Direct Mannich Reaction with Malonates and Simple Imines by Bifunctional Cinchona Alkaloid Catalysts: Enantioselective Synthesis of β-Amino Acids

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General Information: ^{1}H and ^{13}C NMR spectra were recorded on a Varian instrument (400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for ^{1}H NMR are reported as follows: chemical shift (δ, ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz) and integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Infrared spectra were recorded on a Perkin Elmer FT-IR Spectrometer and are reported in frequency of absorption (cm^{-1}). Low resolution mass spectra for all the new compounds were performed by 70SE CI+, and exact mass spectra were recorded on a 70-VSE-B high resolution mass spectrometer. Specific rotations were measured on a Jasco Digital Polarimeter.

High performance liquid chromatography (HPLC) analysis was performed on a Hewlett-Packard 1100 Series instrument equipped with a quaternary pump, using a Daicel Chiralcel OJ, OD Column (250 x 4.6 mm) or Chiralpak AD, AS Column (250 x 4.6 mm) or Regis Pirckle covalent (*R*, *R*) Whelk-O 1 Column (250 x 4.6 mm). UV absorption was monitored at 220 nm.

Materials:

Catalysts Q-**1a**, Q-**1b**, Q-**1d** and QD-**1d** were prepared according to literature procedures.[1] Catalysts **2** and Q-**1c** were prepared according to literature procedures.[2]

Aryl *N*-Boc-Imines **4A-4L** were prepared according to literature procedures.[3]

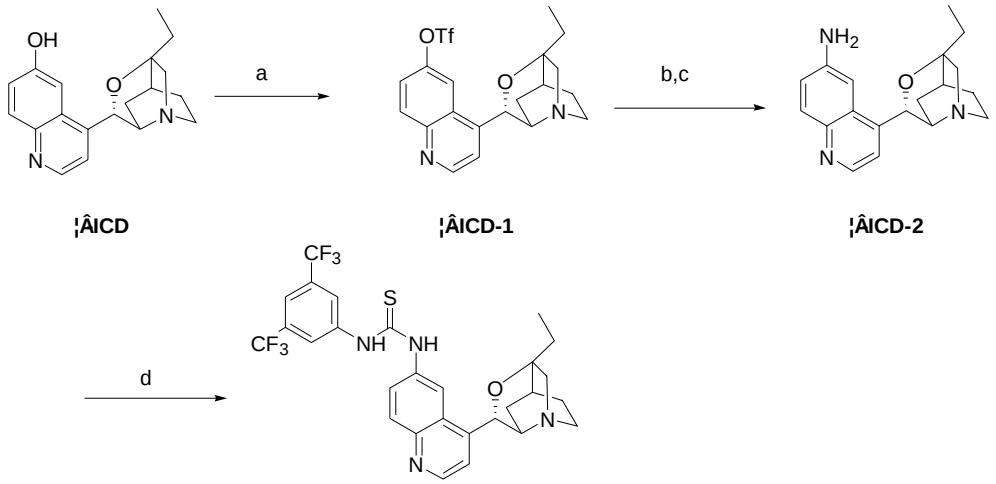
Malonates **5a**, **5b** and β-ketoester **8a** were purchased from Aldrich Inc. Malonate **5c** was purchased from Pfaltz & Bauer, Inc.; β-ketoesters **8b** and **8c** were prepared according to literature procedures.[4]

ACS grade Acetone was used without further purification. Methylene chloride was freshly distilled from calcium hydride under nitrogen atmosphere.

All the commercial reagents were used as received.

[1] Vakulya, B.; Varga, S.; Csámpai, A.; Soós, T. *Org Lett*. **2005**, *7*, 1967
[2] Li, B.; Jiang, L.; Liu, M.; Chen, Y.; Ding, L.; Wu, Y. *Synlett* **2005**, *4*, 603
[3] Wenzel, A. G.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2002**, *124*, 12964
[4] Dezile, R.; Endo, M. US Patent (**1989**), NO. 4831043

1. Preparation of Catalyst 3

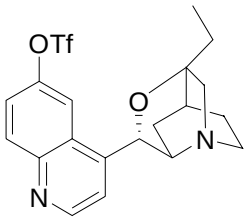


¦ÂICD ¦ÂICD-1 ¦ÂICD-2

3

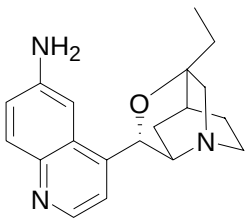
a) $PhNTf_2$, NEt_3, CH_2Cl_2; b) $Pd(OAc)_2$, BINAP, Cs_2CO_3, THF, $Ph_2C{=}NH$; c) NH_2OH HCl, THF, d) $3,5\text{-}(CF_3)_2PhNCS$, THF

The synthesis of **3** was accomplished by using the procedure described by Corey and Zhang.[5] The starting material β-ICD was prepared according to reported procedure.[6]



¦ÂICD-1

To a solution of β-ICD (1.24 g, 4.0 mmol) and *N*-phenyl-bis(trifluoromethanesulfonimide) (1.71g, 4.8 mmol) in anhydrous methylene chloride (40 mL), was added triethylamine (1.01g, 10 mmol) at room temperature. After stirred at room temperature for 15 h, the reaction mixture was transferred to a separation funnel, washed with saturated sodium carbonate aqueous solution (50 mL) and brine (50 mL). The organic layer was collected, dried over anhydrous sodium sulfate and concentrated under reduced pressure. Silica gel flash chromatography of the residue (3% MeOH and 1% $NH_3{\cdot}H_2O$ in EtOAc) gave crude **β-ICD-1** as yellow sticky oil (1.25 g). The crude product was used directly for the next step without further purification.

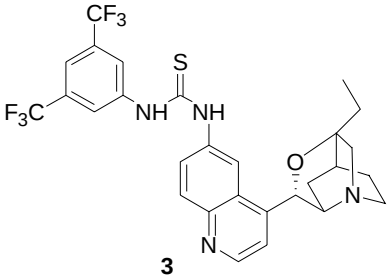


¦ÂICD-2

The crude **β-ICD-1** (1.25 g), palladium acetate (128 mg, 0.57 mmol), BINAP (175 mg, 0.275 mmol), cesium carbonate (1.38 g, 4.23 mmol), and benzophenone imine (1.03 g, 5.7 mmol) were suspended in THF (35 mL). The reaction mixture was refluxed with stirring for 24 h. Then the reaction mixture was cooled to room temperature, diluted with EtOAc (20 mL), washed with 5% sodium carbonate aqueous solution (30 mL) and brine (30 mL). The organic layer was collected, dried over anhydrous sodium sulfate and concentrated under reduced

[5] Corey, E. J.; Zhang, J. *Org. Lett.* **2001**, *3*, 3211
[6] Iwabuchi, Y.; Nakatani, M.; Yokoyama, N.; Hatakeyama, S. *J. Am. Chem. Soc.* **1999**, *121*, 10219

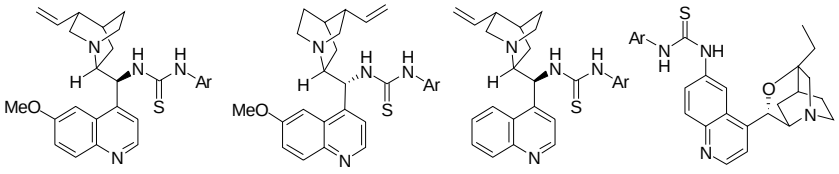
pressure to yield crude imine that was hydrolyzed without further purification. To the solution of the residue (1.05 g) in methanol (25 mL), was added $NH_2OH{\cdot}HCl$ (306 mg, 4.4 mmol) and NaOAc (541 mg, 6.6 mmol). The reaction mixture was stirred for 3 h at room temperature. Then the reaction mixture was concentrated and extracted with saturated Na_2CO_3 (aq.) and CH_2Cl_2 (v : v = 1:1, 20 mL, 8 times). All extractions were combined. Organic layers were collected, washed with brine (60 mL), dried over anhydrous sodium sulfate and concentrated. Pure β-ICD-**2** was obtained as a red foam by flash chromatography (silica gel: EtOAc: MeOH : $NH_3{\cdot}$ H_2O = 90 : 6 : 1) (524 mg, 1.7 mmol, 43% yield from β-ICD). $\mathbf{[\alpha]_D^{25}}$ =141.2 (*c* = 0.72, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.03 (t, *J* = 8.0 Hz, 3H), 1.26 (q, *J* = 6.0 Hz, 1H), 1.46-1.84 (m, 4H), 2.14-2.16 (m, 1H), 2.70 (d, *J* = 13.6 Hz, 1H), 3.02-3.06 (m, 2H), 3.36 (brs, 1H), 3.50-3.62 (m, 2H), 4.12 (s, 2H), 5.88 (s, 1H), 7.06-7.14 (m, 2H) 7.62 (d, *J* = 4.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 8.66 (d, *J* = 4.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 7.31, 23.39, 24.03, 27.34, 32.76, 46.62, 54.63, 56.29, 73.00, 77.07, 102.34, 119.04, 120.83, 126.77, 131.45, 141.44, 142.87, 144.97, 146.38; **IR** (neat) ν 3325, 2962, 1621, 1514; **HRMS**: calc'd for $(M+H)^+$ $C_{19}H_{24}N_3O_6$: 310.1919; found 310.1916.



3

To a solution of **β-ICD-2** (260 mg, 0.85 mmol) in THF (10 mL) was added 3,5-bis-trifluoromethylphenyl isothiocyanate (255 mg, 0.94 mmol) and the reaction mixture was stirred for 16 h at room temperature. The reaction mixture was concentrated and the crude product was purified by flash chromatograph (silica gel: EtOAc : MeOH : $NH_3{\cdot}H_2O$ = 100 : 2 : 1). This yielded **3** as white foam (410 mg, 0.71 mmol, 84% yield). $\mathbf{[\alpha]_D^{25}}$ =75.7 (*c* = 0.63, $CHCl_3$); **^{1}H NMR** (400 MHz, CD_3OD) δ 1.04 (t, *J* = 7.2 Hz, 3H), 1.32-1.42 (m, 1H), 1.50-1.62 (m, 1H), 1.62-1.82 (m, 4H), 2.12-2.18 (m, 1H), 2.80-2.86 (m, 1H), 3.00-3.10 (m, 2H), 3.30 (brs, 1H), 3.45-3.60 (m, 2H), 4.91 (s, 2H), 5.94 (s, 1H), 7.69 (s, 1H), 7.80-7.84 (m, 1H), 7.90-8.08 (m, 3H), 8.25 (s, 1H), 8.83 (d, *J* = 4.4 Hz, 1H); **^{13}C NMR** (100 MHz, CD_3OD) δ 6.39, 23.86, 23.33, 27.11, 32.96, 46.10, 53.82, 56.75, 72.82, 77.41, 117.21, 119.63, 122.18, 123.55, 124.88, 125.84, 127.98, 129.36, 131.48 (q, *J* = 34 Hz), 137.78, 141.92, 145.35, 149.36, 181.53; **IR (neat)** ν 2918, 1614, 1277, 1120, 1174; **HRMS**: calc'd for $(M+H)^+$ $C_{28}H_{27}N_4OSF_6$: 581.1810; found 581.1812.

2. Catalyst Screening

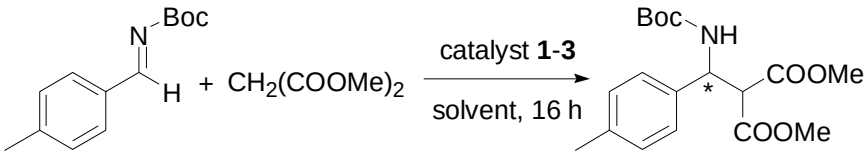


Q-**1** QD-**1** **2** **3**

1a Ar = 4-*t*-Bu-Ph-; **1b** Ar = 2-*i*-Pr-Ph-**;**
1c Ar = Ph-**; 1d** Ar = 3,5-*bis*CF_3Ph-

2,3: Ar = 3,5-*bis*CF_3Ph-

Figure 1. C6' or C9 thiourea cinchona alkaloid derivatives.

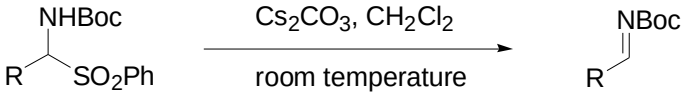


4D **5a** **6Da**

entry	cat.	temp (^{o}C)	solvent	conv./%[b]	ee/%[c]
1	Q-**1a**	RT	CH_2Cl_2	>98	57
2	Q-**1b**	RT	CH_2Cl_2	>98	43
3	Q-**1c**	RT	CH_2Cl_2	>98	62
4	Q-**1d**	RT	CH_2Cl_2	>98	77
5	QD-**1d**	RT	CH_2Cl_2	>98	-74
6	**2**	RT	CH_2Cl_2	>98	65
7	**3**	RT	CH_2Cl_2	>98	72
8	Q-**1d**	RT	CH_3CN	>98	83
9	Q-**1d**	RT	Acetone	>98	77
10	Q-**1d**	-20	CH_2Cl_2	>98	80
11	Q-**1d**	-20	CH_3CN	>98	74
12	Q-**1d**	-20	Acetone	>98	85
13[d]	Q-**1d**	-60	Acetone	>98	93
14[d]	Quinidine	-60	Acetone	>98	25
15[d]	**3**	-60	Acetone	>98	0

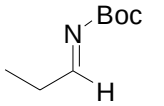
[a] Unless noted, reactions were run with 0.05 mmol of **4D**, 0.15 mmol of **5a** in 0.10 mL of solvent with 10 mol% catalyst at room temperature for 16 h. [b] Determined by ^{1}H NMR analysis. [c] Determined by HPLC analysis. [d] Reaction was run with catalyst (20 mol%) at -60 ^{o}C for 24 h.

3. General procedure for the preparation of *N*-Boc imine **4M**, **4N**, **4O**

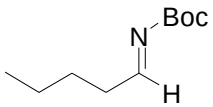


4M-4O

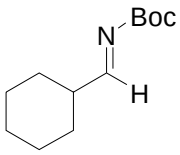
To a round bottom flask (50 mL) was added cesium carbonate (1.64 g, 10.0 mmol). The solids were placed under vacuum and flame-dried. Once cool, anhydrous methylene chloride (10 mL) was added under a positive stream of nitrogen, followed by the addition of *N*-(*tert*-butoxycarbonyl)–α-(phenylsulfonyl)alkylamine (1.0 mmol)[3]. The reaction mixture was stirred at room temperature for 4 to 10 h. Then reaction mixture was cooled to 0°C by ice-water bath, diluted with hexanes (10 mL, pre-cooled with ice-water bath). The organic layer was washed with water (10 mL, twice, precooled with ice-water bath), brine (10 mL) and dried over anhydrous sodium sulfate. Solvent was removed by rotavap under reduced pressure (water bath temperature was kept below 15°C) to give pure *N*-Boc imine. The *N*-Boc imine was used for Mannich reaction immediately.



(**4M**) Reaction was performed in 1.0-mmol scale using the general procedure. After 4 h, **4M** was isolated as a colorless liquid (124 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (t, *J* = 7.2 Hz, 3H), 1.53 (s, 9H), 2.43 (brs, 2H), 8.32 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.67, 27.73, 29.42, 81.96, 161.98, 175.75; IR (neat) ν 2928, 1721, 1667, 1160;



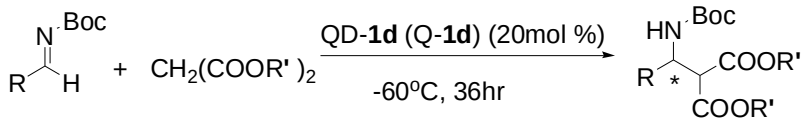
(**4N**) Reaction was performed in 2.0-mmol scale using the general procedure. After 7 h, **4N** was isolated as a colorless liquid (327 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.6 Hz, 3H), 1.39 (q, *J* = 7.2 Hz, 2H), 1.53 (s, 9H), 1.60 (m, 2H), 2.40 (brs, 2H), 8.31 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.62, 22.15, 26.72, 27.67, 35.78, 81.80, 161.98, 175.48; IR (neat) ν 2962, 2928, 1723, 1666, 1456, 1364, 1253, 1160;



(**4O**) Reaction was performed in 5.0-mmol scale using the general procedure. After 10 h, **4O** was obtained as a colorless oil (1.01 g, 96%). The spectrum data was identical to the reported value[7].

