Supporting Information

For

BIFUNCTIONAL-BENZOTHIADIAZINE-CATALYZED REGIO- AND STEREOSELECTIVE ALDOL REACTIONS USING A 1,3-ACETONEDICARBOXYLIC ACID MONOESTER

Yusuke Tokuhiro, Noboru Hayama, Yusuke Kobayashi, Yoshiji Takemoto*

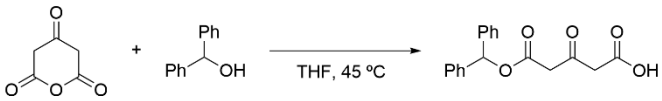
Graduate School of Pharmaceutical Sciences, Kyoto University

CONTENTS

1. General Information

All reactions were carried out under air with no precautions taken to exclude moisture unless otherwise noted. Commercially available reagents that were used as received are noted in the individual reaction procedures. Analytical thin-layer chromatography was performed with Merck Silica gel 60. Column chromatography was performed on Cica silica gel 60N (Spherical, Neutral, 100-210 μm), or Fuji Silysia silica gel (BW-300). ^{1}H NMR spectra were recorded on a JEOL JNM-ECA 500 (500 MHz) and are reported in ppm relative to Me_4Si (δ 0.00) in $CDCl_3$ and internal residual solvents (dimethylsulfoxide-d_6 δ 2.49). Data reported as: integration; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constant(s) in Hz. Proton-decoupled ^{13}C NMR spectra were recorded on a JEOL JNM-ECA 500 (126 MHz) or JEOL JNM-ECZ 600 (150 MHz) and are reported in ppm relative to ($CDCl_3$ δ 77.0, and dimethylsulfoxide-d_6 δ 39.7). Infrared spectra were recorded on a JASCO FT/IR-4100 Fourier-transform infrared spectrometer ATR (attenuated total reflectance). High-resolution mass spectra were obtained on a SHIMADZU LCMS-IT-TOF fitted with an ESI-MS, Bruker microTOF, and JEOL JMS-700 double-focusing mass spectrometer. High performance liquid chromatography (HPLC) analysis was performed on SHIMADZU Prominence Series instrument equipped with a UV detector. Optical rotations were determined with a JASCO P-2200KDT polarimeter and are the average of five measurements and reported as follows: $[\alpha]^{T\,^{\circ}C}_{\lambda}$ concentration (c = g / 100 mL, solvent). All melting points were measured on BÜCHI M-565 melting point apparatus and are uncorrected

2. Preparation of 1,3-Acetonedicarboxylic Acid Monoester



S1 **S2** **1**

A 50 mL round bottom flask was charged with a stir bar, carboxylic anhydride **S1**[1] (1.50 g, 11.7 mmol, 1.0 equiv.), benzhydrol **S2** (2.59 g, 14.1 mmol, 1.2 equiv.), and THF (9.0 mL), and the mixture was stirred at 45 °C for 3 h. Then the mixture was allowed to cool to room temperature, and concentrated under reduced pressure. The residue was dissolved in Et_2O (20 mL), and extracted with saturated aqueous $NaHCO_3$ solution (20 mL + 10 mL x3). The combined aqueous layers were acidified with 1M HCl (50 mL), and extracted with $CHCl_3$ (100 mL x3). The combined organic layers were washed with brine (200 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was washed with hexane (30 mL x2) at −78 °C, and dried *in vacuo* to afford 5-(benzhydryloxy)-3,5-dioxopentanoic acid **1** (2.59 g, 9.26 mmol, 79% yield) as a white solid, which was storable at −20 °C under Ar atmosphere.

5-(Benzhydryloxy)-3,5-dioxopentanoic acid (1)

^{1}H NMR (500 MHz, DMSO-d_6): δ 7.41–7.24 (10H, m), 6.81 (1H, s), 3.87 (2H, s), 3.59 (2H, s) (COO-H proton was not observed).

^{13}C NMR (150 MHz, DMSO-d_6): δ 197.4, 168.3, 166.0, 140.2, 128.5, 127.8, 126.6, 77.1, 49.3, 48.9.

HRMS (FAB+): *m/z* calculated for $C_{18}H_{16}O_5Na$ $[M+Na]^+$: 335.0895, found: 335.0893.

IR (ATR): 3031.6, 1752.0, 1702.8 cm^{-1}

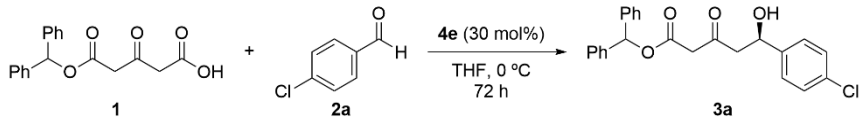
Melting Point: 73.9-76.2 °C

3. Experimental Procedure for the Decaroboxylative Aldol Reaction

Optimezed General Procedure

A 10 mL test tube equipped with a Teflon-coated screw cap was charged with a stir bar, aldehyde **2** (0.100 mmol, 1.0 equiv.), catalyst **4e** (9.7 mg, 0.0301 mmol, 30 mol%), and THF (1.0 mL) before the mixture was cooled to 0 °C.Carboxylic acid **1** (93.6 mg, 0.300 mmol, 3.0 equiv.) was added in portions (0, 24, and 48 h, 1.0 equiv. each) to the stirred mixture. After stirring for 72 h at 0 °C, the solution was concentrated under reduced pressure, and the residue was purified using column chromatography on silica gel eluted by hexane/EtOAc to afford the adduct **3**. The ee values was determined by chiral HPLC analysis.

Benzhydryl (*R*)-5-(4-chlorophenyl)-5-hydroxy-3-oxopentanoate (3a)



According to general procedure, carboxylic acid **1** (93.6 mg, 0.300 mmol, 3.0 equiv.) reacted with aldehyde **2a** (14.1 mg, 0.100 mmol, 1.0 equiv.) and catalyst **4e** (9.7 mg, 0.0301 mmol, 30 mol%) in THF (1.0 mL) at 0 °C to afford **3a** (32.9 mg, 0.0805 mmol, 81% yield, 68% ee) as a colorless oil. The ee value of the product was determined by chiral HPLC analysis: CHIRALPAK IC, 1.0 mL/min, 15% 2-propanol/hexane. λ = 254 mm, $t_{R(ent\text{-}3a)}$ = 10.8 min, $t_{R(3a)}$ = 13.7 min.

^{1}H NMR (500 MHz, DMSO-d_6): δ 7.39–7.31 (12H, m), 7.30–7.25 (2H, m), 6.81 (1H, s), 5.59 (1H, d, J = 4.6 Hz), 5.05–4.99 (1H, m), 3.85–3.75 (2H, m), 2.87–2.75 (2H, m).

^{13}C NMR (150 MHz, DMSO-d_6): δ 201.6, 166.3, 144.0, 140.25, 140.23, 131.4, 128.5, 128.1, 127.82, 127.80, 127.6, 126.63, 126.60, 77.0, 67.7, 52.1, 49.4 (one aromatic carbon peak is missing due to overlapping).

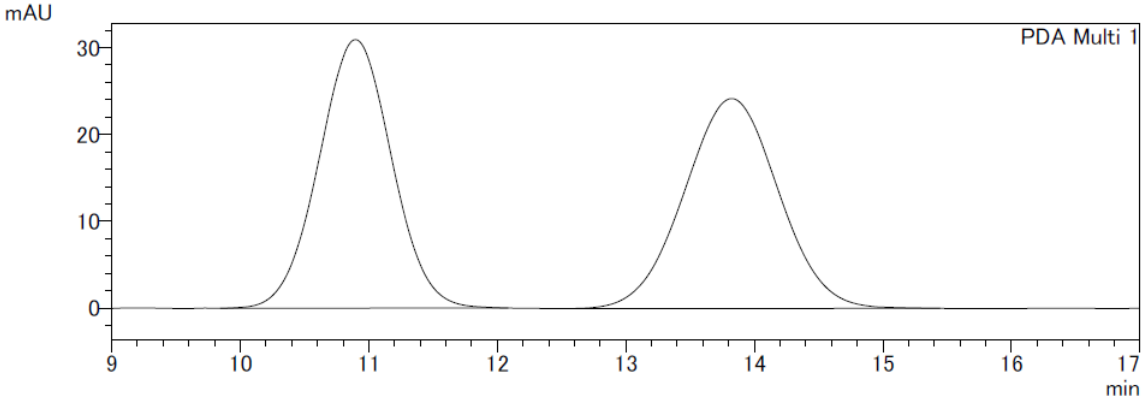
HRMS (ESI+): *m/z* calculated for $C_{24}H_{21}O_4ClNa$ $[M+Na]^+$: 431.1021, found: 431.1008.

IR (ATR): 3484.3, 3032.0, 2927.4, 1740.9, 1214.4 cm^{-1}

Optical Rotation: $[\alpha]^{19}_D$ +19.9 (c 1.29, $CHCl_3$)

Chiral HPLC Analysis for Adduct 3a

<Chromatogram>



1 PDA Multi 1 / 254nm 4nm

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PDA Ch1 254nm 4nm

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2	13.817	1237130	50.313

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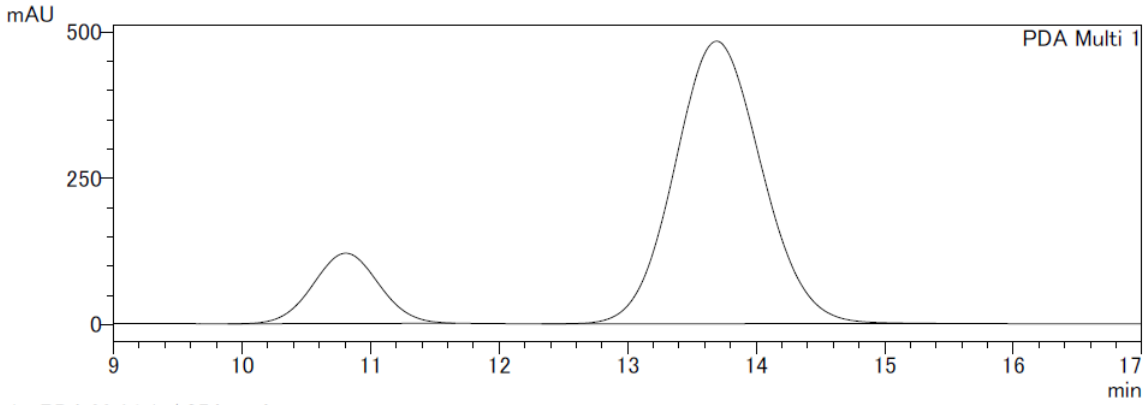


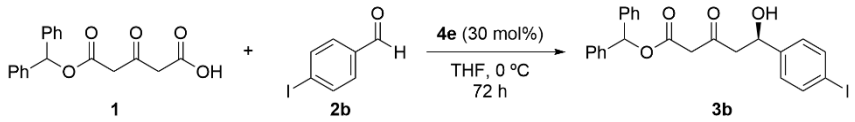
1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	10.802	4297811	15.861
2	13.687	22799257	84.139

Benzhydryl (*R*)-5-hydroxy-5-(4-iodophenyl)-3-oxopentanoate (3b)



According to general procedure, carboxylic acid **1** (93.6 mg, 0.300 mmol, 3.0 equiv.) reacted with aldehyde **2b** (23.2 mg, 0.100 mmol, 1.0 equiv.) and catalyst **4e** (9.7 mg, 0.0301 mmol, 30 mol%) in THF (1.0 mL) at 0 °C to afford **3b** (27.5 mg, 0.0549 mmol, 55% yield, 65% ee) as a colorless oil. The ee value of the product was determined by chiral HPLC analysis: CHIRALPAK IC, 1.0 mL/min, 15% 2-propanol/hexane. λ = 254 mm, $t_{R(ent\text{-}3b)}$ = 11.9 min, $t_{R(3b)}$ = 14.5 min.

^{1}H NMR (500 MHz, DMSO-d_6): δ 7.65 (2H, d, J = 8.6 Hz), 7.41–7.30 (8H, m), 7.30–7.25 (2H, m), 7.14 (2H, d, J = 8.0 Hz), 6.80 (1H, s), 5.57 (1H, d, J = 4.6 Hz), 5.00–4.95 (1H, m), 3.84–3.75 (2H, m), 2.86–2.73 (2H, m).

^{13}C NMR (126 MHz, DMSO-d_6): δ 201.5, 166.2, 144.8, 140.2, 136.8, 128.5, 128.2, 127.80, 127.79, 126.62, 126.59, 92.8, 76.9, 67.9, 52.0, 49.4 (two aromatic carbon peaks are missing due to overlapping).

HRMS (ESI−): *m/z* calculated for $C_{24}H_{20}O_4I$ $[M-H]^-$: 499.0412, found: 499.0417.

IR (ATR): 3465.5, 2927.9, 1737.6, 1715.4 cm^{-1}

Optical Rotation: $[\alpha]^{20}_D$ +14.5 (c 1.16, $CHCl_3$)

Chiral HPLC Analysis for Adduct 3b

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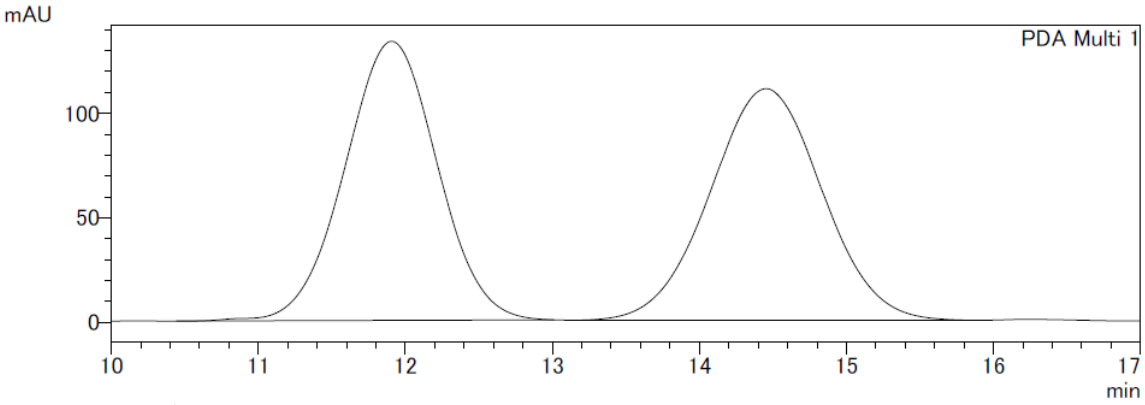

1 PDA Multi 1 / 254nm 4nm

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PDA Ch1 254nm 4nm

peak #	retention time (min)	area	area (%)
1	11.902	5859854	49.861
2	14.448	5892487	50.139

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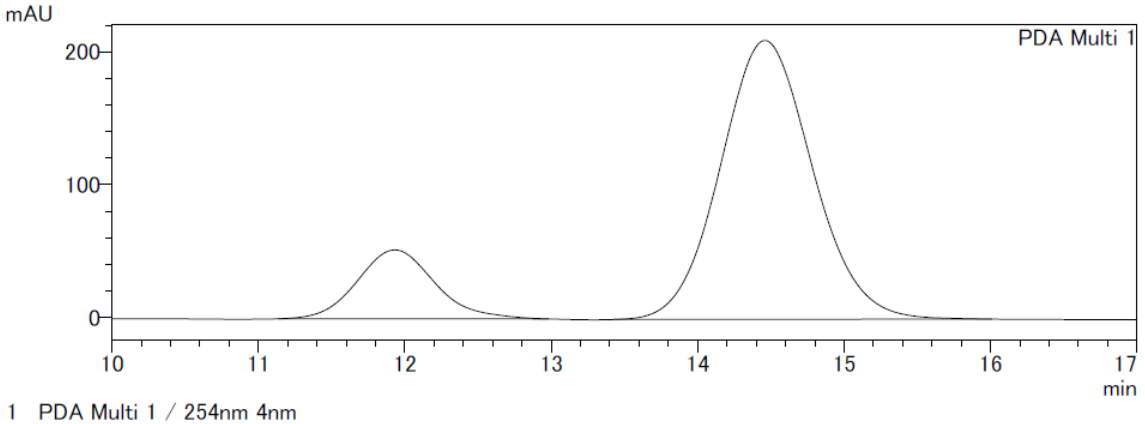

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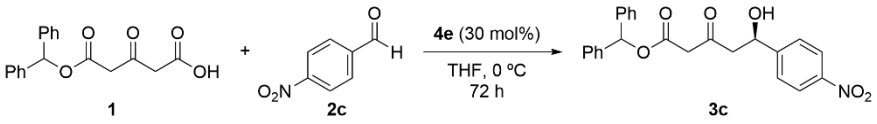
PDA Ch1 254nm 4nm

peak #	retention time (min)	area	area (%)
1	11.926	1916487	17.260
2	14.454	9187146	82.740

Benzhydryl (*R*)-5-hydroxy-5-(4-nitrophenyl)-3-oxopentanoate (3c)



According to general procedure, carboxylic acid **1** (93.6 mg, 0.300 mmol, 3.0 equiv.) reacted with aldehyde **2c** (15.1 mg, 0.0999 mmol, 1.0 equiv.) and catalyst **4e** (9.7 mg, 0.0301 mmol, 30 mol%) in THF (1.0 mL) at 0 °C to afford **3c** (30.5 mg, 0.0727 mmol, 73% yield, 75% ee) as a white solid. The ee value of the product was determined by chiral HPLC analysis: CHIRALPAK IC, 1.0 mL/min, 15% 2-propanol/hexane. λ = 254 mm, $t_{R(ent\text{-}3c)}$ = 16.9 min, $t_{R(3c)}$ = 19.8 min.

^{1}H NMR (500 MHz, DMSO-d_6): δ 8.18 (2H, d, J = 9.2 Hz), 7.62 (2H, d, J = 8.6 Hz), 7.40–7.31 (8H, m), 7.30–7.25 (2H, m), 6.82 (1H, s), 5.84 (1H, d, J = 4.6 Hz), 5.18 (1H, q, J = 5.9 Hz), 3.87–3.78 (2H, m), 2.88 (2H, d, J = 6.9 Hz)..

