Brønsted Acid-Promoted Olefin Aziridination And Formal *anti*-Aminohydroxylation

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Experimental Section

Flame-dried (under vacuum) glassware was used for all reactions. All reagents and solvents were commercial grade and purified prior to use when necessary. Tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were dried by passage through a column of activated alumina as described by Grubbs.[1] The carbamates[2] were prepared as reported in literature.

Thin layer chromatography (TLC) was performed using glass-backed silica gel (250 μm) plates and flash chromatography utilized 230–400 mesh silica gel from Scientific Adsorbents. UV light, and/or the use of ceric ammonium molybdate and potassium iodoplatinate solutions to visualize products.

IR spectra were recorded on a Nicolet Avatar 360 spectrophotometer and are reported in wavenumbers (cm^{-1}). Liquids and oils were analyzed as neat films on a NaCl plate (transmission), whereas solids were applied to a diamond plate (ATR). Nuclear magnetic resonance spectra (NMR) were acquired on either a Varian INOVA-400 (400 MHz), VXR-400 (400 MHz), or Varian INOVA-500 (500 MHz) instrument. Chemical shifts are measured relative to residual solvent peaks as an internal standard set to δ 7.26 and δ 77.1 ($CDCl_3$). Mass spectra were recorded on a Kratos MS-80 spectrometer by use of chemical ionization (CI). Atlantic Microlabs, GA, performed combustion analyses.

General Procedure for Acid Catalyzed Aziridination

A solution of the Michael acceptor (1.0 equiv) in the indicated solvent (0.3 M) was cooled to 0 °C and treated with triflic acid (1.2 equiv). Benzyl azide (1.5 equiv) was then added and the reaction was allowed to stir until complete conversion (generally 12 hours). The reaction mixture was then diluted with ethyl acetate and washed with 1 M aq NaOH. The organic layer was dried and concentrated to an oil that was purified by flash chromatography to provide the desired aziridine in analytically pure form.

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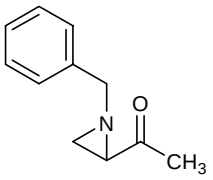
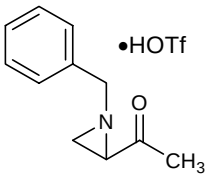
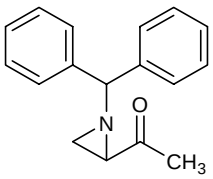
[1] Pangborn, A. B.; Giardello, M.A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.
[2] Kanazawa, A. M.; Denis, J.; Greene, A.E. *J. Org. Chem.* **1994**, *59*, 1238-1240.



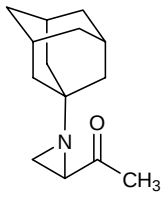
1-(1-Benzyl-aziridin-2-yl)-ethanone (2a). According to the general procedure, **3a** was prepared as a colorless oil (138 mg, 79%). R_f = 0.50 (30% EtOAc/hexanes); IR (film) 3030, 2921, 1701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30-7.20 (m, 5H), 3.58 (d, *J* = 13.4 Hz, 1H), 3.46 (d, *J* = 13.4 Hz, 1H), 2.22-2.20 (m, 2H), 2.04 (s, 3H), 1.80 (dd, *J* = 6.1, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 204.6, 138.2, 128.6, 128.1, 127.5, 64.0, 45.4, 35.0, 25.1; HRMS (EI) Exact mass calcd for $C_{11}H_{13}NO$ $[M]^+$, 175.0997. Found 175.0996.



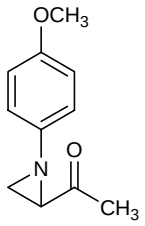
1-(1-Benzyl-aziridin-2-yl)-ethanone triflic acid salt (2a·HOTf). According to the general procedure, **3a** was prepared by recrystallization (ethyl acetate/hexanes) of the crude salt as a colorless crystalline solid (748 mg, 92%). Mp = 97-100 °C; IR (film) 3506, 3067, 1732, 1634 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (br s, 1H), 7.48-7.30 (m, 5H), 4.56 (d, *J* = 13.2 Hz, 1H), 4.44 (d, *J* = 13.2 Hz, 1H), 4.08 (dd, *J* = 7.4, 6.2 Hz, 1H), 3.06 (d, *J* = 6.2 Hz, 1H), 3.01 (d, *J* = 7.4 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 197.8, 130.6, 130.5, 129.7, 129.0, 55.6, 44.4, 35.8, 29.3.



