Electronic Supplementary Material (ESI) for ChemComm.

Organoboron Based Photochromic Gelator

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S1. Experimental Details

General Information

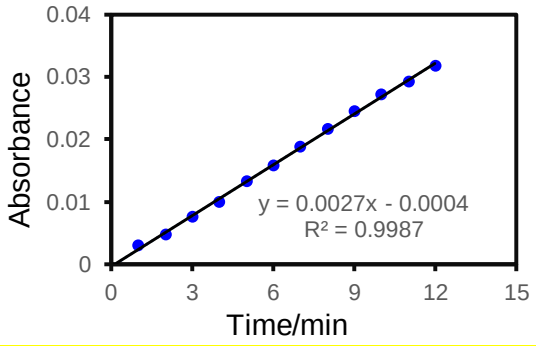
General Procedures and Materials. Unless otherwise specified, all reactions were conducted under an inert atmosphere utilizing standard Schlenk techniques. The starting materials were purchased from either J&K Scientific Ltd. or Energy Chemical Co. and were used as received, without the need for additional purification steps. Before utilization, the solvents were subjected to standard drying procedures to ensure their purity. For the detection and monitoring of reaction progress, thin-layer chromatography (TLC) was employed, utilizing silica gel plates and visualized under UV light at wavelengths of 254 or 365 nm. The purification process involved the use of preparative chromatography with normal-phase silica gel, specifically with a particle size ranging from 300 to 400 mesh. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. High-resolution mass spectra (HRMS) were obtained from an Agilent Q-TOF 6520 LC-MS spectrometer. UV-visible absorption spectra were recorded on a Cary 300 UV-Vis spectrophotometer. Luminescent spectra were recorded on an Edinburgh Instruments FLS980 or Lengguang Tech. F97Pro spectrophotometer. Fluorescent quantum efficiencies were determined using a Hamamatsu C11347-11 Quantaurus-QY spectrometer. The morphologies and sizes of the gel were characterized by using field emission scanning electron microscopy (FE-SEM, JSM-7500F). The rheological characterization was performed using a stress-controlled rheometer (Anton Paar MCR302) at 25 ^{o}C. Hydroxyl-functionalized photochromic boryl unit (compound **1**)[1] was prepared according to literature procedures.

Photoisomerization Quantum Yield Measurement

All preparation and measurements were done with freshly prepared solutions. The photoisomerization quantum yields were determined based on Hatchard-Parker method[2-3] by measuring the rate of isomerization in the initial stage of the reaction at low concentration (absorbance at 365 nm ≈ 0.1) and using B(ppy)Mes_2 as the reference material. The photoisomerization quantum efficiency of B(ppy)Mes_2 was established previously using ferrioxalate actinometry (Organometallics, 2011, 30, 665–668). The absorbance was measured using an Agilent Cary 300 spectrophotometer for collecting absorbance measurements. The monchromated excitation light (365 nm) of an Edinburgh Instruments FLS980 450 W (xenon arc

lamp) was used as the irradiation light source.

The photoisomerization quantum yield of **tripep-triazole-B** was measured in degassed dry toluene solution. The solution was exposed under 365 nm light and the absorbance change was recorded every 1 minute at 580 nm. The absorbance *vs*. time was monitored at 580 nm and the slope of the fitting curve was defined as *m*, which is directly related to the number of moles of the dark isomer units produced over time.



The following equation is used to calculate the quantum yield of isomerization process.

$$\Phi_s = \Phi_r \frac{\frac{m_s V_s}{\varepsilon_s}}{\frac{m_r V_r}{\varepsilon_r}} \frac{A_r}{A_s}$$

Φ_s : quantum yield of testing sample

Φ_r : quantum yield of reference compound

m_s : slope of the fitting curve of absorbance (sample) *vs.* time

V_s : volume of the irradiated volume of the sample

ε_s : the molar extinction coefficient of the formed isomer from the testing sample

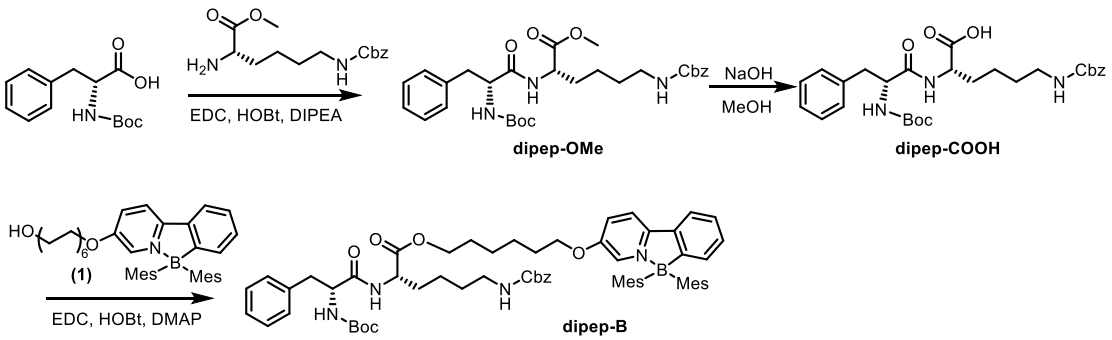
m_r : slope of the fitting curve of absorbance (reference compound) *vs.* time

V_r : volume of the irradiated volume of the reference compound

ε_r : the molar extinction coefficient of the formed isomer from the reference compound

A_r : the absorbance reading of the reference compound at the wavelength of irradiation

A_s : the absorbance reading of the testing sample at the wavelength of irradiation

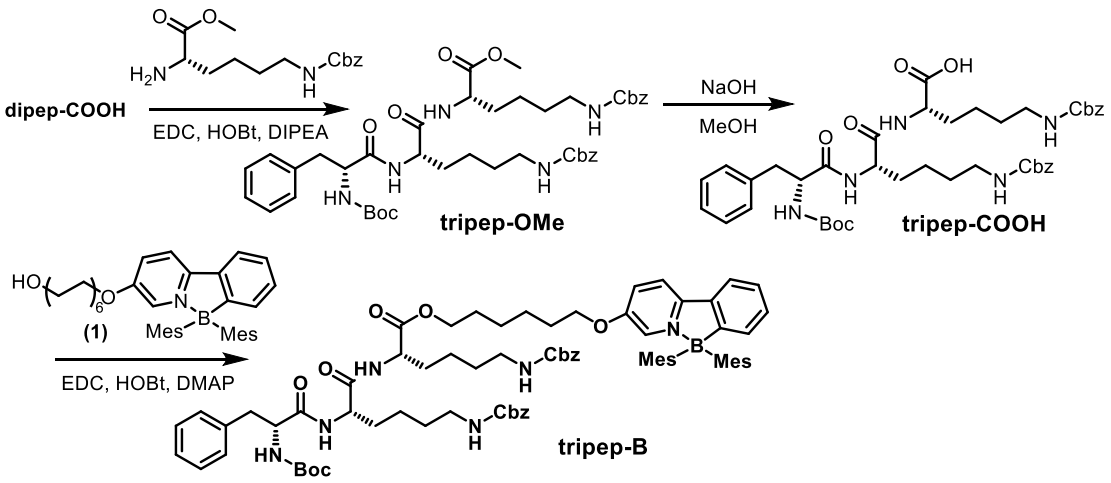


Compound dipep-OMe. Boc-D-phenylalanine (500 mg, 1.89 mmol, 1.0 equiv.), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDC) (728 mg, 3.8 mmol, 2.0 equiv.), 1-hydroxybenzotriazole (HOBt) (513 mg, 3.8 mmol, 2.0 equiv.) and 25 mL dichloromethane were added into a 50 mL Schlenk flask. The solution was cooled to -10°C, and N,N-diisopropylethylamine (DIPEA) (2.3 mL, 14 mmol, 7.5 equiv.) was added. After stirring for 10 minutes, Z-L-lysine methyl ester hydrochloride (676 mg, 2.3 mmol, 1.2 equiv.) was slowly added and the reaction was allowed to warm to room temperature and stirred overnight. After the reaction was complete, the mixture was extracted with dichloromethane, washed with brine solution, and the organic phases were combined and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to obtain the crude product, which was then purified by silica gel column chromatography (PE: EA = 2:1) to yield a white solid powder (818 mg), with a yield of 80%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.29 (s, 1H), 7.30 (m, 11H), 6.84 (d, J = 8.8 Hz, 1H), 4.98 (s, 2H), 4.22 (dt, J = 16.5, 8.7 Hz, 2H), 3.63 (s, 3H), 3.02-2.70 (m, 4H), 1.30 (s, 15H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.98, 172.16, 156.57, 155.56, 138.39, 137.75, 129.72, 128.81, 128.45, 128.20, 126.66, 78.46, 65.60, 55.91, 52.27, 52.21, 38.43, 29.37, 28.24. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{29}H_{40}N_3O_7$, 542.2861; found 542.2887.

Compound dipep-COOH. Compound **dipep-OMe** (500 mg, 0.9 mmol, 1.0 equivalent) was introduced into a 50 mL round-bottom flask and dissolved in 20 mL of methanol. The solution was cooled to 0°C, and then a 5 mL portion of 0.6 M NaOH solution was added dropwise. Following the addition, the reaction mixture was allowed to warm to room temperature and stirred for about 4 hours. Upon completion of the reaction, the solvent was removed under reduced pressure to obtain the crude product. The resulting solid was dissolved in water and subsequently washed with dichloromethane to eliminate organic impurities. The aqueous layer was then acidified with a 2 M HCl solution, added dropwise under an ice bath, and the product was extracted using

dichloromethane. The organic phases were combined and dried over anhydrous sodium sulfate (Na_2SO_4). After the drying process, the solvent was removed under reduced pressure, yielding compound **2** as a white solid (438 mg) with a yield of 90%. Compound **dipep-COOH** was used for the next step without further purification.

Compound dipep-B. Compound **dipep-COOH** (100 mg, 0.19 mmol, 1.0 equiv.) was weighed and placed into a 50 ml Schlenk flask. Under a nitrogen atmosphere, 5 ml of dichloromethane was added. The solution was cooled to 0°C, and then EDC (73 mg, 0.38 mmol, 2.0 equiv.) and HOBt (51 mg, 0.38 mmol, 2.0 equiv.) were added. After stirring for ten minutes, 4-dimethylaminopyridine (DMAP) (9.8 mg, 0.08 mmol, 0.4 equiv.) and compound **1** (88 mg, 0.17 mmol, 0.9 equiv.) were added and the reaction was allowed to slowly warm to room temperature and stirred overnight. After the reaction was complete, the mixture was extracted with dichloromethane, washed with a saturated solution of sodium chloride, and the organic phases were combined and dried over anhydrous Na_2SO_4. The solvent was then removed under reduced pressure. The crude product was then purified by column chromatography (PE : EA = 3:1) to yield a white solid powder (90 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.84 (d, *J* = 10.1 Hz, 1H), 7.71 (d, *J*= 6.1 Hz, 3H), 7.52 (d, *J* = 9.9 Hz, 2H), 7.34 –7.20 (m, 10H), 6.64 (s, 4H), 5.09 (s, 2H), 4.50 (s, 1H), 4.35 (s, 1H), 4.10 (t, *J* = 7.5 Hz, 2H), 3.92 –3.88 (t, *J* = 7.5 Hz, 2H), 3.14 –3.05 (m, 4H), 2.17 (s, 6H), 1.78 –1.64 (m, 16H), 1.45 –1.39 (m, 19H).^{13}C NMR (101 MHz, DMSO-*d*6) δ 171.87, 156.26, 153.88, 151.84, 137.27, 134.12, 132.79, 130.13, 129.42, 129.18, 128.67, 127.97, 127.71, 127.69, 121.44, 78.10, 68.95, 64.11, 28.08, 24.96, 20.31.HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{63}H_{78}BN_4O_8$, 1029.5907; found 1029.5940.



