Supporting Information

General Methods: All manipulations were carried out under an inert atmosphere of nitrogen using dry solvents (KF < 300μg/mL). Reagents were purchased from Aldrich Chemical Co. unless otherwise noted and were used without prior purification. NMR data was obtained in $CDCl_3$ using a Bruker AM400 spectrometer with chemical shifts referenced to the internal solvent signal and coupling constants reported in Hertz. Chromatographic purification of products was accomplished using forced flow chromatography on silica gel (230 mesh) according to the method of Stille.[1] HPLC analysis were carried out on a Hewlett Packard 1100 system. Melting points were determined on a Büchi B-545 apparatus and are uncorrected. Combustion analysis was performed by Quantitative Technologies Inc., Whitehouse, NJ.

General Procedure for the Preparation of Tosyl-Amides[2]: A 1.0-L round-bottomed flask fitted with an addition funnel and an overhead mechanical stirrer was charged with p-toluenesulfinic acid, sodium salt (25 mmol, 1.5 eq) followed by the amide (25 mmol, 1.5 eq). The flask was then charged with acetonitrile (500 mL) and the contents were stirred and placed under a positive pressure of nitrogen. To the resulting slurry was added the aldehyde (16.7 mmol, 1.0 eq) in one portion. The mixture was then cooled to 10 ºC using an ice bath. To the addition funnel was added chlorotrimethylsilane (TMSCl) (33.3 mmol, 2.0 eq) and this was slowly added to the reaction mixture to maintain an internal temperature below 25 ºC (typical addition times 15-30 min). After complete addition of the TMSCl, the reaction was allowed to warm to room temperature (23 ºC). The reaction was then monitored by HPLC until completion (typical reaction times: 24 hours). To the heterogeneous mixture was added water (500mL) and the resulting suspension was stirred for 30 min. The solids were isolated by filtration and the filter cake was washed with water (100 mL). The solids were dried in a vacuum oven at 50 ºC at 30 torr for 24 hours to give the product as a fine white solid.

General Procedure for the Thiazolium Catalyzed Synthesis of N-Acyl β-Amino Ketones: A 50mL flask was charged with the tosyl-amide (3.0 mmol, 1.0 eq) and the thiazolium catalyst (0.3 mmol, 0.1 eq) and purged with nitrogen for 15 min. To the flask was added CH_2Cl_2 (20 mL) followed by the aldehyde (3.3 mmol, 1.1 eq) and the resulting mixture stirred and heated to 35 °C. Triethylamine (45 mmol, 15 eq) was added in one portion via syringe and the corresponding reaction was monitored by HPLC analysis for consumption of the tosyl-amide. After the reaction was complete, it was cooled to 25 °C and water was added (20 mL). The resulting layers were separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. The products were purified by either flash chromatography or crystallization from the crude reaction mixture.

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[1] Still, W. C., Ammon, H. L., DeShong, P.*J. Am. Chem. Soc.* **1995**, *117,* 5166.

[2] All of the tosyl amides prepared by this procedure matched those reported in the literature: (a) Mecozzi, T.; Petrini, M. *J. Org. Chem.* **1999**, *64,* 8970-8972. (b) Sisko, J.; Mellinger, M.; Sheldrake, P.W.; Baine, N.H. *Tetrahedron Lett*. **1996**, *37*, 8113-8116. (c) Unterhalt, B.; Mohr, R. *Synthesis***, 1985**, *10* 973-974.

N-(2-Oxo-1,2-diphenyl-ethyl)-carbamic acid *tert*-butyl ester: The product was isolated from the crude reaction mixture by crystallization from ethyl acetate in 75% yield as small white needles; mp 113-114 ˚C; ^{1}H NMR (400MHz, $CDCl_3$) δ 8.01-7.90 (d, 2H, J = 7.6Hz), 7.53-7.46 (t, 1H, J = 7.6 Hz), 7.43-7.34 (t, 4H, J = 7.6 Hz), 7.32-7.20 (m, 3H), 6.35-6.25 (d, 1H, J = 7.2 Hz), 6.12-6.00 (d, 1H, J = 7.2 Hz), 1.50-1.38 (br, 9H); ^{13}C NMR (100MHz, $CDCl_3$) δ 196.1, 155.2, 137.4, 134.5, 133.5, 129.0, 128.5, 128.2, 128.0, 79.8, 59.7, 28.3; Anal. Calcd for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50. Found: C, 72.91; H, 6.76; N, 4.42.

