Electronic Supplementary Material (ESI) for New Journal of Chemistry.

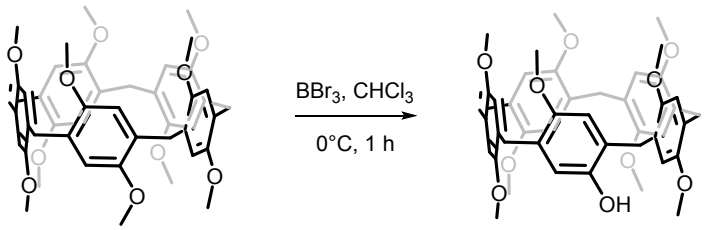

# Supporting Information

**Contents**:

*1. Materials and methods*

Unless otherwise mentioned, materials were obtained from commercial suppliers without further purification. All of solvents were bought from commercial suppliers and used directly. Column chromatography was performed over silica gel (300-400 mesh). NMR spectra were conducted on a Mercury-300BB-300 MHz spectrometer and a Bruker 600 MHz spectrometer. Chemical shifts for proton is reported in parts per million downfield and tetramethylsilane (TMS) was used as the reference and carbon is reported in parts per million and $CDCl_3$ (77.16 ppm) was used as the reference. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. Electrospray ionization (ESI) mass spectra were obtained on a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA). Fluorescence spectra were determined on a Cary Eclipse spectrophotometer, respectively at room temperature. The melting points were obtained on an X-6 melting point apparatus. Thin-layered chromatography (TLC) was performed using silica gel 60 F254 plates.

*2. Synthesis of compound **P1***




To a solution of pillar[5]arene (2.25 g, 3 mmol) in 150 mL of $CHCl_3$ for 10 minutes, 1.1 mL of $BBr_3$ (12 mmol) was added and stirred for 10 minutes at 0°C. After completion, the reaction was quenched by 100 mL of $H_2O$. After a workup, the solvent of organic phase was dried over $Na_2SO_4$ and removed by rotary evaporation. The pure product was obtained by column chromatography ($SiO_2$, PE/EA= 10/1) as a white powder (484.1 mg, 22%). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.00 – 6.48 (m, 10H), 4.70 (s, 1H), 3.98 – 3.31 (m, 37H).$^{13}$C NMR (75 MHz, $CDCl_3$) δ 152.06, 151.31, 151.18, 151.04, 148.96, 147.74, 130.26, 129.64, 128.96, 128.68, 128.61, 128.43, 128.06, 127.14, 125.25, 119.05, 114.79, 114.71, 114.56, 114.38, 114.32, 114.14, 113.28, 113.22, 77.58, 77.16, 76.74, 56.54, 56.52, 56.29, 56.23, 56.15, 56.08, 56.04, 53.22, 31.09, 30.28, 30.08, 29.83, 29.04.

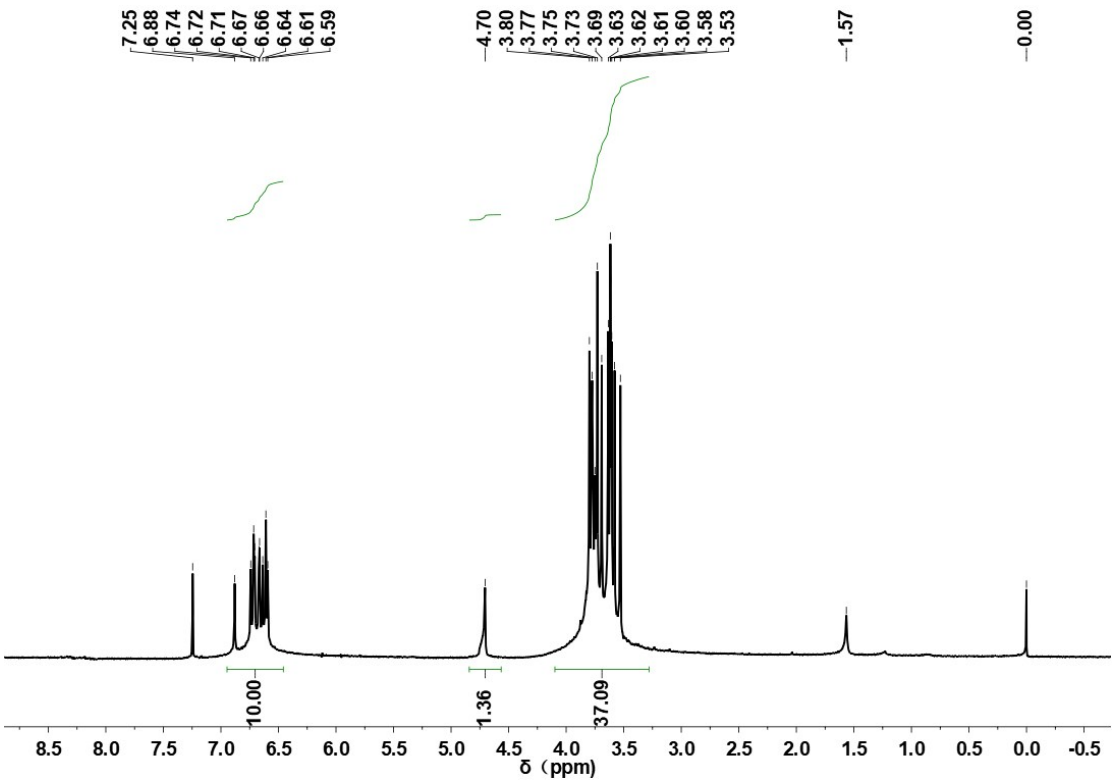



**Fig. S1** $^{1}$H NMR spectroscopy of compound **P1** (300 MHz, $CDCl_3$, 298 K)

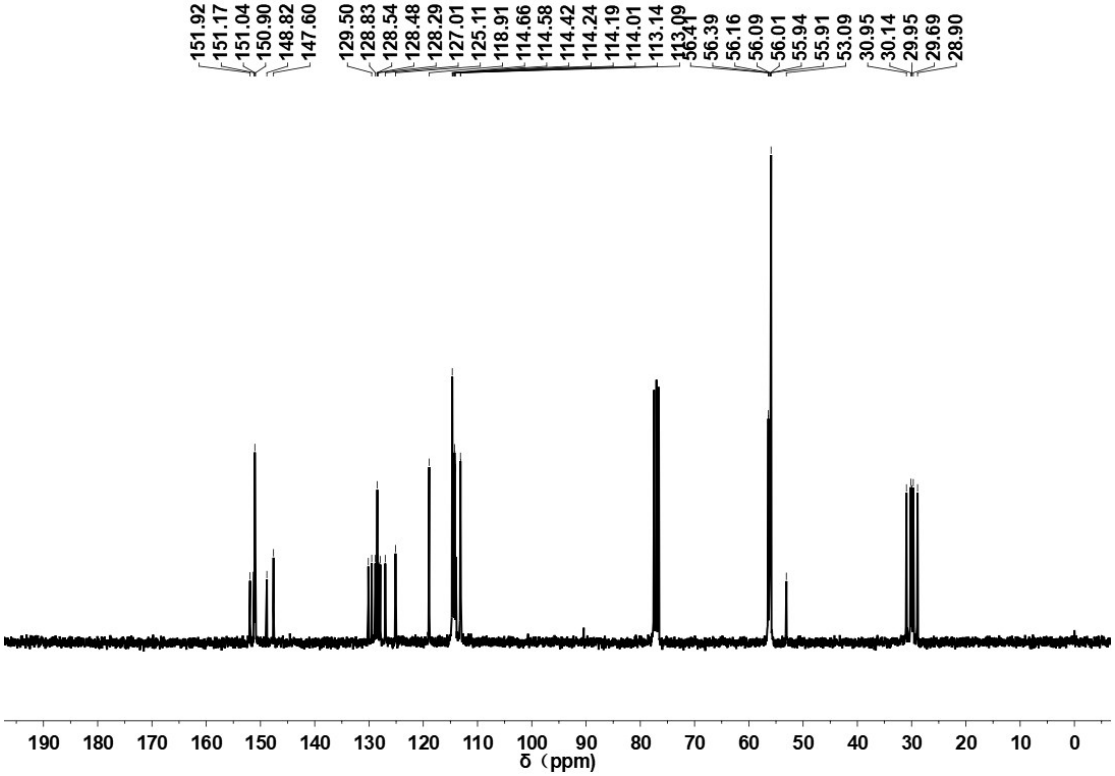
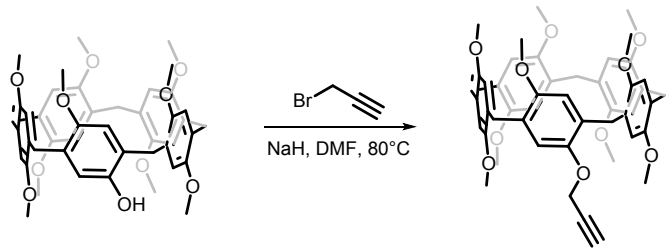



