Supporting Information

Total synthesis of both enantiomers of the biosurfactant aureosurfactin via bidirectional synthesis with a chiral Horner-Wittig building block

*Fabia Mittendorf, Moritz Quambusch and Stefan F. Kirsch**

* Department of Organic Chemistry, Bergische Universität Wuppertal, 42119 Wuppertal, Germany;
ORCID: 0000-0003-2628-8703; Email: sfkirsch@uni-wuppertal.de

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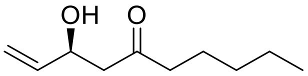
1. General information

General remarks. All commercial reagents and solvents were used as purchased. Thin-layer chromatography (TLC) was conducted with precoated aluminum-backed plates (silica gel 60 F_{254}) and visualized by exposure to UV light (254 nm) or by staining with potassium permanganate ($KMnO_4$) and subsequent heating. Flash column chromatography was performed on silica gel (40–60 µm), the used eluent is reported in the respective experiments. Abbreviations of solvents are as followed: CyHex: cyclohexane, DMF: dimethylformamide, EtOAc: ethyl acetate, MeOH: methanol, THF: tetrahydrofuran. For the preparation of the pH7 buffer solution 8.0 g NaCl, 0.2 g KCl, 1.78 g $Na_2HPO_4•2H_2O$, 0.27 g KH_2PO_4 were solved in 1 L H_2O. IR spectra were measured using ATR-technique in the range of 400–4000 cm^{-1}. ^1H NMR spectra were recorded at 400 MHz or 600 MHz, ^{13}C NMR spectra at 101 MHz or 151 MHz. Chemical shifts are reported in ppm relative to the solvent signal, coupling constants *J* in Hz. Multiplicities were defined by standard abbreviations. Low-resolution mass spectra (LRMS) were recorded using a LC/MS-combination (ESI). High-resolution mass spectra (HRMS) were obtained using ESI ionization (positive) on a Bruker micrOTOF or FD ionization on a JEOL-TOF.

2. Experimental data

(*S*)-3-hydroxydec-1-en-5-one (8)



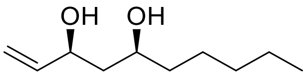
$C_{10}H_{18}O_2$

170.3 g/mol

To a solution of diisopropylamine (1.72 mL, 1.24 g, 12.3 mmol, 2.1 equiv.) in dry THF (58 mL) was added *n*-butyllithium (2.5 M in hexane, 4.91 mL, 3.40 g, 12.3 mmol, 2.1 equiv.) at −78 °C. After the cooling was removed for 15 minutes, building block (6*S*)-**3** (2.00 g, 5.84 mmol, 1.0 equiv.) dissolved in dry THF (19 mL) was added slowly at −78 °C. The solution was allowed to stir for one hour at this temperature. Following the addition of aldehyde **4a** (1.86 mL, 1.51 g, 17.5 mmol, 3.0 equiv.) dissolved in dry THF (10 mL) the reaction was allowed to warm to rt within one hour. After addition of potassium *tert*-butoxide (690 mg, 5.84 mmol, 1.0 equiv.) the reaction mixture was stirred for an additional hour at rt. The reaction was quenched with saturated, aqueous ammonium chloride solution (20 mL) and the aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic layers were washed with hydrochloric acid (2 M, 2 x 20 mL) and the aqueous layer was again extracted with dichloromethane (3 x 20 mL). The combined organic layers were washed with brine (20 mL), dried with sodium sulfate, and filtered. The filtrate was concentrated *in vacuo* and flash chromatography (CyHex/EtOAc 7:3) on silica gel afforded product **8** in 86% yield (850 mg, 4.99 mmol) as a yellow oil.

TLC: $R_f = 0.51$ (CyHex/EtOAc = 7:3) [$KMnO_4$]. **$[\alpha]_D^{20}$:** −19.0 ($c = 1.13$, CH_2Cl_2). **^{1}H NMR** (600 MHz, $CDCl_3$): δ [ppm] = 5.85 (ddd, J = 17.1, 10.5, 5.5 Hz, 1H), 5.28 (dt, J = 17.2, 1.5 Hz, 1H), 5.12 (dt, J = 10.5, 1.4 Hz, 1H), 4.56 (dddd, J = 7.9, 5.7, 4.2, 1.4 Hz, 1H), 2.78–2.75 (m, 1H), 2.65–2.60 (m, 2H), 2.42 (t, J = 7.5 Hz, 2H), 1.57 (p, J = 7.4 Hz, 2H), 1.34–1.20 (m, 4H), 0.88 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ [ppm] = 211.6, 139.2, 115.1, 68.8, 48.8, 43.8, 31.4, 23.4, 22.5, 14.0. **IR** (ATR): $\tilde{\upsilon}$ [cm^{-1}] = 3417, 2957, 2931, 2872, 1708, 1465, 1406, 1377, 1127, 1073, 1028, 992, 922. **HRMS** (ESI) m/z: [M+Na$^+$] calculated for $C_{10}H_{18}NaO_2$: 193.1199; found 193.1199.

(3*S*,5*S*)-dec-1-ene-3,5-diol (5a)



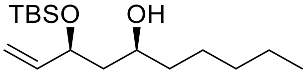
$C_{10}H_{20}O_2$

172.3 g/mol

β-Hydroxyketone **8** (3.20 g, 18.8 mmol, 1.0 equiv.) was dissolved in dry THF/MeOH (188 mL, 4:1) and diethylmethoxyborane (4 M in THF, 5.64 mL, 4.58 g, 22.6 mmol, 1.2 equiv.) was added at −78 °C. After stirring for 20 minutes at −78 °C, sodium borohydride (782 mg, 20.7 mmol, 1.1 equiv.) was added in one portion at −78 °C and the solution was stirred for two hours at this temperature. After addition of 2 M aqueous sodium hydroxide solution (58 mL) and 35% aqueous hydrogen peroxide solution (29 mL), the solution was allowed to stir at rt for 45 minutes. The reaction mixture was diluted by the addition of water (50 mL) and the aqueous layer was extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with brine (50 mL), dried with sodium sulfate, and filtered. The filtrate was concentrated *in vacuo* and flash chromatography (CyHex/EtOAc 7:3) on silica gel afforded product **5a** in 81% yield (6.25 g, 23.5 mmol, *d.r.* > 99:1) as a white solid.

TLC: R$_f$ = 0.23 (CyHex/EtOAc = 4:6). [KMnO$_4$]. **$[\alpha]_D^{20}$:** +5.7 (*c* = 1.02, CH$_2$Cl$_2$). **^{1}H NMR** (600 MHz, CDCl$_3$): δ [ppm] = 5.88 (ddd, *J* = 16.8, 10.4, 5.9 Hz, 1H), 5.25 (d, *J* = 17.2 Hz, 1H), 5.10 (d, *J* = 10.4 Hz, 1H), 4.37 (ddd, *J* = 9.7, 5.4, 3.1 Hz, 1H), 3.88 (dddd, *J* = 9.8, 7.3, 4.9, 2.3 Hz, 1H), 2.63 (s, 2H), 1.66 (dt, *J* = 14.5, 2.7 Hz, 1H), 1.58 (dt, *J* = 14.5, 9.9 Hz, 1H), 1.53–1.35 (m, 3H), 1.37–1.23 (m, 5H), 0.89 (t, *J* = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR** (151 MHz, CDCl$_3$): δ [ppm] = 140.9, 114.5, 74.0, 72.7, 43.2, 38.3, 32.0, 25.2, 22.8, 14.2. **IR** (ATR): $\tilde{\upsilon}$ [cm^{-1}] = 3335, 2954, 2929, 2858, 1457, 1422, 1314, 1135, 1068, 989, 921, 850. **HRMS** (ESI) m/z: [M+Na$^+$] calculated for $C_{10}H_{20}NaO_2$: 195.1356; found 195.1359. The analytical data are in agreement with previously reported one.[2]

(3*S*,5*S*)-3-((*tert*-butyldimethylsilyl)oxy)dec-1-en-5-ol (9)



$C_{16}H_{34}O_2Si$

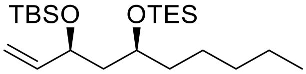
286.5 g/mol

To a solution of diol **5a** (2.50 g, 14.5 mmol, 1.0 equiv.) in dry THF (101 mL) was added *n*-butyllithium (2.5 M in hexane, 7.56 mL, 5.24 g, 14.5 mmol, 2.1 equiv.) dropwise at −78 °C and the reaction was allowed to warm to rt within one hour. Then TBSCl (2.62 g, 17.4 mmol, 1.2 equiv.) was added in one portion and the solution was stirred for additional 30 minutes at rt. After addition of imidazole (49.4 mg, 726 µmol, 0.05 equiv.) the reaction mixture was stirred for 12 hours at rt. The reaction was quenched with saturated aqueous sodium bicarbonate solution (50 mL) and diluted with diethyl ether (20 mL). The aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic layers were washed with brine (20 mL), dried with sodium sulfate, and filtered. The filtrate was concentrated *in vacuo* and flash chromatography (CyHex/EtOAc 9:1) on silica gel afforded product **9** in 67% yield (2.80 g, 9.77 mmol) as a colorless oil.

TLC: R$_f$ = 0.53 (CyHex/EtOAc = 8:2). [KMnO$_4$]. **$[\alpha]_D^{20}$:** −14.2 (*c* = 1.05, CH$_2$Cl$_2$). **^{1}H NMR** (600 MHz, CDCl$_3$): δ [ppm] = 5.82 (ddd, *J* = 17.2, 10.4, 6.8 Hz, 1H), 5.16 (d, *J* = 17.2 Hz, 1H), 5.05 (d, *J* = 10.7 Hz, 1H), 4.35 (td, *J* = 7.7, 5.0 Hz, 1H), 3.79 (dddd, *J* = 9.3, 7.0, 4.6, 2.4 Hz, 1H), 1.68–1.55 (m, 2H), 1.51–1.44 (m, 1H), 1.43–1.36 (m, 2H), 1.35–1.22 (m, 5H), 0.96–0.70

(m, 12H), 0.20–−0.11 (m, 6H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ [ppm] = 141.7, 114.5, 75.2, 71.0, 44.6, 37.8, 32.1, 26.0, 25.2, 22.8, 18.2, 14.2, −3.7, −4.7. **IR** (ATR): $\tilde{\upsilon}$ [cm^{-1}] = 3454, 2955, 2929, 2857, 1463, 1252, 1071, 921, 834, 774. **HRMS** (ESI) m/z: [M+Na^{+}] calculated for $C_{16}H_{34}NaO_2Si$: 309.2220; found 309.2227.

(5*S*,7*S*)-9,9-diethyl-2,2,3,3-tetramethyl-7-pentyl-5-vinyl-4,8-dioxa-3,9-disilaundecane (6)



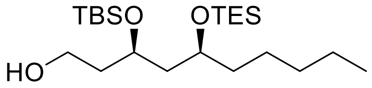
$C_{22}H_{48}O_2Si_2$

400.8 g/mol

To a solution of alcohol **9** (1.63 g, 5.69 mmol, 1.0 equiv.) in DMF (38 mL) were added imidazole (3.10 g, 45.5 mmol, 8.0 equiv.) and TESCl (3.82 mL, 3.43 g, 22.8 mmol, 4.0 equiv.). The solution was allowed to stir at rt for 18 hours. The reaction mixture was diluted with water (20 mL) and dichloromethane (20 mL). The aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic layers were washed with brine (20 mL), dried with sodium sulfate, and filtered. The filtrate was concentrated *in vacuo* and flash chromatography (CyHex/EtOAc 95:5) on silica gel afforded product **6** in 94% yield (2.15 g, 5.36 mmol) as a colorless oil.

TLC: R_f = 0.58 (CyHex/EtOAc = 95:5) [$KMnO_4$]. **$[\alpha]_{D}^{20}$:** −1.0 (*c* = 1.32, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 5.80 (ddd, *J* = 16.9, 10.3, 6.4 Hz, 1H), 5.14 (ddd, *J* = 17.2, 1.8, 1.2 Hz, 1H), 5.03 (ddd, *J* = 10.3, 1.8, 1.0 Hz, 1H), 4.24–4.14 (m, 1H), 3.85–3.69 (m, 1H), 1.71 (ddd, *J* = 13.5, 7.1, 6.3 Hz, 1H), 1.61–1.44 (m, 2H), 1.44–1.19 (m, 7H), 1.02–0.80 (m, 21H), 0.59 (q, *J* = 7.6 Hz, 6H), 0.09–−0.02 (m, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 141.9, 114.0, 71.6, 69.5, 46.2, 37.4, 32.2, 26.0, 25.0, 22.8, 18.3, 14.2, 7.1, 5.4, −4.1, −4.7. **IR** (ATR): $\tilde{\upsilon}$ [cm^{-1}] = 2954, 2929, 2876, 2857, 1461, 1251, 1079, 1004, 922, 865, 834, 774, 723. **HRMS** (ESI) m/z: [M+Na^{+}] calculated for $C_{22}H_{48}NaO_2Si_2$: 423.3085; found 423.3081.

(3*R*,5*S*)-3-((*tert*-butyldimethylsilyl)oxy)-5-((triethylsilyl)oxy)decan-1-ol (10a)



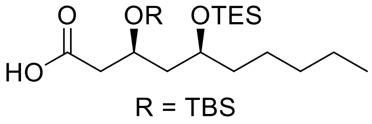
$C_{22}H_{50}O_3Si_2$

418.8 g/mol

To a solution of silylether **6** (2.10 g, 5.24 mmol, 1.0 equiv.) in dry THF (52 mL) was added 9-BBN (0.5 M in THF, 20.9 mL, 10.5 mmol, 2.0 equiv.) dropwise at 0 °C. After stirring at 0 °C for 15 minutes, the reaction was allowed to stir for 18 hours at rt. After addition of 3 M aqueous sodium hydroxide solution (3.5 mL) and 35% aqueous hydrogen peroxide solution (3.5 mL) consecutively at 0 °C, the reaction mixture was stirred for four hours at rt. The solution was diluted with water (20 mL) and diethyl ether (20 mL). The aqueous layer was extracted with diethyl ether (3 x 20 mL). The combined organic layers were washed with brine (20 mL), dried with sodium sulfate, and filtered. The filtrate was concentrated *in vacuo* and flash chromatography (CyHex/EtOAc 9:1) on silica gel afforded product **10a** in 80% yield (1.75 g, 4.18 mmol) as a colorless oil.

TLC: R_f = 0.18 (CyHex/EtOAc = 9:1) [$KMnO_4$]. **$[\alpha]_D^{20}$:** +14.8 (*c* = 1.30, CH_2Cl_2). **^{1}H NMR** (600 MHz, $CDCl_3$): δ [ppm] = 4.12–4.03 (m, 1H), 3.87–3.80 (m, 1H), 3.76–3.61 (m, 2H), 2.51 (s, 1H), 1.99–1.83 (m, 1H), 1.76–1.55 (m, 4H), 1.50–1.39 (m, 2H), 1.32–1.14 (m, 5H), 0.99–0.85 (m, 21H), 0.59 (q, *J* = 7.8 Hz, 6H), 0.14–0.02 (m, 6H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ [ppm] = 69.8, 69.6, 60.4, 44.2, 38.0, 37.9, 32.2, 26.0, 24.9, 22.8, 18.1, 14.2, 7.1, 5.4, −4.3, −4.5. **IR** (ATR): $\tilde{\upsilon}$ [cm^{-1}] = 3433, 2953, 2930, 2867, 2857, 1462, 1253, 1080, 1056, 1004, 835, 773, 740, 724. **HRMS** (ESI) m/z: [M+Na$^+$] calculated for $C_{22}H_{50}NaO_3Si_2$: 441.3191; found 441.3195.

(3*S*,5*S*)-3-((*tert*-butyldimethylsilyl)oxy)-5-((triethylsilyl)oxy)decanoic acid (2a)



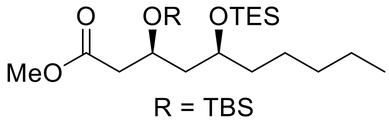
$C_{22}H_{48}O_4Si_2$

432.8 g/mol

To a solution of alcohol **10a** (500 mg, 1.19 mmol, 1.0 equiv.) in ACN/CCl_4/pH 7 buffer (23 mL, 1:1:1.5) were added sodium periodate (774 mg, 3.58 mmol, 3.0 equiv.) and ruthenium(IV) oxide hydrate (30.0 mg, 120 µmol, 0.1 equiv.) consecutively. The solution was stirred at rt for 3 hours. The reaction mixture was then diluted with water (10 mL) and diethyl ether (10 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (3 x 5 mL). The combined organic layers were washed with brine (10 mL), dried with sodium sulfate, and filtered. The filtrate was concentrated *in vacuo* and flash chromatography (CyHex/EtOAc 8:2) on silica gel afforded product **2a** in 70% yield (363 mg, 839 µmol) as a colorless oil.

TLC: R_f = 0.39 (CyHex/EtOAc = 8:2) [$KMnO_4$]. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{20}}$**:** +12.8 (*c* = 1.32, CH_2Cl_2). **^{1}H NMR** (600 MHz, $CDCl_3$): δ [ppm] = 4.25 (p, *J* = 6.2 Hz, 1H), 3.76 (p, *J* = 6.0 Hz, 1H), 2.60 (dd, *J* = 15.0, 5.1 Hz, 1H), 2.47 (dd, *J* = 15.0, 6.6 Hz, 1H), 1.76–1.60 (m, 2H), 1.51–1.38 (m, 2H), 1.35–1.21 (m, 6H), 1.00–0.84 (m, 21H), 0.60 (q, *J* = 8.0 Hz, 6H), 0.12–−0.09 (m, 6H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ [ppm] = 176.8, 69.5, 67.1, 44.6, 42.4, 37.6, 32.2, 25.9, 24.9, 22.8, 18.0, 14.1, 7.1, 5.3, −4.4, −4.7. **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2954, 2930, 2876, 1711, 1462, 1252, 1082, 1004, 835, 775. **HRMS** (ESI) m/z: [M+Na$^+$] calculated for $C_{22}H_{48}NaO_4Si_2$: 455.2983; found 455.2982.

methyl (3*S*,5*S*)-3-((*tert*-butyldimethylsilyl)oxy)-5-((triethylsilyl)oxy)decanoate (11a)



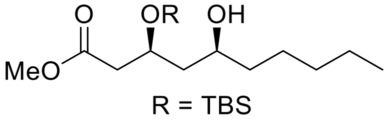
$C_{23}H_{50}O_4Si_2$

446.8 g/mol

To a solution of carboxylic acid **2a** (195 mg, 450 µmol, 1.0 equiv.) in DMF (901 µL) were added potassium carbonate (112 mg, 811 µmol, 1.8 equiv.) and iodomethane (126 µL, 288 mg, 2.03 mmol, 4.5 equiv.) consecutively. The solution was stirred at rt for 18 hours. The reaction mixture was quenched with saturated aqueous ammonium chloride solution (5 mL) and diluted diethyl ether (5 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (3 x 5 mL). The combined organic layers were washed with brine (5 mL), dried with sodium sulfate, and filtered. The filtrate was concentrated *in vacuo* and flash chromatography (CyHex/EtOAc 98:2) on silica gel afforded product **11a** in 86% yield (174 mg, 389 µmol) as a colorless oil.

TLC: R_f = 0.56 (CyHex/EtOAc = 95:5) [$KMnO_4$]. **$[\alpha]_D^{20}$:** +12.5 (*c* = 1.08, CH_2Cl_2). **^{1}H NMR** (600 MHz, $CDCl_3$): δ [ppm] = 4.23 (p, *J* = 6.3 Hz, 1H), 3.75 (p, *J* = 6.1 Hz, 1H), 3.66 (d, *J* = 1.2 Hz, 3H), 2.53 (dd, *J* = 14.6, 4.9 Hz, 1H), 2.43 (dd, *J* = 14.6, 7.4 Hz, 1H), 1.69 (dt, *J* = 13.0, 6.3 Hz, 1H), 1.61 (dt, *J* = 13.4, 6.2 Hz, 1H), 1.48 (dq, *J* = 15.6, 5.2 Hz, 1H), 1.41 (tq, *J* = 10.4, 5.9, 5.2 Hz, 1H), 1.37–1.22 (m, 6H), 1.01–0.86 (m, 21H), 0.60 (q, *J* = 7.9, 7.4 Hz, 6H), 0.08–−0.03 (m, 6H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ [ppm] = 172.2, 69.5, 67.2, 51.5, 45.2, 43.0, 37.4, 32.2, 25.9, 25.0, 22.8, 18.1, 14.2, 7.1, 5.3, −4.3, −4.6. **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2953, 2930, 2876, 2857, 1742, 1461, 1436, 1254, 1193, 1165, 1081, 1004, 835, 775, 741. **HRMS** (ESI) m/z: [$M+Na^+$] calculated for $C_{23}H_{50}NaO_4Si_2$: 469.3140; found 469.3140.

methyl (3*S*,5*S*)-3-((*tert*-butyldimethylsilyl)oxy)-5-hydroxydecanoate (12a)



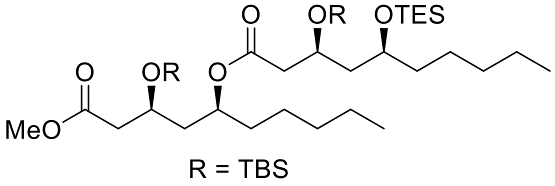
$C_{17}H_{36}O_4Si$

332.6 g/mol

First, HF•pyridine (70% HF, 80.1 µL, 79.2 mg, 559 µmol, 5.0 equiv.) was dissolved in pyridine/MeOH (1.1 mL, 6:1) at 0 °C in a teflon vial. In another teflon vial, silyl ether **11a** (50.0 mg, 112 µmol, 1.0 equiv.) was dissolved in THF (0.98 mL) and the solution was cooled to 0 °C. The prepared HF•pyridine solution was then transferred to the THF solution and the reaction mixture was stirred at rt for 18 hours. Following the addition of an excess of MeOTMS (5 mL) at 0 °C and dilution with toluene (5 mL), the volatile compounds were removed *in vacuo*. The residue was diluted with toluene (2 mL) again and the procedure was repeated three times to remove all of the pyridine. Flash chromatography (CyHex/EtOAc 9:1) on silica gel afforded then the product **12a** in 78% yield (29.0 mg, 87.2 µmol) as a colorless oil.

TLC: R_f = 0.45 (CyHex/EtOAc = 8:2) [$KMnO_4$]. $\boldsymbol{[\alpha]_D^{20}}$**:** +3.2 (*c* = 0.47, CH_2Cl_2). **^{1}H NMR** (600 MHz, C_6D_6): δ [ppm] = 4.46 (p, *J* = 6.2 Hz, 1H), 3.60 (dt, *J* = 8.6, 4.3 Hz, 1H), 3.37 (s, 3H), 2.59–2.43 (m, 2H), 1.83 (s, 1H), 1.70 (td, *J* = 9.0, 8.6, 4.5 Hz, 1H), 1.63 (ddd, *J* = 14.1, 6.6, 2.8 Hz, 1H), 1.50–1.14 (m, 8H), 1.01–0.75 (m, 12H), 0.17–0.02 (m, 6H). **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6): δ [ppm] = 171.7, 69.3, 68.9, 51.1, 45.2, 42.8, 38.5, 32.3, 26.0, 25.6, 23.1, 18.2, 14.3, −4.5, −4.5. **IR** (ATR): $\tilde{\upsilon}$ [cm^{-1}] = 3445, 2954, 2929, 2857, 1741, 1462, 1255, 1165, 1082, 836, 810, 776. **HRMS** (ESI) m/z: [$M+Na^+$] calculated for $C_{17}H_{36}NaO_4Si$: 355.2275; found 355.2273.

(3*S*,5*S*)-3-((*tert*-butyldimethylsilyl)oxy)-1-methoxy-1-oxodecan-5-yl-(3*S*,5*S*)-3-((*tert*-butyldimethylsilyl)oxy)-5-((triethylsilyl)oxy)decanoate (13a)



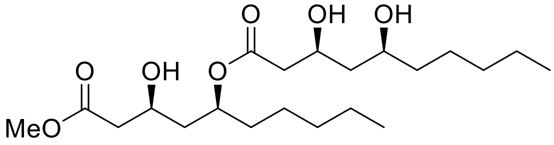
$C_{39}H_{82}O_7Si_3$

747.3 g/mol

To a solution of carboxylic acid **2a** (55.0 mg, 127 µmol, 1.0 equiv.) in dry toluene (4.2 mL) were added triethylamine (21.1 µL, 15.4 mg, 153 µmol, 1.2 equiv.) and 2,4,6-trichlorobenzoylchloride (22.5 µL, 35.2 mg, 140 µmol, 1.1 equiv.) consecutively. The reaction mixture was stirred for 30 minutes and then alcohol **12a** (50.7 mg, 153 µmol, 1.2 equiv.) dissolved in dry toluene (1.4 mL) was added, followed by DMAP (21.7 mg, 178 µmol, 1.4 equiv.). The solution was allowed to stir for one hour at rt and then it was concentrated *in vacuo*. Flash chromatography (CyHex/EtOAc 99:1) on silica gel afforded product **13a** in 92% yield (87.0 mg, 116 µmol) as a colorless oil.

TLC: R_f = 0.61 (CyHex/EtOAc = 95:5) [$KMnO_4$]. $[\alpha]_D^{20}$**:** +5.7 (*c* = 1.21, CH_2Cl_2). **^{1}H NMR** (600 MHz, C_6D_6): δ [ppm] = 5.22 (td, *J* = 7.9, 3.9 Hz, 1H), 4.50 (p, *J* = 6.1 Hz, 1H), 4.40 (td, *J* = 7.1, 3.6 Hz, 1H), 3.97 (p, *J* = 6.0 Hz, 1H), 3.39 (s, 3H), 2.72–2.62 (m, 2H), 2.56 (qd, *J* = 15.0, 6.0 Hz, 2H), 2.03–1.87 (m, 3H), 1.82 (ddd, *J* = 14.0, 7.4, 4.8 Hz, 1H), 1.70–1.18 (m, 16H), 1.08 (t, *J* = 8.0 Hz, 6H), 1.04–0.88 (m, 27H), 0.70 (q, *J* = 8.0 Hz, 6H), 0.26–0.01 (m, 12H). **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6): δ [ppm] = 171.4, 170.8, 71.3, 69.8, 67.3, 67.2, 51.1, 45.4, 43.2, 42.5, 42.3, 37.8, 35.1, 32.6, 32.1, 26.2, 26.0, 25.4, 25.2, 23.1, 23.0, 18.3, 18.2, 14.3, 14.2, 7.3, 5.7, −4.2, −4.4, −4.4, −4.5. **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2954, 2929, 2857, 1738, 1462, 1254, 1167, 1081, 1005, 957, 835, 809, 775. **HRMS** (ESI) m/z: [M+Na$^+$] calculated for $C_{39}H_{82}NaO_7Si_3$: 769.5261; found 769.5261.

(3*S*,5*S*)-3-hydroxy-1-methoxy-1-oxodecan-5-yl (3*S*,5*S*)-3,5-dihydroxydecanoate (1a)



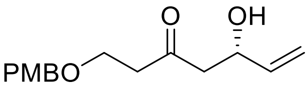
$C_{21}H_{40}O_7$

404.5 g/mol

First, HF•pyridine (70% HF, 280 µL, 277 mg, 1.95 mmol, 20.0 equiv.) was dissolved in pyridine/MeOH (1 mL, 6:1) at 0 °C in a teflon vial. In another teflon vial, silyl ether **13a** (73.0 mg, 97.7 µmol, 1.0 equiv.) was dissolved in THF (0.85 mL) and the solution was cooled to 0 °C. The prepared HF•pyridine solution was then transferred to the THF solution and the reaction mixture was stirred at rt for 18 hours. Following the addition of an excess of MeOTMS (5 mL) at 0 °C and dilution with toluene (5 mL), the volatile compounds were removed *in vacuo*. The residue was diluted with toluene (2 mL) again and the procedure was repeated three times to remove all of the pyridine. Flash chromatography (CH_2Cl_2 → CH_2Cl_2/MeOH = 98:2 → CH_2Cl_2/MeOH = 95:5) on silica gel afforded then the product **1a** in 99% yield (39.0 mg, 96.4 µmol) as a colorless oil.

TLC: R_f = 0.19 (CH_2Cl_2/MeOH = 98:2) [$KMnO_4$]. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{20}}$**:** +20.6 (*c* = 0.70, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 5.15–4.99 (m, 1H), 4.27 (tt, *J* = 8.4, 4.3 Hz, 1H), 4.19–4.03 (m, 1H), 3.94–3.82 (m, 1H), 3.71 (s, 3H), 2.53 (dd, *J* = 16.5, 3.5 Hz, 1H), 2.47–2.38 (m, 3H), 1.85 (dt, *J* = 14.6, 8.4 Hz, 1H), 1.70–1.65 (m, 1H), 1.64–1.54 (m, 4H), 1.51–1.38 (m, 3H), 1.36–1.18 (m, 11H), 0.96–0.79 (m, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 173.2, 172.4, 73.0, 72.4, 69.8, 66.5, 52.0, 42.9, 42.6, 41.3, 40.9, 37.9, 34.7, 32.0, 31.7, 25.2, 25.0, 22.8, 22.6, 14.2, 14.1. **IR** (ATR): $\tilde{\upsilon}$ [cm^{-1}] = 3403, 2954, 2928, 2858, 1727, 1437, 1263, 1163, 1130, 1070. **HRMS** (ESI) m/z: [M+Na^{+}] calculated for $C_{21}H_{40}NaO_7$: 427.2666; found 427.2666.