N-(2-Oxo-1-phenyl-2-(2-bromophenyl)-ethyl)-carbamic acid *tert*-butyl ester: The product was isolated from the crude reaction mixture by crystallization from (2:1) isopropyl acetate/hexanes in 86% yield as opaque crystals: mp 102-103 °C; ^{1}H NMR δ 7.55-7.50 (d, 1H, J = 8.83), 7.31-7.15 (m, 8H), 6.14-6.08 (d, 1H, J = 7.23), 6.08-5.98 (d, 1H, J = 7.23), 1.50-1.32 (s, 9H); ^{13}C NMR δ 198.7, 154.8, 138.8, 133.8, 132.0, 129.3, 129.0, 128.5, 128.1, 127.1, 119.7, 80.1, 63.2, 28.4; Anal. Calcd for $C_{19}H_{20}BrNO_3$: C, 58.47; H, 5.17; N, 3.59. Found: C, 58.49; H, 5.16; N, 3.46.

N-(2-Oxo-1-phenyl-2-(3-methoxyphenyl)-ethyl)-carbamic acid *tert*-butyl ester: The product was isolated from the crude reaction mixture by crystallization from (2:1) isopropylacetate/hexanes in 68% yield as clear prisms: mp 90-91 °C; ^{1}H NMR δ 7.60-7.51 (d, 1H, J = 7.61), 7.48-7.42 (s, 1H), 7.38-7.18 (m, 6H), 7.08-7.00 (dd, 1H, J = 8.41, J = 2.40), 6.30-6.20 (d, 1H, J = 7.21), 6.06-5.95 (d, 1H, J = 7.21), 3.83-3.76 (s, 3H), 1.52-1.31 (s, 9H); ^{13}C NMR δ 28.3, 55.3, 59.8, 79.8, 113.0, 120.2, 121.6, 128.0, 128.2, 129.0, 129.5, 135.8, 137.5, 154.9, 159.7, 195.8; Anal. Calcd for $C_{20}H_{23}NO_4$: C, 70.36; H, 6.79; N, 4.10. Found: C, 70.31; H, 6.89; N, 3.99.

***N*-(2-oxo-1-phenyl-2-pyridin-4-yl-ethyl)-carbamic acid *tert*-butyl ester:** The product was isolated from the crude reaction mixture by flash chromatography using (9:1) ethyl acetate/hexanes as eluent to afford the product as a white crystalline solid in 85% yield; mp 135-136 °C; ^{1}H NMR δ 8.72-8.66 (d, 2H, J = 6.01), 7.70-7.62 (d, 2H, J = 6.01), 7.34-7.20 (m, 5H), 6.22-6.16 (d, 1H, J = 7.21), 6.01-5.90 (d, 1H, J = 7.21), 1.50-1.32 (s, 9H); ^{13}C NMR δ 195.9, 154.9, 150.8, 140.7, 135.8, 129.3, 128.7, 128.1, 121.5, 80.1, 60.4, 28.2; Anal. Calcd for $C_{18}H_{20}N_2O_3$: C, 69.21; H, 6.45; N, 8.97. Found: C, 68.97; H, 6.43; N, 8.82.

