**Enantioselective Synthesis of the Optically Active α -Methylene- β -hydroxy Esters,
Equivalent Compounds to Morita-Baylis-Hillman Adducts,
Using Successive Asymmetric Aldol Reaction and Oxidative Deselenization**

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Supporting Information

S1-5 Spectral Data of Compounds

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(Optically Active Aldol Products)

Methyl (2*S*,3*R*)-3-hydroxy-2-methyl-3-(4-methylphenyl)-2-methylselenopropanoate (**6b**)

HPLC (CHIRALCEL AS, *i*-PrOH/hexane = 1/9, flow rate = 1.0 mL/min): t_R = 5.8 min (3.6%), t_R = 6.9 min (96.4%); IR (neat): 3483, 1716 cm^{-1} ; ^1H NMR (CDCl_3): 7.26 (d, J = 8.2 Hz, 2H, Ar), 7.11 (d, J = 8.1 Hz, 2H, Ar), 5.13 (s, 1H, 3-H), 3.71 (s, 3H, OMe), 3.21 (br s, 1H, OH), 2.32 (s, 3H, ArMe), 2.17 (s, 3H, SeMe), 1.33 (s, 3H, 2-Me); ^{13}C NMR (CDCl_3): 173.1, 137.6, 134.7, 128.6, 127.6, 73.1, 52.6, 52.2, 21.1, 16.4, 4.6; HR MS: calcd for $\text{C}_{13}\text{H}_{18}\text{O}_3\text{SeNa}$ ($\text{M}+\text{Na}^+$) 325.0319, found 325.0318.

Methyl (2*S*,3*R*)-3-hydroxy-3-(4-methoxyphenyl)-2-methyl-2-methylselenopropanoate (**6c**)

HPLC (CHIRALCEL AS, *i*-PrOH/hexane = 1/9, flow rate = 1.0 mL/min): t_R = 8.8 min (2.6%), t_R = 11.4 min (97.4%); IR (neat): 3487, 1716 cm^{-1} ; ^1H NMR (CDCl_3): 7.34-7.27 (m, 2H, Ar), 6.86-6.80 (m, 2H, Ar), 5.11 (s, 1H, 3-H), 3.78 (s, 3H, ArOMe), 3.70 (s, 3H, OMe), 3.27 (br s, 1H, OH), 2.15 (s, 3H, SeMe), 1.33 (s, 3H, 2-Me); ^{13}C NMR (CDCl_3): 173.0, 159.2, 129.8,

128.9, 113.2, 72.9, 55.1, 52.5, 52.1, 16.3, 4.5; HR MS: calcd for $C_{13}H_{18}O_4SeNa$ ($M+Na^+$) 341.0268, found 341.0271.

Methyl (2*S*,3*R*)-3-(4-chlorophenyl)-3-hydroxy-2-methyl-2-methylselenopropionate (6d)

HPLC (CHIRALCEL OD-H, *i*-PrOH/hexane = 1/9, flow rate = 0.5 mL/min): t_R = 13.3 min (2.5%), t_R = 16.4 min (97.5%); IR (neat): 3473, 1716 cm^{-1} ; ^1H NMR ($CDCl_3$): 7.35-7.26 (m, 4H, Ar), 5.12 (s, 1H, 3-H), 3.71 (s, 3H, OMe), 3.34 (br s, 1H, OH), 2.16 (s, 3H, SeMe), 1.29 (s, 3H, 2-Me); ^{13}C NMR ($CDCl_3$): 172.8, 136.3, 133.7, 129.2, 128.1, 72.6, 52.3, 52.3, 16.2, 4.7; HR MS: calcd for $C_{12}H_{15}O_3ClSeNa$ ($M+Na^+$) 344.9773, found 344.9775.