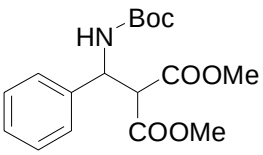
[7] After the submission of this paper, a similar procedure to make **4O** was reported online. Trost, B. M.; Jaratjaroonphong, J.; Reutrakul, V. *J. Am. Chem. Soc.* **2006**, *128*, 2778

4. General Procedure for Enantionselective Mannich Reaction of Malonate 5 to Aryl Imine 4:



4 **5** **5a**: R'=Me; **b**: R'=Bn; **c**: R'=Allyl **6**

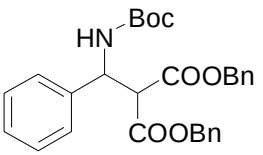
To a solution of imine **4** (0.20 mmol) and chiral catalyst (20 mol%) in acetone (0.40 mL) at –60 °C, was added malonate **5** (0.30 mmol) in one portion. The resulting mixture was kept at –60 °C for 36 h. The reaction mixture was diluted with ethyl ether (5 ml) and allowed to pass through a short silica gel column. Then the filtrate was concentrated and purified by silica gel flash chromatography using the solvent specified below.



6Aa

(+)-6Aa This product was obtained as a white solid (61 mg) in 90% yield after flash chromatography (silica gel: Ethyl ether / Hexane = 1 / 5) and in 97% ee as determined by HPLC [Daicel Chiralpak AD, Hexane / IPA = 90 / 10, 1.0 ml·min^{-1}, λ = 220 nm, t_r (major) = 16.15 min, t_r (minor) = 21.51 min] from a reaction catalyzed by QD-**1d** (20 mol%) at –60 °C for 36 h. $[\alpha]_D^{25}$ = 16.8 (*c* = 0.90, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.42 (s, 9H), 3.63 (s, 3H), 3.73 (s, 3H), 3.94 (s, 1H), 5.49 (brs, 1H), 6.17 (brs, 1H), 7.20-7.40 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.14, 52.41, 52.74, 53.27, 56.55, 79.62, 126.08, 127.53, 128.49, 139.27, 154.98, 167.44, 168.27; **IR** (neat) ν 3387, 1719, 1497, 1246, 1164 ; **HRMS**: calc'd for $(M+Na)^+$ $C_{17}H_{23}NO_6Na$: 360.1423; found 360.1420.

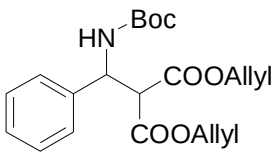
(-)-6Aa This product was obtained as a white solid in 91% yield and 93% ee from a reaction catalyzed by Q-**1d** (20 mol%) at –60 °C for 36 h.



6Ab

(+)-6Ab This product was obtained as a colorless oil (98 mg) in 99% yield after flash chromatography (silica gel: Ethyl acetate / Hexane = 1/15) and in 96% ee as determined by HPLC [Regis Pirckle Covalent (*R*, *R*) Whelk-O 1, Hexane / IPA = 99 / 1, 1.0 ml·min^{-1}, λ = 220 nm, t_r (major) = 14.89 min, t_r (minor) = 12.49 min] from a reaction catalyzed by QD-**1d** (20 mol%) at –60 °C for 36 h. $[\alpha]_D^{25}$ = 14.0 (*c* = 0.98, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.41 (s, 9H), 4.01 (s, 1H), 5.04 (s, 2H), 5.13 (dd, *J* = 8.0 Hz, 12.0 Hz, 2H), 5.56 (brs, 1H), 6.20 (brs, 1H), 7.06-7.12 (m, 2H), 7.20-7.36 (m, 13H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.22, 53.41, 56.81, 67.21, 67.61, 79.65, 126.15, 127.55, 127.98, 128.21, 128.25, 128.35, 128.43, 128.52, 128.53, 134,78, 134.90, 139.21, 154.98, 166.78, 167.76; **IR** (neat) ν 3423, 1720, 1497, 1254, 1162 ; **HRMS**: calc'd for $(M+H)^+$ $C_{29}H_{32}NO_6$: 490.2230; found 490.2227.

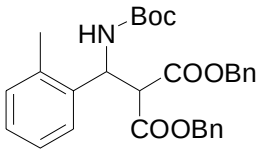
(-)-6Ab This product was obtained as a colorless oil in 99% yield and 94% ee from a reaction catalyzed by Q-**1d** (20 mol%) at –60 °C for 36 h.



6Ac

(+)-6Ac This product was obtained as a colorless oil (71 mg) in 91% yield after flash chromatography (silica get: Ethyl acetate / Hexane = 1 / 6) and in 98% ee as determined by HPLC [Daicel Chiralpak AS, Hexane / IPA = 98 / 2, 1.0 ml·min^{-1}, λ = 220 nm, t_r (major) = 12.63 min, t_r (minor) = 11.00 min] from a reaction catalyzed by QD-**1d** (20 mol%) at –60 °C for 36 h. $[\alpha]_D^{25}$ = 12.3 (*c* = 1.22, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.41 (s, 9H), 3.98 (s, 1H), 4.42-4.72(m, 4H), 5.08-5.18 (m, 2H), 5.20-5.38 (m, 2H), 5.53 (brs, 1H), 5.66-5.80 (m, 1H), 5.82-5.94(m, 1H), 6.20 (brs, 1H), 7.20-7.40 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.23, 53.36, 56.82, 66.07, 66.45, 79.64, 116.68, 118.95, 126.20, 127.58, 128.55, 131,05, 131.21, 139.33, 154.96, 166.68, 167.59; **IR** (neat) ν 3431, 1722, 1497, 1250, 1166; **HRMS**: calc'd for $(M+Na)^+$ $C_{21}H_{27}NO_6Na$: 412.1736; found 412.1727.

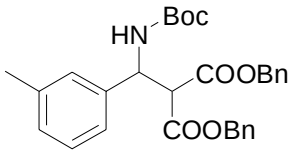
(-)-6Ac This product was obtained as a colorless oil in 86% yield and 92% ee from a reaction catalyzed by Q-**1d** (20 mol%) at –60 °C for 36 h.



6Bb

(+)-6Bb This product was obtained as a colorless oil (99 mg) in 97% yield after flash chromatography (silica gel: Ethyl acetate / Hexane = 1 / 15) and in 99% ee as determined by HPLC [Daicel chiralpak AS, Hexane / IPA = 95 / 5, 1.0 ml·min^{-1}, λ = 220nm, t_r (major) = 11.70 min, t_r (minor) = 7.50 min] from a reaction catalyzed by QD-**1d** at –60 °C for 36 h. $[\alpha]_D^{25}$ = 0.20 (*c* = 2.00, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.38 (s, 9H), 2.40 (s, 3H), 3.86 (s, 1H), 5.00-5.22 (m, 4H), 5.72 (brs, 1H), 6.23 (brs, 1H), 7.06-7.20 (m, 6H), 7.20-7.40 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 19.02, 28.22, 50.41, 55.41, 67.27, 67.51, 79.61, 125.48, 126.23, 127.60, 128.03, 128.29, 128.46, 128.52, 130.73, 134.79, 135.02, 137.58, 154.83, 166.76, 167.75; **IR** (neat) ν 3422, 1718, 1498, 1164; **HRMS**: calc'd for $(M+H)^+$ $C_{30}H_{34}NO_6$: 504.2386; found 504.2382.

(-)-6Bb This product was obtained as a colorless oil in 96% yield and 95% ee from a reaction catalyzed by Q-**1d** (20 mol%) at –60 °C for 36 h.

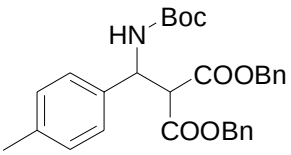


6Cb

(+)- 6Cb This product was obtained as a colorless oil (103 mg) in 99% yield after flash chromatography (silica gel: Ethyl acetate / Hexane = 1 / 12) and in 98% ee as determined by HPLC [Daicel Chiralcel OD, Hexane / IPA = 90 : 10, 0.5 ml·min^{-1}, λ= 220 nm, t_r (major) = 16.61 min, t_r (minor) = 14.19 min] from a reaction catalyzed by QD-**1d** at –60 °C for 36 h. $[\alpha]_D^{25}$ = 15.4 (*c* = 2.00, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.41 (s, 9H), 2.23 (s, 3H), 4.01 (s, 1H), 5.06 (s, 2H), 5.14 (dd, *J* = 8.0 Hz, 12.0 Hz, 2H), 5.53 (brs, 1H), 6.18 (brs, 1H), 7.02-7.12 (m, 5H), 7.13-7.20 (m, 2H), 7.23-7.36 (m, 7H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.40, 28.23, 53.41, 56.85, 67.16, 67.57, 79.59, 123.12, 126.92, 127.92, 128.20, 128.23, 128.33, 128.42, 128.51, 134,84, 134.94, 138.15, 139.15, 148.81, 149.96, 154.99, 166.83, 167.77; **IR** (neat)

ν 3431, 1718, 1497, 1165; **HRMS**: calc'd for $(M+H)^+$ $C_{30}H_{34}NO_6$: 504.2386; found 504.2383.

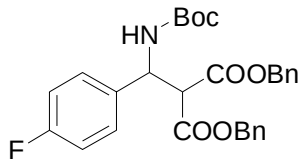
(-)-6Cb This product was obtained as a colorless oil in 99% yield and 97% ee from a reaction catalyzed by Q-**1d** (20 mol%) at –60 °C for 36 h.



6Db

(+)-6Db This product was obtained as a colorless oil (92 mg) in 92% yield after flash chromatography (silica gel: Ethyl acetate / Hexane = 1 / 12) and in 97% ee as determined by HPLC [Regis Pirckle Covalent (*R*, *R*) Whelk-O 1, Hexane / IPA = 99 / 1, 0.5 ml·min^{-1}, λ = 220nm, t_r (major) = 15.74 min, t_r (minor) = 18.03 min] from a reaction catalyzed by QD-**1d** at –60 °C for 36 h. $[\alpha]_D^{25}$ = 14.0 (*c* = 0.98, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.40 (s, 9H), 2.31 (s, 3H), 3.98 (s, 1H), 5.05 (s, 2H), 5.14 (dd, *J* = 8.0, 12.0 Hz, 2H), 5.51 (brs, 1H), 6.13 (brs, 1H), 7.02-7.17 (m, 7H), 7.22-7.36 (m, 7H), **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.02, 28.26, 53.24, 56.93, 67.20, 67.59, 79.61, 126.06, 128.02, 128.25, 128.35, 128.42, 128.53, 129.24, 134,87, 134.97, 136.23, 137.17, 154.99, 166.86, 167.81; **IR** (neat) ν 3430, 2977, 1719, 1498, 1161; **HRMS**: calc'd for $(M+H)^+$ $C_{30}H_{34}NO_6$: 504.2386; found 504.2379.

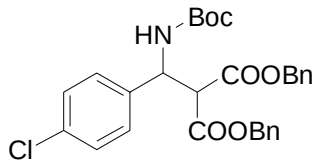
(-)-6Db This product was obtained as a colorless oil in 96% yield and 92% ee from a reaction catalyzed by Q-**1d** (20 mol%) at –60 °C for 36 h.



6Eb

(+)-6Eb This product was obtained as a white solid (102 mg) in 99% yield after flash chromatography (silica gel: Ethyl acetate / Hexane = 1 / 12) and in 98% ee as determined by HPLC [Daicel Chiralcel OD, Hexane / IPA = 90 : 10, 1.0 ml·min^{-1}, λ = 220 nm, t_r (major) = 10.97 min, t_r (minor) = 8.09 min] from a reaction catalyzed by QD-**1d** at –60 °C for 36 h. $[\alpha]_D^{25}$ = 20.3 (*c* = 1.15, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.40 (s, 9H), 3.96 (s, 1H), 5.00-5.20 (m, 4H), 5.51 (brs, 1H), 6.18 (brs, 1H), 6.88-6.96 (m, 2H), 7.06-7.14 (m, 2H), 7.24-7.36 (m, 10H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.18, 52.87, 56.80, 67.29, 67.64, 79.80, 115.36 (d, *J* = 10.6 Hz), 127.87, 127.96, 128.04, 128.22, 128.34, 128.40, 128.44, 128.52, 134.70, 134.75 (d, *J* = 5.3 Hz), 154.87, 162.01 (d, *J* = 122.2Hz), 166.55, 167.62; **IR** (neat) ν 3428, 1720, 1226, 1159 ; **HRMS**: calc'd for $(M+H)^+$ $C_{29}H_{31}NFO_6$: 508.2135; found 508.2120.

(-)-6Eb This product was obtained as a white solid in 98% yield and 94% ee from a reaction catalyzed by Q-**1d** (20mol%) at –60 °C for 36 h.

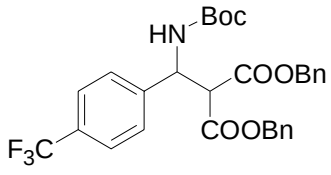


6Fb

(+)-6Fb This product was obtained as a white solid (103 mg) in 98% yield after flash chromatography (silica gel: Ethyl acetate / Hexane = 1/15) and in 99% ee as determined by HPLC [Daicel Chiralcel OD, Hexane / IPA = 90 / 10, 1.0 ml·min^{-1}, λ = 220 nm, t_r (major) = 11.34 min, t_r (minor) = 8.08 min] from a reaction catalyzed by QD-**1d** at –60 °C for

36 h. $[\alpha]_D^{25}$ = 21.0 (*c* = 0.715, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.40 (s, 9H), 3.95 (s, 1H), 5.05 (dd, *J* = 6.4, 12.0 Hz, 2H), 5.14 (dd, *J* = 6.0, 12.4 Hz, 2H), 5.50 (brs, 1H), 6.18 (brs, 1H), 7.05-7.12 (m, 2H), 7.15-7.24 (m, 2H), 7.24-7.35 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.22, 52.95, 56.64, 67.37, 67.74, 79.92, 127.64, 128.08, 128.27, 128.40, 128.46, 128.49, 128.57, 128.69, 133.40, 134.68, 134.79, 137.78, 154.90, 166.54, 167.61; **IR (neat)** ν 3369, 1721, 1493, 1367, 1251, 1161; **HRMS**: calc'd for $(M+H)^+$ $C_{29}H_{31}NClO_6$: 524.1840; found 524.1832.

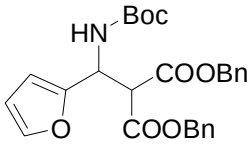
(-)-6Fb This product was obtained as a white solid in 97% yield and 91% ee from a reaction catalyzed by Q-**1d** (20 mol%) at –60 °C for 36 h.



6Gb

(+)-6Gb This product was obtained as a white solid (91 mg) in 81% yield after flash chromatography (silica gel: Ethyl acetate / Hexane = 1 / 12) and in 97% ee as determined by HPLC [Daicel Chiralcel OD, Hexane / IPA = 90 / 10, 1.0 ml·min^{-1}, λ = 220 nm, t_r (major) = 11.13 min, t_r (minor) = 8.13 min] from a reaction catalyzed by QD-**1d** at –60 °C for 36 h. $[\alpha]_D^{25}$ = 24.5 (*c* = 1.05, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.41 (s, 9H), 3.99 (s, 1H), 5.05 (dd, *J* = 7.2, 12 Hz, 2H), 5.16 (dd, *J* = 7.2, 11.6 Hz, 2H), 5.57 (brs, 1H), 6.27 (brs, 1H), 7.09 (d, *J* = 6.0 Hz, 2H), 7.23-7.40 (m, 10H), 7.50(d, *J* = 7.2 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.21, 53.18, 56.42, 67.49, 67.86, 80.07, 125.51, 125.55, 126.65, 128.14, 128.31, 128.49, 128.52, 128.60, 129.80 (q, *J* = 32 Hz), 134.59, 134.74, 139.91, 143.30, 154.93, 166.45, 167.57; **IR** (neat) ν 3383, 1754, 1736, 1687, 1517, 1327, 1296, 1162, 1124; **HRMS**: calc'd for $(M+H)^+$ $C_{30}H_{31}NF_3O_6$: 558.2103; found 558.2096.

