Electronic Supplementary Information (ESI)

Efficient synthesis of diverse hetero-bis-metallated alkenes as modular reagents towards highly conjugated and isolated olefinic systems

Mario Altendorfer[†] and Dirk Menche[‡,*]

[†] *Universität Heidelberg, Institut für Organische Chemie, INF 270, D-69120 Heidelberg, Germany and*
[‡] *Kekulé-Institut für Organische Chemie und Biochemie der Universität Bonn, Gerhard-Domagk-Str. 1, D-53121 Bonn, Germany.*

E-mail: *dirk.menche@uni-bonn.de*

Contents

General Remarks: All reactions were performed under an atmosphere of argon in flame-dried glassware which had been cooled under argon unless stated otherwise. All flasks were equipped with rubber septa and reactants were handled using standard Schlenk techniques. Temperatures above rt (23 °C) refer to oil bath temperatures which were controlled by a temperature modulator. For cooling, the following baths were used: ethanol/liquid nitrogen (-98 °C), acetone/dry ice (–78 °C), water/ice (0 °C). All reagents, anhydrous DMF and anhydrous 1,4-dioxane were purchased from commercial suppliers (Sigma-Aldrich, Alfa Aesar, Strem) in the highest grade available and used without further purification unless otherwise stated. Anhydrous solvents (THF, diethyl ether and dichloromethane) were freshly obtained from a solvent drying system MB SPS-800. Reactions were monitored via TLC on silica gel 60 F_{254} precoated plates (0.2 mm SiO_2, Machery-Nagel) and visualized using UV light and/or staining with a solution of CAM (1 g $Ce(SO_4)_2$, 2.5 g $(NH_4)_6Mo_7O_{24}$, 8 mL conc. H_2SO_4 in 100 mL H_2O) and subsequent heating. For column chromatography, silica gel (pore size 60 Å, 40-63 µm) obtained from Aldrich was

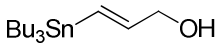
For column chromatography, silica gel (pore size 60 Å, 40-63 µm) obtained from Aldrich was used. Solvents were destilled prior to use. Optical Rotations were measured with a Perkin Elmer 241 polarimeter in a 10 mm cuvette and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-300, DRX-300, AVB-400, DRX-500 and Avance III 600 spectrometers with ^{13}C operating frequencies of 75, 100, 125 and 150 MHz, respectively. Data for ^{1}H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants in Hertz, number of hydrogens). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), br (broad). Mass spectra (MS) and High-resolution - mass spectra (HR-MS) were recorded at the Department of Organic Chemistry on the following mass spectrometers: Bruker ICR APEX-QE, Vacuum Generators ZAB-2F, Finnigan MAT TSQ 700 and JEOL JMS-700. Ionization processes and mol peaks were given.

I. Experimental Details and Characterization Data.

General procedure for hydrostannation of alkynes 4 and 8

Pd_2dba_3 (4.60 mg, 5.00 µmol, 0.5 mol%), tricyclohexylphosphonium tetrafluoroborate (7.40 mg, 20.0 µmol, 2.0 mol%) and diisopropylethylamine (5.20 mg, 40.0 µmol, 4 mol%) were added successively to dry dichloromethane (10 mL) and the resulting mixture was stirred at room temperature for 10 minutes. Alkyne (1.00 mmol, 1.0 eq.) was added and the reaction mixture was cooled to 0 °C. Bu_3SnH (1.20 mmol, 1.2 eq.) was diluted in dry dichloromethane (5 mL) and added dropwise via a syringe over 5 minutes. The reaction was then allowed to stir at 0 °C for 2 hours. The reaction mixture was concentrated under reduced pressure and purified by silica gel chromatography (petroleum ether/ethyl acetate, 9:1) to afford the corresponding vinylstannane.

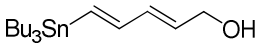
(*E*)-5-(tributylstannyl)prop-2-en-1-ol 5a



5a

The reaction was performed according to the general procedure as described above for Pd_2dba_3 (82.0 mg, 89.0 µmol, 0.5 mol%), tricyclohexylphosphonium tetrafluoroborate (131 mg, 365 µmol, 2.0 mol%), diisopropylethylamine (92.0 mg, 712 µmol, 4 mol%) in dichloromethane (100 mL), propargyl alcohol **4a** (1.00 g, 17.8 mmol, 1.0 eq.), Bu_3SnH (6.23 g, 21.4 mmol, 1.2 eq.) in dichloromethane (50 mL) to give stannane **5a** as a yellow oil (3.88 g, 11.2 mmol, 63%). R_f = 0.34 (*n*-hexane/ethyl acetate, 9:1); ^{1}H NMR (300.132 MHz, $CDCl_3$) δ = 0.90 (m, 15 H), 1.31 (dq, J = 14.5 Hz, J = 7.3 Hz, 6 H), 1.49 (m, 6 H), 4.18 (dd, J = 5.9 Hz, J = 3.2 Hz, 2 H), 6.18 (m, 2 H); ^{13}C NMR (75.48 MHz, $CDCl_3$) δ = 9.4, 13.7, 27.3, 29.1, 66.4, 128.3, 147.0; EI MS (70 eV, *m/z* (%)): 291 ($[M]^+$-C_4H_9, 100).

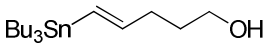
(2*E*,4*E*)-5-(tributylstannyl)penta-2,4-dien-1-ol 5b



5b

The reaction was performed according to the general procedure as described above for Pd_2dba_3 (5.60 mg, 6.10 µmol, 0.5 mol%), tricyclohexylphosphonium tetrafluoroborate (9.60 mg, 24.4 µmol, 2.0 mol%), diisopropylethylamine (6.36 mg, 48.8 µmol, 4.0 mol%) in dry dichloromethane (7 mL), Pent-2,4-diyn-1-ol **4b** (100 mg, 1.22 mmol, 1.0 eq.), Bu_3SnH (426 mg, 1.46 mmol, 1.2 eq.) in dry dichloromethane (4 mL) to give stannane **5b** as a yellow oil (273 mg, 732 mmol, 60%). R_f = 0.24 (*n*-hexane/ethyl acetate, 9:1); ^{1}H NMR (300.132 MHz, $CDCl_3$) δ = 0.90 (m, 15 H), 1.32 (dq, J = 14.8 Hz, J = 7.2 Hz, 6 H), 1.50 (m, 6 H), 4.21 (t, J = 5.4 Hz, 2 H), 5.80 (dt, J = 15.5 Hz, J = 5.8 Hz, 1 H), 6.26 (m, 2 H), 6.55 (dd, J = 18.9 Hz, J = 8.8 Hz, 1 H); ^{13}C NMR (75.48 MHz, $CDCl_3$) δ = 9.5, 13.7, 27.3, 29.1, 63.3, 130.7, 134.6, 135.1, 145.9; HR-MS (EI): *m/z* = 317.0930 ($C_{13}H_{25}OSn$ $[M\text{-}C_4H_9]^+$), calculated *m/z* = 317.0922.

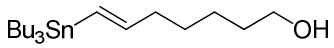
(*E*)-5-(tributylstannyl)pent-4-en-1-ol 9a



9a

The reaction was performed according to the general procedure as described above for Pd_2dba_3 (9.20 mg, 0.01 mmol, 0.5 mol%), tricyclohexylphosphonium tetrafluoroborate (14.8 mg, 0.04 mmol, 2.0 mol%), diisopropylethylamine (10.4 mg, 0.08 mmol, 4.0 mol%) in dichloromethane (10 mL), Pent-4-yn-1-ol **8a** (168 mg, 2.00 mmol, 1.0 eq.), Bu_3SnH (698 mg, 2.40 mmol, 1.2 eq.) in dry dichloromethane (6 mL) to give stannane **9a** as a colourless oil (675 mg, 1.80 mmol, 90%). R_f = 0.31 (*n*-hexane/ethyl acetate, 8:1); ^{1}H NMR (500.130 MHz, $CDCl_3$) δ = 0.88 (m, 15 H), 1.31 (dq, J = 14.8 Hz. J = 7.3 Hz, 6 H), 1.49 (m, 6 H) 1.69 (qiun, J = 7.0 Hz, 2 H), 2.23 (td, J = 7.3 Hz, J = 4.8 Hz, 2 H), 3.67 (m, 2 H), 5.96 (m, 2 H); ^{13}C NMR (125.78 MHz, $CDCl_3$) δ = 9.4, 13.7, 27.3, 29.1, 31.8, 34.1, 62.6, 128.2, 148.6 ; HR-MS (EI): found m/z = 319.1093 ($[M]^+$-C_4H_9), calculated m/z = 319.0645.

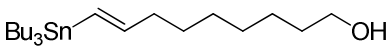
(*E*)-7-(tributylstannyl)hept-6-en-1-ol 9b



9b

The reaction was performed according to the general procedure as described above for Pd_2dba_3 (82.0 mg, 89.0 µmol, 0.5 mol%), tricyclohexylphosphonium tetrafluoroborate (131 mg, 365 µmol, 0.02 eq.), diisopropylethylamine (92.0 mg, 712 µmol, 0.04 eq.) in dry dichloromethane (100 mL), Hept-6-yn-1-ol **8b** (2.00 g, 17.8 mmol, 1.0 eq.), Bu_3SnH (6.23 g, 21.4 mmol, 1.2 eq.) in dry dichloromethane (50 mL) to give stannane **9b** as a colourless oil (5.24 g, 13.0 mmol, 73%). R_f = 0.26 (petroleum ether/ethyl acetate, 9:1); ^{1}H NMR (300.132 MHz, $CDCl_3$) δ = 0.89 (m, 15 H), 1.46 (m, 18 H), 2.17 (m, 2 H), 3.66 (m, 2 H), 5.94 (m, 2 H); ^{13}C NMR (75.48 MHz, $CDCl_3$) δ = 9.4, 13.7, 25.2, 27.2, 28.7, 29.1, 32.6, 37.8, 63.0, 127.3, 149.4; HR-MS (EI): m/z = 347.1400 ($C_{15}H_{31}OSn$ $[M-C_4H_9]^+$), calculated m/z = 347.1391.

(*E*)-9-(tributylstannyl)non-8-en-1-ol 9c



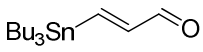
9c

The reaction was performed according to the general procedure as described above for Pd_2dba_3 (82.0 mg, 89.0 µmol, 0.5 mol%), tricyclohexylphosphonium tetrafluoroborate (131 mg, 365 µmol, 0.02 eq.), diisopropylethylamine (92.0 mg, 712 µmol, 0.04 eq.) in dry dichloromethane (100 mL), Non-8-yn-1-ol **8c** (2.50 g, 17.8 mmol, 1.0 eq.), Bu_3SnH (6.23 g, 21.4 mmol, 1.2 eq.) in dry dichloromethane (50 mL) to give stannane **9c** as a light yellow oil (5.81 g, 13.5 mmol, 76%). R_f = 0.28 (petroleum ether/ethyl acetate, 9:1); ^{1}H NMR (300.132 MHz, $CDCl_3$) δ = (m, 15 H), 1.43 (m, 22 H), 2.13 (m, 2 H), 3.64 (m, 2 H), 5.91 (m, 2 H); ^{13}C NMR (75.48 MHz, $CDCl_3$) δ = 9.4, 13.7, 25.7, 27.3, 28.8, 29.1, 29.1, 29.3, 32.8, 37.8, 63.1, 127.1, 149.7; HR-MS (EI): *m/z* = 375.1713 ($C_{17}H_{35}OSn$ $[M\text{-}C_4H_9]^+$), calculated *m/z* = 375.1704.

General procedure for the oxidation of allylic alcohols 5

Activated MnO_2 (1.48 g, 17.0 mmol, 17 eq) was suspended in dichloromethane (10 mL). Allylic alcohol (1.00 mmol, 1 eq) in dichloromethane (6 mL) was added at room temperature and the mixture was stirred for 2 h. The mixture was filtered through a short pad of celite with dichloromethane (30 mL) and ethyl acetate (50 mL). The solvent was evaporated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate; 12:1) to afford the corresponding aldehyde.

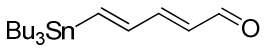
(*E*)-3-(tributylstannyl)acrylaldehyde 6a



6a

The reaction was performed according to the general procedure as described above for, MnO_2 (8.52 g, 97.9 mmol, 17 eq) in dichloromethane (55 mL), (*E*)-5-(tributylstannyl)prop-2-en-1-ol **5a** (2.00 g, 5.76 mmol, 1 eq) in dichloromethane (35 mL) to give the aldehyde **6a** (1.76 g, 5.07 mmol, 88%) as a yellow oil. R_f = 0.75 (*n*-hexane/ethyl acetate; 10:1); ^{1}H NMR (300.132 MHz, $CDCl_3$): δ = 0.90 (m, 10 H), 1.02 (m, 5 H), 1.32 (dq, *J* = 14.8 Hz, *J* = 7.2 Hz, 6 H), 1.53 (m, 6 H), 6.63 (dd, *J* = 19.2 Hz, *J* = 7.5 Hz, 1 H), 7.80 (d, *J* = 19.2 Hz, 1 H), 9.42 (d, *J* = 7.5 Hz, 1 H); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 10.2, 14.0, 27.6, 29.4, 148.0, 163.7, 194.1; HR-MS (EI^+): found *m/z* = 289.0623 ($C_{11}H_{21}OSn$ $[M\text{-}C_4H_9]^+$), calculated *m/z* = 289.0176.

(2*E*,4*E*)-5-(tributylstannyl)penta-2,4-dienal 6b



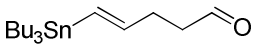
6b

The reaction was performed according to the general procedure as described above for MnO_2 (198 g, 2.28 mmol, 17 eq) in dichloromethane (1.5 mL), (2*E*,4*E*)-5-(tributylstannyl)penta-2,4-dien-1-ol **5b** (50.0 mg, 134 µmol, 1.0 eq) in dichloromethane (0.5 mL) to give the aldehyde **6b** (42.7 mg, 115 µmol, 86%) as a yellow oil. R_f = 0.43 (*n*-pentane/diethyl ether, 100:5); ^{1}H NMR (300.132 MHz, $CDCl_3$) δ = 0.94 (m, 15 H), 1.33 (dq, J = 14.6 Hz, J = 7.2 Hz, 6 H), 1.54 (m, 6 H), 6.07 (dd, J = 15.1 Hz, J = 8.0 Hz, 1 H), 6.80 (m, 1 H), 7.02 (m, 2 H), 9.58 (d, J = 8.0 Hz, 1 H); ^{13}C NMR (75.48 MHz, $CDCl_3$) δ = 9.7, 13.7, 27.2, 29.0, 130.1, 144.2, 151.4, 153.5, 194.4; HR-MS (EI): found m/z = 315.0773 ($C_{13}H_{23}OSn$ $[M\text{-}C_4H_9]^+$), calculated m/z = 317.0765.

General procedure for the oxidation of alcohols 9

To a solution of alcohol (1.00 mmol, 1.0 eq.) in dichloromethane (25 mL) was added a spatula load of dried 4 Å powdered molecular sieves, followed by NMO (351 mg, 3.00 mmol, 3.0 eq.) and TPAP (35.1 mg, 0.10 µmol, 0.1 eq.). The reaction mixture was stirred at 0 °C for 30 min then directly purified by flash chromatography (SiO_2, petroleum ether/ ethyl acetate, 20:1), yielding the corresponding aldehyde.

(*E*)-5-(tributylstannyl)pent-4-enal 10a

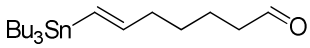


10a

The reaction was performed according to the general procedure as described above for (*E*)-5-(tributylstannyl)pent-4-enol **9a** (50.0 mg, 133 µmol, 1.0 eq.) in dichloromethane (3 mL), NMO (40.8 mg, 400 µmol, 3.0 eq.) and TPAP (4.60 mg, 13.3 µmol, 0.1 eq.) yielding the desired aldehyde **10a** (39.8 mg, 107 µmol, 80%) as a colourless oil. R_f = 0.73 (petroleum ether/ethyl acetate, 10:1); ^{1}H NMR (300.132 MHz, $CDCl_3$) δ = 0.88 (m, 15 H), 1.30 (m, 6 H), 1.49 (m, 6 H), 2.51 (m, 4 H), 5.97 (m, 2 H), 9.78 (t, J = 1.6 Hz, 1 H); ^{13}C NMR (75.48 MHz,

$CDCl_3$) δ = 9.4, 13.7, 27.2, 29.1, 29.9, 42.7, 129.2, 146.3, 202.3; HR-MS (EI): found *m/z* = 317.0947 ($C_{13}H_{25}OSn$ $[M-C_4H_9]^+$), calculated *m/z* = 317.0489.

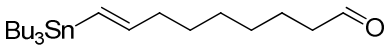
(*E*)-7-(tributylstannyl)hept-6-enal 10b



10b

The reaction was performed according to the general procedure as described above for (*E*)-7-(tributylstannyl)hept-6-en-1-ol **9b** (50.0 mg, 124 µmol, 1.0 eq.) in dichloromethane (3 mL), NMO (43.6 mg, 371 µmol, 3.0 eq.) and TPAP (4.40 mg, 12.4 µmol, 0.1 eq.) yielding the desired aldehyde **10b** (40.3 mg, 100 µmol, 81%) as a colourless liquid. R_f = 0.60 (*n*-hexane/ethyl acetate, 9:1); ^{1}H NMR (300.132 MHz, $CDCl_3$) δ = 0.88 (m, 15 H), 1.31 (dq, *J* = 14.6 Hz, *J* = 7.2 Hz, 6 H), 1.57 (m, 8 H), 2.17 (td, *J* = 7.4 Hz, *J* = 4.4 Hz, 2 H), 2.44 (td, *J* = 7.3 Hz, *J* = 1.8 Hz, 2 H), 5.86 (m, 2 H), 9.77 (t, *J* = 1.9 Hz, 1 H); ^{13}C NMR (75.48 MHz, $CDCl_3$) δ = 9.4, 13.7, 21.6, 27.3, 28.3, 29.1, 37.4, 43.8, 128.0, 148.7, 202.7; HR-MS (ESI): *m/z* = 425.1841 ($C_{19}H_{38}OSnNa$), calculated *m/z* = 425.1840.

(*E*)-9-(tributylstannyl)non-8-enal 10c



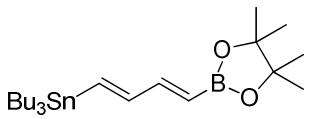
10c

The reaction was performed according to the general procedure as described above for (*E*)-7-(tributylstannyl)non-8-en-1-ol **9c** (50.0 mg, 116 µmol, 1.0 eq.) in dichloromethane (3 mL), NMO (40.8 mg, 348 µmol, 3.0 eq.) and TPAP (4.10 mg, 11.6 µmol, 0.1 eq.) yielding the desired aldehyde **10c** (40.7 mg, 94.8 mmol, 82%) as a colourless liquid. R_f = 0.60 (*n*-hexane/ethyl acetate, 9:1); ^{1}H NMR (300.132 MHz, $CDCl_3$) δ = 0.88 (m, 15 H), 1.47 (m, 20 H), 2.13 (m, 2 H), 2.42 (td, *J* = 7.3 Hz, *J* = 1.8 Hz, 2 H), 5.89 (m, 2 H), 9.77 (t, *J* = 1.8 Hz, 1 H); ^{13}C NMR (75.48 MHz, $CDCl_3$) δ = 9.4, 13.7, 22.0, 27.3, 28.6, 28.8, 29.0, 29.1, 37.7, 43.9, 127.3, 149.5, 202.8; HR-MS (ESI): *m/z* = 453.2153 ($C_{21}H_{42}OSnNa$), calculated *m/z* = 453.2153.

