Supporting Information for *Org. Lett.*:

Enantioselective Synthesis of (–)-Roccellaric Acid

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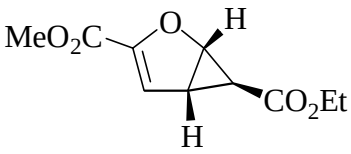
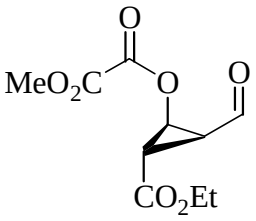
General Remarks: Reactions with moisture-sensitive chemicals were performed under nitrogen in a flame-dried reactionflask. Solvents were dried by standard methods. Chromatography: Macherey-Nagel silica gel (0.03 – 0.06 mm). Uncorrected melting point: Büchi SMP 20. IR: Mattson Genesis Series FT–IR, Perkin Elmer 298, Bruker IFS 66, $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR: Bruker ARX 400, AC 250 F, δ in ppm, *J* in Hz. MS: Finnigan MAT 95, Varian MAT 311A. Elemental analysis: Heraeus CHN–Rapid. XRD: Stoe Imaging Plate System, Siemens Stoe AED2.



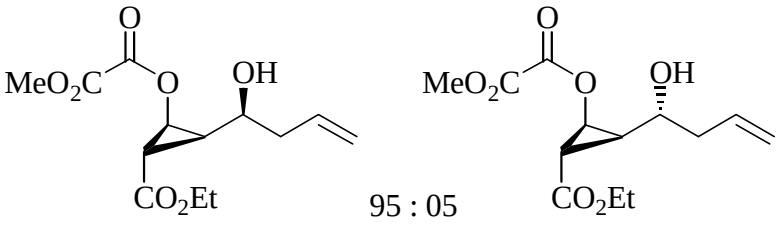
6-Ethyl 3-methyl (1*S*,5*S*,6*S*)-(–)-2-Oxa-bicyclo[3.1.0]hex-3-ene-3,6-dicarboxylate (10): To a mixture of **1** (12.9 mL, 120 mmol, 3 eq.), $Cu(OTf)_2$ (297 mg, 0.82 mmol, 2.0 mol%) and (–)–**14** (303 mg, 1.02 mmol, 2.5 mol%) phenylhydrazine (89 mg, 0.82 mmol, 2.0 mol%) was added under nitrogen at 0 °C. After 30 min, a solution of ethyl diazoacetate (4.685 g, 41.1 mmol, 1 eq.) in abs. CH_2Cl_2 (70 mL) was added via syringe-pump over 12 h in 4 equal amounts. After each addition CH_2Cl_2 was expelled by passing nitrogen through the flask. Excess of **1** was evaporated under high vacuum at room temp. and the residue was purified by chromatography (hexanes/ethylacetate, 10:1, silica gel) to provide 5.494 g **10** as a colorless

oil. Enantiopure product **10** could be obtained by recrystallization from *n*–pentane (4.622 g, 53%). R_f(SiO_2, PE/EE 10:1) = 0.04.– Mp. 42 °C.– $[\alpha]_D^{20}$ = –272 (c = 1.0, CH_2Cl_2).– ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.16 (dd, *J* = 2.7, 1.1 Hz, 1 H, 6–H), 1.23 (t, *J* = 7.1 Hz, 3 H, CH_3), 2.87 (ddd, *J* = 5.3, 2.9, 2.7 Hz, 1 H, 5–H), 3.78 (s, 3 H, OCH_3), 4.12 (q, *J* = 7.1 Hz, 2 H, CH_2), 4.97 (dd, *J* = 5.3, 1.1 Hz, 1 H, 1–H), 6.39 (d, *J* = 2.9 Hz, 1 H, 4–H).– ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.2 (+, *C*H_3), 21.5 (+, C–6), 31.9 (+, C–5), 52.1 (+, OCH_3), 61.0 (–, CH_2), 67.5 (+, C–1), 116.0 (+, C–4), 149.3 (C_{quat}, C–3), 159.5 (C_{quat}, CO), 171.7 (C_{quat}, CO).– IR (KBr): $\tilde{\nu}$ = 3118, 2956, 1720, 1617, 1428, 1380, 1297, 1166, 1124, 1041, 954, 831, 725 cm^{-1}.– MS (70 eV, EI): *m/z* (%) = 212.1 [M^+] (9.8), 153.0 [$M^+ - CO_2Me$] (11.5), 139.0 [$M^+ - CO_2Et$] (100), 124.9 (24.4), 98.9 (28.6), 96.9 (31.7), 78.9 (11.3), 59.0 (13.5), 52.1(11.5).– $C_{10}H_{12}O_5$ (212.2): calc. C 56.60, H 5.70; found C 56.51, H 5.73.



(1*S*,2*S*,3*S*)-(–)-2–Formyl-3-(methoxycarbonyl)cyclopropyl methyl oxalate (11): A solution of (–)-**10** (2.50 g, 11.78 mmol) in dry CH_2Cl_2 (125 mL) was cooled to –78 °C and treated with ozone until the mixture turned blue. Excess ozone was expelled by passing oxygen through the solution, followed by addition of dimethyl sulfide (4.3 mL, 58.91 mmol, 5 eq.). The reaction mixture was allowed to warm to room temp. and stirring was continued for 24 h. Saturated $NaHCO_3$ (1 x 10 mL) was added and layers were separated. The organic layer was washed with water (2 x 10 mL), dried over anhydrous $MgSO_4$ and evaporated. The residue was recrystallized from Et_2O at –27 °C to yield (–)-**11** (2.70 g, 94%) as a colorless solid. Mp. 52 °C.– $[\alpha]_D^{20}$ = –37.7 (c = 1.0, CH_2Cl_2).– ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.28 (t, *J* = 7.1 Hz, 3 H, CH_2CH_3), 2.79 (ddd, *J* = 7.3, 6.0, 4.0 Hz, 1 H, 2–H), 2.90 (dd, *J* = 6.0, 3.6 Hz, 1 H, 3–H), 3.91 (s, 3 H, CO_2CH_3), 4.19 (q, *J* = 7.1 Hz, 2 H, CH_2CH_3) 4.83 (dd, *J* = 7.3, 3.6 Hz, 1 H, 1–H), 9.45 (d, *J* = 4.0 Hz, 1 H, C*H*O).– ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.1 (+, CH_3), 26.4 (+, C–3), 34.9 (+, C–2), 54.0 (+, CO_2CH_3), 58.9 (+, C–1), 62.0 (–, $CO_2CH_2CH_3$), 156.6 (C_{quat}, CO), 156.9 (C_{quat}, CO), 168.1 (C_{quat}, $CO_2CH_2CH_3$), 192.7 (+, CHO).– IR (KBr): $\tilde{\nu}$ = 3066, 3015, 2963, 2892, 1785, 1751, 1735, 1706, 1445, 1345, 1313, 1210, 1167, 1086, 1011, 963, 867, 790, 715, 613, 495 cm^{-1}.– MS (DCI, NH_3): *m/z* (%) =

262.0 [M + NH_4^+] (100), 176.0 (20), 160.0 (55), 120.9 (15).– $C_{10}H_{12}O_7$ (244.2): calc. C 49.19, H 4.95; found C 49.22, H 4.99.



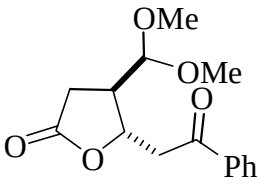
(1*S*,1'*S*/*R*,2*S*,3*S*)-Oxalic acid 2-ethoxycarbonyl-3-(1'-hydroxy-but-3-enyl)-cyclopropyl ester methyl ester (12): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.81 – 1.92 (m, 1 H, 2–H), 2.15 (dd, *J* = 6.2, 2.7 Hz, 1 H, 3–H), 2.31 – 2.51 (m, 4 H), 3.70 (ddd, *J* = 7.3, 7.3, 5.4 Hz, 1 H, 1'–H), 3.88 (s, 3 H, CO_2CH_3), 4.13 (q, *J* = 7.0 Hz, 2 H, $CO_2CH_2CH_3$), 4.72 (dd, *J* = 7.5, 2.8 Hz, 1 H, 1–H), 5.14 – 5.22 (m, 2 H, 4'–H), 5.76 – 5.93 (m, 1 H, 3'–H), characteristic signals of the diastereomer: δ = 4.14 (q, *J* = 7.0 Hz, 2 H, $CO_2CH_2CH_3$), 4.67 (dd, *J* = 6.9, 3.0 Hz, 1 H, 1–H).– ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.1 (+, CH_3), 24.7 (+, C–3), 31.3 (+, C–2), 41.7 (–, C–2'), 53.8 (+, CO_2CH_3), 58.8 (+, C–1), 61.3 (–, $CO_2CH_2CH_3$), 67.8 (+, C–1'), 118.8 (–, C–4'), 133.4 (+, C–3'), 157.2 (C_{quat}, CO), 157.2 (C_{quat}, CO), 170.6 (C_{quat}, CO_2CH_3), characteristic signals of the diastereomer: δ = 25.1 (+, C–3), 41.3 (–, C–2'), 53.6 (+, CO_2CH_3), 58.6 (+, C–1), 61.2 (–, $CO_2CH_2CH_3$), 68.6 (+, C–1'), 118.6 (–, C–4'), 133.5 (+, C–3').

General procedure for the transformation 6 of into 2:

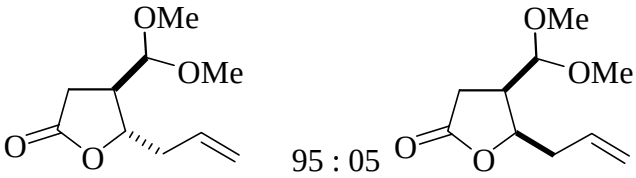
A round–bottomed flask, equipped with the Dean–Stark trap was charged with cyclopropane (1 mmol, 1 eq.), alcohol (2.5 eq.), Sn–catalyst (5 mol%) and benzene. The mixture was gently refluxed for several hours (TLC). The crude mixture was evaporated and purified by chromatography on silica gel (ethyl acetate/hexanes 1:1) to yield the protected aldehyde.

General procedure for the transformation of 6 into 3:

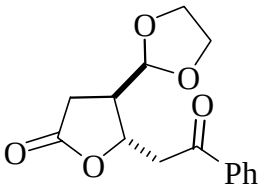
The cyclopropane (1 mmol, 1 eq.) was dissolved in methanol (10 ml) at 0 °C and treated dropwise with a solution of $Ba(OH)_2 \cdot 8\ H_2O$ (0.5 mmol, 1 eq.) in methanol. CH_2Cl_2 (10 ml) and H_20 (10 ml) were added and layers were separated. The aqueous layer was extracted with CH_2Cl_2 (10 x 10 ml). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. Chromatography on silica gel (ethyl acetate/hexanes 1:1) yielded the unprotected aldehyde.



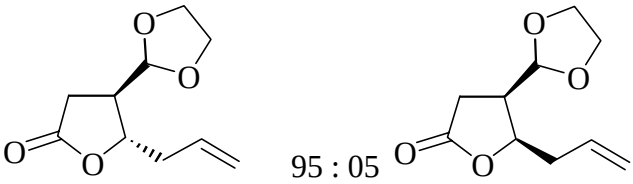
4-Dimethoxymethyl-5-(2'-oxo-2'-phenyl-ethyl)-dihydro-furan-2-one: R_f(SiO_2, PE/EE 1:1) = 0.25.– ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.54 – 2.62 (m, 1 H), 2.66 – 2.75 (m, 2 H), 3.40 (s, 6 H), 3.42 (dd, *J* = 8.6, 6.1 Hz, 2 H, 1'–H), 4.42 (d, *J* = 5.4 Hz, 1 H), 4.98 (dd, *J* = 11.4, 5.4 Hz, 1 H), 7.46 – 7.50 (m, 2 H), 7.57 – 7.61 (m, 1 H), 7.93 – 7.96 (m, 2 H).– ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 30.1 (–, C–3), 43.2 (+, C–4), 43.3 (–, C–1'), 54.3 (+, CH_3), 55.7 (+, CH_3), 77.1 (+, C–5), 105.6 (+, CH), 128.1, 128.7, 133.6, 136.4 (C–Ar), 175.7 (C_{quat}, CO), 196.3 (C–2').– IR (film): $\tilde{\nu}$ = 2960, 2886, 2345, 1777, 1683, 1362, 1188, 1073, 921 cm^{-1}.– MS (EI, 70 eV): *m/z* (%) = 278.1 [M^+] (5), 151.1 (15), 107.1 (70), 73.1 (100).– $C_{11}H_{14}O_5$ (226.2): calc. C 58.40, H 6.24; found C 58.61, H 6.87.



