Supporting Information

A Non-Iterative, Flexible and Highly Stereoselective Synthesis of Polydeoxypropionates – Synthesis of (+)-Vittatalactone

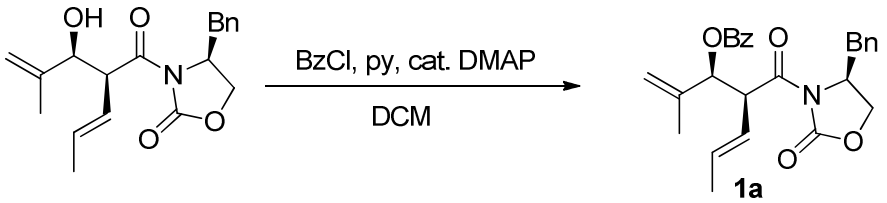
*Christian F. Weise, Matthias Pischl, Andreas Pfaltz and Christoph Schneider**

1 General Methods

Unless otherwise noted, all reactions were carried out in dry solvents under argon atmosphere using standard vacuum line techniques. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution using a Varian Gemini 2000 spectrometer (300 MHz) and Bruker Avance DRX 400 (400 MHz). The signals were referenced to residual chloroform (7.26 ppm, ^{1}H, 77.15 ppm, ^{13}C). Chemical shifts are reported in ppm, multiplicities are indicated by s (singulet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet) and brs (broad singulet). Melting points were determined uncorrected on a Boetius heating table. IR spectra were obtained with a FTIR spectrometer (Genesis ATI Mattson/Unicam). Optical rotations were measured using a Polarotronic polarimeter (Schmidt & Haensch). All ESI mass spectra were recorded on a Bruker APEX II FT-ICR. HPLC analyses were carried out on a Jasco MD-2010 plus instrument with chiral stationary phase column (Daicel Chiralcel OD-H column). Solvents were distilled from indicated drying reagents: dichlormethane (CaH_2), tetrahydrofuran (Na, bezophenone), diethyl ether (Na, benzophenone), toluene (Na, benzophenone). Diethyl ether, ethyl acetate and hexane were technical grade and distilled from KOH. Flash column chromatography was performed by using Merck silica gel 60 230-400 mesh (0.040-0.063 mm). Abbreviations for solvents are used as followed: Diethyl ether (E), ethyl acetate (EA), hexane (Hex), dichloromethane (DCM). Spots were monitored by thin-layer chromatography on precoated TLC Silica gel 60 F_{254} plates (Merck), were visualized by UV and treated with phosphomolybdic acid staining solution, vanillin staining solution, $KMnO_4$ staining solution or formaldehyde staining solution. Hydrogenation experiments were carried out in a Premex MED 1234 autoclave at the indicated reaction conditions.

2 Protection of *Syn*-Aldols

2.1 Synthesis of Benzoate 1a



3.12 g (9.47 mmol, 1.0 eq) of *E*-aldol product were dissolved in 40 mL of DCM and cooled to 0°C. After addition of 1.53 mL (18.9 mmol, 2.0 eq) of pyridine, 1.98 ml (17.1 mmol, 1.8 eq) of benzoyl chloride were added. A catalytic amount of DMAP (tip of spatula) was added and the reaction mixture was stirred over night at RT. The reaction was quenched by the addition of sat. aq. $NaHCO_3$ and diluted with ether . The organic phase was washed twice with 1N HCl and dried over anhydrous Na_2SO_4. After removal of the solvent the crude product was purified by flash column chromatography (EA/Hex 1/7 → 1/5) to give 3.76 g (8.70 mmol, 92%) of **1a** as a colorless, viscous oil.

$[\alpha]_D^{22}$ = + 52.1 (c = 1.21, $CHCl_3$).

TLC: R_f = 0.33 (EA/Hex 1/4).

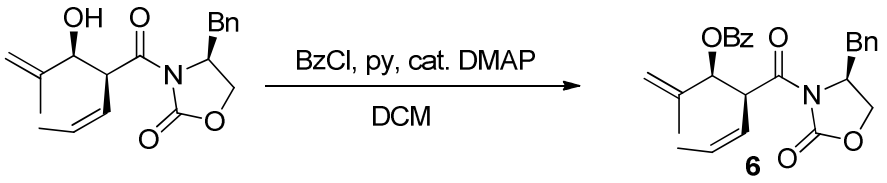
^{1}H-NMR (300 MHz, $CDCl_3$, 26°C): δ = 8.08 – 8.05 (m, 2H), 7.61 – 7.58 (m, 1H), 7.49 – 7.44 (m, 2H), 7.34 – 7.25 (m, 3H), 7.20 – 7.17 (m, 2H), 5.90 (d, *J* = 6.6 Hz, 1H), 5.85 – 5.66 (m, 2H), 5.12 (s, 1H), 5.01 (dd, *J* = 8.7, 6.6 Hz, 1H), 4.98 (s, 1H), 4.62 (m_c, 1H), 4.25 (t, *J* = 8.7 Hz, 1H), 4.16 (dd, *J* = 9.0, 2.7 Hz, 1H), 3.21 (dd, *J* = 13.5, 3.3 Hz, 1H), 2.79 (dd, *J* = 13.5, 9.2 Hz, 1H), 1.84 (s, 3H), 1.71 (dd, *J* = 6.0, 1.2 Hz, 3H) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$, 26°C): δ = 171.6, 165.6, 153.4, 141.3, 135.2, 133.1, 131.9, 130.2, 129.8, 129.7, 129.6, 128.9, 128.5, 127.4, 124.2, 114.3, 76.47, 66.16, 55.39, 49.99, 37.64, 19.06, 18.21 ppm.

IR (Film) ν (cm^{-1}) = 3541, 3379, 3062, 3030, 2972, 2918, 2856, 2255, 1789, 1713, 1651, 1602, 1584, 1478, 1450, 1384, 1268, 1099, 1070, 1026, 969, 911, 830, 804, 761, 712, 671, 644, 595, 566, 506.

HR-MS (ESI): calcd. for: $C_{26}H_{27}NO_5Na$ ($[M+Na]^+$): 456.17814; found: 456.17810.

2.2 Synthesis of Benzoate 7



940 mg (2.85 mmol, 1.0 eq) of *Z*-aldol product were dissolved in 10 mL of DCM and cooled to 0°C. After addition of 0.46 mL (1.49 mmol, 2.0 eq) of pyridine, 0.59 mL (1.34 mmol, 1.8 eq) of benzoyl chloride were added. A catalytic amount of DMAP (tip of spatula) was added and the reaction mixture was stirred over night at RT. The reaction was quenched by the addition of sat. aq. $NaHCO_3$ and diluted with ether. The organic phase was washed twice with 1N HCl and dried over Na_2SO_4. After removal of the solvent the crude product was purified by flash column chromatography (E/Hex 1/3 → 1/1) to give 1.17 g (2.69 mmol, 95%) of **7** as a colorless, viscous oil.

$[\alpha]_D^{24}$ = + 43.0 (c = 1.0, $CHCl_3$).

TLC: R_f = 0.33 (EA/Hex 1/4).

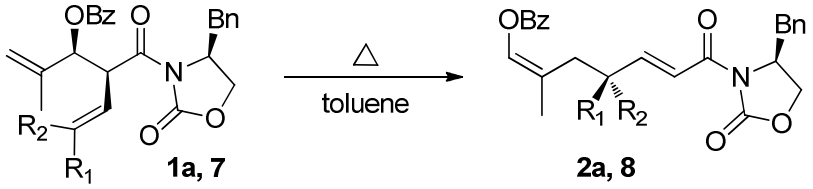
^{1}H-NMR (400 MHz, $CDCl_3$, 26°C): δ = 8.08 – 8.02 (m, 2H), 7.61 – 7.53 (m, 1H), 7.50 – 7.42 (m, 2H), 7.33 – 7.23 (m, 3H), 7.21 – 7.14 (m, 2H), 5.91 (d, *J* = 6.4 Hz, 1H), 5.87 – 5.75 (m, 1H), 5.68 (m_c, 1H), 5.47 (dd, *J* = 9.8, 6.4 Hz, 1H), 5.13 (s, 1H), 4.98 (s, 1H), 4.62 (m_c, 1H), 4.25 (t, *J* = 8.9 Hz, 1H), 4.17 (dd, *J* = 9.0, 2.7 Hz, 1H), 3.20 (dd, *J* = 13.5, 3.3 Hz, 1H), 2.80 (dd, *J* = 13.5, 9.2 Hz, 1H), 1.87 (s, 3H), 1.76 (dd, *J* = 6.8, 1.7 Hz, 3H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, 26°C): δ = 171.7, 165.6, 153.5, 141.4, 135.2, 133.2, 130.5, 130.2, 129.8, 129.6, 129.0, 128.5, 127.4, 123.8, 114.3, 76.71, 66.23, 55.49, 44.82, 37.73, 19.04, 13.95 ppm.

IR (Film) ν (cm^{-1}) = 3063, 3029, 2976, 2920, 1778, 1720, 1653, 1602, 1584, 1493, 1451, 1384, 1360, 1315, 1271, 1208, 1178, 1108, 1070, 1053, 1026, 910, 788, 762, 711, 641, 595, 576, 505.

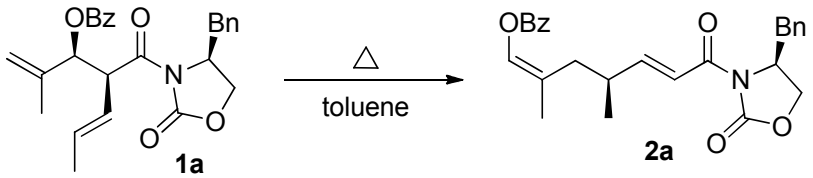
HR-MS (ESI): calcd. for: $C_{26}H_{27}NO_5Na$ ($[M+Na]^+$): 456.17814; found: 456.17820.

3 General Procedure for the Oxy-Cope Rearrangement of *Syn*-Aldols



The substrates were dissolved in toluene (10 mL/g of substrate), transferred into a screw cap-round bottom flask and degassed with a stream of argon for 5 min. The tube was sealed and placed into a heating bath at the reaction conditions indicated for each case. After 4-6 h the solvent was removed under reduced pressure and the products were purified by flash column chromatography (E/Hex 1/2 → 1/1).

3.1 Oxy-Cope Product 2a



According to the general procedure above 3.99 g (9.20 mmol) of **1a** were heated to 180°C over a period of 4 h to give 3.79 g (8.74 mmol, 95%) of **2a** as a viscous, colorless oil after purification. The product solidified on standing.

$[\alpha]_D^{25}$ = - 18.7 (c = 0.97, $CHCl_3$).

TLC: R_f = 0.30 (EA/Hex 1/5).

Melting Point: 87 – 88°C

^{1}H-NMR (300 MHz, $CDCl_3$, 26°C): δ = 8.10 – 8.06 (m, 2H), 7.62 – 7.56 (m, 1H), 7.51 – 7.46 (m, 2H), 7.35 – 7.13 (m, 8H), 4.68 (m_c, 1H), 4.21 – 4.12 (m, 2H), 3.29 (dd, J = 3.3, 13.5 Hz, 1H), 2.75 – 2.67 (m, 2H), 2.38 (d, J = 7.2 Hz, 2H), 1.74 (d, J = 1.5 Hz, 3H), 1.65 (d, J = 6.6 Hz, 3H) ppm.

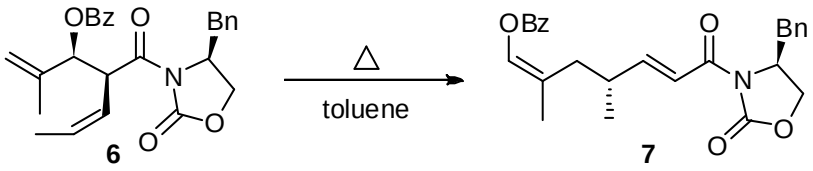
^{13}C-NMR (75 MHz, $CDCl_3$, 26°C): δ = 165.0, 163.5, 155.8, 153.4, 135.4, 133.3, 131.5, 129.8, 129.5, 129.4, 128.9, 128.6, 127.3, 119.8, 118.9, 66.10, 55.34, 37.86, 36.49, 35.06, 19.03, 18.00 ppm.

IR (Film) ν (cm^{-1}) = 3534, 3350, 3068, 3063, 3029, 2964, 2919, 2871, 2740, 2254, 1778, 1731, 1681, 1633, 1601, 1583, 1491, 1479, 1452, 1384, 1266, 1122, 1072, 1053, 1023, 1003, 945, 913, 876, 858, 803, 761, 750, 732, 711, 675, 642, 617, 595, 572, 506.

HR-MS (ESI): calcd. for: $C_{26}H_{27}NO_5Na$ ($[M+Na]^+$): 456.17814; found: 456.17794.

HPLC: Chiralcel OD-H column, hexane/*i*-PrOH = 92/8, flow rate = 0.8 mL min^{-1}; t_R = 28.3 min.

3.2 Oxy-Cope Product 7



According to the general procedure above 1.59 g (3.68 mmol) of **7** were heated to 200°C over a period of 6 h to give 1.338 g (3.09 mmol, 84%, 96:4) of **7** as a viscous, colorless oil after purification.

$[\alpha]_D^{24}$ = +94.0 (c = 1.0, $CHCl_3$).

TLC: R_f = 0.30 (EA/Hex 1/5).

^{1}H-NMR (400 MHz, $CDCl_3$, 26°C): δ = 8.12 – 8.05 (m, 2H), 7.62 – 7.55 (m, 1H), 7.52 – 7.43 (m, 2H), 7.37 – 7.14 (m, 8H), 4.66 (m_c, 1H), 4.21 – 4.11 (m, 2H), 3.29 (dd, *J* = 13.4, 3.2 Hz, 1H), 2.81 – 2.65 (m, 2H), 2.38 (d, *J* = 7.5 Hz, 2H), 1.75 (d, *J* = 1.5 Hz, 3H), 1.15 (d, *J* = 6.7 Hz, 3H) ppm.

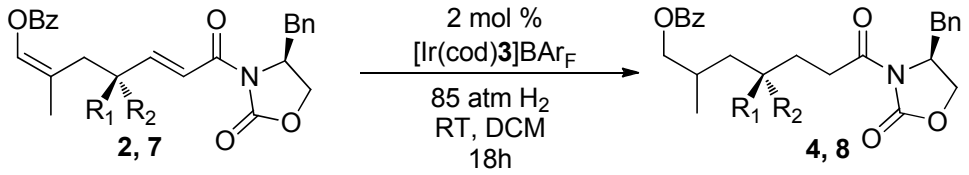
^{13}C-NMR (100 MHz, $CDCl_3$, 26°C): δ = 165.2, 163.6, 156.0, 153.5, 135.5, 133.4, 131.7, 129.9, 129.6, 129.5, 129.0, 128.7, 127.4, 119.9, 119.0, 66.22, 55.42, 37.99, 36.60, 35.12, 19.07, 18.16 ppm.

IR (Film) *v* (cm^{-1}) = 3525, 3088, 3028, 3006, 2970, 2954, 2914, 2885, 2654, 1781, 1718, 1680, 1632, 1601, 1583, 1490, 1477, 1452, 1385, 1356, 1311, 1270, 1207, 1173, 1145, 1122, 1073, 1051, 1026, 1001, 988, 945, 873, 858, 834, 816, 799, 763, 750, 731, 707, 637, 589, 575, 560, 505, 437.

HR-MS (ESI): calcd. for: $C_{26}H_{27}NO_5Na$ ($[M+Na]^+$): 456.17814; found: 456.17814.

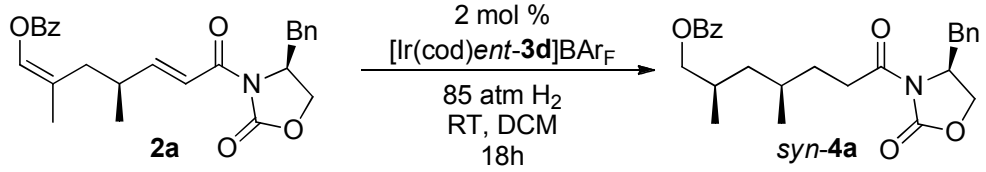
HPLC: Chiralcel OD-H column, hexane/*i*-PrOH = 92/8, flow rate = 0.8 mL min^{-1}; major isomer t_R = 26.4 min; minor isomer t_R = 37.9 min.

4 General Procedure for the Hydrogenation of Oxy-Cope Products



In a glass vial equipped with a magnetic stir bar were weighed the substrate and 2 mol % of the Ir-catalyst. The mixture was dissolved in dry DCM (c = 0.3 – 0.6M). The vial was placed into the hydrogenation autoclave which was sealed and purged once with hydrogen. The reaction was stirred at room temperature under 80 – 90 atm of hydrogen for 18 h. The solvent was removed under reduced pressure and the products were purified by flash column chromatography (E/Hex 1/2 → 1/1). For screening purposes 0.1 mmol of substrate and 2 mol % of Ir-catalyst were dissolved in 0.5 mL of DCM and submitted to the reaction conditions above. The diastereomeric excesses were determined by chiral HPLC.

4.1 Hydrogenation Product *syn*-4a



1.80 g (4.15 mmol) of **2a** and 135 mg (0.083 mmol, 0.02 eq.) of [Ir(cod)*ent*-**3d**]BAr_F were dissolved in 8 mL of DCM and submitted to the reaction conditions above to give 1.78 g (4.06 mmol, 98%, 97:3 *syn/anti*) of *syn*-**4a** as a viscous, colorless oil after purification.

$[\alpha]_D^{22}$ = + 32.0 (c = 1.0, $CHCl_3$).

TLC: R_f = 0.30 (EA/Hex 1/5).

^{1}H-NMR (400 MHz, $CDCl_3$, 26°C): δ = 8.10 – 8.01 (m, 2H), 7.60 – 7.51 (m, 1H), 7.50 – 7.39 (m, 2H), 7.38 – 7.23 (m, 3H), 7.23 – 7.16 (m, 2H), 4.65 (m_c, 1H), 4.28 – 4.05 (m, 4H), 3.28 (dd, J = 13.4, 3.2 Hz, 1H), 2.96 (m_c, 2H), 2.72 (dd, J = 13.4, 9.7 Hz, 1H), 2.15 – 2.01 (m, 1H),

1.85 – 1.63 (m, 2H), 1.57 – 1.44 (m, 2H), 1.21 – 1.10 (m, 1H), 1.05 (d, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.5 Hz, 3H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, 26°C): δ = 173.5, 166.7, 153.5, 135.42, 132.9, 130.5, 129.6, 129.4, 129.0, 128.4, 127.4, 69.77, 66.24, 55.24, 41.17, 37.99, 33.20, 31.01, 30.29, 29.78, 20.02, 17.86 ppm.

IR (Film) *v* (cm^{-1}) = 3062, 3029, 2958, 2925, 1782, 1715, 1602, 1584, 1452, 1387, 1352, 1314, 1274, 1212, 1112, 1070, 1053, 1026, 983, 845, 806, 761, 744, 713, 674, 630, 595, 504.

HR-MS (ESI): calcd. for: $C_{26}H_{31}NO_5Na$ ($[M+Na]^+$): 460.20944; found: 460.20893.

HPLC: Chiralcel OD-H column, hexane/*i*-PrOH = 92/8, flow rate = 0.8 mL min^{-1}; major diastereomer t_R = 35.7 min; minor diastereomer t_R = 39.1 min.

4.2 Hydrogenation Product *anti*-4a

1.14 g (2.62 mmol) of **2a** and 86 mg (0.052 mmol, 0.02 eq.) of [Ir(cod)**3d**]BAr_F were dissolved in 5 mL of DCM and submitted to the reaction conditions above to give 1.11 g (2.53 mmol, 97%, 96:4 *anti/syn*) of *anti*-**4a** as a viscous, colorless oil after purification.

$[\alpha]_D^{24}$ = + 25.0 (c = 1.0, $CHCl_3$).

TLC: R_f = 0.30 (EA/Hex 1/5).

^{1}H-NMR (400 MHz, $CDCl_3$, 26°C): δ = 8.10 – 8.01 (m, 2H), 7.60 – 7.51 (m, 1H), 7.48 – 7.39 (m, 2H), 7.37 – 7.23 (m, 3H), 7.23 – 7.14 (m, 2H), 4.66 (m_c, 1H), 4.26 – 4.04 (m, 4H), 3.28 (dd, *J* = 13.4, 3.1 Hz, 1H), 2.97 (m_c, 2H), 2.76 (dd, *J* = 13.4, 9.6 Hz, 1H), 2.07 (m_c, 1H), 1.84 – 1.49 (m, 3H), 1.39 – 1.23 (m, 2H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.94 (d, *J* = 6.3 Hz, 3H) ppm.

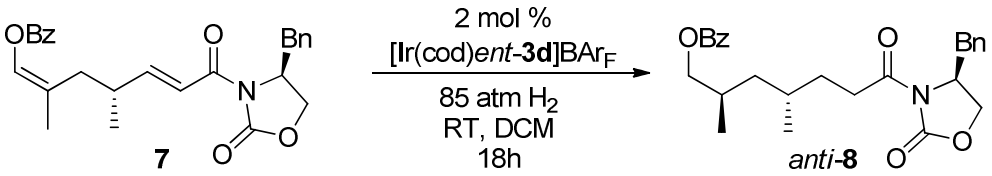
^{13}C-NMR (100 MHz, $CDCl_3$, 26°C): δ = 173.5, 166.6, 153.5, 135.4, 132.9, 130.6, 129.6, 129.5, 129.0, 128.4, 127.4, 70.30, 66.21, 55.21, 40.77, 37.96, 33.34, 31.99, 30.34, 29.73, 19.20, 16.87 ppm.

IR (Film) *v* (cm^{-1}) = 3541, 3063, 3030, 2960, 2925, 1783, 1716, 1602, 1584, 1496, 1452, 1386, 1352, 1314, 1273, 1211, 1111, 1070, 1052, 1026, 982, 936, 788, 712, 675, 631, 594, 565, 505.

HR-MS (ESI): calcd. for: $C_{26}H_{31}NO_5Na$ ($[M+Na]^+$): 460.20944; found: 460.20912.

HPLC: Chiralcel OD-H column, hexane/*i*-PrOH = 92/8, flow rate = 0.8 mL min^{-1}; minor diastereomer t_R = 35.7 min; major diastereomer t_R = 39.1 min.

4.3 Hydrogenation Product *anti*-8



1.12 g (2.58 mmol) of **7** and 84 mg (0.051 mmol, 0.02 eq.) of [Ir(cod)*ent*-**3d**]BAr_F were dissolved in 5 mL of DCM and submitted to the reaction conditions above to give 1.07 g (2.45 mmol, 95%, 94:6 *anti/syn*) of *anti*-**8** as a viscous, colorless oil after purification.

$[\alpha]_D^{24}$ = + 38.0 (c = 1.0, $CHCl_3$).

TLC: R_f = 0.30 (EA/Hex 1/5).

^{1}H-NMR (300 MHz, $CDCl_3$, 26°C): δ = 8.09 – 8.01 (m, 2H), 7.60 – 7.51 (m, 1H), 7.49 – 7.40 (m, 2H), 7.37 – 7.24 (m, 3H), 7.24 – 7.15 (m, 2H), 4.73 – 4.60 (m, 1H), 4.26 – 4.04 (m, 4H), 3.29 (dd, *J* = 13.3, 3.2 Hz, 1H), 2.97 (t, *J* = 7.7 Hz, 2H), 2.76 (dd, *J* = 13.3, 9.6 Hz, 1H), 2.15 – 1.97 (m, 1H), 1.85 – 1.44 (m, 3H), 1.39 – 1.23 (m, 2H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.94 (d, *J* = 6.4 Hz, 3H) ppm.

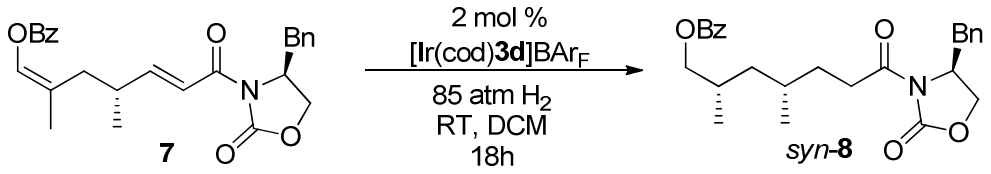
^{13}C-NMR (75 MHz, $CDCl_3$, 26°C): δ = 173.6, 166.7, 153.5, 135.4, 132.9, 130.6, 129.6, 129.5, 129.0, 128.4, 127.4, 70.32, 66.25, 55.25, 40.78, 38.02, 33.39, 32.06, 30.38, 29.78, 19.24 ppm.