General procedure for the Boryl-Takai olefination of aldehydes 6 and 10

The following process was conducted in the dark. A solution of aldehyde (1.00 mmol, 1.0 eq) and dioxaborolane **7** (422 mg, 2.00 mmol, 2.0 eq) in THF (8.5 mL) was added via syringe to a mixture of anhydrous chromium(II) chloride (983 mg, 8.00 mmol, 8 eq) in THF (8.5 mL). A solution of lithium iodide (535 mg, 4.00 mmol, 4.0 eq) in THF (8.5 mL) was added via syringe and the reaction mixture was stirred at 25 °C for 12 h. The reaction was quenched by the addition of water. The organic layer was separated and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic extracts were washed with brine (2 x 20 mL), dried with Na_2SO_4, filtered and concentrated under reduced pressure. The residue was passed through a pad of celite and the filter cake was washed thoroughly with Et_2O. After concentration of the residue the crude product was purified by chromatography (SiO_2, petroleum ether/diethyl ether, 100:1) to afford the corresponding pinacolborane.

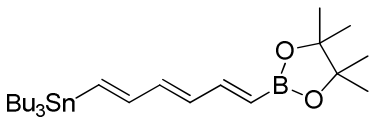
Tributyl((1*E*,3*E*)-4-(4,4,5,5-tetramethyl-1,3,2 dioxaborolan 2 yl)buta-1,3-dienyl)-stannane 2a



2a

The reaction was performed according to the general procedure as described above for (*E*)-3-(tributylstannyl) acrylaldehyde **6a** (200 mg, 0.58 mmol, 1.0 eq) and 2-(dichloromethyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **7** (244 mg, 1.16 mmol, 2.0 eq) in THF (5 mL), anhydrous chromium(II) chloride (548 mg, 4.46 mmol, 8 eq) in THF (5 mL), lithium iodide (298 mg, 2.23 mmol, 4.0 eq) in THF (5 mL) to afford the conjugated diene **2a** (260 mg, 550 mmol, 75%) as a green-clear liquid. R_f = 0.48 (*n*-hexane/ethyl acetate, 100:5); ^{1}H NMR (300.132 MHz, $CDCl_3$): δ = 0.91 (m, 15 H), 1.30 (m, 18 H), 1.50 (m, 6 H), 5.48 (d, J = 17.5 Hz, 1 H), 6.52 (m, 2 H), 6.97 (dd, J = 17.6 Hz, J = 9.0 Hz, 1 H); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 9.1, 13.3, 24.3, 24.5, 26.8, 28.6, 82.7, 140.0, 148.1, 151.8; HR-MS (EI): found m/z = 413.1687 $C_{18}H_{44}BO_2Sn$ ([M-C_4H_9]$^+$), calculated m/z = 413.1235.

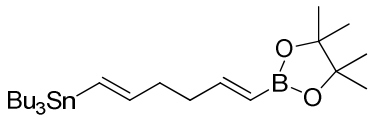
Tributyl((1*E*,3*E*,5*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,3,5-trien-1-yl)stannane 2b



2b

The reaction was performed according to the general procedure as described above for (2*E*,4*E*)-5-(tributylstannyl)penta-2,4-dienal **6b** (531 mg, 1.43 mmol, 1.0 eq) and 2-(dichloromethyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **7** (603 mg, 2.86 mmol, 2.0 eq) in THF (11 mL), anhydrous chromium chloride (1.41 g, 11.4 mmol, 8.0 eq) in THF (11 mL), lithium iodide (766 mg, 5.72 mmol, 4.0 eq) in THF (11 mL) to afford triene **2b** (526 mg, 1.06 mmol, 74%) as an orange oil. R_f = 0.57 (*n*-hexane/diethyl ether, 100:1); ^{1}H NMR (300.132 MHz, $CDCl_3$): δ = 0.92 (m, 15 H), 1.43 (m, 24 H), 5.58 (d, J = 17.6 Hz, 1 H), 6.31 (m, 3 H), 6.60 (m, 1 H), 7.04 (dd, J = 17.6 Hz, J = 9.9 Hz, 1 H); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 9.6, 13.7, 24.8, 26.6, 27.3, 29.1, 83.2, 133.1, 138.6, 138.9, 146.5, 149.8; HR-MS (EI): found *m/z* = 439.1838 $C_{20}H_{46}BO_2Sn$ ($[M-C_4H_9]^+$), calculated *m/z* = 439.1825.

Tributyl((1*E*,5*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,5-dienyl)stannane 3a

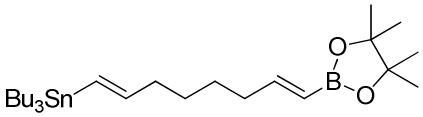


3a

The reaction was performed according to the general procedure as described above for (*E*)-5-(tributylstannyl)pent-4-enal **10a** (715 mg, 1.92 mmol, 1.0 eq) and 2-(dichloromethyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **7** (810 mg, 3.84 mmol, 2.0 eq) in THF (12 mL), anhydrous chromium(II) chloride (1.89 g, 15.4 mmol, 8.0 eq) in THF (12 mL), lithium iodide (1.03 g, 7.68 mmol, 4.0 eq) in THF (12 mL) to afford diene **3a** (740 mg, 1.49 µmol, 76%) as a colourless oil. R_f = 0.38 (*n*-hexane/diethyl ether, 100:5); ^{1}H NMR (300.132 MHz, $CDCl_3$): δ = 0.87 (m, 15 H), 1.30 (m, 18 H), 1.50 (m, 6 H), 2.26 (m, 4 H),

5.45 (d, J = 17.9 Hz, 1 H), 5.94 (m, J = 5.5 Hz, J = 18.8 Hz, 2 H), 6.65 (d, J = 17.9 Hz, 1 H); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 9.0, 13.3, 24.3, 26.8, 28.7, 34.8, 35.8, 82.6, 127.3, 148.0, 153.5. HR-MS (ESI): found m/z = 521.2578 ($C_{24}H_{47}BO_2SnNa$), calculated m/z = 521.2589.

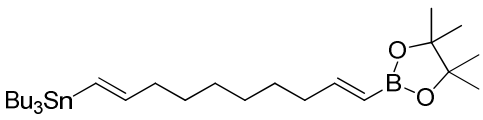
Tributyl((1*E*,7*E*)-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octa-1,7-dien-1-yl)stannane 3b



3b

The reaction was performed according to the general procedure as described above for (*E*)-7-(tributylstannyl)hept-6-enal **10b** (317 mg, 790 µmol, 1.0 eq) and 2-(dichloromethyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **7** (333 mg, 1.58 mmol, 2.0 eq) in THF (6 mL), anhydrous chromium chloride (777 mg, 6.43 mmol, 8.0 eq) in THF (6 mL), lithium iodide (432 mg, 3.16 mmol, 4.0 eq) in THF (6 mL) to afford diene **3b** (404 mg, 769 µmol, 97%) as a colourless liquid. R_f = 0.66 (petroleum ether/ethyl acetate, 100:5); ^{1}H NMR (300.132 MHz, $CDCl_3$): δ = 0.86 (m, 15 H), 1.43 (m, 28 H), 2.13 (m, 4 H), 4.96 (m, 1 H), 5.43 (dt, J = 17.8 Hz, J = 1.5 Hz, 1 H), 5.83 (m, 1 H), 6.63 (dt, J = 18.0 Hz, J = 6.5 Hz, 1 H); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 9.4, 13.7, 24.4, 24.8, 27.3, 28.4, 29.0, 29.1, 33.6, 35.6, 37.7, 83.0, 114.3, 127.2, 138.9, 149.4, 154.5; HR-MS (ESI): m/z = 565.2641 ($C_{26}H_{51}BO_2SnK$), calculated m/z = 565.2643.

Tributyl((1*E*,9*E*)-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)deca-1,9-dien-1-yl)stannane 3c



3c

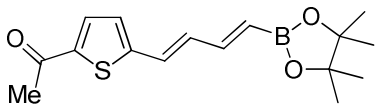
The reaction was performed according to the general procedure as described above for (*E*)-9-(tributylstannyl)non-8-enal **10c** (35.0 mg, 81.5 µmol, 1.0 eq) and 2-(dichloromethyl-4,4,5,5-

tetramethyl-1,3,2-dioxaborolane **7** (34.4 mg, 163 mmol, 2.0 eq) in THF (1 mL), anhydrous chromium(II) chloride (80.1 mg, 652 µmol, 8.0 eq) in THF (1 mL), lithium iodide (43.6 mg, 326 µmol, 4.0 eq) in THF (1 mL) to afford diene **3c** as a colourless oil (40.1 mg, 72.5 µmol, 89%). R_f = 0.64 (petroleum ether/ethyl acetate, 10:1); ^{1}H NMR (300.132 MHz, $CDCl_3$ δ = 0.85 (m, 15 H), 1.38 (m, 32 H), 2.14 (m, 4 H), 5.43 (d, *J*=17.9 Hz, 1 H), 5.90 (m, 2 H), 6.64 (dt, *J*=17.9, 6.4 Hz, 1 H); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 9.4, 13.7, 24.8, 27.3, 27.5, 28.2, 28.8, 28.9, 29.1, 29.1, 35.8, 37.9, 83.0, 114.1, 127.0, 149.8, 154.8; HR-MS (ESI): *m/z* = 425.1841 ($C_{28}H_{55}BO_2SnK$), calculated *m/z* = 425.1840.

General procedure for the Stille coupling reactions of vinylstannanes 2 and 3

The following process was executed in the dark and conducted in an amber glass septum vial. $PdCl_2(CH_3CN)_2$ (2.60 mg, 10.0 µmol, 5 mol%) was added to a solution of 2-Acetyl-5-iodothiophene **11** (25.2 mg, 100 µmol, 1.0 eq.) and the stannane **2** or **3** (200 µmol, 2.0 eq.) in degassed, anhydrous DMF (400 µL). After stirring for 1-2 h the reaction mixture was diluted with diethyl ether (3 mL) and washed with a concentrated aqueous solution of NH_4Cl (4 mL). The organic phase was separated and the aqueous phase was extracted with diethyl ether (3 x 5 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by column chromatography (SiO_2, petroleum ether/ethyl acetate, 10:1) afforded the product **12** or **14**.

1-(5-((1*E*,3*E*)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,3-dien-1-yl)thiophen-2-yl)ethanone 12a

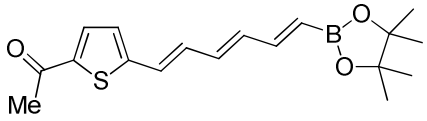


12a

The reaction was performed according to the general procedure as described above for $PdCl_2(CH_3CN)_2$ (2.80 mg, 10.7 µmol, 5 mol%), 2-Acetyl-5-iodothiophene **11** (36.0 mg, 142 µmol, 1.0 eq.) and stannane **2a** (100 mg, 213 µmol, 1.5 eq.) in degassed, anhydrous DMF (400 µL) to afford the product **12a** (42.3 mg, 139 µmol, 98%) as a yellow oil with little impurities of Bu_3SnI. R_f = 0.16 (petroleum ether/ethyl acetate, 10:1); ^{1}H NMR (300.132 MHz,

$CDCl_3$) δ = 1.29 (s, 12 H), 2.53 (s, 3 H), 5.75 (d, J = 17.6 Hz, 1 H), 6.77 (m, 2 H), 7.03 (d, J = 3.8 Hz, 1 H), 7.09 (s, 1 H), 7.56 (d, J = 3.8 Hz, 1 H); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 24.8, 26.6, 83.4, 127.3, 133.0, 133.6, 143.0, 148.1, 150.0, 190.3; HR-MS (ESI): m/z = 327.1196 ($C_{16}H_{21}B0_3SNa$), calculated m/z = 327.1197.

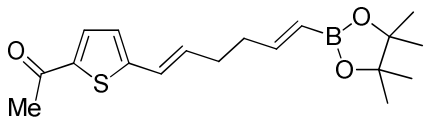
1-(5-((1*E*,3*E*,5*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,3,5-trien-1-yl)thiophen-2-yl)ethanone 12b



12b

The reaction was performed according to the general procedure as described above for $PdCl_2(CH_3CN)_2$ (875 µg, 3.37 µmol, 5 mol%), 2-Acetyl-5-iodothiophene **11** (17.0 mg, 67.3 µmol, 1.0 eq.) and stannane **2b** (50.0 mg, 101 µmol, 1.5 eq.) in degassed, anhydrous DMF (300 µL). to afford the triene **12b** (19.2 mg, 58.1 µmol, 86%) as a dark red solid with little impurities of Bu_3SnI. R_f = 0.16 (petroleum ether/ethyl acetate, 10:1); ^{1}H NMR (300.132 MHz, $CDCl_3$) δ = 1.29 (s, 12 H), 2.53 (s, 3 H), 5.67 (d, J = 17.6 Hz, 1 H), 6.47 (m, 1 H), 6.70 (m, 1 H), 6.81 (m, 1 H), 7.00 (d, J = 3.9 Hz, 1 H), 7.07 (m, 1 H), 7.55 (d, J = 4.0 Hz, 1 H); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 24.8, 26.6, 26.9, 83.4, 126.3, 126.7, 131.9, 133.2, 135.0, 136.9, 142.6, 148.9, 150.6, 190.3; HR-MS (ESI): m/z = 305.1377 ($C_{16}H_{22}B0_3S$), calculated m/z = 305.1380.

1-(5-((1*E*,5*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,5-dien-1-yl)thiophen-2-yl)ethanone 14a

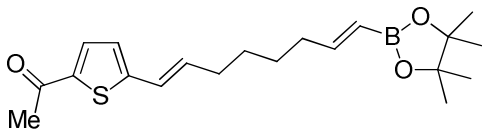


14a

The reaction was performed according to the general procedure as described above for $PdCl_2(CH_3CN)_2$ (521 µg, 2.01 µmol, 5 mol%), 2-Acetyl-5-iodothiophene **11** (10.1 mg,

40.2 µmol, 1.0 eq.) and stannane **3a** (30.0 mg, 60.3 µmol, 1.5 eq.) in degassed, anhydrous DMF (200 µL) to afford the diene **14a** (12.6 mg, 37.8 µmol, 94%) as a yellow oil. R_f = 0.19 (petroleum ether/ethyl acetate, 10:1); ^{1}H NMR (300.132 MHz, $CDCl_3$): δ = 1.27 (s, 12 H), 2.34 (m, 4 H), 2.51 (s, 3 H), 5.49 (d, J = 18.1 Hz, 1 H), 6.28 (d, J = 15.6 Hz, 1 H), 6.50 (m, 1 H), 6.64 (d, J = 17.8 Hz, 1 H), 6.88 (d, J = 3.8 Hz, 1 H), 7.53 (d, J = 3.8 Hz, 1 H); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 24.8, 26.5, 31.5, 34.8, 83.1, 123.2, 125.1, 133.0, 134.2, 141.5, 151.2, 152.6, 190.3; HR-MS (ESI): m/z = 333.1691 ($C_{18}H_{26}B0_3S$), calculated m/z = 333.1693.

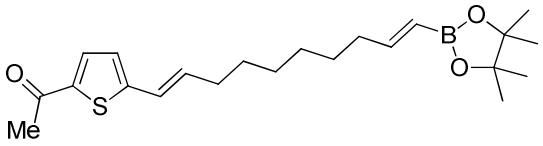
1-(5-((1*E*,7*E*)-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octa-1,7-dien-1-yl)thiophen-2-yl)ethanone 14b



14b

The reaction was performed according to the general procedure as described above for $PdCl_2(CH_3CN)_2$ (824 µg, 3.16 µmol, 5 mol%), 2-Acetyl-5-iodothiophene **11** (16.0 mg, 63.5 µmol, 1.0 eq.) and stannane **3b** (50 mg, 95.2 µmol, 1.5 eq.) in degassed, anhydrous DMF (500 µL) to afford the diene **14b** (16.4 mg, 45.5 µmol, 72%) as an orange oil with little impurities of Bu_3SnI. R_f = 0.19 (petroleum ether/ethyl acetate, 10:1); ^{1}H NMR (600.130 MHz. $CDCl_3$): δ = 1.27 (s, 12 H), 1.49 (m, 4 H), 2.20 (m, 4 H), 2.52 (s, 3 H), 5.45 (d, J = 17.9 Hz, 1 H), 6.27 (dt, J = 15.7 Hz, J = 7.0 Hz, 1 H), 6.48 (d, J = 15.6 Hz, 1 H), 6.63 (dt, J = 17.9 Hz, J = 6.4 Hz, 1 H), 6.88 (d, J = 3.8 Hz, 1 H), 7.54 (d, J = 3.9 Hz, 1 H); ^{13}C NMR (150.90 MHz, $CDCl_3$): δ = 13.6, 17.5, 24.8, 26.5, 26.8, 27.7, 27.8, 28.3, 29.7, 32.8, 35.5, 83.0, 122.9, 124.9, 133.1, 135.2, 141.3, 151.5, 154.2, 190.4; HR-MS (ESI): m/z = 361.2004 ($C_{20}H_{30}B0_3S$), calculated m/z = 361.2007.

1-(5-((1*E*,9*E*)-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)deca-1,9-dien-1-yl)thiophen-2-yl)ethanone 14c



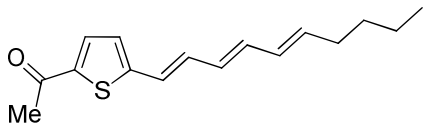
14c

The reaction was performed according to the general procedure as described above for $PdCl_2(CH_3CN)_2$ (825 mg, 3.18 µmol, 5 mol%), 2-Acetyl-5-iodothiophene **11** (16.0 mg, 63.5 µmol, 1.0 eq.) and stannane **3c** (53.0 mg, 95.2 µmol, 1.5 eq.) in degassed, anhydrous DMF (250 µL) to afford the diene **14c** (20.1 mg, 51.8 µmol, 82%) as an orange oil with little impurities of Bu_3SnI. R_f = 0.21 (petroleum ether/ethyl acetate, 10:1); ^{1}H NMR (300.132 MHz, $CDCl_3$): δ = 1.27 (s, 12 H), 1.54 (m, 8 H), 2.18 (dq, J = 13.0 Hz, J = 6.6 Hz, 4 H), 2.52 (s, 3 H), 5.43 (d, J = 18.0 Hz, 1 H), 6.28 (dt, J = 15.7 Hz, J = 6.9 Hz, 1 H), 6.48 (d, J = 15.8 Hz, 1 H), 6.63 (dt, J = 17.9 Hz, J = 6.4 Hz, 1 H), 6.88 (d, J = 3.9 Hz, 1 H), 7.53 (d, J = 3.9 Hz, 1 H); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 13.6, 17.5, 24.8, 26.5, 26.8, 27.8, 28.1, 28.8, 29.0, 29.0, 32.9, 35.7, 83.0, 122.8, 124.9, 133.1, 135.6 (2 C), 141.3, 151.6, 154.6, 190.4; HR-MS (ESI): m/z = 389.2318 ($C_{22}H_{34}B0_3S$), calculated m/z = 389.2320.

General procedure for the Suzuki-Miyaura coupling reactions of pinacolboranes 12 and 14

The reaction was conducted in an amber glass septum vial in absence of light. (*E*)-1-iodohex-1-ene **16** (21.0 mg, 100 µmol, 1.0 eq.) and the pinacol borane (29.5 mg, 140 µmol, 1.4 eq.) were diluted in anhydrous DMF (600 µL). $Pd(dppf)Cl_2$ (11.0 mg, 15.0 µmol, 15 mol%) and $Ba(OH)_2{\cdot}8H_2O$ (94.6 mg, 300 µmol, 3.0 eq.) were added to the vigorous stirring solution sequently. After stirring over night the reaction mixture was quenched with diethyl ether (3 mL) and pH 7 buffer solution (6 mL) and extracted with diethyl ether (3 x 8 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. After purification by column chromatography (SiO_2, petroleum ether/ethyl acetate, 10:1) the corresponding polyene was yielded.