***N*-(2-oxo-1-phenyl-propyl)-carbamic acid *tert*-butyl ester:** The product was isolated from the crude reaction mixture by crystallization from (1:1) methylene chloride/hexanes in 62% yield; mp 82-83 °C; ^{1}H NMR δ 7.28-7.40 (m, 5H), 5.83-5.90 (s, 1H), 5.22-5.29 (d, 1H, J=6.02 Hz), 2.02-2.08 (s, 3H), 1.22-1.45 (s, 9H); ^{13}C NMR δ 27.0, 28.3, 64.8, 79.9, 127.9, 128.5, 129.2, 137.0, 154.9, 203.6; Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.45; H, 7.68; N, 5.62. Found: C, 67.50; H, 7.79; N, 5.53.

***N*-(3-Benzyloxy-2-oxo-1-phenyl-propyl)-carbamic acid *tert*-butyl ester:** The product was isolated from the crude reaction mixture by crystallization from (1:1) methylene chloride/hexanes in 75% yield; mp 60-61 °C; ^{1}H NMR δ 7.20-7.40 (m, 10H), 6.78-6.84 (s, 1H), 5.55-6.0 (d, 1H, J=7.23 Hz), 4.35-4.52 (dd_{AB}, 2H, J_{AB}=11.64 Hz), 4.02-4.10 (s,

1H), 1.22-1.45 (s, 9H); ^{13}C NMR 28.4, 61.2, 72.7, 73.5, 79.9, 128.0 (2C), 128.1, 128.5, 128.6, 129.2, 136.2, 136.9, 154.7, 204.2; Anal. Calcd for $C_{21}H_{25}NO_4$: C, 70.96; H, 7.09; N, 3.94. Found: C, 70.73; H, 7.16; N, 3.87.

4-Methoxy-*N*-(2-oxo-1-phenyl-2-pyridin-4-yl-ethyl)-benzamide: The product was isolated from the crude reaction mixture by filtering through silica gel with several washing of ethyl acetate to yield 97% of product: m.p. 103-105 °C; ^{1}H NMR δ 8.76-8.79 (d, 2H, J = 4.41 Hz), 7.81-7.83 (dd, 2H, J = 6.81 Hz, J = 2.00 Hz,), 7.74-7.76 (d, 2H, J = 4.41 Hz), 7.27-47 (m, 6H), 6.91-6.95 (dd, 2H, J = 6.81 Hz, J = 2.00 Hz), 6.67-6.69 (d, 1H, J = 6.81 Hz), 3.87 (s, 3H); ^{13}C NMR δ 55.3, 59.5, 113.7, 121.6, 125.7, 128.4, 128.8, 129.0, 129.4, 135.7, 140.6, 150.9, 162.4, 166.0, 195.8; Anal. Calcd for $C_{21}H_{18}N_2O_3$: C, 72.82; H, 5.24; N, 8.09. Found: C, 72.21; H, 5.23; N, 7.87.

4-Fluoro-*N*-(2-oxo-1-phenyl-2-pyridin-4-yl-ethyl)-benzamide The product was isolated from the crude reaction mixture by filtering through silica gel with several washing of ethyl acetate to yield 90% of product: m.p. 131-132 °C; ^{1}H NMR δ 8.77 (d, 2H, J = 4.41 Hz), 7.82-7.90 (m, 2H),), 7.74-7.76 (d, 2H, J = 4.41 Hz), 7.41-7.49 (m, 3H), 7.28-7.39 (m, 3H), 7.08-7.16 (t, 2H, J = 8.41 Hz), 6.63-6.67 (d, 1H, J = 6.81 Hz); ^{13}C NMR δ 59.6, 115.5, 115.7, 121.6, 128.4, 129.0, 129.5, 129.6, 135.5, 140.4, 150.9, 163.6, 165.4, 166.1, 195.6; Anal. Calcd for $C_{20}H_{15}FN_2O_2$: C, 71.85; H, 4.52; N, 8.38. Found: C, 71.37; H, 4.58; N, 8.15.