(*S*)-5-hydroxy-1-((4-methoxybenzyl)oxy)hept-6-en-3-one (14)



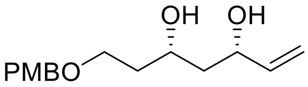
$C_{15}H_{20}O_4$

264.3 g/mol

To a solution of diisopropylamine (6.53 mL, 4.72 g, 36.2 mmol, 2.1 equiv.) in THF (221 mL) was added *n*-butyllithium (2.5 M in hexane, 23.3 mL, 16.2 g, 46.6 mmol, 2.1 equiv.) at −78 °C. After the cooling was removed for 15 minutes, building block (6*S*)-**3** (7.60 g, 22.2 mmol, 1.0 equiv.) dissolved in 74 mL THF was added slowly at −78 °C. The solution was allowed to stir for one hour at this temperature. Following the addition of aldehyde **4b** (12.0 g, 66.6 mmol, 3.0 equiv.) dissolved in 37 mL THF the reaction was allowed to warm to rt within one hour. After addition of potassium *tert*-butoxide (2.62 g, 22.2 mmol, 1.0 equiv.) the reaction mixture was stirred for an additional hour at rt. The reaction was quenched with saturated, aqueous ammonium chloride solution (100 mL) and the aqueous layer was extracted with dichloromethane (3 x 50 mL). The combined organic layers were washed with hydrochloric acid (2 M, 2 x 100 mL) and the aqueous layer was again extracted with dichloromethane (3 x 50 mL). The combined organic layers were washed with brine (100 mL), dried with sodium sulfate, and filtered. The filtrate was concentrated *in vacuo* and flash chromatography (CyHex/EtOAc 7:3) on silica gel afforded product **14** in 89% yield (5.21 g, 19.7 mmol) as a yellow oil.

TLC: $R_f = 0.34$ (CyHex /EtOAc = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.25–7.20 (m, 2H), 6.91–6.83 (m, 2H), 5.85 (ddd, *J* = 17.2, 10.5, 5.5 Hz, 1H), 5.28 (dt, *J* = 17.2, 1.5 Hz, 1H), 5.12 (dt, *J* = 10.5, 1.4 Hz, 1H), 4.64–4.51 (m, 1H), 4.43 (s, 2H), 3.80 (s, 3H), 3.71 (td, *J* = 6.1, 2.0 Hz, 2H), 2.74–2.63 (m, 4H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 209.7, 159.5, 139.2, 130.1, 129.5, 115.1, 114.0, 73.1, 68.7, 64.9, 55.4, 49.7, 43.9. The analytical data are in agreement with previously reported one.[1]

(3*S*,5*R*)-7-((4-methoxybenzyl)oxy)hept-1-ene-3,5-diol (5b)



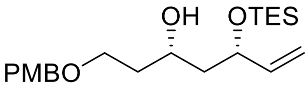
$C_{15}H_{22}O_4$

266.3 g/mol

β-Hydroxyketone **14** (2.20 g, 8.32 mmol, 1.0 equiv.) was dissolved in dry THF/MeOH (82 mL, 4:1) and diethylmethoxyborane (4 M in THF, 2.50 mL, 2.03 g, 10.0 mmol, 1.2 equiv.) was added at −78 °C. After stirring for 20 minutes at −78 °C, sodium borohydride (346 mg, 9.16 mmol, 1.1 equiv.) was added in one portion at −78 °C and the solution was stirred for two hours at this temperature. After addition of 2 M aqueous sodium hydroxide solution (26 mL) and 35% aqueous hydrogen peroxide solution (13 mL), the solution was allowed to stir at rt for 45 minutes. The reaction mixture was diluted by the addition of water (20 mL) and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried with sodium sulfate, and filtered. The filtrate was concentrated *in vacuo* and flash chromatography (CyHex/EtOAc 6:4) on silica gel afforded product **5b** in 96% yield (2.13 g, 8.00 mmol, *d.r.* > 99:1) as a colorless oil.

TLC: R_f = 0.21 (CyHex/EtOAc = 1:1). [$KMnO_4$] $[\alpha]_D^{20}$**:** +10.7 (*c* = 1.22, CH_2Cl_2). **^{1}H NMR** (600 MHz, $CDCl_3$): δ [ppm] = 7.24 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.86 (ddd, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.26 (dt, *J* = 17.2, 1.5 Hz, 1H), 5.08 (dt, *J* = 10.4, 1.5 Hz, 1H), 4.45 (d, *J* = 1.0 Hz, 2H), 4.38 (dddd, *J* = 8.5, 5.5, 2.8, 1.4 Hz, 1H), 4.10 (ddt, *J* = 9.9, 8.5, 3.0 Hz, 1H), 3.81 (s, 3H), 3.70 (ddd, *J* = 9.4, 5.9, 4.4 Hz, 1H), 3.66–3.56 (m, 1H), 1.81 (dtd, *J* = 14.6, 8.4, 4.5 Hz, 1H), 1.73 (dddd, *J* = 14.6, 5.9, 4.2, 3.0 Hz, 1H), 1.60 (dt, *J* = 14.2, 3.0 Hz, 2H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ [ppm] = 159.5, 140.9, 130.0, 129.5, 114.3, 114.1, 73.4, 73.2, 72.3, 68.7, 55.4, 43.4, 37.0. **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3317, 2911, 1644, 1585, 1244, 1075, 1030, 992, 845, 818. **HRMS** (ESI) m/z: [M+Na$^+$] calculated for $C_{15}H_{22}NaO_4$: 289.1410; found 289.1411.

(3*S*,5*S*)-1-((4-methoxybenzyl)oxy)-5-((triethylsilyl)oxy)hept-6-en-3-ol (15)



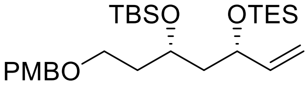
$C_{21}H_{36}O_4Si$

380.6 g/mol

To a solution of diol **5b** (1.90 g, 7.13 mmol, 1.0 equiv.) in dry dichloromethane (24 mL) were added 2,6-lutidine (2.52 mL, 2.32 g, 21.4 mmol, 3.0 equiv.) and DMAP (87.2 mg, 0.713 mmol, 0.1 equiv.). After addition of triethylsilyl chloride (1.45 mL, 1.29 g, 8.56 mmol, 1.2 equiv.) at −78 °C, the solution was firstly stirred for two hours at −78 °C and then for one hour at 0 °C. The reaction mixture was quenched with saturated aqueous sodium bicarbonate solution (20 mL) and diluted with diethyl ether (20 mL). The aqueous layer was extracted with diethyl ether (3 x 20 mL). The combined organic layers were washed with brine (20 mL), dried with sodium sulfate, and filtered. The filtrate was concentrated *in vacuo* and flash chromatography (CyHex/EtOAc 9:1) on silica gel afforded product **15** in 58% yield (1.59 g, 4.18 mmol) as a colorless oil.

TLC: R_f = 0.31 (CyHex/ EtOAc = 8:2). [$KMnO_4$] $[\alpha]_D^{20}$**:** −1.7 (*c* = 1.01, CH_2Cl_2). **^{1}H NMR** (600 MHz, $CDCl_3$): δ [ppm] = 7.25 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.82 (ddd, *J* = 17.3, 10.3, 7.1 Hz, 1H), 5.17 (dt, *J* = 17.2, 1.3 Hz, 1H), 5.06 (dt, *J* = 10.4, 1.2 Hz, 1H), 4.44 (s, 2H), 4.38–4.30 (m, 1H), 3.98–3.90 (m, 1H), 3.80 (s, 3H), 3.64 (ddd, *J* = 9.4, 6.6, 5.5 Hz, 1H), 3.59 (ddd, *J* = 9.4, 6.8, 5.6 Hz, 1H), 3.54 (d, *J* = 1.8 Hz, 1H), 1.80–1.67 (m, 3H), 1.59–1.52 (m, 1H), 0.95 (t, *J* = 8.0 Hz, 9H), 0.62 (q, *J* = 8.0 Hz, 6H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ [ppm] = 159.4, 141.4, 130.6, 129.4, 114.7, 114.0, 74.3, 73.0, 69.0, 67.9, 55.4, 45.0, 37.4, 6.9, 5.1. **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3507, 2951, 2911, 2875, 1612, 1512, 1245, 1084, 1034, 1004, 921, 845, 819, 740, 725. **HRMS** (ESI) m/z: [M+H$^+$] calculated for $C_{21}H_{37}O_4Si$: 381.2456; found 381.2456.

(5*S*,7*S*)-9,9-diethyl-5-(2-((4-methoxybenzyl)oxy)ethyl)-2,2,3,3-tetramethyl-7-vinyl-4,8-dioxa-3,9-disilaundecane (7)



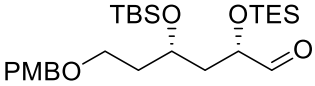
$C_{27}H_{50}O_4Si_2$

494.8 g/mol

To a solution of alcohol **15** (1.90 g, 4.99 mmol, 1.0 equiv.) in DMF (30 mL) were added imidazole (1.36 g, 19.9 mmol, 4.0 equiv.) and TBSCl (1.50 g, 9.98 mmol, 2.0 equiv.). The solution was allowed to stir at rt for 18 hours. The reaction mixture was diluted with water (20 mL) and dichloromethane (20 mL). The aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic layers were washed with brine (20 mL), dried with sodium sulfate, and filtered. The filtrate was concentrated *in vacuo* and flash chromatography (CyHex/EtOAc 95:5) on silica gel afforded product **7** in 95% yield (2.34 g, 4.73 mmol) as a colorless oil.

TLC: $R_f = 0.59$ (CyHex/ EtOAc = 8:2). [$KMnO_4$]. **$[\alpha]_D^{20}$:** −1.4 ($c = 1.12$, CH_2Cl_2). **^{1}H NMR** (600 MHz, $CDCl_3$): δ [ppm] = 7.25 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 5.80 (ddd, J = 17.1, 10.4, 6.5 Hz, 1H), 5.14 (ddt, J = 17.2, 7.6, 1.5 Hz, 1H), 5.02 (ddt, J = 10.4, 5.6, 1.4 Hz, 1H), 4.49–4.34 (m, 2H), 4.24–4.16 (m, 1H), 3.96–3.87 (m, 1H), 3.80 (s, 3H), 3.51 (t, J = 6.7 Hz, 2H), 1.84 (dtd, J = 13.8, 7.0, 5.0 Hz, 1H), 1.74 (tt, J = 13.2, 6.5 Hz, 2H), 1.61–1.53 (m, 1H), 0.94 (t, J = 7.9 Hz, 9H), 0.89–0.85 (m, 9H), 0.58 (q, J = 7.9 Hz, 6H), 0.14–−0.04 (m, 6H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ [ppm] = 159.3, 141.8, 130.9, 129.3, 114.1, 113.9, 72.8, 71.2, 67.1, 66.8, 55.4, 46.3, 37.5, 26.0, 18.2, 7.0, 5.1, −4.2, −4.3. **IR** (ATR): $\tilde{\upsilon}$ [cm^{-1}] = 2952, 2930, 2876, 2856, 1613, 1513, 1247, 1087, 1039, 1005, 834, 773. **HRMS** (ESI) m/z: [$M+Na^+$] calculated for $C_{27}H_{50}NaO_4Si_2$: 517.3140; found 517.3125.

(2*S*,4*S*)-4-((*tert*-butyldimethylsilyl)oxy)-6-((4-methoxybenzyl)oxy)-2-((triethylsilyl)oxy)hexanal (16)



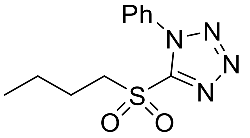
$C_{26}H_{48}O_5Si_2$

496.8 g/mol

To a solution of alkene **7** (2.34 g, 4.73 mmol, 1.0 equiv.) in 1,4-dioxane/H_2O (85 mL, 3:1) were added 2,6-lutidine (1.11 mL, 2.17 g, 16.7 mmol, 2.0 equiv.), sodium periodate (7.19 g, 40.0 mmol, 4.0 equiv.) and osmium tetroxide (4% in H_2O, 1.02 mL, 1.06 g, 0.17 mmol, 2.0 mol%) consecutively. The reaction mixture was stirred at rt for 18 hours and then filtered through a pad of celite. The residue was washed with dichloromethane (3 x 50 mL) and the filtrate was diluted with saturated aqueous sodium thiosulfate solution (50 mL). The layers were separated, and the aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic layers were washed with brine (50 mL), dried with sodium sulfate, and filtered. The filtrate was concentrated *in vacuo* and flash chromatography (CyHex/EtOAc 95:5) on silica gel afforded product **16** in 95% yield (2.44 g, 7.91 mmol) as a colorless oil.

TLC: R_f = 0.46 (CyHex/ EtOAc = 8:2) [$KMnO_4$]. $[\alpha]_D^{20}$**:** −2.4 (c = 1.01, CH_2Cl_2). ^{1}**H NMR** (600 MHz, $CDCl_3$): δ [ppm] = 9.58 (s, 1H), 7.24 (d, J = 8.2 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 4.51–4.22 (m, 2H), 4.14–4.01 (m, 2H), 3.80 (s, 3H), 3.49 (td, J = 6.5, 2.3 Hz, 2H), 1.90–1.73 (m, 4H), 1.03–0.80 (m, 18H), 0.61 (q, J = 7.9 Hz, 6H), 0.10–−0.13 (m, 6H). ^{13}**C{**^{1}**H} NMR** (151 MHz, $CDCl_3$): δ [ppm] = 203.8, 159.3, 130.8, 129.4, 113.9, 74.8, 72.8, 66.5, 66.0, 55.4, 40.9, 37.2, 26.0, 18.1, 6.8, 4.9, −4.2, −4.4. **IR** (ATR): $\tilde{\upsilon}$ [cm^{-1}] = 2953, 2930, 2877, 2856, 1735, 1613, 1512, 1246, 1091, 1037, 1004, 834, 807, 774. **HRMS** (ESI) m/z: [$M+Na^+$] calculated for $C_{26}H_{48}NaO_5Si_2$: 519.2932; found 519.2935.

5-(butylsulfonyl)-1-phenyl-1*H*-tetrazole (17)



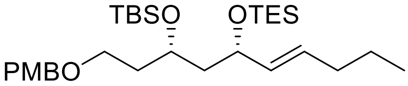
$C_{11}H_{14}N_4O_2S$

266.3 g/mol

To a solution of *n*-butanol (3.00 mL, 2.43 g, 32.8 mmol, 1.0 equiv.) in dry THF (429 mL) were added 1-phenyl-1*H*-tetrazole-5-thiol (11.7 g, 65.6 mmol, 2.0 equiv.), triphenylphosphine (12.9 g, 49.2 mmol, 1.5 equiv.) and diisopropyl azodicarboxylate (12.3 mL, 12.7 g, 59.0 mmol, 1.8 equiv) consecutively at 0 °C. The solution was stirred at 0 °C for 120 minutes. The reaction mixture was concentrated *in vacuo* and flash chromatography (CyHex/EtOAc 95:5) on silica gel afforded the corresponding sulfide as a yellow oil. To a solution of the sulfide (3.00 mL, 2.43 g, 32.8 mmol, 1.0 equiv.) in ethanol (160 mL) was added ammonium molybdate tetrahydrate (7.91 g, 6.40 mmol, 0.20 equiv.) dissolved in a hydrogen peroxide solution (35% in H_2O, 27.4 mL, 31.1 g, 320 mmol, 10 equiv.) at 0 °C. The reaction mixture was stirred at rt for 18 hours. The reaction was diluted with water (100 mL) and dichloromethane (100 mL). The layers were separated and the aqueous layer was extracted with dichloromethane (3 x 100 mL). The combined organic layers were washed with brine (1000 mL), dried with sodium sulfate, and filtered. The filtrate was concentrated *in vacuo* and flash chromatography (CyHex/EtOAc 95:5) on silica gel afforded sulfone **17** in 68% yield (6.00 g, 22.5 mmol) as a colorless solid.

TLC: R_f = 0.55 (CyHex/ EtOAc = 95:5) [$KMnO_4$]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.85 – 7.43 (m, 5H), 3.91 – 3.46 (m, 2H), 2.09 – 1.68 (m, 2H), 1.65 – 1.33 (m, 2H), 1.12 – 0.75 (m, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 153.6, 133.2, 131.6, 129.8, 125.2, 55.9, 24.0, 21.6, 13.6. **HRMS** (ESI) m/z: [$M+Na^+$] calculated for $C_{11}H_{14}N_4NaO_2S$ [$M+Na^+$]: 289.0730; found 289.0728. The analytical data are in agreement with previously reported one.[3]

(5*S*,7*S*)-9,9-diethyl-5-(2-((4-methoxybenzyl)oxy)ethyl)-2,2,3,3-tetramethyl-7-((*E*)-pent-1-en-1-yl)-4,8-dioxa-3,9-disilaundecane (18)



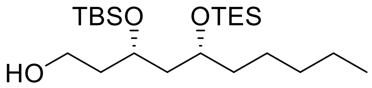
$C_{30}H_{56}O_4Si_2$

536.9 g/mol

To a solution of sulfone **17** (919 mg, 3.54 mmol, 1.15 equiv.) in dry 1,2-dimethoxyethane (60 mL) was added KHMDS (0.5 M in toluene, 7.20 mL, 3.60 mmol, 1.20 equiv.) slowly at −78 °C. The reaction mixture was stirred at −78 °C for 30 minutes. Following the addition of aldehyde **16** (1.49 g, 3.00 mmol, 1.00 equiv.) dissolved in dry 1,2-dimethoxyethane (30 mL) at −78 °C the solution was stirred at this temperature for three hours. The reaction was quenched with pH7 buffer solution (30 mL) and diluted with diethyl ether (30 mL). The layers were separated and the aqueous layer was extracted with diethyl ether (3 x 15 mL). The combined organic layers were washed with brine (20 mL), dried with sodium sulfate, and filtered. The filtrate was concentrated *in vacuo* and flash chromatography (CyHex/EtOAc 99:1) on silica gel afforded product **18** in 93% yield (1.50 g, 2.79 mmol) as a colorless oil.

TLC: R_f = 0.53 (CyHex/EtOAc = 9:1) [$KMnO_4$]. $[\alpha]_D^{20}$**:** −10.2 (*c* = 1.12, CH_2Cl_2). **^{1}H NMR** (600 MHz, $CDCl_3$): δ [ppm] = 7.25 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 5.52 (ddt, *J* = 19.5, 13.0, 6.7 Hz, 1H), 5.41–5.33 (m, 1H), 4.46–4.34 (m, 2H), 4.15 (dq, *J* = 13.1, 6.8 Hz, 1H), 3.89 (tt, *J* = 11.5, 5.8 Hz, 1H), 3.80 (s, 3H), 3.51 (t, *J* = 6.9 Hz, 2H), 2.02–1.91 (m, 2H), 1.83 (dtd, *J* = 13.9, 7.1, 5.3 Hz, 1H), 1.74 (ddt, *J* = 15.7, 13.3, 6.6 Hz, 2H), 1.60–1.50 (m, 1H), 1.42–1.31 (m, 2H), 1.01–0.81 (m, 21H), 0.57 (q, *J* = 8.0 Hz, 6H), 0.13–0.10 (m, 6H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ [ppm] = 159.2, 133.7, 131.0, 129.3, 113.9, 72.7, 71.1, 67.2, 66.9, 55.4, 46.6, 37.5, 34.5, 26.1, 22.5, 18.2, 13.9, 7.0, 5.2, −4.2, −4.2. **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2954, 2930, 2875, 2856, 1613, 1513, 1462, 1247, 1089, 1040, 1004, 835, 774. **HRMS** (ESI) m/z: [M+Na$^+$] calculated for $C_{30}H_{56}NaO_4Si_2$: 559.3609; found 559.3610.

(3*S*,5*R*)-3-((*tert*-butyldimethylsilyl)oxy)-5-((triethylsilyl)oxy)decan-1-ol (10b)



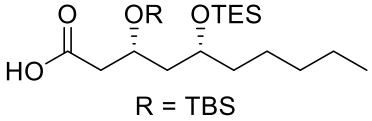
$C_{22}H_{50}O_3Si_2$

418.8 g/mol

Alkene **18** (500 mg, 931 µmol, 1.0 equiv.) was dissolved in CyHex (18 mL) and Pd/C (10% on activated charcoal, 248 mg, 233 µmol, 0.25 equiv.) was added. The reaction mixture was stirred for 48 hours at rt under hydrogen atmosphere (500 psi). The suspension was then filtered through a pad of celite, washing the residue several times with ethyl acetate (3 x 10 mL). The filtrate was concentrated *in vacuo* and flash chromatography (CH/EtOAc 9:1) on silica gel afforded product **10b** in 72% yield (279 mg, 666 µmol) as a colorless oil.

TLC: R_f = 0.18 (CyHex/EtOAc = 9:1). [$KMnO_4$]. $[\alpha]_D^{20}$**:** −9.6 (*c* = 0.81, CH_2Cl_2). **^{1}H NMR** (600 MHz, $CDCl_3$): δ [ppm] = 4.15–4.02 (m, 1H), 3.84 (ddd, *J* = 11.8, 8.1, 4.2 Hz, 1H), 3.69 (dtd, *J* = 29.7, 9.6, 8.2, 5.3 Hz, 2H), 2.52 (s, 1H), 1.90 (ddt, *J* = 13.4, 8.9, 4.7 Hz, 1H), 1.74–1.68 (m, 1H), 1.67–1.60 (m, 2H), 1.43 (tt, *J* = 14.4, 7.4 Hz, 2H), 1.34–1.28 (m, 3H), 1.28–1.21 (m, 3H), 0.96 (t, *J* = 8.4 Hz, 9H), 0.91–0.85 (m, 12H), 0.59 (q, *J* = 7.7 Hz, 6H), 0.16–−0.07 (m, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 69.8, 69.6, 60.4, 44.2, 38.0, 37.9, 32.2, 26.0, 24.9, 22.8, 18.1, 14.2, 7.1, 5.4, −4.3, −4.5. **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3383, 2954, 2930, 2876, 2857, 1462, 1254, 1083, 1058, 1005, 835, 774. **HRMS** (ESI) m/z: [M+Na$^+$] calculated for $C_{22}H_{50}NaO_3Si_2$: 441.3191; found 441.3192.

(3*R*,5*R*)-3-((*tert*-butyldimethylsilyl)oxy)-5-((triethylsilyl)oxy)decanoic acid (2b)



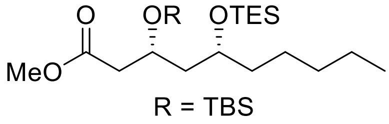
$C_{22}H_{48}O_4Si_2$

432.8 g/mol

To a solution of alcohol **10b** (238 mg, 568 µmol, 1.0 equiv.) in ACN/CCl_4/pH 7 buffer (10.7 mL, 1:1:1.5) were added sodium periodate (368 mg, 1.70 mmol, 3.0 equiv.) and ruthenium(IV) oxide hydrate (60%, 14 mg, 57 µmol, 0.1 equiv.) consecutively. The solution was stirred at rt for 3 hours. The reaction mixture was then diluted with water (10 mL) and diethyl ether (10 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (3 x 5 mL). The combined organic layers were washed with brine (10 mL), dried with sodium sulfate, and filtered. The filtrate was concentrated *in vacuo* and flash chromatography (CyHex/EtOAc 8:2) on silica gel afforded product **2b** in 83% yield (204 mg, 471 µmol) as a colorless oil.

TLC: R_f = 0.39 (CyHex/EtOAc = 8:2) [$KMnO_4$]. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{20}}$**:** −3.9 (*c* = 1.10, CH_2Cl_2). **^{1}H NMR** (400 MHz, C_6D_6): δ [ppm] = 4.53–4.37 (m, 1H), 3.85–3.65 (m, 1H), 2.64–2.41 (m, 2H), 1.88 (ddt, *J* = 13.5, 7.3, 5.0 Hz, 1H), 1.78–1.67 (m, 1H), 1.56–1.43 (m, 2H), 1.42–1.20 (m, 6H), 1.11–0.98 (m, 18H), 0.94–0.88 (m, 3H), 0.66 (q, *J* = 8.0 Hz, 6H), 0.20–0.07 (m, 6H). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ [ppm] = 177.0, 69.7, 67.4, 45.2, 42.7, 37.9, 32.5, 26.1, 25.1, 23.1, 18.2, 14.3, 7.3, 5.6, −4.3, −4.6. **IR** (ATR): $\tilde{\upsilon}$ [cm^{-1}] = 2954, 2929, 2857, 1712, 1471, 1254, 1081, 1004, 834, 808, 774. **HRMS** (ESI) m/z: [M+Na$^+$] calculated for $C_{22}H_{48}NaO_4Si_2$: 455.2983; found 455.2983.

methyl (3*R*,5*R*)-3-((*tert*-butyldimethylsilyl)oxy)-5-((triethylsilyl)oxy)decanoate (11b)



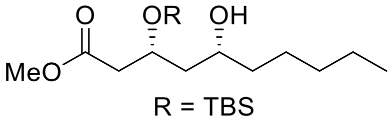
$C_{23}H_{50}O_4Si_2$

446.8 g/mol

To a solution of carboxylic acid **2b** (47.0 mg, 109 µmol, 1.0 equiv.) in DMF (217 µL) were added potassium carbonate (27.0 mg, 195 µmol, 1.8 equiv.) and iodomethane (30.4 µL, 69.4 mg, 488 µmol, 4.5 equiv.) consecutively. The solution was stirred at rt for 18 hours. The reaction mixture was quenched with saturated aqueous ammonium chloride solution (5 mL) and diluted with diethyl ether (5 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (3 x 5 mL). The combined organic layers were washed with brine (5 mL), dried with sodium sulfate, and filtered. The filtrate was concentrated *in vacuo* and flash chromatography (CyHex/EtOAc 98:2) on silica gel afforded product **11b** in 90% yield (43.5 mg, 97.4 µmol) as a colorless oil.

TLC: R$_f$ = 0.56 (CyHex/EtOAc = 95:5). [KMnO$_4$] **$[\alpha]_D^{20}$:** −10.5 (*c* = 1.14, CH$_2$Cl$_2$). **^{1}H NMR** (600 MHz, C$_6$D$_6$): δ [ppm] = 4.47 (p, *J* = 6.4 Hz, 1H), 3.82 (dp, *J* = 48.9, 5.9 Hz, 1H), 3.38 (s, 3H), 2.61–2.41 (m, 2H), 1.98–1.85 (m, 1H), 1.80–1.70 (m, 1H), 1.64–1.48 (m, 2H), 1.46–1.35 (m, 2H), 1.35–1.21 (m, 4H), 1.08–0.97 (m, 18H), 0.91 (t, *J* = 7.1 Hz, 3H), 0.68 (q, *J* = 7.9 Hz, 6H), 0.36–0.13 (m, 6H). **^{13}C{^{1}H} NMR** (151 MHz, C$_6$D$_6$): δ [ppm] = 171.6, 69.8, 67.7, 51.0, 45.5, 43.0, 37.9, 32.5, 26.1, 25.2, 23.1, 18.2, 14.3, 7.3, 5.7, −4.3, −4.5. **IR** (ATR): $\tilde{\upsilon}$ [cm^{-1}] = 2953, 2929, 2857, 1742, 1254, 1165, 1081, 1004, 835, 774, 742. **HRMS** (ESI) m/z: [M+Na$^+$] calculated for C$_{23}$H$_{50}$NaO$_4$Si$_2$: 469.3140; found 469.3141.

methyl (3*R*,5*R*)-3-((*tert*-butyldimethylsilyl)oxy)-5-hydroxydecanoate (12b)



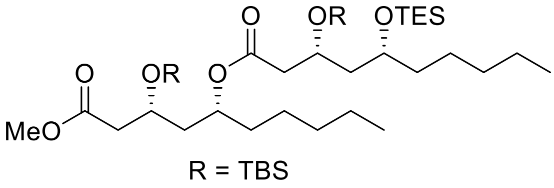
C$_{17}$H$_{36}$O$_4$Si

332.6 g/mol

First, HF•pyridine (70% HF, 80.1 µL, 79.2 mg, 559 µmol, 5.0 equiv.) was dissolved in pyridine/MeOH (1.2 mL, 6:1) at 0 °C in a teflon vial. In another teflon vial, silyl ether **11b** (50 mg, 112 µmol, 1.0 equiv.) was dissolved in THF (1 mL) and the solution was cooled to 0 °C. The prepared HF•pyridine solution was then transferred to the THF solution and the reaction mixture was stirred at rt for 18 hours. Following the addition of an excess of MeOTMS (5 mL) at 0 °C and dilution with toluene (5 mL), the volatile compounds were removed *in vacuo*. The residue was diluted with toluene (2 mL) again and the procedure was repeated three times to remove all of the pyridine. Flash chromatography (CyHex/EtOAc 9:1) on silica gel afforded then the product **12b** in 67% yield (25 mg, 75 µmol) as a colorless oil.

