Supplementary Material for:

Kinetic Resolution of Racemic Lactones by Conjugate Additions of Allylic Organolithium Species: Formation of 3 Centers with High Diatereo- and Enantioselectivities

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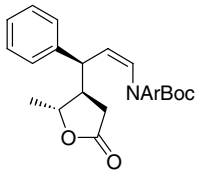
Experimental

General. All air-sensitive reactions were performed in oven or flame dried glassware under nitrogen with freshly distilled solvents. Toluene was distilled over CaH_2, and diethyl ether, tetrahydrofuran (THF) was distilled from sodium and benzophenone. Commercial (–)-sparteine (Aldrich) was distilled and stored under nitrogen. Commercially available TEEDA was used to obtain racemic product and used without purification. *n*-BuLi solution in hexanes (1.6M) was titrated prior to use against *N*-pivaloyl-*o*-toluidine. All other commercial reagents were used without further purification, unless otherwise indicated.

Preparative high-pressure liquid chromatography (HPLC) was performed using Rainin SD 200 pump system equipped with Dynamax-60-A 8 μm silica column (Rainin Instrument Co., 25 cm x 21.4 mm i.d.) and Knauer UV detector (254 nm). Analytical chiral stationary phase HPLC was performed using Rainin HPXL pump systems. Either Whelk-O (Regis Chemical Co., 25 cm x 4.6 mm i.d.) or Chiralpak AD (Chiral Technologies Inc. 25 cm x 4.6 mm i.d.) was used to obtain product enantiomeric purity. Analytical thin layer chromatography (TLC) was done on Merck silica plates (0.25 mm)

with QF-254 indicator. Either UV light or alkaline $KMnO_4$ was used for TLC visualization. Flash chromatography was performed suing 230-400 mesh silica gel. ^1H and ^{13}C NMR spectra were acquired using either a Varian U400 (400 MHz ^1H, 100.6 MHz ^{13}C) or U500 (500 MHz ^1H, 125.7 MHz ^{13}C) spectrometer using $CDCl_3$, acetone-d_6 or DMSO as a solvent. Chemical shifts are reported in ppm relative to the solvent. Mass spectral data was obtained at the University of Illinois Mass Spectrometry Laboratory. Thomas-Hoover capillary melting point apparatus was used to determine uncorrected melting points. Purity of the sample is established to be >95% based on ^{13}C NMR spectra. Diastereomeric purity was determined by ^1H NMR integration.

"Standard workup" refers to dilution with diethyl ether, addition of H_2O, separation of phases, extraction of the aqueous layer with ether (3x), combination of the organic phases, drying with $MgSO_4$ and concentration by rotary evaporation.



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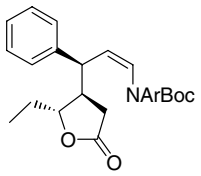
Representative Kinetic Resolution of Racemic Michael Acceptors: Preparation of (3*R*, 2'*R*, 3''*S*)-(4-Methoxy-phenyl)-[3-(2'-methyl-5-oxo-tetrahydro-furan-3-yl)-3''-phenyl-propenyl]-carbamic acid *tert*-butyl ester (4)

To a stirring solution of **1** (249 mg, 0.73 mmol) under a N_2 atmosphere in 10 mL of toluene, (-)-sparteine (0.19 mL, 0.80 mmol) was added. The reaction mixture was cooled to -78 °C, and *n*-BuLi (0.51 mL, 0.80 mmol) was added and stirred for 15 min. The resulting mixture was slowly added to a precooled solution of 5-methyl 5H-furan-2-one (0.17 mL, 1.83 mmol) and TMSCl (0.47 mL, 3.7 mmol) in 5 mL of toluene. After stirring for 1 hr, the reaction mixture was quenched with MeOH, and warmed to rt. 3.7 mL of TBAF (3.7 mmol) was added and stirred for additional 30 mins. The standard work-up afforded the crude product as a yellow oil, which was purified by column chromatography (25% ethyl acetate in hexane) to give the product as a clear oil (246mg, 0.563 mol, 77%). **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ 1.35 (d, 3H, *J* = 6.5Hz), 1.43 (s, 9H),

