Supporting Information-I

Direct Catalytic Asymmetric Synthesis of Highly Functionalized Tetronic acids/Tetrahydro-isobenzofuran-1, 5-diones via Combination of Cascade Three-Component Reductive Alkylations and Michael-Aldol Reactions

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General Methods: The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) for ^{1}H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.0$) for ^{13}C NMR. *In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment, and is given in parentheses.* The coupling constants *J* are given in Hz. Column chromatography was performed using Acme's silica gel (particle size 0.063-0.200 mm). High-resolution mass spectra were recorded on micromass ESI-TOF MS. GCMS mass spectrometry was performed on Shimadzu GCMS-QP2010 mass spectrometer. IR spectra were recorded on JASCO FT/IR-5300. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 analyzer. Mass spectra were recorded on either VG7070H mass spectrometer using EI technique or Shimadzu-LCMS-2010 A mass spectrometer. For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

The enantiomeric excess (ee) of the M and M-A products was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H or OJ-H column and hexane/2-propanol as the eluent or using a Daicel Chiralpak AS-H column and hexane/2-propanol as the eluent. Retention times and solvent ratios are indicated in the respective entries.

- ***Because of solubility problem of cascade TCRA products 7aa-fm in $CDCl_3$, we have used three drops of CD_3OD for NMR analysis.***

Materials: All solvents and commercially available chemicals were used as received.

General Experimental Procedures for the Cascade TCRA and Michael-Aldol Reactions:

Procedure A: Amino Acid-Catalyzed Cascade Three-Component Reductive Alkylation (TCRA) Reactions with Cyclic ✪-keto-Lactones: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.6 mmol of the aldehyde **2**, 0.3 mmol of CH acid **1**, and 0.3 mmol of Hantzsch ester **3** was added 1.0 mL of solvent, and then the catalyst amino acid **4** (0.015 mmol) was added, and the reaction mixture was stirred at 25 °C for the time indicated in Tables 3. The crude reaction mixture was directly loaded onto a silica gel column with or without aqueous workup, and pure cascade products **7aa-7fm** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure B: General Procedure for the Synthesis of 3-Benzyl-4-methoxy-5*H*-furan-2-one 8aa: In an ordinary glass vial equipped with a magnetic stirring bar, to 1.0 mmol of 4-hydroxy-3-benzyl-5*H*-furan-2-one **7aa** in 1.0 mL of ether at 0 °C added an excess ethereal solution of diazomethane and the reaction mixture was stirred at room temperature for the 0.5 h. After evaporation of the solvent and excess diazomethane completely in fume hood, the crude reaction mixture was directly loaded on silica gel column without aqueous work-up and pure products **8aa** were obtained by column chromatography (silica gel, mixture of exane/ethyl acetate).

Procedure C: Preparation for Racemic Michael Products 10 with Triethylamine-Catalysis: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.3 mmol of 4-hydroxy-3-alkyl-5*H*-furan-2-one **7** and 0.9 mmol of methyl vinyl ketone **9a** with a catalytic amount of triethylamine in 1.0 mL of THF solvent and the reaction mixture was stirred at 25 °C for 6-48 h. The crude reaction mixture was worked up with aqueous NH_4Cl solution, and the aqueous layer was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were dried (Na_2SO_4),

filtered, and concentrated. Pure products **10** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

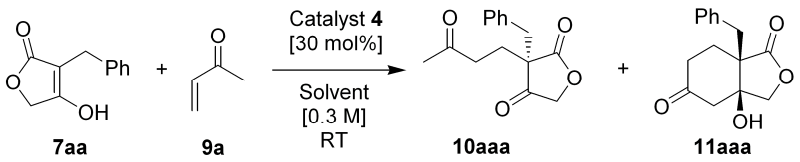
Procedure D: Preparation of Racemic Cascade Michael-Aldol Products 11 with DL-β-Phenylalanine-Catalysis: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.3 mmol of 4-hydroxy-3-alkyl-5*H*-furan-2-one **7** and 0.9 mmol of methyl vinyl ketone **9a** with a catalytic amount of DL-β-phenylalanine in 1.0 mL of THF solvent and the reaction mixture was stirred at 25 °C for 6-48 h. The crude reaction mixture was worked up with aqueous NH_4Cl solution, and the aqueous layer was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated. Pure products **11** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure E: Amino Acid-Catalyzed Asymmetric Cascade Michael-Aldol Reactions: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.3 mmol of 4-hydroxy-3-alkyl-5*H*-furan-2-one **7** and 0.9 mmol of methyl vinyl ketone **9a** was added 1.0 mL of DMSO solvent, and then the catalyst L-proline **4a** (0.09 mmol) was added, and the reaction mixture was stirred at 25 °C for 2 days. The crude reaction mixture was worked up with aqueous NH_4Cl solution, and the aqueous layer was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated. Pure cascade M-A products **11** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure F: Q-NH_2/TCA-Catalyzed Asymmetric Cascade Michael-Aldol Reactions: In an ordinary glass vial equipped with a magnetic stirring bar, to **Q-NH_2 4u** (0.05 mmol) and TCA (32 mg, 0.2 mmol) in THF (5.0 mL) were added and stirred at 25 °C for 10 minutes then 0.5 mmol of 4-hydroxy-3-alkyl-5*H*-furan-2-one **7** and 1.5 mmol of methyl vinyl ketone **9a** was added, and the reaction mixture was stirred at 25 °C for 6-48 h. The crude reaction mixture was worked up with aqueous NH_4Cl solution, and the aqueous layer was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated. Pure cascade M-A products **11** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure G: General Procedure for the Hydrolysis of Cascade Michael-Aldol Products: A solution of bicyclic alcohol compound **11** (0.5 mmol) and *p*-TSA (0.05 mmol) in dry benzene (3.0 mL) was stirred at 80 °C for 1 hr. After cooling, the reaction mixture washed with aqueous sodium bicarbonate solution and the aqueous layer was extracted with dichloromethane (2 x 20 ml). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure products **12** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

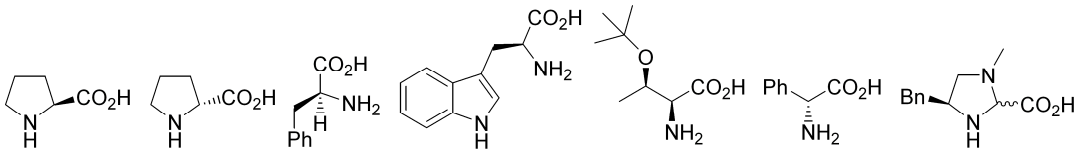
Table S1 Effect of Solvent and Amino acid on the Direct Amino acid Catalyzed Asymmetric Cascade M-A Reaction of **7aa** and **9a**[a]



7aa **9a** **10aaa** **11aaa**

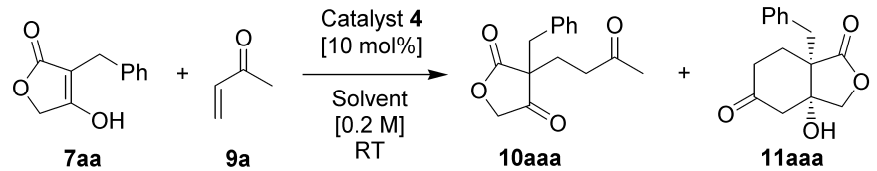
Entry	Catalyst	Solvent	Time [h]	Product **10aaa**		Product **11aaa**	
				Yield [%][b]	ee [%][c]	Yield [%][b]	ee [%][c]
1	**4a**	DMSO	48	10	23	70	52
2	**4a**	Toluene	72	38	0	55	ND
3	**4b**	DMSO	48	10	-21	50	-53
4	**4c**	DMSO	5	40	0	40	ND
5	**4c**	DMSO	6	10	0	79	0
6	**4d**	DMSO	24	31	0	65	ND
7	**4e**	DMSO	24	15	0	75	0
8	**4f**	DMSO	24	58	0	27	ND
9	**4g**	DMSO	168	50	0	31	ND
10	**4g**	Toluene	168	37	0	31	ND

[a] Reactions were carried out in solvent [0.3 M] with 3.0 equiv. of freshly distilled **9a** in the presence of 30 mol% of catalyst **4**. [b] Yield refers to the column purified product. [c] Ee determined by HPLC analysis.



4a **4b** **4c** **4d** **4e** **4f** **4g**

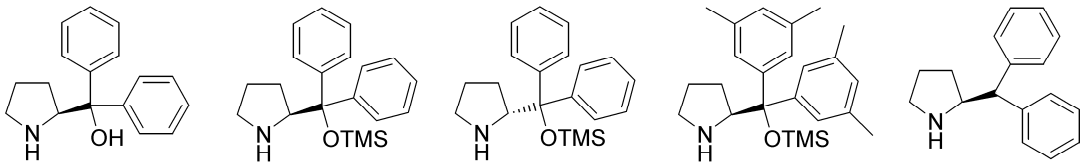
Table S2 Effect of Solvent and Pyrrolidine Catalysts on the Direct Amine Catalyzed Asymmetric Cascade M-A Reaction of **7aa** and **9a**[a]



7aa **9a** **10aaa** **11aaa**

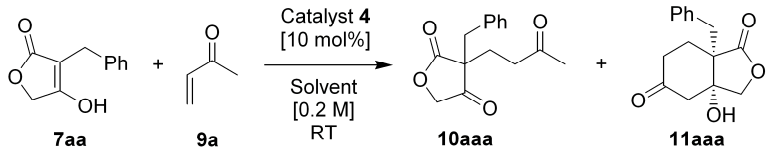
Entry	Catalyst	Solvent	Time [h]	Product **10aaa**		Product **11aaa**	
				Yield [%][b]	ee [%][c]	Yield [%][b]	ee [%][c]
1	**4h**	DMSO	48	60	0	–	–
2	**4h**	$C_6H_5CH_3$	36	74	0	–	–
3	**4i/PhCO$_2$H**	CH_2Cl_2	36	76	0	15	ND
4	**4i/PhCO$_2$H**	$C_6H_5CH_3$	10	77	0	10	ND
5	**4j**	DMSO	48	62	0	–	–
6	**4j**	$C_6H_5CH_3$	36	78	0	–	–
7	**4k/PhCO$_2$H**	$C_6H_5CH_3$	21	77	0	–	–
8	**4l/TFA**	CH_2Cl_2	168	<15	–	–	–

[a] Reactions were carried out in solvent [0.2 M] with 3.0 equiv. of freshly distilled **9a** in the presence of 10 mol% of catalyst **4** and 20 mol% of co-catalyst. [b] Yield refers to the column purified product. [c] Ee determined by HPLC analysis.



4h **4i** **4j** **4k** **4l**

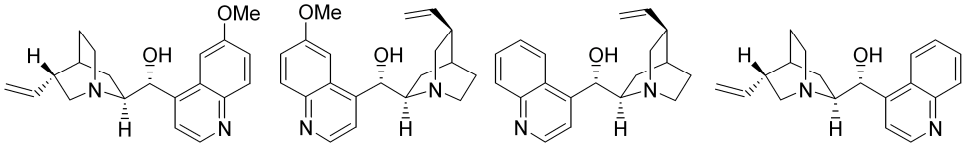
Table S3 Effect of Solvent and 3°-Amine on the Direct Amine-Catalyzed Asymmetric Cascade M-A Reaction of **7aa** and **9a**[a]



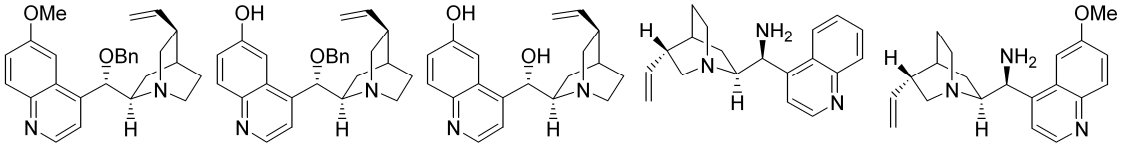
7aa **9a** **10aaa** **11aaa**

Entry	Catalyst	Solvent	Time [h]	Product **10aaa**		Product **11aaa**	
				Yield [%][b]	ee [%][c]	Yield [%][b]	ee [%][c]
1	**4m**	Toluene	24	71	0	–	–
2	**4n**	Toluene	24	80	0	–	–
3	**4o**	Toluene	12	80	0	–	–
4	**4p**	Toluene	12	80	0	–	–
5	**4q**	Toluene	48	70	5	–	–
6	**4r**	Toluene	19	80	2	–	–
7	**4s**	Toluene	24	82	0	–	–
8	**4t**	Toluene	48	73	0	–	–
9	**4u**	Toluene	48	70	0	–	–
10	**4u/TFA**	**Toluene**	**6**	**55**	**7**	**40**	**20**

[a] Reactions were carried out in solvent [0.2 M] with 3.0 equiv. of freshly distilled **9a** in the presence of 10 mol% of catalyst **4** and 40 mol% of co-catalyst. [b] Yield refers to the column purified product. [c] Ee determined by HPLC analysis.

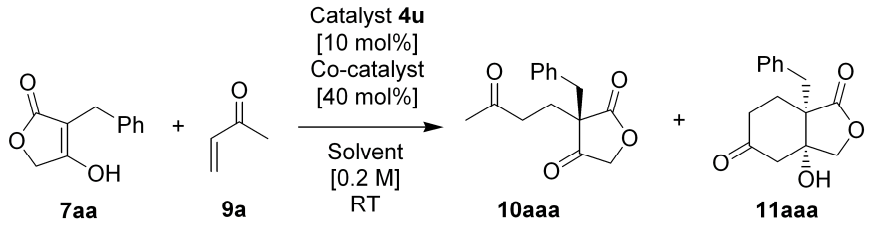


Quinine 4m **Quinidine 4n** **Cinchonine 4o** **Cinchonidine 4p**



QD-OBn 4q **OH-QD-OBn 4r** **OH-QD 4s** **CD-NH$_2$ 4t** **Q-NH$_2$ 4u**

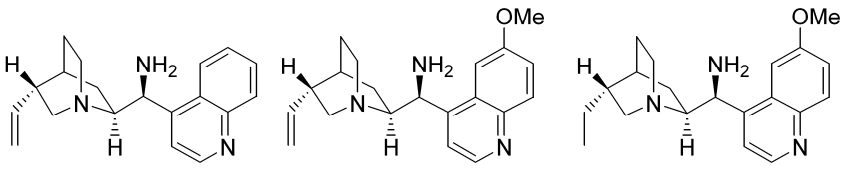
Table S4 Effect of Solvent and Co-catalyst on the Direct Q-NH_2-Catalyzed Asymmetric Cascade M-A Reaction of **7aa** and **9a**[a]



7aa **9a** **10aaa** **11aaa**

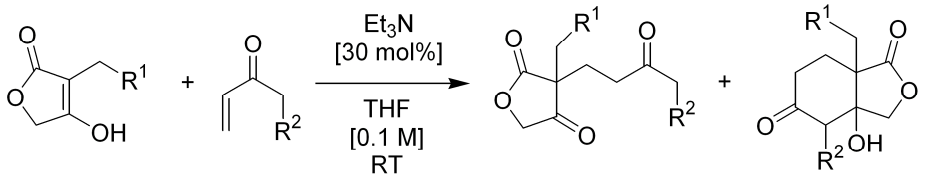
Entry	Catalyst/ Co-catalyst	Solvent	Time [h]	Product **10aaa**		Product **11aaa**	
				Yield [%][b]	ee [%][c]	Yield [%][b]	ee [%][c]
1	**4u/TFA**	Toluene	6	55	7	40	20
2	**4u/TFA**	CH_2Cl_2	4	75	11	–	–
3	**4u/TFA**	**$CHCl_3$**	**10**	**71**	**13**	**19**	**58**
4	**4u/TFA**	THF	3	50	9	40	43
5	**4u/TFA**	DMSO	12	21	35	71	10
6	**4u/TFA**	n-PrOH	24	23	54	44	1
7	**4u/TFA**	i-PrOH	12	15	48	81	15
8	**4u/TCA**	i-PrOH	8	25	69	44	17
9	**4u/TCA**	**THF**	**8**	**60**	**8**	**40**	**55**
10	**4u/3,5-DNBA**	THF	24	30	60	50	36
11	**4t/TFA**	THF	5	40	5	33	46
12	**4t/TCA**	**THF**	**6**	**60**	**2**	**20**	**61**
13	**4v/TCA**	THF	120	45	8	35	57

[a] Reactions were carried out in solvent [0.2 M] with 3.0 equiv. of freshly distilled **9a** in the presence of 10 mol% of catalyst **4** and 40 mol% of co-catalyst. [b] Yield refers to the column purified product. [c] Ee determined by HPLC analysis.