5-Allyl-4-dimethoxymethyl-dihydro-furan-2-one: R_f(SiO_2, PE/EE 1:1) = 0.37.– ^{1}H NMR (400 MHz, C_6D_6): δ = 2.04 – 2.13 (m, 2 H), 2.20 – 2.27 (m, 3 H), 2.89 (s, 3 H, OCH_3), 2.95 (s, 3 H, OCH_3), 3.72 (d, *J* = 6.5 Hz, 1 H), 4.22 (dt, *J* = 6.6, 5.0 Hz, 1 H), 4.97 – 5.04 (m, 2 H), 5.64 – 5.74 (m, 1 H).– ^{13}C NMR (100.6 MHz, C_6D_6): δ = 30.3 (–, C–3), 39.5 (–, C–1'), 42.0 (+, C–4), 53.4 (+, CH_3), 54.6 (+, CH_3), 79.8 (+, C–5), 105.4 (+, CH), 118.5 (–, =CH), 133.1 (+, =CH), 174.8 (C_{quat}, CO), characteristic signals of the diastereomer: δ = 35.1 (–, C–3), 40.6 (–, C–1'), 52.6 (+, CH_3), 53.5 (+, CH_3), 103.0 (+, CH), 117.7 (–, =CH), 134.3 (+, =CH).– IR (film): $\tilde{\nu}$ = 3079, 2940, 2836, 1777, 1683, 1643, 1438, 1420, 1362, 1188, 1126, 1073, 991, 919, 826 cm^{-1}.– MS (EI, 70 eV): *m/z* (%) = 199.1 [M–H^+] (0.17), 159.0 (20.1), 126.9 (49.1), 98.9 (37.0), 74.9 (78.6), 71.0 (100), 47.1 (10.7), 41.1 (19.5); MS (DCI, NH_3): 218.1 [M + NH_4^+] (100).– $C_{10}H_{16}O_4$ (200.2): calc. C 59.98, H 8.05; found C 60.03, H 8.02.



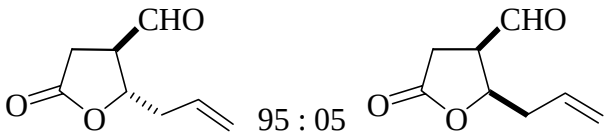
4-[1,3]Dioxolan-2-yl-5-(2'-oxo-2'-phenyl-ethyl)-dihydro-furan-2-one: R_f(SiO_2, PE/EE 1:1) = 0.21.– Mp. 95 – 96 °C.– ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.57 – 2.80 (m, 3 H, 3–H, 4–H), 3.37 (dd, *J* = 17.4, 5.7 Hz, 1 H, 1'–H), 3.49 (dd, *J* = 17.4, 6.1 Hz, 1 H, 1'–H), 3.83 – 4.03 (m, 4 H, OCH_2CH_2O), 5.01 (d, *J* = 3.4 Hz, 1 H, CH), 5.08 (dd, *J* = Hz, 11.2, 5.6 Hz, 1 H, 5–H), 7.41 – 7.51 (m, 2 H, Ar–H), 7.55 – 7.63 (m, 1 H, Ar–H), 7.88 – 7.99 (m, 2 H, Ar–H).– ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 29.5 (–, C–3), 43.3 (+, C–4), 43.4 (–, C–1'), 65.3, 65.4 (–, OCH_2CH_2O), 76.3 (+, C–5), 103.4 (+, CH), 128.0, 128.7, 133.6, 136.4 (C–Ar), 175.6 (C_{quat}, CO), 196.2 (C–2').– IR (KBr): $\tilde{\nu}$ = 2961, 2882, 2360, 2342, 1769, 1685, 1387, 1196, 1013, 939 cm^{-1}.– MS (EI, 70 eV): *m/z* (%) = 276.1 [M^+] (5), 149.1 (15), 105.1 (70), 73.1 (100).– $C_{15}H_{16}O_5$ (276.3): calc. C 65.21, H 5.84; found C 65.02, H 5.84.



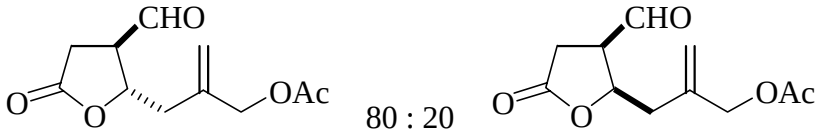
95 : 05

(4*R*,5*S*/*R*)-(–)-5-Allyl-4-[1,3]dioxolan-2-yl-dihydro-furan-2-one (13): R_f(SiO_2, PE/EE 1:1) = 0.34.– $[\alpha]_D^{20}$ = –18.2 (c = 1.0, CH_2Cl_2).– ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.39 – 2.67 (m, 5 H, 1'–H, 3–H, 4–H), 3.83 – 4.01 (m, 4 H, OCH_2CH_2O), 4.51 (m, 1 H, CH), 4.86 (m, 1 H, 5–H), 5.11 – 5.21 (m, 2 H, 3'–H), 5.79 (ddt, *J* = 16.7, 10.6, 6.9 Hz, 1 H, 2'–H), characteristic signals of the diastereomer: δ = 4.06 – 4.18 (m, 4 H, OCH_2CH_2O), 4.60 (ddd, *J* = 8.3, 6.7, 5.8 Hz, 1 H, 5–H), 4.98 (d, *J* = 3.7 Hz, 1 H, CH), 5.85 (ddt, *J* = 7.2, 10.2, 6.7 Hz, 1 H, 2'–H).– ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 29.6 (–, C–3), 39.2 (–, C–1'), 42.5 (+, C–4), 65.4, 65.5 (–, OCH_2CH_2O), 79.7 (+, C–5), 103.5 (+, CH), 119.3 (–, C–3'), 132.0 (+, C–2'), 175.9 (C_{quat}, CO), characteristic signals of the diastereomer: δ = 29.26 (–, CH_2), 34.9 (–, C–1'), 41.4 (+, C–4), 65.1, 65.6 (–, OCH_2CH_2O), 80.3 (+, C–5), 101.8 (+, CH), 118.3 (–, C–3'), 133.2 (+, C–2').– IR (film): $\tilde{\nu}$ = 3078, 2953, 2890, 2760, 1782, 1642, 1420, 1356, 1187, 1131, 1025, 994, 945, 922 cm^{-1}.– MS (DCI, NH_3): *m/z* (%) = 250.3 [MH^+ + 3 NH_3] (10), 233.2 [MH^+ + 2 NH_3]

(5), 216.2 [M + NH_4^+] (100).– $C_{10}H_{14}O_4$ (198.2): calc. C 60.59, H 7.12; found C 60.76, H 7.12.

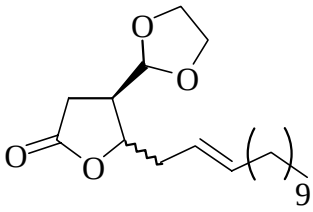


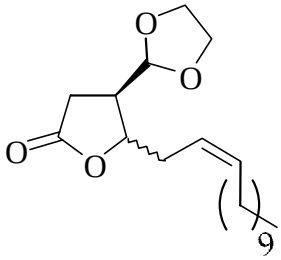
2-Allyl-5-oxo-tetrahydro-furan-3-carbaldehyde: R_f(SiO_2, PE/EE 1:1) = 0.17.– ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.35 – 2.59 (m, 2 H, 1‘–H), 2.71 (dd, *J* = 18.2, 9.9 Hz, 1 H, 3–H), 2.89 (dd, *J* = 18.2, 7.5 Hz, 1 H, 3–H), 3.19 (dddd, *J* = 10.0, 7.3, 6.0, 1.2 Hz, 1 H, 4–H), 4.74 (dd, *J* = 11.9, 6.2 Hz, 1 H, 5–H), 5.10 – 5.27 (m, 2 H, 3‘–H), 5.75 (dddd, *J* = 17.3, 10.0, 7.0, 3.5 Hz, 1 H, 2‘–H), 9.69 (d, *J* = 1.2 Hz, 1 H, CHO), characteristic signals of the diastereomer: δ = 3.00 (dd, *J* = 17.7, 5.8 Hz, 1 H, 3–H), 9.82 (d, *J* = 1.7 Hz, 1 H, CHO).– ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 28.8 (–, C–3), 39.2 (–, C–1‘), 51.2 (+, C–4), 78.0 (+, C–5), 120.4 (–, C–3‘), 130.9 (+, C–2‘), 174.2 (C_{quat}, CO), 197.4 (C_{quat}, CO), characteristic signals of the diastereomer: δ = 30.2 (–, C–3), 39.3 (–, C–1‘), 49.5 (+, C–4), 79.6 (+, C–5), 119.9 (–, C–3‘), 131.4 (+, C–2‘), 174.5 (C_{quat}, CO), 198.2 (C_{quat}, CO).– IR (film): $\tilde{\nu}$ = 3080, 2980, 2939, 2841, 1774, 1727, 1642, 1419, 1359, 1193, 1111, 1000, 924 cm^{-1}.– MS (EI, 70 eV): *m/z* (%) = 154.2 (5) [M^+], 113.1 (100) [M – C_3H_5], 85.1 (95), 57.1 (95).– $C_8H_{10}O_3$ (154.2): calc. C 62.33, H 6.54; found C 62.82, H 6.89.



Acetic acid 2-(3’-formyl-5’-oxo-tetrahydro-furan-2’-ylmethyl)-allyl ester: R_f(SiO_2, PE/EE 1:1) = 0.07.– ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.08 (s, CH_3, 3 H), 2.47 (dd, *J* = 14.7, 6.0 Hz, 1 H, 1’–H), 2.61 (dd, *J* = 14.7, 7.0 Hz, 1 H, 1’–H), 2.76 (dd, *J* = 18.0, 10.0 Hz, 1 H, 4’–H), 2.90 (dd, *J* = 17.9, 7.7 Hz, 1 H, 4’–H), 3.21 (dddd, *J* = 9.9, 7.7., 6.4,1.3 Hz, 1 H, 3’–H), 4.54 (s, 2 H, CH_2OAc), 4.87 (dd, *J* = 13.0, 6.4 Hz, 1 H, 2’–H), 5.13 (m, 1 H, C=CH), 5.25 (bs, 1 H, C=CH), 9.71 (bs, 1 H, CHO), characteristic signals of the diastereomer: δ = 5.03 (dd, *J* = 14.3, 7.5 Hz, 1 H, 2’–H).– ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 20.8 (+, CH_3), 28.9 (–, C–4’), 39.0 (–, CH_2), 51.7 (+, C–3’), 66.6 (–, CH_2OAc), 77.2 (+, C–2’), 117.7 (–, C=CH_2), 138.3 (C_{quat}, C–2‘), 170.5 (C_{quat}, CO), 173.7 (C_{quat}, C–5’), 197.2 (+, CHO), characteristic signals of

the diastereomer: δ = 66.5 (–, CH_2OAc), 78.4 (+, C–2'), 197.9 (+, CO).– IR (film): $\tilde{\nu}$ = 3090, 2938, 1777, 1736, 1655, 1436, 1373, 1233, 1029, 920 cm^{-1}.– MS (EI, 70 eV): *m/z* (%) = 226.2 [M^+] (5), 113.1 (40), 85.1 (50), 57.1 (40), 43.1 (1000).– $C_{11}H_{14}O_5$ (226.2): calc. C 58.40, H 6.24; found C 58.61, H 6.87.

