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Protecting-Group-Directed Stereodivergent Tsuji–Trost Cyclization: Total Synthesis of Oxylipids and (+)-Petromyroxol

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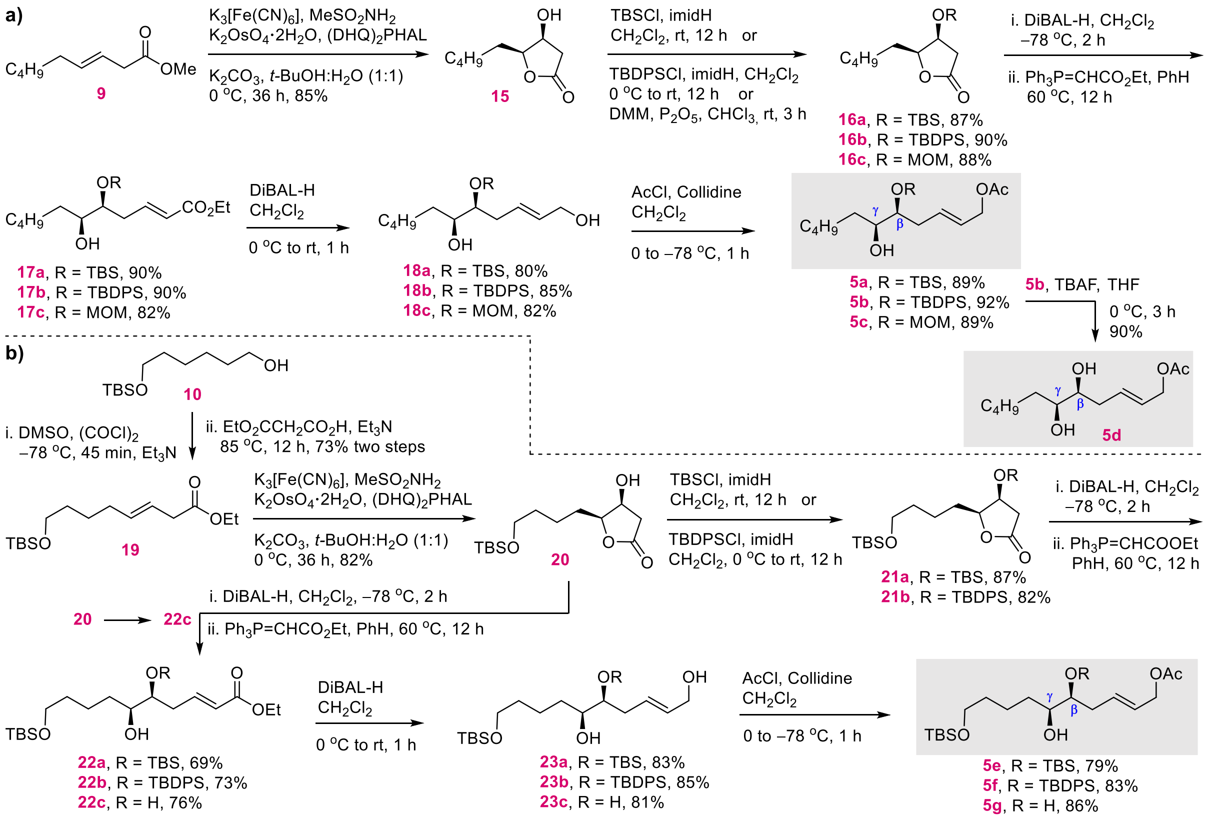
Experimental Data

General Information

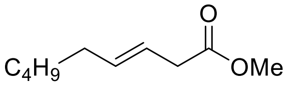
IR spectra were obtained on a Bruker Tensor 27 FT-IR spectrometer by evaporating compounds dissolved in $CHCl_3$ on CsCl pellets. ^{1}H NMR and ^{13}C NMR were recorded with the Bruker Avance III HD and Bruker Avance III 400 spectrometers operating at 500 or 400 and 125 or 100 MHz for proton and carbon nuclei, respectively. The chemical shifts are based on the $CDCl_3$ peaks at $\delta = 7.26$ ppm for proton NMR and $\delta = 77.00$ ppm (t) for carbon NMR. HRMS (ESI-TOF) spectra were recorded on Bruker Maxis Impact Sr no.282001.0008 spectrometer using positive electrospray ionization by the TOF method. Solvents were dried by using standard procedures. Tetrahydrofuran (THF) solvent was dried over sodium metal and CH_2Cl_2 by refluxing with CaH_2. Thin-layer chromatography was performed on EM 250 Kieselgel 60 F254 silica gel plates. The spots were visualized by staining with $KMnO_4$ or by using a UV lamp. For all reactions requiring heating, an oil bath was used.

Synthesis of β,γ-oxygenated allyl acetates 5a-g for Tsuji–Trost cyclization: Various β,γ-oxygenated allyl acetates **5a-g** were prepared as shown in Scheme S1 to validate the protecting-group-directed Tsuji–Trost cyclization. The Sharpless asymmetric dihydroxylation[1] of known (*E*)-β,γ-unsaturated ester **9**[2] with $(DHQ)_2$PHAL provided the γ-lactone **15**,[2] which upon β-OH group varied protection delivered **16a-c** (Scheme S1a). The DIBAL-H reduction of **16a-c** to the lactols and subsequent Wittig olefination furnished the esters **17a-c**, respectively. These were next reduced to allyl alcohols (**18a-c**) and then chemoselective acylation of primary OH furnished the β,γ-oxygenated allyl acetates **5a-c**, respectively. The silyl deprotection in **5b** gave the free diol acetate **5d**. The ester **19** (prepared from **10**[3]) under similar set of reactions[1c,2b] led to β,γ-oxygenated allyl acetates **5e-g** (Scheme S1b) with silyl or free β,γ-OH groups.



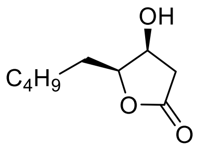
Scheme S1 Synthesis of β,γ-oxygenated allyl acetates **5a-g**.

Methyl (*E*)-non-3-enoate (9):[2]



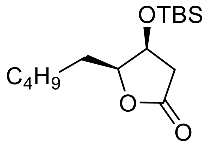
A mixture of heptanal (4.0 g, 35.03 mmol), Et_3N (4.8 mL, 35.03 mmol, 1.0 equiv) and monoethyl malonate (4.62 g, 35.03 mmol, 1.0 equiv) was heated at 85 °C under nitrogen atmosphere. After stirring for 12 h, the reaction mixture was cooled to room temperature and poured at 0 °C into aq. H_2SO_4 solution (20%, 100 mL). The organic phase was separated and the aqueous phase was extracted with EtOAc (3 × 100 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated under vacuum. Silica gel column chromatography of the crude product using petroleum ether/EtOAc (19:1) as eluent gave *β,γ*-unsaturated ester **9** (5.06 g, 85%) as colorless oil. IR ($CHCl_3$): ν_{max} = 2927, 2855, 1741, 1466, 1407, 1369, 1346, 1302, 1248, 1159, 1125, 1097, 1032, 968, 856, 771, 729 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.58–5.42 (m, 2H), 3.64 (s, 3H), 2.99 (d, J = 5.8 Hz, 2H), 1.99 (q, J = 7.2 Hz, 2H), 1.37–1.30 (m, 2H), 1.29–1.22 (m, 4H), 0.85 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 172.6, 134.9, 121.3, 51.7, 37.9, 32.4, 31.3, 28.8, 22.5, 14.0 ppm.

(4*S*,5*S*)-4-Hydroxy-5-pentyldihydrofuran-2(3*H*)-one (15):[2]



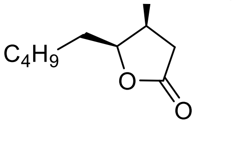
To a mixture of $K_3Fe(CN)_6$ (2.9 g, 8.82 mmol, 3.0 equiv), K_2CO_3 (1.22 g, 8.82 mmol, 3.0 equiv), and $(DHQ)_2$-PHAL (27.3 mg, 0.035 mmol, 1.2 mol%) in *t*-BuOH-H_2O (1:1, 40 mL) cooled at 0 °C was added $K_2OsO_4.2H_2O$ (6.5 mg, 0.0176 mmol, 0.6 mol%) followed by $MeSO_2NH_2$ (280 mg, 2.94 mmol, 1.0 equiv). After stirring for 5 min at 0 °C, the olefin methyl(*E*)-non-3-enoate **9** (500 mg, 2.94 mmol) was added in one portion. The reaction mixture was stirred at 0 °C for 36 h and then quenched with solid Na_2SO_3 (0.5 g). Stirring was continued for an additional 45 min and the solution was extracted with EtOAc (3× 30 mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (3:2) as an eluent gave lactone **15** (430 mg, 85%) as colorless oil. $[\alpha]_D^{25}$ –49.1 (*c* 1.0, $CHCl_3$), lit.[2] $[\alpha]_D^{25}$ –49.4 (*c* 0.8, $CHCl_3$), 96% ee.[2] IR ($CHCl_3$): ν_{max} = 3435, 3020, 2956, 2931, 2862, 1766, 1635, 1467, 1405, 1331, 1169, 1085, 1019, 979, 949, 901, 669 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.48–4.42 (m, 1H), 4.39–4.33 (m, 1H), 2.78 (dd, *J* = 17.8, 5.5 Hz, 1H), 2.54 (d, *J* = 17.8 Hz, 1H), 1.89–1.79 (m, 1H), 1.75–1.65 (m, 1H), 1.53–1.38 (m, 2H), 1.37–1.29 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 176.4, 85.3, 68.9, 39.5, 31.6, 28.2 , 25.2, 22.4, 13.9 ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_9H_{16}O_3Na$ 195.0992; Found 195.0990.

(4*S*,5*S*)-4-(*tert*-Butyldimethylsilyloxy)-5-pentyldihydrofuran-2(3*H*)-one (16a):



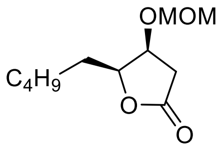
To a solution of alcohol **15** (250 mg, 1.45 mmol) in dry CH_2Cl_2 (10 mL) under argon was added imidazole (197.4, 2.90 mmol, 2 equiv) at 0 °C and the reaction mixture stirred for 30 min. TBAF (327.8 mg, 2.17 mmol, 1.5 equiv) was then added and stirring continued for another 12 h. The reaction mixture was diluted with CH_2Cl_2 (10 mL), H_2O (5 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with water, brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (9:1) as eluent to afford **16a** (362 mg, 87%) as colorless oil. $[\alpha]_D^{25}$ –24.1 (*c* 1.4, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 2931, 2860, 1780, 1464, 1408, 1362, 1254, 1165, 1096, 1028, 939, 839, 777, 697, 678 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.41–4.38 (m, 1H), 4.33–4.29 (m, 1H), 2.69 (dd, *J* = 17.3, 5.2 Hz, 1H), 2.40 (dd, *J* = 17.3, 1.2 Hz, 1H), 1.84–1.75 (m, 1H), 1.65–1.56 (m, 1H), 1.51–1.41 (m, 1H), 1.41–1.26 (m, 5H), 0.90–0.80 (m, 12H), 0.06 (s, 6H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175.6, 85.3, 69.5, 39.8, 31.7, 28.7, 25.6, 25.2, 22.5, 17.9, 14.0, –4.6, –5.2 ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{30}O_3SiNa$ 309.1857; Found 309.1858.

(4*S*,5*S*)-4-(*tert*-Butyldiphenylsilyloxy)-5-pentyldihydrofuran-2(3*H*)-one (16b):



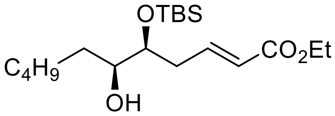
To a solution of alcohol **15** (250 mg, 1.45 mmol) in dry CH_2Cl_2 (10 mL) under argon was added imidazole (129 mg, 1.89 mmol, 1.3 equiv) at 0 °C and the reaction mixture stirred for 30 min. *tert*-Butylchlorodiphenylsilane (519 mg, 1.89 mmol, 1.3 equiv) was then added and stirring continued for another 12 h. The reaction mixture was diluted with CH_2Cl_2 (10 mL), H_2O (5 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with water, brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (9:1) as eluent to afford **16b** (536 mg, 90%) as colorless oil. $[\alpha]_D^{25}$ –20.8 (*c* 1.0, CHCl3). IR (CHCl3): ν_{max} = 3016, 2959, 2935, 2850, 1783, 1461, 1427, 1166, 1102, 1027, 942, 868, 824, 707, 614, 546, 509 cm^{-1}. ^{1}H NMR (500 MHz, CDCl3): δ = 7.66–7.59 (m, 4H), 7.49–7.43 (m, 2H), 7.43–7.37 (m, 4H), 4.47–4.43 (m, 1H), 4.27–4.21 (m, 1H), 2.44–2.34 (m, 2H), 1.96–1.86 (m, 1H), 1.73–1.64 (m, 1H), 1.55–1.43 (m, 1H), 1.35–1.28 (m, 5H), 1.08 (s, 9H), 0.90 (t, *J* = 6.9 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl3): δ = 175.3, 135.8, 135.7, 133.1, 132.5, 130.2, 130.1, 127.91, 127.90, 85.0, 70.7, 39.0, 31.6, 29.0, 26.8, 25.3, 22.5, 19.3, 14.0 ppm. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{25}H_{34}O_3SiNa$ 433.2169; Found 433.2166.

(4*S*,5*S*)-4-(Methoxymethoxy)-5-pentyldihydrofuran-2(3*H*)-one (16c):



To a solution of alcohol **15** (100 mg, 0.580 mmol) in CHCl3 (10 mL) at 0 °C under argon was added dimethoxymethane (0.26 mL, 2.90 mmol, 5 equiv) dropwise. After 5 min phosphorus pentoxide (41.2 mg, 0.29 mmol, 0.5 equiv) was added and resulting mixture stirred for 3 h at rt. The reaction mixture was diluted with CH_2Cl_2 (10 mL), H_2O (5 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were dried (Na_2SO_4) and then concentrated. The crude product was purified by silica gel column chromatography using petroleum ether/EtOAc (4:1) as eluent to get the pure compound **16c** (110.4 mg, 88%) as colorless oil. $[\alpha]_D^{25}$ –3.2 (*c* 1.1, CHCl3). IR (CHCl3): ν_{max} = 2952, 2931, 2862, 1780, 1467, 1409, 1351, 1301, 1203, 1155, 1101, 1042, 919, 810, 758, 667 cm^{-1}. ^{1}H NMR (400 MHz, CDCl3): δ = 4.68–4.59 (m, 2H), 4.46–4.38 (m, 1H), 4.36–4.30 (m, 1H), 4.36 (d, *J* = 1.0 Hz, 3H), 2.74–2.58 (m, 2H), 1.93–1.78 (m, 1H), 1.78–1.63 (m, 1H), 1.54–1.44 (m, 1H) 1.38–1.26 (m, 5H), 0.88 (t, *J* = 5.0 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl3): δ = 175.2, 95.6, 84.1, 73.7, 55.9, 36.8, 31.6, 28.4, 25.2, 22.4, 13.9 ppm. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{11}H_{20}O_4Na$ 239.1254; Found 239.1250.

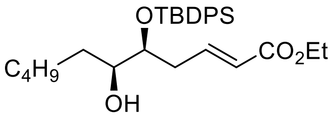
Ethyl (5*S*,6*S*,2*E*)-5-(*tert*-butyldimethylsilyloxy)-6-hydroxyundec-2-enoate (17a):



To a cooled solution of lactone **16a** (180 mg, 0.628 mmol, 1 equiv) in dry CH_2Cl_2 (10 mL) under argon atmosphere was added DiBAL-H (0.49 mL, 0.691 mmol, 1.4 M solution in toluene, 1.1 equiv) dropwise over a period of 15 min. The reaction mixture was stirred at –78 °C for 30 min and then quenched with a saturated aq. solution of Rochelle's salt (3 mL). Stirring was continued for 2 h at room temperature and then the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated to give the crude lactol (180 mg), which was used for the next reaction without further purification.

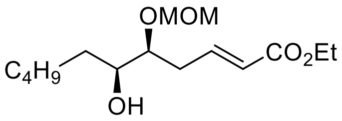
To a stirred solution of (carbethoxymethylene)triphenylphosphorane (328 mg, 0.942 mmol, 1.5 equiv) in benzene (10 mL) was added a solution of above lactol (180 mg) in dry benzene (10 mL) and the mixture stirred for 12 h at 60 °C. It was then quenched with saturated aq. NH_4Cl (5 mL) and the solution extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with water, brine, dried (Na$_2$SO$_4$) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (9:1) as eluent to give **17a** (202.7 mg, 90%) as colorless oil. $[\alpha]_D^{25}$ +25.0 (*c* 0.5, CHCl$_3$). IR (CHCl$_3$): ν_{max} = 3565, 3010, 2956, 2930, 2858, 1714, 1644, 1464, 1416, 1389, 1256, 1182, 1094, 938, 837, 668 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 6.97–6.87 (m, 1H), 5.86 (dt, *J* = 15.8, 1.3 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.67–3.59 (m, 1H), 3.44–3.32 (m, 1H), 2.59–2.49 (m, 1H), 2.39–2.29 (m, 1H), 2.03 (d, *J* = 7.2 Hz, 1H, *OH*), 1.50–1.36 (m, 3H), 1.34–1.24 (m, 8H), 0.91–87 (m, 12H), 0.079 (s, 6H) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 166.3, 144.8, 123.8, 74.0, 73.0, 60.2, 37.0, 33.8, 31.8, 25.8, 25.5, 22.6, 18.1, 14.2, 14.0, –4.2, –4.6 ppm. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{19}$H$_{38}$O$_4$SiNa 381.2432; Found 381.2430.

Ethyl (5*S*,6*S*,2*E*)-5-(*tert*-butyldiphenylsilyloxy)-6-hydroxyundec-2-enoate (17b):



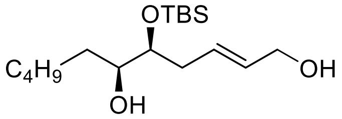
The titled compound was prepared from lactone **16b** (180 mg, 0.438 mmol) by similar procedure as described for **17a** to give **17b** (190 mg, 90%) as colorless oil. $[\alpha]_D^{25}$ +18.0 (*c* 1.0, CHCl$_3$), lit. $[\alpha]_D^{25}$ +17.3 (*c* 5.0, CHCl$_3$). IR (CHCl$_3$): ν_{max} = 3612, 2985, 2945, 2908, 1741, 1463, 1447, 1374, 1243, 1158, 1097, 1048, 938, 917, 848, 785, 758, 634, 608 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.71–7.67 (m, 4H), 7.47–7.42 (m, 2H), 7.41–7.36 (m, 4H), 6.77–6.68 (m, 1H), 5.65 (d, *J* = 15.6 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.74–3.68 (m, 1H), 3.46–3.39 (m, 1H), 2.56–2.48 (m, 1H), 2.27–2.20 (m, 1H), 2.08 (brs, 1H, *OH*), 1.50–1.33 (m, 3H), 1.30–1.21 (m, 8H), 1.09 (s, 9H), 0.87 (t, *J* = 6.9 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 166.1, 144.4, 135.9, 135.8, 133.5, 132.9, 129.9, 129.8, 127.7, 127.6, 127.5, 123.7, 75.0, 72.8, 60.1, 36.3, 33.4, 31.8, 27.0, 25.4, 22.5, 19.4, 14.1, 13.9 ppm. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for C$_{29}$H$_{42}$O$_4$SiNa 505.2745; Found 505.2742.

Ethyl (5*S*,6*S*,2*E*)-6-hydroxy-5-(methoxymethoxy)undec-2-enoate (17c):



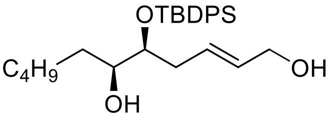
The titled compound was prepared from lactone **16c** (100 mg, 0.462 mmol) by similar procedure as described for **17a** to give **17c** (109 mg, 82%) as a colorless oil. $[\alpha]_D^{25}$ +5.0 (*c* 1.1, CHCl$_3$). IR (CHCl$_3$): ν_{max} = 2932, 1721, 1657, 1466, 1368, 1318, 1268, 1171, 1115, 1099, 1038, 919, 863 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 6.95 (ddd, *J* = 15.2, 7.9, 7.3 Hz, 1H), 5.88 (dd, *J* = 15.5, 0.6 Hz, 1H), 4.68 (d, *J* = 0.41 Hz, 2H), 4.17 (qd, *J* = 7.1 Hz, 0.6 Hz, 2H), 3.56–3.47 (m, 2H), 3.39 (d, *J* = 0.78 Hz, 3H), 2.61–2.50 (m, 1H), 2.49–2.38 (m, 1H), 2.28 (brs, 1H, *OH*), 1.52–1.39 (m, 3H), 1.35–1.22 (m, 8H), 0.87 (t, *J* = 6.5 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 166.2, 144.6, 123.8, 96.9, 80.9, 72.6, 60.2, 55.9, 34.2, 33.1, 31.8, 25.2, 22.6, 14.2, 14.0 ppm. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for C$_{15}$H$_{28}$O$_5$Na 311.1829; Found 311.1821.

(5*S*,6*S*,2*E*)-5-(*tert*-Butyldimethylsilyloxy)undec-2-ene-1,6-diol (18a):



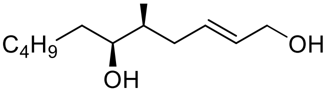
To a stirred solution of *α,β*-unsaturated ester **17a** (200 mg, 0.557 mmol) in dry THF (15 mL) at 0 °C under argon atmosphere was added dropwise DiBAL-H (1.2 mL, 1.67 mmol, 1.4 M solution in toluene, 3.0 equiv). The reaction mixture was stirred for 30 min, warmed to room temperature and stirred for additional 30 min. It was then quenched with a saturated aq. solution of Rochelle's salt (2 mL), stirred for 1 h and then extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (7:3) to give **18a** (141 mg, 80%) as colorless oil. $[\alpha]_D^{25}$ +5.8 (*c* 1.8, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3420, 3018, 2956, 2931, 2859, 1471, 1391, 1256, 1080, 1006, 975, 837, 669 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.72–5.59 (m, 2H), 4.07 (d, *J* = 4.2 Hz, 2H), 3.57–3.50 (m, 1H), 3.44–3.37 (m, 1H), 2.44–2.36 (m, 1H), 2.23–2.14 (m, 1H), 2.10 (brs, 2H, *OH*), 1.46–1.23 (m, 8H), 0.88–0.85 (m, 12H), 0.067 (s, 3H), 0.057 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 131.9, 128.0, 74.5, 72.4, 63.4, 37.0, 34.0, 31.9, 25.8, 25.5, 22.6, 18.0, 14.0, –4.2, –4.7 ppm. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{17}H_{36}O_3SiNa$ 339.2326; Found 339.2322.

(5*S*,6*S*,2*E*)-5-(*tert*-Butyldiphenylsilyloxy) undec-2-ene-1,6-diol (18b):



The titled compound was prepared from **17b** (200 mg, 0.414 mmol) by similar procedure as described for **18a** to give **18b** (155 mg, 85%) as a white solid. M.P. 68–70 °C, $[\alpha]_D^{25}$ +9.0 (*c* 1.0, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3388, 3071, 2931, 2857, 1589, 1471, 1427, 1390, 1188, 1111,1075, 999, 973, 938, 821, 739, 702, 609, 507, 489 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71–7.66 (m, 4H), 7.47–7.36 (m, 6H), 5.48–5.33 (m, 2H), 3.92 (d, *J* = 5.13 Hz, 2H), 3.66–3.60 (m, 1H), 3.48–3.42 (m, 1H), 2.43–2.30 (m, 1H), 2.15–2.07 (m, 1H), 1.77 (brs, 2H, *OH*), 1.52–1.33 (m, 3H), 1.30–1.18 (m, 5H), 1.07 (s, 9H), 0.87 (t, *J* = 6.9 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 135.93, 135.90, 133.9, 133.2, 131.9, 129.9, 129.7, 128.0, 127.7, 127.5, 75.7, 72.7, 63.4, 36.5, 33.8, 31.8, 27.1, 25.5, 22.6, 19.5, 14.0 ppm. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{27}H_{40}O_3SiNa$ 463.2639; Found 463.2632.

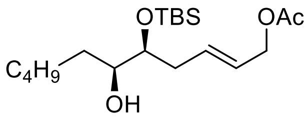
(5S,6S,2*E*)-5-(Methoxymethoxy)undec-2-ene-1,6-diol (18c):



The titled compound was prepared from **17c** (100 mg, 0.347 mmol) by similar procedure as described for **18a** to give **18c** (68 mg, 82%) as colourless oil. $[\alpha]_D^{25}$ +1.1 (*c* 1.2, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3404, 2931, 2871, 1656, 1467, 1379, 1261, 1151, 1103, 1034, 972, 920, 801, 764, 726 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.73–5.63 (m, 2H), 4.73–4.62 (m, 2H), 4.05 (d, *J* = 3.78 Hz, 2H), 3.53–3.46 (m, 1H), 3.46–3.39 (q, *J* = 5.7 Hz, 1H), 3.37 (m, 3H), 2.63 (s, 2H, *OH*), 2.45–2.35 (m, 1H), 2.33–2.21 (m, 1H), 1.49–1.37 (m, 3H), 1.34–1.20 (m, 5H), 0.86 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):

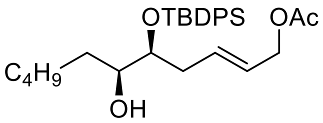
δ = 132.0, 127.8, 96.5, 81.3, 72.3, 63.2, 55.8, 34.0, 33.1, 31.8, 25.2, 22.5, 14.0 ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{26}O_4Na$ 269.1723; Found 269.1720.

(5*S*,6*S*,2*E*)-5-(*tert*-Butyldimethylsilyloxy)-6-hydroxyundec-2-en-1-yl acetate (5a):



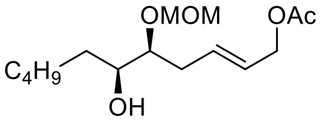
To a stirred solution of allyl alcohol **18a** (60 mg, 0.189 mmol) in dry CH_2Cl_2 (10 mL) at 0 °C was added 2,3,5-collidine (0.049 ml, 0.379 mmol, 2.0 equiv) and the reaction mixture was stirred for 15 min. It was then cooled to −78 °C and acyl chloride (0.016 mL, 0.227 mmol, 1.2 equiv) was added dropwise. The reaction mixture was stirred for 1 h and then warmed to room temperature. It was quenched with water (1 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (9:1) to give **5a** (60.3 mg, 89%) as colorless oil. $[\alpha]_D^{25}$ +3.4 (*c* 0.7, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3478, 2951, 2932, 2857, 1739, 1462, 1385, 1364, 1255, 1083, 1026, 837, 669 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.78–5.68 (m, 1H), 5.66–5.55 (m, 1H), 4.49 (d, *J* = 6.2 Hz, 2H), 3.58–3.51 (m, 1H), 3.44–3.35 (m, 1H), 2.45–2.35 (m, 1H), 2.25–2.15 (m, 1H), 2.07 (d, *J* = 7.1 Hz, 1H, *OH*), 2.03 (s, 3H), 1.44–1.21 (m, 8H), 0.90–0.86 (m, 12H), 0.059 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 170.8, 131.6, 126.7, 74.4, 72.6, 64.9, 37.0, 33.8, 31.8, 25.8, 25.5, 22.6, 20.9, 18.0, 14.0, −4.2, −4.7 ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{38}O_4SiNa$ 381.2432; Found 381.2432.

(5*S*,6*S*,2*E*)-5-(*tert*-Butyldiphenylsilyloxy)-6-hydroxyundec-2-en-1-yl acetate (5b):



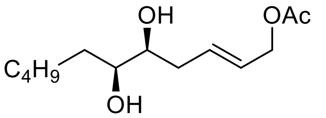
The titled compound was prepared from **18b** (100 mg, 0.227 mmol) by similar procedure as described for **5a** to give **5b** (101 mg, 92%) as a colorless oil. $[\alpha]_D^{25}$ +14.3 (*c* 1.14, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3437, 2930, 1742, 1466, 1243, 1109, 702 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.72–7.66 (m, 4H), 7.47–7.35 (m, 6H), 5.55–5.35 (m, 1H), 5.51–3.44 (m, 1H), 4.37 (d, *J* = 6.0 Hz, 2H), 3.68–3.60 (m, 1H), 3.50–3.42 (m, 1H), 2.43–2.35 (m, 1H), 2.18–2.08 (m, 2H), 2.01 (s, 3H), 1.47–1.37 (m, 3H), 1.33–1.17 (m, 5H), 1.08 (s, 9H), 0.88 (t, *J* = 6.9 Hz, 3H) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ = 170.6, 135.9, 135.8, 133.7, 133.1, 131.3, 129.8, 129.7, 127.7, 127.5, 126.7, 75.5, 72.6, 64.8, 36.4, 33.6, 31.7, 27.0, 25.4, 22.5, 20.8, 19.4, 14.0 ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{29}H_{42}O_4SiNa$ 505.2745*;* Found 505.2742.

(5*S*,6*S*,2*E*)-6-Hydroxy-5-(methoxymethoxy)undec-2-en-1-yl acetate (5c):



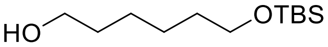
The titled compound was prepared from **18c** (60 mg, 0.244 mmol) by similar procedure as described for **5a** to give **5c** (62.5 mg, 89%) as a colorless oil. $[\alpha]_D^{25}$ +12.0 (*c* 0.5, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3468, 2930, 2859, 1740, 1463, 1378, 1238, 1151, 1102, 1037, 970, 919, 769. 607 1243, 1109, 702 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.82–5.73 (m, 1H), 5.69–5.62 (m, 1H), 4.72–4.65 (m, 2H), 4.51 (dd, J = 6.23, 0.75 Hz, 2H), 3.53–3.48 (m, 1H), 3.46–3.42 (m, 1H), 2.91 (s, 3H), 2.48–2.39 (m, 1H), 2.34–2.24 (m, 1H), 2.05 (s, 3H), 1.51–1.38 (m, 3H), 1.38–1.23 (m, 6H), 0.88 (t, J = 6.5 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 170.8, 131.4, 126.8, 96.8, 81.4, 72.4, 64.9, 55.9, 34.2, 33.1, 31.8, 25.2, 22.6, 20.9, 14.0 ppm. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{15}H_{28}O_5Na$ 311.1829; Found 311.1826.

(5*S*,6*S*,2*E*)-5,6-Dihydroxyundec-2-en-1-yl acetate (5d):



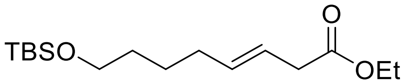
To a solution of **5b** (80 mg, 0.166 mmol) in THF (5 mL) was added (nBu)$_4$NF (0.27 mL, 1M in THF, 0.265 mmol, 1.6 equiv) at room temperature and the mixture was stirred for 1 h. Water (5 mL) was added and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The organic extracts were washed with brine (2 × 10 mL), dried (Na_2SO_4) and the solvent was evaporated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (7:3) as eluent to afford **5d** (36.5 mg, 90%) as a colorless oil. $[\alpha]_D^{25}$ –22.3 (*c* 0.2, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3393, 2956, 1648, 1740, 1462, 1380, 1259, 1240, 1045, 1026, 971, 760 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.85–5.74 (m, 1H), 5.69–5.58 (m, 1H), 4.49 (d, J = 6.2 Hz, 2H), 3.50–3.32 (m, 2H), 2.79 (brd, 2H, *OH*), 2.36–2.15 (m, 2H), 2.03 (s, 3H), 1.54–1.18 (m, 8H), 0.85 (t, J = 6.5 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 171.0, 131.8, 126.8, 73.8, 73.3, 64.9, 36.6, 33.3, 31.7, 25.2, 22.5, 20.9, 13.9 ppm. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{13}H_{24}O_4Na$ 267.1567; Found 267.1562.

6-*tert*-Butyldimethylsilyloxyhexan-1-ol (10):[3]



To a solution of 1,6-hexanediol (2.0 g, 16.9 mmol) in dry CH_2Cl_2 (60 mL) at 0 °C under argon was added imidazole (1.15 g, 16.9 mmol, 1 equiv) at 0 °C and the reaction mixture stirred for 30 min. TBS-Cl (2.55 g, 16.9 mmol, 1 equiv) was then added and stirring continued for another 12 h. The reaction mixture was diluted with H_2O (50 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with water, brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (7:3) as eluent giving the alcohol **10** (3.61 g, 92%) as a colorless oil. IR ($CHCl_3$): ν_{max} = 3365, 2934, 2858, 1646, 1471, 1463, 1361, 1255, 1216, 1059, 1007, 939, 878, 836, 815, 774, 760, 667 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.52–3.42 (m, 5H), 1.48–1.36 (m, 4H), 1.29–1.20 (m, 4H), –0.80 (s, 9H), –0.06 (s, 6H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 63.0, 62.1, 32.6, 32.5, 25.8, 25.5, 25.45, 18.1, –5.5 ppm. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{12}H_{28}O_2SiNa$ 255.1751; Found 255.1742.

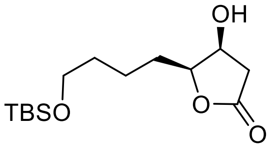
(*E*)-Ethyl 8-(*tert*-butyldimethylsilyloxy)oct-3-enoate (19):



To a solution of DMSO (1.4 mL, 19.36 mmol, 3.0 equiv) in CH_2Cl_2 (50 mL) at −78 °C was added oxalyl chloride (0.83 mL, 9.68 mmol, 1.5 equiv). The resulting solution was stirred for 15 min, and then the solution of alcohol **10** (1.5 g, 6.45 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was added and stirring continued for 45 min. It was then quenched with Et_3N (3.6 mL, 25.8 mmol, 4.5 equiv) and saturated aq. $NaHCO_3$ (50 mL) and the solution extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated. The crude aldehyde (1.62 g) was used without purification for next step.

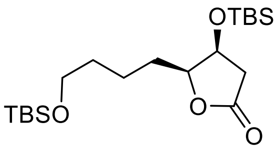
A mixture of aldehyde (1.62 g), Et_3N (0.9 mL, 6.45 mmol, 1.0 equiv) and monoethyl malonate (0.851 g, 6.45 mmol, 1.0 equiv) was heated at 85 °C under nitrogen atmosphere. After stirring for 12 h, the reaction mixture was cooled to room temperature and poured at 0 °C into aq. H_2SO_4 solution (20%, 100 mL). The organic phase was separated and the aqueous phase was extracted with EtOAc (3 × 100 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated under vacuum. Silica gel column chromatography of the crude product using petroleum ether/EtOAc (19:1) as eluent gave *β,γ*-unsaturated ester **19** (1.42 g, 73%), as colorless oil. IR ($CHCl_3$): ν_{max} = 2931, 2858, 1740, 1472, 1369, 1256, 1179, 1158, 1100, 1034, 1006, 969, 939, 913, 837, 776, 734, 662, cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.60–5.47 (m, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.59 (t, *J* = 6.3 Hz, 2H), 3.00 (d, *J* = 5.2 Hz, 2H), 2.04 (q, *J* = 7.4 Hz, 2H), 1.55–1.45 (m, 2H), 1.45–1.35 (m, 2H), 1.25 (t, *J* = 7.3 Hz, 3H), 0.88 (s, 9H), 0.03 (s, 6H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 172.2, 134.6, 121.8, 63.1, 60.5, 38.2, 32.3, 32.2, 26.0, 25.4, 18.4, 14.2, –5.3 ppm. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{16}H_{32}O_3SiNa$ 323.2013; Found 323.2009.

(4*S*,5*S*)-5-(4-*tert*-Butyldimethylsilyloxybutyl)-4-hydroxydihydrofuran-2(3*H*)-one (20):



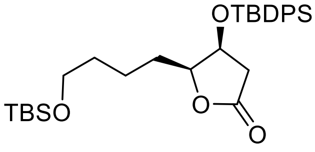
The titled compound was prepared from **19** (1.5 g, 4.99 mmol) by a similar procedure as described for **15** to give lactone **20** (1.18 g, 82%) as colorless oil. $[\alpha]_D^{25}$ –22.1 (*c* 0.25, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3416, 2933, 1760, 1456, 1308, 1166, 1073, 973, 761 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.48 (t, *J* = 3.4 Hz, 1H), 4.38–4.32 (m, 1H), 3.70–3.63 (m, 2H), 2.78 (dd, *J* = 17.8, 5.6 Hz, 1H), 2.55 (d, *J* = 17.7 Hz, 1H), 2.13 (brs, 1H), 1.93–1.73 (m, 2H), 1.65–1.42 (m, 4H), 0.89 (s, 9H), 0.06 (s, 6H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 176.6, 85.2, 68.4, 62.6, 39.3, 32.1, 27.5, 25.8, 21.5, 18.2, –5.42, –5.44 ppm. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{14}H_{28}O_4SiNa$ 311.1649; Found 311.1646.

(4*S*,5*S*)-4-*tert*-Butyldimethylsilyloxy-5-(4-*tert*-butyldimethylsilyloxybutyl)dihydrofuran-2(3*H*)-one (21a):



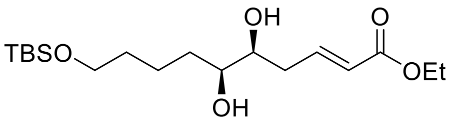
The titled compound was prepared from **20** (1.4 g, 4.85 mmol) by a similar procedure as described for **16a** to give **21a** (1.7 g 87%) as colorless oil. $[\alpha]_D^{25}$ –25.1 (*c* 1.7, CHCl$_3$). IR (CHCl$_3$): ν_{max} = 2953, 2931,2894, 2859, 1780, 1472, 1463, 1408, 1389, 1361, 1295, 1256, 1208, 1187, 1160, 1100, 1026, 1006, 988, 939, 899, 839, 806, 776, 758, 710, 665, 549 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.40–4.36 (m, 1H), 4.33–4.27 (m, 1H), 3.58 (t, *J* = 6.2 Hz, 2H), 2.68 (dd, *J* = 17.1, 5.2 Hz, 1H), 2.58 (dd, *J* = 17.2, 1.3 Hz, 1H), 1.86–1.75 (m, 1H), 1.67–1.36 (m, 5H), 0.86 (s, 9H), 0.85 (s, 9H), 0.043 (s, 6H), 0.008 (s, 6H) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 175.4, 85.1, 69.5, 62.8, 39.7, 32.6, 28.4, 25.5, 21.9, 18.3, 17.9, –4.7, –5.2, –5.4 ppm. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{20}H_{42}NaO_4Si_2$ 425.2514; Found 425.2515.

(4*S*,5*S*)-5-(4-*tert*-Butyldimethylsilyloxybutyl)-4-(*tert*-butyldiphenylsilyloxy) dihydrofuran-2(3*H*)-one (21b):



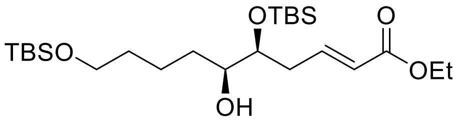
The titled compound was prepared from **20** (1.2 g, 4.16 mmol) by a similar procedure as described for **16b** to give **21b** (1.8 g, 82%) as colorless oil. $[\alpha]_D^{25}$ –15.8 (*c* 1.00, CHCl$_3$). IR (CHCl$_3$): ν_{max} = 3071, 2954, 2932, 2858, 1779, 1589, 1472, 1463, 1428, 1361, 1296, 1250, 1210, 1158, 1111, 1024, 939, 836, 822, 776, 742, 703, 666, 612, 507 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.66–7.59 (m, 4H), 7.48–7.36 (m, 6H), 4.45 (t, *J* = 3.9 Hz, 1H), 4.25 (quint, *J* = 8.7, 4.1 Hz, 1H), 3.65–3.57 (m, 2H), 2.45–2.35 (m, 2H), 1.75–1.63 (m, 1H), 1.64–1.49 (m, 4H), 1.49–1.36 (m, 1H), 1.67 (s, 9H), 0.90 (s, 9H), 0.05 (s, 6H) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 175.3, 135.8, 135.7, 133.1, 132.5, 130.2, 130.17, 128.0, 127.9, 85.0, 70.7, 62.9, 39.0, 32.6, 28.9, 26.9, 26.0, 22.1, 19.3, 18.4, –5.3 ppm. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{30}H_{46}O_4Si_2Na$ 549.2827; Found 549.2825.

Ethyl (5*S*,6*S*,*E*)-10-(*tert*-butyldimethylsilyloxy)-5,6-dihydroxydec-2-enoate (22c):



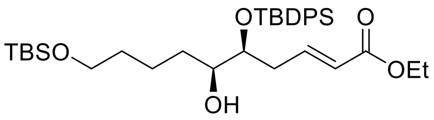
The titled compound was prepared from lactone **20** (600 mg, 2.08 mmol) by similar procedure as described for **17a** to give **22c** (570 mg, 76%) as colorless oil. $[\alpha]_D^{25}$ –18.6 (*c* 0.75, CHCl$_3$). IR (CHCl$_3$): ν_{max} = 3420, 2929, 1704, 1657, 1458, 1369, 1316, 1283, 1208, 1162, 1044, 984, 758, 727 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 6.91 (dt, *J* = 15.3, 7.5 Hz, 1H), 5.64 (dt, *J* = 15.7, 1.5 Hz, 1H), 4.17 (q, *J* = 7.3 Hz, 2H), 3.63–3.54 (m, 3H), 3.48–3.41 (m, 1H), 2.58–2.35 (m, 4H), 1.58–1.48 (m, 6H), 1.27 (t, *J* = 7.2 Hz, 3H), 0.88 (s, 9H), 0.04 (s, 6H) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 166.4, 145.0, 123.8, 73.8, 72.9, 63.1, 60.3, 36.6, 33.2, 32.4, 25.9, 21.9, 18.3, 14.2, –5.3 ppm. HRMS (ESI-TOF) *m/z*: [M + K]$^+$ Calcd for $C_{18}H_{36}O_5SiK$ 399.1964; Found 399.1955.

Ethyl (5*S*,6*S*,*E*)-5,10-bis(tert-butyldimethylsilyloxy)-6-hydroxydec-2-enoate (22a):



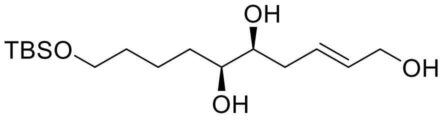
The titled compound was prepared from lactone **21a** (500 mg and 1.241 mmol) by following a similar procedure as described for **17a** to give **22a** (406 mg, 69%) as colorless oil. $[\alpha]_D^{25}$ +0.5 (*c* 1.15, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3398, 2930, 2858, 1723, 1654, 1472, 1461, 1386, 1366, 1320, 1257, 1220, 1172, 1094, 1073, 1051, 1005, 985, 937, 837, 807, 776 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 6.93–6.85 (m, 1H), 5.82 (d, *J* = 15.6 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.64–3.59 (m, 1H), 3.57 (t, *J* = 6.2 Hz, 2H), 3.40–3.34 (m, 1H), 2.56–2.47 (m, 1H), 2.35–2.26 (m, 1H), 2.07 (s, 1H), 1.56–1.45 (m, 3H), 1.42–1.35 (m, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.86 (s, 9H), 0.85 (s, 9H), 0.04 (s, 6H), 0.007 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 166.2, 144.9, 123.7, 74.0, 73.0, 63.1, 60.2, 36.8, 33.5, 32.8, 26.0, 25.8, 22.2, 18.3, 18.0, 14.2, –4.3, –4.6, –5.3 ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{24}H_{50}O_5Si_2Na$ 497.3089; Found 497.3088.

Ethyl (5*S*,6*S*,*E*)-10-(*tert*-butyldimethylsilyloxy)-5-(*tert*-butyldiphenylsilyloxy)-6-hydroxydec-2-enoate (22b):



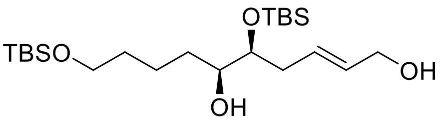
The titled compound was prepared from lactone **21b** (500 mg and 0.949 mmol) by a similar procedure as described for **17a** to give **22b** (415 mg, 73%) as pale yellow oil. $[\alpha]_D^{25}$ +9.4 (*c* 0.5, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3432, 2931, 1720, 1471, 1367, 1268, 1174, 1111, 822, 740, 704, 610, 507 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.68–7.65 (m, 4H), 7.47–7.35 (m, 6H), 6.70 (dt, *J* = 15.3, 7.5 Hz, 1H), 5.64 (d, *J* = 15.8 Hz, 1H), 4.13 (q, *J* = 7.3 Hz, 2H), 3.69 (quint, *J* = 7.7, 4.3 Hz, 1H), 3.56 (t, *J* = 6.3 Hz, 2H), 3.42–3.38 (m, 1H), 2.50 (quint, *J* = 15.2, 7.7 Hz, 1H), 2.24–2.18 (m, 1H), 1.52–1.35 (m, 6H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.07 (s, 9H), 0.89 (s, 9H), 0.04 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 166.2, 144.4, 135.9, 135.85, 134.8, 133.5, 133.0, 130.0, 129.9, 129.6, 127.8, 127.7, 127.65, 123.8, 75.1, 72.8, 63.1, 60.1, 36.3, 33.4, 32.8, 27.1, 26.5, 25.0, 22.1, 19.5, 18.4, 14.2, –5.3 ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{34}H_{54}O_5Si_2Na$ 621.3402; Found 621.3405.

(5*S*,6*S*,*E*)-10-(*tert*-butyldimethylsilyloxy)dec-2-ene-1,5,6-triol (23c):



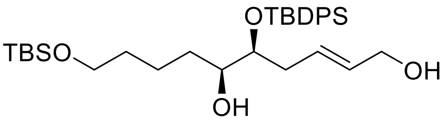
The titled compound was prepared from *α,β*-unsaturated ester **22c** (400 mg, 1.11 mmol) by a similar procedure as described for **18a** to give **23c** (286 mg, 81%) as colorless oil. $[\alpha]_D^{25}$ –4.3 (*c* 1.1, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3471, 3350, 3113, 2926, 2687, 1458, 1274, 1089, 816, 698, 542 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.73–5.63 (m, 2H), 4.04 (d, *J* = 2.4 Hz, 2H), 3.73–3.66 (brs, 1H), 3.59 (t, *J* = 5.8 Hz, 3H), 3.48–3.33 (m, 3H), 2.32–2.11 (m, 2H), 1.59–1.34 (m, 6H), 0.86 (s, 9H), 0.02 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 132.0, 128.5, 73.8, 73.7, 63.1, 63.0, 36.4, 33.0, 32.6, 25.9, 21.9, 18.3, –5.3 ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{34}O_4SiNa$ 341.2119; Found 341.2122.

(5*S*,6*S*,*E*)-5,10-bis(*tert*-Butyldimethylsilyloxy)dec-2-ene-1,6-diol (23a):



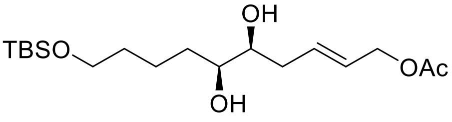
The titled compound was prepared from *α,β*-unsaturated ester **22a** (300 mg and 0.631 mmol) by a similar procedure as described for **18a** to give **23a** (227 mg, 83%) as colorless oil. $[\alpha]_D^{25}$ +5.2 (*c* 1.7, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3369, 2929, 2860, 1473, 1461, 1408, 1391, 1359, 1255, 1094, 1002, 973, 936, 836, 807, 776, 682 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.73–5.60 (m, 2H), 4.11–4.05 (m, 2H), 3.64–3.57 (m, 2H), 3.57–3.52 (m, 1H), 3.47–3.38 (m, 1H), 2.41 (quint, *J* = 6.3 Hz, 1H), 2.25–2.15 (m, 1H), 1.92 (brs, 2H), 1.55–1.38 (m, 6H), 0.89 (s, 9H), 0.88 (s, 9H), 0.07 (s, 6H), 0.03 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 132.0, 128.1, 74.5, 72.4, 63.5, 63.2, 37.0, 33.8, 32.8, 25.9, 22.2, 18.4, 18.1, –4.1, –4.6, –5.3 ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{48}O_4Si_2Na$ 455.2983; Found 455.2988.

(5*S*,6*S*,*E*)-10-(*tert*-Butyldimethylsilyloxy)-5-(*tert*-butyldiphenylsilyloxy)dec-2-ene-1,6-diol (23b):



The titled compound was prepared from *α,β*-unsaturated ester **22b** (300 mg and 0.500 mmol) by a similar procedure as described for **18a** to give **23b** (237 mg, 85%) as pale yellow oil. $[\alpha]_D^{25}$ +5.6 (*c* 1.13, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3351, 2932, 2858, 1469, 1428, 1359, 1190, 1111, 1000, 971, 822, 740, 703, 610, 507 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.69–7.67 (m, 4H), 7.44–7.32 (m, 6H), 5.46–5.33 (m, 2H), 3.91 (d, *J* = 5.3 Hz, 2H), 3.64–3.61 (m, 1H), 3.56 (t, *J* = 6.5 Hz, 2H), 3.47–3.45 (m, 1H), 2.35 (quint, *J* = 14.3, 7.1 Hz, 1H), 2.13–2.08 (m, 1H), 1.86 (brs, 2H), 1.55–1.37 (m, 5H), 1.30–1.21 (m, 1H), 1.06 (s, 9H), 0.89 (s, 9H), 0.04 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 135.92, 135.9, 133.9, 133.1, 132.0, 129.9, 129.8, 128.0, 127.7, 127.5, 75.7, 72.6, 63.4, 63.2, 36.5, 33.6, 32.8, 27.1, 26.0, 25.6, 22.1, 19.5, 18.4, –5.3 ppm. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{32}H_{52}O_4Si_2K$ 595.3036; Found 595.3031.

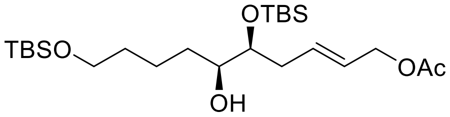
(5*S*,6*S*,*E*)-10-(*tert*-Butyldimethylsilyloxy)-5,6-dihydroxydec-2-en-1-yl acetate (5g):



The titled compound was prepared from alcohol **23c** (300 mg, 0.942 mmol) by a similar procedure as described for **5a** to give **5g** (292 mg, 86%) as colorless oil. $[\alpha]_D^{25}$ –6.1 (*c* 0.5, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3417, 2933, 2866, 1738, 1654, 1455, 1385, 1367, 1251, 1048, 1030, 973, 871, 837, 776, 757, 612, 480 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.84–5.76 (m, 1H), 5.74–5.61 (m, 1H), 4.51 (d, *J* = 6.1 Hz, 2H), 3.60 (t, *J* = 5.76 Hz, 2H), 3.49–3.42 (m, 2H), 2.49 (brs, 2H), 2.37–2.18 (m, 2H), 2.03 (s, 3H), 1.52–1.39 (m, 6H), 0.87 (s, 9H), 0.02 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ =

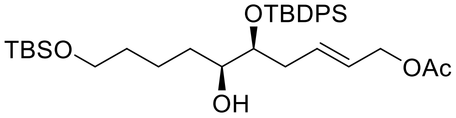
170.9, 131.9, 127.0, 73.7, 73.3, 64.9, 63.1, 36.7, 33.2, 32.5, 25.9, 21.9, 20.9, 18.3, –5.3 ppm. HRMS (ESI-TOF) *m/z*: [M +Na]$^+$ Calcd for $C_{18}H_{36}O_5SiNa$ 383.2224; Found 383.2223.

(5*S*,6*S*,*E*)-5,10-bis(*tert*-Butyldimethylsilyloxy)-6-hydroxydec-2-en-1-yl acetate (5e):



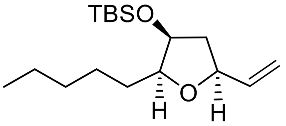
The titled compound was prepared from alcohol **23a** (200 mg and 0.462 mmol) by a similar procedure as described for **5a** to give **5e** (173 mg, 79%) as colorless oil. $[\alpha]_D^{25}$ +1.8 (*c* 1.85, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3484, 2952, 2930, 2858, 1743, 1474, 1461, 1383, 1359, 1254, 1101, 1003, 973, 836, 776 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.78–5.69 (m, 1H), 5.65–5.58 (m, 1H), 4.50 (d, *J* = 5.9 Hz, 2H), 3.59 (t, *J* = 5.6 Hz, 2H), 3.57–3.52 (m, 1H), 3.43–3.37 (m, 1H), 2.45–2.36 (m, 1H), 2.24–2.16 (m, 1H), 2.04 (s, 3H), 1.94 (brs, 1H), 1.57–1.41 (m, 3H), 1.44–1.35 (m, 3H), 0.88 (s, 9H), 0.87 (s, 9H), 0.06 (s, 6H), 0.03 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 170.8, 131.6, 126.8, 74.4, 72.6, 64.9, 63.2, 37.0, 33.7, 32.8, 26.0, 25.9, 22.2, 21.0, 18.4, 18.1, –4.1, –4.6, –5.3 ppm. HRMS (ESI-TOF) *m/z*: [M +Na]$^+$ Calcd for $C_{24}H_{50}O_5Si_2Na$ 497.3089; Found 497.3091.

(5*S*,6*S*,*E*)-10-(*tert*-Butyldimethylsilyloxy)-5-(*tert*-butyldiphenylsilyloxy)-6-hydroxydec-2-en-1-yl acetate (5f):



The titled compound was prepared from alcohol **23b** (200 mg and 0.359 mmol) by a similar procedure as described for **5a** to give **5f** (178 mg, 83%) as pale yellow oil. $[\alpha]_D^{25}$ +5.0 (*c* 1.84, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3419, 1933, 2858, 1740, 1464, 1427, 1386, 1362, 1241, 1111, 1085, 971, 822, 741, 704, 610, 508 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69–7.63 (m, 4H), 7.46–7.35 (m, 6H), 5.52–5.43 (m, 1H), 5.43–5.34 (m, 1H), 4.36 (d, *J* = 6.2 Hz, 2H), 3.61 (quint, *J* = 7.7, 3.7 Hz, 1H), 3.53 (t, *J* = 6.5 Hz, 2H), 3.46–3.39 (m, 1H), 2.36 (quint, *J* = 14.2, 7.0 Hz, 1H), 2.15–2.07 (m, 1H), 2.04 (d, *J* = 1.7 Hz, 1H), 2.01 (s, 3H), 1.53–1.37 (m, 5H), 1.27–1.19 (m, 1H), 1.06 (s, 9H), 0.88 (s, 9H), 0.03 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 170.8, 136.0, 135.9, 134.8, 133.8, 133.2, 131.3, 130.0, 129.8, 127.8, 127.7, 127.6, 126.8, 75.6, 72.6, 64.9, 63.2, 36.5, 33.6, 32.8, 27.1, 26.6, 26.0, 22.2, 21.0, 19.5, 18.4, –5.2 ppm. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{34}H_{54}O_5Si_2Na$ 621.3402; Found 621.3404.

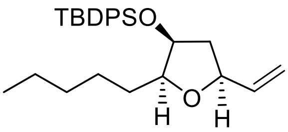
***tert*-Butyldimethyl[(2*S*,3*S*,5*S*)-2-pentyl-5-vinyltetrahydrofuran-3-yloxy]silane (6a):**



To a solution of allylacetate **5a** (71.9 mg, 0.2 mmol) in THF (5 mL) was added $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.1 equiv), PPh_3 (26.2 mg, 0.1 mmol, 0.5 equiv) and pyridine (12.6 mg, 0.16 mmol, 0.8 equiv). The reaction mixture was stirred at 50 °C for 1 h and then filtered through a pad of silica gel. After evaporation of the solvents, the residue was purified by silica gel column chromatography using petroleum ether/EtOAc (9:1) as eluent to afford **6a** (*trans/cis* = 1:9, 54.4 mg, 91%) as a colorless oil. IR ($CHCl_3$):

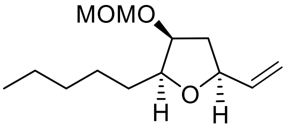
ν_{max} = 2956, 2930, 2858, 1645, 1472, 1362, 1255, 1161, 1097, 922, 836, 774, 671 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.99–5.92 (m, 1H), 5.22–5.15 (m, 1H), 5.06–5.03 (m, 1H), 4.29–4.20 (m, 2H), 3.65–3.61 (m, 1H), 2.37–2.29 (m, 1H), 1.70–1.59 (m, 3H), 1.41–1.25 (m, 6H), 0.92–0.86 (m, 12H), 0.05 (s, 6H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 140.2, 115.3, 83.8, 78.9, 73.1, 42.3, 32.1, 29.5, 26.1, 25.8, 22.7, 18.0, 14.1, –4.5, –5.1 ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{34}O_2SiNa$ 321.2220; Found 321.2220.

***tert*-Butyl[(2*S*,3*S*,5*S*)-2-pentyl-5-vinyltetrahydrofuran-3-yloxy]diphenylsilane (6b):**



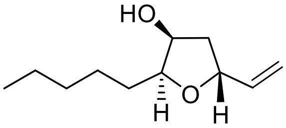
The titled compound was prepared from allyl acetate **5b** (96.6 mg, 0.2 mmol) by similar procedure as described for **6a** to give **6b** (*trans*/*cis* = 1:9, 71.1 mg, 84%) as a colorless oil. IR ($CHCl_3$): ν_{max} = 2962, 2933, 2842, 1648, 1477, 1366, 1209, 1181, 1098, 917, 834, 774, 672 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71–7.65 (m, 4H), 7.47–7.36 (m, 6H), 5.97 (ddd, *J* = 17.5, 10.2, 7.3 Hz 1H), 5.19 (dd, *J* = 17.5, 1.2 Hz, 1H), 5.08 (dd, *J* = 10.20, 1.2 Hz, 1H), 4.39–4.32 (m, 1H), 4.1 (q, *J* = 7.36 Hz, 1H), 3.63–3.54 (m, 1H), 2.1 (ddd, *J* = 13.1, 7.63, 6.26 Hz, 1H), 1.76–1.66 (m, 2H), 1.65–1.56 (m, 1H), 1.51–1.40 (m, 1H), 1.35–1.24 (m, 5H), 1.12–1.08 (m, 9H), 0.89 (t, *J* = 6.6, 3H) ppm. $^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$): δ = 139.9, 134.8, 129.5, 127.6, 115.2, 83.6, 78.0, 73.0, 41.7, 32.0, 28.8, 26.5, 25.9, 22.5, 14.0. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{27}H_{38}O_2SiNa$ 445.2533; Found 445.2533.

(2*S*,3*S*,5*S*)-3-(Methoxymethoxy)-2-pentyl-5-vinyltetrahydrofuran (6c):



The titled compound was prepared from allyl acetate **5c** (57.7 mg, 0.2 mmol) by similar procedure as described for **6a** to give **6c** (*trans*/*cis* = 1:2.4, 40.7 mg, 89%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 5.98–5.89 (m, 1H), 5.88–5.81 (m, 1H), 5.25–5.17 (m, 2H), 5.11–5.06 (m, 2H), 4.72 (d, *J* = 6.9 Hz, 1H), 4.67 (d, *J* = 6.9 Hz, 1H), 4.63 (d, *J* = 6.9 Hz, 1H), 4.60 (d, *J* = 6.8 Hz, 2H), 4.30–4.24 (m, 1H), 4.19–4.14 (m, 2H), 3.93–3.89 (m, 1H), 3.73–3.67 (m, 1H), 3.39 (s, 3H), 3.37 (s, 3H), 2.40–2.30 (m, 1H), 2.27–2.21 (m, 1H), 1.81–1.71 (m, 1H), 1. 71–1.69 (m, 1H), 1.51–1.42 (m, 4H), 1.38–1.28 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 6H) ppm. $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$): δ = 139.5, 139.2, 115.7, 115.2, 95.5, 95.4, 82.7, 82.1, 78.7, 78.0, 77.9, 77.4, 77.3, 77.0, 76.7, 55.6, 39.2, 39.1, 32.1, 29.2, 29.1, 26.1, 26.08, 22.6, 14.0 ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{24}O_3Na$ 251.1618; Found 251.1622.

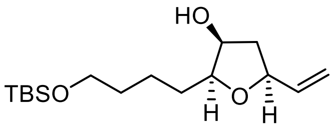
(2*S*,3*S*,5*R*)-2-Pentyl-5-vinyltetrahydrofuran-3-ol (6d):



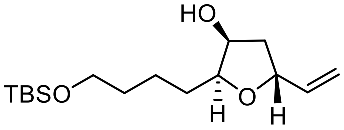
The titled compound was prepared from allyl acetate **5d** (49 mg, 0.2 mmol) by similar procedure as described for **6a** to give **6d** (*trans*/*cis* = 1:0, 36.1 mg, 98%) as a colorless oil. $[\alpha]_D^{25}$ = +1.2 (*c* 0.5, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3420, 2955, 2929, 2859, 1645, 1467, 1326, 1218, 1155, 1031, 987, 925, 869, 758, 671 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.83 (ddd, *J* = 17.2, 10.2, 6.6 Hz, 1H), 5.20 (dt, *J* = 17.1, 1.4 Hz, 1H), 5.1 (dt, *J* = 10.3, 1.2 Hz, 1H), 4.66–4.58 (m, 1H), 4.26–4.20 (m, 1H), 3.81 (td, *J* = 7.59, 2.91 Hz, 1H), 2.19–2.12 (m, 1H), 1.92–1.82 (m, 1H), 1.69–1.50 (m, 2H), 1.47–1.37 (m, 1H), 1.35–1.26 (m, 5H), 0.88 (t, *J* = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 139.1, 115.1, 82.5, 77.7, 73.3, 41.9, 32.0, 28.9, 26.0, 22.5, 14.0 ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_{20}O_2Na$ 207.1356; Found 207.1345.

(2*S*,3*S*,5*R*)-2-(4-*tert*-butyldimethylsilyloxybutyl)-5-vinyltetrahydrofuran-3-ol (6g) and (2*S*,3*S*,5*S*)-2-(4-tert-butyldimethylsilyloxybutyl)-5-vinyltetrahydrofuran-3-ol (6g′):

The titled compound was prepared from allyl acetate **5g** (72.1 mg, 0.2 mmol) by similar procedure as described for **6a** to give **6g** as a mixture of *trans*:*cis* = 12:1, 96%. This mixture was purified further by flash silica gel column chromatography using petroleum ether/EtOAc (3:1) as eluent to give pure **6g′** (4.2 mg, 7%) as colorless oil. Further elution gave pure **6g** (52.9 mg, 88%) as colorless oil.

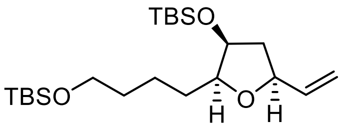


Data for **6g′:** $[\alpha]_D^{25}$ +12.5 (*c* 1.0, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3443, 2949, 2931, 2903, 2859, 1508, 1472, 1463, 1427, 1388, 1361, 1255, 1160, 1100, 1048, 1005, 990, 923, 836, 776, 812, 662 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.01–5.90 (m, 1H), 5.28 (d, *J* = 17.1 Hz, 1H), 5.10 (d, *J* = 10.3 Hz, 1H), 4.31 (q, *J* = 8.4 Hz, 1H), 4.22–4.16 (m, 1H), 3.69–3.59 (m, 3H), 2.47–2.37 (m, 1H), 1.82 (brs, 1H), 1.78–1.60 (m, 4H), 1.59–1.55 (m, 1H), 1.53–1.38 (m, 2H), 0.94–0.83 (m, 9H), 0.14–0.01 (m, 6H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 140.0, 115.3, 83.6, 78.1, 73.0, 62.9, 41.6, 32.7, 28.3, 26.0, 22.4, 18.3, –5.3 ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{32}O_3SiNa$ 323.2013; Found 323.2016.



Data for **6g:** $[\alpha]_D^{25}$ +2.9 (*c* 0.85, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3428, 2933, 2877, 1457, 1330, 1055, 1031, 930, 900, 869, 844, 592, 519 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.87–5.78 (m, 1H), 5.23 (dt, *J* = 17.1, 1.2 Hz, 1H), 5.08 (dt, *J* = 10.3, 1.1 Hz, 1H), 4.63 (q, *J* = 9.2 Hz, 1H), 4.27 (t, *J* = 3.6 Hz, 1H), 3.84–3.81 (m, 1H), 3.67–3.59 (m, 2H), 2.16 (dd, *J* = 13.5, 6.6 Hz, 2H), 1.90–1.83 (m, 1H), 1.72–1.36 (m, 6H) 0.88 (s, 9H), 0.04 (s, 6H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 139.1, 115.1, 82.5, 77.8, 73.1, 62.8, 41.8, 32.6, 28.4, 25.9, 22.3, 18.3, –5.3 ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{32}O_3SiNa$ 323.2013; Found 323.2014.

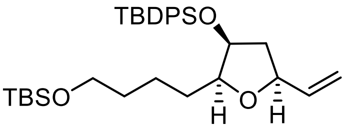
tert-Butyl-(4-[(2*S*,3*S*,5*S*)-3-*tert*-butyldimethylsilyloxy]-5-vinyltetrahydrofuran-2-yl)butoxydimethylsilane (6e):



The titled compound was prepared from **5e** (95 mg and 0.2 mmol) by similar procedure as described for **6a** to give **6e** (78 mg, 94%, *trans:cis* = 1:7) as colorless oil. $[\alpha]_D^{25}$ +15.4 (*c* 1.6, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 2651, 2934, 2856, 1472, 1461, 1255, 1101, 937, 915, 838, 813, 779, 736, 668 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.99–5.91 (m, 1H), 5.17 (d, *J* = 16.5 Hz, 1H), 5.04 (d, *J* = 10.6 Hz, 1H), 4.31–4.17 (m, 2H), 3.65–3.56 (m, 3H), 2.36–2.27 (m, 1H), 1.71–1.51 (m, 7H), 0.89 (s, 9H), 0.88 (s, 9H), 0.05–0.03

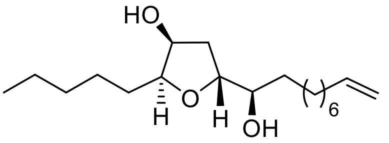
(m, 12H) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 140.2, 115.3, 83.6, 78.9, 73.1, 63.2, 42.3, 33.1, 29.1, 26.0, 25.8, 22.6, 18.4, 18.0, –4.5, –5.1, –5.3 ppm. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{22}H_{46}O_3Si_2Na$ 437.2878; Found 437.2875.

***tert*-Butyl[(2*S*,3*S*,5*S*)-2-(4-*tert*-butyldimethylsilyloxybutyl)-5-vinyltetrahydrofuran-3-yloxy]diphenylsilane (6f):**



The titled compound was prepared from **5f** (111.4 mg and 0.2 mmol) by a similar procedure as described for **6a** to give **6f** (89.5 mg, 83%, *trans:cis* = 1:8) as colorless oil. [α]$_D^{25}$ +32.2 (*c* 1.6, CHCl$_3$). IR (CHCl$_3$): ν_{max} = 3067, 2932, 2858, 1463, 1427, 1390, 1364, 1111, 924, 853, 822, 741, 703, 612, 507, 488 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.71–7.60 (m, 4H), 7.46–7.40 (m, 2H), 7.40–7.34 (m, 4H), 6.00–5.88 (m, 1H), 5.17 (d, *J* = 16.9 Hz, 1H), 5.06 (d, *J* = 10.8 Hz, 1H), 4.39–4.29 (m, 1H), 4.12 (q, *J* = 7.3 Hz, 1H), 3.63–3.53 (m, 3H), 2.04 (quint, *J* = 13.6, 7.4 Hz, 1H), 1.74–1.65 (m, 2H), 1.65–1.59 (m, 2H), 1.54–1.50 (m, 2H), 1.33–1.26 (m, 1H), 1.07 (s, 9H), 0.89 (s, 9H), 0.04 (s, 6H) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 139.6, 136.0, 135.9, 134.1, 133.6, 129.71, 129.66, 127.6, 127.5, 115.5, 82.9, 78.3, 74.4, 63.2, 41.6, 33.1, 29.8, 27.0, 26.0, 22.6, 19.3, 18.4, –5.3 ppm. HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{32}H_{51}O_3Si_2$ 539.3371; Found 539.3372.

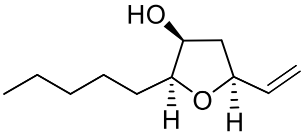
***trans*-Oxylipid (7a)**:[4,5]



Through a stirred solution of **6d** (60 mg, 0.326 mmol) in CH$_2$Cl$_2$ (10 mL) was bubbled ozone (O$_3$) at −78 °C for 10 min. Then dimethylsulfide (0.5 mL) was added and stirred at −78 °C for 2 h and room temperature for 1 h. The mixture was concentrated to give crude aldehyde (60 mg) that was used directly for next reaction.

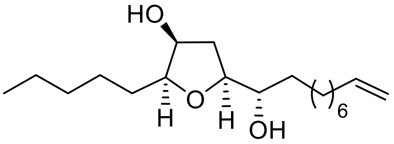
To a stirred solution of above aldehyde (60 mg) in anhydrous DCE (10 mL) at room temperature was added freshly prepared 8-nonenylmagnesium bromide (4.9 mL, 1.95 mmol, 0.4 M, 6.0 equiv). After stirring for 2 h at 80 °C, the reaction mixture was quenched with saturated aq. NH$_4$Cl solution (5 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried (Na$_2$SO$_4$) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (7:3) as eluent to give **7a** (53 mg, 52% over two steps from **6d**) as white solid. M.P. 50–52 °C; [α]$_D^{25}$ +14.6 (*c* 1.0, CHCl$_3$), lit.[4] [α]$_D^{21}$ +15.0 (*c* 1.0, CHCl$_3$), lit.[5] [α]$_D^{25}$ +11.3 (*c* 0.9, CHCl$_3$). IR (CHCl$_3$): ν_{max} = 3416, 2925, 2857, 1639, 1461, 1295, 1263, 1146, 1034, 909, 861, 815 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 5.87–5.76 (m, 1H), 5.05–4.88 (m, 2H), 4.27–4.23 (m, 1H), 4.02 (dt, *J* = 8.9, 6.6 Hz, 1H), 3.75 (td, *J* = 6.9, 2.5 Hz, 1H), 3.42–3.34 (m, 1H), 2.07–1.98 (m, 3H), 1.89–1.84 (m, 1H), 1.68–1.50 (m, 4H), 1.41–1.26 (m, 18H), 0.89 (t, *J* = 6.0 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz; CDCl$_3$): δ = 139.4, 114.3, 82.7, 80.4, 74.3, 73.7, 38.1, 34.0, 33.4, 32.2, 29.8, 29.6, 29.3, 29.1, 29.0, 26.2, 25.8, 22.8, 14.2 ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{36}O_3Na$ 335.2557; Found 335.2561.

(2*S*,3*S*,5*S*)-2-Pentyl-5-vinyltetrahydrofuran-3-ol (11):



To a stirred solution of **6a** (*trans/cis* =1:9, 80 mg, 0.189 mmol) in THF (5 mL) was added TBAF (0.3 mL, 1 M in THF, 0.303 mmol, 1.6 equiv) at room temperature and stirred for 3 h. Water (5 mL) was then added and aqueous layer was extracted with EtOAc (3 × 15 mL). The organic extracts were washed with brine (2 × 10 mL), dried (Na_2SO_4) and the solvent was evaporated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (4:1) as eluent to afford **11** (28.6 mg, 82%) as a colorless oil. Further elution gave **6d** (3.2 mg, 9%) as colorless oil. Data for **11**: $[\alpha]_D^{25}$ +21.3 (*c* 1.25, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3447, 2959, 2925, 2857, 1642, 1457, 1378, 1163, 1163, 1088, 1046, 990, 922, 856, 671 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.95 (ddd, *J* = 17.2, 10.4, 6.8 Hz, 1H), 5.26 (dd, *J* = 17.3, 1.3 Hz, 1H), 5.08 (dd, *J* = 10.3, 1.1 Hz, 1H), 4.35–4.26 (m, 1H), 4.18–4.14 (m, 1H), 3.67–3.58 (m, 1H), 2.46–2.34 (m, 1H), 1.79–1.57 (m, 4H), 1.48–1.28 (m, 6H), 0.87 (t, *J* = 6.6 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 140.0, 115.2, 83.6, 78.0, 73.0, 41.7, 32.0, 28.8, 26.0, 22.5, 14.0 ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_{20}O_2Na$ 207.1356; Found 207.1346. For data of **6d**, see above.