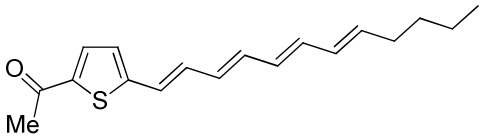
1-(5-((1*E*,3*E*,5*E*)-deca-1,3,5-trien-1-yl)thiophen-2-yl)ethanone 13a



13a

The reaction was performed according to the general procedure as described above for (*E*)-1-iodohex-1-ene **16** (8.80 mg, 41.8 µmol, 1.0 eq.), pinacol borane **12a** (17.8 mg, 58.5 µmol, 1.4 eq.), anhydrous DMF (250 µL), $Pd(dppf)Cl_2$ (4.60 mg, 6.27 µmol, 15 mol%) and $Ba(OH)_2{\cdot}8H_2O$ (39.6 mg, 125 µmol, 3.0 eq.) to obtain triene **13a** (9.80 mg, 37.6 µmol, 90%) as a yellow oil. R_f = 0.33 (petroleum ether/ethyl acetate, 10:1); ^{1}H NMR (300.132 MHz, $CDCl_3$): δ = 0.91 (m, 3 H), 1.38 (m, 4 H), 2.15 (q, *J* = 7.0 Hz, 2 H), 2.53 (s, 3 H), 5.85 (dt, *J* = 14.8 Hz, *J* = 7.2 Hz, 1 H), 6.18 (m, 2 H), 6.40 (dd, *J* = 14.9 Hz, *J* = 10.6 Hz, 1 H), 6.59 (d, *J* = 15.3 Hz, 1 H), 6.79 (dd, *J* = 15.3 Hz, *J* = 10.5 Hz, 1 H), 6.94 (d, *J* = 4.0 Hz, 1 H), 7.54 (d, *J* = 4.0 Hz, 1 H); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 13.9, 22.2, 26.5, 31.3, 32.6, 123.4, 125.8, 129.4, 130.2, 132.9, 133.2, 136.4, 138.1, 141.8, 151.5, 190.2; HR-MS (FAB): *m*/*z* = 261.1345 ($C_{16}H_{21}0S$), calculated *m*/*z* = 261.1308.

1-(5-((1*E*,3*E*,5*E*,7-E)-dodeca-1,3,5,7-tetraen-1-yl)thiophen-2-yl)ethanone 13b

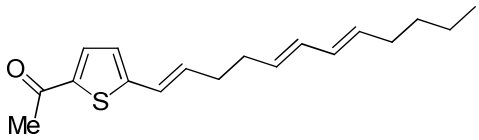


13b

The reaction was performed according to the general procedure as described above for (*E*)-1-iodohex-1-ene **16** (6.09 mg, 29.0 µmol, 1.0 eq.), pinacol borane **12b** (13.4 mg, 40.6 µmol, 1.4 eq.), anhydrous DMF (200 µL), $Pd(dppf)Cl_2$ (3.55 mg, 4.35 µmol, 15 mol%) and $Ba(OH)_2{\cdot}8H_2O$ (27.4 mg, 87.0 µmol, 3.0 eq.) to obtain tetraene **13b** (6.50 mg, 22.7 µmol, 78%) as a dark orange oil. R_f = 0.31 (petroleum ether/ethyl acetate, 10:1); ^{1}H NMR (600.130 MHz. $CDCl_3$): δ = 0.91 (m, 3 H), 1.35 (m, 4 H), 2.14 (q, *J* = 7.1 Hz, 2 H), 2.53 (s, 3 H), 5.81 (dt, *J* = 14.9 Hz, *J* = 7.3 Hz, 1 H), 6.12 (dd, *J* = 14.9 Hz, *J* = 10.8 Hz, 1 H), 6.21 (dd, *J* = 14.7 Hz, *J* = 10.9 Hz, 1 H), 6.31 (dt, *J* = 14.8 Hz, *J* = 10.2 Hz, 2 H), 6.44 (dd, *J* = 14.6 Hz,

J = 11.0 Hz, 1 H), 6.61 (d, *J* = 15.2 Hz, 1 H), 6.81 (dd, *J* = 15.3 Hz, *J* = 10.8 Hz, 1 H), 6.95 (d, *J* = 3.9 Hz, 1 H), 7.55 (d, *J* = 3.9 Hz, 1 H); ^{13}C NMR (150.90 MHz, $CDCl_3$): δ = 13.9, 22.2, 26.50, 31.3, 32.7, 123.7, 126.0, 130.2, 130.4, 130.9, 132.8, 133.3, 135.4, 136.2, 137.4, 141.8, 151.4, 190.3; HR-MS (FAB): *m*/*z* = 286.1389 ($C_{18}H_{22}0S$), calculated *m*/*z* = 286.1391.

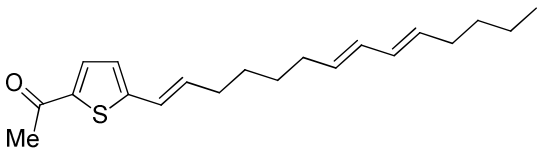
1-(5-((1*E*,5*E*,7*E*)-dodeca-1,5,7-trien-1-yl)thiophen-2-yl)ethanone 15a



15a

The reaction was performed according to the general procedure as described above for (*E*)-1-iodohex-1-ene **16** (5.67 mg, 27.0 µmol, 1.0 eq.), pinacol borane **14a** (12.6 mg, 37.8 µmol, 1.4 eq.), anhydrous DMF (300 µL), $Pd(dppf)Cl_2$ (3.31 mg, 4.05 µmol, 15 mol%) and $Ba(OH)_2{\cdot}8H_2O$ (25.6 mg, 81.0 µmol, 3.0 eq.) to obtain polyene **15a** (7.10 mg, 24.6 µmol, 91%) a light yellow oil. R_f = 0.34 (petroleum ether/ethyl acetate, 10:1); ^{1}H NMR (399.892 MHz, $CDCl_3$): δ = (m, 3 H), 1.34 (m, 4 H), 2.07 (q, *J* = 7.0 Hz, 2 H), 2.28 (m, 4 H), 5.59 (tt, *J* = 13.9 Hz, *J* = 6.7 Hz, 2 H), 6.03 (m, 2 H), 6.29 (dt, *J* = 15.6 Hz, *J* = 6.6 Hz, 1 H), 6.50 (d, *J* = 15.7 Hz, 1 H), 6.89 (d, *J* = 3.8 Hz, 1 H), 7.54 (d, *J* = 3.8 Hz, 1 H); ^{13}C NMR (100.56 MHz, $CDCl_3$): δ = 13.9, 22.2, 26.5, 31.5, 31.9, 32.3, 32.9, 125.1, 130.0, 130.3, 131.3, 133.1, 133.3, 134.5 (2 C), 141.5, 151.3, 190.4; HR-MS (FAB): *m*/*z* = 289.1622 ($C_{18}H_{25}0S$), calculated *m*/*z* = 289.1621.

1-(5-((1*E*,7*E*,9*E*)-tetradeca-1,7,9-trien-1-yl)thiophen-2-yl)ethanone 15b

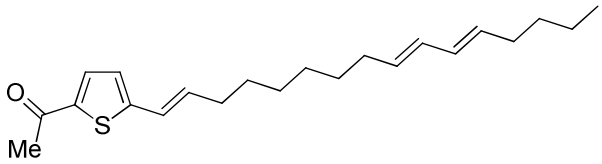


15b

The reaction was performed according to the general procedure as described above for (*E*)-1-iodohex-1-ene **16** (3.70 mg, 17.6 µmol, 1.0 eq.), pinacol borane **14b** (8.90 mg,

24.7 µmol, 1.4 eq.), anhydrous DMF (100 µL), $Pd(dppf)Cl_2$ (1.94 mg, 2.65 µmol, 15 mol%) and $Ba(OH)_2 \cdot 8H_2O$ (16.7 mg, 52.8 µmol, 3.0 eq.) to obtain product **15b** (3.60 mg, 10.7 µmol, 61%) as a light yellow oil. $R_f = 0.36$ (petroleum ether/ethyl acetate, 10:1); ^{1}H NMR (399.892 MHz, $CDCl_3$): $\delta = 0.90$ (m, 3 H), 1.40 (m, 8 H), 2.08 (m, 4 H), 2.21 (m, 2 H), 2.52 (s, 3 H), 5.57 (m, 2 H), 6.01 (m, 2 H), 6.28 (m, 1 H), 6.48 (d, $J = 15.7$ Hz, 1 H), 6.88 (d, $J = 3.8$ Hz, 1 H), 7.54 (d, $J = 3.9$ Hz, 1 H); ^{13}C NMR (100.56 MHz, $CDCl_3$): $\delta = 13.9$, 22.2, 26.5, 28.4, 31.6, 32.3, 32.3, 32.8, 122.9, 124.9, 130.2, 130.7, 131.7, 132.7, 133.1, 135.4 (2 C), 141.4, 151.5, 190.4; HR-MS (FAB): $m/z = 317.1937$ ($C_{20}H_{29}0S$), calculated $m/z = 317.1934$.

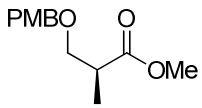
1-(5-((1*E*,9*E*,11*E*)-hexadeca-1,9,11-trien-1-yl)thiophen-2-yl)ethanone 15c



15c

The reaction was performed according to the general procedure as described above for (*E*)-1-iodohex-1-ene **16** (7.50 mg, 35.5 µmol, 1.0 eq.), pinacol borane **14c** (19.3 mg, 49.7 µmol, 1.4 eq.), anhydrous DMF (200 µL), $Pd(dppf)Cl_2$ (3.89 mg, 5.32 µmol, 15 mol%) and $Ba(OH)_2 \cdot 8H_2O$ (33.8 mg, 107 µmol, 3.0 eq.) to obtain product **15c** (7.80 mg, 22.7 µmol, 64%) as a light yellow oil. $R_f = 0.34$ (petroleum ether/ethyl acetate, 10:1); H NMR (399.892 MHz, $CDCl_3$): $\delta = 0.90$ (m, 3 H), 1.40 (m, 12 H), 2.07 (m, 4 H), 2.20 (q, $J = 7.1$ Hz, 2 H), 2.52 (s, 3 H), 5.57 (dtd, $J = 14.2$ Hz, $J = 6.9$ Hz, $J = 6.9$ Hz, $J = 4.2$ Hz, 2 H), 5.99 (m, 2 H), 6.29 (m, 1 H), 6.48 (d, $J = 15.8$ Hz, 1 H), 6.88 (d, $J = 3.8$ Hz, 1 H), 7.54 (d, $J = 3.9$ Hz, 1 H); ^{13}C NMR (100.56 MHz, $CDCl_3$): $\delta = 13.9$, 26.5, 28.8, 29.0, 29.0, 29.3, 31.6, 32.3, 32.5, 32.9, 122.8, 124.9, 130.3, 130.4, 132.2, 132.5, 133.1, 135.6 (2 C), 141.3, 151.6, 190.4; HR-MS (FAB): $m/z = 345.2255$ ($C_{22}H_{33}0S$), calculated $m/z = 345.2247$.

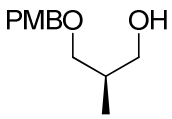
(*S*)-methyl 3-(4-methoxybenzyloxy)-2-methylpropanoate 25



25

To the solution of (*S*)-Roche ester (526 mg, 4.45 mmol, 1.0 eq) in CH_2Cl_2 (6 mL) PMB(HNC)CCl_3 (1.20 g, 4.45 mmol, 1.0 eq) and CSA (62.0 mg, 267 µmol, 0.06 eq) were added and the solution was stirred for 16 h. Then saturated $NaHCO_3$ solution (6 mL) was added and the aqueous layer extracted three times with CH_2Cl_2 (5 mL). The combined organic phases were washed with saturated $NaHCO_3$ solution (10 mL) and brine (10 mL), dried over $MgSO_4$, filtered and the organic solvent was removed under reduced pressure. After purification by chromatography (SiO_2, petroleum ether/ethyl acetate, 4:1) ester **25** was obtained as a colourless, oily liquid (1.05 g, 4.41 mmol, 99%). R_f = 0.78 (petroleum ether/ethyl acetate, 3:1); $[\alpha]^{22}_D$ = +9.26 (c = 1.00, $CHCl_3$) ; ^{1}H NMR (500.130 MHz, $CDCl_3$): δ = 1.18 (d, J = 7.1 Hz, 3 H), 2.78 (sxt, J = 6.9 Hz, 1 H), 3.47 (dd, J = 9.2 Hz, J = 5.9 Hz, 1 H), 3.64 (dd, J = 9.2 Hz, J = 7.3 Hz, 1 H), 3.70 (s, 3 H), 3.81 (s, 3 H), 4.46 (m, 2 H), 6.88 (d, J = 8.5 Hz, 2 H), 7.25 (d, J = 8.5 Hz, 2 H); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 13.7, 39.9, 51.4, 55.0, 71.4, 72.5, 113.4, 128.9, 129.9, 158.9, 175.1; HR-MS (ESI): m/z = 261.1097 ($C_{13}H_{18}0_4Na$), calculated m/z = 261.1103.

(*R*)-3-(4-methoxybenzyloxy)-2-methylpropan-1-ol 26

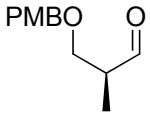


26

A Solution of (*S*)-methyl 3-(4-methoxybenzyloxy)-2-methylpropanoate **25** (1.00 g, 4.20 mmol, 1.0 eq) in CH_2Cl_2 (14 mL) under argon atmosphere was cooled down to -78 °C and treated with DIBAL-H (12.6 mL, 1 M in hexane, 12.6 mmol, 3.0 eq) over a period of 45 min. After stirring for 2 h at -78 °C, the reaction mixture was diluted by adding Et_2O (15 mL), warmed to room temperature an treated with H_2O (6 mL) carefully. The resulting mixture was stirred until a gel was formed. Then NaOH (2 N, 8 mL) was added and stirred

until the gel dissolved. The organic layer was separated, the aqueous phase was extracted with Et_2O (3 x 10 mL) and the combined organic phases were dried over $MgSO_4$, filtrated and concentrated under reduced pressure. After purification by chromatography (SiO_2, *n*-hexane/ethyl acetate 3:1), the desired alcohol **26** was obtained as colourless liquid (799 mg, 3.80 mmol, 90%). R_f = 0.22 (*n*-hexane /ethyl acetate, 3:1); $[\alpha]^{22}_D$ = +15.9 (c = 1.00, $CHCl_3$) ; ^{1}H NMR (300.132 MHz, $CDCl_3$): δ = 0.92 (d, J = 7.0 Hz, 3 H), 2.10 (m, 1 H), 2.46 (br. s, 1 H), 3.44 (m, 1 H), 3.57 (dd, J = 9.1 Hz, J = 4.6 Hz, 1 H), 3.65 (m, 2 H), 3.85 (s, 3 H), 4.49 (s, 2 H), 6.93 (d, J = 8.6 Hz, 2 H), 7.29 (d, J = 8.6 Hz, 2 H); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 13.0, 35.1, 54.8, 67.5, 72.6, 74.7, 113.4, 128.8, 129.7, 158.8; HR-MS (ESI): m/z = 233.1147 ($C_{12}H_{18}0_3Na$), calculated m/z = 233.1148.

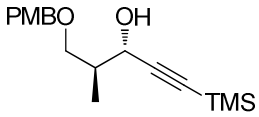
(*S*)-3-(4-methoxybenzyloxy)-2-methylpropanal 27



27

At 0° C Dess-Martin periodinane (565 mg, 1.33 mmol, 1.4 eq) was added to a solution of alcohol **26** (200 mg, 951 µmol, 1.0 eq) in CH_2Cl_2 (10 mL). The solution was allowed to warm to room temperature within 3 h. After evaporation of the solvent in vacuo purification by flash chromatography (SiO_2, petroleum ether/ethyl acetate 10:1) provided the desired aldehyde **27** as a colourless liquid (190 mg, 904 µmol, 95%). R_f = 0.23 (petroleum ether/ethyl acetate, 10:1); $[\alpha]^{22}_D$ = +30.5 (c = 1.00, $CHCl_3$); ^{1}H NMR (300.132 MHz, $CDCl_3$): δ = 1.17 (d, J = 7.3 Hz, 3 H), 2.70 (sxt, J = 7.0 Hz, 1 H), 3.67 (m, 2 H), 3.86 (s, 3 H), 4.51 (s, 2H), 6.93 (d, J = 8.8 Hz, 2 H), 7.29, (d, J = 8.4 Hz, 2 H), 9.76 (d, J = 1.5 Hz, 1 H); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 10.7, 46.8, 55.2, 69.8, 72.9, 113.8, 129.2, 129.9, 159.2, 204.0; HR-MS (EI^+): found m/z = 208.1091 ($C_{12}H_{16}O_3$), calculated m/z = 208.1099.

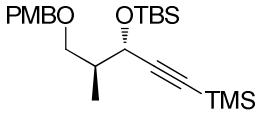
(3*S*,4*S*)-5-(4-methoxybenzyloxy)-4-methyl-1-(trimethylsilyl)pent-1-yn-3-ol 17



17

TMS acetylene (421 µL, 3.04 mmol, 4.0 eq) was added to Et_2Zn (2.76 mL, 1.1 M in toluene, 2.76 mmol, 4.0 eq.) carefully. The mixture was heated to reflux for 1 h, during which time a large amount of grey precipitate formed in the reaction flask. The mixture was cooled to room temperature, and (*R*)-BINOL (87.0 mg, 304 µmol, 0.4 eq.), Et_2O (14 mL) and $Ti(O\mathit{i}Pr)_4$ (226 µL, 759 µmol, 1.0 eq) were added. After 1 h, aldehyde **27** (158 mg, 759 µmol, 1.0 eq.) was added, and the mixture was stirred overnight. The reaction was quenched with 1 M tartaric acid (6 mL) and the mixture was stirred for 30 min. The mixture was partitioned in a separatory funnel, and the aqueous phase was extracted with Et_2O (3 x 7 mL). The combined organic extracts were washed with brine and dried over $MgSO_4$, filtrated and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2, petroleum ether/ethyl acetate, 100:2.5 to 100:5) to afford **17** as a light yellow oil (185 mg, 604 µmol, 80%). R_f = 0.47 (petroleum ether/ethyl acetate, 5:1); $[\alpha]^{22}_D$ = +7.13 (c = 1.00, $CHCl_3$); ^{1}H NMR (300.132 MHz, $CDCl_3$): δ = 0.17 (s, 9 H), 1.05 (d, *J* = 7.0 Hz, 3 H), 2.06 (sxtd, *J* = 6.8 Hz, *J* = 6.8 Hz, *J* = 6.8 Hz, *J* = 6.8 Hz, *J* = 6.8 Hz, *J* = 4.4 Hz, 1 H), 3.44 (dd, *J* = 9.3 Hz, *J* = 6.8 Hz, 1 H), 3.68 (dd, *J* = 9.3 Hz, *J* = 4.2 Hz, 1 H), 3.81 (s, 3 H), 4.40 (d, *J* = 6.2 Hz, 1 H), 4.46 (d, *J* = 2.9 Hz, 2 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 7.26 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = -0.1, 13.2, 39.2, 55.2, 66.8, 73.1, 73.3, 89.9, 105.5, 113.8, 129.2, 129.9, 159.2; HR-MS (ESI): found *m/z* = 329.1547 ($C_{17}H_{26}O_3SiNa$), calculated *m/z* = 329.1543.

