## *Experimental Section*

Azido Acids General: Triflyl anhydride and $Cu^{II}SO_4$ pentahydrate 99.999% were obtained from Aldrich. All other solvents and chemicals were reagent grade or better and obtained from reputable suppliers. All azido acid products were found to be > 95% pure by LC/ESMS with the parent ion detected under negative ionization. Additionally, all products displayed IR bands between 2160-2095 $cm^{-1}$ confirming presence of the azido functionality.

**Synthesis of Azido Glycine (1).** Adapting the general method of Alvarez et al.[17] to account for the acid functionality, sodium azide (5.14 g, 79.2 mmol, 2.1 equiv.) was partially dissolved while stirring in dimethylsulfoxide (DMSO)(220 mL) for 1.5 h. Bromoacetic acid (5.24 g, 37.7 mmol) was added and within minutes the remaining sodium azide dissolved. The reaction was stirred overnight under ambient conditions. The reaction mixture was diluted with $H_2O$ (250 mL), the pH adjusted to 2.5 with conc. HCl and the product extracted with EtOAc (2 × 450 mL). The combined extracts were washed with brine (3×). After drying ($MgSO_4$) and concentration azidoacetic acid (**1**) was obtained as a pale oil (2.58 g, 68 %). $^1$H NMR (300 MHz, $CDCl_3$) δ 3.98 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 174.5, 50.0.

**Azido Acid Synthesis by Diazo Transfer (Differential Extraction Work-up) Synthesis of Azido-Ile (8).** The diazo transfer reactions utilize the method of Wong[11] for carbohydrates with an customized work-up to accommodate the free acid products. Triflyl azide preparation: A solution of sodium azide (1.78 g, 27.45 mmol) was dissolved in distilled $H_2O$ (4.5 mL) with $CH_2Cl_2$ (7.5 mL) and cooled on an ice bath. Triflyl anhydride (0.93 mL, 5.55 mmol) was added slowly over 5 min with stirring continued for 2 h. The mixture was placed in a separatory funnel and the $CH_2Cl_2$ phase removed. The aqueous portion was extracted with $CH_2Cl_2$ (2 × 3.75 mL). The organic fractions, containing the triflyl azide, were pooled and washed once with saturated $Na_2CO_3$ and used without further purification. L-Ile (366 mg, 2.79 mmol) was combined with $K_2CO_3$ (577.5 mg, 4.19 mmol) and $Cu^{II}SO_4$ pentahydrate (6.98 mg, 27.9 μmol) distilled $H_2O$ (9 mL) and $CH_3OH$ (18 mL). The triflyl azide in $CH_2Cl_2$ (15 mL) was added and the mixture was stirred at ambient temperature and pressure overnight. Subsequently, the organic solvents were removed under reduced pressure and the aqueous slurry was diluted with $H_2O$ (50 mL). This was acidified to pH 6 with conc. HCl and diluted with 0.25 M, pH 6.2 phosphate buffer (50 mL) and extracted with EtOAc (4×) to remove sulfonamide by-product. The aqueous phase was then acidified to pH 2 with conc. HCl. The product was obtained from another round of EtOAc extractions (3×). These EtOAc extracts were combined, dried ($MgSO_4$) and evaporated to dryness giving 390 mg of the pale oil (**8**) in 89% yield with no need for further purification. $[\alpha]^{25}_D$ = -33.0 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 3.84 (d, *J* = 5.8 Hz, 1H), 2.15-1.95 (m, 2H), 1.70-1.55 (m, 1H), 1.45-1.25 (m, 1H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 174.5, 66.9, 37.2, 24.9, 15.9, 11.5. Anal. Calcd. for $C_6H_{11}N_3O_2$: C, 45.85; H, 7.05; N, 26.74. Found: C, 46.19; H, 7.29; N, 26.72.

