Supporting Information

Concise organocatalyzed epoxidation based total synthesis of (−)- and (+)-*trans*-posticlures and (−)-(6*Z*,9*Z*,4*S*,5*S*)-*trans*-4,5-epoxynonadeca-6,9-diene

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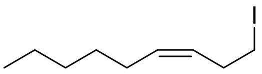
Experimental Section

General Information

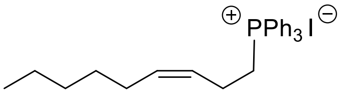
Reagents and solvents were purchased (Sigma-Aldrich, TCI and BLD) and used as received without further purification. NMR spectra were recorded with a Bruker (Germany) Avance III 400 and Bruker (Germany) Avance III HD 500 instruments at room temperature. Chemical shifts (δ) are stated in parts per million (ppm) using the residual $CHCl_3$ (δ = 7.27 ppm for ^1H and 77.00 ppm for ^{13}C [$CDCl_3$]. Coupling constants *J* are given in Hz. Multiplicities are described as singlet (s), broad signal (brs), 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. 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.

(3*Z*)-1-Iodonon-3-ene (7a)



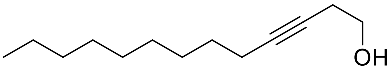
To a solution of triphenylphosphine (1.1 g, 4.22 mmol, 1.2 equiv.) in dry THF (30 mL) was added iodine (584 mg, 4.6 mmol, 1.3 equiv.). The orange precipitate was stirred for 30 min at 0 °C and a solution of *cis*-3-nonen-1-ol **6a** (500 mg, 3.52 mmol, 1.0 equiv.) and imidazole (313 mg, 4.6 mmol, 1.3 equiv.) in THF (1 mL) was added dropwise. The reaction mixture was stirred at room temperature for 6 h and then THF was evaporated. The residue was diluted with water and the solution was extracted with EtOAc (3 x 50 mL). The combined organic extracts were washed with 20% aq. $Na_2S_2O_3$, brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (19:1) as eluent to give (3*Z*)-1-iodonon-3-ene **7a** (568 mg, 64%) as a colorless oil. IR ($CHCl_3$) ν_{max} = 3009, 2956, 2923, 2855, 1457, 1424, 1402, 1378, 1297, 1240, 1167, 1105, 1036, 967, 918, 843, 723, 601 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 5.58–5.49 (m, 1H), 5.36–5.28 (m, 1H), 3.13 (t, *J* = 6.0 Hz, 2H), 2.67–2.60 (m, 2H), 2.06–2.00 (m, 2H), 1.40–1.29 (m, 6H), 0.90 (t, *J* = 6.7 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 132.7, 127.7, 31.5, 31.4, 29.1, 27.4, 22.5, 14.0, 5.5 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_9H_{18}I$ 253.0448; found 253.0449.

(3*Z*)-Non-3-en-1-yltriphenylphosphonium Iodide (8a)



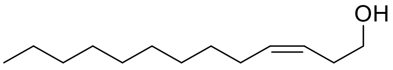
To a solution of triphenylphosphine (438 mg, 1.67 mmol, 1.2 equiv.) in dry benzene (20 mL) was added the iodide **7a** (350 mg, 1.39 mmol, 1.0 equiv.) and the solution refluxed for 36 h. The reaction mixture was cooled to room temperature and benzene was removed under reduced pressure. The sticky solid was triturated with dry Et_2O to remove unreacted starting materials. The residue was dried under high vacuum to a white sticky solid of (3*Z*)-non-3-en-1-yltriphenylphosphoniumiodide **8a** (529.1 mg, 74% yield) and was used as such immediately.

Tridec-3-yn-1-ol (10)



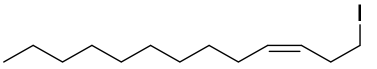
To a stirred solution of but-3-yn-1-ol **9** (250 mg, 3.56 mmol, 1.0 equiv.) in anhydrous THF (30 mL) at –60 °C was added dropwise hexamethylphosphoramide (HMPA, 2.5 mL, 14.26 mmol, 4.0 equiv.) under a nitrogen atmosphere. After 15 min of stirring at the same temperature, *n*-butyllithium (2.5 M in hexane, 3.6 mL, 8.9 mmol, 2.5 equiv.) was added dropwise and the reaction mixture was stirred for an additional 3 h at –30 °C. Subsequently, a solution of 1-iodononane (0.996 g, 3.92 mmol, 1.1 equiv.) in THF (5 mL) was added dropwise and the reaction mixture was gradually warmed to room temperature and stirred for 24 h. The reaction was quenched with saturated aq. $NaHCO_3$ solution and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography using petroleum ether/EtOAc (4:1) as eluent to afford compound **10** (489.2 mg, 70%) as a colorless oil. IR ($CHCl_3$) ν_{max} = 3340, 2923, 2854, 2342, 1462, 1376, 1334, 1220, 1185, 1112, 1044, 849, 722, 720, 635, 562 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.68 (t, *J* = 6.2 Hz, 2H), 2.47–2.40 (m, 2H), 2.19–2.13 (m, 2H), 1.84 (brs, 1H), 1.52–1.44 (m, 2H), 1.39–1.31 (m, 2H), 1.28–1.25 (m, 10H), 0.88 (t, *J* = 6.6 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 82.9, 76.2, 61.4, 31.9, 29.5, 29.3, 29.2, 29.0, 28.9, 23.2, 22.7, 18.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{13}H_{25}O$ 197.1900; found 197.1900.

(3*Z*)-Tridec-3-en-1-ol (6b)



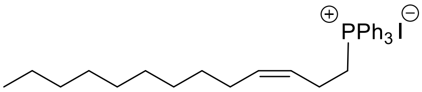
To a stirred solution of compound **10** (200 mg, 1.02 mmol, 1.0 equiv.) in MeOH (8 mL) under a nitrogen atmosphere was added quinoline (132 mg, 1.02 mmol, 1.0 equiv.) at room temperature. Then Palladium on calcium carbonate ($Pd/CaCO_3$, 109.4 mg, 0.053 mmol, 5 mol%) was added under nitrogen atmosphere and the reaction mixture was subjected to hydrogenation at 50 °C under a hydrogen atmosphere. Stirring was continued for 48 h. Upon completion, the reaction mixture was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using petroleum ether/EtOAc (4:1) as eluent to afford compound **6b** (190.2 mg, 94%) as a colorless oil. IR ($CHCl_3$) ν_{max} = 3315, 3008, 2922, 2854, 1461, 1375, 1338, 1241, 1189, 1112, 1047, 872, 721, 633, 596 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 5.55 (q, *J* = 10.0 Hz, 1H), 5.36 (q, *J* = 10.0 Hz, 1H), 3.62 (t, *J* = 6.4 Hz, 2H), 2.35–2.29 (m, 2H), 2.08–2.02 (m, 2H), 1.81 (s, 1H), 1.35–1.25 (m, 14H), 0.87 (t, *J* = 6.7 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 133.4, 124.9, 62.3, 31.9, 30.8, 29.7, 29.6, 29.55, 29.3, 27.4, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{13}H_{27}O$ 199.2057; found 199.2055.

(3*Z*)-1-Iodotridec-3-ene (7b)



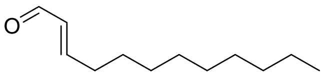
To a solution of triphenylphosphine (793 mg, 3.02 mmol, 1.2 equiv.) in dry THF (30 mL) was added iodine (416 mg, 3.27 mmol, 1.3 equiv.). The orange precipitate was stirred for 30 min at 0 °C and a solution of (*Z*)-tridec-3-en-1-ol **10** (500 mg, 2.52 mmol, 1.0 equiv.) and imidazole (223 mg, 3.27 mmol, 1.3 equiv.) in THF (1 mL) was added dropwise. The reaction mixture was stirred at room temperature for 6 h and then THF was evaporated. The residue was diluted with water and the solution was extracted with EtOAc (3 x 50 mL). The combined organic extracts were washed with 20% aq. $Na_2S_2O_3$, brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (49:1) as eluent to give (*Z*)-1-iodotridec-3-ene **7b** (606 mg, 78%) as a colorless oil. IR ($CHCl_3$) ν_{max} = 3009, 2955, 2921, 2852, 1462, 1424, 1402, 1377, 1296, 1240, 1167, 1116, 1029, 966, 920, 771, 720, 607 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.56–5.49 (m, 1H), 5.36–5.28 (m, 1H), 3.14 (t, *J* = 7.3 Hz, 2H), 2.67–2.60 (m, 2H), 2.06–2.00 (m, 2H), 1.40–1.27 (m, 14H), 0.89 (t, *J* = 6.7 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 132.7, 127.7, 31.9, 31.5, 29.6, 29.5, 29.3, 29.26, 27.4, 22.7, 14.1, 5.5 ppm; HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd. $C_{13}H_{26}I$ 309.1074; found 309.1079.

(3*Z*)-Triphenyl(tridec-3-en-1-yl)phosphonium iodide (8b)



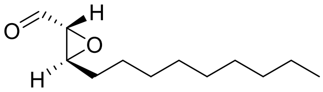
To a solution of triphenylphosphine (613.8 mg, 2.34 mmol, 1.2 equiv.) in dry benzene (20 mL) was added the iodide **7b** (600 mg, 1.95 mmol, 1.0 equiv.) and the solution refluxed for 36 h. The reaction mixture was cooled to room temperature and benzene was removed under reduced pressure. The solid was triturated with dry Et_2O to remove unreacted starting materials. The residue was dried under high vacuum to a white solid of (*Z*)-triphenyl(tridec-3-en-1-yl)phosphonium iodide **8b** (823.3 mg, 74%) and was used as such immediately.

(2*E*)-Dodec-2-enal (4a)



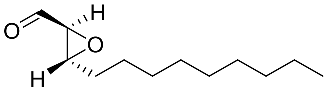
A stirred solution of decanal **5** (1.0 g, 6.4 mmol, 1.0 equiv.) and (formylmethylene)triphenyl phosphorane (3.5 g, 11.52 mmol, 1.8 equiv.) in dry benzene (50 mL) was heated at 70 °C under a nitrogen atmosphere for 14 h. Upon completion of the reaction (monitored by TLC), the mixture was cooled to room temperature and concentrated under reduced pressure. The resulting residue was diluted with petroleum ether (20 mL) and filtered through Celite. The filtrate was concentrated in vacuum and the crude product was purified by silica gel column chromatography using petroleum ether/EtOAc (19:1) as eluent to yield enal **4a** (1.06 g, 91%) as a light-yellow oil. IR ($CHCl_3$) ν_{max} = 2955, 2923, 2854, 2727, 1725, 1691, 1638, 1463, 1378, 1306, 1139, 1102, 1009, 974, 722 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.50 (d, *J* = 1.9 Hz, 1H), 6.89–6.80 (m, 1H), 6.12 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.37–2.29 (m, 2H), 1.55–1.46 (m, 2H), 1.32–1.24 (m, 12H), 0.88 (t, *J* = 6.7 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 194.2, 159.1, 133.0, 32.7, 31.9, 29.5, 29.3, 29.26, 29.1, 27.8, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd. $C_{12}H_{23}O$ 183.1744; found 183.1748.

(2*R*,3*S*)-2,3-Epoxydodecanal (3a)



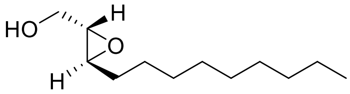
To a stirred solution of enal **4a** (100 mg, 0.549 mmol, 1.0 equiv.) in $CHCl_3$ (10 mL) at 4 °C was added (*R*)-2-(bis(3,5-bis(trifluoromethyl)phenyl)(trimethylsilyloxy)methyl)pyrrolidine **11a** (33 mg, 0.055 mmol, 10 mol%) followed by 30% aq. H_2O_2 (0.09 mL, 0.66 mmol, 1.2 equiv.) and the mixture was stirred for 9 h. The reaction mixture was then diluted with water after completion of the reaction (as monitored by TLC) and then extracted with CH_2Cl_2 (3 x 10 mL). The organic layer was washed with brine, dried (Na_2SO_4), concentrated in vacuo and the residue was purified by silica gel column chromatography using petroleum ether/EtOAc (9:1) as eluent to afford the (*R*,*S*)-epoxy aldehyde **3a** (89.3 mg, 82%) as a colorless oil. $[\alpha]_D^{25}$ = +35.7 (*c* = 1.3, $CHCl_3$), IR ($CHCl_3$) ν_{max} = 2955, 2923, 2854, 2723, 1767, 1730, 1465, 1377, 1308, 1180, 1102, 977, 851, 758, 722 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.01 (d, *J* = 6.3 Hz, 1H), 3.25–3.21 (m, 1H), 3.13 (dd, *J* = 6.2, 1.9 Hz, 1H), 1.70–1.61 (m, 2H), 1.50–1.43 (m, 2H), 1.32–1.24 (m, 12H), 0.87 (t, *J* = 6.7 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 198.6, 59.2, 56.8, 31.9, 31.2, 29.4, 29.3, 29.2, 25.8, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{12}H_{23}O_2$ 199.1694; found 199.1696.

(2*S*,3*R*)-2,3-Epoxydodecanal (*ent*-3a)



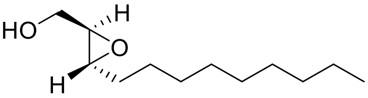
To a stirred solution of enal **4a** (100 mg, 0.549 mmol, 1.0 equiv.) in $CHCl_3$ (10 mL) at 4 °C was added (*S*)-2-(bis(3,5-bis(trifluoromethyl)phenyl)(trimethylsilyloxy)methyl)pyrrolidine (33 mg, 0.055 mmol, 10 mol%) followed by 30% aq. H_2O_2 (0.09 mL, 0.66 mmol, 1.2 equiv.) and the mixture stirred for 9 h. The reaction mixture was diluted with water after completion of the reaction (as monitored by TLC) and then extracted with CH_2Cl_2 (3 x 10 mL). The organic layers were washed with brine, dried (Na_2SO_4), concentrated in vacuo and the residue purified by silica gel column chromatography using petroleum ether/EtOAc (9:1) as eluent to afford (*S*,*R*)-epoxy aldehyde ***ent*-3a** (89.3 mg, 82%) as a colorless oil. $[\alpha]_D^{25}$ = –32.8 (*c* = 1.1, $CHCl_3$), IR ($CHCl_3$) ν_{max} = 2960, 2926, 2855, 2728, 1763, 1718, 1467, 1378, 1311, 1185, 1103, 979, 755, 721, 662 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.98 (d, *J* = 6.3 Hz, 1H), 3.23–3.18 (m, 1H), 3.10 (dd, *J* = 6.2, 1.6 Hz, 1H), 1.67–1.60 (m, 2H), 1.49–1.39 (m, 2H), 1.35–1.22 (m, 12H), 0.85 (t, *J* = 6.5 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 198.5, 59.1, 56.8, 31.8, 31.2, 29.4, 29.3, 29.2, 25.8, 22.6, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{12}H_{23}O_2$ 199.1694; found 199.1695.

(2*S*,3*S*)-2,3-Epoxydodecanol (12)



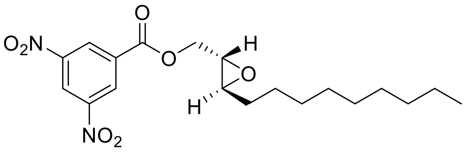
To a stirred solution of (*R*,*S*)-epoxy aldehyde **3a** (50 mg, 0.252 mmol, 1.0 equiv.) in MeOH (5 mL) was added $NaBH_4$ (19 mg, 0.504 mmol, 2.0 equiv.) at 0 °C and stirred for 30 min. The reaction was quenched with saturated aq. NH_4Cl and then extracted with EtOAc (3 x 5 mL). The organic layers were separated, dried (Na_2SO_4), concentrated in vacuo and the residue purified by silica gel column chromatography using petroleum ether/EtOAc (6:1) as eluent to afford 2,3-epoxy alcohol **12** (48.5 mg, 96% yield) as a colorless oil. $[\alpha]_D^{25}$ = –4.9 (*c* = 1.0, $CHCl_3$), IR ν_{max} = 3293, 2955, 2920, 2849, 1460, 1376, 1255, 1132, 1092, 1065, 1049, 1025, 1006, 989, 978, 939, 886, 866, 772, 716, 592 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.94–3.89 (m, 1H), 3.65–3.60 (m, 1H), 2.97–2.92 (m, 2H), 1.85 (brs, 1H), 1.59–1.55 (m, 2H), 1.49–1.21 (m, 14H), 0.88 (t, *J* = 6.1 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 61.7, 58.5, 56.0, 31.9, 31.6, 29.7, 29.5, 29.4, 29.3, 26.0, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{12}H_{25}O_2$ 201.1850; found 201.1850.

(2*R*,3*R*)-2,3-Epoxydodecanol (*ent*-12)



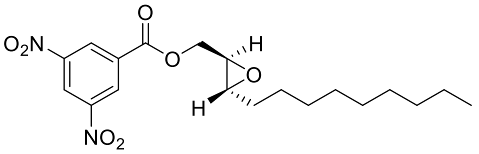
The titled compound was prepared from (*S*,*R*)-epoxy aldehyde ***ent*-3a** (50 mg, 0.252 mmol) by following a similar procedure as described for **12** to give compound ***ent*-12** (46.4 mg, 92%) as a colorless oil. $[\alpha]_D^{25}$ = +18.5 (*c* = 1.0, $CHCl_3$), IR ν_{max} = 3647, 2955, 2924, 2854, 1466, 1377, 1259, 1220, 1131, 1090, 1026, 908, 772, 731, 647, 600 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.93–3.87 (m, 1H), 3.63–3.57 (m, 1H), 2.97–2.89 (m, 2H), 2.22 (brs, 1H), 1.59–1.51 (m, 2H), 1.47–1.38 (m, 2H), 1.37–1.22 (m, 12H), 0.89 (t, *J* = 6.6 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 61.8, 58.6, 56.1, 31.9, 31.6, 29.52, 29.5, 29.4, 29.3, 25.9, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{12}H_{25}O_2$ 201.1850; found 201.1854.

(2*S*,3*S*)-2,3-Epoxydodecyl 3,5-dinitrobenzoate (13)



To a stirred solution of (*S*,*S*)-epoxy alcohol **12** (48 mg, 0.24 mmol, 1.0 equiv.) in dry Et_2O (10 mL) was added dry pyridine (19 mg, 0.24 mmol, 1.0 equiv.) at 0 °C and the mixture was stirred for 30 min and then 3,5-dinitrobenzoyl chloride (72 mg, 0.312 mmol, 1.3 equiv.) was added portion wise at 0 °C. The reaction mixture was stirred for an additional 1 h at room temperature and then quenched with saturated aq. solution of $CuSO_4$ and extracted with Et_2O (3 x 15 mL). The organic layers were separated, dried (Na_2SO_4), concentrated in vacuo and the residue purified by silica gel column chromatography using petroleum ether/EtOAc (9:1) as eluent to afford 3,5-dinitrobenzoate ester **13** (89.9 mg, 95% yield) as a white solid. $[\alpha]_D^{25}$ = –27.4 (*c* = 1.0, $CHCl_3$), IR ν_{max} = 3099, 2956, 2918, 2850, 1728, 1626, 1537, 1461, 1349, 1331, 1281, 1172, 1081, 952, 932, 921, 888, 827, 775, 731, 720, 582 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 9.26 (s, 1H), 9.20 (s, 2H), 4.78 (dd, *J* = 12.2, 2.2 Hz, 1H), 4.27 (dd, *J* = 12.3, 6.8 Hz, 1H), 3.18–3.15 (m, 1H), 2.98–2.94 (m, 1H), 1.65–1.62 (m, 2H), 1.50–1.41 (m, 1H), 1.40–1.31 (m, 12H), 0.88 (t, *J* = 6.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 162.3, 148.7, 133.4, 129.6, 122.6, 67.3, 56.8, 54.7, 31.9, 31.4, 29.5, 29.4, 29.3, 25.8, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$calcd. $C_{19}H_{27}N_2O_7$ 395.1813; found 395.1816.

(2*R*,3*R*)-2,3-Epoxydodecyl 3,5-dinitrobenzoate (*ent*-13)

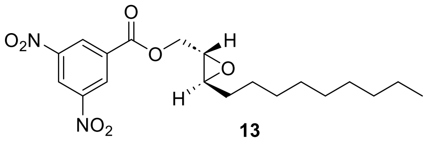


The titled compound was prepared from (*R*,*R*)-epoxy alcohol ***ent*-12** (46 mg, 0.23 mmol) by following a similar procedure as described for **13** to give compound ***ent*-13** (91.8 mg, 97%) as a white solid. = +28.7 (*c* = 1.1, $CHCl_3$), IR ν_{max} = 3102, 2953, 2924, 2854, 1763, 1629, 1598, 1544, 1461, 1343, 1273, 1160, 1075, 967, 920, 892, 826, 771, 719, 645 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.22 (s, 1H), 9.16 (s, 1H), 4.77 (dd, *J* = 12.1, 2.7 Hz, 1H), 4.25 (dd, *J* = 12.1, 6.7 Hz, 1H), 3.15–3.12 (m, 2H), 2.95–2.92 (m, 1H), 1.67–1.55 (m, 2H), 1.48–1.41 (m, 1H), 1.36–1.22 (m, 12H), 0.85 (t, *J* = 6.6 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.3, 148.7, 133.4, 129.6, 122.6, 67.3, 56.8, 54.7, 31.9, 31.4, 29.5, 29.3, 29.26, 25.8, 22.7, 14.1 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$calcd. $C_{19}H_{27}N_2O_7$ 395.1813; found 395.1818.

The enantiomeric purity was determined by HPLC analysis of the 3,5-dinitrobenzoyl ester **13** (chiral column-Chiralpak IG, 4.6 x 250 mm; 30 °C; mobile phase hexane/EtOH, 8.5:1.5; flow rate 1 mL/min; PDA detection at 212 nm): major enantiomer: tR = 29.2 min, minor enantiomer: tR = 35.6 min, 92% ee.

