Supplementary Information

Supramolecular hydrogels based on short peptides linked with conformational switch

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Content

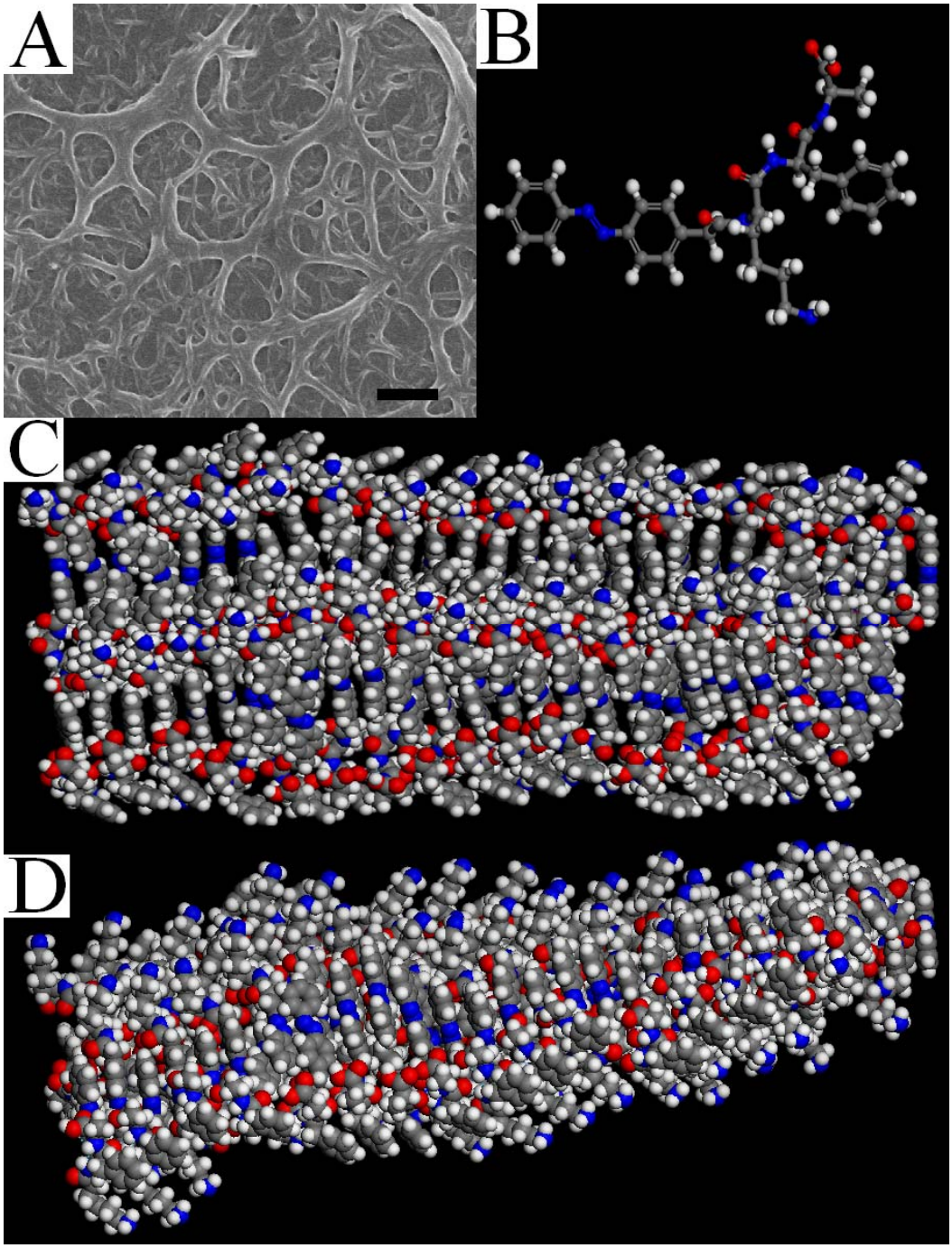


Figure 1 Proposed model of Azo-D-Lys-Phe-Ala a) SEM (scale bar=1μm) b)minimized energy structure of monomer c) top view of molecular self-assemble stacking model after minimized energy calculation d)side view of the model

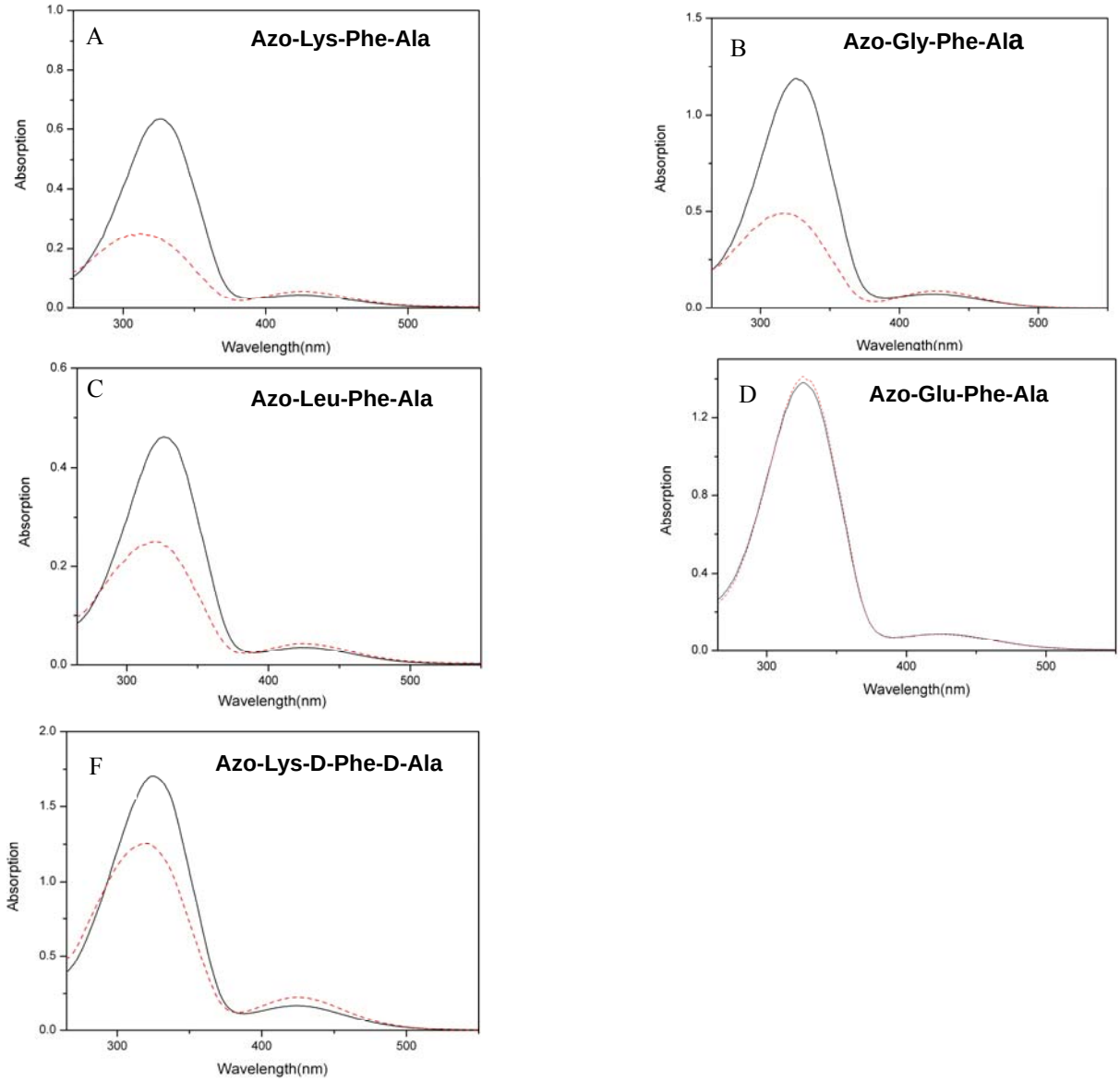


Figure 2 UV absorption of the hydrogels formed by A) Azo-Lys-Phe-Ala B) Azo-Gly-Phe-Ala C) Azo-Leu-Phe-Ala D) Azo-Glu-Phe-Ala E) Azo-Lys-D-Phe-D-Ala before (black solid line) and after (red dash) photo-irradiation

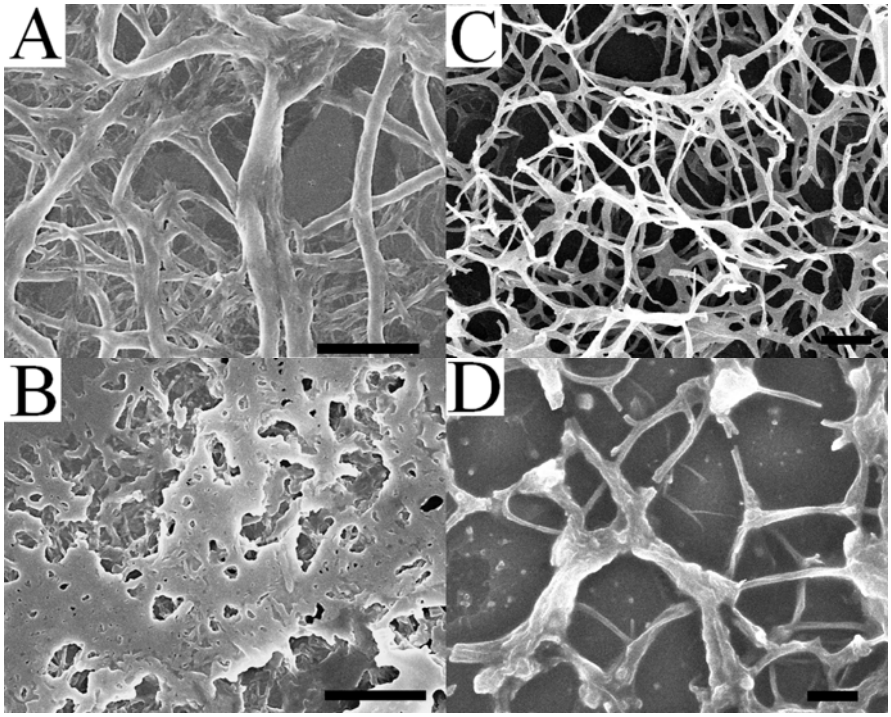


Figure 3 SEM images of the cryo-dried samples of Azo-Lys-D-Phe-D-Ala gel before (A) and after (B) photo-irradiation, Azo-Gln-Phe-Ala gel before (C) and after (D) photo-irradiation (scale bar represents 1μm)

NMR and MS of Azo-peptides.

(4-Phenylazophenyl)acetic Acid: ^{1}H NMR (300 MHz, DMSO-d_6) δ(ppm): 7.89(dd, 2H, *J*=1.7, 7.9 Hz), 7.86(d, 2H, *J*=8.4 Hz), 7.56-7.64(m, 3H), 7.50(d, 2H, *J*=8.4 Hz), 3.71(s, 2H); EI-MS: calc.(M)=240.09, find (M^+)=240.0.

Azo-Phe-Glu: ^{1}H NMR (300MHz,DMSO-d_6) δ (ppm): 8.39(t, 2H, J=7.5Hz), 7.88(dd, 2H, J=8.1Hz, 1.8Hz), 7.75(d, 2H, J=8.4Hz), 7.63-7.53(m, 3H), 7.28-7.17(m, 7H), 4.65-4.57(m, 1H), 4.28-4.21(m, 1H), 3.57-3.45(m, 2H), 3.06(dd, 1H, J=13.8Hz, 3.9Hz), 2.76(dd, 1H, J=14.1Hz, 10.5Hz), 2.33-2.27(m, 2H), 2.07-1.95(m, 1H), 1.87-1.77(m, 1H). ^{13}C NMR(75MHz,DMSO-d_6) δ (ppm): 173.8, 173.1, 171.5, 169.4, 152.0, 150.5, 140.2, 137.8, 131.4, 130.0, 129.5, 129.3, 128.0, 126.2, 122.5, 122.4, 53.7, 51.3, 41.9, 37.7, 30.0, 26.3.

Azo-Glu-Phe: ^{1}H NMR (300MHz,DMSO-d_6) δ (ppm): 8.31-8.23(m, 2H), 7.90-7.82(m, 4H), 7.63-7.55(m, 3H), 7.47(d, 2H, J=8.4Hz), 7.27-7.16(m, 5H), 4.46-4.30(m, 2H), 3.64-3.53(m, 2H), 3.06(dd,

1H, J=13.8Hz, 5.1Hz), 2.76(dd, 1H, J=13.5Hz, 9.0Hz), 2.23(t, 2H, J=7.8Hz),1.93-1.61(m, 2H). ^{13}C NMR(75MHz,DMSO-d_6) δ (ppm): 173.9, 172.8, 171.1, 169.5, 152.0, 150.6, 140.3, 137.4, 131.4, 130.1, 129.45, 129.1, 128.2, 126.4, 122.5, 122.5, 53.5, 51.6, 41.8, 36.5, 30.0, 27.7.

Azo-Phe-Ser: ^{1}H NMR (300MHz,DMSO-d_6) δ (ppm): 8.41-8.35(m, 2H), 7.88(dd, 2H, J=7.8Hz, 1.8Hz), 7.74(d, 2H, J=8.4Hz), 7.63-7.55(m, 3H), 7.30-7.18(m, 7H), 4.74-4.65(m, 2H), 4.33-4.30(m, 1H), 3.78-3.63(m, 2H), 3.56-3.44(m, 2H), 3.12-3.07(m, 1H), 2.79-2.75(m, 1H). ^{13}C NMR (75MHz,DMSO-d_6) δ (ppm): 171.9, 171.5, 169.3, 151.9, 150.5, 140.2, 137.9, 131.4, 123.0, 129.5, 129.3, 128.0, 126.2, 122.5, 122.3, 61.3, 54.7, 53.6, 41.9, 37.8.

Azo-Ser-Phe: ^{1}H NMR (300MHz,DMSO-d_6) δ (ppm): 8.19(d, 1H, J=7.8Hz), 8.05(d, 1H, J=7.8Hz), 7.90-7.81(m, 4H), 7.62-7.56(m, 3H), 7.50-7.44(m, 2H), 7.27-7.18(m, 5H) 4.58-4.35(m, 2H), 3.62-3.50(m, 4H), 3.11-2.87(m, 2H). ^{13}C NMR (75MHz,DMSO-d_6) δ (ppm): 172.6, 169.9, 169.7, 151.9, 150.6, 140.3, 137.3, 131.4, 130.2, 130.1, 129.4, 129.2, 129.1, 128.2, 128.1, 126.4, 122.5, 122.4, 61.7, 55.1, 53.4, 41.8, 36.7.

Azo-Phe-Ala: ^{1}HNMR (300MHz,DMSO-d_6) δ (ppm): 8.44-8.38(m, 2H), 7.88(dd, 2H, J=7.8Hz, 1.8Hz), 7.75(d, 2H, J=8.7Hz), 7.63-7.55(m, 3H), 7.30-7.17(m, 7H), 4.64-4.57(m, 1H), 4.28-4.18(m, 1H), 3.56-3.44(m, 2H), 3.06(dd, 1H, J=14.1Hz, 3.6Hz), 2.75(dd, 1H, J=13.8Hz, 10.5Hz), 1.30(d, 2H, J=7.2Hz). ^{13}C NMR (75MHz,DMSO-d_6) δ (ppm): 174.0, 171.1, 169.3, 151.9, 150.5, 140.2, 137.8, 131.4, 130.0, 129.5, 129.3, 128.0, 126.2, 122.5, 122.3, 53.6, 47.5, 41.9, 37.7, 17.1.

Azo-Ala-Phe: ^{1}H NMR(300MHz,DMSO-d_6) δ (ppm): 8.25(d, 1H, J=7.2Hz), 8.11(d, 1H, J=7.2Hz), 8.00-7.81(m, 4H), 7.62-7.55(m, 3H), 7.47(d, 2H, J=8.4Hz), 7.25-7.17(m, 5H), 4.47-4.33(m, 2H), 3.57(s, 2H), 3.06(dd, 1H, J=13.8Hz, 5.1Hz), 2.91(dd, 1H, J=13.8Hz, 8.7Hz), 1.20(d, 3H, J=7.2Hz). ^{13}C NMR**:** (75MHz,DMSO-d_6) δ (ppm): 172.7, 172.2, 169.2, 151.9, 150.6, 140.3, 137.4, 131.4, 130.1, 129.4, 129.1, 128.2, 126.4, 122.5, 122.4, 53.4, 47.9, 41.7, 36.6, 18.4.

Azo-Phe-Phe: ^{1}H NMR (300MHz,DMSO-d_6) δ (ppm): 8.35(t, 2H, J=7.5Hz), 7.88(d, 2H, J=7.5Hz), 7.84(d, 2H, J=8.4Hz), 7.58(m, 3H), 7.22(m, 12H), 4.64-4.56(m, 1H), 4.50-4.43(m, 1H), 3.54-3.41(m, 2H), 3.12-2.89(m, 3H), 2.76-2.68(m, 1H). ^{13}C NMR:(75MHz,DMSO-d_6) δ (ppm): 172.7, 171.3, 169.2, 151.9, 150.5, 140.2, 137.7, 137.4, 131.4, 131.4, 130.0, 129.5, 129.3, 128.2, 128.0, 126.4, 126.2, 122.5, 122.3, 53.6, 53.5, 41.9, 37.7, 36.6.

