Samarium Barbier Reactions of α -Iodomethyloxazoles and Thiazoles with Aliphatic Aldehydes

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Supporting Information

Experimental procedures and complete characterization data for the compounds of Schemes 1 and 2. General procedures for preparation of SmI₂ and for the Barbier reactions of Table 1. Spectral data for the products of

Table 1 include the ketone of **12**, **15**, **17**, **20**, **22**, **24**, **25**, **27**, **28**, **30**, **31**, **33**, **34**, and **36**.

General.

All compounds were purified by flash chromatography. Compounds that were utilized as mixtures of diastereomers or obtained with minor impurities will be clearly noted in the text.

2-Dichloromethyl-4,5-dihydrooxazole-4-carboxylic acid methyl ester.

Ethyl dichloroacidimidate hydrochloride (5.74 g, 29.8 mmol) and serine methyl ester hydrochloride (4.70 g, 30 mmol) were suspended in CH_2Cl_2 (60 mL) at ambient temperature. Triethylamine (4.15 mL, 30 mmol) was introduced in one portion, and the resulting slurry stirred 16 h during which time the reaction turned pale yellow. The reaction mixture was diluted to 259 mL with Et_2O and filtered through celite. The solids were washed with an additional 100 mL Et_2O . The filtrate was concentrated under reduced pressure to a pale yellow oil that was purified by chromatography with silica gel eluting with 2:1 hexanes:EtOAc to 1:1 hexanes:EtOAc to provide 2-dichloromethyl-4,5-dihydrooxazole-4-carboxylic acid methyl ester (4.55 g, 21.6 mmol, 72%) as a white solid: $R_f = 0.7$ (1:1 hexanes:EtOAc); mp 44–46 °C; ^1H NMR (400 MHz, CDCl_3) δ 6.27 (s, 1H), 4.88 (dd, $J = 8.2, 11.0$ Hz, 1H), 4.73 (dd, $J = 8.2, 8.7$ Hz, 1H), 4.65 (dd, $J = 11.0, 8.7$ Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.1, 164.4, 71.2, 68.0, 60.7, 52.9; IR (neat) 1745, 1665 cm^{-1} ; MS calcd for $\text{C}_6\text{H}_8\text{NO}_3\text{Cl}_2$, 211.9881, found 211.9884. Our spectroscopic data was identical with literature information for this material recently prepared from dichloroacetonitrile as reported by S. A. Hermitage, K. S. Cardwell, T. Chapman, J. W. B. Cooke and R. Newton, *Organic Process Research and Development* **2001**, 5, 37–44.

2-Iodomethyloxazole-4-carboxylic acid methyl ester (**4**).

2-Chloromethyloxazole-4-carboxylic acid methyl ester (**5**) (3.6 g, 20.7 mmol) and NaI (15 g) were dissolved in THF (100 mL) at ambient temperature. After 15 min, the solution was diluted with EtOAc and washed with water (2 X), saturated aqueous NaHSO₃ solution, brine, dried with MgSO₄ and concentrated to provide an oil which crystallized upon addition of ether and hexanes yielding the 2-iodomethyloxazole **4** (4.6 g, 17.2 mmol, 83% yield) as a cream-colored solid: mp 67 °C; lit. mp 66 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.19 (s, 1H), 4.36 (s, 2H), 3.87 (s, 3H); lit. ¹H NMR 3.92 (s, 3H), 4.4 (s, 2H), 8.23 (s, 1H). Our procedure is a modification of the previous report of P. Breuilles, and D. Uguen, *Tetrahedron Lett.* **1998**, 39, 3149–3152.

2-Chloromethyloxazole-4-carboxylic acid methyl ester (**5**).

The 2-dichloromethyloxazoline (4.5 g, 21.6 mmol) was dissolved in CH₂Cl₂ (100 mL) and the resulting colorless solution cooled to 0 °C in an ice bath. DBU (3.5 mL, 25.1 mmol) was then introduced in one portion, resulting in heat evolution and a slight yellowing of the solution. After one minute, the reaction was diluted to 250 mL with Et₂O and washed with saturated NH₄Cl solution, water, brine, dried with MgSO₄ and concentrated to provide **5** (3.63 g, 96% yield) as an off-white solid: R_f = 0.7 (1:1 hexanes:EtOAc); ¹H NMR (400 MHz, CDCl₃) δ 8.19 (s, 1H), 4.62 (s, 2H), 3.92 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) 161.1, 159.9, 145.2, 134.0, 52.4, 35.4; IR (CHCl₃) 1715, 1580 cm⁻¹; MS calcd for C₆H₇NO₃Cl 176.0114, found 176.0119. Our spectroscopic data for compound **5** is the same as described by S. A. Hermitage, K. S. Cardwell, T. Chapman, J. W. B. Cooke and R. Newton, *Organic Process Research and Development* **2001**, 5, 37–44.

Preparation of Aldehyde 6 of Scheme 1:

(3*R*,5*R*,6*E*)-3,5-Dihydroxy-7-phenyl-6-heptenoic acid butyl ester.