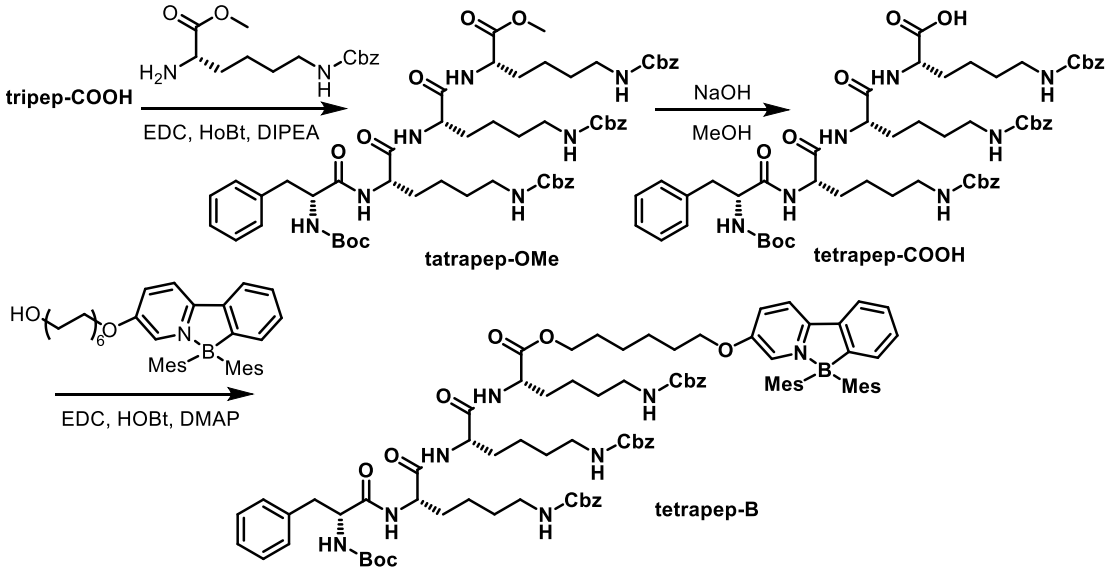
Compound tripep-OMe. Compound **dipep-COOH** (400 mg, 0.76 mmol, 1.0 equiv.), EDC (288

mg, 1.5 mmol, 2.0 equiv.), and HOBt (202 mg, 1.5 mmol, 2.0 equiv.) were added into a 50 mL Schlenk flask and dissolved in 6 mL dichloromethane. The reaction mixture was then cooled to -10°C, and N,N-diisopropylethylamine (DIPEA) (0.9 mL, 5.7 mmol, 7.5 equiv.) was added. After stirring for 10 minutes, CBZ-L-lysine methyl ester hydrochloride (268 mg, 0.9 mmol, 1.2 equiv.) was added to the solution and the reaction mixture stirred overnight at room temperature. Upon completion of the reaction, the mixture was extracted using dichloromethane and then washed with brine to remove water-soluble impurities. The organic layer was dried over anhydrous Na_2SO_4. After the drying process, the solvent was removed under reduced pressure, yielding the crude product which was further purified through silica gel column chromatography (MeOH: DCM = 1:20) to yield a white solid powder (433 mg), with a yield of 71%. ^{1}H NMR (400 MHz, DMSO-*d*6) δ 8.19 (d, *J* = 6.8 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.46 –7.03 (m, 17H), 6.97 (d, *J* = 7.6 Hz, 1H), 5.00 (d, *J* = 6.8 Hz, 4H), 4.25 (d, *J* = 35.2 Hz, 3H), 3.59 (d, *J*= 7.9 Hz, 3H), 2.78 (m, 6H), 1.69–1.26 (m, 21H). HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{43}H_{58}N_5O_{10}$, 804.4178; found 804.4165.

Compound tripep-COOH. Compound **tripep-OMe** (278 mg, 0.35 mmol, 1.0 equiv.) was introduced into a 50 mL round-bottom flask and dissolved in 10 mL of methanol. The solution was cooled to 0°C, and then a 2 mL portion of a 0.6 M NaOH solution was added dropwise. After the addition, the reaction mixture was allowed to warm to room temperature and stirred for about 4 hours. Upon completion of the reaction, the solvent was removed under reduced pressure to obtain the crude product. The resulting solid was dissolved in water and then washed with dichloromethane to remove organic impurities. The aqueous layer was acidified with a 2 M HCl solution, added dropwise under an ice bath, and the product was extracted using dichloromethane. The organic phases were combined and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, yielding compound **tripep-COOH** as a white solid (227 mg) with a yield of 83%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.18 –8.03 (m, 2H), 7.56 – 7.10 (m, 17H), 6.96 (s, 1H), 5.01 (s, 4H), 4.42 – 4.26 (m, 3H), 3.04 – 2.87 (m, 6H), 1.76 – 1.08 (m, 21H). Due to the solubility issue, ^{13}C NMR was not obtained. HRMS(ESI): calcd for $C_{42}H_{56}N_5O_{10}[M+H]^+$: 790.4022; found: 790.4039.

Compound tripep-B. Weighed 120 mg (0.15 mmol, 1.0 equiv.) of **tripep-COOH** into a 50 mL Schlenk flask, and dissolved it in 5 mL of dichloromethane under a nitrogen atmosphere. The solution was cooled to 0°C, then EDC (58 mg, 0.30 mmol, 2.0 equiv.) and HOBt (41 mg, 0.3 mmol, 2.0 equiv.) were added. The mixture was stirred for ten minutes. Subsequently, DMAP (7.0 mg, 0.06

mmol, 0.4 equiv.) and compound **1** (71 mg, 0.14 mmol, 0.9 equiv.) were added. The mixture was allowed to slowly warm to room temperature with continuous stirring, allowing the reaction to proceed overnight. Upon completion of the reaction, it was extracted with dichloromethane, washed with brine, and the organic phases were combined. The combined organic phases were dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to obtain the crude product. The crude product was further purified by silica gel column chromatography (PE: EA = 2:1) to yield a white solid powder: 72 mg, with a yield of 37%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.38 – 8.16 (m, 2H), 8.09 – 7.88 (m, 4H), 7.72 (s, 1H), 7.35 – 7.20 (m, 18H), 6.95 (s, 1H), 6.54 (s, 4H), 5.00 (s, 4H), 4.42 – 4.33 (m, 3H), 4.02 (s, 4H), 3.04 –2.87 (m, 6H), 2.08 (s, 6H), 1.81 – 1.58 (m, 16H), 1.38 – 1.23 (m, 25H).^{13}C NMR (101 MHz, DMSO-d_6) δ 171.99, 156.08, 155.26, 153.88, 151.84, 137.27, 135.12, 132.79, 130.03, 129.42, 129.25, 129.18, 128.67, 127.97, 127.71, 127.69, 121.44, 78.10, 68.95, 65.11, 28.08, 24.96, 20.31. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{77}H_{96}BN_6O_{11}$, 1291.7225; found 1291.7288.



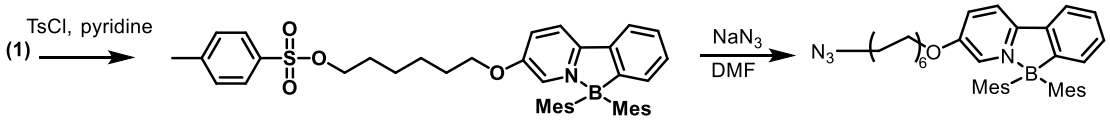
Compound tetrapep-OMe. Compound **tripep-COOH** (400 mg, 0.50 mmol, 1.0 equiv.), EDC (192 mg, 1.0 mmol, 2.0 equiv.), and HOBt (135 mg, 1.0 mmol, 2.0 equiv.) were added into a 50 mL Schlenk flask and dissolved in 6 mL dichloromethane. The reaction mixture was then cooled to -10°C, and N,N-diisopropylethylamine (DIPEA) (0.6 mL, 3.8 mmol, 7.5 equiv.) was added. After stirring for 10 minutes, CBZ-L-lysine methyl ester hydrochloride (176 mg, 0.6 mmol, 1.2 equiv.) was added to the solution and the reaction mixture was stirred overnight at room temperature. Upon completion of the reaction, the mixture was extracted using dichloromethane and then washed with

brine to remove water-soluble impurities. The organic layer was dried over anhydrous Na_2SO_4. Then the solvent was removed under reduced pressure, yielding the crude product which was further purified through silica gel column chromatography (MeOH: DCM = 1: 30) to yield a white solid powder (378 mg), with a yield of 71%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.30 –7.82 (m, 3H), 7.41–7.29 (m, 23H), 6.90 (s, 1H), 5.00 (s, 6H), 4.40–4.25 (m, 4H), 3.59 (s, 3H), 2.97 (s, 8H), 1.67–1.35 (m, 27H). HRMS(ESI): calcd for $C_{57}H_{76}N_7O_{13}$ $[M+H]^+$: 1066.5496; found: 1066.5545.

Compound tetrapep-COOH. Compound **tetrapep-OMe** (290 mg, 0.27 mmol, 1.0 equiv.) was introduced into a 50 mL round-bottom flask and dissolved in 10 mL of methanol. The solution was cooled to 0°C, and then a 1.8 mL portion of a 0.6 M NaOH solution was added dropwise. After the addition, the reaction mixture was allowed to warm to room temperature and stirred for about 4 hours. Upon completion of the reaction, the solvent was removed under reduced pressure to obtain the crude product. The resulting solid was dissolved in water and then washed with dichloromethane to remove organic impurities. The aqueous layer was acidified with a 2 M HCl solution, added dropwise under an ice bath, and the product was extracted using dichloromethane. The organic phases were combined and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, yielding compound **tetrapep-COOH** as a white solid (227 mg) with a yield of 80%. **tetrapep-COOH** was used directly without further purification.

