Supporting Information

Retention of Configuration in Photolytic Decarboxylation of Peresters to Form Chiral Acetals and Ethers

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Supporting Information Contents:

Typical Procedures

Reagents, Solvents, and Solutions. All reagents and solvents employed were purchased from the Aldrich Chemical Company Inc. (Madison, WI), Sigma Chemical Company (St. Louis, MO), or Fisher Scientific Ltd. (Ottawa, ON). Unless otherwise stated, all protected amino acids and derivatives were purchased from the Calbiochem-Novabiochem Corporation (San Diego, CA), Sigma-Aldrich Canada Ltd. (Oakville, ON), or Bachem California Inc. (Torrance, CA). All reagents and solvents were of American Chemical Society (ACS) grade and were used without further purification unless otherwise stated. All processes involving air or moisture sensitive reactants and/or requiring anhydrous conditions were performed under a positive pressure of argon using oven or flame-dried glassware. Acetonitrile and dichloromethane were distilled over calcium hydride prior to use. Methanol was distilled over potassium carbonate.

Purification Techniques. Unless stated otherwise, all reactions and fractions from column chromatography were monitored by thin layer chromatography (TLC) using glass-backed plates (1.5 x 5 cm) pre-coated (0.25 mm) with silica gel containing a UV fluorescent indicator (Merck 60 F_{254}). Compounds were visualized by exposing the plates to UV light, iodine staining, or by

dipping the plates in solutions of $Ce(SO_4)\cdot 4H_2O/(NH_4)MoO_{24}\cdot 4H_2O/H_2SO_4/H_2O$ (5 g:12.5 g:28 mL:472 mL) or phosphomolybdic acid/ethanol (5:95) followed by heating on a hot plate. Flash chromatography was performed using grade 60 silica gel (Rose Scientific, 230-400 mesh).

Instrumentation for Compound Characterization. Nuclear magnetic resonance (NMR) spectra were obtained on Varian Inova 300, 400, 500, and 600 MHz spectrometers. ^{1}H NMR chemical shifts are reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS) using the residual proton resonance of solvents as the reference: $CDCl_3$, δ 7.24; acetone-d_6, 2.04. ^{13}C NMR chemical shifts are reported relative to: $CDCl_3$, δ 77.0; acetone-d_6 28.9. Signals are quoted to within 0.1 ppm except where close peaks necessitate an additional significant figure. Additional assignments were made using pulsed field gradient versions of shift correlation spectroscopy (gCOSY), heteronuclear multiple quantum coherence spectroscopy (gHMQC), and heteronuclear multiple bond correlation spectroscopy (gHMBC).

^{1}H NMR data are reported in the following order: multiplicity (app, apparent; s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; and m, multiplet), number of protons, coupling constant (*J*) in Hertz (Hz), and assignment. When appropriate, the multiplicity is preceded by br, indicating that the signal was broad. The coupling constants reported are within an error range of 0.2-0.4 Hz, and have been rounded to the nearest 0.1 Hz.

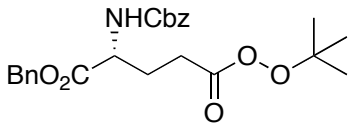
Infrared spectra (IR) were recorded on a Nicholet Magna-IR 750 with Nic-Plan microscope FT-IR spectrometer. Cast refers to the evaporation of a solution on a NaCl plate. Mass spectra (MS) were recorded on a Kratos AEIMS-50 high resolution mass spectrometer (HRMS), using a Micromass ZabSpec Hybrid Sector-TOF positive or negative mode electrospray ionization (ES). Optical rotations were measured on a Perkin Elmer 241

polarimeter with a microcell (10 cm path length, 1 mL) at ambient temperature and are reported in units of 10^{-1} deg cm^2 g^{-1}. All reported optical rotations were referenced against air and were measured at the sodium D line (λ = 589.3 nm).

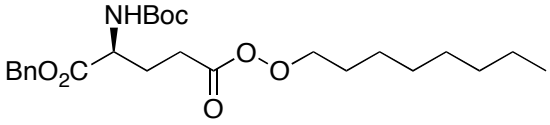
Typical procedure for perester formation. For each equivalent of acid, dissolved in MeCN (10 mL/mmol), an equivalent of hydroperoxide dissolved in CH_2Cl_2 (5 mL/mmol) and a catalytic amount of DMAP (0.05 equivalents) were added, the solution was cooled (usually between -10 and 10 ºC), and an equivalent of DCC dissolved in CH_2Cl_2 (5 mL/mmol) was added. While the mixture was stirred, a white precipitate of DCU began to form. The mixture was stirred until all the starting material was consumed, with typical times of 4-12 h. The reaction mixture was then filtered to remove the DCU precipitate and the solvent was removed *in vacuo*. The resulting oil was purified by flash chromatography on silica gel.

Typical procedure for photolysis of peresters at -196 °C. The liquid starting material (10-200 mg) was spread evenly inside a sealable polyethylene bag and the bag was secured on the bottom of a Dewar vessel, which was filled with liquid nitrogen. The Dewar vessel was covered with a quartz plate and a UV lamp (0.9 A, 254 nm) was used to irradiate the polyethylene bag for 8 to 24 h with periodical liquid nitrogen refills.

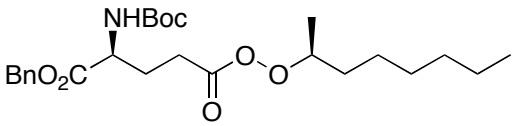
Experimental Details



(2*R*)-Benzyl 2-(benzyloxycarbonylamino)-5-(*tert*-butylperoxy)-5-oxopentanoate (2). The typical procedure for perester synthesis was followed using *N*-Cbz D-glutamic acid γ-benzyl ester (**1**) (1.857 g, 5.00 mmol), *tert*-butyl hydroperoxide (5M in decane, 1.5 mL, 7.50 mmol), DCC (1.032 g, 5.00 mmol), and DMAP (61 mg, 0.50 mmol). The temperature was maintained at -20 °C for 3 h, then allowed to warm to r.t. over 1 h. The solution was filtered, the solvent was removed *in vacuo* and the resulting oil was purified by column chromatography (silica gel, 20% EtOAc/hexanes) to obtain perester **2** (1.990 g, 99%) as a colourless oil: $[\alpha]_D^{26}$ = -2.8° (*c* 1.0, $CHCl_3$); IR ($CHCl_3$ cast) 3351, 3033, 2981, 1772, 1724, 1523, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.31-7.23 (m, 10H, 2x$C_6\underline{H}_5$), 5.60 (d, *J* = 8.0 Hz, 1H, N$\underline{H}$), 5.16 (d, *J* = 12.0 Hz, 1H, C$\underline{H}_a$H$_b$C$_6$H$_5$), 5.09 (d, *J* = 12.0 Hz, 1H, CH$_a\underline{H}_b$C$_6$H$_5$), 5.07 (s, 2H, C$\underline{H}_2$C$_6$H$_5$), 4.44-4.41 (m, 1H, C$\underline{H}$), 2.39-2.26 (m, 2H, CH$_2$C$\underline{H}_2$CO), 2.25-2.19 (m, 1H, CHC$\underline{H}_a$H$_b$CH$_2$), 2.03-1.95 (m, 1H, CHCH$_a\underline{H}_b$CH$_2$), 1.26 (s, 9H, C(C$\underline{H}_3$)$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 171.0, 169.7, 155.7, 135.8, 134.8, 128.8, 128.3, 128.0(x2), 127.8, 127.7, 83.2, 67.1, 66.8, 53.2, 27.3, 27.0, 25.9; HRMS (ES positive) calcd for $C_{24}H_{29}NO_7Na$ 466.1842, found 466.1840 $[MNa]^+$.

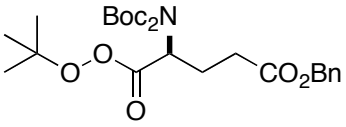


(2*S*)-Benzyl 2-(*tert*-butoxycarbonylamino)-5-(octylperoxy)-5-oxopentanoate (4). The typical procedure for the synthesis of peresters was followed using *N*-Boc L-glutamic acid γ-benzyl ester (**3**) (675 mg, 2.00 mmol), 1-hydroperoxyoctane (292 mg, 2.00 mmol), DMAP (12 mg, 0.10 mmol), and DCC (412 mg, 2.00 mmol) in CH_2Cl_2 at r.t. for 16 h. The resulting oil was purified by column chromatography (silica gel, 10% EtOAc/hexanes) to provide perester **4** (888 mg, 95%) as a colourless oil: $[\alpha]_D^{26}$ = +5.2° (*c* 2.4, $CHCl_3$); IR ($CHCl_3$ cast) 3377, 2929, 2857, 1776, 1716, 1500, 1455, 1367, 1252, 1167 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.32-7.26 (m, 5H, Ar<u>H</u>), 5.23 (d, *J* = 8.0 Hz, 1H, N<u>H</u>), 5.15 (d, *J* = 12.4 Hz, 1H, C<u>H</u>$_a$H$_b$Ph), 5.10 (d, *J* = 12.4 Hz, 1H, CH$_a$<u>H</u>$_b$Ph), 4.37-4.32 (m, 1H, NC<u>H</u>), 4.14 (t, *J* = 6.8 Hz, 2H, OOC<u>H</u>$_2$), 2.34-2.18 (m, 3H, C<u>H</u>$_2$CO$_3$ and NCHC<u>H</u>$_a$H$_b$), 1.99-1.93 (m, 1H, NCHCH$_a$<u>H</u>$_b$), 1.65-1.58 (m, 2H, OOCH$_2$C<u>H</u>$_2$), 1.39-1.21 (m, 19H, (C<u>H</u>$_2$)$_5$ and C(C<u>H</u>$_3$)$_3$), 0.85 (t, *J* = 6.4 Hz, 3H, CH$_2$C<u>H</u>$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.5, 169.8, 155.2, 135.0, 128.4, 128.2, 128.1, 79.8, 76.7, 67.0, 52.7, 31.5, 29.0, 28.9(x2), 28.0, 27.3, 27.0, 25.5, 22.4, 18.8; HRMS (ES positive) calcd for $C_{25}H_{39}NO_7Na$ 488.2619, found 488.2618 $[MNa]^+$.



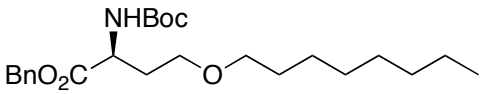
(2*S*)-Benzyl 2-(*tert*-butoxycarbonylamino)-5-((2*S*)-2-octylperoxy)-5-oxopentanoate (5). The typical procedure for perester synthesis was followed using *N*-Boc L-glutamic acid γ-benzyl ester

(**3**) (337 mg, 1.00 mmol), (*2S*)-2-hydroperoxyoctane (146 mg, 1.00 mmol), DMAP (12 mg, 0.10 mmol), and DCC (206 mg, 1.00 mmol) in 2:1 CH_2Cl_2/MeCN at 0 ºC for 16 h. The resulting oil was purified by column chromatography (silica gel, 10% EtOAc/hexanes) to provide perester **5** (234 mg, 50%) as a colourless oil: $[\alpha]_D^{26}$= +5.9° (*c* 3.0, $CHCl_3$); IR ($CHCl_3$ cast) 3366, 2932, 2860, 1774, 1715, 1500, 1455, 1367, 1252, 1165 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.28-7.23 (m, 5H, Ar<u>H</u>), 5.24 (d, *J* = 8.4 Hz, 1H, N<u>H</u>), 5.11 (d, *J* = 12.0 Hz, 1H, OC<u>H</u>$_a$H$_b$Ph), 5.07 (d, *J* = 12.0 Hz, 1H, OCH$_a$<u>H</u>$_b$Ph), 4.32-4.20 (m, 2H, NC<u>H</u> + OC<u>H</u>), 2.35-2.26 (m, 2H, $O_2CC\underline{H}_2$), 2.16-1.90 (m, 2H, NCHC<u>H</u>$_2$), 1.59-1.09 (m, 22H, OCHC<u>H</u>$_3$, NCHC<u>H</u>$_2$CH$_2$, (C<u>H</u>$_2$)$_5$ and C(CH$_3$)$_3$), 0.81 (t, *J* = 6.4 Hz, 3H, (CH$_2$)$_5$C<u>H</u>$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.5, 169.9, 155.1, 135.0, 128.3, 128.2, 128.0, 82.2, 79.7, 67.0, 52.6, 33.7, 31.4, 28.9, 28.0, 27.2, 27.0, 25.0, 22.3, 18.1, 13.8; HRMS (ES positive) calcd for $C_{25}H_{39}NO_7Na$ 488.2619, found 488.2621 $[MNa]^+$.

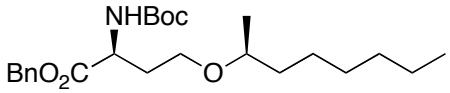


4*S*)-Benzyl 4-(bis(*tert*-butoxycarbonyl)amino)-5-(*tert*-butylperoxy)-5-oxopentanoate (6). The typical procedure for peresters synthesis was followed using the corresponding acid (48 mg, 0.11 mmol), *tert*-butylhydroperoxide (0.1 mL 5M, 0.50 mmol) and CDI (20 mg, 0.12 mmol) in DCM at 0 ºC for 4 h. The resulting oil was purified by column chromatography (silica gel, 10% EtOAc/hexanes) to provide perester **109** (40 mg, 71%) as a colourless oil: IR ($CHCl_3$ cast) 3033, 2978, 2940, 1777, 1739, 1498, 1454, 1367, 1213 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.37-7.31 (m, 5H, C$_6$<u>H</u>$_5$), 5.59 (t, *J* = 5.1 Hz, 1H, C<u>H</u>), 5.14 (s, 2H, C<u>H</u>$_2$C$_6$H$_5$), 3.30 (dd, *J* = 5.1 Hz, 16.0 Hz, 1H, CHC<u>H</u>$_a$H$_b$), 2.84 (dd, *J* = 5.1 Hz, 16.0 Hz, CHCH$_a$<u>H</u>$_b$), 1.50 (s, 18H, 2xCO$_2$C(C<u>H</u>$_3$)$_3$), 1.29 (s, 9H, CO$_3$C(C<u>H</u>$_3$)$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.2, 151.3, 135.8, 128.5, 128.2(x2),

84.1, 83.9, 66.8, 53.6, 35.6, 27.9, 26.0; HRMS (ES positive) Calcd for $C_{26}H_{39}NO_9Na$ 532.2523, found 532.2525 (M+Na).

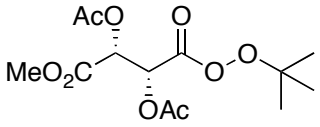


(2*S*)-Benzyl 2-(*tert*-butoxycarbonylamino)-4-(octyloxy)butanoate (8). The typical perester photolysis procedure was followed using perester **4** (128 mg, 0.27 mmol). The resulting oil was purified by column chromatography (silica gel, 10% EtOAc/hexanes) to provide ether **8** (35 mg, 30%) as a colourless oil: $[\alpha]_D^{26}$ = -12.5° (*c* 2.9, $CHCl_3$); IR ($CHCl_3$ cast) 3384, 2930, 2857, 1717, 1499, 1455, 1366, 1248, 1161, 1113, 1059 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.36-7.26 (m, 5H, Ar<u>H</u>), 5.57 (d, *J* = 8.0 Hz, 1H, N<u>H</u>), 5.19 (d, *J* = 12.0 Hz, 1H, C<u>H</u>$_a$H$_b$Ph), 5.13 (d, *J* = 12.0 Hz, 1H, CH$_a$<u>H</u>$_b$Ph), 4.45-4.41 (m, 1H, NC<u>H</u>), 3.47-3.33 (m, 4H, C<u>H</u>$_2$OC<u>H</u>$_2$), 2.10-2.00 (m, 2H, NCHC<u>H</u>$_2$), 1.53-1.14 (m, 21H, CH$_3$(C<u>H</u>$_2$)$_6$ + C(C<u>H</u>$_3$)$_3$), 0.89 (t, *J* = 6.8 Hz, 3H, CH$_2$C<u>H</u>$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.3, 155.8, 135.5, 128.5, 128.2, 128.1, 79.5, 71.3, 67.1, 66.8, 52.2, 31.8, 31.7, 29.6, 29.4, 29.2, 28.3, 26.0, 22.6, 14.0; HRMS (ES positive) calcd for $C_{24}H_{39}NO_5Na$ 444.2720, found 444.2720 $[MNa]^+$.

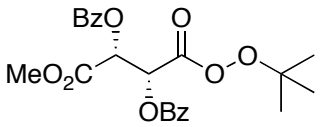


(2*S*)-Benzyl 2-(*tert*-butoxycarbonylamino)-4-((2*S*)-2-octyloxy)butanoate (9). The typical procedure for perester photolysis was followed using perester **5** (109 mg, 0.23 mmol) at -196 ºC for 48 h. The resulting oil was purified by column chromatography (silica gel, 10% EtOAc/hexanes) to provide ether **9** (45 mg, 46%) as a colourless oil: $[\alpha]_D^{26}$ = -9.7° (*c* 2.0, $CHCl_3$);

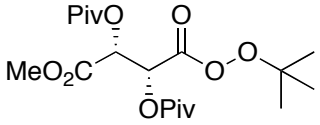
IR ($CHCl_3$ cast) 3388, 2965, 2930, 2859, 1718, 1499, 1455, 1366, 1346, 1248, 1162, 1097 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.36-7.26 (m, 5H, PhH), 5.63 (d, *J* = 7.0 Hz, 1H, NH), 5.17 (d, *J* = 12.0 Hz, 1H, OCH_aH_bPh), 5.14 (d, *J* = 12.0 Hz, 1H, OCH_aH_bPh), 4.46-4.41 (m, 1H, NCH), 3.56-3.51 (m, 1H, OCH), 3.35-3.27 (m, 2H, OCH_2CH_2), 2.08-2.00 (m, 2H, $NCHCH_2$), 1.48-1.21 (m, 19H, $(CH_2)_5$ and $C(CH_3)_3$), 1.07 (d, *J* = 8.0 Hz, 3H, $CHCH_3$), 0.89 (t, *J* = 6.8 Hz, 3H, $(CH_2)_5CH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.3, 155.5, 135.6, 129.1, 128.4, 128.2, 79.5, 75.9, 66.8, 64.6, 52.3, 36.5, 31.8, 31.7, 29.4, 28.3, 25.3, 22.6, 19.2, 14.0; HRMS (ES positive) calcd for $C_{24}H_{39}NO_5Na$ 444.2720, found 444.2722 $[MNa]^+$.



(2*R*,3*R*)-Methyl 2,3-diacetoxy-4-(*tert*-butylperoxy)-4-oxobutanoate (18). The typical procedure for the synthesis of peresters was followed using acid **15** (496 mg, 2.00 mmol), *tert*-butyl hydroperoxide (1 mL 5M, 5.00 mmol), and DCC (412 mg, 2.00 mmol) in CH_2Cl_2 at 0 ºC for 4 h. The resulting oil was purified by column chromatography (silica gel, 25% EtOAc/hexanes) to provide perester **18** (523 mg, 82%) as a colourless oil: $[\alpha]_D^{26}$ = +2.0° (*c* 7.7, $CHCl_3$); IR ($CHCl_3$ cast) 2984, 2959, 1798, 1759, 1438, 1371, 1277, 1211, 1120, 1070, 1025 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.69 (d, *J* = 2.8 Hz, 1H, $CHCO_3$), 5.58 (d, *J* = 2.8 Hz, 1H, $CHCO_2Me$), 3.73 (s, 3H, OCH_3), 2.12 (s, 6H, 2x $COCH_3$), 1.25 (s, 9H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.2, 169.1, 165.8, 163.4, 84.7, 70.4, 69.4, 52.9, 25.7, 20.1, 20.0; HRMS (ES positive) calcd for $C_{13}H_{20}O_9Na$ 343.0999, found 343.0998 $[MNa]^+$.

