Supplementary Information for

Organocatalytic asymmetric direct vinylogous aldol reactions of γ-crotonolactone with aromatic aldehydes

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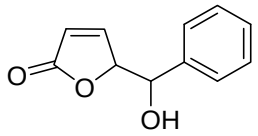
General Procedure for the catalytic vinylogous Mukaiyama aldol reaction:

To the catalyst (0.1 mmol, in a 2 mL Reacti-Vial™ or a standard 3 mL vial) was added the aldehyde (0.5 mmol) followed by γ-crotonolactone (2-(5H)-furanone) (1mmol) and dichloromethane (0.50 mL). The suspension was stirred for 10 days at room temperature (for catalyst **6**) or kept for 7 days at 0 ^{o}C with occassional shaking (for catalyst **5**). The mixture was then diluted with ethyl acetate (1 mL) and aqueous HCl (2N) was added. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined extracts were dried (Na_2SO_4), and concentrated. The residue was purified by flash chromatography (CH_2Cl_2/EtOAc, 10/1). The diastereomeric composition (anti/syn) was determined by ^{1}H NMR analysis of the crude product. The enantiomeric excess was determined by HPLC (Chiralpak AD-H or AS-H column, flow rate 1mL/min, UV detection at 210 or 254 nm) by comparison with reported retention times[1] for compounds **8a-k,** and also by comparison with racemic standards (prepared by using triethylamine as the catalyst) for compounds **8h** and **8i**. The absolute configuration of **8a** was assigned by correlation. Absolute configurations of **8b-k** are assigned by analogy within the series.

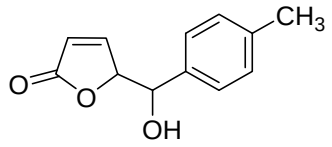
5-(Hydroxy (phenyl) methyl) furan-2(5H)-one (8a):



Reaction of γ-crotonolactone (70.0 μL, 1 mmol) with benzaldehyde (53.0 μL, 0.5 mmol) catalyzed by **6** (54.7 mg, 0.1 mmol) according to the general procedure provided 34.0 mg (35%) of **8a** as a white solid.
IR: 3432, 1728, 1167, 1039, 820 cm^{-1}; ^{1}H NMR (500MHz, $CDCl_3$): **Anti diastereomer:** δ 7.43-7.34 (m, 6H, Ar*H* and COCH=C*H*), 6.19-6.18 (dd, 1H, *J* = 5.8, 1.9 Hz, COC*H*=CH), 5.19-5.18 (br m, 1H, CH=CHC*H*), 5.08-5.10 (br t, 1H, *J* = 4.1 Hz, ArC*H*OH), 2.25 (d, 1H, *J* = 3.8 Hz, O*H*); **Syn diastereomer:** δ 7.42-7.36 (m, 5H, Ar*H*), 7.16-7.18 (dd, 1H, *J* = 5.8, 1.5 Hz, COCH=C*H*), 6.13-6.12 (dd, 1H, *J* = 5.8, 2 Hz,

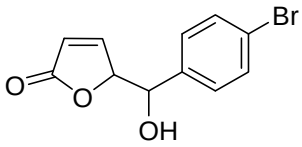
COC*H*=CH), 5.18-5.15 (apparent dt, 1H, *J* = 7, 1.5 Hz, CH=CHC*H*), 4.72-4.70 (d, 1H, *J* = 7.0 Hz, ArC*H*OH), 2.78 (s, 1H, O*H*); MS (APCI pos.): m/z 191.0 (M+1).
HPLC: Chiralpak AS-H, hexanes/2-propanol 90/10, 254 nm, t_1 = 27.8 min (major anti), t_2 = 36.2 min, (syn), t_3 = 49.6 min (syn), t_4 = 66.8 min (minor anti). Ee: 97% (anti).

5-(Hydroxy (p-tolyl) methyl) furan-2(5H)-one (8b):



Reaction of γ-crotonolactone (70.0 µL, 1mmol) with 4-methylbenzaldehyde (59.0 µL, 0.5 mmol) catalyzed by **6** (54.7 mg, 0.1 mmol) according to the general procedure provided 52.0 mg (51%) of **8b** as a white solid.
IR: 3401, 1736, 1325, 1170, 1102, 1079, 1039, 917, 877 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$): **Anti diastereomer:** δ 7.37-7.35 (dd, 1H, *J* = 5.8, 1.4 Hz, COCH=C*H*), 7.29-7.27 (d, 2H, *J* = 8.0 Hz, Ar*H*), 7.21-7.22 (d, 2H, *J* = 8.0 Hz, Ar*H*, ortho to CH_3), 6.18-6.17 (dd, 1 H, *J* = 5.8, 2.0 Hz, COC*H*=CH), 5.17-5.15 (m, 1H, CH=CHC*H*), 5.05-5.03 (br t, 1H, *J* = 4.0 Hz, ArC*H*OH), 2.37 (3H, CH_3), 2.21-2.22 (d, 1H, *J* = 4.0 Hz, O*H*), 2.37 (3H, CH_3); **Syn diastereomer:** δ 7.29-7.27 (d, 2H, *J*= 8.0 Hz, Ar*H*), 7.21-7.22 (d, 2H, *J* = 8.0 Hz, ortho to CH_3), 7.16-7.15 (dd, 1H, *J* = 5.8, 1.6 Hz, COCH=C*H*), 6.13-6.12 (dd, 1H, *J* = 5.8, 2.0 Hz, COC*H*=CH), 5.15-5.17 (m, 1H, CH=CHC*H*), 4.65-4.67 (dd, 1H, *J* = 6.9, 3.0 Hz, ArC*H*OH), 2.58 (d, 1H, *J* = 3.0 Hz, O*H*), 2.37 (3H, CH_3); MS (APCI pos.): m/z 205.0 (M+1).
HPLC: Chiralpak AD-H, hexanes/2-propanol 95/5, 254 nm, t_1 = 20.0 min (major anti), t_2 = 22.2 min, (minor anti), t_3 = 26.8 min (minor syn), t_4 = 29.0 min (major syn). Ee: 95% (anti).

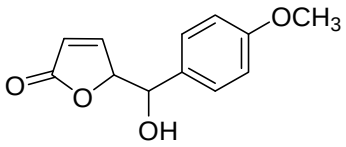
5-((4-Bromophenyl) (hydroxy) methyl) furan-2(5H)-one (8c):



Reaction of γ-crotonolactone (70.0 µL, 1mmol) with 4-bromobenzaldehyde (93.0 mg, 0.5 mmol) catalyzed by **6** (54.7 mg, 0.1 mmol) according to the general procedure provided 83.0 mg (62%) of **8c** as a white solid.
IR: 3343, 1742, 1486, 1399, 1191, 1176, 1095, 1074, 1041, 1008, 917, 880, 831, 808 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$): **Anti diastereomer:** δ 7.54-7.55 (d, 2H, *J* = 8.4 Hz, Ar*H*, ortho to Br), 7.31-7.33 (dd, 1H, *J* = 5.8,1.4 Hz, COCH=C*H*), 7.28-7.30 (d, 2H, *J* = 8.5 Hz, Ar*H*), 6.20-6.18 (dd, 1 H, *J* = 5.8, 2.0 Hz, COC*H*=CH), 5.15-5.13 (m, 1H, CH=CHC*H*), 5.05-5.03 (t, 1H, *J* = 4.0 Hz, ArC*H*OH), 2.47-2.48 (d, 1H, *J* = 4.0 Hz, O*H*); **Syn diastereomer:** δ 7.55-7.54 (d, 2H, *J* = 8.4 Hz, Ar*H*, ortho to Br), 7.30-7.28 (d, 2H, *J* = 8.4 Hz), 7.21-7.19 (dd, 1H, *J* = 5.8, 1.5 Hz, COCH=C*H*), 6.13-6.15 (dd, 1H, *J* = 5.8,

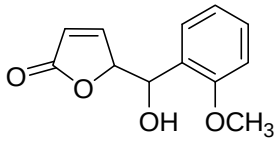
2.0 Hz, COC*H*=CH), 5.13-5.15 (m, 1H, CH=CHC*H*), 4.72-4.74 (dd, 1H, *J* = 6.7, 3.3 Hz, ArC*H*OH), 2.72-2.73 (d, 1H, *J* = 3.3 Hz, O*H*); MS (APCI pos.): m/z 269.1 (M^+).
HPLC: Chiralpak AD-H, hexanes/2-propanol 88/12, 254 nm, t_1 = 9.6 min (major anti), t_2 = 10.4 min (minor syn), t_3 = 10.8 min (minor anti), t_4 = 11.6 min (major syn). Ee: 95% (anti).