Methyl (2*S*,3*R*)-3-hydroxy-2-methyl-2-methylseleno-5-phenylpentanoate (6e)

HPLC (CHIRALCEL OD, *i*-PrOH/hexane = 1/9, flow rate = 1.0 mL/min): t_R = 6.1 min (4.4%), t_R = 8.0 min (95.6%); IR (neat): 3507, 1716 cm^{-1} ; ^1H NMR ($CDCl_3$): 7.31-7.15 (m, 5H, Ph), 3.93 (d, J = 9.9 Hz, 1H, 3-H), 3.70 (s, 3H, OMe), 2.98 (ddd, J = 13.8, 10.0, 4.9 Hz, 1H, 5-H), 2.85 (br s, 1H, OH), 2.68 (ddd, J = 13.8, 9.9, 6.6 Hz, 1H, 5-H), 2.03 (s, 3H, SeMe), 1.91-1.77 (m, 1H, 4-H), 1.67-1.55 (m, 1H, 4-H), 1.43 (s, 3H, 2-Me); ^{13}C NMR ($CDCl_3$): 173.4 (1), 141.9 (Ph), 128.4 (Ph), 128.3 (Ph), 125.8 (Ph), 71.0 (3), 52.2 (OMe), 51.8 (2), 33.4 (4), 33.1 (5), 16.3 (2-Me), 4.0 (SeMe); HR MS: calcd for $C_{14}H_{20}O_3SeNa$ ($M+Na^+$) 339.0476, found 339.0473.

Methyl (2*S*,3*R*)-3-hydroxy-2-methyl-2-methylselenodecanoate (6f)

HPLC (CHIRALCEL OD-H*2, *i*-PrOH/hexane = 1/1000, flow rate = 0.5 mL/min): t_R = 43.4 min (5.0%), t_R = 52.4 min (95.0%); IR (neat): 3508, 1716 cm^{-1} ; ^1H NMR ($CDCl_3$): 3.86 (dd, J = 9.4, 1.5 Hz, 1H, 3-H), 3.72 (s, 3H, OMe), 2.71 (br s, 1H, OH), 2.02 (s, 3H, SeMe), 1.64-1.16 (m, 12H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H), 1.40 (s, 3H, 2-Me), 0.86-0.82 (m, 3H, 10-H); ^{13}C NMR ($CDCl_3$): 173.4, 71.3, 52.2, 52.0, 31.7, 31.5, 29.4, 29.2, 27.0, 22.6, 16.0, 14.0, 3.9; HR MS: calcd for $C_{13}H_{26}O_3SeNa$ ($M+Na^+$) 333.0945, found 333.0946.

Methyl (2*S*,3*R*,4*E*)-3-hydroxy-2-methyl-2-methylseleno-5-phenyl-4-pentenoate (**6g**)

HPLC (CHIRALCEL AS, *i*-PrOH/hexane = 1/9, flow rate = 0.5 mL/min): t_R = 14.3 min (2.9%), t_R = 16.9 min (97.1%); IR (neat): 3483, 1716 cm^{-1} ; ^1H NMR (CDCl_3): 7.40-7.21 (m, 5H, Ph), 6.72 (d, J = 15.8 Hz, 1H, 5-H), 6.21 (dd, J = 15.8, 6.4 Hz, 1H, 4-H), 4.65 (d, J = 6.4 Hz, 1H, 3-H), 3.75 (s, 3H, OMe), 3.12 (br s, 1H, OH), 2.11 (s, 3H, SeMe), 1.50 (s, 3H, 2-Me); ^{13}C NMR (CDCl_3): 173.3, 136.4, 133.5, 128.5, 127.8, 126.6, 125.6, 73.2, 52.3, 51.1, 17.0, 4.3; HR MS: calcd for $\text{C}_{14}\text{H}_{18}\text{O}_3\text{SeNa}$ ($\text{M}+\text{Na}^+$) 337.0319, found 337.0322.