^{13}C NMR (150 MHz, DMSO-d_6): δ 206.4, 171.3, 158.0, 151.6, 145.4, 133.6, 133.0, 132.1, 131.7, 128.6, 128.4, 82.1, 72.7,

56.9, 54.5 (three aromatic carbon peaks are missing due to overlapping).

HRMS (ESI+): *m/z* calculated for $C_{24}H_{21}NO_6Na$ $[M+Na]^+$: 442.1261, found: 442.1242.

IR (ATR): 3477.0, 1759.7, 1713.4, 1506.6 cm^{-1}

Optical Rotation: $[\alpha]^{22}_D$ +20.5 (c 0.86, $CHCl_3$)

Melting Point: 137.9−139.1 °C

Chiral HPLC Analysis for Adduct 3c

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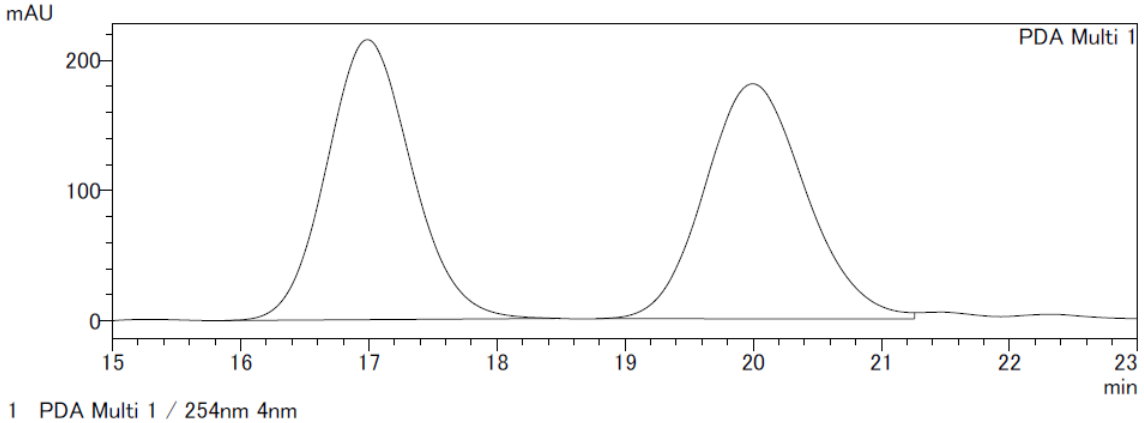

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	16.984	9952616	50.082
2	19.989	9920086	49.918

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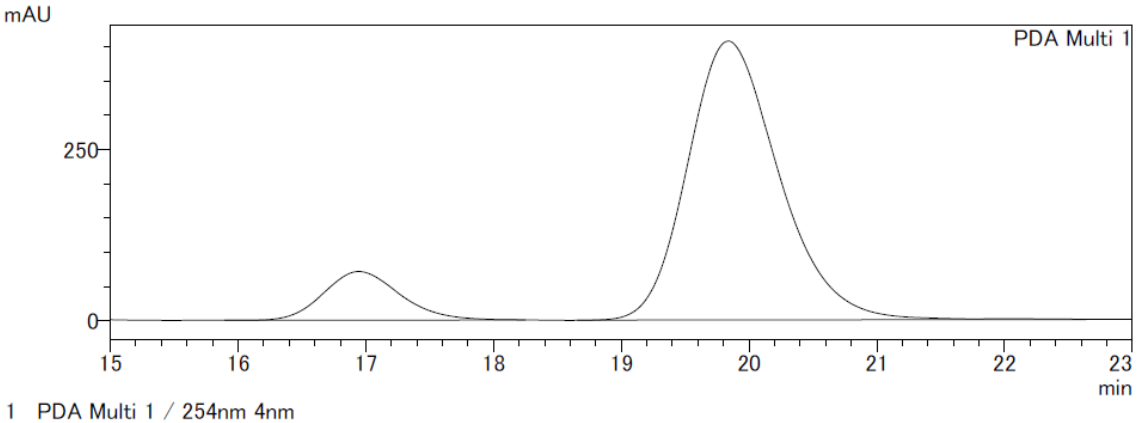


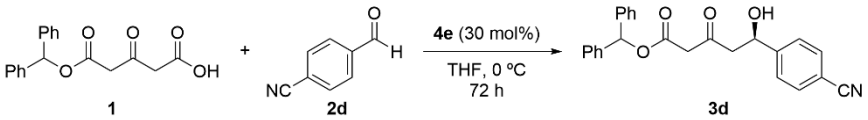
1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	16.942	2938566	12.673
2	19.832	20249691	87.327

Benzhydryl (*R*)-5-(4-cyanophenyl)-5-hydroxy-3-oxopentanoate (3d)



According to general procedure, carboxylic acid **1** (93.6 mg, 0.300 mmol, 3.0 equiv.) reacted with aldehyde **2d** (13.1 mg, 0.0999 mmol, 1.0 equiv.) and catalyst **4e** (9.7 mg, 0.0301 mmol, 30 mol%) in THF (1.0 mL) at 0 °C to afford **3d** (26.9 mg, 0.0673 mmol, 67% yield, 72% ee) as a white solid. The ee value of the product was determined by chiral HPLC analysis: CHIRALPAK IC, 1.0 mL/min, 15% 2-propanol/hexane. λ = 254 mm, $t_{R(ent\text{-}3d)}$ = 21.2 min, $t_{R(3d)}$ = 25.5 min.

^{1}H NMR (500 MHz, DMSO-d_6): δ 7.77 (2H, d, J = 8.0 Hz), 7.53 (2H, d, J = 8.0 Hz), 7.39–7.31 (8H, m), 7.30–7.26 (2H, m), 6.81 (1H, s), 5.75 (1H, d, J = 4.6 Hz), 5.11 (1H, q, J = 5.9 Hz), 3.86–3.76 (2H, m), 2.86–2.82 (2H, m).

^{13}C NMR (150 MHz, DMSO-d_6): δ 201.3, 166.2, 150.7, 140.2, 132.2, 128.51, 128.49, 127.84, 127.82, 126.8, 126.7, 126.6, 119.0, 109.7, 77.0, 67.8, 51.7, 49.4 (one aromatic carbon peak is missing due to overlapping).

HRMS (ESI+): *m/z* calculated for $C_{25}H_{21}NO_4Na$ $[M+Na]^+$: 422.1363, found: 422.1344.

IR (ATR): 3479.4, 3032.5, 2228.3, 1740.9, 1713.4 cm^{-1}

Optical Rotation: $[\alpha]^{23}_D$ +20.0 (c 1.26, $CHCl_3$)

Melting Point: 126.8−129.1 °C

Chiral HPLC Analysis for Adduct 3d

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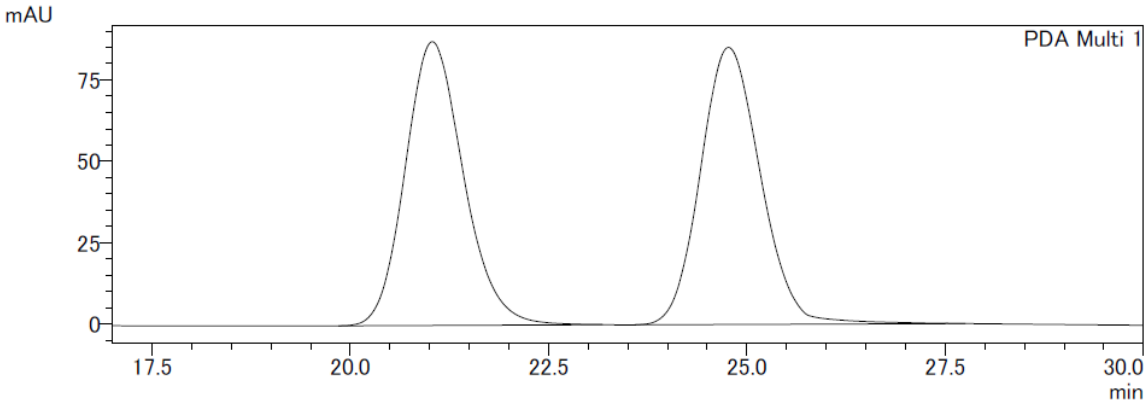

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak #	retention time (min)	area	area (%)
1	21.029	4456960	49.838
2	24.764	4486023	50.162

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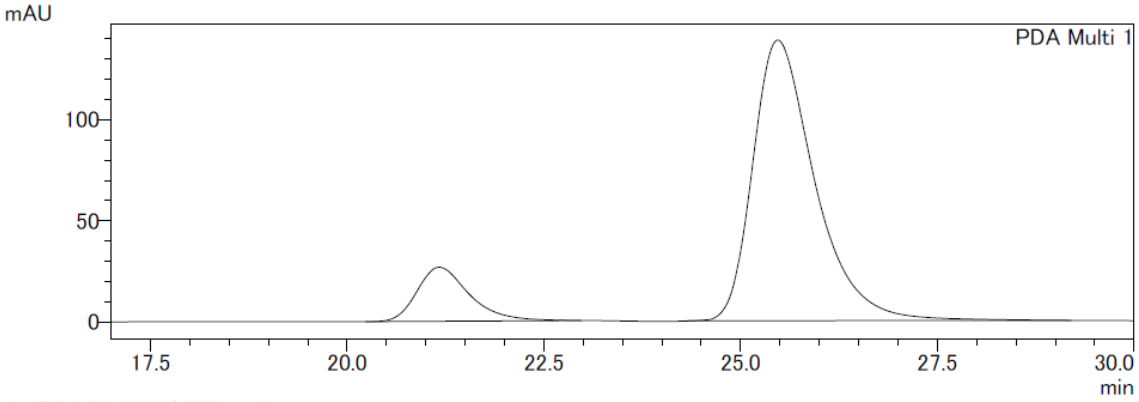


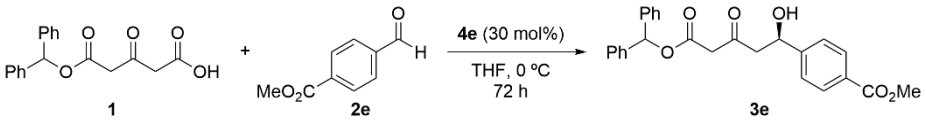
1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	21.170	1231951	13.962
2	25.467	7591778	86.038

Methyl (*R*)-4-(5-(benzhydryloxy)-1-hydroxy-3,5-dioxopentyl)benzoate (3e)



According to general procedure, carboxylic acid **1** (93.6 mg, 0.300 mmol, 3.0 equiv.) reacted with aldehyde **2e** (16.4 mg, 0.0999 mmol, 1.0 equiv.) and catalyst **4e** (9.7 mg, 0.0301 mmol, 30 mol%) in THF (1.0 mL) at 0 °C to afford **3e** (28.7 mg, 0.0663 mmol, 66% yield, 72% ee) as a colorless oil. The ee value of the product was determined by chiral HPLC analysis: CHIRALPAK IC, 1.0 mL/min, 20% 2-propanol/hexane. λ = 254 mm, $t_{R(ent\text{-}3e)}$ = 16.2 min, $t_{R(3e)}$ = 20.3 min.

^{1}H NMR (500 MHz, DMSO-d_6): δ 7.91 (2H, d, J = 8.0 Hz), 7.48 (2H, d, J = 8.6 Hz), 7.39–7.31 (8H, m), 7.30–7.25 (2H, m), 6.81 (1H, s), 5.69 (1H, d, J = 4.6 Hz), 5.13–5.07 (1H, m), 3.86–3.76 (5H, m), 2.90–2.79 (2H, m).

^{13}C NMR (150 MHz, DMSO-d_6): δ 201.5, 166.3, 166.1, 150.5, 140.3, 140.2, 129.1, 128.5, 128.3, 127.8, 126.64, 126.61, 126.1, 77.0, 68.0, 52.1, 51.9, 49.4 (two aromatic carbon peaks are missing due to overlapping).

HRMS (ESI−): *m/z* calculated for $C_{26}H_{23}O_6$ $[M-H]^-$: 431.1500, found: 431.1508.

IR (ATR): 3493.4, 3032.0, 2951.5, 1714.9 cm^{-1}

Optical Rotation: $[\alpha]^{22}_D$ +20.2 (c 1.08, $CHCl_3$)

Chiral HPLC Analysis for Adduct 3e

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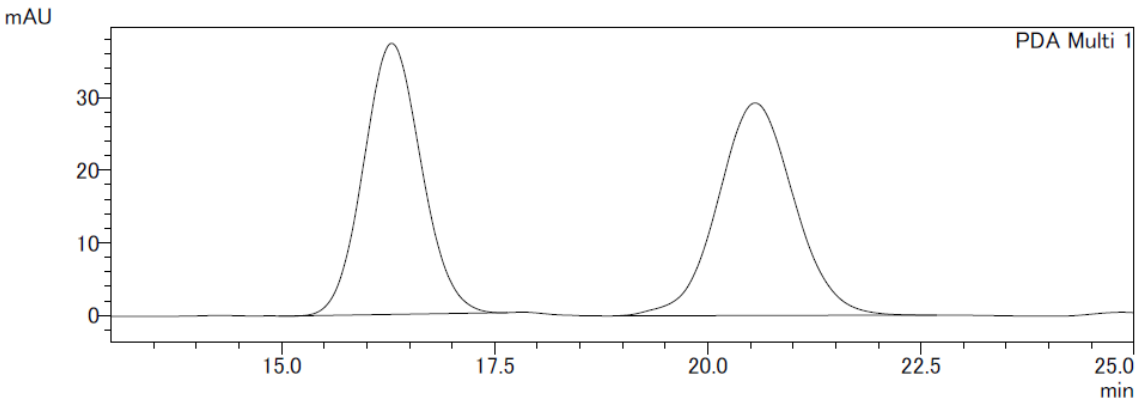

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	16.284	1764519	49.157
2	20.554	1825056	50.843

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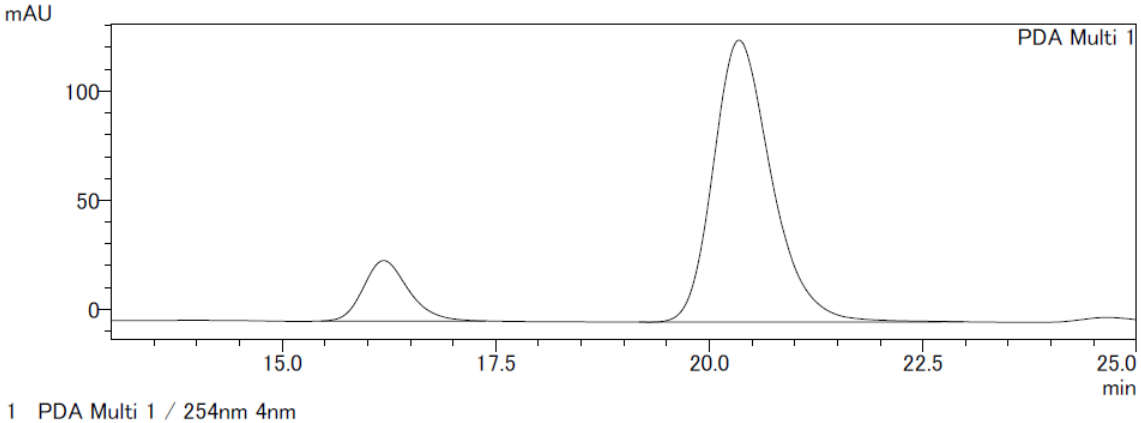


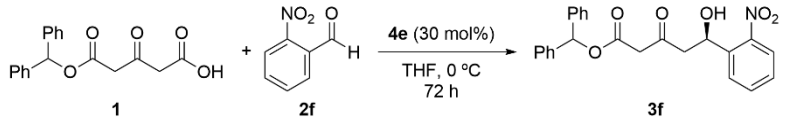
1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	16.181	1015331	14.225
2	20.345	6122567	85.775

Benzhydryl (*R*)-5-hydroxy-5-(2-nitrophenyl)-3-oxopentanoate (3f)



According to general procedure, carboxylic acid **1** (93.6 mg, 0.300 mmol, 3.0 equiv.) reacted with aldehyde **2f** (15.1 mg, 0.0999 mmol, 1.0 equiv.) and catalyst **4e** (9.7 mg, 0.0301 mmol, 30 mol%) in THF (1.0 mL) at 0 °C to afford **3f** 34.2 mg, 0.0815 mmol, 82% yield, 83% ee) as a colorless oil. The ee value of the product was determined by chiral HPLC analysis: CHIRALPAK IC, 1.0 mL/min, 20% 2-propanol/hexane. λ = 254 mm, $t_{R(ent\text{-}3f)}$ = 18.4 min, $t_{R(3f)}$ = 33.3 min.

^{1}H NMR (500 MHz, DMSO-d_6): δ 7.93 (1H, d, J = 8.0 Hz), 7.80 (1H, d, J = 8.0 Hz), 7.73 (1H, t, J = 7.4 Hz), 7.51 (1H, t, J = 7.7 Hz), 7.41–7.37 (4H, m), 7.37–7.31 (4H, m), 7.30-7.25 (2H, m), 6.83 (1H, s), 5.80 (1H, d, J = 4.6 Hz), 5.53–5.48 (1H, m), 3.87–3.77 (2H, m), 2.95–2.85 (2H, m).

^{13}C NMR (150 MHz, DMSO-d_6): δ 200.9, 166.2, 147.1, 140.24, 140.22, 140.0, 133.6, 128.5, 128.38, 128.36, 127.8, 126.64, 126.60, 124.0, 77.1, 63.9, 51.2, 49.4 (two aromatic carbon peaks are missing due to overlapping).

