Supporting Information

Oxidative asymmetric umpolung alkylation of Evans' β-keto imides by dialkylzinc nucleophiles

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Table of Contents

General Experimental Information S2

Experimental Procedures and Characterization Data S3

Preparation of Starting material S27

References S59

General Experimental Information

All reactions were carried out using oven-dried (120 °C) or heat gun dried glassware under a positive pressure of dry argon. All commercially available reagents were used without further purification. The chemical hydroxy(tosyloxy)iodobenzene (Koser's reagent) was handled in the dark. The reactions were magnetically stirred and monitored by thin layer chromatography using Merck Silica Gel 60 F254 plates and visualized by fluorescence quenching under UV light. In addition, TLC plates were stained using potassium permanganate. Chromatographic purification of products (column chromatography) was performed on silica 32-63, 60 Å using a forced flow of eluent at 0.3-0.5 bar. Concentration under reduced pressure was performed by rotary evaporation at 40 °C at the appropriate pressure. Yields refer to chromatographically purified compounds.

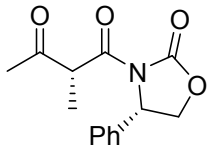
NMR spectra: NMR spectra were recorded on a Bruker Avance I 300 spectrometer operating at 300 MHz and 75 MHz for ^{1}H and ^{13}C acquisitions, respectively, or on Bruker Avance III 400 spectrometers operating at 400 MHz (^{1}H) and 101 MHz (^{13}C) or on a Bruker DPX200 spectrometer operating at 200 MHz (^{1}H) and 50 MHz respectively (^{13}C). Chemical shifts (δ) are reported in ppm with the solvent resonance as the internal standard relative to chloroform (δ 7.26) for ^{1}H, and chloroform (δ 77.0) for ^{13}C. All ^{13}C spectra were measured with complete proton decoupling. Data are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dq = doublet of quartet; coupling constants in Hz. All β-keto imide products were isolated in pure form. While some of the enclosed NMR spectra show a mixture of keto and enol forms in varying proportions depending on compound structure, concentration and solvent, only the data for the keto form has been tabulated. All new compounds are characterized by NMR, IR and HRMS. Known compounds are characterized by NMR only and a reference to a paper describing full characterization is given.

IR spectra: recorded on a Bruker FT-IR (dissolved in $CHCl_3$ unless otherwise stated). Absorptions are given in wavenumbers (cm^{-1}).

Mass spectra: High resolution mass spectra were recorded by the MS service at Technion. ESI-MS (*m*/*z*): was recorded on a Waters Micromass LCT premier instrument at 70eV in the positive or negative mode using 70% acetonitrile/30% water at 0.2 mL flowrate.

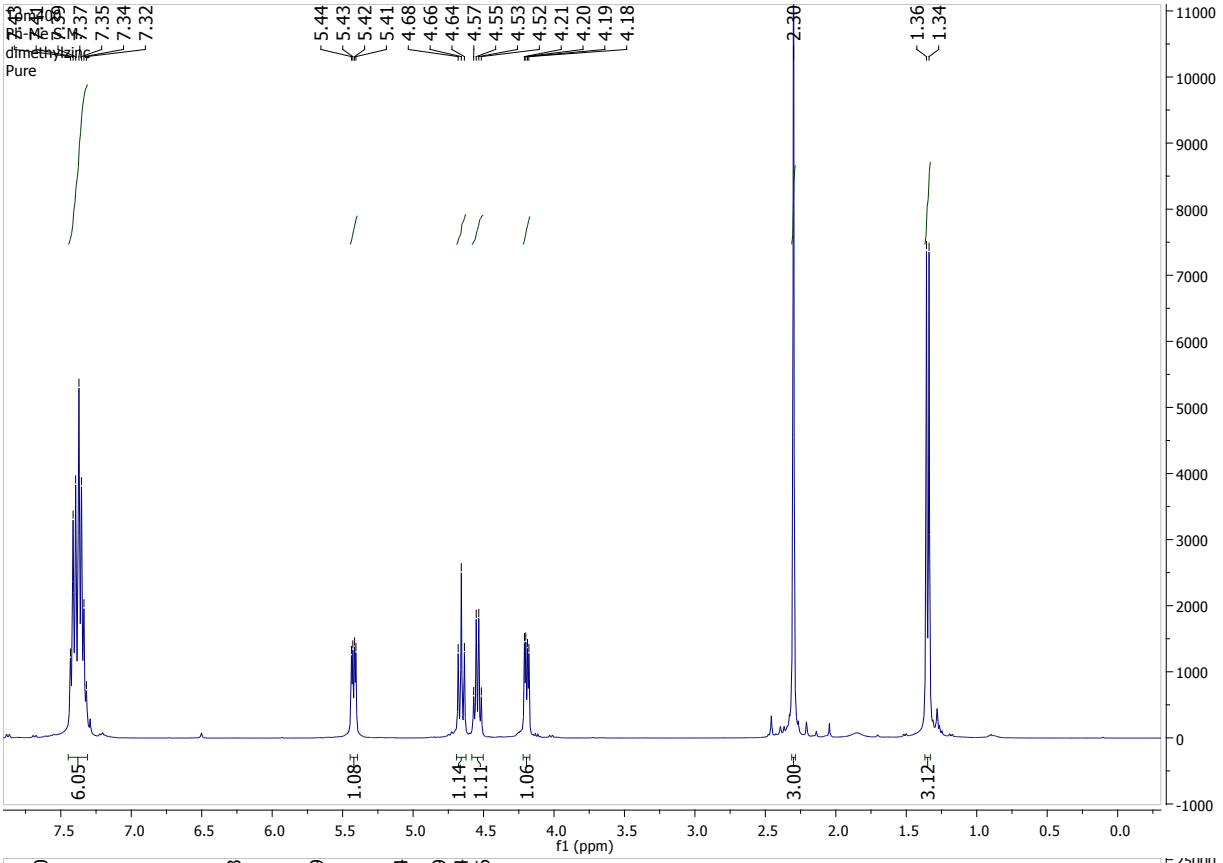
Experimental Procedures and Characterization Data

General procedure 1: Umpolung alkylation reaction
(*R*)-2-methyl-1-((S)-2-oxo-4-phenyloxazolidin-3-yl)butane-1,3-dione (7)



$MgSO_4$ (252 mg, 2.1 mmol, 5.0 equiv) was placed in a flask and dried with a heat-gun for 5 min under vacuum. The flask was allowed to reach r.t. under Argon, Koser's reagent (317 mg, 0.8 mmol, 2.0 equiv) was added and the flask cooled to −78 °C. A solution of (**4**) (100 mg, 0.4 mmol, 1.0 equiv) in toluene (4 mL) was added. The reaction mixture was stirred for 10 min followed by addition of Me_2Zn (0.7 mL, 0.8 mmol, 1.2M in toluene, 2.0 equiv) by syringe, and was allowed to stir for 19 h. Excess Me_2Zn was quenched with 10 mL of water, the mixture was allowed to reach r.t. and was then extracted EtOAc (6×10 mL), the combined extracts were washed with brine (30 mL), dried over Na_2SO_4, filtered, and the solvents removed under reduced pressure. The resulting crude was purified by column chromatography (20% - 35% EtOAc/hexane) to give the product (74 mg, 70% yield, single diastereoisomer) as a white solid. The other diastereoisomer was not observed.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.43 (m, 5H), 5.42 (dd, *J* = 8.8, 3.8, 1H), 4.66 (t, *J* = 8.8, 1H), 4.54 (q, *J* = 7.2, 1H), 4.19 (dd, *J* = 8.8, 3.9, 1H), 2.30 (s, 3H), 1.35 (d, *J* = 7.3, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.0, 169.3, 153.9, 138.4, 128.9 (2C), 128.4, 125.6 (2C), 70.3, 57.5, 52.9, 28.1, 12.1.
R_f: 0.30 (30% EtOAc/hexane).
IR ($CHCl_3$) ν 3028, 2361, 1779, 1720, 1539, 1453, 1387, 1354, 1280, 1223, 1163, 1127, 1074, 939 cm^{-1}.
HRMS (APCI+): *m/z*: Calcd for $C_{14}H_{16}NO_4$ $[M+H]^+$, 262.1074 ; found: 262.1077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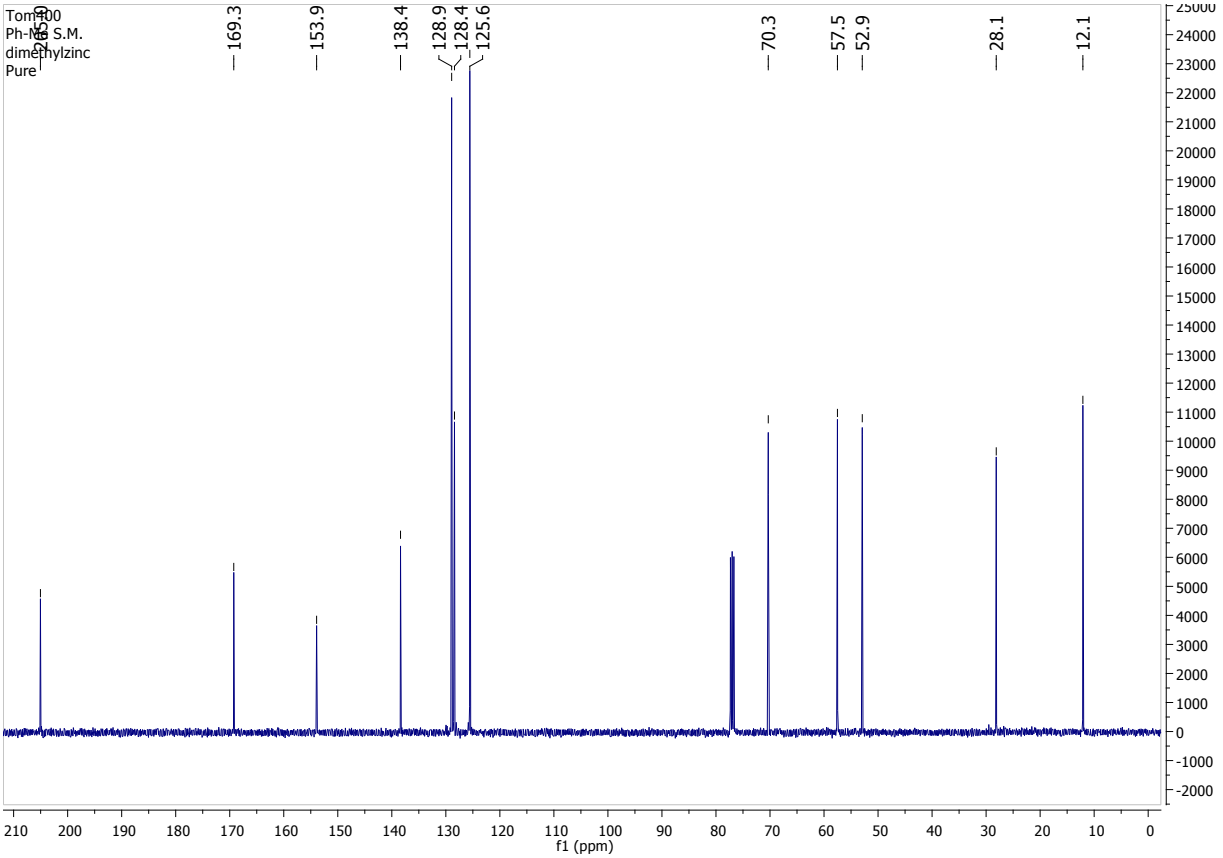
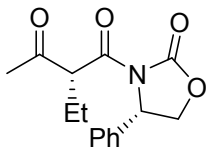
Ph-Me S.M.
dimethylzinc
Pure
7.37
7.35
7.34
7.32
5.44
5.43
5.42
5.41
4.68
4.66
4.64
4.57
4.55
4.53
4.52
4.21
4.20
4.19
4.18
2.30
1.36
1.34
6.05
1.08
1.14
1.11
1.06
3.00
3.12
f1 (ppm)

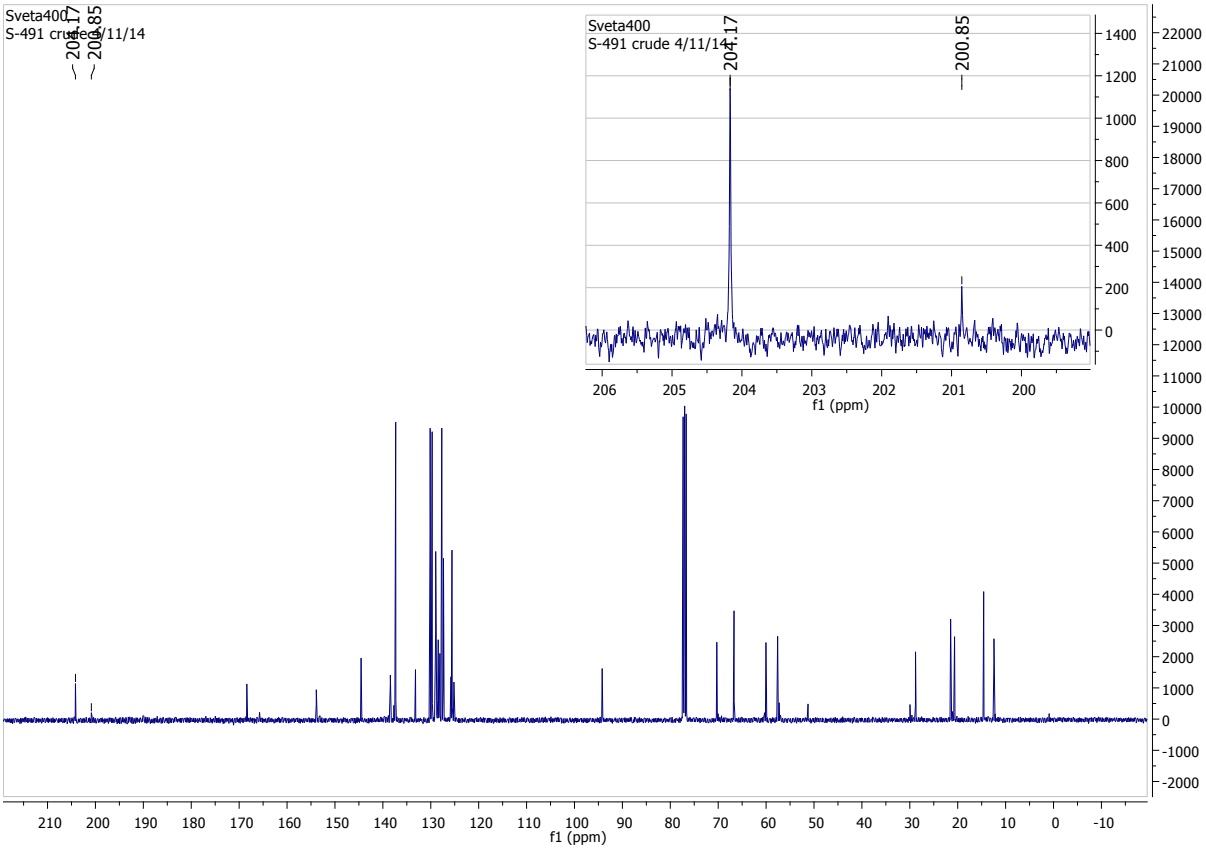

Tom400
Ph-Me S.M.
dimethylzinc
Pure
169.3
153.9
138.4
128.9
128.4
125.6
70.3
57.5
52.9
28.1
12.1
f1 (ppm)

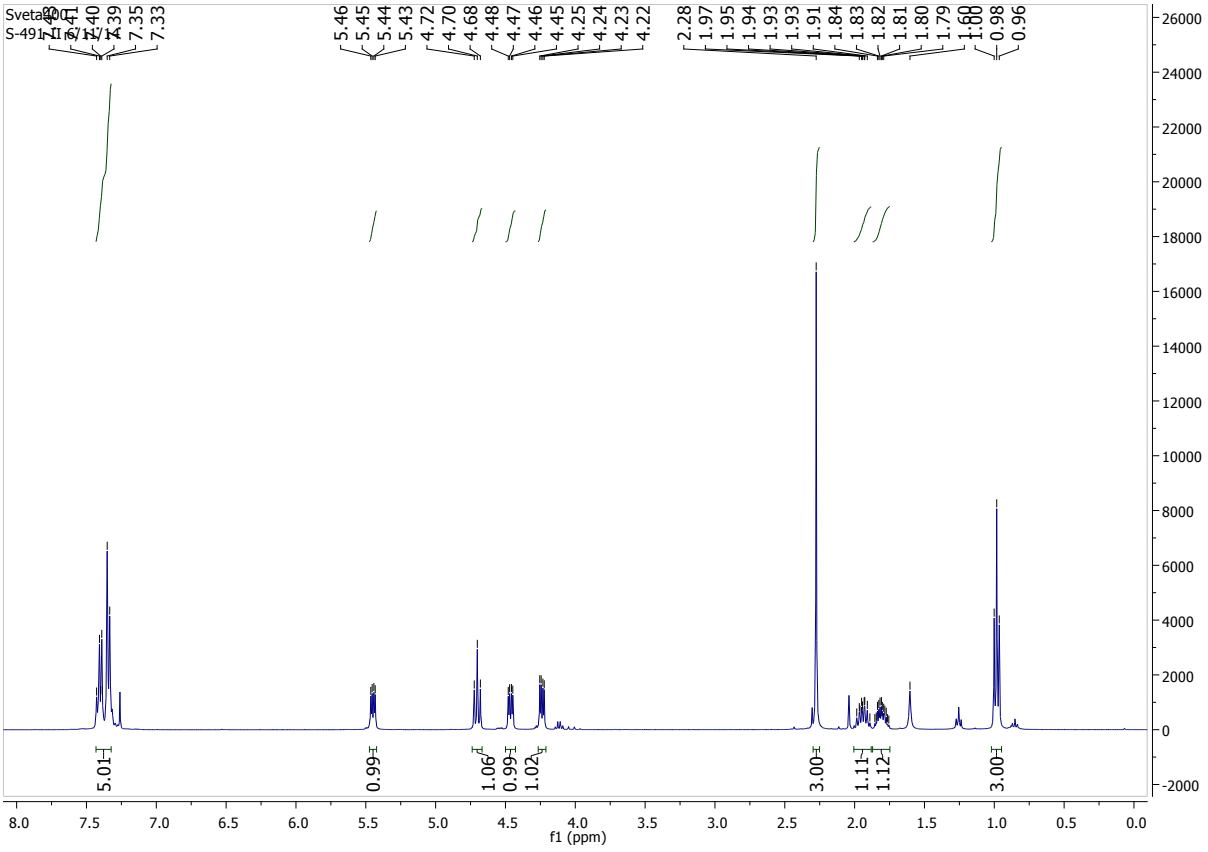
(*R*)-2-ethyl-1-((*S*)-2-oxo-4-phenyloxazolidin-3-yl)butane-1,3-dione (8)



Compound (**8**) was prepared according to general procedure 1 and purified by column chromatography (40% EtOAc/hexane) to give the product (140 mg, 68% yield,) as a white solid. Reaction d.r. *ca.* 6:1 (by crude ^{13}C-NMR). The minor diastereoisomer was not isolated.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.43 (m, 5H), 5.45 (dd, J = 8.8, 3.8, 1H), 4.70 (t, J = 8.8, 1H), 4.46 (dd, J = 9.1, 3.9, 1H), 4.24 (dd, J = 8.8, 3.9, 1H), 2.28 (s, 3H), 1.89 – 1.98 (m, 1H), 1.76 – 1.86 (m, 1H), 0.98 (t, J = 7.4, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 204.3, 168.5, 154.0, 138.4, 129.1(2C), 128.6, 125.7(2C), 70.4, 60.2, 57.7, 28.9, 20.8, 12.5.
R_f: 0.3 (30% EtOAc/hexane).
IR ($CHCl_3$) ν 3029, 2970, 2929, 1779, 1720, 1458, 1385, 1361, 1325, 1276, 1233, 1226, 1194, 1162, 1087, 1050, 998, 957, 917 cm^{-1}.
HRMS (APCI+): *m/z*: Calcd for $C_{15}H_{18}NO_4$ $[M+H]^+$, 276.1230; found: 276.1197

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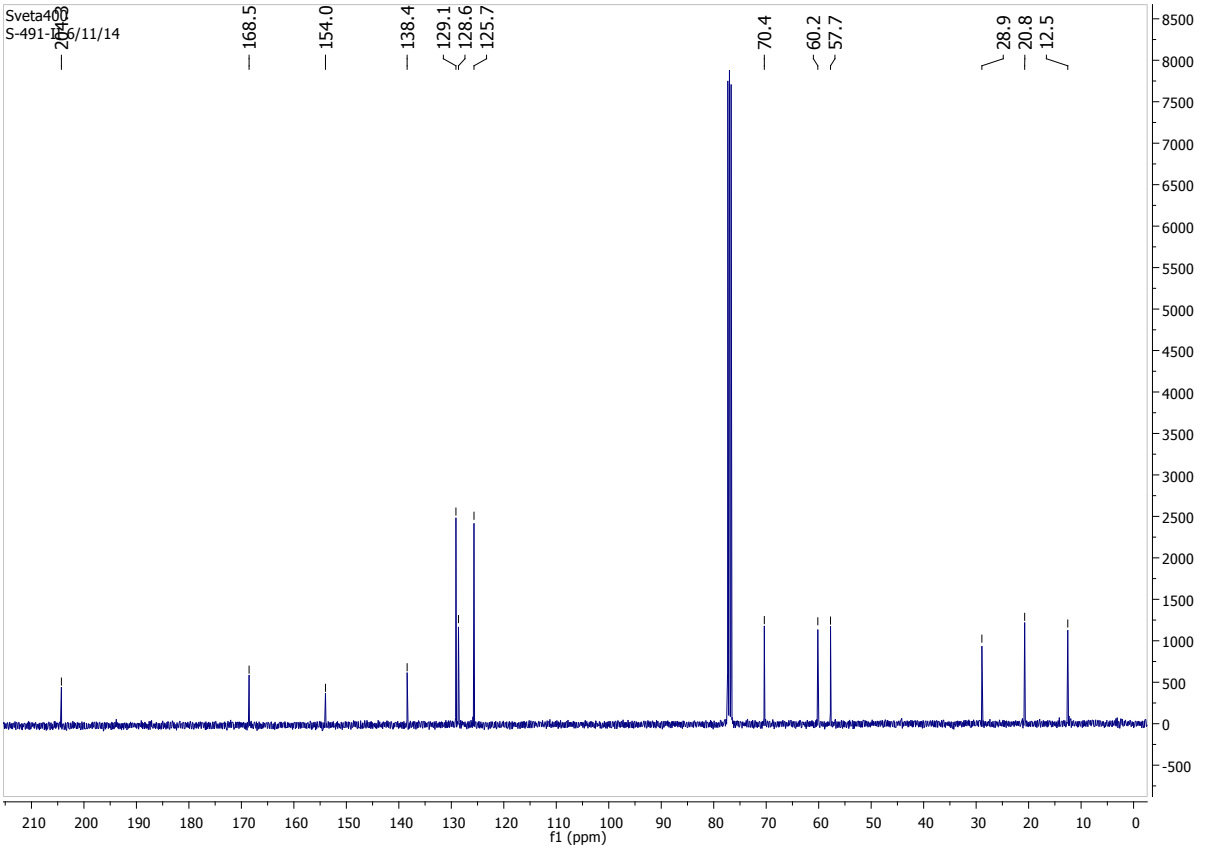
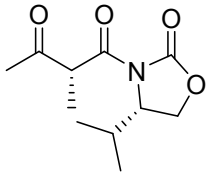
7.41
7.40
7.39
7.35
7.33
5.46
5.45
5.44
5.43
4.72
4.70
4.68
4.48
4.47
4.46
4.45
4.25
4.24
4.23
4.22
2.28
1.97
1.95
1.94
1.93
1.93
1.91
1.84
1.83
1.82
1.81
1.80
1.79
1.60
1.00
0.98
0.96
5.01
0.99
1.06
0.99
1.02
3.00
1.11
1.12
3.00
f1 (ppm)

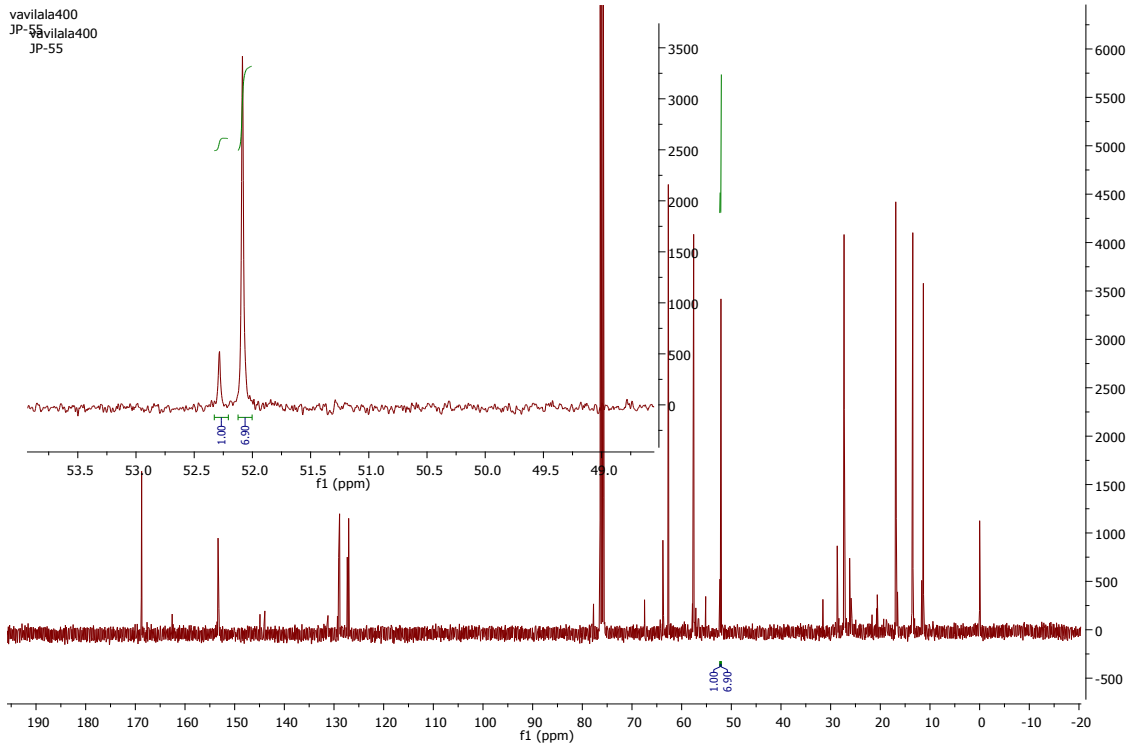

Sveta400
S-491-126/11/14
168.5
154.0
138.4
129.1
128.6
125.7
70.4
60.2
57.7
28.9
20.8
12.5
f1 (ppm)

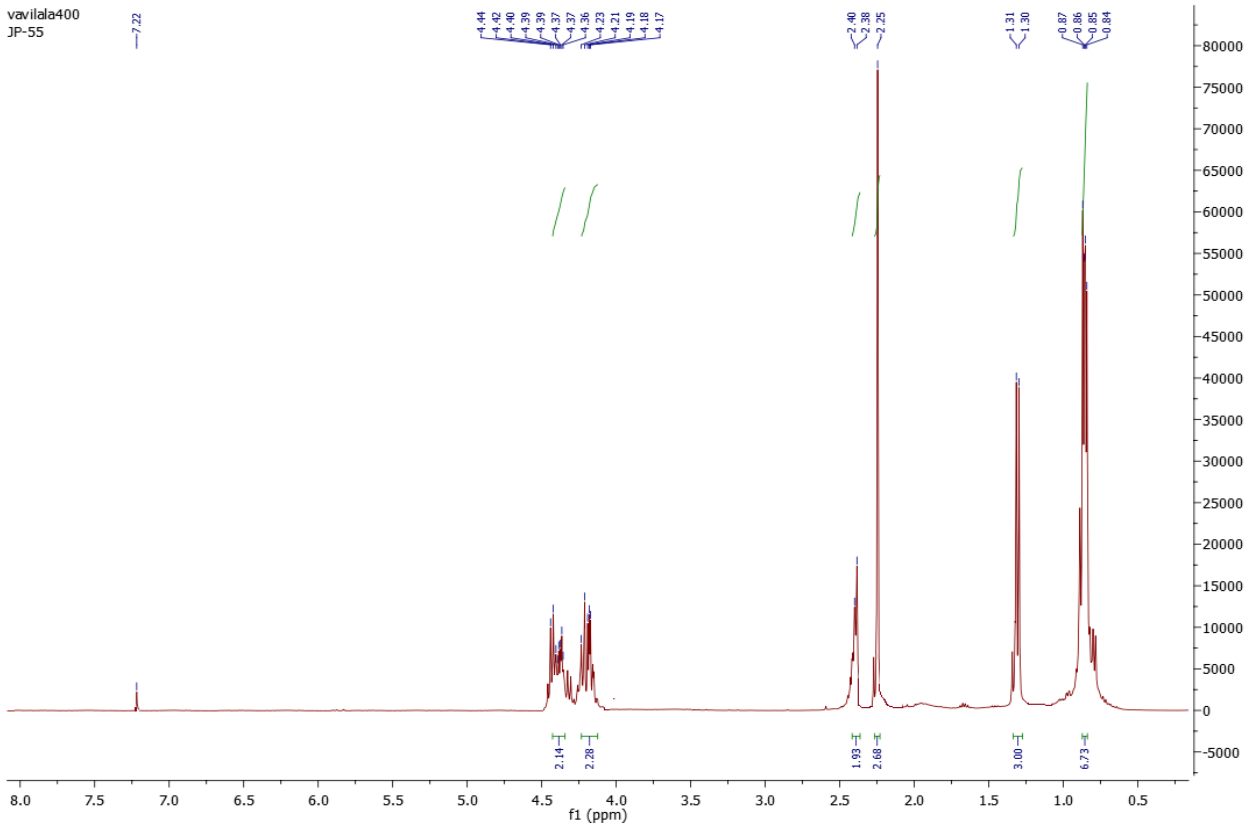
(*R*)-1-((*S*)-4-isopropyl-2-oxooxazolidin-3-yl)-2-methylbutane-1,3-dionedione (9)



Compound (**9**) was prepared according to general procedure 1 and purified by column chromatography (40% EtOAc/hexane) to give the product (42 mg, 70% yield, single diastereoisomer) as a colorless oil. Reaction d.r. *ca.* 6.9:1 (by crude ^{13}C-NMR). The minor diastereoisomer was not isolated.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.36 – 4.44 (m, 2H), 4.17 – 4.23 (m, 2H), 2.38 – 2.43 (m, 1H), 2.29 (s, 3H), 1.35 (d, J = 7.3, 3H), 0.90 (dd, J = 7.0, 4.0, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 204.5, 168.8, 153.4, 62.8, 57.7, 52.2, 27.4, 27.4, 17.0, 13.6, 11.4.
R_f: 0.5 (40% EtOAc/hexane).
IR ($CHCl_3$) ν 3028, 2971, 2879, 1776, 1714, 1601, 1485, 1459, 1385, 1307, 1277, 1227, 1195, 1158, 1094, 1057, 1019, 969, 925 cm^{-1}.
HRMS (ESI−): *m/z*: Calcd for $C_{11}H_{16}NO_4$ $[M-H]^-$, 226.1079; found: 226.1070

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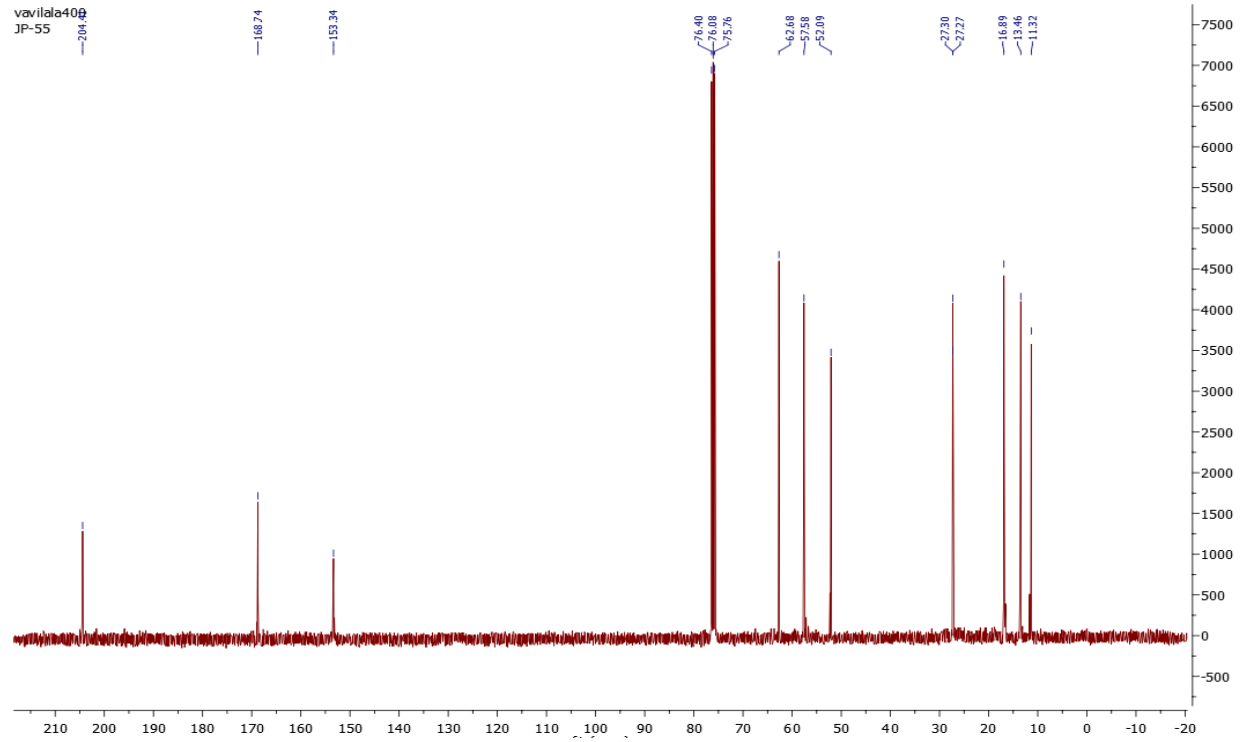
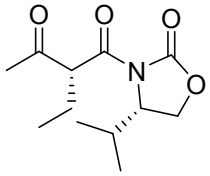
JP-55
7.22
4.44
4.42
4.40
4.39
4.37
4.37
4.36
4.23
4.21
4.19
4.18
4.17
2.40
2.38
2.25
1.31
1.30
0.87
0.86
0.85
0.84
2.14
2.28
1.93
2.68
3.00
6.73
f1 (ppm)

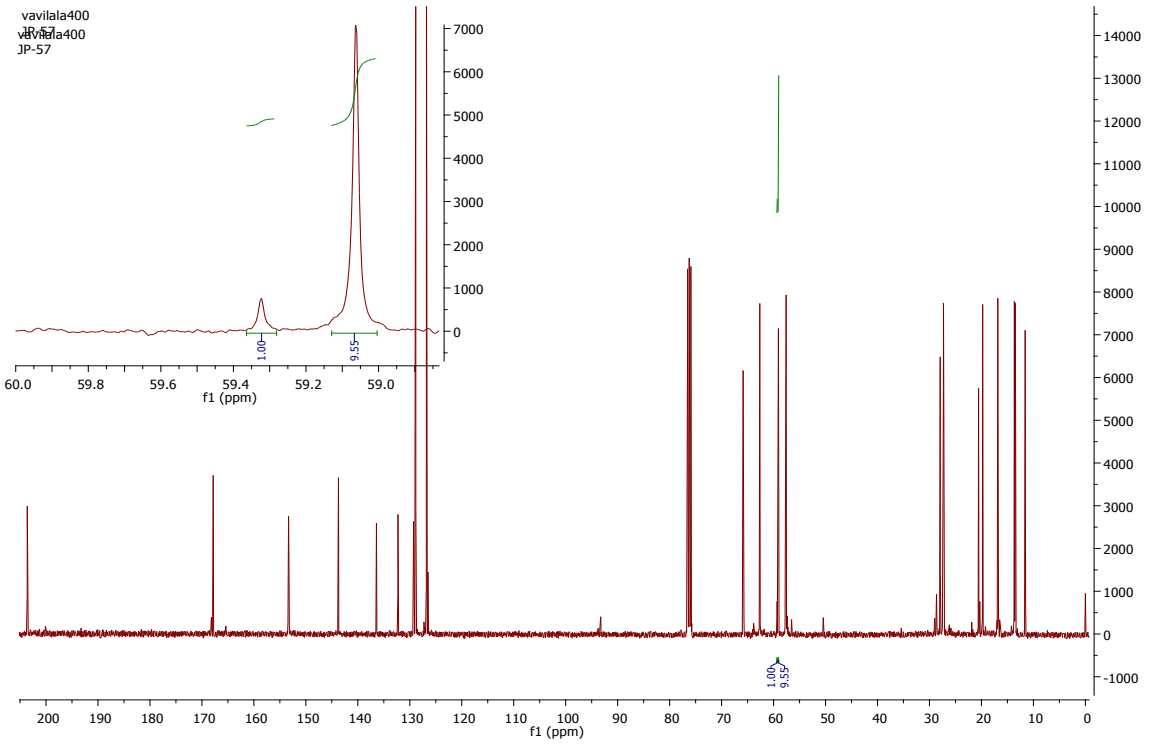

vavilala400
JP-55
204.48
168.74
153.34
76.40
76.08
75.76
62.68
57.58
52.09
27.30
27.27
16.89
13.46
11.32

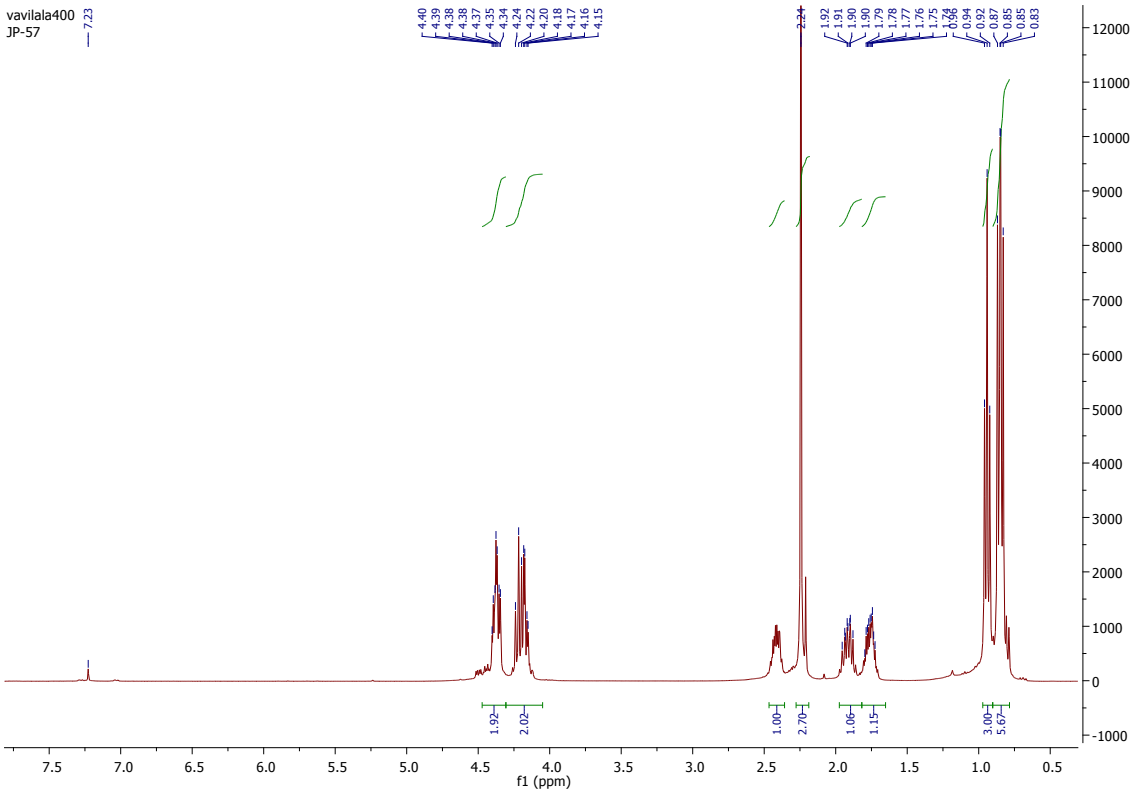
(*R*)-2-ethyl-1-((*S*)-4-isopropyl-2-oxooxazolidin-3-yl)butane-1,3-dione (12)