Compound tetrapep-B. Weighed 150 mg (0.14 mmol, 1.0 equiv.) of **tetrapep-COOH** into a 50 mL Schlenk flask, and dissolved it in 5 mL of dichloromethane under a nitrogen atmosphere. The solution was cooled to 0°C, then EDC (54 mg, 0.28 mmol, 2.0 equiv.) and HOBt (38 mg, 0.28 mmol, 2.0 equiv.) were added. The mixture was stirred for ten minutes. Subsequently, DMAP (7.0 mg, 0.06 mmol, 0.4 equiv.) and compound **1** (68 mg, 0.13 mmol, 0.9 equiv.) were added. The mixture was allowed to slowly warm to room temperature with continuous stirring, allowing the reaction to proceed overnight. Once the reaction was complete, it was extracted with dichloromethane, washed with brine, and the organic phases were combined. The combined organic phases were dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to obtain the crude product. The crude product was further purified by silica gel column chromatography (DCM: MeOH = 50 :1) to yield a white solid powder: 65 mg, with a yield of 30%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.36 –7.86 (m, 8H), 7.34 –7.19 (m, 25H), 6.92 (s, 1H), 6.53 (s, 4H), 4.99 (s, 8H), 4.33–4.09 (m, 4H), 4.01 (s, 4H), 2.96 (s, 8H), 2.07 (s, 6H), 1.76–1.68 (m, 16H), 1.42 –1.22 (m, 31H).^{13}C NMR (101

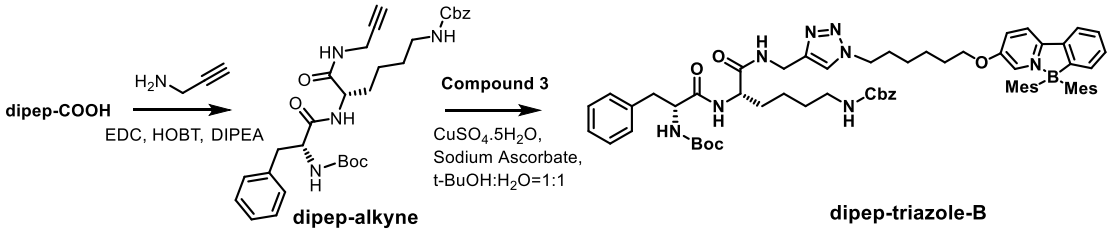
MHz, DMSO-d_6) δ 171.98, 156.08, 153.88, 151.84, 136.98, 132.50, 129.30, 129.13, 128.93, 128.03, 127.69, 127.42, 124.84, 121.16, 118.92, 68.67, 64.82, 63.93, 28.80, 27.80, 24.54, 22.28, 20.02. HRMS (ESI) m/z: $[M + H]^+$calcd for $C_{91}H_{114}BN_8O_{14}$, 1553.8542; found 1553.9688.



Compound 2 Compound 3

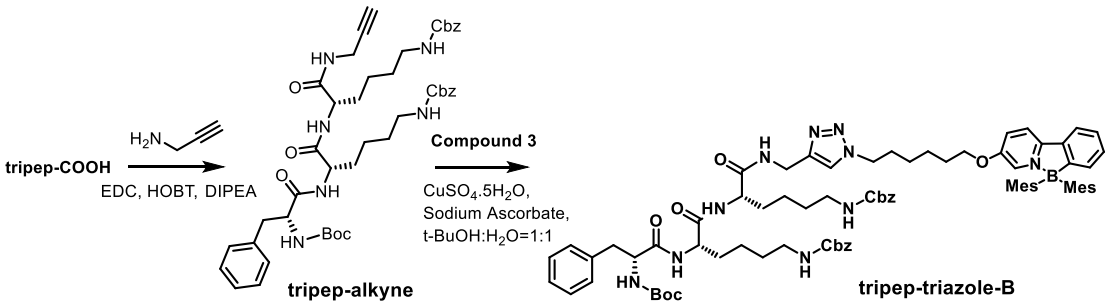
Compound 2. Compound **1** (300 mg, 0.58 mmol, 1.0 equiv.) and pyridine (0.5 ml, 6.38 mmol, 11 equiv.) were added in a 50 mL Schlenk flask. 10 mL dry dichloromethane was added to dissolve the mixture. The solution was cooled to 0°C, then tosyl chloride (165 mg, 0.87 mmol, 1.5 equiv.) was added. The mixture was allowed to slowly warm to room temperature with continuous stirring, allowing the reaction to proceed overnight. Once the reaction was complete, it was extracted with dichloromethane, washed with brine, and the organic phases were combined. The combined organic phases were dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to obtain the crude product and further purified by silica gel column chromatography (PE: EA = 10 :1) to yield a white solid powder: 368 mg, with a yield of 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 2.4 Hz, 1H), 7.85 (d, *J*= 8.9 Hz, 1H), 7.79 (d, *J*= 8.2 Hz, 2H), 7.71 (d, *J*= 7.1 Hz, 2H), 7.51 (dd, *J*= 8.9, 2.6 Hz, 1H), 7.33 (d, *J*= 8.1 Hz, 2H), 7.22 (t, *J*= 5.7 Hz, 2H), 6.64 (s, 4H), 4.03 (t, *J* = 6.4 Hz, 2H), 3.88 (t, *J* = 6.3 Hz, 2H), 2.44 (s, 3H), 2.17 (s, 6H), 1.86 –1.62 (m, 16H), 1.41 –1.33 (m, 4H). HRMS (ESI) m/z: $[M + H]^+$calcd for $C_{42}H_{49}BNO_4S$, 674.3470; found 674.3461.

Compound 3. Compound **2** (114 mg, 0.17 mmol, 1.0 equiv.) and sodium azide (0.5 mL, 6.38 mL, 11 equiv.) were placed into a 50 mL Schlenk flask. 5 mL DMF was used to dissolve the solids. The solution was heated to 80°C and stirred in the dark for 5 hours. After the reaction was complete, it was quenched by water and ethyl acetate was used for extraction. The organic phase was washed with brine solution and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to afford the crude product as a yellow oily liquid (91 mg), with a yield of approximately 99%. The crude product was directly used in the next step without further purification.



Compound dipep-alkyne. Compound **dipep-COOH** (157 mg, 0.30 mmol, 1.0 equiv), EDC (142 mg, 0.75 mmol, 2.5 equiv), and HOBt (81 mg, 0.60 mmol, 2.0 equiv) were dissolved in 6 mL of DCM in a 50 mL Schlenk flask. The solution was cooled to -10°C, then was added DIPEA (0.4 mL, 2.3 mmol, 7.5 equiv) and stirred for ten minutes. Afterward, propargylamine (33 mg, 0.6 mmol, 2.0 equiv) was added and the mixture was allowed to slowly warm to room temperature with stirring overnight. Once the reaction was complete, it was extracted with DCM, washed with brine. The organic phases were combined and dried over anhydrous Na_2SO_4. Remove the solvent under reduced pressure to obtain the crude product which was purified by silica gel column chromatography (DCM : MeOH = 30:1) to yield a white solid powder (156 mg, 92% yield). The ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.18 (m, 10H), 6.96 (s, 1H), 6.22 (s, 1H), 5.10 (s, 2H), 4.97 (s, 1H), 4.83 (s, 1H), 4.35 – 4.26 (m, 1H), 4.19 (q, *J* = 7.2 Hz, 1H), 4.13 – 3.84 (m, 2H), 3.13 (q, *J* = 6.6 Hz, 2H), 3.06 – 2.99 (m, 2H), 2.17 (s, 1H), 1.42 (s, 13H), 1.17 – 0.98 (m, 2H). HRMS (ESI) m/z: [M + H]$^+$calcd for $C_{31}H_{41}N_4O_6$, 565.3021; found 565.3025.

Compound dipep-triazole-B. Compound **dipep-alkyne** (96 mg, 0.17 mmol, 1.0 equiv.), compound **3** (55 mg, 0.17 mmol, 1.0 equiv.), copper(II) sulfate pentahydrate (0.8 mg, 0.003 mmol, 0.02 equiv.) and sodium ascorbate (3.4 mg, 0.02 mmol, 0.1 equiv.) were added into a 25 mL Schlenk flask. The mixture was dissolved in 2.5 mL of tert-butanol and 2.5 mL of distilled water. Stirred the solution at 40°C overnight. After the reaction was completed, extracted with DCM, washed with brine, and combined the organic phases. Dried the organic phase over anhydrous Na_2SO_4. Removed the solvent under reduced pressure to obtain the crude product, which was further purified by silica gel column chromatography (DCM: MeOH = 20:1) to yield pale yellow powder (157 mg, 82% yield). ^{1}H NMR (700 MHz, DMSO-d_6) δ 8.38 –8.29 (m, 2H), 8.10 (d, *J* = 8.0 Hz, 1H), 8.06 (s, 1H), 8.01 (d, *J* = 6.7 Hz, 1H), 7.97 (d, *J* = 6.7 Hz, 1H), 7.81 (s, 1H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.35 –7.15 (m, 13H), 7.06 (s, 1H), 6.54 (s, 4H), 4.98 (s, 2H), 4.37 –4.22 (m, 4H), 4.21 –4.12 (m, 2H), 4.01 (t, *J*= 6.4 Hz, 2H), 2.94 –2.90 (m, 2H), 2.80 –2.74 (m, 1H), 2.08 (s, 6H), 1.86–1.49(m, 14H), 1.47 –1.14 (m, 21H).^{13}C NMR (176 MHz, DMSO-d_6) δ 171.63, 156.05, 153.87, 137.75, 137.26, 132.77, 130.02, 129.59, 129.43, 129.24, 128.33, 128.00, 127.71, 126.21, 125.14, 122.44, 121.46, 119.24, 78.23, 68.92, 65.10, 56.04, 52.41, 49.15, 35.78, 34.40, 29.63, 28.08, 25.56, 24.66, 20.32.HRMS (ESI) m/z: [M + H]$^+$calcd for $C_{66}H_{82}BN_8O_7$, 1109.6394; found 1109.6407.



Compound tripep-alkyne. Compound **tripep-COOH** (500 mg, 0.63 mmol, 1.0 equiv.), EDC (307 mg, 1.6 mmol, 2.5 equiv.), and HOBt (176 mg, 1.3 mmol, 2.0 equiv.) were dissolved in 10 mL of DCM in a 50 mL Schlenk flask. The solution was cooled to -10°C, then was added DIPEA (0.8 mL, 4.7 mmol, 7.5 equiv.) and stirred for ten minutes. Afterward, propargylamine (72 mg, 1.3 mmol, 2.0 equiv.) was added and the mixture was allowed to slowly warm to room temperature with stirring overnight. Once the reaction was complete, it was extracted with DCM, washed with brine. The organic phases were combined and dried over anhydrous Na_2SO_4. Remove the solvent under reduced pressure to obtain the crude product which was purified by silica gel column chromatography (DCM : MeOH = 30:1) to yield a white solid powder (469 mg, 90% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.24 –7.80 (m, 3H), 7.33 –7.18 (m, 17H), 6.98 (d, *J*= 7.3 Hz, 1H), 4.99 (s, 4H), 4.16 (s, 3H), 3.83 (s, 2H), 3.07 (s, 1H), 3.01 –2.68 (m, 6H), 1.72 –1.13 (m, 21H). HRMS (ESI) m/z: $[M + H]^+$calcd for $C_{45}H_{59}N_6O_9$, 827.4338; found 827.4333.

Compound tripep-triazole-B. Compound **tripep-alkyne** (120 mg, 0.14 mmol, 1.0 equiv.), compound **3** (76 mg, 0.14 mmol, 1.0 equiv.), copper(II) sulfate pentahydrate (0.7 mg, 0.003 mmol, 0.02 equiv.) and sodium ascorbate (2.8 mg, 0.014 mmol, 0.1 equiv.) were added into a 25 mL Schlenk flask. The mixture was dissolved in 2.5 mL of tert-butanol and 2.5 mL of distilled water. Stirred the solution at 40°C overnight. After the reaction was completed, extracted with DCM, washed with brine, and combined the organic phases. Dried the organic phase over anhydrous Na_2SO_4. Removed the solvent under reduced pressure to obtain the crude product, which was further purified by silica gel column chromatography (DCM: MeOH = 20:1) to yield pale yellow powder (152 mg, 79% yield). ^{1}H NMR (700 MHz, DMSO-d_6) δ 8.37 –8.15 (m, 2H), 8.12 –7.94 (m, 4H), 7.84 (s, 1H), 7.54 (d, *J*= 7.8 Hz, 1H), 7.35 –7.20 (m, 18H), 7.05 –6.90 (m, 1H), 6.54 (s, 4H), 4.99 (s, 5H), 4.33 –4.14 (m, 7H), 3.99 (d, *J*= 6.4 Hz, 2H), 2.95 (d, *J*= 6.5 Hz, 6H), 2.08 (s, 6H), 1.78 – 1.51 (m, 16H), 1.40 –1.19 (m, 25H).^{13}C NMR (176 MHz, DMSO-d_6) δ 171.52, 156.10, 153.89,

151.87, 146.06, 137.28, 132.80, 130.05, 129.61, 129.45, 129.24, 128.35, 128.03, 127.73, 125.16, 122.59, 121.47, 119.24, 78.16, 68.93, 65.13, 55.98, 49.17, 29.64, 29.14, 25.58, 24.68.HRMS (ESI) m/z: $[M + H]^+$calcd for $C_{80}H_{100}BN_{10}O_{10}$, 1371.7711; found 1371.7777.