TLC: R$_f$ = 0.45 (CyHex/EtOAc = 8:2) [KMnO$_4$] **$[\alpha]_D^{20}$:** −3.2 (*c* = 0.37, CH$_2$Cl$_2$). **^{1}H NMR** (600 MHz, C$_6$D$_6$): δ [ppm] = 4.46 (p, *J* = 6.2 Hz, 1H), 3.65–3.54 (m, 1H), 3.37 (s, 3H), 2.58–2.42 (m, 2H), 1.75 (s, 1H), 1.70 (ddd, *J* = 13.9, 9.1, 6.1 Hz, 1H), 1.63 (ddd, *J* = 14.0, 6.5, 2.9 Hz, 1H), 1.45–1.16 (m, 8H), 0.96 (s, 9H), 0.89 (t, *J* = 7.1 Hz, 3H), 0.14–0.09 (m, 6H). **^{13}C{^{1}H} NMR** (151 MHz, C$_6$D$_6$): δ [ppm] = 171.7, 69.4, 68.9, 51.1, 45.2, 42.8, 38.5, 32.3, 26.0, 25.6, 23.1, 18.2, 14.3, −4.5, −4.5. **IR** (ATR): $\tilde{\upsilon}$ [cm^{-1}] = 3453, 2953, 2928, 2856, 1740, 1462, 1437, 1255, 1081, 1006, 836, 810. 776. **HRMS** (ESI) m/z: [M+Na$^+$] calculated for $C_{17}H_{36}NaO_4Si$: 355.2275; found 355.2279.

(3*R*,5*R*)-3-((*tert*-butyldimethylsilyl)oxy)-1-methoxy-1-oxodecan-5-yl-(3*R*,5*R*)-3-((*tert*-butyldimethylsilyl)oxy)-5-((triethylsilyl)oxy)decanoate (13b)



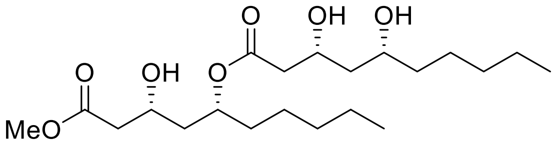
$C_{39}H_{82}O_7Si_3$

747.3 g/mol

To a solution of carboxylic acid **2b** (20 mg, 46 µmol, 1.0 equiv.) in dry toluene (1.5 mL) were added triethylamine (7.7 µL, 5.6 mg, 55 µmol, 1.2 equiv.) and 2,4,6-trichlorobenzoylchloride (8.1 µL, 12 mg, 51 µmol, 1.1 equiv.) consecutively. The reaction mixture was stirred for 30 minutes and then alcohol **12b** (28.4 mg, 55.5 µmol, 1.2 equiv.) dissolved in dry toluene (0.5 mL) was added, followed by DMAP (7.9 mg, 65 µmol, 1.4 equiv.). The solution was allowed to stir for one hour at rt and then it was concentrated *in vacuo*. Flash chromatography (CyHex/EtOAc 99:1) on silica gel afforded product **13b** in 93% yield (32 mg, 43 µmol) as a colorless oil.

TLC: R_f = 0.61 (CyHex/EtOAc = 95:5). [KMnO$_4$] $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{20}}$**:** −5.0 (*c* = 1.03, CH_2Cl_2). **^{1}H NMR** (400 MHz, C_6D_6): δ [ppm] = 5.21 (ddd, *J* = 12.4, 7.6, 5.0 Hz, 1H), 4.48 (h, *J* = 6.1 Hz, 1H), 4.40 (tt, *J* = 7.2, 5.0 Hz, 1H), 3.92 (dt, *J* = 27.9, 5.8 Hz, 1H), 3.39 (s, 3H), 2.74–2.45 (m, 4H), 2.07–1.76 (m, 4H), 1.69–1.42 (m, 6H), 1.37–1.20 (m, 10H), 1.08 (t, *J* = 7.9 Hz, 6H), 1.04–0.98 (m, 27H), 0.70 (q, *J* = 7.8 Hz, 6H), 0.25–0.01 (m, 12H). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ [ppm] = 171.4, 170.8, 71.3, 69.8, 67.3, 67.2, 51.1, 45.4, 43.1, 42.4, 42.3, 37.7, 35.1, 32.6, 32.1, 26.2, 26.0, 25.4, 25.2, 23.1, 23.0, 18.3, 18.2, 14.3, 14.3, 7.3, 5.7, −4.2, −4.4, −4.4, −4.5. **IR** (ATR): $\tilde{\upsilon}$ [cm^{-1}] = 2953, 2928, 2856, 1737, 1462, 1253, 1167, 1080, 1004, 835, 775. **HRMS** (ESI) m/z: [M+Na$^+$] calculated for $C_{39}H_{82}NaO_7Si_3$: 769.5261; found 769.5270.

(3*R*,5*R*)-3-hydroxy-1-methoxy-1-oxodecan-5-yl (3*R*,5*R*)-3,5-dihydroxydecanoate (1b)



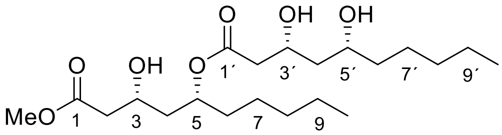
$C_{21}H_{40}O_7$

404.5 g/mol

First, HF•pyridine (70% HF, 123 µL, 121 mg, 856 µmol, 20.0 equiv.) was dissolved in pyridine/MeOH (0.43 mL, 6:1) at 0 °C in a teflon vial. In another teflon vial, silyl ether **13b** (32 mg, 43 µmol, 1.0 equiv.) was dissolved in THF (0.37 mL) and the solution was cooled to 0 °C. The prepared HF•pyridine solution was then transferred to the THF solution and the reaction mixture was stirred at rt for 18 hours. Following the addition of an excess of MeOTMS (5 mL) at 0 °C and dilution with toluene (5 mL), the volatile compounds were removed *in vacuo*. The residue was diluted with toluene (2 mL) again and the procedure was repeated three times to remove all of the pyridine. Flash chromatography ($CH_2Cl_2 \rightarrow CH_2Cl_2$/MeOH = 98:2 → CH_2Cl_2/MeOH = 95:5) on silica gel afforded then the product **1b** in 79% yield (13.6 mg, 33.6 µmol) as a colorless oil.

TLC: R_f = 0.19 (CH_2Cl_2/MeOH = 98:2). [$KMnO_4$] $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{20}}$**:** −19.7 (*c* = 1.03, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 5.14–5.06 (m, 1H), 4.27 (tt, *J* = 8.4, 4.3 Hz, 1H), 4.19–4.01 (m, 1H), 3.92–3.81 (m, 1H), 3.71 (s, 3H), 2.53 (dd, *J* = 16.5, 3.5 Hz, 1H), 2.48–2.39 (m, 3H), 1.86 (dt, *J* = 14.6, 8.4 Hz, 1H), 1.68–1.61 (m, 1H), 1.61–1.53 (m, 4H), 1.51–1.35 (m, 3H), 1.35–1.21 (m, 11H), 0.92–0.77 (m, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 173.2, 172.4, 73.0, 72.4, 69.8, 66.5, 52.0, 42.9, 42.6, 41.3, 40.9, 37.9, 34.7, 32.0, 31.7, 25.2, 25.0, 22.8, 22.6, 14.2, 14.1. **IR** (ATR): $\tilde{\upsilon}$ [cm^{-1}] = 3410, 2954, 2928, 2858, 1727, 1437, 1264, 1193, 1163, 1071. **HRMS** (ESI) m/z: [$M+Na^+$] calculated for $C_{21}H_{40}NaO_7$: 427.2666; found 427.2665.

3. Characterization of synthetic aureosurfactin



(−)-aureosurfactin, **1b**

Comparison table of ^{1}H NMR data: (δ in ppm, *J* in Hz).

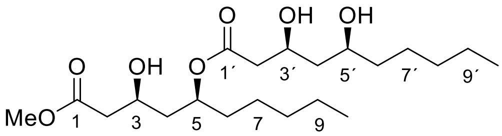
No.	δH natural **1b** (600 MHz, $CDCl_3$)[4]	δH synthetic **1b** (400 MHz, $CDCl_3$)[5]	Δ
5	5.05, m, 1H	5.10, m, 1H	0.05
3´	4.23, m, 1H	4.27, tt (8.4, 4.3), 1H	0.04
3	4.08, m, 1H	4.10, m, 1H	0.02
5´	3.81, m, 1H	3.85, m, 1H	0.04
OMe	3.66, s, 3H	3.71, s, 3H	0.05
2	2.47, m, 1H	2.53, dd (16.5, 3.5), 1H	0.06
2´	2.42, m, 2H,	2.44, m, 3H	0.02
2	2.41, m, 1H		
4	1.80, m, 1H	1.86, dt (14.6, 8.4), 1H	0.06
4	1.62, m, 1H	1.65, m, 1H	0.03
4´/6	1.53, m, 4H	1.56, m, 4H	0.03
6´	1.43, m, 1H	1.43, m, 3H	-
6´/7	1.37, m, 2H		
7/7´	1.26, m, 2H	1.28, m, 11H	0.02
8/8´/9/9´	1.25, m, 8H		
7´	1.24, m, 1H		
10/10´	0.84, m, 6H	0.85, m, 6H	0.01

[5] Referenced to $CDCl_3$ at 7.26 ppm.

Comparison table of $^{13}C\{^1H\}$ NMR data: (δ in ppm).

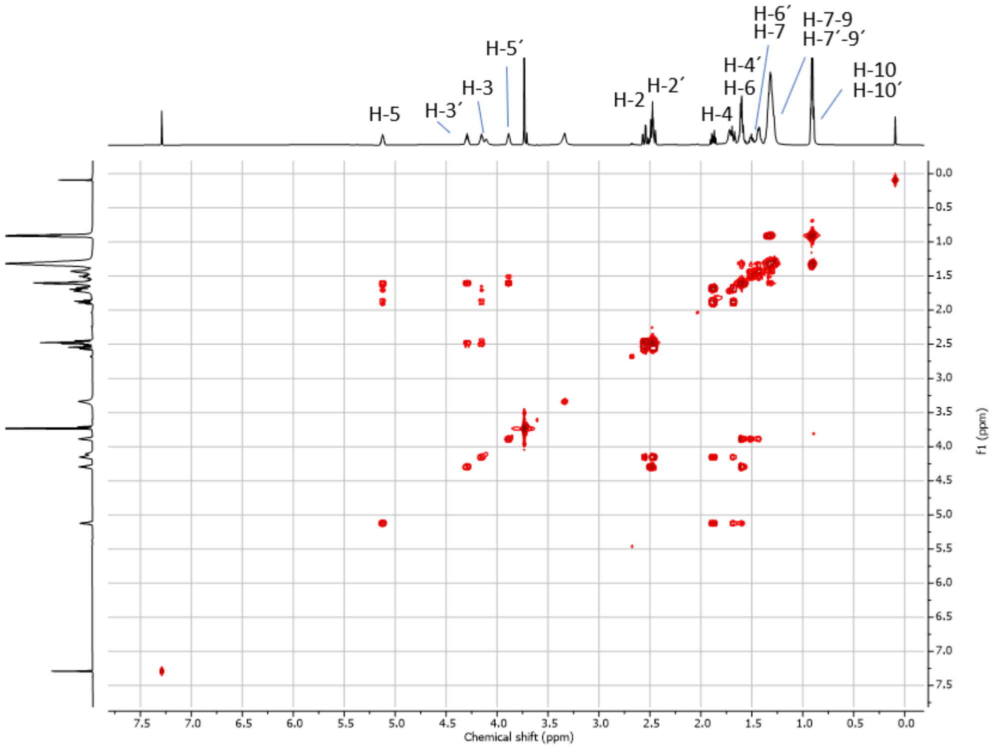
No.	δC natural **1b** (150 MHz, $CDCl_3$)[4]	δC synthetic **1b** (101 MHz, $CDCl_3$)[5]	Δ
1	172.8	173.2	0.4
1´	172.1	172.4	0.3
5	72.7	73.0	0.3
5´	72.1	72.4	0.3
3´	69.5	69.8	0.3
3	66.2	66.5	0.3
OMe	51.8	52.0	0.2
2´	42.7	42.9	0.2
4´	42.3	42.6	0.3
2	41.3	41.3	-
4	40.7	40.9	0.2
6´	37.7	37.9	0.2
6	34.4	34.7	0.3
8´	31.7	32.0	0.3
8	31.5	31.7	0.2
7´	25.0	25.2	0.2
7	24.7	25.0	0.3
9´	22.5	22.8	0.3
9	22.4	22.6	0.2
10´	14.0	14.2	0.2
10	13.9	14.1	0.2

[5] Referenced to $CDCl_3$ at 77.160 ppm.

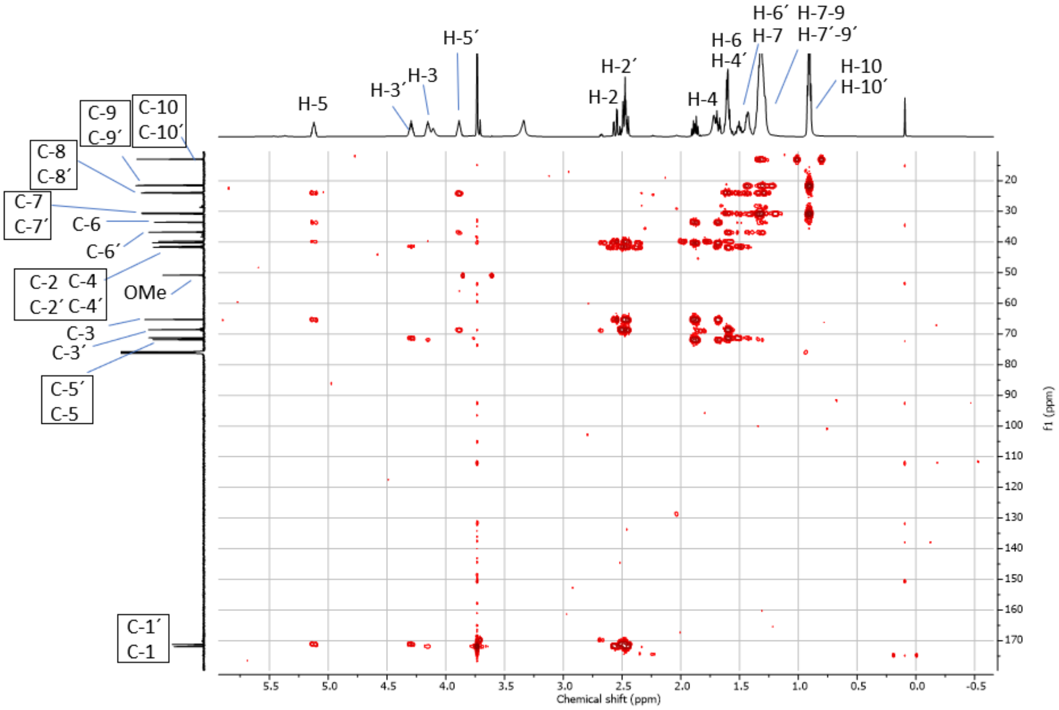


(+)-aureosurfactin, **1a**

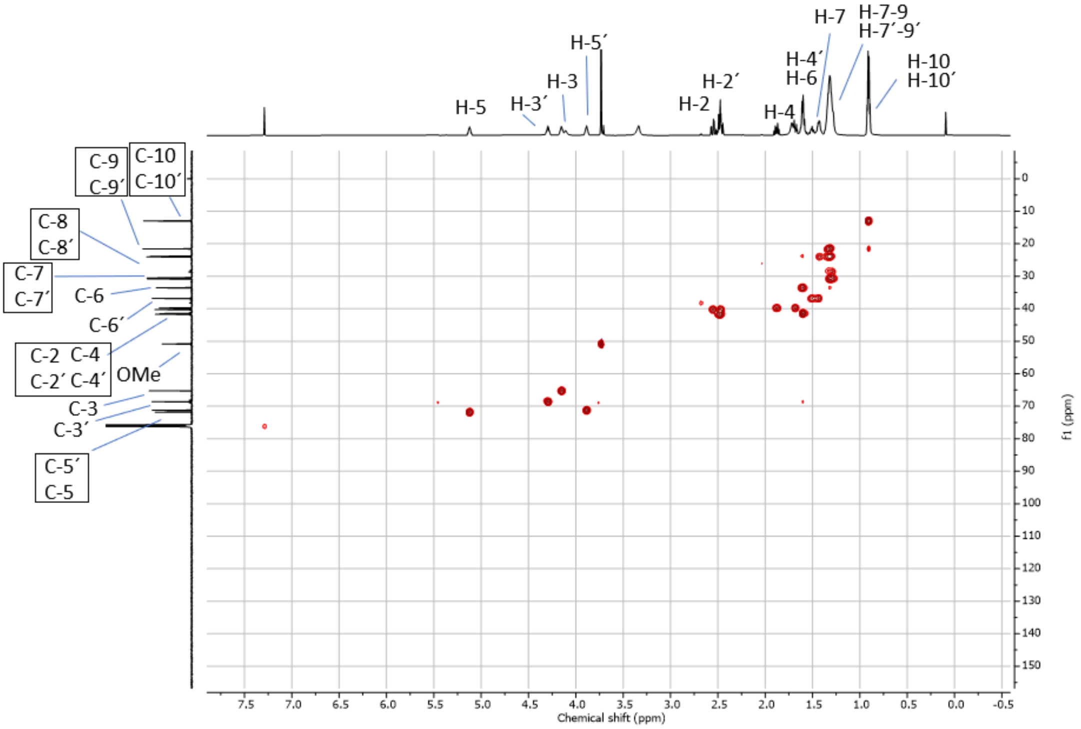
^{1}H-^{1}H COSY spectrum of 1a:



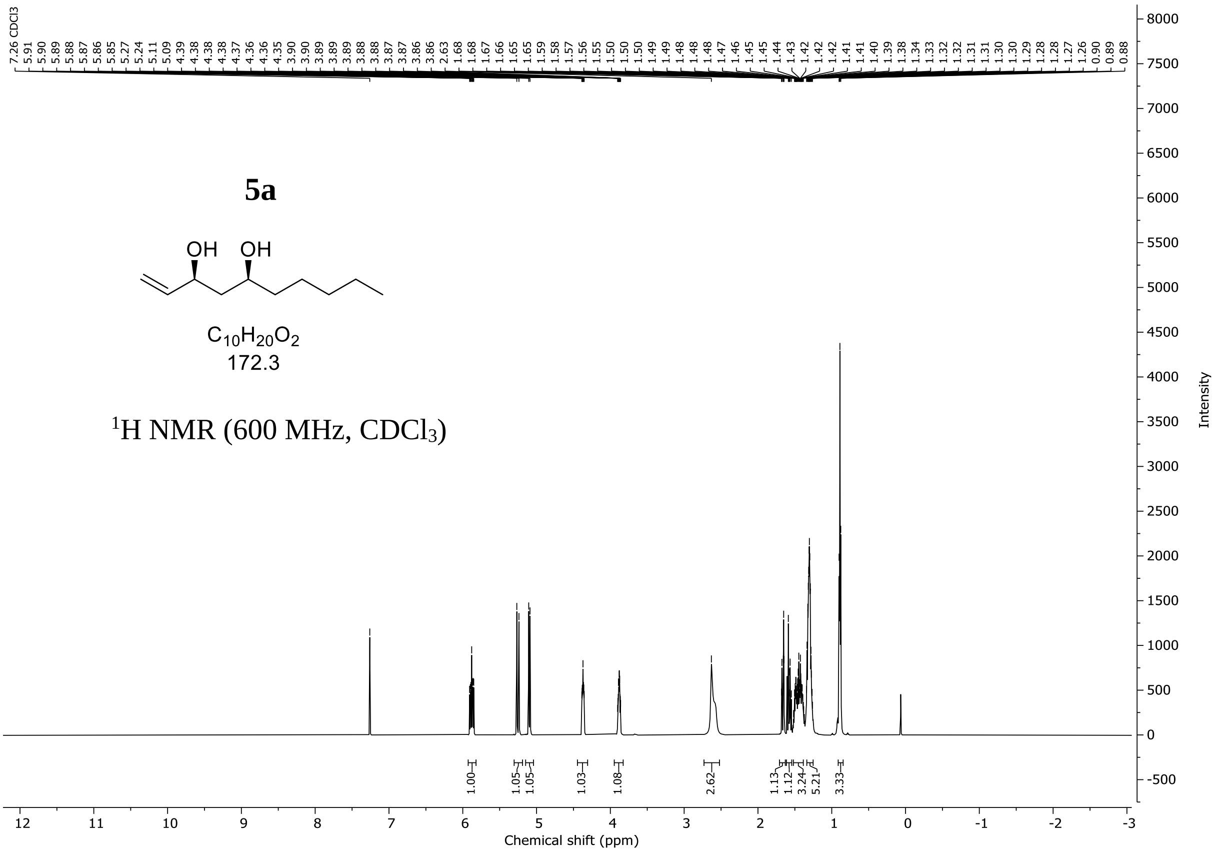
HMBC spectrum of 1a:



HSQC spectrum of 1a:



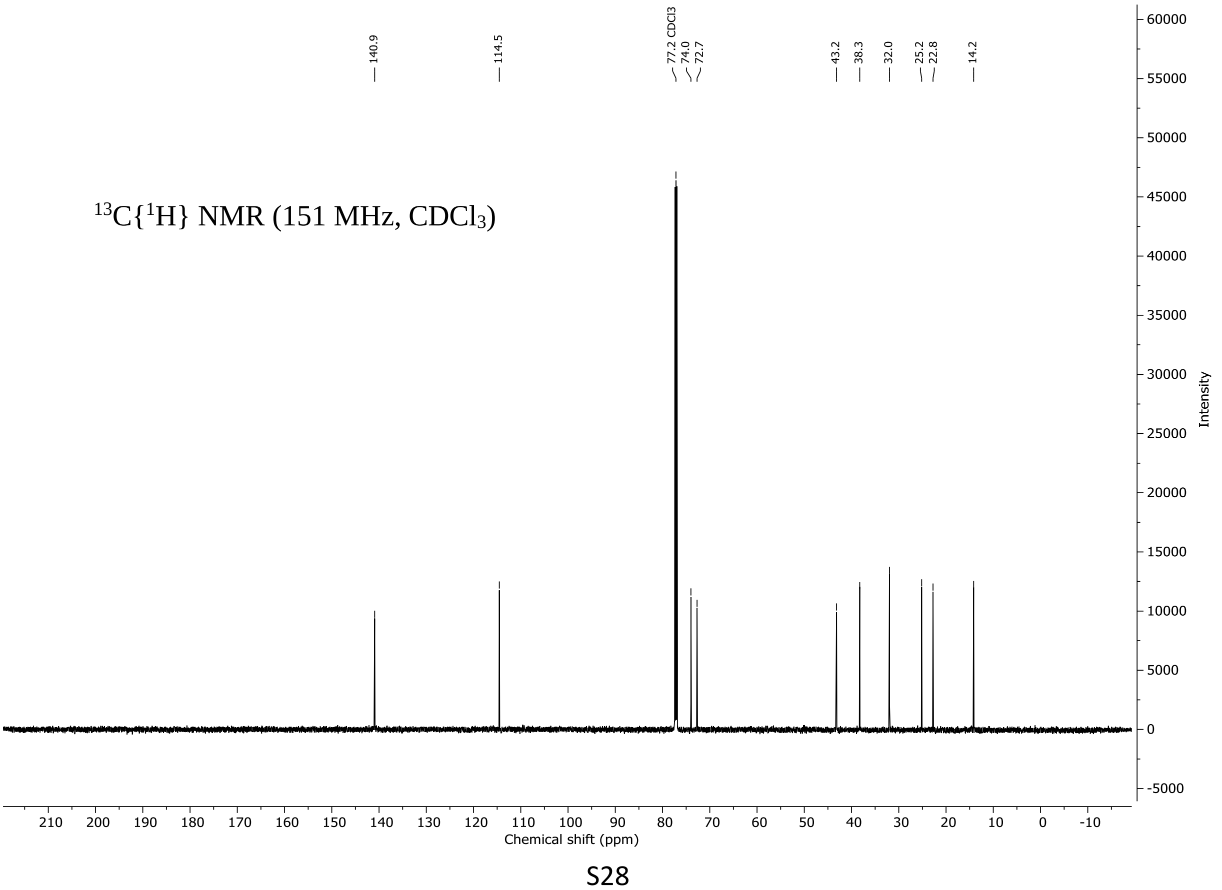
4. ^{1}H - and ^{13}C - NMR spectra of known compounds



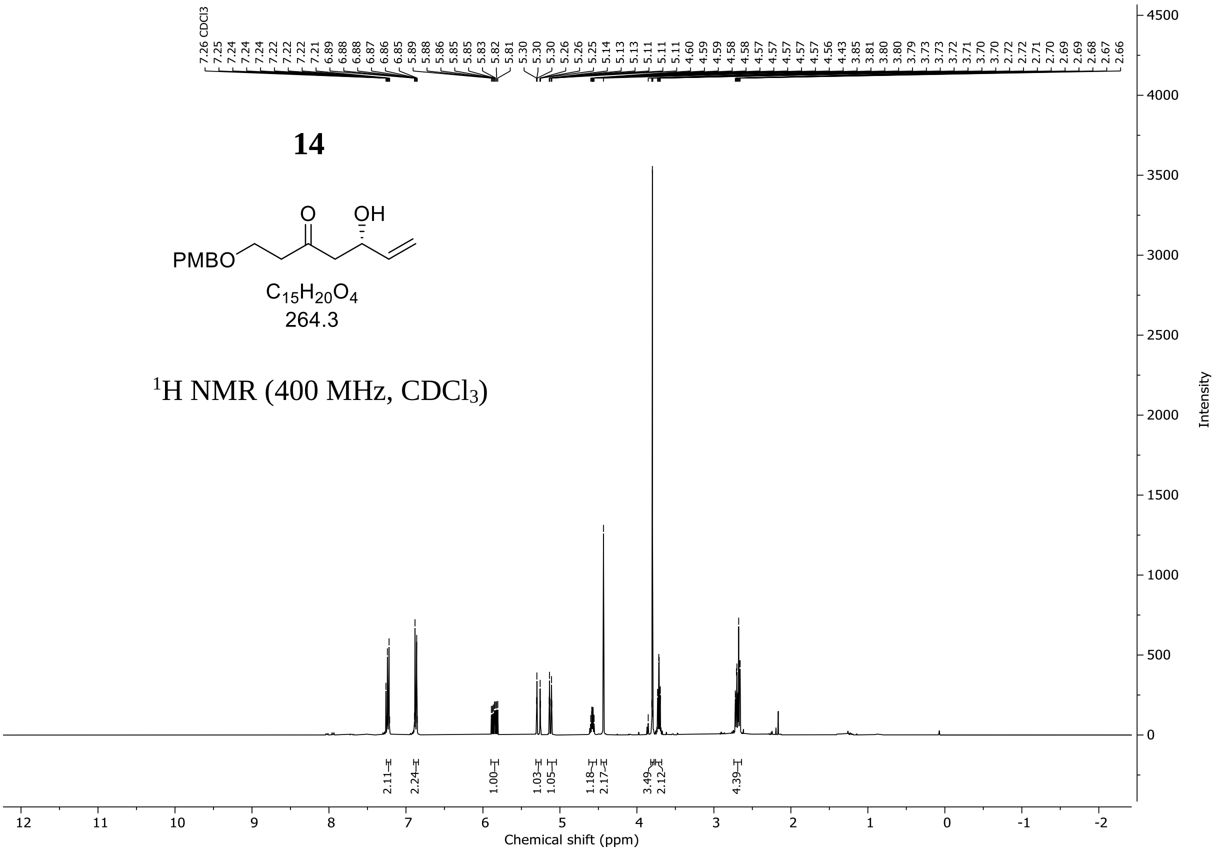
5a

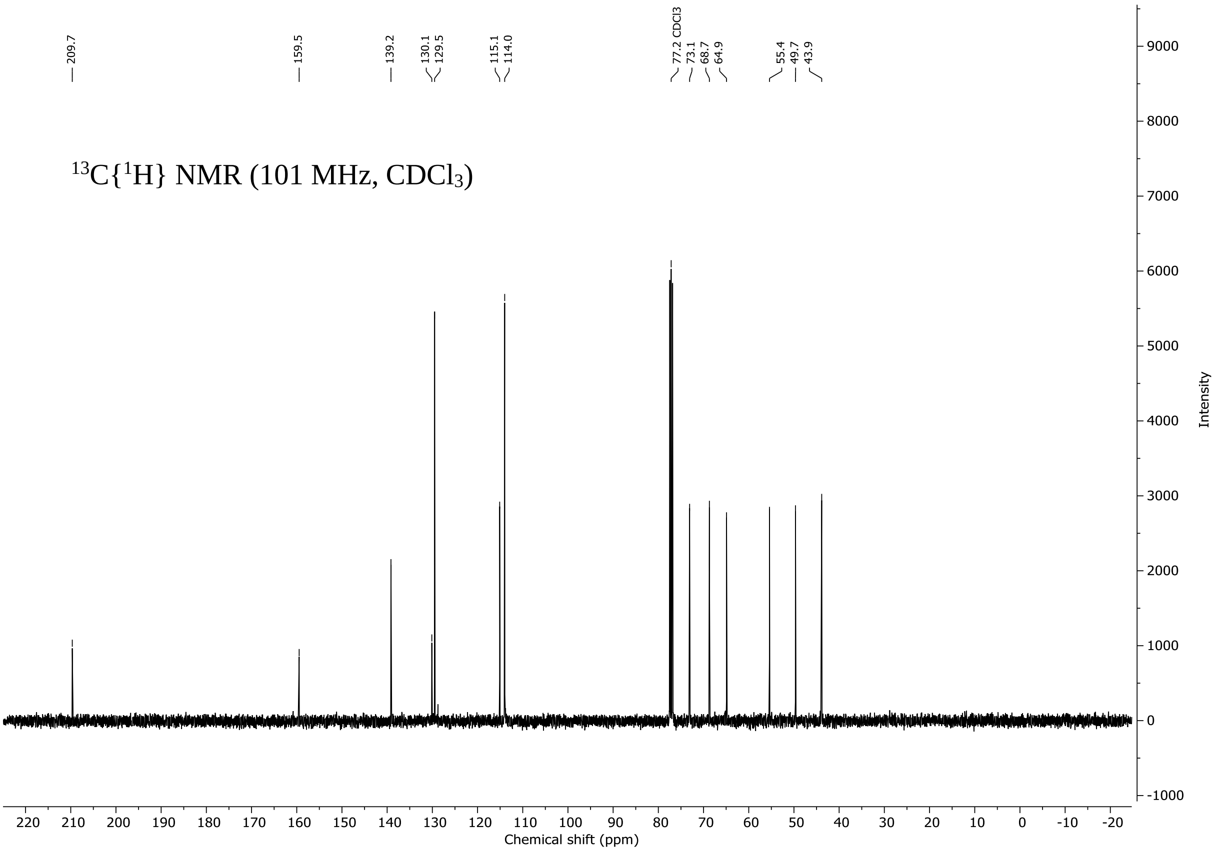
$C_{10}H_{20}O_2$
172.3

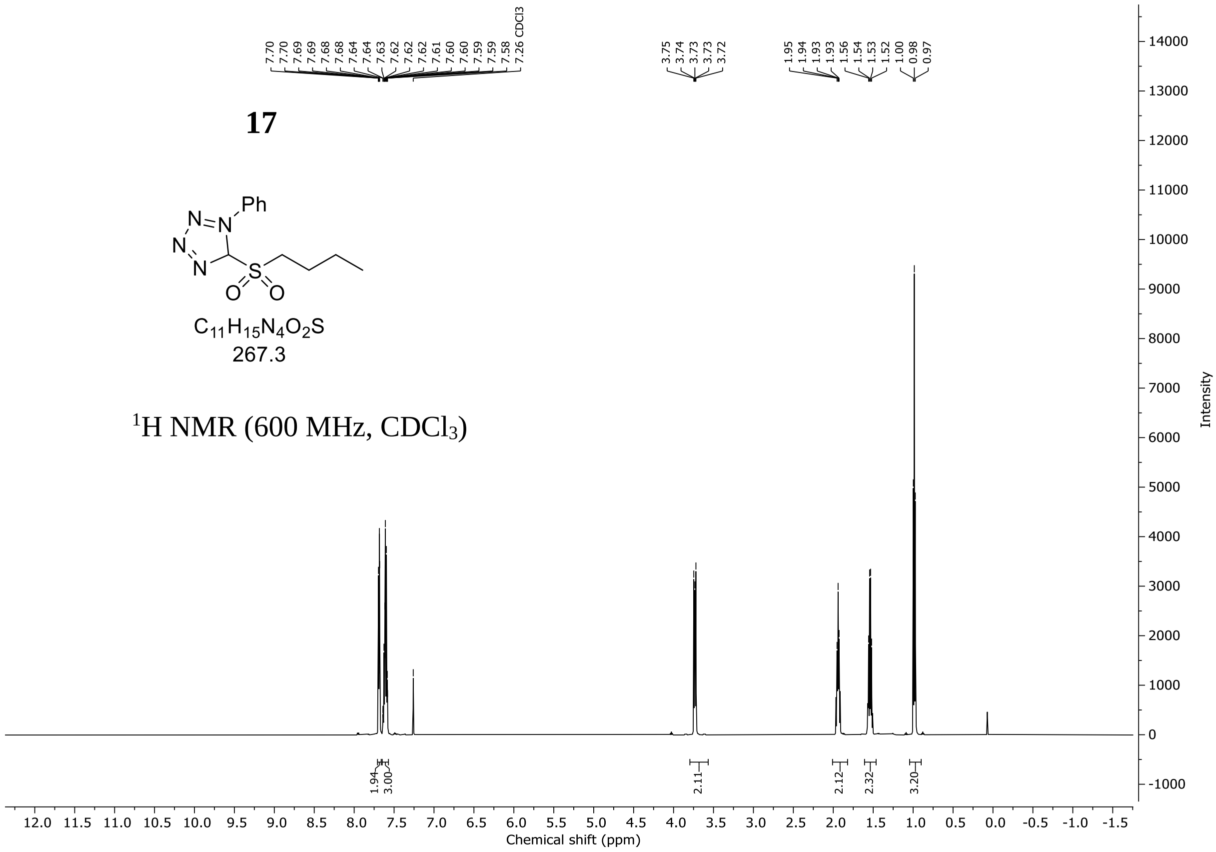
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)