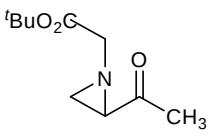
1-(1-Benzhydryl-aziridin-2-yl)-ethanone (2b). According to the general procedure **2b** was prepared as a colorless oil (1.50 g, 88%). R_f = 0.27 (30% EtOAc/hexanes); IR (film) 3061, 3027, 1703, 1493, 1453 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.47-7.23 (m, 10H), 3.63 (s, 1H), 2.31-2.29 (m, 2H), 2.10 (s, 3H), 1.89 (d, *J* = 6.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 207.1, 142.7, 128.7, 127.5, 127.2, 77.9, 45.9, 35.2, 25.1; HRMS (EI) Exact mass calcd for $C_{17}H_{18}NO[M+H]^+$, 252.1388. Found 252.1391. *Anal.* Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.11; H, 6.87; N, 5.59.



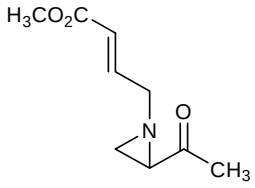
1-(1-Adamantan-1-yl-aziridin-2-yl)-ethanone (2c). According to the general procedure, **2c** was prepared as a white solid (93%). R_f = 0.43 (20% EtOAc/hexanes); IR (film) 2918, 1703. ^1H NMR (400 MHz, $CDCl_3$) δ 2.43 (dd, *J* = 6.8, 2.8 Hz, 1H,), 2.06 (m, 3H), 2.03 (s, 3H), 2.01 (dd, *J* = 6.8, 1.2 Hz, 1H), 1.83 (dd, *J* = 2.8, 1.2 Hz, 1H), 1.58 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) ppm 209.5, 53.4, 40.4, 36.8, 29.6, 26.9, 24.9. HRMS (EI): Exact mass calcd for $C_{14}H_{21}NO$ $[M]^+$, 219.1623. Found 219.1621. *Anal.* Calcd for $C_{14}H_{21}NO$: C, 71.57; H, 6.86; N, 6.39. Found: C, 71.16; H, 6.91; N, 6.27.



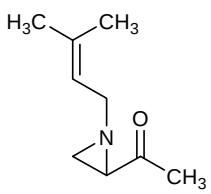
1-[1-(4-Methoxy-phenyl)-aziridin-2-yl]-ethanone (2d). According to the general procedure **2d** was prepared as a yellow oil (30 mg, 43%). R_f = 0.12 (30% EtOAc/hexanes); IR (film) 2918, 2835, 1703, 1507 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.87 (ddd, *J* = 8.8, 3.6, 2.6 Hz, 2H), 6.76 (ddd, *J* = 8.8, 3.6, 2.6 Hz, 2H), 3.73 (s, 3H), 2.65 (dd, *J* = 2.8, 6.8 Hz, 1H), 2.52 (dd, *J* = 2.8, 1.6 Hz, 1H), 2.27 (dd, *J* = 6.8, 1.6 Hz, 1H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 206.8, 155.9, 145.9, 121.5, 114.6, 55.7, 45.6, 34.3, 25.0; HRMS (EI): Exact mass calcd for $C_{11}H_{13}NO_2$ $[M]^+$, 191.0940. Found 191.0946. *Anal.* Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 68.81; H, 6.90; N, 7.48.



(2-Acetyl-aziridin-1-yl)-acetic acid *tert*-butyl ester (2e). According to the general procedure **2e** was prepared as a colorless oil (132 mg, 66%). R_f = 0.56 (40% EtOAc/hexanes); IR (film) 2980, 2927, 1740, 1704, 1368 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.19 (d, *J* = 16.1 Hz, 1H), 2.91 (d, *J* = 16.1 Hz, 1H), 2.23 (d, *J* = 3.3 Hz, 1H), 2.08 (s, 3H), 1.72 (d, *J* = 6.9 Hz, 1H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 206.9, 168.7, 81.9, 61.5, 45.4, 34.3, 28.2, 25.1; HRMS (CI) Exact mass calcd for $C_{10}H_7NO_3$ $[M+H]^+$, 200.1286. Found 200.1284.