S2. Photochromic Property Study

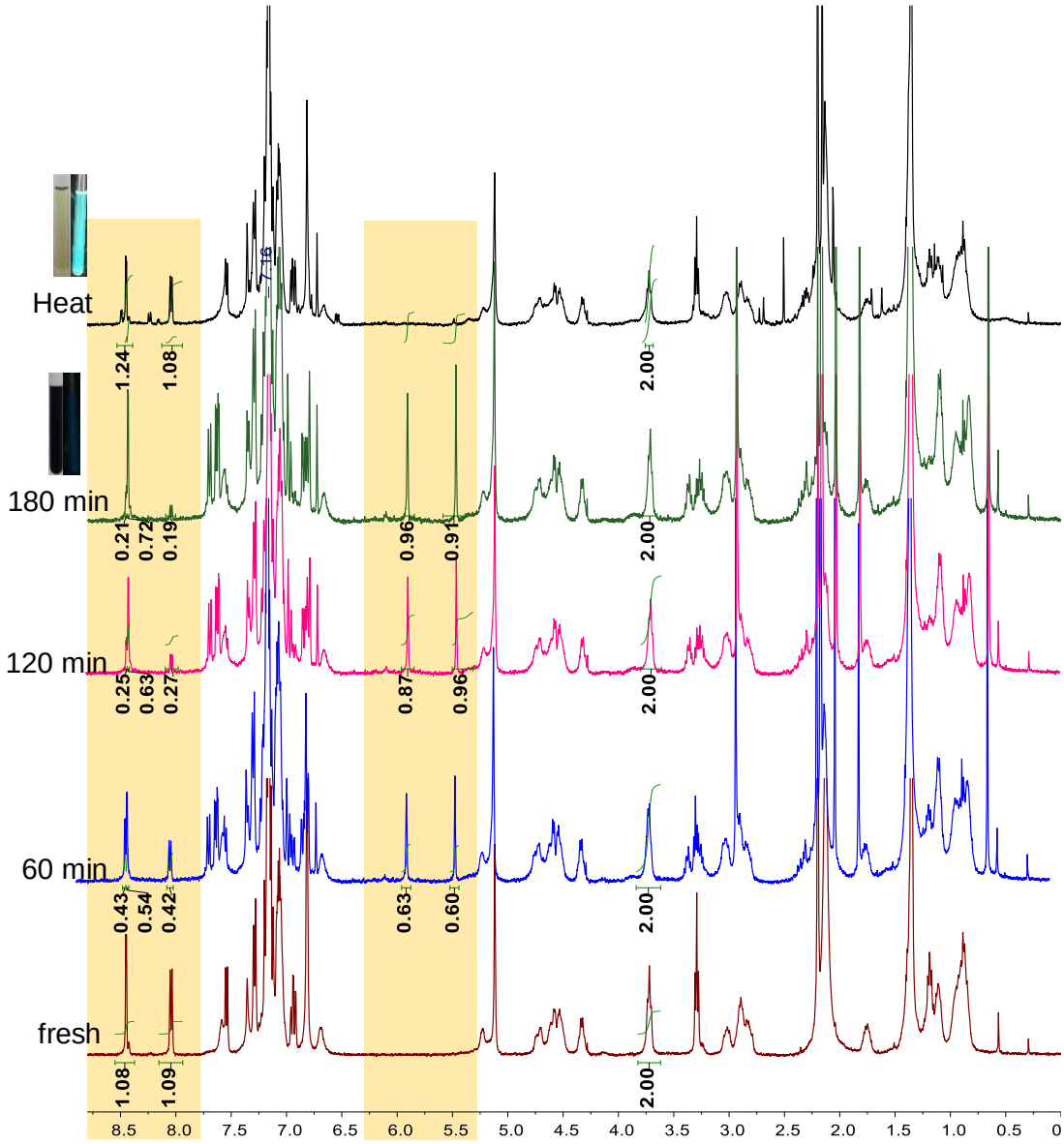


Figure S1. ^{1}H NMR spectral changes of **dipep-triazole-B** in C_6D_6 with 365 nm irradiation → heating to 80 °C for 1 minute and then cooling down (C = 4.2×10^{-5} M). Inset: photographs showing the color of sample after 180 minutes UV irradiation and after heating to 80 °C. The color coded peaks represent the characteristic peaks changing during the structural transformation process.

S2. NMR and Mass spectra

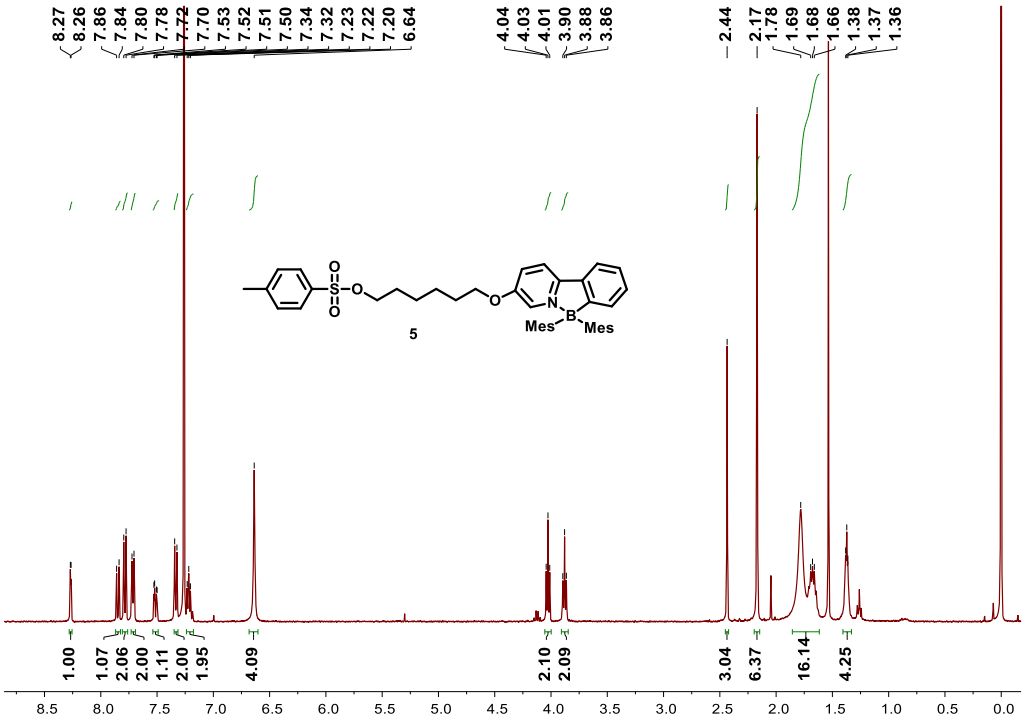


Figure S2. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Compound 2**.

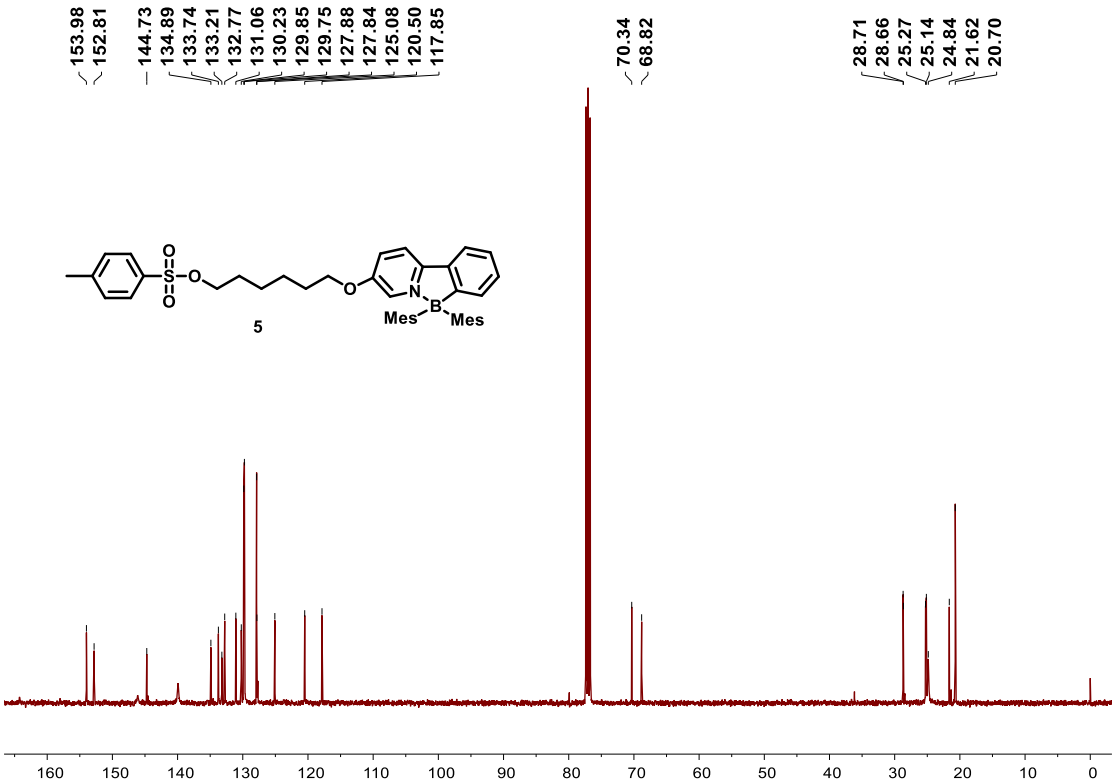


Figure S3. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **Compound 2**.

