Catalytic Asymmetric Rearrangement of Allylic *N*-Aryl Trifluoroacetimidates. A Useful Method for Transforming Prochiral Allylic Alcohols to Chiral Allylic Amines

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Supporting Information

General Experimental Details: The procedure we employed to purify THF and CH₂Cl₂ has been described;¹ other general experimental details also have been described.²

General Procedure for the Synthesis of Allylic *N*-(4-Methoxyphenyl)trifluoroacetimidates. Preparation of (*E*)-2-Hexenyl-*N*-(4-methoxyphenyl)trifluoroacetimidate (**3a**).

Sodium hydride (608 mg, 15.2 mmol) was slurried in THF (13 mL) and cooled to 0 °C. *Trans*-2-hexen-1-ol (1.8 mL, 15.2 mmol) was added dropwise and the reaction was stirred at 0 °C for 30 min. The cooling bath was removed and the reaction was stirred for an additional 1.5 h at room temperature. A solution of *N*-(4-methoxybenzyl)trifluoroacetimidoyl chloride³ (3.0 g, 12.7 mmol) and THF (13 mL) was added in one portion to the alkoxide solution. The reaction was maintained at room temperature for 18 h before concentrating. The residue was redissolved in hexanes, filtered through Celite, and concentrated. The resulting residue was purified by column chromatography on Davisil grade SiO₂ (99.25: 0.75 hexanes: EtOAc to 98.5: 1.5 hexanes: EtOAc) to give 3.4 g (88%) **3a** as a pale yellow oil: ¹H NMR (500 MHz, CDCl₃) δ 6.85 (td, *J* = 8.8, 2.2 Hz, 2H), 6.71–6.84 (m, 2H), 5.79–5.92 (m, 1H), 5.62–5.75 (m, 1H), 4.70 (broad s, 2H), 3.79 (s, 3H), 2.08 (q, *J* = 7.1 Hz, 2H), 1.44 (sextet, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 155.9, 145.1 (q, *J*_{C–F} = 34.5 Hz), 137.4, 137.1, 122.9, 120.5, 116.0 (q, *J*_{C–F} =

¹ Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics*, **1996**, 15, 1518.

² Deng, W.; Overman, L. E. *J. Am. Chem. Soc.* **1994**, 116, 11241.

³ Tamura, K.; Mizukami, H.; Maeda, K.; Watanabe, H.; Uneyama, K. *J. Org. Chem.* **1993**, 58, 32.

283.6 Hz), 113.8, 68.6, 55.4, 34.5, 22.2, 13.8; IR (neat) 2961, 2934, 2876, 2841, 1698, 1505, 1463, 1324, 1243, 1204, 1139, 1038 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{F}_3\text{NO}_2$: C, 59.79; H, 6.02; N, 4.65. Found: C, 60.03; H, 6.15; N, 4.62.

(Z)-2-Hexenyl-N-(4-methoxyphenyl)trifluoroacetimidate (3b). Prepared in 78% yield

following the general procedure: ^1H NMR (500 MHz, CDCl_3) δ 6.84 (td, $J = 8.9, 2.3$ Hz, 2H), 6.76 (broad d, $J = 8.8$ Hz, 2H), 5.63–5.76 (m, 2H), 4.80 (broad d, $J = 4.8$ Hz, 2H), 3.79 (s, 3H), 2.06–2.16 (m, 2H), 1.41 (sextet, $J = 7.4$ Hz, 2H), 0.90 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.2, 145.4 (q, $J_{\text{C-F}} = 32.6$ Hz), 137.6, 136.0, 122.8, 120.8, 116.3 (q, $J_{\text{C-F}} = 284.5$ Hz), 114.1, 64.0, 55.6, 30.5, 23.1, 14.1; IR (neat) 2961, 2934, 2876, 1702, 1509, 1467, 1316, 1243, 1204, 1139, 1038 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{F}_3\text{NO}_2$: C, 59.79; H, 6.02; N, 4.65. Found: C, 60.04; H, 6.09; N, 4.51.

(E)-2-Butenyl-N-(4-methoxyphenyl)trifluoroacetimidate (3c). Prepared in 70% yield

following the general procedure: ^1H NMR (500 MHz, CDCl_3) δ 6.82–6.87 (m, 2H), 6.71–6.81 (m, 2H), 5.83–5.96 (m, 1H), 5.66–5.77 (m, 1H), 4.68 (broad s, 2H), 3.79 (s, 3H), 1.77 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.2, 145.5 (q, $J_{\text{C-F}} = 36.7$ Hz), 137.6, 132.4, 124.2, 120.7, 116.2 (q, $J_{\text{C-F}} = 271.9$ Hz), 113.9, 69.5, 55.3, 17.8; IR (neat) 2953, 1698, 1505, 1328, 1243, 1200, 1135, 1038 cm^{-1} ; HRMS (CI- NH_3) m/z 273.0969 [273.0977 calcd for $\text{C}_{13}\text{H}_{14}\text{F}_3\text{NO}_2$ (M)]. Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{F}_3\text{NO}_2$: C, 57.14; H, 5.16; N, 5.13. Found: C, 57.34; H, 5.16; N, 5.06.

(Z)-2-Butenyl-N-(4-methoxyphenyl)trifluoroacetimidate (3d). Prepared in 83% yield

following the general procedure: ^1H NMR (500 MHz, CDCl_3) δ 6.85–6.82 (m, 2H), 6.76 (d, $J = 7.6$ Hz, 2H), 5.82–5.79 (m, 1H), 5.69 (bs, 1H), 4.82 (d, $J = 4.7$ Hz, 2H), 3.79 (s, 3H), 1.73 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.6, 145.6 (q, $J_{\text{C-F}} = 33.8$ Hz), 137.8, 130.7, 123.7, 120.9, 116.4 (q, $J_{\text{C-F}} = 285.3$ Hz), 114.2, 63.7, 55.5, 13.4; IR (neat) 3035, 2958, 2842, 1699, 1506, 1313, 1244, 1205, 1135, 1035 cm^{-1} ; HRMS (EI) m/z 273.0967 [273.0977 calcd for $\text{C}_{13}\text{H}_{14}\text{F}_3\text{NO}_2$ (M)]. Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{F}_3\text{NO}_2$: C, 57.14; H, 5.16; N, 5.13. Found: C, 57.25; H, 5.19; N, 5.17.