Azo-Phe-Tyr: ^{1}H NMR (300MHz,DMSO-d_6) δ (ppm): 8.34(d, 1H, J=8.7Hz), 8.28(d, 1H, J=8.1Hz),

7.89(dd, 2H, J=8.1Hz, 1.8Hz), 7.74(d, 2H, J=8.4Hz), 7.63-7.56(m, 3H), 7.25-7.17(m, 7H), 7.02(d, 2H, J=8.7Hz), 6.66(d, 2H, J=8.7Hz), 4.64-4.56(m, 1H), 4.41-4.34(m, 1H), 3.55-3.41(m, 2H), 3.05-2.92(m, 2H), 2.85-2.68(m, 2H). ^{13}C NMR: (75MHz,DMSO-d_6) δ (ppm): 172.8, 171.2, 169.2, 156.0, 151.9, 150.5, 140.2, 137.7, 131.4, 130.1, 130.0, 129.4, 129.3, 128.0, 127.3, 126.2, 122.5, 122.3, 115.0, 53.8, 53.6, 41.9, 37.6, 35.9.

Azo-Tyr-Ala: ^{1}H NMR (300MHz,DMSO-d_6) δ (ppm): 8.37(d, 1H, J=7.2Hz), 8.32(d, 1H, J=9.0Hz), 7.88(dd, 2H, J=7.8Hz, 1.8Hz), 7.77(d, 2H, J=8.4Hz), 7.63-7.56(m, 3H), 7.26(d, 2H, J=8.1Hz), 7.05(d, 2H, J=8.4Hz), 6.64(d, 2H, J=8.4Hz), 4.56-4.48(m, 1H), 4.27-4.17(m, 1H), 3.57-3.44(m, 2H), 2.95(dd, 1H, J=13.8Hz, 3.6Hz), 2.63(dd, 1H, J=13.5Hz, 10.5Hz), 1.29(d, 3H, J=7.2Hz).^{13}C NMR (75MHz,DMSO-d_6) δ (ppm): 174.0, 171.3, 169.3, 155.8, 152.0, 150.5, 140.3, 131.4, 130.2, 130.0, 129.5, 127.9, 122.5, 122.4, 114.8, 54.0, 47.5, 41.9, 37.0, 17.1.

Azo-Tyr-Tyr: ^{1}H NMR (300MHz,DMSO-d_6) δ (ppm): 9.19(d, 2H, J=12.3Hz), 8.29-8.21(m, 2H), 7.88(dd, 2H, J=8.1Hz, 1.5Hz), 7.76(d, 2H, J=8.4Hz), 7.62-7.56(m, 3H), 7.24(d, 2H, J=8.4Hz), 7.02(dd, 4H, J=8.4Hz, 1.5Hz), 6.64(dd, 4H, J=9.9Hz, 8.4Hz), 4.55-4.48(m, 1H), 4.40-4.32(m, 1H), 3.57-3.41(m, 2H), 2.97-2.57(m, 4H). ^{13}C NMR (75MHz,DMSO-d_6) δ (ppm): 172.9, 171.4, 169.3, 156.0, 155.8, 152.0, 150.5, 140.2, 131.4, 130.2, 130.1, 130.0, 129.5, 127.8, 127.4, 122.5, 122.4, 115.0, 114.8, 54.0, 53.8, 41.9, 36.9, 36.0.

Azo-Glu-Tyr: ^{1}H NMR (300MHz,DMSO-d_6) δ (ppm): 9.19(s, 1H), 8.27(d, 1H, J=5.1Hz), 8.12(d, 1H, J=7.5Hz), 7.90-7.82(m, 4H), 7.62-7.56(m, 3H), 7.47(d, 2H, J=8.4Hz), 7.00(d, 2H, J=8.7Hz), 6.65(d, 2H, J=8.7Hz), 4.37-4.30(m, 2H), 3.65-3.53(m, 2H), 2.92(dd, 1H, J=14.1Hz, 4.8Hz), 2.79(dd, 1H, J=13.8Hz, 8.4Hz), 2.22(t, 2H, J=7.5Hz), 1.93-1.69(m, 2H). ^{13}C NMR (75MHz,DMSO-d_6) δ (ppm): 173.9, 172.9, 171.1, 169.5, 155.9, 152.0, 150.6, 140.3, 131.4, 130.1, 130.0, 129.5, 127.4, 122.5, 115.0, 53.8, 51.6, 41.8, 35.8, 30.0, 27.7.

Azo-Gln-Tyr: ^{1}H NMR (300MHz,DMSO-d_6) δ (ppm): 9.21(s, 1H), 8.28(d, 1H, J=7.8Hz), 8.12(d, 1H, J=7.5Hz), 7.90-7.82(m, 4H), 7.62-7.56(m, 3H), 7.47(d, 2H, J=8.4Hz), 7.24(s, 1H), 7.00(d, 2H, J=8.7Hz), 6.76(s, 1H), 6.64(d, 2H, J=8.4Hz), 4.37-4.26(m, 2H), 3.64-3.53(m, 2H), 2.91(dd, 1H, J=13.8Hz, 5.1Hz), 2.78(dd, 1H, J=13.8Hz, 8.4Hz), 2.09-2.06(m, 2H), 1.92-1.86(m, 1H), 1.73-1.65(m, 1H). ^{13}C NMR: (75MHz,DMSO-d_6) δ (ppm): 173.8, 172.9, 171.3, 169.5, 156.0, 152.0, 150.6, 140.3, 131.4, 130.2, 130.1, 129.5, 127.3, 122.5, 115.0, 53.8, 52.0, 41.8, 35.9, 31.4, 28.2.

Azo-Gln-Gln: ^{1}H NMR (300MHz,DMSO-d_6) δ (ppm): 8.34-8.27(m, 2H), 7.90-7.83(m, 4H), 7.63-

7.55(m, 3H), 7.48(d, 2H, J=8.4Hz), 7.25(s, 2H), 6.77(s, 2H), 4.33-4.29(m, 1H), 4.17-4.13(m, 1H), 3.62-3.60(m, 2H), 2.15-2.09(m, 4H), 1.99-1.91(m, 2H), 1.79-1.69(m, 2H). ^{13}C NMR (75MHz,DMSO-d_6) δ (ppm): 173.8, 173.5, 173.3, 171.5, 169.6, 152.0, 150.6, 140.3, 131.4, 130.2, 129.5, 122.5, 52.1, 51.6, 41.8, 31.5, 31.3, 28.3, 26.7.

Azo-Glu-Ala: ^{1}H NMR (300MHz,DMSO-d_6) δ (ppm): 8.34(d, 1H, J=8.4Hz), 8.30(d, 1H, J=6.9Hz), 7.90-7.82(m, 4H), 7.63-7.56(m, 3H), 7.48(d, 2H, J=8.4Hz), 4.37-4.29(m, 1H), 4.23-4.13(m, 1H), 3.61(d, 2H, J=2.7Hz), 2.30-2.24(m, 2H), 1.92-1.72(m, 3H), 1.27(d, 2H, J=7.5Hz). ^{13}C NMR (75MHz,DMSO-d_6) δ (ppm): 174.0, 171.0, 169.6, 152.0, 150.6, 140.4, 131.4, 130.1, 129.5, 122.5, 122.5, 51.6, 47.5, 41.8, 30.0, 27.8, 16.9.

Azo-Arg-Ala: ^{1}H NMR (300MHz,DMSO-d_6) δ (ppm): 8.37(d, 1H, J=7.5Hz), 8.20(d, 1H, J=6.9Hz), 7.89-7.76(m, 5H), 7.62-7.48(m, 5H), 7.32-7.00(m, 4H), 4.35-4.14(m, 2H), 3.62(s, 2H), 3.09-3.08(m, 2H), 1.74-1.50(m, 4H), 1.26(d, 3H, J=7.2Hz), 1.12(d, 2H, J=6.3Hz). ^{13}C NMR: (75MHz,DMSO-d_6) δ (ppm): 174.3, 171.1, 169.7, 156.8, 151.9, 150.6, 140.4, 131.4, 130.2, 129.5, 122.5, 51.9, 47.8, 41.8, 29.5, 24.8, 23.1, 17.2.

Azo-Arg-Phe: ^{1}H NMR (300MHz,DMSO-d_6) δ (ppm): 8.33(t, 1H, J=8.1Hz), 8.24(t, 1H, J=8.1Hz), 7.90-7.82(m, 4H), 7.63-7.56(m, 4H), 7.76(d, 2H, J=8.4Hz), 7.26-7.15(m, 10H), 4.44-4.31(m, 2H), 3.60-3.59(m, 2H), 3.09-3.03(m, 1H), 2.94-2.86(m, 1H), 1.64-1.38(m, 4H), 1.12(d, 2H, J=6.3). ^{13}C NMR (75MHz,DMSO-d_6) δ (ppm): 173.2, 171.8, 170.1, 157.2, 152.4, 151.1, 140.8, 137.9, 131.9, 130.6, 129.9, 129.6, 128.6, 126.9, 123.0, 54.0, 52.5, 42.3, 37.1, 29.9, 25.4, 23.6.

Azo-Ser-Ala: ^{1}H NMR (300MHz,DMSO-d_6) δ (ppm): 8.27(d, 1H, J=8.1Hz), 8.16(d, 1H, J=7.2Hz), 7.90-7.81(m, 4H), 7.63-7.47(m, 5H), 4.40-4.34(m, 1H), 4.25-4.20(m, 1H), 3.64-3.53(m, 3H), 1.27(d, 3H, J=7.5Hz). ^{13}C NMR (75MHz,DMSO-d_6) δ (ppm): 174.0, 169.8, 169.7, 152.0, 150.6, 140.4, 131.4, 130.2, 129.5, 122.5, 122.4, 61.8, 55.1, 47.5, 41.9, 17.3.

Azo-Lys-Ala: ^{1}H NMR (300MHz,DMSO-d_6) δ (ppm): 8.34(d, 1H, J=8.7Hz), 8.28(d, 1H, J=7.2Hz), 7.90-7.76(m, 7H), 7.69-7.53(m, 3H), 7.49(d, 2H, J=8.4Hz), 4.35-4.28(m, 1H), 4.24-4.15(m, 1H), 3.60(s, 2H), 2.73(t, 2H, J=6.9Hz), 1.71-1.47(m, 4H), 1.37-1.26(m, 5H). ^{13}C NMR: (75MHz,DMSO-d_6) δ (ppm): 174.0, 171.4, 169.5, 151.9, 150.6, 140.4, 131.4, 130.1, 129.5, 122.5, 122.5, 51.9, 47.5, 41.9, 38.7, 31.74, 26.7, 22.1, 17.0.

Azo-Gln-Phe-Ala: ^{1}H NMR (300M, DMSO-d_6) δ(ppm): 8.29(d, 1H, *J*=7.2 Hz), 8.27(d, 1H, *J*=7.7 Hz),

8.03(d, 1H, *J*=8.4 Hz), 7.89(dd, 2H, *J*=1.5, 8.1 Hz), 7.83(d, 2H, *J*=8.4 Hz), 7.56-7.64 (m, 3H), 7.47(d, 2H, *J*=8.5 Hz), 7.16-7.31 (m, 6 H), 6.78(s, 1H), 4.51-4.58(m, 1H), 4.19-4.28(m, 2H), 3.57(dd, 2H, *J*=14.4, 18.6 Hz), 3.06(dd, 1H, *J*=4.2, 13.5 Hz), 2.79(dd, 1H, *J*=9.3, 14.1 Hz), 2.04-2.09(m, 2H), 1.65-1.90(m, 2H), 1.28(d, 3H, *J*=7.5 Hz); ESI-MS: calc.(M)=586.25, find (M-1)=585.67.

Azo-Glu-Phe-Ala: ^{1}H NMR (300 M, CD_3OD) δ(ppm): 7.90(dd, 2H, *J*=1.5, 8.0 Hz), 7.86(d, 2H, *J*=8.5 Hz), 7.49-7.56(m, 3H), 7.45(d, 2H, *J*=8.5 Hz), 7.14-7.23(m, 5H), 4.65(dd, 1H, *J*=5.2, 9.2 Hz), 4.31-4.41(m, 2H), 3.63(s, 2H), 3.18(dd, 1H, *J*=5.1, 14.0 Hz), 2.86-2.98(m, 2H), 2.26-2.31(m, 2H), 1.83-2.04(m, 2H), 1.36(d, 3H, *J*=8.5 Hz); ESI-MS: calc.(M)=587.24, find (M-1)=586.42.

Azo-Leu-Phe-Ala: ^{1}H NMR (300 M, DMSO-d_6) δ(ppm): 8.25(d, 1H, *J*=8.1 Hz), 8.19(d, 1H, *J*=7.4 Hz), 7.93(d, 1H, *J*=8.4), 7.89(dd, 2H, *J*=1.5, 8.1 Hz), 7.83(d, 2H, *J*=8.6 Hz), 7.56-7.64(m, 3H), 7.46(d, 2H, *J*=8.4 Hz), 7.14-7.23(m, 5H), 4.50-4.57(m, 1H), 4.17-4.29(m, 2H), 3.56(dd, 2H, *J*=14.2, 21.6 Hz), 3.06(dd, 1H, *J*=4.1, 13.8 Hz), 2.82(dd, 1H, *J*=9.5, 14.0 Hz), 1.46-1.56(m, 1H), 1.38(t, 2H, *J*=7.4 Hz), 1.27(d, 3H, *J*=7.2 Hz) , 0.85(d, 3H, *J*=6.5 Hz) , 0.78(d, 3H, *J*=6.6 Hz); ESI-MS: calc.(M)=571.28, find (M-1)=570.75.

Azo-Gly-Phe-Ala: ^{1}H NMR (300 M, DMSO-d_6) δ: (ppm) 8.38(d, 1H, *J*=7.3 Hz), 8.30(t, 1H, *J*=5.4 Hz), 8.12(d, 1H, *J*=8.5 Hz), 7.89(dd, 2H, *J*=1.6, 8.0 Hz) , 7.83(d, 2H, *J*=8.5 Hz), 7.56-7.64(m, 3H), 7.48(d, 2H, *J*=8.2 Hz), 7.16-7.26(m, 5H), 4.54-4.61(m, 1H), 4.22(quint, 1H, *J*=7.3 Hz), 3.77(dd, 1H, *J*=6.1, 16.8 Hz) , 3.59(dd, 1H, *J*=5.4, 16.4 Hz) , 3.58(s, 2H), 3.05(dd, 1H, *J*=3.9, 14.0 Hz) , 2.75(dd, 1H, *J*=9.7, 13.9 Hz), 1.30(d, 3H, *J*=7.4 Hz); ESI-MS: calc.(M)=515.22, find (M-1)=514.50.

Azo-Lys-Phe-Ala: ^{1}H NMR (300 M, DMSO-d_6) δ(ppm): 8.28(d, 2H, *J*=7.1 Hz), 7.99(d, 1H, J=8.0 Hz), 7.89(dd, 2H, *J*=1.7, 8.0 Hz), 7.83(d, 2H, *J*=7.6 Hz), 7,73(br, 2H), 7.56-7.64(m, 3H), 7.47(d, 2H, *J*=7.4 Hz), 7.17-7.24(m, 5H), 4.52-4.59(m, 1H), 4.18-4.27(m, 2H), 3.58(dd, 2H, *J*=14.2, 18.8 Hz), 3.07(dd, 1H, *J*=4.1, 13.9 Hz) , 2.80(dd, 1H, *J*=9.7, 13.9 Hz), 2.70-2.76(m, 2H), 1.40-1.62(m, 4H), 1.28(d, 3H, *J*=7.5 Hz), 1.16-1.29(m, 2H); ESI-MS: calc.(M)=586.29, find (M+1)=587.25.

