Supporting Information

Diastereoselective Formation of Tetrahydrofurans via Pd-AAA: Synthesis of the C13–C29 Subunit of Amphidinolide N

Barry M. Trost* and Jullien Rey

Department of Chemistry, Stanford University,
Stanford, California 94305-5080, United States

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General information

All chemicals were used as received, or purified using standard procedures. Solvents were dried by standard techniques and distilled under nitrogen or argon before use. All experiments were carried out in oven-dried glassware under an inert atmosphere of nitrogen or argon.

Analytical thin layer chromatography (TLC) was performed using EMD silica gel 60 F_{254} plates (0.25 mm); visualization of the developed chromatogram was performed by ultraviolet light and/or treatment with potassium permanganate or *para*-anysaldehyde stains followed by heating as deemed appropriate.

Flash column chromatography was carried out using silica gel (particle size 0.040-0.063 mm) under a positive pressure of nitrogen.

^{1}H and ^{13}C NMR spectra were respectively recorded at 300 MHz and 75 MHz using an NMR spectrometer Varian Inova console Sun Sparcstation 5. Chemical shifts (δ) are quoted in parts per million (ppm) and are referenced to a residual solvent peak.

Mass spectra were recorded using a Micromass Q-Tof API-US mass spectrometer (Waters Corporation, Milford, MA).

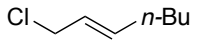
Infrared (IR) spectra were recorded on sodium chloride plates as thin films on a Thermo Scientific Nicolet IR100 FT-IR spectrometer, monitoring from 4000–700 cm^{-1}.

Optical rotations were measured on a Jasco DIP-1000 digital polarimeter using 5 cm cells and the sodium D line (589 nm) at ambient temperature in the solvent and concentration indicated.

Chiral HPLC was performed on Thermo Separation Products Spectra Series P-100 and an Agilent Technologies 1200 Series using Chiralcel© columns. Columns were eluted with heptane / *i*-propanol in ratios indicated. Retention times (R_t) are given in minutes.

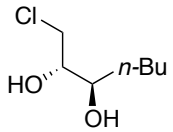
Experimental procedures and analytical data

Synthesis of chloride (9):



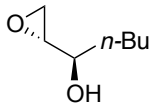
Triphenylphosphine (11.5 g, 43.8 mmol) was added to a solution alcohol **8** (5.00 g, 43.8 mmol, 96% pure from commercial source) in CCl_4 (34 mL) and the mixture was stirred at 80 ºC for 24 h, cooled to rt and concentrated *in vacuo*. The white residue was suspended in pentane, filtered and washed with pentane (× 2). The resulting solution was concentrated *in vacuo* and the crude product purified by flash column chromatography (eluting with hexanes) to yield **9** (4.02 g, 72%) as a colorless oil. The spectroscopic data matches that reported in the literature.[1]

Synthesis of diol (10):



$(DHQD)_2PHAL$ (211 mg, 0.271 mmol), $K_2OsO_4(OH)_4$ (50.0 mg, 0.136 mmol), $K_3Fe(CN)_6$ (26.8 g, 81.4 mmol), K_2CO_3 (11.3 g, 81.4 mmol), $NaHCO_3$ (6.84 g, 81.4 mmol) and $CH_3SO_2NH_2$ (2.58 g, 27.1 mmol) were successively added to a solution of *t*-BuOH (135 mL) and H_2O (135 mL). The mixture was then cooled to 0 ºC and alkene **9** (3.60 g, 27.1 mmol) was added. The dark orange solution was stirred at 0 ºC for 4h and the resulting yellow solution was quenched by addition of sodium metabisulfite and stirred for a further 30 min. The aqueous layer was extracted with EtOAc (× 3) and the combined organic extracts were washed with a 1 N aqueous solution of KOH, a 5% aqueous solution of HCl and brine. The organic phase was dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (eluting with gradient hexanes : EtOAc 7 : 3 to 1 : 1) to yield diol **10** (3.95 g, 87%) as a white solid. Lit: $[\alpha]_D^{25}$ = +11.0 (*c* 2.6, THF): ee = 94%;[2] Calculated for **10**: $[\alpha]_D^{25}$ = +13.2 (*c* 2.6, THF): ee determined for compound **12**. The other spectroscopic data matches that reported in the literature.[2]

Synthesis of epoxide (11):

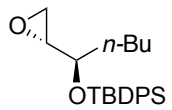


Sodium hydroxide (1.80 g, 45.0 mmol) was added portionwise to a solution of diol **10** (3.75 g, 22.5 mmol) in THF (33 mL) at 0 ºC. The mixture was stirred at 0 ºC for 2 h then diluted with Et_2O and

(1) Wang, Z.-M.; Shen, M. *Tetrahedron: Asymmetry* **1997**, *8*, 3393–3396.
(2) Vanhessche, K. P. M.; Wang, Z.-M.; Sharpless, K. B. *Tetrahedron Lett.* **1994**, *35*, 3469–3472.

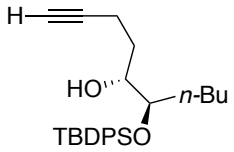
H_2O. The aqueous layer was extracted with Et_2O (× 2) and the combined organic extracts were washed with a saturated aqueous solution of NH_4Cl and brine. The organic phase was dried (Na_2SO_4), filtered and concentrated *in vacuo* to yield epoxide **11** (2.85 g, 97%) as a colorless oil. The spectroscopic data matches that reported in the literature.[2]

Synthesis of silyl ether (12):



Imidazole (1.57 g, 23.0 mmol) and TBDPSCl (2.40 mL, 9.22 mmol) were successively added to a solution of alcohol **11** (1.00 g, 7.68 mmol) in CH_2Cl_2 (30 mL) at 0 ºC. The mixture was stirred at rt for 14 h, diluted with CH_2Cl_2 and washed with H_2O and brine. The organic phase was dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (eluting with hexanes : Et_2O 96 : 4) to yield silyl ether **12** (2.70 g, 95%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73–7.69 (m, 4 H), 7.43–7.34 (m, 6 H), 3.36 (m, 1 H), 3.05 (ddd, $J_{H,H}$ = 6.7 Hz, $J_{H,H}$ = 4.1 Hz, $J_{H,H}$ = 2.7 Hz, 1 H), 2.73 (dd, $J_{H,H}$ = 4.9 Hz, $J_{H,H}$ = 4.1 Hz, 1 H), 2.47 (dd, $J_{H,H}$ = 4.9 Hz, $J_{H,H}$ = 2.7 Hz, 1 H), 1.54–1.46 (m, 2 H), 1.27–1.06 (m, 13 H), 0.78 (t, $J_{H,H}$ = 7.1 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.0, 134.2, 133.9, 129.5, 127.4, 127.3, 75.1, 55.7, 44.9, 34.4, 27.0, 22.6, 19.4, 13.9 ppm. HRMS (ESI): calcd. for $C_{23}H_{32}NaO_2Si$ 391.2064 $[M + Na]^+$; found 391.2054. IR (neat, film): υ_{max} = 3071, 3049, 1590, 1471, 1427, 1390, 1362, 1257, 1111, 1008, 944 cm^{-1}. $[a]_D^{25}$ = −22.3 (*c* 0.16, $CHCl_3$). Chiral HPLC: OD-H eluting with heptane : *i*-PrOH (5000 : 1), 0.8 mL/min, 254 nm, R_t (*major*) = 12.0 min, R_t (*minor*) = 15.3 min, ee = 97%.

Synthesis of alkyne (14):

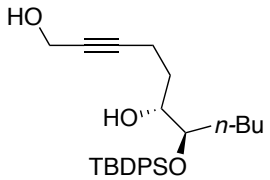


$HgCl_2$ (17 mg, 0.0615 mmol) and a crystal of iodine were added to a suspension of Mg turnings (600 mg, 25.0 mmol) in dry Et_2O (12 mL). The mixture was cooled to 0 ºC and propargyl bromide (**13**) (1.37 mL, 12.3 mmol, 80 wt % in toluene) was added dropwise. The resulting mixture was then stirred at rt for 1 h (exothermic reaction, a condenser is needed) and diluted with 4 mL of Et_2O to yield a 0.77 M solution of allenylmagnesium bromide.

A freshly prepared solution of allenylmagnesium bromide (10.6 mL, 8.14 mmol, 0.77 M in Et_2O) was added dropwise to a solution of epoxide **12** (1.00 g, 2.71 mmol) in Et_2O (60 mL) at –78 ºC. The mixture was stirred at –78 ºC for 30 min and warmed to rt over 1 h. The mixture was cooled to 0 ºC and quenched by addition of a saturated aqueous solution of NH_4Cl. The aqueous layer was extracted with Et_2O (× 4) and the combined organic extracts were washed with brine, dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (eluting with gradient hexanes : Et_2O 95 : 5 to 9 : 1) to yield alkyne **14** (905 mg, 82%) as a colorless oil. ^{1}H

NMR (300 MHz, $CDCl_3$): δ = 7.70–7.66 (m, 4 H), 7.47–7.35 (m, 6 H), 3.67–3.54 (m, 2 H), 2.28–2.21 (m, 3 H), 1.93 (t, $J_{H,H}$ = 2.7 Hz, 3 H), 1.86–1.55 (m, 3 H), 1.37–1.29 (m, 1 H), 1.20–1.00 (m, 13 H), 0.71 (t, $J_{H,H}$ = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.9, 135.8, 133.9, 133.3, 129.8, 129.7, 127.7, 127.5, 84.2, 76.3, 71.5, 68.4, 33.0, 32.7, 27.1, 26.9, 22.6, 19.5, 15.1, 13.9 ppm. HRMS (ESI): calcd. for $C_{26}H_{36}NaO_2Si$ 431.2377 $[M + Na]^+$; found 431.2358. IR (neat, film): υ_{max} = 3460, 3310, 3071, 1471, 1428, 1390, 1111, 1082 cm^{-1}. $[\alpha]_D^{25}$ = −1.80 (*c* 0.34, $CHCl_3$).

Synthesis of propargyl alcohol (15):

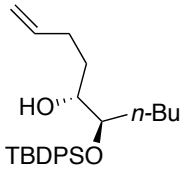


n-BuLi (2.20 mL, 4.85 mmol, 2.20 M in hexanes) was added dropwise to a solution of alkyne **14** (900 mg, 2.20 mmol) in dry Et_2O (5.4 mL) at –78 ºC. The insoluble dianion solution was then slowly warmed to –15 ºC, diluted with dry Et_2O (9.2 mL) and stirred for 1 h. Dry paraformaldehyde (200 mg, 6.60 mmol) was added in one portion and the mixture warmed to rt then stirred at reflux for 3.5 h. The mixture was cooled to rt, quenched by addition of H_2O and the aqueous layer extracted with EtOAc (× 4). The combined organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (eluting with gradient hexanes : Et_2O 65 : 35 to 60 : 40) to yield propargyl alcohol **15** (675 mg, 70%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.70–7.66 (m, 4 H), 7.47–7.36 (m, 6 H), 4.22 (dt, $J_{H,H}$ = 6.0 Hz, $J_{H,H}$ = 2.1 Hz, 2 H), 3.68–3.53 (m, 2 H), 2.31–2.26 (m, 2 H), 2.22 (d, $J_{H,H}$ = 6.9 Hz, 1 H), 1.69–1.51 (m, 3 H), 1.45 (t, $J_{H,H}$ = 6.1 Hz, 1 H), 1.38–1.12 (m, 2 H), 1.07–1.01 (m, 12 H), 0.71 (t, $J_{H,H}$ = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.9, 135.8, 133.9, 133.3, 129.8, 129.7, 127.7, 127.5, 86.1, 78.6, 76.3, 71.6, 51.4, 33.0, 32.7, 27.1, 27.0, 22.6, 19.5, 15.4, 13.9 ppm. HRMS (ESI): calcd. for $C_{27}H_{38}NaO_3Si$ 461.2482 $[M + Na]^+$; found 461.2476. IR (neat, film): υ_{max} = 3389, 3072, 3051, 1471, 1428, 1390, 1111, 1079, 1019 cm^{-1}. $[\alpha]_D^{25}$ = +0.42 (*c* 0.35, $CHCl_3$).

General procedure for the redox isomerisation/oxa-Michael addition:

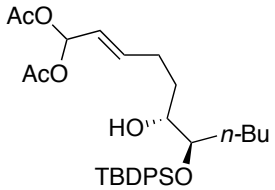
A vial containing a magnetic stirrer, neat propargyl alcohol **15** (1 eq.), $IndRu(PPh_3)_2Cl$ (5 mol %) and CSA (10 to 30 mol %) was purged with Ar several times. Freshly distilled THF (0.2 M) was then added and the solution stirred for 5 min. $In(OTf)_3$ (5 mol %, glove box, stock solution in freshly distilled THF) was added and the mixture was heated (66 ºC or 40 ºC) for 2 h, cooled to rt and concentrated *in vacuo*. The dr and conversion was determined by analysis of the crude ^1H NMR. The crude product was purified by flash column chromatography (eluting with PE : Et_2O 1 : 1) to yield **17** and **18** as an inseparable mixture of isomers.

Synthesis of alkene (22):



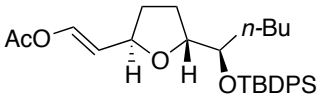
Allylmagnesium bromide (**21**) (8.13 mL, 8.13 mmol, 1 M in Et_2O) was added dropwise to a solution of epoxide **12** (1.00 g, 2.71 mmol) and CuI (78 mg, 0.407 mmol) in THF (27 mL) at –78 ºC. The mixture was then warmed to rt and stirred for 1 h, cooled to 0 ºC and quenched by addition of a saturated aqueous solution of NH_4Cl. The aqueous layer was extracted with Et_2O (× 2) and the combined organic extracts were washed with brine, dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (eluting with gradient hexanes : Et_2O 96 : 4 to 95 : 5) to yield alkene **22** (990 mg, 89%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70–7.67 (m, 4 H), 7.47–7.35 (m, 6 H), 5.85–5.72 (m, 1 H), 5.01–4.92 (m, 2 H), 3.59–3.46 (m, 2 H), 2.20 (d, $J_{H,H}$ = 7.3 Hz, 1 H), 2.19–1.95 (m, 2 H), 1.65–1.43 (m, 3 H), 1.38–1.27 (m, 1 H), 1.17–0.97 (m, 13 H), 0.71 (t, $J_{H,H}$ = 7.1 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.5, 136.0, 135.9 134.1, 133.4, 129.8, 129.6, 127.7, 127.5, 114.6, 76.2, 72.1, 33.1, 33.0, 30.1, 27.1, 27.0, 22.5, 19.5, 13.9 ppm. HRMS (ESI): calcd. for $C_{26}H_{38}NaO_2Si$ 433.2533 $[M + Na]^+$; found 433.2517. IR (neat, film): υ_{max} = 3570, 3463, 3072, 1471, 1428, 1390, 1111, 1076, 912 cm^{-1}. $[\alpha]_D^{25}$ = –2.75 (*c* 0.26, $CHCl_3$).

Synthesis of *gem*-diacetate (19):



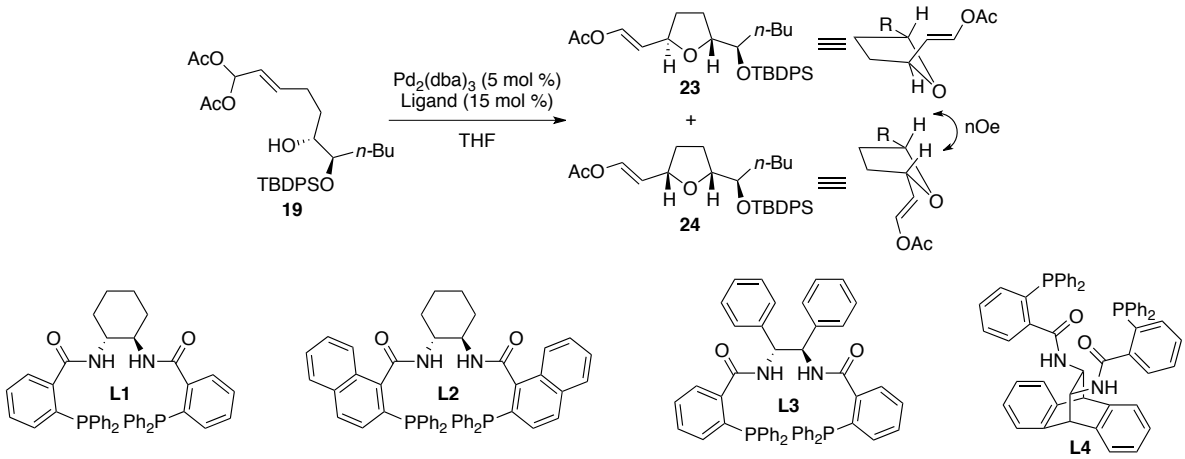
Grubbs catalyst second generation (161 mg, 0.190 mmol) was added to a solution of alkene **22** (2.60 g, 6.33 mmol) and allyl *gem*-diacetate (**20**) (1.97 mL, 12.7 mmol) in degassed CH_2Cl_2 (32 mL). The mixture was then stirred at 40 ºC for 6 h, cooled to rt and concentrated *in vacuo*. The crude product was purified by flash column chromatography (eluting with gradient hexanes : Et_2O 85 : 15 to 75 : 25) to yield alkene **19** (2.46 g, 72%) as a light yellow viscous oil (ratio *E* / *Z* 95 : 5 by the crude ^{1}H NMR). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69–7.65 (m, 4 H), 7.47–7.36 (m, 6 H), 7.08 (d, $J_{H,H}$ = 6.5 Hz, 1 H), 5.98 (dt, $J_{H,H}$ = 15.7 Hz, $J_{H,H}$ = 6.6 Hz, 1 H), 5.49 (dd, $J_{H,H}$ = 15.7 Hz, $J_{H,H}$ = 6.5 Hz, 1 H), 3.56–3.42 (m, 2 H), 2.20 (*app*-d, $J_{H,H}$ = 7.2 Hz, 2 H), 2.08 (*app*-s, 7 H), 1.60–1.27 (m, 4 H), 1.18–0.97 (m, 13 H), 0.71 (t, $J_{H,H}$ = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.7, 137.7, 136.0, 135.9, 133.9, 133.3, 129.8, 129.7, 127.7, 127.5, 123.4, 89.7, 76.2, 71.9, 33.0, 32.7, 28.3, 27.1, 26.9, 22.5, 20.9, 19.5, 13.7 ppm. HRMS (ESI): calcd. for $C_{31}H_{44}NaO_6Si$ 563.2799 $[M + Na]^+$; found 563.2803. IR (neat, film): υ_{max} = 3569, 3072, 3050, 1761, 1471, 1428, 1372, 1243, 1207, 1111, 1050, 1008, 957 cm^{-1}. $[\alpha]_D^{25}$ = +3.16 (*c* 0.26, $CHCl_3$).

Synthesis of *trans*-THF (23):



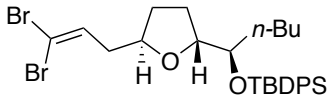
$Pd_2(dba)_3.CHCl_3$ (83.0 mg, 0.081 mmol) and (*R*,*R*)-standard Trost ligand (**L1**) (167 mg, 0.242 mmol) were dissolved in degassed THF (21.5 mL). The mixture was then stirred at rt for 20 min and freshly distilled triethylamine (500 μL, 3.54 mmol) was added. The resulting orange solution was added *via* cannula to neat alkene **19** (1.74 g, 3.22 mmol), stirred at 50 ºC for 18 h, then cooled to rt and concentrated *in vacuo*. The crude ^{1}H NMR showed the presence of two diastereoisomers **23** and **24** with a ratio of 4.6 : 1 in favor of the desired *trans*-THF. The crude mixture was purified by flash column chromatography (eluting with hexanes : Et_2O 95 : 5) to yield a mixture of **23** and **24** (1.27 g, 82%). Repurification of this mixture by flash column chromatography (eluting with hexanes : Et_2O 96.5 : 3.5) led to pure *trans*-THF **23** (1.04 g, 67%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71–7.68 (m, 4 H), 7.42–7.32 (m, 6 H), 7.21 (d, $J_{H,H}$ = 12.5 Hz, 1 H), 5.37 (dd, $J_{H,H}$ = 12.5 Hz, $J_{H,H}$ = 7.6 Hz, 1 H), 4.26–4.19 (m, 1 H), 4.09–4.02 (m, 1 H), 3.63 (dt, $J_{H,H}$ = 5.5 Hz, $J_{H,H}$ = 5.5 Hz, 1 H), 2.13 (s, 3 H), 2.06–1.74 (m, 3 H), 1.64–1.45 (m, 2 H), 1.40–1.28 (m, 1 H), 1.22–1.04 (m, 13 H), 0.73 (t, $J_{H,H}$ = 7.1 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.9, 136.9, 136.0, 135.9, 134.7, 134.2, 129.4, 129.3, 127.3, 127.2, 115.5, 80.8, 76.0, 75.6, 33.4, 32.6, 27.5, 27.1, 22.7, 20.7, 19.6, 13.9 ppm (One carbon obscured in the aliphatic region). HRMS (ESI): calcd. for $C_{29}H_{40}NaO_4Si$ 503.2588 [M + Na]$^+$; found 503.2584. IR (neat, film): υ_{max} = 3072, 1760, 1678, 1471, 1428, 1371, 1220, 1110, 933 cm^{-1}. $[\alpha]_D^{25}$ = –2.85 (*c* 0.60, $CHCl_3$).

