Supplementary Information (SI) for Organic & Biomolecular Chemistry.

Supporting Information

Asymmetric Total Syntheses of Passifetilactones A, C, E and 4-*epi*-Passifetilactone B

Sagar B. Khandekar,[≠] Naga Raju Barnala[≠] and Rodney A. Fernandes*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, Maharashtra, India

Email: rfernand@chem.iitb.ac.in

[≠]These authors contributed equally

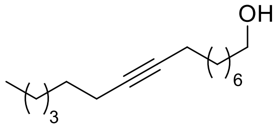
Table of Contents

Experimental Section

General Information

Reagents and solvents were purchased (Sigma-Aldrich, TCI and BLD) and used as received without further purification. NMR spectra were recorded with a Bruker (Germany) Avance III 400 and Bruker (Germany) Avance III HD 500 instruments at room temperature. Chemical shifts (δ) are stated in parts per million (ppm) using the residual $CHCl_3$ δ = 7.27 ppm for ^{1}H and 77.00 ppm for ^{13}C [$CDCl_3$]. Coupling constants *J* are given in Hz. Multiplicities are described as singlet (s), broad signal (br s), doublet (d), triplet (t), quartets (q) and multiplet (m). HRMS were recorded with Bruker Maxis impact mass spectrometer using ESI-TOF techniques in positive mode by dissolving the compound in either methanol or acetonitrile. IR spectra were recorded on Bruker Alpha II instrument in attenuated total reflectance (ATR) mode. Solvents were dried by using standard procedures. HMPA (99%) and DMPU (98%) were vacuum distilled over CaH_2 and stored with dry molecular sieves. 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.

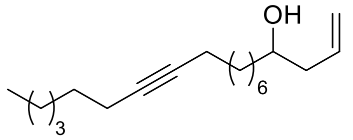
Hexadec-9-yn-1-ol (5)



To a stirred solution of 9-decyn-1-ol **3** (1.97 g, 12.8 mmol, 2.0 equiv) in dry THF (20 mL) and HMPA (6 mL) was added dropwise *n*-BuLi (14.1 mL, 2.0 M, 28.16 mmol, 4.4 equiv) at –78 °C. The reaction mixture was then stirred for 30 min at the same temperature. To this mixture was added dropwise 1-bromohaxane (1.05 g, 6.4 mmol, 1.0 equiv) dissolved in THF (5 mL). The reaction mixture was then stirred for 12 h and then quenched with a saturated aq. solution of NH_4Cl (20 mL). The solution was extracted with Et_2O (3 × 30 mL) and the combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated. The residue was purified by silica gel column chromatography with petroleum ether/EtOAc (4:1) as an eluent to give hexadec-9-yn-1-ol **5** (1.27 g, 83%) as a colorless oil. IR ($CHCl_3$) ν_{max} = 3278, 3192, 2923, 2857, 2268, 1461, 1181, 1072, 969, 825, 693 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* = 3.62 (t, *J* = 6.7 Hz, 2H), 2.17–2.06 (m, 4H), 1.59–1.51 (m, 2H), 1.49–1.42 (m, 4H), 1.38–1.23 (m, 14H), 0.87 (t, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) *δ* = 80.3, 80.1, 63.0, 32.7, 31.3, 29.3, 29.1, 28.7, 28.5, 25.7, 22.5, 18.7, 14.0 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{16}H_{31}O$ 239.2370; found 239.2369.

Hexadec-9-yn-1-ol (5) using DMPU: To a stirred solution of 9-decayn-1-ol **3** (113 mg, 0.72 mmol, 1.2 equiv) in dry THF (6 mL) and DMPU (0.6 mL) was added dropwise *n*-BuLi (0.66 mL, 2.0 M, 1.33 mmol, 2.2 equiv) at −78 °C. The reaction mixture was then stirred for 30 min at the same temperature. To this mixture was added dropwise 1-bromohexane (100 mg, 0.60 mmol, 1.0 equiv) dissolved in THF (5 mL). The reaction mixture was then stirred for 14 h and then quenched with saturated aq. solution of NH_4Cl (20 mL). The solution was extracted with Et_2O (3 × 30 mL). The combined organic layers were washed with water and brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography with petroleum ether/EtOAc (4:1) as an eluent to give hexadec-9-yn-1-ol **5** (103 mg, 65%) as a colorless oil. Spectra data is same as above.

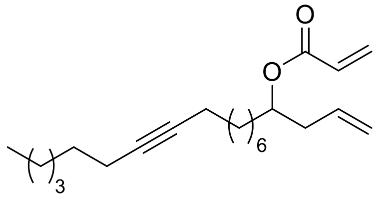
Nonadec-1-en-12-yn-4-ol ((±)-2a)



To a solution of hexadec-9-yn-1-ol **5** (1.0 g, 4.2 mmol, 1.0 equiv) in dry CH_2Cl_2 (55 mL) was added PCC (1.36 g, 6.3 mmol, 1.5 equiv) in portions at 0 °C, and the reaction mixture was allowed to stir for 4 h at room temperature. It was then treated with saturated aq. solutions of $Na_2S_2O_3{\cdot}5H_2O$ (3 mL) and $NaHCO_3$ (3 mL) and stirred for 20 min. The solution was extracted with CH_2Cl_2 (3 × 20 mL) and the combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated to afford the desired aldehyde (0.98 g) that was taken for the next step without further purification.

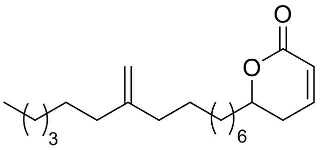
To a solution of above crude aldehyde (0.98 g) in THF (20.0 mL) at 0 °C was added allyl magnesium bromide (5.5 mL, 5.46 mmol, 1.0 M in Et_2O, 1.3 equiv) dropwise. The mixture was left to stir at this temperature before being warmed to room temperature for 1 h. The reaction mixture was quenched at 0 °C with saturated aq. solution of NH_4Cl (5 mL), poured onto saturated aq. NH_4Cl (40 mL) and extracted with Et_2O (3 × 40 mL). The combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated. The residue was purified by silica gel column chromatography with petroleum ether/EtOAc (4:1) as an eluent to afford (±)-**2a** (877 mg, 75% over 2 steps) as a colorless oil. IR ($CHCl_3$) ν_{max} = 3247, 2927, 2859, 2109, 1466, 1251, 1097, 835, 774, 648 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 5.87–5.69 (m, 1H), 5.19–5.03 (m, 2H), 3.73–3.52 (m, 1H), 2.33–2.19 (m, 1H), 2.14–2.07 (m, 5H), 1.71 (brs, 1H), 1.49–1.41 (m, 6H), 1.36–1.20 (m, 14H), 0.86 (t, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 134.8, 117.9, 80.2, 80.1, 70.6, 41.9, 36.7, 31.3, 29.5, 29.1, 28.7, 28.5, 25.6, 22.5, 18.7, 14.0; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{19}H_{35}O$ 279.2683; found 279.2688.

Nonadec-1-en-12-yn-4-yl acrylate (6)



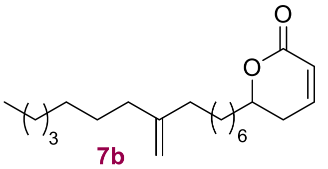
To a stirred solution of acrylic acid (144 mg, 2.0 mmol, 1.2 equiv) in dry CH_2Cl_2 (20 mL) were added DCC (514 mg, 2.49 mmol, 1.5 equiv) and DMAP (81 mg, 0.664 mmol, 0.4 equiv) at 0 °C. The mixture was stirred for 10 min and then a solution of (±)-**2a** (464 mg, 1.66 mmol, 1.0 equiv) in dry CH_2Cl_2 (1 mL) was added dropwise at 0 °C. The reaction mixture was stirred for an additional 5 h at room temperature. It was then filtered through a cotton plug, and the plug was washed with CH_2Cl_2 (5 mL). The filtrate was washed with water and brine, dried (Na_2SO_4), and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (9:1) as an eluent to afford **6** (439 mg, 82%) as a colorless oil. IR ($CHCl_3$) ν_{max} = 3017, 2926, 2852, 2115, 1570, 1447, 1225, 1017, 767, 628 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.37 (dd, *J* = 17.5, 1.3 Hz, 1H), 6.10 (dd, *J* = 18.0, 10.0 Hz, 1H), 5.83–5.68 (m, 2H), 5.11–5.02 (m, 2H), 5.00–4.94 (m, 1H), 2.37–2.28 (m, 2H), 2.12 (apparent t, *J* = 7.0 Hz, 4H), 1.61–1.51 (m, 2H), 1.50–1.43 (m, 4H), 1.35–1.23 (m, 14H), 0.88 (t, *J* = 7.1 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 165.9, 133.7, 130.3, 128.8, 117.6, 80.3, 80.1, 73.6, 38.6, 33.5, 31.4, 29.3, 29.1, 29.08, 29.0, 28.7, 28.5, 25.2, 22.6, 18.73, 18.7, 14.0 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{22}H_{37}O_2$ 333.2789; found 333.2793.

6-(9-Methylenepentadecyl)-5,6-dihydro-2*H*-pyran-2-one (7a) and 6-(8-Methylenepentadecyl)-5,6-dihydro-2*H*-pyran-2-one (7b)



7a

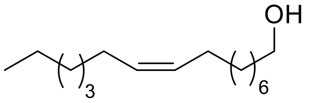
+



7b

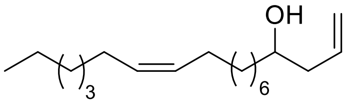
To a stirred and degassed solution of **6** (100 mg, 0.30 mmol, 1.0 equiv) in dry CH_2Cl_2 (50 mL) was added Grubbs second–generation catalyst (25.5 mg, 0.03 mmol, 10 mol%) at room temperature and the mixture refluxed for 4 h. The mixture was cooled and filtered through a small pad of silica gel and the filtrate was concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (4:1) as eluent to give the mixture of **7a** and **7b** (77 mg, 80%) as a colorless oil. IR ($CHCl_3$) ν_{max} = 3025, 2928, 2862, 1717, 1390, 1230, 1049, 835, 765, 692, 633 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.92–6.83 (m, 1H), 6.01 (d, J = 9.4 Hz, 1H), 5.03 (s, 1H), 4.89 (s, 1H), 4.46–4.32 (m, 1H), 2.35–2.26 (m, 2H), 2.21 (apparent t, J = 9.4 Hz, 4H), 1.84–1.71 (m, 1H), 1.69–1.56 (m, 3H), 1.45–1.36 (m, 4H), 1.34–1.27 (m, 14H), 0.87 (t, J = 7.1 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 164.7, 147.9, 145.0, 121.5, 111.34, 111.3, 78.0, 34.9, 34.3, 34.2, 31.8, 29.4, 29.3, 29.2, 28.64, 28.6, 24.8, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{21}H_{37}O_2$ 321.2789; found 321.2795.

(*Z*)-Hexadec-9-en-1-ol (9)



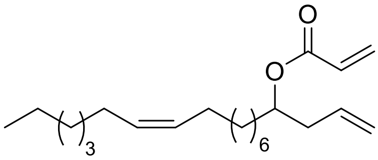
To a stirred solution of $Ni(OAc)_2.4H_2O$ (522 mg, 2.09 mmol, 1.0 equiv) in EtOH (10 mL) under H_2 atmosphere was added $NaBH_4$ (79 mg, 2.09 mmol, 1.0 equiv) in EtOH (10 mL) at room temperature. After stirring for 0.5 h, ethylenediamine (502.4 mg, 8.36 mmol, 4.0 equiv) and alkyne substrate **5** (500 mg, 2.09 mmol, 1.0 equiv) in EtOH (10 mL) were added sequentially. The reaction mixture was allowed to stir for 4 h. Then, EtOH was removed under reduced pressure, and the reaction mixture was diluted with EtOAc (25 mL) and filtered through a pad of Celite and the filtrate was concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (4:1) as eluent to give **9** (497.5 mg, 99%) as a colorless oil. IR ($CHCl_3$) ν_{max} = 3382, 3018, 2929, 1527, 1220, 1155, 1048, 832, 770, 678, 630 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 5.37–5.25 (m, 2H), 3.57 (t, J = 7.2 Hz, 2H), 2.47 (br s, 1H), 2.04–1.90 (m, 4H), 1.59–1.45 (m, 2H), 1.34–1.22 (s, 18H), 0.86 (t, J = 7.5 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 129.8, 129.7, 62.7, 32.6, 31.7, 29.7, 29.65, 29.5, 29.4, 29.2, 28.9, 27.12, 27.1, 25.7, 22.6, 14.0 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{16}H_{33}O$ 241.2526; found 241.2530.

(*Z*)-Nonadeca-1,12-dien-4-ol (10)



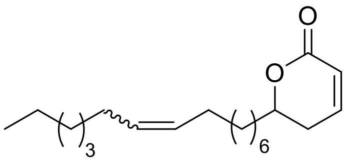
The titled compound was prepared from alcohol **9** (500 mg, 2.08 mmol) by a similar procedure as described for (±)-**2a** to give homoallylic alcohol **10** (449.2 mg, 77% over 2 steps) as a colorless oil. IR ($CHCl_3$) ν_{max} = 3393, 2922, 2857, 1520, 1377, 1274, 1218, 1019, 907, 829, 771, 639 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 5.87–5.75 (m, 1H), 5.37–5.27 (m, 2H), 5.14–5.04 (m, 2H), 3.62 (s, 1H), 2.31–2.21 (m, 1H), 2.17–2.07 (m, 1H), 2.03–1.95 (m, 4H), 1.77 (brs, 1H), 1.45–1.41 (m, 2H), 1.36–1.17 (s, 18H), 0.86 (t, J = 8.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 134.9, 129.9, 129.8, 117.9, 70.6, 41.9, 36.7, 31.7, 29.7, 29.6, 29.5, 29.2, 28.9, 27.2, 27.1, 25.6, 22.6, 14.0 ppm; HRMS (ESI-TOF): *m/z* $[M + NH_4]^+$ calcd. $C_{19}H_{40}ON$ 298.3105; found 298.3103.

(*Z*)-Nonadeca-1,12-dien-4-yl acrylate (11)



The titled compound was prepared from alcohol **10** (200 mg, 0.713 mmol) by a similar procedure as described for **6** to give ester **11** (209 mg, 84%) as a colorless oil. IR ($CHCl_3$) ν_{max} = 2924, 2858, 1726, 1524, 1369, 1270, 1219, 1098, 1023, 838, 771, 700, 636 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.39 (dd, *J* = 17.3, 1.3 Hz, 1H), 6.10 (dd, *J* = 17.6, 10.0 Hz, 1H), 5.84–5.69 (m, 2H), 5.41–5.31 (m, 2H), 5.12–4.95 (m, 3H), 2.41–2.27 (m, 2H), 2.06–1.95 (m, 4H), 1.64–1.51 (m, 4H), 1.32–1.24 (s, 16H), 0.88 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 165.9, 133.7, 130.3, 129.9, 129.9, 128.6, 117.6, 73.6, 38.6, 33.5, 31.8, 29.72, 29.7, 29.4, 29.36, 29.2, 29.0, 27.2, 27.16, 25.2, 22.6, 14.1 ppm; HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd. $C_{22}H_{39}O_2$ 335.2945; found 335.2950.

6-(Pentadec-8-en-1-yl)-5,6-dihydro-2*H*-pyran-2-one (12)



The titled compound was prepared from ester **11** (100 mg, 0.29 mmol) by a similar RCM procedure as described for **7a** and **7b** to give lactone **12** (79 mg, 85%) as a colorless oil. IR ($CHCl_3$) ν_{max} = 2926, 2858, 1720, 1455, 1386, 1252, 1047, 970, 821, 771, 637 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.89–6.84 (m, 1H), 6.00 (dt, *J* = 10.0, 1.4 Hz, 1H), 5.45–5.28 (m, 2H), 4.44–4.35 (m, 1H), 2.35–2.27 (m, 2H), 2.06–1.90 (m, 4H), 1.83–1.73 ((m, 1H), 1.64–1.59 (m, 1H), 1.56–1.48 (m, 1H), 1.43–1.35 (m, 1H), 1.32–1.23 (s, 16H), 0.86 (t, *J* = 6.9 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 164.6, 145.0, 130.4, 130.2, 121.4, 78.0, 34.8, 32.6, 32.5, 31.7, 29.6, 29.55, 29.4, 29.3, 29.29, 29.0, 28.8, 24.8, 22.6, 14.1 ppm; HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd. $C_{20}H_{35}O_2$ 307.2632; found 307.2634.

Table S1: Comparison of ^{1}H NMR of natural passifetilactone A isolated by Schevenels and the present synthetic **1a** and compound **12**

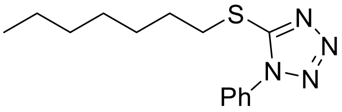
Sr. No.	**Passifetilactone A isolated by Schevenels** *J. Nat. Prod.*, 2024, **87**, 1652	**Synthetic passifetilactone A (1a) This work**	**Synthetic compound 12 This work**
1	6.84 (ddd, *J* = 9.5, 5.3, 3.1 Hz, 1H)	6.92–6.82 (m, 1H)	6.89–6.84 (m, 1H)
2	5.96 (brdd, *J* = 9.7, 1.0 Hz, 1H)	6.01 (d, *J* = 10.0 Hz, 1H)	6.00 (dt, *J* = 10.0, 1.4 Hz, 1H)
3	5.30 (m, 2H)	5.41–5.28 (m, 2H)	5.45–5.28 (m, 2H)
4	4.37 (m, 1H)	4.49–4.34 (m, 1H)	4.44–4.35 (m, 1H)

5	2.29 (m, 2H)	2.34–2.28 (m, 2H)	2.35–2.27 (m, 2H)
6	1.98 (brm, 4H)	2.05–1.95 (m, 4H)	2.06–1.90 (m, 4H)
7	1.74 (m, 1H)	1.83–1.74 (m, 1H)	1.83–1.73 ((m, 1H)
8	1.60 (m, 1H)	1.66–1.59 (m, 1H)	1.64–1.59 (m, 1H)
9	1.47 (m, 1H)	1.52–1.47 (m, 1H)	1.56–1.48 (m, 1H)
10	1.35 (m, 1H)	1.45–1.37 (m, 1H)	1.43–1.35 (m, 1H)
11	1.20–1.13 (brm overlap, 16H)	1.33–1.24 (m, 16H)	1.32–1.23 (m, 16H)
12	0.85 (t, *J* = 6.7 Hz, 3H)	0.87 (t, *J* = 6.8 Hz, 3H)	0.86 (t, *J* = 6.9 Hz, 3H)

Table S2: Comparison of ^{13}C NMR of natural passifetilactone A isolated by Schevenels and the present synthetic **1a** and compound **12**

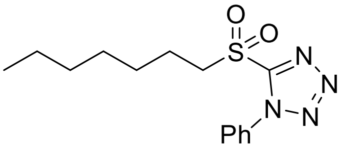
Sr no	**Passifetilactone A isolated by Schevenels** *J. Nat. Prod.*, 2024, **87**, 1652	**Synthetic passifetilactone A (1a)** **This work**	**Synthetic compound 12** **This work**
1	164.6	164.6	164.6
2	145.2	145.0	145.0
3	129.9	130.0	130.4
4	129.9	129.8	130.2
5	121.4	121.5	121.4
6	78.0	78.0	78.0
7	34.9	34.9	34.8
8	32.0	31.8	32.6
9	29.8	29.7	32.5
10	29.7	29.6	31.7
11	29.6	29.4	29.6
12	29.5	29.3	29.55
13	29.4	29.2	29.4
14	29.3	28.8	29.3
15	27.2	27.2	29.29
16	26.9	27.16	29.0
17	24.8	24.8	28.8
18	22.3	22.6	24.8
19	14.0	14.1	22.6
20			14.1

5-(Heptylthio)-1-phenyl-1*H*-tetrazole (14)



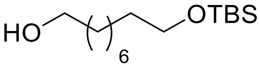
To a stirred solution of 1-heptanol **13** (1.0 g, 8.60 mmol, 1.0 equiv), 1-phenyl-1*H*-tetrazole-5-thiol (1.99 g, 11.18 mmol, 1.3 equiv) and PPh_3 (2.71 g, 10.32 mmol, 1.2 equiv) in THF (40 mL) was added diisopropyl azodicarboxylate (2.20 mL, 11.18 mmol, 1.3 equiv) dropwise at 0 °C and the reaction continued for 3 h. After completely consuming the starting material as judged by TLC, a saturated aq. solution of $NaHCO_3$ was added, and the resulting mixture was extracted with Et_2O (2 × 50 mL). The combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated. The residue was purified by silica gel column chromatography with petroleum ether/EtOAc (4:1) as an eluent to give sulfide **14** (1.90 g, 80%) as a colorless oil. IR ($CHCl_3$) ν_{max} = 2928, 2855, 1696, 1627, 1439, 1282, 1212, 1161, 949, 917, 758, 733, 648, 566 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.63–7.48 (m, 5H), 3.38 (t, *J* = 6.8 Hz, 2H), 1.85–1.74 (m, 2H), 1.47–1.37 (m, 2H), 1.35–1.21 (m, 6H), 0.86 (t, *J* = 7.7 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 154.5, 133.7, 130.0, 129.7, 123.8, 33.3, 31.6, 29.0, 28.6, 28.5, 22.5, 14.0 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{14}H_{21}N_4S$ 277.1482; found 277.1484.

5-(Heptylsulfonyl)-1-phenyl-1*H*-tetrazole (15)



To a solution of sulfide **14** (1.0 g, 3.62 mmol, 1.0 equiv) in EtOH (20 mL), cooled to 0 °C under argon was added a solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (447 mg, 0.36 mmol, 0.1 equiv) and H_2O_2 (3.62 mL, 30%) and then stirred at room temperature for 12 h. The reaction mixture was quenched with H_2O and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with water and brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography with petroleum ether/EtOAc (4:1) as an eluent to give sulfone **15** (971.3 mg, 87%) as a colorless oil. IR ($CHCl_3$) ν_{max} = 2930, 2854, 1504, 1343, 1219, 1151, 1022, 843, 771, 691, 633 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.71–7.64 (m, 2H), 7.63–7.54 (m, 3H), 3.71 (d, *J* = 8.6 Hz, 2H), 2.04–1.84 (m, 2H), 1.53–1.41 (m, 2H), 1.38–1.21 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 153.4, 133.0, 131.4, 129.6, 125.0, 55.9, 31.3, 28.5, 28.0, 22.4, 21.9, 13.9 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{14}H_{21}N_4O_2S$ 309.1380; found 309.1384.

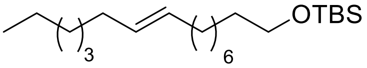
9-(*tert*-Butyldimethylsilyloxy)nonan-1-ol (17)



To the suspension of NaH (60% in oil, 274 mg, 6.86 mmol, 1.1 equiv) in dry THF (50 mL) was added commercially available 1,9-nonane diol **16** (1.0 g, 6.24 mmol, 1.0 equiv) at 0 °C and the mixture stirred for 40 min at room temperature. Then TBSCl (940.5 mg, 6.24 mmol, 1.0 equiv) was added portion-wise at 0 °C and stirred for another 2 h at room temperature. The reaction was quenched with the addition of 10% aq. K_2CO_3. The solution was extracted with Et_2O (3 × 30 mL) and the combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated. The residue was purified by silica gel column chromatography with petroleum ether/EtOAc (9:1) as an eluent to give **17** (1.5 g, 87%) as a colorless oil. IR ($CHCl_3$) ν_{max} = 3400, 2926, 2858, 1517, 1461, 1219, 1060, 835, 771, 688, 642 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.64–3.53 (m, 4H), 1.59–1.42 (m, 4H), 1.34–1.20 (m, 10H), 0.87 (s, 9H), 0.03 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz,

$CDCl_3$) δ = 63.3, 62.9, 32.8, 32.7, 29.5, 29.3, 25.9, 25.73, 25.7, 18.3, –5.3 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{15}H_{35}O_2Si$ 275.2401; found 275.2408.

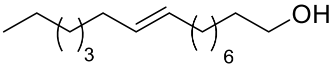
(*E*)-*tert*-Butyl(hexadec-9-en-1-yloxy)dimethylsilane (18)



To a solution of 9-(*tert*-butyldimethylsilyloxy)nonan-1-ol **17** (1.0 g, 3.64 mmol, 1.0 equiv) in dry CH_2Cl_2 (36 mL) was added PCC (1.18 g, 5.46 mmol, 1.5 equiv) in portions at 0 °C. The reaction mixture was allowed to stir for 4 h at room temperature. It was then treated with saturated aq. solutions of $Na_2S_2O_3 \cdot 5H_2O$ (3 mL) and $NaHCO_3$ (3 mL) and stirred for 20 min. The solution was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated to afford the desired aldehyde (900 mg) that was taken for the next step without further purification.

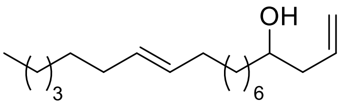
A solution of sulfone **15** (1.12 g, 3.64 mmol, 1.0 equiv) and above crude aldehyde (900 mg) in dimethoxyethane (DME) (33.0 mL) was cooled to –78 °C and KHMDS (3.6 mL, 1.0 M solution in THF, 3.64 mmol, 1.0 equiv) was added via syringe pump over 10 min. The resulting mixture was stirred at –78 °C for 2 h and then was allowed to warm to room temperature over 2 h. Then, a saturated aq. solution of NH_4Cl (1.0 mL) was added and the solution extracted with Et_2O (3 ×10 mL). The combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated. The residue was purified by silica gel column chromatography with petroleum ether/EtOAc (9:1) as an eluent to give *trans*-olefin **18** (1.04 g, 81% over two steps) as a colorless oil. IR ($CHCl_3$) ν_{max} = 2934, 2861, 1594, 1452, 1375, 1277, 1183, 1117, 963, 764, 714 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 5.41–5.34 (m, 2H), 3.59 (t, *J* = 7.0 Hz, 2H), 2.00–1.92 (m, 4H), 1.54–1.47 (m, 2H), 1.33–1.24 (s, 18H), 0.89 (s, 12H), 0.05 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 130.4, 130.3, 63.3, 32.9, 32.6, 31.8, 29.6, 29.5, 29.4, 29.1, 28.8, 26.0, 25.8, 22.6, 18.4, 14.1, –5.3 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{22}H_{47}OSi$ 355.3391; found 355.3393.

(*E*)-Hexadec-9-en-1-ol (19)



To a solution of **18** (1.0 g, 2.82 mmol, 1.0 equiv) in MeOH (28 mL) was added *p*-TsOH·$2H_2O$ (54 mg, 0.282 mmol, 10 mol%) at room temperature. The reaction mixture was stirred at room temperature for 4 h and then MeOH was evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (4:1) as an eluent to give **19** (630.5 mg, 93%) as a colorless oil. IR ($CHCl_3$) ν_{max} = 3499, 3108, 3015, 2921, 1520, 1218, 842, 700, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 5.44–5.32 (m, 2H), 3.62 (t, *J* = 6.6 Hz, 2H), 2.04–1.88 (m, 4H), 1.60–1.50 (m, 2H), 1.44 (brs, 1H), 1.37–1.21 (m, 18H), 0.87 (t, *J* = 7.5 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 130.4, 130.3, 63.0, 32.8, 32.6, 32.56, 31.7, 29.6, 29.44, 29.4, 29.1, 28.8, 25.7, 22.6, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{16}H_{33}O$ 241.2526; found 241.2529.

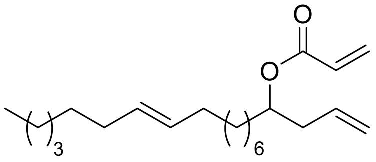
(*E*)-Nonadeca-1,12-dien-4-ol (20)



The titled compound was prepared from alcohol **19** (630 mg, 2.62 mmol) by a similar procedure as described for (±)-**2a** to give homoallylic alcohol **20** (573.2 mg, 78%) as a colorless oil. IR ($CHCl_3$) ν_{max} = 3493, 2928, 2854, 1550, 1452, 1219, 1075, 836, 764, 679, 642 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 5.90–5.75 (m, 1H), 5.42–5.28

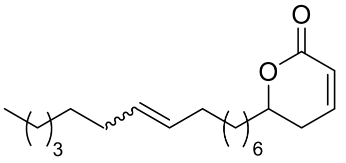
(m, 2H), 5.20–5.04 (m, 2H), 3.68–3.62 (m, 1H), 2.34–2.23 (m, 1H), 2.17–2.06 (m, 1H), 2.04–1.89 (m, 4H), 1.63 (br s, 1H), 1.49–1.39 (m, 3H), 1.37–1.18 (m, 17H), 0.87 (t, *J* = 6.5 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 134.9, 130.4, 130.3, 118.0, 70.7, 41.9, 36.8, 32.6, 32.55, 31.7, 29.6, 29.4, 29.1, 28.8, 25.6, 22.6, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{19}H_{37}O$ 281.2839; found 281.2839.

(*E*)-Nonadeca-1,12-dien-4-yl acrylate (21)



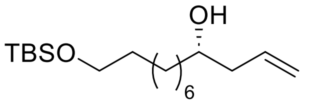
The titled compound was prepared from alcohol **20** (500 mg, 1.78 mmol) by a similar procedure as described for **6** to give ester **21** (512 mg, 86%) as a colorless oil. IR ($CHCl_3$) ν_{max} = 2928, 2854, 1740, 1550, 1452, 104, 1219, 1075, 836, 764, 679, 642 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.37 (dd, *J* = 17.4, 1.4 Hz, 1H), 6.09 (dd, *J* = 16.5, 10.0 Hz, 1H), 5.82–5.68 (m, 2H), 5.42–5.30 (m, 2H), 5.10–4.93 (m, 3H), 2.41–2.24 (m, 2H), 2.02–1.90 (s, 4H), 1.62–1.51 (m, 2H), 1.35–1.22 (m, 18H), 0.87 (t, *J* = 6.5 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 165.9, 133.7, 130.4, 130.3, 130.2, 128.9, 117.6, 73.6, 38.6, 33.5, 32.6, 32.5, 31.7, 29.6, 29.56, 29.4, 29.3, 29.0, 28.8, 25.2, 22.6, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + NH_4]^+$ calcd. $C_{22}H_{42}O_2N$ 352.3210; found 352.3209.

6-(Pentadec-8-en-1-yl)-5,6-dihydro-2*H*-pyran-2-one (12)



The titled compound was prepared from ester **21** (100 mg, 0.299 mmol) by a similar procedure as described for **7a** and **7b** to give lactone **12** (76.1 mg, 83%) as a colorless oil. All spectral and analytical data perfectly matched with the compound **12** obtained from ester **11**.

(*S*)-12-(*tert*-Butyldimethylsilyloxy)dodec-1-en-4-ol (22)

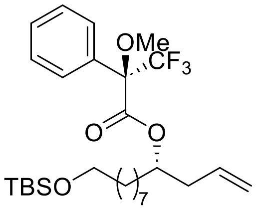


To a solution of 9-(*tert*-butyldimethylsilyloxy)nonan-1-ol **17** (1.0 g, 3.64 mmol, 1.0 equiv) in dry CH_2Cl_2 (36 mL) was added PCC (1.18 g, 5.46 mmol, 1.5 equiv) in portions at 0 °C. The reaction mixture was allowed to stir for 4 h at room temperature. It was then treated with saturated aq. solutions of $Na_2S_2O_3 \cdot 5H_2O$ (3 mL) and $NaHCO_3$ (3 mL) and stirred for 20 min. The solution was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated to afford the desired aldehyde (900 mg) that was taken for the next step without further purification.

A mixture of (*R*)-BINOL (104.2 mg, 0.364 mmol, 0.1 equiv) and $Ti(O^{i}Pr)_4$ (108 µL, 0.364 mmol, 0.1 equiv) in CH_2Cl_2 (15.0 mL) in the presence of 4 Å molecular sieves (1.0 g) was stirred under reflux. After 1 h, the reaction mixture was cooled to room temperature, and the aldehyde (900 mg) as obtained above, was added in CH_2Cl_2 (4.0 mL) and further stirred for 10 min. The reaction mixture was then cooled to −78 °C and allyltributyltin (1.25 mL, 0.40 mmol, 1.1 equiv) was added to it and the stirring continued at −20 °C for 24 h. Then, saturated aq. $NaHCO_3$ solution (10.0 mL) was added to quench the reaction mixture, stirred for an additional 30 min and was then extracted with CH_2Cl_2 (2 × 20). The combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated. The residue was purified by silica gel column chromatography with petroleum ether/EtOAc (9:1) as an eluent to give homoallylic alcohol **22** (927.5 mg, 81% over two steps) as a colorless oil. $[\alpha]_D^{25}$ −2.6 (*c* 1.8, $CHCl_3$); IR ($CHCl_3$) ν_{max} = 3363, 2926, 2857, 1518, 1460, 1252, 1096, 915, 836, 772, 646 cm^{-1}; ^{1}H NMR (400 MHz,

$CDCl_3$) δ = 5.89–5.74 (m, 1H), 5.17–5.08 (m, 2H), 3.67–3.61 (m, 1H), 3.59 (t, J = 7.8 Hz, 2H), 2.36–2.23 (m, 1H), 2.17–2.08 (m, 1H), 1.51–1.48 (m, 2H), 1.46–1.42 (m, 2H), 1.30–1.25 (m, 10H), 0.89 (s, 9H), 0.03 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 134.9, 118.0, 70.7, 63.3, 41.9, 36.8, 32.9, 29.6, 29.5, 29.4, 26.0, 25.8, 25.6, 18.4, –5.3 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{19}H_{39}O_2Si$ 315.2715; found 315.2721.

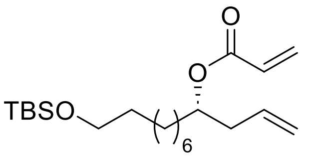
(*S*)-12-(*tert*-Butyldimethylsilyloxy)dodec-1-en-4-yl (*R*)-3,3,3-trifluoro-2-methoxy-2-phenyl propanoate (51)



To a stirred solution of alcohol **22** (20 mg, 0.064 mmol, 1.0 equiv), DCC (20 mg, 0.095 mmol, 1.5 equiv) and DMAP (3.1 mg, 0.0256 mmol, 0.4 equiv) in CH_2Cl_2 (1.0 mL) at room temperature was added (−)-(*S*)-α-methoxy-α-(trifluoromethyl)phenylacetic acid (18.7 mg, 0.08 mmol, 1.2 equiv) in one portion. The reaction mixture was stirred for an additional 5 h at room temperature. It was then filtered through a cotton plug and the plug was washed with CH_2Cl_2 (5 mL). The filtrate was washed with water and brine, dried (Na_2SO_4) and concentrated under vacuum. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (9:1) as an eluent to afford ester **51** (27.2 mg, 80%) as a colorless oil. $[\alpha]_D^{25}$ –17.4 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) ν_{max} = 2927, 2857, 1724, 1603, 1529, 1462, 1219, 1102, 925, 837, 771, 719, 603 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.61–7.51 (m, 2H), 7.40–7.32 (m, 3H), 5.82–5.70 (m, 1H), 5.21–5.03 (m, 3H), 3.63–3.58 (m, 2H), 3.57–3.55 (m, 3H), 2.41 (t, J = 7.0 Hz, 2H), 1.54–1.44 (m, 4H), 1.27–1.21 (m, 10H), 0.89 (s, 9H), 0.047 (s, 6H).

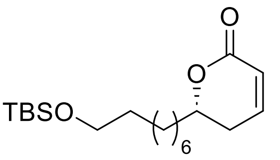
Following similar procedure as above the (*R*)-3,3,3-trifluoro-2-methoxy-2-phenyl ester of racemic (±)-**22** was also prepared and analyzed by proton NMR for two diastereomer peaks (see spectra on page S59). Analysis of the proton NMR data of ester **51** indicated a single diastereomer (>50:1 dr), which means compound **22** to be enantiomerically pure (>98% ee).

(*S*)-12-(*tert*-Butyldimethylsilyloxy)dodec-1-en-4-yl acrylate (23)



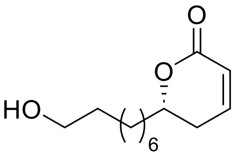
The titled compound was prepared from alcohol **22** (500 mg, 1.59 mmol) by a similar procedure as described for (±)-**2a** to give ester **23** (504 mg, 86%) as a colorless oil. $[\alpha]_D^{25}$ −11.6 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) ν_{max} = 2924, 2853, 1704, 1622, 1537, 1451, 1233, 1180, 1089, 898, 836, 771, 645 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.37 (d, J = 17.0 Hz, 1H), 6.09 (dd, J = 17.0, 6.7 Hz, 1H), 5.84–5.67 (m, 2H), 5.13–5.88 (m, 3H), 3.58 (t, J = 7.0 Hz, 2H), 2.42–2.26 (m, 2H), 1.62–1.53 (m, 2H), 1.52–1.45 (m, 2H), 1.33–1.26 (m, 10H), 0.88 (s, 9H), 0.035 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 165.9, 133.7, 130.3, 128.9, 117.6, 73.6, 63.3, 38.6, 33.5, 32.8, 29.4, 29.36, 29.3, 26.0, 25.7, 25.2, 18.4, –5.3 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{21}H_{41}O_3Si$ 369.2820; found 369.2826.

(*S*)-6-(8-(*tert*-Butyldimethylsilyloxy)octyl)-5,6-dihydro-2*H*-pyran-2-one (24)



The titled compound was prepared from ester **23** (100 mg, 0.27 mmol) by a similar procedure as described for **7a** and **7b** to give lactone **24** (77 mg, 83%) as a colorless oil. $[\alpha]_D^{25}$ −15.7 (*c* 1.2, CHCl$_3$); IR (CHCl$_3$) ν_{max} = 2925, 2859, 1725, 1521, 1460, 1381, 1220, 1077, 837, 771, 689, 639 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ = 6.89–6.84 (m, 1H), 6.01 (td, *J* = 10.0, 1.0 Hz, 1H), 4.45–4.32 (m, 1H), 3.59 (t, *J* = 8.0 Hz, 2H), 2.34–2.29 (m, 2H), 1.83–1.74 (m, 1H), 1.66–1.59 (m, 2H), 1.53–1.47 (m, 2H), 1.42–1.36 (m, 1H), 1.34–1.29 (s, 8H), 0.88 (s, 9H), 0.038 (s, 6H) ppm; ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ = 164.6, 145.0, 121.4, 78.0, 63.3, 34.8, 32.8, 29.4, 29.37, 29.3, 26.0, 25.7, 24.8, 18.4, –5.3 ppm; HRMS (ESI-TOF): *m/z* [M + K]$^+$ calcd. $C_{19}H_{36}O_3Sik$ 379.2068; found 379.2078.

(*S*)-6-(8-Hydroxyoctyl)-5,6-dihydro-2*H*-pyran-2-one (25)

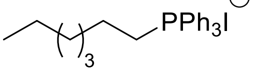


The titled compound was prepared from lactone **24** (77 mg, 0.226 mmol) by a similar procedure as described for **19** to give ester **25** (47.6 mg, 93%) as a colorless oil. $[\alpha]_D^{25}$ +29.6 (*c* 1.7, CHCl$_3$); IR (CHCl$_3$) ν_{max} = 3400, 2922, 2860, 1726, 1515, 1458, 1279, 1128, 1028, 952, 815, 771, 691, 645 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ = 6.91–6.82 (m, 1H), 6.01 (dt, *J* = 10.0, 2.0 Hz, 1H), 4.47–4.33 (m, 1H), 3.63 (t, *J* = 7.8 Hz, 2H), 2.35–2.27 (m, 2H), 1.86–1.72 (m, 1H), 1.68–1.61 (m, 2H), 1.57–1.52 (m, 2H), 1.36–1.31 (s, 9H) ppm; ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ = 164.6, 145.1, 121.4, 78.0. 63.0, 34.8, 32.7, 29.4, 29.35, 29.2, 29.22, 25.7, 24.7 ppm; HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd. $C_{13}H_{23}O_3$ 227.1642; found 227.1646.

Procedure for Wittig Salts (26)

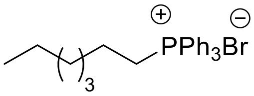
To a solution of 1-haloheptane (2.5 mmol) in toluene (20 mL) was added Ph$_3$P (2.75 mmol). After refluxing for 48 h, the reaction mixture was cooled to rt, and the solvent was removed under reduced pressure. The crude product was dissolved in CH$_2$Cl$_2$ (5 mL) and then added dropwise to Et$_2$O (10 mL). After stirring for 1 h, the precipitate was filtered and dried under vacuum, affording the titled compound in pure form as white powder.

Heptyltriphenylphosphonium iodide (26a)

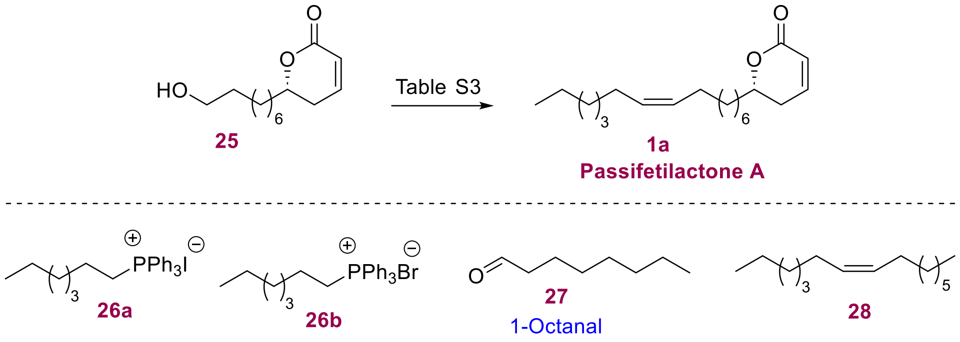


(1.1 g, 90%), white solid, M.P: 120–125 °C, IR (CHCl$_3$) ν_{max} = 2920, 2869, 1556, 1416, 1202, 1108, 995, 748, 679 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.76–7.62 (m, 15H), 3.52 (br s, 2H), 1.58–1.55 (m, 4H), 1.20–1.12 (m, 6H), 0.74 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ = 135.0, 134.95, 133.4, 133.3, 130.5, 130.3, 118.2, 117.4, 31.1, 30.3, 30.1, 28.5, 23.1, 22.6, 22.34, 22.3, 22.2, 13.8 ppm.

Triphenylheptylphosphonium bromide (26b)



(1.06 g, 96%), white solid, M.P: 160–165 °C, IR ($CHCl_3$) ν_{max} = 2919, 2859, 1586, 1436, 1232, 1188, 995, 738, 689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.80–7.63 (m, 15H), 3.64 (br s, 2H), 1.58–1.55 (m, 4H), 1.20–1.13 (m, 6H), 0.75 (t, J = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 135.0, 134.9, 133.5, 133.4, 130.5, 130.3, 118.6, 117.7, 31.2, 30.3, 30.16, 28.7, 22.9, 22.44, 22.4, 22.35, 13.9 ppm.



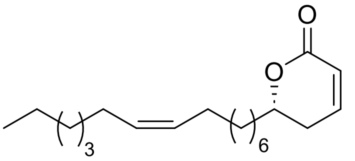
The compound **25** was subjected to IBX oxidation to give the corresponding aldehyde that was next taken for olefination with the iodo-Wittig salt **26a** by using KHMDS as base. In this reaction the starting aldehyde decomposed (Table S3, entry 1). As a model reaction, 1-octanal **27** was treated with the ylide generated from **26a** under the same reaction conditions that led to the formation of the desired *cis*-olefin **28** (entry 2). Hence, the Wittig olefination was optimized and the details are provided in the ESI. Next, we considered different oxidations like Swern oxidation, DMP, TEMPO and PCC oxidation and the aldehyde obtained was then treated with the same ylide from iodo-Wittig salt **26a**. Unfortunately, the Wittig olefination reaction failed in all cases (entries 3-6). Change in base like *n*-BuLi and *t*-BuONa (entries 7 and 8) in ylide generation also proved futile. We finally considered using the bromo-Wittig salt **26b**. Under PCC oxidation, the aldehyde from **25** was treated with the ylide obtained from **26b** using KHMDS, which successfully furnished the desired natural product passifetilactone A (**1a**) in good 80% yield (entry 9).

Table S3 Oxidation of **25** and Wittig olefination.

entry	oxidation of 25/ aldehyde	Wittig salt	conditions	results (yield over 2 steps)
1	IBX oxidation	**26a**	KHMDS, –78 °C, THF, 4 h	decomposition
2	1-octanal **27**	**26a**	KHMDS, –78 °C, THF, 4 h	*cis*-olefin **28**, 82%
3	Swern oxidation	**26a**	KHMDS, –78 °C, THF, 4 h	decomposition
4	DMP oxidation	**26a**	KHMDS, –78 °C, THF, 4 h	decomposition
5	TEMPO oxidation	**26a**	KHMDS, –78 °C, THF, 4 h	decomposition
6	PCC oxidation	**26a**	KHMDS, –78 °C, THF, 4 h	decomposition
7	PCC oxidation	**26a**	*n*-BuLi, –78 °C, THF, 4 h	decomposition
8	PCC oxidation	**26a**	*t*-BuONa, 0 °C, THF, 12 h	aldehyde recovered
9	PCC oxidation	**26b**	KHMDS, –78 °C, THF, 2 h	passifectilactone A (**1a**), 80%

aldehyde (1.0 equiv), Wittig salt (1.3 equiv), base (1.5 equiv)

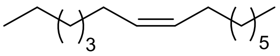
(*S*,*Z*)-6-(Pentadec-8-en-1-yl)-5,6-dihydro-2*H*-pyran-2-one, passifetilactone A (1a)



To a solution of **25** (40 mg, 0.176 mmol, 1.0 equiv) in dry CH_2Cl_2 (10 mL) was added PCC (57 mg, 0.265 mmol, 1.5 equiv) in portions at 0 °C. The reaction mixture was allowed to stir for 4 h at room temperature. It was then treated with saturated aq. solutions of $Na_2S_2O_3{\cdot}5H_2O$ (3 mL) and $NaHCO_3$ (3 mL) and stirred for 20 min. The solution was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated to afford the desired aldehyde (36 mg) that was taken for the next step without further purification.

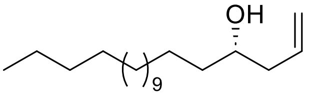
To a stirred slurry of Wittig salt **26b** (102 mg, 0.23 mmol, 1.3 equiv) in THF (5 mL) at –78 °C was added KHMDS (264 µL, 1.0 M solution in THF, 0.264 mmol, 1.5 equiv) dropwise. The mixture was warmed to room temperature over 1 h before recooling to –78 °C. To this was added the above aldehyde (36 mg) in THF (3 mL) dropwise and the mixture stirred for 1 h at –78 °C and then 1 h at room temperature. Then saturated aq. NH_4Cl solution was added and the aqueous layer was separated. This was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried (Na_2SO_4), and the solvent evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (4:1) as eluent to give *passifetilactone* A (**1a**) (45.1 mg, 80%) as a colorless oil. $[\alpha]_D^{21}$ +6.3 (*c* 0.1, MeOH), lit.[1] $[\alpha]_D^{21}$ +6.0 (*c* 0.1, MeOH); IR ($CHCl_3$) ν_{max} = 2923, 2855, 1725, 1456, 1385, 1302, 1247, 1142, 1040, 963, 860, 817, 770, 661 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.92–6.82 (m, 1H), 6.01 (d, *J* = 10.0 Hz, 1H), 5.41–5.28 (m, 2H), 4.49–4.34 (m, 1H), 2.34–2.28 (m, 2H), 2.05–1.95 (m, 4H), 1.83–1.74 (m, 1H), 1.66–1.59 (m, 2H), 1.52–1.47 (m, 1H), 1.30 (s, 16H), 0.87 (t, *J* = 6.8 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 160.6, 145.0, 130.0, 129.8, 121.5, 78.0, 34.9, 31.8, 29.7, 29.6, 29.4, 29.3, 29.2, 29.0, 28.8, 27.2, 27.16, 24.8, 22.6, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + Na]^+$ calcd. $C_{20}H_{34}O_2Na$ 329.2451; found 329.2455.

(*Z*)-Pentadec-7-ene (28)



The titled compound was prepared from 1-octanal **27** (50 mg, 0.39 mmol) by a similar procedure as described for **1a** to give *cis*-olefin **28** (67.3 mg, 82%) as a colorless oil. IR ($CHCl_3$) ν_{max} = 2923, 2855, 1456, 1385, 1302, 1247, 1142, 1040, 963, 860, 817, 770, 661 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.35 (t, *J* = 4.8 Hz, 2H), 2.04–1.97 (m, 4H), 1.33–1.24 (m, 18H), 0.88 (t, *J* = 7.0 Hz, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 129.9, 31.9, 31.8, 29.74, 29.7, 29.3, 29.2, 29.0, 27.2, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + K]^+$ calcd. $C_{15}H_{30}k$ 249.1979; found 249.1984.

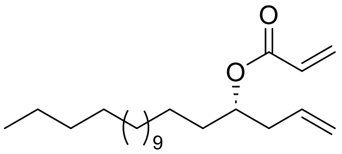
(*S*)-Nonadec-1-en-4-ol (2b)



To a solution of 1-hexadecanol **4** (600 mg, 2.47 mmol, 1.0 equiv) in dry CH_2Cl_2 (10 mL) was added PCC (800 mg, 3.71 mmol, 1.5 equiv) in portions at 0 °C. The reaction mixture was allowed to stir for 4 h at room temperature. It was then treated with saturated aq. solutions of $Na_2S_2O_3{\cdot}5H_2O$ (3 mL) and $NaHCO_3$ (3 mL) and stirred for 20 min. The solution was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated to afford the desired aldehyde **29** (580 mg) that was taken for the next step without further purification.

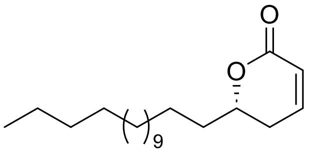
To a stirred solution of $TiCl_4$ (27 µL, 0.247 mmol, 0.1 equiv) in CH_2Cl_2 (5 mL) under N_2 atmosphere, was added Ti(O^{i}Pr)$_4$ (220 µL, 0.741 mmol, 0.3 equiv) at 0 °C. The solution was allowed to warm to room temperature and was stirred for 1 h. Under the exclusion of direct light, Ag_2O (114.5 mg, 0.494 mmol, 0.2 equiv) was added and the stirring was continued for a further 5 h. The reaction mixture was diluted with CH_2Cl_2 (5 mL) and (*R*)–BINOL (141.4 mg, 0.494 mmol, 0.2 equiv) was added and the stirring was continued for an additional 2 h to furnish the chiral catalyst. The resulting mixture was treated with 1–hexadecanal **29** (580) and allyl(tributyl)stannane (1.0 mL, 3.21 mmol, 1.3 equiv) at −20 °C. The temperature was raised to 0 °C and stirring continued for 24 h at the same temperature. The reaction was quenched with saturated aq. $NaHCO_3$ solution (15 mL) and the resulting mixture was stirred for 1 h. The aqueous layer was extracted with CH_2Cl_2 (2 × 15 mL). The combined organic layers were dried (Na_2SO_4), and the solvent evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (4:1) as eluent to give homoallyl alcohol **2b** (607 mg, 87% over two steps) as a white solid. M.P: 46–48 °C, $[\alpha]_D^{25}$ −3.1 (*c* 2.0, $CHCl_3$); IR ($CHCl_3$) ν_{max} = 3386, 3076, 2928, 2852, 1452, 1369, 1214, 1043, 997, 910, 771, 687, 636 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.87–5.79 (m, 1H), 5.15–5.11 (m, 2H), 3.67–3.62 (m, 1H), 2.33–2.27 (m, 1H), 2.17–2.10 (m, 1H), 1.67 (brs, 1H), 1.50–1.41 (m, 3H), 1.36–1.21 (s, 25H), 0.88 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 134.9, 118.0, 70.7, 41.9, 36.8, 31.9, 29.7, 29.64, 29.6, 29.3, 25.7, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd. $C_{19}H_{39}O$ 283.2995; found 283.2989.

(*S*)-Nonadec-1-en-4-yl acrylate (30)



The titled compound was prepared from alcohol **2b** (200 mg, 0.71 mmol) by a similar procedure as described for **6** to give ester **30** (205.5 mg, 86%) as a colorless oil. $[\alpha]_D^{25}$ −17.0 (*c* 1.2 $CHCl_3$); IR ($CHCl_3$) ν_{max} = 2921, 2850, 1691, 1526,1442, 1373, 1309, 1222, 1075, 987, 952, 898, 770, 645 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.38 (dd, *J* = 17.0, 1.3 Hz, 1H), 6.09 (dd, *J* = 17.7, 10.6 Hz, 1H), 5.83–5.69 (m, 2H), 5.10–4.96 (m, 3H), 2.46–2.29 (m, 2H), 1.61–1.54 (m, 2H), 1.33–1.24 (m, 26H), 0.87 (t, *J* = 6.3 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 165.9, 133.7, 130.3, 128.9, 117.6, 73.6, 38.6, 33.6, 31.9, 29.7, 29.64, 29.6, 29.54, 29.5, 29.4, 29.3, 25.2, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd. $C_{22}H_{41}O_2$ 337.3102; found 337.3105.

(*S*)-6-Pentadecyl-5,6-dihydro-2*H*-pyran-2-one, passifetilactone C (1c)



The titled compound was prepared from ester **30** (50 mg, 0.15 mmol) by a similar RCM procedure as described for **7a** and **7b** to give passifetilactone C (**1c**) (37 mg, 80%) as amorphous solid. $[\alpha]_D^{21}$ +2.4 (*c* 0.1, MeOH), lit.^{1} $[\alpha]_D^{21}$ +2.0 (*c* 0.1, MeOH); IR ($CHCl_3$) ν_{max} = 2916, 2851, 1695, 1641, 1467, 1389, 1317, 1264, 1160, 1122, 1032, 910, 863, 770, 722 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.91–6.82 (m, 1H), 6.00 (d, *J* = 9.8 Hz, 1H), 4.45–4.36 (m, 1H), 2.38–2.24 (m, 2H), 1.83–1.73 (m, 1H), 1.69–1.57 (m, 1H), 1.55–1.44 (m, 1H), 1.43–1.36 (m, 1H), 1.35–1.18 (m, 24H), 0.86 (t, *J* = 6.3 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 164.6, 145.0, 121.4, 78.0, 34.8, 31.9, 29.64, 29.6, 29.59, 29.5, 29.4, 29.34, 29.3, 24.8, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd. $C_{20}H_{37}O_2$ 309.2789; found 309.2791.

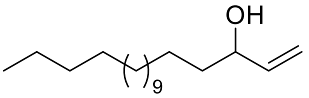
Table S4: Comparison of ^{1}H NMR of natural passifetilactone C isolated by Schevenels and the present synthetic **1c**

Sr. No.	**Passifetilactone C isolated by Schevenels** *J. Nat. Prod.*, 2024, **87**,1652–1659.	**Synthetic Passifetilactone C (1c)** **This work**
1	6.87 (m, 1H)	6.91–6.82 (m, 1H)
2	6.01 (ddd, *J* = 9.6, 2.2, 1.5 Hz, 1H)	6.00 (d, *J* = 9.8 Hz, 1H)
3	4.41 (ddt, *J* = 10.1, 7.3, 5.4 Hz, 1H)	4.45–4.36 (m, 1H)
4	2.32 (m, 2H)	2.38–2.24 (m, 2H)
5	1.79 (m, 1H)	1.83–1.73 (m, 1H)
6	1.63 (m, 1H)	1.69–1.57 (m, 1H)
7	1.50 (m, 1H)	1.55–1.44 (m, 1H)
8	1.39 (m, 1H)	1.43–1.36 (m, 1H)
9	1.32–1.25 (brm overlap, 24H)	1.35–1.18 (m, 24H)
10	0.87 (t, *J* = 6.8 Hz, 3H)	0.86 (t, *J* = 6.3 Hz, 3H)

Table S5: Comparison of ^{13}C NMR of natural passifetilactone C isolated by Schevenels and the present synthetic **1c**

Sr. No.	**Passifetilactone C isolated by Schevenels** *J. Nat. Prod.*, 2024, **87**,1652–1659.	**Synthetic Passifetilactone C (1c)** **This work**
1	164.8	164.6
2	145.2	145.0
3	121.6	121.4
4	78.2	78.0
5	35.0	34.8
6	32.1	31.9
7	29.7	29.64
8	29.7	29.6
9	29.7	29.59
10	29.6	29.5
11	29.6	29.4
12	29.6	29.34, 29.3
13	24.9	24.8
14	22.8	22.7
15	14.3	14.1

Octadec-1-en-3-ol (33)



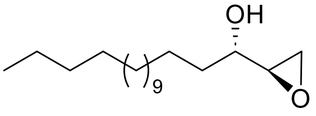
A solution of 1-hexadecanol **4** (1.0 g, 4.12 mmol, 1.0 equiv) in CH_2Cl_2 (25 mL) was added to a suspension of PCC (1.33 g, 6.18 mmol, 1.5 equiv) in CH_2Cl_2 (15 mL) at 0 °C. The mixture was stirred at room temperature until the completion of the reaction (TLC, 4 h) and then diluted by the addition of Et_2O (50 mL) and filtered through a small pad of silica gel (with ether rinsing). The solvent was removed under vacuum and the crude aldehyde (1.0 g) was used without further purification.

To a solution of the above aldehyde (1.0 g) in dry THF (20 mL) cooled to 0 °C was added dropwise vinyl magnesium chloride (1.6 M in THF, 3.9 mL, 6.18 mmol, 1.5 equiv). The solution was stirred for 1 h and then quenched at 0 °C by slow addition of saturated aq. solution of NH_4Cl. The organic layer was separated and the aqueous layer was extracted with EtOAc (2 × 30 mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (9:1) as an eluent to afford **33** (0.984 g, 89% over two steps) as a colourless oil. IR ($CHCl_3$) ν_{max} = 3337, 3265, 3084, 2916, 2851, 1690, 1463, 1316, 1271, 1138, 989, 920, 716, 675 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 5.90–5.81 (m, 1H), 5.20 (d, J = 17.2 Hz, 1H), 5.08 (d, J = 10.4 Hz, 1H), 4.08 (d, J = 5.4 Hz, 1H), 1.62 (s, 1H), 1.57–1.46 (m, 2H), 1.33–1.20 (m, 26H), 0.87 (t, J = 6.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 141.3, 114.5, 73.3, 37.0, 31.9, 29.7, 29.64, 29.6, 29.5, 29.3, 25.3, 22.7, 14.0 ppm; HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd. $C_{18}H_{36}ONa$ 291.2660; found 291.2670.

(*S*)-1-[(*R*)-Oxiran-2-yl]hexadecan-1-ol (32) and (*R*)-Octadec-1-en-3-ol (32′)

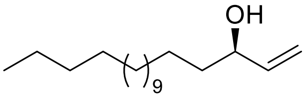
To a suspension of dry 4 Å MS powder (2.5 g) in dry CH_2Cl_2 (15 mL) was added Ti(O-*i*-Pr)$_4$ (0.11 mL, 0.372 mmol, 0.1 equiv) at −20 °C, followed by (+)-DIPT (113.4 mg, 0.484 mmol, 0.13 equiv) and the mixture was stirred for 0.5 h. To this mixture was added allyl alcohol **33** (1.0 g, 3.72 mmol, 1.0 equiv) in dry CH_2Cl_2 (10 mL) dropwise at the same temperature and stirred for 0.5 h. Then, TBHP in decane (0.285 g, 3.162 mmol, 0.85 equiv) was added dropwise and the resultant reaction mixture was stirred at −20 °C. After 18 h, saturated aq. Na_2SO_4 (3 mL) was added and the solution was allowed to warm to room temperature and stirred for 3 h. The solids formed were filtered through a pad of Celite and the filtrate was concentrated in vacuum. The crude product was purified by silica gel column chromatography using petroleum ether/EtOAc (4:1) as an eluent to afford epoxide **32** (455 mg, 43%) as a white solid. M.p. 46–48 °C. Further elution gave allyl alcohol **32′** (399.5 mg, 40%) as a light-yellow oil.

(*S*)-1-((*R*)-Oxiran-2-yl)hexadecan-1-ol (32)



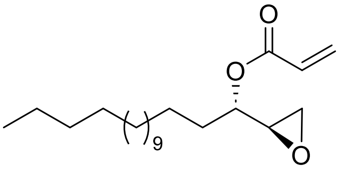
$[\alpha]_D^{25}$ +19.6 (c 1.0, $CHCl_3$); IR ($CHCl_3$) ν_{max} = 3394, 3016, 2918, 2849, 1463, 1377, 1215, 1070, 989, 959, 849, 752, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.81 (d, J = 1.8 Hz, 1H), 3.00 (d, J = 4.0 Hz, 1H), 2.80 (dd, J = 5.0, 2.8 Hz, 1H), 2.72 (t, J = 4.1 Hz, 1H), 1.93 (s, 1H), 1.58–1.45 (m, 3H), 1.44–1.23 (m, 25H), 0.87 (t, J = 6.7 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 68.4, 54.5, 43.4, 33.4, 31.9, 29.7, 29.64, 29.6, 29.56, 29.5, 29.3, 25.3, 22.7, 14.1 ppm; HRMS (ESI-TOF): m/z [M + H]$^+$ calcd. $C_{18}H_{37}O_2$ 285.2788; found 285.2783.

(*R*)-Octadec-1-en-3-ol (32′)



$[\alpha]_D^{25}$ −8.6 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) ν_{max} = 3336, 3263, 3085, 2916, 2851, 2341, 1615, 1463, 1417, 1138, 990, 920, 716, 675 cm^{-1}; 1H NMR (400 MHz, $CDCl_3$) δ = 5.89–5.80 (m, 1H), 5.20 (dt, *J* = 17.1, 1.2 Hz, 1H), 5.10 (dt, *J* = 10.4, 1.2 Hz, 1H), 4.10 (q, 6.3 Hz, 1H), 1.70 (br s, 1H), 1.50–1.40 (m, 2H), 1.36–1.21 (m, 26H), 0.86 (t, *J* = 7.1 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 141.3, 114.4, 73.2, 37.0 31.9, 29.7, 29.6, 29.5, 29.3, 22.6, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + Na]^+$ calcd. $C_{18}H_{36}ONa$ 291.2660; found 291.2670.

(*S*)-1-[(*R*)-Oxiran-2-yl]hexadecyl acrylate (35)



To a stirred solution of compound **32** (500 mg, 1.76 mmol, 1.0 equiv) in dry CH_2Cl_2 (8 mL) at 0 °C was added acrylic anhydride (443.9 mg, 3.52 mmol, 2.0 equiv), triethylamine (356.2 mg, 3.52 mmol, 2.0 equiv) and DMAP (107.5 mg, 0.88 mmol, 0.5 equiv). The resulting mixture was allowed to stir at room temperature for 4 h. After completion (TLC), the reaction was quenched with H_2O and the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (20:1) as an eluent to afford **35** (387.3 mg, 65%) as a colorless oil. $[\alpha]_D^{25}$ +3.2 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) ν_{max} = 2921, 2854, 1728, 1629, 1459, 1404, 1367, 1262, 1185, 1049, 973, 894, 855, 809, 771, 723, 644 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 6.41 (d, *J* = 17.4 Hz, 1H), 6.11 (dd, *J* = 17.4, 10.5 Hz, 1H), 5.84 (d, *J* = 10.4 Hz, 1H), 4.79 (q, 6.2 Hz, 1H), 3.00–2.98 (m, 1H), 2.76–2.73 (m, 2H), 1.71 (q, *J* = 7.4 Hz, 2H), 1.36–1.24 (m, 26H), 0.87 (t, *J* = 6.6 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 165.5, 131.1, 128.3, 73.2, 52.3, 45.6, 31.9, 31.4, 29.7, 29.64, 29.6, 29.5, 29.42, 29.4, 29.3, 24.9, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + NH_4]^+$ calcd. $C_{21}H_{42}O_3N$ 356.3160; found 356.3165.

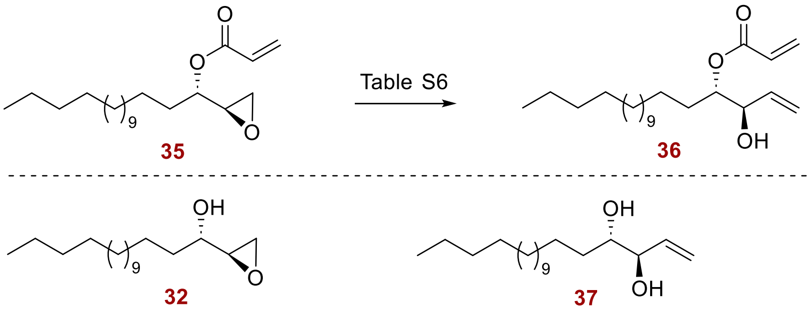


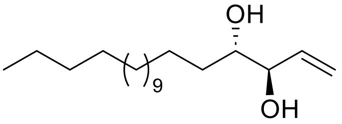
Table S6 Sulfoxonium ylide opening of epoxide **35**.

entry	conditions	equivalent of base	results (yield)
1	Me_3SI, *n*-BuLi, –20 °C, THF, 2 h	2	**32** (72%)
2	Me_3SI, *n*-BuLi, –50 °C, THF, 2 h	2	**32** (67%)

3	Me_3SI, *n*-BuLi, –20 °C, THF, 2 h	1	**32** (70%)
4	Me_3SI, *n*-BuLi, –20 °C, THF, 2 h	3 or more	**37** (67%)
5	Me_3SI, KHMDS, –20 °C, THF, 2 h	1	**32** (69%)
6	Me_3SI, NaH, –20 °C, THF, 2 h	1	**32** (65%)
7	Me_3SI, KHMDS, –20 °C, THF, 2 h	3 or more	**37** (66%)

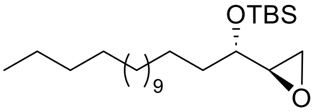
The compound **35** was taken for epoxide opening with sulfoxonium ylide (Table S4). With the use of *n*-BuLi (2.0 equiv) as base to generate the ylide and addition of epoxide, the reactions performed at –20 or –50 °C resulted in only the ester hydrolysis giving epoxy alcohol **32** (entries 1 and 2, Table S2). Change in base concentration to 1.0 equiv also gave same result (entry 3). An increase in base amount to 3.0 or more equiv furnished the epoxide opening product with the ester also being hydrolyzed giving the diol **37** (entry 4). Change in base to KHMDS or NaH (1.0 equiv in each case) also gave the ester hydrolysed product **32** (entries 5 and 6). Increase in base concentration to 3.0 or more equiv resulted in the diol **37** (entry 7). It was difficult to chemoselectively esterify one of the hydroxy groups in diol **37**.

(3*R*,4*S*)-Nonadec-1-ene-3,4-diol (37)



To a suspension of trimethylsulfonium iodide (682.2 mg, 3.10 mmol, 3.0 equiv) in dry THF (10 mL) was added *n*-BuLi (2.5 M in hexanes, 1.25 mL, 3.10 mmol, 3.0 equiv) dropwise at −20 °C and stirred for 1 h. Then a solution of epoxide **35** (350 mg, 1.034 mmol, 1.0 equiv) in dry THF (4 mL) was added dropwise and stirred for 0.5 h. The resultant cloudy suspension was allowed to slowly warm to room temperature and stirred for another 2 h. After consumption of the starting material (monitored by TLC), it was then quenched by the addition of saturated aq. Solution of NH_4Cl (5 mL). The solution was extracted with EtOAc (3 × 15 mL) and the combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (4:1) as an eluent to afford **37** (206.8 mg, 67%) as a colorless oil. $[\alpha]_D^{25}$ −1.8 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) ν_{max} = 3290, 3207, 3037, 2914, 2849, 1466, 1298, 1079, 1035, 997, 921, 770, 711, 645 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 5.98−5.87 (m, 1H), 5.38–5.26 (m, 2H), 4.10 (q, *J* = 3.5 Hz, 1H), 3.72−3.65 (m, 1H), 1.67 (brs, 2H), 1.49–1.45 (m, 2H), 1.42–1.24 (m, 26H), 0.87 (t, *J* = 7.1 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 136.0, 117.7, 75.9, 74.1, 32.2, 31.9, 29.7, 29.6, 29.58, 29.5, 29.4, 25.8, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + Na]^+$ calcd. $C_{19}H_{38}O_2Na$ 321.2764; found 321.2747.

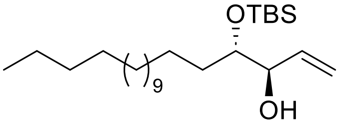
***tert*-Butyldimethyl((*S*)-1-((*R*)-oxiran-2-yl)hexadecyloxy)silane (38)**



To a solution of **32** (300 mg, 1.054 mmol, 1.0 equiv) in dry CH_2Cl_2 (10 mL) was added 2,6-lutidine (226 mg, 2.11 mmol, 2.0 equiv) at 0 °C and stirred for 15 min. To this TBSOTf (418 mg, 1.581 mmol. 1.5 equiv) was added dropwise over 10 min and stirred for 30 min. Then, ice-cooled water was added to the reaction mixture and the organic layer separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL) and the combined organic layers were washed with water and brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography with petroleum ether/EtOAc (20:1) as an eluent to afford **38** (336 mg, 80%) as a colorless oil. $[\alpha]_D^{25}$ +3.8 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) ν_{max} = 2922, 2855, 1462, 1370, 1252, 1095, 998, 926, 837, 777 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.57−3.53 (m, 1H), 2.86−2.84 (m, 1H), 2.68 (dd, *J* = 5.5, 3.9 Hz, 1H), 2.64 (dd, *J* = 5.4, 2.6 Hz, 1H), 1.60−1.48 (m, 2H), 1.30−1.25 (m, 26H), 0.90−0.87 (m, 12H), 0.037 (s, 6H) ppm;

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 71.3, 54.7, 44.8, 35.3, 31.9, 29.7, 29.69, 29.66, 29.6, 29.55, 29.4, 25.9, 25.8, 25.7, 24.9, 22.7, 18.2, 14.1, −4.4, −4.8 ppm; HRMS (ESI-TOF): *m/z* $[M + NH_4]^+$ calcd. $C_{24}H_{54}O_2SiN$ 416.3918; found 416.3910.

(3*R*,4*S*)-4-(*tert*-Butyldimethylsilyloxy)nonadec-1-en-3-ol (*ent*-34)



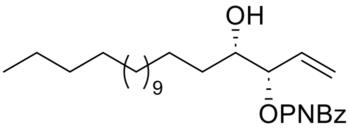
The titled compound was prepared from epoxide **38** (300 mg, 0.752 mmol) by a similar procedure as described for **37** to give ***ent*-34** (217.3 mg, 70%) as a colorless oil. $[\alpha]_D^{25}$ +1.8 (*c* 1.0 $CHCl_3$); IR ($CHCl_3$) ν_{max} = 3345, 2923, 2855, 1462, 1370, 1252, 1095, 998, 926, 837, 777 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 5.88–5.79 (m, 1H), 5.27 (d, *J* = 17.3 Hz, 1H), 5.18 (d, *J* = 10.6 Hz, 1H), 4.10–4.07 (m, 1H), 3.68 (d, *J* = 3.5 Hz, 1H), 2.23 (s, 1H), 1.30–1.24 (m, 28H), 0.90–0.87 (m, 12H), 0.08 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 136.5, 116.4, 75.9, 75.4, 31.9, 31.6, 29.7, 29.68, 29.58, 29.5 29.4, 25.9, 25.6, 22.7, 18.1, 14.1, –4.4, –4.48 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{25}H_{53}O_2Si$ 413.3810; found 413.3816.

(3*S*,4*S*)-4-Hydroxynonadec-1-en-3-yl 4-nitrobenzoate (39a) and (3*R*,4*S*)-4-Hydroxynonadec-1-en-3-yl 4-nitrobenzoate (39b)

To a solution of allylic alcohol ***ent*-34** (300 mg, 0.727 mmol, 1.0 equiv) in dry THF (10 mL) were added PPh_3 (954.7 mg, 3.64 mmol, 5.0 equiv), *p*-nitrobenzoic acid (608.3 mg, 3.64 mmol, 5.0 equiv) and DIAD (736 mg, 3.64 mmol, 5.0 equiv) under a N_2 atmosphere. The resultant mixture was stirred at room temperature for 8 h. After the completion of the reaction, the reaction mixture was concentrated under reduced pressure and was used without further purification.

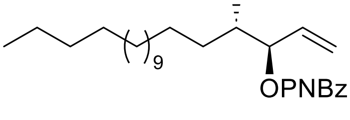
To a solution of above crude compound in MeOH (5 mL) was added *p*-TsOH·H_2O (13.9 mg, 0.073 mmol, 10 mol%) at room temperature. The reaction mixture was stirred at room temperature for 2 h and then MeOH was evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (10:1) as an eluent to give **39a** (169.2 mg, 52%) as a colorless oil and further elution gave **39b** (81.4 mg, 25%) as a colorless oil.

(3*S*,4*S*)-4-Hydroxynonadec-1-en-3-yl 4-nitrobenzoate (39a)



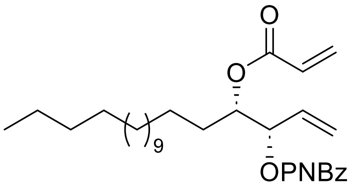
$[\alpha]_D^{25}$ +5.7 (*c* 1.0 $CHCl_3$); IR ($CHCl_3$) ν_{max} = 3319, 3228, 3113, 2917, 2850, 1717, 1680, 1606, 1538, 1461, 1407, 1351, 1271, 1098, 1013, 972, 871, 840, 777, 717, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.28 (d, *J* = 8.8 Hz, 2H), 8.21 (d, *J* = 8.9 Hz, 2H), 5.90 (d, *J* = 1.9 Hz, 2H), 4.86 (d, *J* = 3.5 Hz, 2H), 4.17 (d, *J* = 4.1 Hz, 1H), 1.56–1.52 (m, 2H), 1.34–1.22 (m, 26H), 0.87 (t, *J* = 6.4 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 164.4, 150.6, 138.5, 135.5, 130.7, 123.5, 123.47, 72.0, 65.7, 37.1, 31.9, 29.7, 29.6, 29.56, 29.5, 29.48, 29.3, 25.3, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + NH_4]^+$ calcd. $C_{26}H_{45}O_5N_2$ 465.3323; found 465.3324.

(3*R*,4*S*)-4-Hydroxynonadec-1-en-3-yl 4-nitrobenzoate (39b)



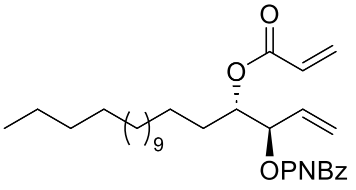
$[\alpha]_D^{25}$ –2.4 (*c* 1.0 $CHCl_3$); IR ($CHCl_3$) ν_{max} = 3319, 3222, 3115, 2917, 2850, 1717, 1679, 1606, 1539, 1461, 1401, 1351, 1271, 1098, 972, 937, 872, 717, 632 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.29 (d, *J* = 8.7 Hz, 2H), 8.22 (d, *J* = 8.9 Hz, 2H), 5.98–5.87 (m, 1H), 5.47–5.17 (m, 3H), 4.30 (d, J = 4.9 Hz, 1H), 1.79–1.74 (m, 2H), 1.53–1.46 (m, 1H), 1.30–1.23 (m, 26H), 0.87 (t, J = 6.9 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 164.6, 150.6, 136.7, 135.6, 130.8, 123.6, 117.4, 77.9, 74.0, 31.9, 30.3, 29.7, 29.6, 29.57, 29.5, 29.4, 29.3, 25.4, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* [M + NH$_4$]$^+$ calcd. $C_{26}H_{45}O_5N_2$ 465.3323; found 465.3327.

(3*S*,4*S*)-4-(Acryloyloxy)nonadec-1-en-3-yl 4-nitrobenzoate (40a)



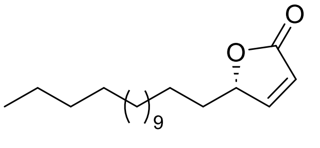
The titled compound was prepared from alcohol **39a** (200 mg, 0.447 mmol) by a similar procedure as described for **35** to give ester **40a** (145.8 mg, 65%) as a colorless oil. $[\alpha]_D^{25}$ +7.5 (c 1.0 $CHCl_3$); IR ($CHCl_3$) ν_{max} = 2923, 2855, 1727, 1687, 1608, 1530, 1457, 1403, 1349, 1270, 1189, 1108, 1046, 974, 870, 813, 774, 720, 645 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.31 (d, J = 8.8 Hz, 2H), 8.24 (d, J = 9.0 Hz, 2H), 6.44 (dd, J = 17.7, 1.5 Hz, 1H), 6.15 (q, J = 10.6 Hz, 1H), 5.92–5.85 (m, 3H), 5.40 (br s, 1H), 4.88 (d, J = 5.27 Hz, 2H), 1.69–1.56 (m, 2H), 1.35–1.23 (m, 26H), 0.89 (t, J = 6.65 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 165.5, 164.3, 150.6, 135.4, 133.6, 130.9, 130.8, 128.6, 125.6, 123.5, 73.7, 65.4, 34.2, 31.9, 29.7, 29.6, 29.5, 29.45, 29.34, 29.3, 25.0, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* [M + NH$_4$]$^+$ calcd. $C_{29}H_{47}O_6N_2$ 519.3429; found 519.3435.

(3*R*,4*S*)-4-(Acryloyloxy)nonadec-1-en-3-yl 4-nitrobenzoate (40b)



The titled compound was prepared from alcohol **39b** (200 mg, 0.447 mmol) by a similar procedure as described for **35** to give ester **40b** (141.3 mg, 63%) as a colorless oil. $[\alpha]_D^{25}$ +3.4 (c 1.0 $CHCl_3$); IR ($CHCl_3$) ν_{max} = 2923, 2855, 1727, 1687, 1608, 1530, 1496, 1457, 1403, 1349, 1270, 1189, 1108, 1046, 974, 870, 842, 774, 645 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.28 (d, J = 8.9 Hz, 2H), 8.18 (d, J = 9.0 Hz, 2H), 6.38 (dd, J = 17.3, 1.3 Hz, 1H), 6.11–6.04 (m, 1H), 5.83–5.79 (m, 2H), 5.58 (t, J = 6.3 Hz, 1H), 5.42–5.29 (m, 3H), 1.75–1.66 (m, 2H), 1.28–1.23 (m, 26H), 0.87 (t, J = 6.6 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 165.0, 164.2, 150.6, 135.4, 132.1, 131.6, 130.8, 127.9, 123.6, 119.8, 75.5, 74.8, 31.9, 30.4, 29.7, 29.6, 29.56, 29.5, 29.33, 29.3, 25.0, 24.95, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* [M + NH$_4$]$^+$ calcd. $C_{29}H_{47}O_6N_2$ 519.3429; found 519.3400.

(*S*)-5-Pentadecylfuran-2(5*H*)-one (41)

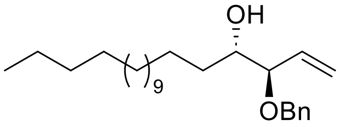


The titled compound was prepared from ester **40a** or **40b** (100 mg, 0.199 mmol) by a similar RCM procedure as described for **7a** and **7b** to give ester **41** (35.7 mg, 61%) as a white solid. M.p. 43–48 °C; $[\alpha]_D^{25}$ +29.6 (c 1.0 $CHCl_3$); IR ($CHCl_3$) ν_{max} = 3086, 2918, 2853, 1792, 1742, 1468, 1367, 1266, 1176, 1101, 1011, 903, 822, 771, 710, 637 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.44 (dd, J = 5.7, 1.2 Hz, 1H), 6.09 (dd, J = 5.7, 1.9 Hz, 1H), 5.02 (q, J = 5.6 Hz, 1H), 1.79–1.65 (m, 2H), 1.45–1.41 (m, 2H), 1.39–1.24 (m, 24H), 0.87 (t, J = 6.7 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 173.2, 156.3, 121.5, 83.4, 33.2, 31.9, 29.7, 29.63, 29.62, 29.6, 29.56, 29.5, 29.34, 29.3, 24.9, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd. $C_{19}H_{35}O_2$ 295.2633; found 295.2639.

(3*R*,4*S*)-3-(Benzyloxy)nonadec-1-en-4-ol (31) and (3*R*,4*S*)-4-(Benzyloxy)nonadec-1-en-3-ol (44)

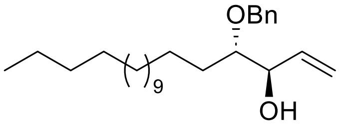
To a suspension of sodium hydride (60% in oil, 58 mg, 1.452 mmol, 1.2 equiv) in dry THF (10 mL) was added dropwise a solution of allylic alcohol ***ent*-34** (500 mg, 1.21 mmol, 1.0 equiv) in THF/DMF (1:1, 40 mL) at 0 °C. Benzyl bromide (248 mg, 1.45 mmol, 1.2 equiv) was added subsequently and the mixture was stirred at 0 °C for 7 h. The reaction mixture was quenched using crushed ice flakes until a clear solution was formed. The solution was extracted with EtOAc (3 × 25 mL). The combined organic layers were washed with water and brine, dried (Na_2SO_4) and concentrated. The residue was used without further purification. To a solution of the above compound (500 mg, 1.21 mmol, 1.0 equiv) in MeOH (15 mL) was added *p*-TsOH·H_2O (230.2 mg, 1.21 mmol, 1.0 equiv) at room temperature. The reaction mixture was stirred at room temperature for 2 h and then MeOH was evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (3:2) as an eluent to afford **31** (207 mg, 44%) as a colorless liquid. Further elution gave compound **44** (136.4 mg, 29%) as a colorless oil.

(3*R*,4*S*)-3-(Benzyloxy)nonadec-1-en-4-ol (31)



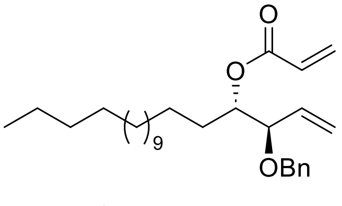
$[\alpha]_D^{25}$ –37.8 (*c* 1.0 $CHCl_3$); IR ($CHCl_3$) ν_{max} = 3585, 3471, 3066, 3030, 2921, 2851, 1496, 1464, 1388, 1302, 1205, 1067, 1027, 996, 926, 732, 696 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* = 7.37–7.28 (m, 5H), 5.90–5.84 (m, 1H), 5.40 (dd, *J* = 10.5, 1.6 Hz, 1H), 5.31 (dd, *J* = 17.5, 1.5 Hz, 1H), 4.64 (d, *J* = 11.9 Hz, 1H), 4.39 (d, *J* = 11.8 Hz, 1H), 3.75–3.71 (m, 2H), 2.19 (s, 1H), 1.48–1.42 (m, 2H), 1.36–1.24 (m, 26H), 0.89 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) *δ* = 138.3, 134.4, 128.3, 127.7, 127.6, 120.1, 83.6, 73.2, 70.2, 32.2, 31.9, 29.7, 29.6, 29.58, 29.56, 29.3, 25.7, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{26}H_{45}O_2$ 389.3414; found 389.3415.

(3*R*,4*S*)-4-(Benzyloxy)nonadec-1-en-3-ol (44)



$[\alpha]_D^{25}$ –2.6 (*c* 1.0 $CHCl_3$); IR ($CHCl_3$) ν_{max} = 3588, 3480, 3069, 2921, 2855, 1495, 1459, 1383, 1303, 1206, 1066, 1027, 995, 927, 733, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* = 7.37–7.34 (m, 4H), 7.32–7.28 (m, 1H), 5.93–5.87 (m, 1H), 5.33 (d, *J* = 17.1 Hz, 1H), 5.22 (d, *J* = 10.6 Hz, 1H), 4.62 (dd, *J* = 11.6, 9.5 Hz, 2H), 4.30 (d, *J* = 2.4 Hz, 1H), 3.45 (q, 3.6 Hz, 1H), 2.26 (s, 1H), 1.64–1.56 (m, 1H), 1.48–1.44 (m, 2H), 1.35–1.24 (m, 25H), 0.89 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) *δ* = 138.4, 136.7, 128.4, 127.8, 127.7, 116.4, 82.1, 73.5, 72.1, 31.9, 29.7, 29.6, 29.57, 29.5, 29.33, 29.3, 25.7, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{26}H_{45}O_2$ 389.3414; found 389.3412.