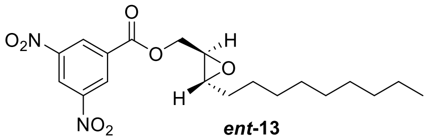
HPLC report of racemic benzoyl ester 13 + *ent*-13

The racemate was prepared by manual mixing of the two enantiomers, **13** and ***ent*-13**

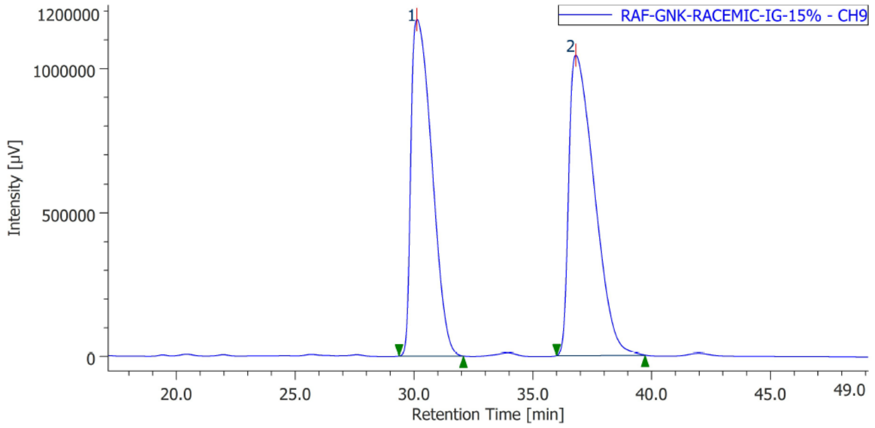


13

+

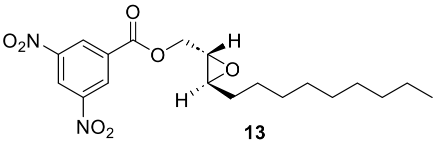


***ent*-13**

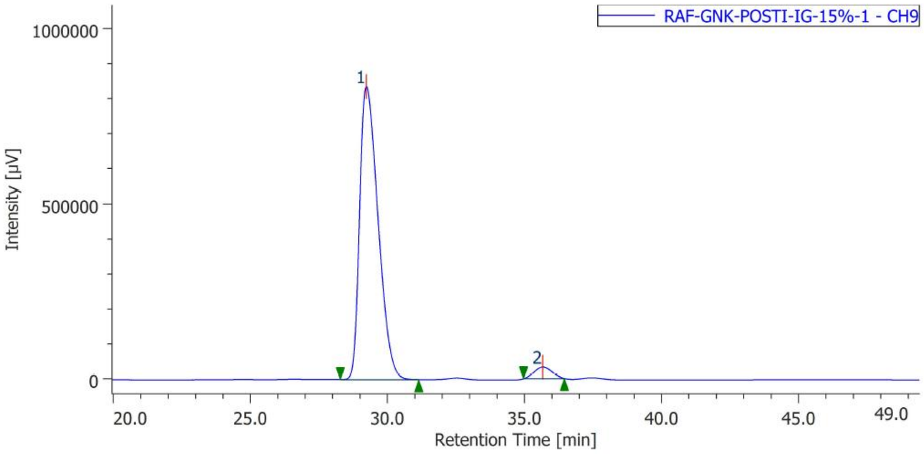


#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	30.120	71368373	1169525	47.879	52.848	N/A	5171	3.638	1.942	
2	Unknown	9	36.807	77692120	1043459	52.121	47.152	N/A	5365	N/A	2.071	

HPLC report of enantiomer 13, 92% ee



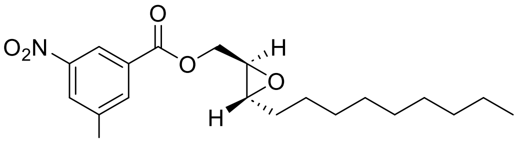
13



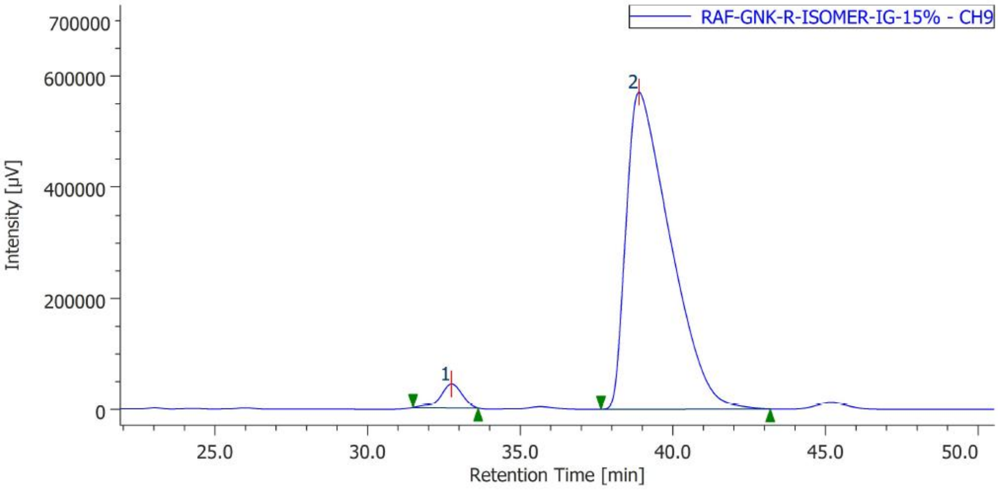
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	29.230	39085341	836296	96.193	96.134	N/A	8768	5.102	1.500	
2	Unknown	9	35.663	1546658	33635	3.807	3.866	N/A	12420	N/A	1.051	

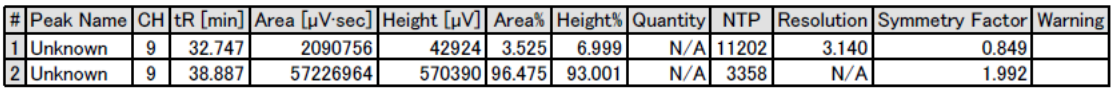
The enantiomeric purity was determined by HPLC analysis of the 3,5-dinitrobenzoyl ester ***ent*-13** (chiral column-Chiralpak IG, 4.6 x 250 mm; 30 °C; mobile phase hexane/EtOH, 8.5:1.5; flow rate 1 mL/min; PDA detection at 212 nm): minor enantiomer: tR = 32.7 min, major enantiomer: tR = 38.8 min, 93% ee.

HPLC report of enantiomer *ent*-13, 93% ee



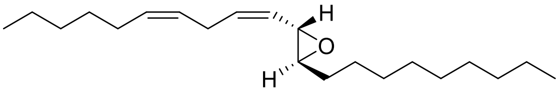
***ent*-13**





#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	32.747	2090756	42924	3.525	6.999	N/A	11202	3.140	0.849	
2	Unknown	9	38.887	57226964	570390	96.475	93.001	N/A	3358	N/A	1.992	

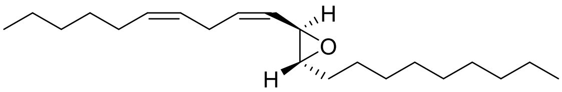
(6*Z*,9*Z*,11*S*,12*S*)-*trans*-11,12-Epoxyhenicosa-6,9-diene, (–)-posticlure (1)



To a stirred solution of freshly prepared (3*Z*)-non-3-en-1-yltriphenylphosphonium iodide **8a** (233.5 mg, 0.454 mmol, 1.8 equiv.) in dry THF (10 mL) at –60 °C was added potassium *tert*-butoxide (37 mg, 0.33 mmol, 1.2 equiv.) and the mixture stirred under nitrogen atmosphere for 1 h, during which time the solution became dark orange. Then, (*R*,*S*)-epoxy aldehyde **3a** (50 mg, 0.252 mmol, 1.0 equiv.) in THF (5 mL) was added dropwise and the reaction was maintained at –60 °C for 1 hour before being allowed to warm to room temperature for 9 h. The reaction mixture was then quenched with saturated aq. $NaHCO_3$ solution and extracted with Et_2O (3 x 10 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), concentrated in vacuum and the residue purified by silica column chromatography using petroleum ether/EtOAc (19:1) as eluent to afford posticlure **1** (63.3 mg, 82%) as a colorless oil. $[\alpha]_D^{25}$ = –9.5 (*c* = 0.8, $CHCl_3$), lit.[1] $[\alpha]_D^{25}$ = –9.6 (*c* = 1.0, $CHCl_3$), IR ($CHCl_3$) ν_{max} = 3011, 2956, 2923, 2854, 1462, 1378, 1247, 1109, 968, 878, 722 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 5.71–5.62

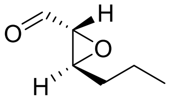
(m, 1H), 5.49–5.42 (m, 1H), 5.41–5.33 (m, 1H), 5.11–5.04 (m, 1H), 3.37 (d, *J* = 8.7 Hz, 1H), 2.97 (t, *J* = 7.5 Hz, 2H), 2.84–2.81 (m, 1H), 2.08 (q, *J* = 6.9 Hz, 2H), 1.60–1.55 (m, 2H), 1.37–1.26 (m, 20H), 0.91–0.86 (m, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, CDCl$_3$) δ = 134.4, 131.2, 127.3, 126.8, 60.2, 54.4, 32.1, 31.9, 31.5, 29.6, 29.54, 29.5, 29.3, 29.27, 27.3, 26.1, 26.0, 22.7, 22.6, 14.1, 14.08 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{21}H_{39}O$ 307.2996; found 307.2996.

(6*Z*,9*Z*,11*R*,12*R*)-*trans*-11,12-Epoxyhenicosa-6,9-diene, (+)-posticlure (*ent*-1)



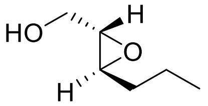
To a stirred solution of freshly prepared (3*Z*)-non-3-en-1-yltriphenylphosphoniumiodide **8a** (233.5 mg, 0.454 mmol, 1.8 equiv.) in dry THF (10 mL) at –60 °C was added potassium *tert*-butoxide (37 mg, 0.33 mmol, 1.2 equiv.) and the mixture stirred under nitrogen atmosphere for 1 h, during which time the solution became dark orange. Further, (*S*,*R*)-epoxy aldehyde ***ent*-3a** (50 mg, 0.252 mmol, 1.0 equiv.) in THF (5 mL) was added dropwise, and the reaction was maintained at –60 °C for 1 hour before being allowed to warm to room temperature for 9 h. The reaction mixture was then quenched with saturated aq. NaHCO$_3$ solution and extracted with Et$_2$O (3 x 10 mL). The combined organic extracts were washed with brine, dried (Na$_2$SO$_4$), concentrated in vacuum and the residue was purified by silica gel column chromatography using petroleum ether/EtOAc (19:1) as eluent to afford (+)-posticlure ***ent*-1** (64.1 mg, 83%) as a colorless oil. $[\alpha]_D^{25}$ = +10.2 (*c* = 1.0, CHCl$_3$), lit.[2] $[\alpha]_D^{24}$ = +10.9 (*c* = 1.09, CHCl$_3$), IR (CHCl$_3$) ν_{max} = 3011, 2956, 2922, 2853, 1464, 1377, 1260, 1187, 1081, 967, 879, 722 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ = 5.71–5.63 (m, 1H), 5.49–5.41 (m, 1H), 5.39–5.32 (m, 1H), 5.11–5.04 (m, 1H), 3.37 (d, *J* = 8.7 Hz, 1H), 2.97 (t, *J* = 7.5 Hz, 2H), 2.84–2.82 (m, 1H), 2.07 (q, *J* = 6.9 Hz, 2H), 1.63–1.57 (m, 2H), 1.35–1.24 (m, 20H), 0.91–0.85 (m, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, CDCl$_3$) δ = 134.4, 131.2, 127.3, 126.8, 60.2, 54.4, 32.1, 31.9, 31.5, 29.6, 29.54, 29.5, 29.3, 29.27, 27.3, 26.1, 25.9, 22.7, 22.6, 14.1, 14.08 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$calcd. $C_{21}H_{39}O$ 307.2996; found 307.2994.

(2*R*,3*S*)-2,3-Epoxyhexanal (3b)



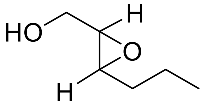
To a stirred solution of commercially obtained *trans*-2-hexanal **4b** (100 mg, 1.02 mmol, 1.0 equiv.) in CHCl$_3$ (10 mL) at 4 °C was added (*R*)-2-(bis(3,5-bis(trifluoromethyl)phenyl)(trimethylsilyloxy)methyl) pyrrolidine **11a** (61 mg, 0.102 mmol, 10 mol%) followed by 30% aq. H$_2$O$_2$ (0.16 mL, 1.224 mmol, 1.2 equiv.) and the mixture stirred for 9 h. The reaction mixture was diluted with water after completion of the reaction (as monitored by TLC) and then extracted with CH$_2$Cl$_2$ (3 x 10 mL). The organic layers were washed with brine, dried (Na$_2$SO$_4$), concentrated in vacuo at low temperature to give **3b** (90.8 mg, 78%) as colourless oil. The compound was volatile and unstable and hence taken without further purification for the next step.

(2*S*,3*S*)-2,3-Epoxyhexanol (14)



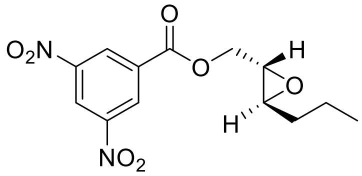
The titled compound was prepared from (*R*,*S*)-epoxy aldehyde **3b** (50 mg, 0.438 mmol) by following a similar procedure as described for **12** to give compound **14** (48.8 mg, 96%) as a colourless oil. This was volatile and hence immediately used for next reaction.

Racemic 2,3-Epoxyhexanol (14′)



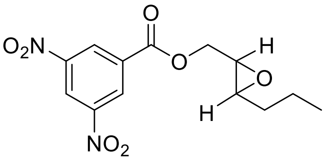
To a solution of *trans*-2-hexenol (500 mg, 5.0 mmol, 1.0 equiv.) in dry CH_2Cl_2 (20 mL) at 0 °C was added *m*-chloroperbenzoic acid (1.3 g, 7.5 mmol, 1.5 equiv.) in small portions. The resulting solution was stirred for 8 h until complete consumption of the starting materials (the progress of the reaction was monitored by TLC). The reaction mixture was quenched with water and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The organic layers were washed with an aq. 10% solution of $NaHCO_3$ (15 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure. The residue (520 mg) was used for next reaction directly.

(2*S*,3*S*)-2,3-Epoxyhexyl 3,5-dinitrobenzoate (15)



The titled compound was prepared from (*S*,*S*)-epoxy alcohol **14** (49 mg, 0.422 mmol, 1.0 equiv.) by following a similar procedure as described for **13** to give compound **15** (120.5 mg, 92%) as a white solid. $[\alpha]_D^{25}$ = –17.3 (*c* = 1.1, $CHCl_3$), IR ν_{max} = 3101, 2961, 2935, 2875, 1732, 1629, 1598, 1542, 1461, 1343, 1272, 1166, 1076, 967, 921, 899, 825, 773, 720, 647 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.26 (t, *J* = 2.2 Hz, 1H), 9.20 (d, *J* = 2.1 Hz, 2H), 4.80 (dd, *J* = 12.1, 3.0 Hz, 1H), 4.29 (dd, *J* = 12.3, 6.8 Hz, 1H), 3.19–3.16 (m, 1H), 3.00–2.96 (m, 1H), 1.65–1.61 (m, 2H), 1.57–1.45 (m, 2H), 1.01 (t, *J* = 7.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.3, 148.7, 133.4, 129.6, 122.6, 67.3, 56.6, 54.7, 33.4, 19.2, 13.8 ppm; HRMS (ESI-TOF): *m/z* $[M + NH_4]^+$ calcd. $C_{13}H_{18}N_3O_7$ 328.1140; found 328.1141.

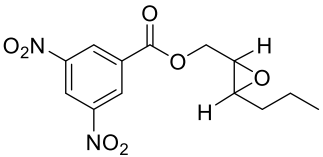
Racemic 2,3-Epoxyhexyl 3,5-dinitrobenzoate (15′)



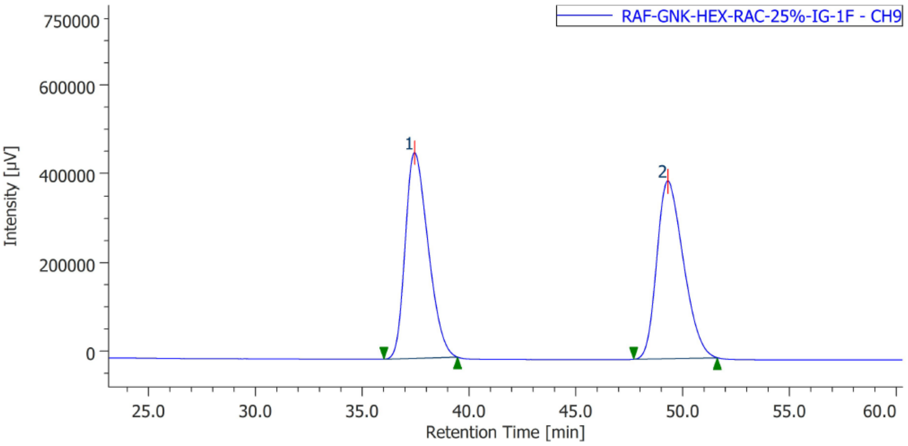
The titled compound was prepared from epoxy alcohol **14′** (50 mg, 0.43 mmol) by following a similar procedure as described for **15** to give compound **15′** (125.5 mg, 94%) as a white solid. IR ν_{max} = 3102, 2961, 2933, 2875, 1732, 1629, 1598, 1541, 1461, 1343, 1270, 1164, 1075, 966, 920, 898, 861, 825, 773, 718, 647 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.24 (t, *J* = 2.1 Hz, 1H), 9.18 (s, 2H), 4.78 (dd, *J* = 12.0, 2.7 Hz, 1H), 4.27 (dd, *J* = 12.4, 6.9 Hz, 1H), 3.17–3.15 (m, 1H), 2.98–2.94 (m, 1H), 1.65–1.59 (m, 2H), 1.55–1.45 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.3, 148.7, 133.4, 129.5, 122.6, 67.2, 56.5, 54.6, 33.4, 19.1, 13.8 ppm; HRMS (ESI-TOF): *m/z* $[M + NH_4]^+$ calcd. $C_{13}H_{18}N_3O_7$ 328.1140; found 328.1142.

The enantiomeric purity was determined by HPLC analysis of 3,5-dinitrobenzoyl ester **15** (chiral column-Chiralpak IG, 4.6 x 250 mm; 30 °C; mobile phase hexane/EtOH, 7.5:2.5; flow rate 1 mL/min; PDA detection at 212 nm): major enantiomer: tR = 39.2 min, minor enantiomer: tR = 45.7 min, 97% ee.

HPLC report of racemic 15′

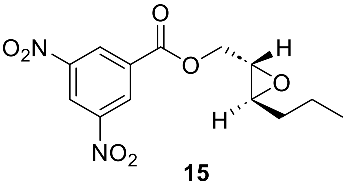


15'

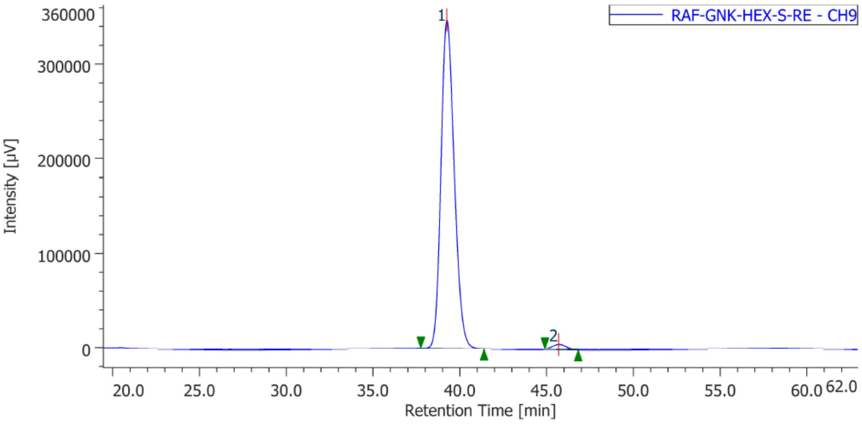


#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	37.447	34596792	462937	49.883	53.656	N/A	5686	5.529	1.323	
2	Unknown	9	49.297	34759749	399849	50.117	46.344	N/A	7277	N/A	1.303	

HPLC report of enantiomer 15, 97% ee

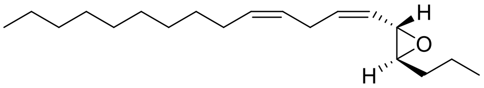


15



#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	39.247	18463869	347622	98.454	98.495	N/A	12608	4.460	1.198	
2	Unknown	9	45.693	289933	5310	1.546	1.505	N/A	14839	N/A	1.132	

(−)-(6*Z*,9*Z*,4*S*,5*S*)-*trans*-4,5-Epoxynonadeca-6,9-diene (2)