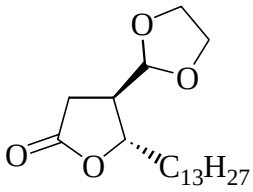




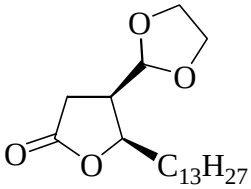
E : *Z* 3.5 : 1, *dv* 95 : 05

(*E*)/(*Z*)-(4*R*,5*S*/*R*)-(–)-4-[1,3]Dioxolan-2-yl-5-tridec-2-enyl-dihydro-furan-2-one (15):

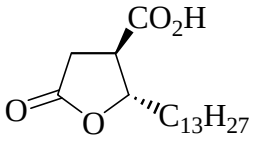
R_f(SiO_2, PE/EE 1:1) = 0.50.– $[\alpha]_D^{20}$ = –13.4 (c = 0.85, CH_2Cl_2).– ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.5 Hz, 3 H, CH_3), 1.23 (bs, 16 H, CH_2), 1.99 (ddt, *J* = 7.0, 7.0, 0.4 Hz, 2 H, 4'–H), 2.27 – 2.60 (m, 5 H, 1'–H, 3–H, 4–H), 3.81 – 4.03 (m, 4 H, OCH_2CH_2O), 4.43 – 4.57 (m, 1 H, CH), 4.86 (dt, *J* = 2.3, 1.3 Hz, 1 H, 5–H), 5.37 (dtt, *J* = 15.2, 6.9, 1.2 Hz, 1 H, =CH–), 5.58 (dtt, *J* = 15.2, 6.6, 1.2 Hz, 1 H, =CH–), characteristic signals of the diastereomer: δ = 4.99 (d, *J* = 3.6 Hz, 1 H, CH).– Major diastereomer: ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.1 (+, CH_3), 22.7 (–, CH_2), 29.16 (–, CH_2), 29.26 (–, CH_2), 29.32 (–, CH_2), 29.47 (–, CH_2), 29.51 (–, CH_2), 29.60 (–, C–3, CH_2), 31.9 (–, CH_2), 32.62 (–, CH_2), 38.0 (–, CH_2), 42.2 (+, C–4), 65.3, 65.4 (–, OCH_2CH_2O), 80.22 (+, C–5), 103.6 (+, CH), 122.9 (+, =CH–), 135.8 (+, =CH–), 176.1 (C_{quat}, CO), characteristic signals of the diastereomer: δ = 29.15 (–, CH_2), 29.23 (–, CH_2), 29.9 (–, C–3), 33.7 (–, CH_2), 34.9 (–, C–1'), 41.4 (+, C–4), 65.1, 65.6 (–, OCH_2CH_2O), 80.94 (+, C–5), 101.9 (+, CH), 124.1 (+, =CH–), 134.7 (+, =CH–), characteristic signals of the diastereomer: δ = 27.5 (–, CH_2), 29.30 (–, CH_2), 29.43 (–, CH_2), 29.62 (–, CH_2), 32.60 (–, CH_2), 42.5 (+, C–4), 80.24 (+, C–5), 122.2 (+, =CH–), 134.4 (+, =CH–), 175.9 (C_{quat}, CO), characteristic signals of the diastereomer: δ = 80.76 (+, C–5), 123.1 (+, =CH–).– IR (Film): $\tilde{\nu}$ = 2924, 2853, 1781, 1465, 1421, 1354, 1181, 1133, 1031, 974, 945, 920 cm^{-1}.– MS (EI, 70 eV): *m/z* (%) = 338.0 [M^+] (1), 210.0 (3), 154.9 (9), 98.9 (4), 82.9 (3), 72.9 (100), 55.0 (6), 45.0 (7), 43.0 (6).– $C_{20}H_{34}O_4$ (338.5): calc. C 70.97, H 10.12; found C 70.70, H 10.02.



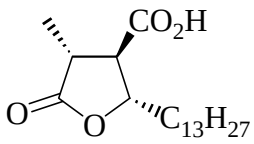
95 : 05



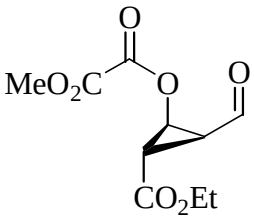
(4*R*,5*S*/*R*)-(–)-4-[1,3]Dioxolan-2-yl-5-tridecyl-dihydro-furan-2-one: R_f(SiO_2, PE/EE 2:1) = 0.30.– Mp. 46 °C.– $[\alpha]_D^{20}$ = –26.5 (c = 1.0, CH_2Cl_2).– ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.5 Hz, 3 H, CH_3), 1.25 (bs, 22 H, CH_2), 1.61 – 1.72 (m, 2 H, CH_2), 2.42 – 2.69 (m, 3 H, 3–H, 4–H), 3.87 – 4.03 (m, 4 H, OCH_2CH_2O), 4.46 (dt, *J* = 7.3, 5.0 Hz, 1 H, CH), 4.88 (d, *J* = 4.9 Hz, 1 H, 2–H), characteristic signals of the diastereomer: δ = 4.98 (d, *J* = 3.8 Hz, 1 H, CH).– ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.1 (+, CH_3), 22.7 (–, CH_2), 25.6 (–, CH_2), 29.25 (–, CH_2), 29.33 (–, CH_2), 29.43 (–, CH_2), 29.51 (–, CH_2), 29.63 (–, C–3, CH_2), 29.66 (–, CH_2), 31.9 (–, CH_2), 35.6 (–, CH_2), 43.6 (+, C–4), 65.36, 65.41 (–, OCH_2CH_2O), 81.0 (+, C–5), 103.6 (+, CH), 176.1 (C_{quat}, CO), characteristic signals of the diastereomer: δ = 26.3 (–, CH_2), 29.35 (–, CH_2), 29.46 (–, CH_2), 29.52 (–, CH_2), 29.61 (–, CH_2), 29.9 (–, C–3), 31.9 (–, CH_2), 41.6 (+, C–4), 65.1, 65.6 (–, OCH_2CH_2O), 81.4 (+, C–5), 102.1 (+, CH). – IR (KBr): $\tilde{\nu}$ = 2919, 2849, 1764, 1466, 1427, 1214, 1153, 1063, 982, 941, 721 cm^{-1}.– MS (DCI, NH_3): *m/z* (%) = 358.5 [M + NH_4^+] (100), 344.5 [M^+] (2), 136.2 (6).– $C_{20}H_{36}O_4$ (340.5): calc. C 70.55, H 10.66, found C 70.37, H 10.60.



(2*S*,3*R*)-(–)-5-Oxo-2-tridecyl-tetrahydro-furan-3-carboxylic acid (16): R_f(SiO_2, $CHCl_3$/EE /HOAc 90:8:2) = 0.24.– Mp. 108 °C, lit.:[7d] 109 – 111 °C.– $[\alpha]_D^{20}$ = –40.5 (c = 0.32, $CHCl_3$), lit.:[7d] –41 (c = 0.5, $CHCl_3$).– ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 3 H, CH_3), 1.26 (bs, 18 H, CH_2), 1.40 – 1.60 (m, 2 H, CH_2), 1.72 – 1.83 (m, 2 H, CH_2), 2.83 (dd, *J* = 17.9, 9.6 Hz, 1 H, 4–H), 2.95 (dd, *J* = 17.9, 8.3 Hz, 1 H, 4–H), 3.10 (ddd, *J* = 9.6, 8.3, 7.2 Hz, 1 H, 3–H), 4.62 (ddd, *J* = 7.4, 7.3, 4.8 Hz, 1 H, 2–H), 8.64 (bs, 1 H, CO_2H).– ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.1 (+, CH_3), 22.7 (–, CH_2), 25.2 (–, CH_2), 29.2 (–, CH_2), 29.37 (–, CH_2), 29.42 (–, CH_2), 29.52 (–, CH_2), 29.63 (–, CH_2), 29.67 (–, CH_2), 29.70 (–, CH_2), 31.91 (–, CH_2), 31.94 (–, CH_2), 35.40 (–, CH_2), 45.4 (+, C–3), 81.8 (+, C–2), 174.2 (C_{quat}, CO), 175.9 (C_{quat}, CO).