Methyl (2*S*,3*R*,4*E*)-3-hydroxy-2-methyl-2-methylseleno-4-hexenoate (**6h**)

HPLC (CHIRALCEL AS, *i*-PrOH/hexane = 1/19, flow rate = 0.5 mL/min): t_R = 12.3 min (2.9%), t_R = 13.5 min (97.1%); IR (neat): 3457, 1716 cm^{-1} ; ^1H NMR (CDCl_3): 5.81 (dq, J = 15.3, 6.5, 1.0 Hz, 1H, 5-H), 5.51 (ddq, J = 15.3, 6.9, 1.5 Hz, 1H, 4-H), 4.41 (dd, J = 6.9, 1.0 Hz, 1H, 3-H), 3.74 (s, 3H, OMe), 3.00 (br s, 1H, OH), 2.08 (s, 3H, SeMe), 1.71 (dd, J = 6.5, 1.5 Hz, 3H, 6-H), 1.44 (s, 3H, 2-Me); ^{13}C NMR (CDCl_3): 173.4, 130.4, 127.3, 73.4, 52.1, 50.8, 17.9, 17.0, 4.0; HR MS: calcd for $\text{C}_9\text{H}_{16}\text{O}_3\text{SeNa}$ ($\text{M}+\text{Na}^+$) 275.0163, found 275.0166.

(Optically Active Morita-Baylis-Hillman Adducts)

Methyl (*R*)-3-hydroxy-2-methylene-3-(4-methylphenyl)propanoate (**7b**)¹

HPLC (CHIRALCEL AS, *i*-PrOH/hexane = 1/9, flow rate = 0.5 mL/min): t_R = 15.2 min (96.8%), t_R = 22.3 min (3.2%); ^1H NMR (CDCl_3): 7.28-7.14 (m, 4H, Ar), 6.33 (dd, J = 1.2, 0.8 Hz, 1H, exo-H), 5.85 (dd, J = 1.2, 1.2 Hz, 1H, exo-H), 5.53 (dd, J = 1.2, 0.8 Hz, 1H, 3-H), 3.72 (s, 3H, OMe), 2.91 (br s, 1H, OH), 2.34 (s, 3H, ArMe); ^{13}C NMR (CDCl_3): 166.8, 141.9, 138.3, 137.5, 129.1, 126.5, 125.9, 73.1, 51.9, 21.1.

Methyl (*R*)-3-hydroxy-3-(4-methoxyphenyl)-2-methylenepropanoate (**7c**)²

HPLC (CHIRALCEL AS, *i*-PrOH/hexane = 1/9, flow rate = 0.5 mL/min): t_R = 25.8 min (97.3%), t_R = 33.1 min (2.7%); ¹H NMR (CDCl₃): 7.32-7.26 (m, 2H, Ar), 6.90-6.85 (m, 2H, Ar), 6.33 (dd, J = 1.0, 0.8 Hz, 1H, exo-H), 5.85 (dd, J = 1.4, 1.0 Hz, 1H, exo-H), 5.53 (dd, J = 1.4, 0.8 Hz, 1H, 3-H), 3.80 (s, 3H, ArOMe), 3.72 (s, 3H, OMe), 2.88 (br s, 1H, OH); ¹³C NMR (CDCl₃): 166.8, 159.2, 142.1, 133.4, 127.9, 125.7, 113.8, 72.8, 55.2, 51.9.

Methyl (*R*)-3-(4-chlorophenyl)-3-hydroxy-2-methylenepropanoate (**7d**)^{1,3}

HPLC (CHIRALCEL OD-H, *i*-PrOH/hexane = 1/50, flow rate = 0.7 mL/min): t_R = 27.8 min (97.5%), t_R = 32.5 min (2.5%); ¹H NMR (CDCl₃): 7.32-7.31 (m, 4H, Ar), 6.34 (dd, J = 1.0, 0.8 Hz, 1H, exo-H), 5.83 (dd, J = 1.6, 1.0 Hz, 1H, exo-H), 5.52 (dd, J = 1.6, 0.8 Hz, 1H, 3-H), 3.73 (s, 3H, OMe), 3.13 (br s, 1H, OH); ¹³C NMR (CDCl₃): 166.6, 141.5, 139.7, 133.6, 128.6, 127.9, 126.4, 72.7, 52.0.