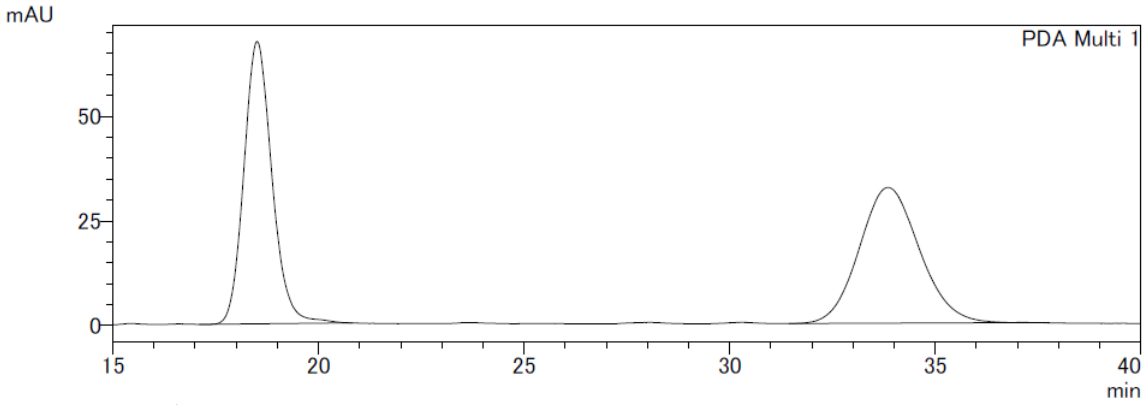
HRMS (ESI−): *m/z* calculated for $C_{24}H_{20}NO_6$ $[M-H]^-$: 418.1296, found: 418.1316.

IR (ATR): 3504.0, 2926.9, 1741.9, 1715.9, 1524.9 cm^{-1}

Optical Rotation: $[\alpha]^{23}_D$ −55.2 (c 1.47, $CHCl_3$)

Chiral HPLC Analysis for Adduct 3f

<Chromatogram>



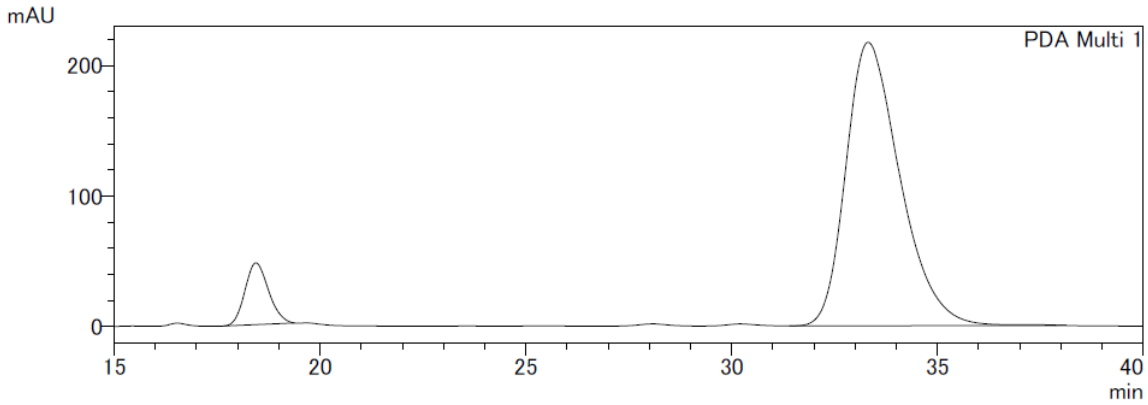
1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	18.503	3220257	49.372
2	33.844	3302154	50.628

<Chromatogram>



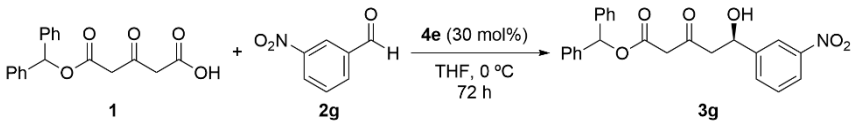
1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	18.439	1885822	8.655
2	33.311	19903845	91.345

Benzhydryl (*R*)-5-hydroxy-5-(3-nitrophenyl)-3-oxopentanoate (3g)



According to general procedure, carboxylic acid **1** (93.6 mg, 0.300 mmol, 3.0 equiv.) reacted with aldehyde **2g** (15.1 mg, 0.0999 mmol, 1.0 equiv.) and catalyst **4e** (9.7 mg, 0.0301 mmol, 30 mol%) in THF (1.0 mL) at 0 °C to afford **3g** (26.1 mg,

0.0622 mmol, 62% yield, 70% ee) as a colorless oil. The ee value of the product was determined by chiral HPLC analysis: CHIRALPAK IC, 1.0 mL/min, 15% ethanol/hexane. λ = 254 mm, $t_{R(ent\text{-}3g)}$ = 11.8 min, $t_{R(3g)}$ = 17.1 min.

^{1}H NMR (500 MHz, DMSO-d_6): δ 8.23 (1H, s), 8.10 (1H, dd, J = 8.0, 1.1 Hz), 7.79 (1H, d, J = 7.4 Hz), 7.61 (1H, t, J = 8.0 Hz), 7.39–7.30 (8H, m), 7.30–7.25 (2H, m), 6.81 (1H, s), 5.84 (1H, d, J = 4.6 Hz), 5.19 (1H, q, J = 5.9 Hz), 3.88–3.78 (2H, m), 2.90 (2H, d, J = 6.3 Hz).

^{13}C NMR (150 MHz, DMSO-d_6): δ 201.3, 166.2, 147.7, 147.4, 140.2, 132.6, 129.7, 128.5, 127.8, 126.62, 126.59, 122.0, 120.4, 77.0, 67.4, 51.8, 49.4 (three aromatic carbon peaks are missing due to overlapping).

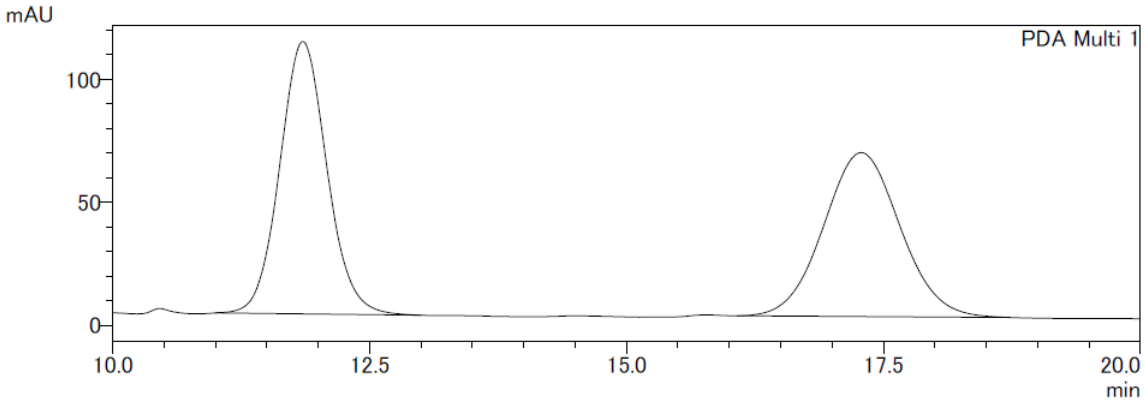
HRMS (ESI−): *m/z* calculated for $C_{24}H_{20}NO_6$ $[M-H]^-$: 318.1296, found: 418.1316.

IR (ATR): 3506.4, 3030.1, 2926.0, 1740.0, 1713.0, 1528.3 cm^{-1}

Optical Rotation: $[\alpha]^{23}_D$ +22.3 (c 1.47, $CHCl_3$)

Chiral HPLC Analysis for Adduct 3g

<Chromatogram>



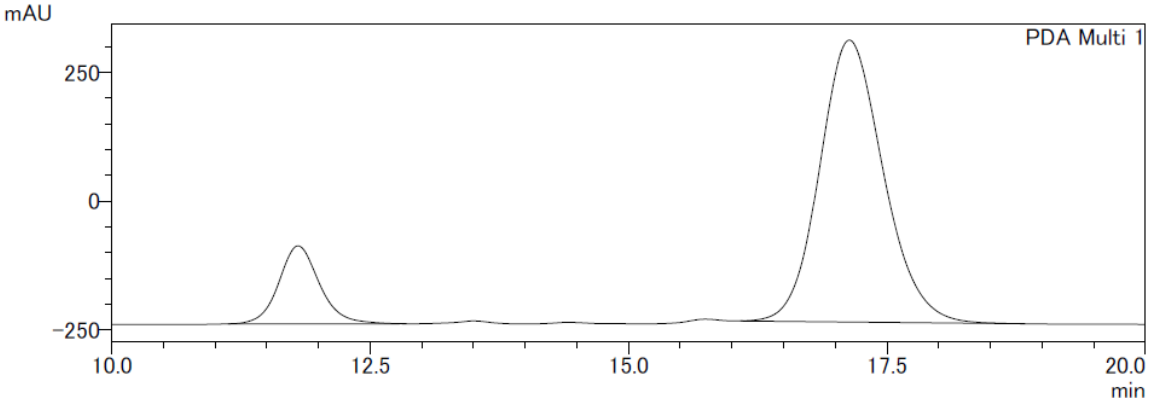
1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	11.845	3544291	50.580
2	17.279	3463067	49.420

<Chromatogram>



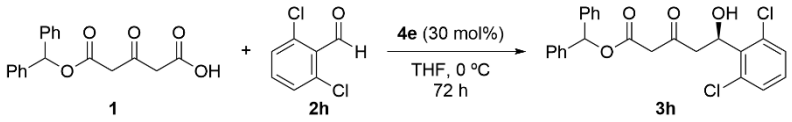
1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	11.798	4157532	15.028
2	17.131	23507746	84.972

Benzhydryl (*R*)-5-(2,6-dichlorophenyl)-5-hydroxy-3-oxopentanoate (3h)



According to general procedure, carboxylic acid **1** (93.6 mg, 0.300 mmol, 3.0 equiv.) reacted with aldehyde **2h** (17.5 mg, 0.0999 mmol, 1.0 equiv.) and catalyst **4e** (9.7 mg, 0.0301 mmol, 30 mol%) in THF (1.0 mL) at 0 °C to afford **3h** (26.2 mg, 0.0592 mmol, 59% yield, 62% ee) as a colorless oil. The ee value of the product was determined by chiral HPLC analysis: CHIRALPAK IC, 1.0 mL/min, 15% 2-propanol/hexane. λ = 254 mm, $t_{R(ent\text{-}3h)}$ = 14.8 min, $t_{R(3h)}$ = 17.6 min.

^{1}H NMR (500 MHz, DMSO-d_6): δ 7.43–7.20 (13H, m), 6.81 (1H, s), 5.83–5.79 (1H, m), 5.67 (1H, d, J = 4.6 Hz), 3.82 (2H, s), 3.47 (1H, dd, J = 16.9, 9.5 Hz), 2.80 (1H, d, J = 17.2 Hz).

^{13}C NMR (150 MHz, DMSO-d_6): δ 201.0, 166.2, 140.24, 140.22, 137.8, 134.0, 129.6, 129.49, 129.48, 127.8, 126.60, 126.57, 77.0, 65.1, 49.5, 47.3 (two aromatic carbon peaks are missing due to overlapping).

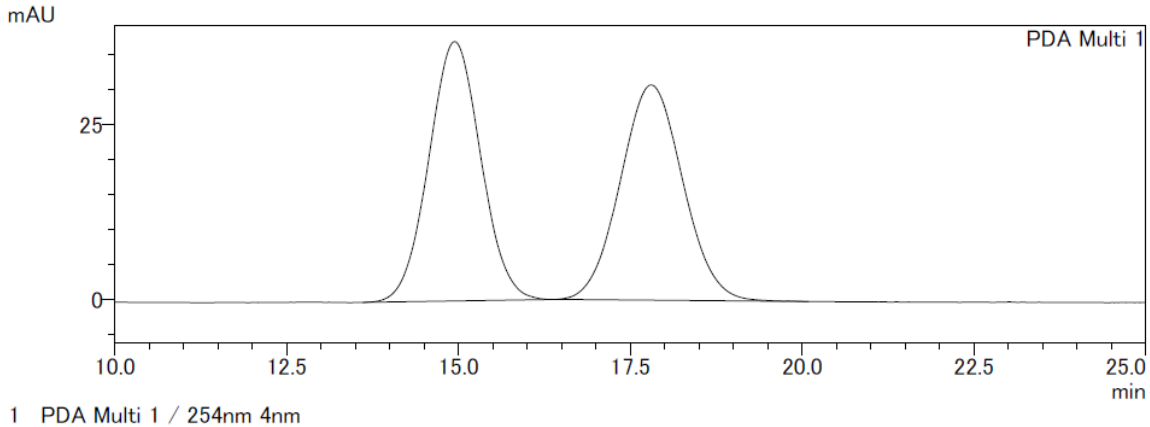
HRMS (ESI+): *m/z* calculated for $C_{24}H_{20}O_4Cl_2Na$ $[M+Na]^+$: 465.0631, found: 465.0621.

IR (ATR): 3459.2, 2927.4, 1743.3, 1718.3 cm^{-1}

Optical Rotation: $[\alpha]^{22}_D$ −9.14 (c 1.49, $CHCl_3$)

Chiral HPLC Analysis for Adduct 3h

<Chromatogram>



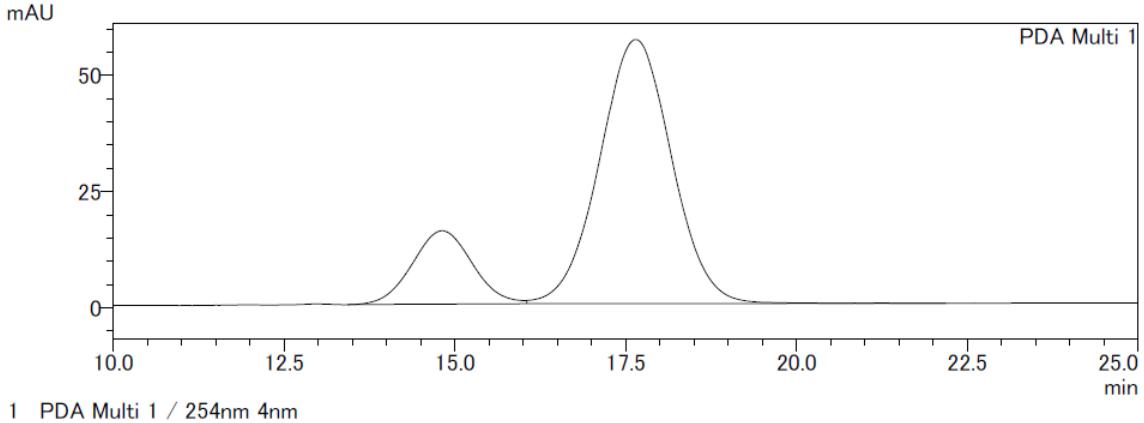
1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	14.941	1949665	50.053
2	17.797	1945565	49.947

<Chromatogram>



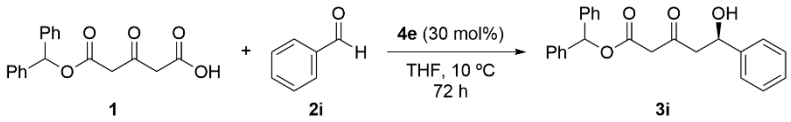
1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	14.805	964460	18.777
2	17.643	4172031	81.223

Benzhydryl (*R*)-5-hydroxy-3-oxo-5-phenylpentanoate (3i)



According to general procedure, carboxylic acid **1** (93.6 mg, 0.300 mmol, 3.0 equiv.) reacted with aldehyde **2i** (10.6 mg, 0.0999 mmol, 1.0 equiv.) and catalyst **4e** (9.7 mg, 0.0301 mmol, 30 mol%) in THF (1.0 mL) at 10 °C to afford **3i** (10.3 mg, 0.0275 mmol, 28% yield, 57% ee) as a colorless oil. The ee value of the product was determined by chiral HPLC analysis: CHIRALPAK IC, 1.0 mL/min, 15% 2-propanol/hexane. λ = 254 mm, $t_{R(ent\text{-}3i)}$ = 13.9 min, $t_{R(3i)}$ = 20.7 min.

^{1}H NMR (500 MHz, DMSO-d_6): δ 7.40–7.21 (15H, m), 6.82 (1H, s), 5.51 (1H, d, J = 4.6 Hz), 5.05–5.00 (1H, m), 3.86–3.75 (2H, m), 2.88–2.75 (2H, m).

^{13}C NMR (150 MHz, DMSO-d_6): δ 201.8, 166.3, 145.0, 140.3, 129.3, 128.6, 128.5, 128.1, 127.8, 127.0, 126.64, 126.61, 125.7, 77.0, 68.5, 52.3, 49.5 (one aromatic carbon peak is missing due to overlapping).

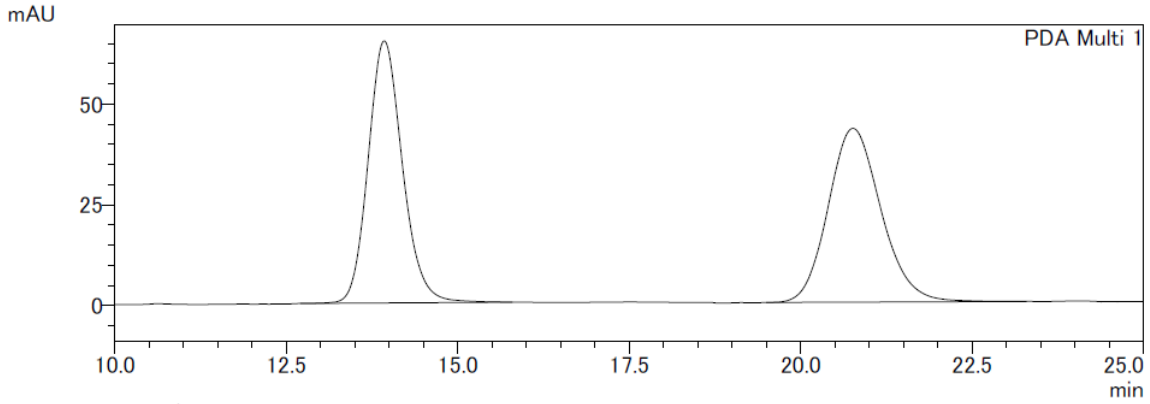
HRMS (ESI+): *m/z* calculated for $C_{24}H_{22}O_4Na$ $[M+Na]^+$: 397.1410, found: 397.1401.