4-(2-Acetyl-aziridin-1-yl)-but-2-enoic acid methyl ester (2f). According to the general procedure **2f** was prepared as a colorless oil (152 mg, 75%). R_f = 0.10 (30% EtOAc/hexanes); IR (film) 3003, 2948, 2834, 1728, 1701, 1445 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.89 (dt, *J* = 15.5, 4.9 Hz, 1H), 6.00 (dt, *J* = 15.5, 1.8 Hz, 1H), 3.67 (s, 3H), 3.06 (ddd, *J* = 16.5, 4.9,1.9 Hz, 2H), 2.12 (d, *J* = 3.2 Hz, 1H), 2.07 (dd, *J* = 7.1, 3.2 Hz, 1H), 2.00 (s, 3H), 1.63 (d, *J* = 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 206.4, 166.5, 144.0, 121.9, 60.3, 51.6, 45.1, 34.6, 25.0; HRMS (EI) Exact mass calcd for $C_9H_{13}NO_3$ $[M+H]^+$, 184.0971. Found 184.0971.

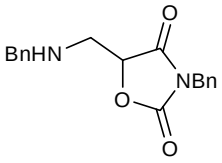


1-[1-(3-Methyl-but-2-enyl)-aziridin-2-yl]-ethanone (2g). According to the general procedure **2f** was prepared as a colorless oil (105 mg, 68%). R_f = 0.28 (30% EtOAc/hexanes); IR (film) 2965, 2921, 2850, 1701, 1353 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.26 (t, *J* = 5.8 Hz, 1H), 2.95 (dd, *J* = 13.2, 5.8 Hz, 1H), 2.91 (dd, *J* = 13.2, 5.8 Hz, 1H), 2.08-2.06 (m, 2H), 2.01 (s, 3H), 1.72 (s, 3H), 1.65 (d, *J* = 7.1 Hz, 1H), 1.60 (s, 3H);); ^{13}C

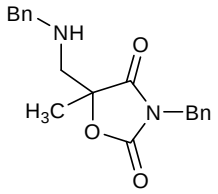
NMR (100 MHz, $CDCl_3$) ppm 208.2, 136.1, 120.7, 58.0, 45.1, 34.7, 25.9, 25.0, 18.3; HRMS (EI) Exact mass calcd for $C_9H_{15}NO$ $[M]^+$, 153.1154. Found 153.1153.

General Procedure for Acid Catalyzed *anti*-Aminohydroxylation

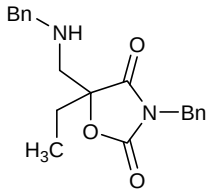
To a vial, the Michael acceptor (1.0 equiv) was added with solvent to generate a 0.3 M solution. The solution was cooled to –20 °C and benzyl azide (2.0 equiv) was added. Triflic acid (2.0 equiv) was then added, and the reaction mixture was stirred until complete conversion (generally 12-48 hours). The reaction was diluted with triethyl amine (5 equiv) and concentrated to an oil that was purified by flash chromatography to give the analytically pure amine.



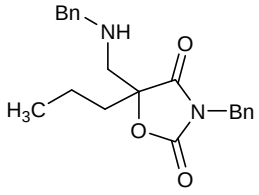
3-Benzyl-5-(benzylamino-methyl)-oxazolidine-2,4-dione (3a). According to the general procedure **3a** was prepared as a colorless oil (143 mg, 84%). R_f = 0.13 (30% EtOAc/hexanes); IR (film) 3350, 3031, 2933, 2840, 1815, 1739, 1439cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.40 (m, 2H), 7.30-7.25 (m, 6H), 7.19-7.17 (m, 2H), 4.84 (t, *J* = 3.3 Hz, 1H), 4.72 (d, *J* = 14.3 Hz, 1H), 4.67 (d, *J* = 14.3 Hz, 1H), 3.77 (s, 2H), 3.21 (dd, *J* = 13.8, 3,3 Hz, 1H), 3.11 (dd, *J* = 13.8, 3.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 172.1, 155.6, 139.4, 134.7, 128.9, 128.6, 128.3, 128.1, 127.3, 80.2, 60.5, 54.0, 47.9, 43.8, 21.2, 14.3; HRMS (EI) Exact mass calcd for $C_{18}H_{19}N_2O_3$ $[M+H]^+$, 311.1395. Found 311.1392. *Anal.* Calcd for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.85; N, 9.03. Found: C, 69.81; H, 5.89; N, 8.91.