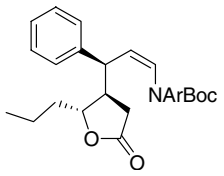
1.91 (dd, 1H, *J* = 17.7, 6.8Hz), 2.20 (m, 1H), 2.28 (dd, 1H, *J* = 17.4, 8.9Hz), 2.89 (bs, 1H), 3.84 (s, 3H), 4.33 (m, 1H), 4.94 (dd, 1H, *J* = 10.5, 9.8 Hz), 6.67 (m, 2H), 6.78 (m, 1H), 6.86 (m, 2H), 7.10 (m, 2H), 7.18 (m, 3H). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.24, 28.1, 33.2, 44.6, 48.2, 55.8, 80.3, 114.3, 126.8, 127.5, 128.5, 129.3, 134.3, 153.5, 158.4, 175.8. HRMS: Calcd for $C_{26}H_{31}N_1O_5$: 437.2202; found: 437.2203. The enantiomeric purity was determined to be 94:6 by CSP-HPLC analysis on a Pirkle concept Whelk-O column with 15% (v/v) isopropyl alcohol/hexane mobile phase by a flow rate 1.2mL/min. The major enantiomer had a retention time of 44.6min and the minor enantiomer had a retention time of 40.0 min.



5

(3*R*, 2'*R*, 3''*S*)-(4-Methoxy-phenyl)-[3-(2'-ethyl-5-oxo-tetrahydro-furan-3-yl)-3''-phenyl-propenyl]-carbamic acid *tert*-butyl ester (3*R*, 2'*R*, 3''*S*)-(5)

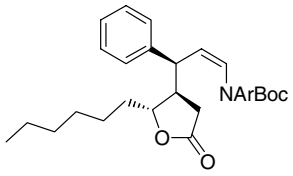
The general kinetic resolution procedure was followed using **1** (183 mg, 0.54 mmol) and 5-ethyl-5H-furan-2-one (152 mg, 1.36 mmol) to afford crude mixture, which was purified by column chromatography (30% ethylacetate in hexane) to afford **5** (152 mg, 0.337 mmol, 62%) as a white crystals, and recovered >32% of 5-ethyl-5H-furan-2-one. Melting point of **5**; 110-112 ^{o}C. $[\alpha]^{20}_{D}$ of 5-ethyl-5H-furan-2-one = +30^{o} (*c* = 8mg/mL, $CHCl_3$) (lit.[9] $[\alpha]^{20}_{D}$ = 103^{o}, *c* = 2.71g/mL, $CHCl_3$, *S*-enantiomer). **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ 0.98 (t, 3H, *J* = 7.8Hz), 1.43 (s, 9H), 1.61 (m, 2H), 1.87 (m, 1H), 2.26 (m, 2H), 2.85 (bs, 1H), 3.83 (s, 3H), 4.20 (m, 1H), 4.91 (t, 1H, *J* = 10.2 Hz), 6.67 (m, 2H), 6.78 (m, 1H), 6.86 (m, 2H), 7.05 (m, 2H), 7.18 (m, 3H). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 9.98, 28.3, 28.60, 32.87, 44.8, 45.48, 55.78, 81.80, 85.17, 114.60, 127.0, 127.84, 128.80, 129.56, 132.93, 134.44, 141.05, 153.76, 158.40, 176.46. HRMS: Calcd for $C_{27}H_{33}N_1O_5$: 451.2359; found: 451.2356. The enantiomeric purity was determined to be 95:5 by CSP-HPLC analysis on a Chiralpak column with 40% (v/v) isopropyl alcohol/hexane mobile phase by a flow rate 1.0mL/min. The major enantiomer had a retention time of 13.6 min and the minor enantiomer had a retention time of 4.6 min.