IR (ATR): 3492.9, 2926.5, 1740.9, 1713.0 cm^{-1}

Optical Rotation: $[\alpha]^{21}_D$ +19.2 (c 0.97, $CHCl_3$)

Chiral HPLC Analysis for Adduct 3i

<Chromatogram>



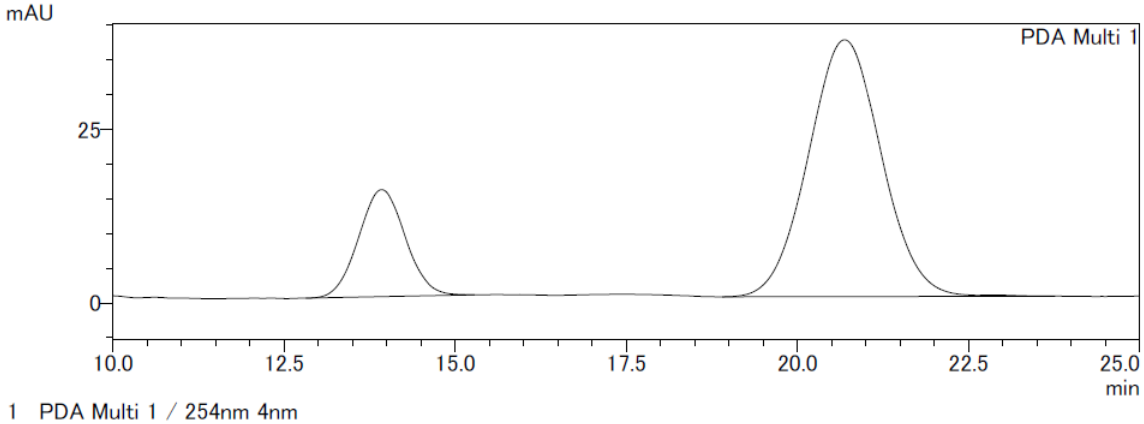
1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	13.925	2268930	49.531
2	20.755	2311909	50.469

<Chromatogram>



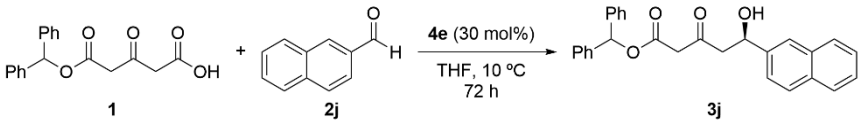
1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	13.923	731360	21.020
2	20.682	2747918	78.980

Benzhydryl (*R*)-5-hydroxy-5-(naphthalen-2-yl)-3-oxopentanoate (3j)



According to general procedure, carboxylic acid **1** (93.6 mg, 0.300 mmol, 3.0 equiv.) reacted with aldehyde **2j** (15.6 mg, 0.0999 mmol, 1.0 equiv.) and catalyst **4e** (9.7 mg, 0.0301 mmol, 30 mol%) in THF (1.0 mL) at 10 °C to afford **3i** (12.9 mg, 0.0304 mmol, 30% yield, 56% ee) as a colorless oil. The ee value of the product was determined by chiral HPLC analysis: CHIRALPAK IC, 1.0 mL/min, 15% 2-propanol/hexane. λ = 254 mm, $t_{R(ent\text{-}3j)}$ = 16.9 min, $t_{R(3j)}$ = 21.7 min.

^{1}H NMR (500 MHz, DMSO-d_6): δ 7.90–7.84 (4H, m), 7.52–7.45 (3H, m), 7.39–7.25 (10H, m), 6.82 (1H, s), 5.67 (1H, d, J = 4.0 Hz), 5.23–5.18 (1H, m), 3.89–3.79 (2H, m), 2.98–2.87 (2H, m).

^{13}C NMR (150 MHz, DMSO-d_6): δ 201.7, 166.3, 142.5, 140.3, 140.2, 132.8, 132.3, 128.5, 127.80, 127.78, 127.75, 127.5,

126.63, 126.60, 126.1, 125.7, 124.4, 124.0, 77.0, 68.6, 52.2, 49.5 (two aromatic carbon peaks are missing due to overlapping).

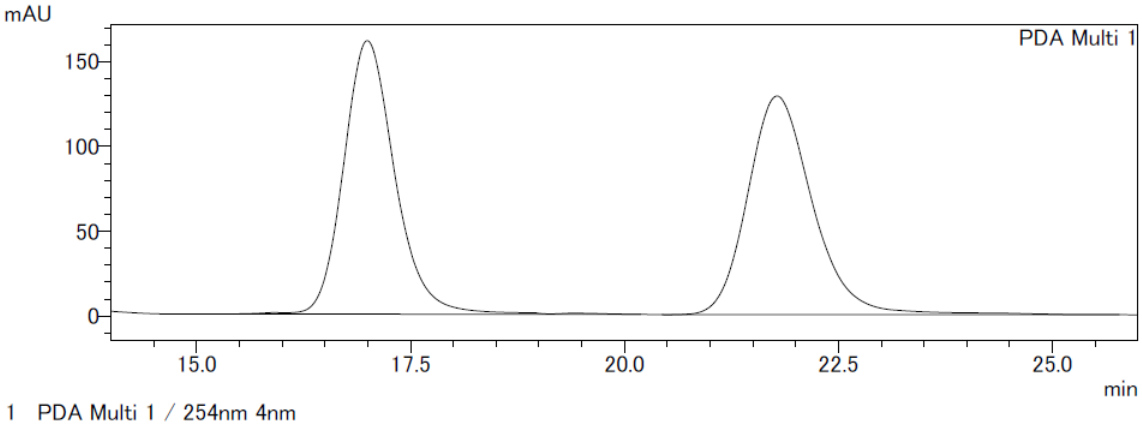
HRMS (ESI+): *m/z* calculated for $C_{28}H_{24}O_4Na$ $[M+Na]^+$: 447.1567, found: 447.1545.

IR (ATR): 3456.8, 2926.9, 1740.0, 1712.5 cm^{-1}

Optical Rotation: $[\alpha]^{24}_D$ +16.4 (c 1.26, $CHCl_3$)

Chiral HPLC Analysis for Adduct 3j

<Chromatogram>



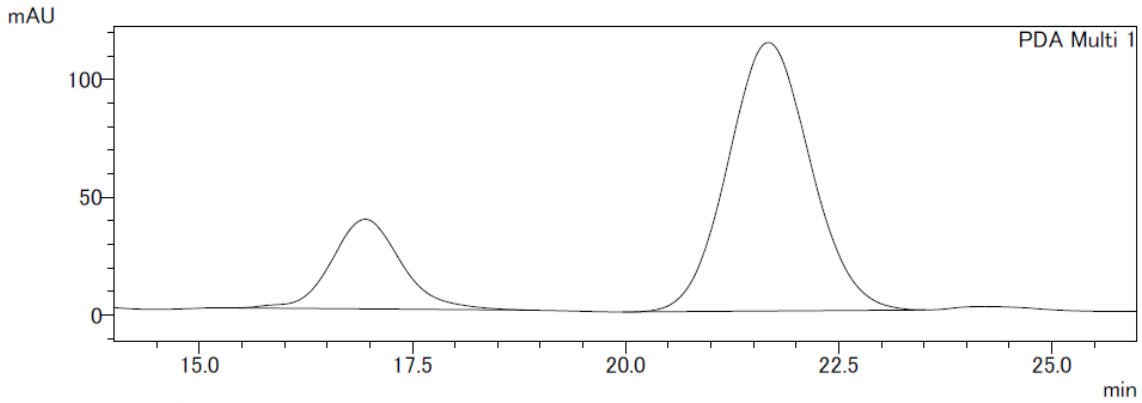
1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	16.990	6763850	49.806
2	21.778	6816559	50.194

<Chromatogram>



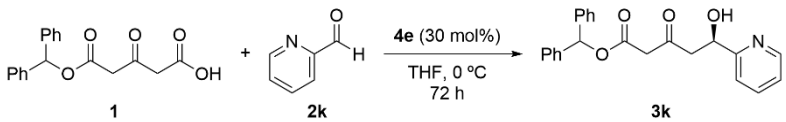
1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	16.940	2172662	22.038
2	21.670	7686107	77.962

Benzhydryl (*R*)-5-hydroxy-3-oxo-5-(pyridin-2-yl)pentanoate (3k)



According to general procedure, carboxylic acid **1** (93.6 mg, 0.300 mmol, 3.0 equiv.) reacted with aldehyde **2k** (10.7mg, 0.0999 mmol, 1.0 equiv.) and catalyst **4e** (9.7 mg, 0.0301 mmol, 30 mol%) in THF (1.0 mL) at 0 °C to afford **3k** (17.3 mg, 0.0461 mmol, 46% yield, 68% ee) as a colorless oil. The ee value of the product was determined by chiral HPLC analysis:

CHIRALPAK IC, 1.0 mL/min, 20% 2-propanol/hexane. λ = 254 mm, $t_{R(ent\text{-}3k)}$ = 21.1 min, $t_{R(3k)}$ = 27.6 min.

^{1}H NMR (500 MHz, DMSO-d_6): δ 8.46 (1H, d, J = 4.6 Hz), 7.78 (1H, td, J = 7.7, 1.5 Hz), 7.50 (1H, d, J = 7.4 Hz), 7.43–7.19 (11H, m), 6.82 (1H, s), 5.72 (1H, d, J = 5.7 Hz), 5.08–5.03 (1H, m), 3.83 (2H, s), 3.03 (1H, dd, J = 15.8, 4.3 Hz), 2.84 (1H, dd, J = 16.0, 8.6 Hz).

^{13}C NMR (150 MHz, DMSO-d_6): δ 201.8, 166.3, 163.2, 148.3, 140.3, 136.8, 128.5, 127.8, 126.62, 126.60, 122.24, 120.20, 77.0, 69.5, 50.3, 49.6 (three aromatic carbon peaks are missing due to overlapping).

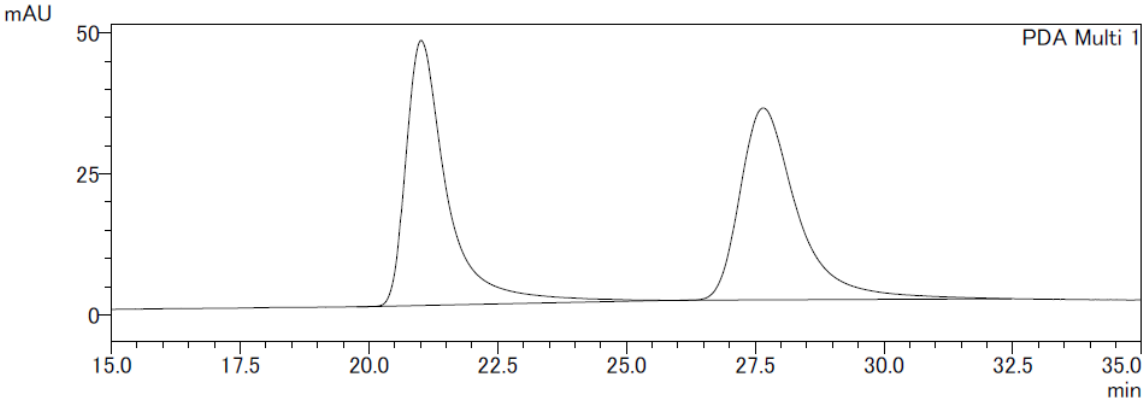
HRMS (ESI−): *m/z* calculated for $C_{23}H_{20}NO_4$ $[M-H]^-$: 374.1398, found: 374.1387.

IR (ATR): 3431.7, 3062.4, 1741.4, 1713.4 cm^{-1}

Optical Rotation: $[\alpha]^{25}_D$ +25.0 (c 1.23, $CHCl_3$)

Chiral HPLC Analysis for Adduct 3k

<Chromatogram>



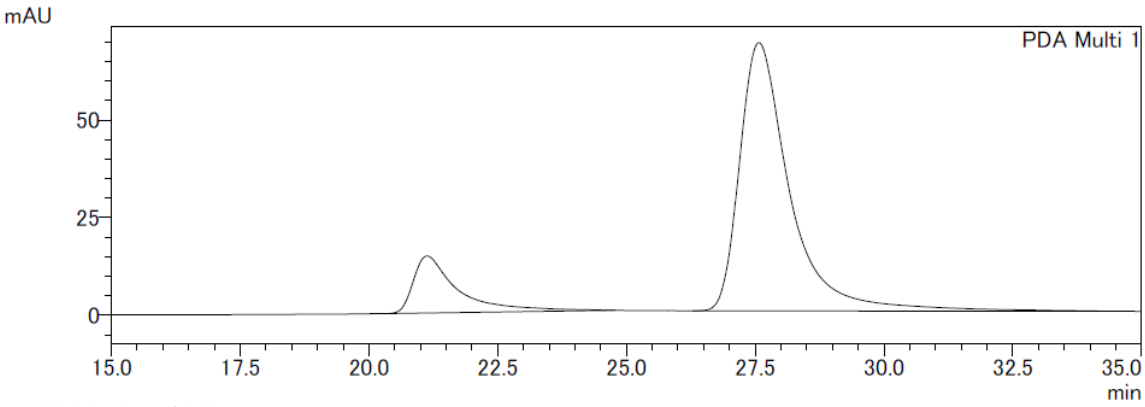
1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	21.012	2627571	49.818
2	27.653	2646777	50.182

<Chromatogram>



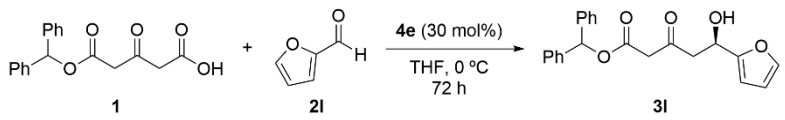
1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	21.125	877625	15.837
2	27.566	4663965	84.163

Benzhydryl (*R*)-5-(furan-2-yl)-5-hydroxy-3-oxopentanoate (3l)



According to general procedure, carboxylic acid **1** (93.6 mg, 0.300 mmol, 3.0 equiv.) reacted with aldehyde **2l** (9.6 mg, 0.0999 mmol, 1.0 equiv.) and catalyst **4e** (9.7 mg, 0.0301 mmol, 30 mol%) in THF (1.0 mL) at 0 °C to afford **3l** (16.1 mg, 0.0442 mmol, 44% yield, 66% ee) as a colorless oil. The ee value of the product was determined by chiral HPLC analysis: CHIRALPAK IC, 1.0 mL/min, 15% 2-propanol/hexane. λ = 254 mm, $t_{R(ent\text{-}3l)}$ = 18.1 min, $t_{R(3l)}$ = 23.5 min.

^{1}H NMR (500 MHz, DMSO-d_6): δ 7.56 (1H, s), 7.39–7.31 (8H, m), 7.30–7.25 (2H, m), 6.81 (1H, s), 6.36 (1H, s), 6.24 (1H, d, J = 2.3 Hz), 5.58 (1H, d, J = 5.7 Hz), 5.00–4.96 (1H, m), 3.81 (2H, s), 3.00–2.90 (2H, m).

^{13}C NMR (150 MHz, DMSO-d_6): δ 201.3, 166.2, 156.7, 142.0, 140.2, 128.5, 127.81, 127.80, 126.62, 126.60, 110.2, 105.6, 77.0, 61.9, 49.3, 48.6 (two aromatic carbon peaks are missing due to overlapping).

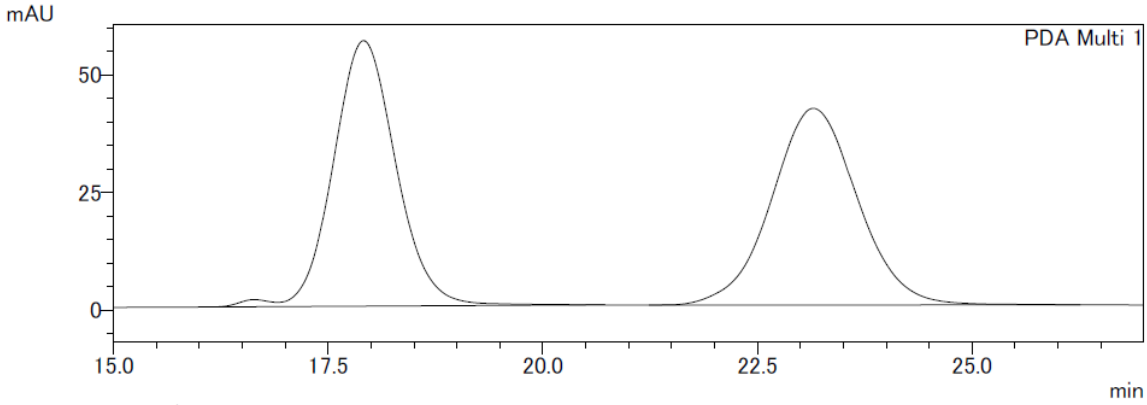
HRMS (ESI−): *m/z* calculated for $C_{22}H_{19}O_5$ $[M-H]^-$: 363.1238, found: 363.1244.