Compound (**12**) was prepared according to general procedure 1 and purified by column chromatography (40% EtOAc/hexane) to give the product (48 mg, 75% yield) as a colorless oil and as a single diastereoisomer. Reaction d.r. *ca.* 9.5:1 (by crude ^{13}C-NMR). The minor diastereoisomer was not isolated.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.34 – 4.40 (ddd, *J* = 12.3, 8.5, 3.5, 2H), 4.21 (m, 2H), 2.45 (m, 1H), 2.27 (s, 3H), 1.95 (ddd, *J* = 14.1, 8.9, 7.3, 1H), 1.79 (m, 1H), 0.97 (t, *J* = 7.4, 3H), 0.88 (dd, *J* = 8.9, 7.1, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 204.5, 168.7, 154.2, 63.5, 60.0, 58.5, 28.9, 28.2, 20.7, 17.8, 14.3, 12.5.
R_f: 0.5 (40% EtOAc/hexane)
IR ($CHCl_3$) ν 3028, 2971, 2879, 1776, 1717, 1603, 1485, 1460, 1385, 1306, 1275, 1241, 1227, 1197, 1158, 1098, 1057, 1019, 968, 926 cm^{-1}.
HRMS (ESI+): *m/z*: Calcd for $C_{12}H_{20}NO_4$ $[M+H]^+$, 242.1392; found: 242.1375

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JP-57
7.23
4.40
4.39
4.38
4.38
4.37
4.35
4.34
4.24
4.22
4.20
4.18
4.17
4.16
4.15
2.24
1.92
1.91
1.90
1.90
1.79
1.78
1.77
1.76
1.75
1.74
0.94
0.92
0.87
0.85
0.85
0.83
1.92
2.02
1.00
2.70
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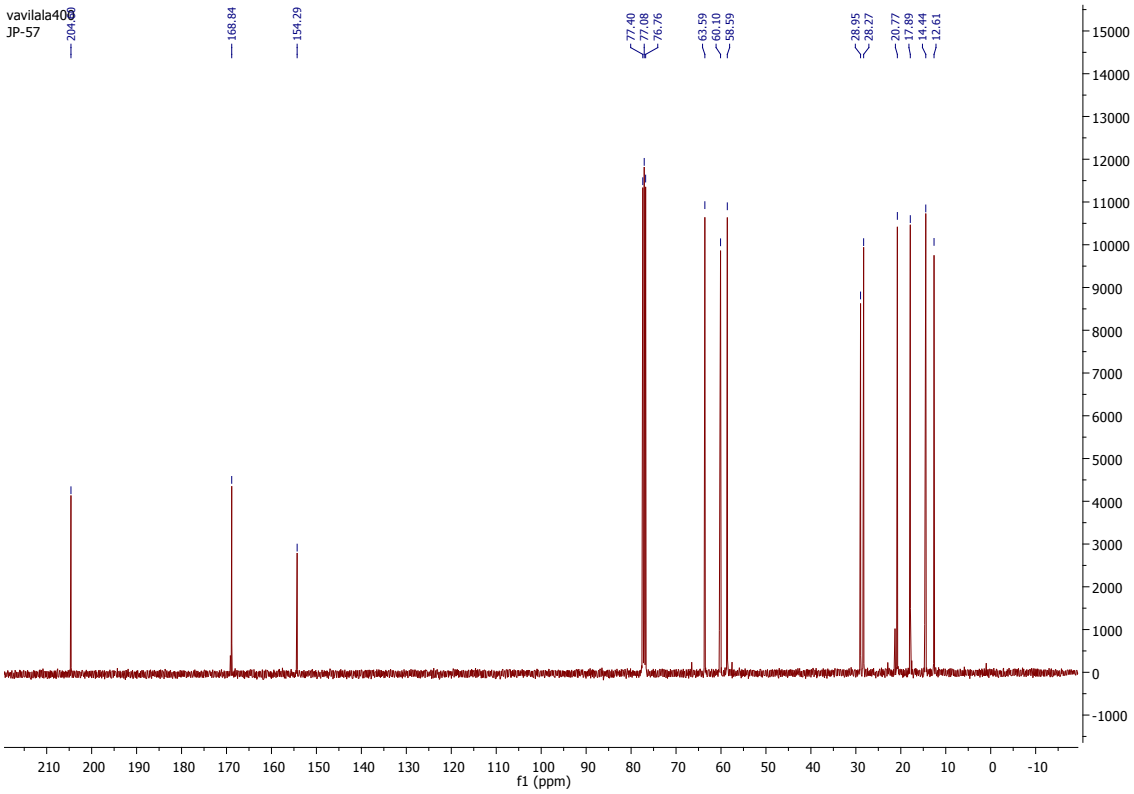
1.15
3.00
5.67
f1 (ppm)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168.84
154.29
77.40
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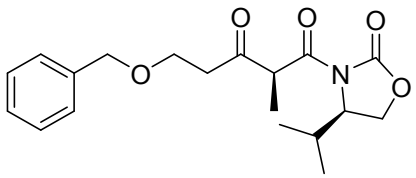
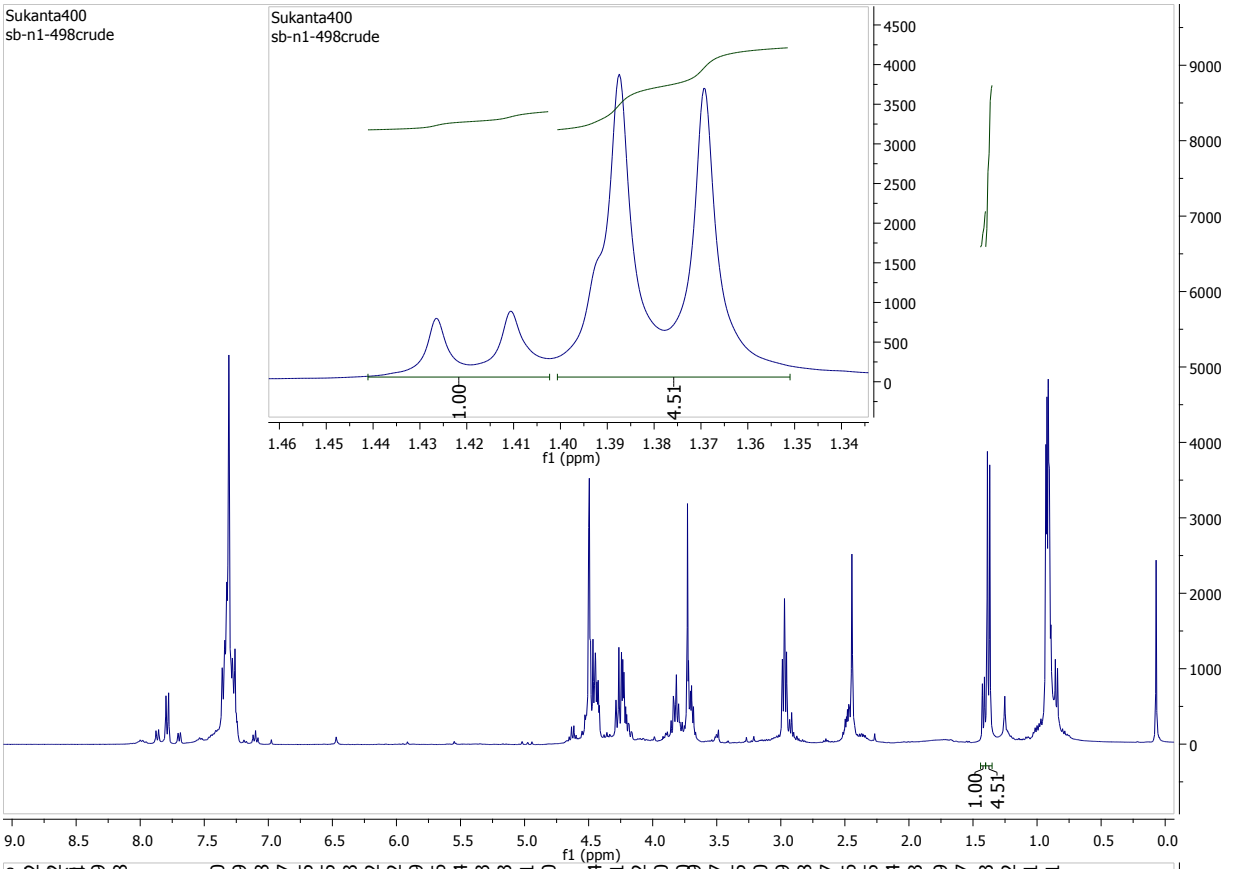
76.76
63.59
60.10
58.59
28.95
28.27
20.77
17.89
14.44
12.61
f1 (ppm)

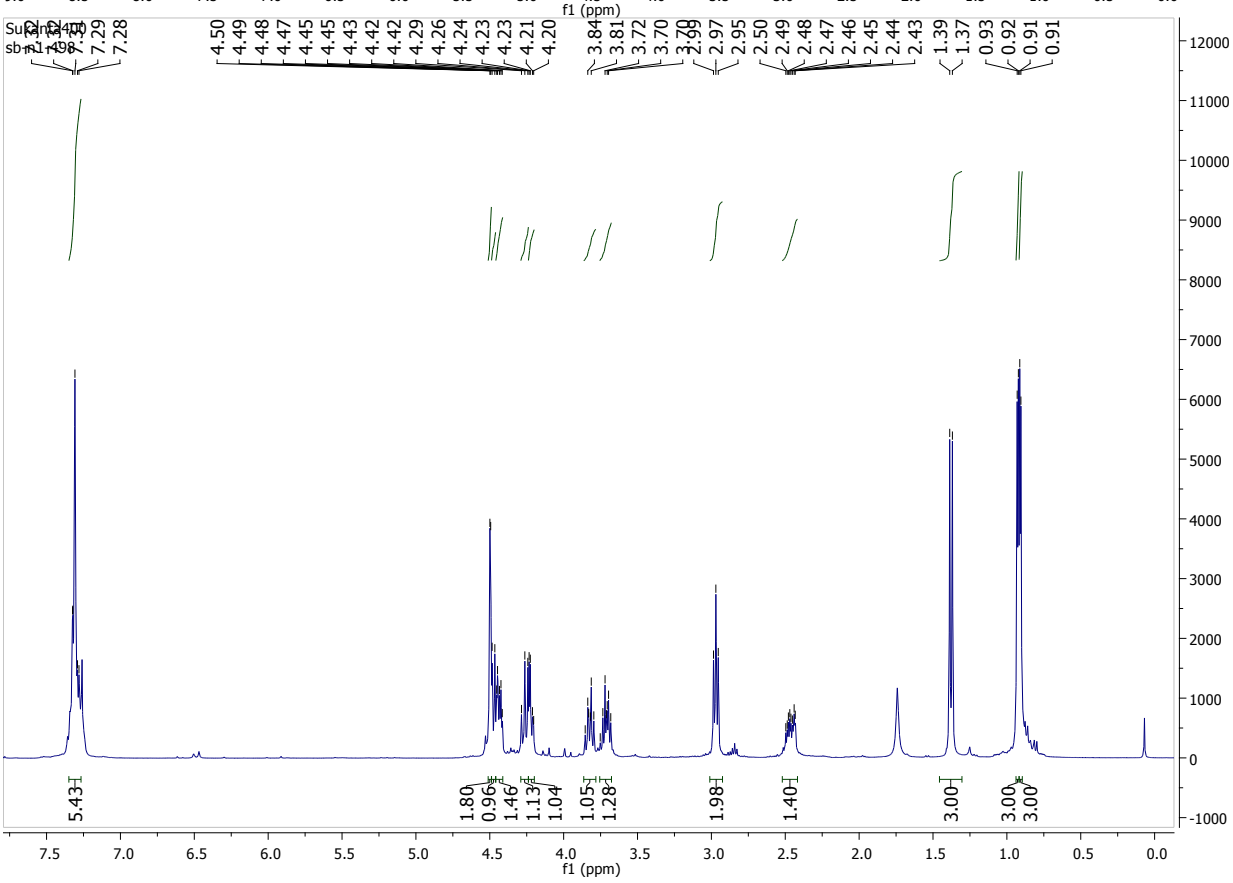
(*S*)-5-(benzyloxy)-1-((*R*)-4-isopropyl-2-oxooxazolidin-3-yl)-2-methylpentane-1,3-dione (13)

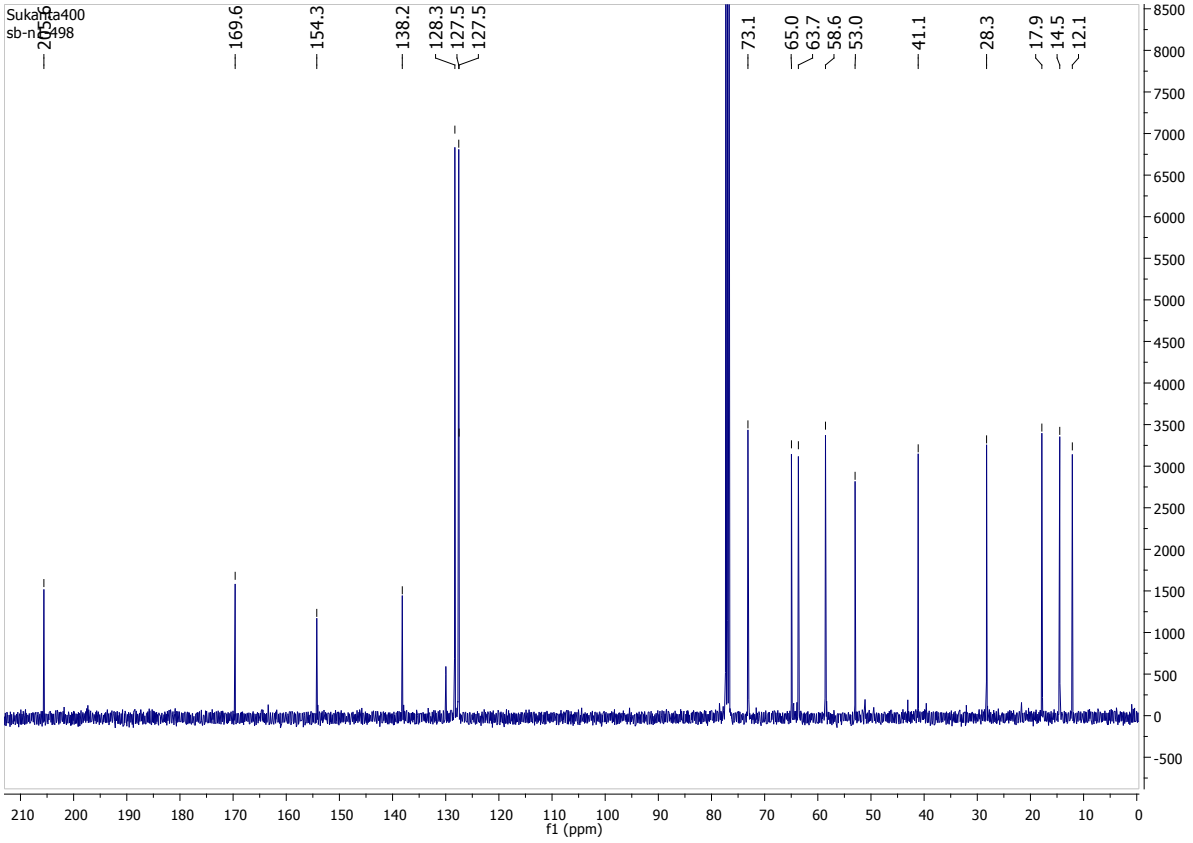


Activated $MgSO_4$ (135 mg, 1.12 mmol, 5 equiv) was taken in a round bottom flask and (R)-5-(benzyloxy)-1-(4-isopropyl-2-oxooxazolidin-3-yl)pentane-1,3-dione (75 mg, 0.23 mmol, 1 equiv), dissolved in 3 mL of toluene, was added to it and the flask was placed at −78 °C. Then Koser reagent (175 mg, 0.45 mmol, 2 equiv) was added in one portion to it and the reaction mixture was allowed to stir for 30 min. Then dimethylzinc (1.2 M, 0.38 ml, 0.46 mmol, 2 equiv) was added dropwise and the reaction was allowed to stir overnight in the dark. The reaction was quenched by adding few drops of water and was diluted with diethylether. Then it was filtered through a mixture of celite and sodium sulfate. Then volatiles were removed and the residue was purified by column chromatography to yield 50 mg of the major product (66% yield), as a colorless oil and as a single diastereoisomer. Reaction d.r. *ca.* 4.5:1 (by crude ^{1}H-NMR). The minor diastereoisomer was not isolated.

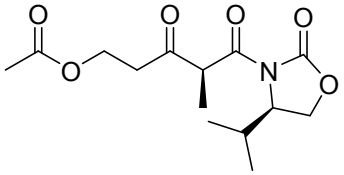
Major diastereoisomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.32 (m, 5H), 4.50 (d, *J* = 2.1, 2H), 4.48 (d, *J* = 7.4, 1H), 4.41– 4.46 (m, 1H), 4.24 – 4.29 (m, 1H), 4.22 (dd, *J* = 9.1, 3.2, 1H), 3.82 (dt, *J* = 9.4, 7.0, 1H), 3.68– 3.76 (m, 1H), 2.97 (t, *J* = 6.5, 2H), 2.43 – 2.50 (m, 1H), 1.38 (d, *J* = 7.3, 3H), 0.93 (d, *J* = 3.2, 3H), 0.91 (d, *J* = 3.1, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.6 169.6, 154.3, 138.2, 128.3 (2C), 127.5 (2C), 127.5, 73.1, 65.0, 63.7, 58.6, 53.0, 41.1, 28.3, 17.9, 14.5, 12.1.
R_f: 0.33 (30% EtOAc/hexane) (major diastereoisomer)
IR ($CHCl_3$) ν 3524, 3034, 3005, 2967, 2875, 1777, 1714, 1603, 1487, 1456, 1387, 1306, 1227, 1195, 1111, 1022, 991 cm^{-1}.
HRMS (ESI+): *m/z*: Calcd for $C_{19}H_{26}NO_5$ $[M+H]^+$, 348.1811; found: 334.1810.


Sukanta400
sb-n1-498crude
Sukanta400
sb-n1-498crude
1.00
4.51
f1 (ppm)
1.00
4.51
f1 (ppm)


7.30
7.29
7.28
4.50
4.49
4.48
4.47
4.45
4.45
4.43
4.42
4.42
4.29
4.26
4.24
4.23
4.23
4.21
4.20
3.84
3.81
3.72
3.70
3.70
2.99
2.97
2.95
2.50
2.49
2.48
2.47
2.46
2.45
2.44
2.43
1.39
1.37
0.93
0.92
0.91
0.91
5.43
1.80
0.96
1.46
1.13
1.04
1.05
1.28
1.98
1.40
3.00
3.00
3.00
f1 (ppm)

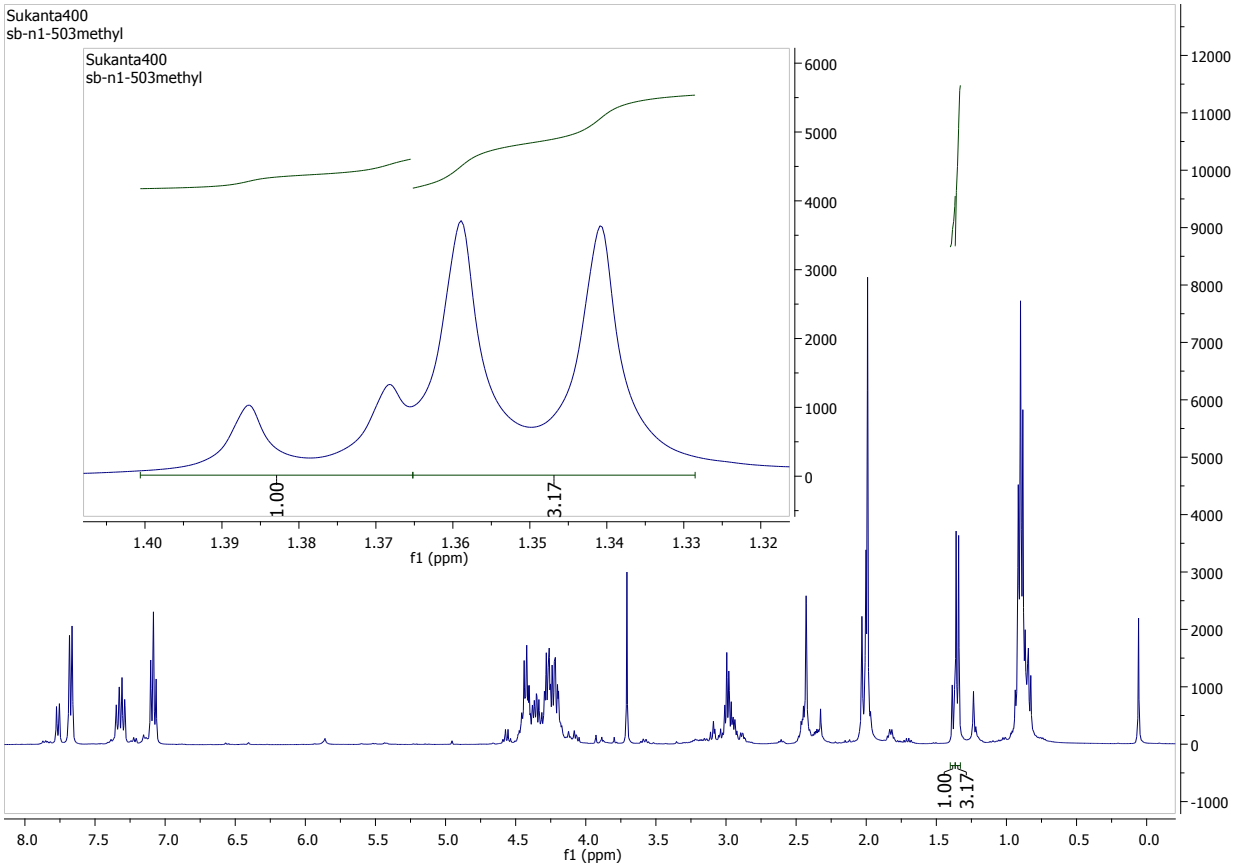


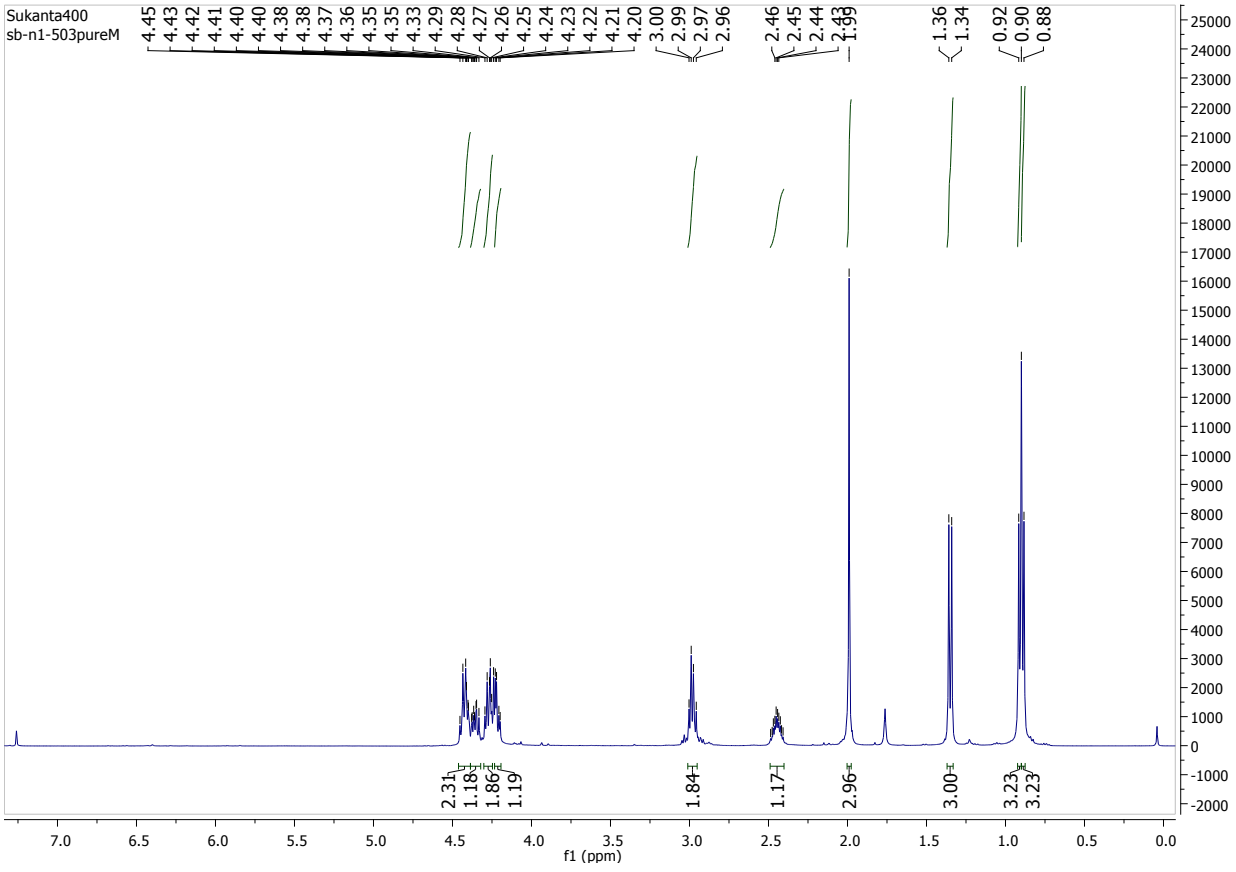
(*S*)-5-((*R*)-4-isopropyl-2-oxooxazolidin-3-yl)-4-methyl-3,5-dioxopentyl acetate (14)

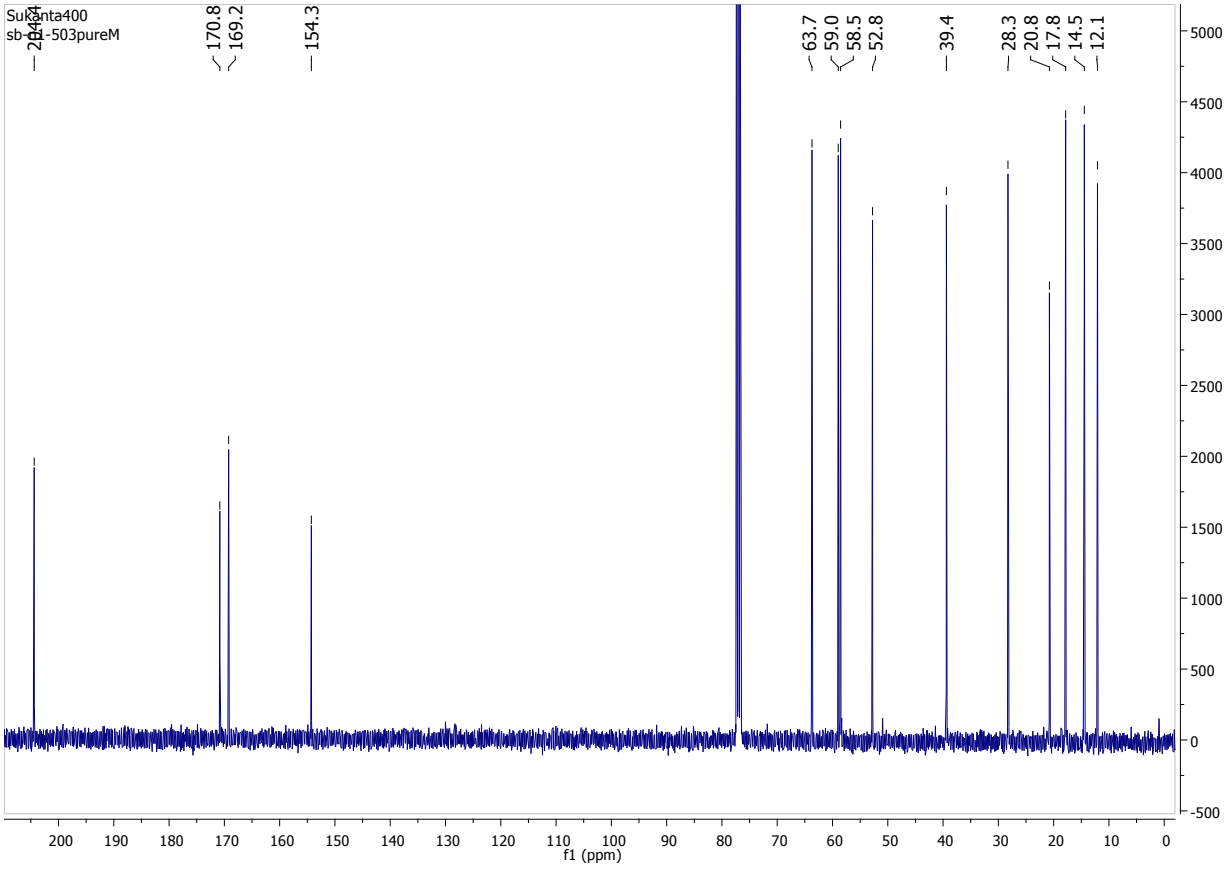


Compound (**14**) was prepared the same way as **(13)**, and isolated as a colorless oil (107 mg, 72% yield) and as a single diastereoisomer. Reaction d.r. *ca.* 3:1 (by crude ^{1}H-NMR). The minor diastereoisomer was not isolated.

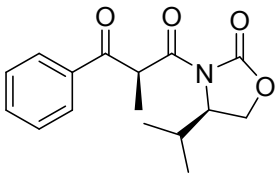
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.40– 4.45 (m, 2H), 4.33– 4.38 (m, 1H), 4.25– 4.29 (m, 2H), 4.21 (dd, *J* = 9.1, 3.2, 1H), 2.98 (dd, *J* = 12.0, 6.3, 2H), 2.43 – 2.46 (m, 1H), 1.99 (s, 3H), 1.35 (d, *J* = 7.3, 3H), 0.91 (d, *J* = 6.7, 3H), 0.89 (d, *J* = 6.6, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 204.4, 170.8, 169.2, 154.3, 63.7, 59.0, 58.5, 52.8, 39.4, 28.3, 20.8, 17.8, 14.5, 12.1.
R_f: 0.3 (30% EtOAc/hexane) (major diastereoisomer)
IR ($CHCl_3$) ν 3675, 3536, 3030, 2969, 2879, 1777, 1732, 1484, 1457, 1378, 1304, 1244, 1237, 1195, 1119, 1076, 1049, 984, 947 cm^{-1}.
HRMS (ESI+): *m/z*: Calcd for $C_{14}H_{22}NO_6$ $[M+H]^+$, 300.1447; found: 300.1448.


Sukanta400
sb-n1-503methyl
Sukanta400
sb-n1-503methyl
1.00
3.17
f1 (ppm)
1.00
3.17
f1 (ppm)


Sukanta400
sb-n1-503pureM
4.45 4.43 4.42 4.41 4.40 4.40 4.38 4.38 4.37 4.36 4.35 4.35 4.33 4.29 4.28 4.27 4.26 4.25 4.24 4.23 4.22 4.21 4.20
3.00 2.99 2.97 2.96
2.46 2.45 2.44 2.43 1.99
1.36 1.34
0.92 0.90 0.88
2.31 1.18 1.86 1.19
1.84
1.17
2.96
3.00
3.23 3.23
f1 (ppm)

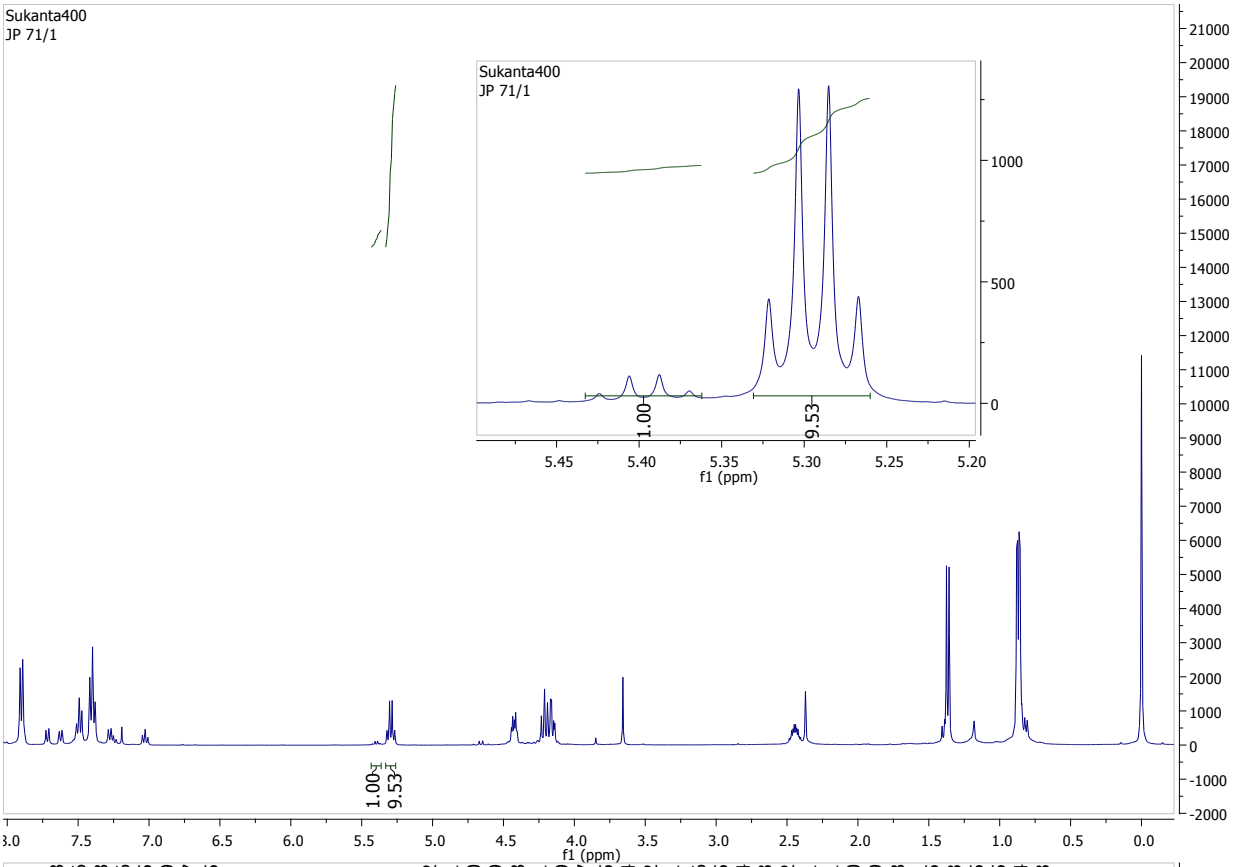


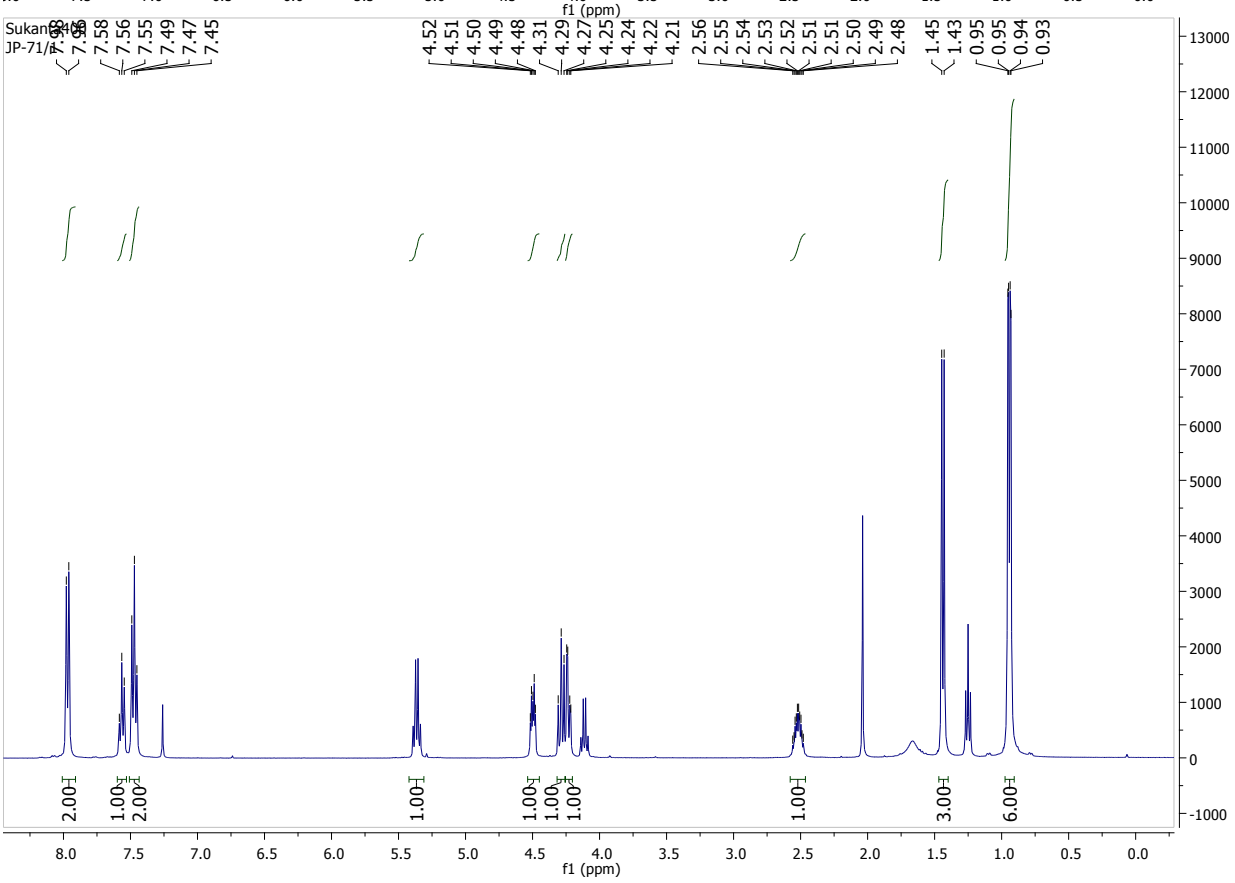
(*S*)-2-methyl-1-((*R*)-4-isopropyl-2-oxooxazolidin-3-yl)-3-phenylpropane-1,3-dione (15)

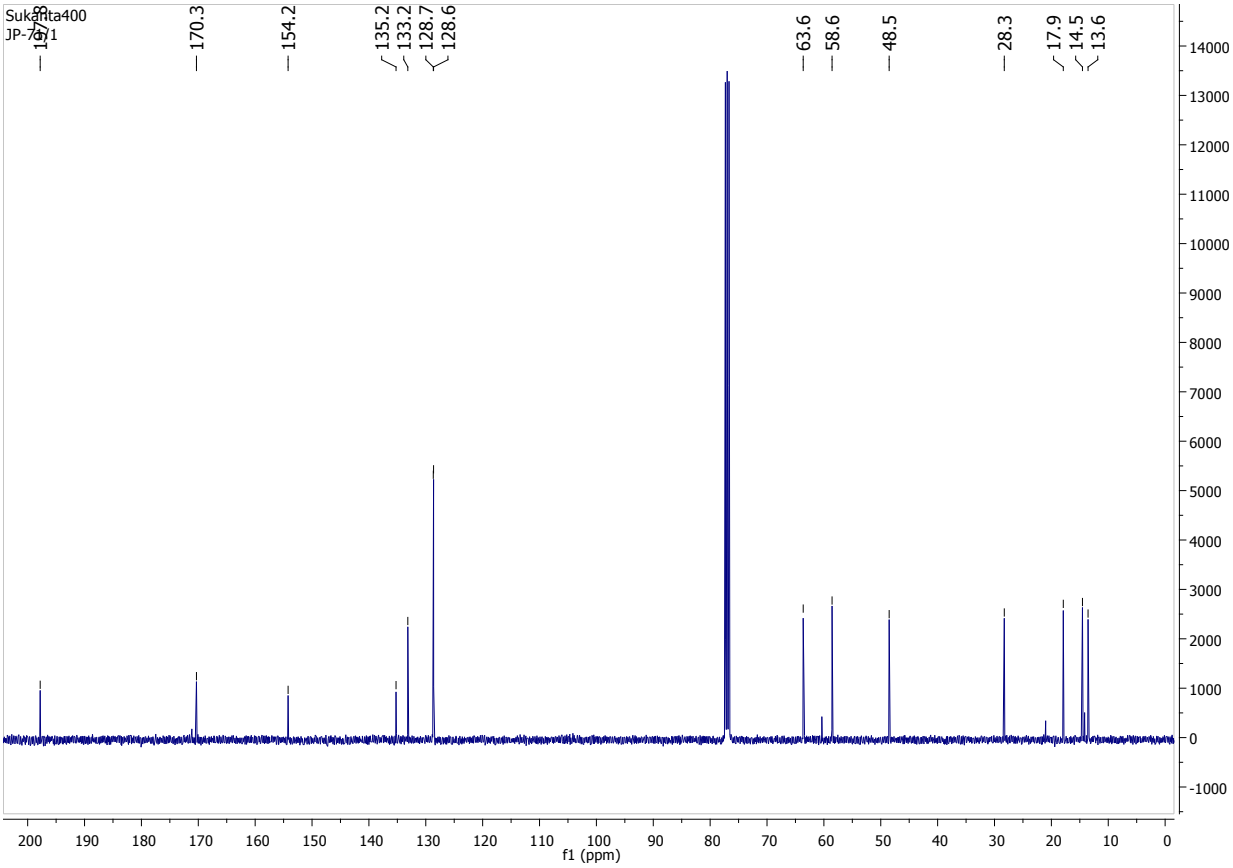


Compound (**15**) was prepared according to general procedure 1 and purified by column chromatography (40% EtOAc/hexane) to give the product (38 mg, 73% yield) as a colorless oil and as a single diastereoisomer. Reaction d.r. *ca.* 9.5:1 (by crude ^{1}H-NMR). The minor diastereoisomer was not isolated.