6

(3*R*, 2'*R*, 3''*S*)-(4-Methoxy-phenyl)-[3-(2'-propyl-5-oxo-tetrahydro-furan-3-yl)-3''-phenyl-propenyl]-carbamic acid *tert*-butyl ester (3*R*, 2'*R*, 3''*S*)-(6)

The general kinetic resolution procedure was followed using **1** (110 mg, 0.32 mmol) and 5-propyl-5H-furan-2-one (90 mg, 0.71 mmol) to afford crude mixture, which was purified by column chromatography (25% ethylacetate in hexane) to afford **6** (93 mg, 0.20 mmol, 62%). **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 0.96 (t, 3H, *J* = 7.0Hz), 1.44 (m, 11H), 1.55 (m, 2H), 1.87 (m, 1H), 2.26 (m, 2H), 2.85 (bs, 1H), 3.85 (s, 3H), 4.28 (m, 1H), 4.91 (t, 1H, *J* = 10.6 Hz), 6.67 (m, 2H), 6.80 (m, 1H), 6.86 (m, 2H), 7.05 (m, 2H), 7.18 (m, 3H). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 13.98, 18.93, 28.33, 32.76, 37.77, 44.75, 46.00, 55.78, 81.86, 83.71, 114.60, 127.02, 127.84, 128.77, 129.56, 134.48, 141.04, 153.75, 158.43, 176.46. HRMS: Calcd for $C_{28}H_{35}N_1O_5$: 465.2515; found: 465.2520. The enantiomeric purity was determined to be 96:4 by CSP-HPLC analysis on a Chiralpak column with 40% (v/v) isopropyl alcohol/hexane mobile phase by a flow rate 1.0 mL/min. The major enantiomer had a retention time of 8.0 min and the minor enantiomer had a retention time of 4.5 min.

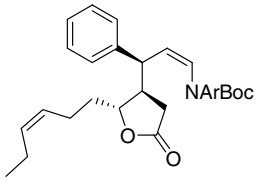


7

(3*R*, 2'*R*, 3''*S*)-(4-Methoxy-phenyl)-[3-(2'-hexyl-5-oxo-tetrahydro-furan-3-yl)-3''-phenyl-propenyl]-carbamic acid *tert*-butyl ester (3*R*, 2'*R*, 3''*S*) -(7)

The general kinetic resolution procedure was followed using **1** (155 mg, 0.46 mmol) and 5-hexyl-5H-furan-2-one (180 mg, 1.07 mmol) to afford crude mixture, which was purified by column chromatography (25% ethylacetate in hexane) to afford **7** (160 mg, 0.32 mmol, 69%). **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ 0.913 (t, 3H, *J* = 7.0Hz), 1.30 (m, 7H), 1.44 (m, 9H), 1.56 (m, 3H), 1.88 (dd, 1H, *J* = 16.7, 4.5 Hz), 2.24 (m, 1H), 2.29

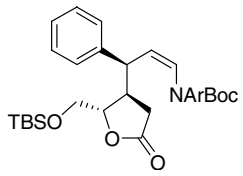
(dd, 1H, *J* = 17.2, 8.6 Hz), 2.84 (bs, 1H), 3.85 (s, 3H), 4.26 (m, 1H), 4.91 (t, 1H, *J* = 10.3 Hz), 6.67 (m, 2H), 6.80 (m, 1H), 6.86 (m, 2H), 7.05 (m, 2H), 7.18 (m, 3H). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 14.30, 22.76, 25.59, 28.35, 29.19, 31.90, 32.78, 35.72, 44.67, 46.02, 55.79, 83.92, 114.62, 127.03, 127.85, 128.77, 129.53, 134.43, 153.75, 158.48, 176.50. HRMS: Calcd for $C_{31}H_{41}N_1O_5$: 507.2985; found: 507.2992. The enantiomeric purity was determined to be 96:4 by CSP-HPLC analysis on a Chiralpak column with 15% (v/v) isopropyl alcohol/hexane mobile phase by a flow rate 0.8 mL/min. The major enantiomer had a retention time of 9.9min and the minor enantiomer had a retention time of 8.0 min.