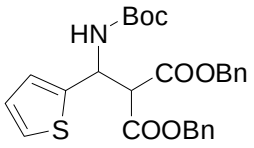
(-)-6Gb This product was obtained as a white solid in 82% yield and 93% ee from a reaction catalyzed by Q-**1d** (20 mol%) at –60 °C for 36 h.



6Hb

(+)- 6Hb This product was obtained as a colorless oil (96 mg) in 99% yield after flash chromatography (silica gel: Ethyl acetate / Hexane = 1 / 12) and in 97% ee as determined by HPLC [Daicel Chiralpak AD, Hexane / IPA = 90 / 10, 1.0 ml·min^{-1}, λ= 220 nm, t_r (major) = 16.36 min, t_r (minor) = 20.40 min] from a reaction catalyzed by QD-**1d** at –60 °C for 36 h. $[\alpha]_D^{25}$ = 5.9 (*c* = 0.68, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.41 (s, 9H), 4.18 (s, 1H), 5.04-5.20 (m, 4H), 5.60 (brs, 1H), 5.96 (d, *J* = 8.8 Hz, 1H), 6.16-6.18 (m, 1H), 6.22-6.26 (m, 1H), 7.19-7.24 (m, 3H), 7.26-7.38(m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.19, 48.30, 54.24, 67.33, 67.63, 79.87, 106.77, 110.40, 128.13, 128.21, 128.30, 128.34, 128.46, 128.50, 134.88, 141.94, 152.00, 154.91, 166.53, 167.55; **IR** (neat) ν 3421, 1732, 1498, 1163; **HRMS**: calc'd for $(M+H)^+$ $C_{27}H_{30}NO_7$: 480.2022; found 480.2019.

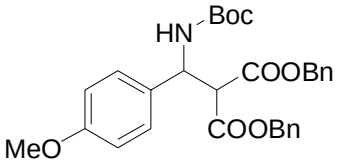
(-)-6Hb This product was obtained as a colorless oil in 99% yield and 96% ee from a reaction catalyzed by Q-**1d** (20 mol%) at –60 °C for 36 h.



6Ib

(+)-6Ib This product was obtained as a colorless oil (94 mg) in 95% yield after flash chromatography (silica gel: Ethyl acetate / Hexane = 1 / 20) and in 97% ee as determined by HPLC [Daicel Chiralcel OD, Hexane / IPA = 98 / 2, 1.0 ml·min^{-1}, λ = 220 nm, t_r (major) = 35.13 min, t_r (minor) = 31.08 min] from a reaction catalyzed by QD-**1d** at –60 °C for 36 h. $[\alpha]_D^{25}$ = 4.1 (*c* = 2.07, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.42 (s, 9H), 4.08 (d, *J* = 4.0 Hz, 1H), 5.11 (s, 2H), 5.14 (dd, *J* = 6.8, 12 Hz, 2H), 5.76 (d, *J* = 4.4 Hz, 1H), 6.16 (d, *J* = 4.8 Hz, 1H), 6.80-6.88 (m, 2H), 7.18-7.22 (m, 3H), 7.25-7.40 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.51, 50.29, 57.03, 67.74, 68.05, 80.21, 124.71, 125.01, 127.16, 128.43, 128.56, 128.64, 128.70, 128.78, 128.84, 135.08, 135.12, 143.69, 155.14, 166.73, 167.92; **IR** (neat) ν 3424, 1719, 1496, 1163**; HRMS**: calc'd for $(M+H)^+$ $C_{27}H_{30}NO_6S$: 496.1794; found 496.1785.

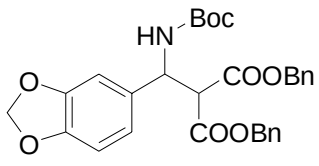
(-)-6Ib This product was obtained as a colorless oil in 96% yield and 88% ee from a reaction catalyzed by Q-**1d** (20 mol%) at –60 °C for 36 h.



6Jb

(+)-6Jb This product was obtained as a white solid (102 mg) in 98% yield after flash chromatography (silica gel: Ethyl acetate / Hexane = 1 / 6) and in 97% ee as determined by HPLC [Daicel Chiralcel OD, Hexane / IPA = 90 / 10, 1.0 ml·min^{-1}, λ = 220 nm, t_r (major) = 13.37 min, t_r (minor) = 10.33 min] from a reaction catalyzed by QD-**1d** at –60 °C for 36 h. $[\alpha]_D^{25}$ = 12.1 (*c* = 1.02, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.40 (s, 9H), 3.77 (s, 3H), 3.96 (s, 1H), 5.06 (dd, *J* = 2.8, 12.0 Hz, 2H), 5.13 (dd, *J* = 5.6, 12.6 Hz, 2H), 5.48 (brs, 1H), 6.11 (brs, 1H), 6.78 (d, *J* = 8.8 Hz, 2H), 7.08-7.14 (m, 2H), 7.17 (d, *J*= 8.8 Hz, 2H), 7.24-7.36 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.25, 53.00, 55.17, 57.03, 67.21, 67.58, 79.63, 113.89, 127.38, 128.03, 128.24, 128.28, 128.36, 128.44, 128.53, 131.30, 134.87, 134.96, 154.96, 158.89, 166.81, 167.82; **IR** (neat) ν 3426, 1720, 1513, 1498, 1249, 1161; **HRMS**: calc'd for $(M+H)^+$ $C_{30}H_{34}NO_7$: 520.2335; found 520.2338.

(-)-6Jb This product was obtained as a white soild in 97% yield and 93% ee from a reaction catalyzed by Q-**1d** (20 mol%) at –60 °C for 36 h.

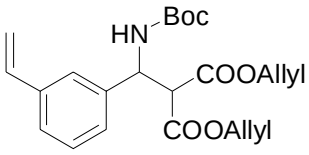


6Kb

(+)-6Kb This product was obtained as a white solid (106 mg) in 99% yield after flash chromatography (silica gel: Ethyl acetate / Hexane = 1 / 7) and in 98% ee as determined by HPLC [Daicel Chiralcel OD, Hexane / IPA = 90 / 10, 1.0 ml·min^{-1}, λ = 220 nm, t_r (major) = 12.59 min, t_r (minor) = 10.79 min] from a reaction catalyzed by QD-**1d** at –60 °C for 36 h. $[\alpha]_D^{25}$ = 13.9 (*c* = 1.00, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.40 (s, 9H), 3.94 (s, 1H), 5.02-5.22 (m, 4H), 5.44 (brs, 1H), 5.89 (s, 2H), 6.14 (brs, 1H), 6.62-6.72 (m, 4H), 6.75 (s, 1H), 7.10-7.16 (m, 2H), 7.22-7.36 (m, 7H); **^{13}C**

NMR (100 MHz, $CDCl_3$) δ 28.26, 53.22, 56.95, 67.20, 67.55, 79.66, 101.00, 106.83, 108.14, 119.48, 127.99, 128.17, 128.25, 128.32, 128.39, 128.48, 133.17, 134.78, 134.86, 146.88, 147.74, 154.85, 166.62, 167.69; **IR** (neat) ν 3423, 1720, 1490, 1240, 1164; **HRMS**: calc'd for $(M+Na)^+$ $C_{30}H_{31}NO_8Na$: 556.1947; found 556.1927.

(-)-6Kb This product was obtained as a white soild in 99% yield and 94% ee from a reaction catalyzed by **Q-1d** (20 mol%) at –60 °C for 36 h.

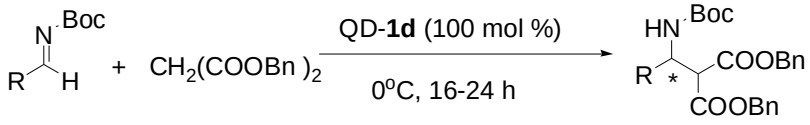


6Lc

(+)-6Lc This product was obtained as a colorless oil (80 mg) in 96% yield after flash chromatography (silica gel: Ethyl acetate / Hexane = 1 / 7) and in 96% ee as determined by HPLC [Daicel Chiralpak AS, Hexane / IPA = 98 / 2, 1.0 ml·min^{-1}, λ = 220 nm, t_r (major) = 13.54 min, t_r (minor) = 11.52 min] from a reaction catalyzed by QD-**1d** at –60 °C for 36 h. $[\alpha]_D^{25}$ = 10.1 (*c* = 0.85, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.40 (s, 9H), 3.96 (s, 1H), 4.44-4.72 (m, 4H), 5.10-5.36 (m, 4H), 5.51 (brs, 1H), 5.66-5.80 (m, 2H), 5.82-5.94 (m, 1H), 6.20 (brs, 1H), 6.68 (dd, *J* = 6.8, 11.2 Hz, 1H), 7.19 (d, *J* = 6.8 Hz, 1H), 7.24-7.34 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.25, 53.36, 56.79, 66.14, 66.49, 79.72, 114.29, 118.80, 119.00, 124.27, 125.41, 125.66, 128.76, 131.05, 131.21, 136.52, 137.84, 139.67, 154.97, 166.66, 167.61; **IR** (neat) ν 3430, 1721, 1497, 1165; **HRMS**: calc'd for $(M+H)^+$ $C_{23}H_{29}NO_6Na$: 438.1893; found 438.1885.

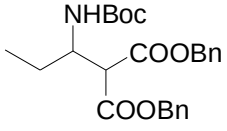
(-)-6Lc This product was obtained as a white soild in 99% yield and 95% ee from a reaction catalyzed by Q-**1d** (20 mol%) at –60 °C for 36 h.

5. General Procedure for Enantionselective Mannich Reaction of Malonate **5** to Alkyl Imine **4**



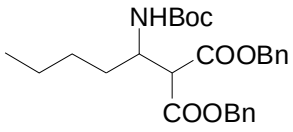
4 **5b** **6**

To a solution of malonate **5b** (0.10 mmol) and QD-**1d** (100 mol%) in dichloromethane (0.30 mL) at 0 °C, was added imine **4** (0.15 mmol) in one portion. The resulting mixture was kept at 0 °C for 16-24 h. Reaction mixture was purified by silica gel flash chromatography using the solvent specified below.

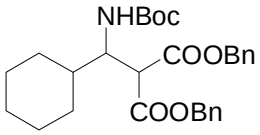


(+)-6Mb This product was obtained as a colorless oil (27 mg) in 63% yield after flash chromatography (silica gel: Ethyl ether / methlene chloride = 1 / 150) and in 89% ee as determined by HPLC [Daicel Chiralcel OD, Hexane / IPA = 98 / 2, 1.0 ml·min^{-1}, λ = 220 nm, t_r (major) = 18.70 min, t_r (minor) = 16.15 min] from a reaction catalyzed by QD-**1d** (100 mol%) at 0 °C for 20 h. Catalyst QD-**1d** (57 mg, 95%) was recycled. $[\alpha]_D^{25}$ = 29.2 (*c* = 1.01, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.2 Hz, 1H), 1.39 (s, 9H), 1.44-

1.58 (m, 2H), 3.70 (d, J = 4.0 Hz, 1H), 4.15-4.22 (m, 1H), 5.04-5.16 (m, 4H), 5.33 (d, J = 9.6 Hz, 1H), 7.24-7.34 (m, 10H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 10.80, 26.64, 28.29, 51.81, 54.78, 67.21, 67.45, 79.25, 128.22, 128.29, 128.34, 128.54, 128.57, 135.07, 155.45, 167.70, 168.11; **IR** (neat) ν 3434, 2963, 1733, 1711, 1500, 1162; **HRMS**: calc'd for $(M+Na)^+$ $C_{25}H_{31}NO_6Na$: 464.2049; found 464.2049.

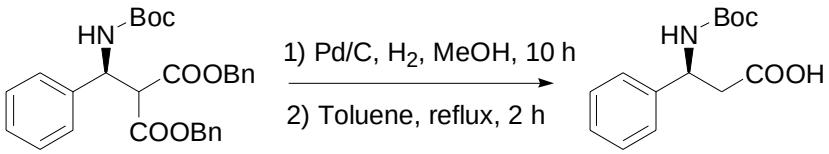


(+)-6Nb This product was obtained as a colorless oil (30 mg) in 64% yield after flash chromatography (silica gel: Hexanes / methlene chloride = 1 / 2) and in 92% ee as determined by HPLC [Daicel Chiralcel OD, Hexane / IPA = 98 / 2, 1.0 ml·min^{-1}, λ = 220 nm, t_r (major) = 16.23 min, t_r (minor) = 14.31 min] from a reaction with catalyzed by QD-**1d** (100 mol%) at 0 °C for 24 h. Catalyst QD-**1d** (59 mg, 98%). **$[\alpha]_D^{25}$** = 42.5 (c = 1.00, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.84 (t, J = 6.8 Hz, 3H), 1.20-1.38 (m, 4H), 1.41 (s, 9H), 1.45-1.58 (m, 2H), 3.71 (d, J = 3.6 Hz, 1H), 4.22-4.30 (m, 1H), 5.06-5.20 (m, 4H), 5.33 (d, J = 9.6 Hz, 1H), 7.33 (s, 10H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.91, 22.30, 28.30, 28.42, 33.20, 50.39, 55.05, 67.20, 67.43, 79.26, 128.29, 128.35, 128.44, 128.55, 128.57, 135.15, 155.36, 167.71, 168.12; **IR** (neat) ν 3424, 1733, 1716, 1496, 1162; **HRMS**: calc'd for $(M+Na)^+$ $C_{27}H_{35}NO_6Na$: 492.2362; found 492.2359.



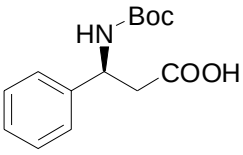
(+)-6Ob This product was obtained as a colorless oil (55 mg) in 55% yield after flash chromatography (silica gel: Ethyl acetate / methlene chloride = 1 / 300) and in 88% ee as determined by HPLC [Daicel Chiralcel OD, Hexane / IPA = 97 / 3, 1.0 ml·min^{-1}, λ = 220 nm, t_r (major) = 10.28 min, t_r (minor) = 8.25 min] from a reaction with **4O** (0.30 mmol) and **5b** (0.20 mmol) in dichloromethane (600 μl) catalyzed by QD-**1d** (100 mol%) at 0 °C for 16 h. Catalyst QD-**1d** (117 mg, 98%) was recycled. **$[\alpha]_D^{25}$** = 41.3 (c = 1.01, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.84-1.14 (m, 4H), 1.41 (s, 9H), 1.48-1.86 (m, 6H), 3.81 (d, J = 4.0 Hz, 1H), 4.07 (dt, J = 3.6, 14.4 Hz, 1H), 5.13 (dd, J = 12.0, 80.0 Hz, 2H), 5.16 (dd, J = 6.0, 12.0 Hz, 2H), 5.55 (d, J = 11.2 Hz, 1H), 7.28-7.40 (m, 10H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 25.82, 25.86, 25.99, 28.32, 29.52, 30.13, 41.16, 52.81, 55.22, 67.19, 67.61, 79.06, 128.30, 128.36, 128.46, 128.55, 128.60, 135.12, 155.61, 168.21, 168.55; **IR** (neat) ν 3434, 2923, 1728, 1713, 1496, 1160; **HRMS**: calc'd for $(M+Na)^+$ $C_{29}H_{37}NO_6Na$: 518.2519; found 518.2514.