**Fig. S2** $^{13}$C NMR spectroscopy of compound **P1** (75 MHz, $CDCl_3$, 298 K)

*3. Synthesis of compound **P2***




To a solution of **P1** (200 mg, 0.27 mmol) dissolved in 3 mL of DMF, NaH (13.04 mg, 0.54 mmol) was added and the mixture was stirred at room temperature for 1 hour. Then, bromo propyne (50.0μL, 0.58 mmol) was added to the solution and the mixture was reacted at 80 °C for 24 hours. After the reaction was completed, the reaction was quenched by 10 mL of $H_2O$ and was extracted with DCM and washed three times with $H_2O$. The organic layer was collected, dried over $Na_2SO_4$ and concentrated. The pure product was collected by column chromatograph ($SiO_2$, DCM) as a white powder (117.6 mg, 56 %). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.07 – 6.54 (m, 10H), 4.42 (d, J = 2.4 Hz, 2H), 4.00 – 3.43 (m, 37H), 1.92 (t, *J* = 2.2 Hz, 1H).$^{13}$C NMR (75 MHz, $CDCl_3$) δ 151.51, 151.03, 150.98, 149.09, 129.23, 128.77, 128.66, 128.61, 128.54, 128.45, 128.23, 115.79, 114.57, 114.51, 114.35, 114.26, 114.16, 79.04, 77.16, 74.73, 56.45, 56.10, 56.06, 56.04, 56.00, 55.95, 53.07, 30.56, 29.91, 29.79, 29.25.

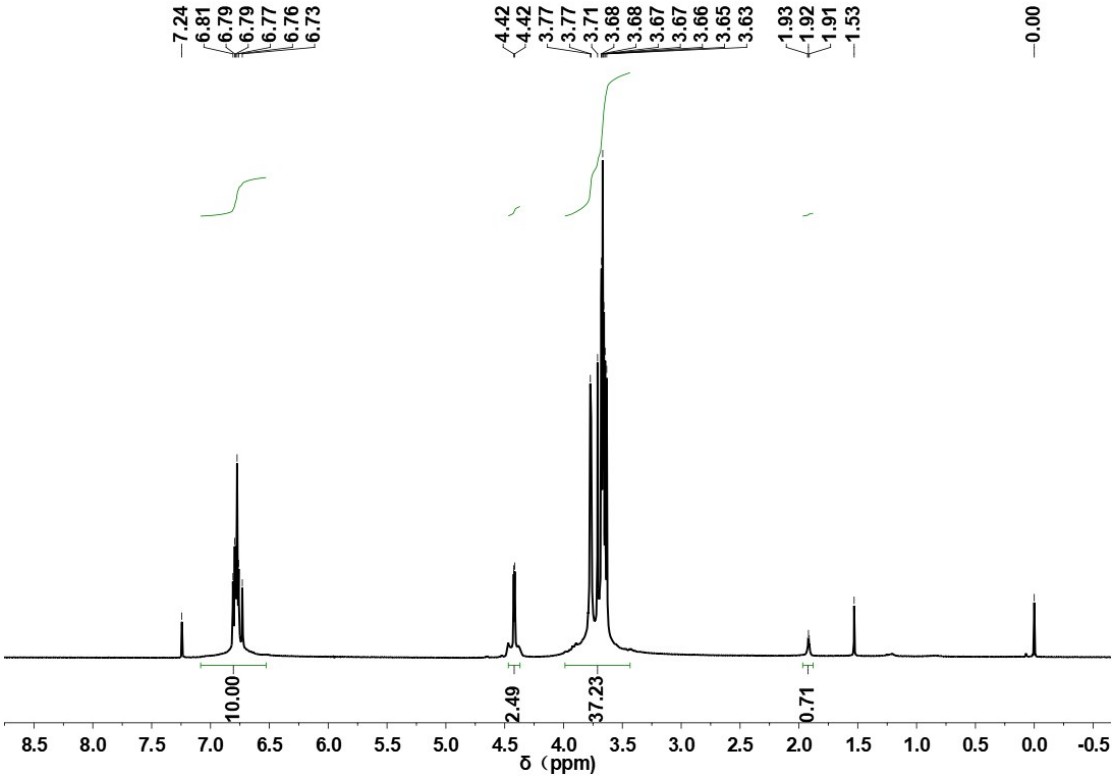



**Fig. S3** $^1$H NMR spectroscopy of compound **P2** (300 MHz, $CDCl_3$, 298 K).

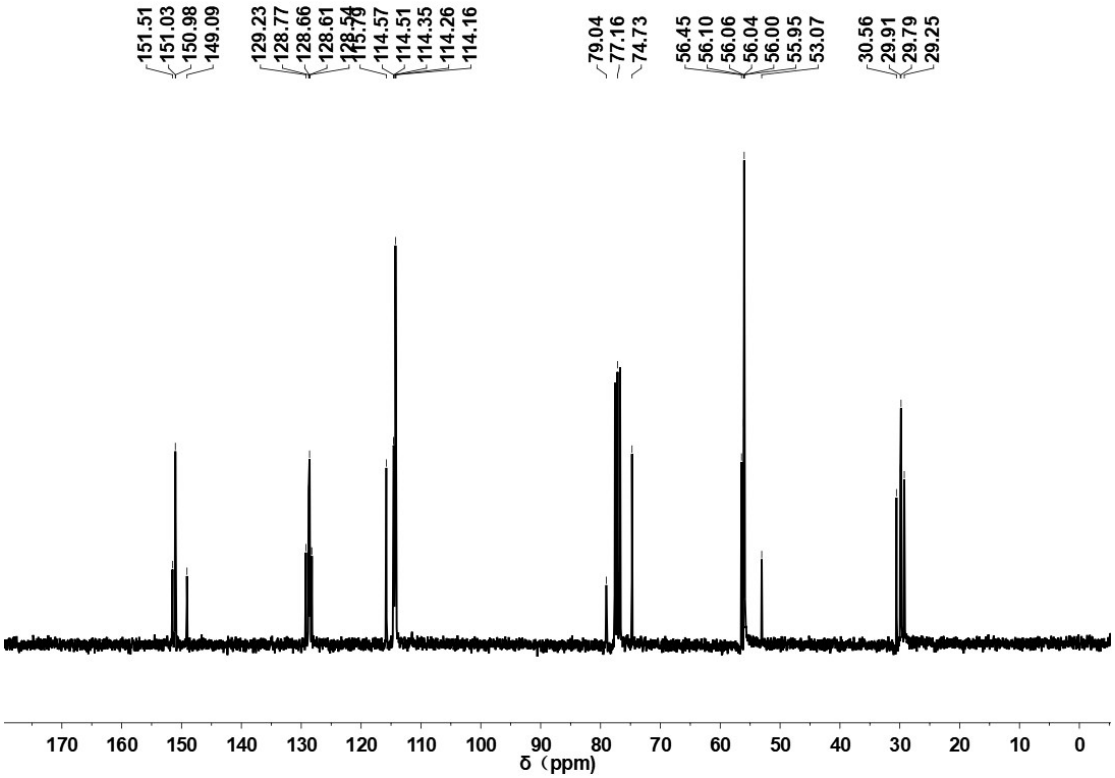
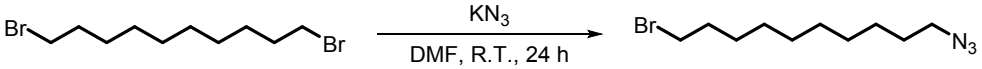



**Fig. S4** $^{13}C$ NMR spectroscopy of compound **P2** (300 MHz, $CDCl_3$, 298 K).

*4. Synthesis of **1-aza-8-bromooctane***




To the solution of 1,8-dibromooctane (2.50 g, 9.19 mmol) in 60 mL of DMF, $KN_3$ (0.69 g, 9.19 mmol) was added portionwise and the reaction mixture was stirred at room temperature for 24 hours. After completion, the reaction was quenched by 60 mL of deionized water and the crude compound was extracted with 200 mL of DCM and the organic layer was washed three times of 200 mL of $H_2O$. The organic layer was collected, dried over $Na_2SO_4$ and concentrated. The pure product (639.90 mg, 32%) was collected by column chromatography ($SiO_2$, PE/DCM = 60/1) as a colorless oil. $^1H$ NMR (300 MHz, $CDCl_3$) δ 3.41 (t, J = 6.8 Hz, 2H), 3.26 (t, *J* = 6.9 Hz, 2H), 1.85 (dd, *J* = 14.6, 6.9 Hz, 2H), 1.68 – 1.53 (m, 2H), 1.49 – 1.25 (m, 8H).