(2*S*,3*R*,4*R*)-(–)-4-Methyl-5-oxo-2-tridecyl-tetrahydro-furan-3-carboxylic acid, Roccellaric acid (17): R_f(SiO_2, $CHCl_3$/EE/HOAc 90:8:2) = 0.25.– Mp. 110 °C, lit.:[6b] 108 °C.– $[\alpha]_D^{20}$ = –26 (c = 0.5, $CHCl_3$), lit.:[6b] –26 (c = 1.93, $CHCl_3$).– ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.5 Hz, 3 H, CH_3), 1.18 – 1.47 (m, 21 H, CH_2), 1.37 (d, *J* = 7.1 Hz, 3 H, CH_3), 1.48 – 1.59 (m, 1 H, 1'–H), 1.65 – 1.77 (m, 1 H, 1'–H), 1.78 – 1.88 (m, 1 H, 1'–H), 2.70 (dd, *J* = 11.4, 9.1 Hz, 1 H, 3–H), 2.99 (dq, *J* = 11.4, 7.1 Hz, 1 H, 4–H), 4.48 (ddd, *J* = 9.1, 8.7, 4.1 Hz, 1 H, 2–H).– ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.1 (+, CH_3), 14.5 (+, CH_3), 22.7 (–, CH_2), 25.3 (–, CH_2), 29.22 (–, CH_2), 29.34 (–, CH_2), 29.38 (–, CH_2), 29.50 (–, CH_2), 29.60 (–, CH_2), 29.64 (–, CH_2), 29.67 (–, CH_2), 31.91 (–, CH_2), 34.92 (–, CH_2), 39.8 (+, C–3), 53.8 (+, C–4), 79.3 (+, C–2), 175.3 (C_{quat}, CO), 176.5 (C_{quat}, CO).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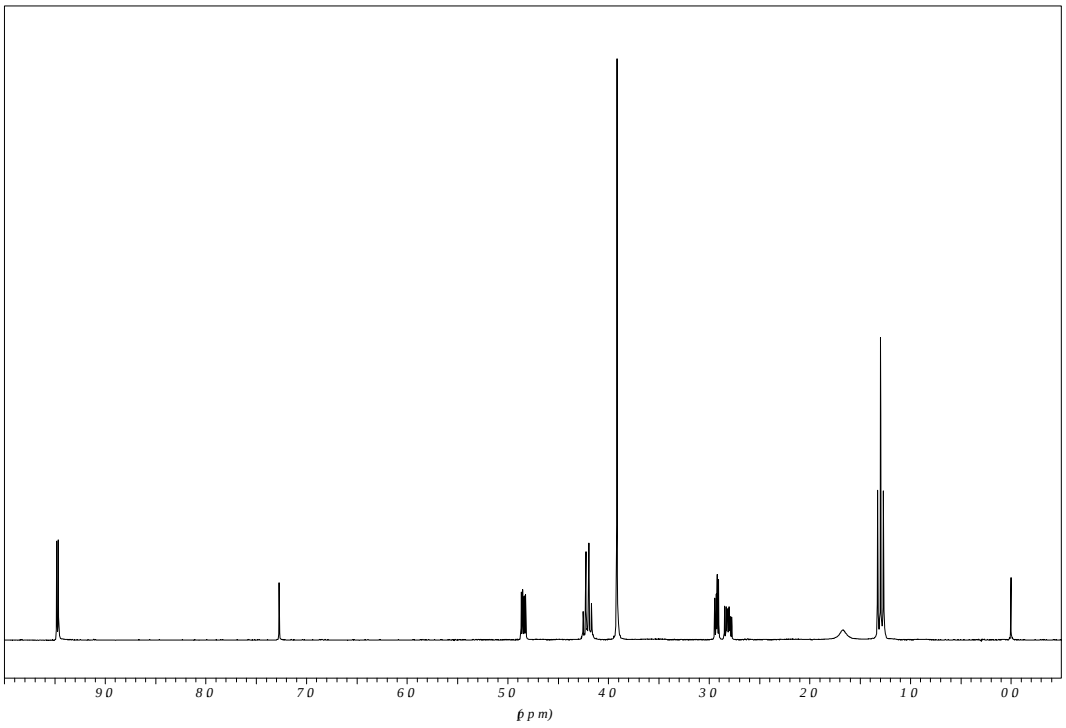
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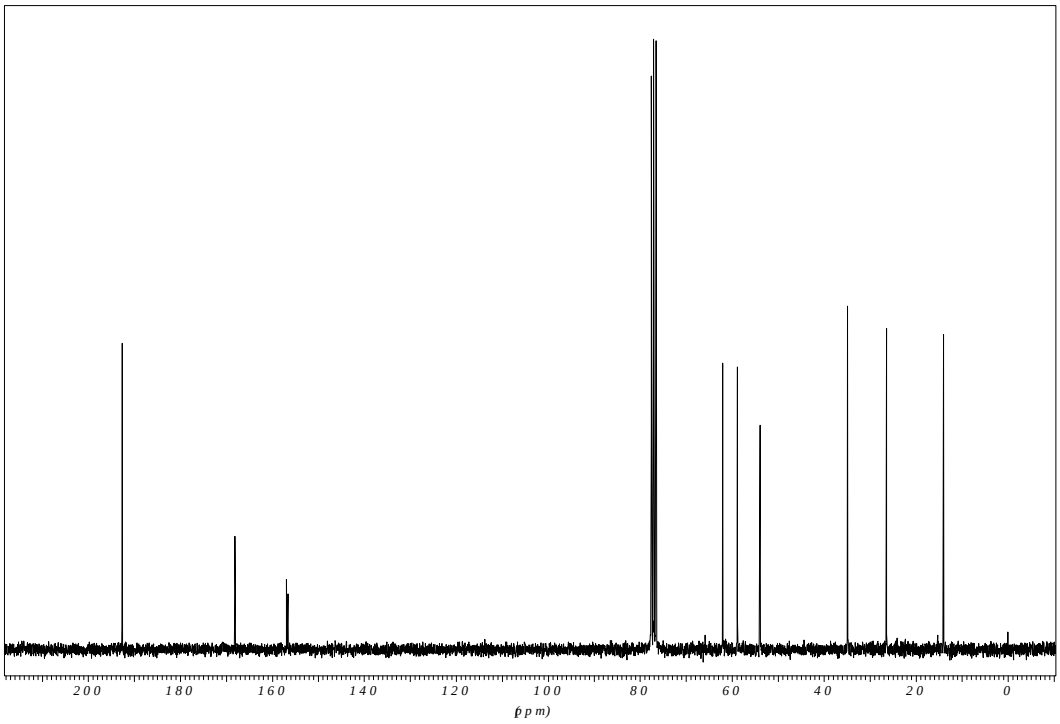
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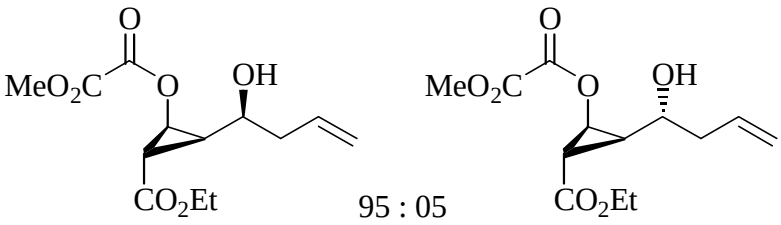