Methyl (*3R,4E*)-3-hydroxy-2-methylene-5-phenylpentanoate (**7e**)⁴

HPLC (CHIRALCEL OD, *i*-PrOH/hexane = 1/9, flow rate = 0.5 mL/min): t_R = 16.2 min (4.0%), t_R = 21.2 min (96.0%); ¹H NMR (CDCl₃): 7.31-7.14 (m, 5H, Ph), 6.24 (d, J = 0.5 Hz, 1H, exo-H), 5.81 (d, 1H, J = 0.5 Hz, 1H, exo-H), 4.42 (t, J = 6.8 Hz, 1H, 3-H), 3.78 (s, 3H, OMe), 2.87-2.63 (m, 2H, 5-H), 2.04-1.89 (m, 2H, 4-H); ¹³C NMR (CDCl₃): 166.9 (1), 142.2 (Ph), 141.6 (2), 128.4 (Ph), 128.3 (Ph), 125.8 (Ph), 125.2 (exo), 70.9 (3), 51.8 (OMe), 37.6 (4), 32.0 (5).

Methyl (*R*)-3-hydroxy-2-methylenedecanoate (**7f**)⁵

HPLC (CHIRALCEL OD-H, *i*-PrOH/hexane = 1/300, flow rate = 0.5 mL/min): t_R = 35.7 min (97.3%), t_R = 47.6 min (2.7%); ^1H NMR (CDCl_3): 6.21 (dd, J = 1.2, 0.3 Hz, 1H, *exo*-H), 5.78 (dd, J = 1.2, 1.2 Hz, 1H, *exo*-H), 4.37 (tdd, J = 6.1, 1.2, 0.3 Hz, 1H, 3-H), 3.77 (s, 3H, OMe), 2.57 (br s, 1H, OH), 1.67-1.58 (m, 2H, 4-H), 1.48-1.20 (m, 10H, 5-H, 6-H, 7-H, 8-H, 9-H), 0.88-0.84 (m, 3H, 10-H); ^{13}C NMR (CDCl_3): 167.0, 142.5, 124.9, 71.7, 51.8, 36.2, 31.8, 29.3, 29.2, 25.8, 22.6, 14.1.

Methyl (3*R*,4*E*)-3-hydroxy-2-methylene-5-phenyl-4-pentenoate (**7g**)^{6,7}

HPLC (CHIRALCEL AS, *i*-PrOH/hexane = 1/9, flow rate = 0.5 mL/min): t_R = 18.3 min (97.5%), t_R = 24.4 min (2.5%); $[\alpha]_D^{23}$ = +17.9 (c 0.913, CHCl_3); ^1H NMR (CDCl_3): 7.43-7.21 (m, 5H, Ph), 6.67 (dd, J = 15.9, 1.3 Hz, 1H, 5-H), 6.31 (dd, J = 1.3, 0.8 Hz, 1H, *exo*-H), 6.30 (dd, J = 15.9, 5.6 Hz, 1H, 4-H), 5.93 (dd, J = 1.1, 0.8 Hz, 1H, *exo*-H), 5.13 (dddd, J = 5.6, 1.3, 1.3, 1.1 Hz, 1H, 3-H), 3.80 (s, 3H, OMe), 2.96 (br s, 1H, OH); ^{13}C NMR (CDCl_3): 166.7, 141.2, 136.4, 131.3, 129.1, 128.5, 127.8, 126.5, 125.8, 71.9, 52.0.

Methyl (3*R*,4*E*)-3-hydroxy-2-methylene-4-hexenoate (**7h**)⁶

HPLC (CHIRALCEL AS, *i*-PrOH/hexane = 1/50, flow rate = 1.5 mL/min): t_R = 9.6 min (97.5%), t_R = 22.4 min (2.5%); ^1H NMR (CDCl_3): 6.24 (dd, J = 1.0, 0.5 Hz, 1H, *exo*-H), 5.84 (dd, J = 1.2, 1.0 Hz, 1H, *exo*-H), 5.81-5.71 (m, 1H, 5-H), 5.64-5.55 (m, 1H, 4-H), 4.89 (dddd, J = 6.6, 1.2, 1.2, 0.5 Hz, 1H, 3-H), 3.79 (s, 3H, OMe), 2.87 (br s, 1H, OH), 1.74-1.71 (m, 3H, 6-H); ^{13}C NMR (CDCl_3): 166.8, 141.6, 130.9, 128.2, 125.2, 71.8, 51.8, 17.7.