5-(Hydroxy (4-methoxyphenyl) methyl) furan-2(5H)-one (8d):



Reaction of γ-crotonolactone (70.0 µL, 1mmol) with 4-methoxybenzaldehyde (63.0 µL, 0.5 mmol) catalyzed by **6** (54.7 mg, 0.1 mmol) according to the general procedure provided 39.0 mg (35%) of **8d** as a white solid.
IR: 3357, 1742, 1585, 1510, 1242, 1171, 1101, 1085, 1029, 1008, 877, 827, 814 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$): **Anti diastereomer:** δ 7.38-7.39 (dd, 1H, *J* = 5.8, 1.5 Hz, COCH=C*H*), 7.31-7.32 (d, 2H, *J* = 8.7 Hz, Ar*H*), 6.92-6.94 (d, 2H, *J* = 8.7 Hz, ortho to OCH_3), 6.17-6.18 (dd, 1 H, *J* = 5.8, 2.0 Hz, COC*H*=CH), 5.14-5.15 (m, 1H, CH=CHC*H*), 4.99-5.01 (t, 1H, *J* = 4.0 Hz, ArC*H*OH), 3.82 (s, 3H, OCH_3), 2.25-2.26 (d, 1H, *J* = 4.0 Hz, O*H*); **Syn diastereomer:** δ 7.31-7.32 (d, 2H, *J* = 8.7 Hz, Ar*H*), 7.15-7.16 (dd, 1H, *J* = 5.8, 1.6 Hz, COCH=C*H*), 6.92-6.94 (d, 2H, *J* = 8.7 Hz, ortho to OCH_3), 6.12-6.13 (dd, 1H, *J* = 5.8, 2.1 Hz, COC*H*=CH), 5.14-5.15 (m, 1H, CH=CHC*H*), 4.64-4.66 (dd, 1H, *J* = 7.1, 3.0 Hz, ArC*H*OH), 3.82 (s, 3H, OCH_3), 2.60-2.61 (d, 1H, *J* = 3.0 Hz, O*H*); MS (APCI pos.): m/z 221.0 (M+1), 203.0 ((M-H_2O)+1).
HPLC: Chiralpak AD-H, hexanes/2-propanol 90/10, 254 nm, t_1 = 15.1 min (major anti), t_2 = 17.7 min, (minor anti), t_3 = 19.0 min (minor syn), t_4 = 20.7 min (major syn). Ee: 97% (anti).

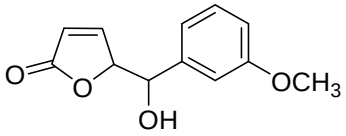
5-(Hydroxy (2-methoxyphenyl) methyl) furan-2(5H)-one (8e):



Reaction of γ-crotonolactone (70.0 µL, 1mmol) with 2-methoxybenzaldehyde (63.0 µL, 0.5 mmol) catalyzed by **6** (54.7 mg, 0.1 mmol) according to the general procedure provided 64.0 mg (58%) of **8e** as a colorless liquid.
IR: 3418, 1733, 1601, 1491, 1462, 1238, 1160, 1095, 1036, 1022, 816 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$): **Anti diastereomer:** δ 7.39-7.40 (dd, 1H, *J* = 5.8, 1.0, COCH=C*H*), 7.31-7.34 (m, 2H, Ar*H* ortho and para to OCH_3), 7.01-7.04 (t, 1 H, *J* = 7.5 Hz, Ar*H*, meta to OCH_3), 6.91-6.93 (d, 1H, *J* = 8.3, Ar*H*), 6.14-6.16 (dd, 1 H, *J* = 5.8, 2.0 Hz, COC*H*=CH), 5.37-5.38 (m, 1H, CH=CHC*H*), 5.30-5.32 (t, 1H, *J* = 5.7 Hz, ArC*H*OH), 3.89 (s, 3H, OCH_3), 2.81-2.82 (d, 1H, *J* = 5.7 Hz, O*H*); **Syn diastereomer:** δ 7.31-7.34

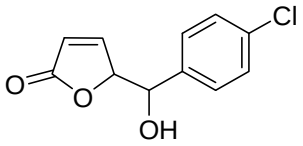
(m, 2H, Ar*H* ortho and para to OCH_3), 7.17-7.19 (dd, 1H, *J* = 5.8, 1.1, COCH=C*H*), 7.01-7.04 (t, 1 H, *J* = 7.5 Hz, Ar*H*, meta to OCH_3), 6.91-6.93 (d, 1H, *J* = 8.3, Ar*H*), 6.11-6.13 (dd, 1H, *J* = 5.8, 2.0 Hz, COC*H*=CH), 5.23-5.24 (br dt, 1H, *J* = 6.6, 1.5, CH=CHC*H*) 5.01-5.03 (t, 1H, *J* = 5.7 Hz, ArC*H*OH), 3.85 (s, 3H, OCH_3), 3.05-3.07 (d, 1H, *J* = 5.7 Hz, O*H*); MS (APCI neg.): m/z 219 (M+); APCI pos. m/z 203.0 ((M-H_2O)+1).
HPLC: Chiralpak AD-H, hexanes/2-propanol 85/15, 254, t_1 = 8.4 min (major anti), t_2 = 11.0 min, (minor anti), t_3 = 12.9 min (major syn), t_4 = 16.3 min (minor syn). Ee: 96% (anti).

5-(Hydroxy (3-methoxyphenyl) methyl) furan-2(5H)-one (8f):



Reaction of γ-crotonolactone (70.0 µL, 1mmol) with 3-methoxybenzaldehyde (63.0 µL, 0.5 mmol) catalyzed by **6** (54.7 mg, 0. 1mmol) according to the general procedure provided 60.0 mg (54%) of **8f** as a colorless liquid.
IR: 3420, 1735,1600, 1585, 1489, 1456, 1435, 1256, 1157, 1034, 825 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$): **Anti diastereomer:** δ 7.29-7.35 (m, 2H, Ar*H*, COCH=C*H*), 6.87-6.97 (m, 3H, Ar*H*), 6.16-6.17 (dd, 1 H, *J* = 5.8, 2.0 Hz, COC*H*=CH), 5.15-5.18 (m, 1H, CH=CHC*H*), 5.07-5.08 (t, 1H, *J* = 4.0 Hz, ArC*H*OH), 3.82 (s, 3H, OCH_3), 2.73(d, 1H, *J* = 4.0 Hz, O*H*); **Syn diastereomer:** δ 7.29-7.35 (m, 1H, Ar*H*), 7.17-7.18 (dd, 1H, *J* = 5.8, 1.4 Hz, COCH=C*H*), 6.87-6.97 (m, 3H, Ar*H*), 6.11-6.12 (dd, 1H, *J* = 5.8,1.9 Hz, COC*H*=CH), 5.15-5.18 (m, 1H, CH=CHC*H*), 4.67-4.69 (dd, 1H, *J* = 7.0, 3.1 Hz, ArC*H*OH), 3.82 (s, 3H, OCH_3), 2.94 (d, 1H, *J* = 3.1 Hz, O*H*); MS (APCI pos.): m/z 221.0 (M+1), 203.0 ((M-H_2O)+1).
HPLC: Chiralpak AD-H, hexanes/2-propanol 90/10, 210 nm, t_1 = 14.2 min (major anti), t_2 = 18.3 min, (minor anti), t_3 = 20.0 min (minor syn), t_4 = 21.4 min (major syn). Ee: 96% (anti).