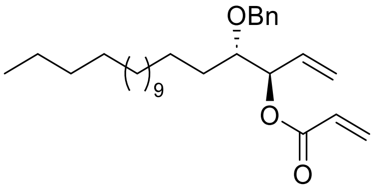
(3*R*,4*S*)-3-(Benzyloxy)nonadec-1-en-4-yl acrylate (45)



The titled compound was prepared from alcohol **31** (300 mg, 0.772 mmol) by a similar procedure as described for **35** to give ester **45** (222.1 mg, 65%) as a colorless oil. $[\alpha]_D^{25}$ –42.4 (*c* 1.0 $CHCl_3$); IR ($CHCl_3$) ν_{max} = 2922, 2852, 1726, 1637, 1495, 1460, 1403, 1294, 1267, 1190, 1068, 986, 965, 929, 807, 733, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* =

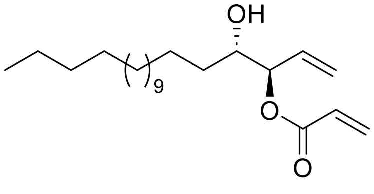
7.38–7.33 (m, 4H), 7.32–7.28 (m, 1H), 6.43 (d, *J* = 16.2 Hz, 1H), 6.15 (dd, *J* = 17.4, 10.4 Hz, 1H), 5.87–5.78 (m, 2H), 5.34 (d, *J* = 16.4 Hz, 2H), 5.12 (q, *J* = 5.5 Hz, 1H), 4.66 (d, *J* = 12.3 Hz, 1H), 4.45 (d, *J* = 12.1 Hz, 1H), 3.89 (t, *J* = 6.6 Hz, 1H), 1.73–1.69 (m, 2H), 1.32–1.24 (m, 26H), 0.90 (t, *J* = 6.8 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 165.7, 138.2, 134.9, 130.5, 128.7, 128.2, 127.5, 127.4, 119.5, 81.2, 75.1, 70.3, 31.9, 29.7, 29.66, 29.62, 29.6, 29.5, 29.45, 29.4, 29.3, 25.3, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + Na]^+$ calcd. $C_{29}H_{46}O_3Na$ 465.3340; found 465.3337.

(3*R*,4*S*)-4-(Benzyloxy)-5-methyloctadec-1-en-3-yl acrylate (46)



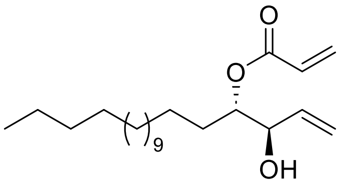
The titled compound was prepared from alcohol **44** (250 mg, 0.643 mmol) by a similar procedure as described for **35** to give ester **46** (185.0 mg, 65%) as a colorless oil. $[\alpha]_D^{25}$ +37.0 (*c* 1.0 $CHCl_3$); IR ($CHCl_3$) ν_{max} = 2922, 2852, 1726, 1620, 1495, 1459, 1403, 1294, 1267, 1190, 1068, 986, 965, 929, 807, 733, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.38–7.33 (m, 4H), 7.32–7.28 (m, 1H), 6.46 (d, *J* = 17.2 Hz, 1H), 6.19 (dd, *J* = 17.3, 10.3 Hz, 1H), 6.01–5.93 (m, 1H), 5.88 (d, *J* = 10.4 Hz, 1H), 5.54 (d, *J* = 5.1 Hz, 1H), 5.38–5.31 (m, 2H), 4.76 (d, *J* = 11.5 Hz, 1H), 4.56 (d, *J* = 11.4 Hz, 1H), 3.58 (t, *J* = 4.6 Hz, 1H), 1.64–1.44 (m, 2H), 1.34–1.28 (m, 26H), 0.91 (t, *J* = 6.8 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 165.3, 138.4, 132.7, 130.9, 128.6, 128.3, 127.9, 127.6, 118.6, 80.2, 76.3, 72.6, 31.9, 30.8, 29.7, 29.6, 29.56, 29.5, 29.3, 25.7, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + Na]^+$ calcd. $C_{29}H_{46}O_3Na$ 465.3340; found 465.3336.

(3*R*,4*S*)-4-Hydroxynonadec-1-en-3-yl acrylate (47)



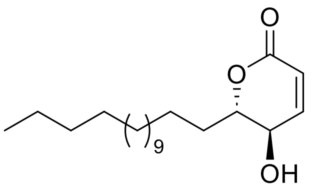
To a stirred solution of **46** (200 mg, 0.452 mmol, 1.0 equiv) in dry CH_2Cl_2 (7 mL) at 0 °C was added a solution of $TiCl_4$ (102.8 mg, 0.542 mmol, 1.2 equiv) in dry CH_2Cl_2 (2 mL) under N_2 and the mixture was stirred from 0 °C to room temperature for 1 h. After the completion of the reaction, the mixture was quenched with saturated aq. Solution of $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (2 × 20 mL). The combined organic phases were washed with brine, dried (Na_2SO_4) and concentrated. The crude residue was purified by silica gel column chromatography using petroleum ether/ EtOAc (4:1) as eluent to give **47** (138.6 mg, 87%) as a colorless oil. $[\alpha]_D^{25}$ +3.0 (*c* 1.0 $CHCl_3$); IR ($CHCl_3$) ν_{max} = 3482, 2921, 2852, 1723, 1637, 1618, 1461, 1405, 1375, 1294, 1270, 1191, 1049, 967, 926, 808, 771, 722, 673 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.42 (d, *J* = 17.7 Hz, 1H), 6.14 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.92–5.83 (m, 2H), 5.36–5.25 (m, 3H), 3.76 (t, *J* = 4.1 Hz, 1H), 2.09 (s, 1H), 1.49–1.39 (m, 2H), 1.37–1.20 (m, 26H), 0.85 (t, *J* = 6.1 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 165.3, 131.8, 131.2, 128.3, 119.6, 78.1, 72.7, 32.3, 31.9, 29.63, 29.6, 29.5, 29.48, 29.3, 25.6, 22.6, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{22}H_{41}O_3$ 353.3051; found 353.3052.

(3*R*,4*S*)-3-Hydroxynonadec-1-en-4-yl acrylate (36)



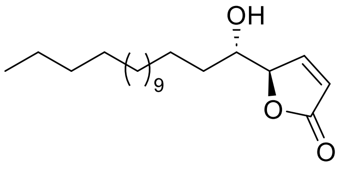
The titled compound was prepared from ester **45** (250 mg, 0.564 mmol) by a similar procedure as described for **47** to give ester **36** (173 mg, 87%) as a colorless oil. $[\alpha]_D^{25}$ −2.8 (*c* 1.0 $CHCl_3$); IR ($CHCl_3$) ν_{max} = 3464, 2921, 2852, 1723, 1637, 1461, 1405, 1375, 1294, 1270, 1191, 1049, 985, 926, 808, 771, 722 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* = 6.43 (d, *J* = 17.3 Hz, 1H), 6.14 (dd, *J* = 17.3, 10.5 Hz, 1H), 5.91–5.82 (m, 2H), 5.34 (d, *J* = 10.1 Hz, 1H), 5.24 (d, *J* = 10.5 Hz, 1H), 5.03–4.98 (m, 1H), 4.25 (s, 1H), 2.21 (br s, 1H), 1.72–1.61 (m, 2H), 1.45–1.21 (m, 26H), 0.87 (t, *J* = 6.9 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) *δ* = 166.4, 135.8, 131.2, 128.4, 117.4, 74.7, 31.9, 29.7, 29.64, 29.6, 29.5, 29.4, 29.38, 29.3, 25.5, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{22}H_{41}O_3$ 353.3051; found 353.3049.

(5*R*,6*S*)-5-Hydroxy-6-pentadecyl-5,6-dihydro-2*H*-pyran-2-one, 4-*epi*-passifetilactone B (48)



The titled compound was prepared from ester **36** (100 mg, 0.284 mmol) by a similar RCM procedure as described for **7a** and **7b** to give lactone **48** (59.9 mg, 65%) as a white solid. M.p. 43–48 °C; $[\alpha]_D^{25}$ −4.0 (*c* 1.0 $CHCl_3$); IR ($CHCl_3$) ν_{max} = 3535, 3353, 3084, 2955, 2916, 2850, 1783, 1741, 1598, 1469, 1383, 1334, 1169, 1113, 1065, 1023, 980, 949, 893, 865, 831, 799, 772, 718 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* = 6.82 (dd, *J* = 9.8, 8.1 Hz, 1H), 5.98 (d, *J* = 9.8 Hz, 1H), 4.30– 4.20 (m, 2H), 2.20 (br s, 1H), 1.86–1.58 (m, 4H), 1.36 –1.20 (m, 24H), 0.87 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) *δ* = 163.1, 148.5, 120.8, 82.6, 66.1, 32.0, 31.9, 29.7, 29.6, 29.5, 29.4, 29.36, 29.3, 24.7, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{20}H_{37}O_3$ 325.2738; found 325.2735.

(*R*)-5-((*S*)-1-Hydroxyhexadecyl)furan-2(5*H*)-one (*ent*-1e)

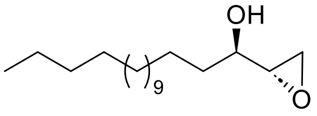


The titled compound was prepared from ester **47** (80 mg, 0.227 mmol) by a similar procedure as described for **7a** and **7b** to give lactone ***ent*-1e** (50.1 mg, 68%) as a white solid. M.p. 43–48 °C; $[\alpha]_D^{25}$ +15.5 (*c* 0.1 MeOH); IR ($CHCl_3$) ν_{max} = 3533, 3385, 3084, 2916, 2850, 1782, 1741, 1598, 1491 1383, 1334, 1169, 1113, 1065, 1023, 981, 949, 893, 865, 831, 799, 772, 718, 652 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* = 7.53 (dd, *J* = 5.8, 1.4 Hz, 1H), 6.19 (dd, *J* = 5.8, 1.9 Hz, 1H), 4.99–4.95 (m, 1H), 3.86 (t, *J* = 3.9 Hz, 1H), 1.61–1.51 (m, 2H), 1.39–1.22 (m, 26H), 0.87 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) *δ* = 173.0, 153.5, 122.8, 86.1, 71.5, 33.0, 31.9, 29.7, 29.62, 29.6, 29.5, 29.46, 29.4, 29.3, 25.5, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{20}H_{37}O_3$ 325.2738; found 325.2736.

(*R*)-1-((*S*)-Oxiran-2-yl)-hexadecan-1-ol (*ent*-32) and (*S*)-Octadec-1-en-3-ol (*ent*-32′)

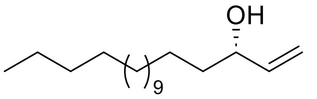
The titled compounds were prepared from **33** (1.5 g, 5.59 mmol) using (–)-DIPT and by following a similar procedure to that described for **32** and **32′** to obtain epoxide ***ent*-32** (699 mg, 44%) as a white solid and ***ent*-32′** (600 mg, 40%) as a light-yellow oil.

Data for *ent*-32



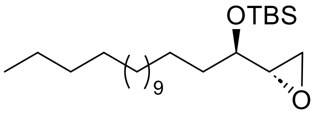
M.p. 46–48 °C; $[\alpha]_D^{25}$ –19.2 (*c* 1.0, CHCl$_3$); IR (CHCl$_3$) ν_{max} = 3390, 3010, 2921, 2853, 1462, 1376, 1217, 1077, 959, 841, 753, 668 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ = 3.81 (d, *J* = 1.8 Hz, 1H), 2.98 (q, *J* = 3.0 Hz, 1H), 2.80 (dd, *J* = 5.0, 2.7 Hz, 1H), 2.72 (t, *J* = 4.1 Hz, 1H), 1.93 (s, 1H), 1.58–1.45 (m, 2H), 1.34–1.21 (m, 26H), 0.90 (t, *J* = 6.70 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ = 68.4, 54.5, 43.4, 33.4, 31.9, 29.7, 29.64, 29.6, 29.56, 29.5, 29.3, 25.3, 22.7, 14.2 ppm; HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd. $C_{18}H_{37}O_2$ 285.2788; found 285.2782.

Data for *ent*-32′



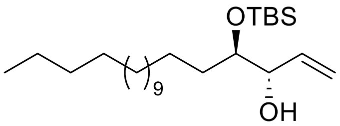
$[\alpha]_D^{25}$ +8.3 (*c* 1.0 CHCl$_3$); IR (CHCl$_3$) ν_{max} = 3336, 3263, 3085, 2916, 2851, 1691, 1615, 1463, 1417, 1138, 990, 920, 716, 675 cm^{-1}; ^{1}H NMR (400 MHz, CDCl3) δ = 5.89–5.80 (m, 1H), 5.20 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.10 (t, *J* = 11.8 Hz, 1H), 4.10 (q, *J* = 6.3 Hz, 1H), 1.77 (s, 1H), 1.50–1.40 (m, 2H), 1.30–1.24 (m, 26H), 0.86 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ = 141.3, 114.4, 73.2, 37.0, 31.9, 29.7, 29.64, 29.6, 29.56, 29.5, 29.3, 25.3, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* [M + Na]$^+$ calcd. $C_{18}H_{36}ONa$ 291.2659; found 291.2670.

tert-Butyldimethyl((*R*)-1-((*S*)-oxiran-2-ylhexadecyloxy)silane (*ent*-38)



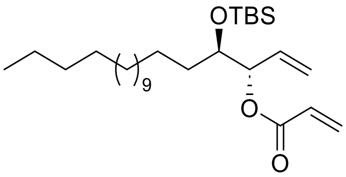
The titled compound was prepared from epoxide ***ent*-32** (450 mg, 1.581 mmol) by a similar procedure as described for **38** to give ***ent*-38** (504.6 mg, 80%) as a colorless oil. $[\alpha]_D^{25}$ –3.7 (*c* 1.0 CHCl$_3$); IR (CHCl$_3$) ν_{max} = 3323, 2917, 2851, 1464, 1254, 1071, 720 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ = 3.56–3.53 (m, 1H), 2.86–2.84 (m, 1H), 2.68 (dd, *J* = 5.5, 3.9 Hz, 1H), 2.64 (dd, *J* = 5.4, 2.6 Hz, 1H), 1.60–1.48 (m, 2H), 1.34–1.25 (m, 26H), 0.89–0.85 (m, 12H), 0.037 (s, 6H) ppm; ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ = 71.3, 54.7, 44.8, 35.3, 31.9, 29.72, 29.7, 29.65, 29.6, 29.55, 29.4, 25.8, 24.9, 22.7, 18.2, 14.1, –4.4, –4.89 ppm; HRMS (ESI-TOF): *m/z* [M + NH$_4$]$^+$ calcd. $C_{24}H_{54}O_2SiN$ 416.3918; found 416.3910.

(3*S*,4*R*)-4-(*tert*-Butyldimethylsilyloxy)nonadec-1-en-3-ol (34)



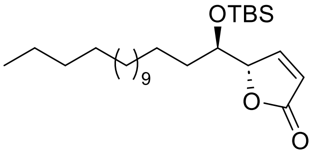
The titled compound was prepared from epoxide ***ent*-38** (400 mg, 1.0 mmol) by a similar procedure as described for **37** to give **34** (289 mg 70% yield) as a colorless oil. $[\alpha]_D^{25}$ –1.9 (*c* 1.0, CHCl$_3$); IR (CHCl$_3$) ν_{max} = 3350, 2922, 2855, 1462, 1370, 1252, 1095, 998, 926, 857, 776, 722, 673 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ = 5.88–5.79 (m, 1H), 5.27 (dt, *J* = 17.3, 1.6 Hz, 1H), 5.18 (dt, *J* = 12.1, 10.6 Hz, 1H), 4.09 (t, *J* = 1.9 Hz, 1H), 3.68 (t, *J* = 3.8 Hz, 1H), 2.23 (d, *J* = 4.2 Hz, 1H), 1.32–1.22 (m, 28H), 0.90–0.86 (m, 12H), 0.08 (s, 6H) ppm; ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) *δ* = 136.5, 116.4, 75.9, 75.4, 31.9, 31.6, 29.74, 29,7, 29.65, 29.6, 29.5, 29.4, 25.9, 25.8, 25.6, 22.7, 18.1, 14.1, −4.4, −4.47 ppm; HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd. $C_{25}H_{53}O_2Si$ 413.3810; found 413.3815.

(3*S*,4*R*)-4-(*tert*-Butyldimethylsilyloxy)nonadec-1-en-3-yl acrylate (49)



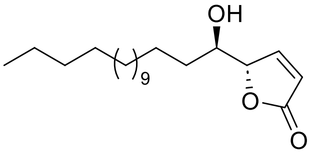
The titled compound was prepared from alcohol **34** (250 mg, 0.605 mmol) by a similar procedure as described for **35** to give **49** (220.3 mg, 78% yield) as a colorless oil. $[\alpha]_D^{25}$ −2.7 (*c* 1.0 CHCl$_3$); IR (CHCl$_3$) ν_{max} = 2923, 2855, 1729, 1632, 1462, 1403, 1369, 1257, 1187, 1104, 1045, 976, 030, 886, 775, 671 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) *δ* = 6.42 (dd, *J* = 17.3, 1.3 Hz, 1H), 6.17–6.07 (m, 1H), 5.97–5.86 (m, 1H), 5.82 (dd, *J* = 10.3, 1.3 Hz, 1H), 5.31–5.23 (m, 3H), 3.81 (q, *J* = 2.7 Hz, 1H), 1.42–1.33 (m, 2H), 1.31–1.20 (m, 26H), 0.90–0.86 (m, 12H), 0.06 (s, 6H) ppm; ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) *δ* = 165.4, 132.5, 130.8, 128.7, 119.2, 78.2, 73.6, 33.7, 31.9, 29.7, 29.6, 29.5, 29.4, 25.9, 25.8, 25.76, 25.4, 22.7, 18.2, 14.1, −4.4, −4.5 ppm; HRMS (ESI-TOF): *m/z* [M + Na]$^+$ calcd. $C_{28}H_{54}O_3SiNa$ 489.3735; found 489.3732.

(*S*)-5-((*R*)-1-(*tert*-Butyldimethylsilyloxy)hexadecyl)furan-2(5*H*)-one (50)



The titled compound was prepared from ester **49** (150 mg, 0.321 mmol) by a similar RCM procedure as described for **7a** and **7b** to give lactone **50** (101.4 mg, 72%) as a colorless oil. $[\alpha]_D^{25}$ −58.8 (*c* 1.0, CHCl$_3$); IR (CHCl$_3$) ν_{max} = 2922, 2855, 1760, 1606, 1462, 1371, 1254, 1154, 1115, 1082, 902, 833, 783, 715 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) *δ* = 7.49 (dd, *J* = 5.8, 1.4 Hz, 1H), 6.13 (dd, *J* = 5.8, 1.9 Hz, 1H), 4.96–4.92 (m, 1H), 3.88 (q, *J* = 5.5 Hz, 1H), 1.45–1.41 (m, 2H), 1.35–1.23 (m, 26H), 0.87 (t, *J* = 7.1 Hz, 3H), 0.84 (s, 9H), 0.04 (s, 6H) ppm; ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) *δ* = 173.0, 154.0, 122.5, 85.5, 72.2, 34.6, 31.9, 29.7, 29.63, 29.6, 29.5, 29.46, 29.3, 25.7, 24.9, 22.7, 18.0, 14.1, −4.6, −4.77 ppm; HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd. $C_{26}H_{51}O_3Si$ 439.3602; found 439.3606.

(*S*)-5-((*R*)-1-Hydroxyhexadecyl)furan-2(5*H*)-one, passifetilactone E (1e)



The titled compound was prepared from ester **50** (50 mg, 0.14 mmol) by a similar procedure as described for **25** to give *passifetilactone E* (**1e**) (37.7 mg, 83%) as a white solid. M.p. 66–67 °C; $[\alpha]_D^{25}$ −16.0 (*c* 0.1, MeOH); lit.[1] $[\alpha]_D^{25}$ −15.0 (c 0.1, MeOH); IR (CHCl$_3$) ν_{max} = 3408, 3106, 2918, 2852 2816, 1747, 1600, 1463, 1326, 1171, 1096, 1035, 826, 719 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) *δ* = 7.53 (dd, *J* = 5.8, 1.4 Hz, 1H), 6.19 (dd, *J* = 5.8, 1.9 Hz, 1H), 4.96–4.91 (m, 1H), 3.86 (t, *J* = 3.9 Hz, 1H), 2.05 (br s, 1H), 1.61–1.51 (m, 2H), 1.39–1.22 (m, 26H), 0.87 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) *δ* = 172.9, 153.4, 122.9, 86.0, 71.6, 33.0, 31.9, 29.7, 29.63, 29.6, 29.5, 29.46, 29.4, 29.3, 25.5, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd. $C_{20}H_{37}O_3$ 325.2737; found 325.2739.

Table S7: Comparison of ^{1}H NMR of natural passifetilactone E isolated by Schevenels and the present synthetic **1e**

Sr. No.	**Passifetilactone E isolated by Schevenels** *J. Nat. Prod.*, 2024, **87**,1652–1659	**Synthetic Passifetilactone E** **This work**
1	7.45 (dd, *J* = 5.8, 1.5 Hz, 1H)	7.53 (dd, *J* = 5.8, 1.4 Hz, 1H)
2	6.16 (dd, *J* = 5.8, 1.9 Hz, 1H)	6.19 (dd, *J* = 5.8, 1.9 Hz, 1H)
3	4.97 (ddd, *J* = 4.8, 2.0, 1.6 Hz, 1H)	4.96–4.91 (m, 1H)
4	3.78 (dt, *J* = 6.3, 4.8 Hz, 3H)	3.86 (t, *J* = 3.9 Hz, 1H)
5	1.57 (m, 1H), 1.50 (m, 1H)	1.61–1.51 (m, 2H)
6	1.42–1.21 (brm overlap, 26H)	1.39–1.22 (m, 26H)
7	0.86 (t, *J* = 6.8 Hz, 3H)	0.87 (t, *J* = 7.1 Hz, 3H)

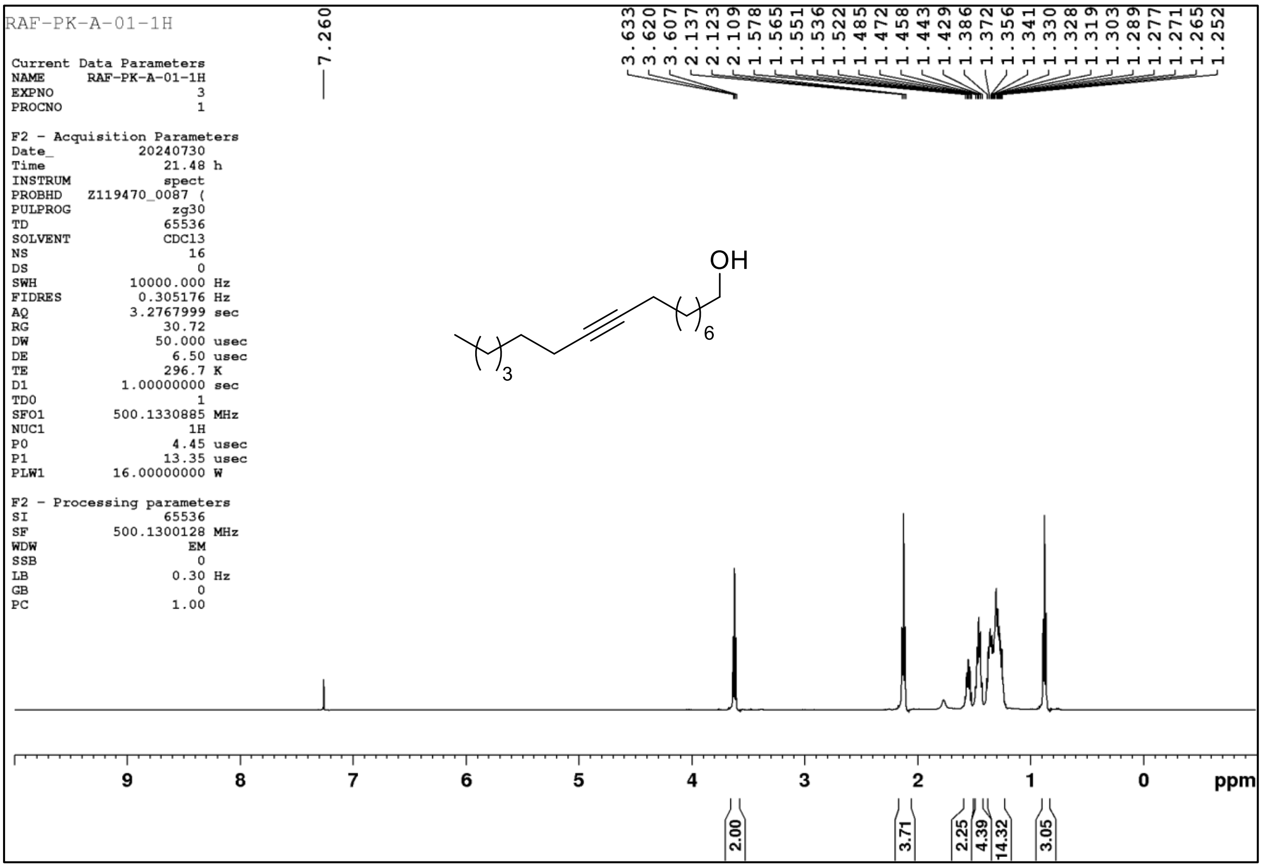
Table S8: Comparison of ^{13}C NMR of natural passifetilactone E isolated by Schevenels and the present synthetic **1e**

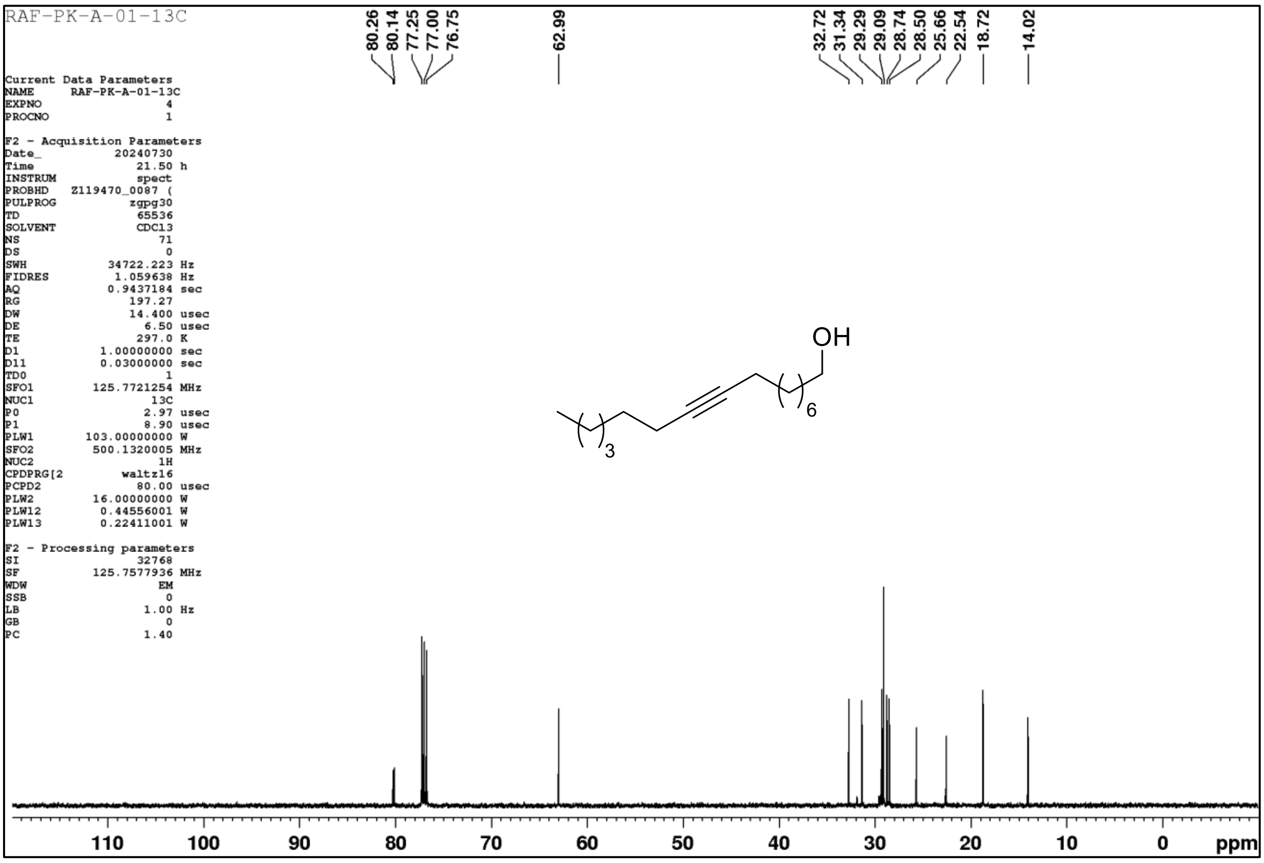
Sr. No.	**Passifetilactone E isolated by Schevenels** *J. Nat. Prod.*, 2024, **87**,1652–1659	**Synthetic Passifetilactone E (1e)** **This work**
1	173.0	172.9
2	153.8	153.4
3	122.9	122.9
4	86.2	86.0
5	72.1	71.6
6	33.4	33.0
7	32.1	31.9
8	29.8	29.7
9	29.7	29.63
10	29.7	29.6
11	29.7	29.5
12	29.6	29.46
13	29.5	29.4
14	29.4	29.3
15	25.6	25.5
16	22.8	22.7
17	14.3	14.1

References

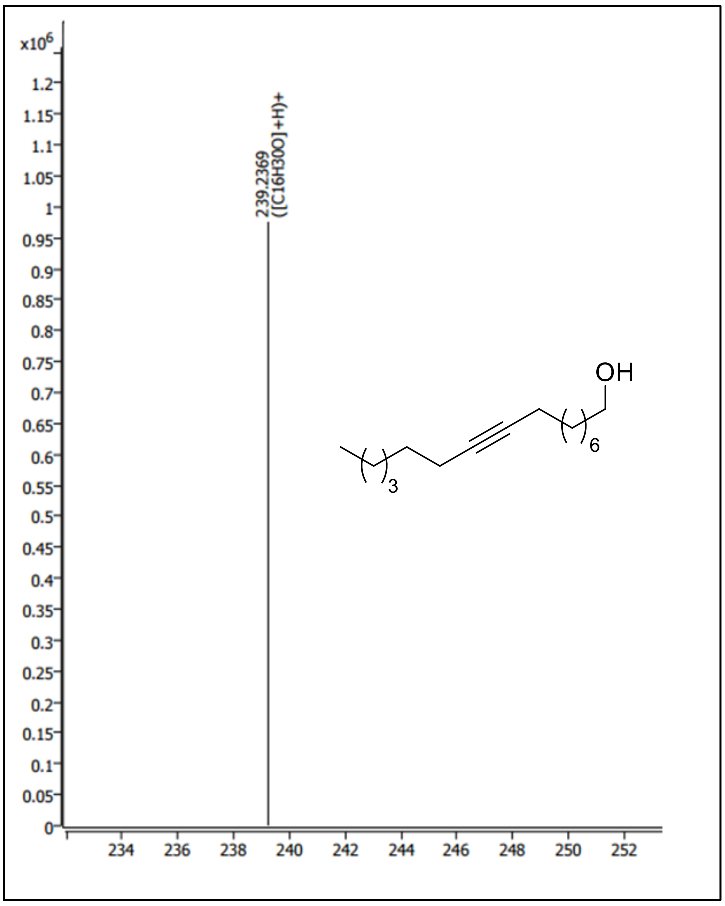
1. K. Ponsuwan, S. Nathabumroong, Lekphrom, R. Lekphrom, S. Sorin, C. Saengboonmee, T. Senawong, S. Tontapha, and F. T. Schevenels, *J. Nat. Prod.,* 2024, **87**, 1652.

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

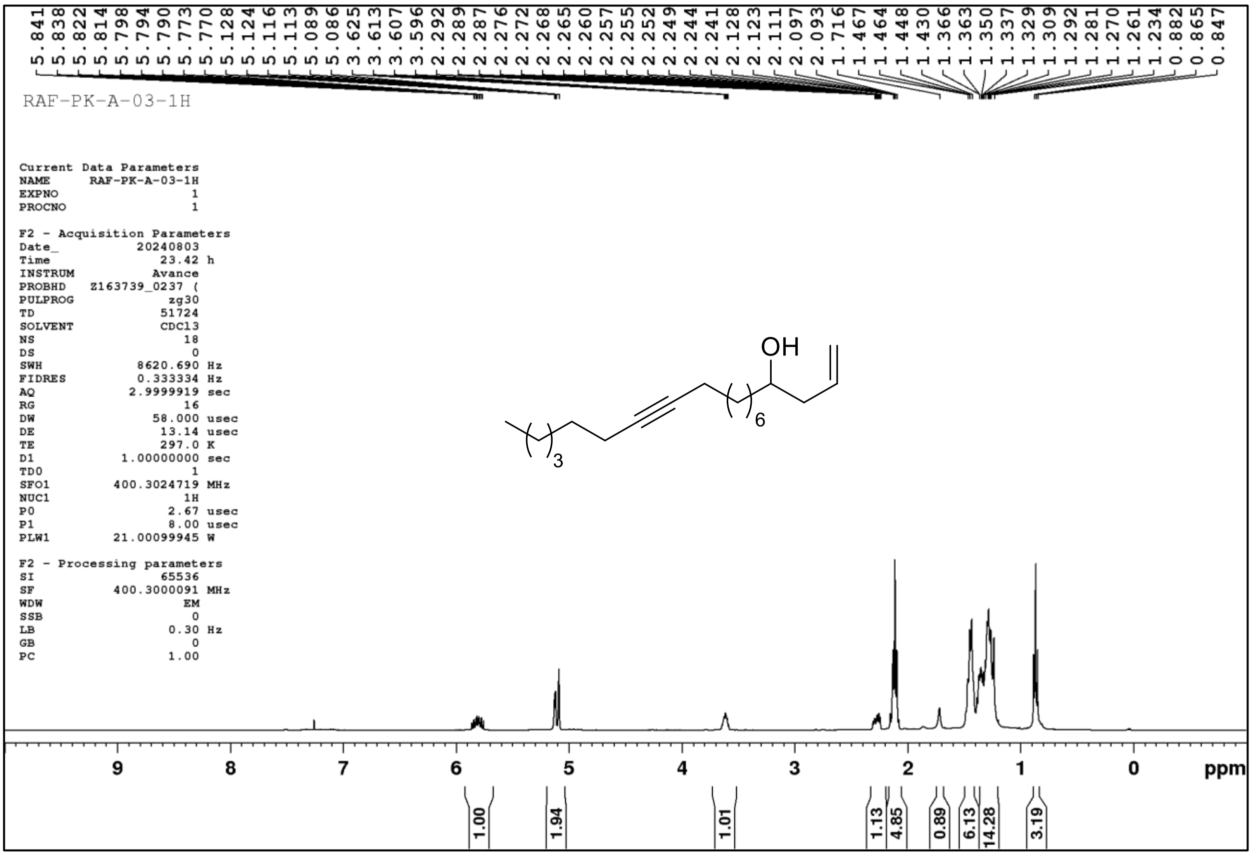


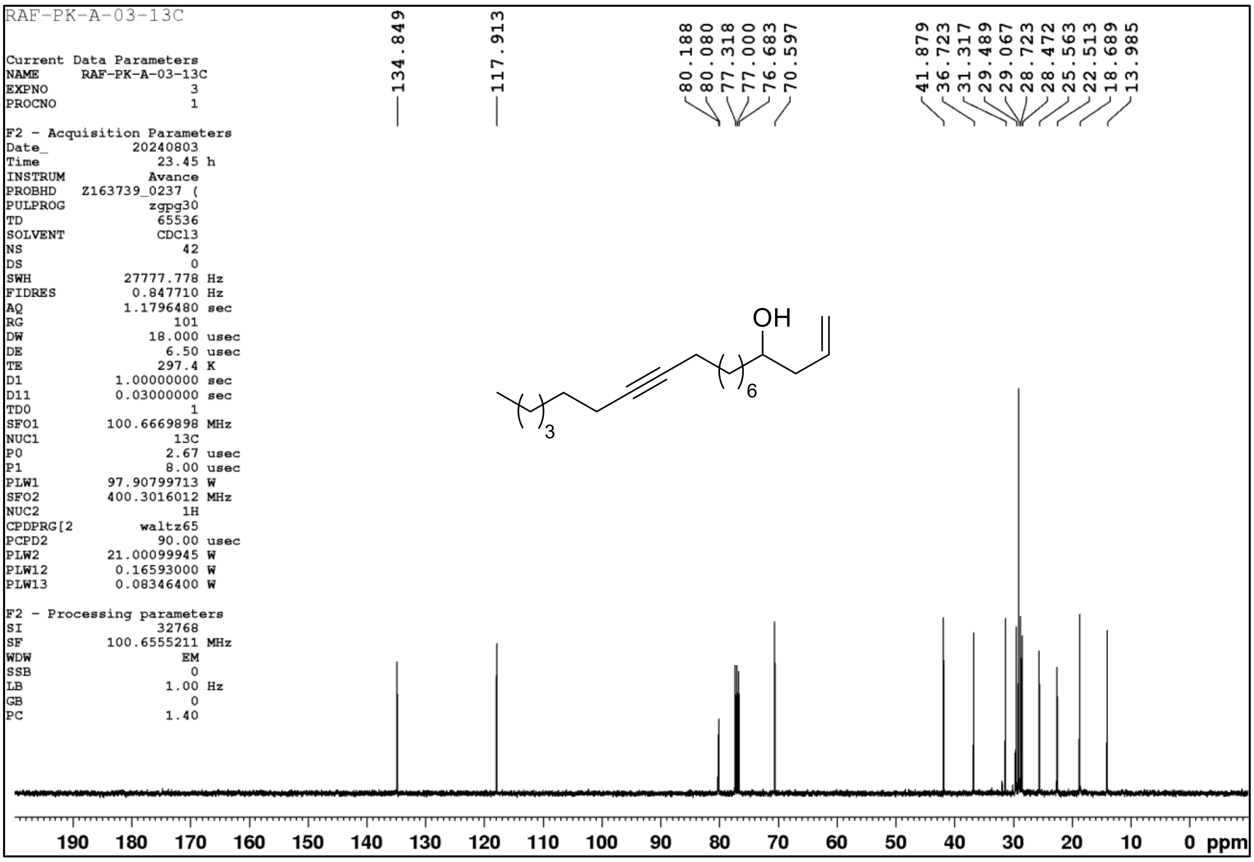


5: HRMS (ESI–TOF) *m/z:* [M + H] $^+$ Calcd for $C_{16}H_{31}O$ 239.2370; Found 239.2369

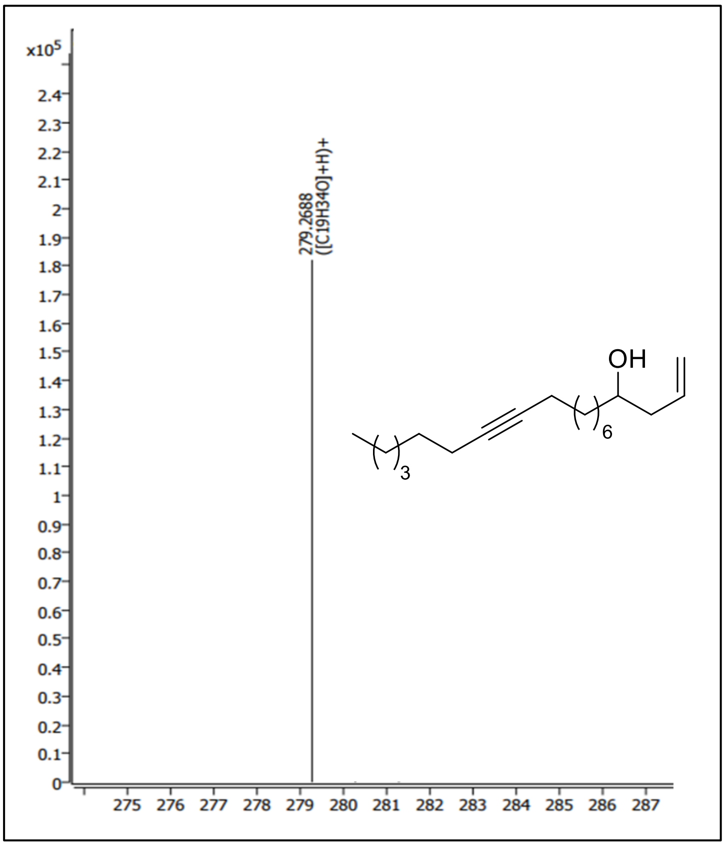


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) of compound (±)-**2a**

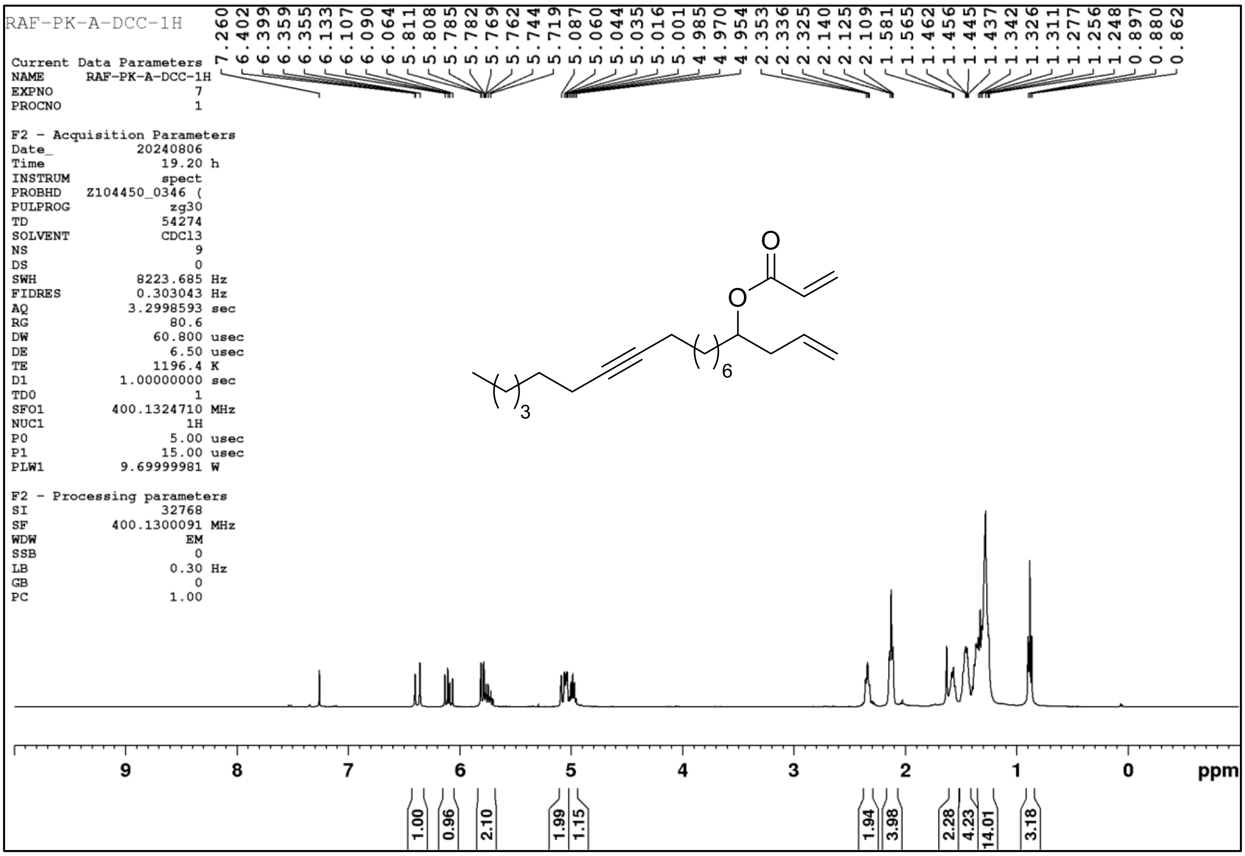




(±)-**2a**: HRMS (ESI–TOF) *m/z:* [M + H]$^+$ Calcd for $C_{19}H_{35}O$ 279.2683; Found 279.2688



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



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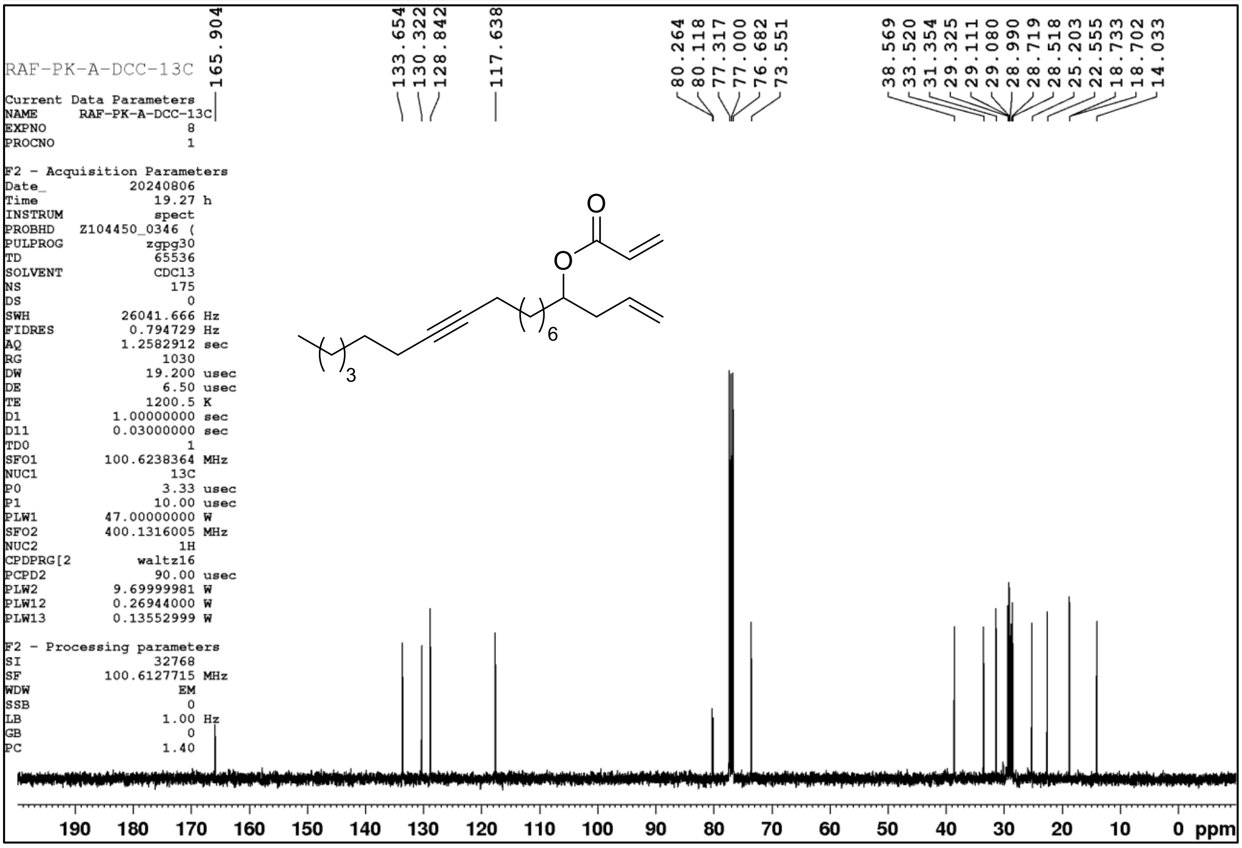
RAF-PK-A-DCC-1H

Current Data Parameters
NAME     RAF-PK-A-DCC-1H
EXPNO                  7
PROCNO                 1

F2 - Acquisition Parameters
Date_           20240806
Time               19.20 h
INSTRUM            spect
PROBHD   Z104450_0346 (
PULPROG             zg30
TD                 54274
SOLVENT            CDCl3
NS                     9
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                1196.4 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           400.1300091 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



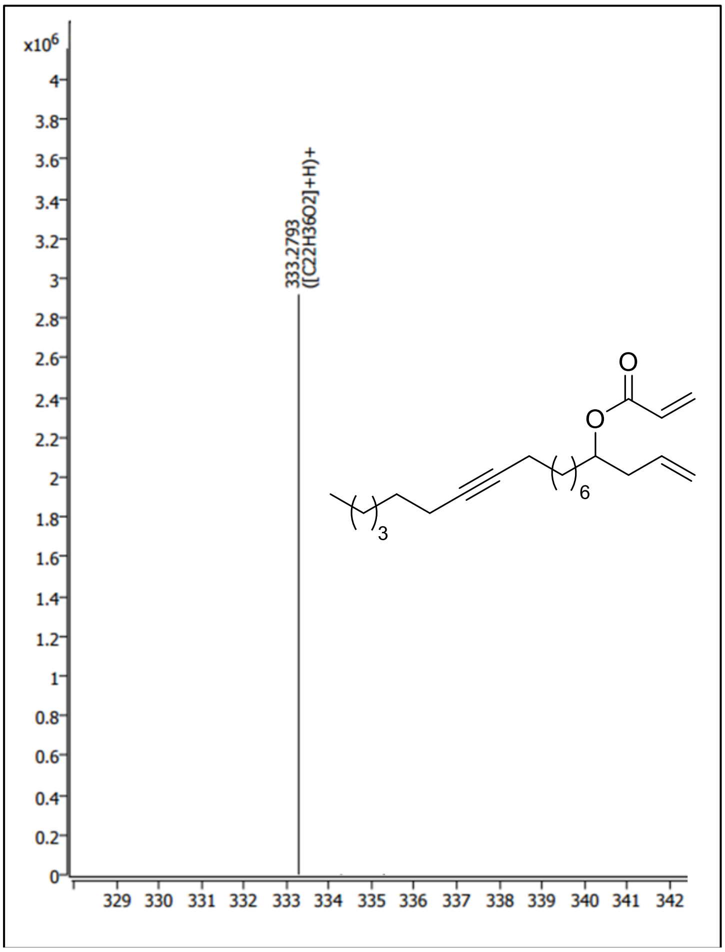
```
RAF-PK-A-DCC-13C

Current Data Parameters
NAME    RAF-PK-A-DCC-13C
EXPNO                  8
PROCNO                 1

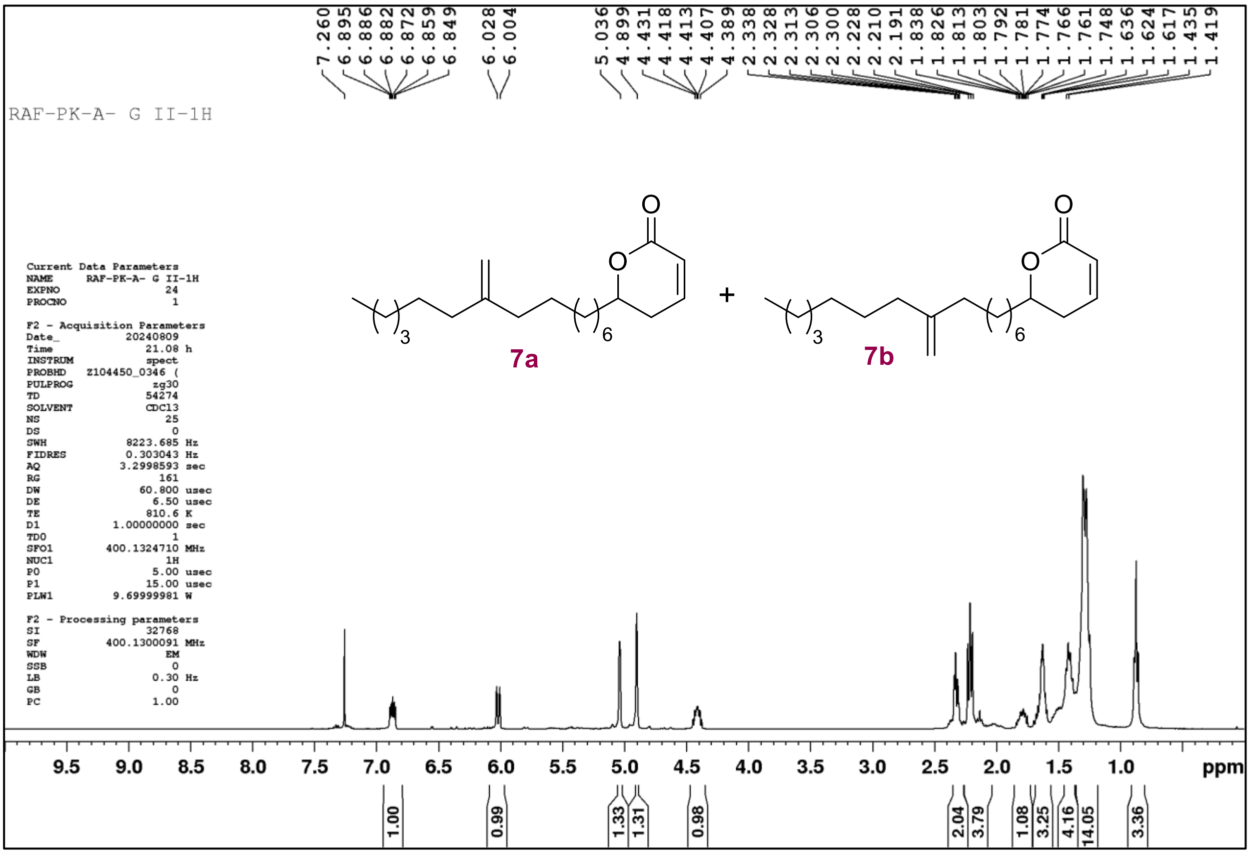
F2 - Acquisition Parameters
Date_           20240806
Time               19.27 h
INSTRUM            spect
PROBHD   Z104450_0346 (
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   175
DS                     0
SWH            26041.666 Hz
FIDRES          0.794729 Hz
AQ             1.2582912 sec
RG                  1030
DW                19.200 usec
DE                  6.50 usec
TE                1200.5 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           100.6127715 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

6: HRMS (ESI–TOF) *m/z:* [M + H]$^+$ Calcd for $C_{22}H_{37}O_2$ 333.2789; Found 333.2793



^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compounds **7a** and **7b**



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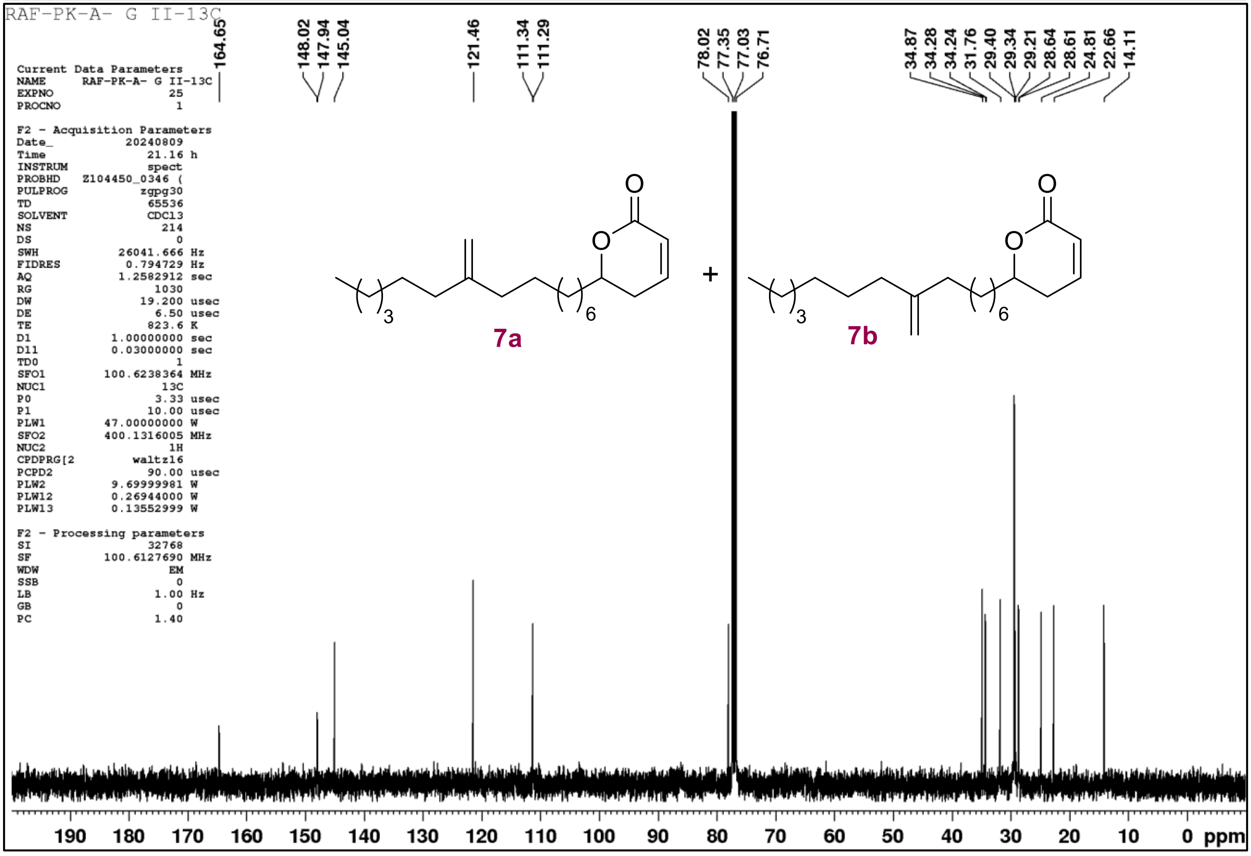
Current Data Parameters
NAME     RAF-PK-A- G II-1H
EXPNO                   24
PROCNO                   1

F2 - Acquisition Parameters
Date_             20240809
Time                 21.08 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                     161
DW                  60.800 usec
DE                    6.50 usec
TE                   810.6 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             400.1300091 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



```
Current Data Parameters
NAME     RAF-PK-A- G II-13C
EXPNO                   25
PROCNO                   1

F2 - Acquisition Parameters
Date_             20240809
Time                 21.16 h
INSTRUM              spect
PROBHD    Z104450_0346 (
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     214
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                   823.6 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             100.6127690 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
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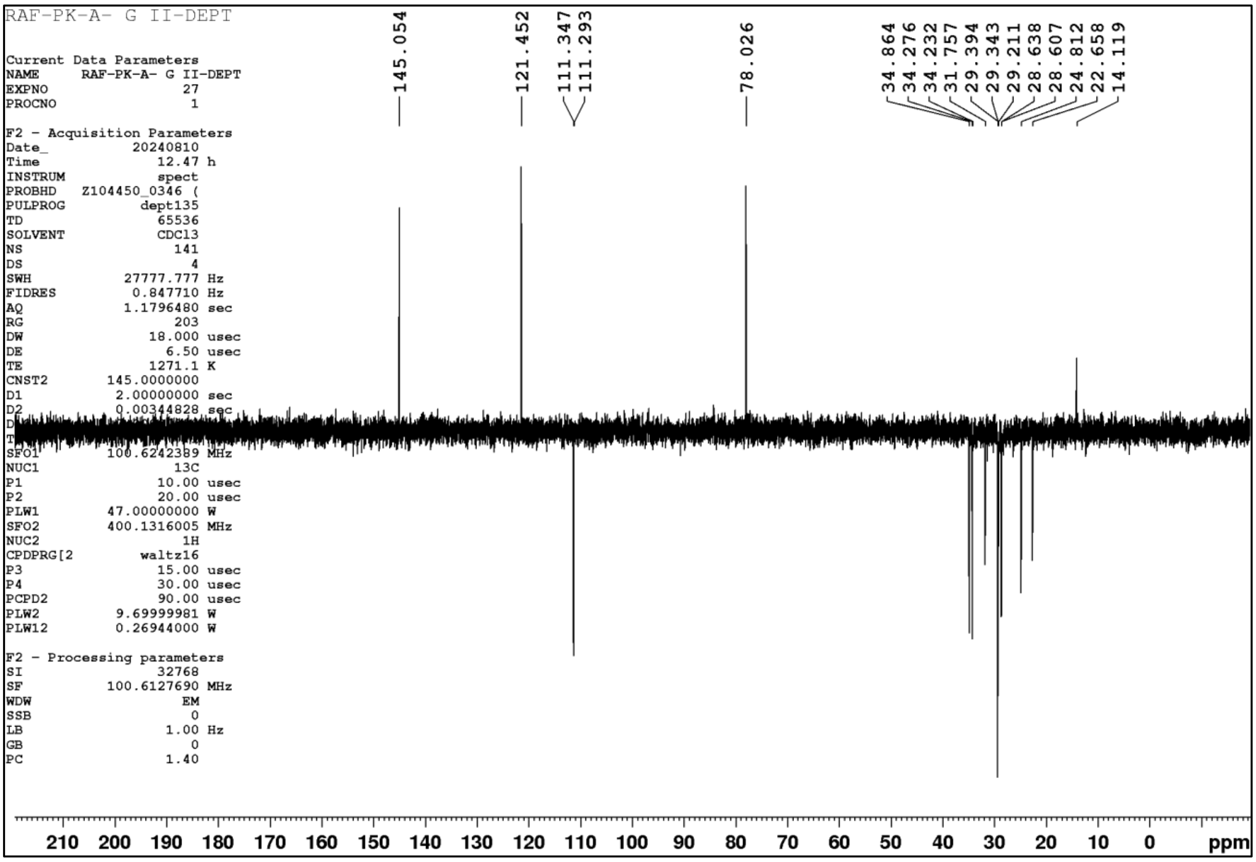
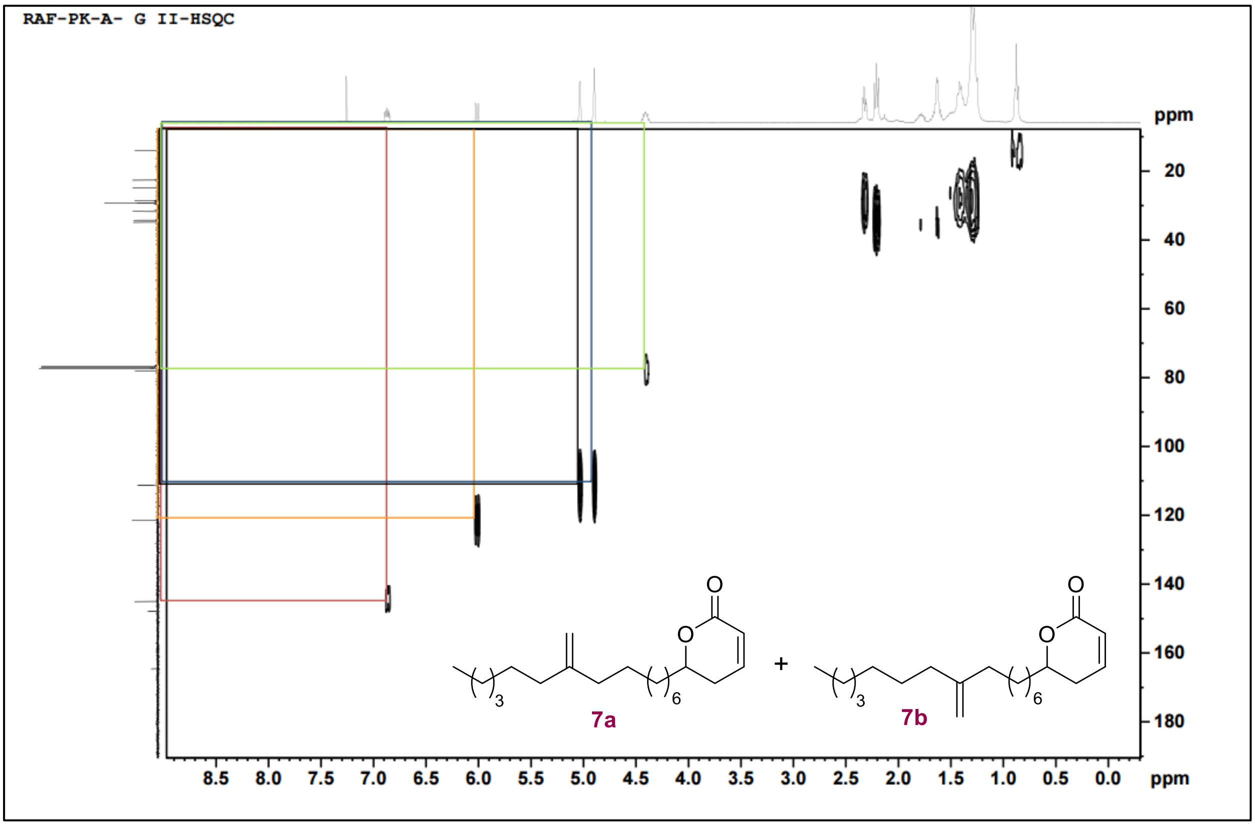
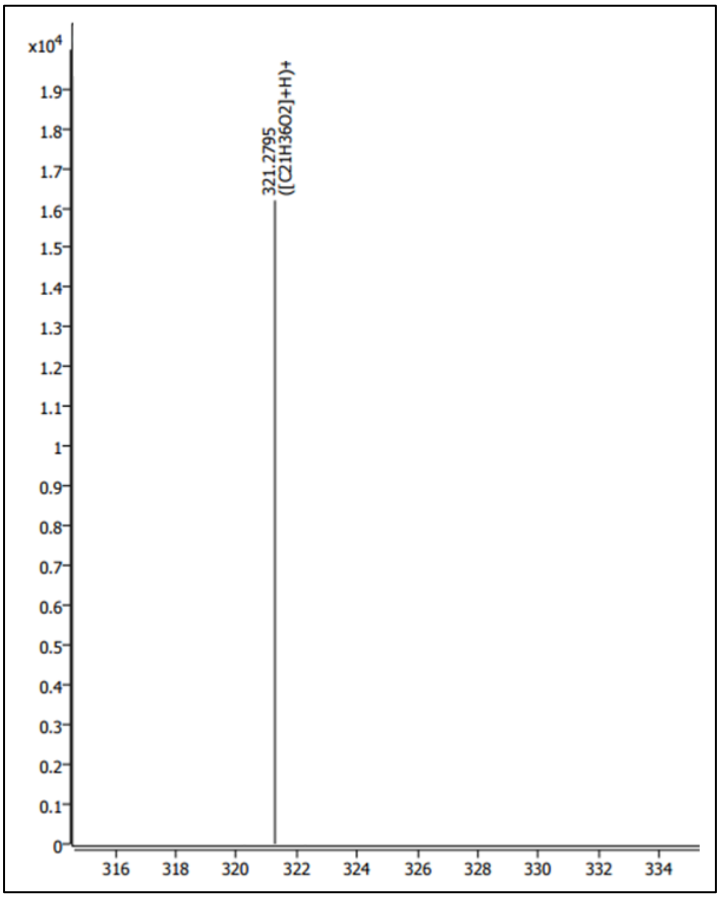


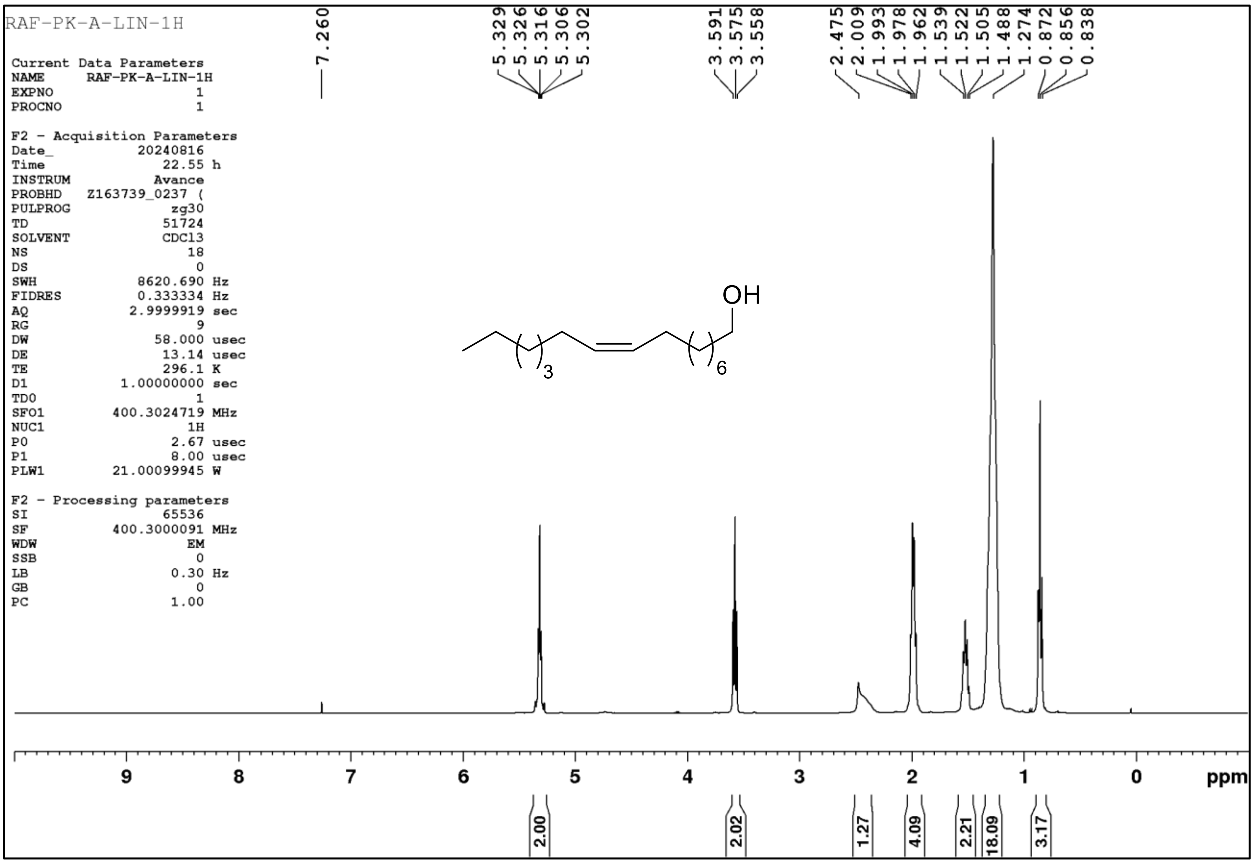
HSQC spectra of compounds **7a** and **7b**



7a and **7b**: HRMS (ESI–TOF) *m/z:* [M + H]$^+$ Calcd for $C_{21}H_{37}O_2$ 321.2789; Found 321.2795



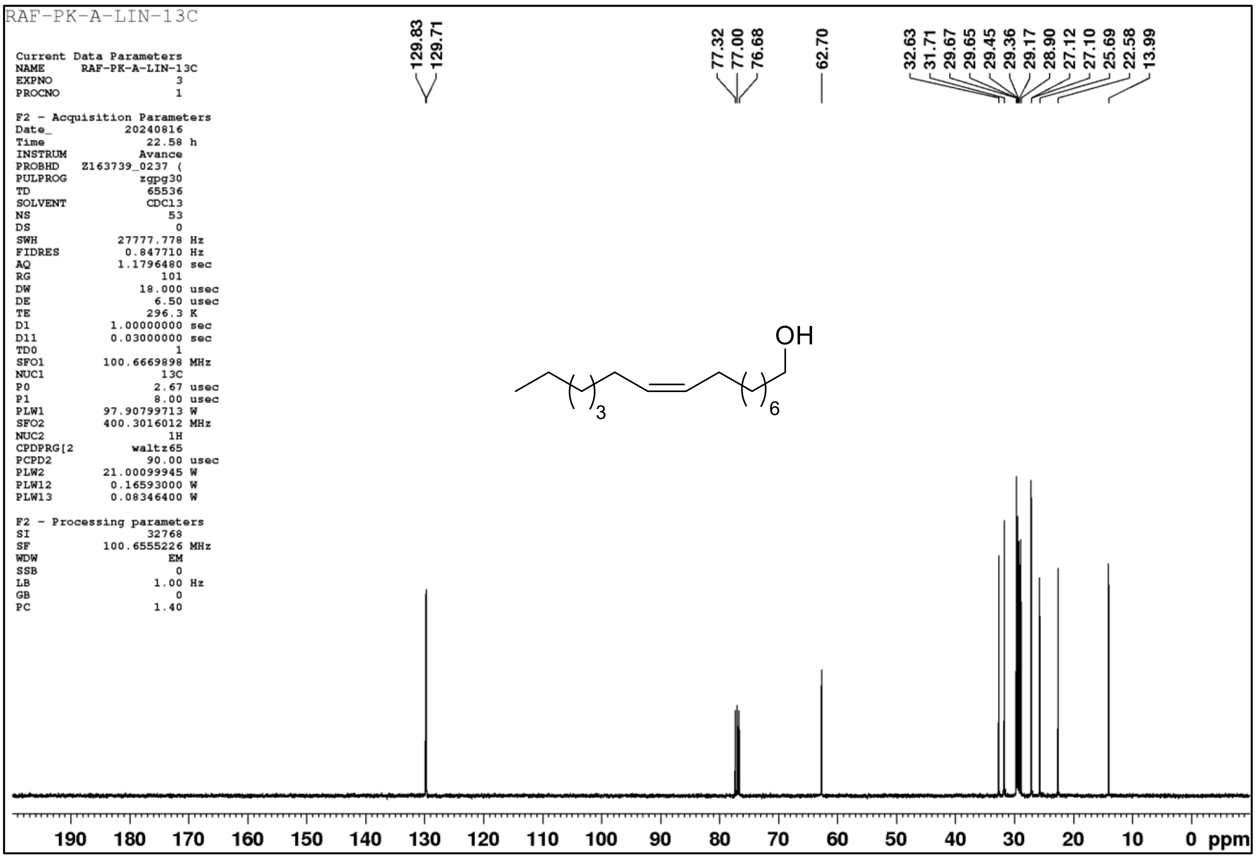
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) of compound **9**



```
Current Data Parameters
NAME      RAF-PK-A-LIN-1H
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20240816
Time                22.55 h
INSTRUM            Avance
PROBHD   Z163739_0237 (
PULPROG              zg30
TD                  51724
SOLVENT             CDCl3
NS                     18
DS                      0
SWH              8620.690 Hz
FIDRES           0.333334 Hz
AQ              2.9999919 sec
RG                      9
DW                 58.000 usec
DE                  13.14 usec
TE                  296.1 K
D1             1.00000000 sec
TD0                     1
SFO1          400.3024719 MHz
NUC1                   1H
P0                   2.67 usec
P1                   8.00 usec
PLW1          21.00099945 W

F2 - Processing parameters
SI                  65536
SF            400.3000091 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

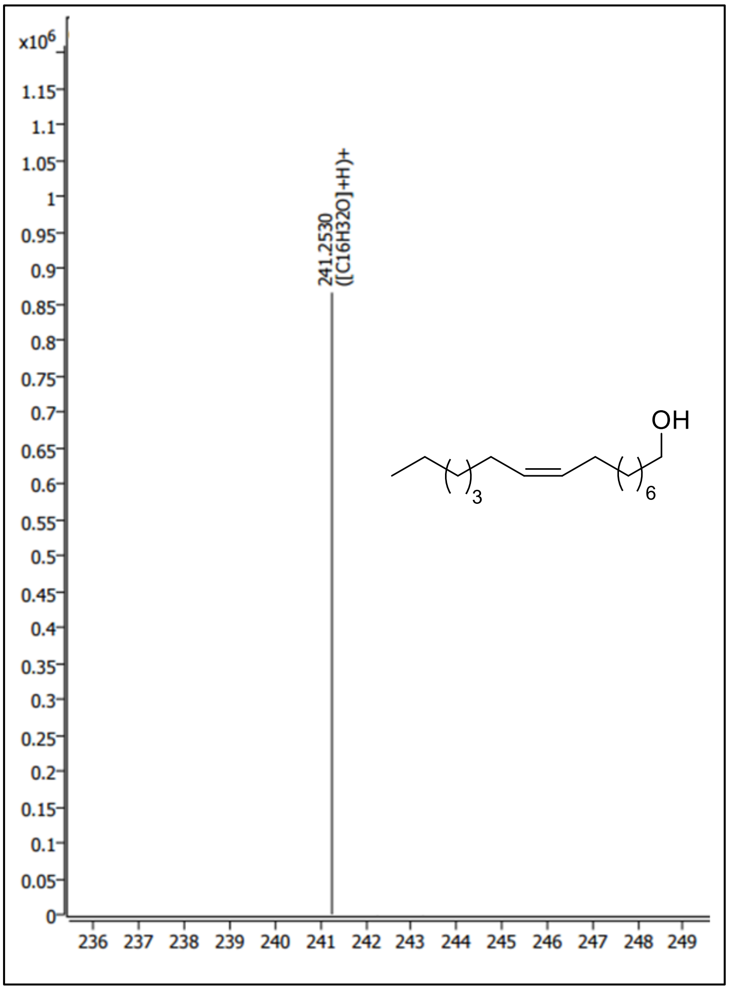


```
Current Data Parameters
NAME      RAF-PK-A-LIN-13C
EXPNO                    3
PROCNO                   1

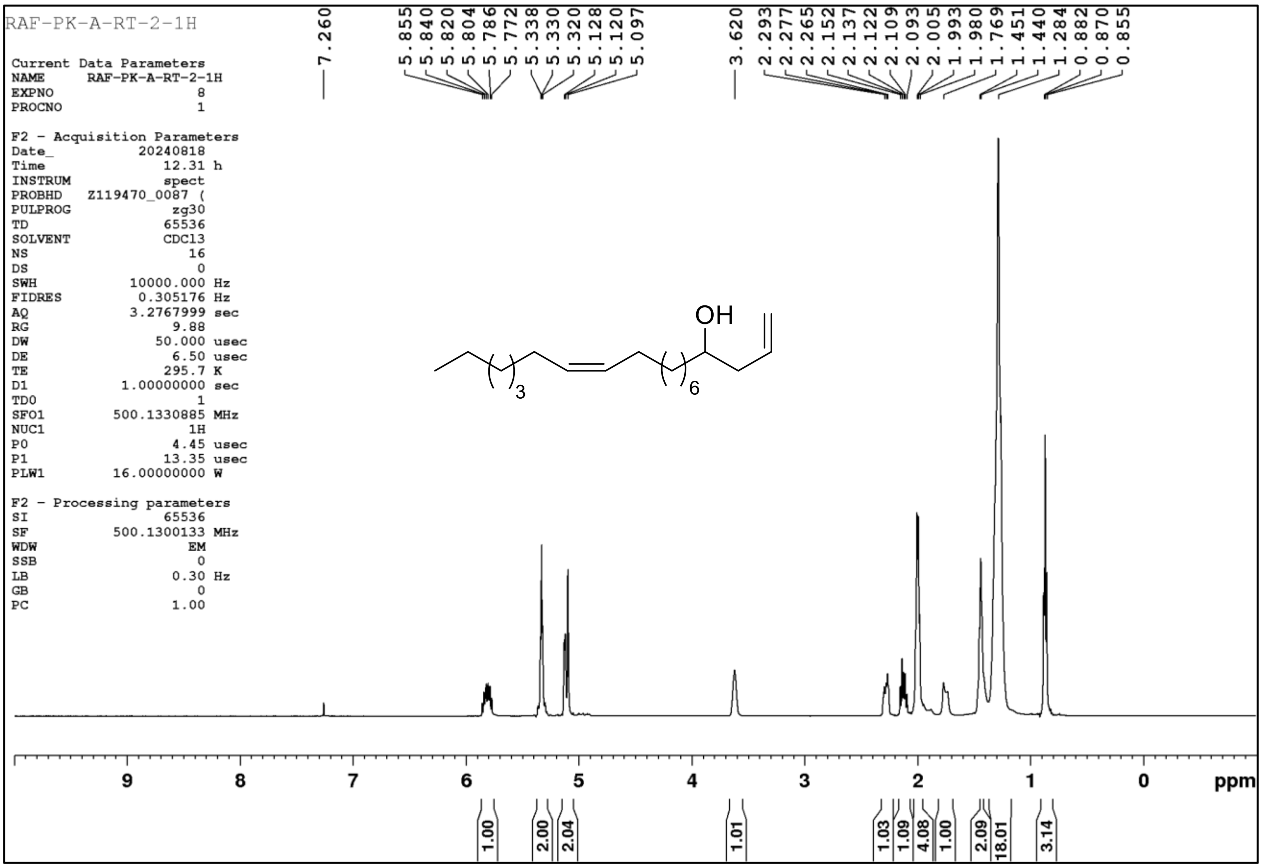
F2 - Acquisition Parameters
Date_            20240816
Time                22.58 h
INSTRUM            Avance
PROBHD   Z163739_0237 (
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     53
DS                      0
SWH             27777.778 Hz
FIDRES           0.847710 Hz
AQ              1.1796480 sec
RG                    101
DW                 18.000 usec
DE                   6.50 usec
TE                  296.3 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          97.90799713 W
SFO2          400.3016012 MHz
NUC2                   1H
CPDPRG[2          waltz65
PCPD2               90.00 usec
PLW2          21.00099945 W
PLW12          0.16593000 W
PLW13          0.08346400 W

F2 - Processing parameters
SI                  32768
SF            100.6555226 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

9: HRMS (ESI–TOF) *m/z:* $[M + H]^+$ Calcd for $C_{16}H_{33}O$ 241.2526; Found 241.2530