7.26 CDCl3
7.25
7.24
7.24
7.24
7.22
7.22
7.22
7.21
6.89
6.88
6.88
6.87
6.86
6.85
5.89
5.88
5.86
5.85
5.85
5.83
5.82
5.81
5.30
5.30
5.30
5.26
5.26
5.25
5.14
5.13
5.13
5.11
5.11
5.11
4.60
4.59
4.59
4.58
4.58
4.57
4.57
4.57
4.57
4.56
4.43
3.85
3.81
3.80
3.80
3.79
3.73
3.73
3.72
3.71
3.70
3.70
2.72
2.72
2.71
2.70
2.69
2.69
2.68
2.67
2.66
14
O
OH
PMBO
C15H20O4
264.3
1H NMR (400 MHz, CDCl3)
2.11
2.24
1.00
1.03
1.05
1.18
2.17
3.49
2.12
4.39
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
Chemical shift (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Intensity

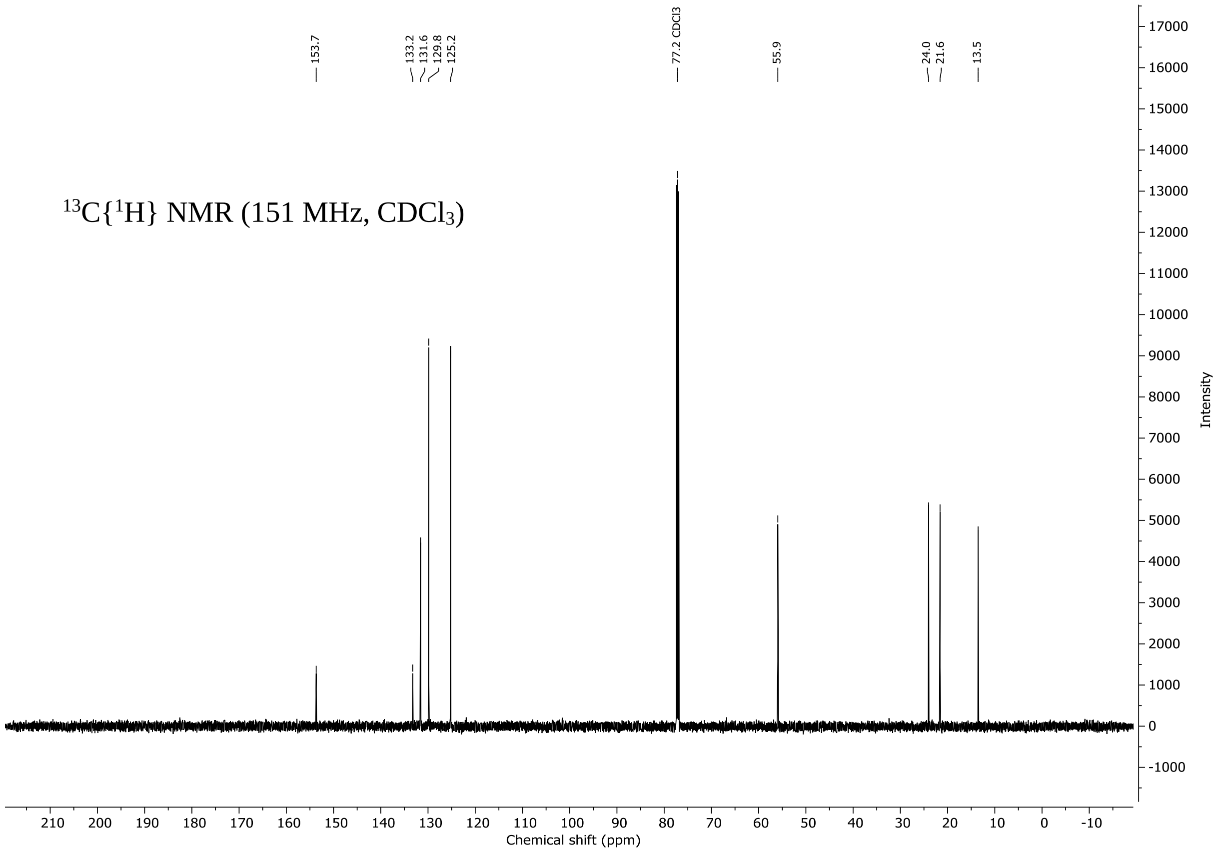

209.7
159.5
139.2
130.1
129.5
115.1
114.0
77.2 CDCl3
73.1
68.7
64.9
55.4
49.7
43.9
13C{1H} NMR (101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
Chemical shift (ppm)
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Intensity



17

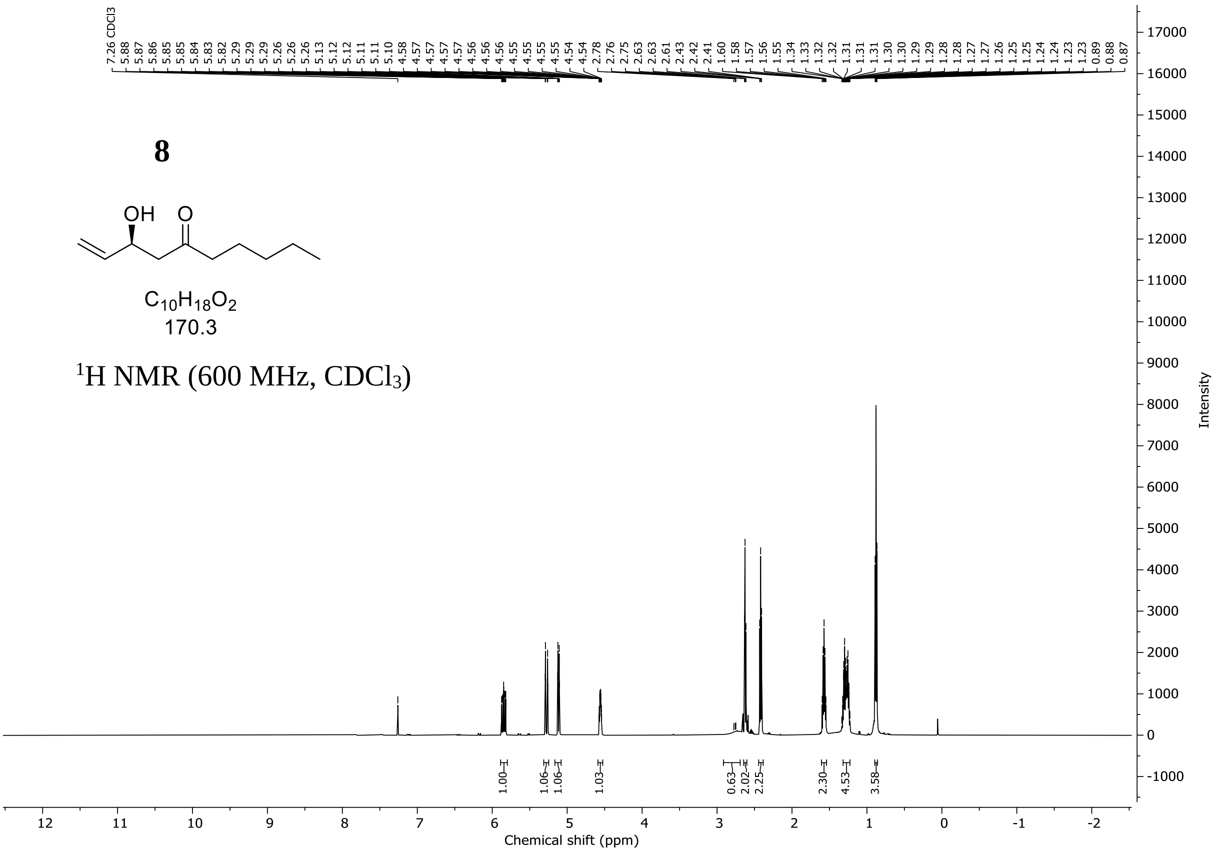
$C_{11}H_{15}N_4O_2S$
267.3

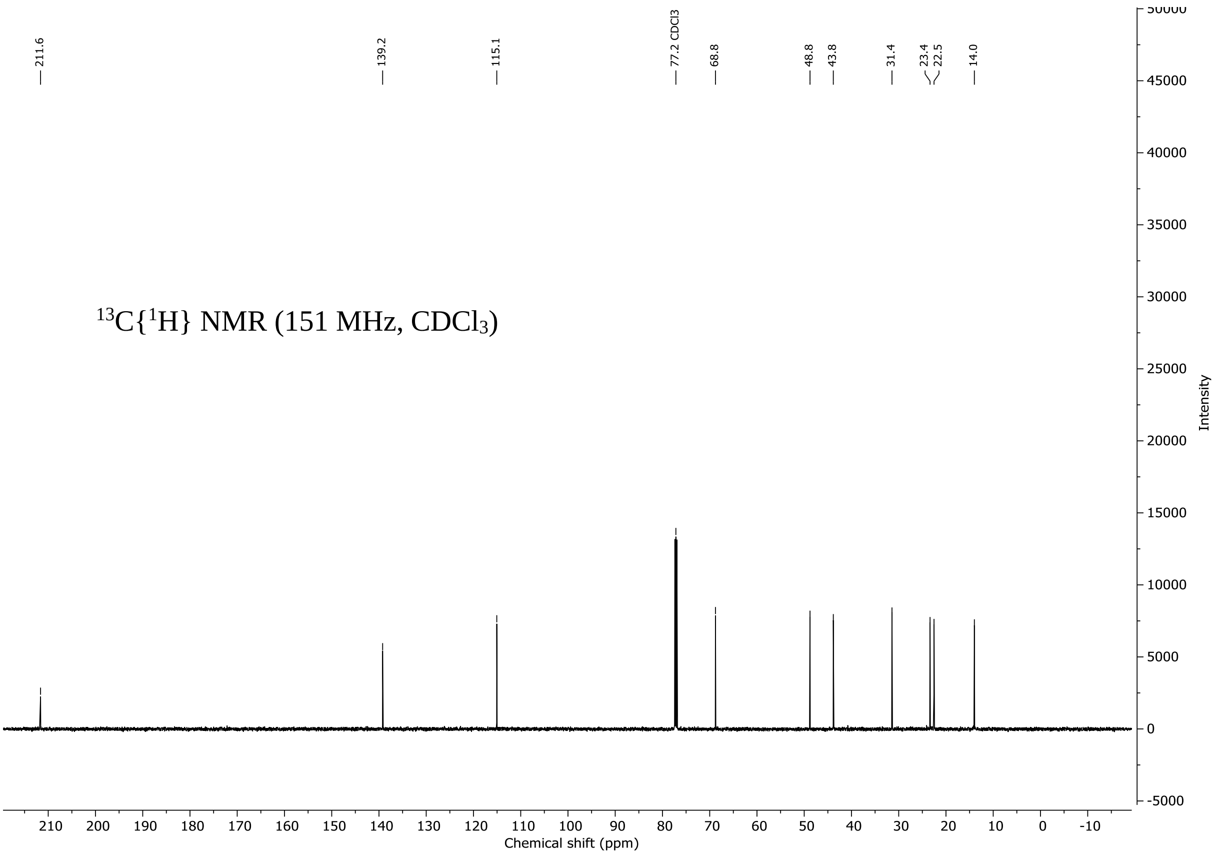
^{1}H NMR (600 MHz, $CDCl_3$)

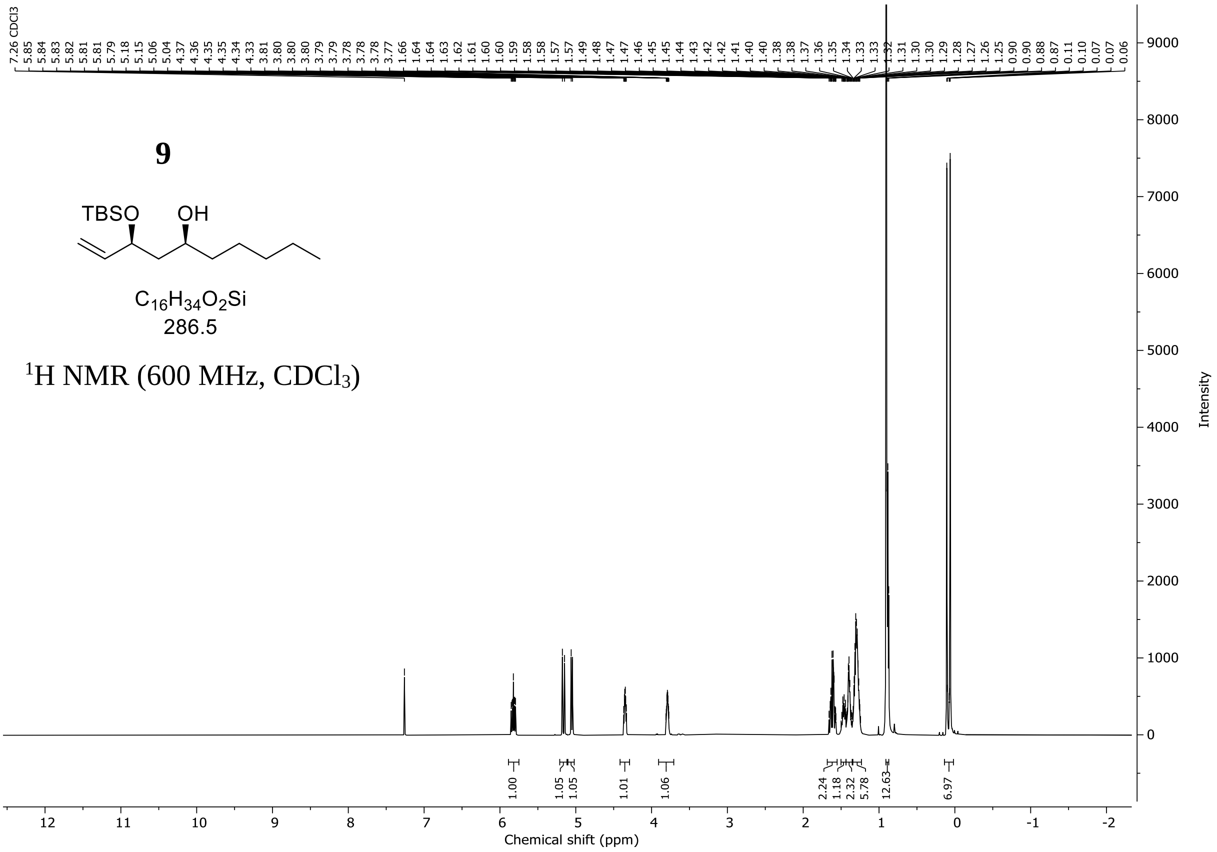


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

5. ^{1}H - and ^{13}C - NMR spectra of new compounds



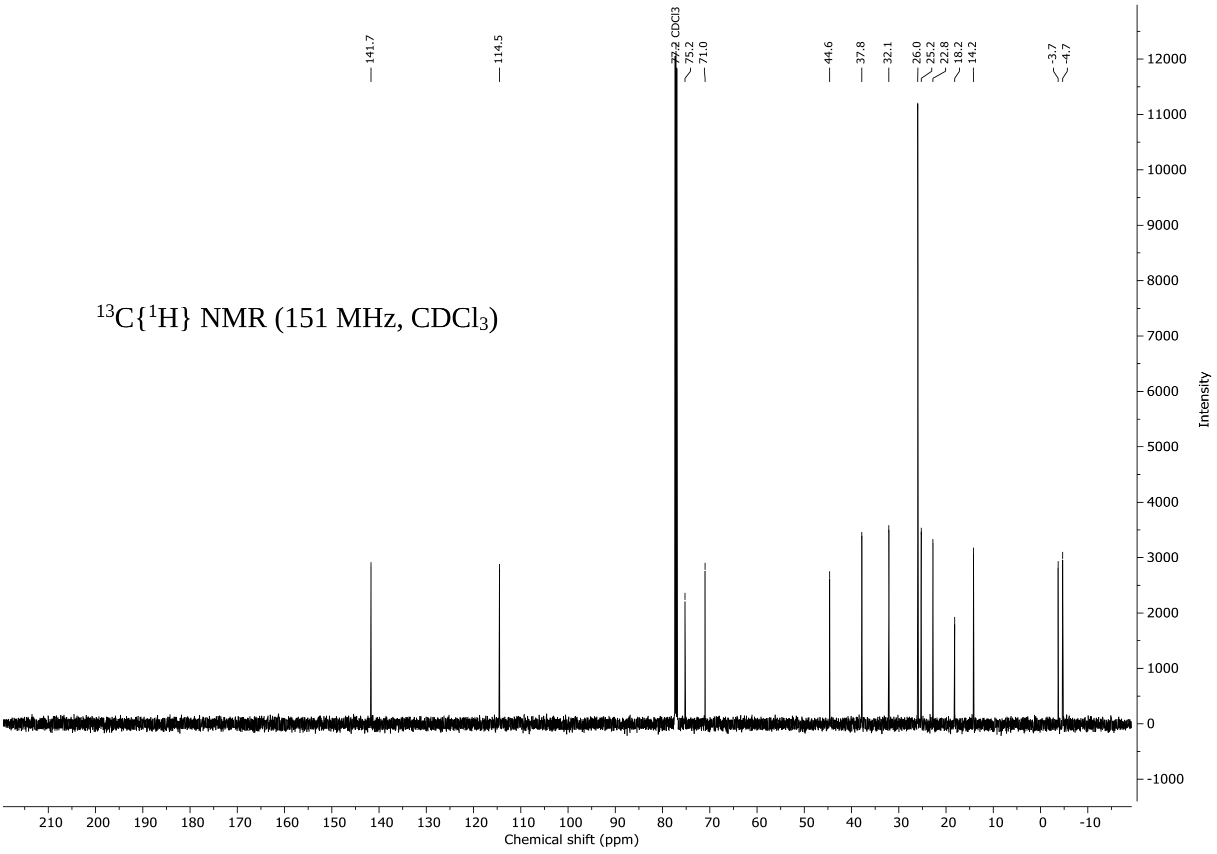




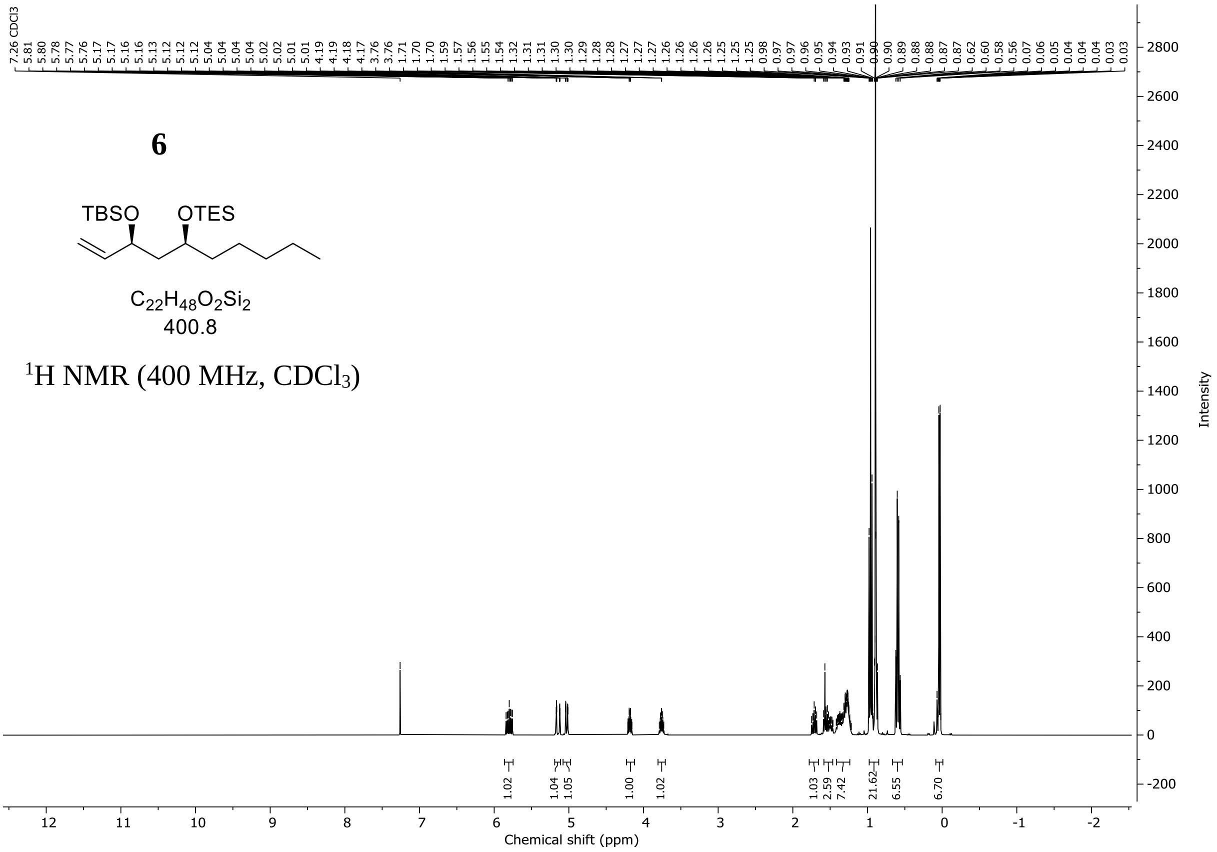
9

$C_{16}H_{34}O_2Si$
286.5

^{1}H NMR (600 MHz, $CDCl_3$)



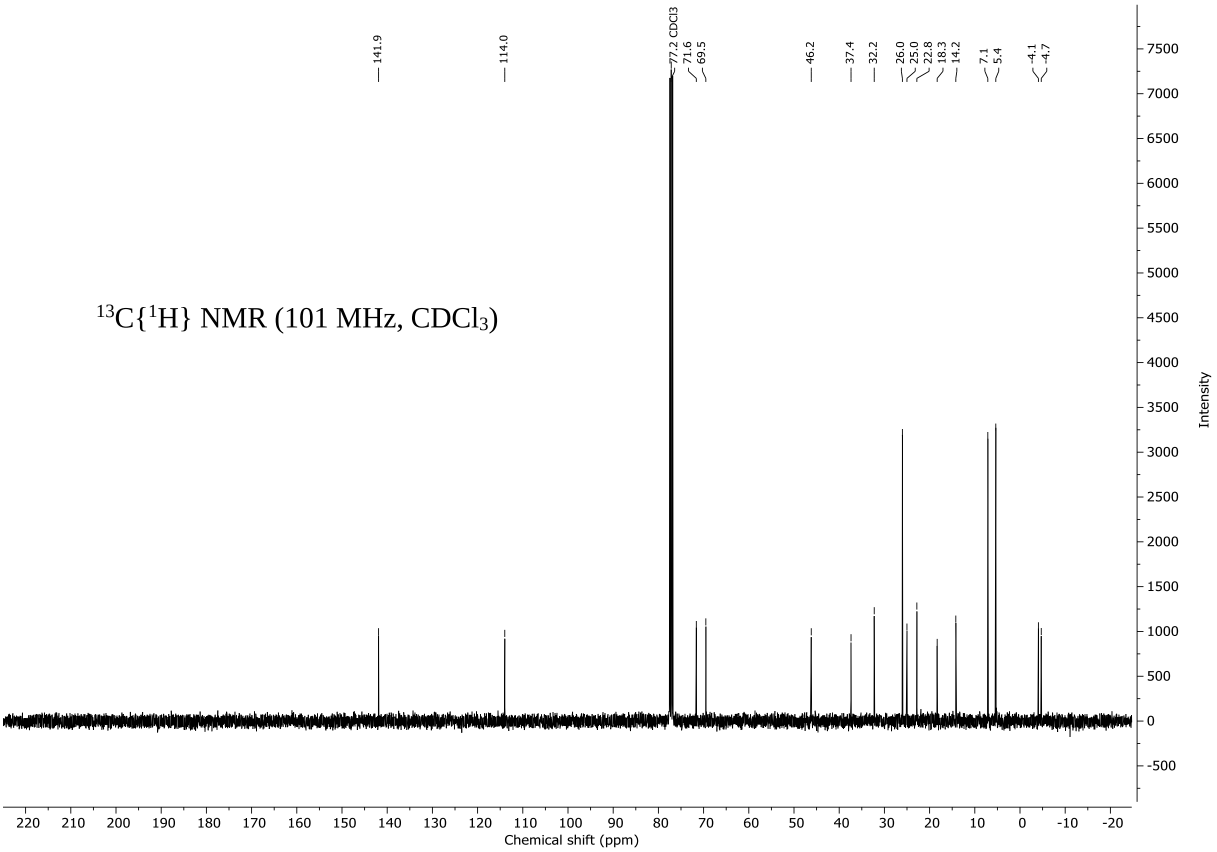
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)