8

(3*R*, 2'*R*, 3''*S*)-[3-(2'-Hex-3-enyl-5-oxo-tetrahydro-furan-3-yl)-3''-phenyl-propenyl]-(4-methoxy-phenyl)-carbamic acid *tert*-butyl ester (3*R*, 2'*R*, 3''*S*)-(8)

The general kinetic resolution procedure was followed using **1** (103 mg, 0.30 mmol) and (3*Z*)-5-hex-3-enyl-5H-furan-2-one (112 mg, 0.67 mmol) to afford crude mixture, which was purified by column chromatography (25% ethylacetate in hexane) to afford **8** (118 mg, 0.23 mmol, 76%). **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ 0.99 (t, 3H, *J* = 7.4Hz), 1.43 (m, 9H), 1.63 (m, 2H), 1.88 (m, 1H), 2.10 (m, 2H), 2.17 (m, 2H), 2.26 (m, 2H), 2.82 (bs, 1H), 3.85 (s, 3H), 4.24 (m, 1H), 4.89 (t, 1H, *J* = 10.1 Hz), 5.31 (m, 1H), 5.47 (m, 1H), 6.69 (m, 2H), 6.82 (m, 1H), 6.86 (m, 2H), 7.05 (m, 2H), 7.19 (m, 3H). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 14.53, 20.78, 23.45, 28.34, 32.93, 35.76, 44.60, 46.22, 55.79, 81.95, 83.33, 114.63, 127.05, 127.49, 127.83, 128.78, 128.86, 129.40, 133.34, 134.37, 141.04, 153.72, 158.51, 176.34. HRMS: Calcd for $C_{31}H_{39}N_1O_5$: 505.2828; found: 505.2824. The enantiomeric purity was determined to be 96:4 by CSP-HPLC analysis on a Chiralpak column with 15% (v/v) isopropyl alcohol/hexane mobile phase by a flow rate 0.8 mL/min. The major enantiomer had a retention time of 11.0 min and the minor enantiomer had a retention time of 8.1 min.



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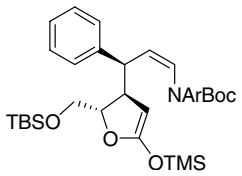
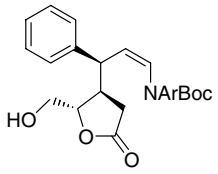


11

(3*S*, 2'*R*, 3''*S*)-{3-[2'-(*tert*-Butyl-dimethyl-silanyloxymethyl)-5-oxo-tetrahydro-furan-3-yl]-3''-phenyl-propenyl}-(4-methoxy-phenyl)-carbamic acid *tert*-butyl ester (3*S*, 2'*R*, 3''*S*)-(10) and **(3*S*, 2'*S*, 3''*S*)-{3-[2'-(*tert*-butyl-dimethyl-silanyloxymethyl)-5-trimethylsilanyloxy-2,3-dihydro-furan-3-yl]-3''-phenyl-propenyl}-(4-methoxy-phenyl)-carbamic acid *tert*-butyl ester (3*S*, 2'*S*, 3''*S*)-(11)**