(E)-5-Phenyl-2-pentenyl-N-(4-methoxyphenyl)trifluoroacetimidate (3e). Prepared in 88% yield following the general procedure: $R_f = 0.72$ (4:1 hexanes/EtOAc); ^1H NMR (500 MHz, CDCl_3) δ 7.32 (dt, $J = 6.9, 1.2$ Hz, 2H), 7.23 (t, $J = 7.3$ Hz, 3H), 6.87 (td, $J = 8.9, 2.0$ Hz, 2H), 6.78 (broad d, $J = 7.0$ Hz, 2H), 5.86–5.99 (m, 1H), 5.68–5.81 (m, 1H), 4.72 (broad s, 2H), 3.81 (s, 3H), 2.77 (t, $J = 7.4$ Hz, 2H), 2.45 (q, $J = 7.5$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.3, 145.3 (q, $J_{\text{C-F}} = 33.0$ Hz), 141.5, 137.6, 136.4, 128.54, 128.47, 126.1, 123.8, 120.9, 116.4 (q, $J_{\text{C-F}} = 282.6$ Hz), 114.2, 68.7, 55.7, 35.7, 34.5; IR (neat) 3088, 3030, 2937, 2837, 1702, 1505, 1455, 1328, 1243, 1204, 1139, 1034 cm^{-1} ; LRMS (ES) m/z 386.24 ($\text{M}+\text{Na}$). Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{F}_3\text{NO}_2$: C, 66.11; H, 5.55; N, 3.85. Found: C, 66.03; H, 5.62; N, 4.04.

(Z)-5-Phenyl-2-pentenyl-N-(4-methoxyphenyl)trifluoroacetimidate (3f). Prepared in 96% yield following the general procedure: ^1H NMR (500 MHz, CDCl_3) δ 7.29–7.34 (m, 2H), 7.18–7.25 (m, 3H), 6.85–6.89 (m, 2H), 6.75–6.84 (m, 2H), 5.75–5.83 (m, 1H), 5.67–5.75 (m, 1H), 4.76 (broad s, 2H), 3.81 (s, 3H), 2.74 (t, $J = 7.6$ Hz, 2H), 2.44–2.55 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.3, 145.2 (q, $J_{\text{C-F}} = 30.0$ Hz), 141.2, 137.5, 134.8, 128.4, 128.3, 126.0, 123.3, 120.7, 116.1 (q, $J_{\text{C-F}} = 285.0$ Hz), 114.0, 63.6, 55.3, 35.5, 29.5; IR (neat) 3030, 2937, 1702, 1505, 1204, 1139, 1034 cm^{-1} ; MS (CI- NH_3) m/z 363.1449 [363.1446 calcd for $\text{C}_{20}\text{H}_{20}\text{F}_3\text{NO}_2$ (M)].

(E)-5-Methyl-2-hexenyl-N-(4-methoxyphenyl)trifluoroacetimidate (3g). Prepared in 71% yield following the general procedure: ^1H NMR (500 MHz, CDCl_3) δ 6.85 (td, $J = 8.8, 2.1$ Hz, 2H), 6.78 (broad d, $J = 7.5$ Hz, 2H), 5.76–5.90 (m, 1H), 5.59–5.74 (m, 1H), 4.73 (broad s, 2H), 3.79 (s, 3H), 2.01 (t, $J = 6.9$ Hz, 2H), 1.69 (septet, $J = 6.7$ Hz, 1H), 0.93 (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.8, 145.7 (q, $J_{\text{C-F}} = 26.9$ Hz), 138.1, 136.7, 124.5, 121.6, 116.7 (q, $J_{\text{C-F}} = 286.4$ Hz), 114.5, 69.0, 55.8, 42.0, 28.4, 22.6; IR (neat) 3042, 2961, 2876, 2841, 1698, 1505, 1467, 1386, 1324, 1289, 1243, 1204, 1139, 1038 cm^{-1} ; LRMS (ES) m/z 338.21 ($\text{M}+\text{Na}$). Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{F}_3\text{NO}_2$: C, 60.94; H, 6.39; N, 4.44. Found: C, 61.12; H, 6.54; N, 4.38.

(Z)-5-Methyl-2-hexenyl-*N*-(4-methoxyphenyl)trifluoroacetimidate (3h). Prepared in

84% yield following the general procedure: ^1H NMR (500 MHz, CDCl_3) δ 6.85 (td, $J = 8.8, 2.1$ Hz, 2H), 6.79 (broad d, $J = 9.4$ Hz, 2H), 5.69–5.79 (m, 2H), 4.82 (broad s, 2H), 3.79 (s, 3H), 2.04 (broad s, 2H), 1.68 (septet, $J = 6.7$ Hz, 1H), 0.94 (d, $J = 6.7$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.3, 145.4 (q, $J_{\text{C}-\text{F}} = 35.1$ Hz), 137.6, 134.9, 123.3, 120.8, 116.3 (q, $J_{\text{C}-\text{F}} = 283.9$ Hz), 114.1, 64.1, 55.7, 37.1, 28.9, 22.7; IR (neat) 2961, 2876, 2841, 1698, 1613, 1505, 1467, 1366, 1316, 1243, 1204, 1139, 1038 cm^{-1} ; LRMS (ES) m/z 338.21 (M+Na). Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{F}_3\text{NO}_2$: C, 60.94; H, 6.39; N, 4.44. Found: C, 61.12; H, 6.42; N, 4.32.

General Procedure for Allylic Imidate Rearrangement Using COP-OCOCF₃ (6b).