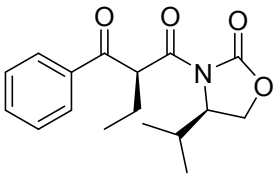
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.4, 2H), 7.56 (t, *J* = 7.3, 1H), 7.47 (t, *J* = 7.6, 2H), 5.36 (q, *J* = 7.2, 1H), 4.48 – 4.52 (m, 1H), 4.29 (t, *J* = 8.7, 1H), 4.23 (dd, *J* = 9.1, 3.1, 1H), 2.48 – 2.56 (m, 1H), 1.44 (d, *J* = 7.3, 3H), 0.95 (d, *J* = 6.9, 3H), 0.94 (d, *J* = 7.0, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 170.3, 154.2, 135.2, 133.2, 128.7 (2C), 128.6 (2C), 63.6, 58.6, 48.5, 28.3, 17.9, 14.5, 13.6.
R_f: 0.35 (40% EtOAc/hexane) (major diastereoisomer)
IR ($CHCl_3$) ν 3034, 2969, 2933, 2879, 1777, 1711, 1602, 1534, 1509, 1485, 1441, 1389, 1312, 1232, 1227, 1194, 1153, 1113, 1061, 1032, 974, 929 cm^{-1}.
HRMS (ESI+): *m/z*: Calcd for $C_{16}H_{20}NO_4$ $[M+H]^+$, 290.1392; found: 290.1360


Sukanta400
JP 71/1
Sukanta400
JP 71/1
1.00
9.53
f1 (ppm)
f1 (ppm)


7.98
7.96
7.58
7.56
7.55
7.49
7.47
7.45
4.52
4.51
4.50
4.49
4.48
4.31
4.29
4.27
4.25
4.24
4.22
4.21
2.56
2.55
2.54
2.53
2.52
2.51
2.51
2.50
2.49
2.48
1.45
1.43
0.95
0.95
0.94
0.93
2.00
1.00
2.00
1.00
1.00
1.00
1.00
3.00
6.00
f1 (ppm)



(*S*)-2-ethyl-1-((*R*)-4-isopropyl-2-oxooxazolidin-3-yl)-3-phenylpropane-1,3-dione (16)



Compound (**16**) was prepared according to general procedure 1 and was purified by column chromatography (40% EtOAc/hexane) to give the product (39 mg, 71% yield, d.r. *ca.* 3.6:1) as a colorless oil. Reaction d.r. *ca.* 3.6:1 (by crude ^{1}H-NMR).

Major diastereoisomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.3, 2H), 7.56 (t, J = 7.4, 1H), 7.47 (t, J = 7.6, 2H), 5.29 (dd, J = 9.2, 3.5, 1H), 4.50 (dt, J = 8.0, 3.3, 1H), 4.29 (t, J = 8.7, 1H), 4.22 (dd, J = 9.2, 3.0, 1H), 2.49 – 2.53 (m, 1H), 2.00– 2.12 (m, 1H), 1.80– 1.92 (m, 1H), 1.02 (t, J = 7.3, 3H), 0.93 (d, J = 6.7, 3H), 0.91 (d, J = 6.3, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0, 169.4, 154.2, 135.8, 133.1, 128.7 (2C), 128.6 (2C), 63.6, 58.6, 55.3, 28.3, 21.8, 17.9, 14.5, 12.7.

Minor diastereoisomer (distinguishable signals only):

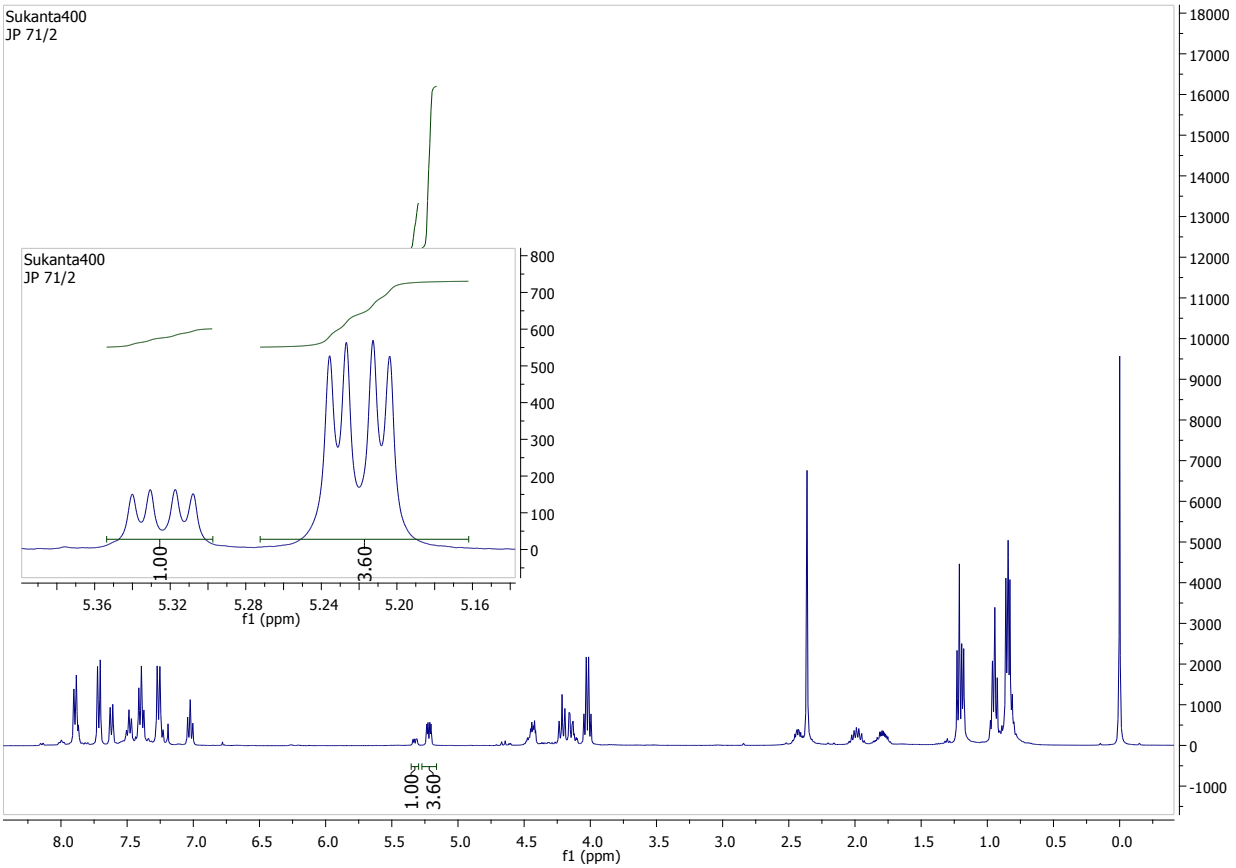
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (dd, J = 9.1, 3.8, 1H), 2.37– 2.45 (m, 1H).

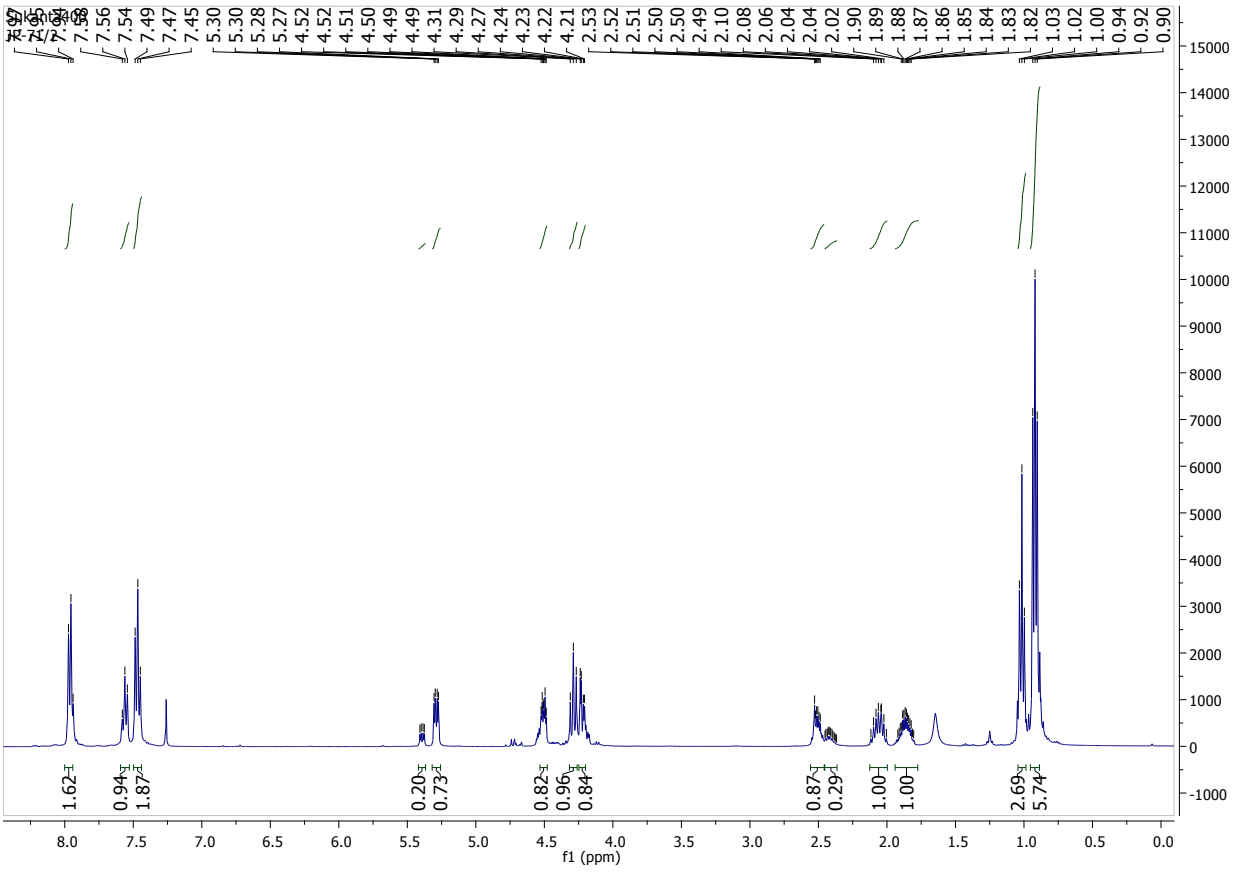
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, 169.5, 133.2, 128.7 (2C), 128.5 (2C), 63.7, 58.7, 55.6, 28.4, 22.3, 14.7.

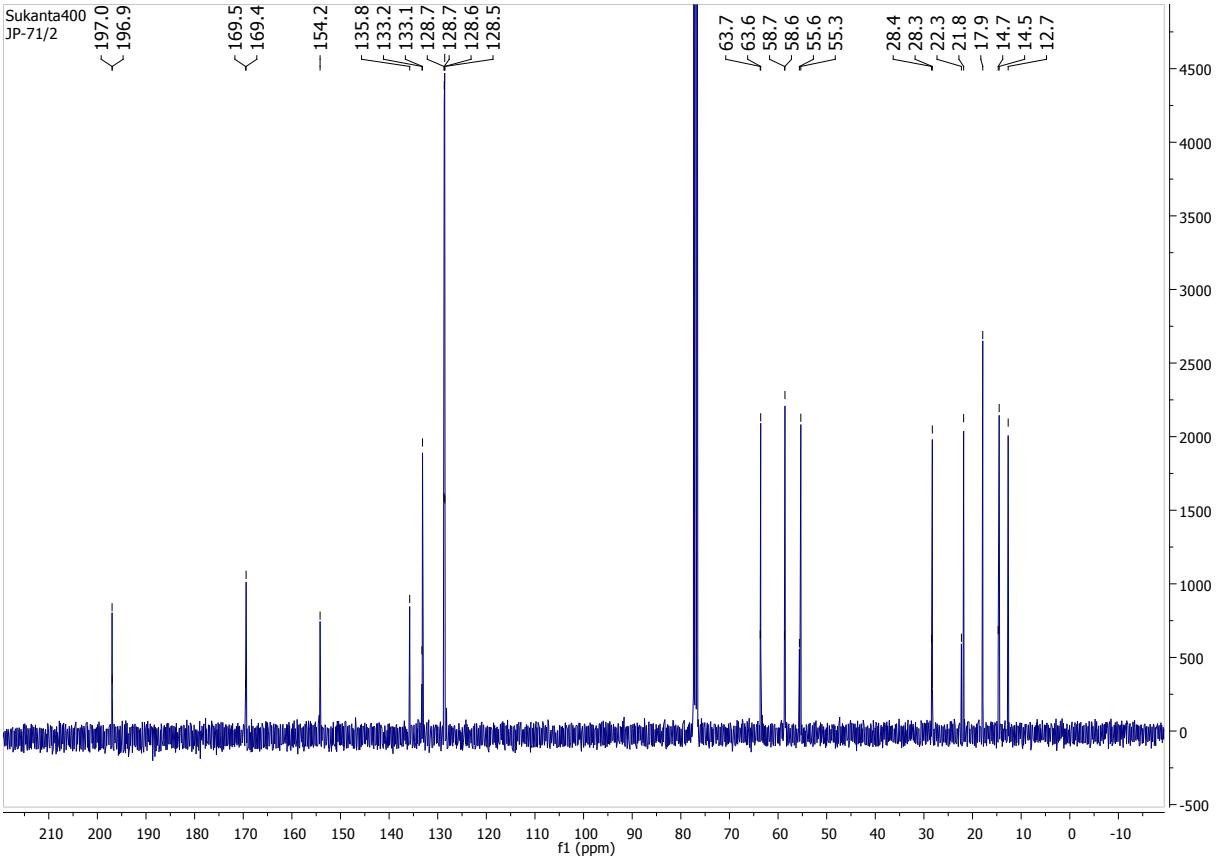
R_f: 0.47 (40% EtOAc/hexane) (both diastereoisomers)

IR ($CHCl_3$) ν 3025, 2970, 2878, 1776, 1711, 1682, 1600, 1452, 1386, 1308, 1281, 1227, 1195, 1119, 1089, 1059, 997, 925 cm^{-1}.

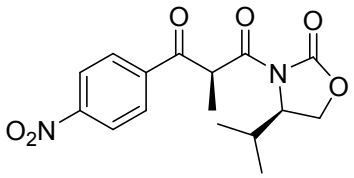
HRMS (ESI+): *m/z*: Calcd for $C_{17}H_{22}NO_4$ $[M+H]^+$, 304.1549; found: 304.1518


Sukanta400
JP 71/2
Sukanta400
JP 71/2
1.00
3.60
f1 (ppm)
1.00
3.60
f1 (ppm)


1.62
0.94
1.87
0.20
0.73
0.82
0.96
0.84
0.87
0.29
1.00
1.00
2.69
5.74
f1 (ppm)

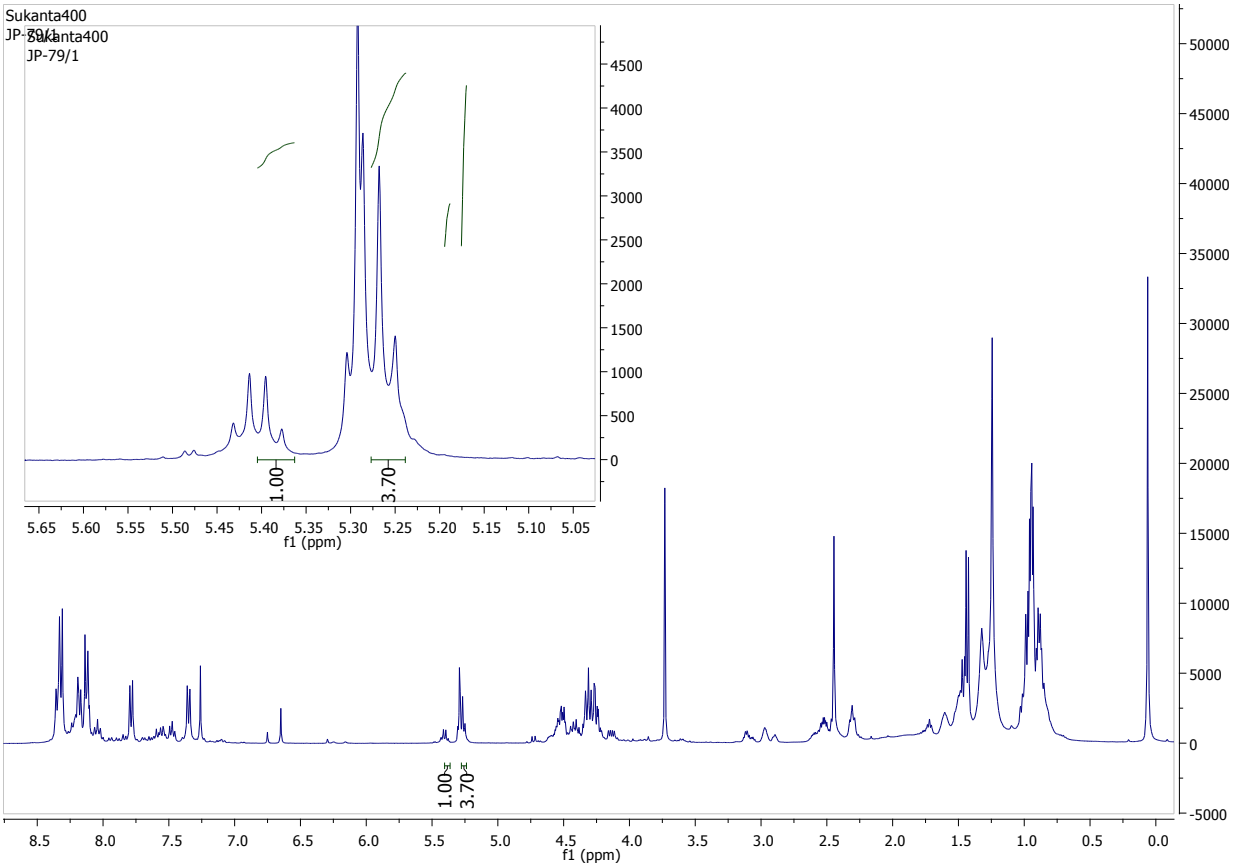


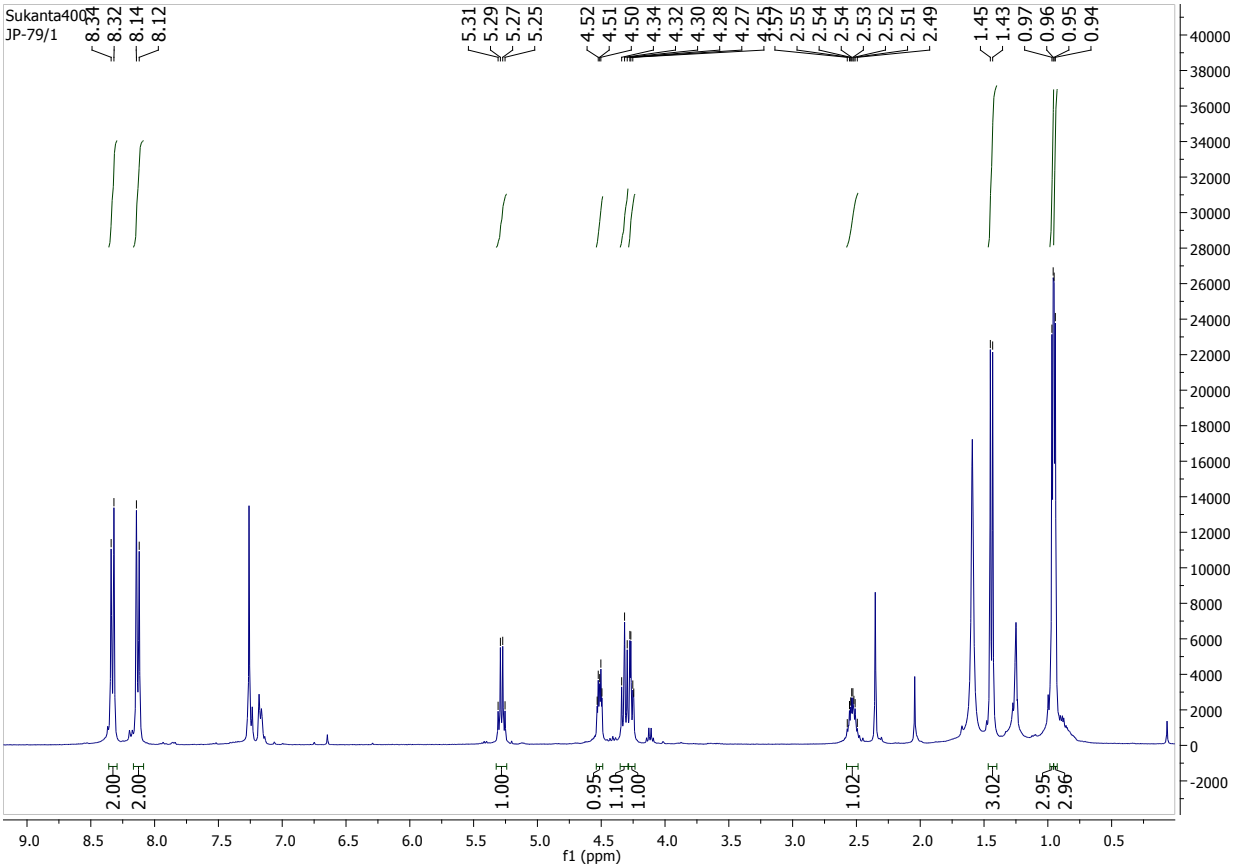
(*S*)-1-((*R*)-4-isopropyl-2-oxooxazolidin-3-yl)-2-methyl-3-(4-nitrophenyl)propane-1,3-dione (17)

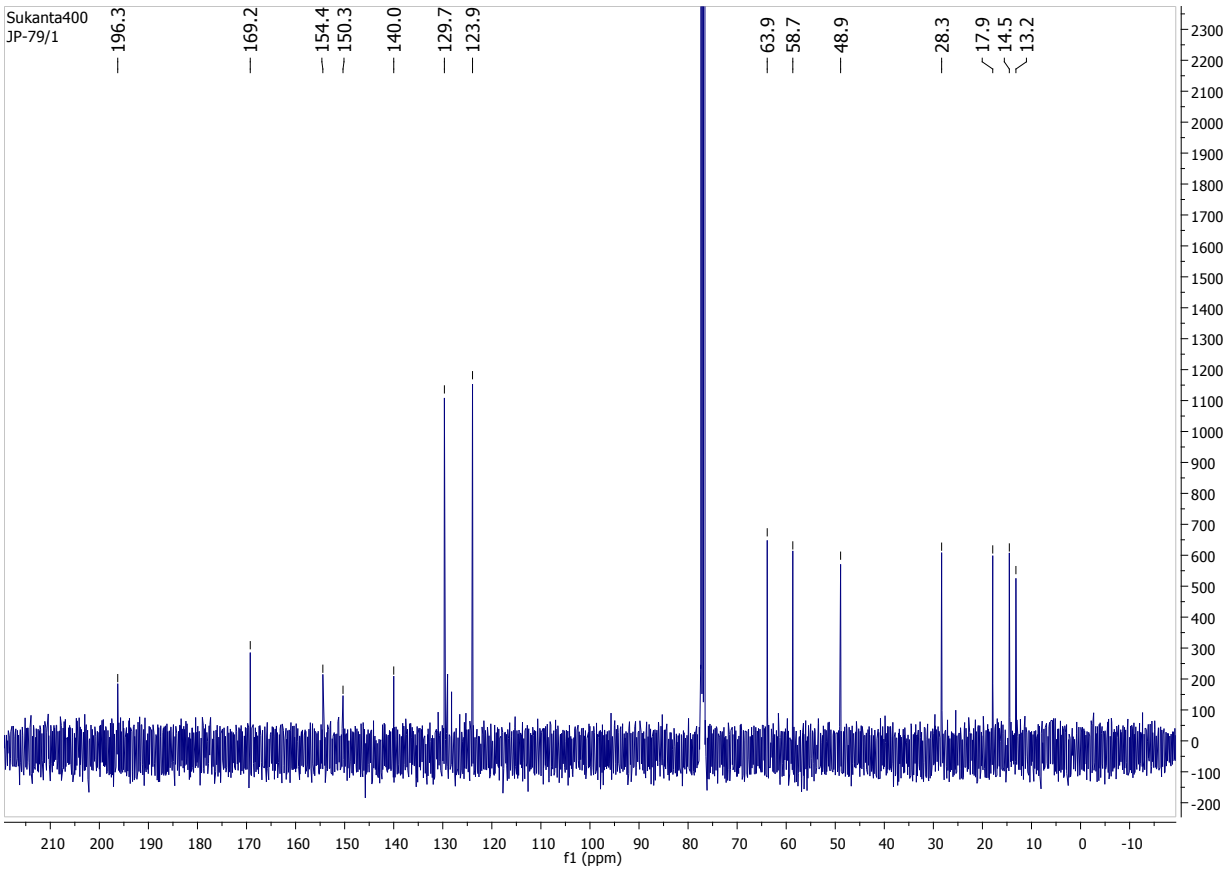


Compound (**17**) was prepared according to general procedure 1 and was purified by column chromatography (40% EtOAc/hexane) to give the product (33 mg, 80% yield) as a colorless oil and as asingle diastereoisomer. Reaction d.r. *ca.* 3.7:1 (by crude ^{1}H-NMR). The minor diastereoisomer was not isolated.

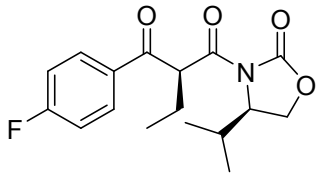
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.8, 2H), 8.13 (d, *J* = 8.8, 2H), 5.28 (q, *J* = 7.3, 1H), 4.50 – 4.52 (m, 1H), 4.32 (t, *J* = 8.7, 1H), 4.26 (dd, *J* = 9.2, 3.1, 1H), 2.49 – 2.57 (m, 1H), 1.44 (d, *J* = 7.3, 3H), 0.96 (d, *J* = 7.0, 3H), 0.95 (d, *J* = 6.8, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 169.2, 154.4, 150.3, 140.0, 129.7 (2C), 123.9 (2C), 63.9, 58.7, 48.9, 28.3, 17.9, 14.5, 13.2.
R_f: 0.2 (40% EtOAc/hexane)
IR ($CHCl_3$) ν 3025, 2966, 1776, 1712, 1601, 1530, 1442, 1390, 1345, 1311, 1227, 1196, 1114, 1058, 1030, 976 cm^{-1}.
HRMS (ESI−): *m/z*: Calcd for $C_{16}H_{17}N_2O_6$ $[M-H]^-$, 333.1087; found: 333.1081


Sukanta400
JP-79/1
1.00
3.70
f1 (ppm)


Sukanta400
JP-79/1
8.34
8.32
8.14
8.12
5.31
5.29
5.27
5.25
4.52
4.51
4.50
4.34
4.32
4.30
4.28
4.27
4.25
2.57
2.55
2.54
2.54
2.53
2.52
2.51
2.49
1.45
1.43
0.97
0.96
0.95
0.94
2.00
2.00
1.00
0.95
1.10
1.00
1.02
3.02
2.95
2.96
f1 (ppm)

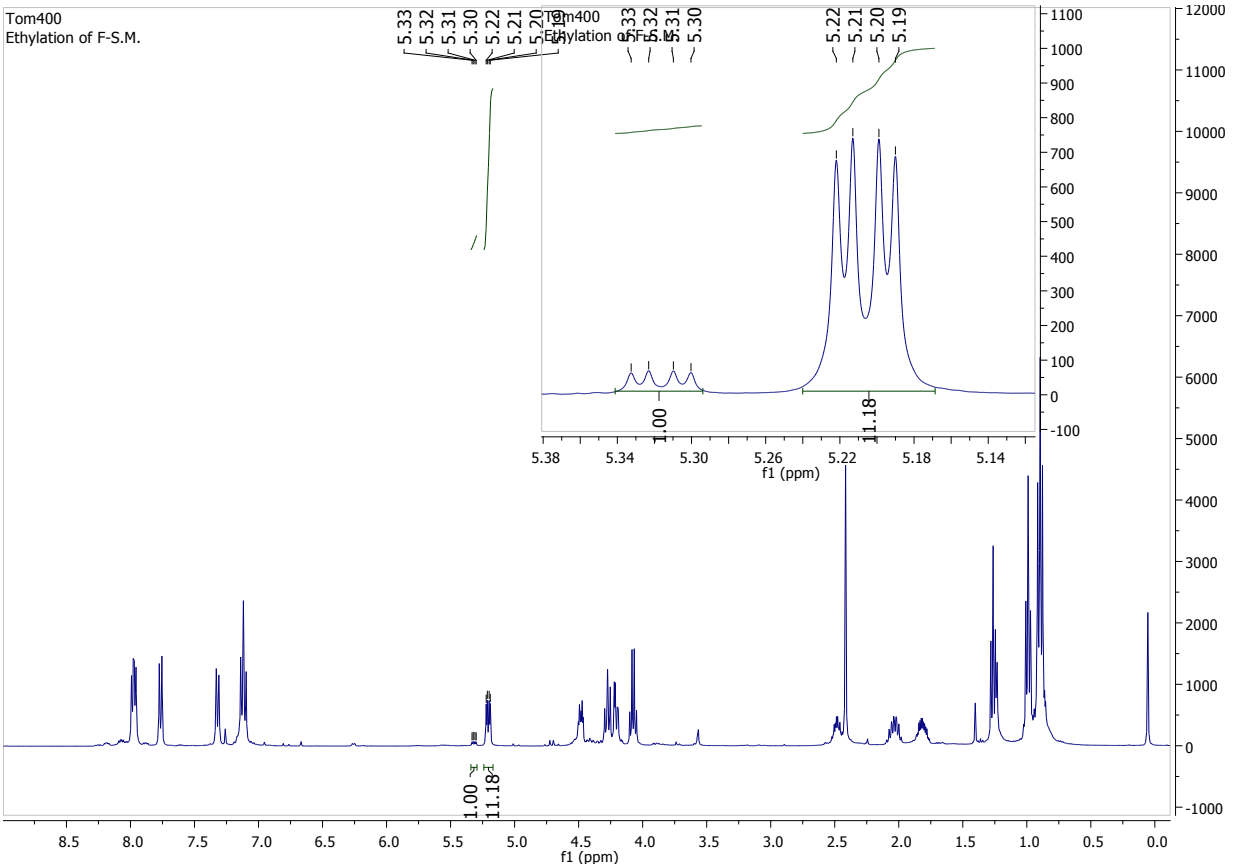


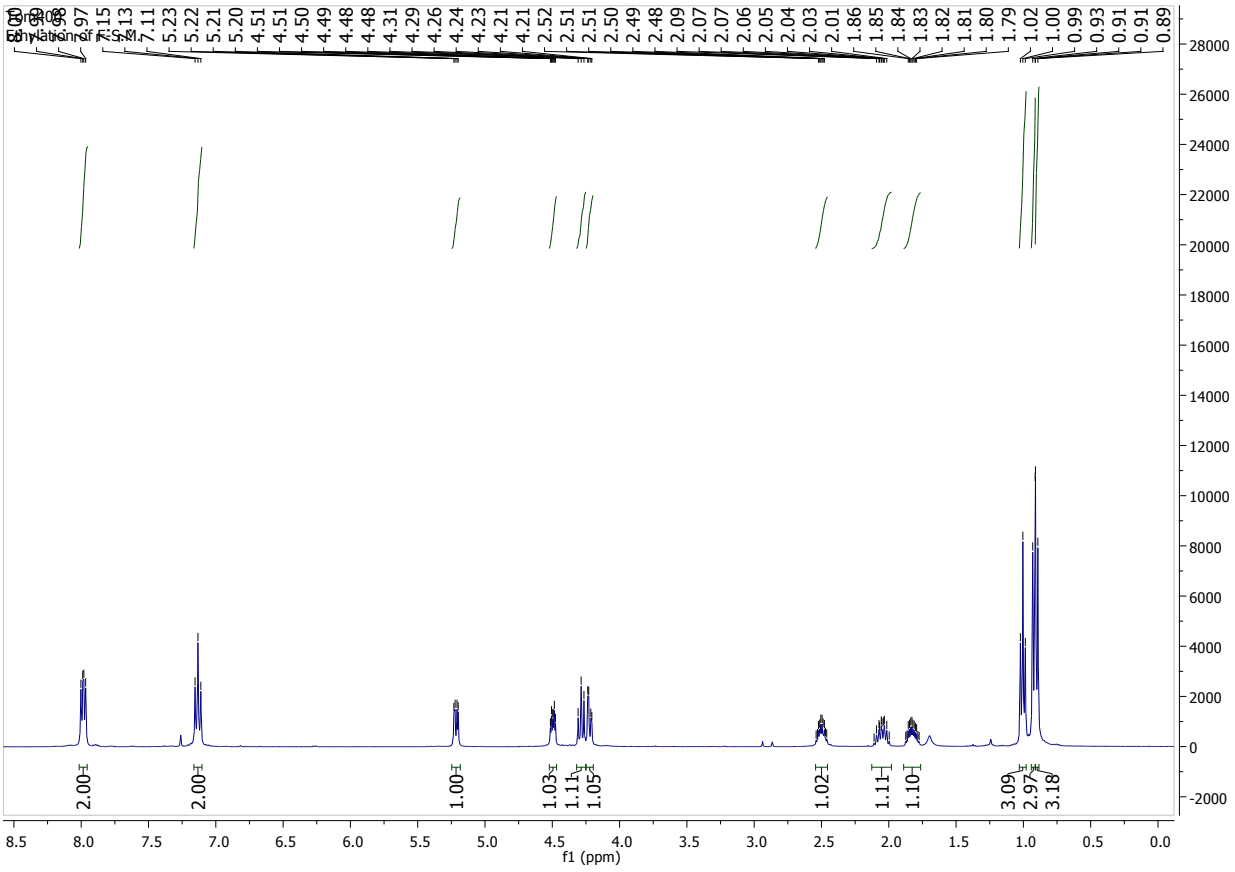
(*S*)-2-ethyl-1-(4-fluorophenyl)-3-((*R*)-4-isopropyl-2-oxooxazolidin-3-yl)propane-1,3-dione (18)

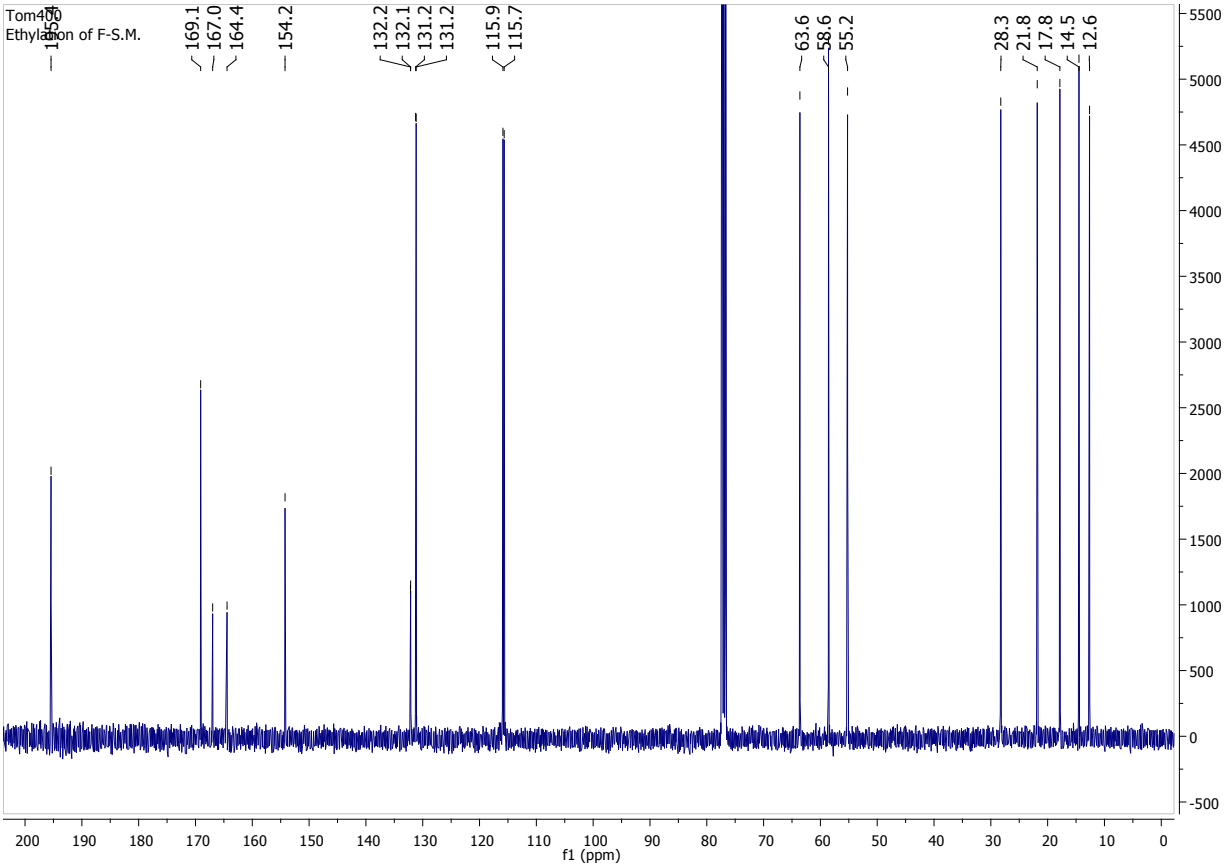


Compound **(18)** was prepared according to general procedure 1. Excess Et_2Zn was quenched with a few drops of water, the mixture was allowed to reach r.t. and was then filtered through celite using Et_2O as a solvent. The solvents removed *in vacuo*, and the crude was purified by column chromatography (15% - 30% EtOAc/hexane) to give the product (34 mg, 55% yield) as a yellow oil and as a single diastereoisomer. Reaction d.r. *ca.* 11:1 (by crude ^{1}H-NMR). The minor diastereoisomer was not isolated.