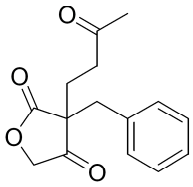


CD-NH_2 4t **Q-NH_2 4u** **DHQ-NH_2 4v**

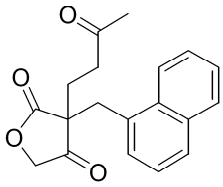
Table S5 Synthesis of Racemic Michael Adducts **10**[a][b]



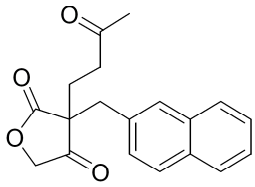
7 **9** **10** *cis*-**11** [10-20%]



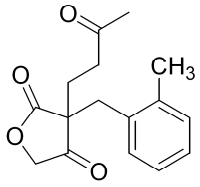
12 h
71% [**10aaa**]



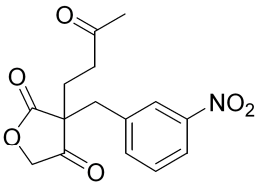
12 h
65% [**10aba**]



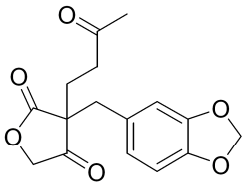
5 h
70% [**10aca**]



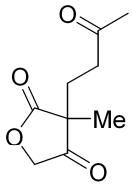
12 h
50% [**10ada**]



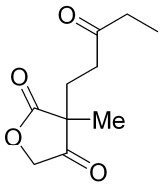
8 h
60% [**10aea**]



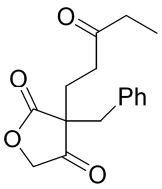
17 h
60% [**10afa**]



6 h
70% [**10ana**]



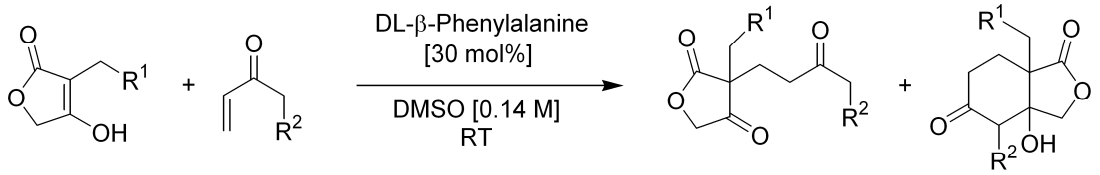
48 h
20% [**10anb**]



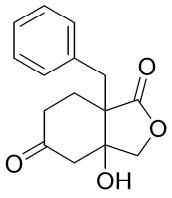
48 h
70% [**10aab**][c]

[a] Reactions were carried out in THF [0.1 M] with 3.0 equiv. of freshly distilled **9** in the presence of 30 mol% of Et_3N. [b] Yield refers to the column purified product. [c] Compound obtained from DL-proline-catalysis in DMSO at RT.

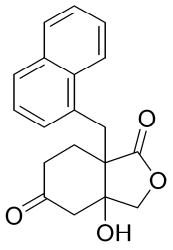
Table S6 Synthesis of Racemic Cascade Michael-Aldol Adducts **11**[a][b]



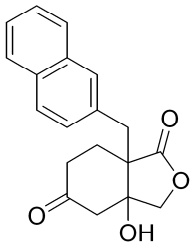
7 **9** **10** [10-20%] *cis*-**11**



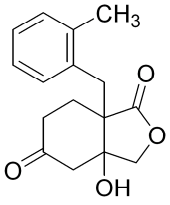
48 h
50% [*cis*-**11aaa**]



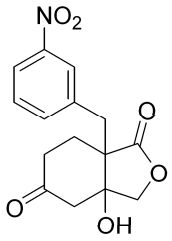
24 h
40% [*cis*-**11aba**]



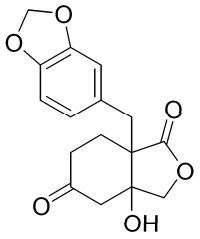
72 h
55% [*cis*-**11aca**]



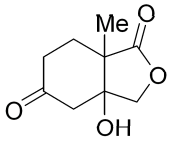
96 h
40% [*cis*-**11ada**]



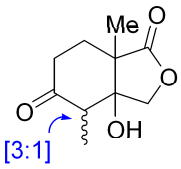
96 h
60% [*cis*-**11aea**]



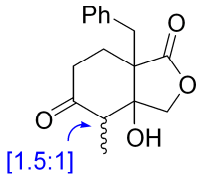
96 h
50% [*cis*-**11afa**]



12 h
30% [*cis*-**11ana**]



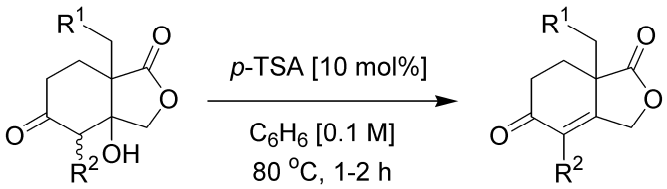
48 h
20% [*cis*-**11anb**][c]



48 h
70% [*cis*-**11aab**][d]

[a] Reactions were carried out in DMSO [0.14 M] with 3.0 equiv. of freshly distilled **9** in the presence of 30 mol% of DL-β-Phenylalanine. [b] Yield refers to the column purified product. [c] Compound obtained from Et_3N-catalysis.[d] Compound obtained from DL-proline-catalysis.

Table S7 Synthesis of Racemic Enones **12**[a]

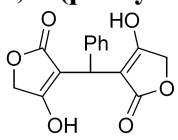


11 **12**

Entry	R^1	R^2	Products yield [%][b] **12**	
1	Ph	H	**12aaa**	70
2	H	H	**12ana**	92
3	H	Me	**12anb**	90
4	Ph	Me	**12aab**	90

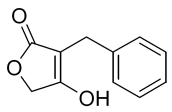
[a] Reactions were carried out in benzene (0.1 M) with 10 mol% of catalyst *p*-TSA as catalyst. [b] Yield refers to the column purified product.

3,3'-(phenylmethanediyl)bis(4-hydroxyfuran-2(5*H*)-one) (6aa): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (neat): ν_{max} 3418, 2934, 2544, 1721, 1644, 1445 and 1117 cm^{-1}; ^{1}H NMR [CD_3OD] δ 7.32 (2H, d, *J* = 7.6 Hz), 7.18 (2H, t, *J* = 7.2 Hz), 7.10 (1H, d, *J* = 7.2 Hz), 4.74 (1H, s), 4.48 (4H, s); ^{13}C NMR [CD_3OD, DEPT-135] δ 183.0 (2 x C), 181.0 (2 x C), 145.0 (C), 129.3 (2 x CH), 128.3 (2 x CH), 127.1 (CH), 100.6 (2 x C), 69.9 (2 x CH_2), 33.9 (CH); LCMS m/z 288.30 (M^+), calcd $C_{15}H_{12}O_6$ 288.0634; Anal. calcd for $C_{15}H_{12}O_6$ (288.0634): C, 62.50; H, 4.20. Found: C, 62.48; H, 4.25%.



6aa

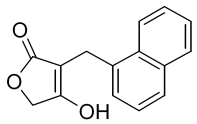
3-Benzyl-4-hydroxy-5*H*-furan-2-one (7aa):[1] Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp.: 158 °C; IR (neat): ν_{max} 2984, 2683, 1589, 1446, 1392, 1099, 1026 and 759 cm^{-1}; ^{1}H NMR [$CDCl_3$ + CD_3OD (three drops)] δ



7aa

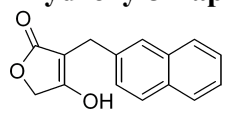
7.27 (4H, s, Ph-*H*), 7.19 (1H, s, Ph-*H*), 4.54 (2H, s, OCH_2), 3.52 (2H, s, PhCH_2), 2.31 (1H, br s, O-H); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 176.7 (C, O-*C*=O), 173.6 (C), 139.0 (C), 128.2 (4 x CH), 126.0 (CH), 100.2 (C), 67.0 (CH_2), 26.9 (CH_2); LCMS m/z 191.05 (M+H$^+$), calcd $C_{11}H_{10}O_3$ 190.0630; HRMS m/z 213.0528 (M+Na), calcd $C_{11}H_{10}O_3Na$ 213.0528; Anal. calcd for $C_{11}H_{10}O_3$ (190.0630): C, 69.46; H, 5.30. Found: C, 69.38; H, 5.35%.

4-Hydroxy-3-naphthalen-1-ylmethyl-5*H*-furan-2-one (7ab): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp.: 182 °C; IR (neat): ν_{max} 2968, 1706, 1658, 1600, 1318, 1110, 1044, 863 and 786 cm^{-1}; ^{1}H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 8.20 (1H, d, *J* = 8.0 Hz), 7.81 (1H, d, *J* = 7.6 Hz), 7.69 (1H, d, *J* = 6.4 Hz), 7.55-7.40 (2H, m), 7.40-7.30 (2H, m), 4.53 (2H, s, OCH_2), 3.93 (2H, s, ArCH_2); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 176.6 (C, O-*C*=O), 174.0 (C), 134.1 (C), 133.5 (C), 131.6 (C), 128.3 (CH), 126.7 (CH), 125.8 (CH), 125.6 (CH), 125.2 (CH), 125.15 (CH), 123.6 (CH), 99.1 (C), 66.8 (CH_2, O*C*H_2), 24.2 (CH_2, Ar*C*H_2); LCMS m/z 241.10 (M+H$^+$), calcd $C_{15}H_{12}O_3$ 240.0786; HRMS m/z 263.0692 (M+Na), calcd $C_{15}H_{12}O_3Na$ 263.0684; Anal. calcd for $C_{15}H_{12}O_3$ (240.0786): C, 74.99; H, 5.03. Found: C, 74.85; H, 5.08%.



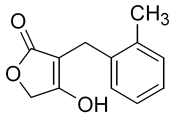
7ab

4-Hydroxy-3-naphthalen-2-ylmethyl-5*H*-furan-2-one (7ac): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp.: 136 °C; IR (neat): ν_{max} 2979, 1753, 1595, 1450 and 1095 cm^{-1}; ^{1}H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 7.76-7.68 (4H, m), 7.42-7.37 (3H, m), 4.56 (2H, s, OCH_2), 3.66 (2H, s, ArCH_2); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 176.8 (C, O-*C*=O), 173.8 (C), 136.4 (C), 133.3 (C), 131.9 (C), 127.7 (CH), 127.3 (2 x CH), 126.9 (CH), 126.1 (CH), 125.7 (CH), 125.0 (CH), 100.0 (C), 67.0 (CH_2, O*C*H_2), 27.0 (CH_2, Ar*C*H_2); LCMS m/z 239.10 (M-H$^+$), calcd $C_{15}H_{12}O_3$ 240.0786; HRMS m/z 263.0683 (M+Na), calcd $C_{15}H_{12}O_3Na$ 263.0684; Anal. calcd for $C_{15}H_{12}O_3$ (240.0786): C, 74.99; H, 5.03. Found: C, 75.12; H, 5.08%.



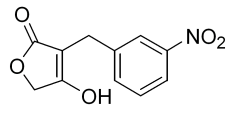
7ac

4-Hydroxy-3-(2-methyl-benzyl)-5*H*-furan-2-one (7ad): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp.: 146 °C; IR (neat): ν_{max} 2987, 2662, 1716, 1603, 1391, 1092 and 1017 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 7.16-7.07 (4H, m), 4.53 (2H, s, OCH_2), 3.46 (2H, s, ArCH_2), 2.34 (3H, s, ArCH_3); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 177.2 (C, O-*C*=O), 174.2 (C), 136.4 (C), 136.1 (C), 129.9 (CH), 128.3 (CH), 126.2 (CH), 125.7 (CH), 99.4 (C), 67.2 (CH_2, O*C*H_2), 24.4 (CH_2, Ar*C*H_2), 19.4 (CH_3, Ar*C*H_3); LCMS m/z 205.05 ($M+H^+$), calcd $C_{12}H_{12}O_3$ 204.0786; HRMS m/z 227.0692 (M+Na), calcd $C_{12}H_{12}O_3Na$ 227.0684; Anal. calcd for $C_{12}H_{12}O_3$ (204.0786): C, 70.57; H, 5.92. Found: C, 70.45; H, 5.98%.



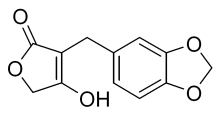
7ad

4-Hydroxy-3-(3-nitro-benzyl)-5*H*-furan-2-one (7ae): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp.: 158 °C; IR (neat): ν_{max} 3417, 2963, 1721, 1492, 1441, 1246 and 1036 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 8.12 (1H, s), 8.04 (1H, d, *J* = 8.4 Hz), 7.65 (1H, d, *J* = 7.6 Hz), 7.45 (1H, t, *J* = 7.6 Hz), 4.63 (2H, s, OCH_2), 3.62 (2H, s, ArCH_2); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 176.3 (C, O-*C*=O), 174.4 (C), 148.0 (C), 141.0 (C), 134.8 (CH), 129.0 (CH), 123.0 (CH), 121.1 (CH), 98.7 (C), 67.0 (CH_2, O*C*H_2), 26.5 (CH_2, Ar*C*H_2); LCMS m/z 236.05 ($M+H^+$), calcd $C_{11}H_9NO_5$ 235.0481; HRMS m/z 258.0372 (M+Na), calcd $C_{11}H_9NO_5Na$ 258.0378; Anal. calcd for $C_{11}H_9NO_5$ (235.0481): C, 56.17; H, 3.86; N, 5.96. Found: C, 56.10; H, 3.82; N, 6.07%.



7ae

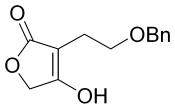
3-Benzo[1,3]dioxol-5-ylmethyl-4-hydroxy-5*H*-furan-2-one (7af): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp.: 210 °C; IR (neat): ν_{max} 2686, 1622, 1447, 1399, 1245, 1034 and 788 cm^{-1}; ^1H NMR (DMSO-D_6) δ 5.62-5.59 (2H, m), 5.51-5.49 (1H, m), 4.76 (2H, s, OCH_2O), 3.46 (2H, s, CH_2O), 2.16 (2H, s, CH_2Ar); ^{13}C NMR (DMSO-D_6, DEPT-135) δ 175.4 (C, O-*C*=O), 174.4 (C), 147.6 (C), 145.8 (C), 133.8 (C), 121.3 (CH), 109.0 (CH), 108.4 (CH), 101.1 (CH_2, O*C*H_2O), 99.1 (C), 67.1 (CH_2, O*C*H_2), 26.6 (CH_2, Ar*C*H_2); LCMS m/z 235.10 ($M+H^+$),



7af

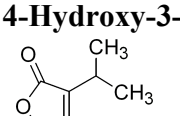
calcd $C_{12}H_{10}O_5$ 234.0528; HRMS m/z 257.0420 (M+Na), calcd $C_{12}H_{10}O_5Na$ 257.0426; Anal. calcd for $C_{12}H_{10}O_5$ (234.0528): C, 61.54; H, 4.30. Found: C, 61.48; H, 4.35%.

3-(2-Benzyloxy-ethyl)-4-hydroxy-5*H*-furan-2-one (7ag): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp.: 80 °C; IR (neat): ν_{max} 3028, 2984, 1725, 1639, 1456, 1394, 1097, 1039, 749 and 696 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 7.31-7.16 (5H, m), 4.54 (2H, s, OC*H*$_2$Ph), 4.44 (2H, s, OC*H*$_2$), 3.66 (2H, t, *J* = 5.6 Hz, OC*H*$_2$CH$_2$), 2.44 (2H, t, *J* = 5.6 Hz, OCH$_2$C*H*$_2$); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 175.5 (C, O-*C*=O), 173.8 (C), 135.8 (C), 128.6 (2 x CH), 128.4 (CH), 128.1 (2 x CH), 98.4 (C), 73.6 (CH_2), 69.5 (CH_2), 66.6 (CH_2), 22.6 (CH_2); LCMS m/z 233.05 ($M-H^+$), calcd $C_{13}H_{14}O_4$ 234.0892; HRMS m/z 257.0789 (M+Na), calcd $C_{13}H_{14}O_4Na$ 257.0790; Anal. calcd for $C_{13}H_{14}O_4$ (234.0892): C, 66.66; H, 6.02. Found: C, 66.75; H, 6.08%.



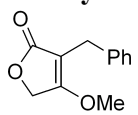
7ag

4-Hydroxy-3-isopropyl-5*H*-furan-2-one (7ah):[2] Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp.: 110 °C; IR (neat): ν_{max} 2968, 1711, 1603, 1430, 1343, 1298, 1116 and 1040 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 4.52 (2H, s, OC*H*$_2$), 2.72 (1H, septet, *J* = 6.8 Hz, C*H*(CH$_3$)$_2$), 1.19 (6H, d, *J* = 6.8 Hz, CH(C*H*$_3$)$_2$); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 176.4 (C, O-*C*=O), 172.1 (C), 105.3 (C), 66.3 (CH_2, O*C*H$_2$), 22.5 (CH), 20.0 (2 x CH_3); LCMS m/z 143.05 ($M+H^+$), calcd $C_7H_{10}O_3$ 142.0630; HRMS m/z 165.0526 (M+Na), calcd $C_7H_{10}O_3Na$ 165.0528; Anal. calcd for $C_7H_{10}O_3$ (142.0630): C, 59.14; H, 7.09. Found: C, 59.21; H, 7.03%.



7ah

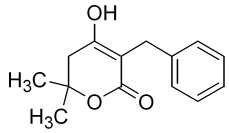
3-Benzyl-4-methoxy-5*H*-furan-2-one (8aa):[3] Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as oil. IR (neat): ν_{mlax} 1749, 1667, 1457, 1381, 1105 and 1046 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.26-7.23 (4H, m), 7.19-7.17 (1H, m), 4.65 (2H, s, OC*H*$_2$), 3.89 (3H, s, OC*H*$_3$), 3.57 (2H, s, PhC*H*$_2$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 174.6 (C, O-*C*=O), 173.2 (C), 138.9 (C), 128.4 (2 x CH), 128.2 (2 x CH), 126.2 (CH), 102.4 (C), 65.2 (CH_2, O*C*H$_2$), 57.6 (CH_3, O*C*H$_3$), 27.6 (CH_2, Ph*C*H$_2$); LCMS 205.05 m/z ($M+H^+$), calcd



8aa

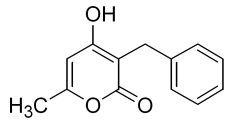
$C_{12}H_{12}O_3$ 204.0786; Anal. calcd for $C_{12}H_{12}O_3$ (204.0786): C, 70.57; H, 5.92. Found: C, 70.65; H, 5.88%.