6. Conversion of *N*-Boc amine **6Ab** to *N*-Boc-protected β-amino acid **7Ab**



***S*-6Ab,** 96% ee ***S*-7Ab,** 94% ee

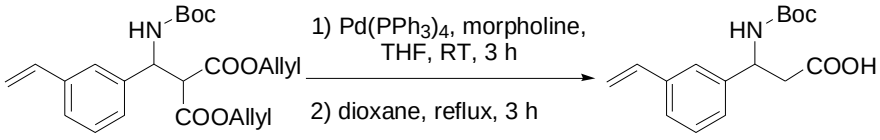
N-Boc amine **6Ab** (48.9 mg, 0.10 mmol) was hydrogenated with 10% palladium on carbon (21 mg) in methanol (3.0 mL) at room temperature under an atmosphere of hydrogen for 10 h. The mixture was filtered with celite to remove insoluble material afterwhich the filtrate was concentrated to give a foam. This was dissolved in toluene (4.0 mL) and the solution was heated at reflux for 2 h. The solvent was removed and the product was purified by flash chromatography.



***S*-7Ab**

***S*-7Ab** This product was obtained as white solid (20 mg) in 76% yield after flash chromatography (silica gel: Hexanes : Ethyl Acetate : Acetic Acid = 80 : 20 : 1) and in 94% ee as determined by HPLC [Daicel Chiralcel OD, Hexane / IPA / TFA = 98 / 2 /0.5, 1.0ml·min^{-1}, λ = 220 nm, 0 ºC, t_r (major) = 14.00 min, t_r (minor) = 18.17 min]. $[\alpha]_D^{25}$ = -50.1 (*c* = 0.71, MeOH); Spectrum data was same as reported and the absolute configure of **7ab** was determined to be *S* by comparing the optical rotation with literature value $[\alpha]_D^{22}$ = -45.6 (*c* = 1.00, MeOH)[8].

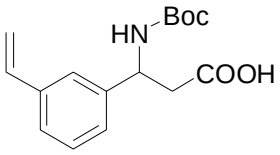
7. Conversion of *N*-Boc amine **6Lc** to *N*-Boc-protected β-amino acid **7Lc**



(+)-6Lc, 96% ee **(-)-7Lc,** 96% ee

To a suspension of **6Lc** (56.0 mg, 0.135 mmol) and terakis(triphenylphosphine)-palladium (15.6 mg 0.0135mmol) in THF (1.5 mL) was added morpholine (36 µl, 0.41 mmol), the resulting reaction mixture was stirred at room temperature for 3 h. Then solvent was removed under reduced pressure, and the residue was dissolved in dioxane (3.0 mL) and refluxed for 3 h. Solvent was removed under reduced pressure and the residue was purified by flash chromatography.

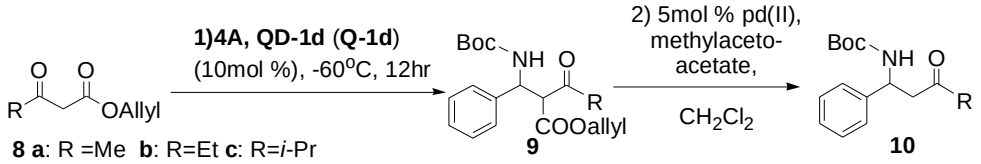
[8] Laschat, S.; Kunz, H. *J. Org. Chem.,* **1991**, *56*, 5883



7Lc

(-)-7Lc This product was obtained as white foam (28 mg) in 72% yield after flash chromatography (silica gel: Hexanes : Ethyl Acetate : Acetic Acid = 88 : 11 : 1) and in 96% ee as determined by HPLC [Daicel Chiralcel OD, Hexane / IPA / TFA = 98 / 2 /0.5, 1.0 ml·min^{-1}, λ = 220 nm, t_r (major) = 32.76 min, t_r (minor) = 38.20 min]. $[\alpha]_D^{25}$ = -23.0 (*c* = 1.10, CH_3Cl); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.41 (s, 9H), 2.85 (brs, 2H), 5.11 (br, 1H), 5.25 (dd, *J* = 2.4, 10.8 Hz, 1H), 5.46 (br, 1H), 5.74 (dd, *J* = 2.4, 17.6 Hz, 1H), 6.70 (ddd, *J* = 2.4, 11.2, 17.2 Hz, 1H), 7.16-7.22 (m, 1H), 7.26-7.36 (m, 3H), 10.6 (br, 1H); **^{13}C NMR** (100 MHz, CD_3OD) δ 28.83, 42.34, 52.94, 80.40, 114.36, 125.37, 126.27, 126.97, 129.84, 138.20, 139.32, 144.22, 157.64, 174.42; **IR** (neat) ν 2979, 1714, 1395, 1164; **HRMS**: calc'd for $(M+H)^+$ $C_{16}H_{22}NO_4$: 292.1549; found 292.1555.

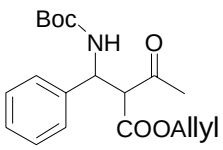
8. General Procedure for Enantionselective Mannich Reaction of Ally β-ketoester **8** to imine **4A,** and transformation of Mannich adduct **9** to amino ketone **10**.



To a solution of imine **4A** (0.20 mmol) and chiral catalyst (10 mol%) in acetone (0.40 ml) at –60 °C, was added β-ketoester **8** (0.30 mmol) in one portion. The resulting mixture was kept at –60 °C for 12 h. The reaction mixture was diluted with ethyl ether (5 ml) and allowed to pass through a short silica gel column. Then the filtrate was concentrated and purified by silica gel flash chromatography using the eluent specified below.

Mannich adduct **9** was converted to **10** by Pd-promoted decarboxylation[9].

To an oven dried round botton flask (10 mL), was added allyl palladium chloride dimmer (1.8mg, 0.005 mmol) and (±) 2,3-O-Isopropyllidene-2,3-dihydroxy-1,4-bis(diphenylphosphino) butane ((±) DIOP) (5.0 mg, 0.010 mmol). The Pd catalyst and ligand were dissolved in methylene chloride (250 μl) and stirred at room temperature for 10 minutes. Methyl acetoacetate (0.023 mL, 0.20 mmol) and isolated product (**9Aa** – **9Ac**, 0.10 mmol) were added successively. The reaction solution was stirred at room temperature overnight and then subjected directly to flash chromatography over silica gel using the eluent specified below.

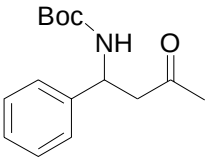


9Aa

9Aa This product was obtained as a white solid (61 mg) in 90% yield after flash chromatography (silica gel: Ethyl acetate / Hexane = 1/8) from a reaction catalyzed by QD-**1d** (10 mol%) at –60 °C for 12 h. **^{1}H NMR** (400 MHz, $CDCl_3$, major diastereomer was reported) δ 1.40 (s,

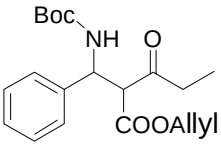
[9] Lou S.; Taoka, B. M.; Ting, A.; Schaus, S. E. *J. Am. Chem. Soc*. **2005**, *127*, 11256

9H), 2.17 (s, 3H), 4.04 (d, J = 6.0 Hz, 1H), 4.56 (d, J = 5.2 Hz, 2H), 5.18-5.28 (m, 2H), 5.45 (brs, 1H), 5.70-5.90 (m, 2H), 7.20-7.40 (m, 5H); **HRMS**: calc'd for $(M+H)^+$ $C_{19}H_{26}NO_5$: 348.1811; found 348.1810.



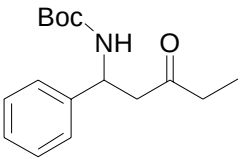
10Aa

(-)-10Aa This product was obtained as a white solid (22 mg) in 83% yield after flash chromatography (silica gel: Ethyl acetate / Hexane = 1 / 3) and in 92% ee as determined by HPLC [Regis Pirckle Covalent (R, R) Whelk-O 1, Hexane / IPA = 85 / 15, 1.0 ml·min^{-1}, λ = 220 nm, t_r (major) = 5.98 min, t_r (minor) = 7.80 min]. $[\alpha]_D^{25}$ = -24.7 (c = 0.55, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.41 (s, 9H), 2.09 (s, 3H), 2.91 (dd, J = 5.6, 16.0 Hz, 1H), 2.9-3.1 (m, 1H), 5.08 (brs, 1H), 5.41 (brs, 1H), 7.20-7.40 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.31, 30.59, 49.30, 51.02, 79.68, 126.19, 127.42, 128.63, 141.50, 155.10, 206.98; **IR** (neat) ν 3384, 1714, 1685, 1516, 1168; **HRMS**: calc'd for $(M+H)^+$ $C_{15}H_{22}NO_3$: 264.1600; found 264.1604.



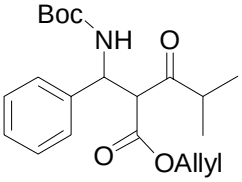
9Ab

9Ab This product was obtained as a white solid (57 mg) in 79% yield after flash chromatography (silica gel: Ethyl acetate / Hexane = 1 / 10) from a reaction catalyzed by QD-**1d** (10 mol %) at –60 °C for 12 h. **^{1}H NMR** (400 MHz, $CDCl_3$, both diastereomers were reported) δ 0.93 (t, J = 6.8 Hz, 3H), 1.08 (t, J = 6.8 Hz, 3H), 1.40 (s, 9H), 1.41 (s, 9H), 1.56 (s, 2H), 2.12-2.22 (m, 1H), 2.55-2.63 (m, 2H), 2.75 (m, 1H), 4.06 (m, 2H), 4.52-4.58 (m, 4H), 5.12-5.28 (m, 2H), 5.44 (brs, 1H), 5.53 (brs, 1H), 5.71-5.83 (m, 2H), 5.99 (brs, 1H), 6.19 (brs, 1H), 7.24-7.35 (m, 10H); **HRMS**: calc'd for $(M+Na)^+$ $C_{20}H_{27}NO_5Na$: 384.1787; found 384.1776.



10Ab

(-)-**10Ab** This product was obtained as a white solid in 81% yield after flash chromatography (silica gel: Ethyl acetate / Hexane = 1 / 15-1 / 5) and in 91% ee as determined by HPLC [Regis Pirckle Covalent (*R*, *R*) Whelk-O 1, Hexane / IPA = 85 / 15, 1.0 ml·min^{-1}, λ = 220 nm, t_r (major) = 5.41 min, t_r (minor) = 7.53 min]. $[\alpha]_D^{25}$ = -19.5 (c = 0.57, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.96 (t, J = 6.8 Hz, 3H), 1.41 (s, 9H), 2.25-2.43 (m, 2H), 2.88 (dd, J = 6.0, 15.6 Hz, 1H), 2.99-3.02 (m, 1H), 5.08 (s, 1H), 5.52 (s, 1H), 7.22-7.34 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 7.35, 28.29, 36.63, 48.04, 51.14, 79.59, 126.12, 127.30, 128.58, 141.62, 155.09, 209.73; **IR** (neat) ν 3380, 1715, 1684, 1519; **HRMS**: calc'd for $(M+H)^+$ $C_{16}H_{24}NO_3$: 278.1756; found 278.1745.

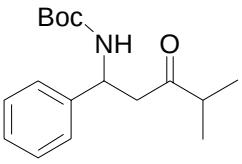


9Ac

QD-**9Ac** This product was obtained as a white solid (58.6 mg) in 78% yield after flash chromatography (silica gel: Ethyl acetate / Hexane = 1 / 10) from a reaction catalyzed by QD-**1d** (10 mol %) at –60 °C for 12 h. **^{1}H NMR** (400 MHz, $CDCl_3$, both diastereomers were reported) δ 0.67 (d, J = 6.8 Hz, 3H), 0.97 (d, J = 6.4 Hz, 3H), 1.08 (m, 3H), 1.19 (d, J = 6.4 Hz, 3H), 1.41 (s, 18 H), 1.58 (s, 2H), 2.40-2.47 (m, 1H), 2.96 (brs, 1H), 4.20-4.23 (m, 2H), 4.52-4.53 (m,

2H), 4.58-4.67 (m, 2H), 5.12-5.17 (m, 2H), 5.24-5.34 (m, 2H), 5.48 (brs, 2H), 5.71-5.78 (m, 1H), 5.84-5.91 (m, 1H), 6.16 (brs, 1H), 6.40 (brs, 1H), 7.22-7.34 (m, 10H); **HRMS**: calc'd for $(M+Na)^+$ $C_{21}H_{29}NO_5Na$: 398.1943; found 398.1932.

Q-**9Ac** This product was obtained as a white soild in 85% yield from a reaction catalyzed by Q-**1d** (10 mol%) at –60 °C for 12 h.

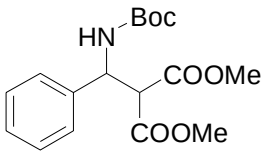


10Ac

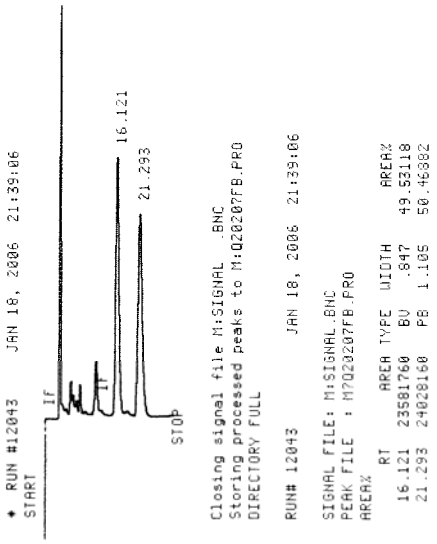
(-)-**10Ac** This product was obtained as a white solid in 66% yield from QD-**9Ac**, after flash chromatography (silica gel: Ethyl acetate / Hexane = 1/15) and in 96% ee as determined by HPLC [Daicel Chiralpak AS, Hexane / IPA = 98 : 2, 1.0 ml·min^{-1}, λ = 220 nm, t_r (major) = 11.76 min, t_r (minor) = 10.54 min]. $[\alpha]_D^{25}$ = -15.0 (*c* = 0.92, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.95 (d, *J* = 7.2 Hz, 3H), 0.99 (d, *J* = 6.4 Hz, 3H), 1.41 (s, 9H), 2.44-2.51 (m, 1H), 2.91 (dd, *J* = 6.0, 16.4 Hz, 1H), 3.06-3.10 (m, 1H), 5.08 (brs, 1H), 5.63 (brs, 1H), 7.21-7.33 (m, 5H); **^{13}C NMR** (100 MHz, CD_4OD) δ 18.14, 28.74, 42.15, 48.09, 52.09, 80.20,127.41, 128.15, 129.45, 144.19, 157.51, 213.91; **IR** (neat) ν 3375, 1711, 1686, 1520; **HRMS**: calc'd for $(M+Na)^+$ $C_{17}H_{25}NO_3Na$: 314.1732; found 314.1727.

(+)-**10Ac** This product was obtained as a white soild in 99% yield and 92% ee from Q-**9Ac**.