IR (ATR): 3465.0, 2928.4, 1741.9, 1716.3 cm^{-1}

Optical Rotation: $[\alpha]^{25}_D$ +12.8 (c 1.19, $CHCl_3$)

Chiral HPLC Analysis for Adduct 3l

<Chromatogram>



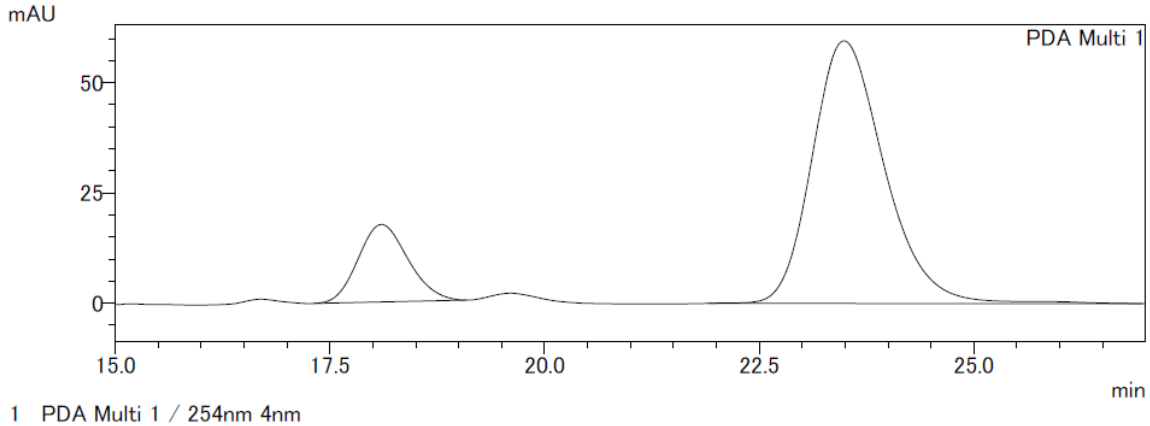
1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	17.910	2890977	49.752
2	23.158	2919779	50.248

<Chromatogram>



1 PDA Multi 1 / 254nm 4nm

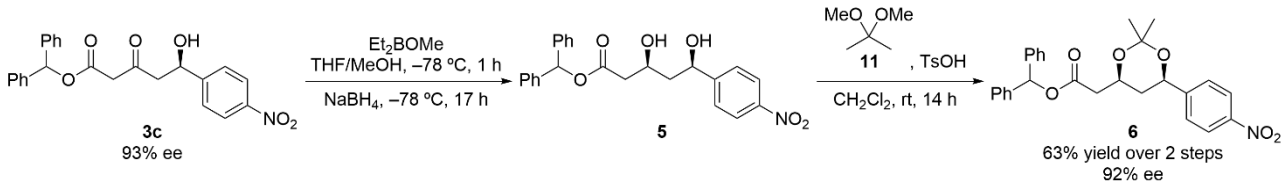
<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	18.095	708663	16.865
2	23.488	3493327	83.135

4. Derivatization of the Aldol Adduct

***Syn*-Selective Reduction**



A 20 mL round bottom flask was charged with a stir bar, recrystallized adduct **3c** (83.9 mg, 0.200 mmol, 1.0 equiv.), THF (0.95 mL), and MeOH (0.24 mL) under Ar atmosphere, before the mixture was cooled to −78 °C. To the mixture was added 1M diethylmethoxyborane solution in THF (0.220 mL, 0.220 mmol, 1.1 equiv.), and the mixture was stirred at −78 °C for 1 h. To the mixture was added sodium borohydride (8.3 mg, 0.219 mmol, 1.1 equiv.), and the mixture was stirred at −78 °C for 17 h. Then the mixture was allowed to warm to room temperature, quenched with saturated aqueous NH_4Cl solution (5.0 mL), extracted with EtOAc (5.0 mL x3). The combined organic layers were washed with brine (5.0 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the crude of diol **5**. Diol **5** was used for the next reaction without further purification.

A 20 mL round bottom flask was charged with a stir bar, the crude of diol **4**, and CH_2Cl_2 (2.0 mL) under Ar atmosphere. To the mixture were added 2,2-dimethoxypropane **11** (0.368 mL, 3.00 mmol, 15 equiv.), *p*-toluenesulfonic acid monohydrate (3.8 mg, 0.0200 mmol, 10 mol%), and the mixture was stirred at room temperature for 14 h. Then the mixture was quenched with solid $NaHCO_3$, and filtered through Celite pad. The filtrate was concentrated under reduced pressure, and the residue was purified using column chromatography on silica bel eluted by hexane/EtOAc (10:1) to afford acetonide **6** (58.5 mg, 0.127 mmol, 63% yield over two steps, 92% ee) as a white solid. The ee value of the product was determined by chiral HPLC analysis: CHIRALPAK IC, 1.0 mL/min, 5% 2-propanol/hexane. λ = 254 mm, $t_{R(\textit{ent}\text{-}6)}$ = 17.3 min, $t_{R(6)}$ = 18.7 min.

Benzhydryl 2-((4*S*,6*R*)-2,2-dimethyl-6-(4-nitrophenyl)-1,3-dioxan-4-yl)acetate (6)

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (2H, d, J = 8.6 Hz), 7.49 (2H, d, J = 8.6 Hz), 7.38–7.26 (10H, m), 6.92 (1H, s), 5.01

(1H, dd, J = 12.0, 2.3 Hz), 4.55–4.49 (1H, m), 2.70 (1H, dd, J = 14.9, 7.4 Hz), 2.54 (1H, dd, J = 15.5, 5.7 Hz), 1.81 (1H, dt, J = 12.8, 2.4 Hz), 1.52 (3H, s), 1.50 (3H, s), 1.41 (1H, q, J = 12.0 Hz).

^{13}C NMR (150 MHz, $CDCl_3$): δ 169.7, 149.3, 147.2, 139.9, 139.8, 128.45, 128.43, 128.0, 127.9, 127.2, 127.0, 126.4, 123.6, 99.5, 77.2, 70.3, 66.0, 41.4, 38.4, 29.9, 19.6.

HRMS (ESI+): *m/z* calculated for $C_{27}H_{27}NO_6Na$ $[M+Na]^+$: 484.1731, found: 484.1716.

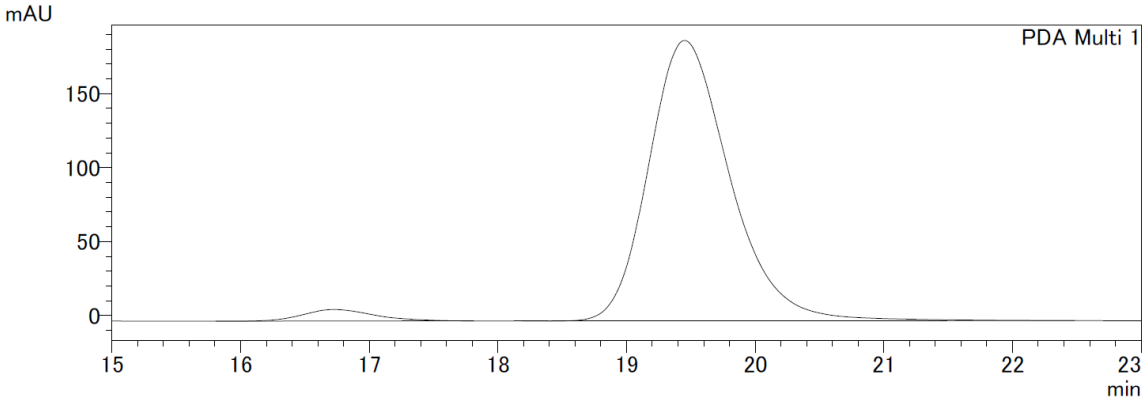
IR (ATR): 2993.9, 1736.1, 1520.1 cm^{-1}

Optical Rotation: $[\alpha]^{17}_D$ +27.9 (c 1.23, $CHCl_3$)

Melting Point: 76.7−79.6 °C

Chiral HPLC Analysis for Recrystalized Adduct 3c

<Chromatogram>



1 PDA Multi 1 / 254nm 4nm

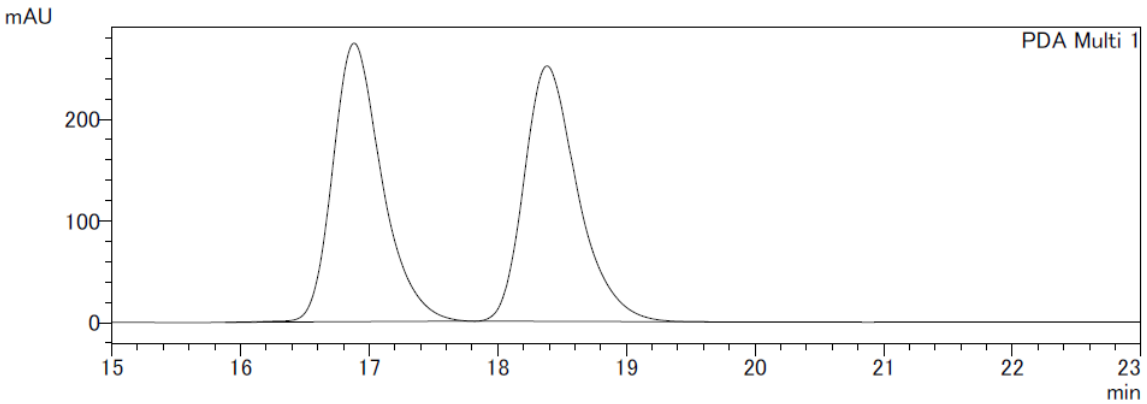
<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	16.723	296238	3.443
2	19.445	8307191	96.557

Chiral HPLC Analysis for Acetonide 6

<Chromatogram>



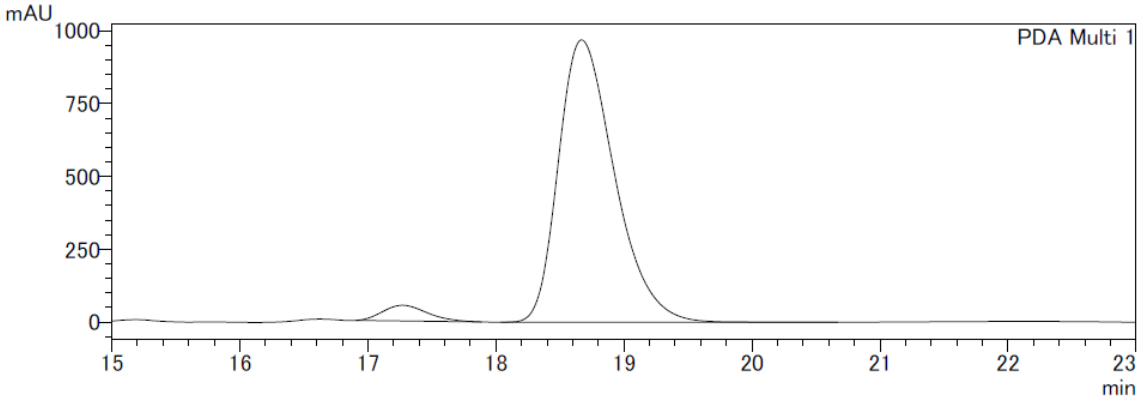
1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	16.878	7293057	50.065
2	18.378	7274199	49.935

<Chromatogram>



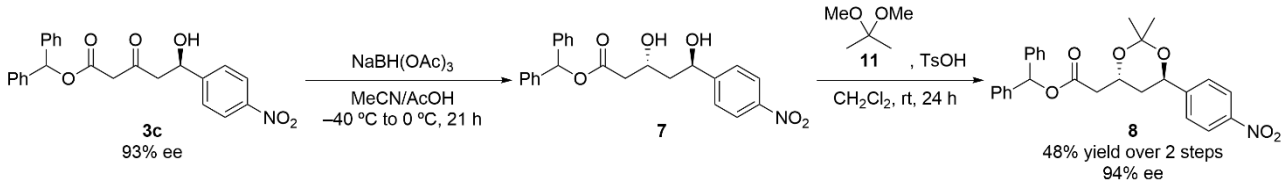
1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	17.265	1299401	4.225
2	18.664	29458932	95.775

***Anti*-Selective Reduction**



A 20 mL round bottom flask was charged with a stir bar, recrystallized adduct **3c** (41.9 mg, 0.0999 mmol, 1.0 equiv.), MeCN (0.25 mL), and AcOH (0.25 mL) under Ar atmosphere, and the mixture was cooled to −40 °C. To the mixture were added sodium triacetoxyborohydride (106.0 mg, 0.500 mmol, 5.0 equiv.) and MeCN(0.50 mL), and the mixture was stirred at 0 °C for 21 h. Then the mixture was quenched with saturated aqueous $NaHCO_3$ solution (5.0 mL), and extracted with EtOAc (5.0 mL x3). The combined organic layers were washed with brine (5.0 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the crude of diol **7**. Diol **7** was used for the next reaction without further purification.

A 20 mL round bottom flask was charged with a stir bar, the crude of diol **7**, and CH_2Cl_2 (1.0 mL) under Ar atmosphere. To the mixture were added 2,2-dimethoxypropane **11** (0.184 mL, 1.50 mmol, 15 equiv.), *p*-toluenesulfonic acid monohydrate (1.9 mg, 0.00999 mmol, 10 mol%), and the mixture was stirred at room temperature for 24 h. Then the mixture was quenched with solid $NaHCO_3$, and filtered through Celite pad. The filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC eluted by hexane/EtOAc (9:1) to afford acetonide **8** (22.2 mg, 0.0481 mmol, 48% yield over two steps, 94% ee) as a colorless oil. The ee value of the product was determined by chiral HPLC analysis: CHIRALPAK IA, 1.0 mL/min, 1% 2-propanol/hexane. λ = 254 mm, $t_{R(\textit{ent}\text{-}\mathbf{8})}$ = 45.6 min, $t_{R(\mathbf{8})}$ = 47.6 min.

Benzhydryl 2-((4*R*,6*R*)-2,2-dimethyl-6-(4-nitrophenyl)-1,3-dioxan-4-yl)acetate (8)

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (2H, d, J = 8.6 Hz), 7.48 (2H, d, J = 9.2 Hz), 7.39–7.26 (10H, m), 6.93 (1H, s), 4.96 (1H, dd, J = 9.7, 6.3 Hz), 4.47–4.40 (1H, m), 2.75 (1H, dd, J = 15.5, 8.0 Hz), 2.63 (1H, dd, J = 15.5, 5.2 Hz), 2.08–2.01 (1H, m), 1.98–1.90 (1H, m), 1.42 (3H, s), 1.37 (3H, s).

^{13}C NMR (150 MHz, $CDCl_3$): δ 169.8, 149.7, 147.1, 139.9, 128.5, 128.4, 128.0, 127.9, 127.3, 127.0,126.4, 123.7, 101.4, 77.2, 67.5, 63.6, 40.9, 39.2, 24.9, 24.4 (one aromatic carbon peak is missing due to overlapping).

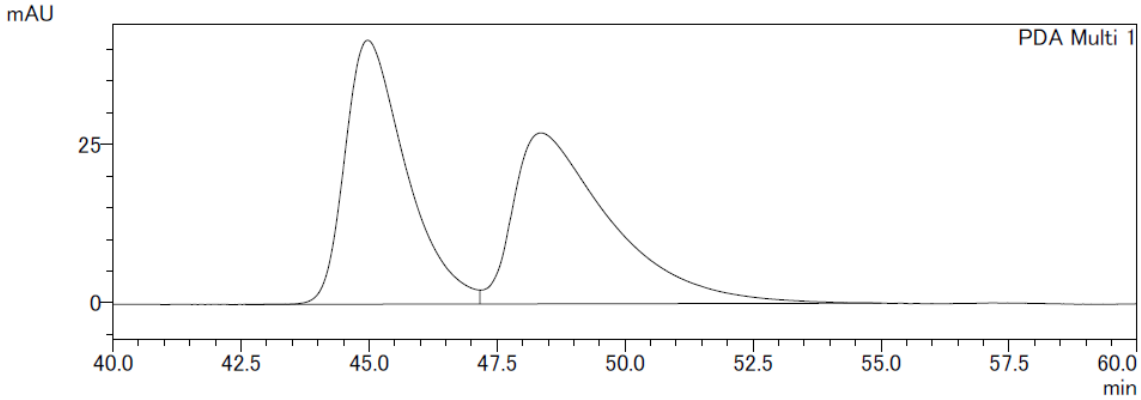
HRMS (ESI+): *m/z* calculated for $C_{27}H_{27}NO_6Na$ $[M+Na]^+$: 484.1731, found: 484.1715.

IR (ATR): 2933.2, 1735.6, 1519.6 cm^{-1}

Optical Rotation: $[\alpha]^{19}_D$ +42.8 (c 1.12, $CHCl_3$)

Chiral HPLC Analysis for Acetonide 8

<Chromatogram>



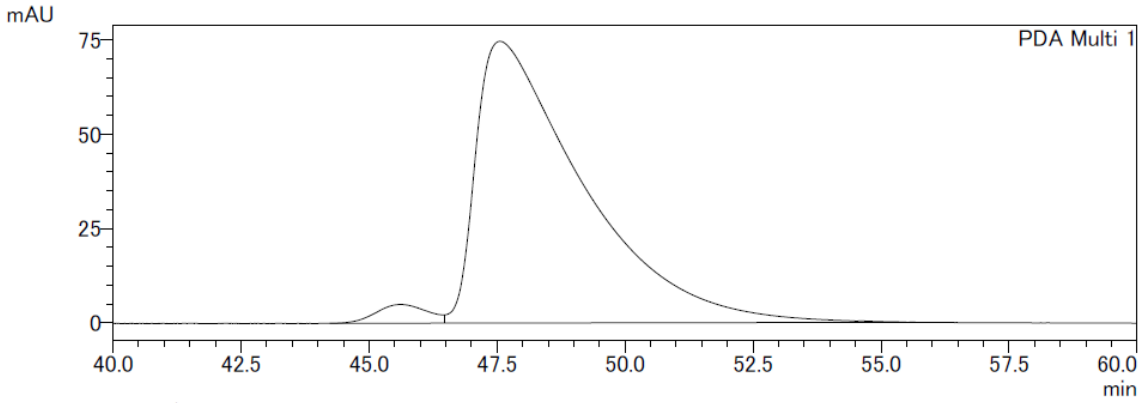
1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	44.968	3474876	49.293
2	48.363	3574519	50.707

<Chromatogram>



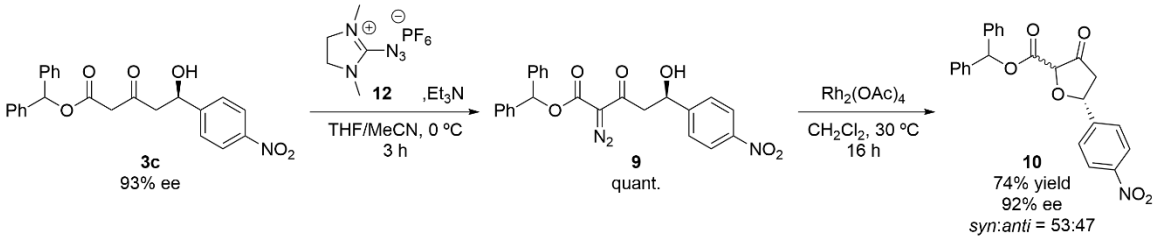
1 PDA Multi 1 / 254nm 4nm

<Peak Report>

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	45.610	351182	3.118
2	47.550	10911024	96.882

Intramolecular O-H Bond Insertion



A 10 mL round bottom flask was charged with a stir bar, 2-azide-1,3-dimethylimidazolinium hexafluorophosphate **12**[2] (34.2 mg, 0.120 mmol, 1.2 equiv.), THF (0.80 mL), and MeCN (0.20 mL) under Ar atmosphere, and the mixture was cooled to 0 °C. To the mixture were added recrystallized adduct **3c** (41.9 mg, 0.0999 mmol, 1.0 equiv.) and triethylamine (0.0278 mL, 0.200 mmol, 2.0 equiv.), and the mixture was stirred at 0 °C for 3 h. Then the mixture was diluted with CH_2Cl_2 (5.0 mL) and washed with water (5.0 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified using column chromatography on silica gel eluted by hexane/EtOAc (3:1) to afford diazo adduct **9** (49.7 mg, quant.) as a yellow oil. Diazo adduct **9** was used for the next reaction without further purification.