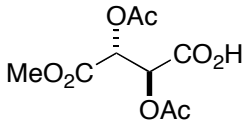


(2*R*,3*S*)-Methyl 2,3-dibenzoyloxy-4-(*tert*-butylperoxy)-4-oxobutanoate (19). The typical procedure for perester synthesis was followed using 1-methyl 2,3-dibenzoyl-L-tartrate (**16**) (1.116 g, 3.00 mmol), *tert*-butyl hydroperoxide (1 mL 5M, 5 mmol), and DCC (618 mg, 3.00 mmol) in MeCN at r.t. for 16 h. The resulting oil was purified by column chromatography (silica gel, 15% EtOAc/hexanes) to provide perester **19** (847 mg, 64%) as a colourless oil: $[\alpha]_D^{26}$ = -53.4° (*c* 2.4, $CHCl_3$); IR ($CHCl_3$ cast) 2982, 1798, 1770, 1732, 1601, 1584, 1452, 1391, 1368, 1244, 1093, 1070 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.13-8.09 (m, 4H, 2x *o*- and *o*'-ArH), 7.61-7.58 (m, 2H, 2x *p*-ArH), 7.49-7.44 (m, 4H, 2x *m*- and *m*'-ArH), 6.08 (d, *J* = 2.8 Hz, 1H, CHCO$_3$), 5.98 (d, *J* = 2.8 Hz, 1H, CHCO$_2$Me), 3.77 (s, 3H, OCH$_3$), 1.25 (s, 9H, C(CH$_3$)$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.9, 165.0, 164.9, 163.5, 133.9, 133.7, 130.0, 129.2, 128.5, 128.4, 128.3, 128.2, 84.8, 71.1, 70.2, 53.0, 25.8; HRMS (ES positive) calcd for $C_{23}H_{24}O_9Na$ 467.1312, found 467.1314 $[MNa]^+$.

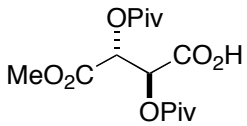


(2*R*,3*R*)-Methyl 2,3-bis(pivaloyloxy)-4-(*tert*-butylperoxy)-4-oxobutanoate (20). The typical procedure for perester synthesis was followed using acid **17** (625 mg, 1.87 mmol), *tert*-butyl hydroperoxide (0.5 mL 5M, 2.50 mmol), DMAP (12 mg, 0.10 mmol), and DCC (386 mg, 1.87 mmol) in 1:1 CH_2Cl_2/MeCN at r.t. for 3 h. The resulting oil was purified by column chromatography (silica gel, 10% EtOAc/hexanes) to provide perester **20** (455 mg, 60%) as a colourless oil: $[\alpha]_D^{26}$ = +3.7° (*c* 3.8, $CHCl_3$); IR ($CHCl_3$ cast) 2980, 2937, 2875, 1801, 1774, 1747, 1481, 1458, 1437, 1398, 1368, 1281 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.64 (d, *J* = 2.8 Hz, 1H,

C<u>H</u>CO_3), 5.52 (d, *J* = 2.8 Hz, 1H, C<u>H</u>CO_2Me), 3.67 (s, 3H, OC<u>H</u>$_3$), 1.23 (s, 9H, OC(C<u>H</u>$_3$)$_3$), 1.17 (s, 18H, 2x CC(C<u>H</u>$_3$)$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.7, 176.4, 166.0, 163.5, 84.5, 70.4, 69.5, 52.6, 38.7, 26.7(x2), 25.9; HRMS (ES positive) calcd for $C_{19}H_{32}O_9Na$ 427.1938, found 427.1938 $[MNa]^+$.

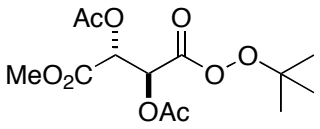


rac*-(2*S*,3*R*)-2,3-Diacetoxy-4-methoxy-4-oxobutanoic acid (24-*rac*).** *meso*-Tartaric acid hydrate (**21**) (5.600 g, 33.30 mmol) was added to a round bottom flask followed by acetic anhydride (15.000 g, 133.30 mmol). The suspension was stirred gently and one drop of sulfuric acid was added. After 4 h of stirring, the acetic acid was removed *in vacuo* and the resulting oil was added to MeOH (15 mL) (exothermic reaction). The solution was stirred for 6 h, then the resulting oil was purified by column chromatography (silica gel, CH_2Cl_2/EtOAc/AcOH = 100: 100: 2) to provide acid **24-*rac (2.121 g, 26%): IR ($CHCl_3$ cast) 3400-2400 (br), 2953, 2630, 1755, 1705, 1239, 1212 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.66 (s, 2H, 2xC<u>H</u>), 3.77 (s, 3H, OC<u>H</u>$_3$), 2.16 (s, 3H, COC<u>H</u>$_3$), 2.14 (s, 3H, COC<u>H</u>$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.9, 169.8, 169.7, 166.1, 70.7, 70.5, 52.9, 20.3, 20.2; HRMS (ES positive) calcd for $C_9H_{12}O_8Na$ 271.0430, found 271.0433 $[MNa]^+$.

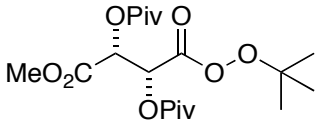


***rac*-(2*R*,3*S*)-4-Methoxy-4-oxo-2,3-bis(pivaloyloxy)butanoic acid (25-*rac*).** *meso*-Tartaric acid hydrate (**21**) (3.36 g, 20 mmol) was added to pivalic acid (5.000 g, 49.00 mmol) at 60 ºC and

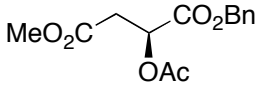
pivaloyl chloride (9.64 g, 80.00 mmol) was added to the suspension. The reaction mixture was maintained at 60 ºC, with the tartaric acid completely dissolving within approximately 20 min. After 3 h at 60 ºC, the reaction mixture was cooled to room temperature and MeOH (30 mL) was added slowly to the mixture. The mixture was stirred at r.t. for 3 h and the solvent was evaporated *in vacuo*. The resulting oil was purified by column chromatography (silica gel, 1% AcOH/$CHCl_3$) to provide acid **25-*rac*** (3.862 g, 58%) as a colourless oil: IR ($CHCl_3$ cast) 3500-2400 (br), 2976, 2938, 2910, 2876, 1747, 1279, 1146 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.62 (s, 2H, 2xOC<u>H</u>), 3.74 (s, 3H, OC<u>H</u>$_3$), 1.19 (s, 18H, 2xC(C<u>H</u>$_3$)$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.9, 176.8, 171.3, 166.2, 70.6, 70.4, 52.7, 38.7, 26.8, 26.7.



rac*-(2*R*,3*S*)-Methyl 2,3-diacetoxy-4-(*tert*-butylperoxy)-4-oxobutanoate (26-*rac*).** The typical procedure for perester synthesis was followed using tartrate **24-*rac (1.470 g, 5.00 mmol), *tert*-butyl hydroperoxide (1.5 mL 5M, 7.50 mmol), and DCC (1.221 g, 6.00 mmol) in CH_2Cl_2 at 0 ºC for 4 h. The resulting oil was purified by column chromatography (silica gel, 25% EtOAc/hexanes) to provide perester **26-*rac*** (618 mg, 53%) as a colourless oil: IR ($CHCl_3$ cast) 2984, 2959, 1758, 1438, 1372, 1216, 1116, 1078, 1044, 1012 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.70 (d, *J* = 2.4 Hz, 1H, C<u>H</u>CO$_3$), 5.57 (d, *J* = 2.4 Hz, 1H, C<u>H</u>CO$_2$Me), 3.79 (s, 3H, OC<u>H</u>$_3$), 2.15 (s, 6H, 2xCOC<u>H</u>$_3$), 1.30 (s, 9H, C(C<u>H</u>$_3$)$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.2, 169.1, 165.7, 163.3, 84.8, 70.6, 69.7, 52.9, 25.8, 20.3, 20.2; HRMS (ES positive) calcd for $C_{13}H_{20}O_9Na$ 343.0999, found 343.0995 $[MNa]^+$.

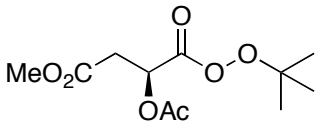


rac*-(2*R*,3*S*)-Methyl 4-(*tert*-butylperoxy)-4-oxo-2,3-bis(pivaloyloxy)butanoate (27-*rac*).** The typical procedure for perester synthesis was followed using acid **25-*rac (910 mg, 2.72 mmol), *tert*-butyl hydroperoxide (0.8 mL 5M, 4.00 mmol), DMAP (12 mg, 0.10 mmol), and DCC (561 mg, 2.72 mmol) in 1:1 CH_2Cl_2/MeCN at r.t. for 16 h. The resulting oil was purified by column chromatography (silica gel, 10% EtOAc/hexanes) to provide perester **27-*rac*** (960 mg, 87%) as a colourless oil: IR ($CHCl_3$ cast) 2980, 2937, 2875, 1800, 1774, 1747, 1481, 1460, 1438, 1398 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.67 (d, *J* = 2.8 Hz, 1H, C<u>H</u>CO_3), 5.57 (d, *J* = 2.8 Hz, 1H, C<u>H</u>CO_2Me), 3.76 (s, 3H, OCH_3), 1.27 (s, 9H, OC(C<u>H</u>$_3$)$_3$), 1.20 (s, 18H, 2x CC(C<u>H</u>$_3$)$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.7, 176.4, 165.9, 163.6, 84.6, 70.5, 69.8, 52.7, 38.7, 26.8, 25.9; HRMS (ES positive) calcd for $C_{19}H_{32}O_9Na$ 427.1938, found 427.1938 $[MNa]^+$.

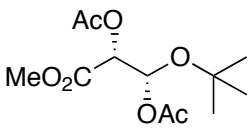


(2*S*)-1-Benzyl 4-methyl 2-acetoxybutanedioate (29). α-Acetyl L-malic acid benzyl ester (**28**) (5.320 g, 20.00 mmol) was dissolved in CH_2Cl_2/MeOH (2:1, 15 mL). DMAP (12 mg, 0.10 mmol) and DCC (4.120 g, 20.00 mmol) were then added with stirring. The stirring was continued for 16 h and the solvent was removed *in vacuo*. EtOAc was added to the white residue (20 mL, in which DCU is only slightly soluble), and the mixture was cooled to 0 °C for 1h, filtered and the solvent removed *in vacuo*. The resulting oil was purified by column chromatography (silica gel, 25% EtOAc/hexanes) to provide ester **29** (5.09 g, 91%) as a

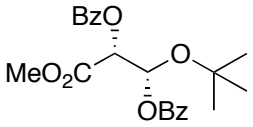
colourless oil: $[\alpha]_D^{26}$= +10.9° (*c* 0.5, $CHCl_3$); IR ($CHCl_3$ cast) 3034, 2955, 1747, 1499, 1456, 1373, 1213 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.33-7.26 (m, 5H, $C_6\underline{H}_5$), 5.49 (t, *J* = 6.4 Hz, 1H, C<u>H</u>), 5.17 (d, *J* = 12.4 Hz, 1H, OC<u>H</u>$_a$H$_b$Ph), 5.13 (d, *J* = 12.4 Hz, 1H, OCH$_a$<u>H</u>$_b$Ph), 3.62 (s, 3H, OC<u>H</u>$_3$), 2.85 (d, *J* = 6.4 Hz, 2H, CHC<u>H</u>$_2$), 2.07 (s, 3H, COC<u>H</u>$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.5, 169.2, 168.4, 134.8, 128.3, 128.8, 127.9, 68.0, 67.1, 51.7, 35.5, 20.2; HRMS (ES positive) calcd for $C_{14}H_{16}O_6Na$ 303.0845, found 303.0840 $[MNa]^+$.



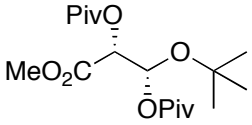
(3*S*)-Methyl 3-acetoxy-4-(*tert*-butylperoxy)-4-oxobutanoate (31). The typical procedure for the synthesis of peresters was followed using α-acetyl L-malic acid methyl ester (**30**) (500 mg, 2.60 mmol), *tert*-butyl hydroperoxide (1 ml 5M, 5.00 mmol), DCC (542 mg, 2.6 mmol), and DMAP (12 mg, 0.1 mmol) in CH_2Cl_2 at r.t. for 12 h. The resulting oil was purified by column chromatography (silica gel, 15% EtOAc/hexanes) to provide perester **31** (485 mg, 70%) as a colourless oil: $[\alpha]_D^{26}$= -19.3° (*c* 6, $CHCl_3$); IR ($CHCl_3$ cast) 2984, 1790, 1752, 1439, 1370, 1228, 1059 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.38 (t, *J* = 6.4 Hz, 1 H, C<u>H</u>), 3.60 (s, 3H, OC<u>H</u>$_3$), 2.78 (d, *J* = 6.4 Hz, 2H, C<u>H</u>$_2$), 2.00 (s, 3H, C<u>H</u>$_3$CO), 1.20 (s, 9H, C(C<u>H</u>$_3$)$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.2, 168.7, 166.3, 84.3, 66.7, 51.8, 35.6, 25.6, 19.9; HRMS (ES positive) calcd for $C_{11}H_{18}O_7Na$ 285.0945, found 285.0945 $[MNa]^+$.



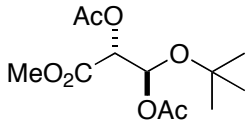
(2*R*,3*R*)-Methyl 2,3-diacetoxy-3-*tert*-butoxypropanoate (32). The typical procedure for perester photolysis was followed using perester **18** (523 mg, 1.60 mmol) for 16 h cooled to -196 ºC with liquid nitrogen. The resulting oil was purified by column chromatography (silica gel, 25% EtOAc/hexanes) to provide acetal **32** (422 mg, 94%[a]) as a colourless oil: $[\alpha]_D^{26}$= -12.4° (*c* 3.8, $CHCl_3$); IR ($CHCl_3$ cast) 2981, 1753, 1438, 1396, 1372, 1282, 1222, 1127, 1078, 1011 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.15 (d, *J* = 4.8 Hz, 1H, C<u>H</u>O*t*-Bu), 4.80 (d, *J* = 4.8 Hz, 1H, C<u>H</u>CO_2Me), 3.57 (s, 3H, OC<u>H</u>$_3$), 1.96 (s, 3H, 3-OCOC<u>H</u>$_3$), 1.89 (s, 3H, 2-OCOC<u>H</u>$_3$), 1.05 (s, 9H, C(C<u>H</u>$_3$)$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.2, 169.1, 166.6, 89.3, 76.7, 73.4, 51.9, 27.5, 20.7, 19.9; HRMS (ES positive) calcd for $C_{12}H_{20}O_7Na$ 299.1101, found 299.1102 $[MNa]^+$.



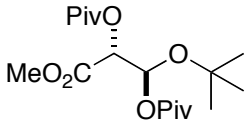
(2*R*,3*S*)-Methyl 2,3-bis(benzoyloxy)-3-*tert*-butoxypropanoate (34). The typical photolysis procedure for peresters was followed using perester **19** (92 mg, 0.2 mmol). The resulting oil was purified by column chromatography (silica gel, 15% EtOAc/hexanes) to provide acetal **34** (54.6 mg, 66%[a]) as a colourless oil: $[\alpha]_D^{26}$= -26.0º (*c* 0.8, $CHCl_3$); IR ($CHCl_3$ cast) 3071, 2981, 2673, 2558, 1768, 1730, 1687, 1601, 1584, 1452, 1423, 1324 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.15-8.09 (m, 4H, 2x *o*- and *o*'-PhH), 7.61-7.57 (m, 2H, 2x *p*-PhH), 7.50-7.44 (m, 4H, 2x *m*- and *m*'-PhH), 6.79 (d, *J* = 5.6 Hz, 1H, OC<u>H</u>O), 5.34 (d, *J* = 5.6 Hz, 1H, C<u>H</u>CO_2CH_3), 3.78 (s, 3H, OC<u>H</u>$_3$), 1.28 (s, 9H, C(C<u>H</u>$_3$)$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.9, 165.0, 164.9, 133.9, 133.7, 130.0, 129.2, 128.5, 128.4, 128.3, 128.2, 90.7, 77.5, 74.3, 52.3, 28.0.



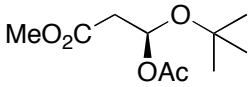
(2*R*,3*R*)-Methyl 3-*tert*-butoxy-2,3-bis(pivaloyloxy)propanoate (36). The typical procedure for perester photolysis was followed using perester **20** (100 mg, 0.25 mmol). The resulting oil was purified by column chromatography (silica gel, 10% EtOAc/hexanes) to provide acetal **36** (76 mg, 85%[a]) as a colourless oil: $[\alpha]_D^{26}$ = -11.2° (*c* 3.3, $CHCl_3$); IR ($CHCl_3$ cast) 2978, 2936, 2874, 1742, 1481, 1461, 1438, 1397 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.28 (d, *J* = 5.2 Hz, 1H, OC<u>H</u>O), 4.85 (d, *J* = 5.2 Hz, 1H, C<u>H</u>CO_2Me), 3.69 (s, 3H, OC<u>H</u>$_3$), 1.18 (s, 27H, OC$(CH_3)_3$ and 2x CC(C<u>H</u>$_3$)$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.2, 176.7, 167.2, 89.9, 76.8, 73.7, 52.0, 38.6, 28.0, 26.8, 26.7; HRMS (ES positive) Calcd for $C_{18}H_{32}O_7Na$ 383.2040, found 383.2040 $[MNa]^+$.



rac*-(2*R*,3*R*)-Methyl 2,3-diacetoxy-3-*tert*-butoxypropanoate (39-*rac*).** The typical perester photolysis procedure was followed using perester **26-*rac (151 mg, 0.55 mmol) for 16 h at -196 °C. The resulting oil was purified by column chromatography (silica gel, 15% EtOAc/hexanes) to provide acetal **39-*rac*** (118 mg, 91%[a]) as a colourless oil: IR ($CHCl_3$ cast) 2926, 2854, 1747, 1439, 1347, 1219, 1116, 1045 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.36 (d, *J* = 4.0 Hz, 1H, C<u>H</u>CO_3), 5.25 (d, *J* = 4.0 Hz, 1H, C<u>H</u>CO_2Me), 3.69 (s, 3H, OC<u>H</u>$_3$), 2.18 (s, 3H, COC<u>H</u>$_3$), 1.98 (s, 3H, COC<u>H</u>$_3$), 1.21 (s, 9H, C(C<u>H</u>$_3$)$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.8, 169.5, 166.4, 89.9, 77.2, 72.5, 52.2, 27.7, 21.0, 20.3; HRMS (ES positive) Calcd for $C_{12}H_{20}O_7Na$ 299.1101, found 299.1103 $[MNa]^+$.

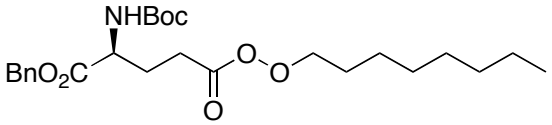


rac*-(2*R*,3*S*)-Methyl 3-*tert*-butoxy-2,3-bis(pivaloyloxy)propanoate (41-*rac*).** The typical procedure for perester photolysis was followed using perester **27-*rac (95 mg, 0.23 mmol). The resulting oil was purified by column chromatography (silica gel, 10% EtOAc/hexanes) to provide acetal **41-*rac*** (71 mg, 84%[a]) as a colourless oil: IR ($CHCl_3$ cast) 2975, 2874, 1744, 1481, 1458, 1437, 1398, 1368, 1278, 1140 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.32 (d, *J* = 4.8 Hz, 1H, OC<u>H</u>O), 5.05 (d, *J* = 4.8 Hz, 1H, C<u>H</u>CO_2Me), 3.68 (s, 3H, OC<u>H</u>$_3$), 1.21 (s, 9H, OC(C<u>H</u>$_3$)$_3$), 1.18 (s, 9H, OCHOCOC(C<u>H</u>$_3$)$_3$), 1.15 (s, 9H, COCHOCOC(C<u>H</u>$_3$)$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.3, 176.9, 166.9, 90.0, 72.7, 52.2, 38.6, 28.1, 26.9, 26.8; HRMS (ES positive) Calcd for $C_{18}H_{32}O_7Na$, found $[MNa]^+$.