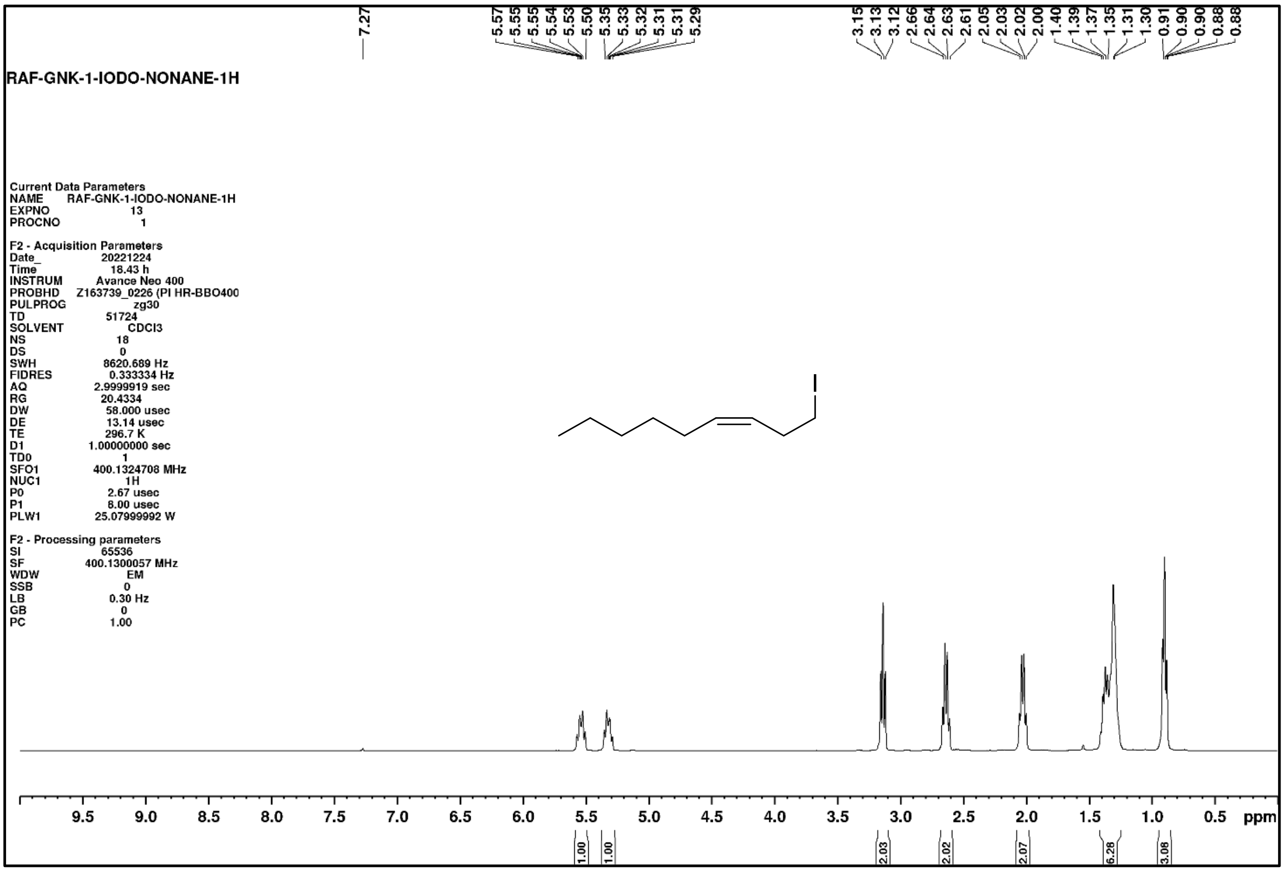


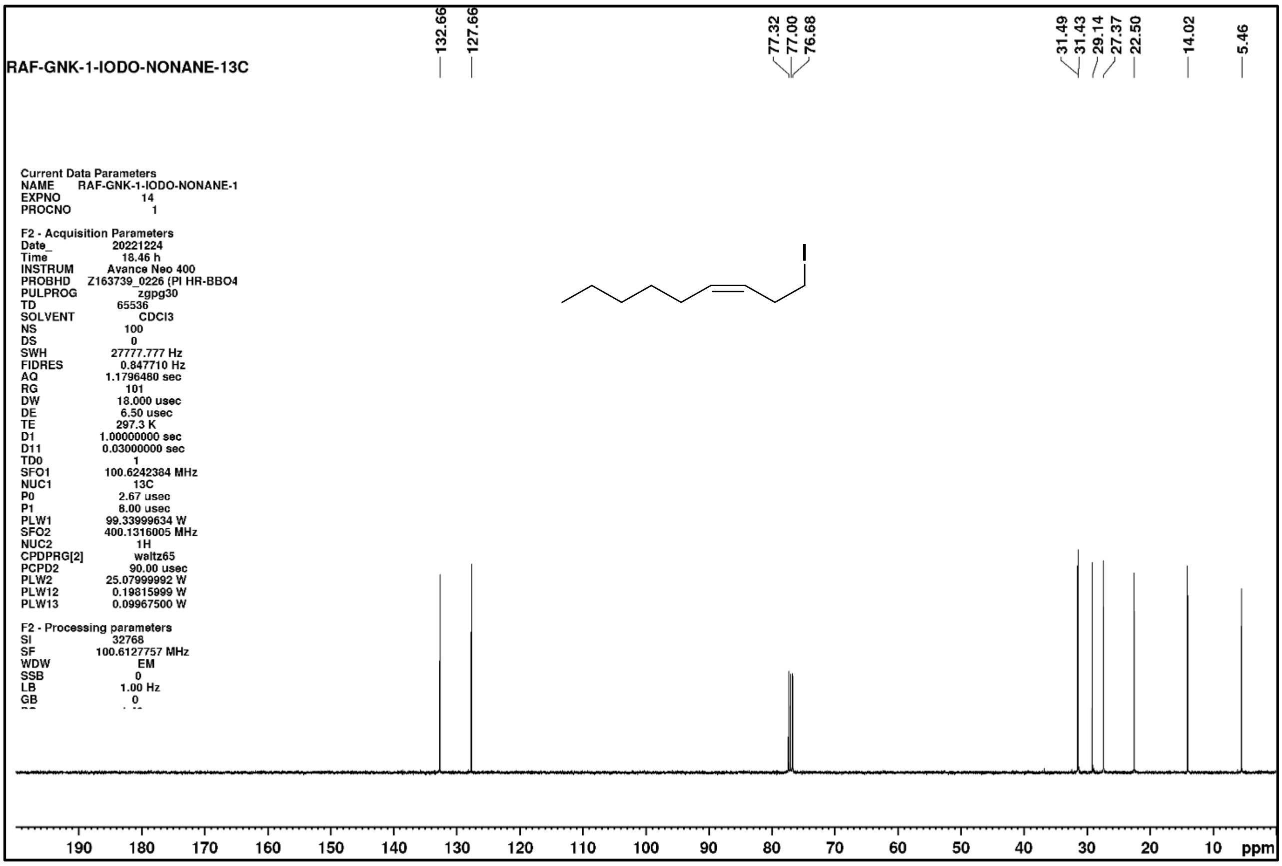
To a stirred solution of freshly prepared (3*Z*)-triphenyl(tridec-3-en-1-yl)phosphoniumiodide **8b** (719.5 mg, 1.261 mmol, 1.8 equiv.) in dry THF (10 mL) at –60 °C was added potassium tert-butoxide (94.3 mg, 0.84 mmol, 1.2 equiv.) and the mixture stirred under nitrogen atmosphere for 1 h, during which time the solution became dark orange. Further, (*R*,*S*)-epoxy aldehyde **3b** (80 mg, 0.70 mmol, 1.0 equiv.) in THF (5 mL) was added dropwise, and the reaction was maintained at –60 °C for 1 h before being allowed to warm to room temperature for 9 h. The reaction mixture was then quenched with saturated aq. $NaHCO_3$ solution and extracted with Et_2O (3 x 10 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), concentrated in vacuo and the residue was purified by silica gel column chromatography using petroleum ether/EtOAc (19:1) as eluent to afford (−)-(6*Z*,9*Z*,4*S*,5*S*)-*trans*-4,5-epoxynonadeca-6,9-diene **2** (150.1 mg, 77%) as a colorless oil. $[\alpha]_D^{25} = -10.7$ (c = 1.1, $CHCl_3$), lit.[1] $[\alpha]_D^{25} = -11.6$ (c = 1.2, $CHCl_3$), IR ($CHCl_3$) ν_{max} = 3013, 2956, 2923, 2854, 1461, 1377, 1217, 1080, 967, 901, 863, 757, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 5.71–5.63 (m, 1H), 5.49–5.41 (m, 1H), 5.39–5.32 (m, 1H), 5.11–5.03 (m, 1H), 3.38 (d, J = 8.9 Hz, 1H), 2.97 (t, J = 7.6 Hz, 2H), 2.84–2.82 (m, 1H), 2.08 (q, J = 7.1 Hz, 2H), 1.62–1.45 (m, 4H), 1.40–1.25 (m, 14H), 0.98 (t, J = 7.7 Hz, 3H), 0.89 (t, J = 6.3 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 134.4, 131.2, 127.3, 126.8, 60,0, 54.3, 34.1, 31.9, 29.7, 29.6, 29.57, 29.4, 27.3, 26.1, 22.7, 19.3, 14.1, 14.0 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. $C_{19}H_{35}O$ 279.2683; found 279.2681.

References

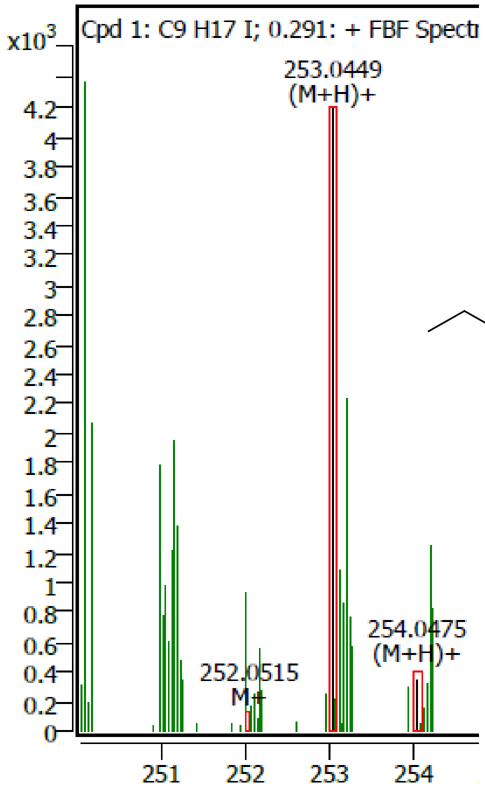
1. B. Kang and R. Britton, *Org. Lett.*, 2007, **9**, 5083.
2. S.-E. Muto and K. Mori, *Eur. J. Org. Chem.*, 2001, **2001**, 4635.

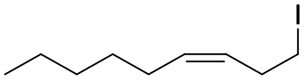
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **7a**



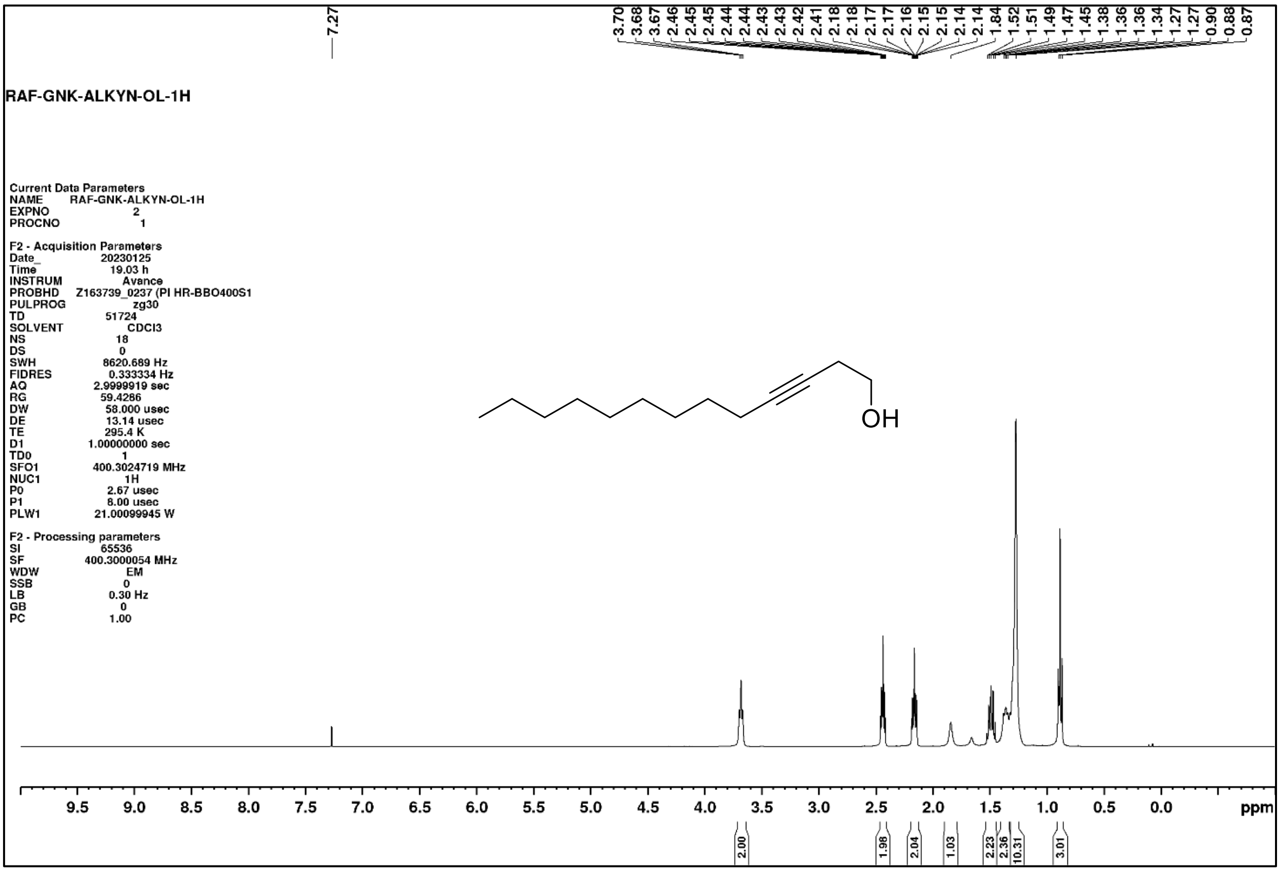


7a: HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd. $C_9H_{18}I$ 253.0448; found 253.0449.





^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **10**



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Current Data Parameters
NAME      RAF-GNK-ALKYN-OL-1H
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_          20230125
Time             19.03 h
INSTRUM          Avance
PROBHD   Z163739_0237 (PI HR-BBO400S1
PULPROG            zg30
TD                51724
SOLVENT           CDCl3
NS                   18
DS                    0
SWH          8620.689 Hz
FIDRES       0.333334 Hz
AQ        2.9999919 sec
RG              59.4286
DW           58.000 usec
DE           13.14 usec
TE              295.4 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       400.3000054 MHz
WDW                  EM
SSB                   0
LB              0.30 Hz
GB                    0
PC                 1.00
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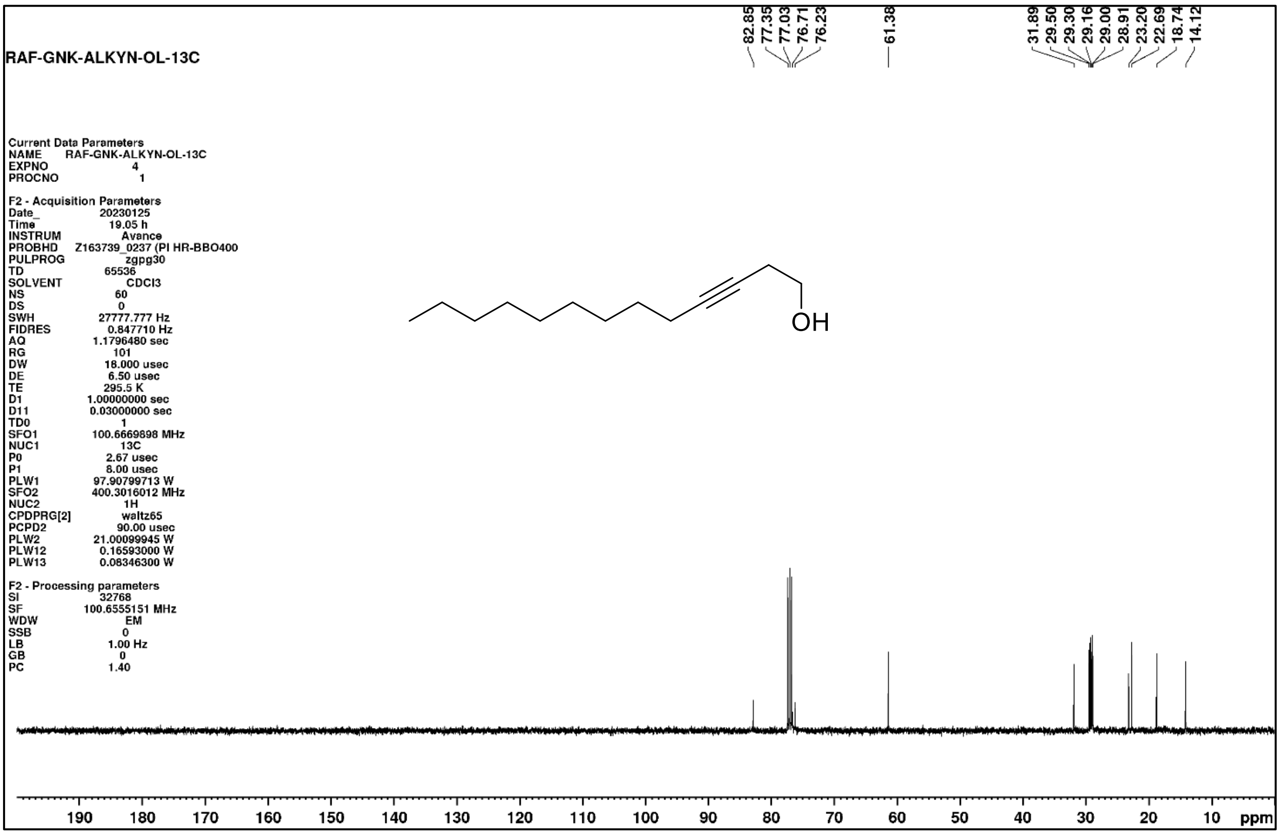

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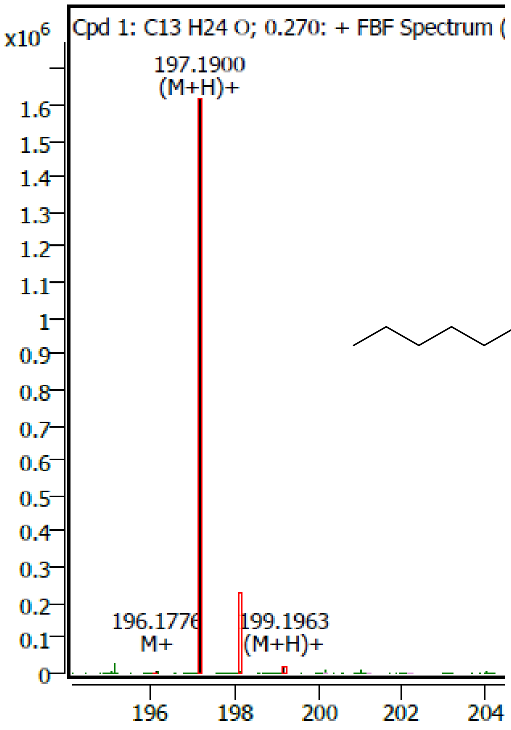
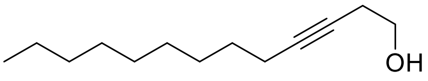
Current Data Parameters
NAME      RAF-GNK-ALKYN-OL-13C
EXPNO                4
PROCNO               1

F2 - Acquisition Parameters
Date_          20230125
Time             19.05 h
INSTRUM          Avance
PROBHD   Z163739_0237 (PI HR-BBO400
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   60
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              295.5 K
D1       1.00000000 sec
D11      0.03000000 sec
TD0                   1
SFO1     100.6669698 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      0.08346300 W

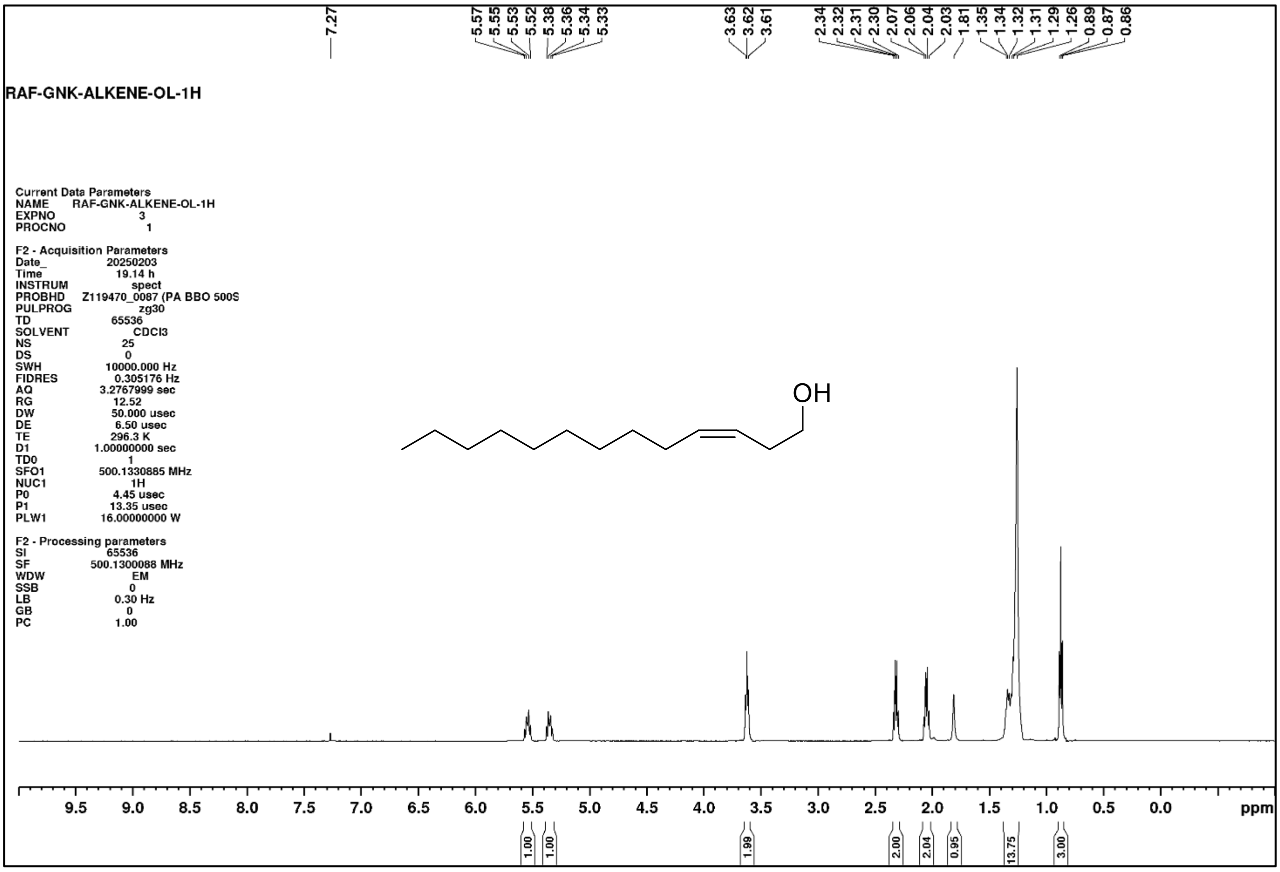
F2 - Processing parameters
SI                32768
SF       100.6555151 MHz
WDW                  EM
SSB                   0
LB              1.00 Hz
GB                    0
PC                 1.40
```

10: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. $C_{13}H_{25}O$ 197. 1900; found 197.1900





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

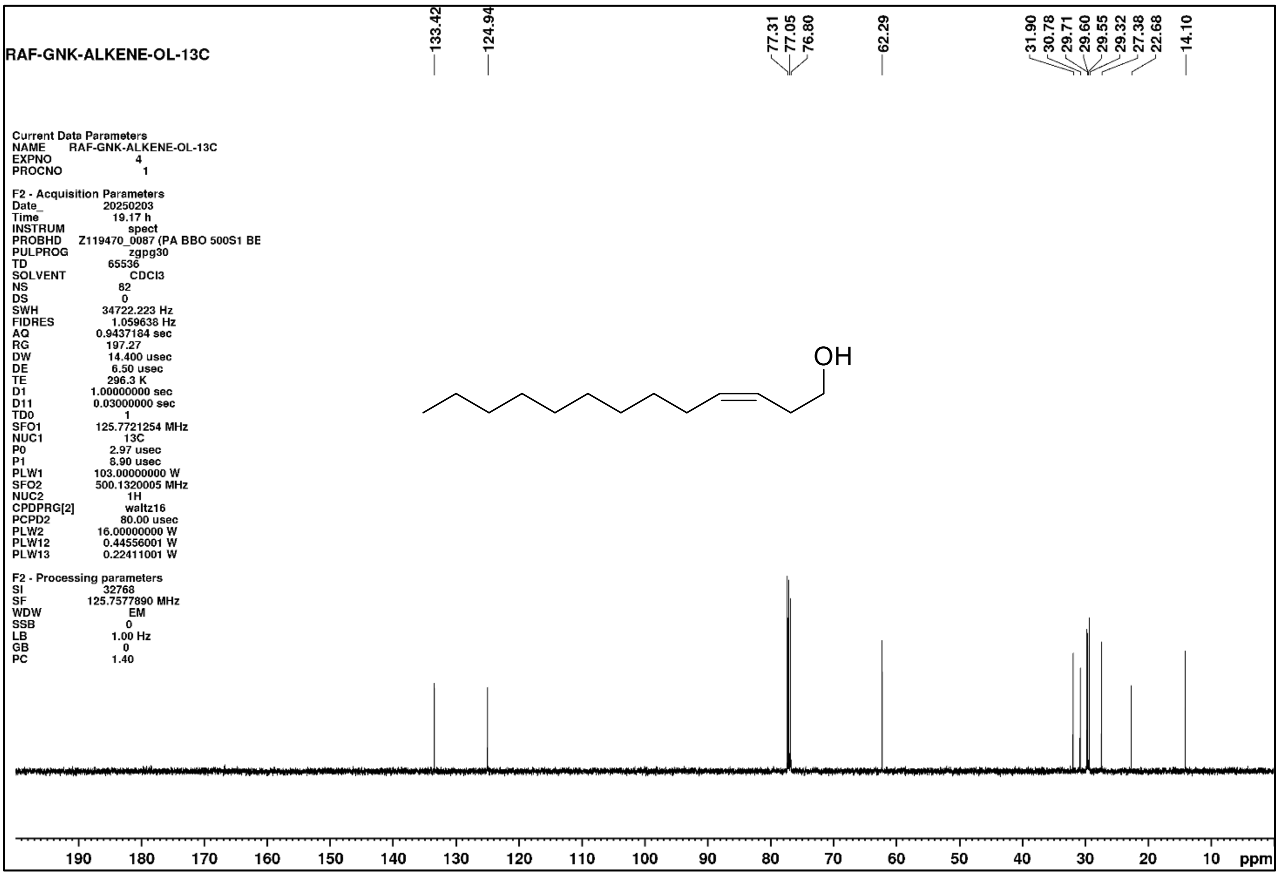


```
RAF-GNK-ALKENE-OL-1H

Current Data Parameters
NAME      RAF-GNK-ALKENE-OL-1H
EXPNO                3
PROCNO               1

F2 - Acquisition Parameters
Date_          20250203
Time             19.14 h
INSTRUM            spect
PROBHD   Z119470_0087 (PA BBO 500S
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               296.3 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       500.1300088 MHz
WDW                   EM
SSB                    0
LB               0.30 Hz
GB                     0
PC                  1.00
```



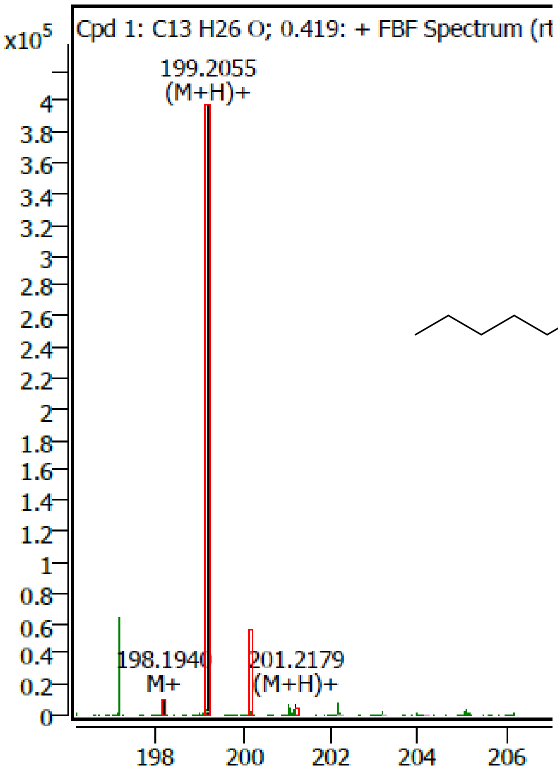
```
RAF-GNK-ALKENE-OL-13C