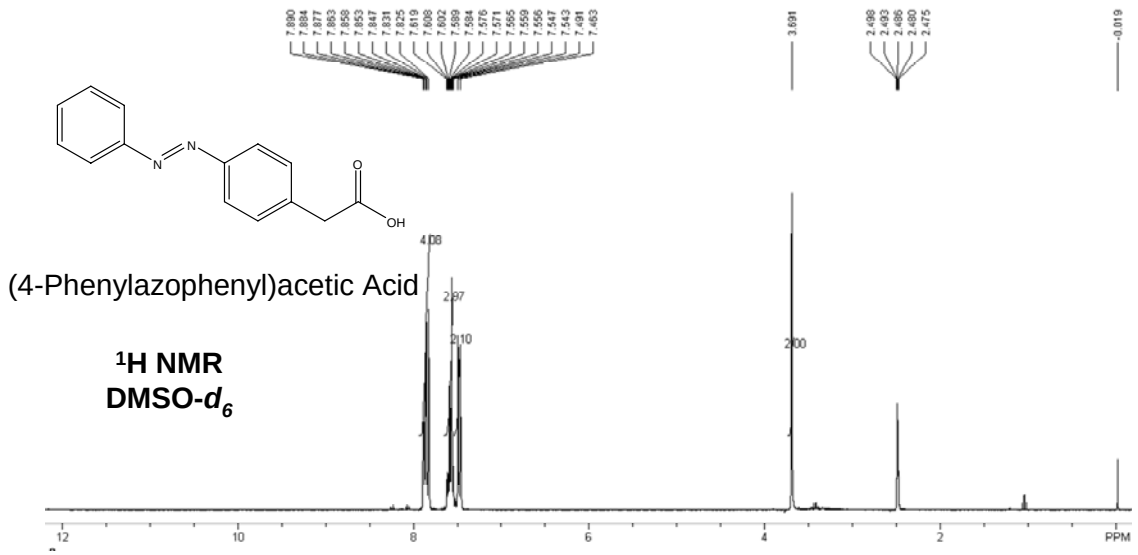
Azo-VYGGG(ESI-MS): calc.(M)= 673.72, find (M-1)=672.58;
Azo-GAGAS(ESI-MS): calc.(M)= 583.59, find (M-1)=582.67;
Azo-SDKP(ESI-MS): calc.(M)=667.71, find (M-1)=666.50;
Azo-VPP(ESI-MS): calc.(M)=533.62, find (M-1)=532.67;
Azo-YIGSR(ESI-MS): calc.(M)=816.90, find (M+1)=817.42;
Azo-IKVAV(ESI-MS): calc.(M)=750.93, find (M+1)=751.75;

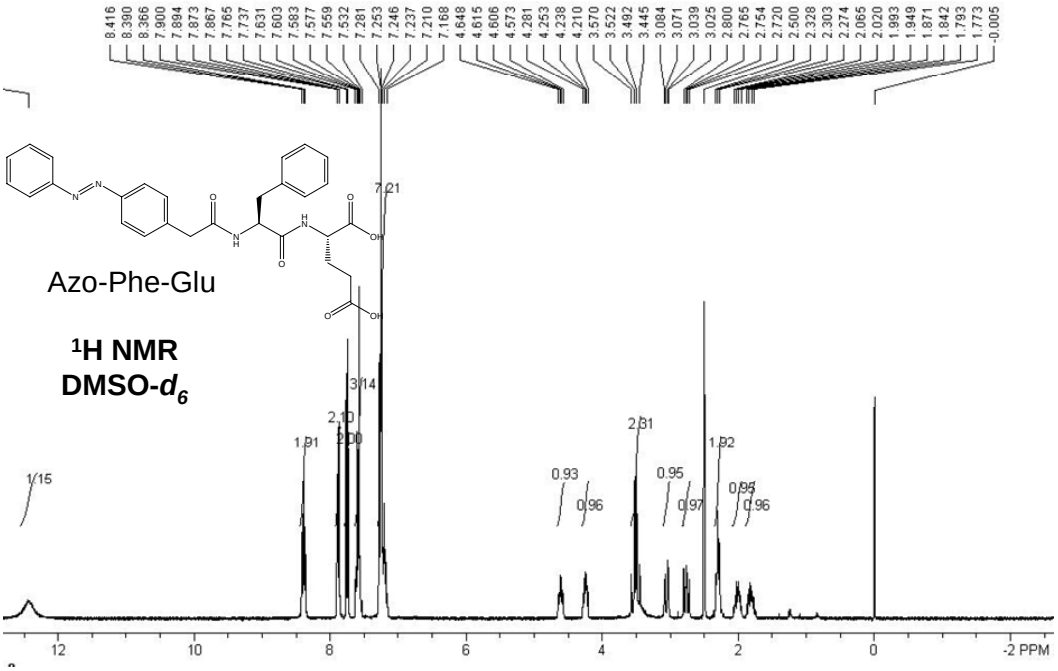
Azo-RGD (ESI-MS): calc.(M)=568.58, find (M+1)=569.42;

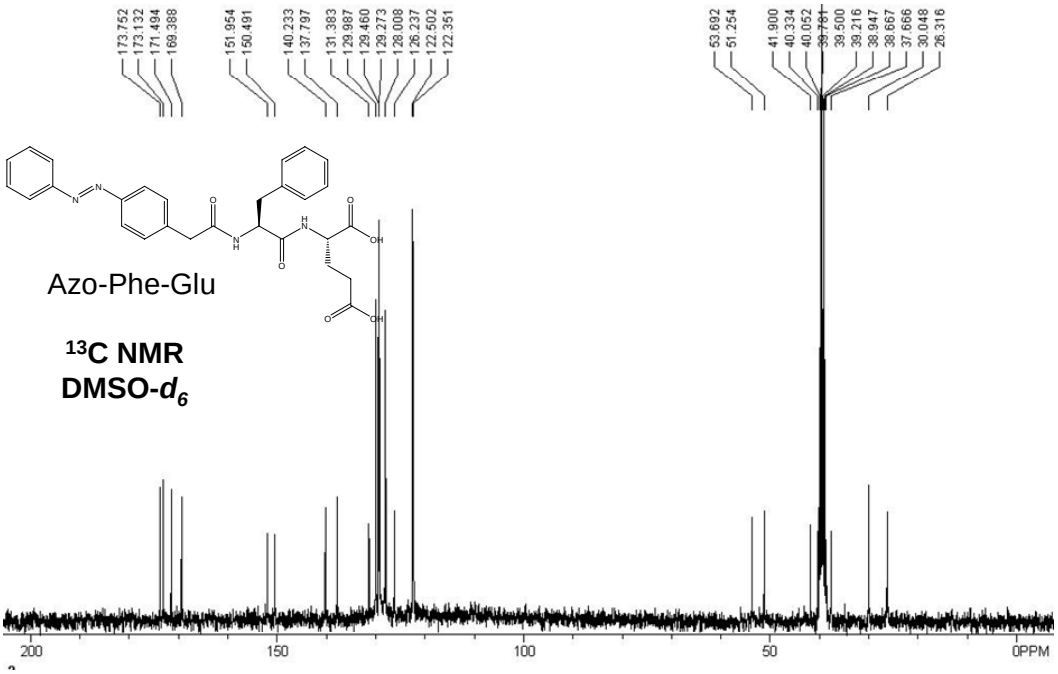
Azo-LGAGGAG (ESI-MS): calc.(M)=723.78, find (M+Na)=746.50;

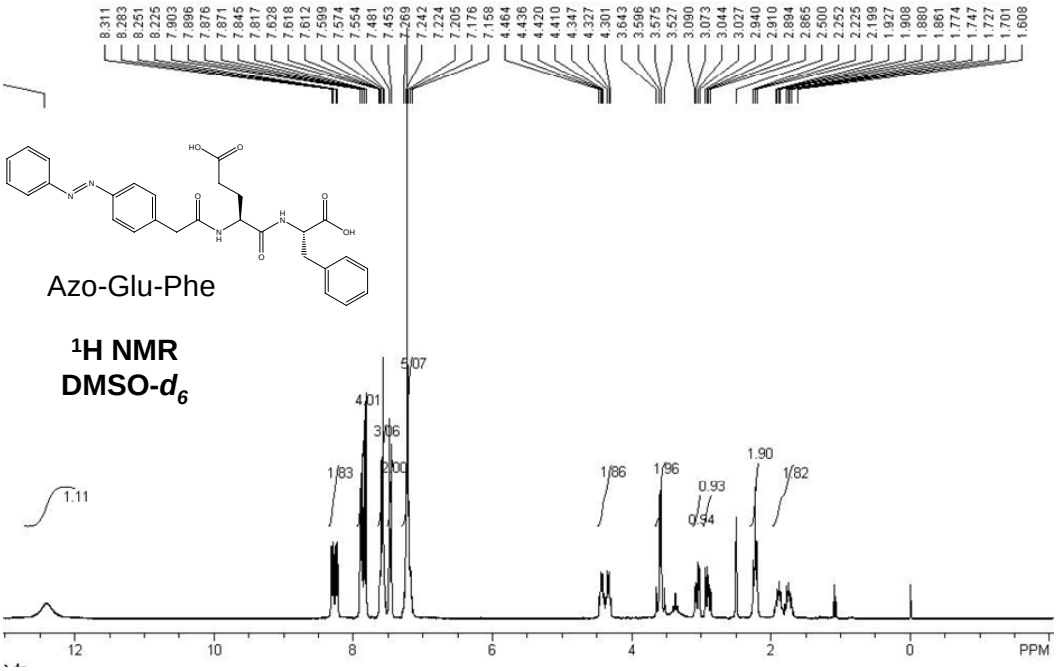
Azo-VVPQ (ESI-MS): calc.(M)=663.76, find (M+1)=664.33;

Azo-YSV (ESI-MS): calc.(M)=589.64, find (M+1)=590.17;




Azo-Phe-Glu
1H NMR
DMSO-d6
12
10
8
6
4
2
0
-2 PPM


Azo-Phe-Glu
13C NMR
DMSO-d6
200
150
100
50
0PPM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7.871
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7.618
7.612
7.599
7.574
7.554
7.481
7.453
7.269
7.242
7.224
7.205
7.176
7.158
4.464
4.436
4.420
4.410
4.347
4.327
4.301
3.643
3.596
3.575
3.527
3.090
3.073
3.044
3.027
2.940
2.910
2.894
2.865
2.500
2.252
2.225
2.199
1.927
1.908
1.880
1.861
1.774
1.747
1.727
1.701
1.608
Azo-Glu-Phe
1H NMR
DMSO-d6
5.07
4.01
3.06
2.00
1.83
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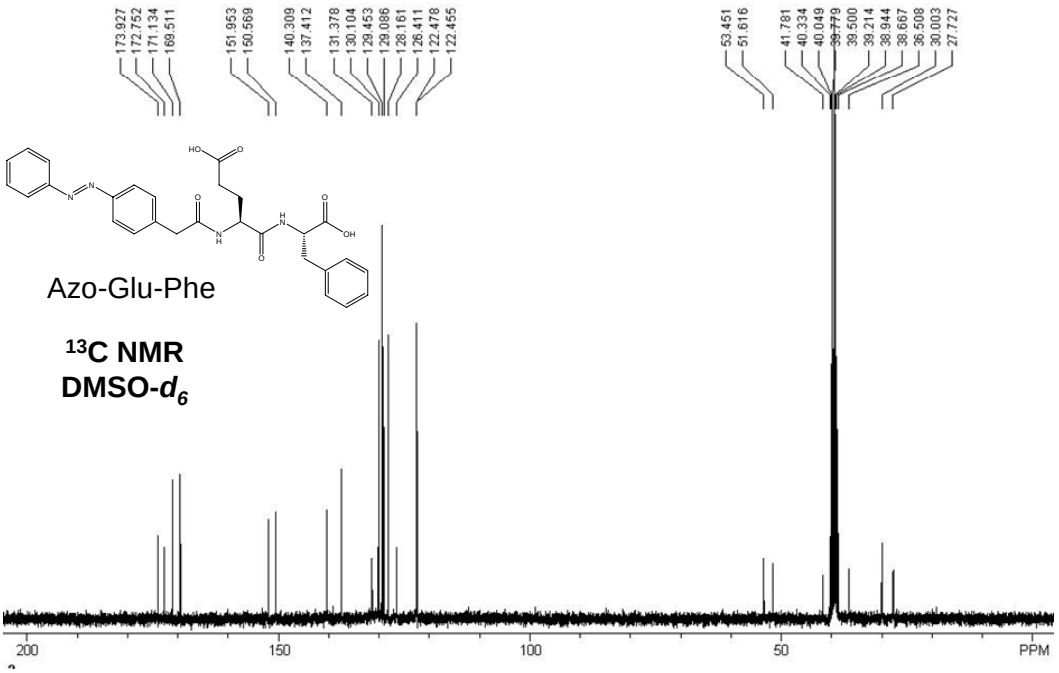
1.96
0.93
0.94
1.90
1.82
12
10
8
6
4
2
0
PPM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171.134
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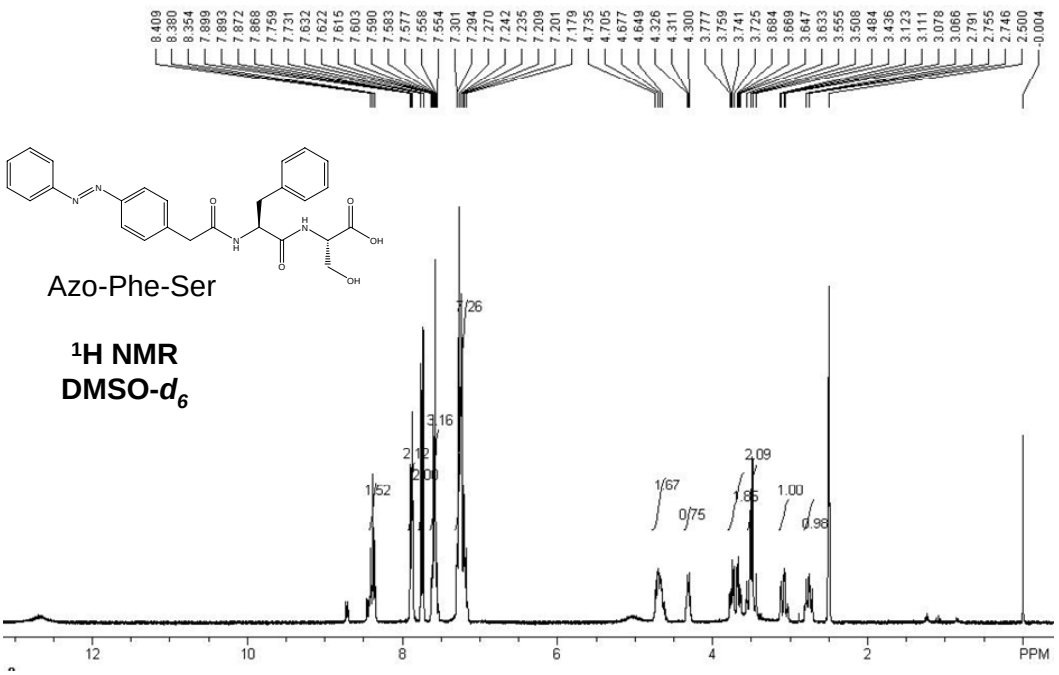
128.161
126.411
122.478
122.455
53.451
51.616
41.781
40.334
40.049
39.779
39.500
39.214
38.944
38.667
36.508
30.003
27.727
Azo-Glu-Phe
13C NMR
DMSO-d6
200
150
100
50
PPM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8.354
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7.759
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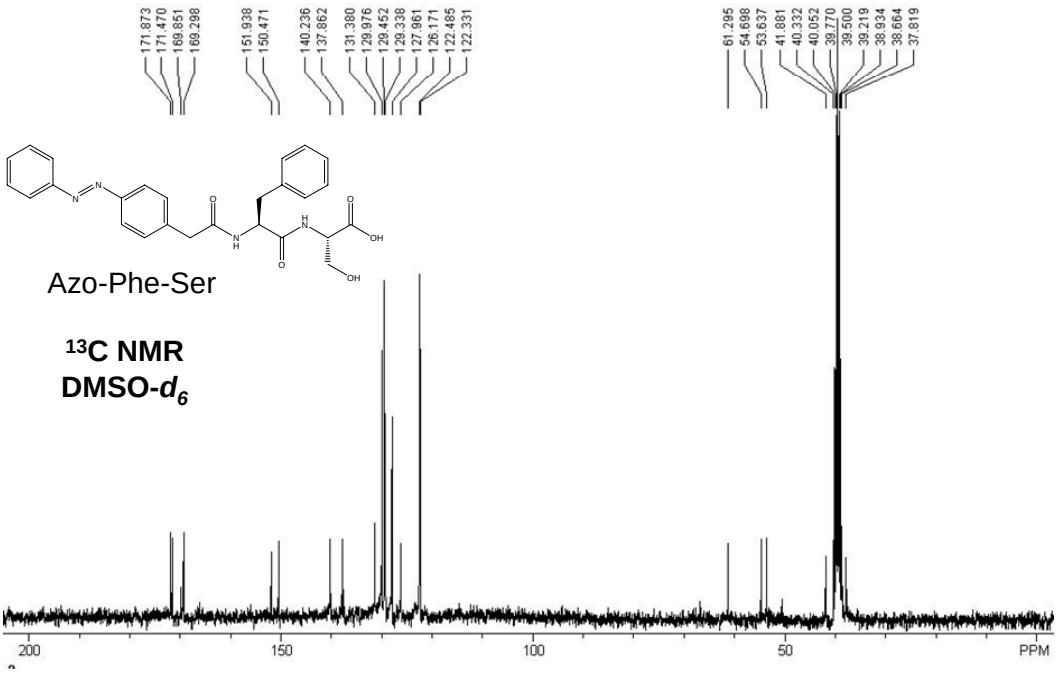
7.622
7.615
7.603
7.590
7.583
7.577
7.558
7.554
7.301
7.294
7.270
7.242
7.235
7.209
7.201
7.179
4.735
4.705
4.677
4.649
4.326
4.311
4.300
3.777
3.759
3.741
3.725
3.684
3.669
3.647
3.633
3.555
3.508
3.484
3.436
3.123
3.111
3.078
3.066
2.791
2.755
2.746
2.500
-0.004
Azo-Phe-Ser
1H NMR
DMSO-d6
7.26
3.16
2.12
2.00
1.52
2.09
1.67
1.86
1.00
0.75
0.98
12
10
8
6
4
2
PPM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137.862
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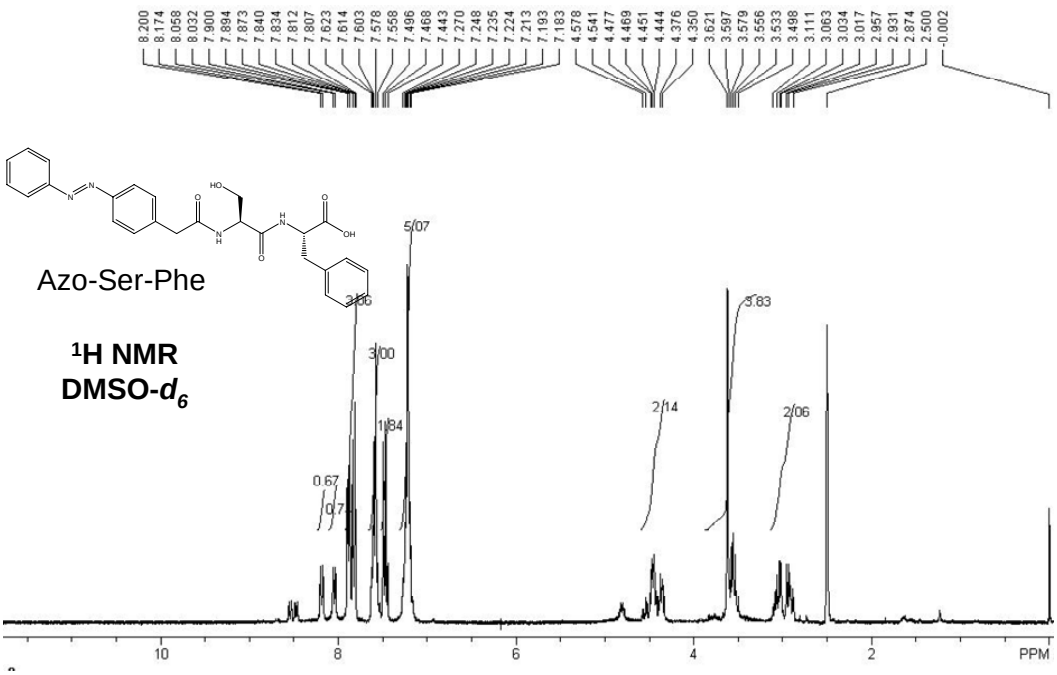
127.961
126.171
122.485
122.331
61.295
54.698
53.637
41.981
40.332
40.052
39.770
39.500
39.219
38.934
38.664
37.819
Azo-Phe-Ser
13C NMR
DMSO-d6
200
150
100
50
PPM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7.840
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7.812
7.807
7.623
7.614
7.603
7.578
7.558
7.496
7.468
7.443
7.270
7.248
7.235
7.224
7.213
7.193
7.183
4.578
4.541
4.477
4.469
4.451
4.444
4.376
4.350
3.621
3.597
3.579
3.556
3.533
3.498
3.111
3.063
3.034
3.017
2.957
2.931
2.874
2.500
-0.002
Azo-Ser-Phe
1H NMR
DMSO-d6
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3.00
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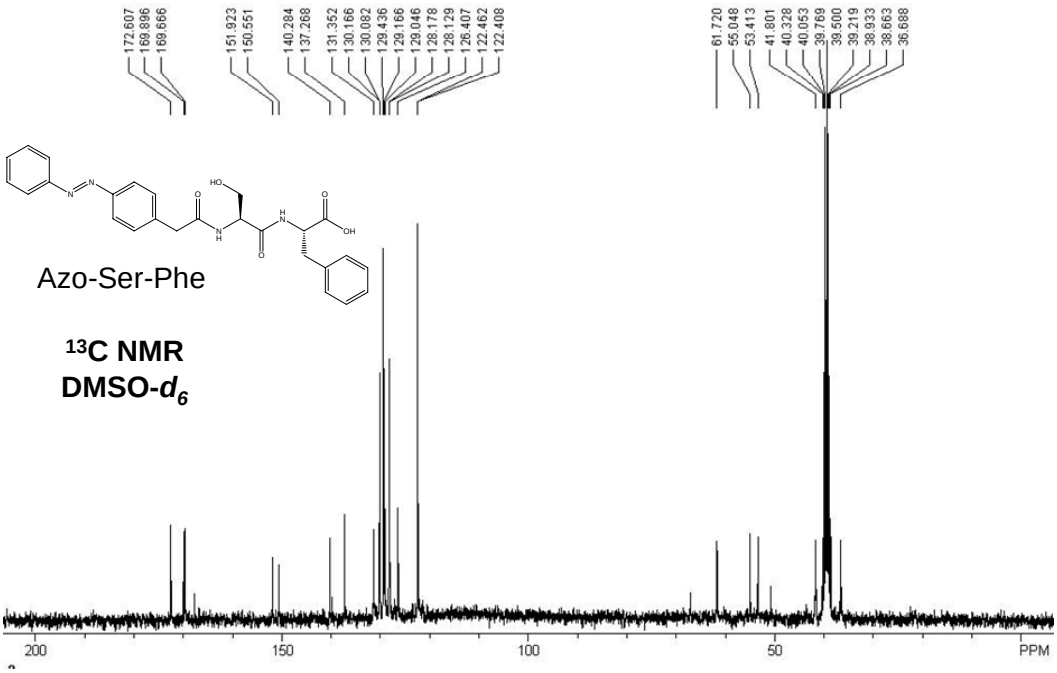
2.06
1.84
0.67
10
8
6
4
2
PPM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122.462
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61.720
55.048
53.413
41.801
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40.053
39.769
39.500
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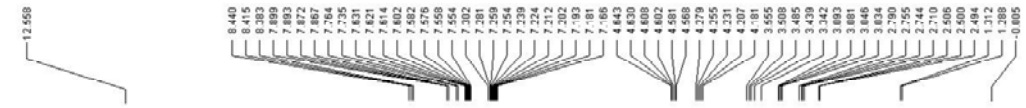
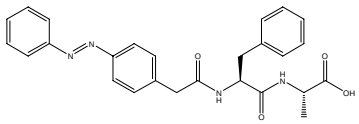
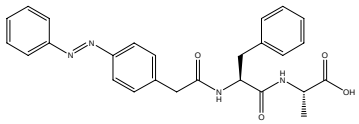
38.663
36.688
Azo-Ser-Phe
13C NMR
DMSO-d6
200
150
100
50
PPM