**Azido-Phe (2).** L-Phe was used in the procedure above to give azido-Phe (**2**), a yellowish oil, in 62% yield. $[\alpha]^{25}_D$ = -74.2 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.50-7.20 (m, 5H), 4.17 (dd, *J* = 5.0, 8.9 Hz, 1H), 3.25 (dd, *J* = 5.0, 14.1 Hz, 1H), 3.05 (dd, *J* = 8.9, 14.1 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.3, 135.6, 129.2, 128.8, 127.5, 63.0, 37.5. Anal. Calcd. for $C_9H_9N_3O_2$: C, 56.54; H, 4.74; N, 21.98. Found: C, 55.90; H, 4.69; N, 21.45.

**Azido-D-Phe (3).** D-Phe was used in the procedure above to give azido-D-Phe (**3**), a yellowish oil, in 68% yield. $[\alpha]^{25}_D$ = +64.0 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.40-7.20 (m, 5H), 4.18 (dd, *J* = 5.0, 8.8 Hz, 1H), 3.25 (dd, *J* = 5.0, 14.1 Hz, 1H), 3.05 (dd, *J* = 8.9, 14.1 Hz, 1H); $^{13}$C NMR (100 MHz,

$CDCl_3$) δ 175.6, 135.6, 129.2, 128.8, 127.5, 63.0, 37.5. Anal. Calcd. for $C_9H_9N_3O_2$: C, 56.54; H, 4.74; N, 21.98. Found: C, 56.27; H, 4.19; N, 21.52.

**Azido-Val (4).** L-Val was used in the procedure above to give azido-Val (**4**), a pale oil, in 75% yield. $[\alpha]^{25}_D$ = -47.8 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 3.78 (d, *J* = 5.7 Hz, 1H), 2.30-2.22 (m, 1H), 1.07 (d, *J* = 6.8 Hz, 3H), 1.02 (d, *J* = 6.7 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.2, 67.9, 30.9, 19.4, 17.7. Anal. Calcd. for $C_5H_9N_3O_2$: C, 41.95; H, 6.34; N, 29.35. Found: C, 41.47; H, 6.32; N, 27.14.

**Azido-D-Val (5).** D-Val was used in the procedure above to give azido-D-Val (**5**), a pale oil, in 80% yield. $[\alpha]^{25}_D$ = +50.8 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 3.79 (d, *J* = 5.7 Hz, 1H), 2.30-2.22 (m, 1H), 1.07 (d, *J* = 6.8 Hz, 3H), 1.02 (d, *J* = 6.7 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.6, 67.9, 30.9, 19.4, 17.7. Anal. Calcd. for $C_5H_9N_3O_2$: C, 41.95; H, 6.34; N, 29.35. Found: C, 41.58; H, 6.25; N, 27.73.

**Azido-Ala (6).** L-Ala was used in the procedure above to give azido-Ala (**6**), a pale oil, in 66% yield. $[\alpha]^{25}_D$ = +22.1 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 4.03 (dd, *J* = 7.2, 14.3 Hz, 1H), 1.55 (d, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.6, 57.1, 16.7. Anal. Calcd. for $C_3H_5N_3O_2$: C, 31.31; H, 4.38; N, 36.51. Found: C, 31.95; H, 4.15; N, 26.31.

**Azido-Leu (7).** L-Leu was used in the procedure above to give azido-Leu (**7**), a pale oil, in 68% yield. $[\alpha]^{25}_D$ = -13.0 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 3.89 (dd, *J* = 5.7, 8.8 Hz, 1H), 2.00-1.70 (m, 3H), 0.99 (t, *J* = 6.4 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.8, 60.0, 39.8, 25.0, 22.8, 21.4. Anal. Calcd. for $C_6H_{11}N_3O_2$: C, 45.85; H, 7.05; N, 26.74. Found: C, 45.33; H, 7.26; N, 26.08.

**Azido-D-Ile (9).** D-Ile was used in the procedure above to give azido-D-Ile (**9**), a pale oil, in 73% yield. $[\alpha]^{25}_D$ = +38.3 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 3.85 (d, *J* = 5.8 Hz, 1H), 2.10-1.95 (m, 1H), 1.70-1.50 (m, 1H), 1.45-1.25 (m, 1H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.7, 67.1, 37.2, 24.9, 15.9, 11.2. Anal. Calcd. for $C_6H_{11}N_3O_2$: C, 45.85; H, 7.05; N, 26.74. Found: C, 44.71; H, 7.20; N, 25.64.