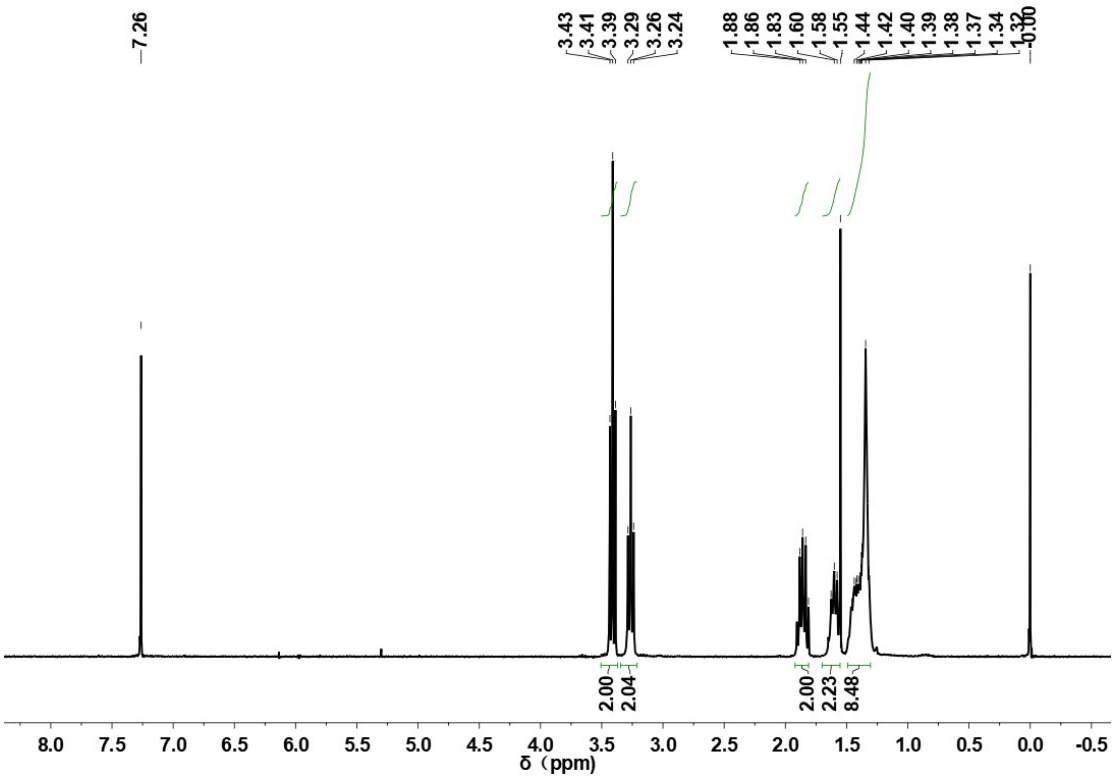
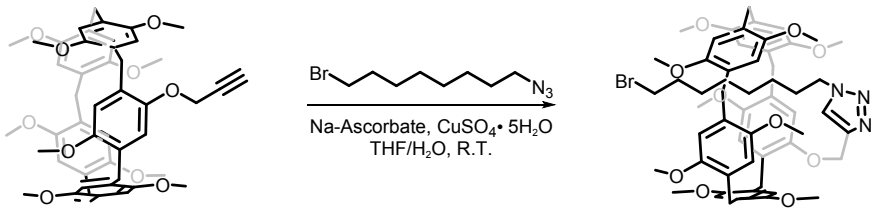



**Fig. S5** $^{1}$H NMR spectroscopy of compound **1-aza-8-bromooctane** (300 MHz, $CDCl_3$, 298 K).

*5. Synthesis of compound **P3***




To the solution of **P2** (115.8 mg, 0.15 mmol) and 1-aza-8-bromooctane (34.85 mg, 0.15 mmol) in 0.8 mL of THF, sodium ascorbate (7.73 mg, 0.04 mmol) and $CuSO_4 \cdot 5H_2O$ (7.87 mg, 0.03 mmol) in 0.2mL $H_2O$ were added to the solution. The mixture was stirred at room temperature for 24 hours, after which the solvent was removed by rotary evaporation. The organic layer was collected, dried over $Na_2SO_4$ and concentrated. The pure compound was purified by column chromatograph ($SiO_2$, PE/EA = 2/1) as a white powder (131.7 mg, 87 %). $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.16 – 6.56 (m, 10H), 5.10 (s, 2H), 4.03 – 3.40 (m, 39H), 2.45 (t, *J* = 7.7 Hz, 2H), 1.66 (s, 1H), 0.71 (s, 1H), 0.50 (s, 2H), -0.24 (d, *J* = 44.5 Hz, 8H). $^{13}$C NMR (75 MHz, $CDCl_3$)δ 151.22, 150.94, 150.80, 150.72, 150.67, 150.59, 150.55, 149.03, 144.09, 129.44, 128.70, 128.60, 128.48, 128.40, 123.31, 115.18, 114.73, 114.11, 113.89, 113.82, 113.72, 77.58, 77.16, 76.74, 62.60, 56.51, 55.94, 55.85, 55.74, 55.70, 53.31, 50.08, 33.96, 32.83, 29.67, 29.45, 29.37, 29.29, 29.08, 28.57, 28.28, 27.79, 25.82.HR-MS: m/z calculated for $[M+H]^+C_{55}H_{67}BrN_3O_{10}^+$, 1008.4004; found 1008.3891.