Preparation of (S)-2,2,2-trifluoro-*N*-(4-methoxyphenyl)-*N*-(1-propylallyl)acetamide (4a) from (E)-2-hexenyl-*N*-(4-methoxyphenyl)trifluoroacetimidate (3a). Palladium

chloride catalyst **6a** (187 mg, 0.13 mmol) and AgOCOCF_3 (113 mg, 0.51 mmol) were dissolved with stirring in CH_2Cl_2 (1.5 mL) under an argon atmosphere and protected from light. After 3 h the resulting mixture, containing COP catalyst **6b**, was filtered through Celite while under Ar and rinsed with CH_2Cl_2 to a final volume of 4.25 mL (0.03M). A portion of this catalyst solution (0.26 mL, 0.03 M, 0.008 mmol) and $i\text{Pr}_2\text{NEt}$ (0.32 mL, 0.016 mmol, 0.1 M in CH_2Cl_2) were added successively at room temperature by syringe to a solution of imidate **3a** (48 mg, 0.16 mmol) and CH_2Cl_2 (0.22 mL). The reaction flask then was then sealed under argon, protected from light and maintained at room temperature. After 30 h the reaction was concentrated. Purification of the residue by chromatography (SiO_2 , 95:5 hexanes/EtOAc) afforded 35 mg (79%) of **4a** as a pale yellow oil: ^1H NMR (500 MHz, CDCl_3) δ 7.06 (app dd, $J = 18.7, 8.6$ Hz, 2H), 6.88 (app t, $J = 7.0$ Hz, 2H), 5.55 (ddd, $J = 17.9, 10.1, 8.3$ Hz, 1H), 5.26 (d, $J = 17.2$ Hz, 1H), 5.19 (dd, $J = 10.2, 0.6$ Hz, 1H), 5.02 (q, $J = 7.6$ Hz, 1H), 3.82 (s, 3H), 1.54–1.64 (m, 1H), 1.39–1.48 (m, 1H), 1.37 (sextet, $J = 7.3$ Hz, 2H), 0.93 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.5, 156.5 (q, $J_{\text{C}-\text{F}} = 34$ Hz), 135.2, 131.6, 130.8, 127.7, 119.0, 116.3 (q, $J_{\text{C}-\text{F}} = 286$ Hz), 113.6, 113.5, 60.6, 55.4, 33.8, 19.6, 13.9; IR (neat) 3083, 2964, 2877, 1690, 1511, 1299, 1250, 1202, 1187, 1148, 1034 cm^{-1} ; LRMS (ES) m/z 324.10 (M+Na). Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{F}_3\text{NO}_2$: C, 59.79; H, 6.02; N, 4.65. Found: C, 60.05; H, 6.10; N, 4.69.

General Procedure for Allylic Imidate Rearrangement Using COP-Cl (6a). **Preparation of (*R*)-2,2,2-trifluoro-*N*-(4-methoxyphenyl)-*N*-(1-propylallyl)acetamide (4a) from (*Z*)-2-hexenyl-*N*-(4-methoxyphenyl)trifluoroacetimidate 3b.** A solution of palladium chloride catalyst **6a** (12 mg, 0.008 mmol) in CH_2Cl_2 (0.26 mL) was added by syringe to imidate **3b** (48 mg, 0.16 mmol). The reaction flask was then sealed, protected from light and maintained at room temperature. After 60 h the reaction was concentrated. Purification of the residue by chromatography (SiO_2 , 95:5 hexanes/EtOAc) afforded 33 mg (70%) of **4a** as a pale yellow oil.

General Procedure for Allylic Imidate Rearrangement Using COP-Cl (6a) at 38 °C. **Preparation of (*R*)-2,2,2-Trifluoro-*N*-(4-methoxyphenyl)-*N*-(1-phenethylallyl)acetamide (4e) from (*Z*)-2-Butenyl-*N*-(4-methoxyphenyl)trifluoroacetimidate 3f.** A

solution of palladium chloride catalyst **6a** (12 mg, 0.008 mmol) in CH_2Cl_2 (0.26 mL) was added by syringe to imidate **3f** (58 mg, 0.16 mmol). The reaction flask was then sealed, protected from light and maintained at 38 °C. After 60 h the reaction was cooled to room temperature and concentrated. Purification of the residue by chromatography (SiO_2 , 95:5 hexanes/EtOAc) afforded 47 mg (81%) of **4e** as a pale yellow oil. 1H NMR (500 MHz, $CDCl_3$) δ 7.29 (t, J = 7.1 Hz, 2H), 7.20 (d, J = 7.3 Hz, 1H), 7.16 (d, J = 7.1 Hz, 2H), 7.11 (d, J = 8.3 Hz, 1H), 7.05 (d, J = 7.9 Hz, 1H), 6.87 (dd, J = 7.7, 1.5 Hz, 2H), 5.59 (ddd, J = 17.3, 10.1, 8.4 Hz, 1H), 5.26–5.34 (m, 2H), 5.08 (q, J = 6.7 Hz, 1H), 3.83 (s, 3H), 2.64 (t, J = 8.0 Hz, 2H), 1.90–2.02 (m, 1H), 1.71–1.82 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 157.4 (q, J_{C-C-F} = 38 Hz), 141.5, 135.6, 132.3, 131.5, 129.0, 128.8, 128.4, 126.6, 120.4, 117.0 (q, J_{C-F} = 287 Hz), 114.4, 114.3, 61.2, 55.8, 33.9, 33.0; IR (neat) 3088, 3030, 2937, 2841, 1695, 1513, 1455, 1417, 1297, 1251, 1204, 1150, 1034 cm^{-1} . Anal. Calcd for $C_{20}H_{20}F_3NO_2$: C, 66.11; H, 5.55; N, 3.85. Found: C, 66.26; H, 5.56; N, 3.86.

Preparation of (*S*)-2,2,2-Trifluoro-*N*-(4-methoxyphenyl)-*N*-(1-methylallyl)acetamide (4c) from (*E*)-2-Butenyl-*N*-(4-methoxyphenyl)trifluoroacetimidate 3c

Using COP-OCOCF₃ (6b). Prepared in 90% yield following the general procedure: 1H NMR (500 MHz, $CDCl_3$) δ 7.05 (dd, J = 11.6, 8.8 Hz, 2H), 6.84–6.91 (m, 2H), 5.75 (ddd, J = 17.1, 10.4, 6.5 Hz, 1H), 5.26 (pentet, J = 6.8 Hz, 1H), 5.17 (d, J = 10.3 Hz, 1H), 5.14–5.16 (m, 1H), 3.83 (s, 3H), 1.18 (d, J = 6.9 Hz, 3H); ^{13}C NMR

(125 MHz, CDCl_3) δ 159.9, 156.7 (q, $J_{\text{C-C-F}} = 35.0$ Hz), 136.5, 131.5, 131.4, 127.5, 117.7, 116.4 (q, $J_{\text{C-F}} = 287.5$ Hz), 113.7, 113.6, 55.4, 55.1, 17.0; IR (neat) 2984, 1691, 1513, 1251, 1189, 1146, 1034 cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{F}_3\text{NO}_2$: C, 57.14; H, 5.16; N, 5.13. Found: C, 57.50; H, 5.15; N, 5.21.

