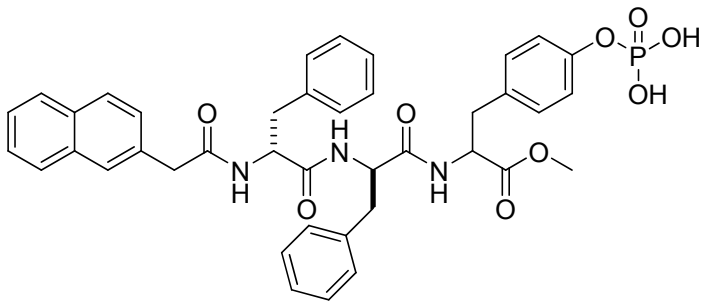
Nap-FFpY-OMe



^{1}H NMR (300 MHz, DMSO-d_6) δ 7.87 (d, J=7.500 Hz, 2H); 7.67 (d, J=7.429 Hz, 2H); 7.37-7.42 (t, 2H); 7.26-7.32 (m, 3H); 7.22-7.24(m, 4H); 7.15 (m, 7H); 7.03-7.07 (m, 2H); 4.44-4.58 (m, 3H); 4.19-4.26 (m, 3H); 3.56 (m, 5H); 2.90-3.03 (m, 4H); 2.63-2.82 (m, 2H). ^{31}P NMR (δ -4.950 ppm); ^{13}C NMR (400 MHz, DMSO-d6): δ 171.49, 171.02, 170.95, 169.74, 150.24, 137.67, 137.39, 133.78, 132.82, 132.29, 131.63, 129.97, 129.12, 127.93, 127.80, 127.50, 127.32, 127.26, 127.14, 126.18, 126.03, 125.85, 125.33, 119.77, 53.67, 53.47, 51.75, 42.11, 37.39, 35.82; MS: calc. M^+ = 848.3, obsvd. $(M+H)^+$ = 849.5;

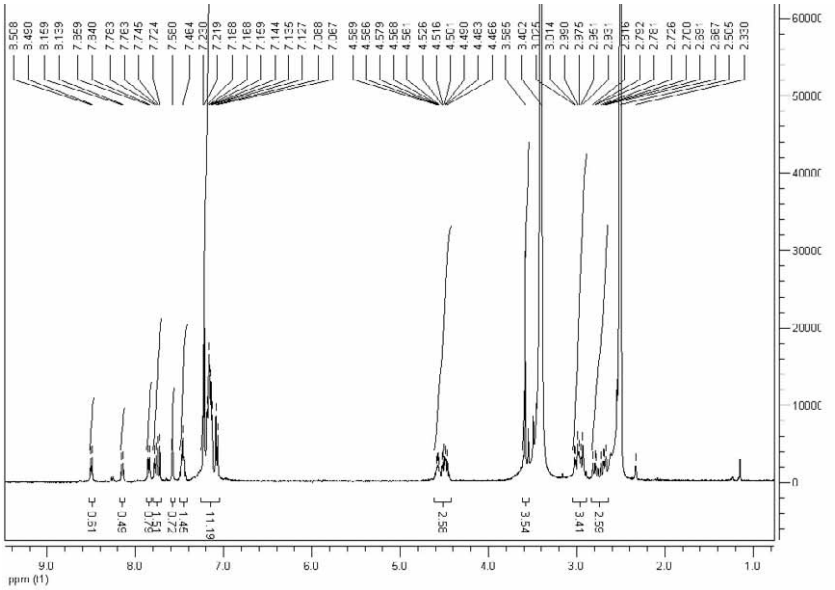


Figure S-1. ^{1}H NMR of compound Nap-FFpY-OMe

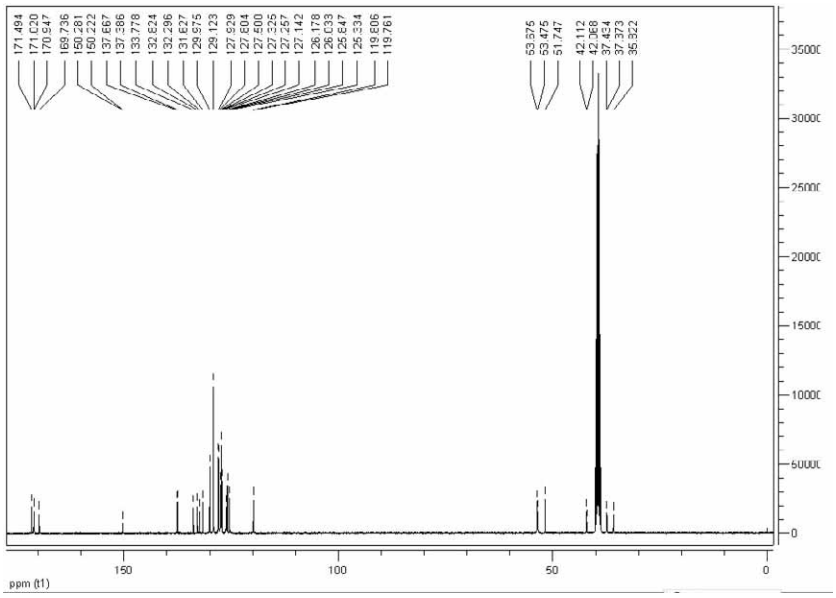
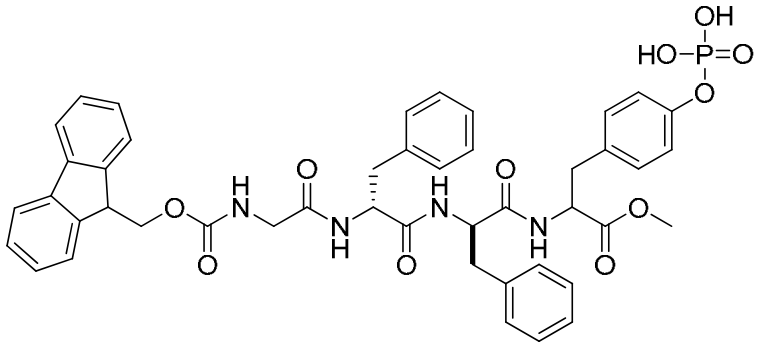


Figure S-2 ^{13}C NMR of compound Nap-FFpY-OMe

Fmoc-GFFpY-OMe



^{1}H NMR (300 MHz, DMSO-d_6) δ 7.87 (d, J=7.500 Hz, 2H); 7.67 (d, J=7.429 Hz, 2H); 7.37-7.42 (t, 2H); 7.26-7.32 (m, 3H); 7.22-7.24(m, 4H); 7.15 (m, 7H); 7.03-7.07 (m, 2H); 4.44-4.58 (m, 3H); 4.19-4.26 (m, 3H); 3.56 (m, 5H); 2.90-3.03 (m, 4H); 2.63-2.82 (m, 2H). ^{31}P NMR (δ -4.950 ppm). ^{13}C NMR (400 MHz, DMSO-d6): δ 171.46, 171.00, 170.66, 168.73, 156.33, 150.20, 150.14, 143.75, 140.62, 137.51, 137.44, 132.39, 130.00, 129.11, 127.97, 127.86, 127.54, 126.99, 126.19, 126.10, 125.15, 112.00, 119.81, 119.76, 65.69, 53.69, 53.51, 51.73, 46.53, 43.22, 37.43, 35.83; MS: calc. M^+ = 848.3, obsvd. $(M+H)^+$ = 849.5.