Attempts at improving the formation of the desired *trans*-THF (23) by Pd-AAA catalysis:



Entry	Conditions	Conversion	dr from the crude ^{1}H NMR (**23** : **24**)
1	**L2** (R,R), 50 °C, 0.15 M	(35%)	**1** : 2
2	**L3** (R,R), 50 °C, 0.15 M	(100%)	**1.1** : 1
3	**L4** (R,R), 50 °C, 0.15 M	(70%)	> **1** : 10
4	**L4** (S,S), 50 °C, 0.15 M	(100%)	**1** : 1.5
5	**L1** (R,R), 35 °C, Et_3N, 0.15 M	(35%)	**4.3** : 1
6	**L1** (R,R), 50 °C, NaF, 0.15 M	(90%)	**3** : 1

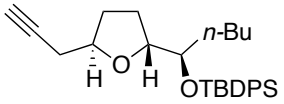
<u>Synthesis of dibromoalkene (25a) *via* aldehyde (17) (first step of the Corey-Fuchs reaction):</u>



Triethylamine (215 μL, 1.55 mmol) was added dropwise to a solution of vinyl acetate **23** (710 mg, 1.48 mmol) in MeOH (30 mL). The mixture was then stirred at rt for 45 min, diluted with $CHCl_3$ and quenched by addition of a saturated aqueous solution of NH_4Cl. The aqueous layer was extracted with $CHCl_3$ (× 3) and the combined organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. Aldehyde **17** was used in the next step with no further purification.

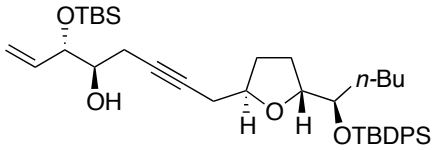
Triphenylphosphine (1.55 g, 5.92 mmol) was added in portions to a solution of carbon tetrabromide (980 mg, 2.96 mmol) in CH_2Cl_2 (10.7 mL) at 0 ºC. The mixture was stirred at 0 ºC for 30 min and a solution of freshly prepared aldehyde **17** (1.48 mmol) in CH_2Cl_2 (4.8 mL) was then added. The mixture was stirred for a further 20 min and quenched by addition onto H_2O. The aqueous layer was extracted with CH_2Cl_2 (× 2) and the combined organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (eluting with gradient hexanes : Et_2O 99 : 1 to 99 : 2) to yield alkene **25a** (700 mg, 80% over 2 steps) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72–7.69 (m, 4 H), 7.43–7.33 (m, 6 H), 6.15 (t, $J_{H,H}$ = 7.2 Hz, 1 H), 4.02–3.95 (m, 1 H), 3.75–3.66 (m, 1 H), 3.60–3.54 (m, 1 H), 2.22–2.04 (m, 2 H), 1.93–1.82 (m, 2 H), 1.66–1.10 (m, 8 H), 1.04 (s, 9 H), 0.78 (t, $J_{H,H}$ = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.0, 135.9, 135.7, 134.6, 134.5, 129.3, 129.2, 127.7, 127.2, 81.5, 76.7, 76.0, 38.9, 32.7, 31.8, 27.8, 27.3, 27.1, 22.8, 19.7, 14.0 ppm (One quaternary carbon obscured). HRMS (ESI): calcd. for $C_{28}H_{38}Br_2NaO_2Si$ 615.0900 $[M + Na]^+$; found 615.0905. IR (neat, film): υ_{max} = 3071, 3048, 1471, 1427, 1110, 822 cm^{-1}. $[\alpha]_D^{25}$ = +16.2 (*c* 0.65, $CHCl_3$).

Synthesis of alkyne (25):



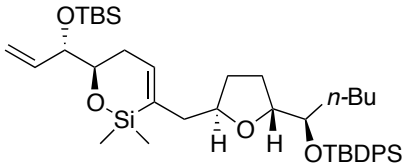
n-BuLi (1.25 mL, 2.65 mmol, 2.15 M in hexanes) was added dropwise to a solution of alkene **25a** (630 mg, 1.06 mmol) in THF (10.6 mL) at –78 ºC. The mixture was stirred at –78 ºC for 20 min, warmed to –30 ºC and stirred for a further 30 min. The mixture was then quenched by addition of a saturated aqueous solution of NH_4Cl at –78 ºC, warmed to rt and extracted with Et_2O (× 3). The combined organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (eluting with hexanes : Et_2O 98 : 2) to yield alkyne **25** (402 mg, 87%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71–7.68 (m, 4 H), 7.43–7.32 (m, 6 H), 4.06 (dt, $J_{H,H}$ = 7.1 Hz, $J_{H,H}$ = 5.2 Hz, 1 H), 3.98–3.89 (m, 1 H), 3.63 (dt, $J_{H,H}$ = 6.4 Hz, $J_{H,H}$ = 5.2 Hz, 1 H), 2.35 (ddd, $J_{H,H}$ = 12.4 Hz, $J_{H,H}$ = 5.0 Hz, $J_{H,H}$ = 2.7 Hz, 1 H), 2.23 (ddd, $J_{H,H}$ = 12.4 Hz, $J_{H,H}$ = 7.3 Hz, $J_{H,H}$ = 2.7 Hz, 1 H), 2.08–1.99 (m, 1 H), 1.93 (t, $J_{H,H}$ = 2.7 Hz, 1 H), 1.92–1.84 (m, 1 H), 1.80–1.58 (m, 2 H), 1.53–1.28 (m, 2 H), 1.22–1.05 (m, 13 H), 0.74 (t, $J_{H,H}$ = 7.1 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.1, 136.0, 134.7, 134.4, 129.3, 127.3, 127.2, 81.4, 81.3, 77.2, 75.6, 69.4, 32.5, 31.5, 27.4, 27.3, 27.1, 25.2, 22.7, 19.6, 13.9 ppm (One carbon obscured (TBDPS)). HRMS (ESI): calcd. for $C_{28}H_{38}NaO_2Si$ 457.2533 $[M + Na]^+$; found 457.2529. IR (neat, film): υ_{max} = 3311, 3071, 3050, 1471, 1428, 1389, 1361, 1110, 939 cm^{-1}. $[\alpha]_D^{25}$ = +33.0 (*c* 0.19, $CHCl_3$).

Synthesis of homopropargyl alcohol (27):



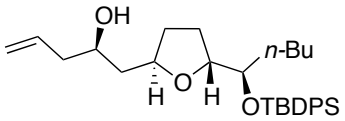
n-BuLi (250 μL, 0.534 mmol, 2.15 M in hexanes) was added dropwise to a solution of alkyne **25** (211 mg, 0.485 mmol) in THF (1.3 mL) at –40 ºC. The mixture was stirred at –40 ºC for 30 min, cooled to –78 ºC and $BF_3.Et_2O$ was added dropwise. A solution of epoxide **26** in THF (0.30 mL) was then added and the resulting mixture was stirred at –78 ºC for 15 min and slowly warmed to rt over 1 h. The mixture was diluted with Et_2O and quenched by addition of a saturated aqueous solution of NH_4Cl. The aqueous phase was extracted with Et_2O (× 3) and the combined organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (eluting with gradient hexanes : Et_2O 96 : 4 to 90 : 10) to yield homopropargyl alcohol **27** (202 mg, 66%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72–7.69 (m, 4 H), 7.43–7.32 (m, 6 H), 5.84 (ddd, $J_{H,H}$ = 17.3 Hz, $J_{H,H}$ = 10.4 Hz, $J_{H,H}$ = 6.7 Hz, 1 H), 5.32–5.20 (m, 2 H), 4.19–4.16 (m, 1 H), 4.08–4.02 (m, 1 H), 3.95–3.88 (m, 1 H), 3.68–3.61 (m, 2 H), 2.46–2.17 (m, 5 H), 2.05–1.85 (m, 2 H), 1.80–1.57 (m, 2 H), 1.53–1.26 (m, 2 H), 1.24–1.05 (m, 13 H), 0.91 (s, 9 H), 0.75 (t, $J_{H,H}$ = 7.1 Hz, 3 H), 0.09 and 0.06 (2 × s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.9, 136.0, 135.9, 134.7, 134.3, 129.3, 127.3, 127.2, 117.3, 81.3, 79.2, 77.5, 77.3, 75.8, 75.6, 73.2, 32.4, 31.6, 27.4, 27.2, 27.1, 25.8, 25.5, 22.7, 22.6, 19.6, 18.1, 13.9, –4.4, –4.9 ppm (One carbon obscured (TBDPS)). HRMS (ESI): calcd. for $C_{39}H_{60}NaO_4Si_2$ 671.3922 $[M + Na]^+$; found 671.3924. IR (neat, film): υ_{max} = 3411, 3072, 1471, 1428, 1254, 1110, 1069, 861, 836 cm^{-1}. $[\alpha]_D^{25}$ = +22.2 (*c* 0.15, $CHCl_3$).

Synthesis of vinylsiloxane (28):



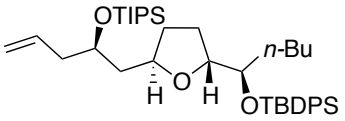
1,1,3,3-Tetramethyldisilazane (11 μL, 0.0606 mmol) was added to homopropargyl alcohol **27** (13.1 mg, 0.0202 mmol) and the neat solution was stirred at 50 ºC for 2.5 h. The mixture was cooled to rt and the volatiles removed under high vacuum for 2 h to yield the corresponding silyl ether. The latter and the $[CpRu(NCMe)_3]PF_6$ catalyst were then dissolved in CH_2Cl_2 (0.20 mL) and the dark brown/orange mixture was stirred at rt for 30 min, diluted with Et_2O, filtered through Florisil® (eluting with Et_2O) and concentrated to yield the crude vinyl siloxane **28** (12.0 mg, 84% over 2 steps) as a light yellow oil. This material was used in the next step with no further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71–7.68 (m, 4 H), 7.43–7.31 (m, 6 H), 6.35 (*app*-br. t, $J_{H,H}$ = 4.4 Hz, 1 H), 5.90 (ddd, $J_{H,H}$ = 17.1 Hz, $J_{H,H}$ = 10.5 Hz, $J_{H,H}$ = 5.2 Hz, 1 H), 5.29–5.09 (m, 2 H), 4.07–3.97 (m, 2 H), 3.93–3.84 (m, 1 H), 3.71–3.61 (m, 2 H), 2.39–2.18 (m, 2 H), 2.07–1.99 (m, 1 H), 1.93–1.73 (m, 2 H), 1.50–1.25 (m, 5 H), 1.21–1.04 (m, 13 H), 0.90 (s, 9 H), 0.72 (t, $J_{H,H}$ = 7.1 Hz, 3 H), 0.14-0.13-0.06 and 0.03 (4 × s, 12 H) ppm.

Synthesis of alcohol (32):



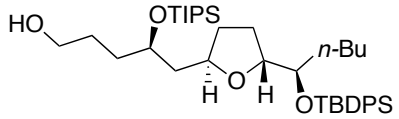
Magnesium bromide (520 mg, 2.81 mmol) was added to a solution of freshly prepared aldehyde **17** (410 mg, 0.936 mmol) in anhydrous Et_2O (5.5 mL) at 0 ºC. The mixture was stirred for 10 min and allyltributyltin (720 μL, 2.34 mmol) was added dropwise and the mixture was slowly warmed to rt over 16 h. The mixture was diluted with Et_2O and quenched by addition of a saturated aqueous solution of $NaHCO_3$. The aqueous layer was extracted with Et_2O (× 3) and the combined organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (eluting with gradient hexanes : Et_2O 90 : 10 to 85 : 15) to yield alcohol **32** (340 mg, 76% over 2 steps from **23**) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74–7.71 (m, 4 H), 7.44–7.35 (m, 6 H), 5.87–5.73 (m, 1 H), 5.11–5.06 (m, 2 H), 4.08–3.98 (m, 2 H), 3.76–3.68 (m, 1 H), 3.63 (dt, $J_{H,H}$ = 5.4 Hz, $J_{H,H}$ = 5.4 Hz, 1 H), 2.87 (d, $J_{H,H}$ = 4.3 Hz, 1 H), 2.29–2.16 (m, 2 H), 1.94–1.84 (m, 2 H), 1.77–1.44 (m, 5 H), 1.38–1.11 (m, 5 H), 1.05 (s, 9 H), 0.76 (t, $J_{H,H}$ = 7.1 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.9 (2 C, TBDPS), 135.2, 134.6, 134.3, 129.3 (2 C, TBDPS), 127.3 (2 C, TBDPS), 117.2, 81.0, 76.7, 75.8, 68.3, 41.8, 40.0, 32.9, 32.0, 27.6, 27.1, 27.0, 22.7, 19.6, 13.9 ppm. HRMS (ESI): calcd. for $C_{30}H_{44}NaO_3Si$ 503.2952 $[M + Na]^+$; found 503.2948. IR (neat, film): υ_{max} = 3466, 3072, 3050, 1471, 1428, 1389, 1110, 999 cm^{-1}. $[\alpha]_D^{25}$ = −2.04 (*c* 0.50, $CHCl_3$).

Synthesis of silyl ether (33):



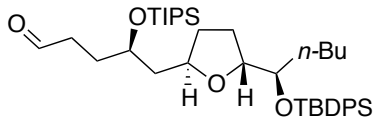
2,6-Lutidine (120 μL, 0.998 mmol) followed by TIPSOTf (215 μL, 0.800 mmol) were added to a solution of alcohol **32** (320 mg, 0.665 mmol) in CH_2Cl_2 (6.7 mL) at 0 ºC. The mixture was stirred at 0 ºC for 2 h and quenched by addition of a saturated aqueous solution of $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 (× 3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (eluting with hexanes : Et_2O 98 : 2) to yield silyl ether **33** (401 mg, 95%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73–7.70 (m, 4 H), 7.44–7.35 (m, 6 H), 5.91–5.83 (m, 1 H), 5.06–5.03 (m, 2 H), 4.06–3.97 (m, 3 H), 3.70 (dt, $J_{H,H}$ = 5.2 Hz, $J_{H,H}$ = 5.2 Hz, 1 H), 2.35–2.25 (m, 2 H), 2.04–1.98 (m, 1 H), 1.88–1.71 (m, 3 H), 1.55–1.43 (m, 3 H), 1.38–1.31 (m, 1 H), 1.19–1.07 (m, 34 H), 0.74 (t, $J_{H,H}$ = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.0, 135.9, 134.9, 134.8, 134.3, 129.4, 129.3, 127.3, 127.2, 116.9, 80.0, 76.3, 75.6, 70.0, 43.2, 42.3, 32.7, 32.5, 27.6, 27.2, 27.1, 22.8, 19.6, 18.2, 13.9, 12.7 ppm. HRMS (ESI): calcd. for $C_{39}H_{64}NaO_3Si_2$ 659.4286 [M + Na]$^+$; found 659.4287. IR (neat, film): υ_{max} = 3072, 3050, 1464, 1428, 1388, 1110, 1064, 999, 883 cm^{-1}. $[\alpha]_D^{25}$ = −10.8 (*c* 0.55, $CHCl_3$).

Synthesis of alcohol (34a) (step 1 to aldehyde (34)):



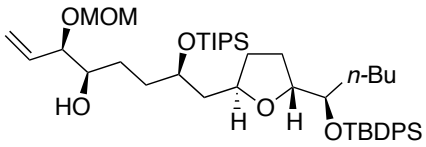
$BH_3.SMe_2$ (300 μL, 0.610 mmol, 2 M in THF) was added dropwise to a solution of alkene **33** (130 mg, 0.204 mmol) in THF (1.0 mL) at 0 ºC. The mixture was slowly warmed to rt over 4 h and cooled to 0 ºC. The mixture was then quenched by the dropwise addition of an aqueous solution of NaOH (2.0 mL, 2.5 M) followed by H_2O_2 (1.0 mL, 30% in H_2O) and stirred for a further 1 h. The aqueous layer was extracted with Et_2O (× 3) and the combined organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (eluting with gradient hexanes : Et_2O 85 : 15 to 80 : 20) to yield alcohol **34a** (104 mg, 78%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71–7.69 (m, 4 H), 7.42–7.34 (m, 6 H), 4.01–3.91 (m, 3 H), 3.67 (dt, $J_{H,H}$ = 5.8 Hz, $J_{H,H}$ = 5.8 Hz, 1 H), 3.60 (*app*-br. s, 2 H), 2.17 (*app*-br. s, 1 H), 2.02–1.96 (m, 1 H), 1.89–1.79 (m, 3 H), 1.73–1.56 (m, 5 H), 1.53–1.40 (m, 2 H), 1.38–1.25 (m, 1 H), 1.17–1.02 (m, 34 H), 0.72 (t, $J_{H,H}$ = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.0, 135.9, 134.8, 134.2, 129.4, 129.3, 127.3, 127.2, 80.0, 76.5, 75.7, 70.3, 63.2, 42.5, 33.6, 32.7, 32.6, 27.5, 27.3, 27.2, 27.1, 22.7, 19.5, 18.2, 13.9, 12.6 ppm. HRMS (ESI): calcd. for $C_{39}H_{66}NaO_4Si_2$ 677.4392 [M + Na]$^+$; found 677.4393. IR (neat, film): υ_{max} = 3367, 3072, 3050, 1464, 1428, 1388, 1110, 1060, 883 cm^{-1}. $[\alpha]_D^{25}$ = −4.08 (*c* 0.60, $CHCl_3$).

Synthesis of aldehyde (34):

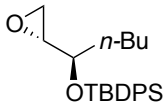


Dess-Martin periodinane (97 mg, 0.229 mmol) was added to a solution of alcohol **34a** (100 mg, 0.153 mmol) and solid $NaHCO_3$ (32 mg, 0.383 mmol) in CH_2Cl_2 (2.0 mL) at 0 ºC. The mixture was stirred at rt for 30 min and directly purified by flash column chromatography (eluting with hexanes : Et_2O 98 : 2) to yield quantitatively aldehyde **34** (100 mg) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.75 (t, $J_{H,H}$ = 1.8 Hz, 1 H), 7.69–7.68 (m, 4 H), 7.42–7.33 (m, 6 H), 3.99–3.95 (m, 2 H), 3.90–3.85 (m, 1 H), 3.66 (dt, $J_{H,H}$ = 5.6 Hz, $J_{H,H}$ = 5.6 Hz, 1 H), 2.58–2.43 (m, 2 H), 2.01–1.81 (m, 5 H), 1.72–1.62 (m, 1 H), 1.59–1.54 (m, 1 H), 1.51–1.29 (m, 3 H), 1.17–1.11 (m, 2 H), 1.08–1.04 (m, 32 H), 0.72 (t, $J_{H,H}$ = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.9, 136.0, 135.9, 134.7, 134.3, 129.4, 129.3, 127.3, 127.2, 80.2, 76.3, 75.6, 69.5, 42.8, 38.8, 32.8, 32.6, 29.1, 27.5, 27.2, 27.1, 22.7, 19.6, 18.2, 13.9, 12.6 ppm. HRMS (ESI): calcd. for $C_{39}H_{64}NaO_4Si_2$ 675.4235 $[M + Na]^+$; found 675.4244. IR (neat, film): υ_{max} = 3071, 3049, 2714, 1728, 1464, 1428, 1388, 1110, 883 cm^{-1}. $[\alpha]_D^{25}$ = −1.46 (*c* 0.17, $CHCl_3$).