3-Benzyl-4-hydroxy-6,6-dimethyl-5,6-dihydro-pyran-2-one (7ba): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp.: 130 °C; IR (neat): ν_{max} 2977, 2940, 2697, 1589, 1380, 1312, 1229 and 1108 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 7.24 (2H, d, *J* = 7.2 Hz), 7.19 (2H, t, *J* = 7.6 Hz), 7.09 (1H, *J* = 6.8 Hz), 4.72 (1H, br s, O-H), 3.62 (2H, s, PhC*H*$_2$), 2.55 (2H, s, RC*H*$_2$), 1.38 (6H, s, 2 x C*H*$_3$); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 169.2 (C, O-*C*=O), 165.1 (C), 140.4 (C), 127.8 (2 x CH), 127.4 (2 x CH), 125.0 (CH), 101.9 (C), 76.6 (C), 38.6 (CH_2), 28.1 (CH_2), 26.7 (2 x CH_3); LCMS m/z 233.05 ($M+H^+$), calcd $C_{14}H_{16}O_3$ 232.1099; HRMS m/z 255.0998 (M+Na), calcd $C_{14}H_{16}O_3Na$ 255.0997; Anal. calcd for $C_{14}H_{16}O_3$ (232.1099): C, 72.39; H, 6.94. Found: C, 72.45; H, 6.88%.



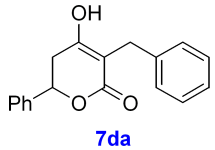
7ba

3-Benzyl-4-hydroxy-6-methyl-pyran-2-one (7ca):[4] Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp.: 166 °C; IR (neat): ν_{max} 3133, 2684, 1639, 1588, 1446, 1401, 1251 and 828 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 7.31 (2H, d, *J* = 7.6 Hz), 7.21 (2H, t, *J* = 7.2 Hz), 7.13 (1H, t, *J* = 7.2 Hz), 5.96 (1H, s, olefinic-*H*), 3.74 (2H, s, PhC*H*$_2$), 2.12 (3H, s, C*H*$_3$); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 167.3 (C, O-*C*=O), 166.5 (C), 160.3 (C), 140.2 (C), 128.4 (2 x CH), 128.0 (2 x CH), 125.7 (CH), 102.0 (C), 100.7 (CH), 28.6 (CH_2), 19.4 (CH_3); LCMS m/z 217.10 ($M+H^+$), calcd $C_{13}H_{12}O_3$ 216.0786; HRMS m/z 239.0678 (M+Na), calcd $C_{13}H_{12}O_3Na$ 239.0684; Anal. calcd for $C_{13}H_{12}O_3$ (216.0786): C, 72.21; H, 5.59. Found: C, 72.11; H, 5.63%.



7ca

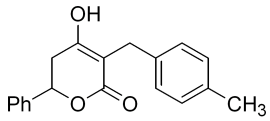
3-Benzyl-4-hydroxy-6-phenyl-5,6-dihydro-pyran-2-one (7da):[5] Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp.: 136 °C; IR (neat): ν_{max} 2998, 2686, 1600, 1448, 1399, 1244, 1034 and 791 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 7.30-7.26 (7H, m), 7.19 (2H, t, *J* = 7.2 Hz), 7.11 (1H, t, *J* = 7.2 Hz), 5.22 (1H, dd, *J* = 12.4, 4.0 Hz), 3.66 (2H, s, C*H*$_2$Ph), 2.79 (1H, dd, *J* = 13.6, 8.8 Hz), 2.59 (1H, dd, *J* = 17.2, 4.0 Hz); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops),



7da

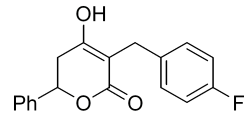
DEPT-135] δ 169.6 (C, O-*C*=O), 166.3 (C), 140.6 (C), 138.3 (C), 128.5 (2 x CH), 128.4 (3 x CH), 128.0 (2 x CH), 125.9 (2 x CH), 125.7 (CH), 103.4 (C), 76.2 (CH), 35.1 (CH_2), 28.8 (CH_2); LCMS m/z 281.10 ($M+H^+$), calcd $C_{18}H_{16}O_3$ 280.1099; HRMS m/z 303.0994 (M+Na), calcd $C_{18}H_{16}O_3Na$ 303.0997; Anal. calcd for $C_{18}H_{16}O_3$ (280.1099): C, 77.12; H, 5.75. Found: C, 77.32; H, 5.71%.

4-Hydroxy-3-(4-methyl-benzyl)-6-phenyl-5,6-dihydro-pyran-2-one (7di):[5] Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp.: 146 °C; IR (neat): ν_{max} 3160, 1641, 1586, 1435, 1401, 1254, 1117 and 994 cm^{-1}; ^1H NMR (DMSO-D_6) δ 7.55-7.35 (5H, m), 7.15 (2H, d, *J* = 8.0 Hz), 7.08 (2H, d, *J* = 8.0 Hz), 5.49 (1H, dd, *J* = 12.0, 4.0 Hz), 3.57 (2H, s), 3.01 (1H, dd, *J* = 16.0, 12.0 Hz), 2.77 (1H, br dd, *J* = 16.0, 4.0 Hz), 2.29 (3H, s); ^{13}C NMR (DMSO-D_6, DEPT-135) δ 168.0 (C, O-*C*=O), 167.0 (C), 139.7 (C), 138.4 (C), 134.8 (C), 129.0 (2 x CH), 128.9 (2 x CH), 128.7 (CH), 128.6 (2 x CH), 126.9 (2 x CH), 102.4 (C), 75.7 (CH), 35.2 (CH_2), 28.6 (CH_2), 21.1 (CH_3); HRMS m/z 317.1154 (M+Na), calcd $C_{19}H_{18}O_3Na$ 317.1154; Anal. calcd for $C_{19}H_{18}O_3$ (294.1256): C, 77.53; H, 6.16. Found: C, 77.48; H, 6.21%.



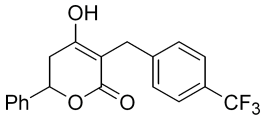
7di

3-(4-Fluoro-benzyl)-4-hydroxy-6-phenyl-5,6-dihydro-pyran-2-one (7dj):[5] Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp.: 170 °C; IR (neat): ν_{max} 3038, 2649, 1594, 1506, 1396, 1221 and 1116 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 7.36-7.31 (5H, m), 7.28-7.25 (2H, m), 6.93-6.88 (2H, m), 5.33 (1H, dd, *J* = 12.0, 4.0 Hz), 3.64 (2H, s), 2.86 (1H, dd, *J* = 17.2, 12.4 Hz), 2.64 (1H, dd, *J* = 17.2, 4.0 Hz); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 169.2 (C, O-*C*=O), 165.9 (C), 161.1 (*C*-F, d, *J* = 241.3 Hz), 138.4 (C), 136.4 (C, d, *J* = 5.1 Hz), 129.8 (2 x CH, d, *J* = 7.7 Hz), 128.5 (2 x CH), 128.4 (CH), 125.9 (2 x CH), 114.6 (2 x CH, d, *J* = 20.9 Hz), 103.6 (C), 76.2 (CH), 35.2 (CH_2), 28.0 (CH_2); LCMS m/z 299.15 ($M+H^+$), calcd $C_{18}H_{15}FO_3$ 298.1005; HRMS m/z 321.0902 (M+Na), calcd $C_{18}H_{15}FO_3Na$ 321.0903; Anal. calcd for $C_{18}H_{15}FO_3$ (298.1005): C, 72.47; H, 5.07. Found: C, 72.35; H, 5.11%.



7dj

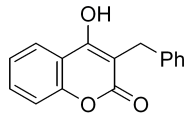
4-Hydroxy-6-phenyl-3-(4-trifluoromethyl-benzyl)-5,6-dihydro-pyran-2-one (7dk):[5]



7dk

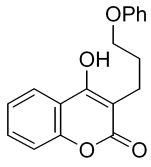
Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp.: 170 °C; IR (neat): ν_{max} 3058, 1592, 1366, 1327, 1236, 1111, 1063 and 920 cm^{-1}; ^{1}H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 7.48 (2H, d, *J* = 8.0 Hz), 7.42 (2H, d, *J* = 8.0 Hz), 7.34-7.32 (5H, m), 5.36 (1H, dd, *J* = 12.0, 4.0 Hz), 4.16 (1H, br s, O-H), 3.73 (2H, s), 2.90 (1H, dd, *J* = 17.2, 12.0 Hz), 2.69 (1H, dd, *J* = 17.2, 4.0 Hz); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 169.3 (C, O-*C*=O), 166.7 (C), 144.98 (C), 144.97 (C), 138.2 (C), 128.7 (2 x CH), 128.41 (2 x CH), 128.37 (CH), 127.7 (C, CF_3, q, *J* = 31.9 Hz), 125.8 (2 x CH), 124.7 (2 x CH, q, *J* = 3.8 Hz), 102.6 (C), 76.2 (CH), 35.0 (CH_2), 28.6 (CH_2); LCMS m/z 349.15 ($M+H^+$), calcd $C_{19}H_{15}F_3O_3$ 348.0973; HRMS m/z 371.0864 (M+Na), calcd $C_{19}H_{15}F_3O_3Na$ 371.0871; Anal. calcd for $C_{19}H_{15}F_3O_3$ (348.0973): C, 65.52; H, 4.34. Found: C, 65.58; H, 4.31%.

3-Benzyl-4-hydroxy-chromen-2-one (7ea):[6] Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp.: 205 °C; IR (neat): ν_{max} 3101, 1656, 1608, 1494, 1394, 1263, 1181, 1110 and 754 cm^{-1}; ^{1}H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 7.89 (1H, d, *J* = 8.0 Hz), 7.52 (1H, t, *J* = 8.0 Hz), 7.33-7.26 (6H, m), 7.18 (1H, t, *J* = 7.2 Hz), 3.98 (2H, s), 2.25 (1H, br s, O-H); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 164.6 (C, O-*C*=O), 161.0 (C), 152.4 (C), 139.0 (C), 131.5 (CH), 128.3 (2 x CH), 128.2 (2 x CH), 126.1 (CH), 123.7 (CH), 123.0 (CH), 116.4 (CH), 116.3 (C), 104.5 (C), 29.3 (CH_2); LCMS m/z 253.10 ($M+H^+$), calcd $C_{16}H_{12}O_3$ 252.0786; HRMS m/z 275.0685 (M+Na), calcd $C_{16}H_{12}O_3Na$ 275.0684; Anal. calcd for $C_{16}H_{12}O_3$ (252.0786): C, 76.18; H, 4.79. Found: C, 76.11; H, 4.83%.



7ea

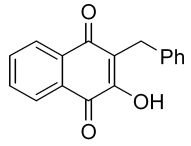
4-Hydroxy-3-(3-phenoxy-propyl)-chromen-2-one (7el): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp.: 126 °C; IR (neat): ν_{max} 2979, 1667, 1601, 1381, 1231, 1107 and 757 cm^{-1}; ^{1}H NMR (CD_3OD) δ 7.92 (1H, d, *J* = 7.6 Hz), 7.58 (1H, t, *J* = 7.2 Hz), 7.34 (2H, t, *J* = 8.0 Hz), 7.22 (2H, t, *J* = 8.0Hz), 6.88 (3H, m), 4.02 (2H, t, *J* = 6.0 Hz), 2.77 (2H, t, *J* = 7.2 Hz), 2.02 (2H, quintet, *J* = 6.4 Hz); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 164.4 (C, O-*C*=O),



7el

161.0 (C), 157.8 (C), 152.2 (C), 131.4 (CH), 129.6 (2 x CH), 123.8 (CH), 123.2 (CH), 121.6 (CH), 116.2 (CH), 116.1 (C), 114.6 (2 x CH), 103.7 (C), 67.6 (CH_2), 27.1 (CH_2), 20.3 (CH_2); LCMS 297.00 m/z (M+H^+), calcd $C_{18}H_{16}O_4$ 296.1049; Anal. calcd for $C_{18}H_{16}O4$ (296.1049): C, 72.96; H, 5.44. Found: C, 72.88; H, 5.51%.

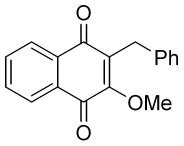
2-Benzyl-3-hydroxy-[1,4]naphthoquinone (7fa): Prepared following the procedure **A**



7fa

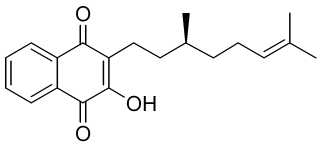
and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp.: 174 °C; IR (neat): ν_{max} 3340, 1658, 1642, 1590, 1369, 1346, 1274, 1221 and 727 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.11 (1H, d, *J* = 7.6 Hz), 8.06 (1H, d, *J* = 7.6 Hz), 7.74 (1H, t, *J* = 7.6 Hz), 7.66 (1H, t, *J* = 7.6 Hz), 7.45 (1H, s, O-H), 7.39 (2H, d, *J* = 7.6 Hz), 7.26 (2H, dt, *J* = 7.6, 2.0 Hz), 7.19-7.16 (1H, m), 3.95 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 184.3 (C), 181.6 (C), 153.0 (C), 138.9 (C), 135.0 (CH), 132.9 (CH), 132.8 (C), 129.3 (C), 129.2 (CH), 128.4 (2 x CH), 126.9 (CH), 126.3 (2 x CH), 126.1 (CH), 123.0 (C), 29.1 (CH_2); LCMS m/z 265.05 (M+H^+), calcd $C_{17}H_{12}O_3$ 264.0786; HRMS m/z 287.0686 (M+Na), calcd $C_{17}H_{12}O_3Na$ 287.0684; Anal. calcd for $C_{17}H_{12}O_3$ (264.0786): C, 77.26; H, 4.58. Found: C, 77.32; H, 4.51%.

2-Benzyl-3-methoxy-[1,4]naphthoquinone (8fa): Prepared following the procedure **B**



8fa

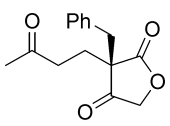
and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp.: 72 °C; IR (neat): ν_{max} 2993, 1763, 1668, 1601, 1334, 1263, 1224, 961 and 726 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.05-7.99 (2H, m), 7.69-7.62 (2H, m), 7.33 (2H, dd, *J* = 7.2, 1.2 Hz), 7.24 (2H, t, *J* = 7.2 Hz), 7.18 (1H, br t, *J* = 7.2 Hz), 4.12 (3H, s, OC*H*$_3$), 3.93 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 185.0 (C), 181.7 (C), 157.6 (C), 139.0 (C), 133.8 (CH), 133.6 (C), 133.2 (CH), 131.8 (C), 131.4 (C), 129.0 (2 x CH), 128.4 (2 x CH), 126.23 (CH), 126.19 (CH), 126.0 (CH), 61.1 (CH_3), 29.3 (CH_2); LCMS m/z 279.15 (M+H^+), calcd $C_{18}H_{14}O_3$ 278.0943; HRMS m/z 301.0845 (M+Na), calcd $C_{18}H_{14}O_3Na$ 301.0841; Anal. calcd for $C_{18}H_{14}O_3$ (278.0943): C, 77.68; H, 5.07. Found: C, 77.56; H, 5.12%.



7fm

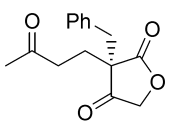
2-[(3*S*)-(+)-3,7-dimethyloct-6-en-1-yl]-3-hydroxynaphthalene-1,4-dione (7fm): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp.: 56 °C; **$[\alpha]^{25}_D$ = +3.5 (*c* 1.42, $CHCl_3$, >99% ee);** IR (neat): ν_{max} 3363, 1649, 1640, 1591, 1351,

1275, 1224 and 728 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.11 (1H, dd, *J* = 8.0, 1.2 Hz), 8.07 (1H, dd, *J* = 8.0, 1.2 Hz), 7.75 (1H, dt, *J* = 7.6, 1.6 Hz), 7.67 (1H, dt, *J* = 7.6, 1.6 Hz), 7.34 (1H, br s, O-H), 5.10 (2H, tt, *J* = 6.8, 1.2 Hz), 2.66-2.54 (2H, m), 2.07-1.91 (2H, m), 1.67 (3H, s), 1.60 (3H, s), 1.56-1.48 (2H, m), 1.45-1.33 (2H, m), 1.25-1.17 (1H, m), 0.98 (3H, d, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 184.6 (C), 181.4 (C), 152.9 (C), 134.8 (CH), 133.0 (C), 132.8 (CH), 131.0 (C), 129.4 (C), 126.7 (CH), 126.0 (CH), 125.2 (C), 124.9 (CH), 36.8 (CH_2), 35.1 (CH_2), 32.7 (CH), 25.7 (CH_3), 25.4 (CH_2), 21.0 (CH_2), 19.4 (CH_3), 17.6 (CH_3); LCMS m/z 313.20 ($M+H^+$), calcd $C_{20}H_{24}O_3$ 312.1725; Anal. calcd for $C_{20}H_{24}O_3$ (312.1725): C, 76.89; H, 7.74. Found: C, 76.95; H, 7.70%.