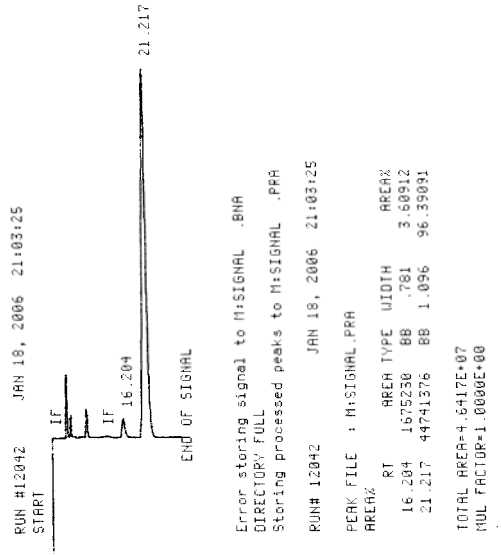
HPLC Condition: Daicel Chiralpak AD, Hexane / IPA = 90 / 10, 1.0 ml·min^{-1}, 220 nm



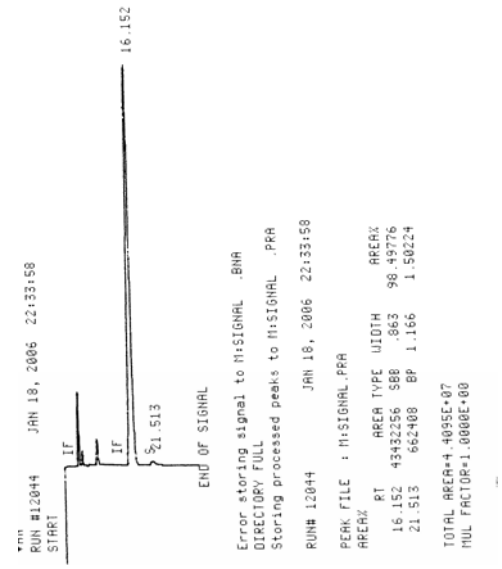
racemic **6Aa**



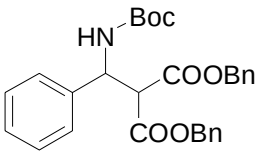
(-)-**6Aa**, 93% ee
Product of Q-**1d** catalyzed reaction



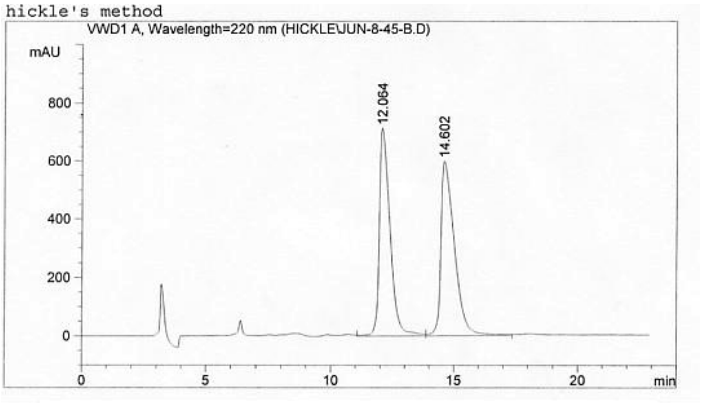
(+)-**6Aa**, 97% ee
Product of QD-**1d** catalyzed reaction



HPLC Condition: Regis Pirckle Covalent (*R*, *R*) Whelk-O 1, Hexane / IPA = 99 / 1, 1.0 ml·min^{-1}, 220 nm



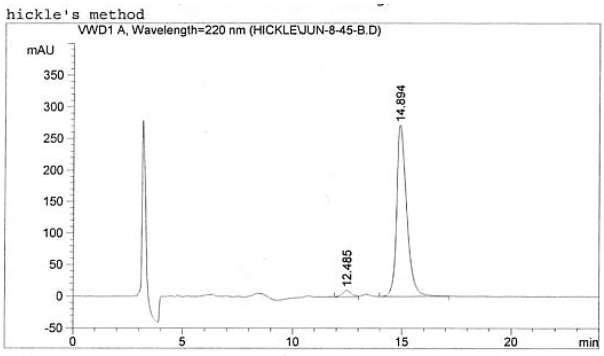
racemic 6**Ab**



Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Sig	Type	Area mAU *s	Height [mAU]	Area %
1	12.064	1	VV	2.16518e4	712.11652	48.5263
2	14.602	1	VB	2.29669e4	596.88727	51.4737
Totals :				4.46186e4	1309.00378	

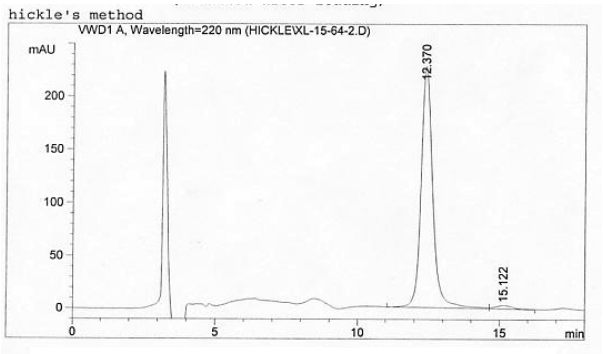
(-)-6**Ab**, 94% ee
Product of Q-**1d** catalyzed reaction



Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Sig	Type	Area mAU *s	Height [mAU]	Area %
1	12.485	1	BV	278.17789	9.92384	3.0802
2	14.894	1	VB	8752.93164	271.07489	96.9198
Totals :				9031.10953	280.99873	

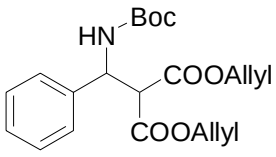
(+)-6**Ab**, 96% ee
Product of QD-**1d** catalyzed reaction



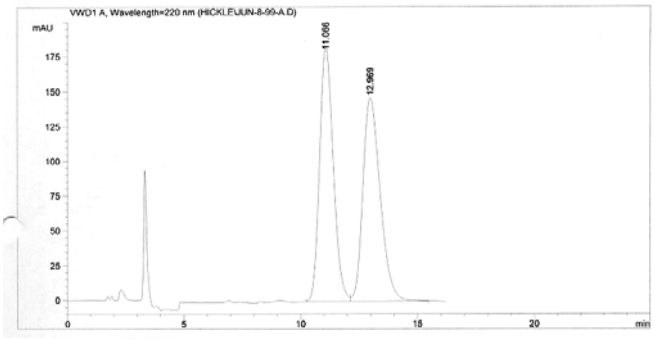
Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Sig	Type	Area mAU *s	Height [mAU]	Area %
1	12.370	1	VB	6460.62549	227.44182	97.9679
2	15.122	1	BB	134.01273	3.34240	2.0321
Totals :				6594.63821	230.78422	

HPLC Condition: Daicel Chiralpak AS, Hexane / IPA = 98 / 2, 1.0 ml·min^{-1}, 220 nm



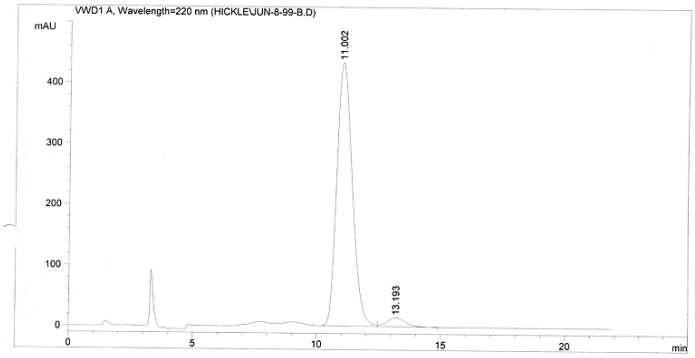
racemic 6**Ac**



Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.066	BV	0.6409	7473.46240	182.46924	49.7056
2	12.969	VB	0.8013	7562.00244	146.23720	50.2944
Totals :				1.50355e4	328.70644	

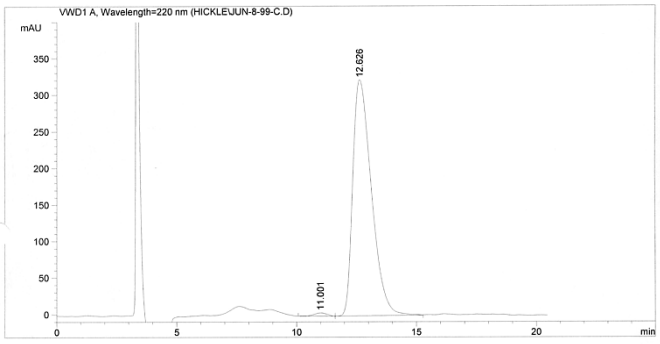
(-)-**6Ac**, 92% ee
Product of Q-**1d** catalyzed reaction



Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.002	BV	0.6828	1.88573e4	433.04745	96.0464
2	13.193	VB	0.8066	776.23462	14.88056	3.9536
Totals :				1.96335e4	447.92801	

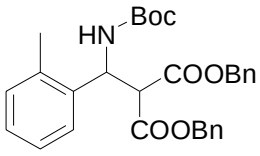
(+)-**6Ac**, 98% ee
Product of QD-**1d** catalyzed reaction



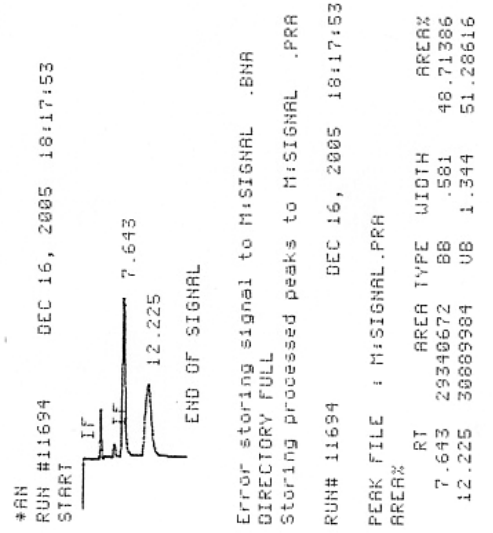
Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.001	BV	0.5889	158.93767	4.47746	0.9018
2	12.626	VB	0.8421	1.74660e4	322.19614	99.0982
Totals :				1.76249e4	326.67359	

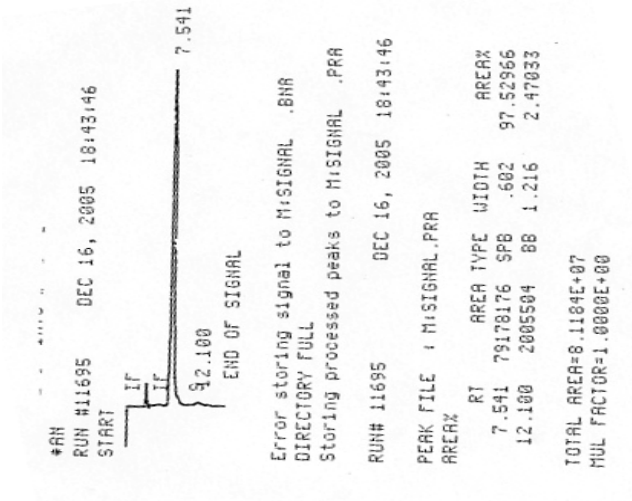
HPLC Condition: Daicel Chiralpak AS, Hexane / IPA = 90 / 10, 1.0 ml·min^{-1}, 220nm



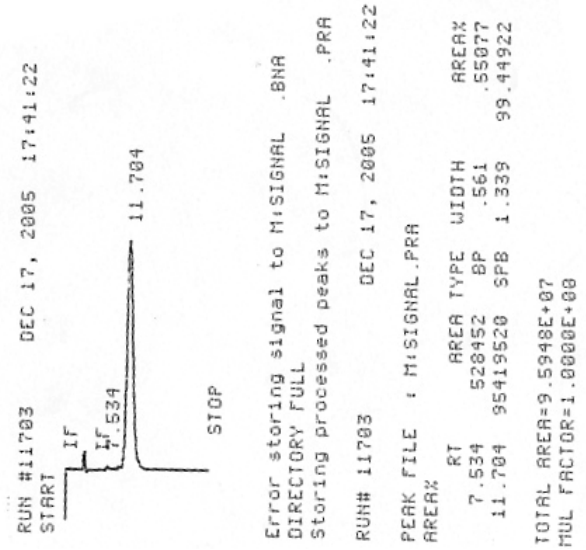
racemic **6Bb**



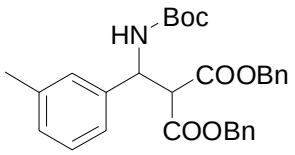
(-)-**6Bb**, 95% ee
Product of Q-**1d** catalyzed reaction



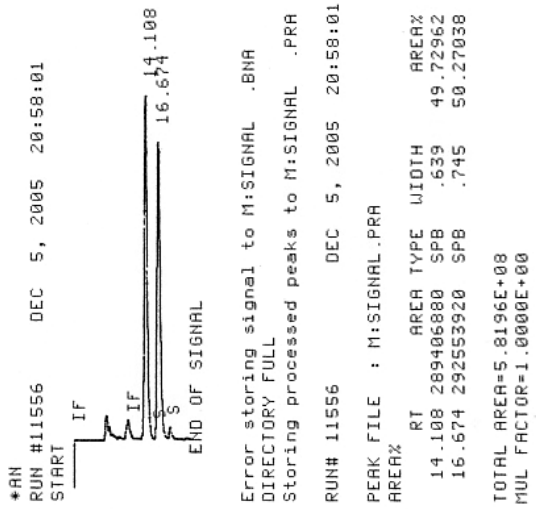
(+)-**6Bb**, 99% ee
Product of QD-**1d** catalyzed reaction



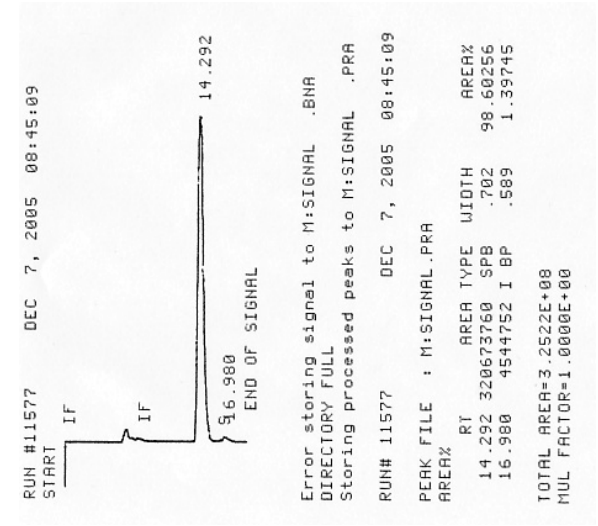
HPLC Condition: Daicel Chiralcel OD, Hexane / IPA = 90 / 10, 0.5 ml·min^{-1}, 220 nm



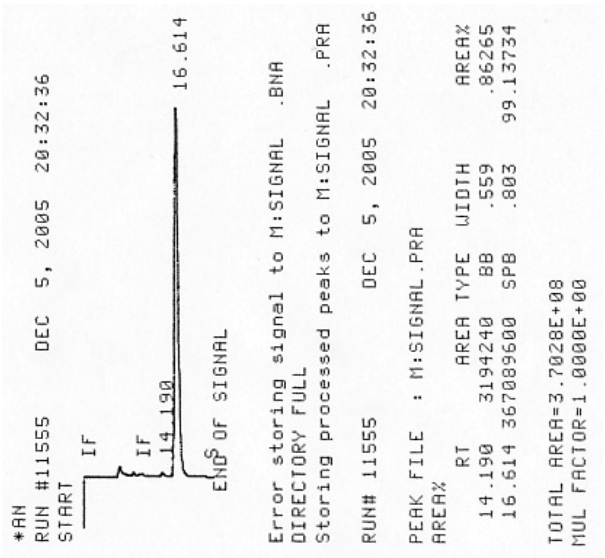
racemic **6Cb**



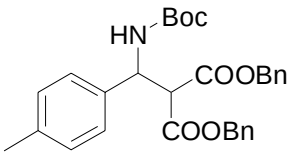
(-)-**6Cb**, 97% ee
Product of Q-**1d** catalyzed reaction



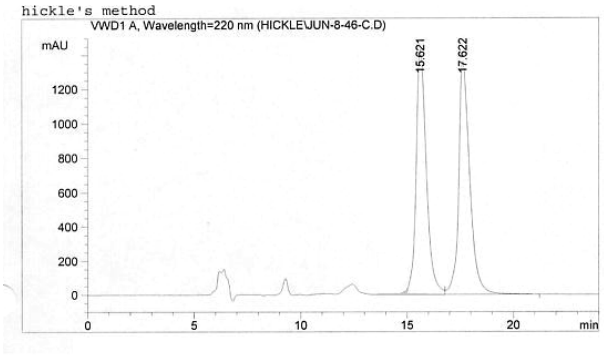
(+)-**6Cb**, 98% ee
Product of QD-**1d** catalyzed reaction



HPLC Condition: Regis Pirckle Covalent (*R*, *R*) Whelk-O 1, Hexane / IPA = 99 / 1, 0.5 ml·min^{-1}, 220 nm