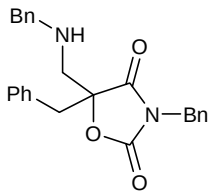
3-Benzyl-5-(benzylamino-methyl)-5-methyl-oxazolidine-2,4-dione (3b). According to the general procedure **3b** was prepared as a colorless oil (123 mg, 88%). R_f = 0.63 (50% EtOAc/hexanes); IR (film) 3400, 3046, 2937, 2844, 1804, 1733, 1411 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.31 (m, 2H), 7.30-7.24 (m, 3H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.3 Hz, 1H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 2H), 4.60 (d, *J* = 14.6 Hz, 1H), 4.54 (d, *J* = 14.6 Hz, 1H), 3.47 (bs, 1H), 3.41 (t, *J* = 6.7 Hz, 2H), 2.21 (dq, *J* = 14.6, 7.3 Hz, 2H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 175.4, 154.7, 147.5, 134.9, 129.5, 129.1, 128.7, 128.5, 118.3, 113.2, 85.2, 43.9, 38.6, 36.3, 23.3; HRMS (EI) Exact mass calcd for $C_{19}H_{20}N_2O_3$ $[M]^+$, 324.1474. Found 324.1463. *Anal.* Calcd for $C_{19}H_{20}N_2O_3$: C, 70.35; H, 6.21; N, 8.64. Found: C, 70.54; H, 6.22; N, 8.62.



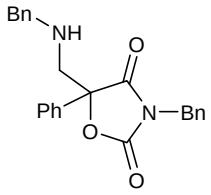
3-Benzyl-5-(benzylamino-methyl)-5-ethyl-oxazolidine-2,4-dione (3c). According to the general procedure **3c** was prepared as a colorless oil (35 mg, 61%). R_f = 0.14 (20% EtOAc/hexanes); IR (film) 3403, 3033, 2927, 1810, 1733, 1603 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 2H), 7.28-7.24 (m, 3H), 7.18-7.13 (m, 2H), 6.75-6.71 (m, 1H), 6.50-6.45 (m, 2H), 4.56 (AB q, *J* = 14.4 Hz, 2H), 3.50 (br s, 1H), 3.14 (t, *J* = 6.6 Hz, 2H), 2.28-2.13 (m, 2H) 1.98-1.89 (m, 2H), 0.82 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 175.0, 155.2, 147.5, 134.9, 129.5, 129.0, 128.8, 128.5, 118.3, 113.2, 88.3, 43.9, 38.5, 35.3, 29.9; HRMS (EI): Exact mass calcd for $C_{20}H_{22}N_2O_3$ $[M]^+$, 338.1630. Found 338.1625. *Anal.* Calcd for $C_{20}H_{22}N_2O_3$: C, 70.99; H, 6.55; N, 8.28. Found: C, 70.85; H, 6.49; N, 8.20.



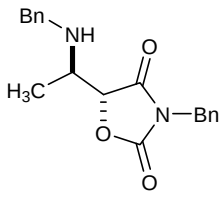
3-Benzyl-5-(benzylamino-methyl)-5-propyl-oxazolidine-2,4-dione (3d). According to the general procedure **3d** was prepared as a colorless oil (35 mg, 60%). R_f = 0.13 (10% EtOAc/hexanes); IR (film) 3394, 2962, 2924, 1810, 1734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42–7.22 (m, 5H), 7.17-7.11 (m, 2H), 6.72 (tt, *J* = 7.6, 1.2 Hz, 1H), 6.46 (m, 2H), 4.55 (AB q, *J* = 14.4 Hz, 2H), 3.12 (t, *J* = 7.2 Hz, 2H), 2.18 (m, 2H), 1.84 (m, 2H), 1.32 (m, 1H), 1.16 (m, 1H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 175.0, 155.1, 147.5, 134.9, 129.5, 129.0, 128.8, 128.5, 118.3, 113.2, 88.0, 43.9, 38.7, 38.5, 35.5, 16.1, 13.9; HRMS (CI): Exact mass calcd for $C_{21}H_{24}N_2O_3$ $[M]^+$, 352.1783. Found 352.1787. *Anal.* Calcd for $C_{21}H_{24}N_2O_3$: C, 71.57; H, 6.86; N, 7.95. Found: C, 71.59; H, 6.86; N, 7.90.