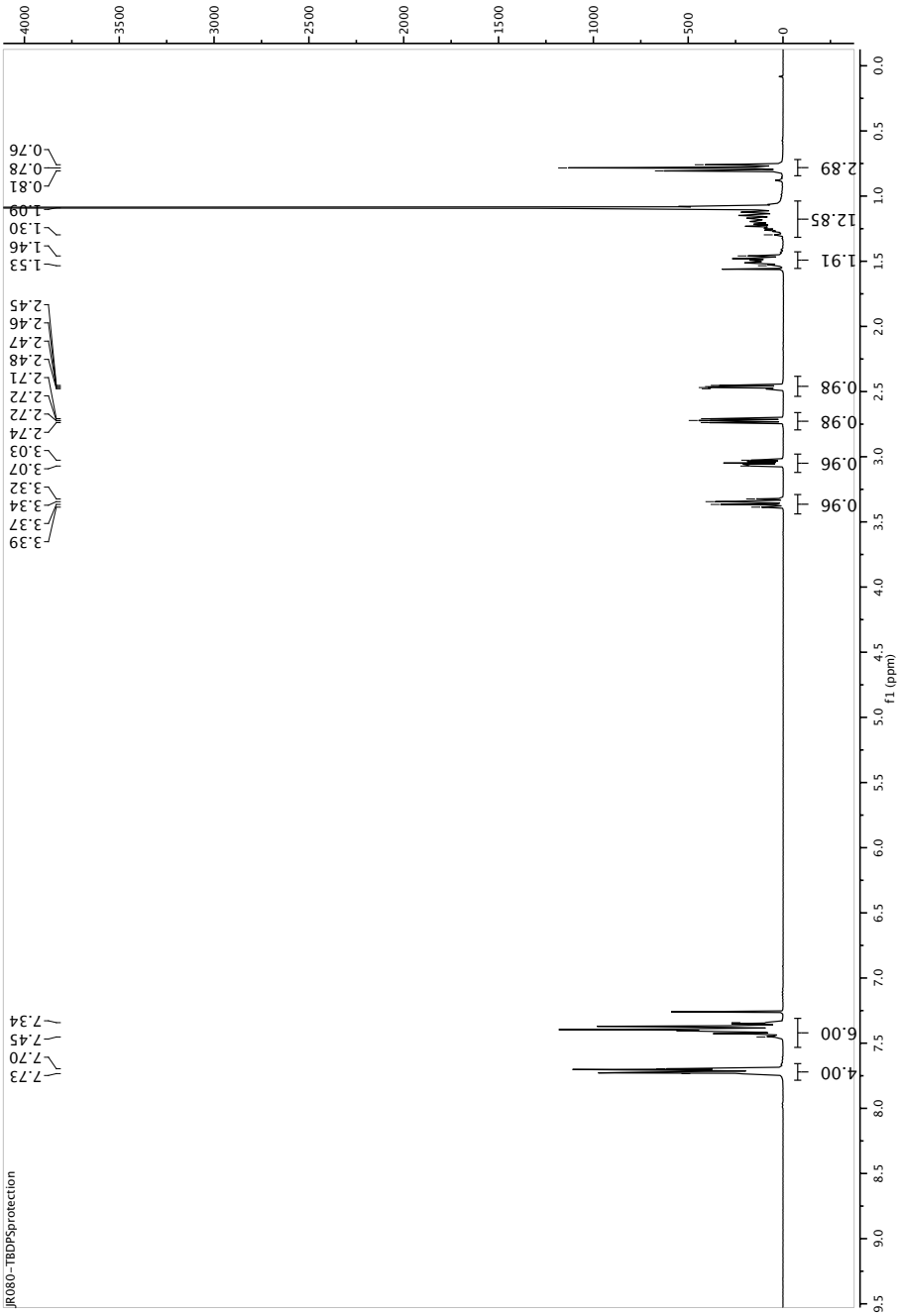
Synthesis of alcohol (36):

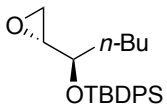


sec-Butyllithium (625 μL, 0.808 mmol, 1.3 M in cyclohexane) was added dropwise to a solution of methoxymethyl allyl ether (**35**) (100 mg, 0.970 mmol) in THF (1.5 mL) at –78 ºC. After the resultant orange solution was stirred at –78 ºC for 30 min, (–)-B-methoxydiisopinocamphenylborane (256 mg, 0.808 mmol) in THF (1.5 mL) was added. The mixture was stirred at –78 ºC for 1 h and $BF_3.Et_2O$ (130 μL, 1.05 mmol) was added followed by a solution of aldehyde **34** (264 mg, 0.404 mmol) in THF (1.0 mL). The mixture was kept at –78 ºC for 3 h then warmed to rt over 1 h. The mixture was cooled to 0 ºC and quenched by addition of a saturated aqueous solution of $NaHCO_3$ (2.0 mL) followed by H_2O_2 (1.0 mL, 30% in H_2O) and further stirred for 30 min. The aqueous layer was extracted with Et_2O (× 3) and the combined organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude product was filtered through silica gel (eluting with CH_2Cl_2 : Et_2O 94 : 6) to remove the boron byproducts and the residue was purified by flash column chromatography (eluting with gradient hexanes : Et_2O 9 : 1 to 8 : 2) to yield alcohol **36** (223 mg, 73%, dr = 92 : 8) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71–7.67 (m, 4 H), 7.44–7.32 (m, 6 H), 5.76–5.62 (m, 1 H), 5.33–5.28 (m, 2 H), 4.74 (d, $J_{H,H}$ = 6.7 Hz, 1 H), 4.58 (d, $J_{H,H}$ = 6.7 Hz, 1 H), 4.01–3.90 (m, 3 H), 3.84 (*app*-t, $J_{H,H}$ = 7.4 Hz, 1 H), 3.70–3.62 (m, 1 H), 3.54–3.47 (m, 1 H), 3.39 (s, 3 H), 2.58 (d, $J_{H,H}$ = 3.5 Hz, 1 H), 2.03–1.94 (m, 1 H), 1.86–1.26 (m, 11 H), 1.18–1.05 (m, 34 H), 0.72 (t, $J_{H,H}$ = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.0, 135.9, 134.8, 134.7, 134.3, 129.3, 129.2, 127.3, 127.2, 120.0, 93.9, 81.5, 80.0, 76.4, 75.6, 73.8, 70.0, 55.7, 43.0, 33.2, 32.6, 32.4, 27.6, 27.2, 27.1, 27.0, 22.7, 19.5, 18.2, 13.9, 12.7 ppm. HRMS (ESI): calcd. for $C_{44}H_{74}NaO_6Si_2$ 777.4916 $[M + Na]^+$; found 777.4928. IR (neat, film): υ_{max} = 3484, 3072, 3049, 1464, 1427, 1388, 1363, 1258, 1152, 1109, 923, 883 cm^{-1}. $[\alpha]_D^{25}$ = −15.1 (*c* 0.71, $CHCl_3$).

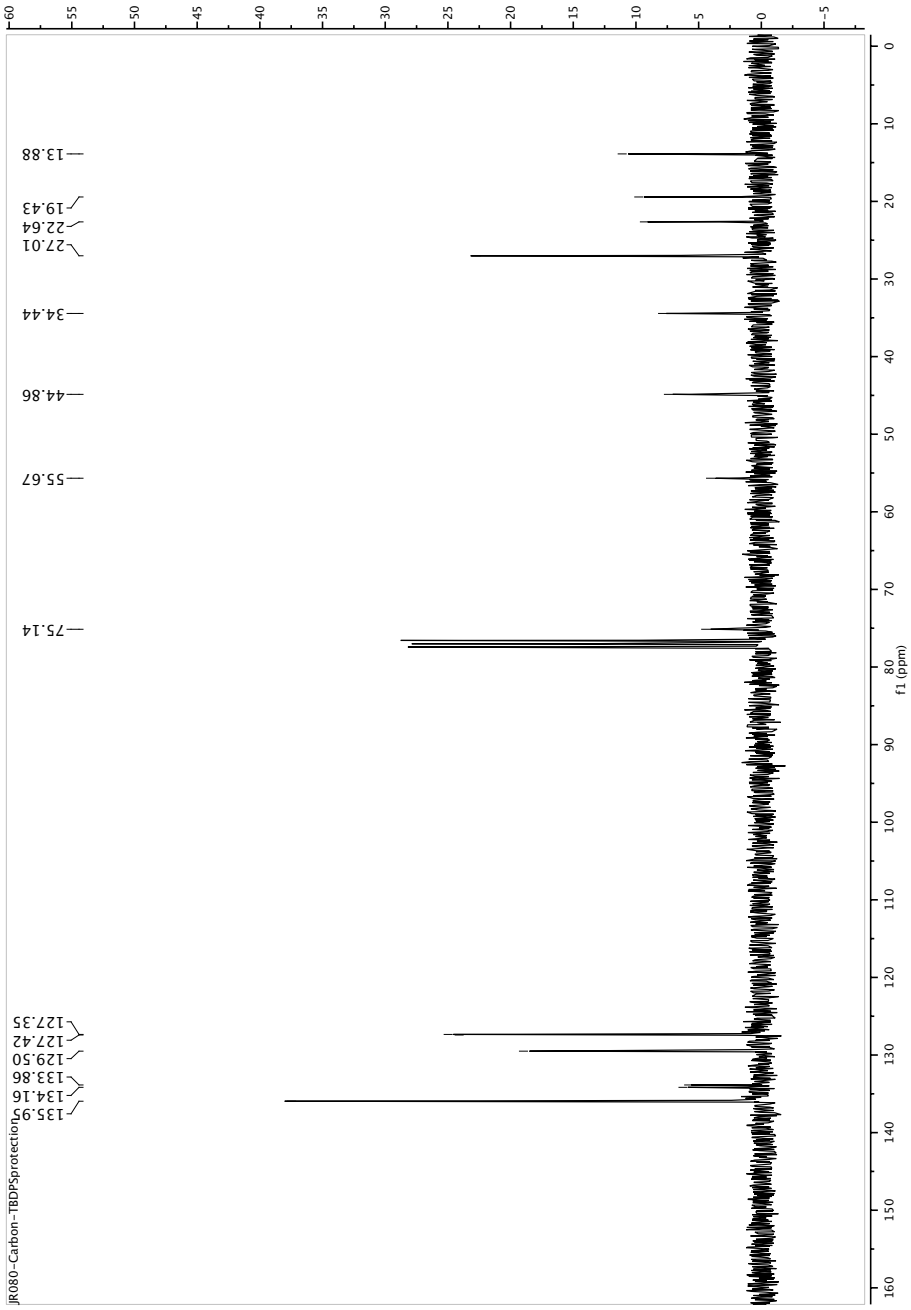

O
n-Bu
OTBDPS

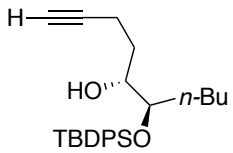
12


JR080-TBDPSprotection
7.73
7.70
7.45
7.34
3.39
3.37
3.34
3.32
3.07
3.03
2.74
2.72
2.72
2.71
2.48
2.47
2.46
2.45
1.53
1.46
1.30
1.09
0.81
0.78
0.76
4.00
6.00
0.96
0.96
0.98
0.98
1.91
12.85
2.89
f1 (ppm)

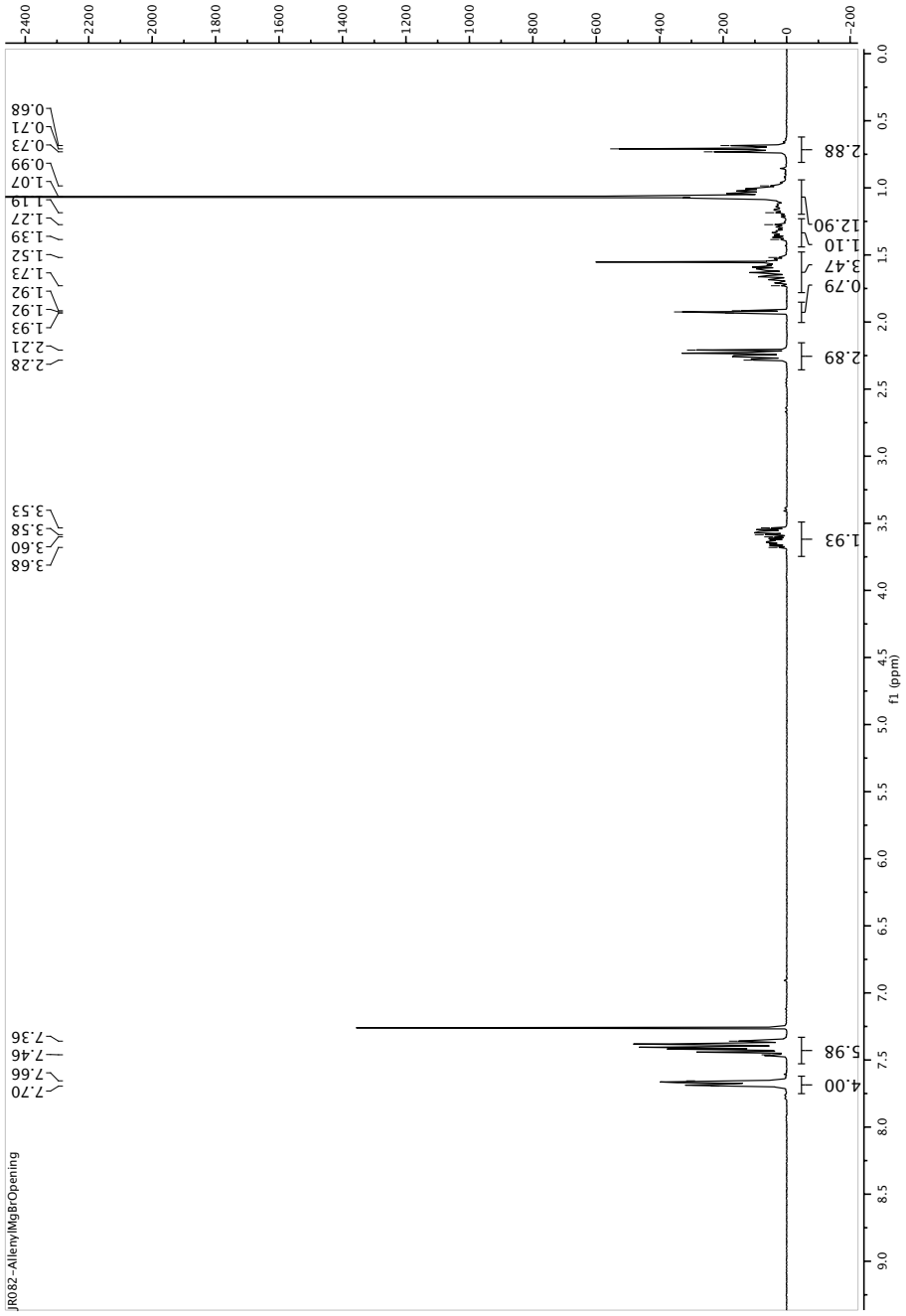

O
n-Bu
OTBDPS

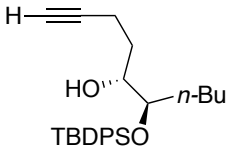
12


JR080-Carbon-TBDPSprotection
135.95
134.16
133.86
129.50
127.42
127.35
75.14
55.67
44.86
34.44
27.01
22.64
19.43
13.88
f1 (ppm)

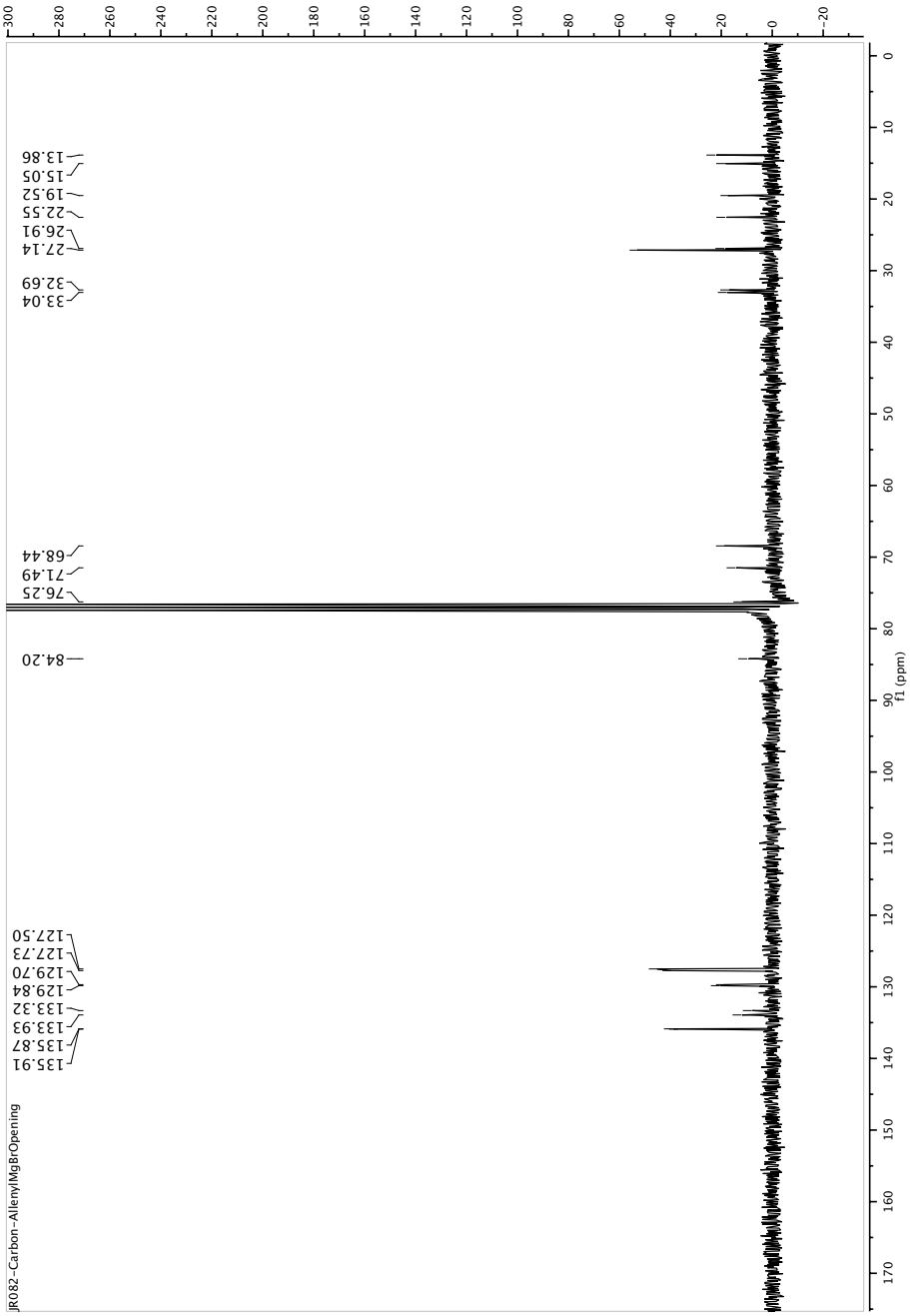

H
HO
n-Bu
TBDPSO

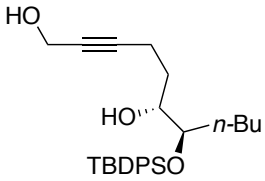
14


jR082-AllenylMgBrOpening
7.70
7.66
7.46
7.36
3.68
3.60
3.58
3.53
2.28
2.21
1.93
1.92
1.92
1.73
1.52
1.39
1.27
1.19
1.07
0.99
0.73
0.71
0.68
4.00
5.98
1.93
2.89
0.79
3.47
1.10
12.90
2.88
f1 (ppm)

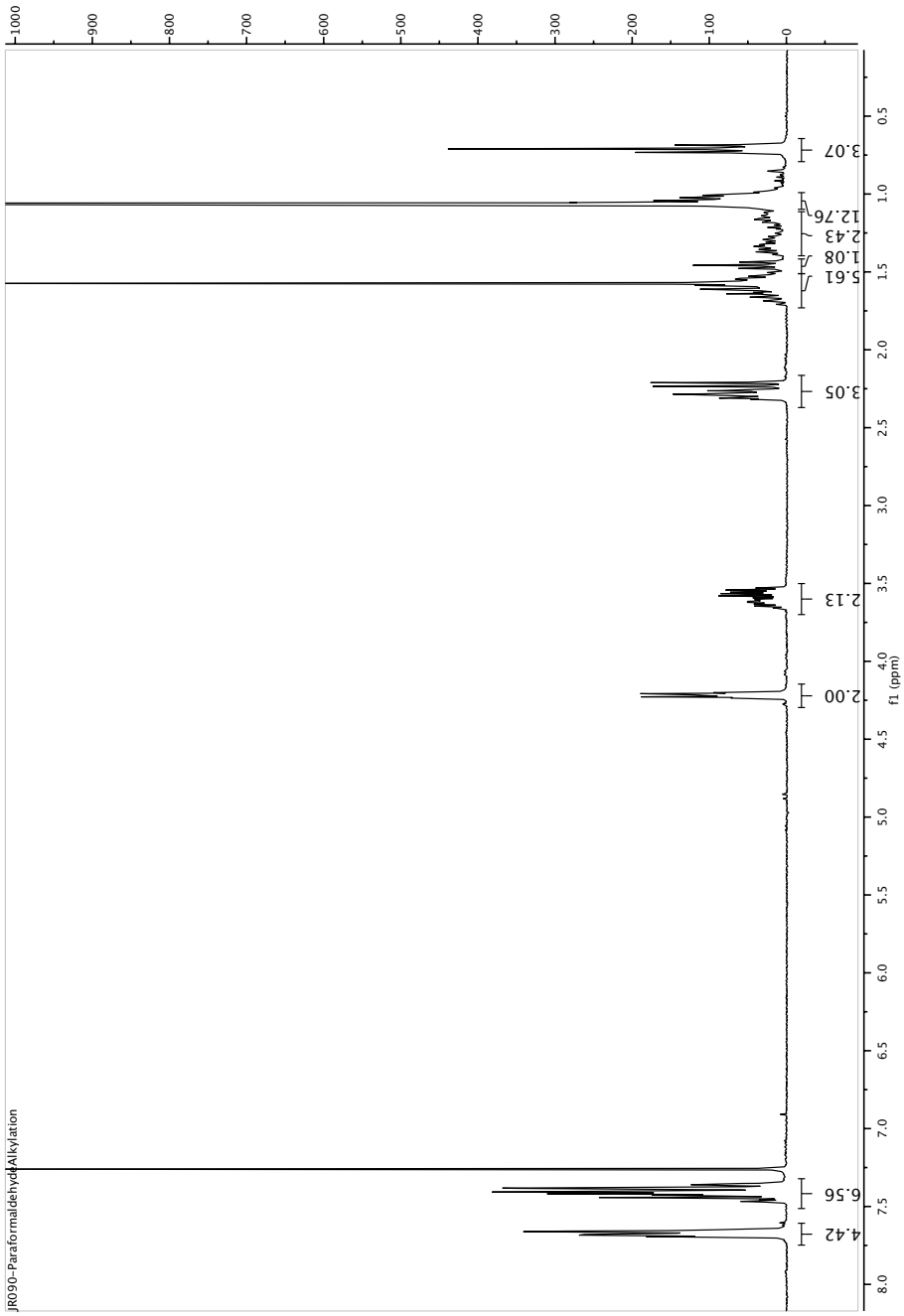

H
HO
n-Bu
TBDPSO

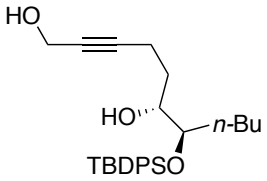
14


JR082-Carbon-AllenylMgBrOpening
135.91
135.87
133.93
133.32
129.84
129.70
127.73
127.50
84.20
76.25
71.49
68.44
33.04
32.69
27.14
26.91
22.55
19.52
15.05
13.86
f1 (ppm)