A 10 mL round bottom flask was charged with a stir bar, diazo adduct **9**, and CH_2Cl_2 (2.0 mL) under Ar atmosphere. To the mixture was added rhodium acetate dimer (1.1 mg, 0.00249 mmol, 2.5 mol%), and the mixture was backdrafted with Ar and stirred at 30 °C for 16 h. Then the mixture was concentrated under reduced pressure, and the residue was purified using column chromatography on silica gel eluted by hexane/EtOAc (85:15) to afford dihydro-3-furanone **10** (31.0 mg, 0.0743 mmol, 74% yield, 92% ee, *syn*:*anti* = 53:47). The ee value of the product was determined by chiral HPLC analysis: CHIRALPAK IC, 1.0 mL/min, 5% 2-propanol/hexane. λ = 254 mm, $t_{R(ent\text{-}9)}$ = 61.0 min, $t_{R(9)}$ = 77.3 min. We could not separate diastereomers on chiral HPLC analysis condition due to isomerization at active methyne carbon center, so the diastereomeric ratio was determined by ^{1}H NMR, and peaks of *syn* isomer were determined by NOESY.

Benzhydryl (5*R*)-5-(4-nitrophenyl)-3-oxotetrahydrofuran-2-carboxylate (10)

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (1.06H, d, J = 8.6 Hz), 8.21 (0.94H, d, J = 8.6 Hz), 7.69 (1.06H, d, J = 8.6 Hz), 7.57 (0.94H, d, J = 8.0 Hz), 7.40–7.29 (10H, m), 6.96 (1H, s), 5.75 (0.47H, dd, J = 10.0, 6.6 Hz), 5.43 (0.53H, dd, J = 10.6, 6.6 Hz), 4.94 (0.47H, s), 4.76 (0.53H, s), 3.06–2.96 (1H, m), 2.59–2.49 (1H, m).

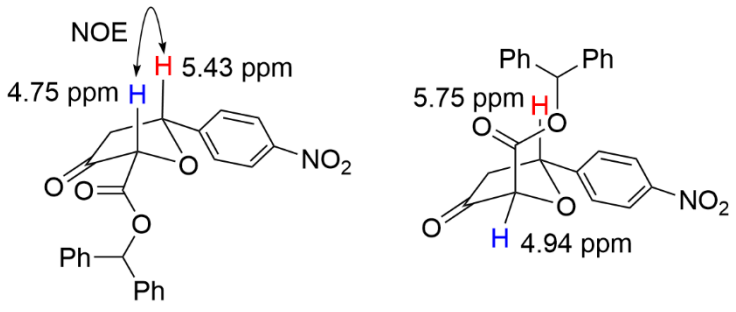
^{13}C NMR (150 MHz, $CDCl_3$): δ 205.2, 204.9, 165.2, 164.5, 147.9, 147.8, 147.0, 146.7, 139.09, 139.07, 139.0, 128.7, 128.62, 128.59, 128.47, 128.46, 128.2, 128.1, 127.51, 127.45, 126.9, 126.8, 126.63, 126.56, 124.0, 80.6, 80.3, 79.1, 79.0, 78.0, 77.2, 44.1, 43.7 (three aromatic carbon peaks are missing due to overlapping).

HRMS (ESI+): *m/z* calculated for $C_{24}H_{18}NO_6$ $[M-H]^-$: 416.1140, found: 416.1157.

IR (ATR): 3032.0, 2924.0, 1771.8, 1742.4, 1520.1 cm^{-1}

Optical Rotation: $[\alpha]^{20}_D$ +59.2 (c 1.46, $CHCl_3$)

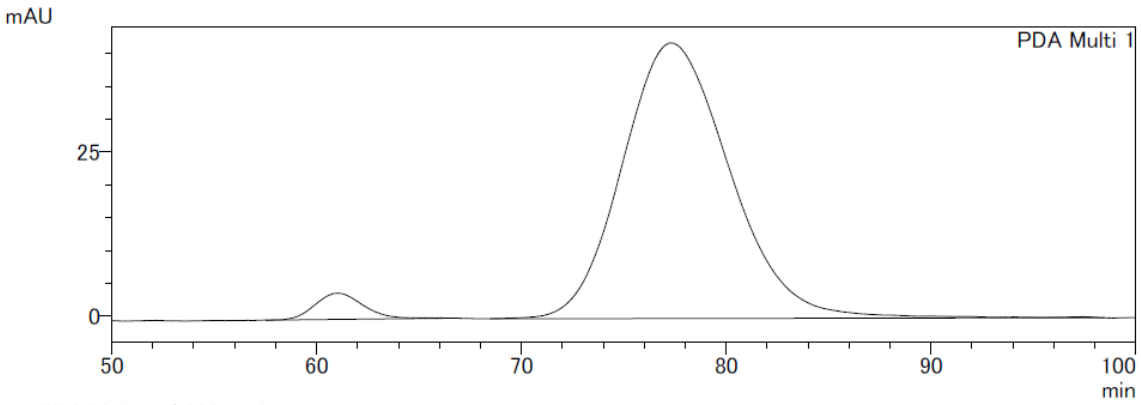
Determination of Relative Configuration by NOESY



syn isomer *anti* isomer

Chiral HPLC Analysis for Dihydro-3-furanone 10

<Chromatogram>



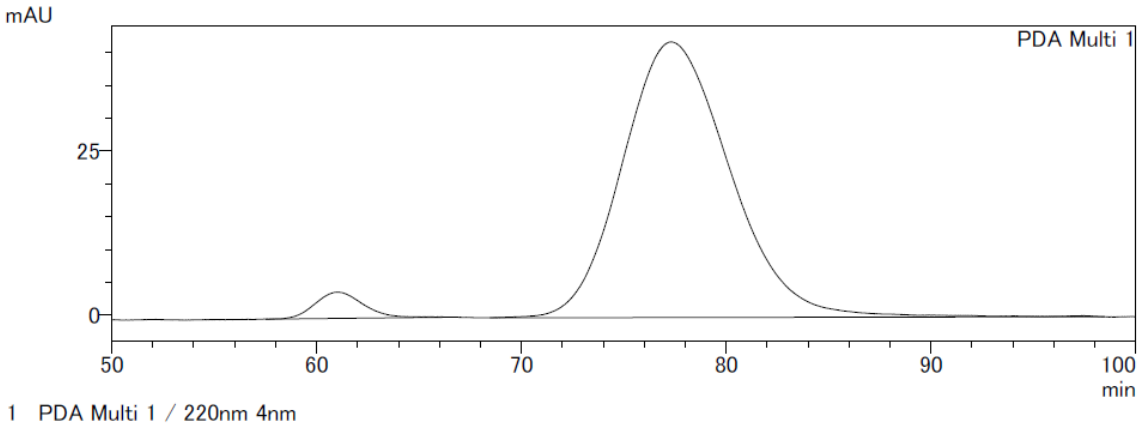
1 PDA Multi 1 / 220nm 4nm

<Peak Report>

PDA Ch1 220nm 4nm

peak#	retention time (min)	area	area (%)
1	60.990	654961	4.092
2	77.293	15352410	95.908

<Chromatogram>



1 PDA Multi 1 / 220nm 4nm

<Peak Report>

PDA Ch1 220nm 4nm

peak#	retention time (min)	area	area (%)
1	60.990	654961	4.092
2	77.293	15352410	95.908

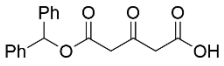
5. References

1) A. K. Kiang, S. F. Tan, and W. S. Wong, *J. Chem. Soc. C.*, 1971, 2721.

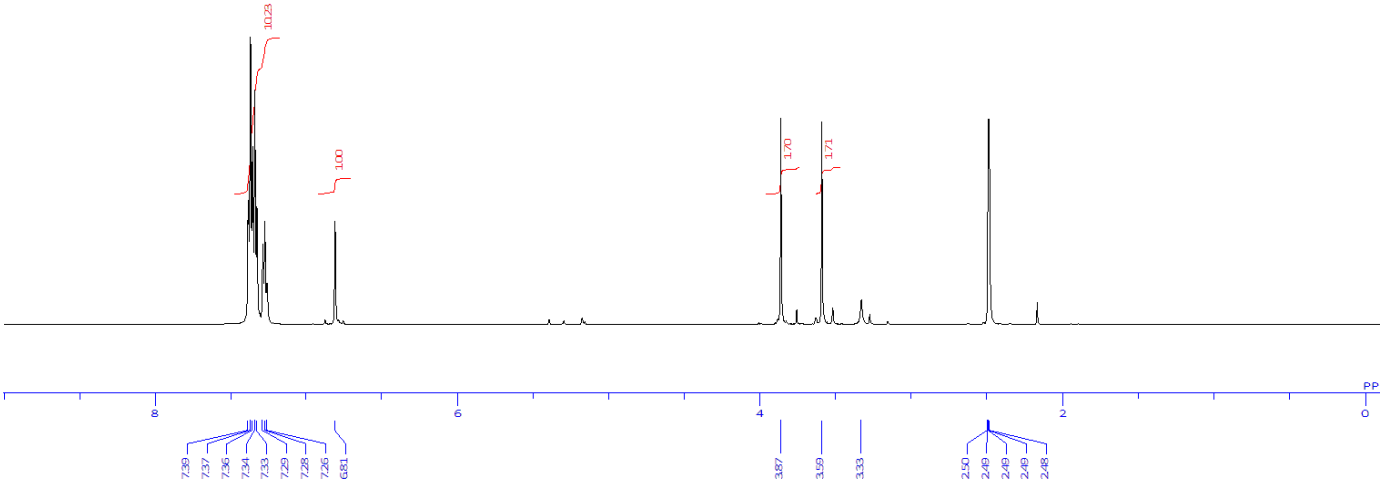
2) M. Kitamura, N. Tashiro, S. Miyagawa, and T. Okauchi, *Synthesis*, 2011, **7**, 1037.

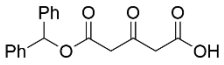
6. Copies of ^{1}H and ^{13}C NMR Charts

5-(Benzhydryloxy)-3,5-dioxopentanoic acid (1)



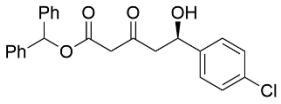
500 MHz, DMSO-d_6



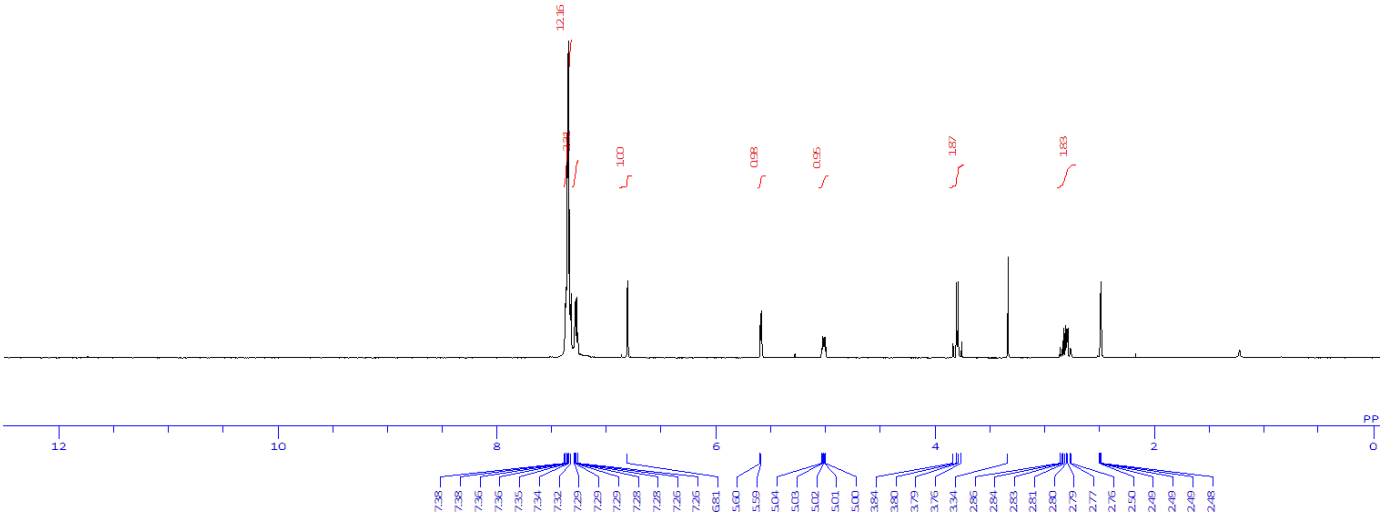


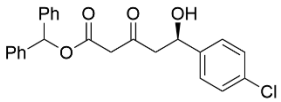
150 MHz, DMSO-d_6

Benzhydryl (*R*)-5-(4-chlorophenyl)-5-hydroxy-3-oxopentanoate (3a)



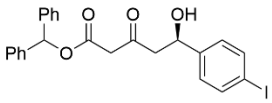
500 MHz, DMSO-d_6



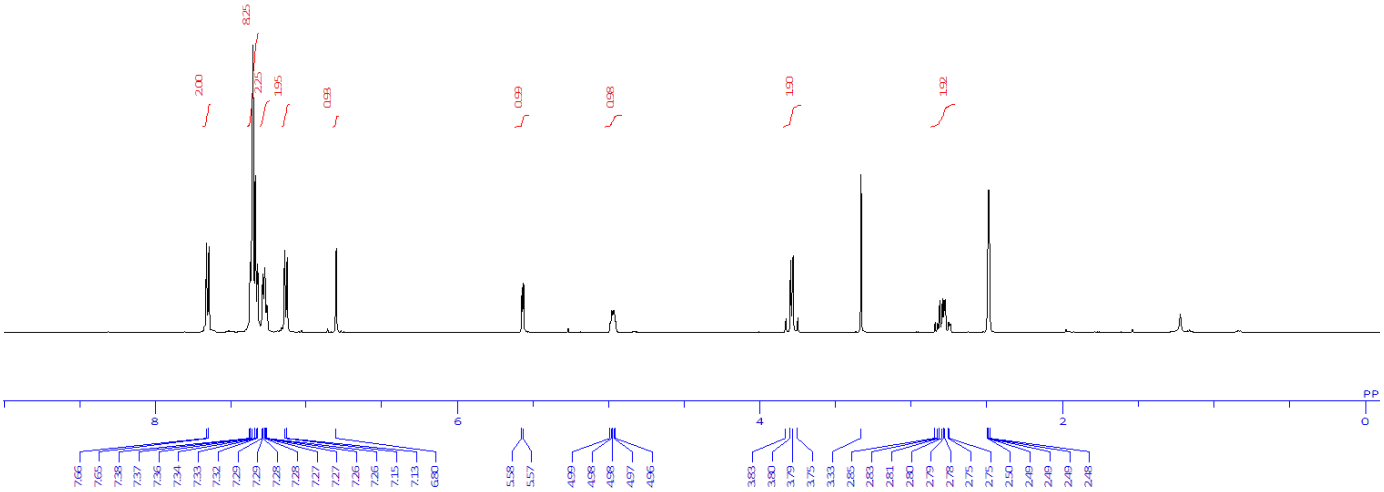


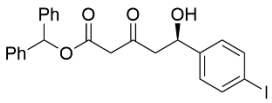
150 MHz, DMSO-d_6

Benzhydryl (*R*)-5-(4-iodophenyl)-5-hydroxy-3-oxopentanoate (3b)



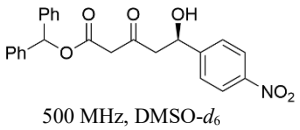
500 MHz, DMSO-d_6



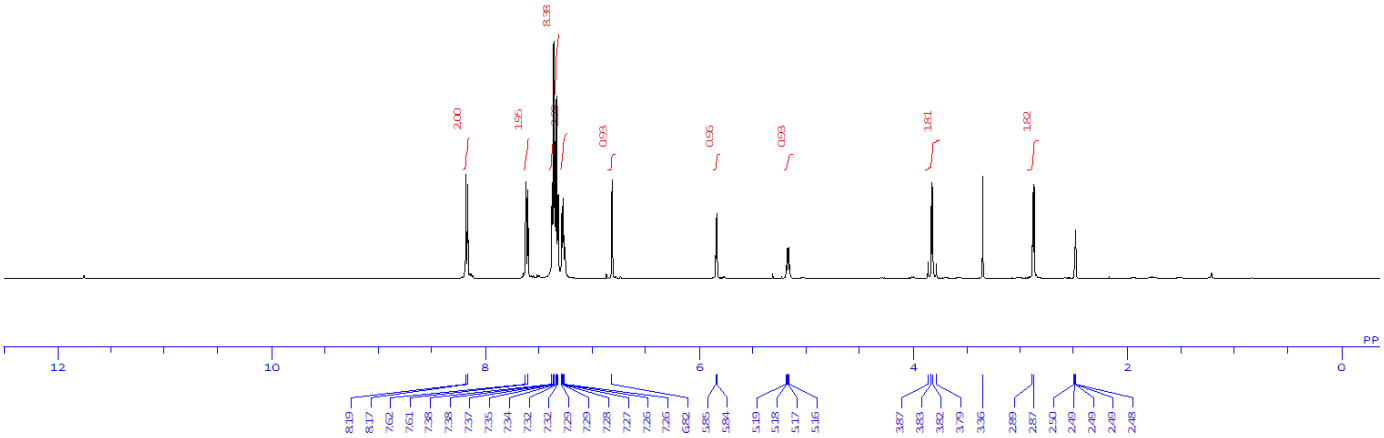


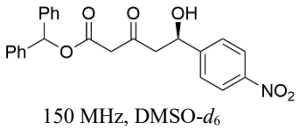
126 MHz, DMSO-d_6

Benzhydryl (*R*)-5-hydroxy-5-(4-nitrophenyl)-3-oxopentanoate (3c)