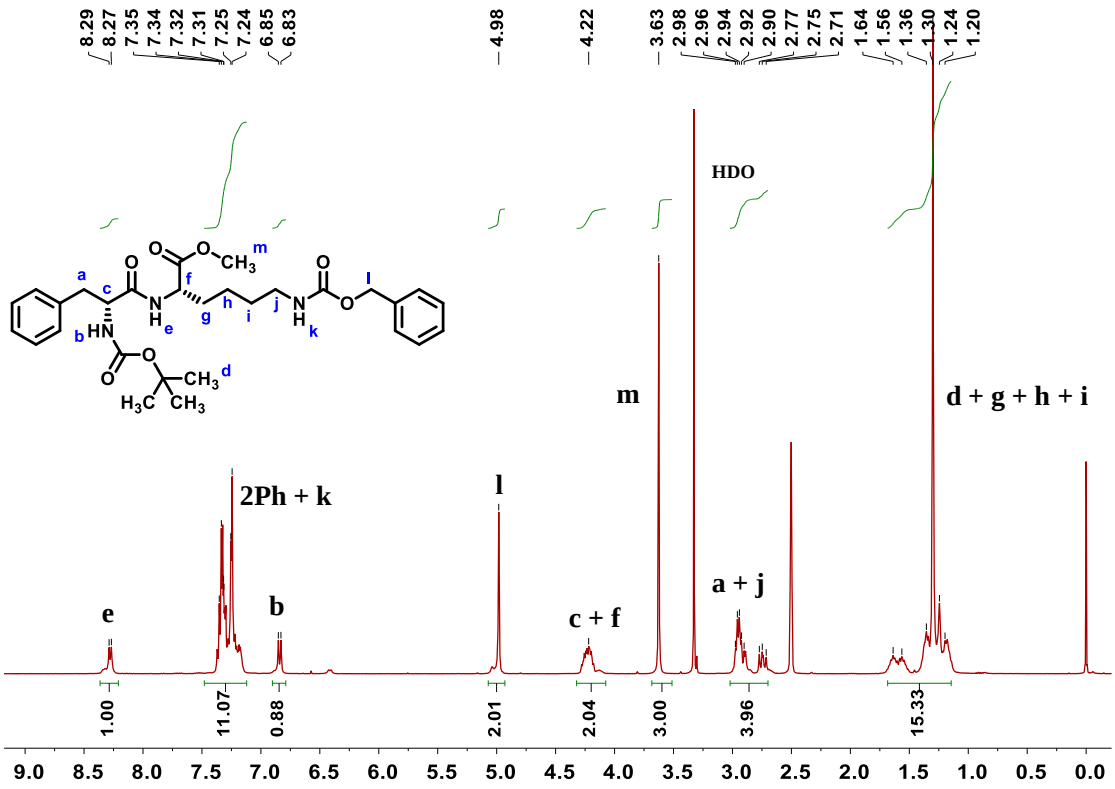


Figure S4. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **dipep-OMe**.

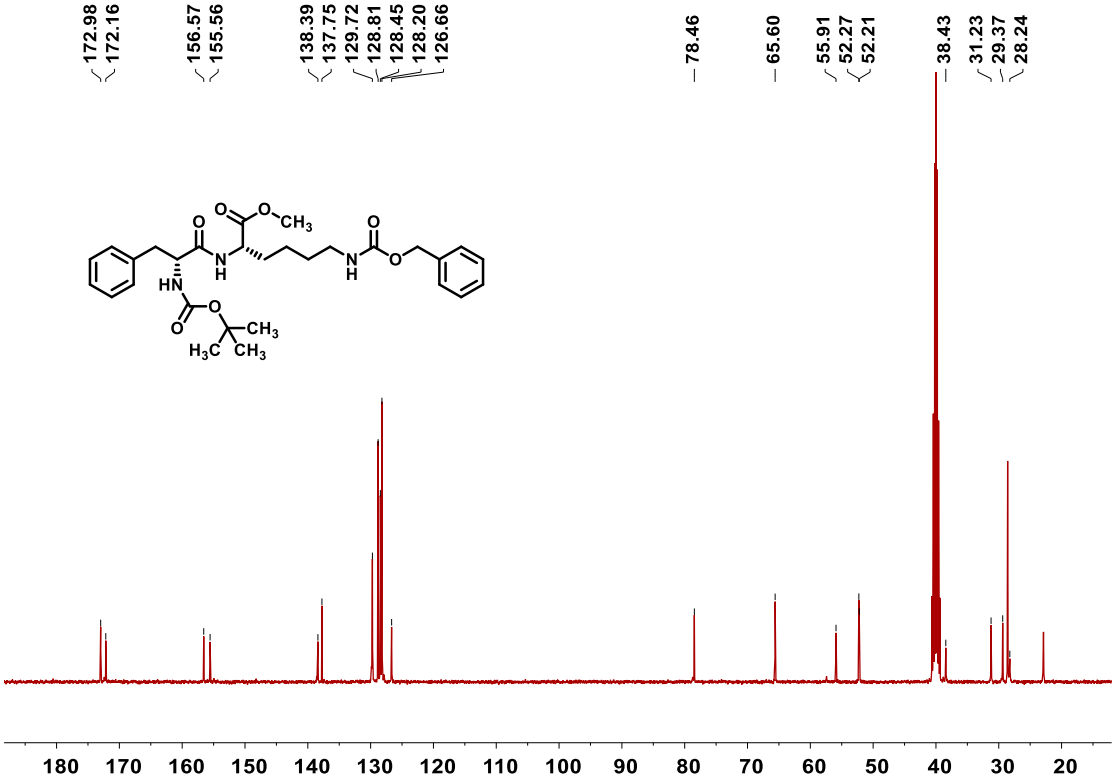


Figure S5. ^{13}C NMR (101 MHz, DMSO-d_6.) spectrum of **dipep-OMe**.

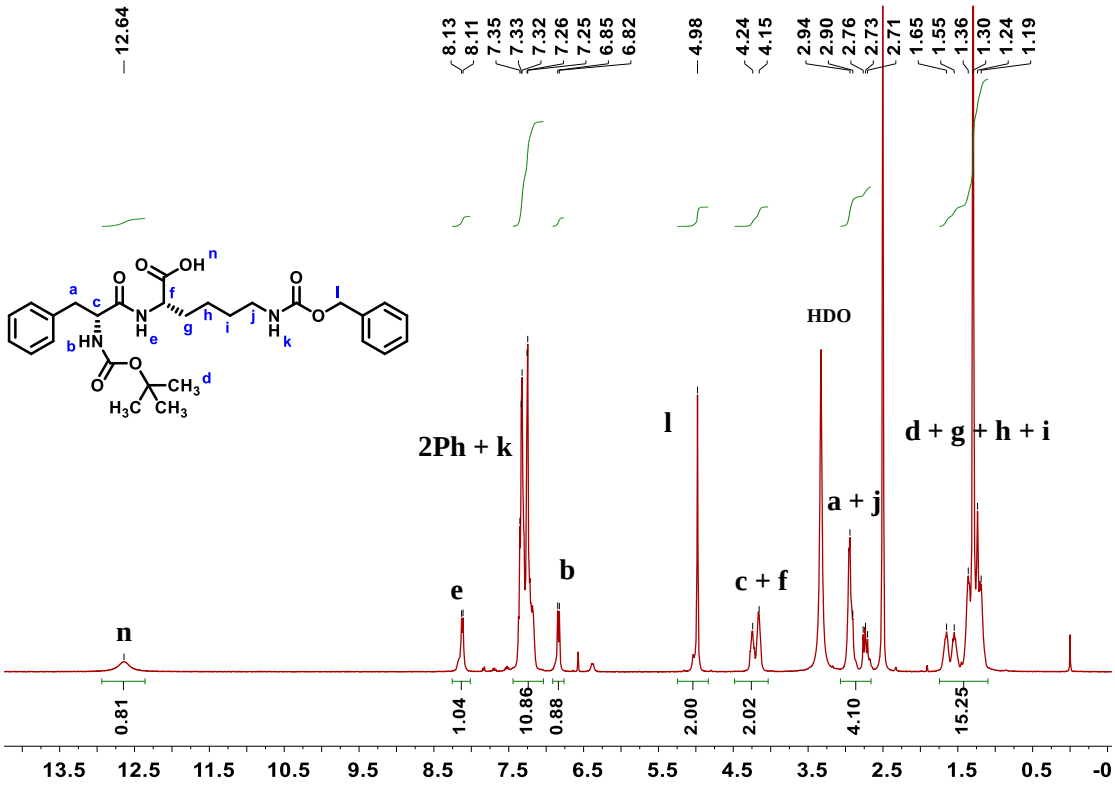


Figure S6. ^{1}H NMR (400 MHz, DMSO-d_6.) spectrum of **dipep-COOH**.

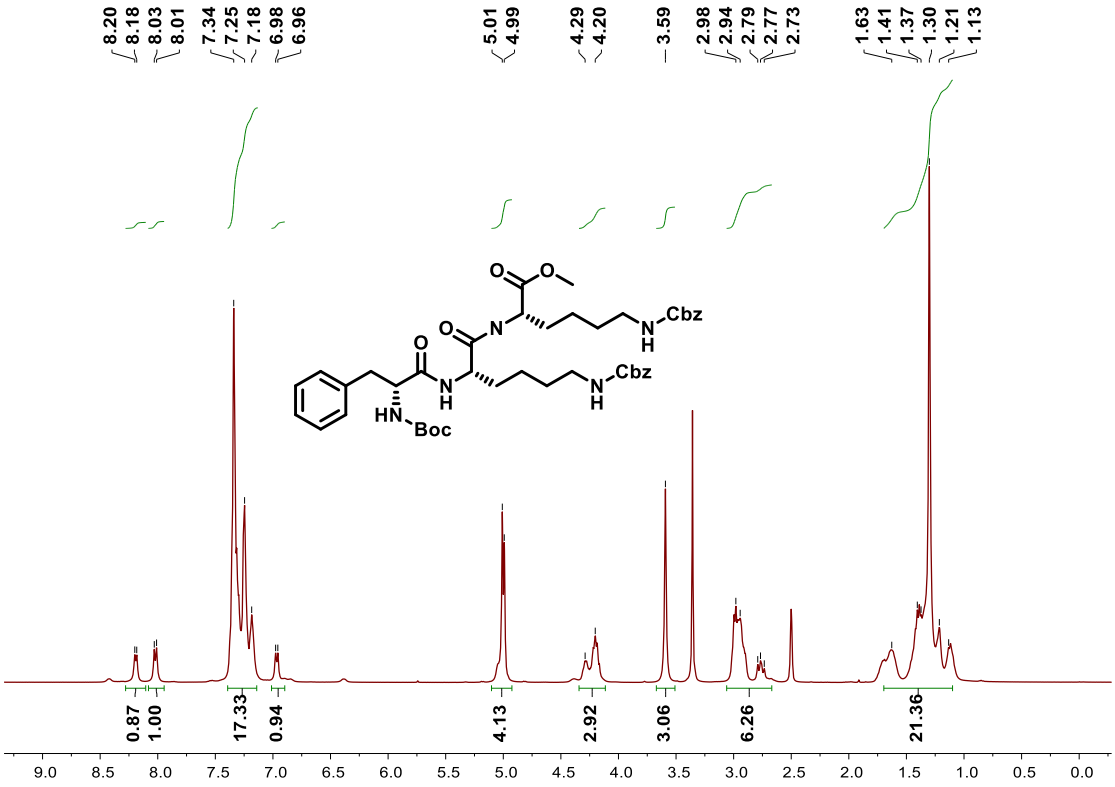


Figure S7. ^{1}H NMR (400 MHz, DMSO-d_6.) spectrum of **tripep-OMe**.