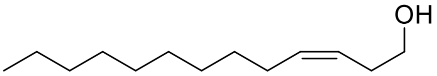
Current Data Parameters
NAME      RAF-GNK-ALKENE-OL-13C
EXPNO                4
PROCNO               1

F2 - Acquisition Parameters
Date_          20250203
Time             19.17 h
INSTRUM            spect
PROBHD   Z119470_0087 (PA BBO 500S1 BE
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    82
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               296.3 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

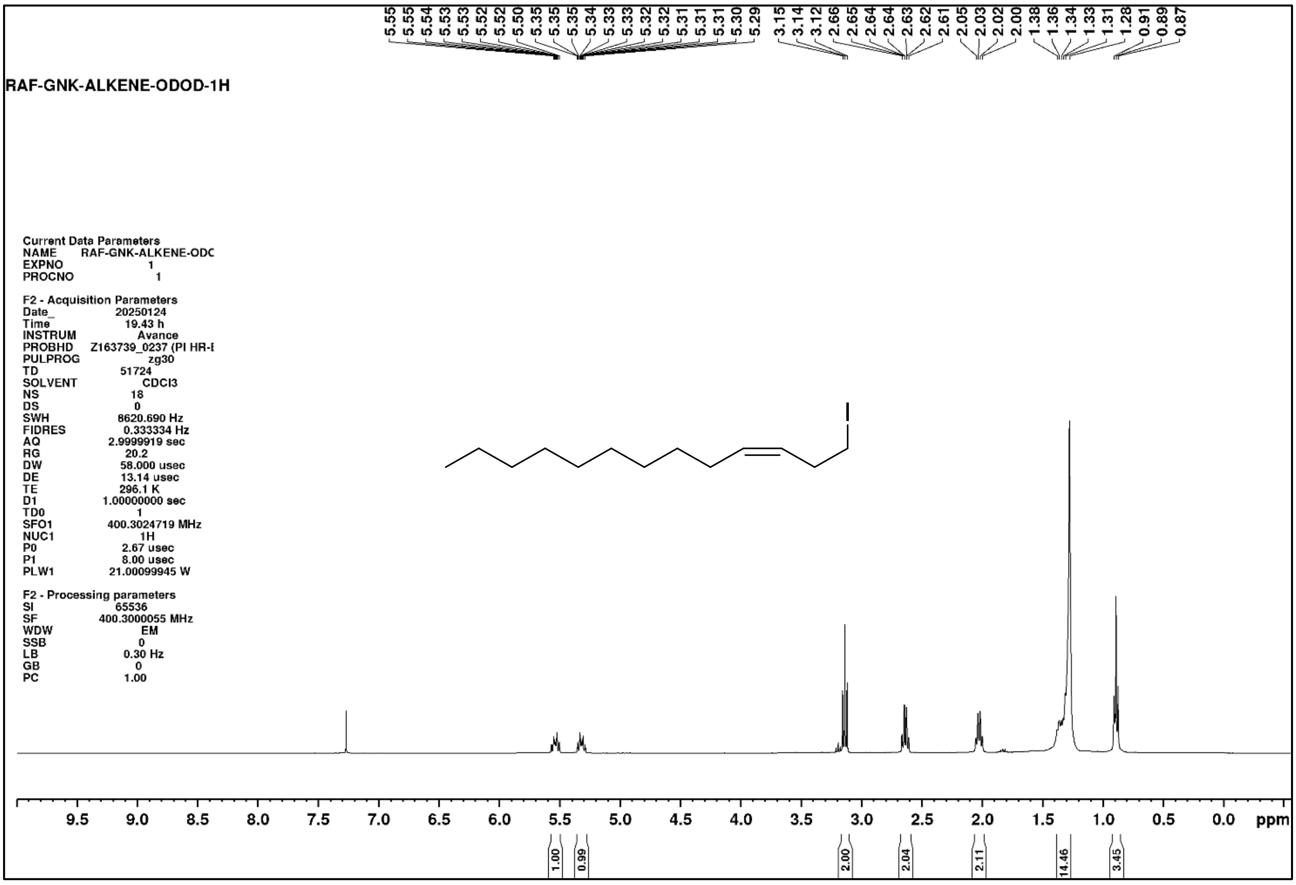
F2 - Processing parameters
SI                 32768
SF       125.7577890 MHz
WDW                   EM
SSB                    0
LB               1.00 Hz
GB                     0
PC                  1.40
```

6b: HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd. $C_{13}H_{27}O$ 199.2057 ; found 199.2055.





^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) of compound **7b**

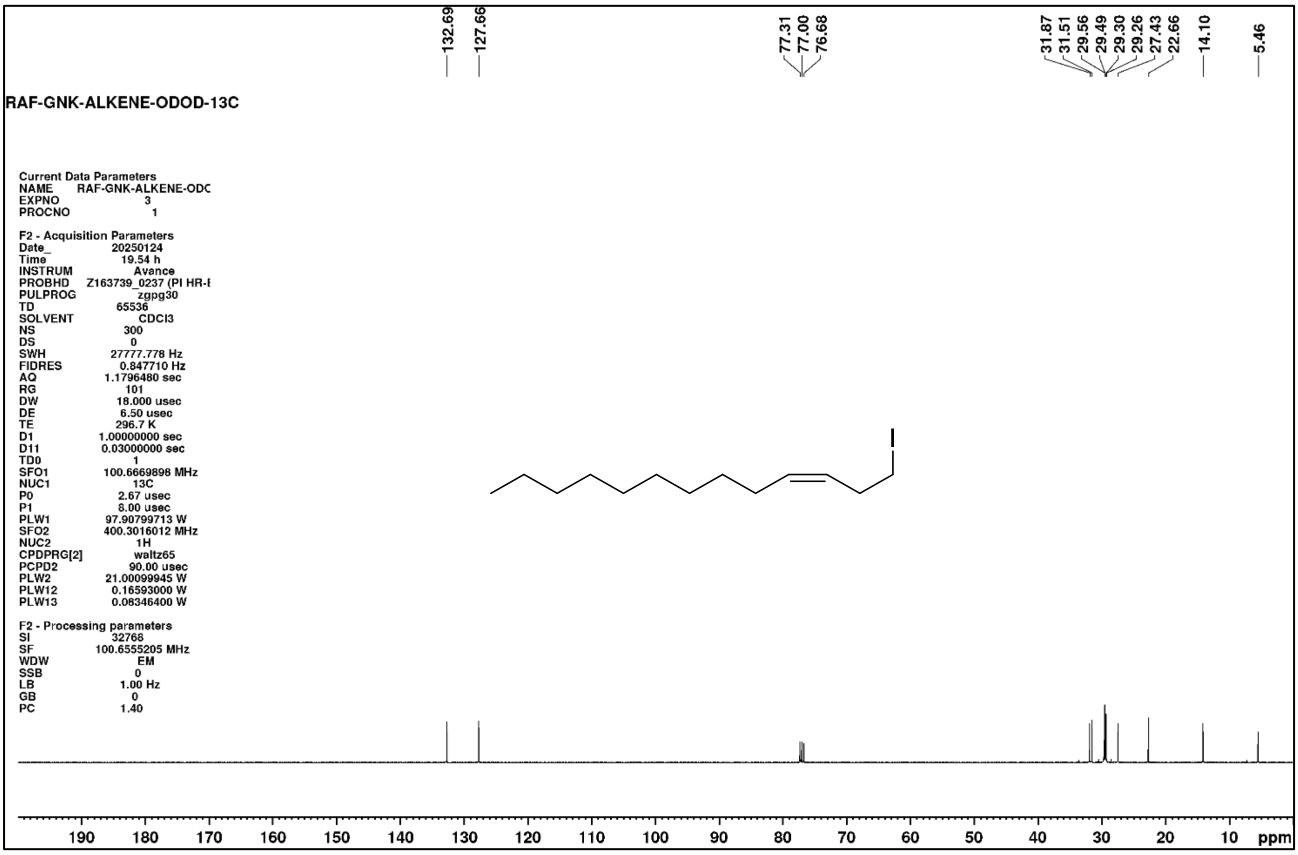


RAF-GNK-ALKENE-ODOD-1H

```
Current Data Parameters
NAME      RAF-GNK-ALKENE-ODC
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_            20250124
Time               19.43 h
INSTRUM             Avance
PROBHD   Z163739_0237 (PI HR-I
PULPROG              zg30
TD               51724
SOLVENT             CDCI3
NS                  18
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                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             400.3000055 MHz
WDW                  EM
SSB                  0
LB                 0.30 Hz
GB                   0
PC                 1.00
```



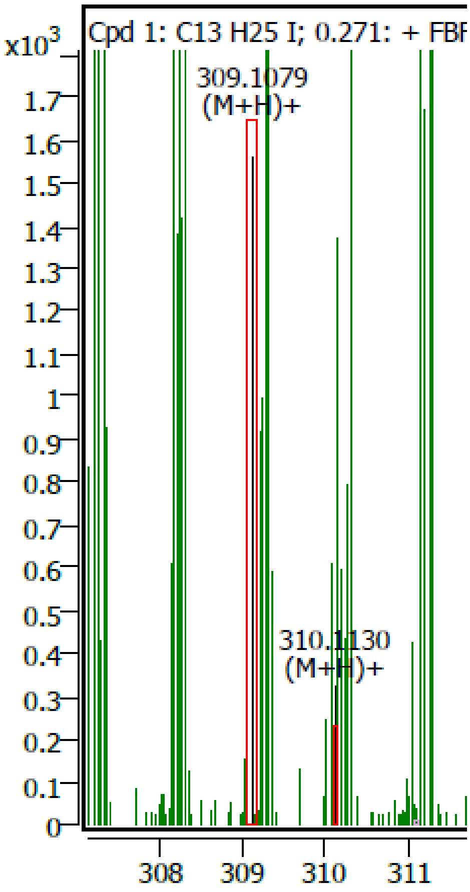
RAF-GNK-ALKENE-ODOD-13C

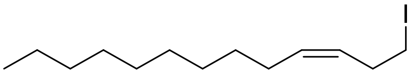
```
Current Data Parameters
NAME      RAF-GNK-ALKENE-ODC
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_            20250124
Time               19.54 h
INSTRUM             Avance
PROBHD   Z163739_0237 (PI HR-I
PULPROG            zgpg30
TD               65536
SOLVENT             CDCI3
NS                  300
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

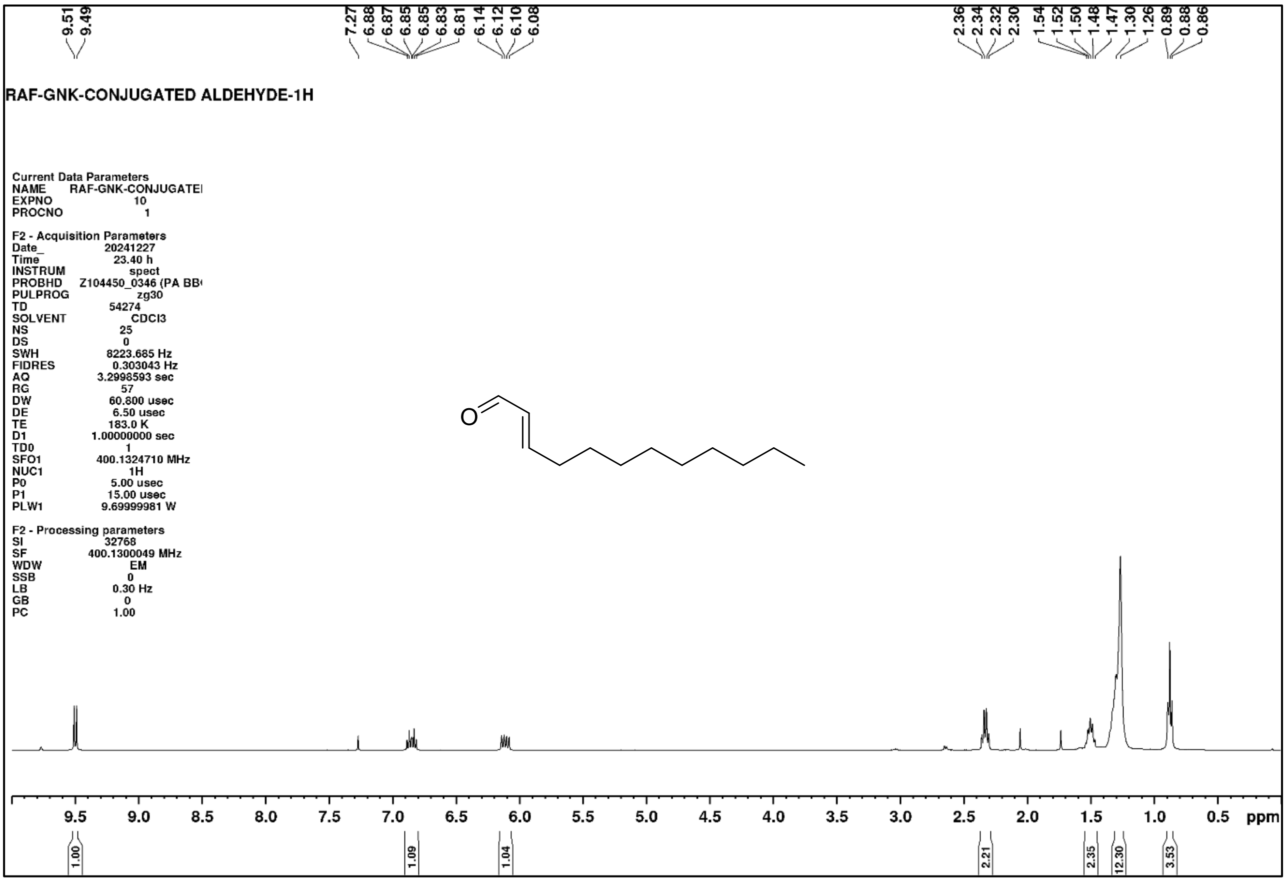
F2 - Processing parameters
SI                32768
SF             100.6555205 MHz
WDW                  EM
SSB                  0
LB                 1.00 Hz
GB                   0
PC                 1.40
```

7b: HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd. $C_{13}H_{26}I$ 309.1074; found 309.1079.





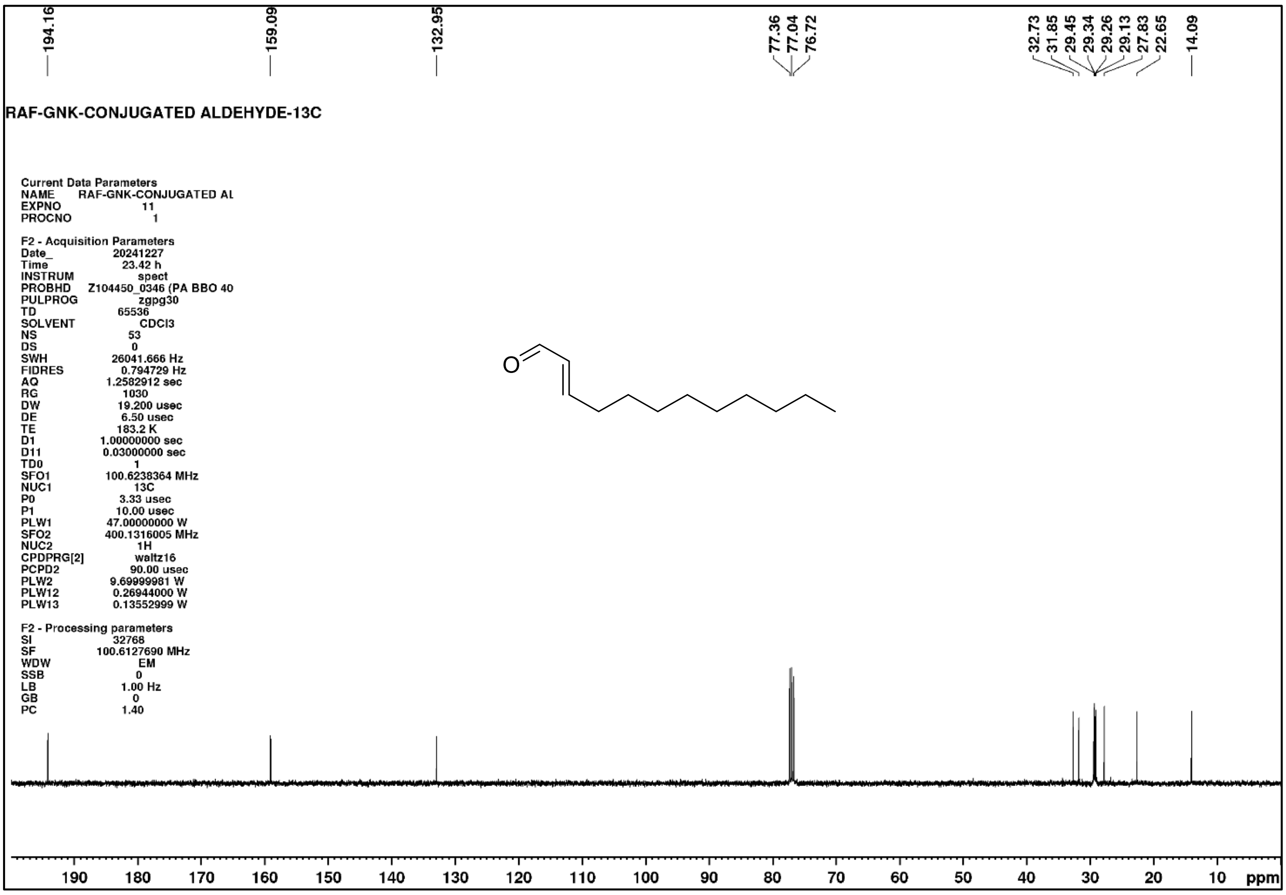
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **4a**



```
Current Data Parameters
NAME     RAF-GNK-CONJUGATEI
EXPNO              10
PROCNO              1

F2 - Acquisition Parameters
Date_          20241227
Time             23.40 h
INSTRUM           spect
PROBHD   Z104450_0346 (PA BB(
PULPROG            zg30
TD              54274
SOLVENT           CDCl3
NS                 25
DS                  0
SWH          8223.685 Hz
FIDRES        0.303043 Hz
AQ          3.2998593 sec
RG                 57
DW             60.800 usec
DE               6.50 usec
TE              183.0 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        400.1300049 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
```

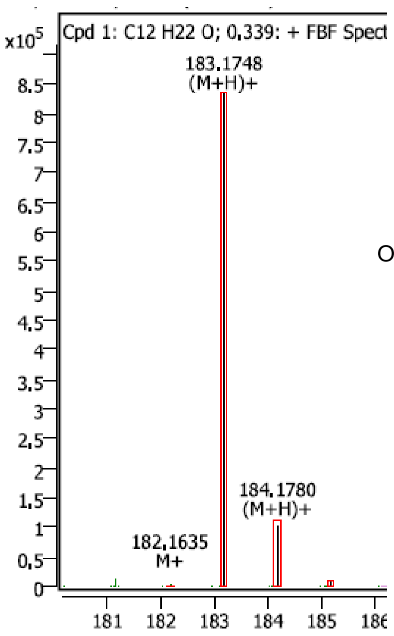


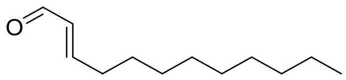
```
Current Data Parameters
NAME     RAF-GNK-CONJUGATED AL
EXPNO              11
PROCNO              1

F2 - Acquisition Parameters
Date_          20241227
Time             23.42 h
INSTRUM           spect
PROBHD   Z104450_0346 (PA BBO 40
PULPROG          zgpg30
TD              65536
SOLVENT           CDCl3
NS                 53
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              183.2 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

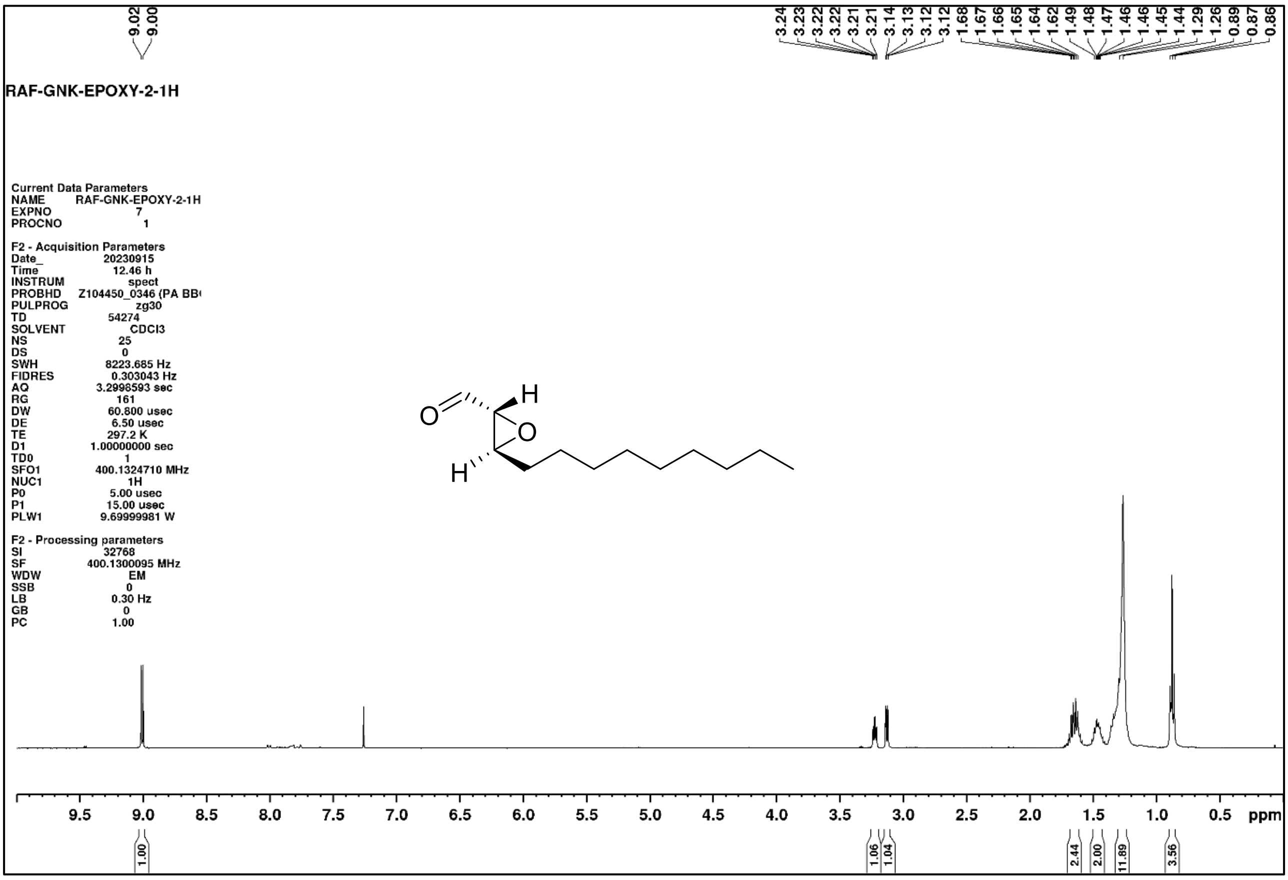
F2 - Processing parameters
SI              32768
SF        100.6127690 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

4a: HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd. $C_{12}H_{22}O$ 183.1744; found 183.1748