IR (Film) *v* (cm^{-1}) = 3468, 3065, 3030, 2961, 2920, 1785, 1718, 1602, 1452, 1385, 1351, 1314, 1273, 1211, 1111, 1070, 1026, 982, 787, 762, 711, 629.

HR-MS (ESI): calcd. for: $C_{26}H_{31}NO_5Na$ ($[M+Na]^+$): 460.20944; found: 460.20925.

HPLC: Chiralcel OD-H column, hexane/*i*-PrOH = 92/8, flow rate = 0.8 mL min^{-1}; minor diastereomer t_R = 29.3 min; major diastereomer t_R = 35.8 min.

4.4 Hydrogenation Product *syn*-8



1.11 g (2.57 mmol) of **7** and 84 mg (0.051 mmol, 0.02 eq.) of [Ir(cod)**3d**]BAr_F were dissolved in 5 mL of DCM and submitted to the reaction conditions above to give 1.10 g (2.52 mmol, 98%, 92:8 *syn/anti*) of *syn*-**8** as a viscous, colorless oil after purification.

$[\alpha]_D^{24}$ = + 34.0 (c = 1.0, $CHCl_3$).

TLC: R_f = 0.30 (EA/Hex 1/5).

^{1}H-NMR (300 MHz, $CDCl_3$, 26°C): δ = 8.09 – 8.00 (m, 2H), 7.61 – 7.50 (m, 1H), 7.50 – 7.39 (m, 2H), 7.37 – 7.23 (m, 3H), 7.23 – 7.15 (m, 2H), 4.64 (m_c, 1H), 4.27 – 4.05 (m, 4H), 3.28 (dd, *J* = 13.4, 3.3 Hz, 1H), 2.96 (t, *J* = 7.7 Hz, 2H), 2.76 (dd, *J* = 13.4, 9.6 Hz, 1H), 2.09 (m_c, 1H), 1.90 – 1.62 (m, 2H), 1.56 – 1.39 (m, 2H), 1.24 – 1.08 (m, 1H), 1.05 (d, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.4 Hz, 3H) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$, 26°C): δ = 173.5, 166.7, 153.5, 135.4, 132.9, 130.6, 129.6, 129.5, 129.0, 128.5, 127.4, 69.78, 66.25, 55.25, 41.10, 38.02, 33.20, 31.01, 30.30, 29.78, 20.08, 17.86 ppm.

IR (Film) ν (cm^{-1}) = 3541, 3063, 3029, 2958, 2925, 2254, 1782, 1715, 1602, 1584, 1452, 1387, 1352, 1314, 1275, 1212, 1112, 1070, 1053, 1026, 983, 915, 845, 806, 761, 713, 674, 631, 594, 504.

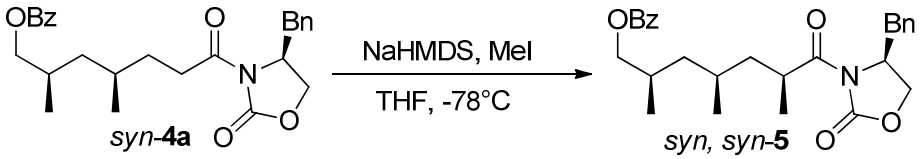
HR-MS (ESI): calcd. for: $C_{26}H_{31}NO_5Na$ ($[M+Na]^+$): 460.20944; found: 460.20926.

HPLC: Chiralcel OD-H column, hexane/*i*-PrOH = 92/8, flow rate = 0.8 mL min^{-1}; major diastereomer t_R = 29.3 min; minor diastereomer t_R = 35.8 min.

5 General Procedure for the α-Methylation of Hydrogenation Products

The hydrogenation products were dissolved in anhydrous THF (c = 0.2 M), cooled to -78°C and a solution of 2M NaHMDS in THF (1.15 eq) was added dropwise. The reaction was stirred for 45 min and MeI (1.50 eq) was added. The reaction was quenched with a few drops of sat. aq. NH_4Cl after TLC analysis indicated full conversion of starting material (3 – 4h). The solvent of the reaction mixture was removed under reduced pressure and the crude mixture was directly subjected to a silica gel column with a plug of anhydrous Na_2SO_4 using toluene. Flash column chromatography (E/Hex 1/3 → 1/1) gave the methylated products. NMR spectra showed only a single diastereomer.

5.1 *alpha*-Methylation of *syn*-4a



3.15 g (7.20 mmol, 1.0 eq) *syn*-**4a** were dissolved in 36 mL THF, treated with 4.14 mL (8.28 mmol, 1.15 eq) of NaHMDS (2M in THF) and 0.67 mL (10.80 mmol, 1.50 eq) MeI according to the general procedure above. Purification of the crude product gave 3.03 g (6.72 mmol, 93%) *syn, syn*-**5** as a colorless, viscous oil.

$[\alpha]_D^{22}$ = + 38.0 (c = 1.0, $CHCl_3$).

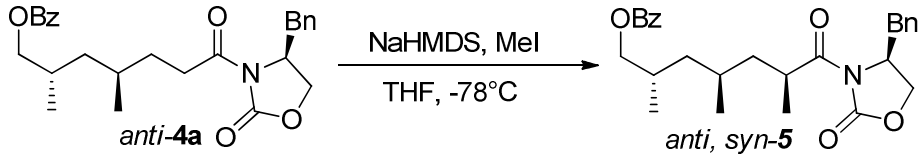
TLC: R_f = 0.39 (EA/Hex 1/5).

^{1}H-NMR (400 MHz, $CDCl_3$, 26°C): δ = 8.07 – 8.03 (m, 2H), 7.59 – 7.52 (m, 1H), 7.49 – 7.41 (m, 2H), 7.37 – 7.24 (m, 3H), 7.23 – 7.17 (m, 2H), 4.66 (m_c, 1H), 4.28 – 4.12 (m, 3H), 4.08 (dd, *J* = 10.7, 6.8 Hz, 1H), 3.91 (m_c, 1H), 3.24 (dd, *J* = 13.4, 3.2 Hz, 1H), 2.76 (dd, *J* = 13.4, 9.5 Hz, 1H), 2.10 (m_c, 1H), 1.94 (m_c, 1H), 1.56 (m_c, 1H), 1.50 – 1.41 (m, 1H), 1.21 (d, *J* = 6.9 Hz, 3H), 1.17 – 1.08 (m, 2H), 1.05 (d, *J* = 6.7 Hz, 3H), 0.93 (d, *J* = 6.5 Hz, 3H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, 26°C): δ = 177.2, 166.8, 153.1, 135.4, 132.9, 130.6, 129.6, 129.6, 129.0, 128.5, 127.4, 69.82, 66.10, 55.33, 41.60, 40.68, 37.94, 35.45, 30.21, 28.29, 20.50, 18.76, 18.00 ppm.

IR (Film) ν (cm^{-1}) = 3541, 3063, 3029, 2960, 2929, 1779, 1715, 1602, 1584, 1453, 1386, 1350, 1314, 1274, 1112, 1071, 1052, 1026, 973, 922, 839, 807, 761, 744, 713, 688, 592, 506.
HR-MS (ESI): calcd. for: $C_{27}H_{33}NO_5Na$ ($[M+Na]^+$): 474.22509; found: 474.22500.

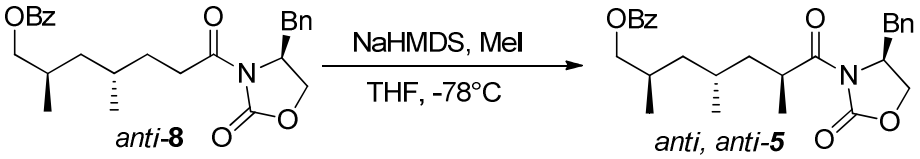
5.2 *alpha*-Methylation of *anti*-4a



658 mg (1.50 mmol, 1.0 eq) *anti*-**4a** were dissolved in 7.5 mL THF, treated with 0.865 mL (1.73 mmol, 1.15 eq) of NaHMDS (2M in THF) and 0.140 mL (2.26 mmol, 1.50 eq) MeI according to the general procedure above. Purification of the crude product gave 630 mg (1.40 mmol, 93%) *anti, syn*-**5** as a colorless, viscous oil.

$[\alpha]_D^{22}$ = + 28.0 (c = 1.0, $CHCl_3$).
TLC: R_f = 0.39 (EA/Hex 1/5).
^{1}H-NMR (400 MHz, $CDCl_3$, 26°C): δ = 8.09 – 8.01 (m, 2H), 7.58 – 7.51 (m, 1H), 7.47 – 7.40 (m, 2H), 7.36 – 7.24 (m, 3H), 7.23 – 7.18 (m, 2H), 4.68 (m_c, 1H), 4.23 – 4.07 (m, 4H), 3.90 (m_c, 1H), 3.24 (dd, J = 13.4, 3.3 Hz, 1H), 2.76 (dd, J = 13.4, 9.5 Hz, 1H), 2.05 (m_c, 1H), 1.90 (m_c, 1H), 1.56 (m_c, 1H), 1.23 (d, J = 6.9 Hz, 3H), 1.30 – 1.16 (m, 3H), 1.01 (d, J = 6.7 Hz, 3H), 0.89 (d, J = 6.5 Hz, 3H) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$, 26°C): δ = 177.3, 166.7, 153.1, 135.4, 132.9, 130.6, 129.6, 129.5, 129.0, 128.4, 127.4, 70.17, 66.08, 55.32, 41.30, 40.84, 37.92, 35.45, 30.29, 28.15, 19.89, 18.53, 17.01 ppm.
IR (Film) ν (cm^{-1}) = 3541, 3063, 3029, 2961, 2929, 2874, 1778, 1715, 1602, 1584, 1453, 1386, 1350, 1314, 1274, 1209, 1112, 1071, 1051, 1026, 973, 922, 839, 806, 761, 745, 713, 624, 593, 506.
HR-MS (ESI): calcd. for: $C_{27}H_{33}NO_5Na$ ($[M+Na]^+$): 474.22509; found: 474.22483.

5.3 *alpha*-Methylation of *anti*-8



505 mg (1.15 mmol, 1.0 eq) *anti*-**8** were dissolved in 6 mL THF, treated with 0.664 mL (1.33 mmol, 1.15 eq) of NaHMDS (2M in THF) and 0.108 mL (1.73 mmol, 1.50 eq) MeI according to the general procedure above. Purification of the crude product gave 484 mg (1.07 mmol, 93%) *anti, anti*-**5** as a colorless, viscous oil.

$[\alpha]_D^{24}$ = + 43.0 (c = 1.0, $CHCl_3$).

TLC: R_f = 0.39 (EA/Hex 1/5).

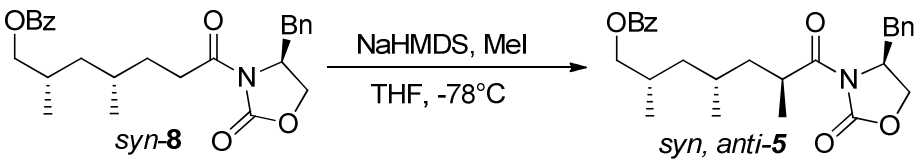
^{1}H-NMR (400 MHz, $CDCl_3$, 26°C): δ = 8.08 – 7.98 (m, 2H), 7.61 – 7.49 (m, 1H), 7.48 – 7.39 (m, 2H), 7.37 – 7.14 (m, 5H), 4.67 (m_c, 1H), 4.28 – 3.99 (m, 4H), 3.87 (m_c, 1H), 3.27 (dd, *J* = 13.3, 3.2 Hz, 1H), 2.77 (dd, *J* = 13.3, 9.6 Hz, 1H), 2.03 (m_c, 1H), 1.73 – 1.53 (m, 2H), 1.42 (m_c, 2H), 1.34 – 1.23 (m, 2H), 1.22 (d, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.1 Hz, 3H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, 26°C): δ = 177.7, 166.7, 153.1, 135.4, 132.9, 130.6, 129.6, 129.5, 129.0, 128.5, 127.4, 70.31, 66.12, 55.52, 41.30, 38.02, 35.45, 30.40, 27.94, 19.19, 17.38, 16.85 ppm.

IR (Film) ν (cm^{-1}) = 3541, 3063, 3029, 2963, 2928, 2255, 1780, 1716, 1602, 1584, 1453, 1387, 1350, 1314, 1274, 1210, 1112, 1070, 1052, 1026, 972, 914, 841, 806, 761, 734, 713, 648, 593, 506.

HR-MS (ESI): calcd. for: $C_{27}H_{33}NO_5Na$ ($[M+Na]^+$): 474.22509; found: 474.22480.

5.4 *alpha*-Methylation of *syn*-8



265 mg (0.605 mmol, 1.0 eq) *syn*-**8** were dissolved in 3 mL THF, treated with 0.348 mL (0.696 mmol, 1.15 eq) of NaHMDS (2M in THF) and 0.057 mL (0.91 mmol, 1.50

eq) MeI according to the general procedure above. Purification of the crude product gave 250 mg (0.557 mmol, 92%) *syn, anti*-**5** as a colorless, viscous oil.

$[\alpha]_D^{24}$ = + 37.0 (c = 1.0, $CHCl_3$).

TLC: R_f = 0.39 (EA/Hex 1/5).

^{1}H-NMR (400 MHz, $CDCl_3$, 26°C): δ = 8.06 – 7.99 (m, 2H), 7.58 – 7.52 (m, 1H), 7.49 – 7.41 (m, 2H), 7.37 – 7.23 (m, 3H), 7.23 – 7.17 (m, 2H), 4.64 (qd, *J* = 6.7, 3.1 Hz, 1H), 4.23 – 4.11 (m, 3H), 4.05 (dd, *J* = 10.7, 6.7 Hz, 1H), 3.85 (m_c, 1H), 3.25 (dd, *J* = 13.3, 3.2 Hz, 1H), 2.76 (dd, *J* = 13.3, 9.6 Hz, 1H), 2.05 (m_c, 1H), 1.71 – 1.60 (m, 1H), 1.61 – 1.51 (m, 1H), 1.48 – 1.38 (m, 2H), 1.20 (d, *J* = 6.8 Hz, 3H), 1.15 – 1.06 (m, 1H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 6.4 Hz, 3H) ppm.

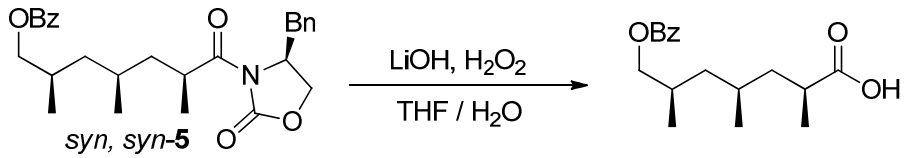
^{13}C-NMR (100 MHz, $CDCl_3$, 26°C): δ = 177.6, 166.8, 153.1, 135.5, 133.0, 130.5, 129.6, 129.6, 129.0, 128.5, 127.4, 69.78, 66.13, 55.49, 41.67, 40.41, 38.00, 35.42, 30.24, 27.99, 20.05, 17.99, 17.28 ppm.

IR (Film) *v* (cm^{-1}) = 3541, 3063, 3029, 2962, 2928, 1780, 1716, 1602, 1584, 1453, 1387, 1350, 1314, 1274, 1210, 1112, 1070, 1053, 1026, 971, 922, 788, 761, 712, 626, 593, 506.

HR-MS (ESI): calcd. for: $C_{27}H_{33}NO_5Na$ ($[M+Na]^+$): 474.22509; found: 474.22482.

6 Derivatization of *syn, syn*-5

6.1 Hydrolytic Cleavage of Auxiliary[1]



185 mg (0.410 mmol, 1.0 eq) *syn, syn*-**5** were dissolved in 8 mL of a 3/1 mixture of THF/water and cooled to 0°C. After the addition of 0.175 mL (2.05 mmol, 5.0 eq) hydrogen peroxide (35%), 65 mg (0.86 mmol, 2.0 eq) LiOH (56%) were added. The reaction was stopped after 90 min by the addition of 1.50 mL (2.25 mmol) 1.5N Na_2SO_3. After removal of the THF under reduced pressure the mixture was buffered with bicarbonate to maintain a basic pH. The aqueous phase was washed twice with DCM and then acidified by dropwise addition of conc. HCl. The aqueous phase was then extracted three times with ethyl acetate and dried over anhydrous Na_2SO_4. After removal of the solvent the crude product was

purified by filtration through a plug of silica (EA/Hex 1/1) to give 96 mg (0.33 mmol , 80%) of the acid as a colorless liquid.

$[\alpha]_D^{24}$ = + 8.0 (c = 1.0, $CHCl_3$).

TLC: R_f = 0.65 (EA/Hex 1/1).

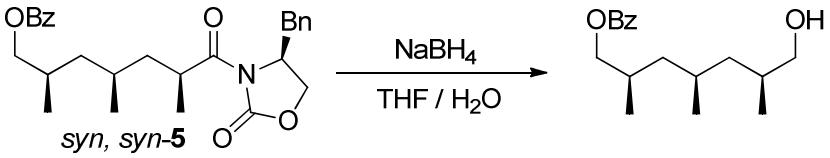
^{1}H-NMR (300 MHz, $CDCl_3$, 26°C): δ = 11.32 (brs, 1H), 8.08 – 8.00 (m, 2H), 7.59 – 7.50 (m, 1H), 7.49 – 7.38 (m, 2H), 4.20 (dd, J = 10.7, 5.4 Hz, 1H), 4.08 (dd, J = 10.7, 6.7 Hz, 1H), 2.58 (m_c, 1H), 2.07 (m_c, 1H), 1.79 (m_c, 1H), 1.65 (m_c, 1H), 1.47 – 1.33 (m, 1H), 1.18 (d, J = 7.0 Hz, 3H), 1.15 – 1.04 (m, 2H), 1.01 (d, J = 6.7 Hz, 3H), 0.95 (d, J = 6.5 Hz, 3H) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$, 26°C): δ = 183.5, 166.8, 132.9, 130.5, 129.6, 128.4, 69.90, 41.46, 40.88, 37.35, 30.15, 28.26, 20.36, 18.13, 17.64 ppm.

IR (Film) ν (cm^{-1}) = 2963, 1719, 1602, 1584, 1453, 1383, 1314, 1274, 1176, 1113, 1070, 1026, 970, 805, 712, 687, 675.

HR-MS (ESI): calcd. for: $C_{17}H_{24}O_4Na$ ($[M+Na]^+$): 315.15668; found: 315.15696.

6.2 Reductive Cleavage of Auxiliary[1]



2.81 g (6.22 mmol, 1.0 eq) of *syn, syn*-**5** were dissolved in 30 mL of a 3/1 mixture of THF/water and cooled to 0°C. 1.41 g (33.3 mmol, 6.0 eq) $NaBH_4$ were added in one portion and the reaction was warmed to RT overnight. After 18h another 2.0 eq $NaBH_4$ were added and the reaction was quenched with sat. aq. NH_4Cl after TLC showed full consumption of the starting material (prolonged reaction time leads to the diol as byproduct). The reaction was diluted with ether and the organic phase was washed with water and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure and purification by flash column chromatography (EA/Hex 1/4 →1/3) gave 1.56 g (5.59 mmol, 90%) of the alcohol as a colorless liquid.

$[\alpha]_D^{22}$ = -12.0 (c = 1.0, $CHCl_3$).

TLC: R_f = 0.57 (EA/Hex 1/2).

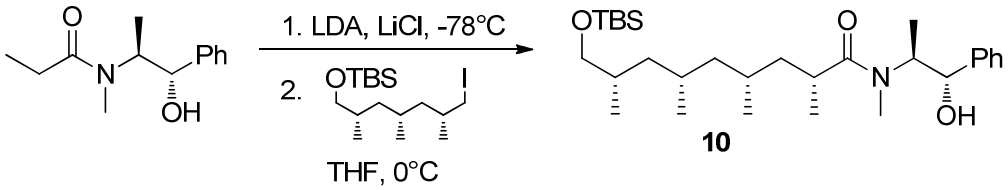
^{1}H-NMR (300 MHz, $CDCl_3$, 26°C): δ = 8.08 – 8.01 (m, 2H), 7.60 – 7.52 (m, 1H), 7.48 – 7.39 (m, 2H), 4.23 (dd, *J* = 10.8, 5.0 Hz, 1H), 4.10 (dd, *J* = 10.8, 6.7 Hz, 1H), 3.51 (dd, *J* = 10.5, 5.1 Hz, 1H), 3.38 (dd, *J* = 10.5, 6.6 Hz, 1H), 2.05 (m_c, 1H), 1.81 – 1.57 (m, 2H), 1.55 – 1.23 (m, 3H), 1.03 (d, *J* = 6.7 Hz, 3H), 1.10 – 0.97 (m, 1H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.90 (d, *J* = 6.7 Hz, 3H) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$, 26°C): δ = 166.8, 133.0, 130.6, 129.6, 128.5, 69.61, 68.17, 41.41, 41.29, 33.14, 30.35, 27.77, 20.93, 18.38, 17.61 ppm.

IR (Film) *v* (cm^{-1}) = 3427, 3063, 2957, 2918, 1719, 1602, 1584, 1452, 1387, 1314, 1274, 1197, 1176, 1114, 1070, 1027, 973, 806, 780, 712, 687, 674.

HR-MS (ESI): calcd. for: $C_{17}H_{24}O_4Na$ ($[M+Na]^+$): 301.17796; found: 301.17752.

6.3 Elongation to Tetradeoxypropionate Chain Applying Myers' Method



To a suspension of 112 mg (2.65 mmol, 6.0 eq) anhydrous LiCl in 1.5 mL THF were added 0.264 mL (1.88 mmol, 4.25 eq) diisopropyl amine and 0.743 mL (1.86 mmol, 4.2 eq) *n*BuLi (2.5M in hexane) at -78°C. The mixture was stirred for 20 min, then a solution of 205 mg (0.928 mmol, 2.1 eq) pseudoephedrine amide in 2 mL THF was added dropwise and stirred for 90 min. The reaction mixture was warmed to 0°C and a solution of 176 mg (0.442 mmol, 1.0 eq) iodide in 1 mL THF was added. The reaction was allowed warm to RT over night and stirred for an additional 18h. Excess enolate was quenched by the addition of sat. aq. NH_4Cl. The mixture was diluted with diethyl ether, washed with water and sat. aq. $NaHCO_3$. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (E/Hex 1/1 → 7/3) to give 162 mg (0.329 mmol, 75%) of tetradeoxypropionate **10** as a viscous, colorless oil.

$[\alpha]_D^{24}$ = +36.0 (c = 1.0, $CHCl_3$).

TLC: R_f = 0.39 (E/Hex 7/3).

^{1}H-NMR (6:1 rotamer ratio, asterisk denotes minor rotamer peaks, 400 MHz, $CDCl_3$, 26°C): δ = 7.40 – 7.20 (m, 5H), 4.65 – 4.51 (m, 1H), 4.40 (brs, 1H), 4.09* (m_c, 1H), 3.45 (dd, *J* = 9.7, 5.0 Hz, 1H), 3.33 (dd, *J* = 9.7, 6.6 Hz, 1H), 3.04 – 2.91* (m, 1H), 2.88* (s, 3H), 2.84 (s, 3H), 2.76 – 2.63 (m, 1H), 2.04 – 1.89* (m, 1H), 1.77 (m_c, 1H), 1.72 – 1.55 (m, 2H), 1.45 (m_c, 1H), 1.28 (m_c, 1H), 1.13 (d, *J* = 6.9 Hz, 3H), 1.05 (d, *J* = 6.7 Hz, 3H), 1.01 – 0.79 (m, 19H), 0.75 (d, *J* = 6.6 Hz, 3H), 0.02 (s, 6H) ppm.

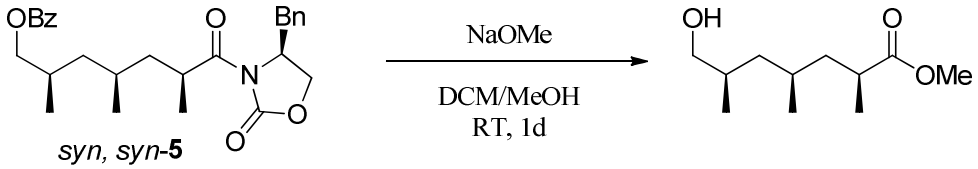
^{13}C-NMR (6:1 rotamer ratio, asterisk denotes minor rotamer peaks, 100 MHz, $CDCl_3$, 26°C): δ = 179.1, 177.8*, 142.7, 141.4*, 128.8*, 128.4, 127.5, 127.1*, 126.4, 76.56, 75.32*, 68.16, 59.25*, 58.17, 45.78*, 45.56, 41.43*, 41.28, 41.08, 34.10, 33.26, 33.18, 28.02*, 27.93, 27.56*, 27.47, 26.11*, 26.07, 21.29*, 21.11*, 20.96, 20.82, 18.93*, 18.45, 18.26, 18.12*, 18.01, 15.56*, 14.52, -5.25 ppm.