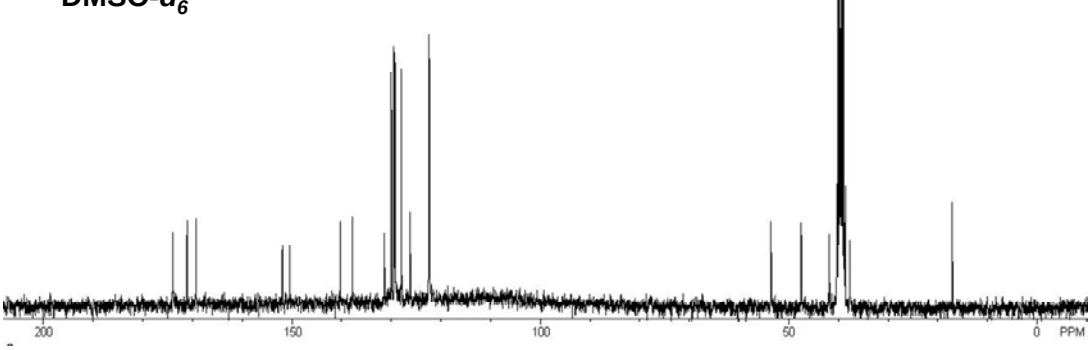
Azo-Phe-Ala

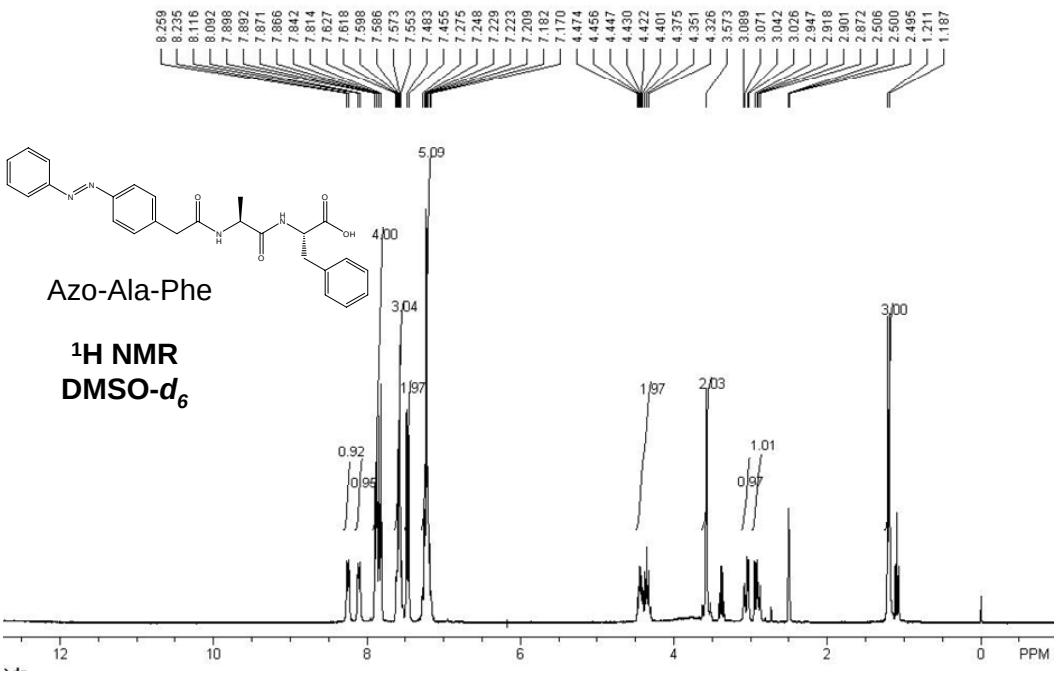
^{1}H NMR
DMSO-*d*$_6$



Azo-Phe-Ala

^{13}C NMR
DMSO-*d*$_6$

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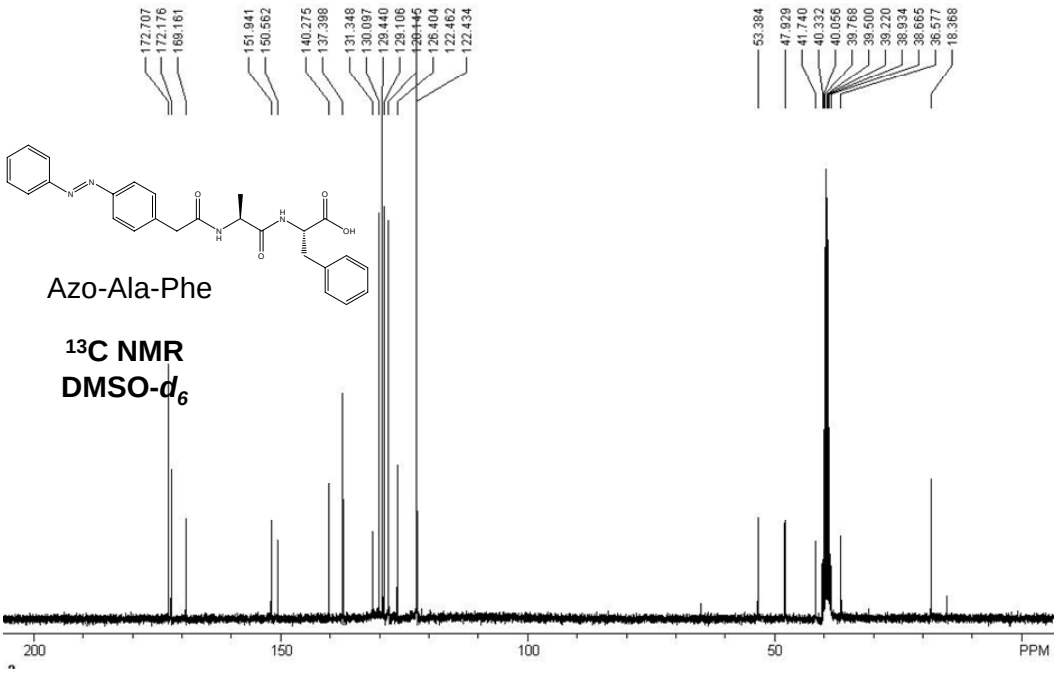
7.814
7.627
7.618
7.598
7.586
7.573
7.553
7.483
7.455
7.275
7.248
7.229
7.223
7.209
7.182
7.170
4.474
4.456
4.447
4.430
4.422
4.401
4.375
4.351
4.326
3.573
3.089
3.071
3.042
3.026
2.947
2.918
2.901
2.872
2.506
2.500
2.495
1.211
1.187
5.09
4.00
3.04
1.97
0.92
0.95
1.97
2.03
1.01
0.97
3.00
Azo-Ala-Phe
1H NMR
DMSO-d6
12
10
8
6
4
2
0
PPM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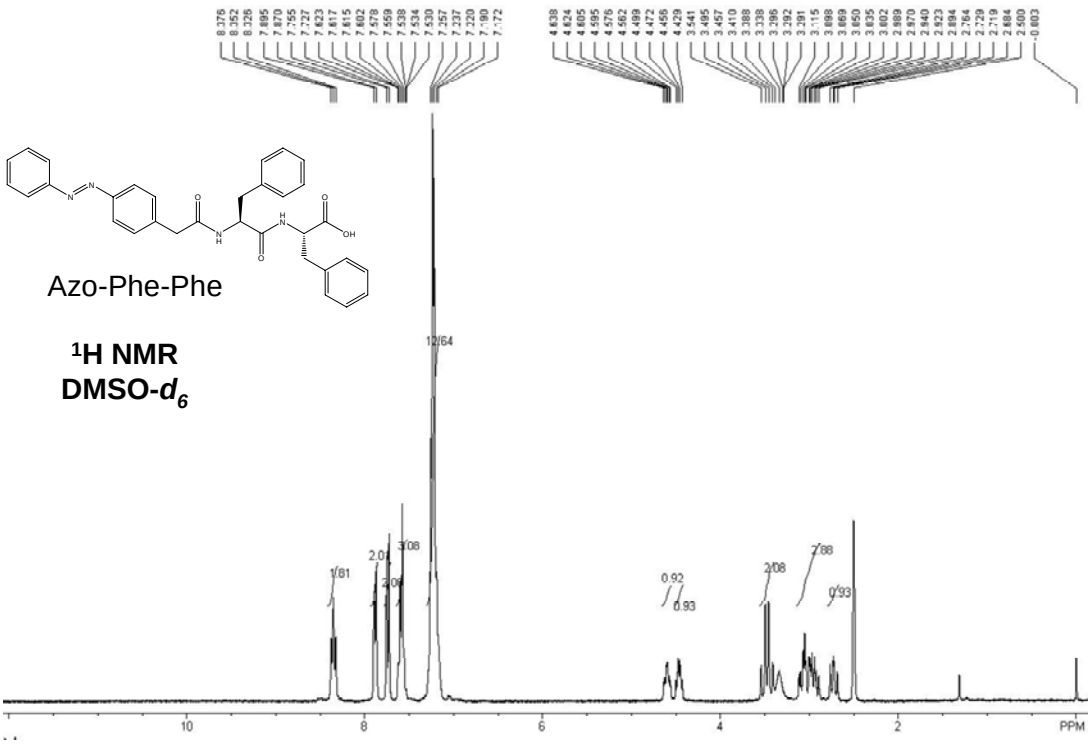
129.106
126.404
122.462
122.434
53.384
47.929
41.740
40.332
40.056
39.768
39.500
39.220
38.934
38.665
36.577
18.368
Azo-Ala-Phe
13C NMR
DMSO-d6
200
150
100
50
PPM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1H NMR
DMSO-d6
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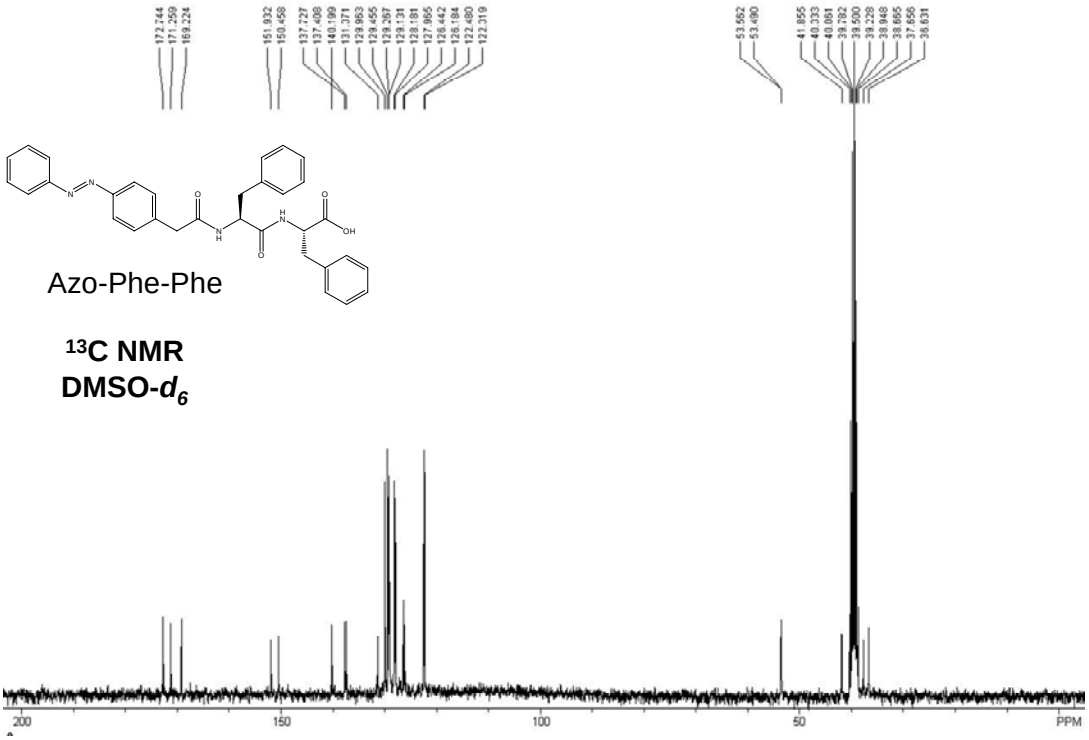
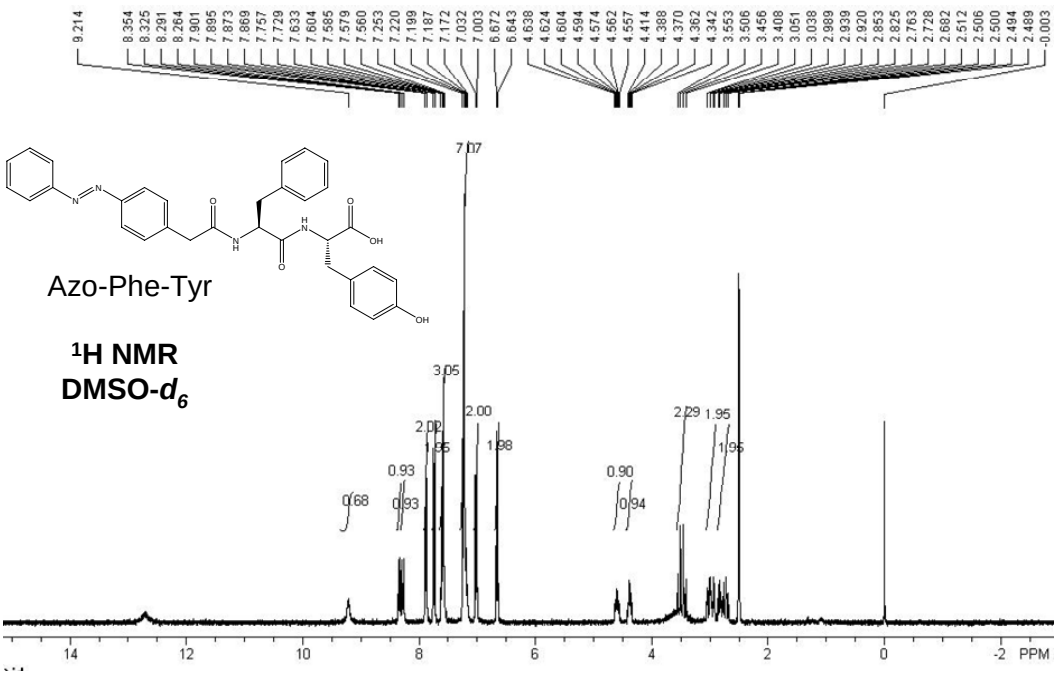
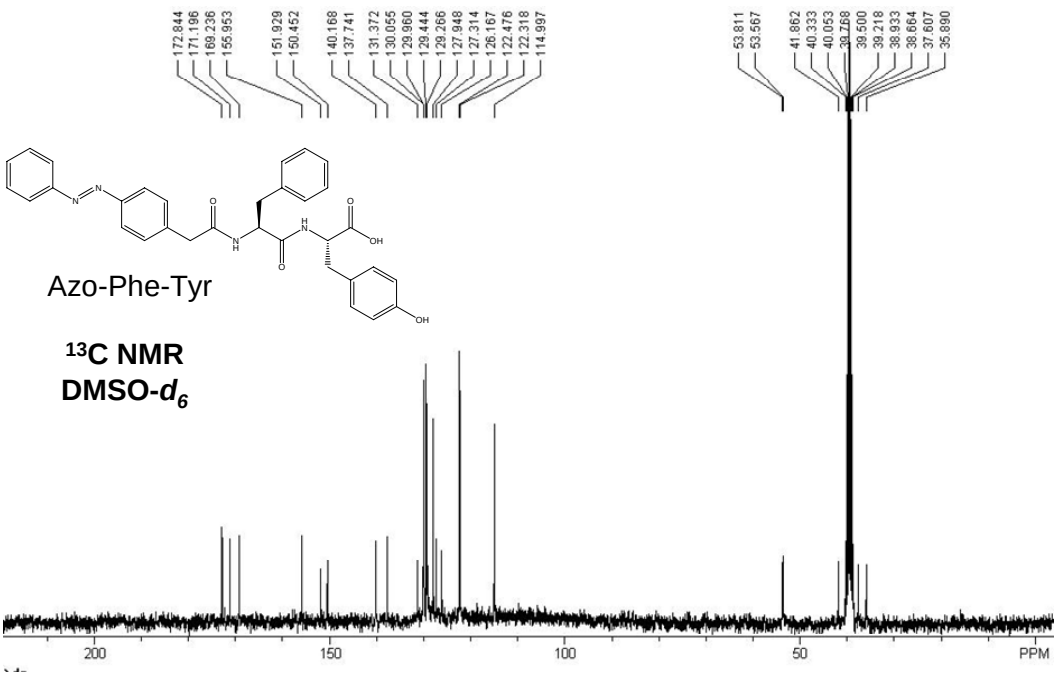
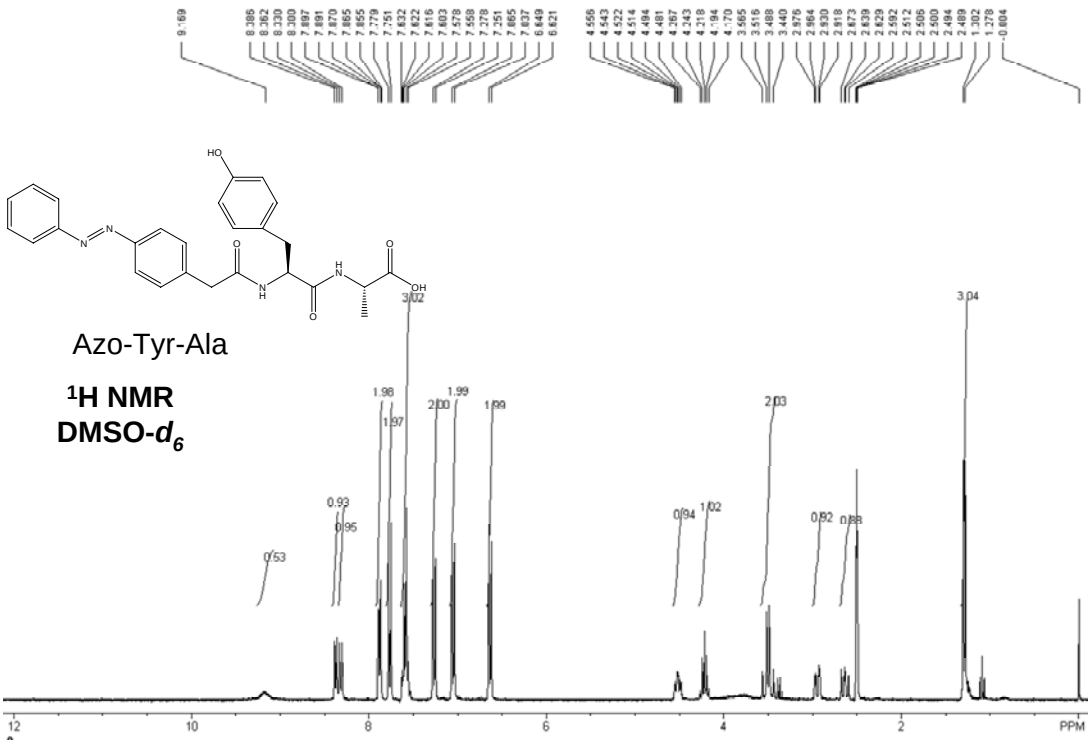
2.04
1.81
0.92
0.93
2.08
2.88
0.93
10
8
6
4
2
PPM