^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **3a**

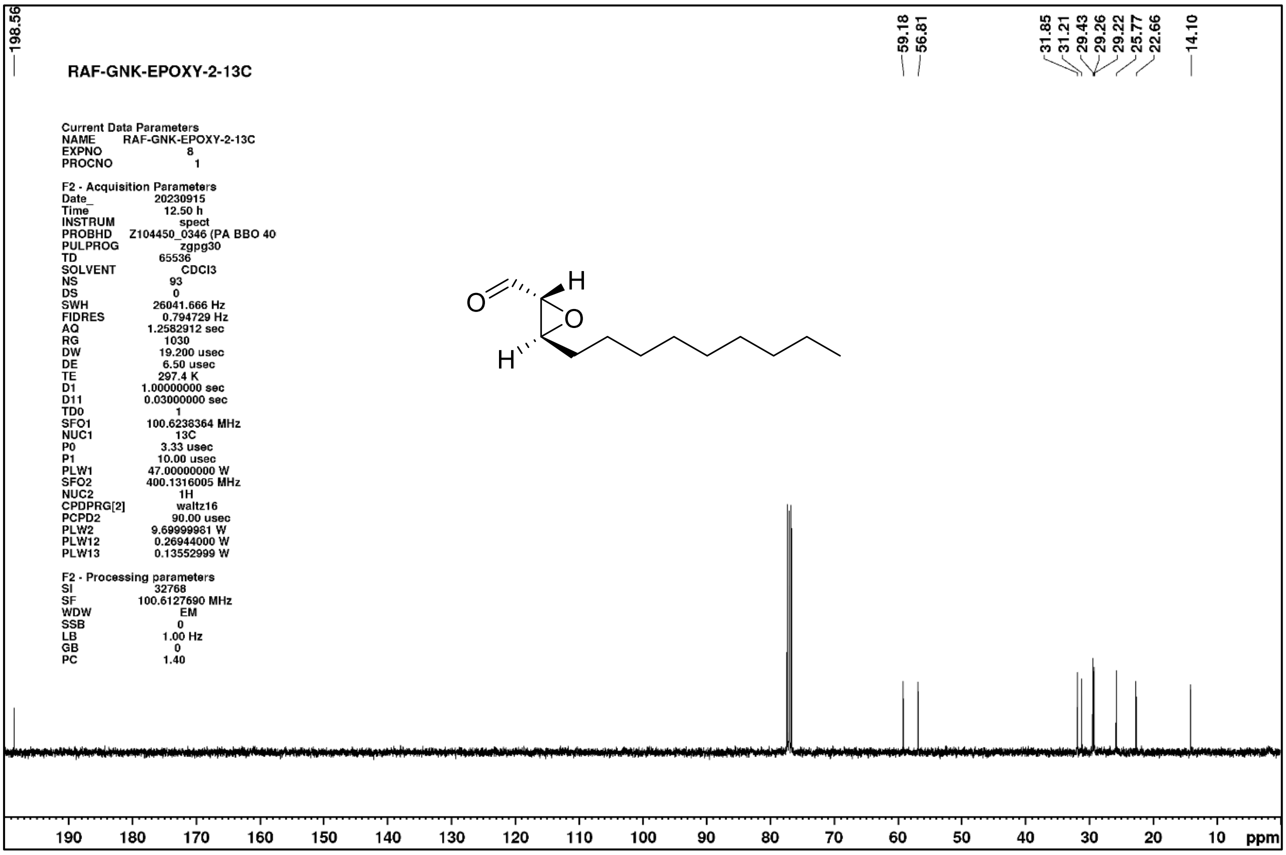


RAF-GNK-EPOXY-2-1H

```
Current Data Parameters
NAME        RAF-GNK-EPOXY-2-1H
EXPNO                    7
PROCNO                   1

F2 - Acquisition Parameters
Date_              20230915
Time                12.46 h
INSTRUM               spect
PROBHD     Z104450_0346 (PA BB(
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                  297.2 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           400.1300095 MHz
WDW                      EM
SSB                       0
LB                  0.30 Hz
GB                        0
PC                     1.00
```



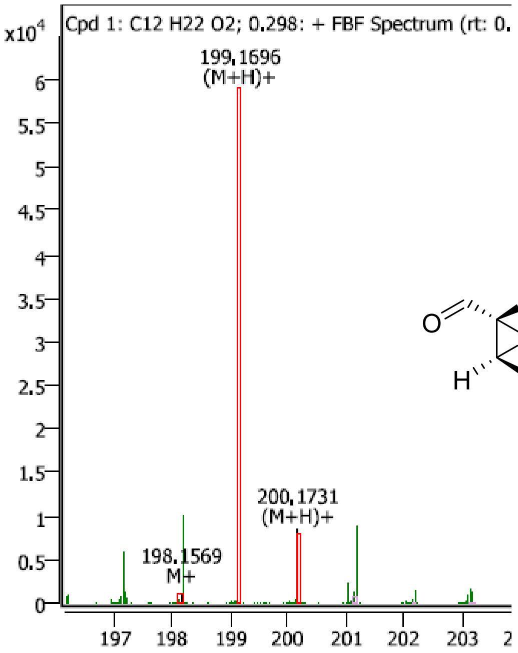
RAF-GNK-EPOXY-2-13C

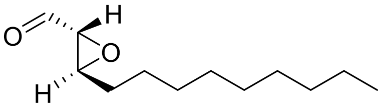
```
Current Data Parameters
NAME        RAF-GNK-EPOXY-2-13C
EXPNO                    8
PROCNO                   1

F2 - Acquisition Parameters
Date_              20230915
Time                12.50 h
INSTRUM               spect
PROBHD     Z104450_0346 (PA BBO 40
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       93
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                  297.4 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

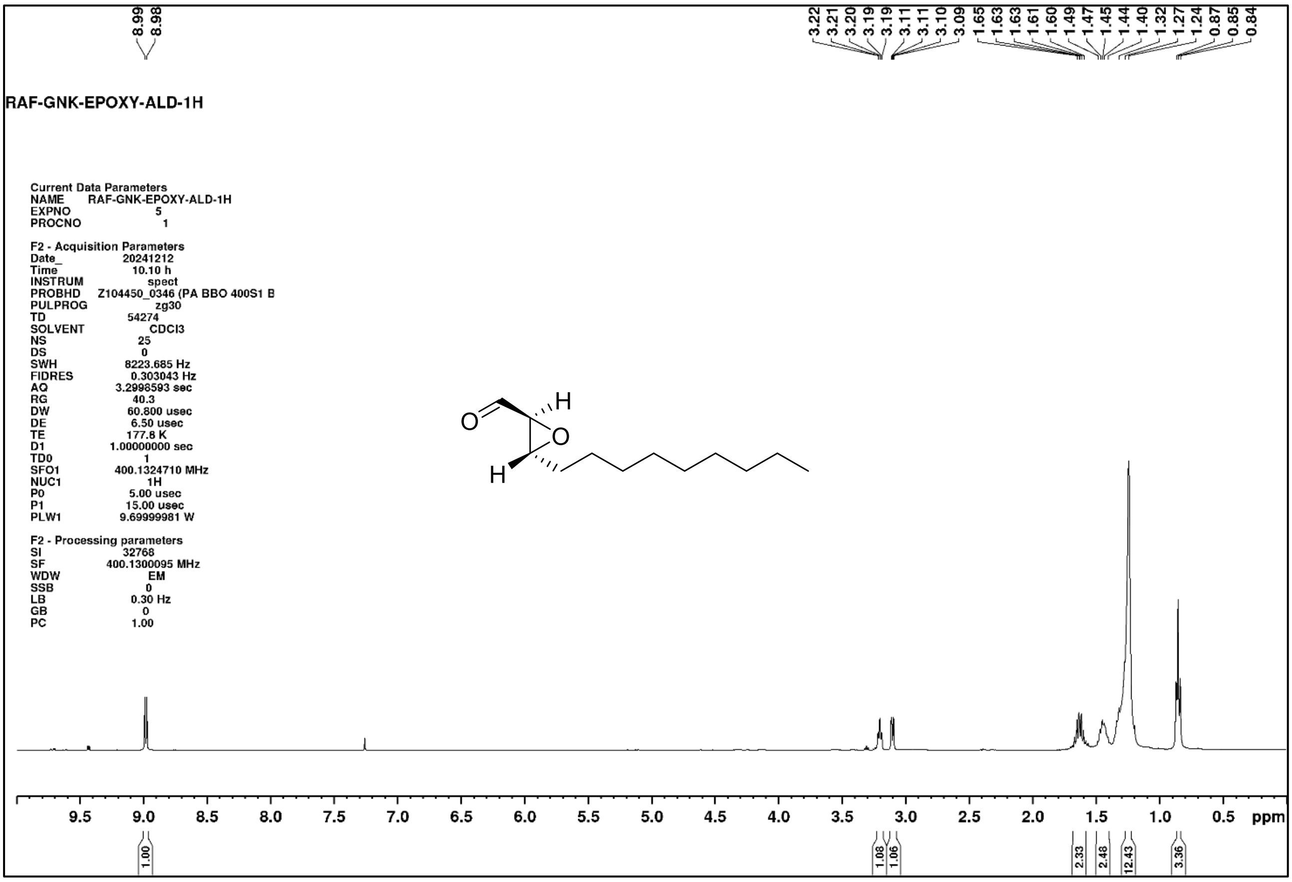
F2 - Processing parameters
SI                    32768
SF           100.6127690 MHz
WDW                      EM
SSB                       0
LB                  1.00 Hz
GB                        0
PC                     1.40
```

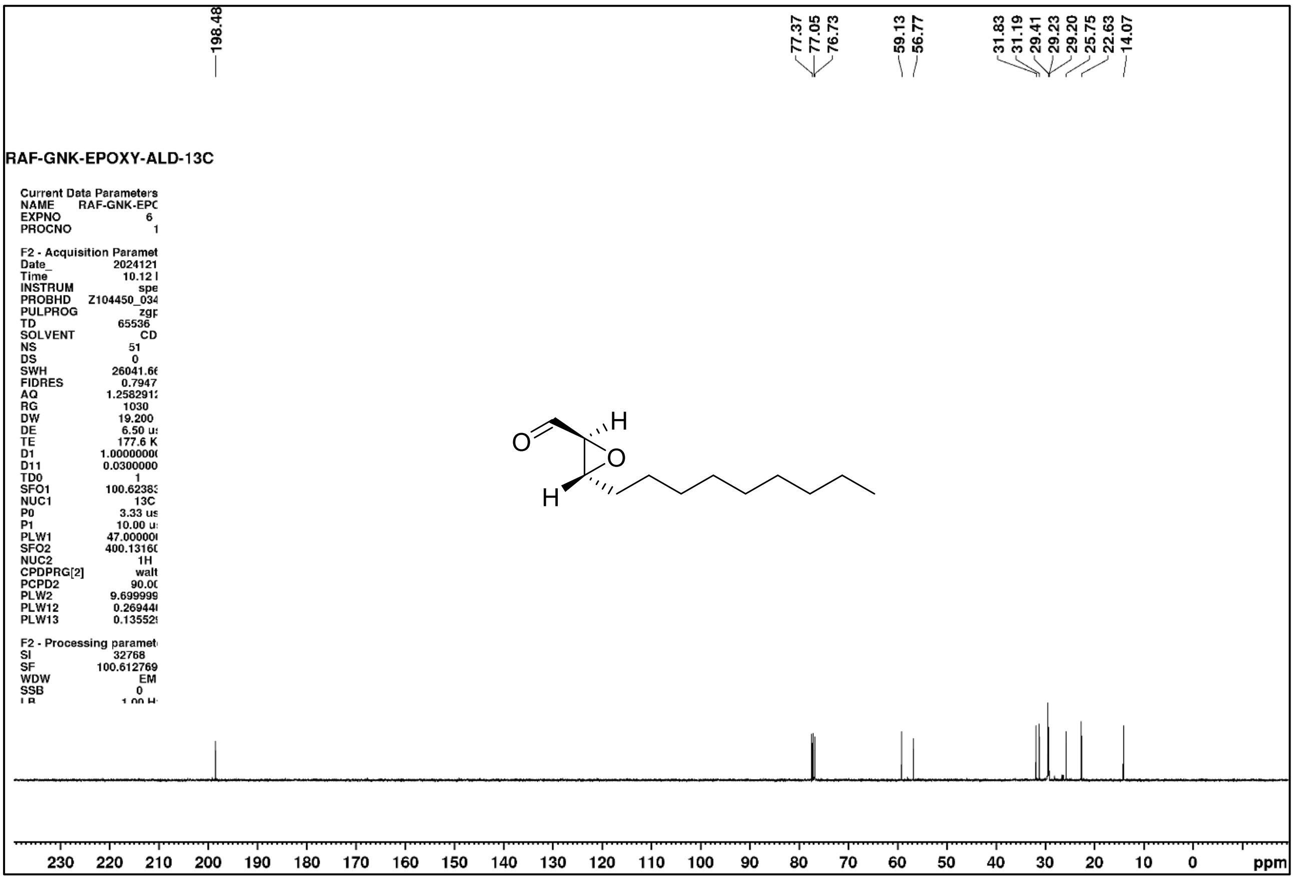
3a: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. $C_{12}H_{23}O$ 199.1694; found 199.1696.



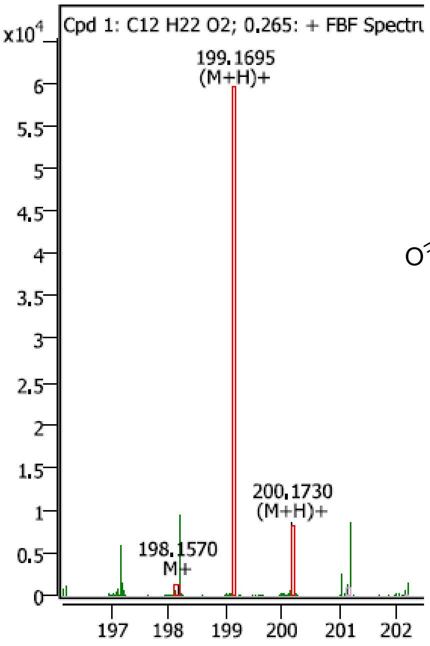


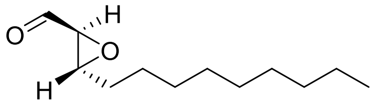
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) of compound ***ent*-3a**



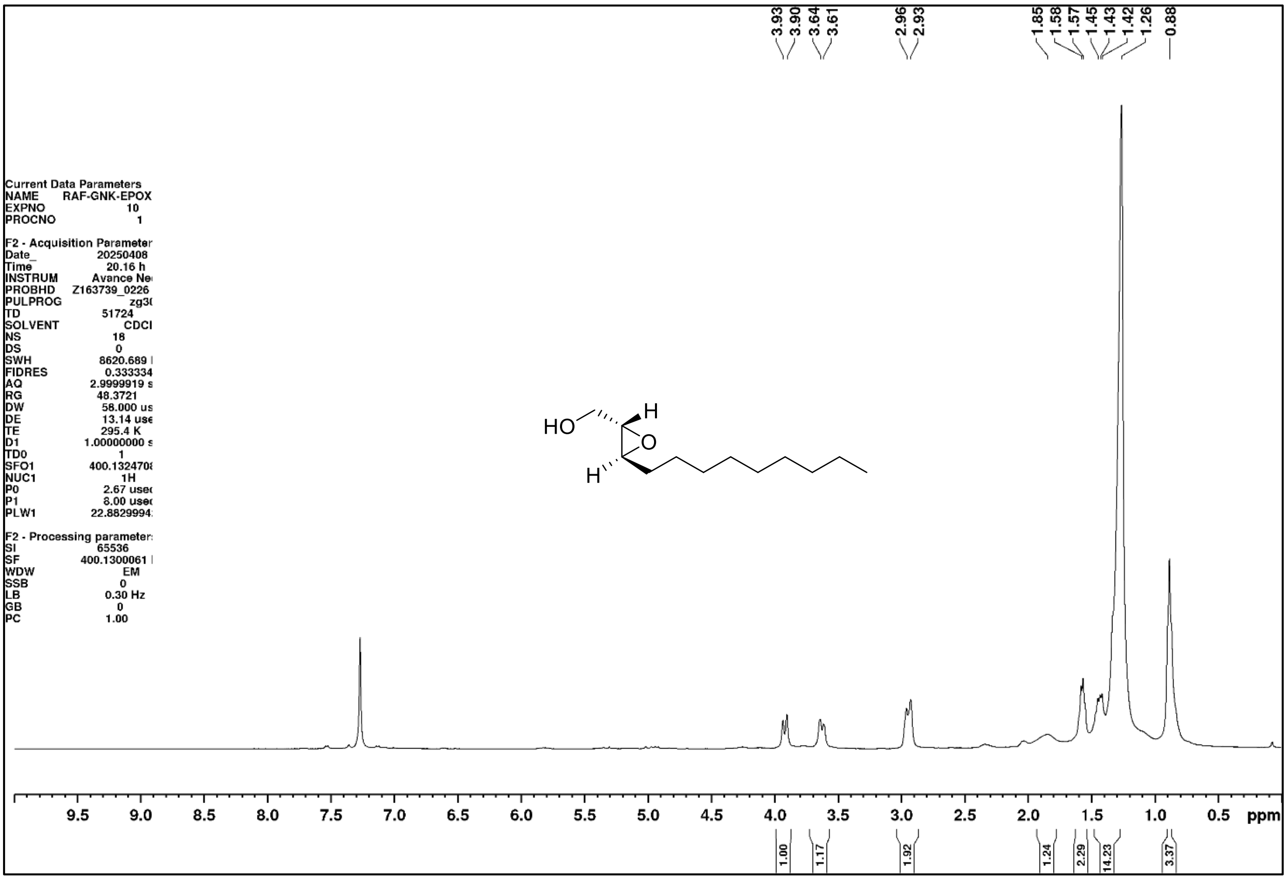


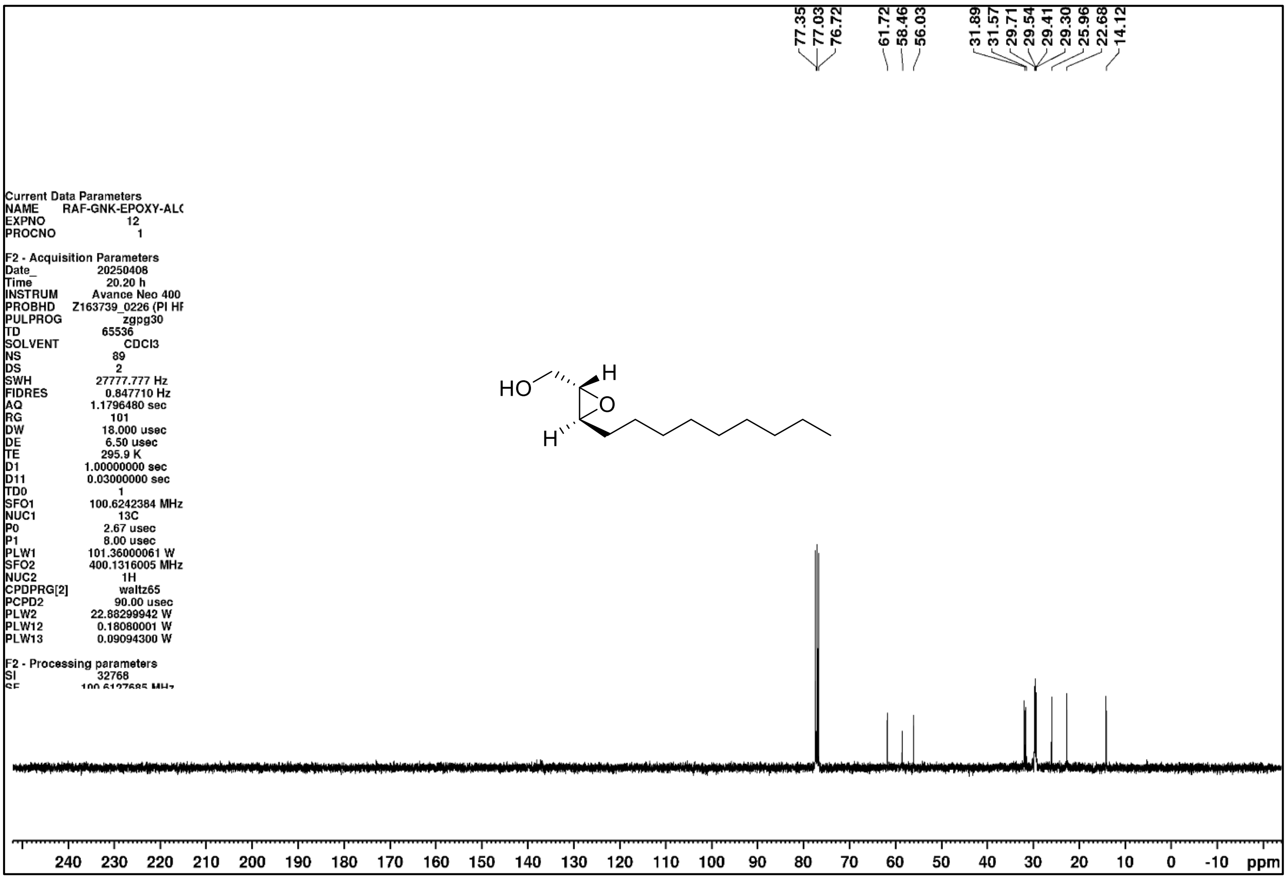
***ent*-3a**: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. $C_{12}H_{23}O_2$ 199.1694; found 199.1695