IR (Film) *v* (cm^{-1}) = 3385, 3063, 3029, 2955, 2928, 2856, 1621, 1462, 1408, 1376, 1298, 1253, 1098, 1051, 1006, 938, 836, 786, 701, 666, 520.

HR-MS (ESI): calcd. for: $C_{29}H_{53}NO_3SiNa$ ($[M+Na]^+$): 514.369242; found: 514.36936.

7 Total Synthesis of (+)-Vittatalactone

7.1 Synthesis of Hydroxy Ester



syn, syn-**5**

To a solution of *syn, syn*-**5** (1.10 g, 2.43 mmol, 1.0 eq) in DCM (24 mL, c = 0.1 M) was added NaOMe (2.24 mL, 5.4 M in MeOH, 12.2 mmol, 5.0 eq). After stirring at room temperature for 24 hours full conversion was indicated by TLC. The reaction mixture was diluted with a phosphate buffer solution pH 7 (30 mL) and water (30 mL) and extracted with ehter (3 x 50mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (EA/Hex 1/6 → 1/4) to afford 347 mg (1.72 mmol, 71 %) of the hydroxy ester as a colorless oil.

$[\alpha]_D^{23}$ = + 41.3 (c = 1.10, $CHCl_3$).

TLC: R_f = 0.77 (EA/Hex 1:1).

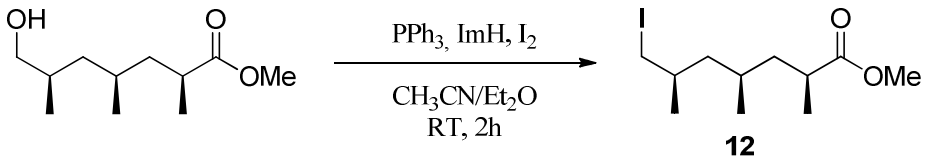
^{1}H-NMR (400 MHz, $CDCl_3$, 26°C): δ = 3.63 (s, 3H), 3.44 (dd, *J* = 5.4, 10.5 Hz, 1H), 3.34 (dd, *J* = 6.5, 10.5 Hz, 1H), 2.54 (m_c, 1H), 1.86 (s, 1H), 1.76 – 1.63 (m, 2H), 1.49 – 1.39 (m, 1H), 1.26 (ddd, *J* = 6.3, 7.4, 13.7 Hz, 1H), 1.11 (d, *J* = 7.0, 3H), 1.01 (ddd, *J* = 4.9, 9.2, 13.9 Hz, 1H), 0.92 (ddd, *J* = 6.3, 7.5, 14.1 Hz, 1H), 0.86 (d, *J* = 6.6 Hz, 6H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$, 26°C): δ = 177.6, 68.26, 51.52, 41.29, 41.21, 37.47, 33.03, 28.38, 20.47, 18.36, 17.12 ppm.

IR (Film) ν (cm^{-1}) = 3434, 2954, 2928, 2874, 1738, 1461, 1437, 1379, 1262, 1196, 1174, 1092, 1041, 987, 827, 764.

HR-MS (ESI): calcd. for $C_{11}H_{23}O_3$ ($[M+H]^+$): 203,16417; found: 203,16418.

Synthesis of Iodo Ester 12



12

To a solution of the hydroxy ester (44.4 mg, 0.219 mmol, 1.0 eq) in a 1/1 mixture of ether/CH_3CN (1.0 mL, c = 0.2 M) was added PPh_3 (98.0 mg, 0.373 mmol, 1.7 eq), imidazole (27.0 mg, 0.394 mmol, 1.9 eq), and I_2 (105 mg, 0.416 mmol, 1.8 eq). The mixture was stirred at room temperature for 2 h until full conversion was indicated by TLC. The residual iodine was reduced with sat. aq. $Na_2S_2O_3$ (10 ml) and stirred for 30 minutes. The mixture was extracted with ether (3 x 10 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure and purification by silica gel chromatography (E/Hex 1/40) gave 64.3 mg (0.206 mmol, 94 %) of iodo ester **12** as a colorless oil.

$[\alpha]_D^{23}$ = + 5.6 (c = 1.10, $CHCl_3$).

TLC: R_f = 0.51 (E/Hex 1:20).

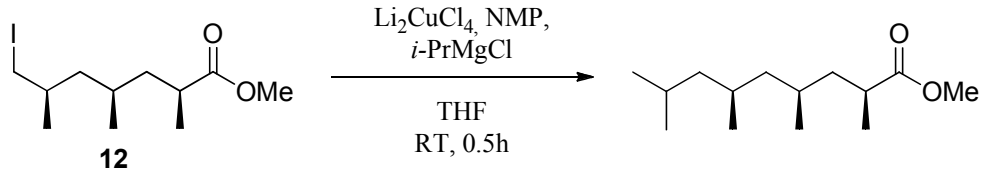
^{1}H-NMR (300 MHz, $CDCl_3$, 26°C): δ = 3.67 (s, 3H), 3.22 (dd, *J* = 4.3, 9.6 Hz, 1H), 3.13 (dd, *J* = 5.8, 9.6 Hz, 1H), 2.58 (m_c, 1H), 1.71(ddd, *J* = 4.5, 9.1, 13.9 Hz, 1H), 1.58 – 1.38 (m, 2H, 6H), 1.29 (ddd, *J* = 6.8, 6.8, 13.6 Hz, 1H), 1.16 (d, *J* = 7.0 Hz, 3H), 1.16 – 0.97 (m, 2H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.89 (d, *J* = 6.5 Hz, 3H) ppm.

^{13}C NMR (75 MHz, CDCl 26°C): δ = 177.4, 51.65, 44.24, 41.40, 37.43, 31.73, 28.35, 21.24, 20.06, 19.25, 18.28, 18.18 ppm.

IR (Film) ν (cm^{-1}) = 2957, 1737, 1460, 1434, 1379, 1311, 1260, 1194, 1171, 1090, 987, 827, 608, 588.

HR-MS (ESI): calcd. for $C_{11}H_{22}IO_2$ ($[M+H]^+$): 313,06590; found: 313,06574.

7.2 (2*S*,4*S*,6*S*)-Methyl 2,4,6,8-tetramethylnonanoate



To a solution of iodide **12** (2.39 g, 7.66 mmol, 1.0 eq) and Li_2CuCl_4 (3.83 mL, 0.38 mmol, c = 1 M in THF, 5 mol %) in a mixture of THF (7.5 mL, 1 M) and NMP (3.0 mL, 30.6 mmol, 4.0 eq) were added dropwise, at room temperature, 10.0 mL isopropyl magnesium chloride (1.0 M solution in THF, 10.0 mmol, 1.3 eq). Stirring was continued for 30 minutes until full conversion was indicated by TLC. The suspension was quenched with sat. aq. NH_4Cl (50 mL) and stirred for another 30 minutes. The mixture was extracted with ether (3 x 50mL) and solvent was removed under reduced pressure. The combined organic extracts were dried over anhydrous Na_2SO_4 and the residue was purified by silica gel chromatography (E/Hex 1/40) to afford 1.35 g (5.91 mmol, 77 %) of the ester as a colorless oil.

$[\alpha]_D^{23}$ = + 5.1 (c = 1.00, $CHCl_3$).

TLC: R_f = 0.67 (E/Hex 1:20).

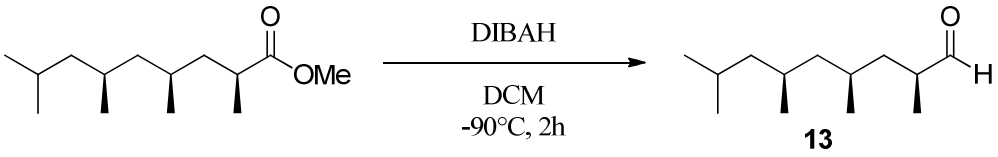
^{1}H-NMR (300 MHz, $CDCl_3$, 26°C): δ = 3.65 (s, 3H), 2.55 (m_c, 1H), 1.71 (ddd, J = 4.2, 9.3, 13.9 Hz, 1H), 1.66-1.40 (m, 3H), 1.13 (d, J = 6.9 Hz, 3H), 1.18 – 0.75 (m, 5H), 0.85 (d, J = 6.6 Hz, 6H), 0.82 (d, J = 6.6 Hz, 3H), 0.79 (d, J = 6.5 Hz, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, 26°C): δ = 176.4, 50.35, 45.74, 44.69, 40.31, 36.36, 27.12, 26.42, 24.16, 22.60, 21.11, 19.25, 19.12, 17.18 ppm.

IR (Film) ν (cm^{-1}) = 2955, 2870, 1740, 1612, 1381, 1261, 1171, 1150, 1081, 794.

HR-MS (ESI): calcd. for $C_{14}H_{28}O_2Na$ ($[M+Na]^+$): 251,19815; found: 251,19816.

(2*S*,4*S*,6*S*)-2,4,6,8-Tetramethylnonanal 13



13

To a solution of the ester (260 mg, 1.14 mmol, 1.0 eq) in 5.5 mL DCM (c = 0.2 M) was added dropwise over 10 minutes at -90°C DIBAH (1.14 ml, 1M in Hexane, 1.0 eq). The solution was warmed to -78°C over 2h and full conversion was indicated by GC-MS. The suspension was quenched with 5 mL methanol and the white residue was dissolved in 5 mL of 2N H_2SO_4. The mixture was extracted with ether (3 x 20 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure and purification by silica gel chromatography (E/Hex 1/20) gave 204 mg (1.03 mmol, 90 %) of aldehyde **13** as a colorless oil.

$[\alpha]_D^{23}$ = - 2.6 (c = 1.10, $CHCl_3$).

TLC: R_f = 0.90 (E/Hex 1/20).

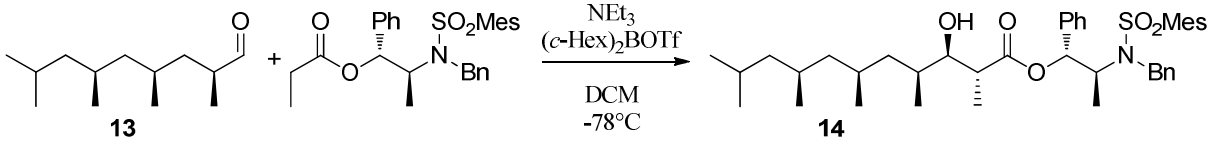
^{1}H-NMR (300 MHz, $CDCl_3$, 26°C): δ = 9.56 (d, J = 2.6 Hz, 1H), 2.43 (m_c, 1H), 1.76 – 1.48 (m, 6H), 1.21 – 1.01 (m, 3H), 1.06 (d, J = 7.0 Hz, 3H), 0.98 – 0.88 (m, 2H), 0.86 (d, J = 6.5 Hz, 3H), 0.85 (d, J = 6.6 Hz, 3H), 0.82 (d, J = 6.5 Hz, 3H), 0.81 (d, J = 6.5 Hz, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, 26°C): δ = 204.3, 45.41, 44.60, 43.06, 37.37, 26.77, 26.53, 24.17, 22.73, 20.95, 19.37, 19.32, 13.36 ppm.

IR (Film) ν (cm^{-1}) = 2956, 1708, 1465, 1415, 1384, 1227, 1093, 1020, 942, 824, 642, 562.

HR-MS (ESI): calcd. for $C_{13}H_{23}ONa$ ($[M+Na]^+$): 221,18759; found: 221,18781.

7.3 Synthesis of Norephedrine Ester 14 by *anti*-Aldol-Reaction



13 14

Into a 25 mL round-bottom flask was placed norephedrine ester (403 mg, 0.84 mmol, 1.0 eq), DCM (4.2 mL, c = 0.2M) and NEt_3 (0.28 mL, 2.02 mmol, 2.4 eq). The solution was cooled to -78°C and 1.85 mL of a freshly prepared solution of dicyclohexylboron triflate (1M in hexane, 1.85 mmol, 2.2 eq) was added over 5 minutes. The reaction mixture was stirred for 2.5 h at -78°C and the freshly prepared aldehyde **13** (200 mg, 1.01 mmol, 1.2 eq) in 1.0 mL DCM was added dropwise to the mixture. The reaction mixture was stirred for 1 h at -78°C and was then allowed to warm to room temperature over 1 h. The mixture was quenched by the addition of a phosphate buffer solution pH 7 (3.4 mL, 4 mL/mmol) and then diluted with methanol (17 mL, 20 mL/mmol) and hydrogen peroxide (1.7 mL, 33 %, 2 mL/mmol). The mixture was stirred overnight, diluted with aq. sat. NaCl and extracted with ether (4 x 20 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (EA/ Hex 1/40 → 1/30 → 1/10) to afford 490 mg (0.72 mmol, 86%) of **14** as a white solid.

$[\alpha]_D^{23}$ = + 11.4 (c = 1.10, $CHCl_3$).

TLC: R_f = 0.61 (EA/Hex 1/5).

Melting Point: 40-43°C

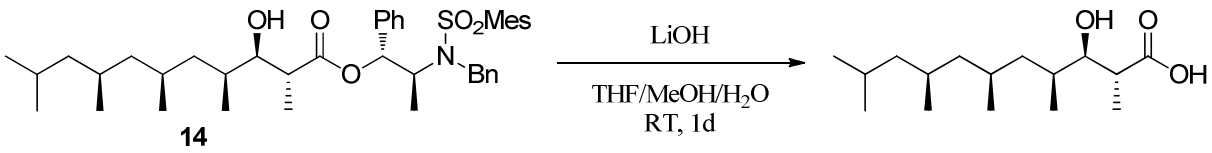
^{1}H-NMR (300 MHz, $CDCl_3$, 26°C): δ = 7.37 – 7.29 (m, 2H), 7.29 – 7.14 (m, 6H), 6.93 – 6.82 (m, 4H), 5.85 (d, *J* = 4.1 Hz, 1H), 4.81 (d, *J* = 16.6 Hz, 1H), 4.58 (d, *J* = 16.6 Hz, 1H), 4.18 – 4.06 (m_c, 1H), 3.66 (dd, *J* = 2.0, 9.2 Hz, 1H), 2.65 – 2.55 (m_c, 1H), 2.51 (s, 6H), 2.29 (s, 3H), 1.82 – 1.39 (m, 5H), 1.18 (d, *J* = 6.7 Hz, 3H), 1.07 (d, *J* = 7.1 Hz, 3H), 1.23 – 0.79 (m, 20H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, 26°C): δ = 175.3, 142.6, 140.4, 138.8, 138.4, 133.5, 132.2, 128.5 128.4, 128.0, 127.8, 127.3, 126.0, 78.37, 74.34, 56.92, 48.37, 46.62, 46.00, 43.78, 41.44, 31.06, 27.65, 27.03, 25.33, 23.92, 23.08, 22.12, 21.02, 20.59, 13.91, 13.61, 13.06 ppm.

IR (Film) ν (cm^{-1}) = 3443, 3032, 2956, 1742, 1630, 1605, 1497, 1456, 1383, 1325, 1251, 1205, 1154, 1056, 1031, 1013, 984, 930, 858, 752, 730, 698, 660, 597, 587, 537, 431, 414.

HR-MS (ESI): calcd. for $C_{42}H_{61}NaNO_5S$ ($[M\text{-}Na]^+$): 700.40062; found: 700.40082.

(2*R*,3*R*,4*S*,6*S*,8*S*)-3-Hydroxy-2,4,6,8,10-pentamethylundecanoic acid



Ester **14** (127.5 mg, 0.188 mmol, 1.0 eq) was dissolved in a mixture of THF/MeOH/H_2O (1/1/1, 1.8 mL, c = 0.1 M) and treated with LiOH (22.6 mg, 0.940 mmol, 5.0 eq). The reaction mixture was stirred for 24 h until full conversion was indicated by TLC. The mixture was diluted with 15 mL water and acidified with 4 N HCl to pH 1. The aqueous layer was extracted with DCM (4 x 10 mL), the combined organic extracts were dried over anhydrous Na_2SO_4 and solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (EA/H 1/10 → EA/ Hex 1/5 + 1 % AcOH) to afford 41.6 mg (0.153 mmol, 81 %) of hydroxy acid as a viscous, colorless oil.

$[\alpha]_D^{23}$ = - 13.0 (c = 1.00, $CHCl_3$).

TLC: R_f = 0.45 (EA/Hex 2/1, 5 % AcOH).

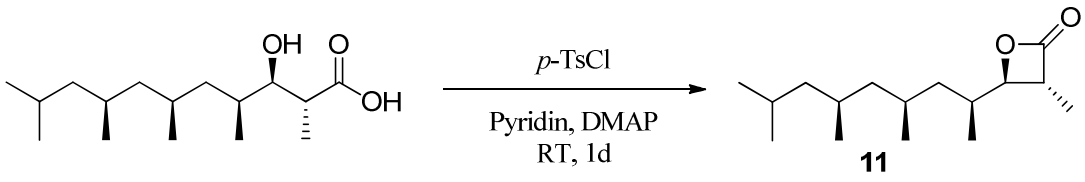
^{1}H-NMR (400 MHz, $CDCl_3$, 26°C): δ = 3.66 (dd, *J* = 2.8, 8.8 Hz, 1H), 2.64 (dq, *J* = 7.1, 14.3 Hz, 1H), 1.75 (ddq, *J* = 2.9, 7.0, 14.0 Hz, 1H), 1.68 – 1.53 (m, 3H), 1.45 (ddd, *J* = 6.2, 7.5, 13.6 Hz, 1H), 1.14-1.20 (m, 1H), 1.17 (d, *J* = 7.1 Hz, 3H), 1.10 (ddd, *J* = 3.5, 8.1, 13.6 Hz, 1H), 1.00 (dd, *J* = 6.9, 13.7 Hz, 1H), 0.96 – 0.90 (m, 2H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H), 0.85 (d, *J* = 6.5 Hz, 3H), 0.84 (d, *J* = 6.5 Hz, 3H), 0.83 (d, *J* = 6.5 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, 26°C): δ = 181.8, 75.04, 46.60, 45.90, 43.59, 41.50, 31.53, 27.69, 27.15, 25.34, 23.94, 22.11, 20.71, 20.65, 14.19, 13.15 ppm.

IR (Film) ν (cm^{-1}) = 2957, 2927, 2029, 1959, 1714, 1461, 1383, 1209, 982, 788.

HR-MS (ESI): calcd. for $C_{42}H_{62}NO_5SNa$ ($[M\text{-}Na]^+$): 700.40062; found: 700.40082.

7.4 (+)-Vittalactone 11



To a solution of the hydroxy acid (38.4 mg, 0.141 mmol, 1.0 eq) in pyridine (0.35 mL, 0.4 M) and DMAP (1.7 mg, 0.014 mmol, 0.1 eq) was added *p*-TsCl (54.0 mg, 0.282 mmol, 2.0 eq) at room temperature. After stirring for 24 h full conversion was indicated by TLC. The reaction mixture was diluted with 10 mL ether and the precipitate was filtered off. The solution was dried over anhydous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (E/ Hex 1/10) to afford 29.3 mg (0.114 mmol, 81 %) of vittatalactone **11** as a colorless oil.

$[\alpha]_D^{23}$ = + 2.5 (c = 0.80, $CHCl_3$). (Lit.: $[\alpha]_D^{23}$= +1.2, c = 1.29, DCM [2], *ent*-**11**: $[\alpha]_D^{23}$= -2.6, c = 0.47 $CHCl_3$[3])

TLC: R_f = 0.66 (EA/Hex 5/1).

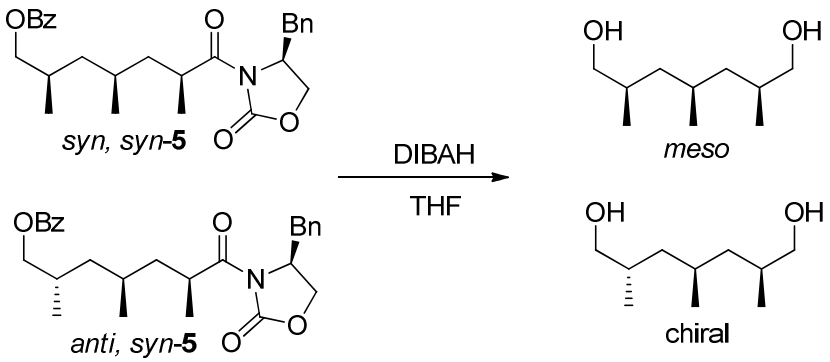
^{1}H-NMR (300 MHz, $CDCl_3$, 26°C): δ = 3.87 (dd, *J* = 4.0, 8.2 Hz, 1H), 3.24 (dq, *J* = 4.1, 7.5 Hz, 1H), 1.87 (m_c, 1H), 1.72 – 1.48 (m, 3H), 1.39 (d, *J* = 7.5 Hz, 3H), 1.27 – 0.96 (m, 4H), 1.02 (d, *J* = 6.6 Hz, 3H), 0.94-0.81 (m, 2H), 0.90 (d, *J* = 6.1 Hz, 3H), 0.88 (d, *J* = 6.1 Hz, 3H), 0.84 (d, *J* = 6.5 Hz, 6H) ppm.

^{13}C NMR (75 MHz, $CDDl_3$, 26°C): δ = 172.3, 83.99, 49.13, 46.24, 45.39, 40.05, 35.03, 27.89, 27.54, 25.43, 24.13, 22.03, 21.26, 20.99, 16.02, 13.13 ppm.

IR (Film) *v* (cm^{-1}) = 2957, 2927, 2029, 1959, 1714, 1461, 1383, 1209, 982, 788.

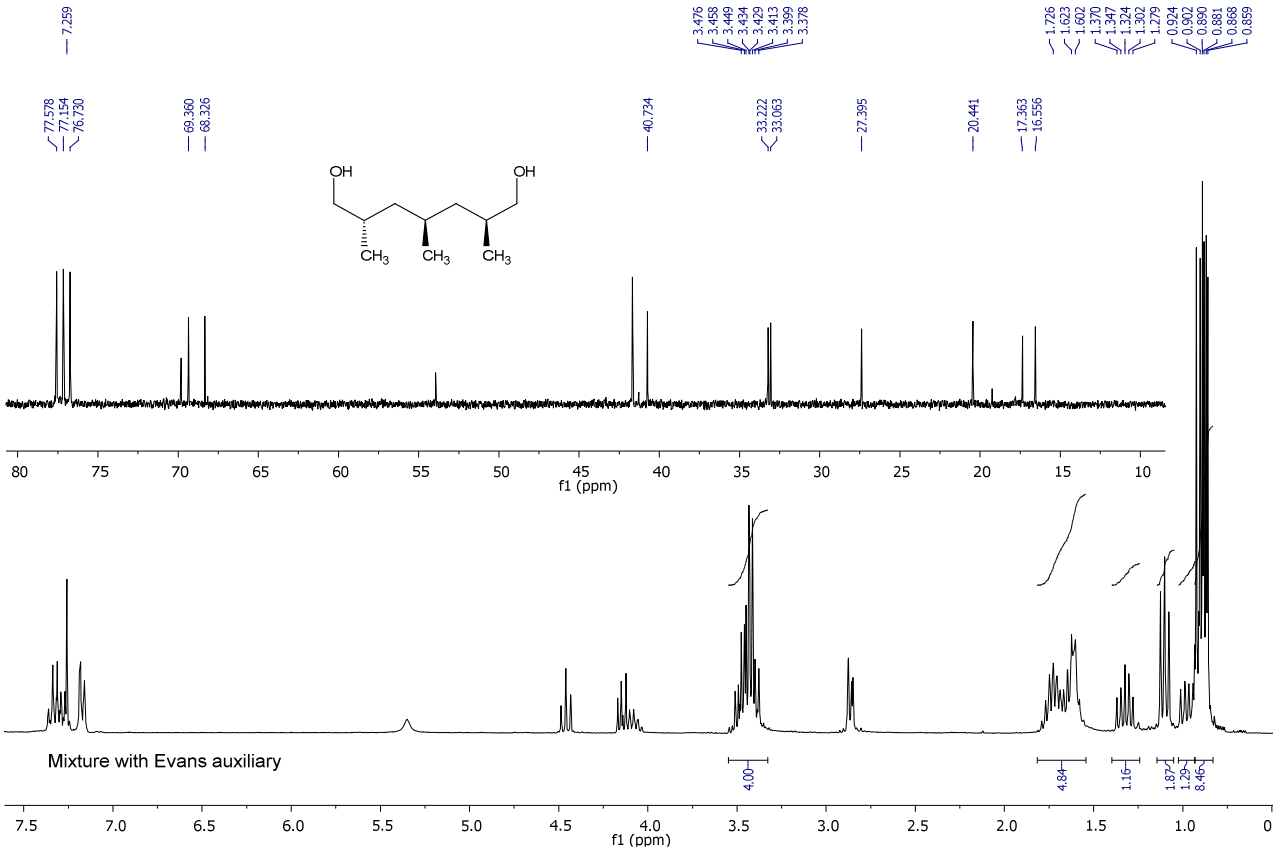
HR-MS (ESI): calcd. for $C_{16}H_{30}O_2Na$ ($[M+Na]^+$): 277.21380; found: 277.21406.