Preparation of (*R*)-2,2,2-Trifluoro-*N*-(4-methoxyphenyl)-*N*-(1-isobutylallyl)-acetamide (4g) from (*Z*)-5-Methyl-2-hexenyl-*N*-(4-methoxyphenyl)-trifluoroacetimidate 3h Using COP-OCO CF_3 (6b). Prepared in 67% yield following

the general procedure: ^1H NMR (500 MHz, CDCl_3) δ 7.07 (d, $J = 8.7$ Hz, 1H), 7.04 (d, $J = 8.7$ Hz, 1H), 6.85–6.92 (m, 2H), 5.54 (ddd, $J = 17.3, 10.2, 8.3$ Hz, 1H), 5.27 (d, $J = 17.2$ Hz, 1H), 5.20 (d, $J = 10.2$ Hz, 1H), 5.15 (q, $J = 7.7$ Hz, 1H), 3.84 (s, 3H), 1.53–1.61 (m, 1H), 1.40–1.48 (m, 1H), 1.30–1.37 (m, 1H), 0.93–0.97 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.8, 156.8 (q, $J_{\text{C-C-F}} = 34.5$ Hz), 135.6, 131.9, 131.1, 127.8, 119.1, 116.5 (q, $J_{\text{C-F}} = 287.1$ Hz), 113.7, 113.6, 58.8, 55.3, 40.5, 24.6, 23.0, 22.0; IR (neat) 3084, 2961, 2876, 1691, 1513, 1467, 1420, 1301, 1251, 1204, 1150, 1034 cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{F}_3\text{NO}_2$: C, 60.94; H, 6.39; N, 4.44. Found: C, 60.90; H, 6.59; N, 4.36.

General Procedure for Deacylation of Allylic Trifluoroacetamides. Preparation of (*S*)-*N*-(4-Methoxyphenyl)-3-amino-1-hexene (11a) from allylic amide 4a. A freshly

prepared solution of sodium ethoxide⁴ (0.23 mL, 3.0 M in ethanol, 0.69 mmol) was added in one portion at room temperature to amide **4a** (35 mg, 0.12 mmol). The resulting solution was warmed to 45 °C. After 18 h, the reaction was allowed to cool to room temperature, CH_2Cl_2 (0.5 mL) and water (0.5 mL) were added and the phases were

separated. The aqueous phase was extracted with CH_2Cl_2 (3 x 1 mL) and the combined organic phase was dried (Na_2SO_4) and concentrated. Purification of the residue by flash chromatography (SiO_2 , 19:1 hexanes/EtOAc) gave 23 mg (96%) of amine **11a** as a pale yellow oil. Chiral HPLC analysis (Chiracel OD-H, 99.8:0.2 *n*-hexane/IPA, 0.8 mL/min) showed that (*S*)-**11a** had been formed in 89% ee (*S*: $[\alpha]_{\text{D}}^{26} = +3.3$, $[\alpha]_{577}^{26} = +2.8$, $[\alpha]_{546}^{26} = +1.9$ (c 0.4, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 6.76 (td, $J = 8.9, 2.9$ Hz, 2H), 6.57 (td, $J = 8.9, 2.9$ Hz, 2H), 5.72 (ddd, $J = 16.9, 10.3, 6.4$ Hz, 1H), 5.19 (td, $J = 17.2, 1.3$ Hz,

⁴ Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley & Sons, Inc.: New York, 1967; Vol. 1, pp 1065–1073.

1H), 5.11 (td, $J = 10.3, 1.1$ Hz, 1H), 3.71–3.76 (m, 1H), 3.74 (s, 3H), 3.37 (broad s, 1H), 1.48–1.63 (m, 2H), 1.40–1.48 (m, 2H), 0.95 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 151.6, 141.6, 140.3, 114.8, 114.6, 114.5, 56.8, 55.8, 38.2, 19.3, 14.2; IR (neat) 3400, 3074, 2958, 2933, 2873, 1513, 1465, 1295, 1237, 1179, 1040 cm^{-1} ; LRMS (ES) m/z 206.14 (M+H). Anal. Calcd for $\text{C}_{13}\text{H}_{19}\text{NO}$: C, 76.06; H, 9.33; N, 6.82. Found: C, 76.02; H, 9.14; N, 6.80.

Preparation of (S)-N-(4-methoxyphenyl)-3-amino-1-butene (11c) from allylic amide 4c. Prepared in 97% yield following the general procedure. Chiral HPLC (Chiracel OD-

H, 99.8:0.8 *n*-hexane/IPA, 0.8 mL/min) showed that **11c** had been formed in 73% ee (*S*): $[\alpha]_{\text{D}}^{26} = +4.9$, $[\alpha]_{577}^{26} = +5.7$, $[\alpha]_{546}^{26} = +3.1$, $[\alpha]_{435}^{26} = -0.9$ (c 0.36, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 6.75–6.79 (m, 2H), 6.56–6.61 (m, 2H), 5.82 (ddd, $J = 17.2, 10.4, 5.8$ Hz, 1H), 5.20 (td, $J = 17.2, 1.4$ Hz, 1H), 5.07 (td, $J = 10.3, 1.3$ Hz, 1H), 3.87–3.95 (m, 1H), 3.74 (s, 3H), 3.34 (broad s, 1H), 1.29 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 152.0, 141.64, 141.58, 114.9, 114.7, 114.0, 55.8, 52.0, 21.7; IR (neat) 3408, 2980, 1513, 1235, 1038 cm^{-1} ; HRMS (CI- NH_3) m/z 177.1152 [177.1154 calcd for $\text{C}_{11}\text{H}_{15}\text{NO}$ (M)]. Anal. Calcd for $\text{C}_{11}\text{H}_{15}\text{NO}$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.58; H, 8.57; N, 7.81.