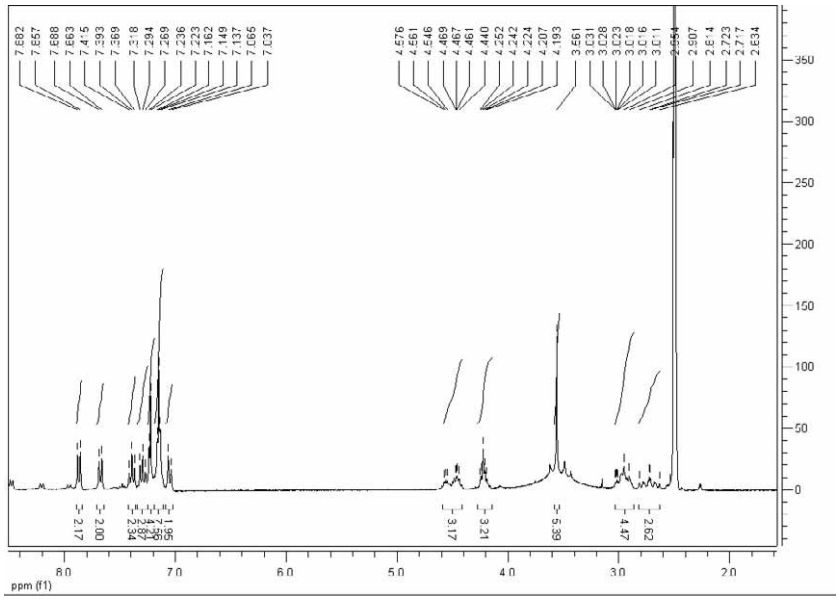


Figure S-3. ^{1}H NMR of compound Fmoc-GFFpY-OMe

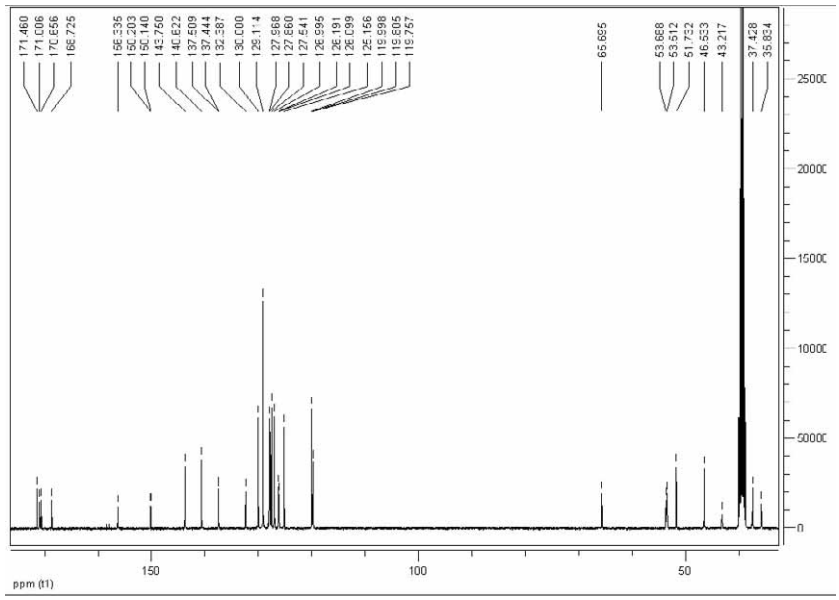
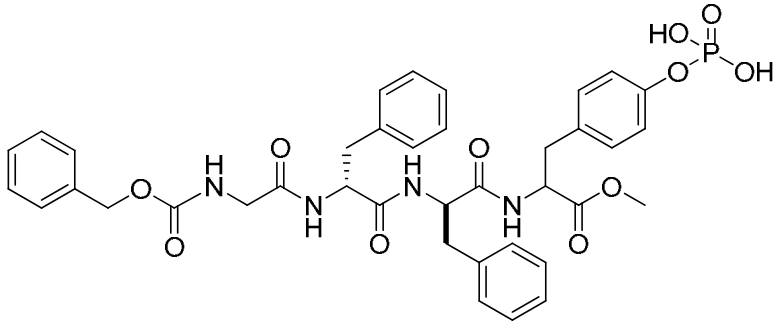


Figure S-4.^{13}C NMR of compound Fmoc-GFFpY-OMe

Cbz-GFFpY-OMe



^{1}H NMR (300 MHz, DMSO-d_6) δ 7.31 (m, 4H); 7.22-7.24 (m, 4H); 7.13-7.16 (m, 9H); 7.03-7.07 (m, 2H); 4.99 (s, 2H); 4.42-4.58 (m, 3H); 3.48-3.57 (m, 5H); 2.89-3.02 (m, 4H); 2.64-2.82 (m, 2H). ^{31}P NMR (δ -5.168 ppm). ^{13}C NMR (400 MHz, DMSO-d6): δ 171.48, 171.04, 170.62, 168.67, 156.29, 150.42, 150.36, 137.46, 136.89, 132.06, 129.91, 129.09, 128.24, 127.96, 127.84, 127.68, 127.58, 126.19, 126.10, 119.76, 119.71, 66.35, 53.69, 53.49, 53.44, 51.72, 43.19, 37.40, 37.39, 35.79. MS: calc. M^+ = 760.3, obsvd. $(M+H)^+$ = 761.6.

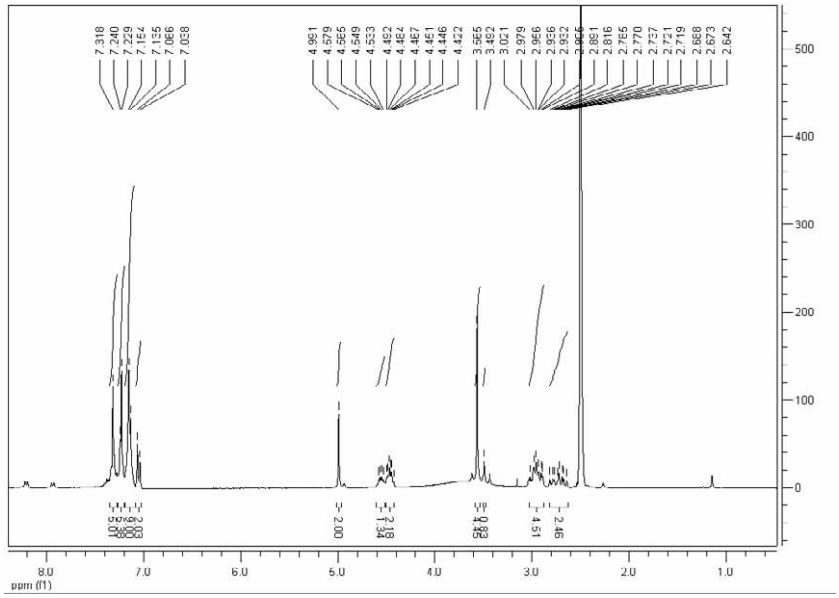


Figure S-5. ^{1}H NMR of compound **Cbz-GFFpY-OMe**

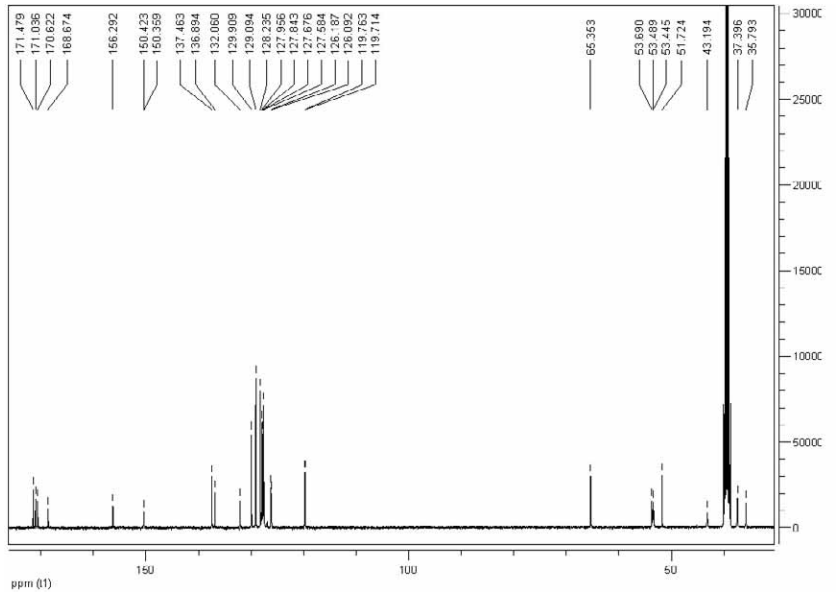
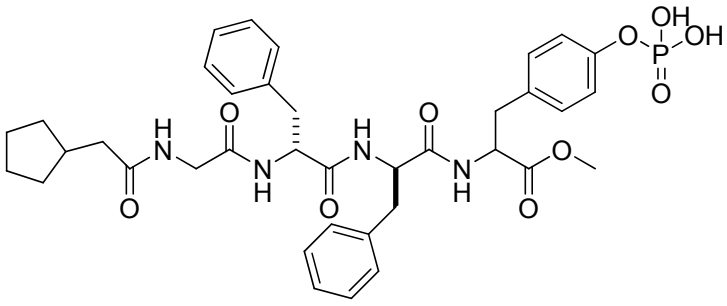


Figure S-6. ^{13}C NMR of compound **Cbz-GFFpY-OMe**

cPen-GFFpY-Ome



^{1}H NMR (300 MHz, DMSO-d_6) δ 7.22-7.25 (m, 4H); 7.12-7.18 (m, 8H); 7.04-7.08 (m, 2H); 4.51-4.56 (m, 1H); 4.43-4.48 (m, 2H); 3.63-3.70 (m, 1H); 3.56 (s, 3H); 3.46-3.52 (m, 1H); 2.89-3.04 (m, 4H); 2.62-2.83 (m, 2H); 2.06 (m, 2H); 1.43-1.66 (m, 7H); 1.05-1.11 (m, 2H). ^{31}P NMR (δ -5.180ppm). ^{13}C NMR (400 MHz, DMSO-d6): δ 177.06, 171.98, 171.46, 171.03, 170.62, 168.72, 150.18, 150.12, 137.50, 132.32, 129.98, 129.08, 127.96, 127.85, 126.17, 126.10, 119.77, 119.73, 53.69, 53.48, 51.73, 41.66, 41.56, 41.12, 41.08, 37.31, 36.44, 35.78, 31.78, 24.36. MS: calc. M^+ = 736.29, obsvd. $(M+H)^+$ = 738.1.