(–)-**10aaa**

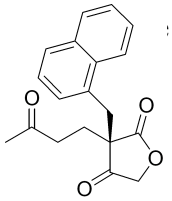
(3*R*)-(◎)-3-benzyl-3-(3-oxobutyl)furan-2,4(3*H*,5*H*)-dione (10aaa): Prepared following the procedure **E** or **F** and purified by column chromatography using EtOAc/hexane and isolated as an oil; The ee was determined by chiral-phase HPLC using a Daicel Chiralpak AS-H column (hexane/*i*-PrOH = 80:20, flow rate 0.8 mL/min, λ = 220 nm), t_R = 15.2 min (minor), t_R = 17.4 min (major); **$[\alpha]^{25}_D$ = –5.2 (*c* 0.33, $CHCl_3$, 63.6% ee);** IR (neat): ν_{max} 2926, 1756, 1714 and 1173 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.26 (3H, m), 7.10 (2H, m), 4.37 (1H, d, *J* = 16.8 Hz), 3.49 (1H, d, *J* = 16.8 Hz), 3.06 (2H, ABq, *J* = 12.8 Hz), 2.60-2.54 (2H, m), 2.23-2.09 (2H, m), 2.13 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 209.8 (C, *C*=O), 207.1 (C, *C*=O), 176.1 (C, O-*C*=O), 133.7 (C), 129.6 (2 x CH), 128.9 (2 x CH), 127.9 (CH), 73.3 (CH_2), 54.2 (C), 43.0 (CH_2), 37.8 (CH_2), 29.8 (CH_3), 28.2 (CH_2); LCMS m/z 261.15 ($M+H^+$), calcd $C_{15}H_{16}O_4$ 260.1049; HRMS m/z 283.0957 (M+Na), calcd $C_{15}H_{16}O_4Na$ 283.0946; Anal. calcd for $C_{15}H_{16}O_4$ (260.1049): C, 69.22; H, 6.20. Found: C, 69.35; H, 6.16%.



(+)-**10aaa**

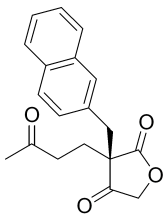
(3*S*)-(+)-3-benzyl-3-(3-oxobutyl)furan-2,4(3*H*,5*H*)-dione (10aaa): Prepared following the procedure **E** or **F** and purified by column chromatography using EtOAc/hexane and isolated as an oil; The ee was determined by chiral-phase HPLC using a Daicel Chiralpak AS-H column (hexane/*i*-PrOH = 80:20, flow rate 0.8 mL/min, λ = 220 nm), t_R = 15.2 min (major), t_R = 17.4 min (minor); **$[\alpha]^{25}_D$ = +1.4 (*c* 0.5, $CHCl_3$, 23% ee).**

(3*R*)-3-Naphthalen-1-ylmethyl-3-(3-oxo-butyl)-furan-2,4-dione (10aba): Prepared following the procedure **F** and purified by column chromatography using EtOAc/hexane


10aba

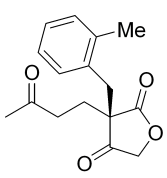
and isolated as an oil. The ee was determined by chiral-phase HPLC using a Daicel Chiralpak AS-H column (hexane/*i*-PrOH = 80:20, flow rate 0.8 mL/min, λ = 220 nm), t_R = 16.0 min (major), t_R = 20.5 min (minor); ee = 13%.; IR (neat): ν_{max} 2925, 1753, 1710, 1369, 1228, 1051 and 828 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.01 (1H, d, *J* = 8.0 Hz), 7.81 (1H, d, *J* = 8.0 Hz), 7.77 (1H, d, *J* = 8.0 Hz), 7.53 (1H, t, *J* = 7.2 Hz), 7.47 (1H, t, *J* = 8.0 Hz), 7.38 (1H, t, *J* = 7.6 Hz), 7.32 (1H, d, *J* = 6.8 Hz), 4.23 (1H, d, *J* = 16.8 Hz), 3.65 (1H, d, *J* = 13.6 Hz), 3.53 (1H, d, *J* = 13.6 Hz), 3.24 (1H, d, *J* = 16.8 Hz), 2.61-2.55 (2H, m), 2.34-2.23 (2H, m), 2.14 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 209.6 (C, *C*=O), 207.1 (C, *C*=O), 176.2 (C, O-*C*=O), 133.8 (C), 131.4 (C), 130.0 (C), 128.8 (CH), 128.7 (CH), 128.5 (CH), 126.5 (CH), 126.1 (CH), 125.3 (CH), 123.7 (CH), 73.3 (CH_2), 54.0 (C), 39.0 (CH_2), 37.9 (CH_2), 29.9 (CH_3), 28.3 (CH_2); HRMS m/z 333.1104 (M+Na), calcd $C_{19}H_{18}O_4Na$ 333.1103; Anal. calcd for $C_{19}H_{18}O_4$ (310.1205): C, 73.53; H, 5.85. Found: C, 73.65; H, 5.81%.

(3*R*)-3-Naphthalen-2-ylmethyl-3-(3-oxo-butyl)-furan-2,4-dione (10aca): Prepared following the procedure **F** and purified by column chromatography using EtOAc/hexane and isolated as an oil. The ee was determined by chiral-phase HPLC using a Daicel Chiralpak AS-H column (hexane/*i*-PrOH = 80:20, flow rate 0.2 mL/min, λ = 220 nm), t_R = 108.7 min (major), t_R = 115.0 min (minor); ee = 11%.; IR (neat): ν_{max} 1753 and 1709 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.80-7.74 (3H, m), 7.58 (1H, s), 7.48-7.46 (2H, m), 7.21 (1H, dd, *J* = 8.4, 1.6 Hz), 4.34 (1H, d, *J* = 16.8 Hz), 3.46 (1H, d, *J* = 16.8 Hz), 3.23 (2H, ABq, *J* = 12.8 Hz), 2.62-2.57 (2H, m), 2.26-2.16 (2H, m), 2.14 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 209.8 (C, *C*=O), 207.1 (C, *C*=O), 176.2 (C, O-*C*=O), 133.2 (C), 132.6 (C), 131.2 (C), 128.68 (CH), 128.64 (CH), 127.9 (CH), 127.6 (CH), 127.2 (CH), 126.4 (CH), 126.3 (CH), 73.3 (CH_2), 54.2 (C), 43.0 (CH_2), 37.8 (CH_2), 29.9 (CH_3), 28.3 (CH_2); LCMS m/z 309.05 ($M-H^+$), calcd $C_{19}H_{18}O_4$ 310.1205; Anal. calcd for $C_{19}H_{18}O_4$ (310.1205): C, 73.53; H, 5.85. Found: C, 73.45; H, 5.89%.



10aca

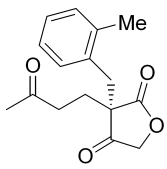
(3*R*)-3-(2-Methyl-benzyl)-3-(3-oxo-butyl)-furan-2,4-dione (10ada): Prepared following the procedure **F** and purified by column chromatography using EtOAc/hexane and isolated as an oil; The ee was



10ada

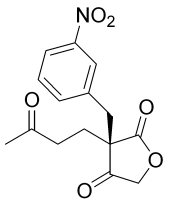
determined by chiral-phase HPLC using a Daicel Chiralcel OJ-H column (hexane/ethanol = 70:30, flow rate 1.0 mL/min, λ = 220 nm), t_R = 13.4 min (major), t_R = 14.6 min (minor); ee = 10%.; IR (neat): ν_{max} 1802 and 1755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.14-7.06 (4H, m), 4.36 (1H, d, *J* = 16.4 Hz), 3.55 (1H, d, *J* = 16.4 Hz), 3.15 (2H, ABq, *J* = 13.6 Hz), 2.62-2.47 (2H, m), 2.27 (3H, s, CH_3), 2.24-2.15 (2H, m), 2.12 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 209.6 (C, *C*=O), 207.1 (C, *C*=O), 176.5 (C, O-*C*=O), 136.8 (C), 132.2 (C), 131.1 (CH), 129.6 (CH), 127.9 (CH), 126.3 (CH), 73.2 (CH_2), 53.7 (C), 39.3 (CH_2), 37.8 (CH_2), 29.8 (CH_3), 28.2 (CH_2), 19.5 (CH_3); LCMS m/z 275.15 ($M+H^+$), calcd $C_{16}H_{18}O_4$ 274.1205; HRMS m/z 297.1101 (M+Na), calcd $C_{16}H_{18}O_4Na$ 297.1103; Anal. calcd for $C_{16}H_{18}O_4$ (274.1205): C, 70.06; H, 6.61. Found: C, 70.12; H, 6.65%.

(3*S*)-3-(2-Methyl-benzyl)-3-(3-oxo-butyl)-furan-2,4-dione (10ada): Prepared following the procedure **E** and purified by column chromatography using EtOAc/hexane and isolated as an oil; The ee was determined by chiral-phase HPLC using a Daicel Chiralcel OJ-H column (hexane/ethanol = 70:30, flow rate 1.0 mL/min, λ = 220 nm), t_R = 13.4 min (minor), t_R = 14.6 min (major); ee = 16%.



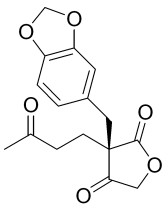
10ada

(3*R*)-3-(3-Nitro-benzyl)-3-(3-oxo-butyl)-furan-2,4-dione (10aea): Prepared following the procedure **F** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp.: 88 °C; The ee was determined by chiral-phase HPLC using a Daicel Chiralcel OJ-H column (hexane/ethanol = 70:30, flow rate 1.0 mL/min, λ = 220 nm), t_R = 44.0 min (minor), t_R = 50.1 min (major); ee = 15%.; IR (neat): ν_{max} 1750, 1712, 1531, 1355, 1076 and 1036 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.10 (1H, td, *J* = 7.2, 2.4 Hz), 7.93 (1H, br s), 7.46-7.45 (2H, m), 4.50 (1H, d, *J* = 17.2 Hz), 3.74 (1H, d, *J* = 17.2 Hz), 3.14 (2H, s), 2.67-2.53 (2H, m), 2.22-2.09 (2H, m), 2.12 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 208.7 (C, *C*=O), 207.0 (C, *C*=O), 175.3 (C, O-*C*=O), 148.3 (C), 135.9 (C), 135.8 (CH), 129.8 (CH), 124.6 (CH), 122.9 (CH), 73.1 (CH_2), 53.4 (C), 40.9 (CH_2), 37.3 (CH_2), 29.8 (CH_3), 28.4 (CH_2); LCMS m/z 306.15 ($M+H^+$), calcd $C_{15}H_{15}NO_6$ 305.0899; HRMS m/z 328.0789 (M+Na), calcd $C_{15}H_{15}NO_6Na$ 328.0797; Anal. calcd for $C_{15}H_{15}NO_6$ (305.0899): C, 59.01; H, 4.95; N, 4.59. Found: C, 59.12; H, 4.88; N, 4.65%.



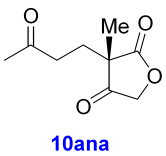
10aea

(3*R*)-3-Benzo[1,3]dioxol-5-ylmethyl-3-(3-oxo-butyl)-furan-2,4-dione (10afa):

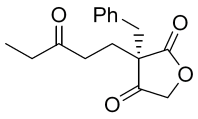

10afa

Prepared following the procedure **F** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp.: 114 °C; The ee was determined by chiral-phase HPLC using a Daicel Chiralpak AS-H column (hexane/ethanol = 80:20, flow rate 1.0 mL/min, λ = 220 nm), t_R = 17.7 min (major), t_R = 26.0 min (minor); ee = 8%.; IR (neat): ν_{max} 2944, 1749, 1717, 1492, 1447, 1250, 1224, 1040, 928 and 814 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.69 (1H, d, *J* = 8.0 Hz), 6.58-6.55 (2H, m), 5.93 (2H, s, OC*H*$_2$O), 4.42 (1H, d, *J* = 16.4 Hz), 3.69 (1H, d, *J* = 16.8 Hz), 2.98 (2H, ABq, *J* = 9.6 Hz), 2.58-2.53 (2H, m), 2.18-2.11 (1H, m), 2.13 (3H, s, CH_3), 2.09-2.03 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 210.0 (C, *C*=O), 207.2 (C, *C*=O), 176.2 (C, O-*C*=O), 147.8 (C), 147.2 (C), 127.2 (C), 122.9 (CH), 109.9 (CH), 108.5 (CH), 101.2 (CH_2, O*C*H$_2$O), 73.4 (CH_2), 54.2 (C), 42.7 (CH_2), 37.7 (CH_2), 29.8 (CH_3), 28.1 (CH_2); LCMS m/z 303.10 ($M-H^+$), calcd $C_{16}H_{16}O_6$ 304.0947; HRMS m/z 327.0834 (M+Na), calcd $C_{16}H_{16}O_6Na$ 327.0845; Anal. calcd for $C_{16}H_{16}O_6$ (304.0947): C, 63.15; H, 5.30. Found: C, 63.25; H, 5.28%.

3-Methyl-3-(3-oxo-butyl)-furan-2,4-dione (10ana): Prepared following the procedure **E** or **F** and purified by column chromatography using EtOAc/hexane and isolated as oil. IR (neat): ν_{max} 2922, 1756, 1712, 1099 and 1043 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.64 (2H, ABq, *J* = 16.8 Hz), 2.51 (2H, t, *J* = 8.0 Hz), 2.08 (3H, s, CH_3), 2.03-1.91 (2H, m), 1.27 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 209.0 (C, *C*=O), 207.4 (C, *C*=O), 176.8 (C, O-*C*=O), 72.2 (CH_2), 46.4 (C), 37.2 (CH_2), 29.8 (CH_3), 28.1 (CH_2), 20.0 (CH_3); LCMS m/z 183.10 ($M-H^+$), calcd $C_9H_{12}O_4$ 184.0736; HRMS m/z 207.0630 (M+Na), calcd $C_9H_{12}O_4Na$ 207.0633.

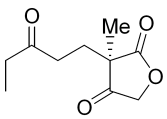

10ana

(3*S*)-3-benzyl-3-(3-oxopentyl)furan-2,4(3*H*,5*H*)-dione (10aab): Prepared following the procedure **E** (first step from eq. 4) and purified by column chromatography using EtOAc/hexane and isolated as an oil. The ee was determined by chiral-phase HPLC using a Daicel Chiralpak AS-H column (hexane/iso-propanol = 85:15, flow rate 0.25 mL/min, λ = 220 nm), t_R = 48.2 min (minor), t_R = 51.8 min (major); IR (neat): ν_{max} 1799, 1755, 1713, 1078, 1047 and 703 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.27-7.26 (3H, m), 7.10 (2H, d, *J* = 4.4 Hz), 4.38 (1H, d, *J* = 16.8 Hz), 3.49 (1H, d, *J* = 16.8 Hz), 3.06 (2H, ABq, *J* = 12.8 Hz), 2.59-2.48 (2H, m),


10aab

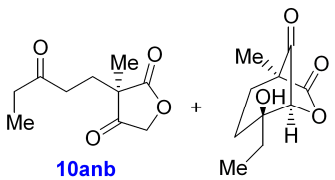
2.40 (2H, q, *J* = 7.2 Hz), 2.23-2.06 (2H, m), 1.02 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 210.0 (C, C=O), 209.8 (C, C=O), 176.2 (C, O-C=O), 133.6 (C), 129.5 (2 x CH), 128.8 (2 x CH), 127.8 (CH), 73.3 (CH_2), 54.2 (C), 43.1 (CH_2), 36.4 (CH_2), 35.8 (CH_2), 28.2 (CH_2), 7.5 (CH_3); LCMS m/z 275.00 ($M+H^+$), calcd $C_{16}H_{18}O_4$ 274.1205. Anal. calcd for $C_{16}H_{18}O_4$ (274.1205): C, 70.06; H, 6.61. Found: C, 70.18; H, 6.65%.

3-Methyl-3-(3-oxo-pentyl)-furan-2,4-dione (10anb):[7] Prepared following the procedure **E (first step from eq. 4)** and purified by column chromatography using EtOAc/hexane and isolated as oil. IR (neat): ν_{max} 1800, 1754, 1711, 1377 and 1042 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.70 (2H, ABq, *J* = 16.8 Hz), 2.54 (2H, t, *J* = 7.6 Hz), 2.41 (2H, q, *J* = 7.2 Hz), 2.12-1.97 (2H, m), 1.33 (3H, s, CH_3), 1.03 (3H, t, *J* = 7.2 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 210.3 (C, *C*=O), 209.0 (C, *C*=O), 176.8 (C, O-*C*=O), 72.3 (CH_2), 46.6 (C), 36.03 (CH_2), 35.94 (CH_2), 28.3 (CH_2), 20.4 (CH_3), 7.6 (CH_3); LCMS m/z 199.15 ($M+H^+$), calcd $C_{10}H_{14}O_4$ 198.0892; HRMS m/z 221.0787 (M+Na), calcd $C_{10}H_{14}O_4Na$ 221.0790.



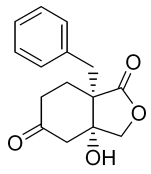
10anb

3-Methyl-3-(3-oxo-pentyl)-furan-2,4-dione (10anb) and 4-Ethyl-4-hydroxy-1-methyl-6-oxa-bicyclo[3.2.1]octane-7,8-dione (13anb): Prepared following the procedure **E (second step from Scheme 3)** and purified by column chromatography using EtOAc/hexane and isolated as oil. IR (neat): ν_{max} 2936, 1805, 1758, 1711, 1377 and 1043 cm^{-1}; ^{1}H NMR ($CDCl_3$, 1:1 mixture of **10anb/13anb**, data for **13anb**) δ 4.35 (1H, s), 2.57-2.53 (2H, m), 2.11-1.97 (2H, m), 1.84-1.73 (2H, m), 1.25 (3H, s), 1.00 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135, 1:1 mixture of **10anb/13anb**, data for **13anb**) δ 206.3 (C, *C*=O), 173.6 (C, O-*C*=O), 83.7 (CH), 80.1 (C), 51.2 (C), 35.2 (CH_2), 32.7 (CH_2), 30.4 (CH_2), 11.6 (CH_3), 6.6 (CH_3); LCMS m/z 199.15 ($M+H^+$), calcd $C_{10}H_{14}O_4$ 198.0892.