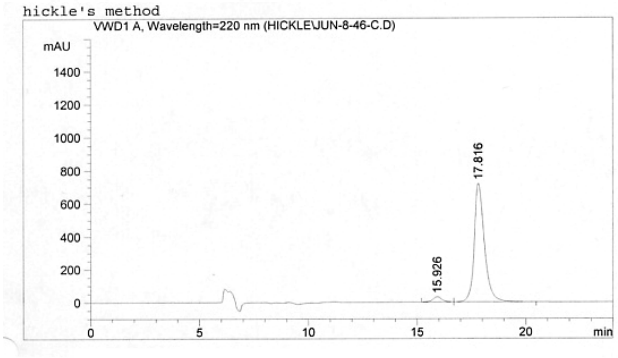
racemic **6Db**



Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Sig	Type	Area mAU *s	Height [mAU]	Area %
1	15.621	1	BV	4.82044e4	1429.71765	49.2814
2	17.622	1	VB	4.96102e4	1359.73657	50.7186

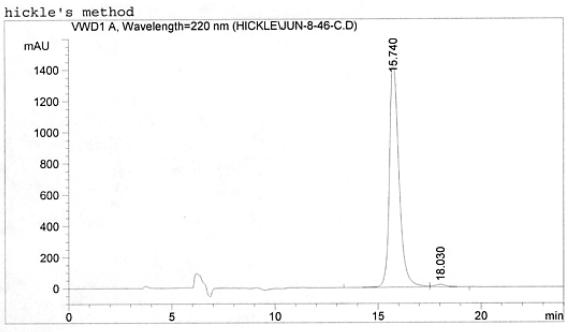
(-)-**6Db**, 92% ee
Product of Q-**1d** catalyzed reaction



Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Sig	Type	Area mAU *s	Height [mAU]	Area %
1	15.926	1	BV	977.26251	32.62965	3.9814
2	17.816	1	VB	2.35686e4	719.15088	96.0186
Totals :				2.45459e4	751.78053	

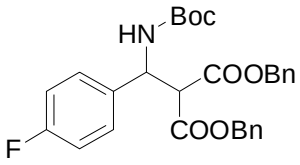
(+)-**6Db**, 97% ee
Product of QD-**1d** catalyzed reaction



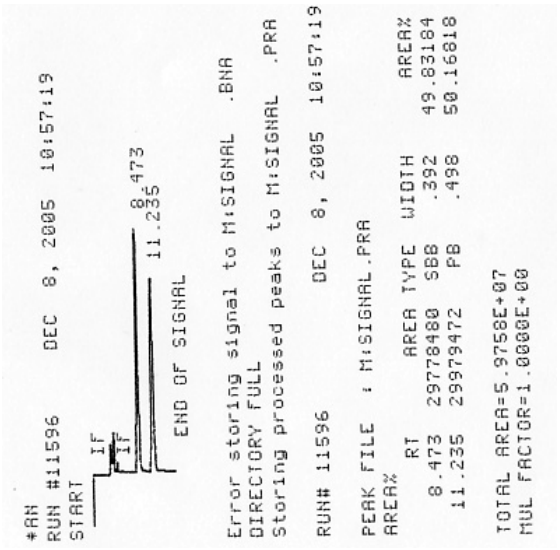
Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Sig	Type	Area mAU *s	Height [mAU]	Area %
1	15.740	1	BV	4.68023e4	1447.52808	98.4714
2	18.030	1	VB	726.52606	16.99037	1.5286
Totals :				4.75288e4	1464.51845	

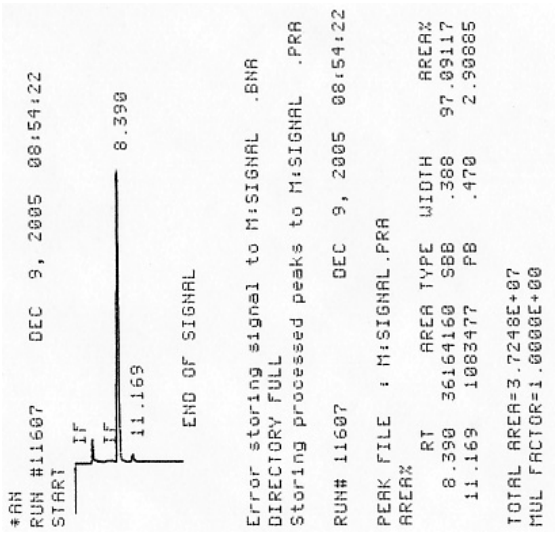
HPLC Condition: Daicel Chiralcel OD, Hexane / IPA = 90 / 10, 1.0 ml·min^{-1}, 220 nm



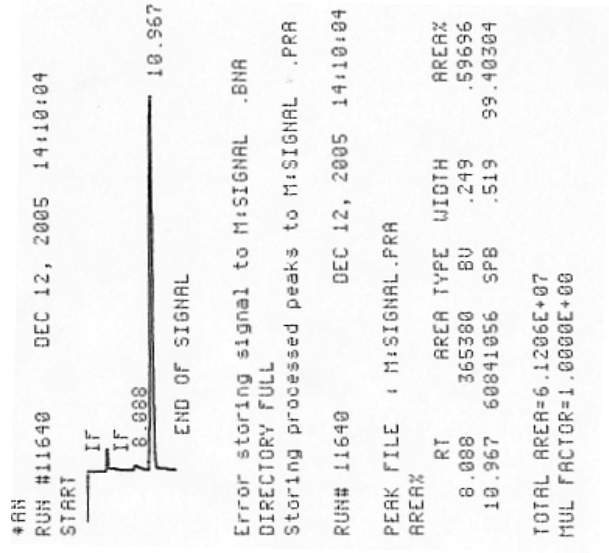
racemic **6Eb**



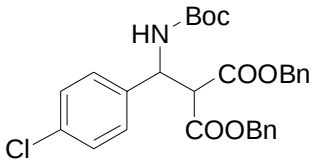
(-)-**6Eb**, 94% ee
Product of Q-**1d** catalyzed reaction



(+)-**6Eb**, 99% ee
Product of QD-**1d** catalyzed reaction

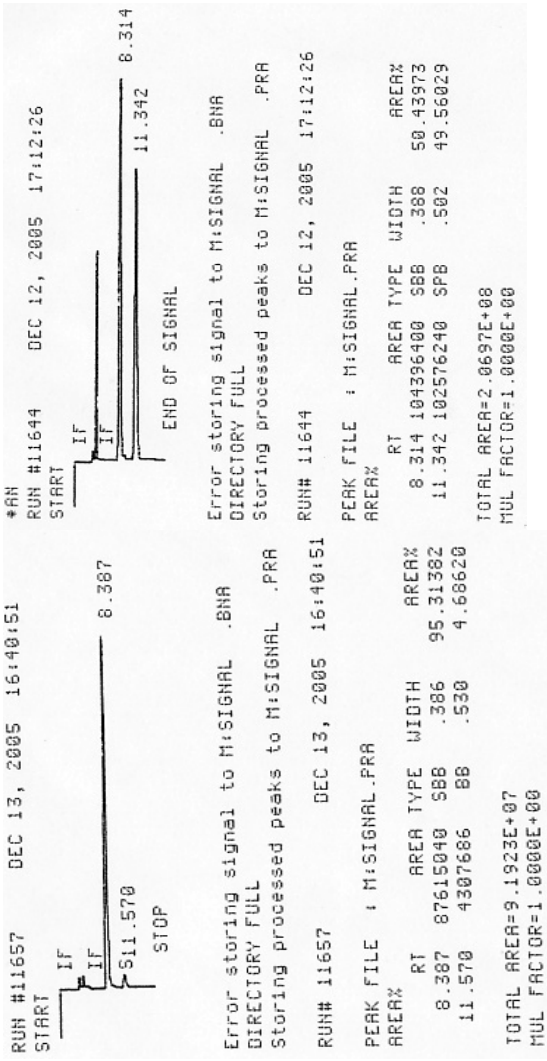


HPLC Condition: Daicel Chiralcel OD, Hexane / IPA = 90 / 10, 1.0 ml·min^{-1}, 220 nm

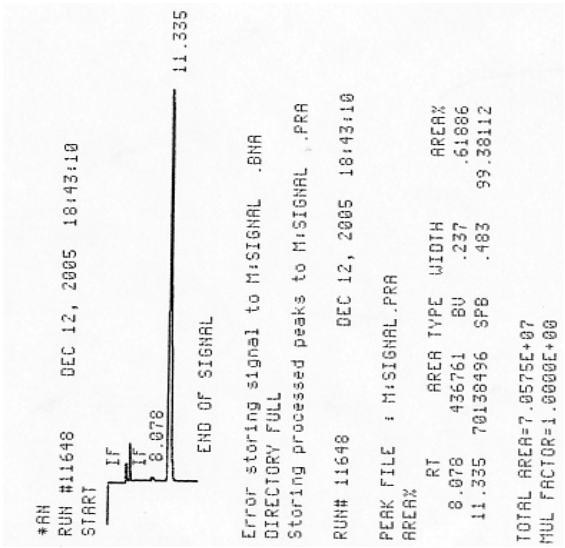


racemic **6Fb**

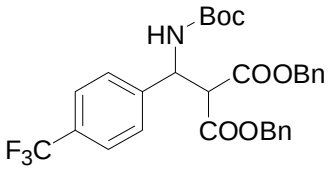
(-)-**6Fb**, 91% ee
Product of Q-**1d** catalyzed reaction



(+)-**6Fb**, 99% ee
Product of QD-**1d** catalyzed reaction

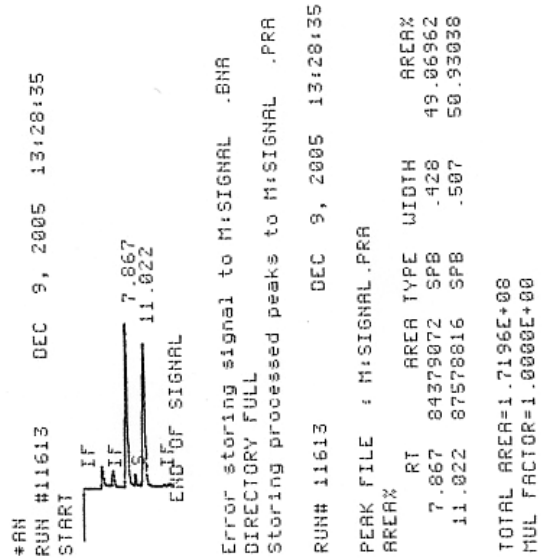


HPLC Condition: Daicel Chiralcel OD, Hexane / IPA = 90 / 10, 1.0 ml·min^{-1}, 220 nm

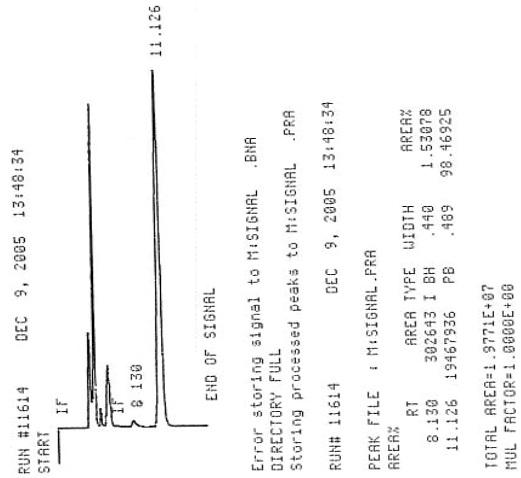


racemic 6**Gb**

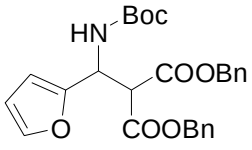
(-)-**6Gb**, 93% ee
Product of Q-**1d** catalyzed reaction



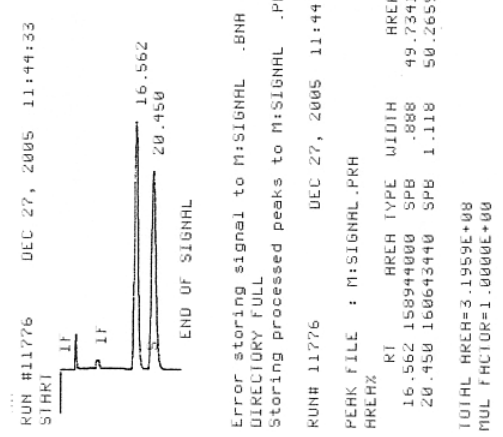
(+)-**6Gb**, 97% ee
Product of QD-**1d** catalyzed reaction



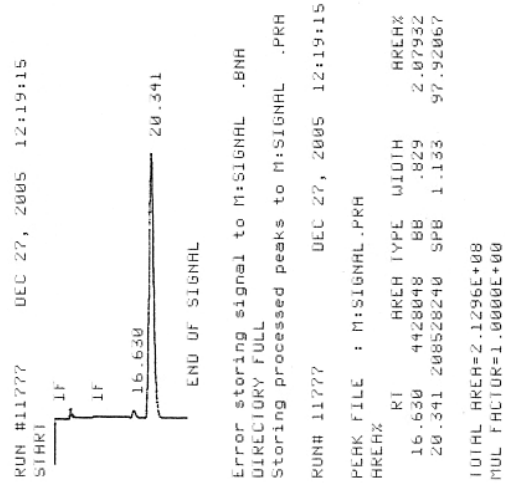
HPLC Condition: Daicel Chiralcel AD, Hexane / IPA = 85 / 15, 1.0 ml·min^{-1}, 220 nm



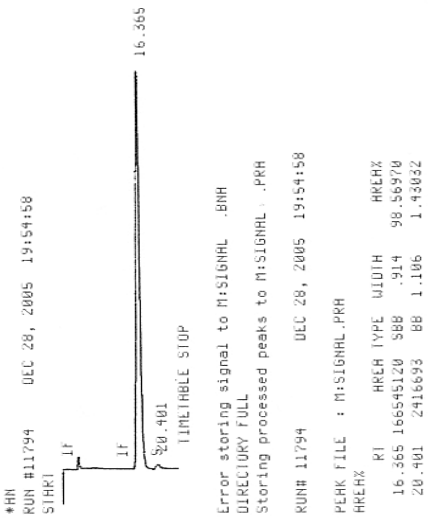
racemic **6Hb**



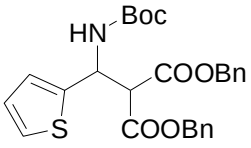
(-)-**6Hb**, 96% ee
Product of Q-**1d** catalyzed reaction



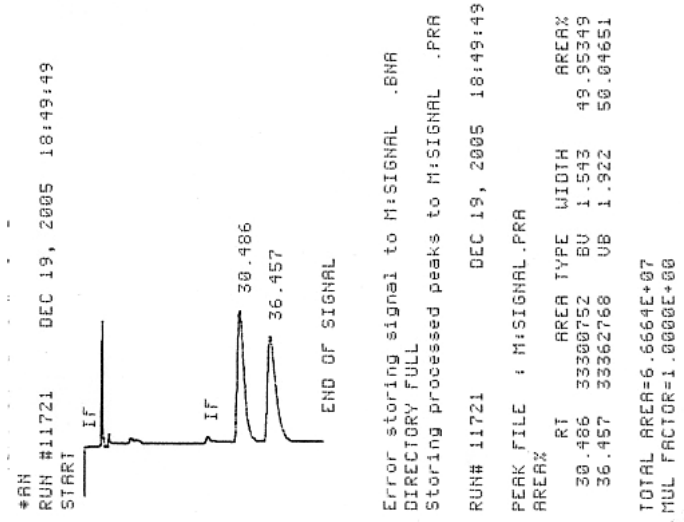
(+)-**6Hb**, 97% ee
Product of QD-**1d** catalyzed reaction



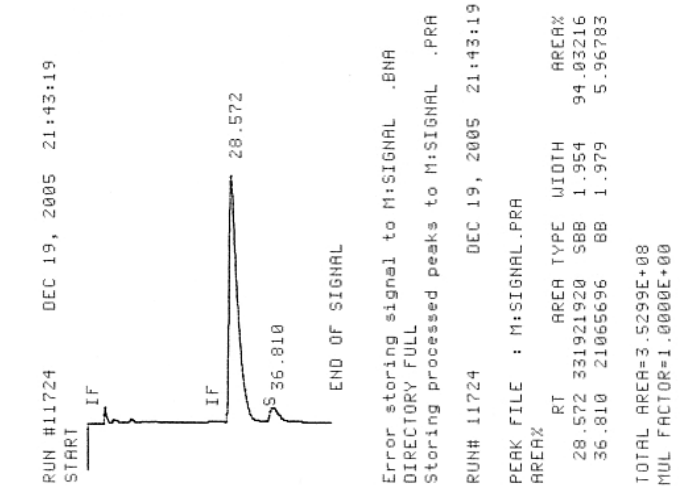
HPLC Condition: Daicel Chiralcel OD, Hexane / IPA = 98 / 2, 1.0 ml·min^{-1}, 220 nm