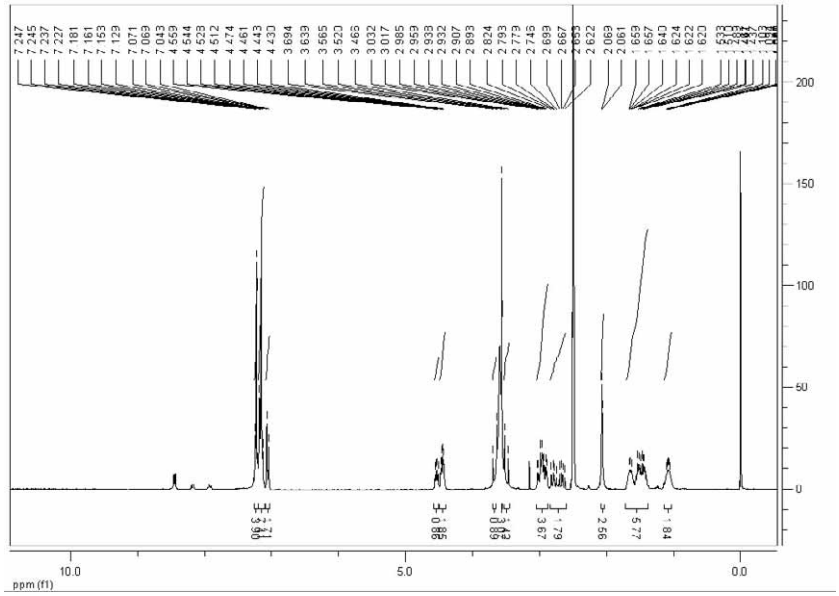


Figure S-7. ^{1}H NMR of compound **cPen-GFFpY-OMe**

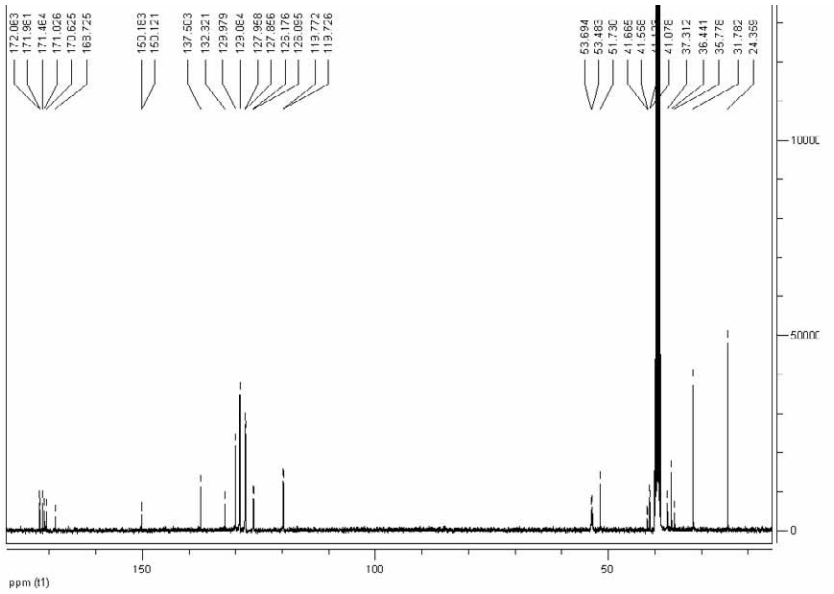
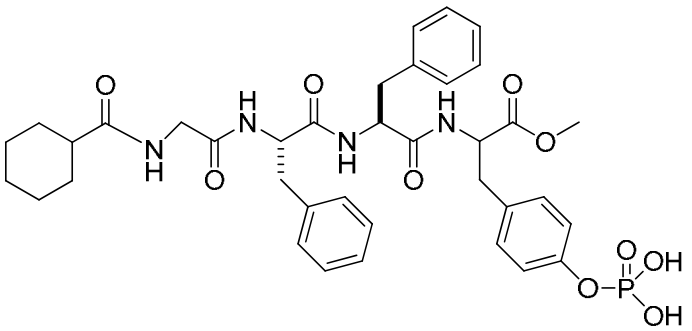


Figure S-8. ^{13}C NMR of compound **cPen-GFFpY-OMe**

cHex-GFFpY-OMe



^{1}H NMR (300 MHz, DMSO-d_6) δ 7.23-7.25 (m, 4H); 7.14-7.19 (m, 8H); 7.04-7.07 (m, 2H); 4.41-4.46 (m, 2H); 3.63-3.68 (m, 1H); 3.56 (m, 3H); 3.44-3.51 (m, 1H); 2.29-3.04 (m, 3H); 2.63-2.83 (m, 2H); 2.07-2.14 (m, 1H); 1.61-1.65 (m, 6H); 1.14-1.28 (m, 6H). ^{31}P NMR (δ -5.176 ppm). ^{13}C NMR (400 MHz, DMSO-d6): δ 175.48, 171.47, 171.04, 171.57, 168.85, 150.23, 150.17, 137.50, 137.44, 132.28, 129.97, 129.11, 129.07, 129.97, 127.87, 126.19, 126.10, 119.78, 119.74, 53.75, 53.48, 51.73, 43.53, 41.71, 37.30, 35.79, 28.98, 25.35, 25.11. MS: calc. M^+ = 736.3, obsvd. $(M+H)^+$ = 737.0.