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¹H NMR spectrum of compound 10a in CDCl₃. The x-axis is chemical shift in ppm, ranging from 0 to 10. The spectrum shows several peaks with integration values. Aromatic protons appear as a multiplet between 7.1 and 7.3 ppm (integration 5.06). A broad peak at 3.954 ppm (integration 3.954) is assigned to the NH group. A large peak at 2.942 ppm (integration 3.01) is assigned to the CH₂ group. Other peaks in the 1.4-3.1 ppm range are assigned to various protons in the molecule, including the CH₃ group at 1.432 ppm (integration 3.10).

Chemical Shift (ppm)	Integration
7.313	
7.286	
7.269	
7.260	
7.225	
7.213	
7.200	
7.184	
5.06	
3.954	3.954
3.917	
3.701	
3.687	
3.032	
3.013	
2.979	
2.963	
2.942	3.01
2.925	
2.856	
2.743	
2.719	
2.707	
2.682	
2.668	
2.657	
2.632	
2.035	
1.876	
1.860	
1.845	
1.826	
1.809	
1.771	
1.669	
1.628	
1.432	3.10
1.10	
1.10	
1.02	
0.90	
1.00	
0.99	
2.93	

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 P13 1.00 ms
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 CTMP 17.0 c
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 CLEXR 0.00
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 OBATN 511
 LOOP1 1

C:\NMR95\WINNMR95\yama\M.B.H\oct\AutoINON_E1_FT.als
Octa-BH

DFILE
COMMT
DATIM
EXMOD
OBNUC
OBPRQ
OBSET
OBFIN
POINT
FREQU
CLPNT
TODAT
CLFRQ
SCANS
ACQTM
PD
PW1
PW2
PW3
P11
P12
P13
IRNUC
CTEMP
SLVNT
EXREF
CLEXR
RGAIN
OBRIN
LOOP1

Octa-BH
Tue Feb 15 22:48:43 2005
NON
1H
270.05 MHz
112.00 KHz
5800.0 Hz
32768
5405.4 Hz
1
1
100.0 Hz
16
6.062 sec
0.935 sec
6.0 us
10.0 us
10.0 us
1.000 ms
1.000 ms
1.00 ms
1H
21.5 C
CDCL3
7.26 ppm
0.00
12
511
1

C:\NMR95\WINNMR95\yamai\aldol\chinnam syn\AutoINON EI_FT.als
cinna

DFILE C:\NMR95\WINNMR95\yamai\aldol\chir
 COMMT cinna
 DATIM Sat Jan 22 18:24:00 2005
 EXMOD NON
 OBNUC 1H
 OBFREQ 270.05 MHz
 OBSET 112.00 KHz
 OBFIN 5800.0 Hz
 POINT 32768
 FREQU 5405.4 Hz
 CLPNT 1
 TODAT 1
 CLFREQ 100.0 Hz
 SCANS 16
 ACQTM 6.062 sec
 PD 0.935 sec
 FW1 6.0 us
 FW2 10.0 us
 FW3 10.0 us
 FI1 1.000 ms
 FI2 1.000 ms
 FI3 1.00 ms
 IRENUC 1H
 CTEMP 18.8 C
 SLVNT CDCL3
 EXREF 0.00 ppm
 CLEXR 0.00
 RGAIN 15
 OBTATN 511
 LOOP1 1

OBRO	270.05 MHz	
OBRO	112.00 KHz	
OBSET	5800.0 Hz	
OBFIN	3768	
POINT	5405.4 Hz	
FREQU	1	
CLPNT	1	
TODAT	100.0 Hz	
CLFRQ	6.062 sec	
SCANS	0.935 sec	
ACQTM	6.0 us	
PD	10.0 us	
PW1	10.0 us	
PW2	10.0 us	
PW3	1.000 ms	
P11	1.000 ms	
P12	1.000 ms	
P13	1.00 ms	
IRNUC	1H	
CTEMP	21.5 C	
SVNFT	CDCL3	
EXREF	7.26 ppm	
CLEXR	0.00	
RGAIN	22	
OBATN	511	
LOOP1	1	