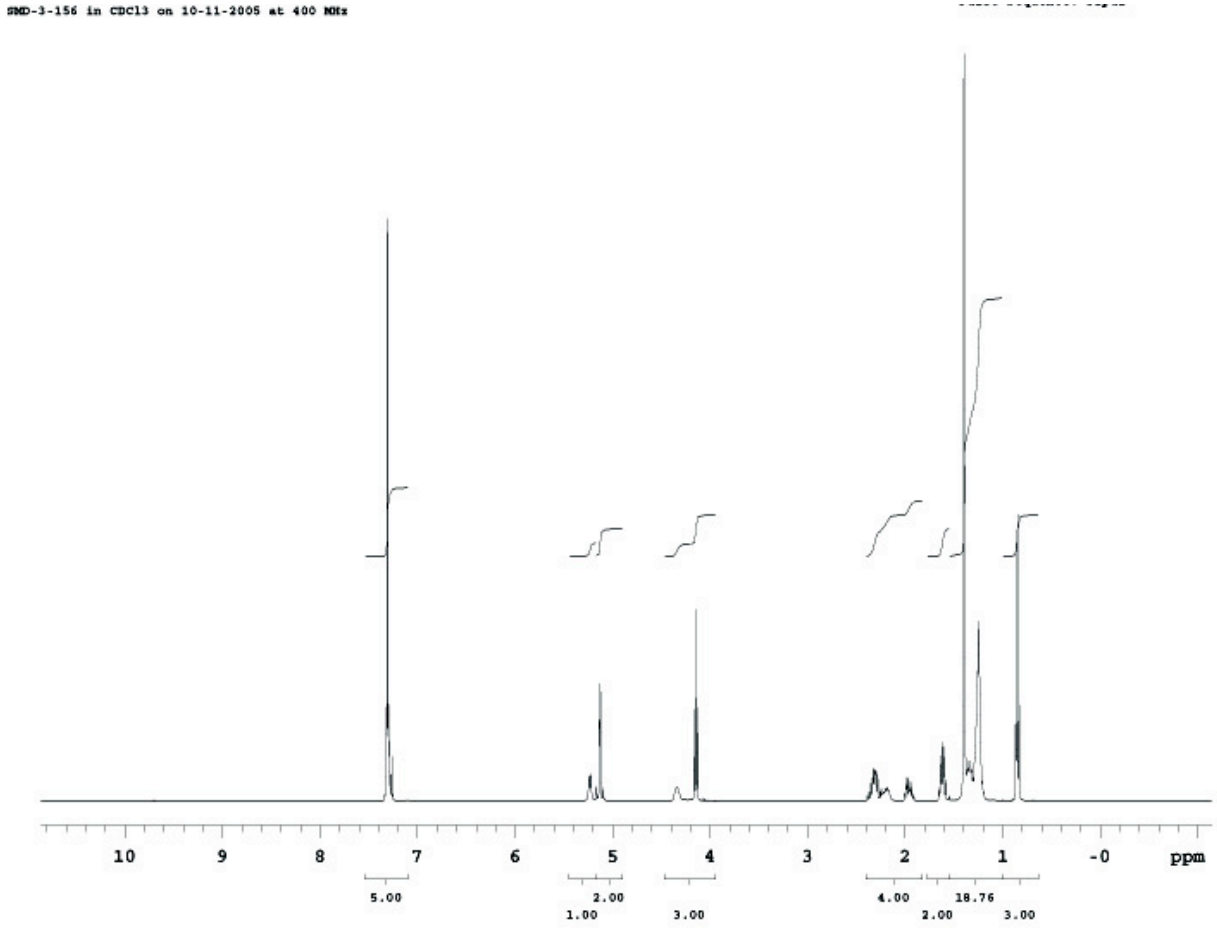
(3*S*)-Methyl 3-acetoxy-3-*tert*-butoxypropanoate (42). The typical procedure for photolysis of peresters was followed using perester **31** (138 mg, 0.52 mmol). The resulting oil was purified by column chromatography (silica gel, 15% EtOAc/hexanes) to provide **42** (76 mg, 66%[a]) as a colourless oil: $[\alpha]_D^{26}$ = +13.9° (*c* 0.4, $CHCl_3$); IR ($CHCl_3$ cast) 2978, 2932, 1745, 1654, 1520, 1438, 1396, 1368, 1311, 1241, 1196 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.35 (dd, *J* = 4.4 Hz, 7.2 Hz, 1H, C<u>H</u>), 3.68 (s, 3H, OC<u>H</u>$_3$), 2.73 (dd, *J* = 4.4 Hz, 16 Hz, 1H, C<u>H</u>$_a$<u>H</u>$_b$), 2.66 (dd, *J* = 7.2 Hz, 16 Hz, 1H, CH$_a$<u>H</u>$_b$), 2.02 (s, 3H, C<u>H</u>$_3$CO), 1.23 (s, 9H, C(C<u>H</u>$_3$)$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.0, 169.2, 90.8, 76.4, 51.6, 41.2, 28.1, 21.5; HRMS (ES positive) Calcd for $C_{10}H_{18}O_5Na$ 241.1046, found 241.1047 $[MNa]^+$.

[a]Quoted yield corresponds to that of diastereomeric mixture.

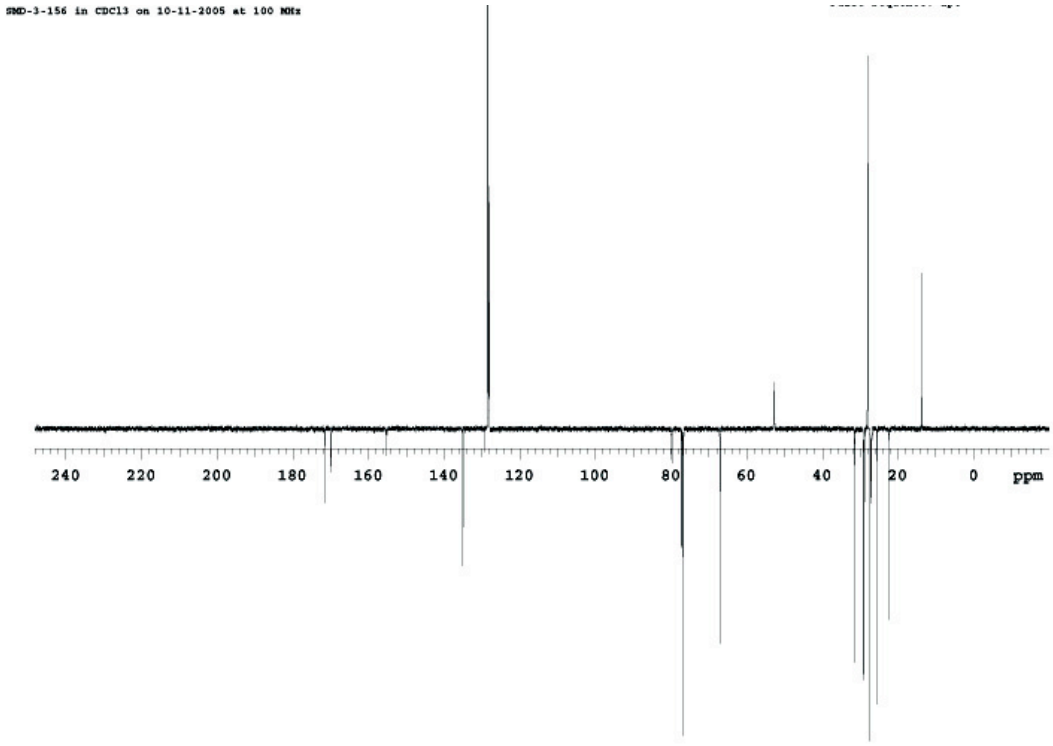


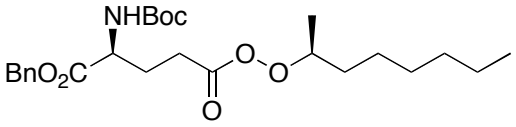
4

^{1}H NMR (400 MHz; $CDCl_3$)



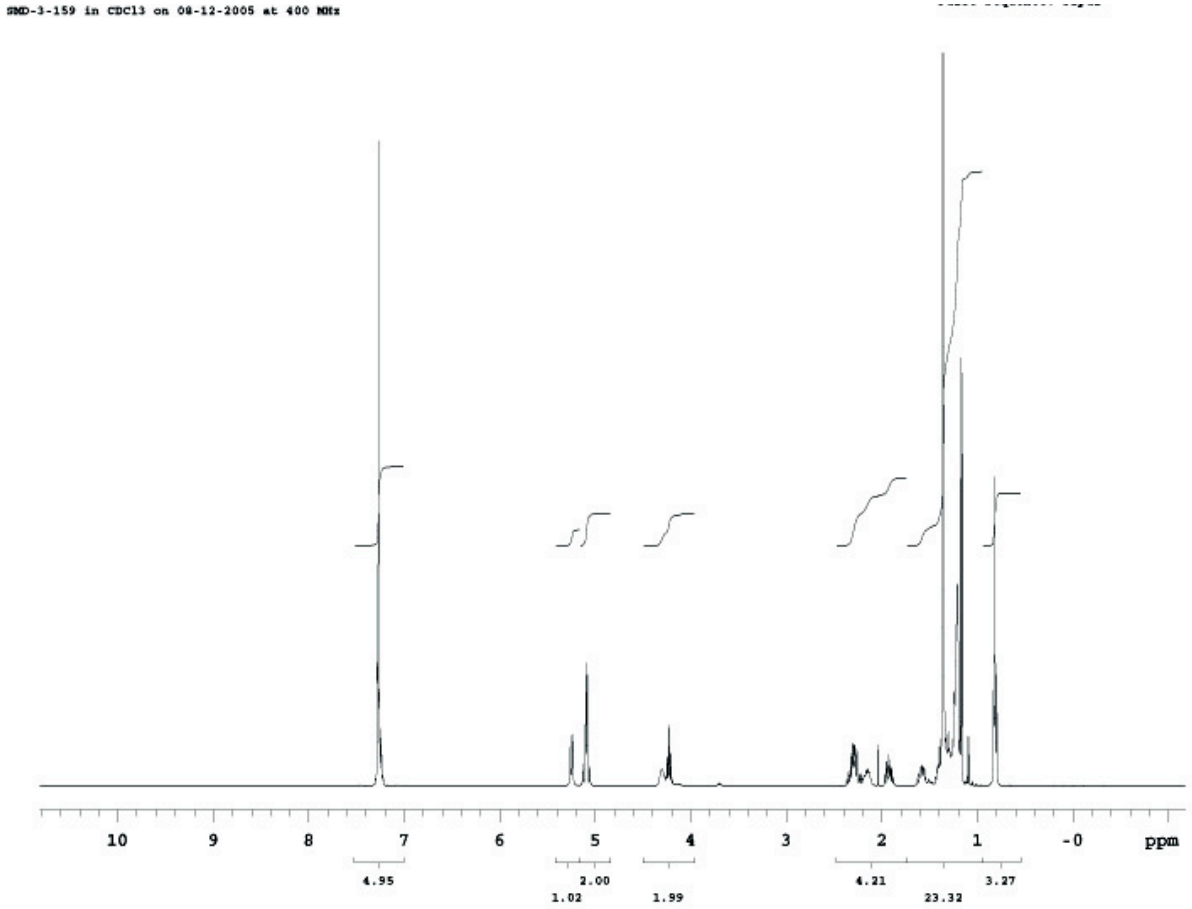
^{13}C NMR (100 MHz; $CDCl_3$)



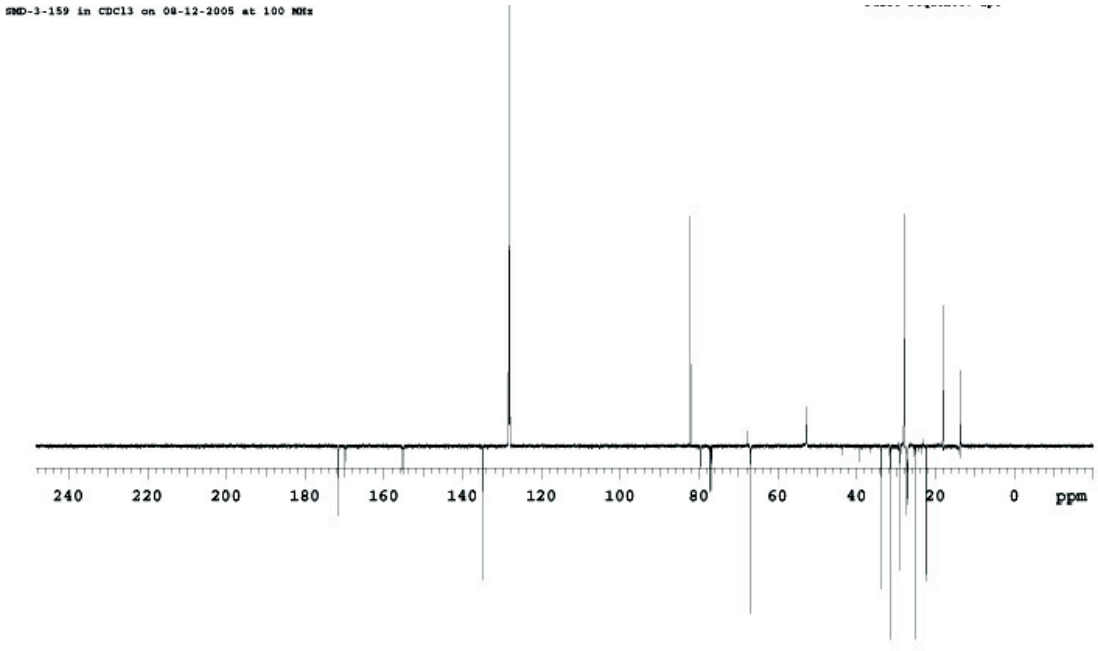


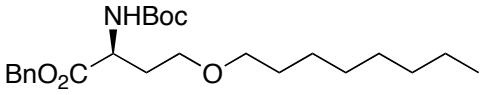
5

^{1}H NMR (400 MHz; $CDCl_3$)



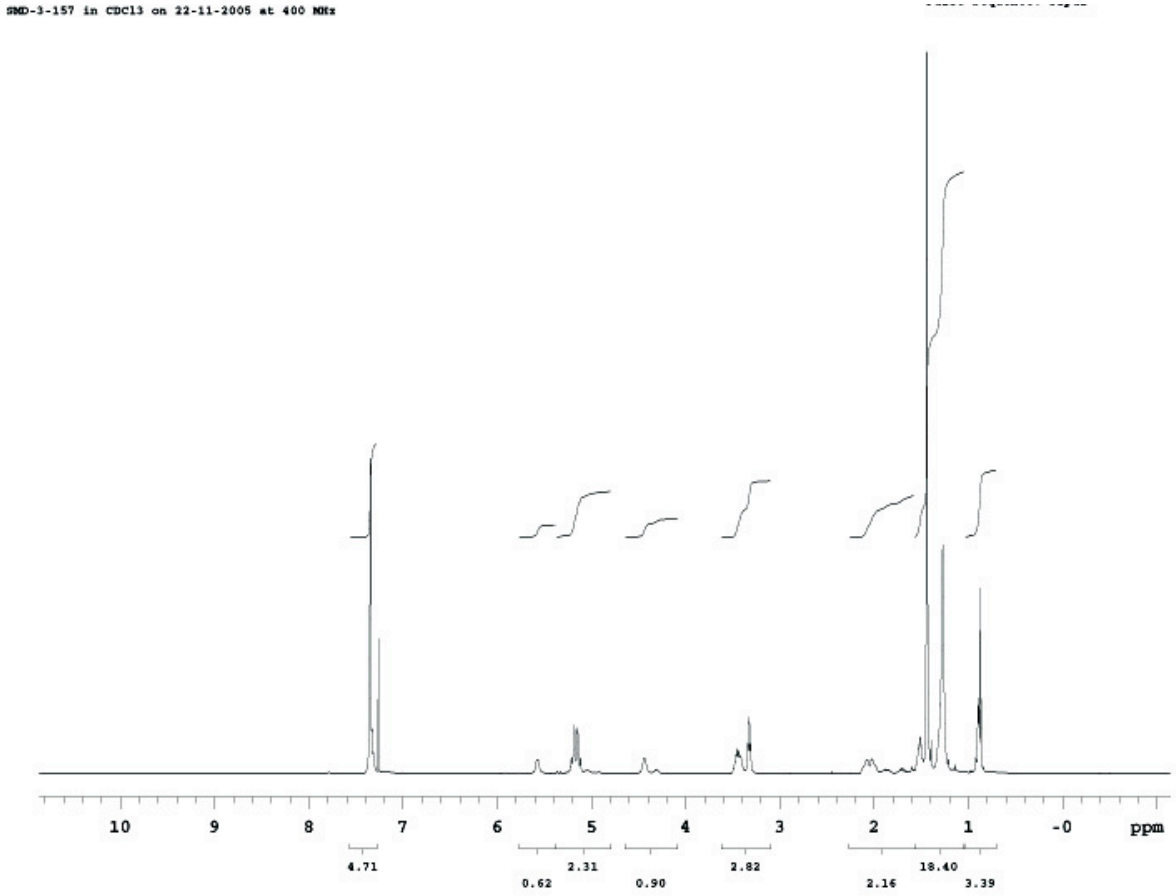
^{13}C NMR (100 MHz; $CDCl_3$)



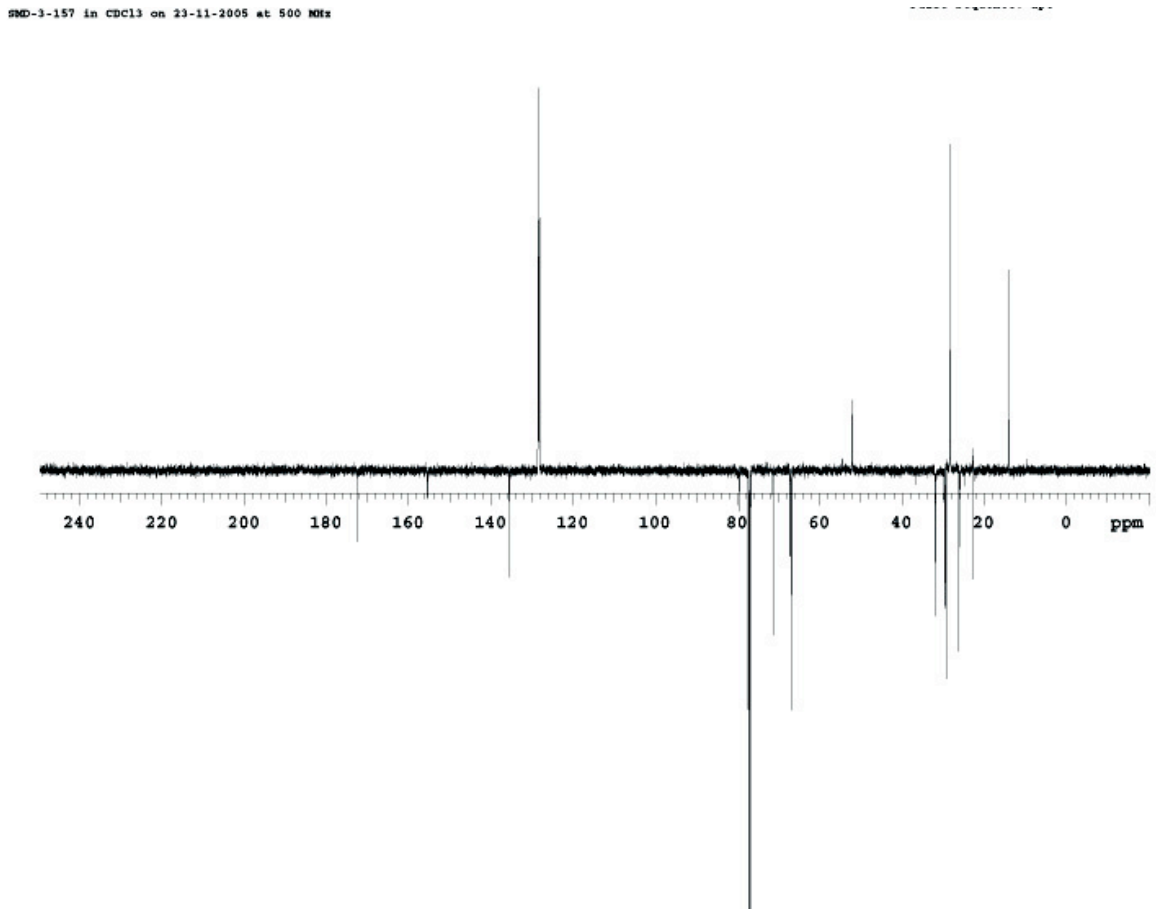


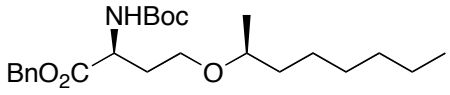
7

^{1}H NMR (400 MHz; $CDCl_3$)