**Azido-D-*allo*-Ile (10).** D-*allo*-Ile was used in the procedure above to give azido-D-*allo*-Ile (**10**), a pale oil, in 76% yield. $[\alpha]^{25}_D$ = +108.6 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 4.01 (d, *J* = 4.5 Hz, 1H), 2.15-2.00 (m, 1H), 1.65-1.50 (m, 1H), 1.50-1.30 (m, 1H), 0.97 (d, *J* = 5.9 Hz, 3H), 0.96 (t, *J* = 6.9 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 177.2, 66.5, 37.9, 26.9, 15.1, 12.0. Anal. Calcd. for $C_6H_{11}N_3O_2$: C, 45.85; H, 7.05; N, 26.74. Found: C, 45.53; H, 6.84; N, 26.04.

**Azido-*tert*-Leu (11).** L-*tert*-Leu was used in the procedure above to give azido-*tert*-Leu (**11**), a clear crystalline solid, in 80% yield. mp 66-68°C; $[\alpha]^{25}_D$ = -69.6 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 3.75 (s, 1H), 1.08 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 174.1, 71.7, 35.7, 26.6. Anal. Calcd. for $C_6H_{11}N_3O_2$: C, 45.85; H, 7.05; N, 26.74. Found: C, 45.92; H, 7.33; N, 26.75.

**Azido-Phg (12).** L-Phg was used in the procedure above to give azido-Phg (**12**), a golden oil, in 85% yield. $[\alpha]^{25}_D$ = +145.9 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.55-7.35 (m, 5H), 5.05 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.8, 133.2, 129.6, 129.3, 127.7, 65.1. Anal. Calcd. for $C_8H_7N_3O_2$: C, 54.24; H, 3.98; N, 23.72. Found: C, 53.64; H, 3.72; N, 23.15.

**Azido-D-Phg (13).** D-Phg was used in the procedure above to give azido-D-Phg (**13**), a golden oil, in 87% yield. $[\alpha]^{25}_{D}$ = -163.6 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.50-7.30 (m, 5H), 5.05 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 174.0, 133.2, 129.6, 129.3, 127.7, 65.1. Anal. Calcd. for $C_8H_7N_3O_2$: C, 54.24; H, 3.98; N, 23.72. Found: C, 54.13; H, 3.68; N, 23.60.

**Azido-Asn (14).** L-Asn was used in the procedure above with five final acidic EtOAc extractions of the polar product, azido-Asn (**14**), in 48% yield. $[\alpha]^{25}_{D}$ = -98.0 (*c* = 1.0 in MeOH); $^1$H NMR (300 MHz, $CD_3OD$) δ 4.32 (dd, *J* = 4.8, 8.5 Hz, 1H), 2.67 (dd, *J* = 4.9, 15.6 Hz, 1H), 2.51 (dd, *J* = 8.5, 15.6 Hz, 1H); $^{13}$C NMR (100 MHz, $CD_3OD$) δ 174.9, 173.6, 60.5, 38.4. Anal. Calcd. for $C_4H_6N_4O_3$: C, 30.39; H, 3.82; N, 35.43. Found: C, 29.86; H, 4.28; N, 32.18.

**Azido-Gln (15).** L-Gln was used in the procedure above with five final acidic EtOAc extractions of the polar product, azido-Gln (**15**), in 49% yield. $[\alpha]^{25}_{D}$ = -73.3 (*c* = 1.0 in MeOH); $^1$H NMR (300 MHz, $CD_3OD$) δ 4.20 (dd, *J* = 4.8, 8.7 Hz, 1H), 2.60-2.45 (m, 2H), 2.40-2.20 (m, 1H), 2.15-2.00 (m, 1H); $^{13}$C NMR (100 MHz, $CD_3OD$) δ 177.9, 173.9, 63.1, 32.8, 28.9. Anal. Calcd. for $C_5H_8N_4O_3$: C, 34.89; H, 4.68; N, 32.55. Found: C, 34.89; H, 4.93; N, 31.48.