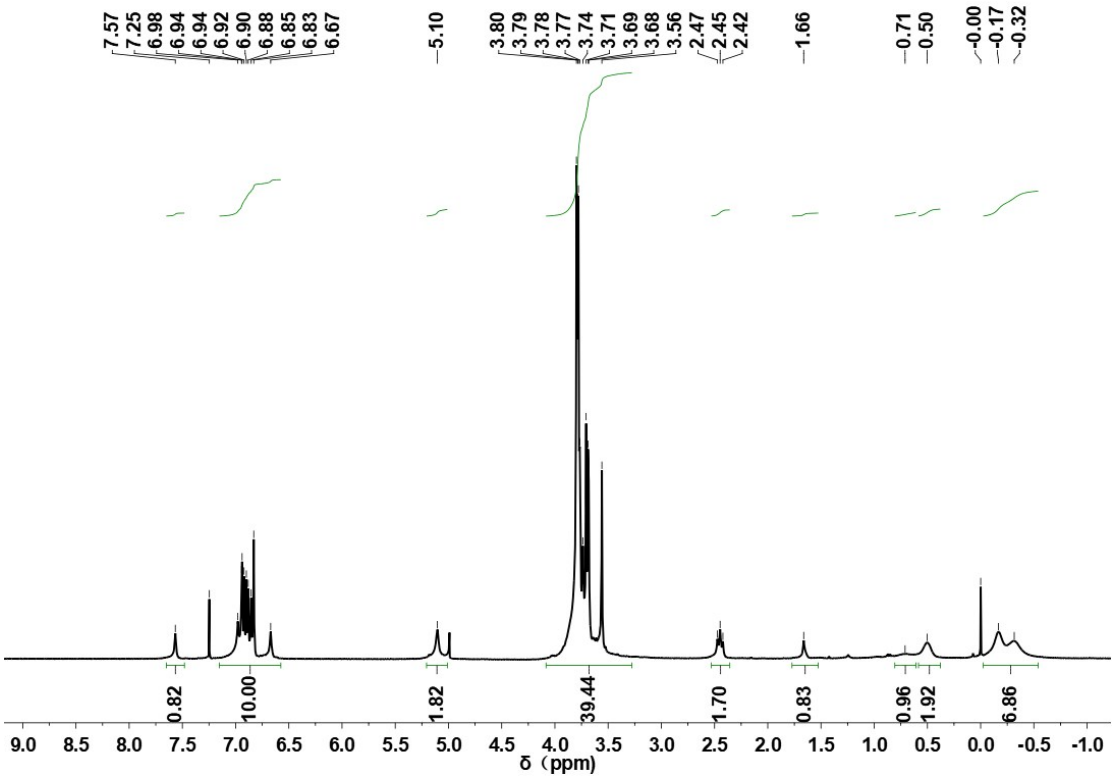



**Fig. S6** $^{1}$H NMR spectroscopy of compound **P3** (300 MHz, $CDCl_3$, 298 K).

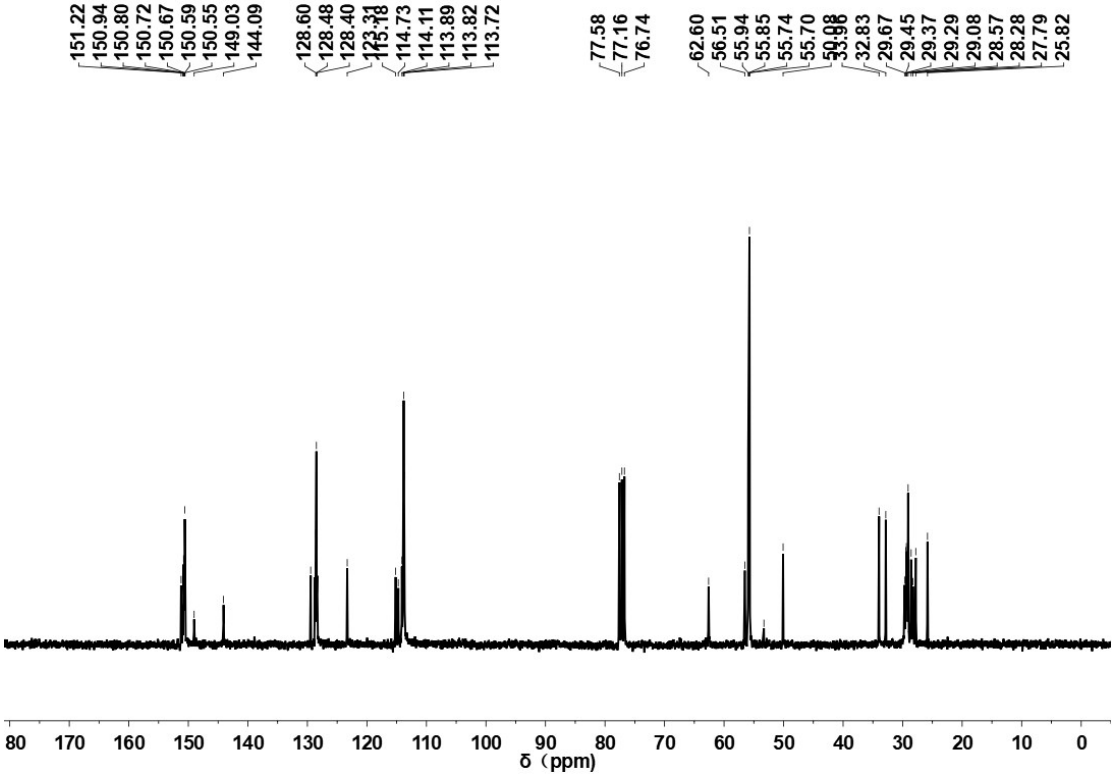



**Fig. S7** $^{13}$C NMR spectroscopy of compound **P3** (300 MHz, $CDCl_3$, 298 K).

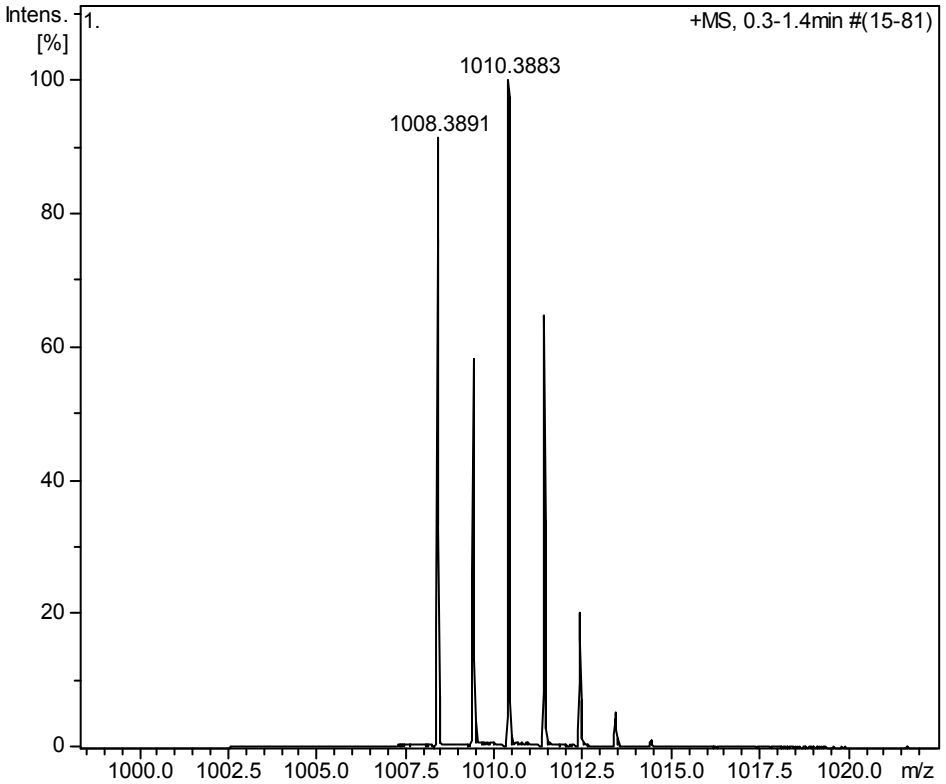
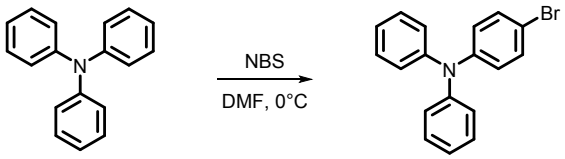



**Fig. S8** Mass spectroscopy of compound **P3**. HR-MS: m/z calculated for $[M+H]^+$ $C_{55}H_{67}BrN_3O_{10}^+$, 1008.4004; found 1008.3891.

*6. Synthesis of compound **M1***




To a solution of triphenylamine (100.00 mg, 0.40 mmol) in 1.2 mL of DMF, NBS (91.77 mg, 0.40 mmol) in 0.8 mL of DMF was added dropwise and the solution was stirred at ice bath for 4 hours. After completion, 4 mL of $H_2O$ was added to quench the reaction and the crude product was extracted with DCM and $H_2O$. The organic layer was collected, dried over $Na_2SO_4$ and concentrated. The pure product was collected by column chromatograph ($SiO_2$, PE) as a white powder (77.4 mg, 60%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.20 (m, 6H), 7.11 – 6.99 (m, 6H), 6.96 – 6.91 (m, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 147.52, 147.17, 132.28, 129.51, 125.26, 124.55, 123.36, 114.90, 77.16.