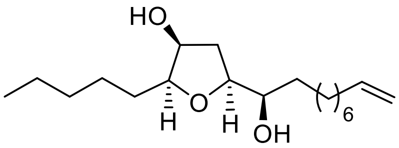
***cis*-Oxylipid (7b):**[5]



Through a stirred solution of **11** (50 mg, 0.272 mmol) in CH_2Cl_2 (10 mL) was bubbled ozone (O_3) at −78 °C for 10 min. Then dimethylsulfide (0.45 mL) was added and stirred at −78 °C for 2 h and room temperature for 1 h. The mixture was concentrated to give crude aldehyde (50 mg) that was used directly for next reaction.

To a stirred solution of above aldehyde (50 mg) in anhydrous DCE (5 mL) at room temperature was added freshly prepared 8-nonenylmagnesium bromide (4.1 mL, 1.632 mmol, 0.4 M, 6.0 equiv). After stirring for 2 h at 80 °C, the reaction mixture was quenched with saturated aq. NH_4Cl solution (5 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (7:3) as eluent to give **7b** (42.4 mg, 50% over two steps from **11**) as white solid. M.P. 47–49 °C; $[\alpha]_D^{25}$ + 19.4 (*c* 0.5, $CHCl_3$), lit.[5] $[\alpha]_D^{24}$ +18.0 (*c* 0.3, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3346, 3079, 2925, 2855, 1729, 1640, 1465, 1283, 1128 ppm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.86–5.74 (m, 1H), 5.03–4.88 (m, 2H), 4.03 (dd, *J* = 5.4, 2.7 Hz, 1H), 3.94 (dt, *J* = 9.4, 2.5 Hz, 1H), 3.62 (td, *J* = 6.8, 2.6 Hz, 1H), 3.47 (ddd, *J* = 8.5, 5.0, 2.2 Hz, 1H), 2.38 (ddd, *J* = 14.6, 9.4, 5.4 Hz, 1H), 2.03 (dd, *J* = 14.4, 6.8 Hz, 2H), 1.83 (dd, *J* = 14.3, 3.6 Hz, 1H), 1.73 (br s, 1H), 1.68–1.62 (m, 2H), 1.59–1.53 (m, 1H), 1.39–1.25 (m, 18H), 0.88 (t, *J* = 6.6 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 139.4, 114.4, 84.6, 79.3, 74.1, 71.8, 39.0, 34.6, 34.0, 32.3, 29.7, 29.6, 29.3, 29.1, 29.0, 26.2, 26.1, 22.8, 14.3 ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{36}O_3Na$ 335.2557; Found 335.2557.

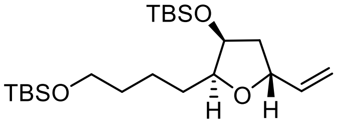
6-*epi*-*cis*-Oxylipid (7c):[6]



Through a stirred solution of **6a** (60 mg, 0.20 mmol) in CH_2Cl_2 (10 mL) was bubbled ozone (O_3) at −78 °C for 10 min. Then dimethylsulfide (0.5 mL) was added and stirred at −78 °C for 2 h and room temperature for 1 h. The mixture was concentrated to give crude aldehyde (60 mg) that was used directly for next reaction.

To a stirred solution of above aldehyde (60 mg) in anhydrous DCE (5 mL) at room temperature was added freshly prepared 8-nonenylmagnesium bromide (3 mL, 1.2 mmol, 0.4 M, 6.0 equiv). After stirring for 2 h at 80 °C, the reaction mixture was quenched with saturated aq. NH_4Cl solution (5 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (4:1) as eluent to give **7c** (30.6 mg, 49% overall from **6a**) as colorless oil. $[\alpha]_D^{25}$ +20.9 (*c* 0.9, $CHCl_3$), lit.[6] for *ent*-**7c**, $[\alpha]_D^{20}$ −22.8 (*c* 1.0, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3346, 2926, 2854, 1640, 1466, 1289, 1185, 1088, 1035, 910, 667 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.80 (dddd, *J* =16.9, 10.1, 6.8, 6.8 Hz, 1H), 4.98 (dd, *J* = 17.4, 1.6 Hz, 1H), 4.92 (d, *J* =11.2 Hz, 1H), 4.03–3.98 (m, 2H), 3.84–3.80 (m, 1H), 3.59 (td, *J* = 6.7, 2.5 Hz, 1H), 2.18 (ddd, *J* = 14.2, 9.8, 5.4 Hz, 1H), 2.03 (q, *J* = 6.5 Hz, 2H), 1.90 (dd, *J* = 14.2, 3.3 Hz, 1H), 1.68–1.59 (m, 2H), 1.42–1.24 (m, 18H), 0.88 (t, *J* = 6.7 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 139.3, 114.4, 84.0, 80.1, 72.2, 71.4, 34.5, 33.9, 33.5, 32.2, 29.6, 29.5, 29.2, 29.04, 29.0, 26.2, 26.1, 22.8, 14.2 ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{36}O_3Na$ 335.2557; Found 335.2554.

***tert*-Butyl(4-[(2*S*,3*S*,5*R*)-3-*tert*-butyldimethylsilyloxy]-5-vinyltetrahydrofuran-2-ylbutoxy)dimethylsilane (12):**

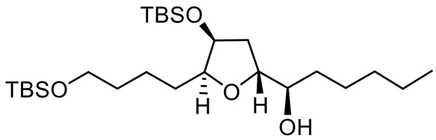


To a solution of alcohol **6g** (140 mg, 0.466 mmol) in CH_2Cl_2 (5 mL) at 0 °C was added imidazole (47.6 mg, 0.699 mmol, 1.5 equiv). The reaction mixture was stirred at 0 °C for 30 min and then TBSCl (84.4 mg, 0.56 mmol, 1.2 equiv) was added and the solution stirred at room temperature for 12 h. The reaction mixture was poured into water (5 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography using petroleum ether/EtOAc (9:1) as eluent to produce **12** (166 mg, 86%) as colorless oil. $[\alpha]_D^{25}$ –0.8 (*c* 0.85, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 2950, 2929, 2859, 1472, 1388, 1256, 1193, 1099, 1051, 937, 837, 809, 779, 661 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.87–5.79 (m, 1H), 5.24 (dd, *J* = 17.1, 1.4 Hz, 1H), 5.08 (dd, *J* = 10.3, 1.1 Hz, 1H), 4.61–4.55 (m, 1H), 4.24 (t, *J* = 2.9 Hz, 1H), 3.84 (td, *J* = 6.6, 3.3 Hz, 1H), 3.60 (t, *J* = 6.7 Hz, 2H), 2.03–1.98 (m, 1H), 1.81–1.74 (m, 1H), 1.63–1.52 (m, 4H), 1.42–1.36 (m, 2H), 0.89 (s, 9H), 0.88 (s, 9H), 0.07–0.03 (m, 12H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 139.3, 115.3, 83.2, 78.1, 73.4, 63.3, 42.5, 33.1, 29.4, 26.0, 25.7, 22.6, 18.4, 18.0, –4.5, –5.1, –5.3 ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{46}O_3Si_2Na$ 437.2878; Found 437.2875.

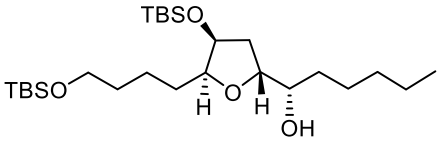
(*R*)-1-[(2*R*,4*S*,5*S*)-4-*tert*-butyldimethylsilyloxy-5-(4-*tert*-butyldimethylsilyloxybutyl) tetrahydrofuran-2-yl]hexan-1-ol (13) and (*S*)-1-[(2*R*,4*S*,5*S*)-4-*tert*-butyldimethylsilyloxy-5-(4-*tert*-butyldimethylsilyloxybutyl)tetrahydrofuran-2-yl]hexan-1-ol (13′):

Through a stirred solution of **12** (157 mg, 0.378 mmol) in CH_2Cl_2 (20 mL) was bubbled ozone (O_3) at −78 °C for 10 min. Then dimethylsulfide (0.11 mL) was added and stirred at −78 °C for 2 h and room temperature for 1 h. The mixture was concentrated to give crude aldehyde (155 mg) that was used directly for next reaction.

To a stirred solution of above aldehyde (155 mg) in anhydrous Et_2O (5mL) was added freshly prepared *n*-pentylmagnesium bromide (69 μL, 0.556 mmol, 1.5 equiv). After stirring for 2 h at –78 °C, the reaction mixture was quenched with saturated aq. NH_4Cl solution (10 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 10mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated. The residue was purified by flash silica gel column chromatography using petroleum ether/EtOAc (9:1) as eluent to give alcohol **13** (90.6 mg, 49% yield) as colorless oil. Further elution gave **13′** (29.6 mg, 16%) as colorless oil.

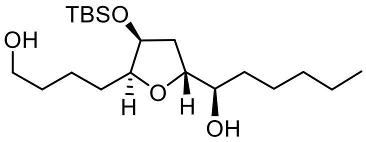


Data for **13:** $[\alpha]_D^{25}$ +3.6 (*c* 1.3, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3478, 2930, 2858, 1471, 1361, 1255, 1098, 940, 837, 780, 757 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.23–4.22 (m, 1H), 4.05–3.96 (m, 1H), 3.75–3.70 (m, 1H), 3.60 (t, *J* = 6.6 Hz, 2H), 3.40–3.32 (m, 1H), 1.88–1.79 (m, 2H), 1.59–1.51 (m, 4H), 1.42–1.25 (m, 10H), 0.92–0.86 (m, 21H), 0.01–0.02 (s, 12H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 83.3, 80.4, 74.2, 73.6, 63.2, 38.5, 33.6, 33.1, 31.9, 29.2, 26.0, 25.8, 25.4, 22.7, 22.6, 18.4, 18.1, 14.1, –4.5, –5.0, –5.3 ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{26}H_{56}O_4Si_2Na$ 511.3609; Found 511.3597.



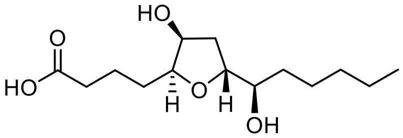
Data for **13′:** $[\alpha]_D^{25}$ +5.1 (*c* 1.2, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3458, 2944, 2858, 1470, 1364, 1255, 1102, 944, 827, 786, 747 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 4.27–4.22 (m, 1H), 4.17–4.07 (m, 1H), 3.88–3.75 (m, 2H), 3.60 (t, *J* = 3.6 Hz, 2H), 2.04–1.94 (m, 1H), 1.75–1.67 (m, 3H), 1.61–1.52 (m, 4H), 1.37–1.25 (m, 8H), 0.91–0.86 (m, 21H), 0.09–0.03 (m, 12H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 84.0, 80.2, 73.4, 71.7, 63.2, 34.5, 33.1, 32.2, 31.8, 29.4, 26.0, 25.7, 25.6, 22.6, 22.55, 18.4, 18.0, 14.0, –4.5, –5.0, –5.3 ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{26}H_{56}O_4Si_2Na$ 511.3609; Found 511.3600.

(***R***)-1-[(2***R***,4***S***,5***S***)-4-(***tert***-butyldimethylsilyloxy)-5-(4-hydroxybutyl)tetrahydro furan-2-yl]hexan-1-ol (14):



To a solution of **13** (163 mg, 0.333 mmol) in dry CH_2Cl_2 (5 mL) was added $BF_3{\cdot}OEt_2$ (0.11 mL, 0.334 mmol, 1.0 equiv, 45% solution) at 0 °C under N_2 atmosphere and the mixture stirred for 30 min. It was then quenched with saturated aq. $NaHCO_3$ (3 mL) and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 5mL) and the combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (9:1) as eluent to afford **14** (83.6 mg, 67%) as colorless oil. $[\alpha]_D^{25}$ +32.1 (*c* 0.4, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3410, 2930, 2861, 1470, 1285, 1256, 1144, 1059, 954, 838, 775, 741, 668 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 4.25–4.20 (m, 1H), 4.04–3.97 (m, 1H), 3.78–3.72 (m, 1H), 3.64 (t, *J* = 6.5 Hz, 2H), 3.39–3.33 (m, 1H), 1.98 (brs, 2H), 1.89–1.79 (m, 2H), 1.69–1.49 (m, 6H), 1.43–1.34 (m, 4H), 1.32–1.28 (m, 4H), 0.89 (s, 12H), 0.07 (s, 3H), 0.05 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 83.2, 80.4, 74.2, 73.6, 62.8, 38.4, 33.5, 32.8, 31.9, 29.1, 25.7, 25.3, 22.6, 22.5, 18.0, 14.0, –4.5, –5.0 ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{42}O_4SiNa$ 397.2745; Found 397.2755.

(+)–Petromyroxol (8):[7]



To a vigorously stirred solution of alcohol **14** (38 mg, 0.101 mmol) in CH_2Cl_2 (2 mL) and H_2O (1 mL) was added TEMPO (3.2 mg, 0.0203 mmol, 20 mol%) and (bis(acetyoxy)iodo)benzene (BAIB) (81.5 mg, 0.253 mmol, 2.5 equiv). Stirring was continued for 12 h at room temperature. The reaction was quenched by addition of a saturated aq. $Na_2S_2O_3$ solution (2 mL). The organic layer was separated and washed with brine, dried (Na_2SO_4) and concentrated. The crude acid was treated with $BF_3{\cdot}OEt_2$ (64 μL, 0.202 mmol, 2.0 equiv, 45% solution) in CH_2Cl_2 (3 mL) at 0 °C for 2 h. It was then quenched with saturated aq. $NaHCO_3$ (3 mL) and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 5mL) and the combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated. Purification of the crude product by silica gel column chromatography using petroleum ether/EtOAc (1:9) as eluent afforded (+)-petromyroxol **8** (14.7 mg, 53%) as colorless oil. $[\alpha]_D^{25}$ +16.2 (*c* 0.4, $CHCl_3$); lit.[7] $[\alpha]_D^{25}$ +17.0 (*c* 0.36, $CHCl_3$). IR ($CHCl_3$): ν_{max} = 3408, 2929, 2858, 1714, 1516, 1462, 1414, 1377, 1339, 1251, 1161, 1128, 1060, 1025, 940, 922, 865, 824, 794, 757, 705 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 4.29 (d, *J* = 3.0 Hz, 1H), 4.06 (dd, *J* = 6.7, 6.6 Hz, 1H), 3.99 (brs, 2H), 3.80–3.77 (m, 1H), 3.39 (d, *J* = 6.2 Hz, 1H), 2.41 (d, *J* = 3.2 Hz, 2H), 2.02 (dd, *J* = 13.2, 6.6 Hz, 1H), 1.90–1.84 (m, 1H), 1.76–1.63 (m, 4H), 1.49 (d, *J* = 7.2 Hz, 1H), 1.41–1.33 (m, 2H), 1.31–1.24 (m, 5H), 0.88 (t, *J* = 6.8 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 177.6, 82.4, 80.6, 74.1, 73.2, 37.5, 33.6, 33.0, 31.8, 28.1, 25.2, 22.6, 21.2, 14.0. ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{26}O_5Na$ 297.1672; Found 297.1670.

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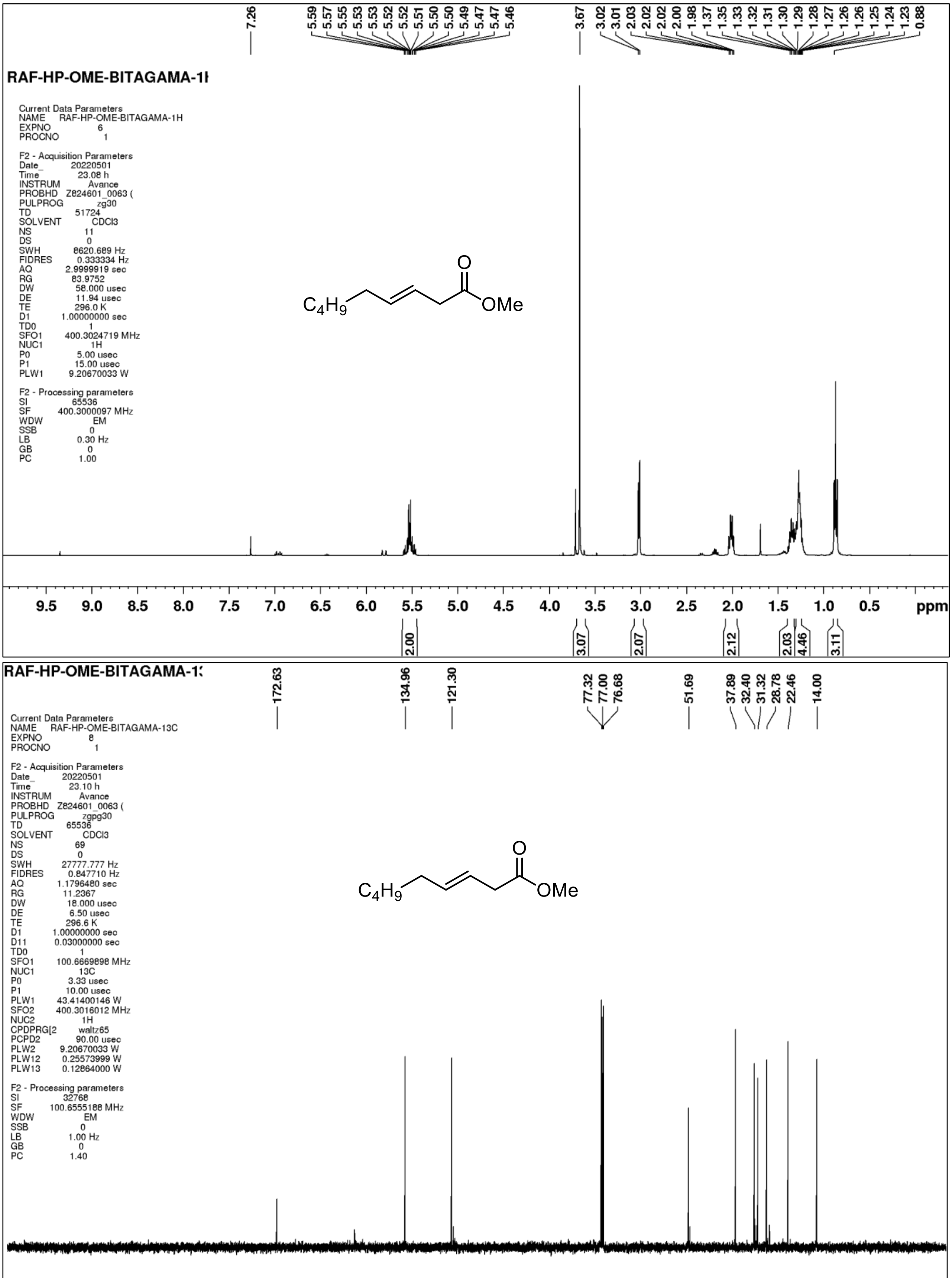
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **9**



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PROCNO             1

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TD                51724
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NS                   11
DS                    0
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FIDRES      0.333334 Hz
AQ        2.9999919 sec
RG              83.9752
DW          58.000 usec
DE           11.94 usec
TE              296.0 K
D1       1.00000000 sec
TD0                   1
SFO1    400.3024719 MHz
NUC1                 1H
P0            5.00 usec
P1           15.00 usec
PLW1     9.20670033 W

F2 - Processing parameters
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SSB                   0
LB              0.30 Hz
GB                    0
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Current Data Parameters
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EXPNO              8
PROCNO             1

F2 - Acquisition Parameters
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Time            23.10 h
INSTRUM          Avance
PROBHD   Z824601_0063 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   69
DS                    0
SWH        27777.777 Hz
FIDRES      0.847710 Hz
AQ        1.1796480 sec
RG              11.2367
DW          18.000 usec
DE            6.50 usec
TE              296.6 K
D1       1.00000000 sec
D11      0.03000000 sec
TD0                   1
SFO1    100.6669898 MHz
NUC1                13C
P0            3.33 usec
P1           10.00 usec
PLW1    43.41400146 W
SFO2    400.3016012 MHz
NUC2                 1H
CPDPRG[2        waltz65
PCPD2        90.00 usec
PLW2     9.20670033 W
PLW12    0.25573999 W
PLW13    0.12864000 W

F2 - Processing parameters
SI                32768
SF      100.6555188 MHz
WDW                  EM
SSB                   0
LB              1.00 Hz
GB                    0
PC                 1.40
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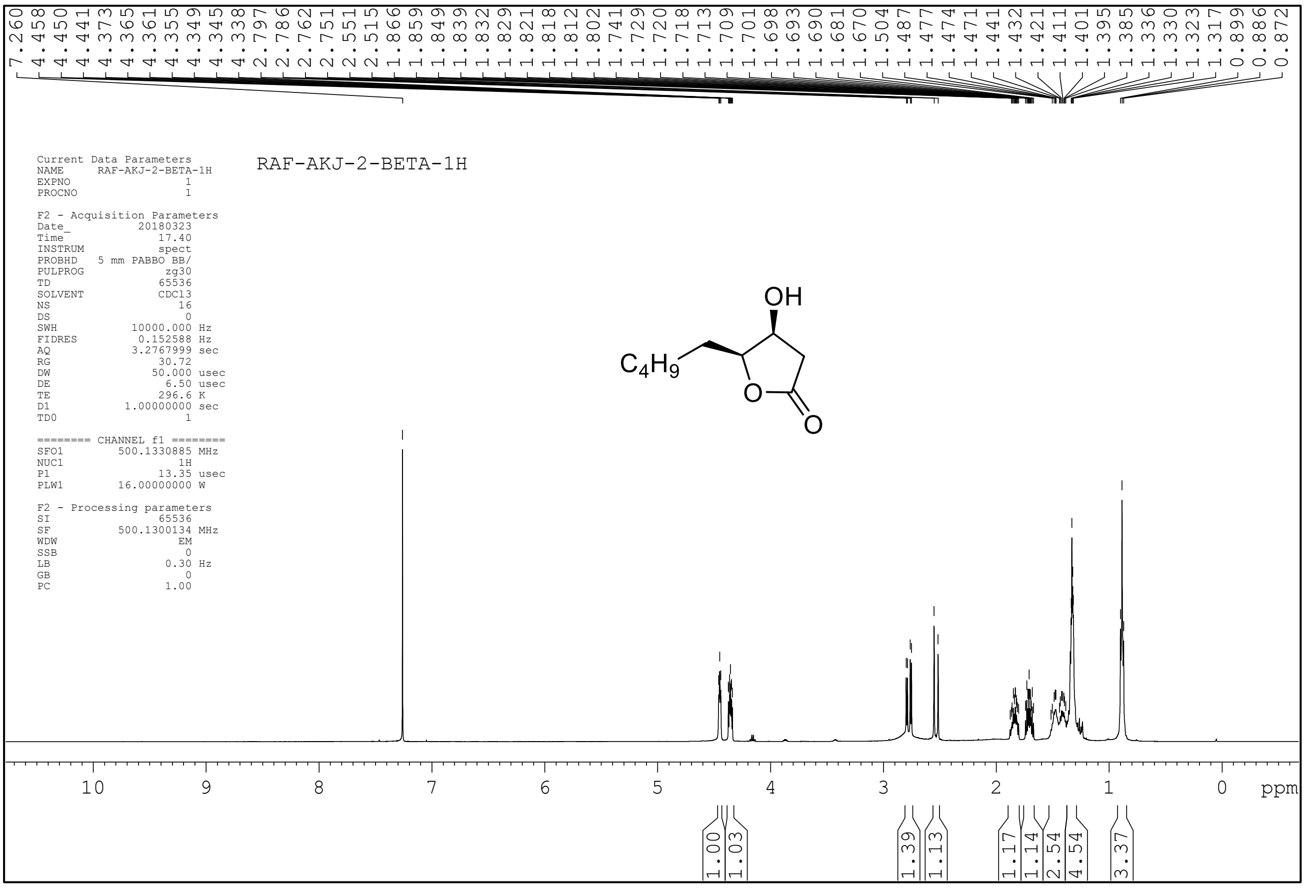
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) of compound **15**



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EXPNO                    1
PROCNO                   1

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Time                 17.40
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PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       0
SWH              10000.000 Hz
FIDRES            0.152588 Hz
AQ               3.2767999 sec
RG                   30.72
DW                  50.000 usec
DE                    6.50 usec
TE                   296.6 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           500.1330885 MHz
NUC1                    1H
P1                   13.35 usec
PLW1           16.00000000 W

F2 - Processing parameters
SI                   65536
SF             500.1300134 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
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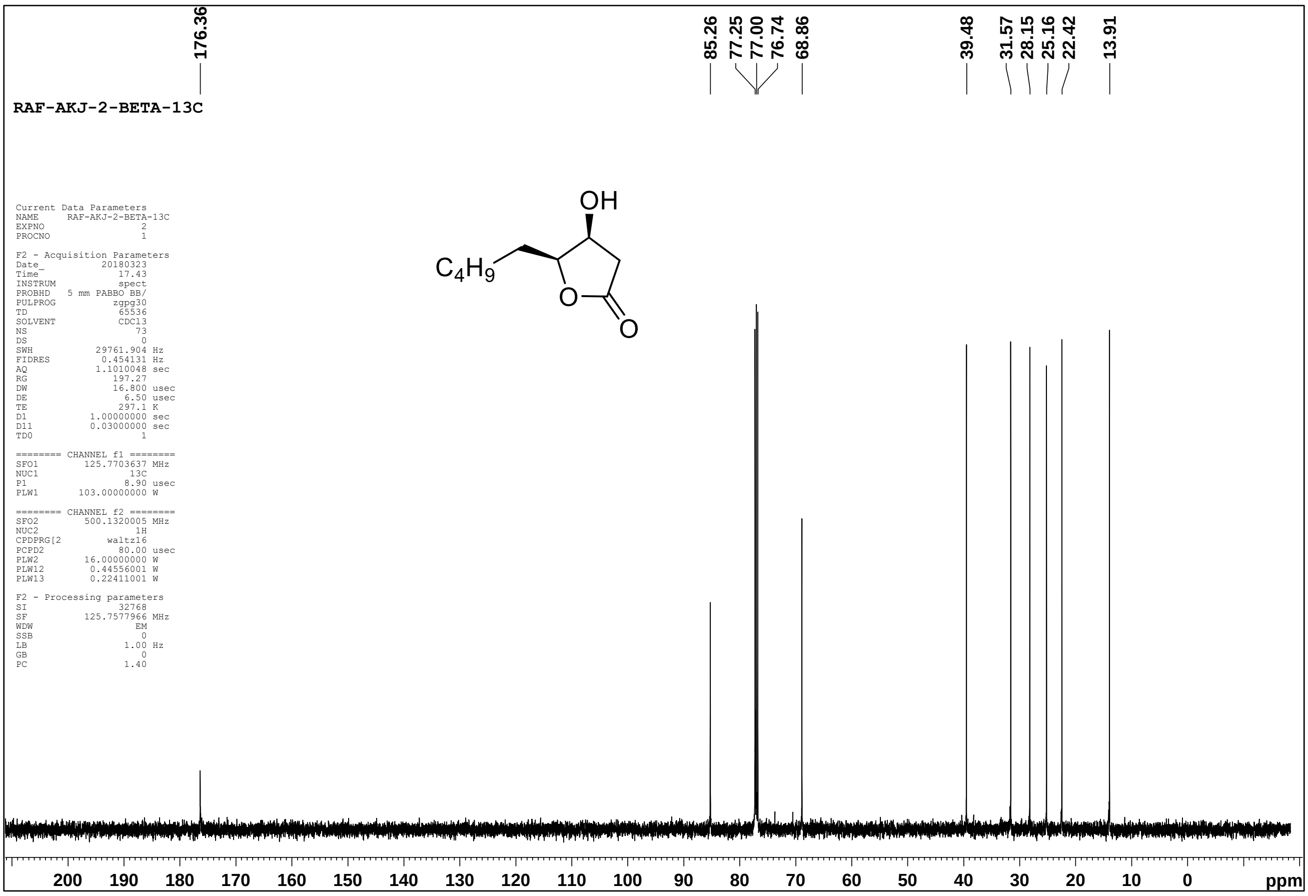

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EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
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Time                 17.43
INSTRUM              spect
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PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      73
DS                       0
SWH              29761.904 Hz
FIDRES            0.454131 Hz
AQ               1.1010048 sec
RG                  197.27
DW                  16.800 usec
DE                    6.50 usec
TE                   297.1 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           125.7703637 MHz
NUC1                   13C
P1                    8.90 usec
PLW1          103.00000000 W

======== CHANNEL f2 ========
SFO2           500.1320005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           16.00000000 W
PLW12           0.44556001 W
PLW13           0.22411001 W

F2 - Processing parameters
SI                   32768
SF             125.7577966 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
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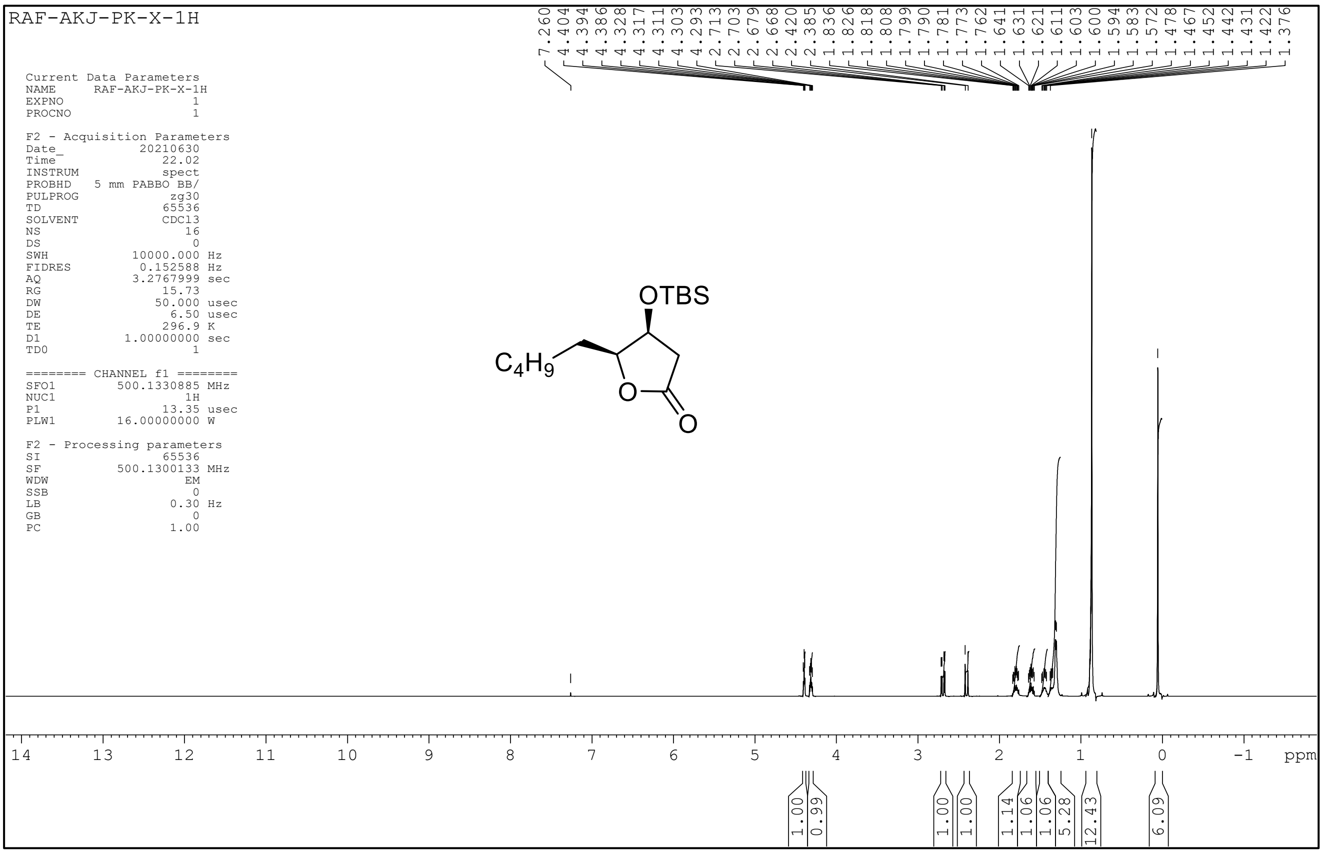
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **16a**



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RAF-AKJ-PK-X-1H

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  PULPROG             zg30
  TD                 65536
  SOLVENT            CDCl3
  NS                    16
  DS                     0
  SWH            10000.000 Hz
  FIDRES          0.152588 Hz
  AQ             3.2767999 sec
  RG                 15.73
  DW                50.000 usec
  DE                  6.50 usec
  TE                 296.9 K
  D1            1.00000000 sec
  TD0                    1

  ======== CHANNEL f1 ========
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  P1                 13.35 usec
  PLW1         16.00000000 W

  F2 - Processing parameters
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  SSB                    0
  LB                  0.30 Hz
  GB                     0
  PC                  1.00
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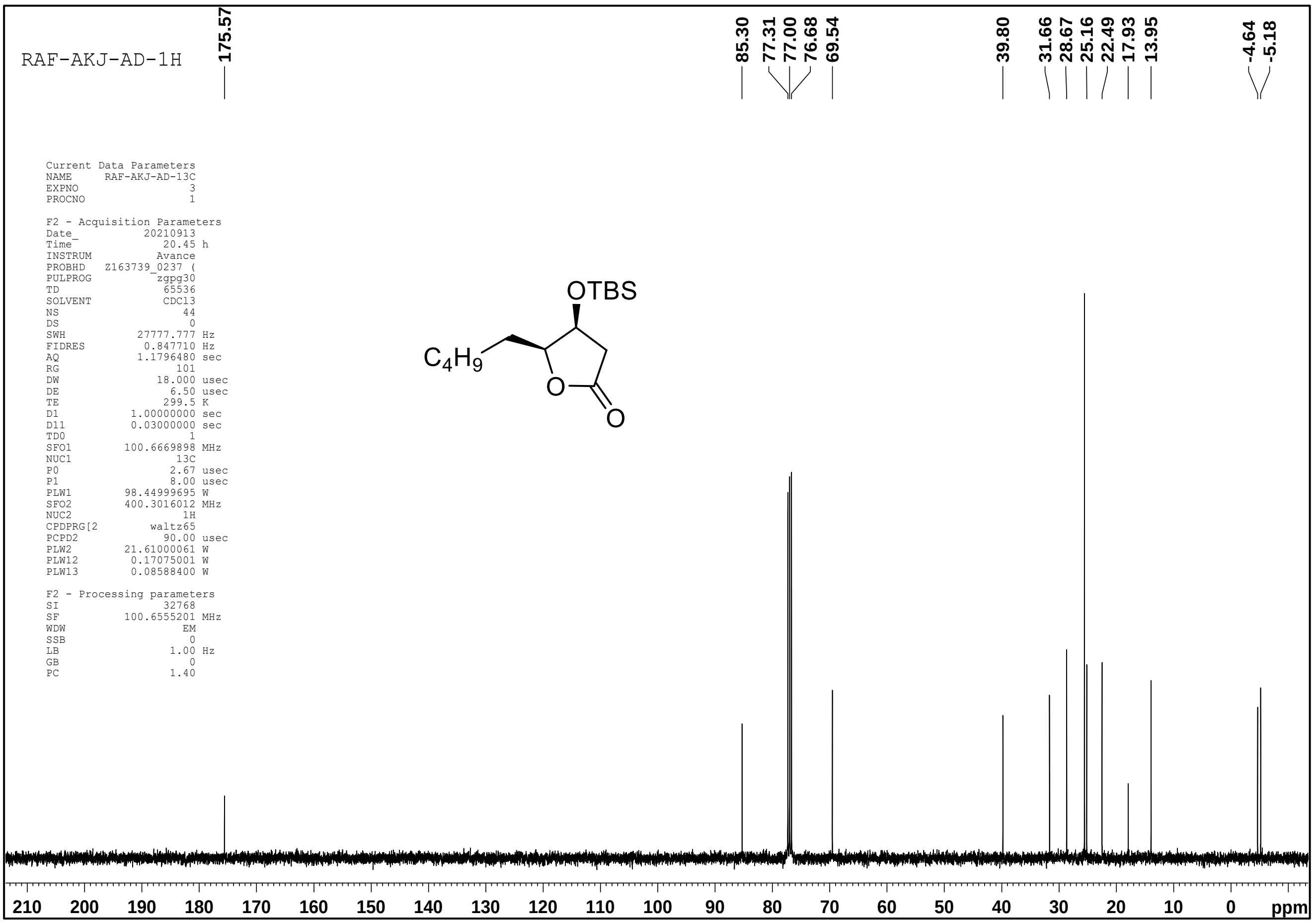

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RAF-AKJ-AD-1H

  Current Data Parameters
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  EXPNO                 3
  PROCNO                1

  F2 - Acquisition Parameters
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  Time              20.45 h
  INSTRUM          Avance
  PROBHD   Z163739_0237 (
  PULPROG         zgpg30
  TD                65536
  SOLVENT           CDCl3
  NS                   44
  DS                    0
  SWH           27777.777 Hz
  FIDRES         0.847710 Hz
  AQ            1.1796480 sec
  RG                  101
  DW               18.000 usec
  DE                 6.50 usec
  TE                299.5 K
  D1           1.00000000 sec
  D11          0.03000000 sec
  TD0                   1
  SFO1        100.6669898 MHz
  NUC1                13C
  P0                 2.67 usec
  P1                 8.00 usec
  PLW1        98.44999695 W
  SFO2        400.3016012 MHz
  NUC2                 1H
  CPDPRG[2        waltz65
  PCPD2             90.00 usec
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  F2 - Processing parameters
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  SSB                   0
  LB                 1.00 Hz
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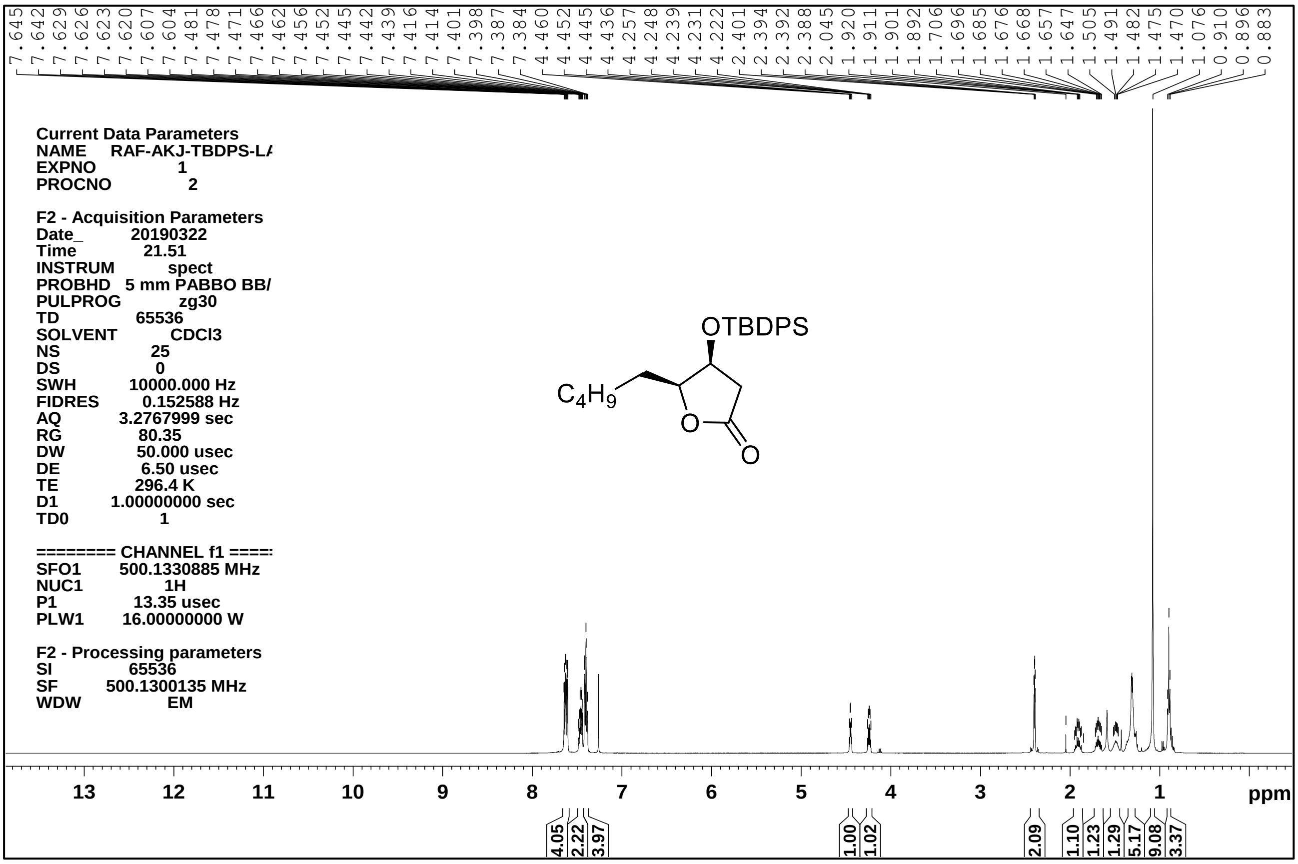
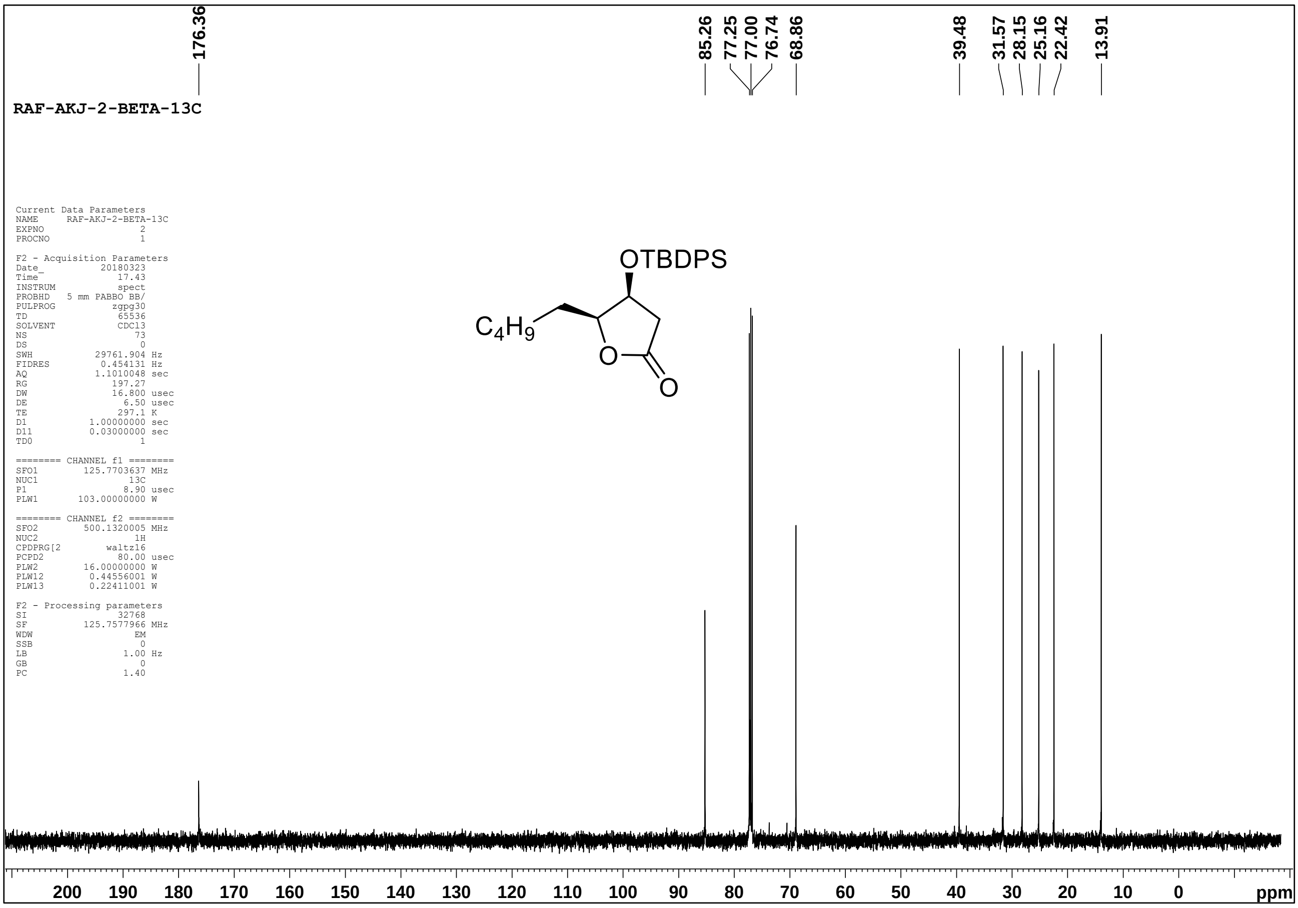
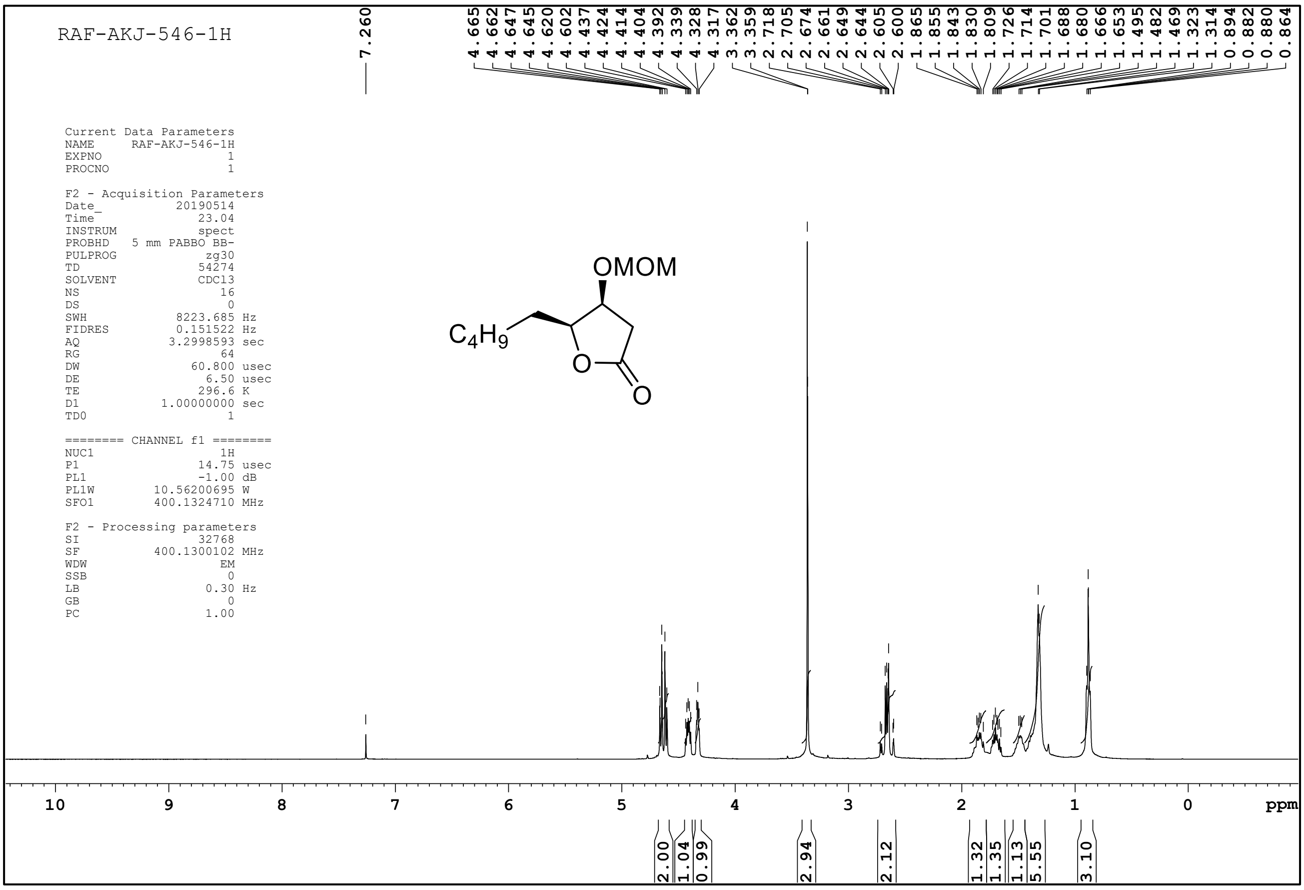
^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) of compound **16b**





^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of compound **16c**



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Current Data Parameters
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PROCNO                1

F2 - Acquisition Parameters
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PULPROG            zg30
TD                54274
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            8223.685 Hz
FIDRES         0.151522 Hz
AQ            3.2998593 sec
RG                   64
DW               60.800 usec
DE                 6.50 usec
TE                296.6 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.75 usec
PL1               -1.00 dB
PL1W        10.56200695 W
SFO1        400.1324710 MHz

F2 - Processing parameters
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SSB                   0
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GB                    0
PC                 1.00
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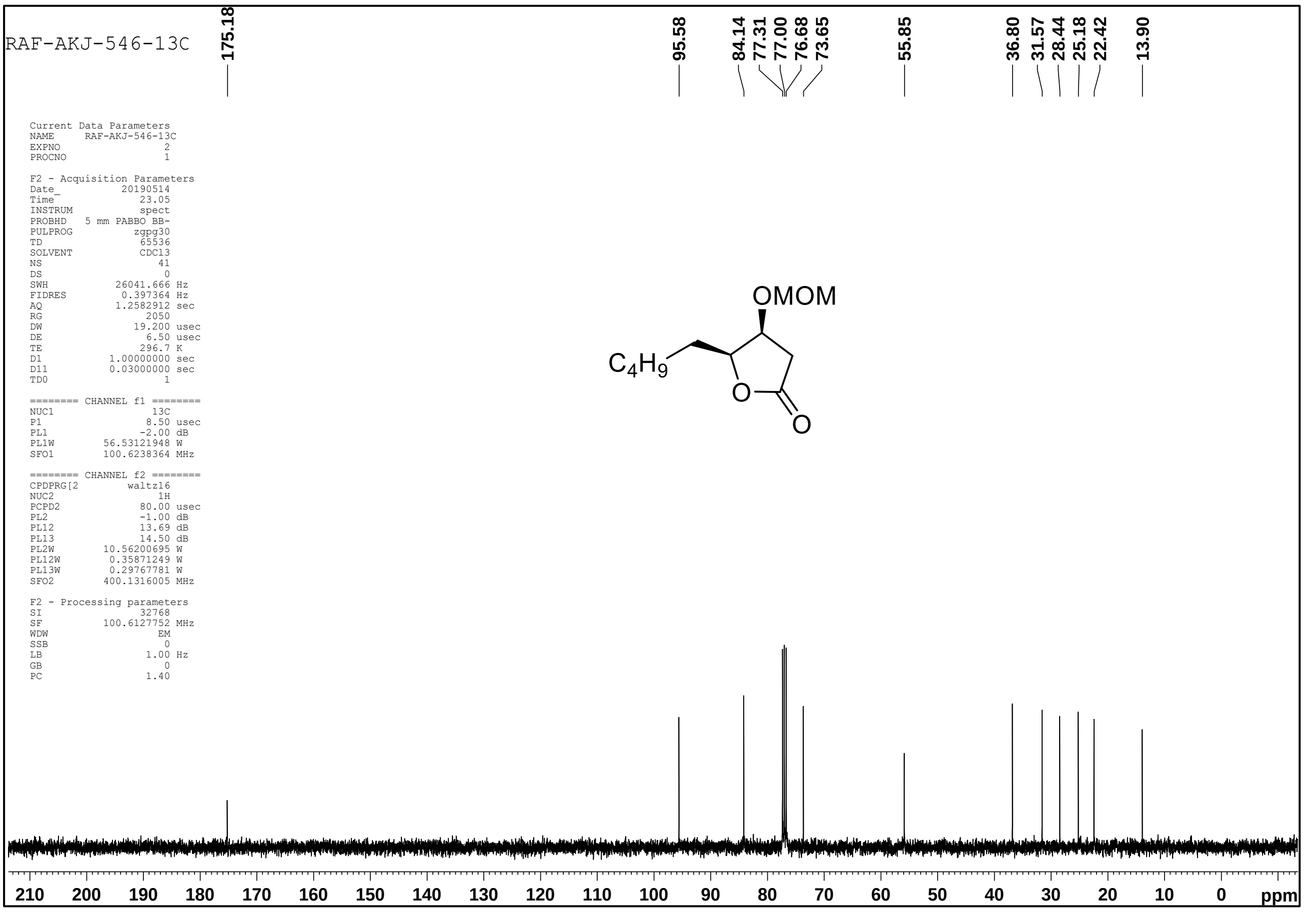

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Current Data Parameters
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PROCNO                1

F2 - Acquisition Parameters
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PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   41
DS                    0
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FIDRES         0.397364 Hz
AQ            1.2582912 sec
RG                 2050
DW               19.200 usec
DE                 6.50 usec
TE                296.7 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 8.50 usec
PL1               -2.00 dB
PL1W        56.53121948 W
SFO1        100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -1.00 dB
PL12              13.69 dB
PL13              14.50 dB
PL2W        10.56200695 W
PL12W        0.35871249 W
PL13W        0.29767781 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127752 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
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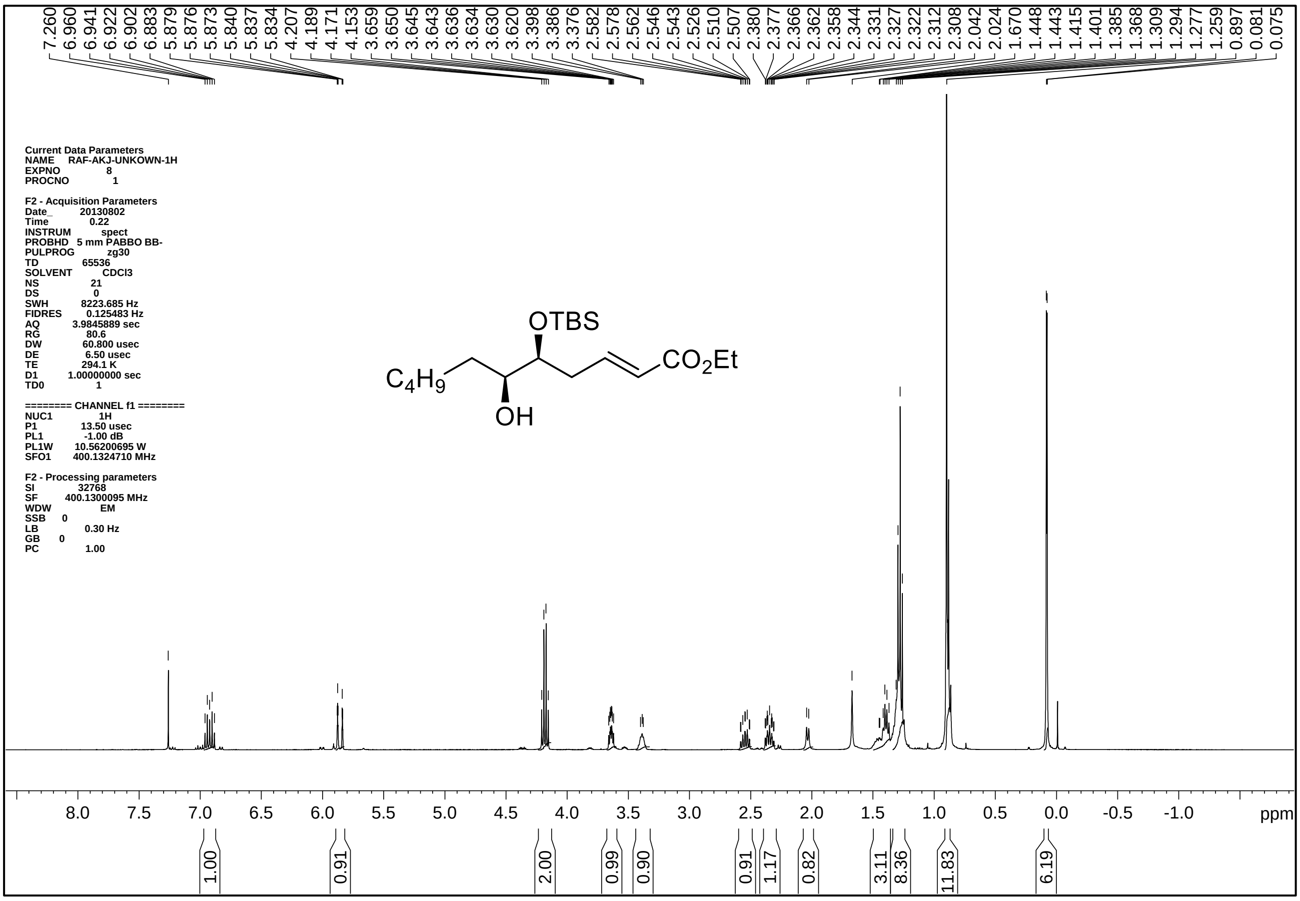
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **17a**



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Current Data Parameters
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EXPNO              8
PROCNO             1

F2 - Acquisition Parameters
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Time              0.22
INSTRUM          spect
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PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  21
DS                   0
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FIDRES       0.125483 Hz
AQ         3.9845889 sec
RG                80.6
DW          60.800 usec
DE            6.50 usec
TE             294.1 K
D1        1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1          13.50 usec
PL1           -1.00 dB
PL1W      10.56200695 W
SFO1      400.1324710 MHz

F2 - Processing parameters
SI               32768
SF        400.1300095 MHz
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GB       0
PC                1.00
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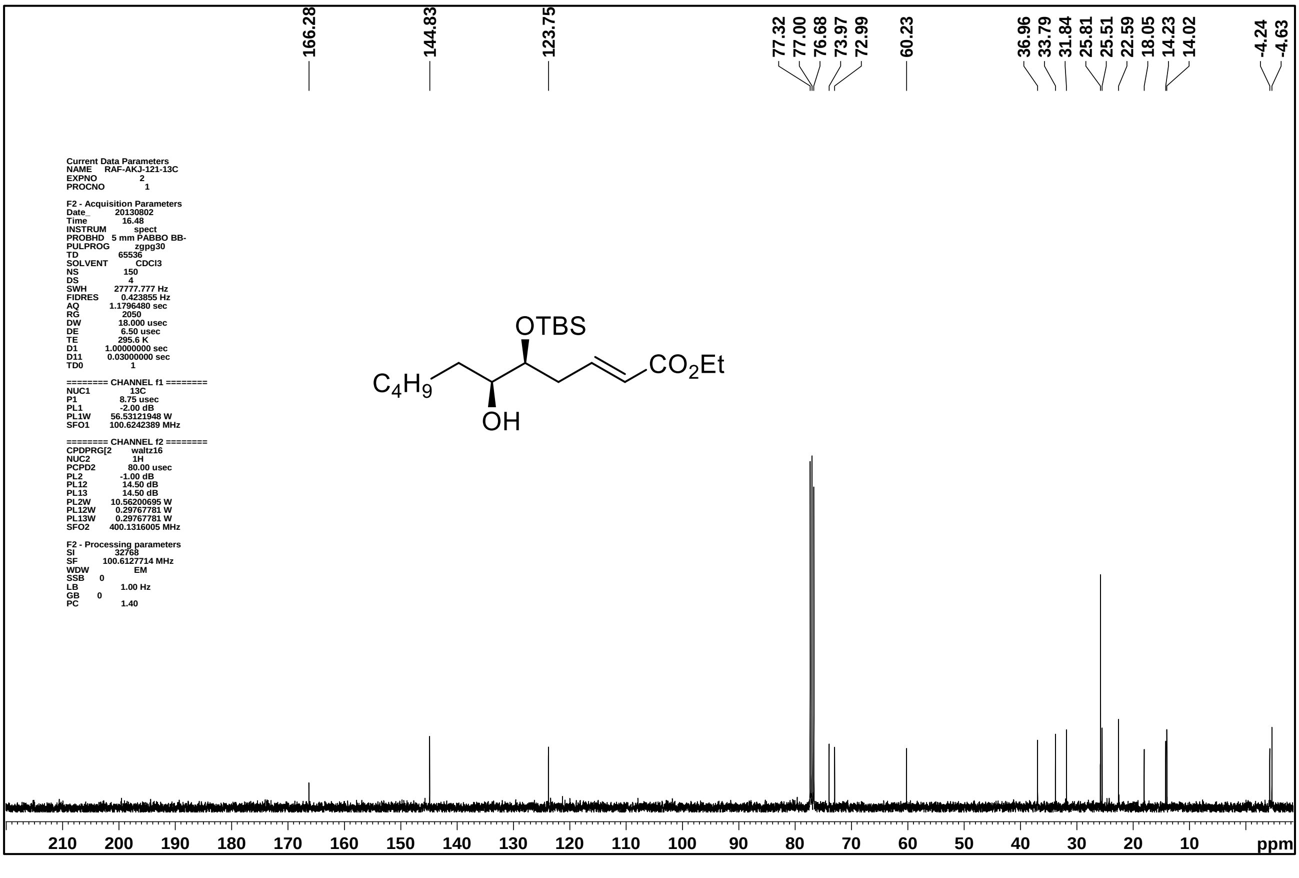

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PROCNO             1

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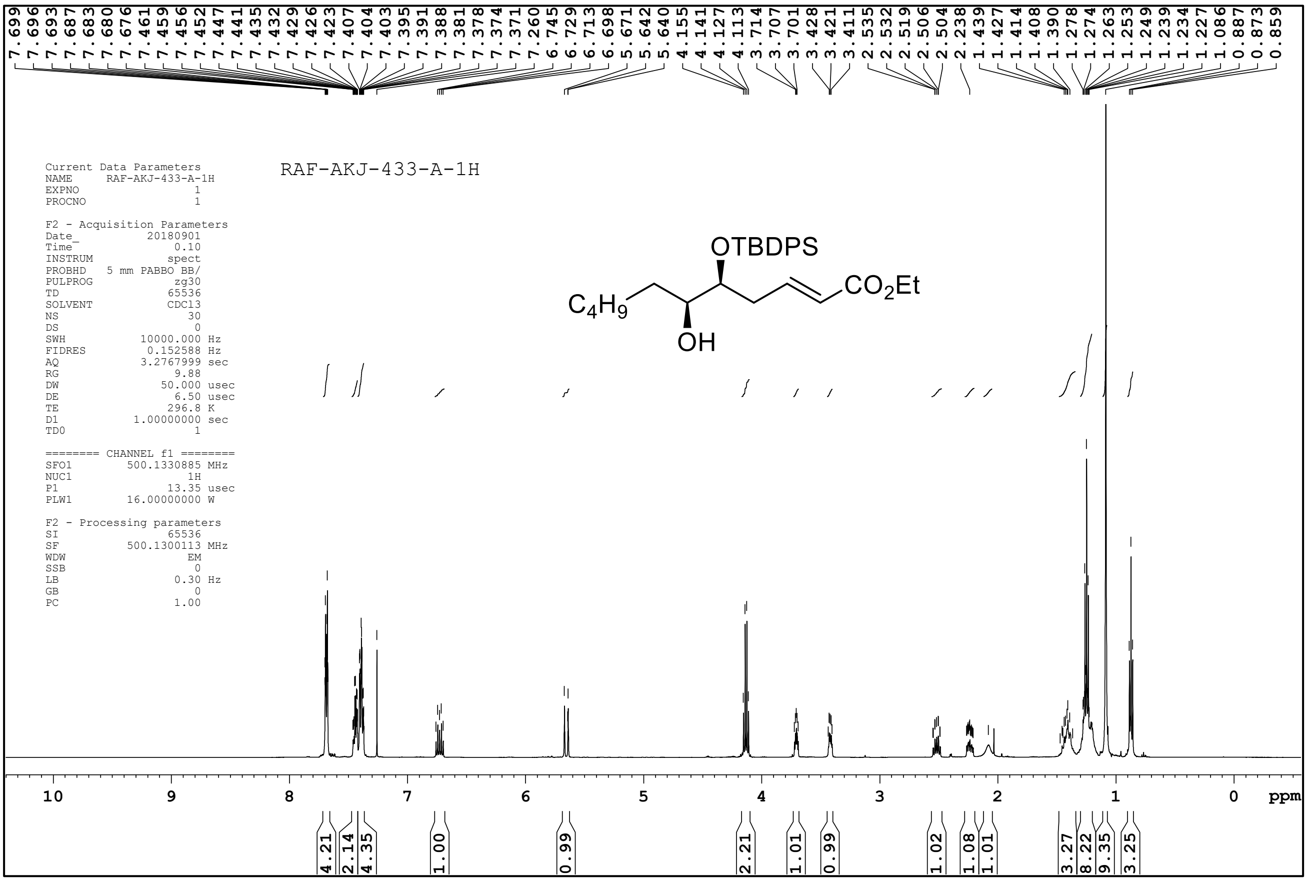
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 150
DS                   4
SWH        27777.777 Hz
FIDRES       0.423855 Hz
AQ         1.1796480 sec
RG                2050
DW          18.000 usec
DE            6.50 usec
TE             295.6 K
D1        1.00000000 sec
D11       0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1           8.75 usec
PL1           -2.00 dB
PL1W      56.53121948 W
SFO1      100.6242389 MHz

======== CHANNEL f2 ========
CPDPRG[2       waltz16
NUC2                1H
PCPD2        80.00 usec
PL2           -1.00 dB
PL12          14.50 dB
PL13          14.50 dB
PL2W      10.56200695 W
PL12W      0.29767781 W
PL13W      0.29767781 W
SFO2      400.1316005 MHz

F2 - Processing parameters
SI               32768
SF        100.6127714 MHz
WDW                 EM
SSB      0
LB             1.00 Hz
GB       0
PC                1.40
```

^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) of compound **17b**

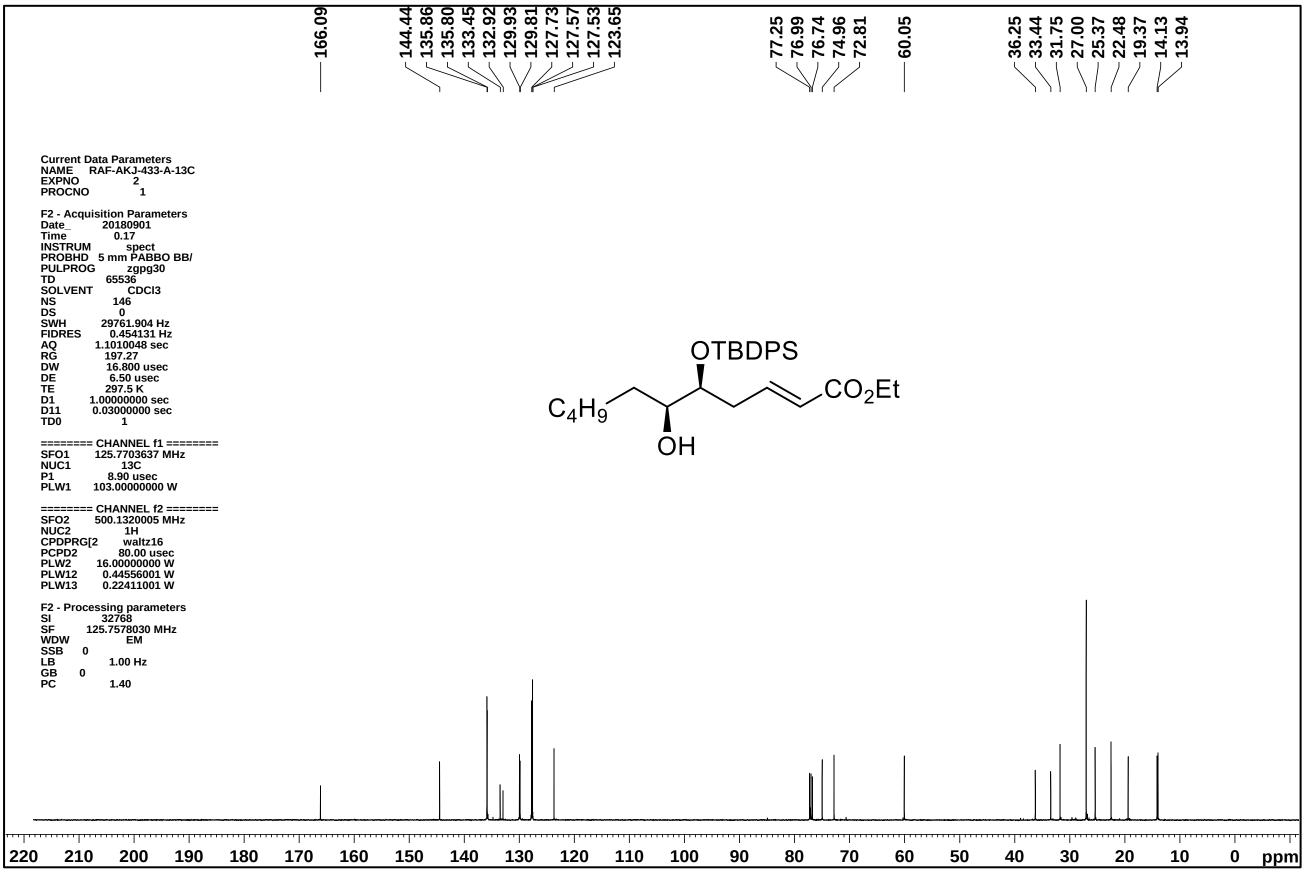


```
Current Data Parameters
NAME     RAF-AKJ-433-A-1H
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180901
Time                 0.10
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     30
DS                      0
SWH             10000.000 Hz
FIDRES           0.152588 Hz
AQ              3.2767999 sec
RG                   9.88
DW                 50.000 usec
DE                   6.50 usec
TE                  296.8 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          500.1330885 MHz
NUC1                   1H
P1                  13.35 usec
PLW1          16.00000000 W

F2 - Processing parameters
SI                  65536
SF            500.1300113 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



```
Current Data Parameters
NAME     RAF-AKJ-433-A-13C
EXPNO              2
PROCNO             1

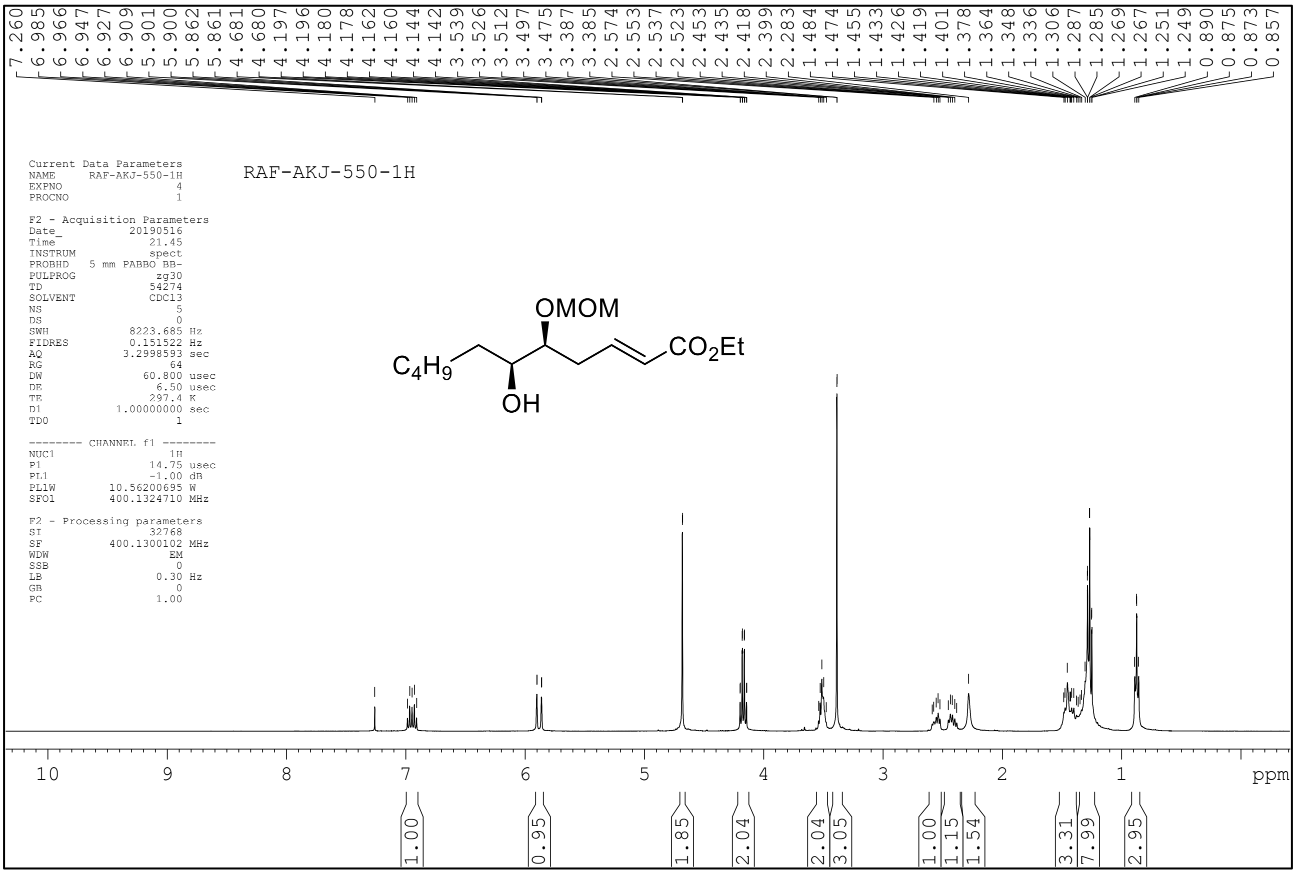
F2 - Acquisition Parameters
Date_         20180901
Time             0.17
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD              65536
SOLVENT          CDCl3
NS                146
DS                  0
SWH         29761.904 Hz
FIDRES       0.454131 Hz
AQ          1.1010048 sec
RG             197.27
DW             16.800 usec
DE               6.50 usec
TE              297.5 K
D1         1.00000000 sec
D11        0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1       125.7703637 MHz
NUC1              13C
P1               8.90 usec
PLW1     103.00000000 W

======== CHANNEL f2 ========
SFO2       500.1320005 MHz
NUC2               1H
CPDPRG[2       waltz16
PCPD2           80.00 usec
PLW2      16.00000000 W
PLW12      0.44556001 W
PLW13      0.22411001 W

F2 - Processing parameters
SI              32768
SF         125.7578030 MHz
WDW                EM
SSB     0
LB               1.00 Hz
GB      0
PC               1.40
```