***N*-(2-oxo-1-phenyl-2-pyridin-4-yl-ethyl)-carbamic acid benzyl ester:** The product was isolated from the crude reaction mixture by chromatography over silica gel (60% EtOAc/40% Hexane) to yield 96% of product: m.p. 95-96 °C; ^{1}H NMR δ 8.70-8.77 (d, 2H, J = 6.01 Hz), 7.65-7.71 (d, 2H, J = 6.01 Hz), 7.28-7.42 (m, 10H), 6.20-6.26 (d, 1H, J = 6.81 Hz), 6.15-6.19 (d, 1H, J = 6.81 Hz), 5.03-5.17 (dd_{AB}, 2H, J_{AB} = 12.01 Hz); ^{13}C NMR δ 60.8, 67.1, 121.6, 128.1, 128.2, 128.5, 128.9, 129.4, 135.7, 136.0, 140.4, 150.8, 155.4, 195.3; Anal. Calcd for $C_{21}H_{18}N_2O_3$: C, 72.82; H, 5.24; N, 8.09. Found: C, 72.75; H, 5.18; N, 7.91.

***N*-(2-oxo-1-phenyl-2-pyridin-4-yl-ethyl)-acetamide:** The product was isolated from the crude reaction mixture by chromatography over silica gel (98% EtOAc/2% MeOH) to yield 94% of product: m.p. 142-144 °C; ^{1}H NMR δ 8.72-8.77 (d, 2H, J = 4.41 Hz), 7.65-7.72 (d, 2H, J = 4.41 Hz), 7.27-7.38 (m, 5H), 6.75-6.83 (d, 1H, J = 7.21 Hz), 6.43-6.50 (d, 1H, J = 7.21 Hz), 2.02-2.10 (s, 3H); ^{13}C NMR δ 22.9, 59.1, 121.6, 128.2, 128.8, 129.4, 135.6, 140.5, 150.8, 169.3, 195.6; Anal. Calcd for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.63; H, 5.50; N, 10.76.

***N*-(2-oxo-1-phenyl-2-pyridin-4-yl-ethyl)-formamide:** The product was isolated from the crude reaction mixture by chromatography over silica gel (100% EtOAc) to yield 86% of product: m.p. 134-135 °C; ^{1}H NMR δ 8.72-8.78 (d, 2H, J = 4.41Hz), 8.27 (s, 1H), 7.69-7.71 (d, 2H, J = 4.41 Hz), 7.27-7.39 (m, 5H), 7.05-7.13 (d, 1H, J = 7.21 Hz), 6.52-6.57 (d, 1H, J = 7.21 Hz); ^{13}C NMR δ 57.8, 121.6, 128.2, 129.0, 129.5, 135.3, 140.2,

150.9, 160.1, 194.9; Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.63; H, 5.02; N, 11.41.

***N*-(2-oxo-1-phenyl-2-pyridin-4-yl-ethyl)-benzamide:** The product was isolated from the crude reaction mixture by chromatography over silica gel (70% EtOAc/30% Hexane) to yield 88% of product: m.p. 144-145 °C; ^{1}H NMR δ 8.73-8.80 (d, 2H, J = 4.41 Hz), 7.81-7.86 (m, 2H), 7.74-7.76 (d, 2H, J = 4.41 Hz), 7.41-7.56 (m, 6H), 7.28-7.39 (m, 3H), 6.65-6.70 (d, 1H, J = 6.81 Hz); ^{13}C NMR δ 59.6, 121.6, 127.1, 128.4, 128.5, 128.9, 129.5, 131.8, 133.4, 135.6, 140.5, 150.9, 166.5, 195.6; Anal. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.67; H, 5.05; N, 8.70.

***N*-(2-oxo-1-phenyl-2-pyridin-4-yl-ethyl)-cyclohexanecarboxamide:** The product was isolated from the crude reaction mixture by chromatography over silica gel (70% EtOAc/30% Hexane) to yield 98% of product: m.p. 162-163 °C; ^{1}H NMR δ 8.70-8.74 (d, 2H, J = 4.41Hz), 7.69-7.71 (d, 2H, J = 4.41 Hz), 7.27-7.48 (m, 5H), 6.65-6.72 (d, 2H, J = 7.21 Hz), 6.43-6.48 (d, 2H, J = 7.21 Hz), 2.2 (tt, 1H, J = 11.61 Hz, J = 3.20 Hz), 1.61-1.95 (m, 5H), 1.35-1.50 (m, 2H), 1.15-1.34 (m, 3H); ^{13}C NMR δ 25.5 (2 C), 25.6, 29.3, 29.4, 44.9, 58.9, 121.6, 128.2, 128.7, 129.4, 135.7, 140.7, 150.8, 175.3, 195.9; Anal. Calcd for $C_{20}H_{22}N_2O_2$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.41; H, 6.94; N, 8.65.