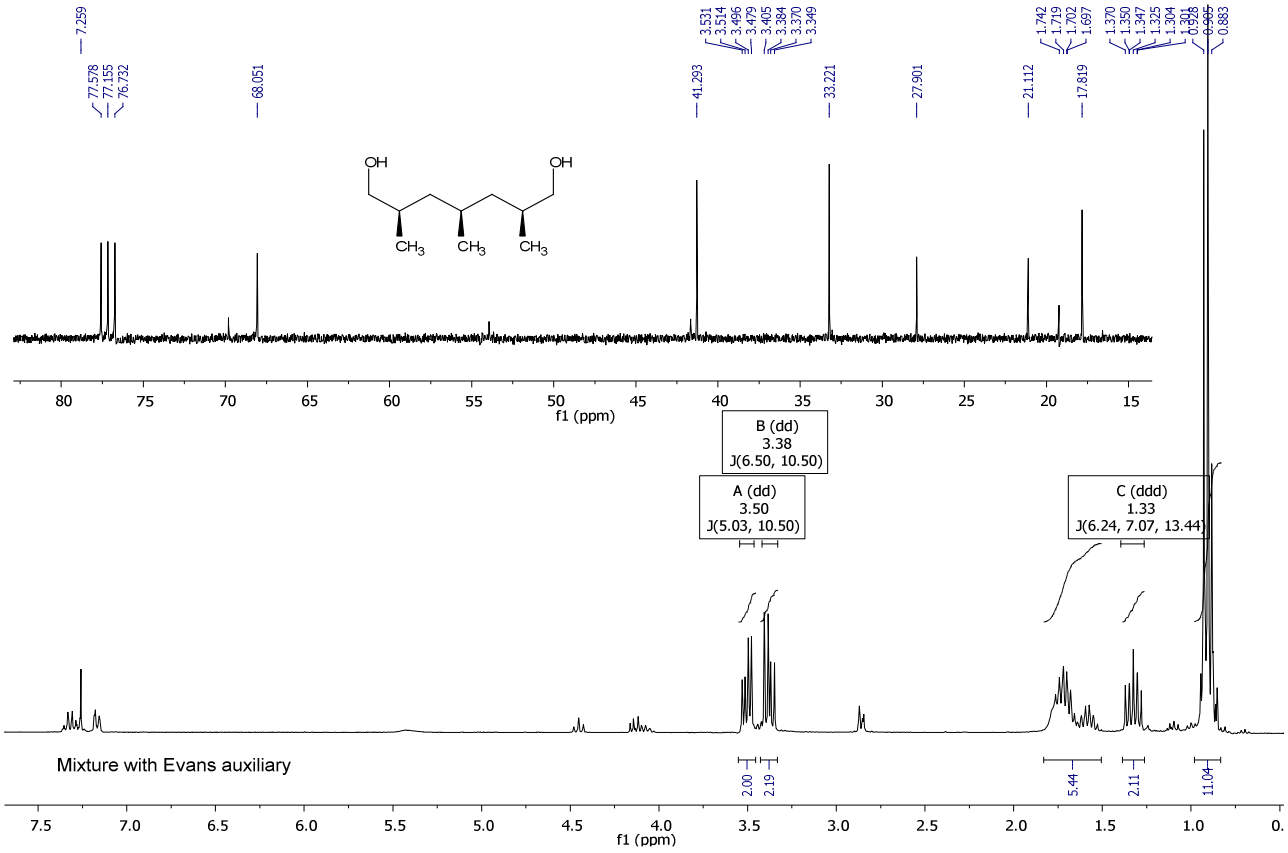
8 Determination of Relative Configuration of Trideoxypropionates



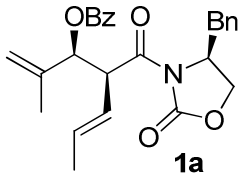
To determine the stereoinduction of [Ir(cod)**3d**]BAr_F and of [Ir(cod)*ent*-**3d**]BAr_F the two *alpha*-methylation products *syn, syn*-**5** and *anti, syn*-**5** were treated with DIBAH in THF

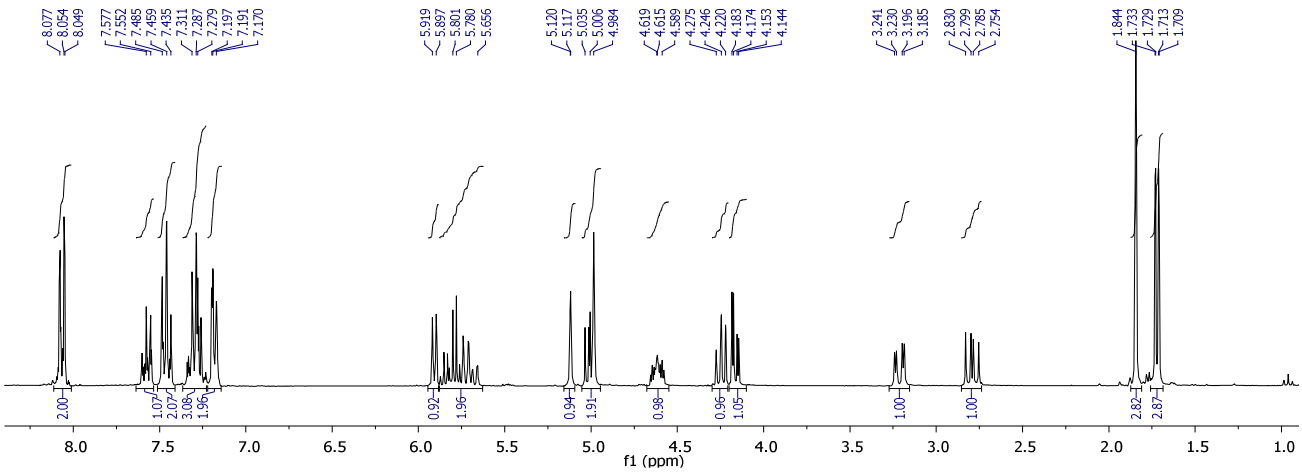
to give the corresponding, fully reduced diols. Whereas the diol derived from *anti, syn*-**5** shows a full set of signals (10 carbon signals) in the ^{13}C- and ^{1}H-NMR spectrum, the diol derived from *syn, syn*-**5**, due to its *meso*-nature, shows only a reduced set of singals (6 carbon signals). The spectra of the diols are shown below. Since the diols could not be separated from the cleaved auxiliary, optical rotation could not be used for analysis of the diols.

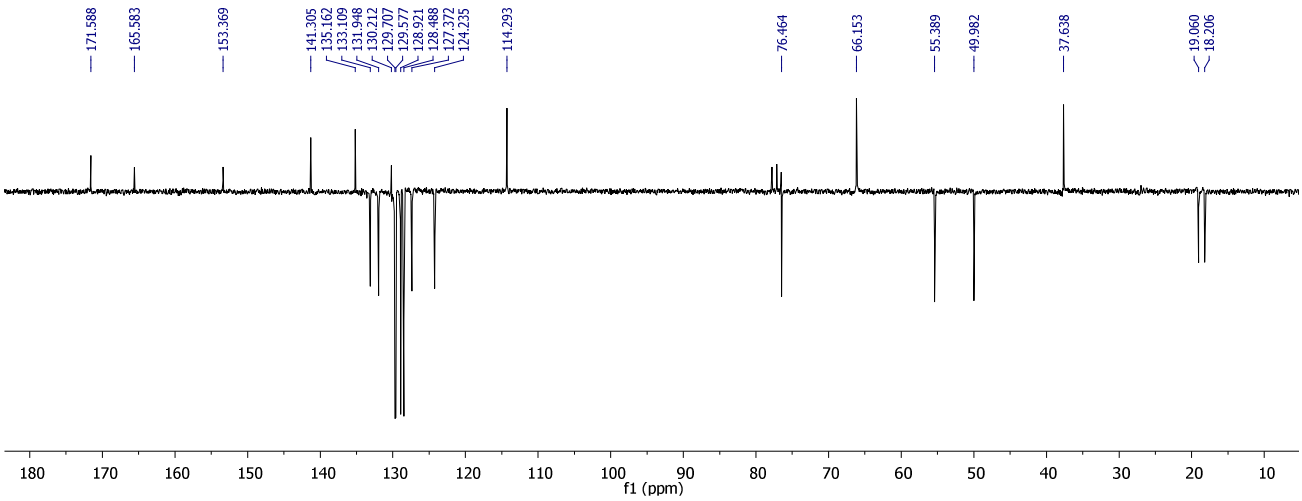


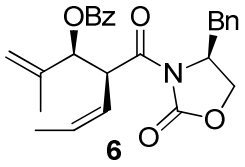


9 NMR Spectra

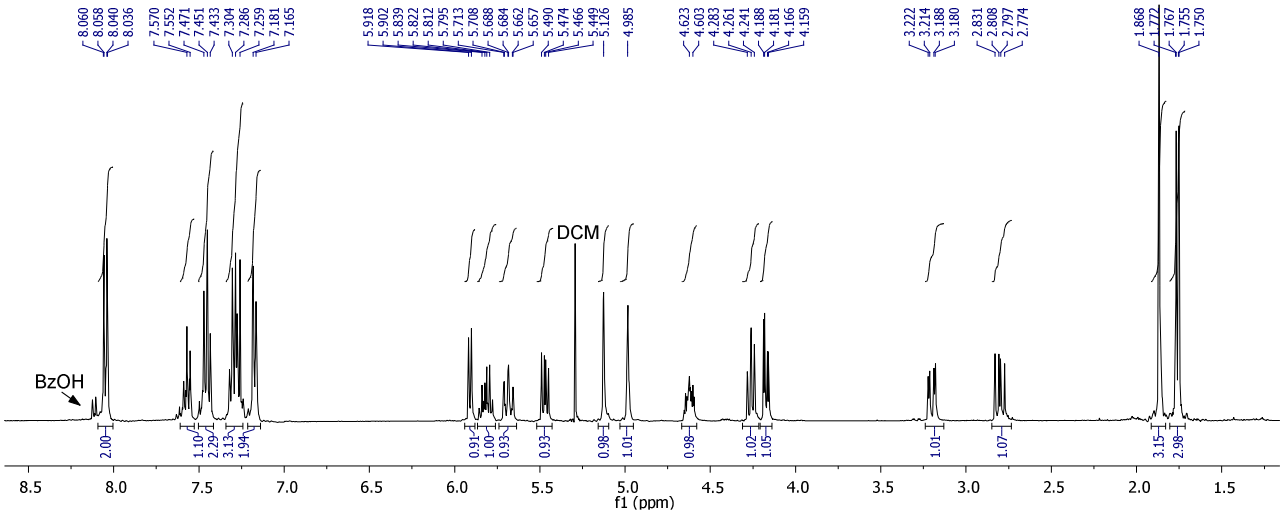


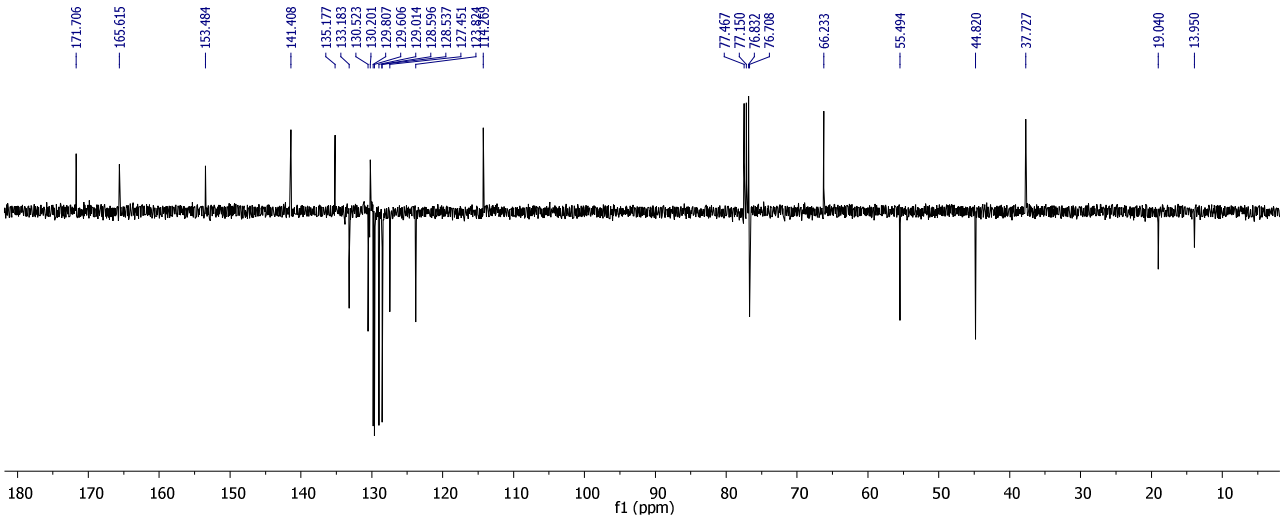


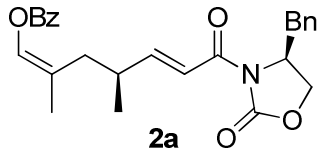

171.588
165.583
153.369
141.305
135.162
133.109
131.948
130.212
129.707
129.577
128.921
128.488
127.372
124.235
114.293
76.464
66.153
55.389
49.982
37.638
19.060
18.206
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



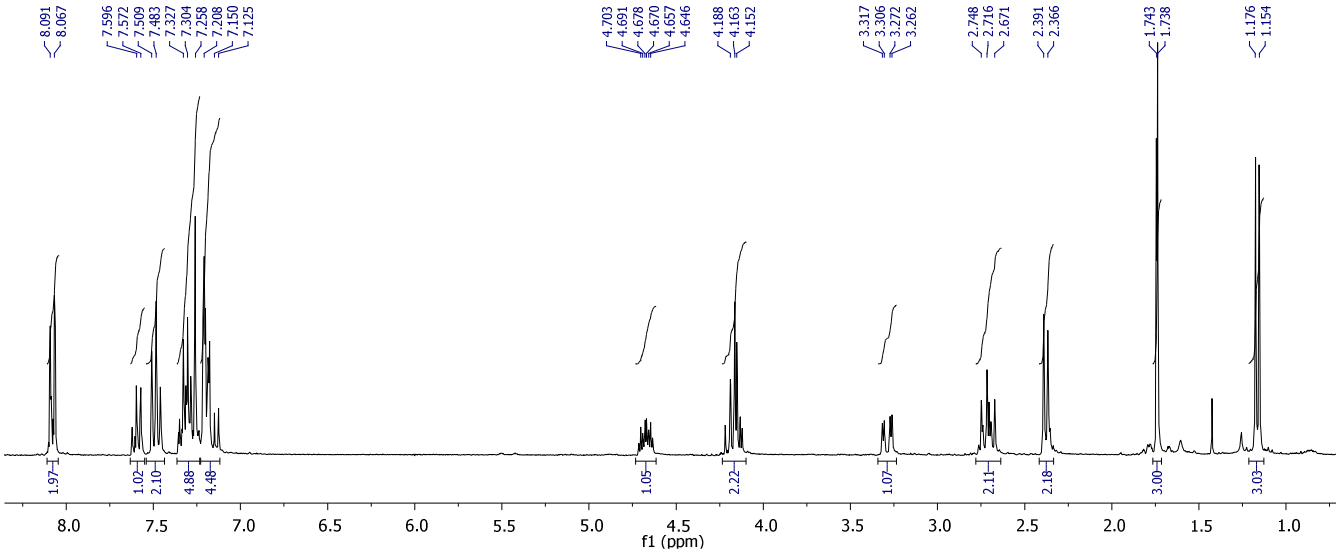
6






OBz
O
Bn
N
O
O

2a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7.596
7.572
7.509
7.483
7.327
7.304
7.258
7.208
7.150
7.125
4.703
4.691
4.678
4.670
4.657
4.646
4.188
4.163
4.152
3.317
3.306
3.272
3.262
2.748
2.716
2.671
2.391
2.366
1.743
1.738
1.176
1.154
1.97
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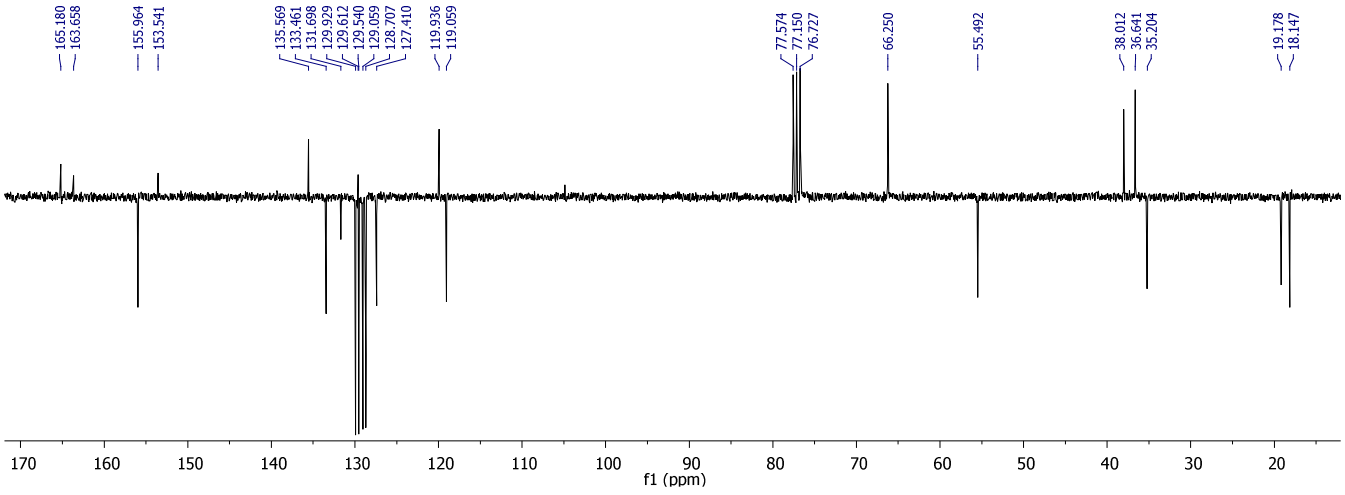
1.07
2.11
2.18
3.00
3.03
f1 (ppm)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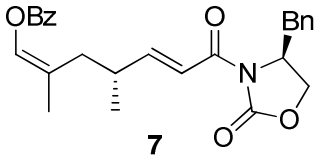
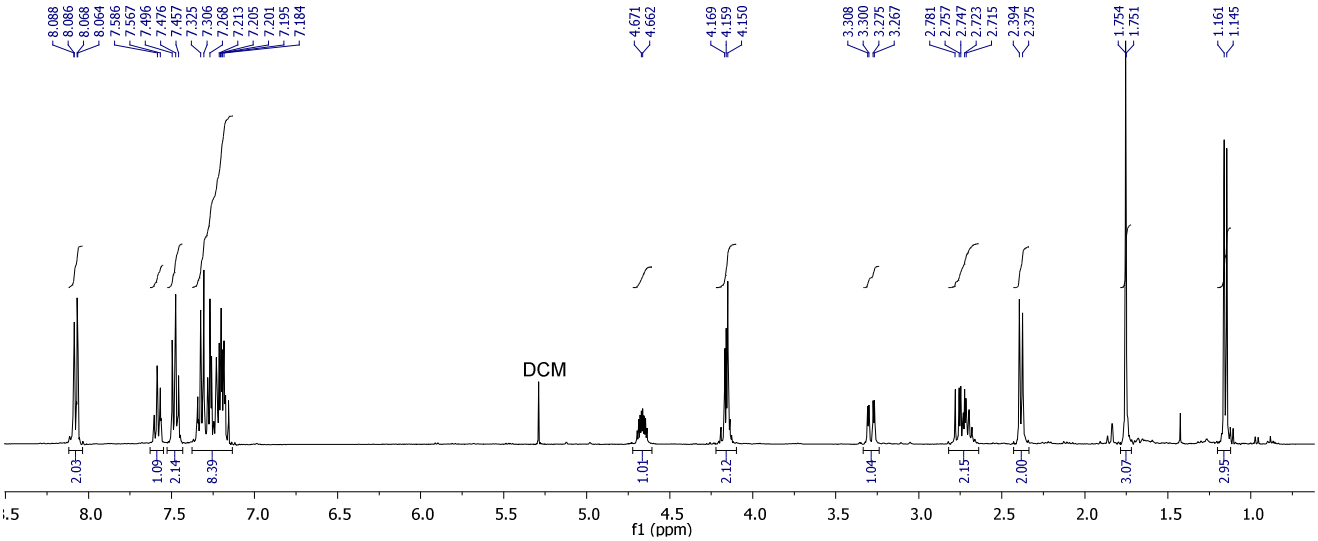
155.964
153.541
135.569
133.461
131.698
129.929
129.612
129.540
129.059
128.707
127.410
119.936
119.059
77.574
77.150
76.727
66.250
55.492
38.012
36.641
35.204
19.178
18.147
f1 (ppm)