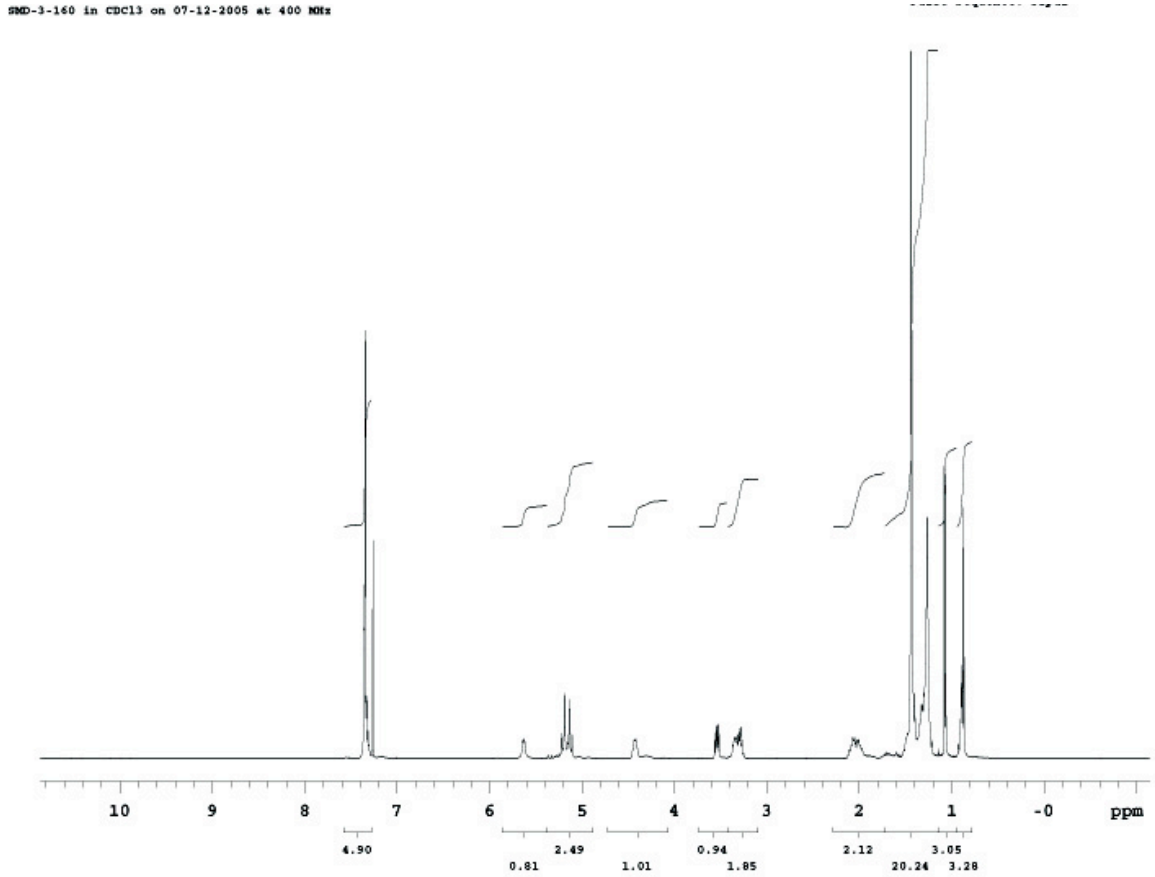
^{13}C NMR (125 MHz; $CDCl_3$)



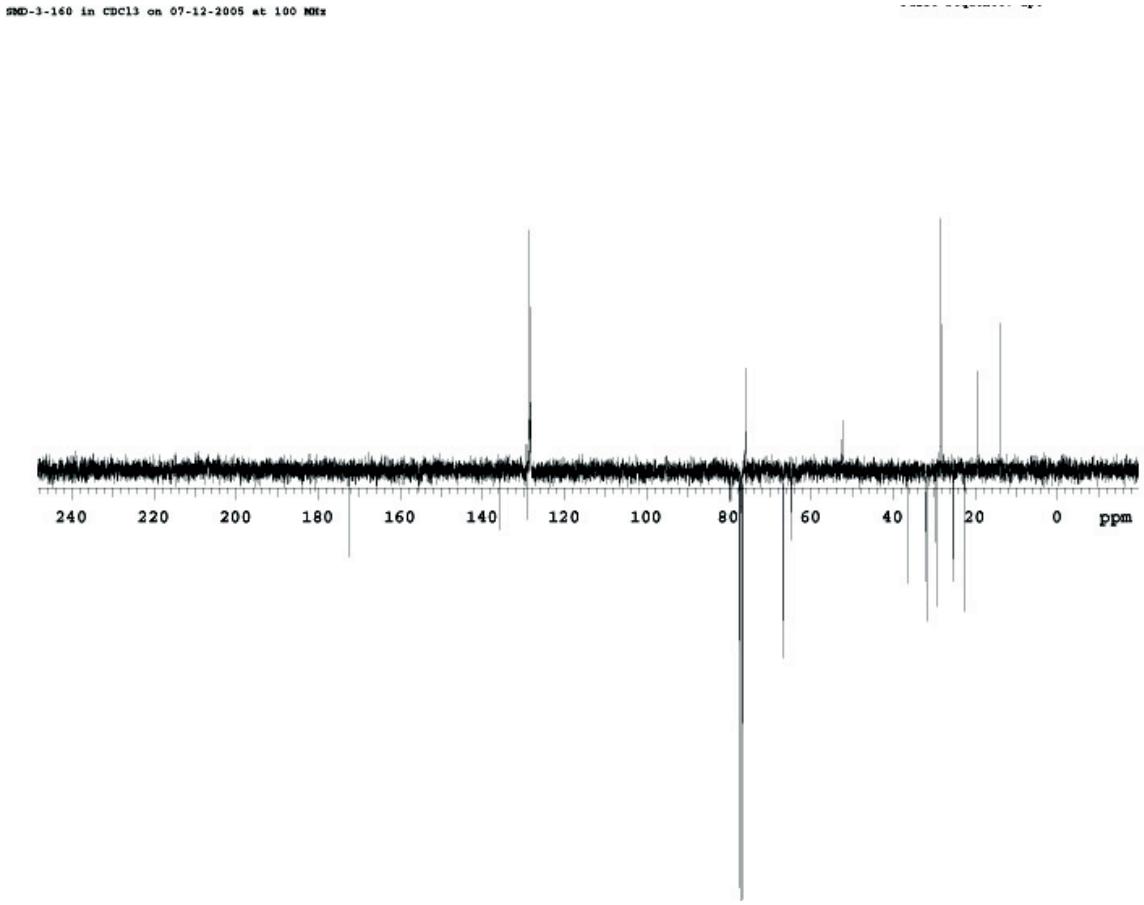


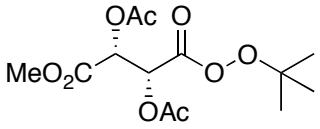
8

^{1}H NMR (400 MHz; $CDCl_3$)



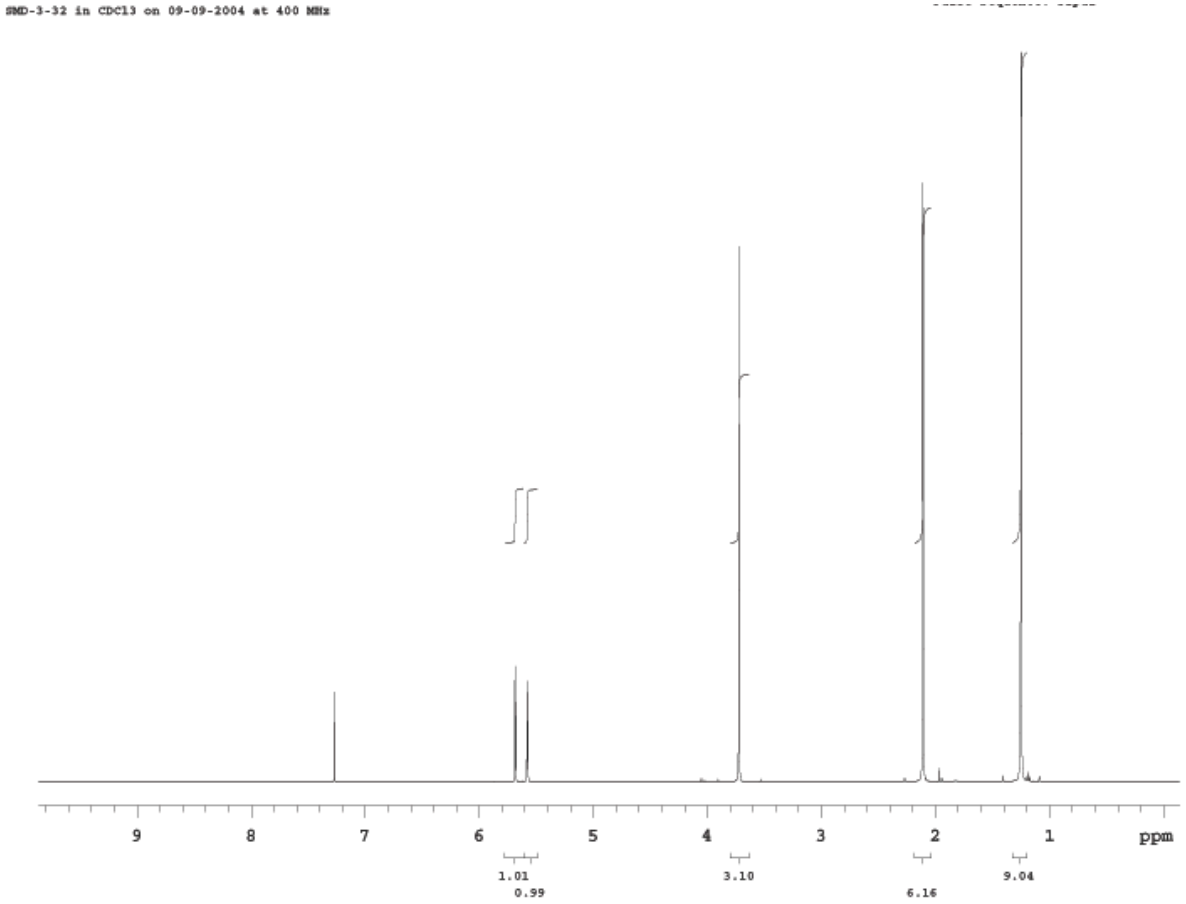
^{13}C NMR (100 MHz; $CDCl_3$)



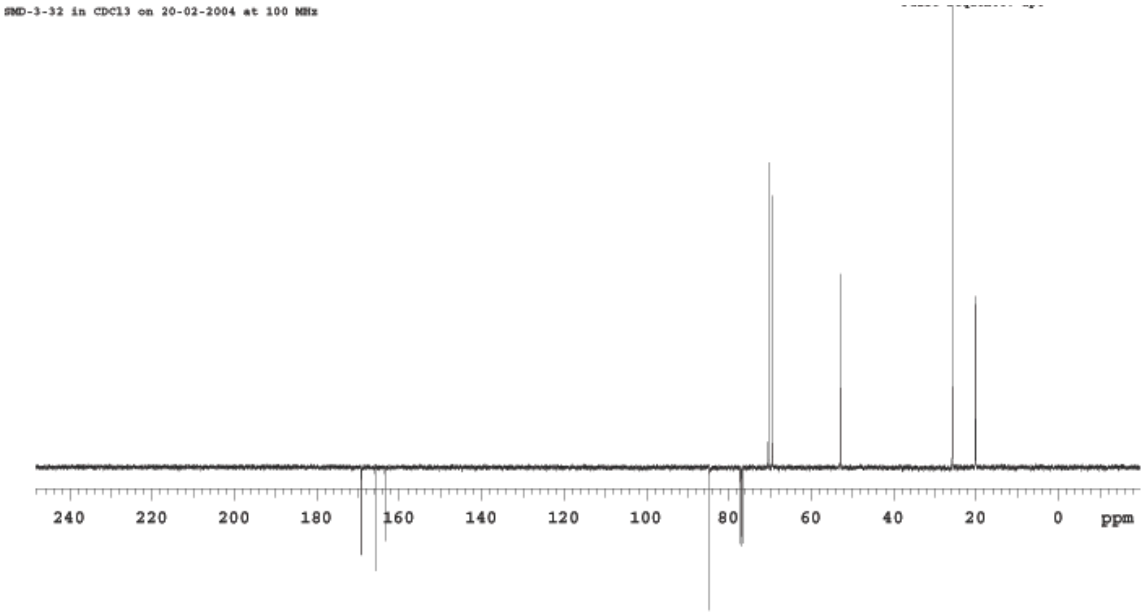


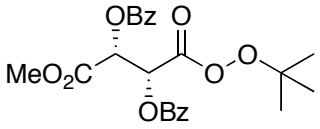
17

^{1}H NMR (400 MHz; $CDCl_3$)



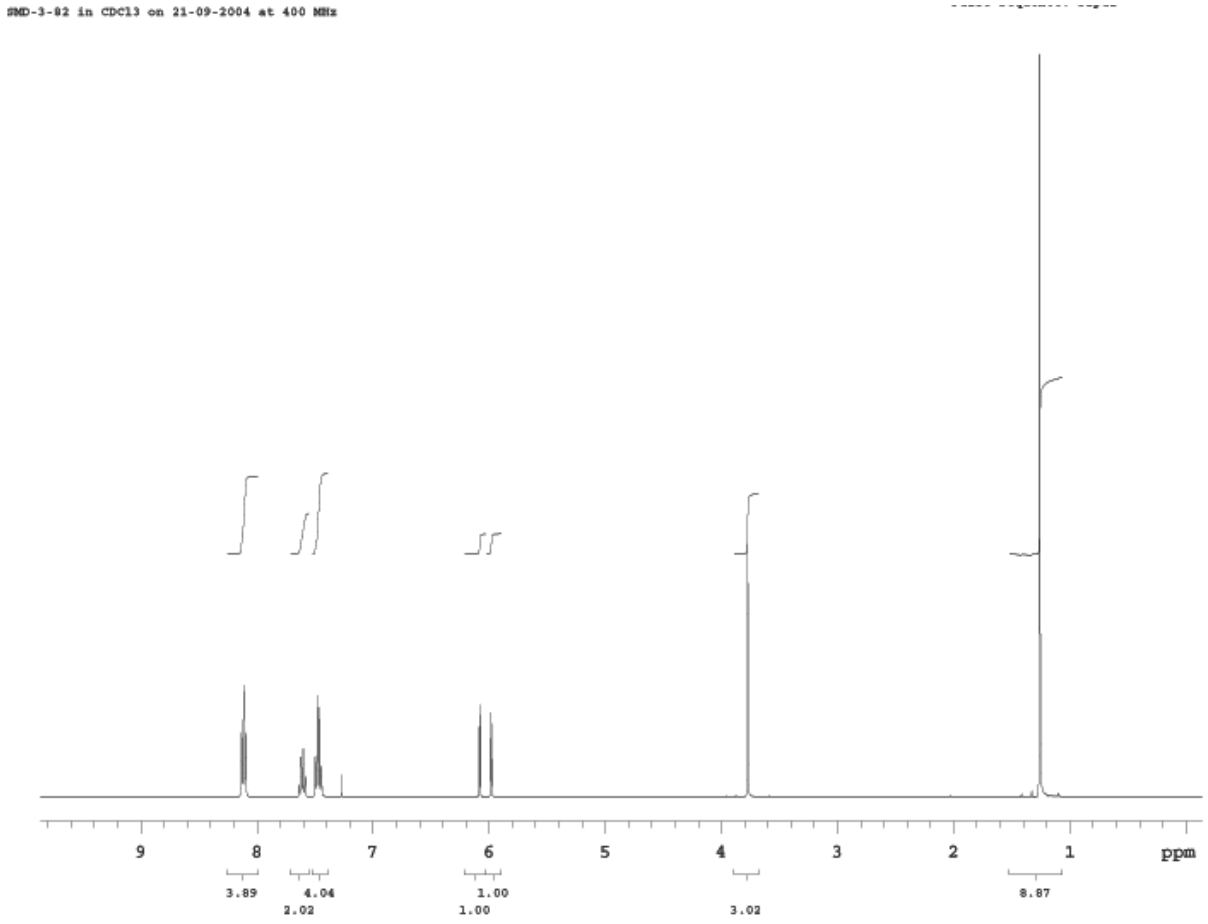
^{13}C NMR (100 MHz; $CDCl_3$)



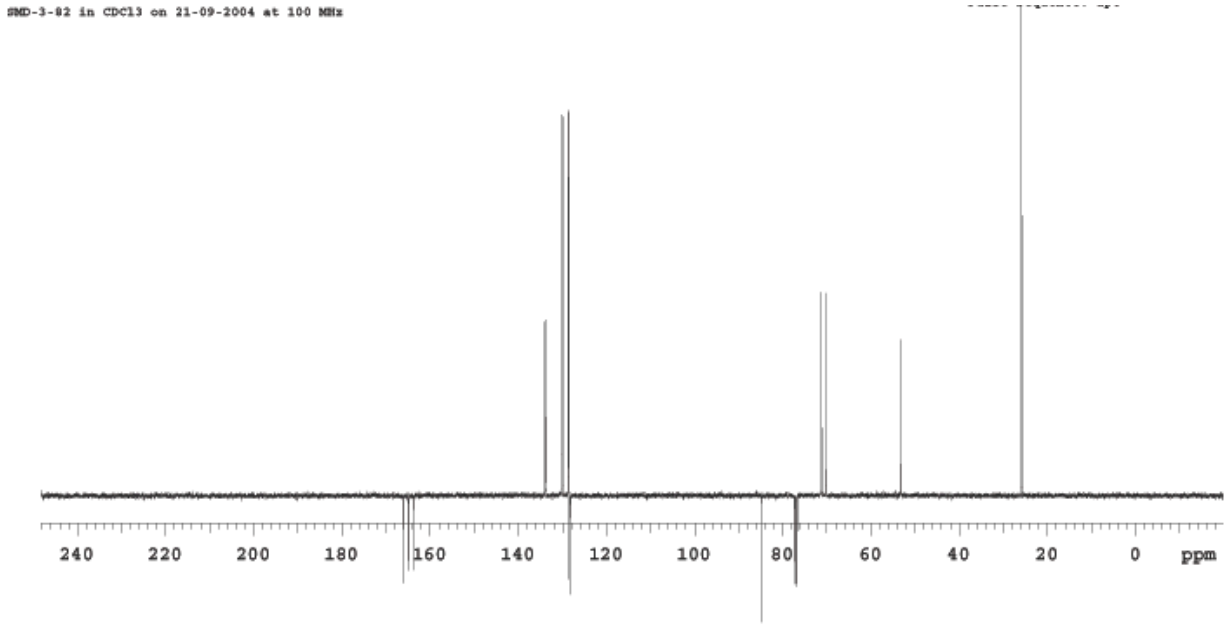


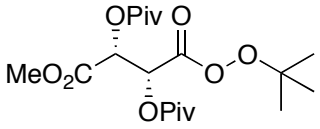
18

^{1}H NMR (400 MHz; $CDCl_3$)