Tetramethylammonium triacetoxyborohydride (14.4 g, 55 mmol, 5 equiv) was dissolved in 35 mL anhydrous AcOH and stirred 30 min at ambient temperature. The starting (5*R*,6*E*)-5-hydroxy-3-oxo-7-phenyl-6-heptenoic acid butyl ester (3.18 g, 10.95 mmol) was dissolved in 35 mL anhydrous acetonitrile and cooled to $-40\text{ }^{\circ}\text{C}$. The borohydride solution was then transferred via cannula into the cold solution of the hydroxyketone, and the resulting slurry was maintained at $-20\text{ }^{\circ}\text{C}$ for 36 h. At this time, a distillation head was fitted to the reaction flask and the acetonitrile, and a majority of the acetic acid, were removed under reduced pressure (0.5 mmHg) at a bath temperature of $\leq 25\text{ }^{\circ}\text{C}$. The resulting liquid was dissolved in diethyl ether and the residual acetic acid was neutralized by careful portionwise addition of an aqueous NaHCO_3 slurry. The layers were separated and the aqueous layer was extracted with Et_2O . The combined organic layers were washed with saturated NaHCO_3 solution and brine, dried with MgSO_4 and concentrated to a thick oil that was purified by flash chromatography with silica gel (gradient of 2:1 hexanes:EtOAc to EtOAc). A total of 2.94 g (10.1 mmol, 92% yield) of diol was isolated as a colorless oil as a 92:8 ratio of *syn:anti* diastereomers: $R_f = 0.2$ (2:1 hexanes:EtOAc); $[\alpha]_D^{24} 6.0$ (c 0.055, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.36 (m, 2H), 7.30 (m, 2H), 7.22 (m, 1H), 6.64 (dd, $J = 1.2, 15.9$ Hz, 1H), 6.26 (dd, $J = 5.9, 15.9$ Hz, 1H), 4.62 (dddd, $J = 1.5, 3.3, 5.8, 7.5$ Hz, 1H), 4.38 (dddd, $J = 3.1, 4.2, 7.0, 9.1$ Hz, 1H), 4.10 (t, $J = 6.6$ Hz, 2), 2.53 (A of ABX, $J_{AB} = 16.4$ Hz, $J_{AX} = 9.25$ Hz, 1H), 2.49 (B of ABX, $J_{AB} = 16.4$ Hz, $J_{BX} = 3.2$ Hz, 1H), 1.83 (ddd, A of ABXY, $J_{AB} = 14.4$ Hz, $J_{AX} = 3.4$ Hz, $J_{AY} = 9.2$ Hz, 1H), 1.73 (ddd, B of ABXY, $J_{AB} = 14.4$ Hz, $J_{BX} = 3.0$ Hz, $J_{BY} = 7.7$ Hz, 1H), 1.60 (m, 2H), 1.35 (m, 2H), 0.91 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.8, 136.6, 131.8, 129.8, 128.5, 127.5, 126.4, 69.7, 65.5, 64.6, 42.1, 41.3, 3.5, 19.0, 13.6; IR (neat) 3425 (br), 2959, 2933, 2873, 1729, 1449, 1420, 1406, 1163, 1069, 1065, 967, 749, 694 cm^{-1} ; MS (CI/ CH_4) m/z 274, 256, 218, 200, 172, 158, 131, 115, 91; HRMS (CI/ CH_4) calcd for $\text{C}_{17}\text{H}_{24}$, 292.1675; found, 292.1679.

(3*R*,5*R*,6*E*)-3,5-Bis(*tert*-butyldimethylsilyloxy)-7-phenyl-6-heptenoic acid butyl ester.

Starting diol (2.85 g, 9.75 mmol), *tert*-butylchlorodimethylsilane (3.67 g, 24.3 mmol) and imidazole (2.6 g, 39 mmol) were combined in CH₂Cl₂ (30 mL) at ambient temperature. After 16 h, the reaction mixture was diluted with Et₂O and washed with water (3 X), brine, dried with MgSO₄ and concentrated. The resulting clear oil was purified by chromatography with silica gel (30:1 hexanes:EtOAc) to provide 4.3 g (8.3 mmol, 85% yield) of the corresponding bis(silyl) ether as a colorless oil: $R_f = 0.6$ (10:1 hexanes:EtOAc); $[\alpha]_D^{24} 16$ (c 0.015, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.4–7.25 (m, 5H), 6.45 (d, $J = 15.9$ Hz, 1H), 6.12 (dd, $J = 15.9, 7.3$ Hz, 1H), 4.36 (ddt, $J = 1.0, 5.2, 7.3$ Hz, 1H), 4.27 (dq, $J = 7.0, 5.9$ Hz, 1H), 4.04 (dt, A of ABX², $J_{AB} = 10.4$ Hz, $J_{AX} = 6.9$ Hz, 1H), 4.02 (dt, B of ABX², $J_{BA} = 10.4$ Hz, $J_{BC} = 7.0$ Hz, 1H), 2.53 (dd, A of ABX, $J_{AB} = 14.5$ Hz, $J_{AX} = 5.2$ Hz, 1H), 2.46 (dd, B of ABX, $J_{BA} = 14.5$ Hz, $J_{BX} = 7.2$ Hz, 1H), 1.82 (ddd, A of ABXY, $J_{AB} = 13.9$ Hz, $J_{AX} = 6.2$ Hz, $J_{AY} = 7.5$ Hz, 1H), 1.74 (dt, B of ABXY, $J_{BA} = 13.9$ Hz, $J_{BC} = J_{BD} = 5.5$ Hz, 1H), 1.57 (m, 2H), 1.35 (m, 2H), 0.90 (t, $J = 7.0$ Hz 3H), 0.89 (s, 9H), 0.85 (s, 9H), 0.073 (s, 3H), 0.070 (s, 3H), 0.029 (s, 3H), 0.023 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.47, 136.86, 133.13, 129.58, 128.55, 127.48, 126.39, 71.31, 67.10, 64.23, 46.74, 43.66, 30.62, 25.93, 25.89, 25.79, 19.15, 18.16, 17.97, 13.70, –3.68, –4.31, –4.49, –4.57; IR (cm^{–1}) 2957, 2930, 2895, 2887, 2856, 1737, 1253, 1163, 1093, 1076, 966; MS (CI/CH₄) m/z 75, 101, 157, 201, 231, 272, 321, 388, 463, 505; HRMS (CI/CH₄) for C₂₈H₄₉O₄Si₂ (M–CH₃)⁺, calculated: 505.3169; found: 505. 3183.

(3*R*,5*R*,6*E*)-3,5-Bis(*tert*-butyldimethylsilyloxy)-7-phenyl-6-heptenal.

Butyl ester (15.0 g, 28.8 mmol) was dissolved in CH₂Cl₂ (200 mL) and cooled to –78 °C in a dry ice-acetone bath. A solution of diisobutylaluminum hydride (1.0 M in hexanes, 32 mL, 32 mmol) was introduced in a slow stream and the reaction maintained at –78 °C until the reduction was complete (15 min). Acetone (2 mL) was then introduced to quench any unreacted DIBAL and the solution warmed to ambient temperature. Addition of a half-saturated solution of Rochelle's salt to the reaction resulted in an emulsion that was stirred vigorously until the phases separated upon cessation of stirring (2 hrs). The organic layer was removed, washed