Preparation of (R)-N-(4-methoxyphenyl)-3-amino-5-phenyl-1-pentene (11e) from allylic amide 4f. Prepared in 88% yield following the general procedure. Chiral HPLC

(Chiracel OD-H, 98.2:1.8 *n*-hexane/IPA, 0.8 mL/min) showed that **11e** had been formed in 96% ee (*R*): $[\alpha]_{\text{D}}^{26} = -8.3$, $[\alpha]_{577}^{26} = -9.0$, $[\alpha]_{546}^{26} = -9.1$ (c 0.38, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 7.40 (t, $J = 8.3$ Hz, 2H), 7.31 (app t, $J = 8.0$ Hz, 3H), 6.87 (td, 8.9, 3.6 Hz, 2H), 6.64 (td, $J = 8.9, 3.5$ Hz, 2H), 5.87 (ddd, $J = 16.7, 10.3, 6.3$ Hz, 1H), 5.32 (d, $J = 17.2$ Hz, 1H), 5.26 (dd, $J = 10.3, 1.1$ Hz, 1H), 3.86 (q, $J = 6.6$ Hz, 1H), 3.84 (s, 3H), 2.86 (t, $J = 7.8$ Hz, 2H), 1.95–2.08 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 152.0, 141.7, 141.6, 140.1, 128.42, 128.36, 125.9, 115.3, 114.8, 114.7, 56.3, 55.7, 37.2, 32.2; IR (neat) 3393, 3084, 3065, 2934, 2833, 1513, 1455, 1235, 1181, 1038 cm^{-1} ; LRMS (ES) m/z 268.14 (M+H). Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{NO}$: C, 80.86; H, 7.92; N, 5.24. Found: C, 80.86; H, 8.01; N, 5.13.

Preparation of (R)-N-(4-methoxyphenyl)-3-amino-5-methyl-1-hexene (11g) from allylic amide 4h. Prepared in 99% yield following the general procedure. Chiral HPLC

(Chiracel OD-H, 99.5:0.5 *n*-hexane/IPA, 0.8 mL/min) showed that **11g** had been formed in 97% ee (*R*): $[\alpha]_D^{26} = -7.0$, $[\alpha]_{577}^{26} = -4.9$, $[\alpha]_{546}^{26} = -5.7$ (c 0.42, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 6.76 (td, *J* = 8.9, 2.9 Hz, 2H), 6.58 (td, *J* = 9.0, 2.9 Hz, 2H), 5.70 (ddd, *J* = 17.0, 10.3, 6.5 Hz, 1H), 5.18 (td, *J* = 17.2, 1.3 Hz, 1H), 5.09 (td, *J* = 10.3, 1.1 Hz, 1H), 3.78 (q, *J* = 6.9 Hz, 1H), 3.74 (s, 3H), 1.78 (septet, *J* = 6.7 Hz, 1H), 1.41–1.52 (m, 2H), 0.94 (app dd, *J* = 11.8, 6.6 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 151.9, 141.8, 140.8, 114.80, 114.75, 114.7, 55.8, 55.1, 45.3, 24.7, 22.7; IR (neat) 3394, 3094, 2956, 2856, 2870, 2833, 1511, 1466, 1237, 1180, 1039 cm⁻¹; LRMS (ES) *m/z* 242.23 (M+Na). Anal. Calcd for C₁₄H₂₁NO: C, 76.67; H, 9.65; N, 6.39. Found: C, 76.62; H, 9.55; N, 6.31.

General Procedure for Oxidative Dearylation to Provide Primary Allylic Amines.

Preparation of 3-amino-1-hexene maleic acid salt (12a).

Ceric ammonium nitrate (CAN, 207 mg, 0.38 mmol) was dissolved in H₂O (2.7 mL) and cooled to 0 °C. A solution of amine **11a** (31 mg, 0.15 mmol) and acetonitrile (2.0 mL) was added dropwise over 6 minutes. The reaction was maintained at 0 °C for 3 h, Et₂O (2.0 mL) and H₂O (2.0 mL) were added, the phases were separated and the organic phase was washed with H₂O (2.0 mL). The aqueous phase was basified to pH 10 with Na₂CO₃ and extracted with EtOAc (4 x 5 mL). The combined EtOAc extracts were dried (Na₂SO₄), filtered into a flask containing maleic acid (21.0 mg, 0.18 mmol) and the resulting solution was concentrated *in vacuo*. Purification of the residue by column chromatography (SiO₂, 95:5 → 9:1 MeOH/CH₂Cl₂) provided 25 mg (74%) of **12a** as a pale brown semi-solid: ¹H NMR (500 MHz, CD₃OD) δ 6.24 (s, 2H), 5.81 (ddd, *J* = 17.3, 10.4, 7.9 Hz, 1H), 5.38–5.43 (m, 2H), 3.64–3.72 (m, 1H), 1.58–1.74 (m, 2H), 1.31–1.47 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (125 MHz, CD₃OD) δ 171.1, 136.8, 135.7, 121.0, 55.3, 36.4, 19.7, 14.0; IR (neat) 3397, 2964, 2582, 1617, 1571, 1467, 1359 cm⁻¹; HRMS (GCMS-EI) *m/z* 98.0971 [98.0970 calcd for C₆H₁₄N (M-H)].

3-Amino-5-phenyl-1-pentene maleic acid salt (12e). Prepared in 80% yield following

the general procedure: ¹H NMR (500 MHz, CD₃OD) δ 7.18–7.24 (m, 2H), 7.08–7.16 (m, 3H), 6.23 (s, 2H), 5.87 (ddd, *J* = 17.2, 10.5, 7.9 Hz, 1H), 5.31–5.39 (m, 2H),

3.54–3.62 (m, 1H), 2.51–2.68 (m, 2H), 1.91–2.01 (m, 1H), 1.79–1.90 (m, 1H); ^{13}C NMR (125 MHz, CD_3OD) δ 171.3, 142.0, 136.6, 136.1, 129.8, 129.5, 127.5, 121.1, 55.0, 36.4, 32.6; IR (neat) 3405, 2934, 1544, 1455, 1355 cm^{-1} ; HRMS (GCMS-EI) m/z 161.1203 [161.1204 calcd for $\text{C}_{11}\text{H}_{15}\text{N}$ (M)].