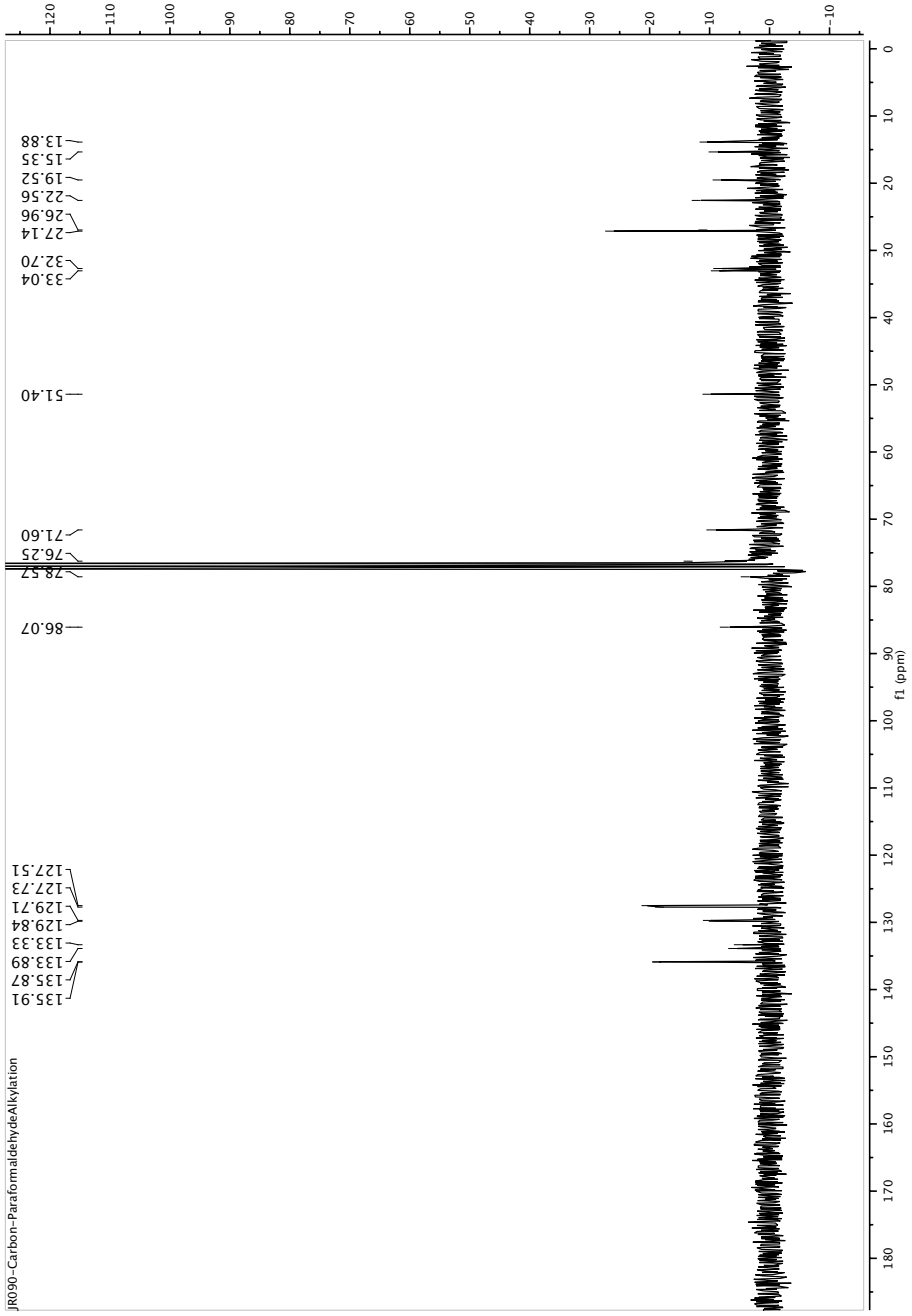

HO
HO
n-Bu
TBDPSO

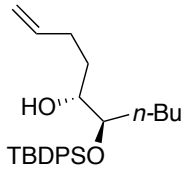
15


JR090-ParaformaldehydeAlkylation
4.42
6.56
2.00
2.13
3.05
5.61
1.08
2.43
12.76
3.07
f1 (ppm)

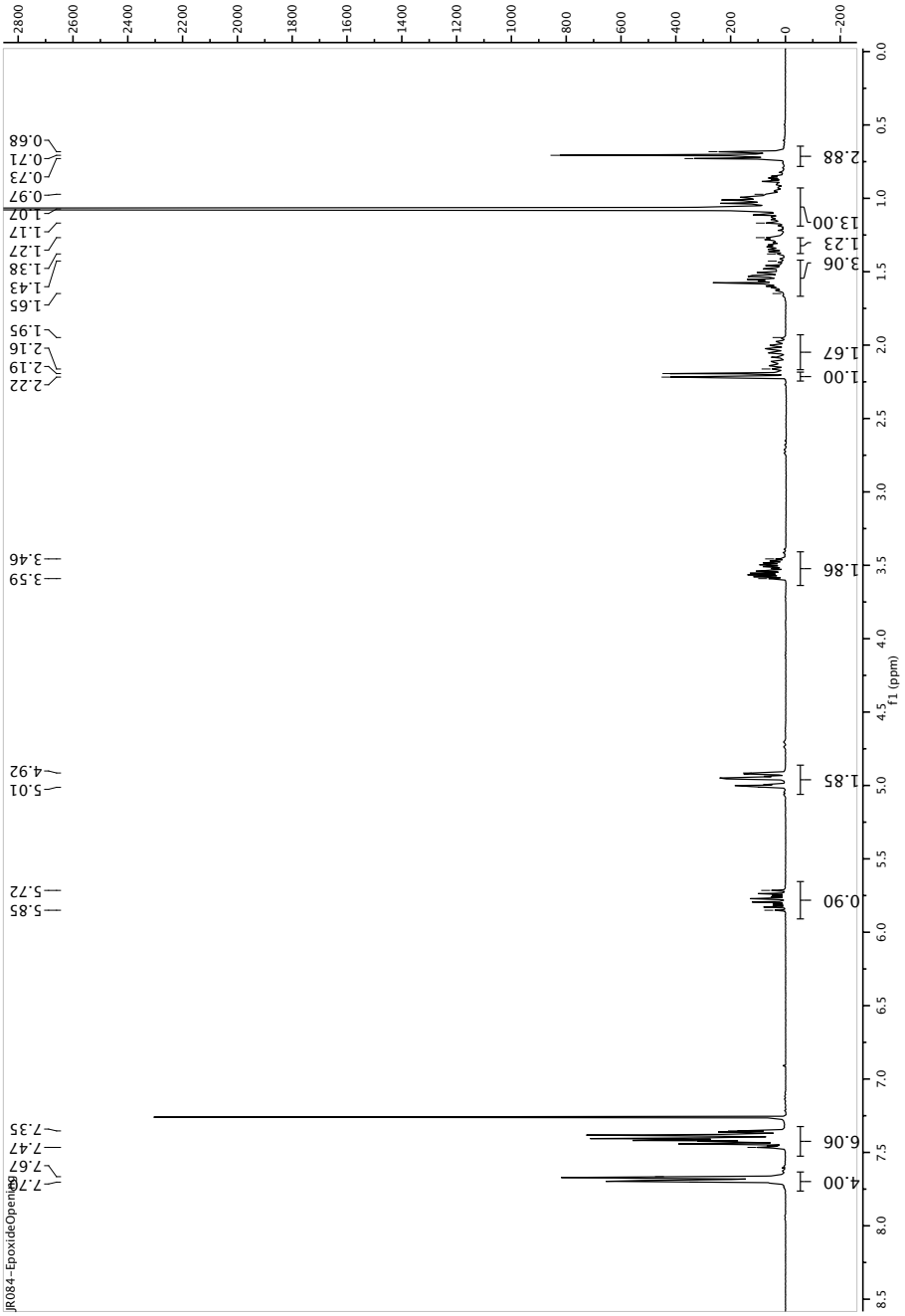

HO
HO
n-Bu
TBDPSO

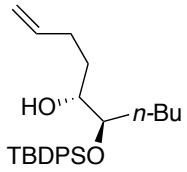
15


JR090-Carbon-ParaformaldehydeAlkylation
135.91
135.87
133.89
133.33
129.84
129.71
127.73
127.51
86.07
78.57
76.25
71.60
51.40
33.04
32.70
27.14
26.96
22.56
19.52
15.35
13.88
f1 (ppm)

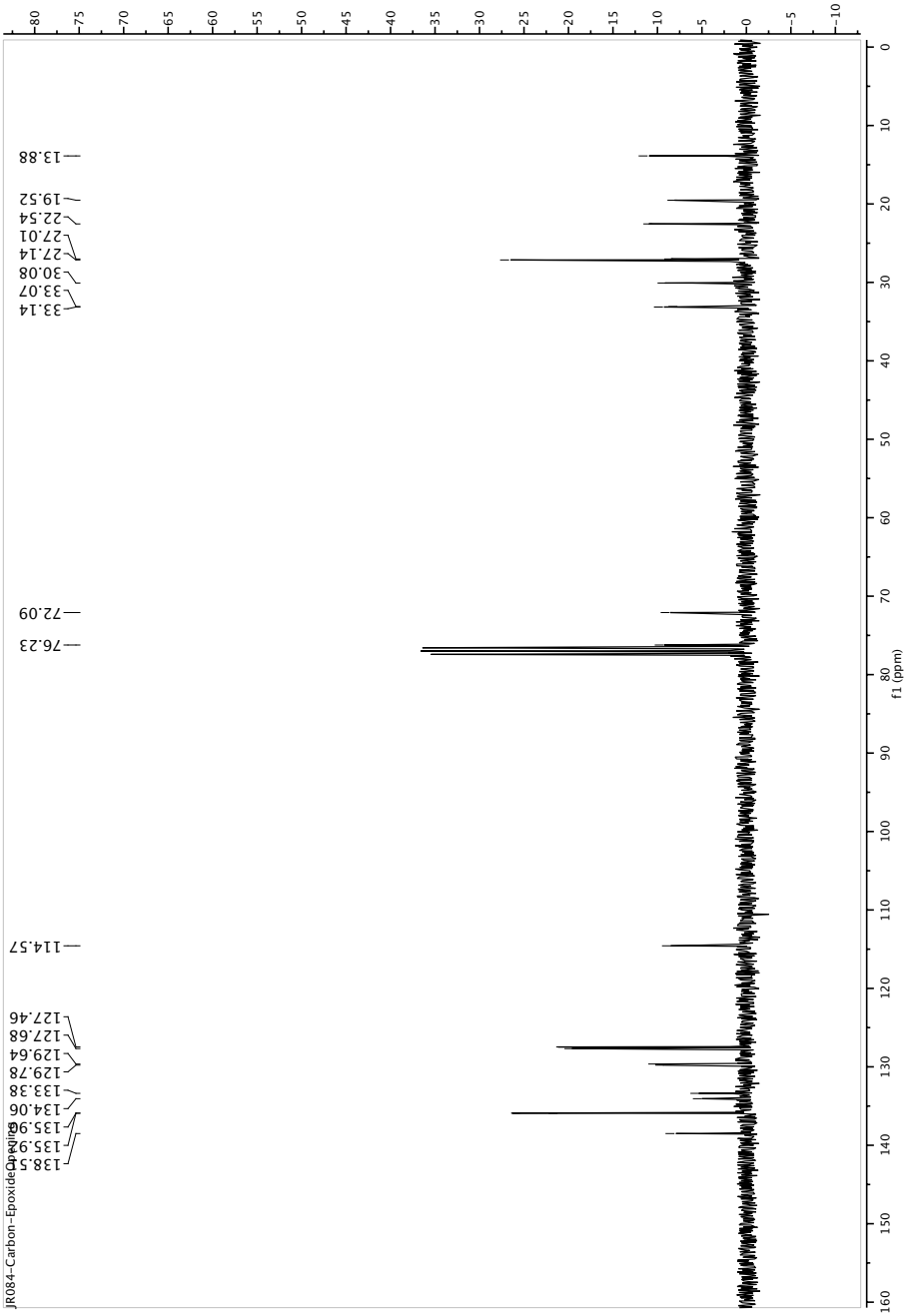

HO
n-Bu
TBDPSO

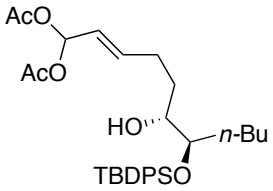
22


JR084-EpoxideOpening
7.70
7.67
7.47
7.35
5.85
5.72
5.01
4.92
3.59
3.46
2.22
2.19
2.16
1.95
1.65
1.43
1.38
1.27
1.17
1.07
0.97
0.73
0.71
0.68
4.00
6.06
0.90
1.85
1.86
1.00
1.67
3.06
1.23
13.00
2.88
f1 (ppm)

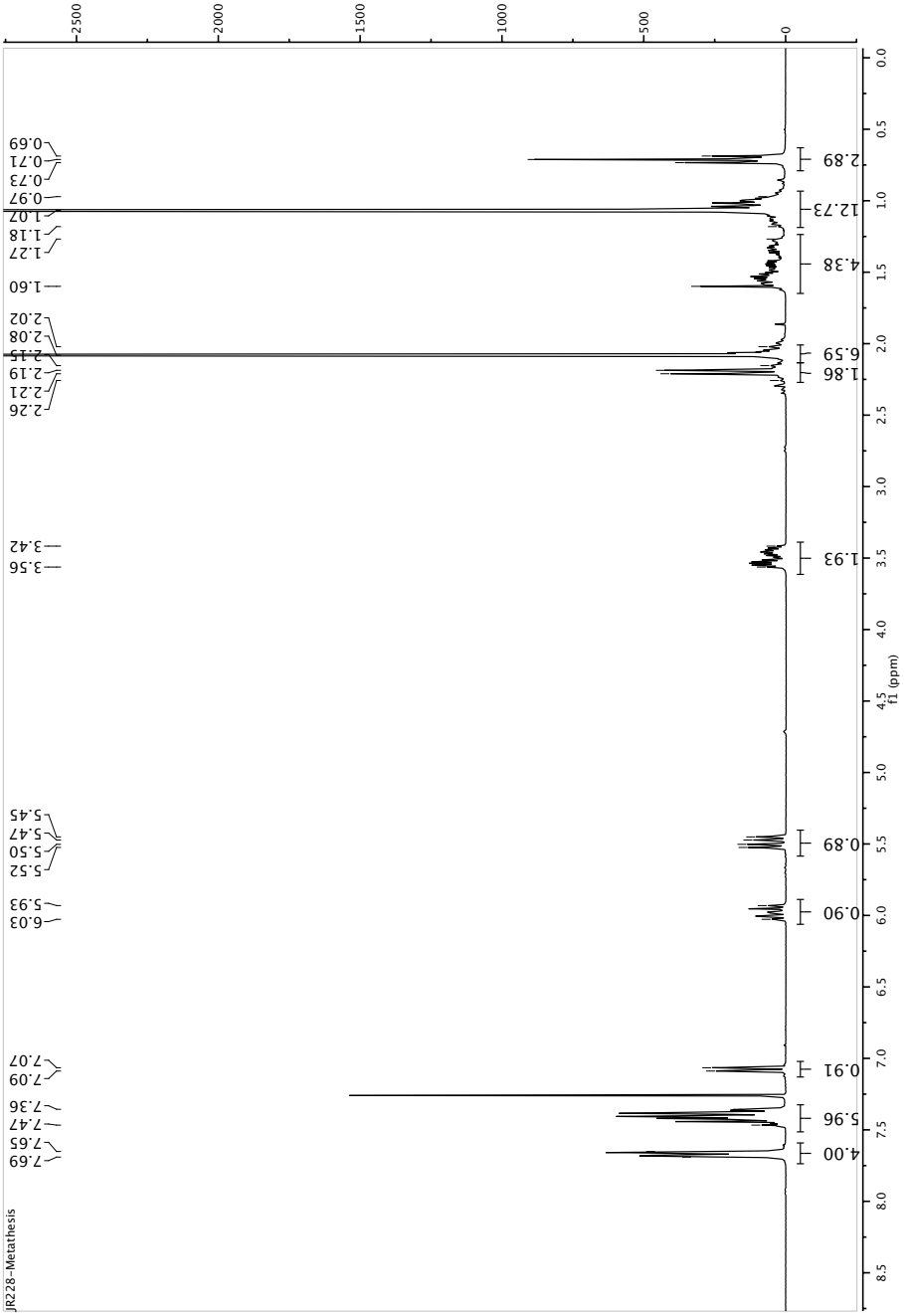

HO
n-Bu
TBDPSO

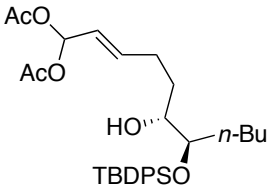
22


JR084-Carbon-Epoxide-Opening
138.57
135.92
135.90
134.06
133.38
129.78
129.64
127.68
127.46
114.57
76.23
72.09
33.14
33.07
30.08
27.14
27.01
22.54
19.52
13.88
f1 (ppm)

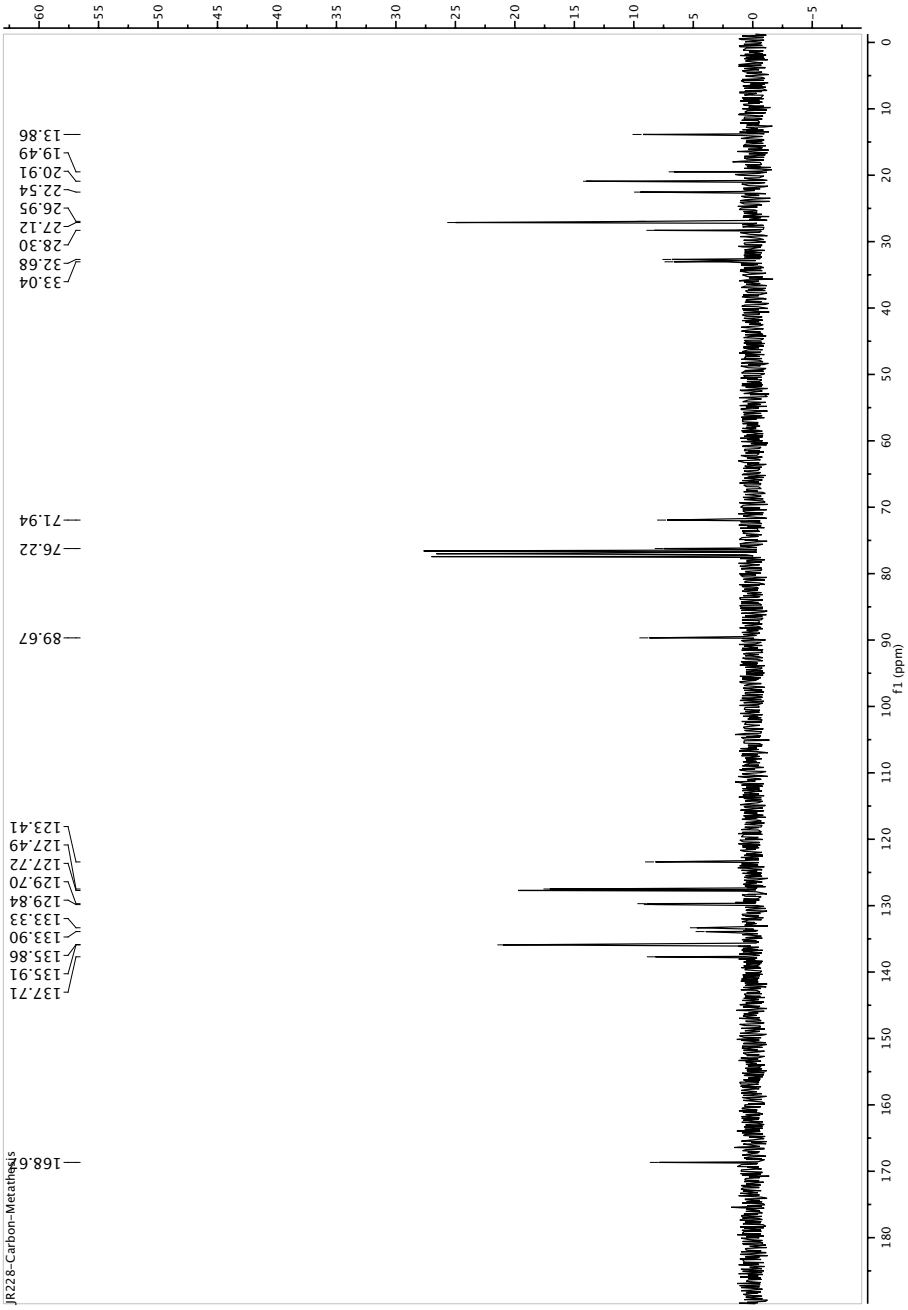

AcO
AcO
HO
n-Bu
TBDPSO

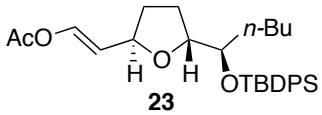
19


JR228-Metathesis
7.69
7.65
7.47
7.36
7.09
7.07
6.03
5.93
5.52
5.50
5.47
5.45
3.56
3.42
2.26
2.21
2.19
2.15
2.08
2.02
1.60
1.27
1.18
1.07
0.97
0.73
0.71
0.69
4.00
5.96
0.91
0.90
0.89
1.93
1.86
6.59
4.38
12.73
2.89
f1 (ppm)