**Azido-Asp(*t*-Bu) (16).** L-Asp(*t*-Bu) was used in the procedure above to give azido-Asp(*t*-Bu) (**16**), a pale oil, in 82% yield. $[\alpha]^{25}_{D}$ = -65.9 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 4.38 (dd, *J* = 5.6, 6.9 Hz, 1H), 2.83 (dd, *J* = 5.6, 17.0 Hz, 1H), 2.72 (dd, *J* = 7.2, 16.4 Hz, 1H), 1.47 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.5, 168.7, 82.4, 58.3, 37.3, 28.0. Anal. Calcd. for $C_8H_{13}N_3O_4$: C, 44.65; H, 6.09; N, 19.53. Found: C, 44.31; H, 6.12; N, 19.04.

**Azido-Glu(Bzl) (17).** L-Glu(Bzl) was used in the procedure above to give azido-Glu(Bzl) (**17**), a pale oil, in 42% yield. $[\alpha]^{25}_{D}$ = -46.8 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.45-7.30 (m, 5H), 5.14 (s, 2H), 4.10 (dd, *J* = 5.0, 8.6 Hz, 1H), 2.65-2.45 (m, 2H), 2.35-2.15 (m, 1H), 2.15-2.00 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 174.7, 172.1, 135.6, 128.6, 128.4, 128.3, 66.7, 60.7, 30.0, 26.4. Anal. Calcd. for $C_{12}H_{13}N_3O_4$: C, 54.75; H, 4.98; N, 15.96. Found: C, 51.98; H, 4.48; N, 16.26.

**Azido-Ser(*t*-Bu) (18).** L-Ser(*t*-Bu) was used in the procedure above to give azido-Ser(*t*-Bu) (**18**), a pale oil, in 84% yield. $[\alpha]^{25}_{D}$ = +29.3 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 3.97 (t, *J* = 4.4 Hz, 1H), 3.83 (dd, *J* = 1.8, 4.7 Hz, 2H), 1.24 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.9, 74.5, 62.6, 61.3, 27.2. Anal. Calcd. for $C_7H_{13}N_3O_3$: C, 44.91; H, 7.00; N, 22.45. Found: C, 44.04; H, 7.05; N, 21.03.

**Azido-D-Ser(*t*-Bu) (19).** D-Ser(*t*-Bu) was used in the procedure above to give azido-D-Ser(*t*-Bu) (**19**), a pale oil, in 84% yield. $[\alpha]^{25}_{D}$ = -27.4 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 3.99 (t, *J* = 4.4 Hz, 1H), 3.84 (dd, *J* = 1.4, 3.9 Hz, 1H), 1.24 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 172.7, 74.7, 62.5, 61.1, 27.2. Anal. Calcd. for $C_7H_{13}N_3O_3$: C, 44.91; H, 7.00; N, 22.45. Found: C, 44.45; H, 7.14; N, 22.15.

**Azido-Thr(*t*-Bu) (20).** L-Thr(*t*-Bu) was used in the procedure above to give azido-Thr(*t*-Bu) (**20**), a white solid, in 80% yield. mp 76-78°C; $[\alpha]^{25}_{D}$ = +31.6 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 4.13 (dq, *J* = 4.2, 12.6 Hz, 1H), 3.82 (d, *J* = 4.1 Hz, 1H), 1.27 (d, *J* = 6.3 Hz, 3H), 1.25 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.9, 75.5, 68.8, 66.2, 28.2, 20.1. Anal. Calcd. for $C_8H_{15}N_3O_3$: C, 47.75; H, 7.51; N, 20.88. Found: C, 47.89; H, 7.76; N, 20.75.