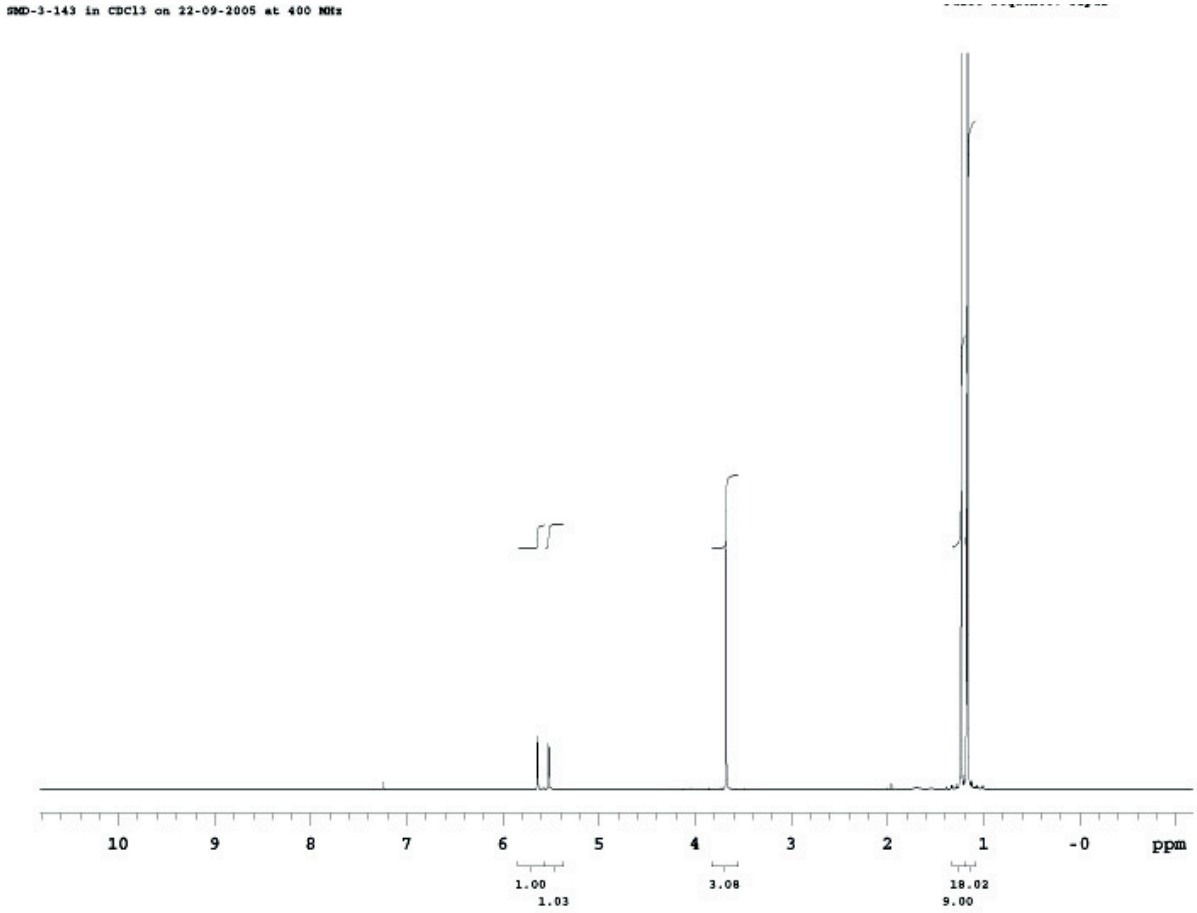
^{13}C NMR (100 MHz; $CDCl_3$)



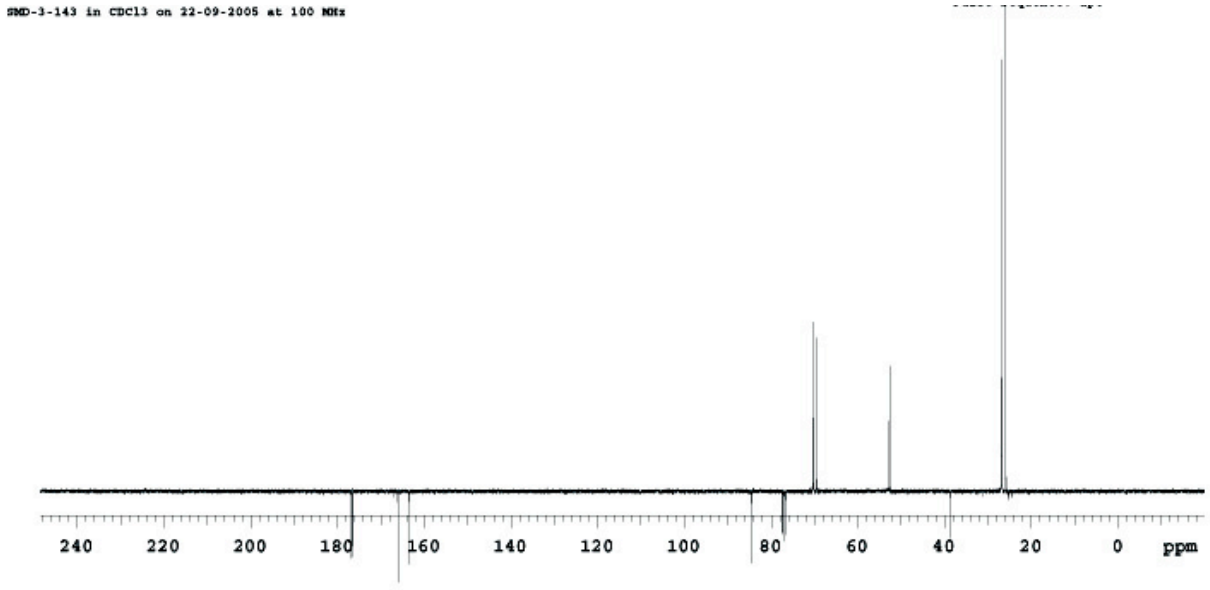


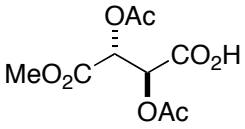
19

^{1}H NMR (400 MHz; $CDCl_3$)

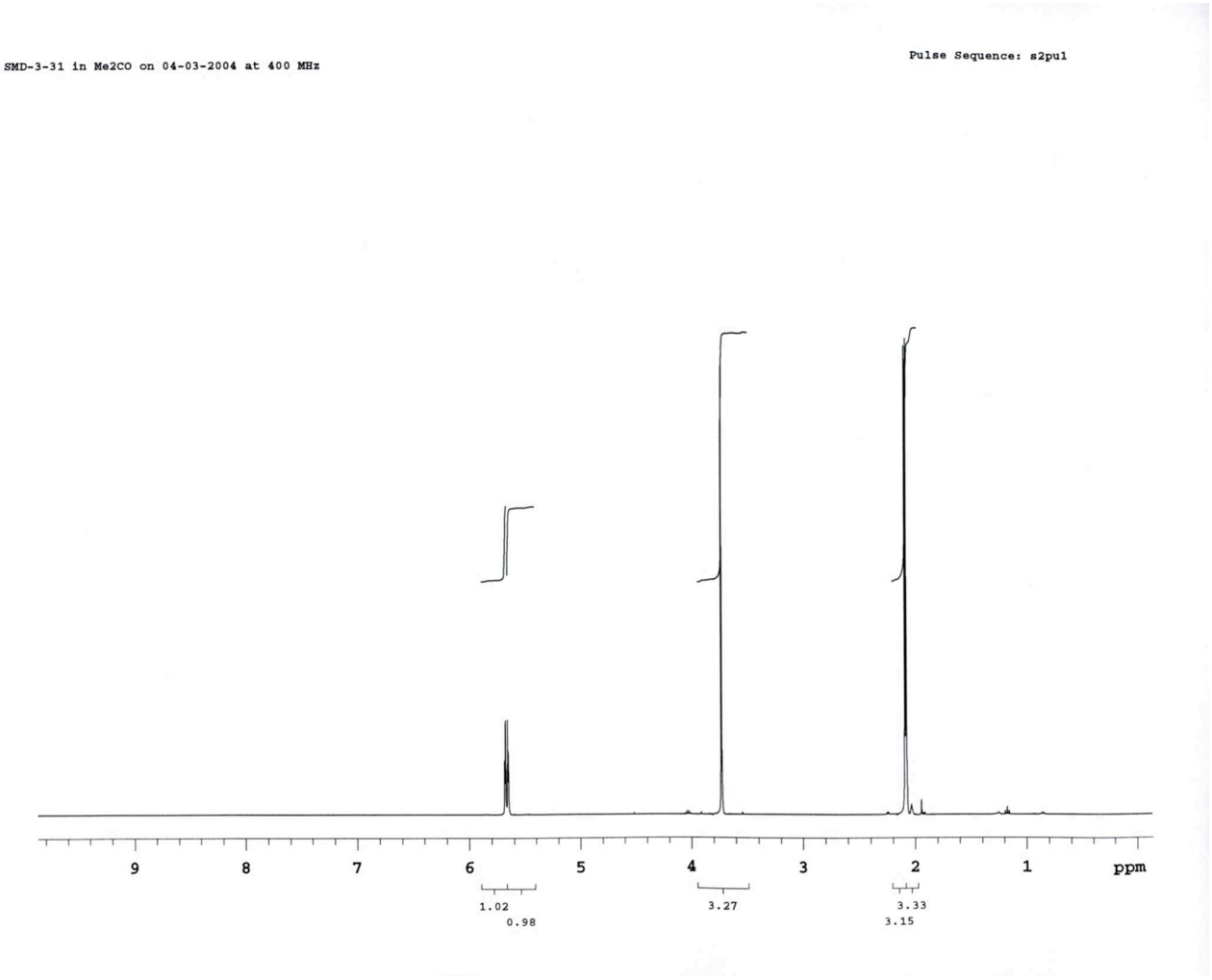


^{13}C NMR (100 MHz; $CDCl_3$)

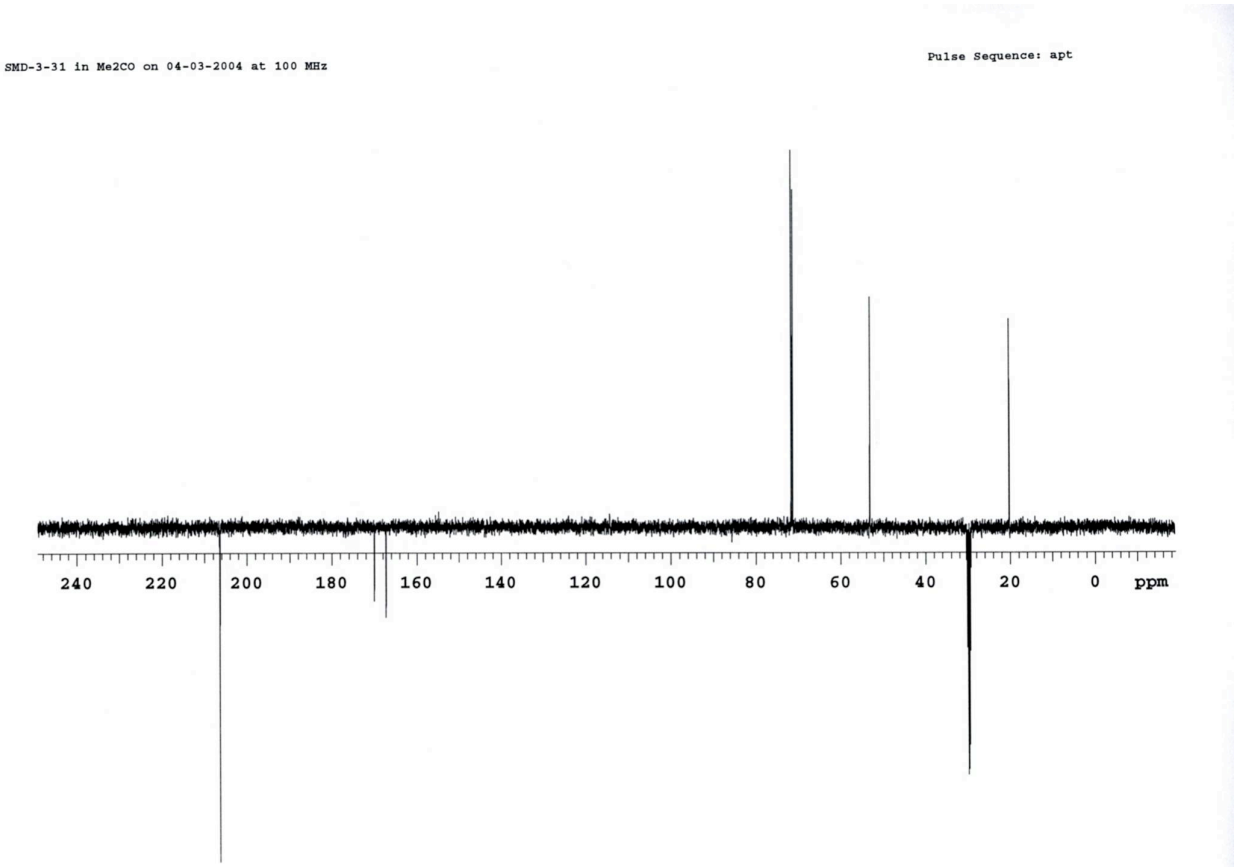




23-*rac*

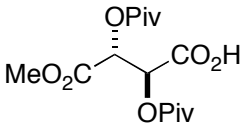


^{1}H NMR (400 MHz; acetone-d_6)

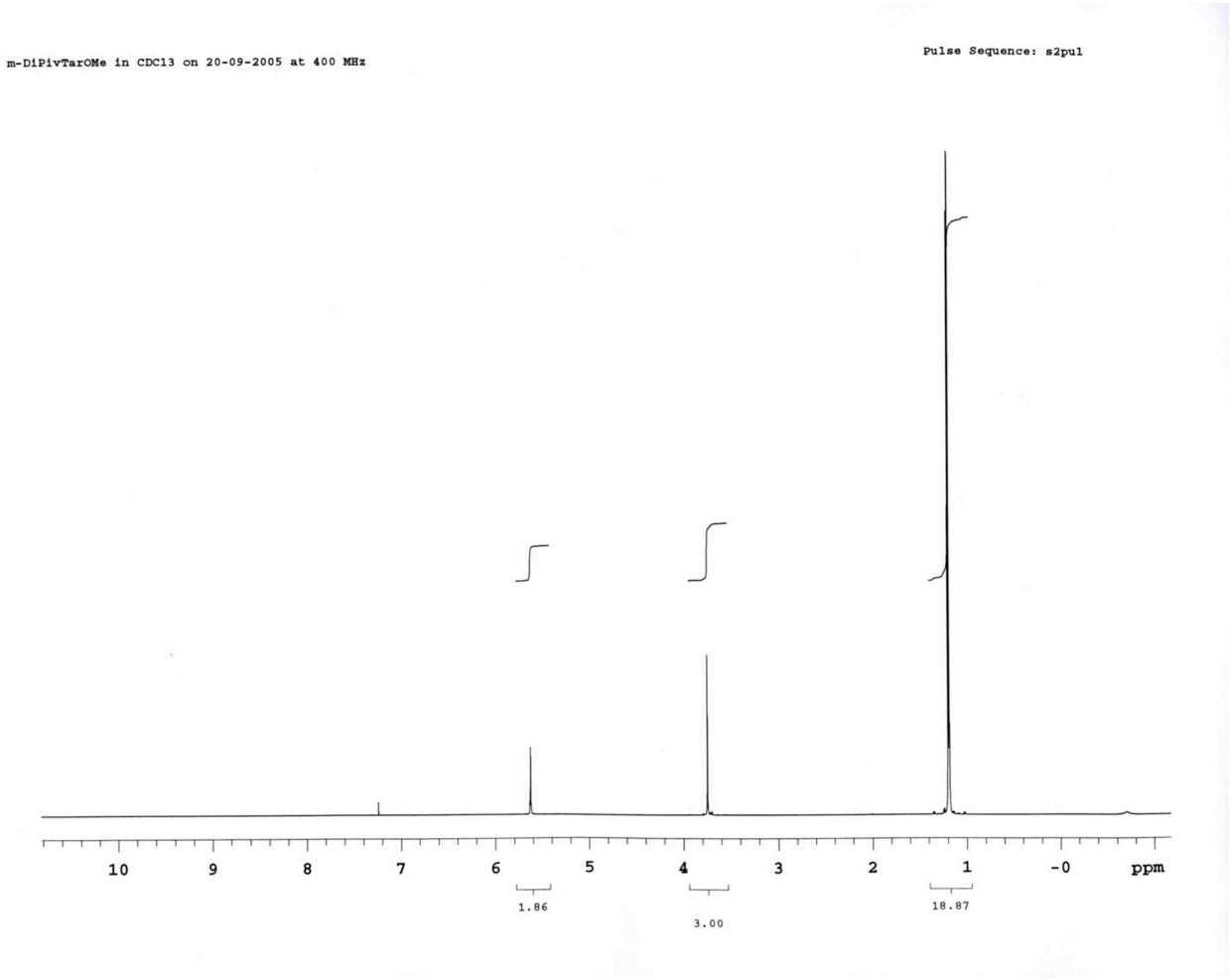


1

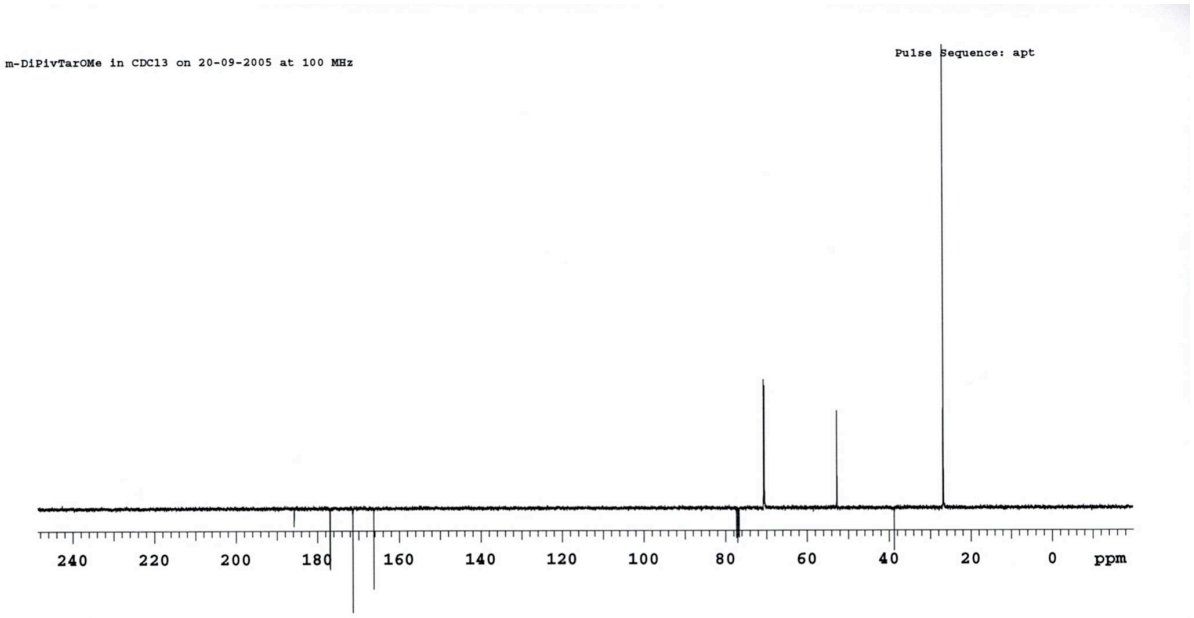
^{3}C NMR (100 MHz; acetone-d_6)