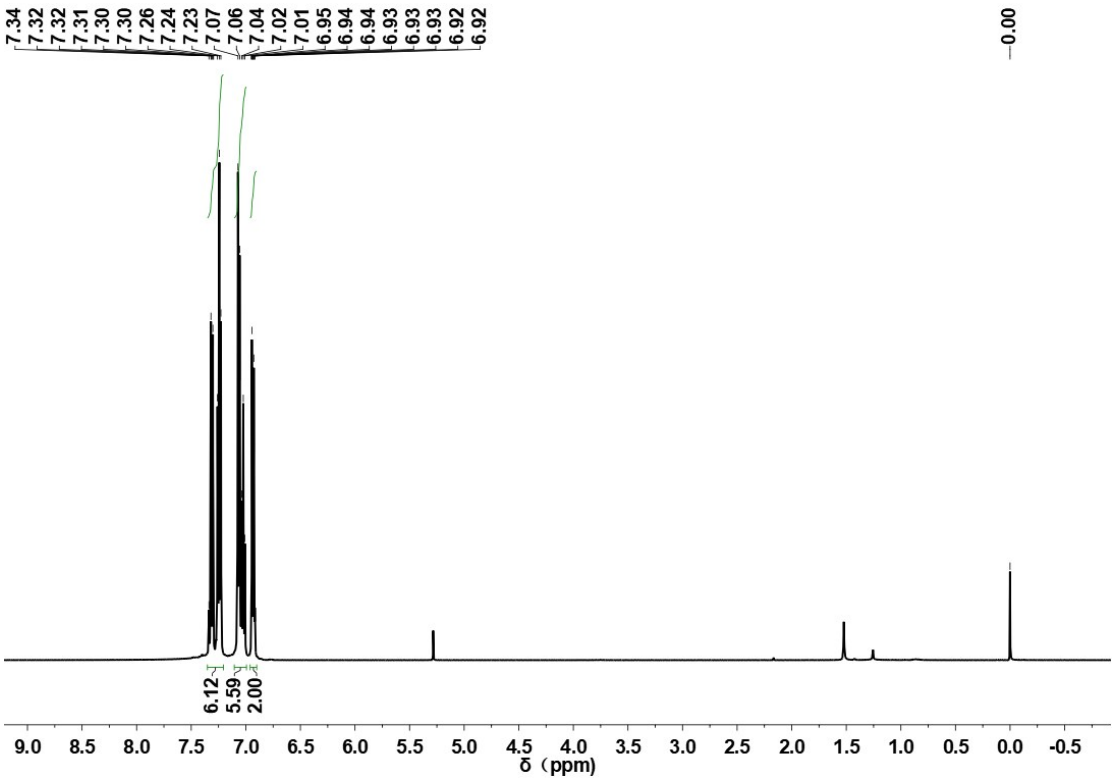



**Fig. S9** $^{1}$H NMR spectroscopy of compound **M1** (300 MHz, $CDCl_3$, 298 K).

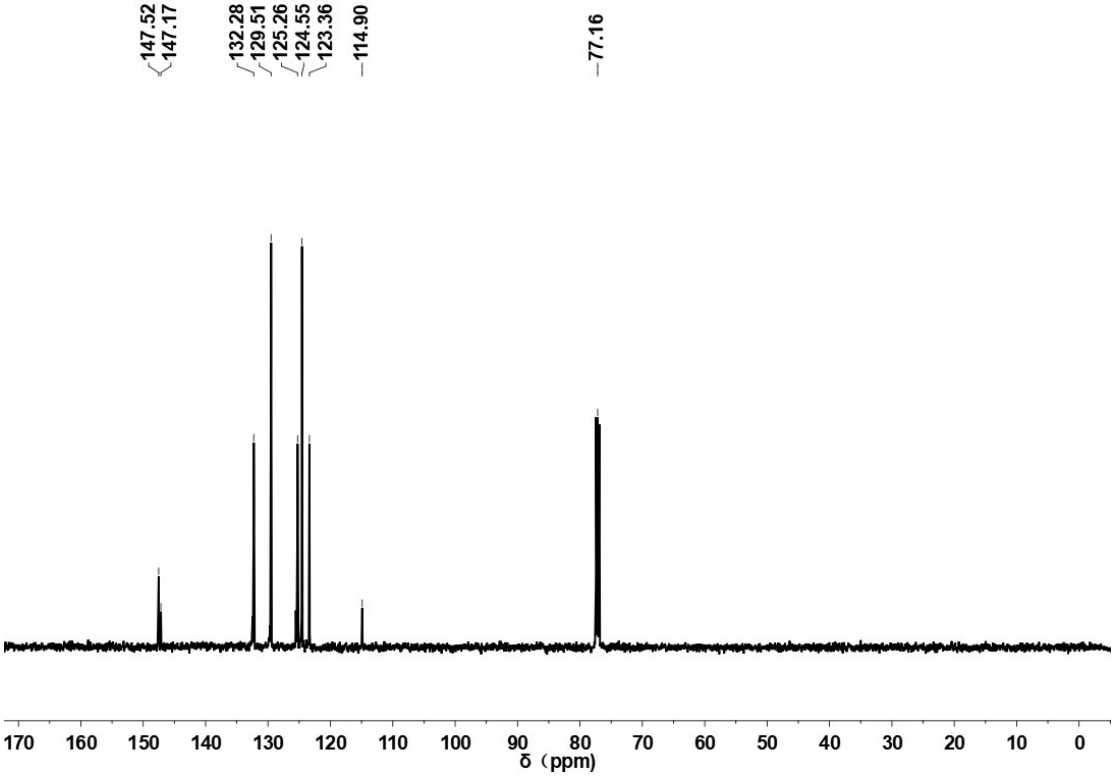
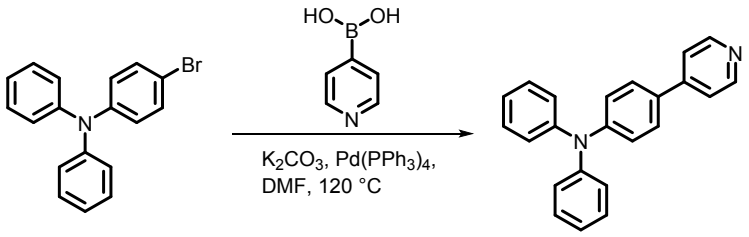



**Fig. S10** $^{13}$C NMR spectroscopy of compound **M1** (300 MHz, $CDCl_3$, 298 K).

*7. Synthesis of compound **M2***




To a solution of **M1** (100.00 mg, 0.30 mmol), pyridine-4-boronic acid (45.50 mg, 0.32 mmol) and $K_2CO_3$ (82.75 mg, 0.60 mmol) in 3mL of anhydrous DMF, $Pd(PPh_3)_4$ (17.33 mg, 0.02 mmol) was added under inert gas atmosphere. The solution was stirred at 120 °C for 24 hours and the solvent was removed by rotary evaporation after completion. The pure compound was collected after a column chromatograph purification ($SiO_2$, PE/EA = 30/1) as a buff powder (32.40 mg, 67 %).$^1$H NMR (300 MHz, $CDCl_3$) δ 8.62 (s, 2H), 7.58 – 7.50 (m, 2H), 7.49 – 7.43 (m, 2H), 7.34 – 7.23 (m, 4H), 7.14 (dd, J = 9.3, 1.8 Hz, 6H), 7.07 (t, J = 7.3 Hz, 2H).$^{13}$C NMR (75 MHz, $CDCl_3$) δ 150.22, 149.08, 147.81, 147.36, 131.03, 129.55, 127.76, 125.11, 123.73, 123.02, 121.01, 77.58, 77.16, 76.74.