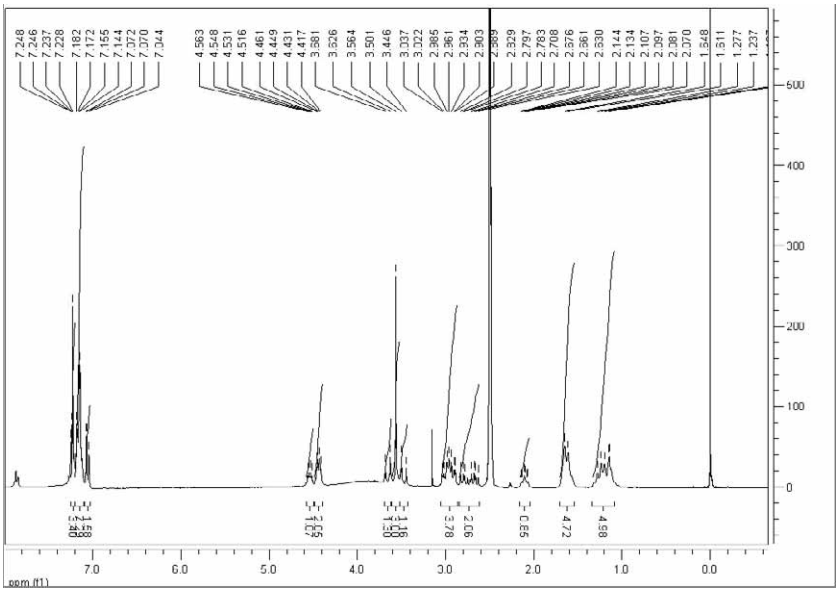


Figure S-9. ^{1}H NMR of compound **cHex-GFFpY-OMe**

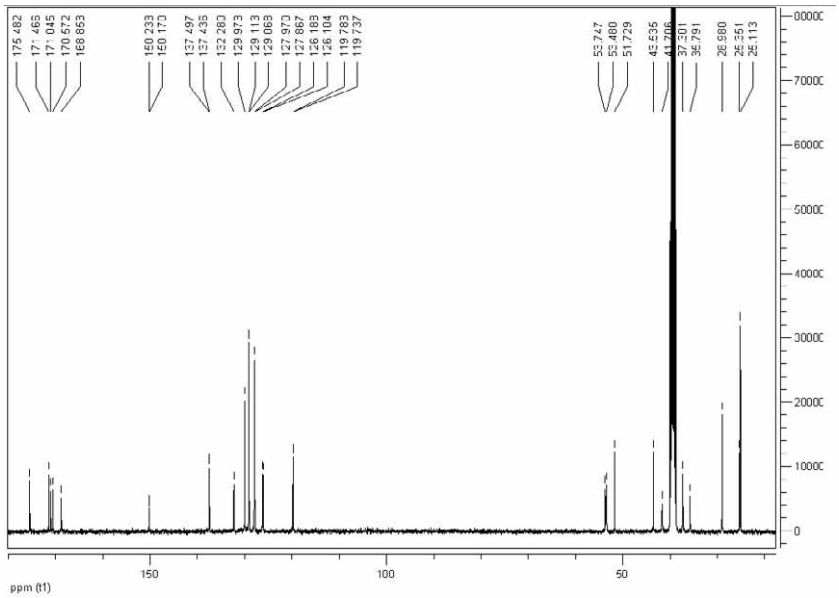
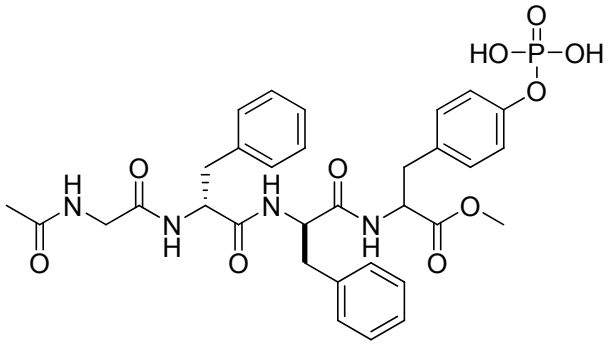


Figure S-10. ^{13}C NMR of compound **cHex-GFFpY-OMe**

Ac-GFFpY-OMe



^{1}H NMR (300 MHz, DMSO-d_6) δ 7.24-7.27 (m, 4H); 7.17-7.21 (m, 8H); 7.06-7.09 (m, 2H); 4.52-4.57 (m, 2H); 4.45-4.48 (m, 2H); 3.64-3.68 (m, 2H); 3.58 (s, 3H); 2.90-3.05 (m, 5H); 1.81 (s, 3H). ^{31}P NMR (δ -6.265ppm): ^{13}C NMR (400 MHz, DMSO-d6): δ 171.47, 171.03, 170.95, 170.65, 170.58, 169.52, 169.44, 168.69, 168.61, 150.16, 150.09, 137.54, 137.46, 132.36, 129.99, 129.08, 127.97, 127.87, 126.20, 126.11, 119.78, 119.73, 53.68, 53.41, 51.74, 41.64, 37.27, 35.75, 22.22. MS: calc. M^+ = 668.2, obsvd. $(M+H)^+$ = 669.3.

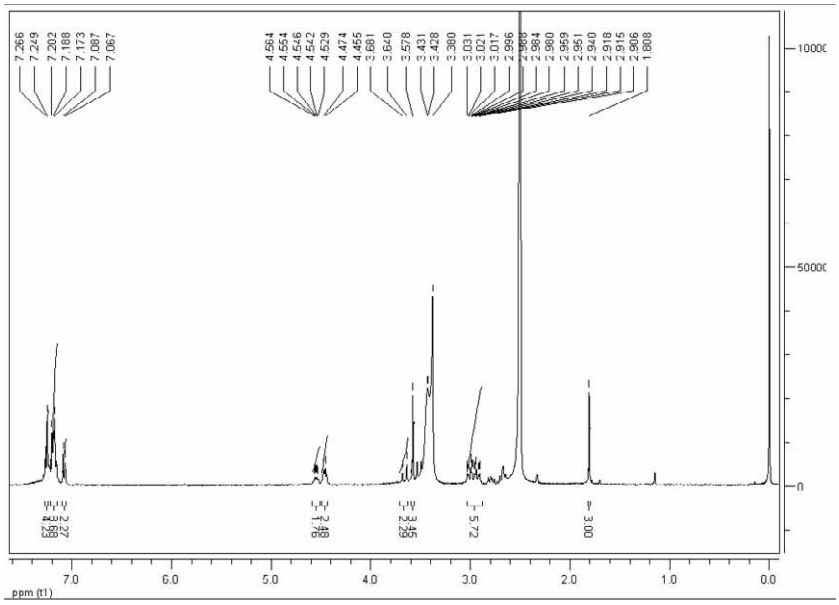


Figure S-11. ^{1}HNMR of compound **Ac-GFFpY-OMe**

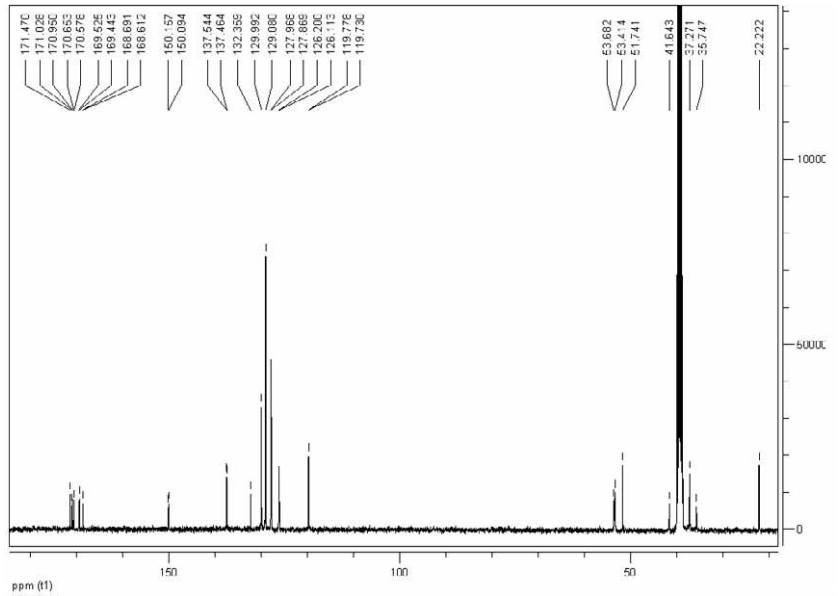
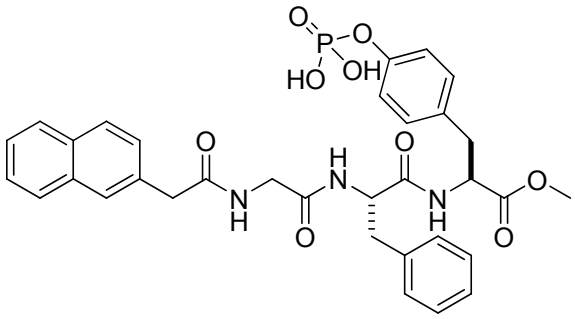


Figure S-12. ^{13}C NMR of compound **Ac-GFFpY-OMe**

Nap-GFpY-OMe



^{1}H NMR (300 MHz, DMSO-d$_6$) δ 7.81-7.88 (m, 3H); 7.76 (s, 1H); 7.41-7.49 (m, 3H); 7.16-7.24 (m, 7H); 7.06-7.08 (m, 2H); 4.53-4.57 (m, 1H); 4.41-4.47 (m, 1H); 3.61-3.63 (m, 3H); 3.58 (m, 4H); 2.87-3.00 (m, 3H); 2.67-2.73 (m, 1H). ^{13}C NMR (400 MHz, DMSO-d6): δ 171.51, 171.07, 170.34, 170.26, 168.43, 150.15, 150.09, 137.48, 133.78, 132.87, 132.43, 131.67, 129.98, 129.06, 127.91, 127.62, 127.45, 127.35, 127.27, 126.16, 125.91, 125.38, 119.77, 119.72, 53.67, 51.74, 42.03, 41.00, 37.46, 35.71. ^{31}P NMR (δ -6.213 ppm). MS: calc. M^+ = 647.2, obsvd. $(M+H)^+$ = 647.9.