Azo-Phe-Phe
13C NMR
DMSO-d6
200
150
100
50
PPM


Azo-Phe-Tyr
1H NMR
DMSO-d6
PPM


Azo-Phe-Tyr
13C NMR
DMSO-d6
PPM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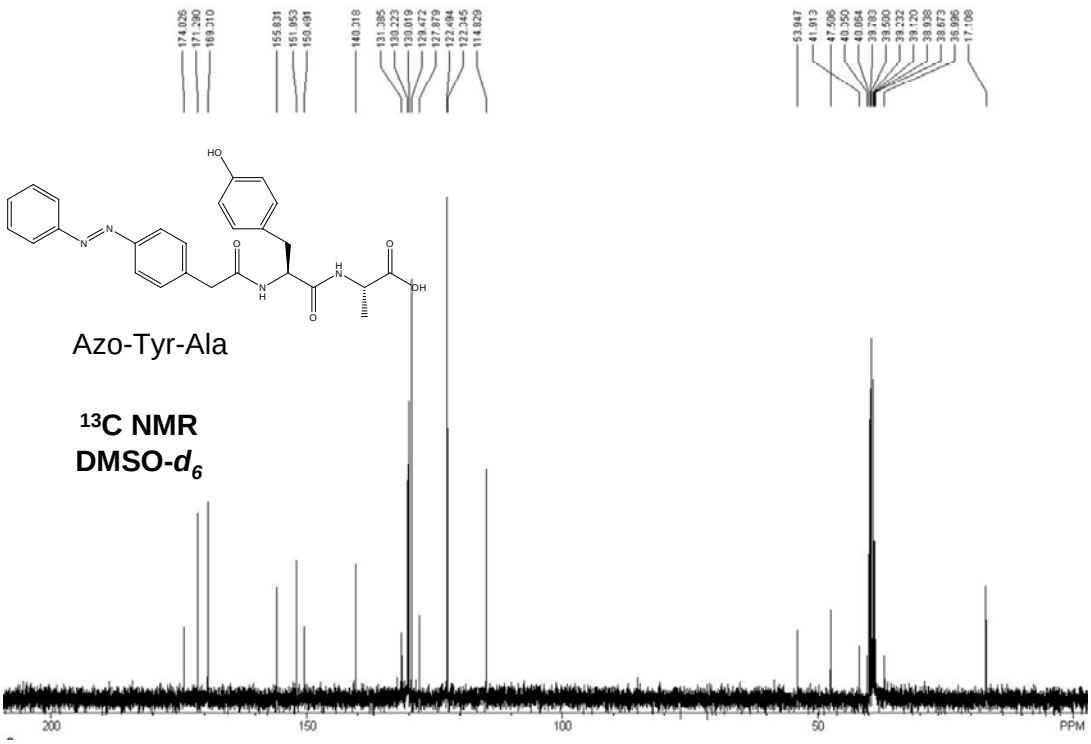
1H NMR
DMSO-d6
PPM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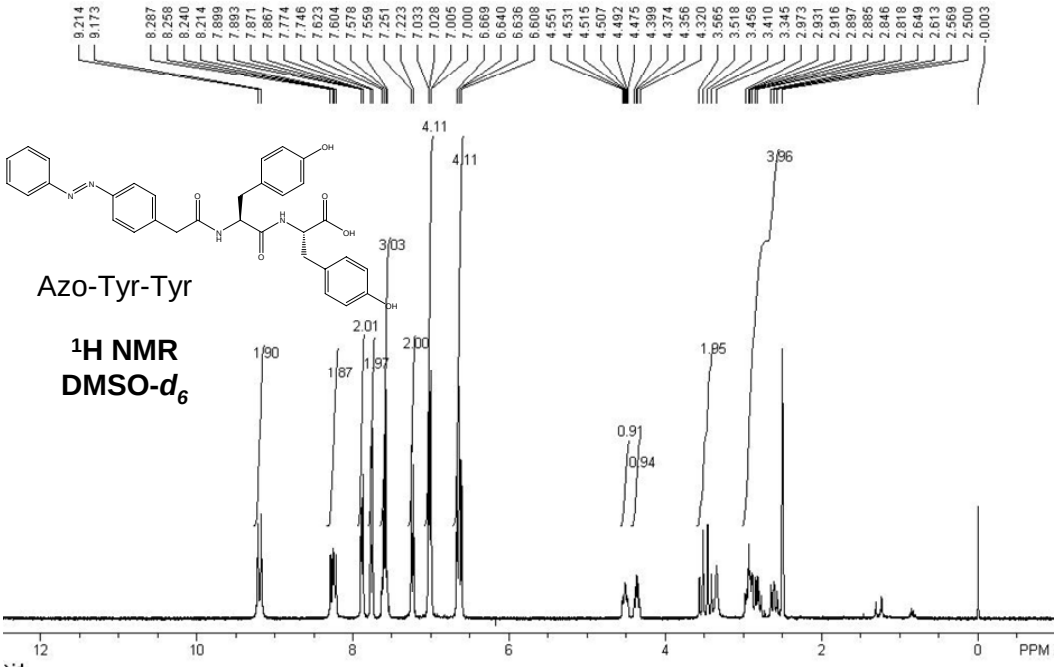
13C NMR
DMSO-d6
PPM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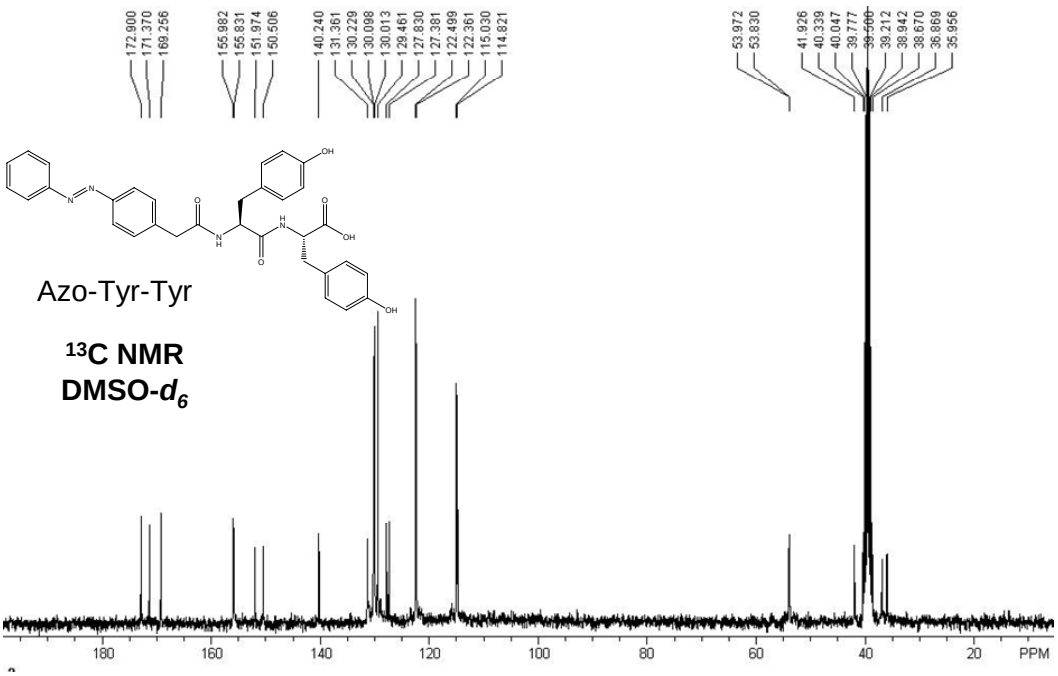
DMSO-d6
PPM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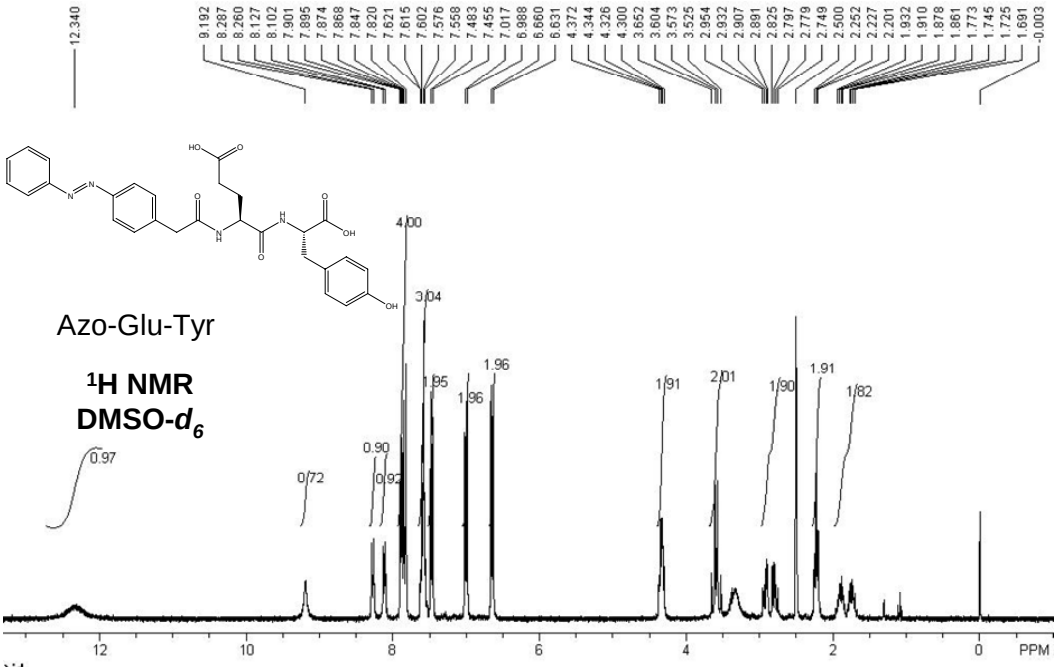
DMSO-d6
PPM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7.820
7.621
7.615
7.602
7.576
7.558
7.483
7.455
7.017
6.988
6.660
6.631
4.372
4.344
4.326
4.300
3.652
3.604
3.573
3.525
2.954
2.932
2.907
2.891
2.825
2.797
2.779
2.749
2.500
2.252
2.227
2.201
1.932
1.910
1.878
1.861
1.773
1.745
1.725
1.691
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Azo-Glu-Tyr
1H NMR
DMSO-d6
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3.04
1.96
1.95
1.96
1.91
2.01
1.90
1.91
1.82
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0.72
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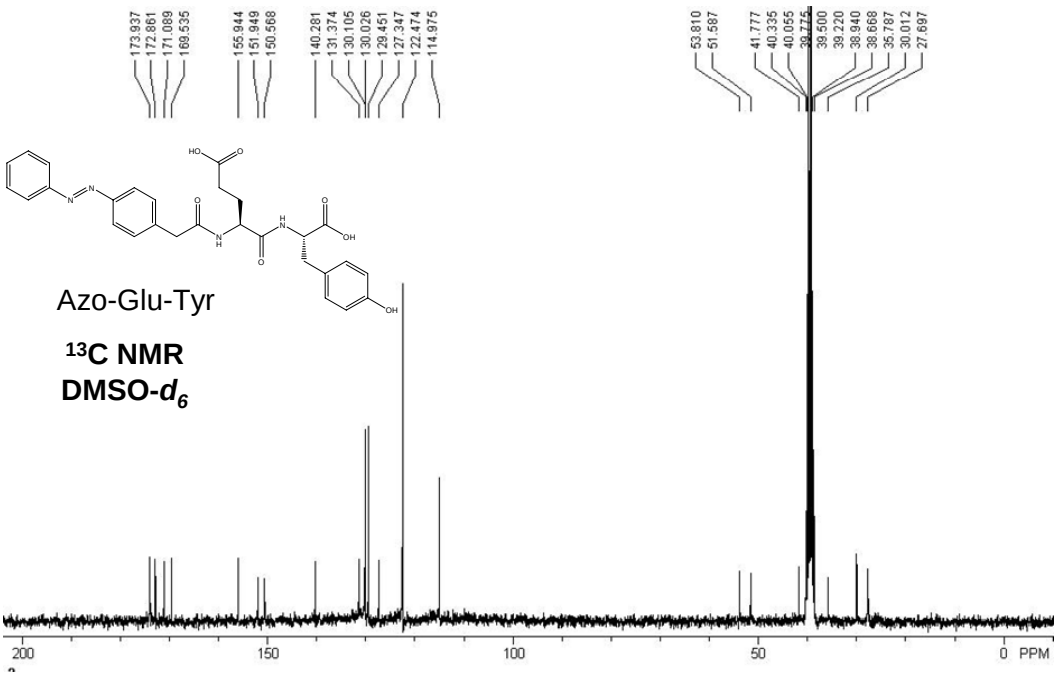
10
8
6
4
2
0
PPM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130.026
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122.474
114.975
53.810
51.587
41.777
40.335
40.055
39.775
39.500
39.220
38.940
38.668
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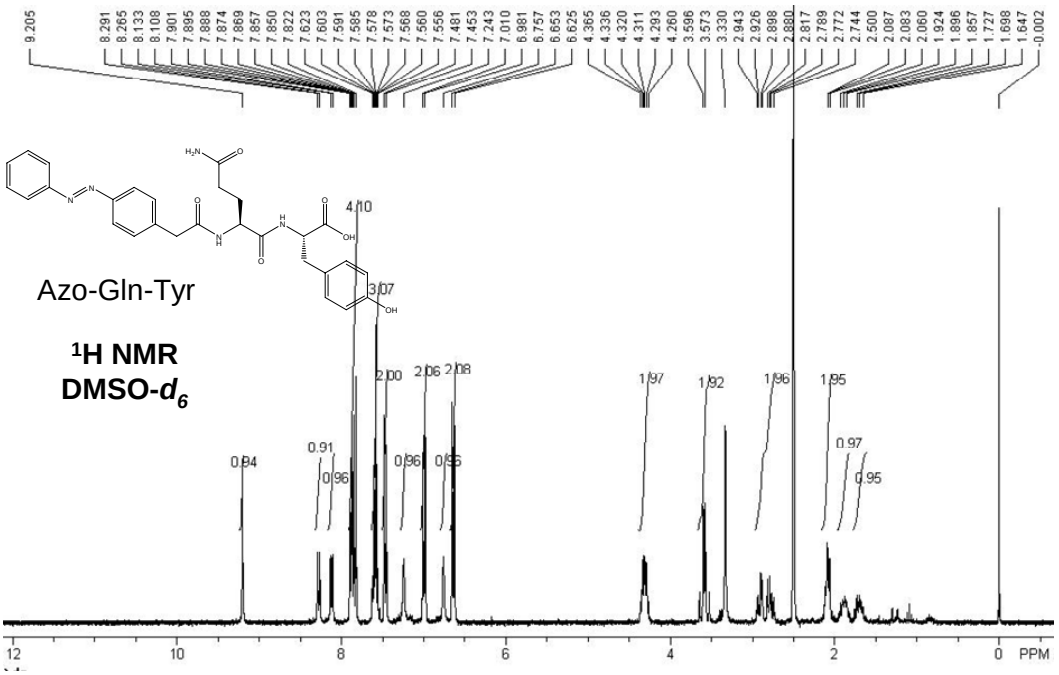
27.697
Azo-Glu-Tyr
13C NMR
DMSO-d6
200
150
100
50
0
PPM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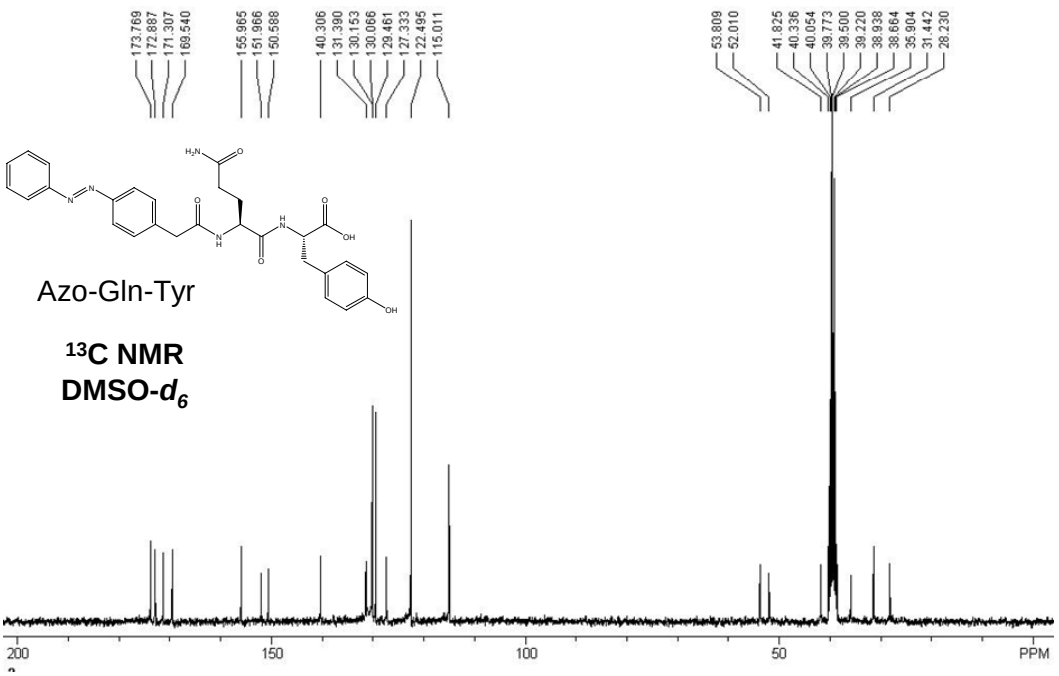
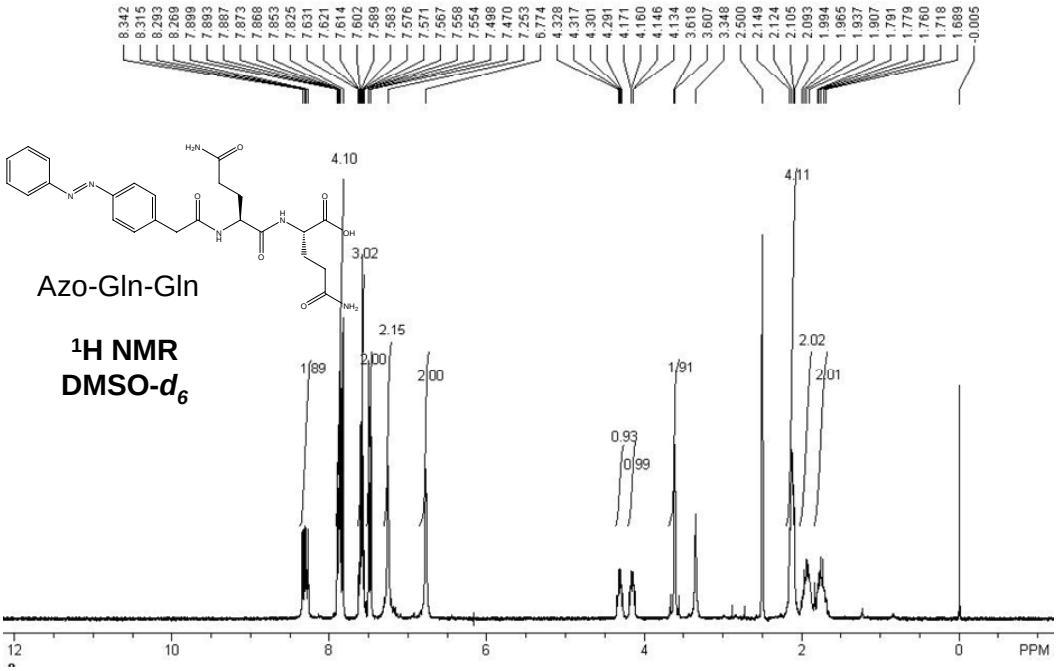
1H NMR
DMSO-d6
PPM


Azo-Gln-Tyr
13C NMR
DMSO-d6
PPM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7.614
7.602
7.589
7.583
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7.567
7.558
7.554
7.498
7.470
7.253
6.774
4.328
4.317
4.301
4.291
4.171
4.160
4.146
4.134
3.618
3.607
3.348
2.500
2.149
2.124
2.105
2.093
1.994
1.965
1.937
1.907
1.791
1.779
1.760
1.718
1.689
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Azo-Gln-Gln
1H NMR
DMSO-d6
4.10
3.02
2.15
2.00
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10
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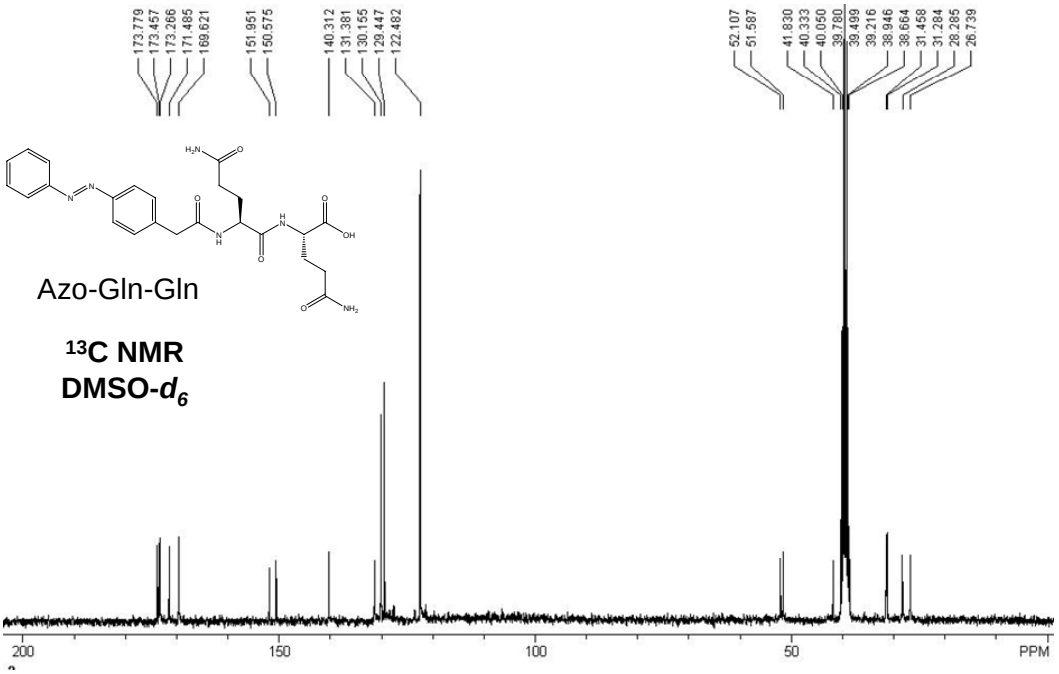
PPM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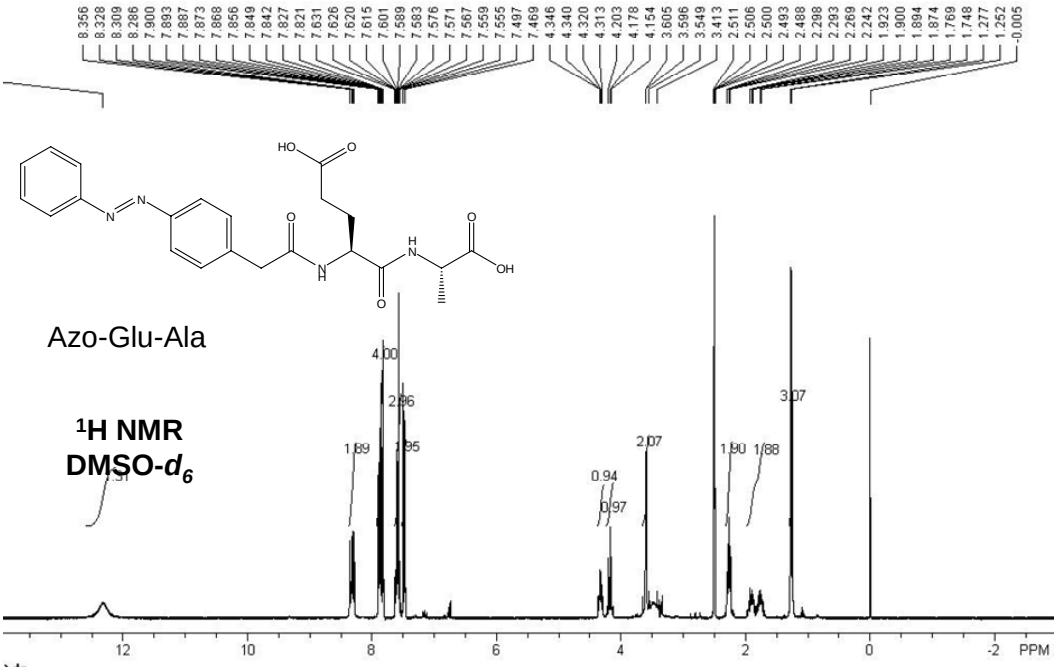
52.107
51.587
41.830
40.333
40.050
39.780
39.499
39.216
38.946
38.664
31.458
31.284
28.285
26.739
Azo-Gln-Gln
13C NMR
DMSO-d6
200
150
100
50
PPM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1H NMR
DMSO-d6
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1.95
2.07
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0.97
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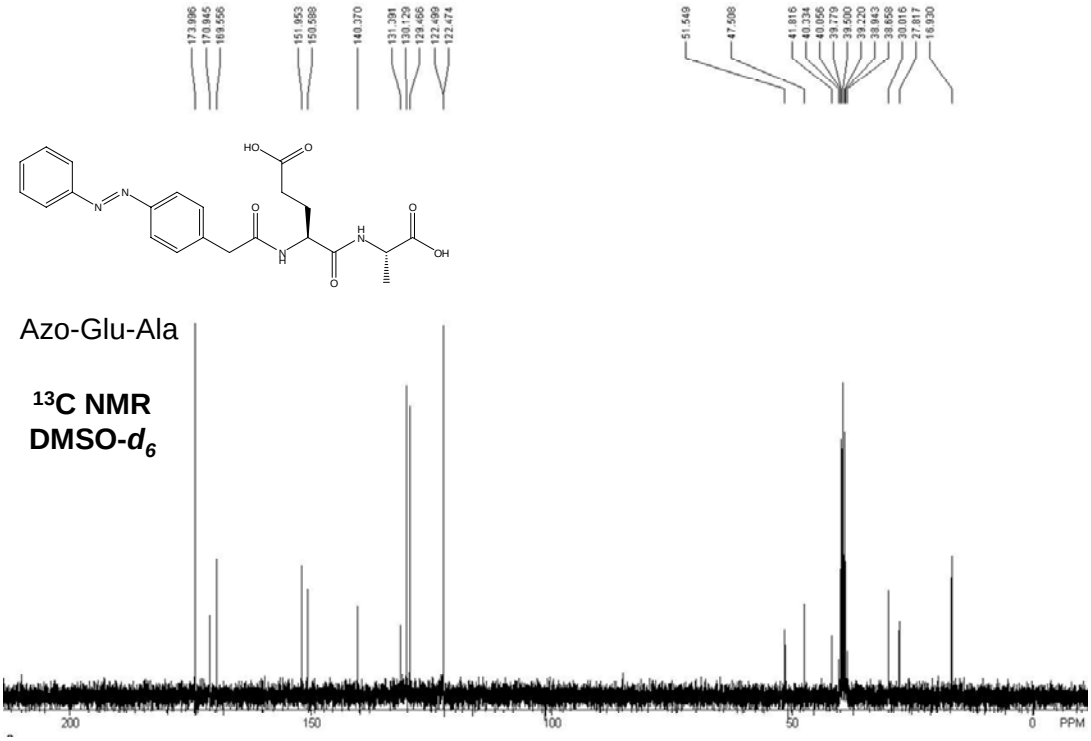
1.88
3.07
PPM