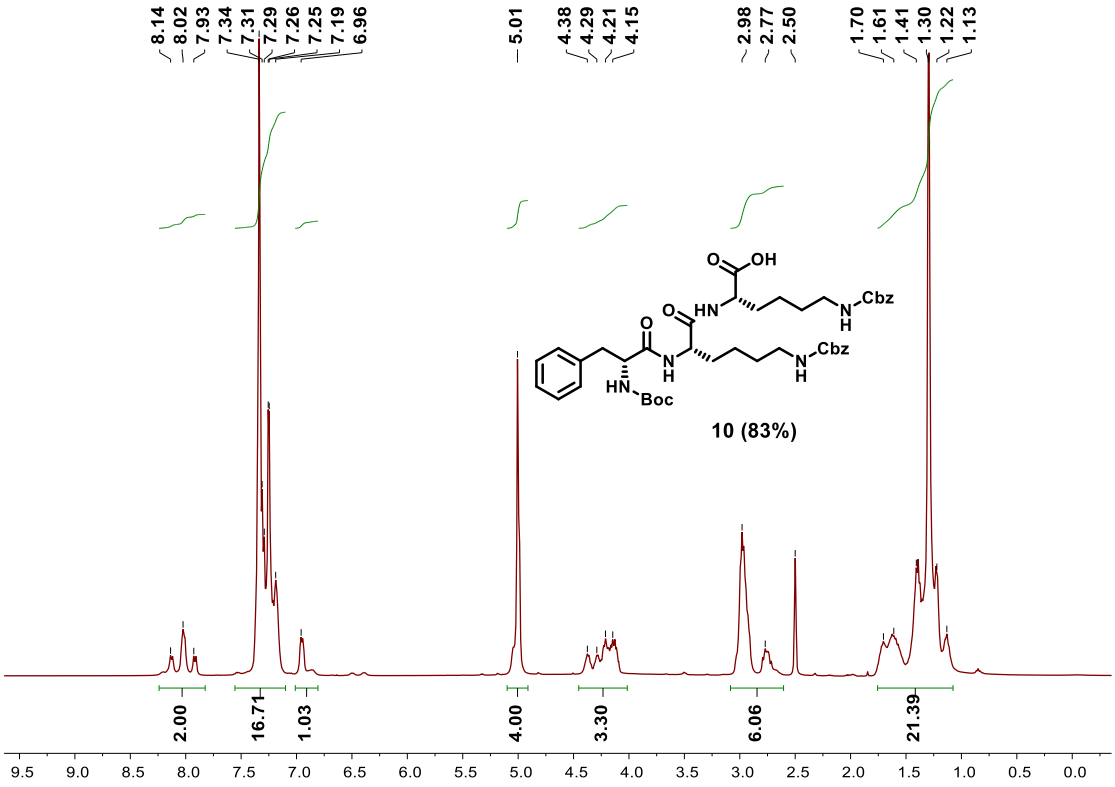


Figure S8. ^{1}H NMR (400 MHz, DMSO-d_6.) spectrum of **tripep-COOH**.

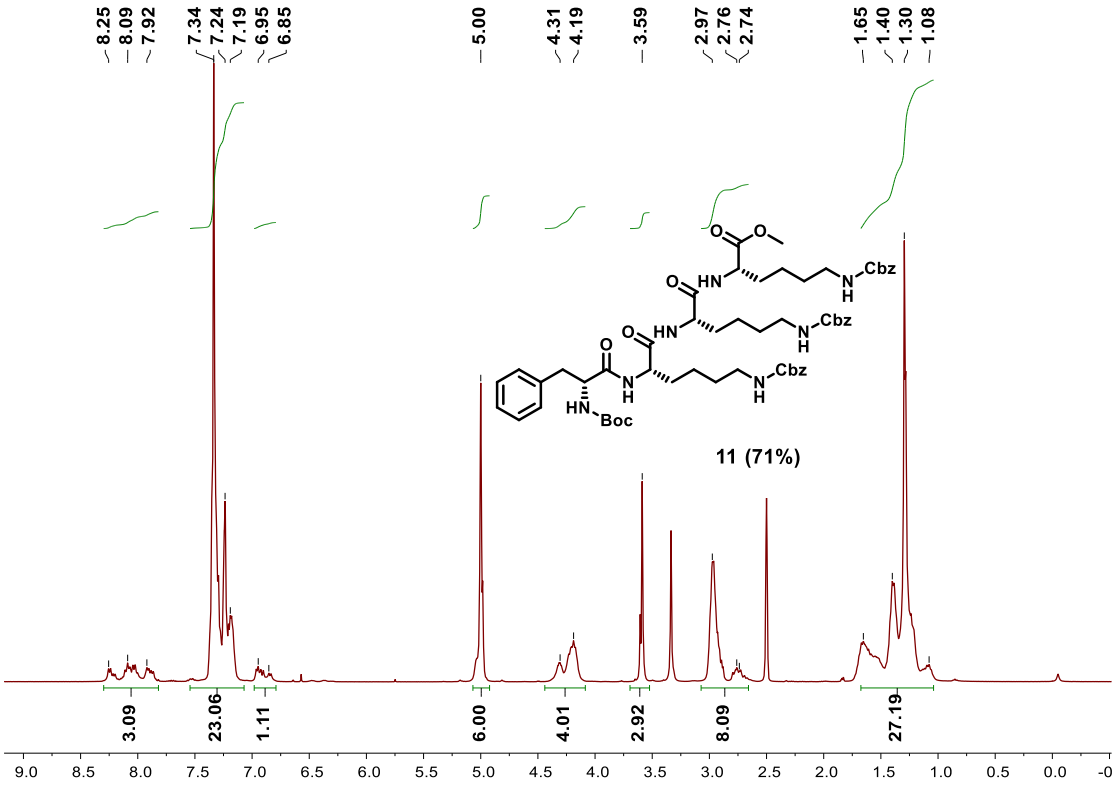


Figure S9. ^{1}H NMR (400 MHz, DMSO-d_6.) spectrum of **tetrapep-OMe.**

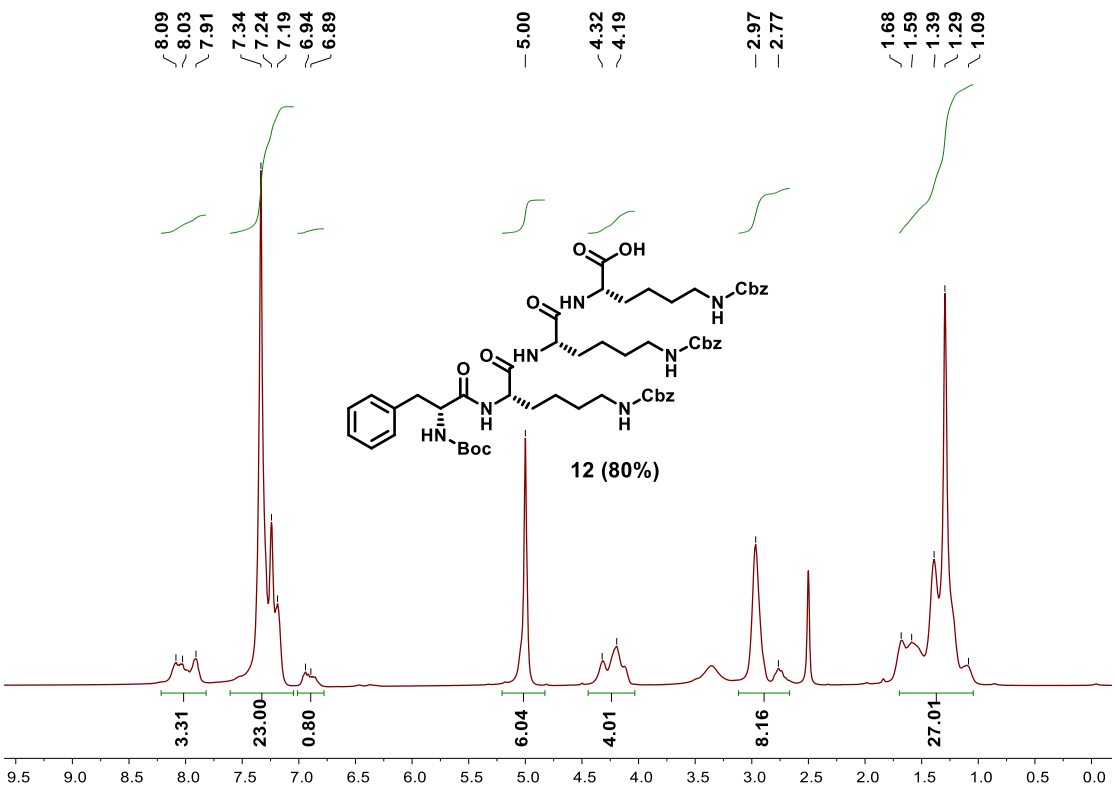


Figure S10. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **tetrapep-COOH.**