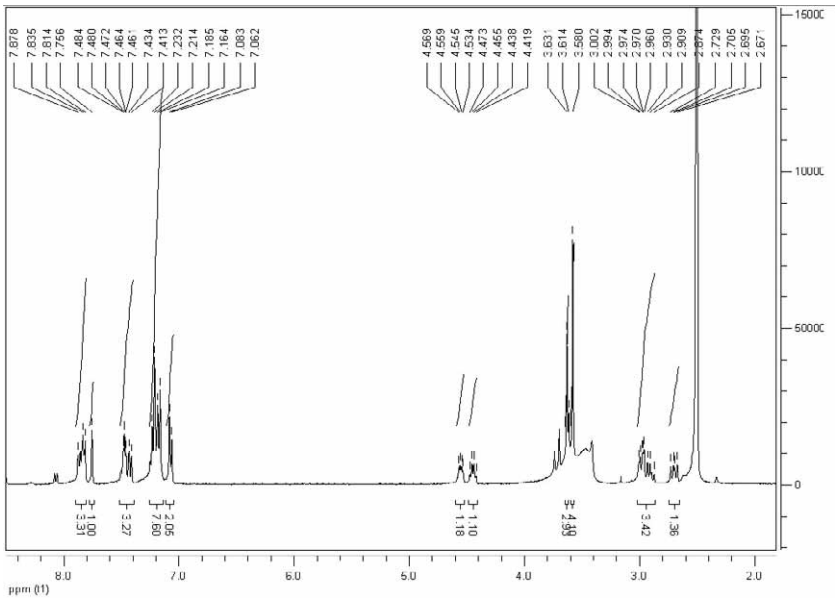


Figure S-13. ^{1}H NMR of compound **Nap-GFpY-OMe**

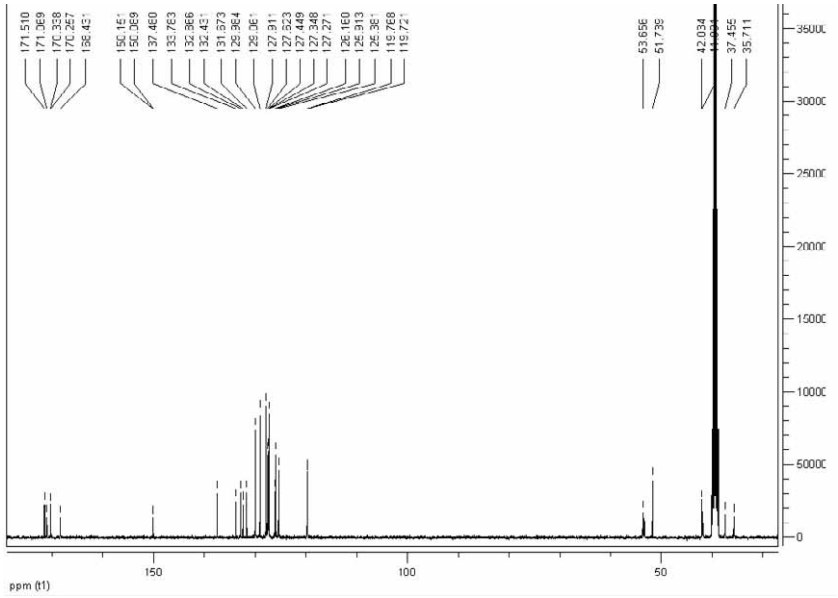
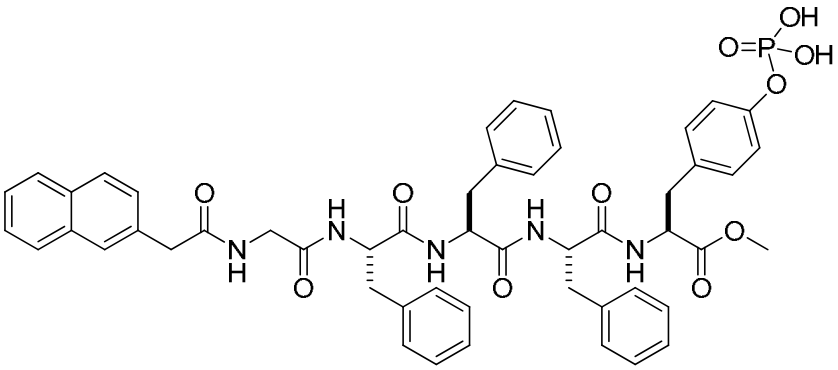


Figure S-14. ^{13}C NMR of compound **Nap-GFpY-OMe**

Nap-GFFFpY-OMe



^{1}H NMR (300 MHz, DMSO-d$_6$) δ 7.80-7.86 (m, 3H); 7.72 (s, 1H); 7.37-7.47 (m, 3H); 7.22-7.25 (m, 4H); 7.12-7.18 (m, 13H); 7.04-7.08 (m, 2H); 4.56-4.62 (m, 2H); 4.45-4.49 (m, 3H); 3.67-3.73 (m, 3H); 3.60 (s, 3H); 2.90-3.04 (m, 4H); 2.58-2.87 (m, 4H). ^{13}C NMR (400 MHz, DMSO-d6): δ 171.45, 170.95, 170.64, 170.56, 170.27, 168.40, 150.23, 150.17, 137.56, 137.36, 133.77, 132.87, 132.28, 131.67, 129.96, 129.09, 129.05, 127.95, 127.89, 127.85, 127.61, 127.45, 127.34, 127.27, 126.17, 126.07, 125.91, 125.38, 119.79, 119.74, 53.66, 53.53, 51.74, 42.03, 41.86, 37.49, 37.37, 37.31, 35.85. ^{31}P NMR (δ -5.168 ppm). MS: calc. M^+ = 941.3, obsvd. $(M+H)^+$ = 942.1.

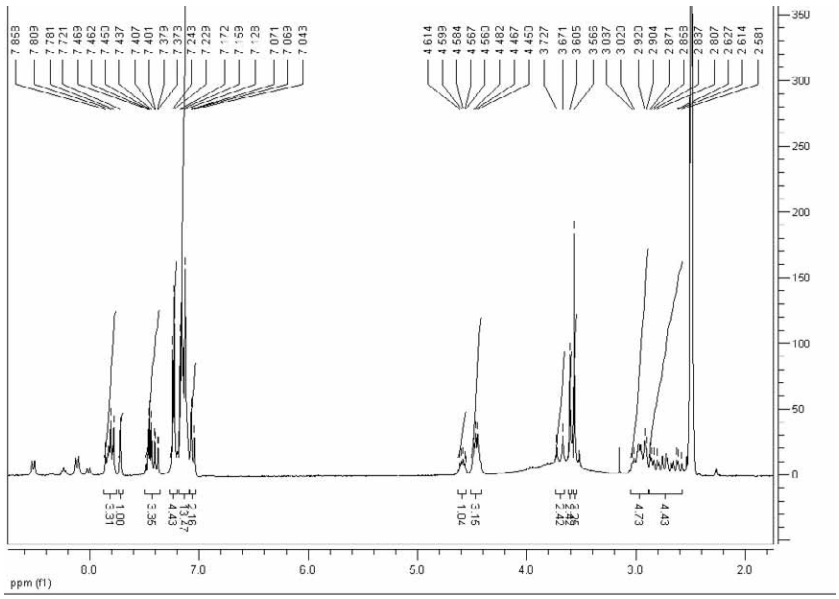


Figure S-15. ^{1}H NMR of compound **Nap-GFFFpY-OMe**

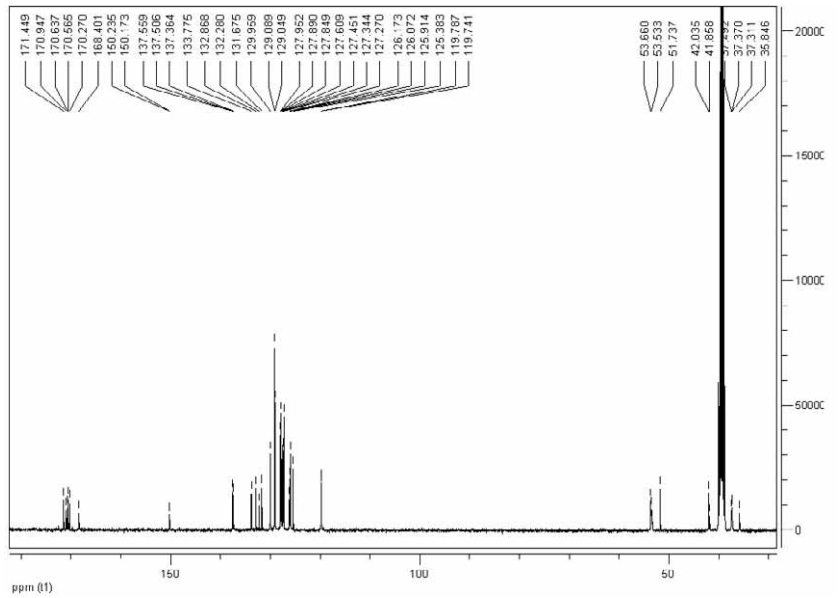
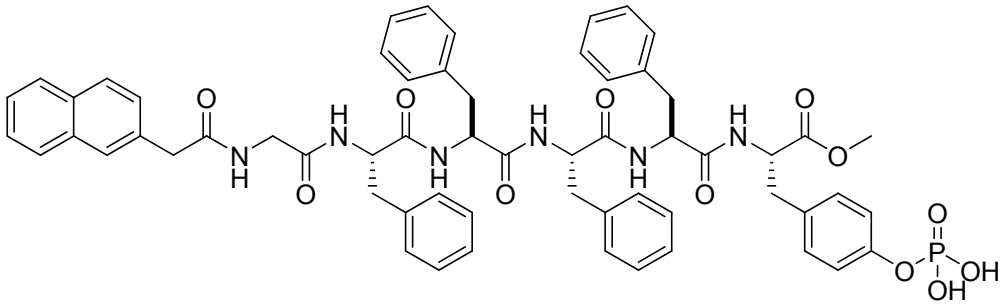