**Azido-Met (21).** L-Met was used in the procedure above to give azido-Met (**21**), a golden oil, in 86% yield. $[\alpha]^{25}_{D}$ = -98.5 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 4.25 (dd, *J* = 4.6, 8.9 Hz, 1H), 2.85-

2.60 (m, 2H), 2.25-2.00 (m, 2H), 2.13 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.3, 60.2, 30.4, 30.1, 15.3. Anal. Calcd. for $C_5H_9N_3O_2S$: C, 34.28; H, 5.18; N, 23.98. Found: C, 33.62; H, 5.38; N, 23.19.

**Azido-IBA (22).** Aminoisobutyric acid was used in the procedure above to give azido-IBA (**22**), a pale oil, in 75% yield. $^1$H NMR (300 MHz, $CDCl_3$) δ 1.53 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 178.8, 62.9, 24.3. Anal. Calcd. for $C_4H_7N_3O_2$: C, 37.21; H, 5.46; N, 32.54. Found: C, 35.86; H, 4.97; N, 25.96.

**Azido Acid Synthesis by Diazo Transfer (Partitioning anion workup) Synthesis of azido-Trp(*t*-Boc) (23).** The diazo transfer reaction was carried out as described above beginning with L-Trp(*t*-Boc). After the reaction was completed the organic solvents were evaporated and $H_2O$ (100 mL) was added. The immediate opaque appearance indicated lack of solubility for the anion which partitioned into EtOAc 3 × 100 mL leaving the sulfonamide in the aqueous phase. The combined organics were washed twice with $H_2O$ adjusted to pH 3 with 6 N HCl. After drying ($MgSO_4$) and concentration, 790 mg of the yellow oil (**23**) was obtained (86% yield). $[\alpha]^{25}_D$ = +31.0 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.55 (s, 1H), 7.37-7.31 (m, 1H), 7.30-7.24 (m, 1H), 4.29 (dd, *J* = 4.9, 8.6 Hz, 1H), 3.34 (dd, *J* = 5.0, 15.4 Hz, 1H), 3.15 (dd, *J* = 8.6, 15.1 Hz, 1H), 1.68 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.7, 149.6, 135.4, 129.9, 124.7, 124.6, 122.7, 118.6 115.5, 114.6, 83.9, 61.6, 28.7, 27.3. Anal. Calcd. for $C_{16}H_{18}N_4O_4$: C, 58.17; H, 5.49; N, 16.96. Found: C, 53.60; H, 5.18; N, 14.94.

**Azido Acid Synthesis by Diazo Transfer (Partial partitioning by the anion) Synthesis of azido-Cys(4-MeO-Bzl) (24).** The diazo transfer reaction was carried out as described above beginning with L-Cys(4-MeO-Bzl). In this situation partial partitioning of the anion product made sulfonamide removal difficult to manage. This was found to be the case in instances where side chain protecting groups provide enhanced lipophilic character. Upon completion of the reaction following the general procedure above both the sulfonamide and product are partitioned between EtOAc 3 × 100 mL and $H_2O$ (pH 3, 100 mL). The organic phase was dried ($MgSO_4$) and concentrated. About 100 mg of crude material was purified by reversed-phase HPLC on a Gilson dual pump (model 306) system equipped with a Gilson 215 automated liquid handler in combination with a YMC (20 × 50 mm, 120 Å, 5μ) preparative column. The mobile phase consisted of acetonitrile (solvent A) and $H_2O$ (solvent B) without an acid component to prevent protecting group cleavage. Purification was carried out at a flow rate of 20 mL/min with linear gradients of 10% A to 100% A over 10 min. The effluent was monitored by UV detection at 220 and 255 nm. After RP-HPLC purification the golden oil, azido-Cys(4-MeO-Bzl) (**24**), was obtained in 41% yield. $[\alpha]^{25}_D$ = -53.0 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 4.03 (dd, *J* = 5.3, 7.4 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 2H), 2.89 (dd, *J* = 5.3, 14.1 Hz, 1H), 2.75 (dd, *J* = 7.5, 14.2 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 172.8, 158.9, 130.1, 129.3, 114.1, 62.1, 55.3, 36.3, 32.2. Anal. Calcd. for $C_{11}H_{13}N_3O_3S$: C, 49.43; H, 4.90; N, 15.72. Found: C, 48.70; H, 5.00; N, 15.57.