***N*-(2-oxo-1-phenyl-2-pyridin-2-yl-ethyl)-cyclohexanecarboxamide:** The product was isolated from the crude reaction mixture by chromatography over silica gel (60% CH_2Cl_2/30% EtOAc/10% Hexane) to yield 79% of product: m.p. 148-149 °C; ^{1}H NMR δ 8.63-8.69 (d, 1H, J = 4.81 Hz), 7.98-8.03 (d, 1H, J = 7.61 Hz), 7.72-7.80 (dt, 1H, J = 7.61 Hz, J = 1.60 Hz), 7.42-7.49 (d, 2H, J = 7.21 Hz), 7.37-7.42 (dd, 1H, J = 7.61 Hz, J = 4.81 Hz), 7.21-7.29 (t, 2H, J = 7.21 Hz), 7.19-7.21 (d, 1H, J = 7.21 Hz), 7.10-7.15 (d, 1H, J = 7.21 Hz), 6.80-6.90 (d, 1H, J = 7.21 Hz), 2.14-2.24 (tt, 1H, J = 11.61 Hz, J=3.20 Hz), 1.61-1.95 (m, 5H), 1.35-1.52 (m, 2H), 1.15-1.34 (m, 3H); ^{13}C NMR δ 25.6 (2 C), 25.7, 29.4, 29.5, 45.1, 57.3, 123.1, 127.4, 127.8, 128.3, 128.5, 128.6, 136.7, 136.9, 148.9, 151.2, 175.0, 196.9; Anal. Calcd for $C_{20}H_{22}N_2O_2$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.38; H, 6.96; N, 8.56.

***N*-(2-oxo-1-phenyl-2-pyridin-3-yl-ethyl)-carbamic acid *tert*-butyl ester:** The product was isolated from the crude reaction mixture by chromatography over silica gel (60% EtOAc/40% Hexane) to yield 79% of product: m.p. 113-114 °C ; ^{1}H NMR δ 9.13-9.16 (dd, 1H, J = 2.41 Hz, J = 0.80 Hz), 8.68-8.71 (dd, 1H, J = 4.82 Hz, J = 1.61 Hz), 8.18-8.21 (td, 1H, J = 8.03 Hz, J = 1.61 Hz), 7.27-7.40 (m, 6H), 6.18-6.22 (d, 1H, J = 7.23 Hz), 5.90-5.95 (d, 1H, J = 7.23 Hz), 1.30-1.48 (s, 9H); ^{13}C NMR δ 28.2, 60.3, 80.1, 123.5, 128.1, 128.6, 129.3, 130.0, 136.1, 136.3, 150.2, 153.2, 154.9, 195.1; Anal. Calcd for $C_{18}H_{20}N_2O_3$: C, 69.21; H, 6.45; N, 8.97. Found: C, 68.61; H, 6.48; N, 8.78.

***N*-(2-Furan-2-yl-2-oxo-1-phenyl-ethyl)-carbamic acid *tert*-butyl ester:** The product was isolated from the crude reaction mixture by crystallizition from isopropyl acetate to yield 73% of product: m.p. 110-111 °C; ^{1}H NMR δ 7.55-7.56 (dd, 1H, J = 1.61 Hz, J =