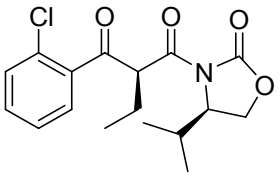
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, J = 8.8, 5.4, 2H), 7.13 (t, J = 8.6, 2H), 5.22 (dd, J = 9.2, 3.6, 1H), 4.50 (dt, J = 8.1, 3.3, 1H), 4.29 (t, J = 8.7, 1H), 4.22 (dd, J = 9.2, 3.0, 1H), 2.48 – 2.52 (m, 1H), 2.01 – 2.09 (m, 1H), 1.79 – 1.86 (m, 1H), 1.00 (t, J = 7.3, 3H), 0.92 (d, J = 7.3, 3H), 0.90 (d, J = 7.1, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 195.4, 169.1, 165.7 (d, J = 254.9), 154.2, 132.1 (d, J = 3.0), 131.2 (d, J = 9.3, 2C), 115.8 (d, J = 22.0, 2C), 63.6, 58.6, 55.2, 28.3, 21.8, 17.8, 14.5, 12.6.
R_f: 0.50 (30% EtOAc/hexane)
IR ($CHCl_3$) ν 3032, 2971, 2878, 1775, 1711, 1681, 1599, 1508, 1461, 1387, 1306, 1281, 1235, 1227, 1194, 1153, 1119, 1089, 1056, 998, 912 cm^{-1}.
HRMS (ESI+): *m/z*: Calcd for $C_{17}H_{21}NO_4F$ $[M+H]^+$, 322.1455; found: 322.1422


Tom400
Ethylation of F-S.M.
f1 (ppm)


Tom400
Ethylation of F-S.M.
f1 (ppm)

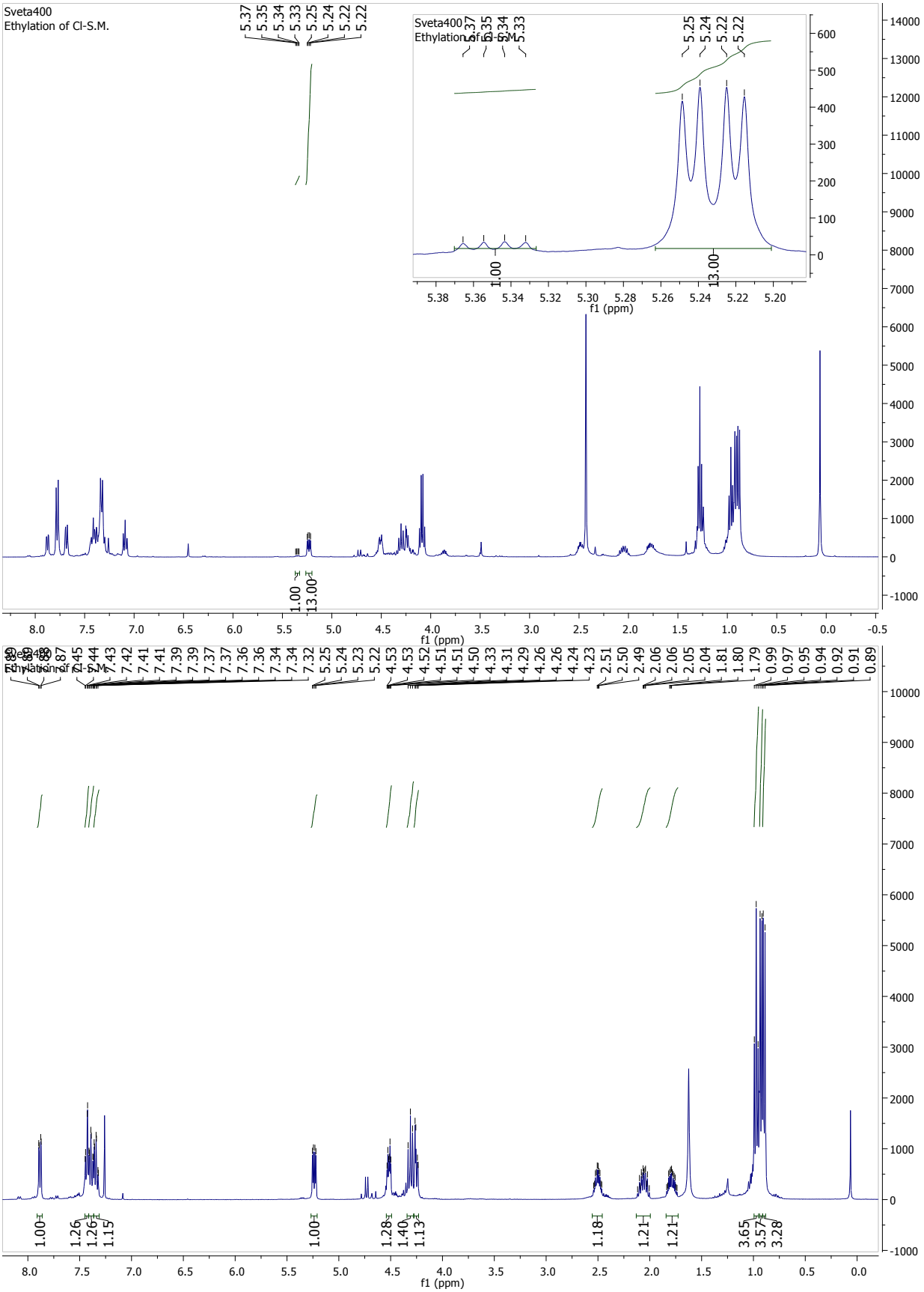


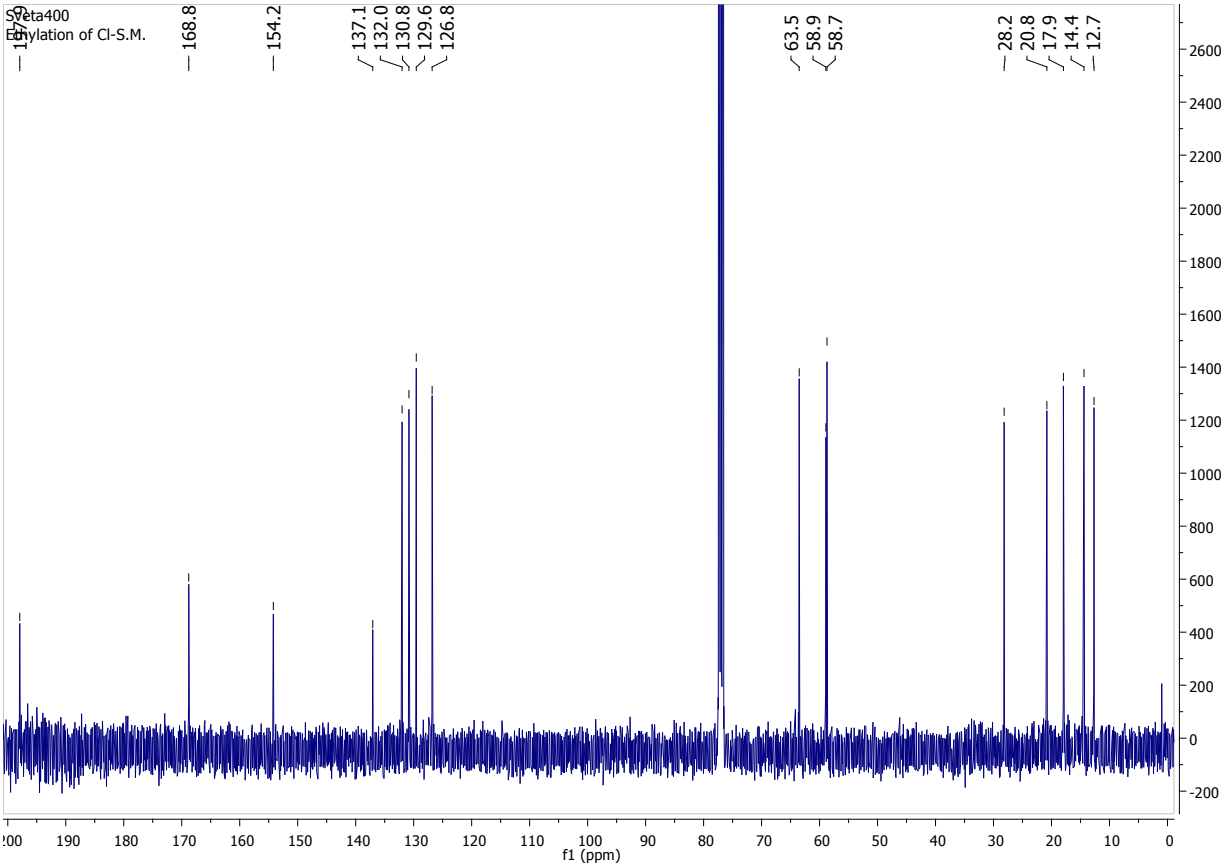
(*S*)-1-(2-chlorophenyl)-2-ethyl-3-((*R*)-4-isopropyl-2-oxooxazolidin-3-yl)propane-1,3-dione (19)



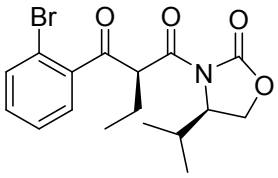
Compound (**19**) was prepared according to general procedure 1. Excess Et_2Zn was quenched with a few drops of water, the mixture was allowed to reach r.t. and was then filtered through celite using Et_2O as a solvent. The solvents removed *in vacuo*, and the crude was purified by column chromatography (20% - 30% EtOAc/hexane) to give the product (30 mg, 55% yield) as a yellow oil and as a single diastereoisomer. Reaction d.r. *ca.* 13:1 (by crude ^{1}H-NMR). The minor diastereoisomer was not isolated.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 7.6, 1.7, 1H), 7.44 (dd, *J* = 7.9, 1.4, 1H), 7.39 (td, *J* = 7.6, 1.8, 1H), 7.34 (td, *J* = 7.4, 1.6, 1H), 5.24 (dd, *J* = 9.5, 3.8, 1H), 4.52 (dt, *J* = 8.1, 3.2, 1H), 4.23 – 4.33 (m, 1H), 4.25 (dd, *J* = 9.1, 3.0, 1H), 2.49 – 2.51 (m, 1H), 2.00 – 2.12 (m, 1H), 1.73 – 1.84 (m, 1H), 0.97 (t, *J* = 7.3, 3H), 0.93 (d, *J* = 7.1, 3H), 0.90 (d, *J* = 6.9, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 168.8, 154.2, 137.1, 132.0, 130.8, 129.6, 126.8, 63.5, 58.9, 58.7, 28.2, 20.8, 17.9, 14.4, 12.7. The C-Cl carbon was not observed.
R_f: 0.48 (30% EtOAc/hexane)
IR ($CHCl_3$) ν 3030, 2970, 2878, 1777, 1712, 1592, 1464, 1435, 1387, 1305, 1279, 1231, 1227, 1194, 1117, 1091, 1062, 994, 913 cm^{-1}.
HRMS (ESI+): *m/z*: Calcd for $C_{17}H_{21}NO_4Cl$ $[M+H]^+$, 338.1159; found: 338.1165


Sveta400
Ethylation of Cl-S.M.
f1 (ppm)

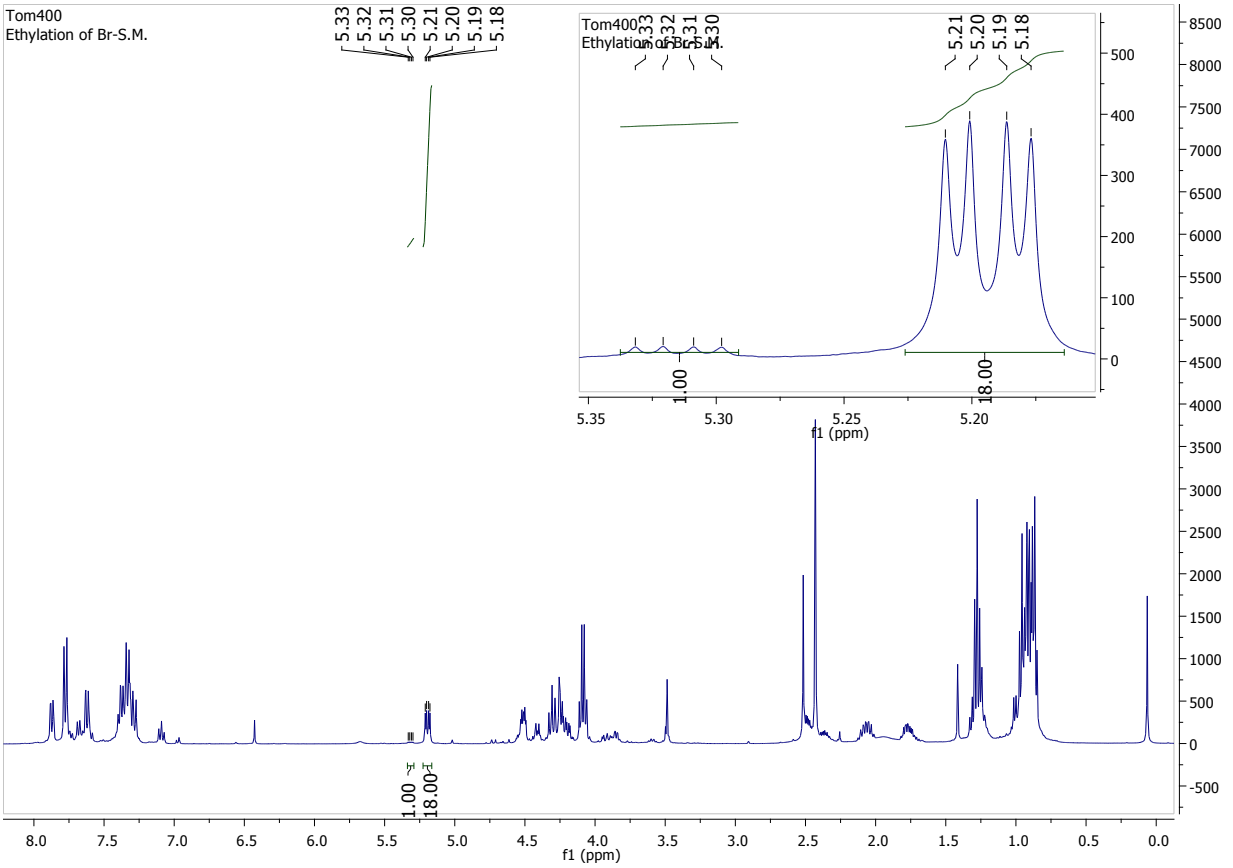


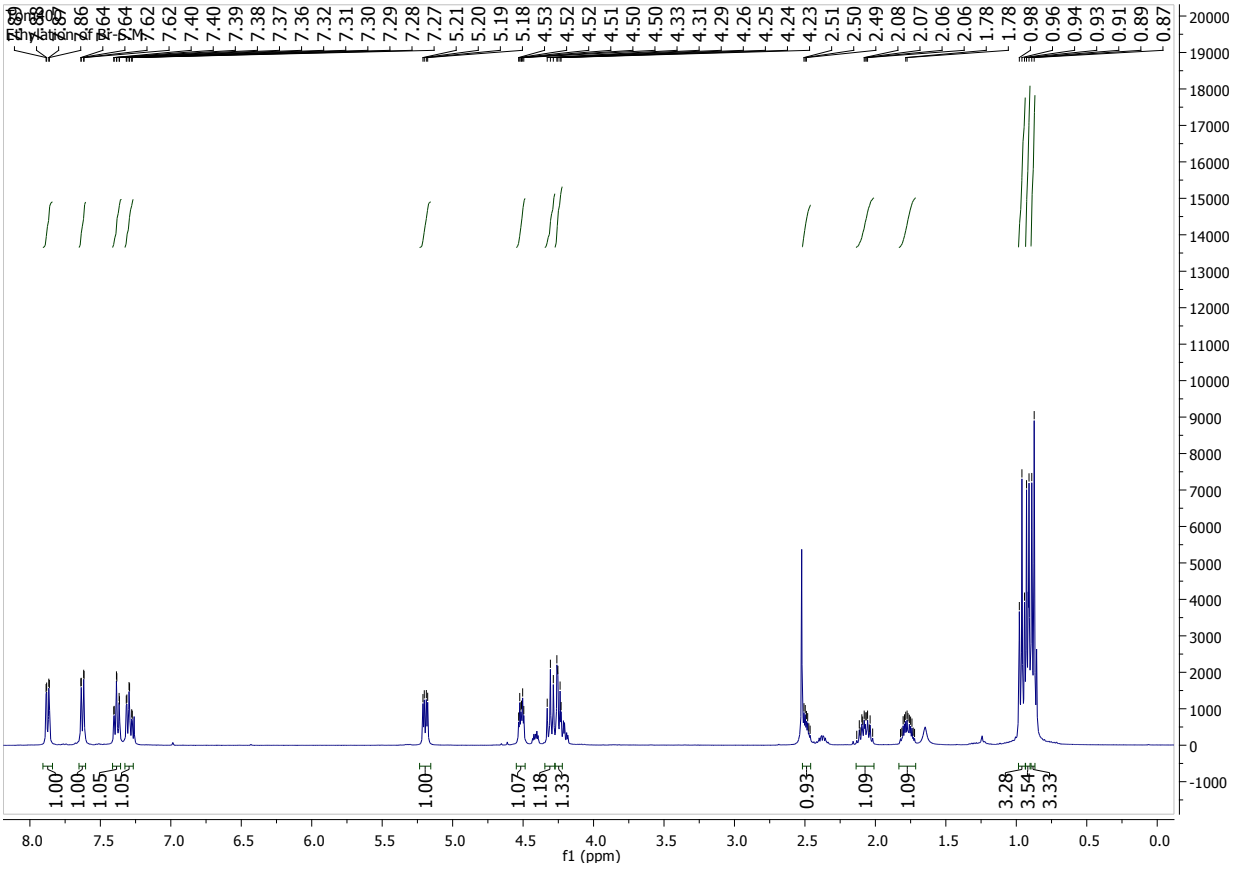
(*S*)-1-(2-bromophenyl)-2-ethyl-3-((*R*)-4-isopropyl-2-oxooxazolidin-3-yl)propane-1,3-dione (20)

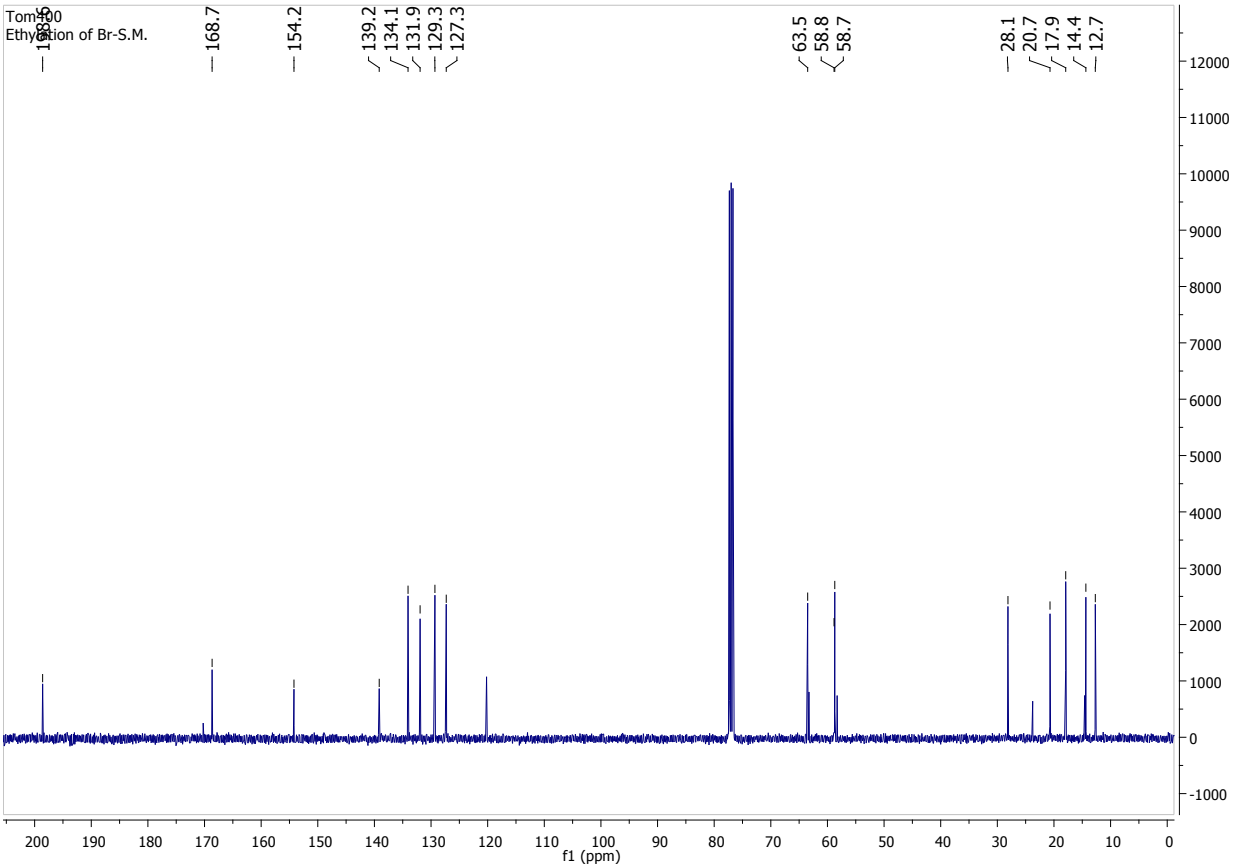


Compound (**20**) was prepared according to general procedure 1. Excess Et_2Zn was quenched with a few drops of water, the mixture was allowed to reach r.t. and was then filtered through celite using Et_2O as a solvent. The solvents removed *in vacuo*, and the crude was purified by column chromatography (15% - 30% EtOAc/hexane) to give the product (23 mg, 40% yield) as a yellow oil and as a single diastereoisomer. Reaction d.r. *ca.* 18:1 (by crude ^{1}H-NMR). The minor diastereoisomer was not isolated.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.7, 1.6, 1H), 7.63 (dd, *J* = 7.9, 0.9, 1H), 7.38 (td, *J* = 7.6, 1.1 Hz, 1H), 7.29 (td, *J* = 7.8, 1.7, 1H), 5.19 (dd, *J* = 9.6, 3.8, 1H), 4.51 (dt, *J* = 8.1, 3.2, 1H), 4.31 (t, *J* = 8.7, 1H), 4.25 (dd, *J* = 9.1, 2.9, 1H), 2.49 – 2.51 (m, 1H), 2.01 – 2.14 (m, 1H), 1.71 – 1.83 (m, 1H), 0.96 (t, *J* = 7.3, 3H), 0.92 (d, *J* = 7.1, 3H), 0.88 (d, *J* = 6.9, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.6, 168.7, 154.2, 139.2, 134.1, 131.9, 129.3, 127.3, 63.5, 58.8, 58.7, 28.1, 20.7, 17.9, 14.4, 12.7. The C-Br carbon was not observed.
R_f: 0.48 (30% EtOAc/hexane)IR ($CHCl_3$) ν 3028, 2971, 2935, 2878, 1777, 1709, 1588, 1463, 1431, 1384, 1305, 1282, 1231, 1226, 1194, 1145, 1122, 1088, 1059, 1023, 991, 914 cm^{-1}.
HRMS (ESI+): *m/z*: Calcd for $C_{17}H_{21}NO_4Br$ $[M+H]^+$, 382.0654; found: 382.0641

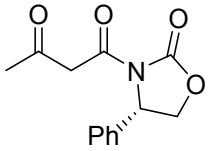

Tom400
Ethylation of Br-S.M.
5.33
5.32
5.31
5.30
5.21
5.20
5.19
5.18
1.00
18.00
f1 (ppm)


Tom400
Ethylation of Br-S.M.
1.00
1.00
1.05
1.05
1.00
1.07
1.18
1.33
0.93
1.09
1.09
3.28
3.54
3.33
f1 (ppm)



Preparation of Starting Materials

(*S*)-1-(2-oxo-4-phenyloxazolidin-3-yl)butane-1,3-dione (4)



To a solution of (*S*)-4-phenyl-2-oxazolidinone (450 mg, 2.76 mmol, 1.0 equiv) in toluene (14 mL) 2,2,6-trimethyl-4H-1,3-dioxin-4-one (0.55 mL, 4.14 mmol, 1.5 equiv) was added dropwise and stirred for 15 min at r.t. under Argon. The mixture was refluxed for 22 h until full consumption of the oxazolidinone (TLC). The mixture was allowed to reach r.t., and the solvent was removed *in vacuo*. The crude was purified by column chromatography (20%-25% EtOAc/hexane) to give the product (590 mg, 86% yield) as a yellow solid.

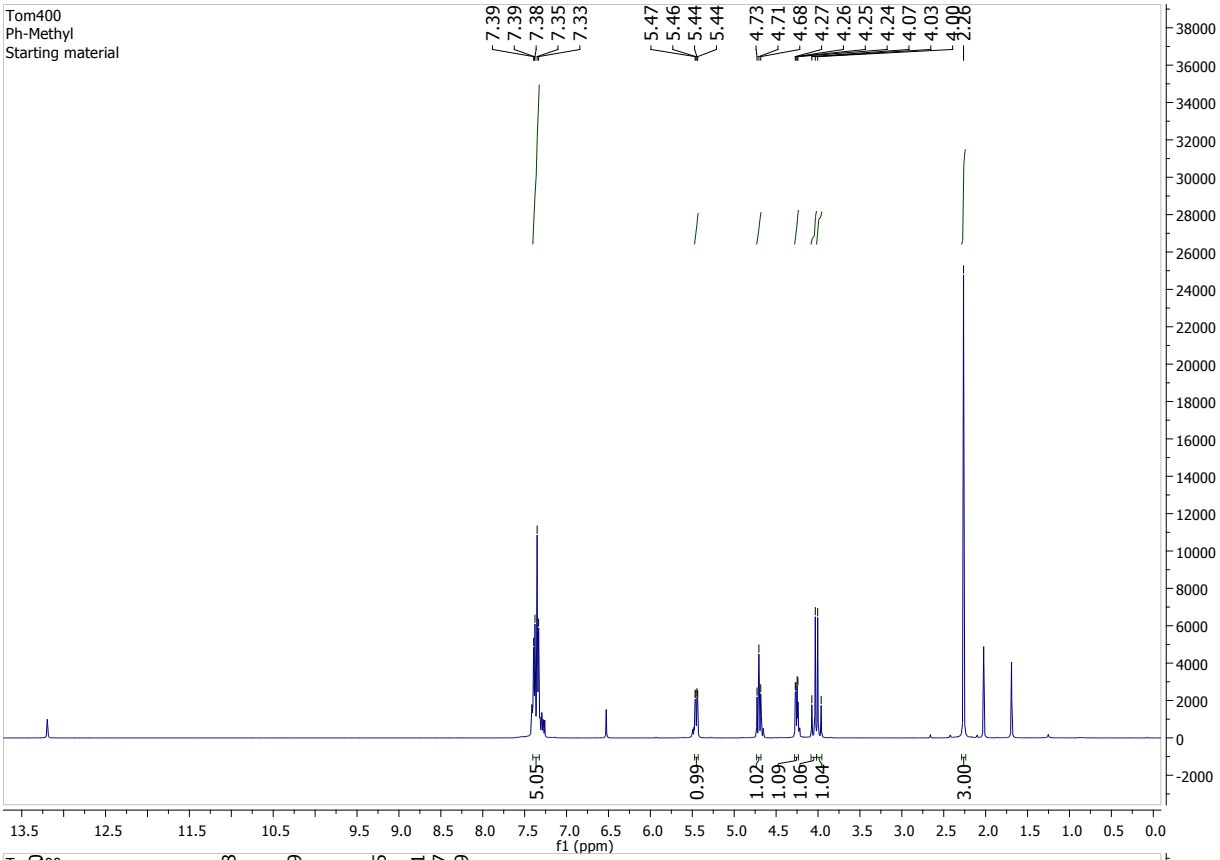
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.39 (m, 5H), 5.45 (dd, *J* = 8.8, 3.8, 1H), 4.71 (t, *J* = 8.9, 1H), 4.26 (dd, *J* = 8.9, 3.8, 1H), 4.05 (d, *J* = 16.6, 1H), 3.98 (d, *J* = 16.6, 1H), 2.26 (s, 3H).

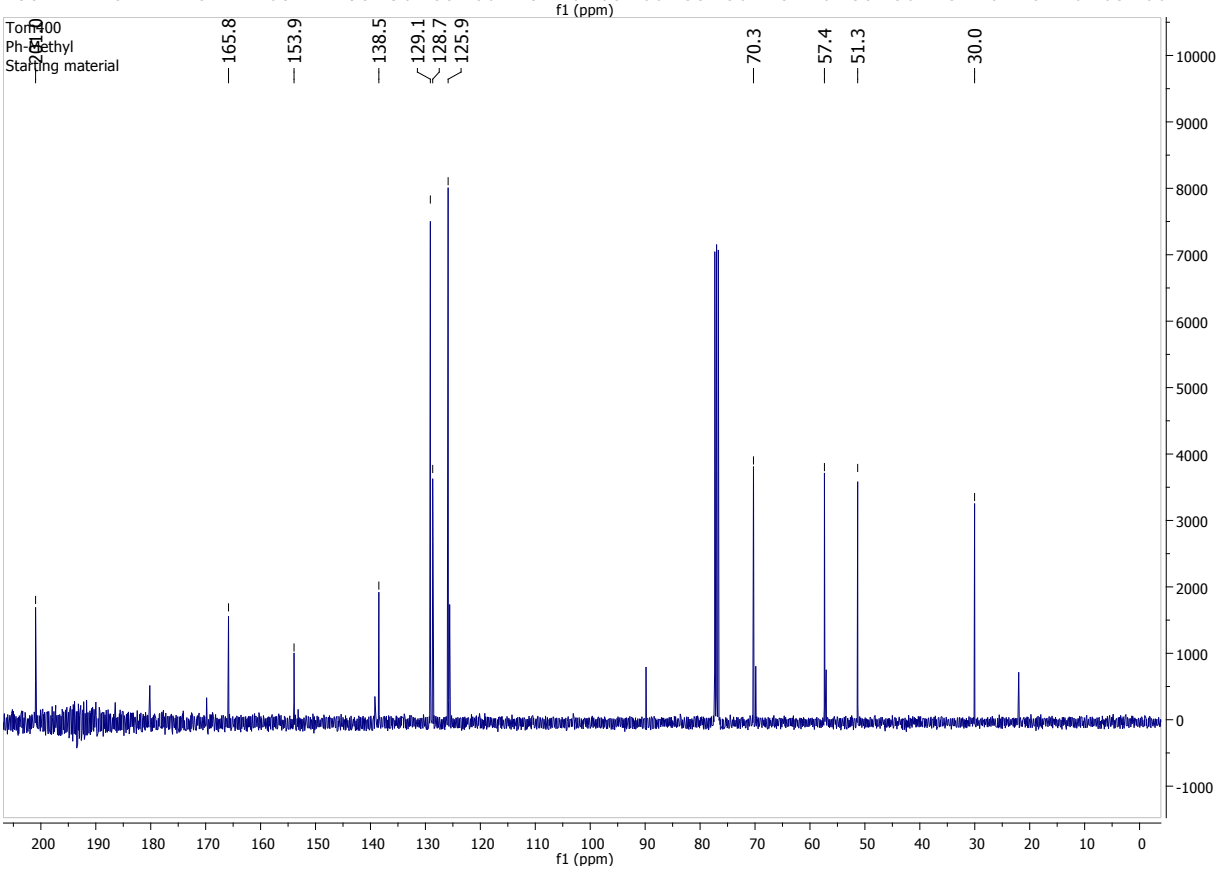
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.0, 165.8, 153.9, 138.5, 129.1 (2C), 128.7, 125.9 (2C), 70.3, 57.4, 51.3, 30.0.

R_f: 0.30 (30% EtOAc/hexane).

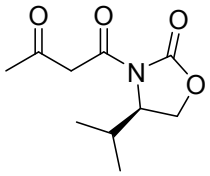
IR (ATR) ν 2924, 1773, 1711, 1490, 1455, 1394, 1357, 1321, 1214, 1187, 1161, 1122, 1061, 1036, 954 cm^{-1}.

HRMS (ESI+): *m/z*: Calcd for $C_{13}H_{14}NO_4$ $[M+H]^+$, 248.0923; found: 248.0957.


Tom400
Ph-Methyl
Starting material
7.39
7.39
7.38
7.35
7.33
5.47
5.46
5.44
5.44
4.73
4.71
4.68
4.27
4.26
4.25
4.24
4.07
4.03
4.00
2.28
5.05
0.99
1.02
1.09
1.06
1.04
3.00
f1 (ppm)


Tom400
Ph-Methyl
Starting material
165.8
153.9
138.5
129.1
128.7
125.9
70.3
57.4
51.3
30.0
f1 (ppm)

(*R*)-1-(4-isopropyl-2-oxooxazolidin-3-yl)butane-1,3-dione (5)



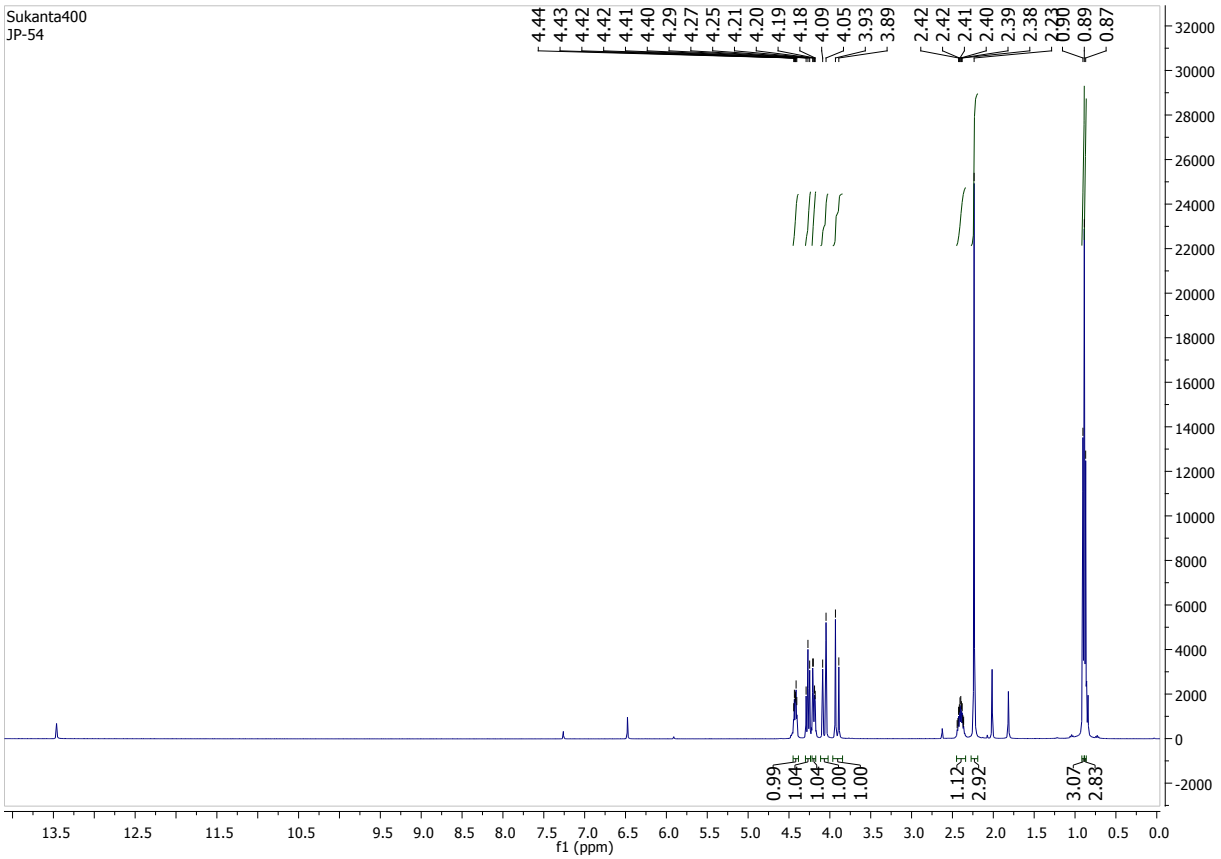
Compound (**5**) was prepared the same way as (**4**), and was purified by column chromatography (20% EtOAc/hexane) to give the product (440 mg, 89%) as a pale yellow oil.