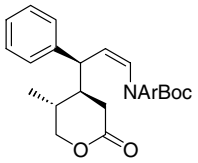
The general kinetic resolution procedure was followed using **1** (203 mg, 0.60 mmol) and 5-(*tert*-butyl-dimethyl-silanyloxymethyl)-5H-furan-2-one (180 mg, 0.78 mmol) to afford crude mixture, which was purified by column chromatography (25% ethylacetate in hexane) to afford **10** (240 mg, 0.42 mmol, 70 %), and **11** (68 mg, 10.6 mmol, 18%). **10**: **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ 0.05 (s, 3H), 0.07 (s, 3H), 0.88 (s, 9H), 1.42 (s, 9H), 1.81 (bd, 1H, *J* = 17.9 Hz), 2.39 (dd, 1H, *J* = 17.9, 9.2 Hz), 2.55 (m, 1H), 2.81 (bs, 1H), 3.60 (dd, 1H, *J* = 11.4, 2.3 Hz), 3.84 (s, 3H), 3.86 (dd, 1H, *J* = 11.4, 2.7Hz), 4.37 (bs, 1H), 4.89 (t, 1H, *J* = 10.2Hz), 6.69 (m, 2H), 6.82 (m, 1H), 6.86 (m, 2H), 7.03 (m, 2H), 7.18 (m, 3H). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ -5.37, -5.30, 18.39, 26.01, 28.35, 33.51, 42.44, 45.04, 55.78, 65.20, 83.08, 83.11, 114.64, 126.97, 127.85, 128.77, 129.75, 134.35, 141.13, 153.77, 158.46, 177.04. HRMS: Calcd for $C_{32}H_{45}N_1O_6Si$: 567.3016; found: 567.3023. **11**: **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ -0.12 (s, 9H), 0.02 (s, 3H), 0.04 (s, 3H), 0.89 (s, 9H), 1.42 (s, 9H), 1.77(bd, 1H, *J* = 4.6Hz), 2.31 (m, 1H), 2.83 (bs, 1H), 3.37 (m, 2H), 3.80 (s, 3H), 4.32 (m, 1H), 5.00 (bt, 1H, *J* = 10.4Hz), 6.73 (m, 4H), 6.86 (m, 1H), 6.93 (m, 2H), 7.12 (m, 3H). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ -5.17, -2.08, 18.4, 25.9, 28.1, 35.3, 44.6, 46.3, 55.8, 64.9, 81.8, 114.3, 126.9, 128.0, 128.6, 134.1, 153.6, 178.9. HRMS: Calcd for $C_{35}H_{53}N_1O_6Si_2$: 639.3411; found: 639.3407.



12

(3*S*, 2'*R*, 3''*S*)-[3-(2'-Hydroxymethyl-5-oxo-tetrahydro-furan-3-yl)-3''-phenyl-propenyl]-(4-methoxy-phenyl)-carbamic acid *tert*-butyl ester (3*S*, 2'*R*, 3''*S*) -(12)

From **10**: To a stirring solution of **10** (976 mg, 1.72 mmol) in 15 mL of THF, 1.9 mL of TBAF (1.9 mmol) was added and stirred for 30 min. The solvent was removed and the resulting oil was purified by column chromatography (50% ethylacetate in hexane) to afford **12** (765 mg, 1.69 mmol, 98%). From **11**: To a stirring solution of **11** (54 mg, 0.085 mmol) in 15 mL of THF, 0.17 mL of TBAF (0.17 mmol) was added and stirred for 30 min. The solvent was removed and the resulting oil was purified by column chromatography (50% ethylacetate in hexane) to afford **12** (35 mg, 0.077 mmol, 91%). **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ 1.44 (s, 9H), 1.92 (dd, 1H, *J* = 18.3, 5.8Hz), 2.23 (bs, 1H), 2.36 (dd, 1H, *J* = 18.3, 9.3 Hz), 2.60 (m, 1H), 2.92 (bs, 1H), 3.61 (m, 1H), 3.85 (s, 3H), 3.88 (m, 1H), 4.33 (m, 1H), 4.95 (dd, 1H, *J* = 10.6, 9.4Hz), 6.69 (m, 2H), 6.78 (bd, 1H, *J* = 9.2 Hz), 6.87 (m, 2H), 7.06 (m, 2H), 7.18 (m, 3H). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 28.4, 33.5, 41.8, 45.0, 55.8, 64.3, 82.1, 83.9, 114.6, 127.1, 127.7, 128.6, 128.8, 129.7, 134.5, 140.8, 153.8, 158.4, 176.6. HRMS: Calcd for $C_{26}H_{31}N_1O_6$: xxxx; found: xxxx.