^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **17c**

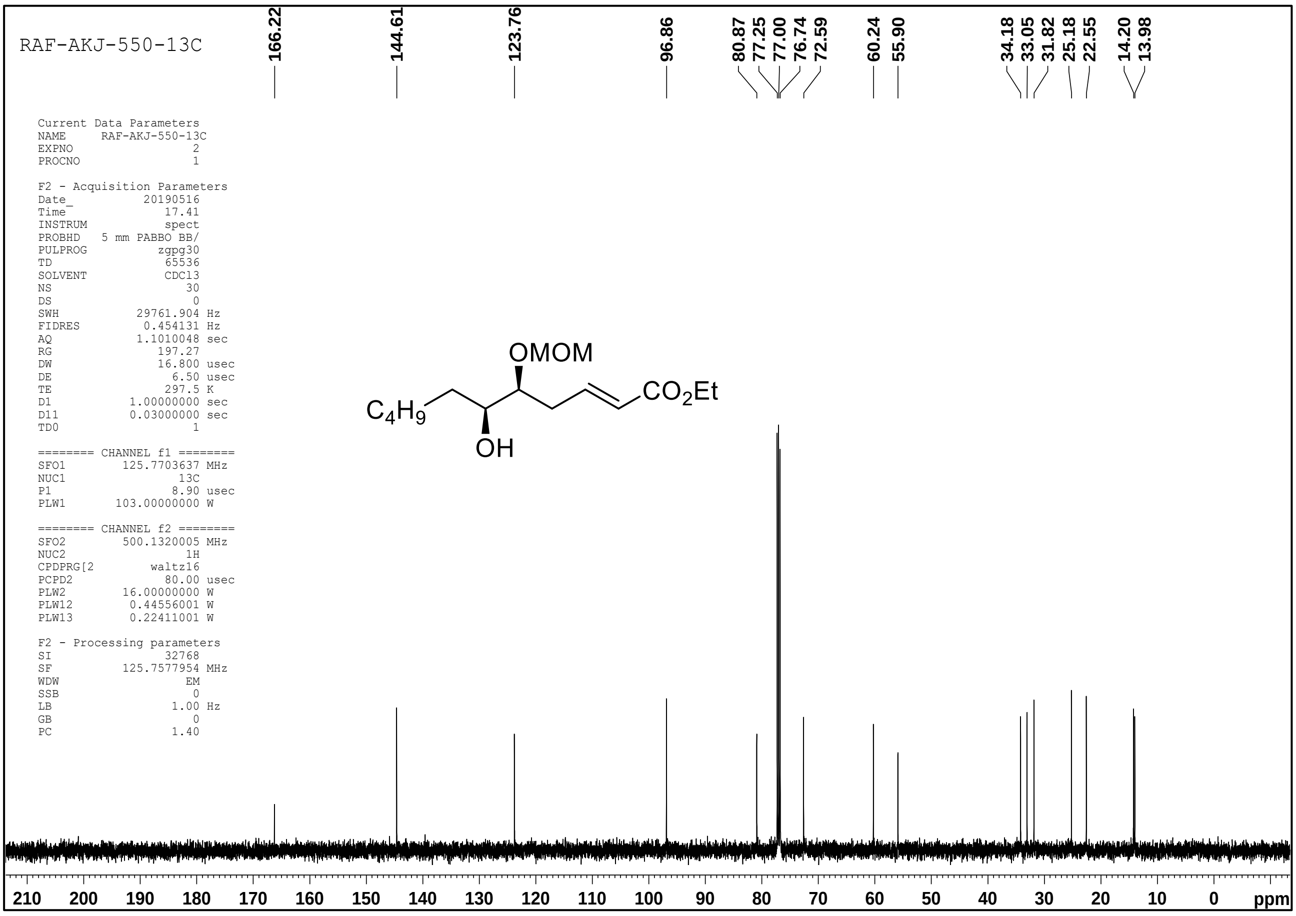


```
Current Data Parameters
NAME     RAF-AKJ-550-1H
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
Date_          20190516
Time              21.45
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                54274
SOLVENT           CDCl3
NS                    5
DS                    0
SWH            8223.685 Hz
FIDRES         0.151522 Hz
AQ            3.2998593 sec
RG                   64
DW               60.800 usec
DE                 6.50 usec
TE                297.4 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.75 usec
PL1               -1.00 dB
PL1W        10.56200695 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300102 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



```
Current Data Parameters
NAME     RAF-AKJ-550-13C
EXPNO                 2
PROCNO                1

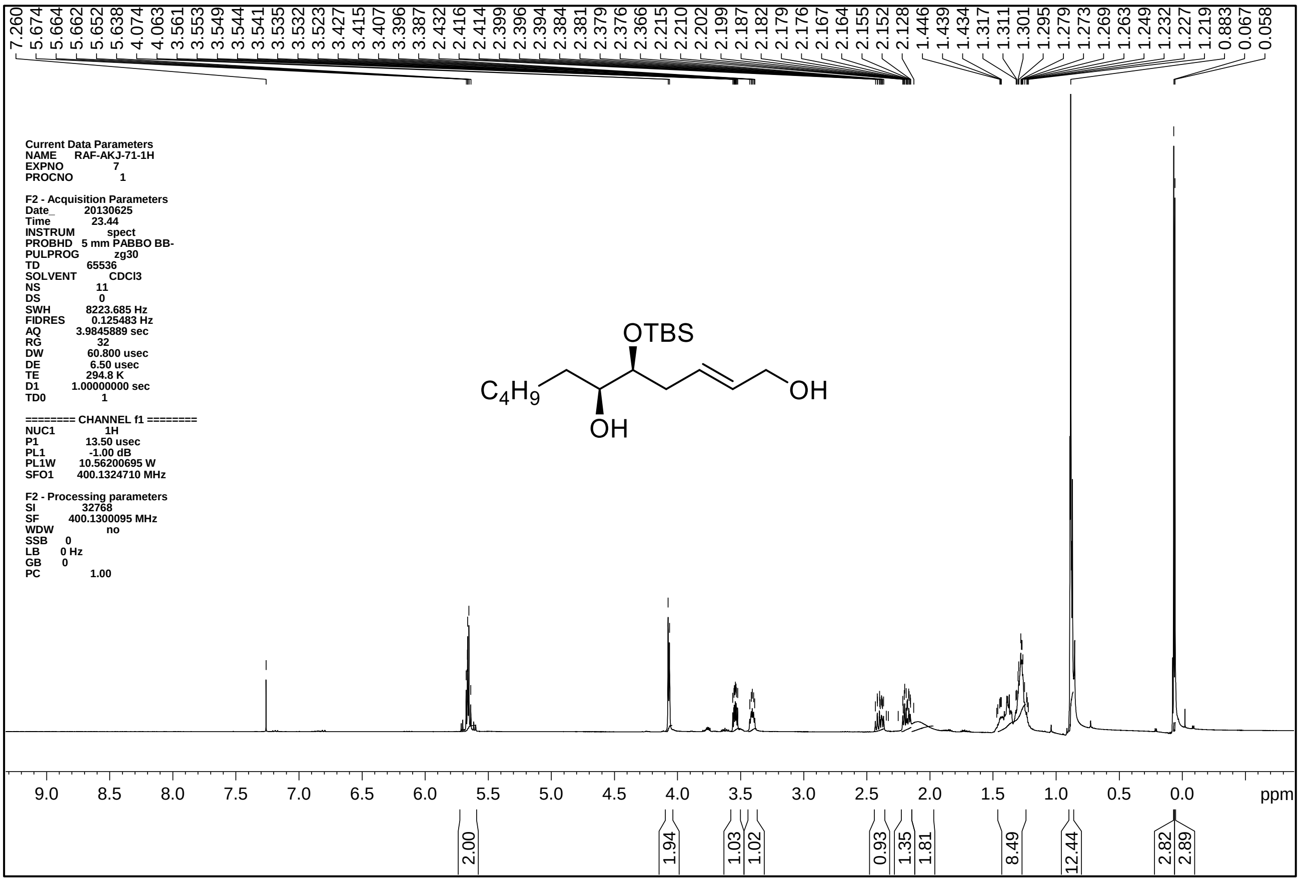
F2 - Acquisition Parameters
Date_          20190516
Time              17.41
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   30
DS                    0
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG               197.27
DW               16.800 usec
DE                 6.50 usec
TE                297.5 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        125.7703637 MHz
NUC1                13C
P1                 8.90 usec
PLW1       103.00000000 W

======== CHANNEL f2 ========
SFO2        500.1320005 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2        16.00000000 W
PLW12        0.44556001 W
PLW13        0.22411001 W

F2 - Processing parameters
SI                32768
SF          125.7577954 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **18a**

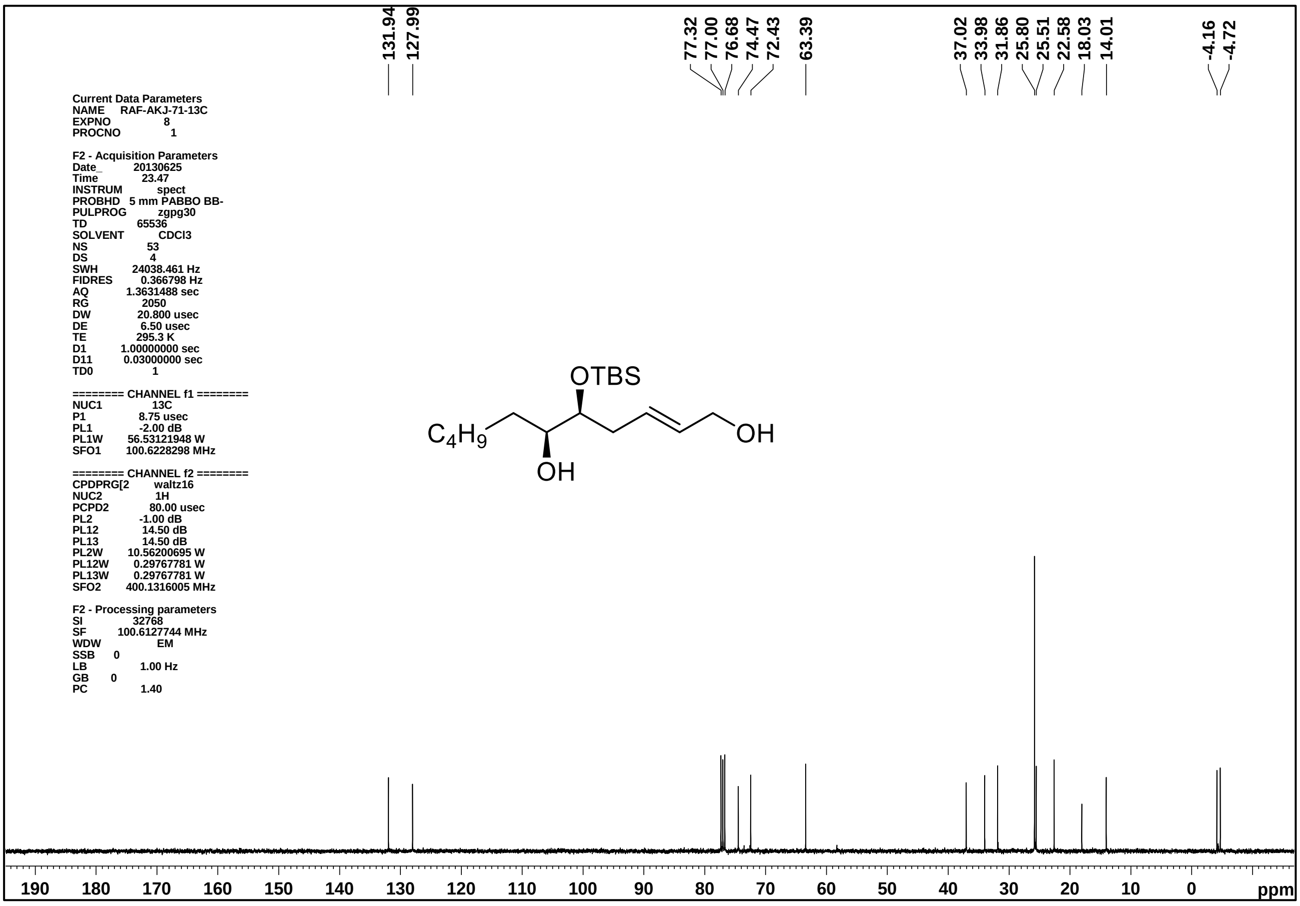


```
Current Data Parameters
NAME     RAF-AKJ-71-1H
EXPNO          7
PROCNO         1

F2 - Acquisition Parameters
Date_        20130625
Time           23.44
INSTRUM        spect
PROBHD   5 mm PABBO BB-
PULPROG        zg30
TD           65536
SOLVENT        CDCl3
NS             11
DS              0
SWH        8223.685 Hz
FIDRES      0.125483 Hz
AQ        3.9845889 sec
RG             32
DW          60.800 usec
DE            6.50 usec
TE           294.8 K
D1       1.00000000 sec
TD0             1

======== CHANNEL f1 ========
NUC1            1H
P1           13.50 usec
PL1          -1.00 dB
PL1W     10.56200695 W
SFO1     400.1324710 MHz

F2 - Processing parameters
SI           32768
SF       400.1300095 MHz
WDW             no
SSB     0
LB      0 Hz
GB      0
PC            1.00
```



```
Current Data Parameters
NAME     RAF-AKJ-71-13C
EXPNO          8
PROCNO         1

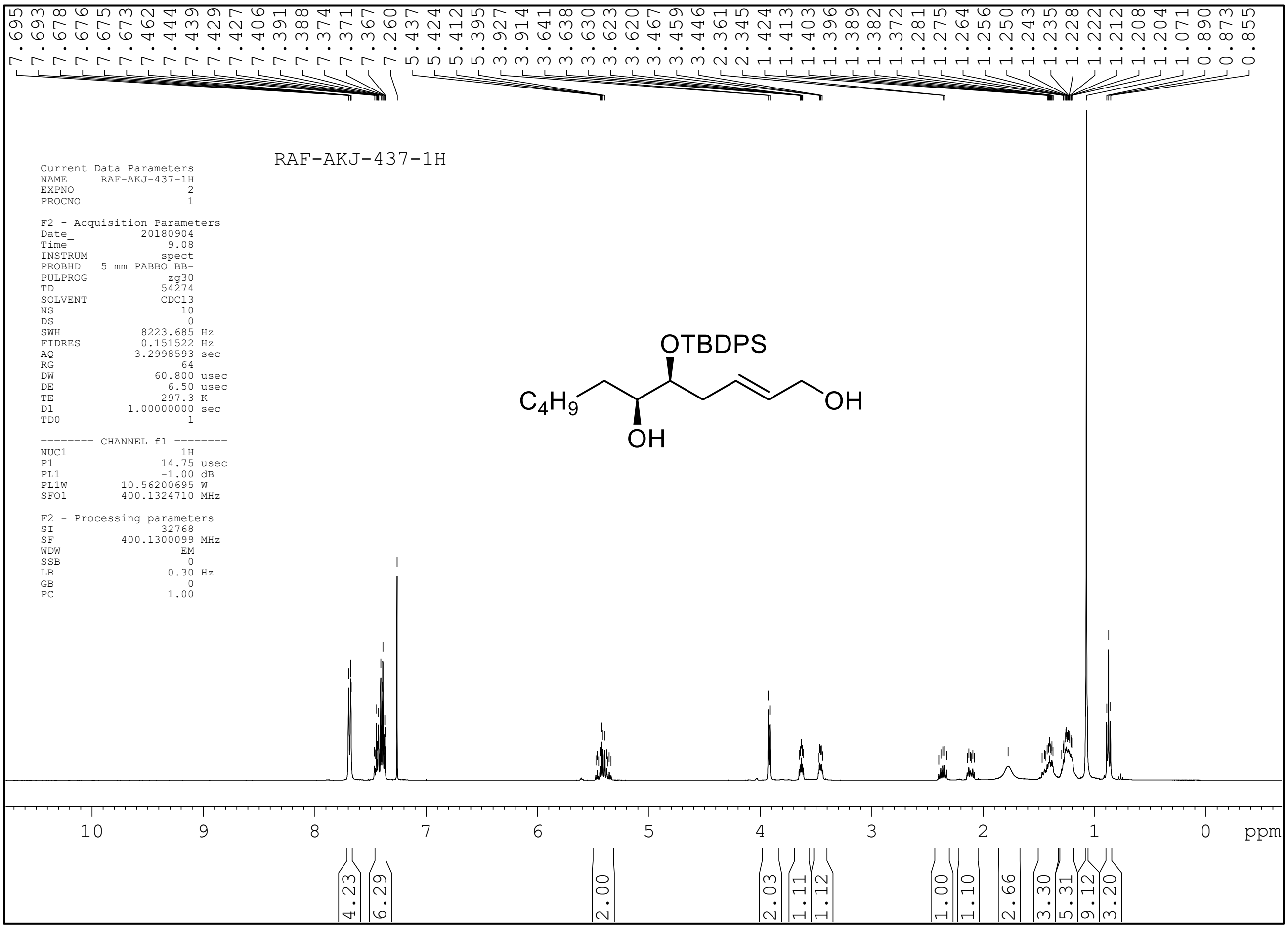
F2 - Acquisition Parameters
Date_        20130625
Time           23.47
INSTRUM        spect
PROBHD   5 mm PABBO BB-
PULPROG        zgpg30
TD           65536
SOLVENT        CDCl3
NS             53
DS              4
SWH       24038.461 Hz
FIDRES      0.366798 Hz
AQ        1.3631488 sec
RG            2050
DW          20.800 usec
DE            6.50 usec
TE           295.3 K
D1       1.00000000 sec
D11      0.03000000 sec
TD0             1

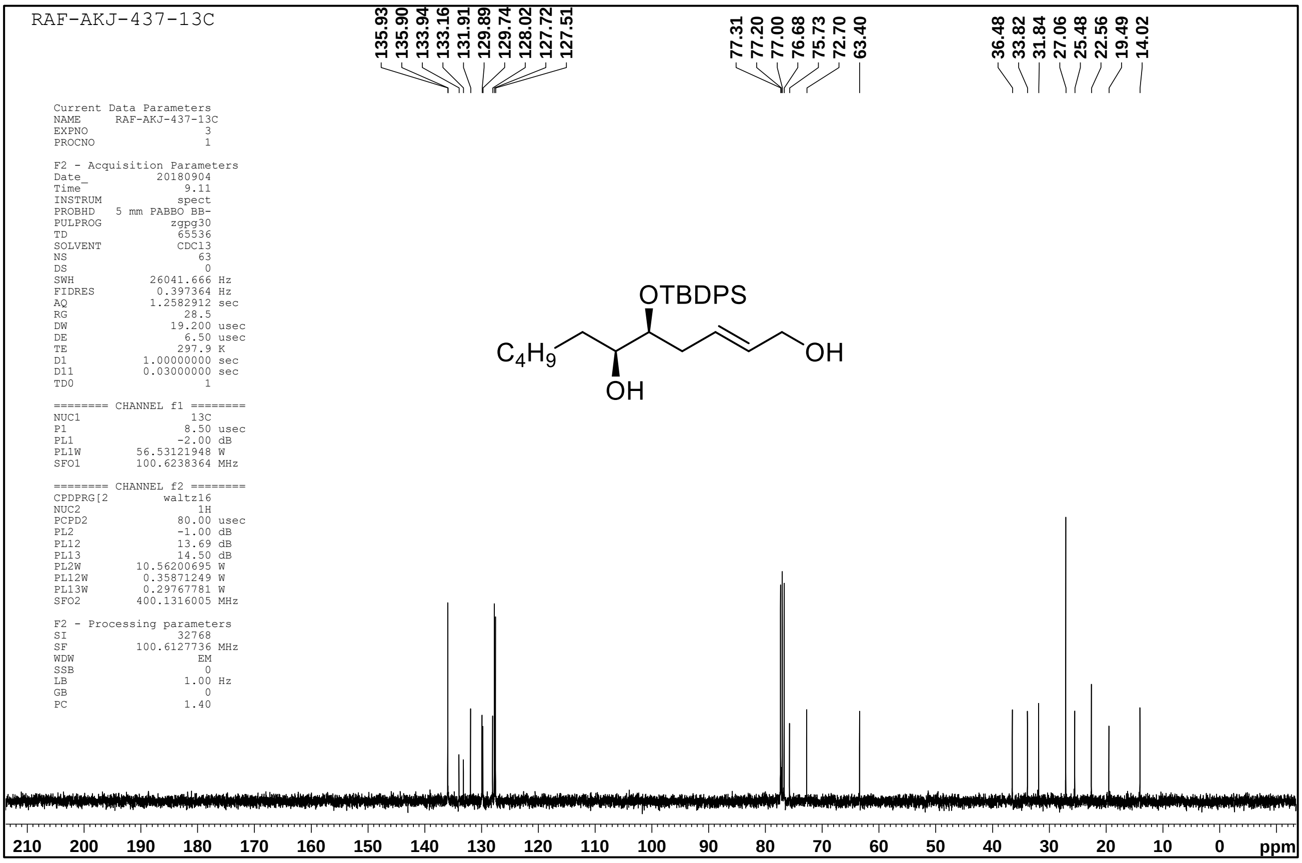
======== CHANNEL f1 ========
NUC1            13C
P1            8.75 usec
PL1          -2.00 dB
PL1W     56.53121948 W
SFO1     100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2       waltz16
NUC2            1H
PCPD2        80.00 usec
PL2          -1.00 dB
PL12         14.50 dB
PL13         14.50 dB
PL2W     10.56200695 W
PL12W     0.29767781 W
PL13W     0.29767781 W
SFO2     400.1316005 MHz

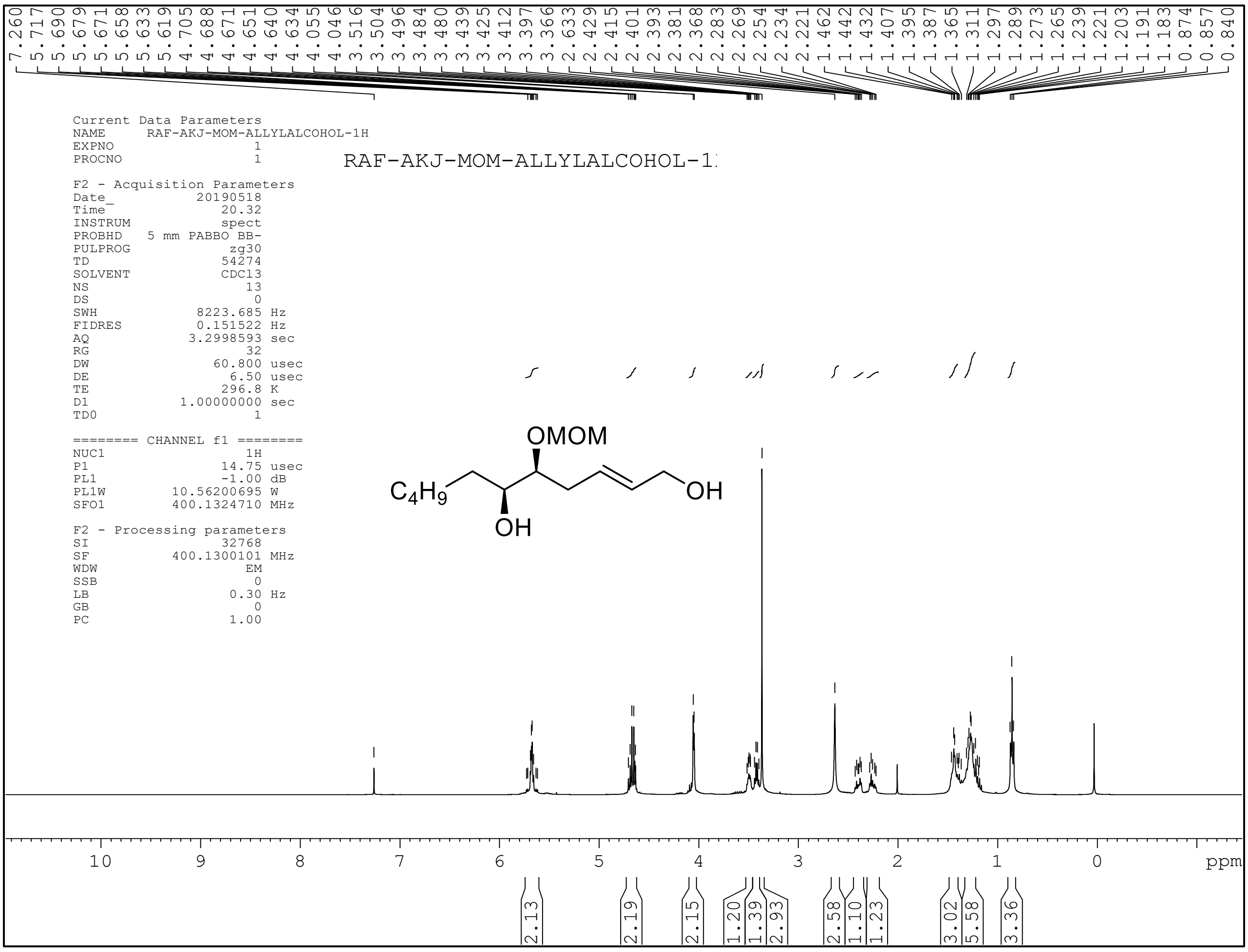
F2 - Processing parameters
SI           32768
SF       100.6127744 MHz
WDW             EM
SSB     0
LB            1.00 Hz
GB      0
PC            1.40
```

^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **18b**





^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) of compound **18c**

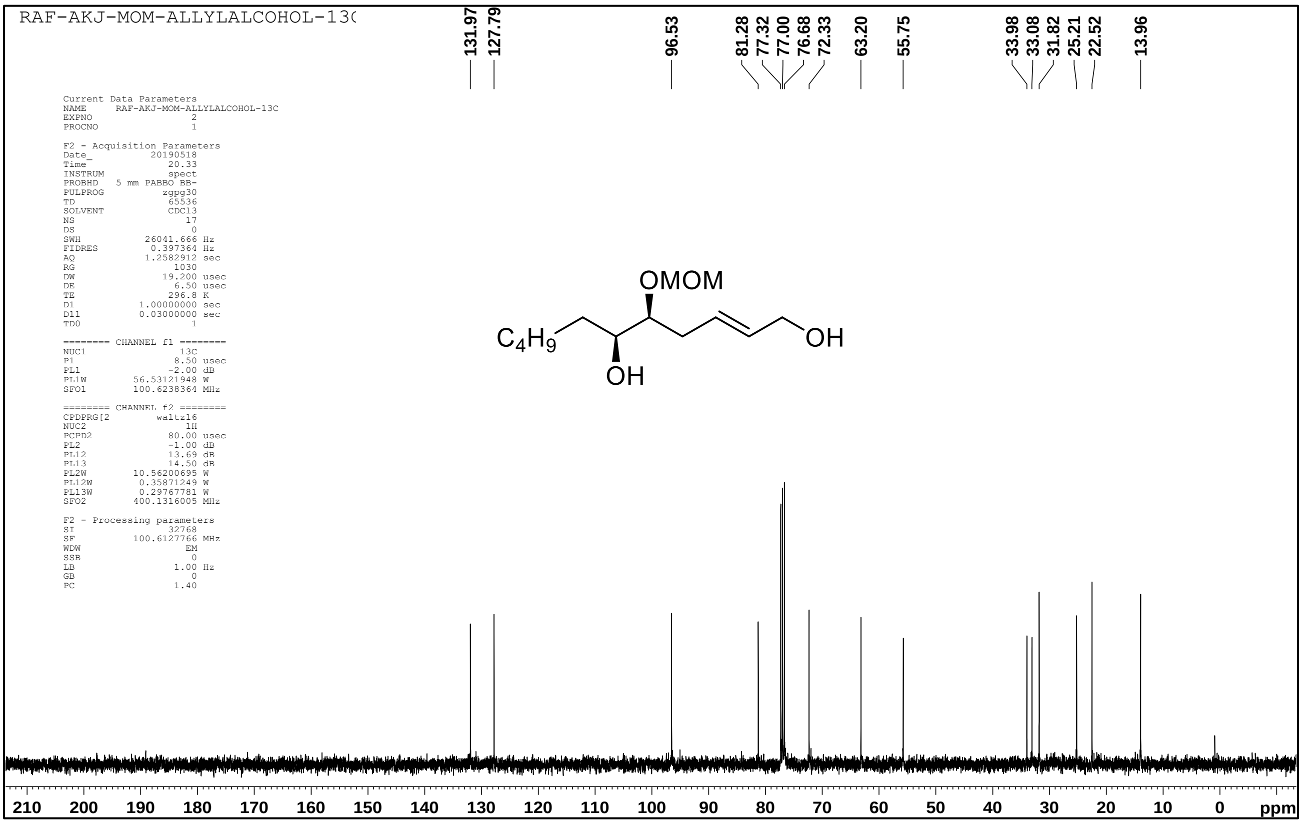


```
Current Data Parameters
NAME     RAF-AKJ-MOM-ALLYLALCOHOL-1H
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20190518
Time              20.32
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                54274
SOLVENT           CDCl3
NS                   13
DS                    0
SWH            8223.685 Hz
FIDRES         0.151522 Hz
AQ            3.2998593 sec
RG                   32
DW               60.800 usec
DE                 6.50 usec
TE                296.8 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.75 usec
PL1               -1.00 dB
PL1W        10.56200695 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300101 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



```
Current Data Parameters
NAME     RAF-AKJ-MOM-ALLYLALCOHOL-13C
EXPNO                 2
PROCNO                1

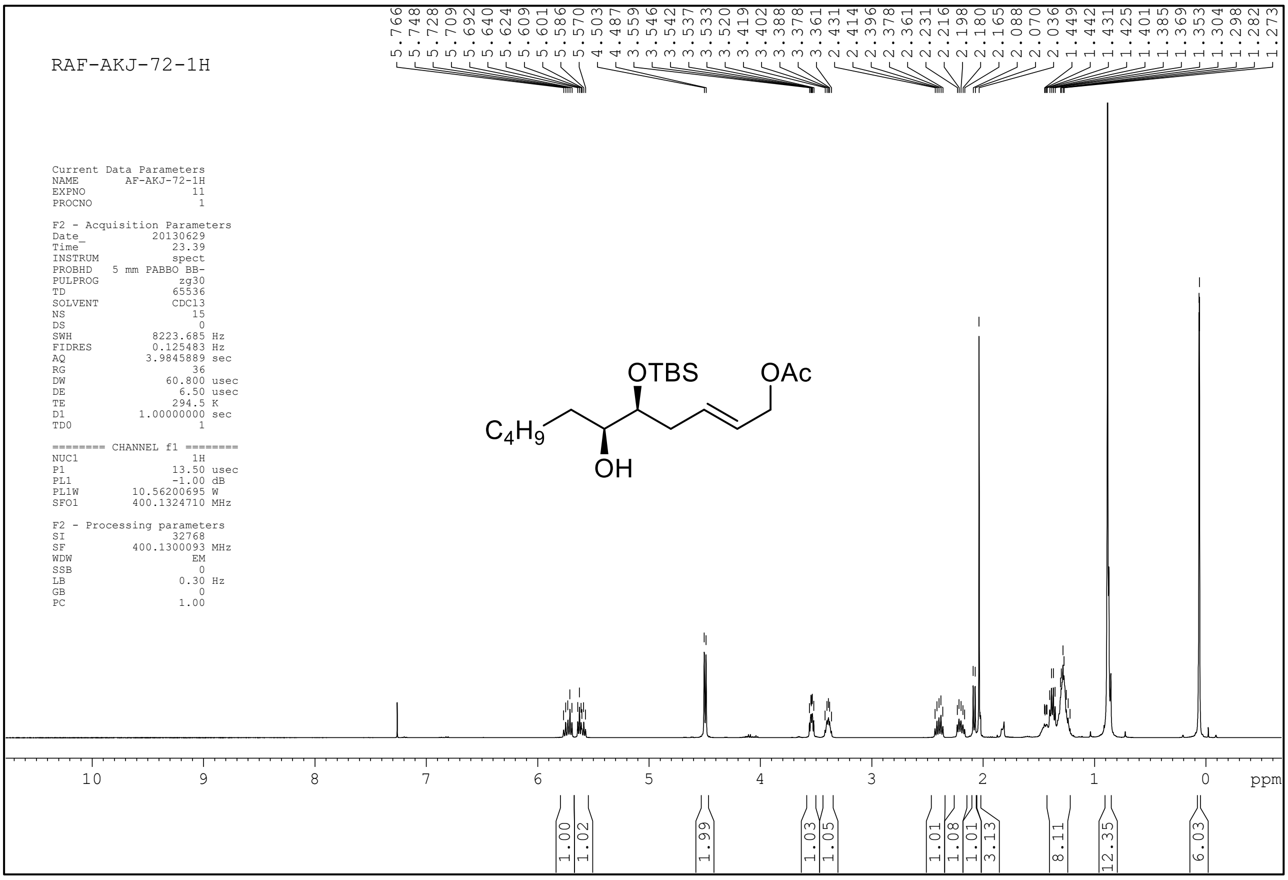
F2 - Acquisition Parameters
Date_          20190518
Time              20.33
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   17
DS                    0
SWH           26041.666 Hz
FIDRES         0.397364 Hz
AQ            1.2582912 sec
RG                 1030
DW               19.200 usec
DE                 6.50 usec
TE                296.8 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 8.50 usec
PL1               -2.00 dB
PL1W        56.53121948 W
SFO1        100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -1.00 dB
PL12              13.69 dB
PL13              14.50 dB
PL2W        10.56200695 W
PL12W        0.35871249 W
PL13W        0.29767781 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127766 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **5a**

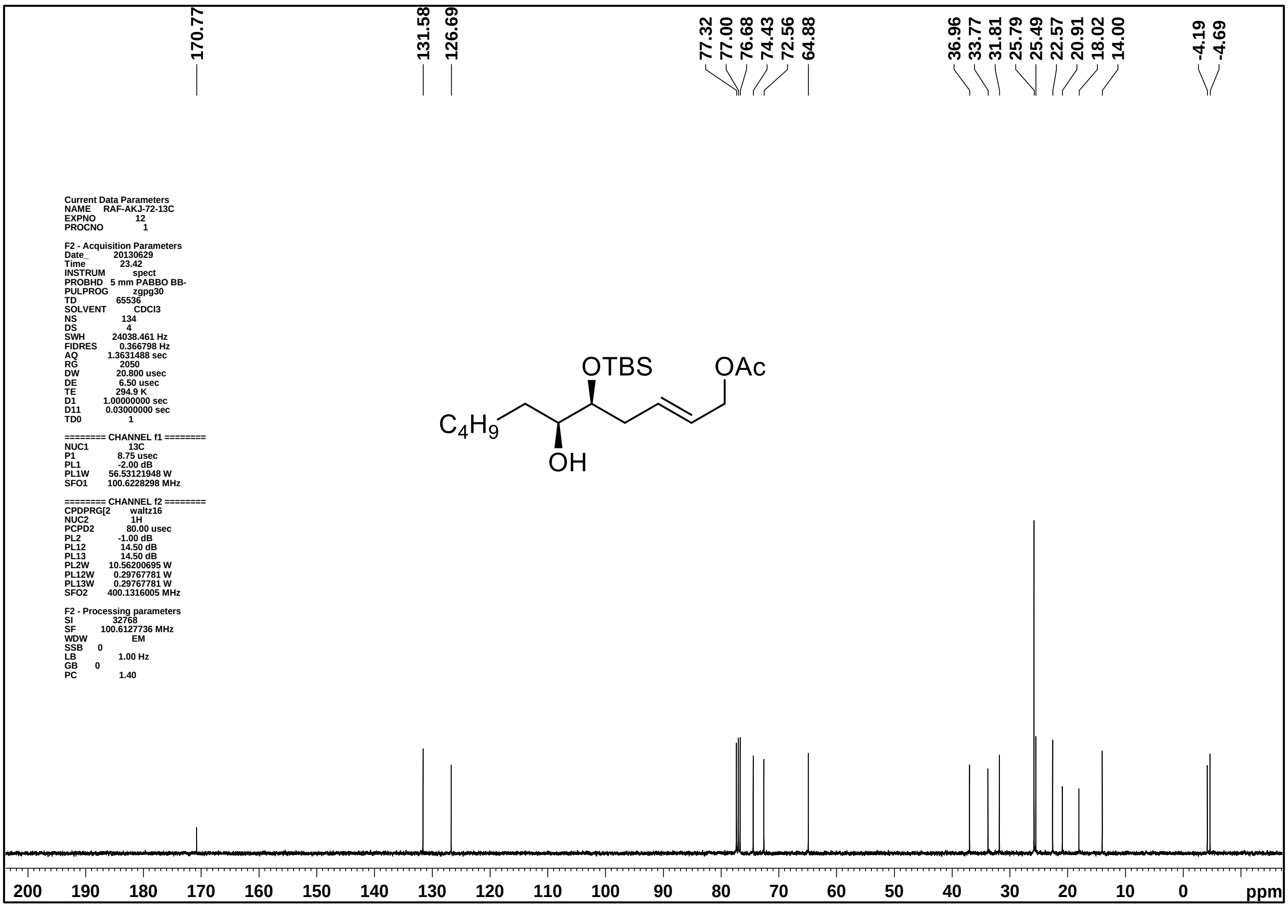


```
Current Data Parameters
NAME       AF-AKJ-72-1H
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20130629
Time              23.39
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   15
DS                    0
SWH            8223.685 Hz
FIDRES         0.125483 Hz
AQ            3.9845889 sec
RG                   36
DW               60.800 usec
DE                 6.50 usec
TE                294.5 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                13.50 usec
PL1               -1.00 dB
PL1W        10.56200695 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300093 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



```
Current Data Parameters
NAME     RAF-AKJ-72-13C
EXPNO             12
PROCNO             1

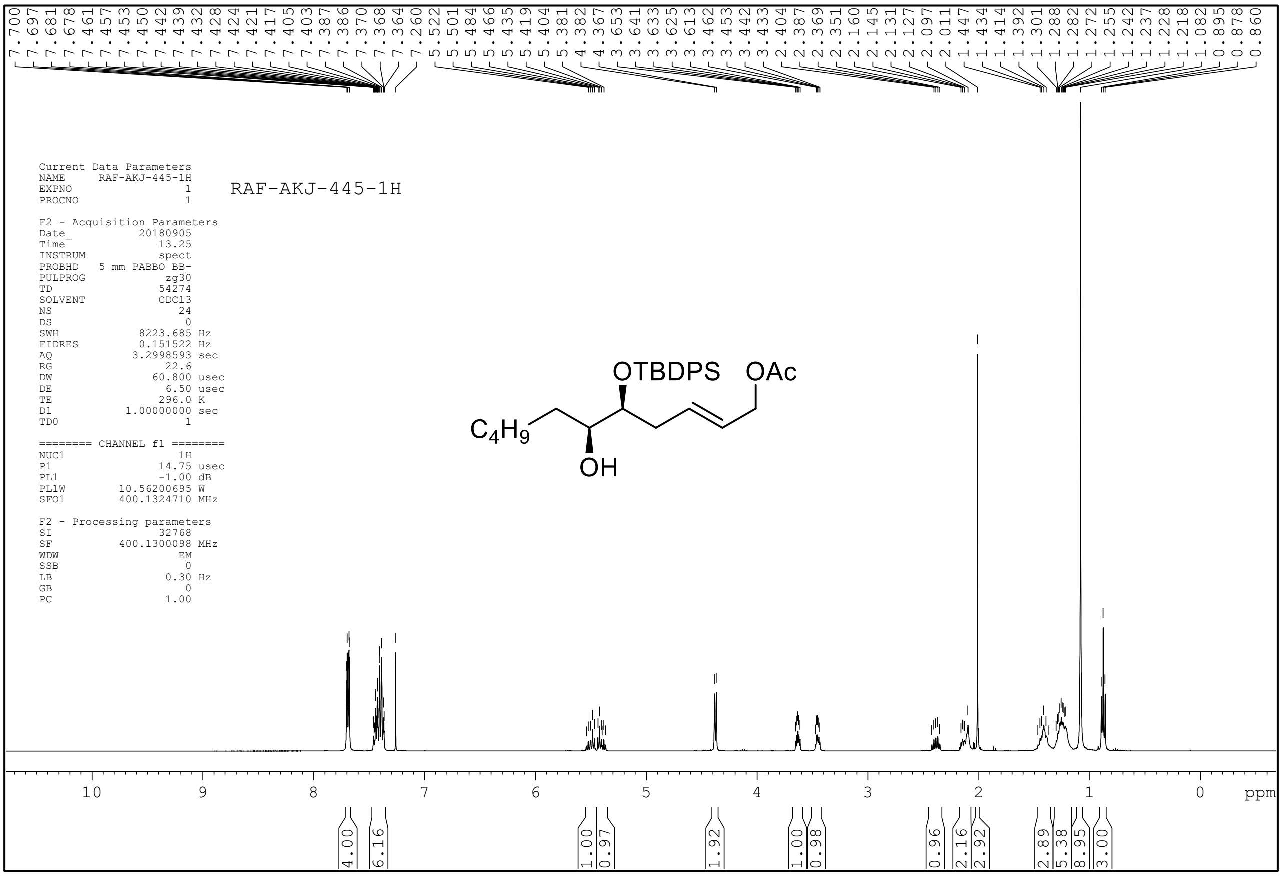
F2 - Acquisition Parameters
Date_         20130629
Time             23.42
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD             65536
SOLVENT          CDCl3
NS               134
DS                 4
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ         1.3631488 sec
RG              2050
DW             20.800 usec
DE              6.50 usec
TE             294.9 K
D1        1.00000000 sec
D11       0.03000000 sec
TD0                1

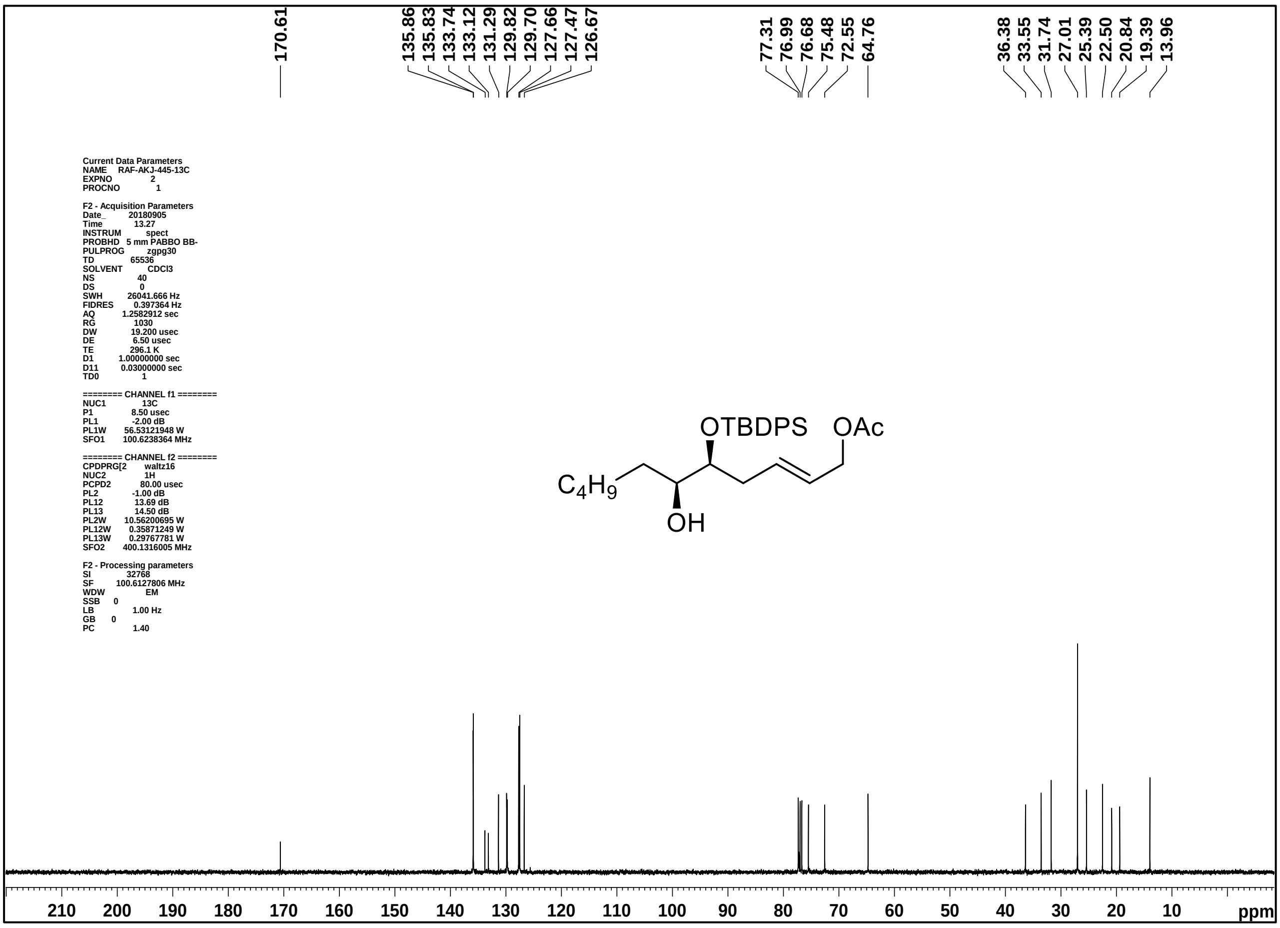
======== CHANNEL f1 ========
NUC1              13C
P1             8.75 usec
PL1            -2.00 dB
PL1W      56.53121948 W
SFO1      100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2       waltz16
NUC2               1H
PCPD2          80.00 usec
PL2            -1.00 dB
PL12           14.50 dB
PL13           14.50 dB
PL2W      10.56200695 W
PL12W      0.29767781 W
PL13W      0.29767781 W
SFO2      400.1316005 MHz

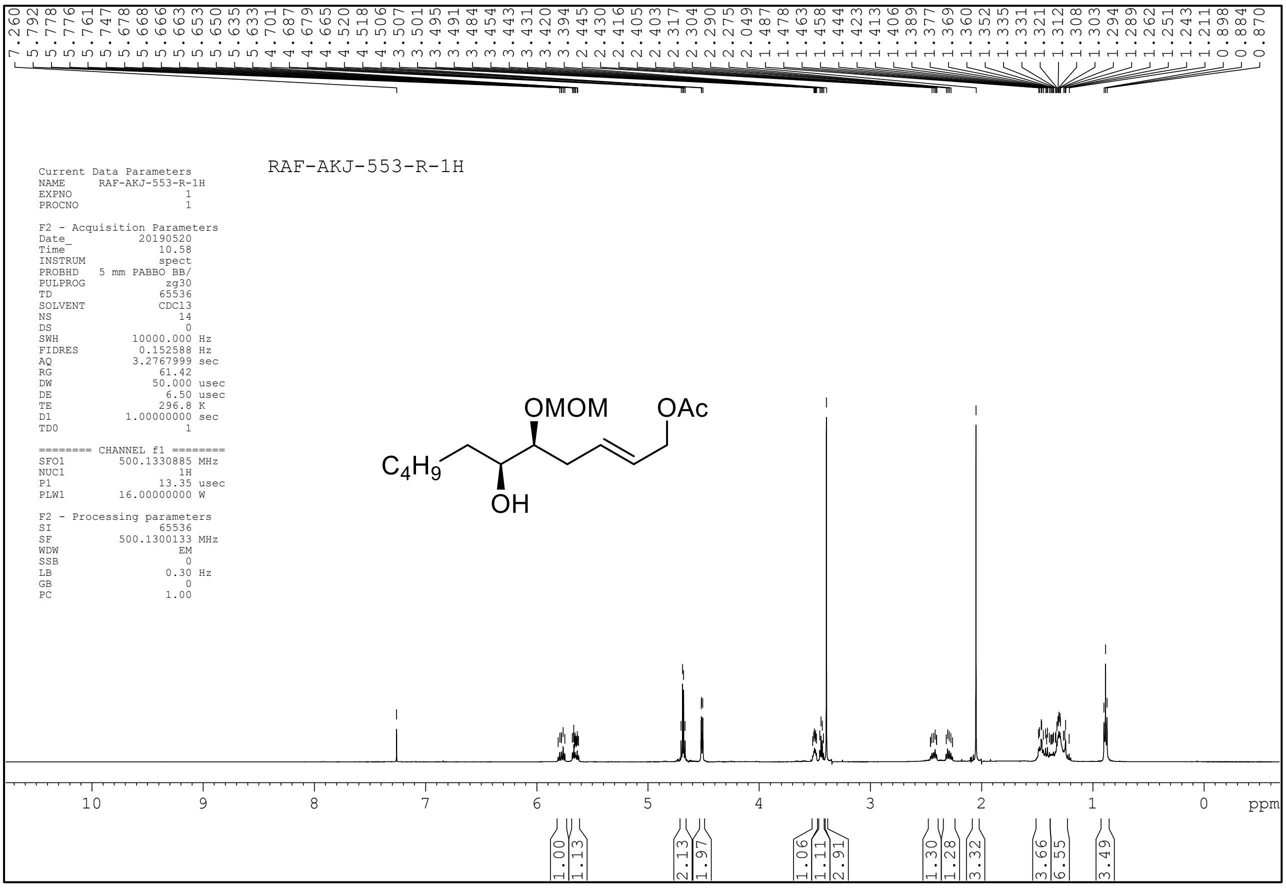
F2 - Processing parameters
SI             32768
SF        100.6127736 MHz
WDW                EM
SSB     0
LB             1.00 Hz
GB      0
PC             1.40
```

^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **5b**





^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) of compound **5c**

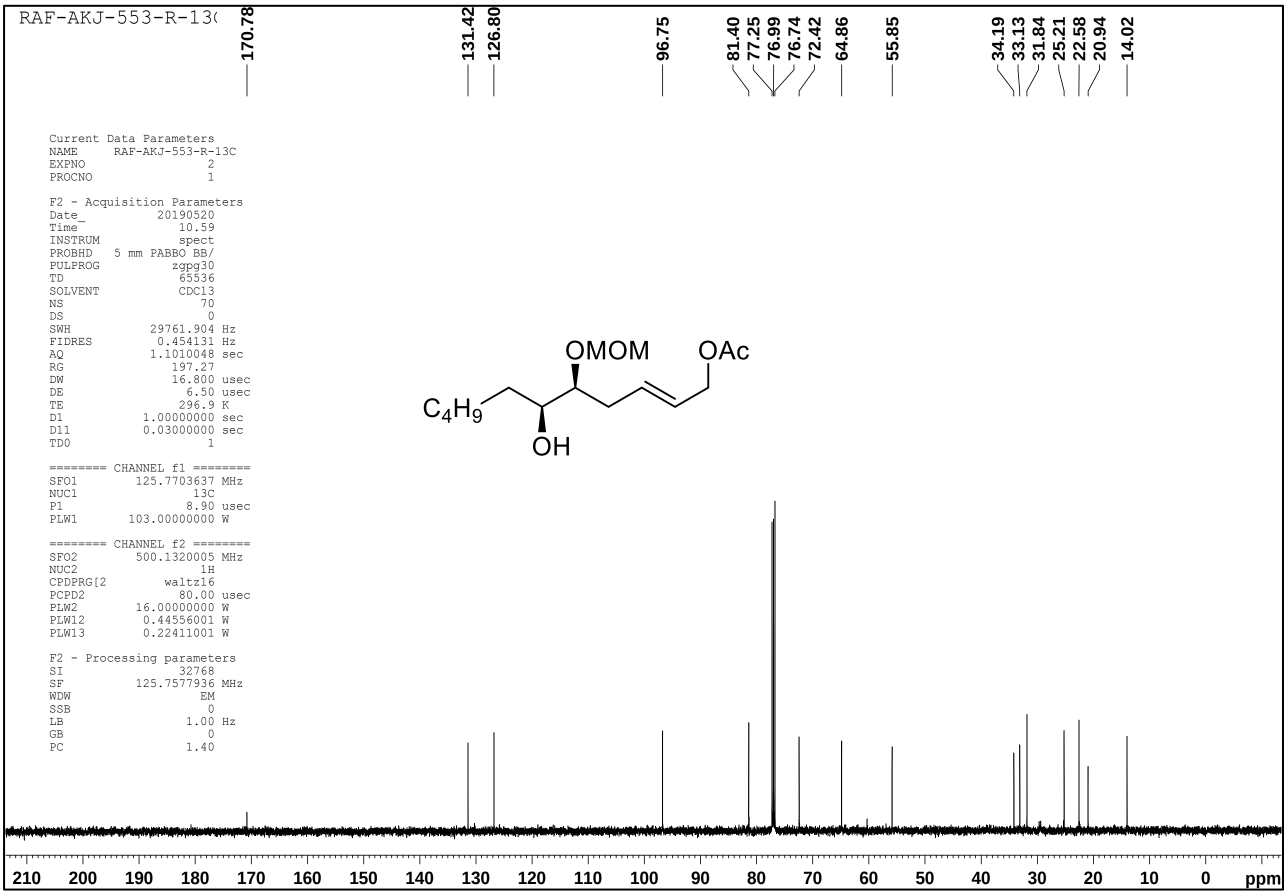


```
Current Data Parameters
NAME     RAF-AKJ-553-R-1H
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20190520
Time                10.58
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     14
DS                      0
SWH             10000.000 Hz
FIDRES           0.152588 Hz
AQ              3.2767999 sec
RG                  61.42
DW                 50.000 usec
DE                   6.50 usec
TE                  296.8 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          500.1330885 MHz
NUC1                   1H
P1                  13.35 usec
PLW1          16.00000000 W

F2 - Processing parameters
SI                  65536
SF            500.1300133 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



```
Current Data Parameters
NAME     RAF-AKJ-553-R-13C
EXPNO                   2
PROCNO                  1

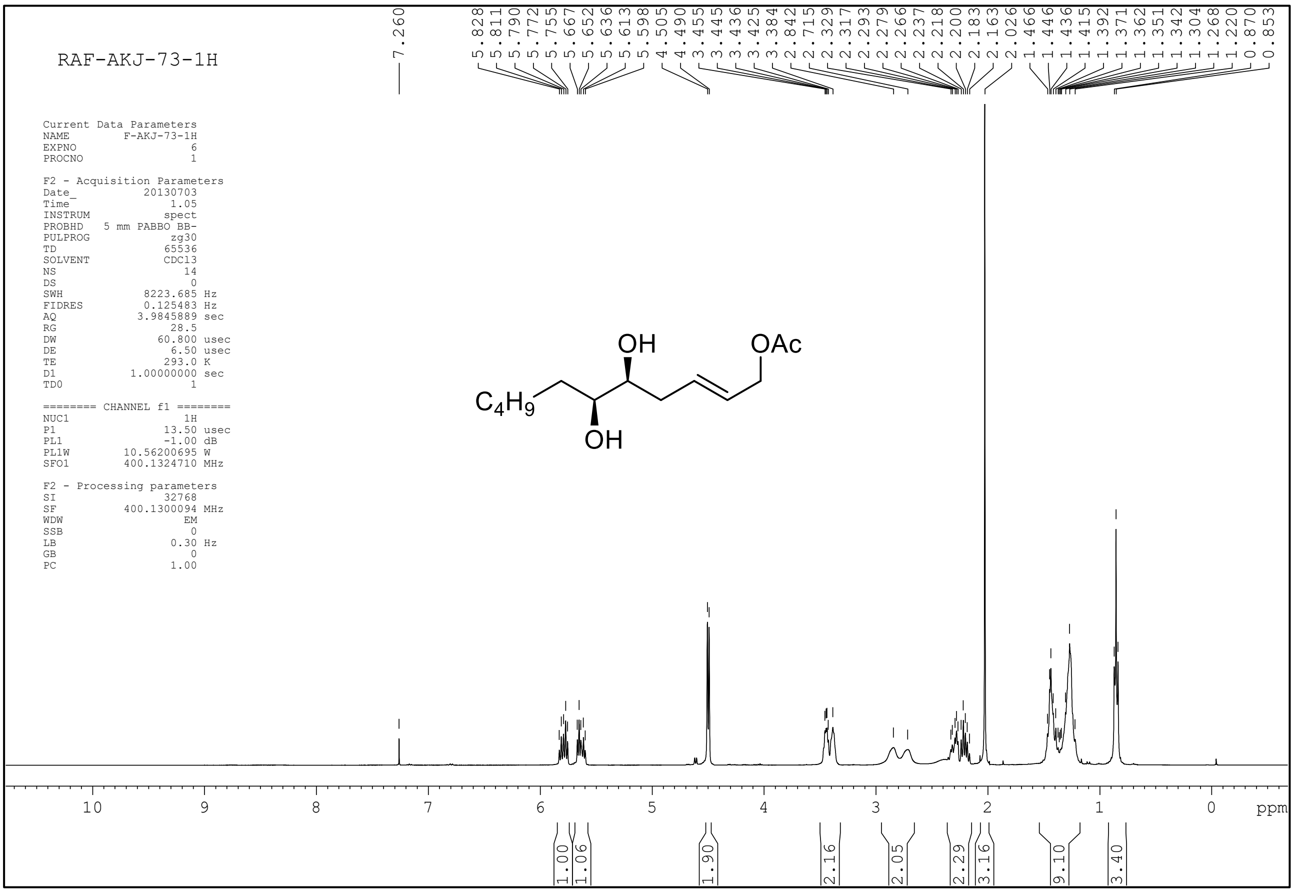
F2 - Acquisition Parameters
Date_            20190520
Time                10.59
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     70
DS                      0
SWH             29761.904 Hz
FIDRES           0.454131 Hz
AQ              1.1010048 sec
RG                 197.27
DW                 16.800 usec
DE                   6.50 usec
TE                  296.9 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                     1

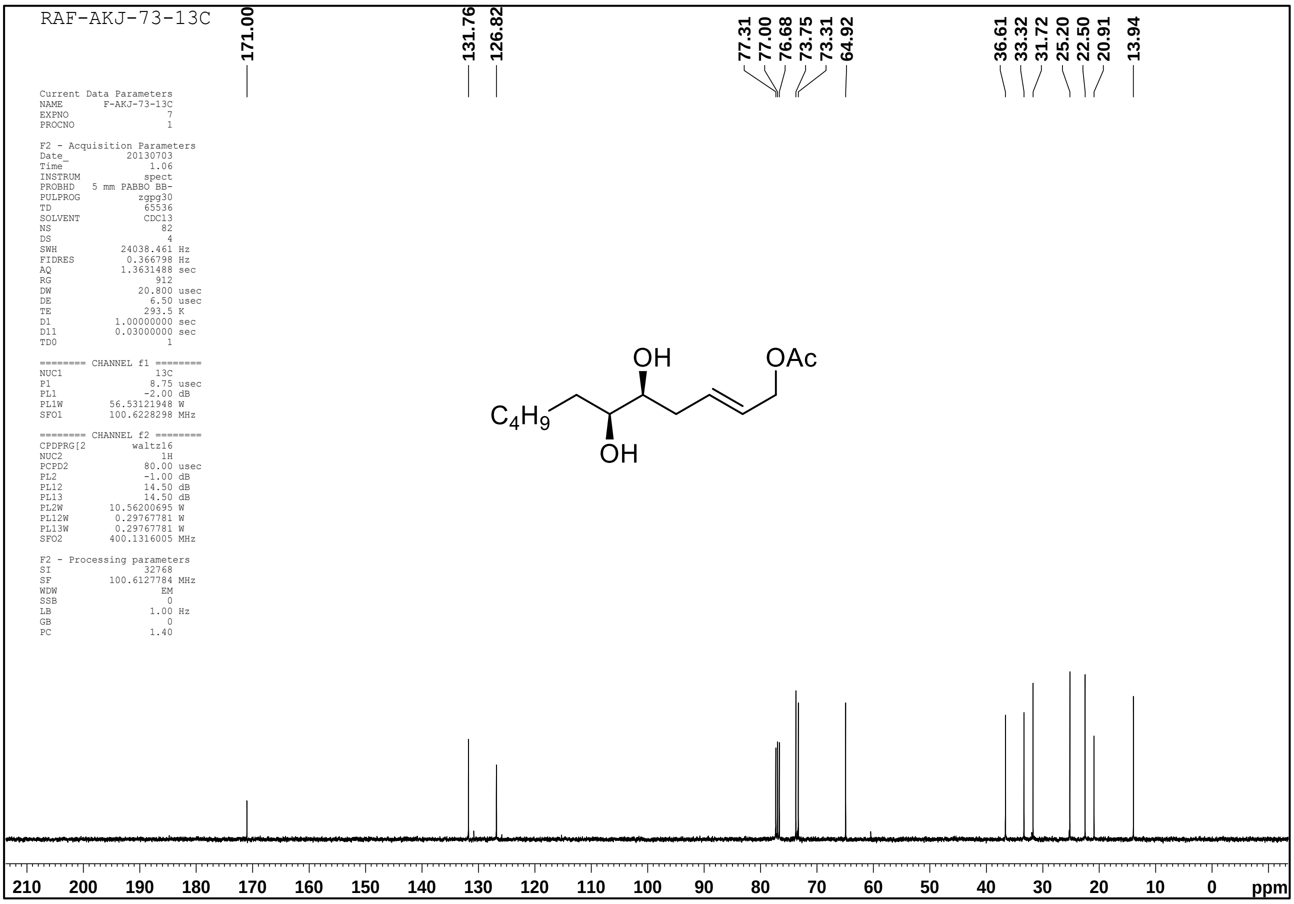
======== CHANNEL f1 ========
SFO1          125.7703637 MHz
NUC1                  13C
P1                   8.90 usec
PLW1         103.00000000 W

======== CHANNEL f2 ========
SFO2          500.1320005 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          16.00000000 W
PLW12          0.44556001 W
PLW13          0.22411001 W

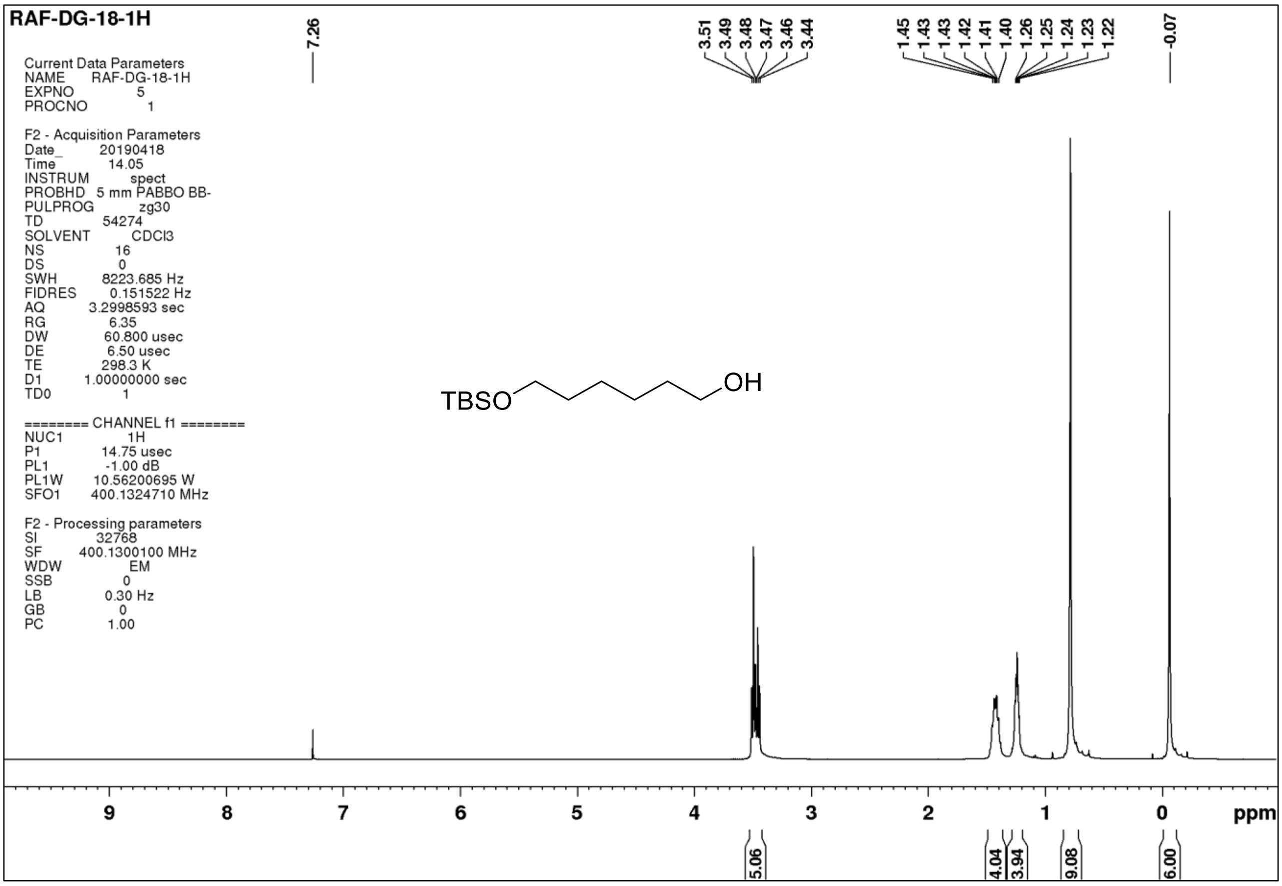
F2 - Processing parameters
SI                  32768
SF            125.7577936 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

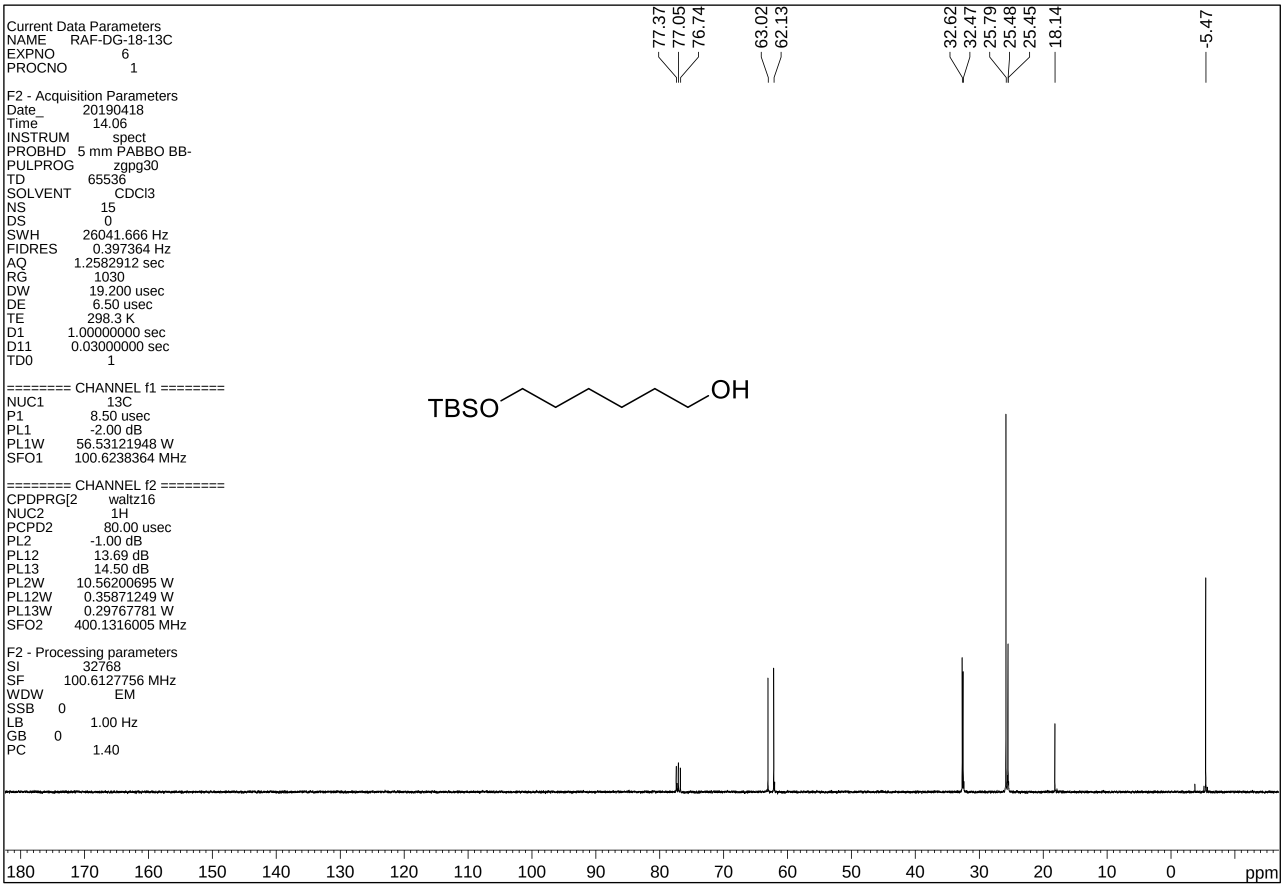
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **5d**



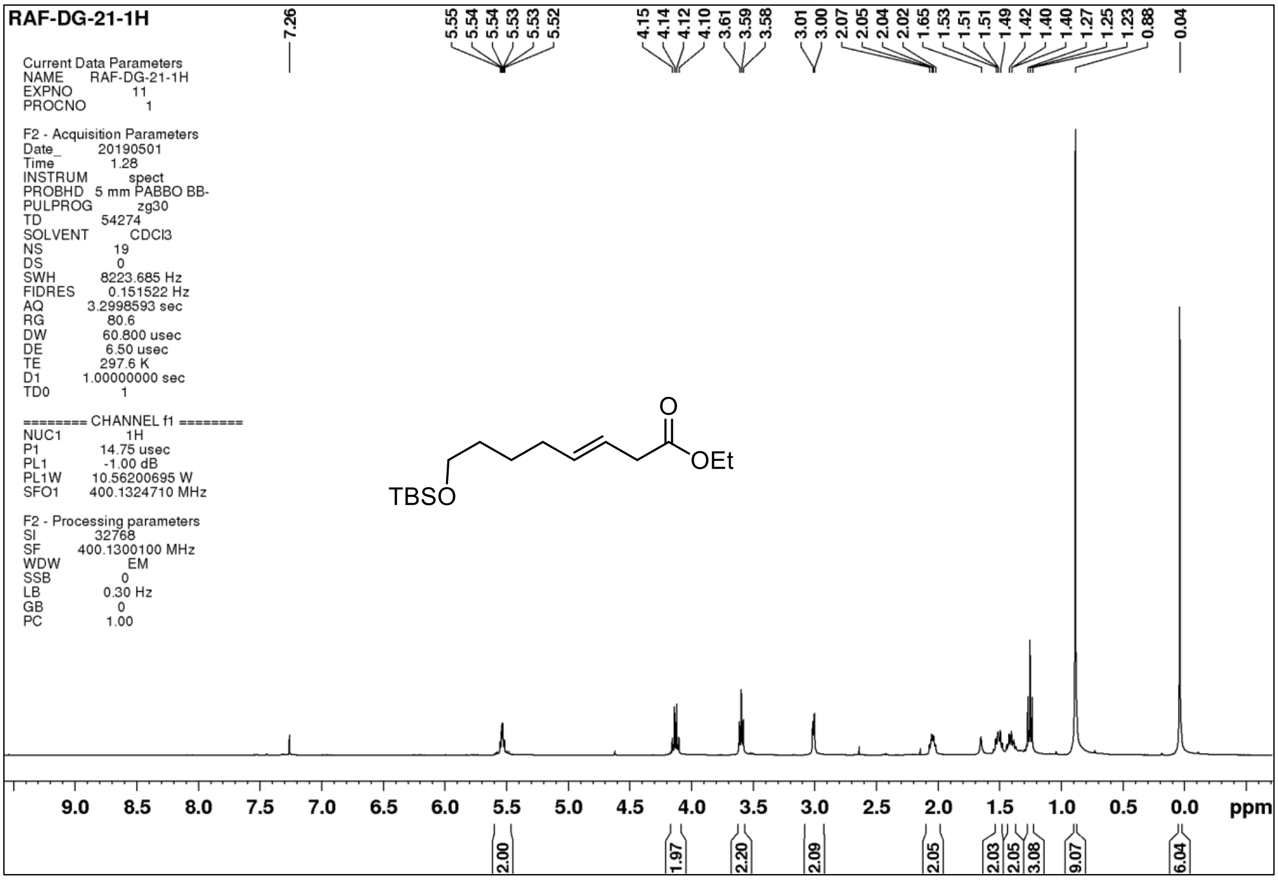


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) of compound **10**





^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **19**

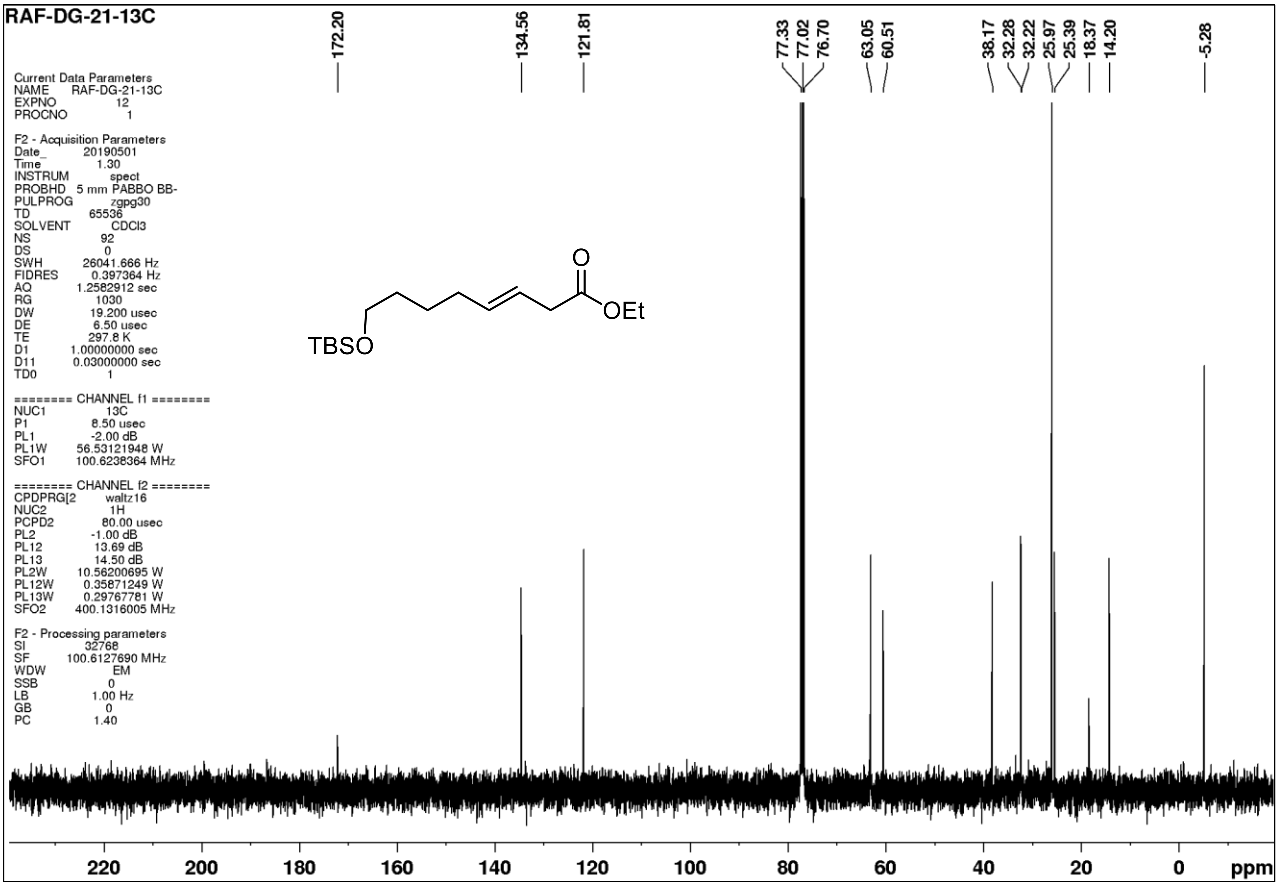