OBz
O
Bn
N
O
O

7


8.088
8.086
8.068
8.064
7.586
7.567
7.496
7.476
7.457
7.325
7.306
7.268
7.213
7.205
7.201
7.195
7.184
4.671
4.662
4.169
4.159
4.150
3.308
3.300
3.275
3.267
2.781
2.757
2.747
2.723
2.715
2.394
2.375
1.754
1.751
1.161
1.145
DCM
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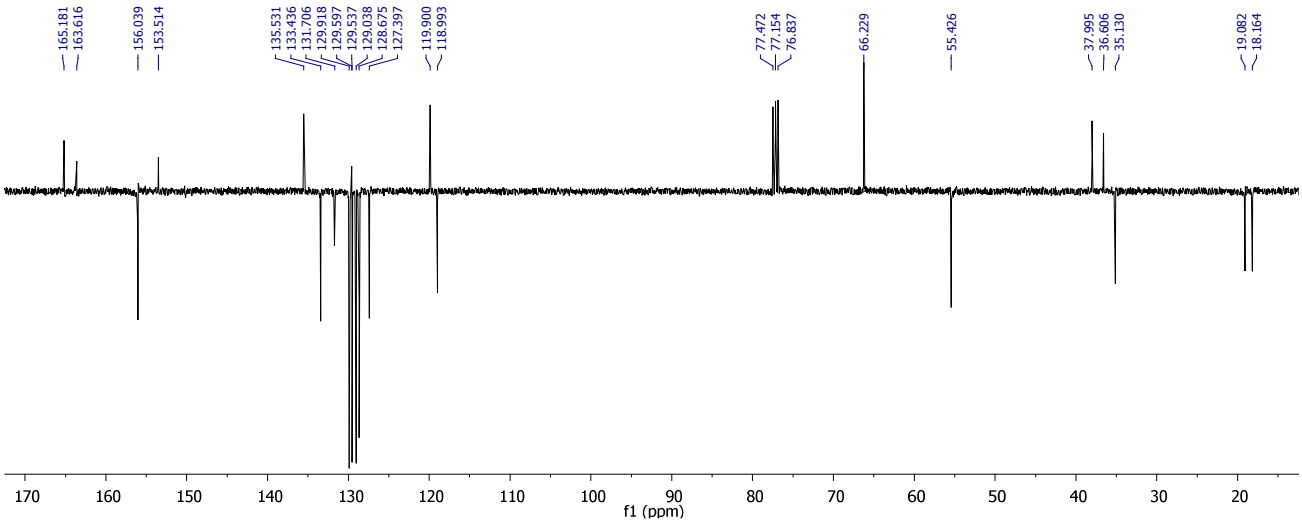
1.04
2.15
2.00
3.07
2.95
f1 (ppm)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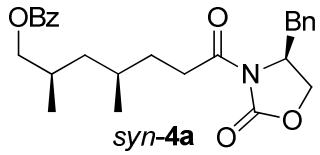
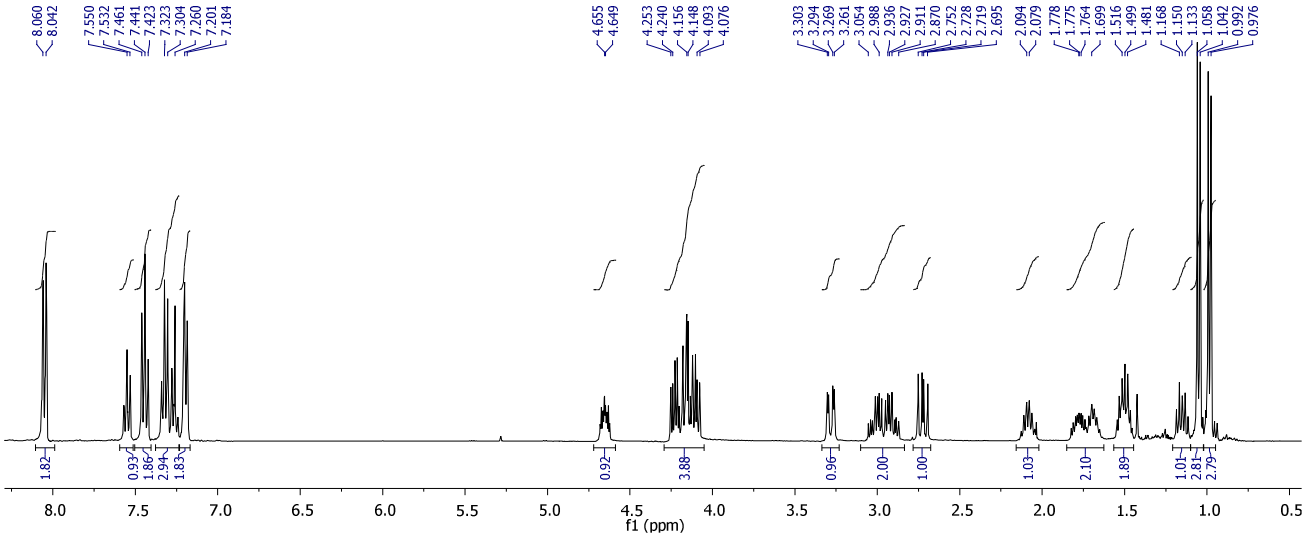
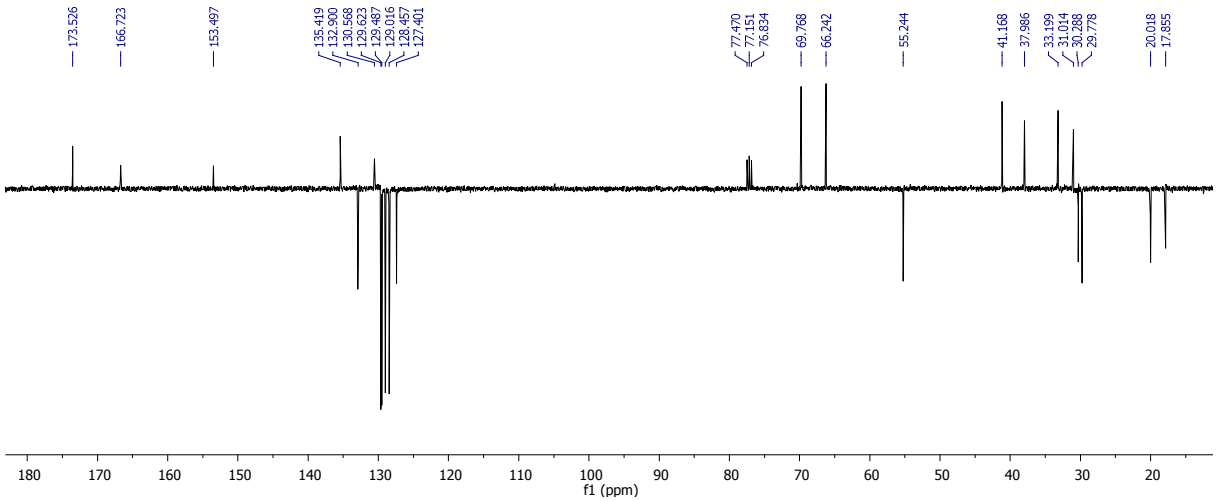
163.616
156.039
153.514
135.531
133.436
131.706
129.918
129.597
129.537
129.038
128.675
127.397
119.900
118.993
77.472
77.154
76.837
66.229
55.426
37.995
36.606
35.130
19.082
18.164
f1 (ppm)


OBz
O
Bn
N
O
O

syn-**4a**


8.060
8.042
7.550
7.532
7.461
7.441
7.423
7.323
7.304
7.260
7.201
7.184
4.655
4.649
4.253
4.240
4.156
4.148
4.093
4.076
3.303
3.294
3.269
3.261
3.054
2.988
2.936
2.927
2.911
2.870
2.752
2.728
2.719
2.695
2.094
2.079
1.778
1.775
1.764
1.699
1.516
1.499
1.481
1.168
1.150
1.133
1.058
1.042
0.992
0.976
1.82
0.93
1.86
2.94
1.83
0.92
3.88
0.96
2.00
1.00
1.03
2.10
1.89
1.01
2.81
2.79
f1 (ppm)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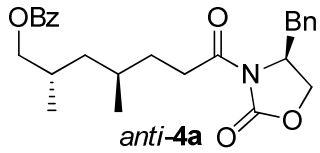
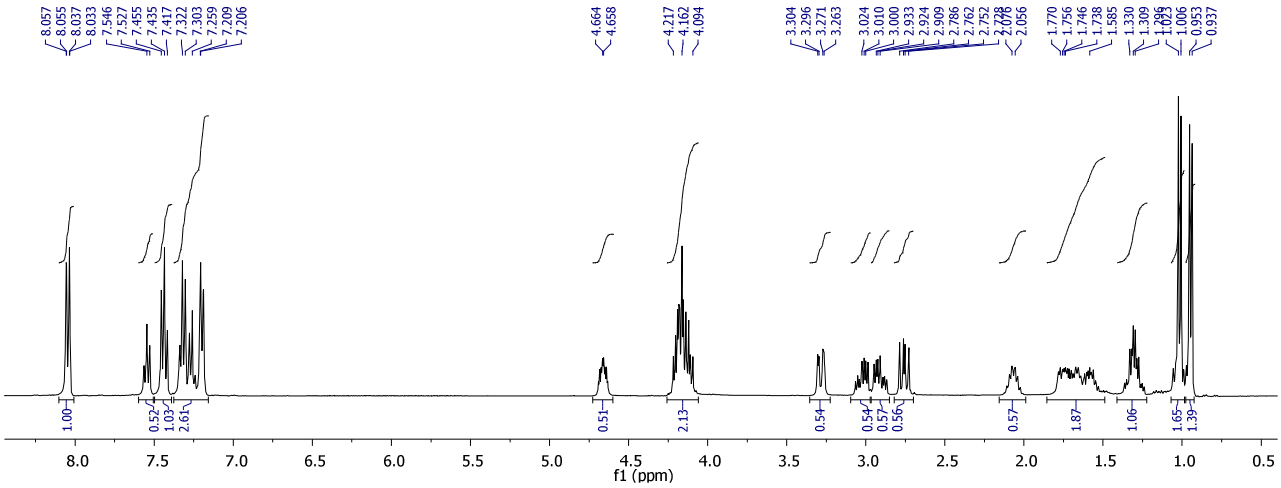
166.723
153.497
135.419
132.900
130.568
129.623
129.487
129.016
128.457
127.401
77.470
77.151
76.834
69.768
66.242
55.244
41.168
37.986
33.199
31.014
30.288
29.778
20.018
17.855
f1 (ppm)


OBz
O
Bn
N
O
O

anti-**4a**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8.037
8.033
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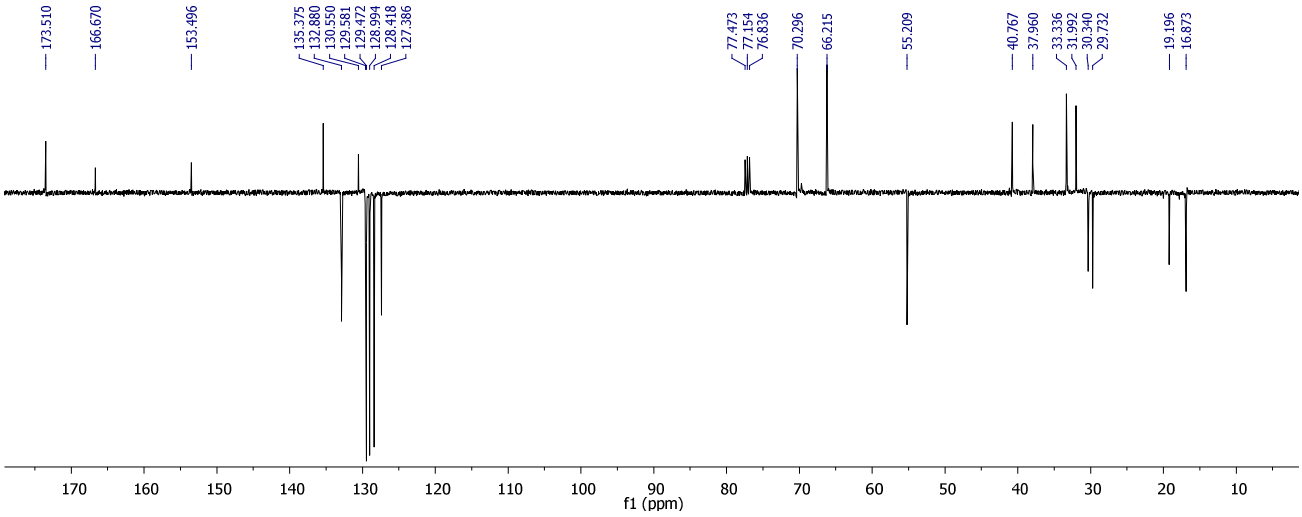
7.527
7.455
7.435
7.417
7.322
7.303
7.259
7.209
7.206
4.664
4.658
4.217
4.162
4.094
3.304
3.296
3.271
3.263
3.024
3.010
3.000
2.933
2.924
2.909
2.786
2.762
2.752
2.728
2.078
2.056
1.770
1.756
1.746
1.738
1.585
1.330
1.309
1.006
0.953
0.937
1.00
0.52
1.05
2.61
0.51
2.13
0.54
0.54
0.57
0.56
0.57
1.87
1.06
1.65
1.39
f1 (ppm)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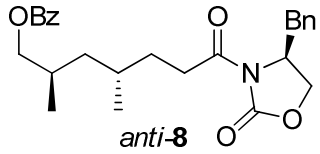
130.550
129.581
129.472
128.994
128.418
127.386
77.473
77.154
76.836
70.296
66.215
55.209
40.767
37.960
33.336
31.992
30.340
29.732
19.196
16.873
f1 (ppm)


OBz
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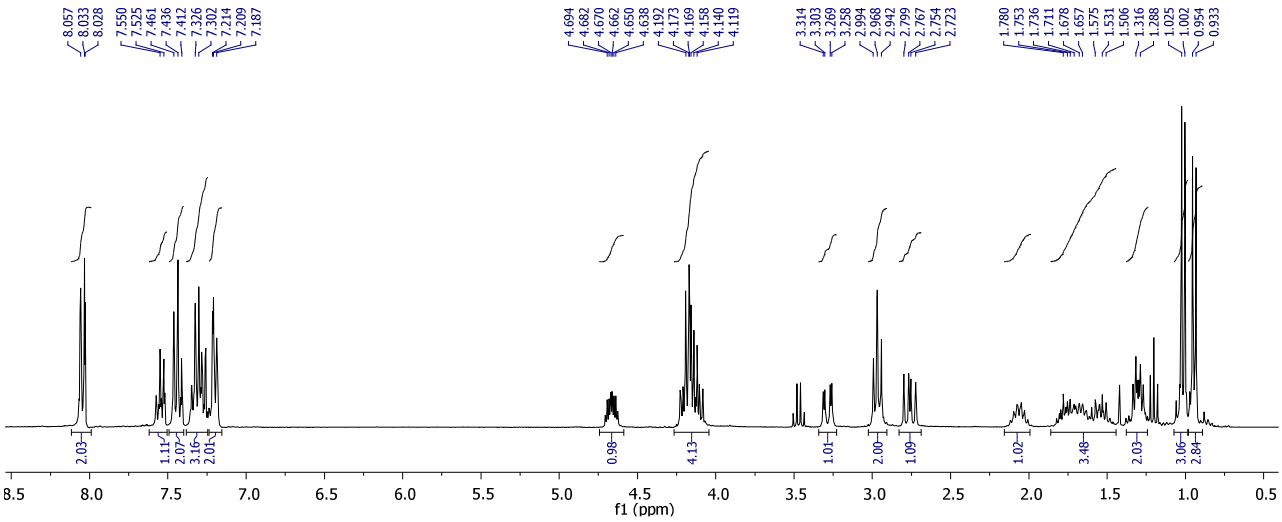
Bn
N
O
O

anti-**8**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8.028
7.550
7.525
7.461
7.436
7.412
7.326
7.302
7.214
7.209
7.187
4.694
4.682
4.670
4.662
4.650
4.638
4.192
4.173
4.169
4.158
4.140
4.119
3.314
3.303
3.269
3.258
2.994
2.968
2.942
2.799
2.767
2.754
2.723
1.780
1.753
1.736
1.711
1.678
1.657
1.575
1.531
1.506
1.316
1.288
1.025
1.002
0.954
0.933
2.03
1.11
2.07
3.16
2.01
0.98
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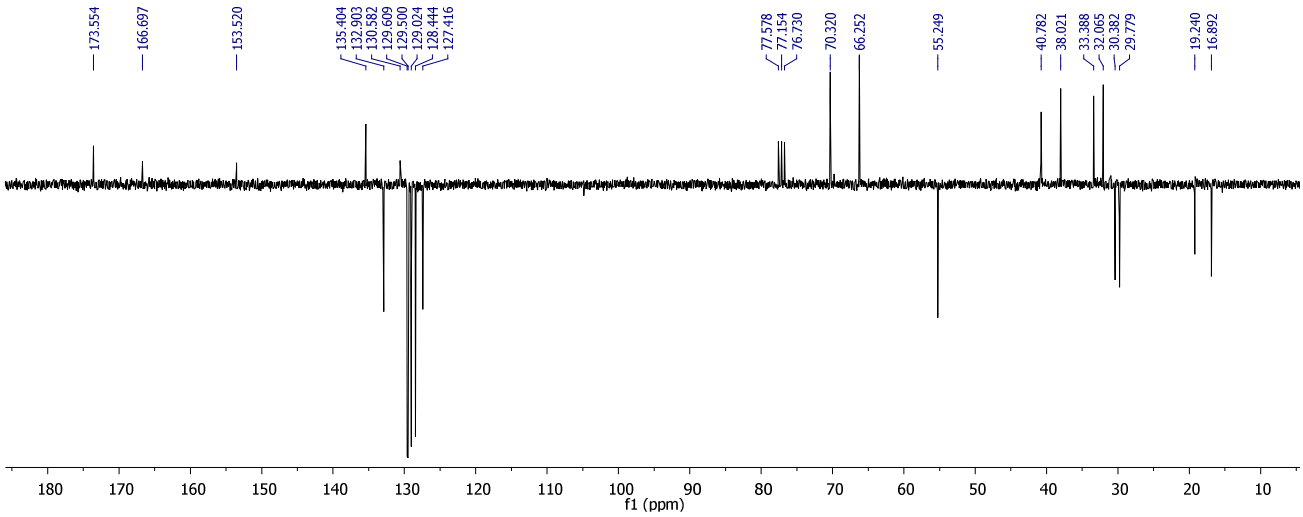
1.01
2.00
1.09
1.02
3.48
2.03
3.06
2.84
f1 (ppm)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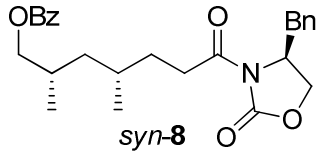
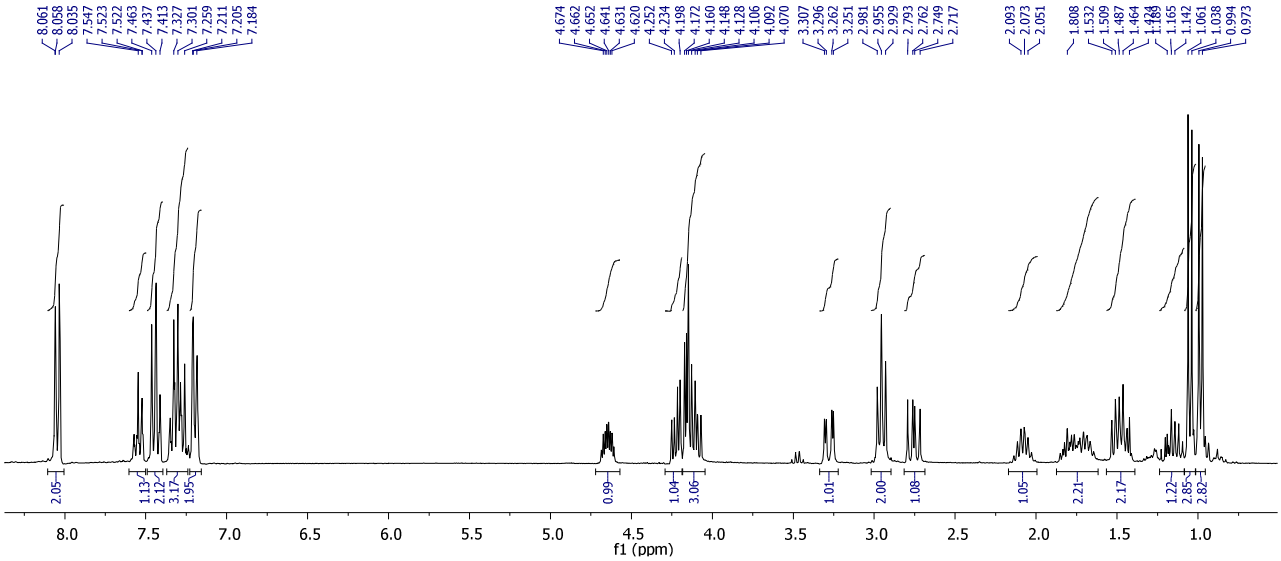
132.903
130.582
129.609
129.500
129.024
128.444
127.416
77.578
77.154
76.730
70.320
66.252
55.249
40.782
38.021
33.388
32.065
30.382
29.779
19.240
16.892
f1 (ppm)


OBz
O
Bn
N
O
O

syn-**8**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8.058
8.035
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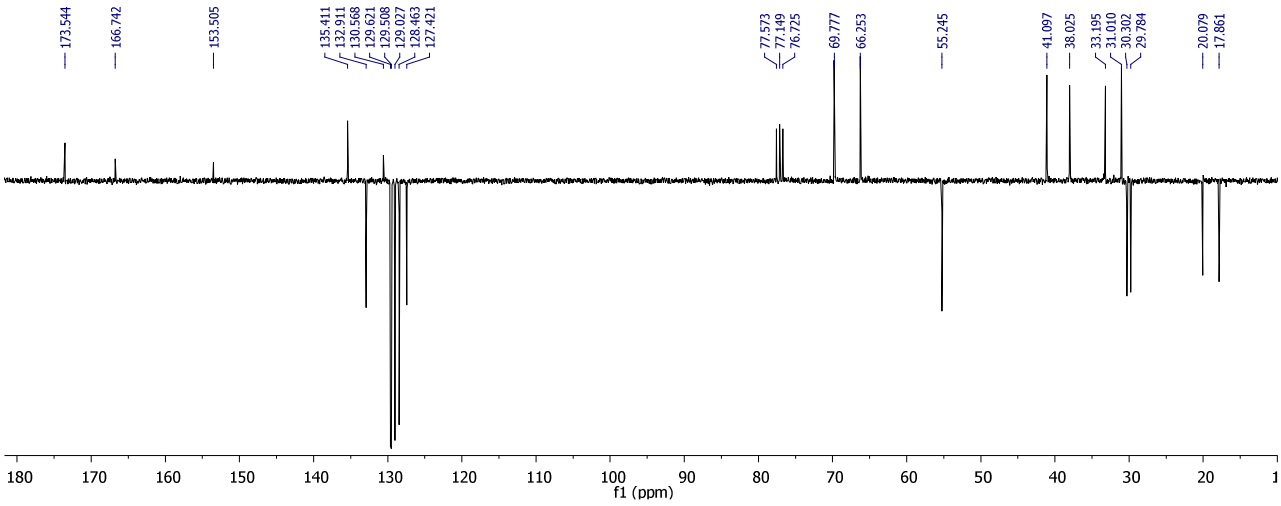
7.523
7.522
7.463
7.437
7.413
7.327
7.301
7.239
7.211
7.205
7.184
4.674
4.662
4.652
4.641
4.631
4.620
4.252
4.234
4.198
4.172
4.160
4.148
4.128
4.106
4.092
4.070
3.307
3.296
3.262
3.251
2.981
2.955
2.929
2.793
2.762
2.749
2.717
2.093
2.073
2.051
1.808
1.532
1.509
1.487
1.464
1.165
1.142
1.061
1.038
0.994
0.973
2.05
1.13
2.12
3.17
1.95
0.99
1.04
3.06
1.01
2.00
1.08
1.05
2.21
2.17
1.22
2.85
2.82
f1 (ppm)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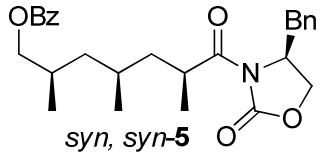
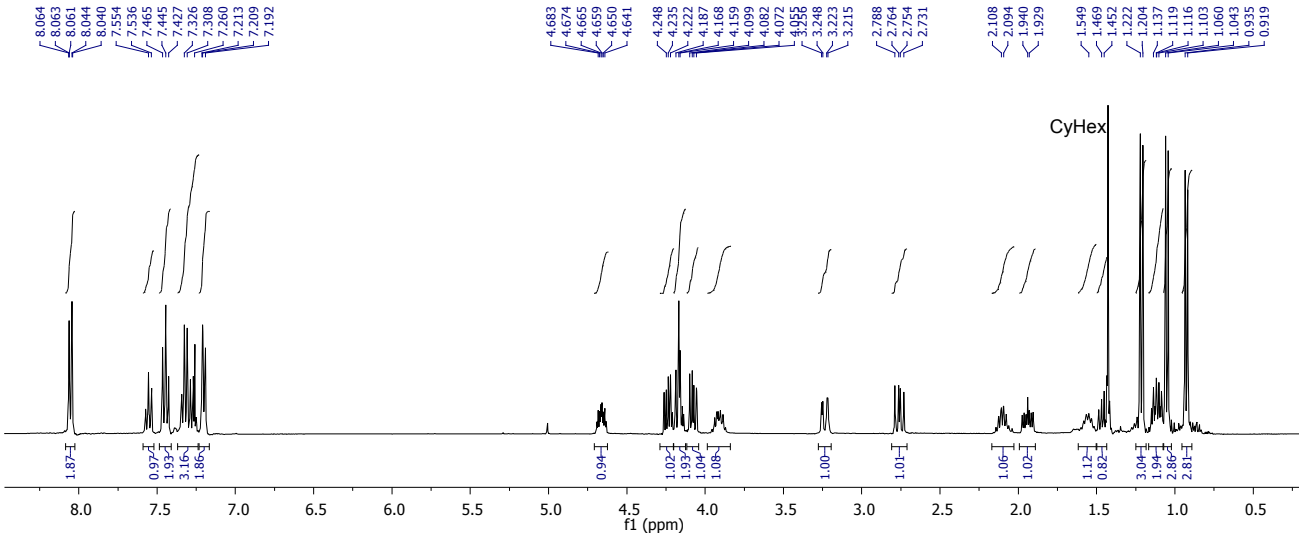
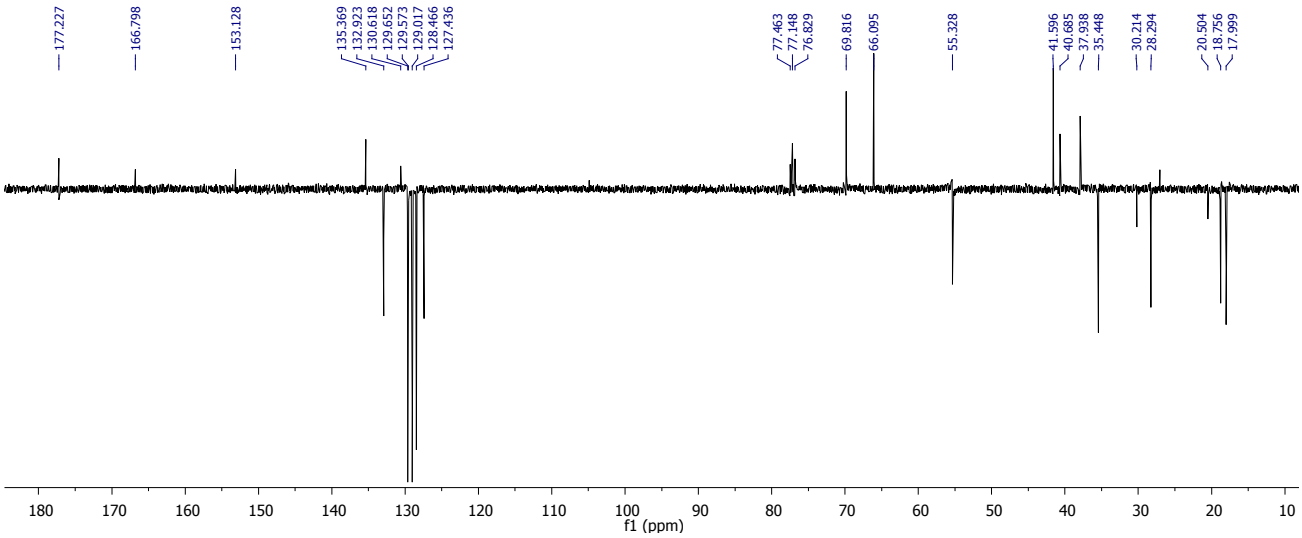
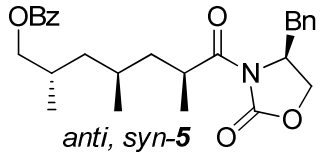
132.911
130.568
129.621
129.508
129.027
128.463
127.421
77.573
77.149
76.725
69.777
66.253
55.245
41.097
38.025
33.195
31.010
30.302
29.784
20.079
17.861
f1 (ppm)