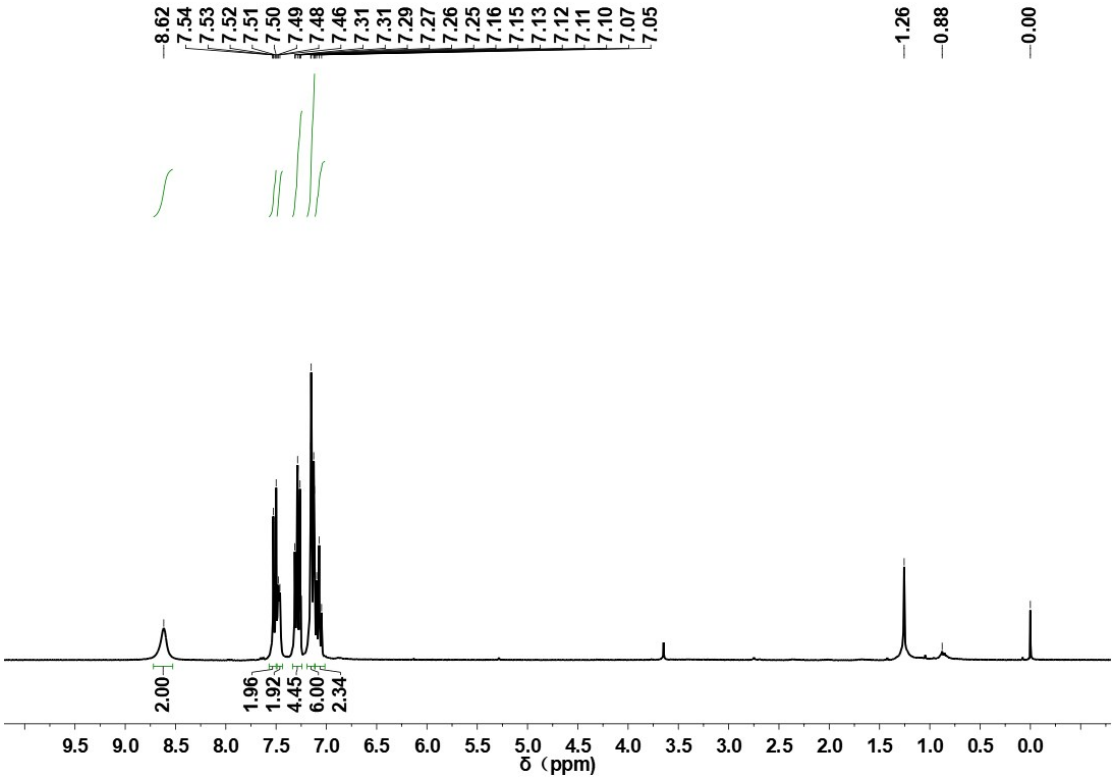



**Fig. S11** $^1$H NMR spectroscopy of compound **M2** (300 MHz, $CDCl_3$, 298 K).

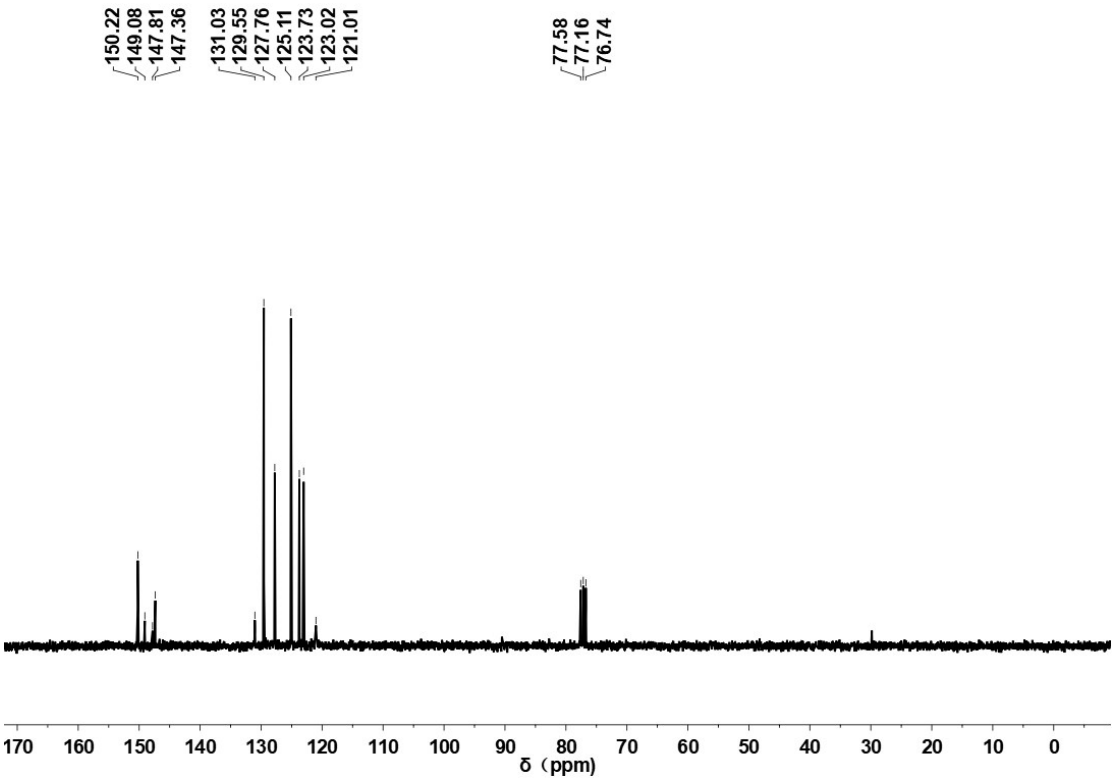
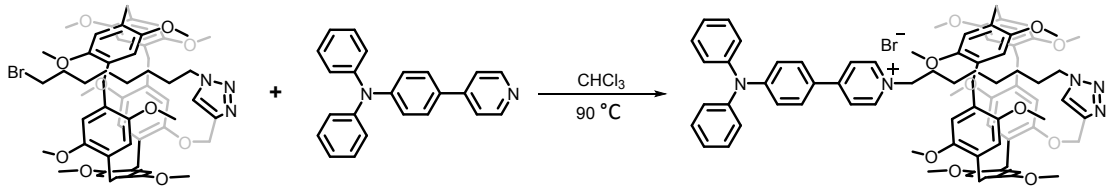



**Fig. S12** $^{13}$C NMR spectroscopy of compound **M2** (300 MHz, $CDCl_3$, 298 K).

*8. Synthesis of compound **P4***




To a 25 mL sealed tube, compound **M2** (49.6 mg, 0.15 mmol), compound **P3** (109.6 mg, 0.11 mmol) were dissolved in 1 mL of chloroform and the solution was heated at 90 °C for 24 hours. After completion, the solvent was removed by rotary evaporation to obtain a crude product. The pure product was prepared through a column chromatography purification ($SiO_2$, DCM/MeOH = 60/1) as an orange solid (24.1 mg, 18 %). Melting point 136.6-138.7 °C; $^1$H NMR (600 MHz, $CD_3OD$-$d_4$) δ 8.18 (s, 1H), 7.92 (d, *J* = 8.6 Hz, 2H), 7.75 (s, 2H), 7.44 (t, *J* = 7.8 Hz, 5H), 7.34 – 7.23 (m, 6H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.96 (dd, *J* = 63.0, 38.5 Hz, 7H), 6.79 – 6.50 (m, 3H), 5.86 (s, 2H), 5.47 – 5.38 (m, 1H), 5.09 (s, 1H), 4.56 (s, 2H), 3.93 – 3.37 (m, 37H), 1.95 (d, *J* = 35.3 Hz, 2H), 1.08 (s, br., 4H), 0.67 (s, br., 4H), -0.24 (s, br., 2H), -1.11 (d, *J* = 40.5 Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 154.01, 152.32, 151.39, 151.16, 151.08, 150.75, 150.66, 150.50, 149.25, 145.97, 144.99, 143.30, 143.19, 129.99, 129.37, 128.98, 128.88, 128.74, 128.58, 128.21, 126.49, 125.56, 124.07, 123.69, 122.16, 120.43, 115.17, 115.13, 115.09, 115.06, 114.80, 114.51, 114.30, 113.83, 64.44, 56.96, 56.73, 56.34, 56.23, 56.16, 56.09, 53.32, 50.69, 50.21, 29.85, 29.75, 29.33, 29.19, 28.56, 27.95, 25.70, 25.29. LC-ESI-MS: m/z calculated for $[M]^+$ $C_{78}H_{84}N_5O_{10}^+$, 1250.6213; found 1250.5798.