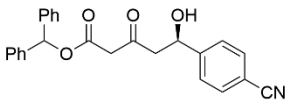
500 MHz, DMSO-d_6



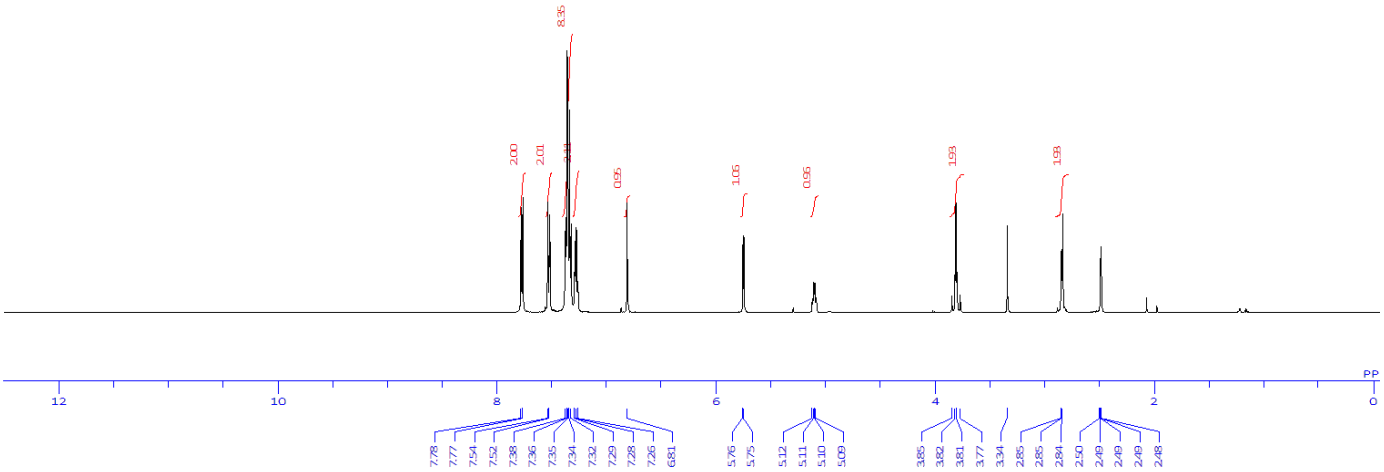


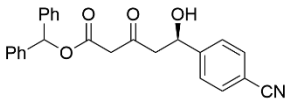
150 MHz, DMSO-d_6

Benzhydryl (*R*)-5-(4-cyanophenyl)-5-hydroxy-3-oxopentanoate (3d)



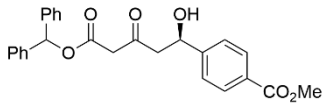
500 MHz, DMSO-d_6



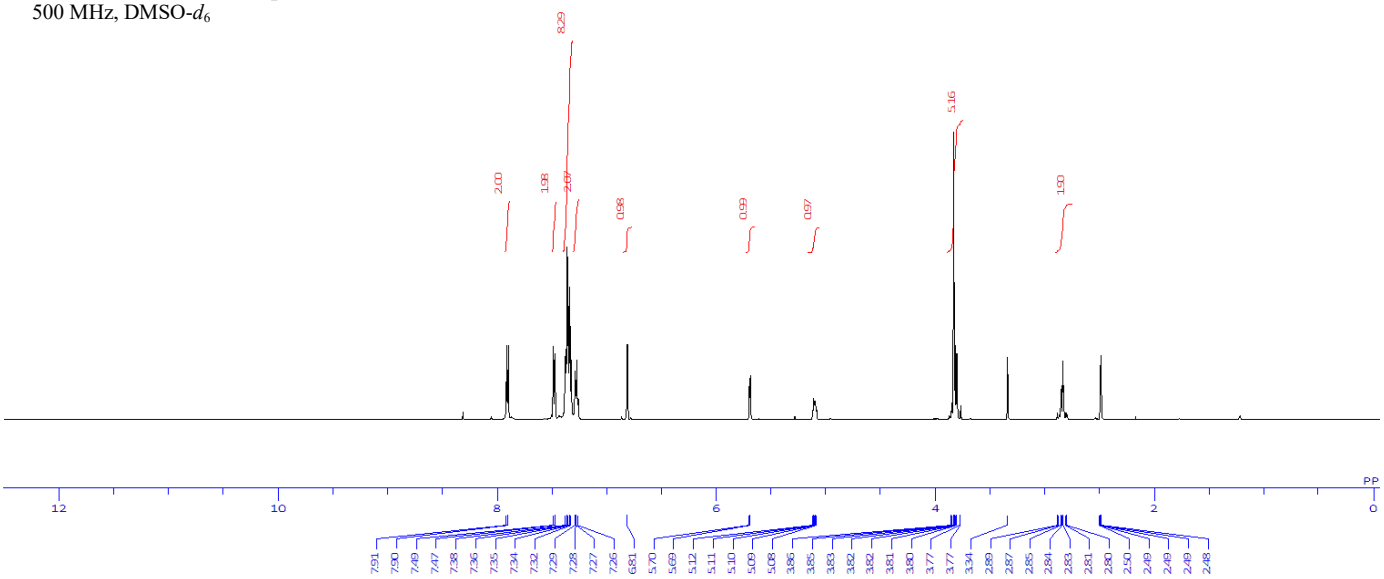


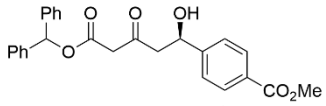
150 MHz, DMSO-d_6

Methyl (*R*)-4-(5-(benzhydryloxy)-1-hydroxy-3,5-dioxopentyl)benzoate (3e)



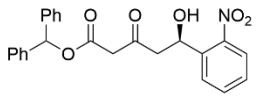
500 MHz, DMSO-d_6



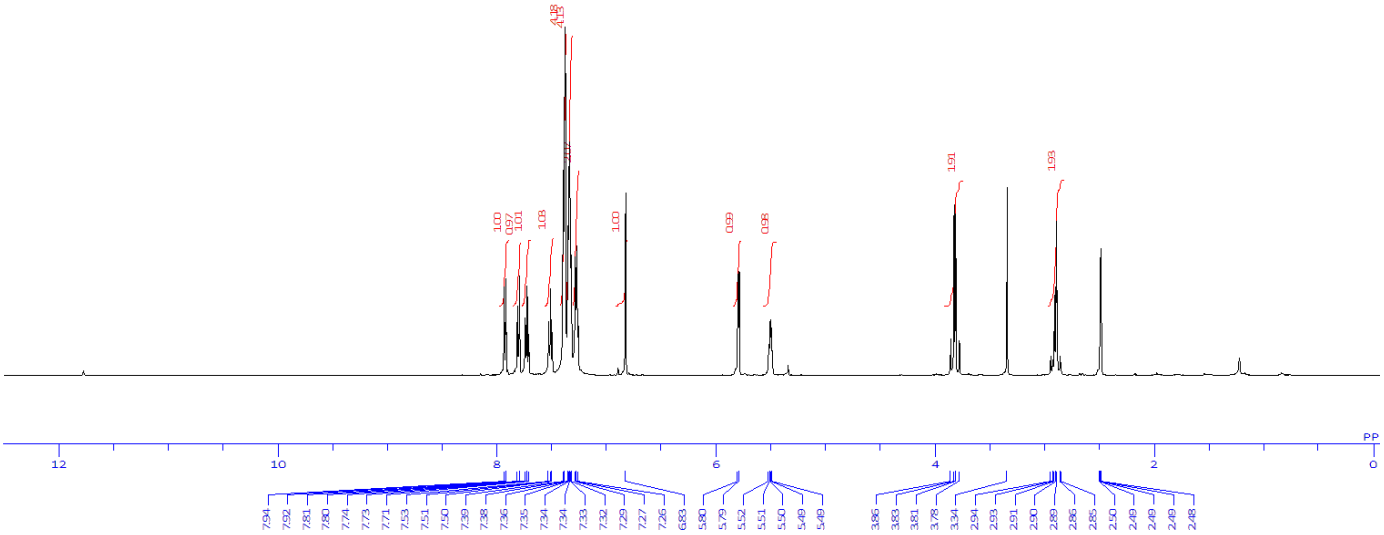


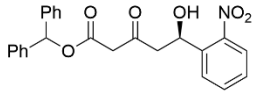
150 MHz, DMSO-d_6

Benzhydryl (*R*)-5-hydroxy-5-(2-nitrophenyl)-3-oxopentanoate (3f)



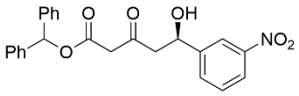
500 MHz, DMSO-d_6



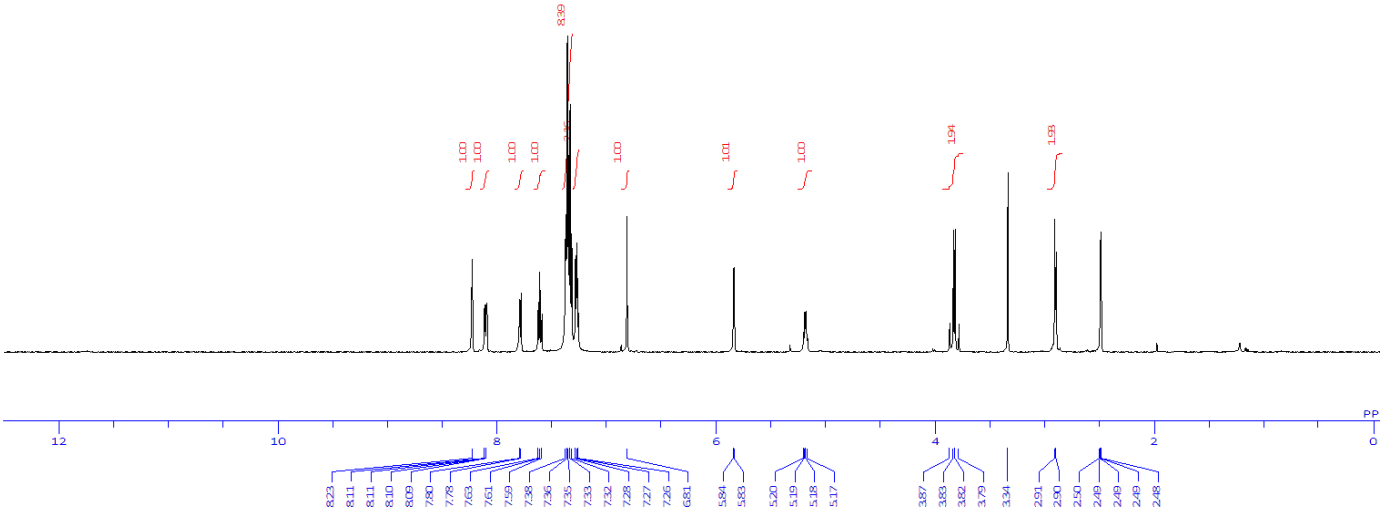


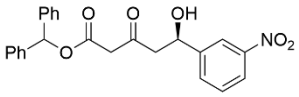
150 MHz, DMSO-d_6

Benzhydryl (*R*)-5-hydroxy-5-(3-nitrophenyl)-3-oxopentanoate (3g)



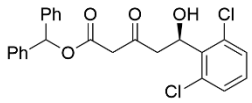
500 MHz, DMSO-d_6



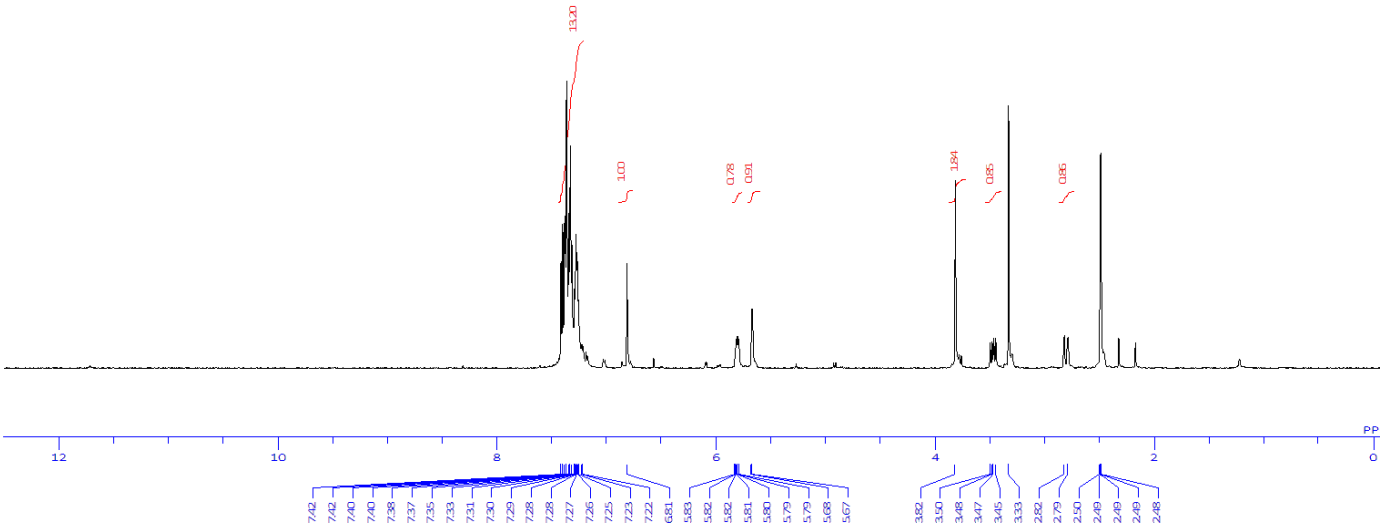


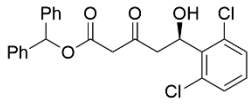
150 MHz, DMSO-d_6

Benzhydryl (*R*)-5-(2,6-dichlorophenyl)-5-hydroxy-3-oxopentanoate (3h)



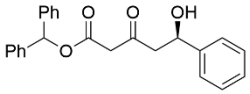
500 MHz, DMSO-d_6



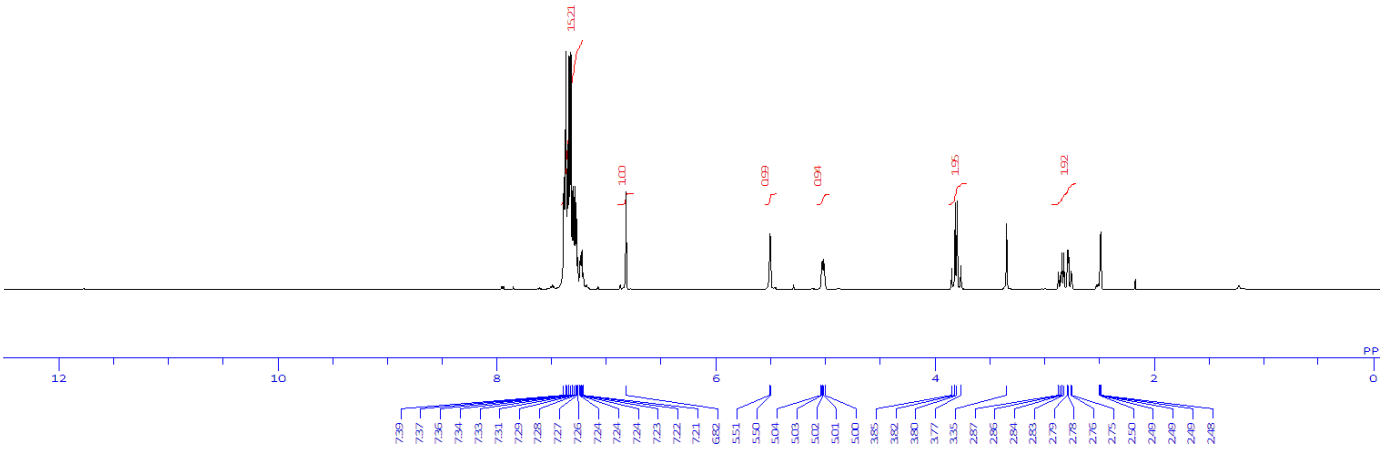


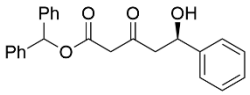
150 MHz, DMSO-d_6

Benzhydryl (*R*)-5-hydroxy-3-oxo-5-phenylpentanoate (3i)



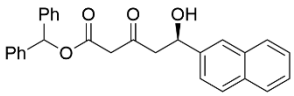
500 MHz, DMSO-d_6



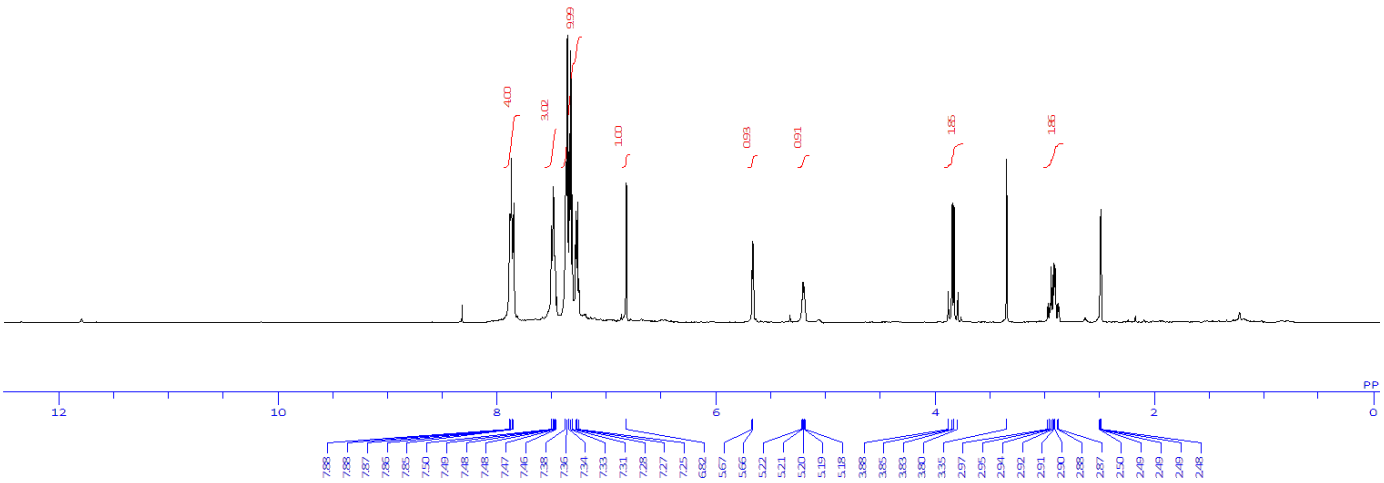


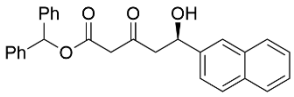
150 MHz, DMSO-d_6

Benzhydryl (*R*)-5-hydroxy-5-(naphthalen-2-yl)-3-oxopentanoate (3j)