10anb [1:1] 13anb

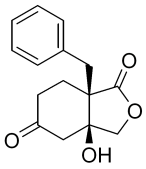
(3a*R*,7a*S*)-(+)-7a-benzyl-3a-hydroxytetrahydro-2-benzofuran-1,5(3*H*,4*H*)-dione (11aaa): Prepared following the procedure **F** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp. 152 °C.; The ee was determined by chiral-phase HPLC using a Daicel Chiralcel OD-H column (hexane/*i*-PrOH = 80:20, flow rate 0.5 mL/min, λ = 220 nm), t_R = 20.9 min (minor), t_R = 23.8 min (major). **$[\alpha]^{25}_D$ = +16.2 (*c* 0.82, $CHCl_3$, 92%**



(+)-11aaa

ee); IR (neat): ν_{max} 3312, 1766, 1710, 1188, 1113, 1033 and 704 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 7.34-7.26 (5H, m), 3.92 (2H, s), 3.13 (2H, ABq, *J* = 14.0 Hz), 2.64 (2H, ABq, *J* = 15.6 Hz), 2.39 (1H, br s, O-H), 2.26 (2H, t, *J* = 6.4 Hz), 2.14-2.00 (2H, m); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 209.1 (C, *C*=O), 178.6 (C, O-*C*=O), 135.8 (C), 130.7 (2 x CH), 128.3 (2 x CH), 127.2 (CH), 78.5 (C), 74.8 (CH_2), 49.8 (C), 49.2 (CH_2), 37.5 (CH_2), 36.3 (CH_2), 28.3 (CH_2); HRMS m/z 283.0947 (M+Na), calcd $C_{15}H_{16}O_4Na$ 283.0946; Anal. calcd for $C_{15}H_{16}O_4$ (260.1049): C, 69.22; H, 6.20. Found: C, 69.15; H, 6.25%.

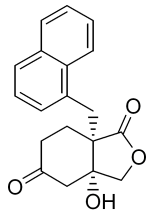
(3a*S*,7a*R*)-(+)-7a-benzyl-3a-hydroxytetrahydro-2-benzofuran-1,5(3*H*,4*H*)-dione



(–)-11aaa

(11aaa): Prepared following the procedure **E** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp. 152 °C.; The ee was determined by chiral-phase HPLC using a Daicel Chiralcel OD-H column (hexane/*i*-PrOH = 80:20, flow rate 0.5 mL/min, λ = 220 nm), t_R = 20.9 min (major), t_R = 23.8 min (minor). **$[\alpha]^{25}_D$ = –14.5 (*c* 1.71, $CHCl_3$, 72% ee)**.

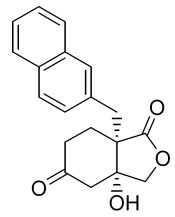
(3a*R*,7a*S*)-(+)-3a-hydroxy-7a-(naphthalen-1-ylmethyl)tetrahydro-2-benzofuran-



(+)-11aba

1,5(3*H*,4*H*)-dione (11aba): Prepared following the procedure **F** and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp.: 174 °C; The ee was determined by chiral-phase HPLC using a Daicel Chiralcel OJ-H column (hexane/EtOH = 80:20, flow rate 0.75 mL/min, λ = 220 nm), t_R = 30.6 min (major), t_R = 39.3 min (minor). **$[\alpha]^{25}_D$ = +24.4 (*c* 0.23, $CHCl_3$, 81% ee);** IR (neat): ν_{max} 3398, 1743, 1723, 1405, 1196, 1159, 1014 and 781 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 8.19 (1H, d, *J* = 8.4 Hz), 7.85 (1H, d, *J* = 8.4 Hz), 7.76 (1H, d, *J* = 8.4 Hz), 7.54-7.37 (4H, m), 4.23 (1H, d, *J* = 9.6 Hz), 4.00 (1H, d, *J* = 9.6 Hz), 3.67 (2H, ABq, *J* = 14.8 Hz), 3.04 (2H, s), 2.22-2.07 (2H, m), 2.02-1.89 (2H, m); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 209.1 (C, *C*=O), 178.5 (C, O-*C*=O), 133.8 (C), 132.9 (C), 132.1 (C), 129.2 (CH), 128.8 (CH), 128.0 (CH), 126.0 (CH), 125.5 (CH), 125.0 (CH), 123.8 (CH), 78.6 (C), 74.6 (CH_2), 49.9 (C), 48.9 (CH_2), 36.5 (CH_2), 31.6 (CH_2), 27.5 (CH_2); HRMS m/z 333.1119 (M+Na), calcd $C_{19}H_{18}O_4Na$ 333.1103; Anal. calcd for $C_{19}H_{18}O_4$ (310.1205): C, 73.53; H, 5.85. Found: C, 73.64; H, 5.80%.

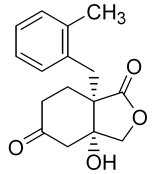
(3a*R*,7a*S*)-(+)-3a-hydroxy-7a-(naphthalen-2-ylmethyl)tetrahydro-2-benzofuran-1,5(3*H*,4*H*)-dione (11aca): Prepared following the procedure **F** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 144 °C; The ee was determined by chiral-phase HPLC using a Daicel Chiralcel OJ-H column (hexane/*i*-PrOH = 60:40, flow rate 0.5 mL/min, λ = 220 nm), t_R = 42.8 min (minor), t_R = 101.4 min (major).



(+)-11aca

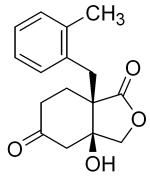
$[\alpha]^{25}_D$ = +10.6 (*c* 0.34, $CHCl_3$, 70.2% ee); IR (neat): ν_{max} 3431, 3324, 1769, 1708, 1098 and 1014 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 7.79-7.76 (4H, m), 7.50-7.44 (3H, m), 3.93 (2H, ABq, *J* = 9.2 Hz), 3.36 (1H, d, *J* = 14.0 Hz), 3.24 (1H, d, *J* = 14.0 Hz), 2.64 (2H, ABq, *J* = 15.2 Hz), 2.27-2.24 (2H, m), 2.19-2.12 (1H, m), 2.07-2.02 (1H, m); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 209.1 (C, *C*=O), 178.9 (C, O-*C*=O), 133.4 (C), 133.1 (C), 132.3 (C), 129.4 (CH), 128.7 (CH), 127.6 (CH), 127.5 (CH), 127.4 (CH), 126.0 (CH), 125.7 (CH), 78.2 (C), 74.8 (CH_2), 49.9 (CH_2), 48.7 (C), 37.4 (CH_2), 36.2 (CH_2), 28.1 (CH_2); LCMS m/z 293.15 ($M+H^+-H_2O$), calcd $C_{19}H_{18}O_4$ 310.1205; Anal. calcd for $C_{19}H_{18}O_4$ (310.1205): C, 73.53; H, 5.85. Found: C, 73.61; H, 5.80%.

(3a*R*,7a*S*)-(+)-3a-hydroxy-7a-(2-methylbenzyl)tetrahydro-2-benzofuran-1,5(3*H*,4*H*)-dione (11ada): Prepared following the procedure **F** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 160 °C; The ee was determined by chiral-phase HPLC using a Daicel Chiralcel OJ-H column (hexane/*i*-PrOH = 90:10, flow rate 0.5 mL/min, λ = 220 nm), t_R = 91.9 min (minor), t_R = 98.9 min (major); **$[\alpha]^{25}_D$ = +2.8 (*c* 0.666, $CHCl_3$, 60.4% ee);** IR (neat): ν_{max} 3324, 1777, 1711, 1102 and 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.26 (1H, d, *J* = 6.4 Hz), 7.18-7.13 (3H, m), 4.15 (1H, d, *J* = 9.2 Hz), 4.02 (1H, d, *J* = 9.2 Hz), 3.54 (1H, br s, O-H), 3.19 (2H, ABq, *J* = 14.4 Hz), 2.70 (2H, ABq, *J* = 15.6 Hz), 2.36 (3H, s, CH_3), 2.33-2.28 (2H, m), 2.14-2.11 (2H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 208.9 (C, *C*=O), 177.9 (C, O-*C*=O), 137.2 (C), 133.7 (C), 131.2 (CH), 130.9 (CH), 127.4 (CH), 125.9 (CH), 79.5 (C), 74.5 (CH_2), 49.7 (C), 49.6 (CH_2), 36.5 (CH_2), 33.3 (CH_2), 27.9 (CH_2), 19.9 (CH_3); LCMS m/z 275.15 ($M+H^+$), calcd $C_{16}H_{18}O_4$ 274.1205; HRMS m/z 297.1103 (M+Na), calcd $C_{16}H_{18}O_4Na$ 297.1103; Anal. calcd for $C_{16}H_{18}O_4$ (274.1205): C, 70.06; H, 6.61. Found: C, 70.12; H, 6.67%.



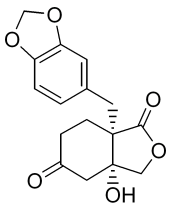
(+)-11ada

(3a*S*,7a*R*)-(–)-3a-hydroxy-7a-(2-methylbenzyl)tetrahydro-2-benzofuran-1,5(3*H*,4*H*)-dione (11ada): Prepared following the procedure **E** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 160 °C; The ee was determined by chiral-phase HPLC using a Daicel Chiralcel OJ-H column (hexane/*i*-PrOH = 90:10, flow rate 0.5 mL/min, λ = 220 nm), t_R = 91.9 min (major), t_R = 98.9 min (minor); **$[\alpha]^{25}_D$ = –2.5 (*c* 0.2, $CHCl_3$, 50.0% ee).**



(–)-11ada

(3a*R*,7a*S*)-(+)-3a-hydroxy-7a-(3-nitrobenzyl)tetrahydro-2-benzofuran-1,5(3*H*,4*H*)-dione (11aea): Prepared following the procedure **F** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 146 °C; The ee was determined by chiral-phase HPLC using a Daicel Chiralcel OJ-H column (hexane/ethanol = 80:20, flow rate 1.0 mL/min, λ = 220 nm), t_R = 13.9 min (minor), t_R = 19.5 min (major). **$[\alpha]^{25}_D$ = +14.4 (*c* 0.833, $CHCl_3$, 65% ee);** IR (neat): ν_{max} 3363, 2500, 1761, 1712, 1532, 1353, 1117, 1028, 1008 and 657 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 8.27 (1H, s), 8.15 (1H, d, *J* = 8.0 Hz), 7.73 (1H, d, *J* = 7.6 Hz), 7.55-7.50 (1H, m), 4.02 (1H, d, *J* = 9.2 Hz), 3.95 (1H, d, *J* = 9.2 Hz), 3.37 (1H, d, *J* = 14.0 Hz), 3.15 (1H, d, *J* = 14.0 Hz), 2.70 (2H, ABq, *J* = 15.6 Hz), 2.38-2.29 (2H, m), 2.11-2.03 (2H, m); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 208.4 (C, C=O), 178.4 (C, O-C=O), 147.6 (C), 137.9 (C), 136.9 (CH), 128.8 (CH), 125.4 (CH), 121.8 (CH), 77.4 (C), 74.9 (CH_2), 49.6 (C), 48.8 (CH_2), 36.4 (CH_2), 35.4 (CH_2), 27.4 (CH_2); LCMS m/z 306.15 ($M+H^+$), calcd $C_{15}H_{15}NO_6$ 305.0899; HRMS m/z 328.0804 (M+Na), calcd $C_{15}H_{15}NO_6Na$ 328.0797; Anal. calcd for $C_{15}H_{15}NO_6$ (305.0899): C, 59.01; H, 4.95; N, 4.59. Found: C, 58.92; H, 4.99; N, 4.52%.

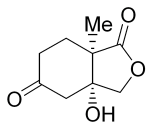


(+)-11afa

(3a*R*,7a*S*)-(+)-7a-(1,3-benzodioxol-5-ylmethyl)-3a-hydroxytetrahydro-2-benzofuran-1,5(3*H*,4*H*)-dione (11afa): Prepared following the procedure **F** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 200 °C; The ee was determined by chiral-phase HPLC using a Daicel Chiralcel OJ-H column (hexane/ethanol = 70:30, flow rate 1.0 mL/min, λ = 220 nm), t_R = 19.6 min (minor), t_R = 22.7 min (major). **$[\alpha]^{25}_D$ = +4.9 (*c* 1.11, $CHCl_3$, 40% ee);** IR (neat): ν_{max} 3372, 1736, 1726, 1493, 1249, 1197 and 1037 cm^{-1}; ^1H NMR ($CDCl_3$)

δ 6.86 (1H, s), 6.78 (2H, m), 5.95 (2H, s, OC*H*$_2$O), 3.93 (2H, ABq, *J* = 19.2 Hz), 3.09 (2H, ABq, *J* = 14.0 Hz), 2.67 (2H, ABq, *J* = 16.4 Hz), 2.31 (2H, t, *J* = 6.8 Hz), 2.12-2.07 (2H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 208.5 (C), 178.4 (C), 147.7 (C), 146.9 (C), 129.1 (C), 123.7 (CH), 110.9 (CH), 108.3 (CH), 101.1 (CH_2, O*C*H$_2$O), 79.1 (C), 74.9 (CH_2), 50.0 (C), 49.4 (CH_2), 37.6 (CH_2), 36.2 (CH_2), 28.6 (CH_2); LCMS m/z 305.05 (M+H$^+$), calcd $C_{16}H_{16}O_6$ 304.0947; HRMS m/z 327.0847 (M+Na), calcd $C_{16}H_{16}O_6Na$ 327.0845; Anal. calcd for $C_{16}H_{16}O_6$ (304.0947): C, 63.15; H, 5.30. Found: C, 63.11; H, 5.34%.

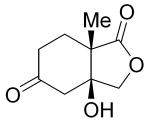
(3a*R*,7a*R*)-3a-Hydroxy-7a-methyl-tetrahydro-isobenzofuran-1,5-dione (11ana):



(3a*R*,7a*R*)-11ana

Prepared following the procedure **F** and purified by column chromatography using EtOAc/hexane and isolated a solid. Mp 126 °C; The enantiomeric excess (ee) of **11ana** was determined via enone product **12ana** by chiral stationary phase HPLC analysis as shown below (see preparation of (–)-**12ana**); IR (neat): ν_{max} 3434, 1765, 1704, 1096 and 1013 cm^{-1}; ^{1}H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 4.16 (1H, d, *J* = 9.6 Hz), 4.06 (1H, d, *J* = 9.2 Hz), 3.00 (1H, br s, O-H), 2.64 (2H, ABq, *J* = 15.2 Hz), 2.51-2.32 (2H, m), 2.08-1.97 (2H, m), 1.38 (3H, s, CH_3); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 208.4 (C), 180.1 (C), 78.1 (C), 74.9 (CH_2), 47.7 (CH_2), 45.7 (C), 36.0 (CH_2), 30.1 (CH_2), 15.6 (CH_3); LCMS m/z 183.00 (M-H), calcd $C_9H_{12}O_4$ 184.0736; HRMS m/z 207.0624 (M+Na), calcd $C_9H_{12}O_4Na$ 207.0633.

(3a*S*,7a*S*)-3a-Hydroxy-7a-methyl-tetrahydro-isobenzofuran-1,5-dione (11ana):



(3a*S*,7a*S*)-11ana

Prepared following the procedure **E** and purified by column chromatography using EtOAc/hexane and isolated a solid. Mp 126 °C; The enantiomeric excess (ee) of **11ana** was determined via enone product **12ana** by chiral stationary phase HPLC analysis as shown below (see preparation of (+)-**12ana**); IR (neat): ν_{max} 3434, 1765, 1704, 1096 and 1013 cm^{-1}; ^{1}H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 4.16 (1H, d, *J* = 9.6 Hz), 4.06 (1H, d, *J* = 9.2 Hz), 3.00 (1H, br s, O-H), 2.64 (2H, ABq, *J* = 15.2 Hz), 2.51-2.32 (2H, m), 2.08-1.97 (2H, m), 1.38 (3H, s, CH_3); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 208.4 (C, *C*=O), 180.1 (C, O-*C*=O), 78.1 (C), 74.9 (CH_2), 47.7 (CH_2), 45.7 (C), 36.0

(CH_2), 30.1 (CH_2), 15.6 (CH_3); LCMS m/z 183.00 (M-H), calcd $C_9H_{12}O_4$ 184.0736; HRMS m/z 207.0624 (M+Na), calcd $C_9H_{12}O_4Na$ 207.0633.