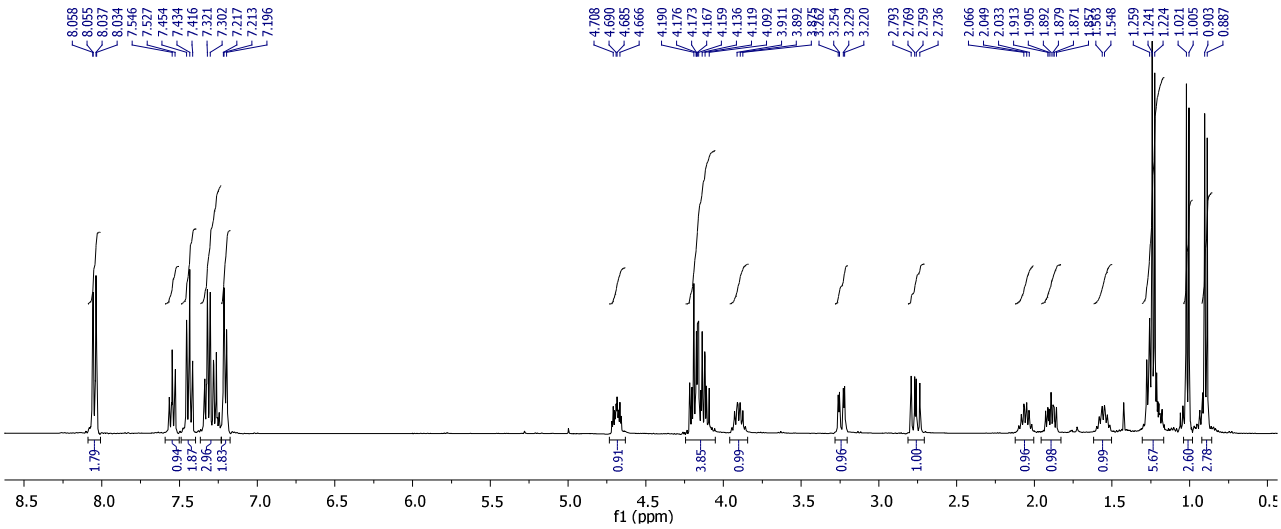
syn, syn-**5**






OBz
O
Bn
N
O
O

*anti, syn-**5***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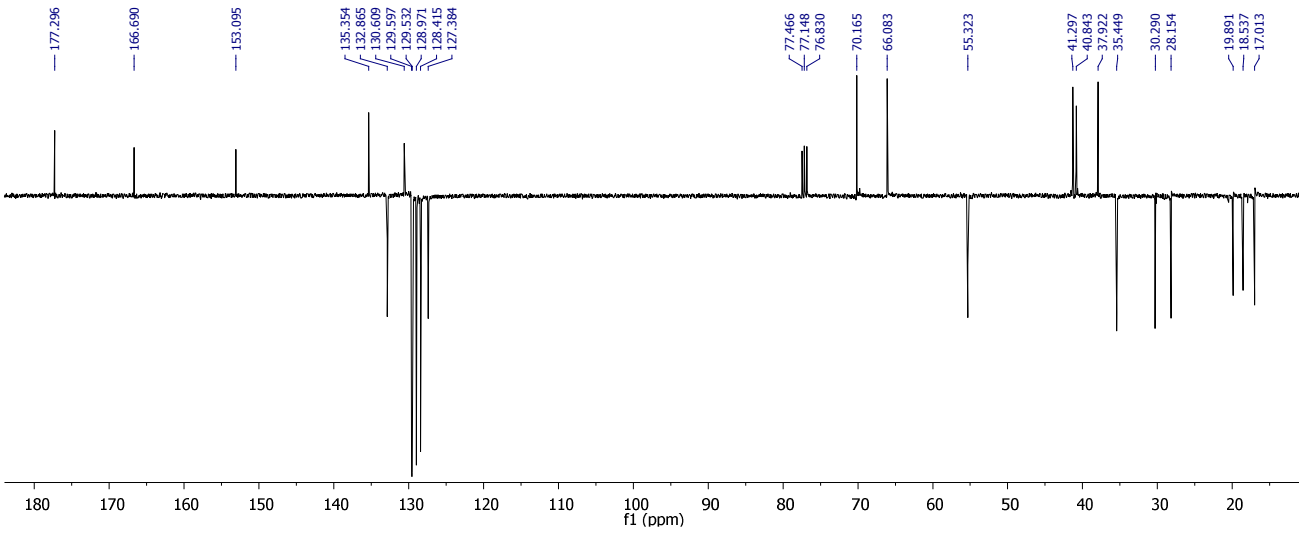
7.434
7.416
7.321
7.302
7.217
7.213
7.196
4.708
4.690
4.685
4.666
4.190
4.176
4.173
4.167
4.159
4.136
4.119
4.092
3.911
3.892
3.254
3.229
3.220
2.793
2.769
2.759
2.736
2.066
2.049
2.033
1.913
1.905
1.892
1.879
1.871
1.548
1.259
1.241
1.224
1.021
1.005
0.903
0.887
1.79
0.94
1.87
2.96
1.83
0.91
3.85
0.99
0.96
1.00
0.96
0.98
0.99
5.67
2.60
2.78
f1 (ppm)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129.532
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76.830
70.165
66.083
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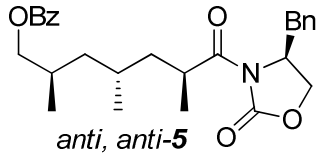
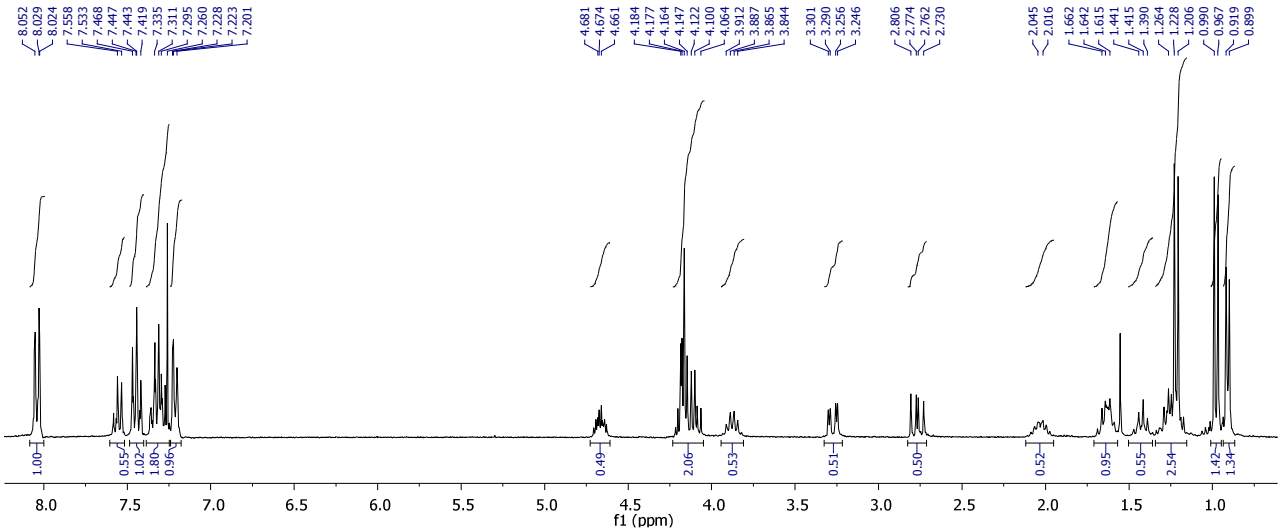
40.843
37.922
35.449
30.290
28.154
19.891
18.537
17.013
f1 (ppm)


OBz
O
Bn
N
O
O

*anti, anti-**5***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7.419
7.335
7.311
7.295
7.260
7.228
7.223
7.201
4.681
4.674
4.661
4.184
4.177
4.164
4.147
4.122
4.100
4.064
3.912
3.887
3.865
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3.301
3.290
3.256
3.246
2.806
2.774
2.762
2.730
2.045
2.016
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1.642
1.615
1.441
1.415
1.390
1.264
1.228
1.206
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0.967
0.919
0.899
1.00
0.55
1.02
1.80
0.96
0.49
2.06
0.53
0.51
0.50
0.52
0.95
0.55
2.54
1.42
1.34
8.0
7.5
7.0
6.5
6.0
5.5
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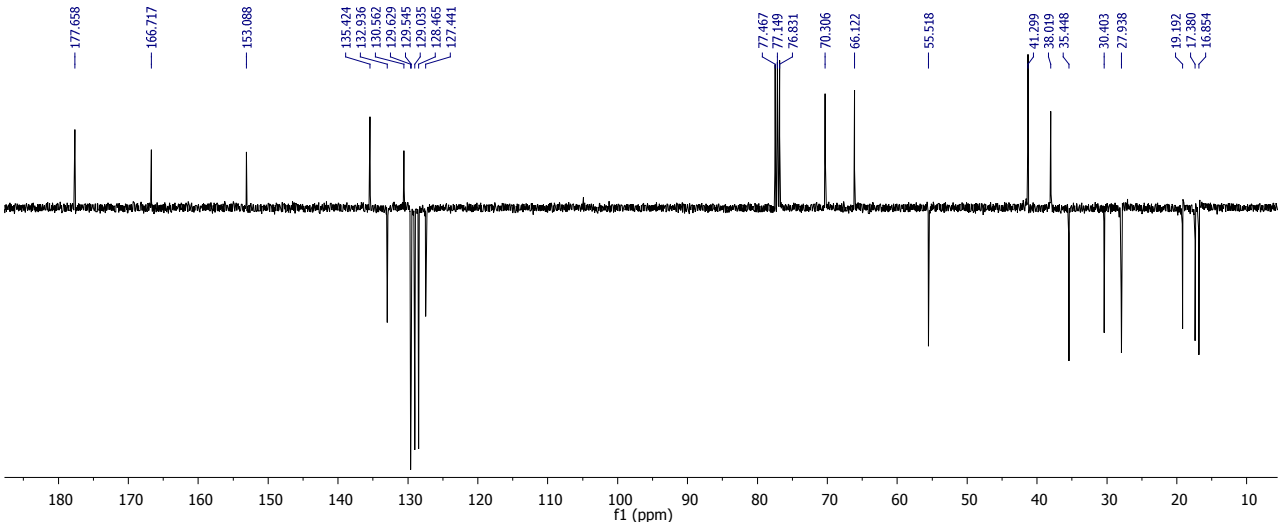
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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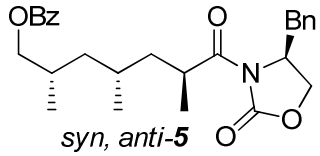
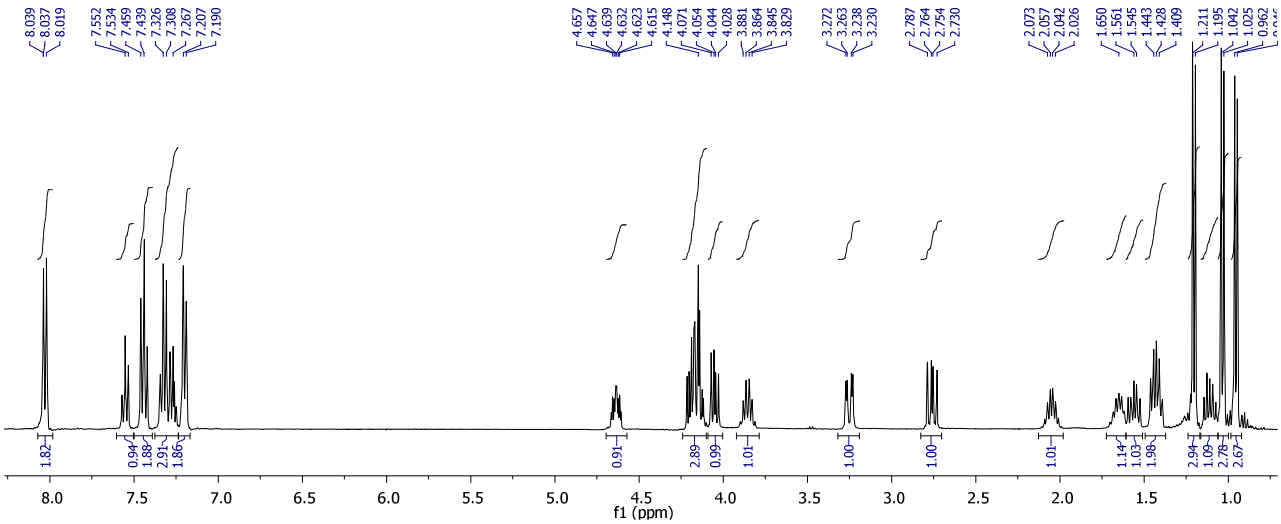
129.545
129.035
128.465
127.441
77.467
77.149
76.831
70.306
66.122
55.518
41.299
38.019
35.448
30.403
27.938
19.192
17.380
16.854
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


OBz
O
Bn
N
O
O

*syn, anti-**5***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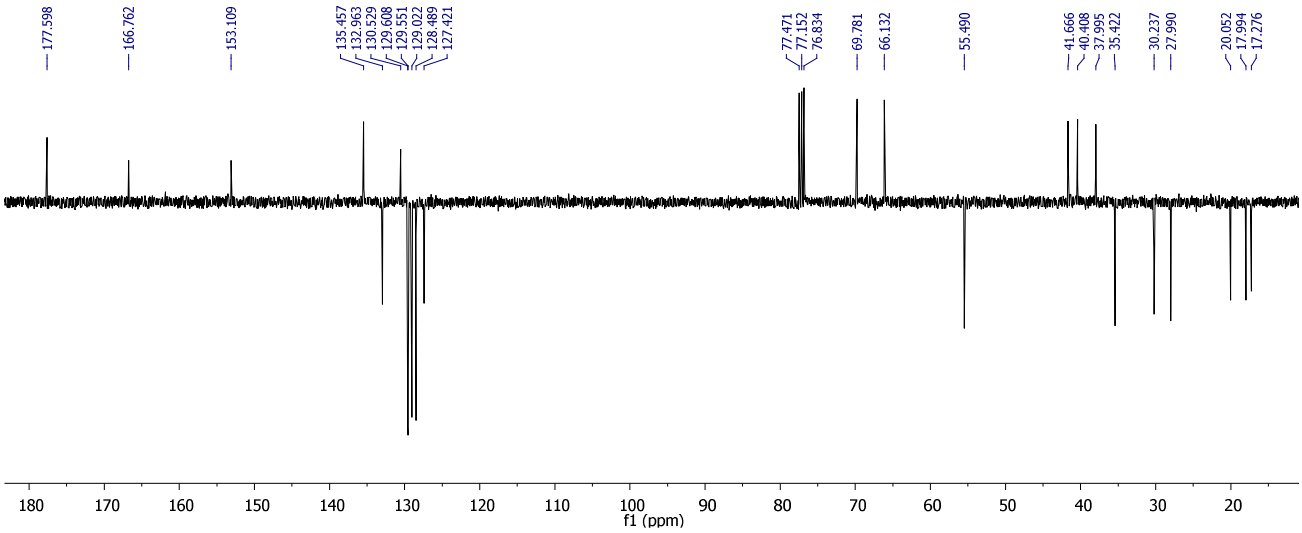
7.267
7.207
7.190
4.657
4.647
4.639
4.632
4.623
4.615
4.148
4.071
4.054
4.044
4.028
3.881
3.864
3.845
3.829
3.272
3.263
3.238
3.230
2.787
2.764
2.754
2.730
2.073
2.057
2.042
2.026
1.650
1.561
1.545
1.443
1.428
1.409
1.211
1.195
1.042
1.025
0.962
1.82
0.94
1.88
2.91
1.86
0.91
2.89
0.99
1.01
1.00
1.00
1.01
1.14
1.03
1.98
2.94
1.09
2.78
2.67
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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129.022
128.489
127.421
77.471
77.152
76.834
69.781
66.132
55.490
41.666
40.408
37.995
35.422
30.237
27.990
20.052
17.994
17.276
180
170
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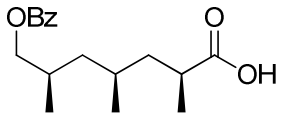
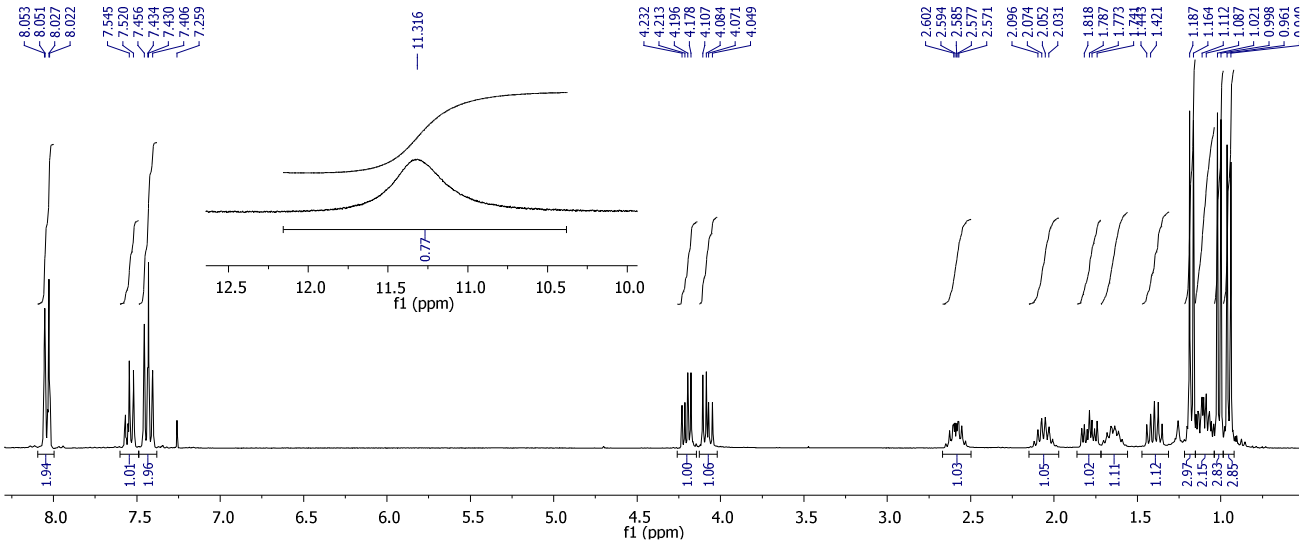
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


OBz
O
OH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8.027
8.022
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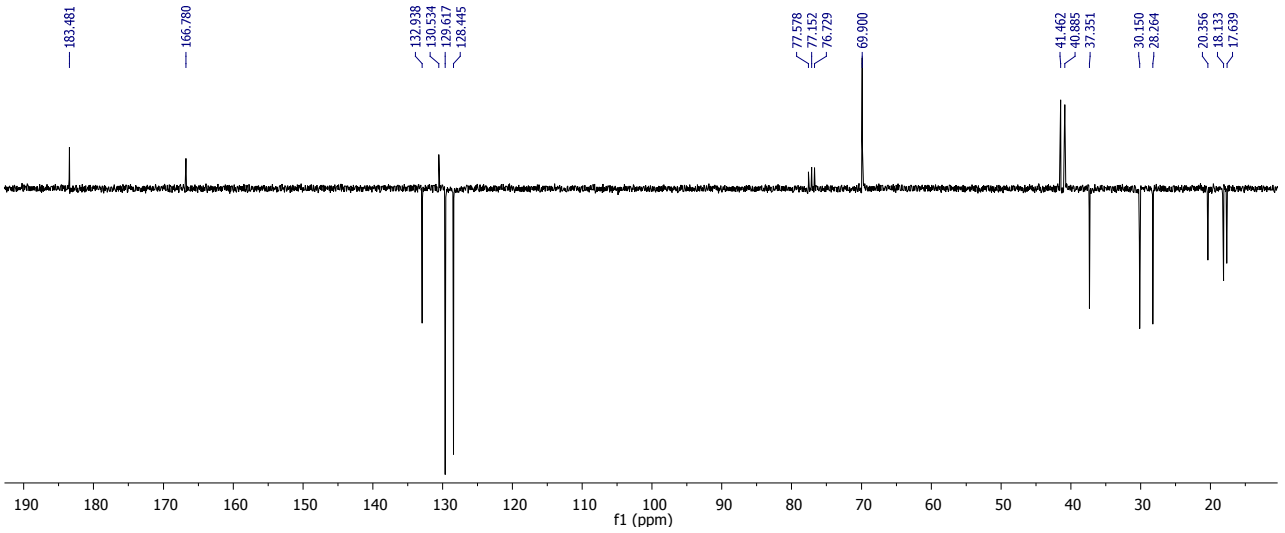
7.520
7.456
7.434
7.430
7.406
7.259
11.316
4.232
4.213
4.196
4.178
4.107
4.084
4.071
4.049
2.602
2.594
2.585
2.577
2.571
2.096
2.074
2.052
2.031
1.818
1.787
1.773
1.421
1.187
1.164
1.112
1.087
1.021
0.998
0.961
0.77
12.5
12.0
11.5
11.0
10.5
10.0
f1 (ppm)
1.94
1.01
1.96
1.00
1.06
1.03
1.05
1.02
1.11
1.12
2.97
2.15
2.83
2.85
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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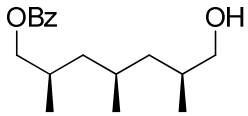
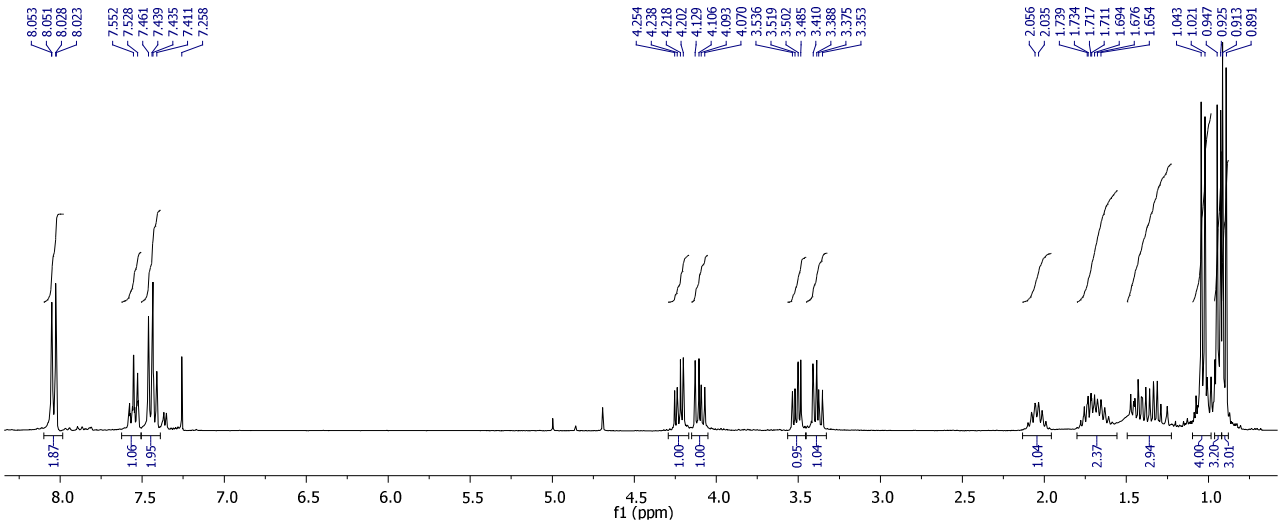
77.152
76.729
69.900
41.462
40.885
37.351
30.150
28.264
20.356
18.133
17.639
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