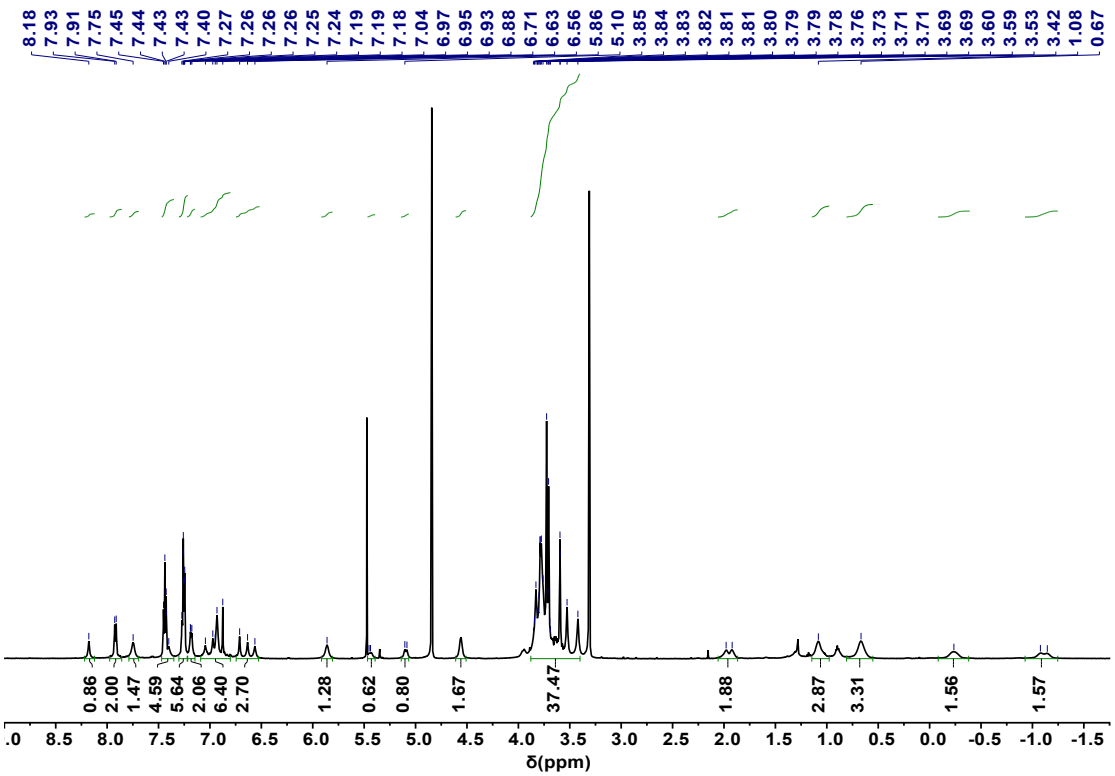



**Fig. S13** $^{1}$H NMR spectroscopy of compound **P4** (600 MHz, $CD_3OD$-$d_4$, 298K).

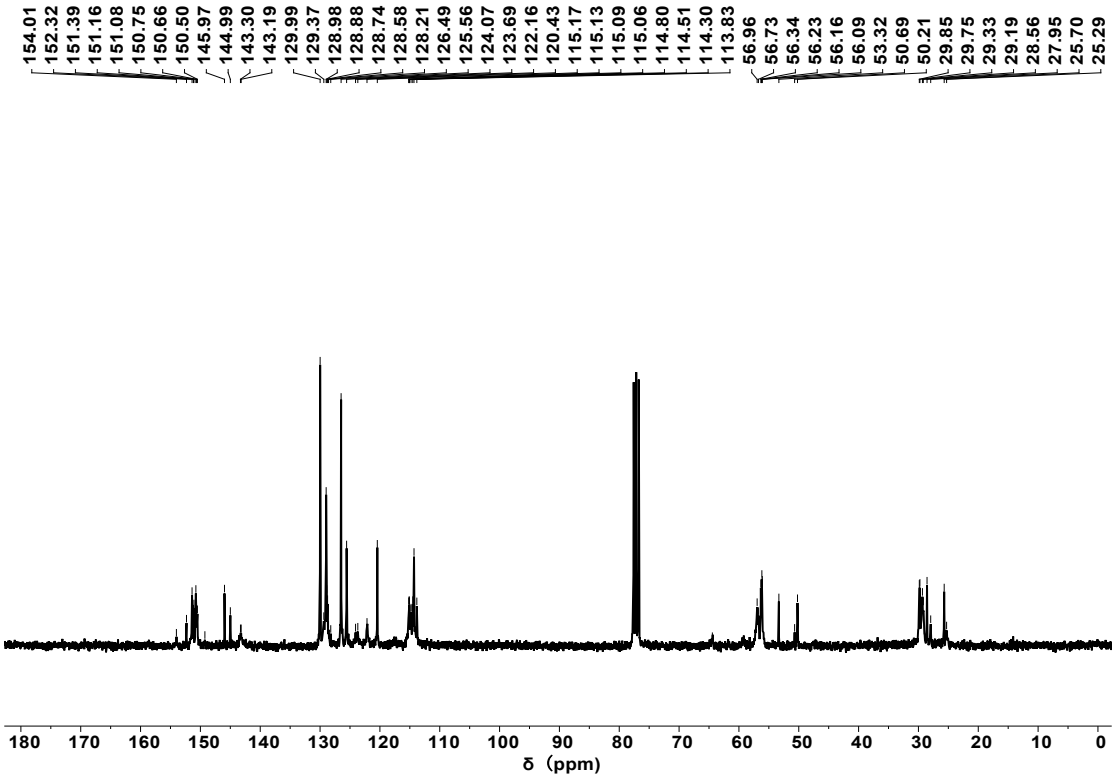



**Fig. S14** $^{13}$C NMR spectroscopy of compound **P4** (75 MHz, $CDCl_3$, 298 K).

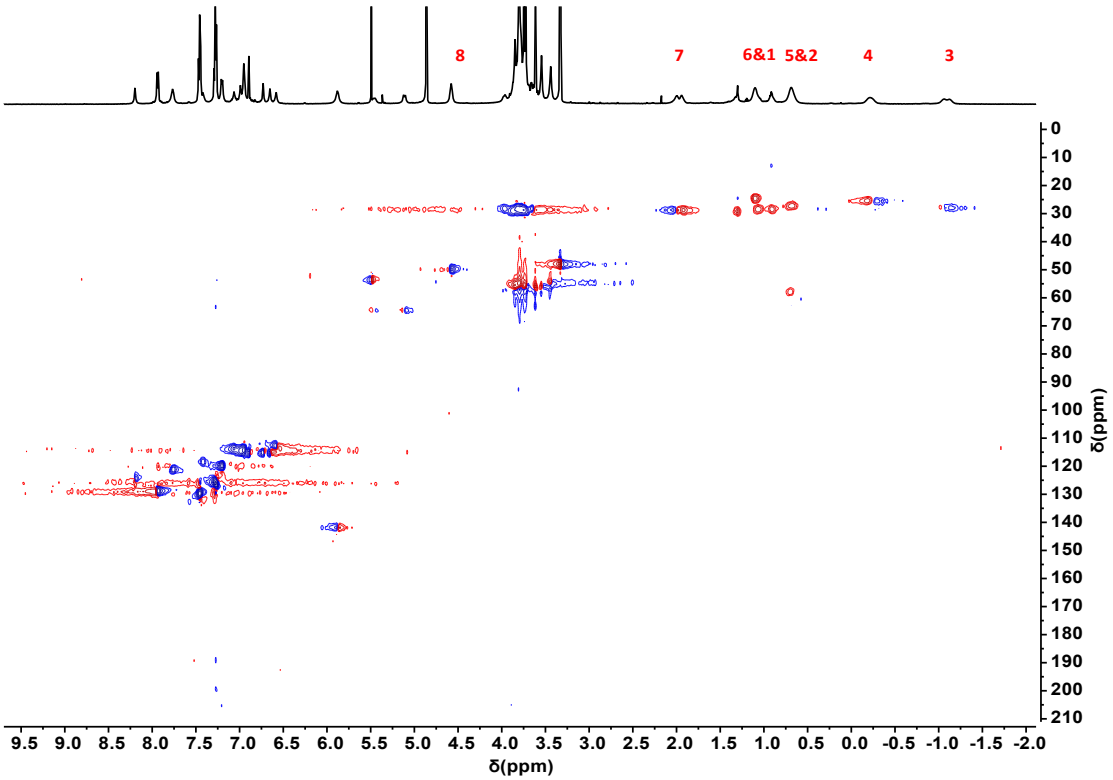



**Fig. S15** 2D $^{1}$H-$^{1}$H HSQC NMR spectroscopy of compound **P4** (600 MHz, $CD_3OD$-$d_4$, 298K).

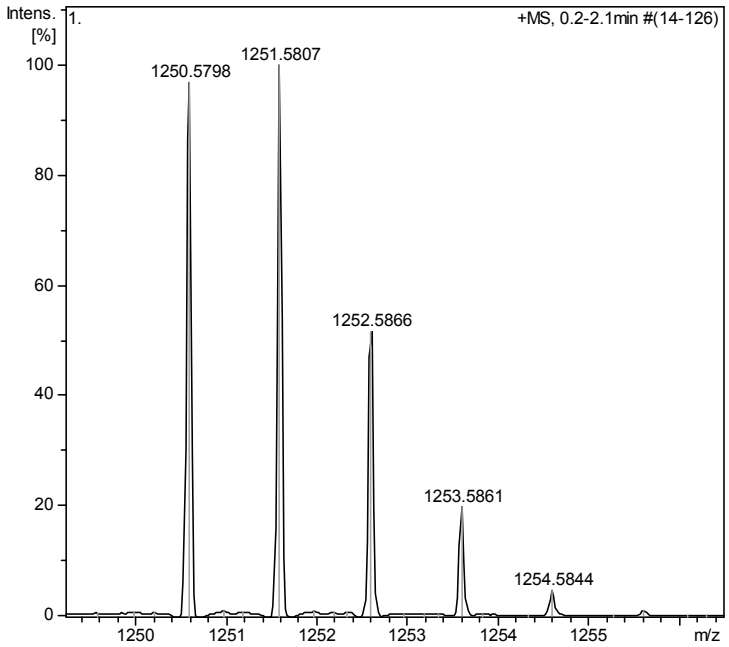
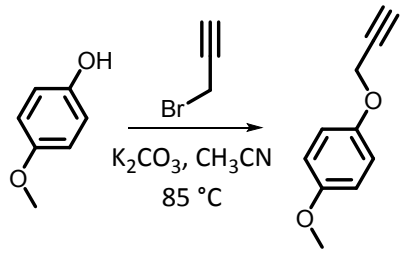



**Fig. S16** Mass spectroscopy of compound **P4**. HR-MS: m/z calculated for $[M]^+$ $C_{78}H_{84}N_5O_{10}^+$, 1250.6213; found 1250.5798.