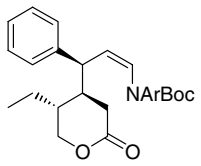


14

(3*R*, 5'*R*, 3''*R*)-(4-Methoxy-phenyl)-[3-(5'-methyl-2-oxo-tetrahydro-pyran-4-yl)-3''-phenyl-propenyl]-carbamic acid *tert*-butyl ester (3*R*, 5'*R*, 3''*R*)-(14)

The general kinetic resolution procedure was followed using **1** (76 mg, 0.22 mmol) and 5-methyl-5,6-dihydro-pyran-2-one (55 mg, 0.49 mmol) to afford crude mixture which was purified by column chromatography (35% ethylacetate in hexane) to afford **14** (68 mg, 0.15 mmol, 68%) as a mixture of diasteromers (75:25 dr). Using TEEDA as a ligand, rac-**14** (83 mg, 0.18 mmol, 62%) was obtained with 98:2 dr from **1** (101 mg, 0.30 mmol) and 5-methyl-5,6-dihydro-pyran-2-one (44 mg, 0.39 mmol). Major diastereomers: **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ 0.97 (d, 3H, *J* = 7.0 Hz), 1.42 (s, 9H), 1.74 (m, 1H), 1.89 (bs, 1H), 1.91 (dd, 1H, *J* = 15.9, 7.8 Hz), 2.17 (dd, 1H, *J* = 16.0, 7.0

Hz), 2.93 (m, 1H), 3.83 (s, 3H), 3.87 (dd, 1H, *J* = 11.4, 6.0 Hz), 4.11 (dd, 1H, *J* = 11.4, 4.0 Hz), 5.05 (dd, 1H, *J* = 10.8, 9.5 Hz), 6.69 (m, 2H), 6.76 (m, 1H), 6.82 (m, 2H), 7.01 (m, 2H), 7.17 (m, 3H) **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 18.90, 28.37, 30.91, 32.31, 43.82, 46.47, 55.79, 71.98, 81.71, 114.46, 126.87, 127.96, 128.44, 128.60, 129.34, 134.65, 153.84, 158.24, 172.98. HRMS: Calcd for $C_{27}H_{33}N_1O_5$: 451.2359; found: 451.2365. The enantiomeric purity was determined to be 98:2 for major and 93:7 for minor diastereomer by CSP-HPLC analysis on a Chiralpak column with 20% (v/v) isopropyl alcohol/hexane mobile phase by a flow rate 0.6 mL/min. For major diastereomer, the major enantiomer had a retention time of 25.3 min and the minor enantiomer had a retention time of 10.5min. For minor diastereomer, the major enantiomer had a retention time of 11.5 min and the minor enantiomer had a retention time of 6.0 min.

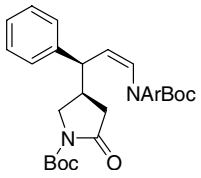


15

(3*R*, 5'*R*, 3''*R*)-(4-Methoxy-phenyl)-[3-(5'-ethyl-2-oxo-tetrahydro-pyran-4-yl)-3''-phenyl-propenyl]-carbamic acid *tert*-butyl ester (3*R*, 5'*R*, 3''*R*)-(15)