^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) of compound **10**

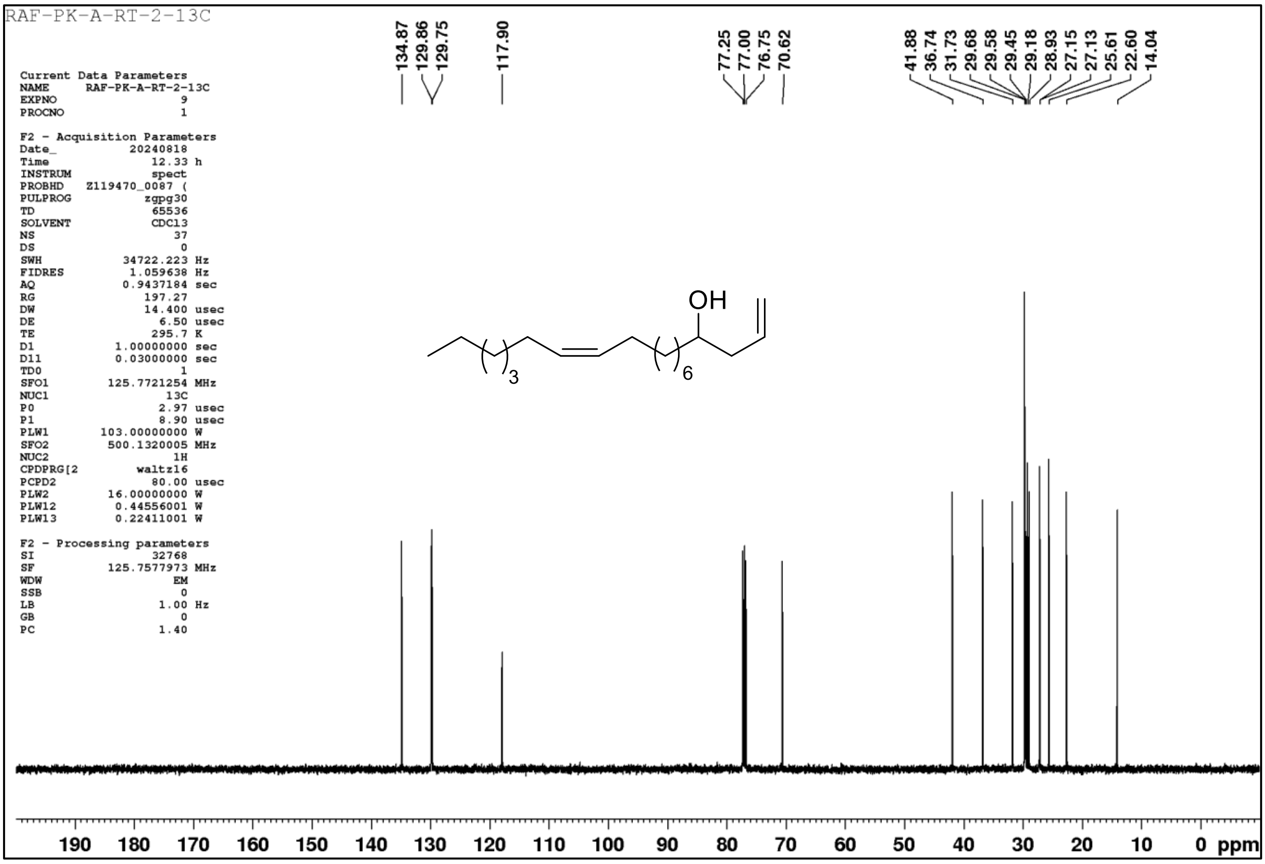


```
RAF-PK-A-RT-2-1H

Current Data Parameters
NAME      RAF-PK-A-RT-2-1H
EXPNO                    8
PROCNO                   1

F2 - Acquisition Parameters
Date_             20240818
Time                 12.31 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                    9.88
DW                  50.000 usec
DE                    6.50 usec
TE                   295.7 K
D1              1.00000000 sec
TD0                      1
SFO1           500.1330885 MHz
NUC1                    1H
P0                    4.45 usec
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
```



```
RAF-PK-A-RT-2-13C

Current Data Parameters
NAME      RAF-PK-A-RT-2-13C
EXPNO                    9
PROCNO                   1

F2 - Acquisition Parameters
Date_             20240818
Time                 12.33 h
INSTRUM              spect
PROBHD   Z119470_0087 (
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      37
DS                       0
SWH              34722.223 Hz
FIDRES            1.059638 Hz
AQ               0.9437184 sec
RG                  197.27
DW                  14.400 usec
DE                    6.50 usec
TE                   295.7 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                      1
SFO1           125.7721254 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           16.00000000 W
PLW12           0.44556001 W
PLW13           0.22411001 W

F2 - Processing parameters
SI                   32768
SF             125.7577973 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
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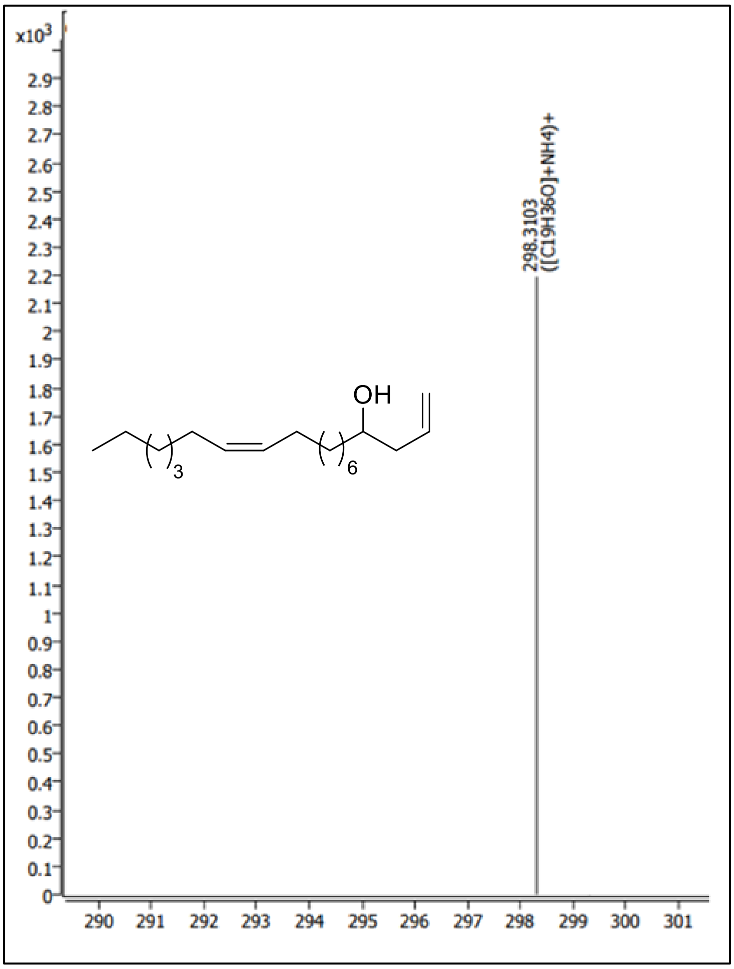
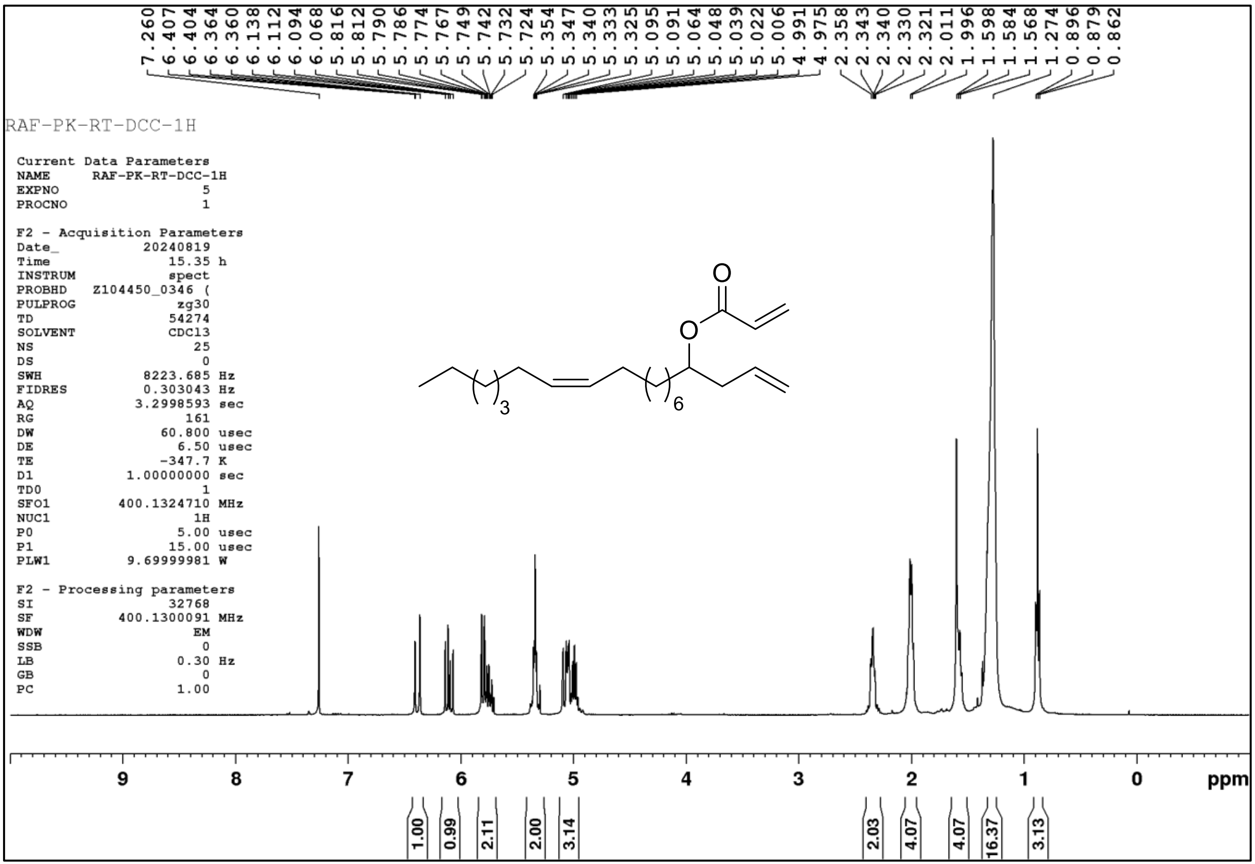
10: HRMS (ESI–TOF) *m/z:* $[M + NH_4]^+$ Calcd for $C_{19}H_{40}ON$ 298.3105; Found 298.3103



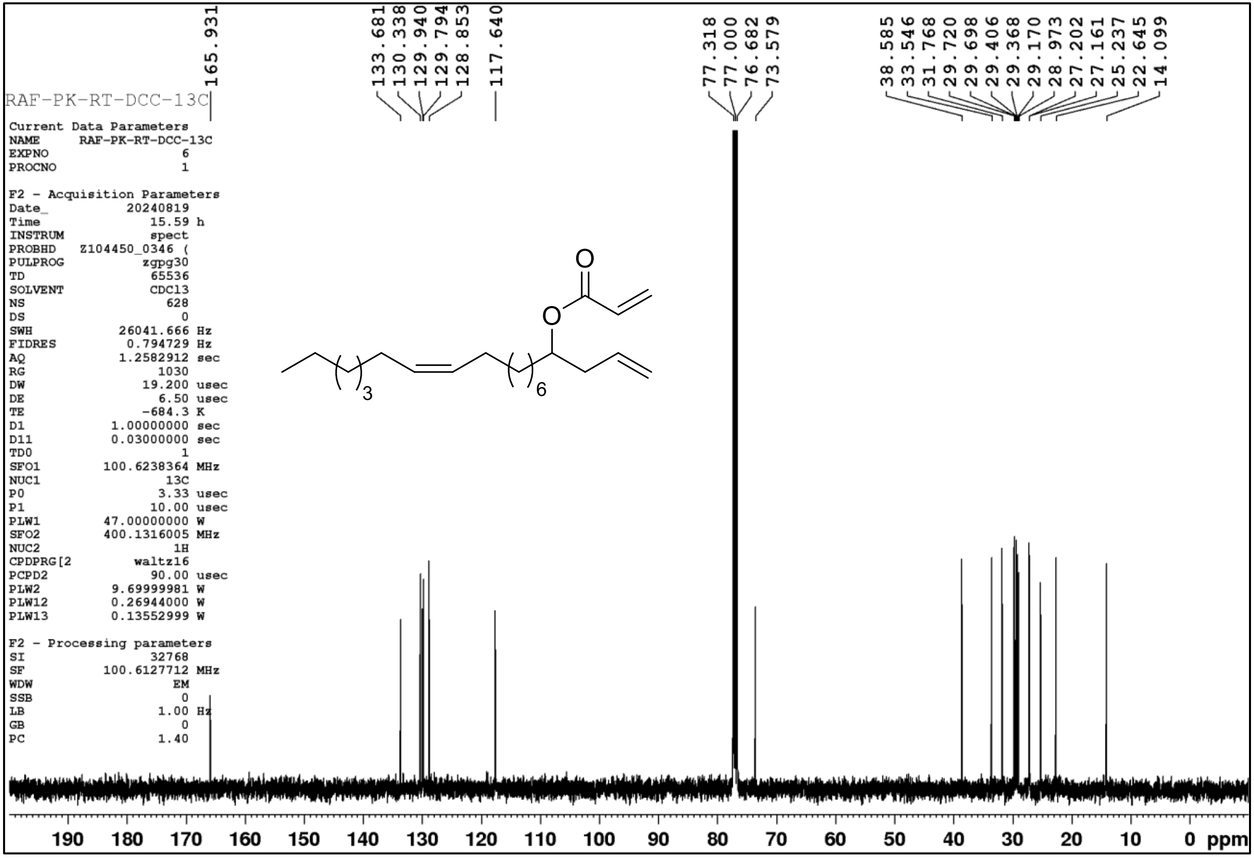
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **11**



```
Current Data Parameters
NAME       RAF-PK-RT-DCC-1H
EXPNO                     5
PROCNO                    1

F2 - Acquisition Parameters
Date_              20240819
Time                15.35 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                      161
DW               60.800 usec
DE                 6.50 usec
TE                 -347.7 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          400.1300091 MHz
WDW                      EM
SSB                       0
LB                  0.30 Hz
GB                        0
PC                     1.00
```

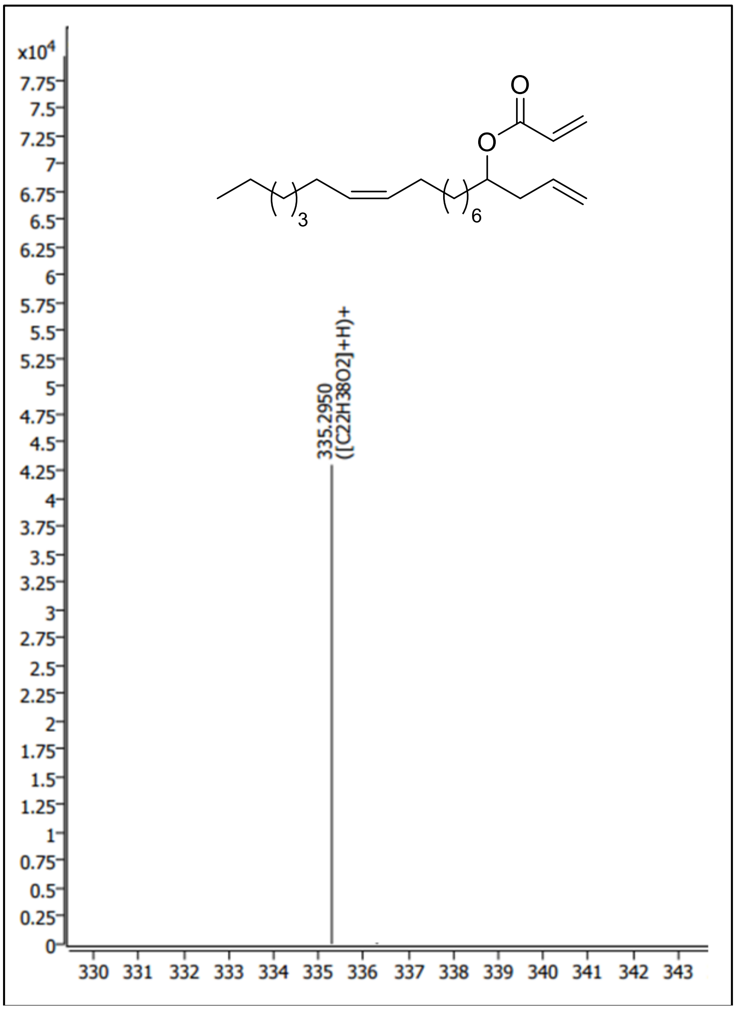


```
Current Data Parameters
NAME      RAF-PK-RT-DCC-13C
EXPNO                     6
PROCNO                    1

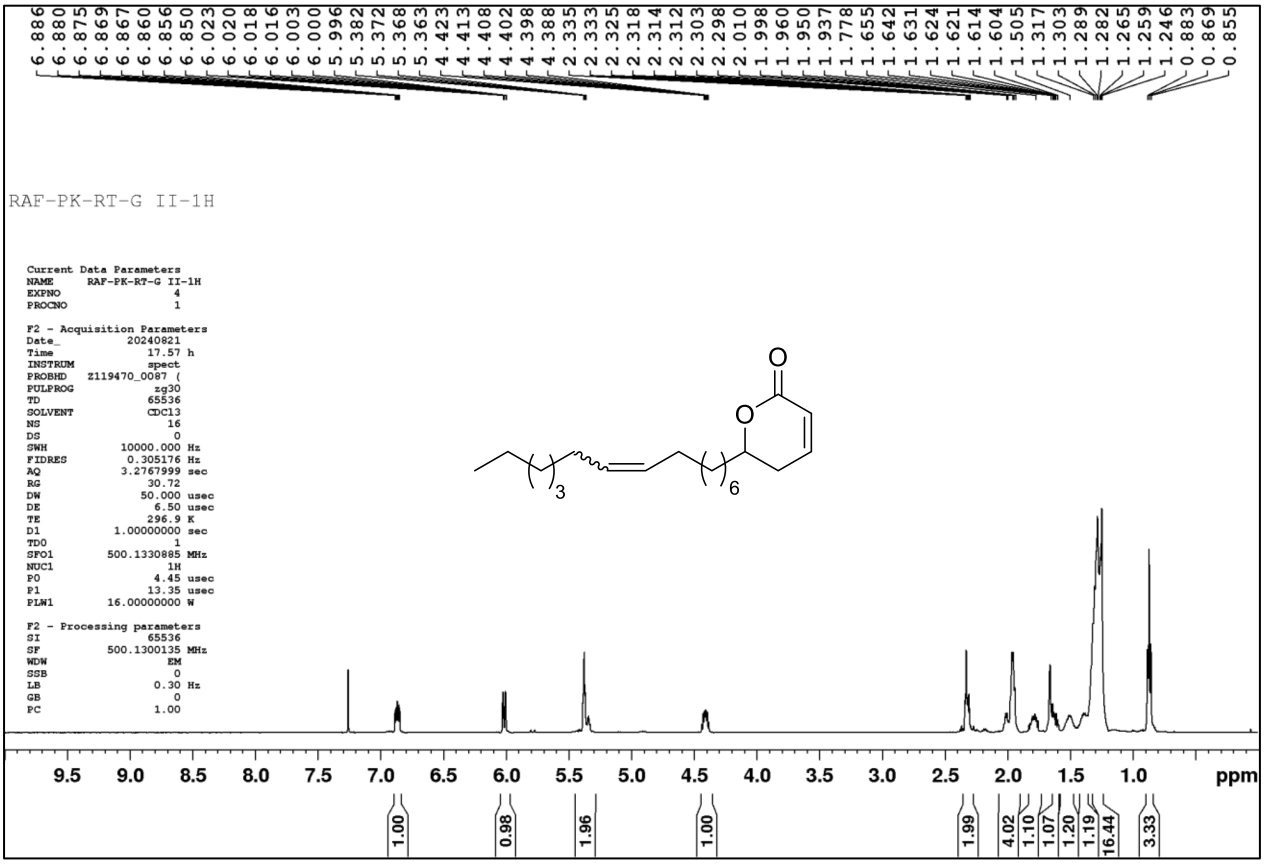
F2 - Acquisition Parameters
Date_              20240819
Time                15.59 h
INSTRUM               spect
PROBHD   Z104450_0346 (
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      628
DS                        0
SWH            26041.666 Hz
FIDRES          0.794729 Hz
AQ             1.2582912 sec
RG                     1030
DW               19.200 usec
DE                 6.50 usec
TE                 -684.3 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          100.6127712 MHz
WDW                      EM
SSB                       0
LB                  1.00 Hz
GB                        0
PC                     1.40
```

11: HRMS (ESI–TOF) *m/z:* [M + H]$^+$ Calcd for $C_{22}H_{39}O_2$ 335.2945; Found 335.2950



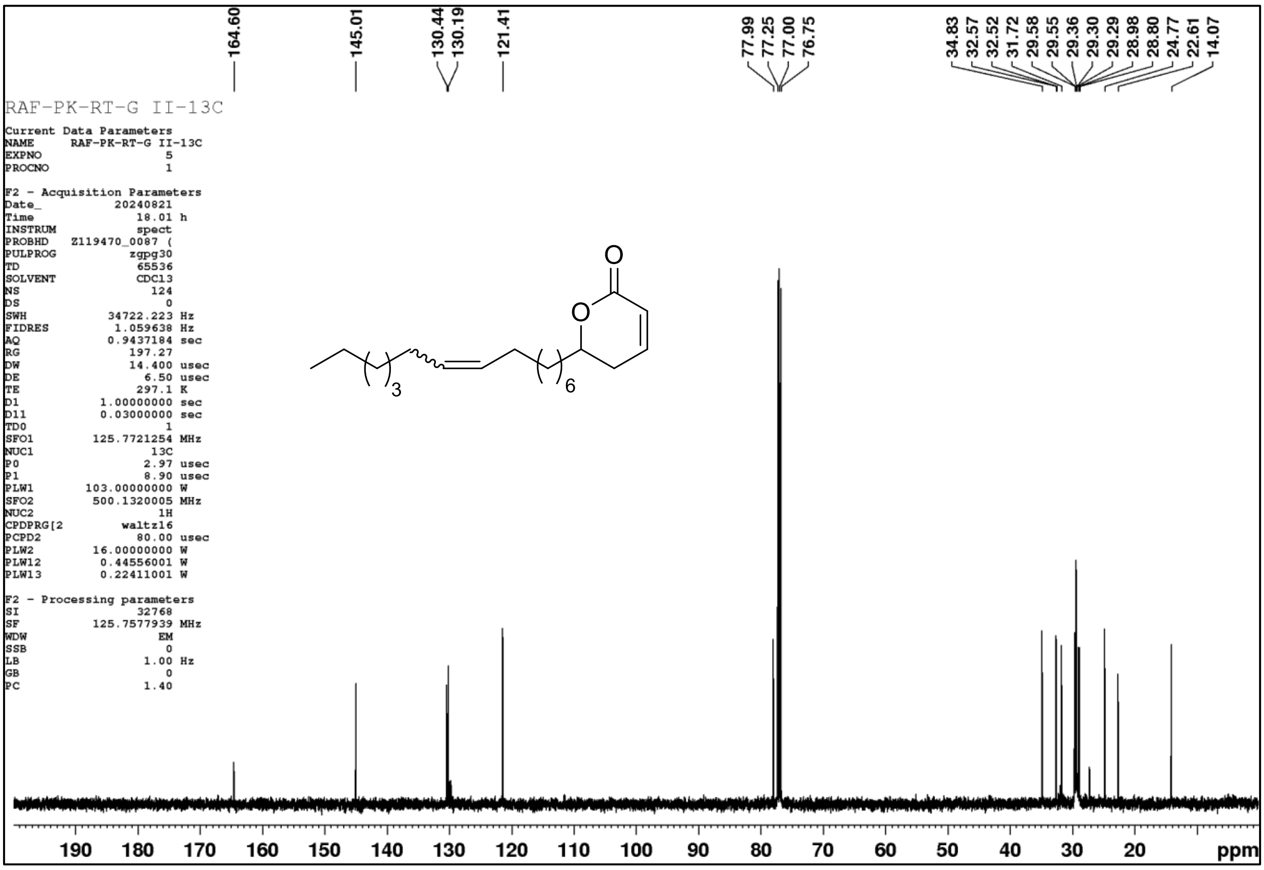
^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) of compound **12**



```
Current Data Parameters
NAME      RAF-PK-RT-G II-1H
EXPNO                     4
PROCNO                    1

F2 - Acquisition Parameters
Date_          20240821
Time              17.57 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                296.9 K
D1           1.00000000 sec
TD0                   1
SFO1        500.1330885 MHz
NUC1                 1H
P0                 4.45 usec
P1                13.35 usec
PLW1        16.00000000 W

F2 - Processing parameters
SI                65536
SF          500.1300135 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

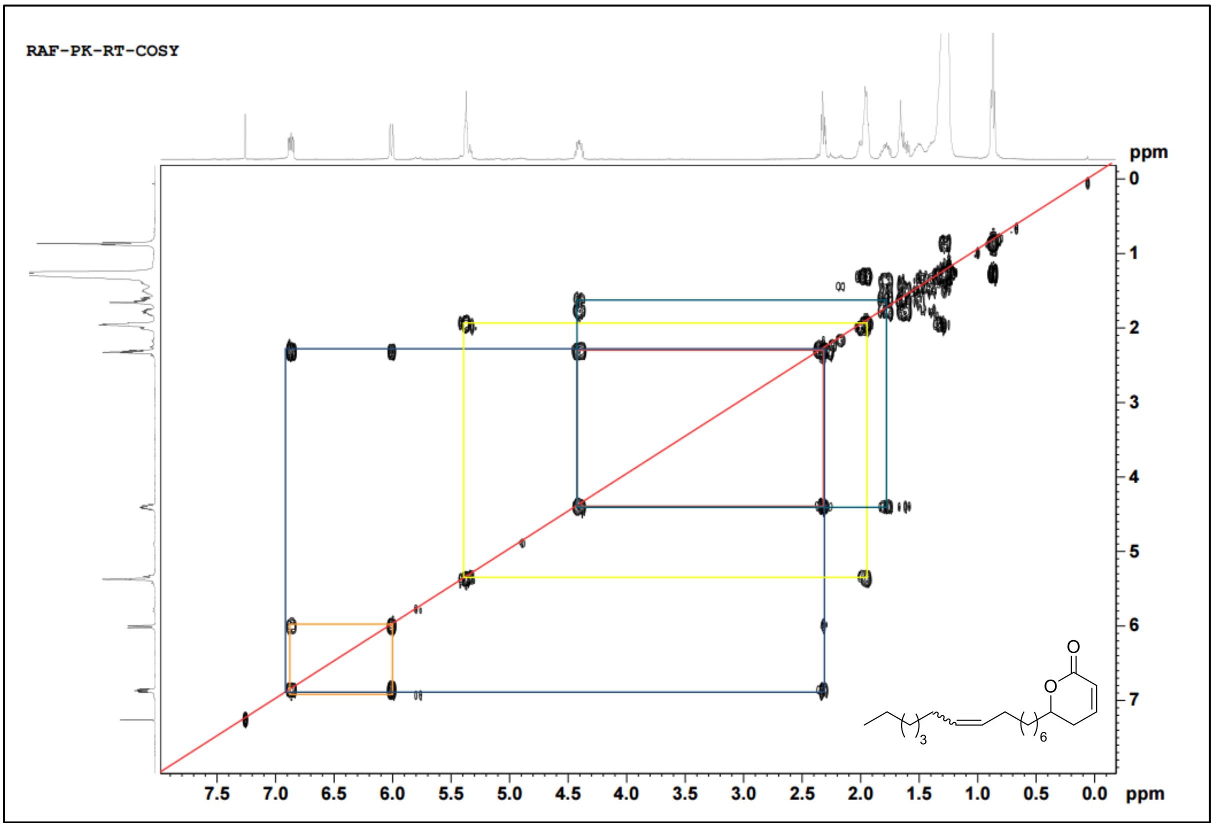


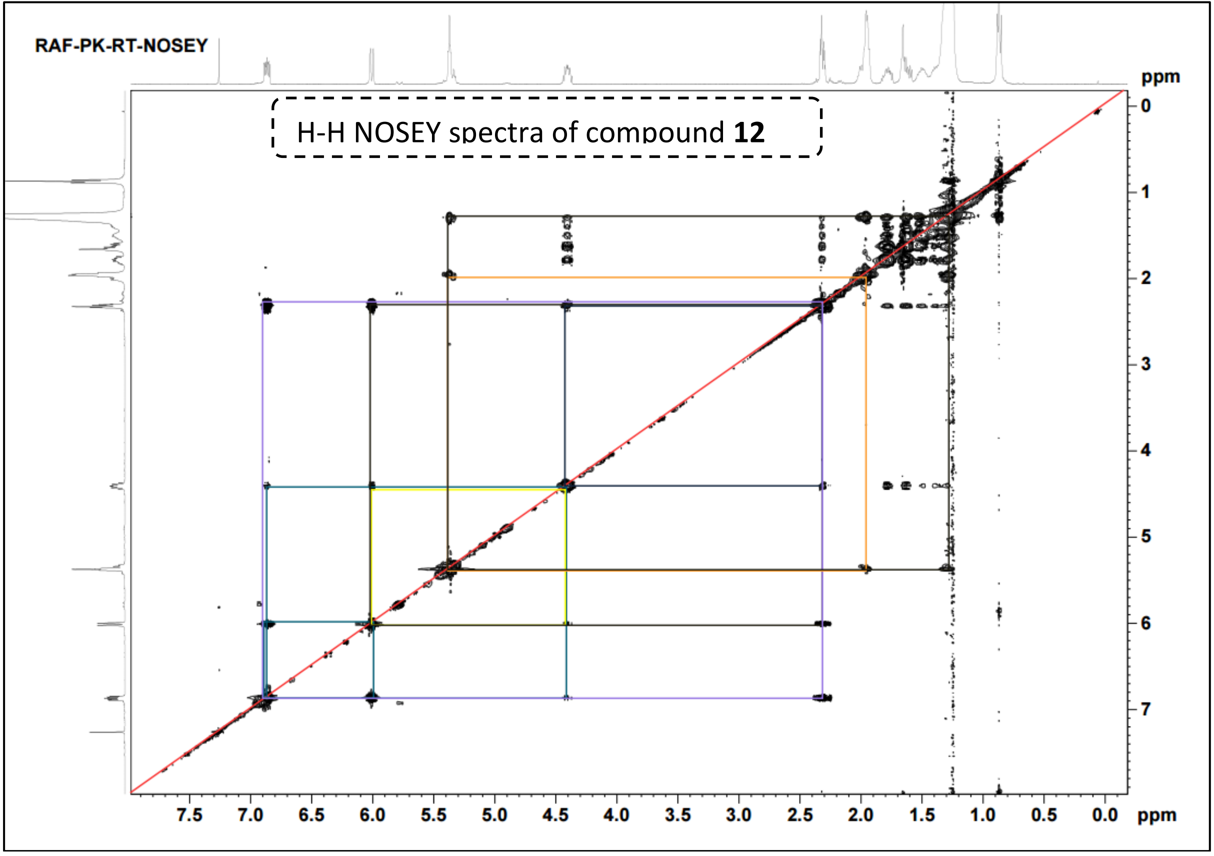
```
Current Data Parameters
NAME      RAF-PK-RT-G II-13C
EXPNO                     5
PROCNO                    1

F2 - Acquisition Parameters
Date_          20240821
Time              18.01 h
INSTRUM           spect
PROBHD   Z119470_0087 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  124
DS                    0
SWH           34722.223 Hz
FIDRES         1.059638 Hz
AQ            0.9437184 sec
RG               197.27
DW               14.400 usec
DE                 6.50 usec
TE                297.1 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        125.7721254 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        16.00000000 W
PLW12        0.44556001 W
PLW13        0.22411001 W

F2 - Processing parameters
SI                32768
SF          125.7577939 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

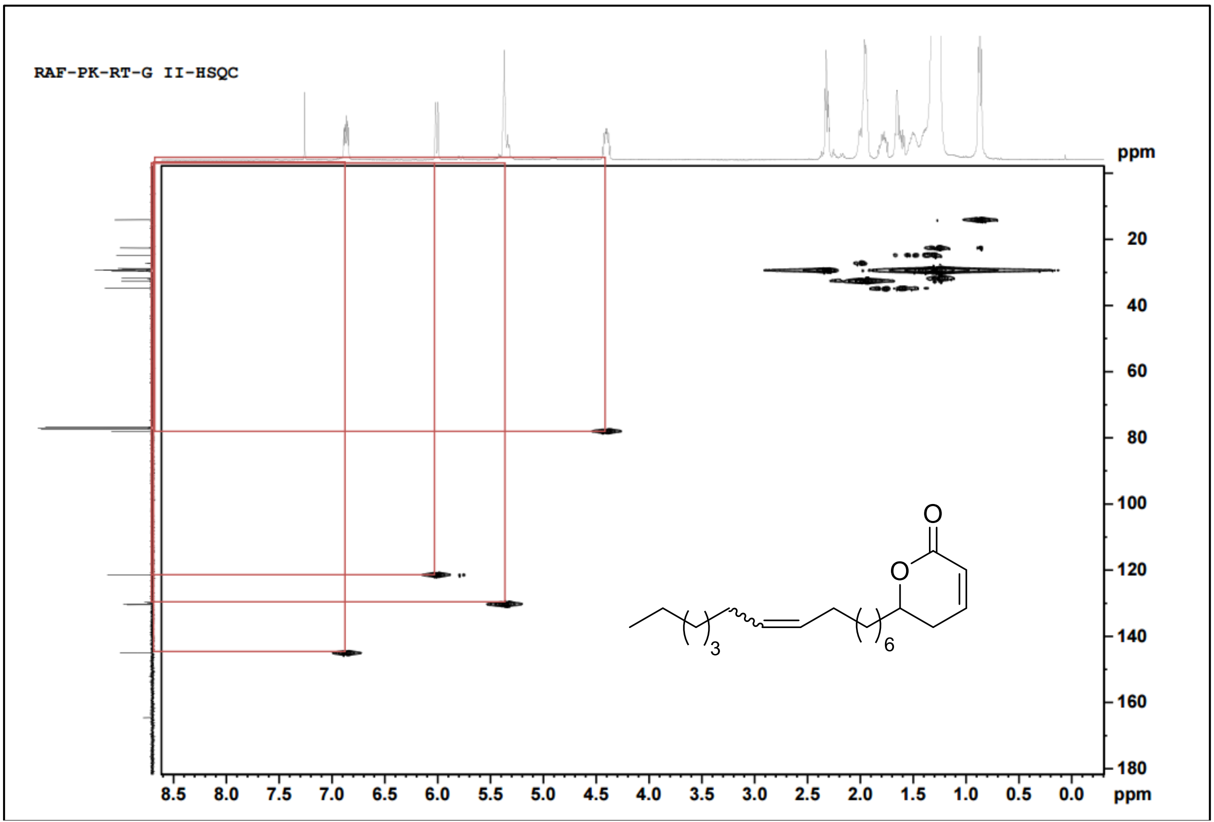
H-H COSY spectra of compound **12**



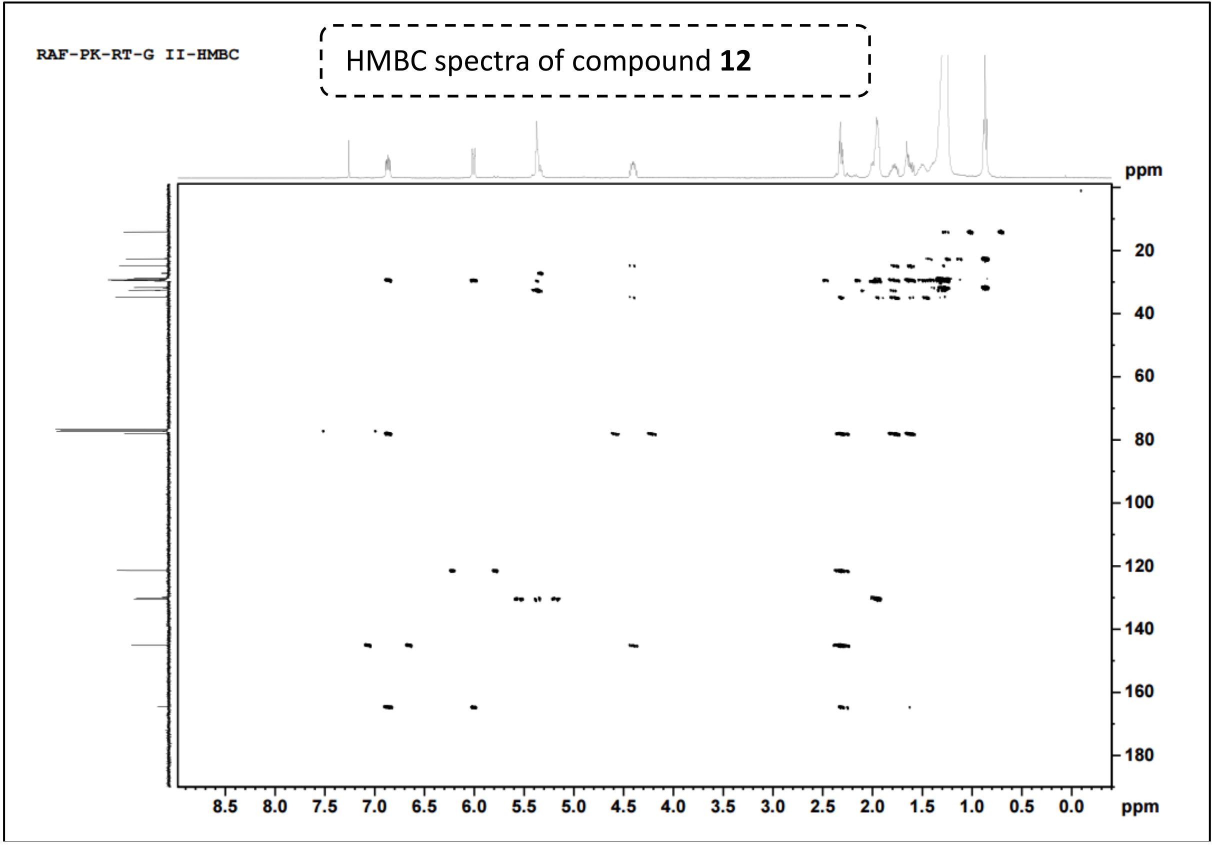


H-H NOSEY spectra of compound **12**

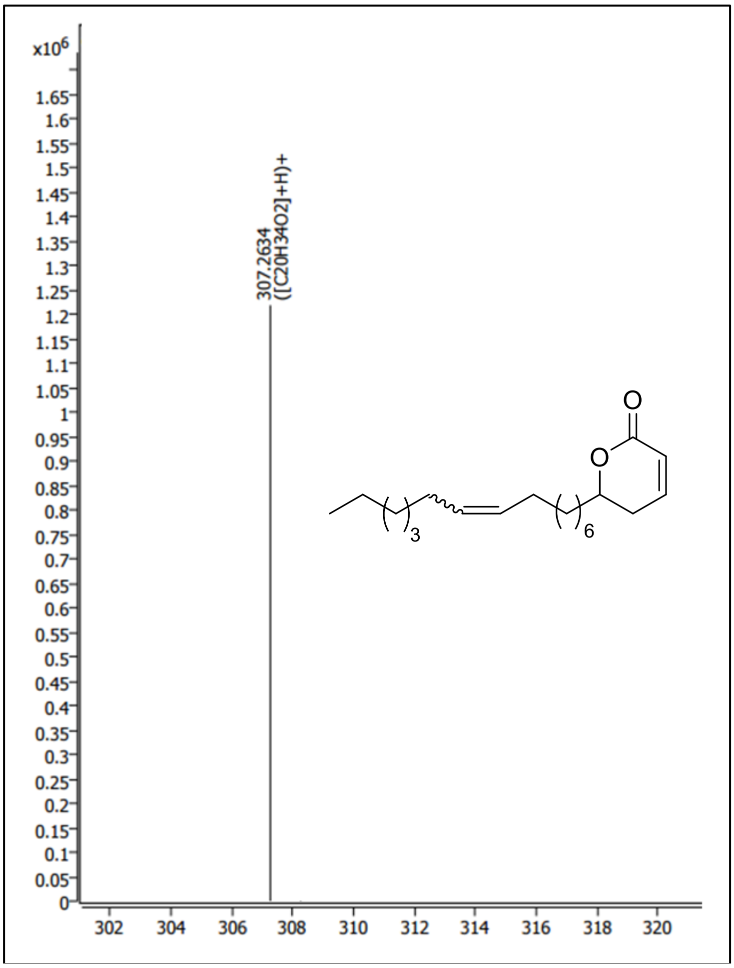
HSQC spectra of compound **12**



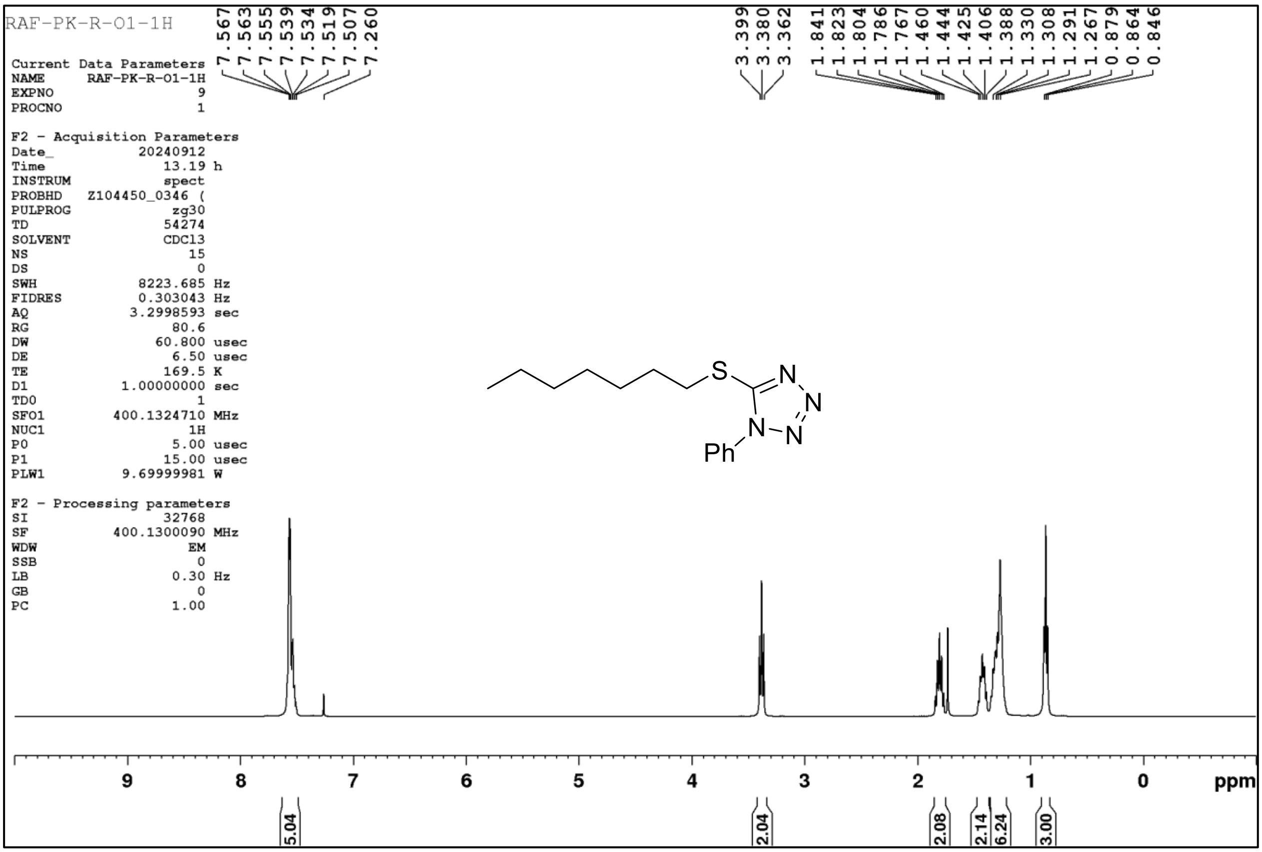
HMBC spectra of compound **12**

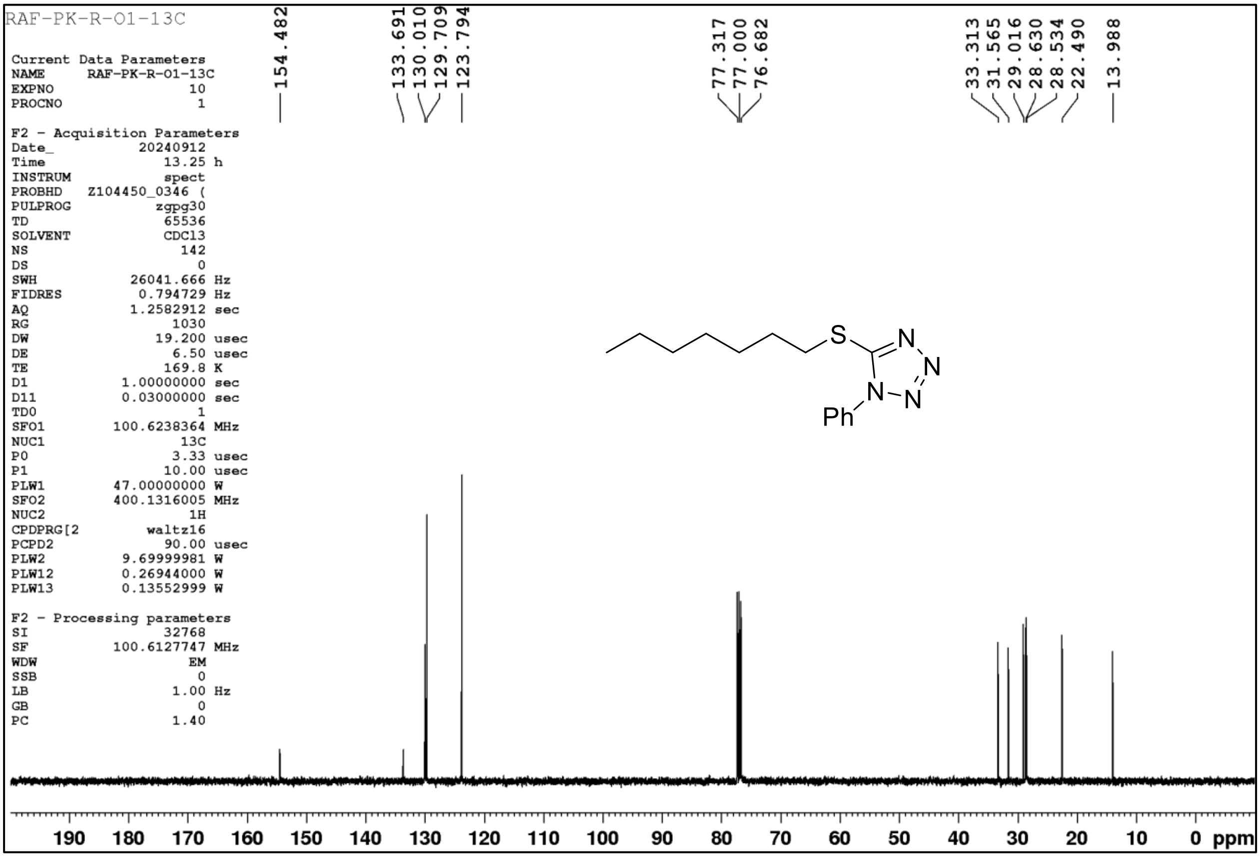


12: HRMS (ESI–TOF) *m/z:* [M + H]$^+$ Calcd for $C_{20}H_{35}O_2$ 307.2632; Found 307.2634

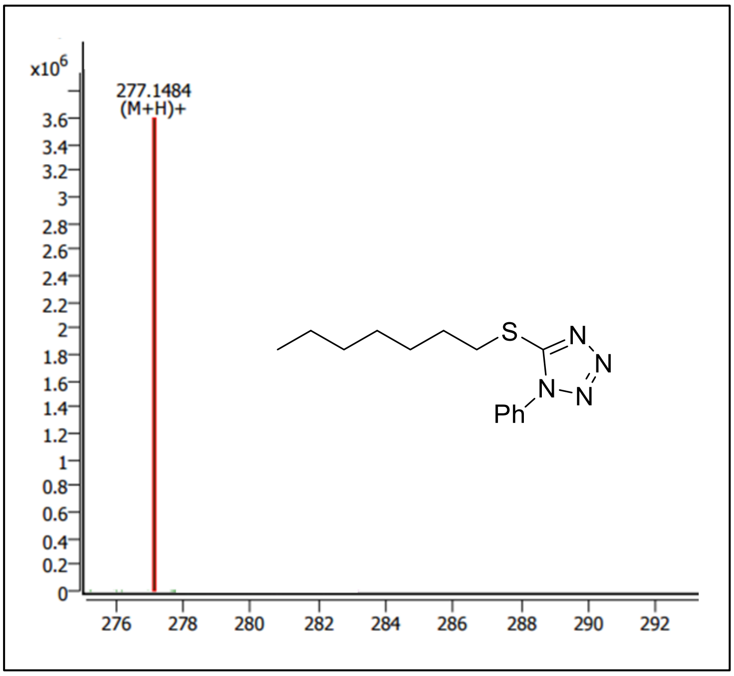


^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **14**

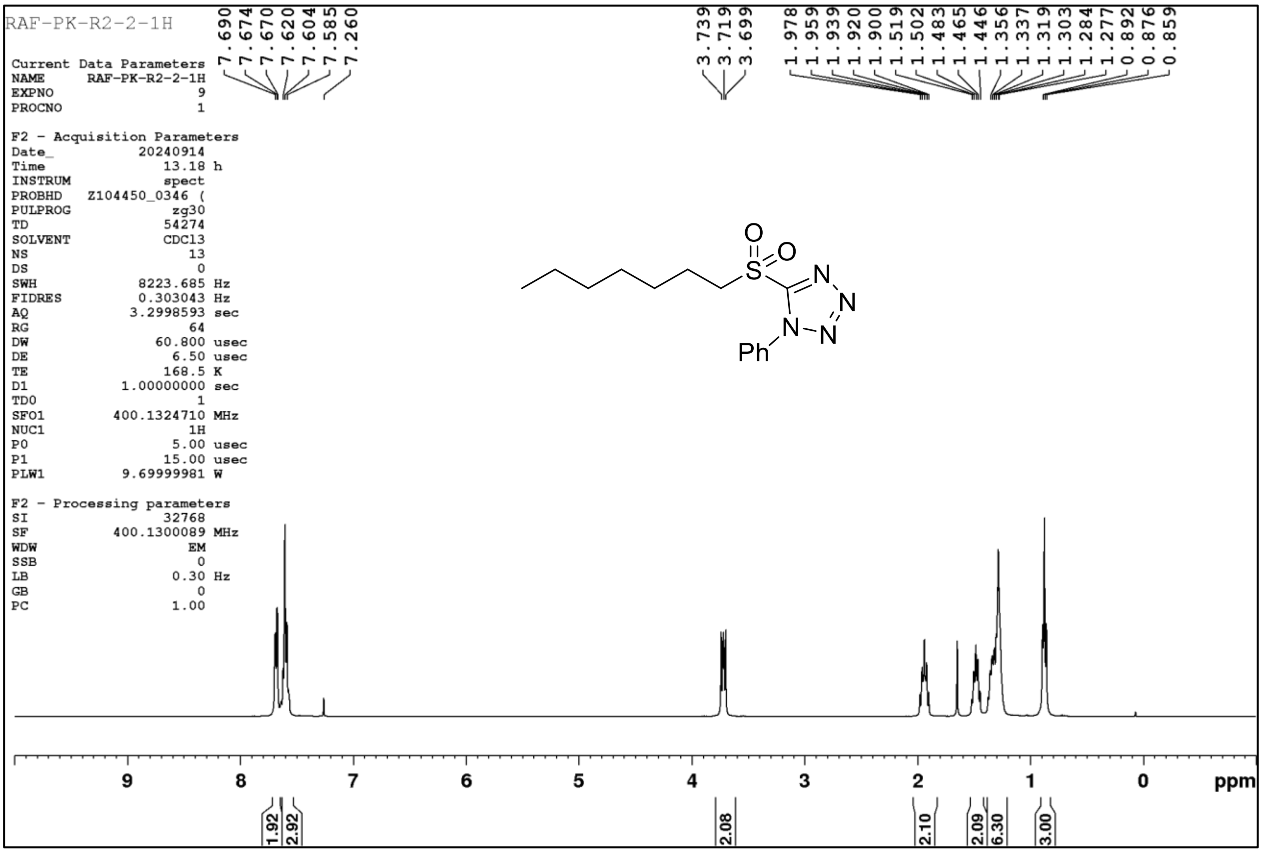




14: HRMS (ESI–TOF) *m/z:* [M + H]$^+$ Calcd for $C_{14}H_{21}N_4S$ 277.1482; Found 277.1484



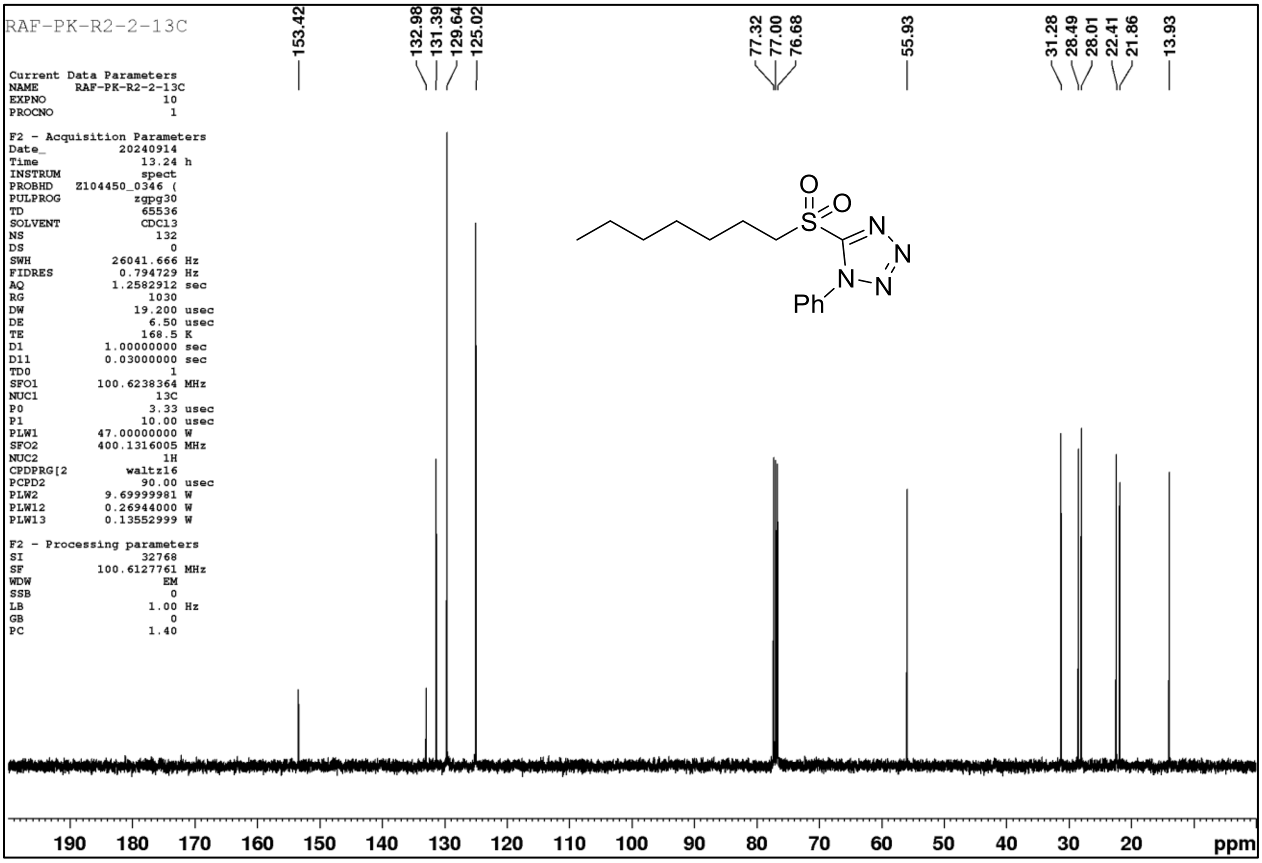
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) of compound **15**



```
Current Data Parameters
NAME      RAF-PK-R2-2-1H
EXPNO                  9
PROCNO                 1

F2 - Acquisition Parameters
Date_           20240914
Time               13.18 h
INSTRUM            spect
PROBHD   Z104450_0346 (
PULPROG             zg30
TD                 54274
SOLVENT            CDCl3
NS                    13
DS                     0
SWH             8223.685 Hz
FIDRES          0.303043 Hz
AQ             3.2998593 sec
RG                    64
DW                60.800 usec
DE                  6.50 usec
TE                 168.5 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           400.1300089 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

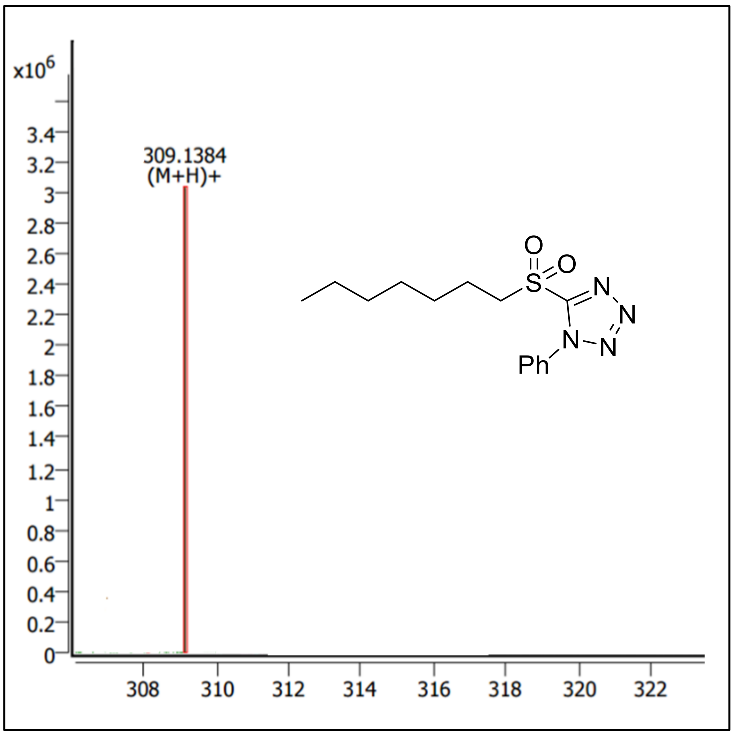


```
Current Data Parameters
NAME     RAF-PK-R2-2-13C
EXPNO                 10
PROCNO                 1

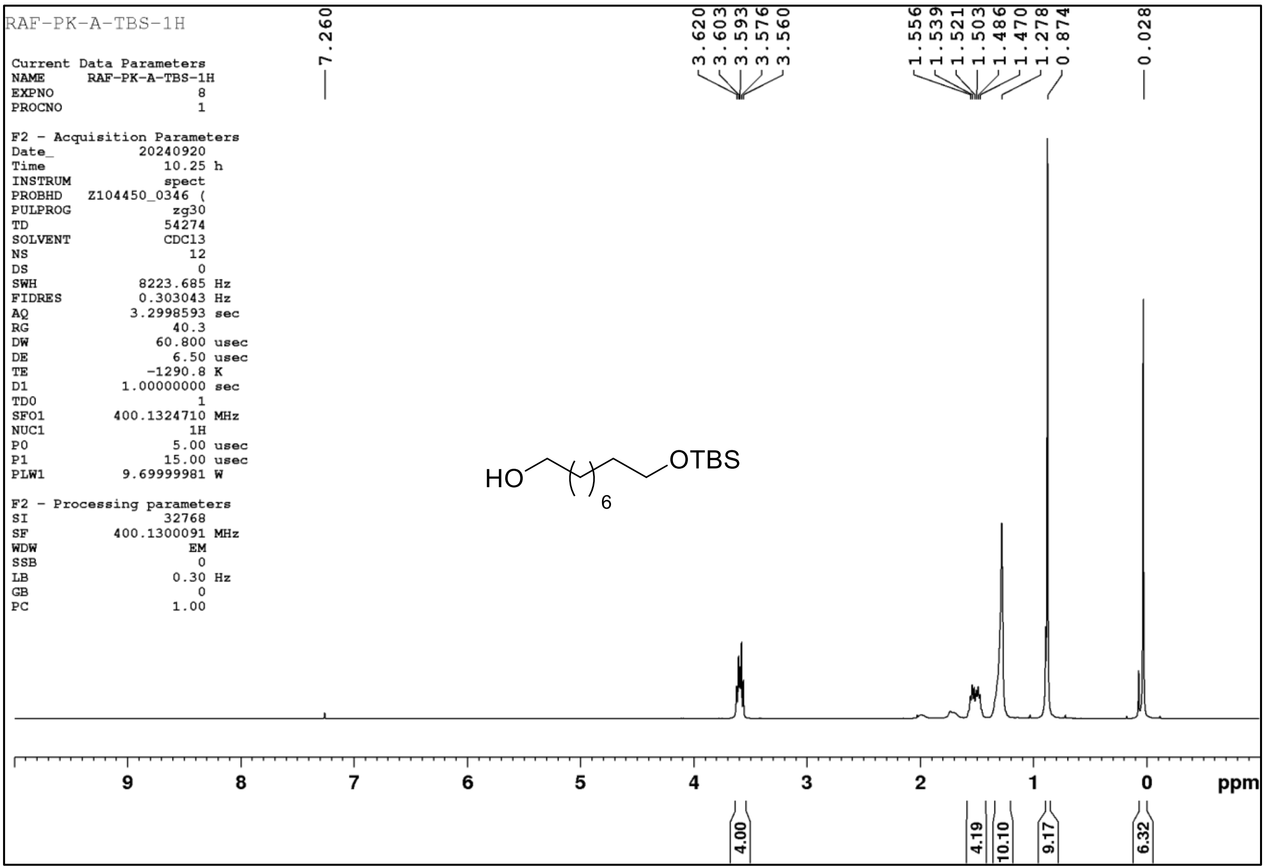
F2 - Acquisition Parameters
Date_           20240914
Time               13.24 h
INSTRUM            spect
PROBHD   Z104450_0346 (
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   132
DS                     0
SWH            26041.666 Hz
FIDRES          0.794729 Hz
AQ             1.2582912 sec
RG                  1030
DW                19.200 usec
DE                  6.50 usec
TE                 168.5 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

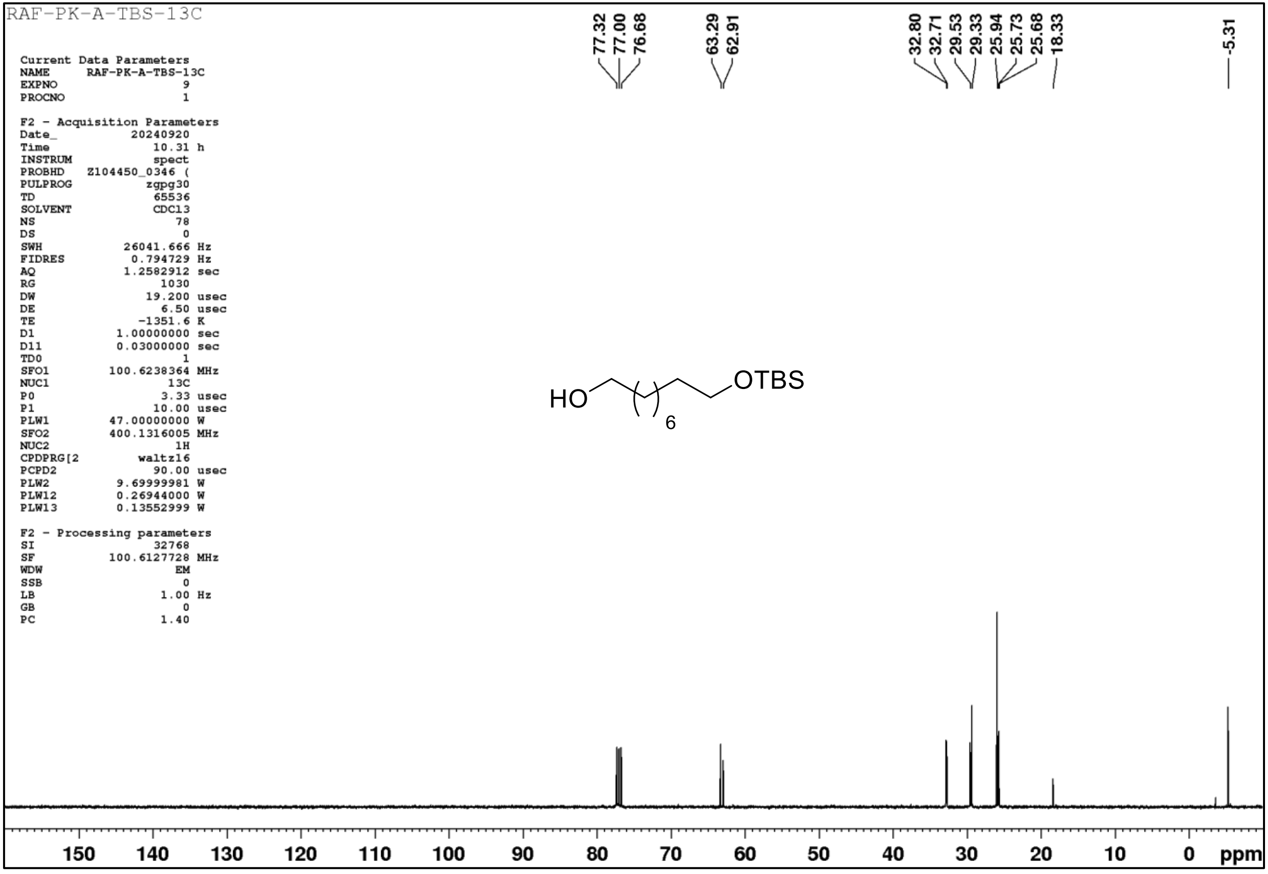
F2 - Processing parameters
SI                 32768
SF           100.6127761 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

15: HRMS (ESI–TOF) *m/z:* $[M + H]^+$ Calcd for $C_{14}H_{21}N_4O_2S$ 309.1380; Found 309.1384

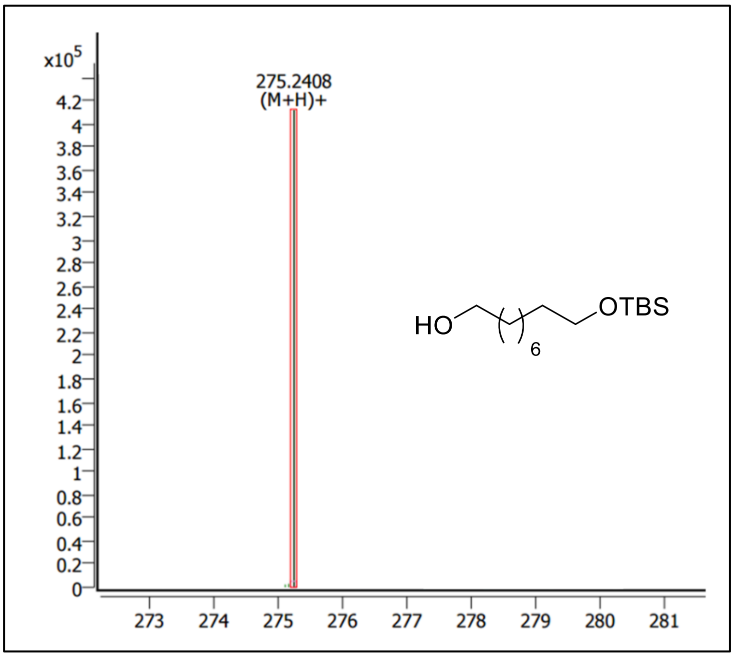


^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **17**

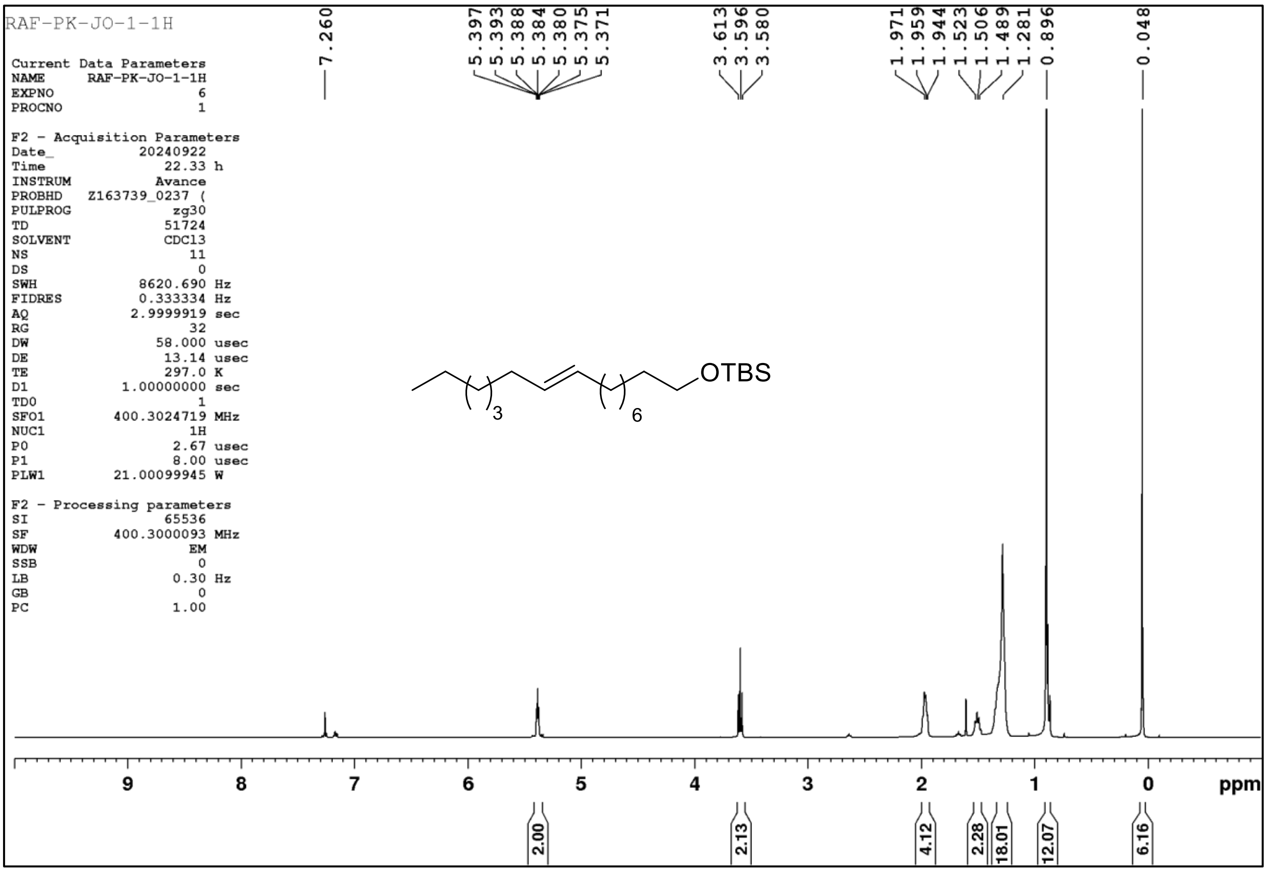




17: HRMS (ESI–TOF) *m/z:* [M + H]$^+$ Calcd for $C_{15}H_{35}O_2Si$ 275.2401; Found 275.2408



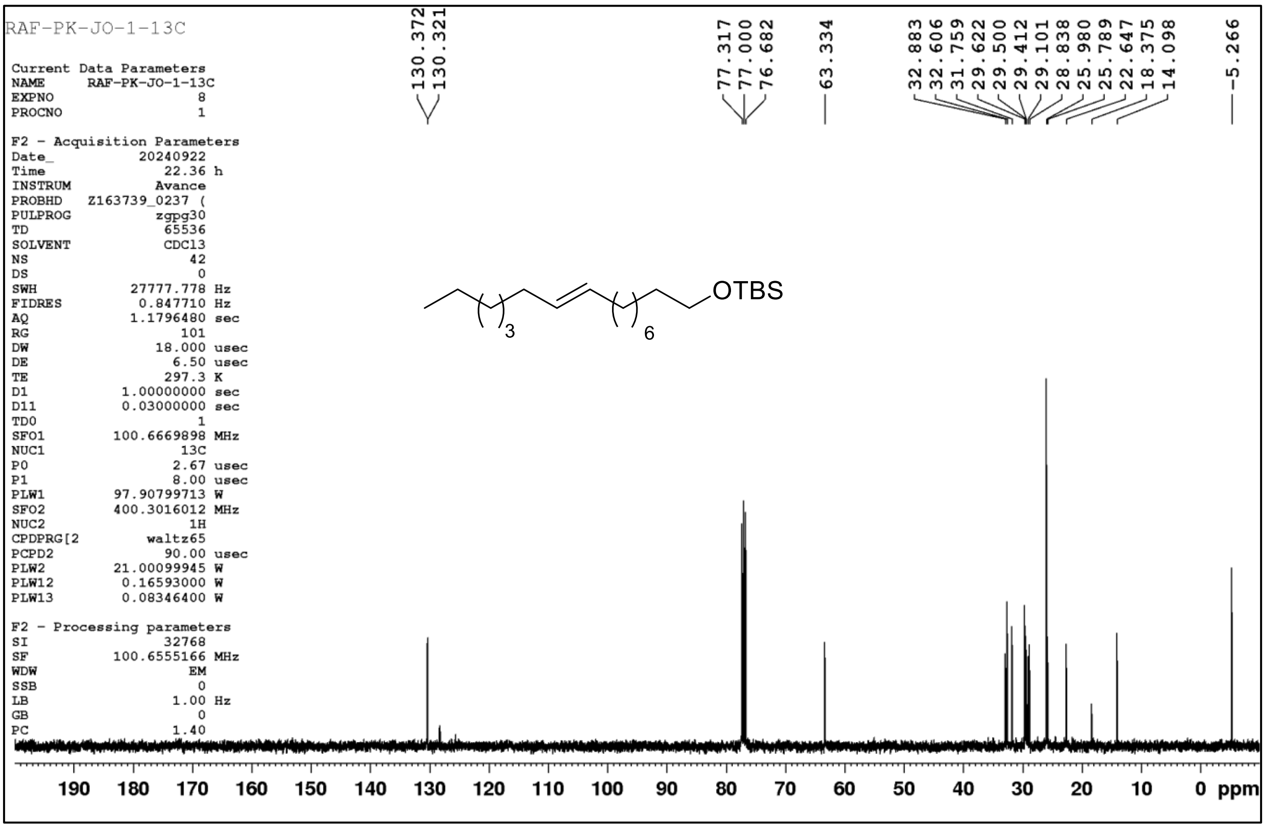
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **18**



```
Current Data Parameters
NAME       RAF-PK-JO-1-1H
EXPNO                   6
PROCNO                  1

F2 - Acquisition Parameters
Date_            20240922
Time                22.33 h
INSTRUM            Avance
PROBHD    Z163739_0237 (
PULPROG              zg30
TD                  51724
SOLVENT             CDCl3
NS                     11
DS                      0
SWH              8620.690 Hz
FIDRES           0.333334 Hz
AQ              2.9999919 sec
RG                     32
DW                 58.000 usec
DE                  13.14 usec
TE                  297.0 K
D1             1.00000000 sec
TD0                     1
SFO1          400.3024719 MHz
NUC1                   1H
P0                   2.67 usec
P1                   8.00 usec
PLW1          21.00099945 W

F2 - Processing parameters
SI                  65536
SF            400.3000093 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

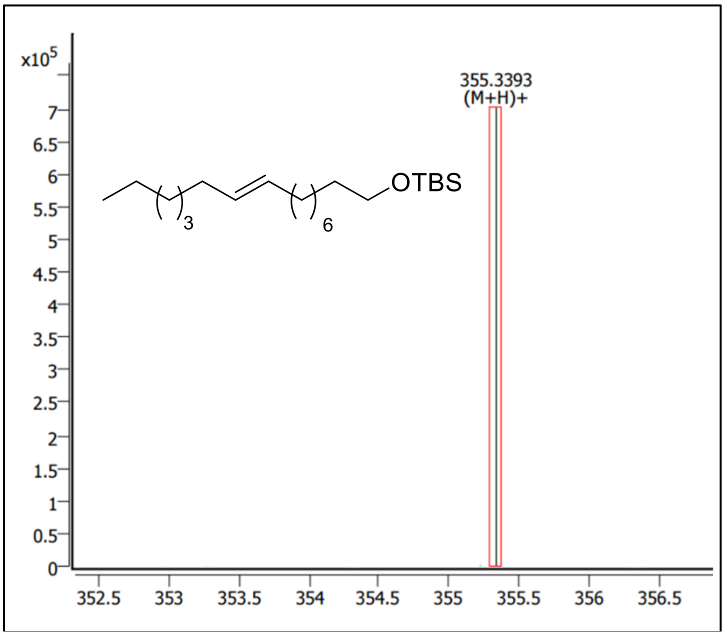


```
Current Data Parameters
NAME      RAF-PK-JO-1-13C
EXPNO                   8
PROCNO                  1

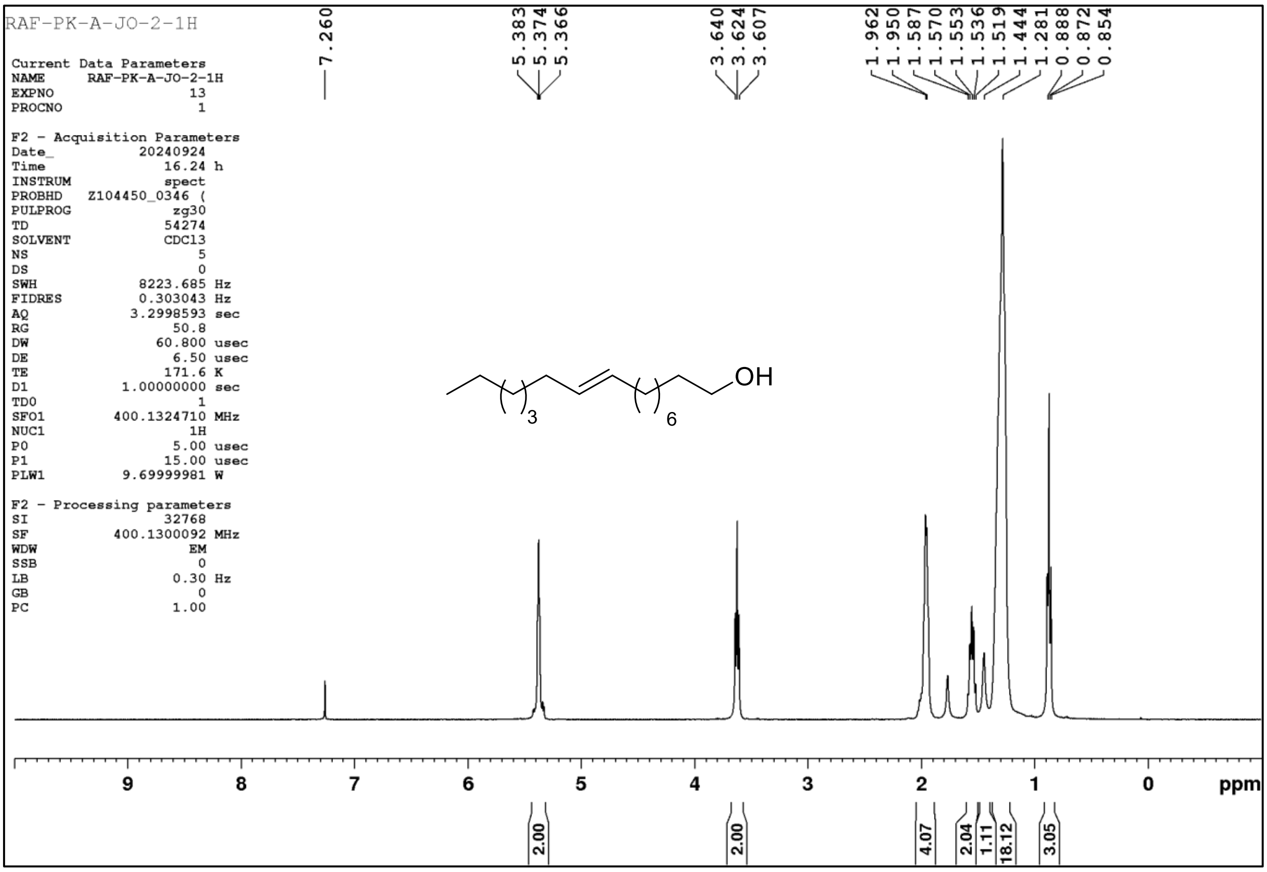
F2 - Acquisition Parameters
Date_            20240922
Time                22.36 h
INSTRUM            Avance
PROBHD    Z163739_0237 (
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     42
DS                      0
SWH             27777.778 Hz
FIDRES           0.847710 Hz
AQ              1.1796480 sec
RG                    101
DW                 18.000 usec
DE                   6.50 usec
TE                  297.3 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          97.90799713 W
SFO2          400.3016012 MHz
NUC2                   1H
CPDPRG[2          waltz65
PCPD2               90.00 usec
PLW2          21.00099945 W
PLW12          0.16593000 W
PLW13          0.08346400 W

F2 - Processing parameters
SI                  32768
SF            100.6555166 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

18: HRMS (ESI–TOF) *m/z:* $[M + H]^+$ Calcd for $C_{22}H_{47}OSi$ 355.3391; Found 355.3393



^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **19**

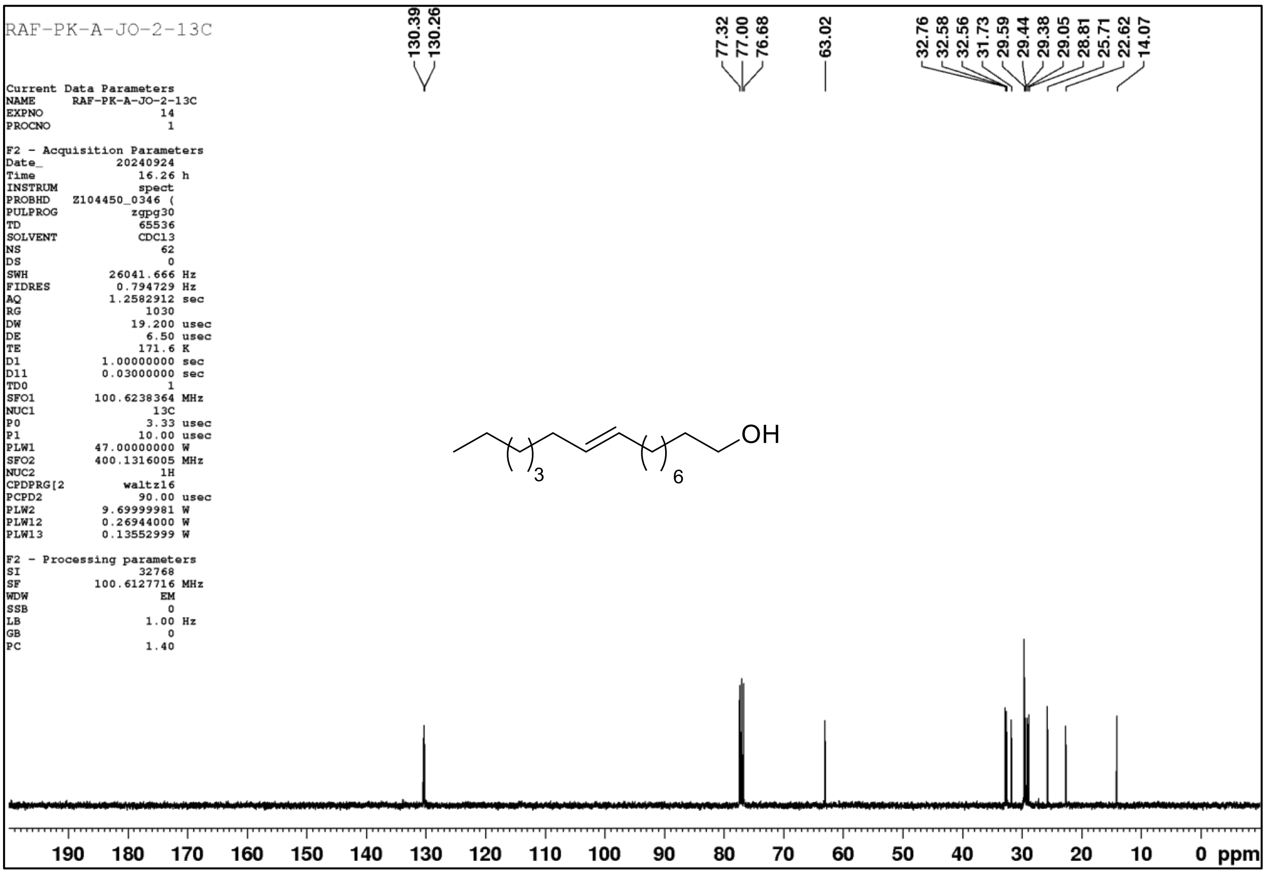


```
RAF-PK-A-JO-2-1H

Current Data Parameters
NAME     RAF-PK-A-JO-2-1H
EXPNO                  13
PROCNO                  1

F2 - Acquisition Parameters
Date_           20240924
Time               16.24 h
INSTRUM            spect
PROBHD   Z104450_0346 (
PULPROG             zg30
TD                 54274
SOLVENT            CDCl3
NS                     5
DS                     0
SWH             8223.685 Hz
FIDRES          0.303043 Hz
AQ             3.2998593 sec
RG                  50.8
DW                60.800 usec
DE                  6.50 usec
TE                 171.6 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
```



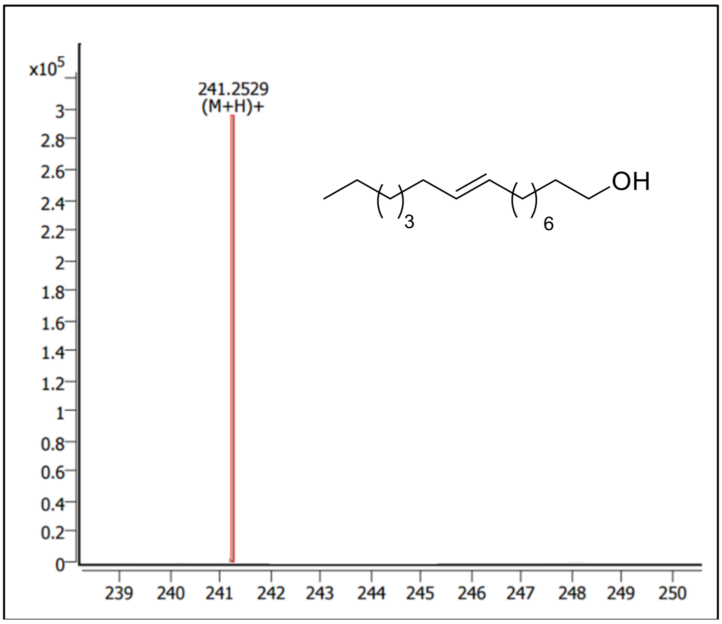
```
RAF-PK-A-JO-2-13C

Current Data Parameters
NAME     RAF-PK-A-JO-2-13C
EXPNO                  14
PROCNO                  1