3-Amino-5-methyl-1-hexene maleic acid salt (12g). Prepared in 70% yield following

the general procedure: ^1H NMR (500 MHz, CD_3OD) δ 6.24 (s, 2H), 5.80 (ddd, $J = 17.3, 10.4, 8.0$ Hz, 1H), 5.42 (d, $J = 17.2$ Hz, 1H), 5.38 (d, $J = 10.4$ Hz, 1H), 3.68–3.77 (m, 1H), 1.61–1.72 (m, 1H), 1.46–1.60 (m, 2H), 0.95 (dd, $J = 10.2, 6.5$ Hz, 6H); ^{13}C NMR (125 MHz, CD_3OD) δ 170.9, 136.6, 135.5, 121.5, 54.0, 43.2, 25.7, 23.5, 21.9; IR (neat) 3393, 2961, 1698, 1617, 1571, 1467, 1355 cm^{-1} ; HRMS (GCMS-EI) m/z 112.1131 [112.1126 calcd for $\text{C}_7\text{H}_{14}\text{N}$ (M-H)].

Di- μ -chlorobis[(η^5 -(*S*)-(*pR*)-2-(2'-(4'-methylethyl)oxazolinyl)cyclopentadienyl, 1-*C*, 3'-*N*)(η^4 -tetraphenylcyclobutadiene)cobalt]dipalladium (6a). To a

solution of Di- μ -acetobis[(η^5 -(*S*)-(*pR*)-2-(2'-(4'-methylethyl)oxazolinyl)cyclopentadienyl, 1-*C*, 3'-*N*)(η^4 -tetraphenylcyclobutadiene)cobalt]dipalladium (4.5 g, 3.0 mmol) in acetone (2.0 L) was added 2N aqueous sodium chloride (1.1 L). The reaction was maintained for 36 hours. The product was collected by filtration and dried under vacuum to provide **COP-Cl** (4.1 g, 94%) as a mustard colored solid: ^1H NMR (500 MHz, CDCl_3 , 1.0:0.7 mixture of dimers) δ 7.66–7.71 (m, 8H), 7.58–7.62 (m, 8H), 7.23–7.30 (m, 12H), 7.16–7.22 (m, 12H), 4.99 (d, $J = 1.5$ Hz, 1H), 4.98 (d, $J = 1.5$ Hz, 1H), 4.73 (d, $J = 2.0$ Hz, 1H), 4.70 (d, $J = 2.0$ Hz, 1H), 4.40 (t, $J = 2.5$ Hz, 1H), 4.28 (t, $J = 2.5$ Hz, 1H), 4.16–4.22 (m, 2H), 3.43 (t, $J = 8.9$ Hz, 1H), 3.34 (t, $J = 9.0$ Hz, 1H), 3.03–3.15 (m, 2H), 2.20–2.33 (m, 2H), 0.80 (d, $J = 7.0$ Hz, 3H), 0.76 (d, $J = 6.8$ Hz, 3H), 0.70–0.74 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.1, 171.2, 135.6, 135.5, 129.5, 129.4, 128.3, 128.2, 126.5, 126.4, 98.7, 98.6, 87.1, 85.7, 84.9, 84.8, 84.5, 84.2, 81.0, 80.5, 76.8, 76.5, 71.5, 71.4, 66.0, 65.6, 29.2, 29.0, 19.02, 19.00, 14.5, 14.3; IR (thin film) 3061, 2961, 1602, 1502, 1370, 1185 cm^{-1} .

Di- μ -chlorobis[(η^5 -(*S*)-(*R*)-2-(2'-(1'-{1-tert-butylethyl}imidazol)cyclopentadienyl, 1-*C*, 3'-*N*)(η^4 -tetraphenylcyclobutadiene)cobalt]-dipalladium (7a**).**

To a solution of di- μ -acetobis[(η^5 -(*S*)-(*R*)-2-(2'-(1'-{1-tert-butylethyl}imidazol)cyclopentadienyl, 1-*C*, 3'-*N*)(η^4 -tetraphenylcyclobutadiene)cobalt]dipalladium (1.03 g, 0.65 mmol) in 95:5 CH_2Cl_2 /acetone (500 mL) was added $NiPr_4Br$ (0.010 g, 0.04 mmol) and saturated aq. NaCl (500 mL). The reaction was maintained for 24 h. The two layers were separated, the organic layer evaporated and the resulting yellow solid recrystallised (CH_2Cl_2 /hexane) to give **7a** (0.70 g, 70 %) as a

yellow crystalline solid: 1H NMR (250 MHz, $CDCl_3$, 1.0:0.6 mixture of dimers) δ 7.55 – 7.40 (m, 16 H), 7.30 – 7.10 (m, 24 H), 6.81 (d, $J = 2$ Hz, 1 H), 6.77 (d, $J = 2$ Hz, 1 H), 6.54 (d, $J = 2$ Hz, 1 H), 6.51 (d, $J = 2$ Hz, 1 H), 4.83 (d, $J = 3$ Hz, 1 H), 4.79 (d, $J = 3$ Hz, 1 H), 4.65 (d, $J = 3$ Hz, 1 H), 4.60 (d, $J = 3$ Hz, 1 H), 4.46 (t, $J = 3$ Hz, 1 H), 4.36 (d, $J = 3$ Hz, 1 H), 3.75 (q, $J = 7$ Hz, 1 H), 3.70 (q, $J = 7$ Hz, 1 H), 0.84 (s, 9 H), 0.77 (s, 9 H), 0.73 (d, $J = 7$ Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 135.1, 127.9, 127.0, 125.6, 125.0, 124.7, 113.3, 100.7, 100.1, 89.7, 84.6, 84.0, 81.4, 76.0, 74.9, 60.7, 34.6, 25.5, 13.9.