with brine, dried with MgSO_4 and concentrated to an oil that was purified by chromatography with silica gel (15:1 hexanes:EtOAc). Aldehyde product **6** was isolated as a clear, colorless oil (11.94 g, 92% yield): $R_f = 0.55$ (10:1 hexanes:EtOAc); $[\alpha]_D^{25} +21$ (c 0.031, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ 9.78 (dd, $J = 2.2, 3.0$ Hz, 1H), 7.4–7.2 (m, 5H), 6.44 (d, $J = 15.9$ Hz, 1H), 6.11 (dd, $J = 15.9, 7.5$ Hz, 1H), 4.34 (m, 2H), 2.61 (ddd, A of ABXY, $J_{AB} = 15.7$ Hz, $J_{AX} = 2.0$ Hz, $J_{AY} = 4.8$ Hz, 1H), 2.54 (ddd, B of ABXY, $J_{BA} = 15.7$ Hz, $J_{BX} = 3.0$ Hz, $J_{BY} = 6.5$ Hz, 1H), 1.85 (dt, A of ABXY, $J_{AB} = 13.6$ Hz, $J_{AX} = J_{AY} = 6.6$ Hz, 1H), 1.82 (dt, B of ABXY, $J_{BA} = 13.6$ Hz, $J_{BC} = J_{BD} = 5.7$ Hz, 1H), 0.88 (s, 9H), 0.86 (s, 9H), 0.87 (s, 3H), 0.065 (s, 3H), 0.048 (s, 3H), 0.024 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 202.0, 136.6, 132.7, 129.9, 128.6, 127.6, 126.4, 71.3, 65.8, 51.6, 46.8, 25.9, 25.9, 25.8, 18.2, 18.0, -3.7 , -4.2 , -4.4 ; IR (neat) 2955, 2930, 2887, 2856, 1726, 1471, 1462, 1255, 1122, 1072, 1030, 1004, 968, 837, 808, 775, 748, 692 cm^{-1} ; MS (CI/ CH_4) m/z 75, 91, 129, 157, 247, 321, 347, 391, 430; HRMS (CI/ CH_4) calcd for $\text{C}_{25}\text{H}_{42}\text{O}_2\text{Si}_2$ ($\text{M}-\text{H}_2\text{O}$) $^+$ 430.2723, found 430.2725.

2-[(2*RS*,4*R*,6*R*,7*E*)-4,6-Bis(*tert*-butyldimethylsilyloxy)-2-hydroxy-8-phenyl-7-octenyl]-oxazole-4-carboxylic acid methyl ester (7**).**

A solution of SmI_2 in THF was prepared by slow addition of CH_2I_2 (807 μL , 10 mmol) to a suspension of Sm powder (1.51 g, 10.1 mmol) in anhydrous, degassed THF (40 mL) maintained at ambient temperature with a water bath. This mixture was stirred 2–3 h until a majority of the Sm metal had been consumed. In another flask, aldehyde **6** (1.79 g, 4.0 mmol) and oxazole iodide **4** (1.07 g, 4.0 mmol) were dissolved in anhydrous, degassed THF (5 mL) and this mixture was introduced via cannula to the stirring solution of SmI_2 over 2 min. Once the addition was complete, the reaction mixture was diluted with Et_2O (40 mL) and a saturated aqueous solution of Na•K tartrate (100 mL) and the resulting emulsion stirred vigorously until the organic phase separated on cessation of stirring. The layers were separated and the aqueous layer extracted twice with 1:1 hexanes:EtOAc. The combined organic layers were washed with brine, dried with MgSO_4 and concentrated in the absence of light to a pale yellow oil that was purified by chromatography with silica gel (eluting with 4:1 hexanes:EtOAc to 2:1 hexanes:EtOAc). The resulting light yellow oil (**7**, 1.53 g, 66% yield;

50:50 mixture of diastereomers at C33) rapidly darkens to an orange-red oil on exposure to light and was usually employed directly in the next reaction without delay; $R_f = 0.6$ (2:1 hexanes:EtOAc). The following data are reported for the diastereomeric mixture obtained in this reaction: $[\alpha]_D^{25} +2.0$ (c 0.018, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ 8.13 (s, 0.5H), 8.10 (s, 0.5H), 7.35–7.20 (m, 5H), 6.42 (d, $J = 16.9$ Hz, 0.5H), 6.40 (d, $J = 16.9$ Hz, 0.5H), 6.09 (dd, $J = 16.9, 7.3$ Hz, 0.5 H), 6.08 (dd, $J = 16.9, 7.3$ Hz, 0.5H), 4.45 (m, 0.5H), 4.25 (m, 1.5H), 4.13 (m, 0.5H), 3.98 (m, 0.5H), 3.88 (s, 3H), 3.0–2.85 (m, 4H), 0.86 (br s, 18H), 0.078 (s, 1.5H), 0.078 (s, 1.5H), 0.066 (s, 3H), 0.050 (s, 1.5H), 0.046 (s, 1.5H), 0.014 (s, 1.5H), 0.007 (s, 1.5H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.4, 163.3, 161.6, 161.6, 143.9, 136.6, 136.6, 133.2, 133.1, 132.6, 132.4, 130.1, 129.9, 128.6, 127.6, 126.4, 71.5, 69.8, 68.9, 68.0, 66.5, 52.1, 46.9, 44.9, 43.4, 41.5, 36.4, 36.1, 25.9, 25.8, 25.8, 18.2, 17.9, –3.8, –3.9, –4.0, –4.4, –4.5, –4.6, –4.6, –4.7; IR (neat) 3488 (br), 2953, 2930, 2857, 1740, 1586, 1472, 1462, 1439, 1360, 1325, 1256, 1138, 1111, 1069, 1032, 1005, 968, 835, 808, 775, 746, 692 cm^{-1} ; MS (CI/ CH_4) m/z 75, 129, 167, 247, 270, 308, 400, 457, 532; HRMS (CI/ CH_4) calcd for $\text{C}_{27}\text{H}_{42}\text{NO}_6\text{Si}_2$ ($\text{M}-\text{C}_4\text{H}_9$) $^+$ 532.2550, found 532.2537.

2-[(4*R*,6*R*,7*E*)-4,6-Bis(*tert*-butyldimethylsilyloxy)-2-oxo-8-phenyl-7-octenyl]-oxazole-4-carboxylic acid methyl ester (8**).**