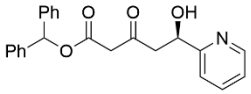
500 MHz, DMSO-d_6



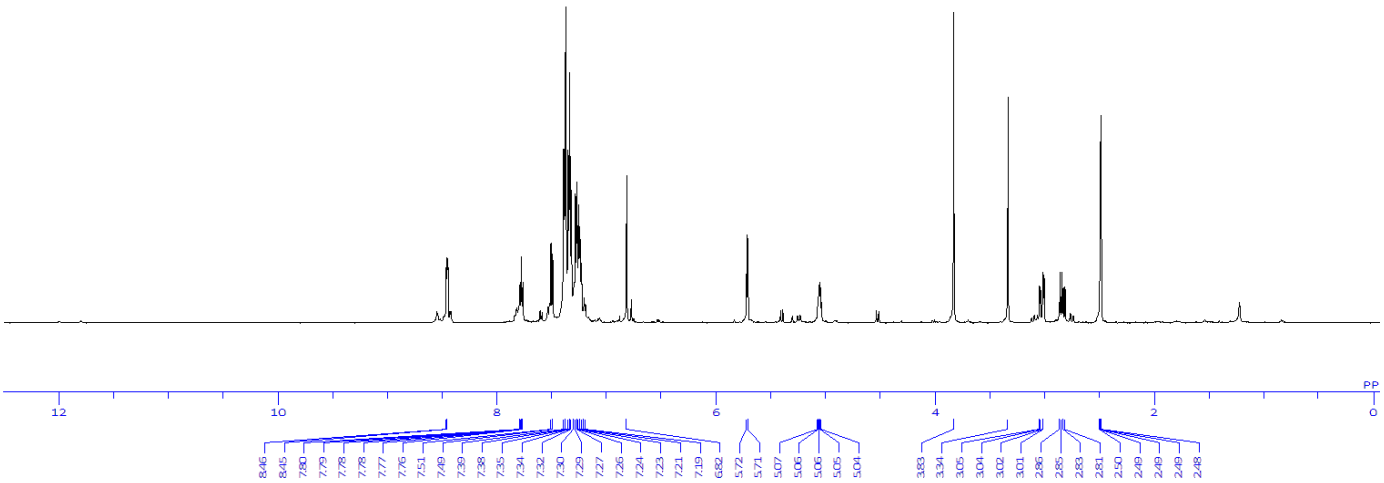


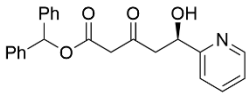
150 MHz, DMSO-d_6

Benzhydryl (*R*)-5-hydroxy-3-oxo-5-(pyridin-2-yl)pentanoate (3k)



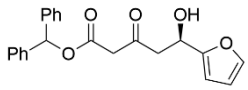
500 MHz, DMSO-d_6



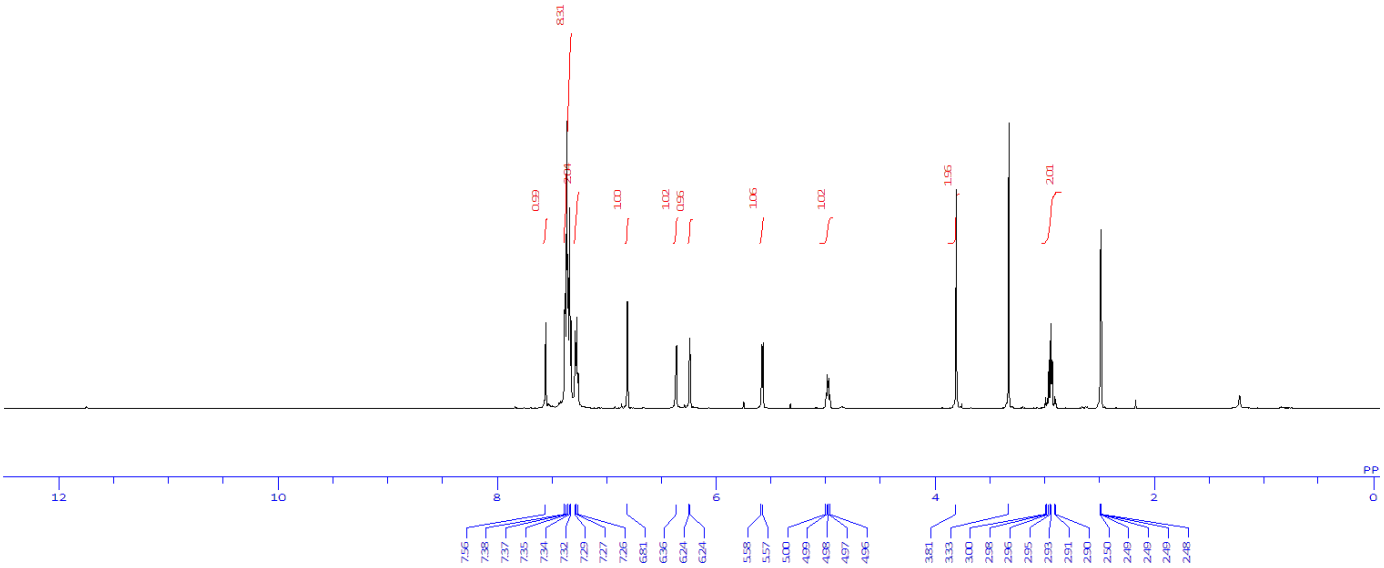


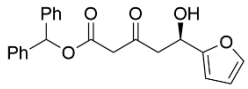
150 MHz, DMSO-d_6

Benzhydryl (*R*)-5-(furan-2-yl)-5-hydroxy-3-oxopentanoate (3l)



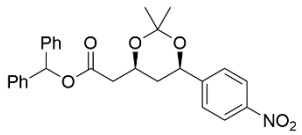
500 MHz, DMSO-d_6



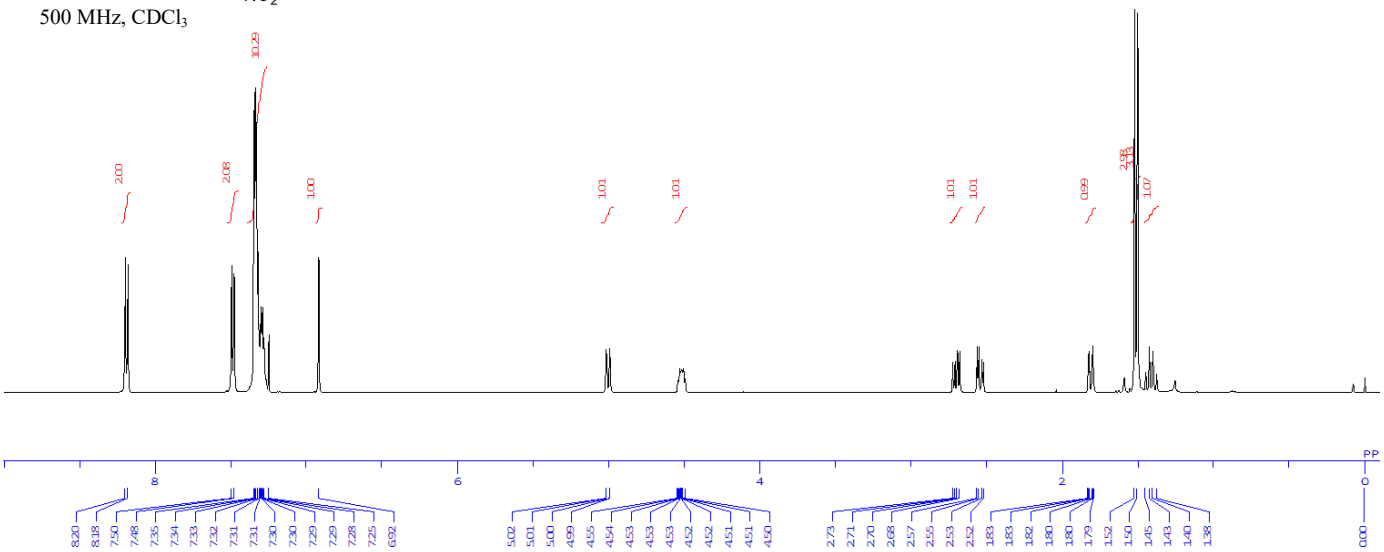


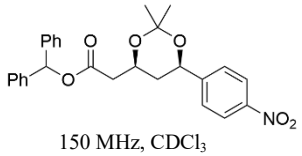
150 MHz, DMSO-d_6

Benzhydryl 2-((4*S*,6*R*)-2,2-dimethyl-6-(4-nitrophenyl)-1,3-dioxan-4-yl)acetate (6)

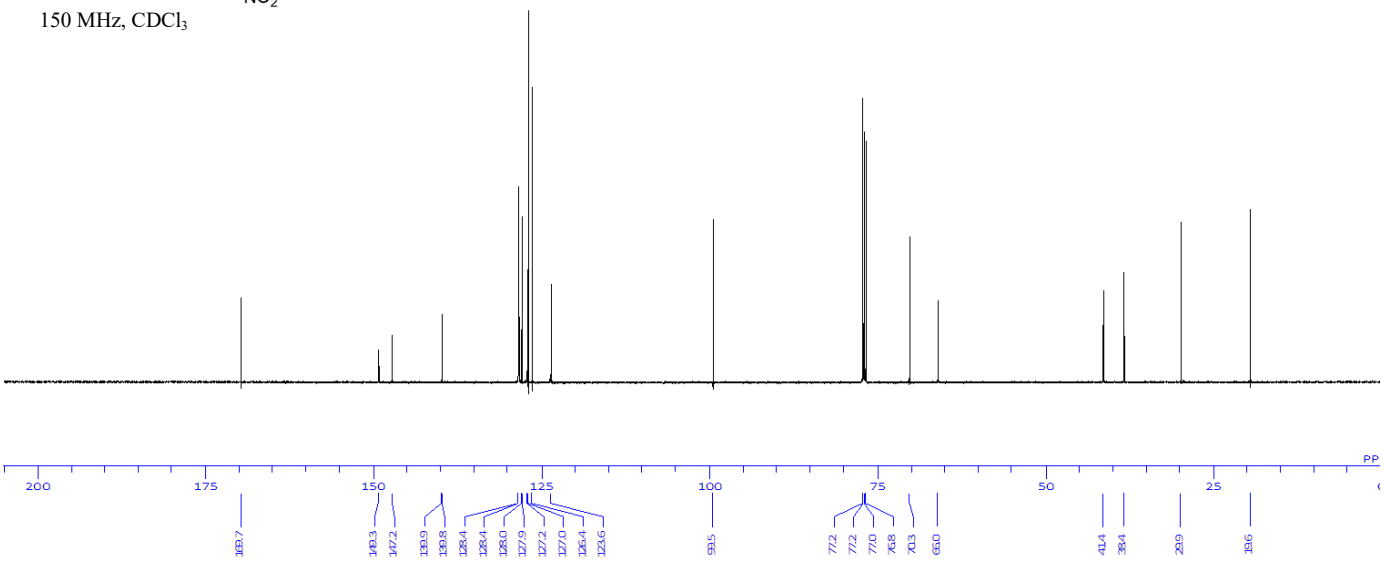


500 MHz, $CDCl_3$

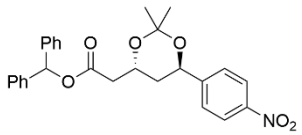




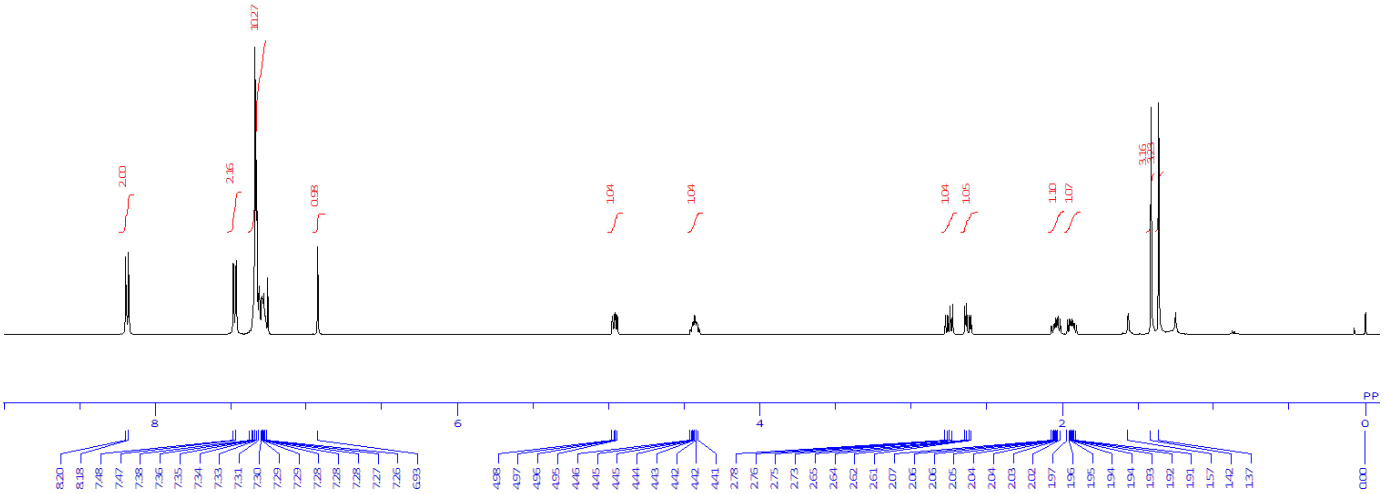
150 MHz, $CDCl_3$

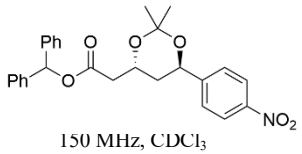


Benzhydryl 2-((4*R*,6*R*)-2,2-dimethyl-6-(4-nitrophenyl)-1,3-dioxan-4-yl)acetate (8)



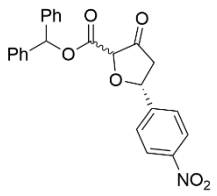
500 MHz, $CDCl_3$



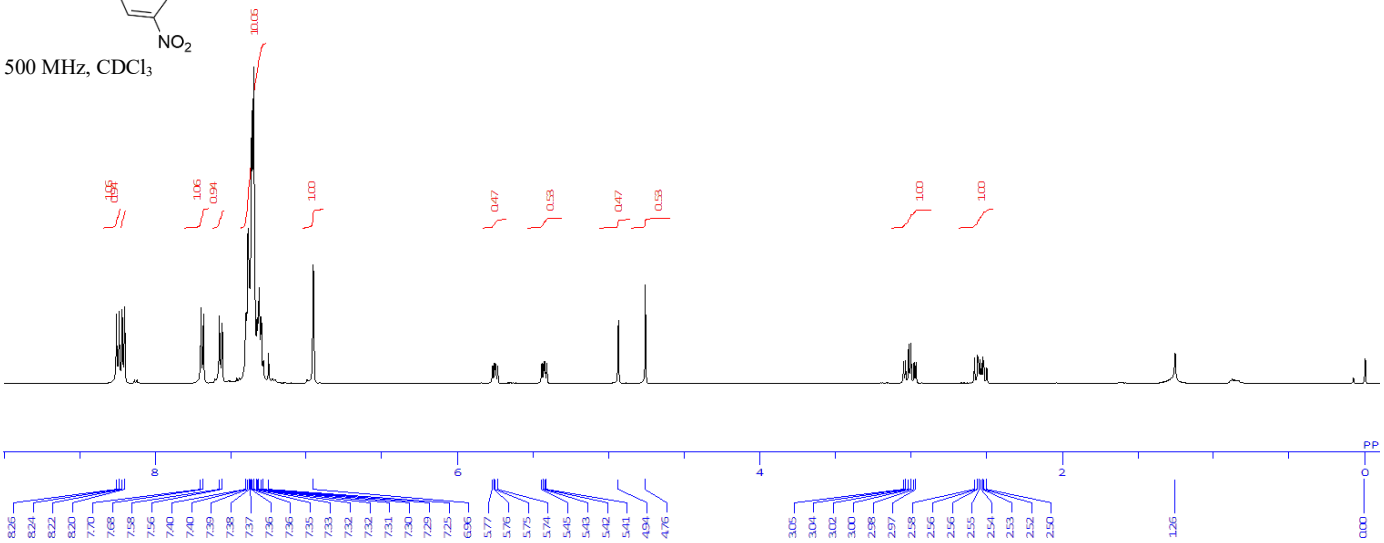


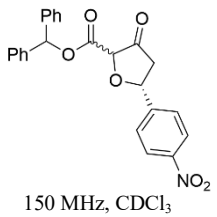
150 MHz, $CDCl_3$

Benzhydryl (5*R*)-5-(4-nitrophenyl)-3-oxotetrahydrofuran-2-carboxylate (10)



500 MHz, $CDCl_3$





150 MHz, $CDCl_3$