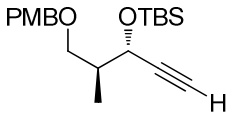
***tert*-butyl(((3*S*,4*S*)-5-((4-methoxybenzyl)oxy)-4-methyl-1-(trimethylsilyl)pent-1-yn-3-yl)oxy)dimethylsilane 28**



28

2,6-Lutidine (587 mg, 5.48 mmol, 4.2 eq.) and *tert*-butyldimethylsilyl trifluromethanesulfonate (1.10 g, 4.18 mmol, 3.2 eq.) were added slowly to a solution of alcohol **17** (400 mg, 1.31 mmol, 1.0 eq.) in CH_2Cl_2 (5 mL) at -78° C. After stirring for 1 h, the reaction was quenched by addition of aqueous saturated $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (3 x 7 mL). The combined organic phases were dried with $MgSO_4$, concentrated under reduced pressure and purified by flash chromatography (SiO_2, *n*-hexane/ethyl acetate, 50:1) to afford the protected alcohol **28** as a colourless liquid (528 mg, 1.25 mmol, 96%). R_f = 0.33 (petroleum ether/ethyl acetate, 50:1); $[\alpha]^{22}_D$ = -13.3 (c = 1.00, $CHCl_3$); ^{1}H NMR (300.132 MHz, $CDCl_3$): δ = 0.10 (s, 3 H) 0.14 (s, 3 H) 0.16 (s, 9 H) 0.90 (s, 9 H) 1.01 (d, *J* = 7.0 Hz, 3 H) 2.02 (spt, *J* = 6.5 Hz, 1 H) 3.39 (dd, *J* = 9.3 Hz, *J* = 6.0 Hz, 1 H) 3.50 (dd, *J* = 9.3 Hz, *J* = 6.0 Hz, 1 H) 3.81 (s, 3 H) 4.44 (m, 3 H) 6.88 (d, *J* = 8.6 Hz, 2 H) 7.26 (d, *J* = 8.6 Hz, 2 H); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = -5.1, -4.5, -0.2, 12.7, 18.2, 25.8, 40.5, 55.2, 65.2, 71.1, 72.7, 89.7, 106.1, 113.7, 129.1, 130.8, 159.0; HR-MS (ESI): found *m/z* = 443.2410 ($C_{23}H_{40}O_3Si_2Na$), calculated *m/z* = 443.2408.

tert-butyl(((3*S*,4*S*)-5-((4-methoxybenzyl)oxy)-4-methylpent-1-yn-3-yl)oxy)dimethylsilane 29

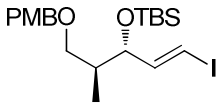


29

Potassium carbonate (63.3 mg, 458 µmol, 1.1 eq.) was added to a solution of the TMS-protected alkyne **28** (175 mg, 416 µmol, 1.0 eq) in MeOH (1.5 mL). The reaction mixture was stirred vigorously at room temperature for 1 h. The reaction was quenched by addition of saturated aqueous NH_4Cl and the volatiles were removed in vacuo. The residue was extracted with diethyl ether (3 x 1 mL), the combined organic phases were washes with water (1 mL), brine (1 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash chromatography (SiO_2, petroleum ether/ethyl acetate 50:1) provided the desired terminal alkyne **29** (141 mg, 404 µmol, 97%). R_f = 0.17 (petroleum ether/ethyl acetate, 50:1); $[\alpha]^{22}_D$ = -10.7 (c = 1.00, $CHCl_3$) ; ^{1}H NMR (300.132 MHz, $CDCl_3$): δ = 0.11 (s, 3 H), 0.15 (s, 3 H), 0.91 (s, 9 H), 1.03 (d, *J* = 7.0 Hz, 3 H), 2.06 (spt, *J* = 6.4 Hz, 1 H), 2.37 (d, *J* = 2.0 Hz, 1 H), 3.40 (dd, *J* = 9.3 Hz, *J* = 5.8 Hz, 1 H), 3.49 (dd, *J* = 9.3 Hz, *J* = 7.0 Hz, 1 H),

3.82 (s, 3 H), 4.44 (s, 2 H), 6.89 (d, J = 8.6 Hz, 2 H), 7.26 (d, J = 8.6 Hz, 2 H); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = -5.2, -4.6, 12.3, 18.2, 25.8, 40.5, 55.3, 64.5, 71.6, 72.7, 73.1, 83.8, 113.7, 129.1, 130.7, 159.1; HR-MS (ESI): found m/z = 371.2022 ($C_{20}H_{32}O_3SNa$), calculated m/z = 371.2013.

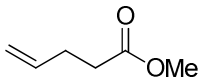
tert-butyl(((3_S_,4_S_,_E_)-1-iodo-5-((4-methoxybenzyl)oxy)-4-methylpent-1-en-3-yl)oxy)dimethylsilane 18



18

To $ZrCp_2Cl_2$ (45.0 mg, 157 µmmol, 1.1 eq.) in THF (250 µL) cooled to 0 °C was added slowly a solution DIBAL-H (156 µL, 1 M in THF, 156 µmol, 1.0 eq.) under argon. The resultant suspension was stirred for 30 min at 0 °C, followed by addition of alkyne **29** (50.0 mg, 143 µmol, 1.0 eq.) in THF (150 µL). The mixture was warmed to room temperature and stirred until a homogenous solution resulted and then cooled to -78 °C, followed by addition of I_2 (47.2 mg, 186 µmol, 1.30 eq.) in THF (200 µL). After 1 h at -78°C the reaction mixture was quenched with 1 N HCl, extracted with diethyl ether, washed successively with saturated aqueous $Na_2S_2O_3$, $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated. Flash chromatography (SiO_2, petroleum ether) afforded vinyl iodide **18** as colourless liquid (46.5 mg, 97.6 µmol, 62%). R_f = 0.19 (petroleum ether/ethyl acetate, 50:1); $[\alpha]^{22}_D$ = +1.39 (c = 1.00, $CHCl_3$); ^{1}H NMR (300.132 MHz, $CDCl_3$): δ = 0.02 (s, 3 H), 0.04 (s, 3 H), 0.89 (m, 12 H), 1.92 (dquin, J = 12.8 Hz, J = 6.5 Hz, J = 6.5 Hz, J = 6.5 Hz, 1 H), 3.34 (m, 2 H), 3.82 (s, 3 H), 4.15 (m, 1 H), 4.41 (m, 2 H), 6.14 (dd, J = 14.4 Hz, J = 1.0 Hz, 1 H), 6.48 (dd, J = 14.4 Hz, J = 6.7 Hz, 1 H), 6.89 (d, J = 8.7 Hz, 2 H), 7.25 (d, J = 9.2 Hz, 2 H); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = -5.0, -4.5, 12.5, 18.2, 25.8, 39.9, 55.3, 71.5, 72.7, 76.4, 76.5, 113.8, 129.2, 130.6, 147.1, 159.1; HR-MS (ESI): found m/z = 499.1132 ($C_{20}H_{33}IO_3SiNa$), calculated m/z = 499.1136.

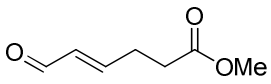
Methyl-pent-4-enoate 30



30

A solution of Pent-4-enoic acid **24** (10.0 g, 100 mmol, 1.0 eq.) in dried CH_3OH (170 mL, 420 mol, 42 eq.) was treated with concentrated H_2SO_4 (1.00 mL). After refluxing for 3 h, the reaction mixture was washed with water (2 x 140 mL) and the resulting mixture was extracted with Et_2O (3 x 200 mL), dried with $MgSO_4$ and concentrated. The residue was purified by vigreux destillation to afford the pure ester **30** as a colourless liquid (8.24 g, 72.2 mmol, 72%). R_f = 0.63 (*n*-hexane/ethyl acetate, 8:1) ; ^{1}H NMR (300.132 MHz, CDCl3) δ = 2.39 (m, 4 H), 3.68 (s, 3 H), 5.03 (m, 2 H), 5.82 (m, 1 H); ^{13}C NMR (75.48 MHz, $CDCl_3$) δ = 28.4, 33.9, 51.1, 115.1, 136.2, 173.1; EI MS (70 eV, *m/z* (%)): 114 ([M]$^+$, 27.5), 55 (100).

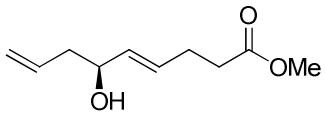
(*E*)-Methyl 6-oxohex-4-enoate 31



31

Crotonaldehyde (6.14 g, 87.6 mmol, 10 eq.) dissolved in dried CH_2Cl_2 (30 mL) was added to a solution of olefin **30** (1.00 g, 8.76 mmol, 1.0 eq.) in deaeterated CH_2Cl_2 (10 mL). Hoveyda-Grubbs catalyst second generation (165 mg, 3.0 mol%) was added and the reaction mixture was heated to 40 °C under an argon atmosphere for 2 h. After stirring, the mixture was concentrated under reduced pressure and purified by flash chromatography (SiO_2, *n*-hexane/ethyl acetate, 4:1) to afford aldehyde **31** as a brown liquid (1.16 g, 8.16 mmol, 93%). R_f = 0.24 (*n*-hexane/ethyl acetate, 4:1); ^{1}H NMR (300.132 MHz, $CDCl_3$) δ = 2.53 (m, 2 H), 2.65 (m, 2 H), 3.68 (s, 3 H), 6.12 (dd, *J* = 15.3 Hz, *J* = 7.8 Hz, 1 H), 6.85 (dt, *J* = 15.7 Hz, *J* = 6.4 Hz, 1 H), 9.49 (d, *J* = 7.7 Hz, 1 H) ; ^{13}C NMR (75.48 MHz, $CDCl_3$) δ = 27.1, 31.4, 51.4, 132.9, 155.3, 172.0, 193.3 ; HR-MS (EI) found *m/z* = 142.0654 ($C_7H_{10}O_3$), calculated *m/z* = 142.0630.

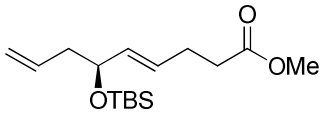
(*S*,*E*)-Methyl 6-hydroxynona-4,8-dienoate 32



32

Allylmagnesium bromide (5.63 mL, 1.00 M in diethyl ether, 5.63 mmol, 4.0 eq.) was added dropwise to a well-stirred solution of (-)-$(Ipc)_2BOMe$ (1.78 g, 5.63 mmol, 4.0 eq.) in diethyl ether (6 mL) at 0 C. Following addition, stirring was continued for 1 h at room temperature and ether was removed under vacuum. The residue was carefully extracted with pentane (2 x 25 mL) under argon while the reaction mixture was stirred. Next, stirring was discontinued to permit the Mg^{2+} salts to settle, and the clear supernatant pentane extract was transferred into another flask with a double-ended needle through a filter. The combined organic phases were concentrated under vacuum. The residue was solved in diethyl ether (5 mL) and cooled to -98° C. To the resulting mixture a solution of aldehyde **31** (200 mg, 1.41 mmol, 1.0 eq.) in diethyl ether (2.5 mL) was added slowly and stirred at -98° C. After 3 h the reaction mixture was allowed to warm to room temperature, treated with NaOH (550 µL, 3 N) and H_2O_2 (1.5 mL, 30 %) and then heat to reflux for 1 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution and the organic phase separated. The aqueous layer was extracted with diethyl ether (2 x 3.5 mL), MTBE (2 x 2.5 mL) and ethyl acetate (2 x 1.5 mL). The combined organic layers were dried over $MgSO_4$ and evaporated under vacuum. The residue was purified by flash chromatography (SiO_2, *n*-hexane/ethyl acetate, 3:1) to afford **32** as an orange liquid (233 mg, 1.26 mmol, 90%). R_f = 0.21 (*n*-hexane/ethyl acetate; 5:1); $[\alpha]^{22}_D$ = -7.40 (c = 1.00, $CHCl_3$); ^{1}H NMR (300.132 MHz, $CDCl_3$) δ = 2.29 (m, 2 H), 2.39 (m, 4 H), 3.67 (s, 3 H), 4.13 (q, J = 6.2 Hz, 1 H), 5.11 (t, J = 1.3 Hz, 1 H), 5.15 (m, 1 H), 5.54 (m, 1 H), 5.75 (m, 2 H); ^{13}C NMR (75.48 MHz, $CDCl_3$) δ = 27.4, 33.6, 41.9, 51.5, 71.4, 118.2, 129.5, 133.3, 134.2, 173.4; HR-MS (ESI): found *m/z* = 207.0994 ($C_{10}H_{16}O_3Na$), calculated *m/z* = 207.0992.

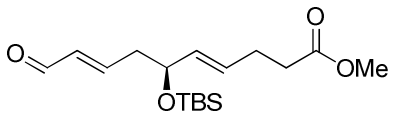
(*S*,*E*)-Methyl 6-(*tert*-butyldimethylsilyloxy)nona-4,8-dienoate 33



33

2,6-Lutidine (609 mg, 5.69 mmol, 2.1 eq.) and *tert*-butyldimethylsilyl trifluromethanesulfonate (1.15 g, 4.34 mmol, 1.6 eq.) were added slowly to a solution of alcohol **32** (500 mg, 2.71 mmol, 1.0 eq.) in CH_2Cl_2 (8 mL) at -78° C. After stirring for 1 h, the reaction was quenched by addition of aqueous saturated $NaHCO_3$ and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried with $MgSO_4$, concentrated under reduced pressure and purified by flash chromatography (SiO_2, *n*-hexane/ethyl acetate, 30:1) to afford the protected alcohol **33** as a colourless liquid (803 mg, 2.69 mmol, 99%). R_f = 0.29 (*n*-hexane/ethyl acetate; 30:1); $[\alpha]^{22}_D$ = -2.30 (c = 1.00, $CHCl_3$); ^{1}H NMR (300.132 MHz, $CDCl_3$) δ = 0.01 (s, 3 H), 0.03 (s, 3 H), 0.88 (s, 9 H), 2.22 (m, 2 H), 2.36 (m, 4 H), 3.67 (s, 3 H), 4.08 (m, 1 H), 5.00 (s, 1 H), 5.04 (d, *J*=5.1 Hz, 1 H), 5.47 (m, 1 H), 5.57 (m, 1 H), 5.76 (m, 1 H); ^{13}C NMR (75.48 MHz, $CDCl_3$) δ = -4.8, -4.4, 18.2, 25.8, 27.4, 33.8, 43.1, 51.5, 73.0, 116.7, 128.0, 134.3, 135.1, 173.4; HR-MS (ESI): found *m/z* = 321.1860 ($C_{16}H_{30}O_3SiNa$), calculated *m/z* = 321.1856.

(*S*,4*E*,8*E*)-Methyl 6-(*tert*-butyldimethylsilyloxy)-10-oxodeca-4,8-dienoate 34

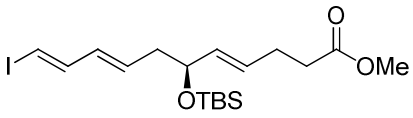


34

The protected Alcohol **33** (1.00 g, 3.35 mmol, 1.0 eq.) solved in CH_2Cl_2 (3 mL) was added to a well stirred solution of crotonaldehyde (0.70 g, 10.0 mmol, 3.0 eq.) in CH_2Cl_2 (7 mL). After Grubbs-Catalyst second generation (142 mg, 5.0 mol%) was added, the reaction mixture was heated to 40° C for 2 h, concentrated under reduced pressure and purified by flash chromatography (SiO_2, *n*-hexane/ethyl acetate, 10:1) to afford aldehyde **34** as a yellow-brown liquid (940 mg, 2.88 mmol, 86%). R_f = 0.28 (*n*-hexane/ethyl acetate; 10:1); $[\alpha]^{22}_D$ = +0.65 (c = 1.00, $CHCl_3$); ^{1}H NMR (300.132 MHz, $CDCl_3$) δ = 0.02 (s, 3 H), 0.03 (s, 3 H), 0.88 (s, 9

H), 2.37 (m, 4 H), 2.50 (ddd, J = 7.2 Hz, J = 5.9 Hz, J = 1.5 Hz, 2 H), 3.67 (s, 3 H), 4.24 (m, 1 H), 5.47 (m, 1 H), 5.63 (m, 1 H), 6.12 (ddt, J = 15.7 Hz, J = 7.9 Hz, J = 1.2 Hz, J = 1.2 Hz, 1 H), 6.82 (dt, J = 15.7 Hz, J = 7.3 Hz, 1 H), 9.50 (d, J = 8.1 Hz, 1 H); ^{13}C NMR (75.48 MHz, $CDCl_3$) δ = -5.3, -4.7, 17.7, 25.3, 26.8, 33.2, 41.2, 51.1, 71.5, 128.8, 133.0, 134.4, 154.4, 172.8, 193.5; HR-MS (ESI): found m/z = 349.1807 ($C_{17}H_{30}O_4SiNa$), calculated m/z = 349.1811.

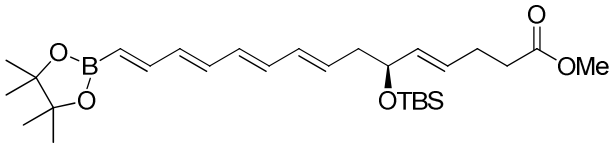
(*S*,4*E*,8*E*,10*E*)-Methyl 6-(*tert*-butyldimethylsilyloxy)-11-iodoundeca-4,8,10-trieno-ate 19



19

To a cooled (0° C) suspension of $CrCl_2$ (2.11 g, 17.2 mmol, 14 eq.) in mixed solvent (THF/dioxane, 1:6, 15 mL) was added dropwise a solution of aldehyde **34** (400 mg, 1.23 mmol, 1.00 eq.) and iodoform (4.25 g, 10.8 mmol, 8.8 eq.) in mixed solvent (THF/dioxane, 1:6, 15 mL and 6 mL washing). The resulted brown mixture was stirred at room temperature for 4 h in the absence of light, quenched by sequential additions of aqueous saturated NH_4Cl (70 mL), saturated $Na_2S_2O_3$ (35 mL) and water (70 mL). The resulted mixture was extracted with diethyl ether (3 x 100 mL) and the combined organic phases were washed with saturated $Na_2S_2O_3$ (70 mL) and brine (70 mL), dried over $MgSO_4$ and concentrated under vacuum. Flash chromatography (SiO_2, *n*-hexane/ethyl acetate, 40:1 to 20:1) provided vinyl iodide **19** as a yellow oil (480 mg, 1.07 mmol, 87%, E/Z = 7:1 based on ^{1}H NMR integrations). R_f = 0.48 (*n*-hexane/ethyl acetate; 10:1); $[\alpha]^{22}_D$ = +3.50 (c = 1.00, $CHCl_3$); ^{1}H NMR (300.132 MHz, $CDCl_3$) δ = 0.00 (s, 3 H), 0.02 (s, 3 H), 0.87 (s, 9 H), 2.20 (t, J = 6.7 Hz, 2 H), 2.36 (m, 4 H), 3.67 (s, 3 H), 4.09 (m, 1 H), 5.44 (m, 1 H), 5.62 (m, 2 H), 5.97 (dd, J = 15.2 Hz, J = 10.6 Hz, 1 H), 6.18 (d, J = 14.3 Hz, 1 H), 6.98 (dd, J = 14.3 Hz, J = 10.5 Hz, 1 H); ^{13}C NMR (75.48 MHz, $CDCl_3$) δ = -4.4, -3.9, 18.6, 26.3, 27.8, 34.2, 42.1, 52.0, 73.2, 128.8, 132.5, 132.7, 134.6, 145.8, 173.8 ; HR-MS (ESI): found m/z = 473.0979 ($C_{18}H_{31}IO_3SiNa$), calculated m/z = 473.0985.