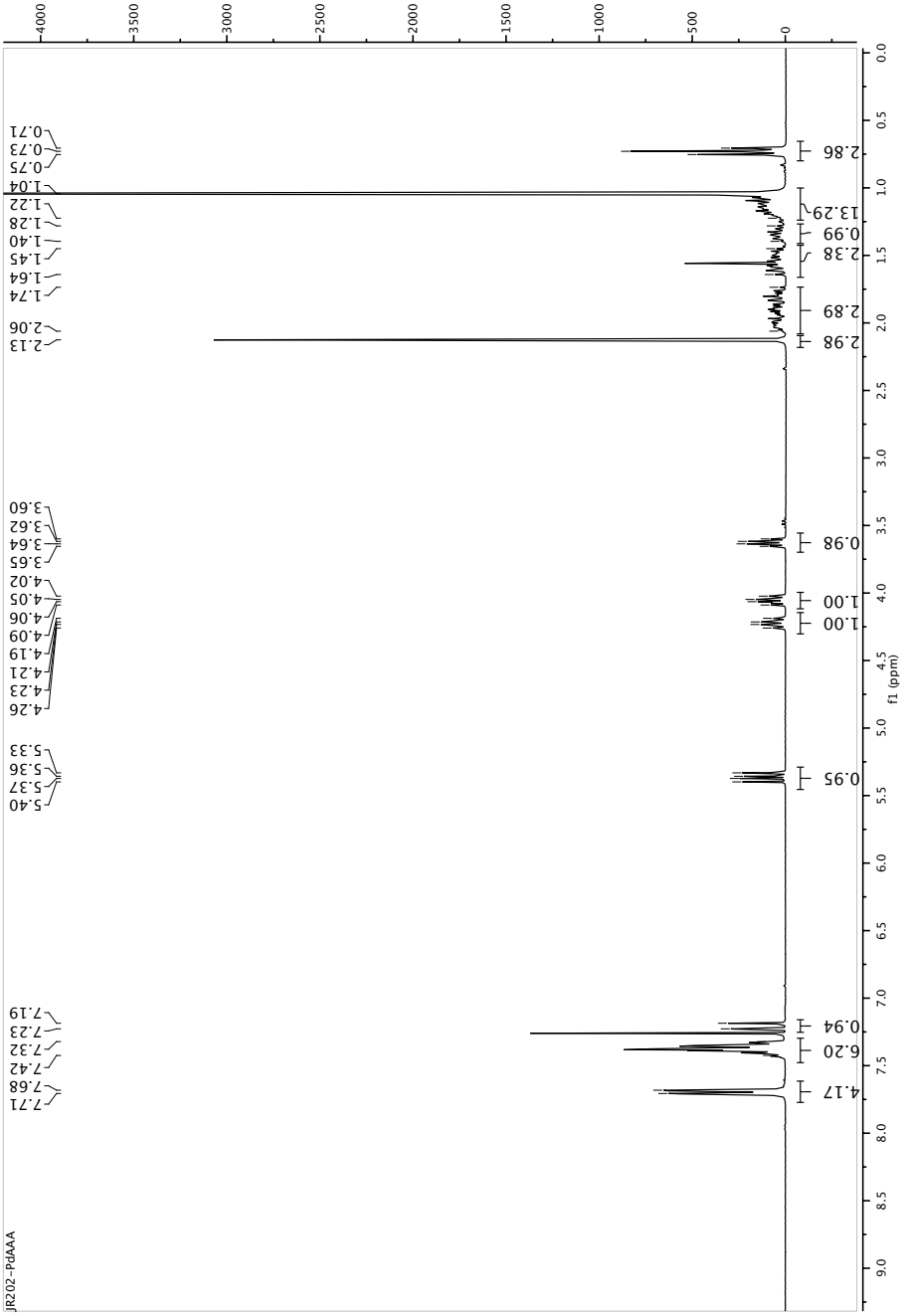

AcO
AcO
HO
n-Bu
TBDPSO

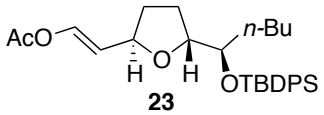
19


JR228-Carbon-Metathesis
168.61
137.71
135.91
135.86
133.90
133.33
129.84
129.70
127.72
127.49
123.41
89.67
76.22
71.94
33.04
32.68
28.30
27.12
26.95
22.54
20.91
19.49
13.86
f1 (ppm)

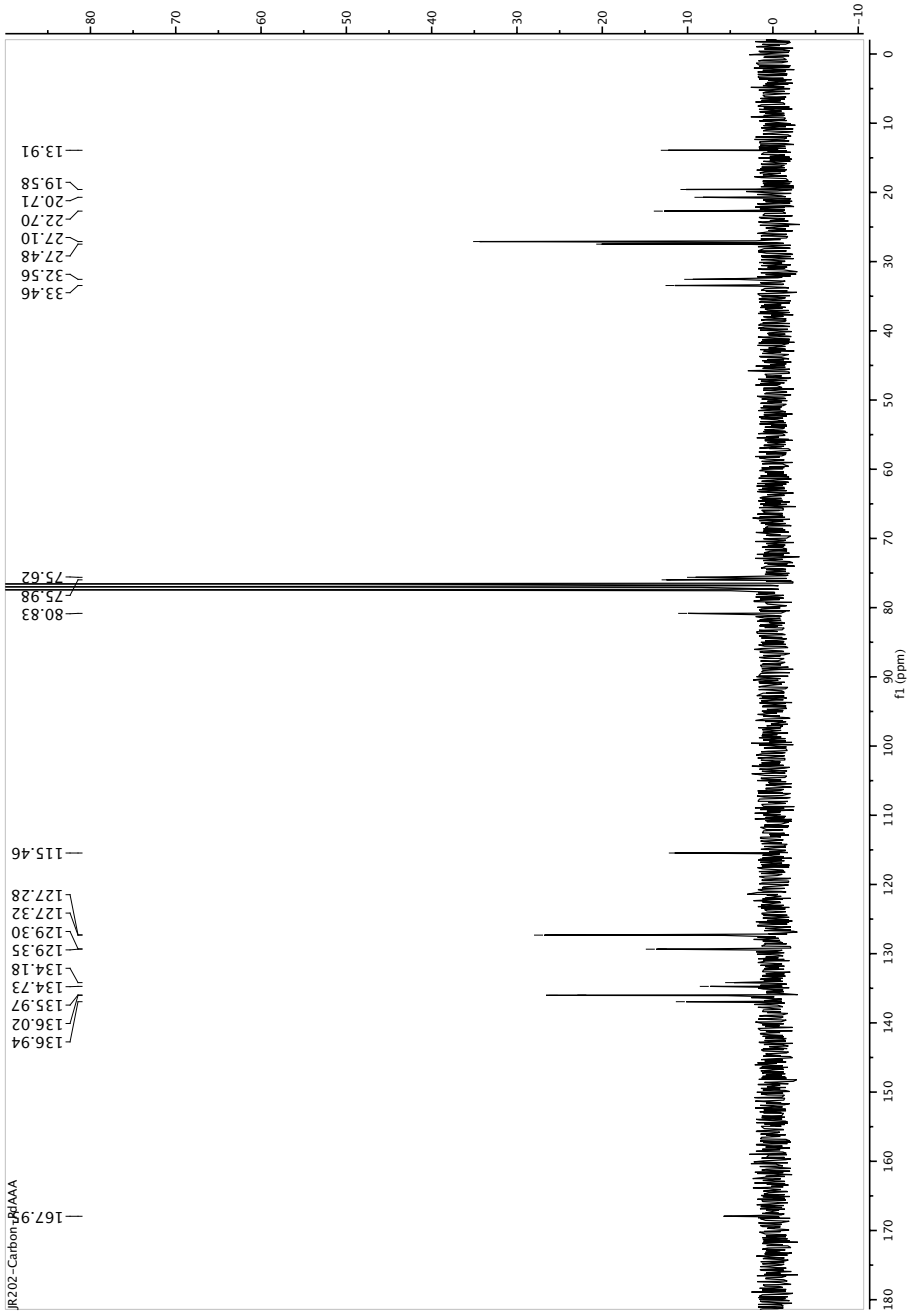

AcO
n-Bu
H
O
H
OTBDPS

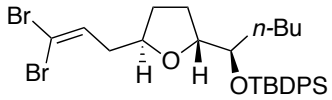
23


JR202-PdAAA
f1 (ppm)
7.71
7.68
7.42
7.32
7.23
7.19
5.40
5.37
5.36
5.33
4.26
4.23
4.21
4.19
4.09
4.06
4.05
4.02
3.65
3.64
3.62
3.60
2.13
2.06
1.74
1.64
1.45
1.40
1.28
1.22
1.04
0.75
0.73
0.71
4.17
6.20
0.94
0.95
1.00
1.00
0.98
2.98
2.89
2.38
0.99
13.29
2.86

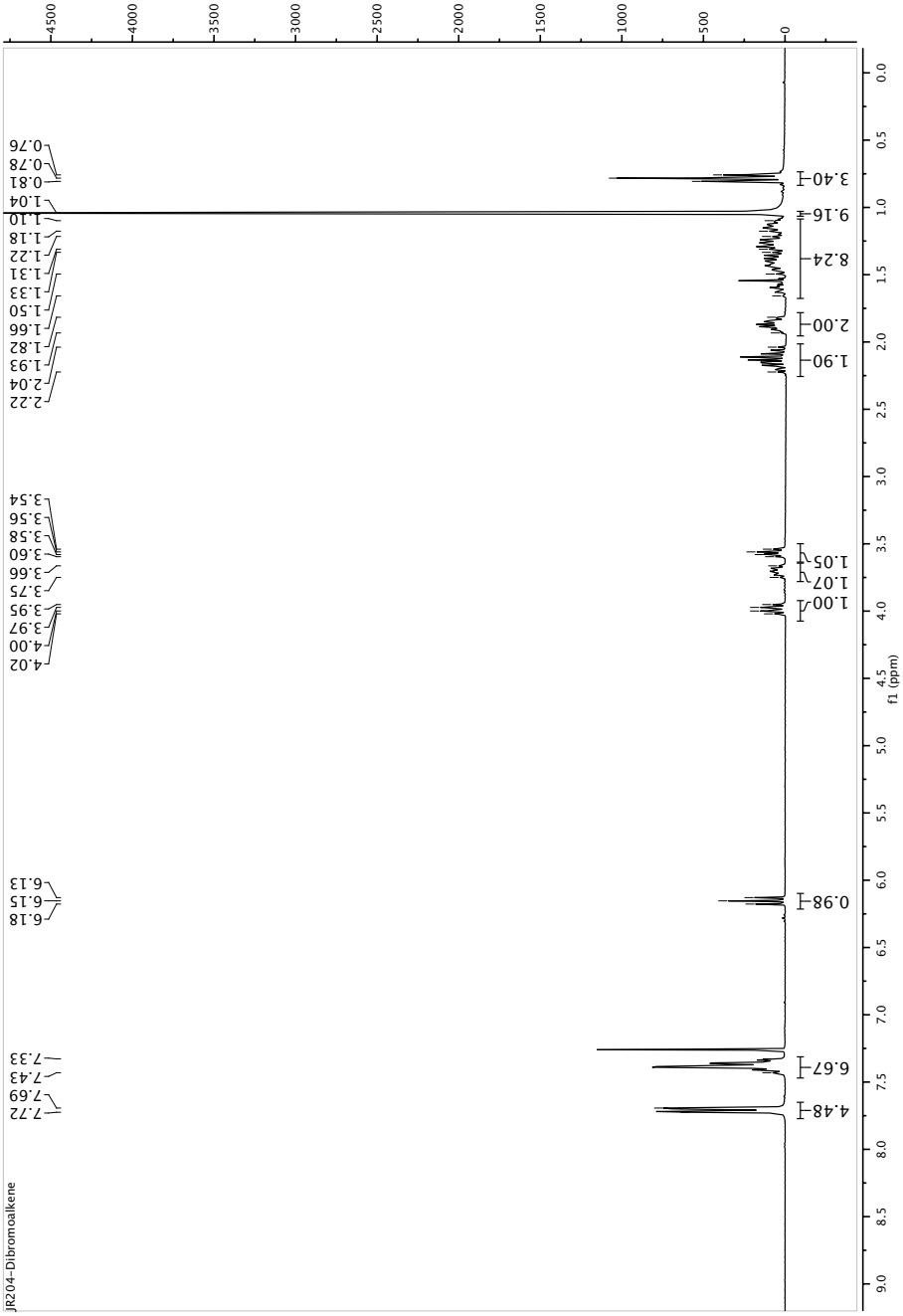

AcO
H
O
H
n-Bu
OTBDPS

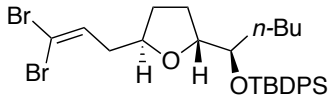
23


JR202-Carbon-pr.AAA
167.97
136.94
136.02
135.97
134.73
134.18
129.35
129.30
127.32
127.28
115.46
80.83
75.98
75.62
33.46
32.56
27.48
27.10
22.70
20.71
19.58
13.91
f1 (ppm)

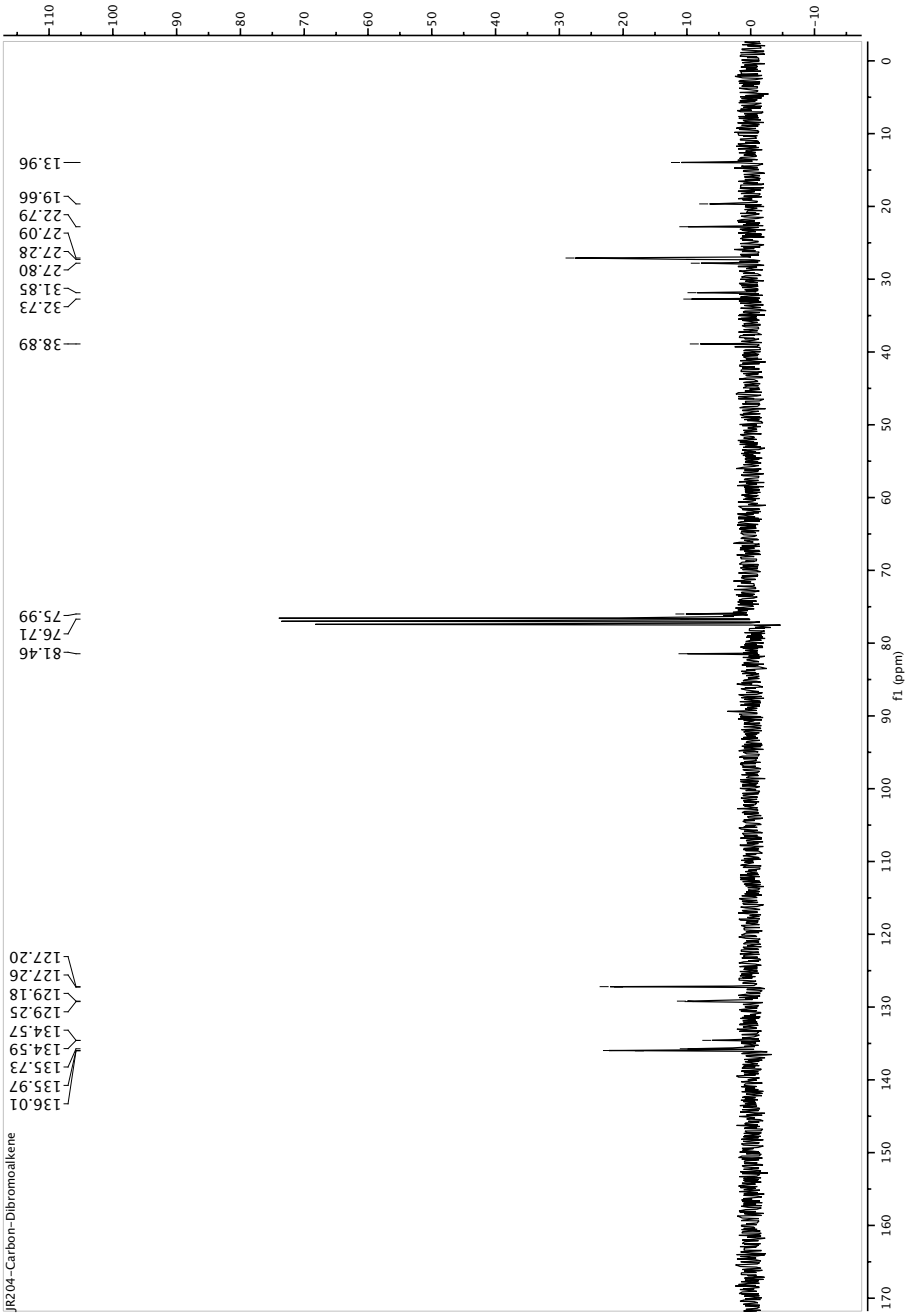

Br
Br
H
O
H
n-Bu
OTBDPS

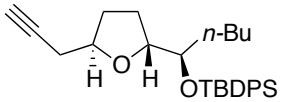
25a


JR204-Dibromoalkene
7.72
7.69
7.43
7.33
6.18
6.15
6.13
4.02
4.00
3.97
3.95
3.75
3.66
3.60
3.58
3.56
3.54
2.22
2.04
1.93
1.82
1.66
1.50
1.33
1.31
1.22
1.18
1.10
1.04
0.81
0.78
0.76
4.48
6.67
0.98
1.00
1.07
1.05
1.90
2.00
8.24
9.16
3.40
f1 (ppm)

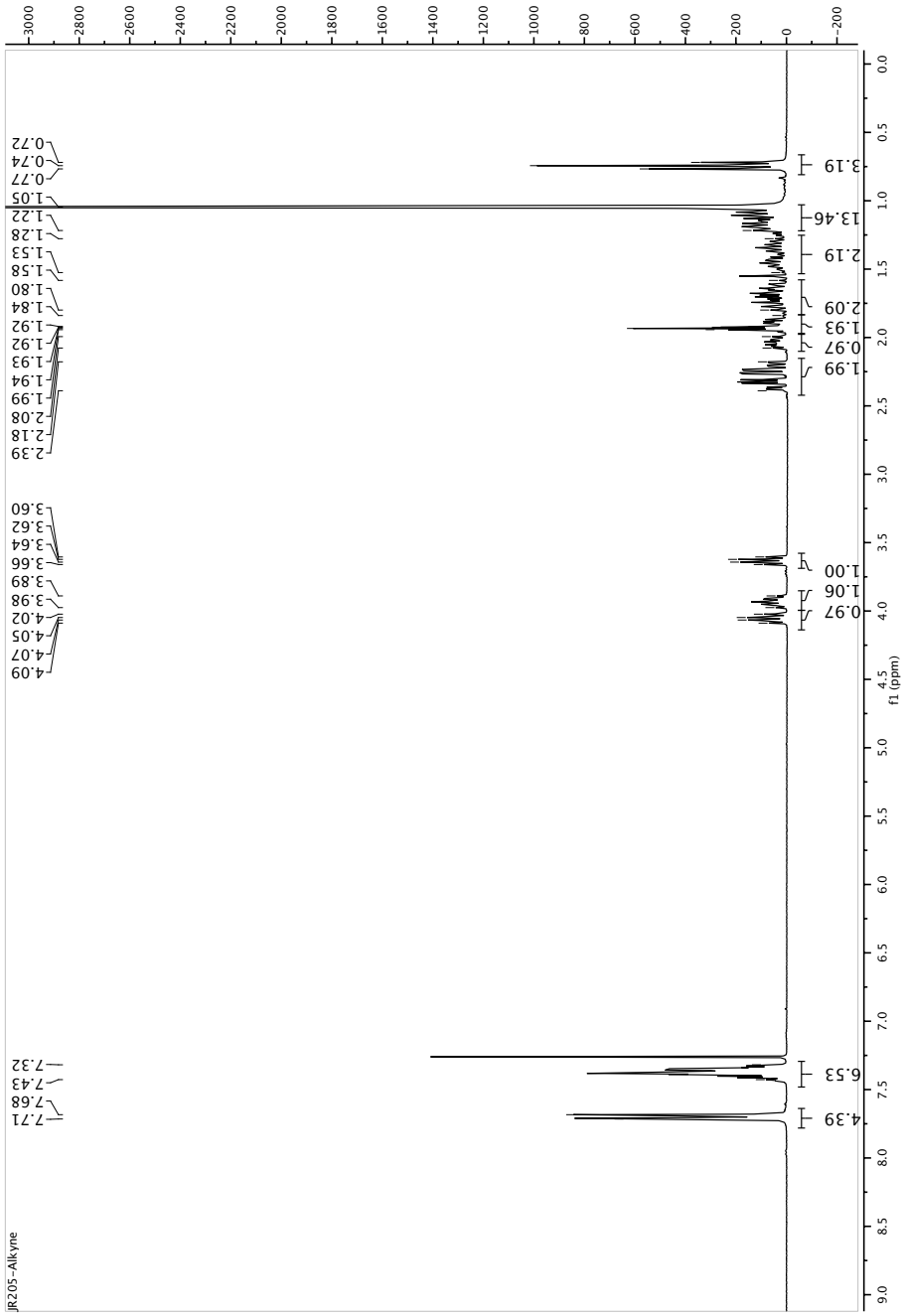

Br
Br
H
O
H
n-Bu
OTBDPS

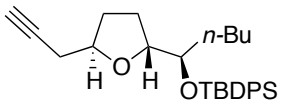
25a


JR204-Carbon-Dibromoalkene
136.01
135.97
135.73
134.59
134.57
129.25
129.18
127.26
127.20
81.46
76.71
75.99
38.89
32.73
31.85
27.80
27.28
27.09
22.79
19.66
13.96
f1 (ppm)