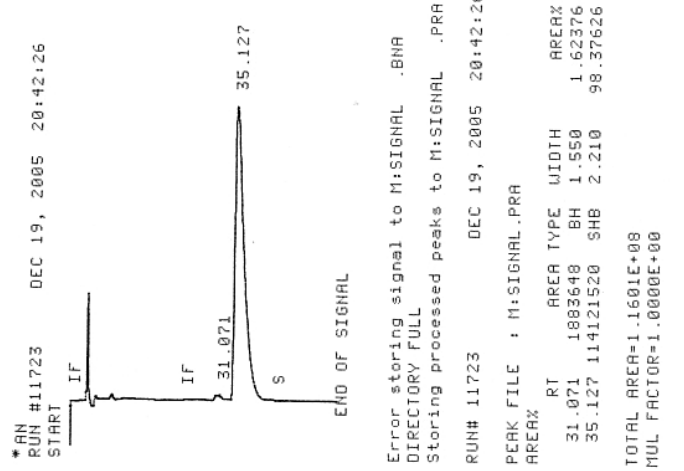
racemic **6Ib**



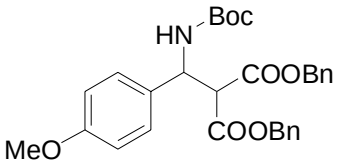
(-)-**6Ib**, 88% ee
Product of Q-**1d** catalyzed reaction



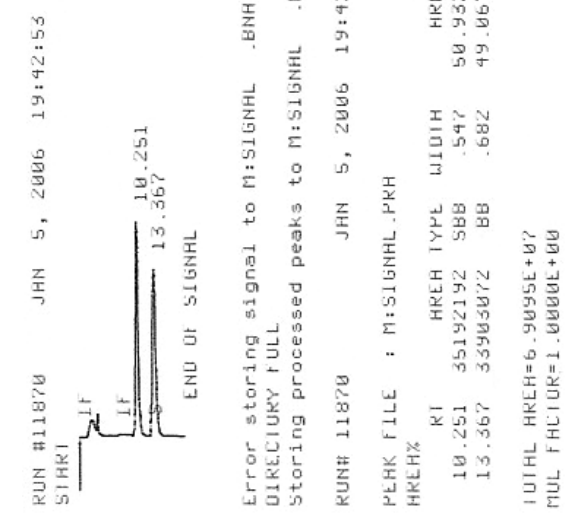
(+)-**6Ib**, 97% ee
Product of QD-**1d** catalyzed reaction



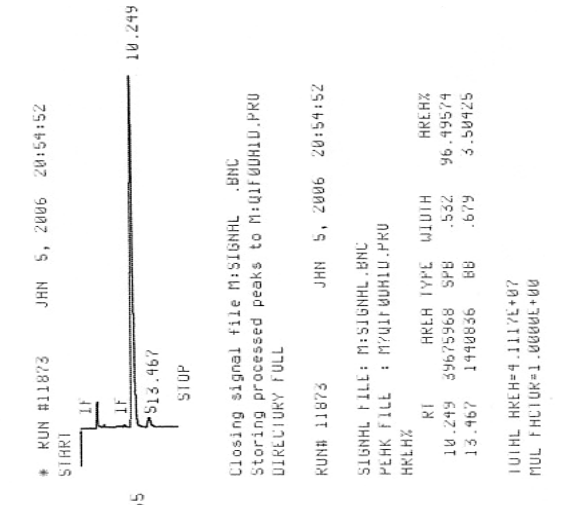
HPLC Condition: Daicel Chiralcel OD, Hexane / IPA = 90 / 10, 1.0 ml·min^{-1}, 220 nm



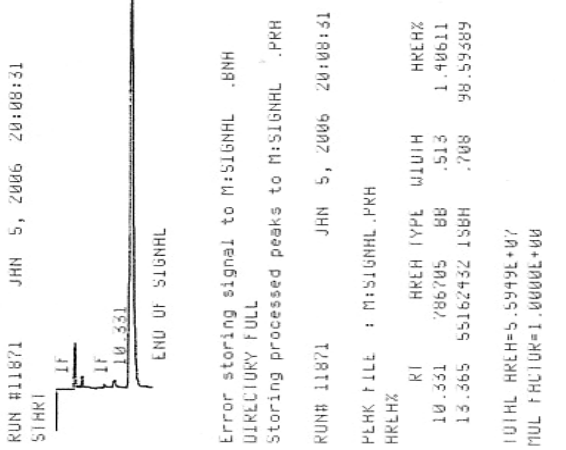
racemic **6Jb**



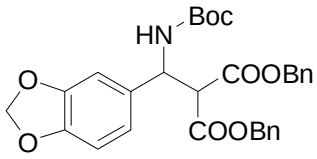
(-)-**6Jb**, 93% ee
Product of Q-**1d** catalyzed reaction



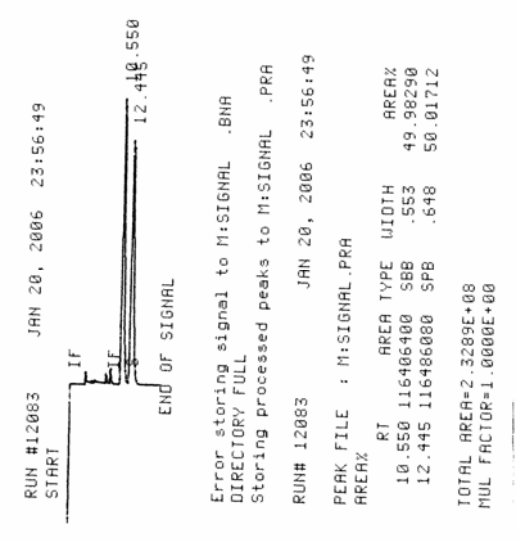
(+)-**6Jb**, 97% ee
Product of QD-**1d** catalyzed reaction



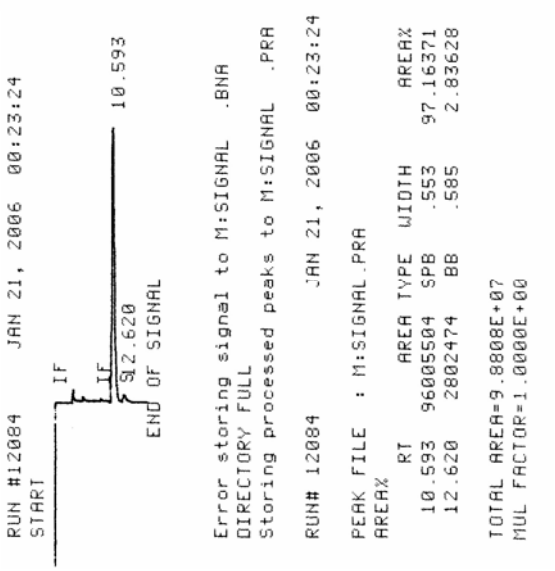
HPLC Condition: Daicel Chiralcel OD, Hexane / IPA = 90 / 10, 1.0 ml·min^{-1}, 220 nm



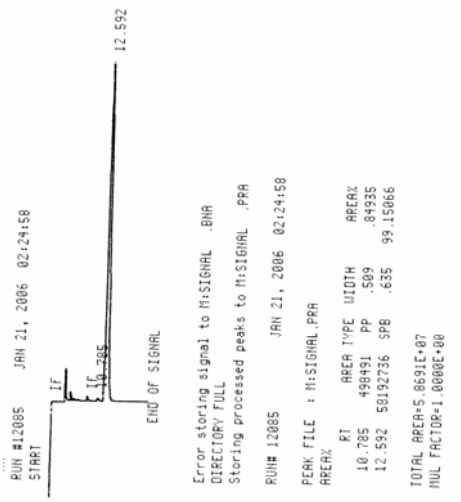
racemic **6Kb**



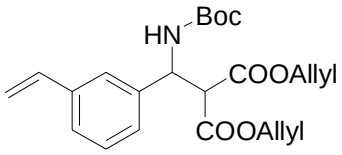
(-)-**6Kb**, 94% ee
Product of Q-**1d** catalyzed reaction



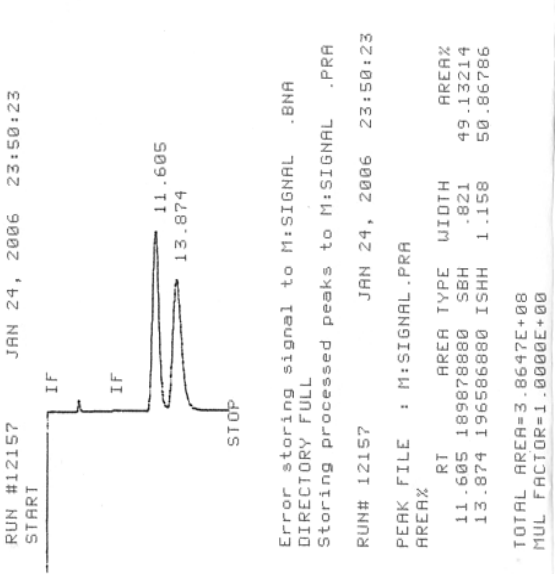
(+)-**6Kb**, 98% ee
Product of Q-**1d** catalyzed reaction



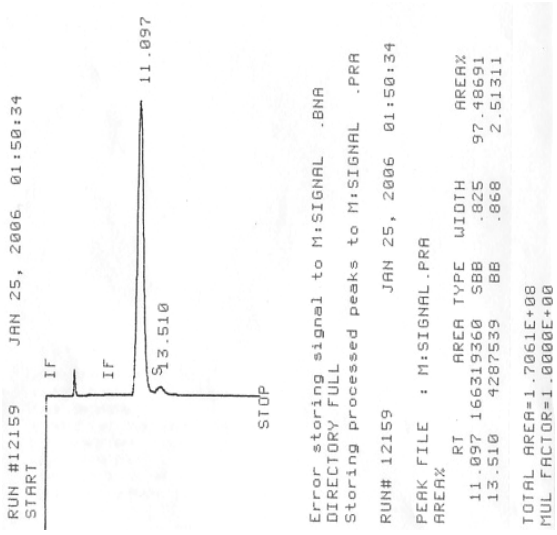
HPLC Condition: Daicel Chiralpak AS, Hexane / IPA = 98 / 2, 1.0 ml·min^{-1}, 220 nm



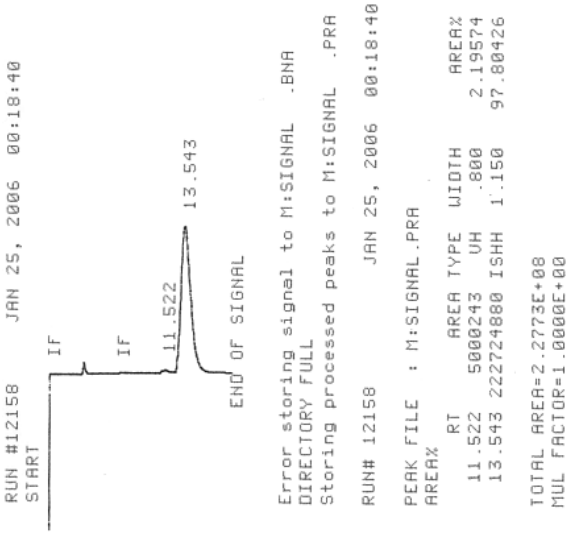
racemic **6Lc**



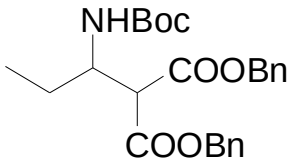
(-)-**6Lc**, 95% ee
Product of Q-**1d** catalyzed reaction



(+)-**6Lc**, 96% ee
Product of QD-**1d** catalyzed reaction



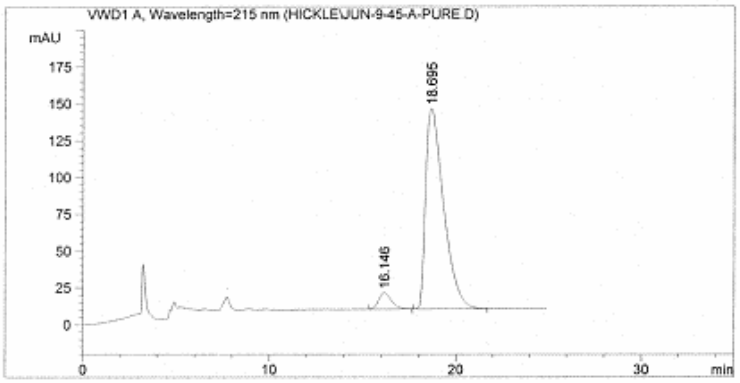
HPLC Condition: Daicel Chiralcel OD, Hexane / IPA = 98 / 2, 1.0 ml·min^{-1}, 220 nm



racemic **6Mb**

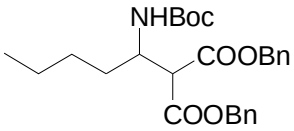
```
*AN
RUN #12907      MAR 21, 2006   09:31:10
START
                IF
                IF
                    15.800
                    18.684
                  END OF SIGNAL

Error storing signal to M:SIGNAL   .BNA
DIRECTORY FULL
Storing processed peaks to M:SIGNAL   .PRA

RUN# 12907           MAR 21, 2006   09:31:10

PEAK FILE   : M:SIGNAL.PRA
AREA%
      RT       AREA TYPE  WIDTH       AREA%
  15.800   73090112  SPB    .962    49.23227
  18.684   75369664 ISPP   1.294    50.76773

TOTAL AREA=1.4846E+08
MUL FACTOR=1.0000E+00
```

(+)-**6Mb**, 89% ee
Product of QD-**1d** catalyzed reaction



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.146	BB	0.7518	535.06702	11.04039	5.5841
2	18.695	BB	1.0102	9046.86133	135.79890	94.4159
Totals :				9581.92834	146.83929	

HPLC Condition: Daicel Chiralcel OD, Hexane / IPA = 98 / 2, 1.0 ml·min^{-1}, 220 nm



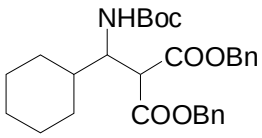
racemic **6Nb**

```
*AN
RUN #13018      MAR 31, 2006  00:41:18
START
                IF
                IF
                                14.092
                                16.315
                  END OF SIGNAL

Error storing signal to M:SIGNAL  .BNA
DIRECTORY FULL
Storing processed peaks to M:SIGNAL  .PRA

RUN# 13018           MAR 31, 2006  00:41:18

PEAK FILE  : M:SIGNAL.PRA
AREA%
      RT       AREA TYPE  WIDTH      AREA%
  14.092   32275392   BV    .792    49.66435
  16.315   32711648   VB    .925    50.33563

TOTAL AREA=6.4987E+07
MUL FACTOR=1.0000E+00
```

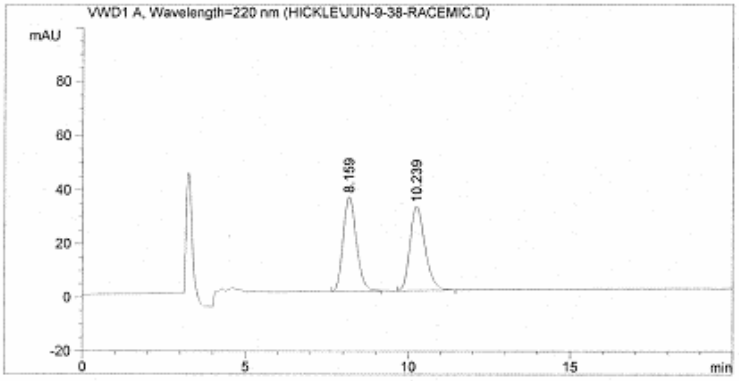
(+)-**6Nb**, 92% ee
Product of QD-**1d** catalyzed reaction

```
*AN
RUN #13019      MAR 31, 2006  01:29:41
START
                IF
                IF
                14.312                  16.226
                  END OF SIGNAL

Error storing signal to M:SIGNAL  .BNA
DIRECTORY FULL
Storing processed peaks to M:SIGNAL  .PRA

RUN# 13019           MAR 31, 2006  01:29:41

PEAK FILE  : M:SIGNAL.PRA
AREA%
      RT       AREA TYPE  WIDTH      AREA%
  14.312    1503932   PV    .795     3.97286
  16.226   36351200   VV    .899    96.02717

TOTAL AREA=3.7855E+07
MUL FACTOR=1.0000E+00
```