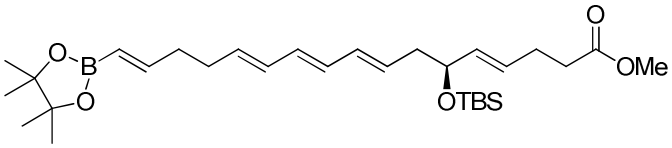
(*S*,4*E*,8*E*,10*E*,12*E*,14*E*)-methyl-6-(tert-butyldimethylsilyloxy)-15-(4,4,5,5-tetra-methyl-1,3,2-dioxaborolan-2-yl)pentadeca-4,8,10,12,14-pentaenoate 20



20

The following process was executed in the dark. $PdCl_2(CH_3CN)_2$ (6.25 mg, 24.1 µmol, 5.0 mol%) was added to a solution of the iodide **19** (217.0 mg, 482 µmol, 1.0 eq.) and the stannane **2a** (325 mg, 963 µmol, 2.0 eq.) in degassed, anhydrous DMF (1.7 mL). After stirring for 4 h the reaction mixture was diluted with diethyl ether (10 mL) and washed with a concentrated aqueous solution of NH_4Cl (20 mL). The organic phase was separated and the aqueous phase was extracted with diethyl ether (3 x 10 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by column chromatography (SiO_2, petroleum ether/ethyl acetate, 40:1-20:1) afforded the product **20** (194 mg, 385 µmol, 80%) as a yellow oil with little impurities of Bu_3SnI. R_f = 0.21 (petroleum ether/ethyl acetate, 20:1); $[\alpha]^{22}_D$ = +2.00 (c = 1.00, $CHCl_3$); ^{1}H NMR (600.130 MHz, $CDCl_3$): δ = 0.00 (s, 3 H), 0.02 (s, 3 H), 0.88 (m, 9 H), 1.28 (s, 12 H), 2.27 (m, 2 H), 2.36 (m, 4 H), 3.66 (s, 3 H), 4.10 (m, 1 H), 5.47 (dd, *J* = 15.3 Hz, *J* = 6.3 Hz, 1 H), 5.57 (m, 2 H), 5.72 (dt, *J* = 15.1, *J* = 7.6 Hz, 1 H), 6.10 (dd, *J* = 15.1 Hz, *J* = 10.6 Hz, 1 H), 6.17 (dd, *J* = 14.8 Hz, *J* = 10.8 Hz, 1 H), 6.28 (dd, *J* = 14.7 Hz, *J* = 10.6 Hz, 2 H), 6.38 (m, 1 H), 7.04 (dd, *J* = 17.7 Hz, *J* = 10.6 Hz, 1 H); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = -4.8, -4.4, 13.6, 17.5, 24.6, 24.8, 25.8, 26.8, 27.8, 33.8, 42.1, 51.5, 73.1, 83.2, 128.2, 130.7, 132.6, 132.6, 133.8, 134.3, 135.3, 136.7, 149.7, 173.4; HR-MS (ESI): found *m*/*z* = 525.3187 ($C_{28}H_{47}0_5SiNa$), calculated *m*/*z* = 525.3183.

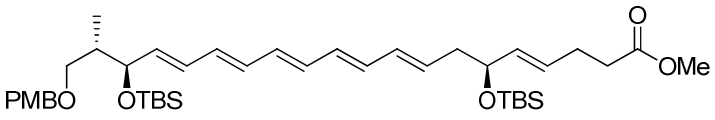
(*S*,4*E*,8*E*,10*E*,12*E*,16*E*)-methyl 6-hydroxy-17-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptadeca-4,8,10,12,16-pentaenoate 21



21

The following process was executed in the dark. $PdCl_2(CH_3CN)_2$ (1.44 mg, 5.55 µmol, 5.0 mol%) was added to a solution of the iodide **19** (50.0 mg, 111 µmol, 1.0 eq.) and the stannane **3a** (55.2 mg, 111 µmol, 1.0 eq.) in degassed, anhydrous DMF (400 µL) in an amber glass septum vial. After stirring for 4 h the reaction mixture was diluted with 6 mL of diethyl ether and washed with saturated aqueous solution of NH_4Cl (6 mL). The organic phase was separated and the aqueous phase was extracted with diethyl ether (3 x 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by column chromatography (SiO_2, petroleum ether/ethyl acetate, 40:1-20:1) afforded the product **21** (40.1 mg, 75.6 µmol, 68%) as a slightly yellow liquid. R_f = 0.21 (petroleum ether/ethyl acetate, 20:1); $[\alpha]^{22}_D$ = +7.60 (c = 1.00, $CHCl_3$); ^{1}H NMR (300.132 MHz, $CDCl_3$): δ = 0.00 (s, 3 H), 0.02 (s, 3 H), 0.88 (s, 9 H), 1.27 (s, 12 H), 2.24 (m, 6 H), 2.36 (m, 4 H), 3.67 (s, 3 H), 4.07 (q, J = 6.1 Hz, 1 H), 5.57 (m, 5 H), 6.09 (m, 4 H), 6.63 (dt, J = 18.0 Hz, J = 5.8 Hz, 1 H); ^{13}C NMR (75.57 MHz, $CDCl_3$): δ = -4.8, -4.4, 18.2, 24.8, 25.9, 27.4, 31.4, 33.8, 35.5, 42.1, 51.5, 73.3, 83.0, 128.0, 130.2, 130.8, 131.0, 131.2, 132.6, 133.4, 153.4, 173.4; HR-MS (ESI): m/z = 553.3504 ($C_{30}H_{51}B0_5SiNa$), calculated m/z = 553.3497.

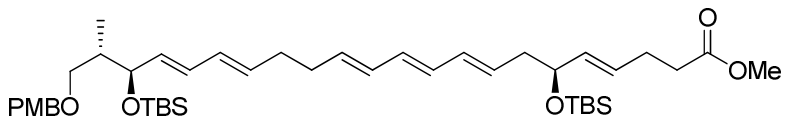
(4*E*,6*S*,8*E*,10*E*,12*E*,14*E*,16*E*,18*R*,19*S*)-Methyl-6,18-bis((tert-butyldimethylsilyl)oxy)-20-((4-methoxybenzyl)oxy)-19-methylicosa-4,8,10,12,14,16-hexaenoate 22



22

The following process was executed in the absence of light and conducted in an amber glass septum vial. The iodide **18** (6.77 mg, 14.2 µmol, 1.0 eq.) and the borane **20** (10.0 mg, 19.9 µmol, 1.4 eq.) were diluted in anhydrous DMF (100 µL). $Pd(dppf)Cl_2$ (3.12 mg, 4.26 µmol, 30 mol%) and $Ba(OH)_2{\cdot}8H_2O$ (13.4 mg, 42.6 µmol, 3.0 eq.) were added to the vigorous stirring solution sequently and the reaction mixture was stirred for 4 h. For purification diethyl ether (6 mL) and water (10 mL) was added. After separation of the organic phase the aqueous phase was extracted with diethyl ether (3 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. After purification by column chromatography (SiO_2, petroleum ether/ethyl acetate, 40:1) the product **22** (7.90 mg, 10.9 µmol, 77%) was obtained as a clear, yellow liquid. $R_f = 0.17$ (petroleum ether/ethyl acetate, 20:1); $[\alpha]^{22}_D = +12.03$ (c = 1.00, $CHCl_3$); ^{1}H NMR (500.132 MHz, $CDCl_3$): $\delta = 0.00$ (s, 3 H), 0.02 (s, 3 H), 0.03 (s, 3 H), 0.04 (s, 3 H), 0.89 (m, 21 H), 1.93 (dt, $J = 12.3$ Hz, $J = 6.2$ Hz, 1 H), 2.34 (m, 2 H), 2.26 (m, 2 H), 3.32 (dd, $J = 8.8$ Hz, $J = 6.3$ Hz, 1 H), 3.41 (dd, $J = 8.8$ Hz, $J = 6.3$ Hz, 1 H), 3.67 (s, 3 H), 3.81 (s, 3 H), 4.16 (m, 2 H), 4.37 (d, $J = 11.5$ Hz, 1 H), 4.45 (d, $J = 11.5$ Hz, 1 H), 5.48 (dd, $J = 15.4$ Hz, $J = 6.0$ Hz, 1 H), 5.57 (m, 1 H), 5.62 (m, 1 H), 5.68 (m, 1 H), 6.19 (m, 8 H), 6.88 (d, $J = 8.5$ Hz, 2 H), 7.26 (d, $J = 9.3$ Hz, 2 H); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = -4.9$, -4.8, -4.4, -4.2, 12.9, 14.2, 18.2, 18.2, 25.8, 25.9, 27.4, 33.8, 40.5, 42.2, 51.5, 55.2, 60.4, 72.0, 72.6, 73.2, 74.6, 113.7, 128.1, 129.2, 130.8, 130.9, 131.3, 131.4, 132.3, 132.4, 132.5, 132.8, 133.1, 133.2, 134.3, 135.1, 159.0, 173.4; HR-MS (ESI): found $m/z = 747.4452$ ($C_{42}H_{68}O_6Si_2Na$), calculated $m/z = 747.4447$.

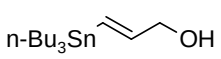
(4*E*,6*S*,8*E*,10*E*,12*E*,16*E*,18*E*,20*R*,21*S*)-Methyl-6,20-bis((tert-butyldimethylsilyl)oxy)-22-((4-methoxybenzyl)oxy)-21-methyldocosa-4,8,10,12,16,18-hexaenoate 23



23

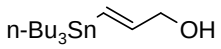
The following process was executed in the dark and conducted in an amber glass septum vial. The iodide **18** (6.43 mg, 13.5 µmol, 1.00 eq.) and the pinacol borane **21** (10.0 mg, 18.9 µmol, 1.4 eq.) were diluted in anhydrous DMF (50 µL). $Pd(dppf)Cl_2$ (2.96 mg, 1.60 µmol, 30 mol%) and $Ba(OH)_2{\cdot}8H_2O$ (12.7 mg, 40.5 µmol, 3.0 eq.) were added to the vigorous stirring solution sequently. The reaction mixture was stirred for 4 h. For purification diethyl ether (6 mL) and

water (10 mL) was added to the reaction mixture. After separation of the organic phase the aqueous phase was extracted with diethyl ether (3 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. After purification by column chromatography (SiO_2, petroleum ether/ethyl acetate, 40:1) the product **23** (8.40 mg, 11.2 µmol, 83%) was obtain as a clear, slightly yellow liquid. R_f = 0.33 (petroleum ether/ethyl acetate, 40:1); $[\alpha]^{22}_D$ = +76.1 (c = 1.00, $CHCl_3$); ^{1}H NMR (600.130 MHz, $CDCl_3$): δ = 0.00 (s, 3 H), 0.01 (s, 3 H), 0.03 (s, 6 H), 0.88 (s, 21 H), 1.91 (dquin, J = 12.8 Hz, J = 6.5 Hz, 1 H), 2.22 (m, 6 H), 2.35 (t, J = 6.2 Hz, 2 H), 2.39 (m, 2 H), 3.30 (dd, J = 9.1 Hz, J = 6.7 Hz, 1 H), 3.43 (dd, J = 9.0 Hz, J = 5.9 Hz, 1 H), 3.67 (s, 3 H), 3.81 (s, 3 H), 4.08 (m, 1 H), 4.12 (t, J = 6.5 Hz, 1 H), 4.38 (d, J = 11.6 Hz, 1 H), 4.44 (d, J = 11.6 Hz, 1 H), 5.47 (m, 2 H), 5.62 (m, 4 H), 6.06 (m, 6 H), 6.88 (d, J = 8.5 Hz, 2 H), 7.26 (d, J = 9.9 Hz, 2 H); ^{13}C NMR (150.90 MHz, $CDCl_3$): δ = -4.9, -4.8, -4.4, -4.1, 13.0, 18.2, 18.2, 25.9, 25.9, 27.4, 32.5, 32.5, 33.8, 40.4, 42.1, 51.5, 55.2, 72.1, 72.6, 73.3, 74.7, 113.7, 128.0, 129.1, 130.2, 130.2, 130.8, 130.9, 130.9, 131.0, 131.1, 132.6, 132.6, 133.1, 133.5, 134.3, 159.0, 173.5; HR-MS (ESI): m/z = 775.4757 ($C_{44}H_{72}0_6Si_2Na$), calculated m/z = 775.4759.



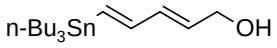
5a

solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz



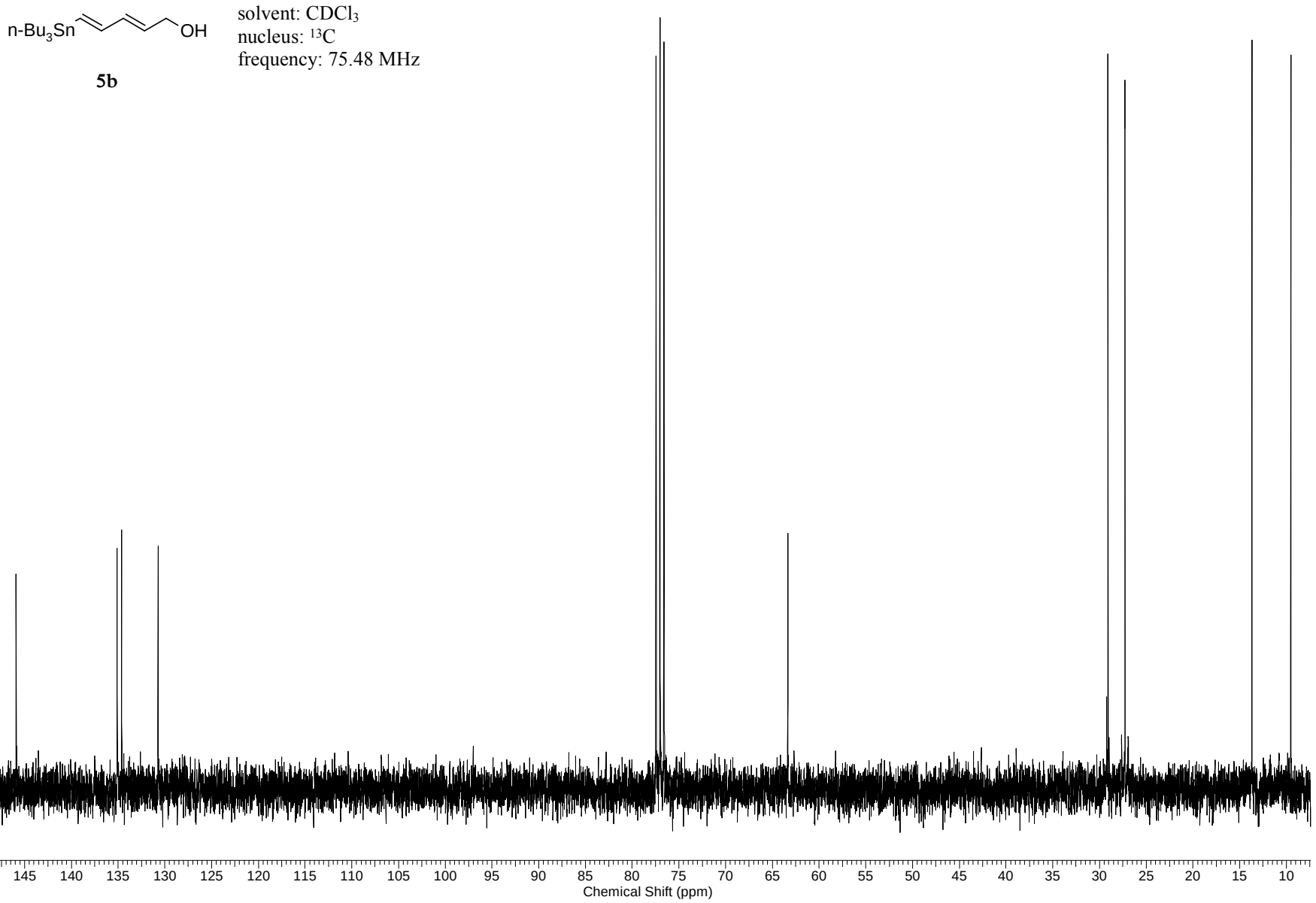
5a

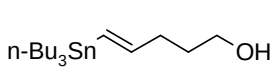
solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz



5b

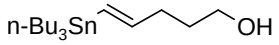
solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz





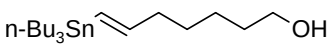
9a

solvent: $CDCl_3$
nucleus: ^1H
frequency: 500.130 MHz



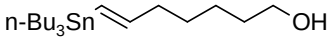
9a

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 125.78 MHz



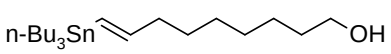
9b

solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz



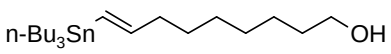
9b

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz



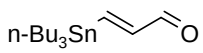
9c

solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz



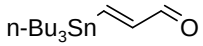
9c

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz



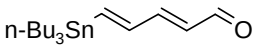
6a

solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz



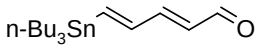
6a

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz



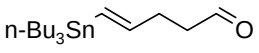
6b

solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz



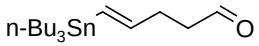
6b

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz



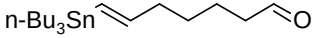
10a

solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz



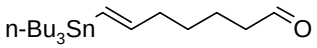
10a

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz



10b

solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz

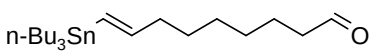


10b

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz

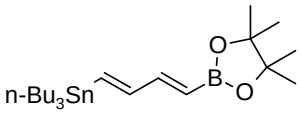
10c

solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz



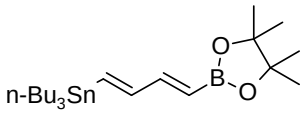
10c

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz



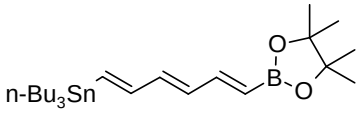
2a

solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz



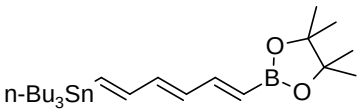
2a

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz



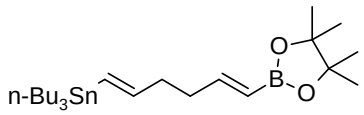
2b

solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz



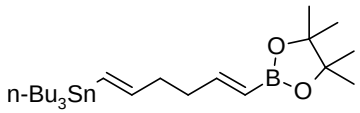
2b

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 100.61 MHz



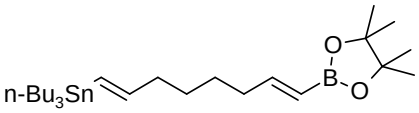
3a

solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz



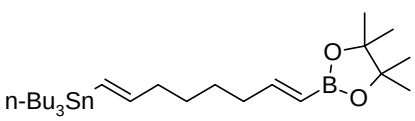
3a

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz



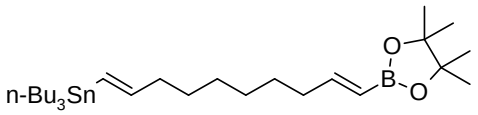
3b

solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz



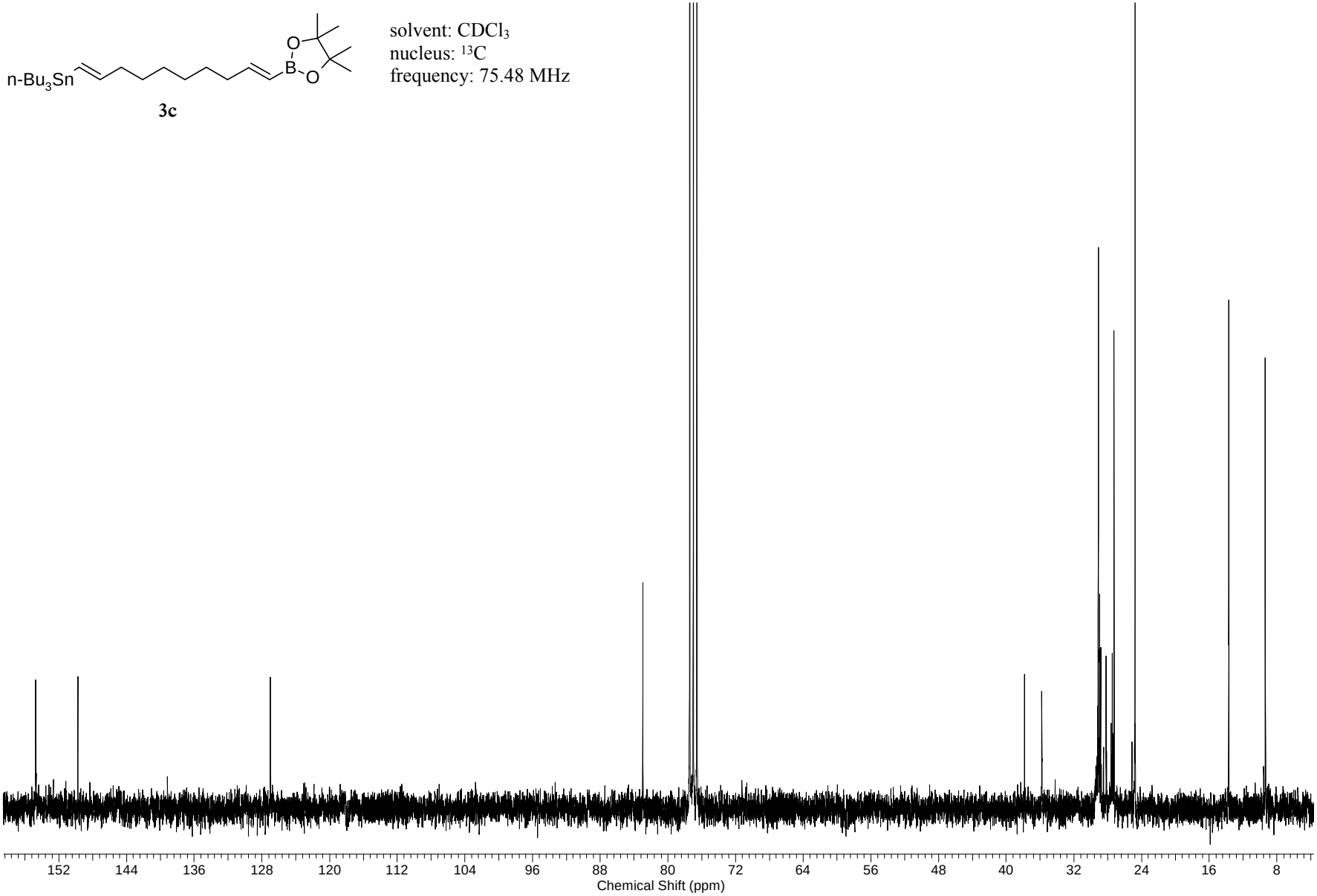
3b

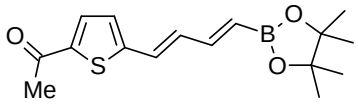
solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz



3c

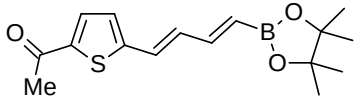
solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz





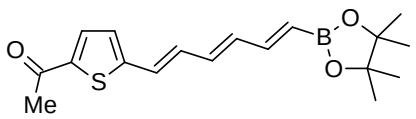
12a

solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz



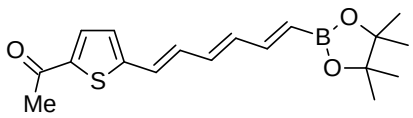
12a

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz



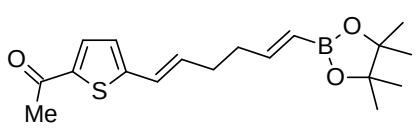
12b

solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz



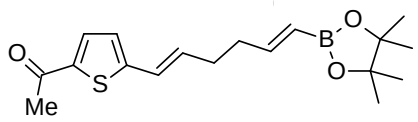
12b

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz



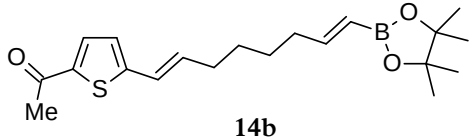
14a

solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz



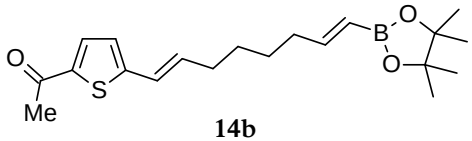
14a

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz



14b

solvent: $CDCl_3$
nucleus: ^1H
frequency: 600.130 MHz

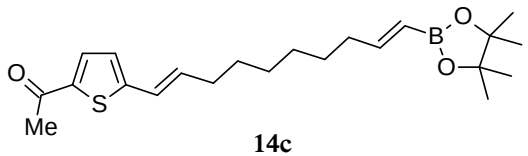


14b

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 150.90 MHz

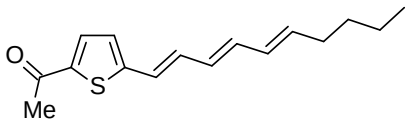
14c

solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz



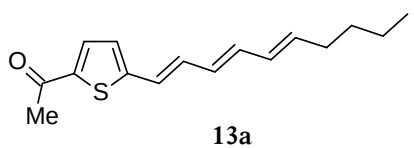
14c

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz



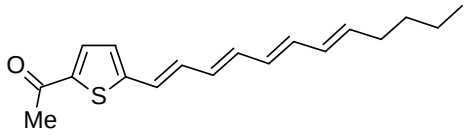
13a

solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz



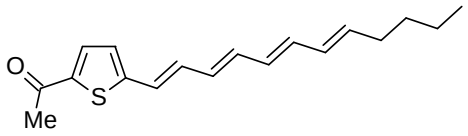
13a

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz



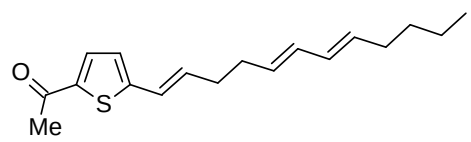
13b

solvent: $CDCl_3$
nucleus: ^1H
frequency: 600.130 MHz



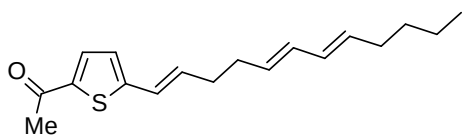
13b

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 150.90 MHz



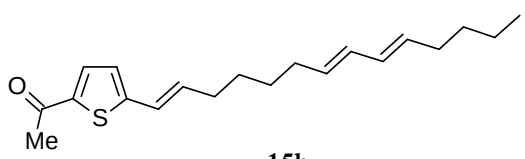
15a

solvent: $CDCl_3$
nucleus: ^1H
frequency: 399.982 MHz



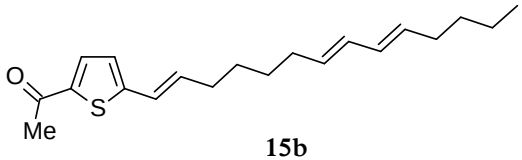
15a

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 100.56 MHz



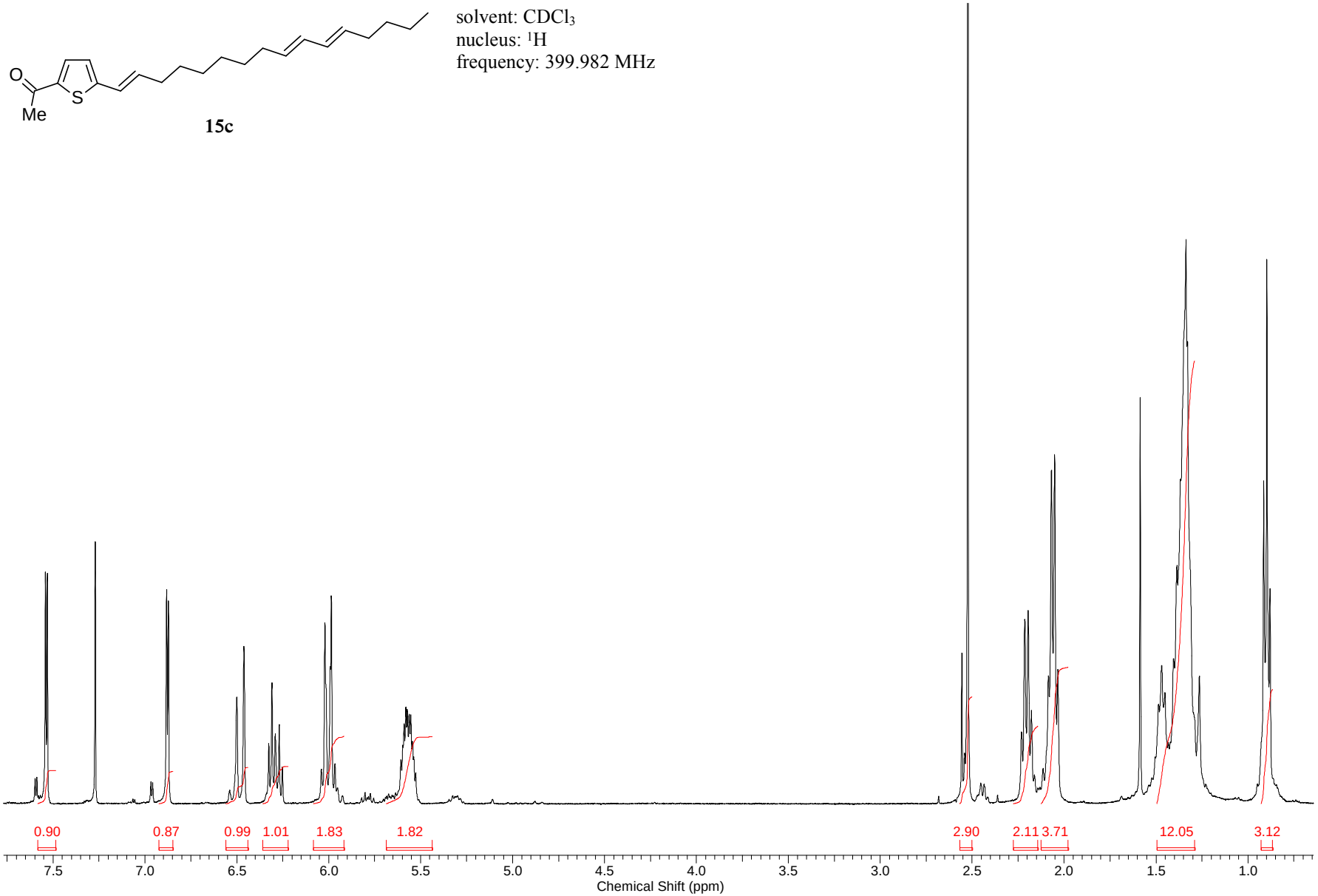
15b

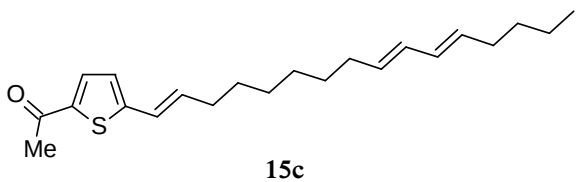
solvent: $CDCl_3$
nucleus: ^1H
frequency: 399.982 MHz



15b

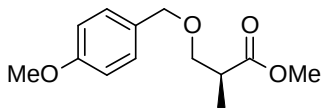
solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 100.56 MHz





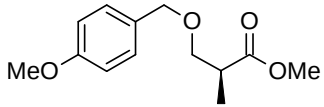
15c

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 100.56 MHz



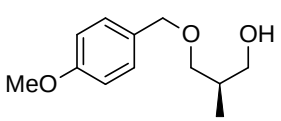
25

solvent: $CDCl_3$
nucleus: ^1H
frequency: 500.130 MHz



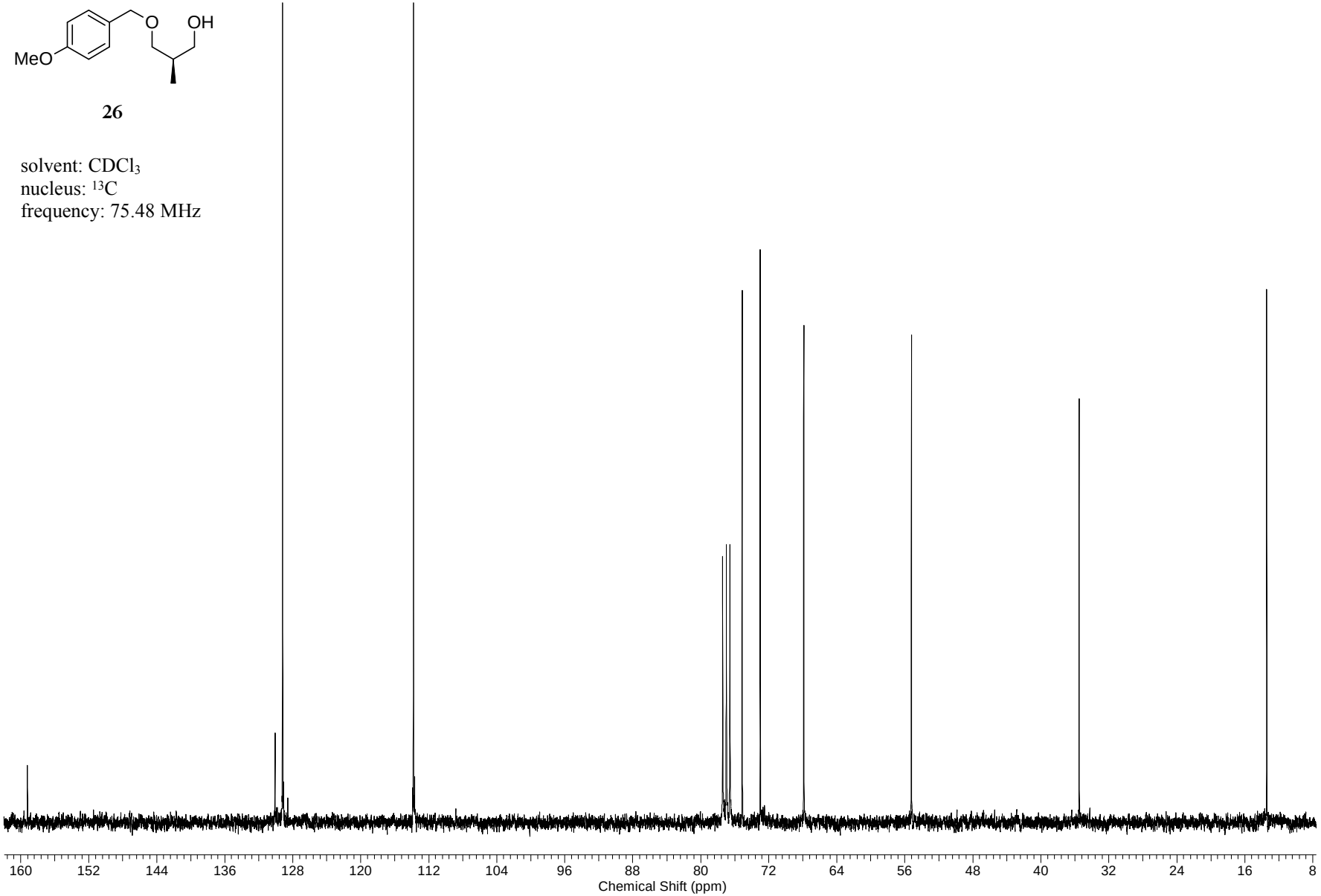
25

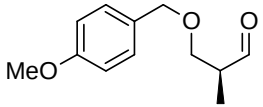
solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 125.76 MHz



26

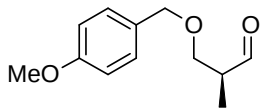
solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz





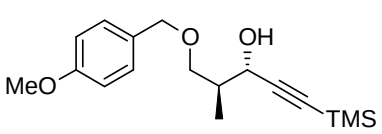
27

solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz



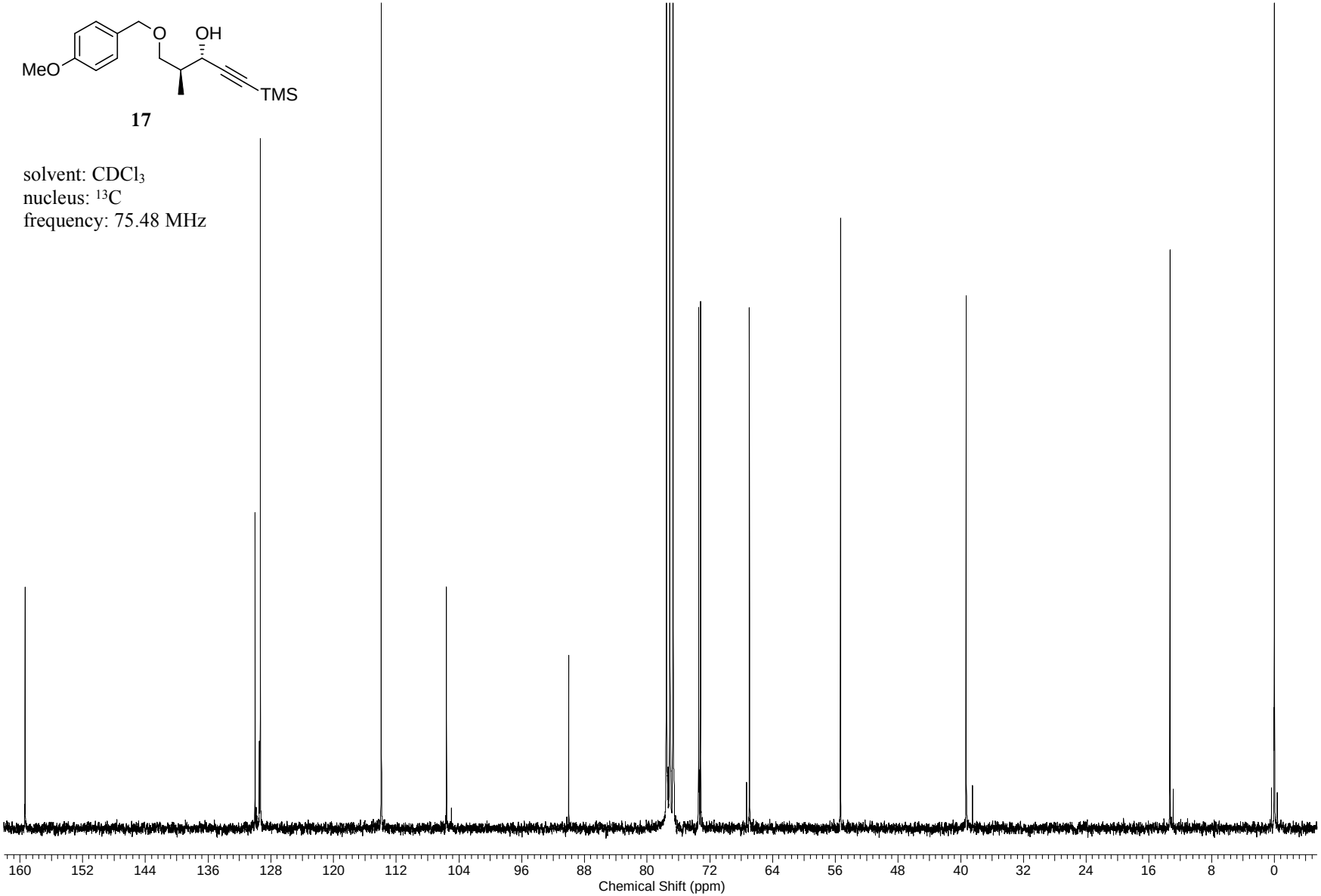
27

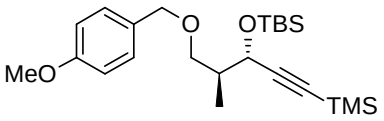
solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz



17

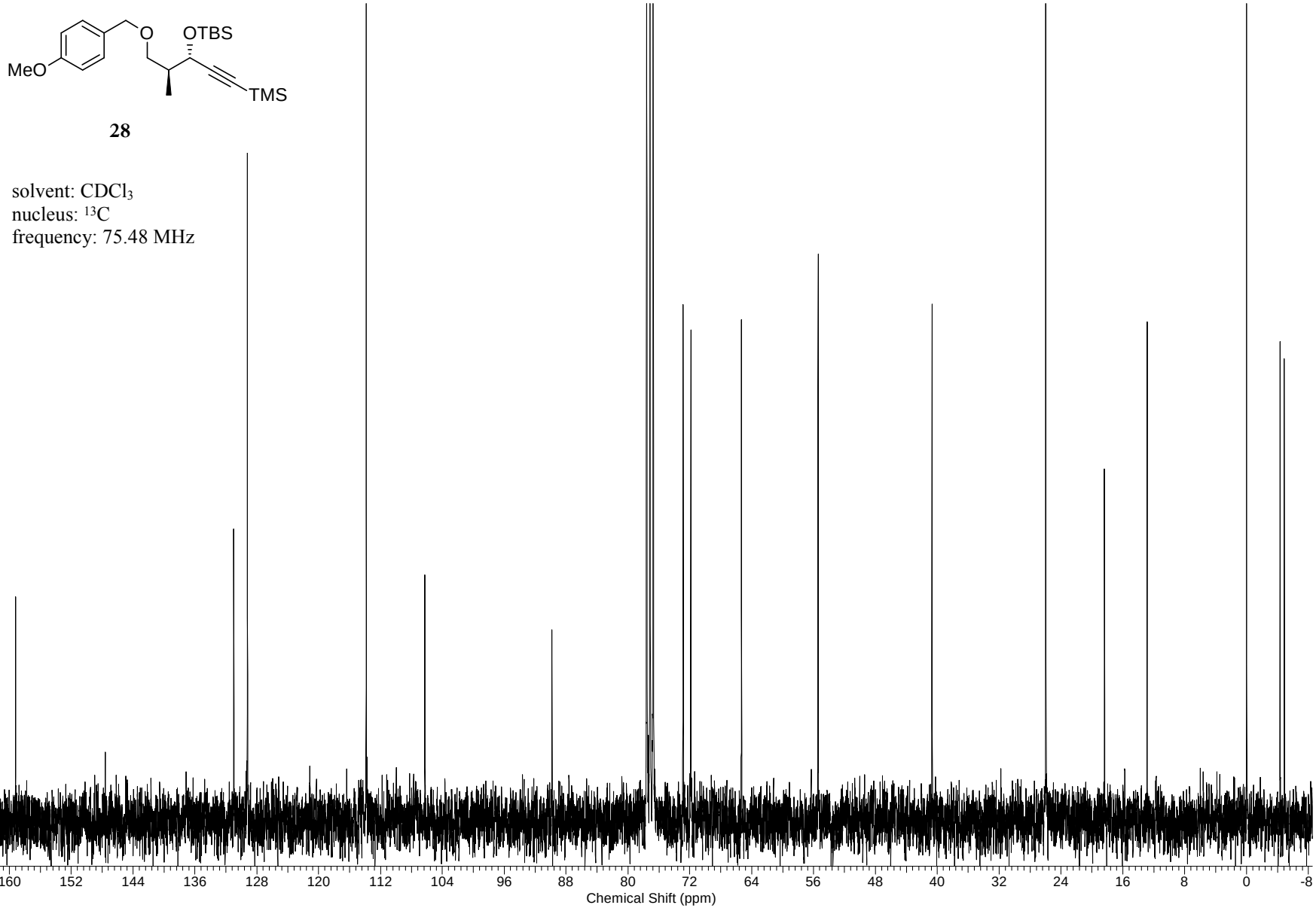
solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz

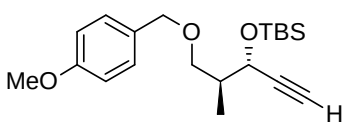

MeO
O
OH
TMS
17
solvent: CDCl3
nucleus: 13C
frequency: 75.48 MHz
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)



28

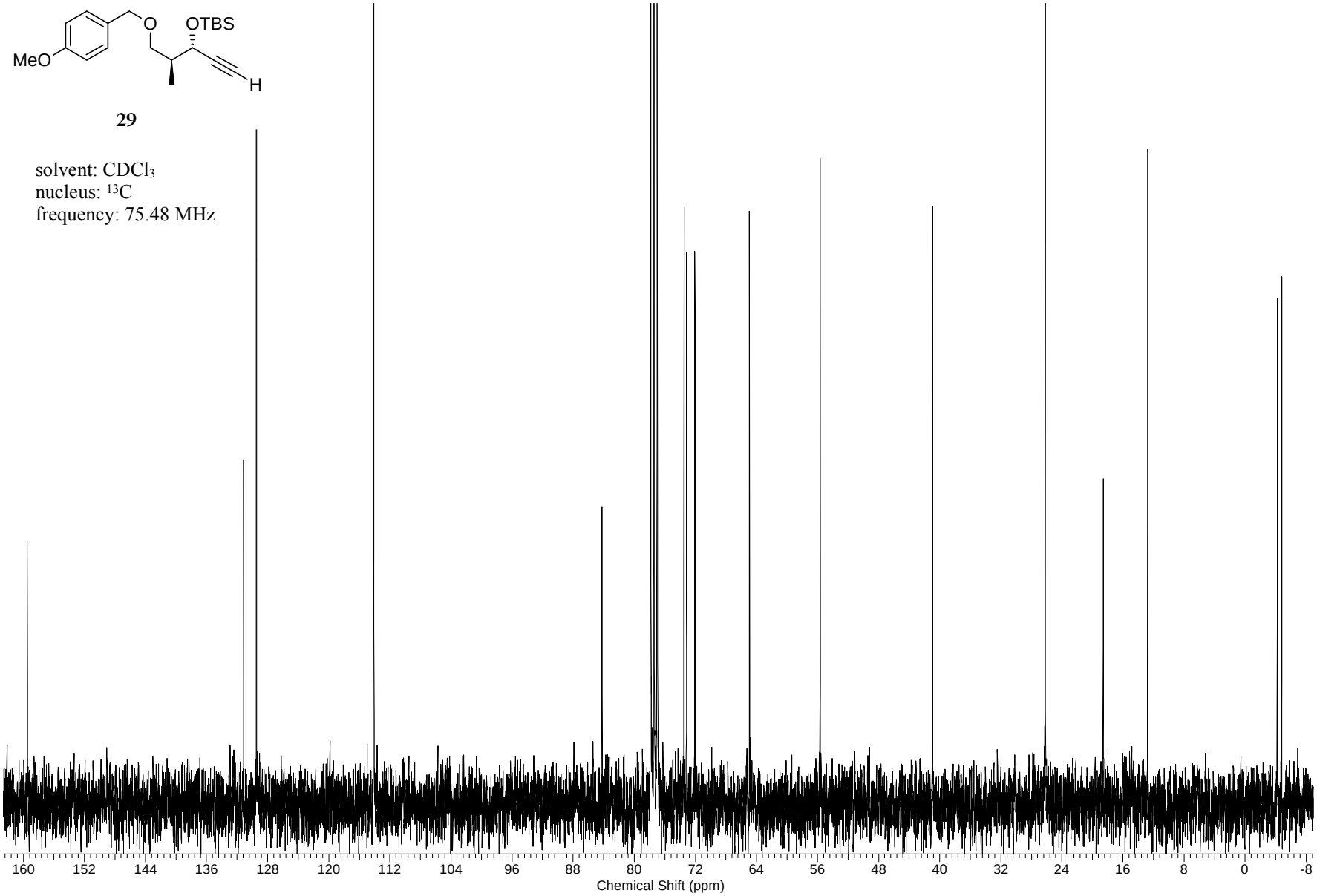
solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz

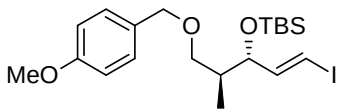




29

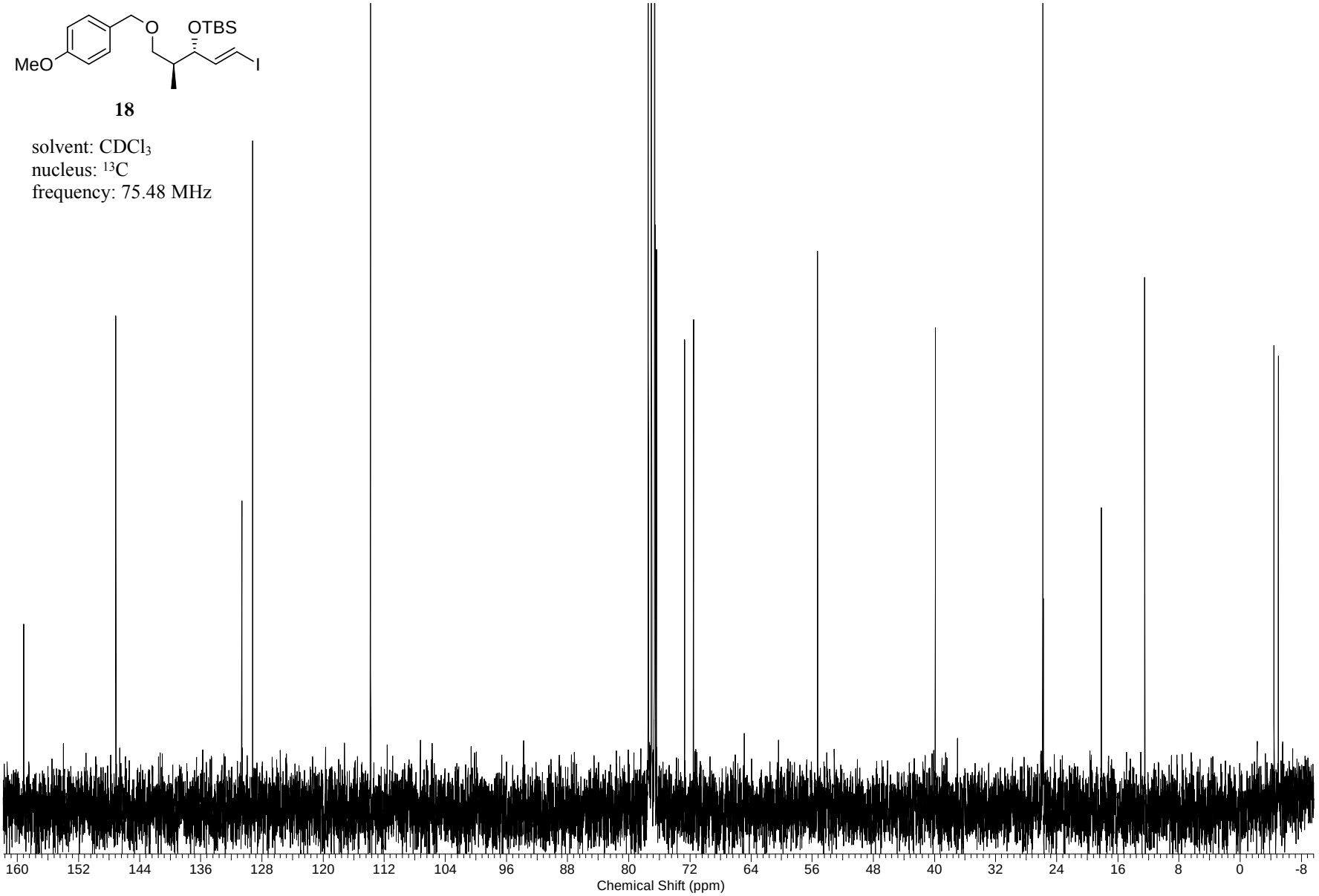
solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz

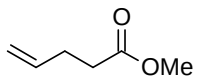




18

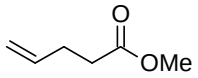
solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz





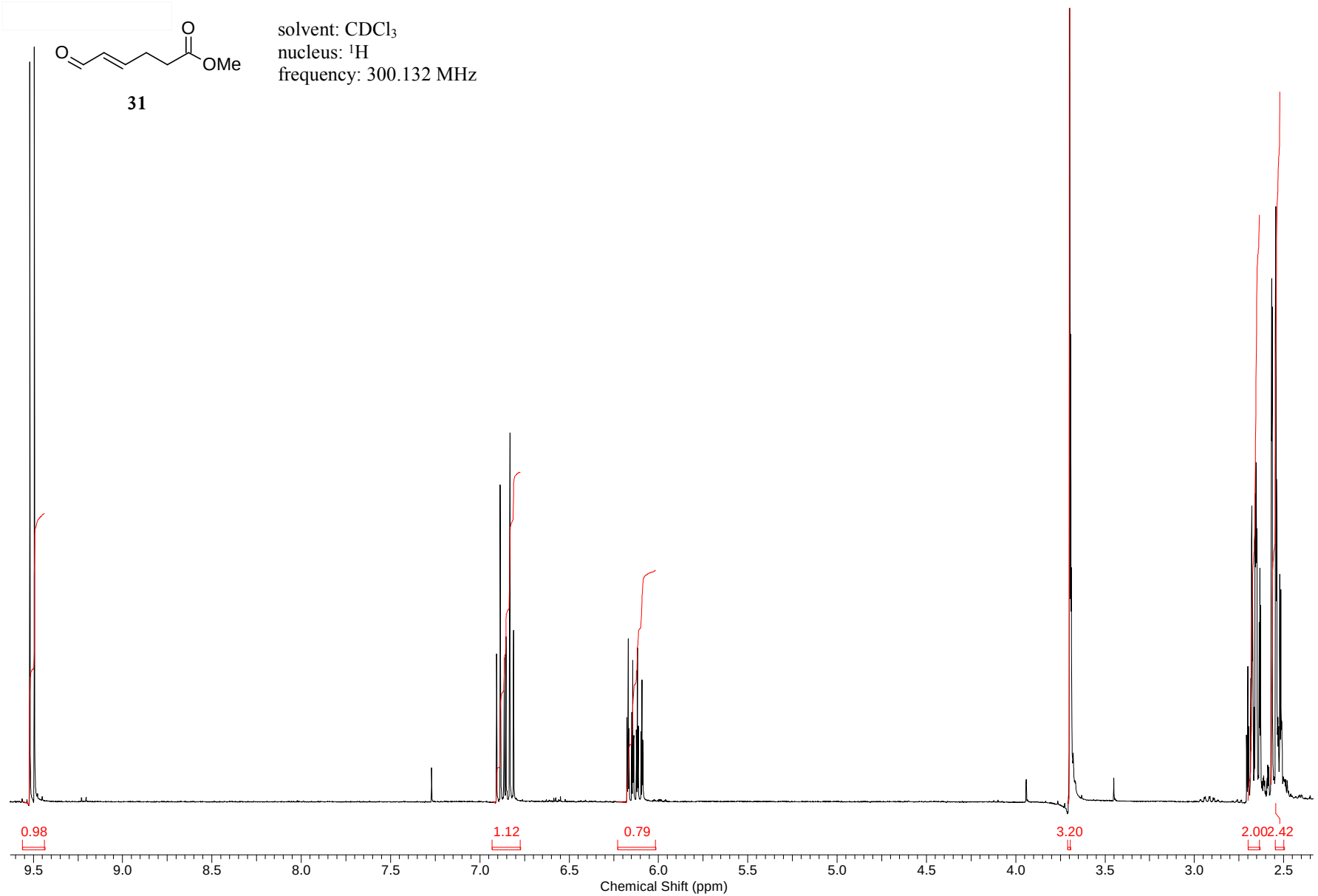
30

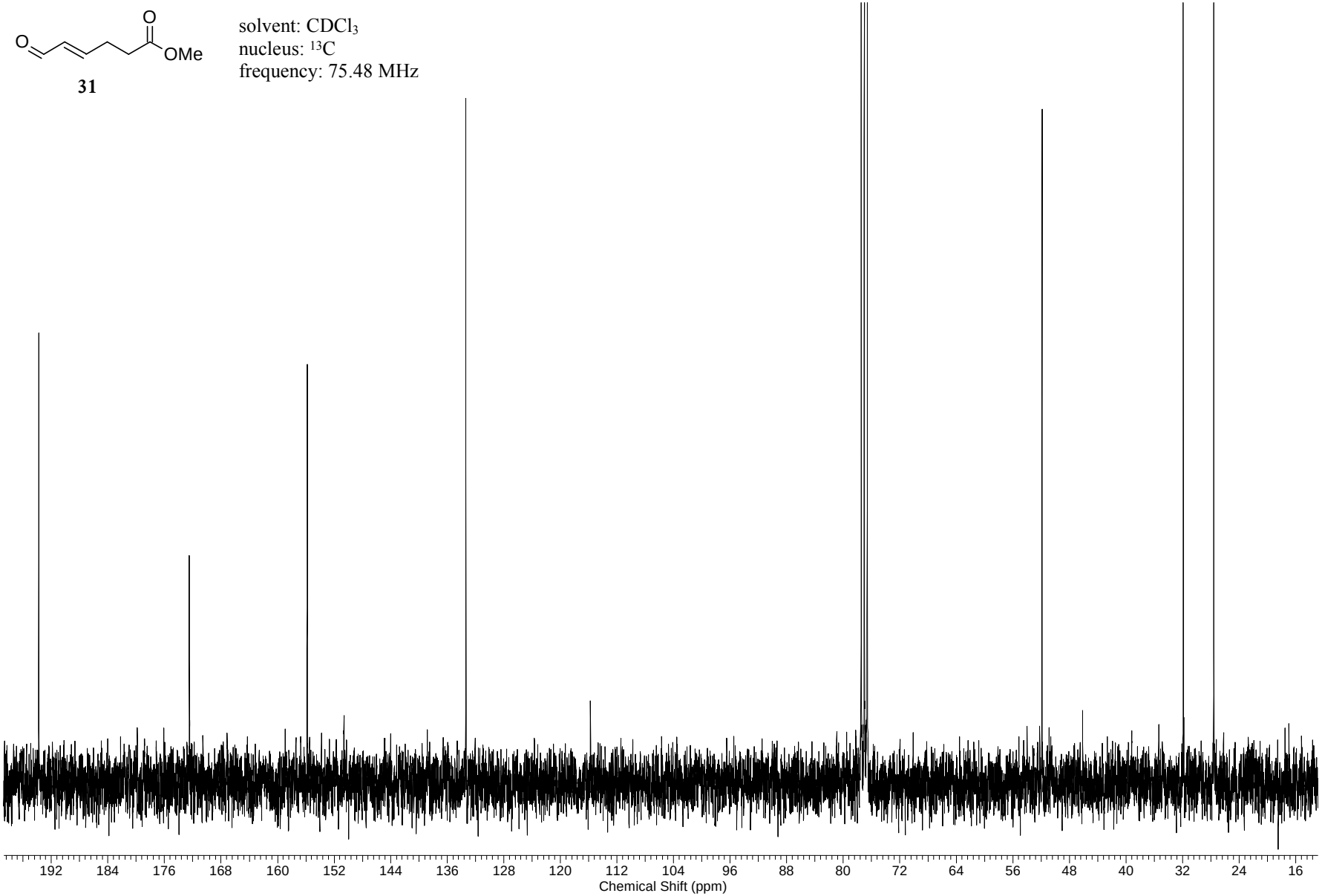
solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz

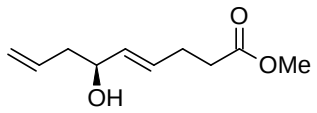


30

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz

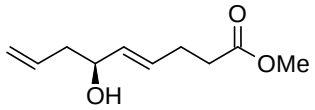






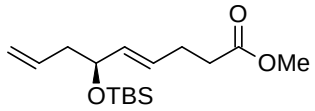
32

solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz



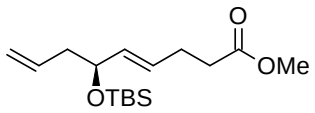
32

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz



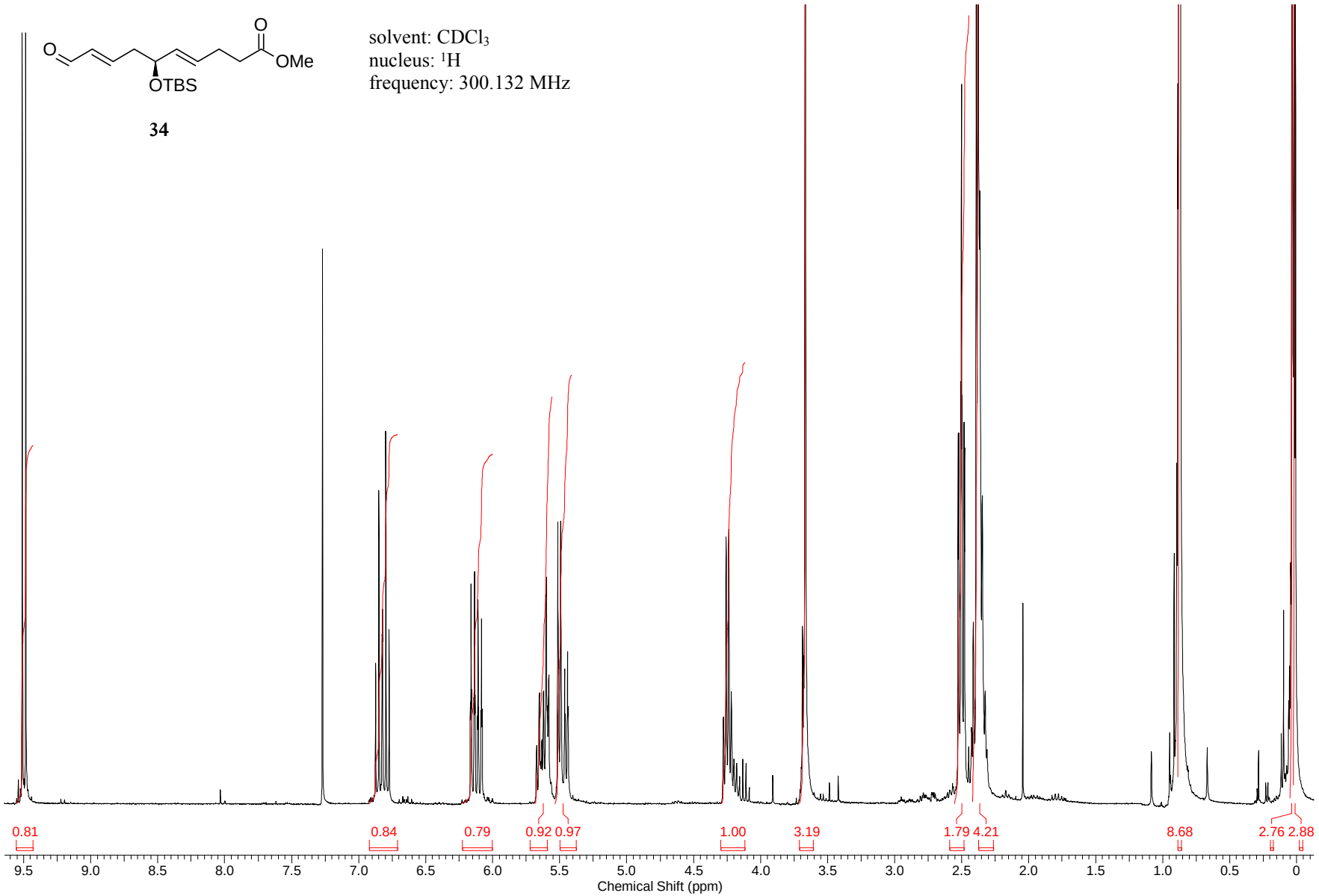
33

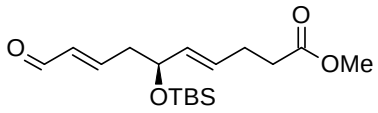
solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz



33

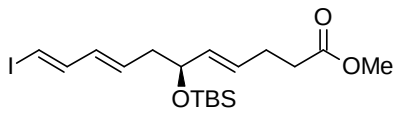
solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz





34

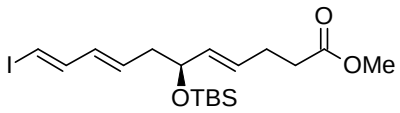
solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz



19

E/*Z* = 7:1

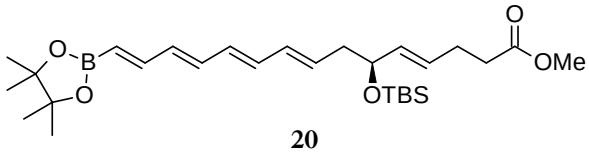
solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz



19

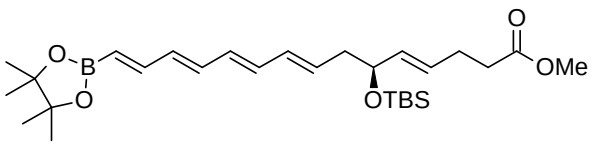
E/*Z* = 7:1

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz



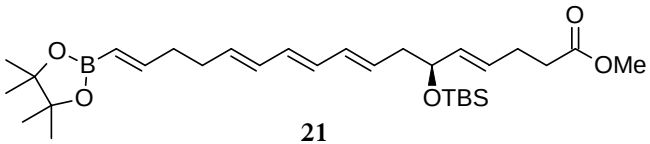
20

solvent: $CDCl_3$
nucleus: ^1H
frequency: 600.130 MHz



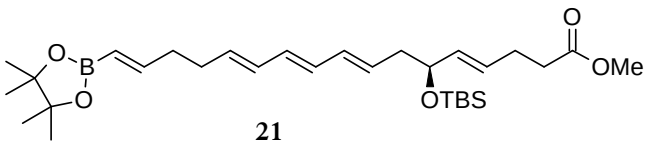
20

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz



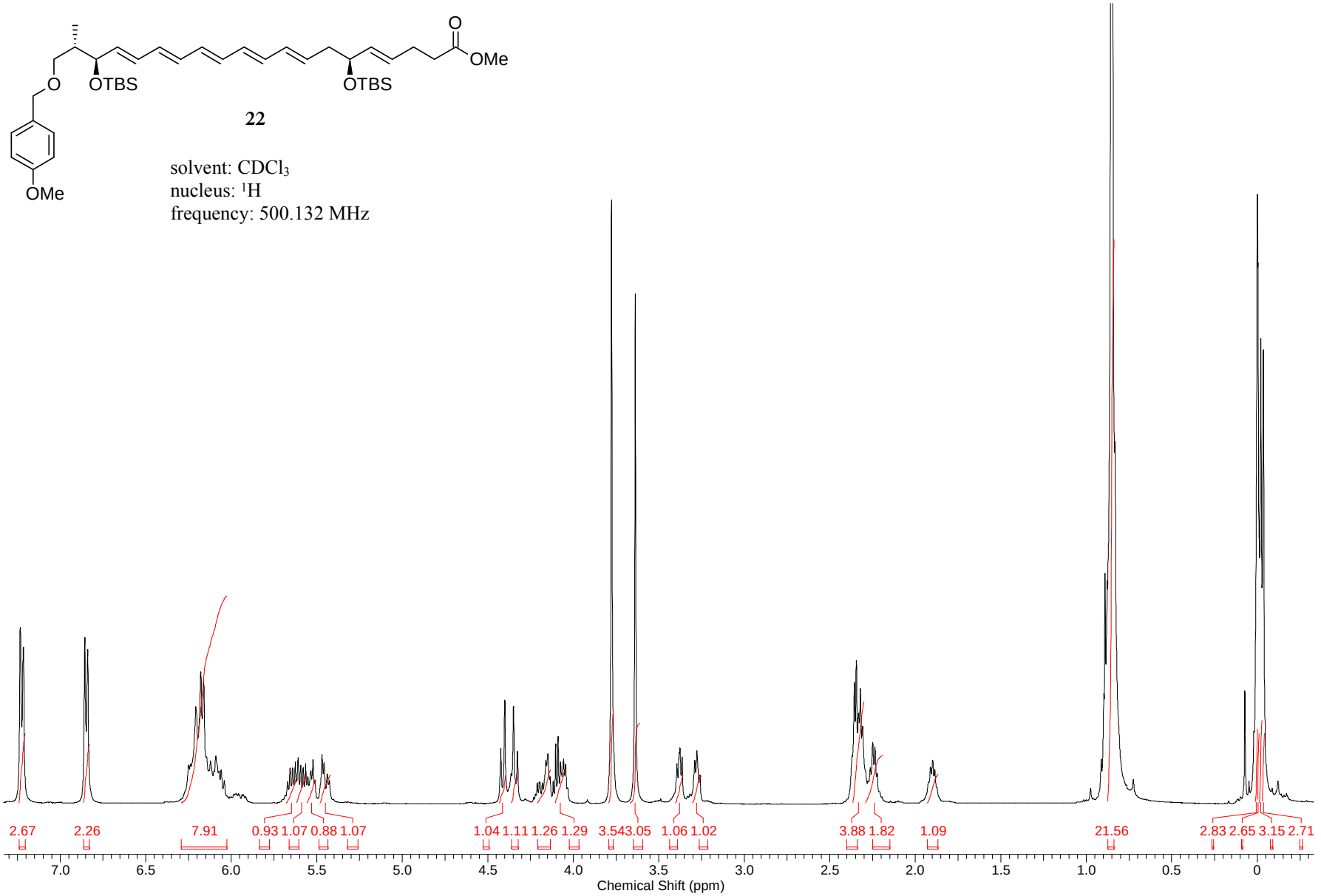
21

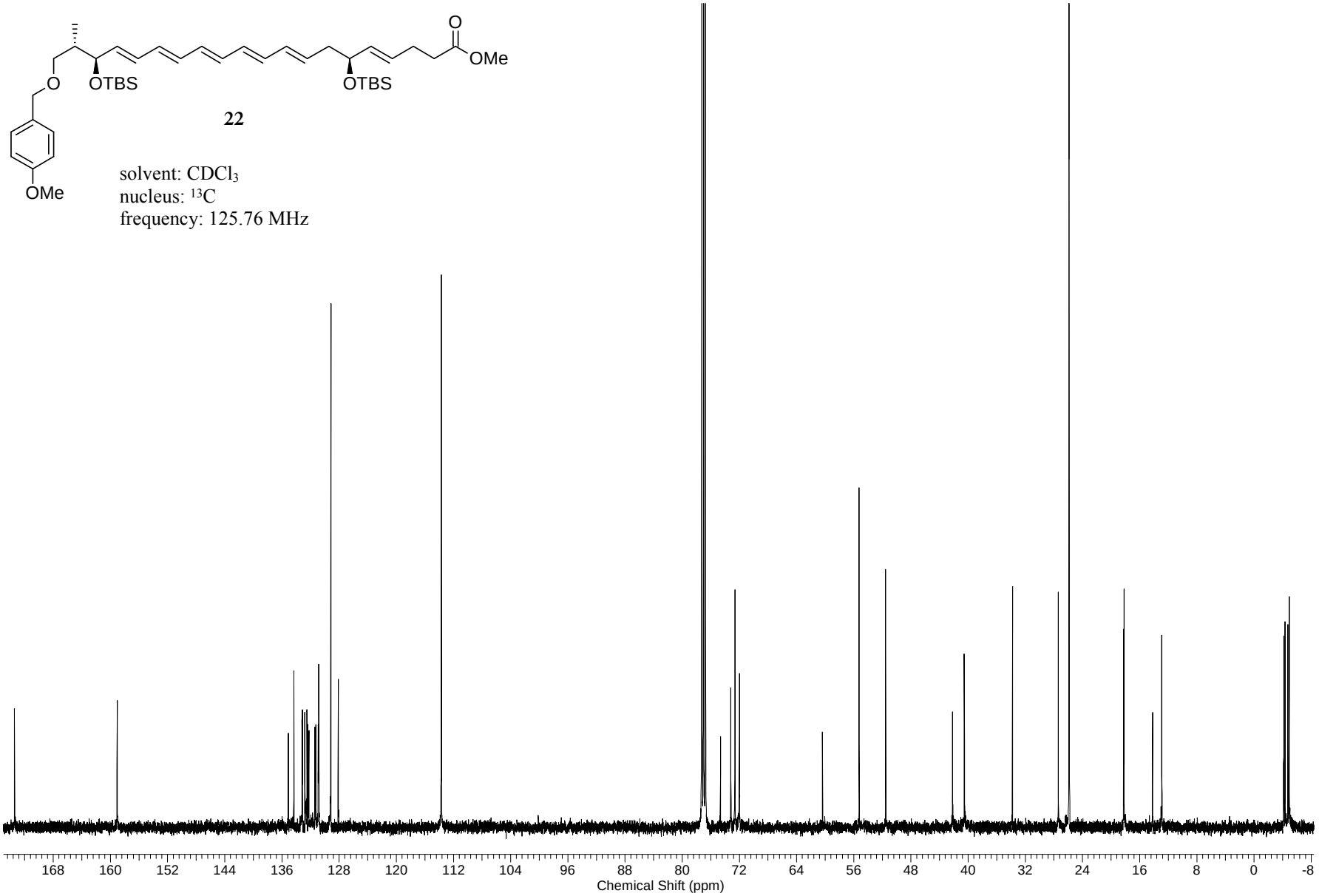
solvent: $CDCl_3$
nucleus: ^1H
frequency: 300.132 MHz

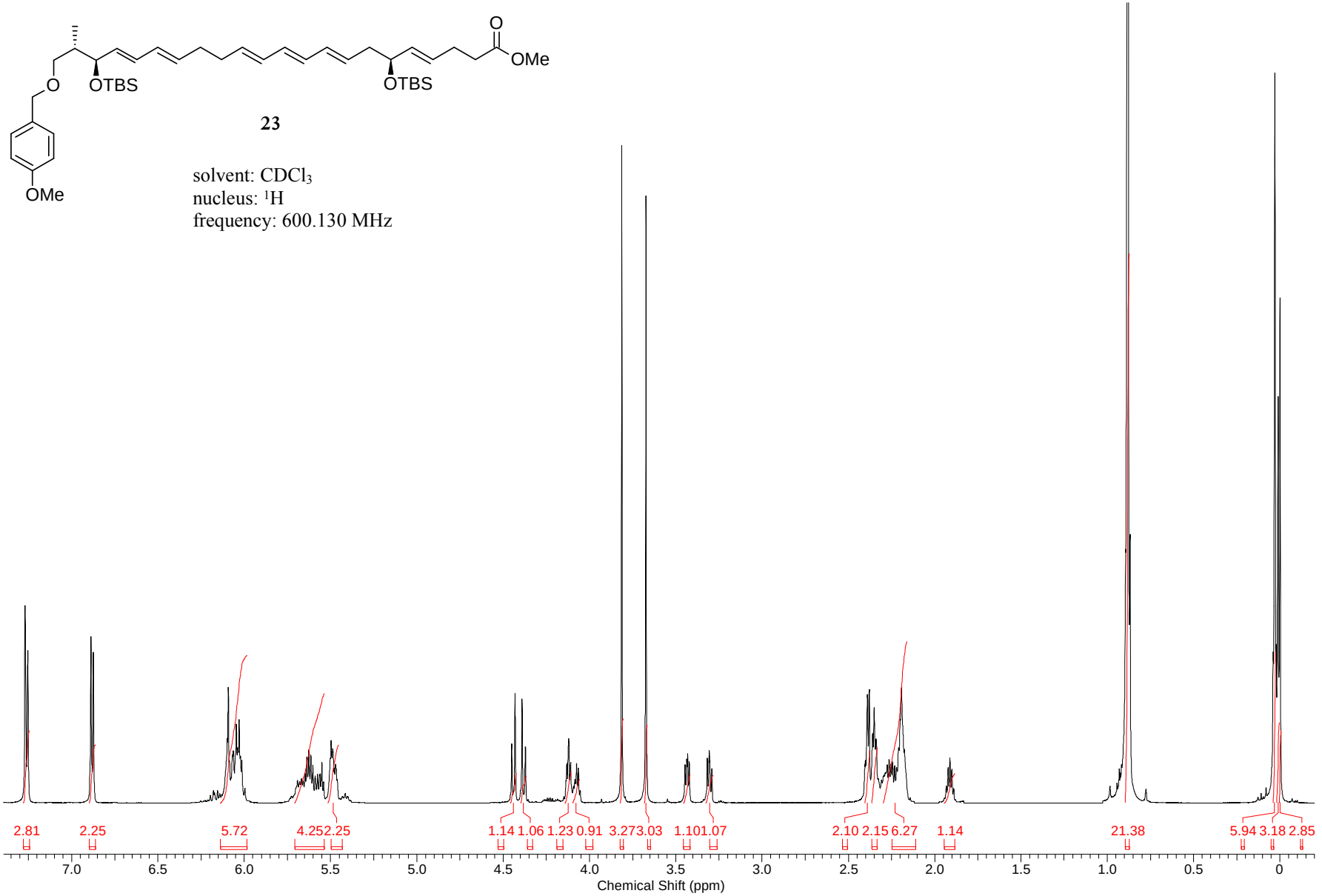


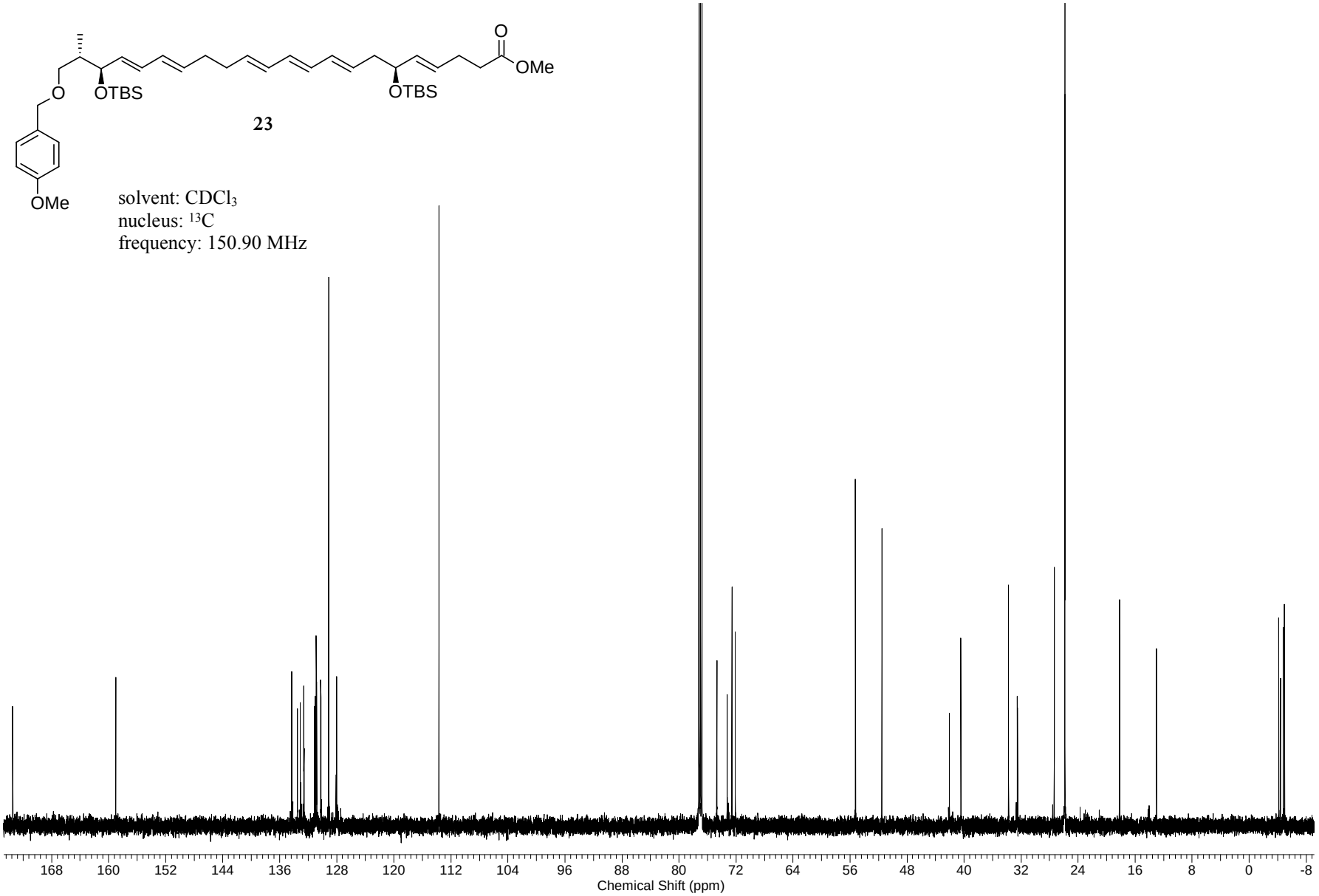
21

solvent: $CDCl_3$
nucleus: ^{13}C
frequency: 75.48 MHz









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