```
Current Data Parameters
NAME      RAF-DG-21-1H
EXPNO             11
PROCNO             1

F2 - Acquisition Parameters
Date_       20190501
Time            1.28
INSTRUM        spect
PROBHD   5 mm PABBO BB-
PULPROG         zg30
TD             54274
SOLVENT        CDCl3
NS                19
DS                 0
SWH         8223.685 Hz
FIDRES      0.151522 Hz
AQ         3.2998593 sec
RG              80.6
DW            60.800 usec
DE              6.50 usec
TE             297.6 K
D1        1.00000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1              1H
P1             14.75 usec
PL1            -1.00 dB
PL1W     10.56200695 W
SFO1     400.1324710 MHz

F2 - Processing parameters
SI             32768
SF       400.1300100 MHz
WDW               EM
SSB                0
LB              0.30 Hz
GB                 0
PC              1.00
```



```
Current Data Parameters
NAME      RAF-DG-21-13C
EXPNO             12
PROCNO             1

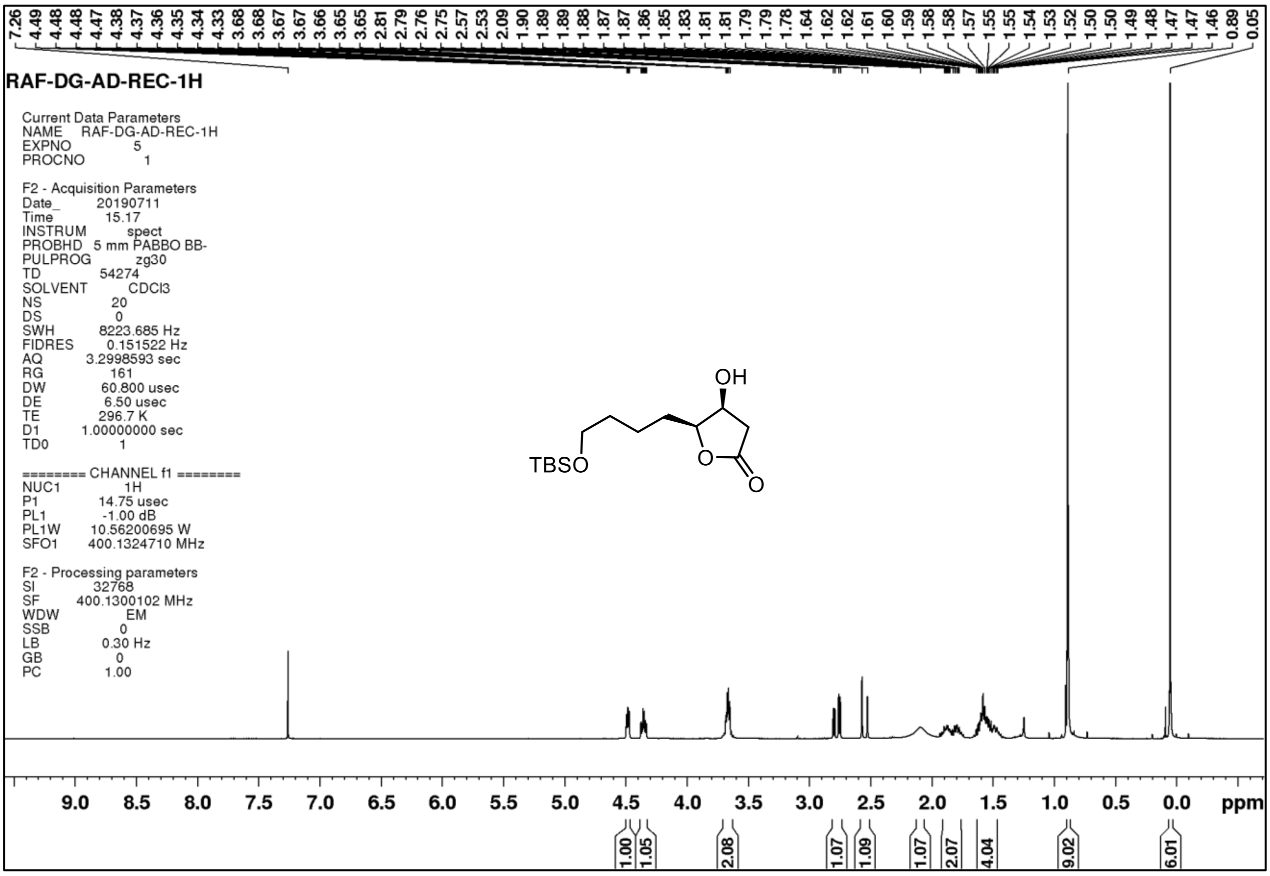
F2 - Acquisition Parameters
Date_       20190501
Time            1.30
INSTRUM        spect
PROBHD   5 mm PABBO BB-
PULPROG       zgpg30
TD             65536
SOLVENT        CDCl3
NS                92
DS                 0
SWH        26041.666 Hz
FIDRES      0.397364 Hz
AQ         1.2582912 sec
RG              1030
DW            19.200 usec
DE              6.50 usec
TE             297.8 K
D1        1.00000000 sec
D11       0.03000000 sec
TD0                1

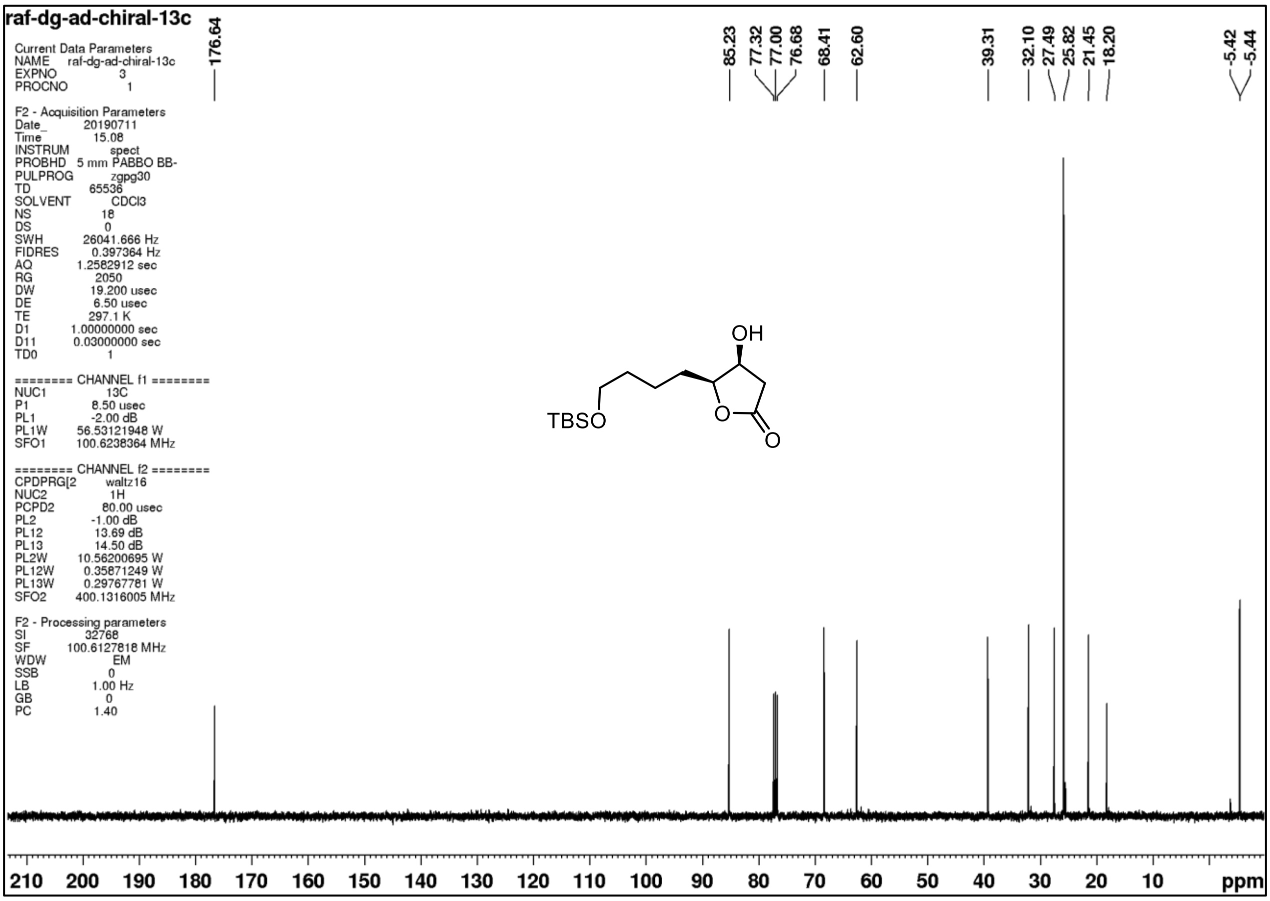
======== CHANNEL f1 ========
NUC1             13C
P1              8.50 usec
PL1            -2.00 dB
PL1W     56.53121948 W
SFO1     100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG[2     waltz16
NUC2              1H
PCPD2          80.00 usec
PL2            -1.00 dB
PL12           13.69 dB
PL13           14.50 dB
PL2W     10.56200695 W
PL12W     0.35871249 W
PL13W     0.29767781 W
SFO2     400.1316005 MHz

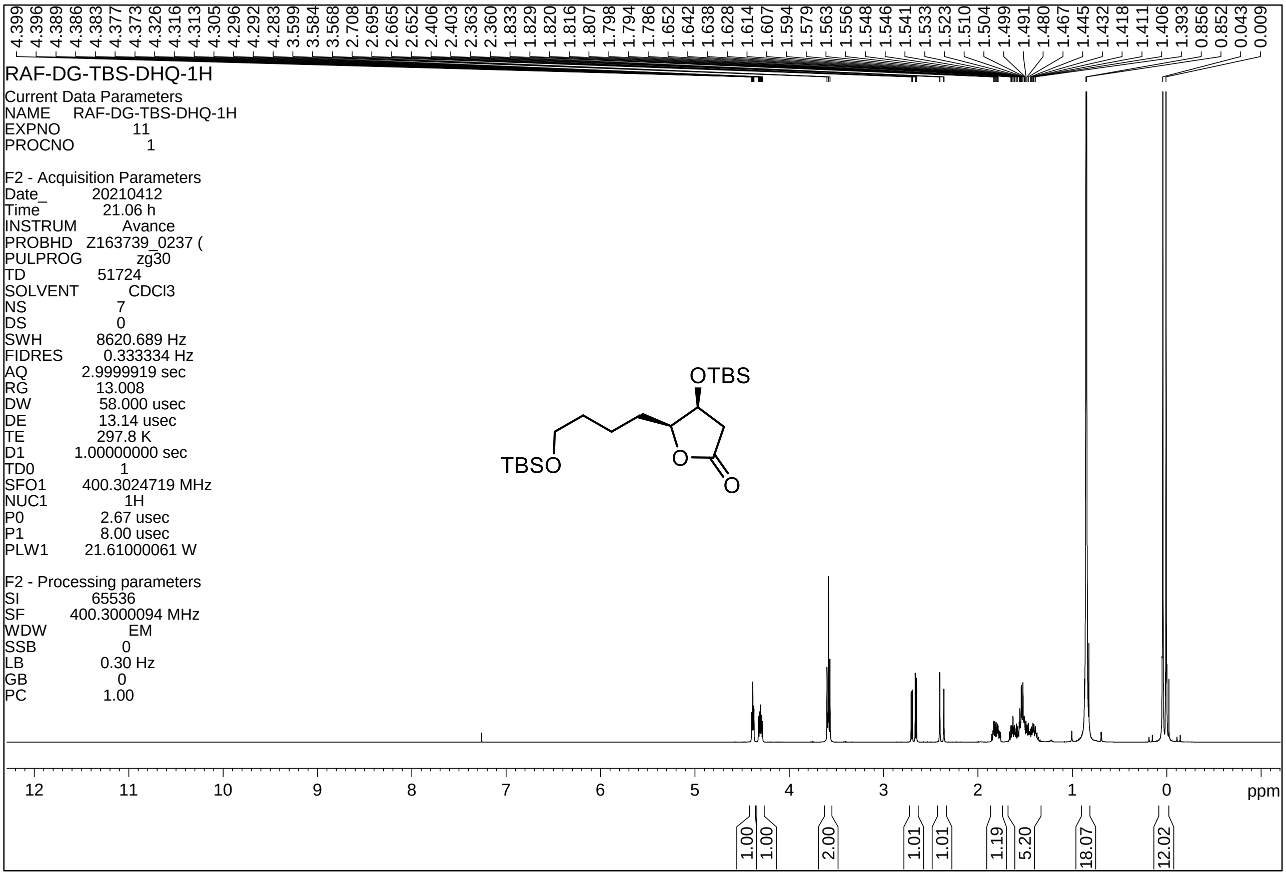
F2 - Processing parameters
SI             32768
SF       100.6127690 MHz
WDW               EM
SSB                0
LB              1.00 Hz
GB                 0
PC              1.40
```

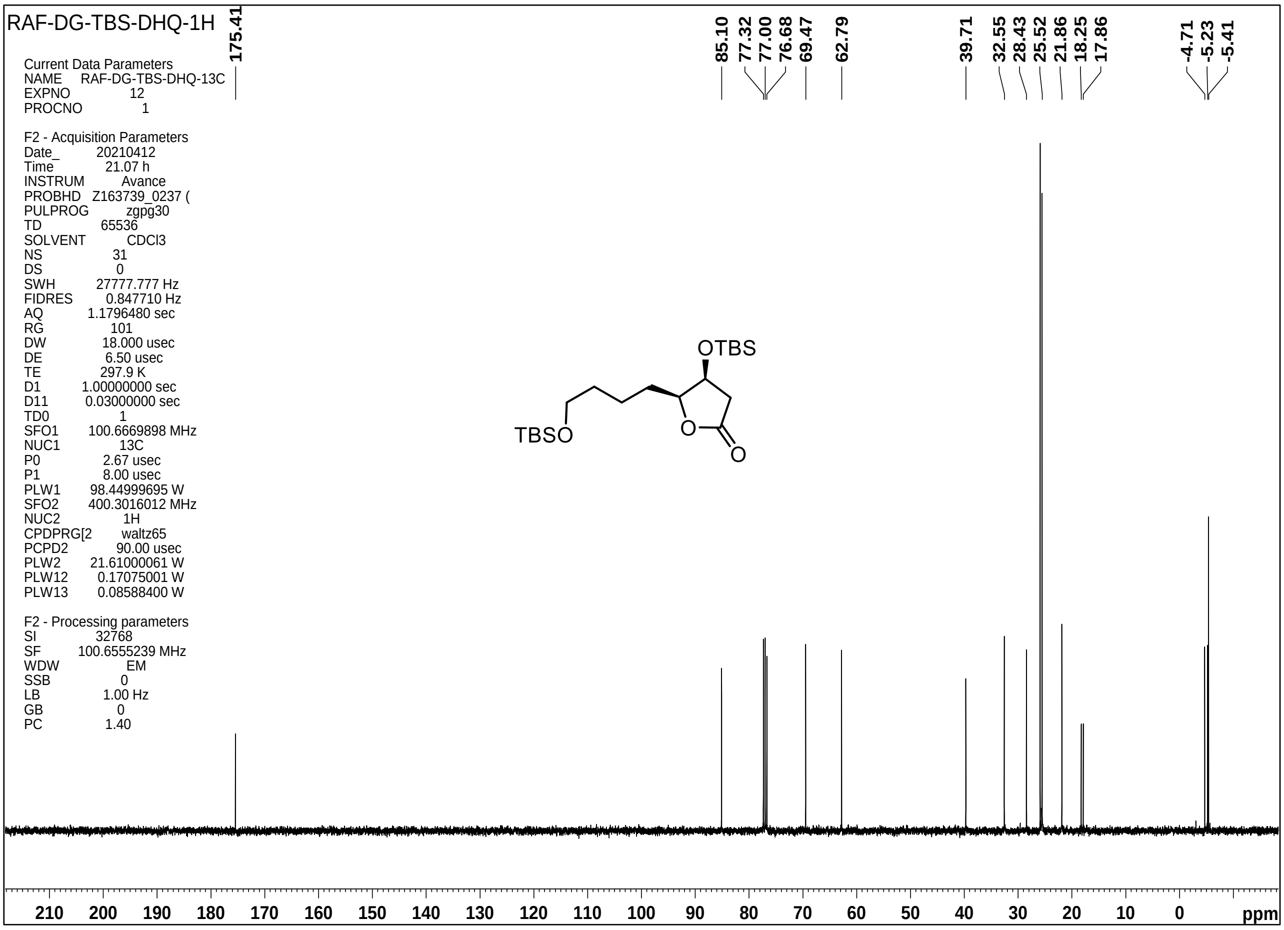
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **20**



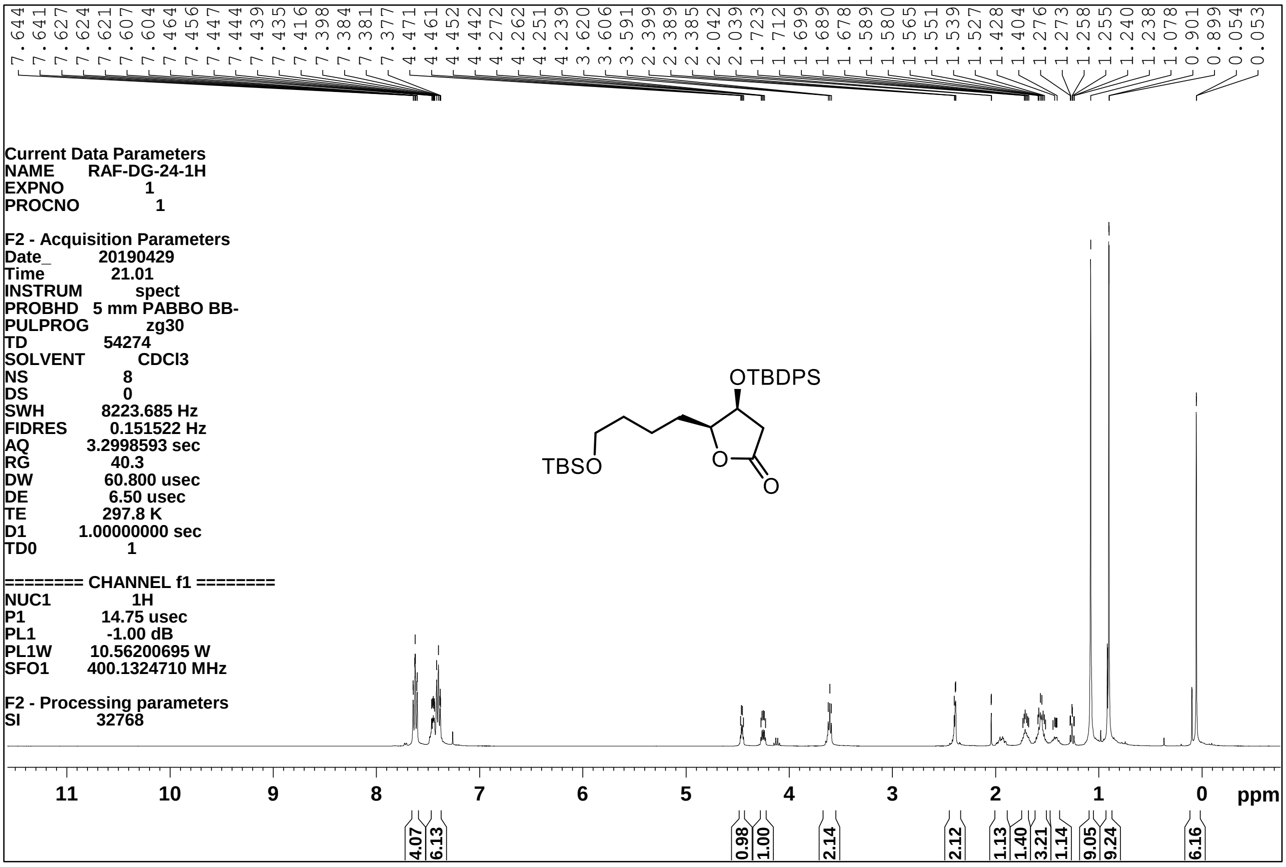


^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **21a**





^{771}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **21b**

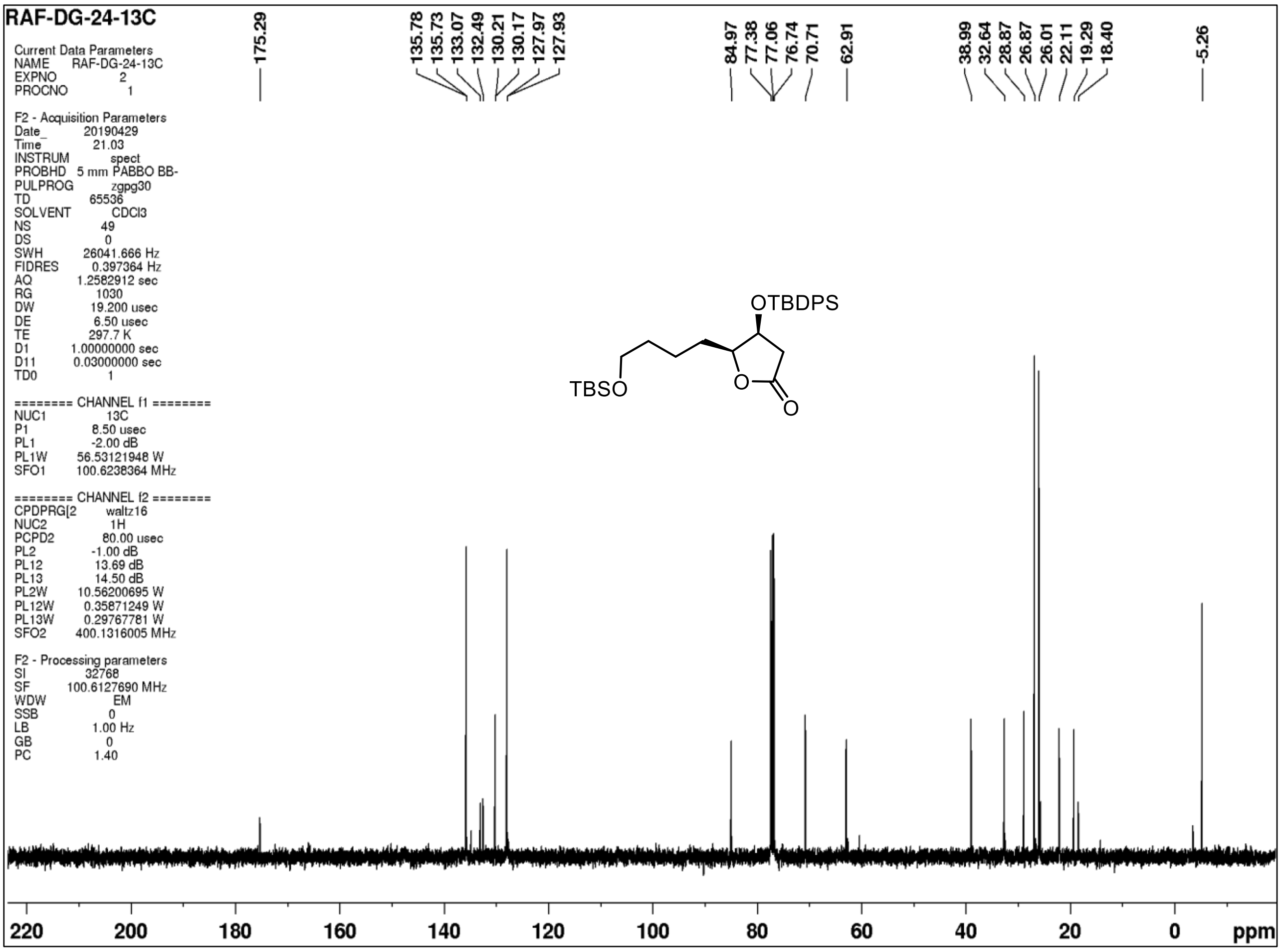


Current Data Parameters
NAME RAF-DG-24-1H
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190429
Time 21.01
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 54274
SOLVENT CDCl3
NS 8
DS 0
SWH 8223.685 Hz
FIDRES 0.151522 Hz
AQ 3.2998593 sec
RG 40.3
DW 60.800 usec
DE 6.50 usec
TE 297.8 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.75 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768



RAF-DG-24-13C

Current Data Parameters
NAME RAF-DG-24-13C
EXPNO 2
PROCNO 1

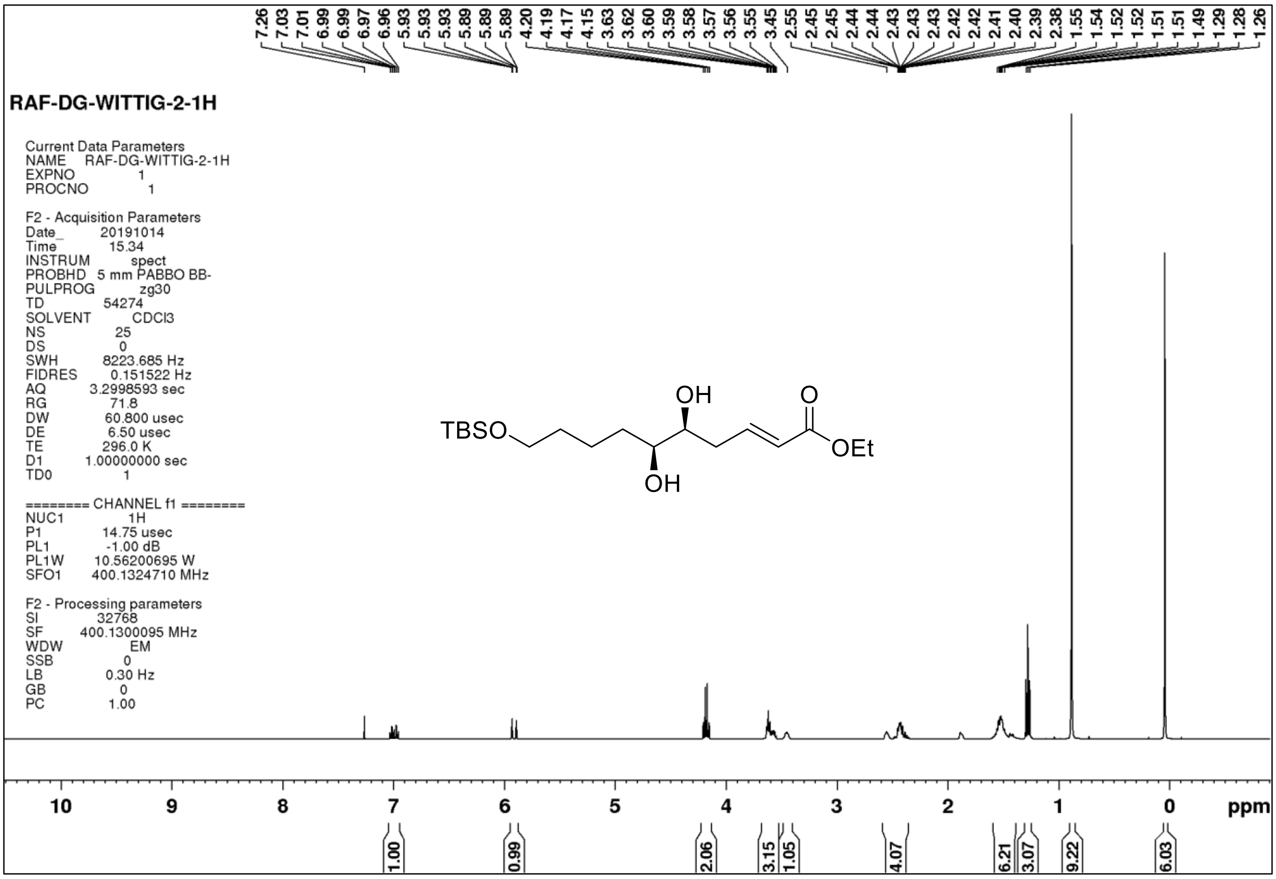
F2 - Acquisition Parameters
Date_ 20190429
Time 21.03
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 49
DS 0
SWH 26041.666 Hz
FIDRES 0.397364 Hz
AQ 1.2582912 sec
RG 1030
DW 19.200 usec
DE 6.50 usec
TE 297.7 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 13.69 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.35871249 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **22c**

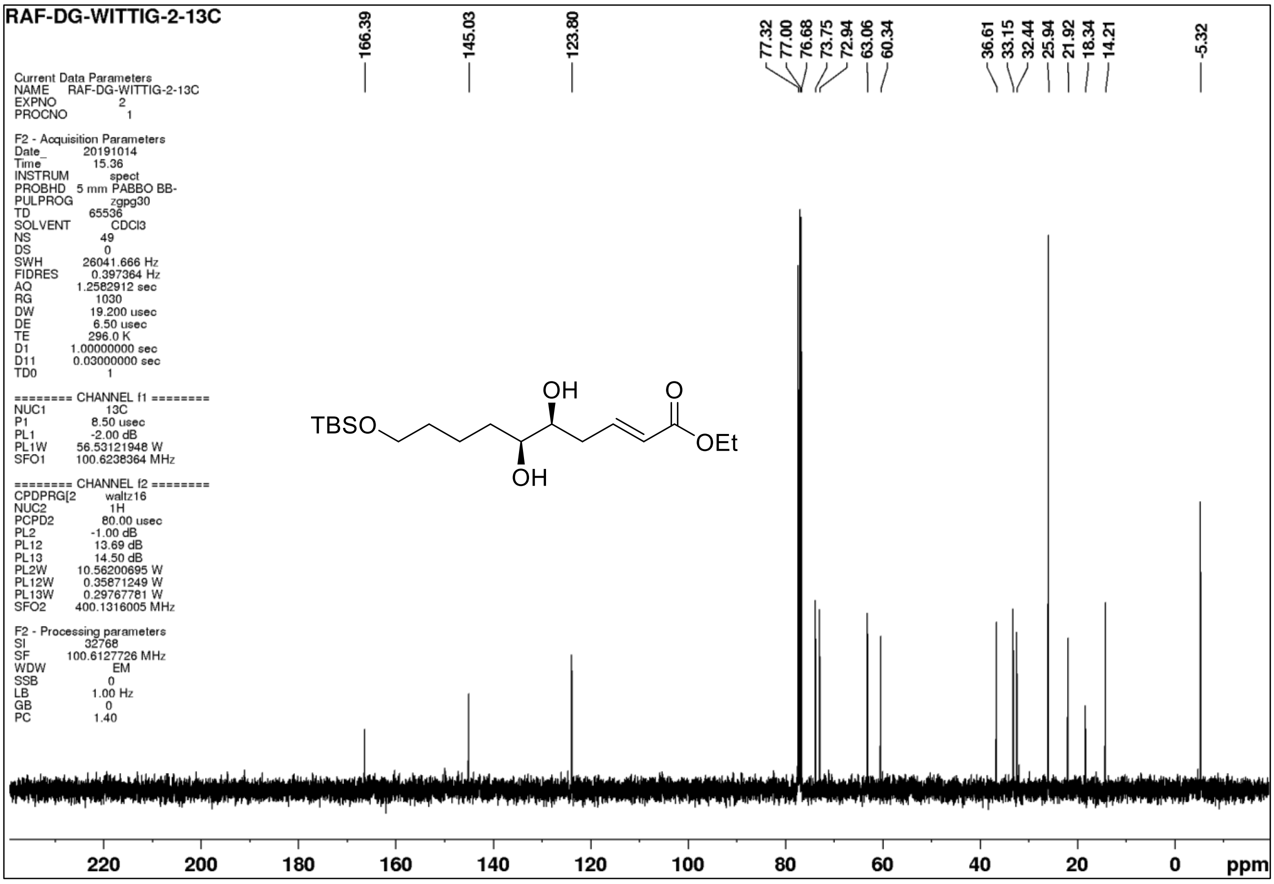


```
Current Data Parameters
NAME     RAF-DG-WITTIG-2-1H
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_        20191014
Time            15.34
INSTRUM         spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              54274
SOLVENT         CDCl3
NS                 25
DS                  0
SWH          8223.685 Hz
FIDRES       0.151522 Hz
AQ          3.2998593 sec
RG               71.8
DW             60.800 usec
DE               6.50 usec
TE              296.0 K
D1         1.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               1H
P1              14.75 usec
PL1             -1.00 dB
PL1W      10.56200695 W
SFO1      400.1324710 MHz

F2 - Processing parameters
SI              32768
SF        400.1300095 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
```



```
Current Data Parameters
NAME     RAF-DG-WITTIG-2-13C
EXPNO              2
PROCNO             1

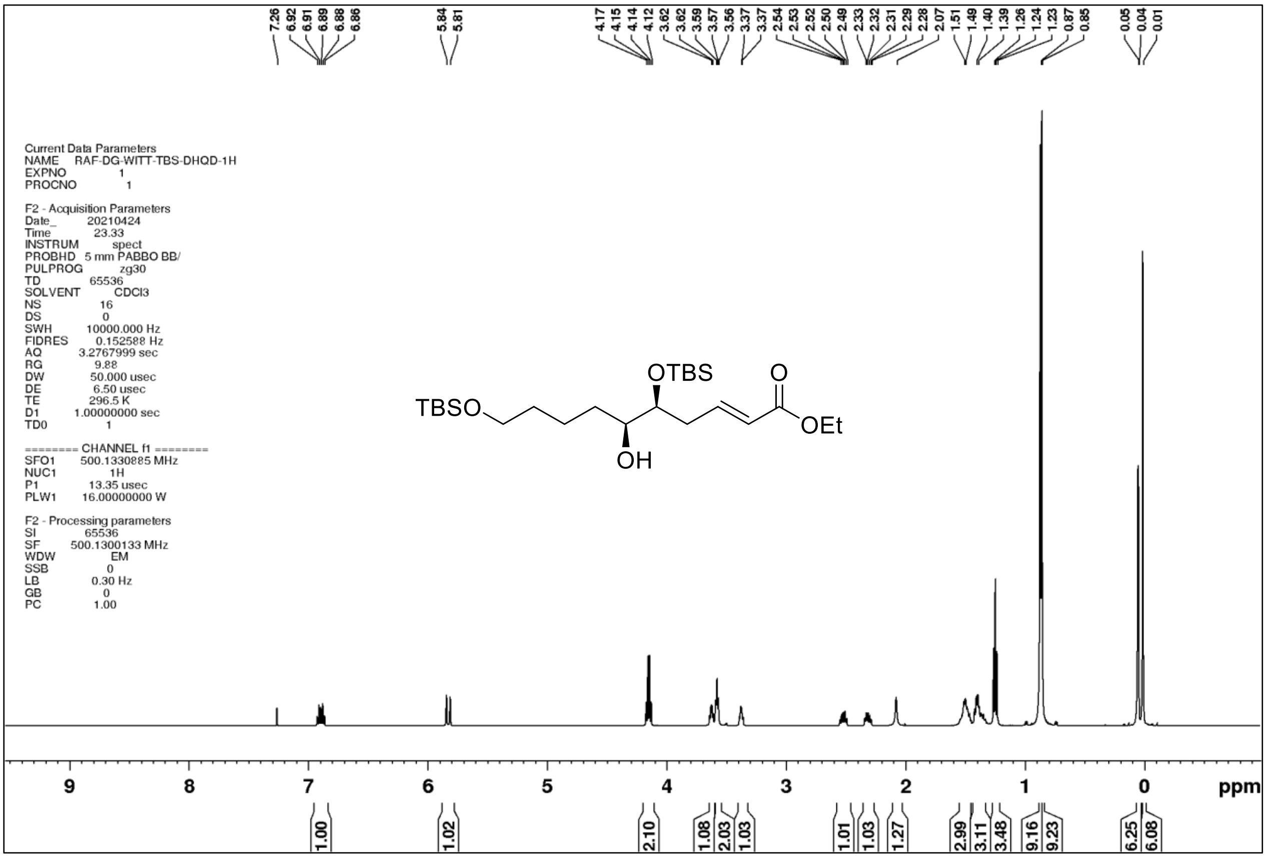
F2 - Acquisition Parameters
Date_        20191014
Time            15.36
INSTRUM         spect
PROBHD   5 mm PABBO BB-
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                 49
DS                  0
SWH         26041.666 Hz
FIDRES       0.397364 Hz
AQ          1.2582912 sec
RG               1030
DW             19.200 usec
DE               6.50 usec
TE              296.0 K
D1         1.00000000 sec
D11        0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1              13C
P1               8.50 usec
PL1             -2.00 dB
PL1W      56.53121948 W
SFO1      100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG[2      waltz16
NUC2               1H
PCPD2           80.00 usec
PL2             -1.00 dB
PL12            13.69 dB
PL13            14.50 dB
PL2W      10.56200695 W
PL12W      0.35871249 W
PL13W      0.29767781 W
SFO2      400.1316005 MHz

F2 - Processing parameters
SI              32768
SF        100.6127726 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) of compound **22a**

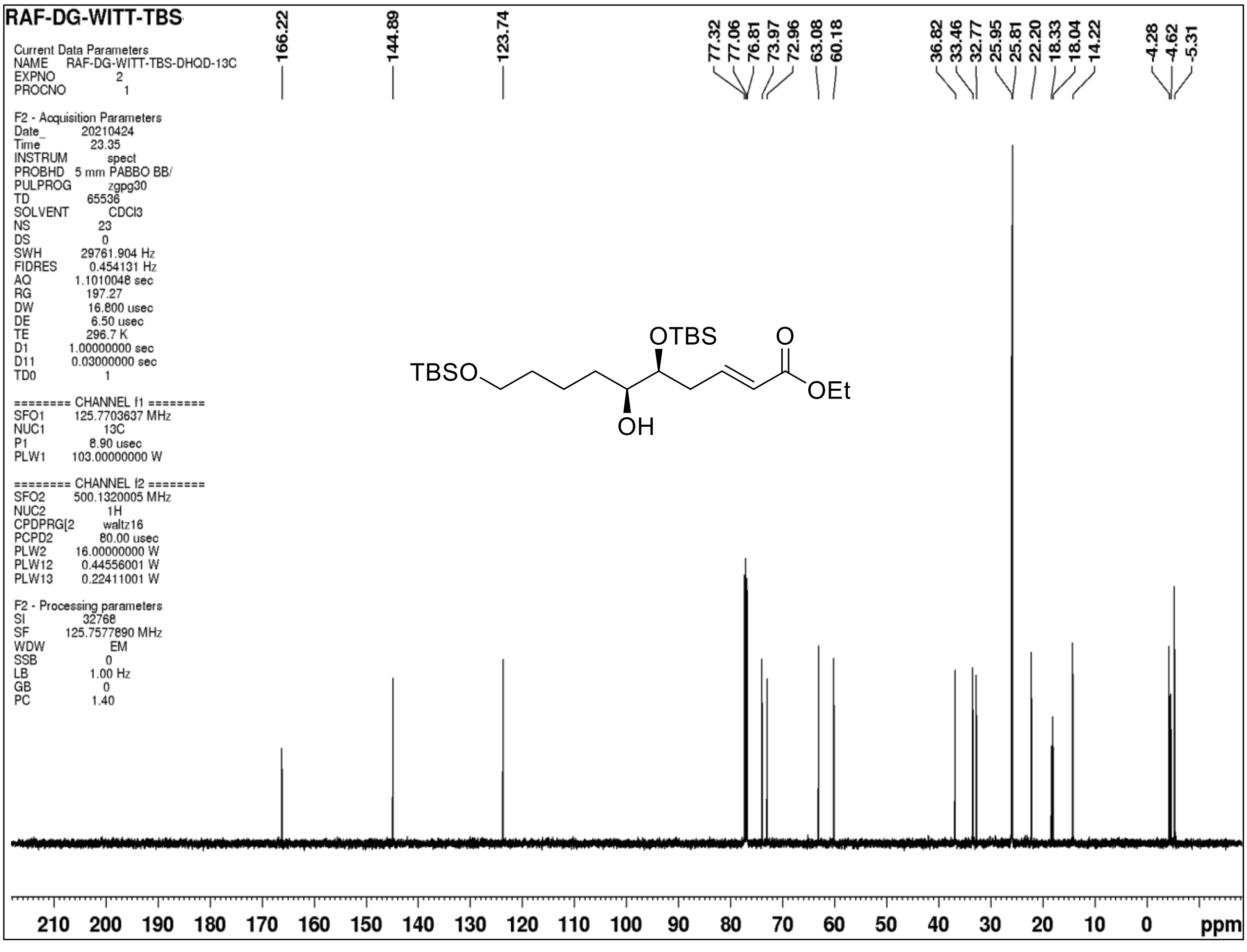


```
Current Data Parameters
NAME     RAF-DG-WITT-TBS-DHQD-1H
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_          20210424
Time              23.33
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD              65536
SOLVENT          CDCl3
NS                 16
DS                  0
SWH         10000.000 Hz
FIDRES       0.152588 Hz
AQ          3.2767999 sec
RG               9.88
DW             50.000 usec
DE               6.50 usec
TE              296.5 K
D1         1.00000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1      500.1330885 MHz
NUC1               1H
P1              13.35 usec
PLW1      16.00000000 W

F2 - Processing parameters
SI              65536
SF        500.1300133 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
```



```
Current Data Parameters
NAME     RAF-DG-WITT-TBS-DHQD-13C
EXPNO              2
PROCNO             1

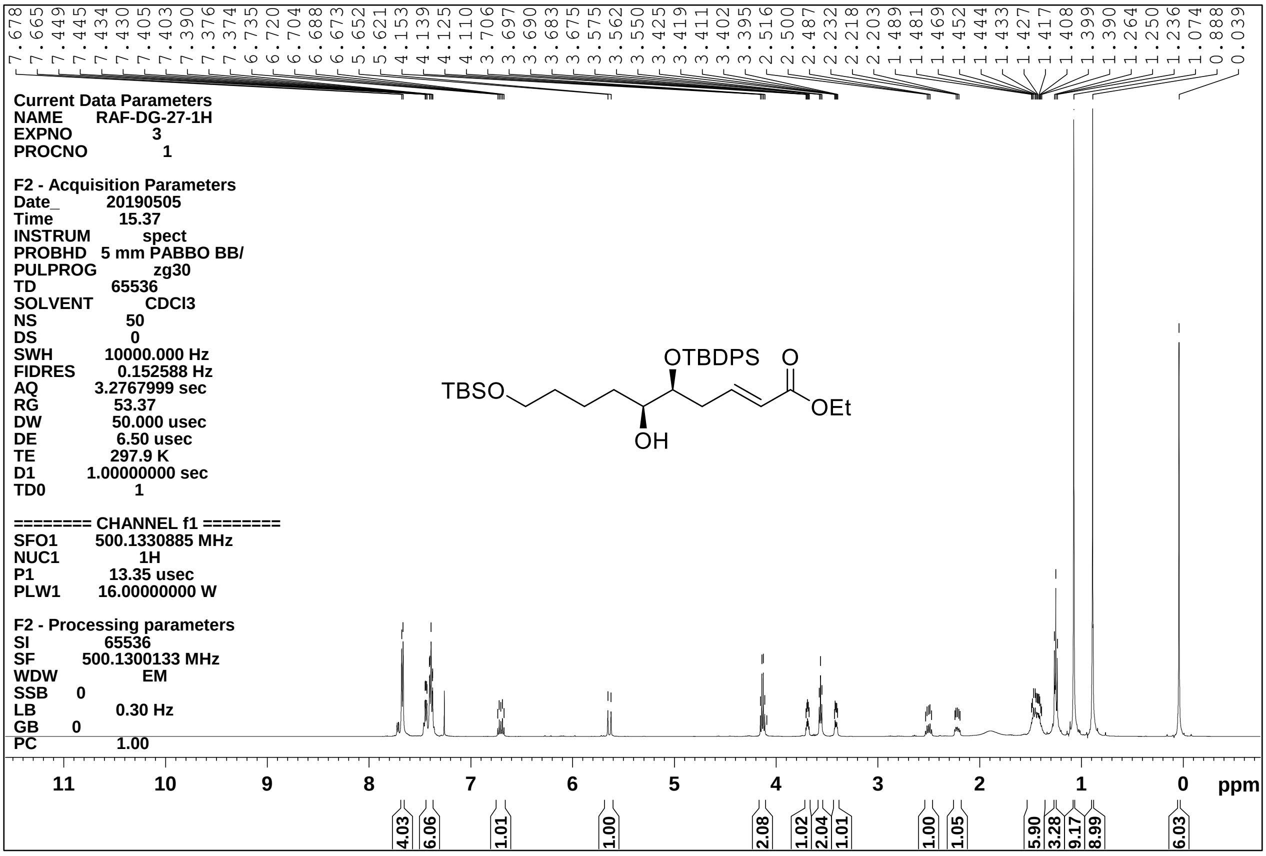
F2 - Acquisition Parameters
Date_          20210424
Time              23.35
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD              65536
SOLVENT          CDCl3
NS                 23
DS                  0
SWH         29761.904 Hz
FIDRES       0.454131 Hz
AQ          1.1010048 sec
RG             197.27
DW             16.800 usec
DE               6.50 usec
TE              296.7 K
D1         1.00000000 sec
D11        0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1      125.7703637 MHz
NUC1              13C
P1               8.90 usec
PLW1     103.00000000 W

======== CHANNEL f2 ========
SFO2      500.1320005 MHz
NUC2               1H
CPDPRG[2       waltz16
PCPD2           80.00 usec
PLW2      16.00000000 W
PLW12      0.44556001 W
PLW13      0.22411001 W

F2 - Processing parameters
SI              32768
SF        125.7577890 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) of compound **22b**

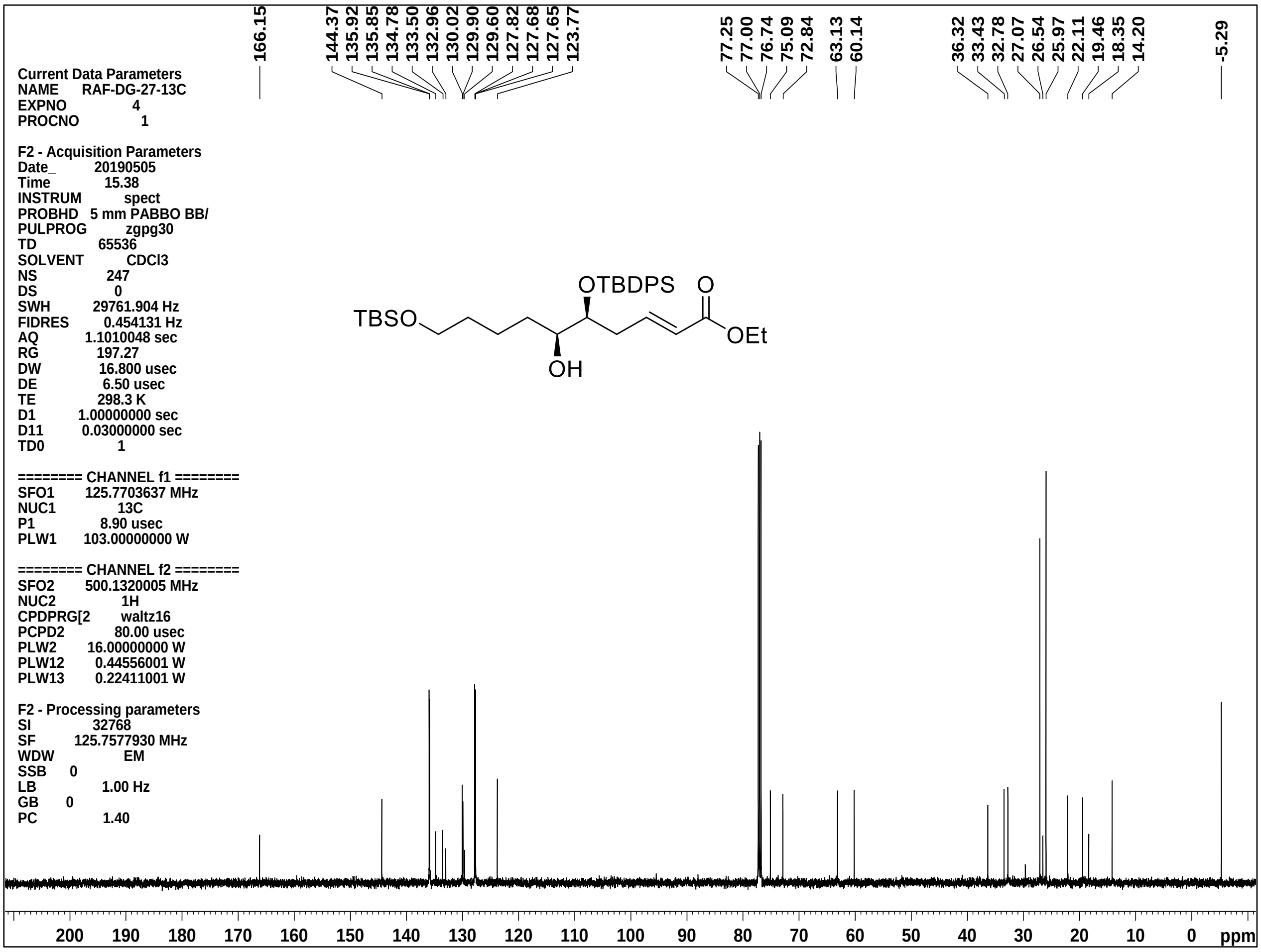


Current Data Parameters
NAME RAF-DG-27-1H
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190505
Time 15.37
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 50
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 53.37
DW 50.000 usec
DE 6.50 usec
TE 297.9 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 13.35 usec
PLW1 16.00000000 W

F2 - Processing parameters
SI 65536
SF 500.1300133 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME RAF-DG-27-13C
EXPNO 4
PROCNO 1

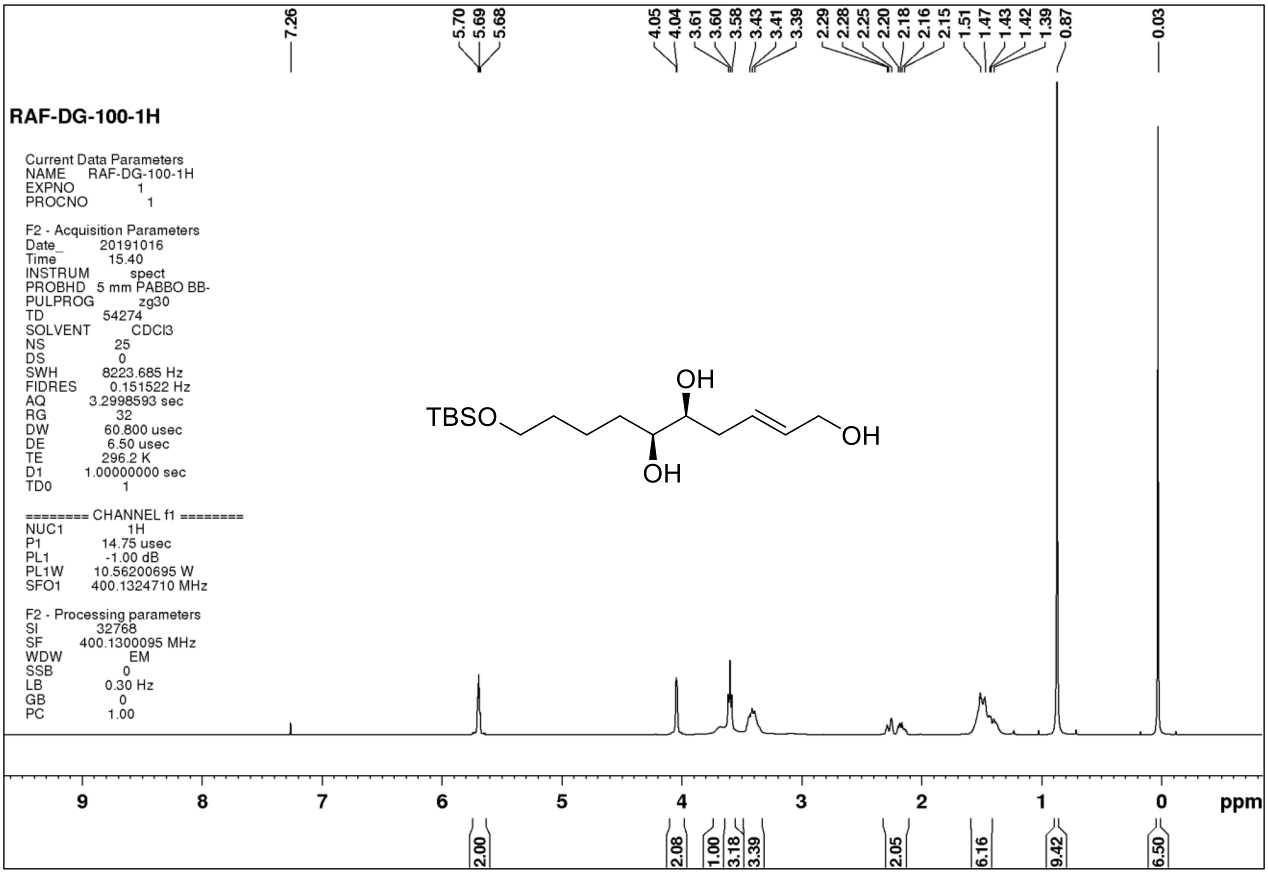
F2 - Acquisition Parameters
Date_ 20190505
Time 15.38
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 247
DS 0
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 197.27
DW 16.800 usec
DE 6.50 usec
TE 298.3 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

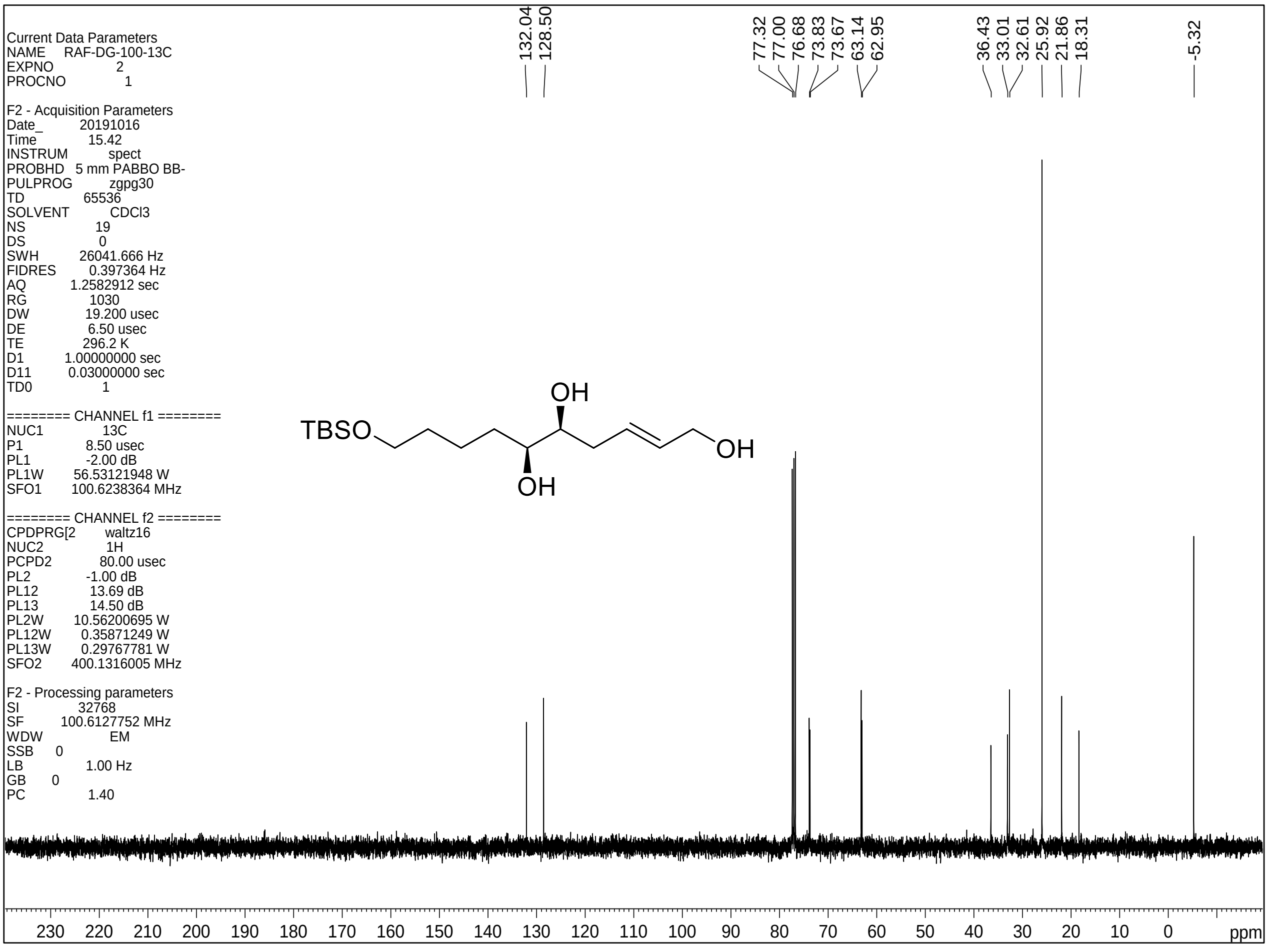
======== CHANNEL f1 ========
SFO1 125.7703637 MHz
NUC1 13C
P1 8.90 usec
PLW1 103.00000000 W

======== CHANNEL f2 ========
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 16.00000000 W
PLW12 0.44556001 W
PLW13 0.22411001 W

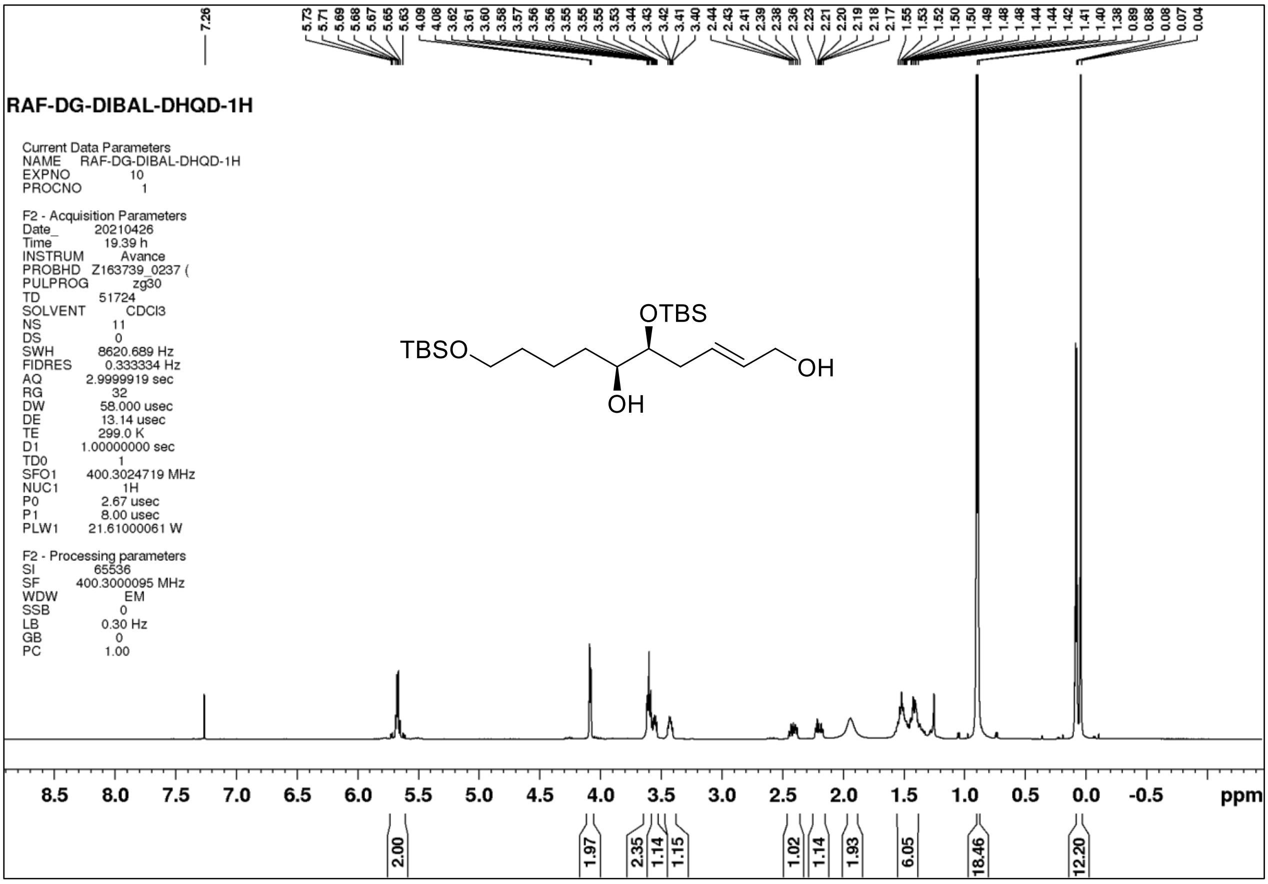
F2 - Processing parameters
SI 32768
SF 125.7577930 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

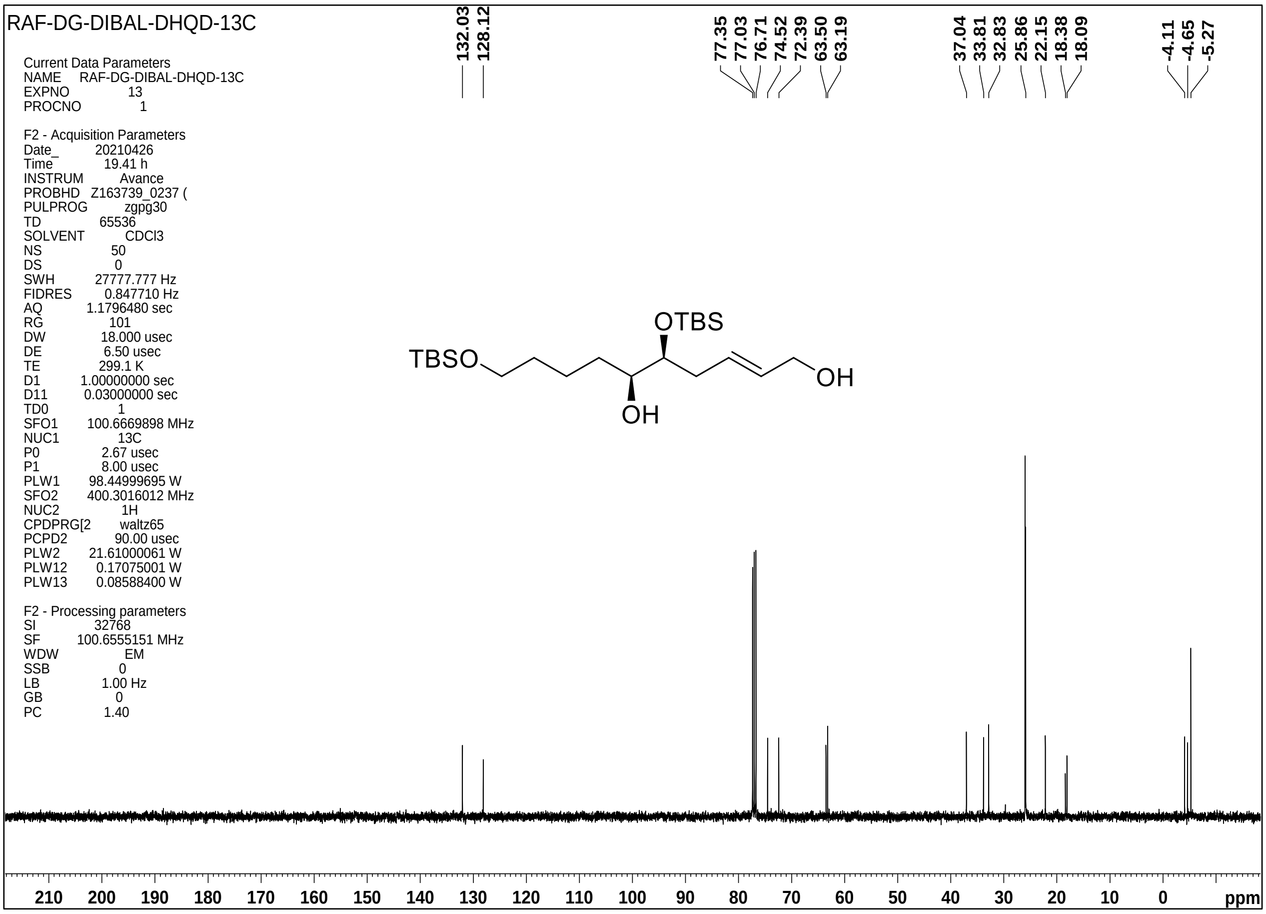
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **23c**



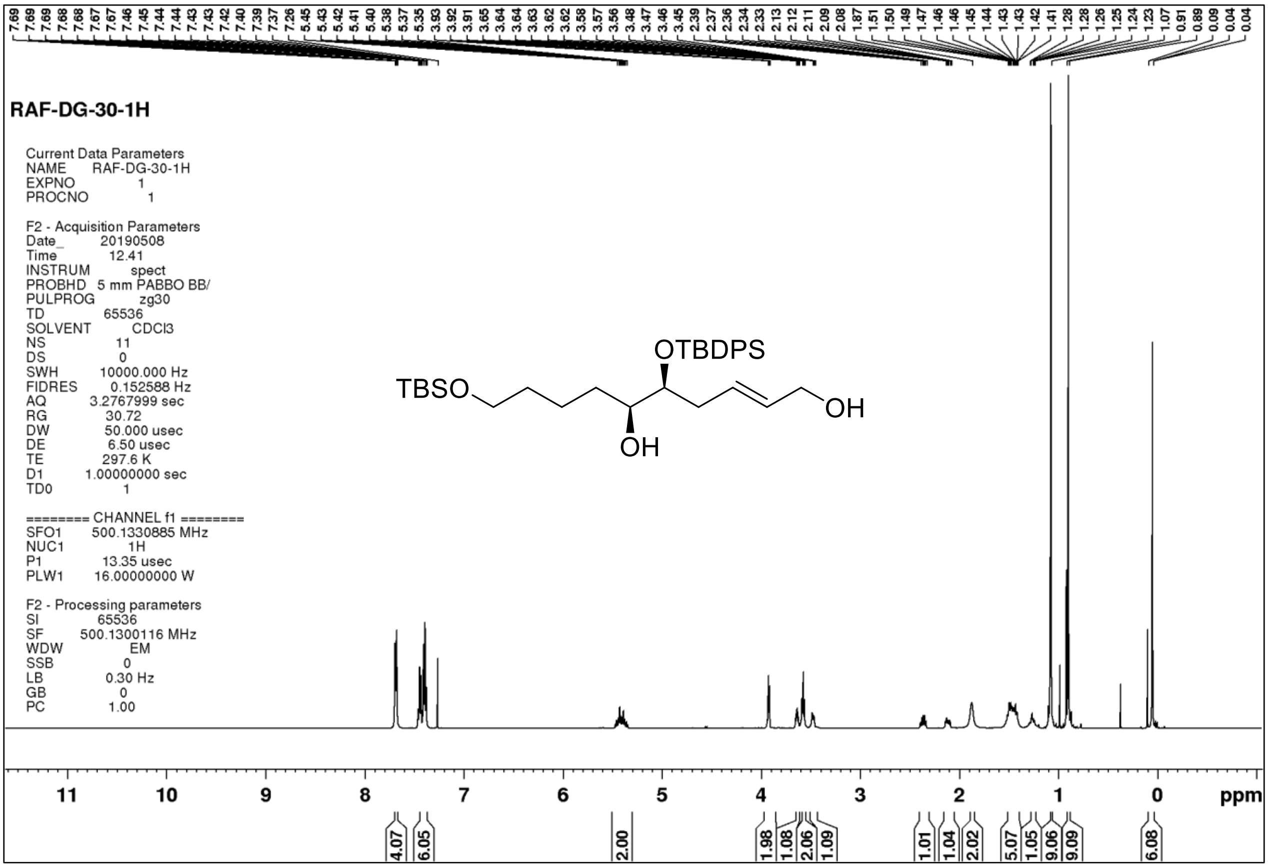


^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **23a**





^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **23b**

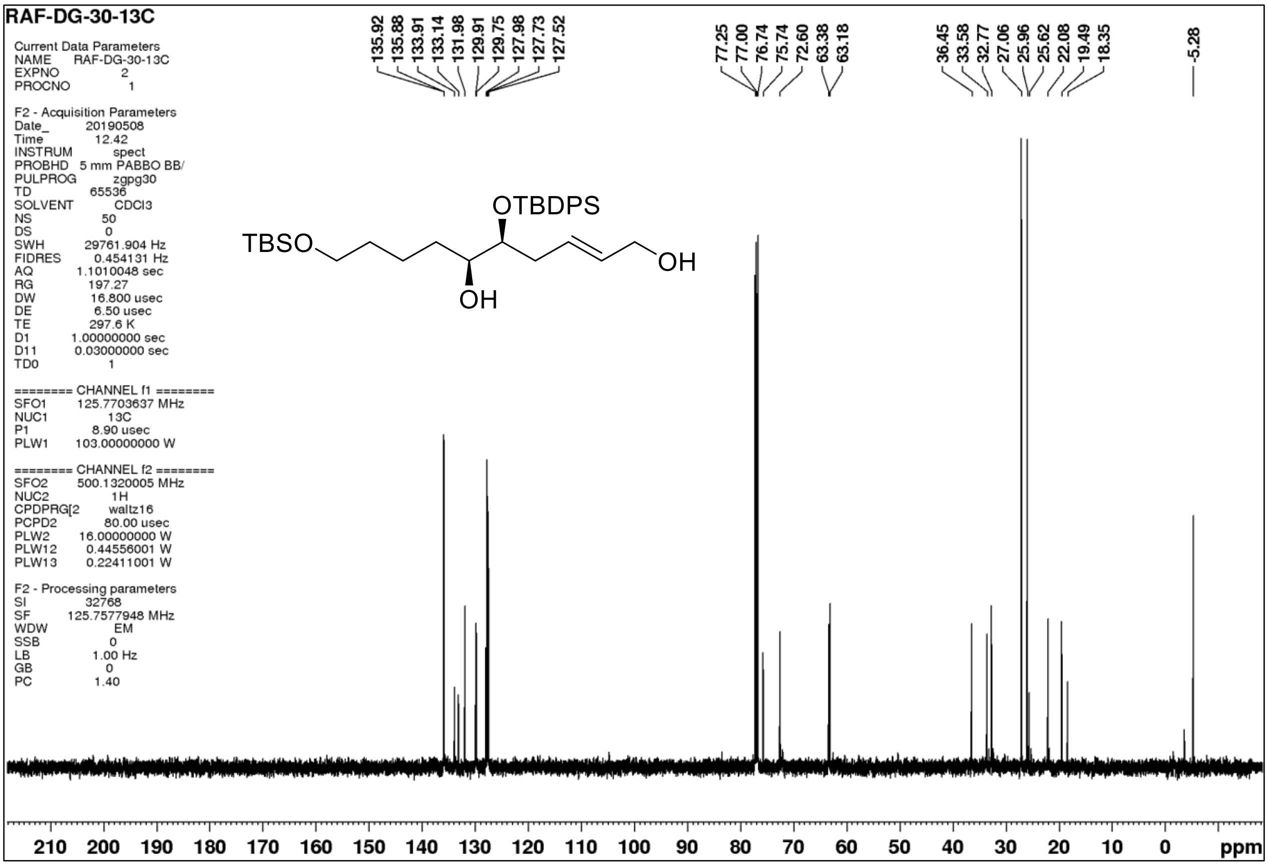