HPLC Condition: Daicel Chiralcel OD, Hexane / IPA = 97 / 3, 1.0 ml·min^{-1}, 220 nm



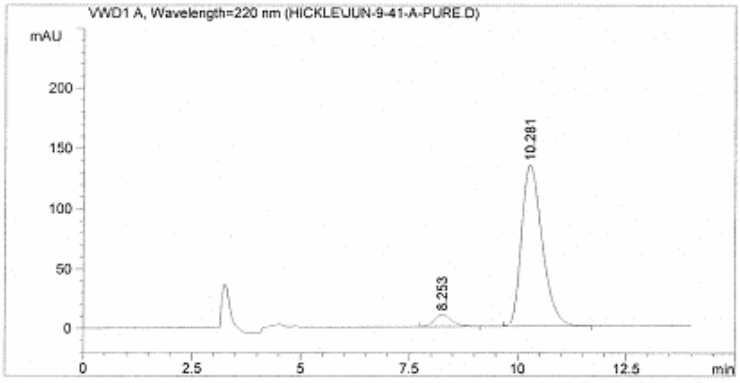
racemic **6Ob**



Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.159	BB	0.4384	985.72864	35.08925	49.4882
2	10.239	BB	0.4965	1006.11560	31.37090	50.5118
Totals :				1991.84424	66.46015	

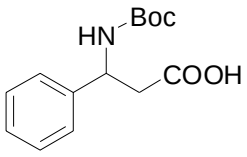
(+)-**6Ob**, 88% ee
Product of QD-**1d** catalyzed reaction



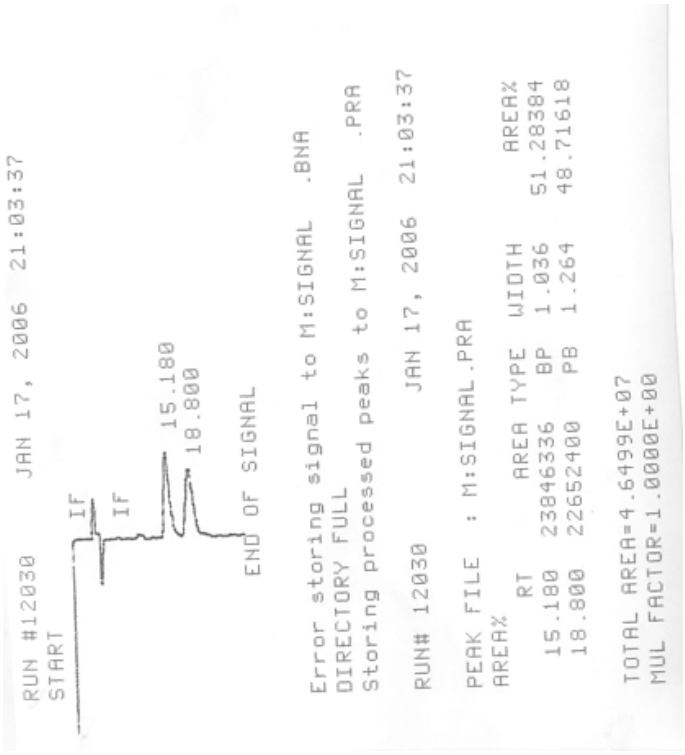
Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.253	BB	0.4310	281.01743	10.05146	5.9256
2	10.281	BB	0.5156	4461.37402	134.33229	94.0744
Totals :				4742.39145	144.38375	

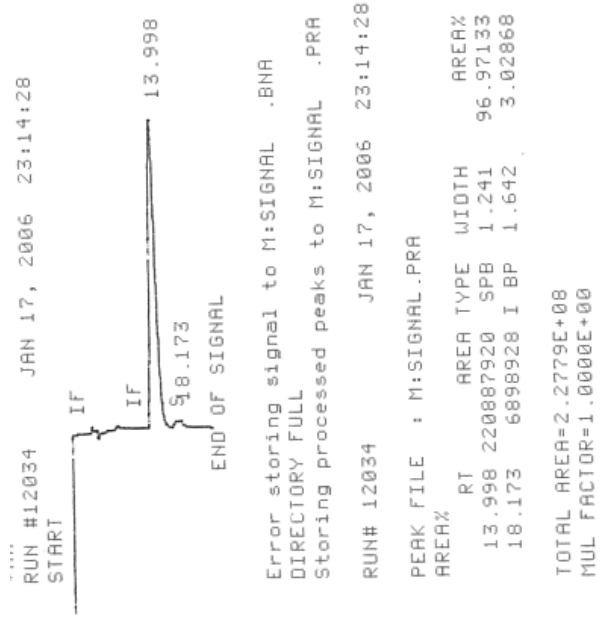
HPLC Condition: Daicel Chiralcel OD, Hexane / IPA / TFA = 95 / 5 / 0.1, 1.0 ml·min^{-1}, 220 nm, 0^{o}C



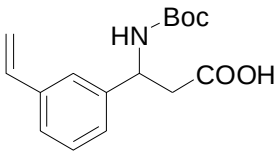
racemic **7Ab**



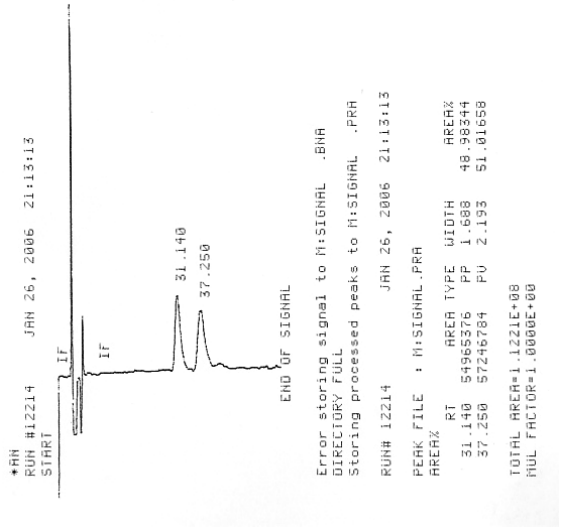
(S)(-)-**7Ab**, 94% ee
derived from (+)-**6Ab**



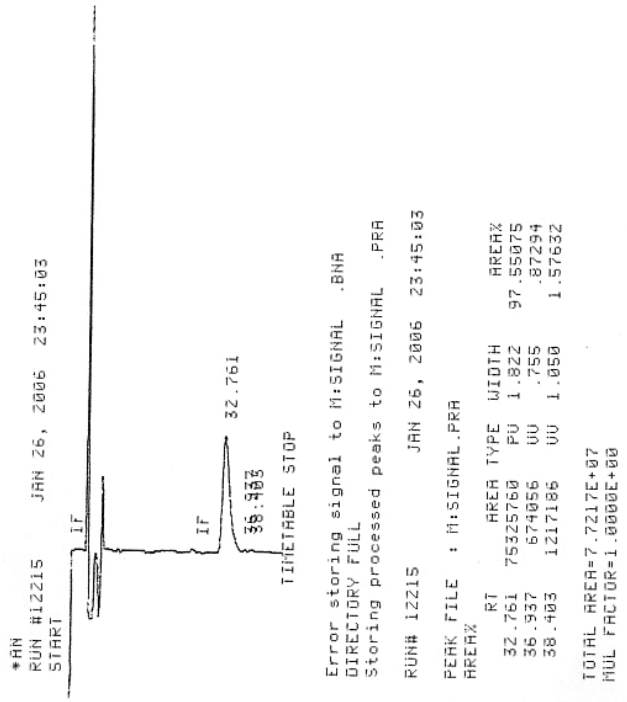
HPLC Condition: Daicel Chiralcel OD, Hexane / IPA / TFA = 98 / 2 / 0.1, 1.0 ml·min^{-1}, 220 nm.



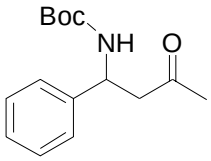
racemic **7Lc**



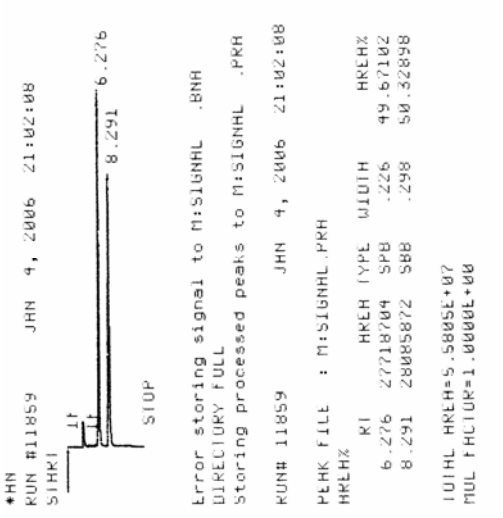
(-)-**7Lc** 97% ee
derived from (+)-**6Lc**



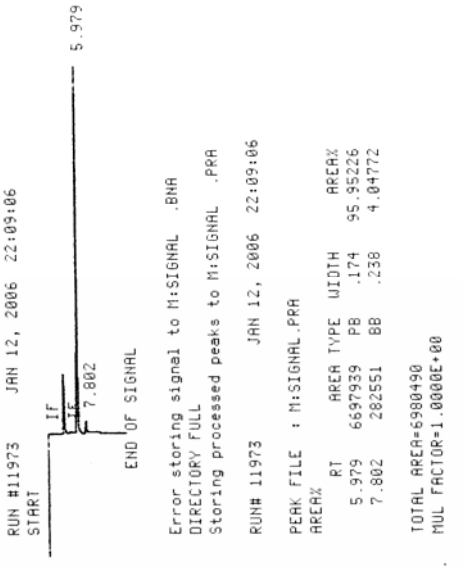
HPLC Condition: Regis Pirckle Covalent (*R*, *R*) Whelk-O 1, Hexane / IPA = 85 / 15, 1.0 ml·min^{-1}, 220 nm



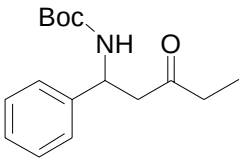
racemic **10Aa**



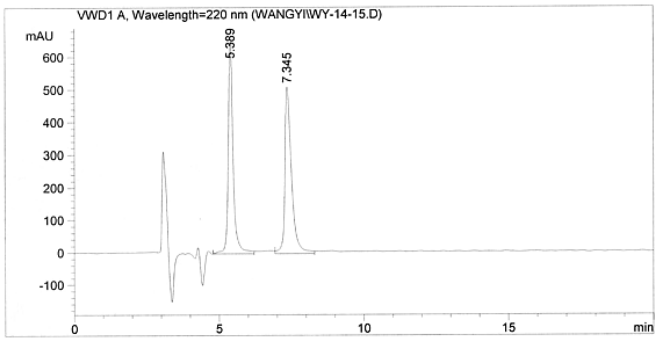
(-)-**10Aa**, 92% ee derived from **9Aa** (Product of QD-**1d** catalyzed reaction)



HPLC Condition: Regis Pirckle Covalent (*R*, *R*) Whelk-O 1 Column, Hexane / IPA = 85 / 15, 1.0 ml·min^{-1},



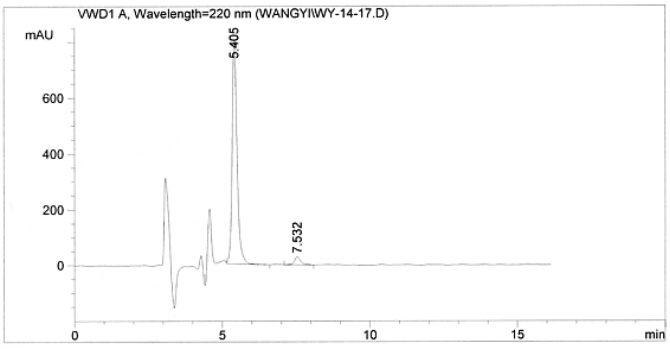
racemic **10Ab**



Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.389	BV	0.1766	7760.27588	652.31592	48.3264
2	7.345	VV	0.2386	8297.76758	511.93216	51.6736
Totals :				1.60580e4	1164.24808	

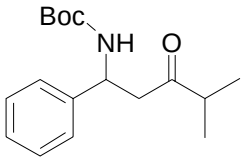
(-)-**10Ab**, 91% ee
derived from **9Ab** (Product of QD-**1d** catalyzed reaction)



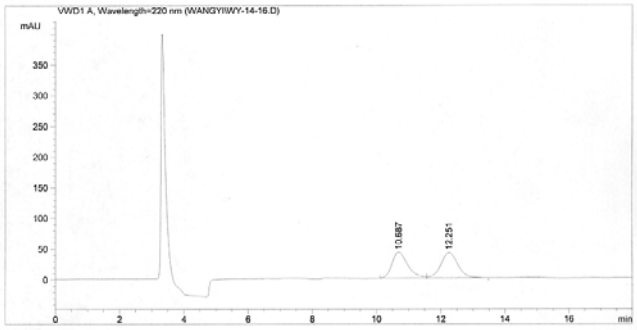
Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.405	VV	0.1756	9224.90430	798.40521	95.2762
2	7.532	VV	0.2238	457.36768	29.63161	4.7238
Totals :				9682.27197	828.03683	

HPLC Condition: Daicel Chiralpak AS, Hexane / IPA = 98 / 2, 1.0 ml·min^{-1}, 220 nm



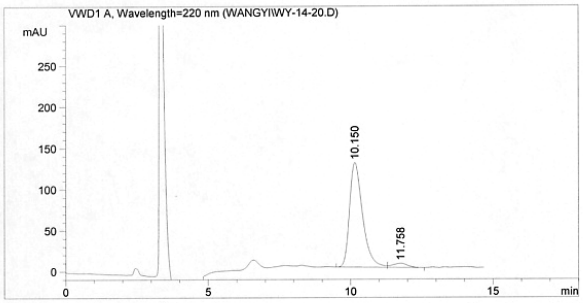
racemic **10Ac**



Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.687	BV	0.5283	1449.13538	42.24953	48.8940
2	12.251	VB	0.5607	1514.69287	41.20287	51.1060
Totals :				2963.82825	83.45240	

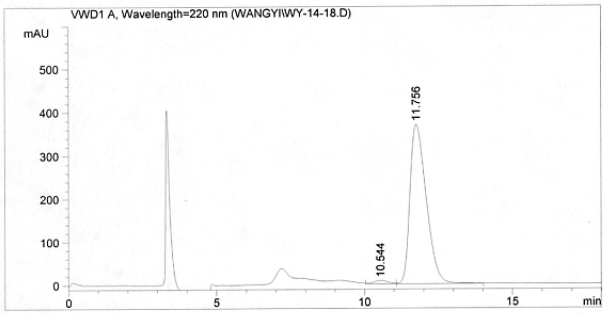
(+)-**10Ac**, 92% ee
derived from **9Ac** (Product of Q-**1d** catalyzed reaction)



Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.150	VV	0.4888	4064.66064	127.36127	95.7944
2	11.758	VV	0.5512	178.44716	4.98920	4.2056
Totals :				4243.10780	132.35047	

(-)-**10Ac**, 96% ee
derived from **9Ac** (Product of QD-**1d** catalyzed reaction)



Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.544	BV	0.5050	261.05579	7.83969	1.8134
2	11.756	VB	0.5987	1.41352e4	368.69211	98.1866
Totals :				1.43963e4	376.53180	