(3a*S*,7a*R*)-(–)-7a-benzyl-3a-hydroxy-4-methyltetrahydro-2-benzofuran-1,5(3*H*,4*H*)-dione (11aab): Prepared following the procedure **E** (second step from eq. 4) and purified by column chromatography using EtOAc/hexane and isolated as a solid. The enantiomeric excess (ee) of **11aab** was determined via enone product **12aab** by chiral stationary phase HPLC analysis as shown below (see preparation of (+)-**12aab**); **$[\alpha]^{25}_D$ = –4.2 (*c* 0.5, $CHCl_3$, 86% ee);** IR (neat): ν_{max} 3302, 1762, 1709, 1669, 1188, 1114 and 742 cm^{-1}; ^1H NMR [$CDCl_3$, 1.5:1 mixture of isomers] δ 7.54-7.52 (2H, m), 7.36-7.27 (6H, m), 7.25-7.22 (2H, m), 4.16 (1H, d, *J* = 9.2 Hz), 4.07 (1H, d, *J* = 10.4 Hz), 3.99 (1H, d, *J* = 10.4 Hz), 3.78 (1H, d, *J* = 9.6 Hz), 3.72 (1H, br s, O-H), 3.50 (1H, br s, O-H), 3.37 (1H, d, *J* = 14.0 Hz), 3.25 (1H, d, *J* = 14.4 Hz), 3.20 (1H, d, *J* = 14.0 Hz), 3.00 (1H, d, *J* = 14.0 Hz), 2.83 (1H, q, *J* = 6.8 Hz), 2.69 (1H, q, *J* = 6.4 Hz), 2.44-2.39 (2H, m), 2.27-2.18 (2H, m), 2.15-2.04 (3H, m), 1.80-1.72 (1H, m), 1.14 (3H, d, *J* = 6.4 Hz), 1.12 (3H, d, *J* = 6.8 Hz); ^{13}C NMR [$CDCl_3$, DEPT-135, 1.5:1 mixture of isomers] δ 210.8 (C, *C*=O), 208.9 (C, *C*=O), 179.7 (C, O-*C*=O), 178.1 (C, O-*C*=O), 136.3 (C), 135.2 (C), 130.8 (2 x CH), 130.4 (2 x CH), 128.5 (2 x CH), 128.3 (2 x CH), 127.3 (CH), 127.2 (CH), 82.8 (C), 82.1 (C), 73.4 (CH_2), 72.1 (CH_2), 51.0 (C), 50.3 (C), 49.6 (CH), 48.7 (CH), 39.0 (CH_2), 36.4 (CH_2), 36.3 (CH_2), 35.7 (CH_2), 28.5 (CH_2), 27.7 (CH_2), 7.12 (CH_3), 7.08 (CH_3); LCMS m/z 273.35 ($M–H^+$), calcd $C_{16}H_{18}O_4$ 274.1205. Anal. calcd for $C_{16}H_{18}O_4$ (274.1205): C, 70.06; H, 6.61. Found: C, 70.12; H, 6.57%.

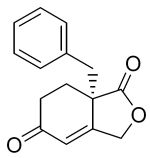
(–)-11aab

(3a*S*,7a*S*)-3a-Hydroxy-4,7a-dimethyl-tetrahydro-isobenzofuran-1,5-dione (11anb): Prepared following the procedure **E** and purified by column chromatography using EtOAc/hexane and isolated as a solid. mp 144 °C; The enantiomeric excess (ee) of **11anb** was determined via enone product **12anb** by chiral stationary phase HPLC analysis as shown below (see preparation of (+)-**12anb**); IR (neat): ν_{max} 1666, 1602, 1496, 1381, 1233 and 757 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (three drops), 3:1 mixture of isomers] δ 4.24 (1H, d, *J* = 9.6 Hz), 4.14 (1H, d, *J* = 10.4 Hz), 4.06 (1H, d, *J* = 9.6 Hz), 3.99 (1H, d, *J* = 10.8 Hz), 3.42 (2H, br s, 2 x O-H), 2.75 (1H, q, *J* = 6.8 Hz), 2.63-2.55 (2H, m), 2.42-2.33 (3H, m), 2.31-2.24 (1H,

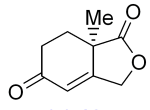
(3aS,7aS)-11anb

m), 2.06-2.00 (1H, m), 1.94-1.87 (1H, m), 1.84 (1H, dt, *J* = 14.0, 4.0 Hz), 1.45 (3H, s, CH_3), 1.32 (3H, s, CH_3), 1.14 (3H, d, *J* = 7.2 Hz), 1.11 (3H, d, *J* = 7.2 Hz); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135, 3:1 mixture of isomers] δ 210.8 (C), 208.8 (C), 180.6 (C), 180.2 (C), 82.0 (C), 80.5 (C), 73.2 (CH_2), 72.6 (CH_2), 49.3 (CH), 49.2 (CH), 47.1 (C), 46.1 (C), 35.9 (CH_2), 35.8 (CH_2), 30.7 (CH_2), 29.5 (CH_2), 18.3 (CH_3), 13.7 (CH_3), 7.5 (CH_3), 6.7 (CH_3); LCMS m/z 199.15 (M+H), calcd $C_{10}H_{14}O_4$ 198.0892; HRMS m/z 221.0786 (M+Na), calcd $C_{10}H_{14}O_4Na$ 221.0790.

(7a*S*)-(–)-7a-benzyl-7,7a-dihydro-2-benzofuran-1,5(3*H*,6*H*)-dione(12aaa): Prepared following the procedure **G** and purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 160 °C; The ee was determined by chiral-phase HPLC using a Daicel Chiralpak AS-H column (hexane/*i*-PrOH = 70:30, flow rate 1.0 mL/min, λ = 254 nm), t_R = 29.4 min (minor), t_R = 46.5 min (major). **[α]$^{25}_D$ = ◎342.7 (*c* 0.566, $CHCl_3$, 92.6% ee);** IR (neat): ν_{max} 2923, 1781, 1674, 1212, 1121, 1029 and 1009 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.32-7.31 (3H, m), 7.19-7.16 (2H, m), 6.02 (1H, s, olefinic-*H*), 4.52 (1H, d, *J* = 14.4 Hz), 3.70 (1H, dd, *J* = 14.4, 2.0 Hz), 3.20 (2H, ABq, *J* = 12.8 Hz), 2.76-2.67 (1H, m), 2.61-2.55 (1H, m), 2.41 (1H, dd, *J* = 13.6, 5.2 Hz), 2.14 (1H, dt, *J* = 13.6, 5.6 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 196.3 (C, C=O), 177.0 (C, O-C=O), 161.1 (C), 134.3 (C), 129.5 (2 x CH), 128.9 (2 x CH), 128.0 (CH), 123.2 (CH), 69.2 (CH_2), 47.8 (C), 42.2 (CH_2), 32.7 (CH_2), 29.7 (CH_2); LCMS m/z 243.05 (M+H$^+$), calcd $C_{15}H_{14}O_3$ 242.0943; HRMS m/z 265.0841 (M+Na), calcd $C_{15}H_{14}O_3Na$ 265.0841; Anal. calcd for $C_{15}H_{14}O_3$ (242.0943): C, 74.36; H, 5.82. Found: C, 74.45; H, 5.78%.


(–)-12aaa

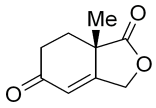
(7a*R*)-(–)-7a-methyl-7,7a-dihydro-2-benzofuran-1,5(3*H*,6*H*)-dione (12ana): Prepared following the procedure **G** and purified by column chromatography using EtOAc/hexane and isolated as an oil. The ee was determined by chiral-phase HPLC using a Daicel Chiralcel OJ-H column (hexane/ethanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 22.3 min (minor), t_R = 25.9 min (major). **[α]$^{25}_D$ = ◎56.6 (*c* 0.416, $CHCl_3$, 47.4% ee);** IR (neat): ν_{max} 3147, 2684, 1786, 1665, 1638, 1448, 1401 and 1250 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.98 (1H, d, *J* = 0.8 Hz), 5.08 (1H, dd, *J* = 14.4, 2.0 Hz), 4.91 (1H, dd, *J* = 14.4, 0.8 Hz), 2.65-2.51 (2H, m), 2.26 (1H, ddd, *J* = 13.6, 4.8, 2.8 Hz), 2.11 (1H, dt, *J* = 13.2, 6.8 Hz), 1.55 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$,



(–)-12ana

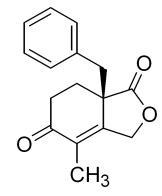
DEPT-135) δ 196.3 (C, C=O), 177.4 (C, O-C=O), 161.5 (C), 122.3 (CH), 68.1 (CH_2), 41.3 (C), 32.6 (CH_2), 29.5 (CH_2), 20.8 (CH_3); LCMS m/z 167.05 ($M+H^+$), calcd $C_9H_{10}O_3$ 166.0630. Anal. calcd for $C_9H_{10}O_3$ (166.0630): C, 65.05; H, 6.07. Found: C, 65.12; H, 5.98%.

(*S*)-(+)-7a-methyl-7,7a-dihydro-2-benzofuran-1,5(3*H*,6*H*)-dione (12ana): Prepared following the procedure **G** and purified by column chromatography using EtOAc/hexane and isolated as an oil. The ee was determined by chiral-phase HPLC using a Daicel Chiralcel OJ-H column (hexane/ethanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 22.3 min (major), t_R = 25.9 min (minor). **$[\alpha]^{25}_D$ = +20.3 (*c* 0.583, $CHCl_3$, 30.0% ee)**.



(+)-12ana

(*S*)-(+)-4,7a-dimethyl-7,7a-dihydro-2-benzofuran-1,5(3*H*,6*H*)-dione (12anb): Prepared following the procedure **G** and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 90 °C; The ee was determined by chiral-phase HPLC using a Daicel Chiralcel OJ-H column (hexane/ethanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 17.2 min (major), t_R = 19.2 min (minor). **$[\alpha]^{25}_D$ = +129.5 (*c* 0.666, $CHCl_3$, 72% ee);** IR (neat): ν_{max} 1780, 1668, 1353, 1185, 1103 and 1006 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.00 (2H, s), 2.68-2.53 (2H, m), 2.22 (1H, ddd, *J* = 13.2, 5.2, 2.4 Hz), 2.10 (1H, dt, *J* = 13.6, 6.0 Hz), 1.74 (3H, s, CH_3), 1.52 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 196.5 (C, C=O), 178.2 (C, O-C=O), 154.4 (C), 128.7 (C), 67.2 (CH_2), 41.2 (C), 32.4 (CH_2), 29.4 (CH_2), 21.1 (CH_3), 10.7 (CH_3); HRMS m/z 203.0688 (M+Na), calcd $C_{10}H_{12}O_3Na$ 203.0684.



(+)-12aab

(7a*R*)-(+)-7a-benzyl-4-methyl-7,7a-dihydro-2-benzofuran-1,5(3*H*,6*H*)-dione (12aab): Prepared following the procedure **G** and purified by column chromatography using EtOAc/hexane and isolated as a solid. The ee was determined by chiral-phase HPLC using a Daicel Chiralpak AS-H column (hexane/ethanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 13.5 min (major), t_R = 23.6 min (minor). **$[\alpha]^{25}_D$ = +169.4 (*c* 0.633, $CHCl_3$, 86% ee);** IR (neat): ν_{max} 1772, 1666, 1445, 1361, 1149, 1024 and 703 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.31-7.30 (3H, m), 7.14-7.12 (2H, m), 4.60 (1H, d, *J* = 14.4 Hz), 3.63 (1H, dd, *J* = 14.4, 1.6 Hz), 3.15 (2H, ABq, *J* = 12.8 Hz), 2.81-2.71 (1H, m), 2.60 (1H, ddd, *J* = 18.8, 5.6, 0.8

Hz), 2.37 (1H, ddd, J = 13.6, 5.6, 1.2 Hz), 2.13 (1H, dt, J = 13.6, 6.0 Hz), 1.73 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 196.4 (C, *C*=O), 177.7 (C, O-*C*=O), 154.1 (C), 134.6 (C), 129.7 (C), 129.4 (2 x CH), 128.7 (2 x CH), 127.8 (CH), 68.2 (CH_2), 47.6 (C), 42.5 (CH_2), 32.4 (CH_2), 29.4 (CH_2), 10.8 (CH_3); LCMS m/z 257.00 ($M+H^+$), calcd $C_{16}H_{16}O_3$ 256.1099. Anal. calcd for $C_{16}H_{16}O_3$ (256.1099): C, 74.98; H, 6.29. Found: C, 74.85; H, 6.35%.

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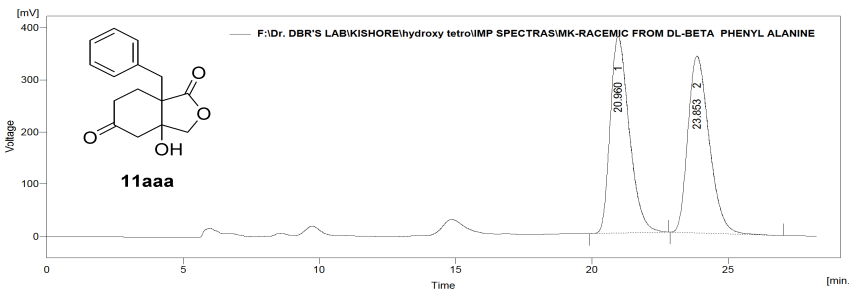
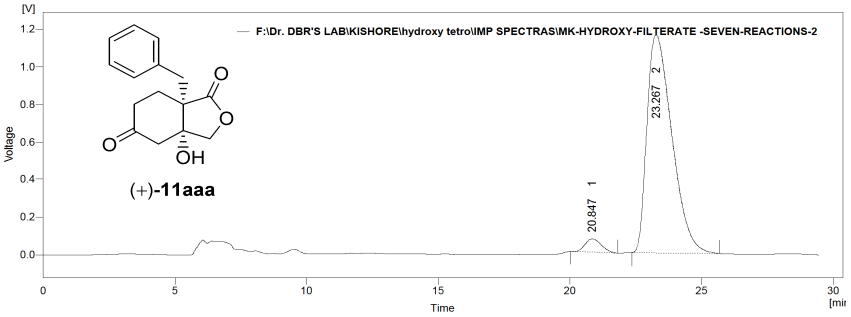
Racemic-11aaa



DAICEL CHIRAL CEL OD-H COLUMN, Hexane/i-PrOH = 80:20,

Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\hydroxy tetro\IMP SPECTRAS\MK-RACEMIC FROM DL-BETA PHENYL ALANINE)

Chiral-(+)-11aaa

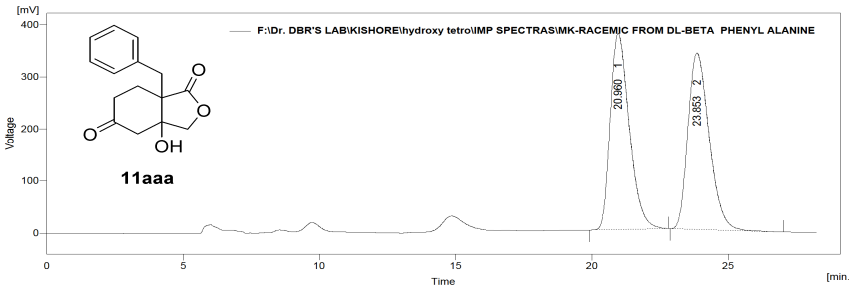


DAICEL CHIRAL CEL OD-H COLUMN, Hexane/i-PrOH = 80:20, FLOW RATE 0.5 mL/min, λ_{max} 220nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\hydroxy tetro\IMP SPECTRAS\MK-HYDROXY-FILTERATE -SEVEN-REACTIONS-2)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	20.847	1995.901	46.760	3.8	5.7	0.68
2	23.267	50756.798	772.690	96.2	94.3	1.03
	Total	52752.700	819.451	100.0	100.0	

Racemic-11aaa

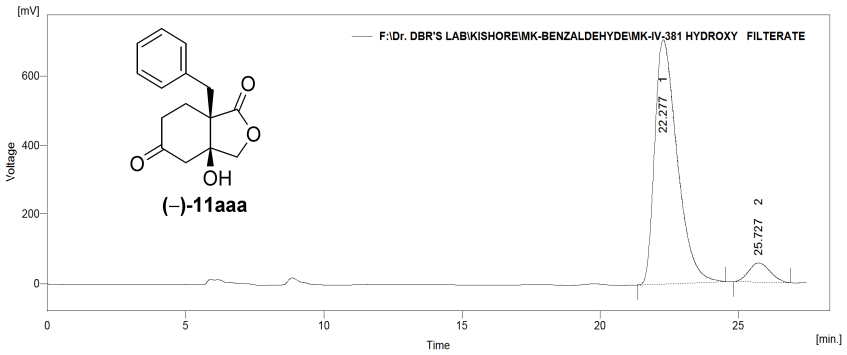


DAICEL CHIRAL CEL OD-H COLUMN, Hexane/i-PrOH = 80:20, FLOW RATE 0.5 mL/min, λ_{max} 220nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\hydroxy tetro\IMP SPECTRAS\MK-RACEMIC FROM DL-BETA PHENYL ALANINE)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	20.960	12166.337	250.633	49.8	52.6	0.75
2	23.853	12245.756	225.970	50.2	47.4	0.84
	Total	24412.094	476.603	100.0	100.0	

Chiral (–)-11aaa

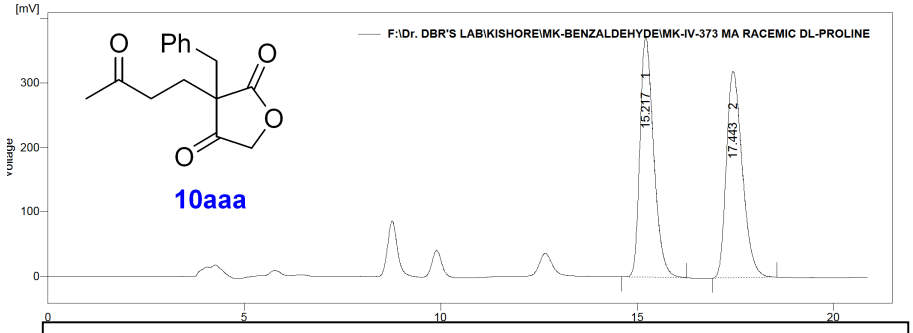


DAICEL CHIRALCEL OD-H COLUMN, Hexane/i-PrOH = 80:20, FLOW RATE 0.5 mL/min, λ_{max} 220nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\MK-BENZALDEHYDE\MK-IV-381 HYDROXY FILTERATE)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	22.277	26466.772	469.959	93.1	92.8	0.87
2	25.727	1972.247	36.725	6.9	7.2	0.85
	Total	28439.019	506.683	100.0	100.0	