```
Current Data Parameters
NAME      RAF-DG-30-1H
EXPNO            1
PROCNO           1

F2 - Acquisition Parameters
Date_       20190508
Time          12.41
INSTRUM        spect
PROBHD   5 mm PABBO BB/
PULPROG         zg30
TD          65536
SOLVENT        CDCl3
NS             11
DS              0
SWH       10000.000 Hz
FIDRES     0.152588 Hz
AQ        3.2767999 sec
RG            30.72
DW           50.000 usec
DE             6.50 usec
TE            297.6 K
D1       1.00000000 sec
TD0              1

======== CHANNEL f1 ========
SFO1     500.1330885 MHz
NUC1              1H
P1            13.35 usec
PLW1      16.00000000 W

F2 - Processing parameters
SI           65536
SF       500.1300116 MHz
WDW              EM
SSB               0
LB             0.30 Hz
GB                0
PC             1.00
```



```
Current Data Parameters
NAME      RAF-DG-30-13C
EXPNO            2
PROCNO           1

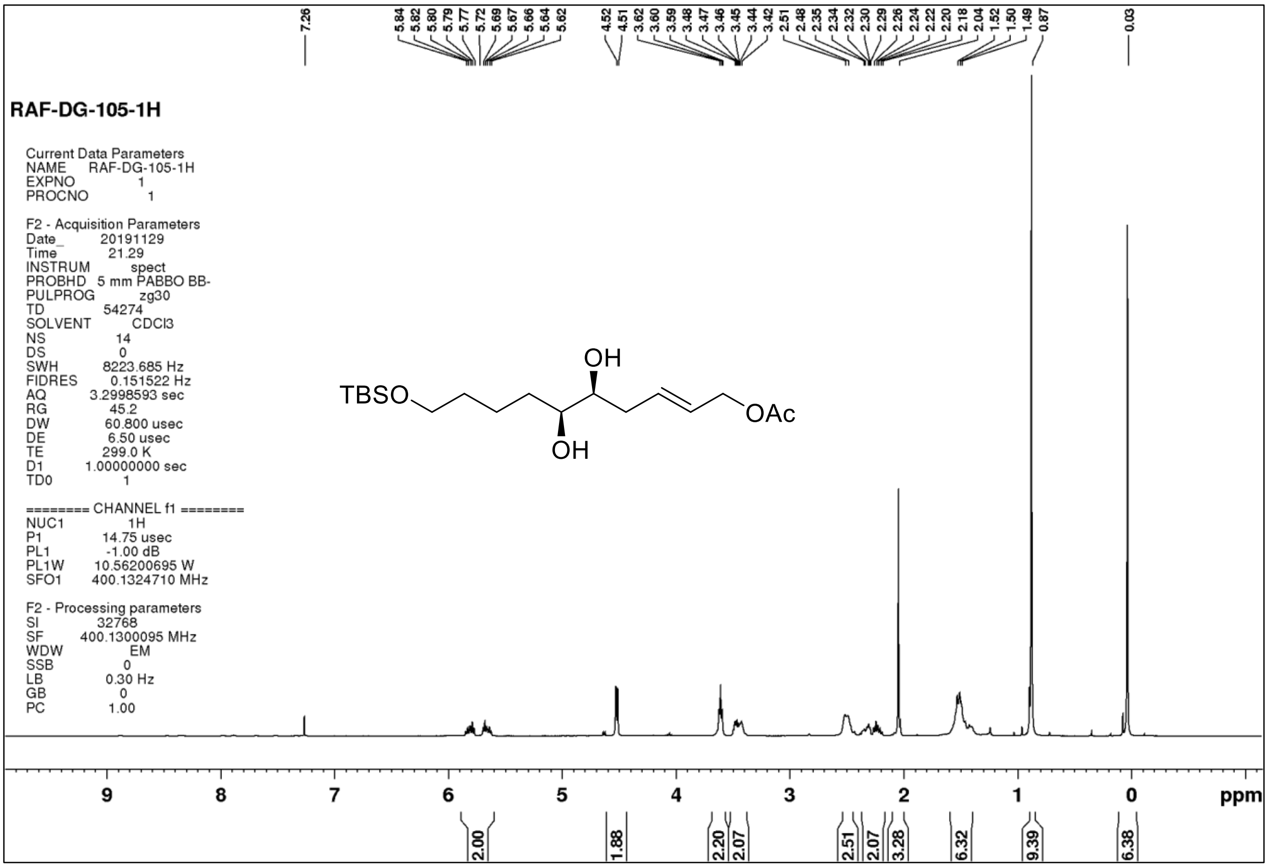
F2 - Acquisition Parameters
Date_       20190508
Time          12.42
INSTRUM        spect
PROBHD   5 mm PABBO BB/
PULPROG       zgpg30
TD          65536
SOLVENT        CDCl3
NS             50
DS              0
SWH       29761.904 Hz
FIDRES     0.454131 Hz
AQ        1.1010048 sec
RG           197.27
DW           16.800 usec
DE             6.50 usec
TE            297.6 K
D1       1.00000000 sec
D11      0.03000000 sec
TD0              1

======== CHANNEL f1 ========
SFO1     125.7703637 MHz
NUC1             13C
P1             8.90 usec
PLW1     103.00000000 W

======== CHANNEL f2 ========
SFO2     500.1320005 MHz
NUC2              1H
CPDPRG[2        waltz16
PCPD2          80.00 usec
PLW2      16.00000000 W
PLW12      0.44556001 W
PLW13      0.22411001 W

F2 - Processing parameters
SI           32768
SF       125.7577948 MHz
WDW              EM
SSB               0
LB             1.00 Hz
GB                0
PC             1.40
```

^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **5g**

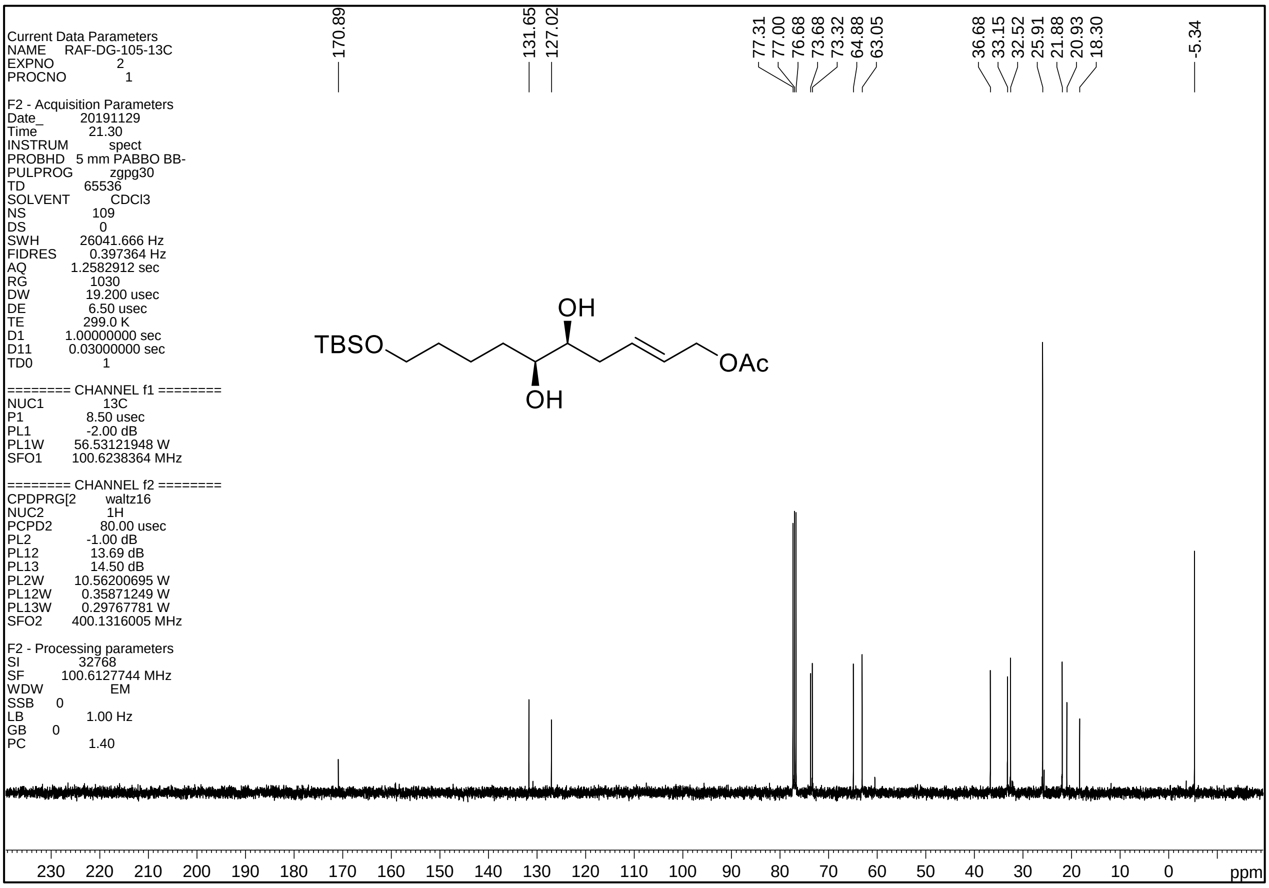


```
Current Data Parameters
NAME     RAF-DG-105-1H
EXPNO            1
PROCNO           1

F2 - Acquisition Parameters
Date_       20191129
Time          21.29
INSTRUM        spect
PROBHD   5 mm PABBO BB-
PULPROG         zg30
TD            54274
SOLVENT        CDCl3
NS               14
DS                0
SWH        8223.685 Hz
FIDRES     0.151522 Hz
AQ        3.2998593 sec
RG               45.2
DW          60.800 usec
DE            6.50 usec
TE             299.0 K
D1       1.00000000 sec
TD0               1

======== CHANNEL f1 ========
NUC1              1H
P1           14.75 usec
PL1           -1.00 dB
PL1W     10.56200695 W
SFO1     400.1324710 MHz

F2 - Processing parameters
SI             32768
SF        400.1300095 MHz
WDW               EM
SSB                0
LB           0.30 Hz
GB                 0
PC              1.00
```



```
Current Data Parameters
NAME     RAF-DG-105-13C
EXPNO            2
PROCNO           1

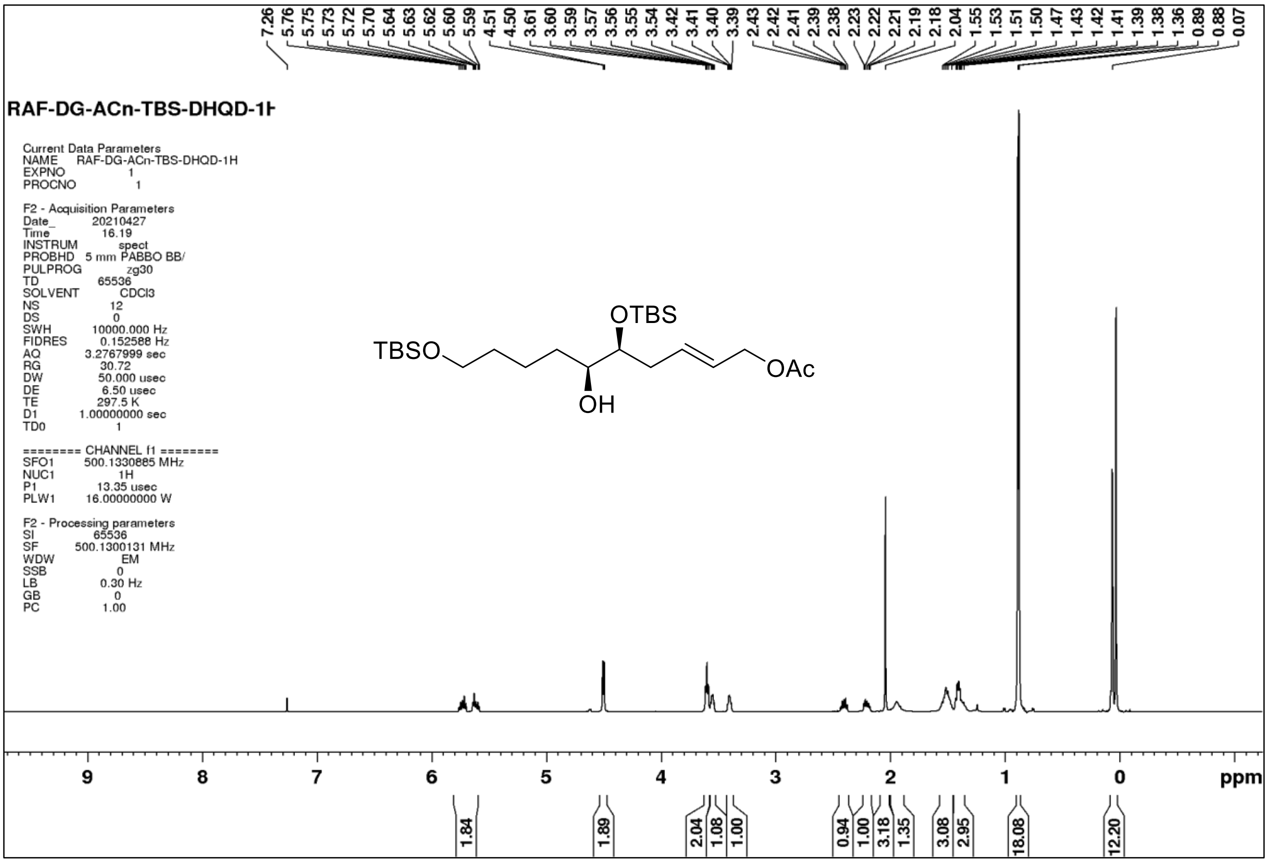
F2 - Acquisition Parameters
Date_       20191129
Time          21.30
INSTRUM        spect
PROBHD   5 mm PABBO BB-
PULPROG       zgpg30
TD            65536
SOLVENT        CDCl3
NS              109
DS                0
SWH       26041.666 Hz
FIDRES     0.397364 Hz
AQ        1.2582912 sec
RG              1030
DW          19.200 usec
DE            6.50 usec
TE             299.0 K
D1       1.00000000 sec
D11      0.03000000 sec
TD0               1

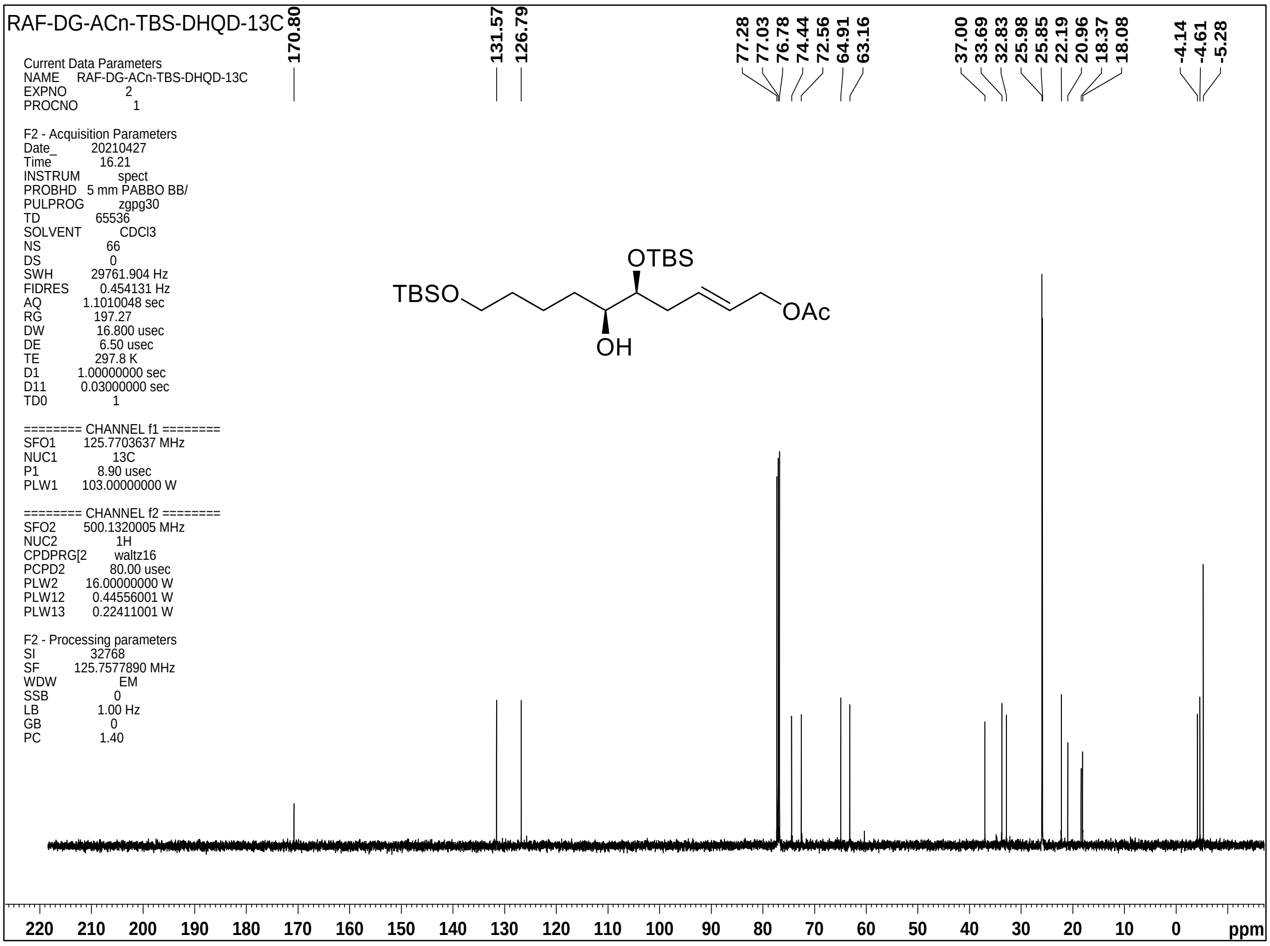
======== CHANNEL f1 ========
NUC1             13C
P1            8.50 usec
PL1           -2.00 dB
PL1W     56.53121948 W
SFO1     100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2              1H
PCPD2        80.00 usec
PL2           -1.00 dB
PL12          13.69 dB
PL13          14.50 dB
PL2W     10.56200695 W
PL12W     0.35871249 W
PL13W     0.29767781 W
SFO2     400.1316005 MHz

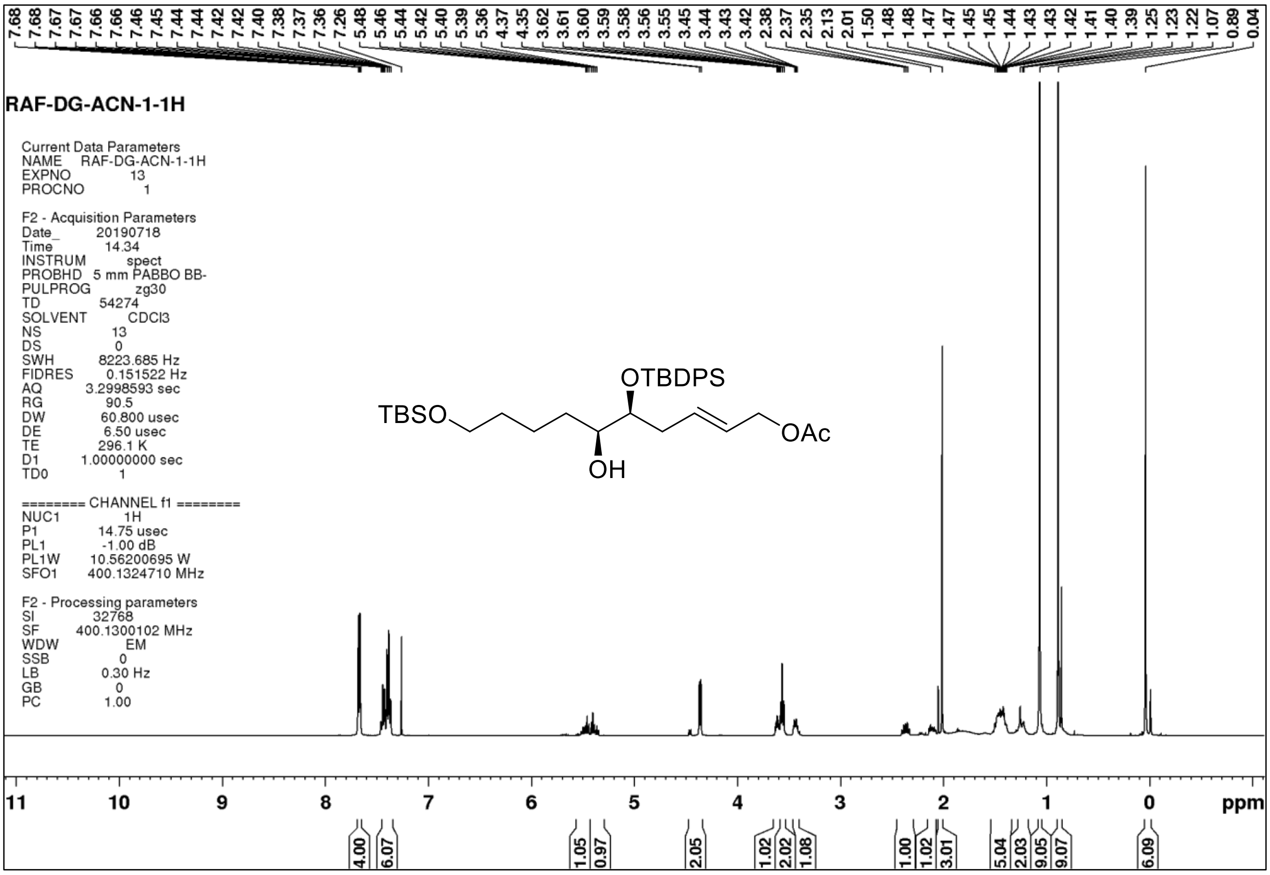
F2 - Processing parameters
SI             32768
SF        100.6127744 MHz
WDW               EM
SSB     0
LB           1.00 Hz
GB      0
PC              1.40
```

^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) of compound **5e**





^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) of compound **5f**



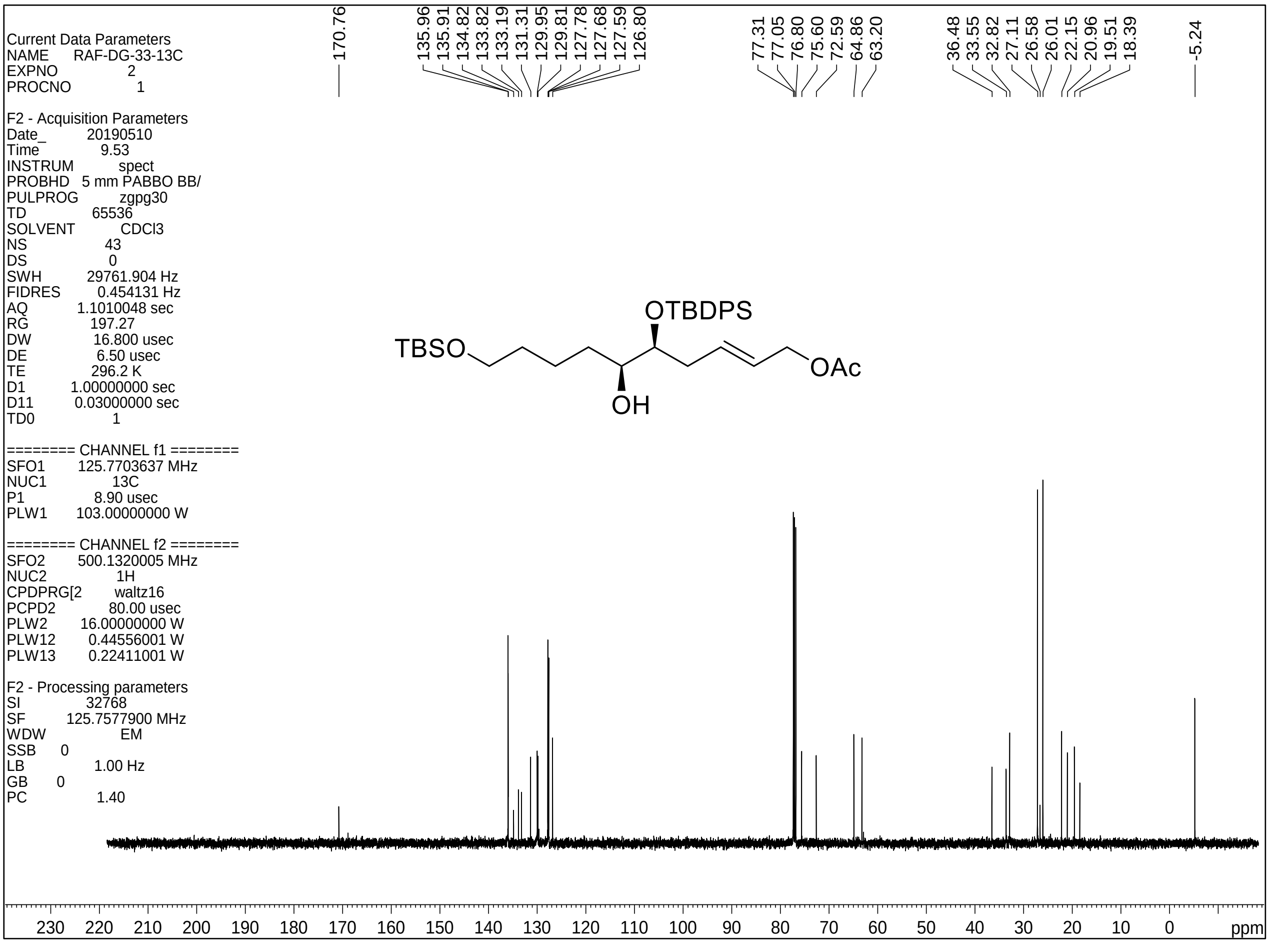
RAF-DG-ACN-1-1H

```
Current Data Parameters
NAME     RAF-DG-ACN-1-1H
EXPNO              13
PROCNO              1

F2 - Acquisition Parameters
Date_        20190718
Time            14.34
INSTRUM         spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              54274
SOLVENT         CDCl3
NS                 13
DS                  0
SWH        8223.685 Hz
FIDRES     0.151522 Hz
AQ       3.2998593 sec
RG               90.5
DW         60.800 usec
DE           6.50 usec
TE              296.1 K
D1     1.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               1H
P1         14.75 usec
PL1          -1.00 dB
PL1W    10.56200695 W
SFO1   400.1324710 MHz

F2 - Processing parameters
SI              32768
SF     400.1300102 MHz
WDW                EM
SSB                 0
LB            0.30 Hz
GB                  0
PC               1.00
```



```
Current Data Parameters
NAME      RAF-DG-33-13C
EXPNO               2
PROCNO              1

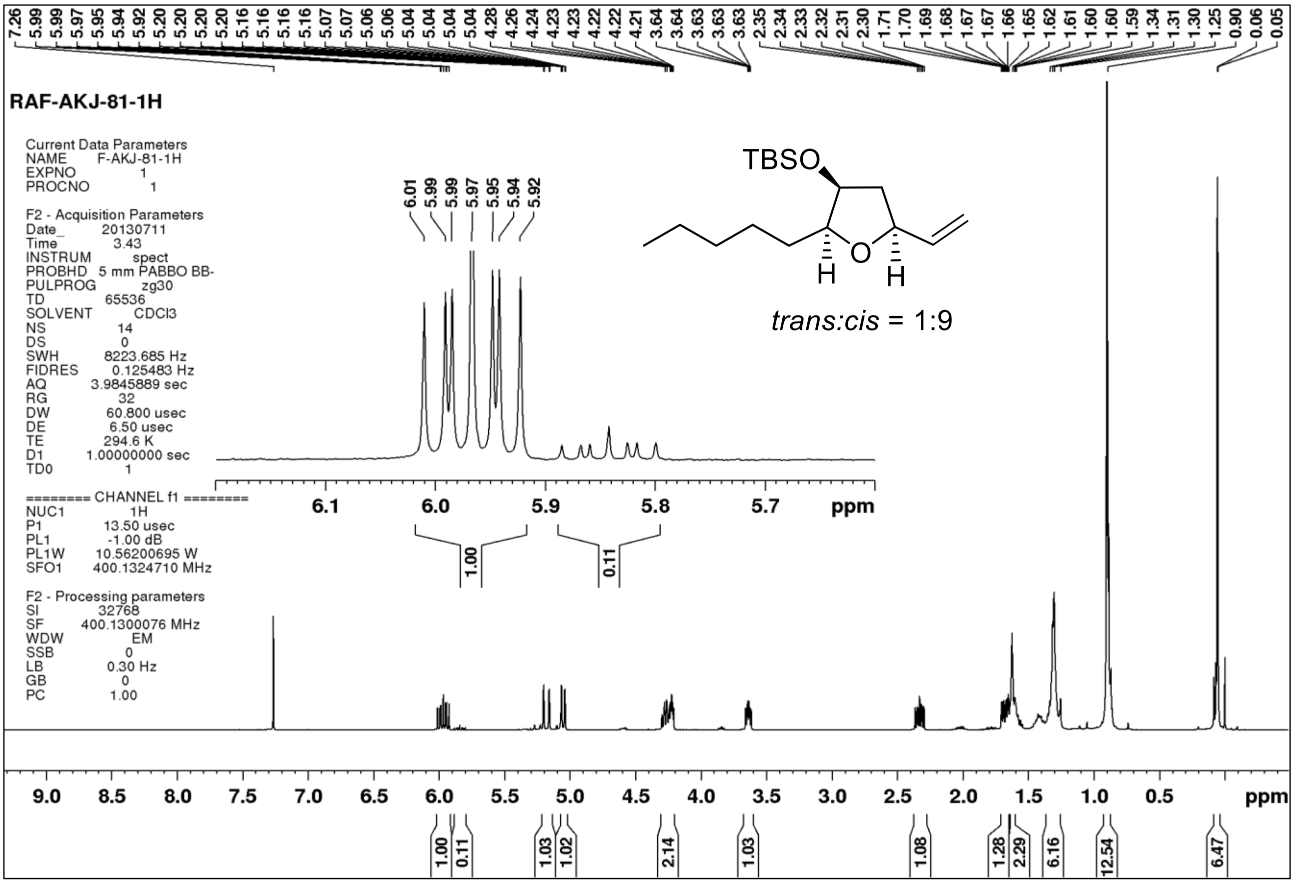
F2 - Acquisition Parameters
Date_        20190510
Time             9.53
INSTRUM         spect
PROBHD   5 mm PABBO BB/
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                 43
DS                  0
SWH       29761.904 Hz
FIDRES     0.454131 Hz
AQ       1.1010048 sec
RG             197.27
DW         16.800 usec
DE           6.50 usec
TE              296.2 K
D1     1.00000000 sec
D11    0.03000000 sec
TD0                 1

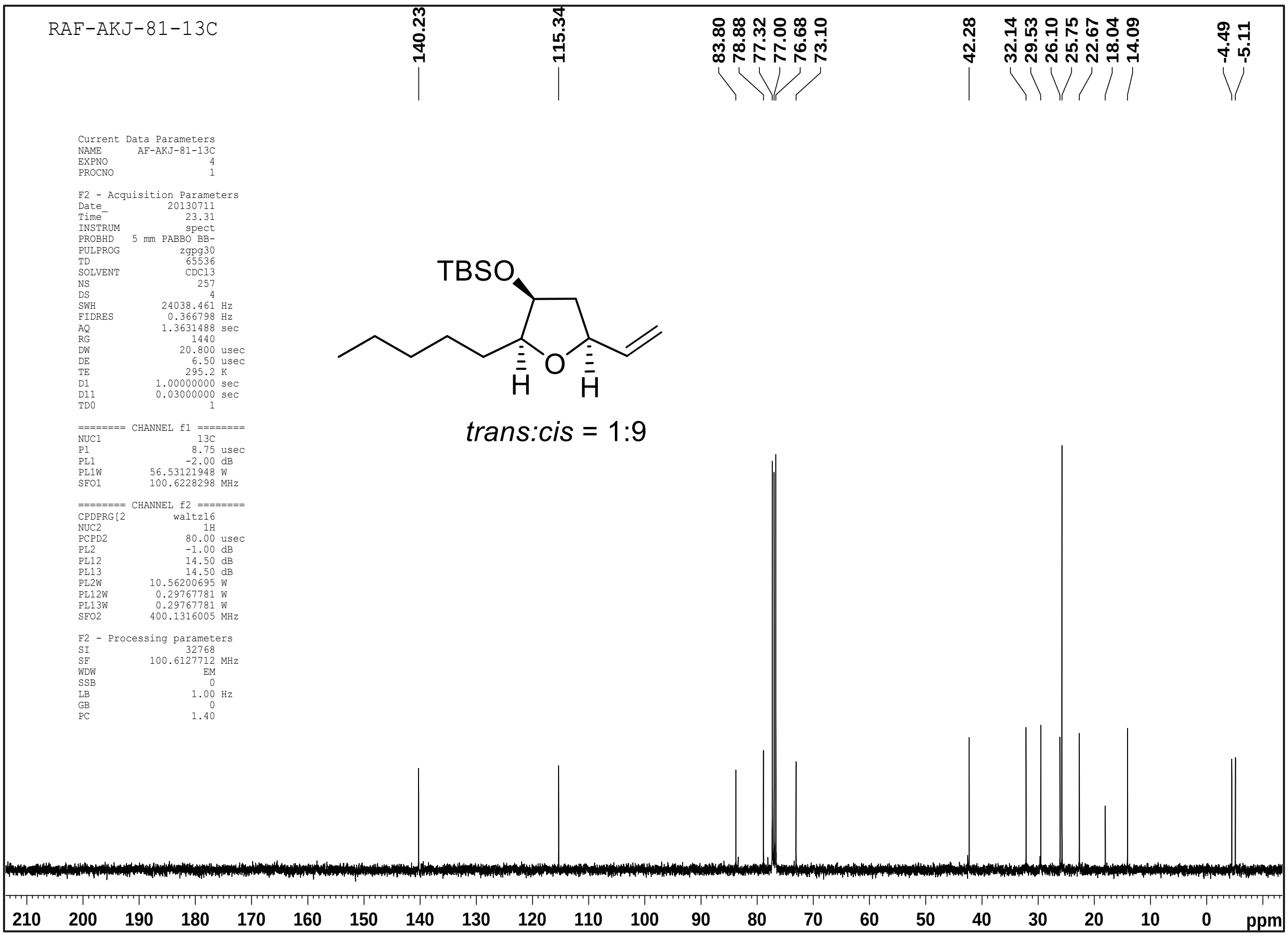
======== CHANNEL f1 ========
SFO1   125.7703637 MHz
NUC1              13C
P1          8.90 usec
PLW1   103.00000000 W

======== CHANNEL f2 ========
SFO2   500.1320005 MHz
NUC2               1H
CPDPRG[2       waltz16
PCPD2       80.00 usec
PLW2    16.00000000 W
PLW12    0.44556001 W
PLW13    0.22411001 W

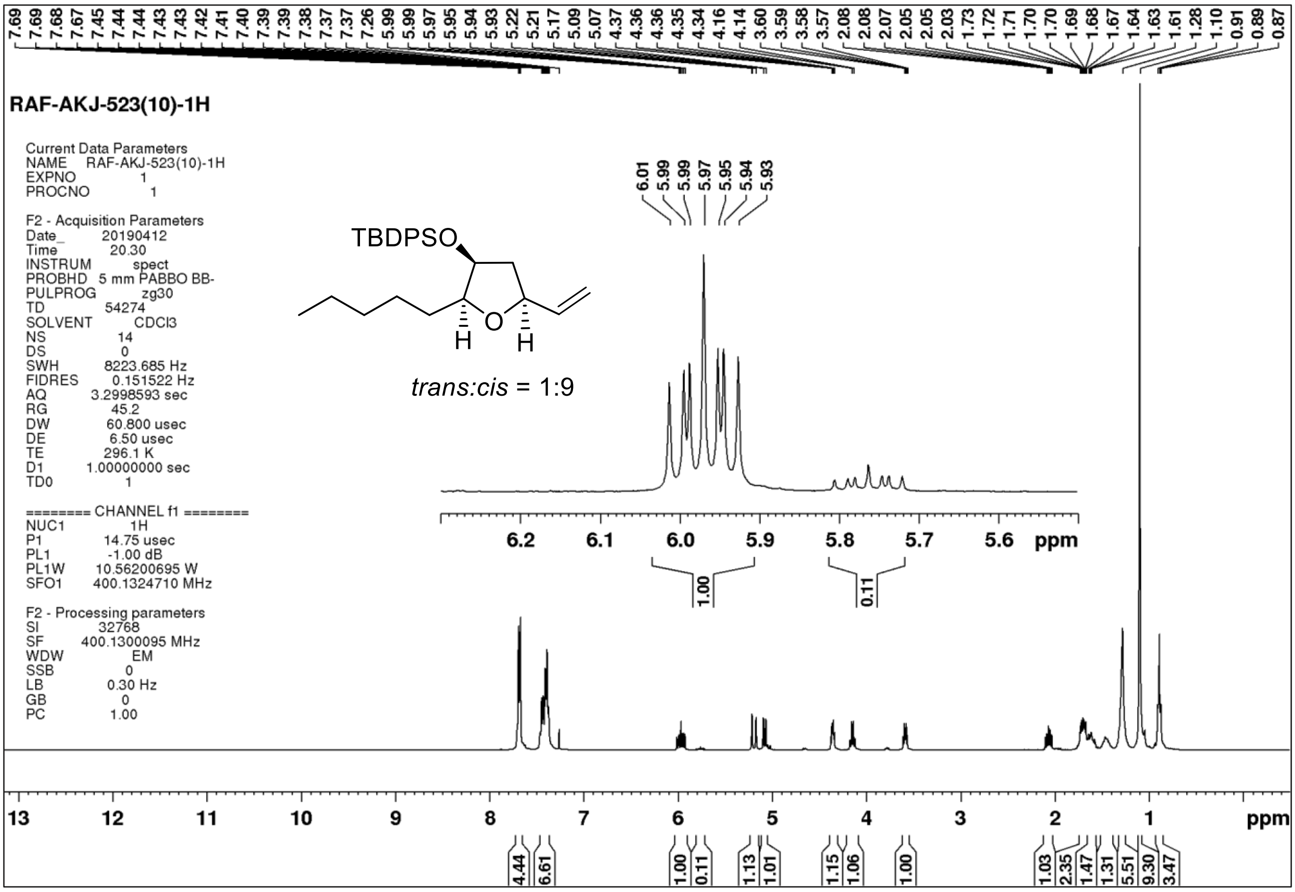
F2 - Processing parameters
SI              32768
SF     125.7577900 MHz
WDW                EM
SSB    0
LB            1.00 Hz
GB     0
PC               1.40
```

^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **6a**





^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **6b**

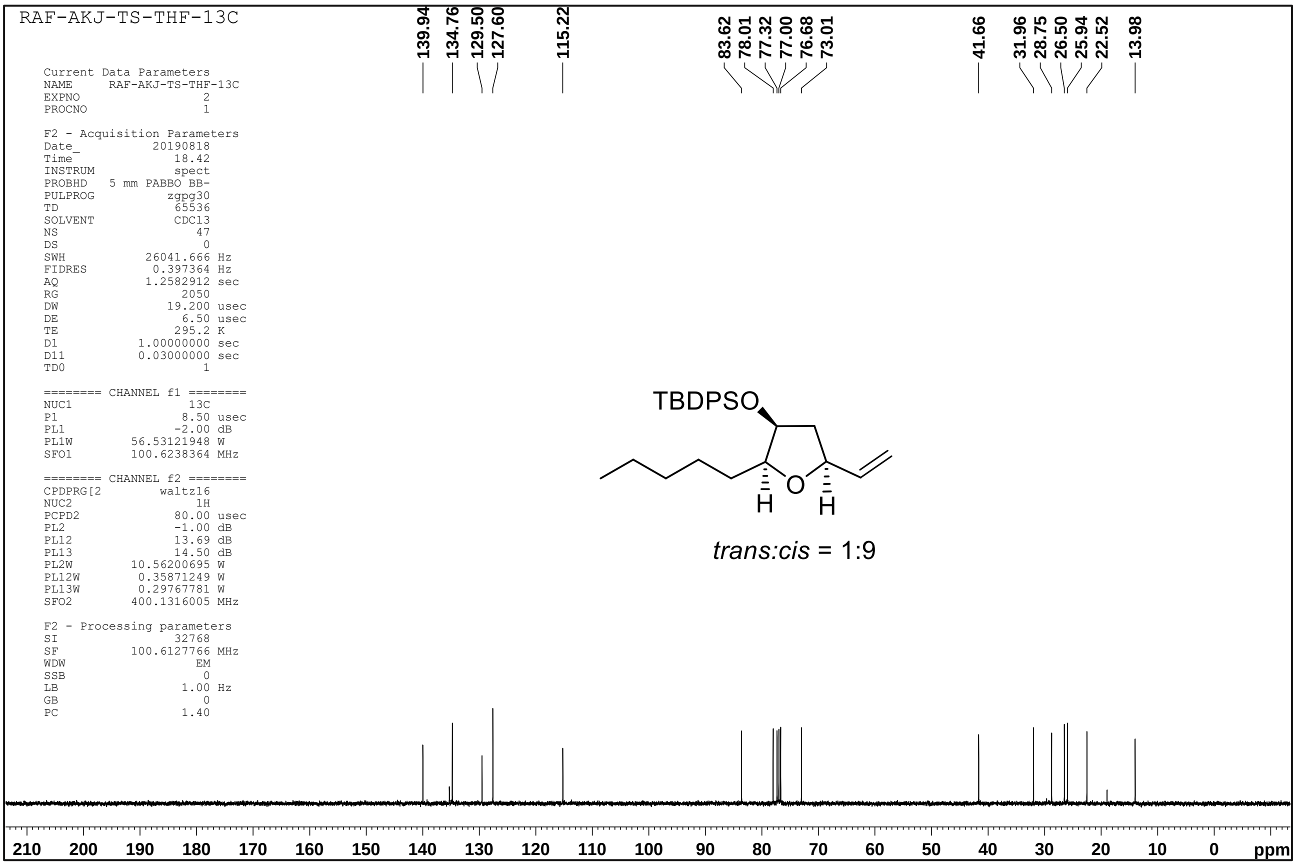


```
Current Data Parameters
NAME    RAF-AKJ-523(10)-1H
EXPNO            1
PROCNO           1

F2 - Acquisition Parameters
Date_       20190412
Time           20.30
INSTRUM        spect
PROBHD  5 mm PABBO BB-
PULPROG         zg30
TD             54274
SOLVENT        CDCl3
NS                14
DS                 0
SWH      8223.685 Hz
FIDRES   0.151522 Hz
AQ     3.2998593 sec
RG              45.2
DW        60.800 usec
DE          6.50 usec
TE           296.1 K
D1    1.00000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1              1H
P1        14.75 usec
PL1         -1.00 dB
PL1W   10.56200695 W
SFO1  400.1324710 MHz

F2 - Processing parameters
SI             32768
SF    400.1300095 MHz
WDW               EM
SSB                0
LB           0.30 Hz
GB                 0
PC              1.00
```



```
Current Data Parameters
NAME      RAF-AKJ-TS-THF-13C
EXPNO                     2
PROCNO                    1

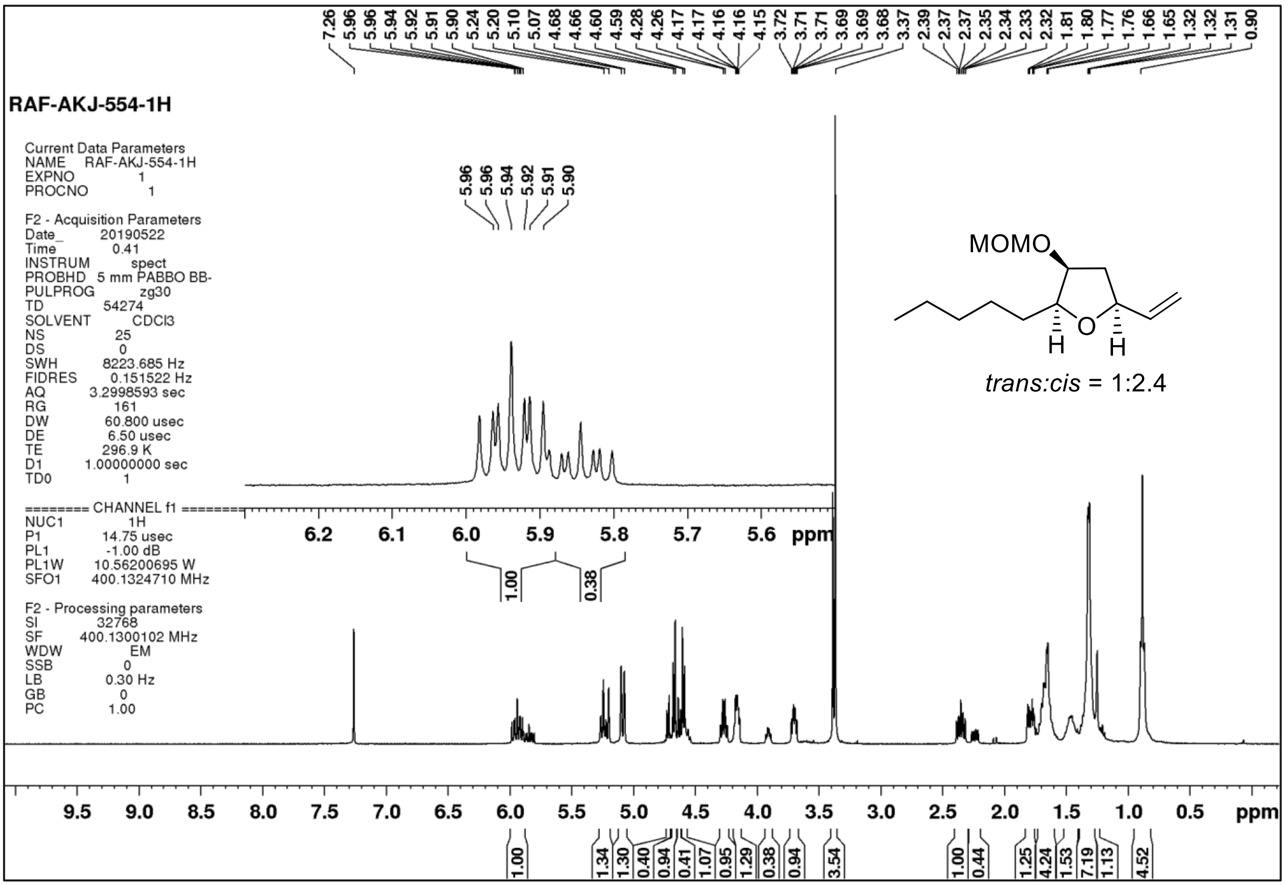
F2 - Acquisition Parameters
Date_            20190818
Time                18.42
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    47
DS                     0
SWH            26041.666 Hz
FIDRES          0.397364 Hz
AQ             1.2582912 sec
RG                  2050
DW                19.200 usec
DE                  6.50 usec
TE                 295.2 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                    1

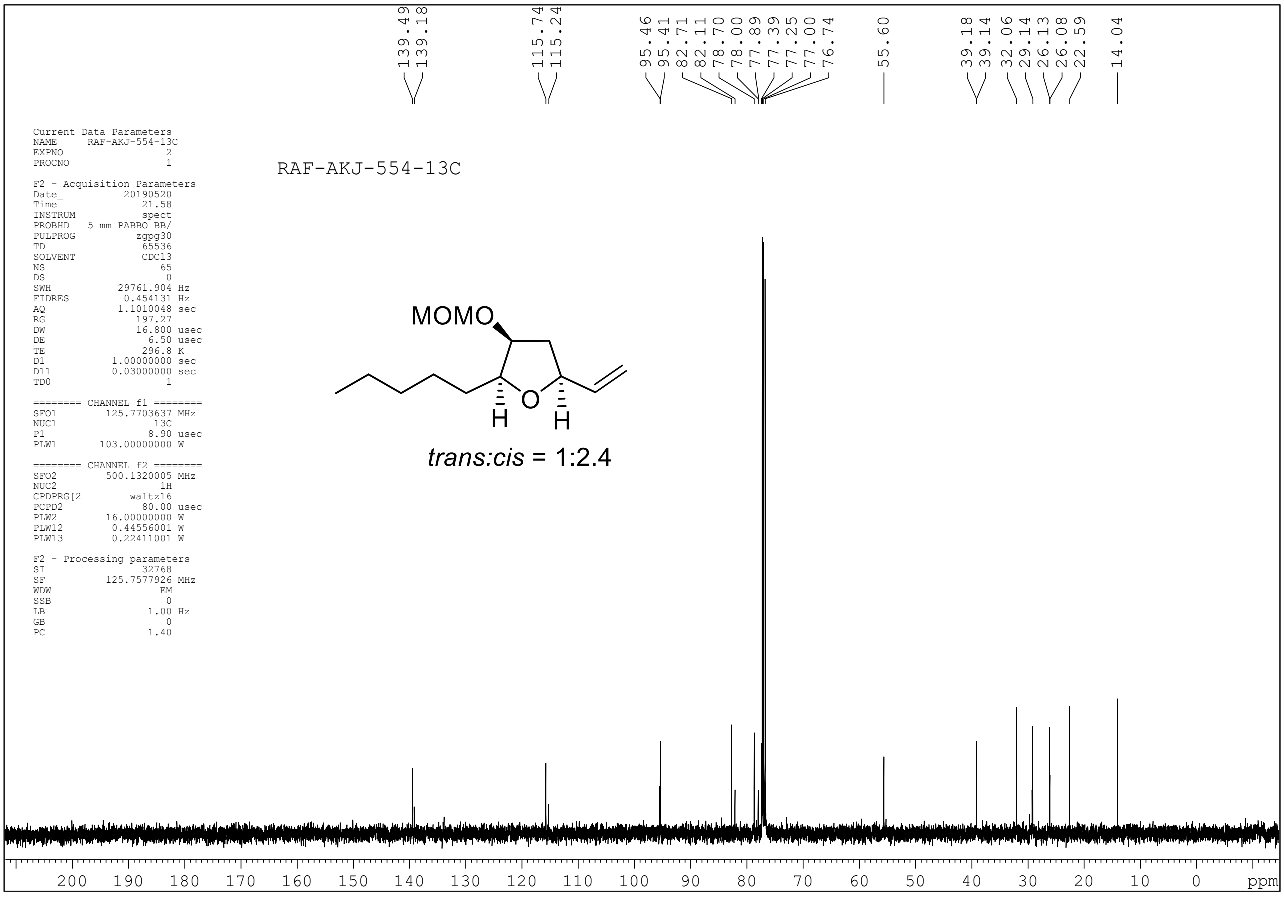
======== CHANNEL f1 ========
NUC1                 13C
P1                  8.50 usec
PL1                -2.00 dB
PL1W         56.53121948 W
SFO1         100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               13.69 dB
PL13               14.50 dB
PL2W         10.56200695 W
PL12W         0.35871249 W
PL13W         0.29767781 W
SFO2         400.1316005 MHz

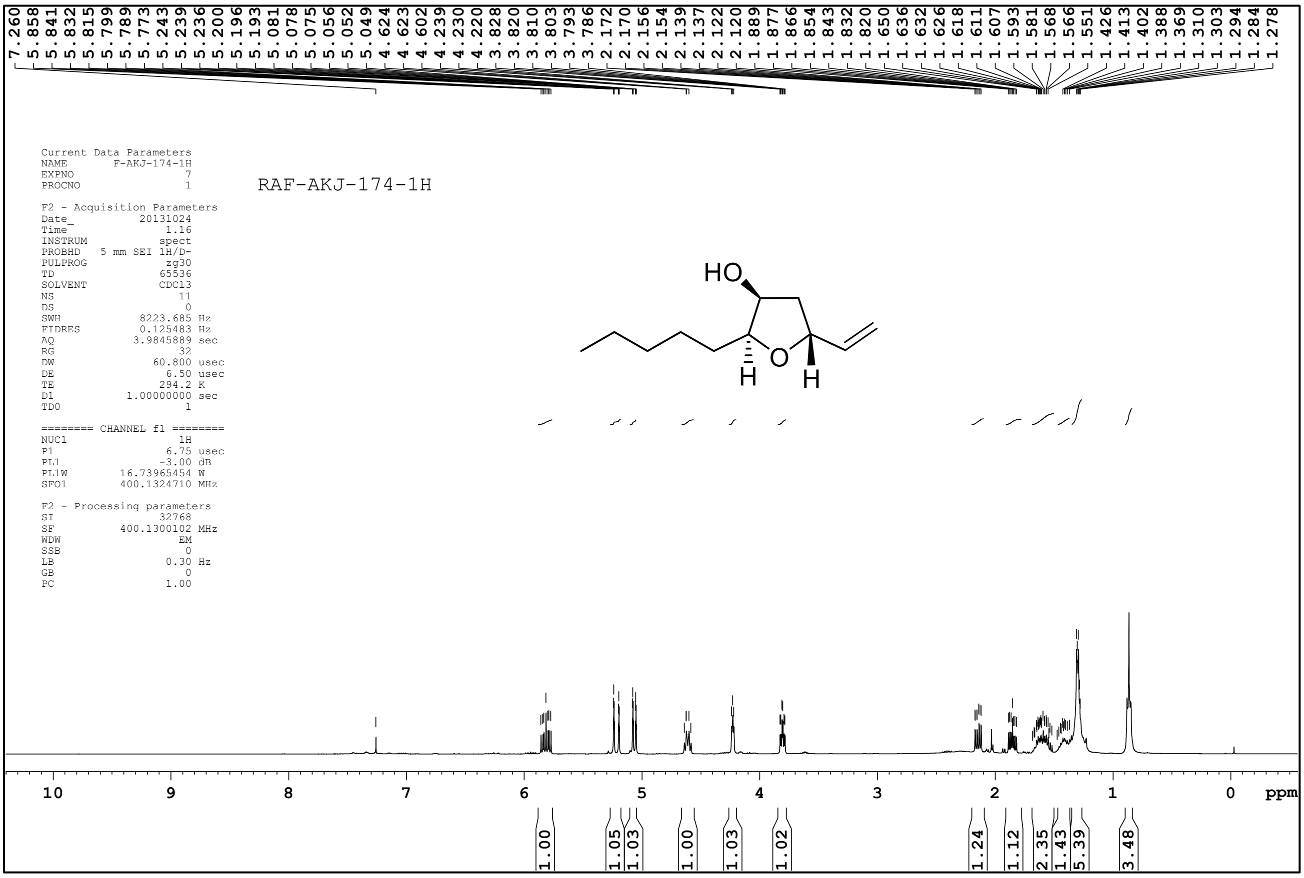
F2 - Processing parameters
SI                 32768
SF           100.6127766 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (125 MHz, CDCl$_3$) of compound **6c**





^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **6d**

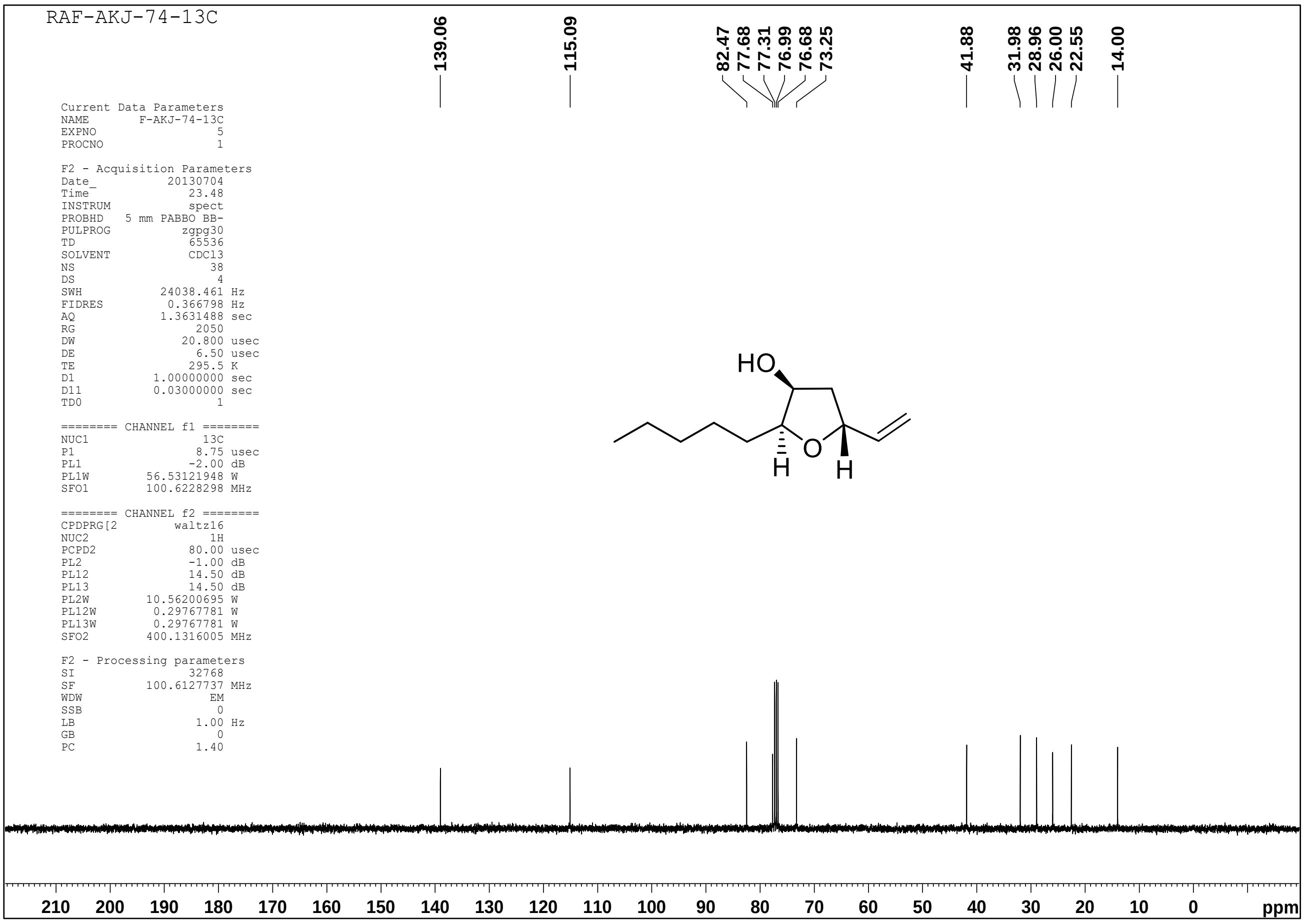


```
Current Data Parameters
NAME       F-AKJ-174-1H
EXPNO                 7
PROCNO                1

F2 - Acquisition Parameters
Date_          20131024
Time               1.16
INSTRUM           spect
PROBHD   5 mm SEI 1H/D-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   11
DS                    0
SWH            8223.685 Hz
FIDRES         0.125483 Hz
AQ            3.9845889 sec
RG                   32
DW               60.800 usec
DE                 6.50 usec
TE                294.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                 6.75 usec
PL1               -3.00 dB
PL1W        16.73965454 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300102 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



```
Current Data Parameters
NAME        F-AKJ-74-13C
EXPNO                  5
PROCNO                 1

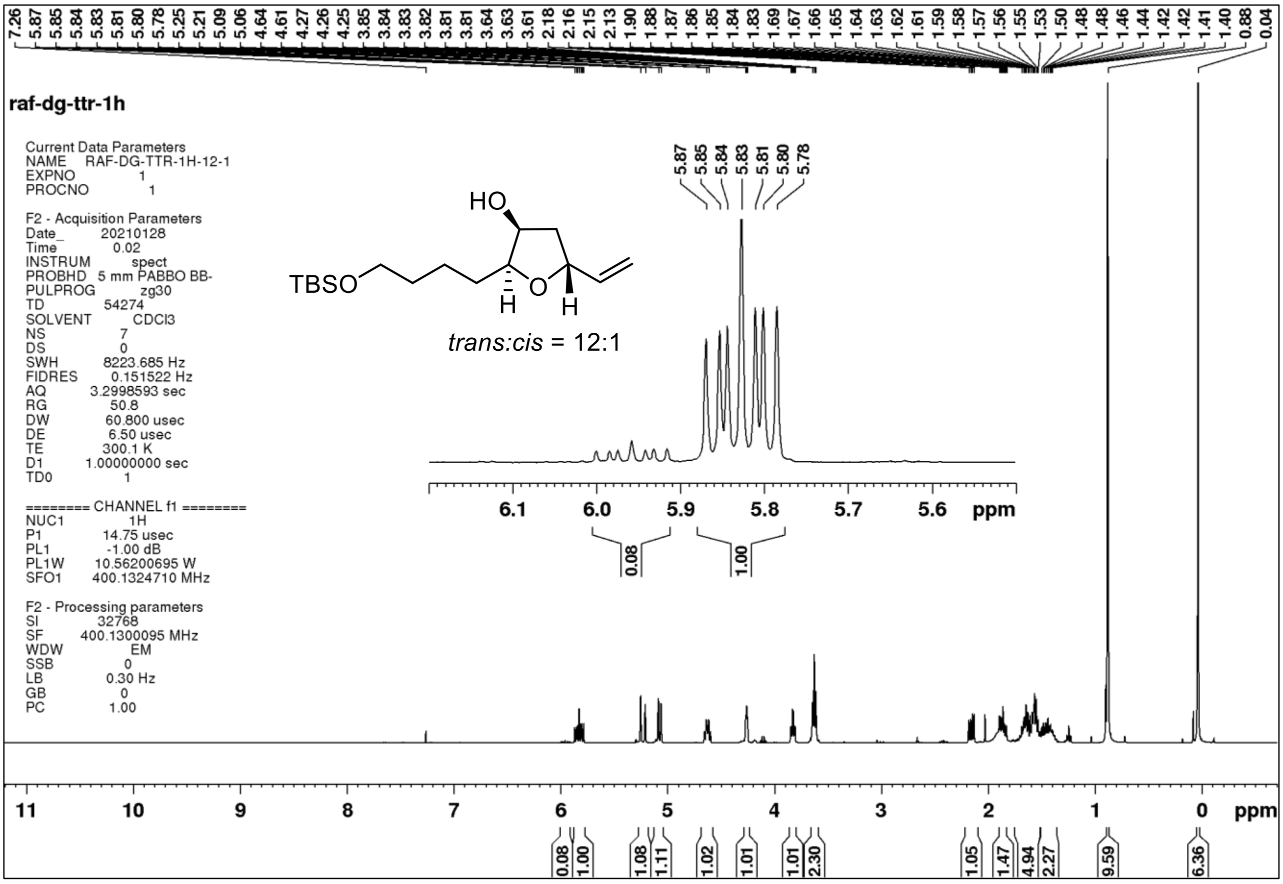
F2 - Acquisition Parameters
Date_           20130704
Time               23.48
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    38
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631488 sec
RG                  2050
DW                20.800 usec
DE                  6.50 usec
TE                 295.5 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.75 usec
PL1                -2.00 dB
PL1W         56.53121948 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               14.50 dB
PL13               14.50 dB
PL2W         10.56200695 W
PL12W         0.29767781 W
PL13W         0.29767781 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127737 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

^{1}H NMR (400 MHz, $CDCl_3$) of compound **6g** (*trans:cis* = 12:1)



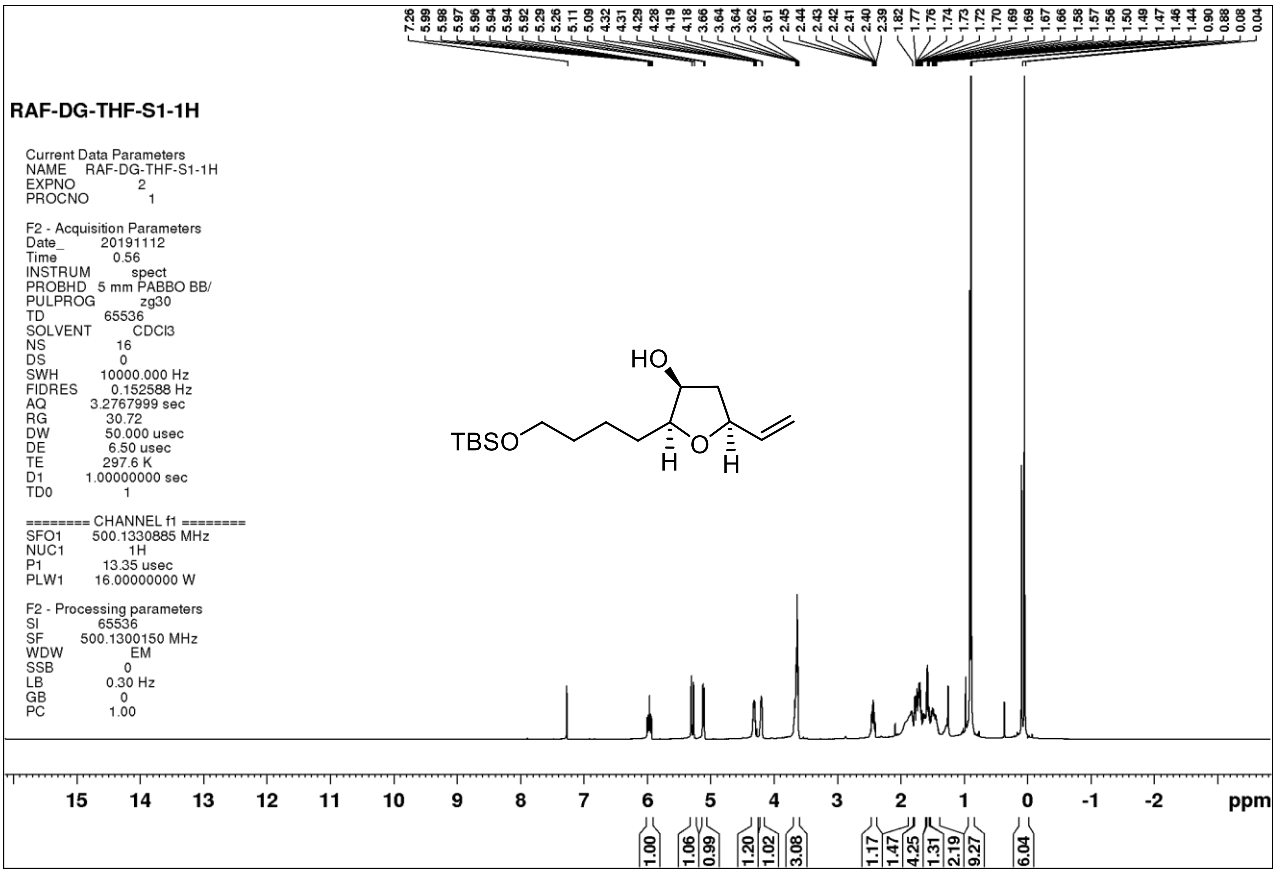
```
Current Data Parameters
NAME    RAF-DG-TTR-1H-12-1
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_       20210128
Time            0.02
INSTRUM         spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD             54274
SOLVENT         CDCl3
NS                 7
DS                 0
SWH         8223.685 Hz
FIDRES      0.151522 Hz
AQ         3.2998593 sec
RG              50.8
DW            60.800 usec
DE              6.50 usec
TE             300.1 K
D1        1.00000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1              1H
P1             14.75 usec
PL1            -1.00 dB
PL1W     10.56200695 W
SFO1     400.1324710 MHz

F2 - Processing parameters
SI             32768
SF       400.1300095 MHz
WDW               EM
SSB                0
LB              0.30 Hz
GB                 0
PC              1.00
```