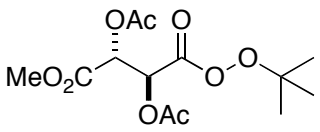
24-*rac*



^{1}H NMR (400 MHz; $CDCl_3$)

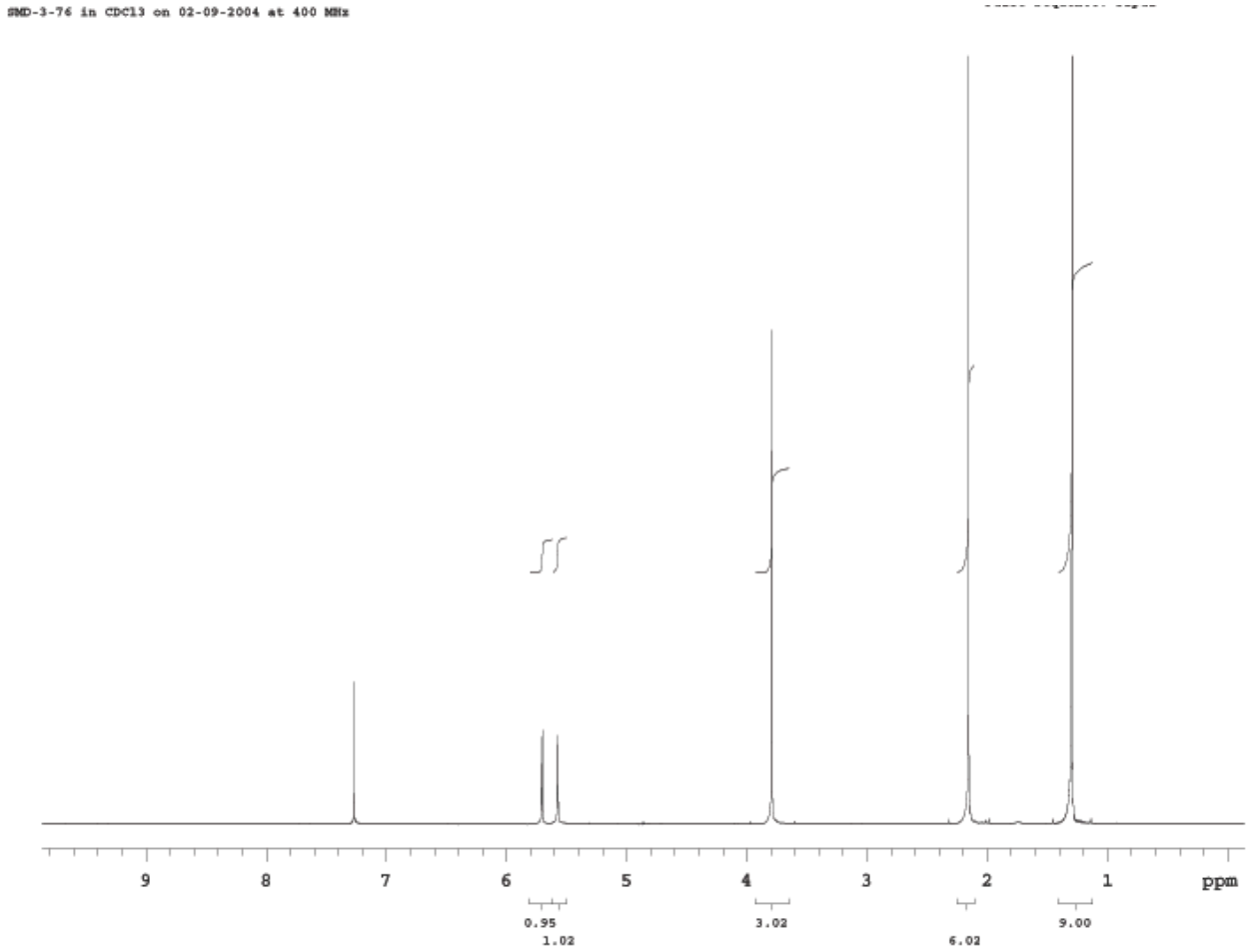


^{13}C NMR (100 MHz; $CDCl_3$)

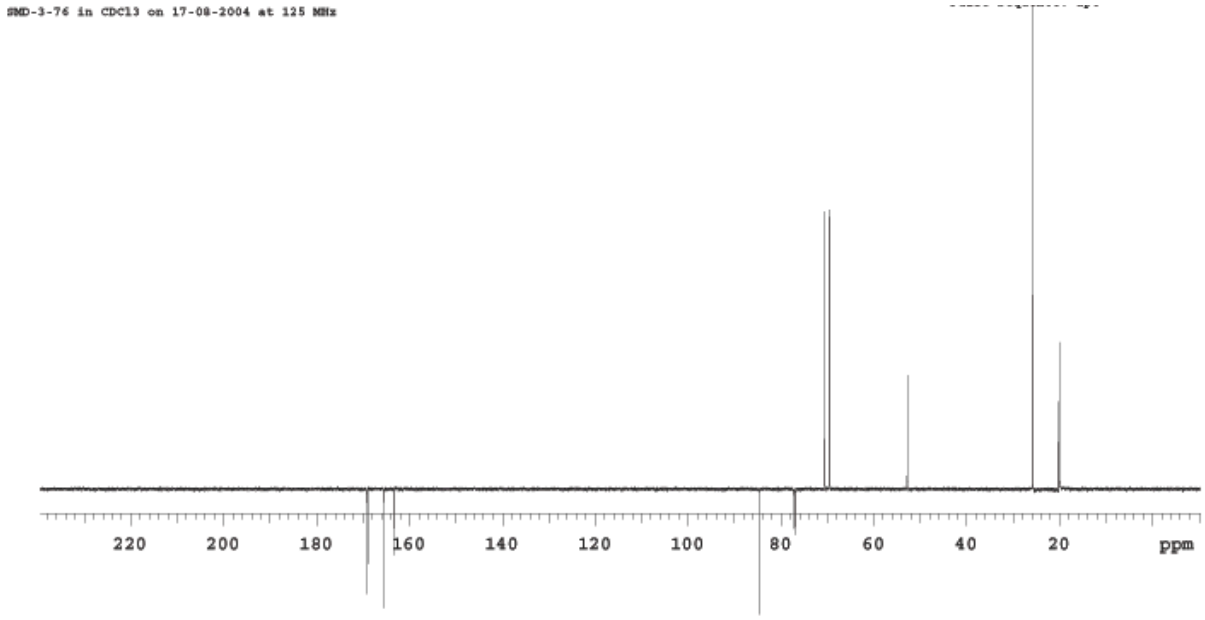


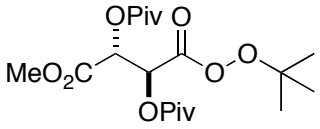
25-*rac*

^{1}H NMR (400 MHz; $CDCl_3$)



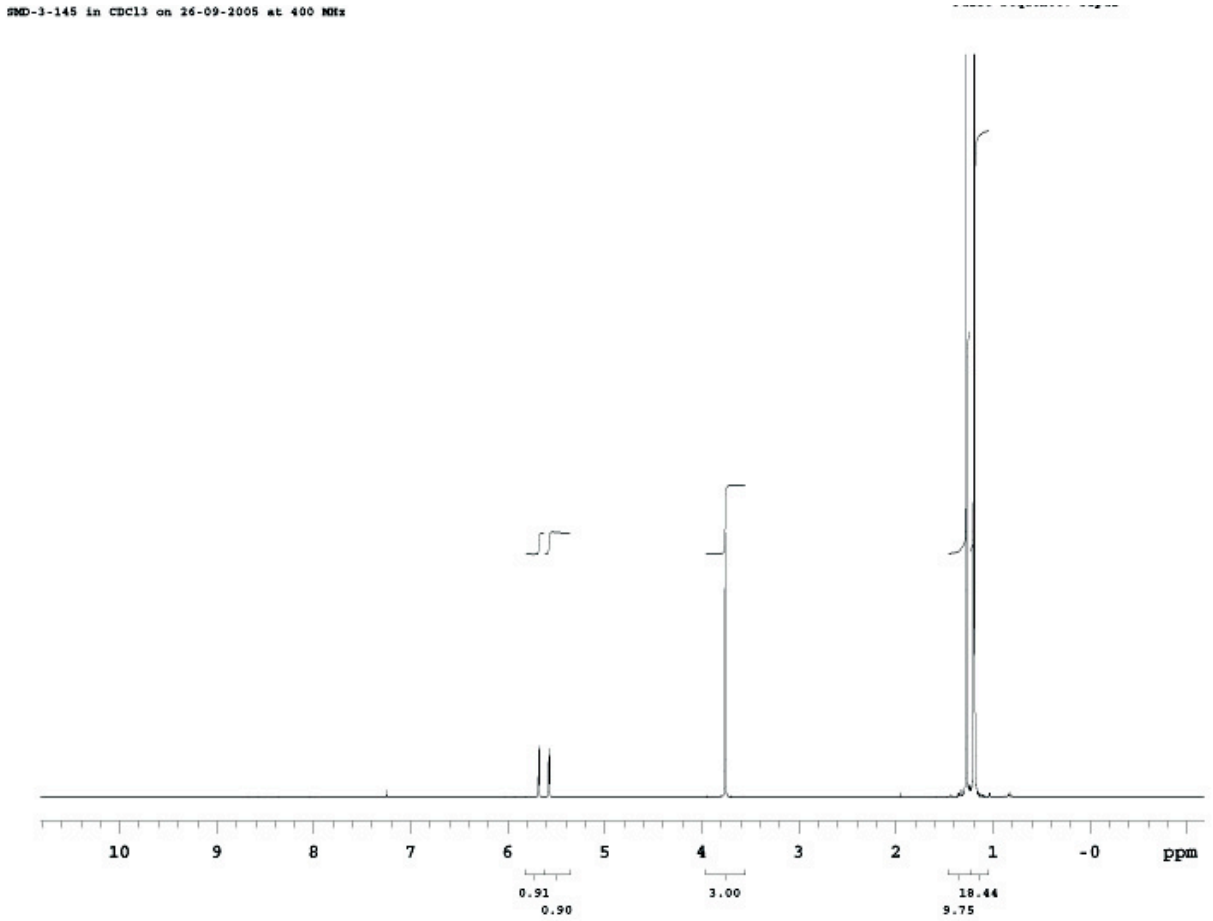
^{13}C NMR (100 MHz; $CDCl_3$)



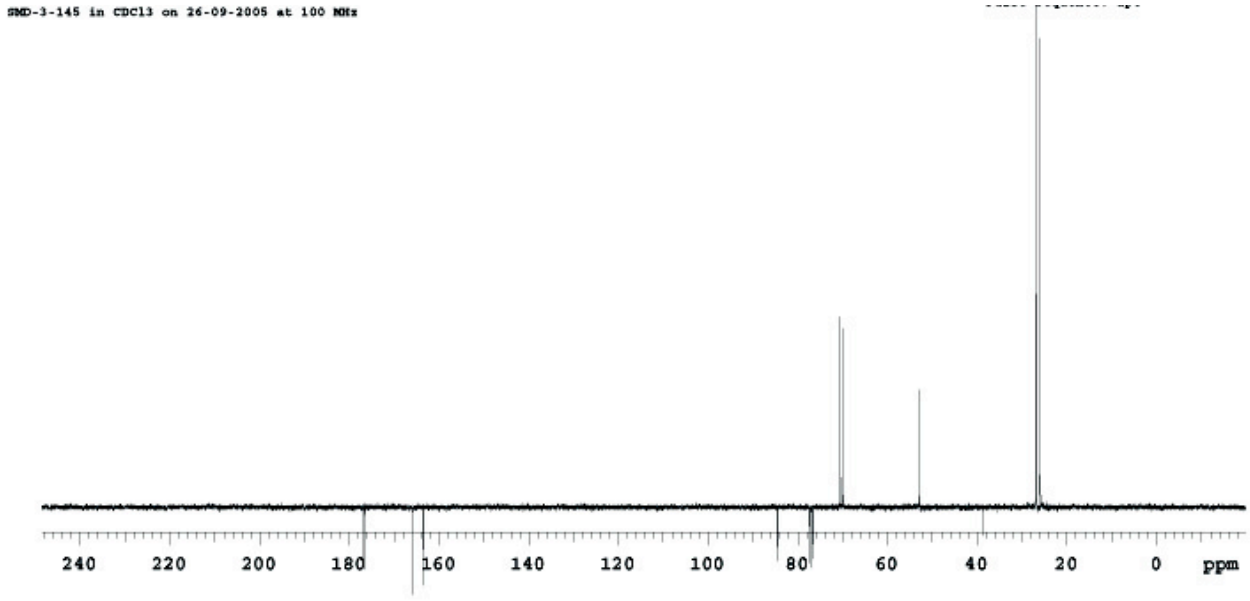


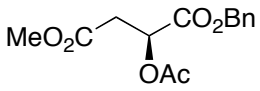
26-*rac*

^{1}H NMR (400 MHz; $CDCl_3$)

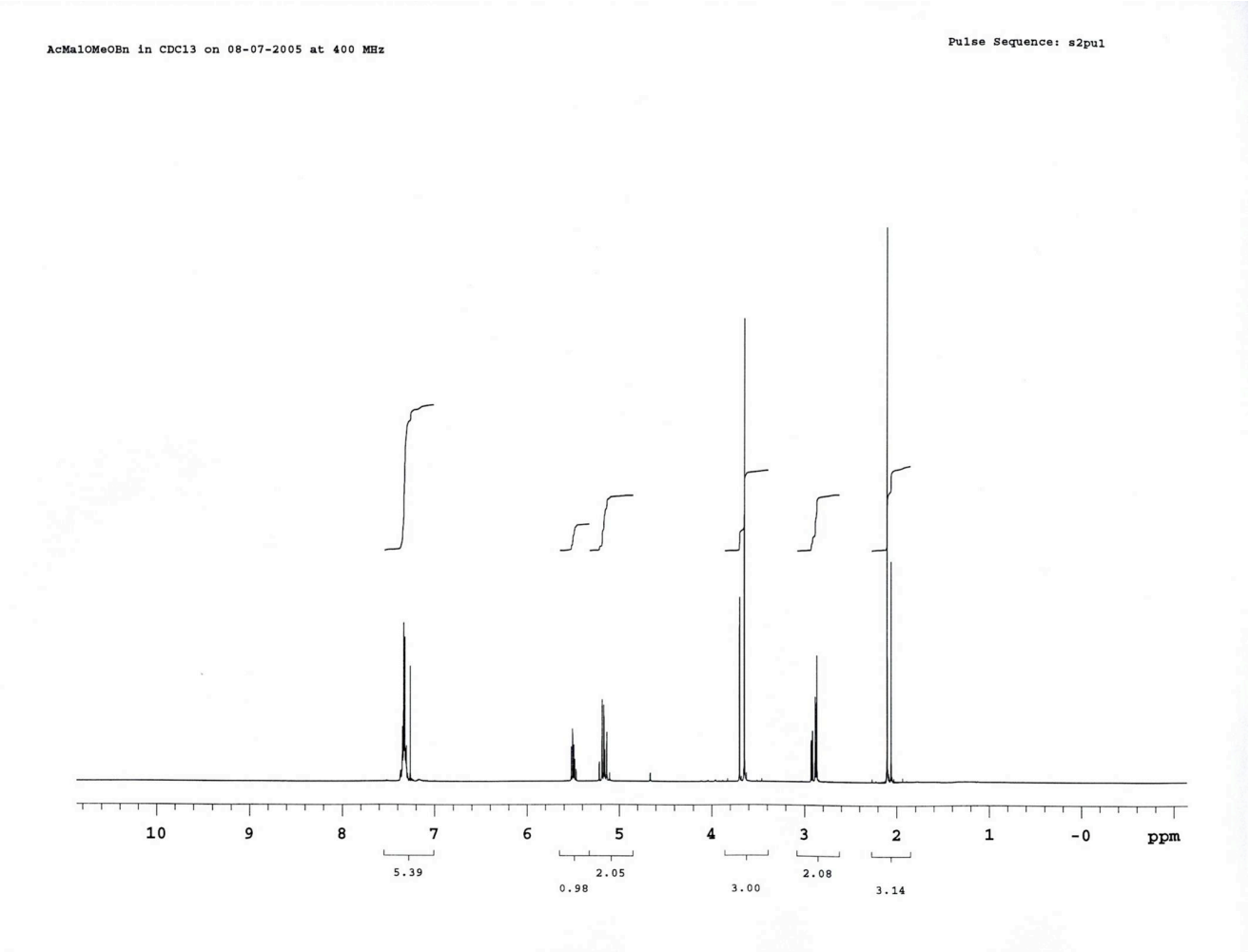


^{13}C NMR (100 MHz; $CDCl_3$)

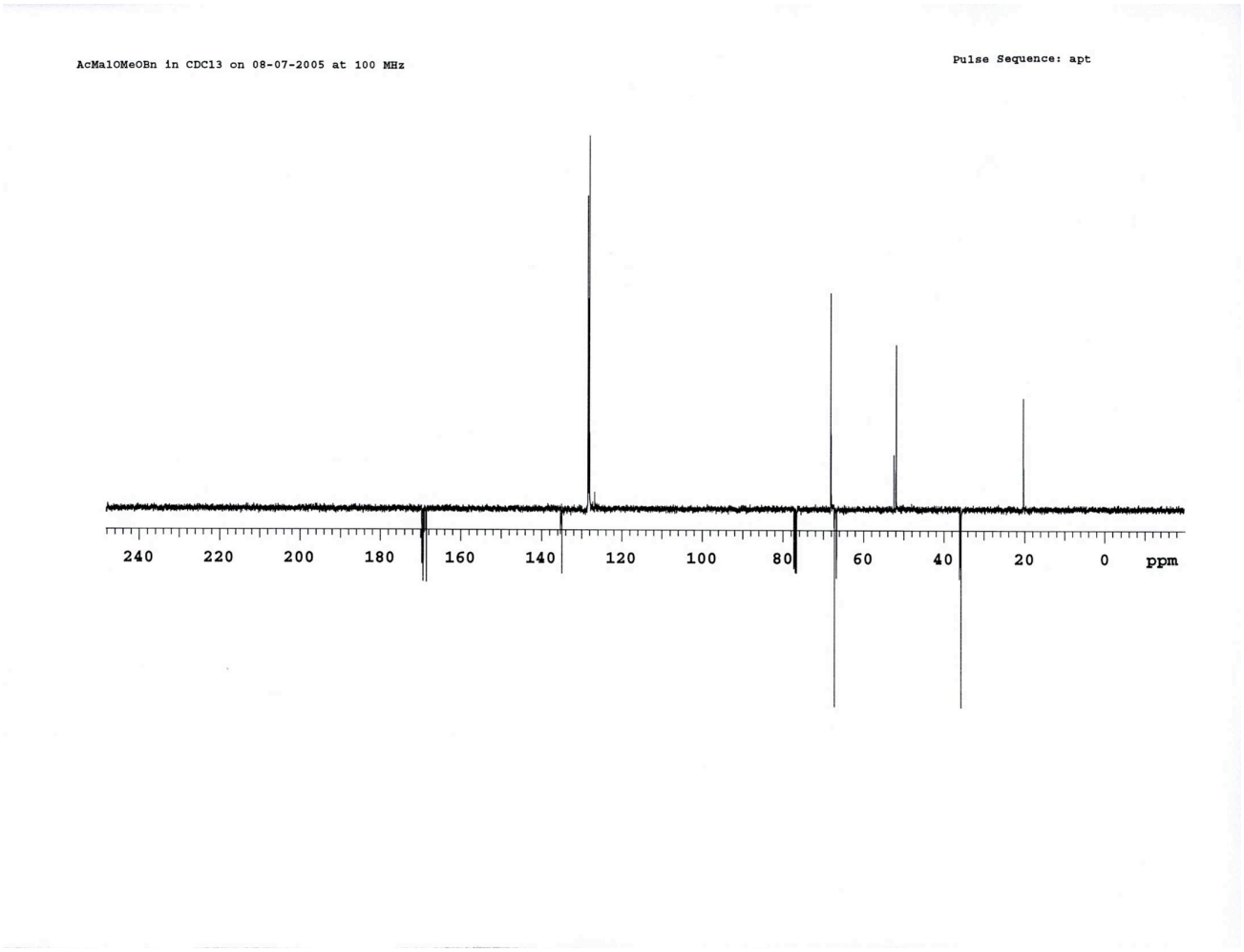




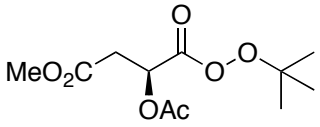
28



^{1}H NMR (400 MHz; $CDCl_3$)