¹H spectrum

¹H spectrum

HMP 1.191
13C spectrum with 1H decoupling

¹H spectrum ¹³C spectrum with ¹H decoupling

¹H spectrum ¹³C spectrum with ¹H decoupling

¹H spectrum ¹³C spectrum with ¹H decoupling

¹³C spectrum with ¹H decoupling

Data File D:\DATA\CEO\03140201.D

Sample Name: ceo-IV-67

```
=====
Injection Date   : 3/14/02 2:34:10 PM      Seq. Line :    1
Sample Name      : ceo-IV-67              Location  : Vial 61
Acq. Operator    : ceo                    Inj       :    1
                                           Inj Volume: 5 µl

Acq. Method      : D:\METHODS\CEOODH.M
Last changed     : 3/12/02 8:32:45 AM by ceo
Analysis Method  : D:\METHODS\CEOODH3.M
Last changed     : 4/5/02 10:40:48 AM by ceo
ODH
99.8:0.2 nHex/IPA
0.8 mL/MIN
no guard
=====
```

Area Percent Report

```
=====
Sorted By       : Signal
Multiplier      : 1.0000
Dilution        : 1.0000
=====
```

Signal 1: DAD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.031	BV	0.6136	7673.76807	189.83095	49.7997
2	22.656	VBA	0.6609	7735.49609	175.28296	50.2003

Totals : 1.54093e4 365.11391

Results obtained with enhanced integrator!

*** End of Report ***

Data File C:\HPCHEM\1\DATA\MMP\03210303.D

Sample Name: mmp-i-216b

```
=====
Injection Date   : 3/21/03 5:01:45 PM      Seq. Line :    3
Sample Name      : mmp-i-216b              Location  : Vial 63
Acq. Operator    : mmp                     Inj       :    1
                                           Inj Volume: 5 µl

Acq. Method      : D:\METHODS\CEODH.M
Last changed     : 3/18/03 8:39:54 PM by ceo
Analysis Method  : D:\METHODS\CEODH4.M
Last changed     : 7/15/02 11:59:26 AM by ceo
ODH
98.2:1.8 nHEX:IPA
0.8 mL/MIN
no guard
=====
```

=====
Area Percent Report
=====

Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.713	BV	0.6974	3.56595e4	836.38580	95.9899
2	22.325	VB	0.5787	1489.71863	39.43964	4.0101

Totals : 3.71492e4 875.82545

Results obtained with enhanced integrator!

=====
*** End of Report ***

Data File D:\DATA\CEO\08190201.D

Sample Name: ceo-IV-293A

```
=====
Injection Date   : 8/19/02 10:44:11 AM      Seq. Line :    1
Sample Name      : ceo-IV-293A              Location  : Vial 41
Acq. Operator    : ceo                      Inj       :    1
                                           Inj Volume: 5 µl

Acq. Method      : D:\METHODS\CEODH.M
Last changed     : 5/30/02 12:12:59 PM by ceo
Analysis Method  : D:\METHODS\CEODH.M
Last changed     : 8/24/02 9:28:44 AM by ceo
ODH
99.8:0.2 nHEX:IPA
0.8 mL/MIN
no guard
=====
```

Signal 1: DAD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.015	BP	0.4599	86.66575	2.80949	2.4247
2	21.431	VB	0.5533	3487.63306	96.12479	97.5753

Totals : 3574.29881 98.93429

Results obtained with enhanced integrator!

*** End of Report ***

Data File D:\DATA\CEO\08240201.D

Sample Name: ceo-IV-105 rac

```
=====
Injection Date   : 8/24/02 10:15:14 AM      Seq. Line :    1
Sample Name      : ceo-IV-105 rac           Location  : Vial 46
Acq. Operator    : ceo                     Inj       :    1
                                           Inj Volume: 5 µl

Method           : D:\METHODS\CEODH.M
Last changed     : 8/24/02 9:28:44 AM by ceo
ODH
99.8:0.2 nHEX:IPA
0.8 mL/MIN
no guard
=====
```

=====
Area Percent Report
=====

```
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
```

Signal 1: DAD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.534	BB	0.6878	1520.28687	33.86224	50.0171
2	28.905	BB	0.7622	1519.24731	30.65727	49.9829

Totals : 3039.53418 64.51951

Results obtained with enhanced integrator!

=====
*** End of Report ***

Data File D:\DATA\MMP\01270305.D

Sample Name: mmp-i-179a

```
=====
Injection Date   : 1/27/03 2:38:51 PM      Seq. Line :    5
Sample Name      : mmp-i-179a              Location  : Vial 65
Acq. Operator    : mmp                     Inj       :    1
                                           Inj Volume: 5 µl

Acq. Method      : D:\METHODS\CEOODH.M
Last changed     : 1/27/03 10:04:00 AM by mmp
Analysis Method  : D:\METHODS\CEOODH4.M
Last changed     : 7/15/02 11:59:26 AM by ceo
ODH
98.2:1.8 nHEX:IPA
0.8 mL/MIN
no guard
=====
```

Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.728	BB	0.8139	3.66805e4	646.56927	91.0771
2	32.208	BB	0.8139	3593.64404	66.76664	8.9229

Totals : 4.02742e4 713.33591

Results obtained with enhanced integrator!

*** End of Report ***

Data File C:\HPCHEM\1\DATA\MMP\04210305.D

Sample Name: MMP.I.192a

```
=====
Injection Date   : 4/21/03 9:08:09 PM      Seq. Line :    1
Sample Name      : MMP.I.192a              Location  : Vial 65
Acq. Operator    : mmp                     Inj       :    1
                                           Inj Volume: 5 µl

Acq. Method      : D:\METHODS\CEODH.M
Last changed     : 4/21/03 8:26:58 PM by mmp
Analysis Method  : D:\METHODS\CEODH4.M
Last changed     : 7/15/02 11:59:26 AM by ceo
ODH
98.2:1.8 nHEX:IPA
0.8 mL/MIN
no guard
=====
```

Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.973	BB	0.6387	616.22980	13.96717	6.7231
2	30.413	BB	0.7870	8549.68945	158.57234	93.2769

Totals : 9165.91925 172.53951

Results obtained with enhanced integrator!