Figure S-16. ^{13}C NMR of compound **Nap-GFFFpY-OMe**

Nap-GFFFFpY-OMe



^{1}H NMR (300 MHz, DMSO-d_6) δ 7.76-7.85 (m, 3H); 7.71 (s, 1H); 7.42-7.47 (m, 2H); 7.35-7.39 (m, 1H); 7.18-7.23 (m, 7H); 7.05-7.16 (m, 17H); 4.51-4.63 (m, 1H); 4.38-4.50 (m, 4H); 3.68-3.74 (m, 1H); 3.60 (m, 3H); 3.57 (s, 3H); 2.78-3.03 (m, 7H); 2.60-2.73 (m, 3H). ^{13}C NMR (400 MHz, DMSO-d6): δ 171.48, 170.99, 170.58, 170.52, 170.20, 170.12, 168.36, 137.57, 137.45, 137.35, 133.78, 132.83, 131.64, 129.89, 129.07, 127.94, 127.85, 127.60, 127.42, 127.33, 127.26, 126.03, 125.90, 125.37, 119.70, 119.65, 53.64, 51.74, 42.01, 41.00, 37.43, 37.37. ^{31}P NMR (δ -4.960 ppm). MS: calc. M^+ = 1088.4, obsvd. $(M+H)^+$ = 1090.1.

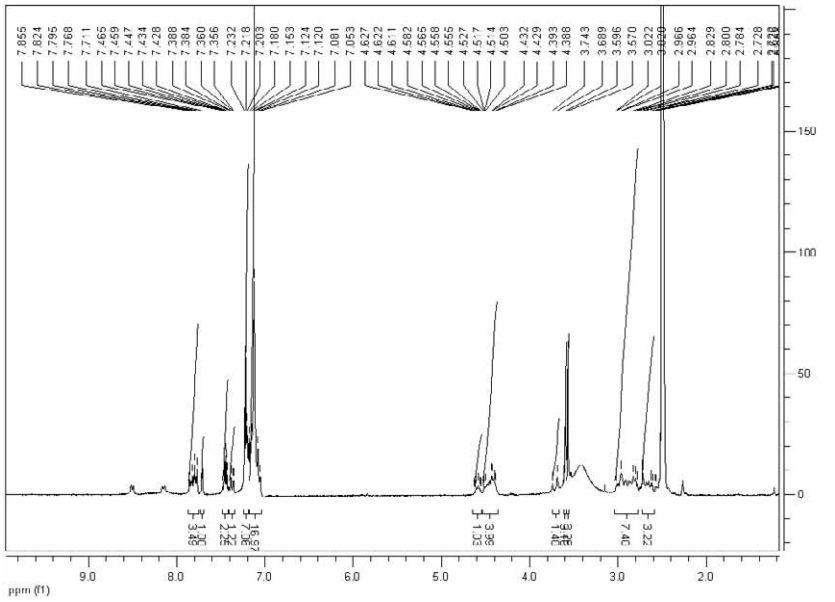


Figure S-17. ^{1}H NMR of compound **Nap-GFFFFpY-OMe**

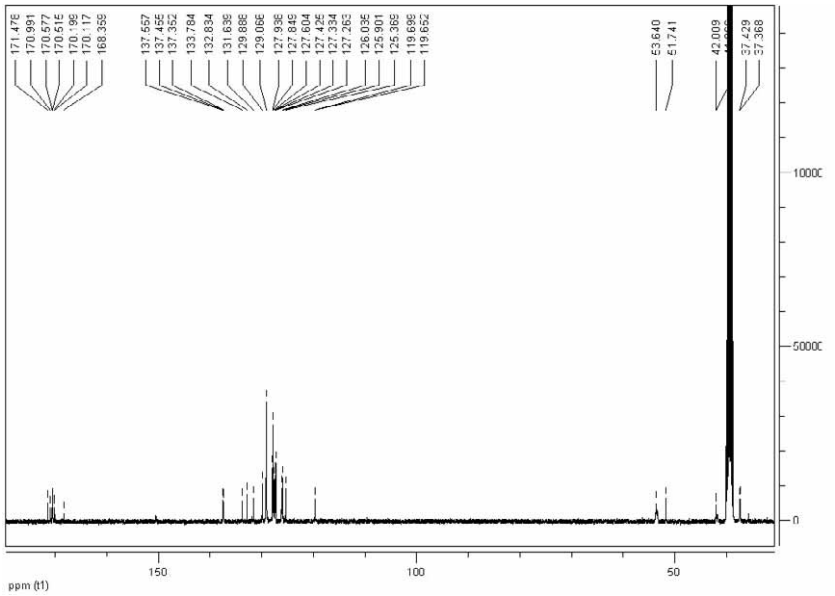
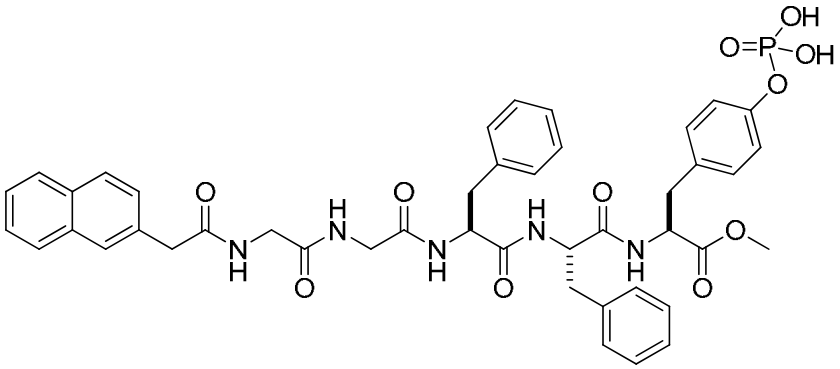


Figure S-18. ^{13}C NMR of compound **Nap-GFFFFpY-OMe**

Nap-GGFFpY-OMe



^{1}H NMR (300 MHz, DMSO-d_6) δ 7.81-7.88 (m, 3H); 7.76 (s, 1H); 7.42-7.51 (m, 4H); 7.06-7.25 (m, 14H); 4.55-4.57 (m, 1H); 4.46-4.48 (m, 2H); 3.72 (s, 2H); 3.65-3.68 (m, 3H), 3.57 (m, 4H); 2.90-3.03 (m, 4H); 2.76-2.83 (m, 1H); 2.63-2.68 (m, 1H). ^{13}C NMR (400 MHz, DMSO-d6): δ 171.47, 171.02, 170.65, 170.53, 170.45, 169.11, 168.40, 150.22, 150.16, 137.63, 137.47, 133.75, 132.89, 132.36, 131.70, 129.99, 129.11, 127.97, 127.89, 127.66, 127.47, 127.35, 127.32, 126.20, 126.10, 125.93, 125.40, 119.80, 119.75, 53.69, 53.61, 51.73, 42.10, 42.06, 41.73, 41.64, 37.39, 37.29, 35.83. ^{31}P NMR (δ -6.219 ppm). MS: calc. M^+ = 851.3, obsvd. $(M+H)^+$ = 852.0.