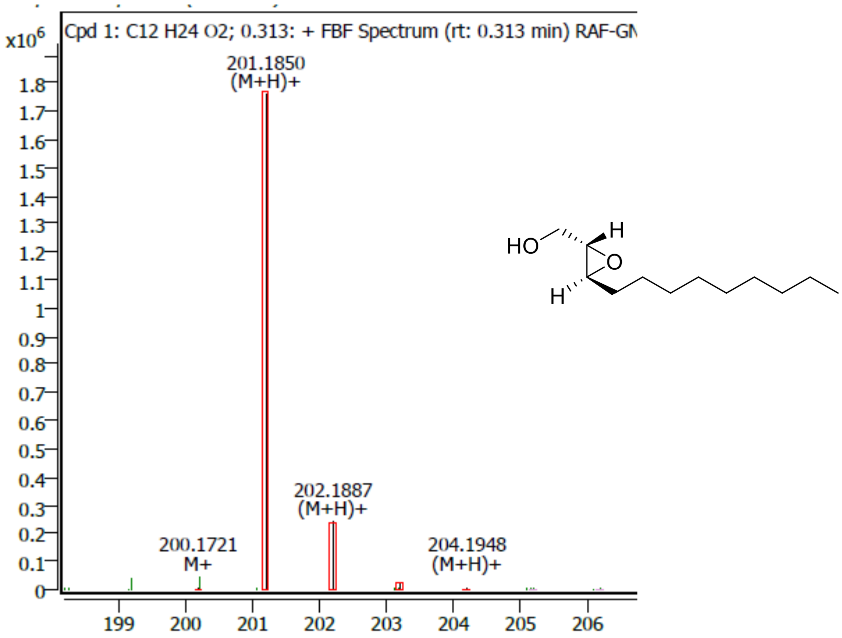


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **12**

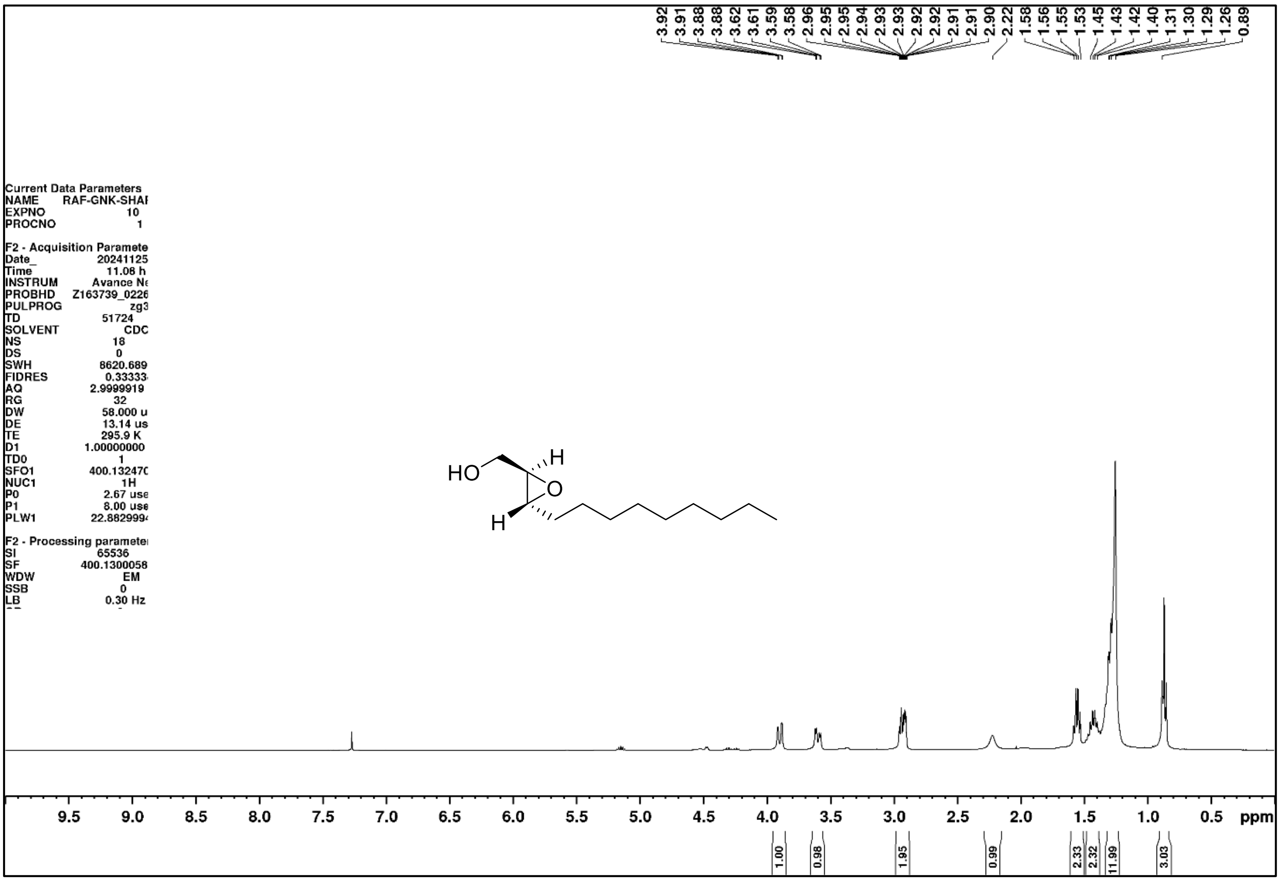


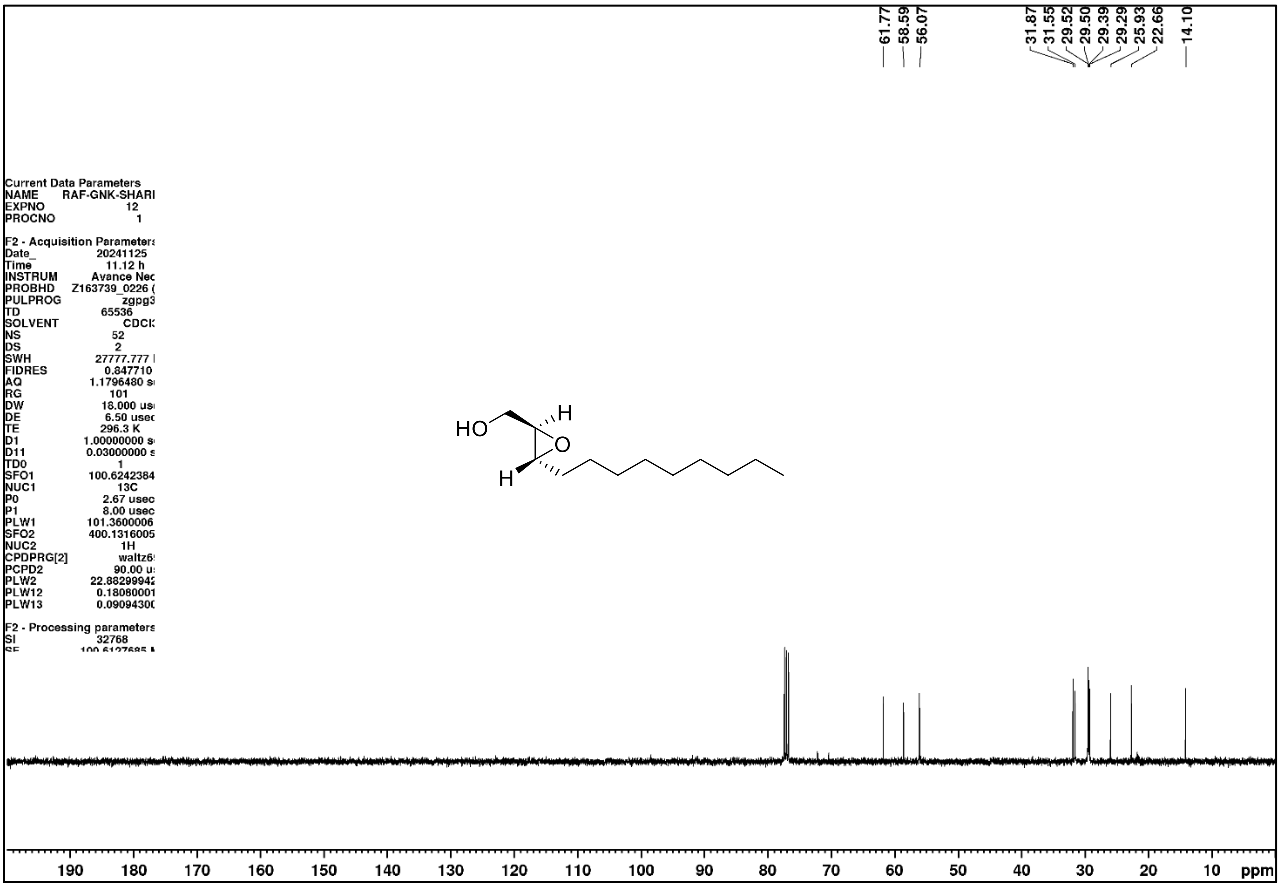


12: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. $C_{12}H_{25}O_2$ 201.1850; found 201.1850.

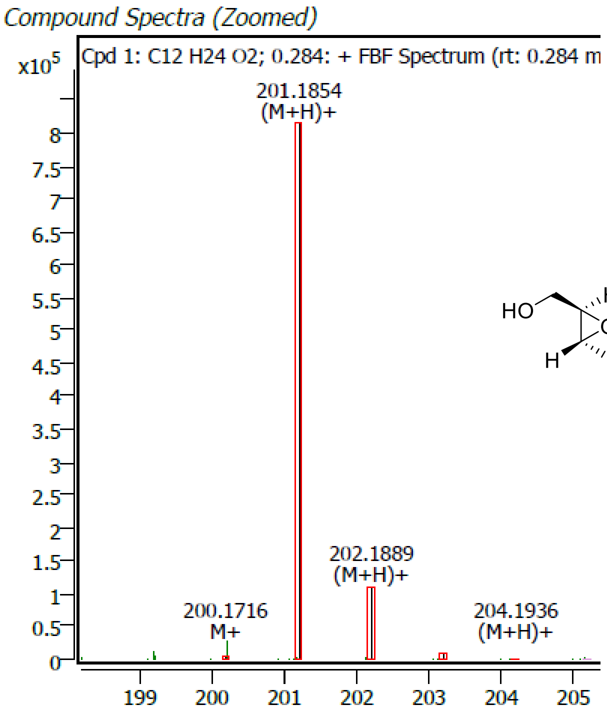


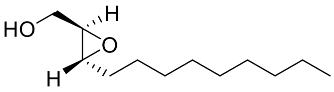
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound ***ent*-12**



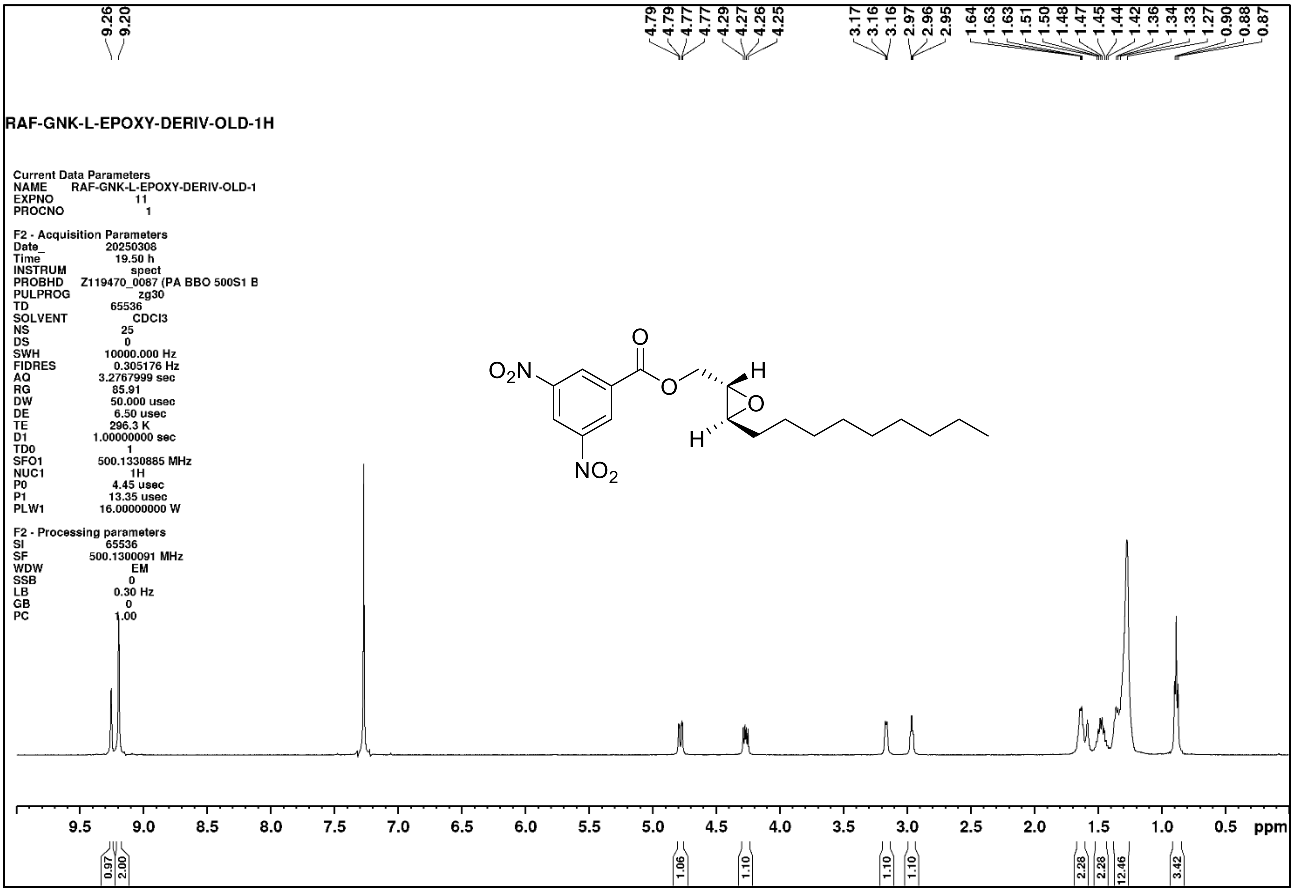


***ent*-12**: HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd. $C_{12}H_{25}O_2$ 201.1850; found 201.1854.





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

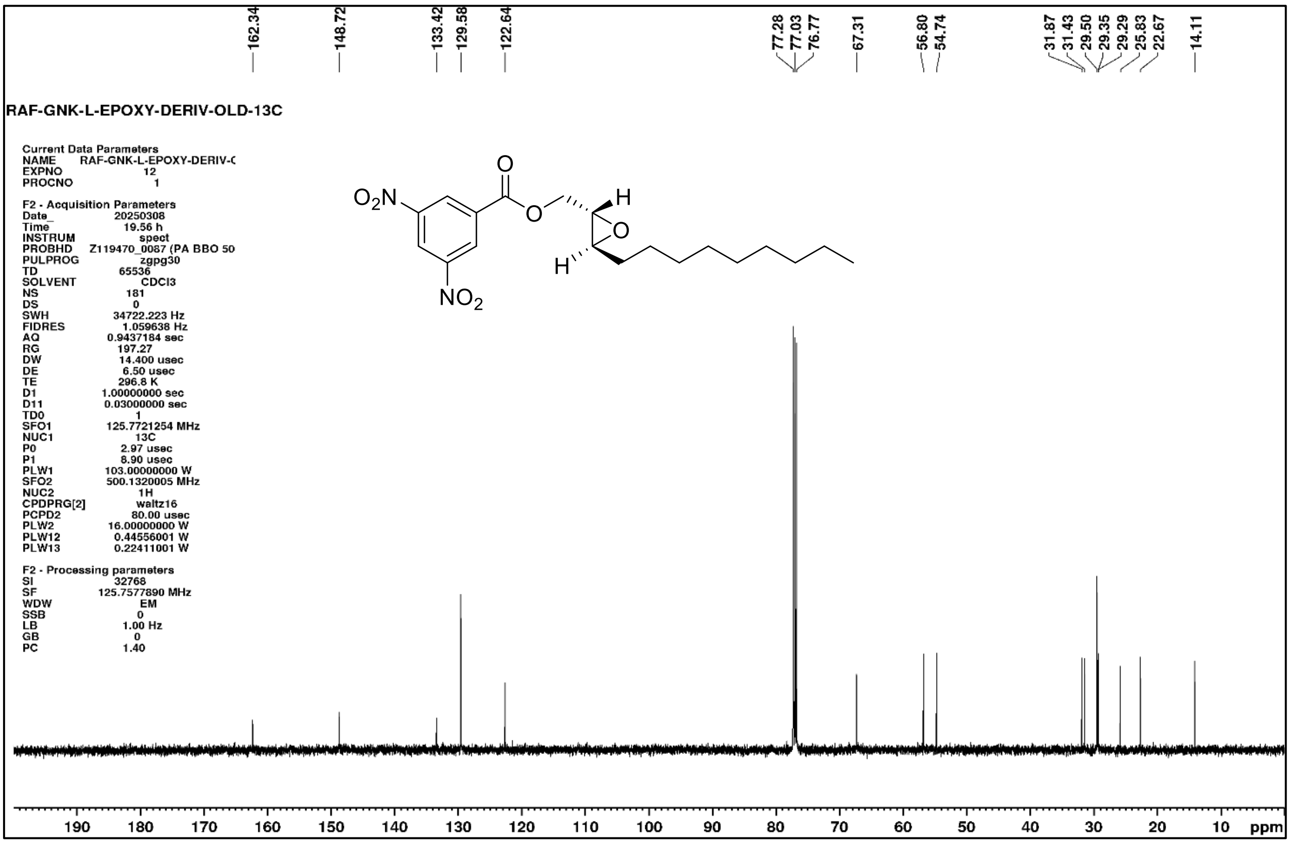


```
RAF-GNK-L-EPOXY-DERIV-OLD-1H

Current Data Parameters
NAME       RAF-GNK-L-EPOXY-DERIV-OLD-1
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20250308
Time                 19.50 h
INSTRUM               spect
PROBHD    Z119470_0087 (PA BBO 500S1 B
PULPROG                zg30
TD                 65536
SOLVENT               CDCl3
NS                    25
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                296.3 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            500.1300091 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                  1.00
```



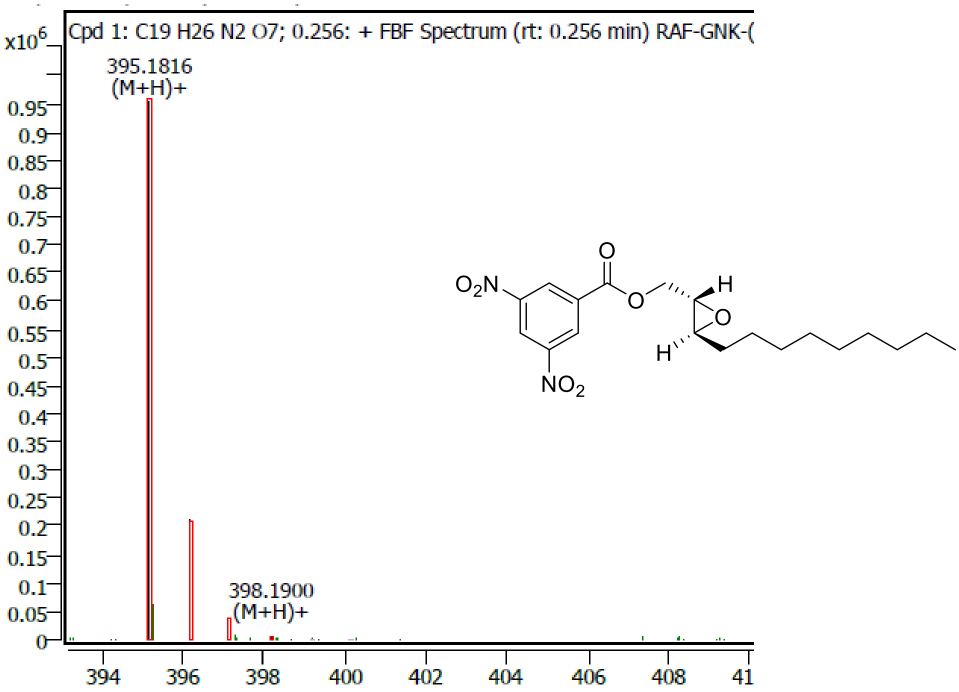
```
RAF-GNK-L-EPOXY-DERIV-OLD-13C

Current Data Parameters
NAME       RAF-GNK-L-EPOXY-DERIV-(
EXPNO                  12
PROCNO                  1

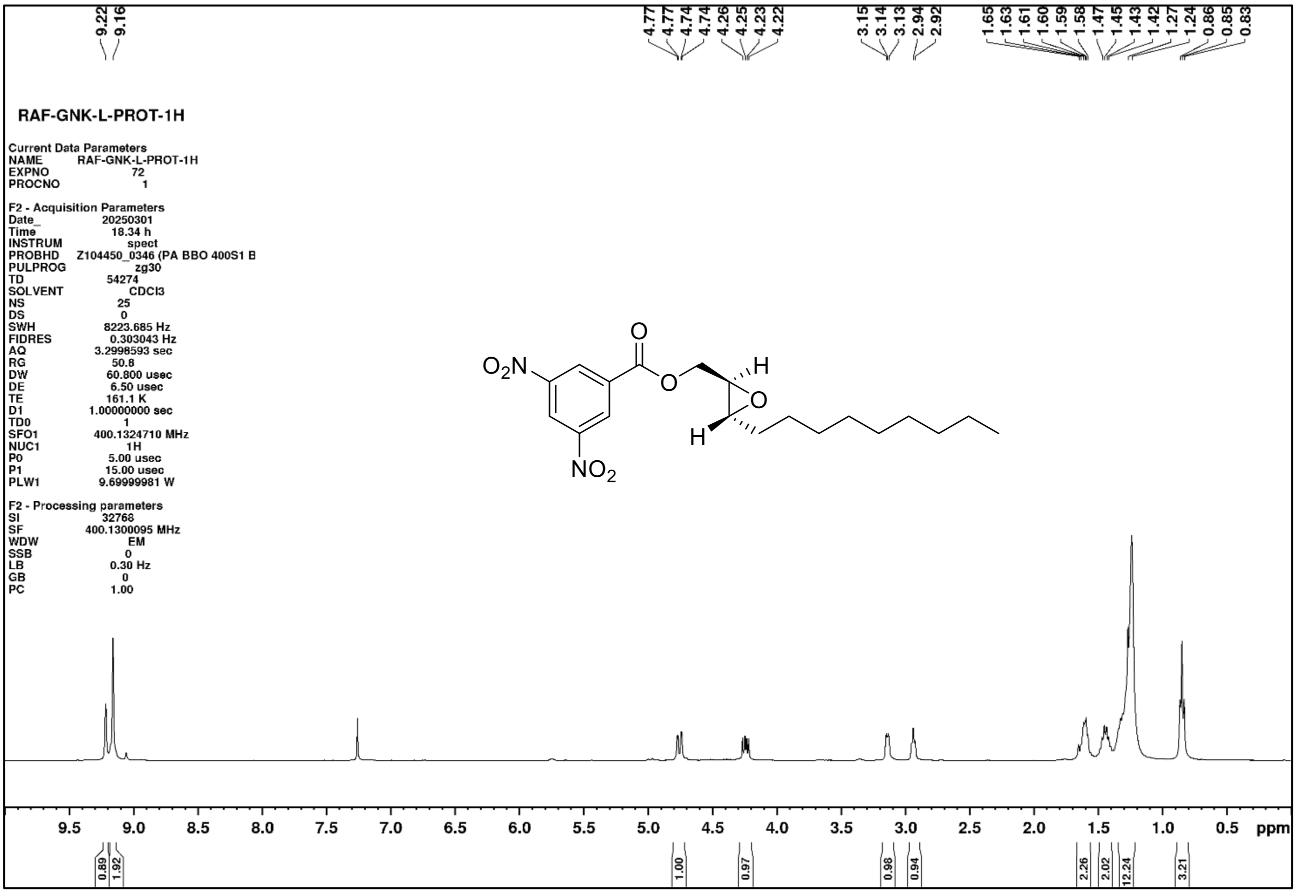
F2 - Acquisition Parameters
Date_              20250308
Time                 19.56 h
INSTRUM               spect
PROBHD    Z119470_0087 (PA BBO 50
PULPROG              zgpg30
TD                 65536
SOLVENT               CDCl3
NS                   181
DS                     0
SWH             34722.223 Hz
FIDRES             1.059638 Hz
AQ              0.9437184 sec
RG                197.27
DW                14.400 usec
DE                 6.50 usec
TE                296.8 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            125.7577890 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                  1.40
```

13: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. $C_{19}H_{27}N_2O_7$ 395.1813; found 395.1816.