OBz
OH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8.051
8.028
8.023
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7.528
7.461
7.439
7.435
7.411
7.258
4.254
4.238
4.218
4.202
4.129
4.106
4.093
4.070
3.536
3.519
3.502
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2.035
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1.694
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1.043
1.021
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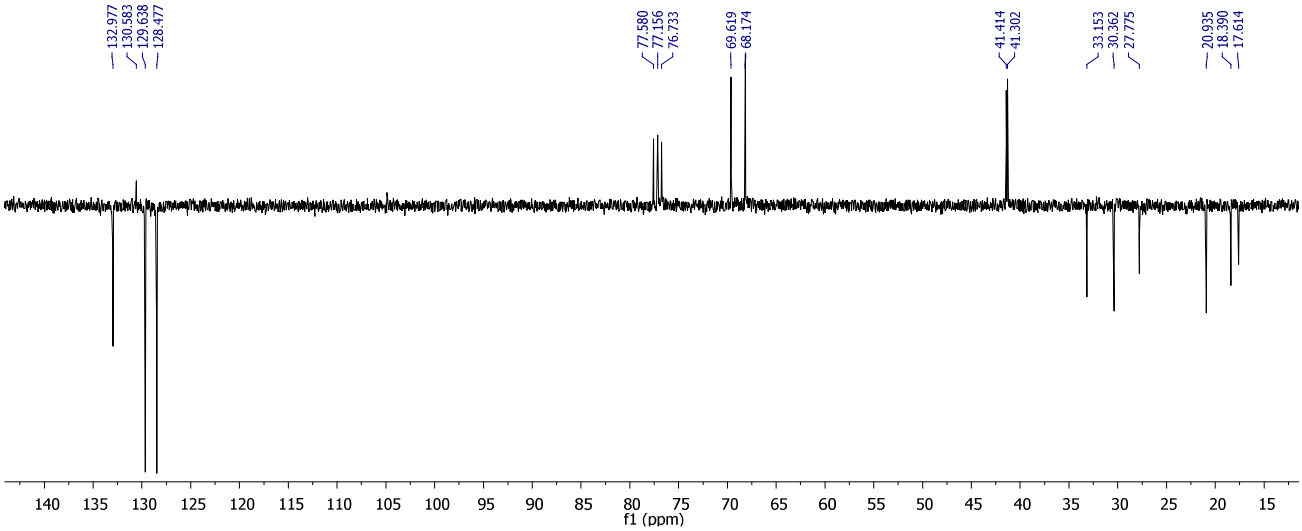
0.925
0.913
0.891
1.87
1.06
1.95
1.00
1.00
0.95
1.04
1.04
2.37
2.94
4.00
3.20
3.01
f1 (ppm)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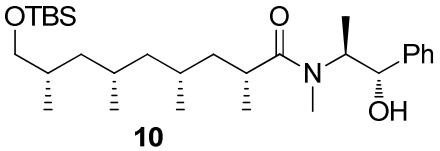
130.583
129.638
128.477
77.580
77.156
76.733
69.619
68.174
41.414
41.302
33.153
30.362
27.775
20.935
18.390
17.614
f1 (ppm)



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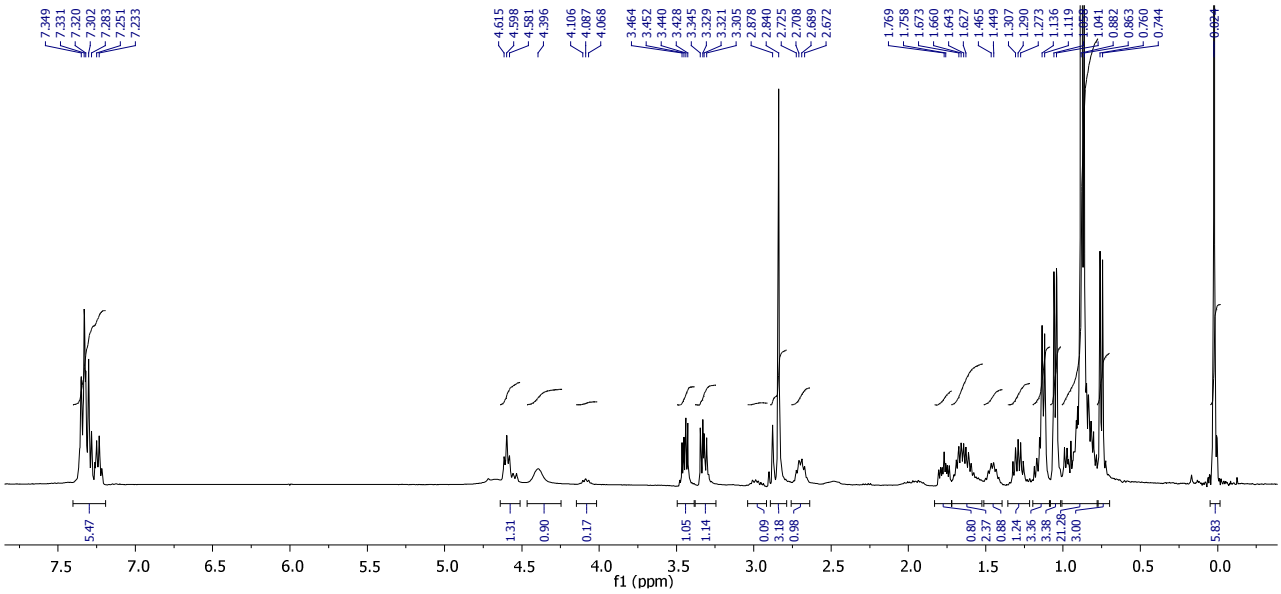
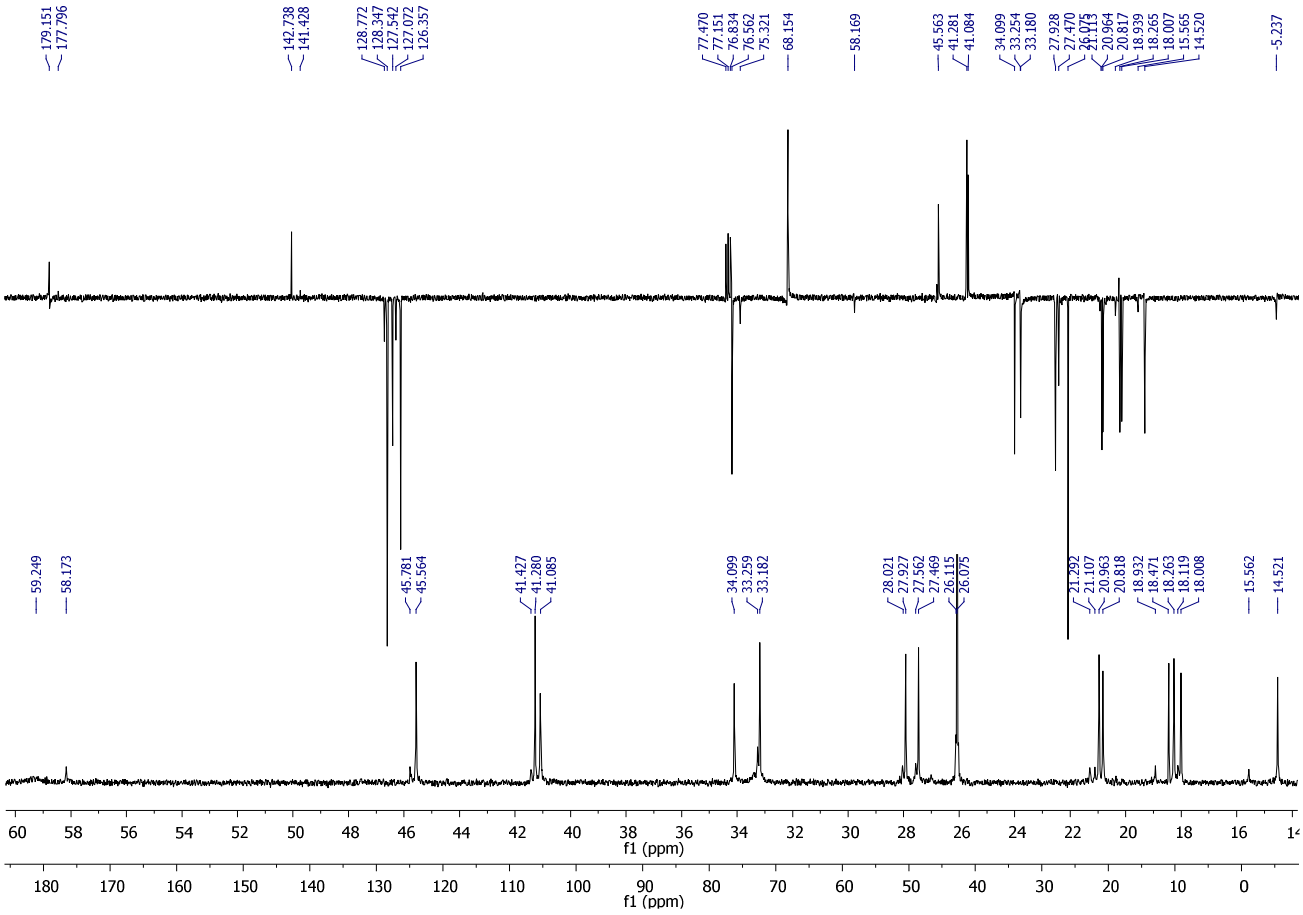
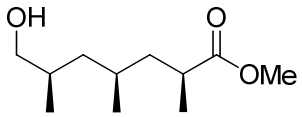
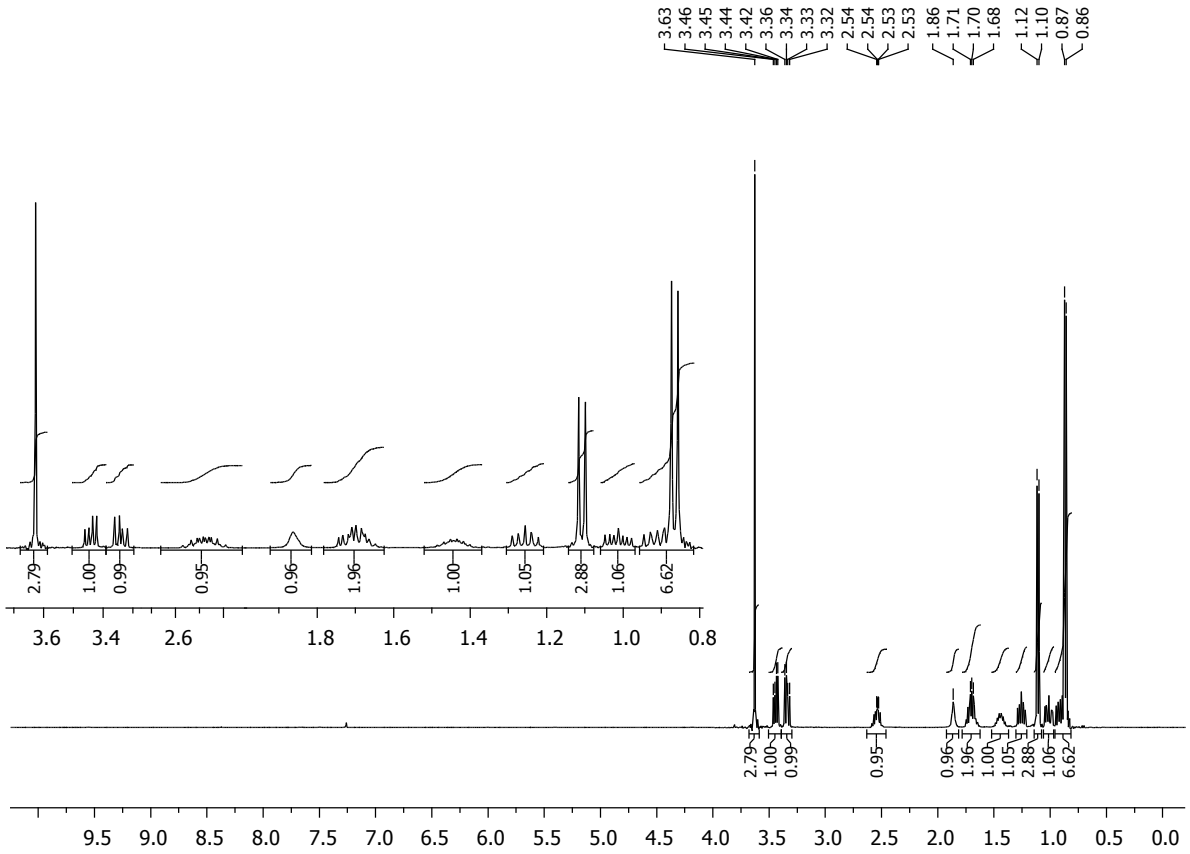
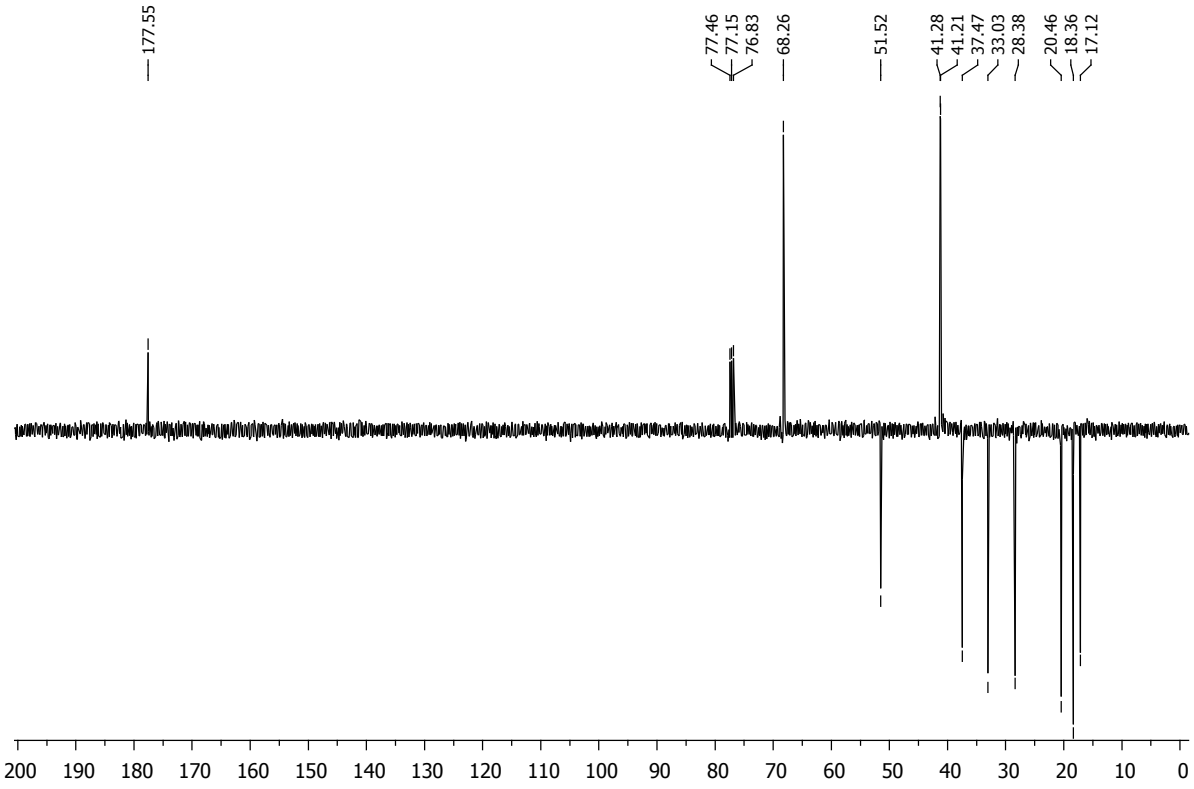





OH
O
OMe


3.63
3.46
3.45
3.44
3.42
3.36
3.34
3.33
3.32
2.54
2.54
2.53
2.53
1.86
1.71
1.70
1.68
1.12
1.10
0.87
0.86
2.79
1.00
0.99
0.95
0.96
1.96
1.00
1.05
2.88
1.06
6.62
3.6
3.4
2.6
1.8
1.6
1.4
1.2
1.0
0.8
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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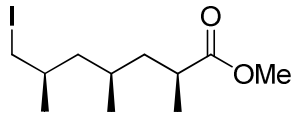
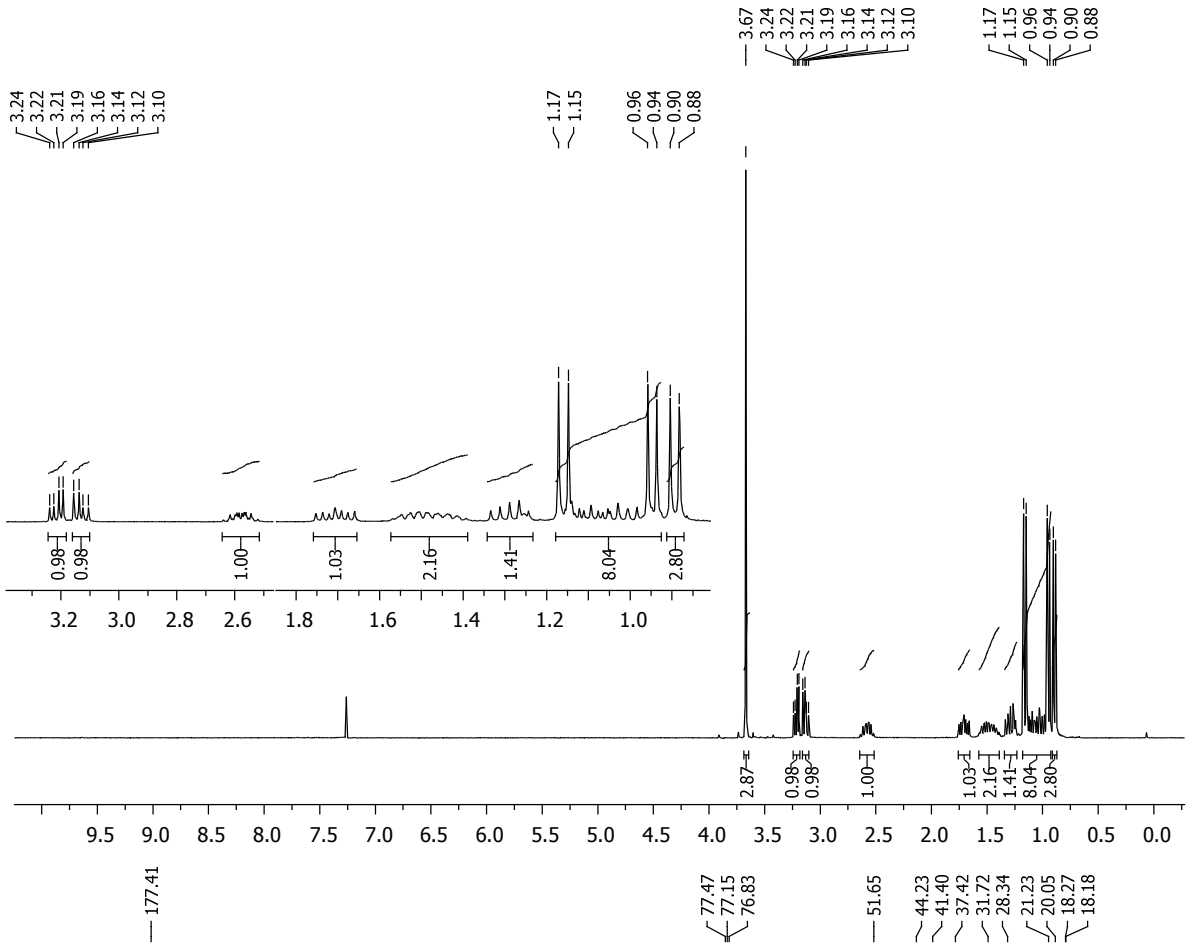
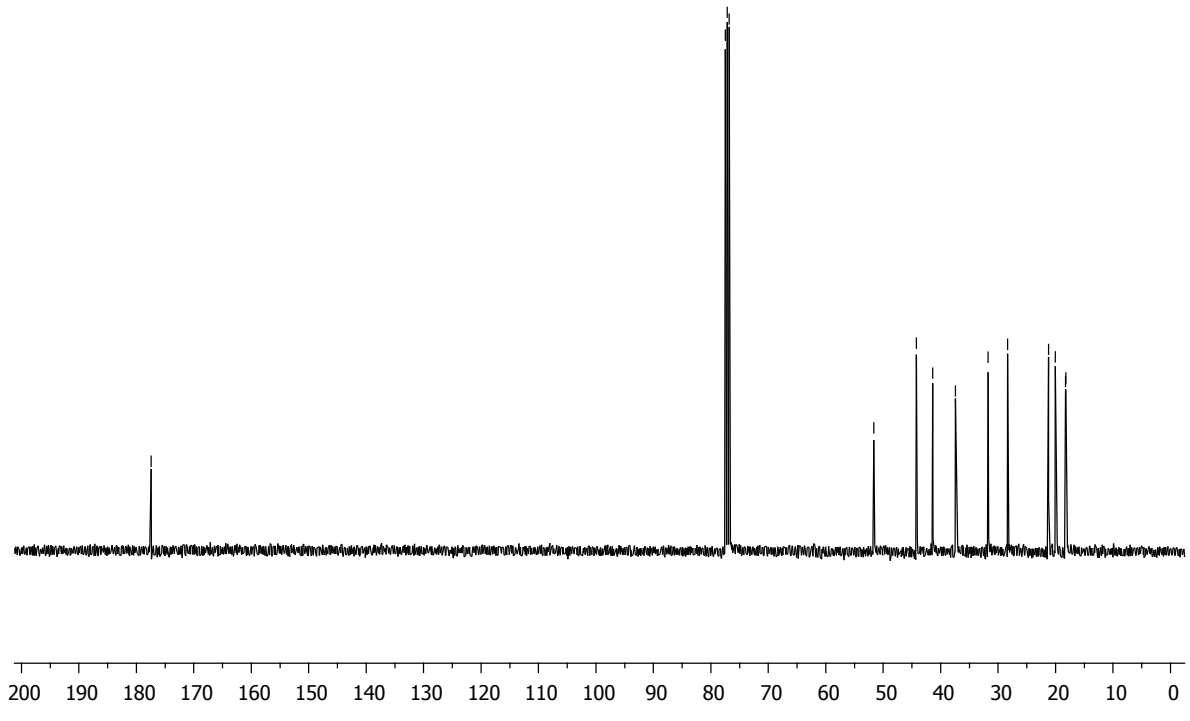
77.46
77.15
76.83
68.26
51.52
41.28
41.21
37.47
33.03
28.38
20.46
18.36
17.12
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