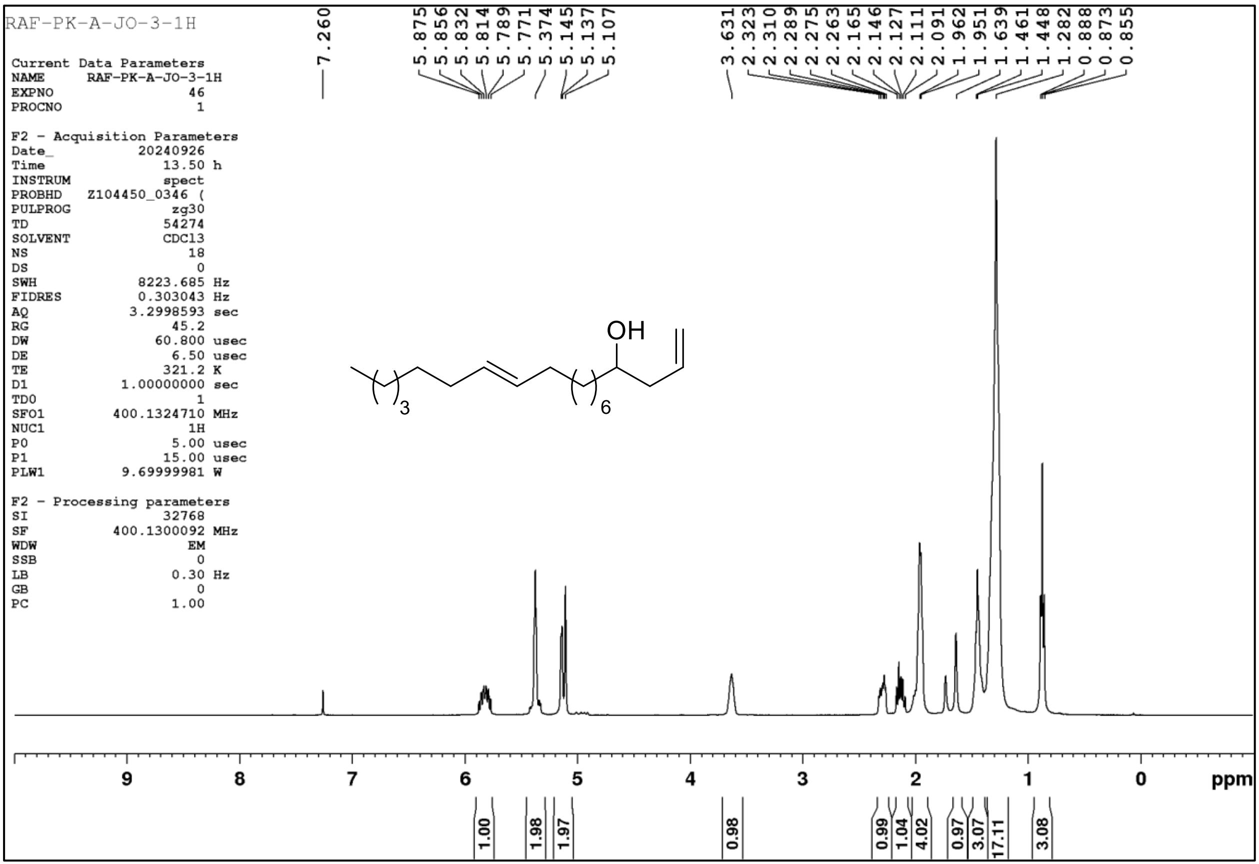
F2 - Acquisition Parameters
Date_           20240924
Time               16.26 h
INSTRUM            spect
PROBHD   Z104450_0346 (
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    62
DS                     0
SWH            26041.666 Hz
FIDRES          0.794729 Hz
AQ             1.2582912 sec
RG                  1030
DW                19.200 usec
DE                  6.50 usec
TE                 171.6 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           100.6127716 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

19: HRMS (ESI–TOF) *m/z:* $[M + H]^+$ Calcd for $C_{16}H_{33}O$ 241.2526; Found 241.2529



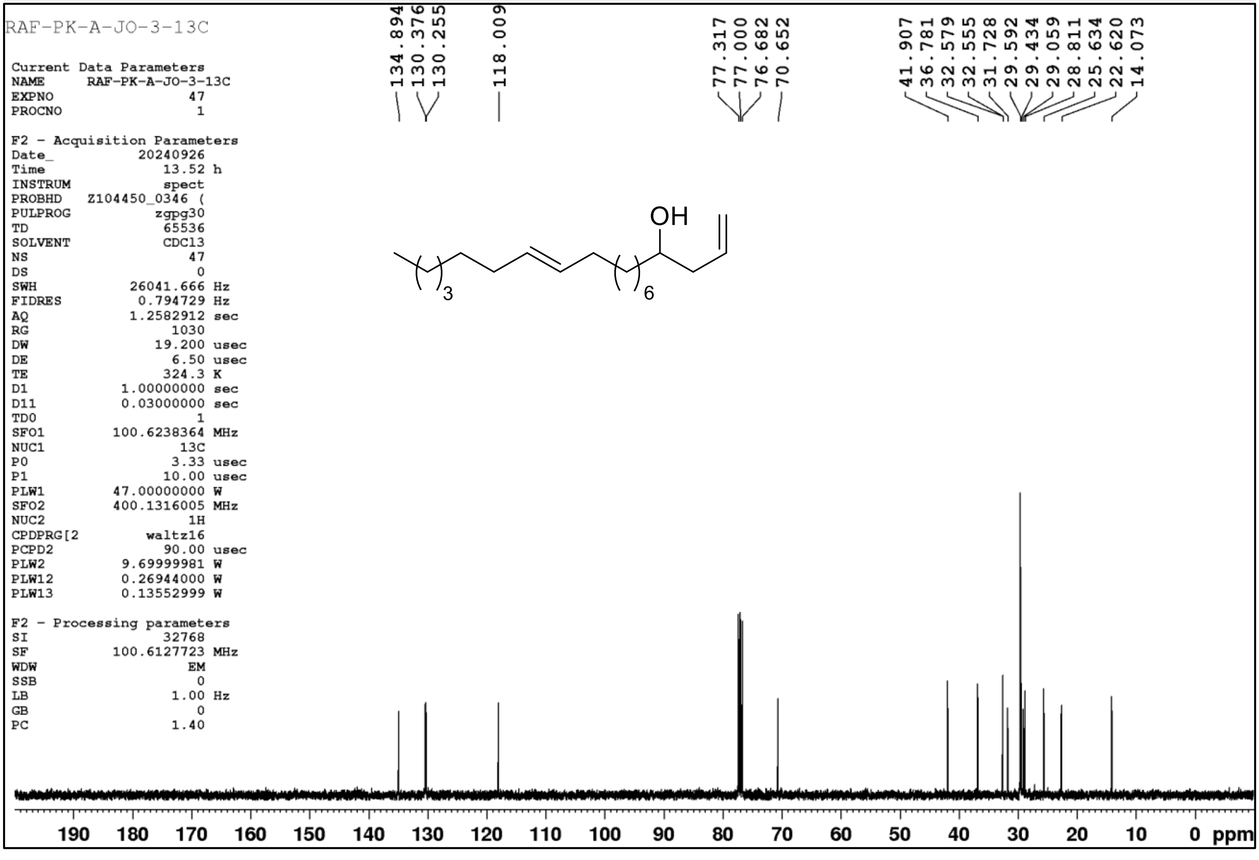
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) of compound **20**



```
Current Data Parameters
NAME      RAF-PK-A-JO-3-1H
EXPNO                 46
PROCNO                 1

F2 - Acquisition Parameters
Date_           20240926
Time               13.50 h
INSTRUM            spect
PROBHD   Z104450_0346 (
PULPROG             zg30
TD                 54274
SOLVENT            CDC13
NS                    18
DS                     0
SWH             8223.685 Hz
FIDRES          0.303043 Hz
AQ             3.2998593 sec
RG                  45.2
DW                60.800 usec
DE                  6.50 usec
TE                 321.2 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
```

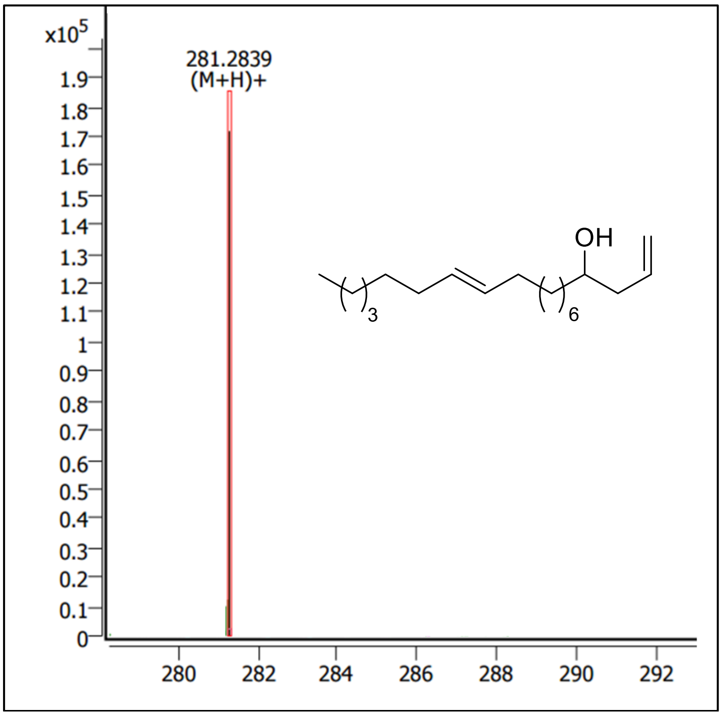


```
Current Data Parameters
NAME      RAF-PK-A-JO-3-13C
EXPNO                 47
PROCNO                 1

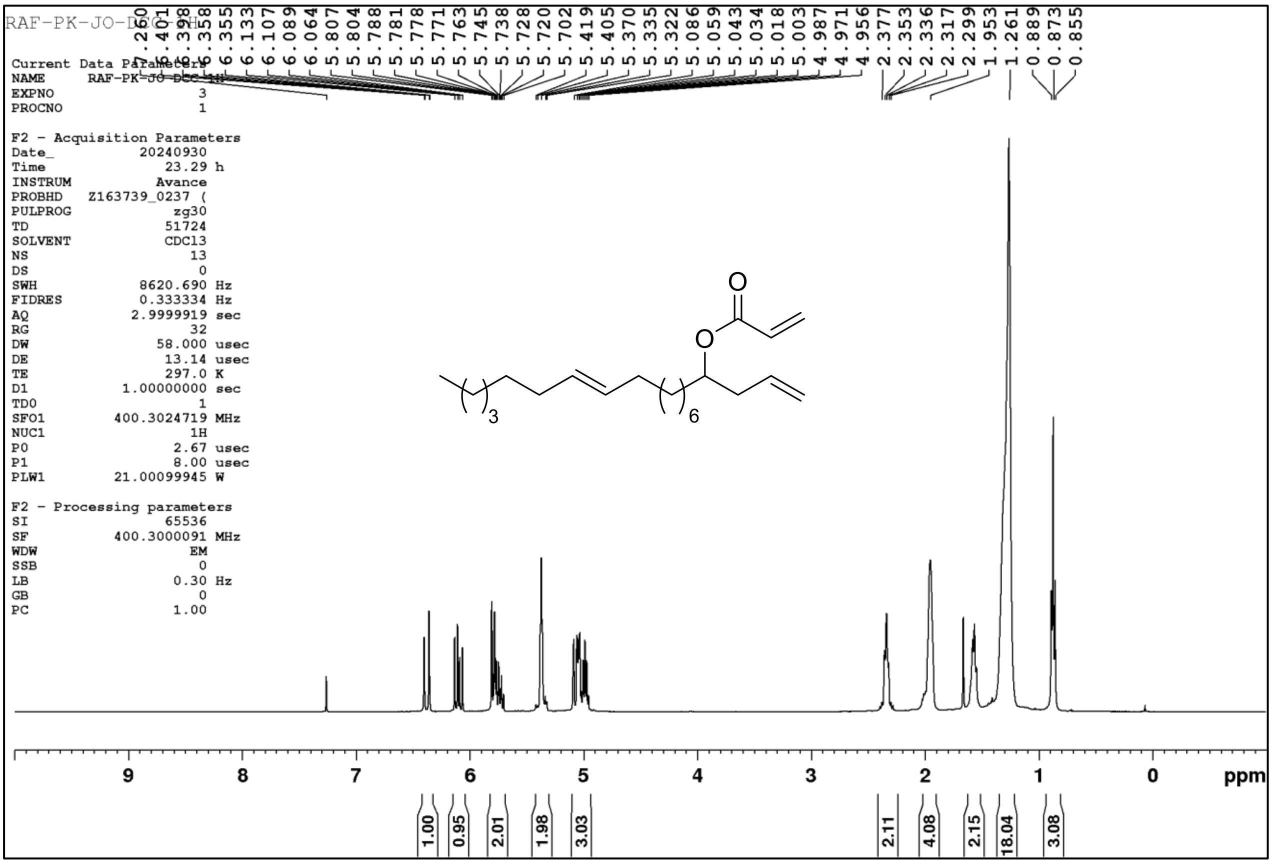
F2 - Acquisition Parameters
Date_           20240926
Time               13.52 h
INSTRUM            spect
PROBHD   Z104450_0346 (
PULPROG           zgpg30
TD                 65536
SOLVENT            CDC13
NS                    47
DS                     0
SWH            26041.666 Hz
FIDRES          0.794729 Hz
AQ             1.2582912 sec
RG                  1030
DW                19.200 usec
DE                  6.50 usec
TE                 324.3 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           100.6127723 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

20: HRMS (ESI–TOF) *m/z:* [M + H]$^+$ Calcd for $C_{19}H_{37}O$ 281.2839; Found 281.2839



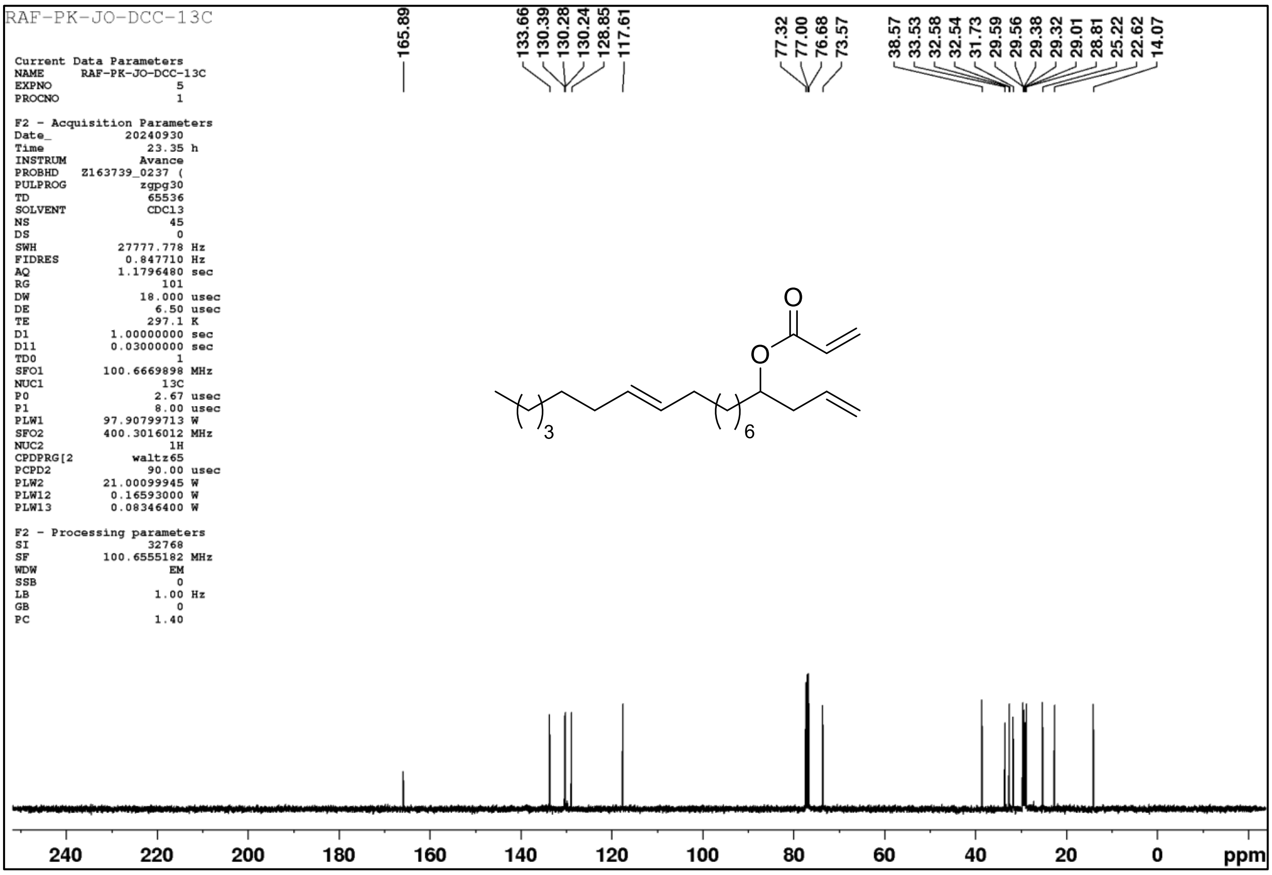
^1H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) of compound **21**



```
Current Data Parameters
NAME      RAF-PK-JO-DCC-1H
EXPNO                3
PROCNO               1

F2 - Acquisition Parameters
Date_         20240930
Time             23.29 h
INSTRUM         Avance
PROBHD   Z163739_0237 (
PULPROG           zg30
TD               51724
SOLVENT          CDCl3
NS                  13
DS                   0
SWH           8620.690 Hz
FIDRES        0.333334 Hz
AQ           2.9999919 sec
RG                  32
DW              58.000 usec
DE               13.14 usec
TE               297.0 K
D1          1.00000000 sec
TD0                  1
SFO1       400.3024719 MHz
NUC1                1H
P0                2.67 usec
P1                8.00 usec
PLW1       21.00099945 W

F2 - Processing parameters
SI               65536
SF         400.3000091 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```

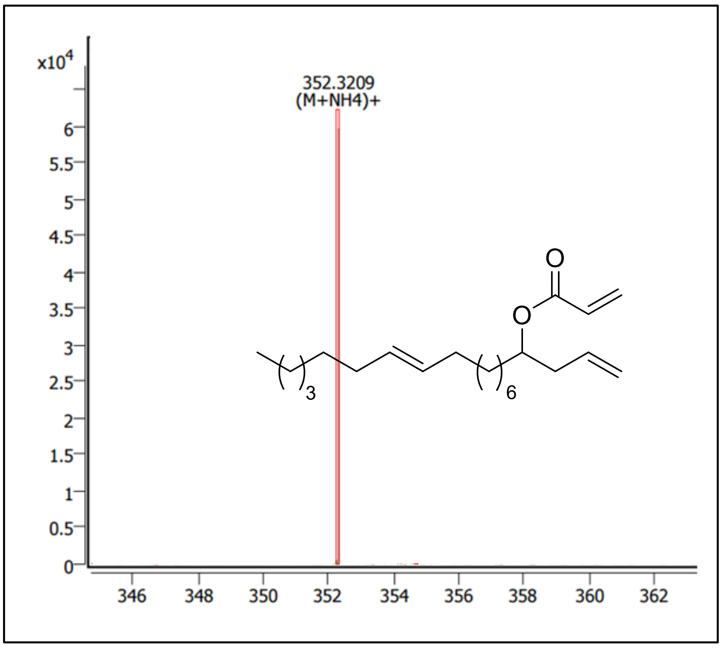


```
Current Data Parameters
NAME      RAF-PK-JO-DCC-13C
EXPNO                5
PROCNO               1

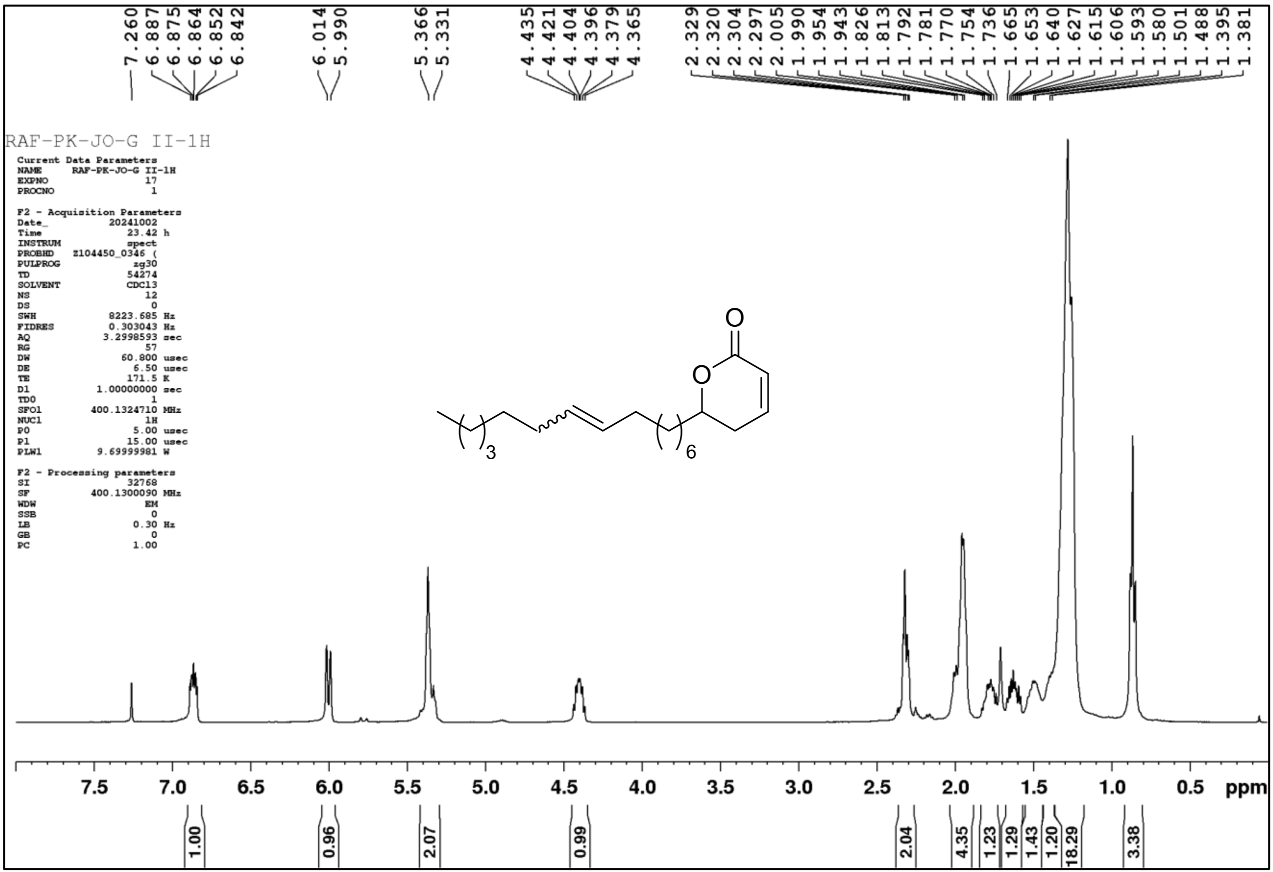
F2 - Acquisition Parameters
Date_         20240930
Time             23.35 h
INSTRUM         Avance
PROBHD   Z163739_0237 (
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                  45
DS                   0
SWH          27777.778 Hz
FIDRES        0.847710 Hz
AQ           1.1796480 sec
RG                 101
DW              18.000 usec
DE                6.50 usec
TE               297.1 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       97.90799713 W
SFO2       400.3016012 MHz
NUC2                1H
CPDPRG[2        waltz65
PCPD2            90.00 usec
PLW2       21.00099945 W
PLW12       0.16593000 W
PLW13       0.08346400 W

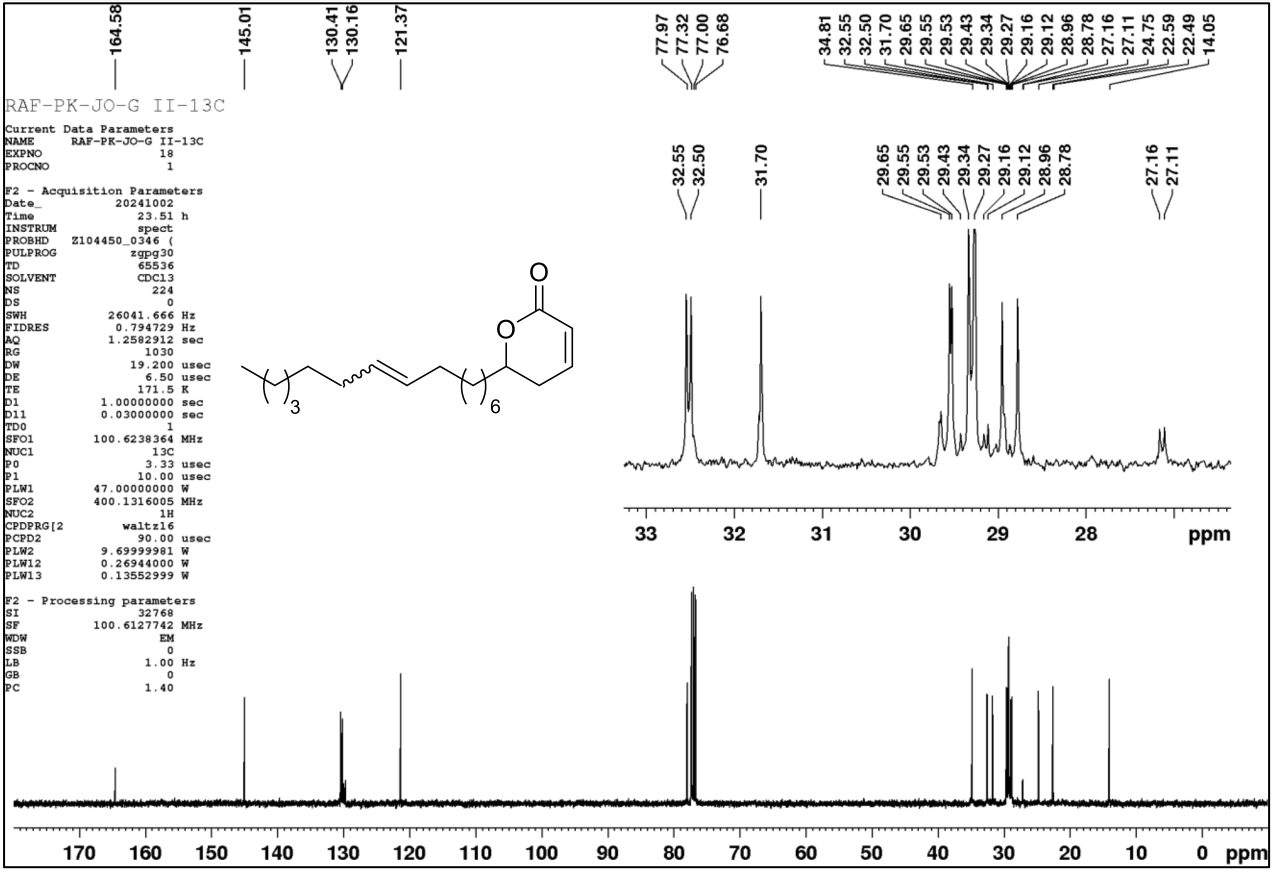
F2 - Processing parameters
SI               32768
SF         100.6555182 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

21: HRMS (ESI–TOF) *m/z:* $[M + NH_4]^+$ Calcd for $C_{22}H_{42}O_2N$ 352.3210; Found 352.3209

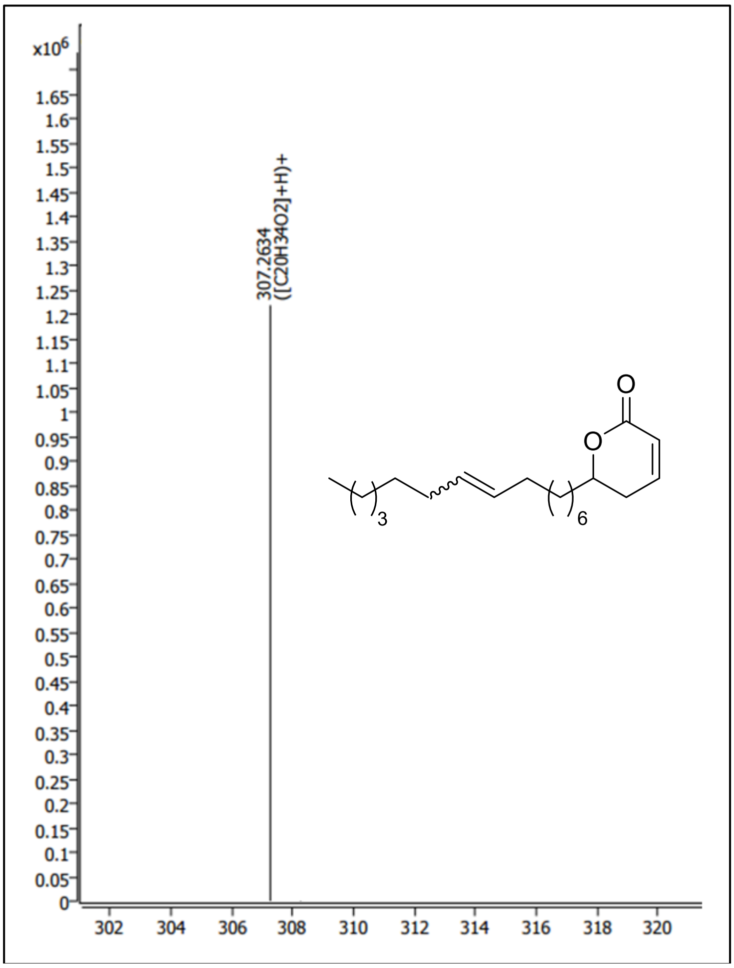


^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **12** from **21**

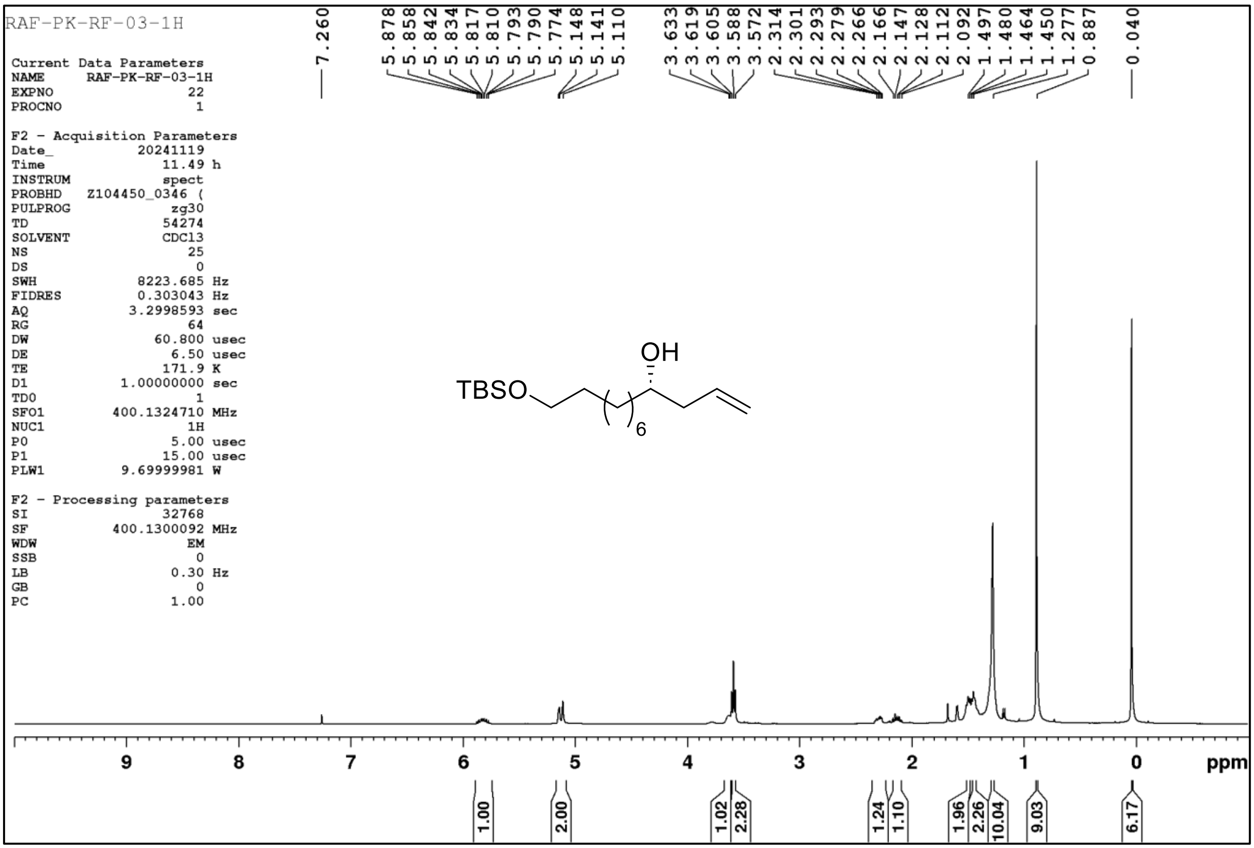




12 (obtained from **21**): HRMS (Q–TOF) *m/z:* [M + H]$^+$ Calcd for $C_{20}H_{35}O_2$ 307.2632; Found 307.2634



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

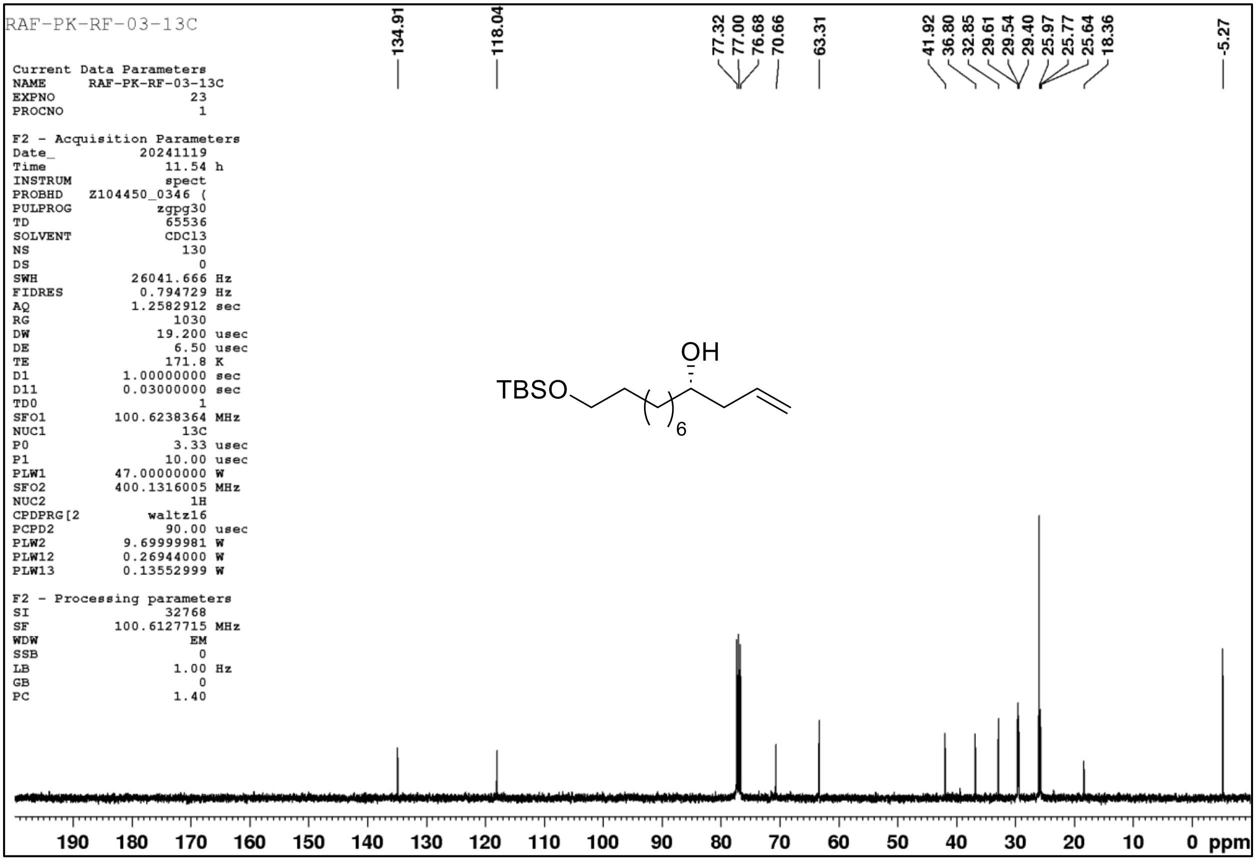


```
RAF-PK-RF-03-1H

Current Data Parameters
NAME      RAF-PK-RF-03-1H
EXPNO                  22
PROCNO                  1

F2 - Acquisition Parameters
Date_          20241119
Time              11.49 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                   64
DW               60.800 usec
DE                 6.50 usec
TE                171.9 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
```



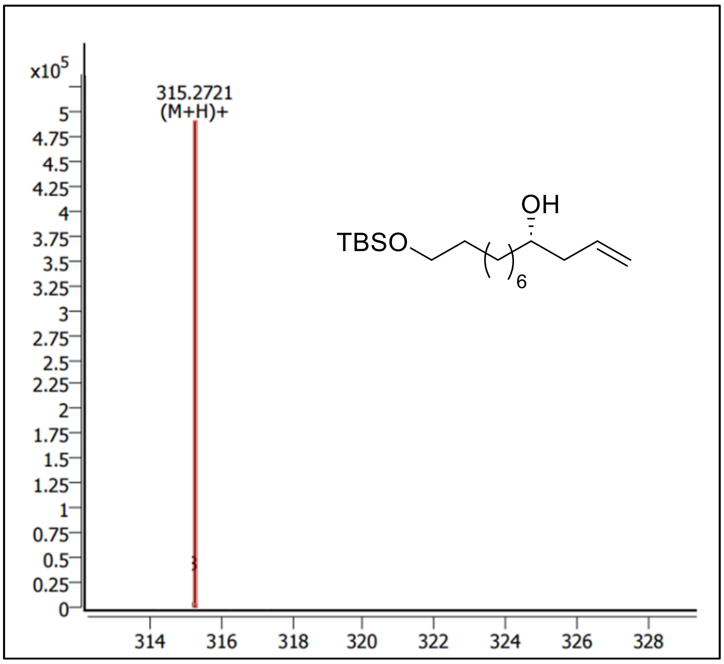
```
RAF-PK-RF-03-13C

Current Data Parameters
NAME      RAF-PK-RF-03-13C
EXPNO                  23
PROCNO                  1

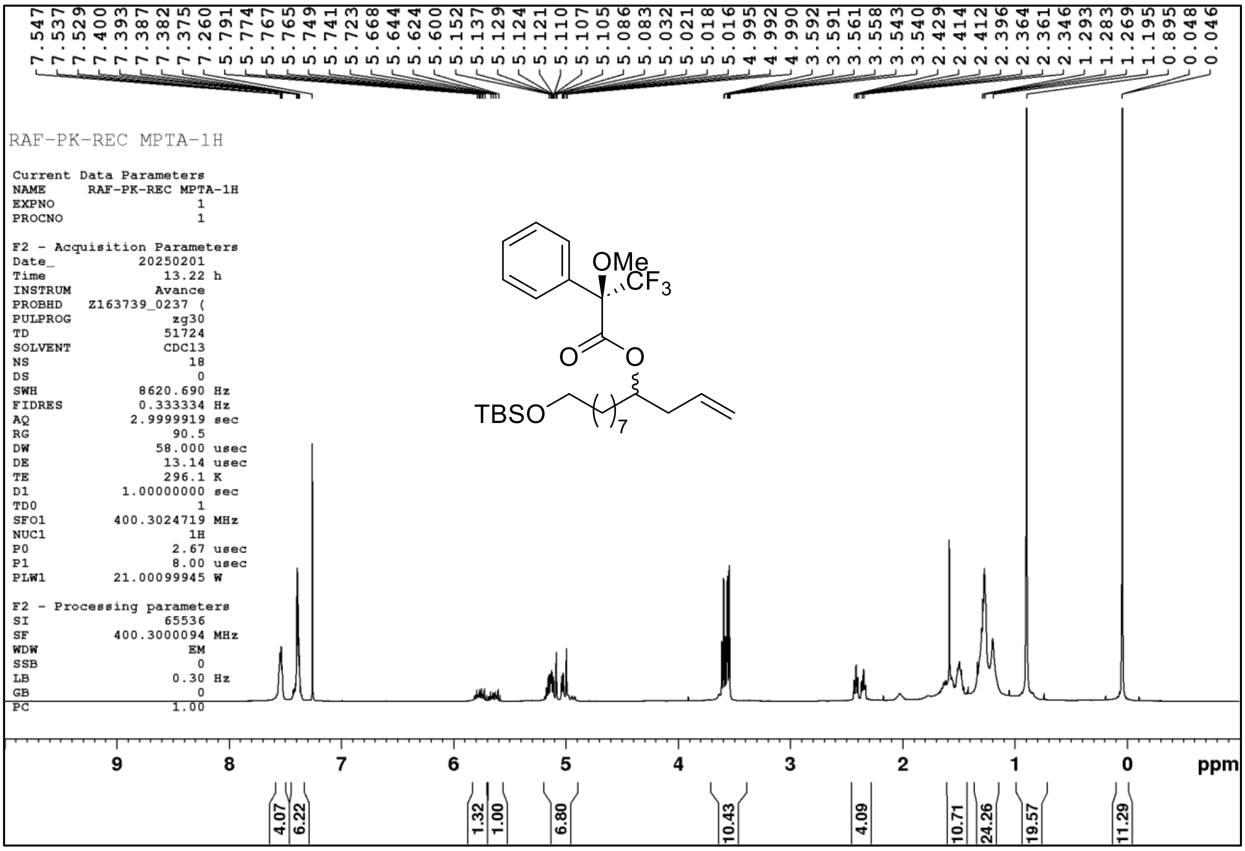
F2 - Acquisition Parameters
Date_          20241119
Time              11.54 h
INSTRUM           spect
PROBHD   Z104450_0346 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  130
DS                    0
SWH           26041.666 Hz
FIDRES         0.794729 Hz
AQ            1.2582912 sec
RG                 1030
DW               19.200 usec
DE                 6.50 usec
TE                171.8 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          100.6127715 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

22: HRMS (ESI–TOF) *m/z:* $[M + H]^+$ Calcd for $C_{19}H_{39}O_2Si$ 315.2715; Found 315.2721



^{1}H NMR (400 MHz, $CDCl_3$ compound diastereomeric **51**



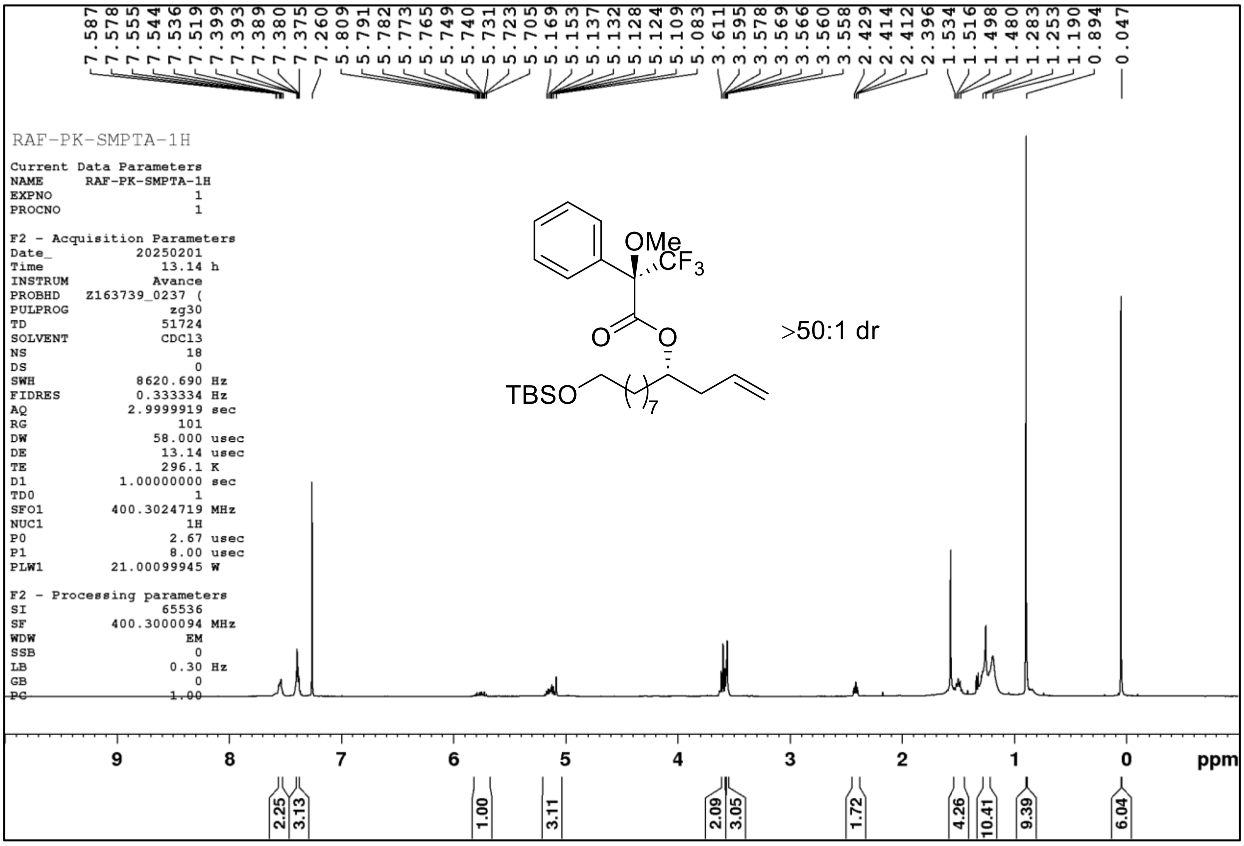
```
RAF-PK-REC MPTA-1H

Current Data Parameters
NAME     RAF-PK-REC MPTA-1H
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20250201
Time                13.22 h
INSTRUM              Avance
PROBHD   Z163739_0237 (
PULPROG                zg30
TD                    51724
SOLVENT               CDCl3
NS                       18
DS                        0
SWH              8620.690 Hz
FIDRES           0.333334 Hz
AQ              2.9999919 sec
RG                     90.5
DW                 58.000 usec
DE                  13.14 usec
TE                  296.1 K
D1             1.00000000 sec
TD0                       1
SFO1         400.3024719 MHz
NUC1                     1H
P0                   2.67 usec
P1                   8.00 usec
PLW1          21.00099945 W

F2 - Processing parameters
SI                    65536
SF           400.3000094 MHz
WDW                      EM
SSB                       0
LB                   0.30 Hz
GB                        0
PC                     1.00
```

^{1}H NMR (400 MHz, $CDCl_3$ compound **51**



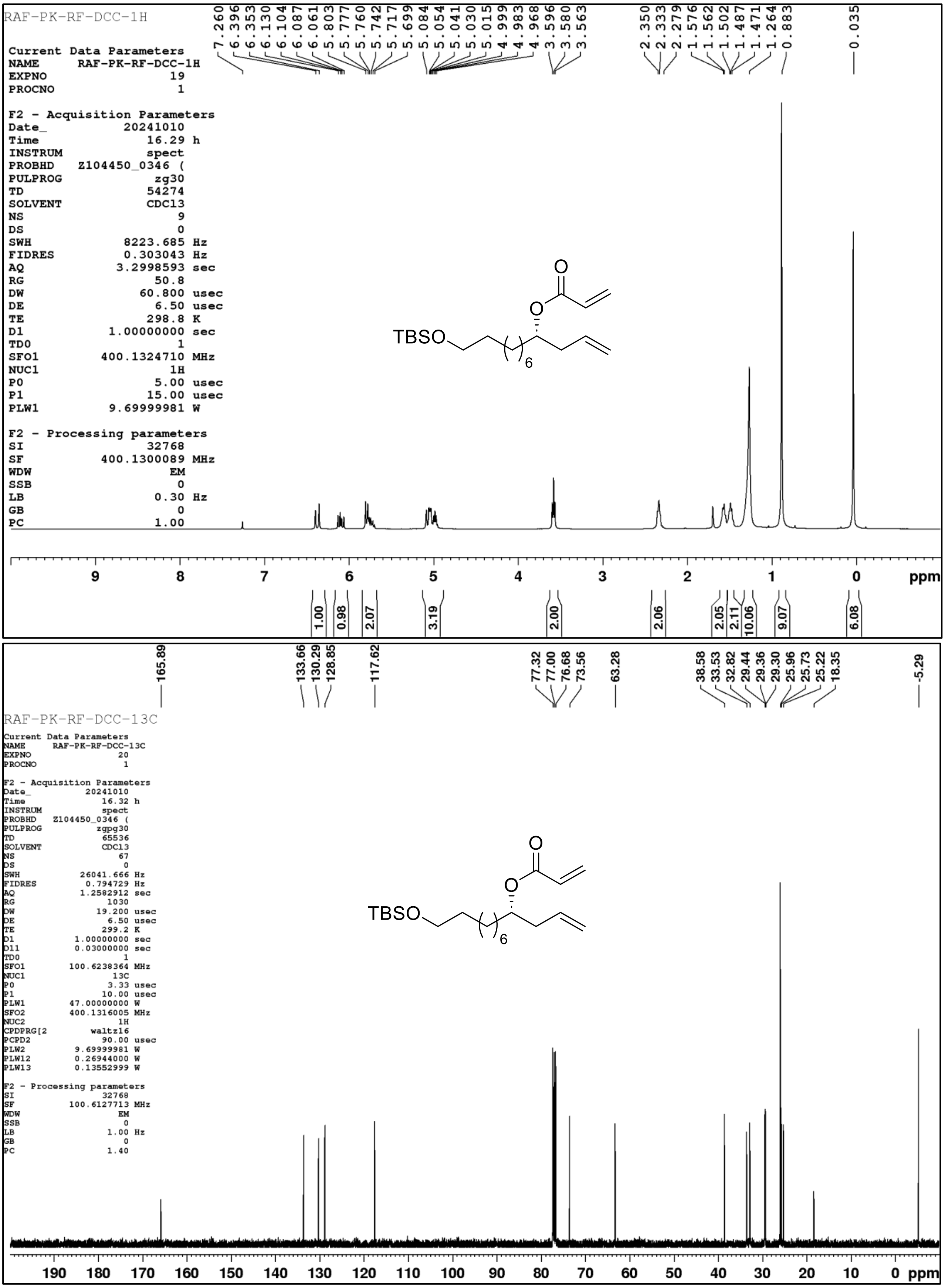
```
RAF-PK-SMPTA-1H

Current Data Parameters
NAME     RAF-PK-SMPTA-1H
EXPNO                     1
PROCNO                    1

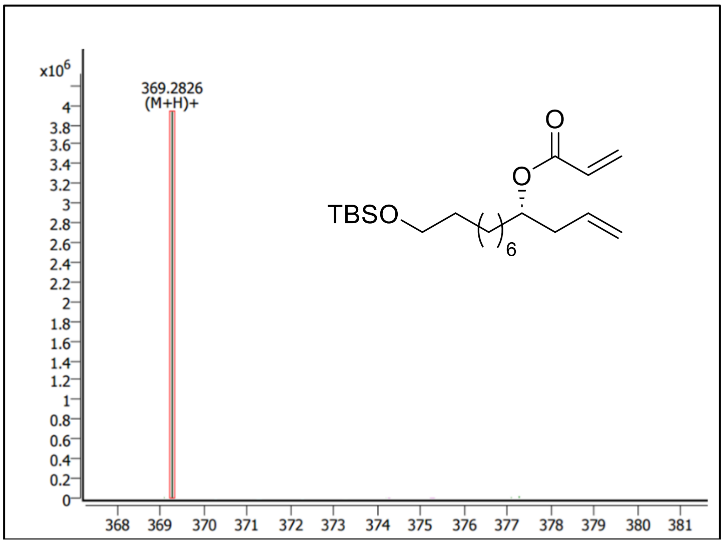
F2 - Acquisition Parameters
Date_              20250201
Time                13.14 h
INSTRUM              Avance
PROBHD   Z163739_0237 (
PULPROG                zg30
TD                    51724
SOLVENT               CDCl3
NS                       18
DS                        0
SWH              8620.690 Hz
FIDRES           0.333334 Hz
AQ              2.9999919 sec
RG                      101
DW                 58.000 usec
DE                  13.14 usec
TE                  296.1 K
D1             1.00000000 sec
TD0                       1
SFO1         400.3024719 MHz
NUC1                     1H
P0                   2.67 usec
P1                   8.00 usec
PLW1          21.00099945 W

F2 - Processing parameters
SI                    65536
SF           400.3000094 MHz
WDW                      EM
SSB                       0
LB                   0.30 Hz
GB                        0
PC                     1.00
```

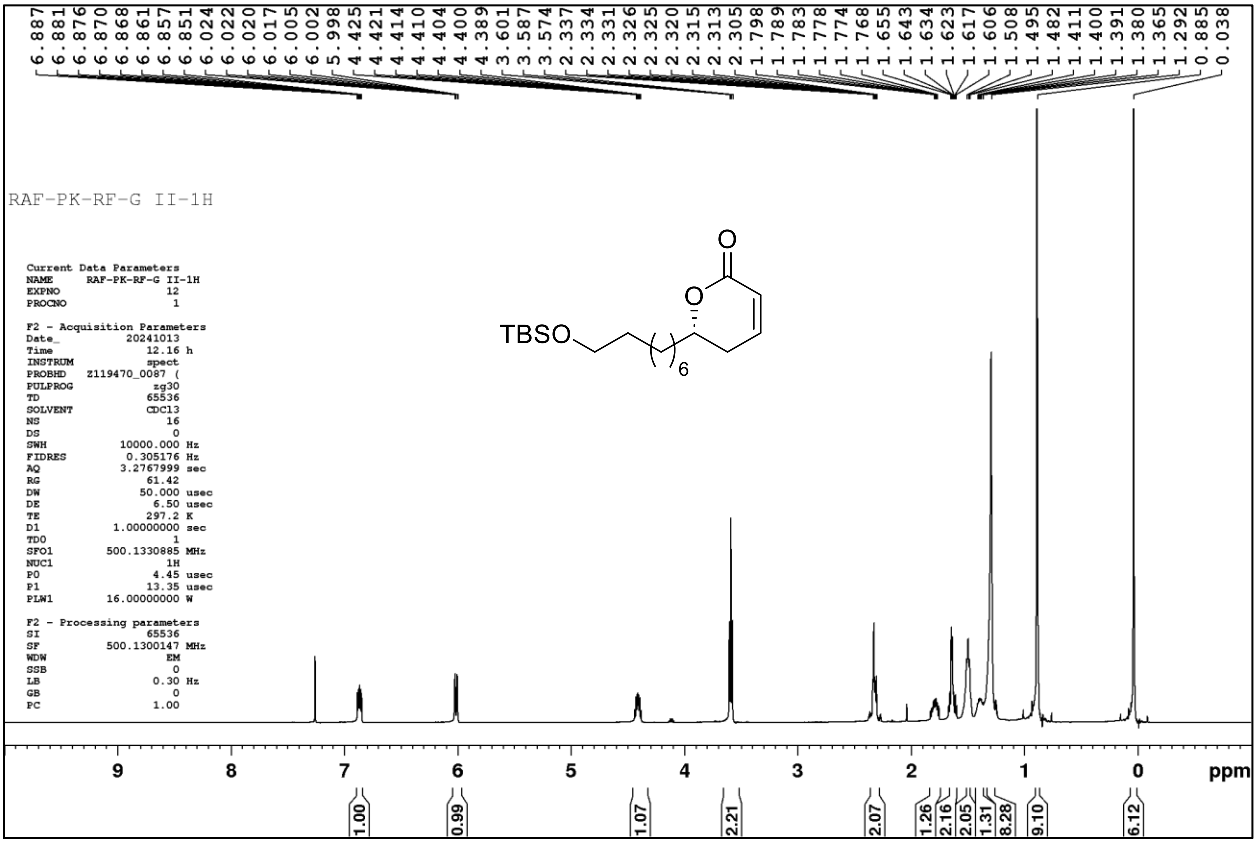
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) of compound **23**

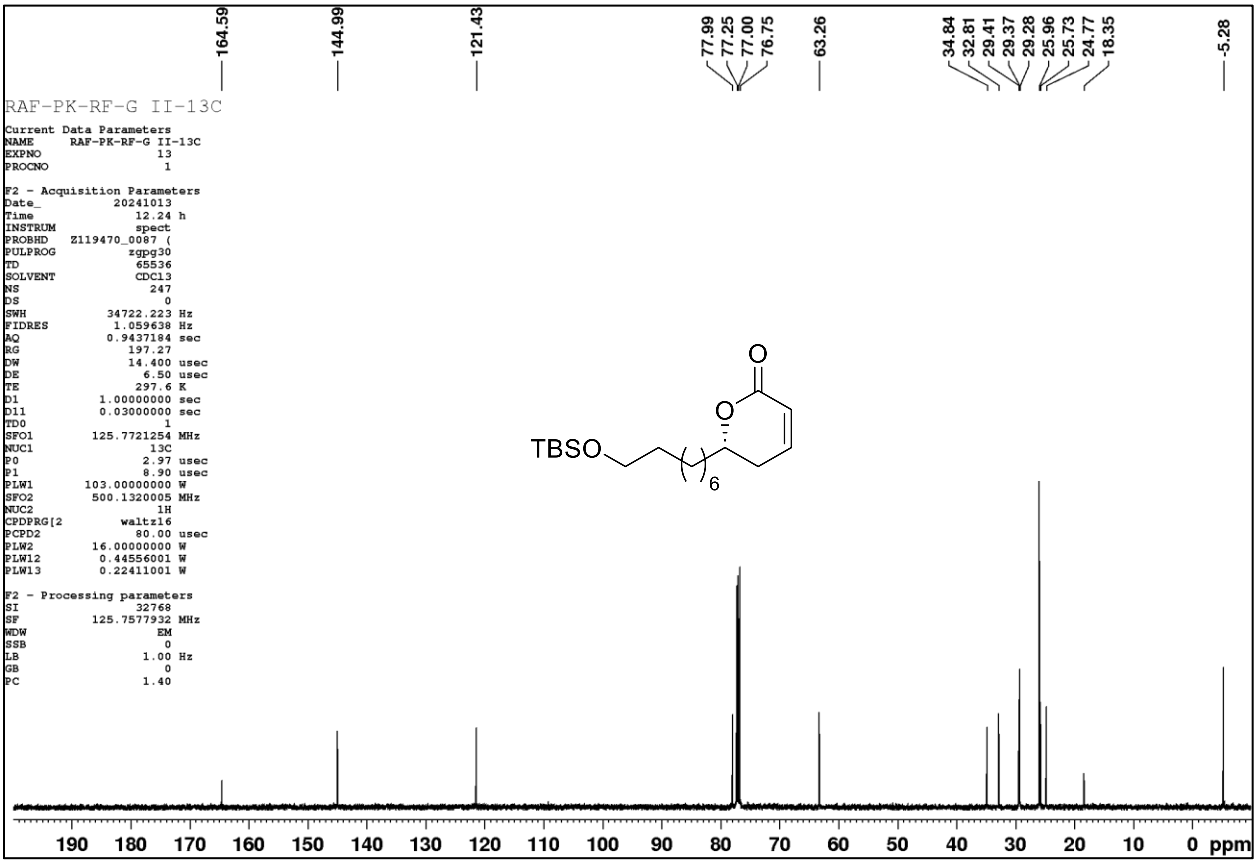


23: HRMS (ESI–TOF) *m/z:* $[M + H]^+$ Calcd for $C_{21}H_{41}O_3Si$ 369.2820; Found 369.2826

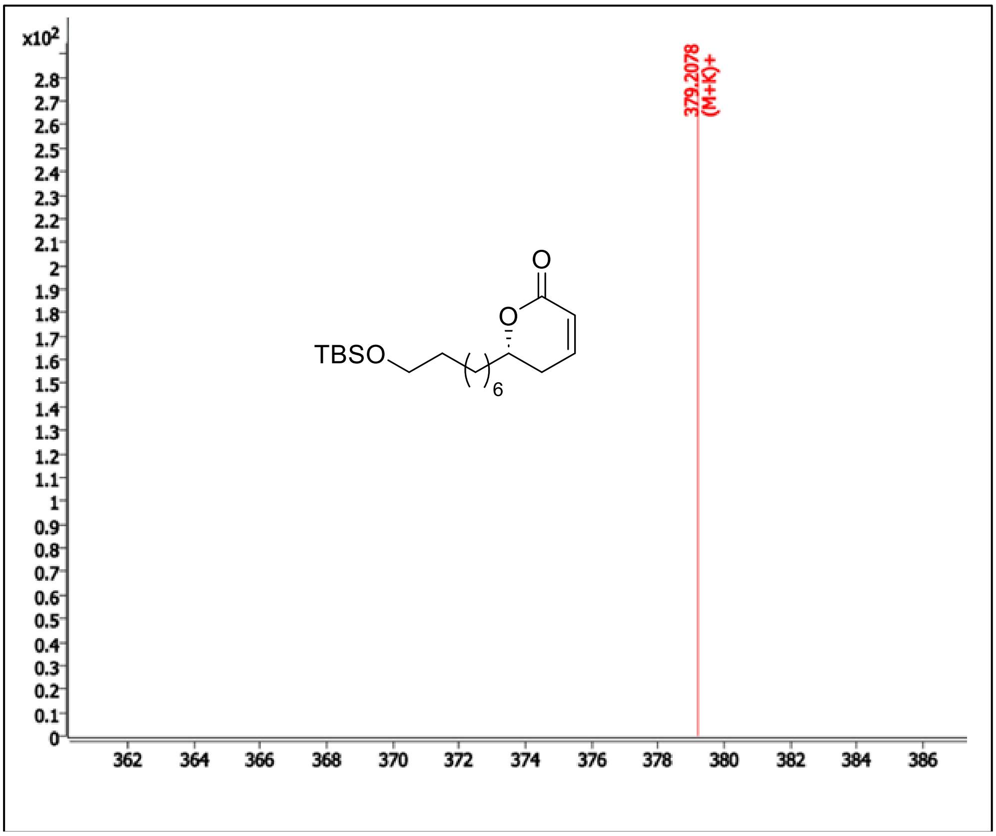


^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) of compound **24**

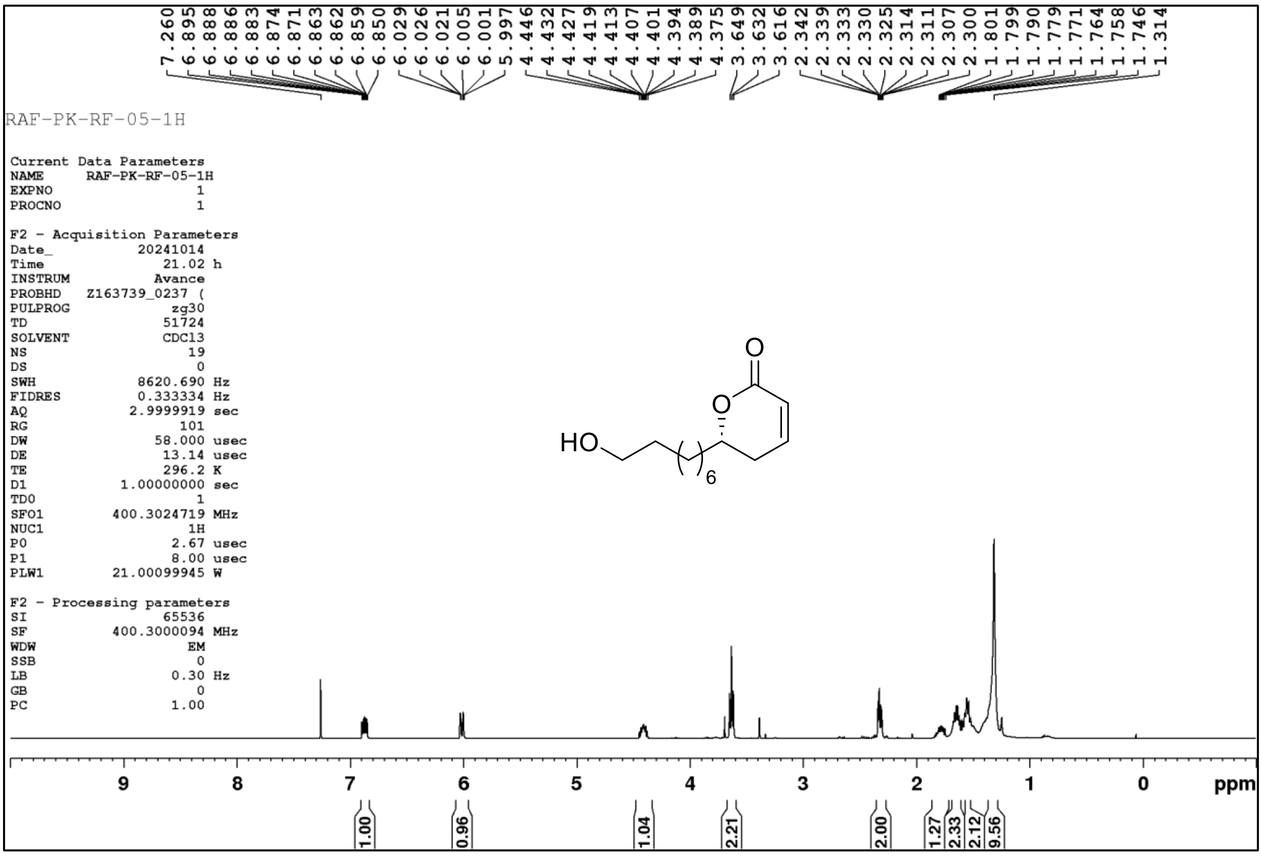




24: HRMS (ESI–TOF) *m/z:* $[M + K]^+$ Calcd for $C_{19}H_{36}O_3SiK$ 379.2068; Found 379.2078



^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **25**

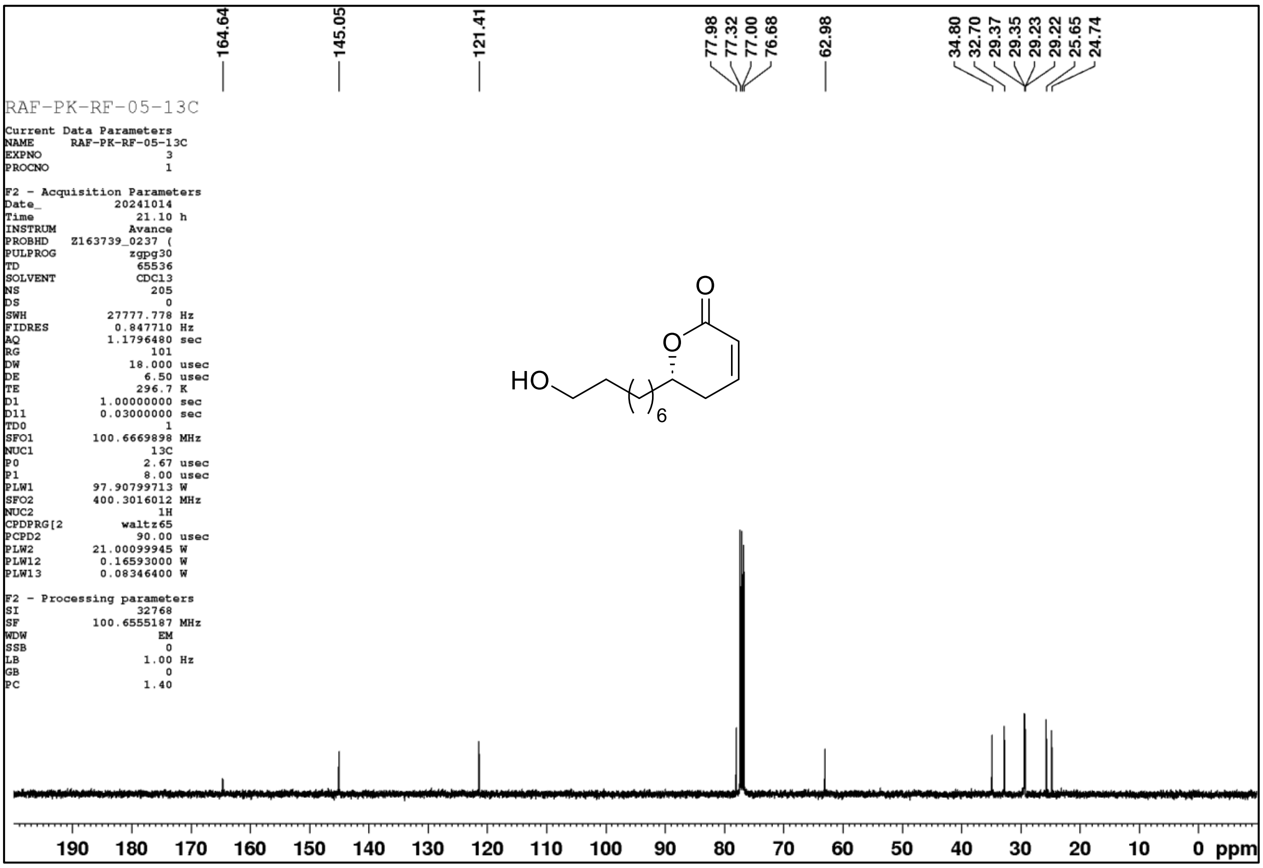


```
RAF-PK-RF-05-1H

Current Data Parameters
NAME       RAF-PK-RF-05-1H
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20241014
Time                 21.02 h
INSTRUM             Avance
PROBHD     Z163739_0237 (
PULPROG               zg30
TD                   51724
SOLVENT              CDCl3
NS                      19
DS                       0
SWH               8620.690 Hz
FIDRES            0.333334 Hz
AQ               2.9999919 sec
RG                     101
DW                  58.000 usec
DE                   13.14 usec
TE                   296.2 K
D1              1.00000000 sec
TD0                      1
SFO1           400.3024719 MHz
NUC1                    1H
P0                    2.67 usec
P1                    8.00 usec
PLW1           21.00099945 W

F2 - Processing parameters
SI                   65536
SF             400.3000094 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



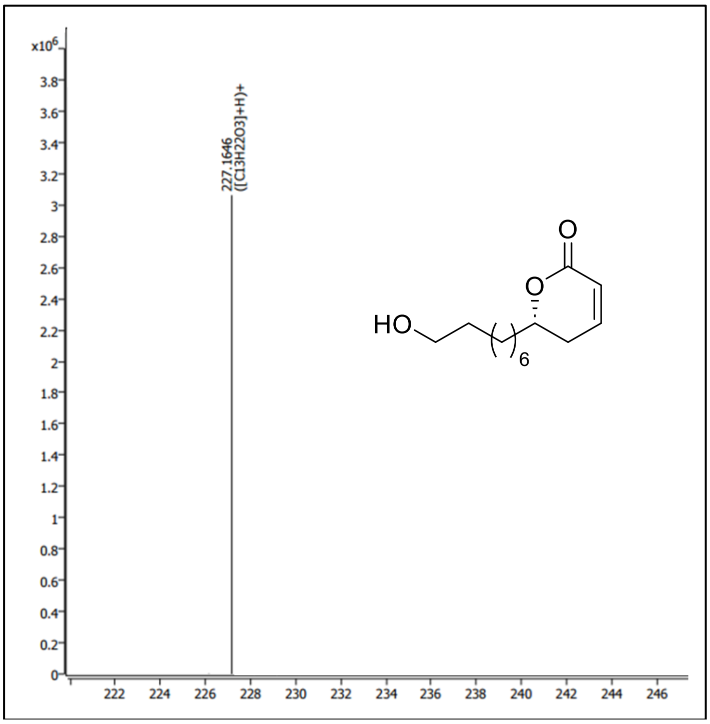
```
RAF-PK-RF-05-13C

Current Data Parameters
NAME      RAF-PK-RF-05-13C
EXPNO                    3
PROCNO                   1

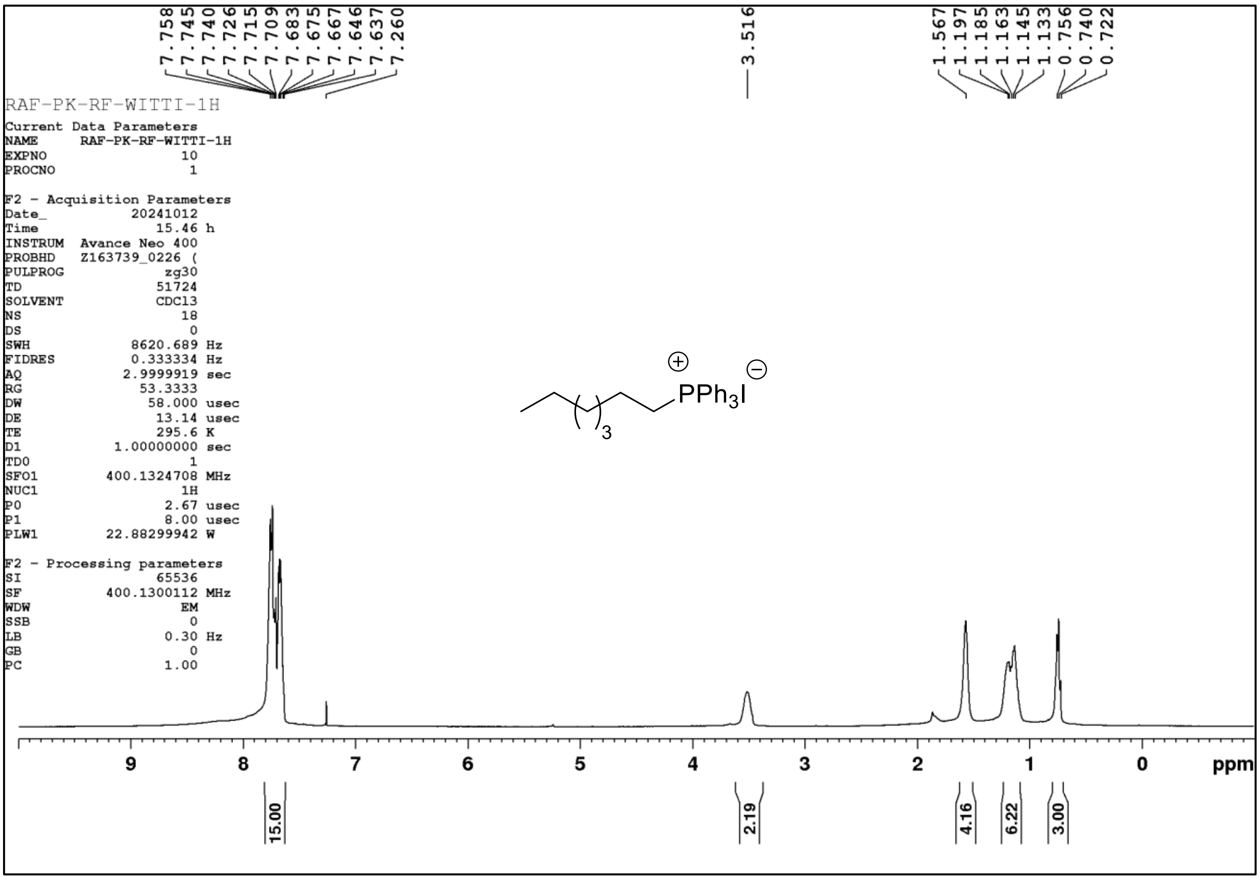
F2 - Acquisition Parameters
Date_             20241014
Time                 21.10 h
INSTRUM             Avance
PROBHD     Z163739_0237 (
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     205
DS                       0
SWH              27777.778 Hz
FIDRES            0.847710 Hz
AQ               1.1796480 sec
RG                     101
DW                  18.000 usec
DE                    6.50 usec
TE                   296.7 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           97.90799713 W
SFO2           400.3016012 MHz
NUC2                    1H
CPDPRG[2           waltz65
PCPD2                90.00 usec
PLW2           21.00099945 W
PLW12           0.16593000 W
PLW13           0.08346400 W

F2 - Processing parameters
SI                   32768
SF             100.6555187 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

25: HRMS (ESI–TOF) *m/z:* $[M + H]^+$ Calcd for $C_{13}H_{23}O_3$ 227.1642 Found 227.1646



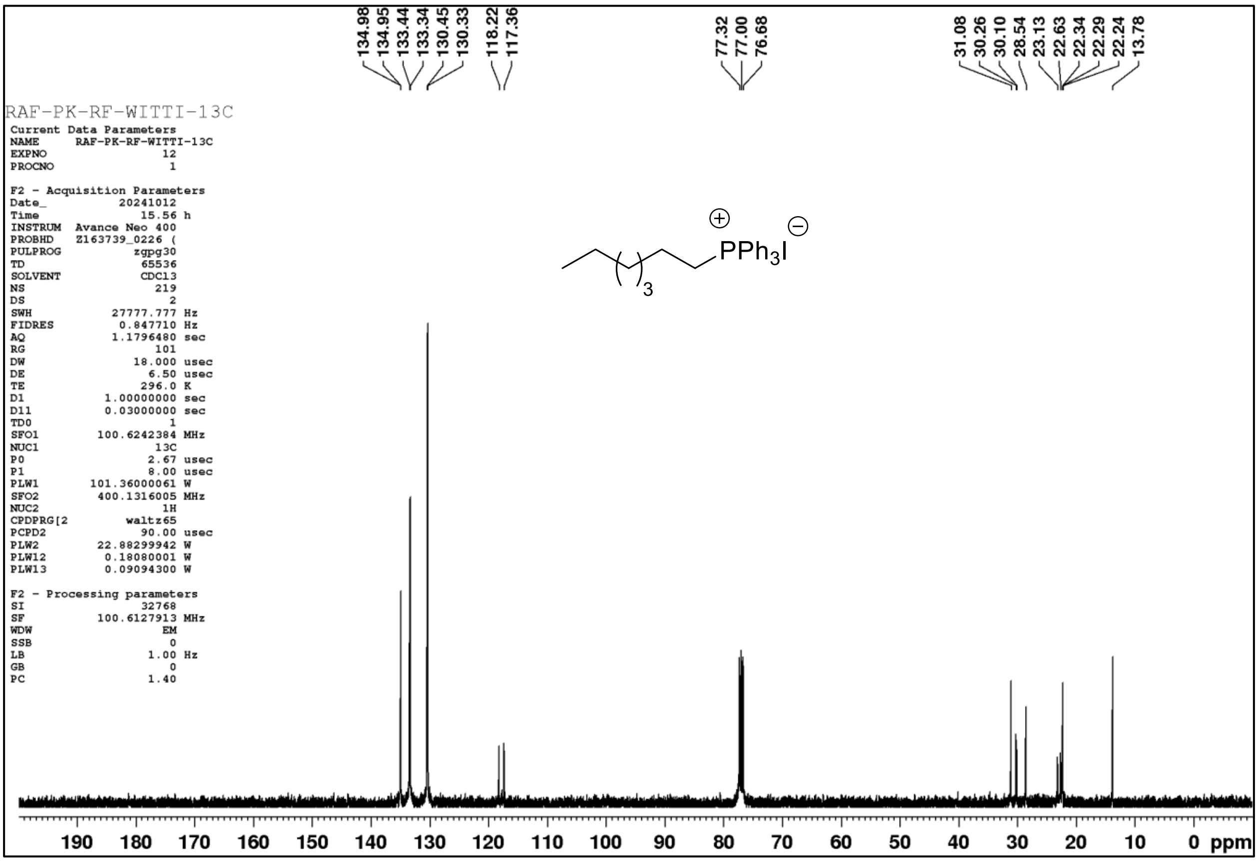
^{1}H NMR (400 MHz, $CDCl_3$), $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) and $^{31}P\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **26a**



```
RAF-PK-RF-WITTI-1H
Current Data Parameters
NAME     RAF-PK-RF-WITTI-1H
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_            20241012
Time                15.46 h
INSTRUM  Avance Neo 400
PROBHD   Z163739_0226 (
PULPROG              zg30
TD                  51724
SOLVENT             CDCl3
NS                     18
DS                      0
SWH              8620.689 Hz
FIDRES           0.333334 Hz
AQ              2.9999919 sec
RG                53.3333
DW                 58.000 usec
DE                  13.14 usec
TE                  295.6 K
D1             1.00000000 sec
TD0                     1
SFO1          400.1324708 MHz
NUC1                   1H
P0                   2.67 usec
P1                   8.00 usec
PLW1          22.88299942 W

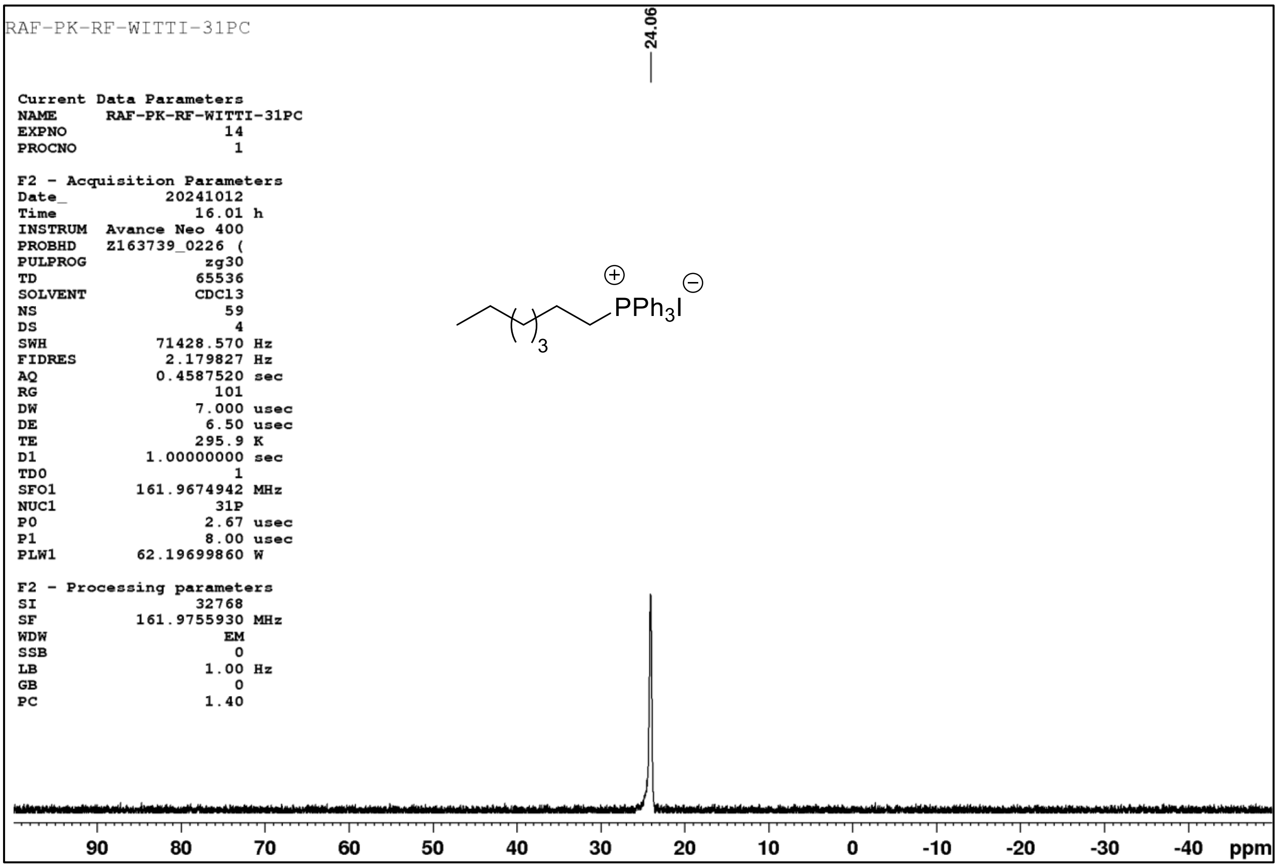
F2 - Processing parameters
SI                  65536
SF            400.1300112 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



```
RAF-PK-RF-WITTI-13C
Current Data Parameters
NAME     RAF-PK-RF-WITTI-13C
EXPNO                  12
PROCNO                  1

F2 - Acquisition Parameters
Date_            20241012
Time                15.56 h
INSTRUM  Avance Neo 400
PROBHD   Z163739_0226 (
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    219
DS                      2
SWH             27777.777 Hz
FIDRES           0.847710 Hz
AQ              1.1796480 sec
RG                    101
DW                 18.000 usec
DE                   6.50 usec
TE                  296.0 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                     1
SFO1          100.6242384 MHz
NUC1                  13C
P0                   2.67 usec
P1                   8.00 usec
PLW1         101.36000061 W
SFO2          400.1316005 MHz
NUC2                   1H
CPDPRG[2          waltz65
PCPD2               90.00 usec
PLW2          22.88299942 W
PLW12          0.18080001 W
PLW13          0.09094300 W

F2 - Processing parameters
SI                  32768
SF            100.6127913 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