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95 : 05
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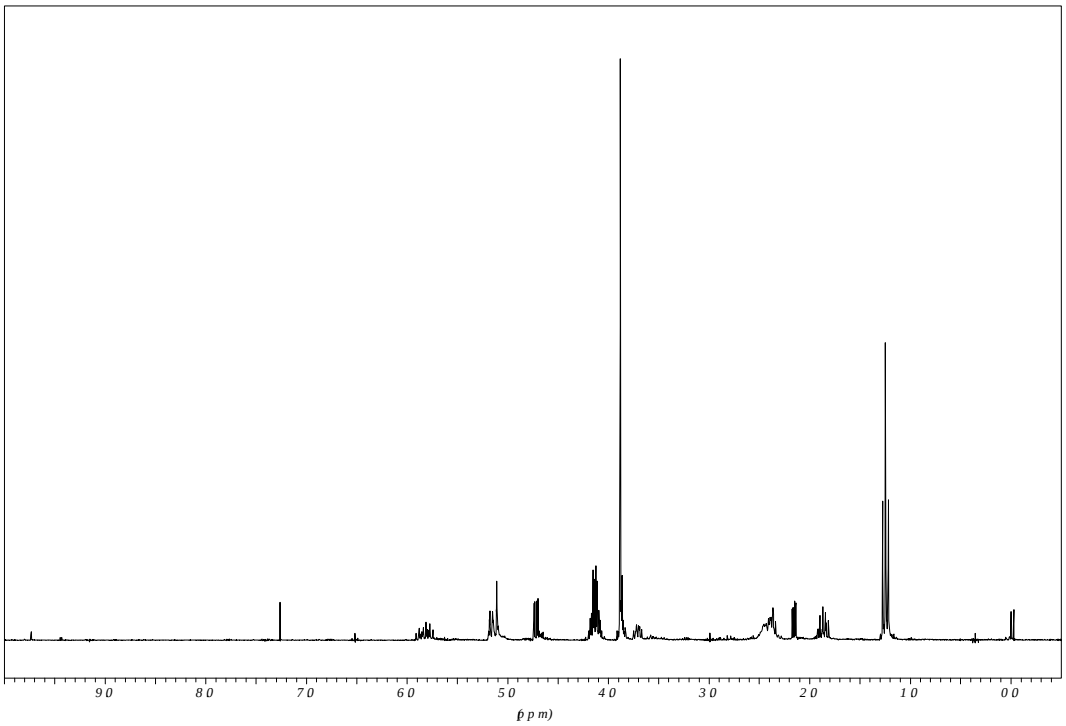
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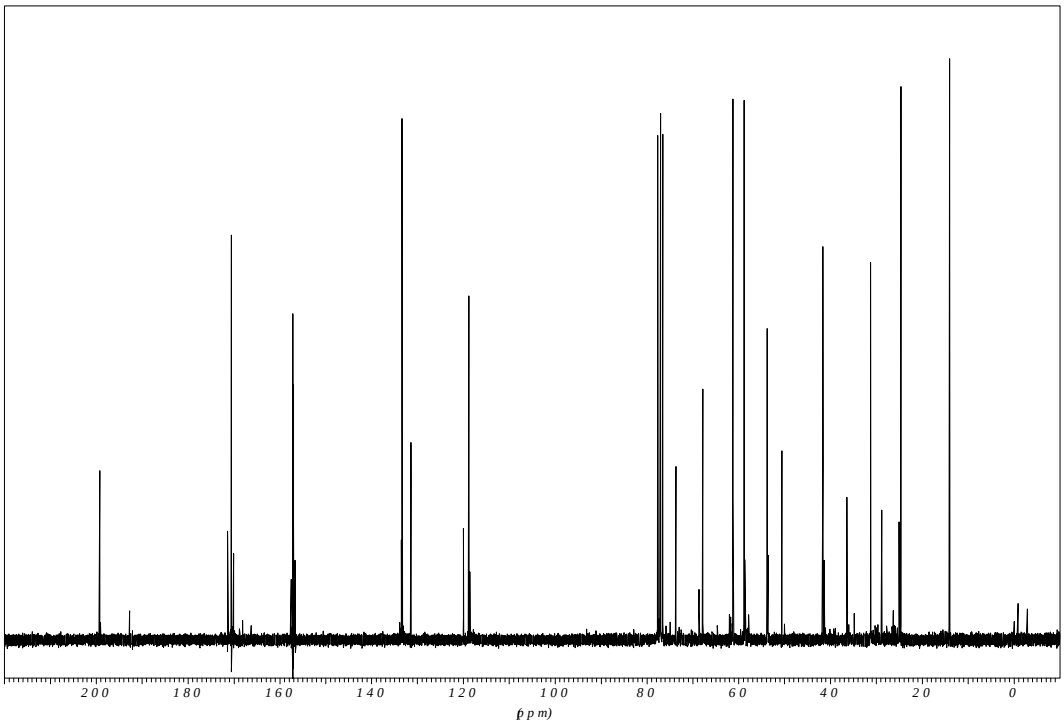
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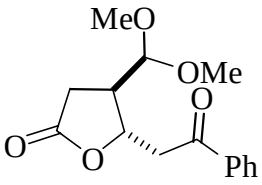
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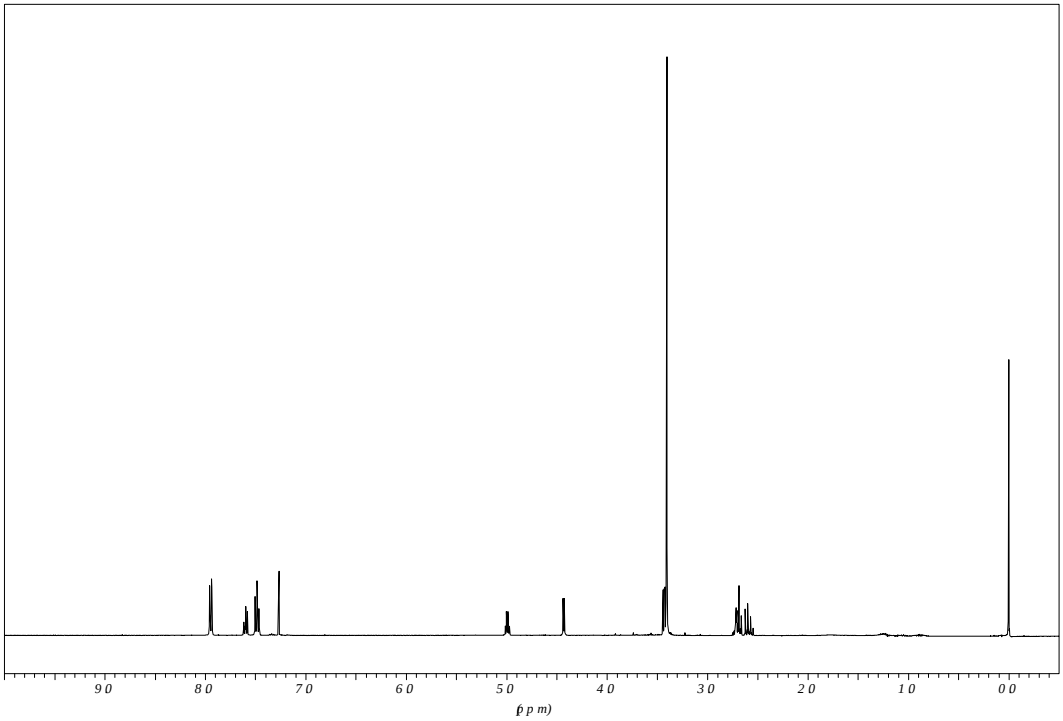
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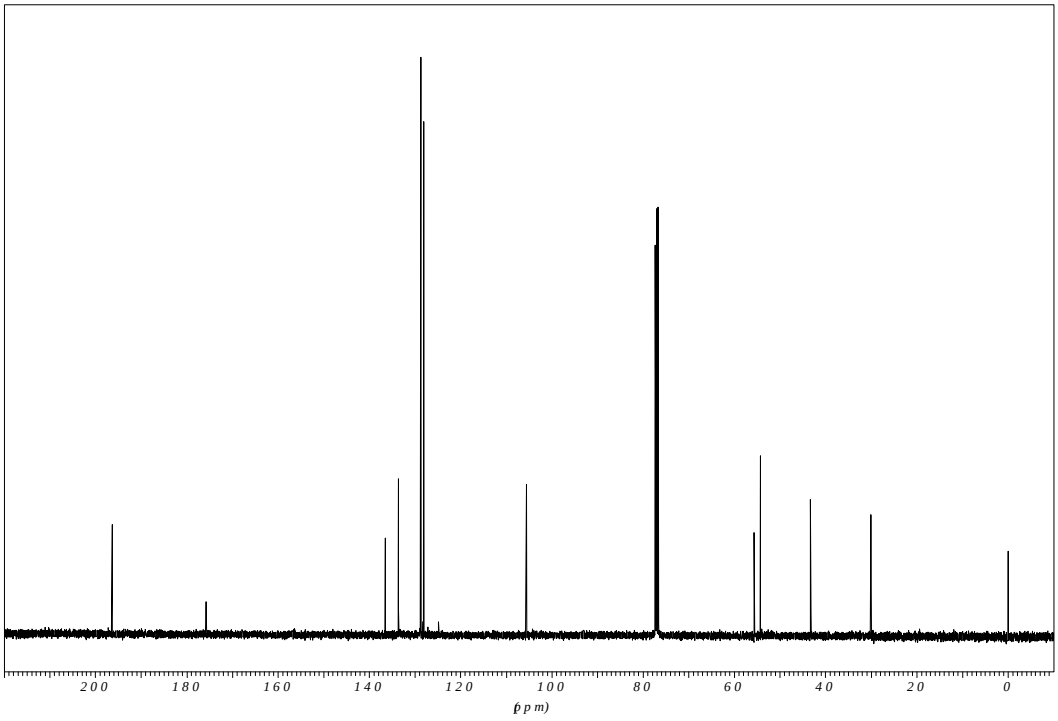
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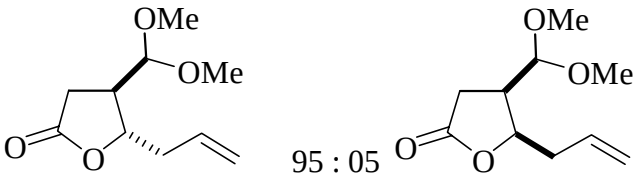
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95 : 05
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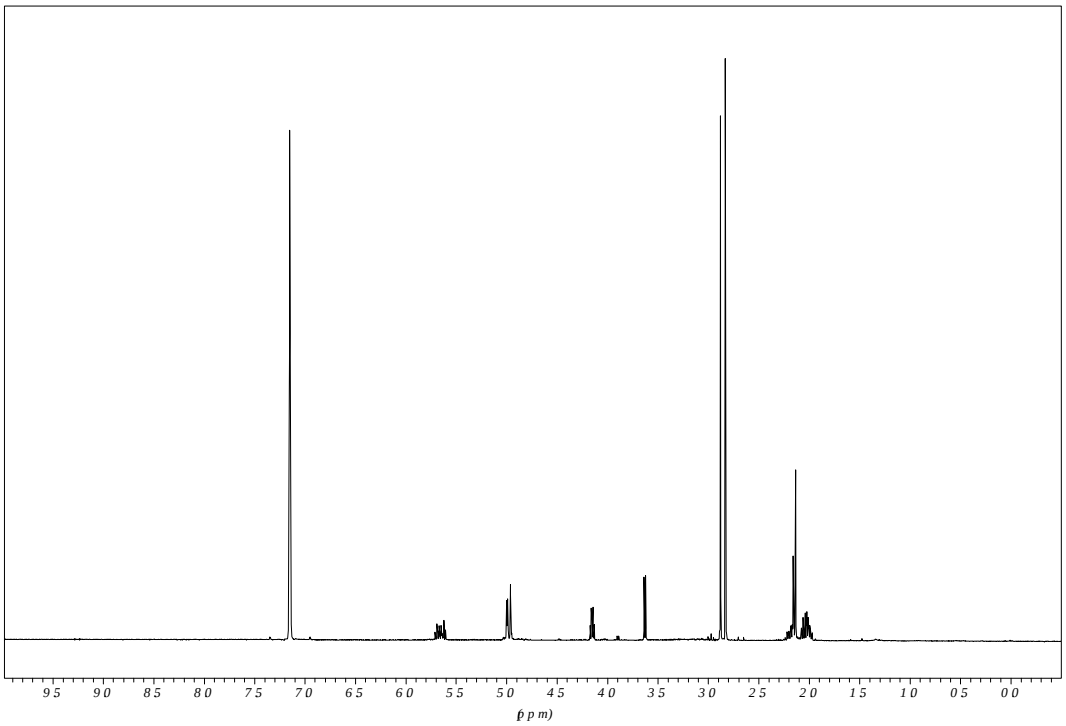
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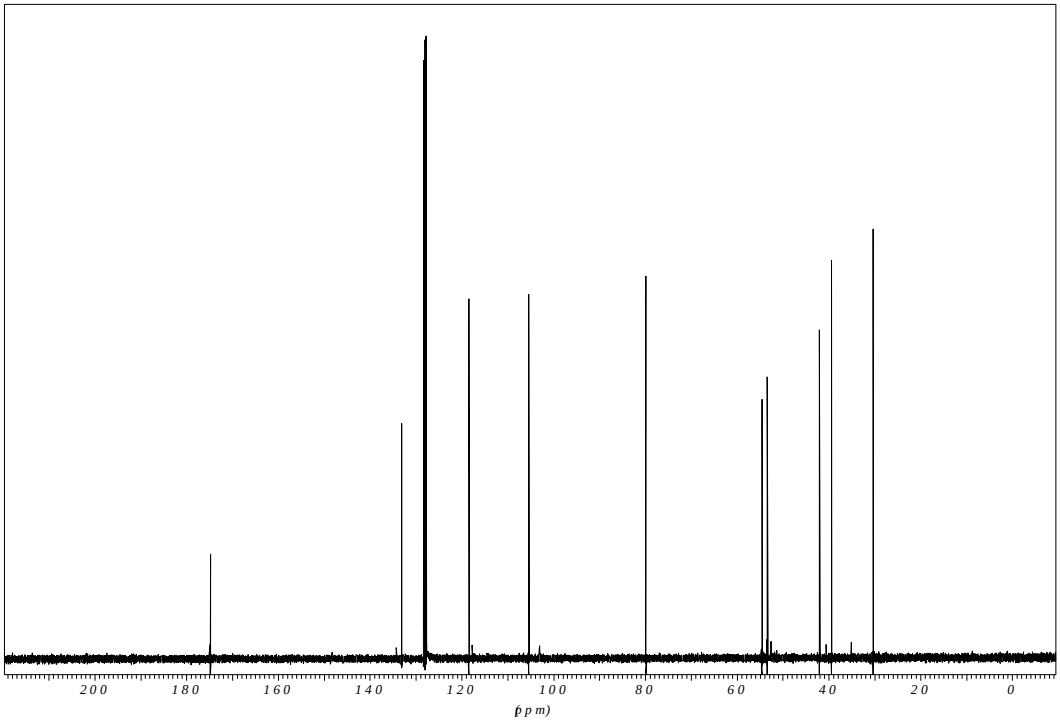
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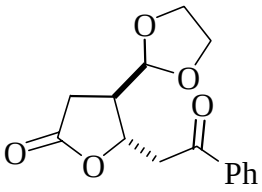
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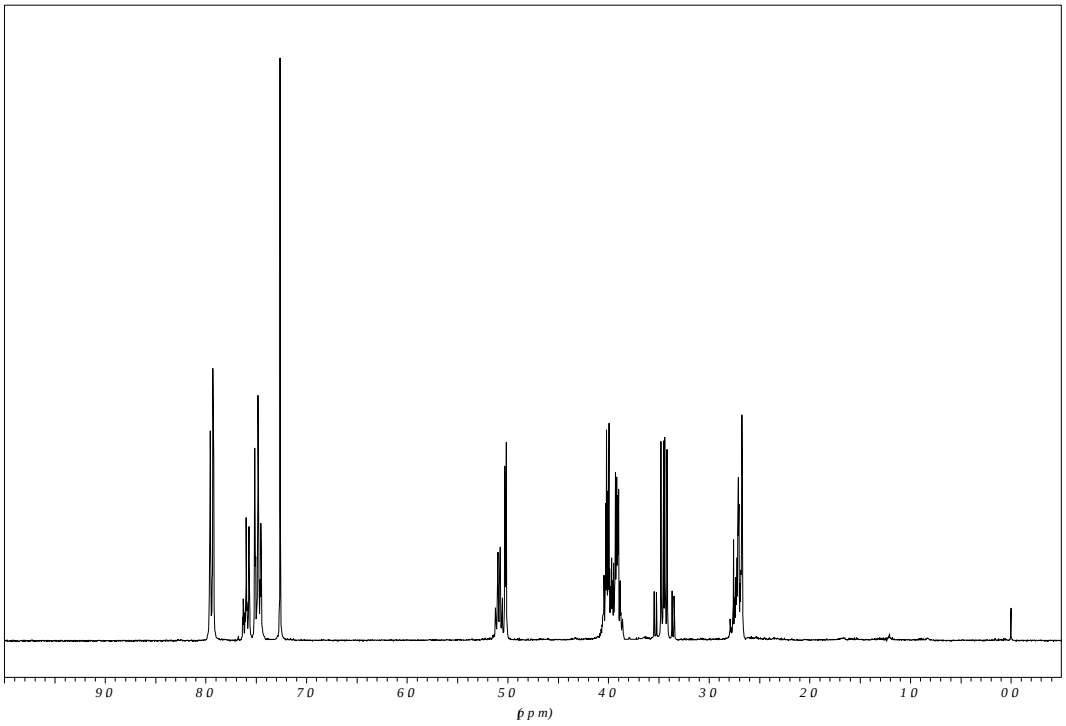
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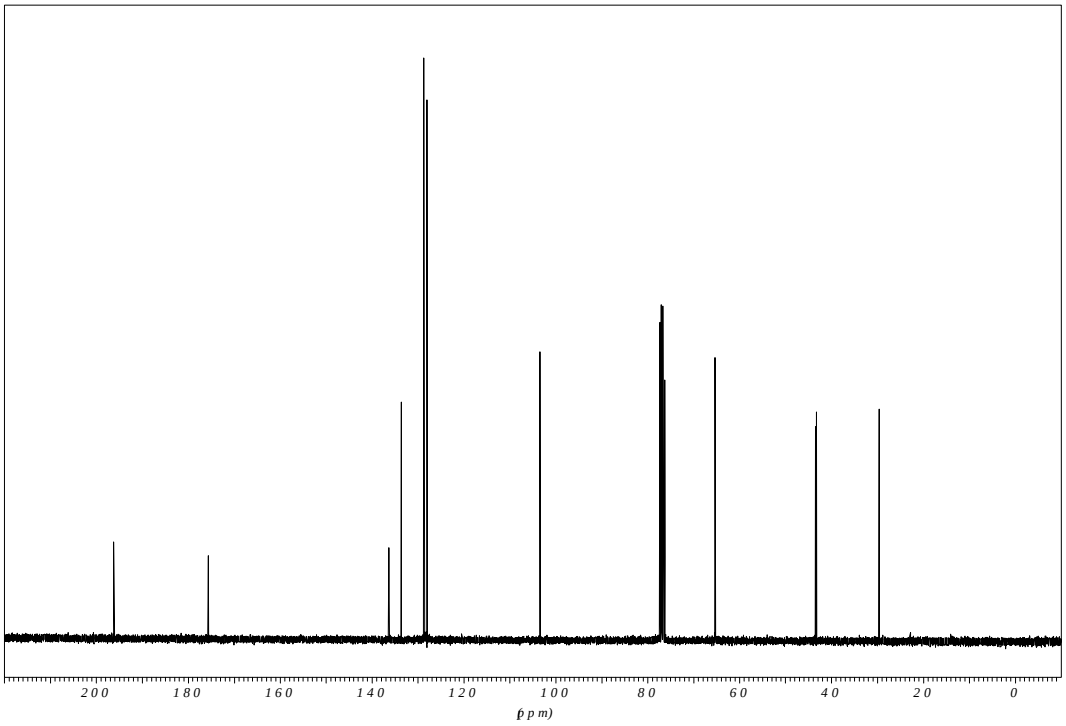