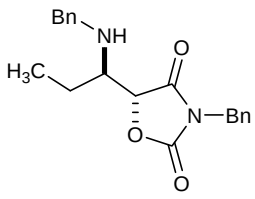
3,5-Dibenzyl-5-(benzylamino-methyl)-oxazolidine-2,4-dione (3e). Compound **3e** was prepared according to the general procedure except it was allowed to react in a sealed tube and heated at 50 ^oC for 7 days. Colorless oil (27 mg, 46%). R_f = 0.15 (20% EtOAc/hexanes); IR (film) 3403, 3031, 2924, 1815, 1734, 1603 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20-7.11 (m, 10H), 6.93-6.89 (m, 2H), 6.77-6.71 (m, 1H), 6.53-6.48 (m, 2H), 4.24 (AB q, *J* = 14.4 Hz, 2H), 3.50 (br s, 1H), 3.23 (m, 2H), 3.17 (s, 2H), 2.44-2.36 (m, 1H), 2.32-2.24 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 174.2, 154.6, 147.5, 134.4, 132.3, 130.4, 129.5, 128.9, 128.8, 128.1, 128.0, 118.4, 113.2, 54.2, 43.6, 42.5, 38.6, 35.7; HRMS (CI): Exact mass calcd for $C_{25}H_{24}N_2O_3$ $[M]^+$, 400.1787. Found 400.1794. *Anal.* Calcd for $C_{25}H_{24}N_2O_3$: C, 74.98; H, 6.04; N, 7.00. Found: C, 74.96; H, 6.13; N, 6.85.



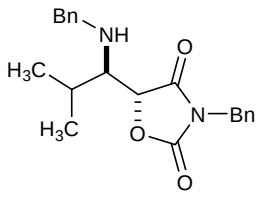
3-Benzyl-5-(benzylamino-methyl)-5-phenyl-oxazolidine-2,4-dione (3f). According to the General Procedure, **3f** was prepared as a colorless oil (28 mg, 86%). R_f = 0.46 (20% EtOAc/hexanes); IR (film) 3034, 2955, 1742, 1674, 1615 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64-7.58 (m, 2H), 7.45-7.38 (m, 3H), 7.34-7.24 (m, 5H), 7.18-7.12 (m, 2H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.45 (d, *J* = 8.8 Hz, 2H), 4.60 (dd, *J* = 14.8, 4.0 Hz, 2H), 3.48 (br s, 1H), 3.18 (m, 2H), 2.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 173.5, 154.6, 147.4, 137.8, 134.6, 129.5, 129.3, 129.2, 129.1, 128.61, 128.56, 124.7, 118.3, 113.3, 87.4, 44.2, 38.8, 38.4; HRMS (CI): Exact mass calcd for $C_{24}H_{22}N_2O_3$ $[M]^+$ 386.1630. Found 386.1629.



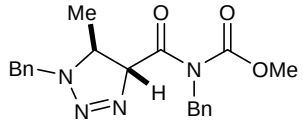
3-Benzyl-5-(1-benzylamino-ethyl)-oxazolidine-2,4-dione (3g). According to the general procedure **3g** was prepared as a colorless oil (131 mg, 94%). R_f = 0.30 (30% EtOAc/hexanes). IR (film) 3300, 3063, 2933, 2850, 1814, 1733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41-7.23 (m, 10H), 4.82 (d, *J* = 3.1 Hz, 1H), 4.72-4.64 (m, 3H), 3.84 (d, *J* = 13.2 Hz, 1H), 3.78(d, *J* = 13.2 Hz, 1H), 3.30-3.23 (m, 1H), 1.43 (bs, 1H), 1.14 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 171.7, 155.6, 139.6, 134.7, 129.1, 129.0, 128.9, 128.7, 128.6, 128.4, 128.1, 127.3, 82.0, 53.5, 51.8, 43.7, 15.1; HRMS (EI): Exact mass calcd for $C_{19}H_{21}N_2O_3$ $[M+H]^+$, 325.1553. Found 325.156. *Anal.* Calcd for $C_{18}H_{18}N_2O_3$: C, 70.35; H, 6.21; N, 8.64. Found: C, 70.54; H, 6.22; N, 8.51. Relative configuration was assigned by X-ray analysis of the β-dibenzylamino derivative.