^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of benzoyl ester ***ent*-13**

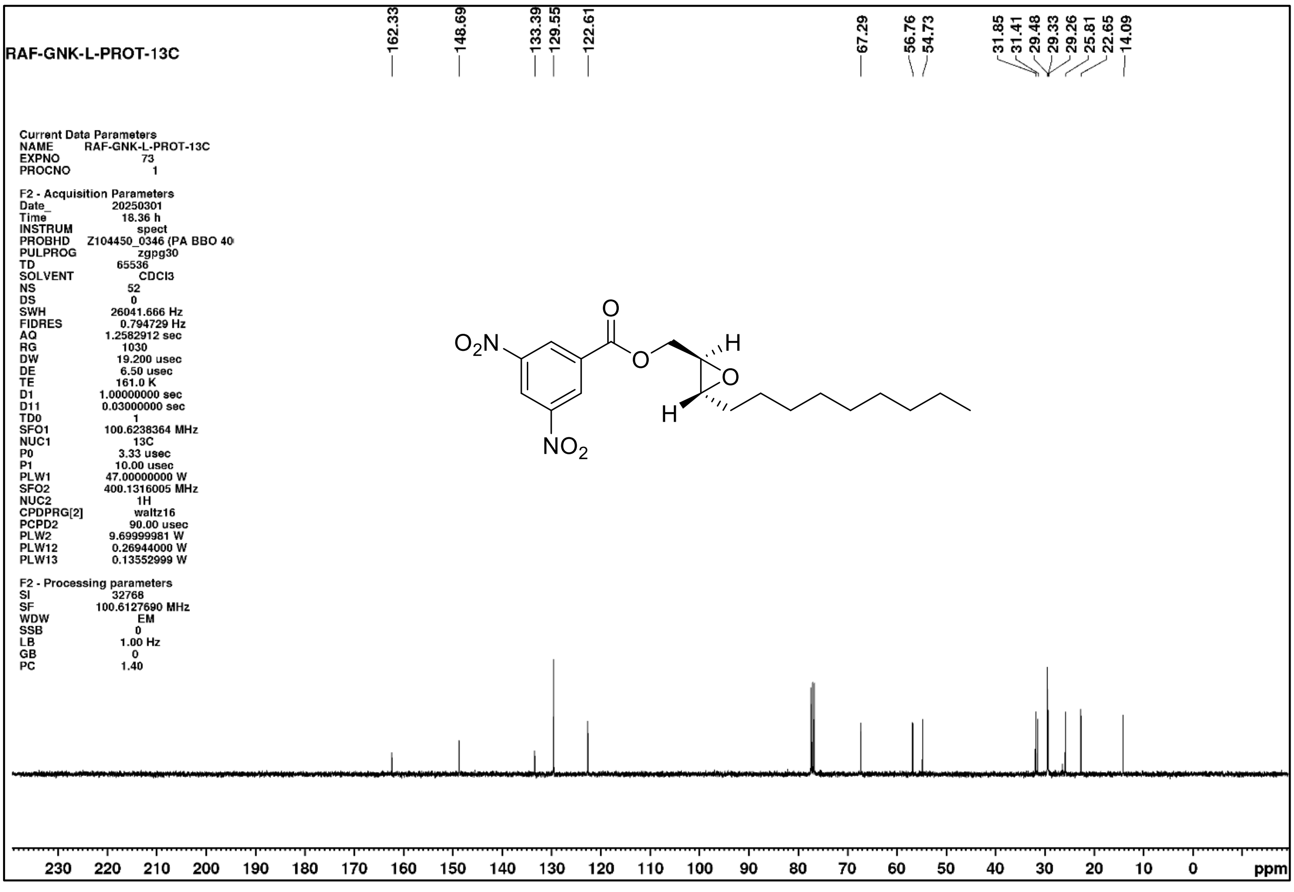


```
RAF-GNK-L-PROT-1H

Current Data Parameters
NAME        RAF-GNK-L-PROT-1H
EXPNO                 72
PROCNO                 1

F2 - Acquisition Parameters
Date_              20250301
Time                18.34 h
INSTRUM              spect
PROBHD     Z104450_0346 (PA BBO 400S1 B
PULPROG              zg30
TD                 54274
SOLVENT              CDCl3
NS                   25
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               161.1 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
LB                 0.30 Hz
GB                     0
PC                  1.00
```



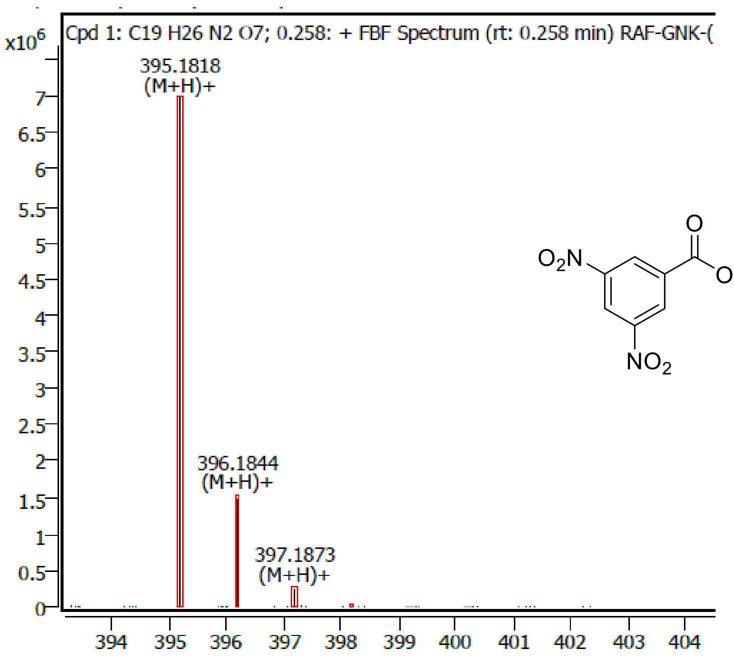
```
RAF-GNK-L-PROT-13C

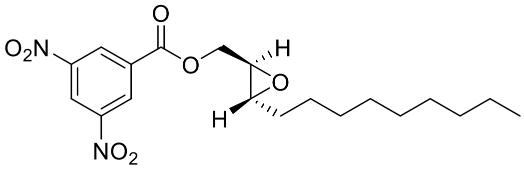
Current Data Parameters
NAME        RAF-GNK-L-PROT-13C
EXPNO                 73
PROCNO                 1

F2 - Acquisition Parameters
Date_              20250301
Time                18.36 h
INSTRUM              spect
PROBHD     Z104450_0346 (PA BBO 40
PULPROG             zgpg30
TD                 65536
SOLVENT              CDCl3
NS                   52
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               161.0 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

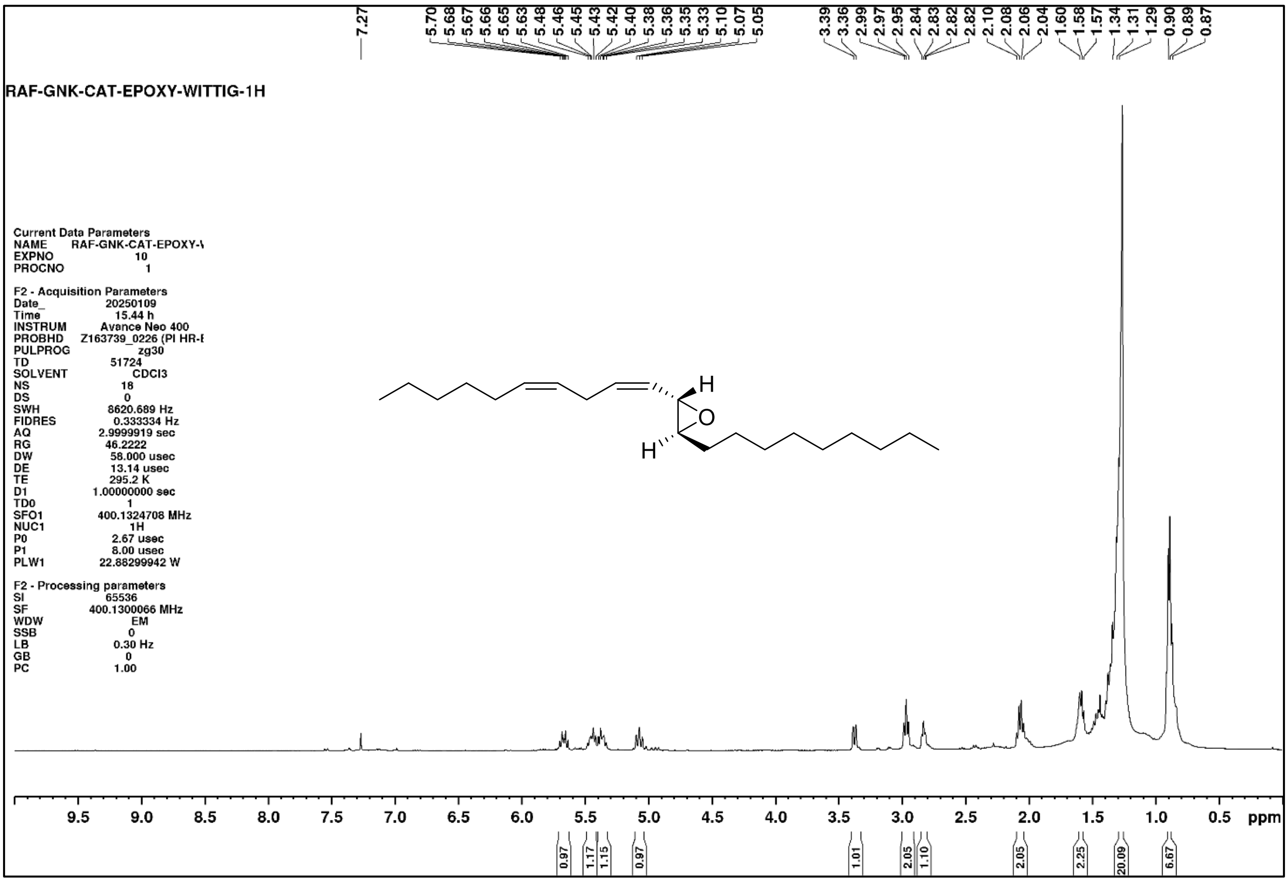
F2 - Processing parameters
SI                 32768
SF            100.6127690 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                  1.40
```

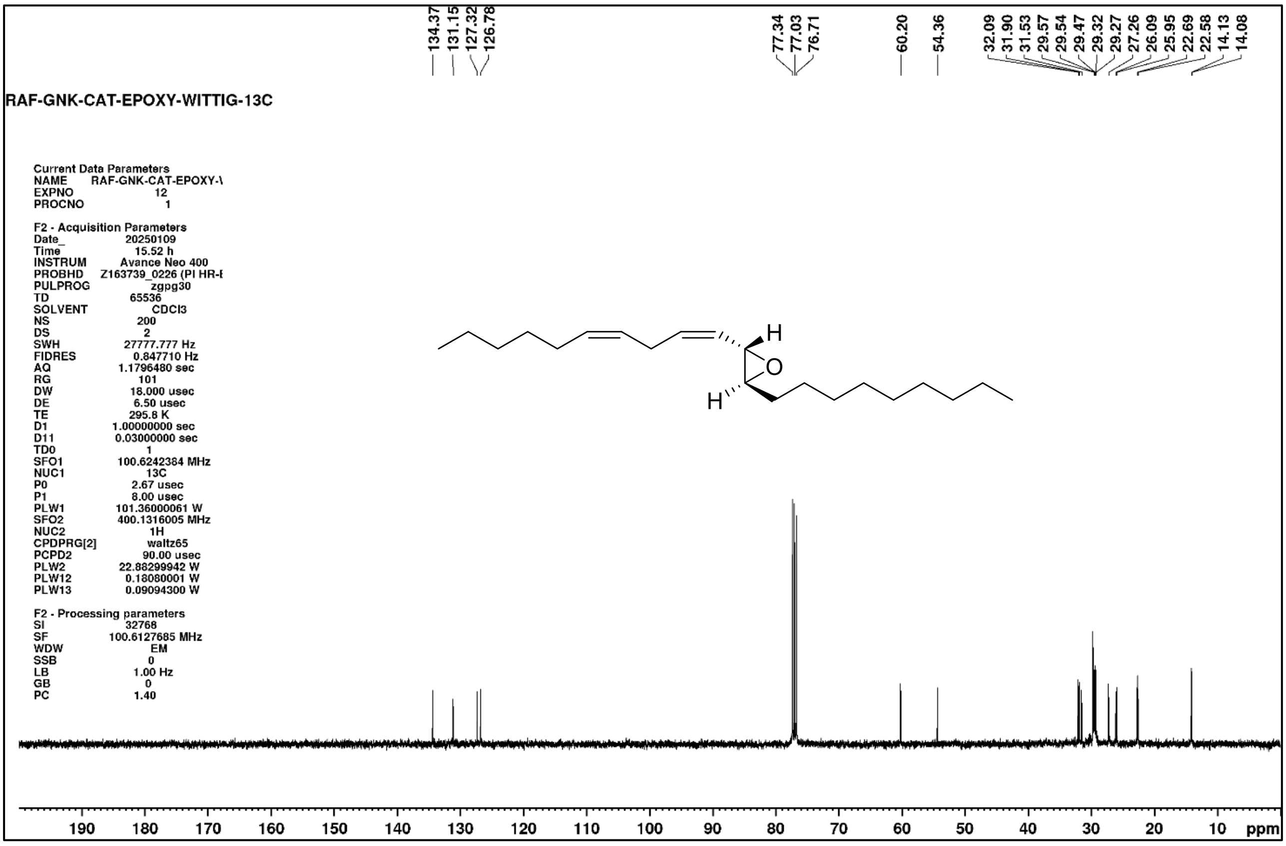
***ent*-13**: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. $C_{19}H_{27}N_2O_7$ 395.1813; found 395.1818.



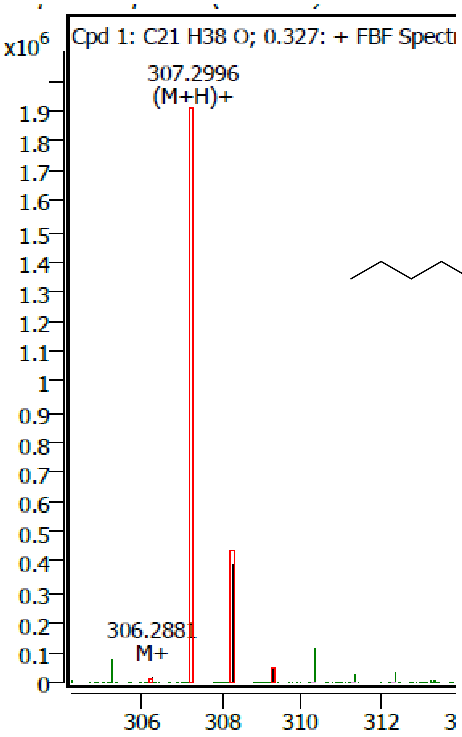


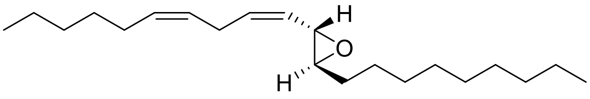
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **1**



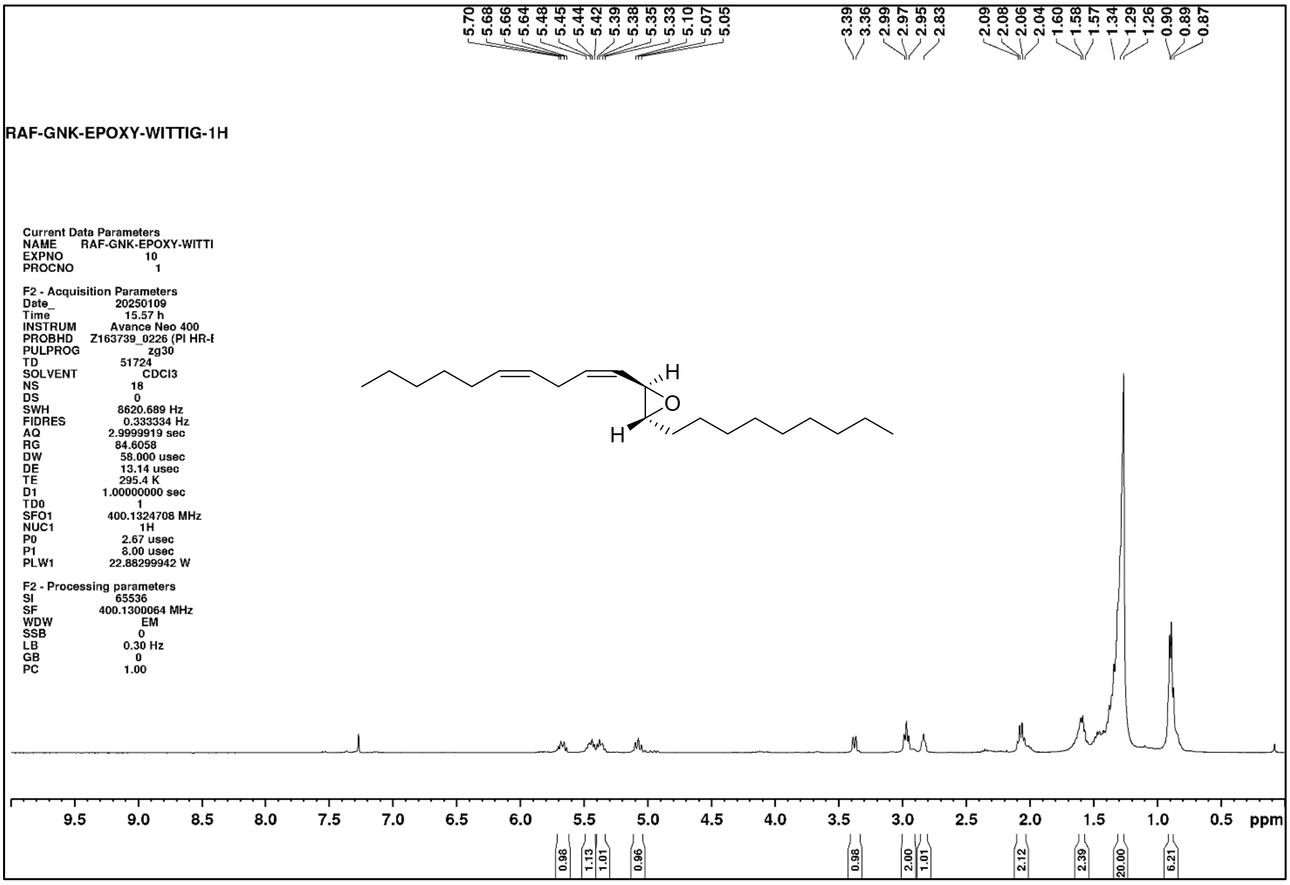


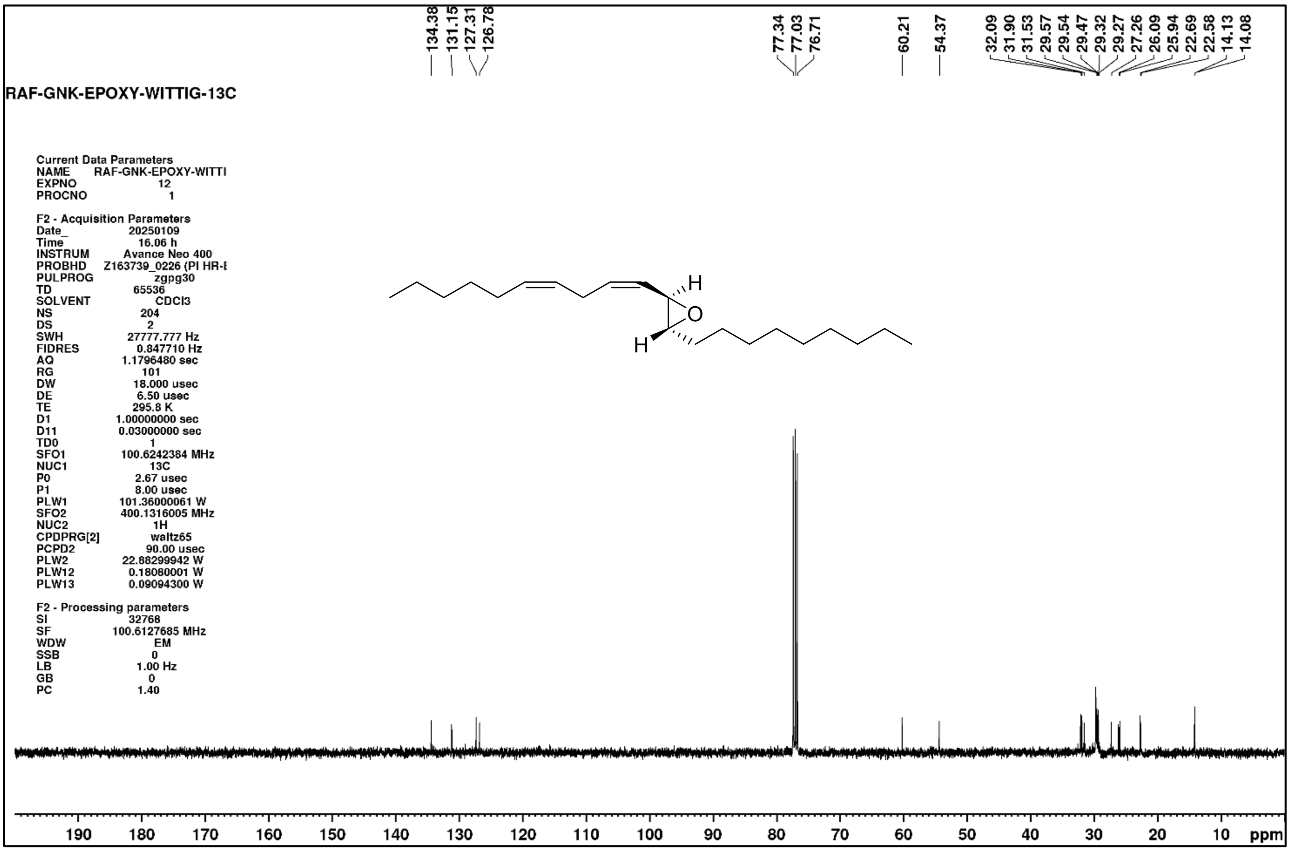
1: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. $C_{21}H_{39}O$ 307.2996; found 307.2996.



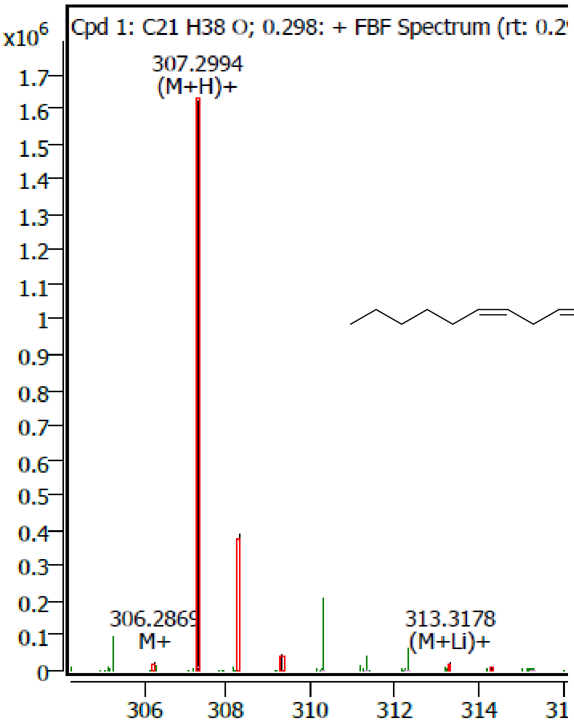


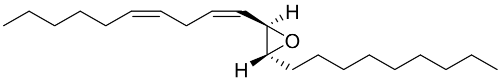
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound ***ent*-1**