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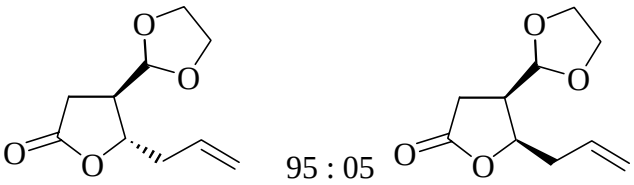
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95 : 05
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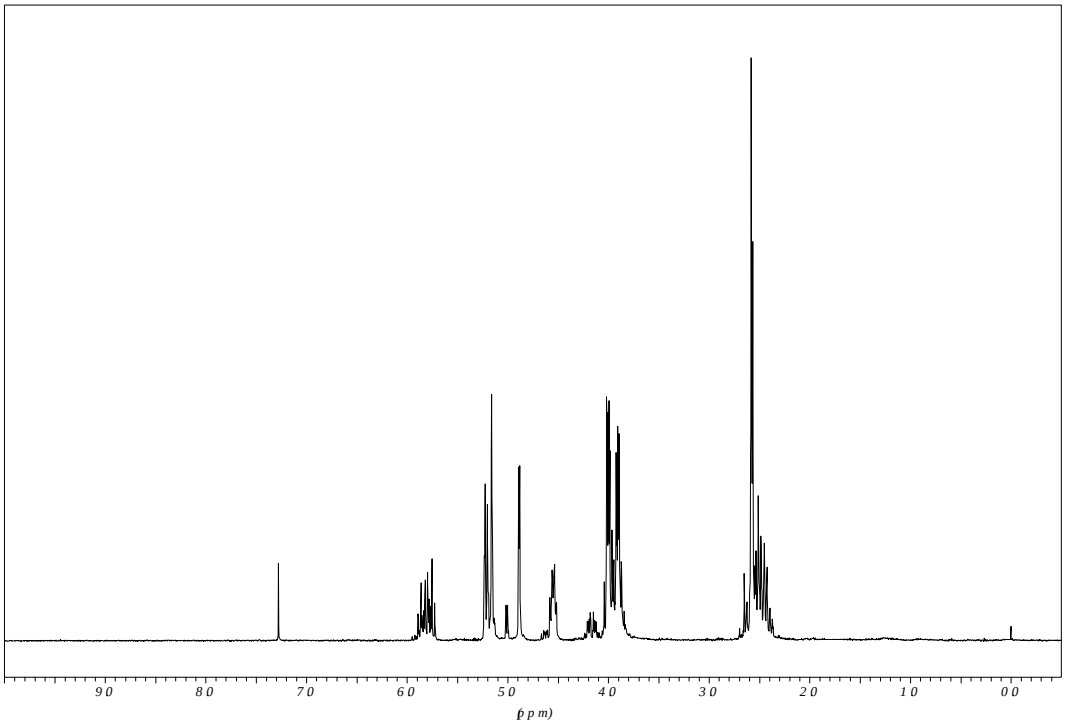
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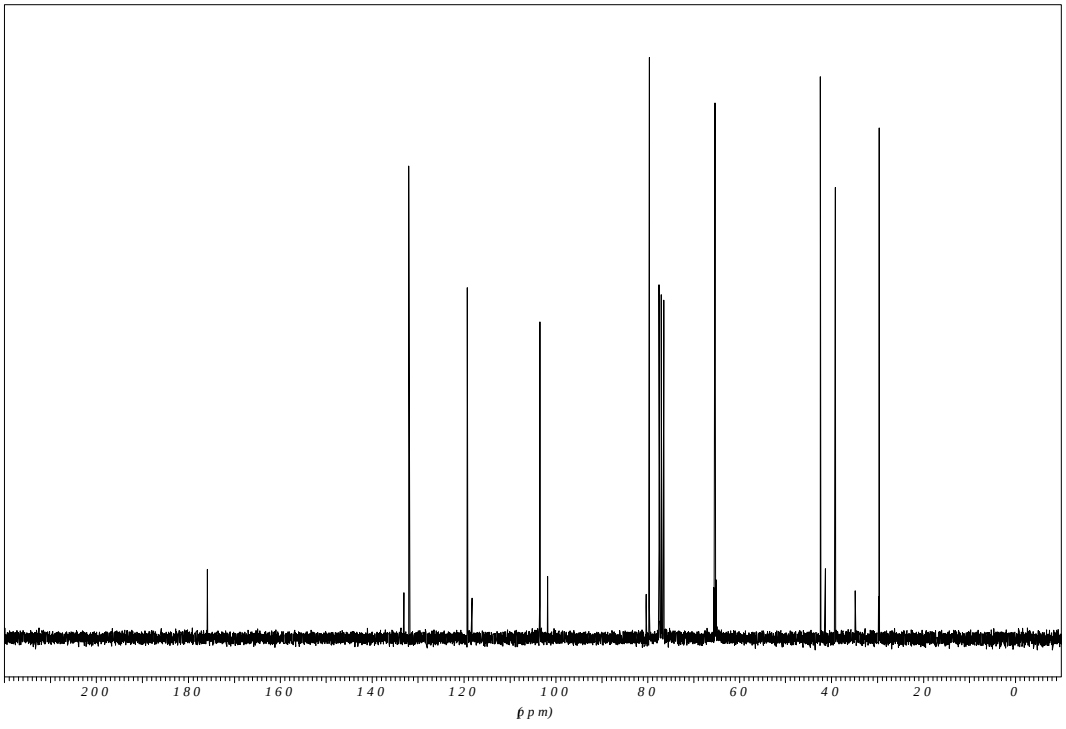
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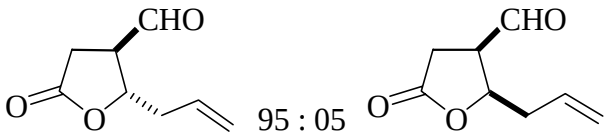
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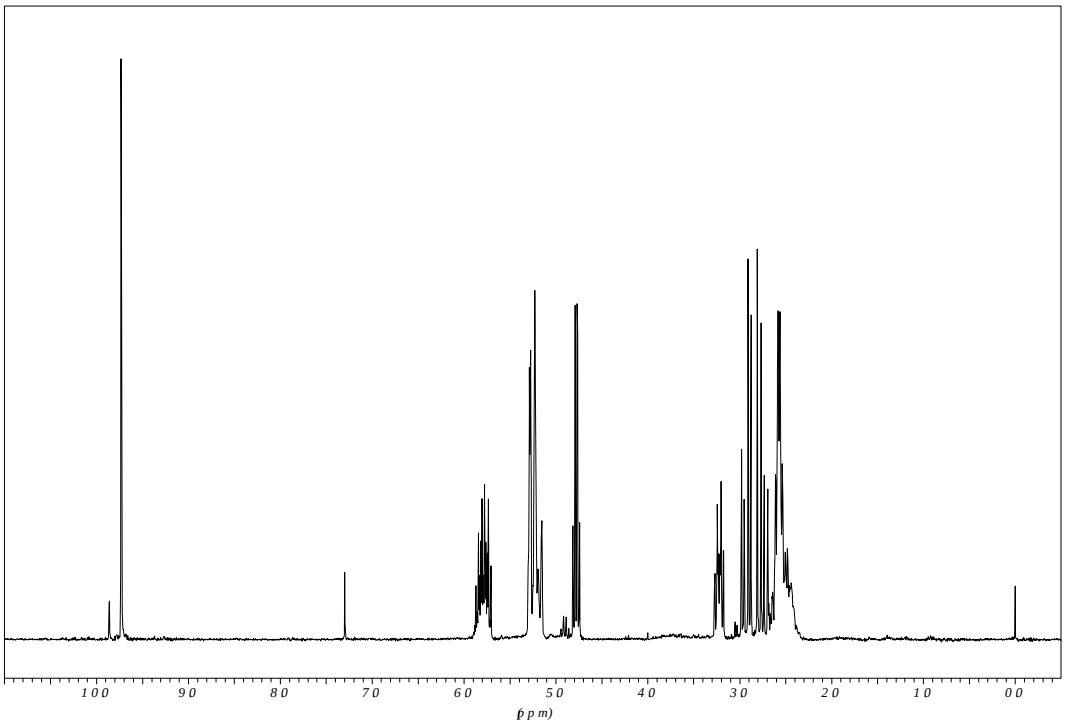
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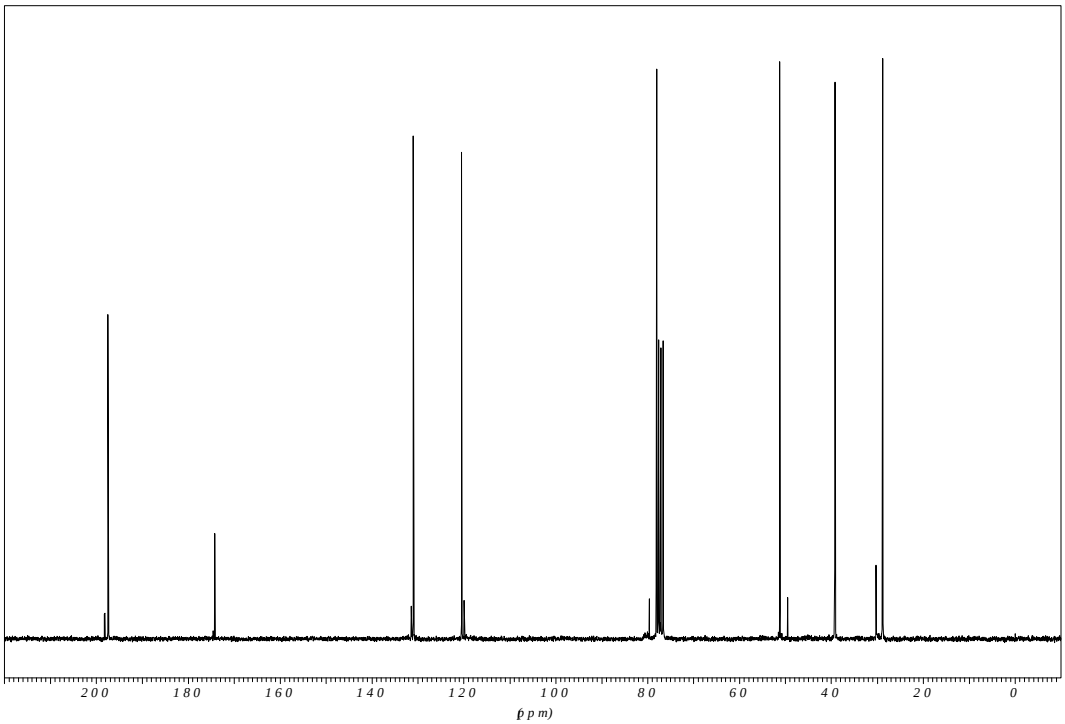
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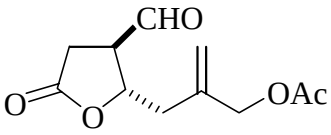
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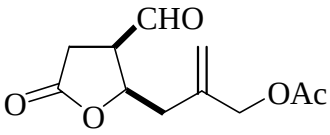
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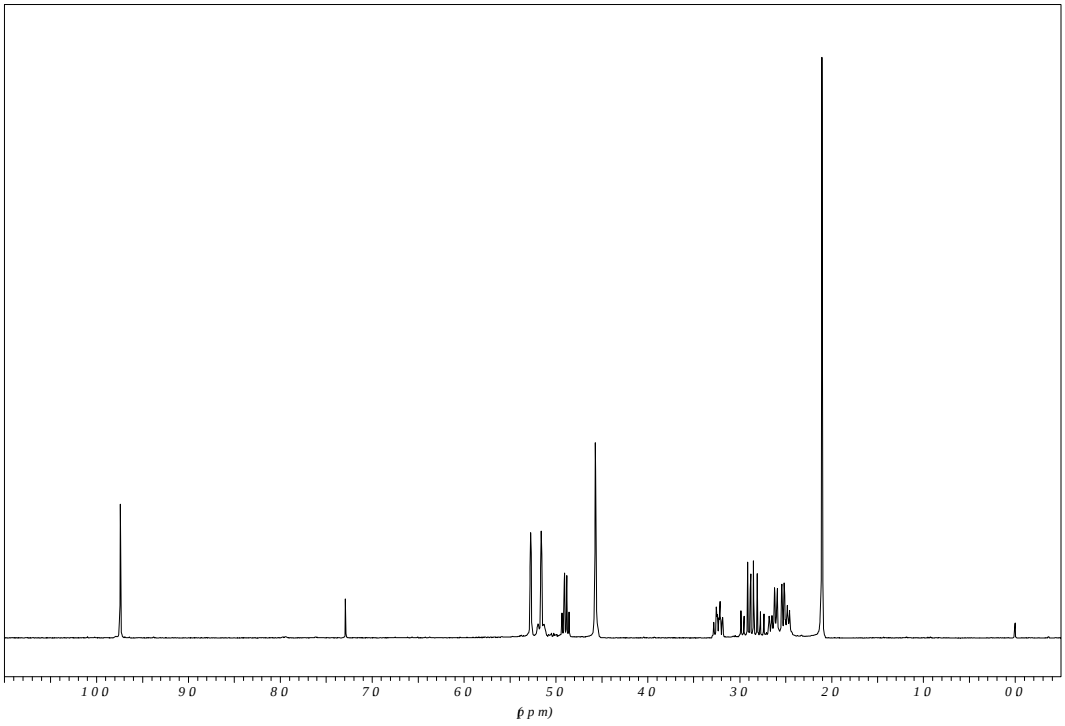
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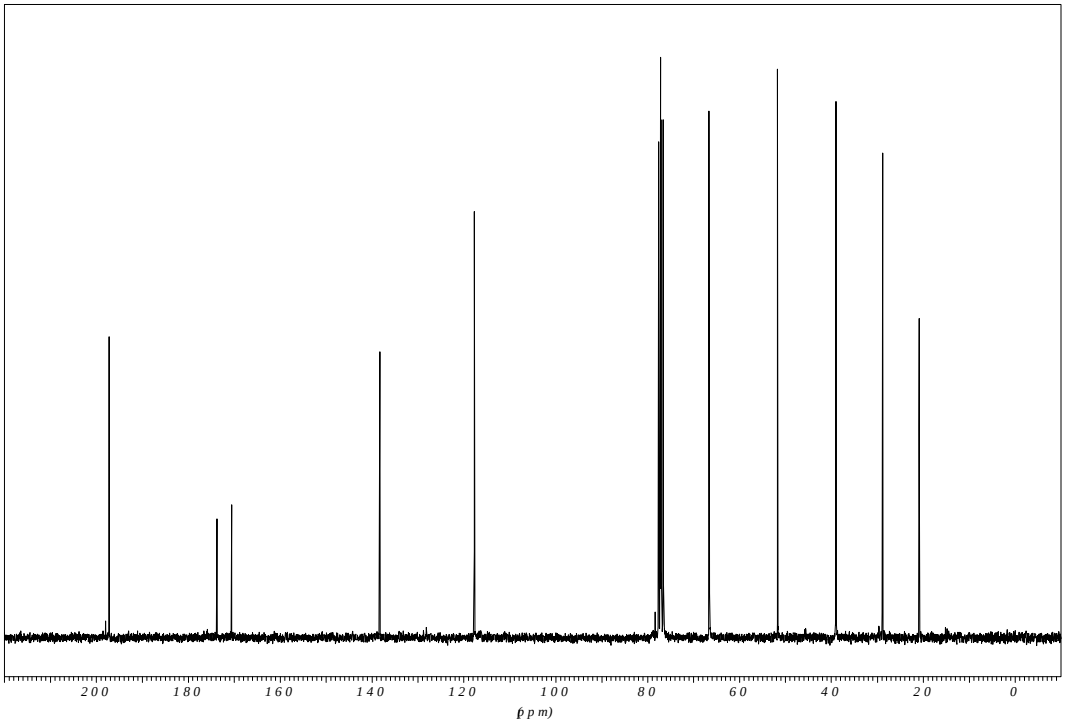
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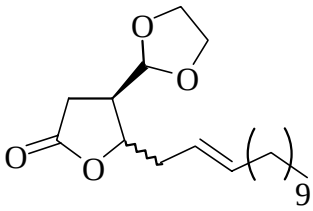
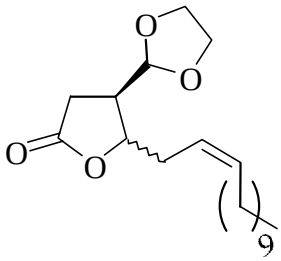
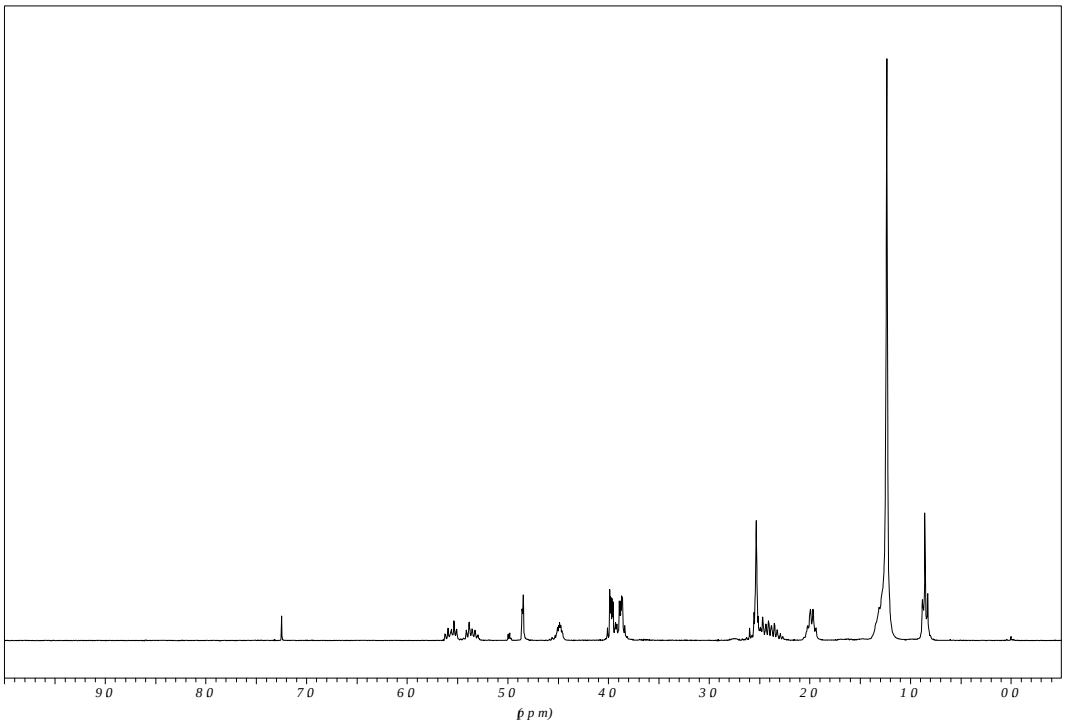
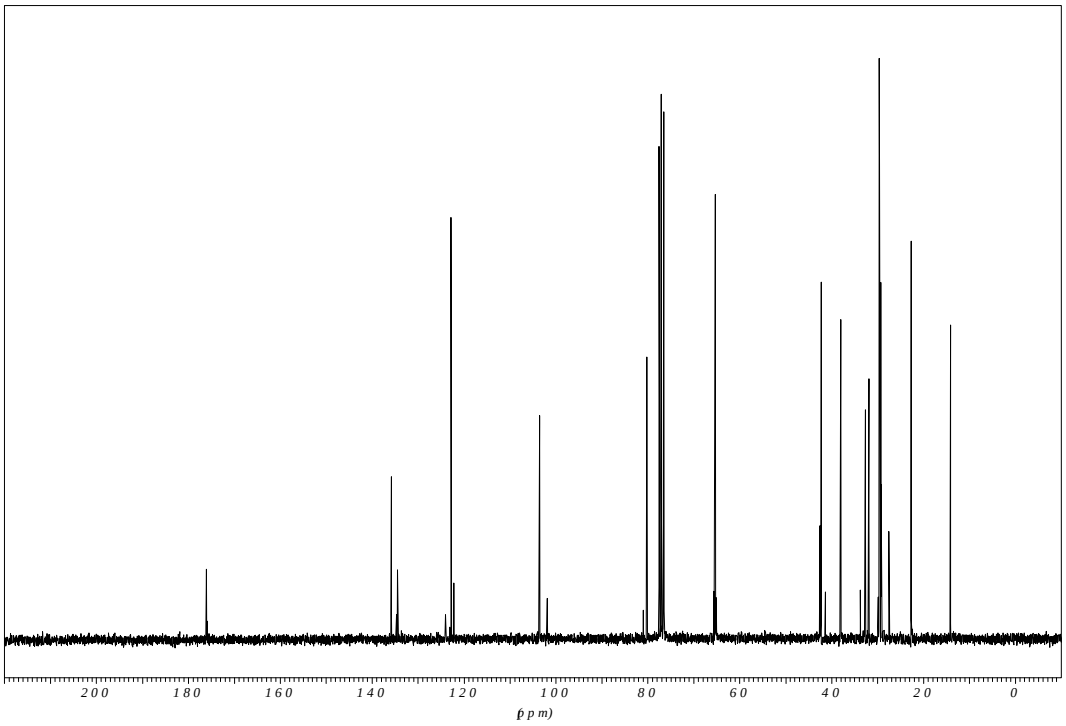
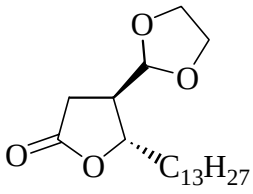