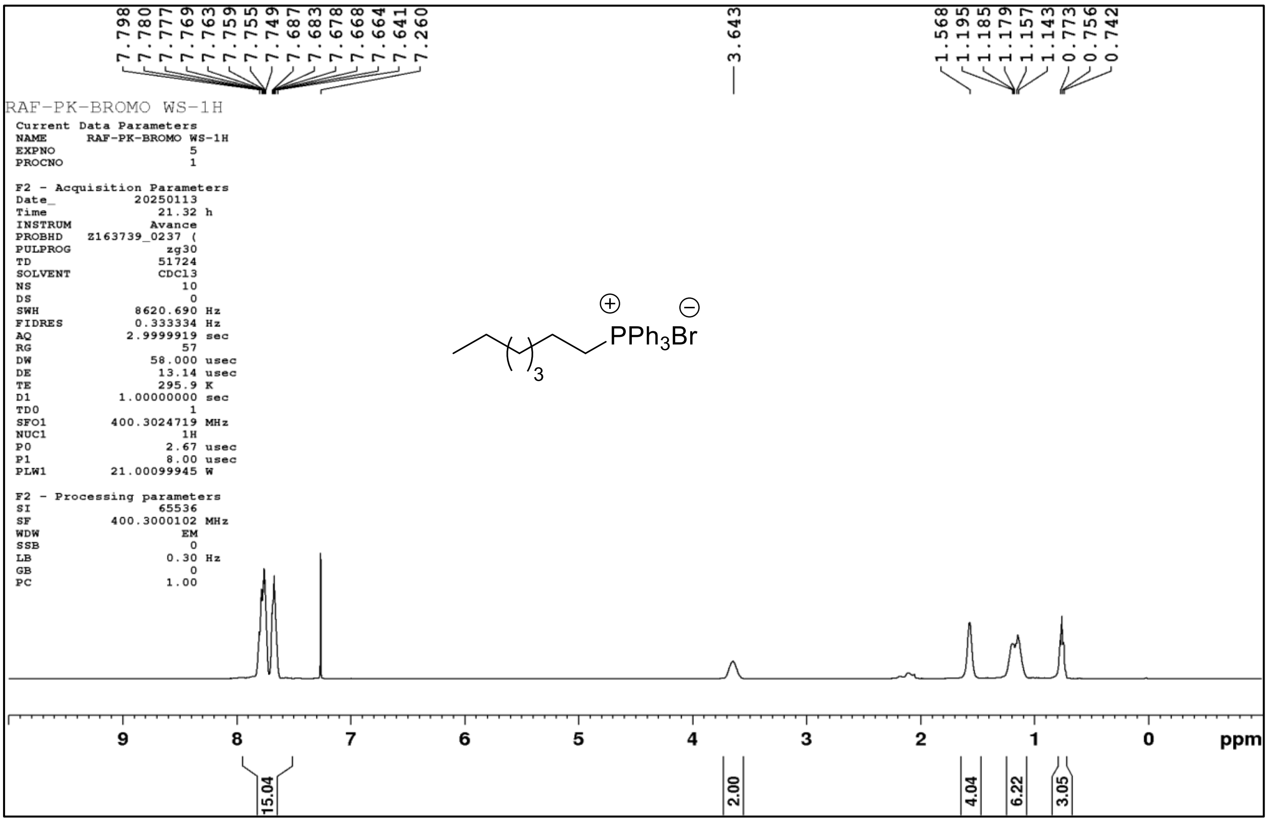
```
RAF-PK-RF-WITTI-31PC

Current Data Parameters
NAME      RAF-PK-RF-WITTI-31PC
EXPNO                   14
PROCNO                   1

F2 - Acquisition Parameters
Date_             20241012
Time                 16.01 h
INSTRUM  Avance Neo 400
PROBHD   Z163739_0226 (
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      59
DS                       4
SWH              71428.570 Hz
FIDRES            2.179827 Hz
AQ               0.4587520 sec
RG                     101
DW                   7.000 usec
DE                    6.50 usec
TE                   295.9 K
D1              1.00000000 sec
TD0                      1
SFO1           161.9674942 MHz
NUC1                   31P
P0                    2.67 usec
P1                    8.00 usec
PLW1           62.19699860 W

F2 - Processing parameters
SI                   32768
SF             161.9755930 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

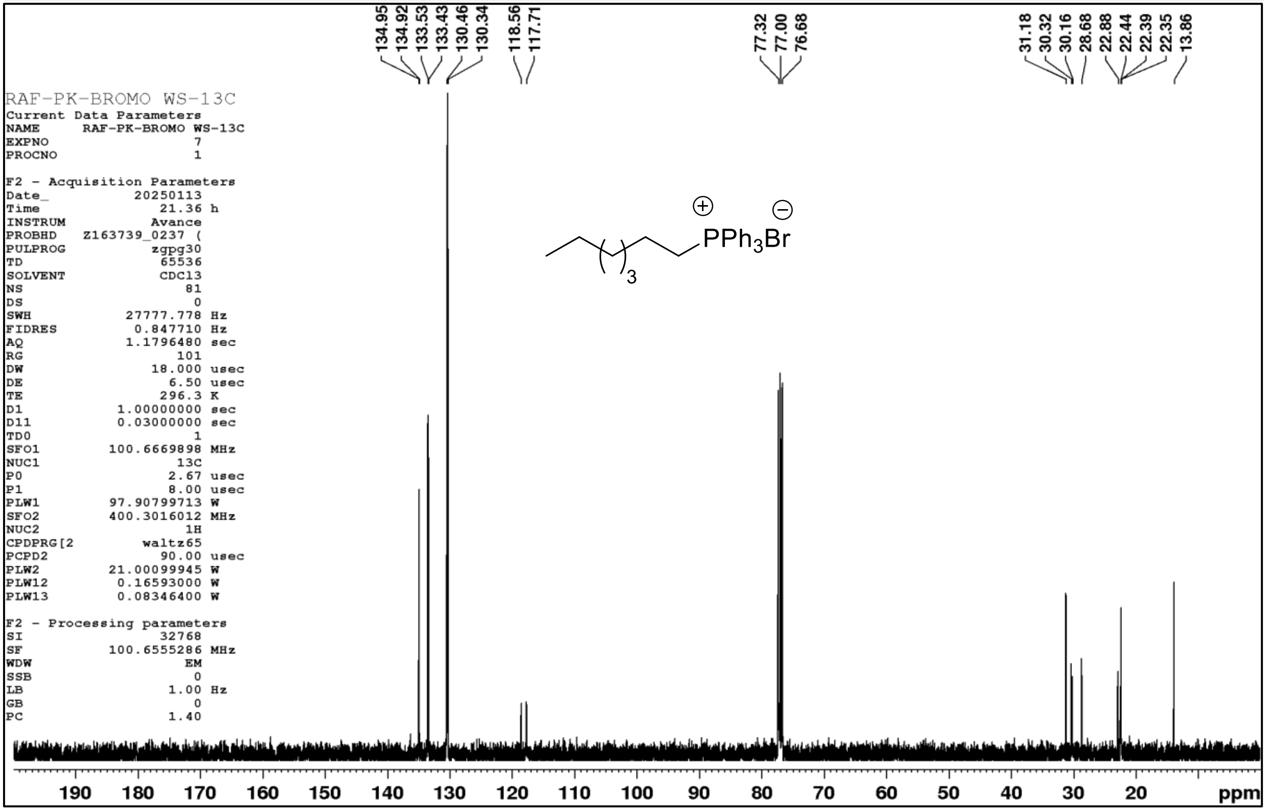
^{1}H NMR (400 MHz, CDCl$_3$), ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) and ^{31}P{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **26b**



```
Current Data Parameters
NAME     RAF-PK-BROMO WS-1H
EXPNO                    5
PROCNO                   1

F2 - Acquisition Parameters
Date_             20250113
Time                 21.32 h
INSTRUM             Avance
PROBHD   Z163739_0237 (
PULPROG               zg30
TD                   51724
SOLVENT              CDCl3
NS                      10
DS                       0
SWH               8620.690 Hz
FIDRES            0.333334 Hz
AQ               2.9999919 sec
RG                      57
DW                  58.000 usec
DE                   13.14 usec
TE                   295.9 K
D1              1.00000000 sec
TD0                      1
SFO1           400.3024719 MHz
NUC1                    1H
P0                    2.67 usec
P1                    8.00 usec
PLW1           21.00099945 W

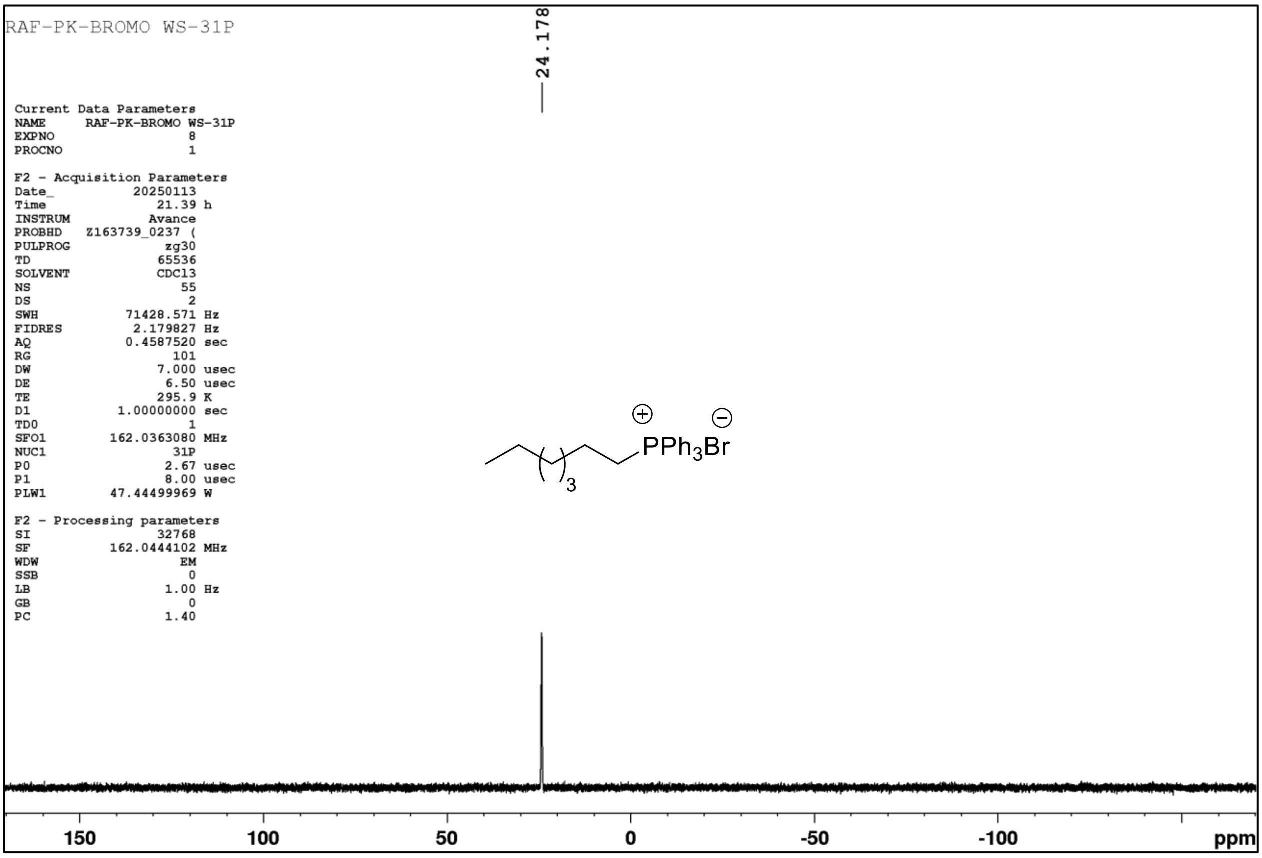
F2 - Processing parameters
SI                   65536
SF             400.3000102 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



```
Current Data Parameters
NAME     RAF-PK-BROMO WS-13C
EXPNO                    7
PROCNO                   1

F2 - Acquisition Parameters
Date_             20250113
Time                 21.36 h
INSTRUM             Avance
PROBHD   Z163739_0237 (
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      81
DS                       0
SWH              27777.778 Hz
FIDRES            0.847710 Hz
AQ               1.1796480 sec
RG                     101
DW                  18.000 usec
DE                    6.50 usec
TE                   296.3 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           97.90799713 W
SFO2           400.3016012 MHz
NUC2                    1H
CPDPRG[2           waltz65
PCPD2                90.00 usec
PLW2           21.00099945 W
PLW12           0.16593000 W
PLW13           0.08346400 W

F2 - Processing parameters
SI                   32768
SF             100.6555286 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

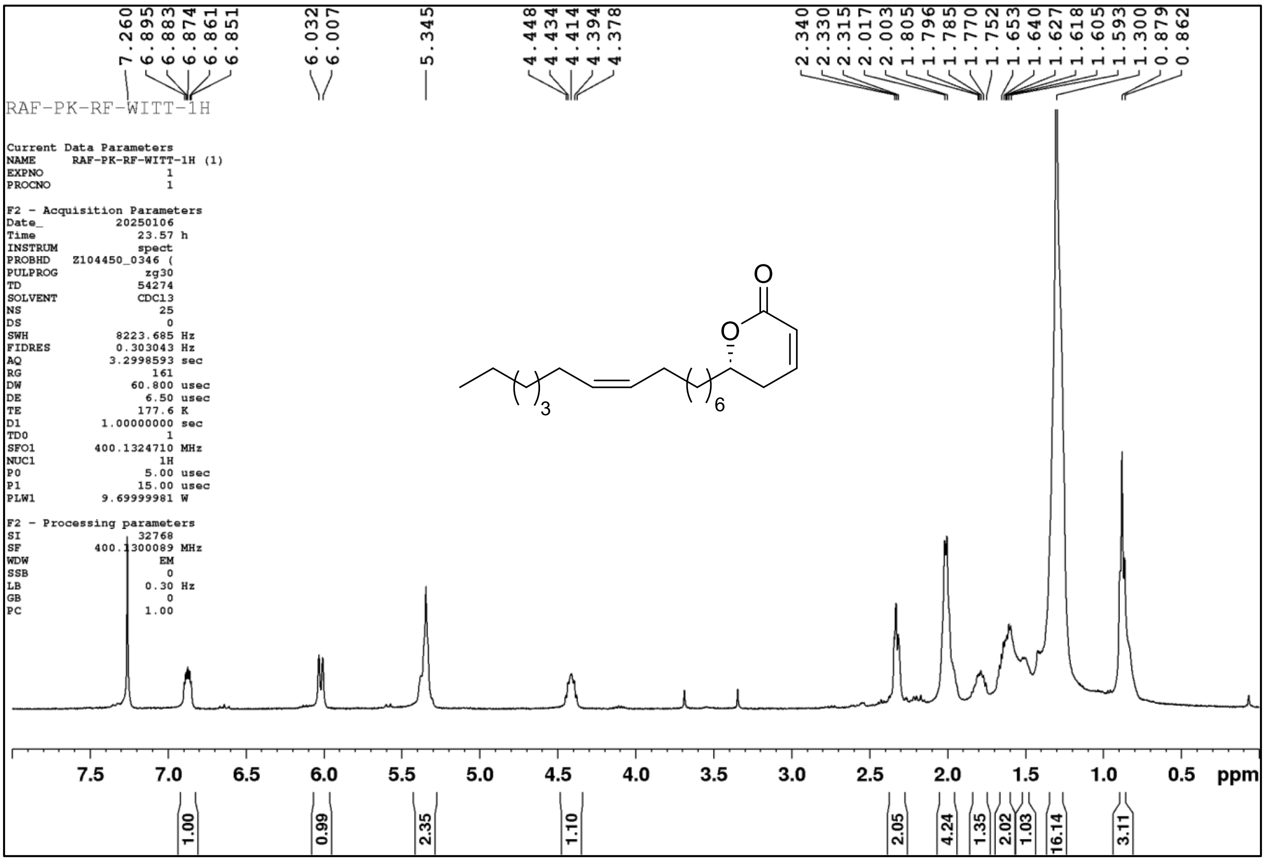


```
Current Data Parameters
NAME       RAF-PK-BROMO WS-31P
EXPNO                     8
PROCNO                    1

F2 - Acquisition Parameters
Date_              20250113
Time                  21.39 h
INSTRUM              Avance
PROBHD    Z163739_0237 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       55
DS                        2
SWH               71428.571 Hz
FIDRES             2.179827 Hz
AQ                0.4587520 sec
RG                      101
DW                    7.000 usec
DE                     6.50 usec
TE                    295.9 K
D1               1.00000000 sec
TD0                       1
SFO1            162.0363080 MHz
NUC1                    31P
P0                     2.67 usec
P1                     8.00 usec
PLW1            47.44499969 W

F2 - Processing parameters
SI                    32768
SF              162.0444102 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

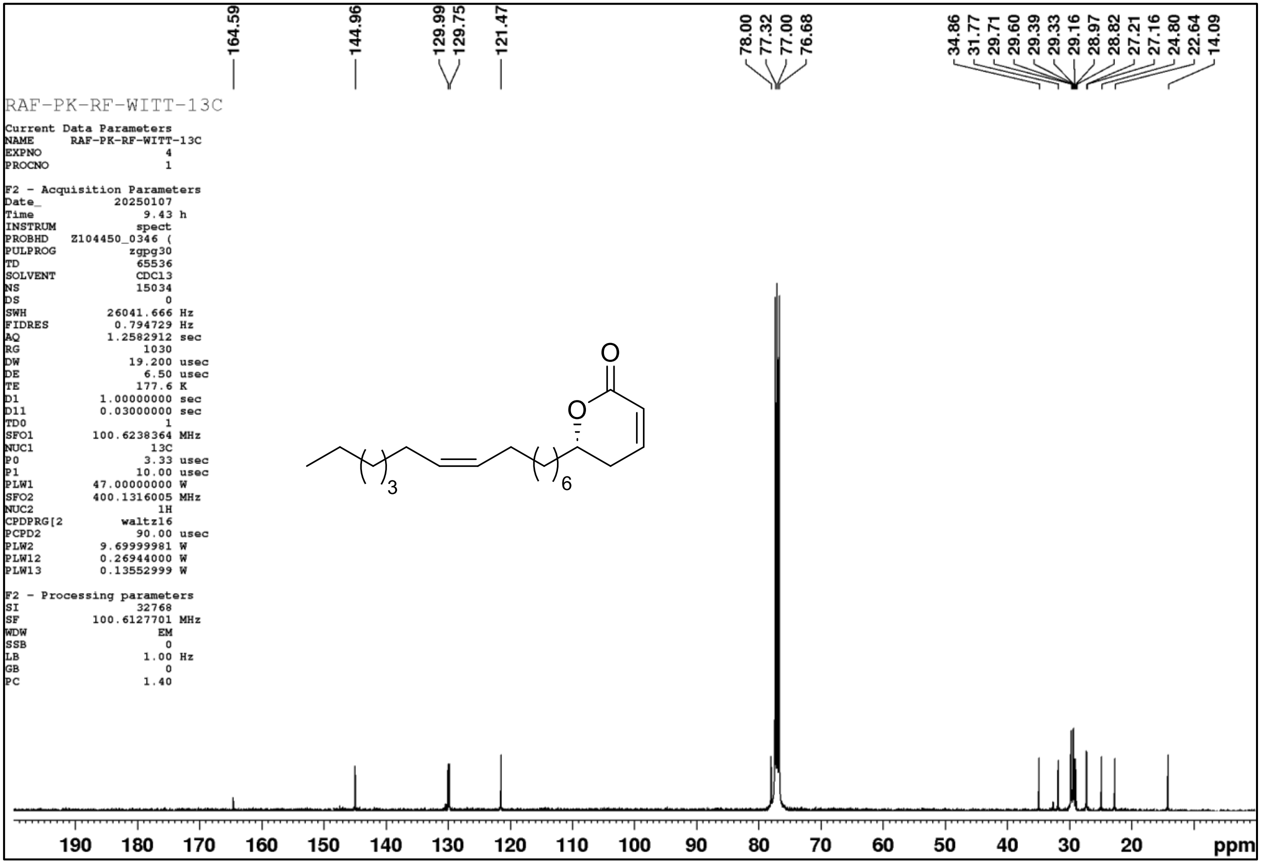
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **1a**



```
Current Data Parameters
NAME     RAF-PK-RF-WITT-1H (1)
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_         20250106
Time             23.57 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                 161
DW              60.800 usec
DE                6.50 usec
TE               177.6 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         400.1300089 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```

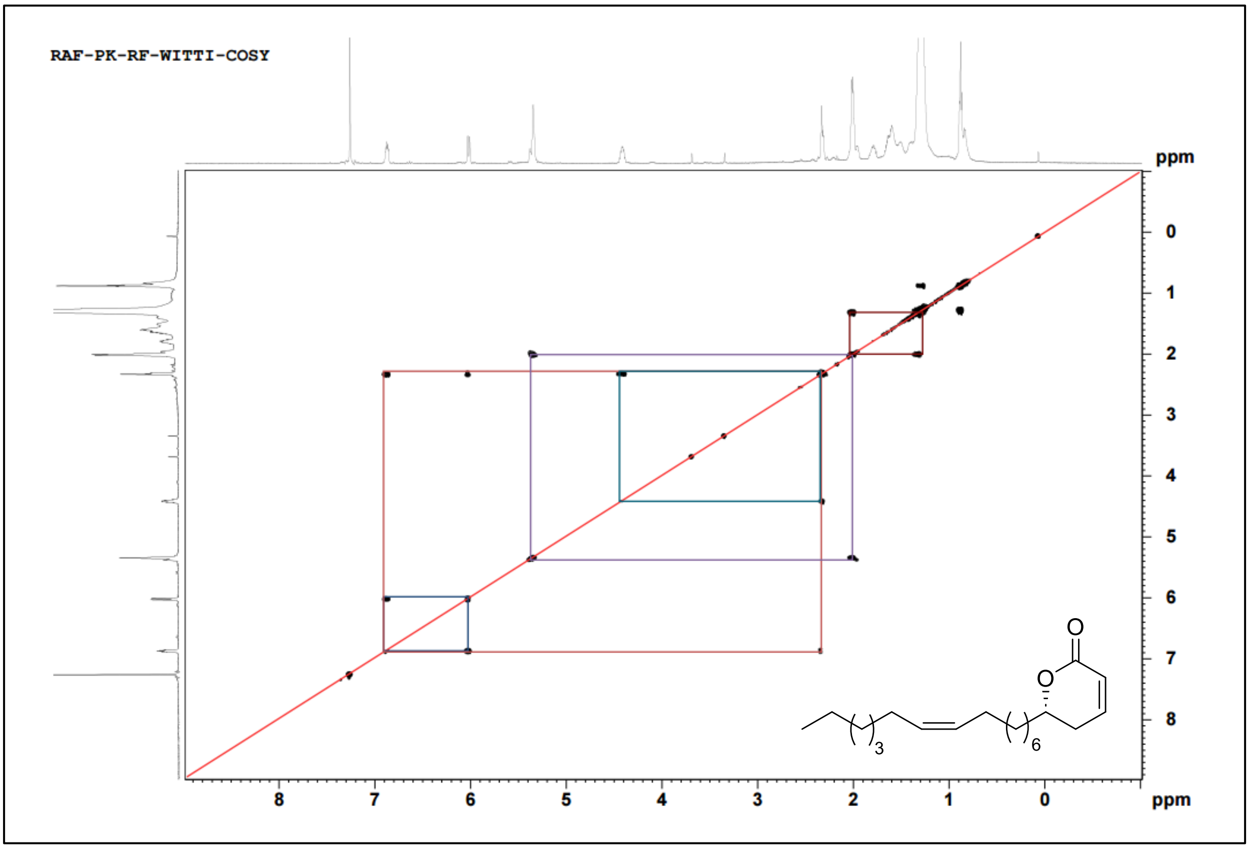


```
Current Data Parameters
NAME     RAF-PK-RF-WITT-13C
EXPNO              4
PROCNO             1

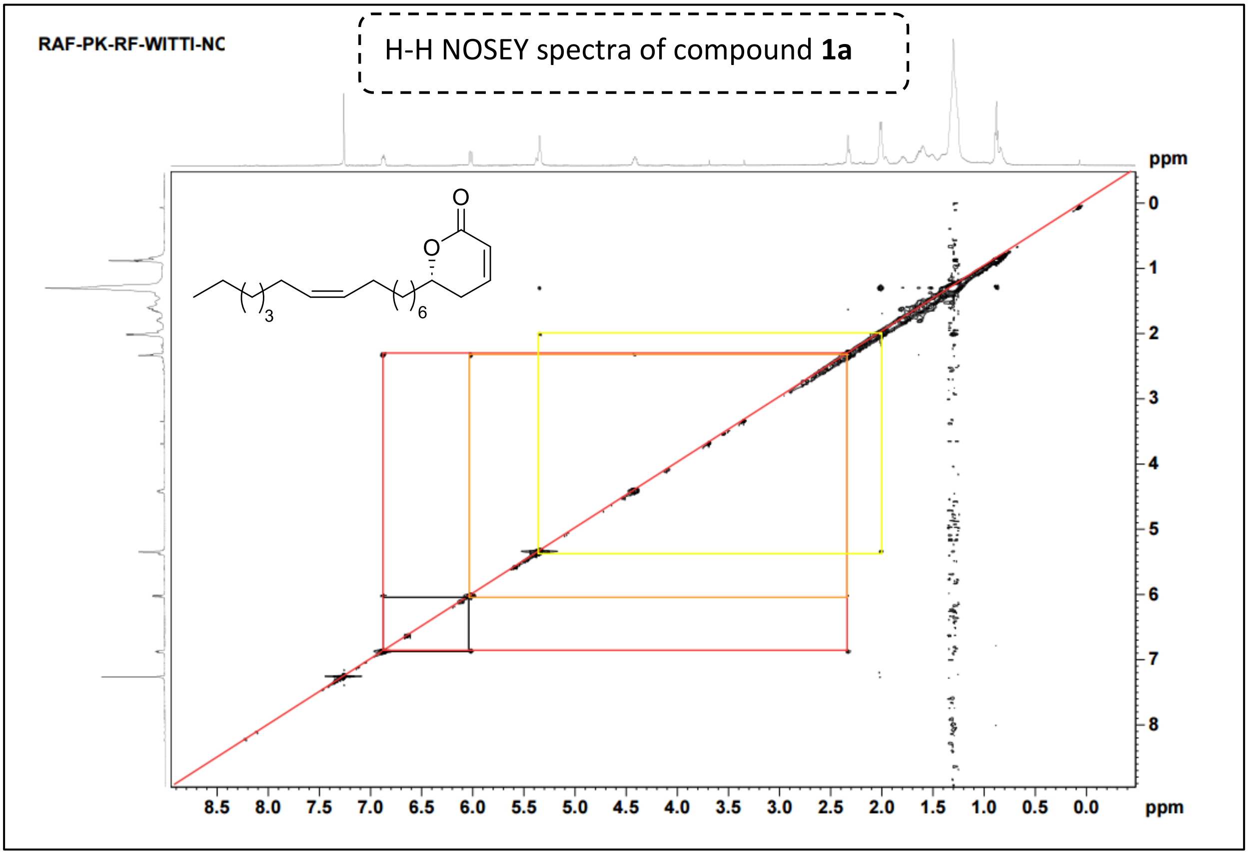
F2 - Acquisition Parameters
Date_         20250107
Time              9.43 h
INSTRUM          spect
PROBHD   Z104450_0346 (
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS               15034
DS                   0
SWH          26041.666 Hz
FIDRES        0.794729 Hz
AQ           1.2582912 sec
RG                1030
DW              19.200 usec
DE                6.50 usec
TE               177.6 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         100.6127701 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

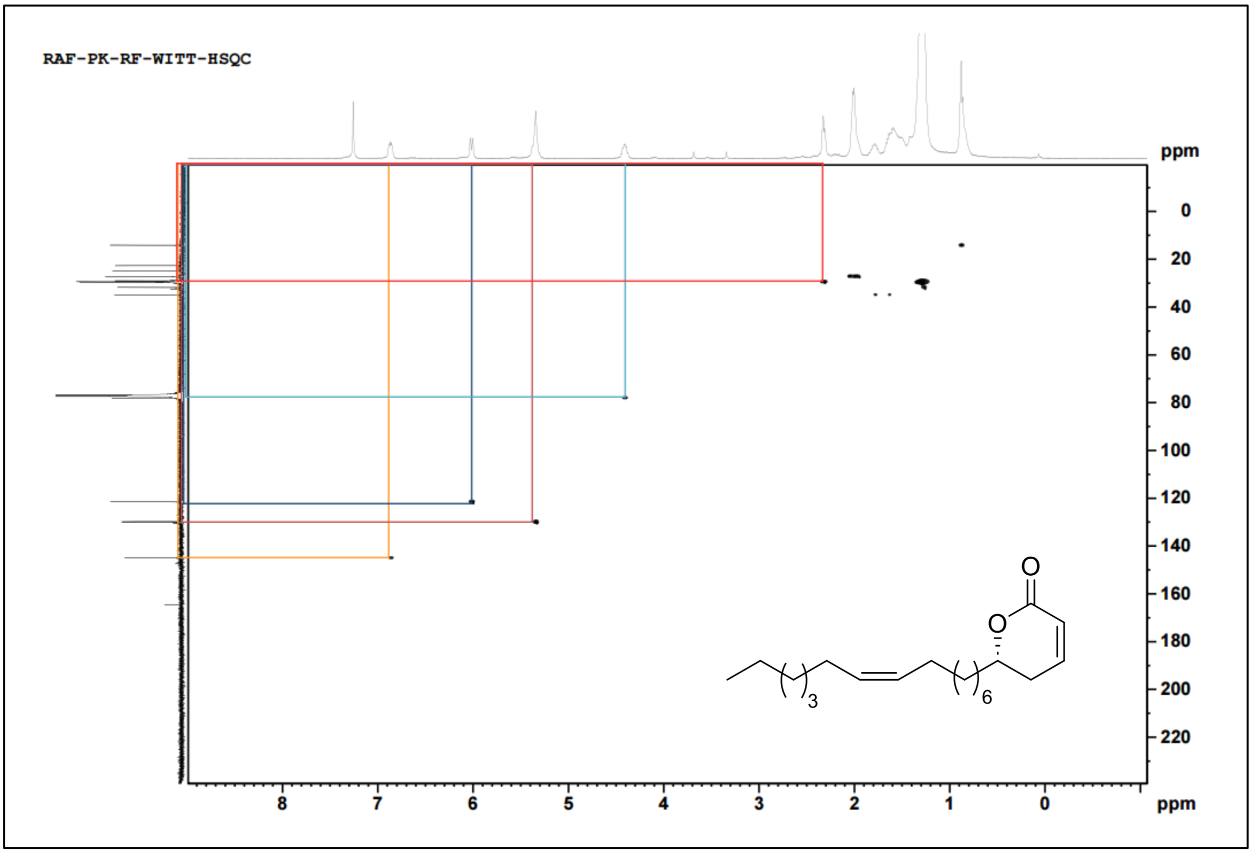
H-H COSY spectra of compound **1a**



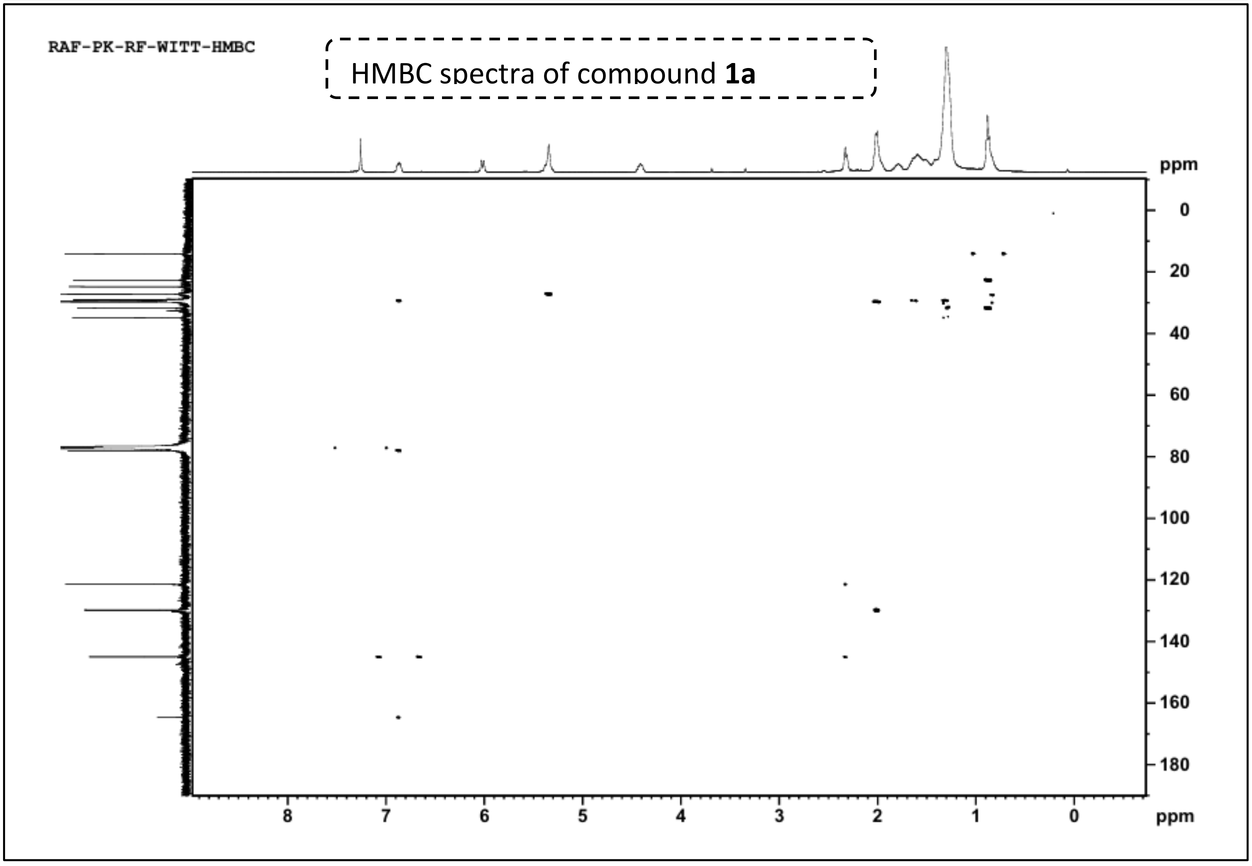
H-H NOSEY spectra of compound **1a**



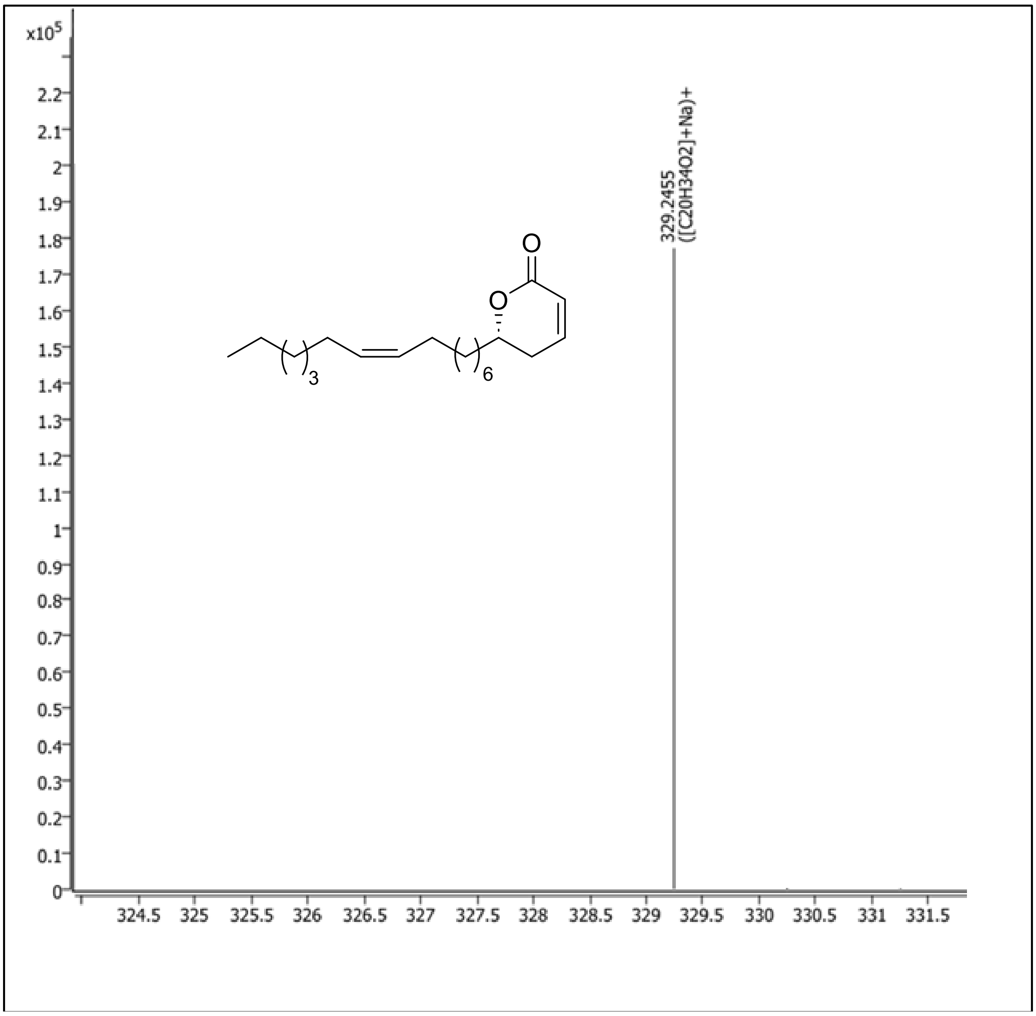
HSQC spectra of compound **1a**



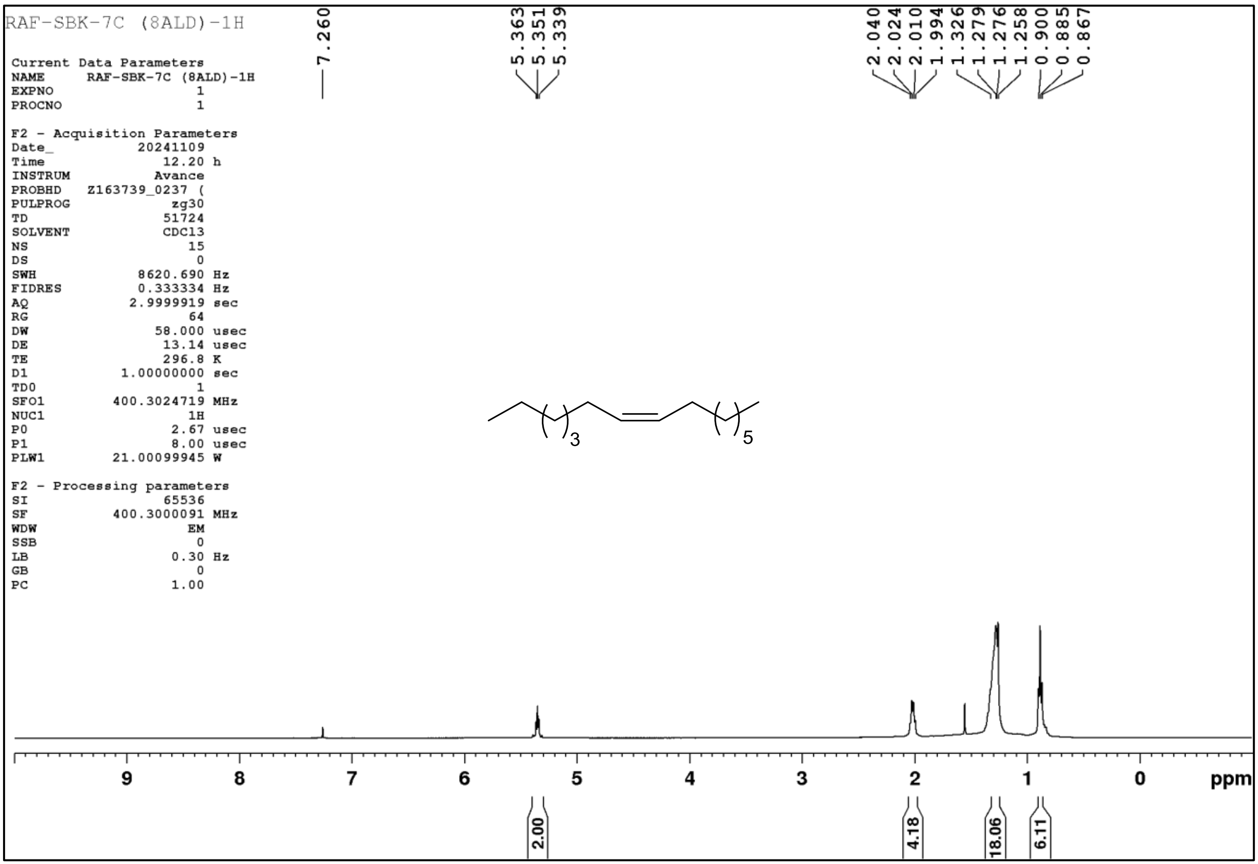
HMBC spectra of compound **1a**



1a: HRMS (ESI–TOF) *m/z:* $[M + Na]^+$ Calcd for $C_{20}H_{34}O_2Na$ 329.2451; Found 329.2455



^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **28**



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Current Data Parameters
NAME      RAF-SBK-7C (8ALD)-1H
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20241109
Time                 12.20 h
INSTRUM             Avance
PROBHD    Z163739_0237 (
PULPROG               zg30
TD                   51724
SOLVENT              CDCl3
NS                      15
DS                       0
SWH               8620.690 Hz
FIDRES            0.333334 Hz
AQ               2.9999919 sec
RG                      64
DW                  58.000 usec
DE                   13.14 usec
TE                   296.8 K
D1              1.00000000 sec
TD0                      1
SFO1           400.3024719 MHz
NUC1                    1H
P0                    2.67 usec
P1                    8.00 usec
PLW1           21.00099945 W

F2 - Processing parameters
SI                   65536
SF             400.3000091 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
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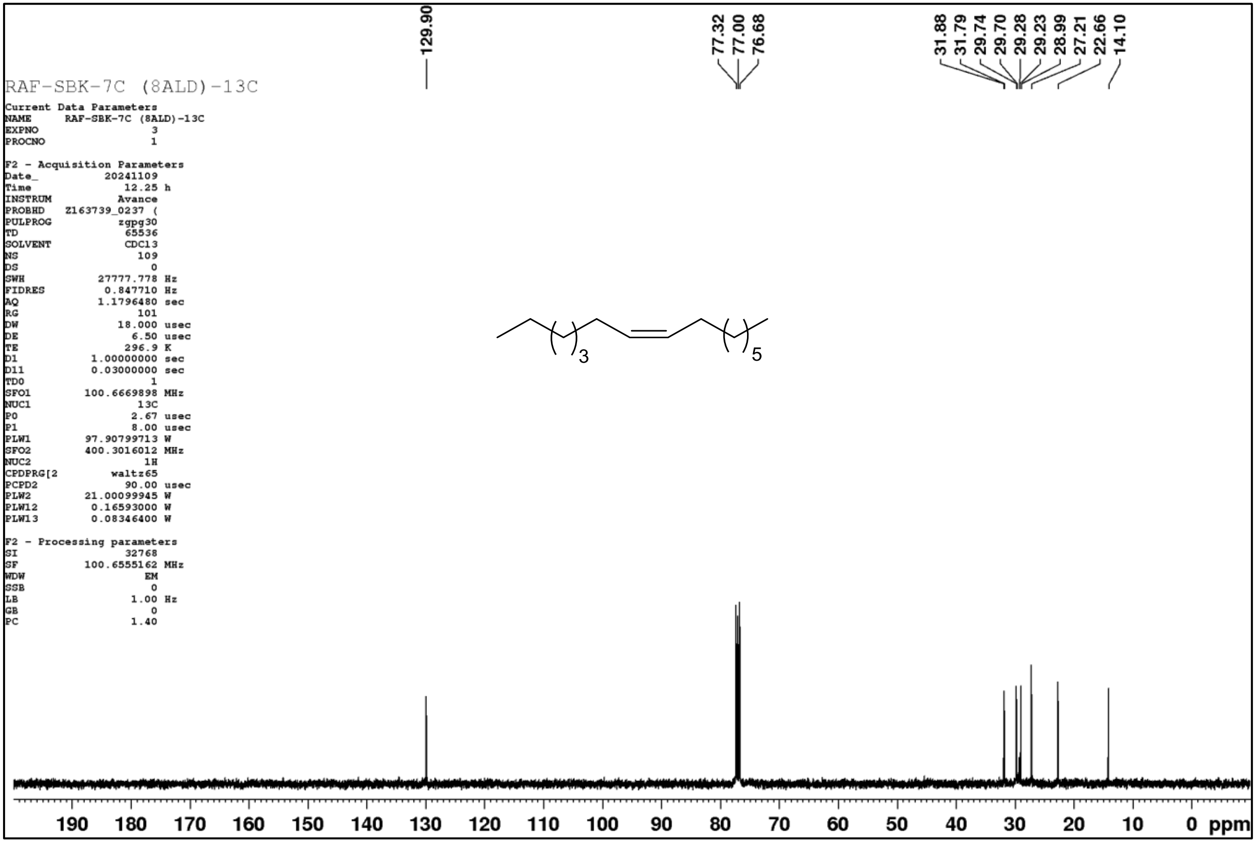

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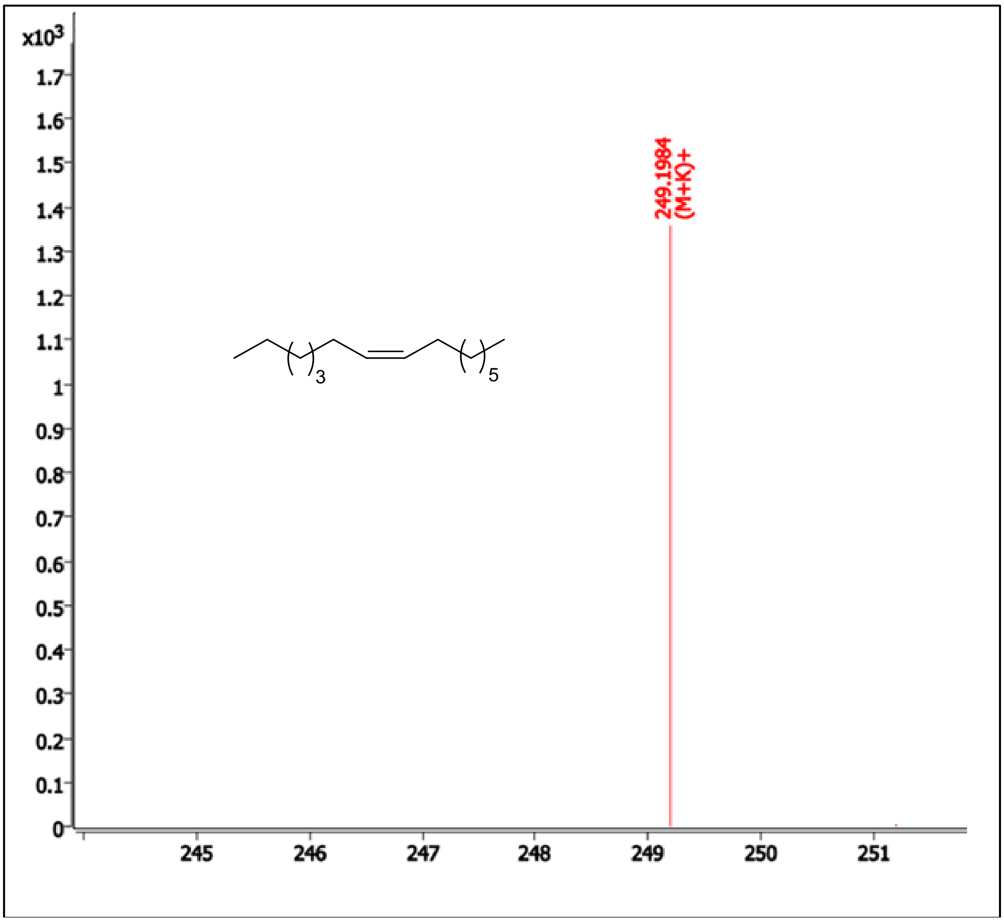
Current Data Parameters
NAME      RAF-SBK-7C (8ALD)-13C
EXPNO                    3
PROCNO                   1

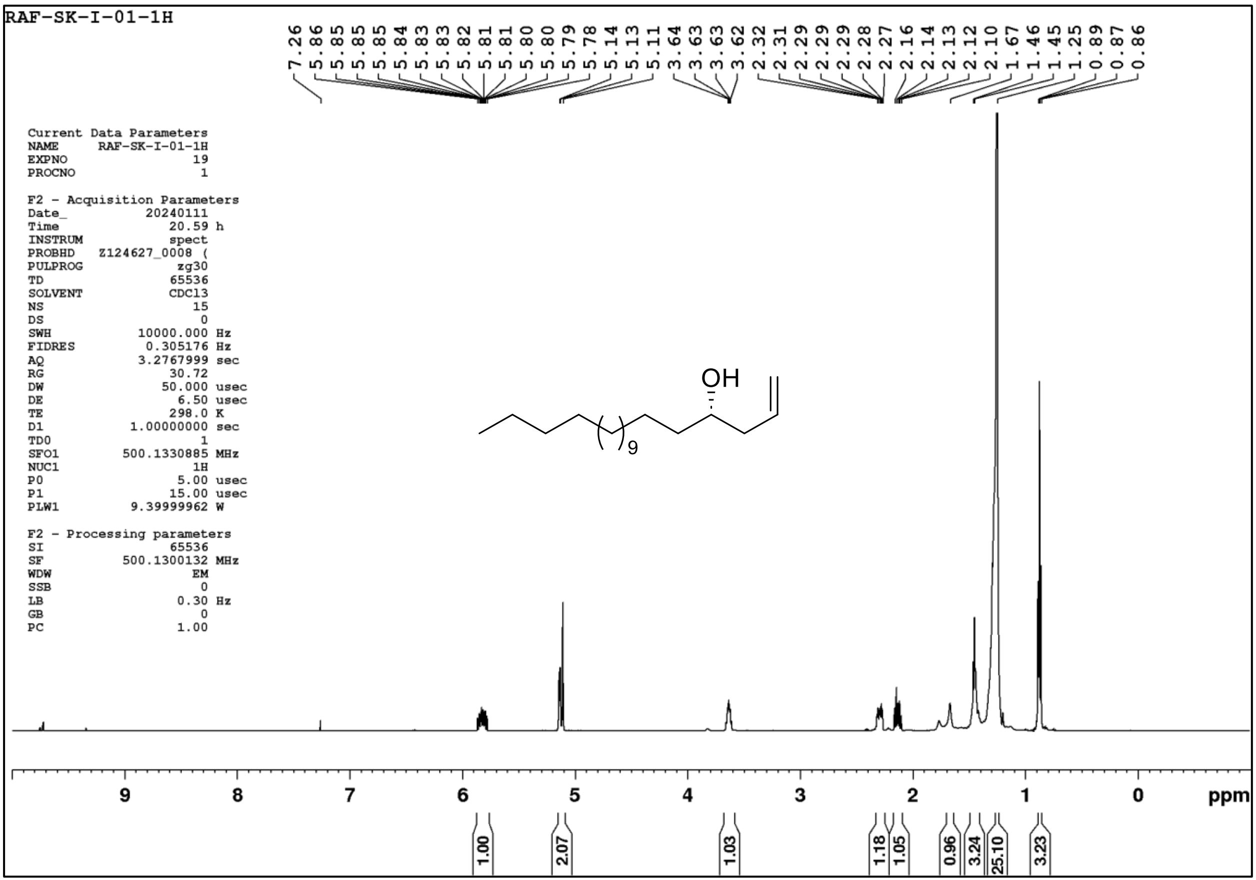
F2 - Acquisition Parameters
Date_             20241109
Time                 12.25 h
INSTRUM             Avance
PROBHD    Z163739_0237 (
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     109
DS                       0
SWH              27777.778 Hz
FIDRES            0.847710 Hz
AQ               1.1796480 sec
RG                     101
DW                  18.000 usec
DE                    6.50 usec
TE                   296.9 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           97.90799713 W
SFO2           400.3016012 MHz
NUC2                    1H
CPDPRG[2           waltz65
PCPD2                90.00 usec
PLW2           21.00099945 W
PLW12           0.16593000 W
PLW13           0.08346400 W

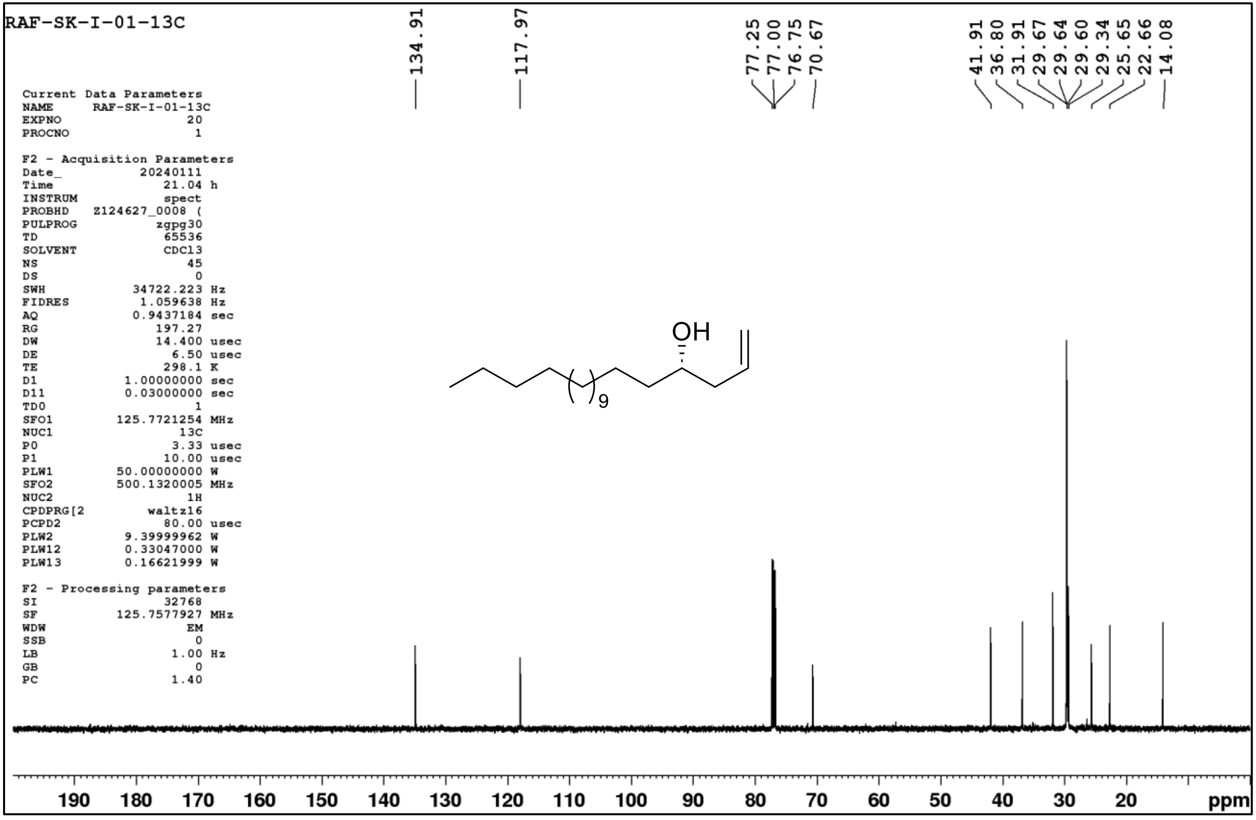
F2 - Processing parameters
SI                   32768
SF             100.6555162 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

28: HRMS (ESI–TOF) *m/z:* [M + K]$^+$ Calcd for $C_{15}H_{30}K$ 249.1979; Found 249.1984

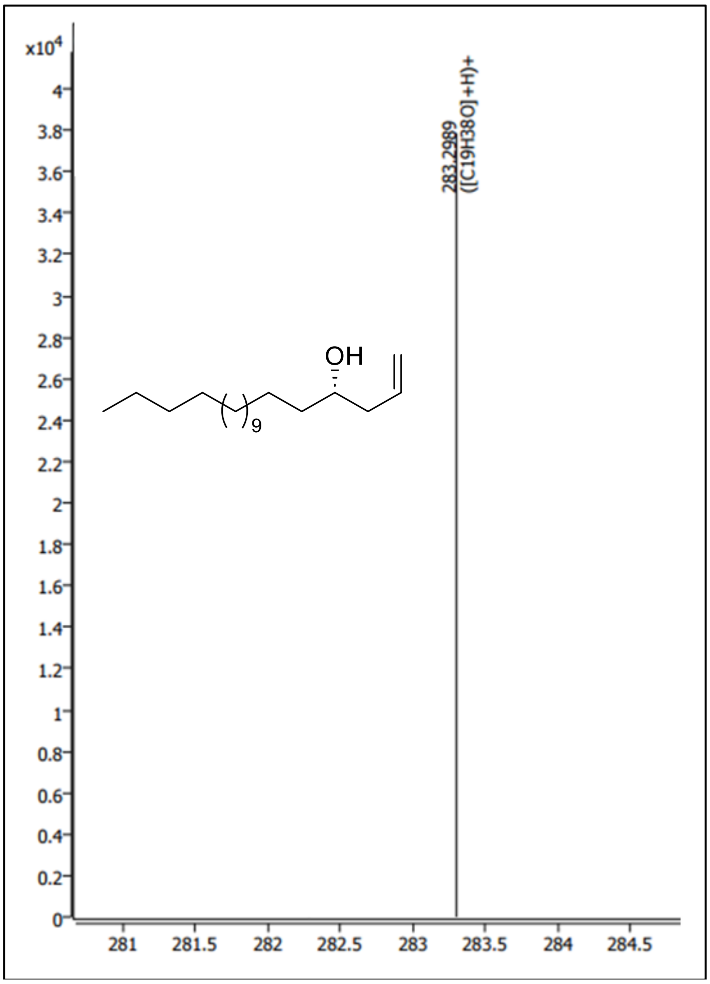


^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) of compound **2b**

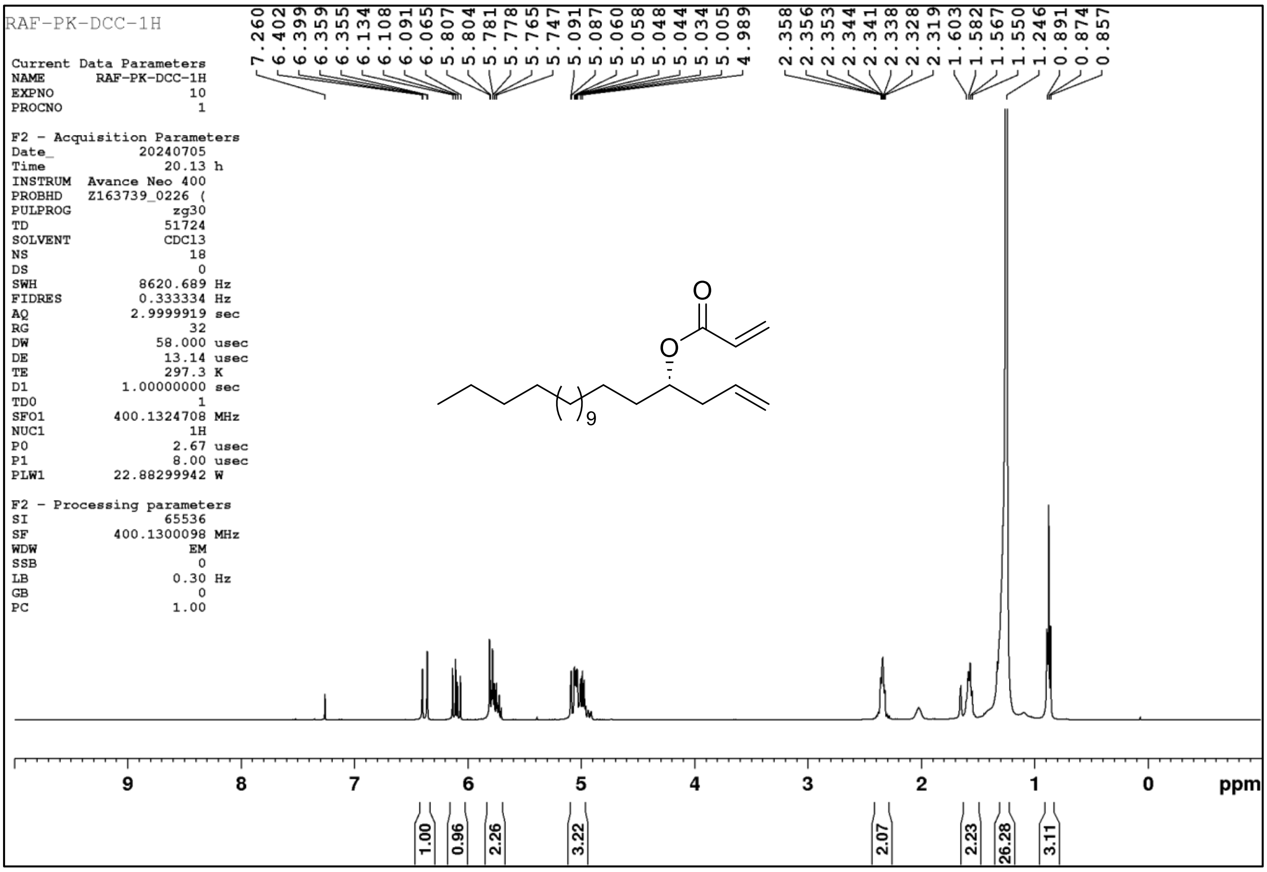


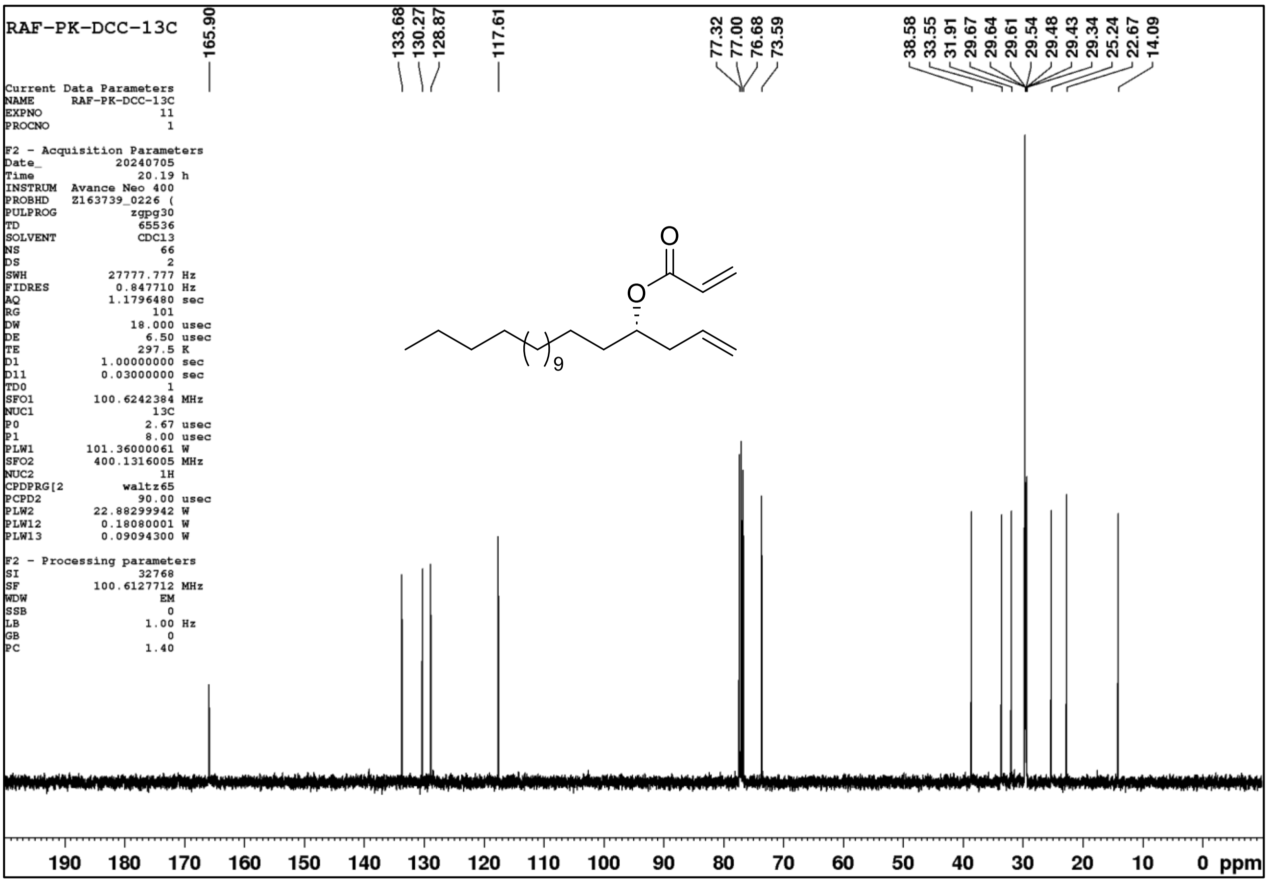


2b: HRMS (ESI–TOF) *m/z:* $[M + H]^+$ Calcd for $C_{19}H_{39}O$, 283.2995; Found 283.2989

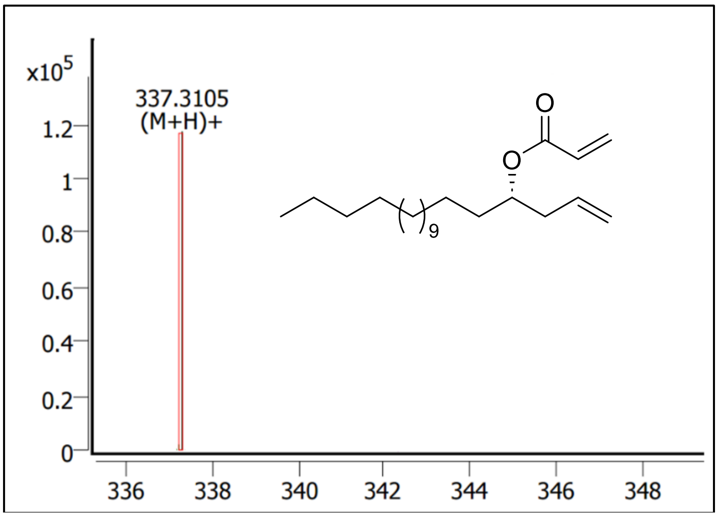


^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **30**

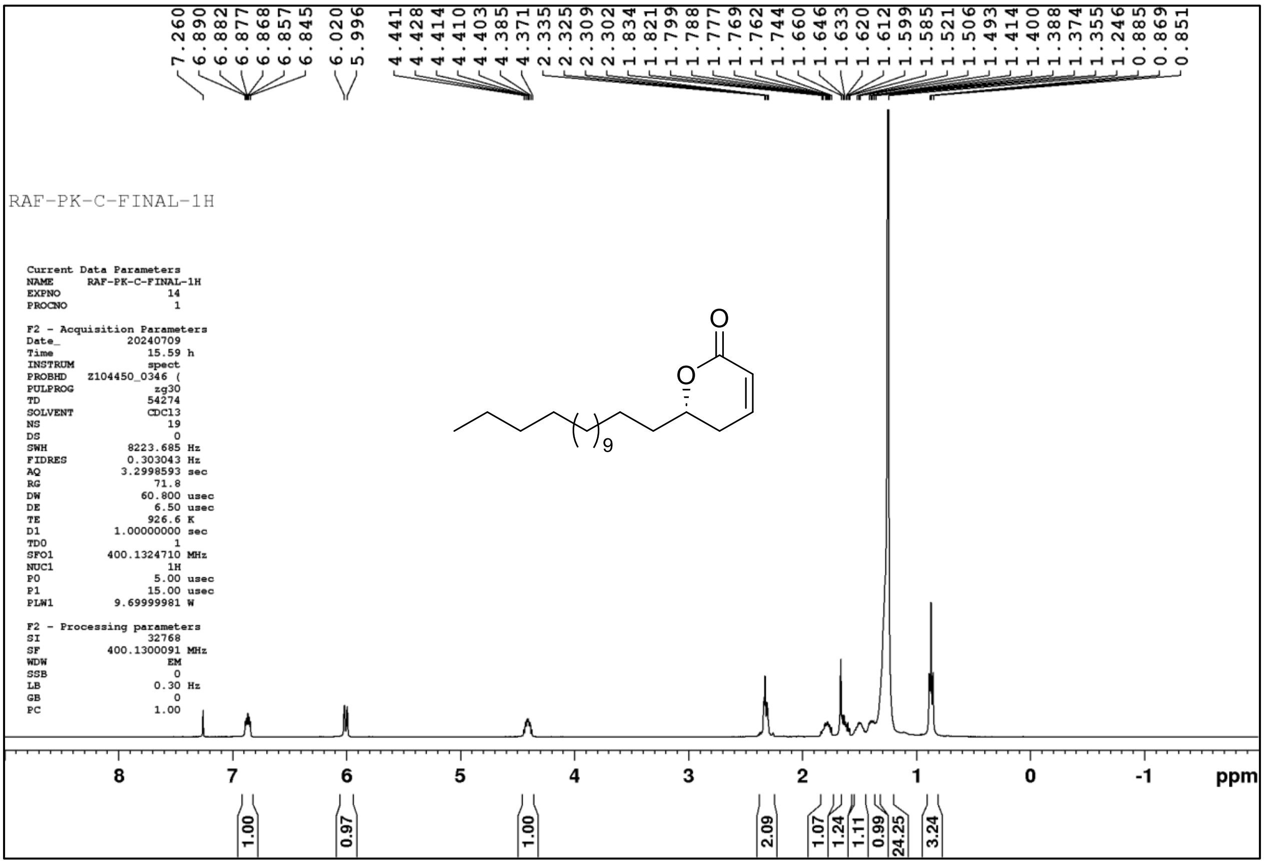


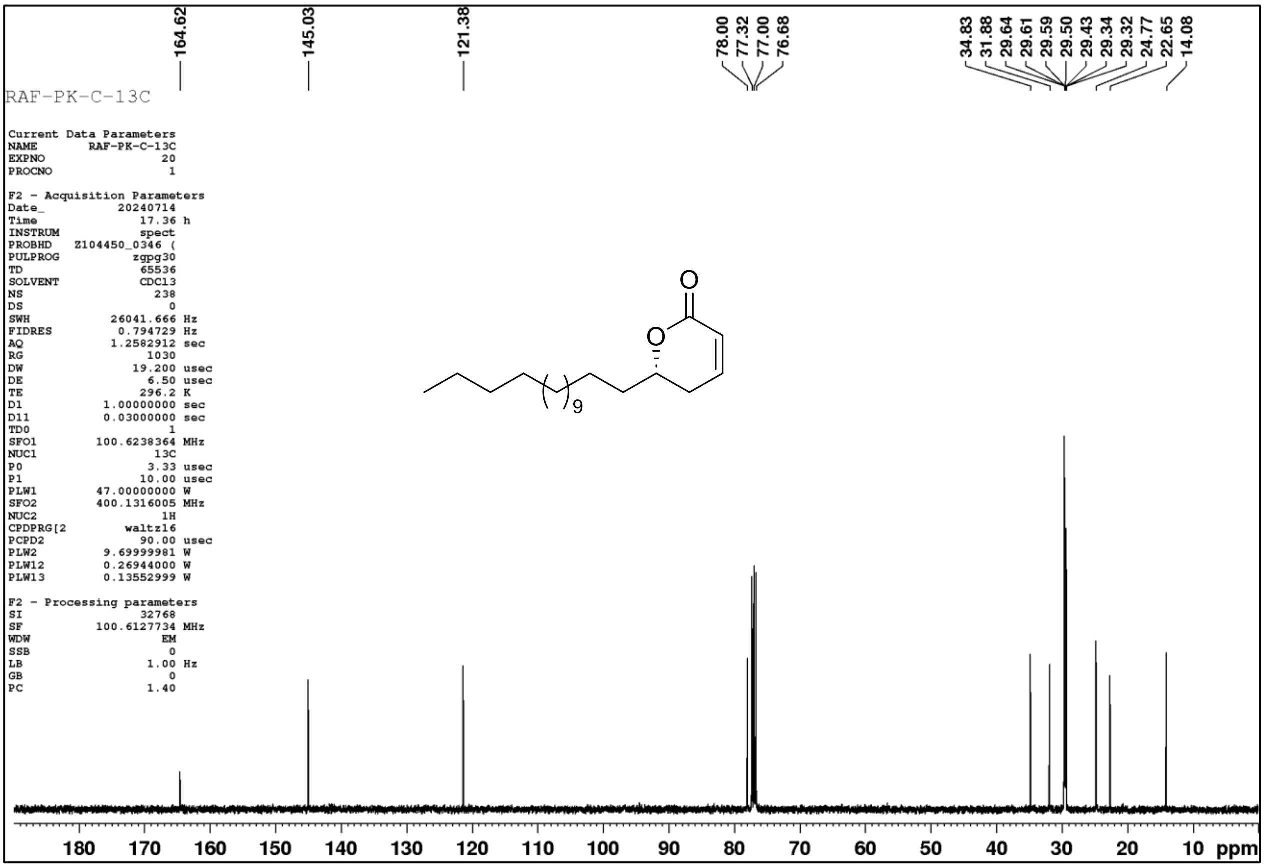


30: HRMS (ESI–TOF) *m/z:* [M + H]$^+$ Calcd for $C_{22}H_{41}O_2$, 337.3102; Found 337.3105

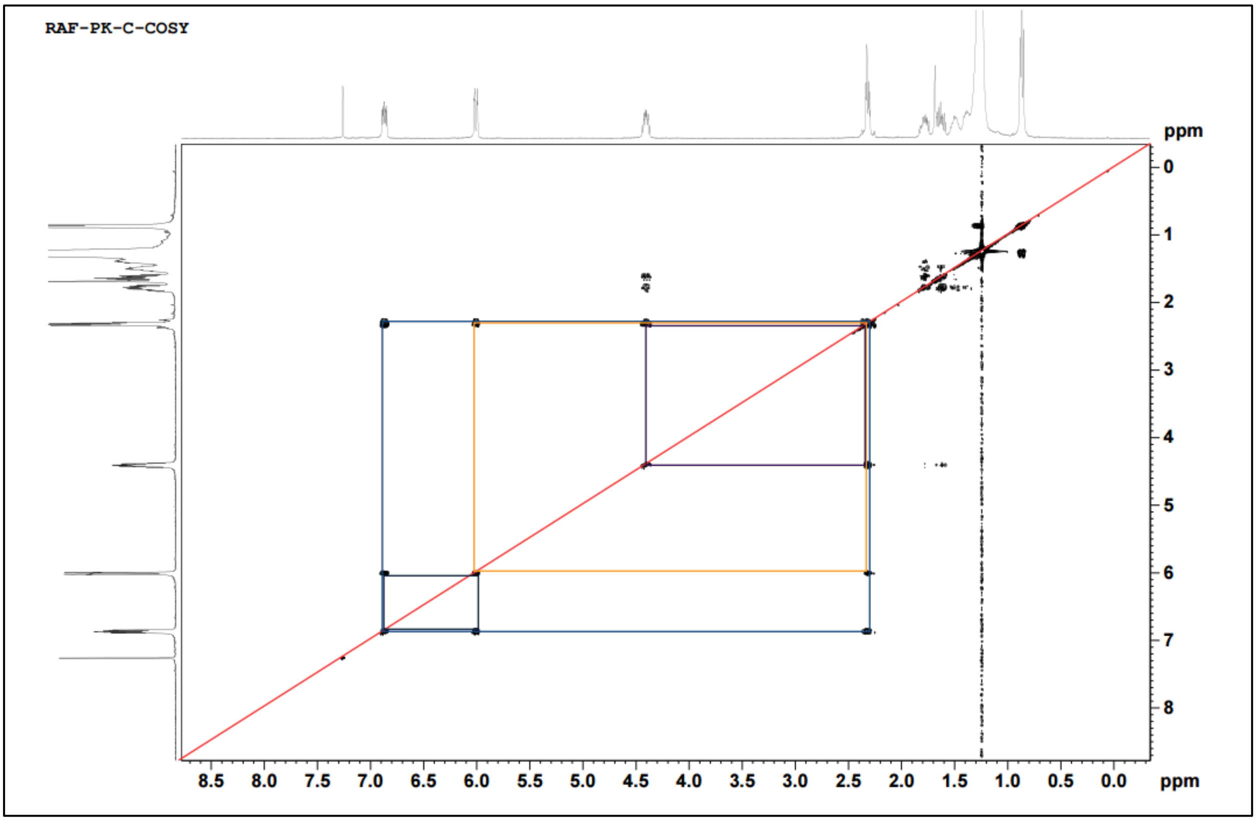


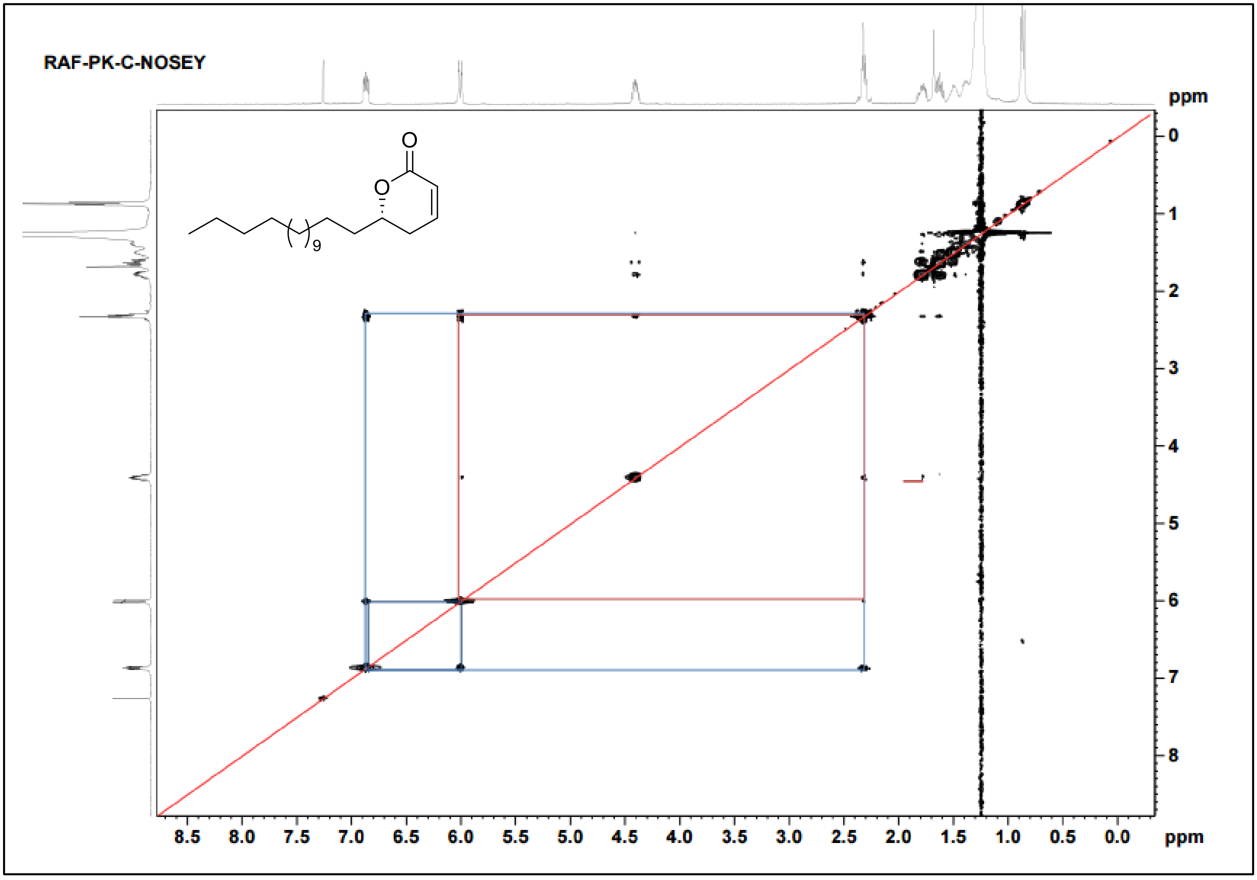
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **1c**





H-H COSY spectra of compound **1c**


RAF-PK-C-COSY
ppm
0
1
2
3
4
5
6
7
8
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


RAF-PK-C-NOSEY
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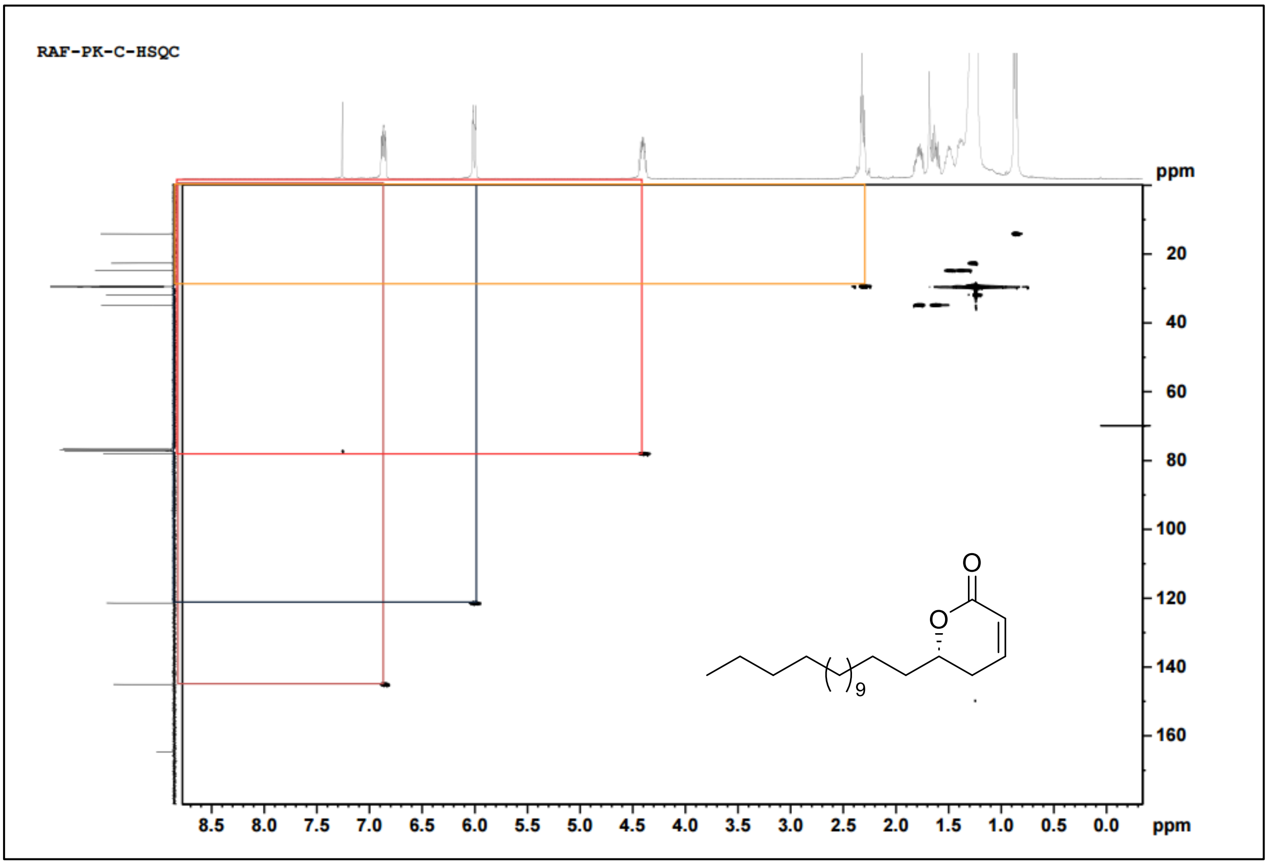
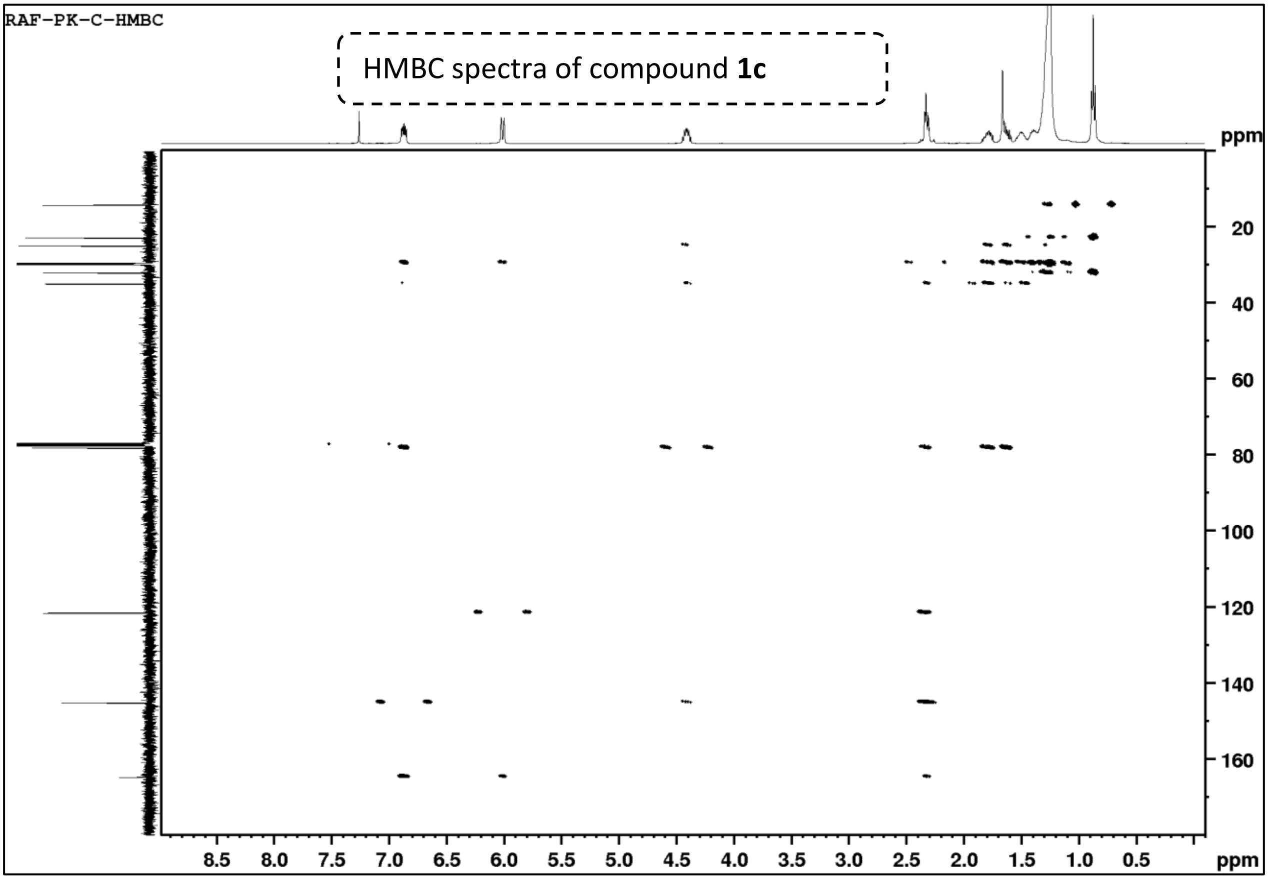
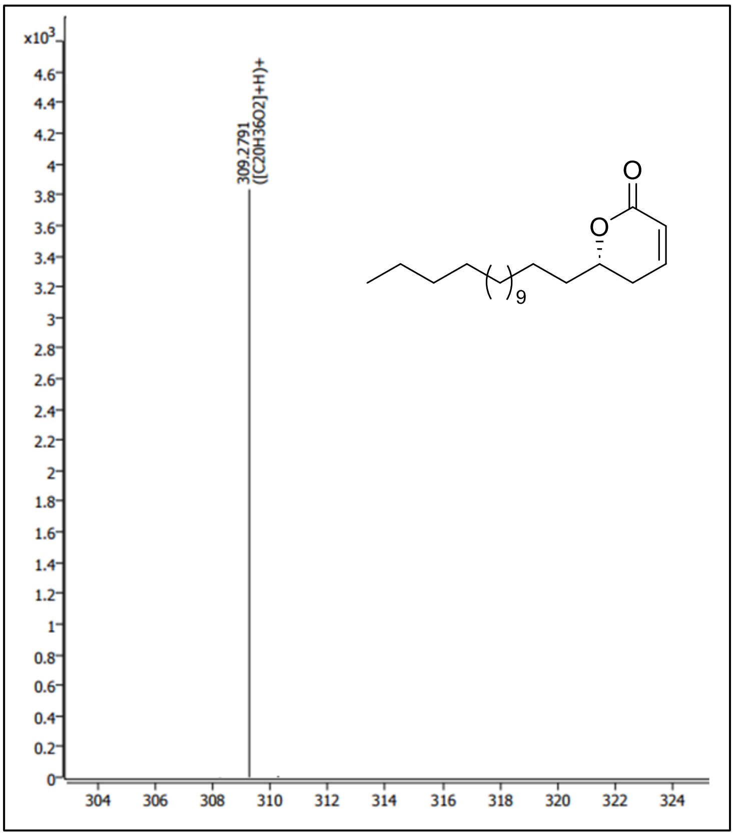
O
9
ppm
0
1
2
3
4
5
6
7
8
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