3-Benzyl-5-(1-benzylamino-propyl)-oxazolidine-2,4-dione (3h). According to the general procedure **3h** was prepared as a colorless oil (125 mg, 82%). Major diastereomer. R_f = 0.20 (30% EtOAc/hexanes). IR (film) 2920, 2849, 1735, 1646 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.18 (m, 10H), 4.84 (dd, *J* = 2.8 Hz, 1H), 4.67 (d, *J* = 7.2 Hz, 2H), 3.80 (d, *J* = 4.0 Hz, 2H), 3.12 (m, 1H), 1.60 (m, 2H), 0.97 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) ppm 172.0, 155.8, 139.9, 134.9, 129.0, 128.8, 128.7, 128.5, 128.3, 127.4, 81.7, 60.0, 53.2, 43.8, 23.3, 11.0. HRMS (EI): Exact mass calcd for $C_{20}H_{22}N_2O_3$ $[M-H]^+$, 337.1552. Found 337.1542.



3-Benzyl-5-(1-benzylamino-2-methyl-propyl)-oxazolidine-2,4-dione (3i). According to the general procedure **3i** was prepared as a colorless oil (26 mg, 61%). Major diastereomer; R_f = 0.20 (30% EtOAc/hexanes). IR (film) 3430, 2923, 2852, 1735, 1656 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (m, 2H) 7.29-7.21 (m, 6H), 7.13 (m, 2H), 4.95 (d, *J* = 2.8 Hz, 1H), 4.68 (dd, *J* = 14.4, 10.8 Hz, 2H), 3.78 (dd, *J* = 14.4, 10.8 Hz, 2H), 2.78 (dd, *J* = 8.8, 3.2 Hz, 1H), 2.00 (m, 1H), 1.05 (d, *J* = 6.4 Hz, 3H), 1.01 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) ppm 172.0, 156.1, 139.9, 134.9, 128.9, 128.7, 128.6, 128.5, 128.3, 127.4, 81.8, 65.2, 55.3, 43.8, 29.9, 20.6, 20.1. HRMS (EI) Exact mass calcd for $C_{21}H_{24}N_2O_3$ $[M+H]^+$, 351.1709. Found 351.1710. *Anal.* Calcd for $C_{21}H_{24}N_2O_3$: C, 71.57; H, 6.86; N, 7.95. Found: C, 71.16; H, 6.91; N, 7.70.



Benzyl-(1-benzyl-5-methyl-[1,2,3]triazolidine-4-carbonyl)-carbamic acid methyl ester (4). Imide **1g** (160 mg, 683 μmol) was stirred in neat benzyl azide (10 equivalents) at ambient temperature in the dark for 1 week (70% conversion by ^1H NMR). Concentration of the reaction mixture and chromatography of the residue (SiO_2, 10% ethyl acetate in hexanes) furnished the triazoline as a colorless oil (138 mg, 79%). R_f = 0.13 (20% EtOAc/hexanes); IR (neat) (cm^{-1}): 3031, 2957, 2094, 1746, 1695; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.20 (m, 10H), 5.66 (d, *J* = 11.2 Hz, 1H), 4.93 (dd, *J* = 13.2, 9.2 Hz, 2H), 4.92 (d, *J* = 14.8 Hz, 1H), 4.63 (d, *J* = 14.8 Hz, 1H), 3.83 (s, 3H), 3.72 (m, 1H), 1.16 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 170.2, 155.1, 137.2, 135.9, 132.6, 128.8, 128.6, 128.3, 128.0, 127.7, 127.6, 86.3, 54.8, 54.2, 52.4, 48.3, 17.2. HRMS (ES) Exact mass calcd for $C_{20}H_{22}NaN_4O_3$ $[M+Na]^+$, 367.1765. Found 367.1764.