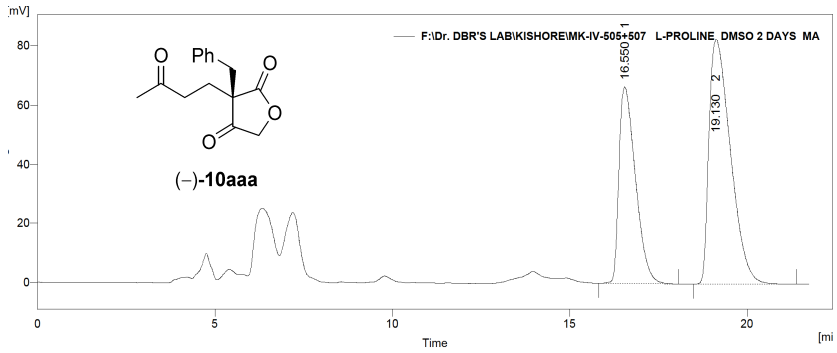
Racemic- 10aaa



DAICEL CHIRALPAK AS-H COLUMN, Hexane/i-PrOH = 80:20, FLOW RATE 0.8 mL/min, λ_{max} 220nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\MK-BENZALDEHYDE\MK-IV-373 MA RACEMIC DL-PROLINE)

Chiral (–)-10aaa

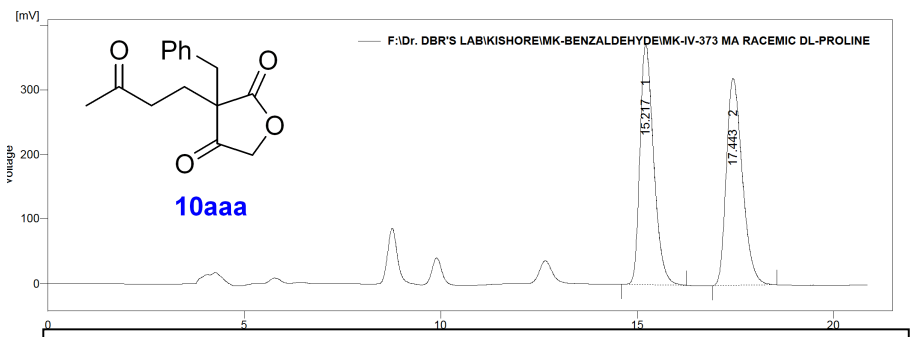


DAICEL CHIRALPAK AS-H COLUMN, Hexane/i-PrOH = 80:20, FLOW RATE 0.8 mL/min, λ_{max} 220nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\MK-IV-505+507 L-PROLINE DMSO 2 DAYS MA)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	16.550	1432.495	44.283	38.2	44.6	0.51
2	19.130	2313.426	55.078	61.8	55.4	0.67
	Total	3745.921	99.361	100.0	100.0	

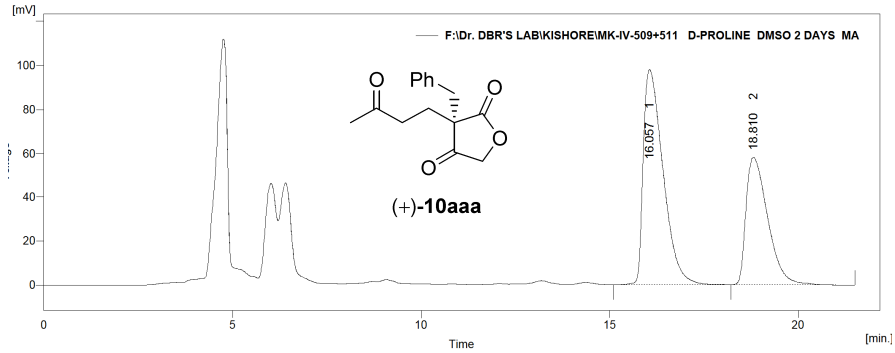
Racemic-10aaa



DAICEL CHIRALPAK AS-H COLUMN, Hexane/i-PrOH = 80:20, FLOW RATE 0.8 mL/min, λ_{max} 220nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\MK-BENZALDEHYDE\MK-IV-373 MA RACEMIC DL-PROLINE)

Chiral (+)-10aaa

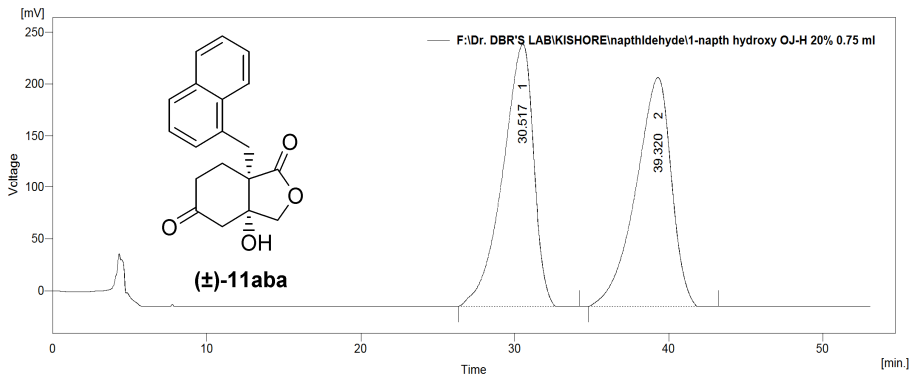


DAICEL CHIRALPAK AS-H COLUMN, Hexane/i-PrOH = 80:20, FLOW RATE 0.8 mL/min, λ_{max} 220nm.

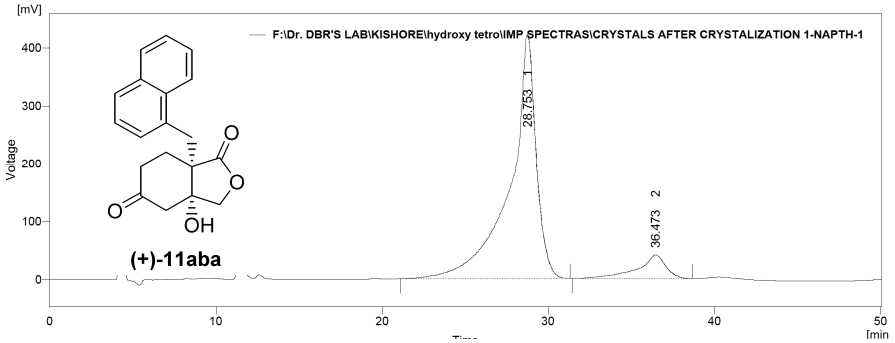
Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\MK-IV-509+511 D-PROLINE DMSO 2 DAYS MA)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	16.057	2382.963	65.229	60.6	62.7	0.57
2	18.810	1549.701	38.850	39.4	37.3	0.62
	Total	3932.664	104.079	100.0	100.0	

Racemic-11aba



Chiral-11aba

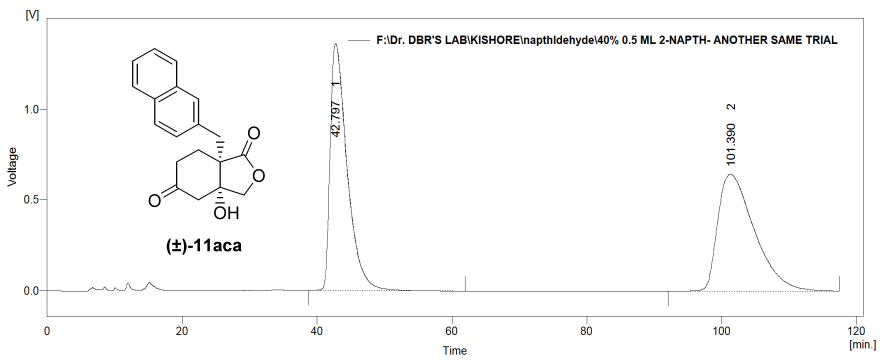


DAICEL CHIRALCEL OJ-H COLUMN, Hexane/EtOH = 80:20, FLOW RATE 0.75 mL/min, λ_{max} 220 nm.

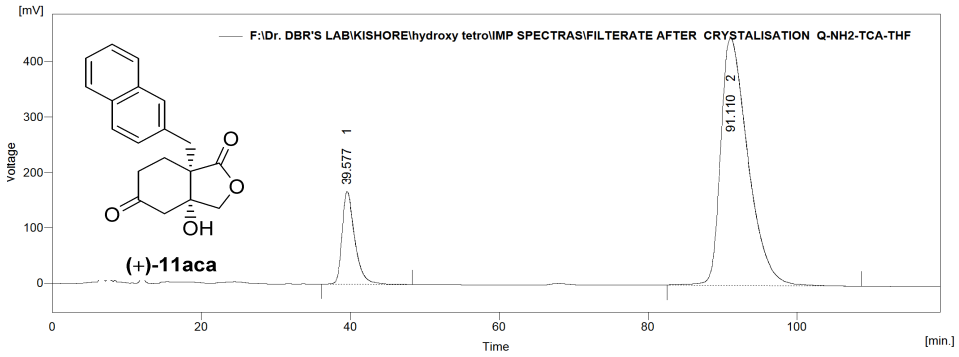
Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\hydroxy tetro\IMP SPECTRAS\CRYSTALS AFTER CRYSTALIZATION 1-NAPTH-1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	28.753	30643.685	281.017	90.5	91.2	1.11
2	36.473	3204.930	27.127	9.5	8.8	1.40
	Total	33848.615	308.144	100.0	100.0	

Racemic -11aca



Chiral-11 aca

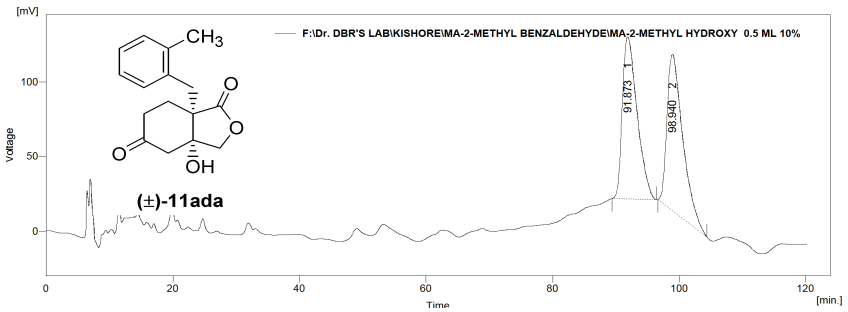


DAICEL CHIRALCEL OJ-H COLUMN, Hexane/i-PrOH = 60:40, FLOW RATE 0.5 mL/min, λ_{max} 220nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\hydroxy tetro\IMP SPECTRAS\FILTERATE AFTER CRYSTALISATION Q-NH2-TCA-THF)

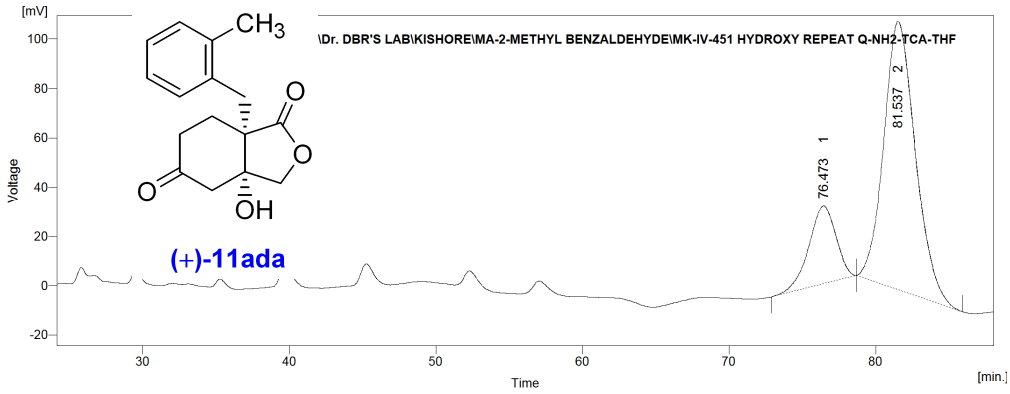
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	39.577	13179.557	110.429	14.9	27.1	1.76
2	91.110	75374.344	297.444	85.1	72.9	3.84
	Total	88553.901	407.873	100.0	100.0	

Racemic-11ada



DAICEL CHIRALCEL OJ-H COLUMN, Hexane/i-PrOH = 90:10, FLOW RATE 0.5 mL/min, λ_{max} 220nm.

Chiral-(+)-11ada

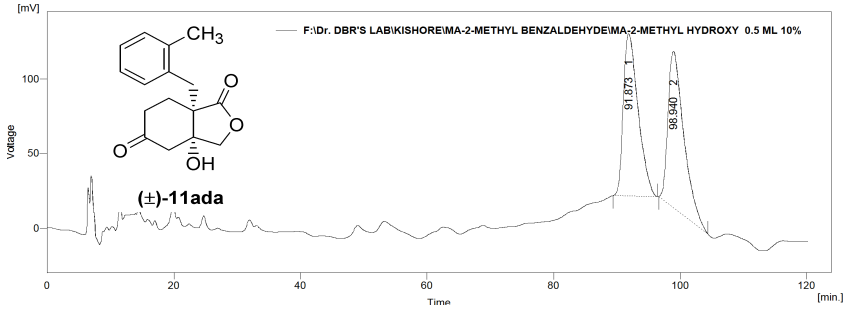


DAICEL CHIRALCEL OJ-H COLUMN, Hexane/i-PrOH = 90:10, FLOW RATE 0.5 mL/min, λ_{max} 220 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\MA-2-METHYL BENZALDEHYDE\MK-IV-451 HYDROXY REPEAT Q-NH2-TCA-THF)

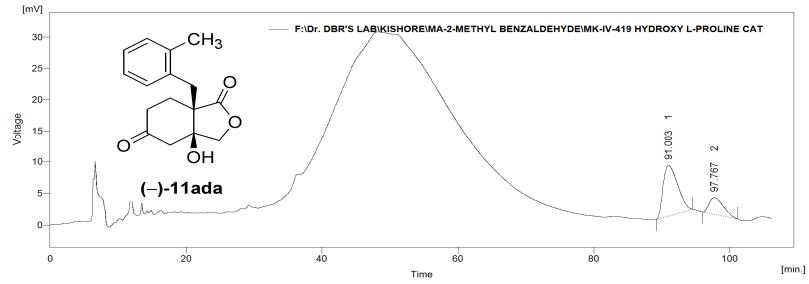
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	76.473	2688.148	20.970	19.8	22.4	1.98
2	81.537	10889.521	72.493	80.2	77.6	2.27
	Total	13577.669	93.464	100.0	100.0	

Racemic sample



DAICEL CHIRALCEL OJ-H COLUMN, Hexane/i-PrOH =

Chiral-(–)-11ada

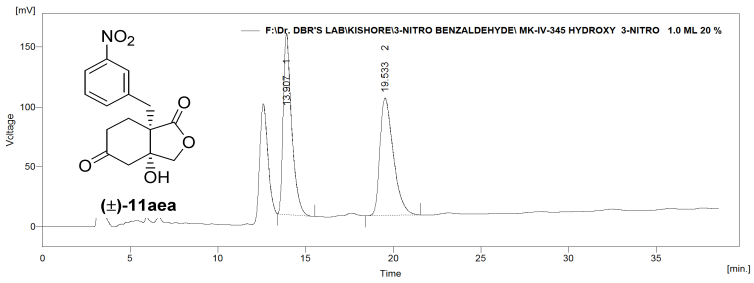


DAICEL CHIRALCEL OJ-H COLUMN, Hexane/i-PrOH = 90:10, FLOW RATE 0.5 mL/min, λ_{max} 220 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\MA-2-METHYL BENZALDEHYDE\MK-IV-419 HYDROXY L-PROLINE CAT)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	91.003	793.826	5.321	75.3	75.0	2.56
2	97.767	260.612	1.772	24.7	25.0	2.24
	Total	1054.438	7.093	100.0	100.0	

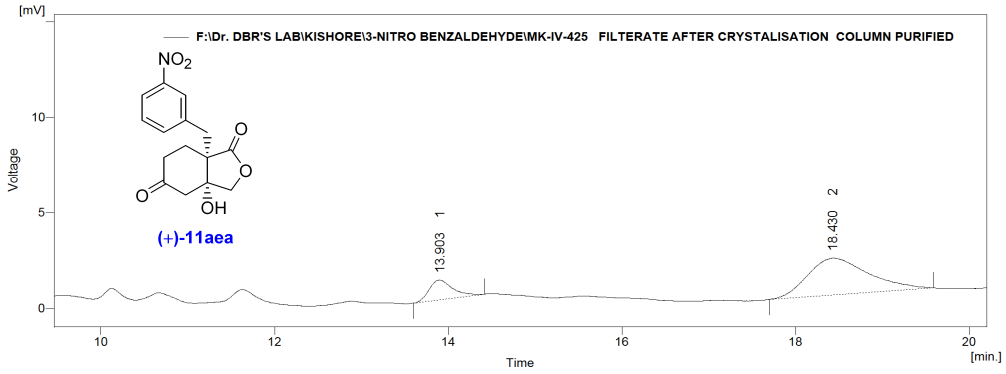
Racemic-11aea



DAICEL CHIRALCEL OJ-H COLUMN, Hexane/EtOH = 80:20, FLOW RATE 1.0 mL/min, λ_{max} 220 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\3-NITRO BENZALDEHYDE\ MK-IV-345