HSQC spectra of compound **1c**

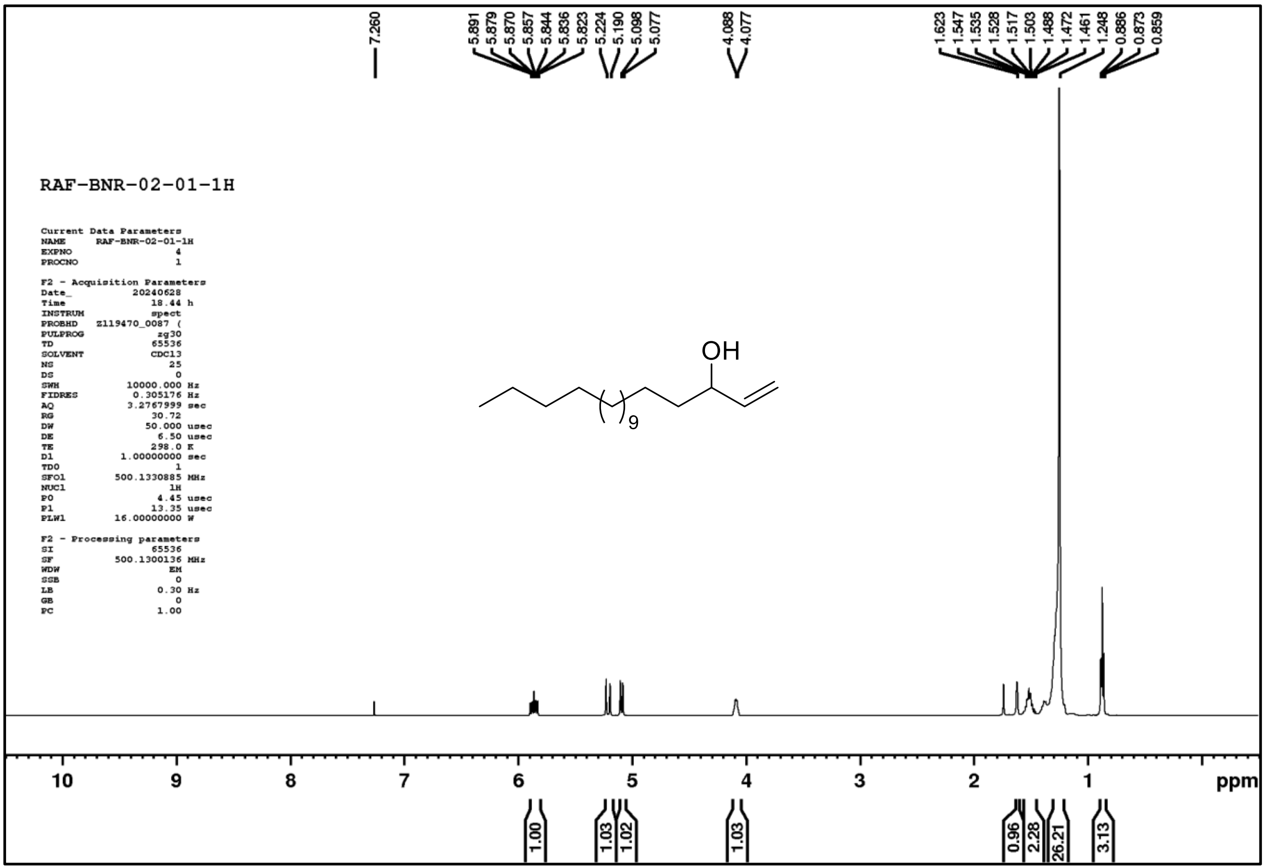



HMBC spectra of compound **1c**

1c: HRMS (ESI–TOF) *m/z:* [M + H]$^+$ Calcd for $C_{20}H_{37}O_2$, 309.2789; Found 309.2791



^1H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) of compound **33**



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Current Data Parameters
NAME      RAF-BNR-02-01-1H
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_             20240628
Time                 18.44 h
INSTRUM              spect
PROBHD    Z119470_0087 (
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      25
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                   298.0 K
D1              1.00000000 sec
TD0                      1
SFO1           500.1330885 MHz
NUC1                    1H
P0                    4.45 usec
P1                   13.35 usec
PLW1           16.00000000 W

F2 - Processing parameters
SI                   65536
SF             500.1300136 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
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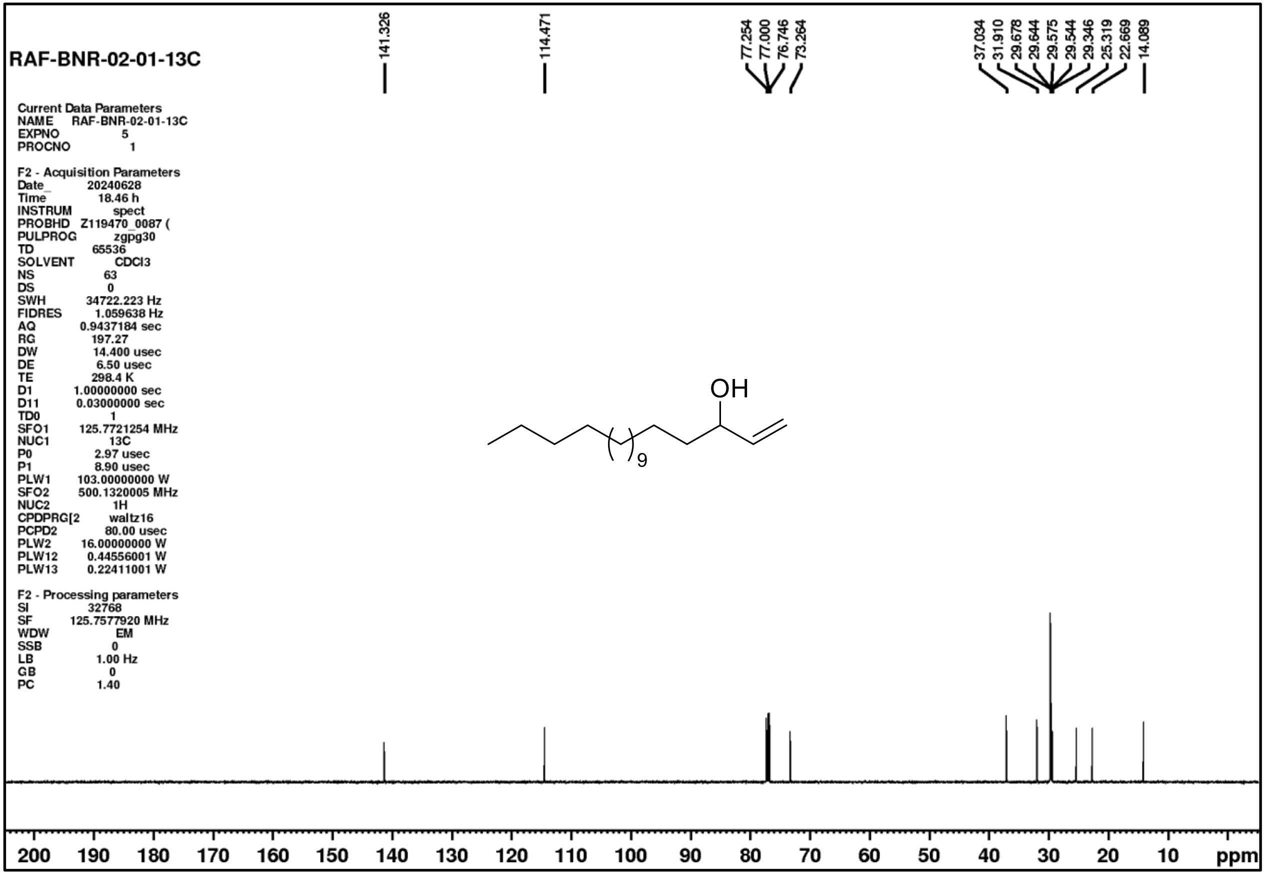

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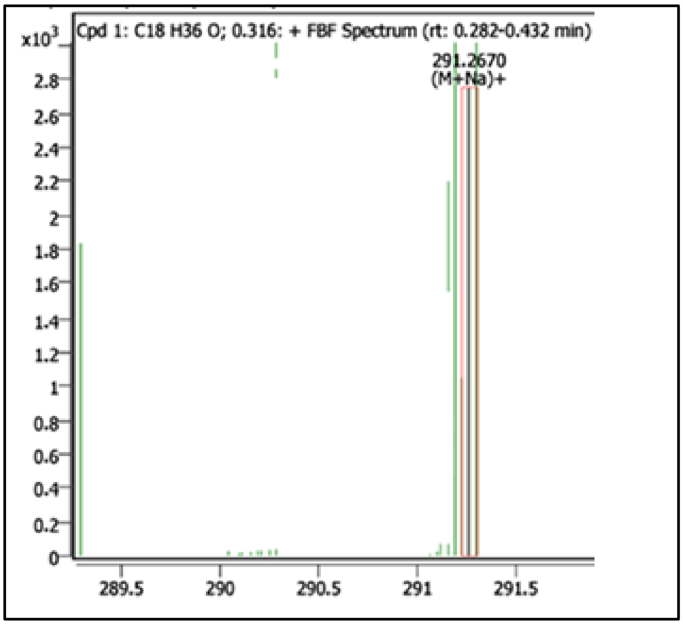
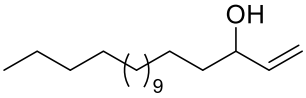
Current Data Parameters
NAME     RAF-BNR-02-01-13C
EXPNO          5
PROCNO         1

F2 - Acquisition Parameters
Date_        20240628
Time            18.46 h
INSTRUM         spect
PROBHD   Z119470_0087 (
PULPROG        zgpg30
TD           65536
SOLVENT          CDCl3
NS            63
DS             0
SWH        34722.223 Hz
FIDRES      1.059638 Hz
AQ        0.9437184 sec
RG           197.27
DW           14.400 usec
DE             6.50 usec
TE            298.4 K
D1       1.00000000 sec
D11      0.03000000 sec
TD0             1
SFO1     125.7721254 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     16.00000000 W
PLW12     0.44556001 W
PLW13     0.22411001 W

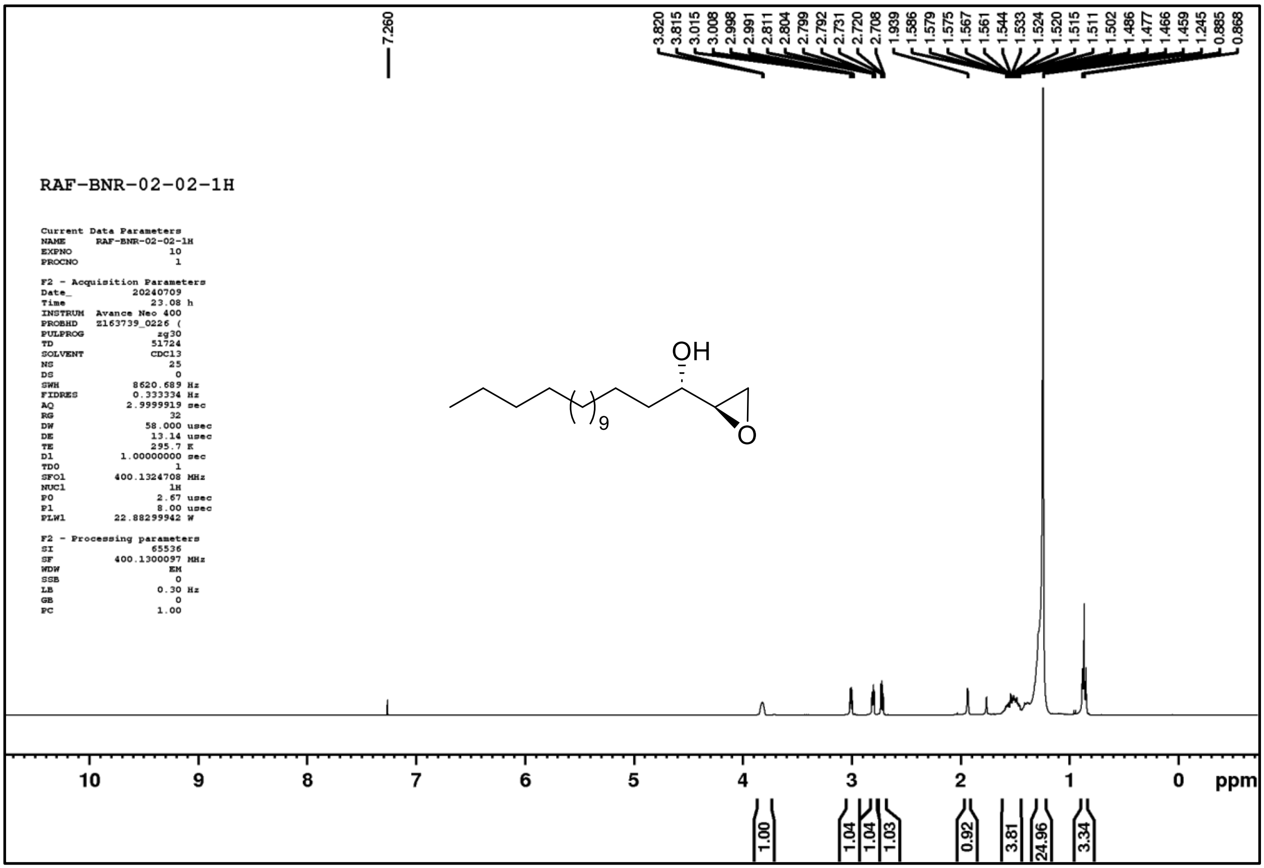
F2 - Processing parameters
SI           32768
SF      125.7577920 MHz
WDW             EM
SSB              0
LB            1.00 Hz
GB               0
PC            1.40
```

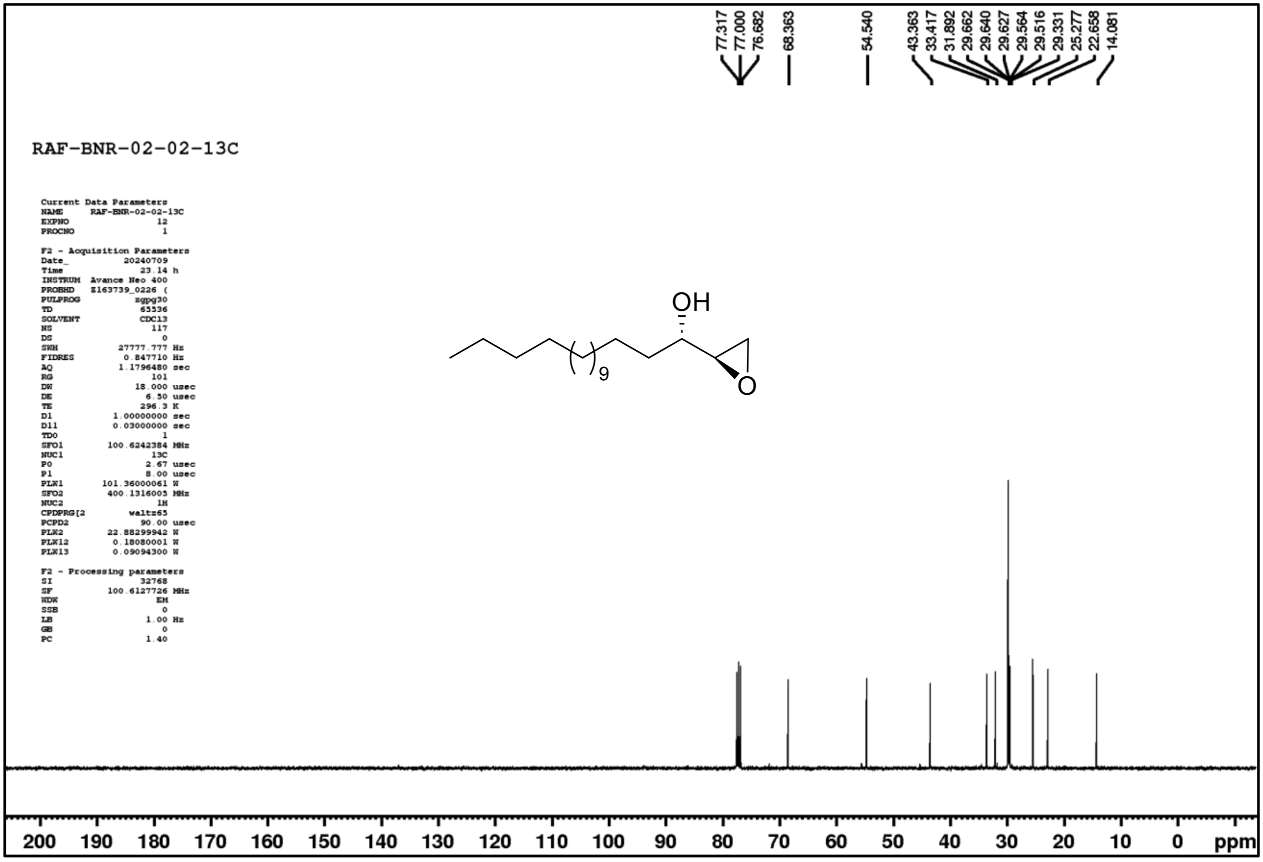
33: HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{36}ONa$ 291.2660; Found: 291.2670



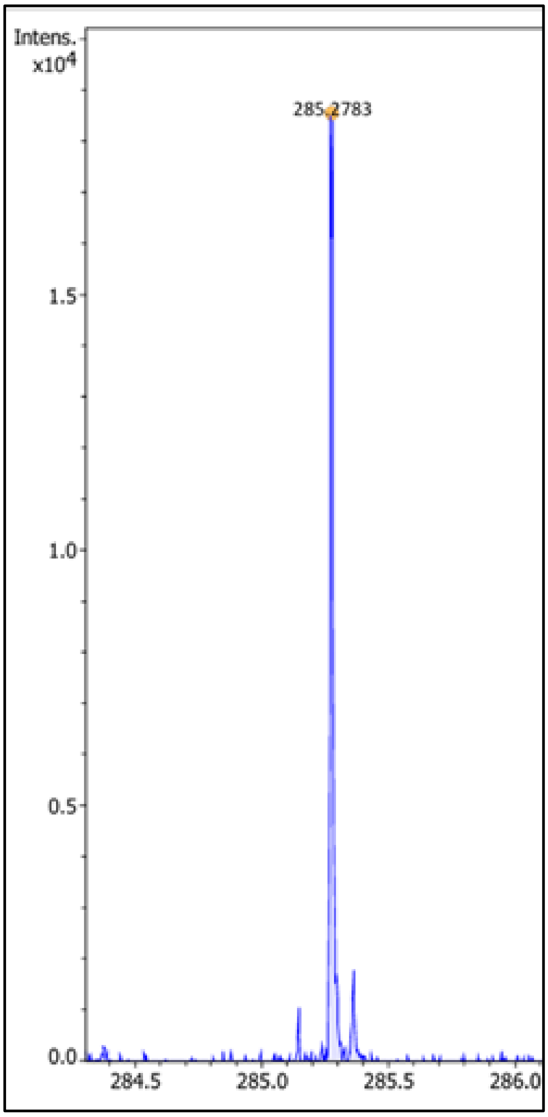


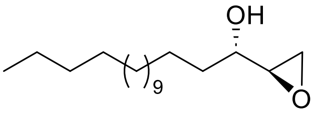
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **32**



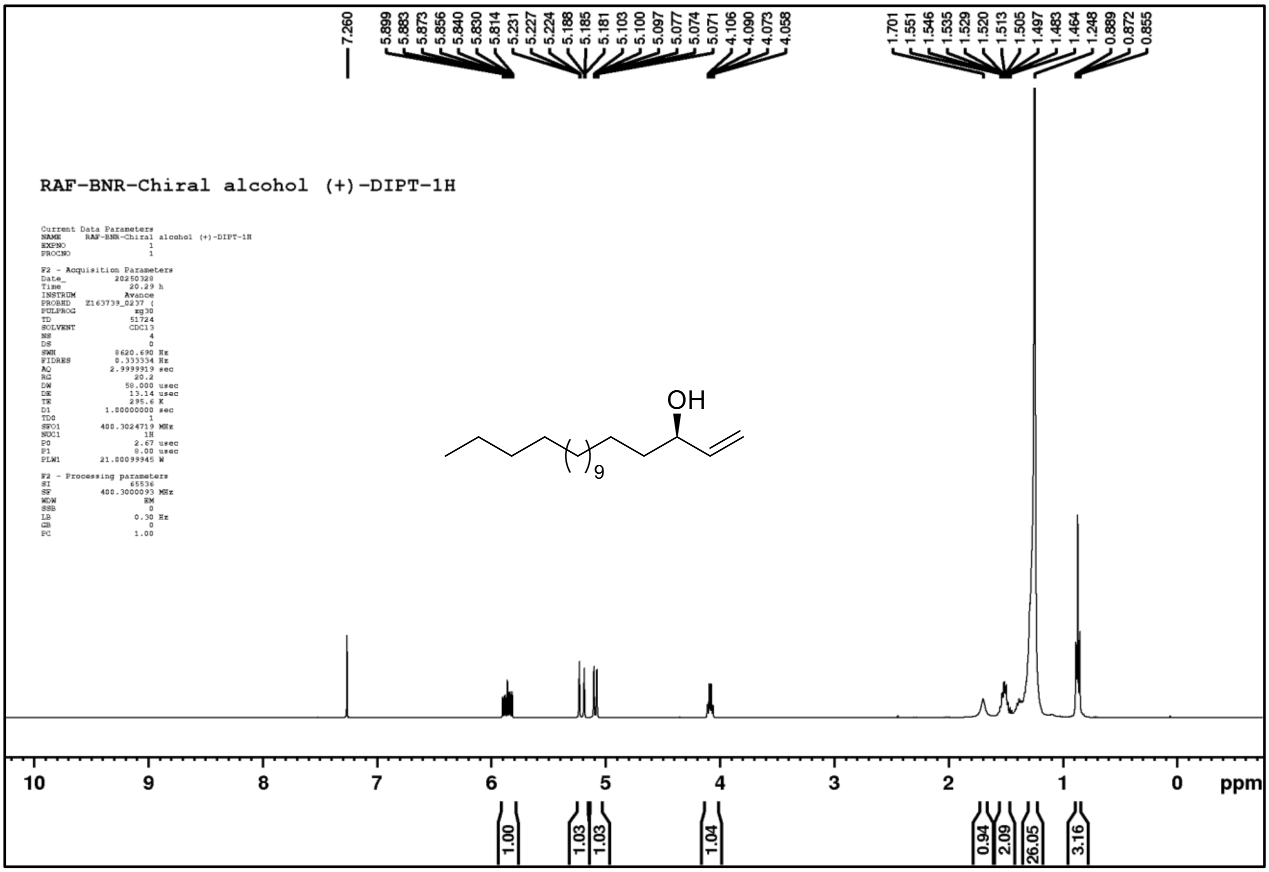


32: HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{18}H_{37}O_2$ 285.2788; Found: 285.2783





^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **32'**



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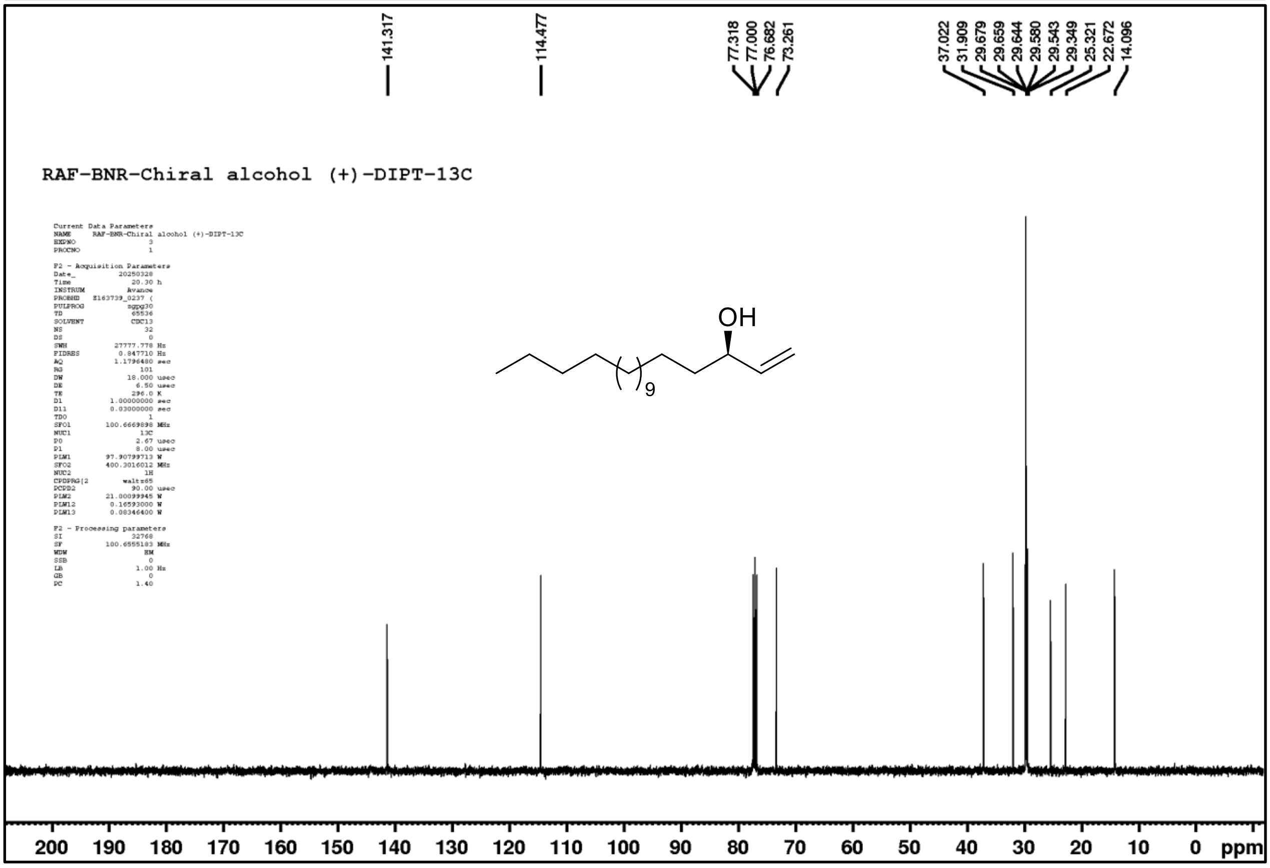
Current Data Parameters
NAME     RAF-BNR-Chiral alcohol (+)-DIPT-1H
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20250328
Time              20.29 h
INSTRUM          Avance
PROBHD   Z163739_0237 (
PULPROG            zg30
TD                51724
SOLVENT           CDCl3
NS                    4
DS                    0
SWH            8620.690 Hz
FIDRES         0.333334 Hz
AQ            2.9999919 sec
RG                 20.2
DW               58.000 usec
DE                13.14 usec
TE                295.6 K
D1           1.00000000 sec
TD0                   1
SFO1        400.3024719 MHz
NUC1                 1H
P0                 2.67 usec
P1                 8.00 usec
PLW1        21.00099945 W

F2 - Processing parameters
SI                65536
SF          400.3000093 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

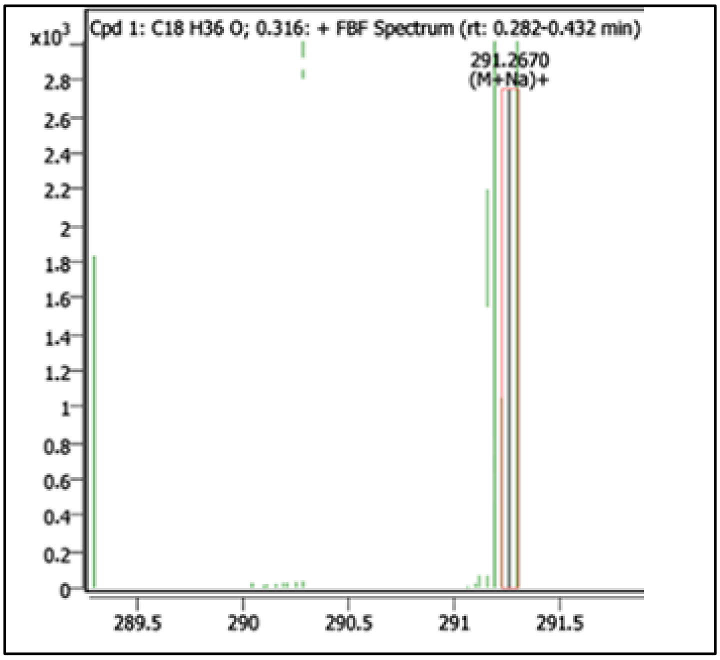


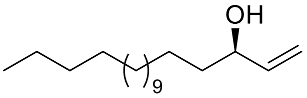
```
Current Data Parameters
NAME     RAF-BNR-Chiral alcohol (+)-DIPT-13C
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20250328
Time              20.30 h
INSTRUM          Avance
PROBHD   Z163739_0237 (
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    0
SWH           27777.778 Hz
FIDRES         0.847710 Hz
AQ            1.1796480 sec
RG                  101
DW               18.000 usec
DE                 6.50 usec
TE                296.0 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        97.90799713 W
SFO2        400.3016012 MHz
NUC2                 1H
CPDPRG[2         waltz65
PCPD2             90.00 usec
PLW2        21.00099945 W
PLW12        0.16593000 W
PLW13        0.08346400 W

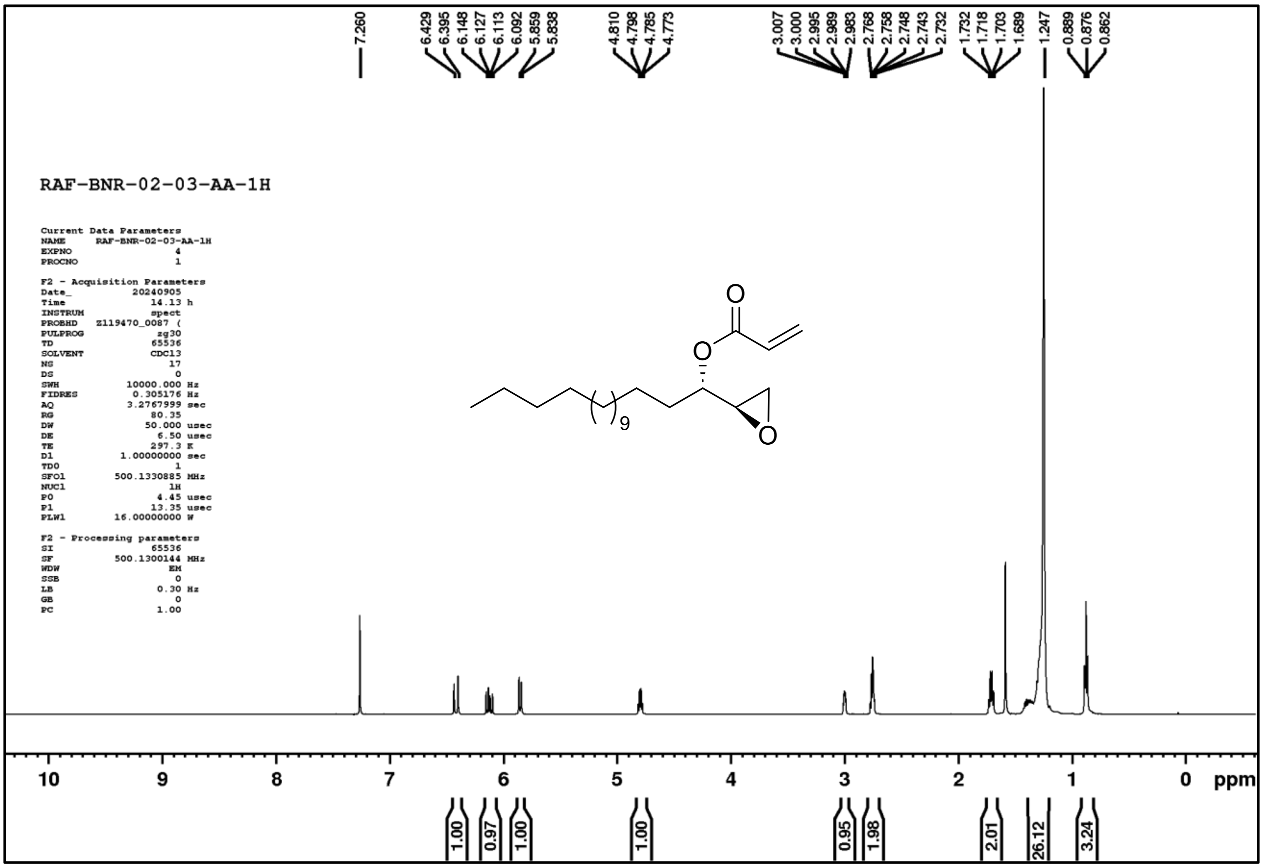
F2 - Processing parameters
SI                32768
SF          100.6555183 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

32': HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{18}H_{36}ONa$ 291.2660; Found: 291.2670





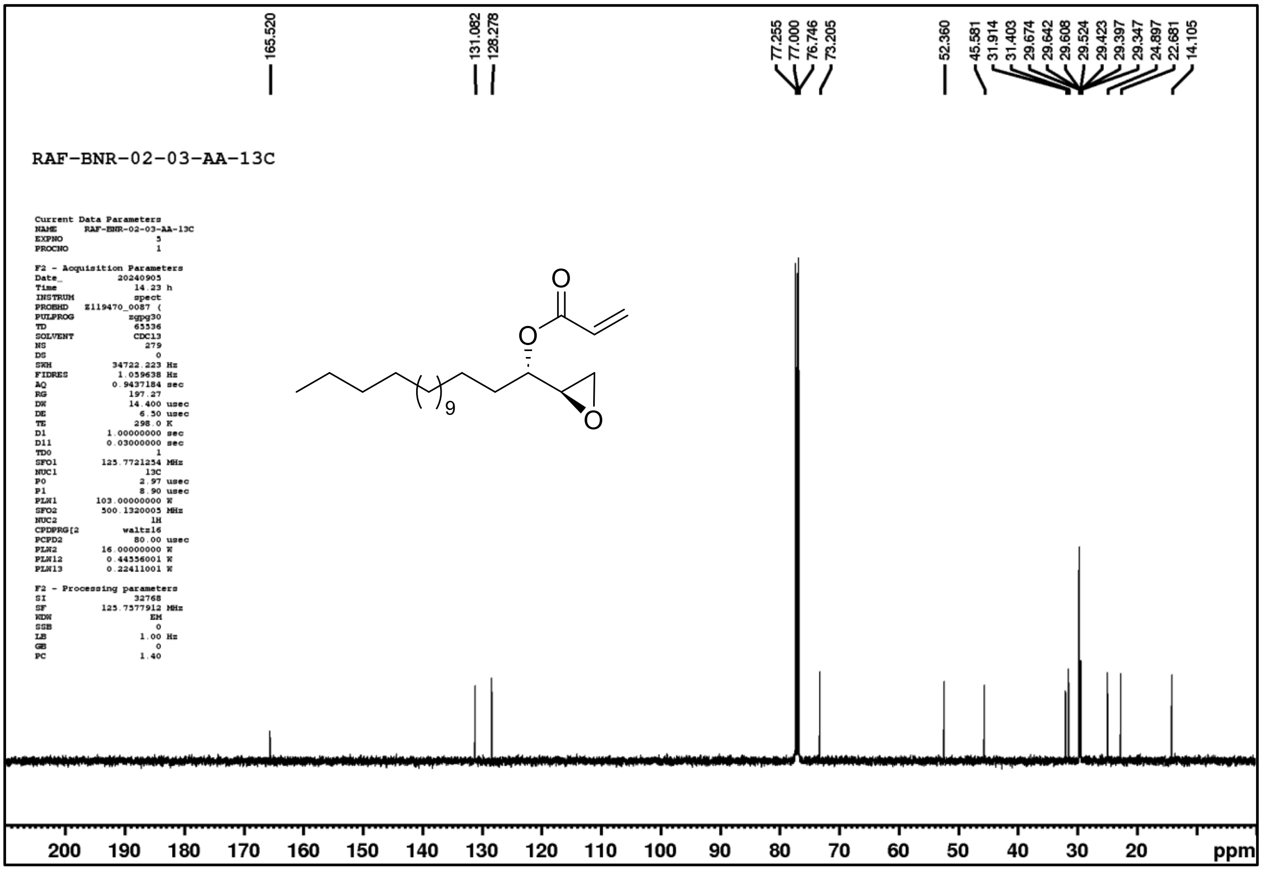
^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) of compound **35**



```
Current Data Parameters
NAME      RAF-BNR-02-03-AA-1H
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20240905
Time                14.13 h
INSTRUM             spect
PROBHD   Z119470_0087 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     17
DS                      0
SWH             10000.000 Hz
FIDRES           0.305176 Hz
AQ              3.2767999 sec
RG                  80.35
DW                 50.000 usec
DE                   6.50 usec
TE                  297.3 K
D1             1.00000000 sec
TD0                     1
SFO1          500.1330885 MHz
NUC1                   1H
P0                   4.45 usec
P1                  13.35 usec
PLW1          16.00000000 W

F2 - Processing parameters
SI                  65536
SF            500.1300144 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



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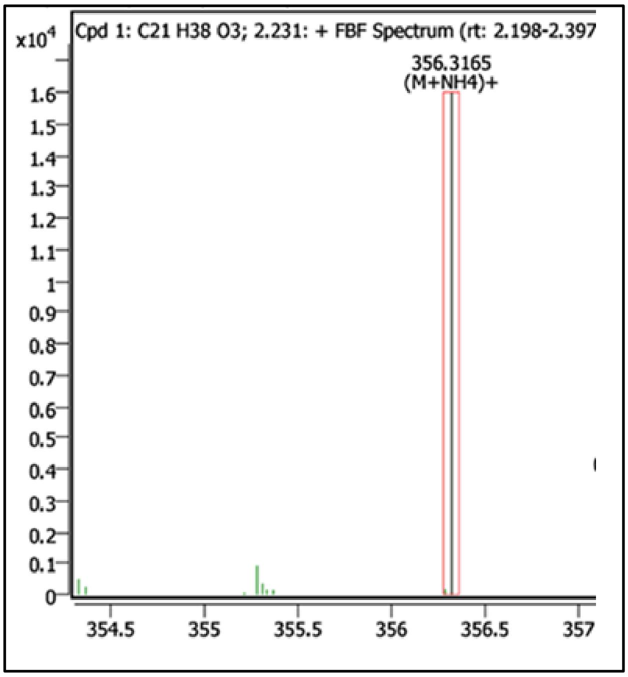
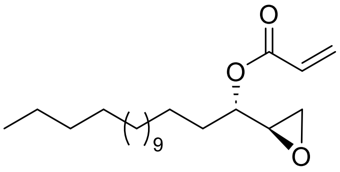
Current Data Parameters
NAME      RAF-BNR-02-03-AA-13C
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_            20240905
Time                14.23 h
INSTRUM             spect
PROBHD   Z119470_0087 (
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    279
DS                      0
SWH             34722.223 Hz
FIDRES           1.059638 Hz
AQ              0.9437184 sec
RG                 197.27
DW                 14.400 usec
DE                   6.50 usec
TE                  298.0 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                     1
SFO1          125.7721254 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          16.00000000 W
PLW12          0.44556001 W
PLW13          0.22411001 W

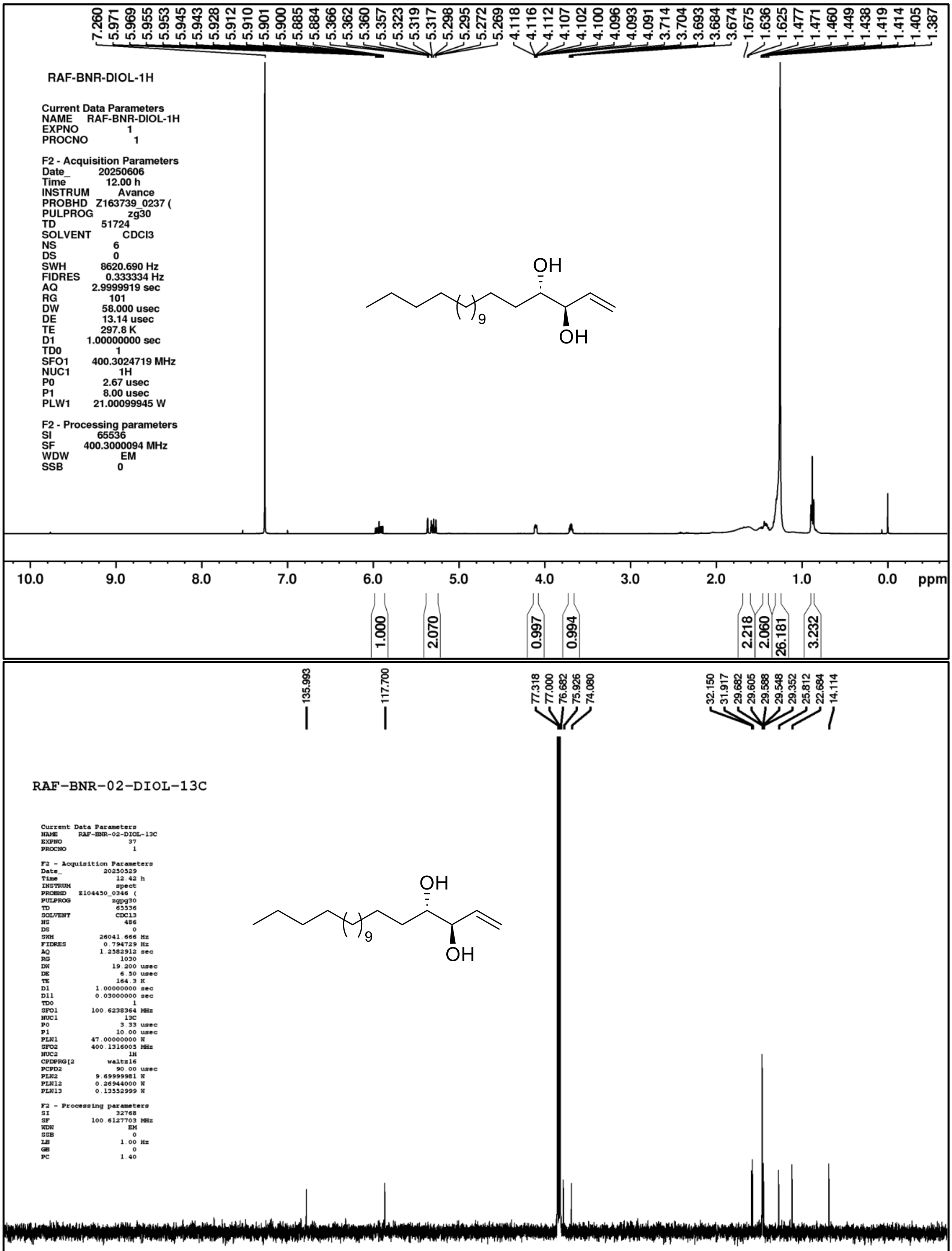
F2 - Processing parameters
SI                  32768
SF            125.7577912 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

35: HRMS (Q-TOF) *m/z*: $[M + NH_4]^+$ Calcd for $C_{21}H_{42}O_3N$ 356.3160; Found: 356.3165

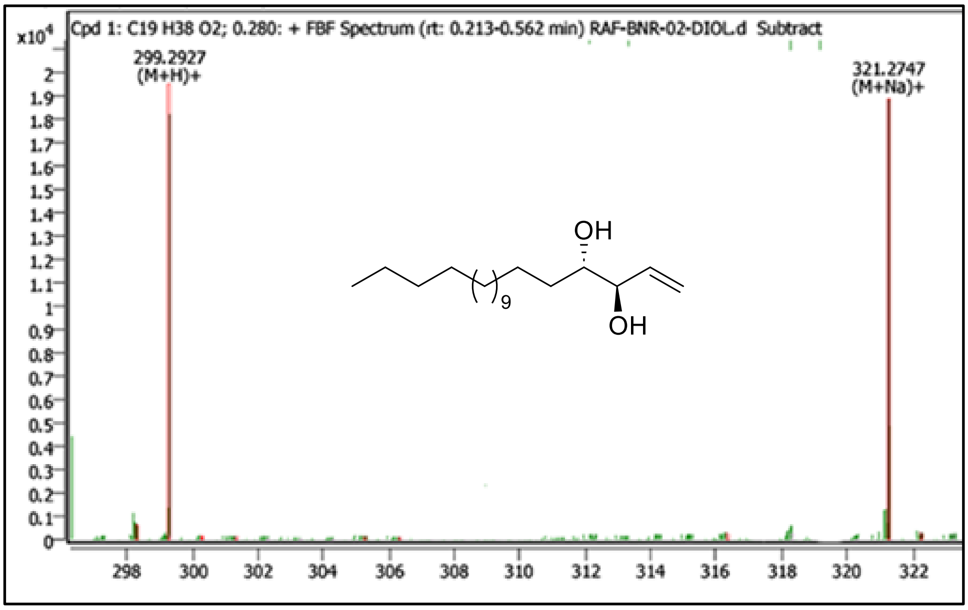




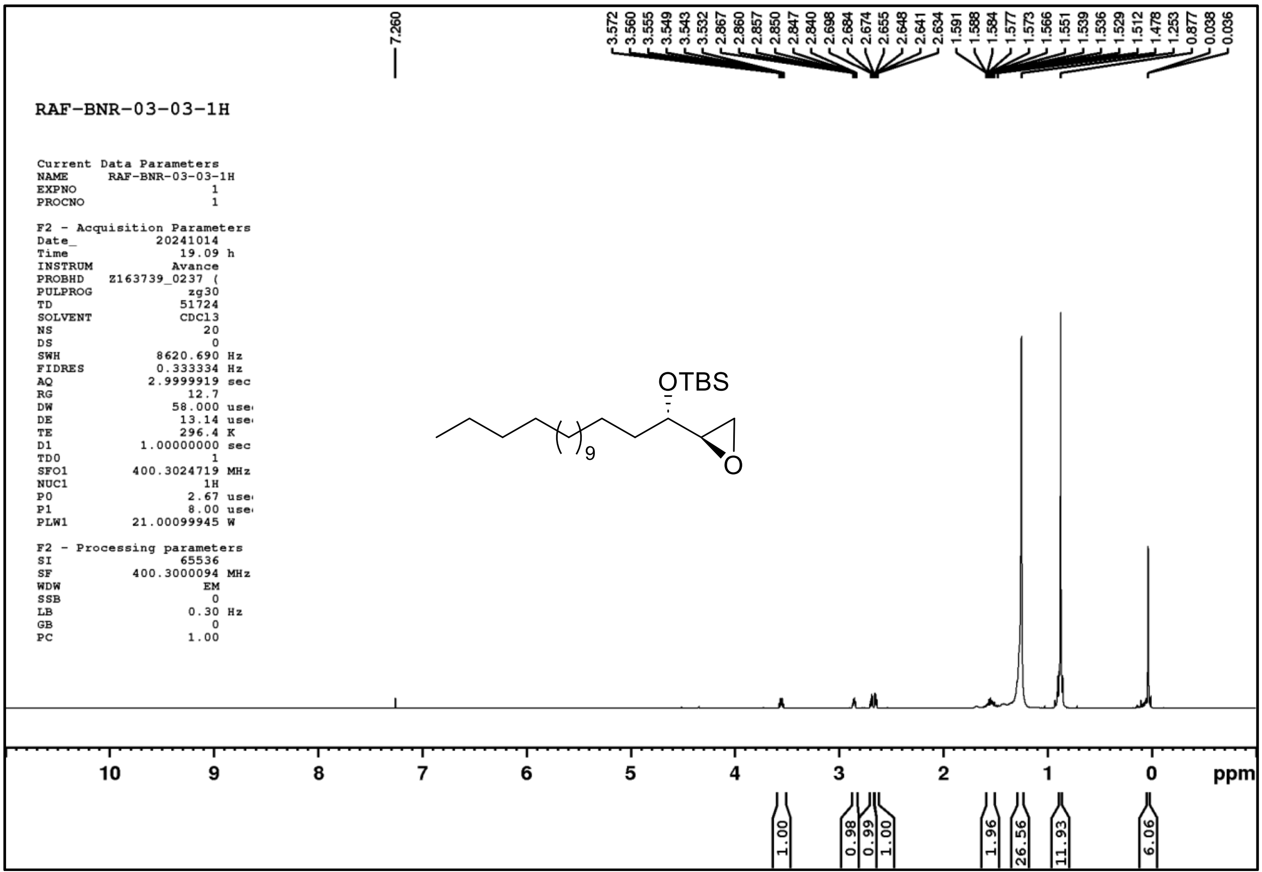
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **37**



37: HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{19}H_{38}O_2Na$ 321.2764; Found: 321.2747



^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **38**

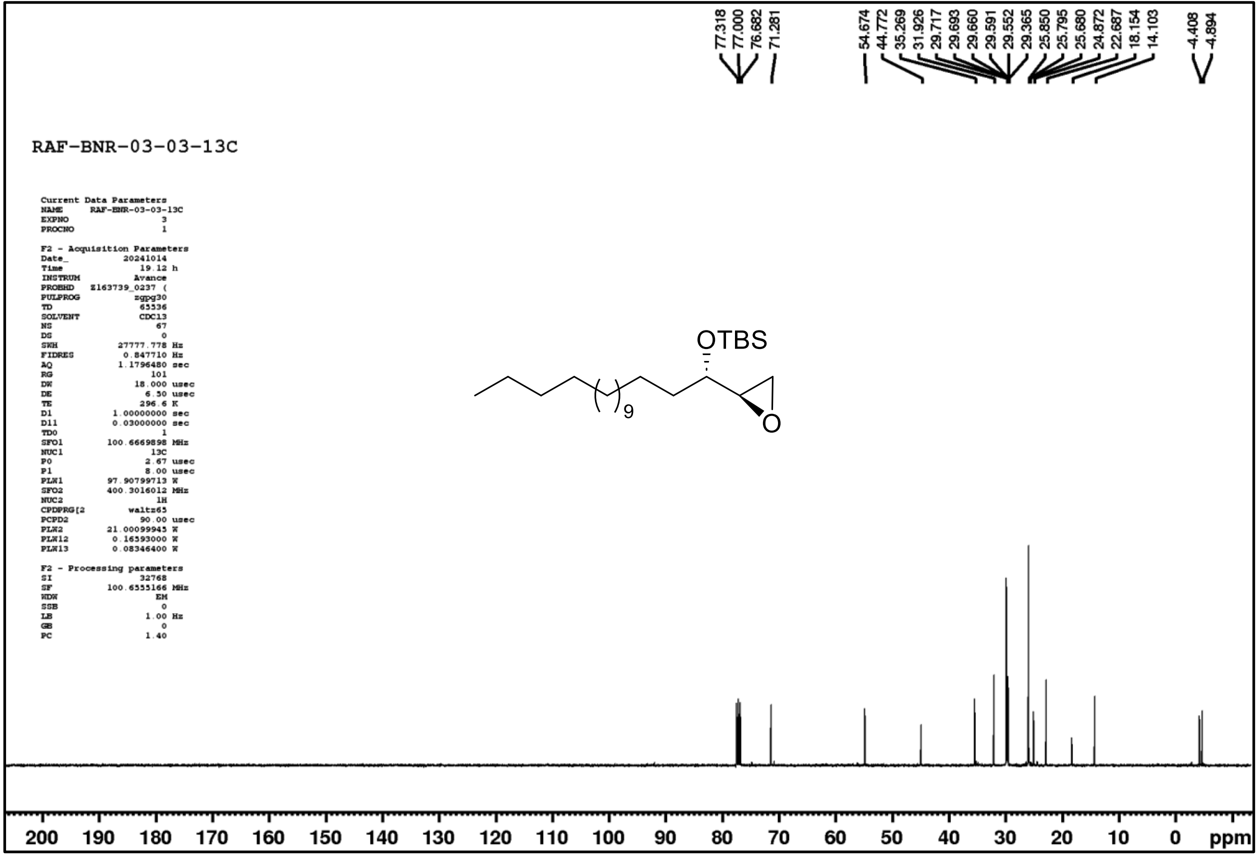


```
RAF-BNR-03-03-1H

Current Data Parameters
NAME      RAF-BNR-03-03-1H
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20241014
Time                 19.09 h
INSTRUM             Avance
PROBHD    Z163739_0237 (
PULPROG               zg30
TD                   51724
SOLVENT              CDCl3
NS                      20
DS                       0
SWH               8620.690 Hz
FIDRES            0.333334 Hz
AQ               2.9999919 sec
RG                    12.7
DW                  58.000 use
DE                   13.14 use
TE                   296.4 K
D1              1.00000000 sec
TD0                      1
SFO1           400.3024719 MHz
NUC1                    1H
P0                    2.67 use
P1                    8.00 use
PLW1           21.00099945 W

F2 - Processing parameters
SI                   65536
SF             400.3000094 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



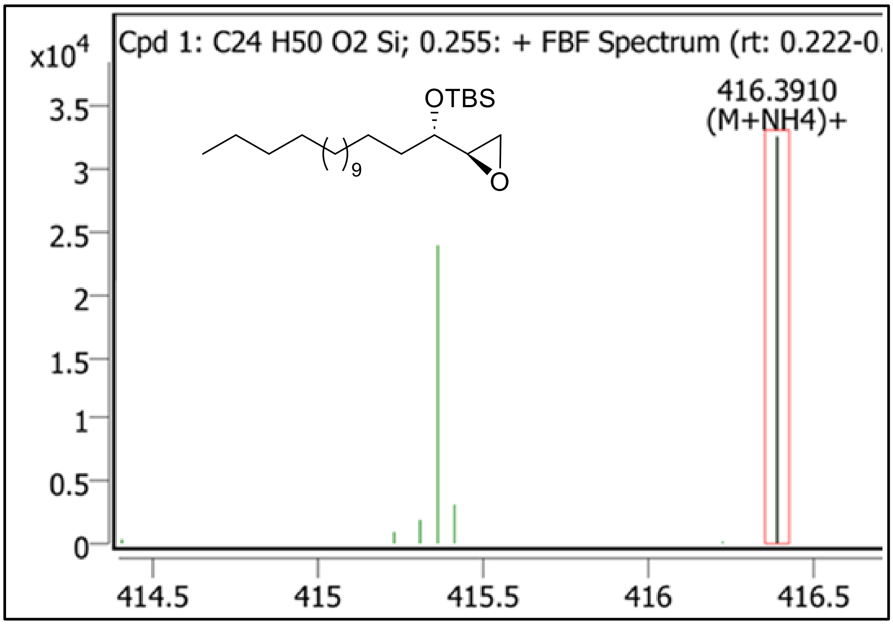
```
RAF-BNR-03-03-13C

Current Data Parameters
NAME      RAF-BNR-03-03-13C
EXPNO                    3
PROCNO                   1

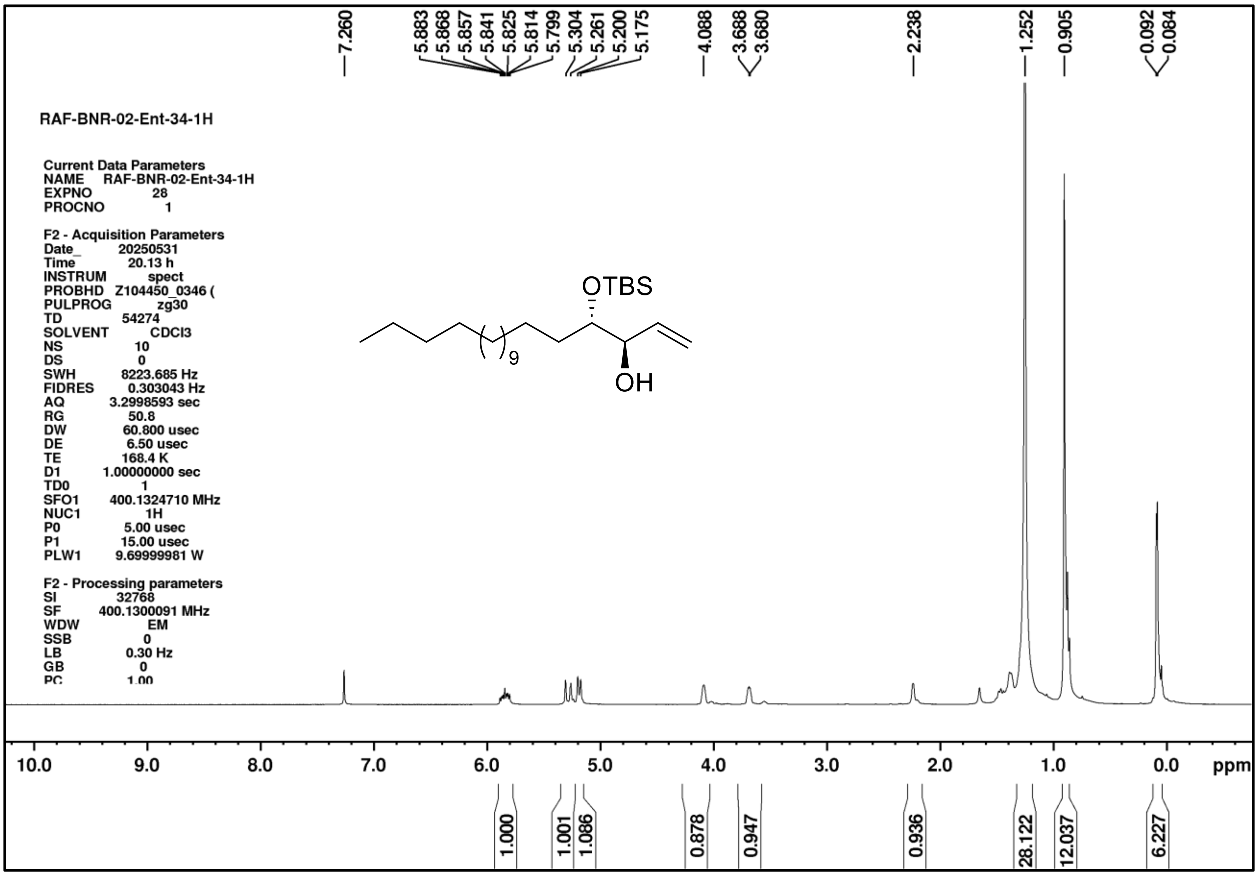
F2 - Acquisition Parameters
Date_             20241014
Time                 19.12 h
INSTRUM             Avance
PROBHD    Z163739_0237 (
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      67
DS                       0
SWH              27777.778 Hz
FIDRES            0.847710 Hz
AQ               1.1796480 sec
RG                     101
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                    2.67 usec
P1                    8.00 usec
PLW1           97.90799713 W
SFO2           400.3016012 MHz
NUC2                    1H
CPDPRG[2          waltz65
PCPD2                90.00 usec
PLW2           21.00099945 W
PLW12           0.16593000 W
PLW13           0.08346400 W

F2 - Processing parameters
SI                   32768
SF             100.6555166 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

38: HRMS (ESI-TOF) *m/z*: [M + NH$_4$]$^+$ Calcd for $C_{24}H_{54}O_2SiN$ 416.3918; Found: 416.3910.



^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound ***ent*-34**

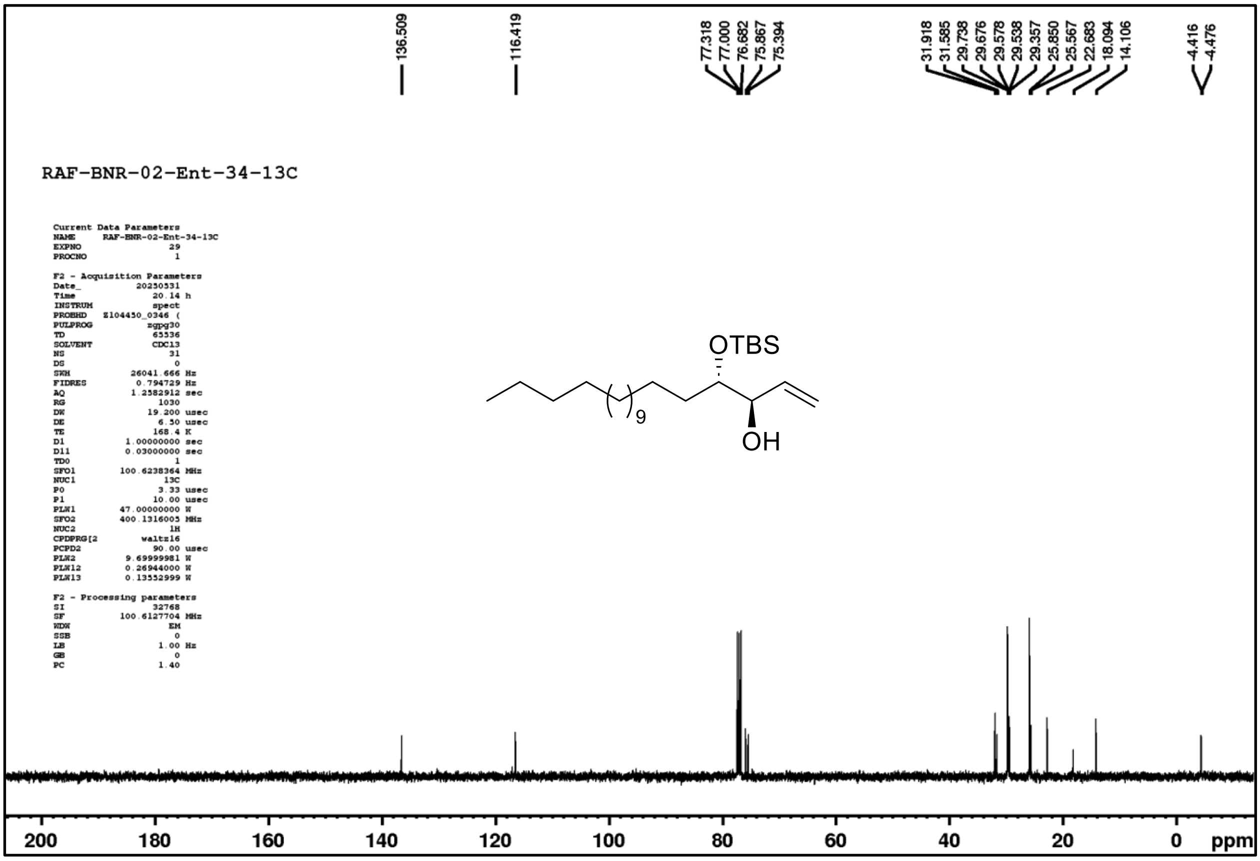


```
RAF-BNR-02-Ent-34-1H

Current Data Parameters
NAME    RAF-BNR-02-Ent-34-1H
EXPNO           28
PROCNO           1

F2 - Acquisition Parameters
Date_        20250531
Time            20.13 h
INSTRUM         spect
PROBHD  Z104450_0346 (
PULPROG          zg30
TD           54274
SOLVENT         CDCl3
NS              10
DS               0
SWH           8223.685 Hz
FIDRES        0.303043 Hz
AQ          3.2998593 sec
RG              50.8
DW            60.800 usec
DE              6.50 usec
TE             168.4 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        400.1300091 MHz
WDW              EM
SSB               0
LB             0.30 Hz
GB                0
PC             1.00
```



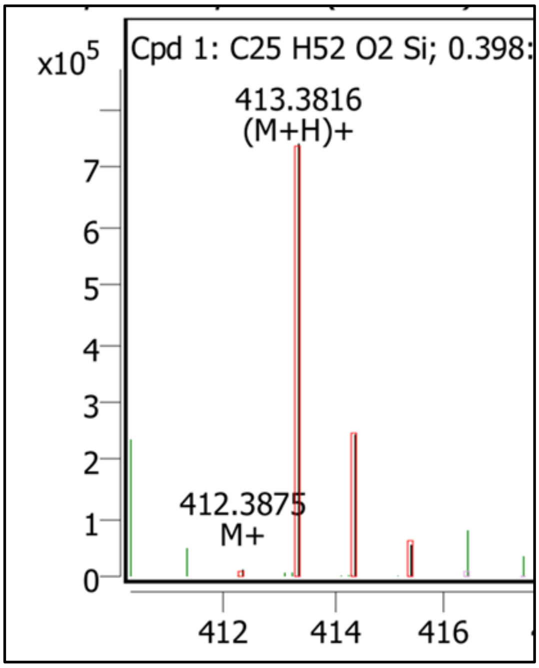
```
RAF-BNR-02-Ent-34-13C

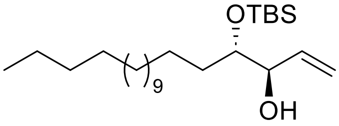
Current Data Parameters
NAME       RAF-BNR-02-Ent-34-13C
EXPNO                    29
PROCNO                    1

F2 - Acquisition Parameters
Date_              20250531
Time                  20.14 h
INSTRUM               spect
PROBHD     Z104450_0346 (
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       31
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                    168.4 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

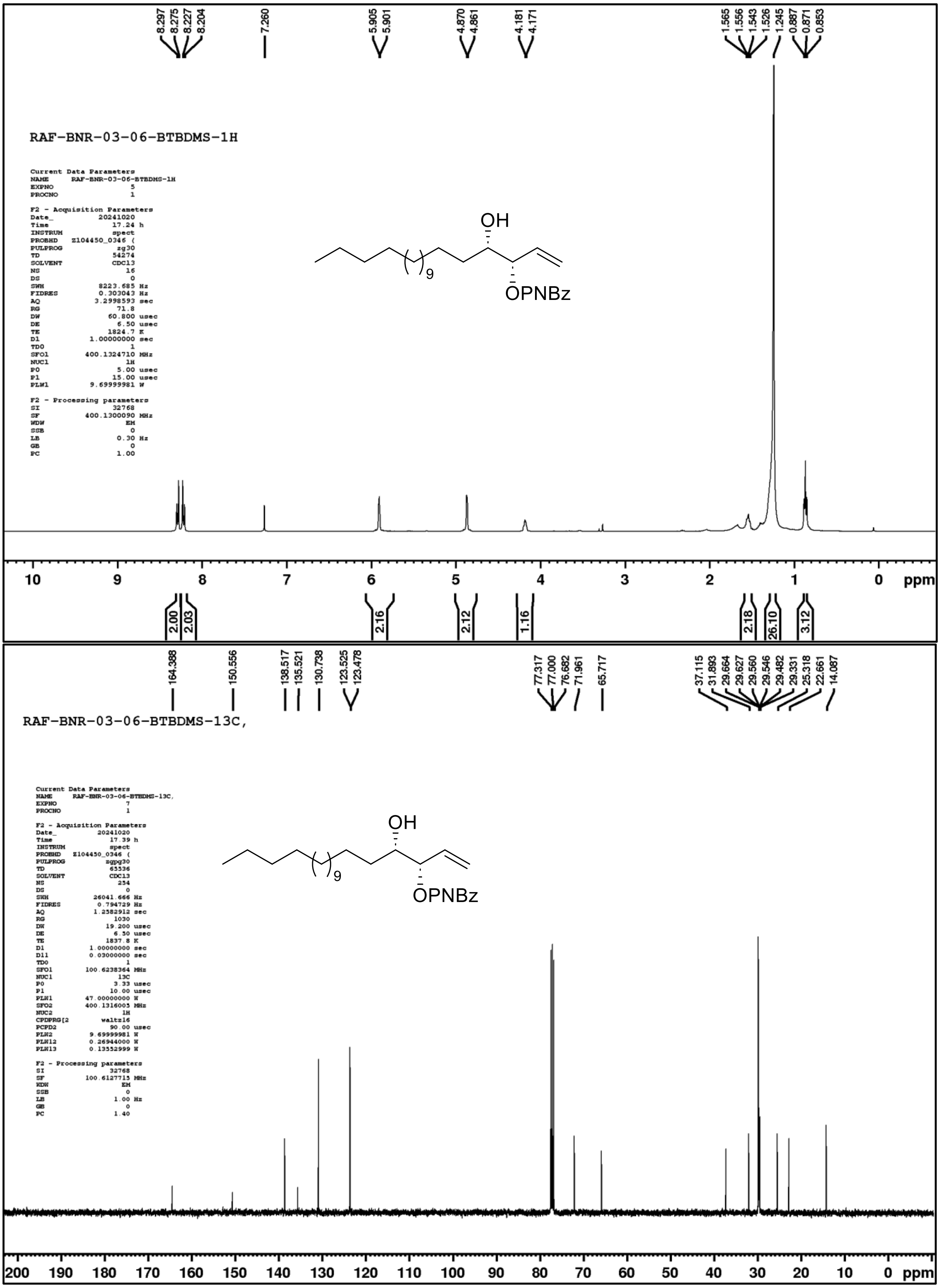
F2 - Processing parameters
SI                    32768
SF              100.6127704 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

***ent*-34**: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{53}O_2Si$ 413.3810; Found: 413.3816

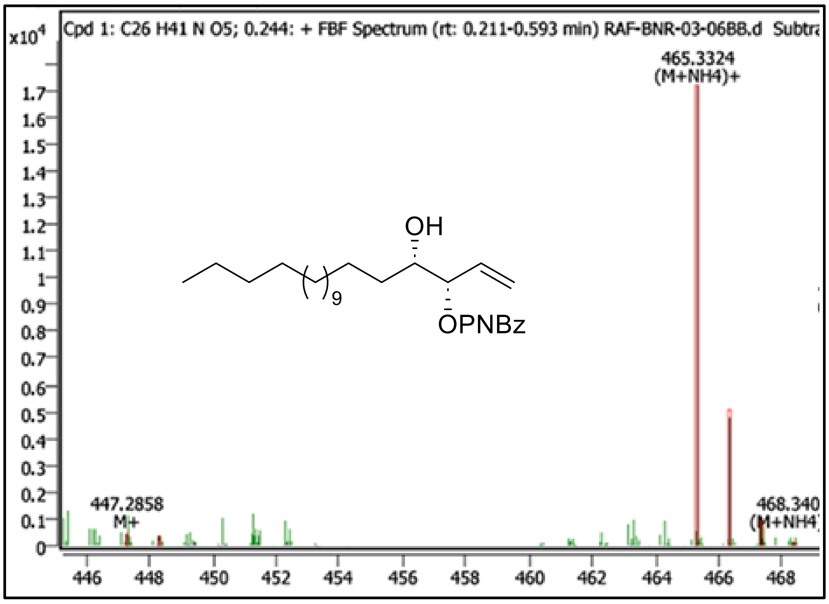




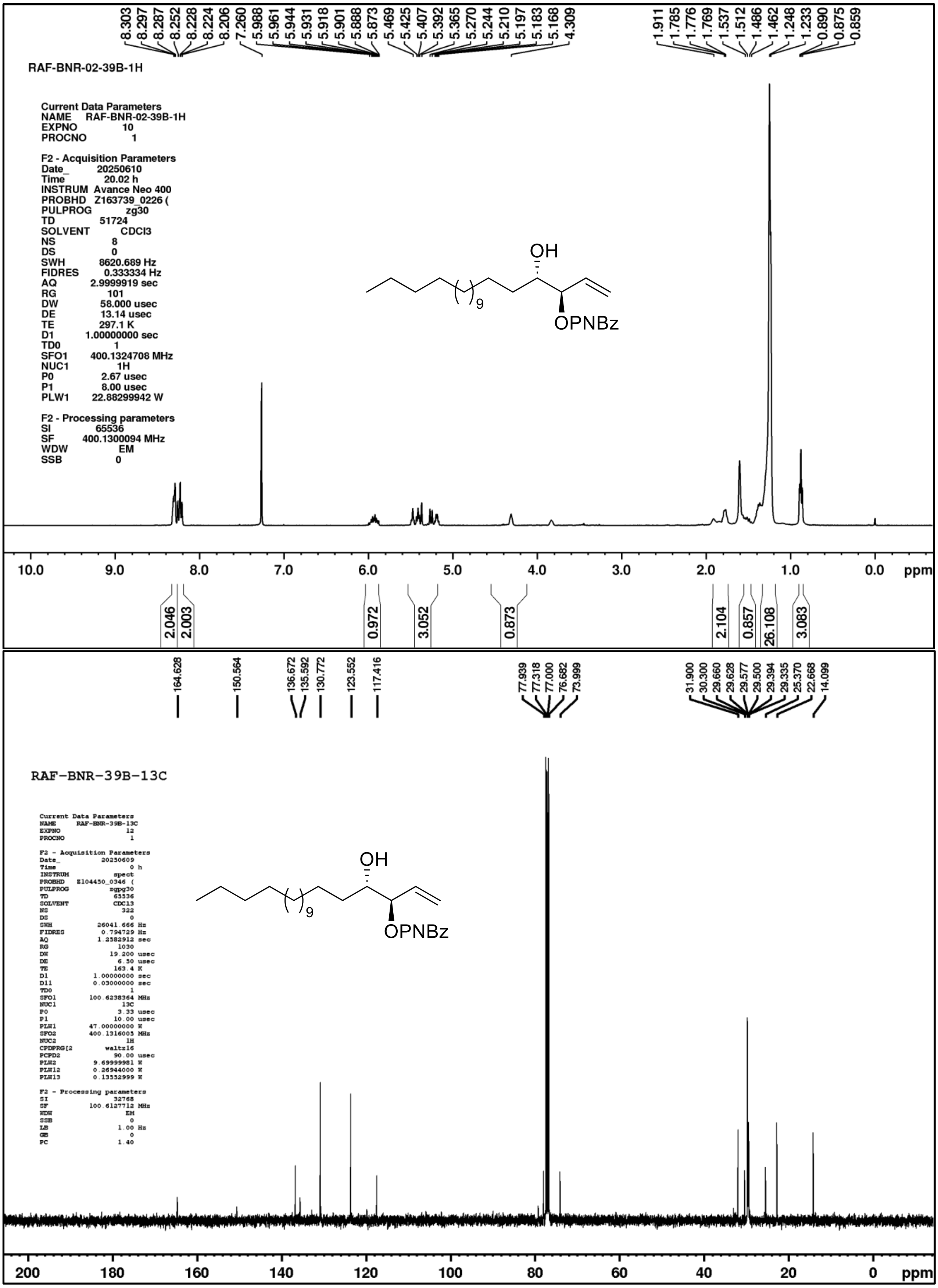
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **39a**



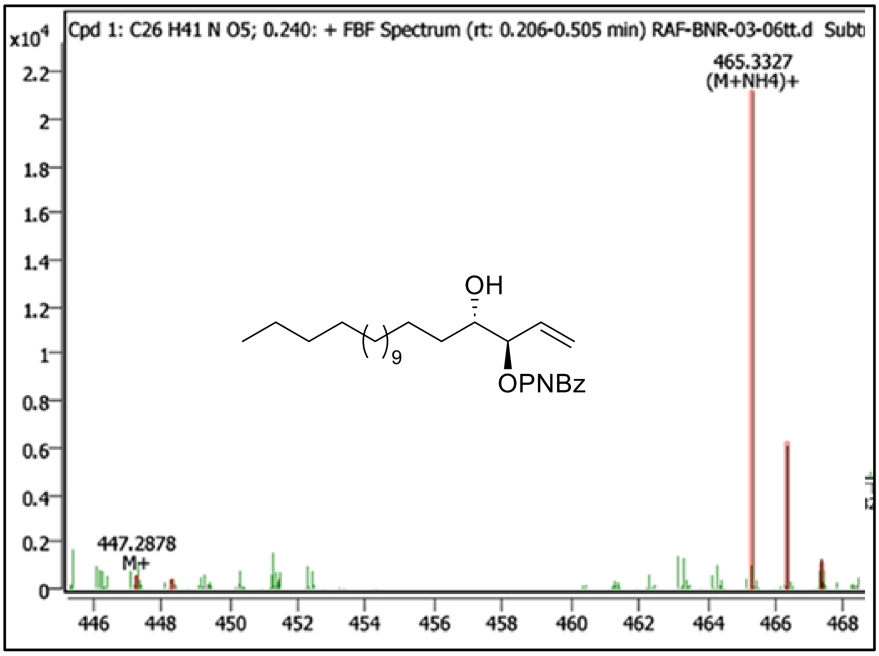
39a: HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ Calcd for $C_{26}H_{45}O_5N_2$ 465.3323; Found: 465.3324



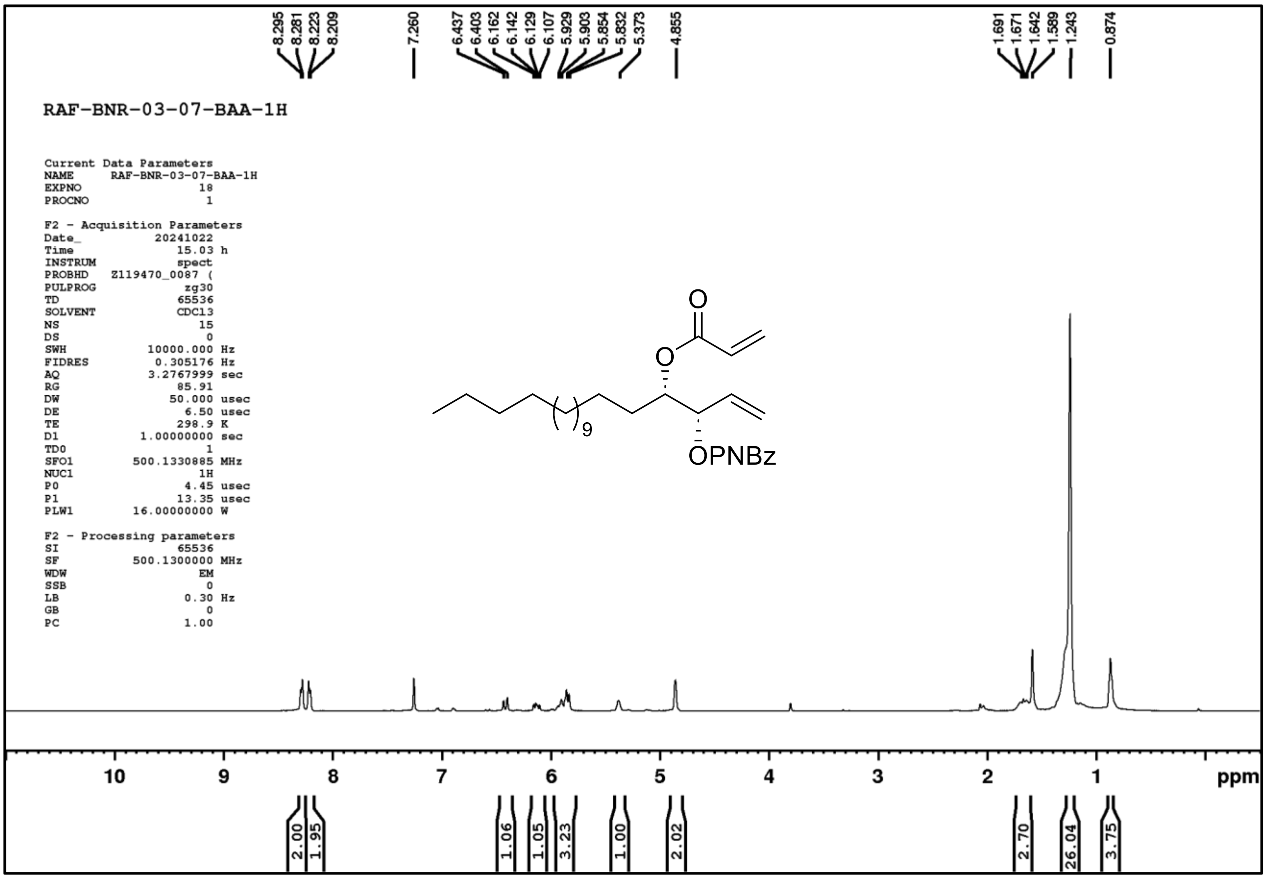
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **39b**



39b: HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ Calcd for $C_{26}H_{45}O_5N_2$ 465.3323; Found: 465.3327