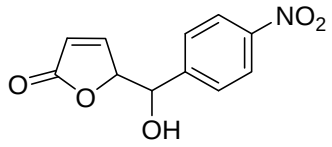
5-((4-Chlorophenyl) (hydroxy) methyl) furan-2(5H)-one (8g):



Reaction of γ-crotonolactone (70.0 µL, 1mmol) with 4-chlorobenzaldehyde (70.0 mg, 0.5 mmol) catalyzed by **5** (45.0 mg, 0.1 mmol) according to the general procedure provided 56.0 mg (50%) of **8g** as a white solid.
IR: 3420, 1732, 1491, 1175, 1093, 1078, 1042, 917, 852, 812 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$): **Anti diastereomer:** δ 7.31-7.40 (m, 6H, Ar*H*, COCH=C*H*), 6.19-6.20 (dd, 1 H, *J* = 5.8, 2.0 Hz, COC*H*=CH), 5.13-5.15 (m, 1H, CH=CHC*H*), 5.04-5.06 (t, 1H, *J* = 4.0 Hz, ArC*H*OH), 2.37-2.38 (d, 1H, *J* = 4.0 Hz, O*H*); **Syn diastereomer:** δ 7.31-7.40 (m,

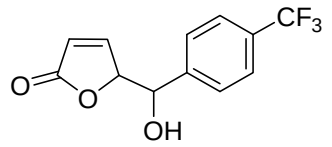
5H, Ar*H*), 7.19-7.20 (dd, 1H, *J* = 5.8, 1.5 Hz, COCH=C*H*), 6.13-6.15 (dd, 1H, *J* = 5.8,2.0 Hz, COCH=C*H*), 5.13-5.15 (m, 1H, CH=CHC*H*), 4.73-4.75 (dd, 1H, *J* = 6.8, 3.2 Hz, ArC*H*OH), 2.66-2.67 (d, 1H, *J* = 3.2 Hz, O*H*); MS (APCI pos.): m/z 225.0 (M+1), 207.0 ((M-H_2O)+1).
HPLC: Chiralpak AD-H hexanea/2-propanol 95/5, 210 nm, t_1 = 21.1 min (major anti), t_2 = 24.2 min, (minor anti), t_3 = 25.9 min (major syn), t_4 = 29.4 min (minor syn). Ee: 94% (anti).

5-(Hydroxy (4-nitrophenyl) methyl) furan-2(5H)-one (8h):



Reaction of γ-crotonolactone (70.0 µL, 1mmol) with 4-nitrobenzaldehyde (76.0 mg, 0.5 mmol) catalyzed by **6** (54.7 mg, 0.1 mmol) according to the general procedure provided 59.0 mg (50%) of **8h** as a yellow solid.
IR: 3438, 1746, 1515, 1348, 1169, 1103, 1039, 916, 833 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$): **Anti diastereomer:** δ 8.25-8.27 (d, 2H, *J* = 8.7 Hz, Ar*H*, ortho to NO_2), 7.59-7.66 (d, *J* = 8.7, 2H, Ar*H*), 7.29-7.30 (dd, 1H, *J* = 5.9,1.6 Hz, COCH=C*H*), 6.16-6.17 (dd, 1 H, *J* = 5.9, 1.8 Hz, COC*H*=CH), 5.19-5.21(m, 2H, CH=CHC*H*, ArC*H*OH), 2.76-2.77 (d, 1H, *J* = 3.7 Hz, O*H*); **Syn diastereomer:** δ 8.28-8.30 (d, 2H, *J* = 8.7 Hz, Ar*H*, ortho to NO_2), 7.59-7.66 (m, 2H, Ar*H*), 7.21 (m, 1H, COCH=C*H*), 6.23-6.25 (dd, 1 H, *J* = 5.8, 1.4 Hz, COC*H*=CH), 4.98-5.0 (m, 2H, CH=CHC*H*, ArC*H*OH), 2.58-2.59 (d, 1H, *J* = 3.5 Hz, O*H*); MS (APCI pos.): m/z 236.1 (M+1).
HPLC: Chiralpak AD-H, hexanes/2-propanol 95/5, 254 nm, t_1 = 52.4 min (major anti), t_2 = 59.1 min, (major syn), 70.5 (minor syn). Ee: >99% (anti).

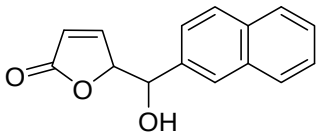
5-((4-(Trifluoromethyl) phenyl) (hydroxy) methyl) furan-2(5H)-one (8i):



Reaction of γ-crotonolactone (70.0 µL, 1mmol) with 4-trifluoromethylbenzaldehyde (67.0 µL, 0.5 mmol) catalyzed by **6** (54.7 mg, 0.1 mmol) according to the general procedure provided 78.0 mg (60%) of **8i** as a colorless solid.
IR: 3413, 1739, 1322, 1161, 1100, 1065, 1040, 1016, 816 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$): **Anti diastereomer:** δ 7.67-7.69 (d, 2H, *J* = 8.1 Ar*H*), 7.54-7.56 (d, 2H, *J* = 8.1), 7.30-7.31 (dd, 1H, *J* = 5.8, 1.4 Hz, COCH=C*H*), 6.20-6.21 (dd, 1 H, *J* = 5.8, 2.0 Hz, COC*H*=CH), 5.14-5.19 (m, 2H, CH=CHC*H*O, ArC*H*OH) 2.37-2.38 (d, 1H, *J* = 3.9 Hz, O*H*); **Syn diastereomer:** δ 7.67-7.69 (d, 2H, *J* = 5.7, Ar*H*), 7.54-7.56 (d, 2H, *J* = 5.7), 7.23-7.25 (dd, 1H, *J* = 5.8, 1.5 Hz, COCH=C*H*), 6.14-6.15 (dd, 1 H, *J* = 5.8, 2.0 Hz,

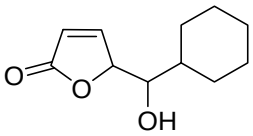
COC*H*=CH), 5.14-5.19 (m, 1H, CH=CHC*H*), 4.91 m, 1H, ArC*H*OH), 2.37-2.38 (d, 1H, *J* = 3.4 Hz, O*H*); MS (APCI pos.): m/z 259.2 (M+1), 241.1 ((M-H_2O)+1).
HPLC: Chiralpak AD-H, hexanes/2-propanol 97/3, 254 nm, t_1 = 28.9 min (major anti), t_2 = 32.4 min, (minor anti). Ee: 95% (anti).

5-(Hydroxy (naphthalen-2-yl) methyl) furan-2(5H)-one (8j):



Reaction of γ-crotonolactone (70.0 μL, 1mmol) with 2-naphthaldehyde (78.0 mg, 0.5 mmol) catalyzed by **6** (54.7 mg, 0.1 mmol) according to the general procedure provided 88.0 mg (73%) of **8j** as a pale yellow solid.
IR: 3359, 1752, 1731, 1172, 1077, 1041, 824 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$): **Anti diastereomer:** δ 7.85-7.90 (m, 4H, Ar*H*), 7.50-7.53 (m, 3H, Ar*H*), 7.35-7.36 (dd, 1H, *J* = 5.8, 1.4 Hz COCH=C*H*), 6.18-6.20 (dd, 1 H, *J* = 5.8, 1.9 Hz, COC*H*=CH), 5.26-5.29 (m, 2H, CH=CHC*H*, ArC*H*OH), 2.50-2.51 (d, 1H, *J* = 3.7 Hz, O*H*); **Syn diastereomer:** δ 7.85-7.90 (m, 4H, Ar*H*), 7.50-7.53 (m, 3H, Ar*H*), 7.17-7.19 (dd, 1H, *J* = 5.8, 1.6 Hz, COCH=C*H*), 6.12-6.14 (dd, 1H, *J* = 5.8, 2.0 Hz, COC*H*=CH), 5.26-5.29 (m, 2H, CH=CHC*H*), 4.87-4.89 (dd, 1H, *J* = 7.1, 3.1 Hz, ArC*H*OH), 2.81 (d, 1H, *J* = 3.1 Hz, O*H*); MS (APCI pos.): m/z 241.0 (M+1), 223.0 ((M-H_2O)+1).
HPLC: Chiralpak AD-H, hexanes/2-propanol 85/15, 254 nm, t_1 = 9.5 min (major anti), t_2 = 11.8 min, (minor anti), t_3 = 12.6 min (major syn), t_4= 13.6 min (minor syn). Ee: 95% (anti).