Trifluoroacetic anhydride (310 μL , 2.20 mmol) was dissolved in CH_2Cl_2 (2 mL) and cooled to -78°C in a dry ice-acetone bath. A solution of dimethylsulfoxide (235 μL , 3.3 mmol) in CH_2Cl_2 (2 mL) was introduced dropwise, and the resulting slurry maintained at -78°C for 15 min. A solution of alcohol **7** (650 mg, 1.10 mmol) in CH_2Cl_2 (3 mL) was then added dropwise to the TFAA/DMSO adduct, and the resulting yellow slurry stirred another 30 min at -78°C . At this time, triethylamine (760 μL , 5.5 mmol) was added in one portion and the reaction gradually warmed to 0°C before being diluted with Et_2O and poured into a separatory funnel. The organic layer was washed with water, aqueous NH_4Cl solution (2 X), water, brine, dried with MgSO_4 and concentrated in the absence of light to a light yellow oil. Purification by flash chromatography with silica gel (eluting with a gradient of 3:1 hexanes:EtOAc to 2:1 hexanes:EtOAc) provided β -ketooxazole **8** as a thick

yellow oil (540 mg, 919 μmol , 84% yield) that was protected from light during routine handling: $R_f = 0.70$ (2:1 hexanes:EtOAc); $[\alpha]_D^{25} +8.1$ (c 0.062, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.16 (s, 1H), 7.40–7.20 (m, 5H), 6.44 (d, $J = 15.9$ Hz, 1H), 6.09 (dd, $J = 15.9$ Hz, 7.4 Hz, 1H), 4.33 (m, 2H), 3.99 (d, A of AB, $J = 17.4$ Hz, 1H), 3.91 (d, B of AB, $J = 17.4$ Hz, 1H), 3.89 (s, 3H), 2.71 (d, $J = 5.8$ Hz, 2H), 1.81 (dt, A of ABX^2 , $J_{\text{AB}} = 14.0$ Hz, $J_{\text{AX}} = 7.0$ Hz, 1H), 1.74 (dt, B of ABX^2 , $J_{\text{BA}} = 14.0$ Hz, $J_{\text{BX}} = 5.3$ Hz, 1H), 0.87 (s, 9H), 0.85 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H), 0.02 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.3, 161.4, 158.9, 144.7, 136.7, 133.5, 132.8, 129.8, 128.6, 128.6, 127.6, 126.4, 71.3, 66.6, 52.2, 50.6, 46.3, 43.8, 25.9, 25.9, 25.8, 18.2, 18.0, –3.8, –4.4, –4.5, –4.6; IR (neat) 2955, 2930, 2895, 2857, 1748, 1730, 1586, 1325, 1254, 1134, 1113, 1092, 1072, 1005, 837, 808, 775 cm^{-1} ; MS (CI/ CH_4) m/z 75, 101, 130, 216, 268, 324, 398, 455, 530, 569, 587; HRMS (CI/ CH_4) calcd for $\text{C}_{31}\text{H}_{47}\text{NO}_5\text{Si}_2$ ($\text{M}-\text{H}_2\text{O}$) $^+$ 569.2993, found 569.2979.

2-(2*S*,4*R*,6*R*(1*E*))-4-Hydroxy-2-methoxy-6-(2-phenylethenyl)tetrahydro-2*H*-pyranylmethyl)oxazole-4-carboxylic acid methyl ester (9).

Bis(silyl) ether **8** (540 mg, 919 μmol) was dissolved in MeOH (15 mL) containing a catalytic amount of camphorsulfonic acid (10 mg). After stirring 16 h at ambient temperature, the acid was neutralized by addition of solid NaHCO_3 followed by removal of the volatiles by rotary evaporation and partitioning of the light orange residue between EtOAc and water. The aqueous layer was extracted twice with EtOAc, and the combined organic layers washed with brine, dried with MgSO_4 and concentrated to a light yellow oil that was purified by flash chromatography with silica gel (eluting with a gradient of 1:1 hexanes:EtOAc to 1:2 hexanes:EtOAc). The resulting viscous oil was redissolved in CH_2Cl_2 and concentrated to a pale yellow foam that solidified under full vacuum (0.5 mmHG). A total of 296 mg (792 μmol , 86% yield of cyclic hemiacetal **9**) was isolated as a single diastereomer: $R_f = 0.25$ (1:2 hexanes:EtOAc); mp 45 $^\circ\text{C}$; $[\alpha]_D^{25} -16.5$ (c 0.094, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 8.19 (s, 1H), 7.38 (m, 2H), 7.31 (m, 2H), 7.23 (m, 1H), 6.60 (d, $J = 15.9$ Hz, 1H), 6.18 (dd, $J = 15.9$, 6.2 Hz, 1H), 4.22 (dddd, $J = 1.2$, 2.1, 6.2, 11.6 Hz, 1H), 4.11 (tt, $J = 4.7$, 11.1 Hz, 1H), 3.90 (s, 3H), 3.38 (d, A of AB, $J = 14.8$ Hz, 1H), 3.34 (s, 3H), 3.13 (d, B of AB, $J = 14.8$ Hz, 1H), 2.17 (ddd, $J = 1.8$, 4.7, 12.6 Hz,

1H), 2.07 (ddt, $J = 4.3, 12.3, 2.1$ Hz, 1H), 1.53 (dd, $J = 11.2, 12.8$ Hz, 1H), 1.50 (br s, -OH, 1H), 1.33 (dt, $J = 11.6, 11.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.5, 161.0, 144.3, 136.4, 133.3, 130.7, 128.7, 128.5, 127.7, 126.4, 99.8, 70.3, 64.2, 52.0, 48.0, 42.3, 40.1, 35.6; IR (neat) 3407 (br), 2951, 1740, 1584, 1449, 1439, 1329, 1221, 1200, 1148, 1113, 1030, 1005, 958, 766, 748, 694 cm^{-1} ; MS (CI/ CH_4) m/z 81, 100, 115, 141, 155, 183, 198, 254, 282, 324, 341; HRMS (CI/ CH_4) calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_5$ ($\text{M}-\text{CH}_4\text{O}$) $^+$ 341.1263, found 341.1262.

Ketone of **12**
(R = TBMPs: *tert*-butyl-4-methoxyphenylsilyl)

Preparation and Characterization of the Ketone Derived from Diastereomeric Alcohols **12:** A solution of SmI_2 in THF was prepared by addition of CH_2I_2 (0.09 mL, 1.08 mmol) to a suspension of Sm° powder (0.17 g, 1.08 mmol) in anhydrous, degassed THF (2 mL). This mixture was stirred in the dark for 2 h at room temperature. A pre-mixed solution of aldehyde **11** (0.24 mg, 0.27 mmol) and oxazole iodide **10** (0.10 g, 0.30 mmol) in degassed THF (1 mL) was introduced dropwise to the stirring solution of SmI_2 . After stirring for 15 min at room temperature, the reaction mixture was diluted with ether (50 mL) and brine (80 mL). The biphasic mixture was separated. The aqueous phase was extracted with ether (30 mL). The combined organic phases were dried (MgSO_4), filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (15 g SiO_2 , 8% EtOAc/hexanes) to afford 220 mg (76%) of the β -hydroxyoxazole **12** (95% purity) as a 1:1 mixture of diastereomers. The alcohols **12** were fully characterized upon oxidation to the corresponding ketone.