**Azido-Tyr(*t*-Bu) (25).** L-Tyr(*t*-Bu) was used in the general diazo transer procedure to produce azido-Tyr(*t*-Bu) (**25**). The crude mixture was purified by the acid free RP-HPLC method described for compound **24** to give the yellow oil, **25**, in 70% yield. $[\alpha]^{25}_D$ = -40.7 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 4.12 (dd, *J* = 5.2, 8.8 Hz, 1H), 3.20 (dd, *J* = 4.9, 14.2 Hz, 1H), 3.00 (dd, *J* = 9.3, 14.2 Hz, 1H), 1.34 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.1, 154.4, 130.6, 129.8, 124.5, 79.0, 63.2, 37.0, 28.8. Anal. Calcd. for $C_{13}H_{17}N_3O_3$: C, 59.30; H, 6.51; N, 15.96. Found: C, 58.00; H, 6.55; N, 15.80.

**Azido-Arg(Mtr) (26).** L-Arg(Mtr) was used in the general diazo transer procedure to produce azido-Arg(Mtr) (**26**). The crude mixture was purified by the acid free RP-HPLC method described above to give the pale oil, **26**, in 46% yield. $[\alpha]^{25}_D$ = -19.5 (*c* = 1.0 in MeOH); $^1$H NMR (300 MHz, $CD_3OD$) δ 6.57 (s, 1H), 3.82 (dd, *J* = 5.2, 7.7 Hz, 1H), 3.75 (s, 3H), 3.10 (t, *J* = 6.7 Hz, 2H), 2.59 (s, 3H), 2.53 (s, 3H), 2.04 (s, 3H), 1.80-1.40 (m, 4H); $^{13}$C NMR (100 MHz, $CD_3OD$) δ 174.2, 160.4, 158.4, 140.0, 138.3, 135.6,

126.3, 113.3, 63.5, 56.5, 42.1, 30.1, 27.5, 24.9, 19.3, 12.6. Anal. Calcd. for $C_{16}H_{24}N_6O_5S$: C, 46.59; H, 5.86; N, 20.37. Found: C, 46.37; H, 5.90; N, 19.36.

**Azido-Lys(*t*-Boc) (27).** L-Lys(*t*-Boc) was used in the general diazo transer procedure to produce azido-Lys(*t*-Boc) (**27**). The crude mixture was purified by the acid free RP-HPLC method described above to give the pale oil, **27**, in 66% yield. $[\alpha]^{25}_{D}$ = -19.0 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 3.93 (t, *J* = 5.0 Hz, 1H), 3.13 (m, 2H), 2.10-1.80 (m, 2H), 1.70-1.45 (m, 4H), 1.45 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 174.5, 156.3, 79.7, 61.9, 40.2, 31.0, 29.5, 28.4, 22.9. Anal. Calcd. for $C_{11}H_{20}N_4O_4$: C, 48.52; H, 7.40; N, 20.58. Found: C, 48.04; H, 6.93; N, 20.16.

**Azido-His (28).** L-His was used in the procedure above with EtOAc extractions at pH 2 to remove the sulfonamide by-product. After concentration of the aqueous phase the product was purified and desalted using the above RP-HPLC system with heptafluorobutyric acid 0.1% added to solvents A and B to help retain polar azido-His (**28**) on the column. Also, a linear gradient of 0% A to 100% A over 10 min was used to give purified Azido-His (**28**) in (86% as the hydrate) yield. $[\alpha]^{25}_{D}$ = -102.1 (*c* = 1.0 in MeOH); $^1$H NMR (300 MHz, $CD_3OD$) δ 8.74 (s, 1H), 7.35 (s, 1H), 4.31 (dd, *J* = 5.1, 7.3 Hz, 1H), 3.18 (dd, *J* = 5.0, 15.4 Hz, 1H), 3.10 (dd, *J* = 7.3, 15.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CD_3OD$) δ 174.5, 135.3, 132.0, 118.9, 64.2, 28.8. Anal. Calcd. for $C_6H_7N_5O_2$: C, 39.78; H, 3.89; N, 38.66. Found: C, 33.09; H, 3.32; N, 26.05.