The general kinetic resolution procedure was followed using **1** (84 mg, 0.25 mmol) and 5-ethyl-5,6-dihydro-pyran-2-one (69 mg, 0.55 mmol) to afford crude mixture, which was purified by column chromatography (35% ethylacetate in hexane) to afford **15** (75 mg, 0.16 mmol, 65%) as a mixture of diastereomers (80:20 dr). Using TEEDA as a ligand, rac-**15** (460 mg, 0.99 mmol, 73%) was obtained with 89:11 dr from **1** (457 mg, 1.35 mmol) and 5-ethyl-5,6-dihydro-pyran-2-one (220 mg, 1.75 mmol). **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ 0.90 (t, 3H, *J* = 7.5 Hz), 1.33 (m, 2H), 1.42 (s, 9H), 1.69 (m, 1H), 1.79 (bs, 1H), 1.86 (dd, 1H, *J* = 15.4, 7.7 Hz), 2.07 (dd, 1H, *J* = 16.0, 7.0 Hz), 2.89 (m, 1H), 3.83 (s, 3H), 4.01 (dd, 1H, *J* = 11.7, 4.8 Hz), 4.08 (dd, 1H, *J* = 11.5, 4.3 Hz), 5.03 (dd, 1H, *J* = 10.9, 9.2 Hz), 6.68 (m, 2H), 6.73 (m, 1H), 6.82 (m, 2H), 7.01 (m, 2H), 7.15 (m, 3H) **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 11.66, 26.13, 28.36, 32.62, 37.43, 42.23, 47.00, 55.79, 69.26, 81.70, 114.48, 126.87, 127.86, 128.45, 128.63, 129.46, 134.77, 153.81,

158.22, 173.27. HRMS: Calcd for $C_{28}H_{35}N_1O_5$: 465.2515q; found: 465.2513. The enantiomeric purity was determined to be 98:2 for major and 93:7 for minor diastereomer by CSP-HPLC analysis on a Chiralpak column with 20% (v/v) isopropyl alcohol/hexane mobile phase by a flow rate 0.6 mL/min. For major diastereomer, the major enantiomer had a retention time of 21.4 min and the minor enantiomer had a retention time of 9.7 min. For minor diastereomer, the major enantiomer had a retention time of 11.0 min and the minor enantiomer had a retention time of 13.3 min.

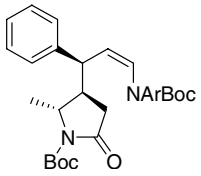


18

(4*R*, 1'*R*)-4-{3-[*tert*-Butoxycarbonyl-(4-methoxy-phenyl)-amino]-1'-phenyl-allyl}-2-oxo-pyrrolidine-1-carboxylic acid *tert*-butyl ester (4*R*, 1'*R*)-(18)

A solution of **1** (246 mg, 0.73 mmol) and (-)-sparteine (0.18 mL, 0.80 mmol) in 15 mL of toulene was cooled to -78 °C, and *n*-BuLi (0.50 mL, 0.80 mmol) was added dropwise. After stirring for 30 min, premixed solution of **16** (199 mg, 1.09 mmol) and TMSCl (0.21 mL, 1.64 mmol) in 5 mL of toluene was added at -78 °C. The reaction mixture was stirred for 1 h, and then quenched with MeOH. The solution was warmed to rt, and TBAF (1.64 mL, 1.64 mmol) was added. Standard workup and flash chromatography (35% ethyl acetate in hexane) provided **18** (220 mg, 0.42 mmol, 58%) with 87:13 dr. The diastereomers were separated using preparative HPLC (12% ethylacetate in hexane to 20% ethylacetate in hexane) to provide a single diastereomer (185 mg, 35 mmol, 48%). Major diastereomer: **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ 1.41 (s, 9H), 1.55 (s, 9H), 1.88 (dd, 1H, *J* = 18.2, 8.6 Hz), 2.12 (dd, 1H, *J* = 17.7, 8.2), 2.31 (m, 1H), 2.72 (bs, 1H), 3.39 (m, 1H), 3.75 (dd, 1H, *J* = 11.1, 7.9 Hz), 3.83 (s, 3H), 4.92 (t, 1H, *J* = 9.9 Hz), 6.69 (bd, 2H, *J* = 7.0 Hz), 6.79 (m, 1H), 6.83 (m, 2H), 6.99 (m, 2H), 7.15 (m, 3H). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 28.27, 28.33, 37.20, 37.77, 45.0, 50.1, 55.8, 81.78, 83.0, 114.49, 126.90, 127.79, 128.67, 134.37, 141.45, 153.71, 158.46, 173.30. HRMS: Calcd for $C_{30}H_{38}N_2O_6$: 522.2730; found: 522.2728. The enantiomeric purity was determined to be 83:17 by CSP-HPLC analysis on a Chiralpak column with

40% (v/v) isopropyl alcohol/hexane mobile phase by a flow rate 0.6mL/min. The major enantiomer had a retention time of 19.8 min and the minor enantiomer had a retention time of 8.33 min.