To a cold (-78°C) solution of trifluoroacetic anhydride (0.06 mL, 0.44 mmol) in CH_2Cl_2 (2 mL) was added dimethylsulfoxide (0.06 mL, 0.88 mmol). The resulting slurry was maintained at -78°C for 15 min. A solution of the β -hydroxyoxazole **12** (0.19 g, 0.17 mmol) in CH_2Cl_2 (0.5 mL) was then added dropwise to the TFAA/DMSO adduct, and the resulting yellow slurry stirred another 20 min at -78°C . At this time triethylamine (0.20 mL, 1.42 mmol) was added in one portion and the reaction was gradually warmed to -30°C . The solution was diluted with ether (80 mL) and then washed with aqueous saturated NaHCO_3 (2 X 50 mL). The combined aqueous phases were back extracted with ether (40 mL). The combined organic phases

were dried (MgSO₄), filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (10 g SiO₂, 8% EtOAc/hexanes) to afford 134 mg (71%) of the β -ketooxazole of **12**: R_f = 0.43 in 20% EtOAc/hexanes; ¹H NMR (400 MHz, CDCl₃) δ 7.72–7.58 (m, 6H), 7.52 (s, 1H), 7.43–7.22 (m, 9H), 5.86 (dd, J = 7.2, 6.8 Hz, 1H), 5.00 (s, 1H), 4.99 (s, 1H), 4.34–4.31 (m, 2H), 4.03–3.80 (m, 4H), 3.55 (s, 1.5H), 3.54 (s, 1.5H), 3.51 (dd, J = 12.0, 5.2 Hz, 1H), 2.74–2.66 (m, 2H), 2.17–2.04 (m, 1H), 1.67–1.50 (m, 3H), 1.20 (s, 9H), 1.06 (d, J = 10.4 Hz, 3H), 1.03 (s, 9H), 0.95 (s, 9H), 0.87 (s, 4.5H), 0.86 (s, 4.5H), 0.75 (s, 4.5H), 0.73 (s, 4.5H), 0.13 (s, 1.5H), 0.11 (s, 1.5H), 0.05 (s, 1.5H), 0.04 (s, 1.5H), –0.04 (s, 3H), –0.24 (s, 3H); IR (neat) 3080, 1730, 1650, 1575 cm^{–1}; HRMS (CI/CH₄) calcd for C₅₅H₈₄NO₉Si₄ (M–C₄H₉)⁺.

General Procedure for Preparation of Heterocyclic Iodides from their Corresponding Alcohols.

To a cold (0 °C) solution of triphenylphosphine (0.58 g, 0.221 mmol) and imidazole (30.0 mg, 0.440 mmol) in CH₂Cl₂ (1.0 mL) was added iodine (56.0 mg, 0.220 mmol). The mixture was stirred at 0 °C for 30 min. The alcohol (0.067 mmol) was added as a solution in CH₂Cl₂ (0.4 mL) into the reaction mixture. After 15 min, the mixture was diluted with CH₂Cl₂ (~30 mL) and washed with H₂O (2 X 25 mL). The combined aqueous phases were extracted with CH₂Cl₂ (15 mL), and the combined organic phases were dried (MgSO₄), filtered and concentrated *in vacuo*. The crude residue was purified by flash chromatography using silica gel to afford the desired iodide (75–95% yield).

General Procedure for Preparation of Samarium Diiodide.

To improve the purity of commercial 1,2-diiodoethane, the crude reagent was dissolved in ether and washed with saturated aqueous Na₂SO₃. The ether solution was dried over anhydrous MgSO₄, filtered and concentrated. The resulting white solid was protected from light and dried for at least one hour under high vacuum prior to use. A 250 mL flame-dried Schlenk flask was charged with Sm metal (1.26g; 8.38 mmol). The flask was evacuated and purged with argon three times, and protected from light. The 1,2-diiodoethane (1.18 g; 4.19 mmol) in dry, deoxygenated THF (42 mL) was added rapidly via cannula with vigorous stirring. The suspension was stirred in the dark at 22 °C for at least 5 h to produce a dark blue solution of samarium diiodide (0.1 M in THF). This solution was freshly prepared for the reduction/metalation of 0.863 mmol of the starting α -iodomethyl heterocycles of Table 1.

General Procedure for Samarium Diiodide-Barbier Reactions of Iodomethyl Heterocycles with Aldehydes of Table 1.

A general procedure was utilized for the samarium Barbier reactions of Table 1. A mixture of starting aldehyde (0.86 mmol) and freshly purified heterocyclic iodide (0.86 mmol) was dissolved in anhydrous, deoxygenated THF (8.6 mL). This solution was added via cannulation into a flask containing a dark blue solution of freshly prepared SmI_2 (0.1 M in THF), which was estimated to contain 3.0 mmol of reagent, and stirring was then continued for 5 min. If the reaction mixture failed to maintain a dark blue color, and starting reactants persisted as indicated by TLC, then an additional amount of SmI_2 solution was introduced. Reactions were quenched by the introduction of saturated aqueous potassium sodium tartrate and subsequent stirring for 30 min. After dilution with Et_2O (20 mL), the layers were separated, and the aqueous phase was extracted with Et_2O (3 X 10 mL). Combined organic phases were washed with brine, dried (MgSO_4), filtered, and concentrated *in vacuo*. The resulting oil was purified by flash chromatography on silica gel with appropriate mixtures of EtOAc in hexanes. Individual products are fully characterized as follows:

Methyl 2-(2-hydroxy-4-phenylbutyl)oxazole-4-carboxylate (15). ^1H NMR (400 MHz, CDCl_3) δ 8.15 (s, 1H), 7.30–7.16 (m, 5H), 4.20–4.13 (m, 1H), 3.89 (s, 3H), 3.01–2.69 (m, 5H), 1.95–1.79 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.8, 161.7, 144.0, 141.6, 133.2, 128.6, 126.1, 68.3, 52.4, 38.4, 36.0, 31.9; IR (neat) 3401, 2950, 2924, 2853, 1741, 1588, 1435, 1323, 1200, 1111 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_4$ (M^+) 275.1152, found 275.1157.