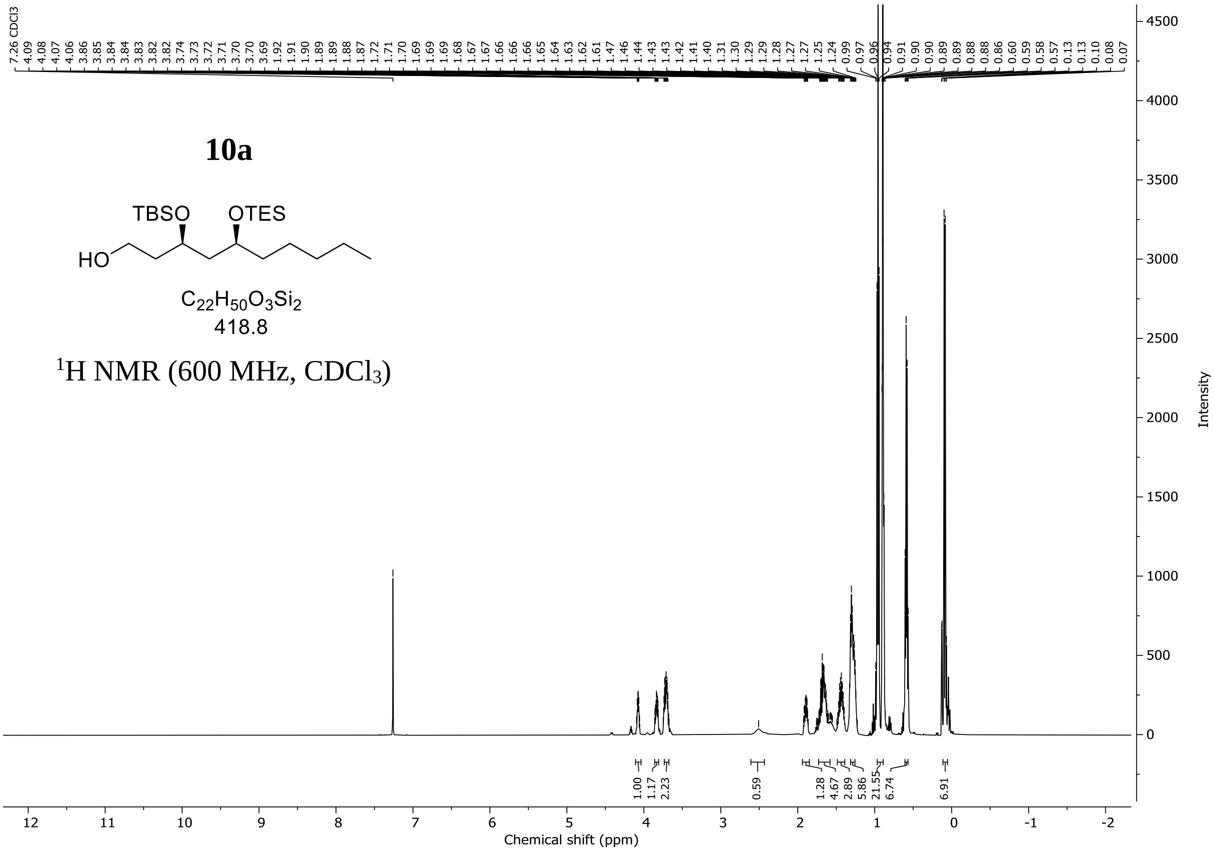
6

$C_{22}H_{48}O_2Si_2$
400.8

^{1}H NMR (400 MHz, CDCl$_3$)



^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)

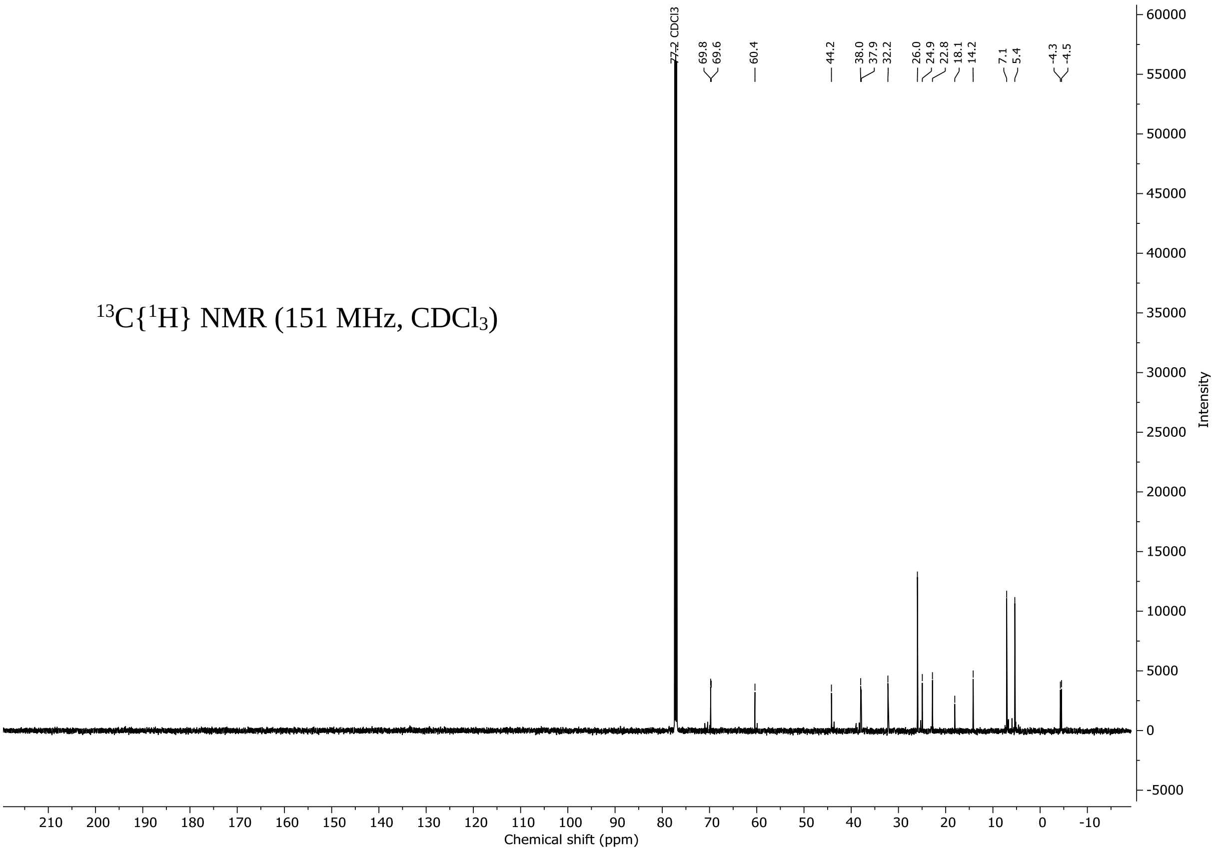


10a

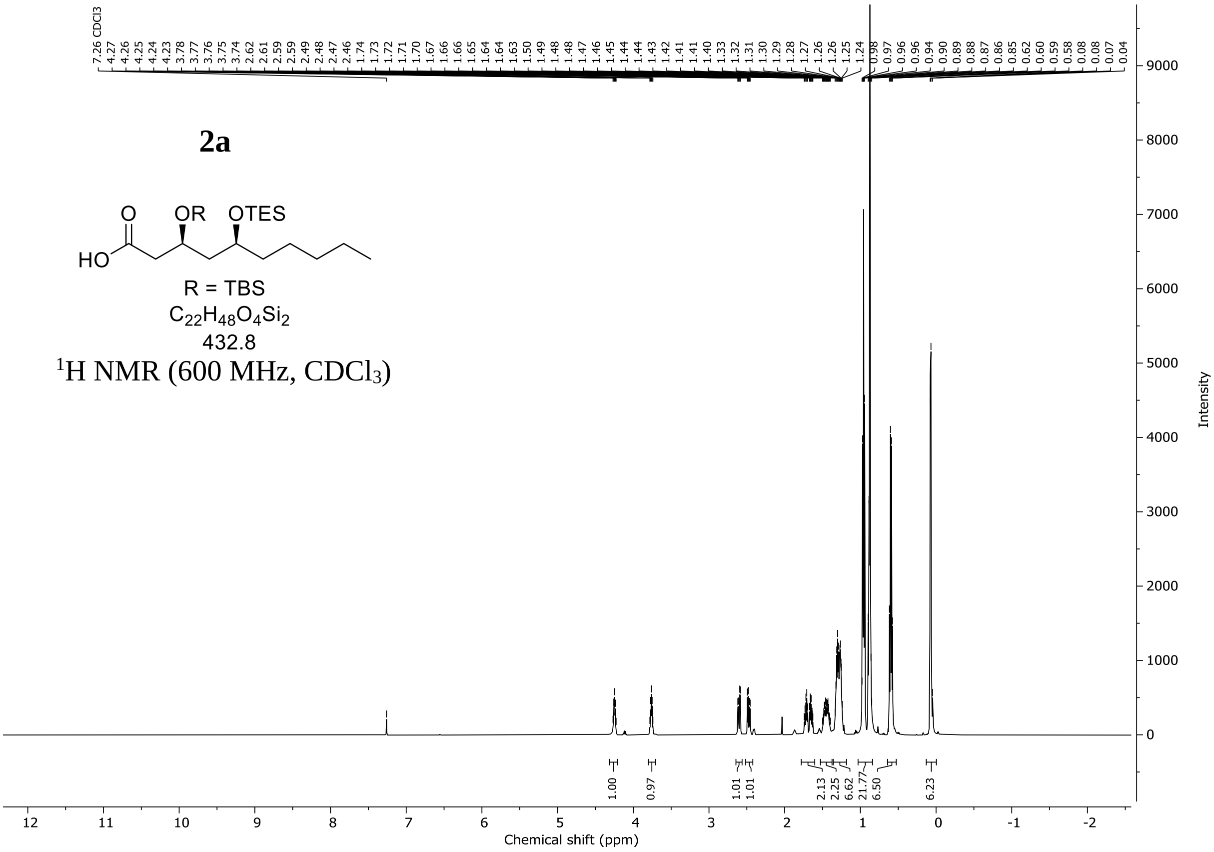
$C_{22}H_{50}O_3Si_2$

418.8

^1H NMR (600 MHz, $CDCl_3$)



$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$)



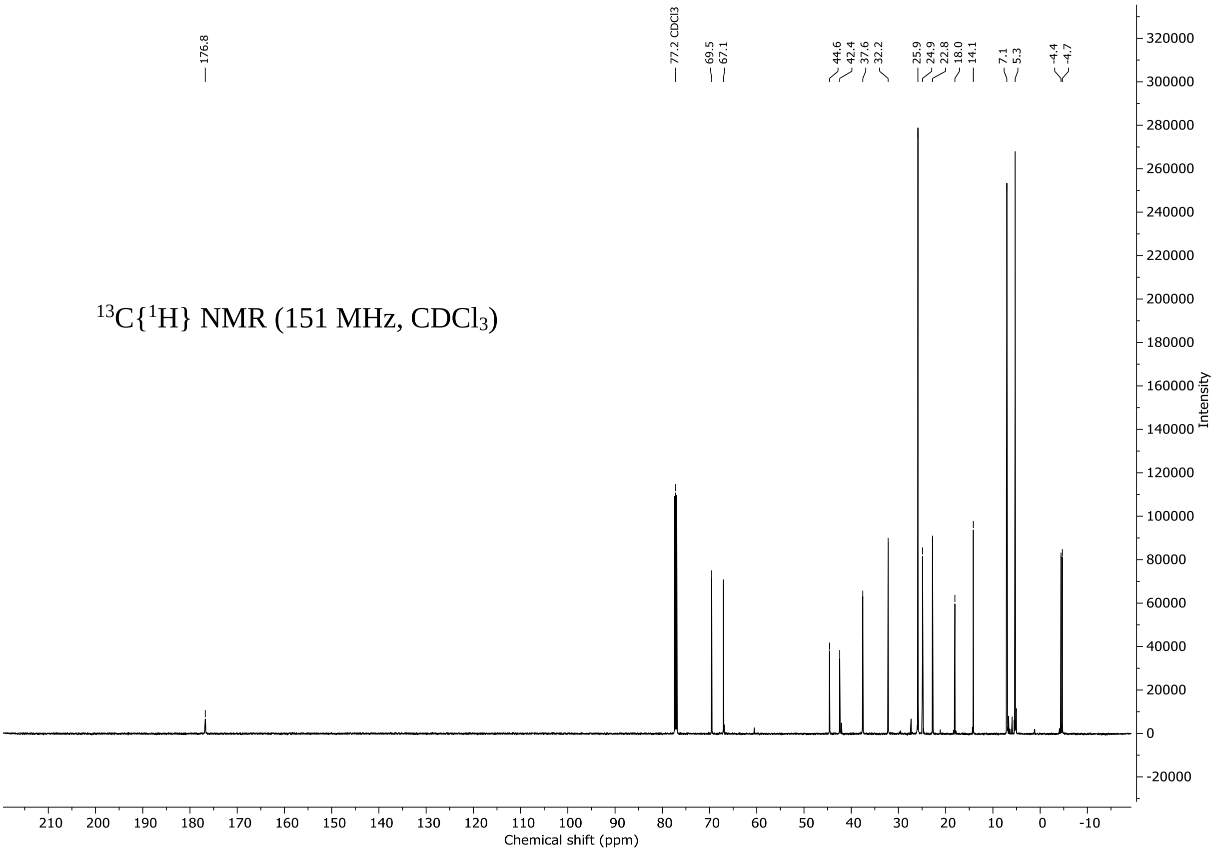
2a

R = TBS

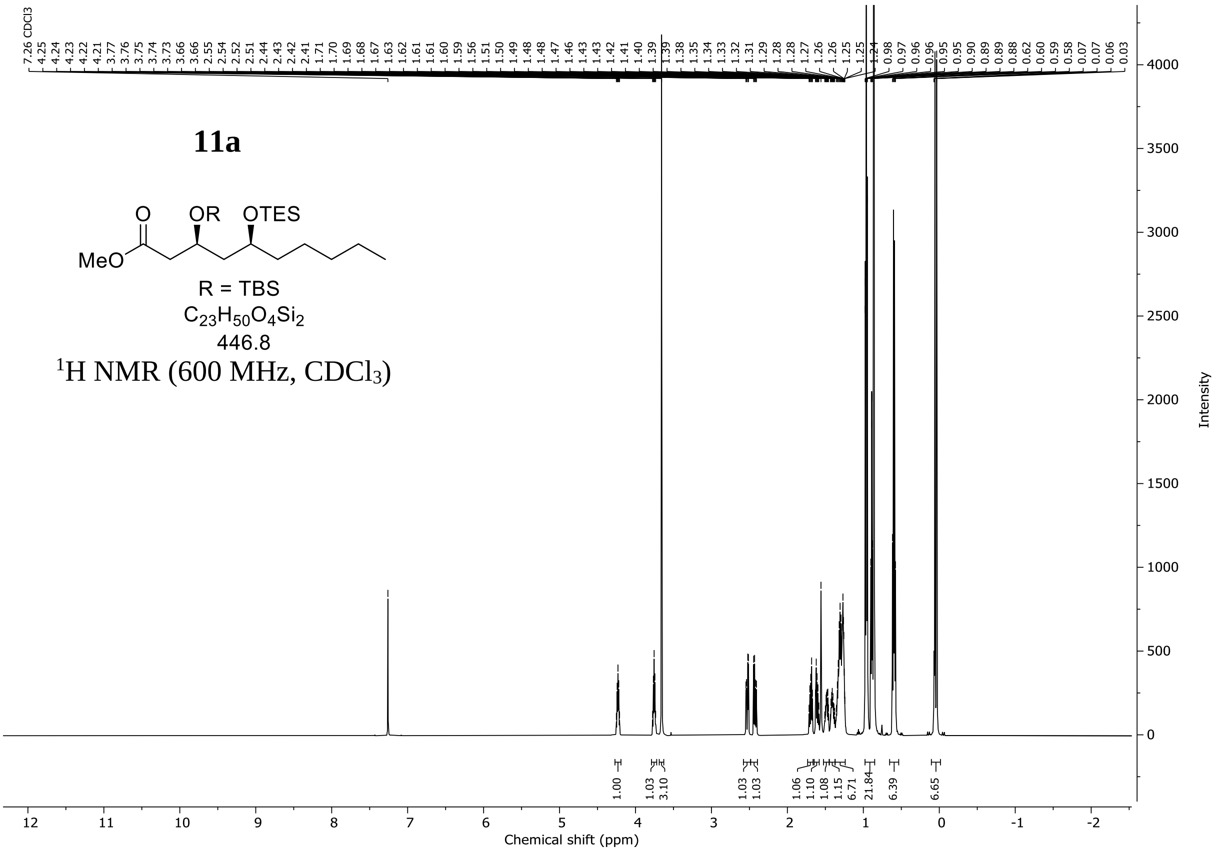
$C_{22}H_{48}O_4Si_2$

432.8

^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)



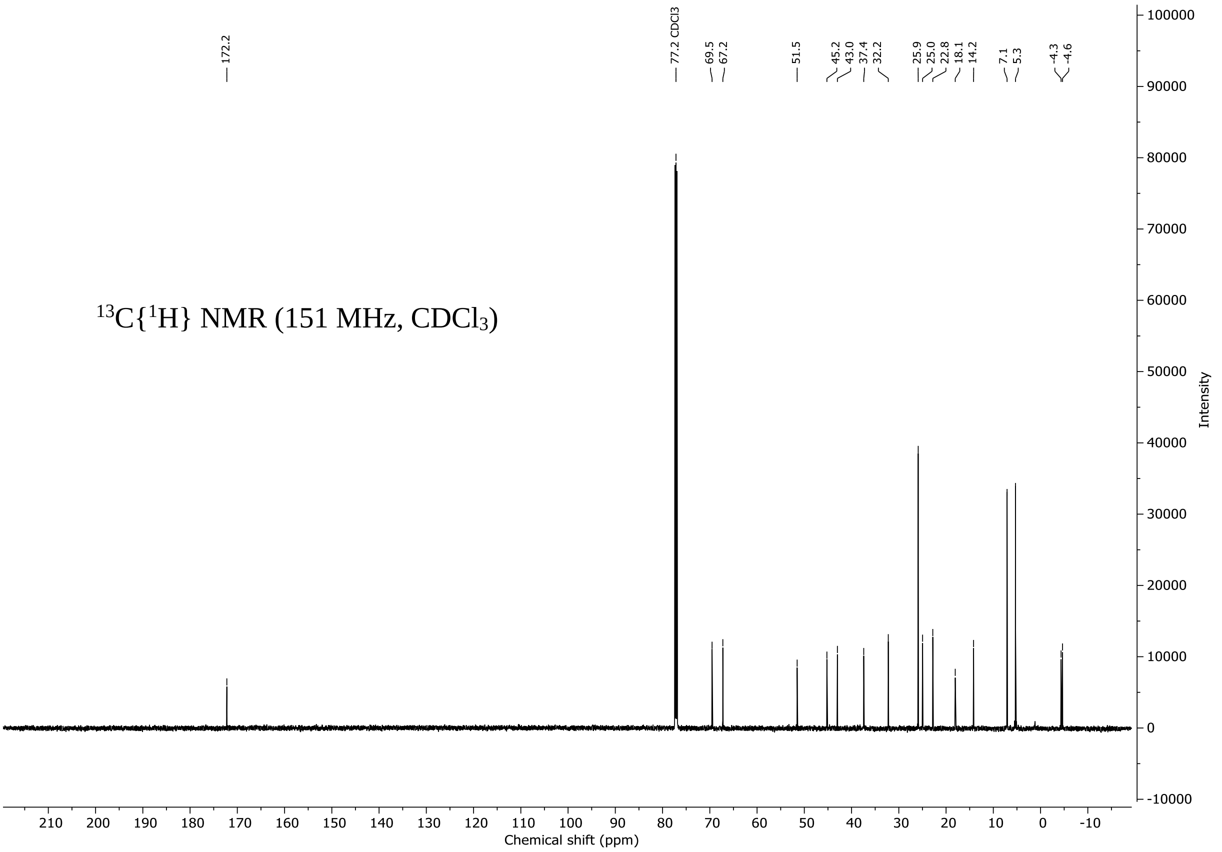
11a

R = TBS

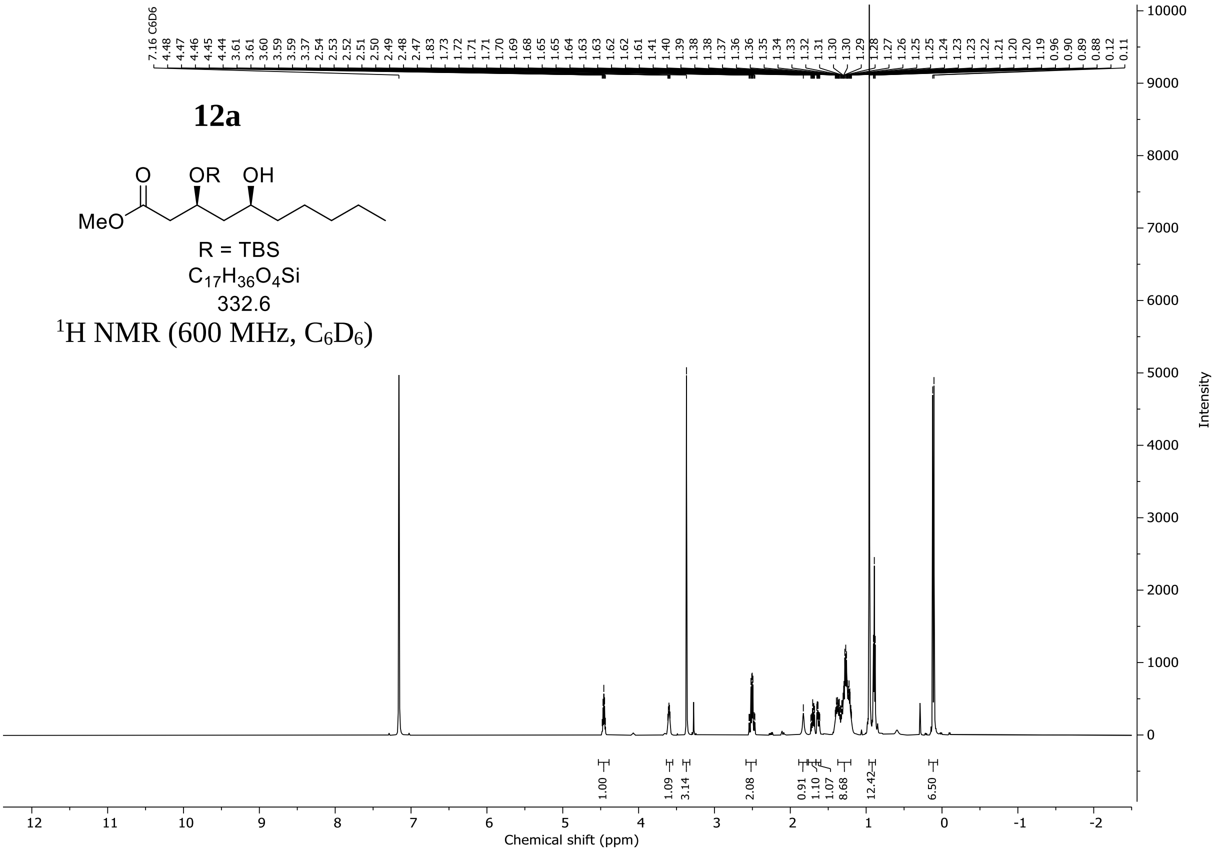
$C_{23}H_{50}O_4Si_2$

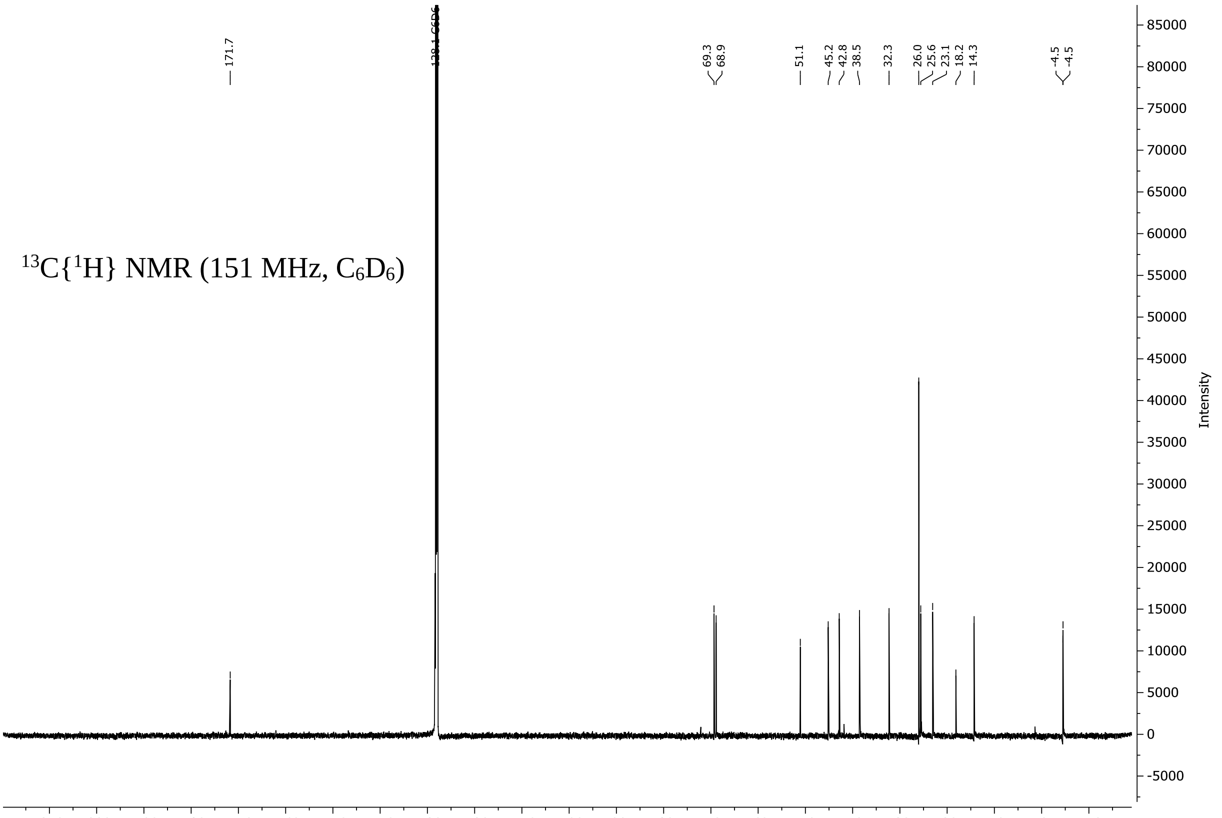
446.8

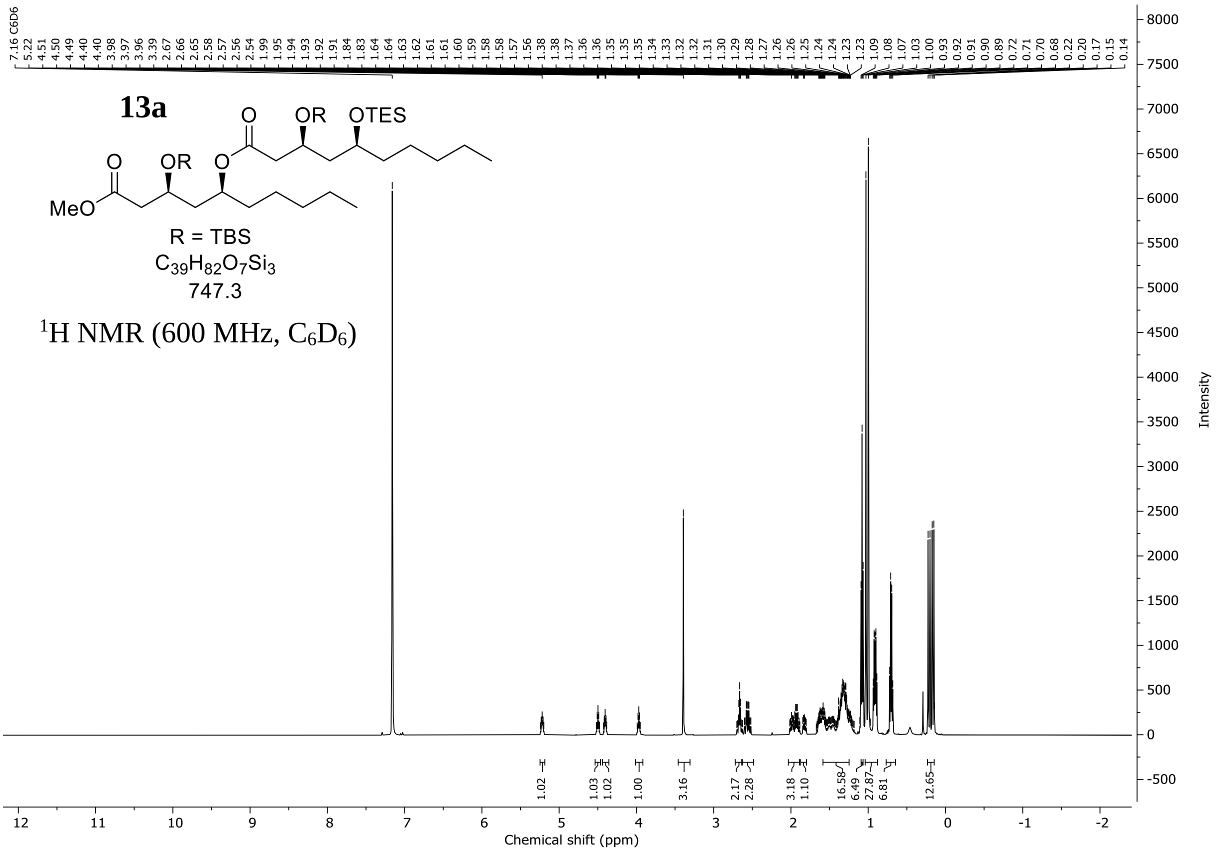
^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$)