I
O
OMe

12


3.67
3.24
3.22
3.21
3.19
3.16
3.14
3.12
3.10
1.17
1.15
0.96
0.94
0.90
0.88
2.87
0.98
0.98
1.00
1.03
2.16
1.41
8.04
2.80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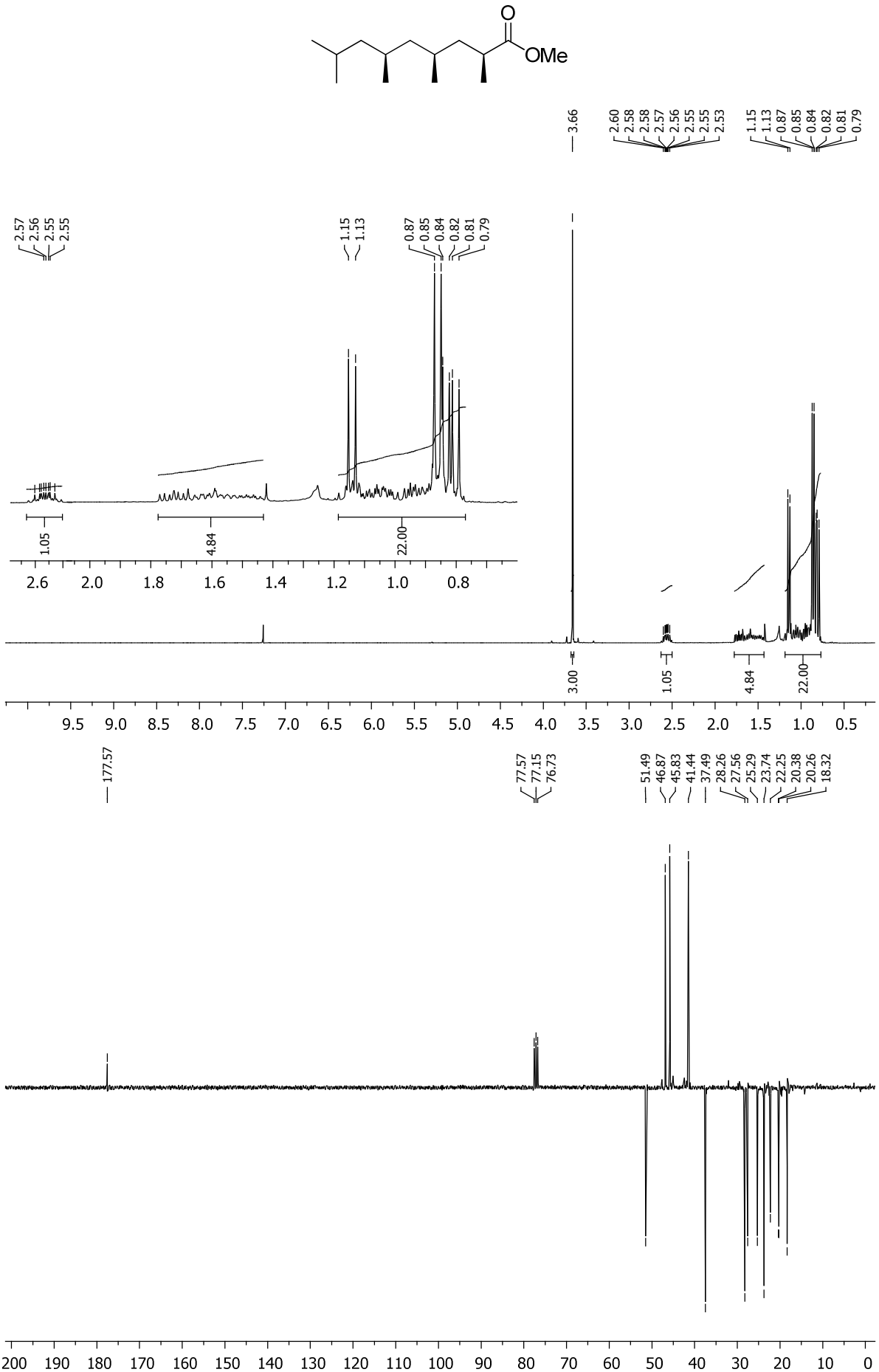
77.47
77.15
76.83
51.65
44.23
41.40
37.42
31.72
28.34
21.23
20.05
18.27
18.18


O
OMe
3.66
2.60
2.58
2.58
2.57
2.56
2.55
2.55
2.53
1.15
1.13
0.87
0.85
0.84
0.82
0.81
0.79
2.57
2.56
2.55
2.55
1.15
1.13
0.87
0.85
0.84
0.82
0.81
0.79
1.05
4.84
22.00
3.00
1.05
4.84
22.00
177.57
77.57
77.15
76.73
51.49
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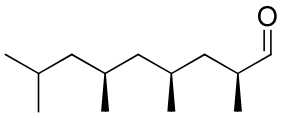
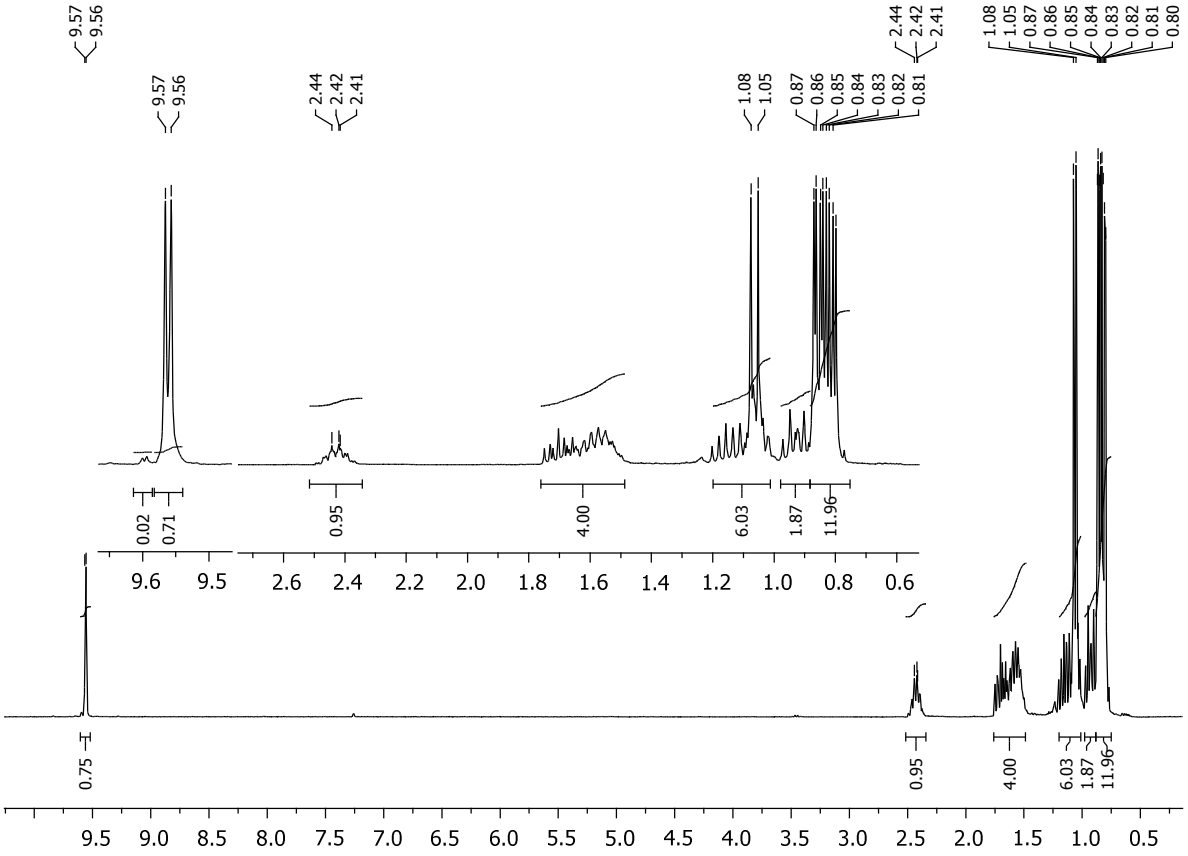
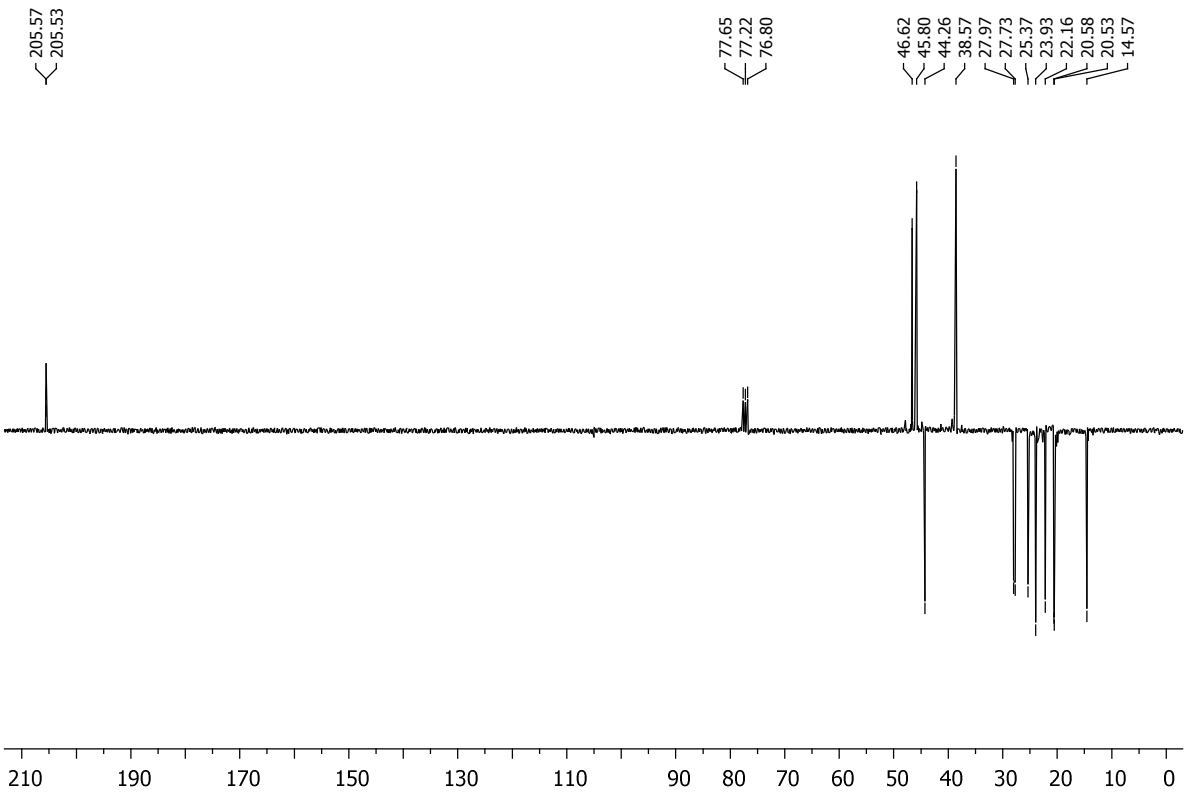
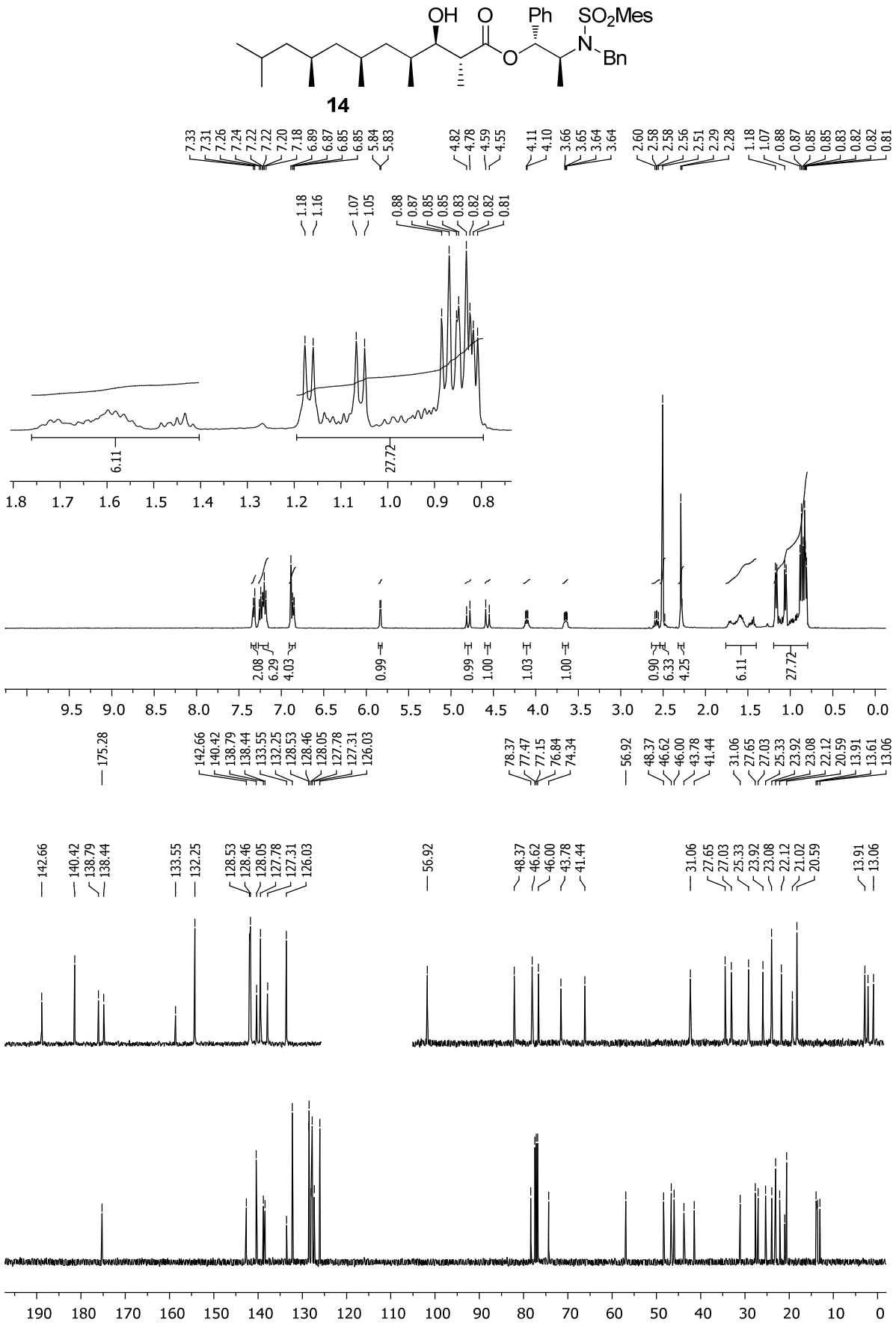
23.74
22.25
20.38
20.26
18.32

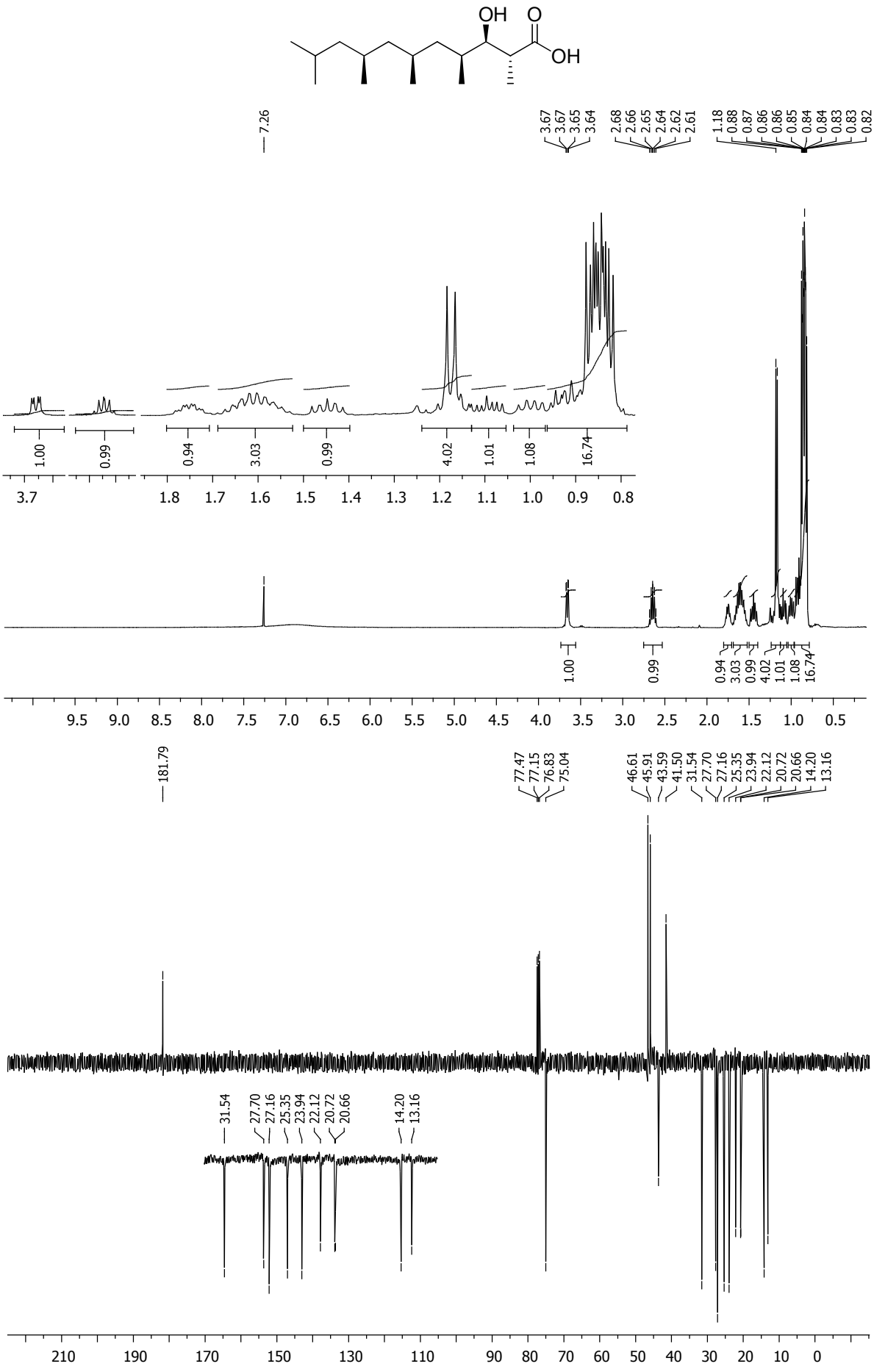


13






OH
O
Ph
SO2Mes
N
Bn
O
14


OH
O
OH
7.26
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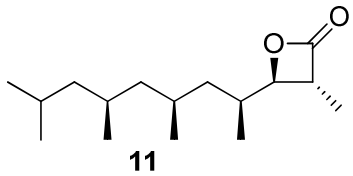
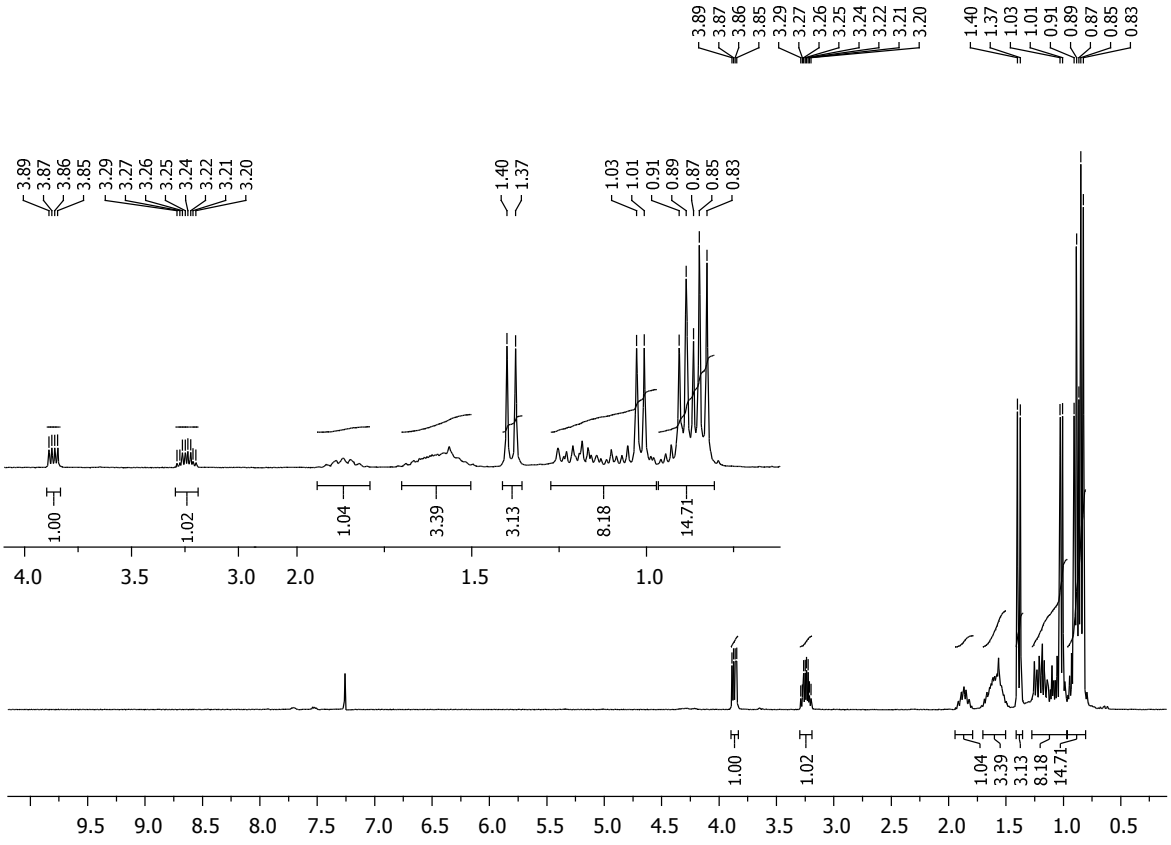
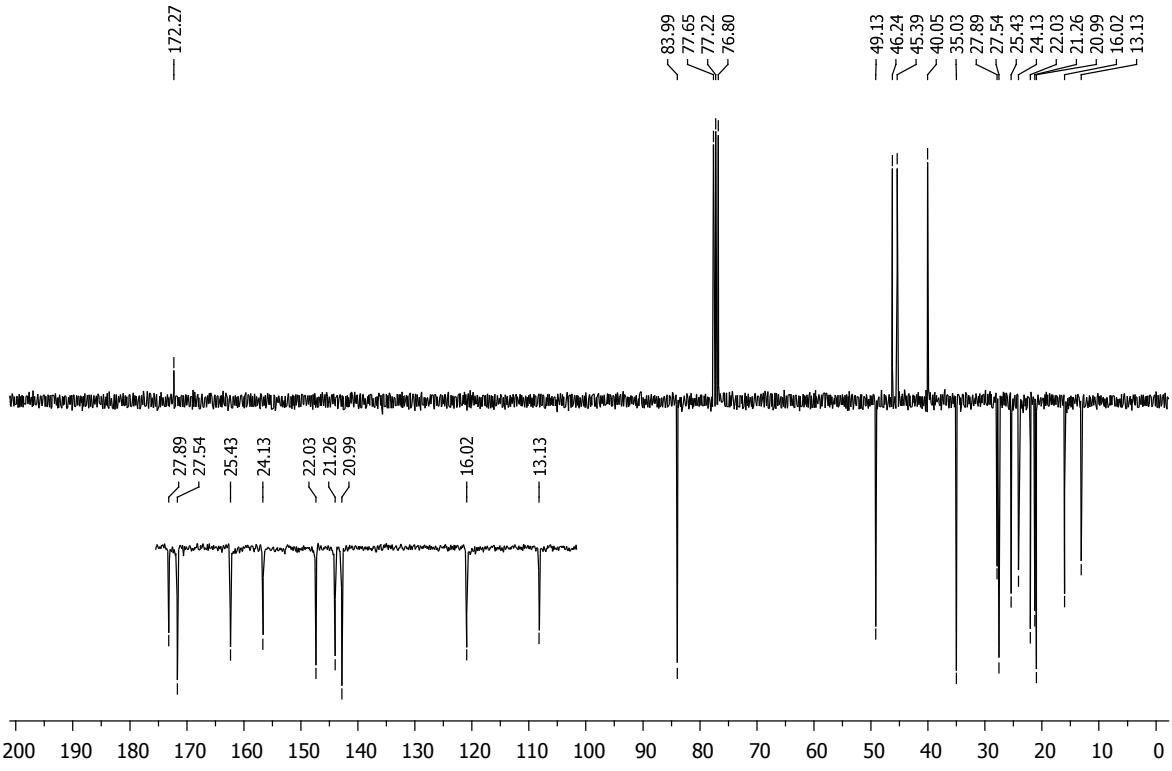
3.67
3.65
3.64
2.68
2.66
2.65
2.64
2.62
2.61
1.18
0.88
0.87
0.86
0.86
0.85
0.84
0.84
0.83
0.83
0.82
1.00
0.99
0.94
3.03
0.99
4.02
1.01
1.08
16.74
181.79
77.47
77.15
76.83
75.04
46.61
45.91
43.59
41.50
31.54
27.70
27.16
25.35
23.94
22.12
20.72
20.66
14.20
13.16



11


3.89
3.87
3.86
3.85
3.29
3.27
3.26
3.25
3.24
3.22
3.21
3.20
1.40
1.37
1.03
1.01
0.91
0.89
0.87
0.85
0.83
1.00
1.02
1.04
3.39
3.13
8.18
14.71


172.27
83.99
77.65
77.22
76.80
49.13
46.24
45.39
40.05
35.03
27.89
27.54
25.43
24.13
22.03
21.26
20.99
16.02
13.13

10 References

[1] A. Schmauder, S. Müller, M. E. Maier, *Tetrahedron*, **2008**, 6263.

[2] Y. Schmidt, K. Lehr, U. Breuninger, G. Brand, T. Reiss and B. Breit, *J. Org. Chem.*, **2010**, *75*, 4424.

[3] Y. Schmidt, B. Breit, *Org.Lett.*, **2009**, 4764.