0.80 Hz), 7.38-7.42 (m, 2H), 7.26-7.36 (m, 3H), 7.24-7.26 (dd, 1H, J = 3.61 Hz, J = 0.80 Hz), 6.47-6.49(dd, 1H, J = 3.61 Hz, J = 1.61 Hz), 6.02-6.08 (d, 1H, J = 7.23 Hz), 5.87-5.95 (d, 1H, J = 7.23 Hz), 1.30-1.50 (s, 9H); ^{13}C NMR δ 25.2, 59.8, 79.9, 112.4, 119.2, 127.9, 128.2, 128.9, 137.0, 147.0, 150.6, 154.8, 184.7; Anal. Calcd for $C_{17}H_{19}NO_4$: C, 67.76; H, 6.36; N, 4.65. Found: C, 67.47; H, 6.46; N, 4.56.

***N*-[2-(4-cyano-phenyl)-2-oxo-1-phenyl-ethyl]-carbamic acid *tert*-butyl ester:** The product was isolated from the crude reaction mixture by chromatography over silica gel (70% EtOAc/30% Hexane) to yield 80% of product: m.p. 115-117 °C; ^{1}H NMR δ 7.98-8.02 (d, 2H, J = 8.41 Hz), 7.68-7.71 (d, 2H, J = 8.41 Hz), 7.27-7.35 (m, 5H), 6.20-6.24 (d, 1H, J=7.21 Hz), 5.82-5.90 (d, 1H, J=7.21 Hz), 1.35-1.50 (s, 9H); ^{13}C NMR δ 28.2, 60.3, 80.2, 116.6, 117.6, 128.1, 128.7, 129.2, 129.4, 132.4, 136.1, 137.7, 154.9, 195.1; Anal. Calcd for $C_{20}H_{20}N_2O_3$: C, 71.41; H, 5.99; N, 8.33. Found: C, 71.34; H, 5.96; N, 8.10.

***N*-(2-oxo-1,4-diphenyl-*trans*-but-3-enyl)-cyclohexanecarboxamide:** The product was isolated from the crude reaction mixture by crystallization from hot ethanol to yield 80% of product: m.p. 183-185 °C; ^{1}H NMR δ 7.69-7.73 (d, 1H, J = 16.02 Hz), 7.46-7.49 (dd, 2H, J = 8.01 Hz, J= 2.00 Hz), 7.29-7.40 (m, 8H), 6.95-7.00 (d, 1H, J = 6.41 Hz), 6.68-6.74(d, 1H, J = 16.02 Hz), 5.82-5.88 (d, 1H, J = 6.41 Hz), 2.14-2.24 (m, 1H), 1.65-1.93 (m, 5H), 1.35-1.51 (m, 2H), 1.15-1.33 (m, 3H); ^{13}C NMR δ 25.6 (3 C), 29.4 (2 C), 45.1, 61.5, 122.4, 128.1, 128.3, 128.5, 128.8, 129.1, 130.9, 133.9, 136.8, 144.6, 175.2, 194.5; Anal. Calcd for $C_{23}H_{25}NO_2$: C, 79.51; H, 7.25; N, 4.03. Found: C, 78.79; H, 7.26; N, 3.92.

N-[1-(4-Methoxy-phenyl)-2-oxo-2-pyridin-4-yl-ethyl]-formamide: The product was isolated from crude reaction mixture by chromatography over silica gel (100% EtOAc) to yield 84% of product: ^{1}H NMR δ 8.73-8.76 (d, 2H, J = 4.41 Hz), 8.27 (s, 1H), 7.68-7.71 (d, 2H, J = 4.41Hz), 7.26-7.29 (m, 2H), 6.90-7.10 (m, 1H), 6.84-6.88 (m, 2H), 6.49-6.53 (d, 1H, J = 7.21Hz); ^{13}C NMR δ 55.2, 57.2, 114.9, 121.6, 127.1, 129.5, 140.3, 150.9, 160.0, 194.8.