**General Peptide Synthesis.** The leader portion of peptides (sequences prior to iminophosphorane/ester condensations) and DKP forming standards (**29**–**32**, all Fmoc method) were synthesized using Wang resin solid phase methodology.[3] Generally resin bound methodology was carried out in parallel on a 100 μmol scale using 3 mL filtration tubes equipped with stopcocks in combination with a Burdick and Jackson multiport vacuum manifold system for resin washing. Each filtration tube was fitted with a cap for horizontal agitation on an orbital shaker during coupling reactions. Amide bond synthesis was carried out by activating 400 μmol of the requisite *N*-α-Fmoc protected amino acids or α-azido acids with 400 μmol each of HOBt and DCC (1M in $CH_2Cl_2$) in 1.5 mL DMF. These activated monomers were used to treat the resin-bound amines. Reactions were carried out for at least 1h with Kaiser test[14] monitoring and recoupled as necessary. For condensations with the secondary amino group of Pro residues, recoupling was routinely performed.

**Iminophosphorane mediated synthesis of DKP forming tripeptides (29–32) and peptides containing Ile diasteriomers for racemization analysis (33–36).** To each resin bound azido-dipeptide precursor was added the requisite *N*-α-Fmoc-OSu monomer (400 μmol, 4 equiv.) in dioxane (1.45 mL). Next, trimethylphosphine (1M in toluene) was added (150 μL, 1.5 equiv.) with effervescence noted for about 20 min. The reaction tube was capped and agitated 18 h on the orbital shaker. The solvent is removed by vacuum filtration and the resin is washed with DMF (5×), $CH_2Cl_2$ (5×), and $CH_3OH$ (3×). For peptides used in $^1$H-NMR racemization analysis (**33**–**36**) the Fmoc group was removed for clarity with 20% piperidine in DMF and washed as above. The resin was dried by aspiration for 20 min after which time TFA:$CH_2Cl_2$ (1:1) (1.5 mL) was added for 1 h. The crude peptide was collected into a glass tube and the resin washed an additional time with the cleavage solution. The crude peptides were concentrated under reduced pressure and those for racemization analysis (**33**–**36**) were used unpurified in $^1$H-NMR experiments. The DKP prone tripeptides (**29**–**32**) were purified with the general protocol and the linear gradient outlined for azido acid **24**, except that solvents A and B contained TFA 0.1%. After purification and concentration the tripeptides were analyzed by LC/MS and were found to be of greater than 95% purity with yields for **29**–**32** reported in Table 2.

**Synthesis of azido tetrapeptides utilizing the reduction-hydrolysis-coupling protocol (37–44).** The appropriate Wang resin bound azido dipeptide (50 μmol) was suspended in a mixture of dioxane (800 μL) and $H_2O$ (200 μL) to hydrolyze the iminophosphorane upon formation. Trimethylphosphine (1M in toluene) was added (300 μL, 300 μmol, 6.0 equiv.), capped, and shaken for 40 min. This was washed with anhydrous dioxane (3×) to remove excess trimethylphosphine. The next azido acid (200 μmol) to be

coupled was dissolved in 1.5 mL dioxane with *N*-hydroxysuccinimide (23 mg, 200 μmol). This was stirred on an ice bath while DCC 1M (200 μL, 200 μmol) was added and stirred for 45 min. This was subsequently used to treat the resin bound amine, with the resulting mixture capped and agitated for 18 h. The resin bound azido tripeptide was then washed with DMF (5×), $CH_2Cl_2$ (5×), and $CH_3OH$ (3×) and dried by aspiration. The coupling procedure was repeated to add the fourth monomer of the sequence. The azido tetrapeptides (**37**–**44**) were washed, cleaved and purified as described above with yields appearing in Table 2. Each was found to be of greater than 95% purity by LC/MS.