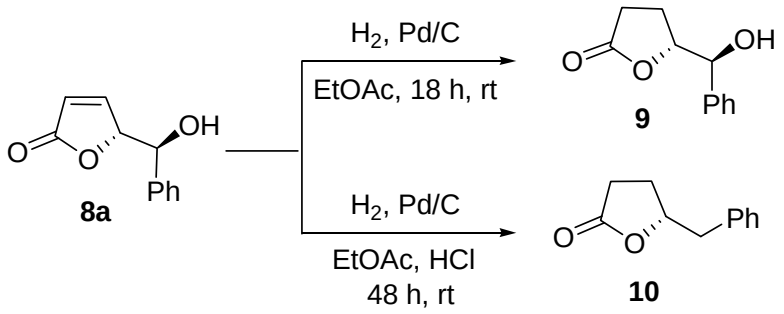
5-(Cyclohexyl (hydroxy) methyl) furan-2(5H)-one (8k):



Reaction of γ-crotonolactone (70.05 μL, 1mmol) with cyclohexanecarboxaldehyde (60.17 μL, 0.5mmol) catalyzed by **5** (45.0 mg, 0.1 mmol) according to the general procedure provided 49.0 mg (50%) of **8k** as a white solid.
IR: 3420, 1747, 1715, 1154, 1112, 1096, 1029, 1004, 870, 845 829 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$): **Anti diastereomer:** δ 7.58-7.60 (dd, 1H, *J* = 5.8, 1.4 Hz, COCH=C*H*), 6.18-6.20 (dd, 1 H, *J* = 5.8, 1.9 Hz, COC*H*=CH), 5.09-5.10 (dt, 1H, *J* = 5.7, 1.6 Hz, CH=CHC*H*), 3.60-3.61 (apparent q, 1H, *J* = 5.6 Hz, ArC*H*OH), 1.96-1.98 (m, 1H, C*H*CH_2), 1.54-1.82 (m, 4H, CH_2), 1.1-1.33 (m, 6H, CH_2); **Syn diastereomer:** δ 7.44-7.45 (dd, 1H, *J* = 5.8, 1.5 Hz, COCH=C*H*), 6.18-6.20 (dd, 1 H, *J* = 5.8, 1.9 Hz, COC*H*=CH), 5.18 (m, 1H, CH=CHC*H*), 3.45-3.49 (m, 1H, ArC*H*OH), 1.96-1.98 (m, 1H, C*H*CH_2), 1.54-1.82 (m, 4H, CH_2), 1.1-1.33 (m, 6H, CH_2); MS (APCI pos.): m/z 197.0 (M+1), 179.1 ((M-H_2O)+1).

HPLC: Chiralpak AD-H, hexanes/2-propanol 95/5, 210 nm, t_1= 15.4 min (major anti), t_2 = 17.5 min (major syn). Ee: >99% (anti).

Determination of the absolute configuration of 8a:

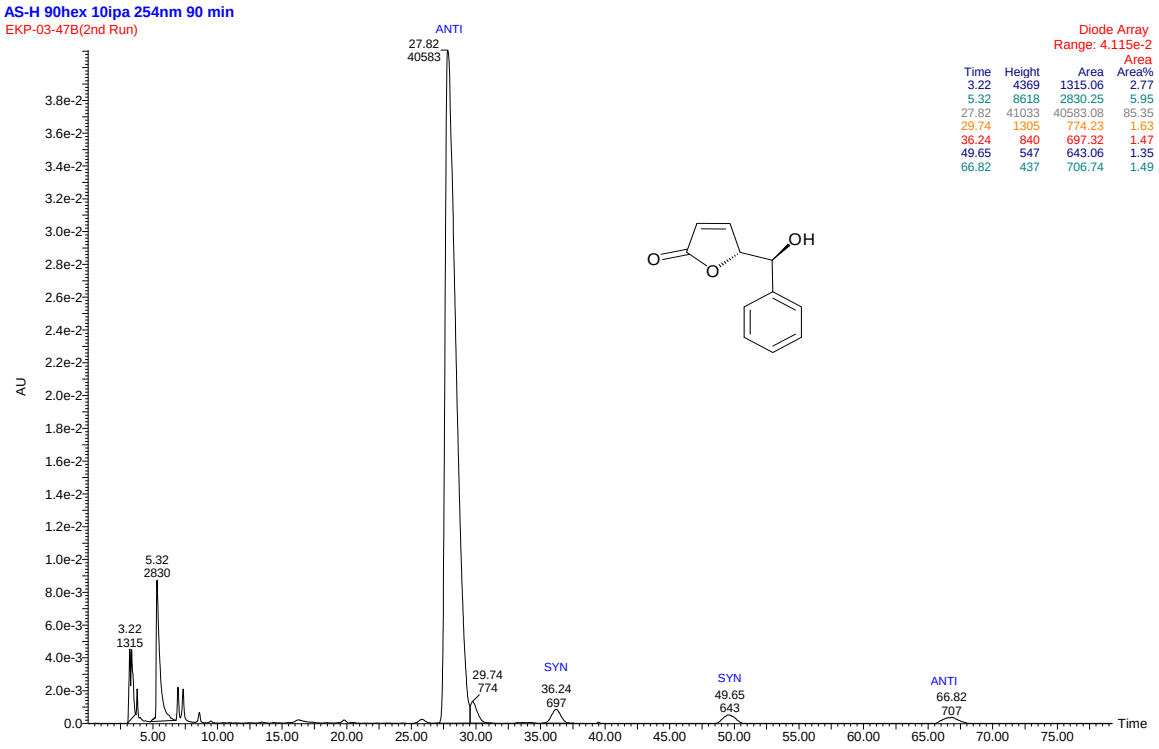


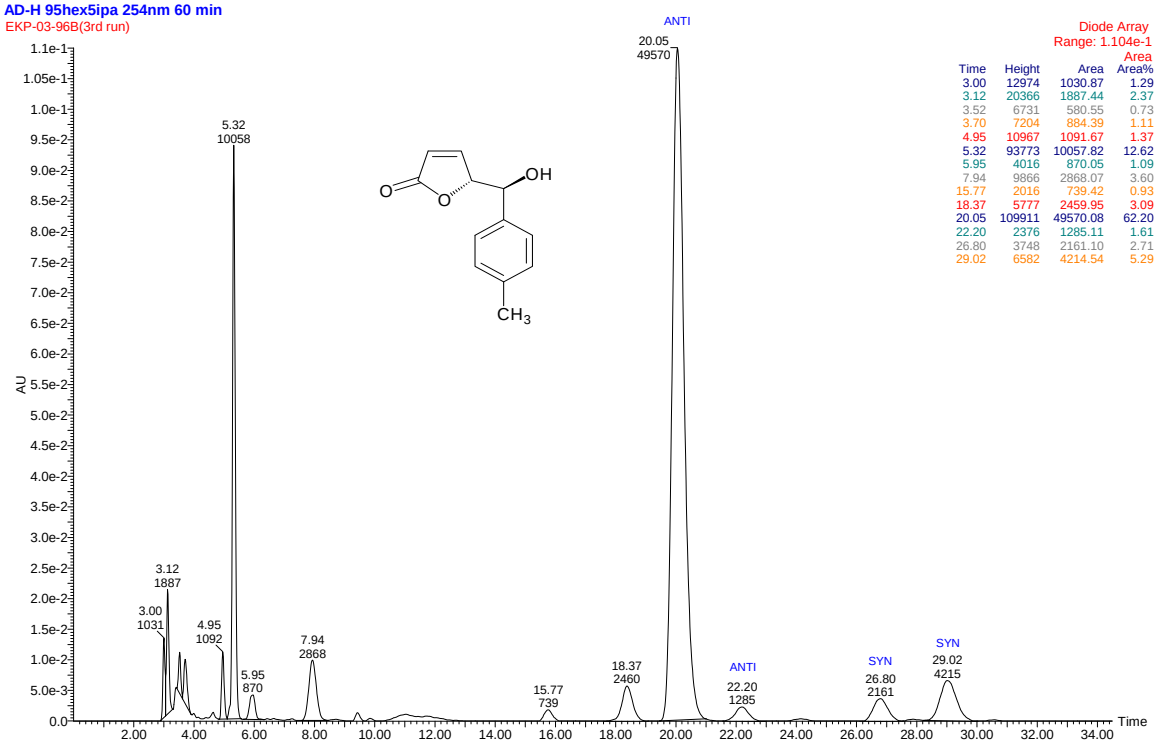
To a solution of **8a** in ethylacetate was added Pd/C and the mixture was stirred under an atmosphere of hydrogen for 18 h. Filtration and concentration of the filtrate provided **9** which was dextrorotatory ($[\alpha]^{23}_D$ = + 50.7 (c 1, $CHCl_3$), 88% ee). The positive rotation indicates that lactone **9** is enantiomeric to the previously reported[2] 5*S*,1'*R* isomer ($[\alpha]^{25}_D$ = - 53.3 (c 0.22, $CHCl_3$) for **9** with 92% ee). Hydrogenolysis of **9** by adaptation of the literature procedure[3] provided **10** which was assigned the *R* configuration on the basis of chiral HPLC retention times[4] (Chiralcel OD-H, hexanes/2-propanol 80/20, 1 mL/min, 214 nm, t_S = 5.95 min, t_R = 6.74 min). Lactone **9** is therefore assigned the 5*R*,1'*S* configuration, and compounds **8a-l** are also assigned the 5*R*,1'*S* configuration by analogy.

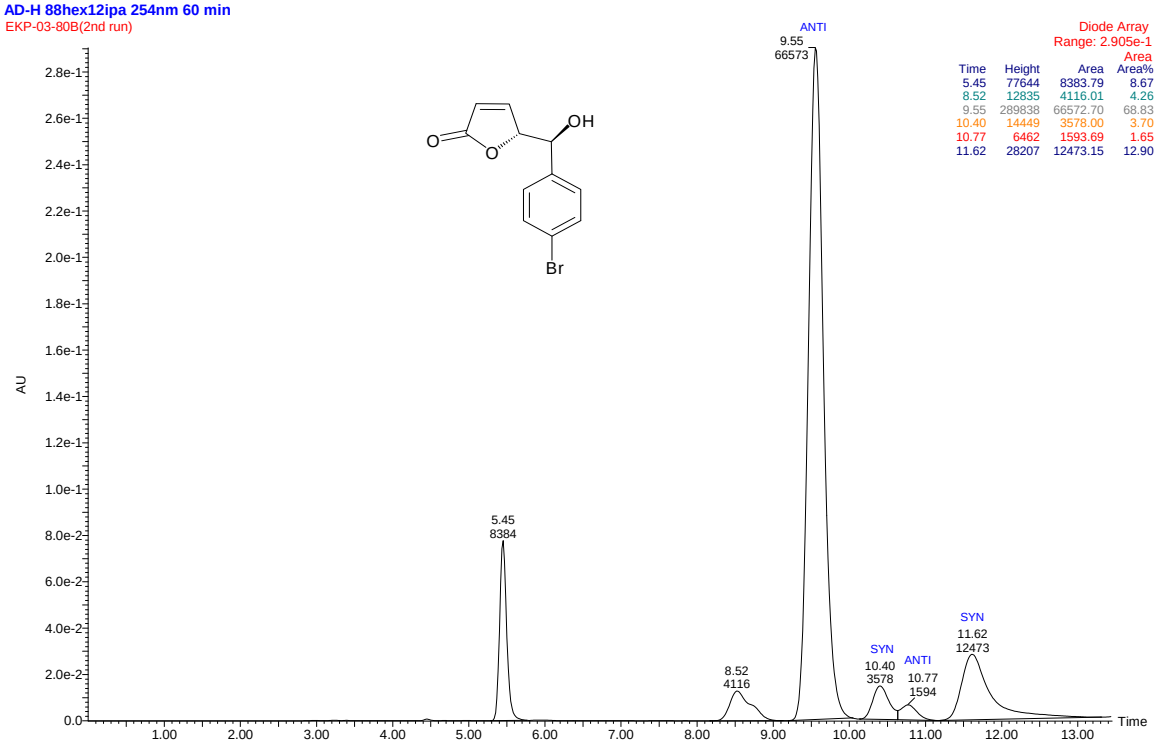
References:

1) (a) Y. Yang, K. Zheng, J. Zhao, L. Lin, X. Liu and X. Feng, *J. Org. Chem.* 2010, **75**, 5382; (b) N. Zhu, B. C. Ma, Y. Zhang and W. Wang, Adv. Synth. Catal. 2010, **352**, 1291.
2) L. Emmanuvel and A. Sudalai, *Tetrahedron Lett.* 2008, **49**, 5736.
3) H. Ube, N. Shimada and M. Terada, *Angew. Chem., Int. Ed.* 2010, **49**, 1858.
4) G. Hoge, *J. Am. Chem. Soc.* 2003, **125**, 10219.