19

(3*R*, 1'*S*, 2''*R*)-3-{3-[*tert*-Butoxycarbonyl-(4-methoxy-phenyl)-amino]-1-phenyl-allyl}-2-methyl-5-oxo-pyrrolidine-1-carboxylic acid *tert*-butyl ester (3*R*, 1'*S*, 2''*R*)-(19)

The general kinetic resolution procedure was followed using **1** (97 mg, 0.29 mmol) and **17** (169 mg, 0.86 mmol) to afford crude mixture, which was purified by column chromatography (25% ethylacetate in hexane) to afford a major diasteromer of **19** (90 mg, 0.165 mmol, 58%), and a mixture of minor diastereomer and electrophile. The mixture was purified with preparatory HPLC (12% ethylacetate in hexane) to afford minor diastereomer of **19** (45 mg, 0.083 mmol, 29%) and recovered **17** (102 mg, 0.52 mmol, 60%). With TEEDA as a ligand rac-**19** (52 mg, 0.10 mmol, 36%) was obtained as a single diastereomer from **1** (90.7 mg, 0.27 mmol) and **17** (79 mg, 0.40 mmol). $[\alpha]^{20}_{D}$ of **17** = +17° (*c* = 23mg/mL, $CHCl_3$) (lit.[12] $[\alpha]^{20}_{D}$ = 145°, *c* = 1g/mL, $CHCl_3$, *S*-enantiomer). **Major diastereomoer**: **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ 1.29 (d, 3H, *J* = 7.0Hz), 1.45 (s, 9H), 1.62 (s, 9H), 1.77 (d, 1H, *J* = 18.5 Hz), 1.84 (t, 1H, *J* = 9.0 Hz), 2.36 (dd, 1H, *J* = 18.2, 8.6 Hz), 2.51 (bs, 1H), 3.86 (s, 3H), 4.11 (q, 1H, *J* = 6.3 Hz), 4.82 (dd, 1H, *J* = 11.0, 9.9 Hz), 6.67 (m, 2H), 6.87 (m, 3H), 6.99 (m, 2H), 7.16 (m, 3H). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 20.89, 28.35, 28.38, 35.19, 44.11, 44.56, 55.87, 57.49, 82.90, 114.67, 126.85, 128.05, 128.67, 129.00, 134.01, 141.38, 150.19, 153.71, 158.77, 173.20. HRMS: Calcd for $C_{31}H_{40}N_2O_6$: 536.2886; found: 536.2868. The enantiomeric purity was determined to be 53:47 by CSP-HPLC analysis on a Chiralpak column with 20% (v/v) isopropyl alcohol/hexane mobile phase by a flow rate 0.6mL/min. The major enantiomer had a retention time of 12.8 min and the minor enantiomer had a retention time of 10.7 min. **Minor diastereomer**: **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ 1.30 (d, 3H, *J* = 6.7Hz),

1.42 (s, 9H), 1.62 (s, 9H), 1.77 (d, 1H, J = 18.3 Hz), 1.85 (t, 1H, J = 9.6 Hz), 2.36 (dd, 1H, J = 18.1, 8.6 Hz), 2.51 (bs, 1H), 3.87 (s, 3H), 4.11 (q, 1H, J = 5.6 Hz), 4.82 (dd, 1H, J = 10.7, 10.0 Hz), 6.67 (m, 2H), 6.87 (m, 3H), 6.99 (m, 2H), 7.16 (m, 3H).