Methyl 2-(4-(benzyloxy)-2-hydroxybutyl)oxazole-4-carboxylate (17). ^1H NMR (300 MHz, CDCl_3) δ 8.15 (s, 1H), 7.36–7.26 (m, 5H), 4.50 (s, 2H), 4.39–4.31 (m, 1H), 3.89 (s, 3H), 3.76–3.62 (m, 2H), 3.52 (s, 1H), 2.98 (d, J = 6.6 Hz, 2H), 1.88–1.82 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.7, 161.7, 144.0, 137.9, 133.3, 128.6,

127.9, 127.8, 73.5, 68.7, 68.4, 52.2, 36.0, 36.0; IR (neat) 3426, 2947, 2925, 2851, 1738, 1589, 1456, 1437, 1326, 1114 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_5$ (M^+) 305.1258, found 305.1262.

1-(4-((tert-Butyldiphenylsilyloxy)methyl)oxazol-2-yl)-3-methylbutan-2-ol (20). ^1H NMR (400 MHz, CDCl_3) δ 7.70 (m, 4H), 7.40 (m, 7H), 4.66 (m, 2H), 3.82 (m, 1H), 3.31 (br s, 1H), 2.90 (A of ABX, $J_{\text{AB}} = 16.0$ Hz, $J_{\text{AX}} = 2.7$ Hz, 1H), 2.79 (B of ABX, $J_{\text{AB}} = 16.0$ Hz, $J_{\text{BX}} = 9.5$ Hz, 1H), 1.76 (dsept, $J = 6.7, 6.7$ Hz, 1H), 1.09 (s, 9H), 1.01 (d, $J = 6.8$ Hz, 3H), 0.97 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.5, 140.6, 135.5, 134.8, 133.2, 129.8, 127.7, 73.6, 59.2, 33.1, 32.4, 26.8, 19.2, 18.4, 17.9; IR (neat) 3420, 3071, 3048, 2959, 2931, 2893, 2858, 1560, 1472, 1428, 1113 cm^{-1} ; HRMS (CI/ CH_4) calcd for $\text{C}_{25}\text{H}_{34}\text{NO}_3\text{Si}$ ($\text{M}+\text{H}$) $^+$ 424.2302, found 424.2293.

1-(Benzyloxy)-3-(4-((tert-butyldiphenylsilyloxy)methyl)oxazol-2-yl)propan-2-ol (22). ^1H NMR (400 MHz, CDCl_3) δ 7.70 (m, 4H), 7.44–7.31 (m, 12H), 4.65 (m, 2H), 4.57 (s, 2H), 4.28 (m, 1H), 4.11 (br s, 1H), 3.55 (d, $J = 5.2$ Hz, 2H), 2.97 (m, 2H), 1.08 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.5, 140.9, 138.1, 135.7, 135.1, 135.0, 133.4, 133.0, 129.0, 128.3, 128.0, 73.6, 73.2, 68.3, 59.4, 32.4, 27.0, 19.4; IR (neat) 3417, 3066, 2956, 2929, 2860, 1727, 1573, 1425, 1108 cm^{-1} ; HRMS (CI/ CH_4) calcd for $\text{C}_{26}\text{H}_{26}\text{NO}_4\text{Si}$ ($\text{M}-\text{C}_4\text{H}_9$) $^+$ 444.1626, found 444.1622.

1-(Benzo[d]oxazol-2-yl)-3-methylbutan-2-ol (24). ^1H NMR (400 MHz, CDCl_3) δ 7.64 (m, 1H), 7.47 (m, 1H), 7.32–7.27 (m, 2H), 3.99 (m, 1H), 3.52 (br s, 1H), 3.08 (A of ABX, $J_{\text{AB}} = 16.0$ Hz, $J_{\text{AX}} = 2.7$ Hz, 1H), 3.00 (B of ABX, $J_{\text{AB}} = 16.0$ Hz, $J_{\text{BX}} = 9.7$ Hz, 1H), 1.82 (dsept, $J = 6.4$, 6.4 Hz, 1H), 1.03 (d, $J = 6.8$ Hz, 3H), 1.01 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.7, 150.5, 140.8, 124.6, 124.2, 119.4, 110.3, 73.6, 32.3, 33.1, 18.5, 17.7; IR (neat) 3420, 3043, 2964, 1610, 1562, 1453, 1286, 1242, 1155, 1106, 1001 cm^{-1} ; HRMS (CI/ CH_4) calcd for $\text{C}_{12}\text{H}_{16}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$ 206.1176, found 206.1168.

1-(Benzo[d]oxazol-2-yl)-3-(benzyloxy)propan-2-ol (25). ^1H NMR (400 MHz, CDCl_3) δ 7.66 (m, 1H), 7.48 (m, 1H), 7.33–7.28 (m, 7H), 4.58, (s, 2H), 4.45 (m, 1H), 3.66–3.58 (m, 2H), 3.33 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.5, 150.5, 141.0, 137.7, 128.4, 127.7, 127.7, 124.7, 124.2, 119.5, 110.4, 73.4, 73.0, 68.0, 33.0; IR (neat) 3368, 3062, 3029, 2914, 2857, 1607, 1568, 1450, 1241, 1105 cm^{-1} ; HRMS (CI/ CH_4) calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_3$ ($\text{M}+\text{H}$) $^+$ 284.1281, found 284.1270.

1-(Benzo[d]thiazol-2-yl)-3-methylbutan-2-ol (27). ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 8.1$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.48–7.38 (m, 2H), 3.93 (m, 1H), 3.25 (A of ABX, $J_{\text{AB}} = 15.6$ Hz, $J_{\text{AX}} = 2.4$ Hz, 1H), 3.14 (B of ABX, $J_{\text{AB}} = 15.6$, $J_{\text{BX}} = 9.5$ Hz, 1H), 1.82 (dsept, $J = 6.7$, 6.7 Hz, 1H), 1.04 (d, $J = 7.0$ Hz, 3H), 1.01 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.1, 152.9, 134.8, 126.2, 125.0, 122.7, 121.6, 75.4, 38.1, 33.5, 18.7, 18.0; IR (neat) 3420, 3060, 3026, 2963, 1502, 1434, 1313, 1148, 1077 cm^{-1} ; HRMS (CI/ CH_4) calcd for $\text{C}_{12}\text{H}_{16}\text{NOS}$ ($\text{M}+\text{H}$) $^+$ 222.0947, found 222.0948.

1-(Benzo[d]thiazol-2-yl)-3-(benzyloxy)propan-2-ol (28). ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.84 d, (*J* = 8.0 Hz, 1H), 7.48–7.28 (m, 7H), 4.58, (s, 2H), 4.39 (m, 1H), 3.60 (br s, 1H), 3.60 (d, *J* = 5.4 Hz, 2H), 3.40–3.24 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 169.0, 153.3, 138.3, 135.4, 128.9, 128.2, 128.2, 16.5, 125.4, 123.0, 121.9, 73.9, 73.6, 69.9, 38.2; IR (neat) 3420, 3060, 2963, 1502, 1455, 1434, 1313, 1148, 1077 cm⁻¹; HRMS (CI/CH₄) calcd for C₁₇H₁₈NO₂S (M+H)⁺ 300.1053, found 300.1044.