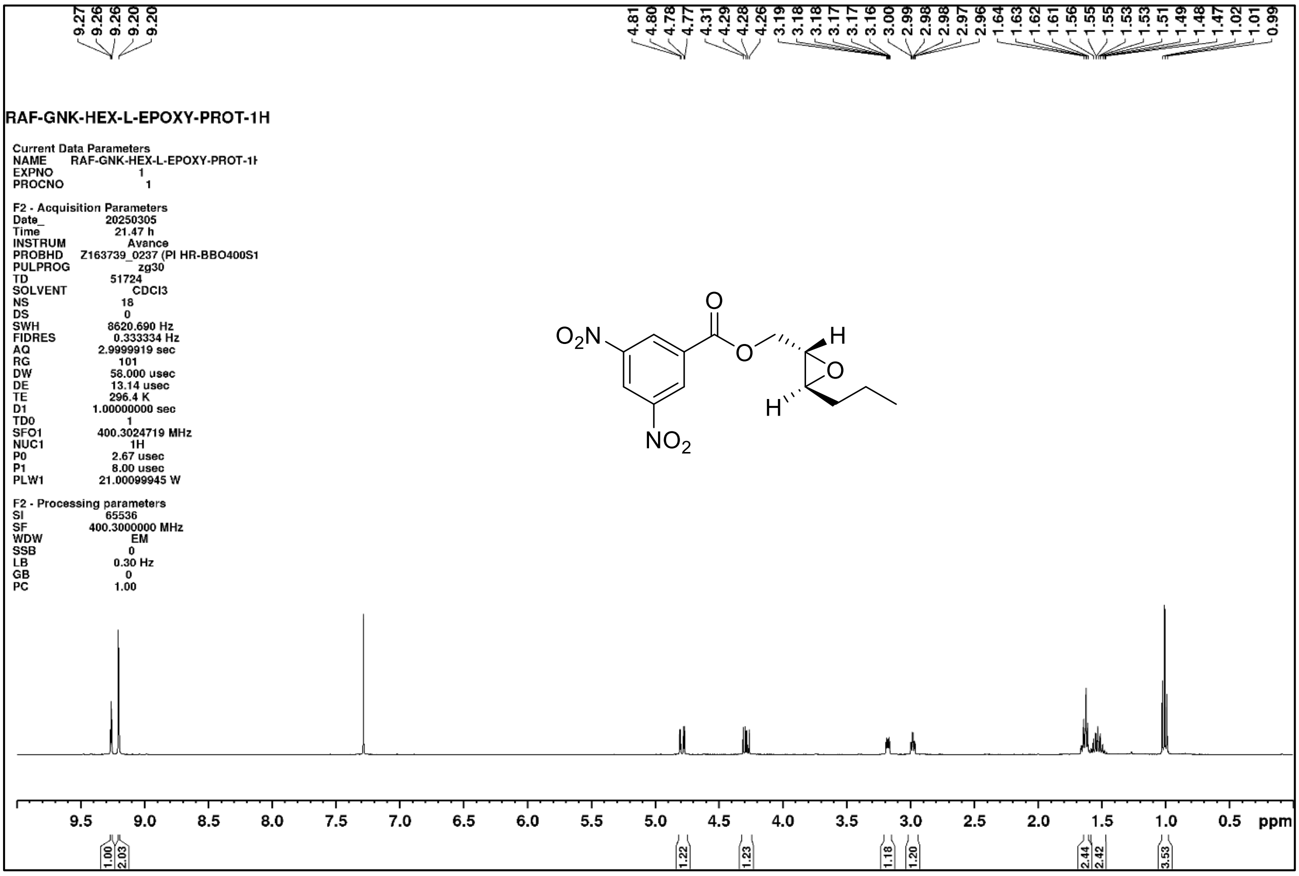


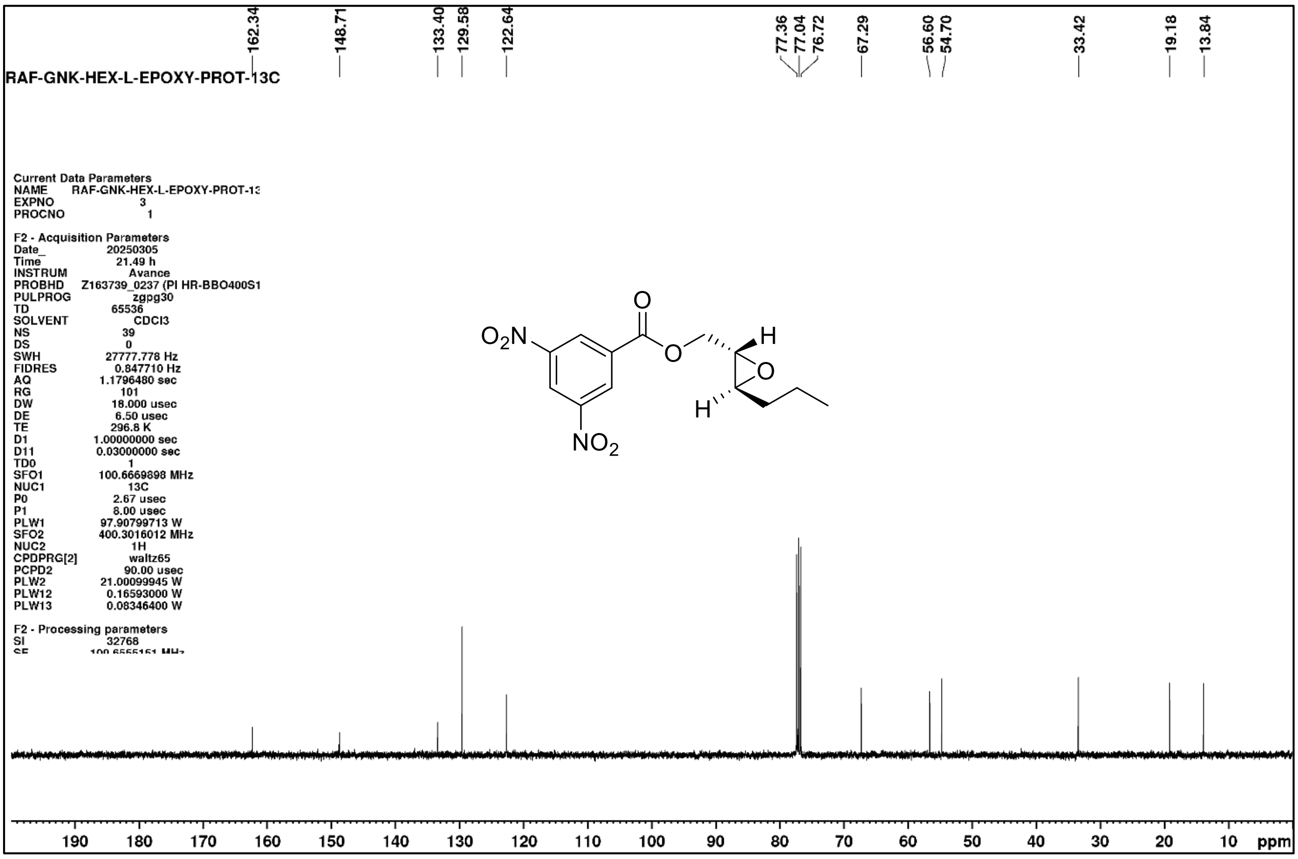
***ent*-1**: HRMS (ESI-TOF) *m/z*: [M + H]+ calcd. $C_{21}H_{39}O$ 307.2996; found 307.2994.



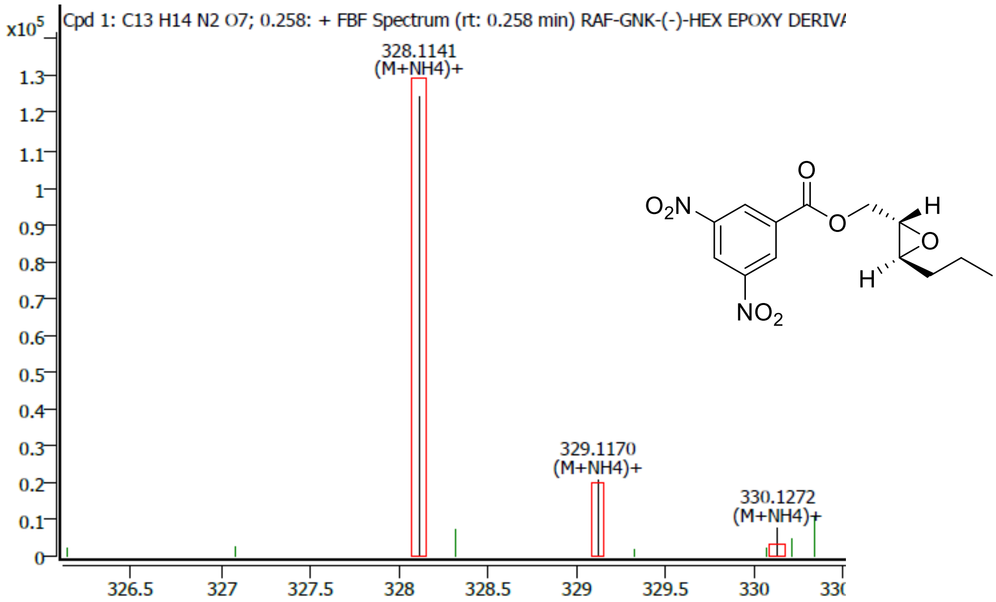


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) of benzoyl ester **15**

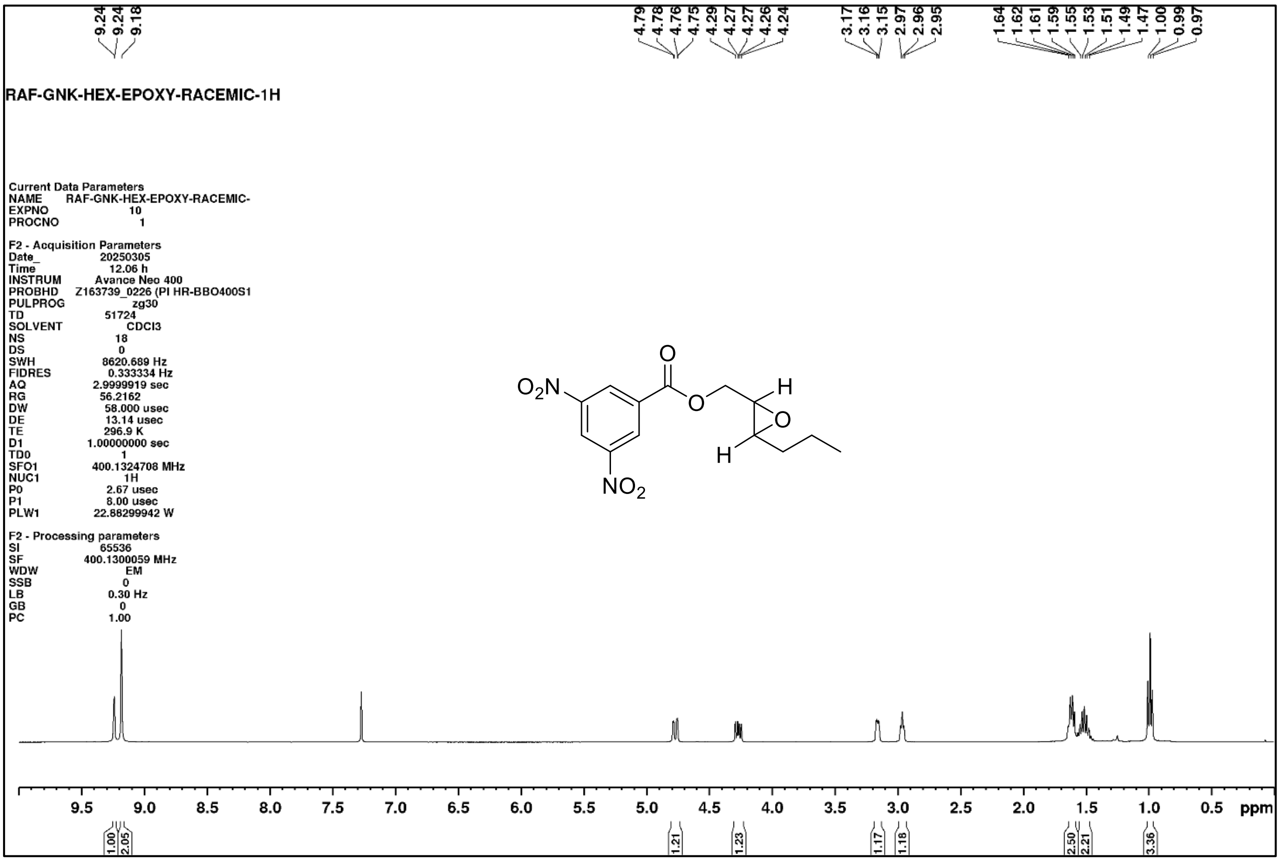




15: HRMS (ESI-TOF) *m/z* [M + NH$_4$]$^+$calcd. $C_{13}H_{18}N_3O_7$ 328.1140; found 328.1141.



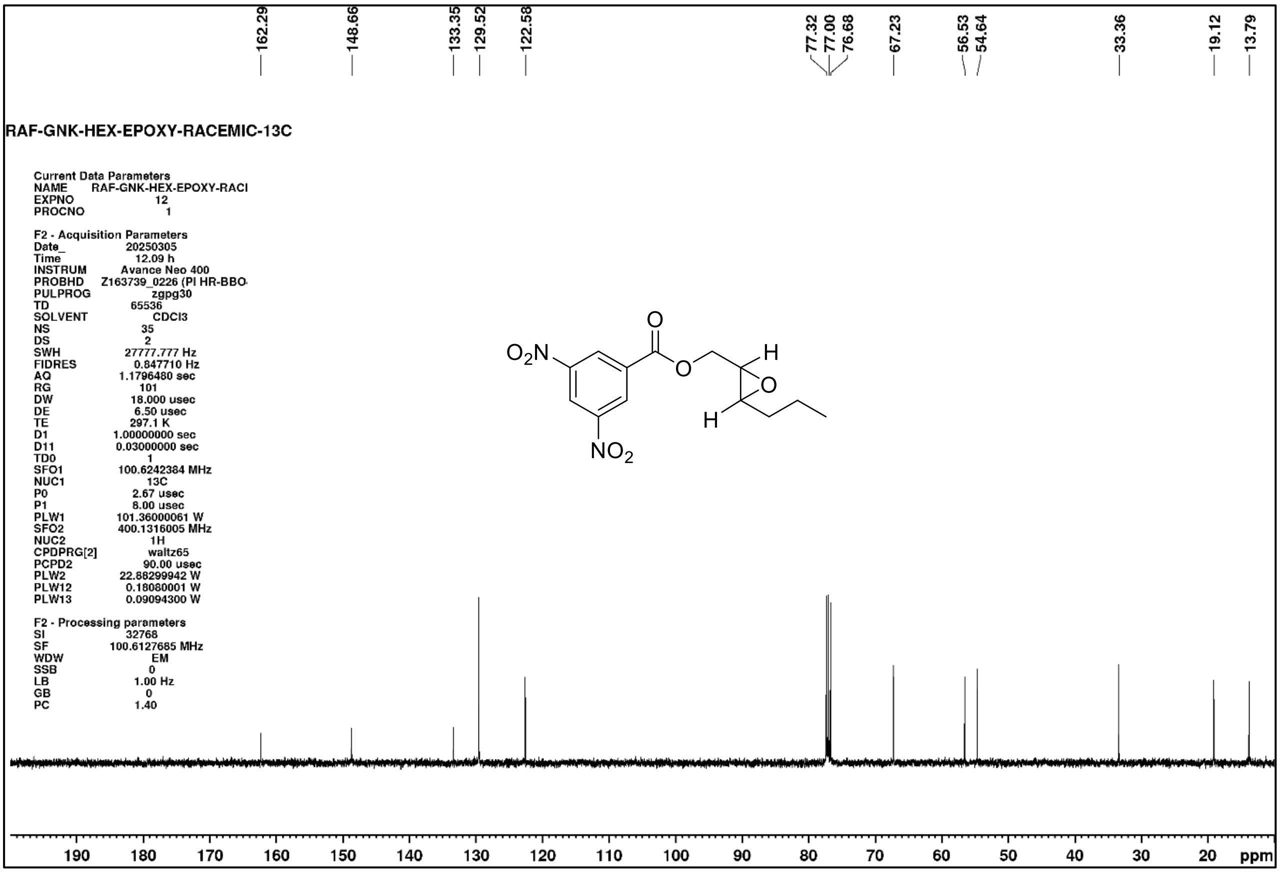
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) of racemic benzoyl ester **15′**



```
Current Data Parameters
NAME      RAF-GNK-HEX-EPOXY-RACEMIC-
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_             20250305
Time               12.06 h
INSTRUM        Avance Neo 400
PROBHD    Z163739_0226 (PI HR-BBO400S1
PULPROG              zg30
TD                51724
SOLVENT              CDCl3
NS                  18
DS                   0
SWH              8620.689 Hz
FIDRES           0.333334 Hz
AQ             2.9999919 sec
RG               56.2162
DW                58.000 usec
DE                13.14 usec
TE                296.9 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            400.1300059 MHz
WDW                  EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```

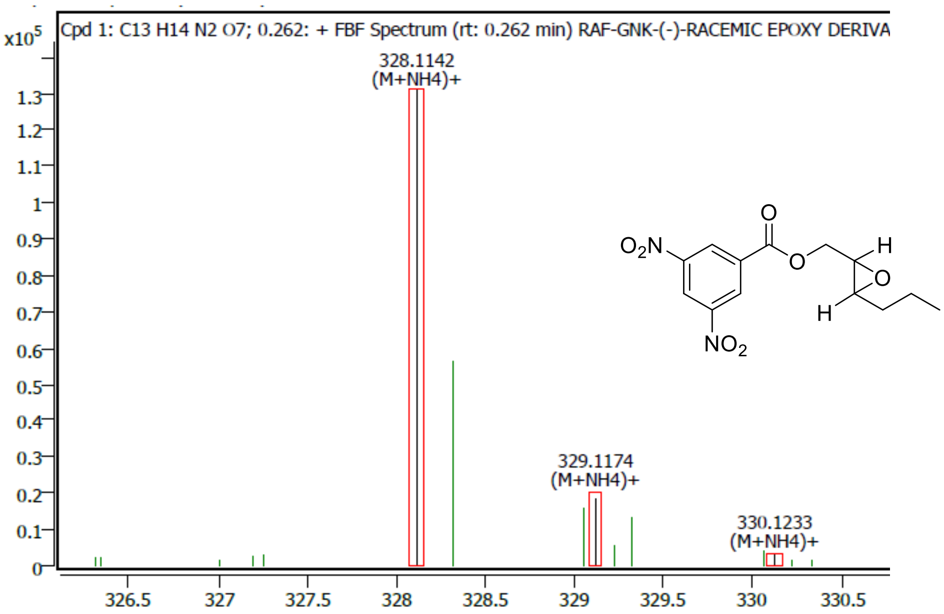


```
Current Data Parameters
NAME      RAF-GNK-HEX-EPOXY-RACI
EXPNO                 12
PROCNO                 1

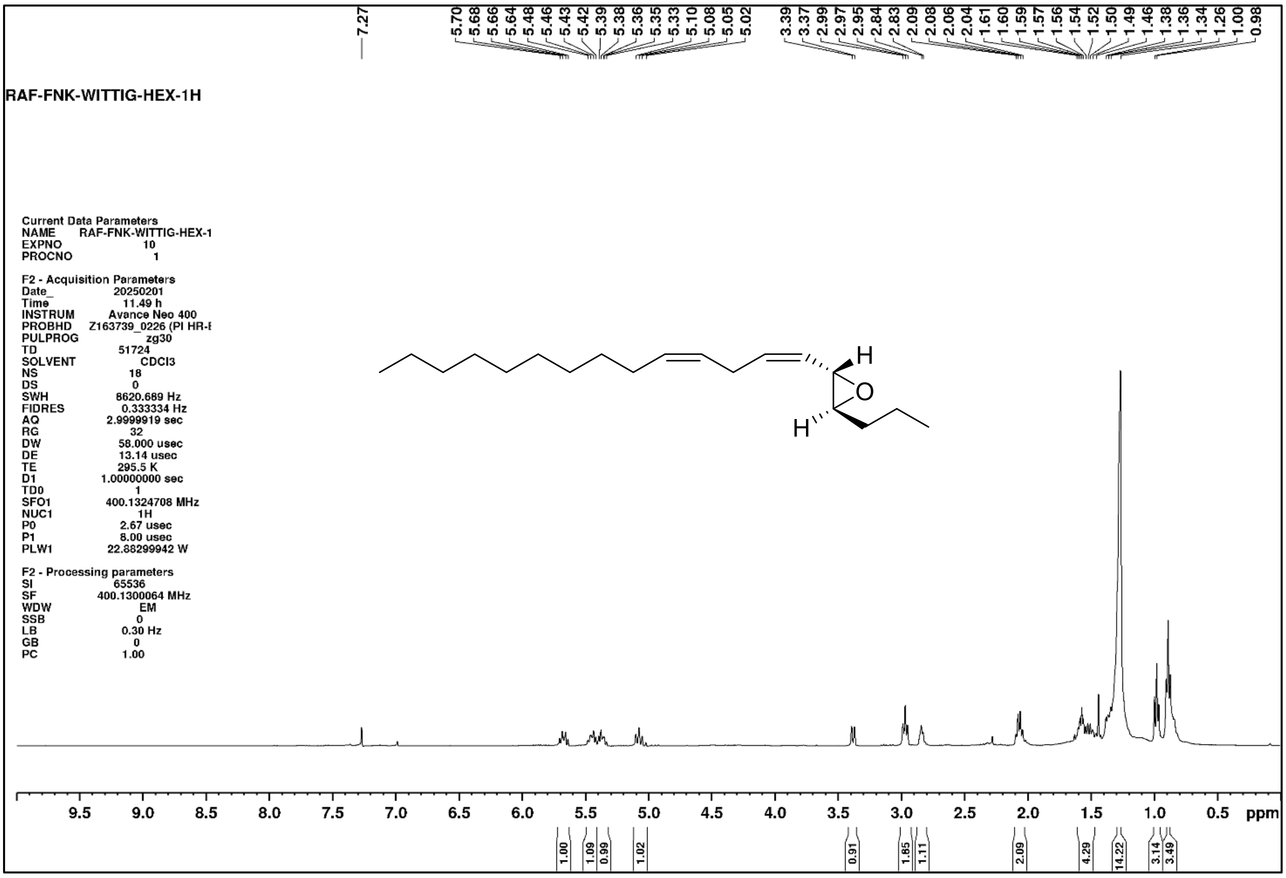
F2 - Acquisition Parameters
Date_             20250305
Time               12.09 h
INSTRUM        Avance Neo 400
PROBHD    Z163739_0226 (PI HR-BBO
PULPROG             zgpg30
TD                65536
SOLVENT              CDCl3
NS                  35
DS                   2
SWH             27777.777 Hz
FIDRES           0.847710 Hz
AQ             1.1796480 sec
RG                 101
DW                18.000 usec
DE                 6.50 usec
TE                297.1 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            100.6127685 MHz
WDW                  EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

15′: HRMS (ESI-TOF) *m/z* [M + NH$_4$]$^+$calcd. C$_{13}$H$_{18}$N$_3$O$_7$ 328.1140; found 328.1142.



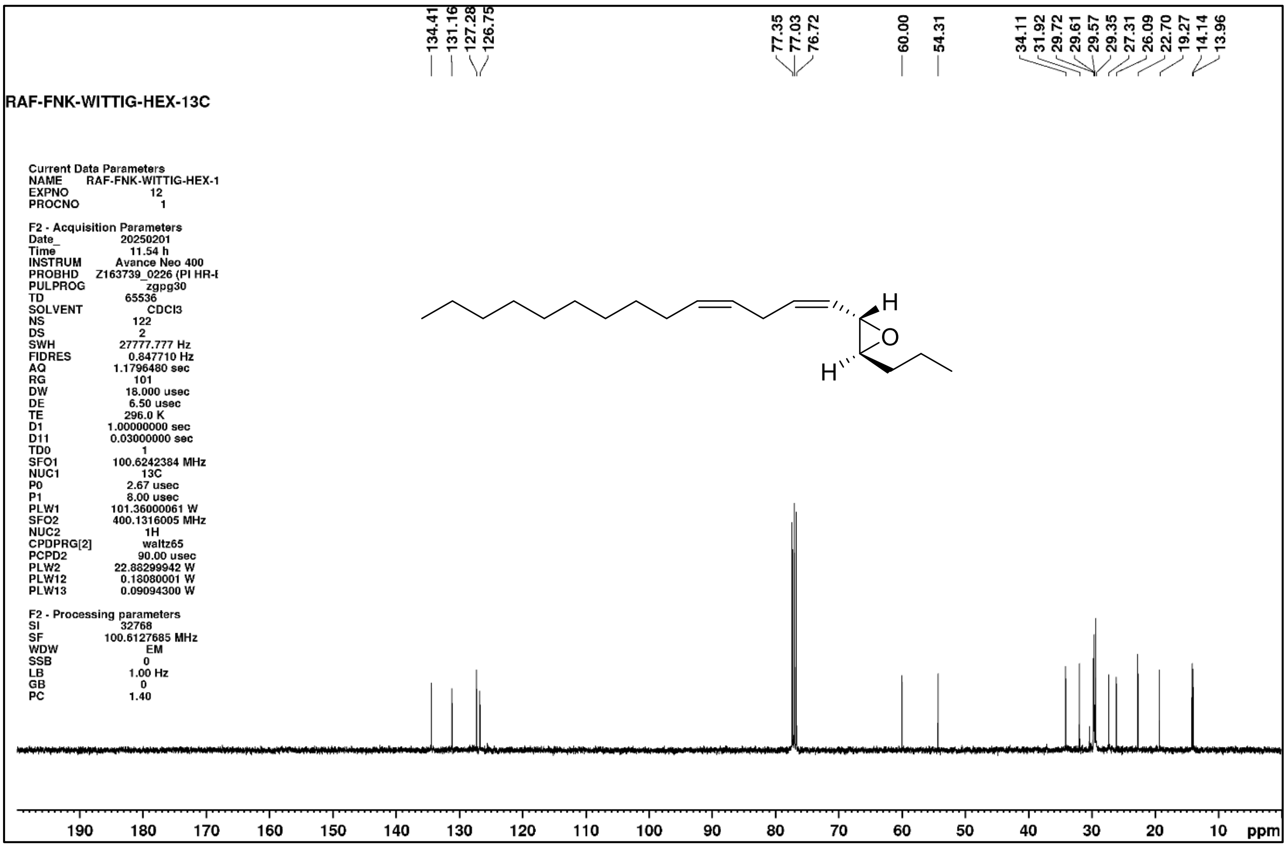
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) of compound **2**



```
Current Data Parameters
NAME        RAF-FNK-WITTIG-HEX-1
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_            20250201
Time              11.49 h
INSTRUM      Avance Neo 400
PROBHD   Z163739_0226 (PI HR-I
PULPROG              zg30
TD               51724
SOLVENT             CDCl3
NS                  18
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               295.5 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          400.1300064 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```



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Current Data Parameters
NAME        RAF-FNK-WITTIG-HEX-1
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_            20250201
Time              11.54 h
INSTRUM      Avance Neo 400
PROBHD   Z163739_0226 (PI HR-I
PULPROG            zgpg30
TD               65536
SOLVENT             CDCl3
NS                 122
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          100.6127685 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

2: HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. $C_{19}H_{35}O$ 279.2683; found 279.2681