7.16 C6D6
4.48
4.47
4.46
4.45
4.44
3.61
3.61
3.60
3.59
3.59
3.37
2.54
2.53
2.52
2.51
2.50
2.49
2.48
2.47
1.83
1.73
1.72
1.71
1.71
1.70
1.69
1.68
1.65
1.65
1.64
1.63
1.63
1.62
1.62
1.61
1.41
1.40
1.39
1.38
1.38
1.37
1.36
1.36
1.35
1.34
1.33
1.32
1.31
1.30
1.30
1.30
1.29
1.28
1.27
1.26
1.25
1.25
1.24
1.23
1.23
1.22
1.21
1.20
1.19
0.96
0.90
0.89
0.88
0.12
0.11
12a
O
OR
OH
MeO
R = TBS
C17H36O4Si
332.6
1H NMR (600 MHz, C6D6)
1.00
1.09
3.14
2.08
0.91
1.10
1.07
8.68
12.42
6.50
Chemical shift (ppm)
Intensity


171.7
128.1 C6D6
69.3
68.9
51.1
45.2
42.8
38.5
32.3
26.0
25.6
23.1
18.2
14.3
-4.5
-4.5
13C{1H} NMR (151 MHz, C6D6)
Chemical shift (ppm)
Intensity



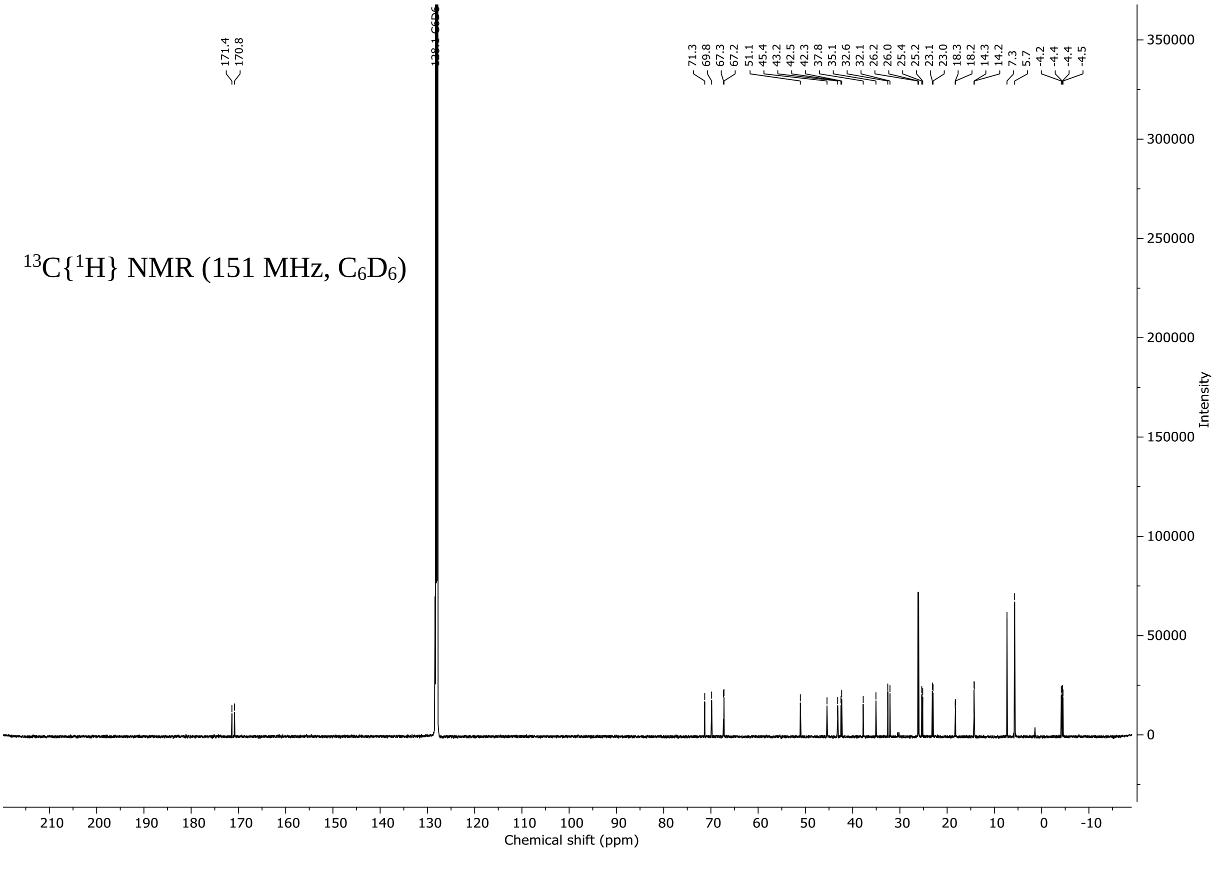
13a

R = TBS

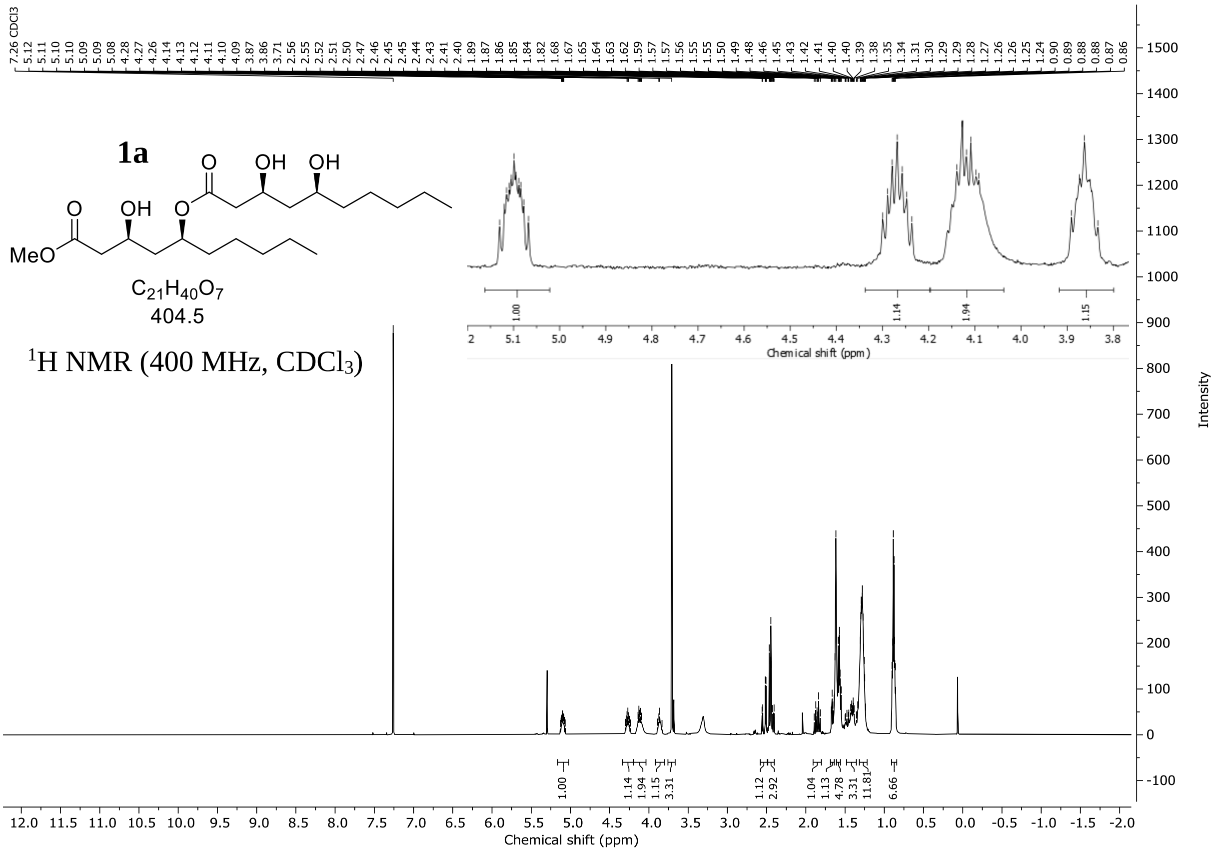
$C_{39}H_{82}O_7Si_3$

747.3

^{1}H NMR (600 MHz, C_6D_6)



^{13}C{^{1}H} NMR (151 MHz, C_6D_6)


1a
MeO
O
OH
OH
OH
$C_{21}H_{40}O_7$
404.5
^{1}H NMR (400 MHz, CDCl$_3$)
7.26 CDCl3
5.12
5.11
5.10
5.09
5.09
5.08
4.28
4.27
4.26
4.14
4.13
4.12
4.11
4.10
4.09
3.87
3.86
3.71
2.56
2.55
2.52
2.51
2.50
2.47
2.46
2.45
2.45
2.44
2.43
2.41
2.40
1.89
1.87
1.86
1.85
1.84
1.82
1.68
1.67
1.65
1.64
1.63
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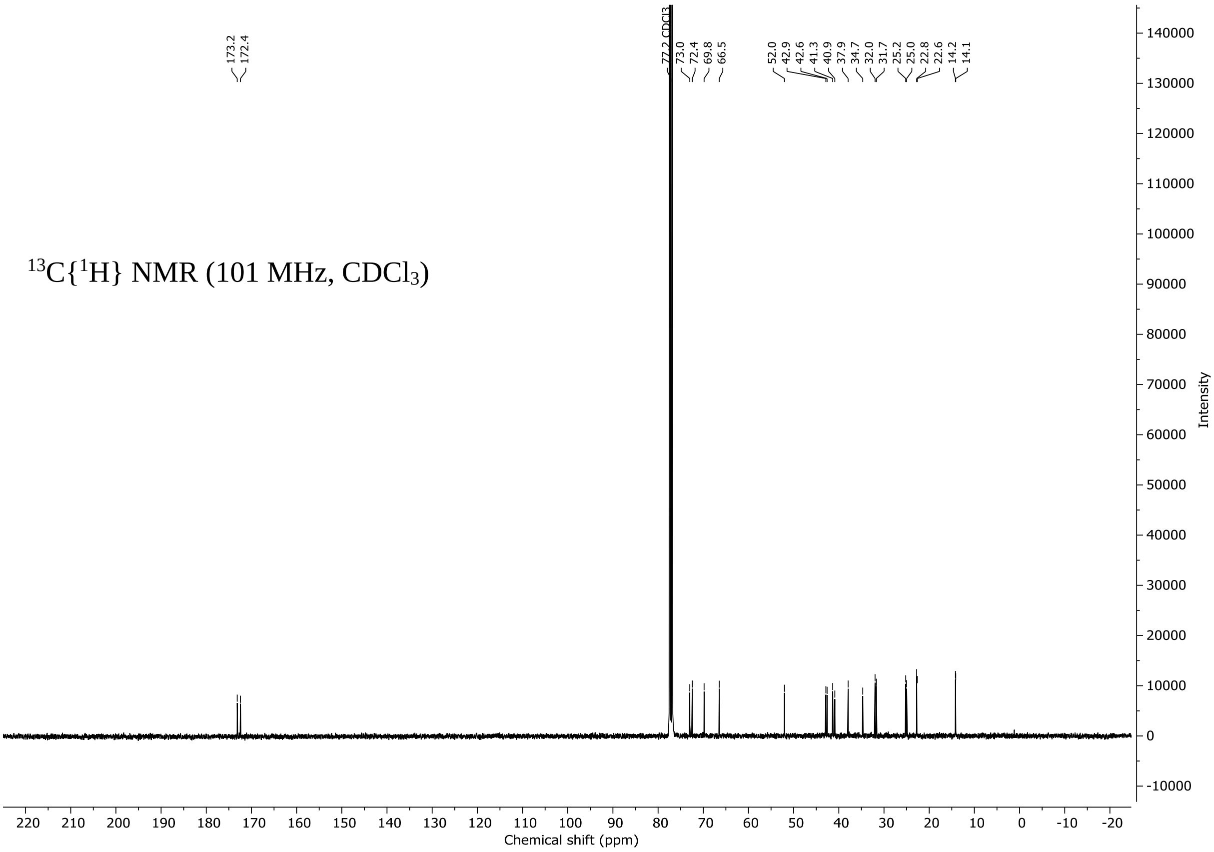
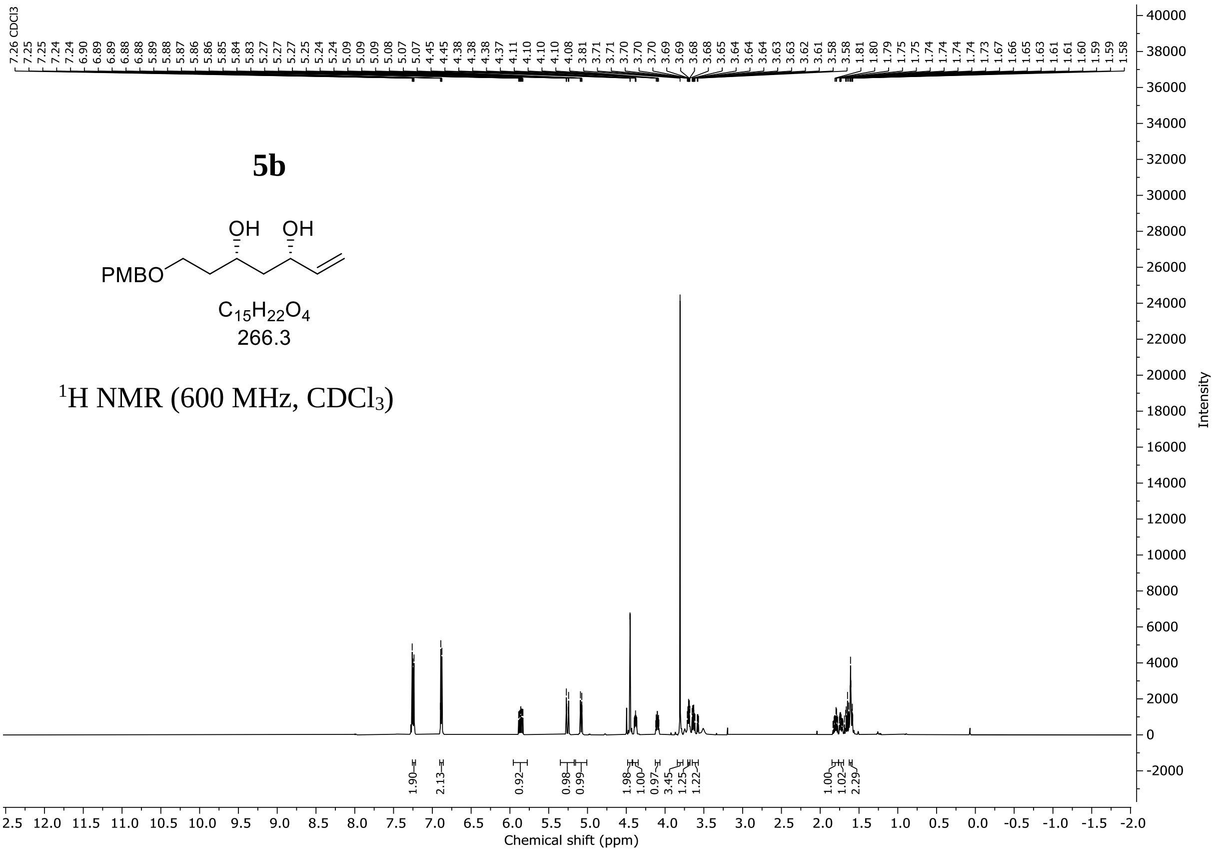
1.57
1.56
1.55
1.55
1.50
1.49
1.48
1.46
1.45
1.43
1.42
1.41
1.40
1.40
1.39
1.38
1.35
1.34
1.31
1.30
1.29
1.29
1.28
1.27
1.26
1.25
1.24
0.90
0.89
0.88
0.88
0.87
0.86
1.00
1.14
1.94
1.15
Chemical shift (ppm)
1.00
1.14
1.94
1.15
3.31
1.12
2.92
1.04
1.13
4.78
3.31
11.81
6.66
Chemical shift (ppm)
Intensity

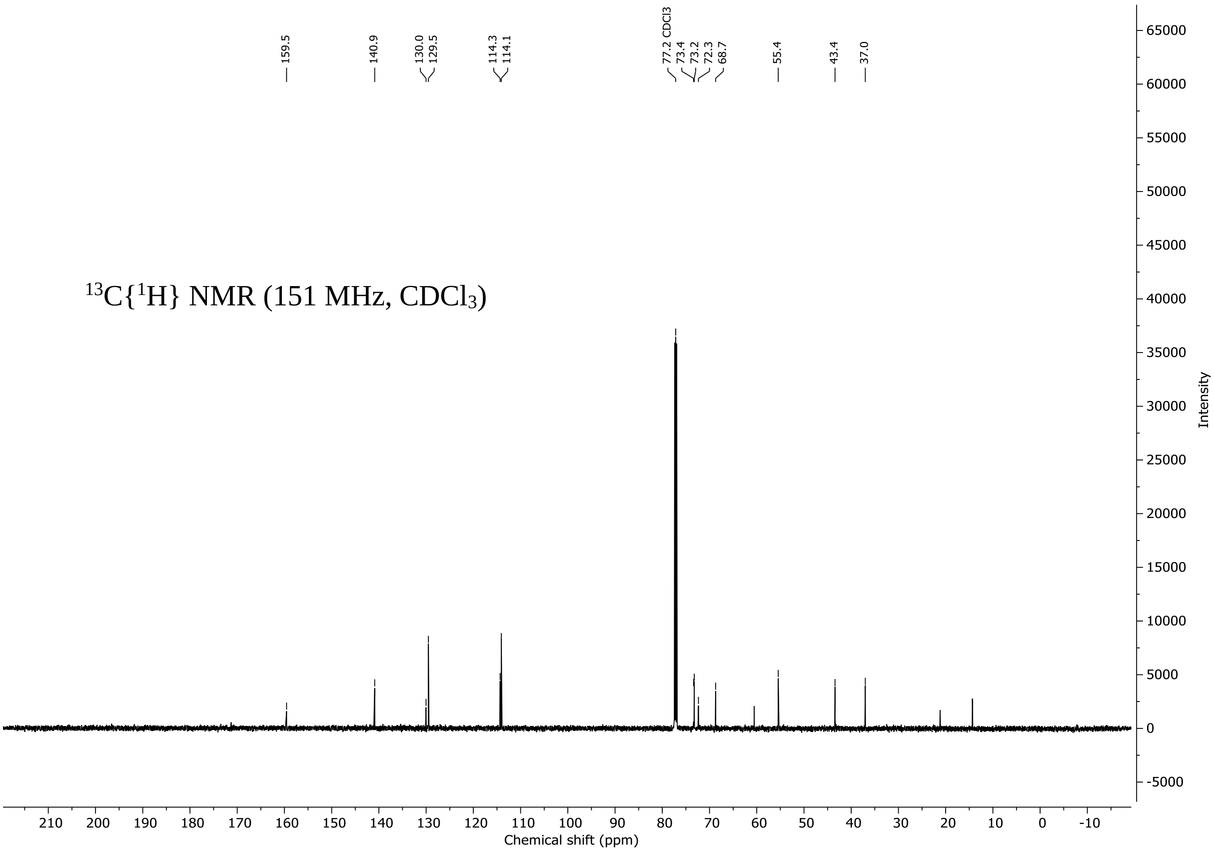

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)
173.2
172.4
77.2 CDCl3
73.0
72.4
69.8
66.5
52.0
42.9
42.6
41.3
40.9
37.9
34.7
32.0
31.7
25.2
25.0
22.8
22.6
14.2
14.1
Chemical shift (ppm)
Intensity



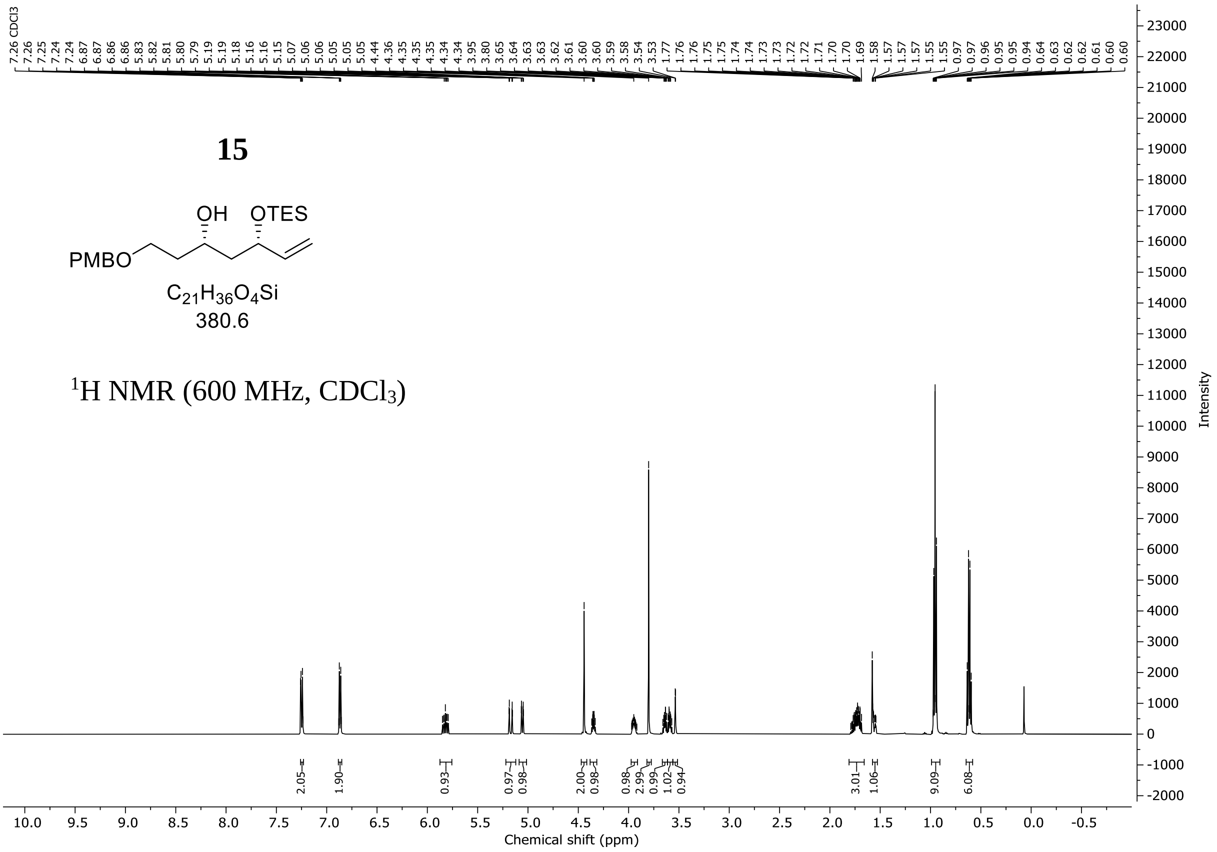
5b

$C_{15}H_{22}O_4$
266.3

^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$)



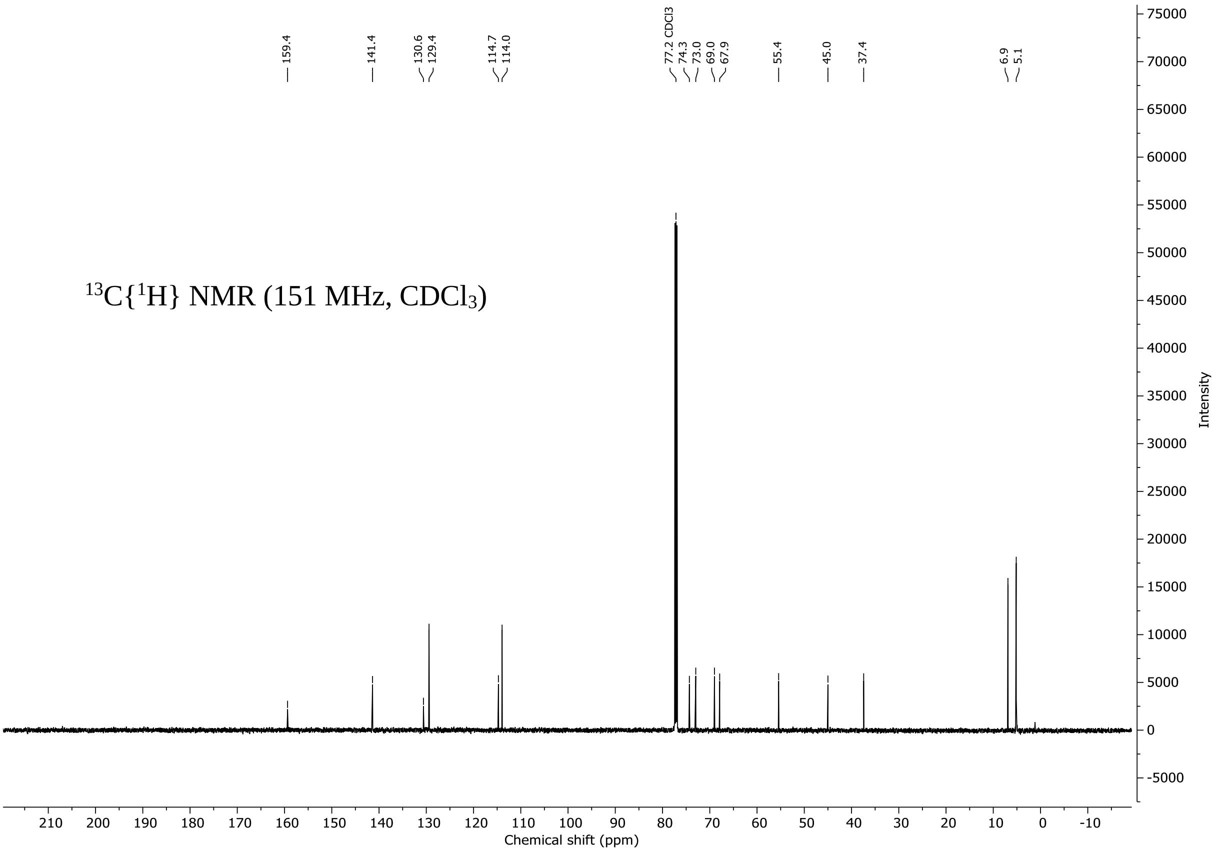
15

PMBO, OH, OTES

$C_{21}H_{36}O_4Si$

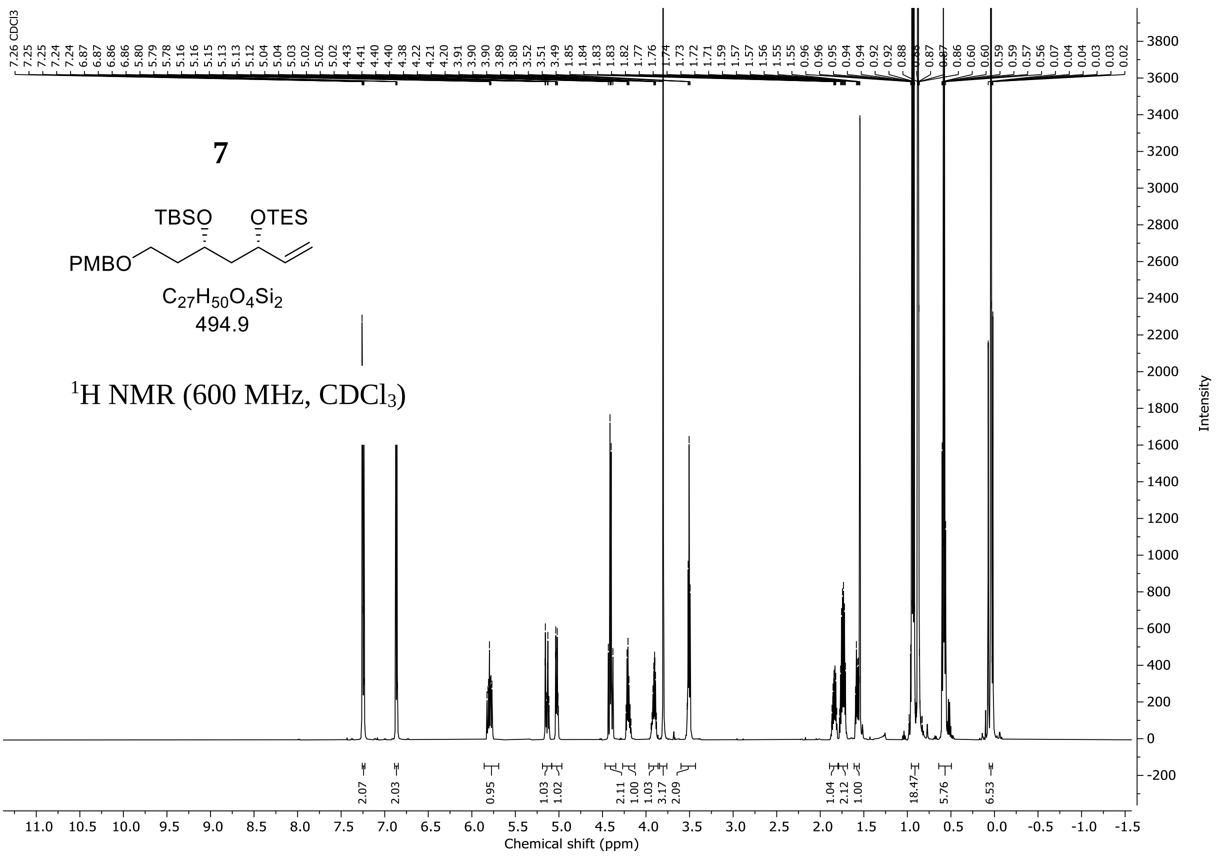
380.6

^{1}H NMR (600 MHz, $CDCl_3$)