1-(2-Isopropylthiazol-4-yl)-3-methylbutan-2-ol (30). ¹H NMR (400 MHz, CDCl₃) δ 6.79 (s, 1H), 4.49 (s, 1H), 3.61 (m, 1H), 3.24 (sept, *J* = 7.0 Hz, 1H), 2.87 (dd, *J* = 2.3, 14.7 Hz, 1H), 2.71 (dd, *J* = 9.4, 14.7 Hz, 1H), 1.68 (dsept, *J* = 6.4, 6.4 Hz, 1H), 1.35 (d, *J* = 7.0 Hz, 6H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.94 (d, *J* = 6.7 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 178.1, 154.2, 112.6, 76.0, 35.1, 33.5, 33.2, 23.1, 18.8, 18.1; IR (neat) 3375, 3102, 2965, 2928, 2869, 1512, 1459, 1165 cm⁻¹; HRMS (CI/CH₄) calcd for C₁₁H₂₀NOS (M+H)⁺ 214.1260, found 214.1268.

1-(Benzyloxy)-3-(2-isopropylthiazol-4-yl)propan-2-ol (31). ¹H NMR (400 MHz, CDCl₃) δ 7.36–7.26 (m, 5H), 6.82 (s, 1H), 4.57 (s, 2H), 4.22–4.08 (m, 2H), 3.52 (A of ABX, *J*_{AB} = 9.5 Hz, *J*_{AX} = 6.0 Hz, 1H), 3.47 (B of ABX, *J*_{AB} = 9.5, *J*_{BX} = 5.2 Hz, 1H), 3.27 (sept, *J* = 6.9 Hz, 1H), 2.98 (dd, *J* = 3.6, 14.8 Hz, 1H), 2.88 (dd *J* = 8.1, 14.8 Hz, 1H), 1.37 (d, *J* = 7.0 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 178.3, 153.1, 138.5, 128.5, 128.1, 127.8, 113.2, 73.8, 73.6, 70.3, 35.1, 33.3, 23.3; IR (neat) 3392, 3029, 2963, 2926, 2866, 1525, 1455, 1102 cm⁻¹; HRMS (CI/CH₄) calcd for C₁₆H₂₂NO₂S (M+H)⁺ 292.1366, found 292.1365.

33 (R = CHMe₂)

1-(2'-Isopropyl-2,4'-bithiazol-4-yl)-3-methylbutan-2-ol (33). ¹H NMR (400 MHz, CDCl₃) δ 7.77 (s, 1H), 6.97 (s, 1H), 4.12 (br s, 1H), 3.70 (m, 1H), 3.36 (sept, *J* = 6.8 Hz, 1H), 2.97 (A of ABX, *J*_{AB} = 14.8 Hz, *J*_{AX} = 2.2 Hz, 1H), 2.83 (B of ABX, *J*_{AB} = 14.8 Hz, *J*_{BX} = 9.4 Hz, 1H), 1.73 (dsept, *J* = 6.6, 6.6 Hz, 1H), 1.42 (d, *J* = 7.0 Hz, 6H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 178.9, 163.1, 155.8, 148.6, 115.0, 114.8, 76.1, 35.3, 33.5, 29.8, 23.2, 18.8, 18.1; IR (neat) 3258, 3101, 2959, 2924, 2875, 1518, 1312, 1183, 1123, 1001 cm⁻¹; HRMS (CI/CH₄) calcd for C₁₆H₂₅N₂OS₂ (M+CH₃)⁺ 325.1403, found 325.1400.

34 (R = (CH₂)₂OCH₂Ph)

1-(Benzyloxy)-3-(2'-isopropyl-2,4'-bithiazol-4-yl)propan-2-ol (34). ¹H NMR (400 MHz, CDCl₃) δ 7.76 (s, 1H), 7.35–7.28 (m, 5H), 6.99 (s, 1H), 4.57 (s, 2H), 4.22 (m, 1H), 3.85 (br s, 1H), 3.52 (m, 2H), 3.37 (sept, *J* = 6.8 Hz, 1H), 3.04 (A of ABX, *J*_{AB} = 15.0 Hz, *J*_{AX} = 4.2 Hz, 1H), 2.97 (B of ABX, *J*_{AB} = 15.0 Hz, *J*_{BX} = 7.6 Hz, 1H), 1.43 (d, *J* = 6.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 178.9, 163.1, 154.6, 148.7, 138.3, 128.6, 127.9, 127.8, 115.4, 114.8, 77.5, 73.6, 70.1, 35.1, 33.5, 23.3; IR (neat) 3403, 2966, 2924, 2867, 1457, 1102 cm⁻¹; HRMS (CI/CH₄) calcd for C₁₉H₂₃O₂N₂S₂ (M+H)⁺ 375.1195, found 375.1179.

1-(2-((4-Methoxybenzyloxy)methyl)oxazol-4-yl)-3-methylbutan-2-ol (36). ¹H NMR (400 MHz, CDCl₃) δ 7.46 (s, 1H), 7.28 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.55 (s, 2H), 4.54 (s, 2H), 3.81 (s, 3H), 3.64 (m,

1H), 2.94 (d, $J = 3.2$ Hz, 1H), 2.72 (A of ABX, $J_{AB} = 15.0$ Hz, $J_{AX} = 2.5$ Hz, 1H), 2.56 (B of ABX, $J_{AB} = 15.0$ Hz, $J_{BX} = 9.5$ Hz, 1H), 1.73 (dqq, $J = 6.8, 6.8, 6.8$ Hz, 1H), 0.99 (d, $J = 6.8$ Hz, 3H), 0.97 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.0, 159.7, 138.8, 136.0, 129.9, 129.3, 114.1, 75.7, 72.8, 63.6, 55.4, 33.5, 30.3, 18.8, 17.9; IR (neat) 3391, 2953, 2913, 2849, 1609, 1514, 1460, 1245, 1086, 1029 cm^{-1} ; HRMS (CI/ CH_4) calcd for $\text{C}_{17}\text{H}_{24}\text{O}_4\text{N}_1$ ($\text{M}+\text{H}$) $^+$ 306.1700, found 306.1705.