Azo-Glu-Ala
13C NMR
DMSO-d6
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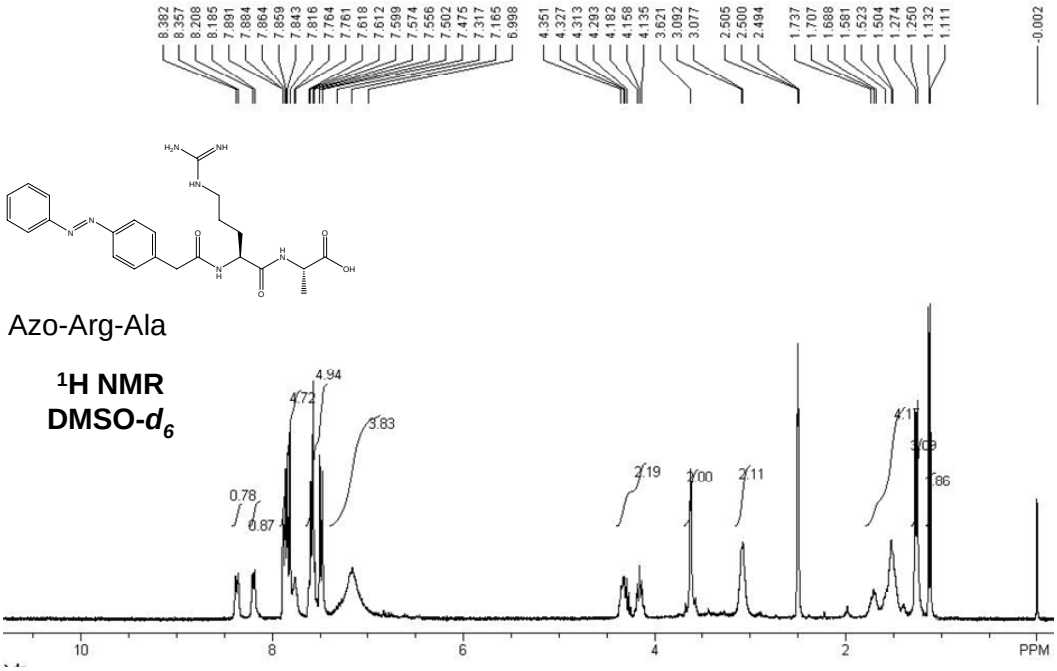
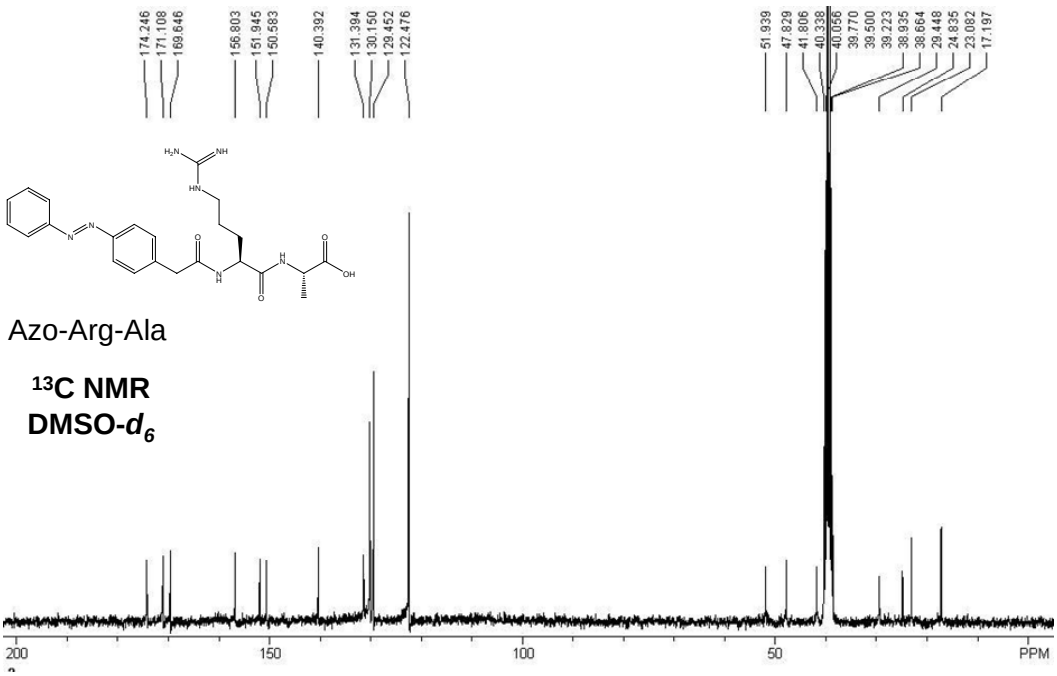