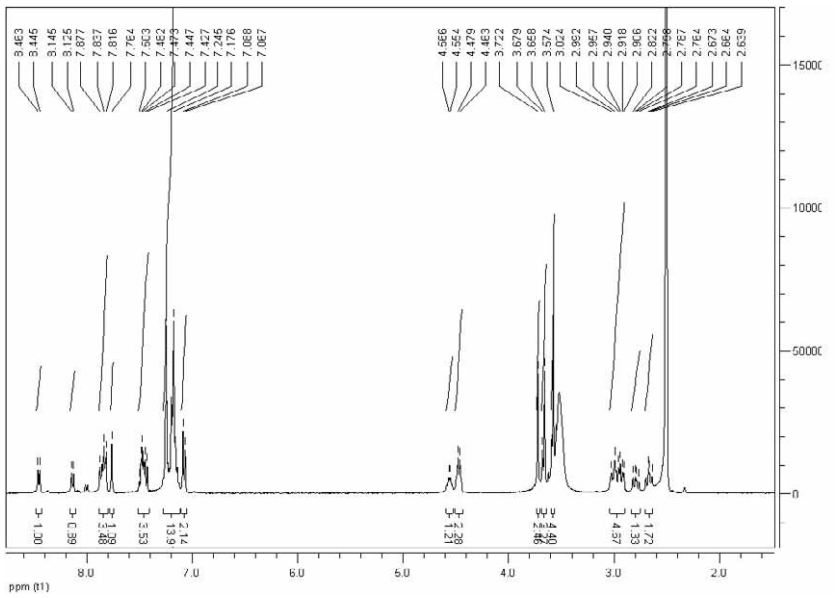


Figure S-19. ^{1}H NMR of compound **Nap-GGFFpY-OMe**

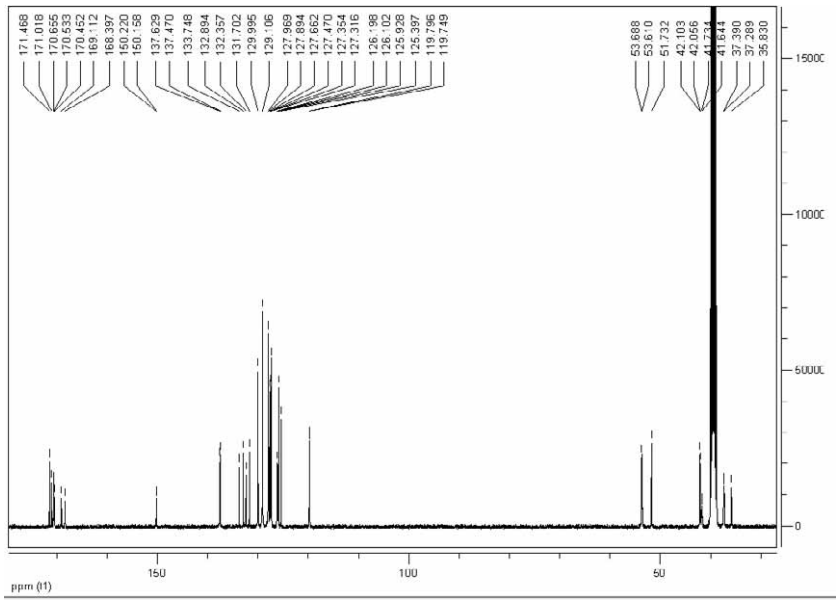
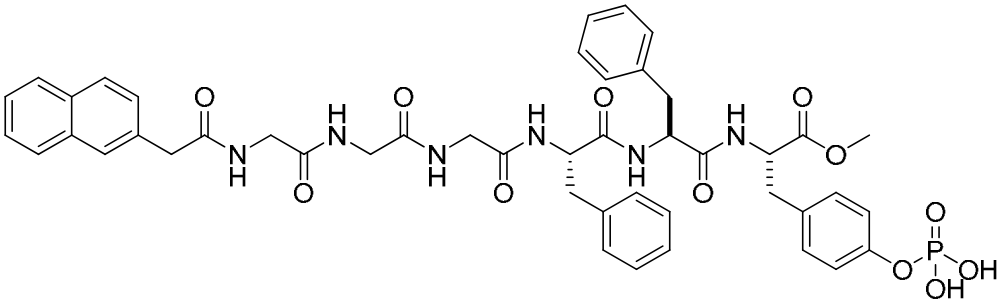


Figure S-20. ^{13}C NMR of compound **Nap-GGFFpY-OMe**

Nap-GGGFFpY-OMe



^{1}H NMR (300 MHz, DMSO-d_6) δ 7.79-7.86 (m, 3H); 7.74 (s, 1H); 7.40-7.47 (m, 3H); 7.72-7.24 (m, 4H); 7.13-7.17 (m, 8H); 7.03-7.07 (d, 2H); 4.41-4.57 (m, 4H); 3.65 (s, 4H); 3.70-3.75 (m, 6H); 2.90-3.03 (m, 4H), 2.62-2.82 (m, 2H). ^{13}C NMR (400 MHz, DMSO-d6): δ 171.47, 171.02, 170.69, 170.43, 170.35, 169.24, 168.93, 168.30, 150.39, 150.33, 137.60, 137.46, 133.78, 132.87, 132.10, 131.68, 129.92, 129.09, 127.96, 127.88, 127.66, 127.45, 127.35, 126.29, 126.19, 126.10, 125.92, 125.39, 119.76, 119.71, 53.68, 53.57, 51.72, 42.10, 37.36, 35.80. ^{31}P NMR (δ -5.006 ppm). MS: calc. M^+ = 908.3, obsvd. $(M+H)^+$ = 910.1.

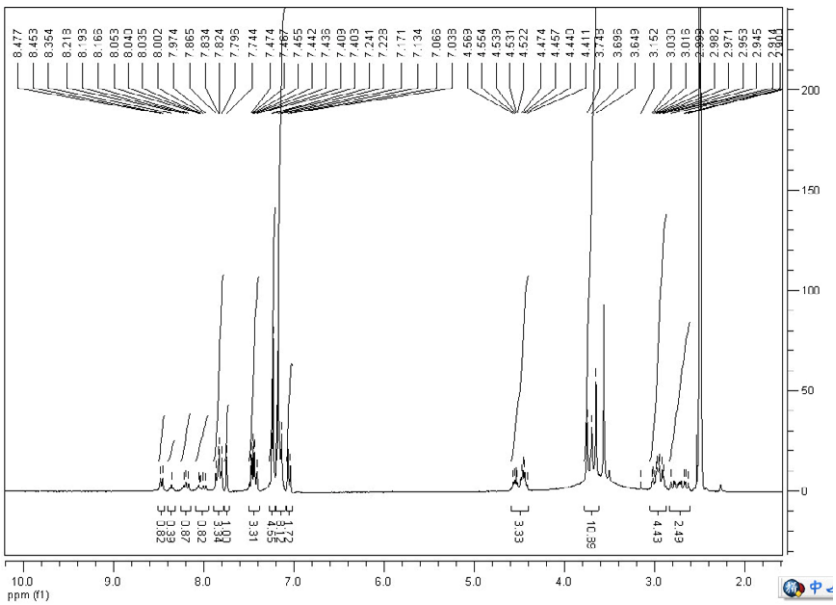


Figure S-21. ^{1}H NMR of compound **Nap-GGGFFpY-OMe**

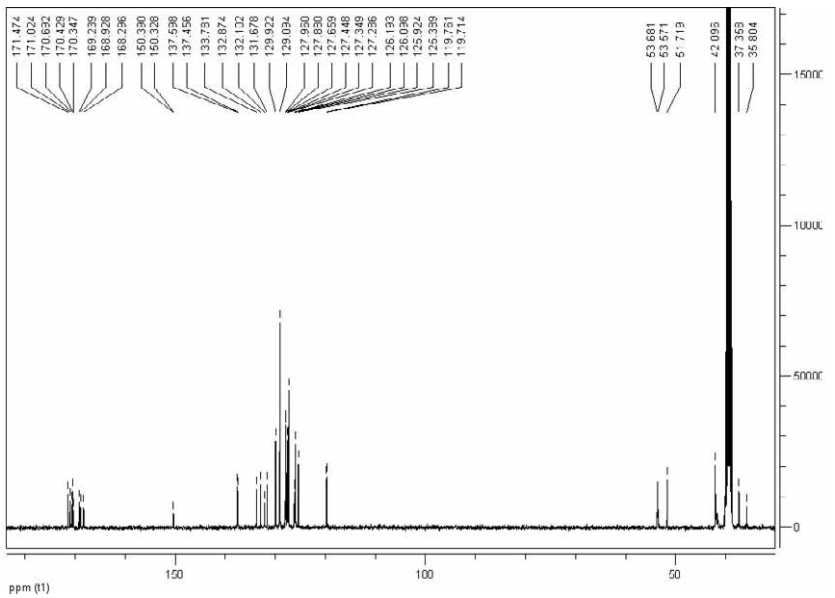
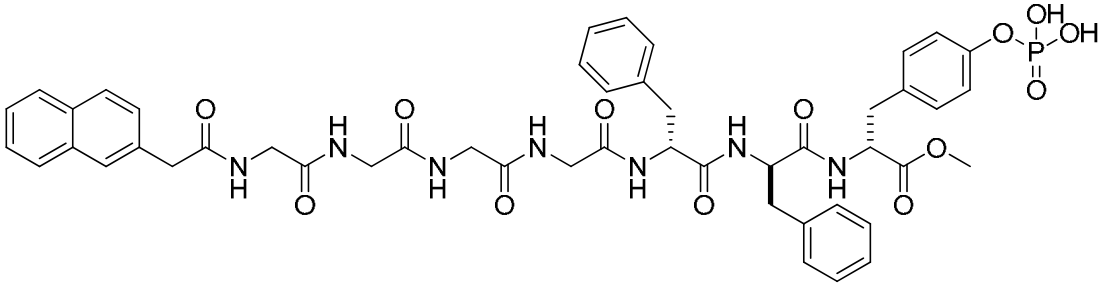