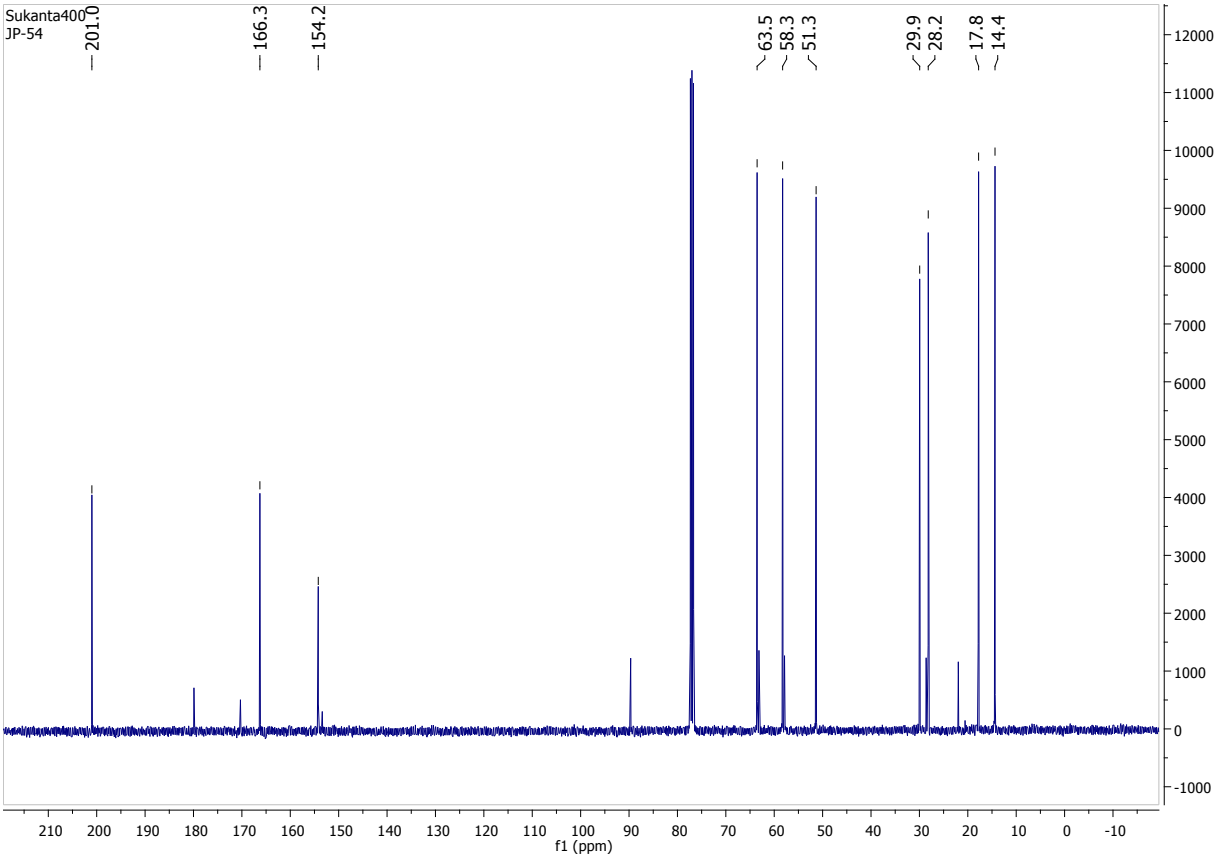
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.40 – 4.44 (m, 1H), 4.27 (t, *J* = 8.7, 1H), 4.19 (dd, *J* = 9.1, 3.0, 1H), 4.07 (d, *J* = 16.5, 1H), 3.91 (d, *J* = 16.5, 1H), 2.38 – 2.42 (m, 1H), 2.23 (s, 3H), 0.90 (d, *J* = 6.8, 3H), 0.88 (d, *J* = 6.7, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.0, 166.3, 154.2, 63.5, 58.3, 51.3, 29.9, 28.2, 17.8, 14.4.

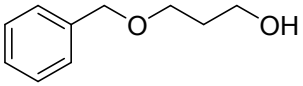
R_f: 0.37 (40% EtOAc/hexane).

HRMS (APCI+): *m/z*: Calcd for $C_{10}H_{16}NO_4$ $[M+H]^+$, 214.1074; found: 214.1070.



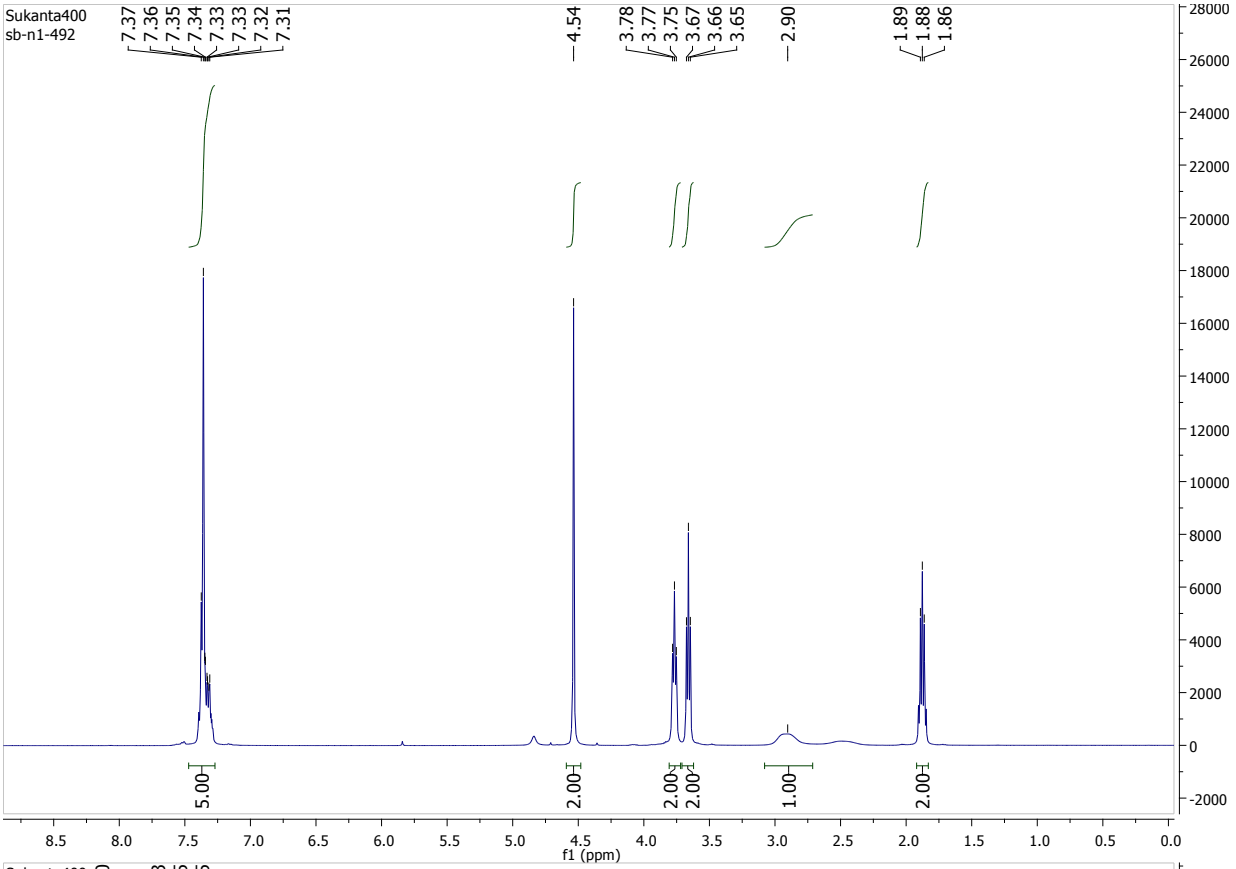


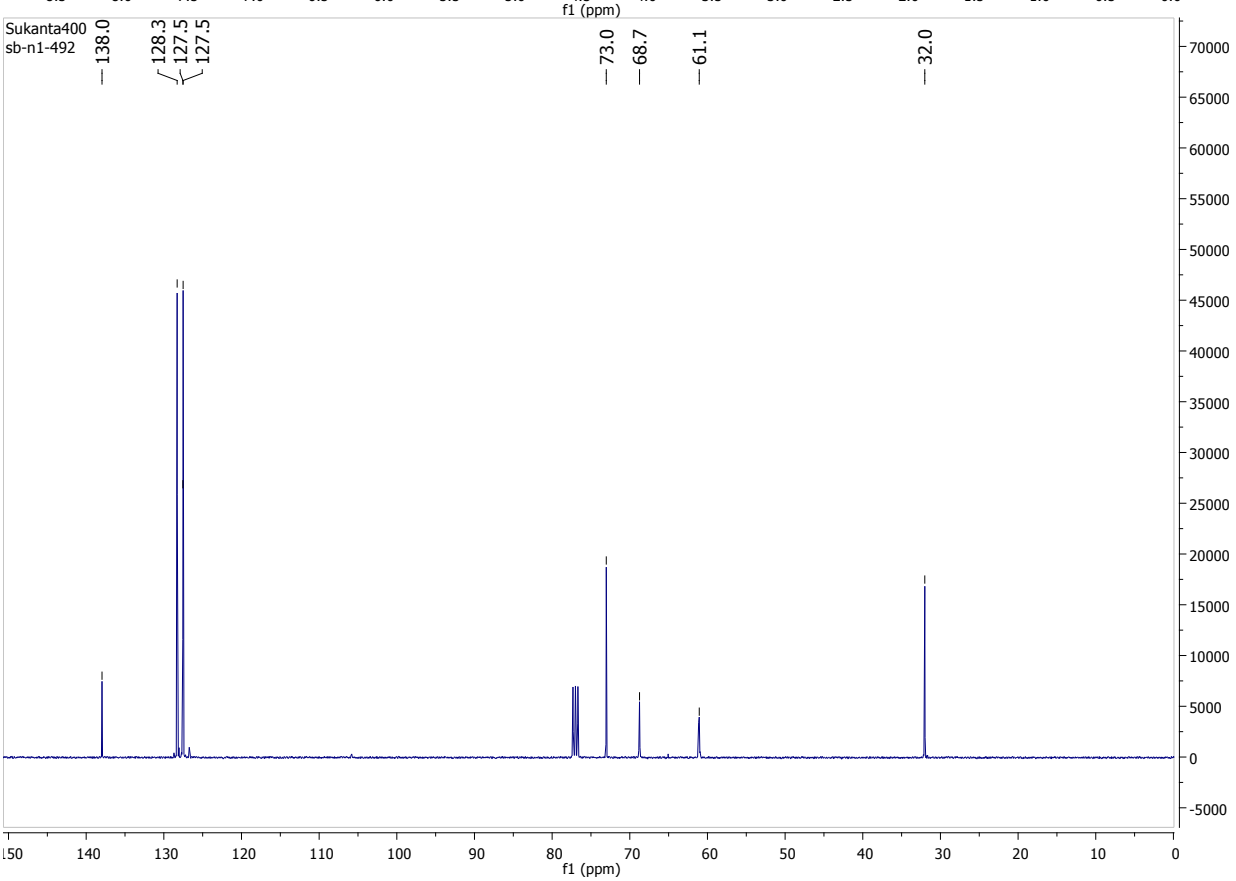
3-(benzyloxy)propan-1-ol (I)[2, 3]



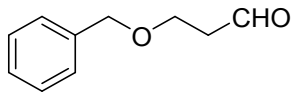
A suspension of NaH (2.6 g 60% dispersion in mineral oil, 65 mmol, 1 equiv) in 25 mL of THF was treated with 1,3-propanedilol (5.0 g, 65.7 mmol, 1 equiv) dropwise at 0 °C. The reaction was stirred at rt for 30 min and a solution of benzyl bromide (11.2 g, 65.8 mmol, 1 equiv) in 30 mL of THF was added dropwise at rt. The reaction was stirred at reflux overnight, cooled and quenched with water. The mixture was extracted with 3×75 mL of ether, the combined organics were washed with brine, dried over sodium sulfate and volatiles were removed by rotary evaporator. The residue was purified by column chromatography to give the product (5.0 g, 46% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.41 (m, 5H), 4.54 (s, 2H), 3.77 (t, J = 5.7, 2H), 3.66 (t, J = 5.9, 2H), 2.90 (s, 1H), 1.88 (quin, J = 5.9, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 128.3 (2C), 127.5, 127.5 (2C), 73.0, 68.7, 61.1, 32.0.


Sukanta400
sb-n1-492
7.37
7.36
7.35
7.34
7.33
7.33
7.32
7.31
4.54
3.78
3.77
3.75
3.67
3.66
3.65
2.90
1.89
1.88
1.86
5.00
2.00
2.00
2.00
1.00
2.00
f1 (ppm)

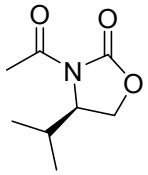

Sukanta400
sb-n1-492
138.0
128.3
127.5
127.5
73.0
68.7
61.1
32.0
f1 (ppm)

3-(benzyloxy)propanal (II)[2, 4]



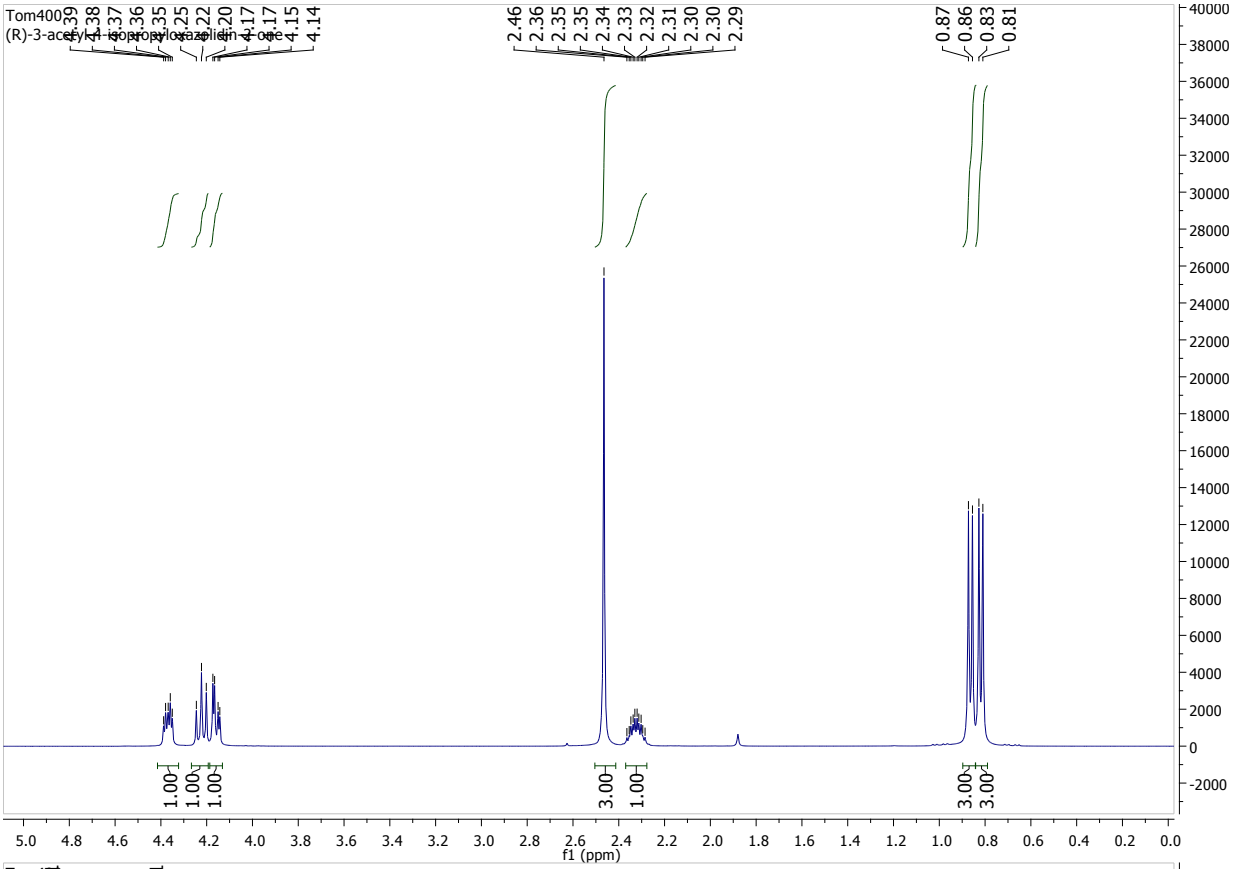
Oxalyl chloride (6.0 g, 48 mmol, 2 equiv) was added to a round bottom flask cooled at −78 °C containing 20 mL of dry DCM. Then DMSO (7.4 g, 96 mmol, 4 equiv) dissolved in 40 mL of DCM was added dropwise to it via a dropping funnel and the reaction mixture was allowed to stir for 20 min. Alcohol (**I**) (4 g, 24 mmol, 1 equiv) dissolved in 80 ml of DCM was added slowly via a dropping funnel and the reaction was allowed to stir for 2 h. Triethylamine (14.4 g, 144 mmol, 6 equiv) dissolved in 80 mL of DCM was added to the reaction mixture slowly via a dropping funnel and the reaction mixture was allowed to stir for 30 min. The reaction was followed by TLC and was quenched upon completion with sat. ammonium chloride and the reaction mixture was washed with brine. Volatiles were removed and the crude aldehyde (3.4 g, 86% yield) was immediately used in the next step without further purification.

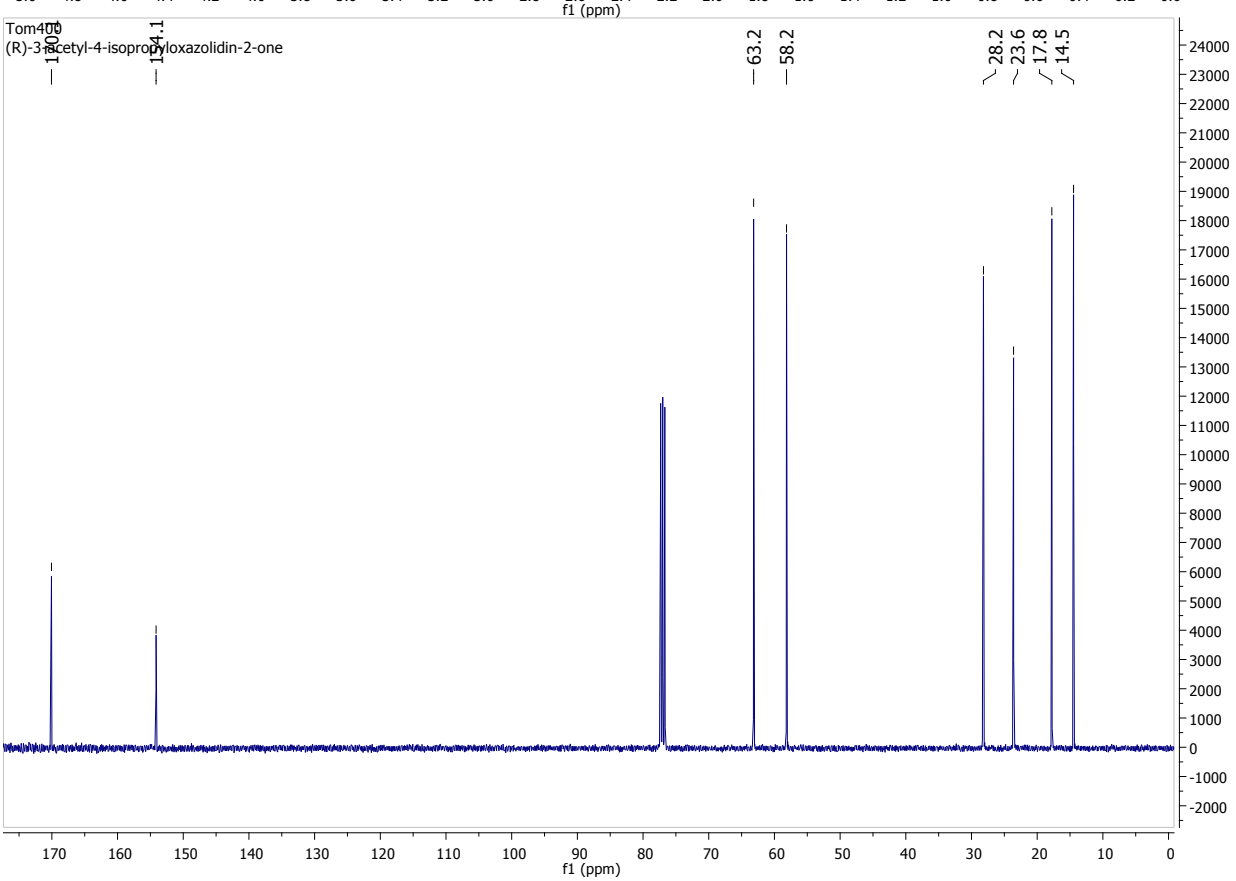
(*R*)-3-acetyl-4-isopropyl-2-oxazolidinone (III)



(*R*)-4-isopropyl-2-oxazolidinone (3.00 g, 23.2 mmol, 1.0 equiv) was dissolved in dry THF (30 mL) and cooled to −78 °C (dry ice/acetone) under Argon. After 10 min, *n*-BuLi (1.54 M in hexane) was added dropwise (16.6 mL, 25.6 mmol, 1.1 equiv) by syringe and stirred for 30 min, after which freshly-distilled acetyl chloride (2.0 mL, 27.9 mmol, 1.2 equiv) was added in one portion. The mixture was allowed to stir for 30 min at −78 °C before being allowed to reach r.t. and stir overnight. The reaction was quenched with sat. ammonium chloride solution (20 mL) and brine (30 mL) was added. The resulting solution was extracted with EtOAc (5×30 mL). The combined organics were dried over Na_2SO_4, filtered, and the solvent was removed *in vacuo*. The crude was purified by column chromatography (10%-30% EtOAc/Hexane) to give the product (3.15 g, 18.4 mmol, 79% yield) as a yellow liquid.

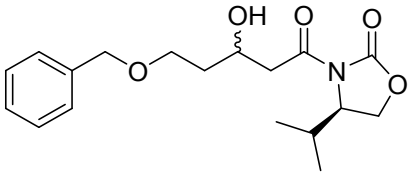
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.35 – 4.39 (m, 1H), 4.22 (t, *J* = 8.7, 1H), 4.16 (dd, *J* = 9.1, 3.0, 1H), 2.46 (s, 3H), 2.29 – 2.36 (m, 1H), 0.86 (d, *J* = 7.1, 3H), 0.82 (d, *J* = 6.9, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 154.1, 63.2, 58.2, 28.2, 23.6, 17.8, 14.5.
R_f: 0.50 (30% EtOAc/Hexane)
IR ($CHCl_3$) ν 2964, 1775, 1699, 1370, 1296, 1204, 1147, 1121, 1061, 1038, 966 cm^{-1}.
HRMS (APCI+): *m/z*: Calcd for $C_8H_{14}NO_3$ $[M+H]^+$, 172.0968; found: 172.1017 .


Tom400
(R)-3-acetyl-4-isopropyloxazolidin-4-one
4.39 4.38 4.37 4.36 4.35 4.25 4.22 4.20 4.17 4.17 4.15 4.14
2.46 2.36 2.35 2.35 2.34 2.33 2.32 2.31 2.30 2.30 2.29
0.87 0.86 0.83 0.81
1.00 1.00 1.00 3.00 1.00 3.00 3.00
f1 (ppm)


Tom400
(R)-3-acetyl-4-isopropyloxazolidin-2-one
170.0 154.1 63.2 58.2 28.2 23.6 17.8 14.5
f1 (ppm)

General procedure 2: Aldol reaction

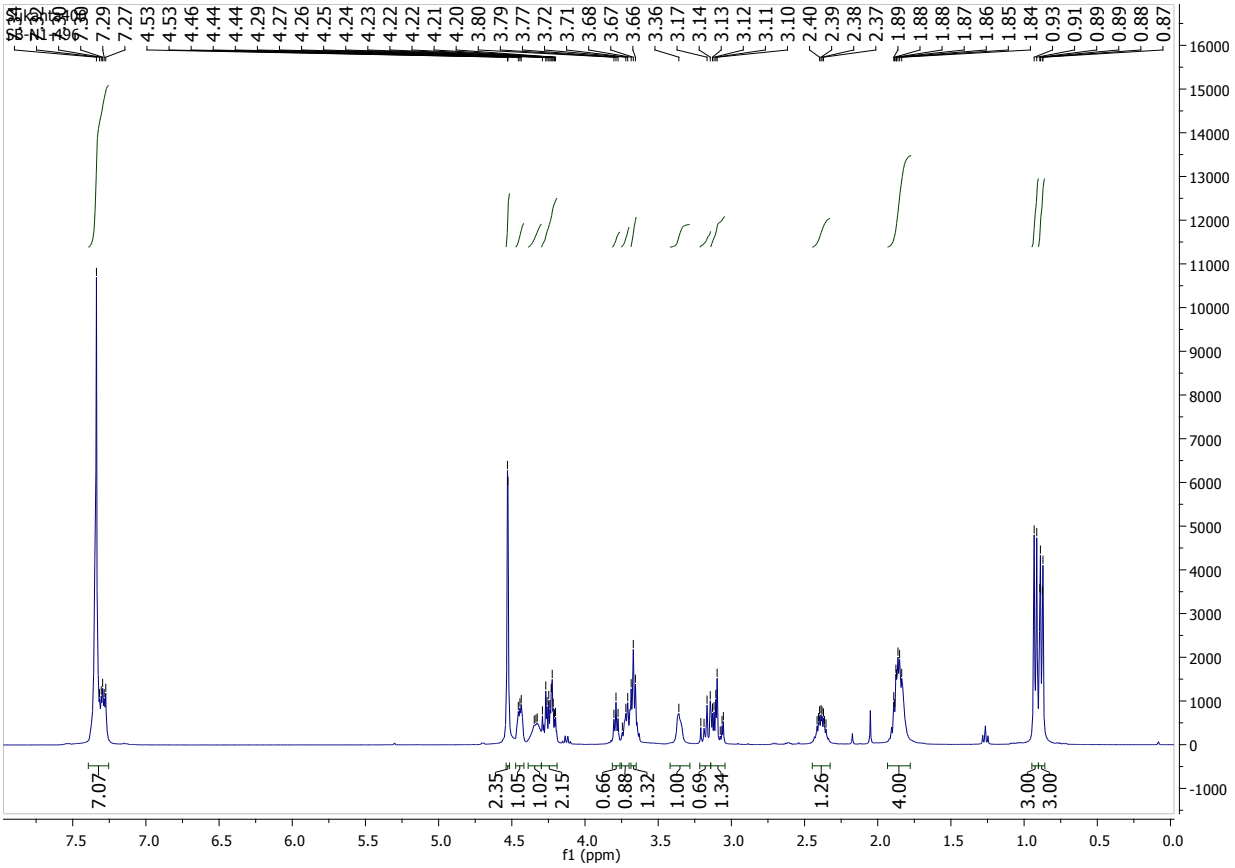
(4*R*)-3-(5-(benzyloxy)-3-hydroxypentanoyl)-4-isopropyloxazolidin-2-one (IV)



$TiCl_4$ (1.098 g, 5.8 mmol, 2 equiv) was added to a round bottom flask placed in −78 °C containing 10 mL of DCM. N-acetyl oxazolidinone (**III**) (0.5 g, 2.9 mmol, 1 equiv) dissolved in 5 ml of DCM added slowly to it via syringe. After 15 min DIPEA (1 mL, 5.8 mmol, 2 equiv) was added to the reaction mixture and was allowed to stir for 1 h. Then aldehyde (**II**) (1.5 g, 8.7 mmol, 3 equiv) dissolved in 5 ml of DCM was added to the reaction mixture and was allowed to stir overnight. Upon completion of the reaction (TLC) it was quenched by sat. ammonium chloride solution at −78 °C. The reaction mixture was extracted at r.t. with 5×20 mL of DCM and the combined organics were washed with brine and dried over Na_2SO_4 and filtered. Volatiles were removed and the residue was purified by column chromatography to get the aldol product (diastereomeric mixture, 680 mg, 70% yield), as a colorless oil.

Major diastereoisomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.34 (m, 5H), 4.53 (s, 2H), 4.44 – 4.46 (m, 1H), 4.33 – 4.35 (m, 1H), 4.20 – 4.29 (m, 2H), 3.66 – 3.68 (m, 1H), 3.36 (s, 1H), 3.05 – 3.13 (m, 1H), 2.35 – 2.41 (m, 1H), 1.84 – 1.89 (m, 4H), 0.92 (d, J = 7.0, 3H), 0.88 (d, J = 6.9, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 154.0, 138.1, 128.3 (2C), 127.6 (2C), 73.1, 67.6, 66.4, 63.4, 58.4, 42.6, 36.2, 28.3, 17.9, 14.6
R_f: 0.2 (30% EtOAc/hexane)
IR ($CHCl_3$) ν 3670, 3511, 3011, 2965, 2872, 1782, 1696, 1488, 1456, 1385, 1305, 1236, 1227, 1194, 1098, 1026, 974, 913 cm^{-1}.
HRMS (ESI+): *m/z*: Calcd for $C_{18}H_{26}NO_5$ $[M+H]^+$, 336.1811; found: 336.1804.

Minor diastereoisomer (distinguishable signals only):
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.53 (s, 2H), 3.79 (t, J = 5.6, 1H), 3.72 (m, 1H), 3.14 – 3.21 (m, 1H), 0.88 (d, J = 6.9, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 138.0, 128.4 (2C), 127.6 (2C), 73.2, 69.3, 67.7, 66.5, 63.5, 61.7, 36.0, 32.1, 28.4, 14.6.


Sukanta400
SB-N1-496
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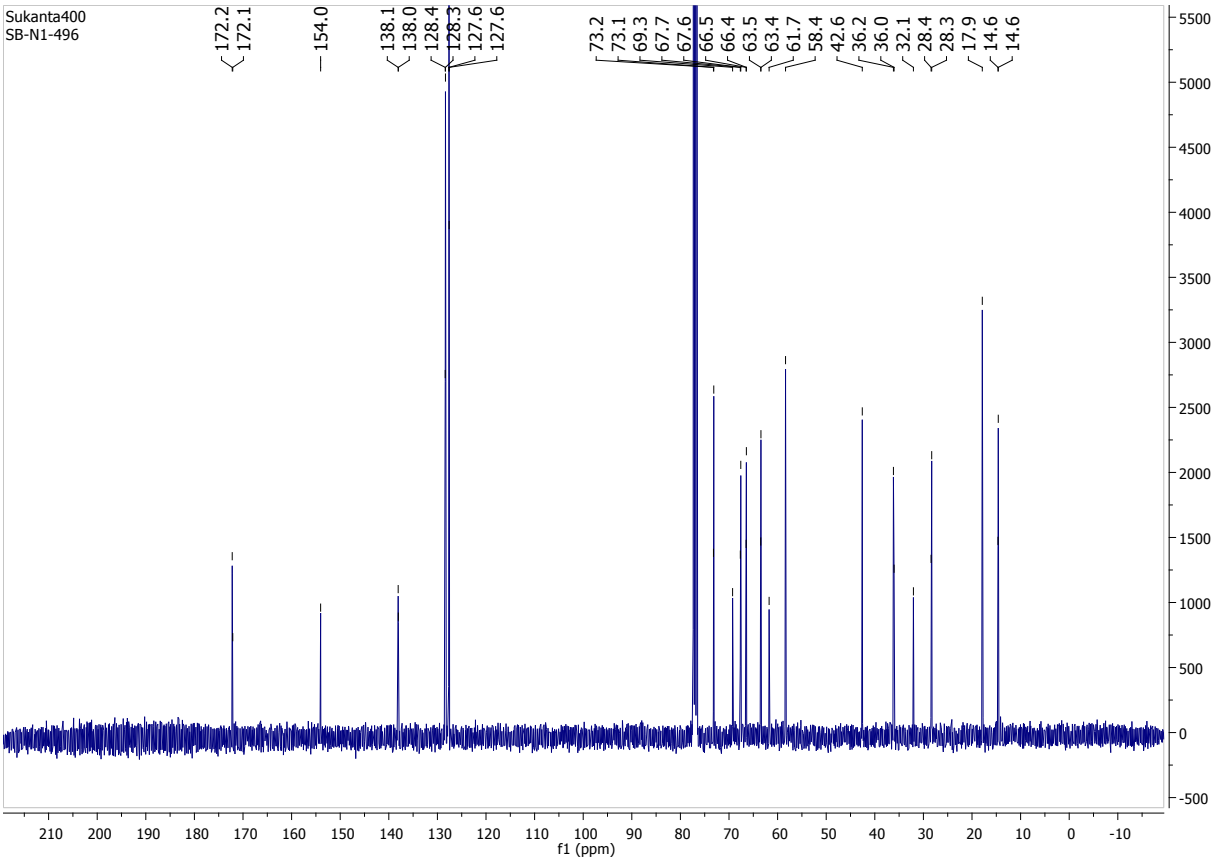
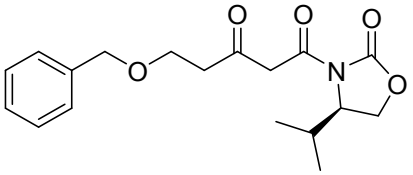
7.27
4.53
4.46
4.44
4.44
4.29
4.27
4.26
4.25
4.24
4.23
4.22
4.22
4.21
4.20
3.80
3.79
3.77
3.72
3.71
3.68
3.67
3.66
3.36
3.17
3.14
3.13
3.12
3.11
3.10
2.40
2.39
2.38
2.37
1.89
1.88
1.88
1.87
1.86
1.85
1.84
0.93
0.91
0.89
0.89
0.88
0.87
7.07
2.35
1.05
1.02
2.15
0.66
0.88
1.32
1.00
0.69
1.34
1.26
4.00
3.00
3.00
f1 (ppm)

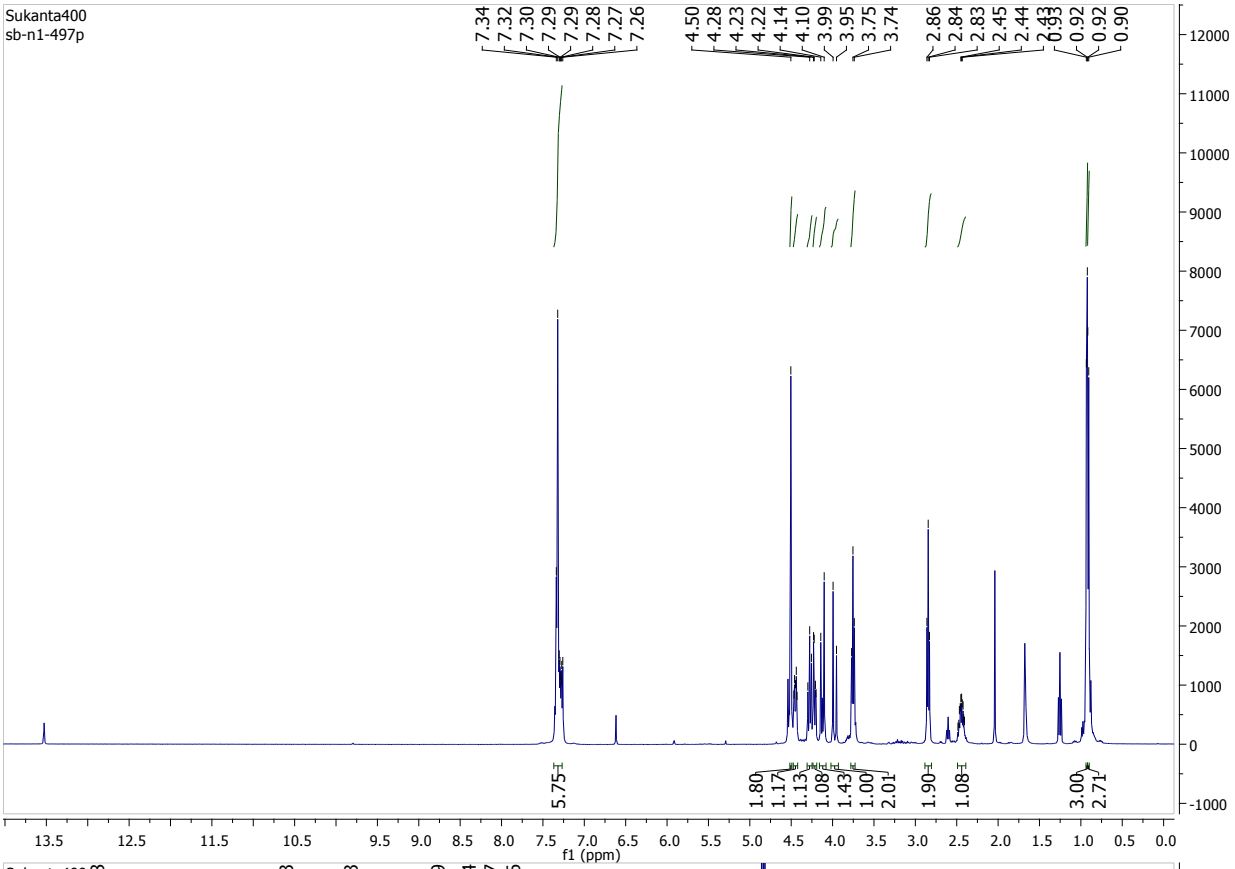

Sukanta400
SB-N1-496
172.2
172.1
154.0
138.1
138.0
128.4
128.3
127.6
127.6
73.2
73.1
69.3
67.7
67.6
66.5
66.4
63.5
63.4
61.7
58.4
42.6
36.2
36.0
32.1
28.4
28.3
17.9
14.6
14.6
f1 (ppm)

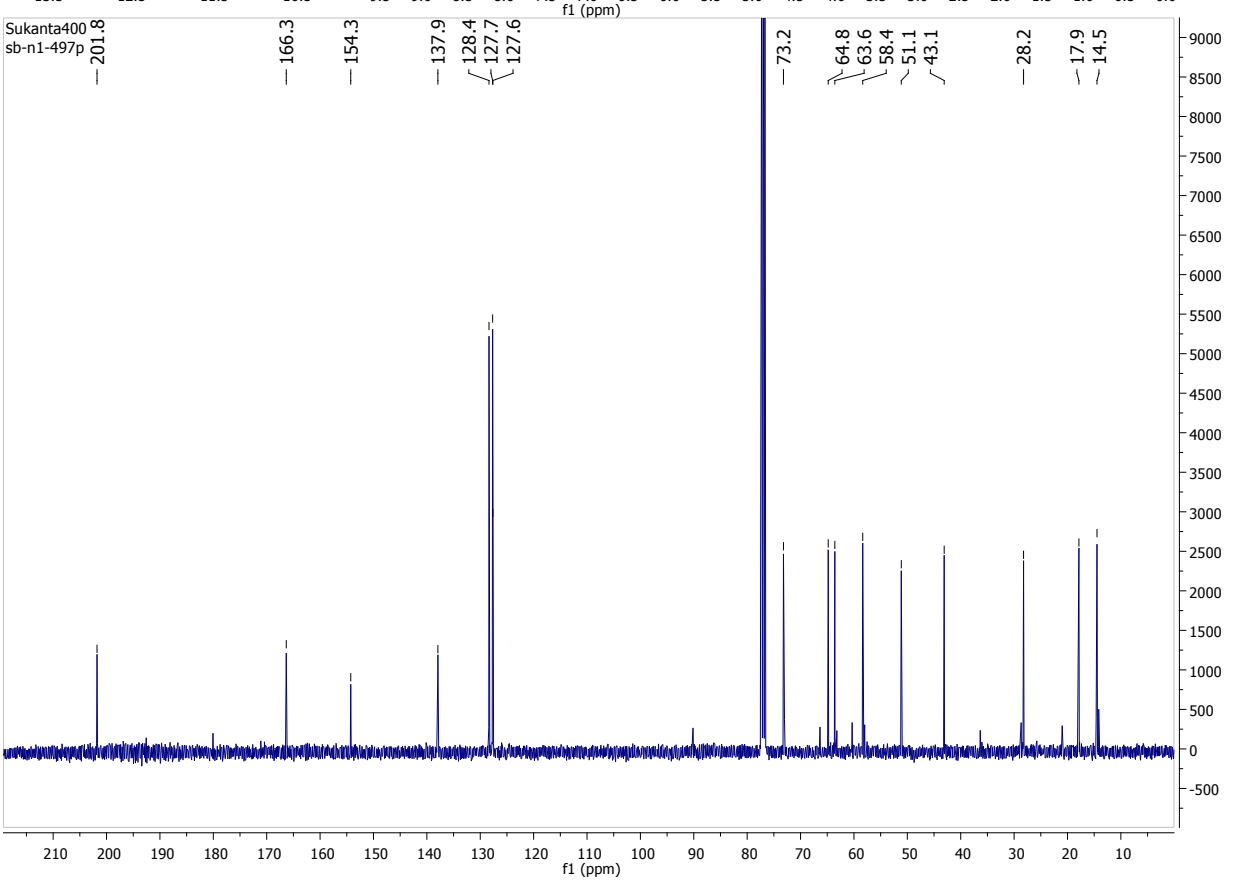
(*R*)-5-(benzyloxy)-1-(4-isopropyl-2-oxooxazolidin-3-yl)pentane-1,3-dione (V)



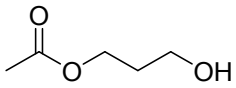
The aldol product (**IV**) (300 mg, 0.89 mmol, 1 equiv) was dissolved in 20 mL of DCM and one spoon full of celite was added to it and the reaction mixture was stirred at r.t. Then PCC (580 mg, 2.69 mmol, 3 equiv) was added to the reaction mixture and was allowed to stir for 24 h. Upon completion of the reaction (TLC), volatiles were removed and the resulting slurry was subjected to column chromatography to get the product (150 mg, 50% yield), as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.34 (m, 5H), 4.50 (s, 2H), 4.42– 4.48 (m, 1H), 4.28 (t, *J* = 8.7, 1H), 4.21 (dd, *J* = 9.1, 3.1, 1H), 4.12 (d, *J* = 16.5, 1H), 3.97 (d, *J* = 16.6, 1H), 3.75 (t, *J* = 6.5, 2H), 2.84 (t, *J* = 6.2, 2H), 2.41 – 2.49 (m, 1H), 0.93 (d, *J* = 4.6, 3H), 0.91 (d, *J* = 4.5, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8, 166.3, 154.3, 137.9, 128.4 (2C), 127.7 (2C), 127.6, 73.2, 64.8, 63.6, 58.4, 51.1, 43.1, 28.2, 17.9, 14.5.
R_f: 0.3 (30% EtOAc/hexane)
IR ($CHCl_3$) ν 3534, 3032, 2968, 2877, 1779, 1703, 1607, 1487, 1457, 1393, 1328, 1227, 1194, 1177, 1112, 1065, 974, 914 cm^{-1}.
HRMS (ESI+): *m/z*: Calcd for $C_{18}H_{24}NO_5$ $[M+H]^+$, 334.1654; found: 334.1650.