E : *Z* 3.5 : 1, *dv* 95 : 05



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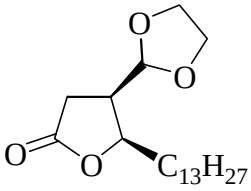
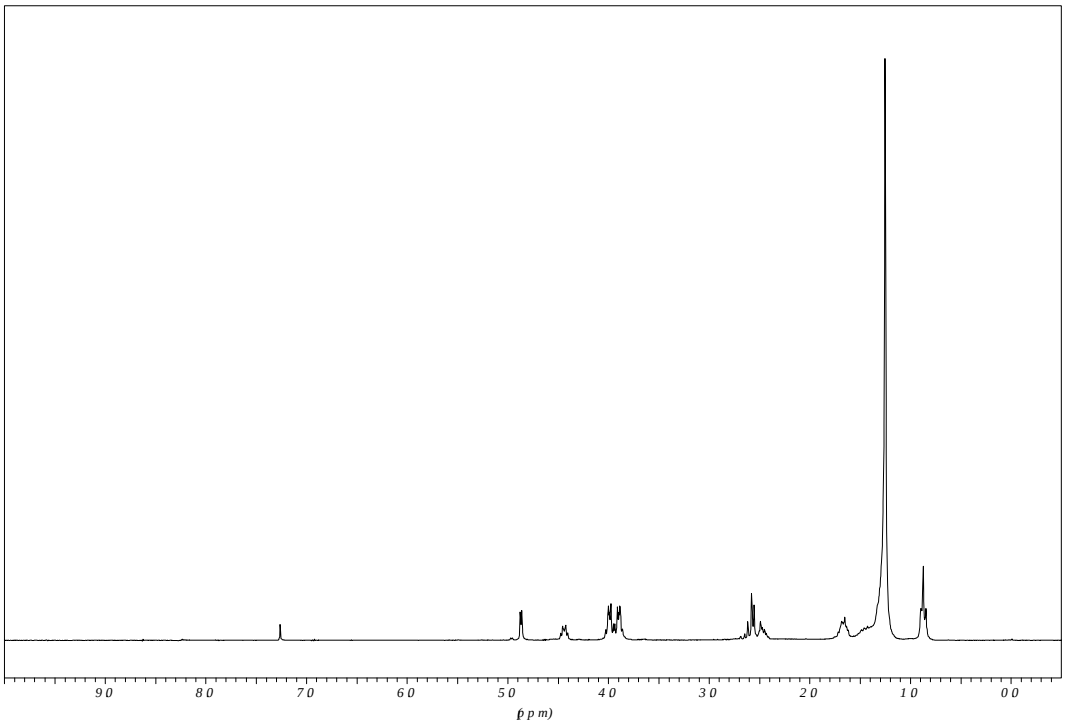
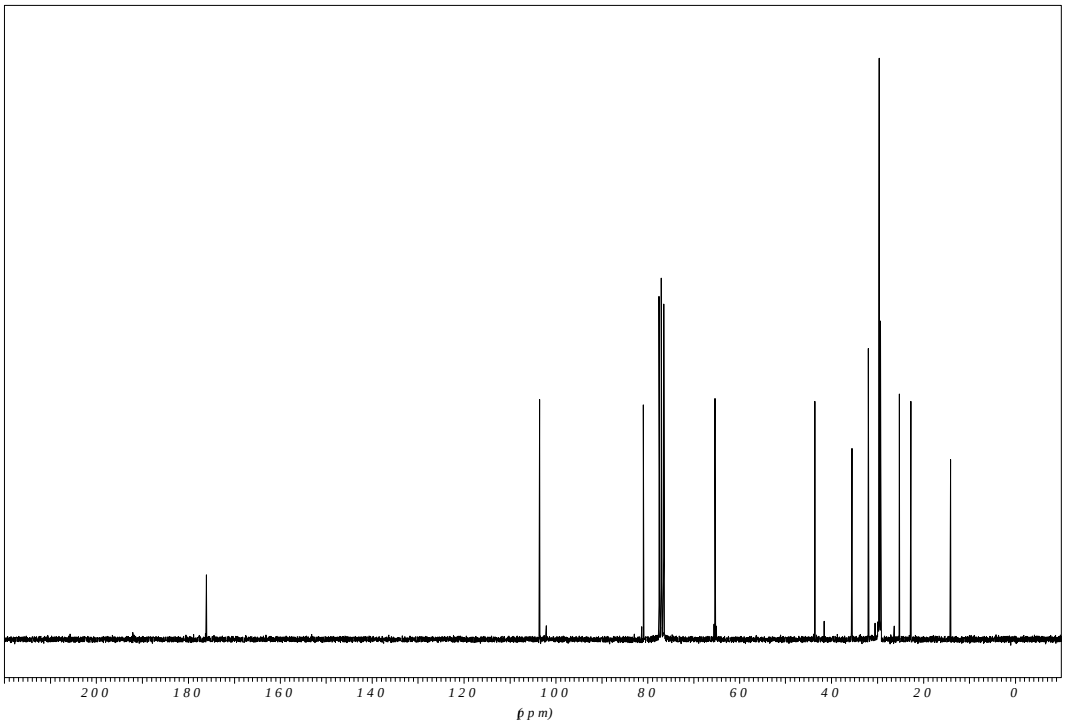
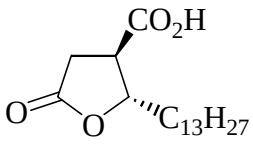
$C_{13}H_{27}$