Chiral-11aea

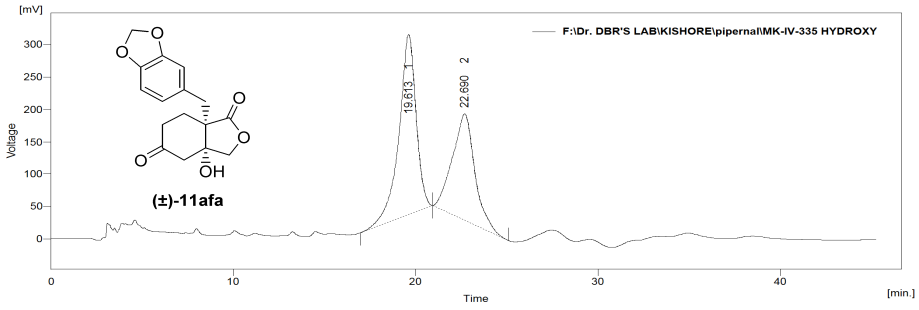


DAICEL CHIRALCEL OJ-H COLUMN, Hexane/EtOH = 80:20, FLOW RATE 1.0 mL/min, λ_{max} 220 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\3-NITRO BENZALDEHYDE\MK-IV-425 FILTERATE AFTER CRYSTALISATION COLUMN PURIFIED)

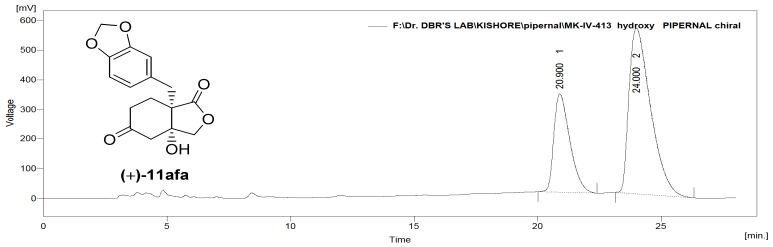
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	13.903	13.021	0.690	17.4	35.2	0.31
2	18.430	62.003	1.272	82.6	64.8	0.80
	Total	75.025	1.962	100.0	100.0	

Racemic-11afa



DAICEL CHIRALCEL OJ-H COLUMN, Hexane/EtOH = 70:30,

Chiral-11afa

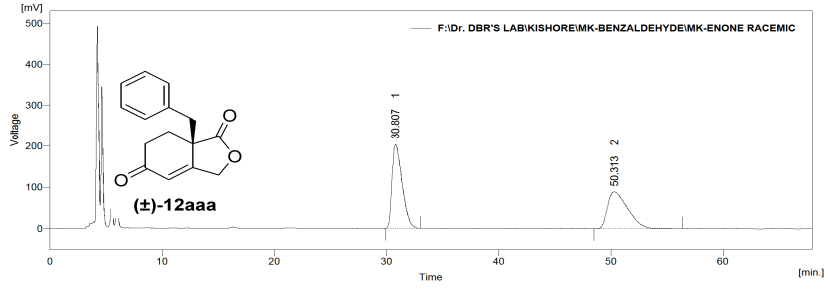


DAICEL CHIRALCEL OJ-H COLUMN, Hexane/EtOH = 70:30, FLOW RATE 1.0 mL/min, λ_{max} 220nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\pipernal\MK-IV-413 hydroxy PIPERNAL chiral)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	20.900	9891.296	221.633	30.4	37.3	0.69
2	24.000	22592.794	372.253	69.6	62.7	0.94
	Total	32484.090	593.886	100.0	100.0	

Racemic-12aaa

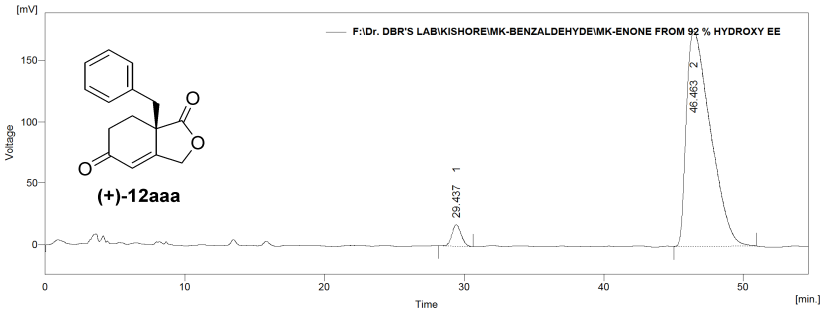


DAICEL CHIRALPAK AS-H COLUMN, Hexane/i-PrOH = 70:30, FLOW RATE 1.0 mL/min, λ_{max} 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\MK-BENZALDEHYDE\MK-ENONE RACEMIC)

	Reten. Time	Area	Height	Area	Height	W05

Chiral-12aaa

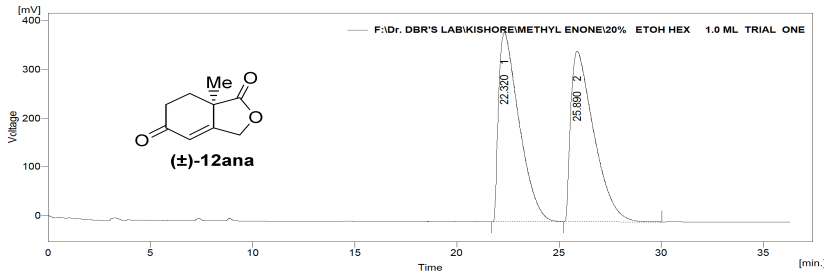


DAICEL CHIRALPAK AS-H COLUMN, Hexane/i-PrOH = 70:30, FLOW RATE 1.0 mL/min, λ_{max} 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\MK-BENZALDEHYDE\MK-ENONE FROM 92 % HYDROXY EE)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	29.437	535.164	11.562	3.7	9.0	0.72
2	46.463	13950.357	116.673	96.3	91.0	1.90
	Total	14485.521	128.235	100.0	100.0	

Racemic-12ana

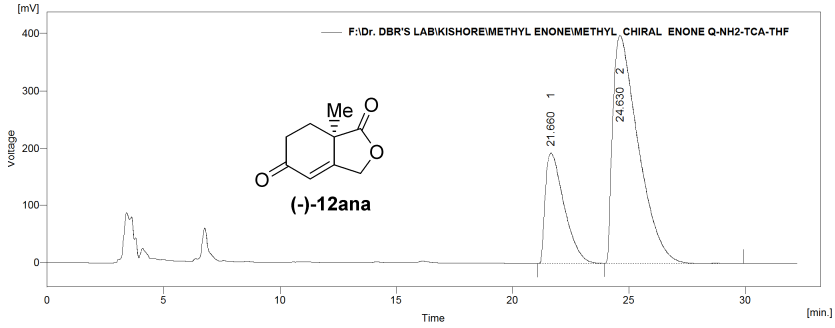


DAICEL CHIRALCEL OJ-H COLUMN, Hexane/EtOH = 80:20, FLOW RATE 1.0 mL/min, λ_{max} 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\METHYL ENONE\20% ETOH HEX 1.0 ML TRIAL ONE)

	Reten. Time	Area	Height	Area	Height	W05

Chiral-12ana

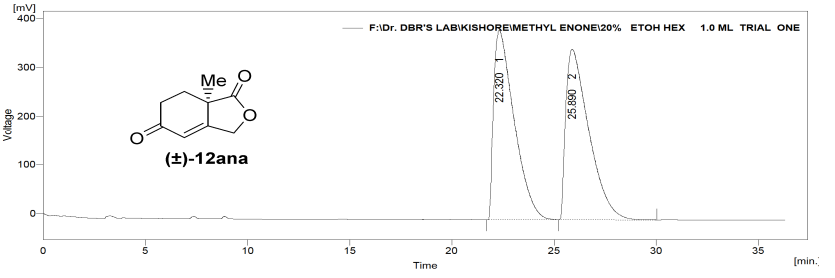


DAICEL CHIRALCEL OJ-H COLUMN, Hexane/EtOH = 80:20, FLOW RATE 1.0 mL/min, λ_{max} 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\METHYL ENONE\METHYL CHIRAL ENONE Q-NH2-TCA-THF)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	21.660	7172.027	128.884	26.3	32.7	0.87
2	24.630	20122.794	265.238	73.7	67.3	1.18
	Total	27294.821	394.122	100.0	100.0	

Racemc -12ana

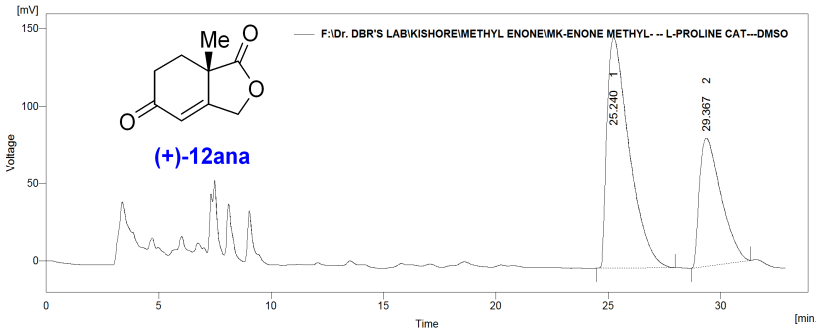


DAICEL CHIRALCEL OJ-H COLUMN, Hexane/EtOH = 80:20, FLOW RATE 1.0 mL/min, λ_{max} 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\METHYL ENONE\20% ETOH HEX 1.0 ML TRIAL ONE)

	Reten. Time	Area	Height	Area	Height	W05

Chiral-(+)-12ana

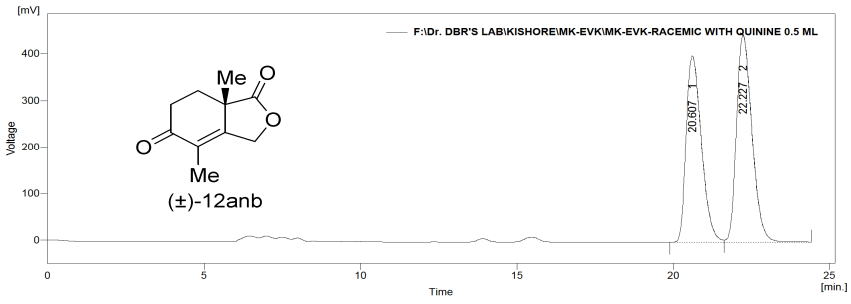


DAICEL CHIRALCEL OJ-H COLUMN, Hexane/EtOH = 80:20. FLOW RATE 1.0 mL/min. λ_{max} 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\METHYL ENONE\MK-ENONE METHYL- -- L-PROLINE CAT---DMSO)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	25.240	6863.916	99.242	65.0	64.2	1.07
2	29.367	3689.916	55.449	35.0	35.8	1.07
	Total	10553.832	154.691	100.0	100.0	

Racemic-12anb

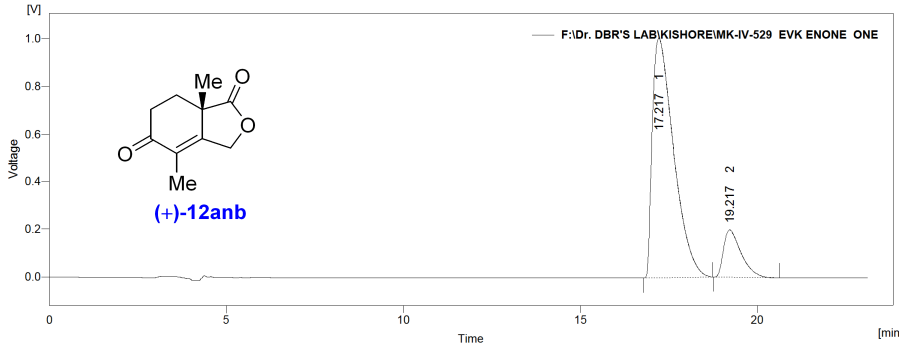


DAICEL CHIRALCEL OJ-H COLUMN, Hexane/EtOH = 80:20, FLOW RATE 1.0 mL/min, λ_{max} 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\MK-EVK\MK-EVK-RACEMIC WITH QUININE 0.5 ML)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	20.607	9058.490	266.825	47.0	47.4	0.53
2	22.227	10235.344	296.446	53.0	52.6	0.54
	Total	19293.834	563.271	100.0	100.0	

Chiral-(+)-12anb

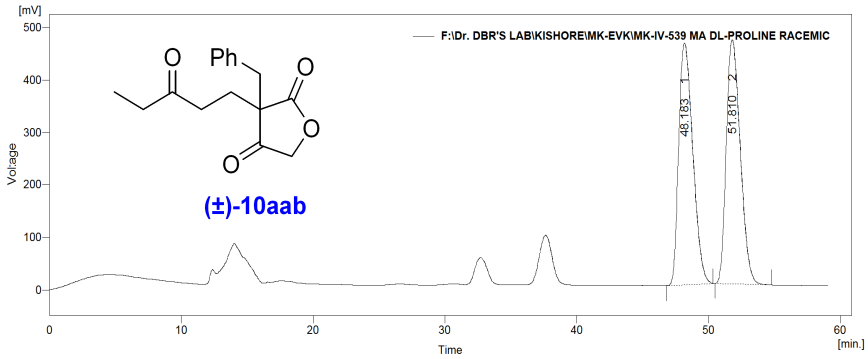


DAICEL CHIRALCEL OJ-H COLUMN, Hexane/EtOH = 80:20, FLOW RATE 1.0 mL/min, λ_{max} 254 nm.

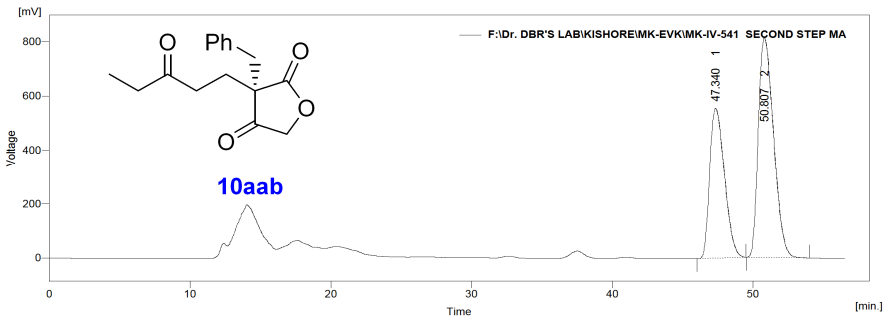
Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\MK-IV-529 EVK ENONE ONE)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	17.217	27909.835	670.517	85.9	83.5	0.65
2	19.217	4589.327	132.168	14.1	16.5	0.53
	Total	32499.162	802.684	100.0	100.0	

Racemic-(±)-10aab



Chiral-10aab

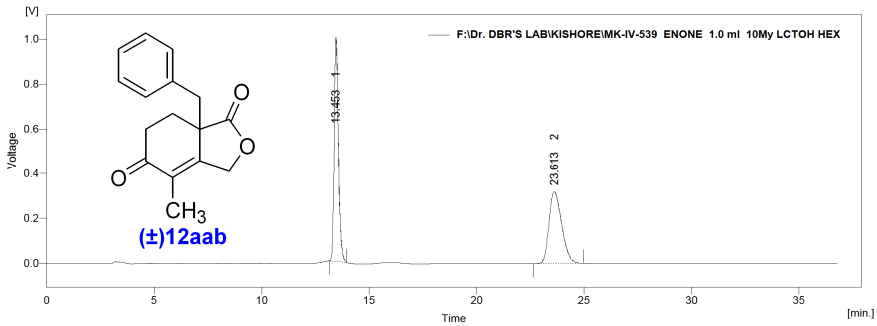


DAICEL CHIRALPAK AS-H COLUMN, Hexane/i-PrOH = 85:15, FLOW RATE 0.25 mL/min, λ_{max} 220 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\MK-EVK\MK-IV-541 SECOND STEP MA)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	47.340	26992.395	370.680	39.7	40.6	1.16
2	50.807	40974.091	541.696	60.3	59.4	1.20
	Total	67966.485	912.376	100.0	100.0	

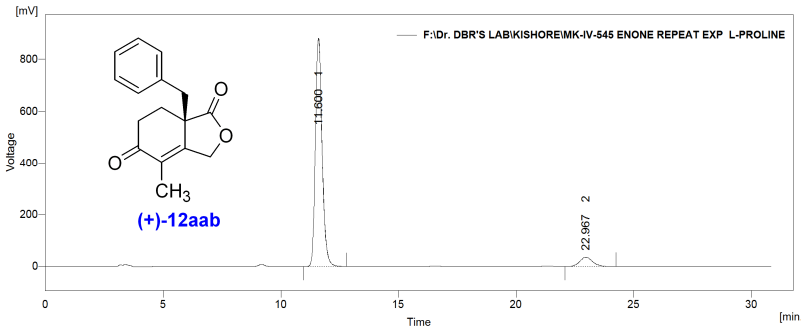
Ra



DAICEL CHIRALPAK AS-H COLUMN, Hexane/EtOH = 90:10, FLOW RATE 1.0 mL/min, λ_{max} 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\MK-IV-539 ENONE 1.0 ml 10My LCTOH HEX)

Chiral-(+)-12aab



DAICEL CHIRALPAK AS-H COLUMN, Hexane/EtOH = 90:10, FLOW RATE 1.0 mL/min, λ_{max} 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\KISHORE\MK-IV-545 ENONE REPEAT EXP L-PROLINE)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	11.600	11773.889	587.908	93.0	96.2	0.31
2	22.967	881.882	23.452	7.0	3.8	0.58
	Total	12655.772	611.360	100.0	100.0	