Figure S-22. ^{13}C NMR of compound **Nap-GGGFFpY-OMe**

Nap-GGGGFFpY-OMe



^{1}H NMR (300 MHz, DMSO-d_6) δ 7.79-7.86 (s, 1H); 7.75 (s, 1H); 7.40-7.47 (m, 4H); 7.03-7.24 (m, 15H); 4.50-4.56 (m, 1H); 4.40-4.46 (m, 2H); 3.73-3.76 (m, 4H); 3.60-3.67 (m, 5H); 3.54-3.61 (m, 4H); 2.87-3.02 (m, 4H); 2.59-2.81 (m, 2H). ^{13}C NMR (400 MHz, DMSO-d6): δ 171.46, 171.01, 170.65, 170.43, 170.49, 169.19, 169.15, 168.30, 150.20, 150.13, 137.61, 137.47, 133.78, 132.89, 132.37, 131.69, 129.99, 129.09, 127.95, 127.88, 127.67, 127.45, 127.35, 127.29, 126.18, 126.09, 125.92, 125.39, 119.77, 119.73, 53.68, 53.69, 51.72, 42.11, 42.06, 37.37, 35.81. ^{31}P NMR (δ -4.814 ppm). MS: calc. M+ = 965.3, obsvd. $(M+H)^{+}$ = 966.6.

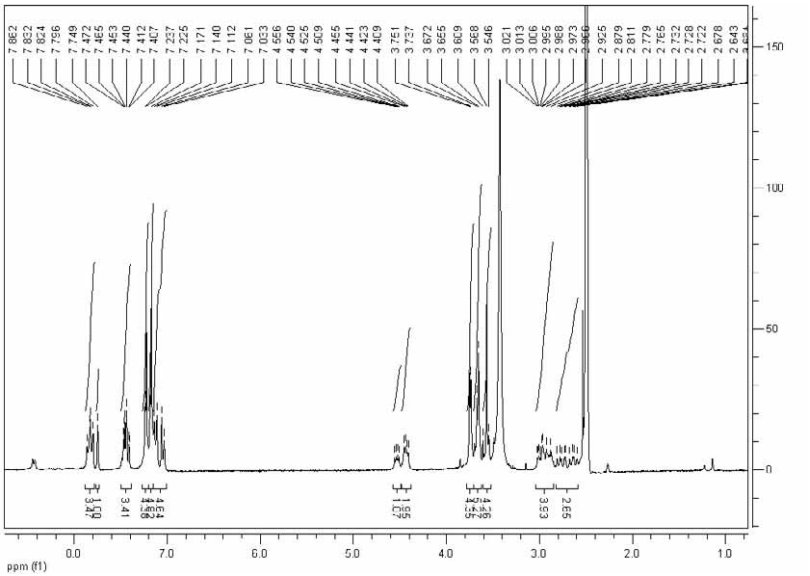


Figure S-23. ^{1}H NMR of compound **Nap-GGGGFFpY-OMe**

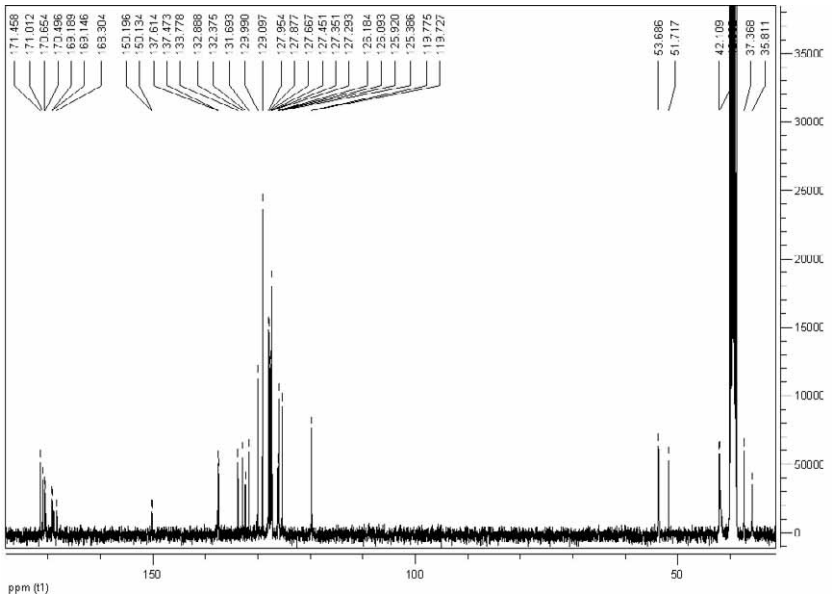


Figure S-24. ^{13}C NMR of compound **Nap-GGGGFFpY-OMe**

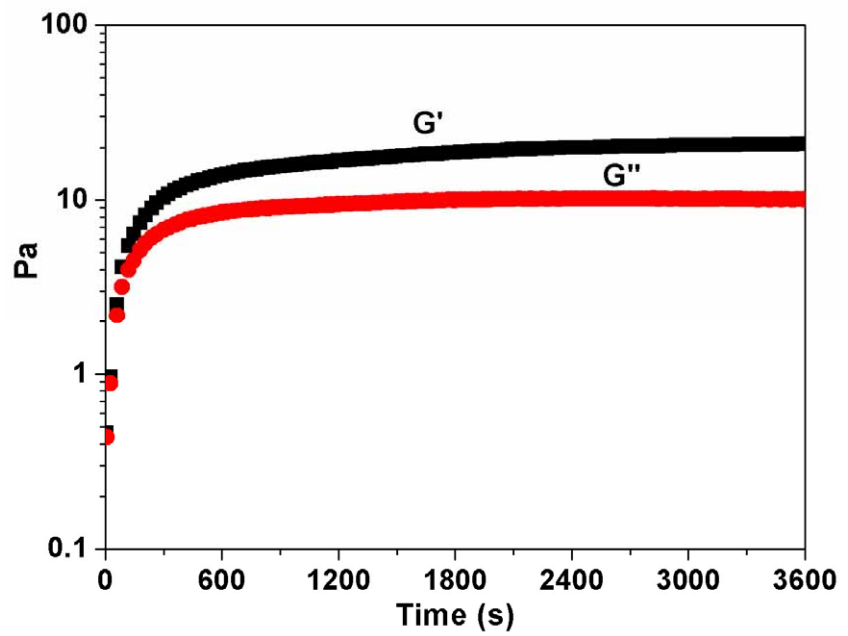


Figure S-25. The rheological measurement with the mode of dynamic time sweep for aqueous solutions containing 0.1 wt% of Nap-GFFpY-OH and 60 U/mL of the enzyme (strain = 2% and frequency = 2 rad/s)

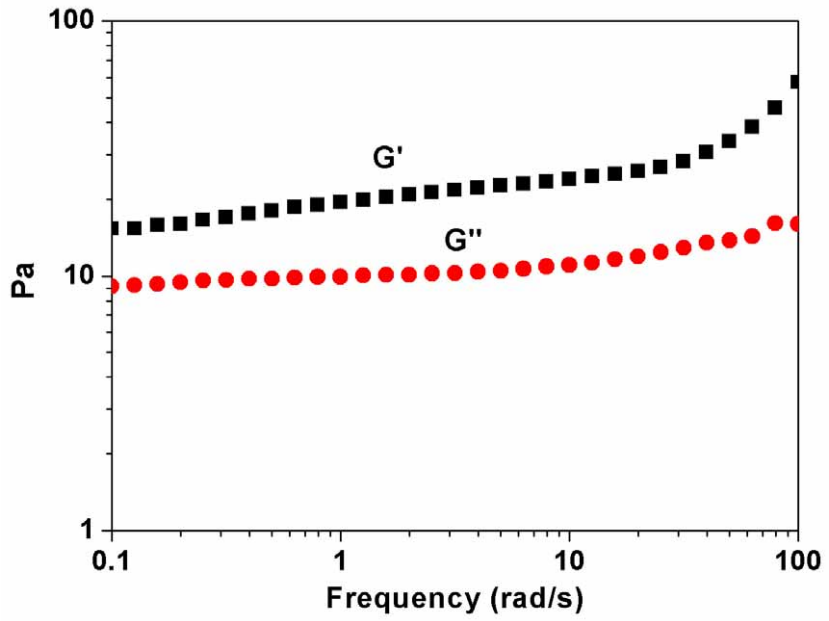


Figure S-26. The rheological measurement with the mode of dynamic frequency sweep for gel of Nap-GFFpY-OH formed 2 hours after the addition of 60 U/mL of the enzyme at the strain of 2% (initial concentration = 0.1 wt%)