Sukanta400
sb-n1-497p
7.34
7.32
7.30
7.29
7.29
7.28
7.27
7.26
4.50
4.28
4.23
4.22
4.14
4.10
3.99
3.95
3.75
3.74
2.86
2.84
2.83
2.45
2.44
0.93
0.92
0.92
0.90
5.75
1.80
1.17
1.13
1.08
1.43
1.00
2.01
1.90
1.08
3.00
2.71
f1 (ppm)

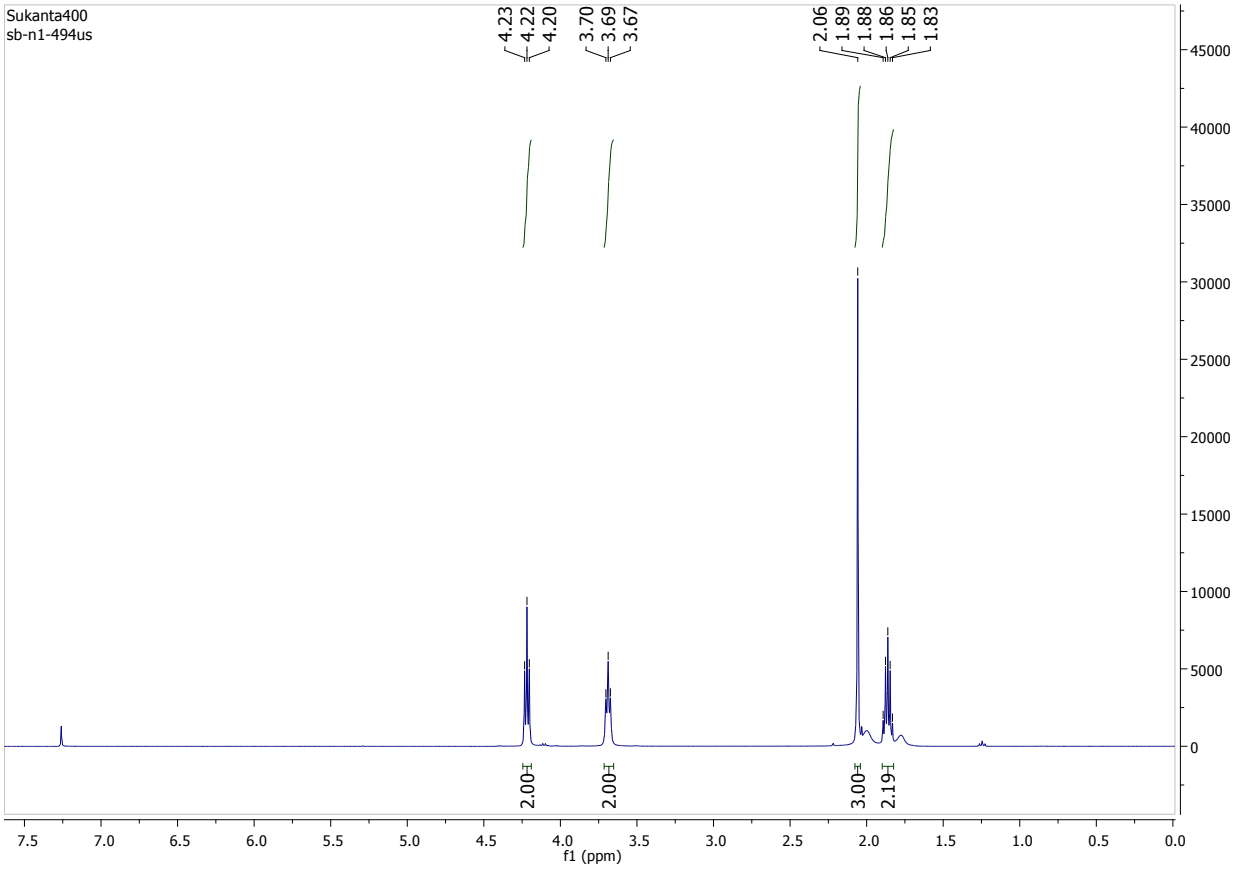

Sukanta400
sb-n1-497p
201.8
166.3
154.3
137.9
128.4
127.7
127.6
73.2
64.8
63.6
58.4
51.1
43.1
28.2
17.9
14.5
f1 (ppm)

3-hydroxypropyl acetate (VI)[5]

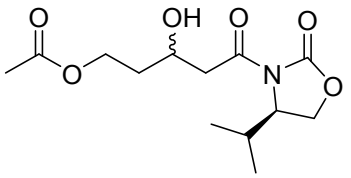


A suspension of NaH (2.6 g, 60% dispersion in mineral oil, 65 mmol, ~1 equiv) in 25 mL of THF was treated with 1,3-propanediol (5.0 g, 65.7 mmol, 1 equiv) which was added dropwise at 0 °C. The reaction was stirred at rt for 30 min and a solution of acetic anhydride (6.7 g, 65.8 mmol, 1 equiv) in 30 mL of THF was added dropwise at rt. The reaction was stirred at rt overnight, cooled and quenched with water. The mixture was extracted 3×75 mL of ether, the combined organics were washed with brine and 10% sodium bicarbonate solution, dried over sodium sulfate and volatiles were removed by rotary evaporator. The residue was purified by column chromatography to yield the product (3.1 g, 40% yields) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (t, J = 6.2, 2H), 3.69 (t, J = 5.9, 2H), 2.06 (s, 3H), 1.86 (quin, J= 6.1, 2H).



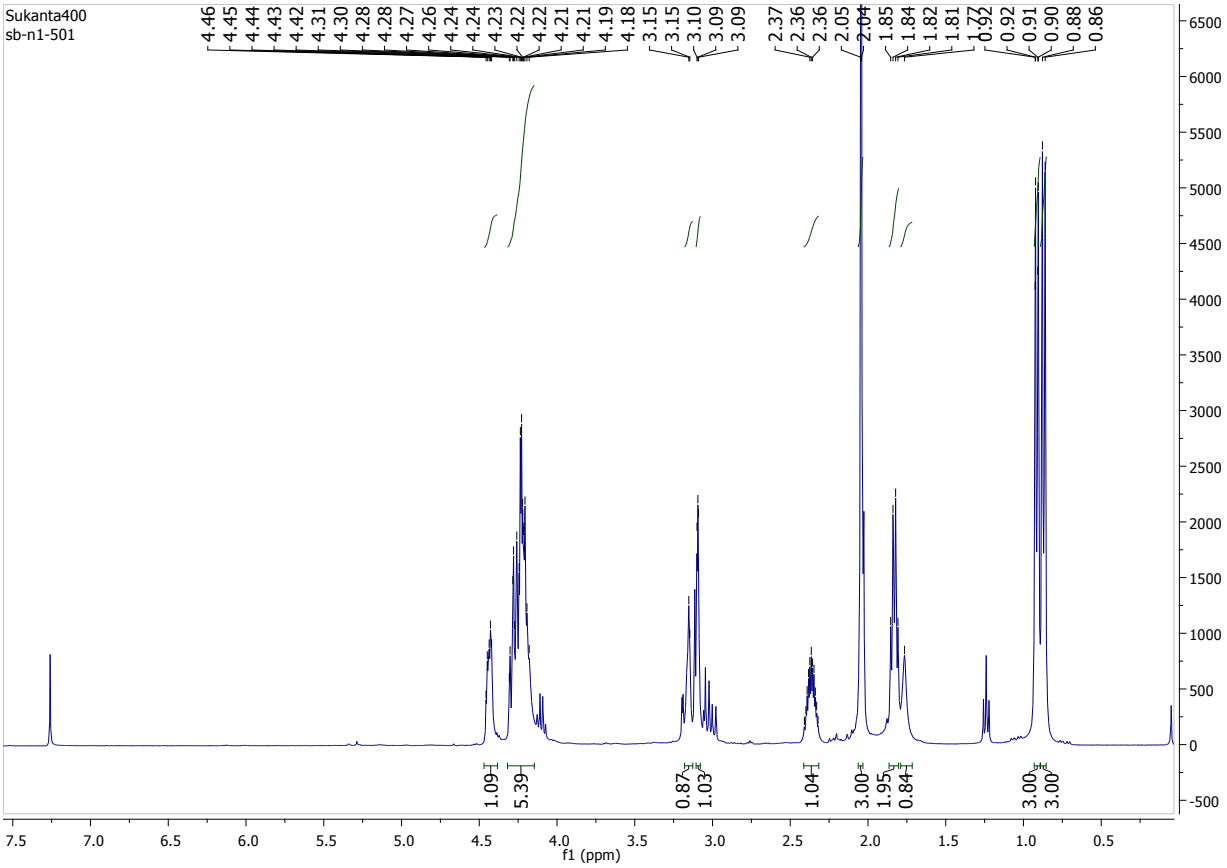
3-hydroxy-5-((*R*)-4-isopropyl-2-oxooxazolidin-3-yl)-5-oxopentyl acetate (VII)

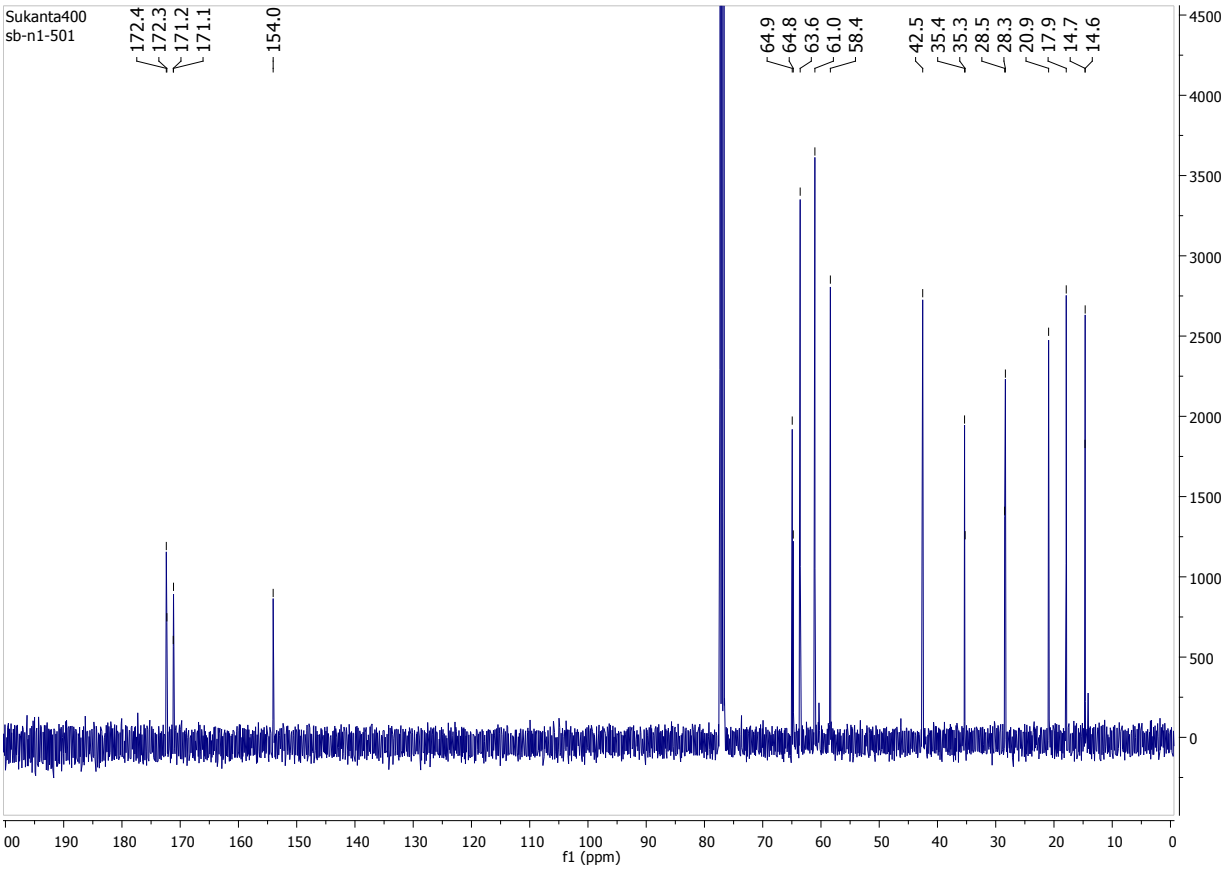


Compound (**VII**) was prepared according to general procedure 2 and isolated as a colorless oil (540 mg, 65% yield, diastereomeric mixture).

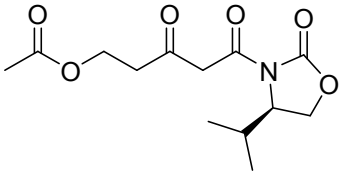
Major diastereoisomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.42 – 4.46 (m, 1H), 4.18– 4.31 (m, 5H), 3.13 – 3.18 (m, 1H), 3.09 – 3.10 (m, 1H), 2.32 – 2.41 (m, 1H), 2.04 (s, 3H), 1.83 (dd, *J* = 12.8, 6.0, 2H), 1.77 (s, 1H), 0.91 (d, *J* = 7.0, 3H), 0.87 (d, *J* = 6.9, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 171.1, 154.0, 64.9, 63.6, 61.0, 58.4, 42.5, 35.4, 28.3, 20.9, 17.9, 14.6.
R_f: 0.2 (30% EtOAc/hexane)
IR ($CHCl_3$) ν 3679, 3546, 3026, 2967, 2880, 2457, 1782, 1732, 1694, 1606, 1462, 1385, 1304, 1236, 1194, 1102, 1055, 1025, 975 cm^{-1}.
HRMS (ESI+): *m/z*: Calcd for $C_{13}H_{22}NO_6$ $[M+H]^+$, 288.1447; found: 288.1419.

Minor diastereoisomer (distinguishable signals only):
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (d, *J* = 7.0, 3H), 2.05 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 171.2, 154.0, 64.8, 35.3, 28.5, 14.7


Sukanta400
sb-n1-501
4.46 4.45 4.44 4.43 4.42 4.31 4.30 4.28 4.28 4.27 4.26 4.24 4.24 4.23 4.22 4.22 4.21 4.21 4.19 4.18 3.15 3.15 3.10 3.09 3.09 2.37 2.36 2.36 2.05 2.04 1.85 1.84 1.82 1.81 0.92 0.92 0.91 0.90 0.88 0.86
1.09 5.39 0.87 1.03 1.04 3.00 1.95 0.84 3.00 3.00
f1 (ppm)


Sukanta400
sb-n1-501
172.4 172.3 171.2 171.1 154.0 64.9 64.8 63.6 61.0 58.4 42.5 35.4 35.3 28.5 28.3 20.9 17.9 14.7 14.6
f1 (ppm)

(*R*)-5-(4-isopropyl-2-oxooxazolidin-3-yl)-3,5-dioxopentyl acetate (VIII)



Compound (**VIII**) was prepared the same way as compound **(V)** and isolated as a colorless oil (198 mg, 50% yield)

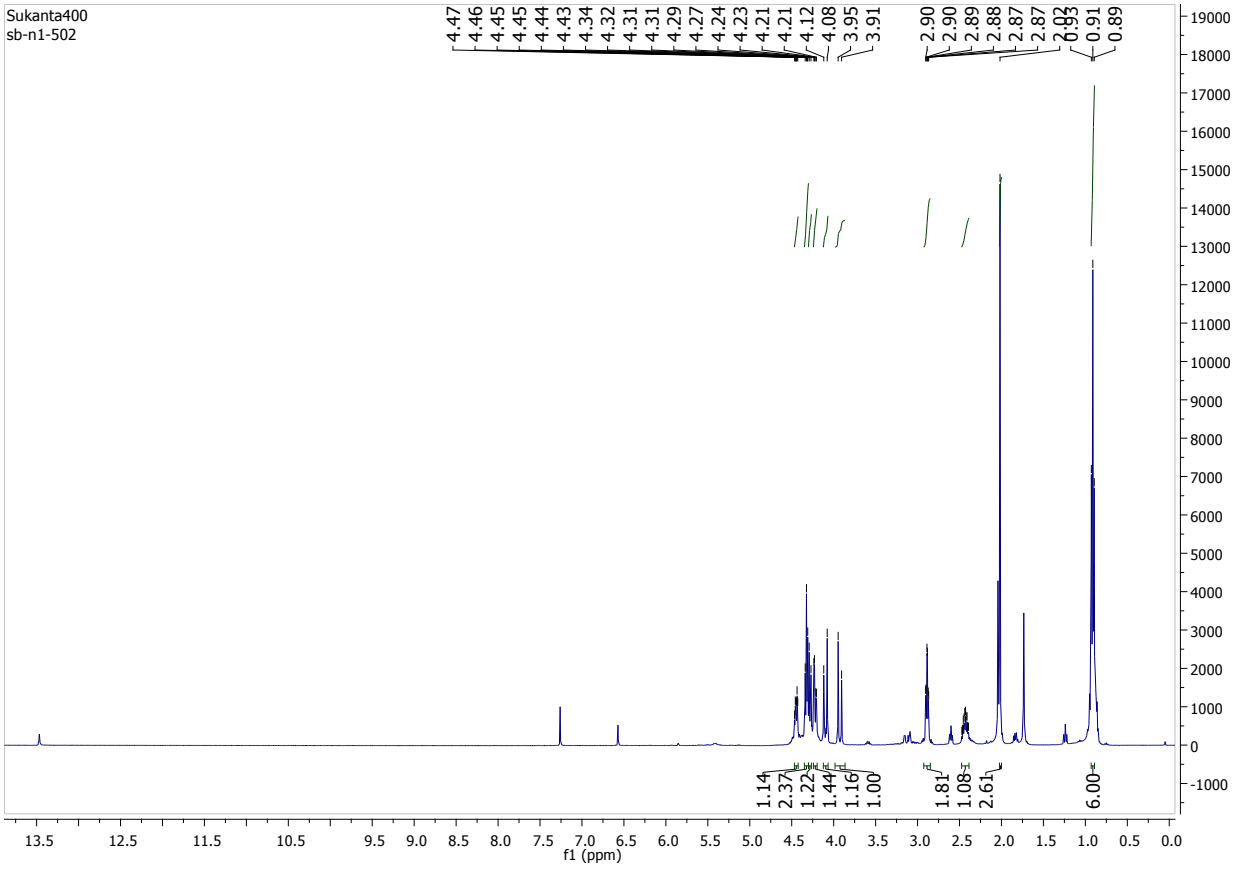
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.43 – 4.47 (m, 1H), 4.32 (d, *J* = 8.1, 2H), 4.28 (d, *J* = 8.5, 1H), 4.22 (dd, *J* = 9.1, 3.0, 1H), 4.10 (d, *J* = 16.5, 1H), 3.93 (d, *J* = 16.5, 1H), 2.89 (td, *J* = 6.1, 2.0, 2H), 2.39 – 2.47 (m, 1H), 2.02 (s, 3H), 0.92 (d, *J* = 7.0, 3H), 0.90 (d, *J* = 6.8, 3H).

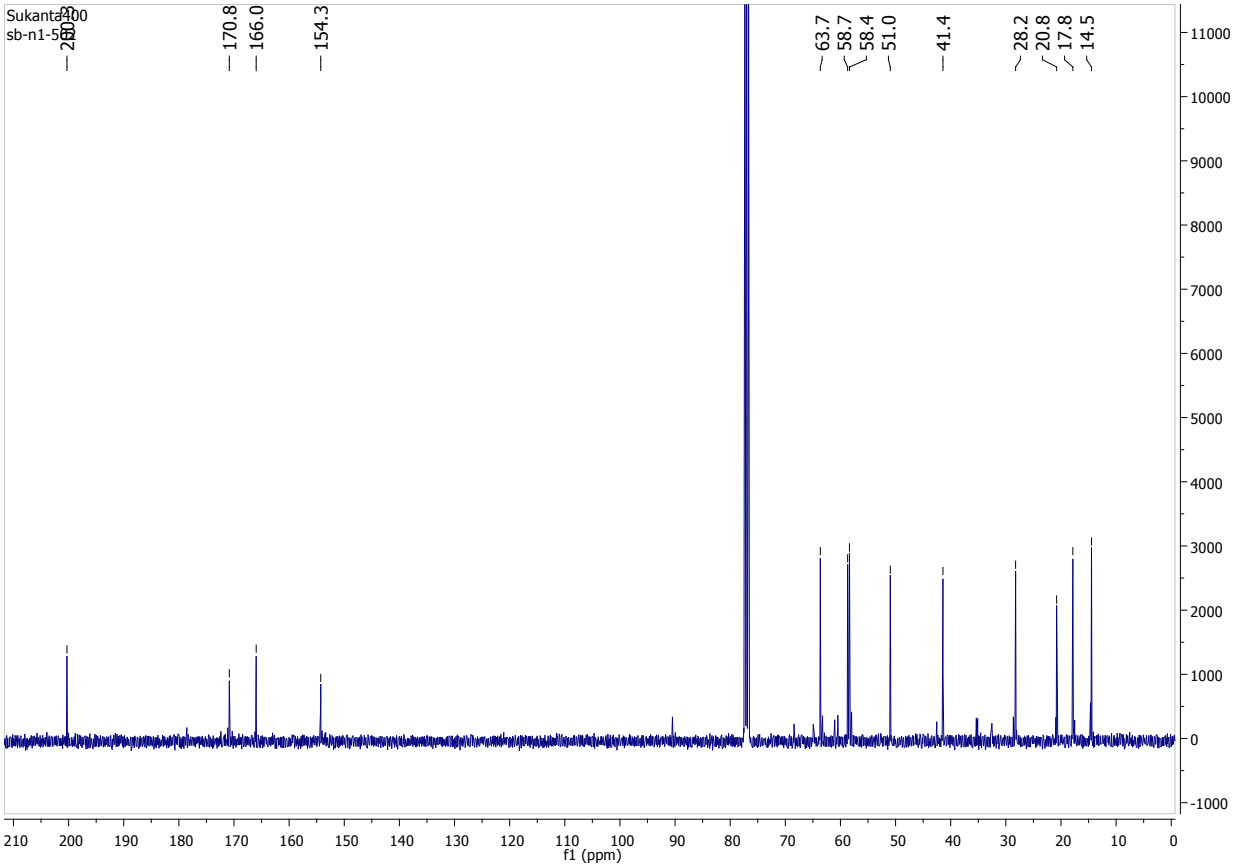
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.3, 170.8, 166.0, 154.3, 63.7, 58.7, 58.4, 51.0, 41.4, 28.2, 20.8, 17.8, 14.5.

R_f: 0.35 (30% EtOAc/hexane)

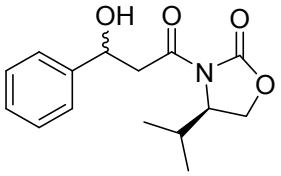
IR ($CHCl_3$) ν 3673, 3466, 3030, 2968, 2879, 2456, 1779, 1735, 1703, 1628, 1484, 1461, 1392, 1329, 1237, 1194, 1178, 1114, 1058, 975 cm^{-1}.

HRMS (ESI+): *m/z*: Calcd for $C_{13}H_{19}NO_6Na$ $[M+Na]^+$, 308.1110; found: 308.1114.



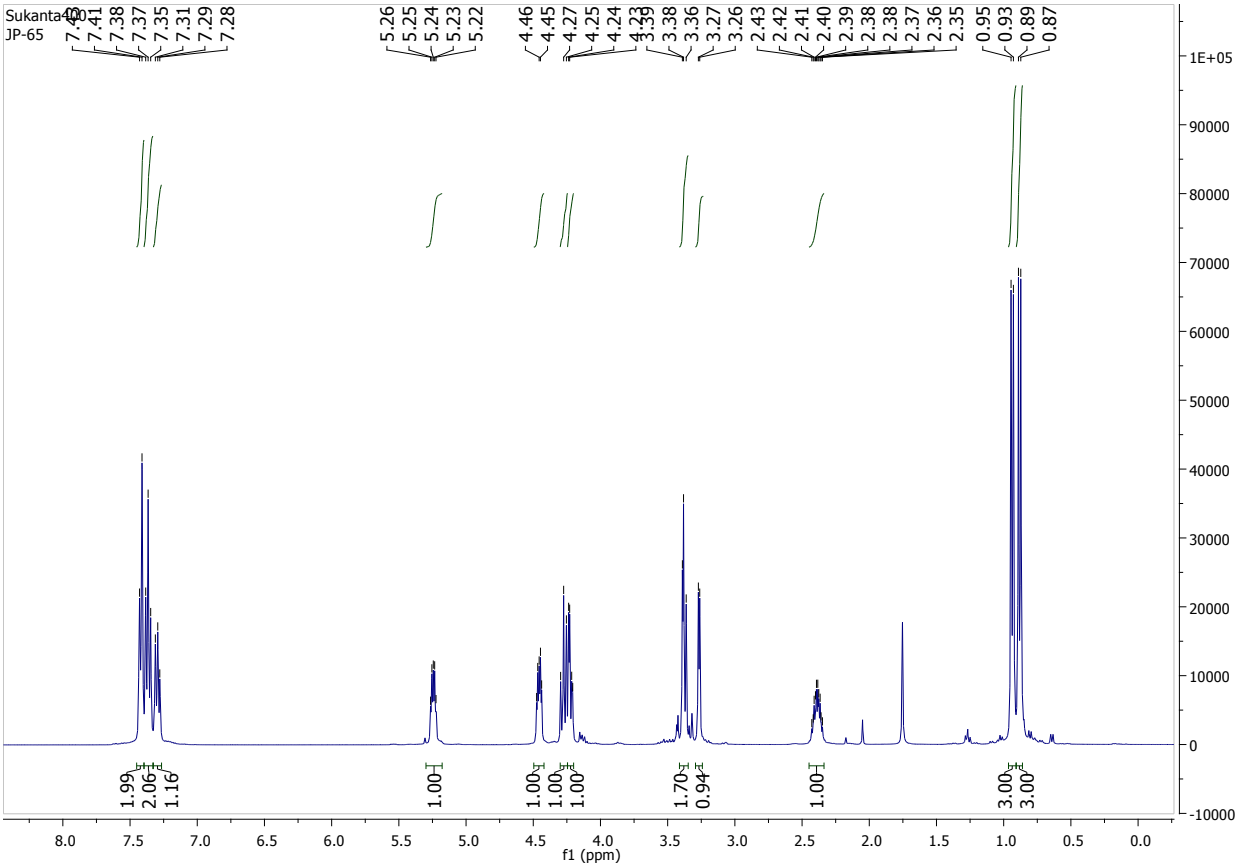


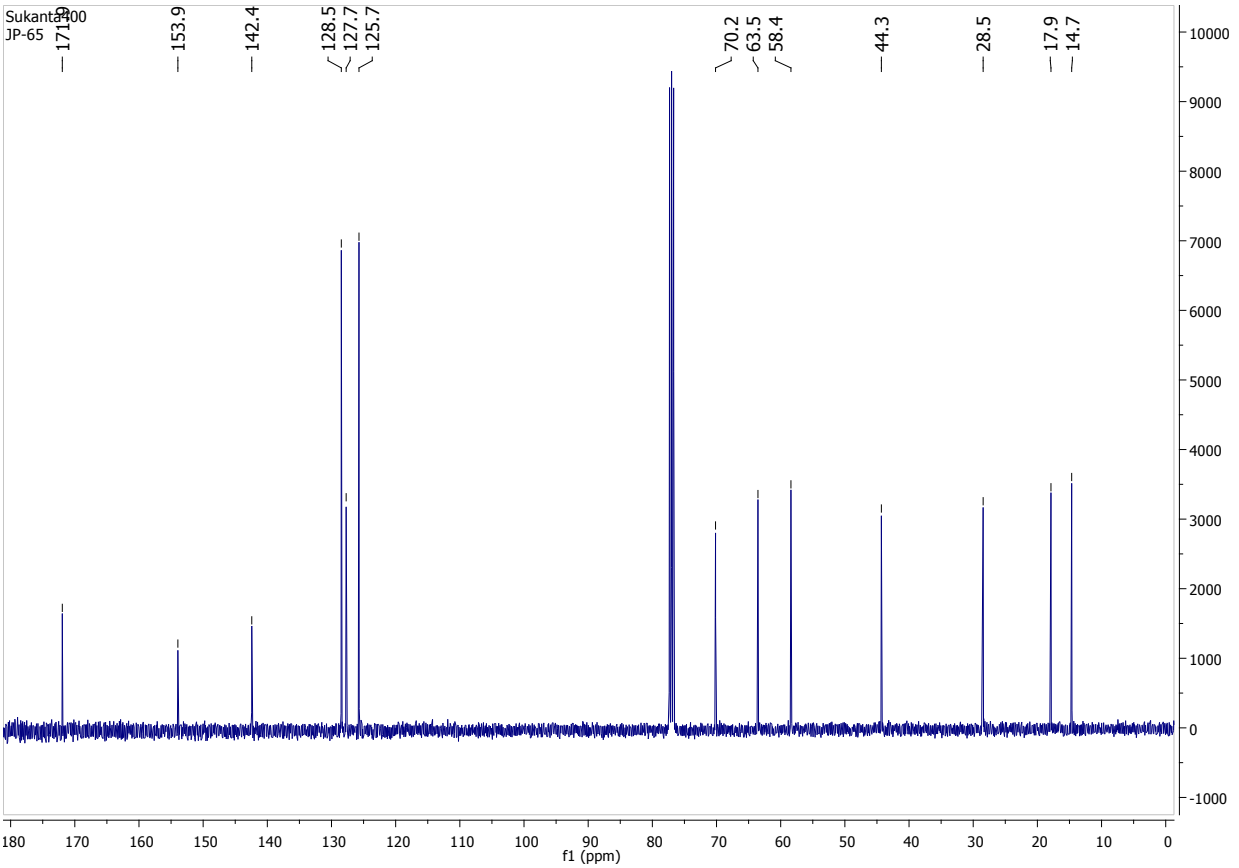
(4*R*)-3-(3-hydroxy-3-phenylpropanoyl)-4-isopropyloxazolidin-2-one (IX)



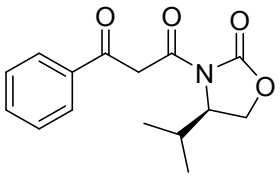
Compound (**IX**) was prepared according to general procedure 2 and purified by column chromatography (40% EtOAc/hexane) to give the product as a colorless oil (143 mg, 69% yield). The minor diastereoisomer wasn't isolated.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.3, 2H), 7.37 (t, *J* = 7.4, 2H), 7.29 (t, *J* = 7.4, 1H), 5.24 (dt, *J* = 8.1, 3.9, 1H), 4.44 – 4.48 (m, 1H), 4.27 (t, *J* = 8.6, 1H), 4.22 (dd, *J* = 9.1, 3.1, 1H), 3.38 (t, *J* = 5.7, 2H), 3.27 (d, *J* = 4.0, 1H), 2.35 – 2.43 (m, 1H), 0.94 (d, *J* = 7.0, 3H), 0.88 (d, *J* = 6.9, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 153.9, 142.4, 128.5 (2C), 127.7, 125.7 (2C), 70.2, 63.5, 58.4, 44.3, 28.5, 17.9, 14.7.
R_f: 0.3 (40% EtOAc/hexane)
IR (ATR) ν 3441, 3059, 3032, 2965, 2928, 2875, 1778, 1677, 1489, 1455, 1378, 1306, 1278, 1209, 1145, 1109, 1078, 1054, 1017, 968, 910 cm^{-1}.
HRMS (APCI+): *m/z*: Calcd for $C_{15}H_{20}NO_4$ $[M+H]^+$, 278.1387; found: 278.1398.