N-[1-(4-Fluoro-phenyl)-2-oxo-2-pyridin-4-yl-ethyl]-formamide: The product was isolated from crude reaction mixture by chromatography over silica gel (95% EtOAc/5% MeOH) to yield 76% of product: m.p. 126-127 °C; ^{1}H NMR δ 8.75-8.78 (d, 2H, J = 4.41 Hz), 8.27 (s, 1H), 7.67-7.70 (d, 2H, J = 4.41Hz), 7.32-7.37 (m, 2H), 7.07-7.13 (d, 1H, J = 7.21Hz), 7.00-7.06 (m, 2H), 6.53-6.57 (d, 1H, J = 7.21Hz); ^{13}C NMR δ 56.9, 116.6 (d, J_{CF} = 21.6 Hz), 121.5, 130.5 (d, J_{CF} = 8.8 Hz), 131.2 (d, J_{CF} = 4.0 Hz), 140.0, 151.0, 160.0, 162.8 (d, J_{CF} = 249.9 Hz), 194.6.

N-(2-oxo-2-[4]pyridyl-ethyl)-benzamide: This compound was synthesized using a modified procedure. To a 50mL flask was charged the corresponding tosyl amide (289mg, 1.0mmol) and 3,4-dimethyl-5-(2-hydroxyethyl)thiazolium iodide (30mg, 0.1mmol). The flask was purged with N_2 for 10 minutes and then charged with THF (5 mL) and 4-pyridinecarboxaldehyde (161mg, 1.5mmol). The contents were stirred and heated to 60 °C. At this point, solid K_2CO_3 was quickly added in one portion and the

reaction monitored by HPLC until completion. The reaction was cooled and filtered to remove the solids. The filtrate was diluted with ethyl acetate (20 mL) and extracted with water (3 x 10 mL). The organic layer was dried and concentrated in vacuo. The crude solid was redissolved in a 3:1 mixture of isopropyl acetate / isopropanol and product was isolated as long white needles by the slow addition of hexanes (140 mg, 58%). The compound matched previously reported characterization data.[3]

Cross-over experiment 1: To a 25ml flask was charged N-(α-tosylbenzyl) cyclohexanecarboxamide (0.50g, 1.35mmol, 1.0 equiv), *N*-[2-(4-cyano-phenyl)-2-oxo-1-phenyl-ethyl]-carbamic acid *tert*-butyl ester (0.23g, 0.68mmol, 0.5 equiv), thiazolium catalyst (0.04g, 0.14mmol, 0.1 equiv), CH_2Cl_2 (10 mL) and the flask was then heated to 40 °C in an oil bath. To the stirred solution at 40 °C was then added 4-pyridinecarboxaldehyde (0.14mL, 1.49mmol, 1.1 equiv) followed by triethylamine (2.8mL, 15 equiv). After 30min at 40 °C the reaction had gone to completion with formation of the expected *N*-(2-oxo-1-phenyl-2-pyridin-4-yl-ethyl)-cyclohexanecarboxamide. Reaction was allowed to stir at 40 °C for 22hrs at which point, no crossover products were observed by HPLC.

Cross-over experiment 2: To a 25ml flask was charged *tert*-Butyl N-(α-tosylbenzyl) carbamate (0.50g, 1.38mmol, 1.0 equiv), *N*-(2-oxo-1-phenyl-2-pyridin-4-yl-ethyl)-cyclohexanecarboxamide (0.22g, 0.69mmol, 0.5 equiv), thiazolium catalyst (0.04g, 0.14mmol, 0.1 equiv), 4-cyanobenzaldehyde (0.20g, 1.52mmol, 1.1 equiv), CH_2Cl_2 (10mL) and the flask was then heated to 40 °C in an oil bath. To the stirred solution at 40 °C was then added triethylamine (2.9ml, 15 equiv). After 30min at 40 °C the reaction had gone to completion with formation of the expected *N*-[2-(4-cyano-phenyl)-2-oxo-1-phenyl-ethyl]-carbamic acid *tert*-butyl ester. Reaction was allowed to stir at 40 °C for 22hrs at which point, no crossover products were observed by HPLC.

[3] van der Meer et al.; *Recl. Trav. Chim. Pays-Bas.* **1953**, *72*, 244.