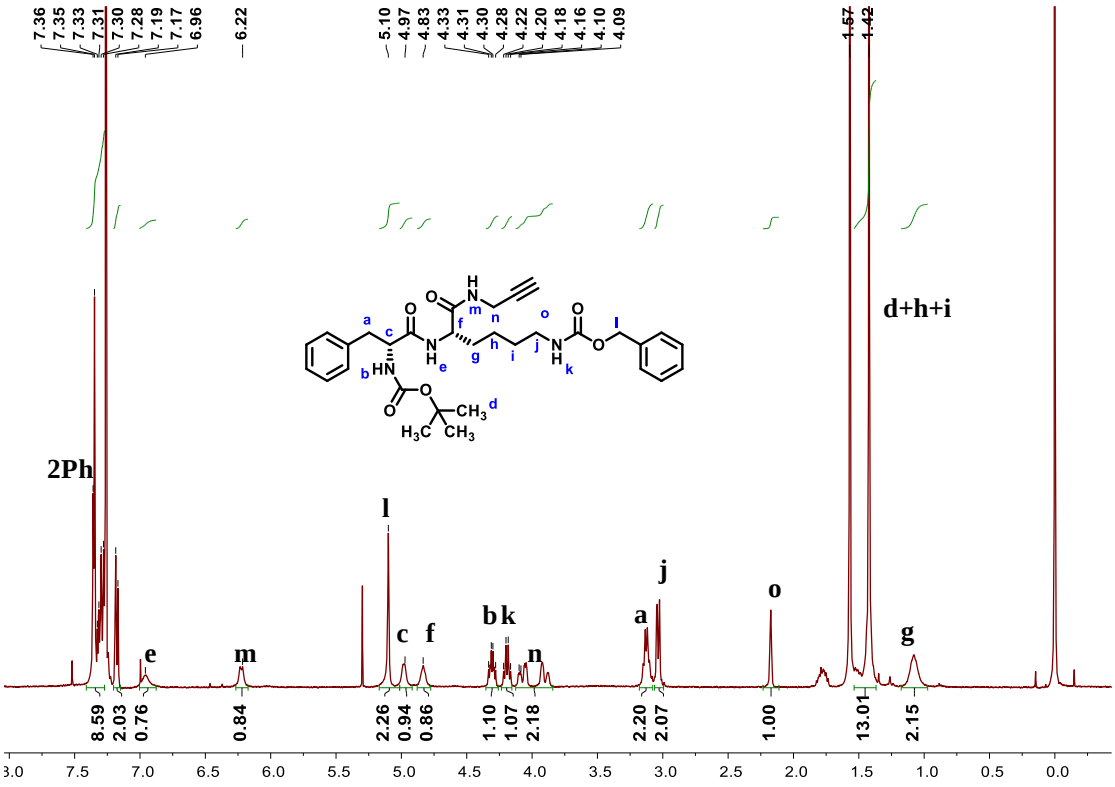


Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **dipep-alkyne.**

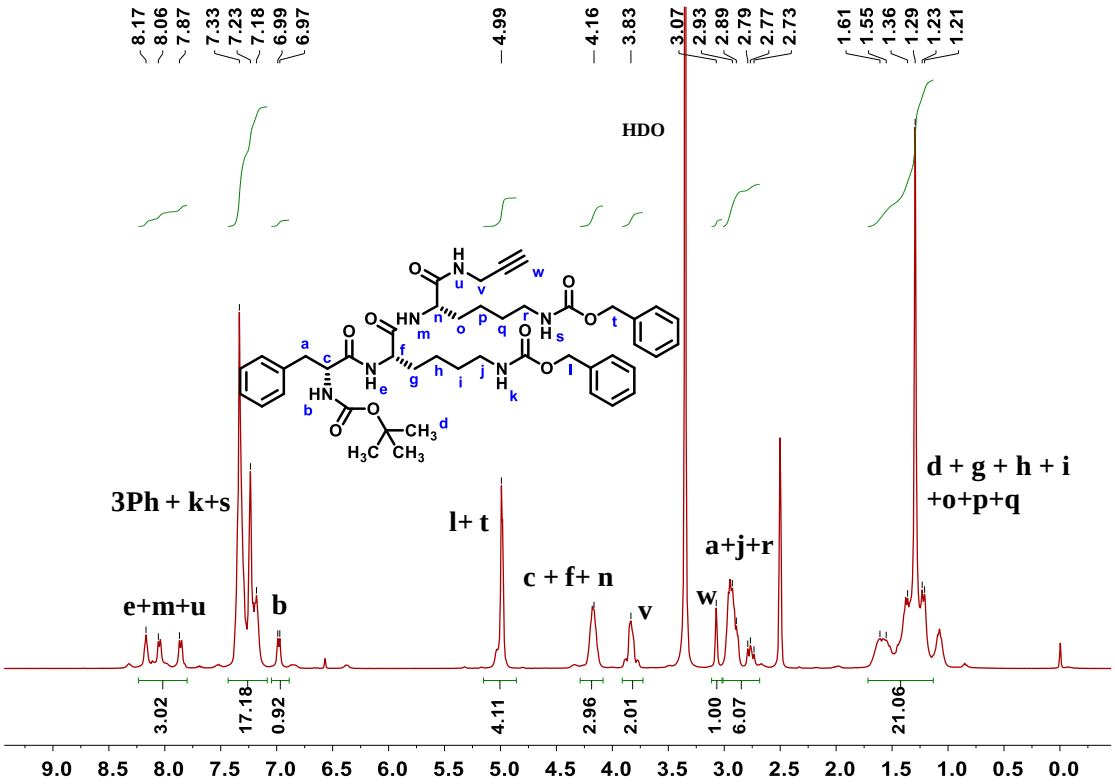


Figure S12. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **tripep-alkyne.**