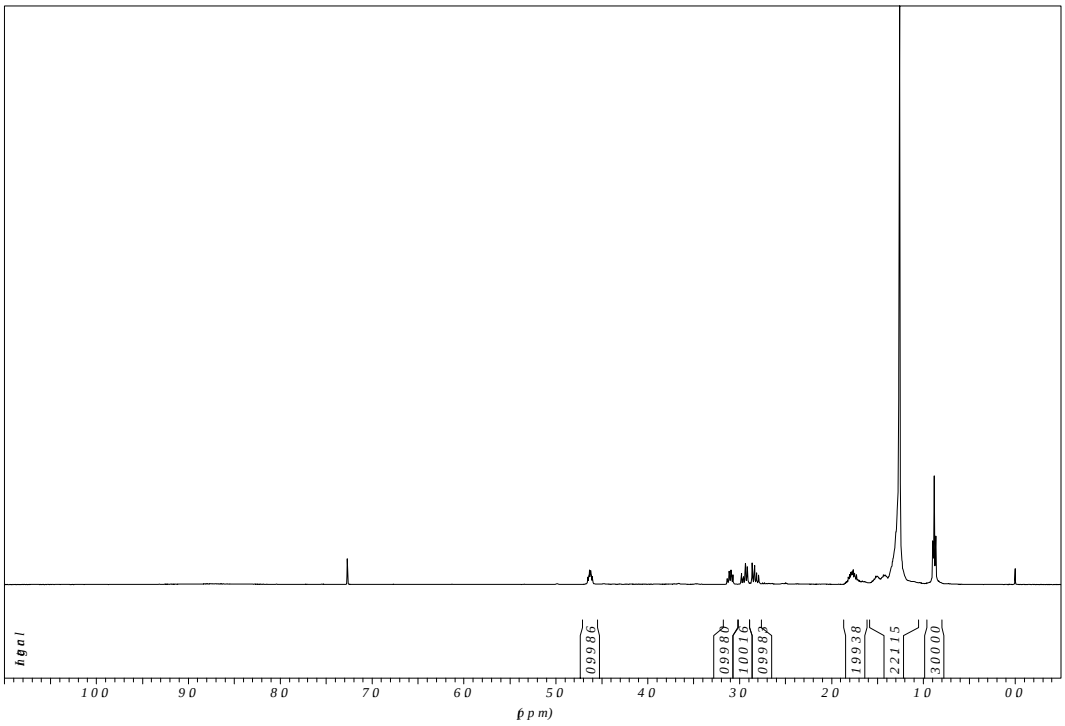
95 : 05

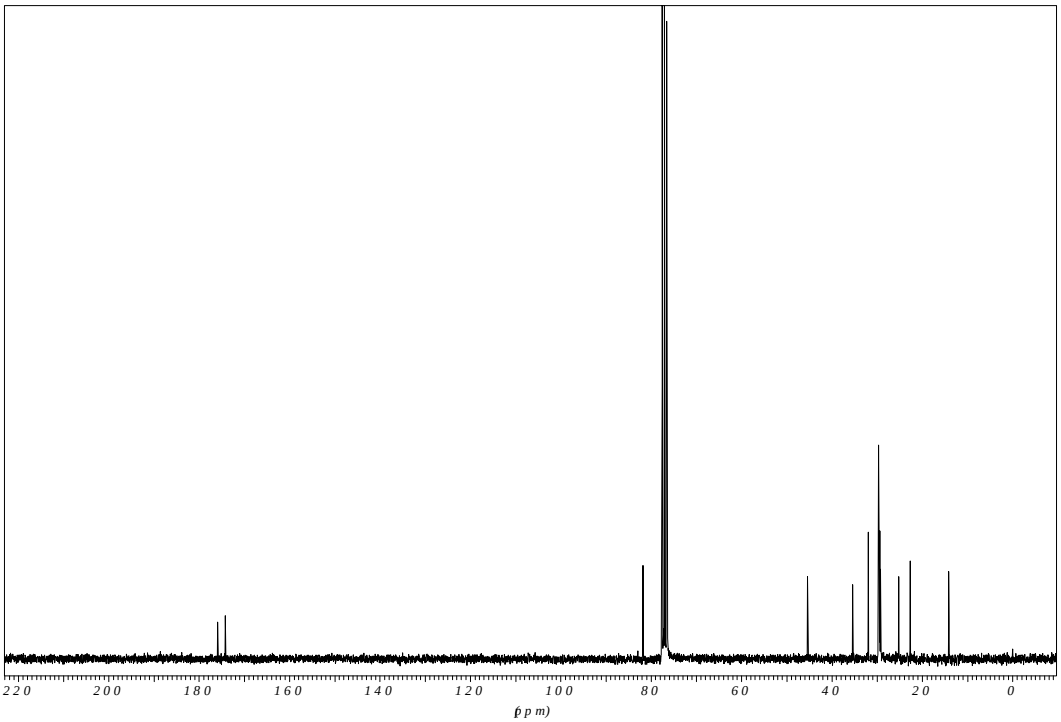

O
O
O
O
$C_{13}H_{27}$

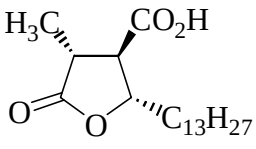

90
80
70
60
50
40
30
20
10
00
(ppm)

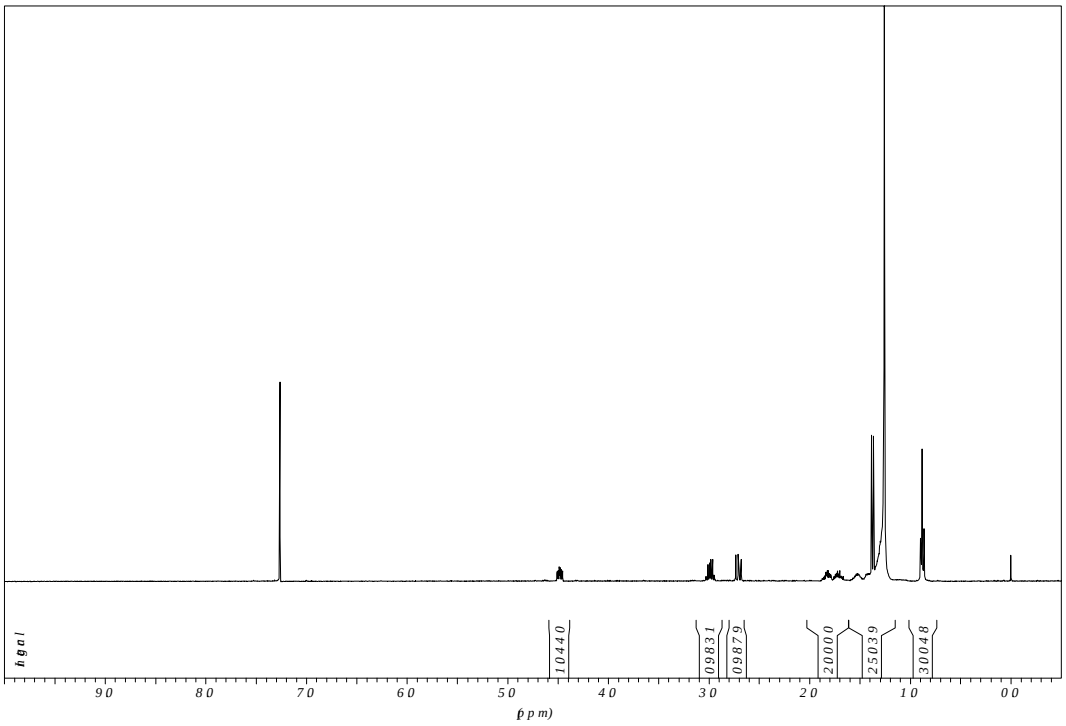

200
180
160
140
120
100
80
60
40
20
0
(ppm)

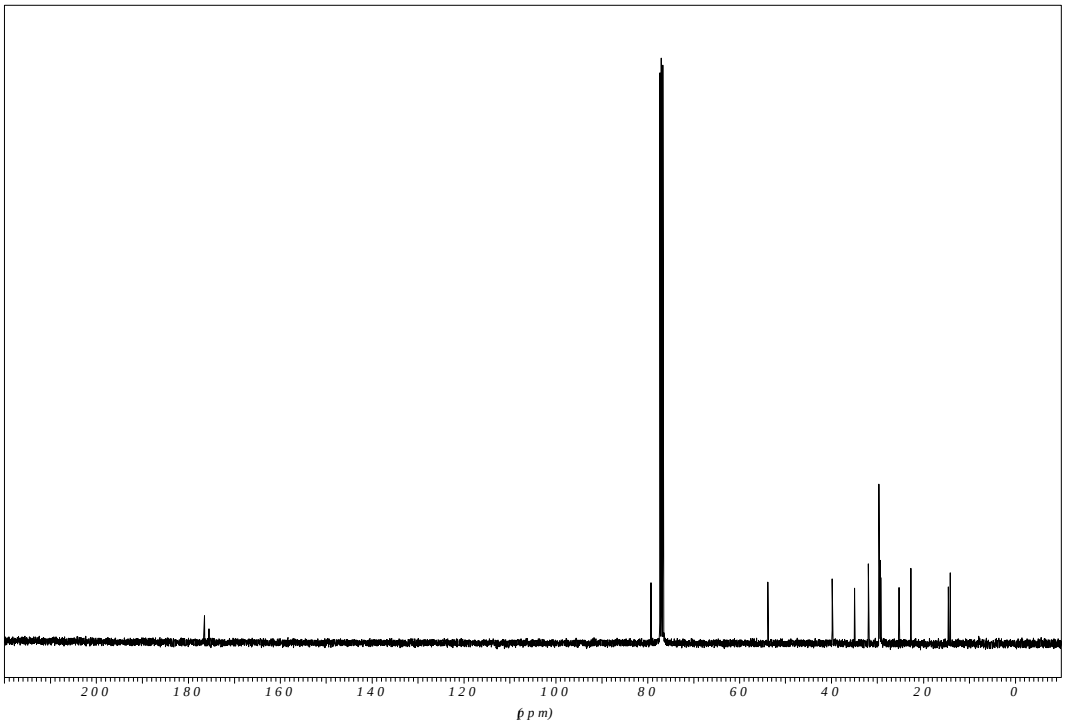

CO2H
O
O
C13H27


hgal
0.9986
0.9980
1.0016
0.9982
1.9938
2.2115
3.0000
100
90
80
70
60
50
40
30
20
10
00
(ppm)


220
200
180
160
140
120
100
80
60
40
20
0
(ppm)


H3C
CO2H
O
O
C13H27


hgal
10440
09831
09879
20000
25039
30048
90
80
70
60
50
40
30
20
10
00
(ppm)


200
180
160
140
120
100
80
60
40
20
0
(ppm)

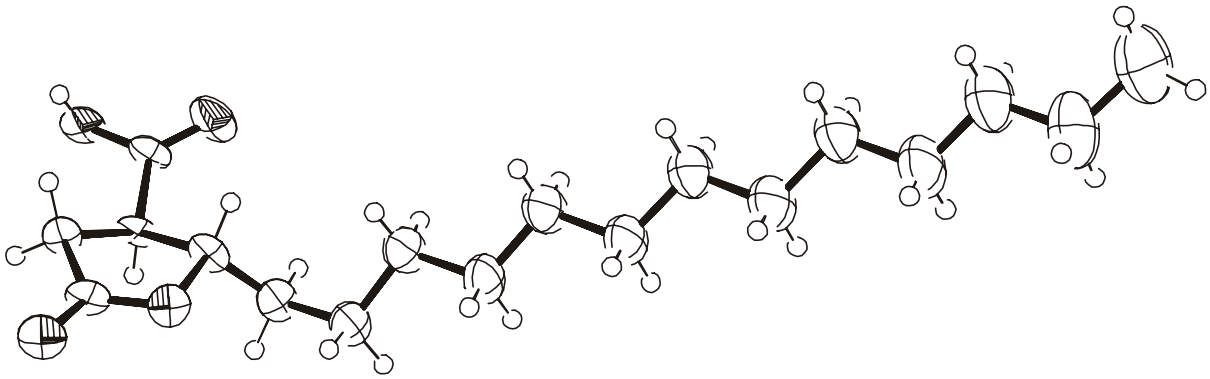


Figure 1. ORTEP-Plot of (–)-**16**.

Table 1. Crystal data and structure refinement for (–)-**16**.

Crystal Data	
Empirical formula	$C_{18}H_{32}O_4$
Formula weight	312.44
Crystal size	0.60 x 0.40 x 0.04 mm
Crystal description	platelike
Crystal colour	translucent, clear
Crystal system	Triclinic
Space group	P 1
Unit cell dimensions	a = 5.3320(10) Å α = 87.67(4) °
	b = 5.3460(10) Å β = 86.76(4) °
	c = 33.137(14) Å γ = 83.23(3) °
Volume	935.9(5) A³
Z, Calculated density	2, 1.109 Mg/m³
Absorption coefficient	0.610 mm^{-1}
F(000)	344
Measurement device type	Enraf-Nonius CAD-4 diffractometer
Measuremnet method	\Q-scan
Temperature	293(1) K
Wavelength	1.54180 Å
Monochromator	graphite
Theta range for data collection	4.01 to 64.77 °
Index ranges	-6<=h<=4, -6<=k<=4, -38<=l<=38

Reflections collected / unique	3397 / 3397 [R(int) = 0.0000]
Reflections greater I>2\\s(I)	2989
Refinement method	Full-matrix least-squares on F^2
Hydrogen treatment	constr
Data / restraints / parameters	3397 / 3 / 398
Goodness-of-fit on F^2	1.101
Final R indices [I>2σ(I)]	R_1 = 0.0772, ωR2 = 0.2029
R indices (all data)	R_1 = 0.0842, ωR2 = 0.2136
Absolute structure parameter	0.4(4)
Extinction coefficient	0.023(4)
Largest diff. peak and hole	0.529 and -0.575 e.A^{-3}