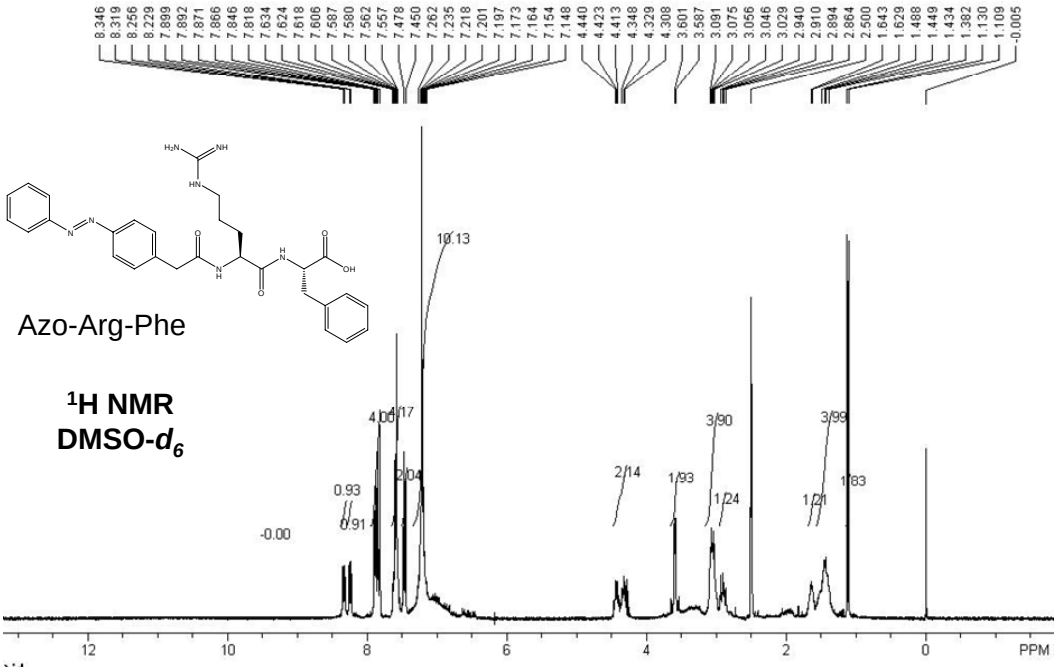
Azo-Arg-Ala

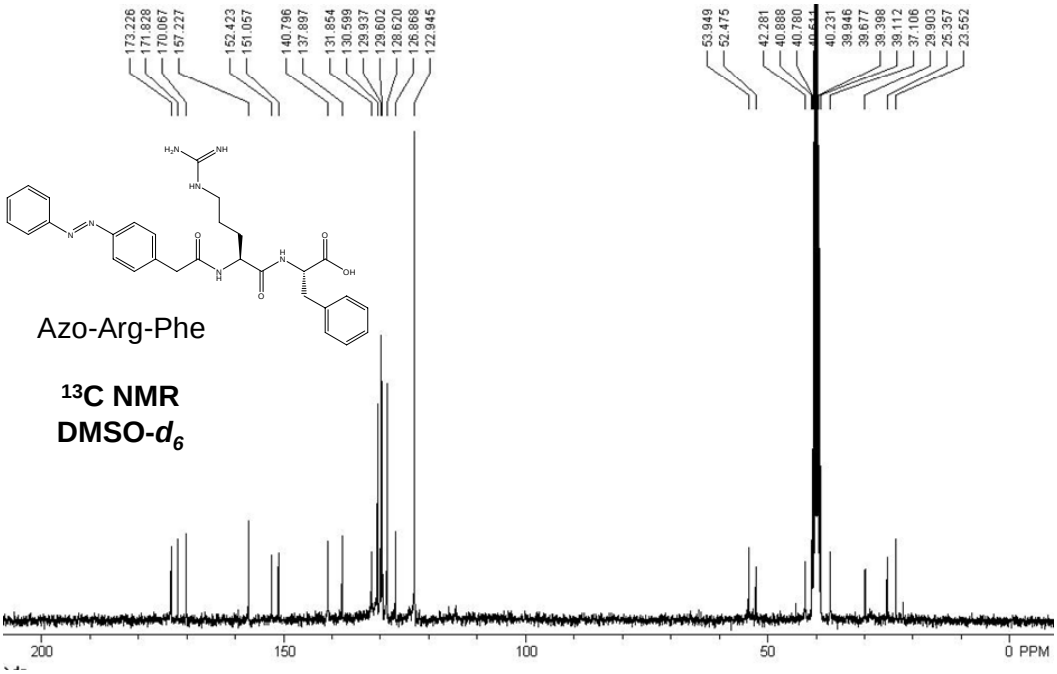
^{1}H NMR
DMSO-*d*$_6$

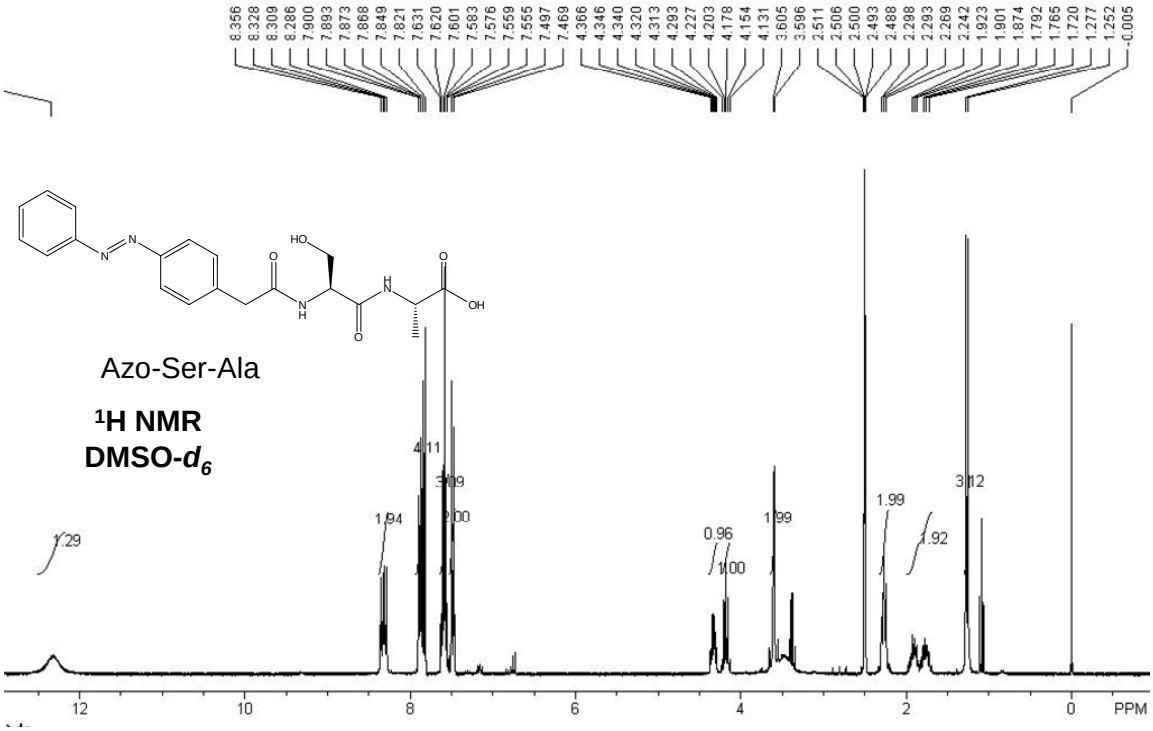


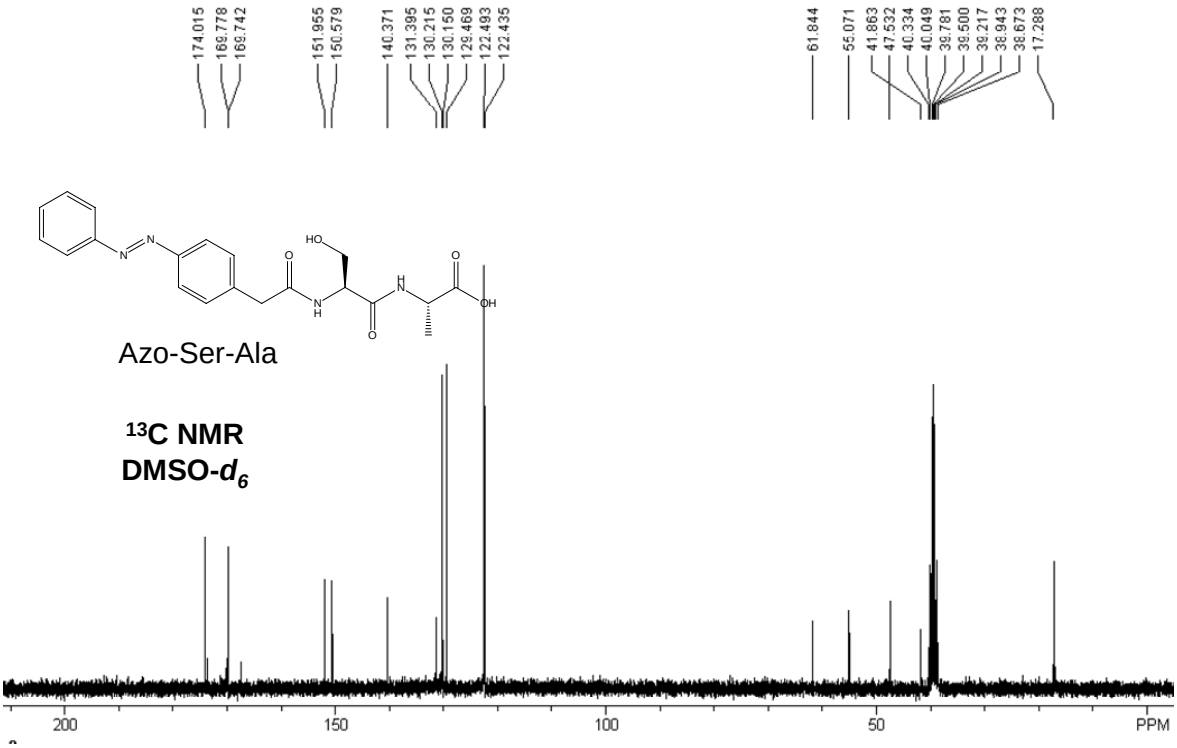
Azo-Arg-Ala

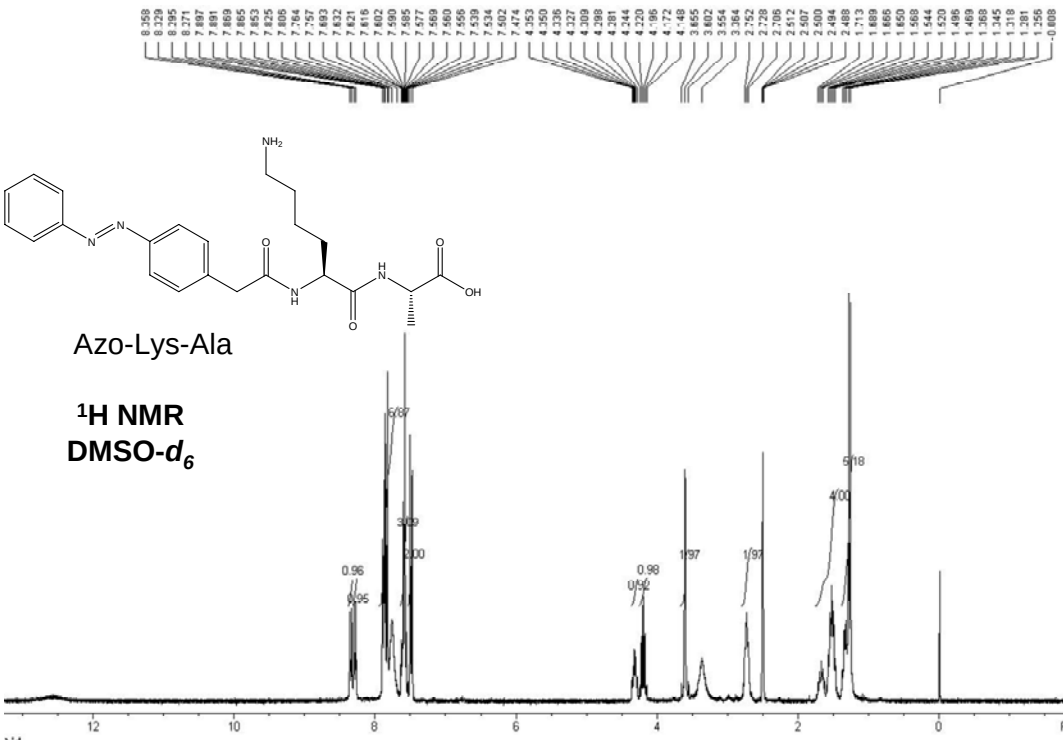
^{13}C NMR
DMSO-*d*$_6$

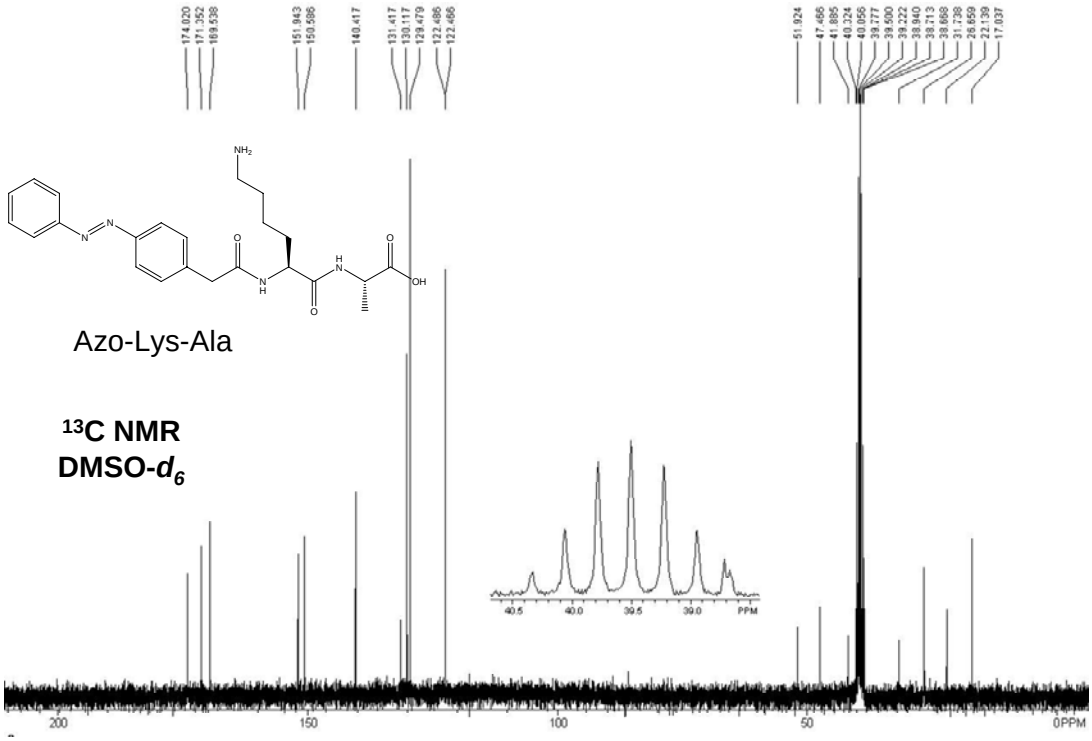

Azo-Arg-Phe
1H NMR
DMSO-d6
10.13
4.00
4.17
2.04
0.93
0.91
-0.00
2.14
1.93
3.90
1.24
3.99
1.21
1.83
12
10
8
6
4
2
0
PPM

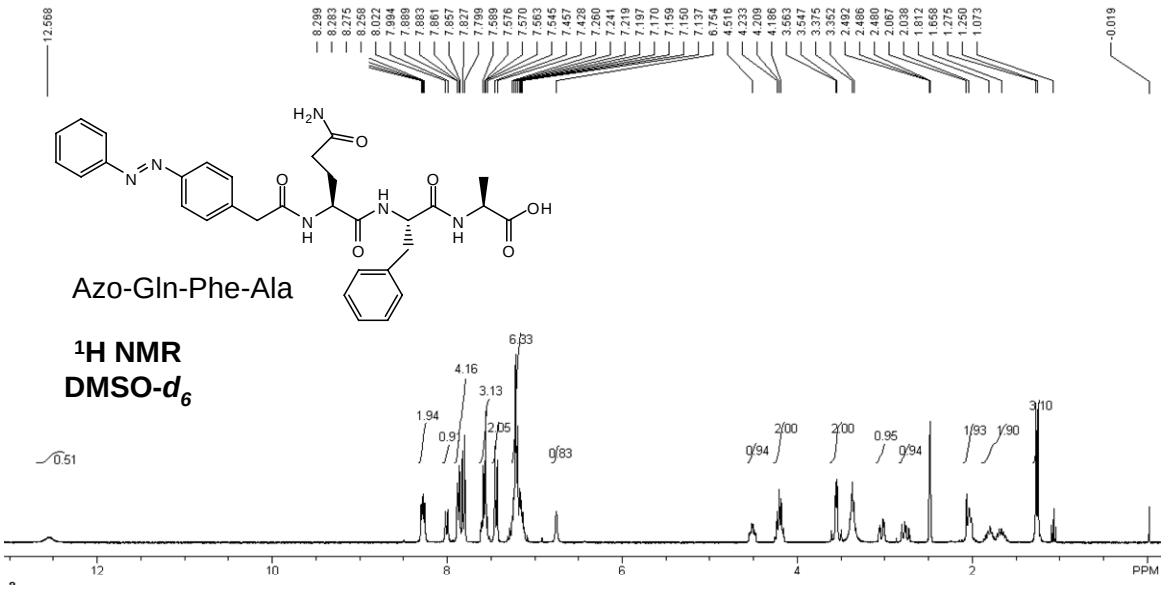

Azo-Arg-Phe
13C NMR
DMSO-d6
200
150
100
50
0 PPM


8.356
8.328
8.309
8.286
7.900
7.893
7.873
7.868
7.849
7.821
7.631
7.620
7.601
7.583
7.576
7.559
7.555
7.497
7.469
4.366
4.346
4.340
4.320
4.313
4.293
4.227
4.203
4.178
4.154
4.131
3.605
3.596
2.511
2.506
2.500
2.493
2.488
2.298
2.293
2.269
2.242
1.923
1.901
1.874
1.792
1.765
1.720
1.277
1.252
-0.005
HO
O
N
H
O
N
H
O
OH
Azo-Ser-Ala
1H NMR
DMSO-d6
1.29
1.94
4.11
3.09
3.00
0.96
1.00
1.99
1.99
1.92
3.12
12
10
8
6
4
2
0
PPM


174.015
169.778
169.742
151.955
150.579