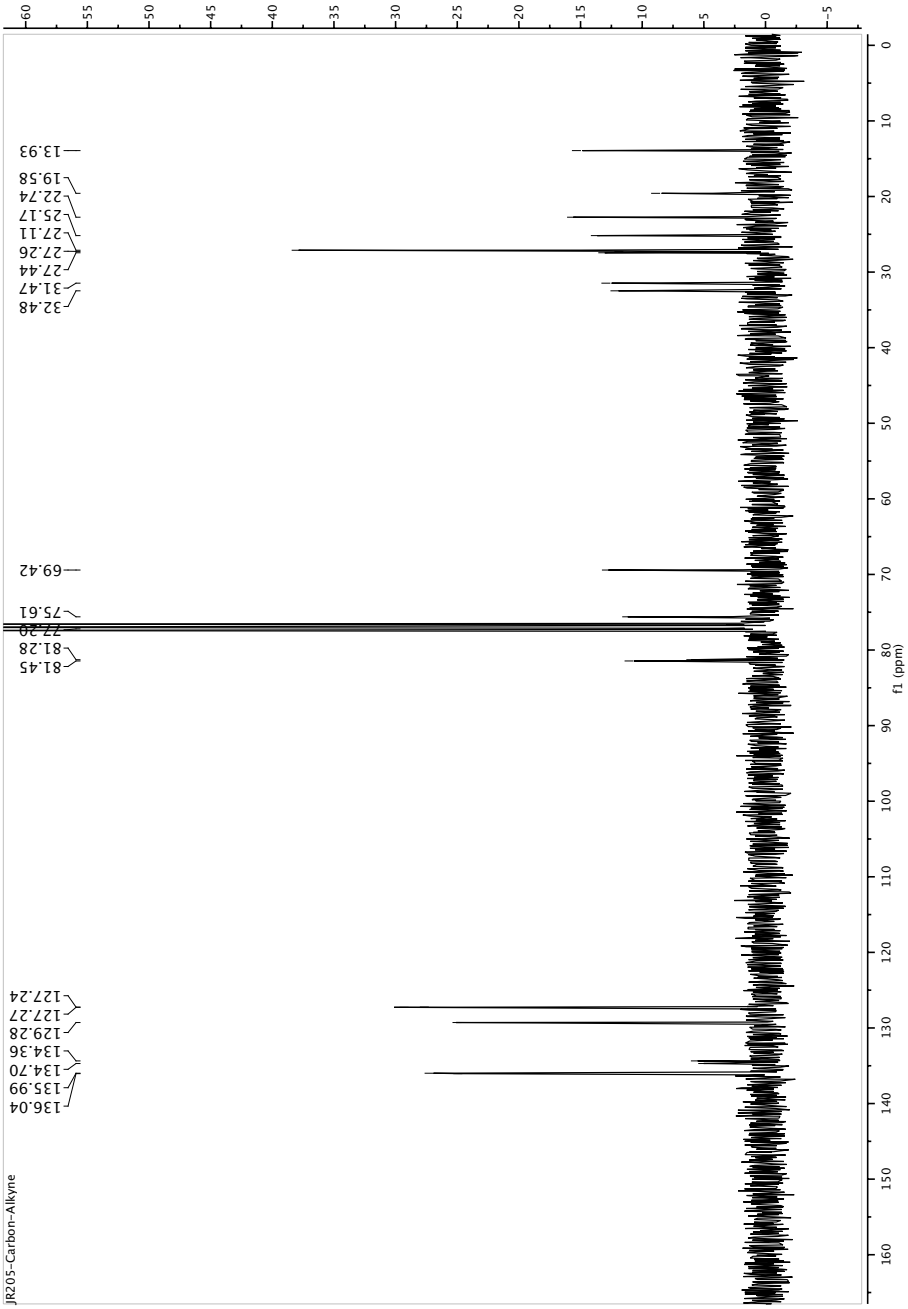

n-Bu
H
O
H
OTBDPS

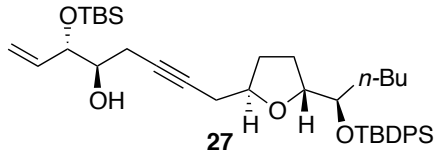
25


JR205-Alkyne
f1 (ppm)
7.71
7.68
7.43
7.32
4.09
4.07
4.05
4.02
3.98
3.89
3.66
3.64
3.62
3.60
2.39
2.18
2.08
1.99
1.94
1.93
1.92
1.92
1.84
1.80
1.58
1.53
1.28
1.22
1.05
0.77
0.74
0.72
4.39
6.53
0.97
1.06
1.00
1.99
0.97
1.93
2.09
2.19
13.46
3.19

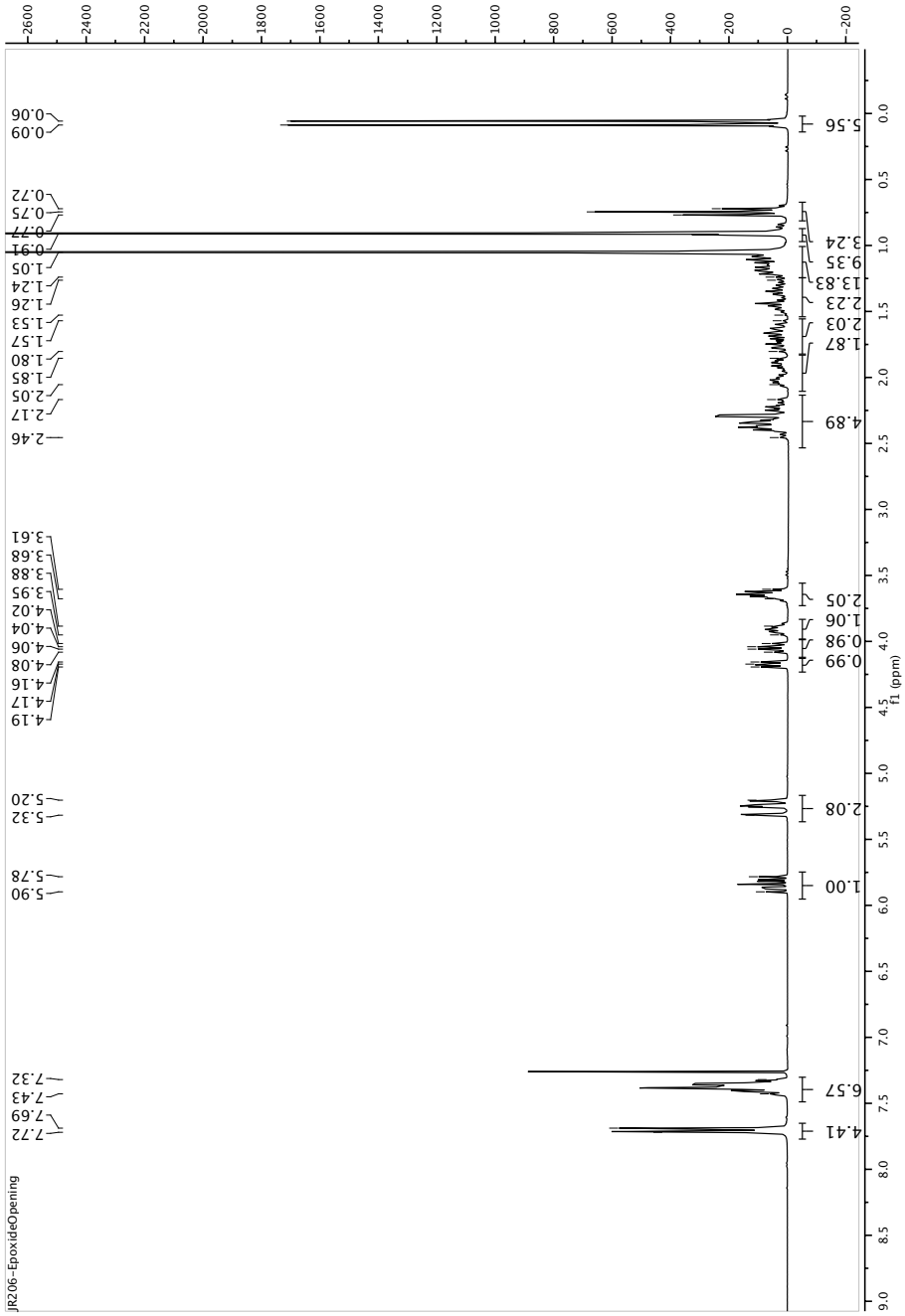

n-Bu
H
O
H
OTBDPS

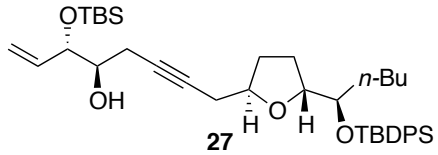
25


JR205-Carbon-Alkyne
136.04
135.99
134.70
134.36
129.28
127.27
127.24
81.45
81.28
77.29
75.61
69.42
32.48
31.47
27.44
27.26
27.11
25.17
22.74
19.58
13.93
f1 (ppm)

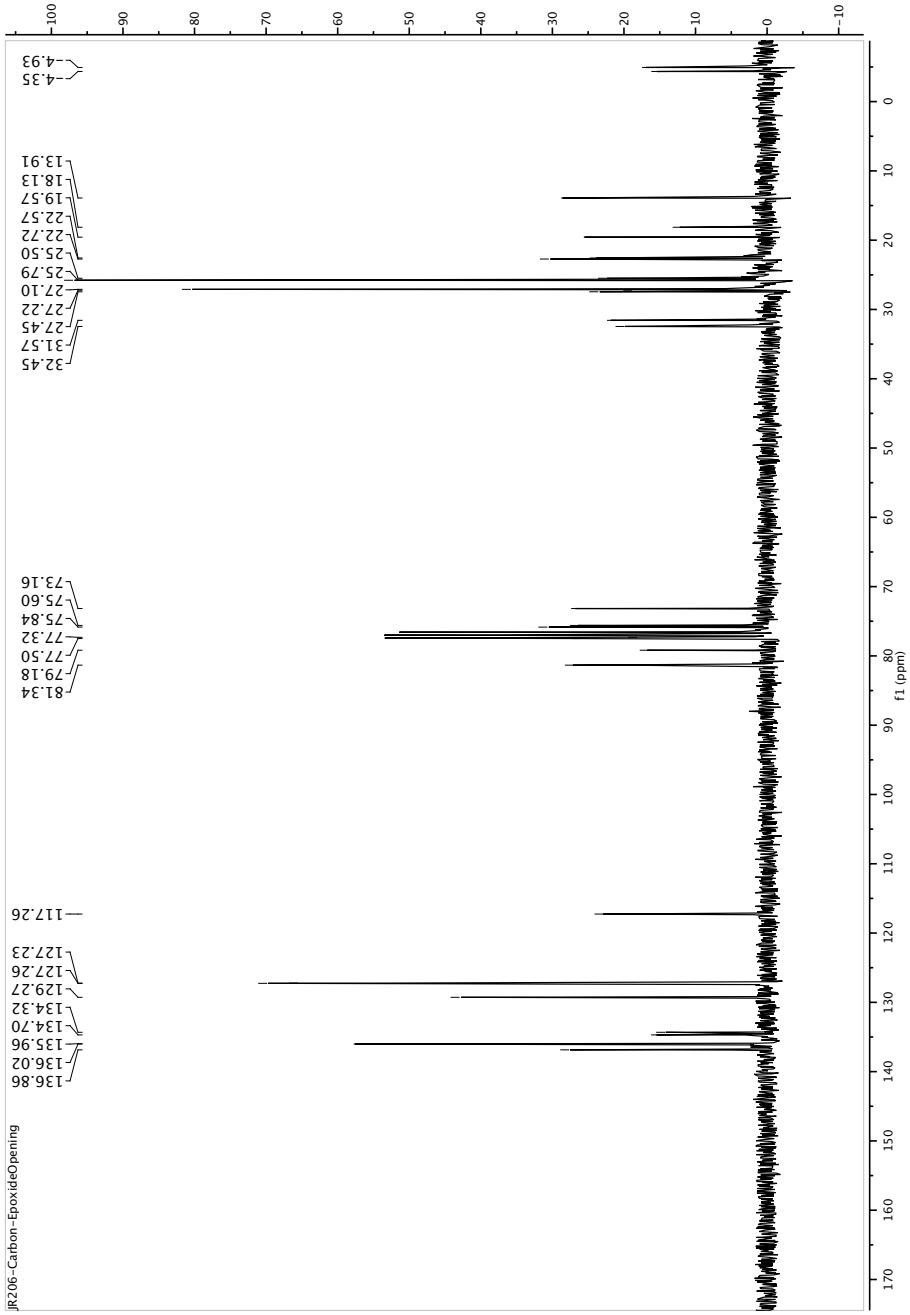

OTBS
OH
H
O
H
n-Bu
OTBDPS

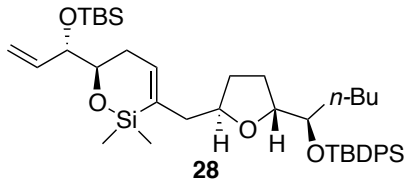
27


JR206-EpoxideOpening
f1 (ppm)
7.72
7.69
7.43
7.32
5.90
5.78
5.32
5.20
4.19
4.17
4.16
4.08
4.06
4.04
4.02
3.95
3.88
3.68
3.61
2.46
2.17
2.05
1.85
1.80
1.57
1.53
1.26
1.24
1.05
0.91
0.77
0.75
0.72
0.09
0.06
5.56
3.24
9.35
13.83
2.23
2.03
1.87
4.89
2.05
1.06
0.98
0.99
2.08
1.00
6.57
4.41

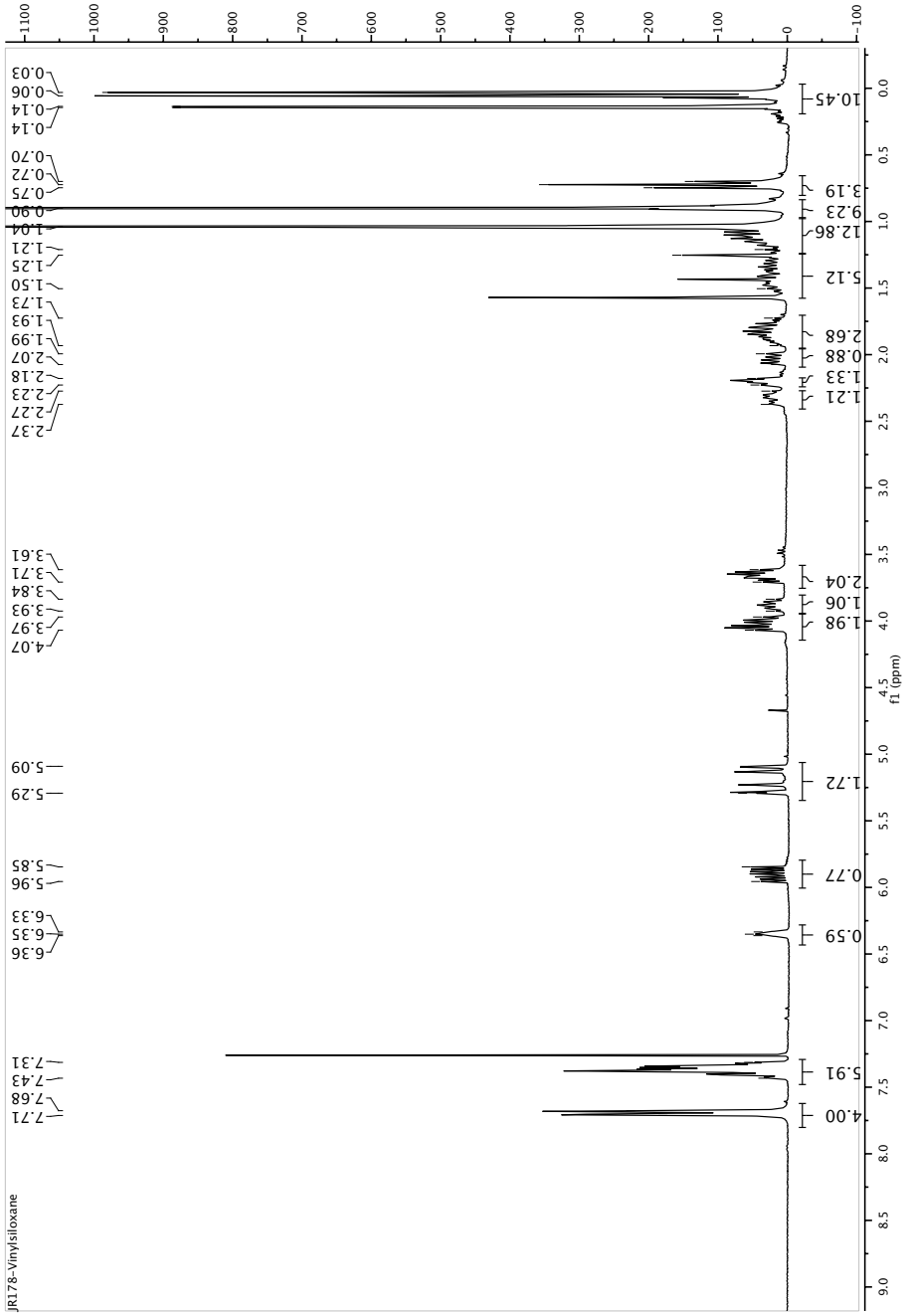

OTBS
OH
H
O
H
n-Bu
OTBDPS

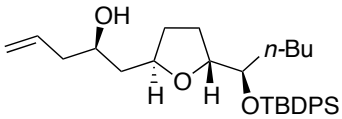
27


JR206-Carbon-EpoxideOpening
f1 (ppm)
136.86
136.02
135.96
134.70
134.32
129.27
127.26
127.23
117.26
81.34
79.18
77.50
77.32
75.84
75.60
73.16
32.45
31.57
27.45
27.22
27.10
25.79
25.50
22.72
22.57
19.57
18.13
13.91
-4.35
-4.93