Sukanta400
JP-65
7.40
7.41
7.38
7.37
7.35
7.31
7.29
7.28
5.26
5.25
5.24
5.23
5.22
4.46
4.45
4.27
4.25
4.24
4.23
4.39
3.38
3.36
3.27
3.26
2.43
2.42
2.41
2.40
2.39
2.38
2.38
2.37
2.36
2.35
0.95
0.93
0.89
0.87
1.99
2.06
1.16
1.00
1.00
1.00
1.00
1.70
0.94
1.00
3.00
3.00
f1 (ppm)

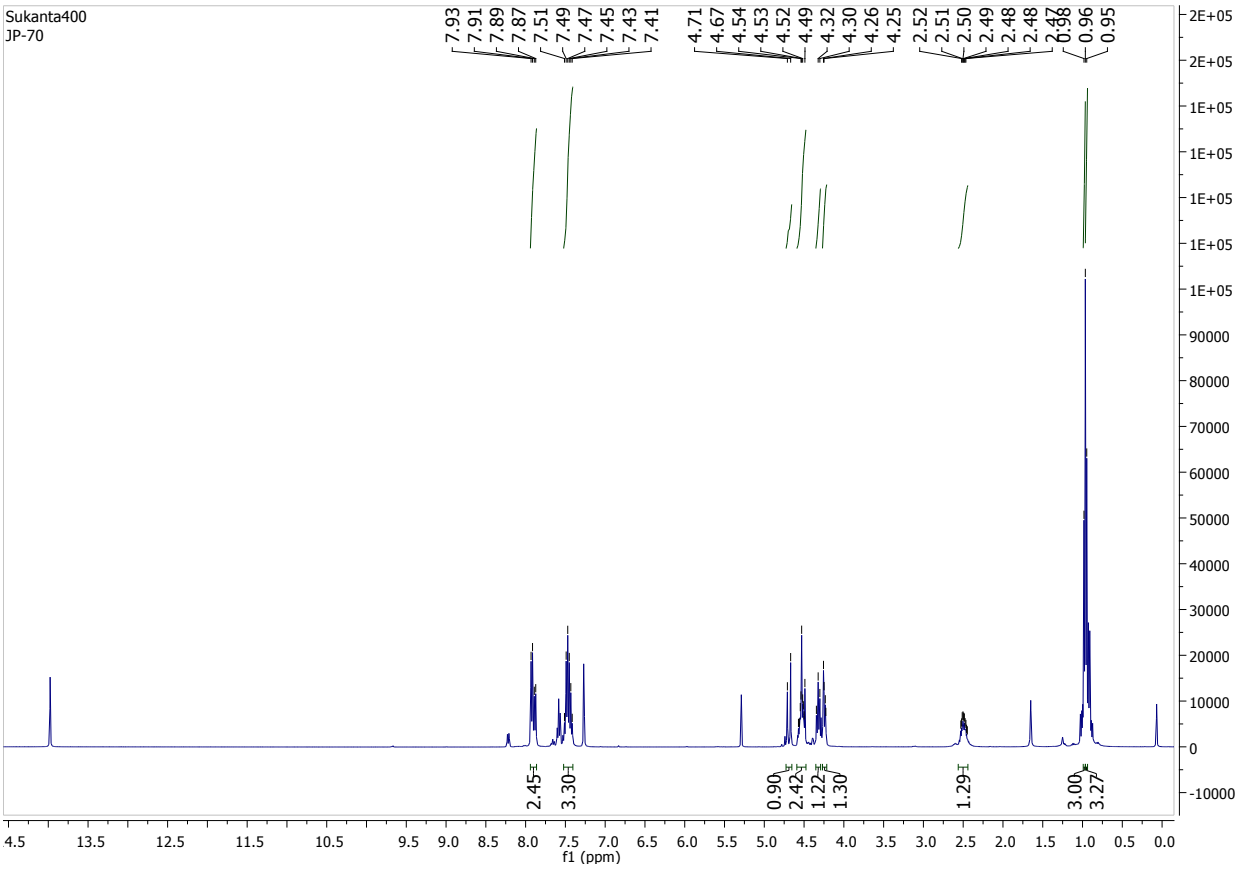

Sukanta400
JP-65
171.9
153.9
142.4
128.5
127.7
125.7
70.2
63.5
58.4
44.3
28.5
17.9
14.7
f1 (ppm)

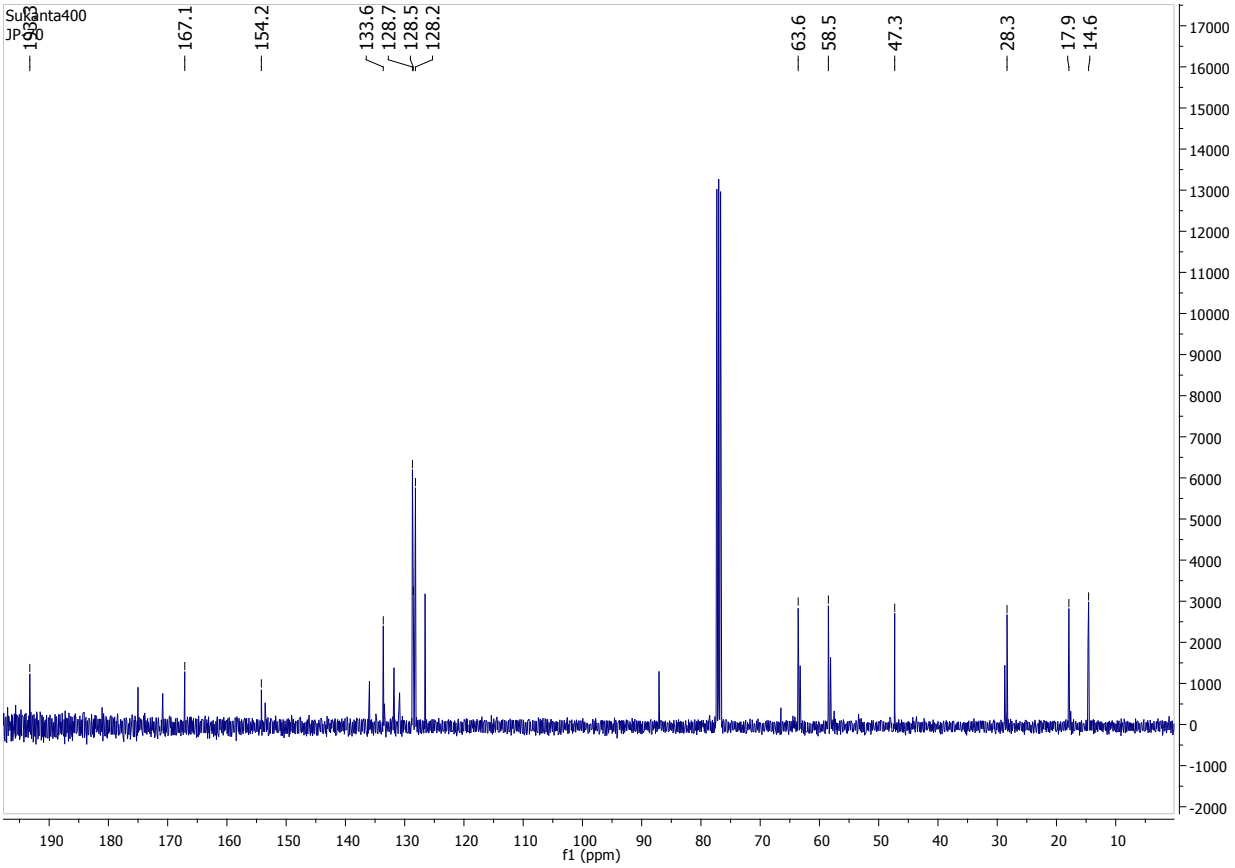
(*R*)-1-(4-isopropyl-2-oxooxazolidin-3-yl)-3-phenylpropane-1,3-dione (X)



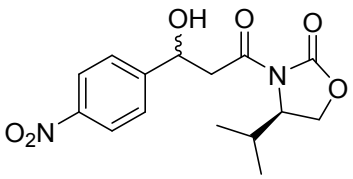
Compound **(IX)** (50 mg, 0.18 mmol, 1.0 equiv) was dissolved in 2 mL DCM at r.t., PCC (77 mg, 0.36 mmol, 2.0 equiv) was added and the reaction was stirred overnight. Celite was added to the flask and the solvent was removed under reduced pressure. The resulting slurry was purified by column chromatography (15% EtOAc/hexane) to give the product as a colorless oil (35 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 16.2, 7.3, 2H), 7.41 – 7.51 (m, 3H), 4.69 (d, *J* = 16.4, 1H), 4.48– 4.58 (m, 2H), 4.32 (t, *J* = 8.7, 1H), 4.24 (dd, *J* = 9.1, 2.8, 1H), 2.45 – 2.53 (m, 1H), 0.97 (d, *J* = 6.9, 3H), 0.96 (d, *J* = 7.1, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 193.3, 167.1, 154.2, 133.6, 128.7 (2C), 128.5, 128.2 (2C), 63.6, 58.5, 47.3, 28.3, 17.9, 14.6.
R_f: 0.66 (40% ethyl acetate/hexane)
IR ($CHCl_3$) ν 3028, 2969, 2936, 1780, 1709, 1687, 1613, 1600, 1577, 1486, 1463, 1451, 1422, 1389, 1373, 1329, 1308, 1262, 1225, 1218, 1207, 1185, 1142, 1121, 1107, 1061, 1037, 1011, 1002, 973 cm^{-1}.
HRMS (APCI+): *m/z*: Calcd for $C_{15}H_{18}NO_4$ $[M+H]^+$, 276.1230; found: 276.1175.



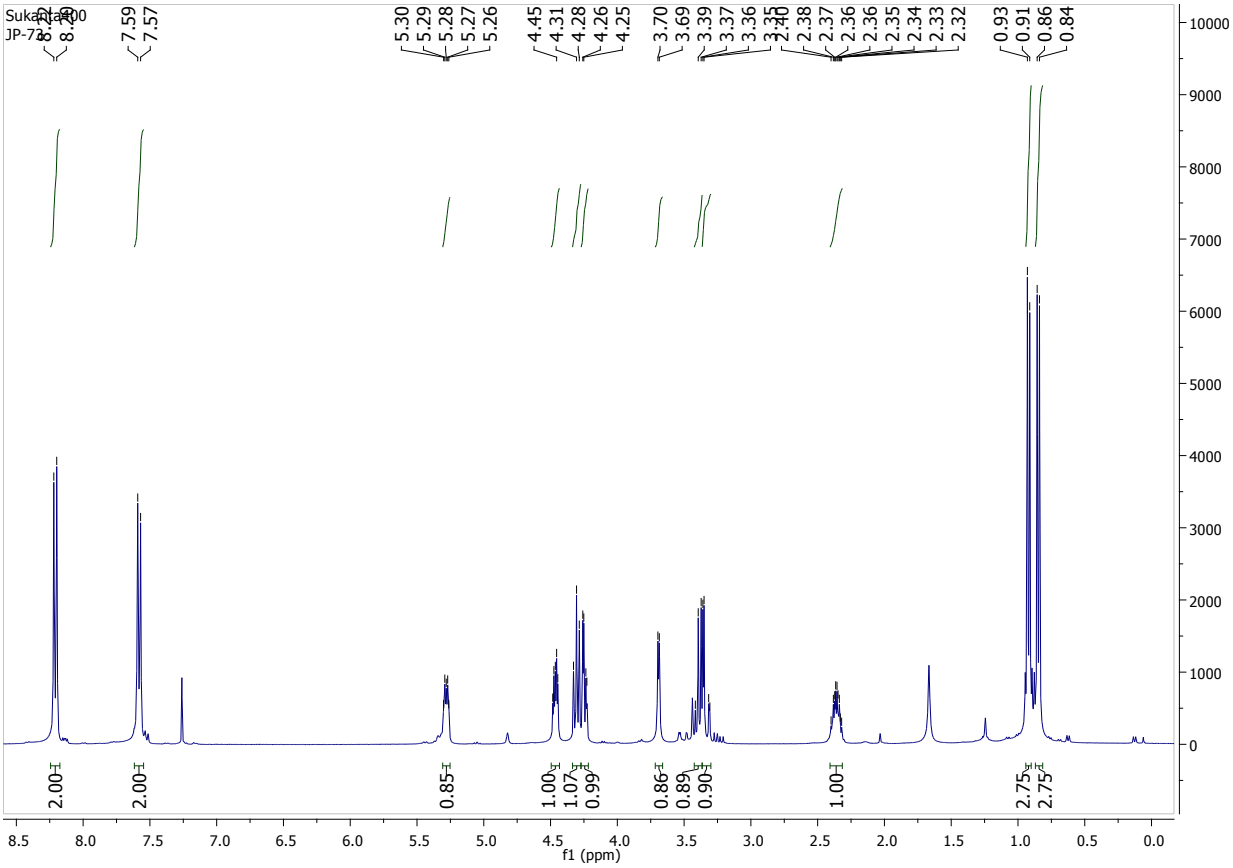


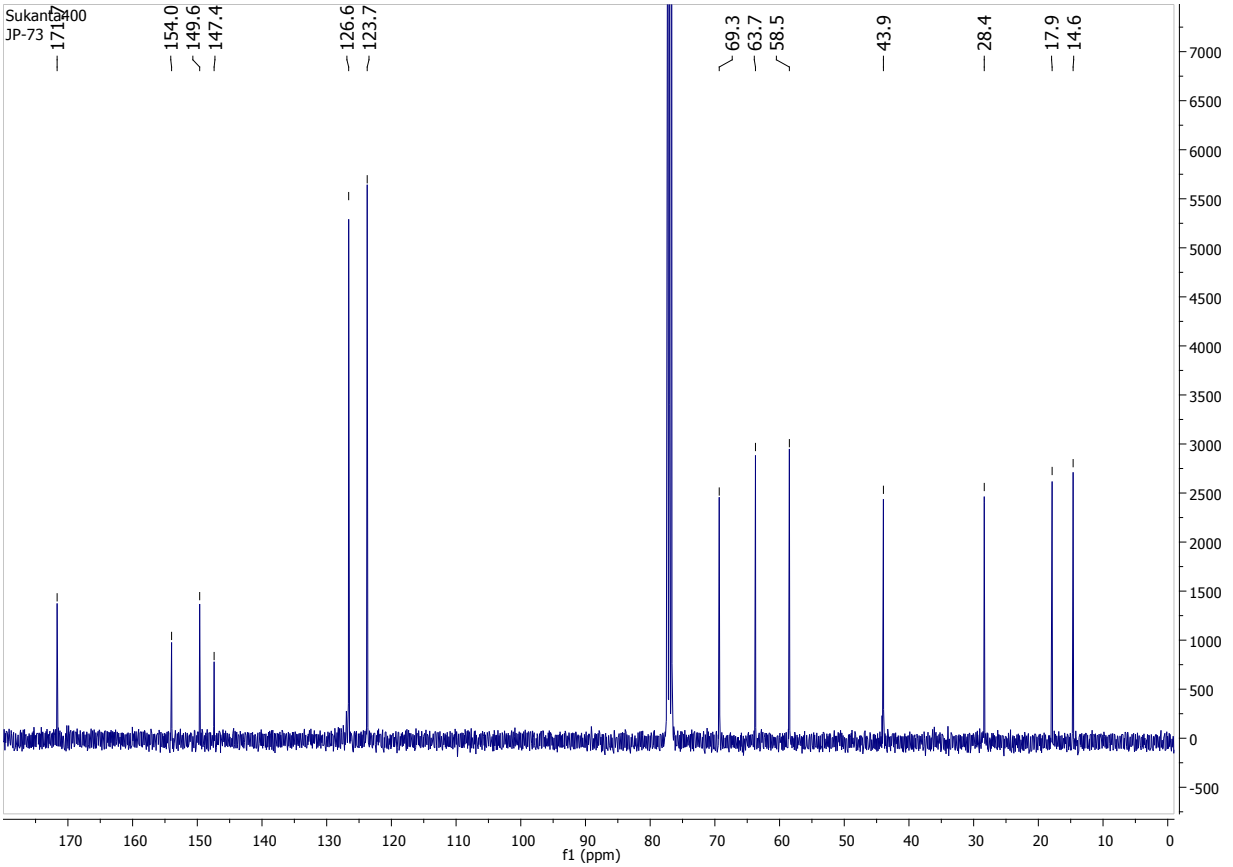
(4*R*)-3-(3-hydroxy-3-(4-nitrophenyl)propanoyl)-4-isopropyloxazolidin-2-one (XI)



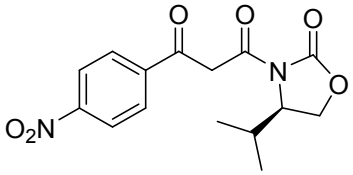
Compound (**XI**) was prepared according to general procedure 2 and purified by column chromatorgraphy (40% EtOAc/hexane) to give the product as a colorless oil (70% yield). The minor diastereoisomer wasn't isolated.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.7, 2H), 7.58 (d, *J* = 8.6, 2H), 5.26 – 5.30 (m, 1H), 4.45 – 4.48 (m, 1H), 4.31 (t, *J* = 8.7, 1H), 4.24 (dd, *J* = 9.2, 3.0, 1H), 3.69 (d, *J* = 4.2, 1H), 3.37 – 3.42 (m, 1H), 3.33 (dd, *J* = 17.4, 3.6, 1H), 2.32 – 2.40 (m, 1H), 0.92 (d, *J* = 7.0, 3H), 0.85 (d, *J* = 6.9, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 154.0, 149.6, 147.4, 126.6 (2C), 123.7 (2C), 69.3, 63.7, 58.5, 43.9, 28.4, 17.9, 14.6.
R_f: 0.3 (40% EtOAc/hexane)
IR (ATR) ν 3416, 3118, 2966, 2879, 2450, 2257, 2108, 1938, 1780, 1692, 1601, 1514, 1377, 1341, 1296, 1195, 1116, 1059, 974, 910 cm^{-1}.
HRMS (APCI+): *m/z*: Calcd for $C_{15}H_{19}N_2O_6$ $[M+H]^+$, 323.1238; found: 323.1243.


Sukanta400
JP-73
8.21
8.20
7.59
7.57
5.30
5.29
5.28
5.27
5.26
4.45
4.31
4.28
4.26
4.25
3.70
3.69
3.39
3.37
3.36
3.35
2.40
2.38
2.37
2.36
2.36
2.35
2.34
2.33
2.32
0.93
0.91
0.86
0.84
2.00
2.00
0.85
1.00
1.07
0.99
0.86
0.89
0.90
1.00
2.75
2.75
f1 (ppm)


Sukanta400
JP-73
171.7
154.0
149.6
147.4
126.6
123.7
69.3
63.7
58.5
43.9
28.4
17.9
14.6
f1 (ppm)

(*R*)-1-(4-isopropyl-2-oxooxazolidin-3-yl)-3-(4-nitrophenyl)propane-1,3-dione (XII)



Compound (**XII**) was prepared the same way as **(X)** and purified by column chromatography (40% EtOAc/hexane) to give the product as a colorless oil (50% yield).

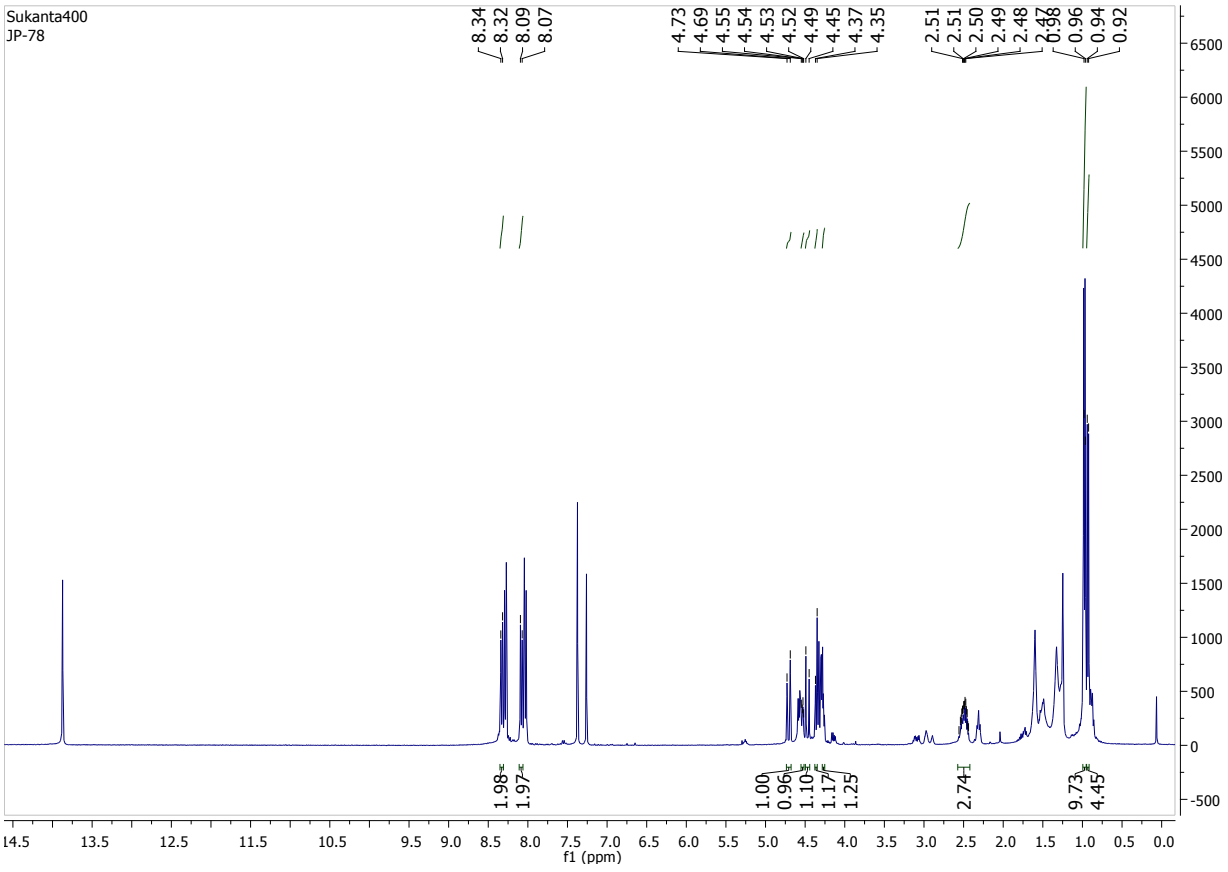
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.9, 2H), 8.08 (d, *J* = 8.9, 2H), 4.71 (d, *J* = 16.5, 1H), 4.53 (dd, *J* = 7.7, 4.1, 1H), 4.47 (d, *J* = 16.5, 1H), 4.36 (d, *J* = 8.5, 1H), 4.27 (dd, *J* = 5.9, 3.2, 1H), 2.44 – 2.56 (m, 1H), 0.97 (d, *J* = 7.1, 3H), 0.93 (d, *J* = 6.9, 3H).

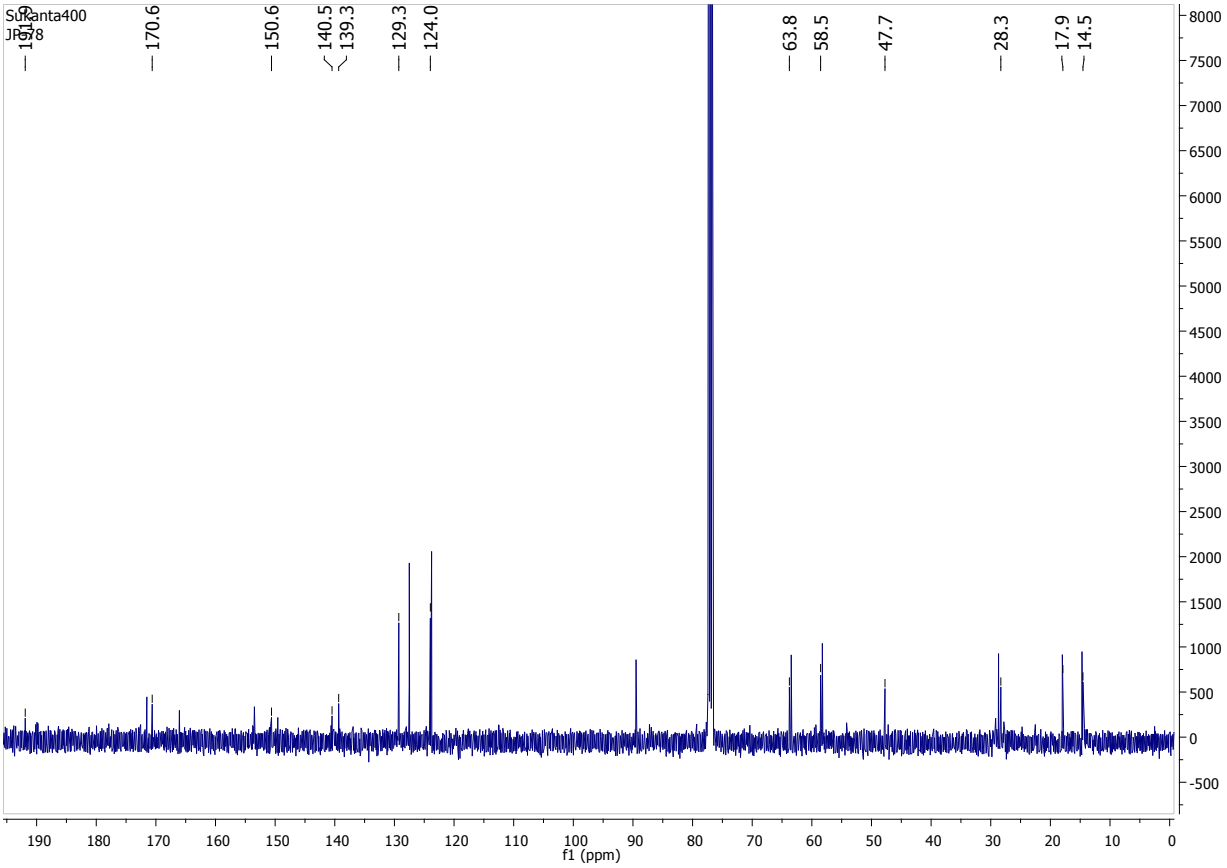
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 170.6, 150.6, 140.5, 139.3, 129.3 (2C), 124.0 (2C), 63.8, 58.5, 47.7, 28.3, 17.9, 14.5.

R_f: 0.30 (40% EtOAc/hexane)

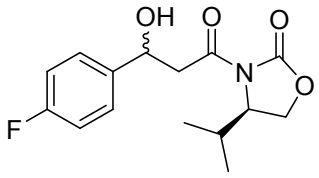
IR ($CHCl_3$) ν 3023, 2966, 1777, 1716, 1597, 1529, 1439, 1392, 1344, 1241, 1227, 1195, 1112, 1068, 1036, 961, 931 cm^{-1}.

HRMS (ESI−): *m/z*: Calcd for $C_{15}H_{15}N_2O_6$ $[M-H]^-$, 319.0930; found: 319.0921





(4*R*)-3-(3-(4-fluorophenyl)-3-hydroxypropanoyl)-4-isopropyloxazolidin-2-one (XIII)

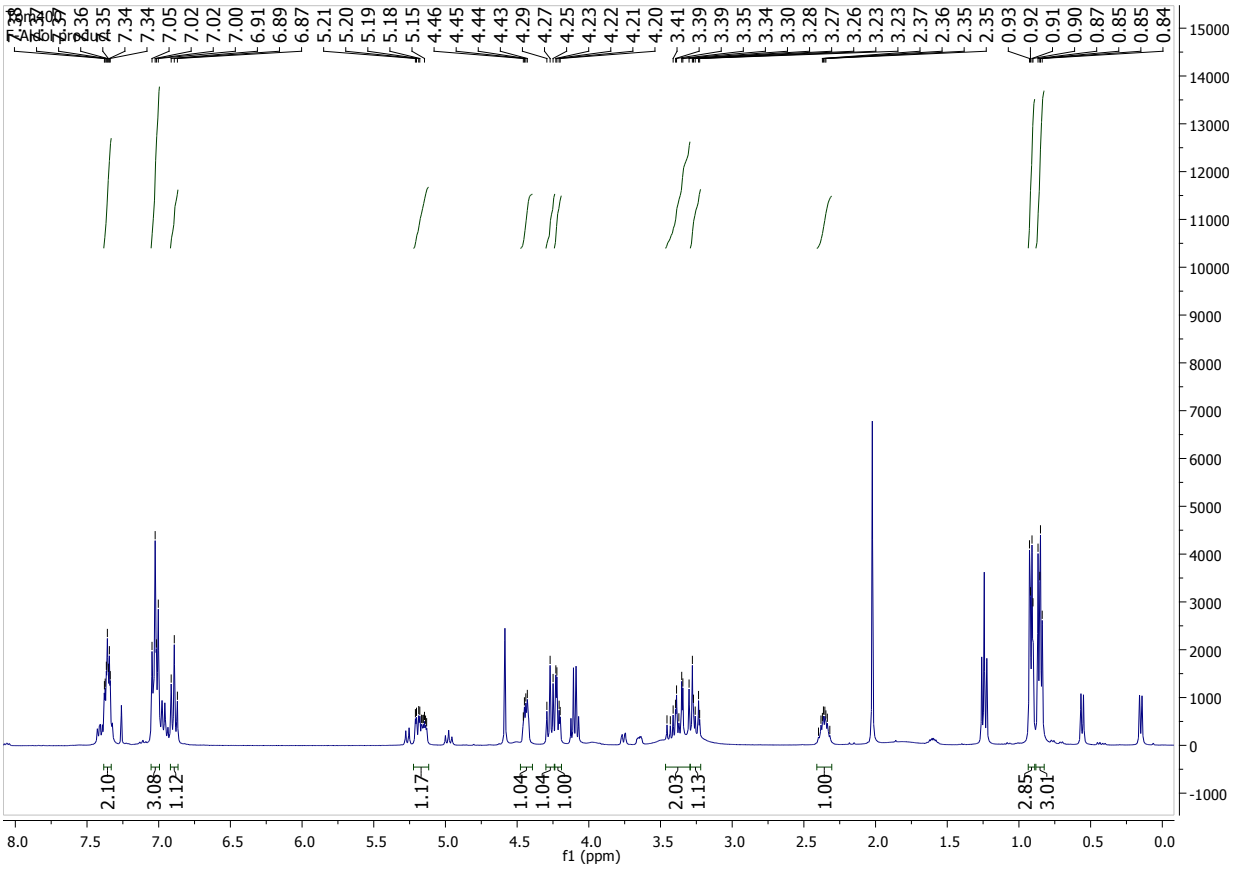


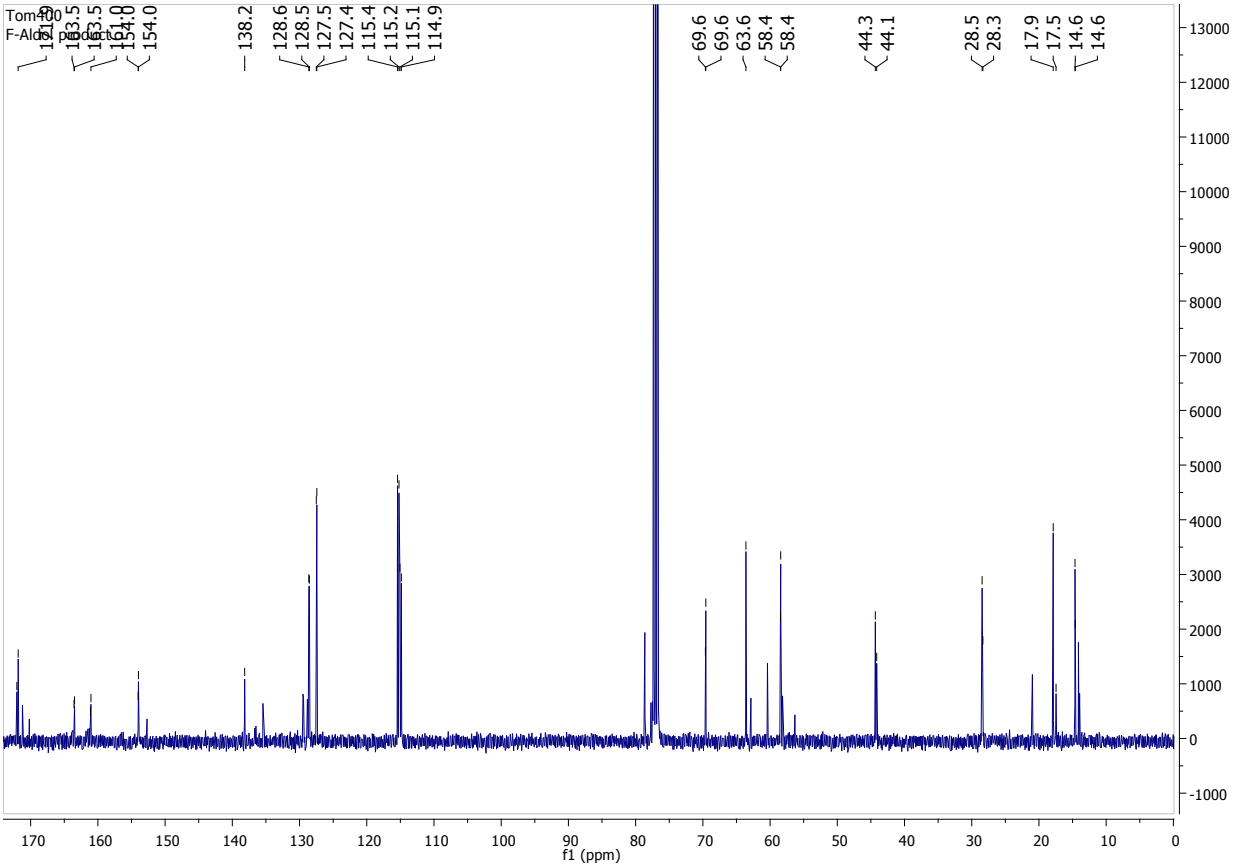
Compound (**XIII**) was prepared according to general procedure 2, with the exception of the aldehyde being added neat, and in 5 equivalents. Reaction time was three hours. The residue was purified by column chromatography (25% - 40% EtOAc/hexane) to give the product (250 mg, 72% yield, diastereomeric mixture) as a yellow oil.

Major diastereoisomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.38 (m, 2H), 7.00 – 7.05 (m, 2H), 5.13 – 5.21 (m, 1H), 4.43 – 4.46 (m, 1H), 4.27 (t, *J* = 8.7, 1H), 4.21 (dd, *J* = 9.2, 2.9, 1H), 3.30 – 3.46 (m, 2H), 3.23 – 3.28 (m, 1H), 2.32 – 2.40 (m, 1H), 0.92 (d, *J* = 7.0, 3H), 0.86 (d, *J* = 6.9, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 162.3 (d, *J* = 245.9), 154.0, 138.2, 127.5 (d, *J* = 8.2, 2C), 115.3 (d, *J* = 21.4, 2C), 69.6, 63.6, 58.4, 44.3, 28.5, 17.9, 14.6.
R_f: 0.39, 0.47 (40% EtOAc/hexane)

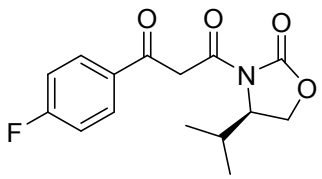
Minor diastereoisomer (distinguishable signals only):
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 – 6.91 (m, 2H), 0.91 (d, *J* = 7.0, 3H), 0.85 (d, *J* = 6.8, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 162.3 (d, *J* = 246.2), 154.0, 128.6 (d, *J* = 8.1, 2C), 115.0 (d, *J* = 21.4, 2C), 69.6, 58.4, 44.1, 28.3, 17.5, 14.6.
IR (ATR) ν 3424, 2967, 2930, 2878, 1775, 1691, 1603, 1507, 1473, 1387, 1370, 1336, 1301, 1260, 1211, 1153, 1123, 1102, 1047, 1017, 977, 935 cm^{-1}.
HRMS (ESI+): *m/z*: Calcd for $C_{15}H_{18}NO_4FNa$ $[M+Na]^+$, 318.1118; found: 318.1103.





(R)-1-(4-fluorophenyl)-3-(4-isopropyl-2-oxooxazolidin-3-yl)propane-1,3-dione (XIV)



Aldol product (**XIII**) (184 mg, 0.62 mmol, 1.0 equiv) was dissolved in DCM (3.1 mL) and PCC (208 mg, 0.97 mmol, 1.6 equiv) was added. The mixture was stirred at r.t. for 23 h and was then filtered through celite, and the solvent was removed *in vacuo*. The residue was purified by column chromatography (10% - 30% EtOAc/hexane) to give the product (61 mg, 34% yield) as a yellow oil.

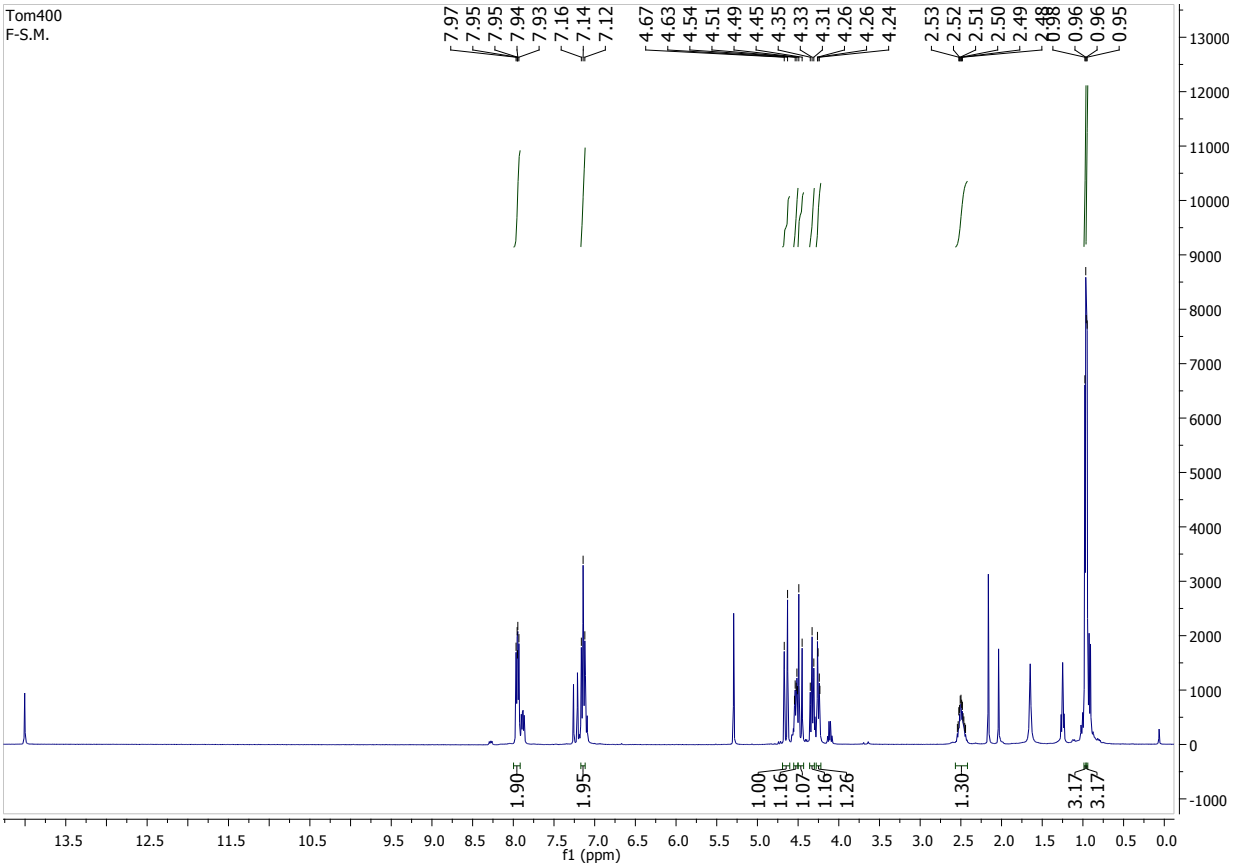
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, J = 8.7, 5.4, 2H), 7.14 (t, J = 8.6, 2H), 4.65 (d, J = 16.3, 1H), 4.51 – 4.54 (m, 1H), 4.47 (d, J = 16.3, 1H), 4.33 (t, J = 8.7, 1H), 4.25 (dd, J = 9.1, 2.9, 1H), 2.44 – 2.54 (m, 1H), 0.97 (d, J = 6.8, 3H), 0.96 (d, J = 7.0, 3H).

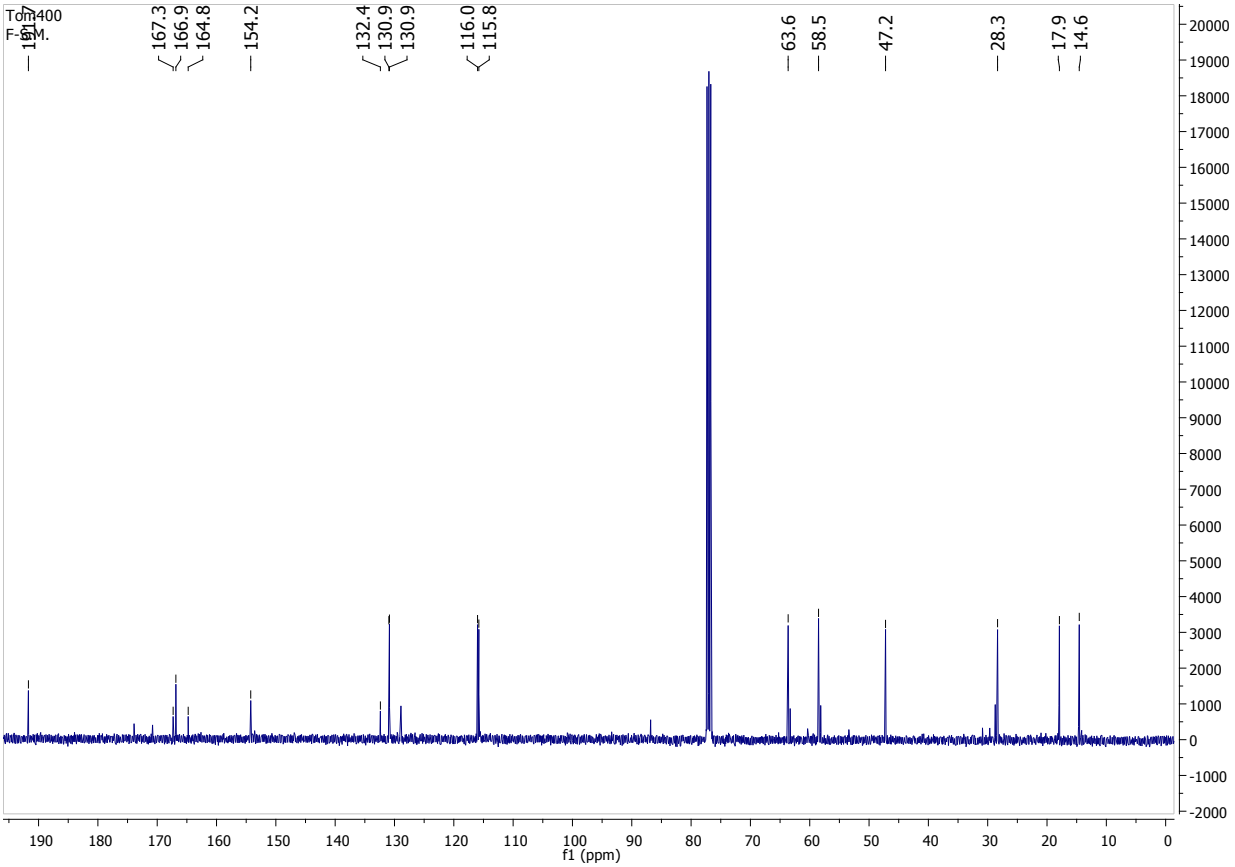
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 166.9, 166.0 (d, J = 255.6), 154.2, 132.4, 130.9 (d, J = 9.5, 2C), 115.9 (d, J = 22.1, 2C), 63.6, 58.5, 47.2, 28.3, 17.9, 14.6.

