°	90.610(10)
γ/°	90
Volume/Å^3	2348.5(5)
Z	4
ρ_{calc}g/cm^3	1.144
μ/mm^{-1}	0.121
F(000)	888.0
Crystal size/mm^3	0.423 × 0.254 × 0.019
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.18 to 49.984

Index ranges	$-23 \leq h \leq 23$, $-12 \leq k \leq 12$, $-13 \leq l \leq 13$
Reflections collected	25653
Independent reflections	4136 [R_{int} = 0.1616, R_{sigma} = 0.1051]
Data/restraints/parameters	4136/0/259
Goodness-of-fit on F^2	1.015
Final R indexes [I>=2σ (I)]	R_1 = 0.0770, wR_2 = 0.1697
Final R indexes [all data]	R_1 = 0.1585, wR_2 = 0.2161
Largest diff. peak/hole / e $Å^{-3}$	0.32/-0.22

(3aR,3bS,3cR,5S,6aR,7aS,8S,8aS)-8a-hydroxy-5-(triisopropylsilyl)-8-vinyl-3a,3b,3c,4,5,6,6a,7a,8,8a-decahydrodicyclopenta[a,f]pentalen-7(1H)-one (22b)

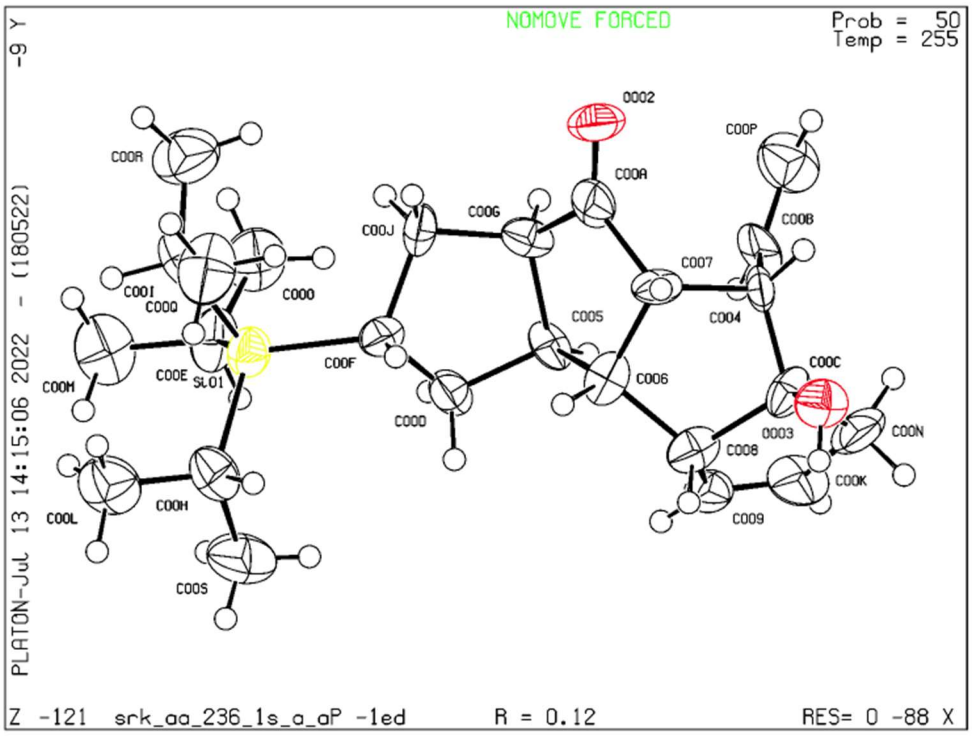

Table 1 Crystal data and structure refinement for SRK_AA_236_1S_A_autored.

Identification code	SRK_AA_236_1S_A_autored
Empirical formula	$C_{25}H_{40}O_2Si$
Formula weight	400.66
Temperature/K	255(18)
Crystal system	triclinic
Space group	P-1
a/Å	7.8153(14)
b/Å	11.4880(16)
c/Å	13.368(4)
α/°	90.921(19)
β/°	103.97(2)
γ/°	98.740(13)
Volume/Å^3	1149.4(5)
Z	2
ρ_{calc}g/cm^3	1.158
μ/mm^{-1}	0.120
F(000)	440.0
Crystal size/mm^3	0.667 × 0.12 × 0.031
Radiation	Mo Kα (λ = 0.71073)

2Θ range for data collection/°	3.592 to 34.998
Index ranges	$-6 \leq h \leq 6$, $-9 \leq k \leq 9$, $-11 \leq l \leq 11$
Reflections collected	16995
Independent reflections	1457 [R_{int} = 0.1679, R_{sigma} = 0.0652]
Data/restraints/parameters	1457/0/260
Goodness-of-fit on F^2	1.165
Final R indexes [I>=2σ (I)]	R_1 = 0.1229, wR_2 = 0.3490
Final R indexes [all data]	R_1 = 0.1352, wR_2 = 0.3555
Largest diff. peak/hole / e $Å^{-3}$	0.53/-0.35