140.371
131.395
130.215
130.150
129.469
122.493
122.435
61.844
55.071
41.863
47.532
40.334
40.049
39.781
39.500
39.217
38.943
38.673
17.288
HO
O
N
H
O
N
H
O
OH
Azo-Ser-Ala
13C NMR
DMSO-d6
200
150
100
50
PPM

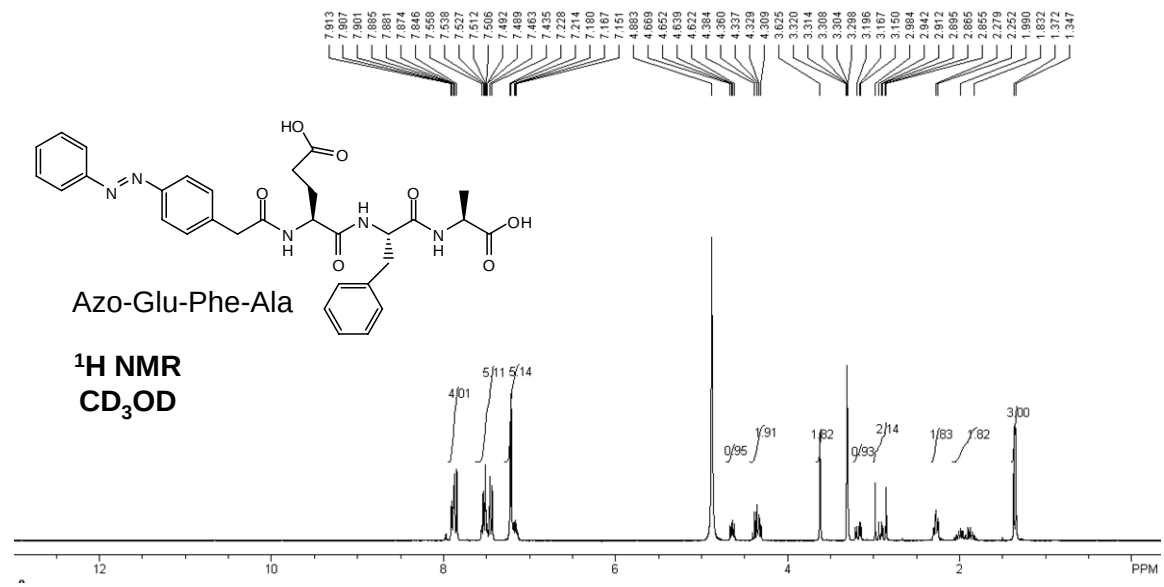

Azo-Lys-Ala
1H NMR
DMSO-d6
PPM


Azo-Lys-Ala
13C NMR
DMSO-d6
PPM



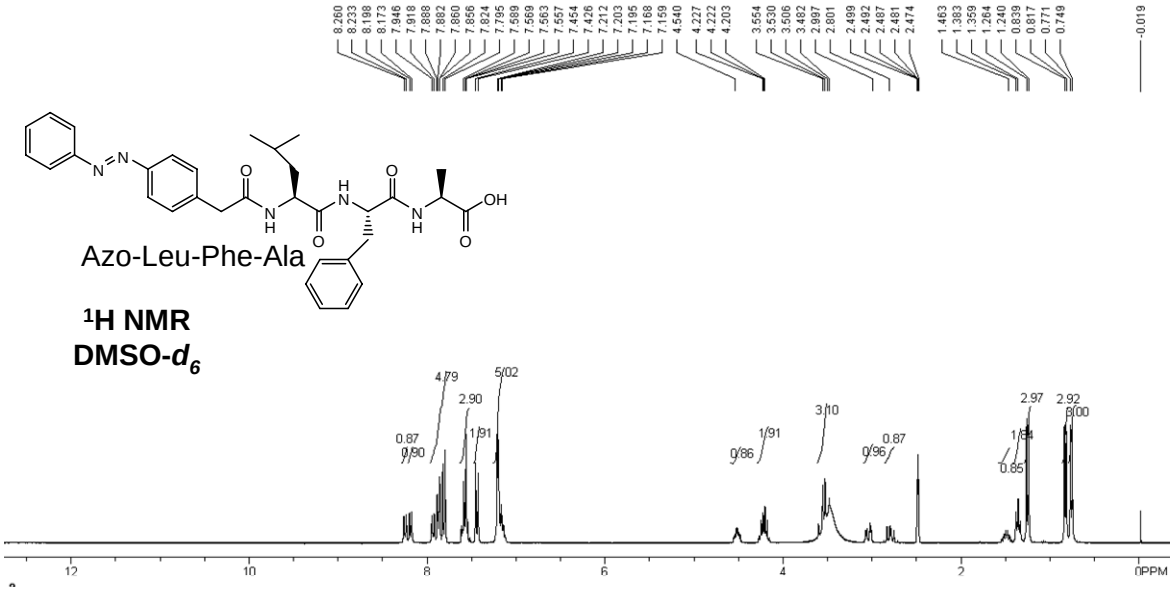
Azo-Gln-Phe-Ala

^{1}H NMR
DMSO-*d*$_6$



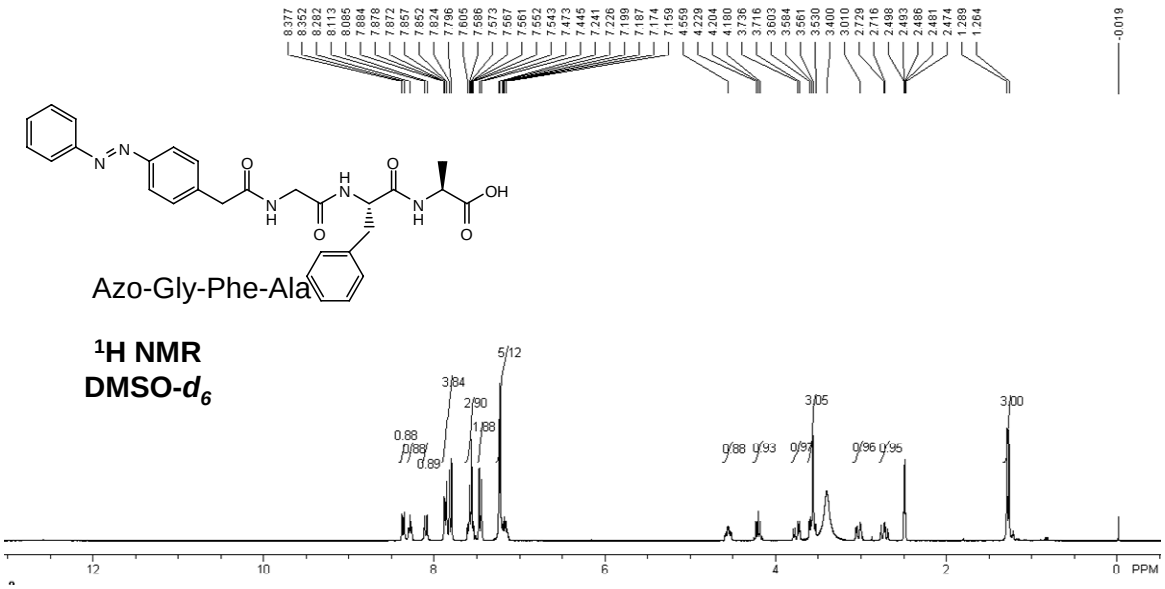
Azo-Glu-Phe-Ala

^{1}H NMR
CD_3OD



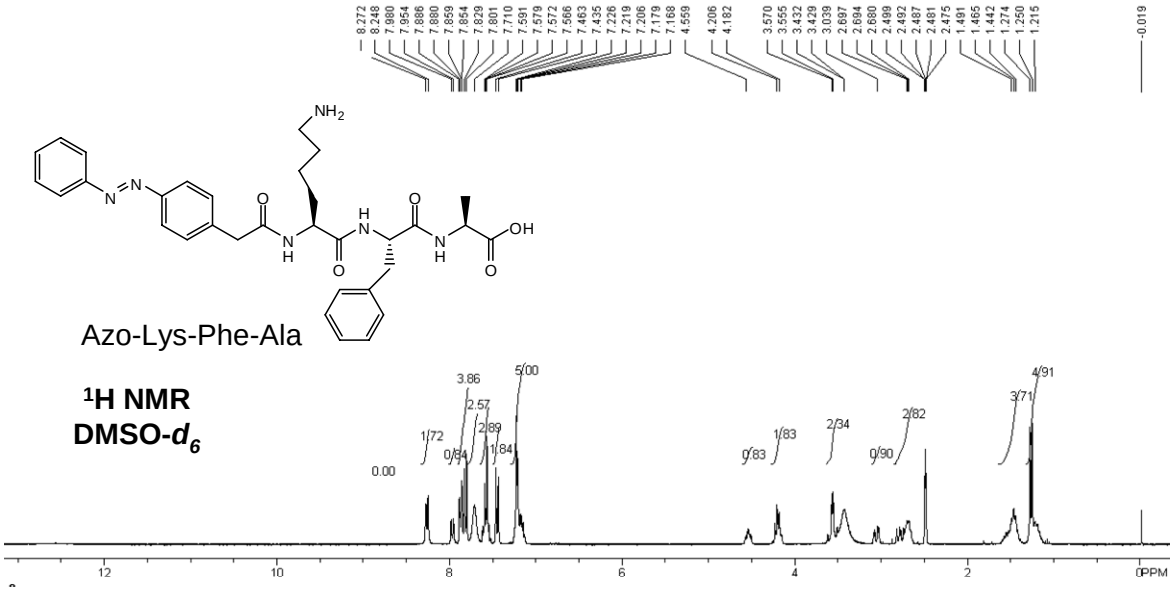
Azo-Leu-Phe-Ala

^{1}H NMR
DMSO-*d*$_6$



Azo-Gly-Phe-Ala

^{1}H NMR
DMSO-*d*$_6$


8.272
8.248
7.980
7.954
7.886
7.880
7.859
7.854
7.829
7.801
7.710
7.591
7.579
7.572
7.566
7.463
7.435
7.226
7.219
7.206
7.179
7.168
4.559
4.206
4.182
3.570
3.555
3.432
3.429
3.039
2.697
2.694
2.680
2.499
2.492
2.487
2.481
2.475
1.491
1.465
1.442
1.274
1.250
1.215
-0.019
NH2
OH
Azo-Lys-Phe-Ala
1H NMR
DMSO-d6
0.00
1.72
0.84
3.86
2.57
2.89
1.84
5.00
0.83
1.83
2.34
0.90
2.82
3.71
4.91
12
10
8
6
4
2
0PPM