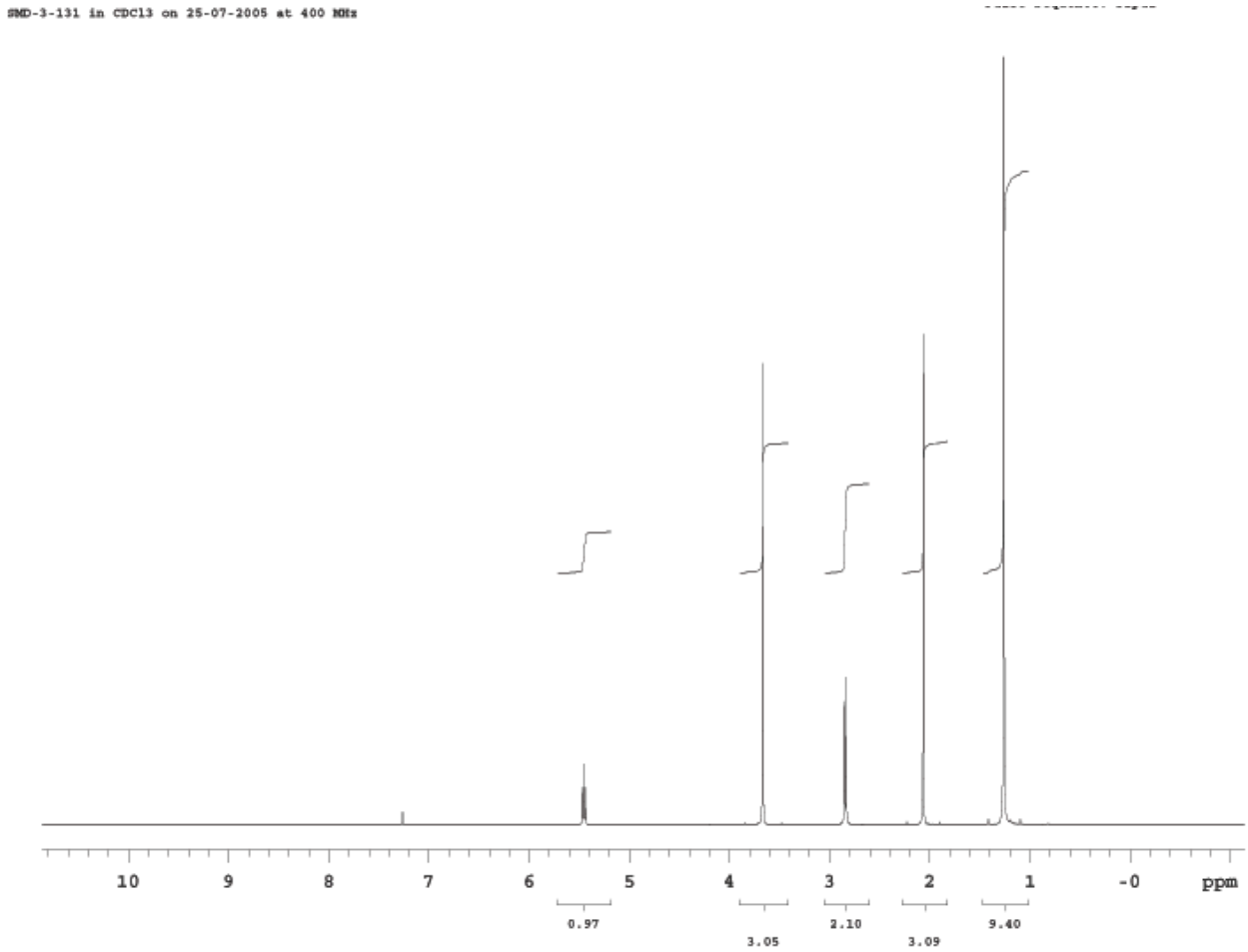


^{13}C NMR (100 MHz; $CDCl_3$)

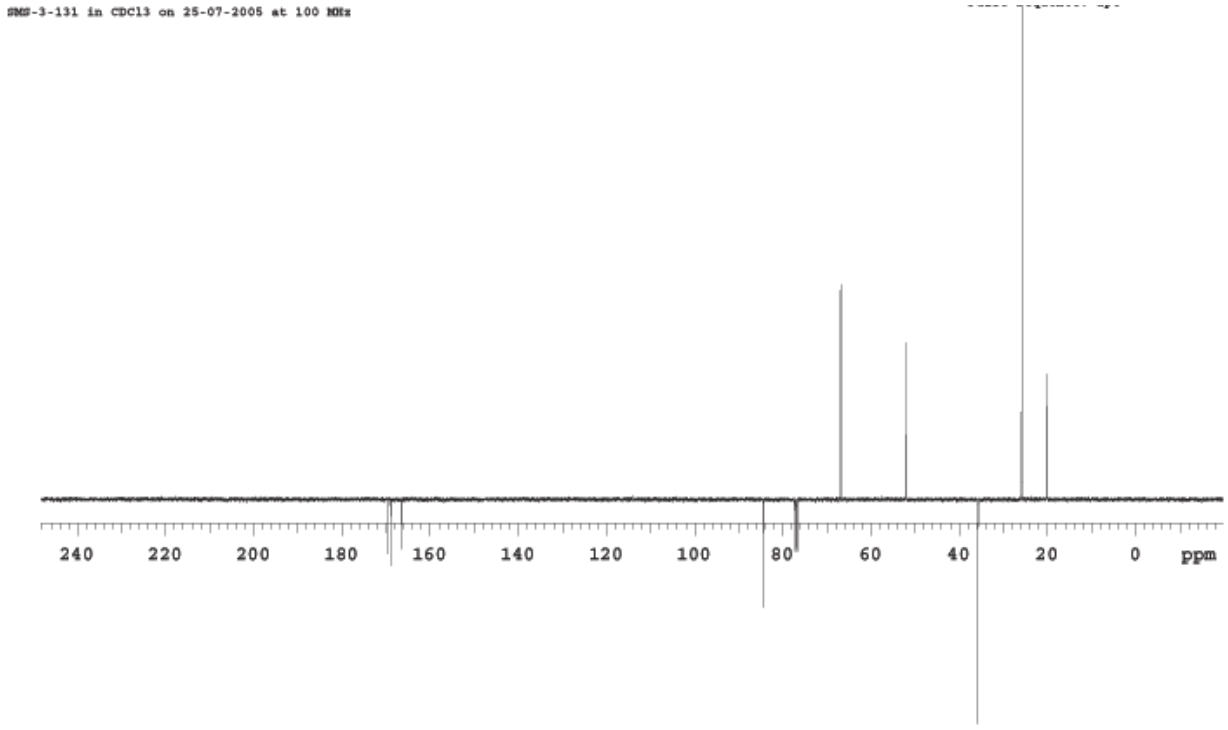


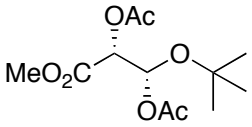
30

^{1}H NMR (400 MHz; $CDCl_3$)



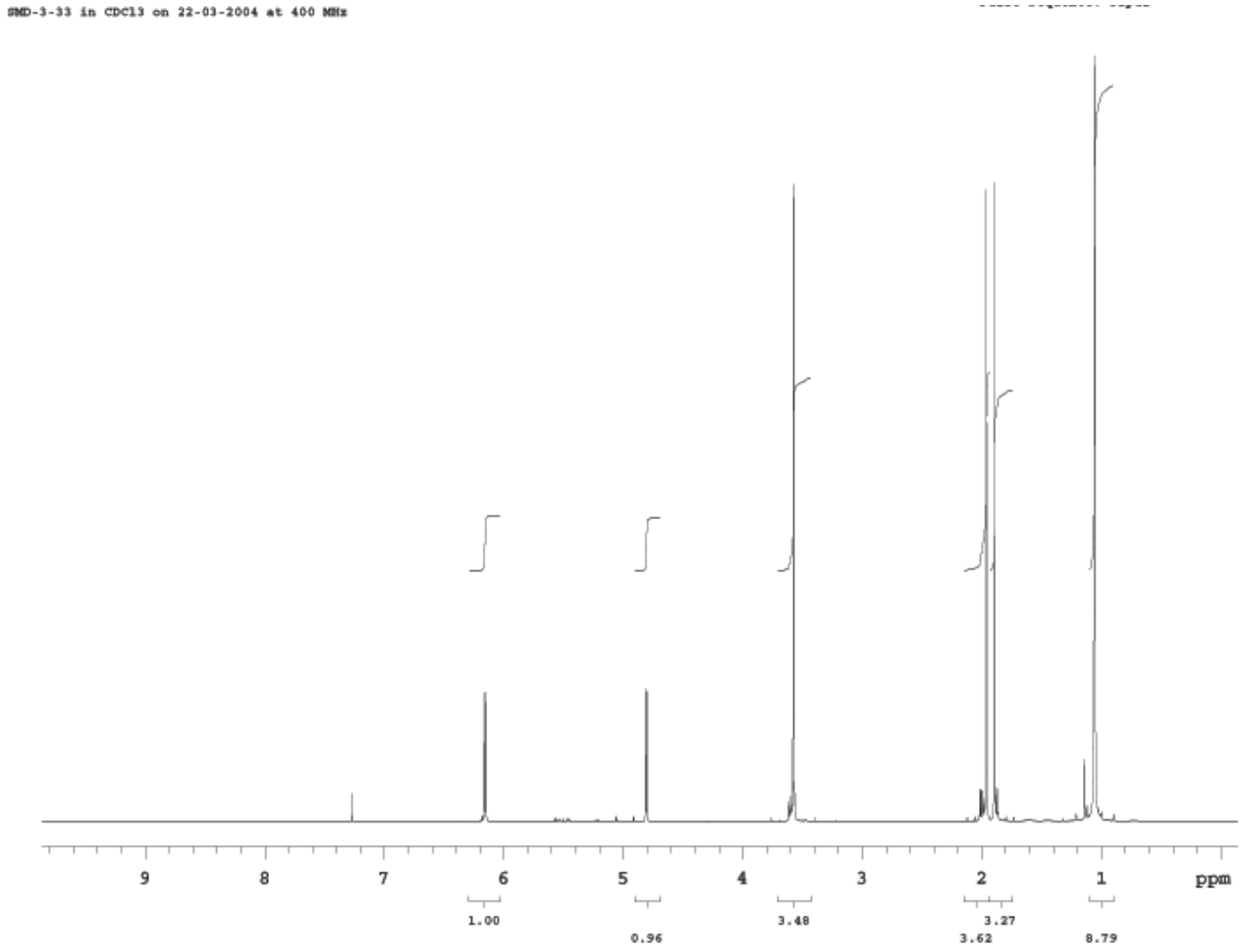
^{13}C NMR (100 MHz; $CDCl_3$)



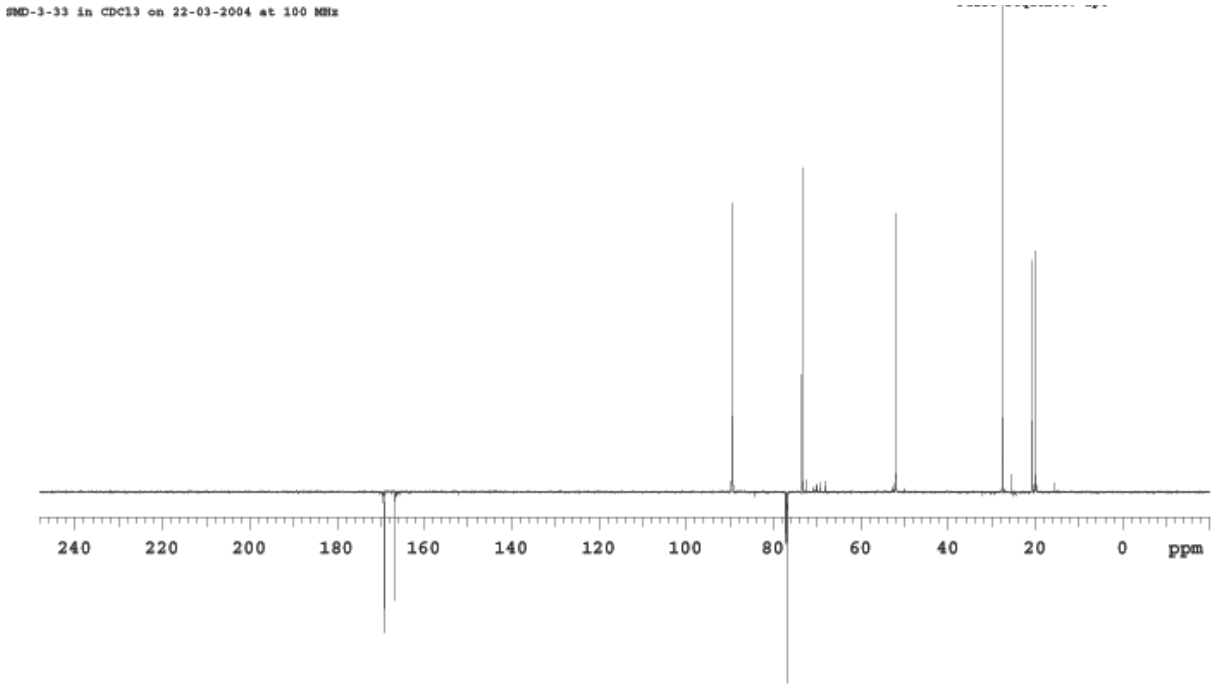


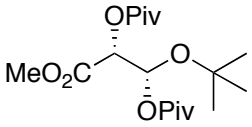
31

^{1}H NMR (400 MHz; $CDCl_3$)



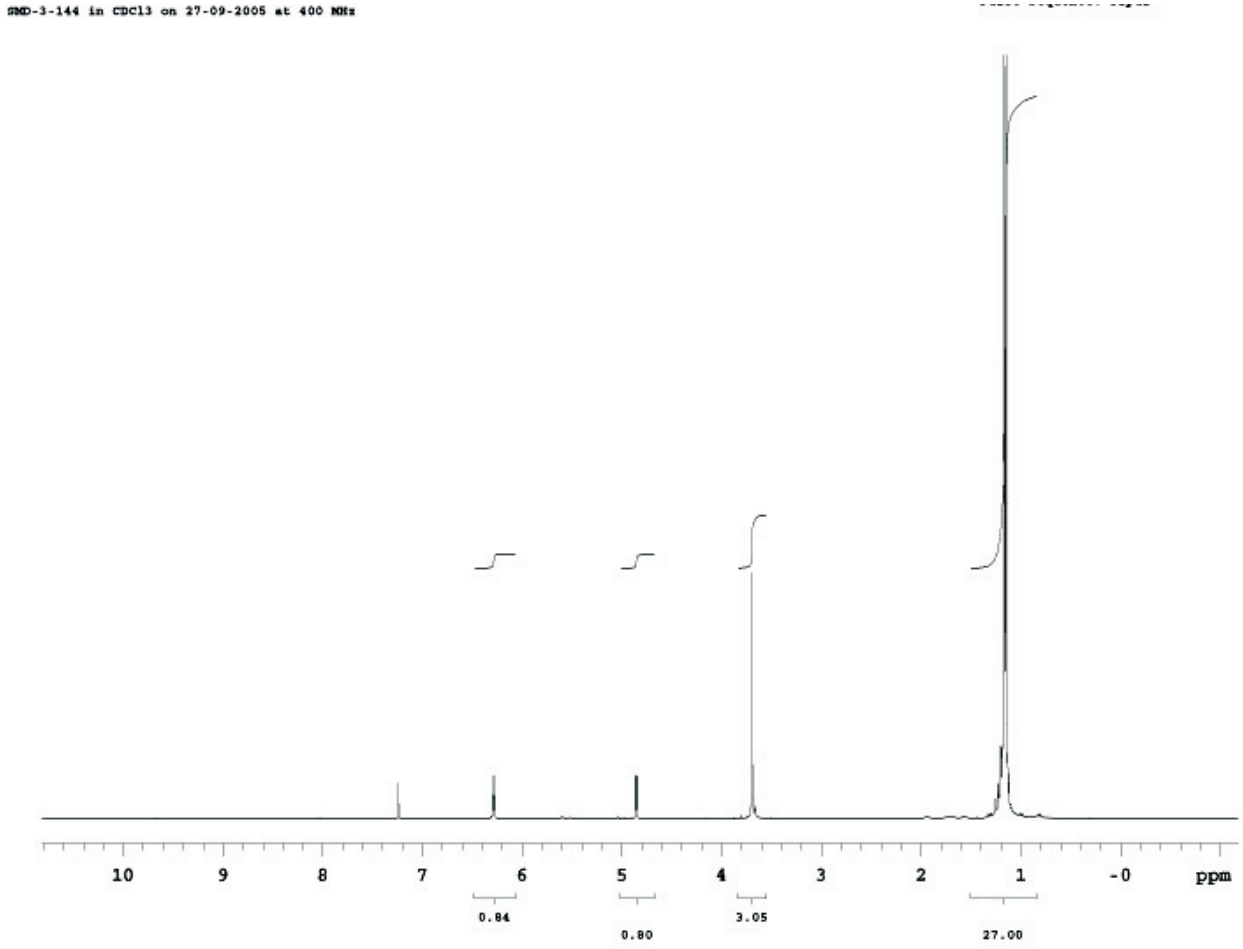
^{13}C NMR (100 MHz; $CDCl_3$)