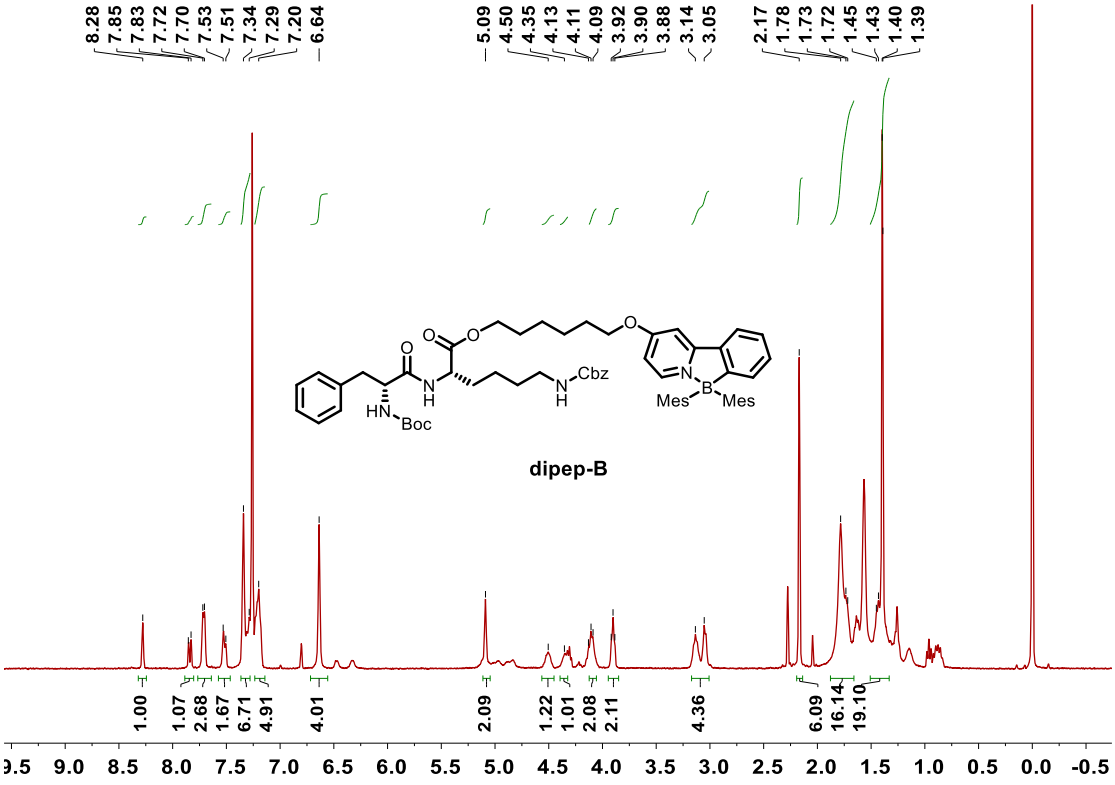


Figure S13. ^{1}H NMR (400 MHz,$CDCl_3$.) spectrum of **dipep-B**

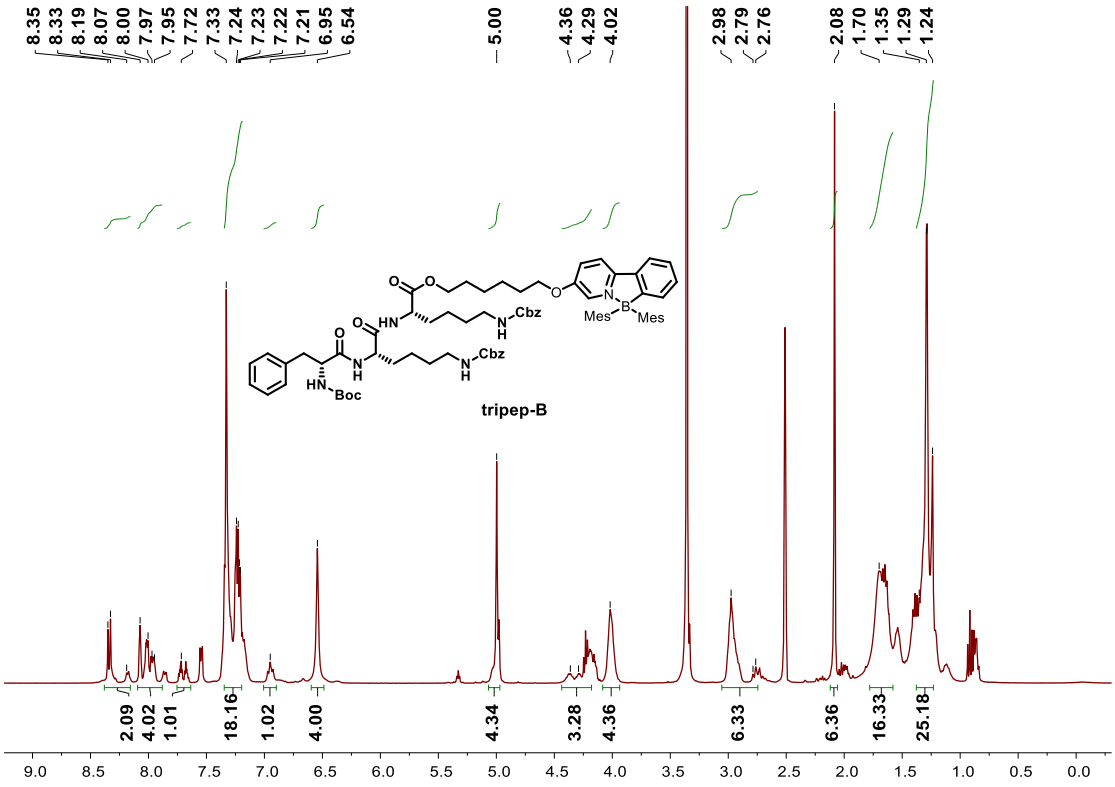


Figure S14. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **tripep-B**

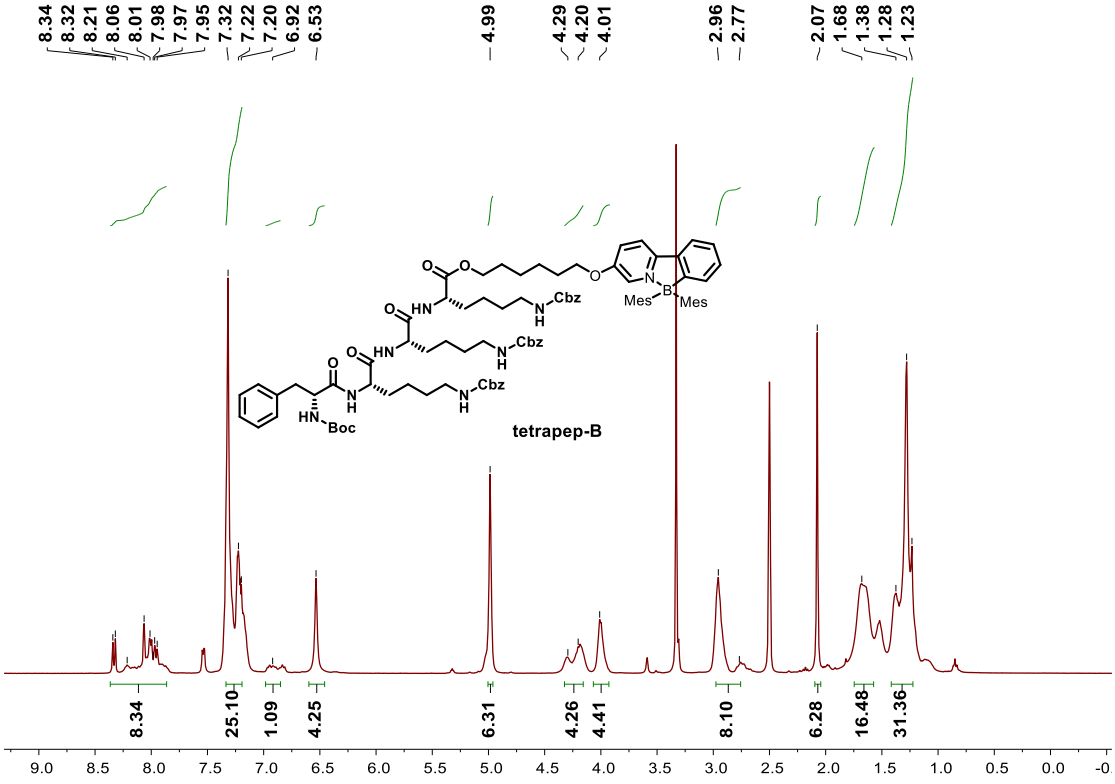


Figure S15. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **tetrapep-B**

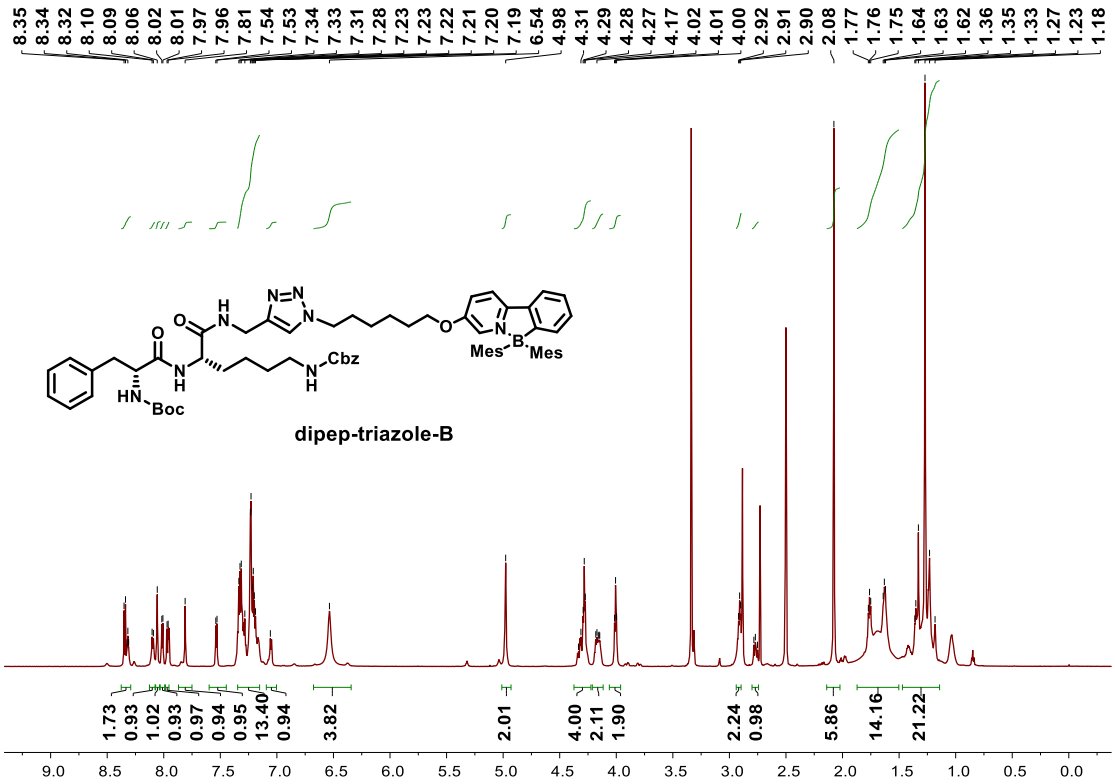


Figure S16. ^{1}H NMR (700 MHz, DMSO-d_6) spectrum of **dipep-triazole-B**

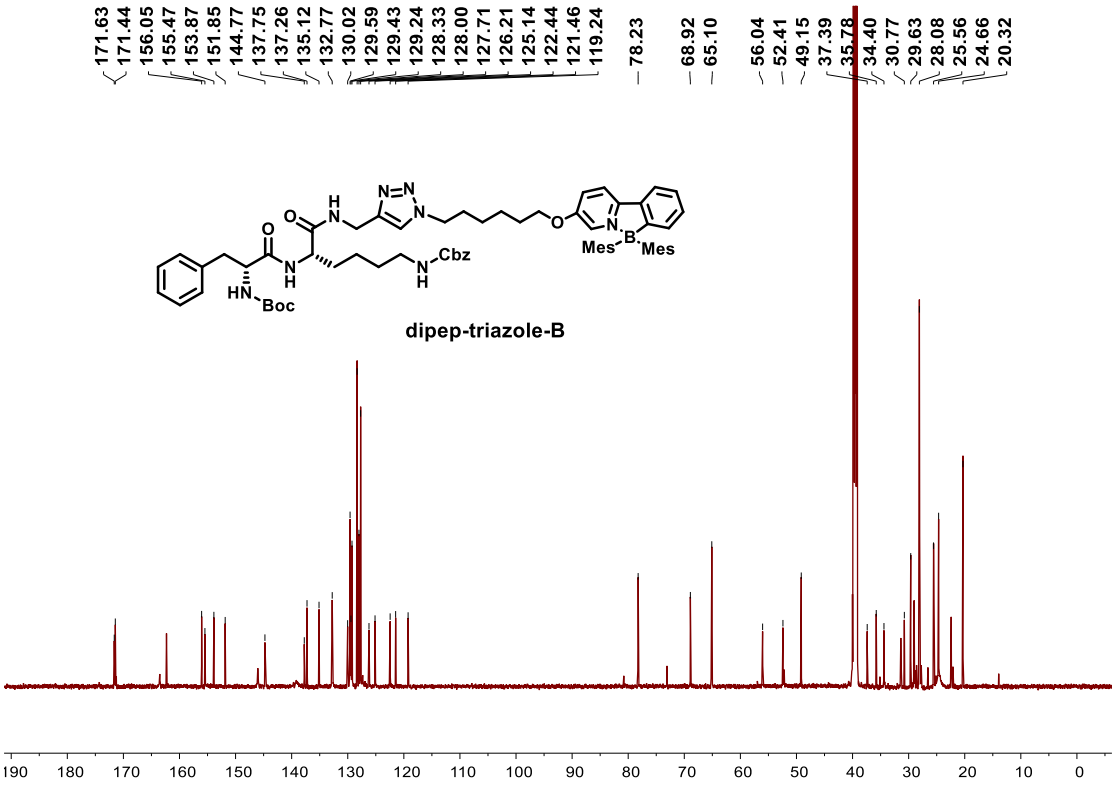


Figure S17. ^{13}C NMR (176 MHz, DMSO-d_6) spectrum of **dipep-triazole-B**

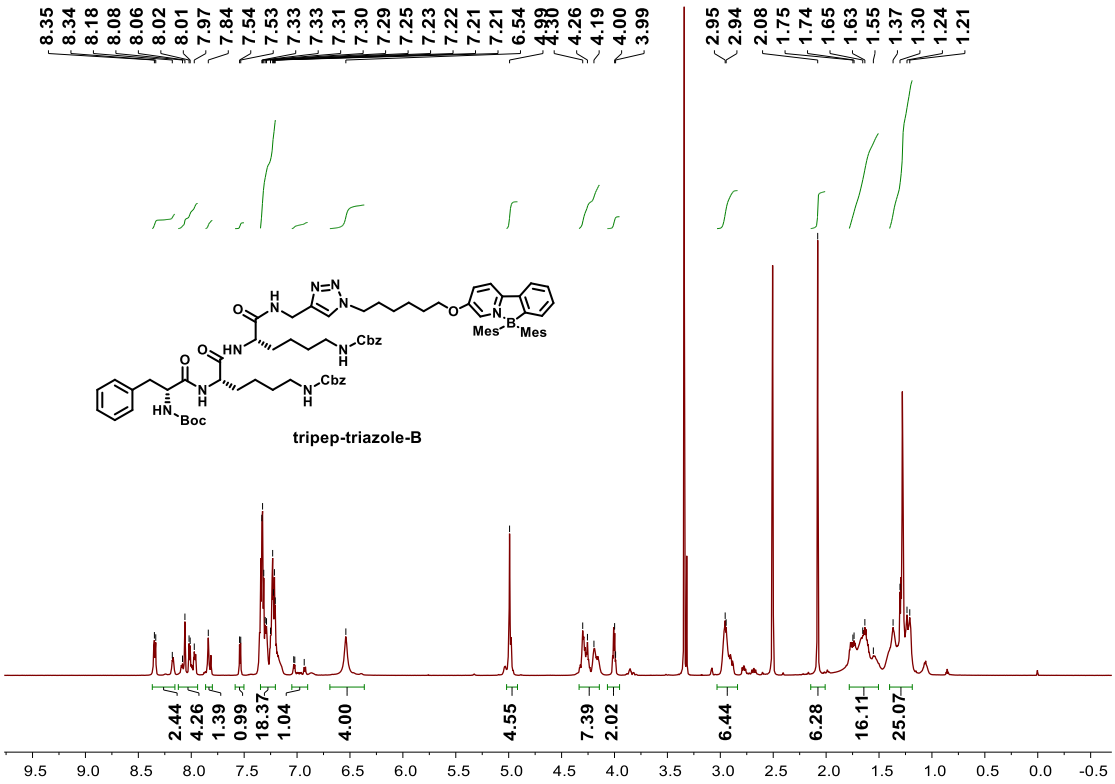


Figure S18. ^{1}H NMR (700 MHz, DMSO-d_6) spectrum of **tripep-triazole-B**

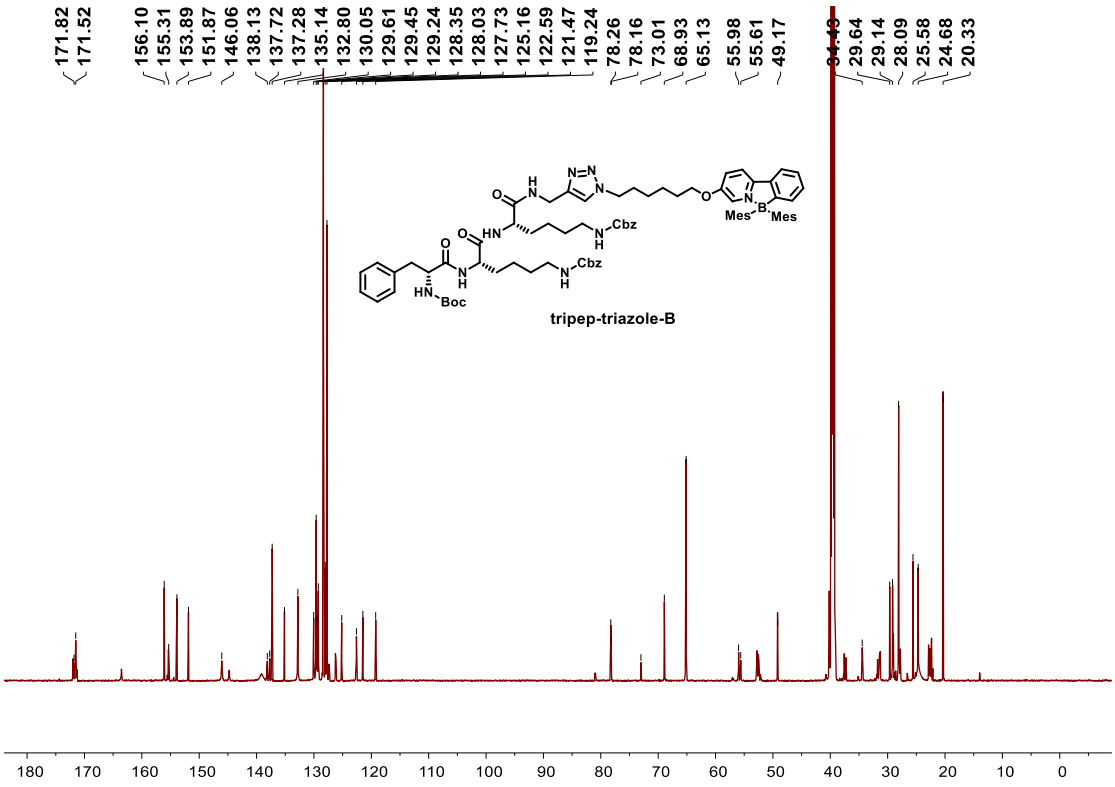


Figure S19. ^{13}C NMR (176 MHz, DMSO-d_6) spectrum of **tripep-triazole-B**

Reference

1. J. Wang, B. Jin, N. Wang, T. Peng, X. Li, Y. Luo and S. Wang, *Macromolecules*, 2017, **50**, 4629-4638.

2. C.A. Parker, A New Sensitive Chemical Actinometer. I. Some Trials with Potassium Ferrioxal *Proc. R. Soc. London A* **1953**, *220*, 104-116.
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