HPLC data for compounds 8a-k



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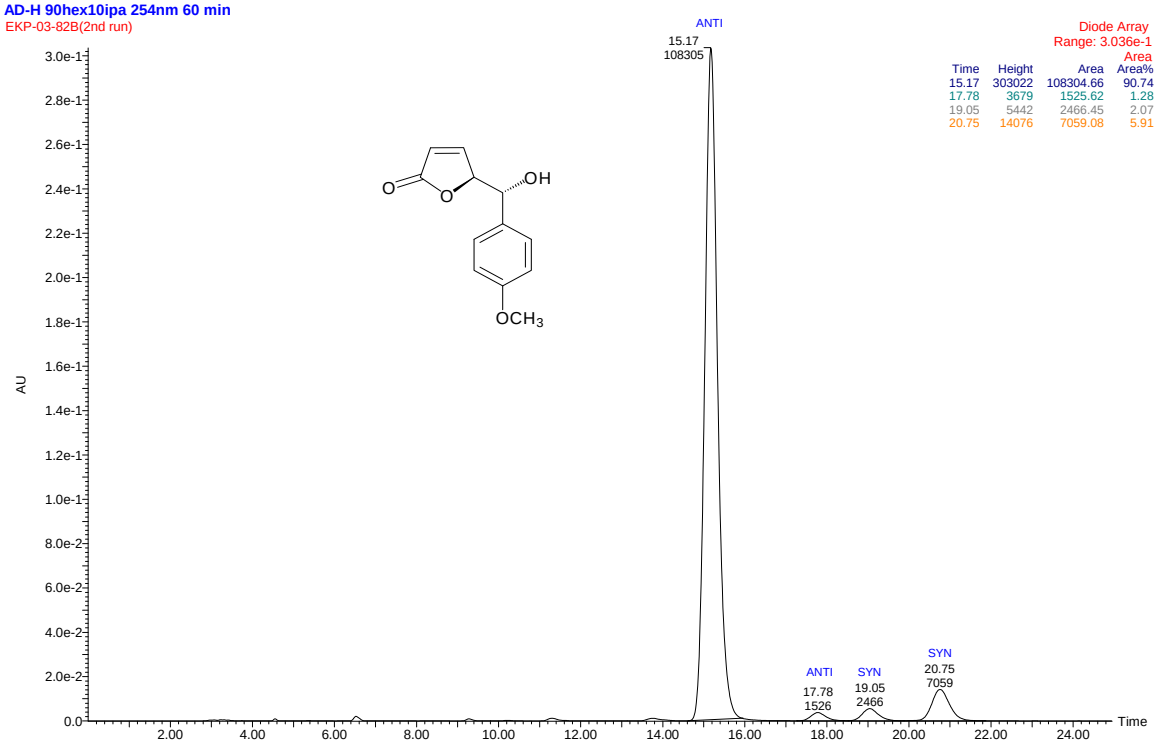
Time Height Area Area%
5.45 77644 8383.79 8.67
8.52 12835 4116.01 4.26
9.55 289838 66572.70 68.83
10.40 14449 3578.00 3.70
10.77 6462 1593.69 1.65
11.62 28207 12473.15 12.90
ANTI
9.55
66573
5.45
8384
8.52
4116
SYN
10.40
3578
ANTI
10.77
1594
SYN
11.62
12473
OH
O
O
Br
AU
Time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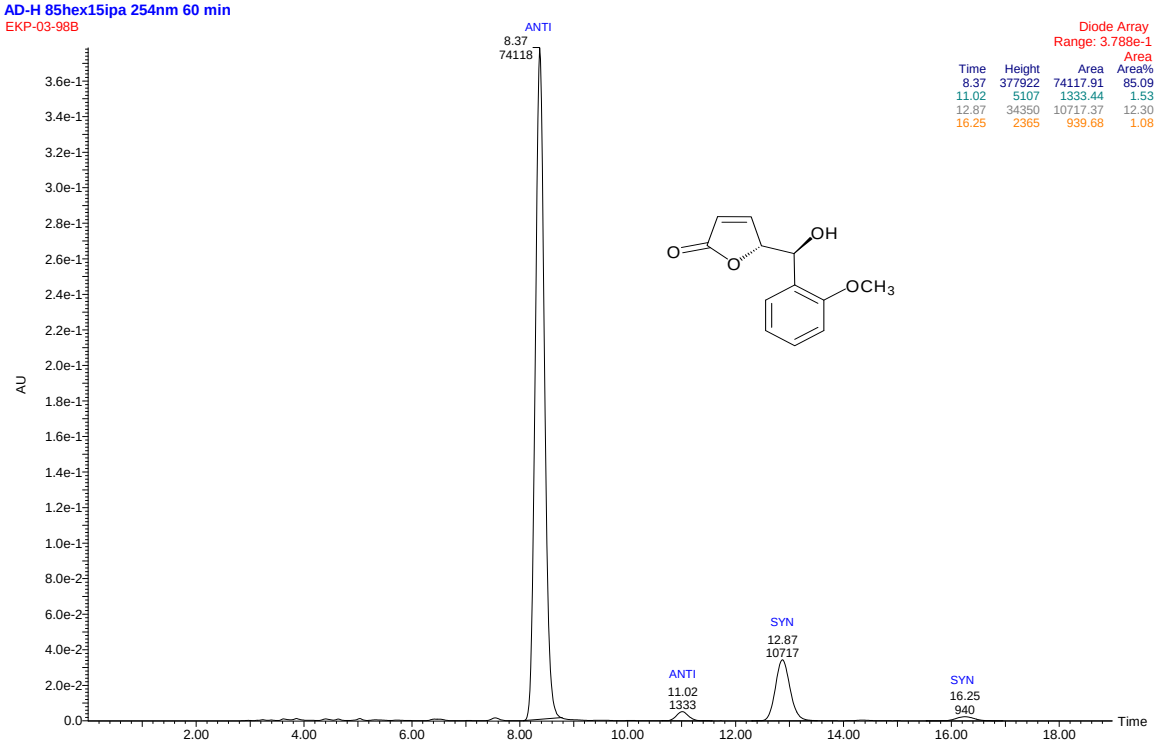
EKP-03-82B(2nd run)
Diode Array
Range: 3.036e-1
Time Height Area Area%
15.17 303022 108304.66 90.74
17.78 3679 1525.62 1.28
19.05 5442 2466.45 2.07
20.75 14076 7059.08 5.91
ANTI
15.17
108305
ANTI
17.78
1526
SYN
19.05
2466
SYN
20.75
7059
OH
O
O
OCH3
AU
Time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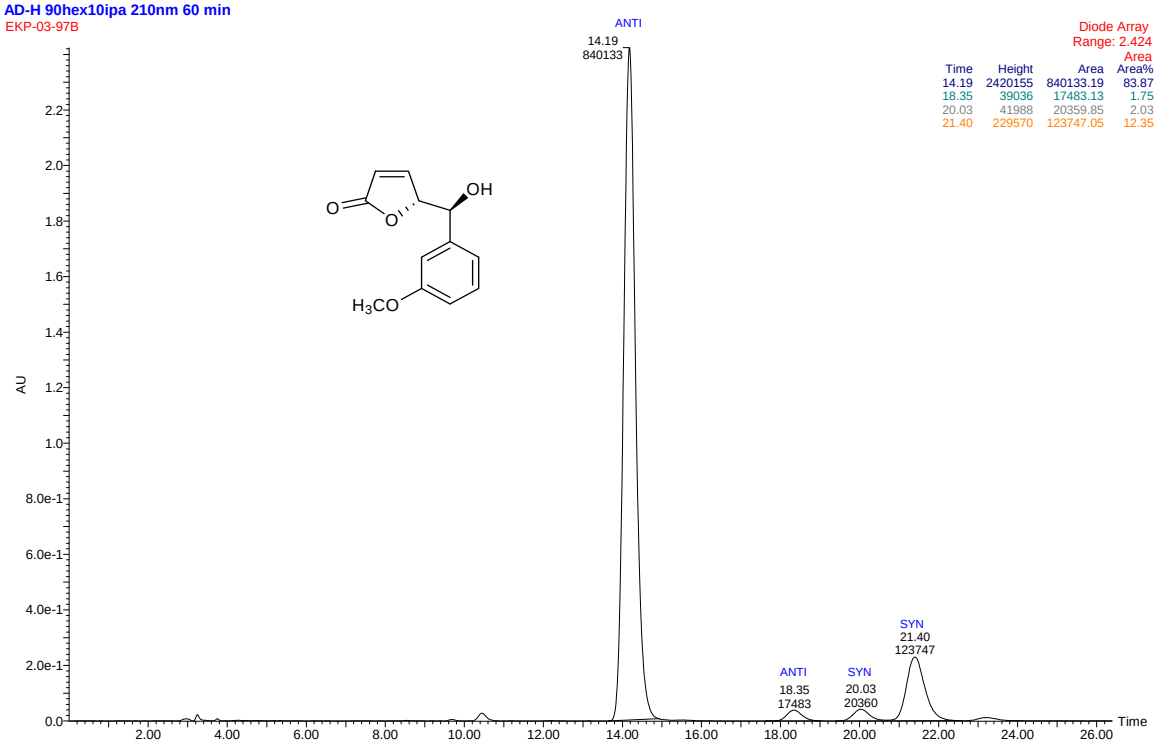
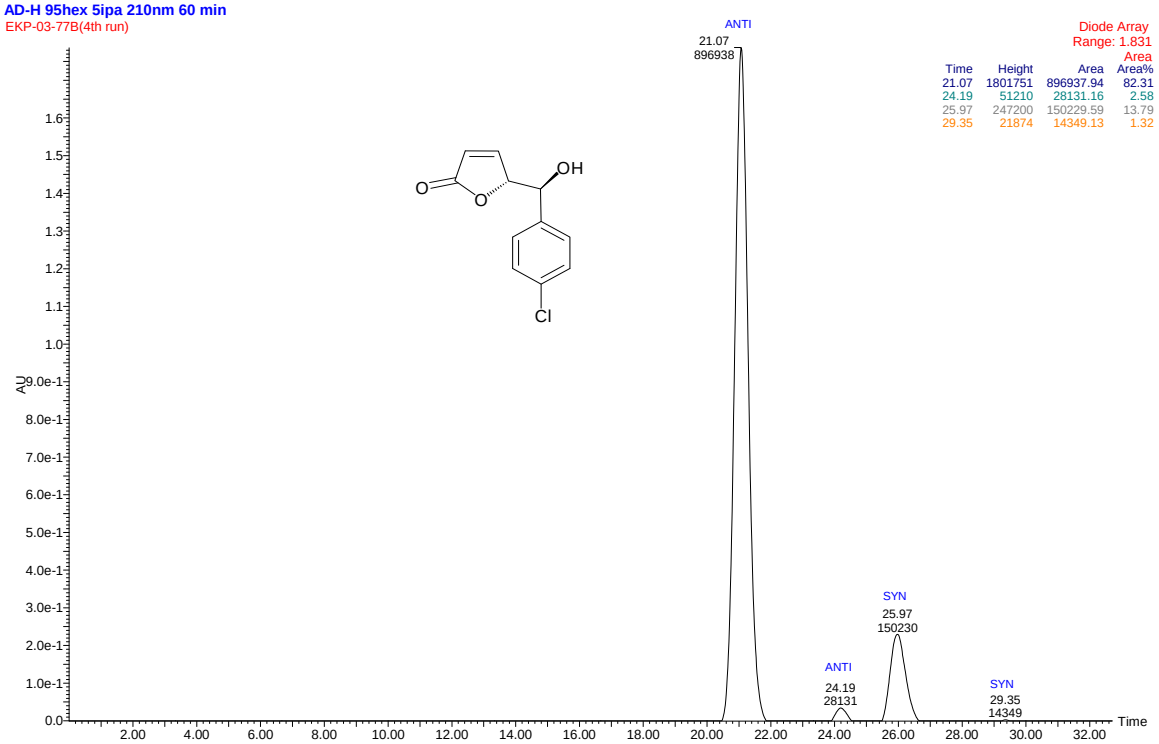
EKP-03-98B
ANTI
8.37
74118
Diode Array
Range: 3.788e-1
Time Height Area Area%
8.37 377922 74117.91 85.09
11.02 5107 1333.44 1.53
12.87 34350 10717.37 12.30
16.25 2365 939.68 1.08
OH
O
O
OCH3
SYN
12.87
10717
ANTI
11.02
1333
SYN
16.25
940
AU
Time