^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **6g′**



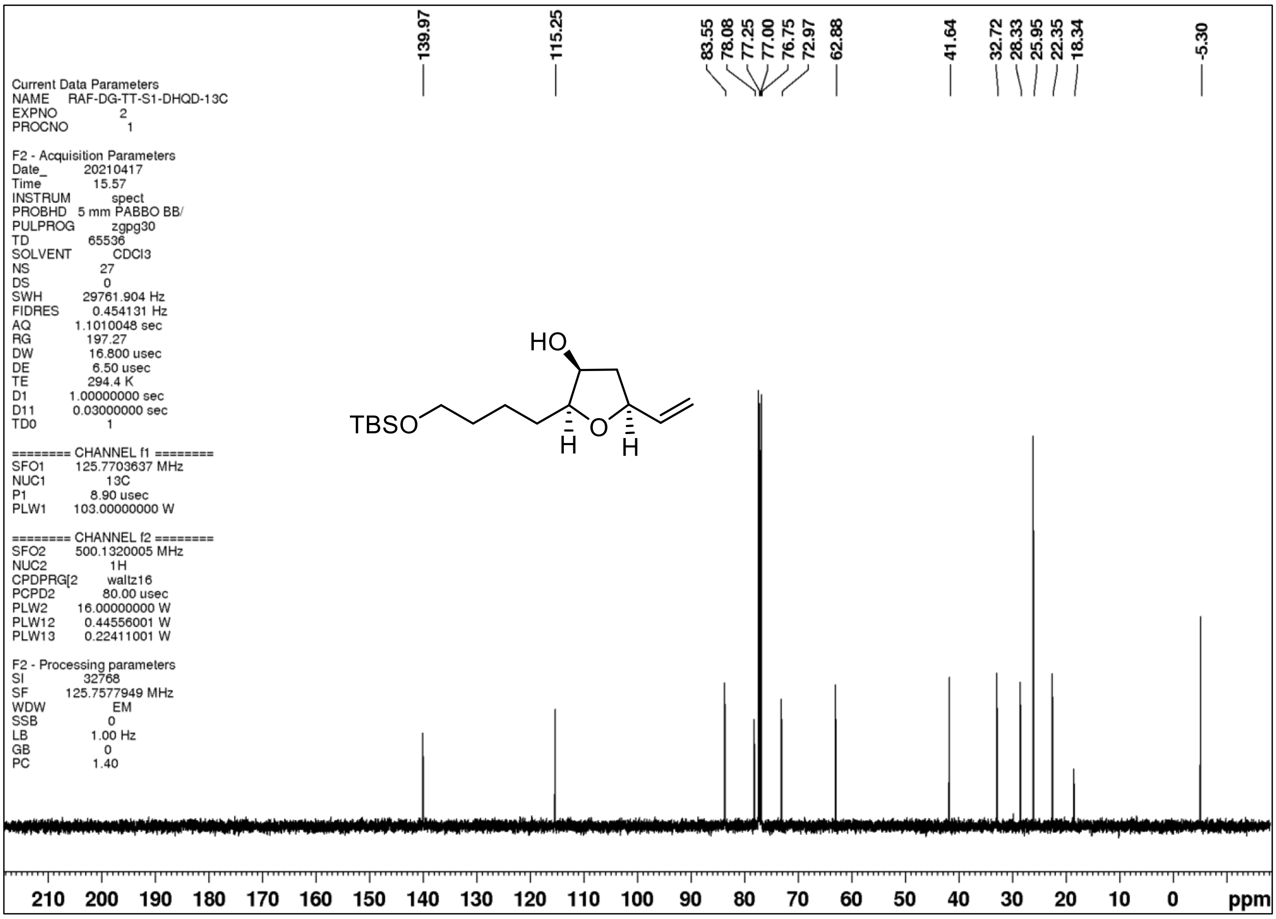
RAF-DG-THF-S1-1H

Current Data Parameters
NAME RAF-DG-THF-S1-1H
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20191112
Time 0.56
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 30.72
DW 50.000 usec
DE 6.50 usec
TE 297.6 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 13.35 usec
PLW1 16.00000000 W

F2 - Processing parameters
SI 65536
SF 500.1300150 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME RAF-DG-TT-S1-DHQD-13C
EXPNO 2
PROCNO 1

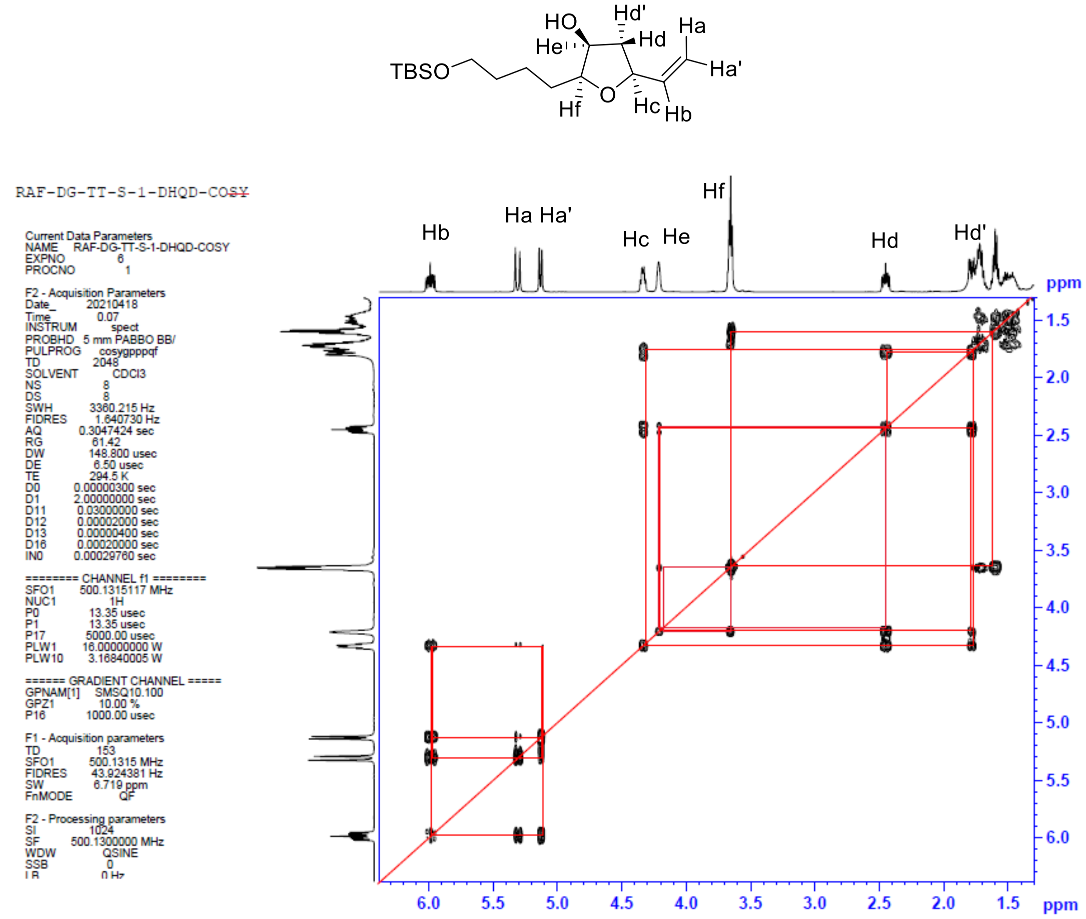
F2 - Acquisition Parameters
Date_ 20210417
Time 15.57
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 27
DS 0
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 197.27
DW 16.800 usec
DE 6.50 usec
TE 294.4 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 125.7703637 MHz
NUC1 13C
P1 8.90 usec
PLW1 103.00000000 W

======== CHANNEL f2 ========
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 16.00000000 W
PLW12 0.44556001 W
PLW13 0.22411001 W

F2 - Processing parameters
SI 32768
SF 125.7577949 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

H-H COESY spectra of compound **6g′**



```
RAF-DG-TT-S-1-DHQD-CO~~SY~~

Current Data Parameters
NAME     RAF-DG-TT-S-1-DHQD-COSY
EXPNO              6
PROCNO             1

F2 - Acquisition Parameters
Date_         20210418
Time            0.07
INSTRUM         spect
PROBHD   5 mm PABBO BB/
PULPROG      cosygpppqf
TD             2048
SOLVENT         CDCl3
NS               8
DS               8
SWH         3360.215 Hz
FIDRES       1.640730 Hz
AQ         0.3047424 sec
RG             61.42
DW          148.800 usec
DE             6.50 usec
TE            294.5 K
D0        0.00000300 sec
D1        2.00000000 sec
D11       0.03000000 sec
D12       0.00002000 sec
D13       0.00000400 sec
D16       0.00020000 sec
IN0       0.00029760 sec

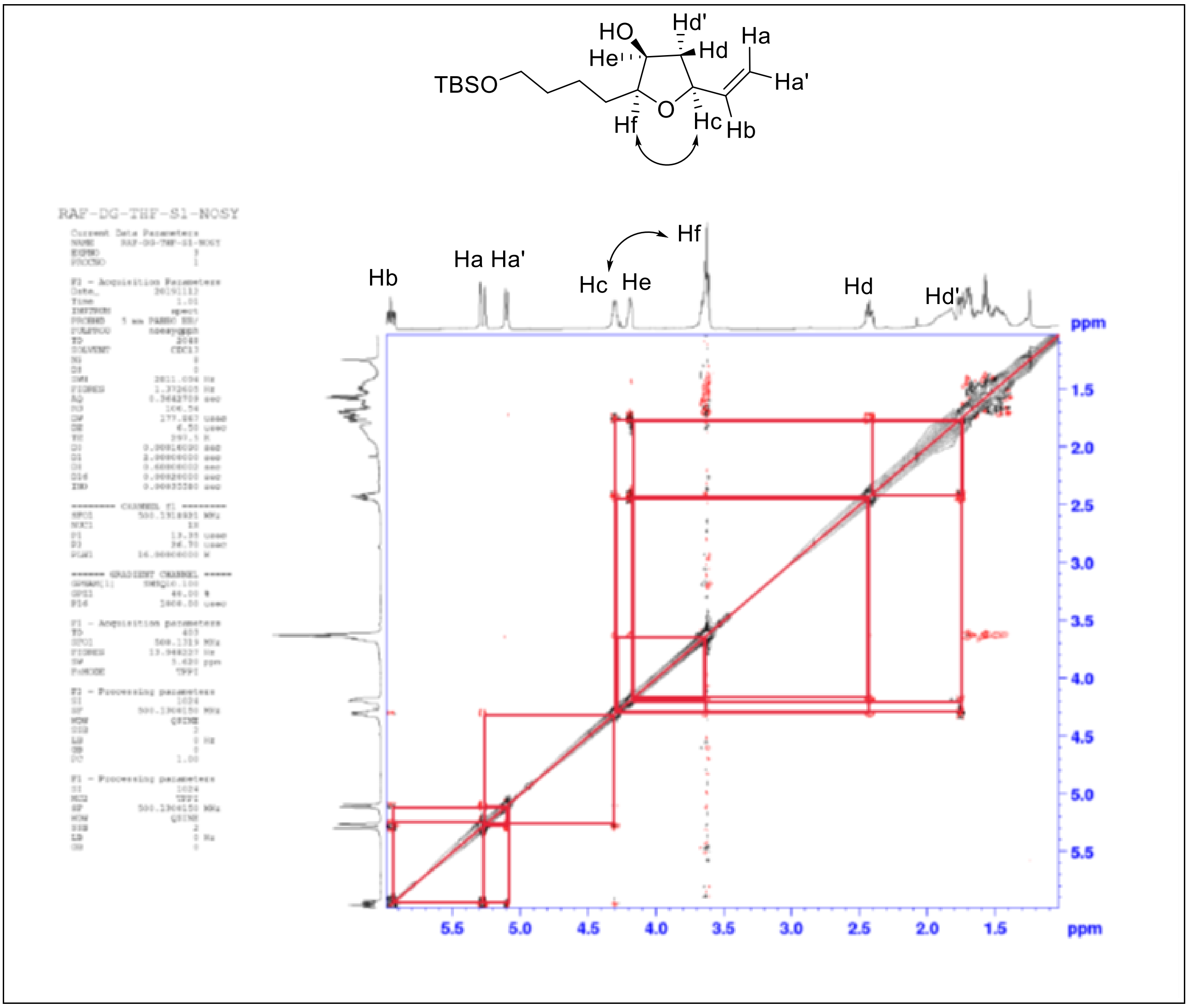
======== CHANNEL f1 ========
SFO1      500.1315117 MHz
NUC1              1H
P0             13.35 usec
P1             13.35 usec
P17          5000.00 usec
PLW1     16.00000000 W
PLW10     3.16840005 W

====== GRADIENT CHANNEL =====
GPNAM[1]    SMSQ10.100
GPZ1          10.00 %
P16         1000.00 usec

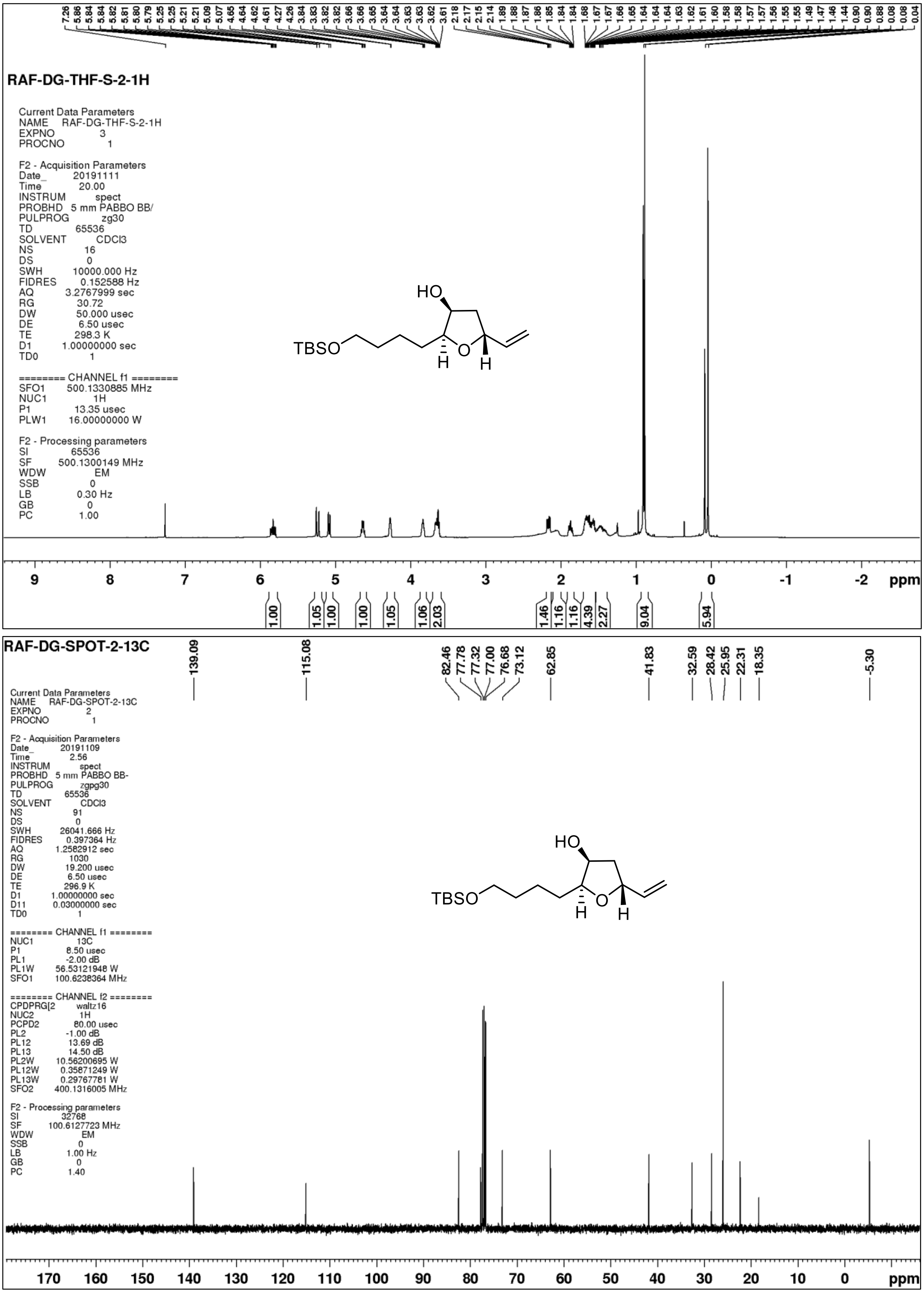
F1 - Acquisition parameters
TD               153
SFO1        500.1315 MHz
FIDRES     43.924381 Hz
SW             6.719 ppm
FnMODE            QF

F2 - Processing parameters
SI             1024
SF        500.1300000 MHz
WDW           QSINE
SSB              0
LB               0 Hz
```

NOESY spectra of compound **6g′**



^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **6g**



```
Current Data Parameters
NAME     RAF-DG-THF-S-2-1H
EXPNO              3
PROCNO             1

F2 - Acquisition Parameters
Date_          20191111
Time              20.00
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    0
SWH        10000.000 Hz
FIDRES      0.152588 Hz
AQ        3.2767999 sec
RG                30.72
DW           50.000 usec
DE             6.50 usec
TE              298.3 K
D1       1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1     500.1330885 MHz
NUC1                  1H
P1            13.35 usec
PLW1      16.00000000 W

F2 - Processing parameters
SI                65536
SF       500.1300149 MHz
WDW                  EM
SSB                   0
LB              0.30 Hz
GB                    0
PC                 1.00
```

```
Current Data Parameters
NAME     RAF-DG-SPOT-2-13C
EXPNO              2
PROCNO             1

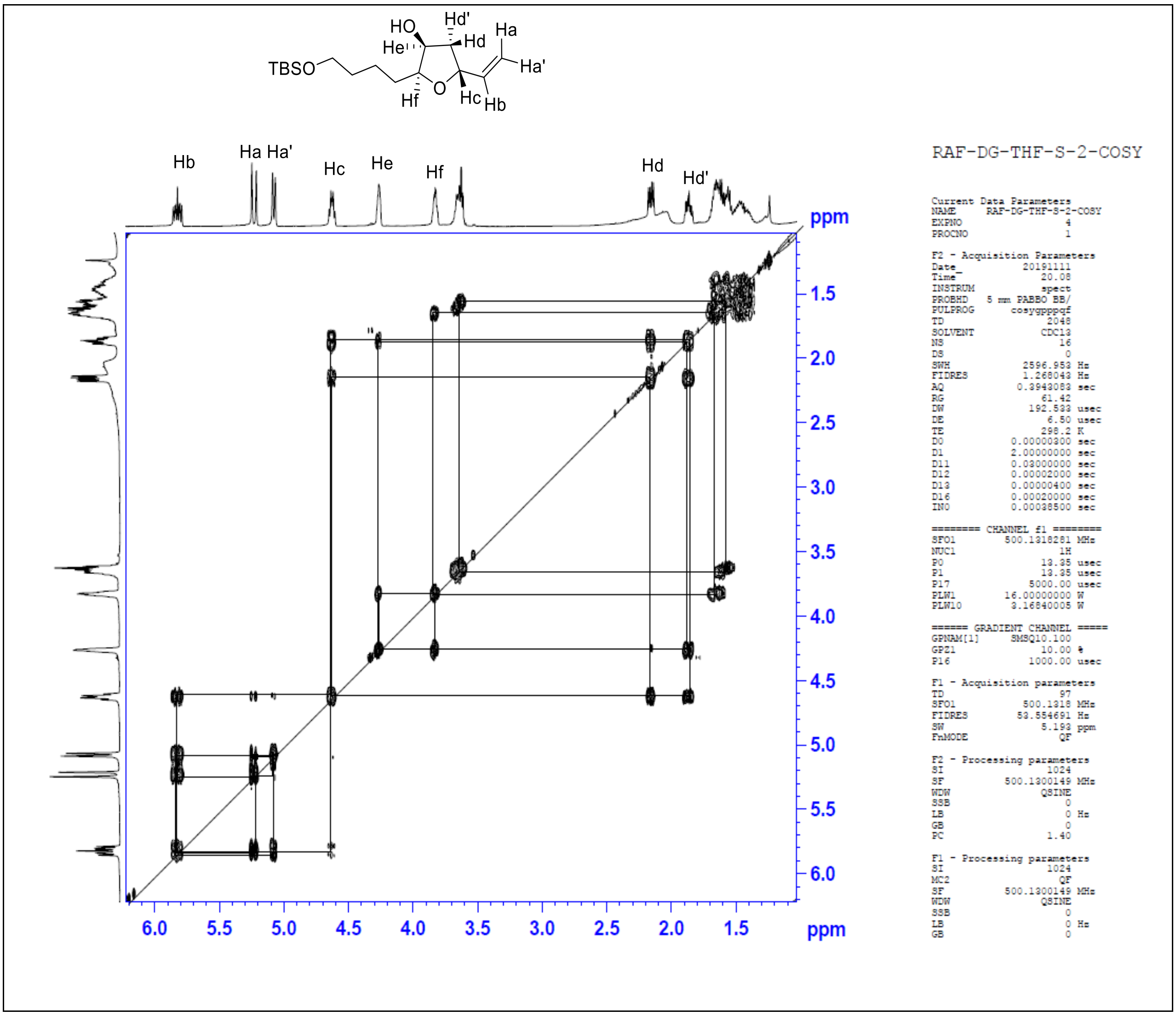
F2 - Acquisition Parameters
Date_          20191109
Time               2.56
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   91
DS                    0
SWH        26041.666 Hz
FIDRES      0.397364 Hz
AQ        1.2582912 sec
RG                 1030
DW           19.200 usec
DE             6.50 usec
TE              296.9 K
D1       1.00000000 sec
D11      0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1             8.50 usec
PL1             -2.00 dB
PL1W      56.53121948 W
SFO1     100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2         80.00 usec
PL2             -1.00 dB
PL12            13.69 dB
PL13            14.50 dB
PL2W      10.56200695 W
PL12W      0.35871249 W
PL13W      0.29767781 W
SFO2     400.1316005 MHz

F2 - Processing parameters
SI                32768
SF       100.6127723 MHz
WDW                  EM
SSB                   0
LB              1.00 Hz
GB                    0
PC                 1.40
```

H-H COESY spectra of compound **6g**



```
RAF-DG-THF-S-2-COSY

Current Data Parameters
NAME     RAF-DG-THF-S-2-COSY
EXPNO                     4
PROCNO                    1

F2 - Acquisition Parameters
Date_              20191111
Time                  20.08
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG           cosygpppqf
TD                     2048
SOLVENT               CDCl3
NS                       16
DS                        0
SWH                2596.953 Hz
FIDRES             1.268043 Hz
AQ                0.3943083 sec
RG                    61.42
DW                  192.533 usec
DE                     6.50 usec
TE                    298.2 K
D0               0.00000300 sec
D1               2.00000000 sec
D11              0.03000000 sec
D12              0.00002000 sec
D13              0.00000400 sec
D16              0.00020000 sec
IN0              0.00038500 sec

======== CHANNEL f1 ========
SFO1            500.1318281 MHz
NUC1                     1H
P0                    13.35 usec
P1                    13.35 usec
P17                 5000.00 usec
PLW1            16.00000000 W
PLW10            3.16840005 W

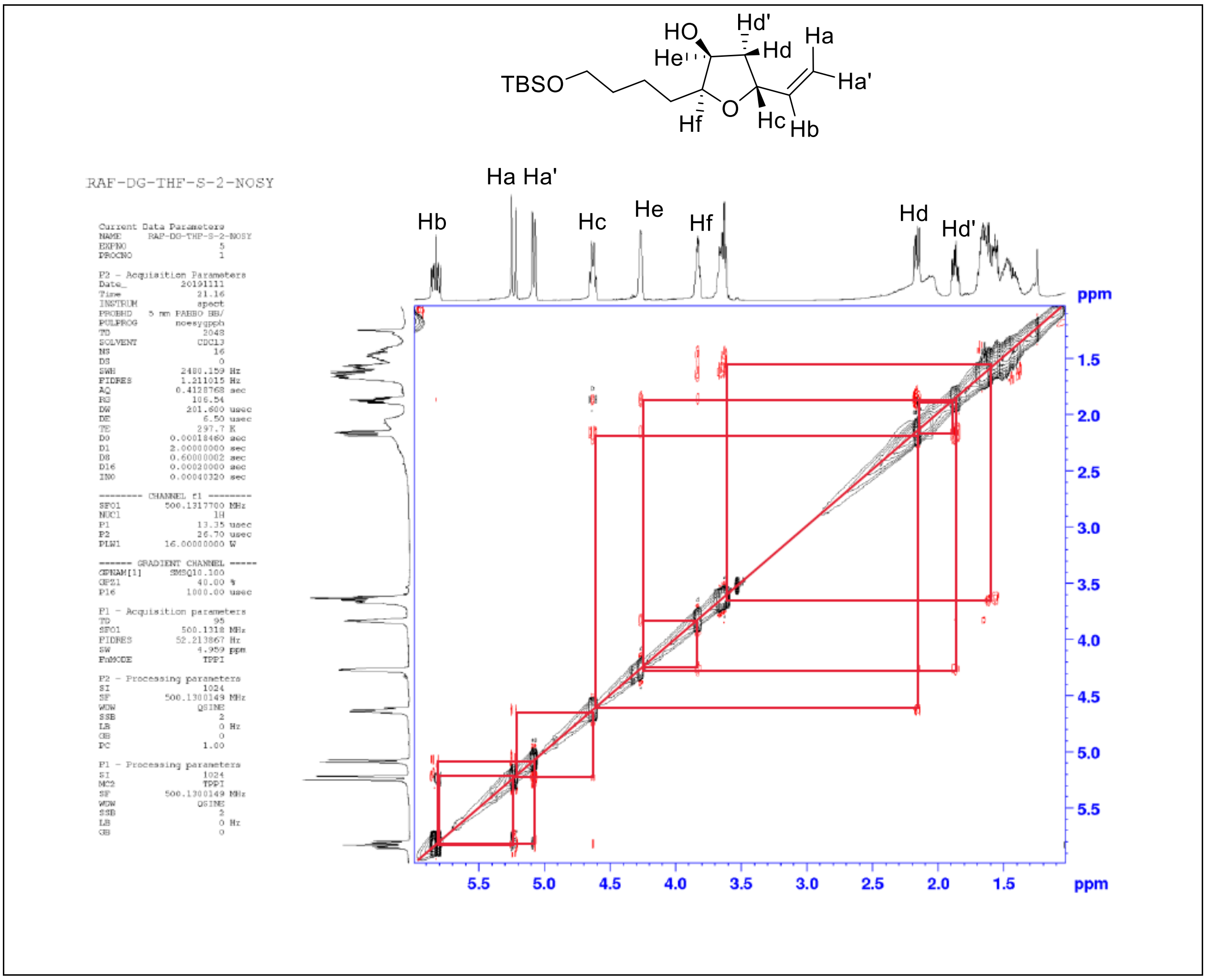
====== GRADIENT CHANNEL =====
GPNAM[1]         SMSQ10.100
GPZ1                  10.00 %
P16                 1000.00 usec

F1 - Acquisition parameters
TD                       97
SFO1               500.1318 MHz
FIDRES            53.554691 Hz
SW                    5.193 ppm
FnMODE                   QF

F2 - Processing parameters
SI                     1024
SF              500.1300149 MHz
WDW                   QSINE
SSB                       0
LB                        0 Hz
GB                        0
PC                     1.40

F1 - Processing parameters
SI                     1024
MC2                      QF
SF              500.1300149 MHz
WDW                   QSINE
SSB                       0
LB                        0 Hz
GB                        0
```

NOESY spectra of compound **6g**



```
RAF-DG-THF-S-2-NOSY

Current Data Parameters
NAME     RAF-DG-THF-S-2-NOSY
EXPNO                     5
PROCNO                    1

F2 - Acquisition Parameters
Date_              20191111
Time                  21.16
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG           noesygpph
TD                     2048
SOLVENT               CDCl3
NS                       16
DS                        0
SWH                2480.159 Hz
FIDRES             1.211015 Hz
AQ                0.4128768 sec
RG                   106.54
DW                  201.600 usec
DE                     6.50 usec
TE                    297.7 K
D0               0.00018460 sec
D1               2.00000000 sec
D8               0.60000002 sec
D16              0.00020000 sec
IN0              0.00040320 sec

======== CHANNEL f1 ========
SFO1            500.1317700 MHz
NUC1                     1H
P1                    13.35 usec
P2                    26.70 usec
PLW1            16.00000000 W

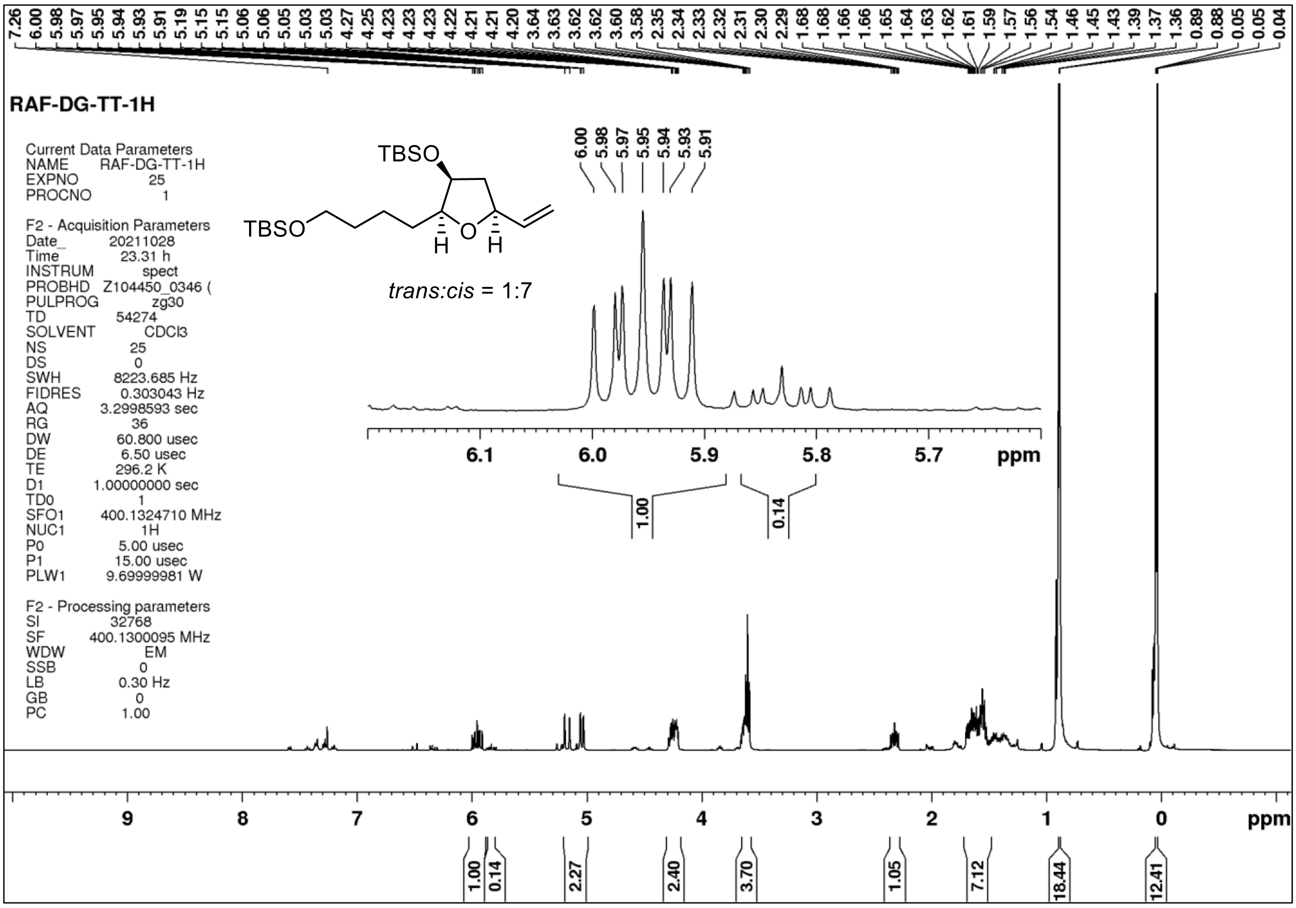
====== GRADIENT CHANNEL =====
GPNAM[1]         SMSQ10.100
GPZ1                  40.00 %
P16                 1000.00 usec

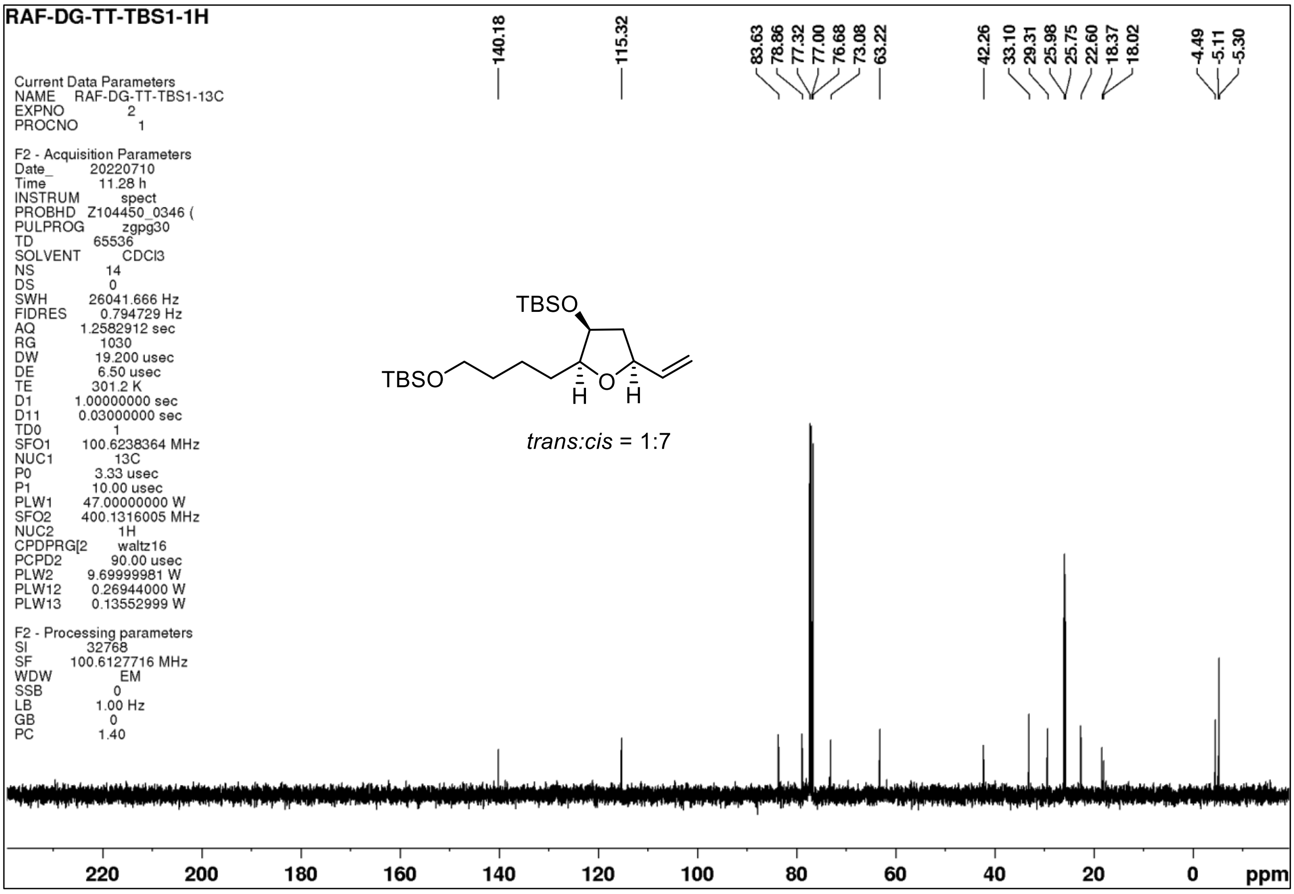
F1 - Acquisition parameters
TD                       95
SFO1               500.1318 MHz
FIDRES            52.213867 Hz
SW                    4.959 ppm
FnMODE                 TPPI

F2 - Processing parameters
SI                     1024
SF              500.1300149 MHz
WDW                   QSINE
SSB                       2
LB                        0 Hz
GB                        0
PC                     1.00

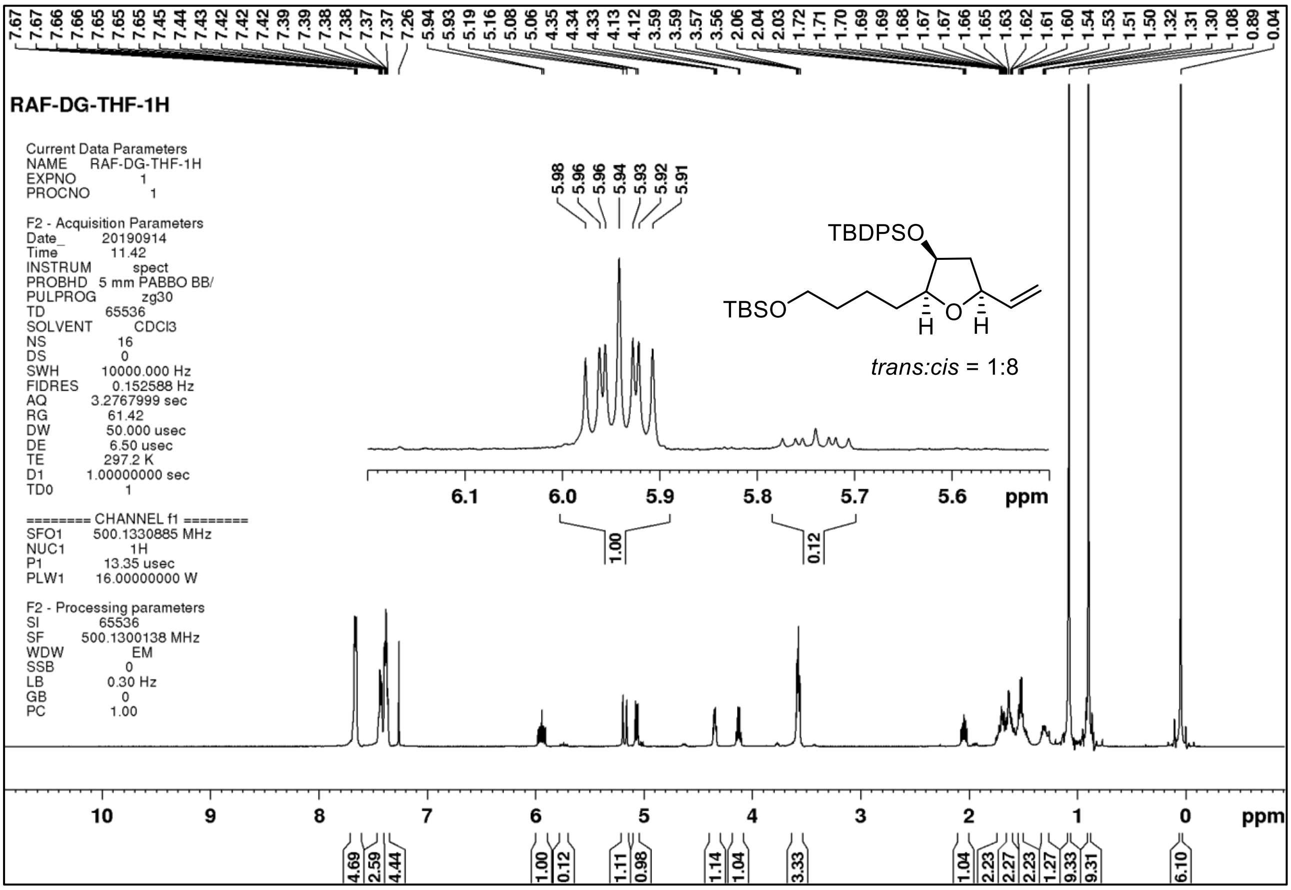
F1 - Processing parameters
SI                     1024
MC2                    TPPI
SF              500.1300149 MHz
WDW                   QSINE
SSB                       2
LB                        0 Hz
GB                        0
```

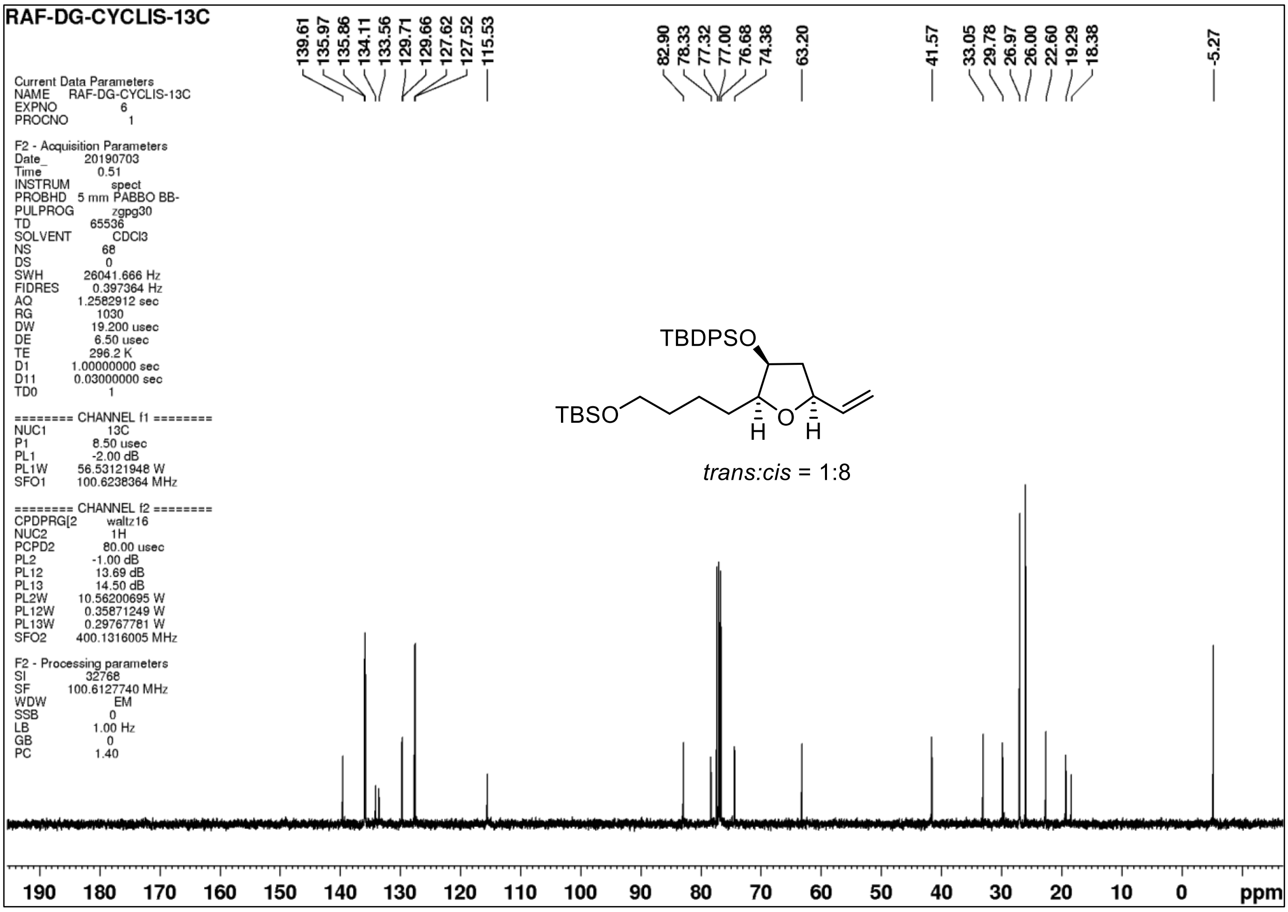
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **6e**



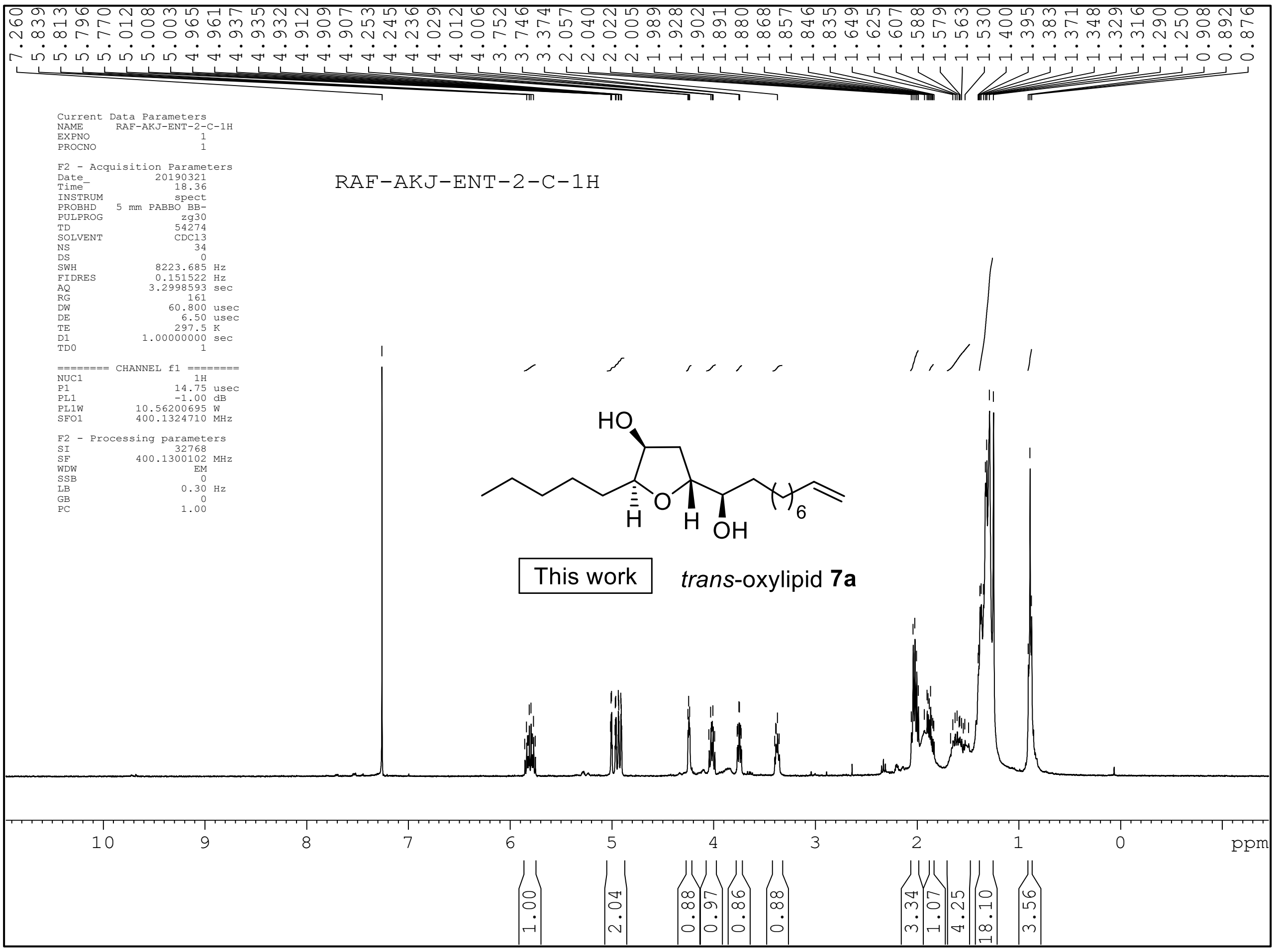


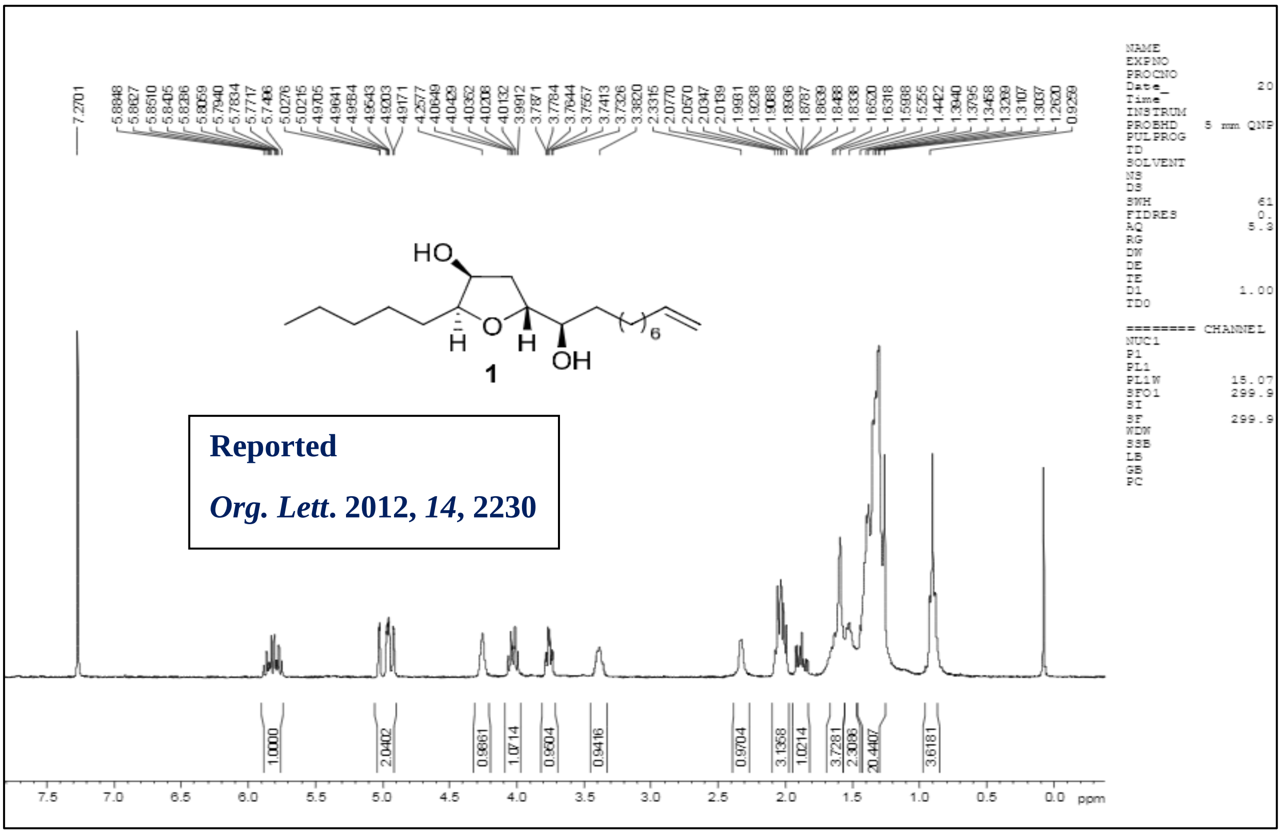
^{1}H NMR (500 MHz, CDCl$_3$)) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **6f**



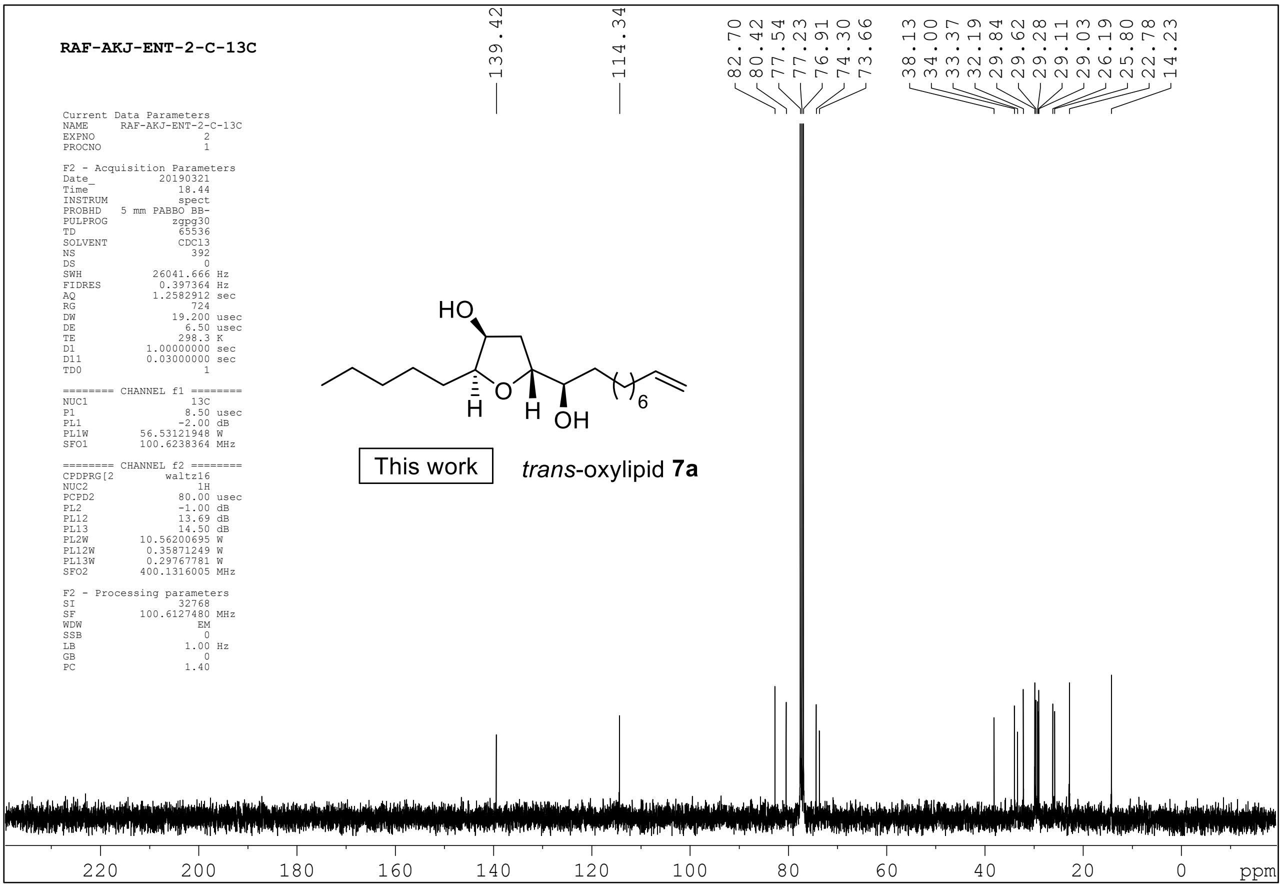


^{1}H NMR (400 MHz, CDCl$_3$) of compound **7a** and reported compound **7a** spectra





$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) of compound **7a** and reported compound **7a** spectra



```
Current Data Parameters
NAME     RAF-AKJ-ENT-2-C-13C
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190321
Time               18.44
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   392
DS                     0
SWH            26041.666 Hz
FIDRES          0.397364 Hz
AQ             1.2582912 sec
RG                   724
DW                19.200 usec
DE                  6.50 usec
TE                 298.3 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                    1

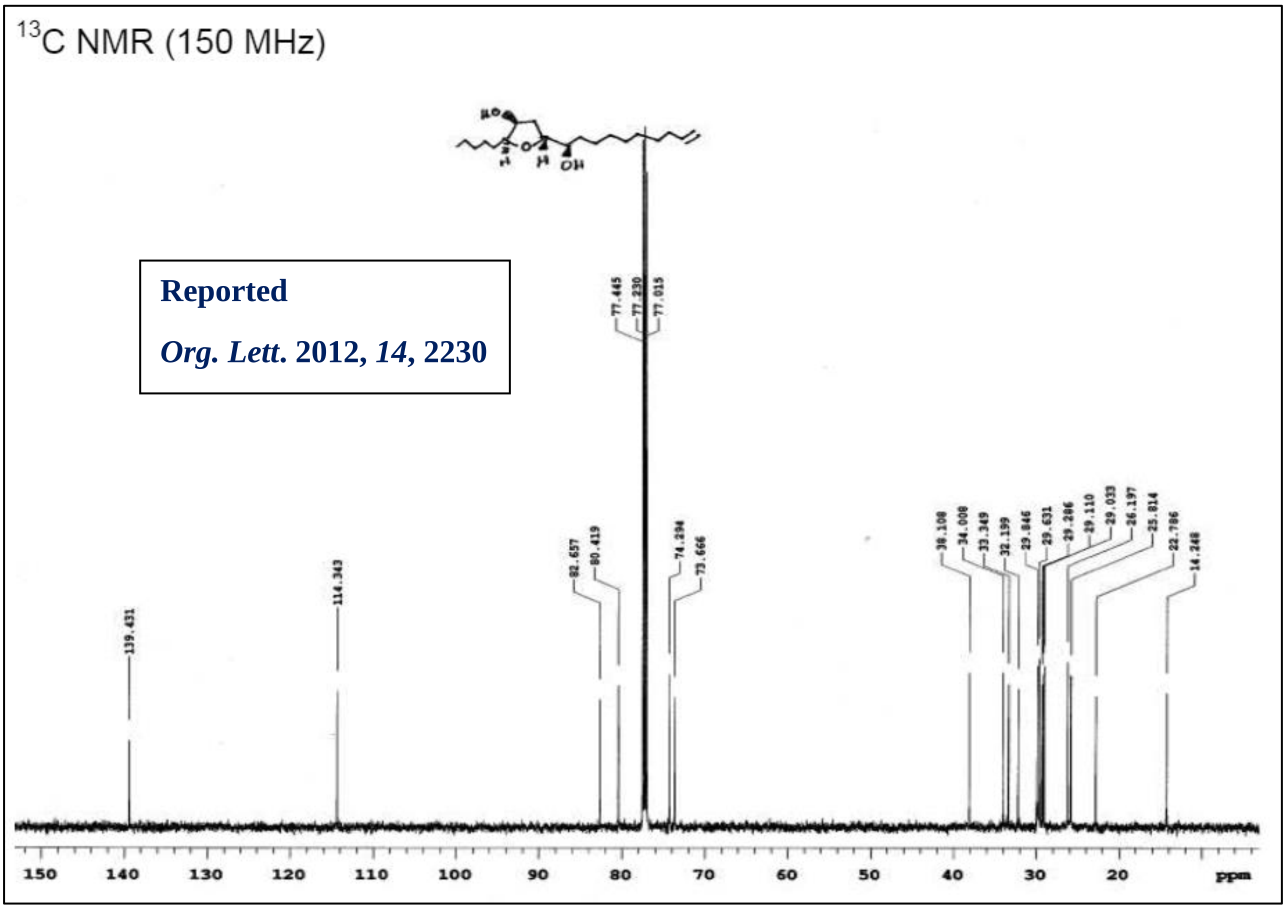
======== CHANNEL f1 ========
NUC1                 13C
P1                  8.50 usec
PL1                -2.00 dB
PL1W         56.53121948 W
SFO1         100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               13.69 dB
PL13               14.50 dB
PL2W         10.56200695 W
PL12W         0.35871249 W
PL13W         0.29767781 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127480 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

This work

trans-oxylipid **7a**



Reported

***Org. Lett.* 2012, *14*, 2230**

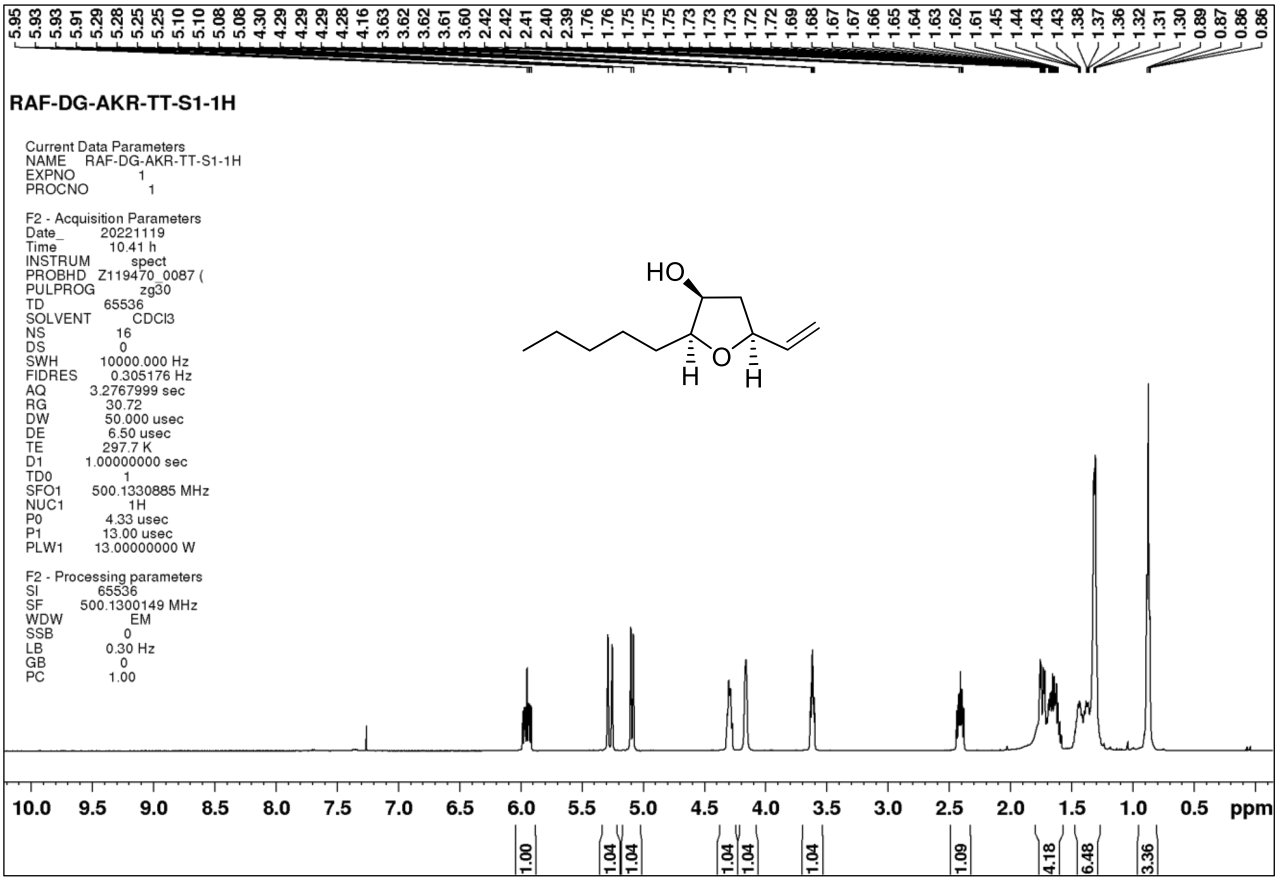
^{1}H NMR Comparison data of compound **7a**: Reported and our work

^{1}H NMR **Reported by Spilling** ***Org. Lett.* 2012, *14*, 2230**	**^{1}H NMR** **This work**
5.82 (m, 1H)	5.87–5.76 (m, 1H)
4.96 (m, 2H)	5.05–4.88 (m, 2H)
4.26 (m, 1H)	4.27–4.23 (m, 1H)
4.03 (dt, J = 6.6, 8.9 Hz, 1H)	4.02 (dt, J = 6.6, 8.9 Hz, 1H)
3.76 (td, J = 2.6, 6.9 Hz, 1H)	3.75 (td, J = 2.5, 6.9 Hz, 1H)
3.38 (m, 1H), 2.33 (brs, 1H)	3.42–3.34 (m, 1H)
2.04 (m, 3H)	2.07–1.98 (m, 3H)
1.88 (ddd, J = 4.5, 9.0, 13.5 Hz, 1H)	1.89–1.84 (m, 1H)
1.63 (m, 1H), 1.44–1.26 m, 20H)	1.68–1.50 (m, 4H), 1.41–1.26 (m, 18H)
0.90 (t, J = 5.8 Hz, 3H)	0.89 (t, J = 6.0 Hz, 3H)

^{13}C NMR Comparison data of compound **7a**: Reported and our work

^{13}C NMR **Reported by** **D. Spilling (*Org. Lett.* 2012, *14*, 2230)**	**^{13}C NMR** **Our Work**
139.4	139.4
114.3	114.3
82.7	82.7
80.4	80.4
74.3	74.3
73.7	73.7
38.1	38.1
34.0	34.0
33.4	33.4
32.2	32.2
29.9	29.8
29.7	29.6
29.3	29.3
29.1	29.1
29.0	29.0
26.2	26.2
25.8	25.8
22.8	22.8
14.2	14.2

^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) of compound **11**

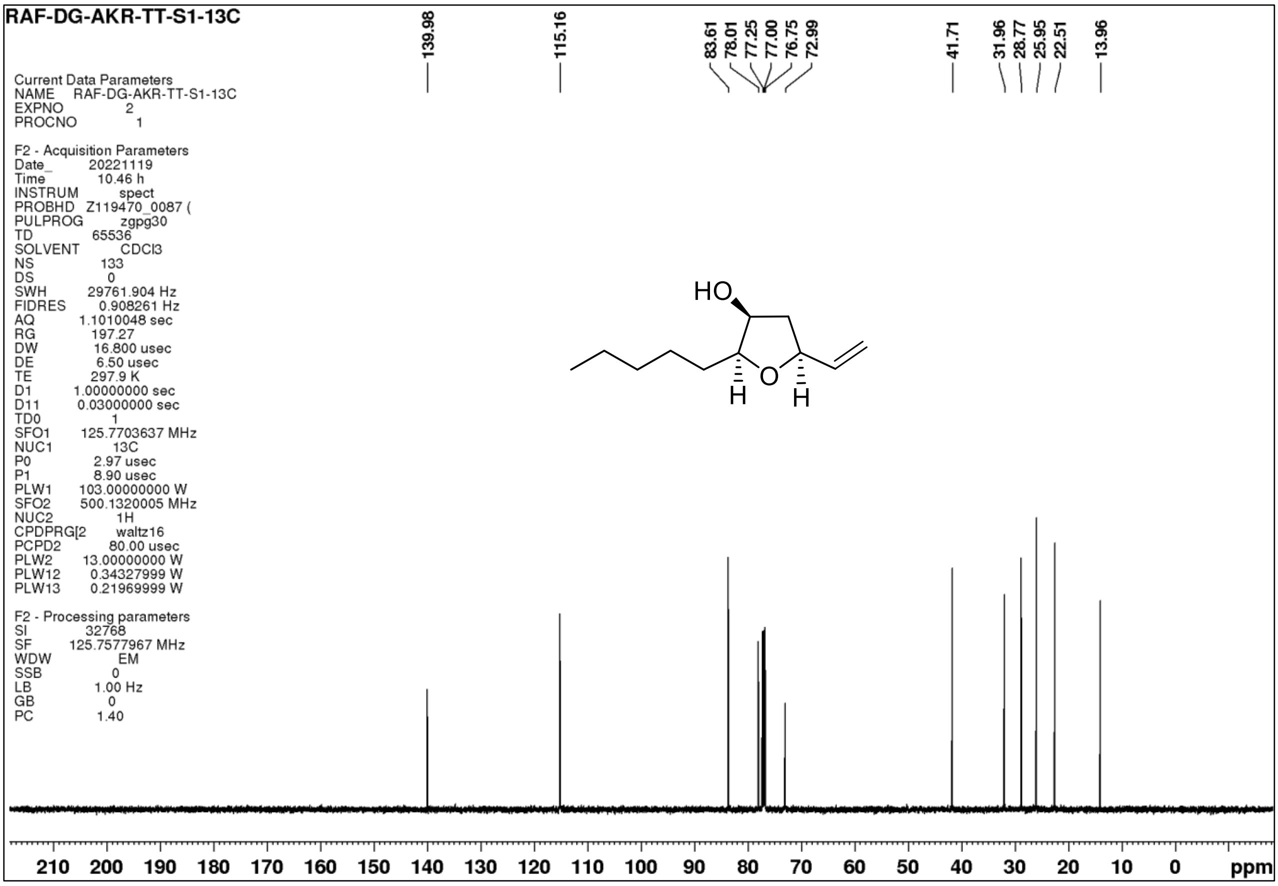


RAF-DG-AKR-TT-S1-1H

Current Data Parameters
NAME RAF-DG-AKR-TT-S1-1H
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20221119
Time 10.41 h
INSTRUM spect
PROBHD Z119470_0087 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 30.72
DW 50.000 usec
DE 6.50 usec
TE 297.7 K
D1 1.00000000 sec
TD0 1
SFO1 500.1330885 MHz
NUC1 1H
P0 4.33 usec
P1 13.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 500.1300149 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



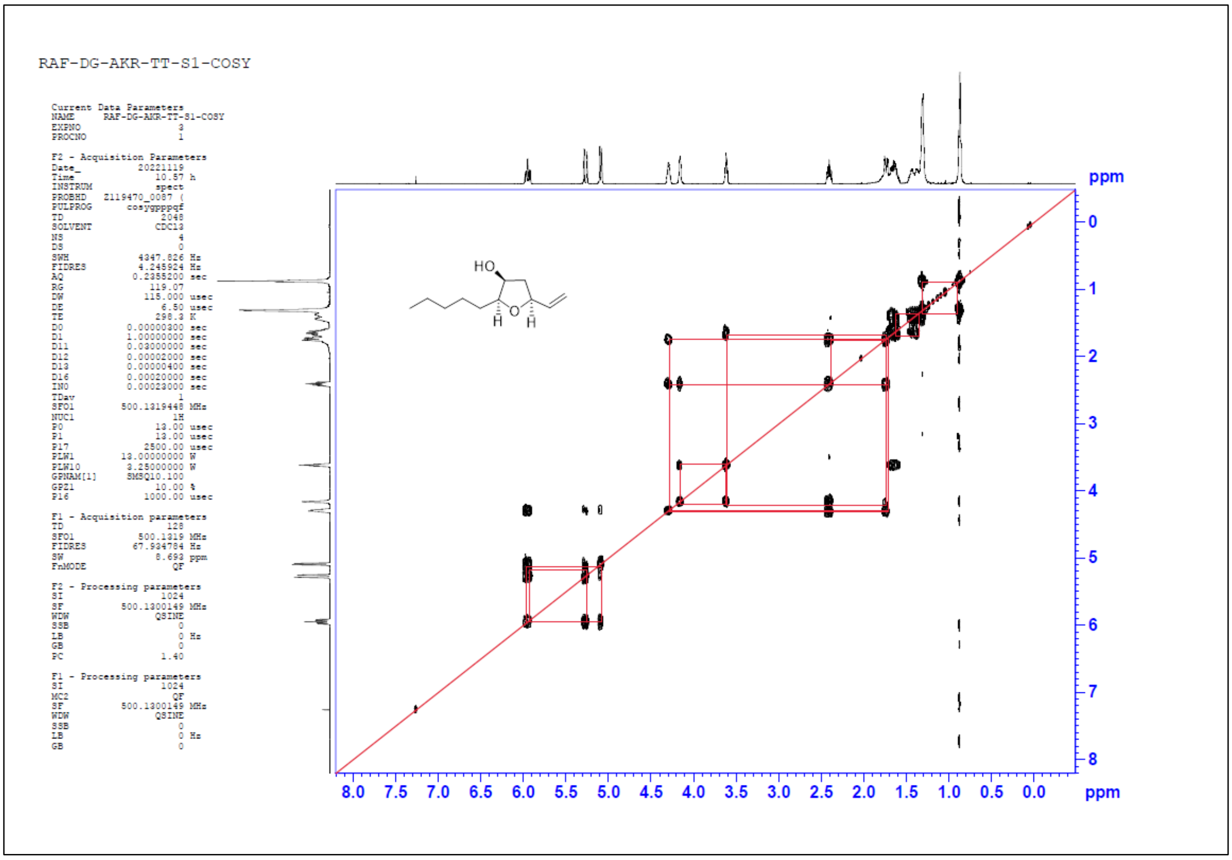
RAF-DG-AKR-TT-S1-13C

Current Data Parameters
NAME RAF-DG-AKR-TT-S1-13C
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20221119
Time 10.46 h
INSTRUM spect
PROBHD Z119470_0087 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 133
DS 0
SWH 29761.904 Hz
FIDRES 0.908261 Hz
AQ 1.1010048 sec
RG 197.27
DW 16.800 usec
DE 6.50 usec
TE 297.9 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7703637 MHz
NUC1 13C
P0 2.97 usec
P1 8.90 usec
PLW1 103.00000000 W
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.00000000 W
PLW12 0.34327999 W
PLW13 0.21969999 W

F2 - Processing parameters
SI 32768
SF 125.7577967 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

H-H COSY spectra of compound **11**



RAF-DG-AKR-TT-S1-COSY

```
Current Data Parameters
NAME     RAF-DG-AKR-TT-S1-COSY
EXPNO                      3
PROCNO                     1