^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **40a**

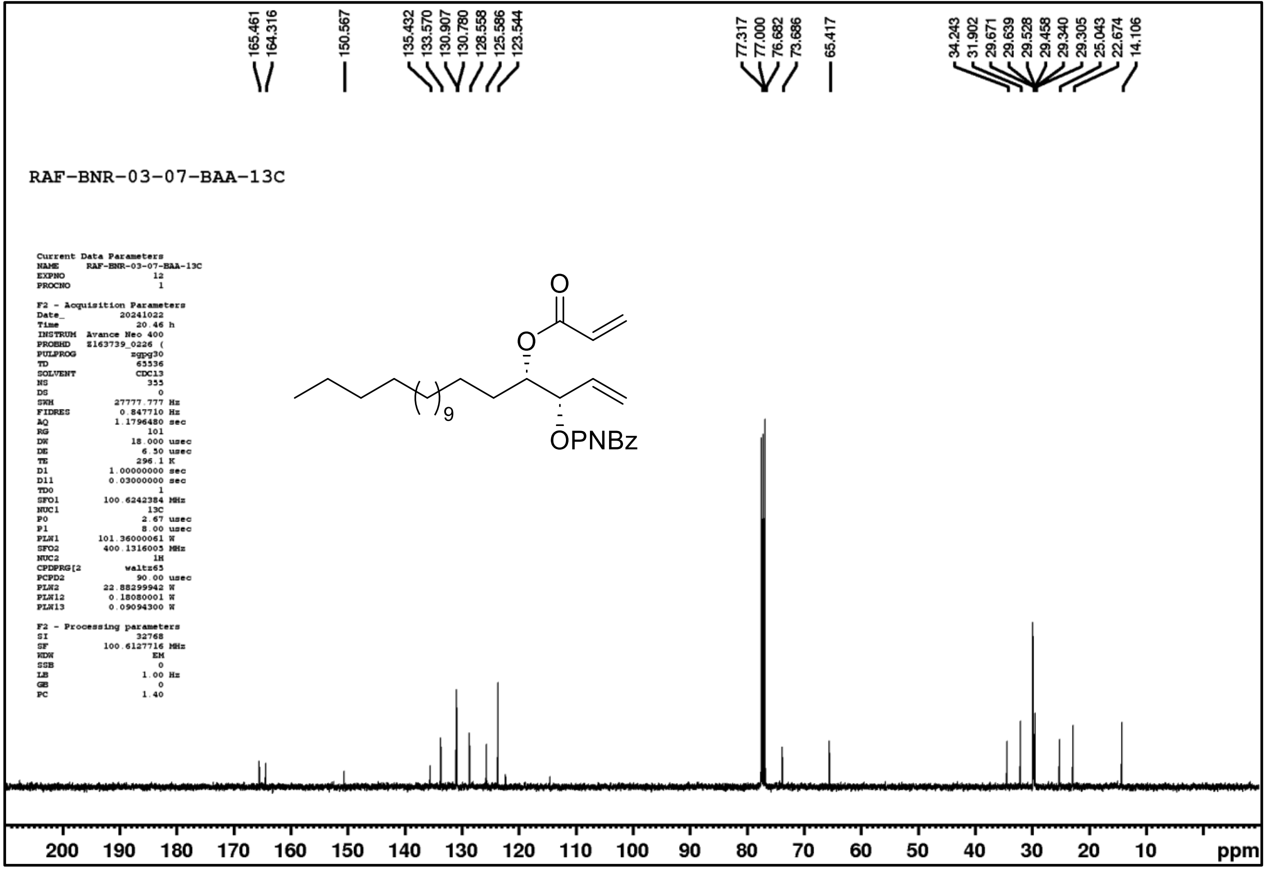


```
RAF-BNR-03-07-BAA-1H

Current Data Parameters
NAME     RAF-BNR-03-07-BAA-1H
EXPNO                  18
PROCNO                  1

F2 - Acquisition Parameters
Date_            20241022
Time                15.03 h
INSTRUM             spect
PROBHD   Z119470_0087 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     15
DS                      0
SWH             10000.000 Hz
FIDRES           0.305176 Hz
AQ              3.2767999 sec
RG                  85.91
DW                 50.000 usec
DE                   6.50 usec
TE                  298.9 K
D1             1.00000000 sec
TD0                     1
SFO1          500.1330885 MHz
NUC1                   1H
P0                   4.45 usec
P1                  13.35 usec
PLW1          16.00000000 W

F2 - Processing parameters
SI                  65536
SF            500.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



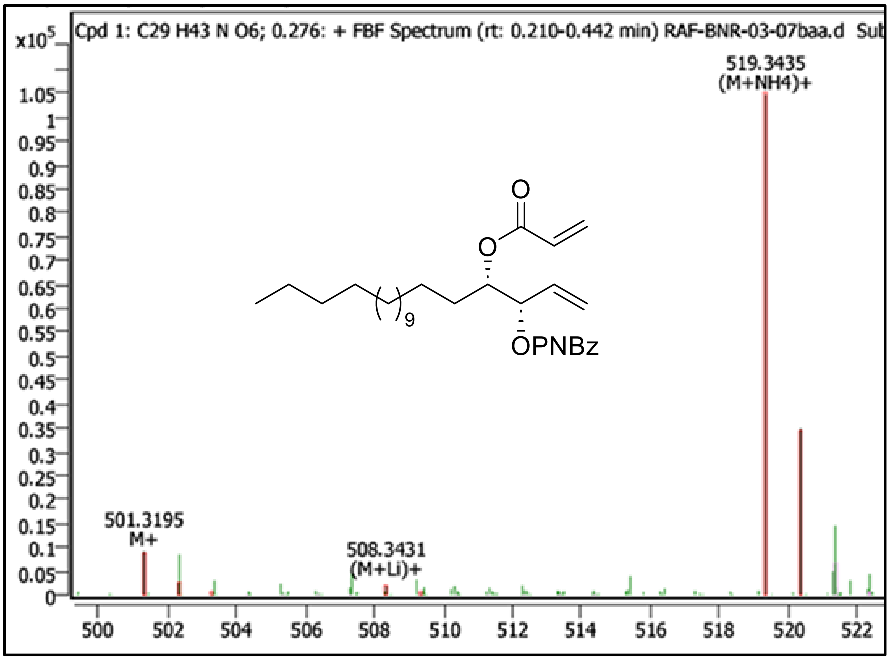
```
RAF-BNR-03-07-BAA-13C

Current Data Parameters
NAME     RAF-BNR-03-07-BAA-13C
EXPNO                  12
PROCNO                  1

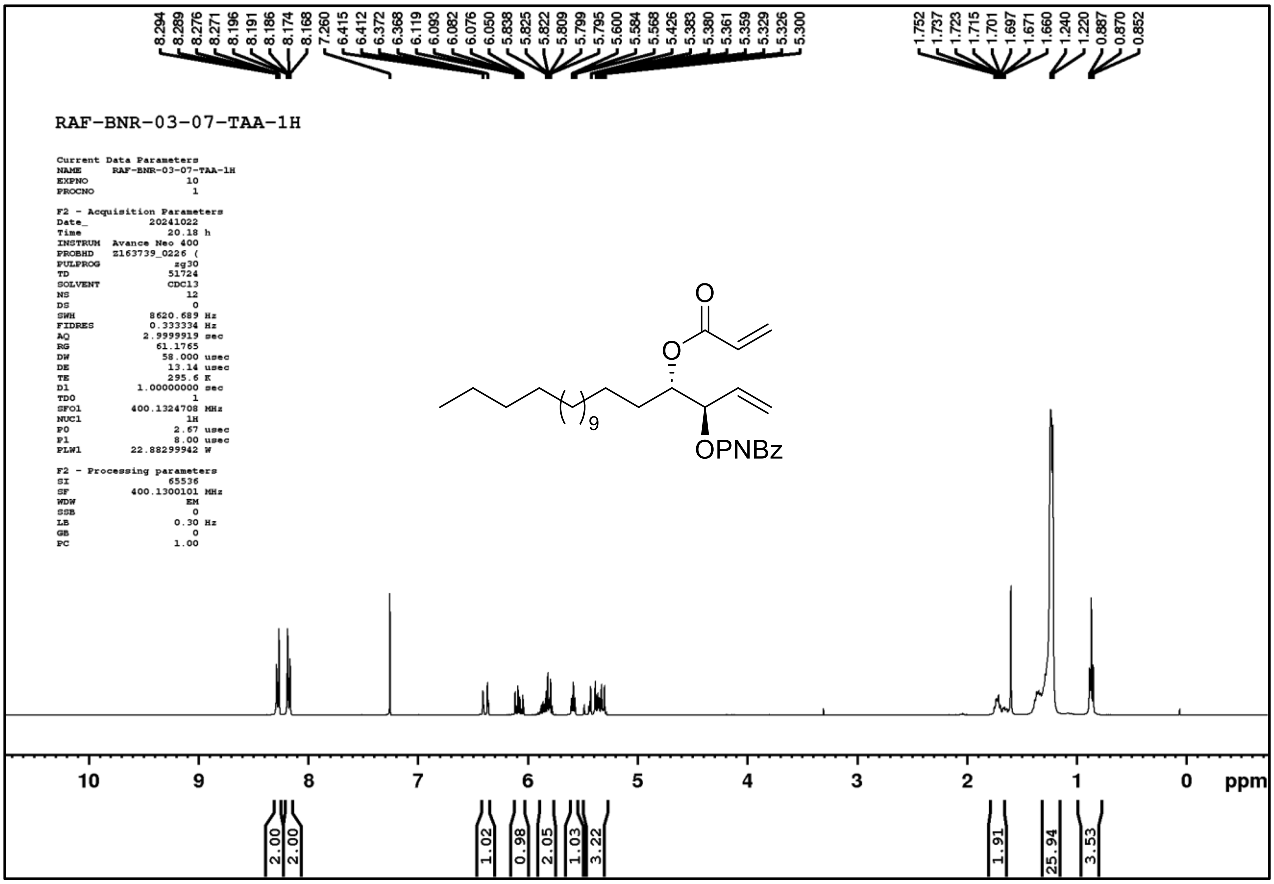
F2 - Acquisition Parameters
Date_            20241022
Time                20.46 h
INSTRUM  Avance Neo 400
PROBHD   Z163739_0226 (
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    355
DS                      0
SWH             27777.777 Hz
FIDRES           0.847710 Hz
AQ              1.1796480 sec
RG                    101
DW                 18.000 usec
DE                   6.50 usec
TE                  296.1 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                     1
SFO1          100.6242384 MHz
NUC1                  13C
P0                   2.67 usec
P1                   8.00 usec
PLW1         101.36000061 W
SFO2          400.1316005 MHz
NUC2                   1H
CPDPRG[2           waltz65
PCPD2               90.00 usec
PLW2          22.88299942 W
PLW12          0.18080001 W
PLW13          0.09094300 W

F2 - Processing parameters
SI                  32768
SF            100.6127716 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

40a: HRMS (ESI-TOF) *m/z*: [M + NH$_4$]$^+$ Calcd for $C_{29}H_{47}O_6N_2$ 519.3429; Found: 519.3435



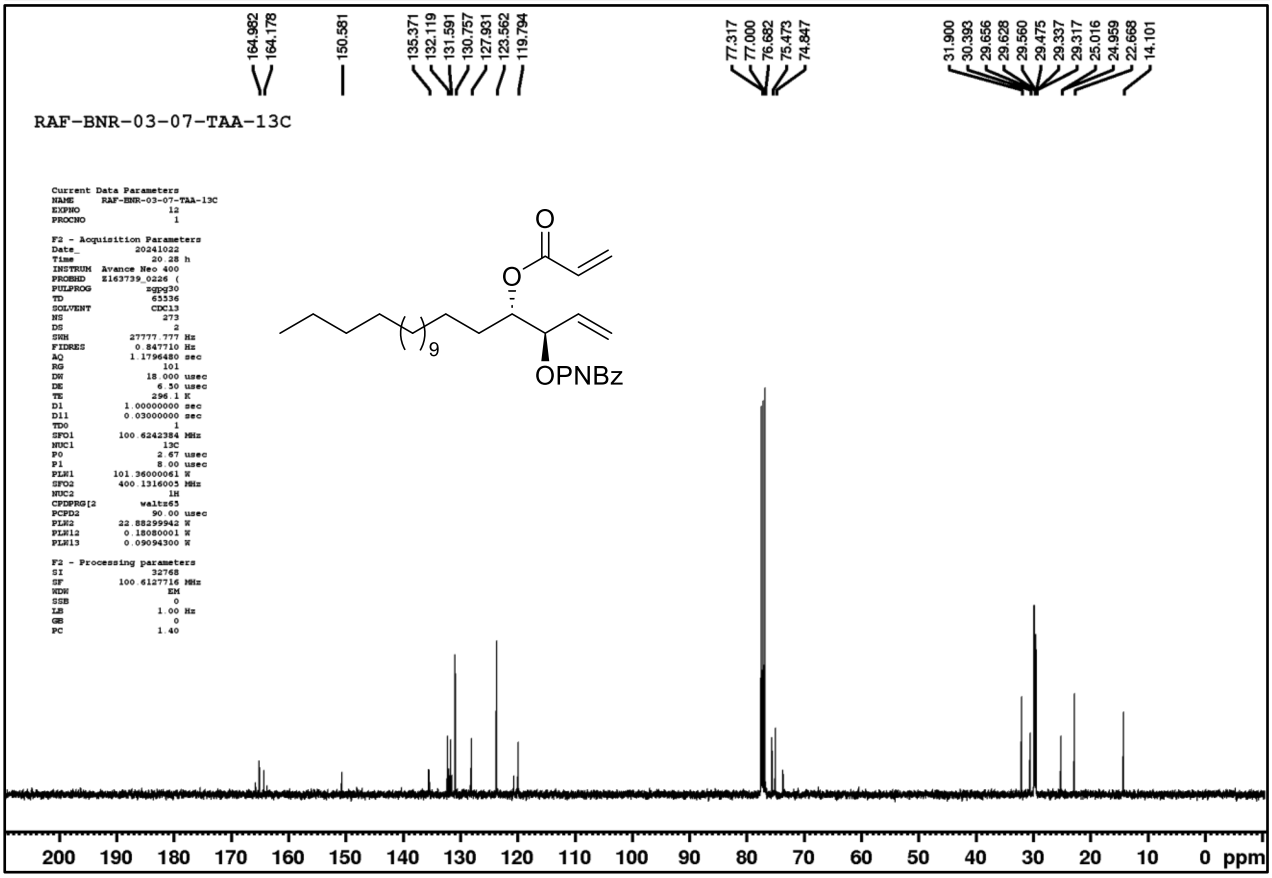
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **40b**



```
Current Data Parameters
NAME      RAF-BNR-03-07-TAA-1H
EXPNO                       10
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20241022
Time                   20.18 h
INSTRUM   Avance Neo 400
PROBHD    Z163739_0226 (
PULPROG                   zg30
TD                       51724
SOLVENT                  CDCl3
NS                          12
DS                           0
SWH                   8620.689 Hz
FIDRES                0.333334 Hz
AQ                   2.9999919 sec
RG                     61.1765
DW                      58.000 usec
DE                       13.14 usec
TE                       295.6 K
D1                  1.00000000 sec
TD0                          1
SFO1               400.1324708 MHz
NUC1                        1H
P0                        2.67 usec
P1                        8.00 usec
PLW1               22.88299942 W

F2 - Processing parameters
SI                       65536
SF                 400.1300101 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```

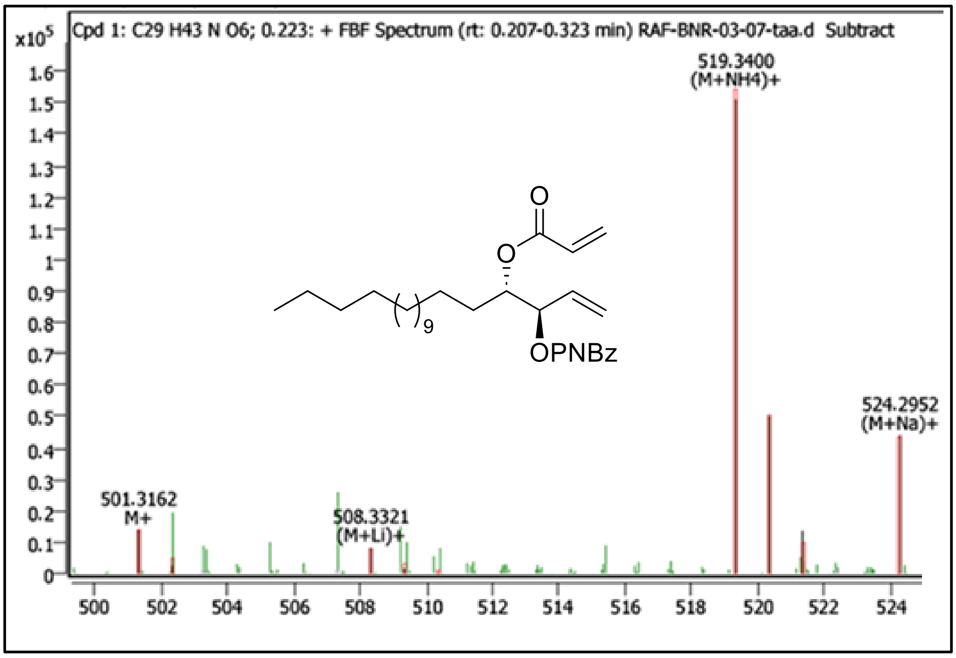


```
Current Data Parameters
NAME      RAF-BNR-03-07-TAA-13C
EXPNO                       12
PROCNO                       1

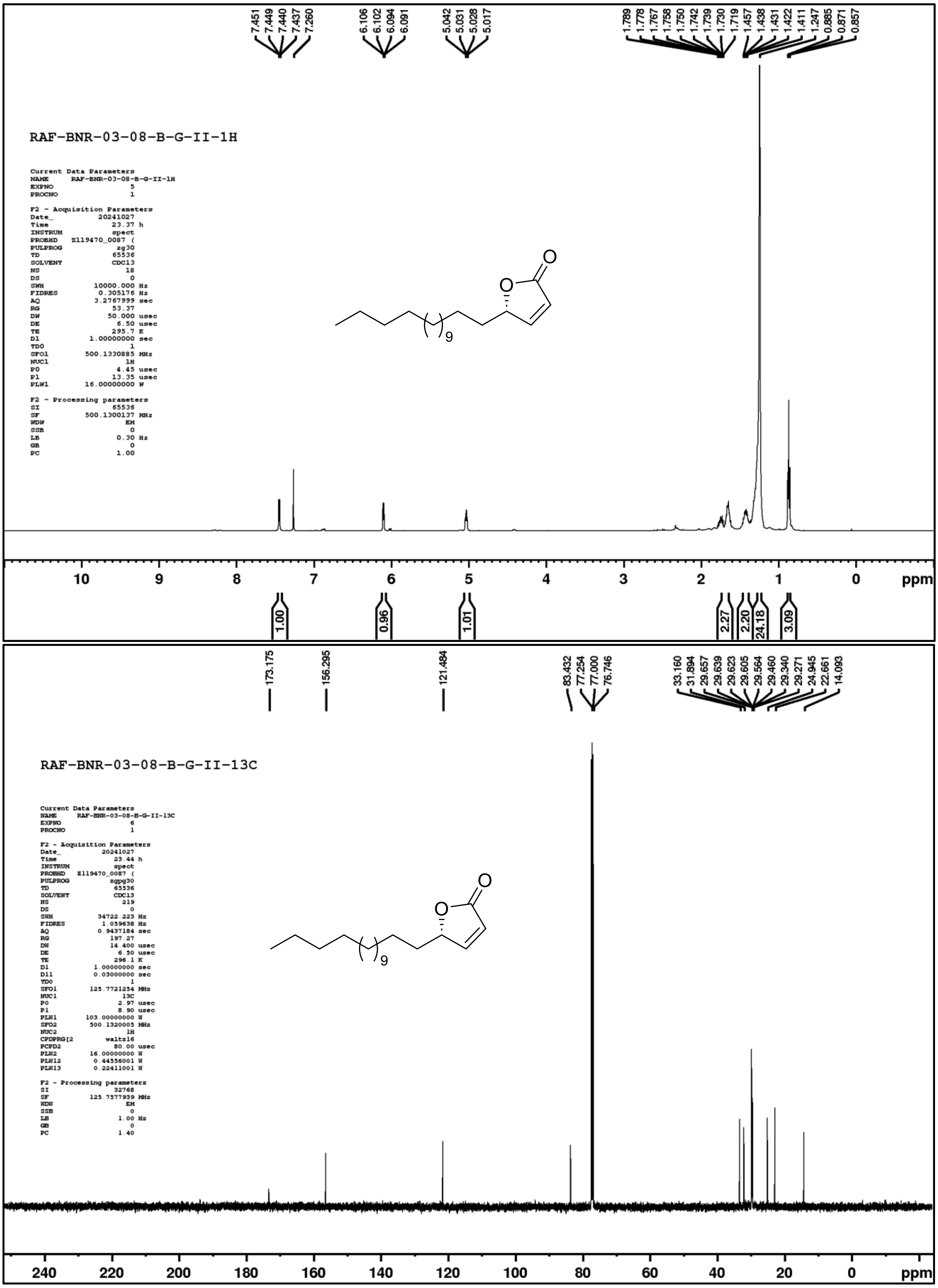
F2 - Acquisition Parameters
Date_                 20241022
Time                   20.28 h
INSTRUM   Avance Neo 400
PROBHD    Z163739_0226 (
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         273
DS                           2
SWH                  27777.777 Hz
FIDRES                0.847710 Hz
AQ                   1.1796480 sec
RG                         101
DW                      18.000 usec
DE                        6.50 usec
TE                       296.1 K
D1                  1.00000000 sec
D11                 0.03000000 sec
TD0                          1
SFO1               100.6242384 MHz
NUC1                       13C
P0                        2.67 usec
P1                        8.00 usec
PLW1              101.36000061 W
SFO2               400.1316005 MHz
NUC2                        1H
CPDPRG[2               waltz65
PCPD2                    90.00 usec
PLW2               22.88299942 W
PLW12               0.18080001 W
PLW13               0.09094300 W

F2 - Processing parameters
SI                       32768
SF                 100.6127716 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```

40b: HRMS (ESI-TOF) *m/z*: [M + NH$_4$]$^+$ Calcd for $C_{29}H_{47}O_6N_2$ 519.3429; Found: 519.3400



^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) of compound **41**



```
RAF-BNR-03-08-B-G-II-1H

Current Data Parameters
NAME      RAF-BNR-03-08-B-G-II-1H
EXPNO                    5
PROCNO                   1

F2 - Acquisition Parameters
Date_             20241027
Time                 23.37 h
INSTRUM              spect
PROBHD   Z119470_0087 (
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      18
DS                       0
SWH              10000.000 Hz
FIDRES            0.305176 Hz
AQ               3.2767999 sec
RG                   53.37
DW                  50.000 usec
DE                    6.50 usec
TE                   295.7 K
D1              1.00000000 sec
TD0                      1
SFO1           500.1330885 MHz
NUC1                    1H
P0                    4.45 usec
P1                   13.35 usec
PLW1           16.00000000 W

F2 - Processing parameters
SI                   65536
SF             500.1300137 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

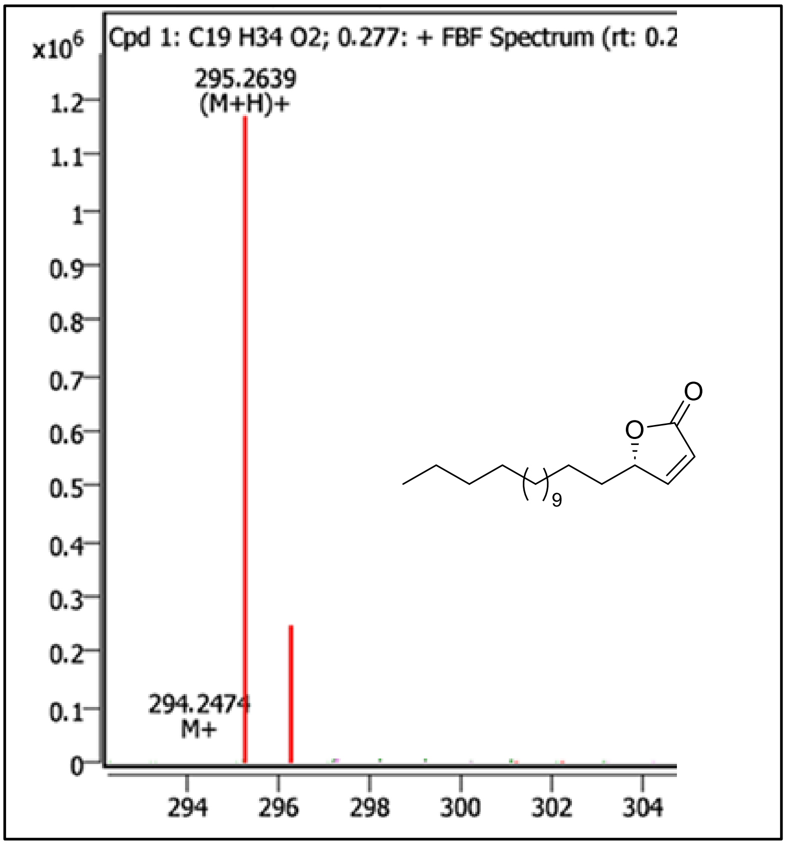
```
RAF-BNR-03-08-B-G-II-13C

Current Data Parameters
NAME      RAF-BNR-03-08-B-G-II-13C
EXPNO                    6
PROCNO                   1

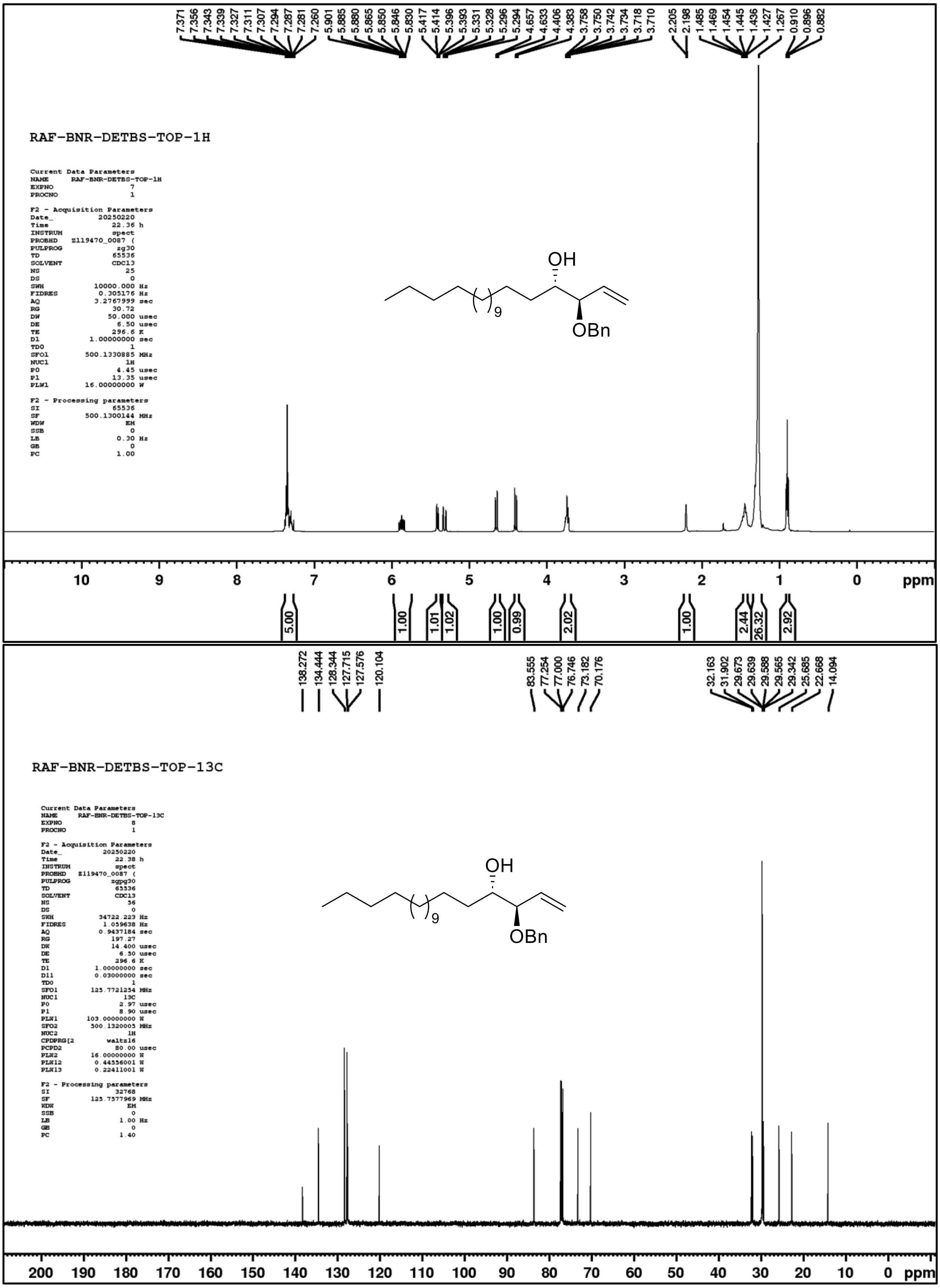
F2 - Acquisition Parameters
Date_             20241027
Time                 23.44 h
INSTRUM              spect
PROBHD   Z119470_0087 (
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     219
DS                       0
SWH              34722.223 Hz
FIDRES            1.059638 Hz
AQ               0.9437184 sec
RG                  197.27
DW                  14.400 usec
DE                    6.50 usec
TE                   296.1 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                      1
SFO1           125.7721254 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           16.00000000 W
PLW12           0.44556001 W
PLW13           0.22411001 W

F2 - Processing parameters
SI                   32768
SF             125.7577939 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

41: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{35}O_2$ 295.2633; Found: 295.2639



^1H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) of compound **31**



```
Current Data Parameters
NAME     RAF-BNR-DETBS-TOP-1H
EXPNO                       7
PROCNO                      1

F2 - Acquisition Parameters
Date_               20250220
Time                   22.36 h
INSTRUM                spect
PROBHD   Z119470_0087 (
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        25
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                     296.6 K
D1                1.00000000 sec
TD0                        1
SFO1             500.1330885 MHz
NUC1                      1H
P0                      4.45 usec
P1                     13.35 usec
PLW1             16.00000000 W

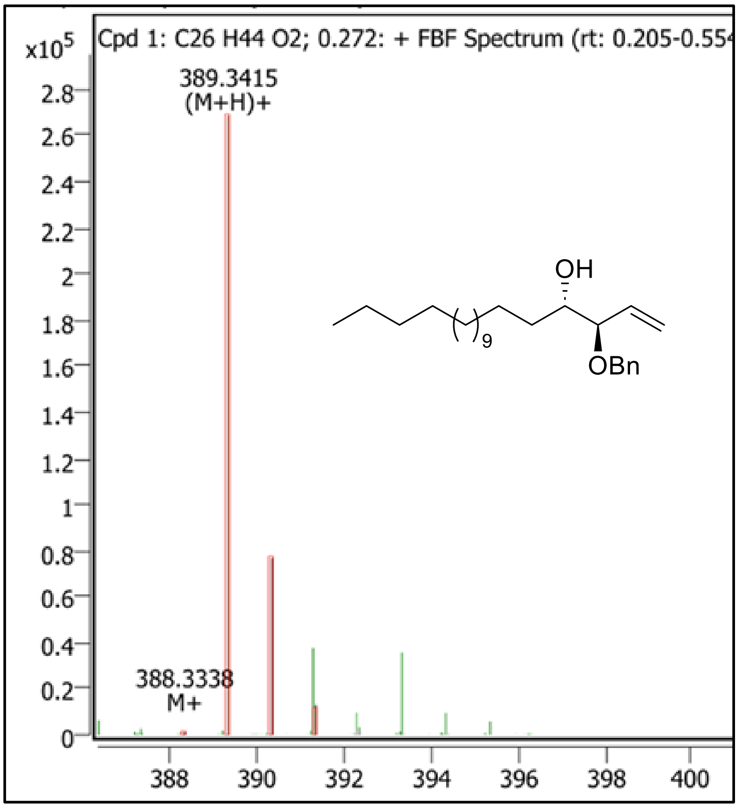
F2 - Processing parameters
SI                     65536
SF               500.1300144 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

```
Current Data Parameters
NAME     RAF-BNR-DETBS-TOP-13C
EXPNO                       8
PROCNO                      1

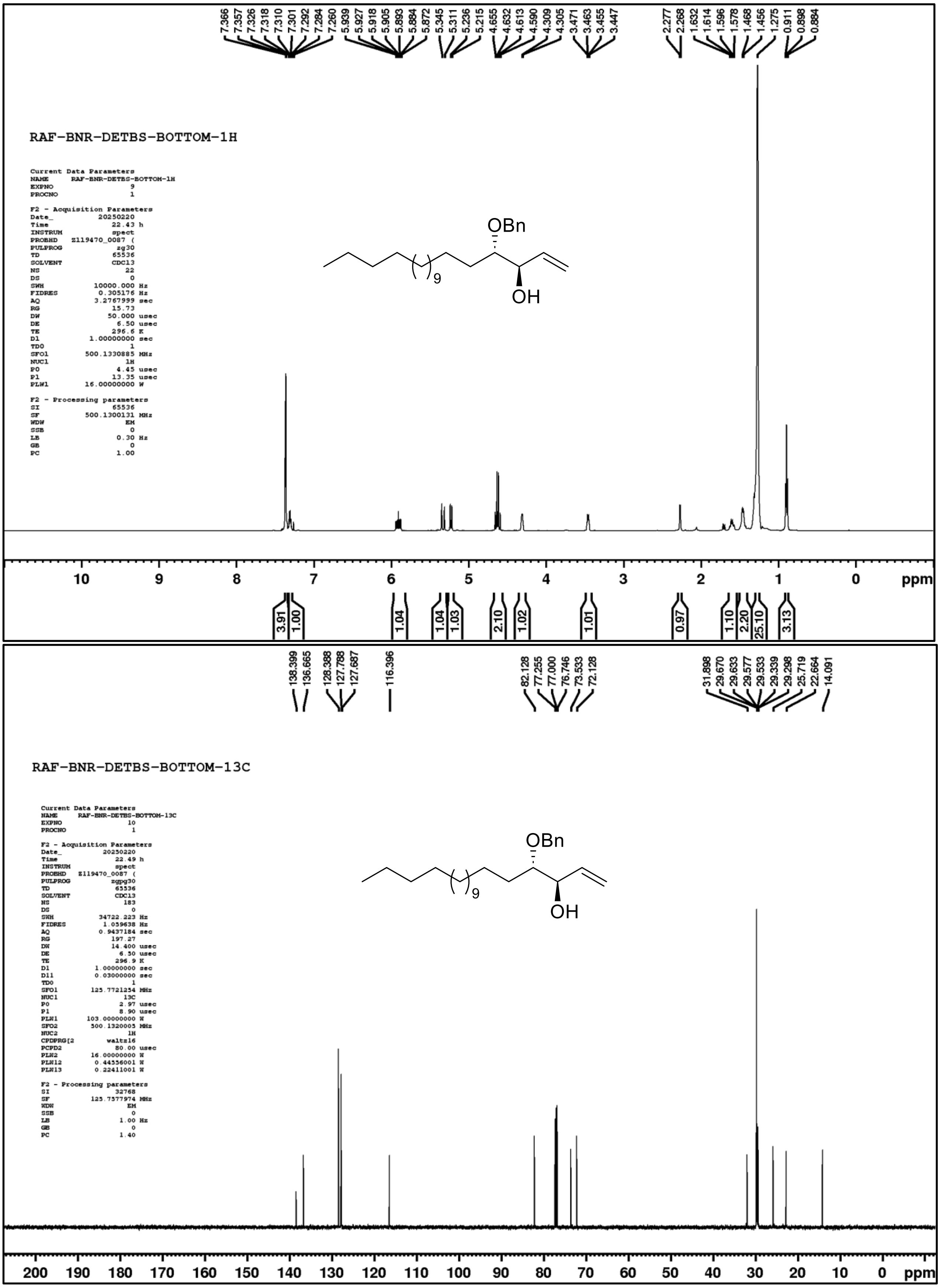
F2 - Acquisition Parameters
Date_               20250220
Time                   22.38 h
INSTRUM                spect
PROBHD   Z119470_0087 (
PULPROG               zgpg30
TD                     65536
SOLVENT                CDCl3
NS                        56
DS                         0
SWH                34722.223 Hz
FIDRES              1.059638 Hz
AQ                 0.9437184 sec
RG                    197.27
DW                    14.400 usec
DE                      6.50 usec
TE                     296.6 K
D1                1.00000000 sec
D11               0.03000000 sec
TD0                        1
SFO1             125.7721254 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             16.00000000 W
PLW12             0.44556001 W
PLW13             0.22411001 W

F2 - Processing parameters
SI                     32768
SF               125.7577969 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

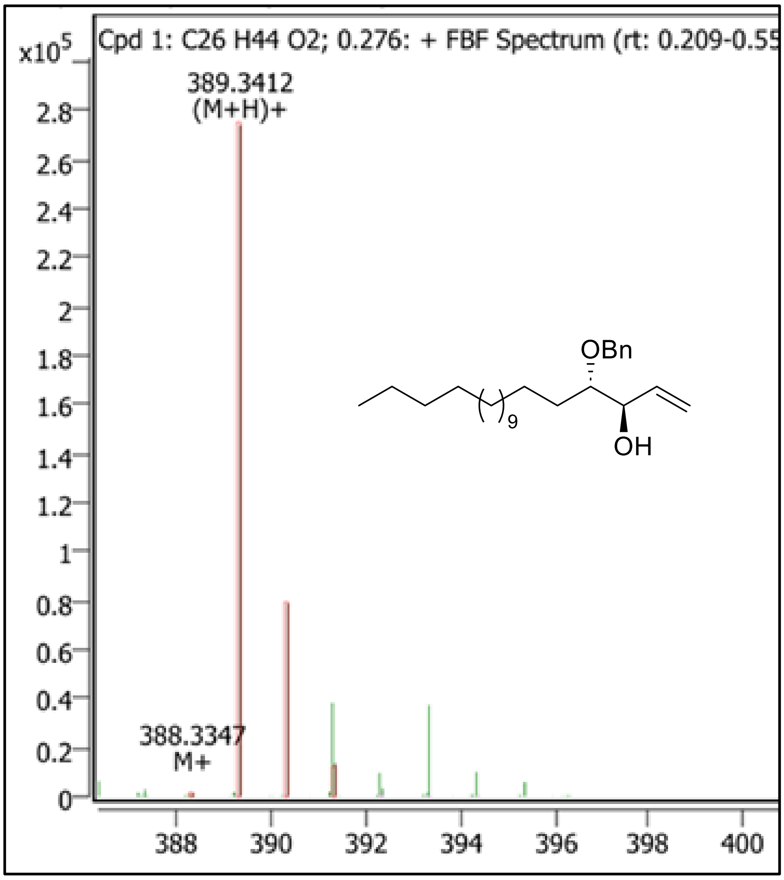
31: HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{26}H_{45}O_2$ 389.3414; Found: 389.3415



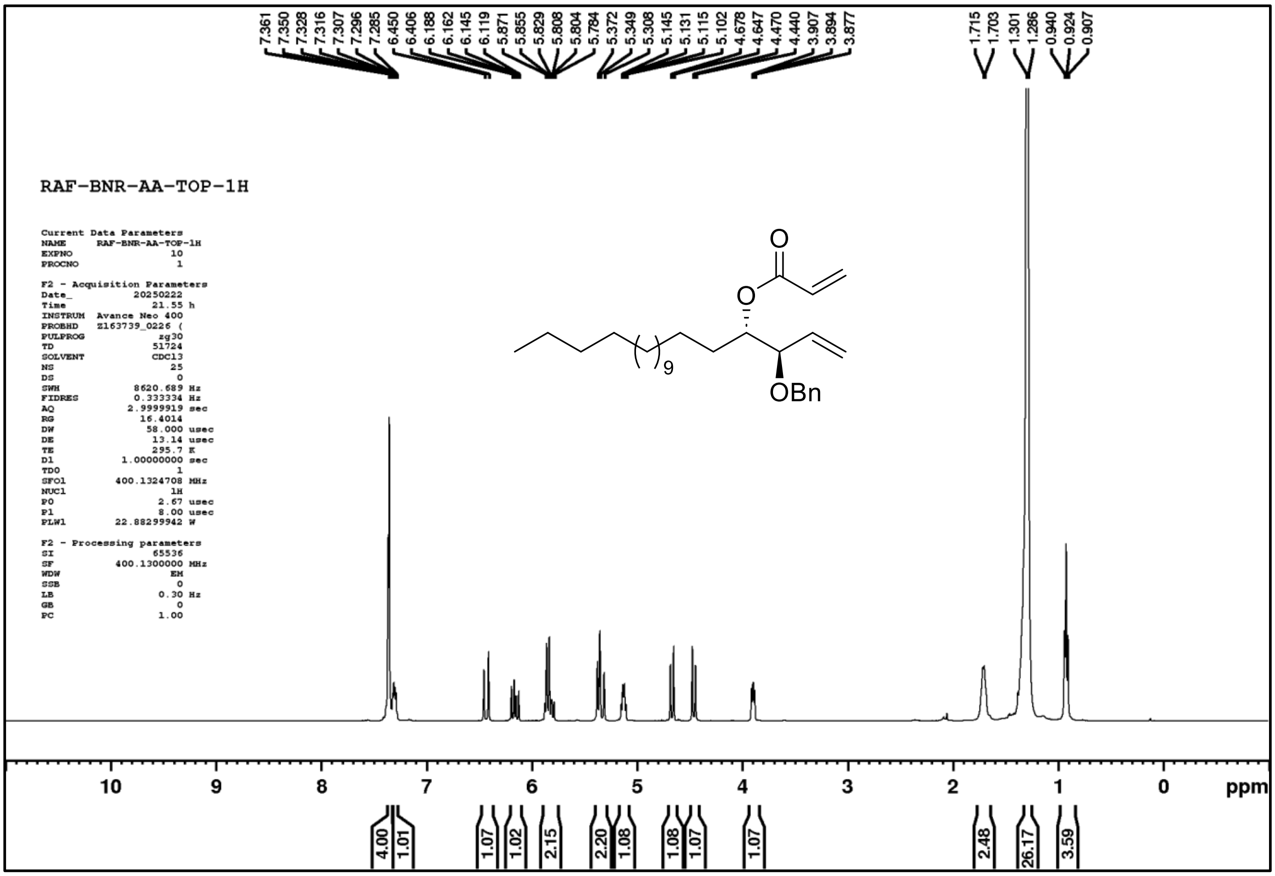
^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **44**

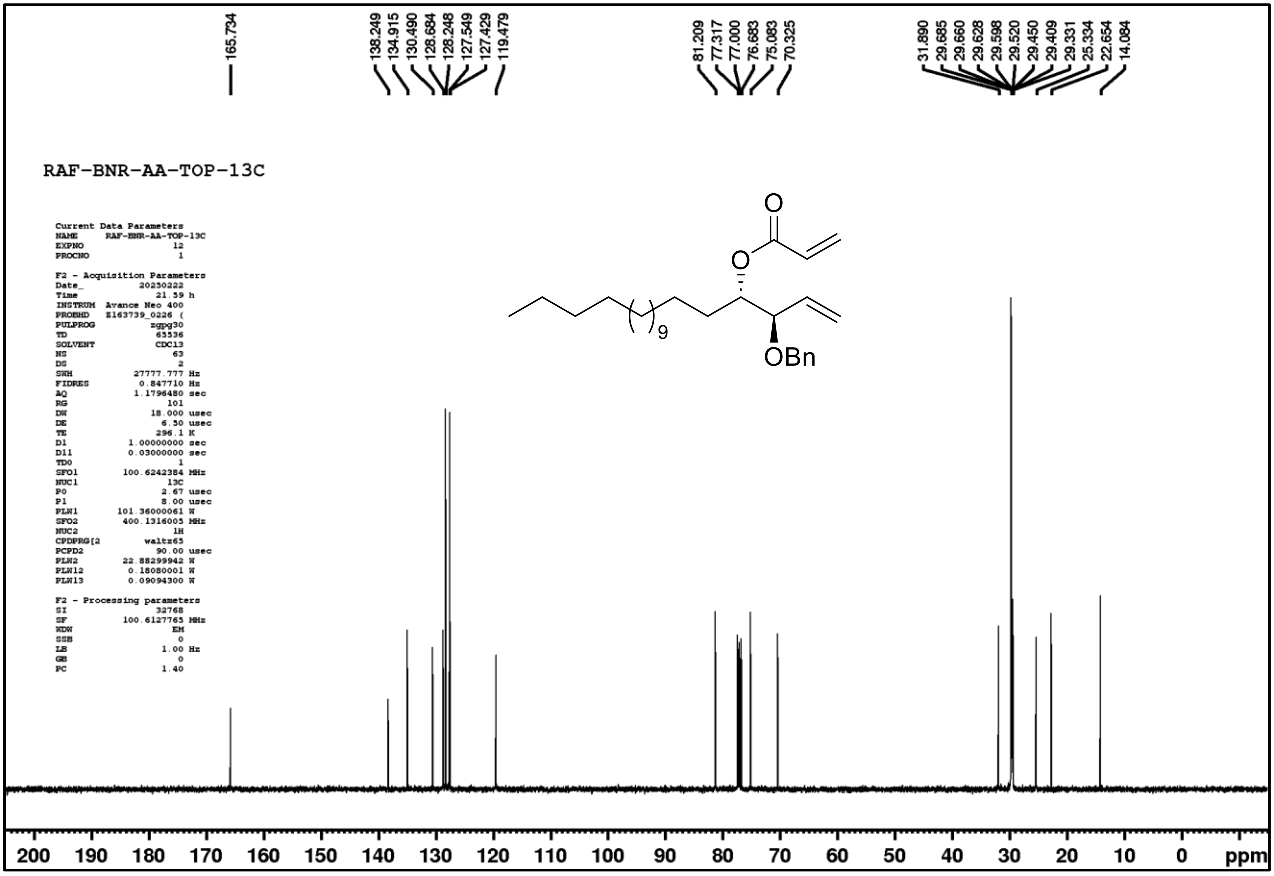


44: HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{26}H_{45}O_2$ 389.3414; Found: 389.3412

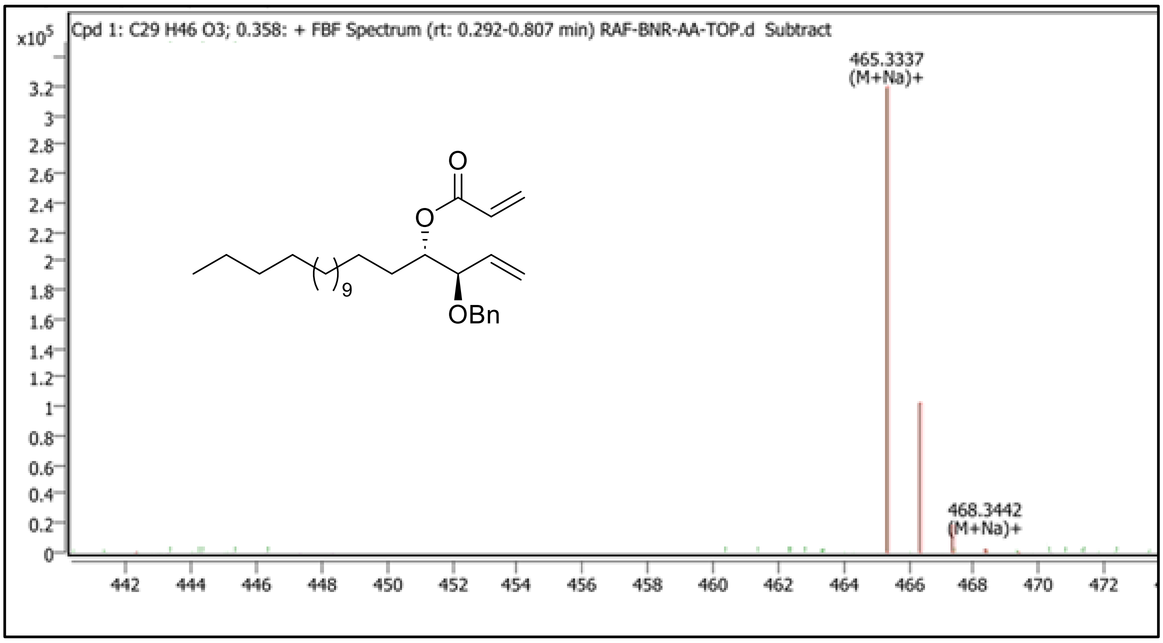


^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **45**

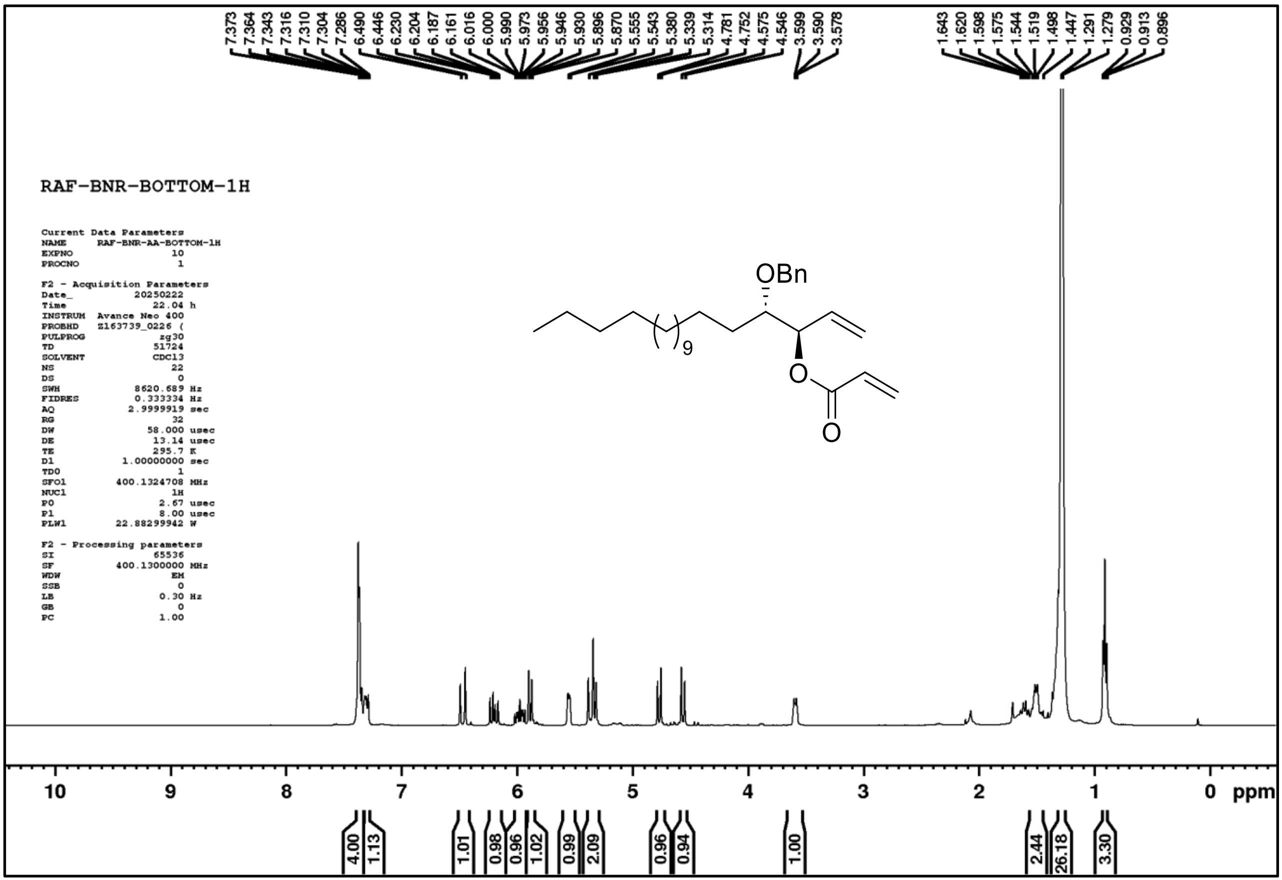




45: HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{29}H_{46}O_3Na$ 465.3340; Found: 465.3337



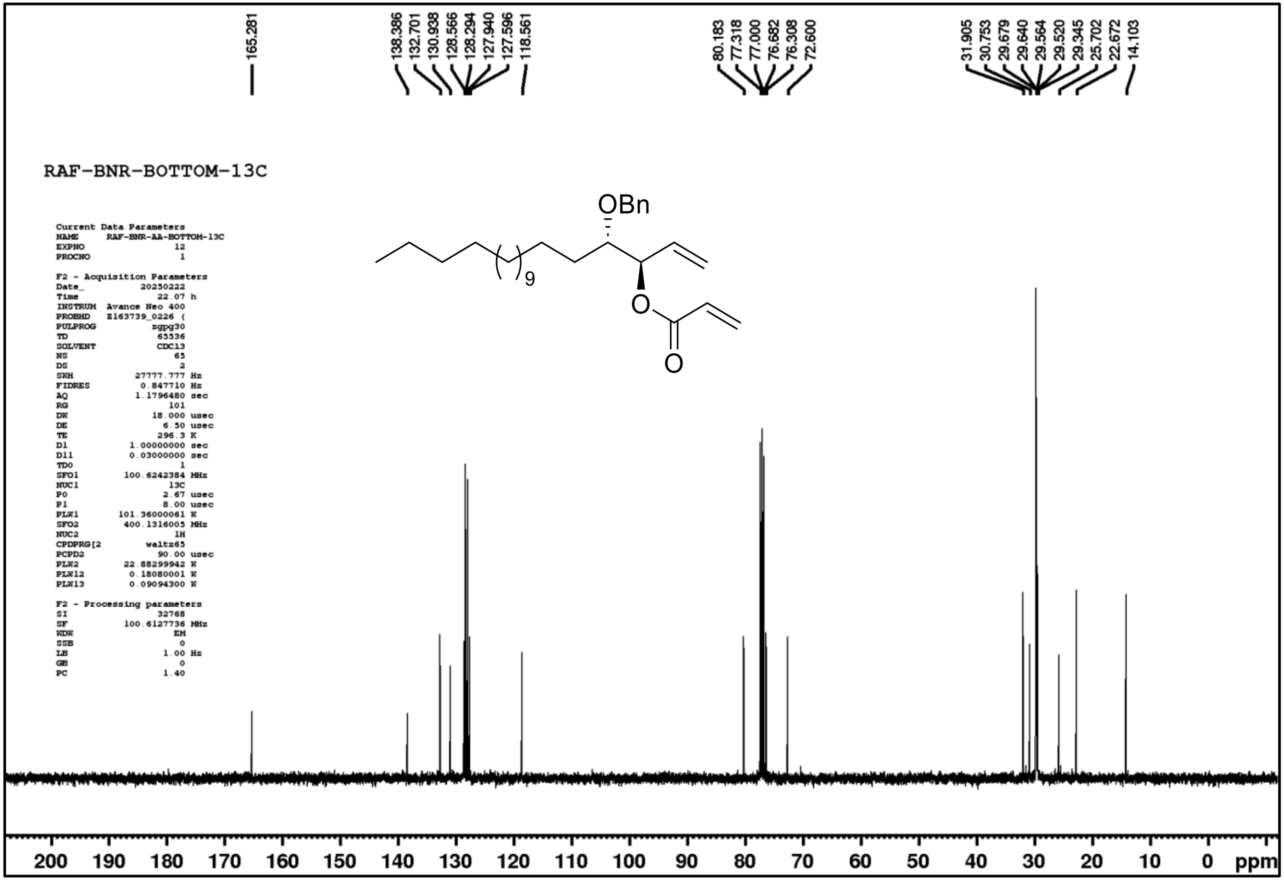
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **46**



```
Current Data Parameters
NAME     RAF-BNR-AA-BOTTOM-1H
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_            20250222
Time                22.04 h
INSTRUM  Avance Neo 400
PROBHD   Z163739_0226 (
PULPROG              zg30
TD                  51724
SOLVENT             CDCl3
NS                     22
DS                      0
SWH              8620.689 Hz
FIDRES           0.333334 Hz
AQ              2.9999919 sec
RG                     32
DW                 58.000 usec
DE                  13.14 usec
TE                  295.7 K
D1             1.00000000 sec
TD0                     1
SFO1          400.1324708 MHz
NUC1                   1H
P0                   2.67 usec
P1                   8.00 usec
PLW1          22.88299942 W

F2 - Processing parameters
SI                  65536
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

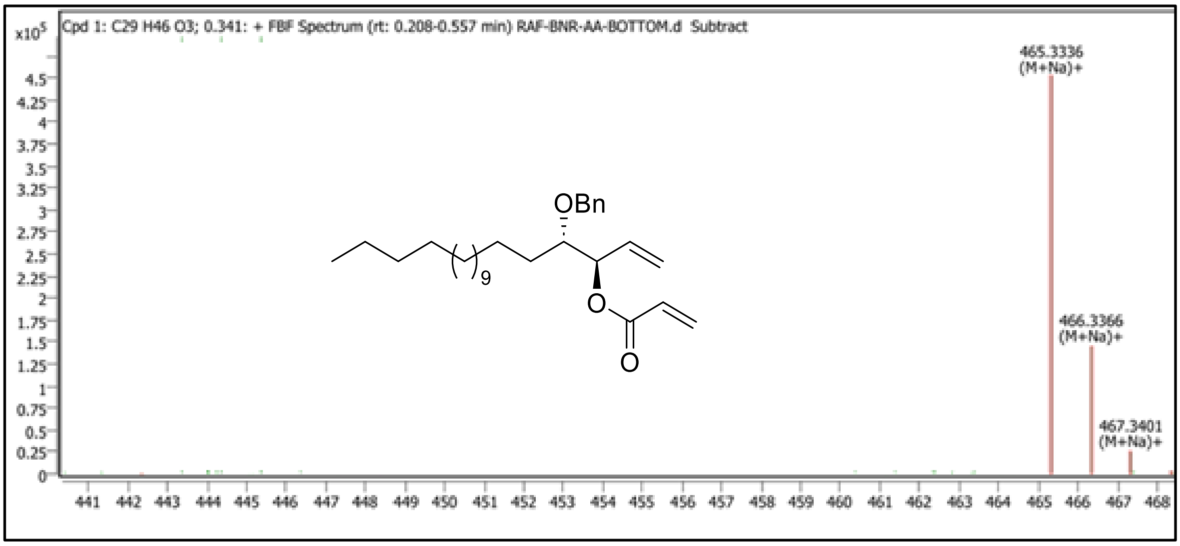


```
Current Data Parameters
NAME     RAF-BNR-AA-BOTTOM-13C
EXPNO                  12
PROCNO                  1

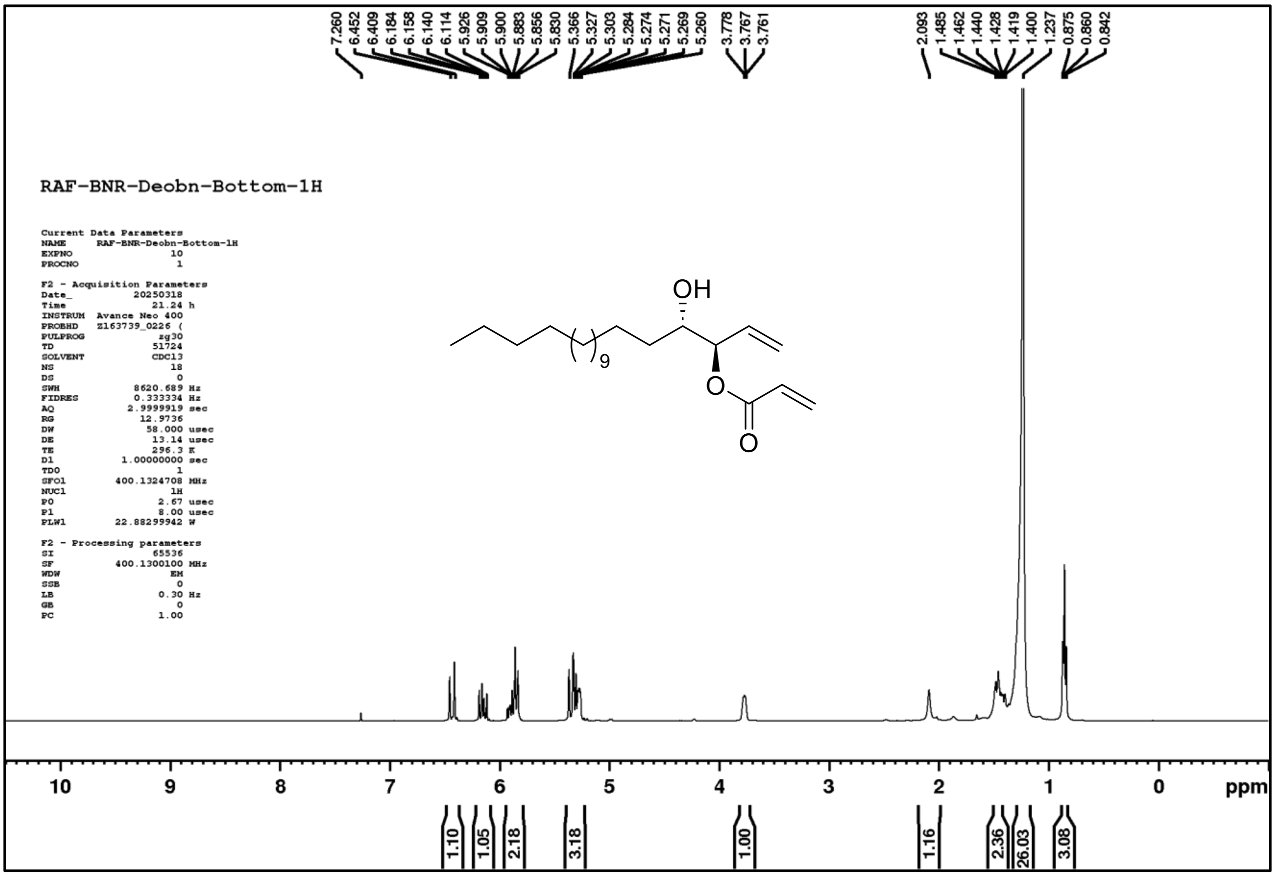
F2 - Acquisition Parameters
Date_            20250222
Time                22.07 h
INSTRUM  Avance Neo 400
PROBHD   Z163739_0226 (
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     65
DS                      2
SWH             27777.777 Hz
FIDRES           0.847710 Hz
AQ              1.1796480 sec
RG                    101
DW                 18.000 usec
DE                   6.50 usec
TE                  296.3 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                     1
SFO1          100.6242384 MHz
NUC1                  13C
P0                   2.67 usec
P1                   8.00 usec
PLW1         101.36000061 W
SFO2          400.1316005 MHz
NUC2                   1H
CPDPRG[2          waltz65
PCPD2               90.00 usec
PLW2          22.88299942 W
PLW12          0.18080001 W
PLW13          0.09094300 W

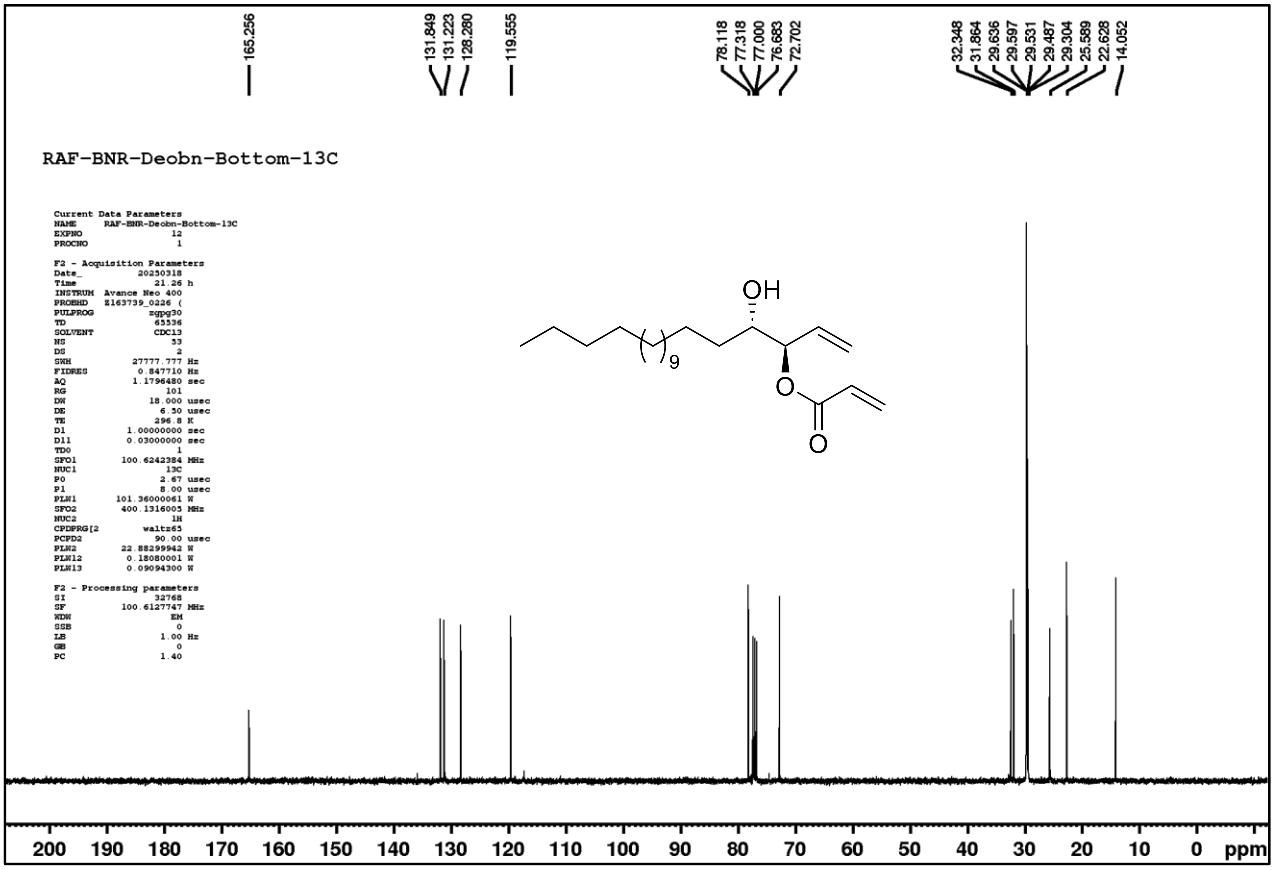
F2 - Processing parameters
SI                  32768
SF            100.6127736 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

46: HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{29}H_{46}O_3Na$ 465.3340; Found: 465.3336

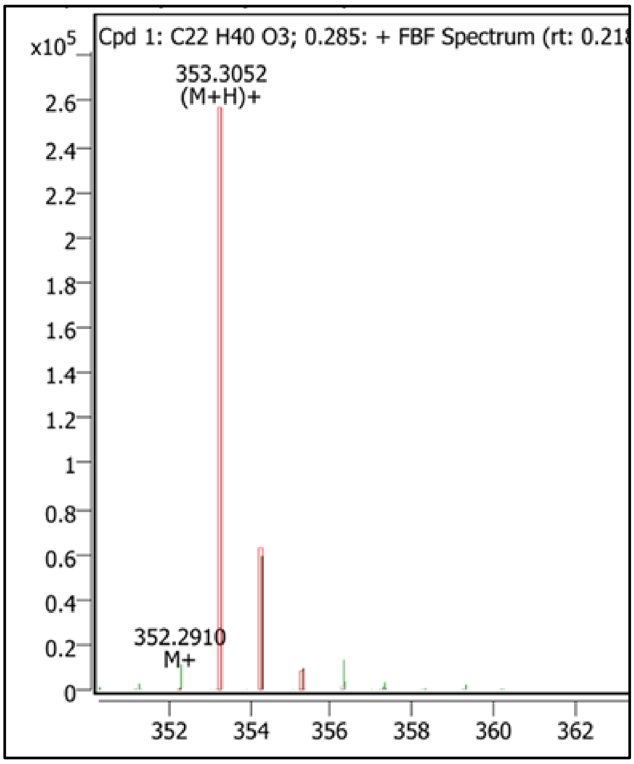


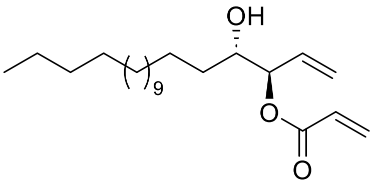
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **47**



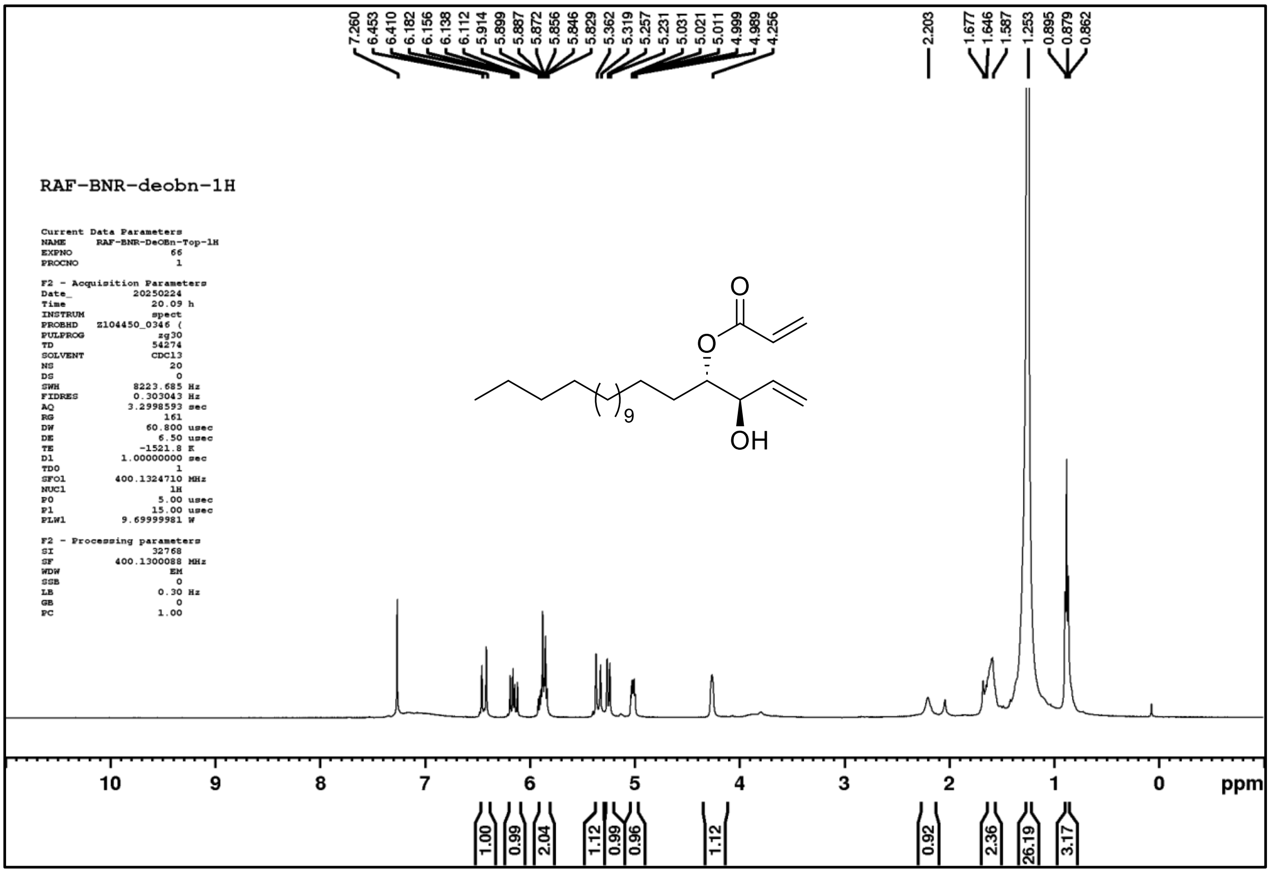


47: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{41}O_3$ 353.3051; Found: 353.3052





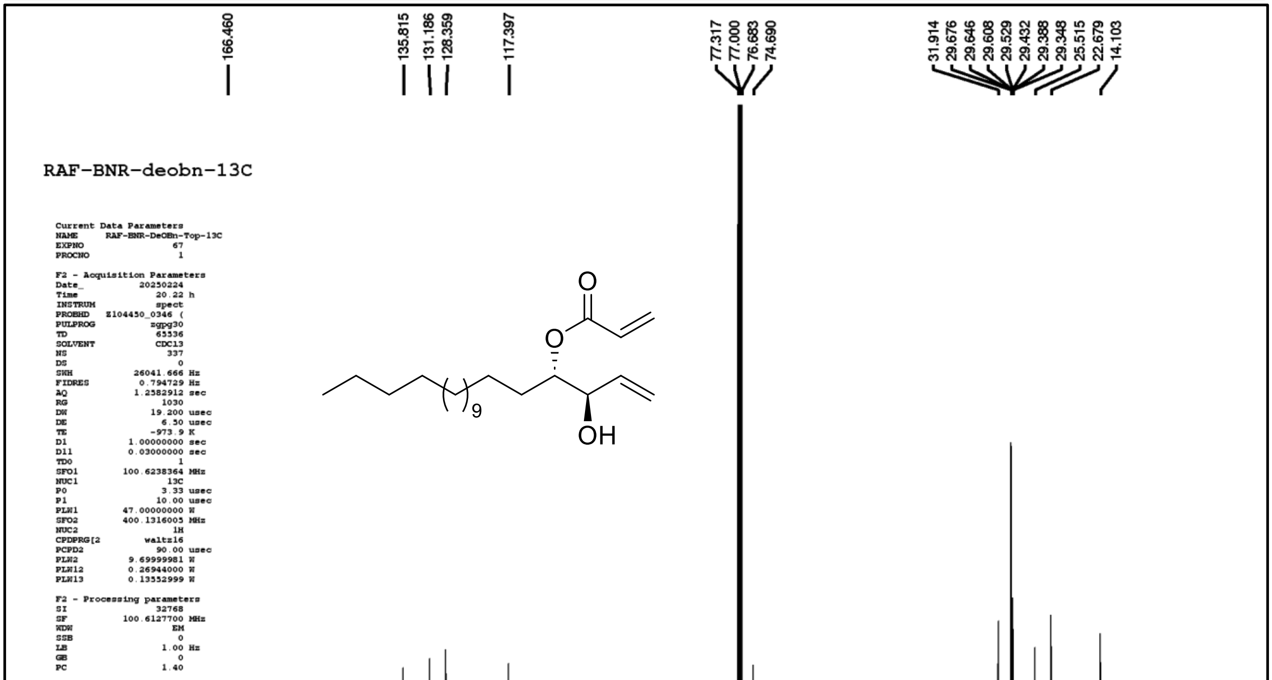
^1H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) of compound **36**



```
Current Data Parameters
NAME      RAF-BNR-DeOBn-Top-1H
EXPNO                   66
PROCNO                   1

F2 - Acquisition Parameters
Date_             20250224
Time                 20.09 h
INSTRUM              spect
PROBHD   Z104450_0346 (
PULPROG               zg30
TD                   54274
SOLVENT              CDCl3
NS                      20
DS                       0
SWH               8223.685 Hz
FIDRES            0.303043 Hz
AQ               3.2998593 sec
RG                     161
DW                  60.800 usec
DE                    6.50 usec
TE                 -1521.8 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             400.1300088 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

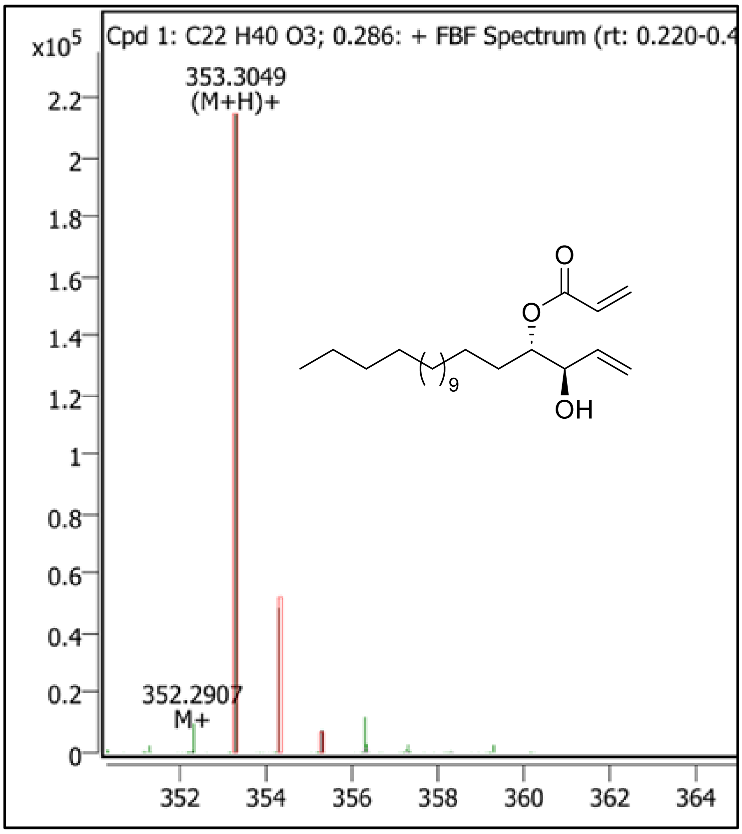


```
Current Data Parameters
NAME      RAF-BNR-DeOBn-Top-13C
EXPNO                   67
PROCNO                   1

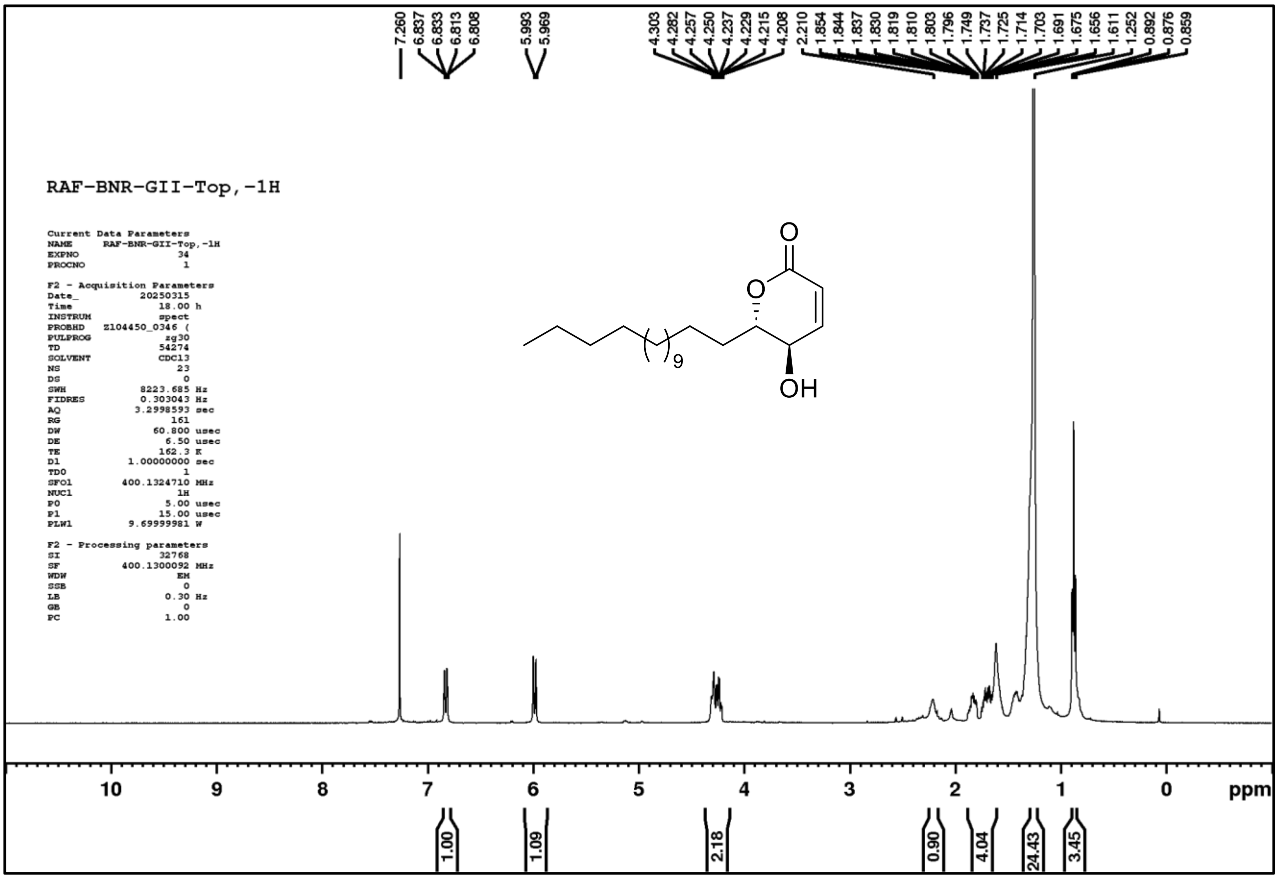
F2 - Acquisition Parameters
Date_             20250224
Time                 20.22 h
INSTRUM              spect
PROBHD   Z104450_0346 (
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     337
DS                       0
SWH              26041.666 Hz
FIDRES            0.794729 Hz
AQ               1.2582912 sec
RG                    1030
DW                  19.200 usec
DE                    6.50 usec
TE                  -973.9 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

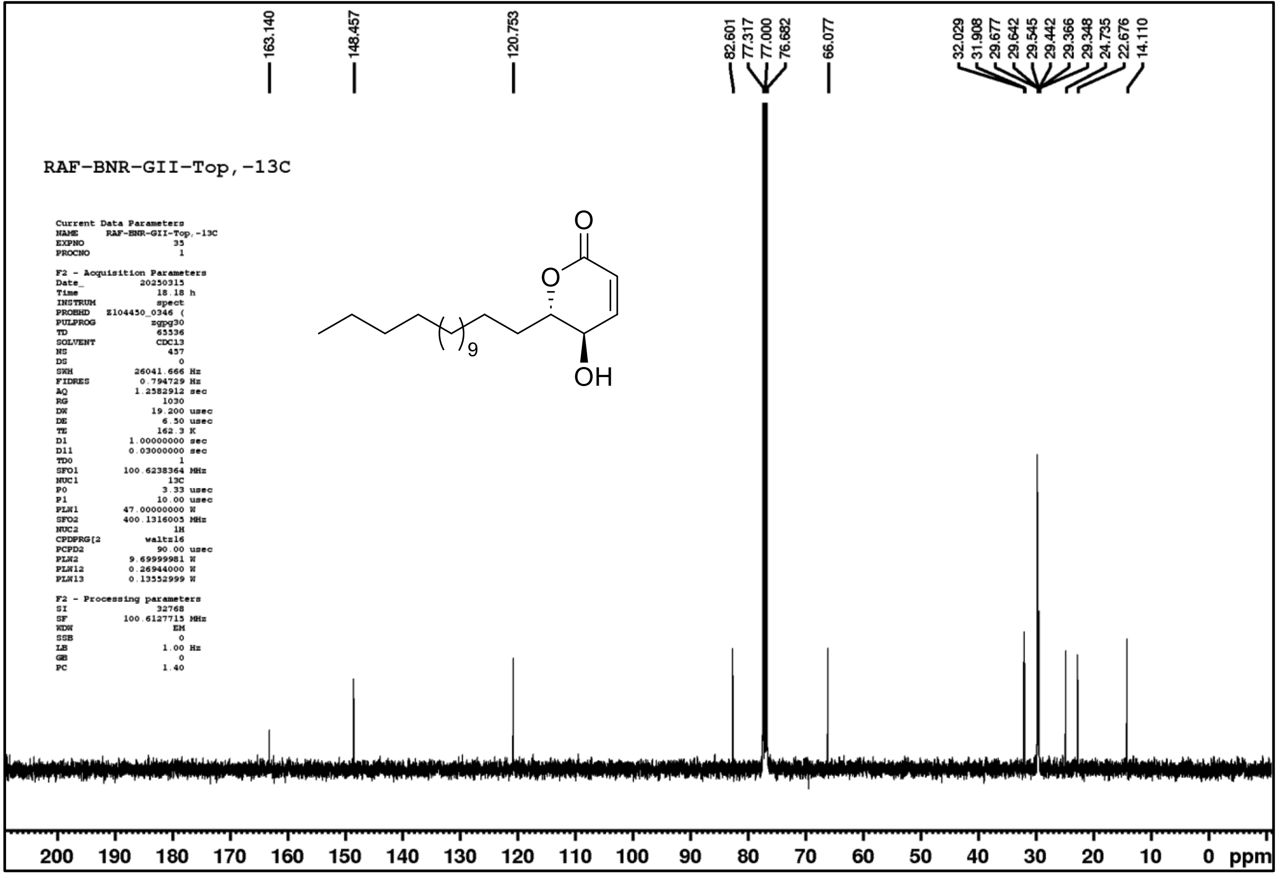
F2 - Processing parameters
SI                   32768
SF             100.6127700 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

36: HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{22}H_{41}O_3$ 353.3051; Found: 353.3049