AD-H 90hex10ipa 210nm 60 min
EKP-03-97B
ANTI
14.19
840133
Diode Array
Range: 2.424
Time Height Area Area%
14.19 2420155 840133.19 83.87
18.35 39036 17483.13 1.75
20.03 41988 20359.85 2.03
21.40 229570 123747.05 12.35
OH
O
O
H3CO
SYN
21.40
123747
ANTI
18.35
17483
SYN
20.03
20360
AU
Time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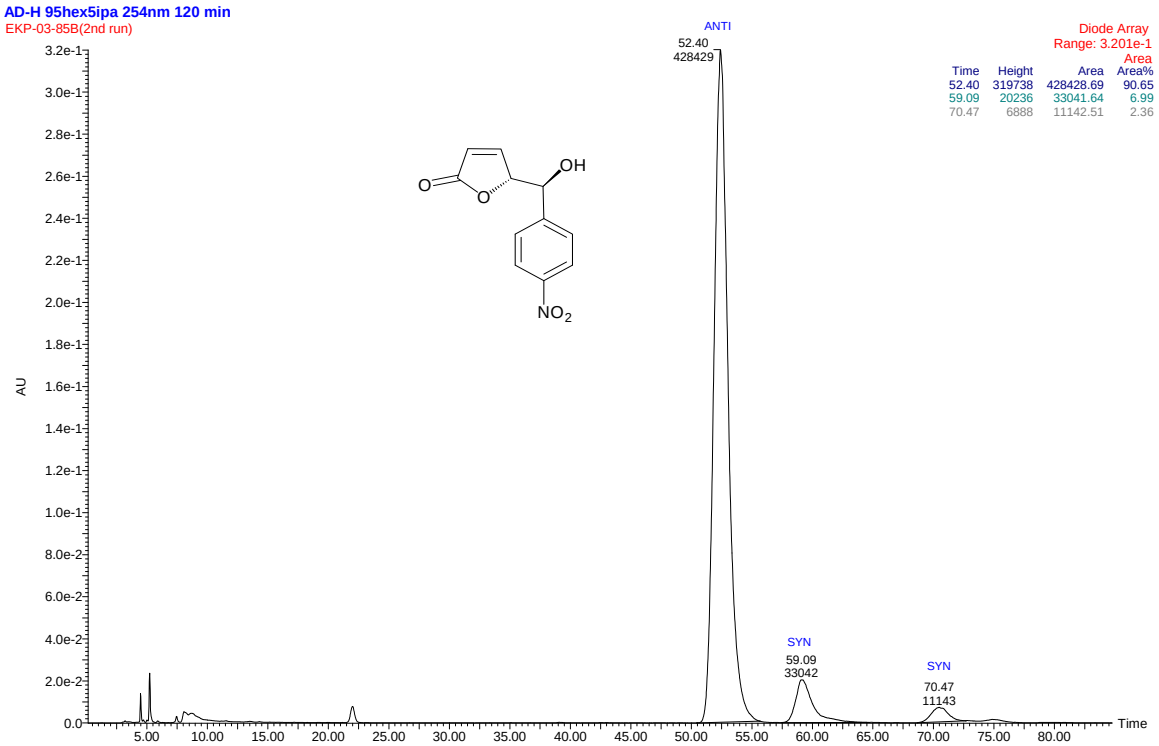
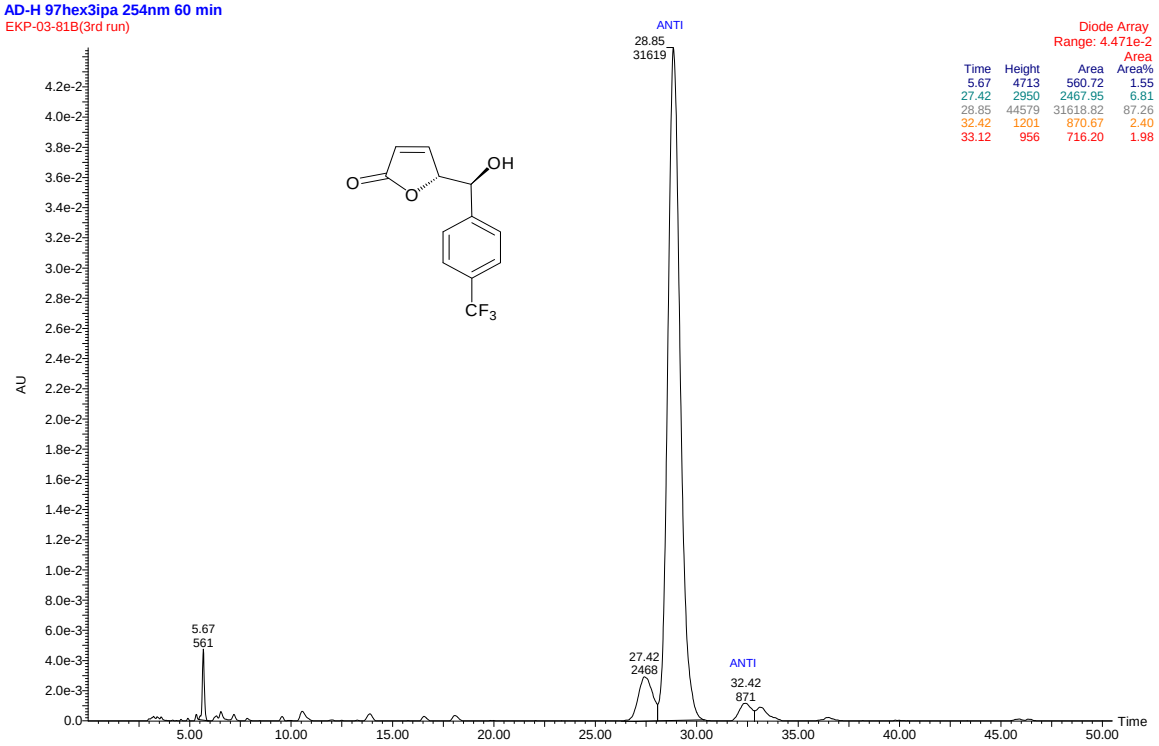
EKP-03-77B(4th run)
ANTI
21.07
896938
Diode Array
Range: 1.831
Time Height Area Area%
21.07 1801751 896937.94 82.31
24.19 51210 28131.16 2.58
25.97 247200 150229.59 13.79
29.35 21874 14349.13 1.32
OH
O
O
Cl
SYN
25.97
150230
ANTI
24.19
28131
SYN
29.35
14349
AU
Time