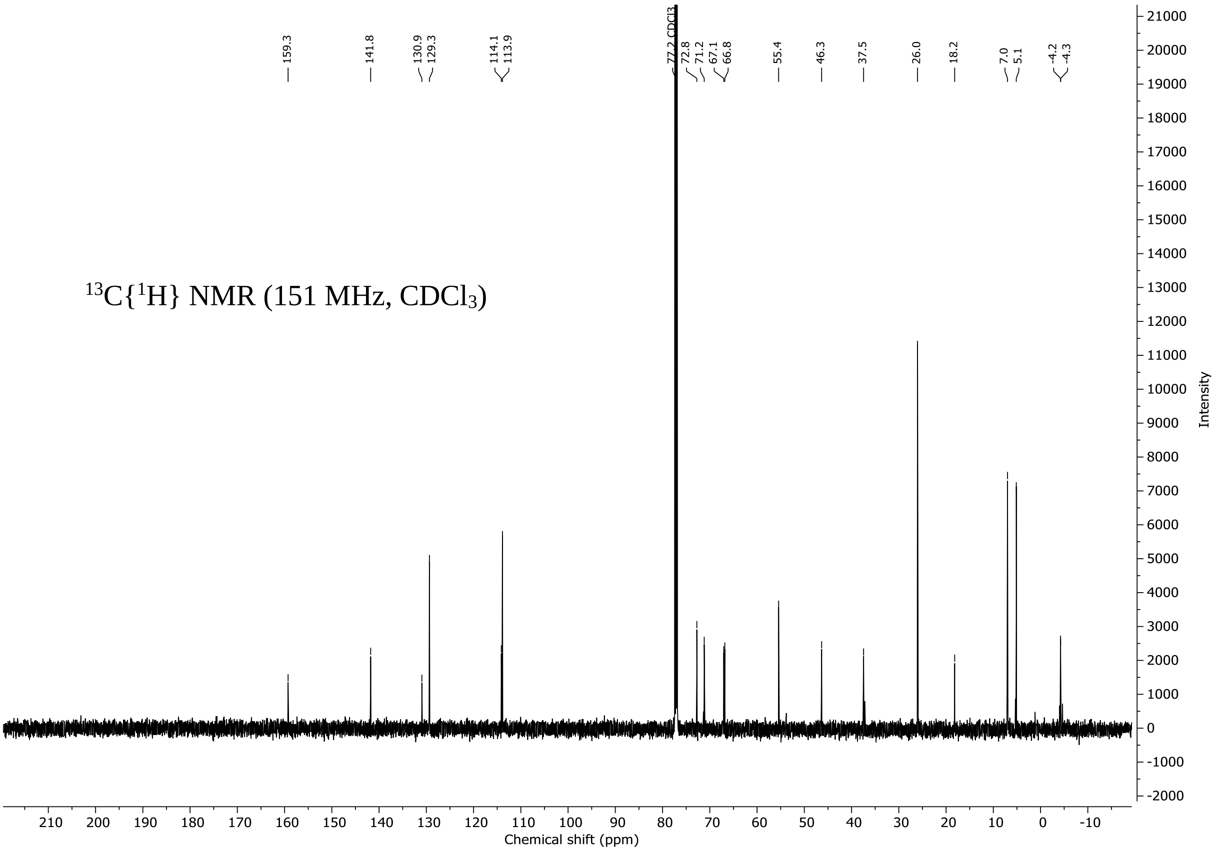
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

7

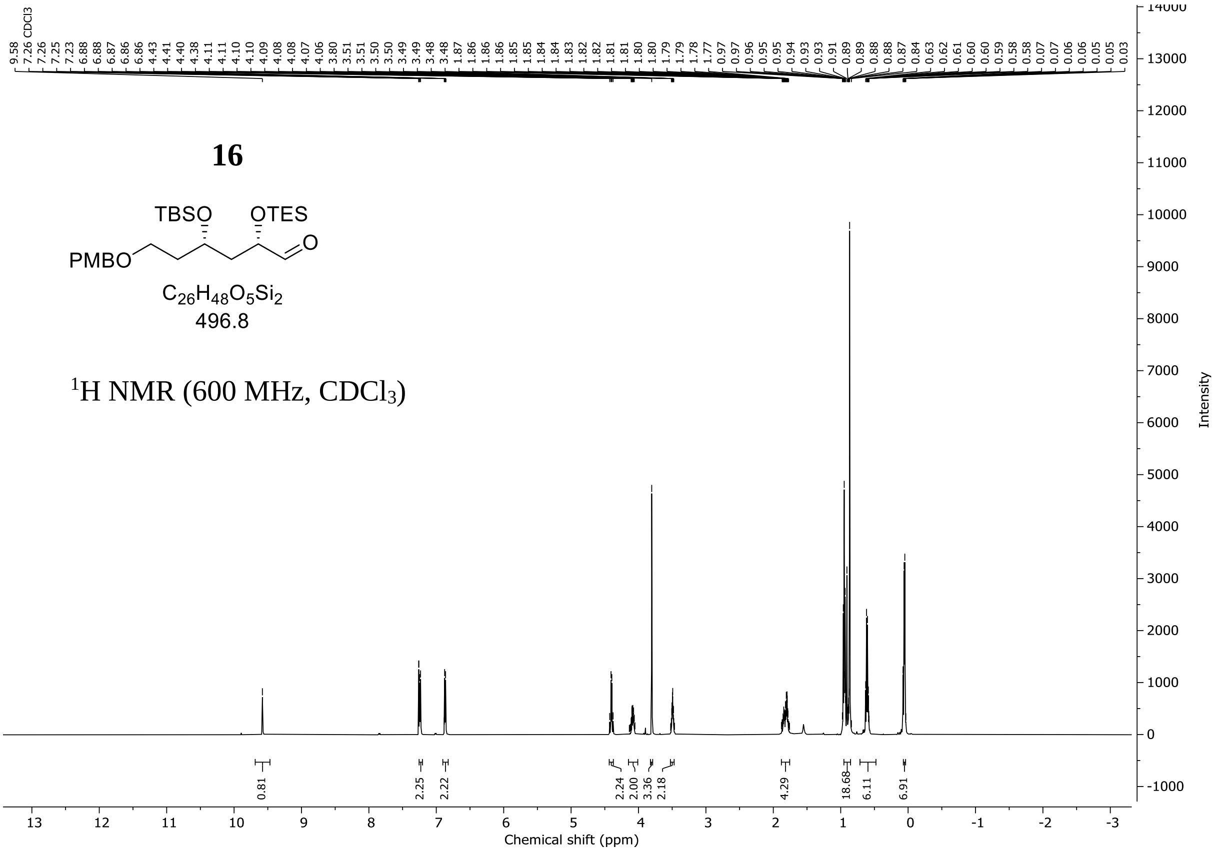


$C_{27}H_{50}O_4Si_2$
494.9

^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$)

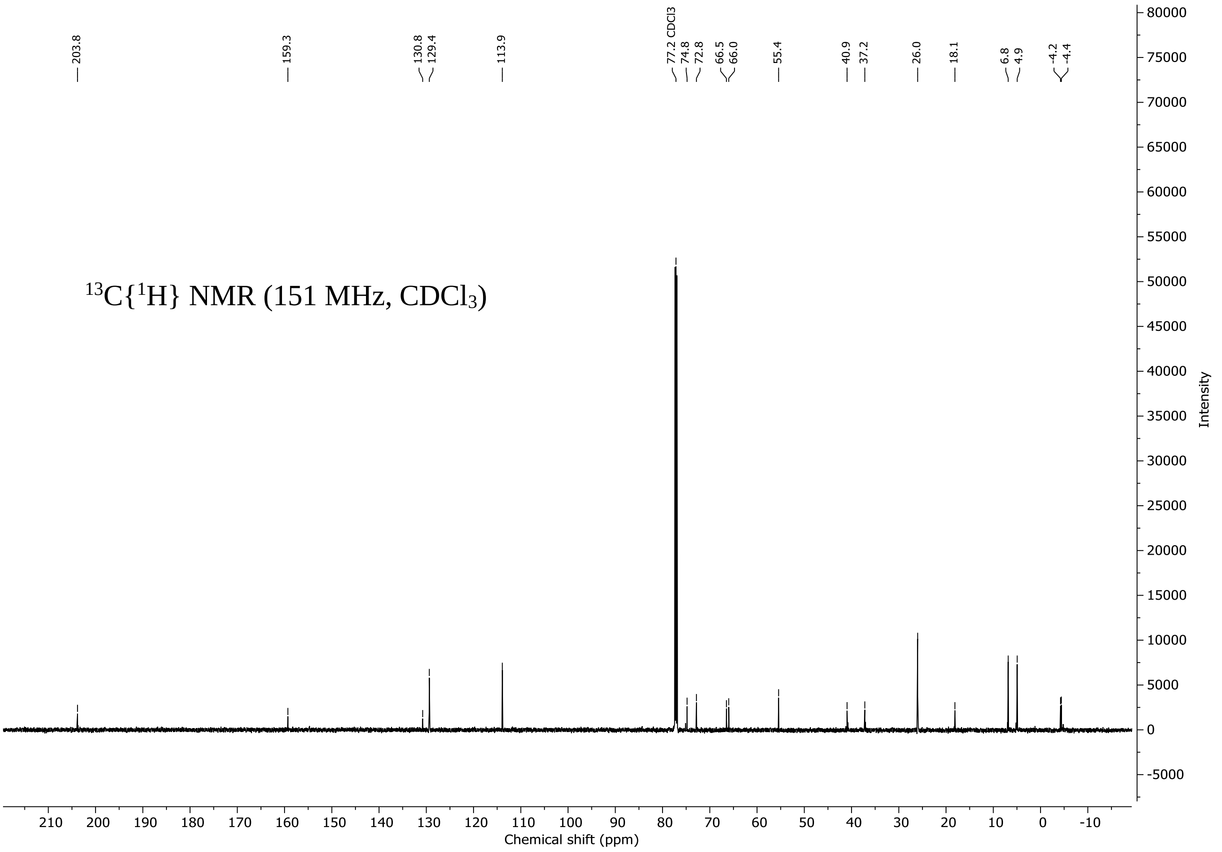


16

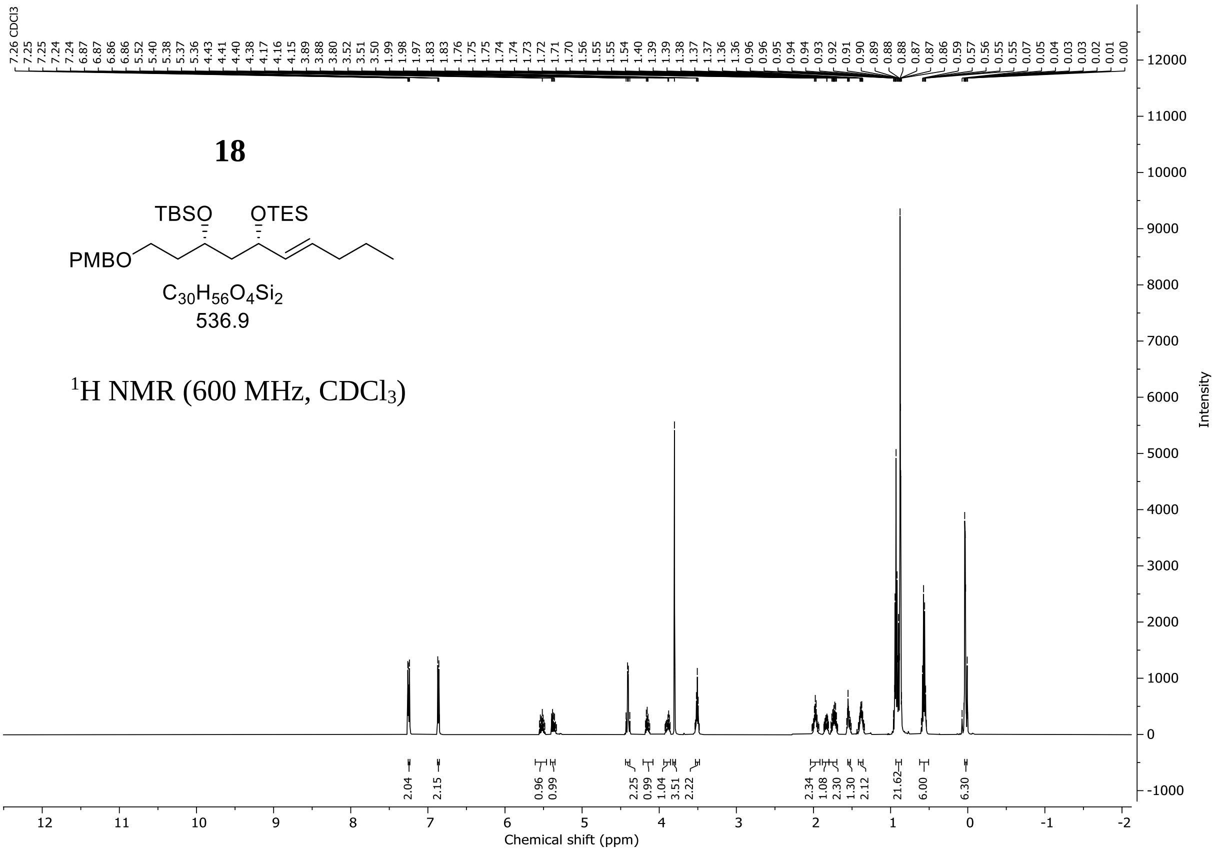
$C_{26}H_{48}O_5Si_2$

496.8

^{1}H NMR (600 MHz, CDCl$_3$)



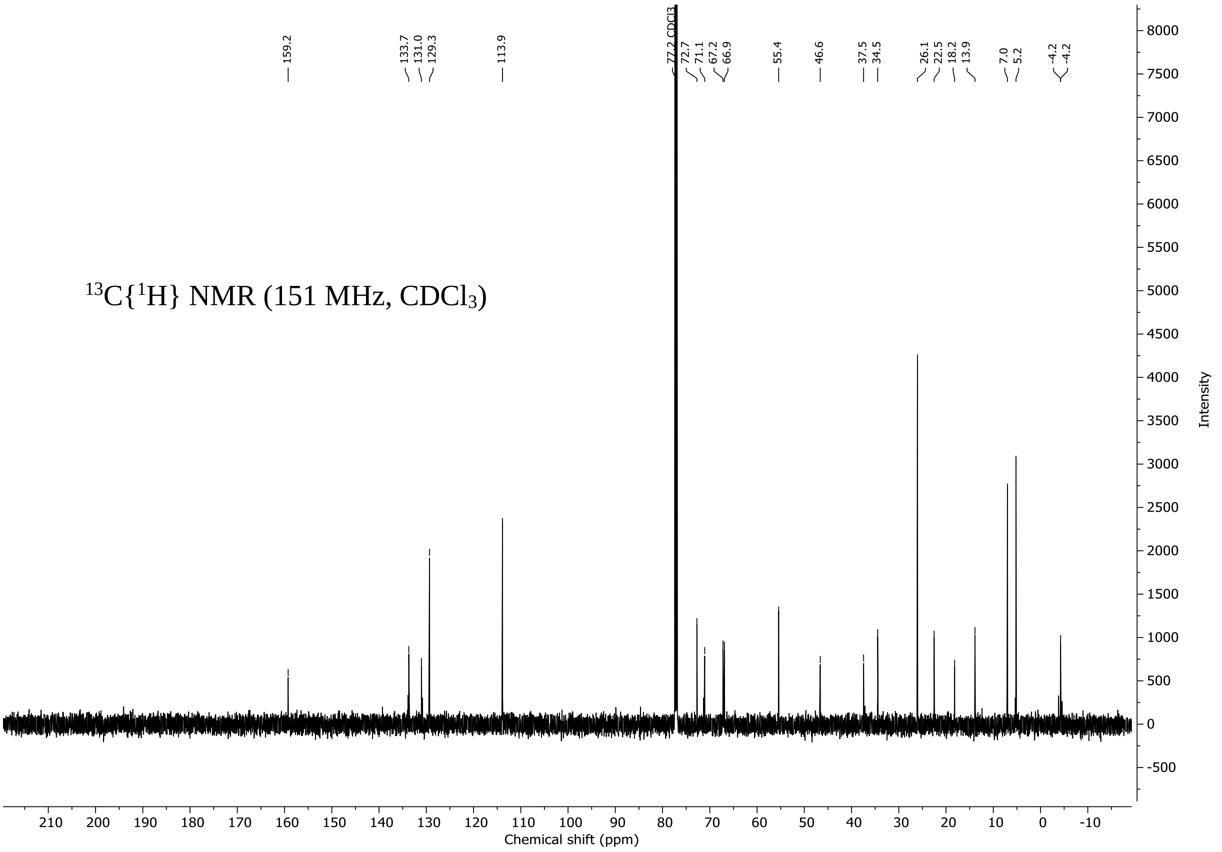
^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$)



18

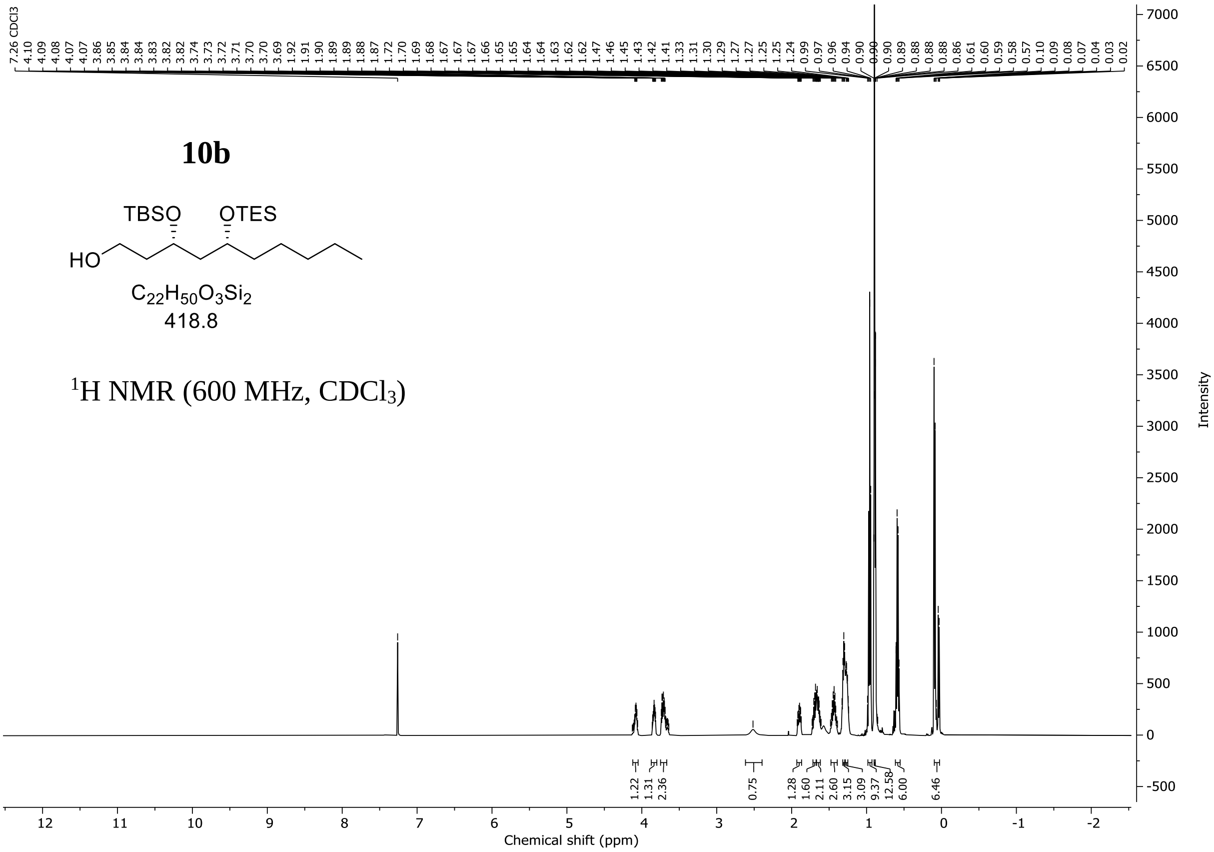
$C_{30}H_{56}O_4Si_2$
536.9

^{1}H NMR (600 MHz, CDCl$_3$)



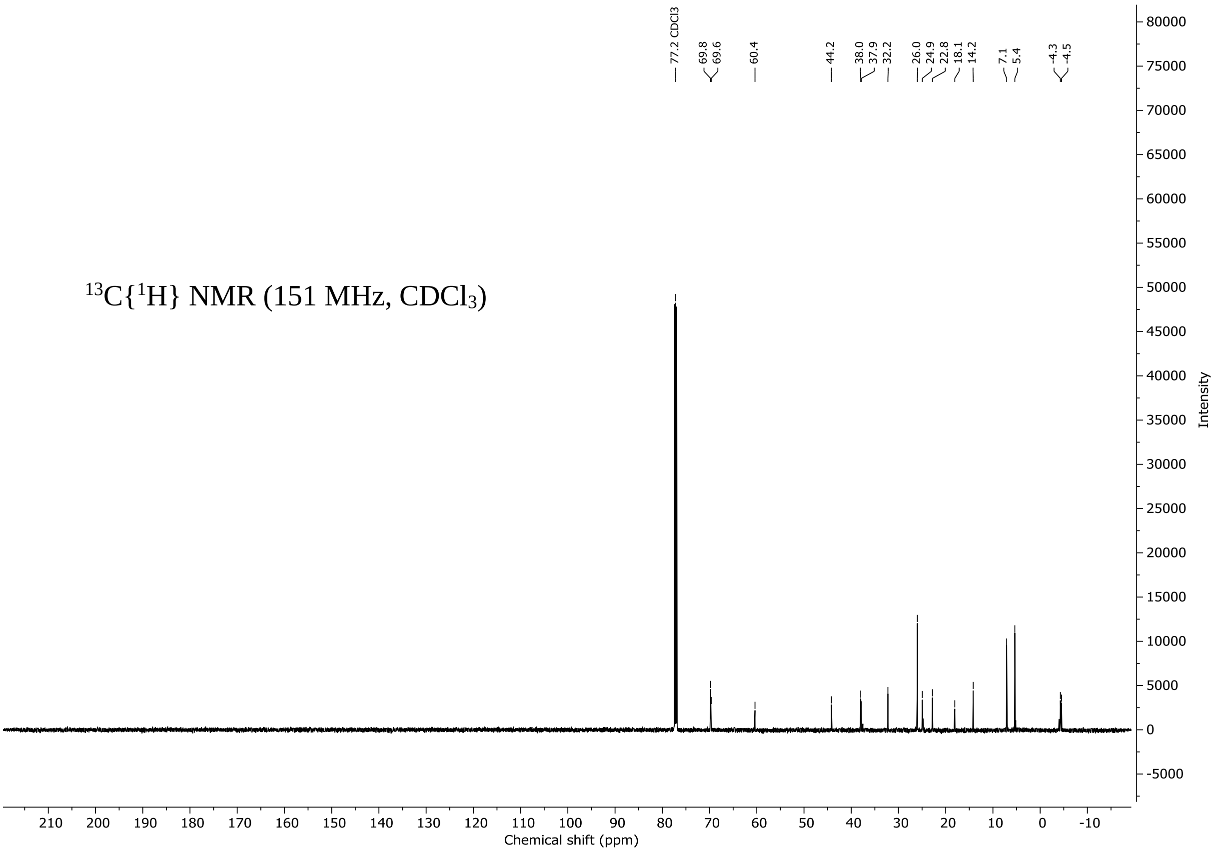
^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$)

10b

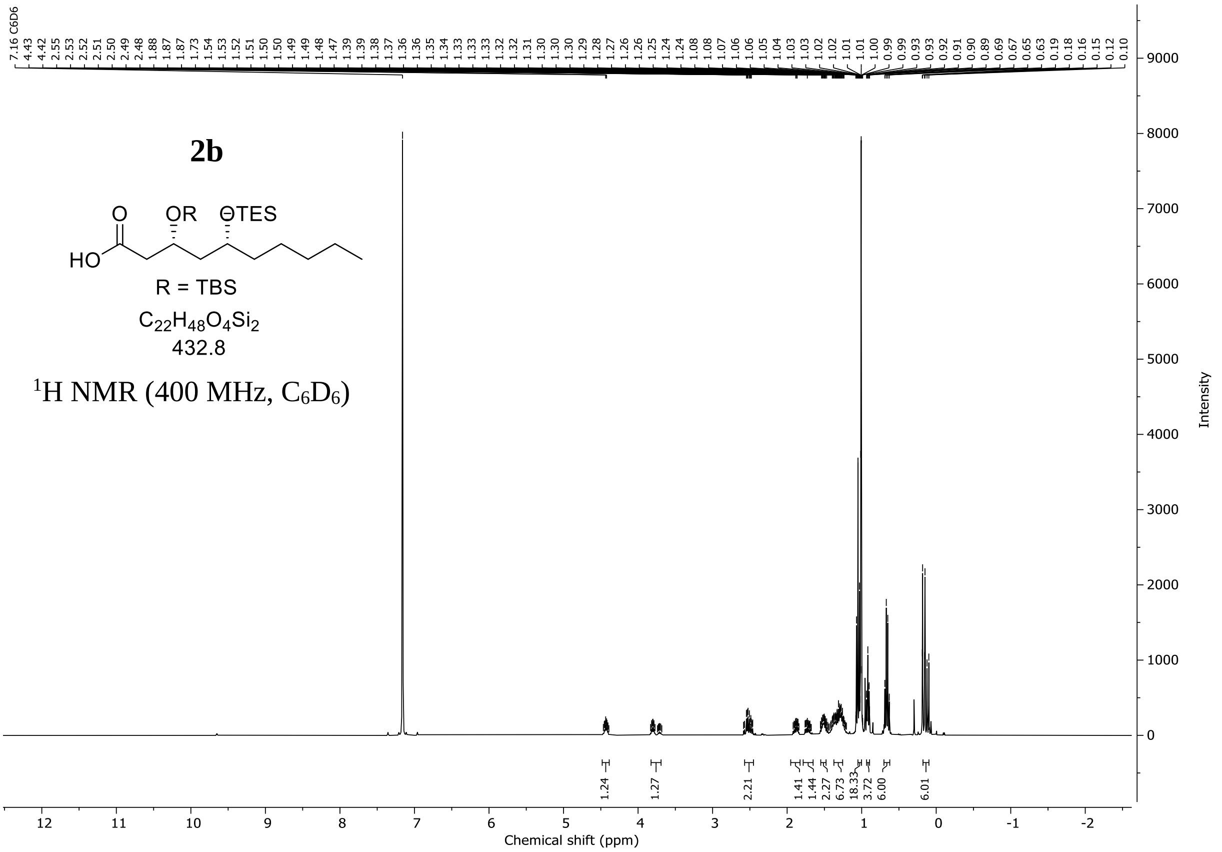


$C_{22}H_{50}O_3Si_2$
418.8

^{1}H NMR (600 MHz, CDCl$_3$)

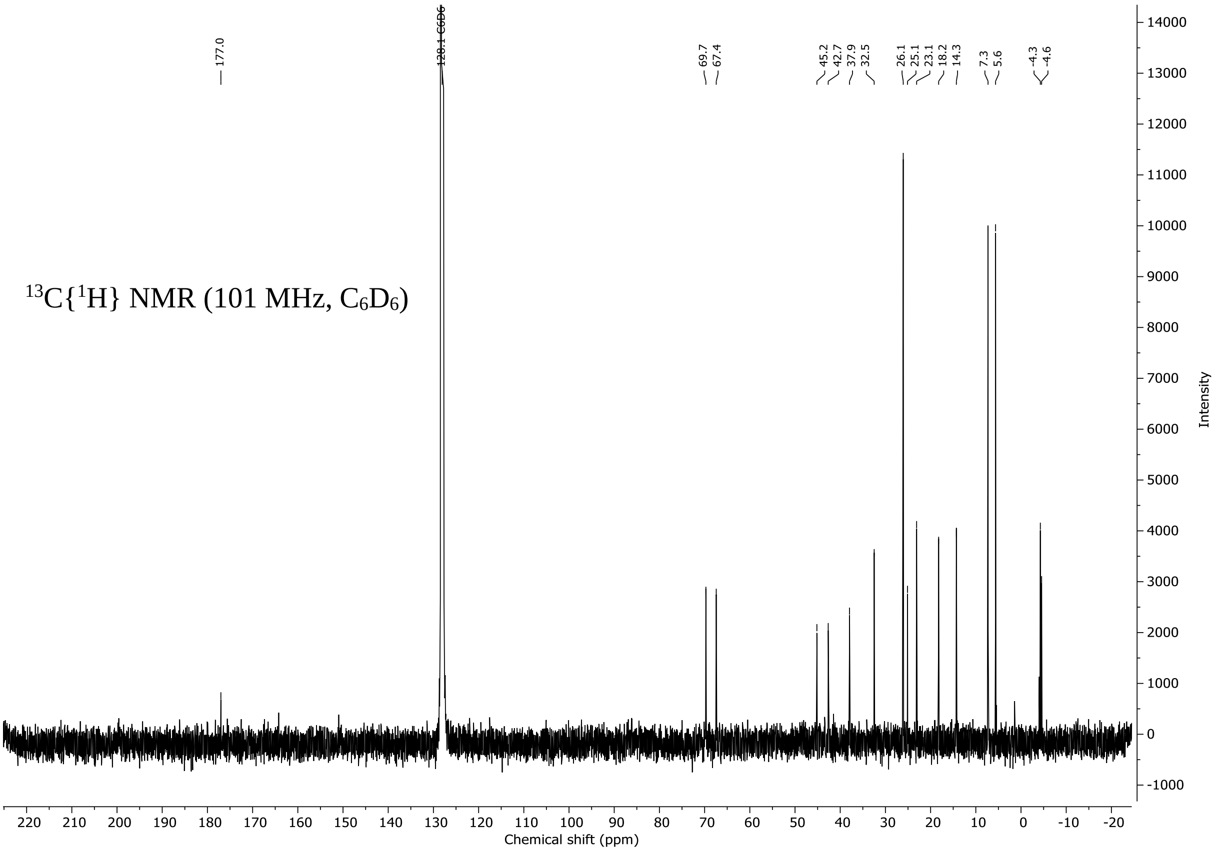


^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$)