*** End of Report ***

Data File D:\DATA\CEO\08230218.D

Sample Name: ceo-IV-113 rac

```
=====
Injection Date   : 8/23/02 7:45:15 PM      Seq. Line : 18
Sample Name      : ceo-IV-113 rac          Location  : Vial 49
Acq. Operator    : ceo                    Inj       : 1
                                           Inj Volume: 5 µl

Acq. Method      : D:\METHODS\CEODH4.M
Last changed     : 8/23/02 8:16:22 PM by ceo
                  (modified after loading)
Analysis Method  : D:\METHODS\CEODH4.M
Last changed     : 7/15/02 11:59:26 AM by ceo
ODH
98.2:1.8 nHEX:IPA
0.8 mL/MIN
no guard
=====
```

=====
Area Percent Report
=====

```
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
```

Signal 1: DAD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.741	BV	0.6416	5113.91016	122.86996	49.6482
2	23.324	VB	0.6784	5186.37988	116.71748	50.3518

Totals : 1.03003e4 239.58744

Results obtained with enhanced integrator!

=====
*** End of Report ***

Data File D:\DATA\CEO\08260207.D

Sample Name: ceo-V-24A

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=====
Injection Date   : 8/26/02 10:07:45 PM      Seq. Line :    7
Sample Name     : ceo-V-24A                Location  : Vial 47
Acq. Operator   : ceo                      Inj       :    1
                                           Inj Volume: 5 µl

Acq. Method     : D:\METHODS\CEOODH4.M
Last changed    : 7/15/02 11:59:26 AM by ceo
Analysis Method : D:\METHODS\CEOODH4.M
Last changed    : 8/28/02 7:53:01 PM by ceo
                  (modified after loading)

```

ODH
 98.2:1.8 nHEX:IPA
 0.8 mL/MIN
 no guard

Signal 1: DAD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.669	BB	0.6389	5570.85840	131.85728	93.8291
2	23.389	BP	0.5774	366.38019	8.16719	6.1709

Totals : 5937.23859 140.02448

Results obtained with enhanced integrator!

*** End of Report ***

Data File D:\DATA\CEO\08230219.D

Sample Name: ceo-V-21A

```
=====
Injection Date   : 8/23/02 8:17:19 PM      Seq. Line :   19
Sample Name      : ceo-V-21A              Location  : Vial 50
Acq. Operator    : ceo                    Inj       :    1
                                           Inj Volume: 5 µl

Acq. Method      : D:\METHODS\CEODH4.M
Last changed     : 8/23/02 8:16:30 PM by ceo
                  (modified after loading)
Analysis Method  : D:\METHODS\CEODH4.M
Last changed     : 7/15/02 11:59:26 AM by ceo
ODH
98.2:1.8 nHEX:IPA
0.8 mL/MIN
no guard
=====
```

Signal 1: DAD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.068	MM	0.7248	58.64140	1.34848	1.5981
2	23.382	BB	0.6691	3610.80396	82.74234	98.4019

Totals : 3669.44535 84.09082

Results obtained with enhanced integrator!

*** End of Report ***

Data File D:\DATA\CEO\03170206.D

Sample Name: ceo-IV-68

```
=====
Injection Date   : 3/17/02 6:59:34 PM      Seq. Line :    5
Sample Name      : ceo-IV-68              Location  : Vial 64
Acq. Operator    : ceo                    Inj       :    1
                                           Inj Volume: 5 µl

Acq. Method      : D:\METHODS\CEOODH2.M
Last changed     : 3/17/02 5:28:08 PM by ceo
Analysis Method  : D:\METHODS\CEOODH3.M
Last changed     : 4/5/02 10:40:48 AM by ceo
ODH
99.5:0.5 nHex/IPA
0.8 mL/MIN
no guard
=====
```

=====
Area Percent Report
=====

```
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
```

Signal 1: DAD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.647	BB	0.2345	938.30737	61.32387	50.0594
2	10.423	BB	0.2549	936.08124	56.60690	49.9406

Totals : 1874.38861 117.93077

Results obtained with enhanced integrator!

=====
*** End of Report ***

Data File D:\DATA\MMP\03030302.D

Sample Name: mmp-i-202b

```
=====
Injection Date   : 3/3/03 2:37:29 PM      Seq. Line :    2
Sample Name      : mmp-i-202b             Location  : Vial 62
Acq. Operator    : mmp                    Inj       :    1
                                           Inj Volume: 5 µl

Acq. Method      : D:\METHODS\CEODH2.M
Last changed     : 1/17/03 1:55:19 PM by ceo
Analysis Method  : D:\METHODS\CEODH4.M
Last changed     : 7/15/02 11:59:26 AM by ceo
ODH
98.2:1.8 nHEX:IPA
0.8 mL/MIN
no guard
=====
```

=====
Area Percent Report
=====

Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.842	BB	0.2395	9076.90820	590.11646	97.1817
2	10.763	BB	0.2522	263.22934	15.97787	2.8183

Totals : 9340.13754 606.09433

Results obtained with enhanced integrator!

=====
*** End of Report ***

Data File D:\DATA\CEO\08230214.D

Sample Name: ceo-V-16A

```

=====
Injection Date   : 8/23/02 4:32:23 PM           Seq. Line :   14
Sample Name     : ceo-V-16A                   Location  : Vial 44
Acq. Operator   : ceo                         Inj       :    1
                                           Inj Volume: 5 µl

Acq. Method     : D:\METHODS\CEODH2.M
Last changed    : 8/23/02 4:31:33 PM by ceo
                  (modified after loading)
Analysis Method : D:\METHODS\CEODH2.M
Last changed    : 7/27/02 1:33:40 PM by ceo
ODH
99.5:0.5 nHEX:IPA
0.8 mL/MIN ,
no guard

```

Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.218	BP	0.2179	65.35452	4.65307	1.5551
2	10.064	BB	0.2455	4137.19336	263.06421	98.4449

Totals : 4202.54788 267.71728

Results obtained with enhanced integrator!

*** End of Report ***