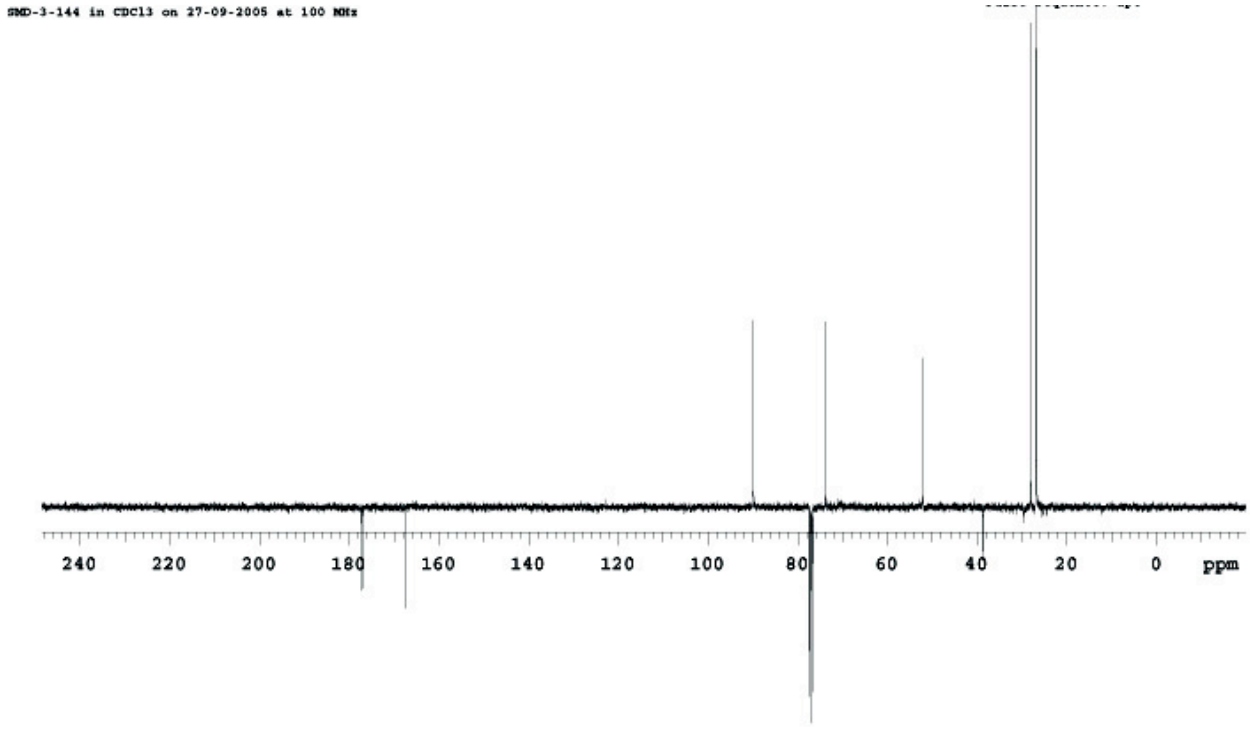


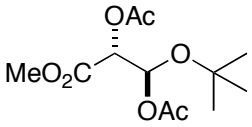
35

^{1}H NMR (400 MHz; $CDCl_3$)



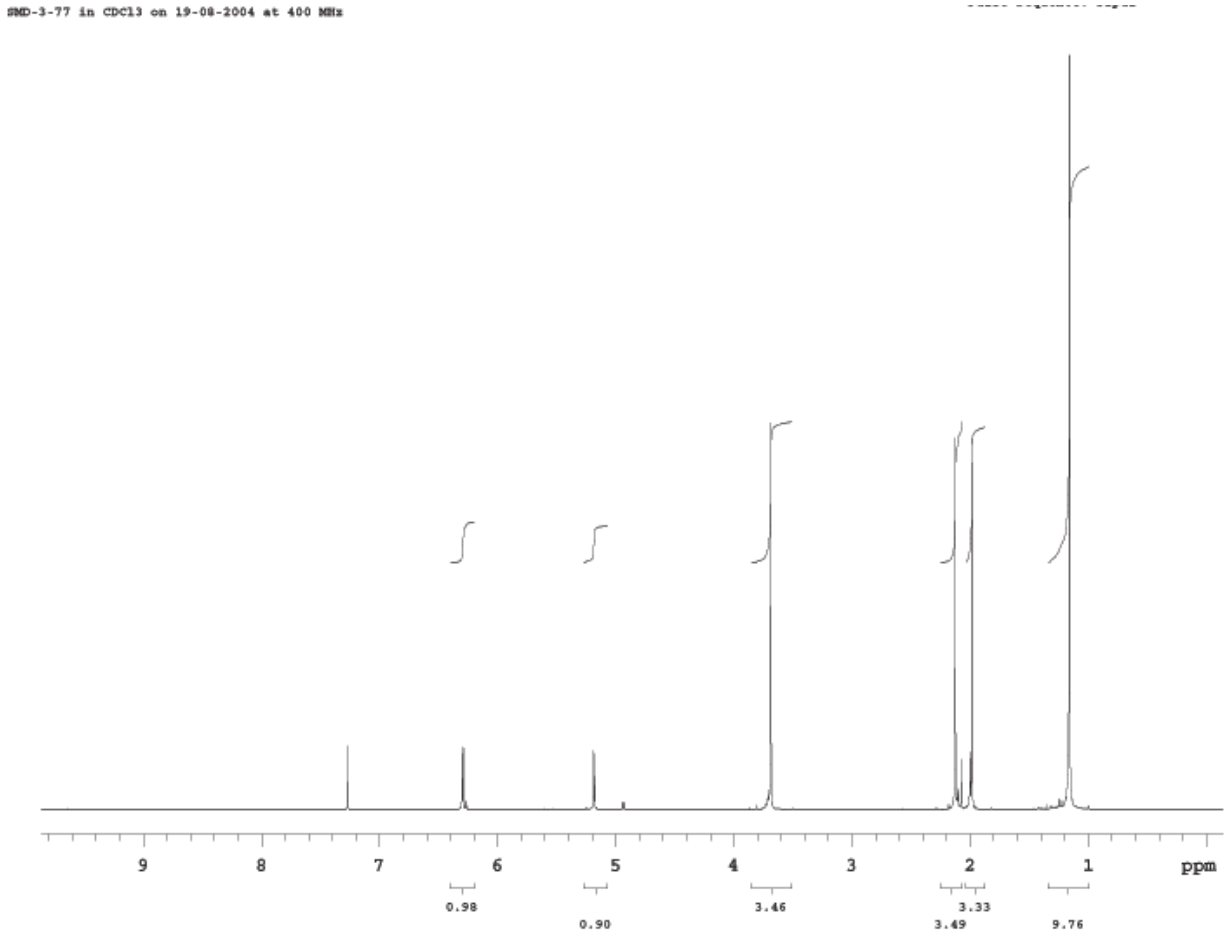
^{13}C NMR (100 MHz; $CDCl_3$)



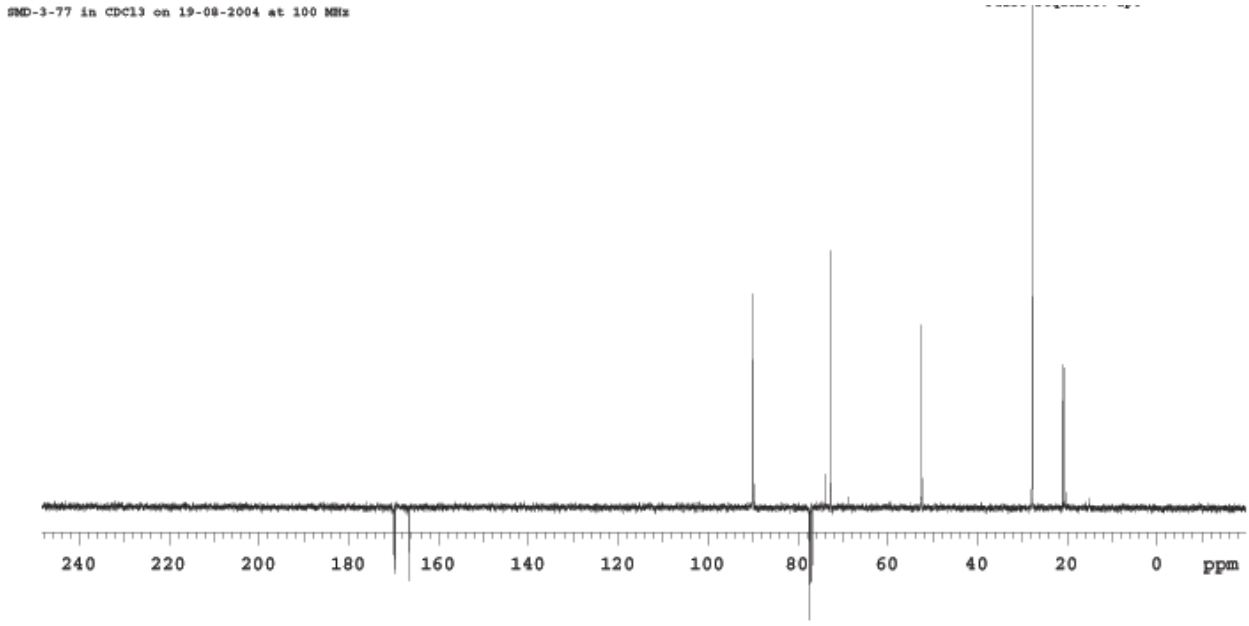


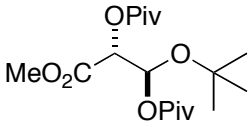
38-*rac*

^{1}H NMR (300 MHz; $CDCl_3$)



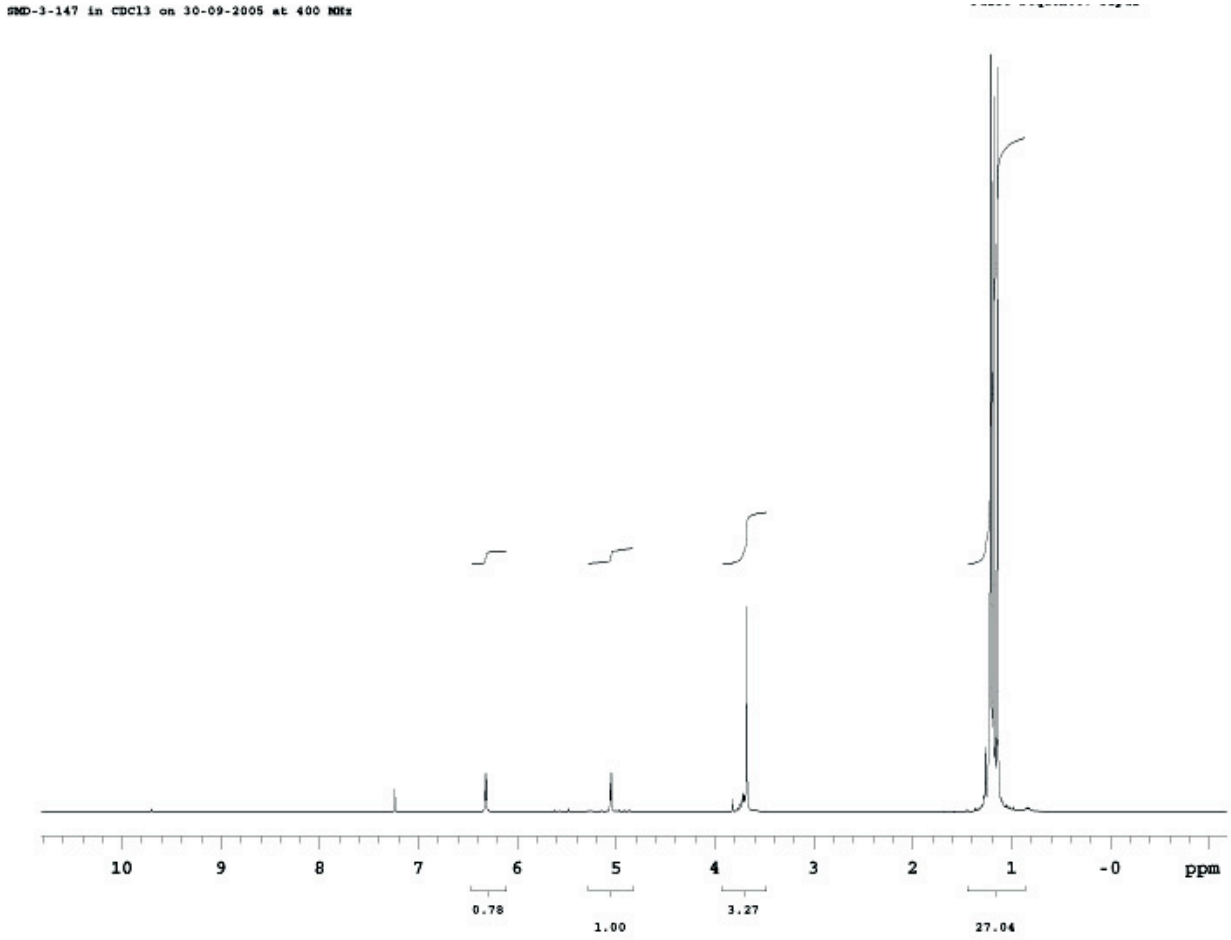
^{13}C NMR (100 MHz; $CDCl_3$)



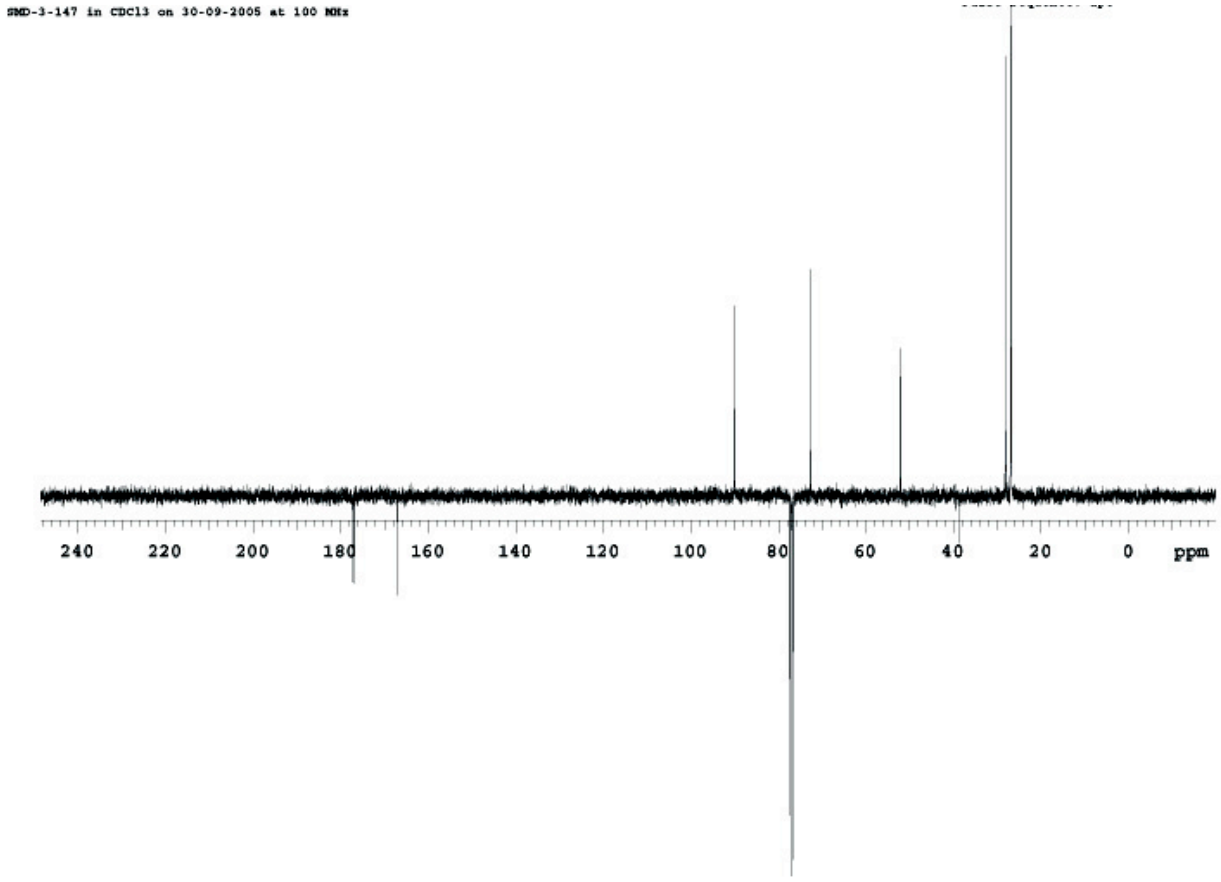


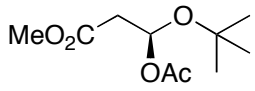
40-*rac*

^{1}H NMR (400 MHz; $CDCl_3$)



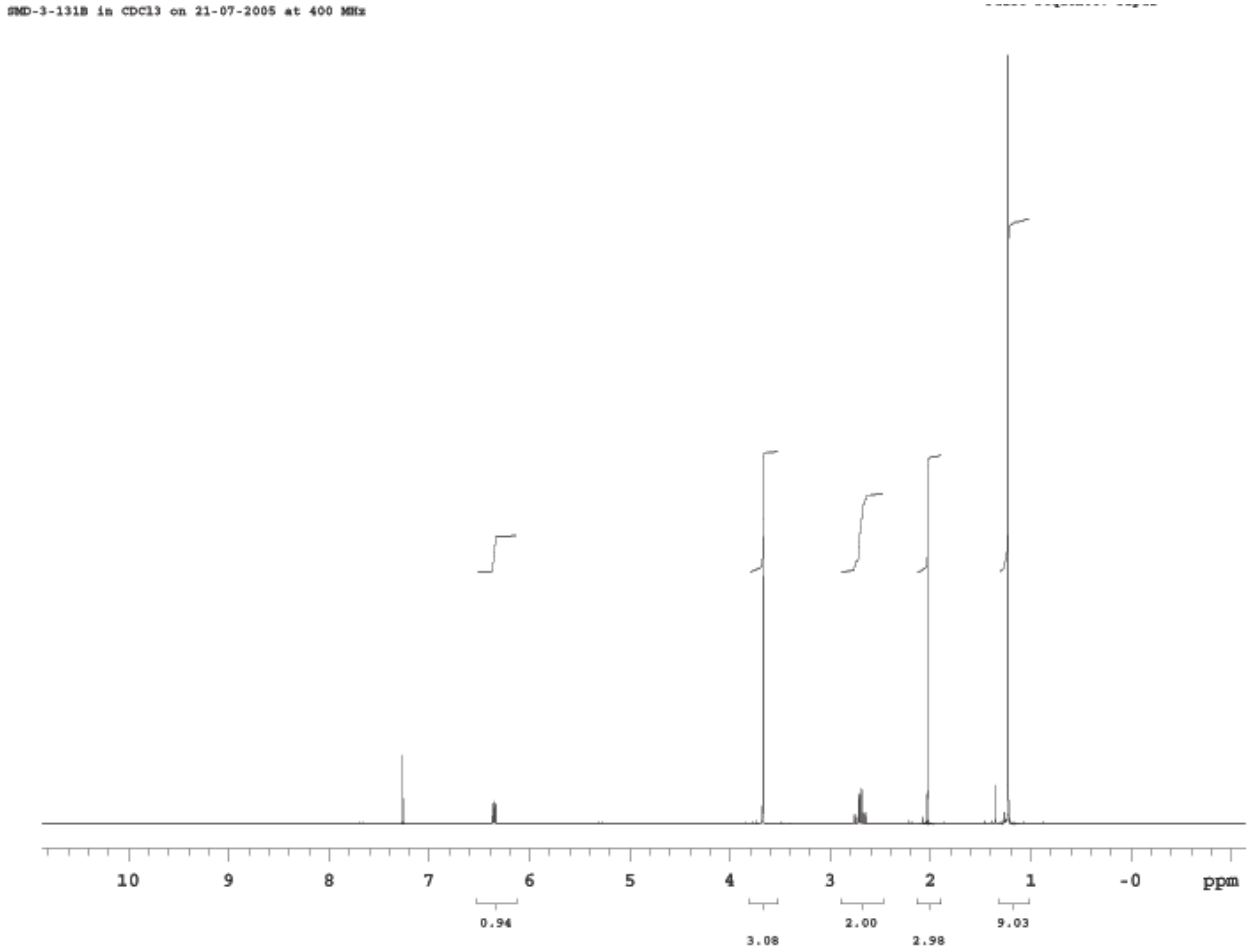
^{13}C NMR (100 MHz; $CDCl_3$)





41

^{1}H NMR (400 MHz; $CDCl_3$)



^{13}C NMR (100 MHz; $CDCl_3$)