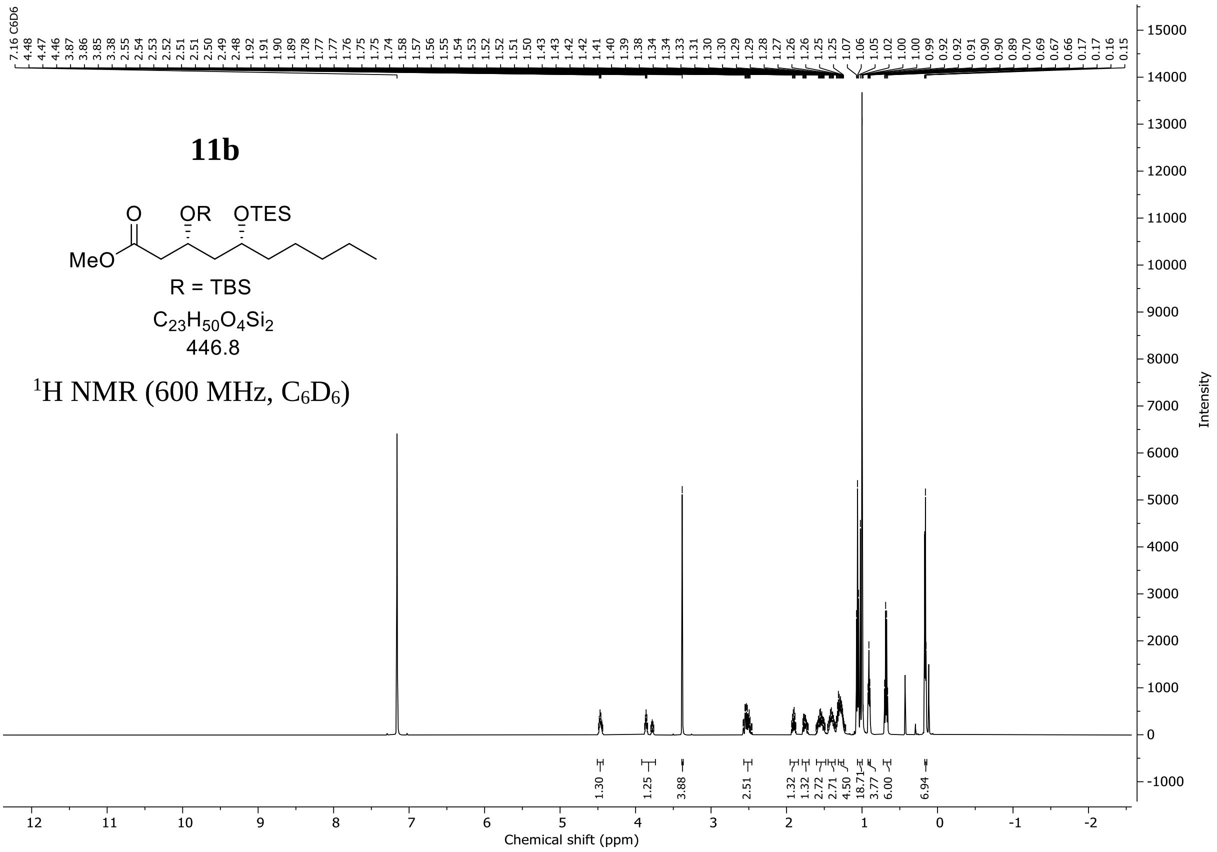


2b

^{1}H NMR (400 MHz, C_6D_6)



$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6)



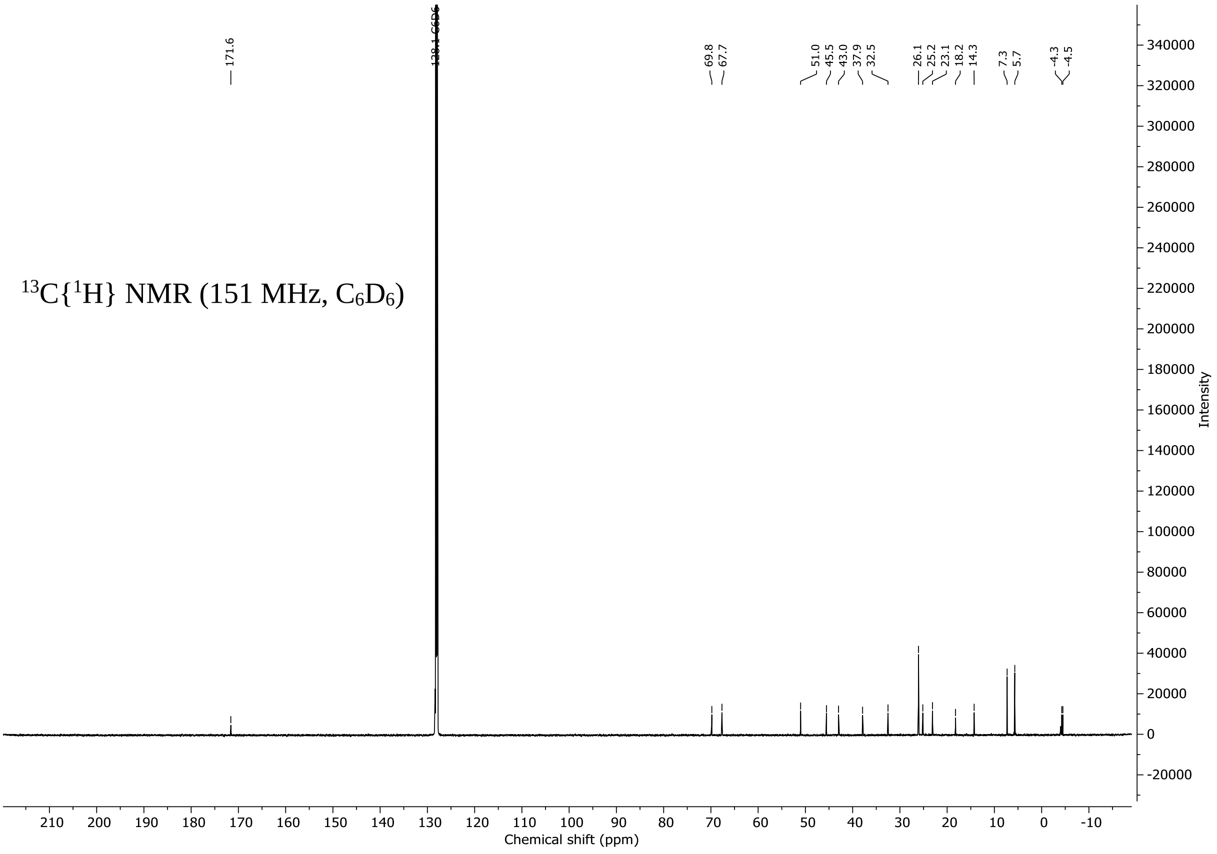
11b

R = TBS

$C_{23}H_{50}O_4Si_2$

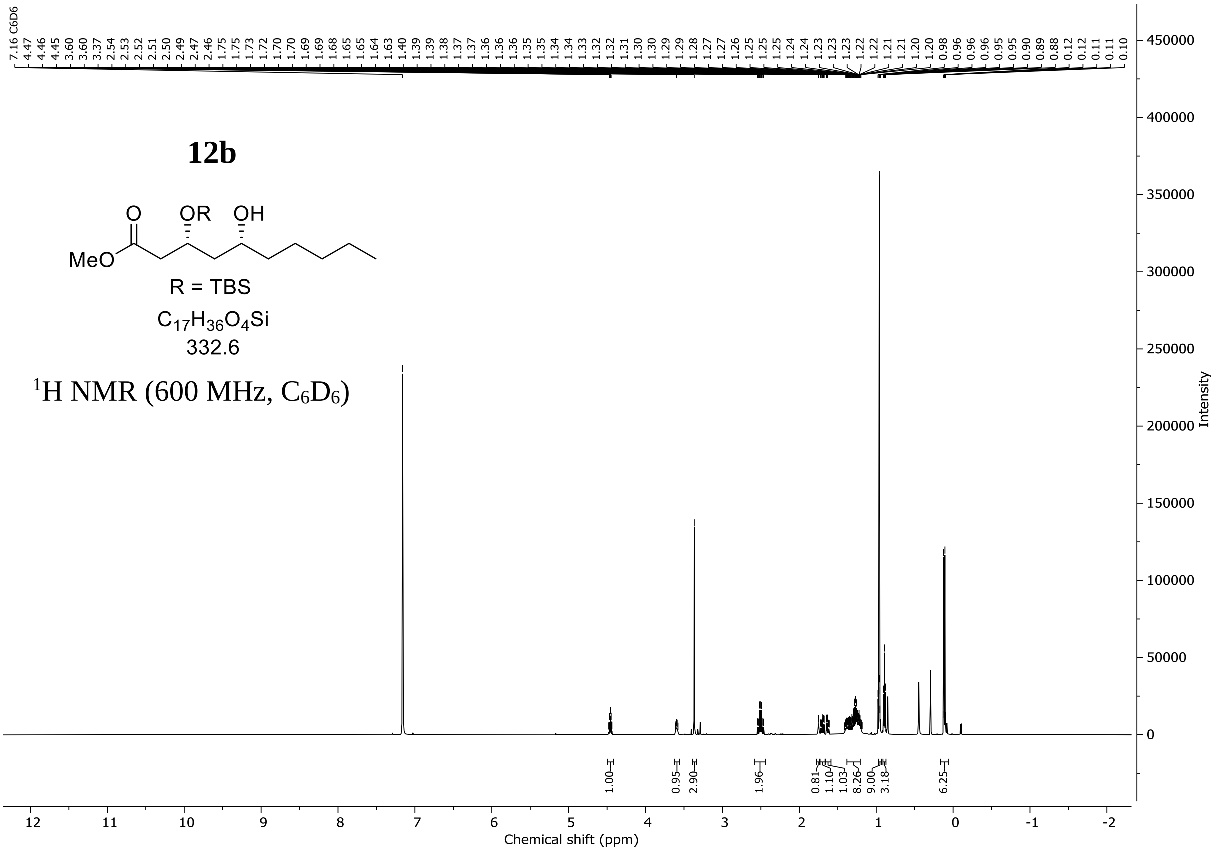
446.8

^{1}H NMR (600 MHz, C_6D_6)



^{13}C{^{1}H} NMR (151 MHz, C_6D_6)

12b

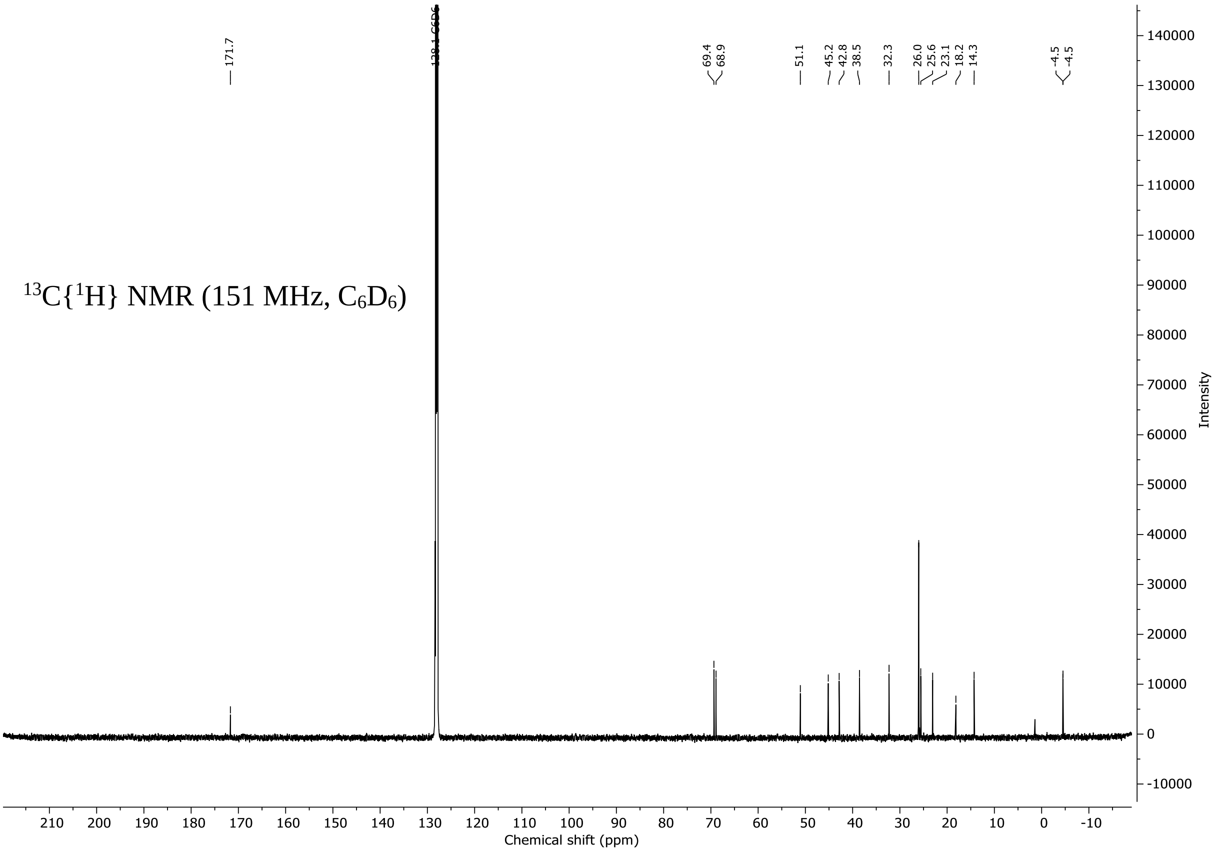


R = TBS

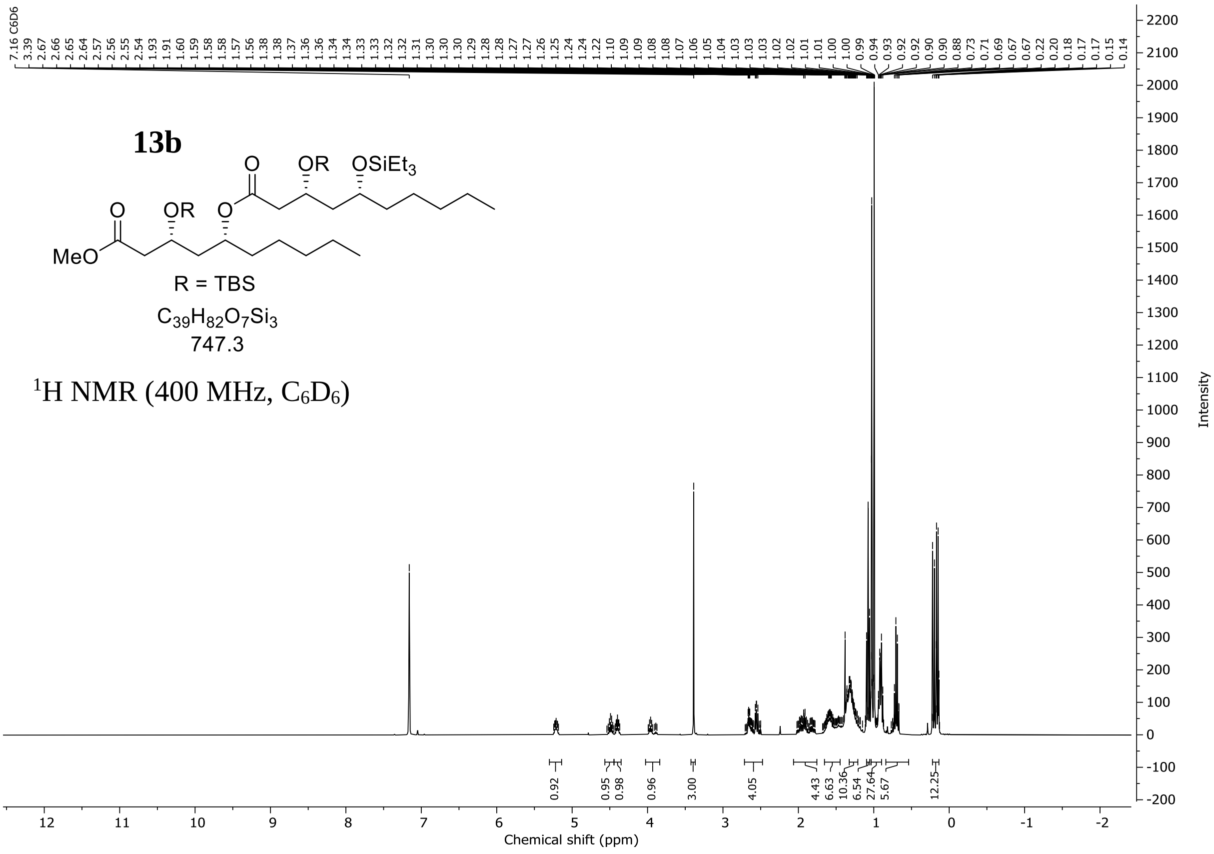
$C_{17}H_{36}O_4Si$

332.6

^1H NMR (600 MHz, C_6D_6)



$^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6)



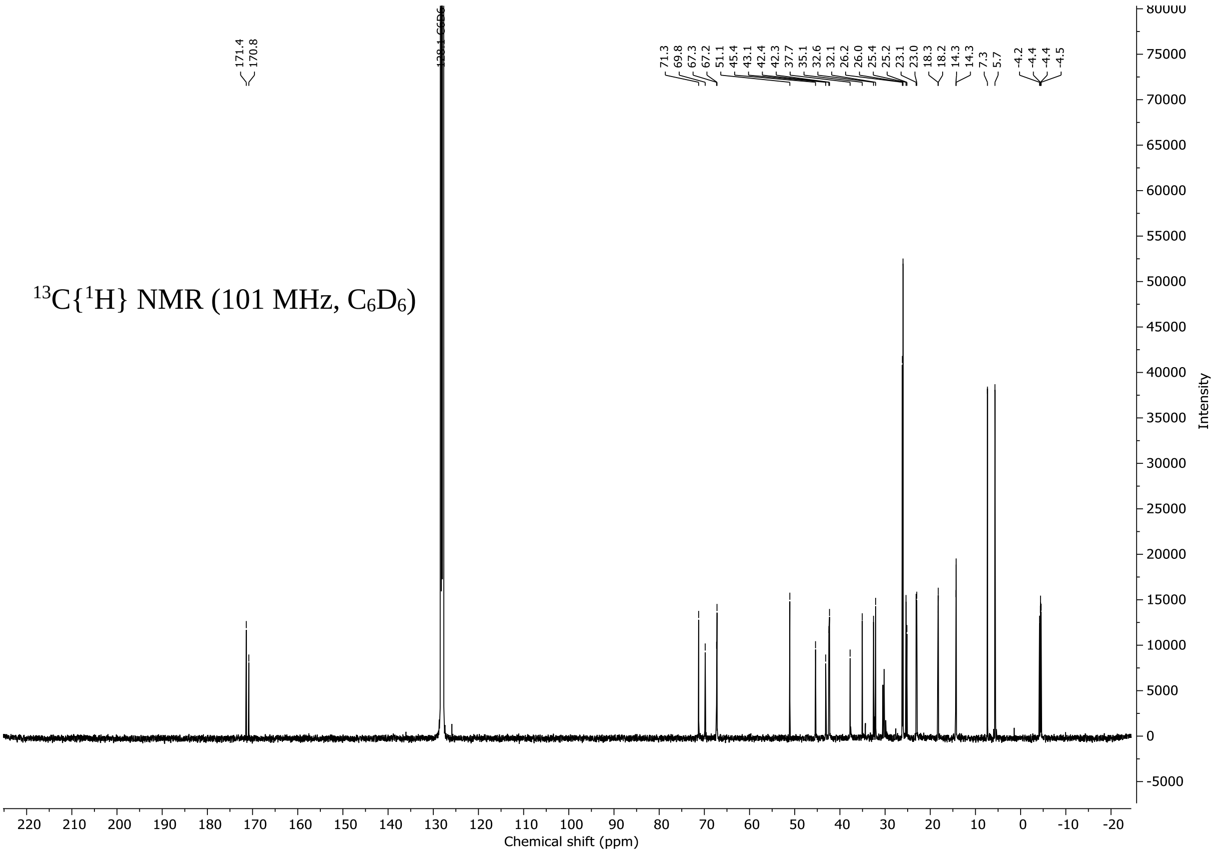
13b

R = TBS

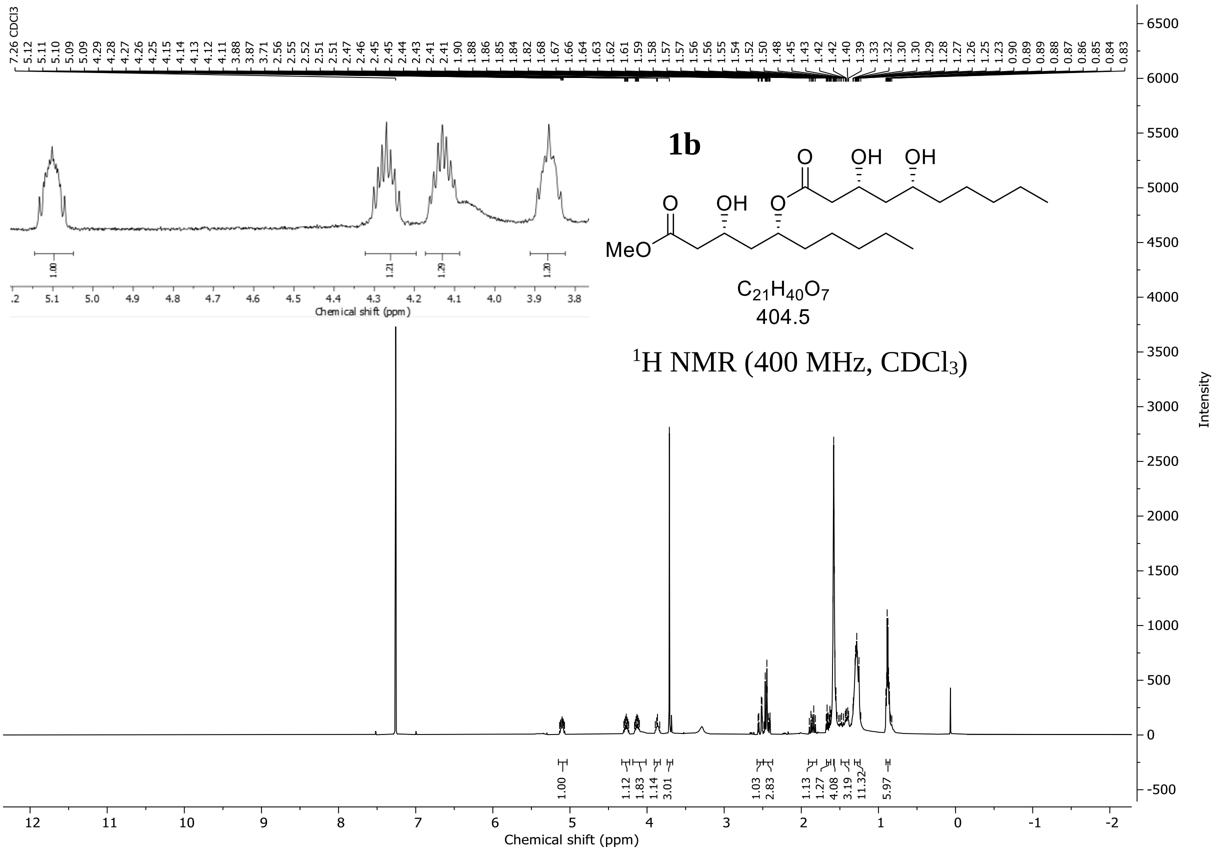
$C_{39}H_{82}O_7Si_3$

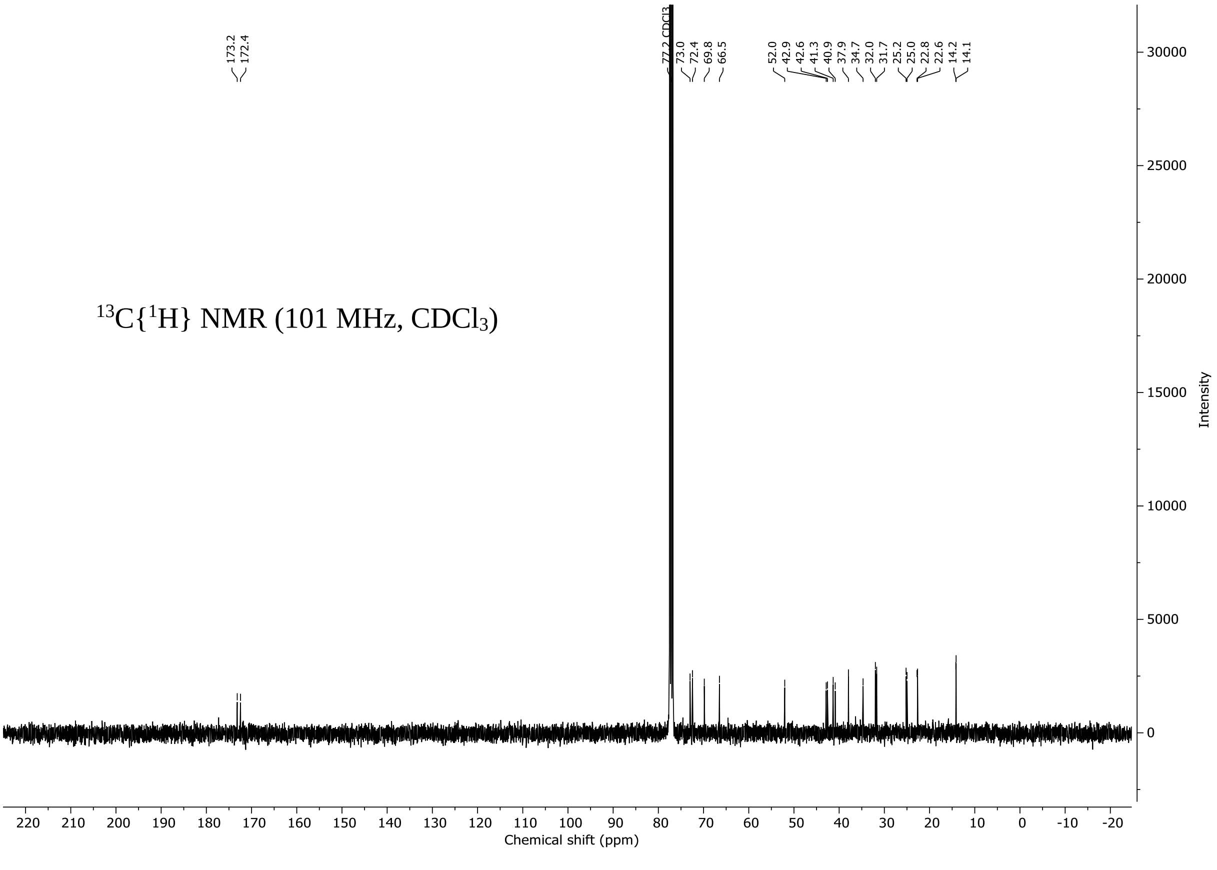
747.3

^{1}H NMR (400 MHz, C_6D_6)



^{13}C{^{1}H} NMR (101 MHz, C_6D_6)


7.26 CDCl3
5.12
5.11
5.10
5.09
4.29
4.28
4.27
4.26
4.25
4.15
4.14
4.13
4.12
4.11
3.88
3.87
3.71
2.56
2.55
2.52
2.51
2.51
2.47
2.46
2.45
2.45
2.44
2.43
2.41
2.41
1.90
1.88
1.86
1.85
1.84
1.82
1.68
1.67
1.66
1.64
1.63
1.62
1.61
1.59
1.58
1.57
1.57
1.56
1.56
1.55
1.54
1.52
1.50
1.48
1.45
1.43
1.42
1.42
1.40
1.39
1.33
1.32
1.30
1.30
1.29
1.28
1.27
1.26
1.25
1.23
0.90
0.89
0.89
0.88
0.87
0.86
0.85
0.84
0.83
1b
O
OH
OH
O
OH
O
MeO
C21H40O7
404.5
1H NMR (400 MHz, CDCl3)
1.00
1.21
1.29
1.20
Chemical shift (ppm)
1.00
1.12
1.83
1.14
3.01
1.03
2.83
1.13
1.27
4.08
3.19
11.32
5.97
Chemical shift (ppm)
Intensity


173.2
172.4
77.2 CDCl3
73.0
72.4
69.8
66.5
52.0
42.9
42.6
41.3
40.9
37.9
34.7
32.0
31.7
25.2
25.0
22.8
22.6
14.2
14.1
13C{1H} NMR (101 MHz, CDCl3)
Chemical shift (ppm)
Intensity

6. Literature

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