AD-H 95hex5ipa 254nm 120 min
EKP-03-85B(2nd run)
ANTI
52.40
428429
Diode Array
Range: 3.201e-1
Time Height Area Area%
52.40 319738 428428.69 90.65
59.09 20236 33041.64 6.99
70.47 6888 11142.51 2.36
OH
O
O
NO2
SYN
59.09
33042
SYN
70.47
11143
AU
Time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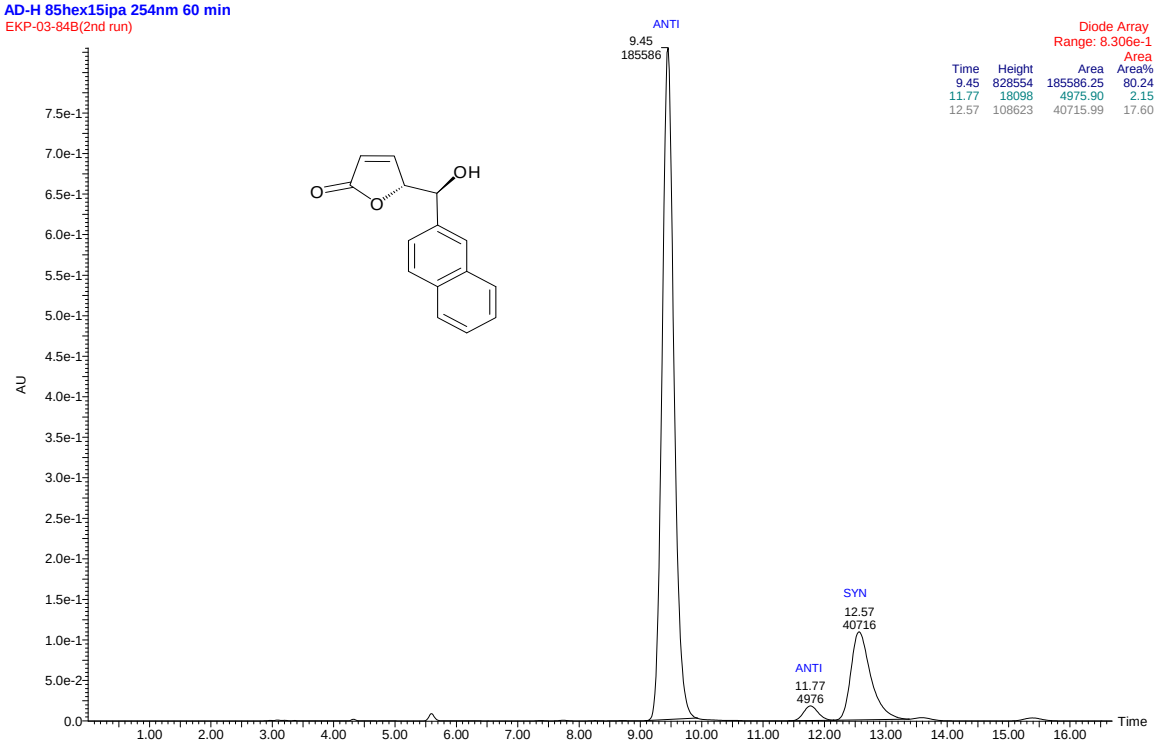
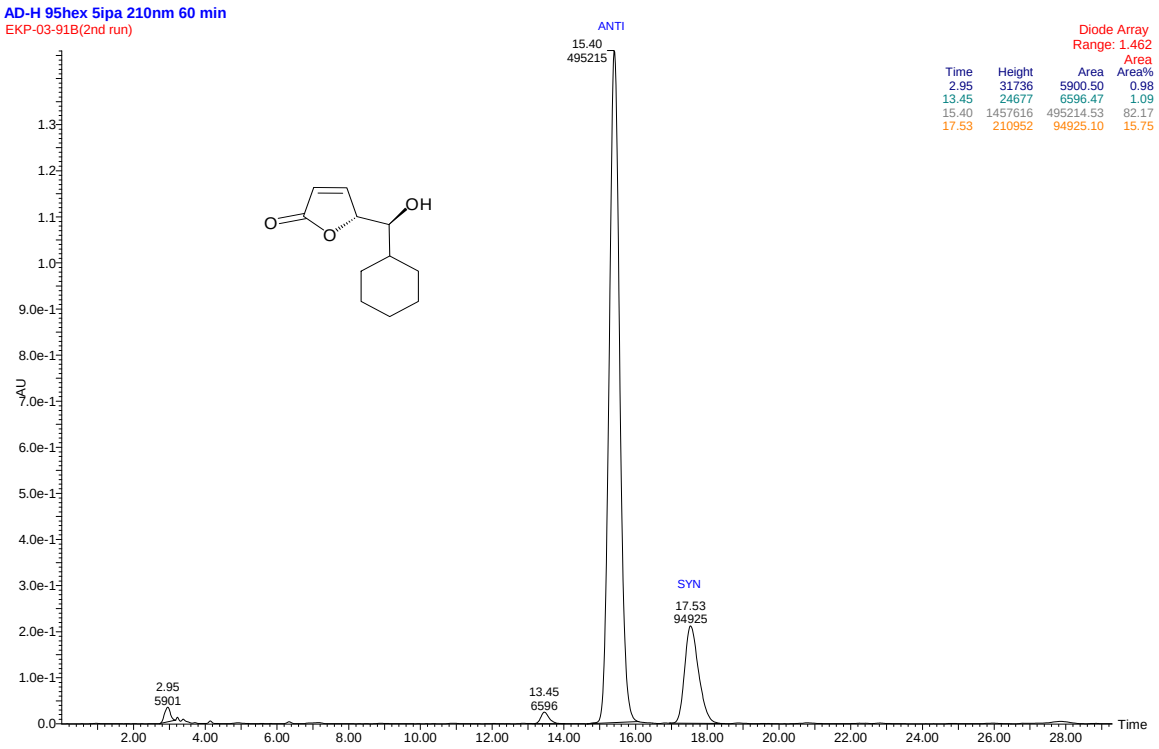
EKP-03-81B(3rd run)
Diode Array
Range: 4.471e-2
Time Height Area Area%
5.67 4713 560.72 1.55
27.42 2950 2467.95 6.81
28.85 44579 31618.82 87.26
32.42 1201 870.67 2.40
33.12 956 716.20 1.98
ANTI
28.85
31619
5.67
561
27.42
2468
ANTI
32.42
871
OH
O
O
CF3
AU
Time


AD-H 85hex15ipa 254nm 60 min
EKP-03-84B(2nd run)
Diode Array
Range: 8.306e-1
Time Height Area Area%
9.45 828554 185586.25 80.24
11.77 18098 4975.90 2.15
12.57 108623 40715.99 17.60
ANTI
9.45
185586
SYN
12.57
40716
ANTI
11.77
4976
OH
O
O
AU
Time


AD-H 95hex 5ipa 210nm 60 min
EKP-03-91B(2nd run)
Diode Array
Range: 1.462
Time Height Area Area%
2.95 31736 5900.50 0.98
13.45 24677 6596.47 1.09
15.40 1457616 495214.53 82.17
17.53 210952 94925.10 15.75
ANTI
15.40
495215
SYN
17.53
94925
2.95
5901
13.45
6596
OH
O
O
AU
Time