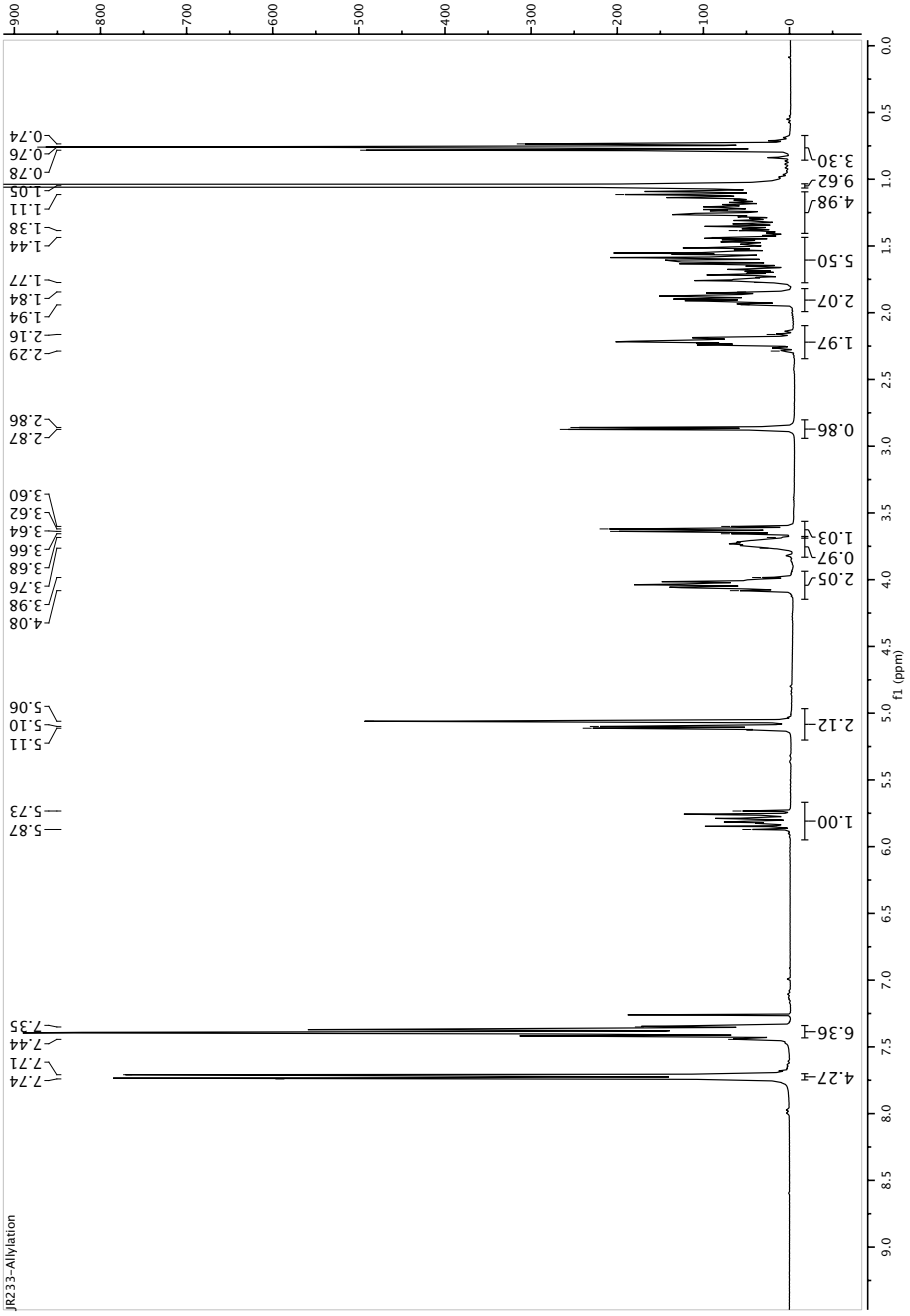

OTBS
O
Si
H
O
H
n-Bu
OTBDPS

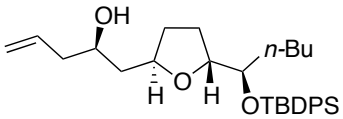
28


JR178–Vinylsiloxane
f1 (ppm)
10.45
3.19
9.23
12.86
5.12
2.68
0.88
1.33
1.21
1.98
1.06
2.04
1.72
0.77
0.59
5.91
4.00
0.03
0.06
0.14
0.14
0.70
0.72
0.75
0.90
1.04
1.21
1.25
1.50
1.73
1.93
1.99
2.07
2.18
2.23
2.27
2.37
3.61
3.71
3.84
3.93
3.97
4.07
5.09
5.29
5.85
5.96
6.33
6.35
6.36
7.31
7.43
7.68
7.71

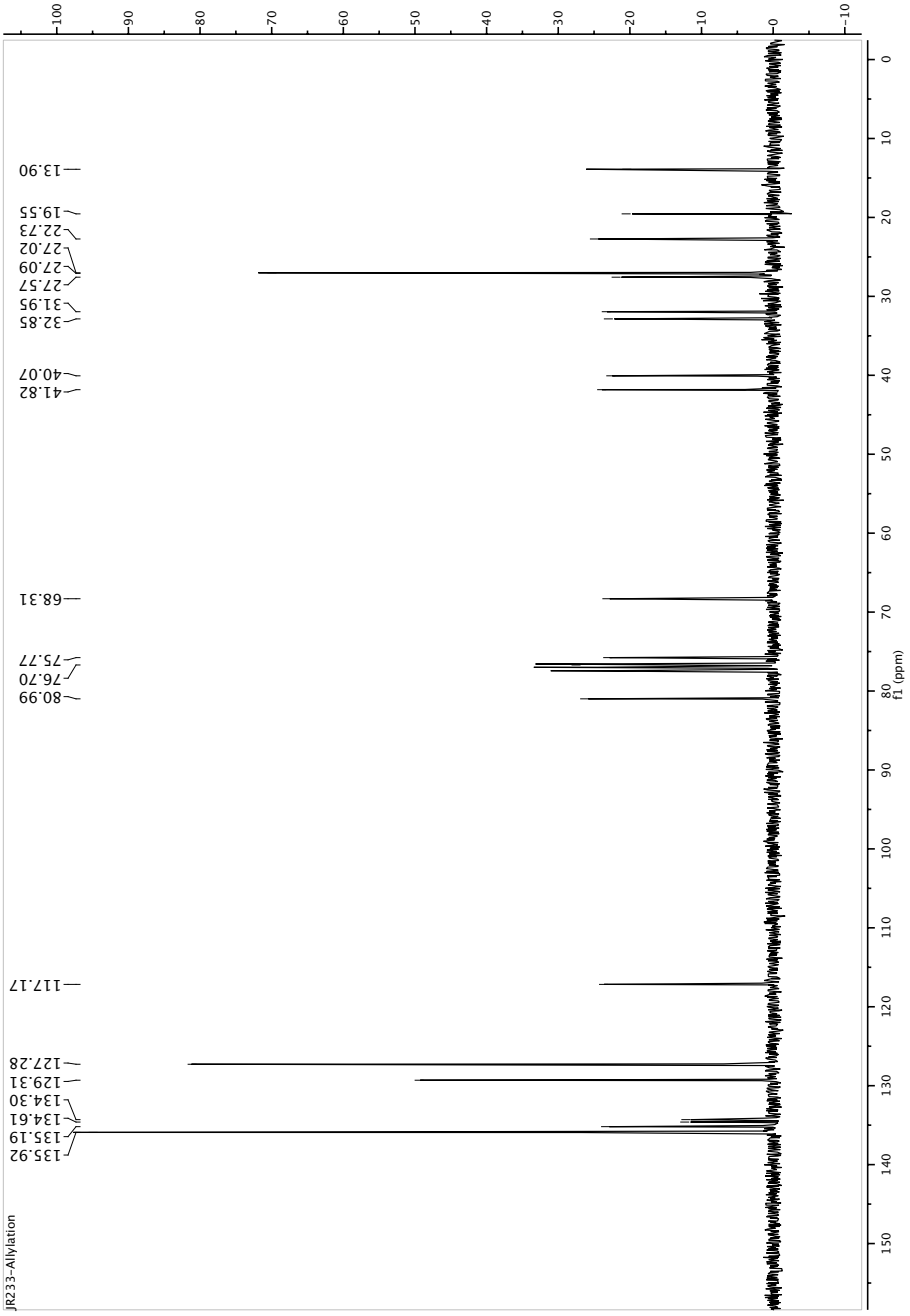

OH
n-Bu
H
O
H
OTBDPS

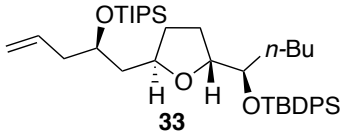
32


JR233-Allylation
7.74
7.71
7.44
7.35
5.87
5.73
5.11
5.10
5.06
4.08
3.98
3.76
3.68
3.66
3.64
3.62
3.60
2.87
2.86
2.29
2.16
1.94
1.84
1.77
1.44
1.38
1.11
1.05
0.78
0.76
0.74
4.27
6.36
1.00
2.12
2.05
0.97
1.03
0.86
1.97
2.07
5.50
4.98
9.62
3.30
f1 (ppm)

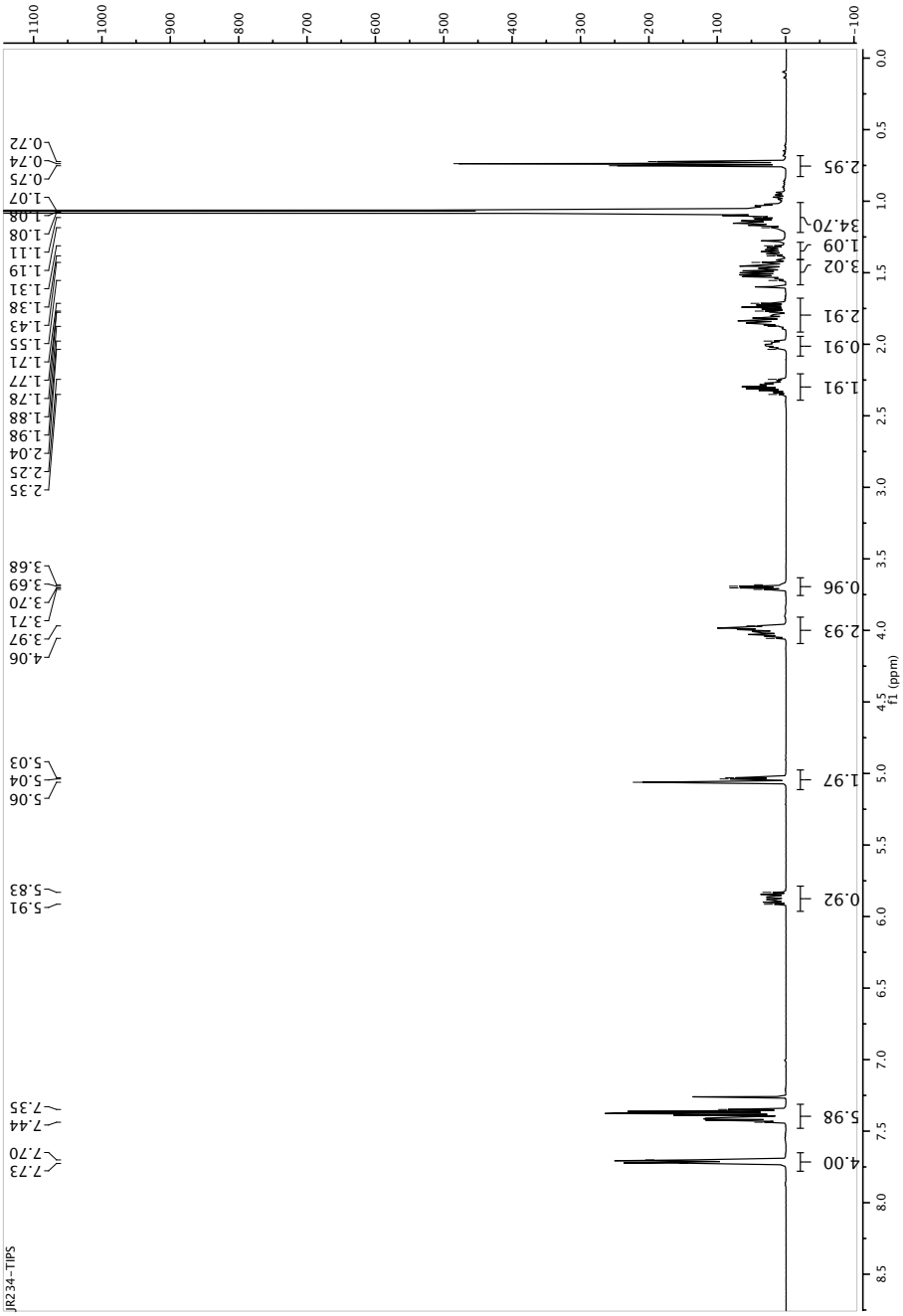

OH
n-Bu
H
O
H
OTBDPS

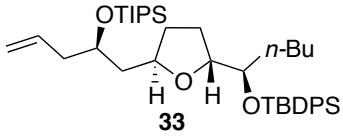
32


JR233-Allylation
135.92
135.19
134.61
134.30
129.31
127.28
117.17
80.99
76.70
75.77
68.31
41.82
40.07
32.85
31.95
27.57
27.09
27.02
22.73
19.55
13.90
f1 (ppm)

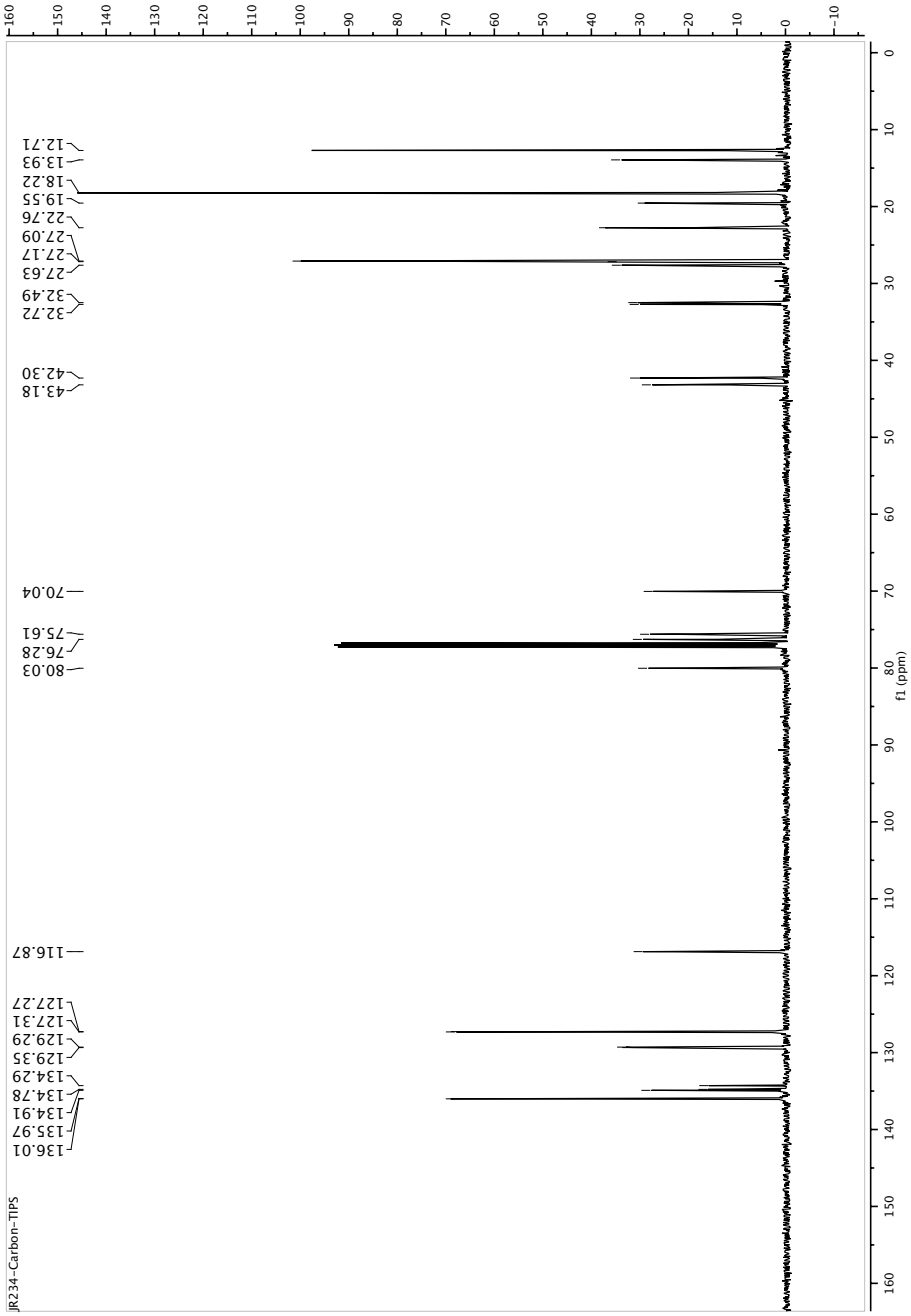

OTIPS
n-Bu
H
O
H
OTBDPS

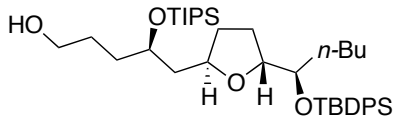
33


JR234-TIPS
f1 (ppm)
7.73
7.70
7.44
7.35
5.91
5.83
5.06
5.04
5.03
4.06
3.97
3.71
3.70
3.69
3.68
2.35
2.25
2.04
1.98
1.88
1.78
1.77
1.71
1.55
1.43
1.38
1.31
1.19
1.11
1.08
1.08
1.07
0.75
0.74
0.72
4.00
5.98
0.92
1.97
2.93
0.96
1.91
0.91
2.91
3.02
1.09
34.70
2.95

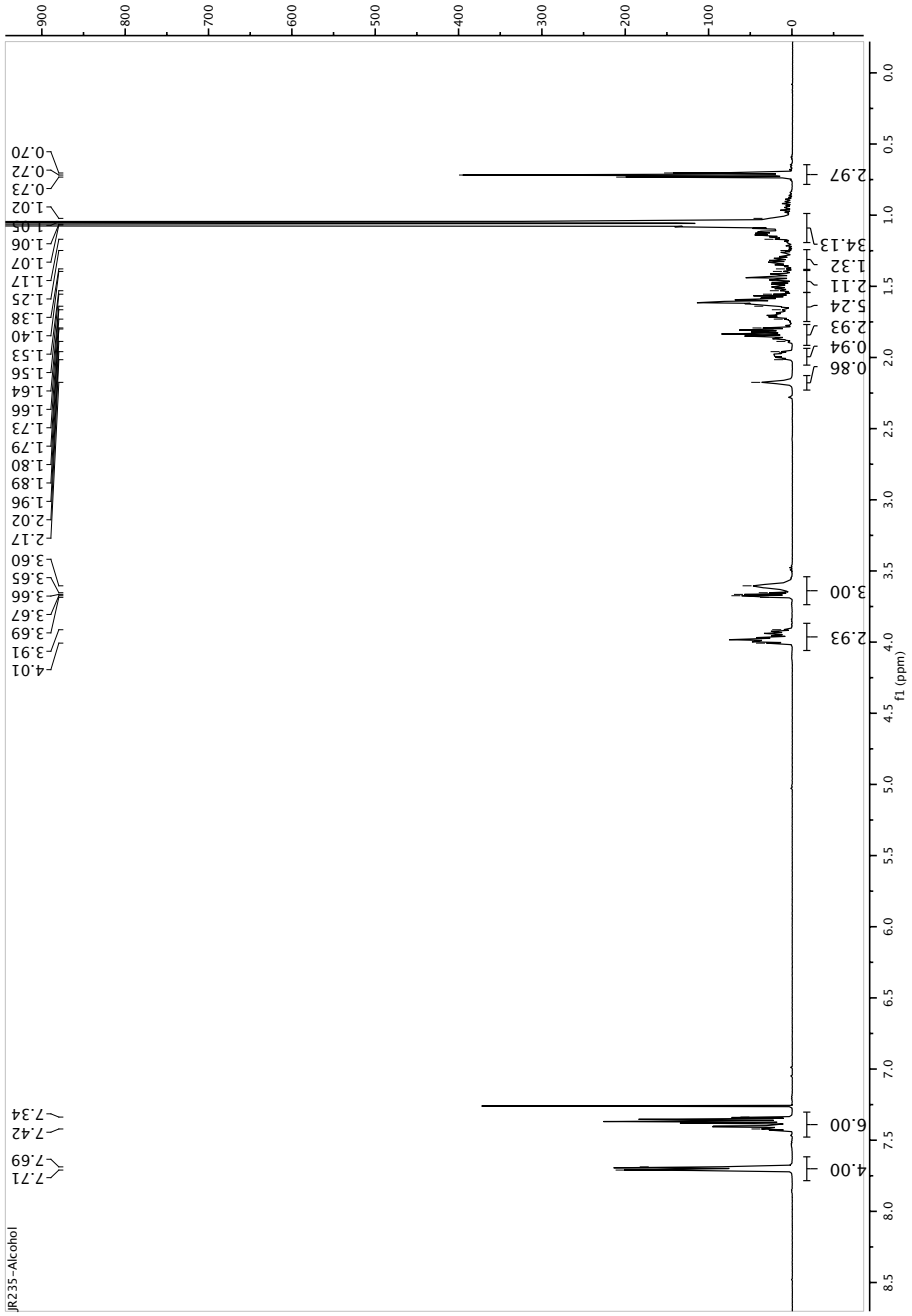

OTIPS
n-Bu
H
O
H
OTBDPS

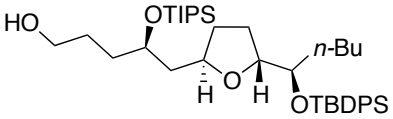
33


JR234-Carbon-TIPS
136.01
135.97
134.91
134.78
134.29
129.35
129.29
127.31
127.27
116.87
80.03
76.28
75.61
70.04
43.18
42.30
32.72
32.49
27.63
27.17
27.09
22.76
19.55
18.22
13.93
12.71
f1 (ppm)