R_f: 0.53 (40% EtOAc/hexane)

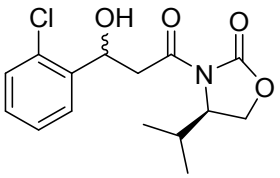
IR ($CHCl_3$) ν 3029, 2968, 2931, 2879, 1779, 1710, 1600, 1509, 1486, 1438, 1394, 1327, 1234, 1194, 1187, 1156, 1111, 1060, 1034, 1007, 975, 909 cm^{-1}.

HRMS (ESI+): *m/z*: Calcd for $C_{15}H_{17}NO_4F$ $[M+H]^+$, 294.1142; found: 294.1137


Tom400
F-S.M.
7.97
7.95
7.95
7.94
7.93
7.16
7.14
7.12
4.67
4.63
4.54
4.51
4.49
4.45
4.35
4.33
4.31
4.26
4.26
4.24
2.53
2.52
2.51
2.50
2.49
0.96
0.96
0.95
1.90
1.95
1.00
1.16
1.07
1.16
1.26
1.30
3.17
3.17
f1 (ppm)

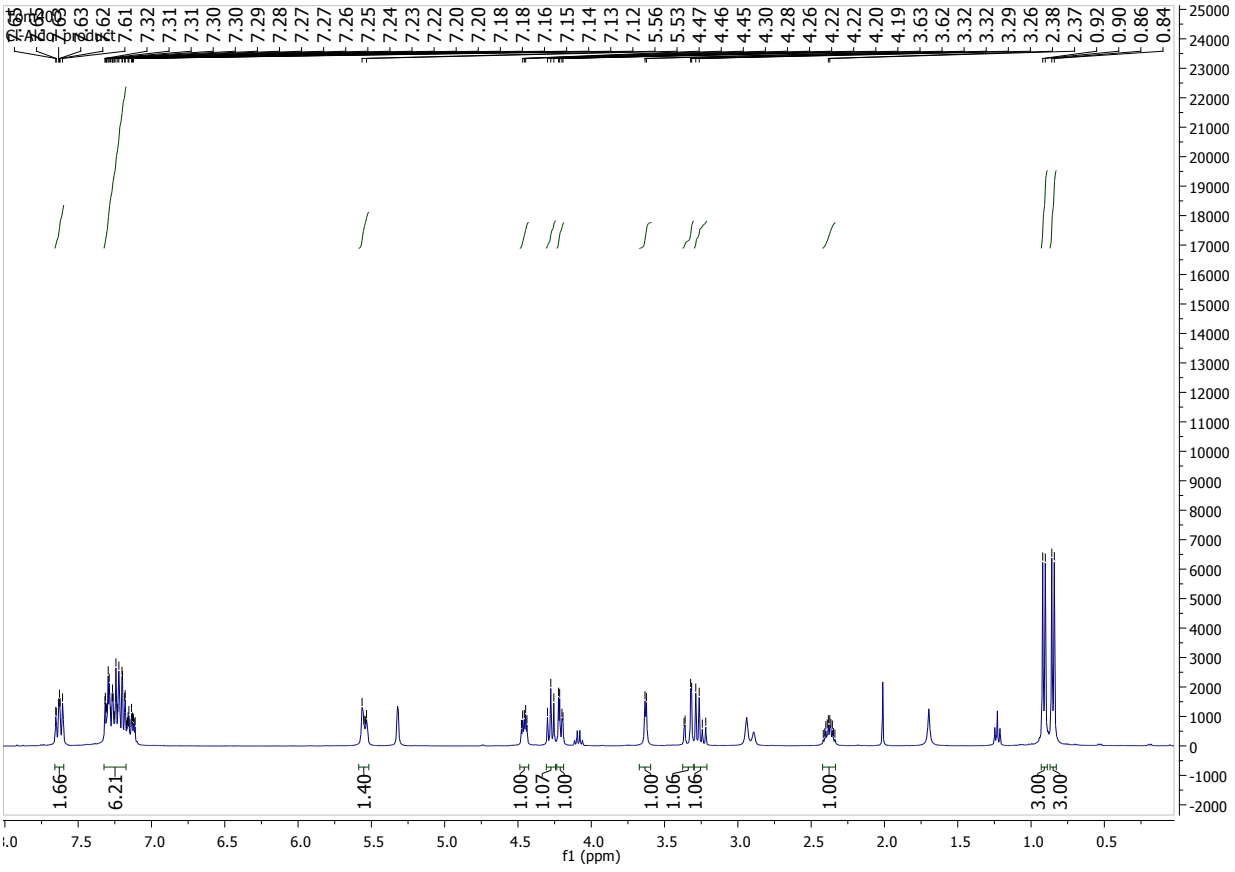

Tom400
F-S.M.
167.3
166.9
164.8
154.2
132.4
130.9
130.9
116.0
115.8
63.6
58.5
47.2
28.3
17.9
14.6
f1 (ppm)

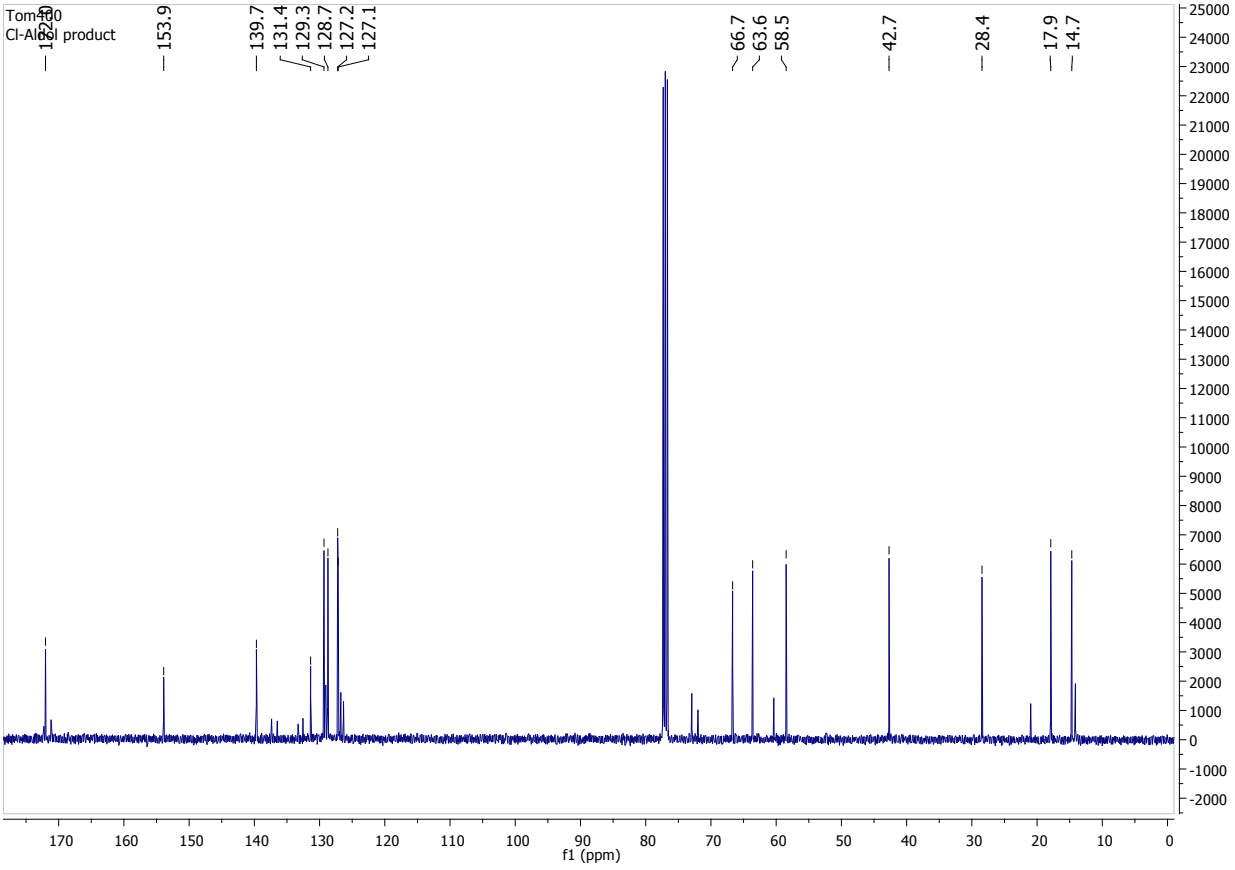
(4*R*)-3-(3-(2-chlorophenyl)-3-hydroxypropanoyl)-4-isopropyloxazolidin-2-one (XV)



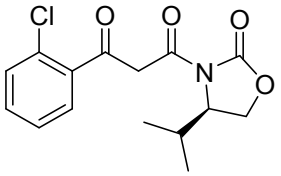
Compound (**XV**) was prepared according to general procedure 2, with the exception of the aldehyde being added neat, and in 5 equivalents. Reaction time was 17 hours. The residue was purified by column chromatography (20% - 35% EtOAc/hexane) to give the product (275 mg, 76% yield) as a yellow oil. The minor diastereoisomer wasn't isolated.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.65 (m, 2H), 7.17 – 7.33 (m, 2H), 5.53 – 5.56 (m, 1H), 4.44 – 4.48 (m, 1H), 4.28 (t, *J* = 8.7, 1H), 4.21 (dd, *J* = 9.2, 3.0, 1H), 3.63 (d, *J* = 3.8, 1H), 3.34 (dd, *J* = 17.9, 2.8, 1H), 3.25 (dd, *J* = 17.9, 9.3, 1H), 2.34 – 2.42 (m, 1H), 0.91 (d, *J* = 7.0, 3H), 0.85 (d, *J* = 6.9, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 153.9, 139.7, 131.4, 129.3, 128.7, 127.2, 127.1, 66.7, 63.6, 58.5, 42.7, 28.4, 17.9, 14.7.
R_f: 0.53 (40% EtOAc/hexane)
IR (ATR) ν 3439, 2962, 2931, 1777, 1675, 1618, 1476, 1439, 1382, 1308, 1276, 1204, 1149, 1113, 1089, 1054, 1020, 968, 910 cm^{-1}.
HRMS (APCI+): *m/z*: Calcd for $C_{15}H_{19}ClNO_4$ $[M+H]^+$, 312.0997; found: 312.1022 .



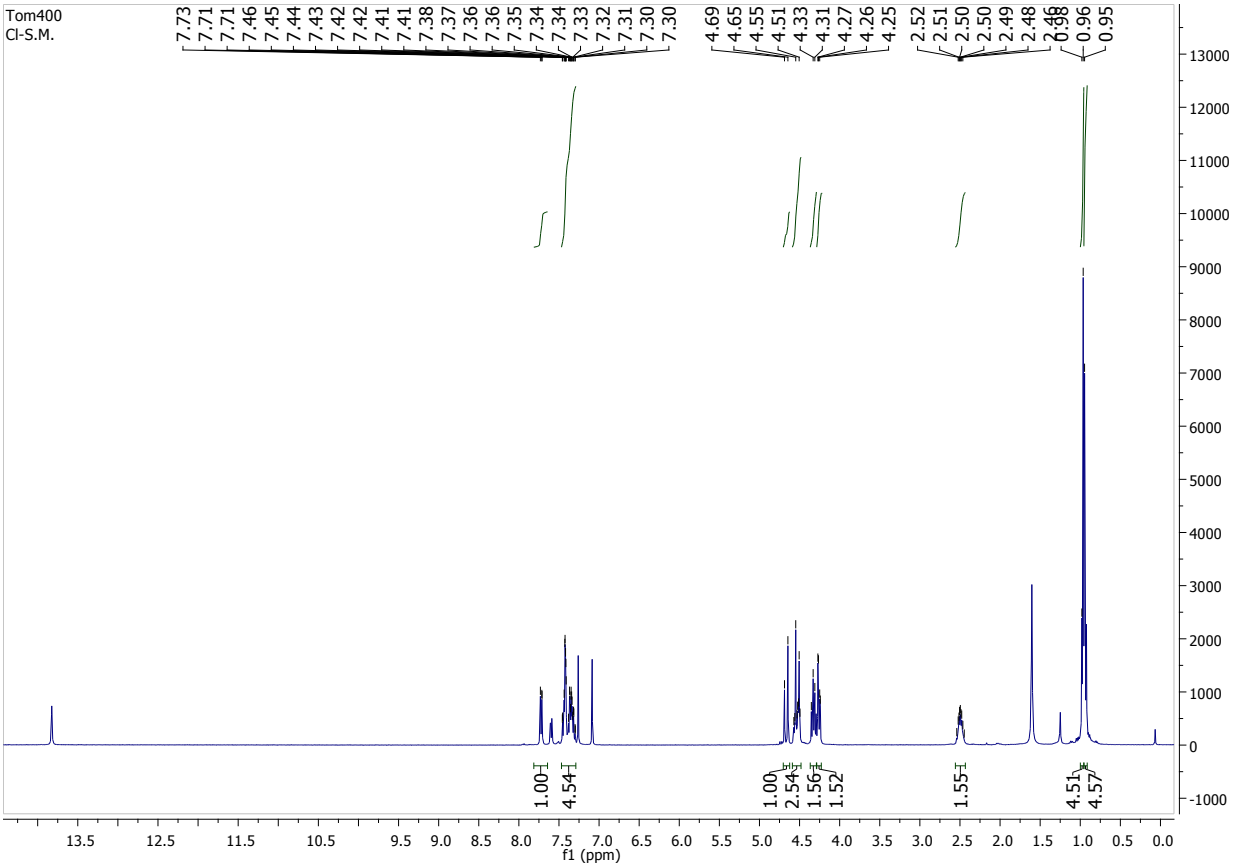


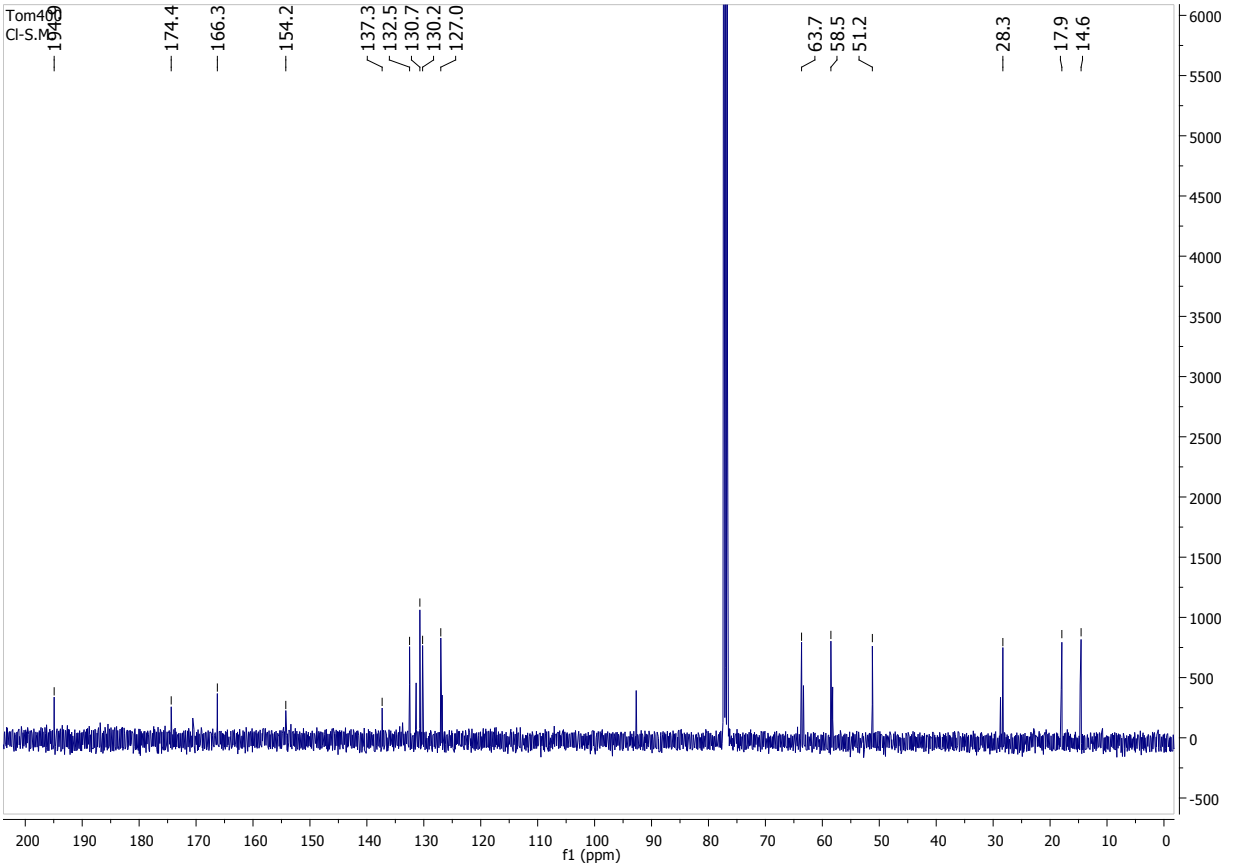
(*R*)-1-(2-chlorophenyl)-3-(4-isopropyl-2-oxooxazolidin-3-yl)propane-1,3-dione (XVI)



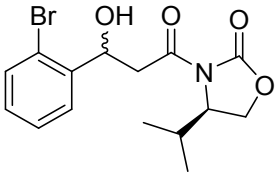
Compound (**XVI**) was prepared the same was as compound (**XIV)**, and purified by column chromatography (20% - 30% EtOAc/hexane) to give the product (56 mg, 26% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.73 (m, 1H), 7.29 – 7.46 (m, 3H), 4.67 (d, *J* = 16.9, 1H), 4.49 – 4.58 (m, 1H), 4.53 (d, *J* = 17.0, 1H), 4.33 (t, *J* = 8.7, 1H), 4.26 (dd, *J* = 9.1, 3.0, 1H), 2.45 – 2.54 (m, 1H), 0.97 (d, *J* = 6.7, 3H), 0.95 (d, *J* = 6.9, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 174.4, 166.3, 154.2, 137.3, 132.5, 130.7, 130.2, 127.0, 63.7, 58.5, 51.2, 28.3, 17.9, 14.6.
R_f: 0.58 (40% EtOAc/hexane).
IR ($CHCl_3$) ν 3028, 2969, 1779, 1709, 1616, 1477, 1438, 1392, 1324, 1262, 1227, 1194, 1109, 1064, 1031, 929 cm^{-1}.
HRMS (ESI+): *m/z*: Calcd for $C_{15}H_{17}NO_4Cl$ $[M+H]^+$, 310.0846; found: 310.0836


Tom400
Cl-S.M.
7.73 7.71 7.71 7.46 7.45 7.44 7.43 7.42 7.42 7.41 7.41 7.38 7.37 7.36 7.36 7.35 7.34 7.34 7.33 7.32 7.31 7.30 7.30
4.69 4.65 4.55 4.51 4.33 4.31 4.27 4.26 4.25
2.52 2.51 2.50 2.50 2.49 2.48 2.46 0.98 0.96 0.95
1.00 4.54 1.00 2.54 1.56 1.52 1.55 4.51 4.57
f1 (ppm)


Tom400
Cl-S.M.
194.0
174.4
166.3
154.2
137.3 132.5 130.7 130.2 127.0
63.7 58.5 51.2
28.3
17.9 14.6
f1 (ppm)

(4*R*)-3-(3-(2-bromophenyl)-3-hydroxypropanoyl)-4-isopropyloxazolidin-2-one (XVII)

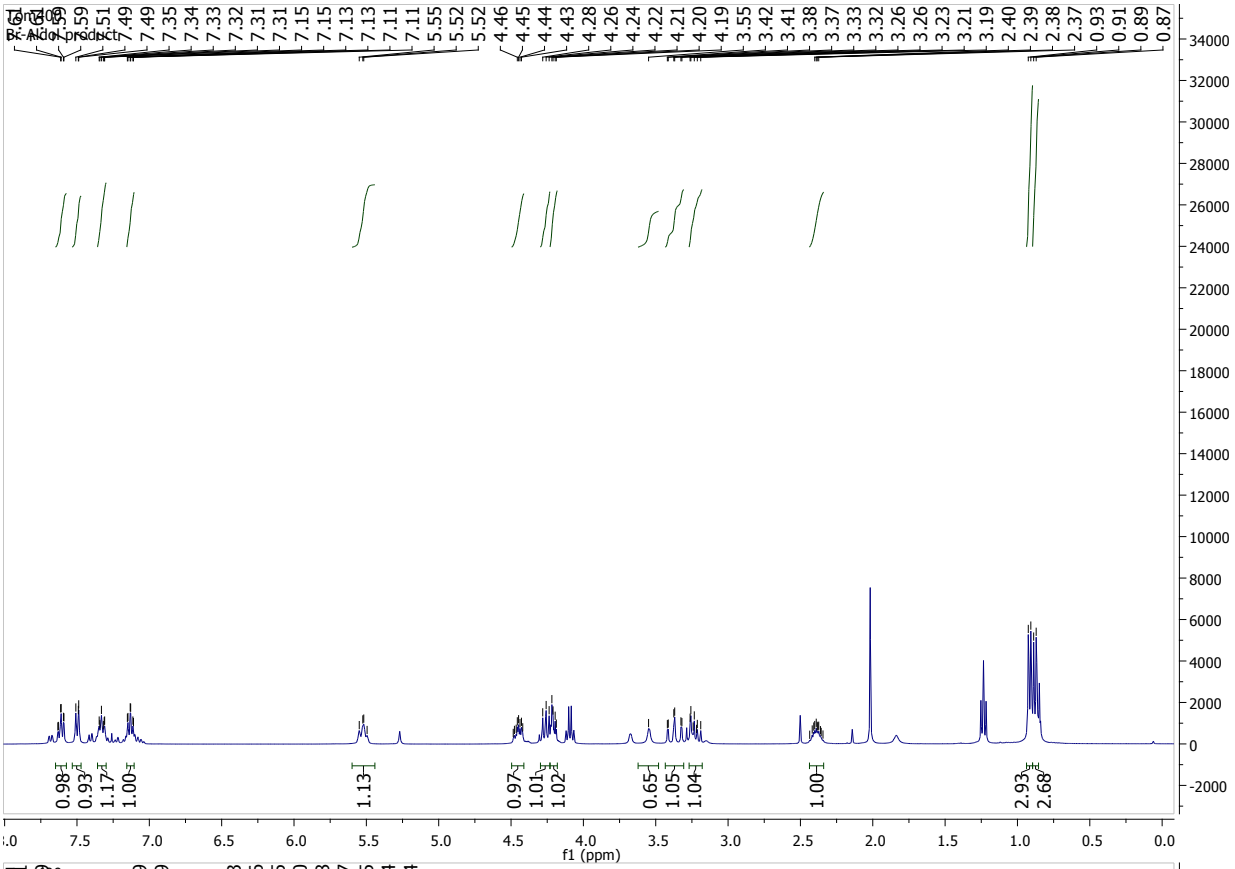


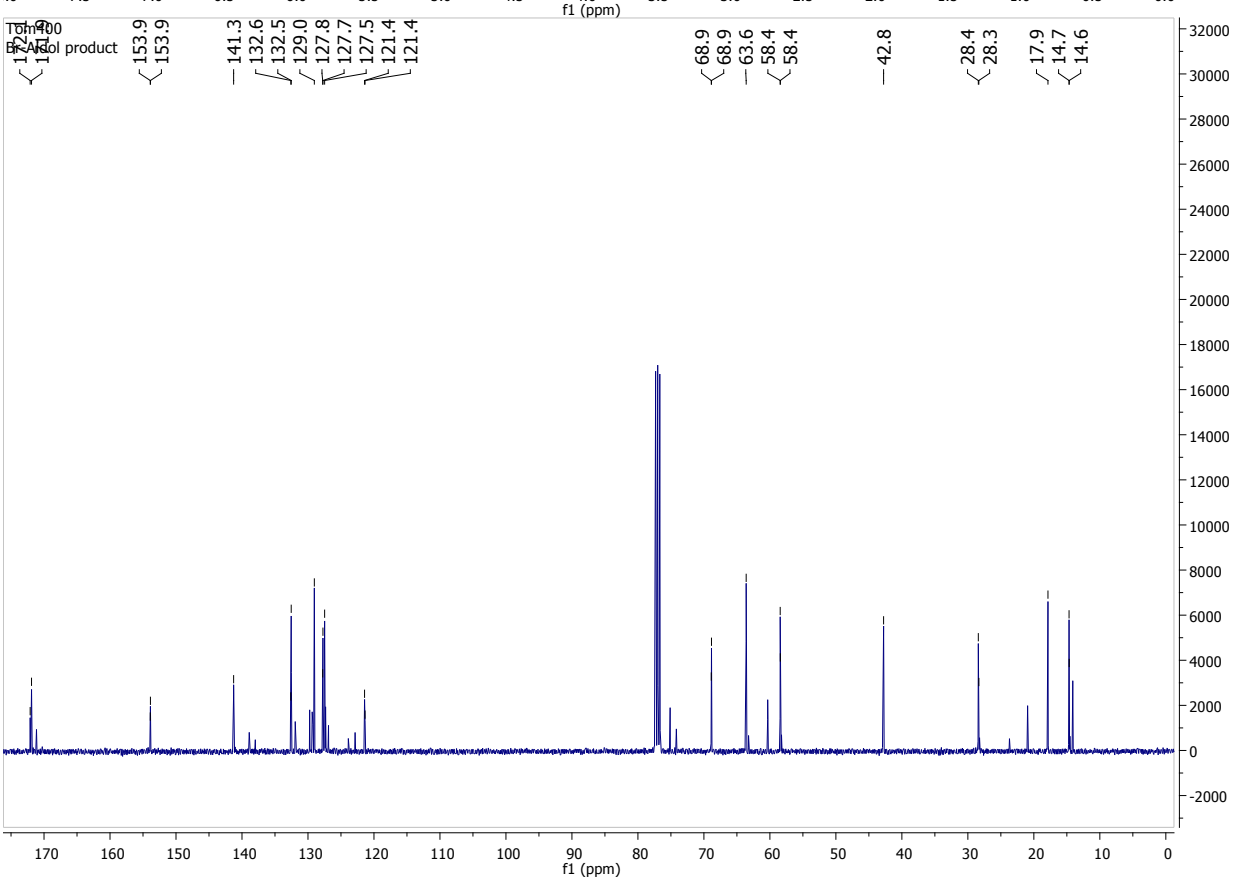
Compound (**XVII**) was prepared according to general procedure 2, with the exception of the aldehyde being added neat, and in 5 equivalents. Reaction time was three hours. The residue was purified by column chromatography (20% - 40% EtOAc/hexane) to give the product (357 mg, 86% yield, diastereomeric mixture) as a yellow oil.

Major diastereoisomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (td, *J* = 7.7, 1.4, 1H), 7.49 – 7.51 (m, 1H), 7.31 – 7.35 (m, 1H), 7.13 (td, *J* = 7.8, 1.6, 1H), 5.49 – 5.55 (m, 1H), 4.42 – 4.48 (m, 1H), 4.24 – 4.28 (m, 1H), 4.20 (dd, *J* = 9.1, 3.2, 1H), 3.53 – 3.57 (m, 1H), 3.32 – 3.42 (m, 1H), 3.19 – 3.26 (m, 1H), 2.34 – 2.44 (m, 1H), 0.92 (d, *J* = 7.0, 3H), 0.88 (d, *J* = 6.9, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 153.9, 141.3, 132.5, 129.0, 127.7, 127.5, 121.4, 68.9, 63.6, 58.4, 42.8, 28.4, 17.9, 14.7.
R_f: 0.39, 0.53 (40% EtOAc/hexane)

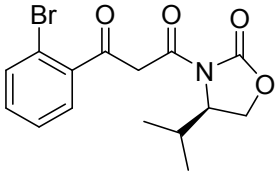
Minor diastereoisomer (distinguishable signals only):
^{1}H NMR (400 MHz, $CDCl_3$) - no distinguishable signals.
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 153.9, 132.6, 127.8, 121.4, 68.9, 58.4, 28.3, 14.6.

IR (ATR) ν 3475, 2966, 1775, 1753, 1705, 1487, 1461, 1433, 1369, 1325, 1298, 1278, 1198, 1145, 1100, 1062, 1056, 1016, 971, 913 cm^{-1}.
HRMS (ESI+): *m/z*: Calcd for $C_{15}H_{19}NO_4Br$ $[M+H]^+$, 356.0497; found: 356.0470 .


Tom400
Br Aldol product
7.59
7.51
7.49
7.49
7.35
7.34
7.33
7.32
7.31
7.31
7.15
7.15
7.13
7.13
7.11
7.11
5.55
5.52
4.46
4.45
4.44
4.43
4.28
4.26
4.24
4.22
4.21
4.20
4.19
3.55
3.42
3.41
3.38
3.37
3.33
3.32
3.26
3.26
3.23
3.21
3.19
2.40
2.39
2.38
2.37
0.93
0.91
0.89
0.87
0.98
0.93
1.17
1.00
1.13
0.97
1.01
1.02
0.65
1.05
1.04
1.00
2.93
2.68
f1 (ppm)

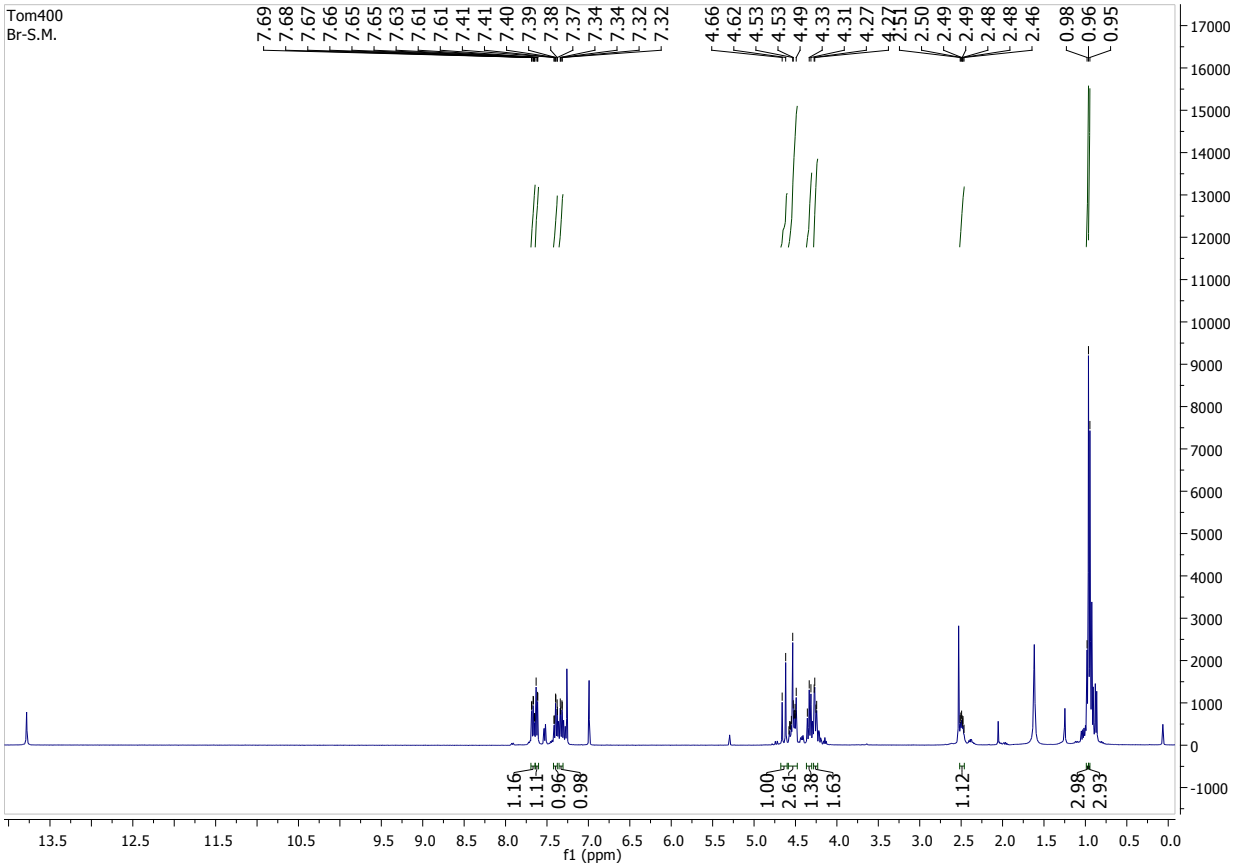

Tom400
Br Aldol product
153.9
153.9
141.3
132.6
132.5
129.0
127.8
127.7
127.5
121.4
121.4
68.9
68.9
63.6
58.4
58.4
42.8
28.4
28.3
17.9
14.7
14.6
f1 (ppm)

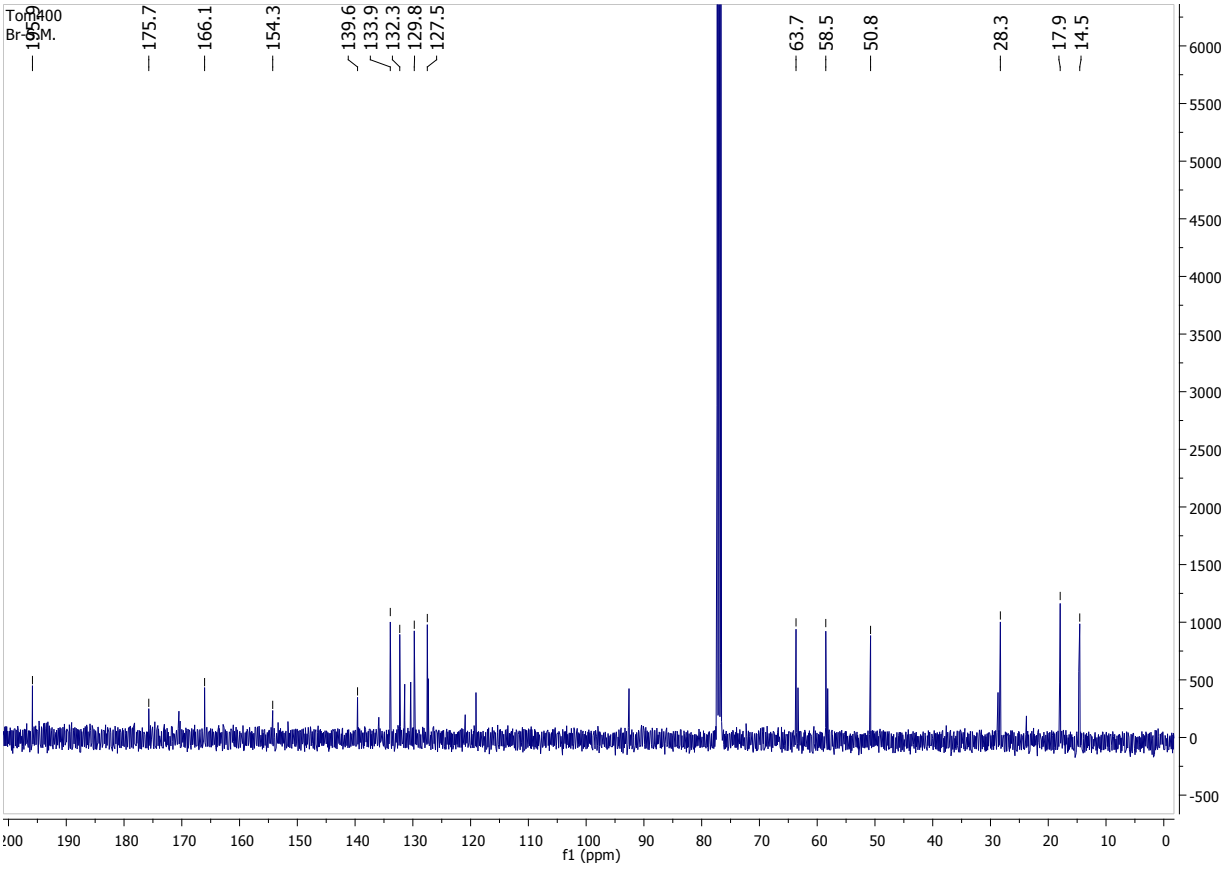
(*R*)-1-(2-bromophenyl)-3-(4-isopropyl-2-oxooxazolidin-3-yl)propane-1,3-dione (XVIII)



Compound (**XVIII**) was prepared the same way as compound **(XIV)**, and purified by column chromatography (20% - 30% EtOAc/hexane) to give the product (55 mg, 20% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.69 (m, 1H), 7.61 – 7.63 (m, 1H), 7.39 (td, *J* = 7.5, 1.1, 1H), 7.33 (dd, *J* = 7.8, 1.7, 1H), 4.64 (d, *J* = 17.0, 1H), 4.48 – 4.58 (m, 1H), 4.51 (d, *J* = 17.0 Hz, 1H), 4.31 – 4.36 (m, 1H), 4.26 (dd, *J* = 9.2, 3.1, 1H), 2.46 – 2.51 (m, 1H), 0.97 (d, *J* = 6.8, 3H), 0.95 (d, *J* = 6.9, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 195.9, 175.7, 166.1, 154.3, 139.6, 133.9, 132.3, 129.8, 127.5, 63.7, 58.5, 50.8, 28.3, 17.9, 14.5.
R_f: 0.58 (40% EtOAc/hexane)
IR ($CHCl_3$) ν 3027, 2968, 2930, 2879, 1780, 1708, 1615, 1466, 1425, 1391, 1312, 1262, 1231, 1227, 1194, 1111, 1061, 1029, 980, 909 cm^{-1}.
HRMS (ESI+): *m/z*: Calcd for $C_{15}H_{17}NO_4Br$ $[M+H]^+$, 354.0341; found: 354.0350




Tom400
Br-5M.
175.7
166.1
154.3
139.6
133.9
132.3
129.8
127.5
63.7
58.5
50.8
28.3
17.9
14.5
f1 (ppm)

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(3) S. Lin, L. Deiana, A. Tseggai and A. Córdova, *Eur. J. Org. Chem.* 2012, **2**, 398–408.

(4) F. Fu and T.-P. Loh, *Tetrahedron Letters,* 2009, **50**, 3530–3533.

(5) C. Chen and S. H. Hong, *Organic Letters,* 2012, **12**, 2992–2995.