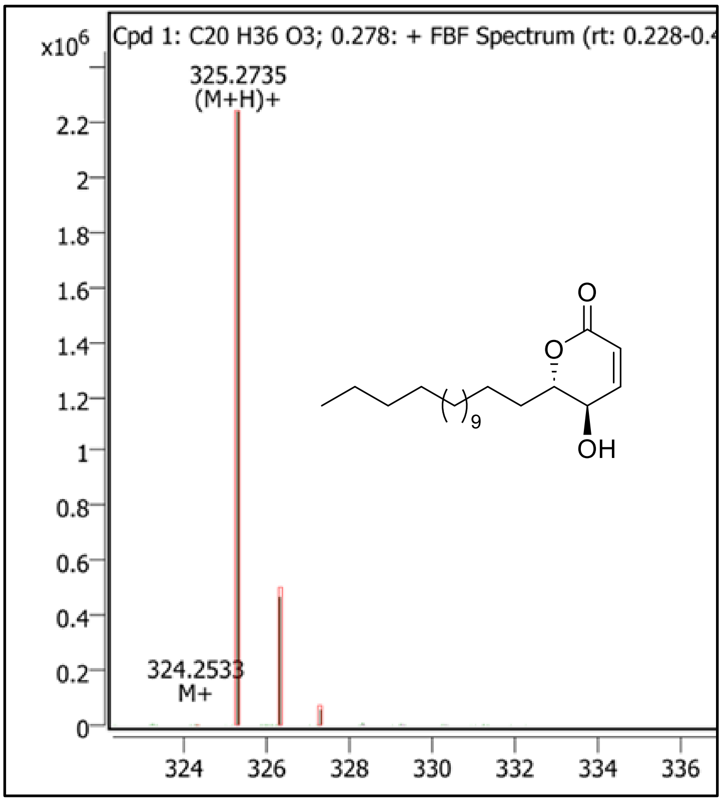


^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **48**

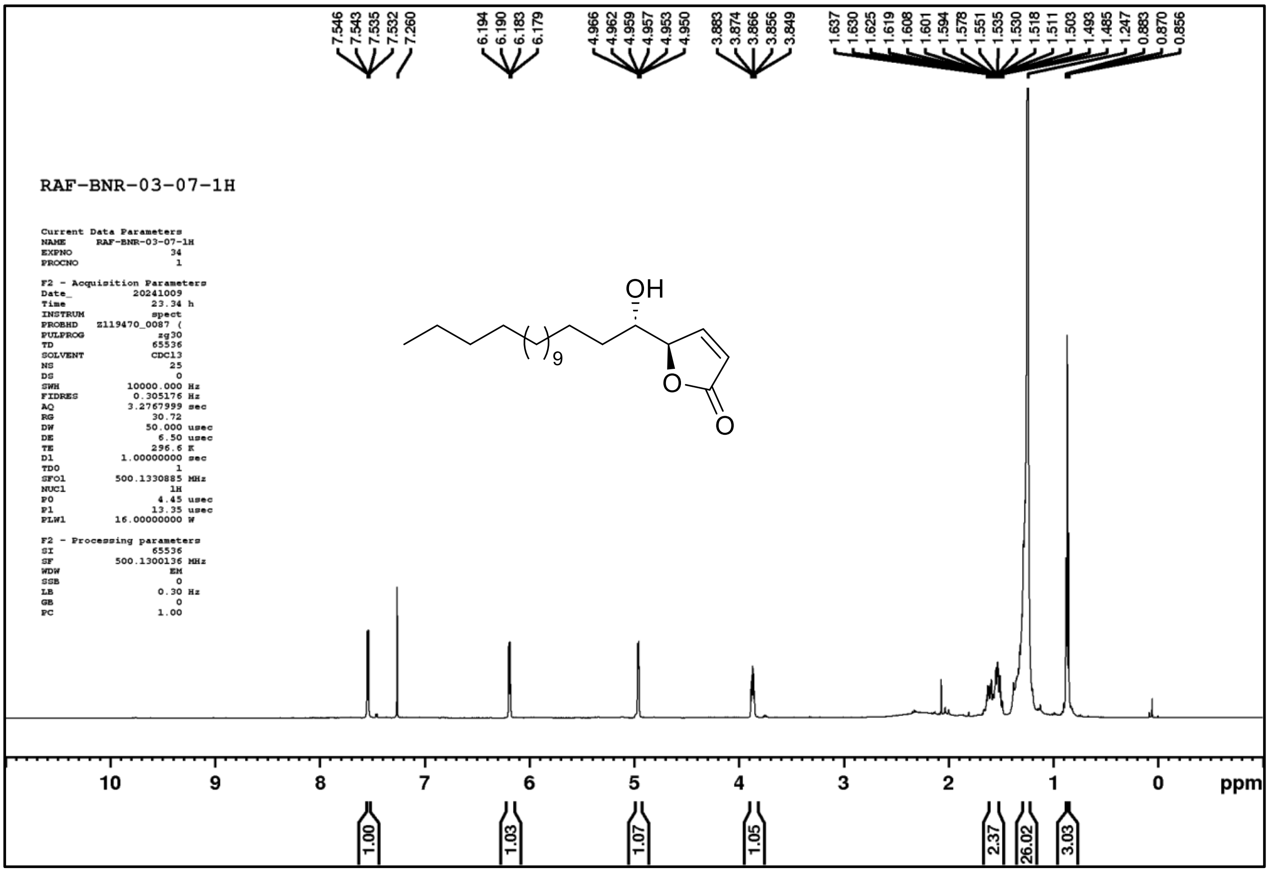




48: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{37}O_3$ 325.2738; Found: 325.2735



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

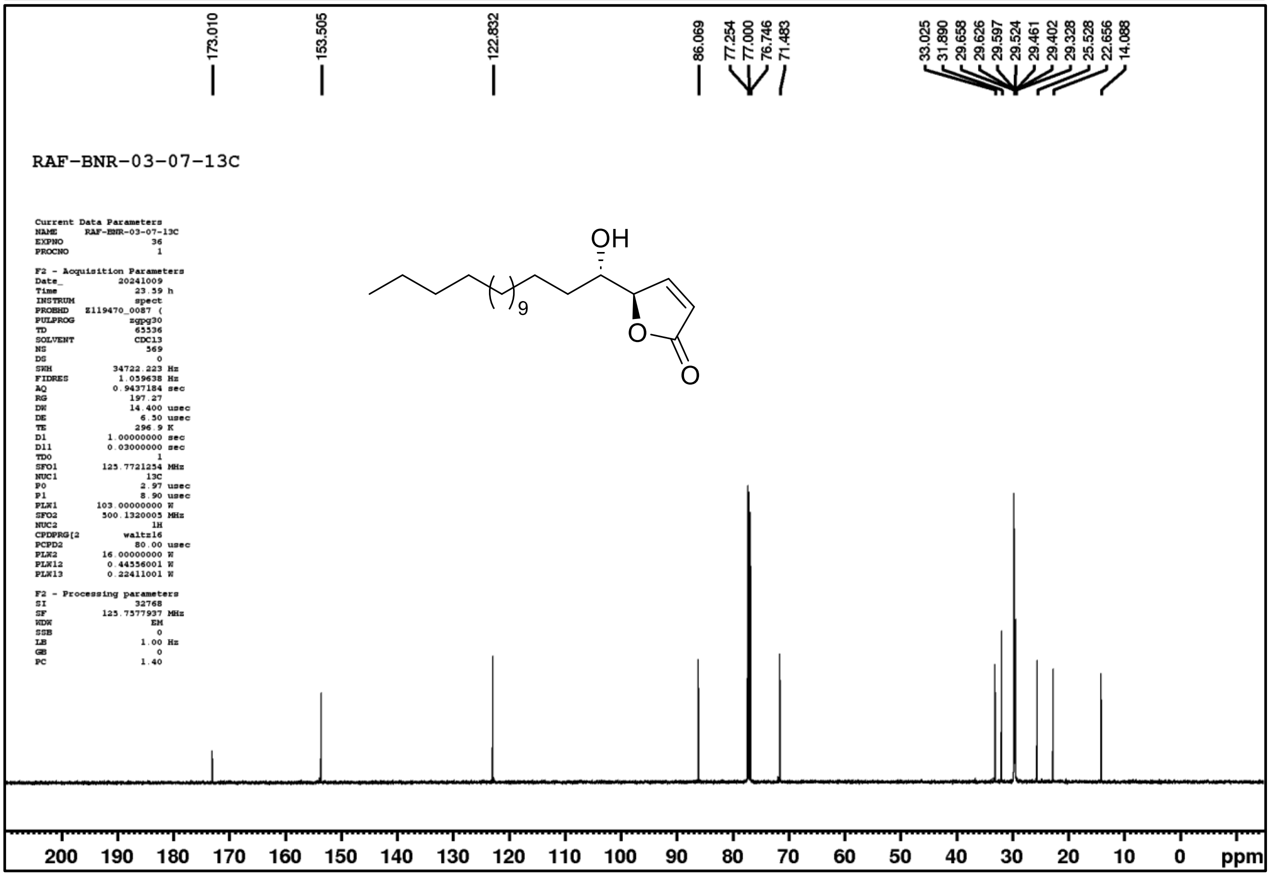


```
RAF-BNR-03-07-1H

Current Data Parameters
NAME      RAF-BNR-03-07-1H
EXPNO                   34
PROCNO                   1

F2 - Acquisition Parameters
Date_             20241009
Time                 23.34 h
INSTRUM              spect
PROBHD   Z119470_0087 (
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      25
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                   296.6 K
D1              1.00000000 sec
TD0                      1
SFO1           500.1330885 MHz
NUC1                    1H
P0                    4.45 usec
P1                   13.35 usec
PLW1           16.00000000 W

F2 - Processing parameters
SI                   65536
SF             500.1300136 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



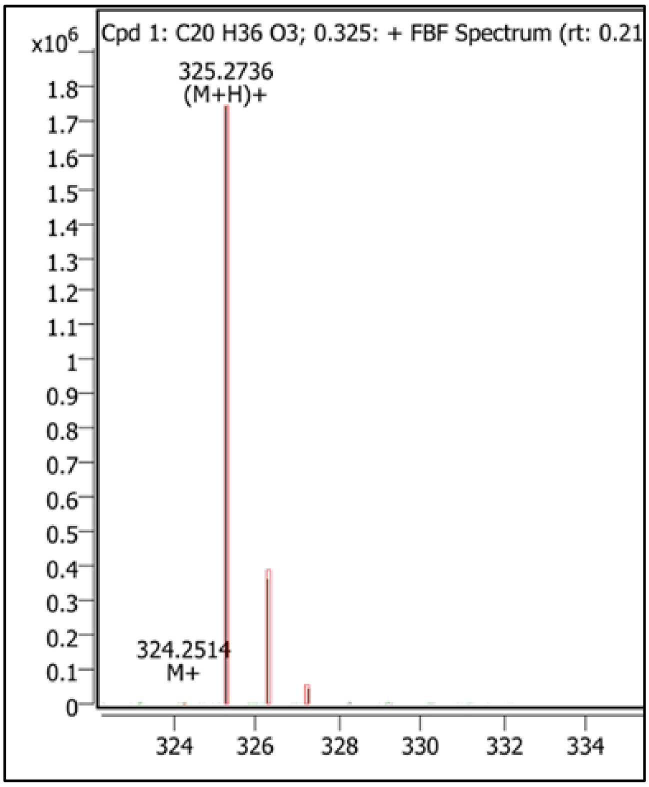
```
RAF-BNR-03-07-13C

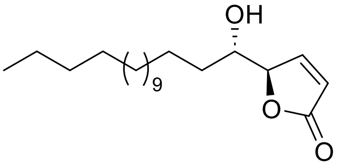
Current Data Parameters
NAME      RAF-BNR-03-07-13C
EXPNO                   36
PROCNO                   1

F2 - Acquisition Parameters
Date_             20241009
Time                 23.59 h
INSTRUM              spect
PROBHD   Z119470_0087 (
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     569
DS                       0
SWH              34722.223 Hz
FIDRES            1.059638 Hz
AQ               0.9437184 sec
RG                  197.27
DW                  14.400 usec
DE                    6.50 usec
TE                   296.9 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                      1
SFO1           125.7721254 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           16.00000000 W
PLW12           0.44556001 W
PLW13           0.22411001 W

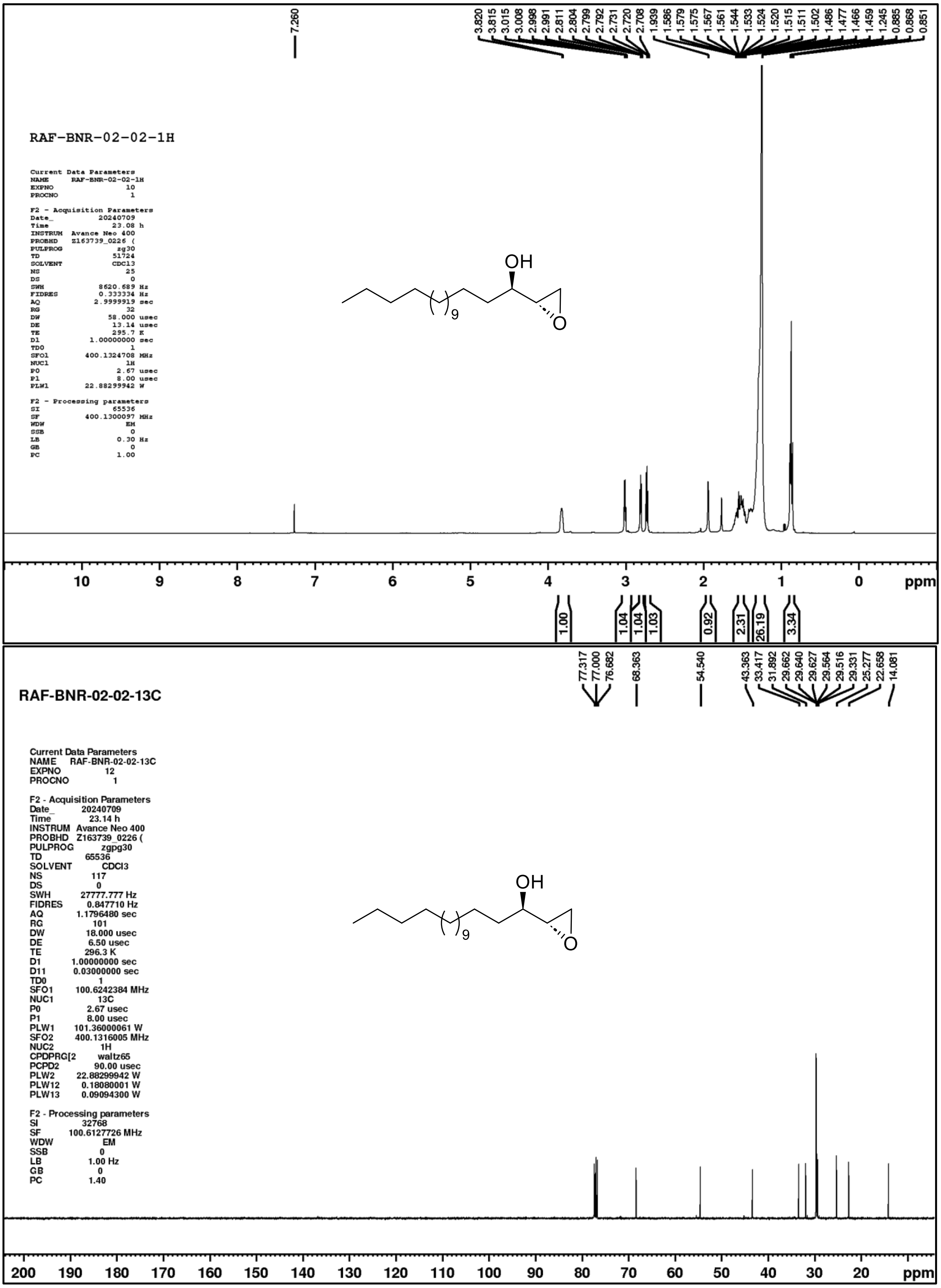
F2 - Processing parameters
SI                   32768
SF             125.7577937 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

***ent*-1e**: HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{20}H_{37}O_3$ 325.2738; Found: 325.2736

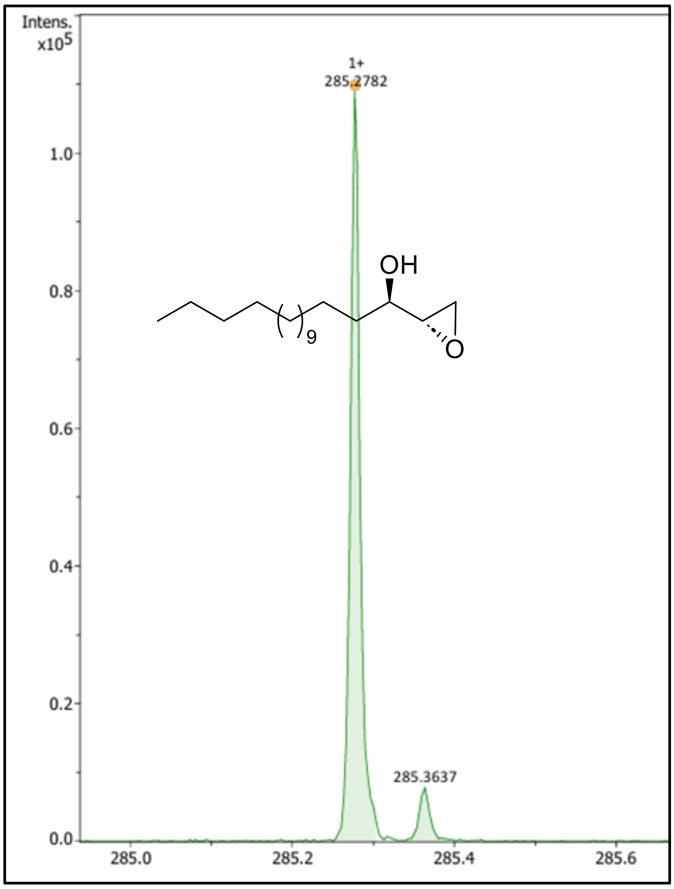




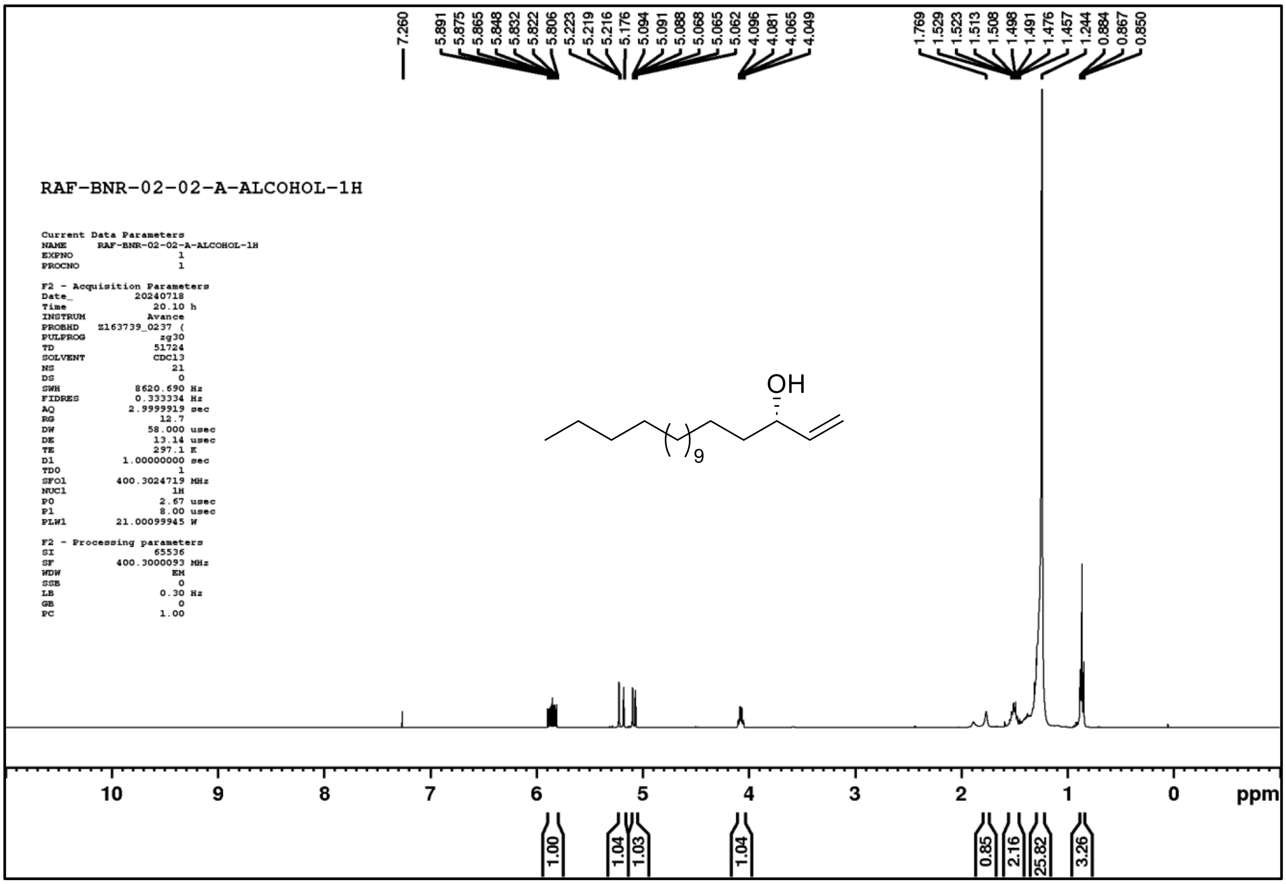
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound ***ent*-32**



***ent*-32**: HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{18}H_{37}O_2$ 285.2788; Found: 285.2782



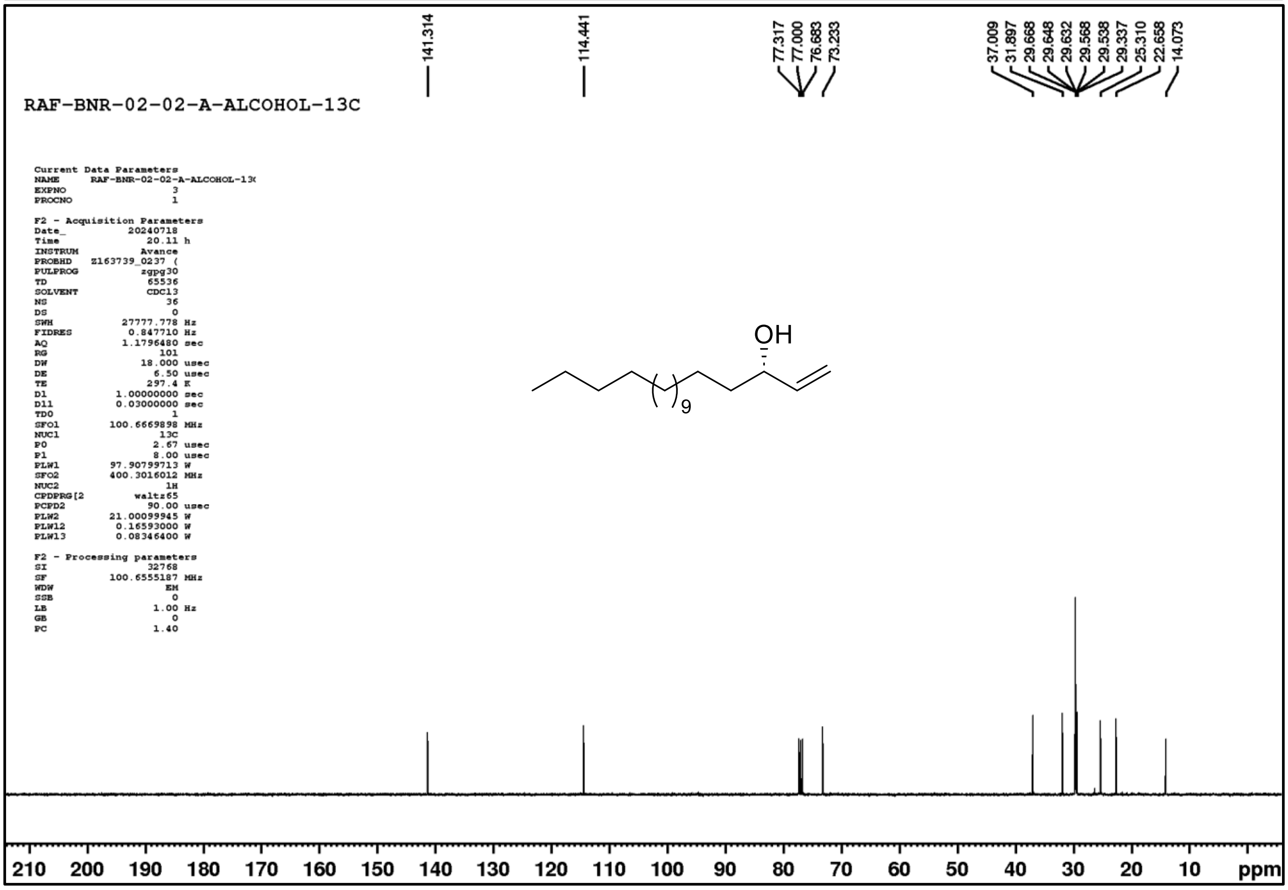
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound ***ent*-32'**



```
Current Data Parameters
NAME      RAF-BNR-02-02-A-ALCOHOL-1H
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20240718
Time                 20.10 h
INSTRUM             Avance
PROBHD    Z163739_0237 (
PULPROG               zg30
TD                   51724
SOLVENT              CDCl3
NS                      21
DS                       0
SWH               8620.690 Hz
FIDRES            0.333334 Hz
AQ               2.9999919 sec
RG                    12.7
DW                  58.000 usec
DE                   13.14 usec
TE                   297.1 K
D1              1.00000000 sec
TD0                      1
SFO1           400.3024719 MHz
NUC1                    1H
P0                    2.67 usec
P1                    8.00 usec
PLW1           21.00099945 W

F2 - Processing parameters
SI                   65536
SF             400.3000093 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

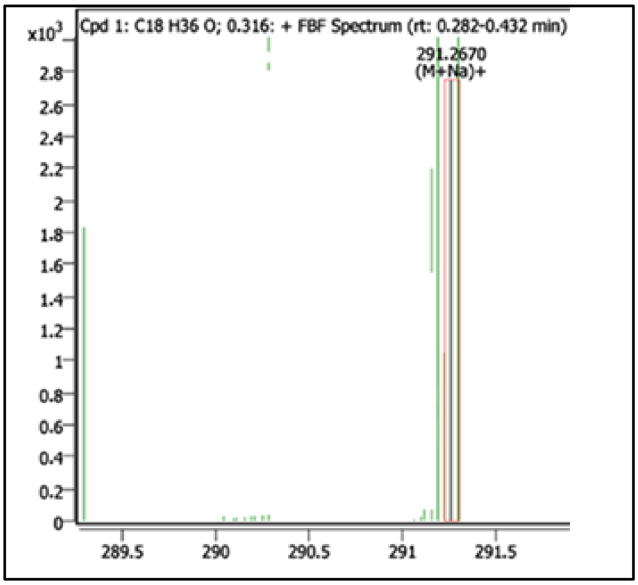


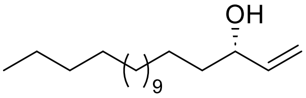
```
Current Data Parameters
NAME      RAF-BNR-02-02-A-ALCOHOL-13C
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_             20240718
Time                 20.11 h
INSTRUM             Avance
PROBHD    Z163739_0237 (
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      36
DS                       0
SWH              27777.778 Hz
FIDRES            0.847710 Hz
AQ               1.1796480 sec
RG                     101
DW                  18.000 usec
DE                    6.50 usec
TE                   297.4 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           97.90799713 W
SFO2           400.3016012 MHz
NUC2                    1H
CPDPRG[2           waltz65
PCPD2                90.00 usec
PLW2           21.00099945 W
PLW12           0.16593000 W
PLW13           0.08346400 W

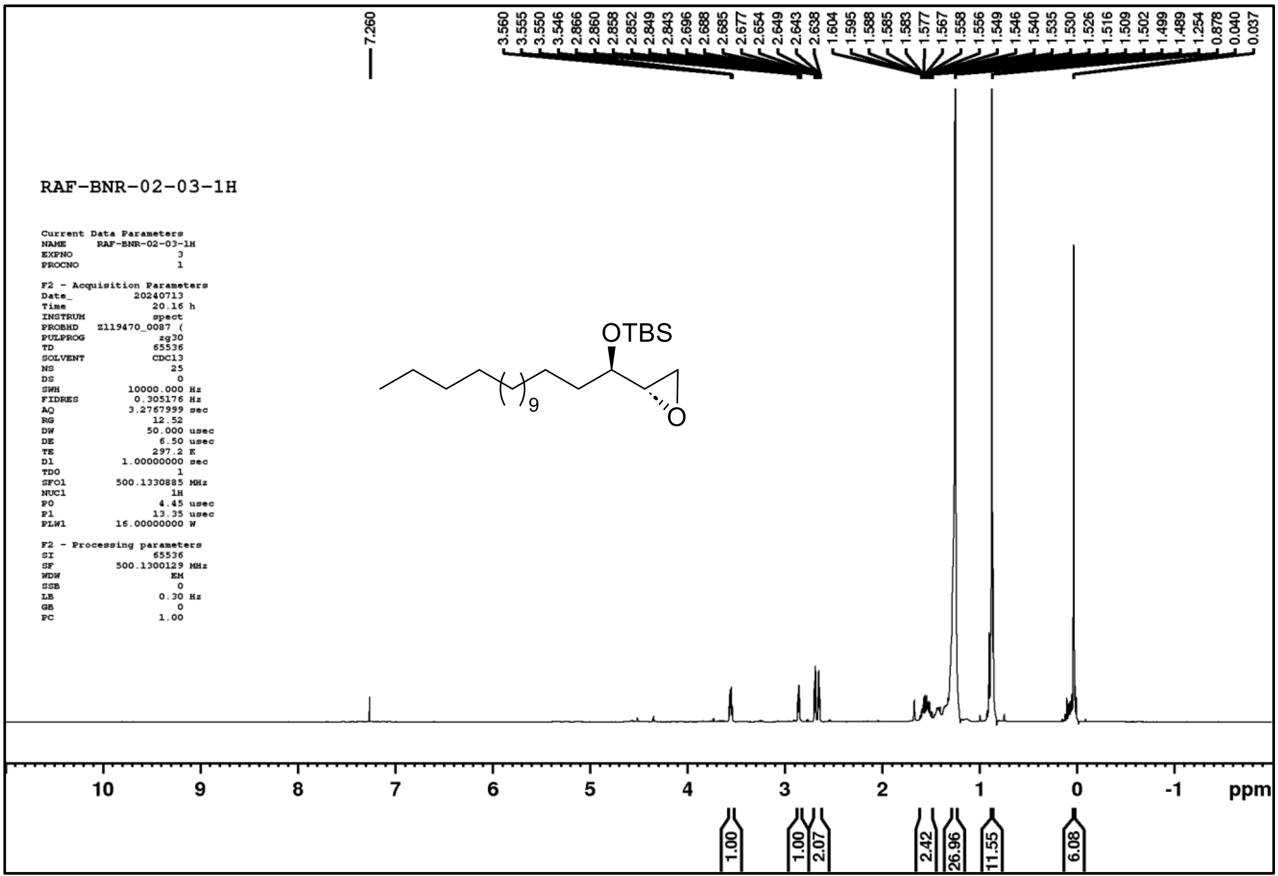
F2 - Processing parameters
SI                   32768
SF             100.6555187 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

***ent*-32'**: HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{18}H_{36}ONa$ 291.2659; Found: 291.2670





^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) of compound ***ent*-38**

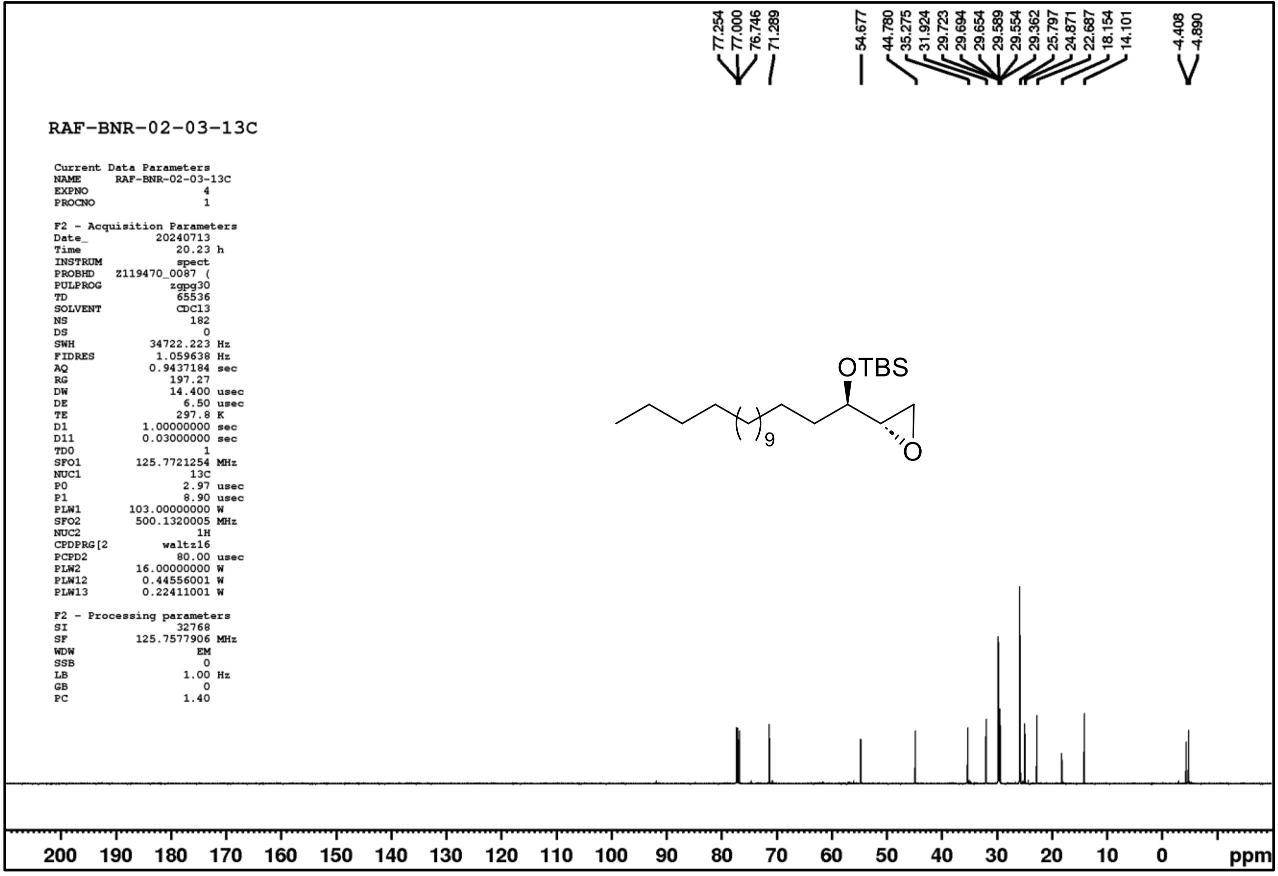


```
RAF-BNR-02-03-1H

Current Data Parameters
NAME      RAF-BNR-02-03-1H
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_             20240713
Time                 20.16 h
INSTRUM              spect
PROBHD    Z119470_0087 (
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      25
DS                       0
SWH              10000.000 Hz
FIDRES            0.305176 Hz
AQ               3.2767999 sec
RG                   12.52
DW                  50.000 usec
DE                    6.50 usec
TE                   297.2 K
D1              1.00000000 sec
TD0                      1
SFO1           500.1330885 MHz
NUC1                    1H
P0                    4.45 usec
P1                   13.35 usec
PLW1           16.00000000 W

F2 - Processing parameters
SI                   65536
SF             500.1300129 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



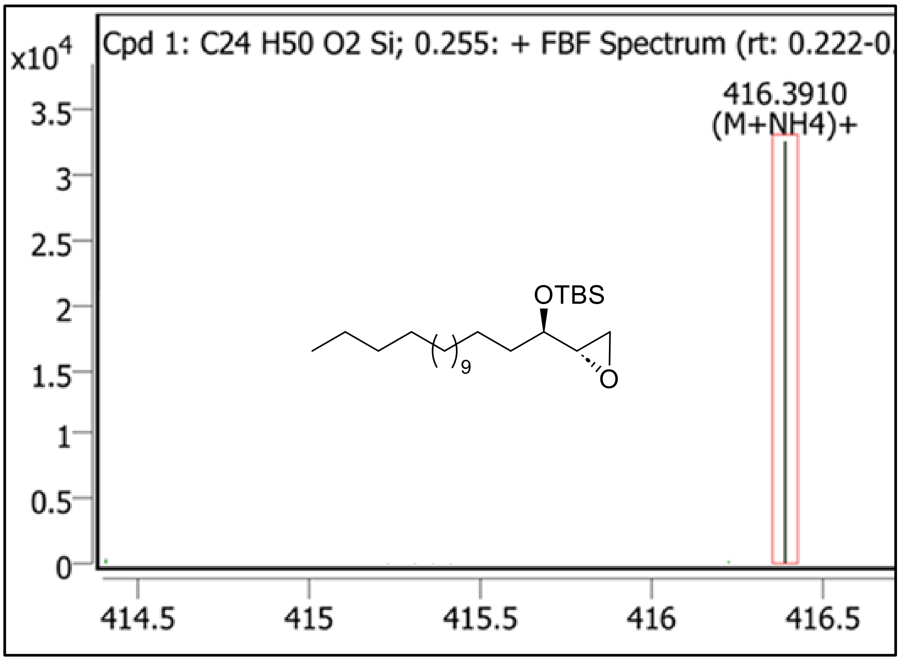
```
RAF-BNR-02-03-13C

Current Data Parameters
NAME      RAF-BNR-02-03-13C
EXPNO                    4
PROCNO                   1

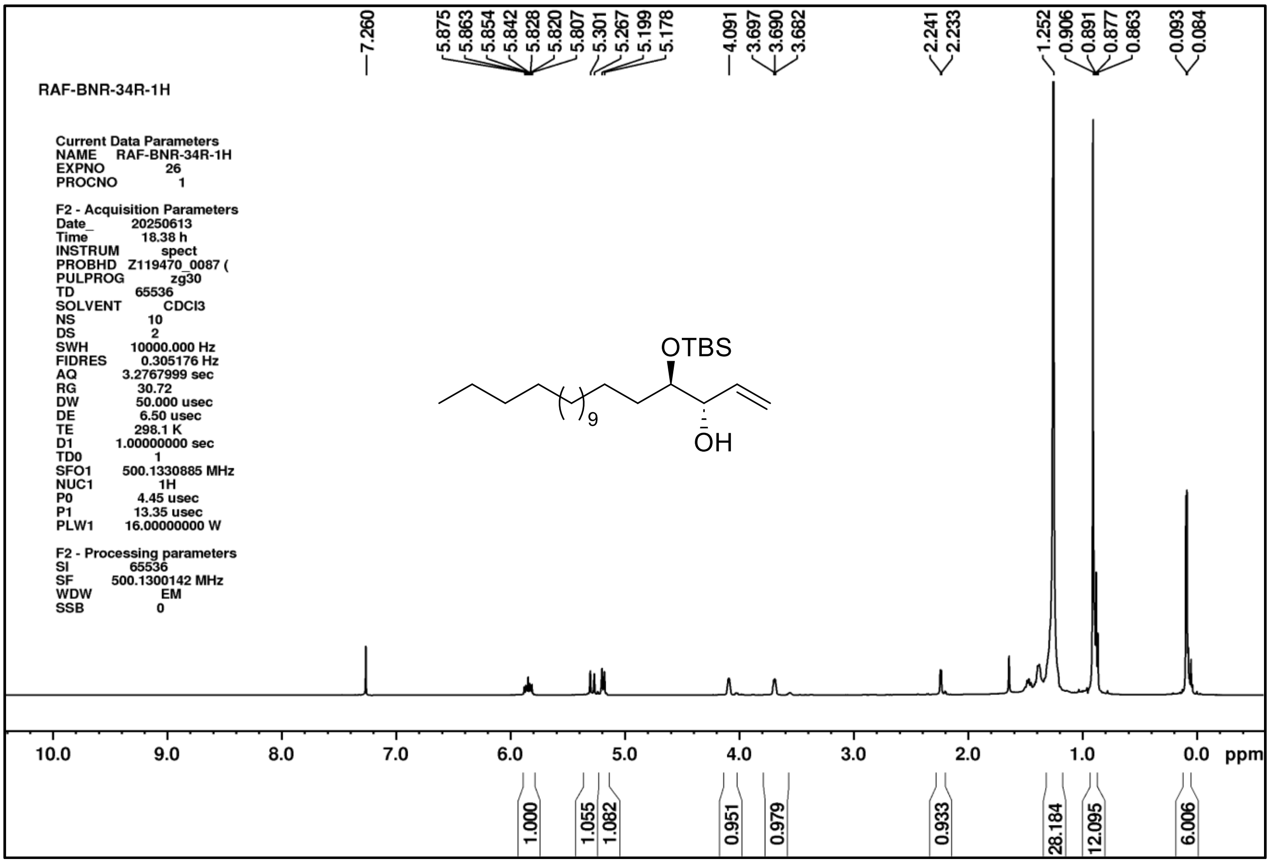
F2 - Acquisition Parameters
Date_             20240713
Time                 20.23 h
INSTRUM              spect
PROBHD    Z119470_0087 (
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     182
DS                       0
SWH              34722.223 Hz
FIDRES            1.059638 Hz
AQ               0.9437184 sec
RG                  197.27
DW                  14.400 usec
DE                    6.50 usec
TE                   297.8 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                      1
SFO1           125.7721254 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           16.00000000 W
PLW12           0.44556001 W
PLW13           0.22411001 W

F2 - Processing parameters
SI                   32768
SF             125.7577906 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

***ent*-38**: HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ Calcd for $C_{24}H_{54}O_2SiN$ 416.3918; Found: 416.3910



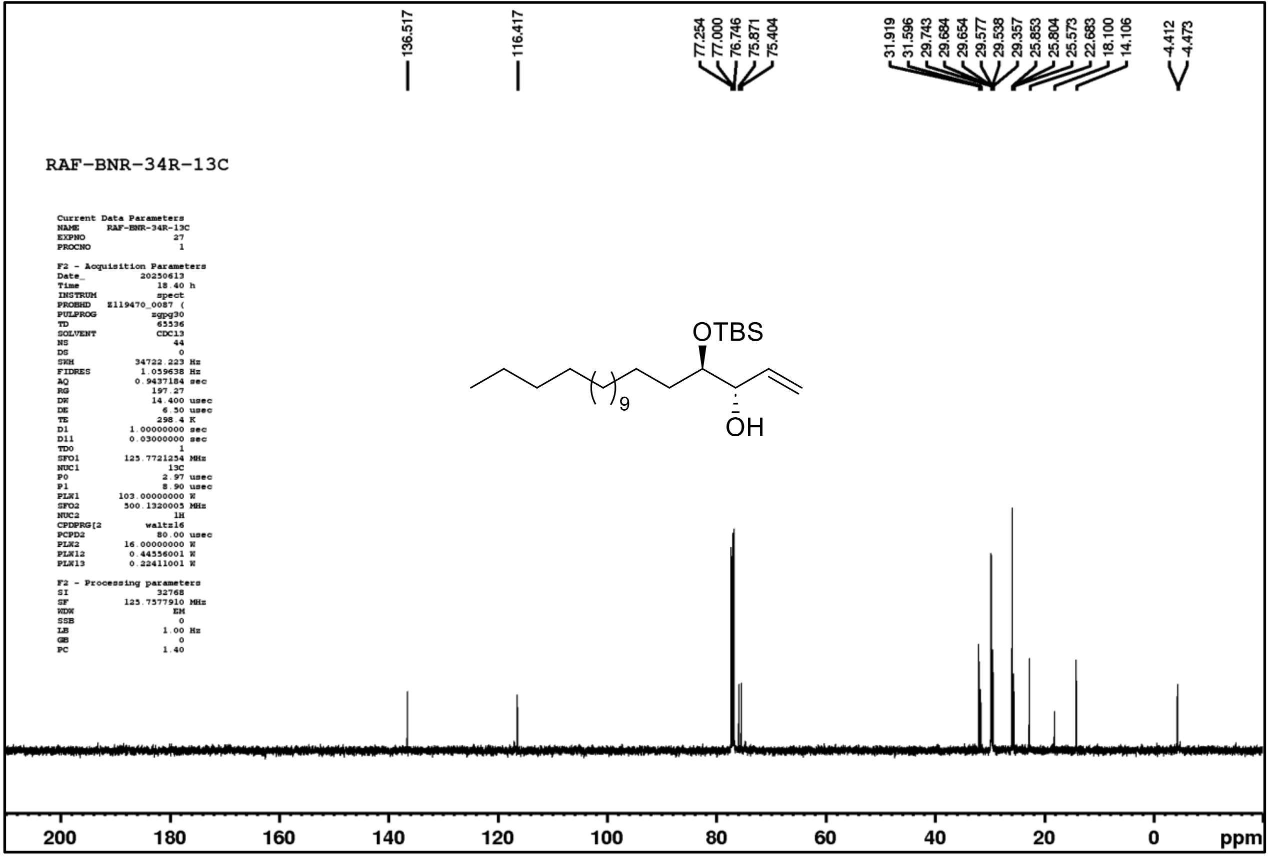
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) of compound **34**



```
Current Data Parameters
NAME    RAF-BNR-34R-1H
EXPNO            26
PROCNO            1

F2 - Acquisition Parameters
Date_       20250613
Time         18.38 h
INSTRUM        spect
PROBHD  Z119470_0087 (
PULPROG         zg30
TD             65536
SOLVENT        CDCl3
NS                10
DS                 2
SWH       10000.000 Hz
FIDRES     0.305176 Hz
AQ        3.2767999 sec
RG             30.72
DW            50.000 usec
DE             6.50 usec
TE            298.1 K
D1       1.00000000 sec
TD0                1
SFO1    500.1330885 MHz
NUC1              1H
P0              4.45 usec
P1             13.35 usec
PLW1     16.00000000 W

F2 - Processing parameters
SI             65536
SF       500.1300142 MHz
WDW               EM
SSB                0
```

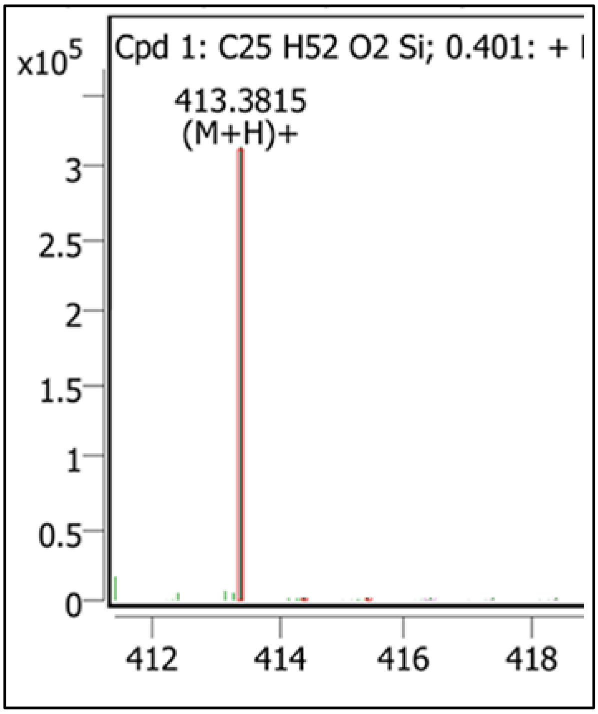


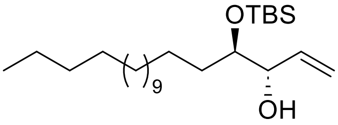
```
Current Data Parameters
NAME       RAF-BNR-34R-13C
EXPNO                   27
PROCNO                   1

F2 - Acquisition Parameters
Date_             20250613
Time                 18.40 h
INSTRUM              spect
PROBHD    Z119470_0087 (
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      44
DS                       0
SWH              34722.223 Hz
FIDRES            1.059638 Hz
AQ               0.9437184 sec
RG                  197.27
DW                  14.400 usec
DE                    6.50 usec
TE                   298.4 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                      1
SFO1           125.7721254 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           16.00000000 W
PLW12           0.44556001 W
PLW13           0.22411001 W

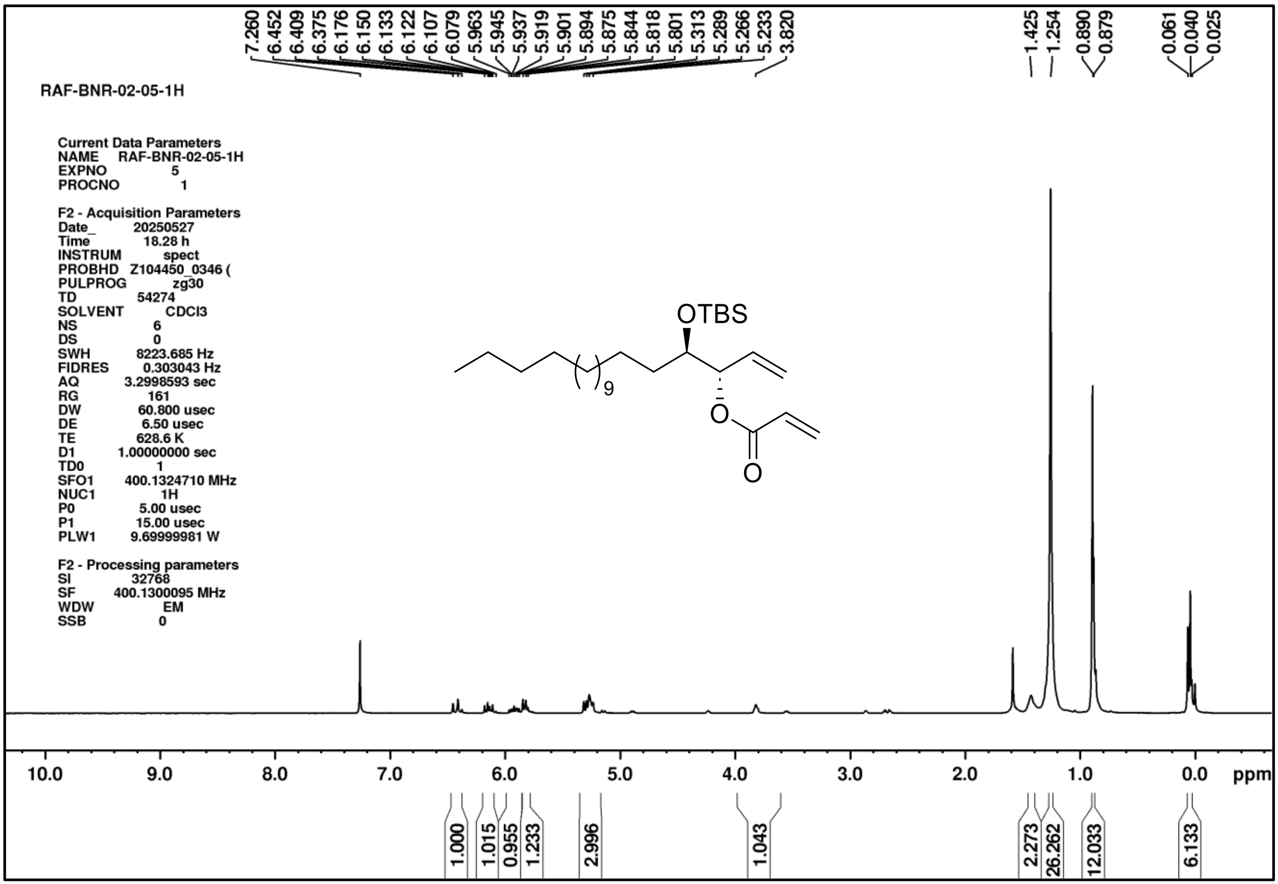
F2 - Processing parameters
SI                   32768
SF             125.7577910 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

34: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{53}O_2Si$ 413.3810; Found: 413.3815





^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) of compound **49**



```
RAF-BNR-02-05-1H

Current Data Parameters
NAME     RAF-BNR-02-05-1H
EXPNO              5
PROCNO             1

F2 - Acquisition Parameters
Date_          20250527
Time             18.28 h
INSTRUM          spect
PROBHD   Z104450_0346 (
PULPROG          zg30
TD              54274
SOLVENT          CDCl3
NS                 6
DS                 0
SWH          8223.685 Hz
FIDRES       0.303043 Hz
AQ          3.2998593 sec
RG               161
DW             60.800 usec
DE              6.50 usec
TE             628.6 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        400.1300095 MHz
WDW               EM
SSB                0
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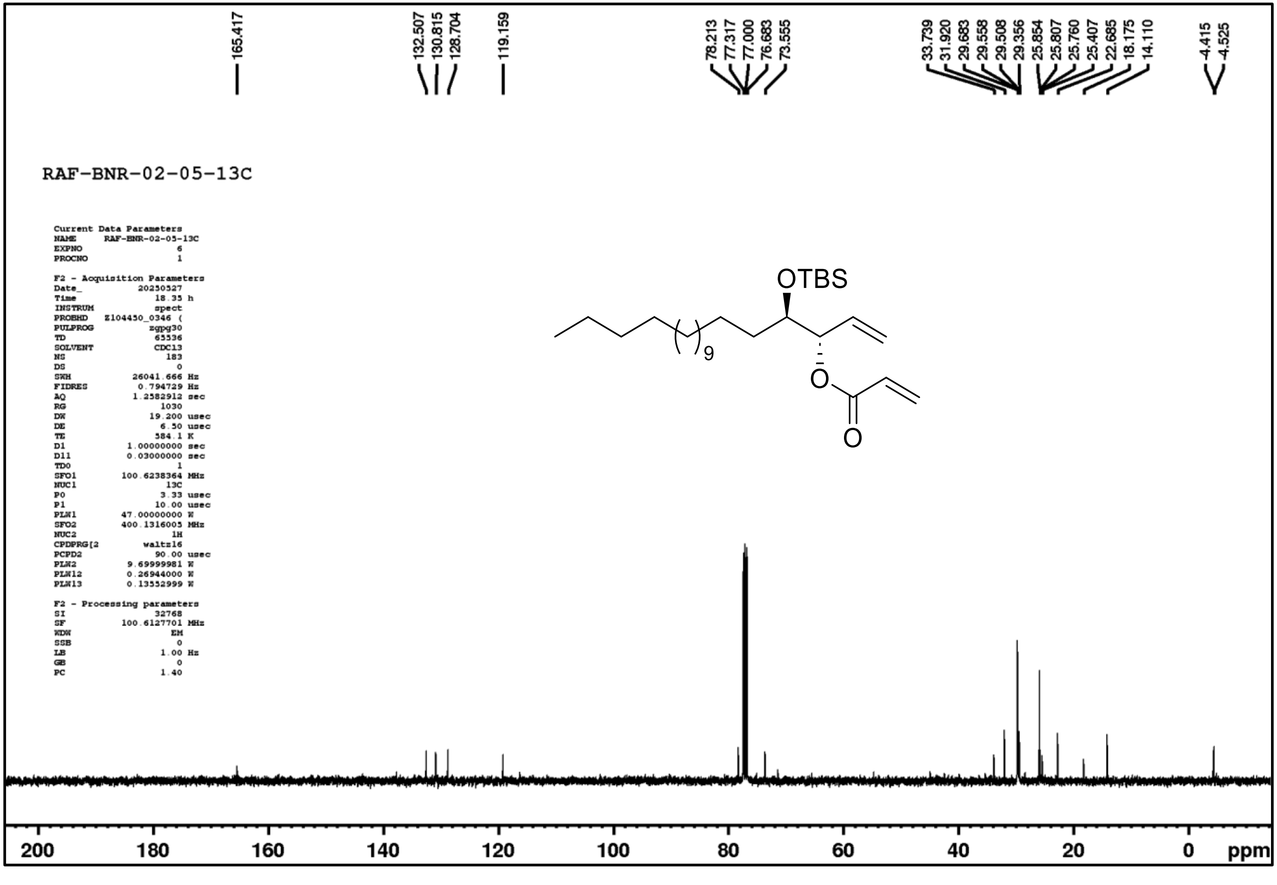


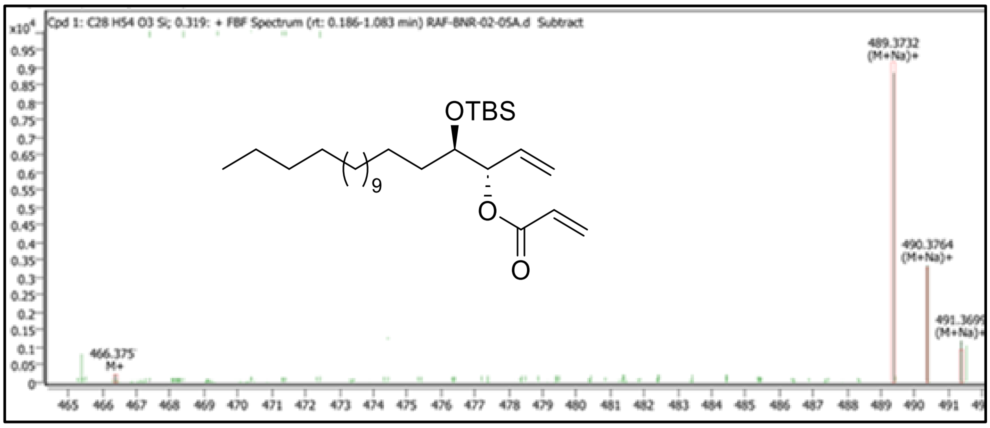
```
RAF-BNR-02-05-13C

Current Data Parameters
NAME      RAF-BNR-02-05-13C
EXPNO                 6
PROCNO                1

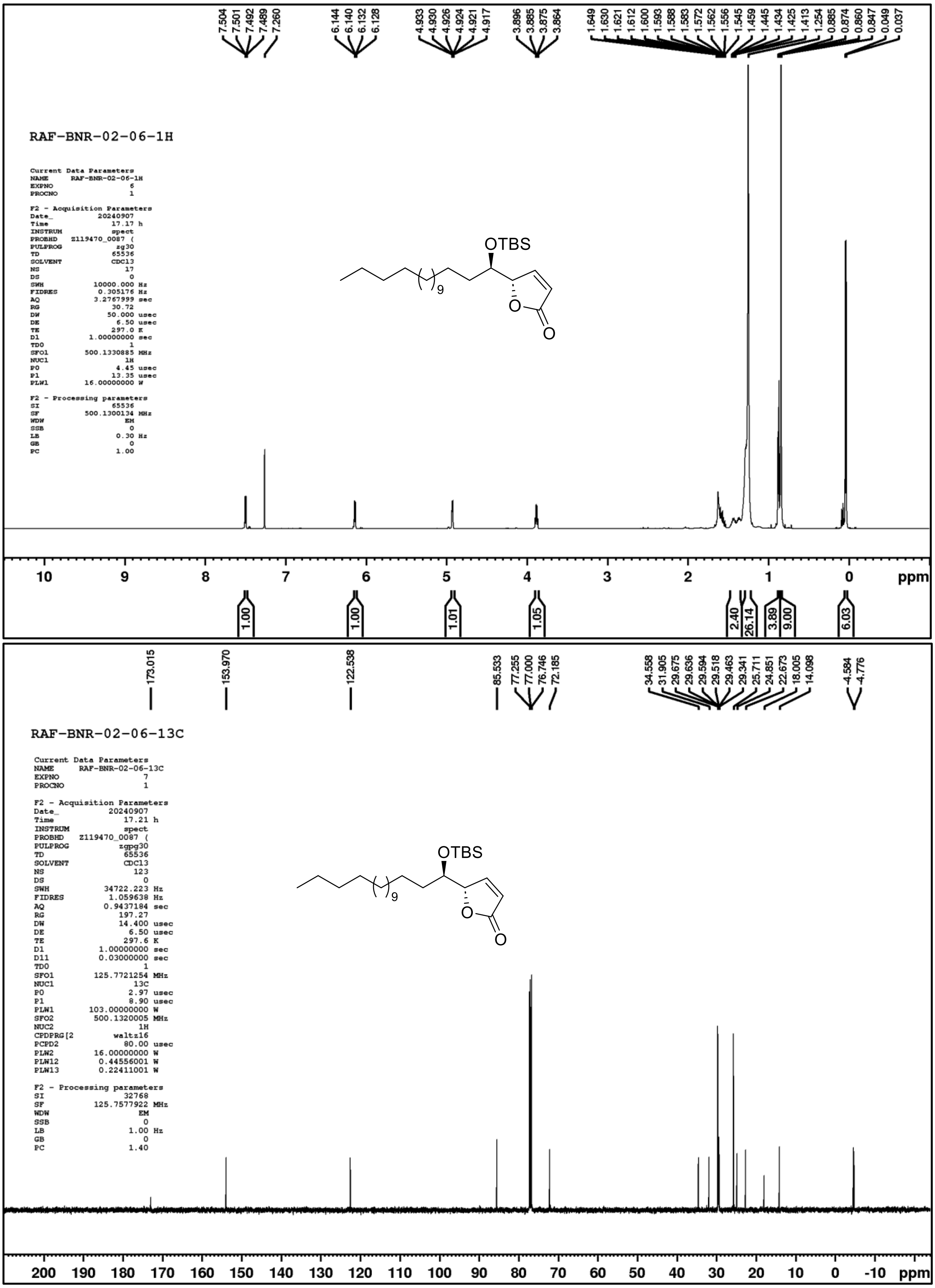
F2 - Acquisition Parameters
Date_          20250527
Time              18.35 h
INSTRUM           spect
PROBHD    Z104450_0346 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  183
DS                    0
SWH           26041.666 Hz
FIDRES         0.794729 Hz
AQ            1.2582912 sec
RG                 1030
DW               19.200 usec
DE                 6.50 usec
TE                584.1 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          100.6127701 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

49: HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{28}H_{54}O_3SiNa$ 489.3735; Found: 489.3732



^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) of compound **50**



```
RAF-BNR-02-06-1H

Current Data Parameters
NAME       RAF-BNR-02-06-1H
EXPNO                     6
PROCNO                    1

F2 - Acquisition Parameters
Date_              20240907
Time                  17.17 h
INSTRUM               spect
PROBHD     Z119470_0087 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       17
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                    297.0 K
D1               1.00000000 sec
TD0                       1
SFO1            500.1330885 MHz
NUC1                     1H
P0                     4.45 usec
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
```

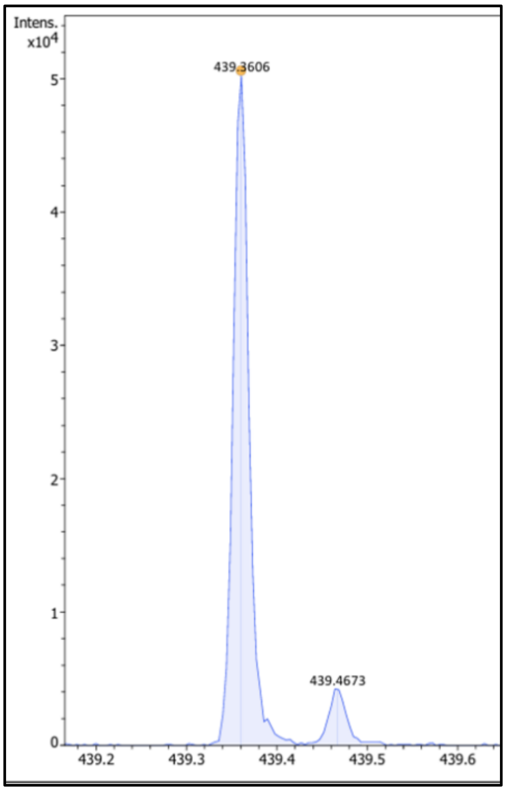
```
RAF-BNR-02-06-13C

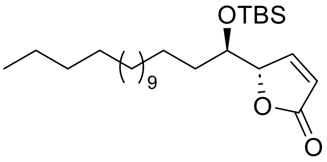
Current Data Parameters
NAME       RAF-BNR-02-06-13C
EXPNO                     7
PROCNO                    1

F2 - Acquisition Parameters
Date_              20240907
Time                  17.21 h
INSTRUM               spect
PROBHD     Z119470_0087 (
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      123
DS                        0
SWH               34722.223 Hz
FIDRES             1.059638 Hz
AQ                0.9437184 sec
RG                   197.27
DW                   14.400 usec
DE                     6.50 usec
TE                    297.6 K
D1               1.00000000 sec
D11              0.03000000 sec
TD0                       1
SFO1            125.7721254 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            16.00000000 W
PLW12            0.44556001 W
PLW13            0.22411001 W

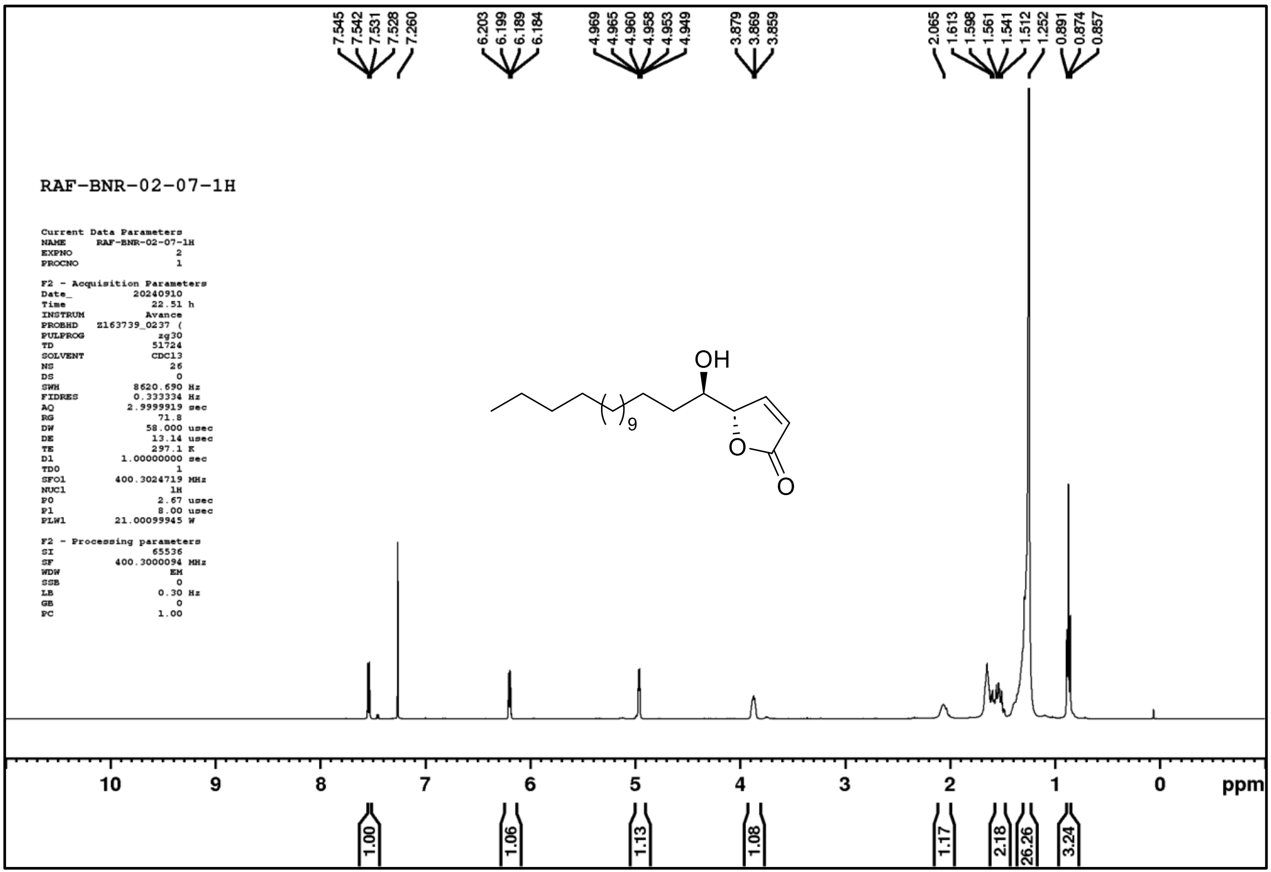
F2 - Processing parameters
SI                    32768
SF              125.7577922 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

50: HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{26}H_{51}O_3Si$ 439.3602; Found: 439.3606





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

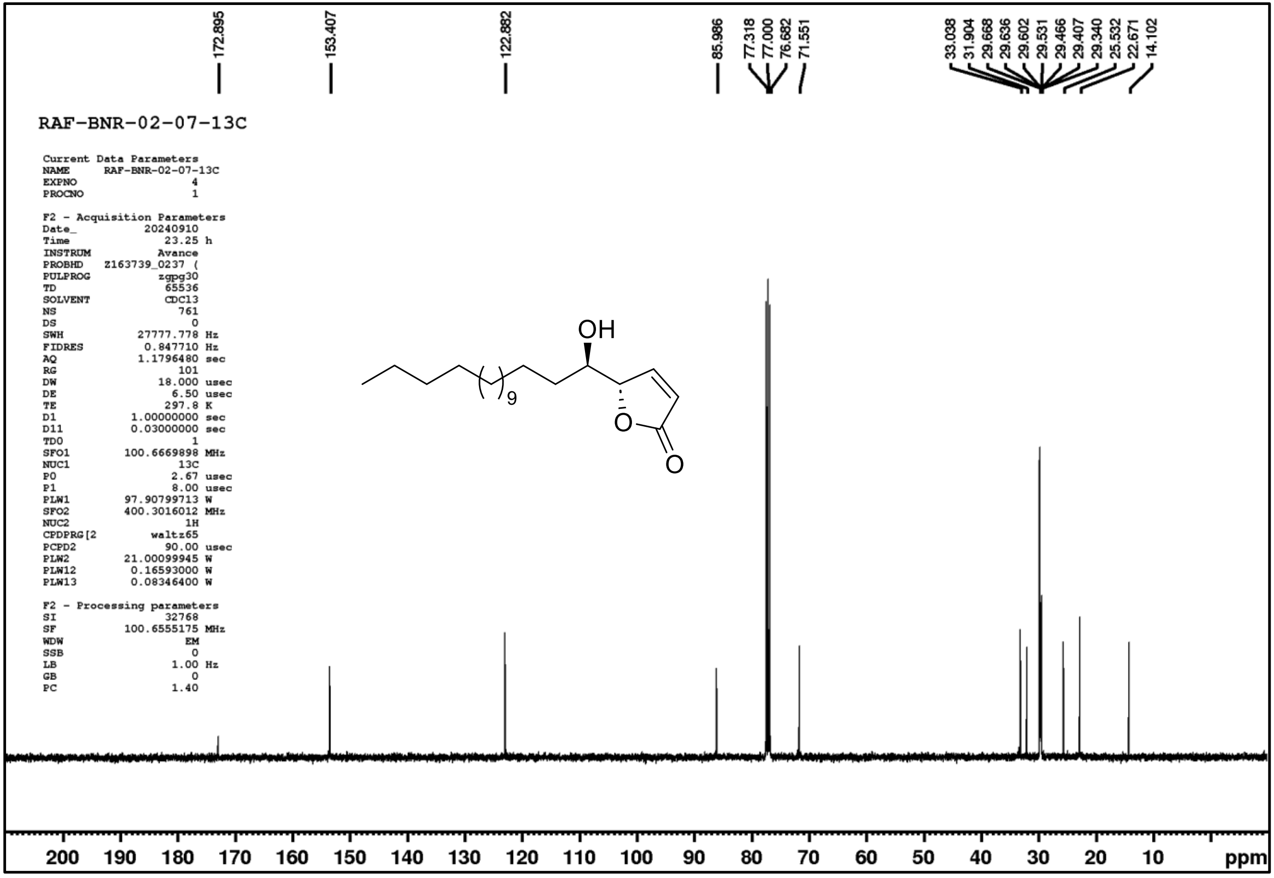


```
RAF-BNR-02-07-1H

Current Data Parameters
NAME     RAF-BNR-02-07-1H
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20240910
Time                22.51 h
INSTRUM            Avance
PROBHD   Z163739_0237 (
PULPROG              zg30
TD                  51724
SOLVENT             CDCl3
NS                     26
DS                      0
SWH              8620.690 Hz
FIDRES           0.333334 Hz
AQ              2.9999919 sec
RG                   71.8
DW                 58.000 usec
DE                  13.14 usec
TE                  297.1 K
D1             1.00000000 sec
TD0                     1
SFO1          400.3024719 MHz
NUC1                   1H
P0                   2.67 usec
P1                   8.00 usec
PLW1          21.00099945 W

F2 - Processing parameters
SI                  65536
SF            400.3000094 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



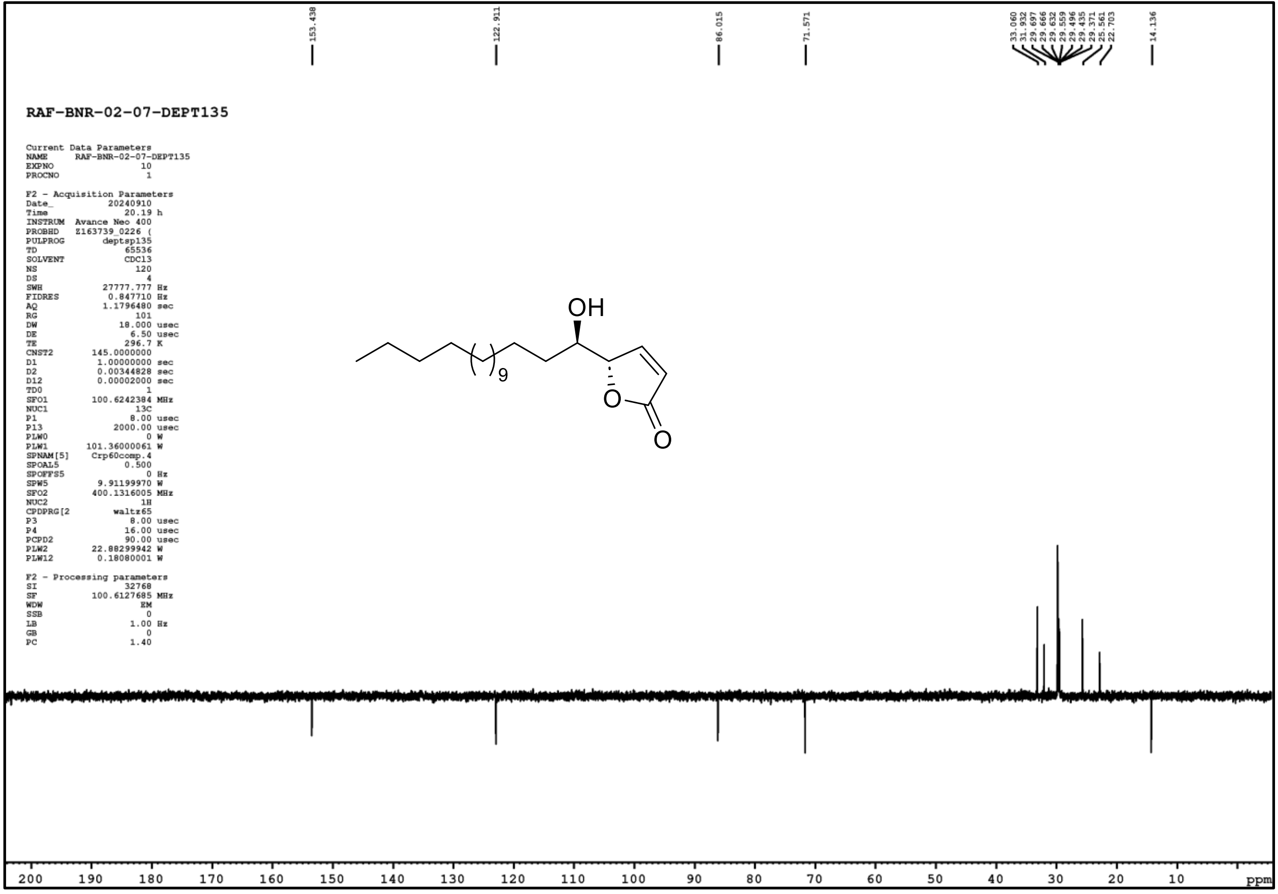
```
RAF-BNR-02-07-13C

Current Data Parameters
NAME     RAF-BNR-02-07-13C
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20240910
Time                23.25 h
INSTRUM            Avance
PROBHD   Z163739_0237 (
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    761
DS                      0
SWH             27777.778 Hz
FIDRES           0.847710 Hz
AQ              1.1796480 sec
RG                    101
DW                 18.000 usec
DE                   6.50 usec
TE                  297.8 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          97.90799713 W
SFO2          400.3016012 MHz
NUC2                   1H
CPDPRG[2          waltz65
PCPD2               90.00 usec
PLW2          21.00099945 W
PLW12          0.16593000 W
PLW13          0.08346400 W

F2 - Processing parameters
SI                  32768
SF            100.6555175 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

DEPT135 $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) of compound **1e**



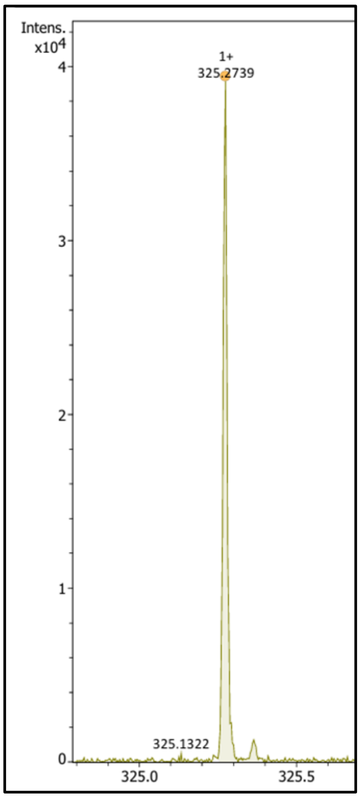
```
RAF-BNR-02-07-DEPT135

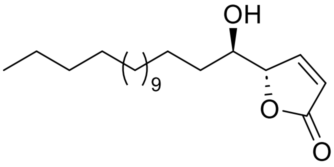
Current Data Parameters
NAME     RAF-BNR-02-07-DEPT135
EXPNO                   10
PROCNO                   1

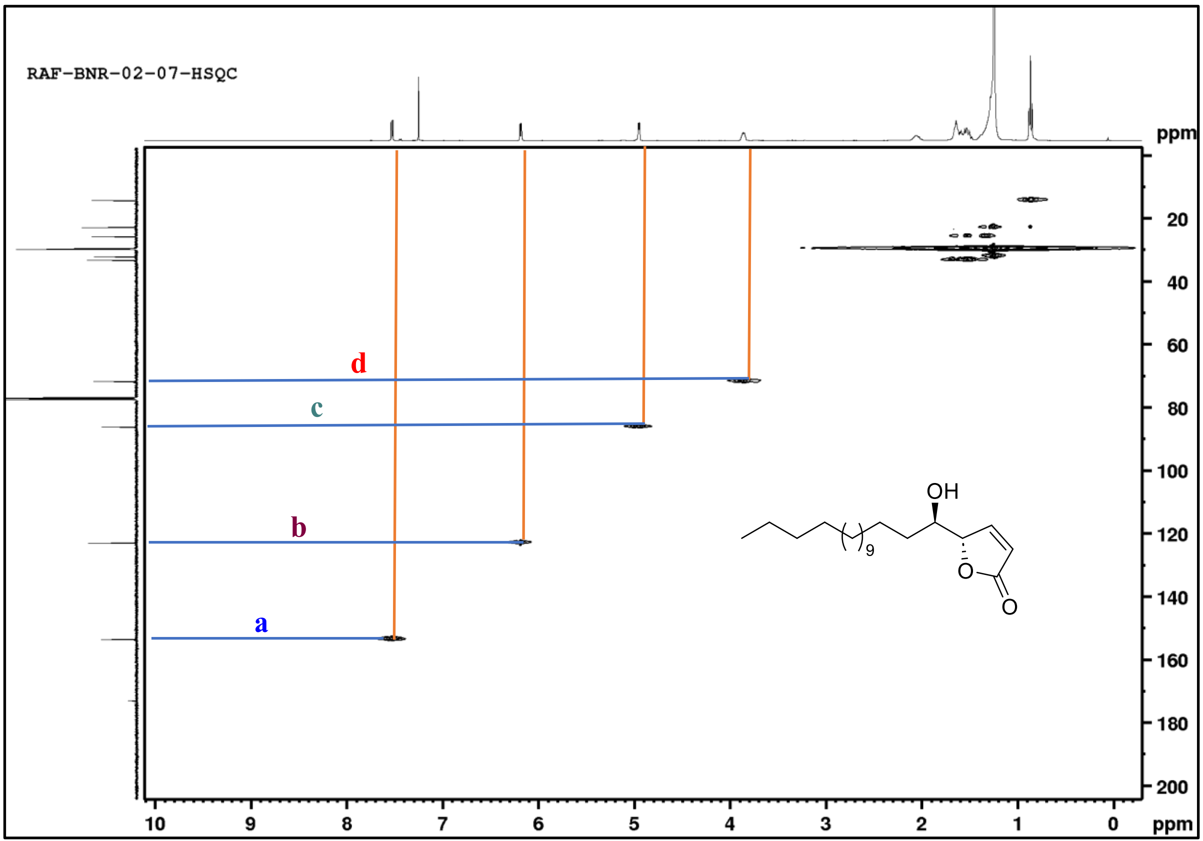
F2 - Acquisition Parameters
Date_             20240910
Time                 20.19 h
INSTRUM  Avance Neo 400
PROBHD   Z163739_0226 (
PULPROG          deptsp135
TD                   65536
SOLVENT              CDC13
NS                     120
DS                       4
SWH              27777.777 Hz
FIDRES            0.847710 Hz
AQ               1.1796480 sec
RG                     101
DW                  18.000 usec
DE                    6.50 usec
TE                   296.7 K
CNST2          145.0000000
D1              1.00000000 sec
D2              0.00344828 sec
D12             0.00002000 sec
TD0                      1
SFO1           100.6242384 MHz
NUC1                   13C
P1                    8.00 usec
P13                2000.00 usec
PLW0                     0 W
PLW1          101.36000061 W
SPNAM[5]       Crp60comp.4
SPOAL5               0.500
SPOFFS5                  0 Hz
SPW5            9.91199970 W
SFO2           400.1316005 MHz
NUC2                    1H
CPDPRG[2          waltz65
P3                    8.00 usec
P4                   16.00 usec
PCPD2                90.00 usec
PLW2           22.88299942 W
PLW12           0.18080001 W

F2 - Processing parameters
SI                   32768
SF             100.6127685 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

1e: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{37}O_3$ 325.2737; Found: 325.2739






RAF-BNR-02-07-HSQC
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80
100
120
140
160
180
200
10
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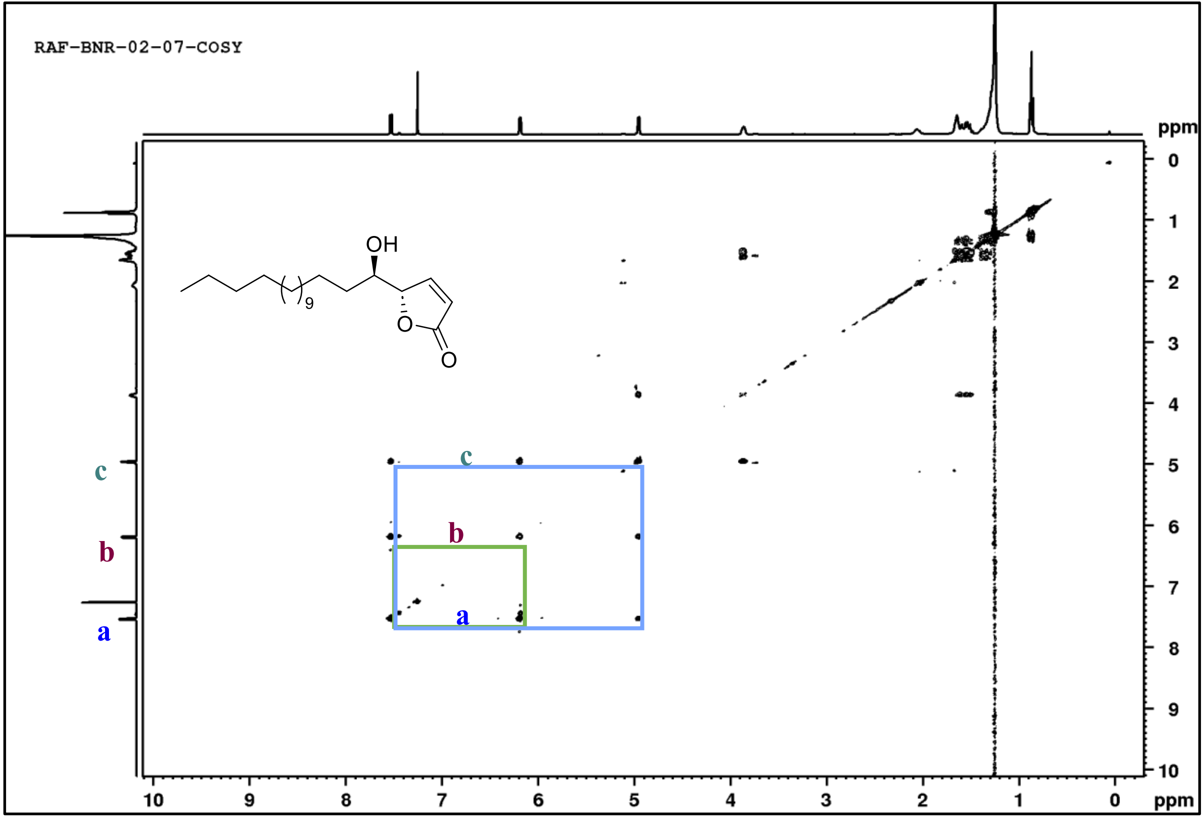
8
7
6
5
4
3
2
1
0
ppm
d
c
b
a
OH
9
O
O


RAF-BNR-02-07-COSY
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8
7
6
5
4
3
2
1
0
ppm
OH
9
O
O
c
b
a
c
b
a

H-H NOESY spectra of compound **1e**