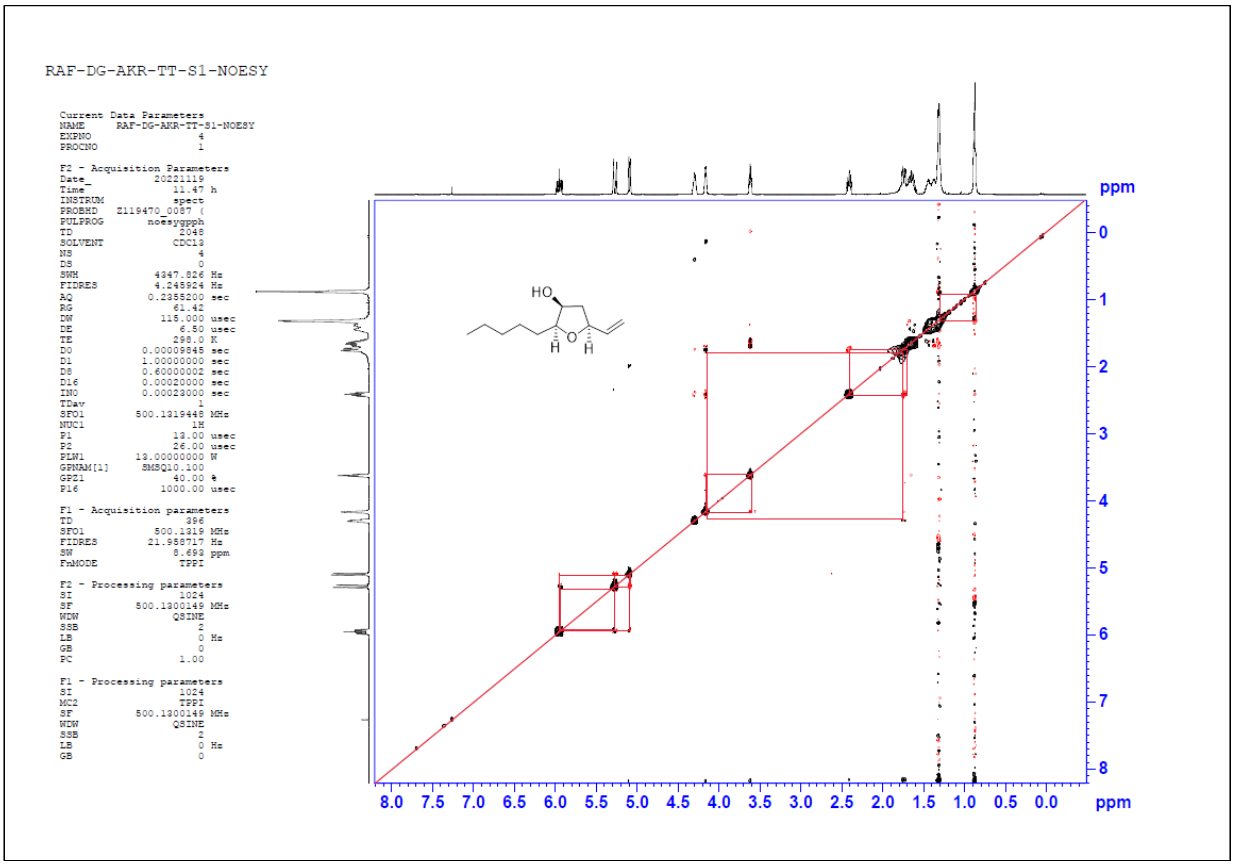
F2 - Acquisition Parameters
Date_              20221119
Time                  10.57 h
INSTRUM               spect
PROBHD   Z119470_0087 (
PULPROG           cosygpppqf
TD                     2048
SOLVENT               CDCl3
NS                        4
DS                        0
SWH                4347.826 Hz
FIDRES             4.245924 Hz
AQ                0.2355200 sec
RG                   119.07
DW                  115.000 usec
DE                     6.50 usec
TE                    298.3 K
D0               0.00000300 sec
D1               1.00000000 sec
D11              0.03000000 sec
D12              0.00002000 sec
D13              0.00000400 sec
D16              0.00020000 sec
IN0              0.00023000 sec
TDav                      1
SFO1            500.1319448 MHz
NUC1                     1H
P0                    13.00 usec
P1                    13.00 usec
P17                 2500.00 usec
PLW1            13.00000000 W
PLW10            3.25000000 W
GPNAM[1]         SMSQ10.100
GPZ1                  10.00 %
P16                 1000.00 usec

F1 - Acquisition parameters
TD                      128
SFO1               500.1319 MHz
FIDRES            67.934784 Hz
SW                    8.693 ppm
FnMODE                   QF

F2 - Processing parameters
SI                     1024
SF              500.1300149 MHz
WDW                   QSINE
SSB                       0
LB                        0 Hz
GB                        0
PC                     1.40

F1 - Processing parameters
SI                     1024
MC2                      QF
SF              500.1300149 MHz
WDW                   QSINE
SSB                       0
LB                        0 Hz
GB                        0
```

NOESY spectra of compound **11**



RAF-DG-AKR-TT-S1-NOESY

```
Current Data Parameters
NAME     RAF-DG-AKR-TT-S1-NOESY
EXPNO                      4
PROCNO                     1

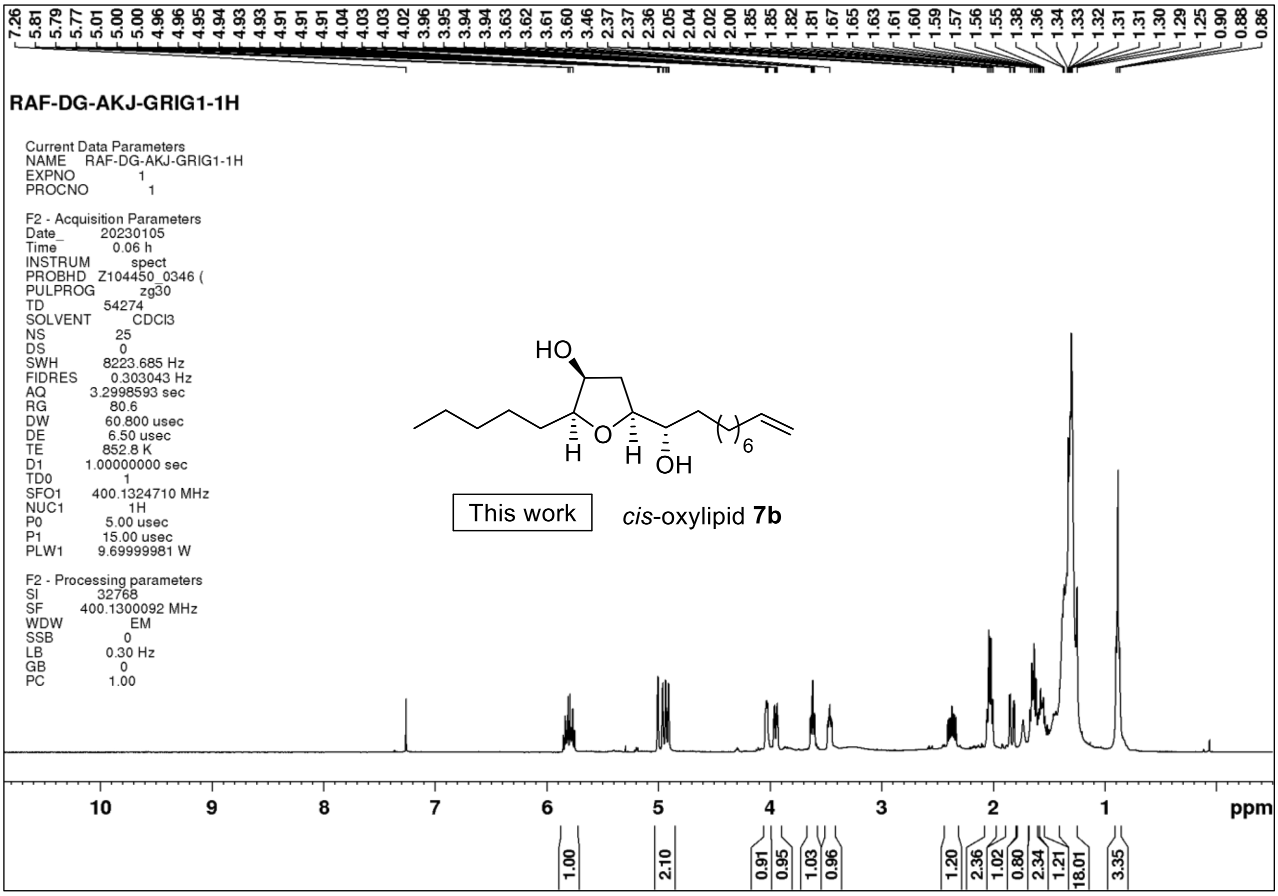
F2 - Acquisition Parameters
Date_              20221119
Time                  11.47 h
INSTRUM               spect
PROBHD   Z119470_0087 (
PULPROG           noesygpph
TD                     2048
SOLVENT               CDCl3
NS                        4
DS                        0
SWH                4347.826 Hz
FIDRES             4.245924 Hz
AQ                0.2355200 sec
RG                    61.42
DW                  115.000 usec
DE                     6.50 usec
TE                    298.0 K
D0               0.00009845 sec
D1               1.00000000 sec
D8               0.60000002 sec
D16              0.00020000 sec
IN0              0.00023000 sec
TDav                      1
SFO1            500.1319448 MHz
NUC1                     1H
P1                    13.00 usec
P2                    26.00 usec
PLW1            13.00000000 W
GPNAM[1]         SMSQ10.100
GPZ1                  40.00 %
P16                 1000.00 usec

F1 - Acquisition parameters
TD                      396
SFO1               500.1319 MHz
FIDRES            21.958717 Hz
SW                    8.693 ppm
FnMODE                 TPPI

F2 - Processing parameters
SI                     1024
SF              500.1300149 MHz
WDW                   QSINE
SSB                       2
LB                        0 Hz
GB                        0
PC                     1.00

F1 - Processing parameters
SI                     1024
MC2                    TPPI
SF              500.1300149 MHz
WDW                   QSINE
SSB                       2
LB                        0 Hz
GB                        0
```

^{1}H NMR (400 MHz, CDCl$_3$) of compound **7b** and reported compound **7b** spectra

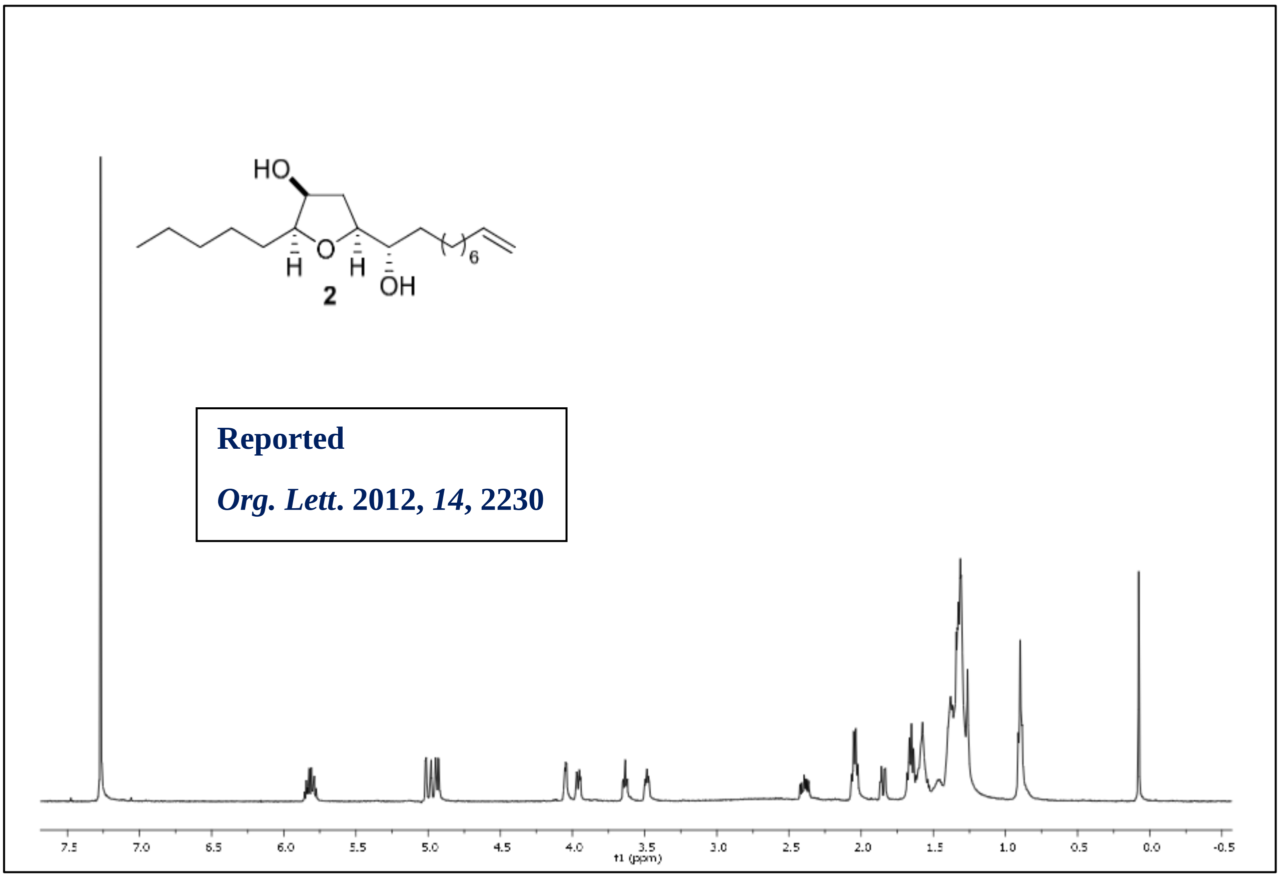


RAF-DG-AKJ-GRIG1-1H

```
Current Data Parameters
NAME     RAF-DG-AKJ-GRIG1-1H
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_         20230105
Time              0.06 h
INSTRUM          spect
PROBHD   Z104450_0346 (
PULPROG           zg30
TD               54274
SOLVENT          CDCl3
NS                  25
DS                   0
SWH          8223.685 Hz
FIDRES        0.303043 Hz
AQ           3.2998593 sec
RG                80.6
DW              60.800 usec
DE                6.50 usec
TE               852.8 K
D1          1.00000000 sec
TD0                  1
SFO1       400.1324710 MHz
NUC1                1H
P0                5.00 usec
P1               15.00 usec
PLW1        9.69999981 W

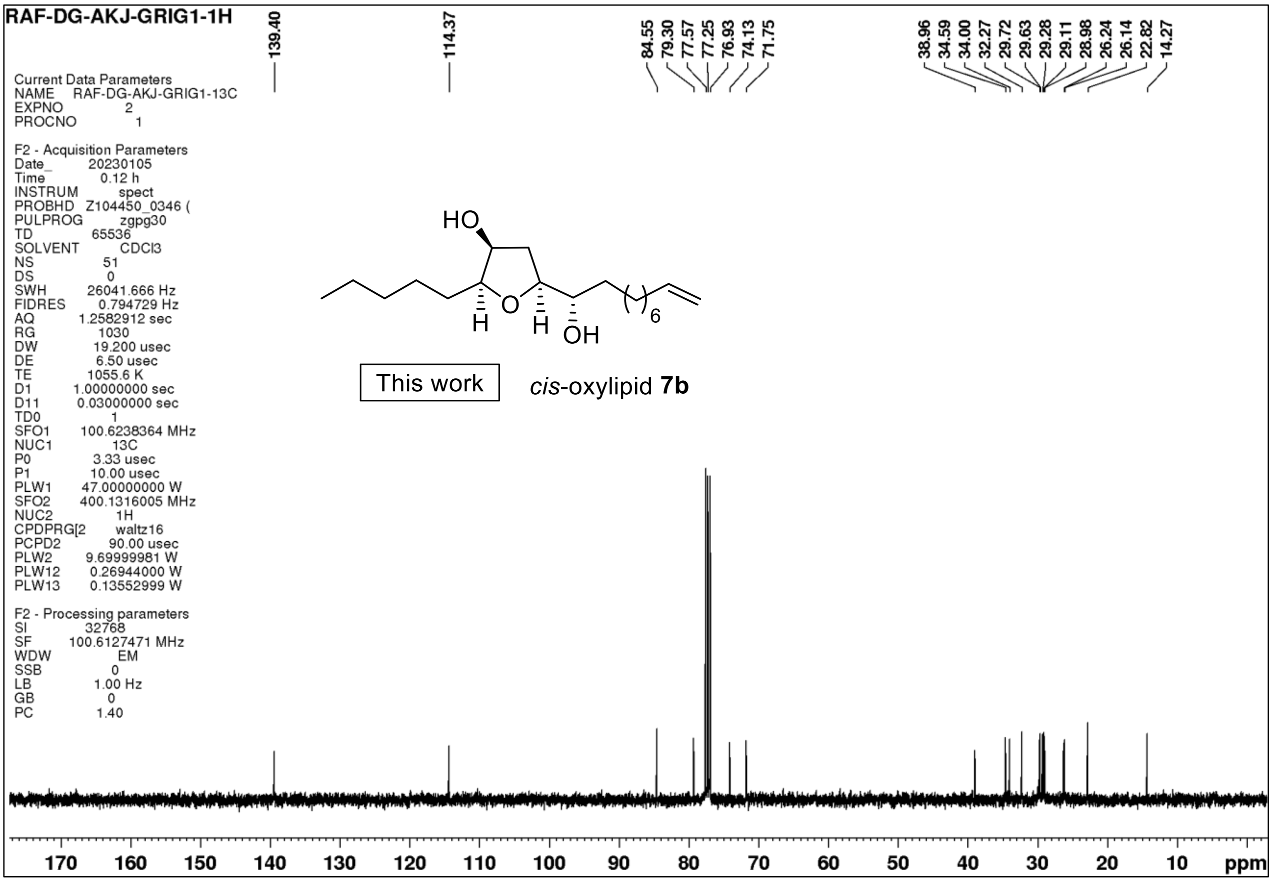
F2 - Processing parameters
SI               32768
SF         400.1300092 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```



Reported

***Org. Lett.* 2012, *14*, 2230**

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **7b** and reported compound **7b** spectra



```
RAF-DG-AKJ-GRIG1-1H

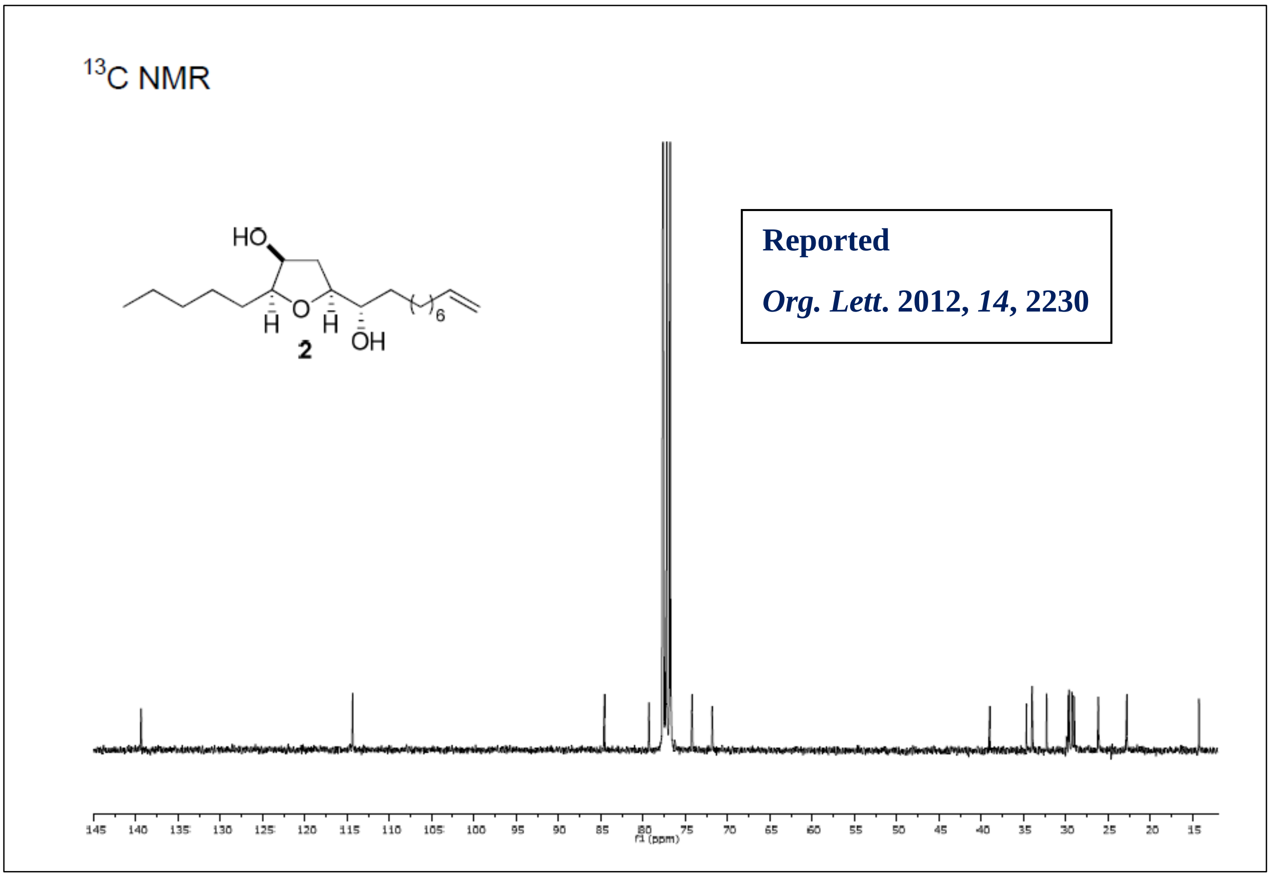
Current Data Parameters
NAME     RAF-DG-AKJ-GRIG1-13C
EXPNO             2
PROCNO            1

F2 - Acquisition Parameters
Date_        20230105
Time           0.12 h
INSTRUM        spect
PROBHD   Z104450_0346 (
PULPROG        zgpg30
TD           65536
SOLVENT        CDCl3
NS             51
DS              0
SWH         26041.666 Hz
FIDRES       0.794729 Hz
AQ         1.2582912 sec
RG            1030
DW           19.200 usec
DE            6.50 usec
TE          1055.6 K
D1        1.00000000 sec
D11       0.03000000 sec
TD0             1
SFO1      100.6238364 MHz
NUC1           13C
P0            3.33 usec
P1           10.00 usec
PLW1      47.00000000 W
SFO2      400.1316005 MHz
NUC2            1H
CPDPRG[2      waltz16
PCPD2         90.00 usec
PLW2       9.69999981 W
PLW12      0.26944000 W
PLW13      0.13552999 W

F2 - Processing parameters
SI            32768
SF        100.6127471 MHz
WDW             EM
SSB              0
LB            1.00 Hz
GB               0
PC            1.40
```

This work

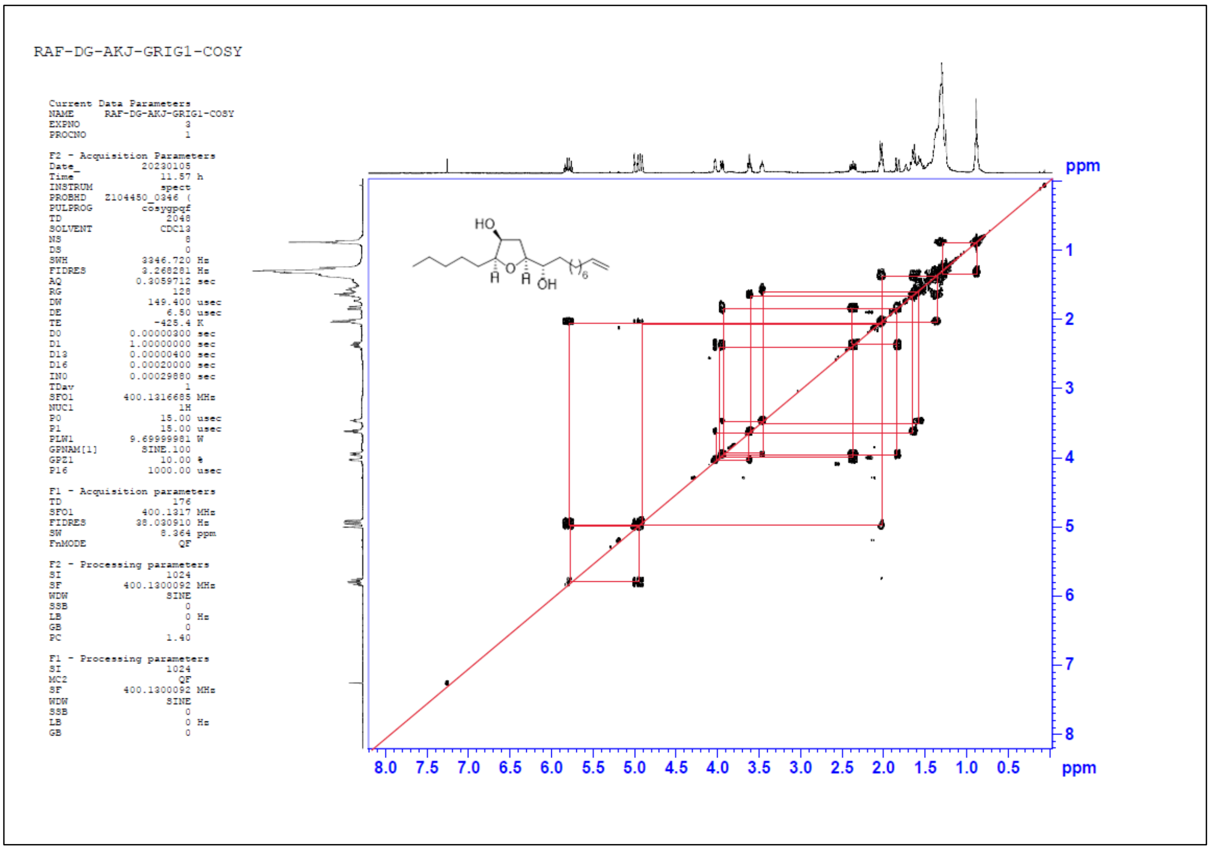
cis-oxylipid **7b**



Reported

***Org. Lett.* 2012, *14*, 2230**

H-H COSY spectra of compound **7b**



```
RAF-DG-AKJ-GRIG1-COSY

Current Data Parameters
NAME     RAF-DG-AKJ-GRIG1-COSY
EXPNO                    3
PROCNO                   1

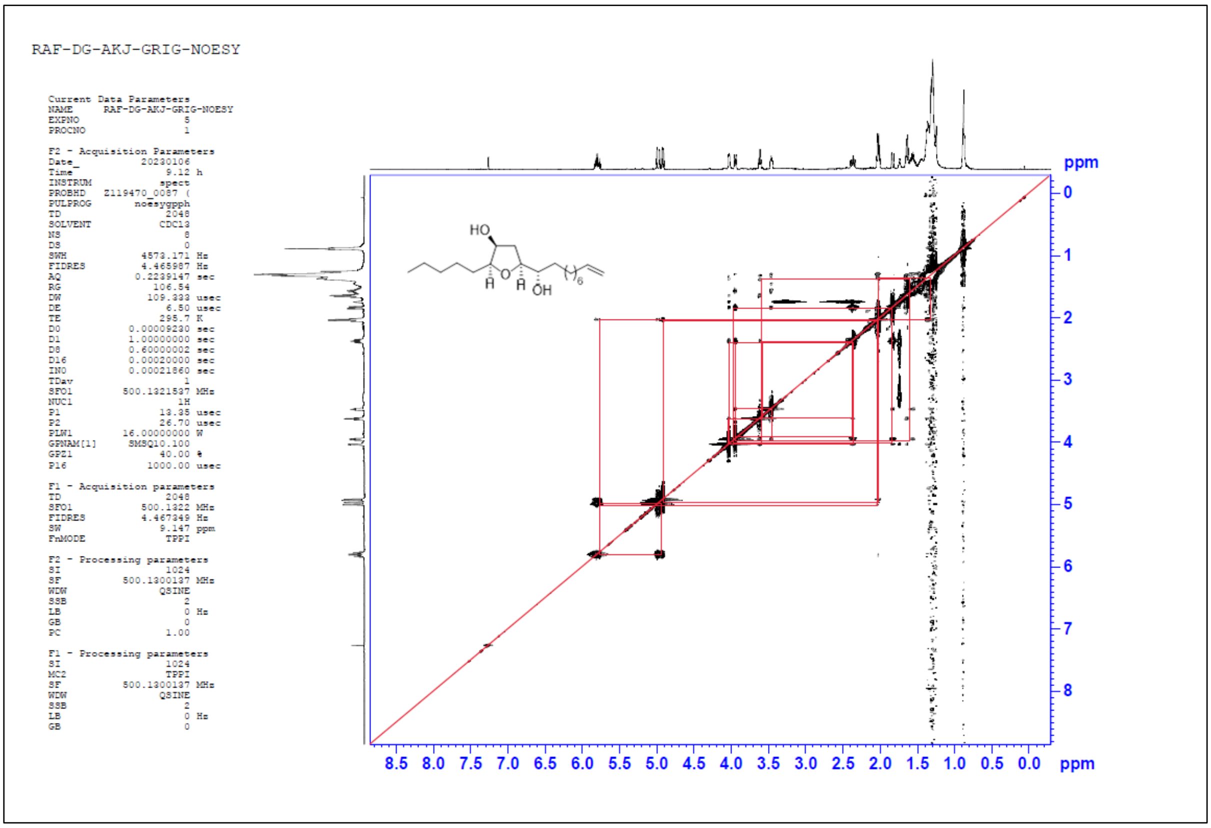
F2 - Acquisition Parameters
Date_             20230105
Time                 11.57 h
INSTRUM              spect
PROBHD   Z104450_0346 (
PULPROG           cosygpqf
TD                    2048
SOLVENT              CDCl3
NS                       8
DS                       0
SWH               3346.720 Hz
FIDRES            3.268281 Hz
AQ               0.3059712 sec
RG                     128
DW                 149.400 usec
DE                    6.50 usec
TE                  -425.4 K
D0              0.00000300 sec
D1              1.00000000 sec
D13             0.00000400 sec
D16             0.00020000 sec
IN0             0.00029880 sec
TDav                     1
SFO1           400.1316685 MHz
NUC1                    1H
P0                   15.00 usec
P1                   15.00 usec
PLW1            9.69999981 W
GPNAM[1]          SINE.100
GPZ1                 10.00 %
P16                1000.00 usec

F1 - Acquisition parameters
TD                     176
SFO1              400.1317 MHz
FIDRES           38.030910 Hz
SW                   8.364 ppm
FnMODE                  QF

F2 - Processing parameters
SI                    1024
SF             400.1300092 MHz
WDW                   SINE
SSB                      0
LB                       0 Hz
GB                       0
PC                    1.40

F1 - Processing parameters
SI                    1024
MC2                     QF
SF             400.1300092 MHz
WDW                   SINE
SSB                      0
LB                       0 Hz
GB                       0
```

NOESY spectra of compound **7b**



```
RAF-DG-AKJ-GRIG-NOESY

Current Data Parameters
NAME     RAF-DG-AKJ-GRIG-NOESY
EXPNO                    5
PROCNO                   1

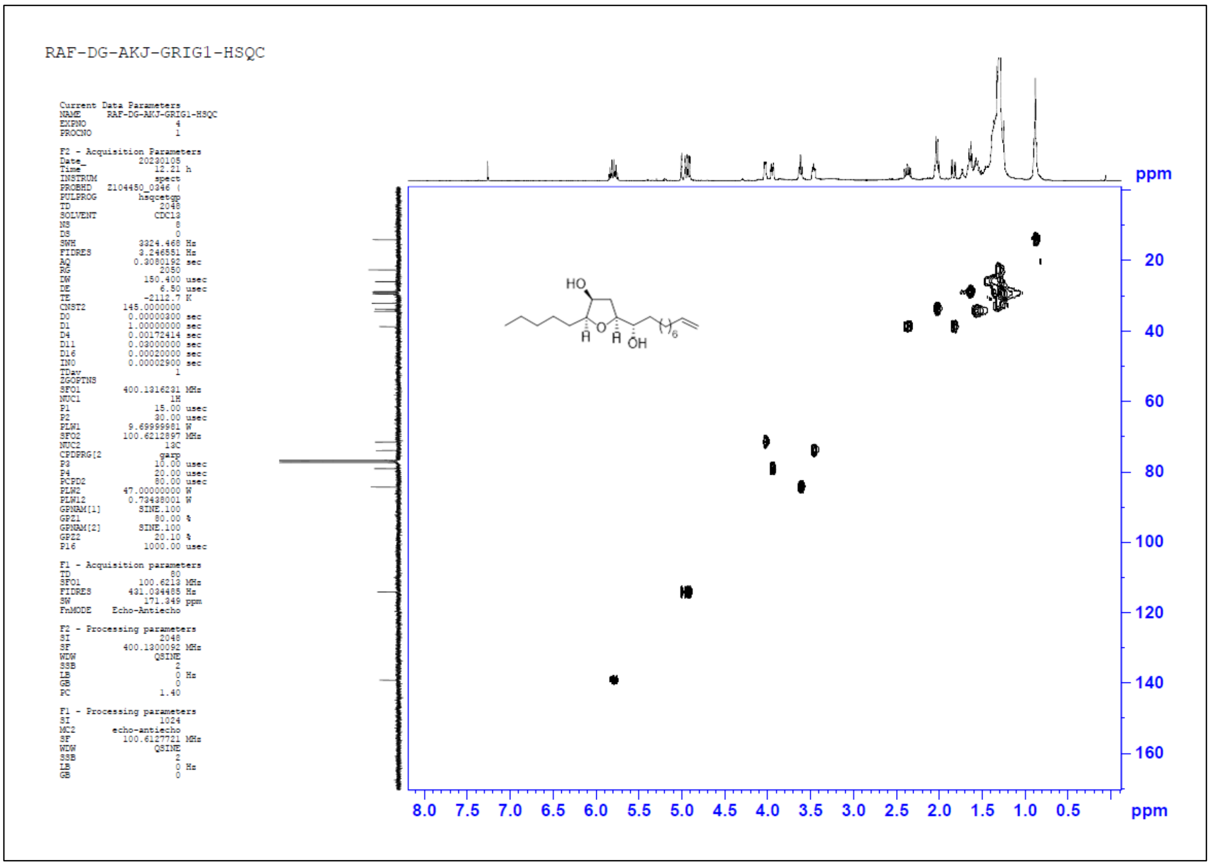
F2 - Acquisition Parameters
Date_             20230106
Time                  9.12 h
INSTRUM              spect
PROBHD   Z119470_0087 (
PULPROG          noesygpph
TD                    2048
SOLVENT              CDCl3
NS                       8
DS                       0
SWH               4573.171 Hz
FIDRES            4.465987 Hz
AQ               0.2239147 sec
RG                  106.54
DW                 109.333 usec
DE                    6.50 usec
TE                   295.7 K
D0              0.00009230 sec
D1              1.00000000 sec
D8              0.60000002 sec
D16             0.00020000 sec
IN0             0.00021860 sec
TDav                     1
SFO1           500.1321537 MHz
NUC1                    1H
P1                   13.35 usec
P2                   26.70 usec
PLW1           16.00000000 W
GPNAM[1]         SMSQ10.100
GPZ1                 40.00 %
P16                1000.00 usec

F1 - Acquisition parameters
TD                    2048
SFO1              500.1322 MHz
FIDRES            4.467349 Hz
SW                   9.147 ppm
FnMODE                TPPI

F2 - Processing parameters
SI                    1024
SF             500.1300137 MHz
WDW                  QSINE
SSB                      2
LB                       0 Hz
GB                       0
PC                    1.00

F1 - Processing parameters
SI                    1024
MC2                   TPPI
SF             500.1300137 MHz
WDW                  QSINE
SSB                      2
LB                       0 Hz
GB                       0
```

HSQC spectra of compound **7b**



```
Current Data Parameters
NAME     RAF-DG-AKJ-GRIG1-HSQC
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20230105
Time                12.21 h
INSTRUM             spect
PROBHD   Z104450_0346 (
PULPROG          hsqcetgp
TD                   2048
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              3324.468 Hz
FIDRES           3.246551 Hz
AQ              0.3080192 sec
RG                   2050
DW                150.400 usec
DE                   6.50 usec
TE                -2112.7 K
CNST2         145.0000000
D0             0.00000300 sec
D1             1.00000000 sec
D4             0.00172414 sec
D11            0.03000000 sec
D16            0.00020000 sec
IN0            0.00002900 sec
TDav                    1
ZGOPTNS
SFO1          400.1316231 MHz
NUC1                   1H
P1                  15.00 usec
P2                  30.00 usec
PLW1           9.69999981 W
SFO2          100.6212897 MHz
NUC2                  13C
CPDPRG[2             garp
P3                  10.00 usec
P4                  20.00 usec
PCPD2               80.00 usec
PLW2          47.00000000 W
PLW12          0.73438001 W
GPNAM[1]         SINE.100
GPZ1                80.00 %
GPNAM[2]         SINE.100
GPZ2                20.10 %
P16               1000.00 usec

F1 - Acquisition parameters
TD                     80
SFO1             100.6213 MHz
FIDRES         431.034485 Hz
SW                171.349 ppm
FnMODE       Echo-Antiecho

F2 - Processing parameters
SI                   2048
SF            400.1300092 MHz
WDW                 QSINE
SSB                     2
LB                      0 Hz
GB                      0
PC                   1.40

F1 - Processing parameters
SI                   1024
MC2          echo-antiecho
SF            100.6127721 MHz
WDW                 QSINE
SSB                     2
LB                      0 Hz
GB                      0
```

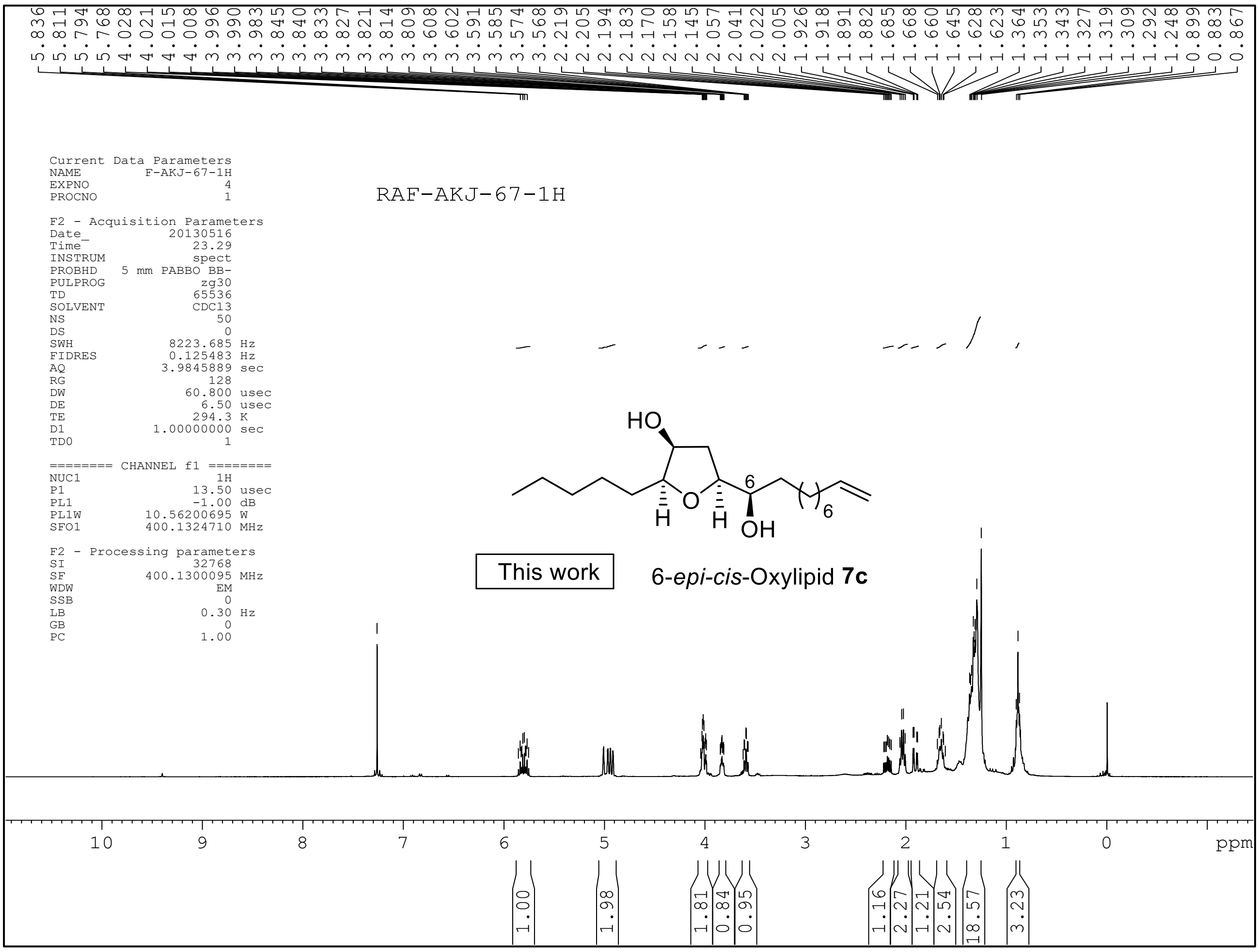
^{1}H NMR Comparison data of compound **7b**: Reported and our work

^{1}**H NMR Reported by Spilling** ***Org. Lett.* 2012, *14*, 2230**	^{1}**H NMR** **This work**
5.82 (m, 1H)	5.86–5.74 (m, 1H)
4.96 (m, 1H) (as per spectra this should be 2H)	5.03–4.88 (m, 2H)
4.05 (dd, *J* = 2.7, 5.3 Hz, 1H)	4.03 (dd, *J* = 5.4, 2.7 Hz, 1H)
3.96 (dt, *J* = 2.8, 9.7 Hz, 1H)	3.94 (dt, *J* = 9.4, 2.5 Hz, 1H)
3.64 (td, *J* = 2.6, 6.8 Hz, 1H)	3.62 (td, *J* = 6.8, 2.6 Hz, 1H)
3.48 (ddd, *J* = 2.2, 5.1, 8.7 Hz, 1H)	3.47 (ddd, *J* = 8.5, 5.0, 2.2 Hz, 1H)
2.39 (ddd, *J* = 5.6, 9.2, 14.7 Hz, 1H)	2.38 (ddd, *J* = 14.6, 9.4, 5.4 Hz, 1H)
2.04 (dd, *J* = 6.9, 14.3 Hz, 3H)	2.03 (dd, *J* = 14.4, 6.8 Hz, 2H)
1.85 (dd, *J* = 3.4, 14.1 Hz, 1H)	1.83 (dd, *J* = 14.3, 3.6 Hz, 1H)
1.68–1.54 (m, 1H), 1.39–1.26 m, 19H)	1.73 (br s, 1H), 1.68–1.62 (m, 2H), 1.59–1.53 (m, 1H), 1.39–1.25 (m, 18H)
0.90 (t, *J* = 6.8 Hz, 3H)	0.88 (t, *J* = 6.6 Hz, 3H)

^{13}C NMR Comparison data of compound **7b**: Reported and our work

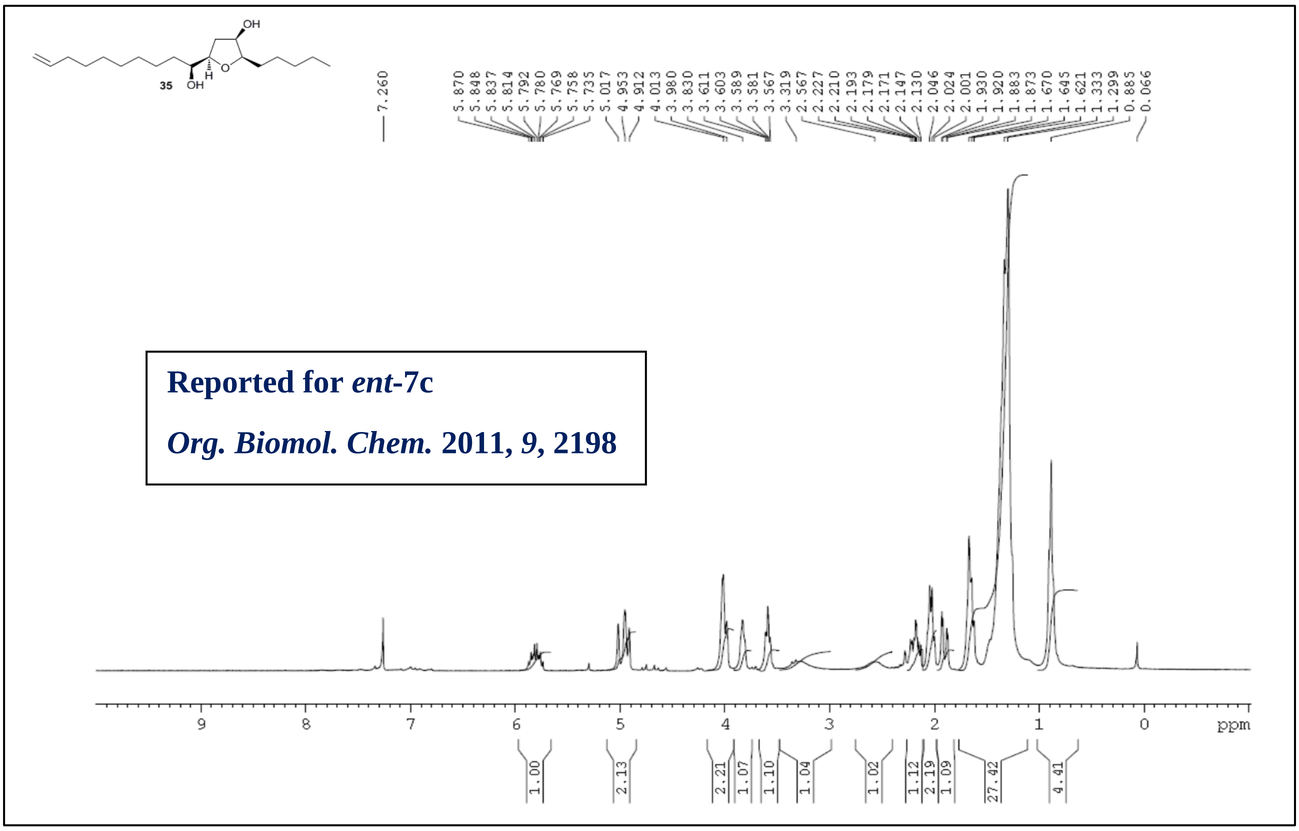
^{13}C NMR Reported by Spilling (*Org. Lett.* 2012, *14*, 2230)	**^{13}C NMR Our Work**
139.4	139.4
114.4	114.4
84.6	84.6
79.3	79.3
74.2	74.1
71.8	71.8
39.0	39.0
34.6	34.6
34.4 (as per spectra this should be 34.0)	34.0
32.3	32.3
29.7	29.7
29.6	29.6
29.3	29.3
29.1	29.1
29.0	29.0
26.2	26.2
26.1	26.1
22.8	22.8
14.3	14.3

^{1}H NMR (400 MHz, $CDCl_3$) of compound **7c** and reported compound ***ent*-7c** spectra



This work

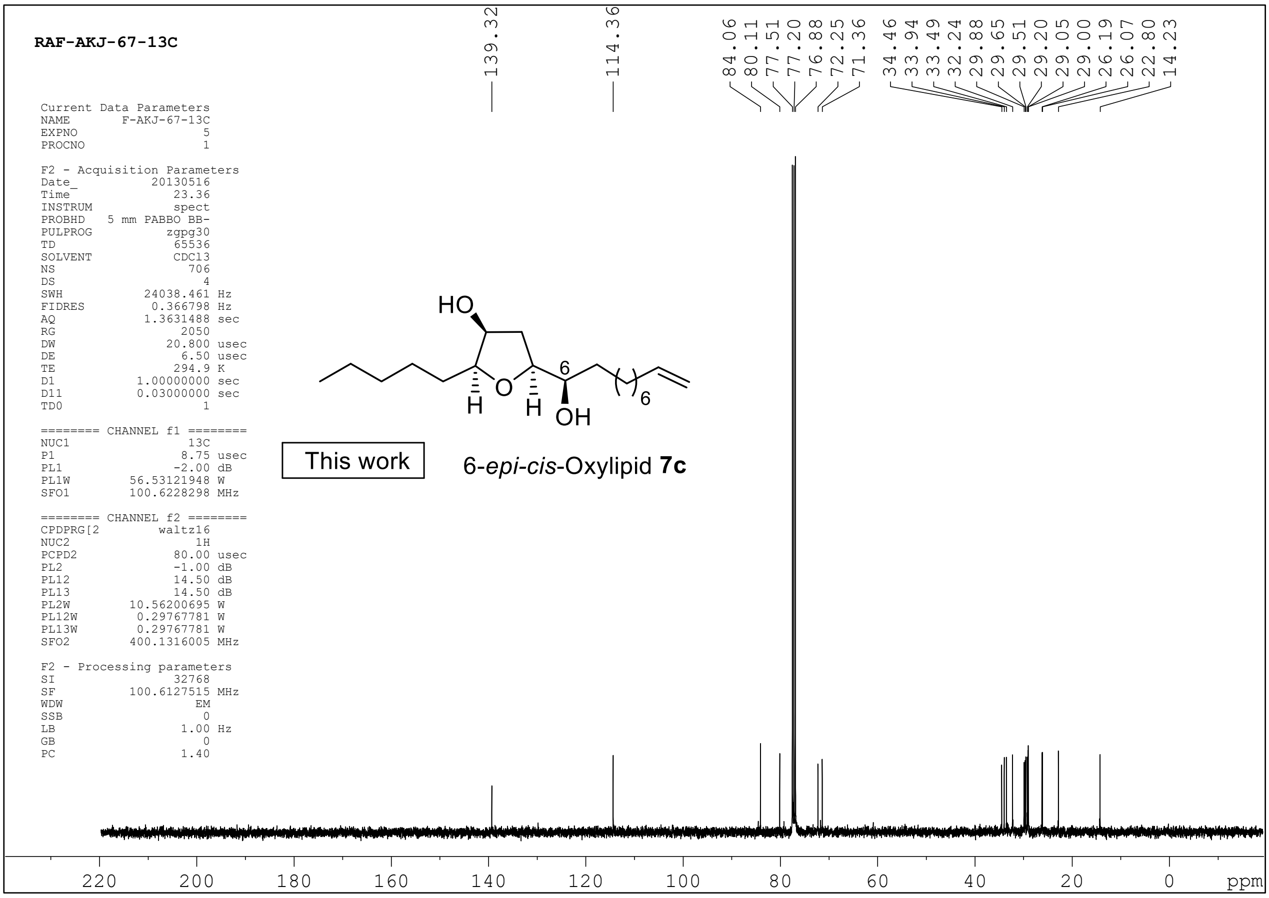
6-*epi*-*cis*-Oxylipid **7c**



Reported for *ent*-7c

***Org. Biomol. Chem.* 2011, *9*, 2198**

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **7c** and reported compound ***ent*-7c** spectra



```
RAF-AKJ-67-13C

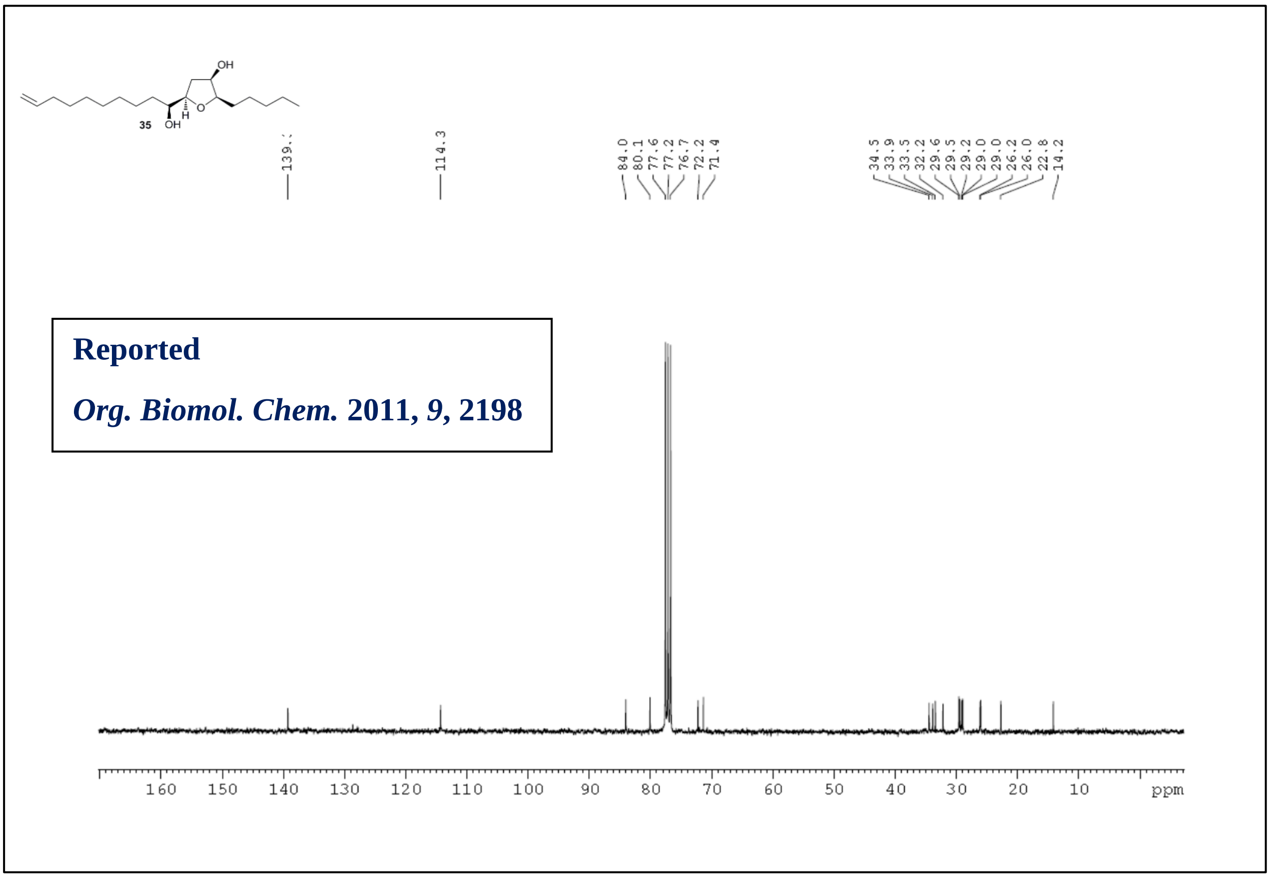
Current Data Parameters
NAME       F-AKJ-67-13C
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20130516
Time              23.36
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  706
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631488 sec
RG                 2050
DW               20.800 usec
DE                 6.50 usec
TE                294.9 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 8.75 usec
PL1               -2.00 dB
PL1W        56.53121948 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -1.00 dB
PL12              14.50 dB
PL13              14.50 dB
PL2W        10.56200695 W
PL12W        0.29767781 W
PL13W        0.29767781 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127515 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

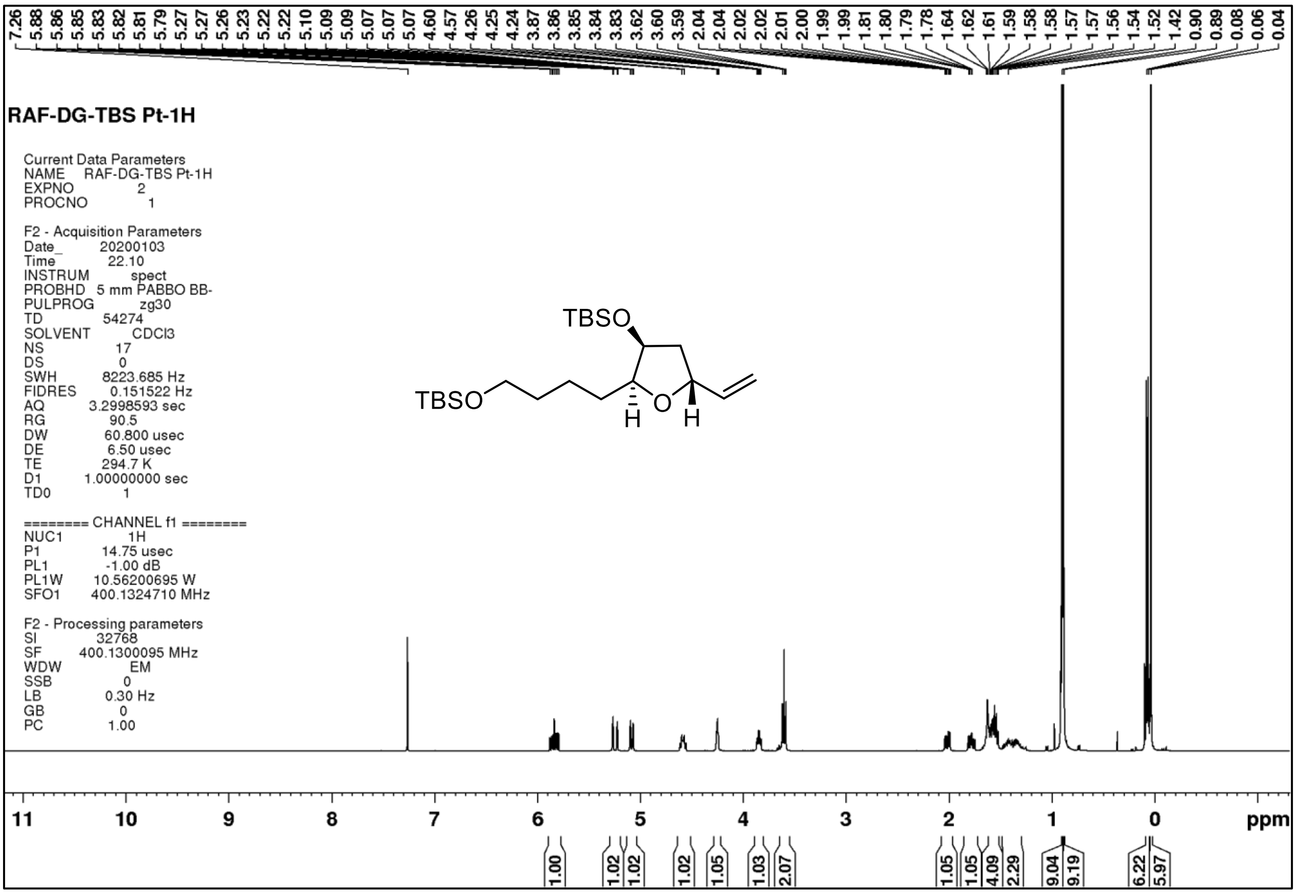


^{1}H NMR Comparison data of compound **7c**: Reported for *ent*-**7c** and our work

^{1}H NMR *ent*-7c **McErlean (*Org. Biomol. Chem.* 2011, *9*, 2198)**	**^{1}H NMR** **This work**
5.80 (dddd, *J* =16.8, 10.2, 6.6, 6.6 Hz, 1H)	5.80 (dddd, *J* = 16.9, 10.1, 6.8, 6.8 Hz, 1H)
4.99 (dd, *J* = 17.4, 1.8 Hz 1H) 4.93 (d, *J* = 11.1 Hz 1H)	4.98 (dd, *J* = 17.4, 1.6 Hz 1H) 4.92 (d, *J* = 11.1 Hz 1H)
4.02–3.97 (m, 1H)	4.03–3.98 (m, 2H)
3.83–3.81 (m, 1H)	3.84–3.80 (m, 1H)
3.59 (ddd, *J* = 6.9, 6.9, 2.4 Hz, 1H)	3.59 (td, *J* = 6.7, 2.5 Hz, 1H)
3.26 (brs, 1H)	
2.49 (brs, 1H)	
2.18 (ddd, *J* = 14.1, 9.9, 5.4 Hz, 1H)	2.18 (ddd, *J* = 14.2, 9.8, 5.4 Hz, 1H)
2.03 (dd, *J* = 13.5, 6.6 Hz, 2H)	2.03 (q, *J* = 6.5 Hz, 2H)
1.92 (dd, *J* = 14.1, 3.3 Hz, 1H)	1.90 (dd, *J* = 14.2, 3.3 Hz, 1H)
1.69–1.62 (m, 1H)	1.68–1.59 (m, 2H)
1.36–1.25 (m, 19H)	1.42–1.24 (m, 18H)
0.89 (app t, *J* = 6.5 Hz, 3H)	0.88 (t, *J* = 6.7 Hz, 3H)

^{13}C NMR McErlean **(*Org. Biomol. Chem,* 2011, *9*, 2198)**	**^{13}C NMR** **Our Work**
139.3	139.3
114.3	114.4
84.0	84.0
80.1	80.1
72.2	72.2
71.4	71.4
34.5	34.5
33.9	33.9
33.5	33.5
32.2	32.2
29.6	29.6
29.5	29.5
29.2	29.2
29.02	29.04
28.97	29.0
26.2	26.2
26.0	26.1
22.8	22.8
14.2	14.2

^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **12**



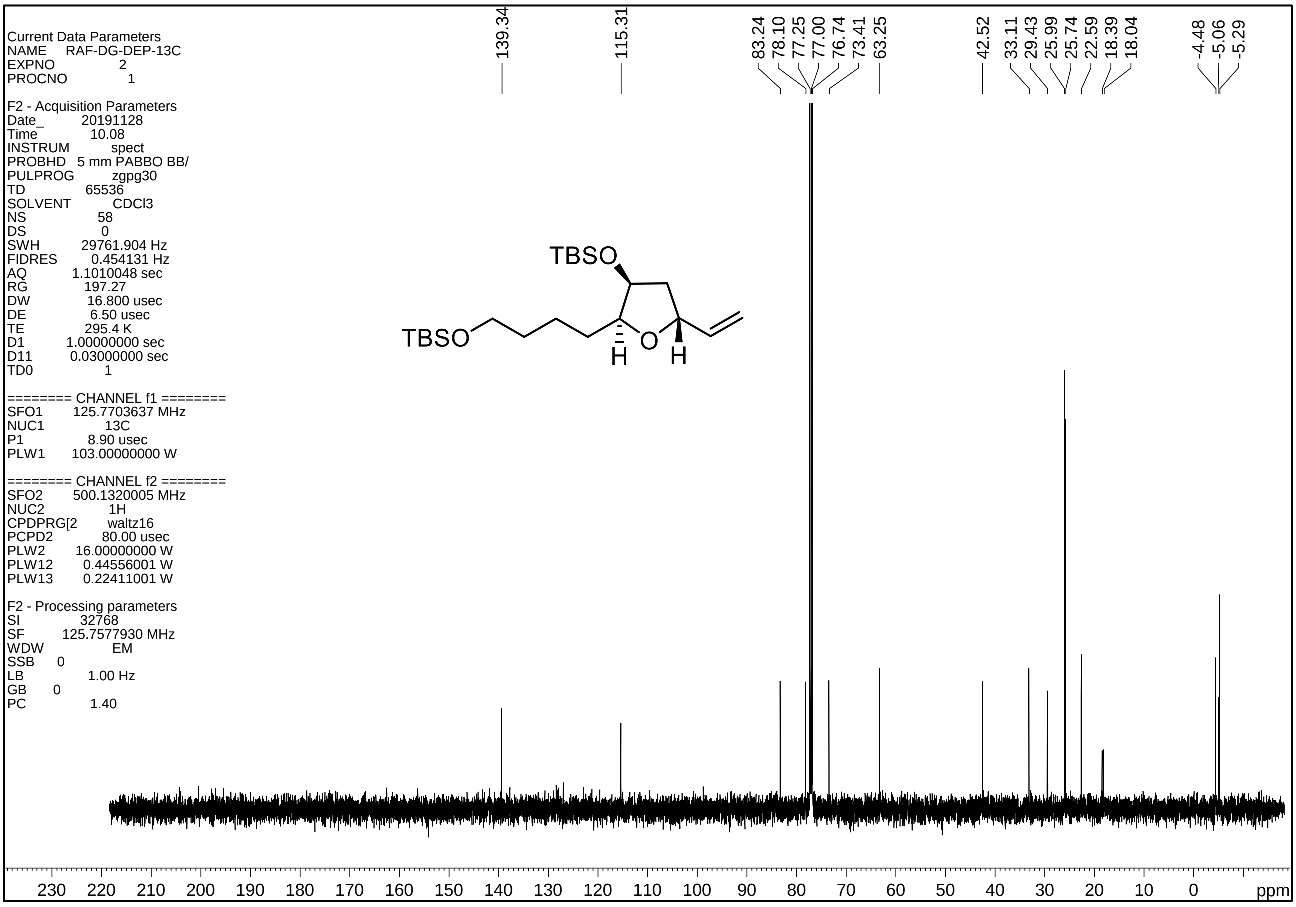
RAF-DG-TBS Pt-1H

```
Current Data Parameters
NAME     RAF-DG-TBS Pt-1H
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_        20200103
Time            22.10
INSTRUM         spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              54274
SOLVENT         CDCl3
NS                 17
DS                  0
SWH       8223.685 Hz
FIDRES    0.151522 Hz
AQ      3.2998593 sec
RG               90.5
DW         60.800 usec
DE          6.50 usec
TE            294.7 K
D1     1.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               1H
P1        14.75 usec
PL1         -1.00 dB
PL1W  10.56200695 W
SFO1  400.1324710 MHz

F2 - Processing parameters
SI              32768
SF     400.1300095 MHz
WDW                EM
SSB                 0
LB            0.30 Hz
GB                  0
PC               1.00
```



```
Current Data Parameters
NAME     RAF-DG-DEP-13C
EXPNO              2
PROCNO             1

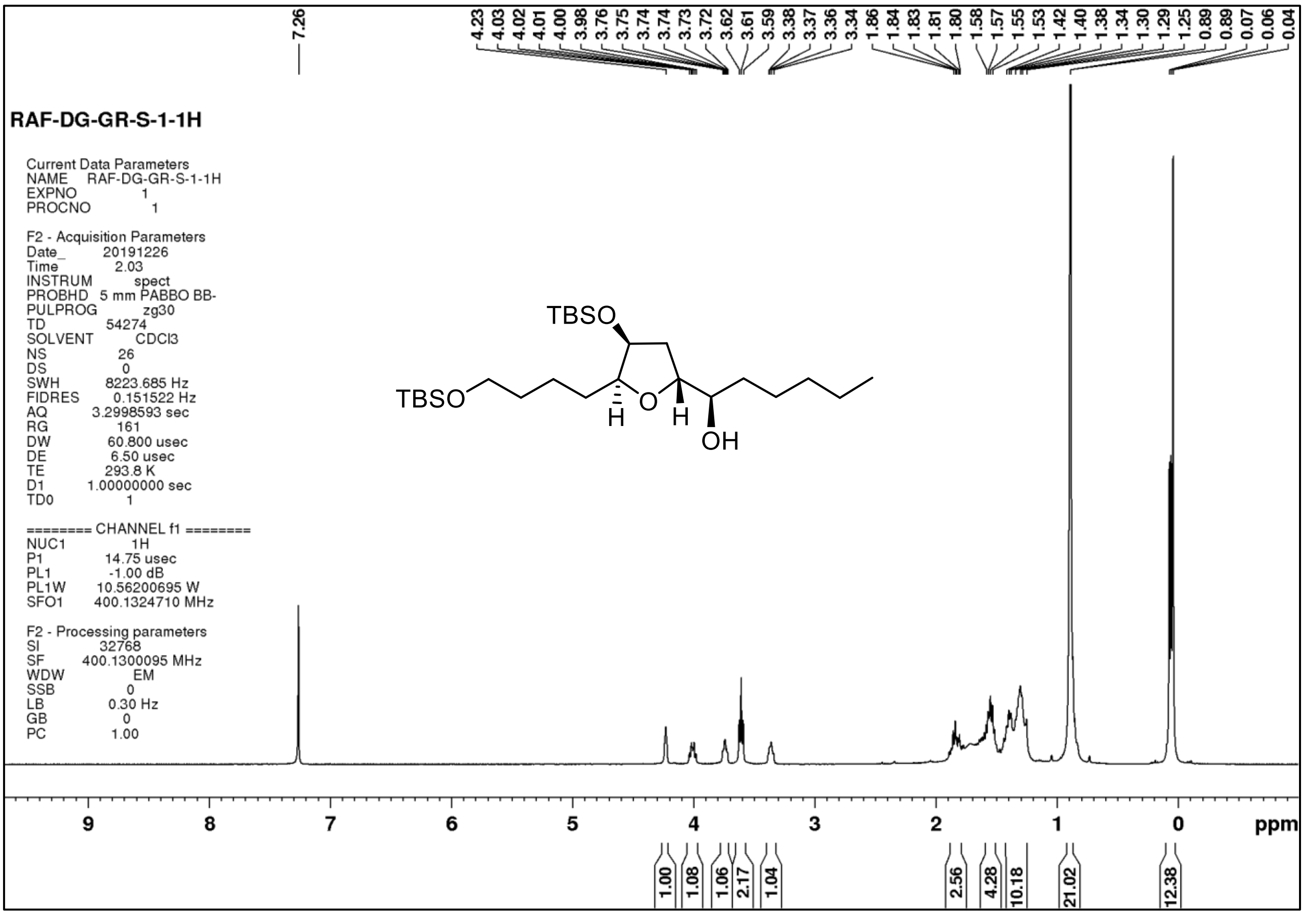
F2 - Acquisition Parameters
Date_        20191128
Time            10.08
INSTRUM         spect
PROBHD   5 mm PABBO BB/
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                 58
DS                  0
SWH      29761.904 Hz
FIDRES    0.454131 Hz
AQ      1.1010048 sec
RG             197.27
DW         16.800 usec
DE          6.50 usec
TE            295.4 K
D1     1.00000000 sec
D11    0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1  125.7703637 MHz
NUC1              13C
P1          8.90 usec
PLW1  103.00000000 W

======== CHANNEL f2 ========
SFO2  500.1320005 MHz
NUC2               1H
CPDPRG[2      waltz16
PCPD2     80.00 usec
PLW2  16.00000000 W
PLW12  0.44556001 W
PLW13  0.22411001 W

F2 - Processing parameters
SI              32768
SF     125.7577930 MHz
WDW                EM
SSB     0
LB            1.00 Hz
GB      0
PC               1.40
```

^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **13**

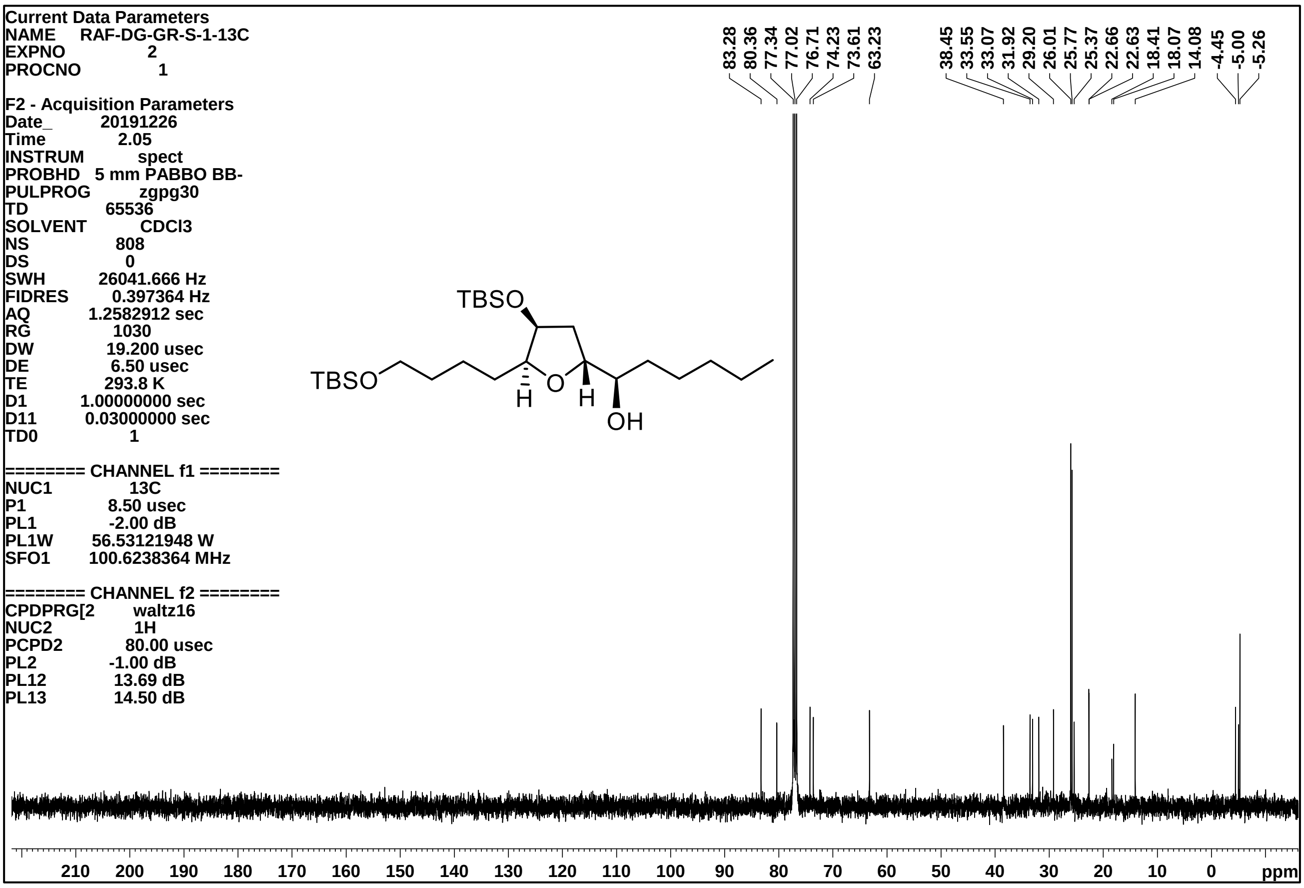