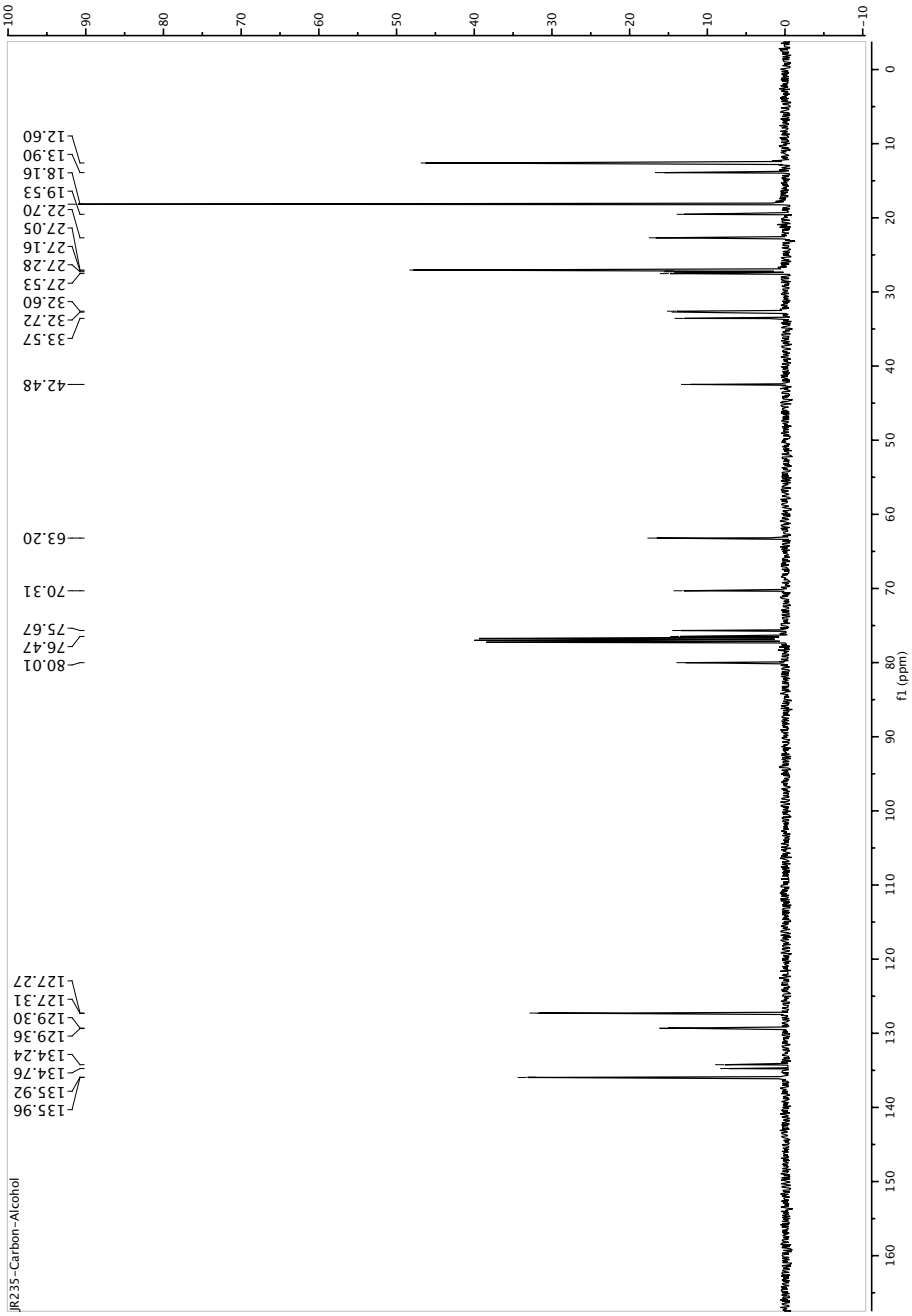

HO
OTIPS
n-Bu
H
O
H
OTBDPS

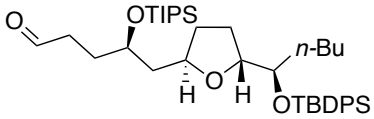
34a


JR235-Alcohol
f1 (ppm)
7.71
7.69
7.42
7.34
4.01
3.91
3.69
3.67
3.66
3.65
3.60
2.17
2.02
1.96
1.89
1.80
1.79
1.73
1.66
1.64
1.56
1.53
1.40
1.38
1.25
1.17
1.07
1.06
1.05
1.02
0.73
0.72
0.70
0.86
0.94
2.93
5.24
2.11
1.32
34.13
2.97
2.93
3.00
6.00
4.00

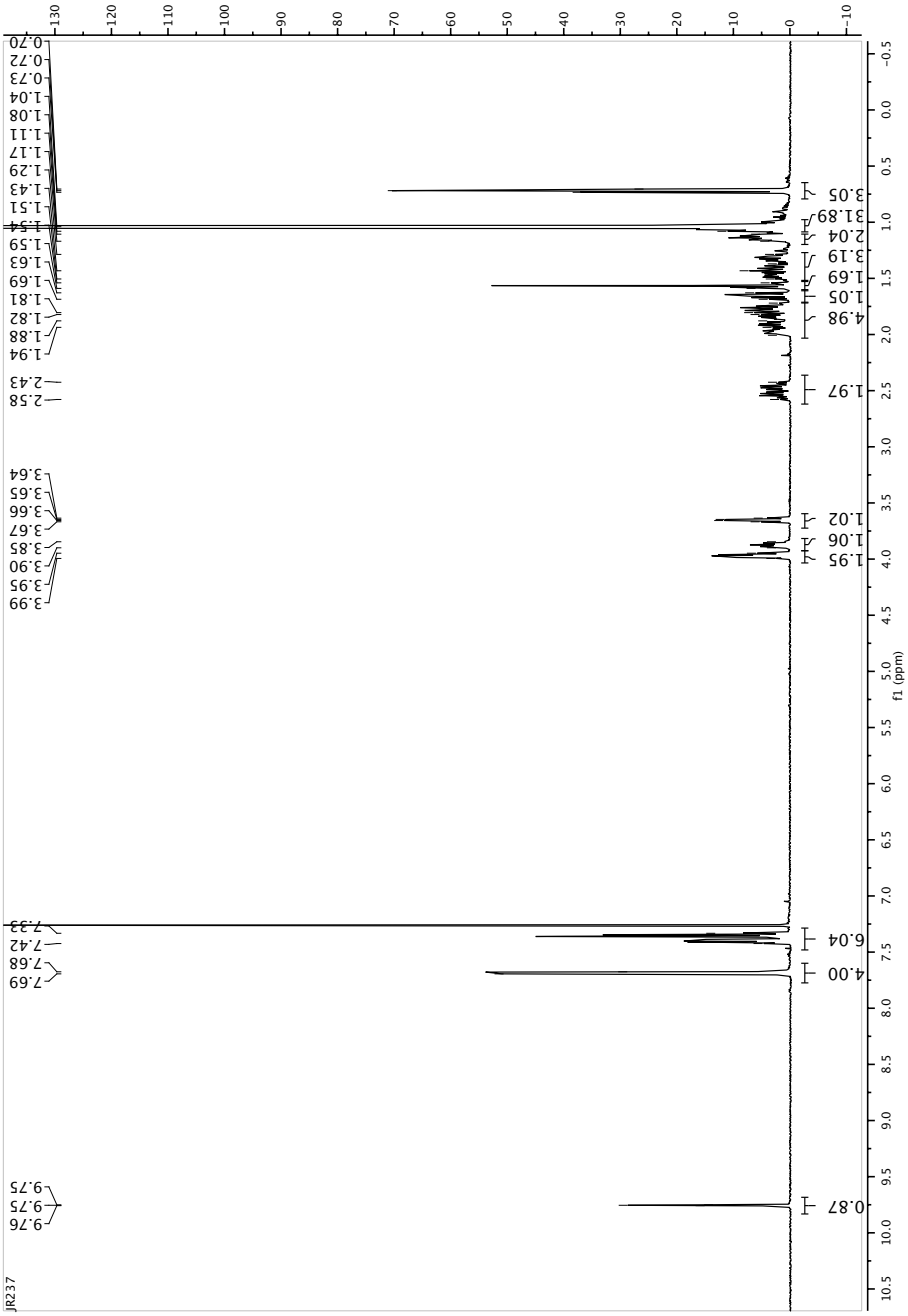

HO
OTIPS
n-Bu
H
O
H
OTBDPS

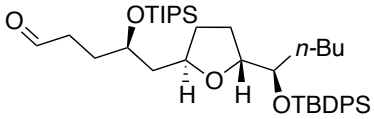
34a


JR235-Carbon-Alcohol
135.96
135.92
134.76
134.24
129.36
129.30
127.31
127.27
80.01
76.47
75.67
70.31
63.20
42.48
33.57
32.72
32.60
27.53
27.28
27.16
27.05
22.70
19.53
18.16
13.90
12.60
f1 (ppm)

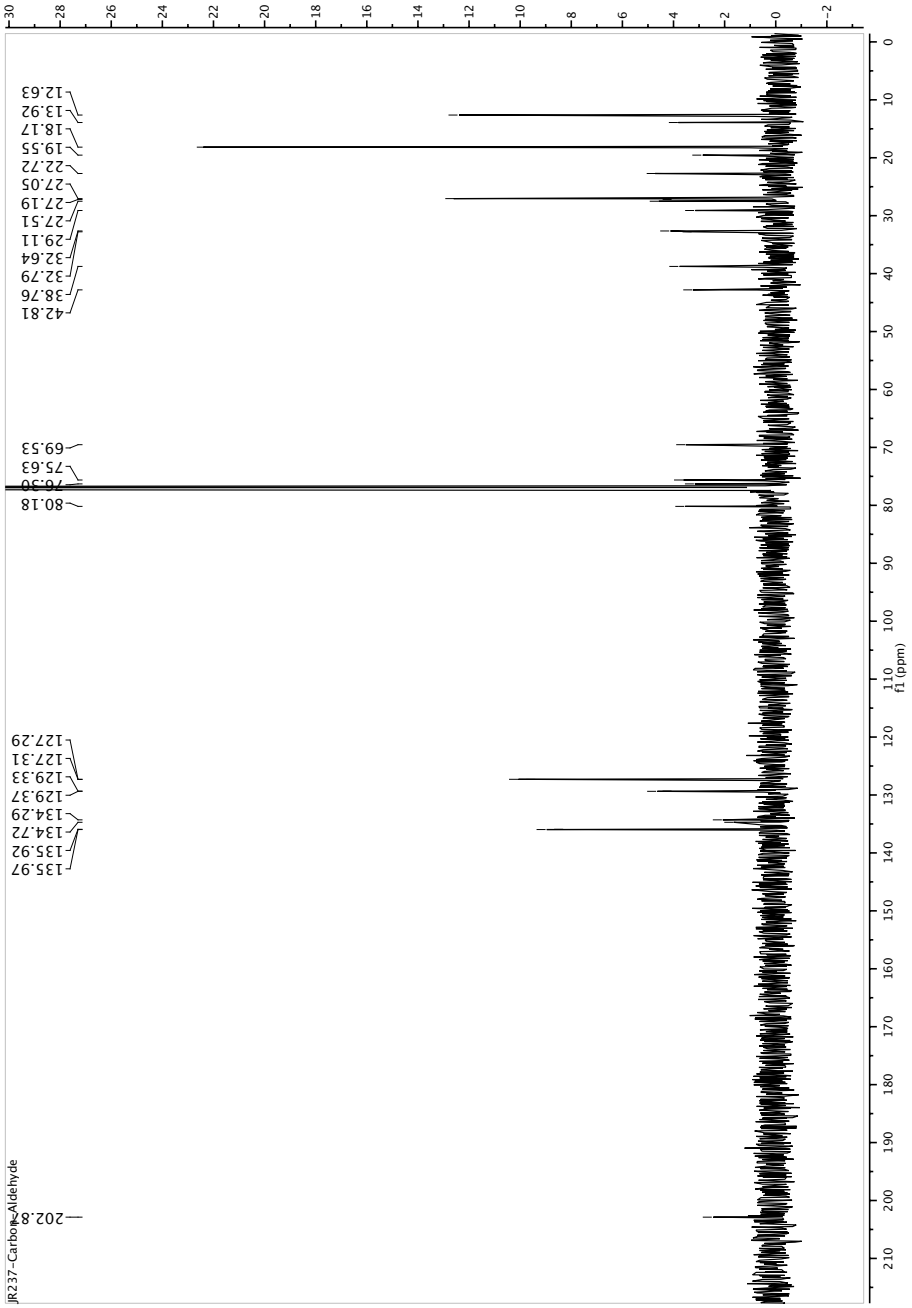

OTIPS
n-Bu
H
O
H
OTBDPS
O

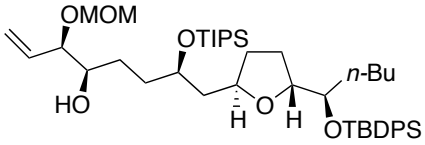
34


JR237
f1 (ppm)
9.76
9.75
9.75
7.69
7.68
7.42
7.33
3.99
3.95
3.90
3.85
3.67
3.66
3.65
3.64
2.58
2.43
1.94
1.88
1.82
1.81
1.69
1.63
1.59
1.54
1.51
1.43
1.29
1.17
1.11
1.08
1.04
0.73
0.72
0.70
0.87
4.00
6.04
1.02
1.06
1.95
1.97
4.98
1.05
1.69
3.19
2.04
31.89
3.05

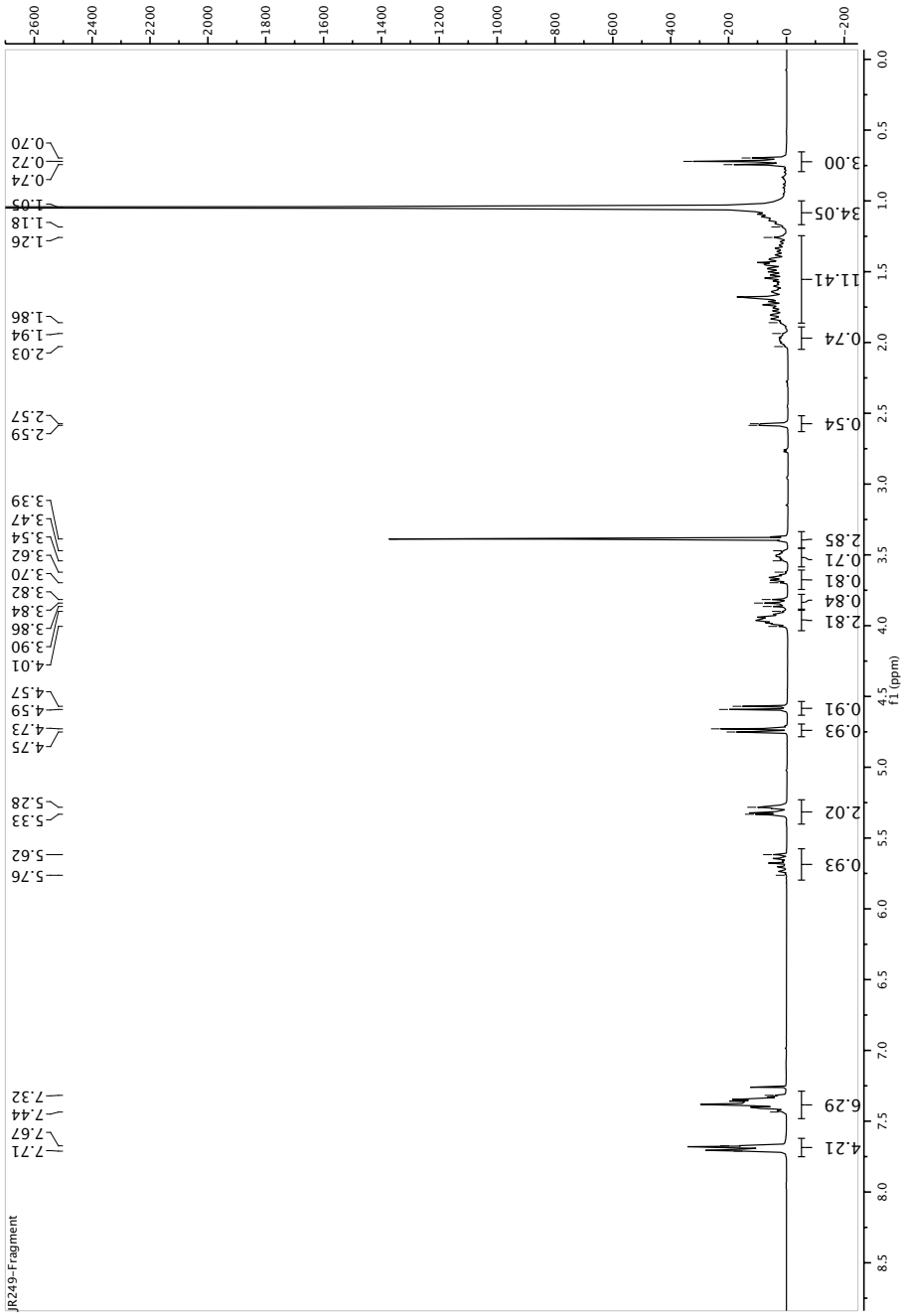

O
OTIPS
n-Bu
H
O
H
OTBDPS

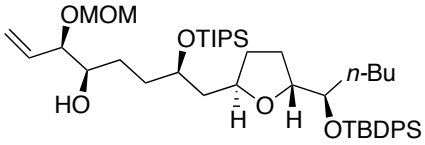
34


JR237-Carbon-Aldehyde
202.87
135.97
135.92
134.72
134.29
129.37
129.33
127.31
127.29
80.18
76.50
75.63
69.53
42.81
38.76
32.79
32.64
29.11
27.51
27.19
27.05
22.72
19.55
18.17
13.92
12.63
f1 (ppm)

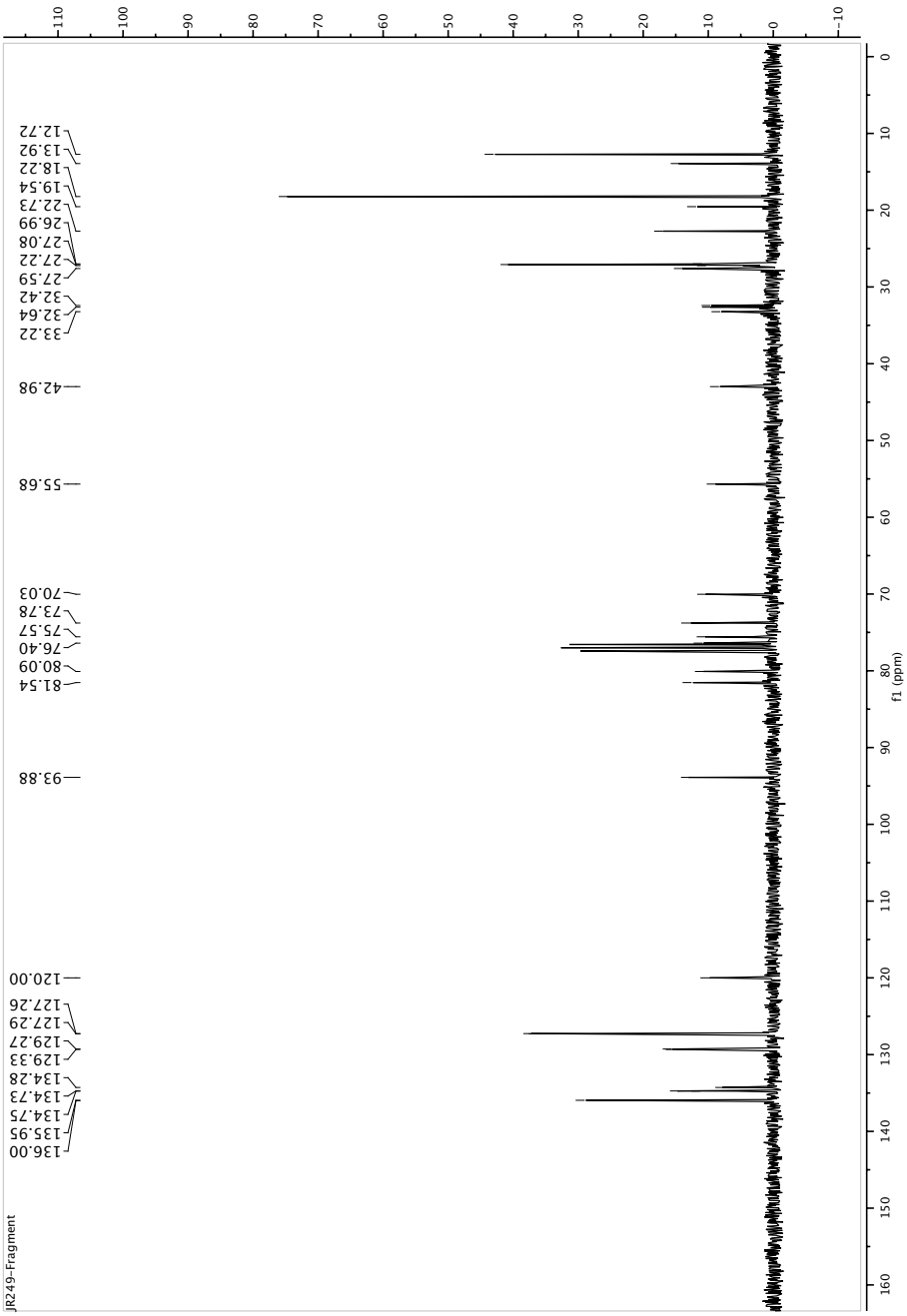

OMOM
OTIPS
n-Bu
HO
H
O
H
OTBDPS

36


JR249-Fragment
f1 (ppm)
7.71
7.67
7.44
7.32
5.76
5.62
5.33
5.28
4.75
4.73
4.59
4.57
4.01
3.90
3.86
3.84
3.82
3.70
3.62
3.54
3.47
3.39
2.59
2.57
2.03
1.94
1.86
1.26
1.18
1.05
0.74
0.72
0.70
4.21
6.29
0.93
2.02
0.93
0.91
2.81
0.84
0.81
0.71
2.85
0.54
0.74
11.41
34.05
3.00


OMOM
OTIPS
n-Bu
HO
H
O
H
OTBDPS

36


JR249-Fragment
136.00
135.95
134.75
134.73
134.28
129.33
129.27
127.29
127.26
120.00
93.88
81.54
80.09
76.40
75.57
73.78
70.03
55.68
42.98
33.22
32.64
32.42
27.59
27.22
27.08
26.99
22.73
19.54
18.22
13.92
12.72
f1 (ppm)