C:\NMR95\WINNMR95\yamai\aldol\croton_syn\AutolNON_E1_FT.als
croton_syn

DFILE C:\NMR95\WINNMR95\yamai\aldol\croton_syn
COMPT croton_syn
DATIM Fri Jan 21 12:54:55 2005
EXMOD NON
OBNUC 1H
OBPRO 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.0 Hz
POINT 32768
FREQU 5405.4 Hz
CLPNT 1
TODAT 1
CLPRO 100.0 Hz
SCANS 16
ACQTM 6.062 sec
PD 0.935 sec
FW1 6.0 us
FW2 10.0 us
FW3 10.0 us
P11 1.000 ms
P12 1.000 ms
P13 1.00 ms
IRNUC 1H
CTEMP 20.4 c
SLVNT CDCL3
EXREF 7.26 ppm
CLEXR 0.00
RGAIN 12
OBAIN 511
LOOP1 1

C:\My Documents\NMR95\WINNMR95\yama1\m.b.h\crotonone\Auto1NON_E1_FT.als
crotonone

DFILE
COMNT crotonone
DATIM Fri Aug 05 15:16:11 2005
EXMOD NON
OBNUC 1H
OBRQ 270.05 MHz
OBSE 112.00 KHz
OBFIN 5800.0 Hz
POINT 32768
FREQU 5405.4 Hz
CLENT 1
TODAT 1
CLFRQ 100.0 Hz
SCANS 16
ACQIM 6.062 sec
PD 0.935 sec
PW1 6.0 us
PW2 10.0 us
PW3 10.0 us
P11 1.000 ms
P12 1.000 ms
P13 1.00 ms
IRNUC 1H
CTEMP 22.1 c
SLVNT CDCL3
EXREF 7.26 ppm
CLEXR 0.00
RGAIN 19
OBAIN 511
LOOP1 1

Comparison of the Chemical Shifts of Several Tetra-substituted Ketene Silyl Acetals

(Z)-1-Methoxy-1-(trimethylsiloxy)-2-phenylselenopropene: (E)-1-Methoxy-1-(trimethylsiloxy)-2-phenylselenopropene:

(Z)-KSA 1:

^1H NMR (C_6D_6):

7.52-7.48 (m, 2H, Ph),

7.09-6.95 (m, 3H, Ph),

3.32 (s, 3H, OMe),

2.23 (s, 3H, 3-H),

0.25 (s, 9H, TMS)

(E)-KSA 1:

^1H NMR (C_6D_6):

7.52-7.48 (m, 2H, Ph),

7.09-6.95 (m, 3H, Ph),

3.41 (s, 3H, OMe),

2.12 (s, 3H, 3-H),

0.16 (s, 9H, TMS)

(Z)-1-Methoxy-2-methylseleno-1-(trimethylsiloxy)propene: (E)-1-Methoxy-2-methylseleno-1-(trimethylsiloxy)propene:

(Z)-KSA 2:

^1H NMR (C_6D_6):

3.30 (s, 3H, OMe),

2.13 (s, 3H, 3-H),

1.87 (s, 3H, SeMe),

0.30 (s, 9H, TMS)

(E)-KSA 2:

^1H NMR (C_6D_6):

3.44 (s, 3H, OMe),

2.05 (s, 3H, 3-H),

1.87 (s, 3H, SeMe),

0.16 (s, 9H, TMS)

(Z)-1-Ethoxy-1-(trimethylsiloxy)-2-methylthiopropene:⁸

(Z)-KSA 2':

^1H NMR (C_6D_6):

3.72 (q, $J = 7.0$ Hz, 2H, OEt),

2.08 (s, 3H, SMe),

2.02 (s, 3H, 3-H),

1.06 (t, $J = 7.0$ Hz, 3H, OEt),

0.32 (s, 9H, TMS)

(E)-1-Ethoxy-1-(trimethylsiloxy)-2-methylthiopropene:⁸

(E)-KSA 2':

^1H NMR (C_6D_6):

3.90 (q, $J = 7.0$ Hz, 2H, OEt),

2.07 (s, 3H, SMe),

2.00 (s, 3H, 3-H),

1.10 (t, $J = 7.0$ Hz, 3H, OEt),

0.18 (s, 9H, TMS)

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