```
Current Data Parameters
NAME     RAF-DG-GR-S-1-1H
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_          20191226
Time               2.03
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                54274
SOLVENT           CDCl3
NS                   26
DS                    0
SWH         8223.685 Hz
FIDRES      0.151522 Hz
AQ        3.2998593 sec
RG                  161
DW          60.800 usec
DE            6.50 usec
TE              293.8 K
D1       1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1           14.75 usec
PL1            -1.00 dB
PL1W      10.56200695 W
SFO1     400.1324710 MHz

F2 - Processing parameters
SI                32768
SF       400.1300095 MHz
WDW                  EM
SSB                   0
LB              0.30 Hz
GB                    0
PC                 1.00
```



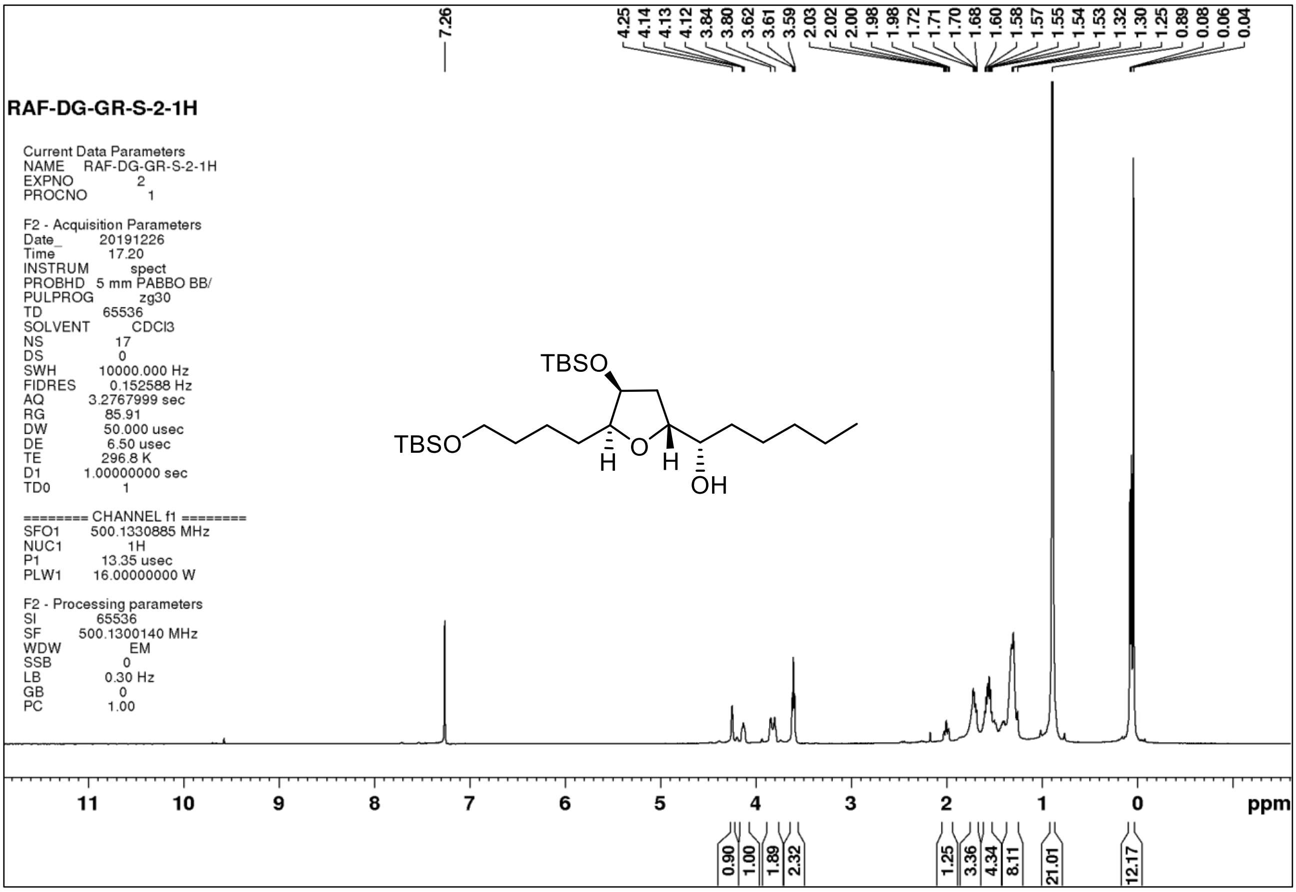
```
Current Data Parameters
NAME     RAF-DG-GR-S-1-13C
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_          20191226
Time               2.05
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  808
DS                    0
SWH        26041.666 Hz
FIDRES      0.397364 Hz
AQ        1.2582912 sec
RG                 1030
DW          19.200 usec
DE            6.50 usec
TE              293.8 K
D1       1.00000000 sec
D11      0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1            8.50 usec
PL1            -2.00 dB
PL1W      56.53121948 W
SFO1     100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2        80.00 usec
PL2            -1.00 dB
PL12           13.69 dB
PL13           14.50 dB
```

^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) of compound **13′**



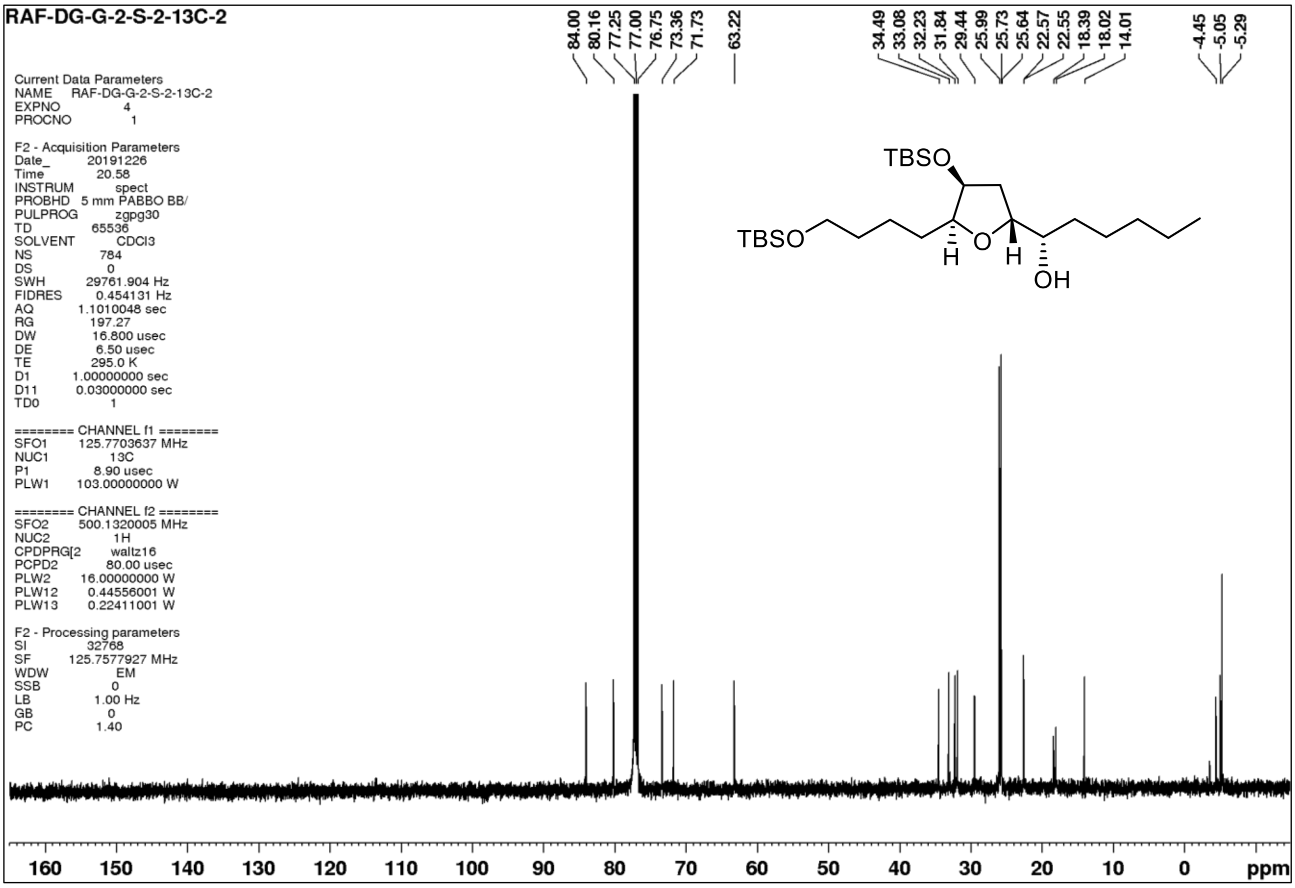
RAF-DG-GR-S-2-1H

```
Current Data Parameters
NAME     RAF-DG-GR-S-2-1H
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_        20191226
Time            17.20
INSTRUM         spect
PROBHD   5 mm PABBO BB/
PULPROG          zg30
TD              65536
SOLVENT         CDCl3
NS                 17
DS                  0
SWH        10000.000 Hz
FIDRES      0.152588 Hz
AQ         3.2767999 sec
RG              85.91
DW             50.000 usec
DE               6.50 usec
TE              296.8 K
D1         1.00000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1      500.1330885 MHz
NUC1               1H
P1              13.35 usec
PLW1      16.00000000 W

F2 - Processing parameters
SI              65536
SF        500.1300140 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
```



RAF-DG-G-2-S-2-13C-2

```
Current Data Parameters
NAME     RAF-DG-G-2-S-2-13C-2
EXPNO              4
PROCNO             1

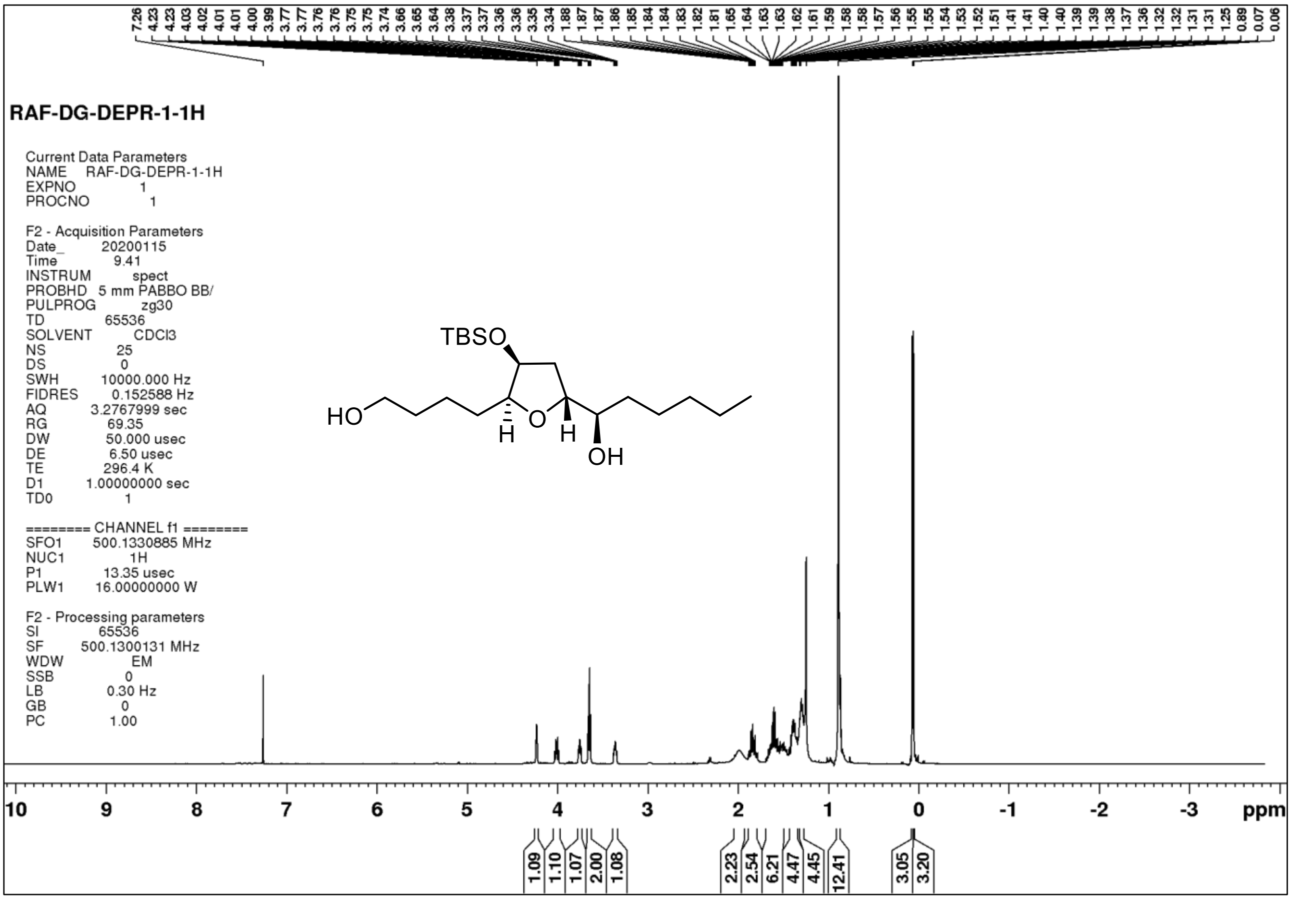
F2 - Acquisition Parameters
Date_        20191226
Time            20.58
INSTRUM         spect
PROBHD   5 mm PABBO BB/
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                784
DS                  0
SWH        29761.904 Hz
FIDRES      0.454131 Hz
AQ         1.1010048 sec
RG             197.27
DW             16.800 usec
DE               6.50 usec
TE              295.0 K
D1         1.00000000 sec
D11        0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1      125.7703637 MHz
NUC1              13C
P1               8.90 usec
PLW1     103.00000000 W

======== CHANNEL f2 ========
SFO2      500.1320005 MHz
NUC2               1H
CPDPRG[2       waltz16
PCPD2           80.00 usec
PLW2      16.00000000 W
PLW12      0.44556001 W
PLW13      0.22411001 W

F2 - Processing parameters
SI              32768
SF        125.7577927 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) of compound **14**



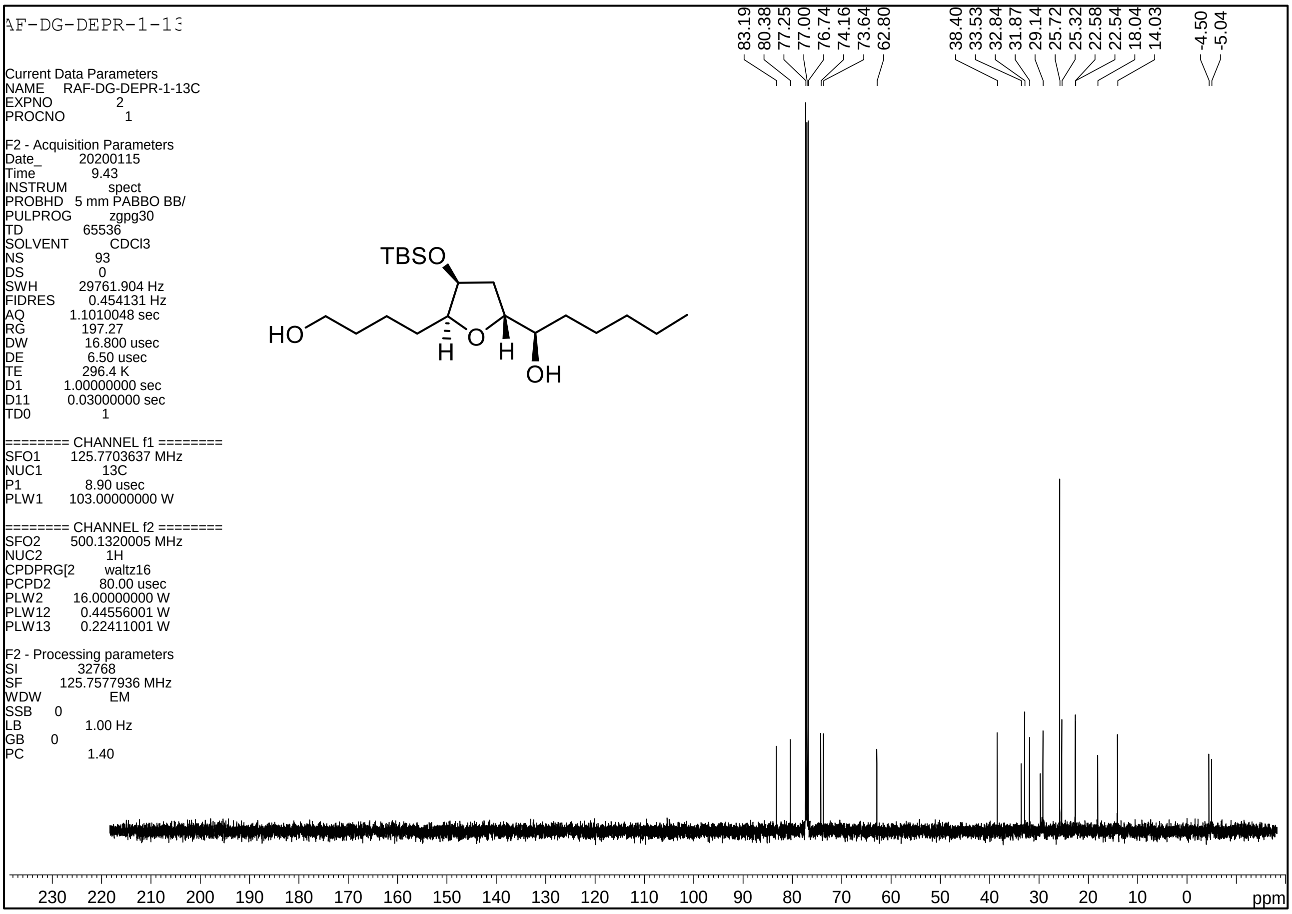
RAF-DG-DEPR-1-1H

```
Current Data Parameters
NAME    RAF-DG-DEPR-1-1H
EXPNO            1
PROCNO           1

F2 - Acquisition Parameters
Date_       20200115
Time           9.41
INSTRUM        spect
PROBHD  5 mm PABBO BB/
PULPROG         zg30
TD            65536
SOLVENT        CDCl3
NS               25
DS                0
SWH      10000.000 Hz
FIDRES    0.152588 Hz
AQ       3.2767999 sec
RG            69.35
DW          50.000 usec
DE           6.50 usec
TE            296.4 K
D1      1.00000000 sec
TD0               1

======== CHANNEL f1 ========
SFO1     500.1330885 MHz
NUC1              1H
P1             13.35 usec
PLW1      16.00000000 W

F2 - Processing parameters
SI            65536
SF       500.1300131 MHz
WDW              EM
SSB               0
LB             0.30 Hz
GB                0
PC             1.00
```



AF-DG-DEPR-1-13

```
Current Data Parameters
NAME    RAF-DG-DEPR-1-13C
EXPNO            2
PROCNO           1

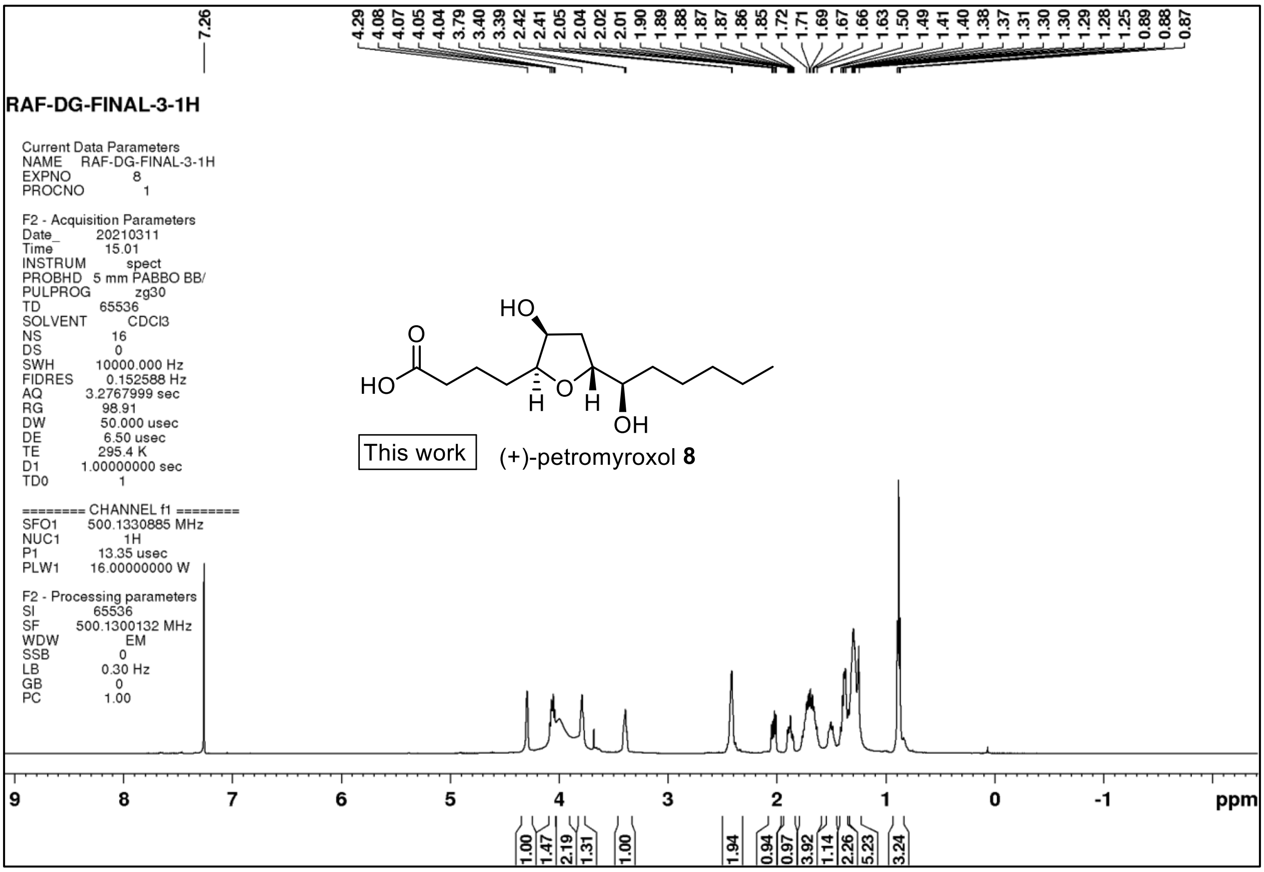
F2 - Acquisition Parameters
Date_       20200115
Time           9.43
INSTRUM        spect
PROBHD  5 mm PABBO BB/
PULPROG       zgpg30
TD            65536
SOLVENT        CDCl3
NS               93
DS                0
SWH      29761.904 Hz
FIDRES    0.454131 Hz
AQ       1.1010048 sec
RG           197.27
DW          16.800 usec
DE           6.50 usec
TE            296.4 K
D1      1.00000000 sec
D11     0.03000000 sec
TD0               1

======== CHANNEL f1 ========
SFO1     125.7703637 MHz
NUC1             13C
P1              8.90 usec
PLW1     103.00000000 W

======== CHANNEL f2 ========
SFO2     500.1320005 MHz
NUC2              1H
CPDPRG[2      waltz16
PCPD2          80.00 usec
PLW2      16.00000000 W
PLW12      0.44556001 W
PLW13      0.22411001 W

F2 - Processing parameters
SI            32768
SF       125.7577936 MHz
WDW              EM
SSB    0
LB             1.00 Hz
GB     0
PC             1.40
```

^{1}H NMR (500 MHz, $CDCl_3$) of compound **8** and reported compound **8** spectra



RAF-DG-FINAL-3-1H

Current Data Parameters
NAME RAF-DG-FINAL-3-1H
EXPNO 8
PROCNO 1

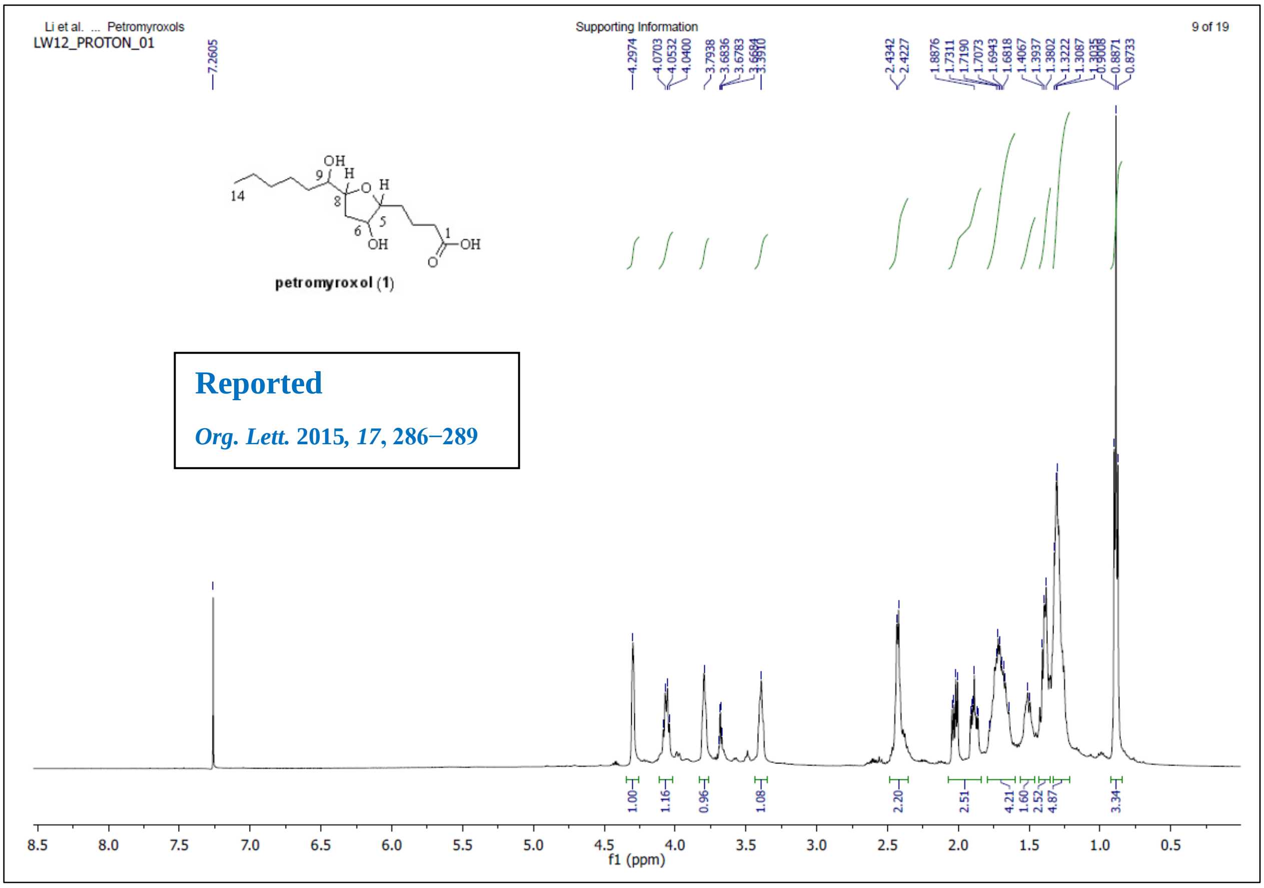
F2 - Acquisition Parameters
Date_ 20210311
Time 15.01
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 98.91
DW 50.000 usec
DE 6.50 usec
TE 295.4 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 13.35 usec
PLW1 16.00000000 W

F2 - Processing parameters
SI 65536
SF 500.1300132 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

This work

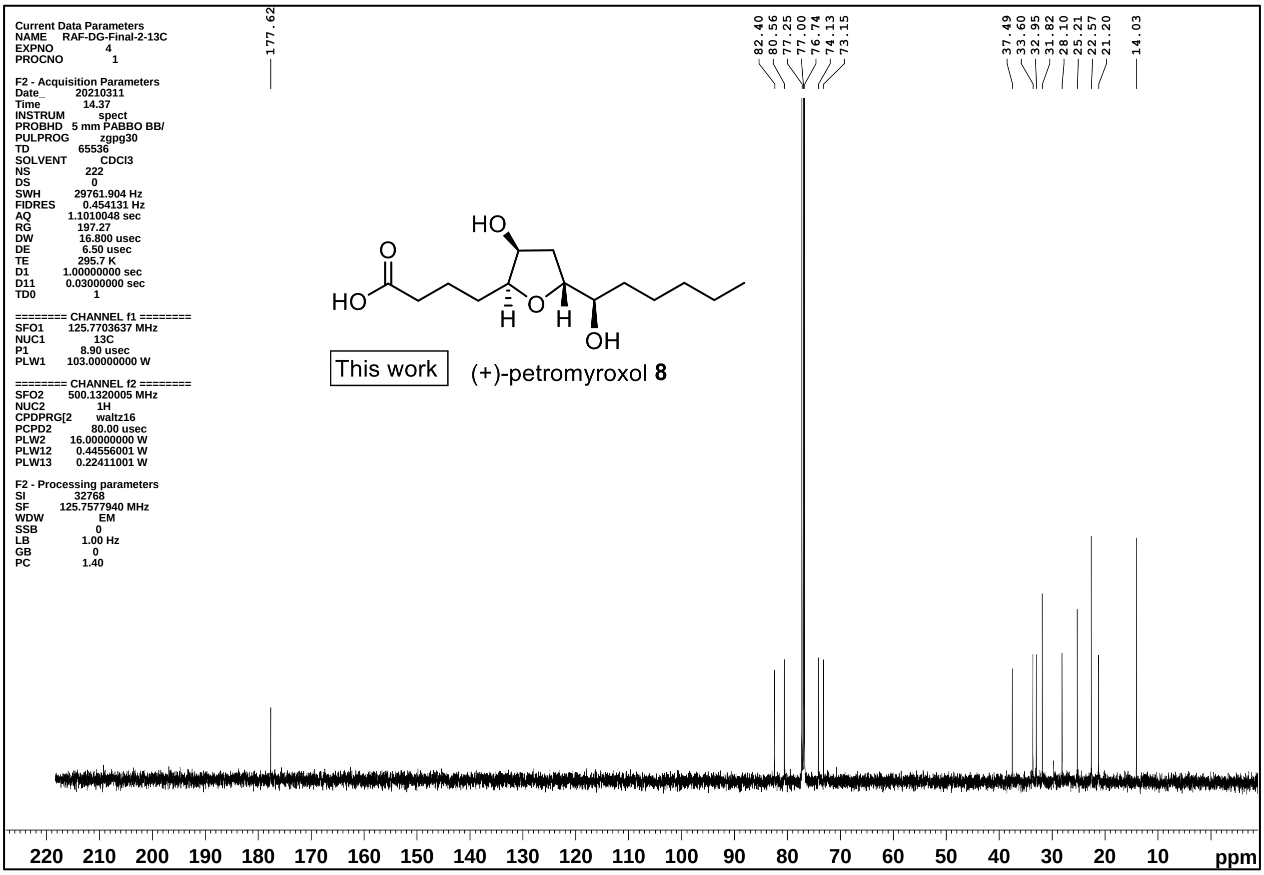
(+)-petromyroxol **8**



Reported

Org. Lett. 2015, *17*, 286−289

^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) of compound **8** and reported compound **8** spectra



```
Current Data Parameters
NAME     RAF-DG-Final-2-13C
EXPNO              4
PROCNO             1

F2 - Acquisition Parameters
Date_          20210311
Time             14.37
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD              65536
SOLVENT          CDCl3
NS                 222
DS                   0
SWH         29761.904 Hz
FIDRES       0.454131 Hz
AQ          1.1010048 sec
RG              197.27
DW              16.800 usec
DE               6.50 usec
TE               295.7 K
D1         1.00000000 sec
D11        0.03000000 sec
TD0                  1

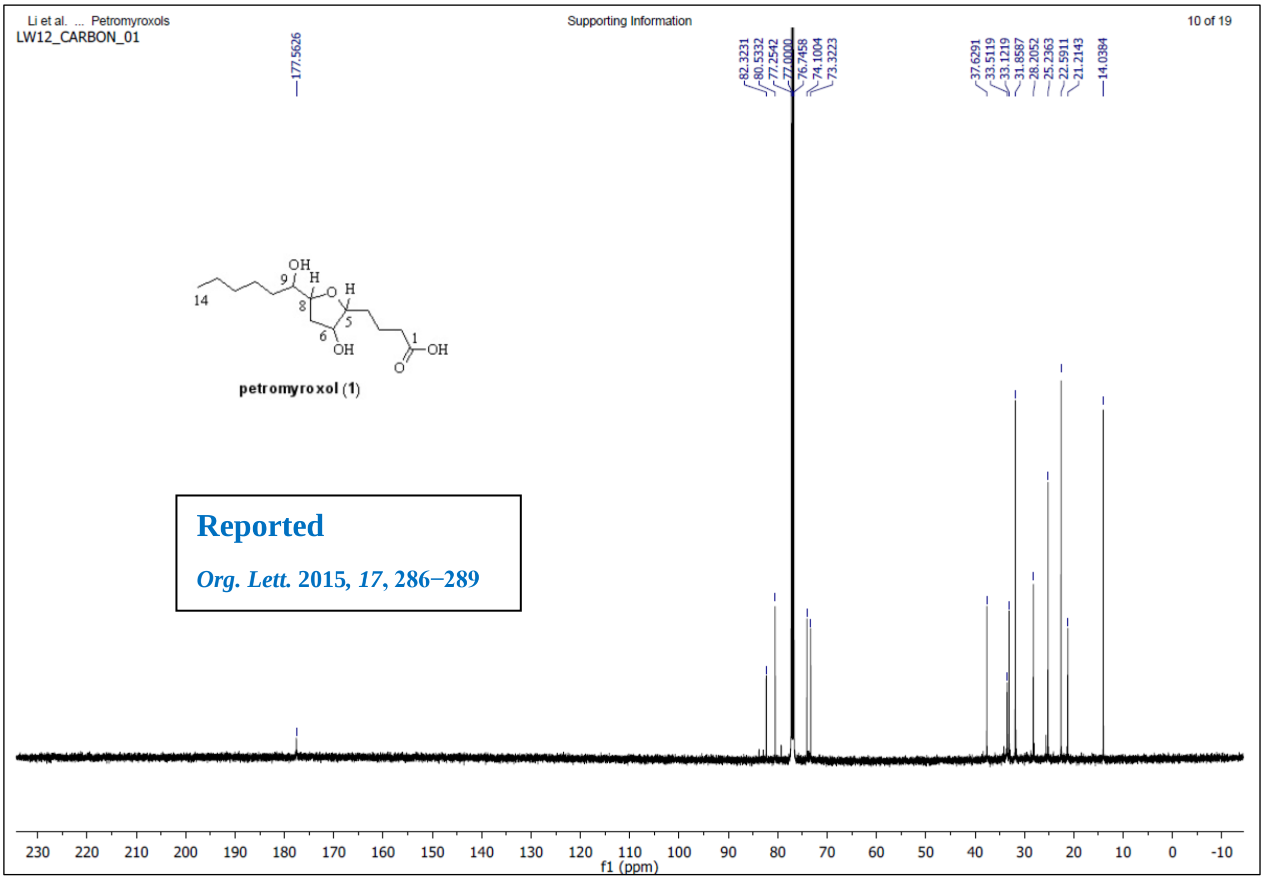
======== CHANNEL f1 ========
SFO1      125.7703637 MHz
NUC1               13C
P1                8.90 usec
PLW1      103.00000000 W

======== CHANNEL f2 ========
SFO2      500.1320005 MHz
NUC2                1H
CPDPRG[2       waltz16
PCPD2            80.00 usec
PLW2       16.00000000 W
PLW12       0.44556001 W
PLW13       0.22411001 W

F2 - Processing parameters
SI               32768
SF        125.7577940 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

This work

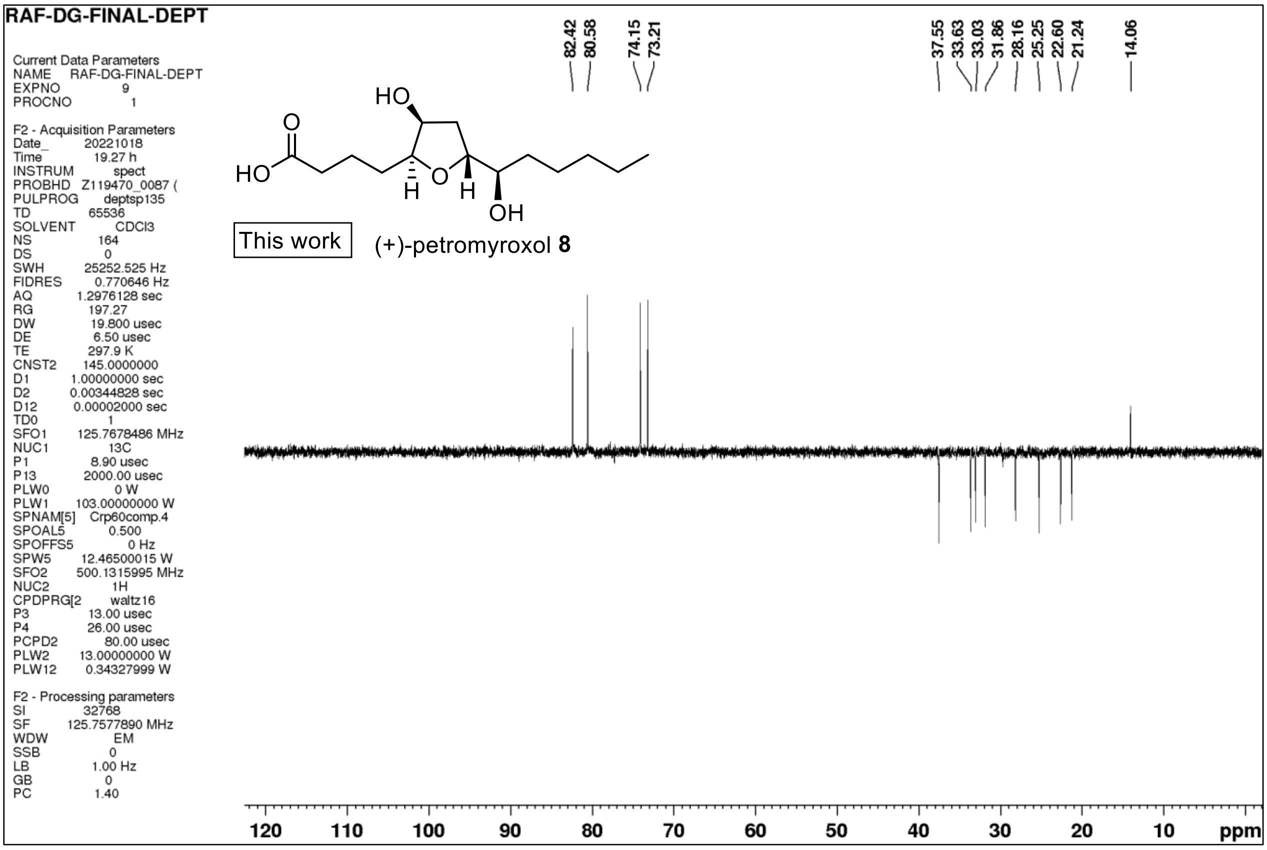
(+)-petromyroxol **8**



Reported

Org. Lett. **2015**, *17*, **286−289**

$^{13}C\{^1H\}$ NMR DEPT (125 MHz, $CDCl_3$) of compound **8** and reported compound **8** spectra

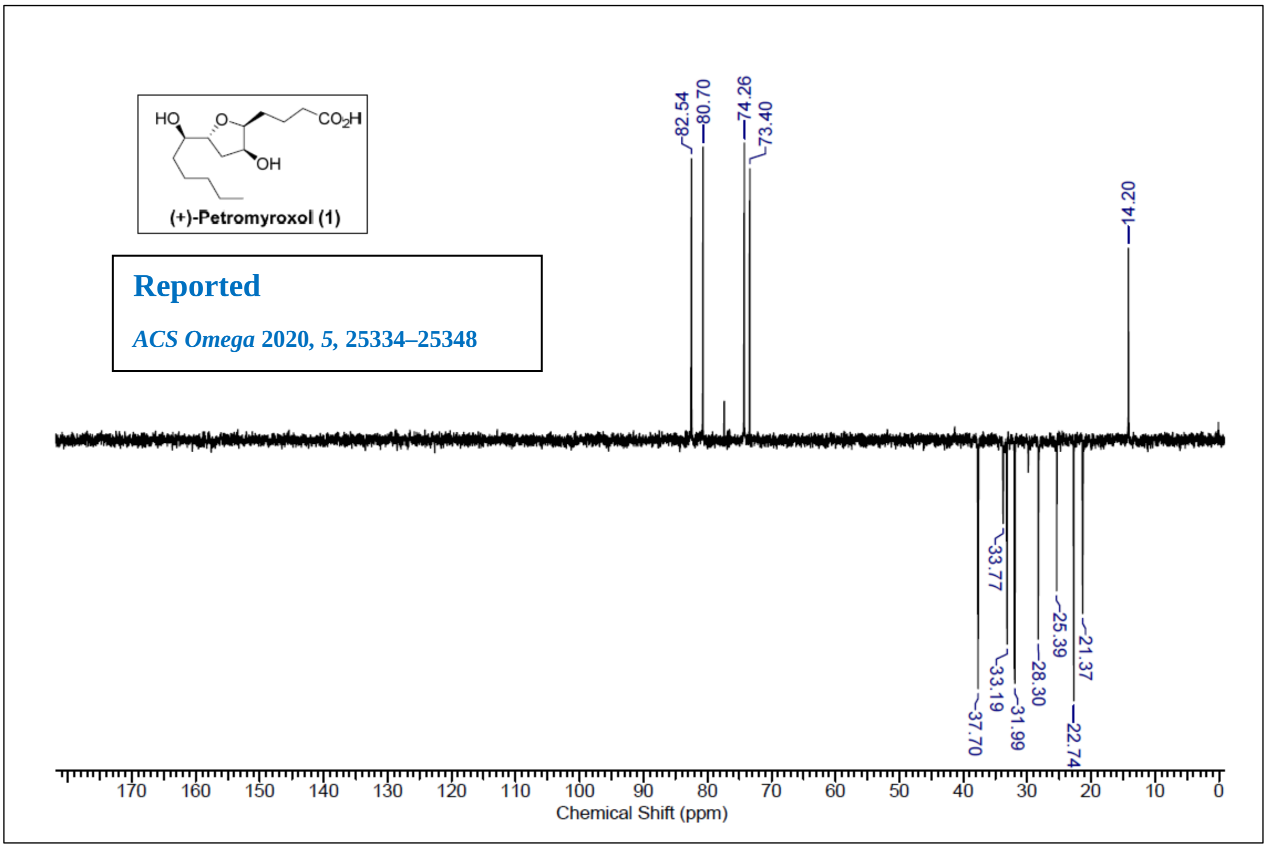


RAF-DG-FINAL-DEPT

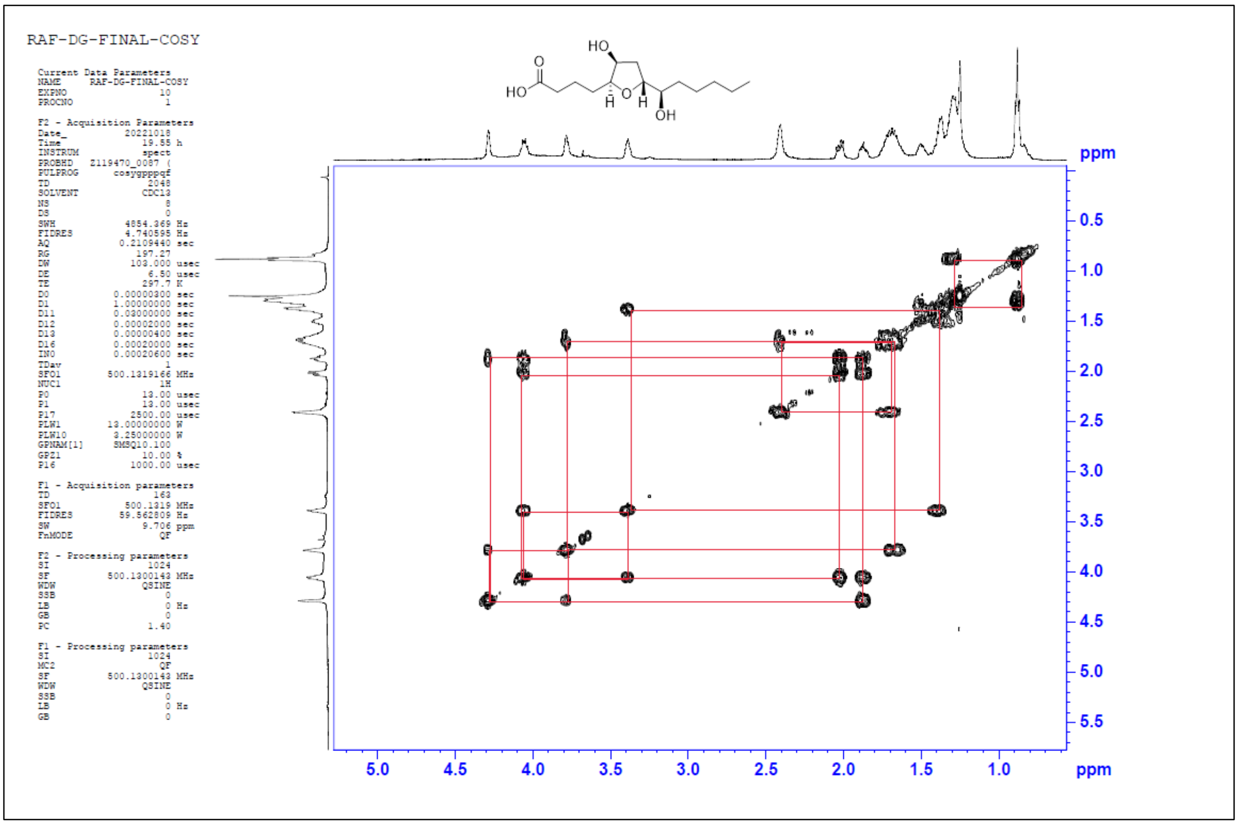
```
Current Data Parameters
NAME     RAF-DG-FINAL-DEPT
EXPNO               9
PROCNO              1

F2 - Acquisition Parameters
Date_          20221018
Time             19.27 h
INSTRUM          spect
PROBHD   Z119470_0087 (
PULPROG       deptsp135
TD             65536
SOLVENT          CDCl3
NS                164
DS                 0
SWH          25252.525 Hz
FIDRES        0.770646 Hz
AQ           1.2976128 sec
RG              197.27
DW              19.800 usec
DE                6.50 usec
TE               297.9 K
CNST2        145.0000000
D1          1.00000000 sec
D2          0.00344828 sec
D12         0.00002000 sec
TD0                  1
SFO1       125.7678486 MHz
NUC1               13C
P1                8.90 usec
P13            2000.00 usec
PLW0                 0 W
PLW1      103.00000000 W
SPNAM[5]   Crp60comp.4
SPOAL5           0.500
SPOFFS5              0 Hz
SPW5       12.46500015 W
SFO2       500.1315995 MHz
NUC2                1H
CPDPRG[2        waltz16
P3               13.00 usec
P4               26.00 usec
PCPD2            80.00 usec
PLW2       13.00000000 W
PLW12       0.34327999 W

F2 - Processing parameters
SI              32768
SF         125.7577890 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```



H-H COSY spectra of compound **8** and reported spectra



```
RAF-DG-FINAL-COSY

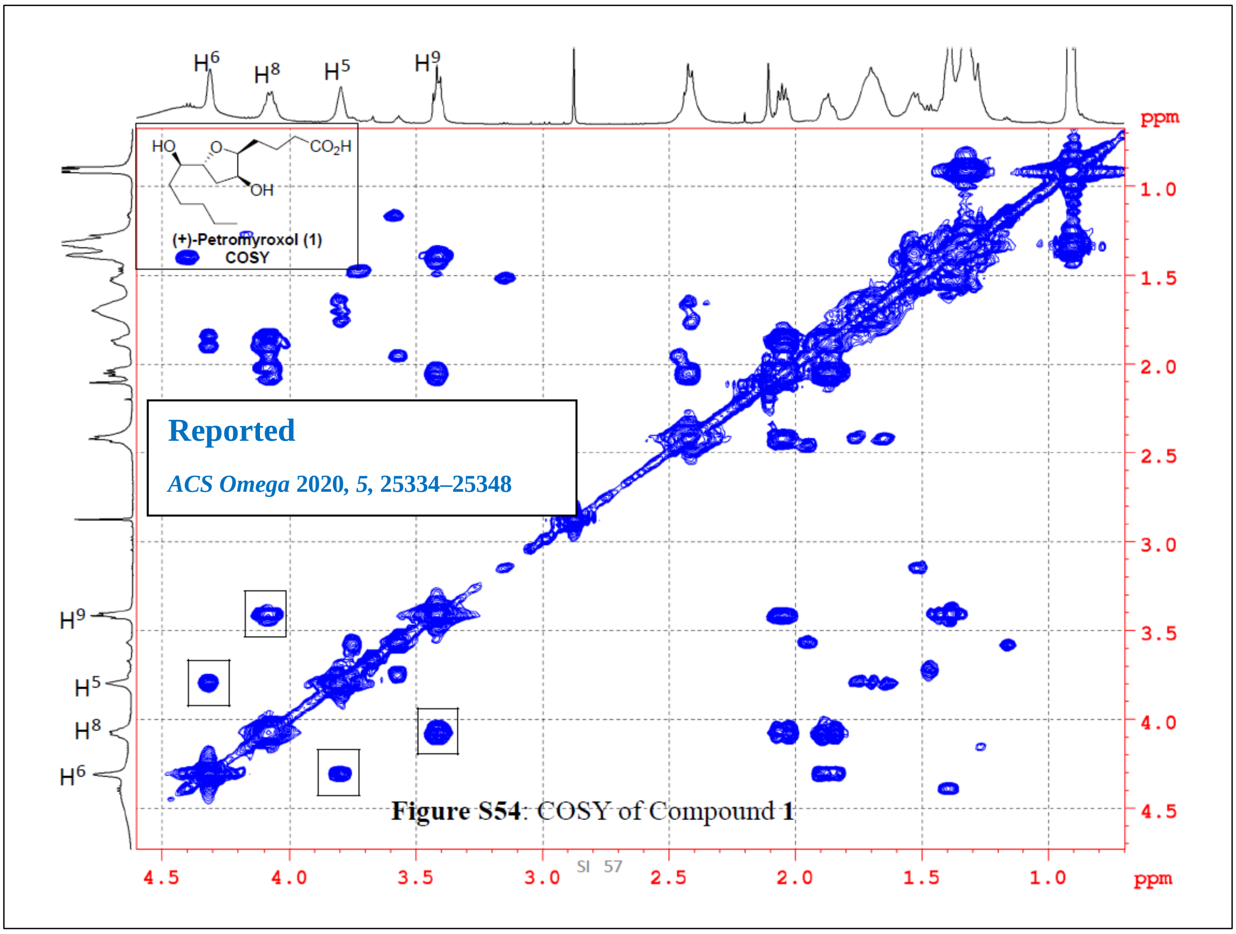
Current Data Parameters
NAME     RAF-DG-FINAL-COSY
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_             20221018
Time                 19.55 h
INSTRUM              spect
PROBHD   Z119470_0087 (
PULPROG         cosygpppqf
TD                    2048
SOLVENT              CDCl3
NS                       8
DS                       0
SWH               4854.369 Hz
FIDRES            4.740595 Hz
AQ               0.2109440 sec
RG                  197.27
DW                 103.000 usec
DE                    6.50 usec
TE                   297.7 K
D0              0.00000300 sec
D1              1.00000000 sec
D11             0.03000000 sec
D12             0.00002000 sec
D13             0.00000400 sec
D16             0.00020000 sec
IN0             0.00020600 sec
TDav                     1
SFO1           500.1319166 MHz
NUC1                    1H
P0                   13.00 usec
P1                   13.00 usec
P17                2500.00 usec
PLW1           13.00000000 W
PLW10           3.25000000 W
GPNAM[1]        SMSQ10.100
GPZ1                 10.00 %
P16                1000.00 usec

F1 - Acquisition parameters
TD                     163
SFO1              500.1319 MHz
FIDRES           59.562809 Hz
SW                   9.706 ppm
FnMODE                  QF

F2 - Processing parameters
SI                    1024
SF             500.1300143 MHz
WDW                  QSINE
SSB                      0
LB                       0 Hz
GB                       0
PC                    1.40

F1 - Processing parameters
SI                    1024
MC2                     QF
SF             500.1300143 MHz
WDW                  QSINE
SSB                      0
LB                       0 Hz
GB                       0
```



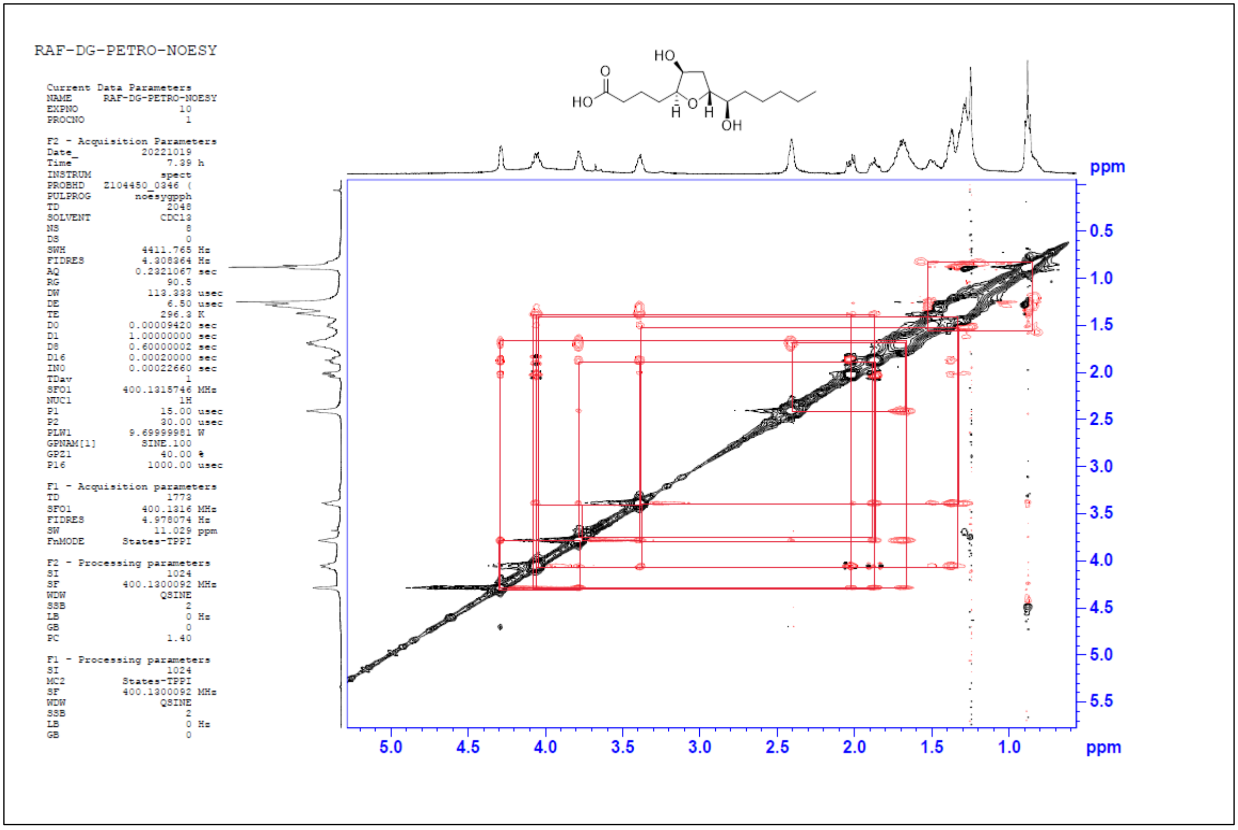
Reported

ACS Omega 2020, *5*, 25334–25348

Figure S54: COSY of Compound **1**

SI 57

NOESY spectra of compound **8** and reported spectra



RAF-DG-PETRO-NOESY

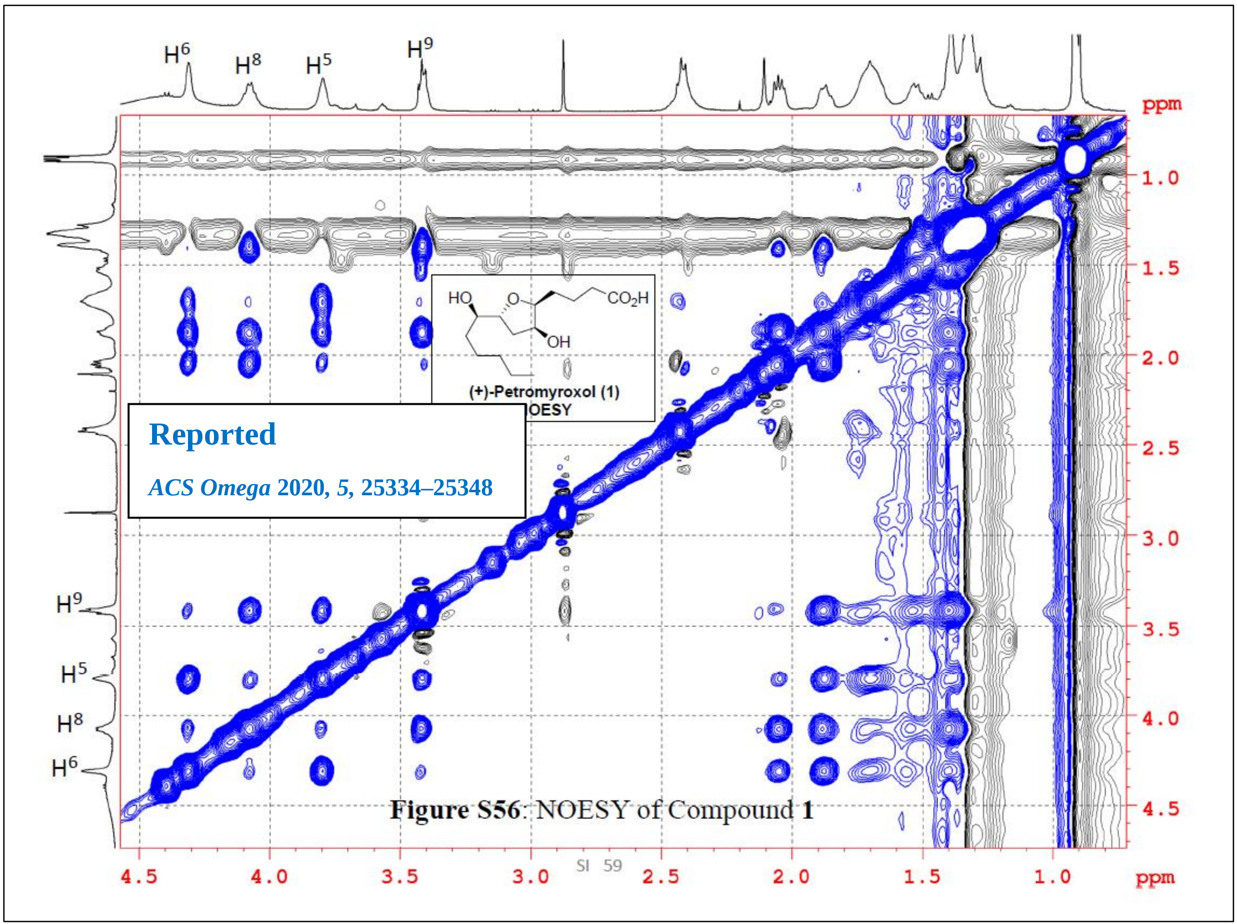
```
Current Data Parameters
NAME      RAF-DG-PETRO-NOESY
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_               20221019
Time                    7.39 h
INSTRUM                spect
PROBHD    Z104450_0346 (
PULPROG           noesygpph
TD                      2048
SOLVENT                CDCl3
NS                         8
DS                         0
SWH                 4411.765 Hz
FIDRES              4.308364 Hz
AQ                 0.2321067 sec
RG                      90.5
DW                   113.333 usec
DE                      6.50 usec
TE                     296.3 K
D0                0.00009420 sec
D1                1.00000000 sec
D8                0.60000002 sec
D16               0.00020000 sec
IN0               0.00022660 sec
TDav                       1
SFO1             400.1315746 MHz
NUC1                      1H
P1                     15.00 usec
P2                     30.00 usec
PLW1              9.69999981 W
GPNAM[1]            SINE.100
GPZ1                   40.00 %
P16                  1000.00 usec

F1 - Acquisition parameters
TD                      1773
SFO1                400.1316 MHz
FIDRES              4.978074 Hz
SW                    11.029 ppm
FnMODE           States-TPPI

F2 - Processing parameters
SI                      1024
SF               400.1300092 MHz
WDW                    QSINE
SSB                        2
LB                         0 Hz
GB                         0
PC                      1.40

F1 - Processing parameters
SI                      1024
MC2              States-TPPI
SF               400.1300092 MHz
WDW                    QSINE
SSB                        2
LB                         0 Hz
GB                         0
```

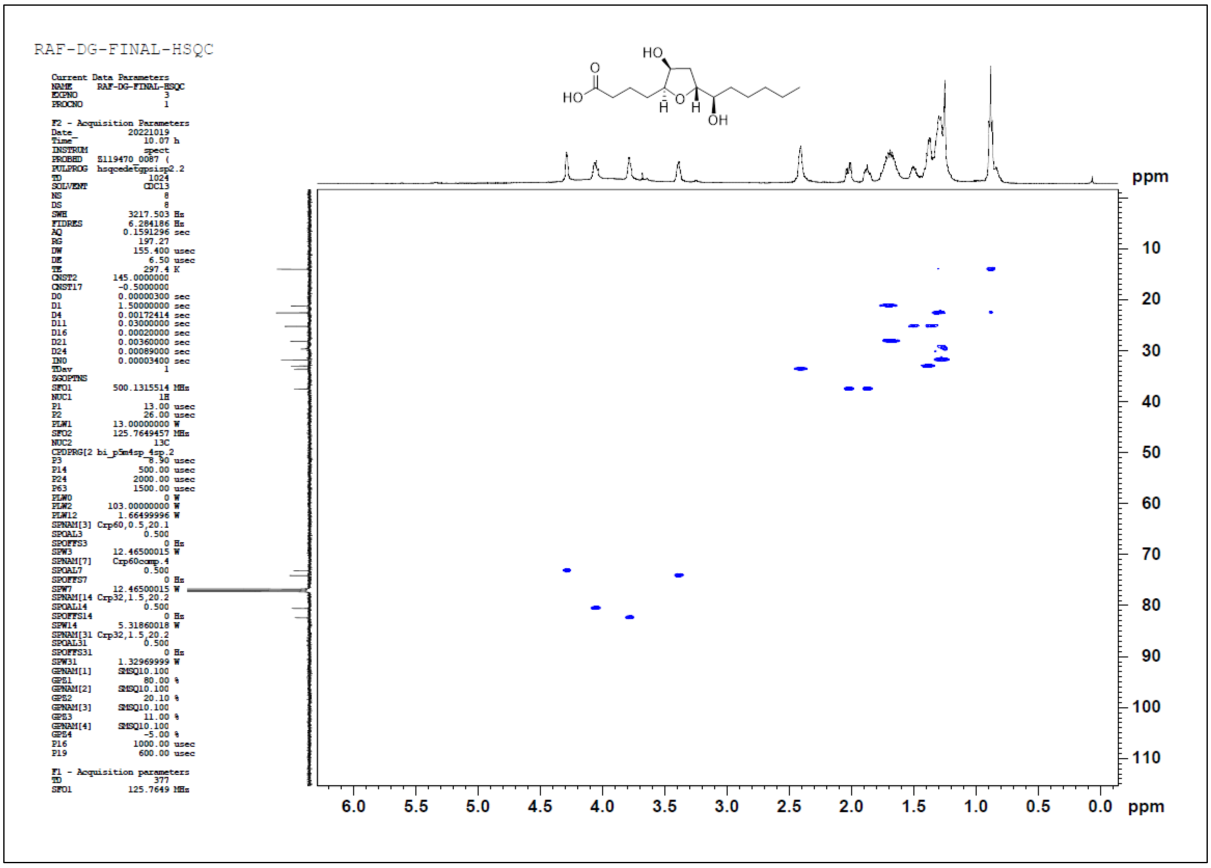


Reported

ACS Omega 2020, *5*, 25334–25348

Figure S56: NOESY of Compound **1**

HSQC spectra of compound **8** and reported spectra

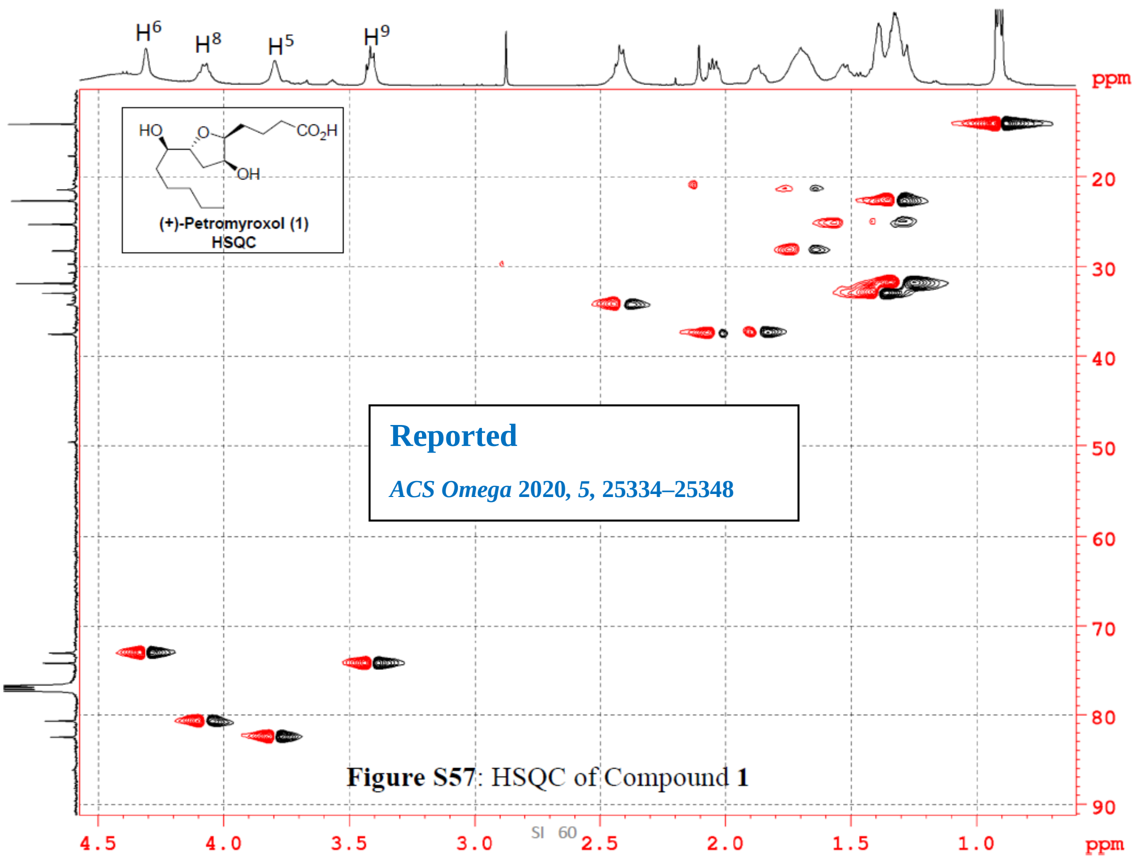


```
RAF-DG-FINAL-HSQC

Current Data Parameters
NAME     RAF-DG-FINAL-HSQC
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_             20221019
Time               10.07 h
INSTRUM              spect
PROBHD   Z119470_0087 (
PULPROG  hsqcedetgpsisp2.2
TD                    1024
SOLVENT              CDCl3
NS                       8
DS                       8
SWH               3217.503 Hz
FIDRES            6.284186 Hz
AQ               0.1591296 sec
RG                  197.27
DW                 155.400 usec
DE                    6.50 usec
TE                   297.4 K
CNST2          145.0000000
CNST17          -0.5000000
D0              0.00000300 sec
D1              1.50000000 sec
D4              0.00172414 sec
D11             0.03000000 sec
D16             0.00020000 sec
D21             0.00360000 sec
D24             0.00089000 sec
IN0             0.00003400 sec
TDav                     1
SGOPTNS
SFO1           500.1315514 MHz
NUC1                    1H
P1                   13.00 usec
P2                   26.00 usec
PLW1           13.00000000 W
SFO2           125.7649457 MHz
NUC2                   13C
CPDPRG[2 bi_p5m4sp_4sp.2
P3                    8.90 usec
P14                 500.00 usec
P24                2000.00 usec
P63                1500.00 usec
PLW0                     0 W
PLW2          103.00000000 W
PLW12           1.66499996 W
SPNAM[3] Crp60,0.5,20.1
SPOAL3               0.500
SPOFFS3                  0 Hz
SPW3           12.46500015 W
SPNAM[7]     Crp60comp.4
SPOAL7               0.500
SPOFFS7                  0 Hz
SPW7           12.46500015 W
SPNAM[14 Crp32,1.5,20.2
SPOAL14              0.500
SPOFFS14                 0 Hz
SPW14           5.31860018 W
SPNAM[31 Crp32,1.5,20.2
SPOAL31              0.500
SPOFFS31                 0 Hz
SPW31           1.32969999 W
GPNAM[1]      SMSQ10.100
GPZ1                 80.00 %
GPNAM[2]      SMSQ10.100
GPZ2                 20.10 %
GPNAM[3]      SMSQ10.100
GPZ3                 11.00 %
GPNAM[4]      SMSQ10.100
GPZ4                 -5.00 %
P16                1000.00 usec
P19                 600.00 usec

F1 - Acquisition parameters
TD                     377
SFO1           125.7649 MHz
```



Reported

ACS Omega 2020, *5*, 25334–25348

Figure S57: HSQC of Compound **1**

^{1}H NMR and ^{13}C NMR Comparison data of compound **8**: Reported and our work

Position	**Natural isolated** ***Org. Lett.* 2015, *17*, 286**		**This work**	
	^{1}H NMR	**^{13}C NMR**	**^{1}H NMR**	**^{13}C NMR**
1		177.6		177.6
2	2.43 m (Σ*J*s = 18)	33.7	2.41 (d, *J* = 3.2 Hz, 2H)	33.6
3	1.77 m, 1.70 m	21.4	1.76–1.63 (m, 4H)	21.2
4	1.72 m, 1.67 m	28.4		28.1
5	3.79 ddd (ca. 2.5, 6.5, 6.5)	82.5	3.80–3.77 (m, 1H)	82.4
6	4.30 dd (ca. 3.5, 3.5)	73.5	4.29 (d, *J* = 3.0 Hz, 1H)	73.2
7a	1.89 ddd (4.6, 9.2, 13.7)		1.90–1.84 (m, 1H)	
7b	2.02 dd (6.6, 13.4)	37.8	2.02 (dd, *J* = 13.2, 6.6 Hz, 1H)	37.5
8	4.06 ddd (6.5, 6.5, 8.9)	80.7	4.06 (dd, *J* = 6.7, 6.6 Hz, 1H)	80.6
9	3.39 m (Σ*J*s = 18)	74.3	3.39 (d, *J* = 6.2 Hz, 1H)	74.1
10	1.40 m	33.3	1.41–1.33 (m, 2H)	33.0
11	1.51 m, 1.38 m	25.4	1.49 (d, *J* = 7.2 Hz, 1H)	25.2
12	1.29 m	32.0	1.31–1.24 (m, 5H)	31.8
13	1.31 m	22.8		22.6
14	0.89 t (6.9)	14.2	0.88 (t, *J* = 6.8 Hz, 3H)	14.0
			3.99 (brs, 2H)	