6

7

8

MAB 2-286-2
1H of Baribier product

File: exp (Varian Data)
Date: Nov 30 1998

Acquisition Parameters:

Nucleus: H1 at 300.069 MHz
Solvent: CDCl3
tof -233.6
av 4000.0 Hz (13.330 ppm)
pw 8.00 usec
cpwr 51
cl 0.370 sec
xp 29120
st 3.640 sec
bs/ss 8/0
nt/ct 64/19
Hz/pt 0.137

Processing Parameters:

lb 0.10
fn 65536
lp/rp -132.8/10.0
ppm/cm 0.38
Hz/pt 0.061

MAB 2-286-3
 13C of Oxazole Sm Barbier Product

File: exp (Varian Data)
 Date: Nov 30 1998

Acquisition Parameters:

Nucleus: C13 at 75.461 MHz
 Solvent: CDCl3
 tof 1515.0
 pw 19000.0 Hz (251.786 ppm)
 tpwr 2.00 usec
 dl 53
 cl 0.275 sec
 xp 65536
 at 1.725 sec
 bs/ss 16/0
 nt/ct 1024/400
 Hz/pt 0.290

Decoupling Parameters:

Nucleus: H1, dof: 0.0
 dm = 'jfp', dnm = 'w', homo = 'n'
 qpwr 38

Processing Parameters:

lb 0.80
 fn 262144
 lp/xp -128.8/-76.5
 ppm/cm 7.20
 Hz/pt 0.072

INDEX	FREQUENCY	PPM	HEIGHT
1	12347.157	163.623	10.1
2	12183.208	161.450	8.6
3	10853.058	143.823	19.3
4	10669.395	141.389	12.8
5	10040.415	133.054	10.3
6	9689.758	128.407	51.2
7	9687.728	128.380	45.3
8	9502.615	125.927	23.5
9	5842.095	77.419	171.7
10	5810.204	76.996	178.3
11	5778.313	76.573	175.4
12	5143.679	68.163	21.2
13	3935.586	52.154	26.7
14	2890.862	38.309	22.1
15	2706.039	35.860	18.7
16	2398.579	31.786	20.4

MA3 3-73-2
 Flashed reaction product
 Sm Ozonole reaction w/ benzoyloxypropanal

File: exp (Varian Data)
 Date: Apr 5 1999

Acquisition Parameters:

Nucleus: H1 at 399.820 MHz
 Solvent: CDCl3
 tof -425.6
 sw 5500.6 Hz (13.758 ppm)
 pw 4.00 usec

tpwz 55
 d1 0.270 sec
 xp 40960
 at 3.723 sec
 bs/ss 8/2
 ht/ct 8/8
 Hz/pt 0.134

Processing Parameters:

lb 0.10
 lp/xp -117.7/139.4
 ppm/cm 0.38
 Hz/pt 0.084

NAB 3-73-3
Flashed reaction product
Sm oxazole rxn w/ benzyloxypropanal

File: exp (Varian Data)
Date: Apr 5 1999

Acquisition Parameters:
Nucleus: C13 at 100.545 MHz
Solvent: CDCl3
tof 970.5
sw 23068.1 Hz (229.430 ppm)
pw 3.20 usec
tpwr 61
dl 0.690 sec
xp 60416
at 1.310 sec
bs/ss 32/0
st/ct 512/128
Ex/pt 0.382

Decoupling Parameters:
Nucleus: H1, dof: -426.0
dm = 'xy', dnm = 'w', homo = 'n',
cprc 47

Processing Parameters:
lb 1.00
fn 65536
lp/rp 44.2/114.8
kpm/cm 7.20
Hz/pt 0.352

INDEX	FREQUENCY	PPM	HEIGHT
1	16424.211	163.352	57.6
2	16224.978	161.370	35.8
3	14853.004	143.747	120.8
4	13834.185	137.592	39.8
5	13355.464	132.831	36.0
6	12889.414	128.196	219.3
7	12819.718	127.502	149.2
8	12811.270	127.418	241.5
9	7773.428	77.313	34.8
10	7741.748	76.998	38.5
11	7709.363	76.676	36.0
12	7345.394	73.056	134.3
13	6846.256	68.091	124.1
14	6828.856	67.916	125.2
15	5211.563	51.833	102.1
16	3593.765	35.743	110.7
17	3586.725	35.673	131.4

17

bws-3-238-3

Pulse Sequence: s2pul

Date: Dec 29 2003

VXP400

PULSE SEQUENCE: standard
OBSERVE H1

STANDARD 1H OBSERVE

bws-3-291-2

Pulse Sequence: s2pul

Date: Dec 23 2003

GEM300

PULSE SEQUENCE: standard

OBSERVE H1

bmw-5-287-5

Pulse Sequence: zgpg

Date: Dec 21 2003

VR400

PULSE SEQUENCE: standard
OBSERVE: H1

bmw-3-287-4

Pulse Sequence: zgpg30

Date: Sep 14, 2003

VX400

PULSE SEQUENCE: standard
OBSERVE: H1

bmw-9-287-4c

Pulse Sequence: zgpg30

Date: Sep 14 2003

V090400

PULSE SEQUENCE: standard

OBSERVE: C13

DECOUPLE: H1

bws-3-285-1

Pulse Sequence: s2pul

Date: Dec 24 2003

GEM300

PULSE SEQUENCE: standard

OBSERVE H1

bws-3-285-2

Pulse Sequence: s2pul

Date: Dec 24 2003

GEM300

PULSE SEQUENCE: standard
OBSERVE H1

bme-3-283-1

Pulse Sequence: zgpg30

Date: Dec 21, 2003

VXRM400

PULSE SEQUENCE: standard
OBSERVE: ¹H

bms-3-281-f

Pulse Sequence: zgpg30

Date: Dec 23 2003

VXPH400

PULSE SEQUENCE: standard

OBSERVE: H1

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INDEX	FREQUENCY	PPM	HEIGHT
1	16195.652	160.975	4.8
2	16061.294	159.640	6.7
3	13960.699	138.761	4.8
4	13662.040	135.792	12.8
5	13067.025	129.878	23.2
6	13011.746	129.329	6.6
7	11474.688	114.051	25.8
8	7794.041	77.468	850.9
9	7761.795	77.148	856.1
10	7730.317	76.835	845.4
11	7614.385	75.682	13.4
12	7325.707	72.813	13.2
13	6401.322	63.625	15.2
14	5577.514	55.437	11.8
15	3367.130	33.467	13.8
16	3043.134	30.247	14.2
17	1887.654	18.762	11.7
18	1803.968	17.930	11.6

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