*9. Synthesis of compound **M3***




4-methoxyphenol (200 mg, 0.27 mmol), $K_2CO_3$ (13.04 mg, 0.54 mmol) and 3-brominated acetylene (50 µL, 0.58 mmol) were dissolved in 3 mL of $CH_3CN$, and stirred at 85 °C for 24 h. After completion, the suspension was filtered and the solution was concentrated by rotary evaporation, the pure compound was collected by column chromatograph ($SiO_2$, DCM) as a white powder (117.6 mg, 56 %). $^1$H NMR (300 MHz, $CDCl_3$) δ 6.88(d, *J* = 16.5 Hz, Ar*H*, 4H), 4.64 (d, *J* = 2.4 Hz, 2H), 3.77 (s, 3H),2.50 (s, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 154.63, 151.82, 116.29, 114.75, 79.04,77.16, 75.42, 56.75, 55.81.

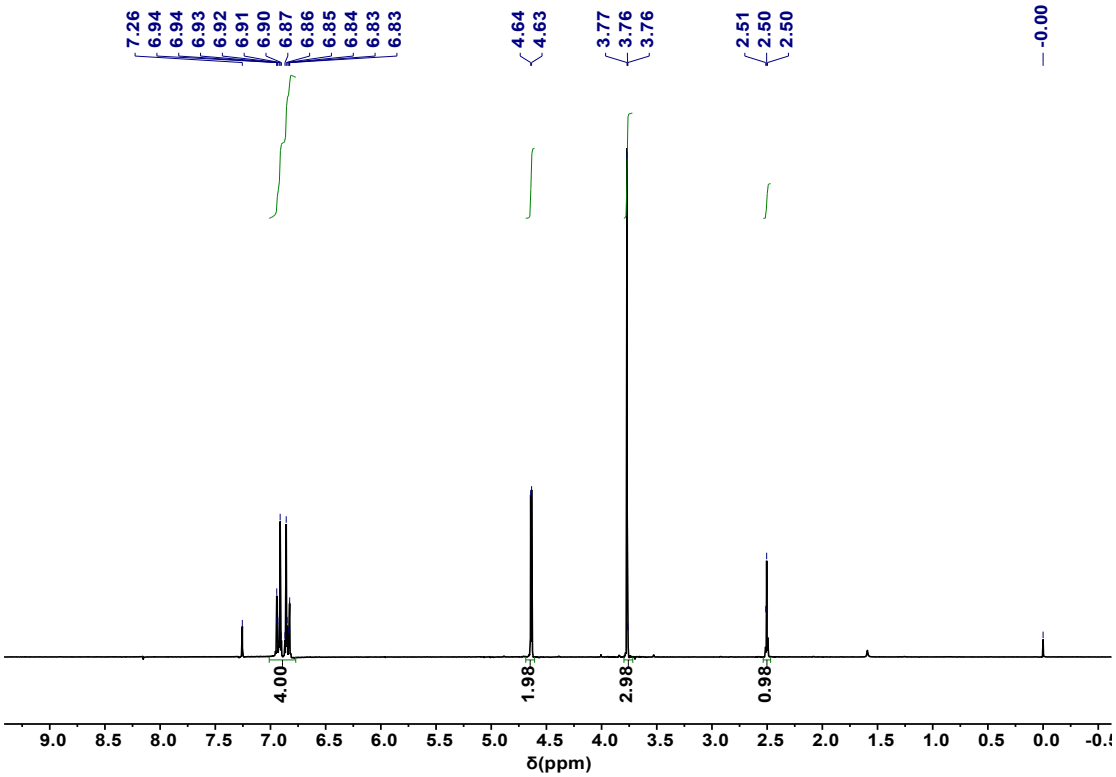



**Fig. S17** $^1$H NMR spectroscopy of compound **M3** (300 MHz, $CDCl_3$, 298 K).

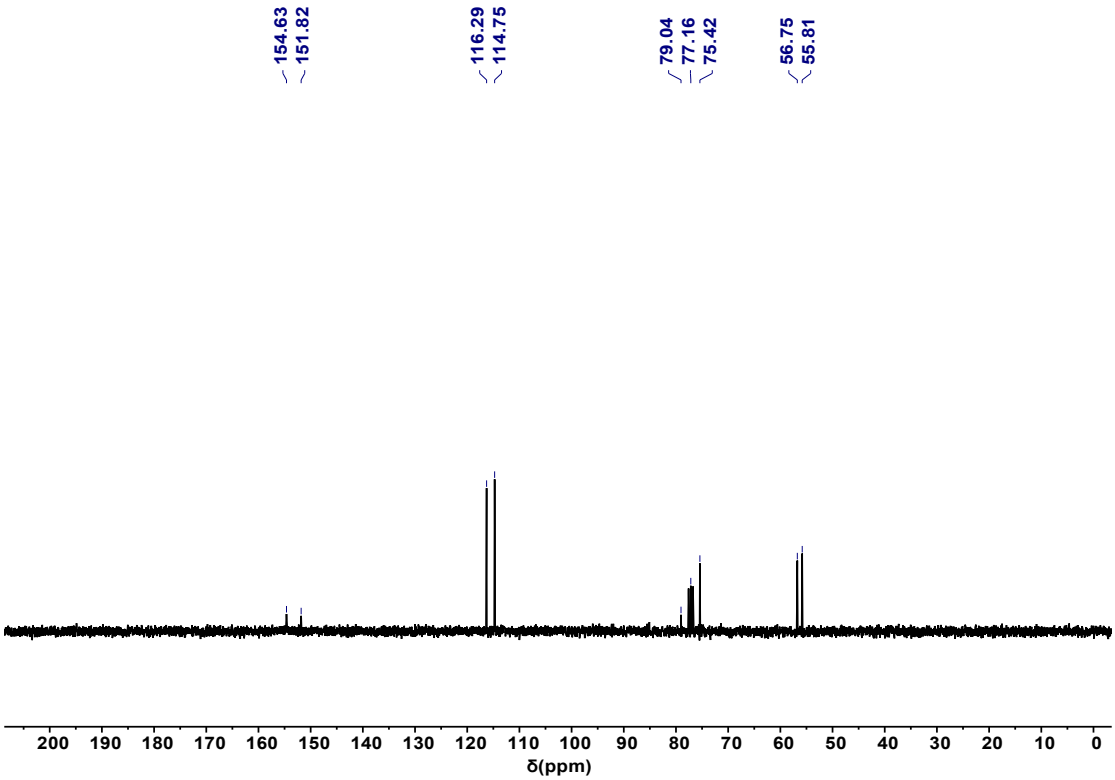
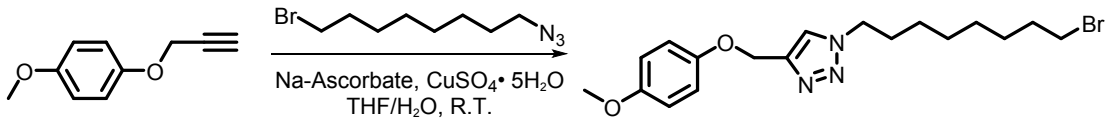



**Fig. S18** $^{13}$C NMR spectroscopy of compound **M3** (75 MHz, $CDCl_3$, 298 K).

*10. Synthesis of compound **M4***




To a solution of compound **M3** (48.64 mg, 0.30 mmol) and 1-aza-8-bromooctane (93.20 mg, 0.30 mmol) in 1.6 mL of THF, an aqueous solution of sodium ascorbate (15.45 mg, 0.08 mmol) and $CuSO_4$□$5H_2O$ (15.73 mg, 0.06 mmol) in 0.4 mL of water was added, then the color of solution varied from blue to brown, and kept the solution stirring at room temperature for 24 hours. After the reaction was completed, the solvent was removed by rotary evaporation and the pure compound was collected by column chromatography ($SiO_2$, DCM/MeOH = 30/1) as a white powder (91.80 mg, 75 %). Melting point 76.6 $^{o}$C; $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.57 (s, 1H), 6.99 – 6.76 (m, 4H), 5.16 (s, 2H), 4.34 (t, *J* = 7.2 Hz, 2H), 3.76 (d, *J* = 1.5 Hz, 3H), 3.40 (t, *J* = 6.8 Hz, 2H), 1.98 – 1.74 (m, 4H), 1.49 – 1.21 (m, 8H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 154.28, 152.46, 144.56, 122.49, 115.96, 114.77, 77.16, 62.95, 55.81, 50.49, 34.03, 32.77, 30.33, 28.89, 28.59, 28.08, 26.46. MS (m/z): HRMS (ESI) calculated for $[M+H]^+$ $C_{18}H_{27}BrN_3O_2^+$ 396.1281; found 396.1278.

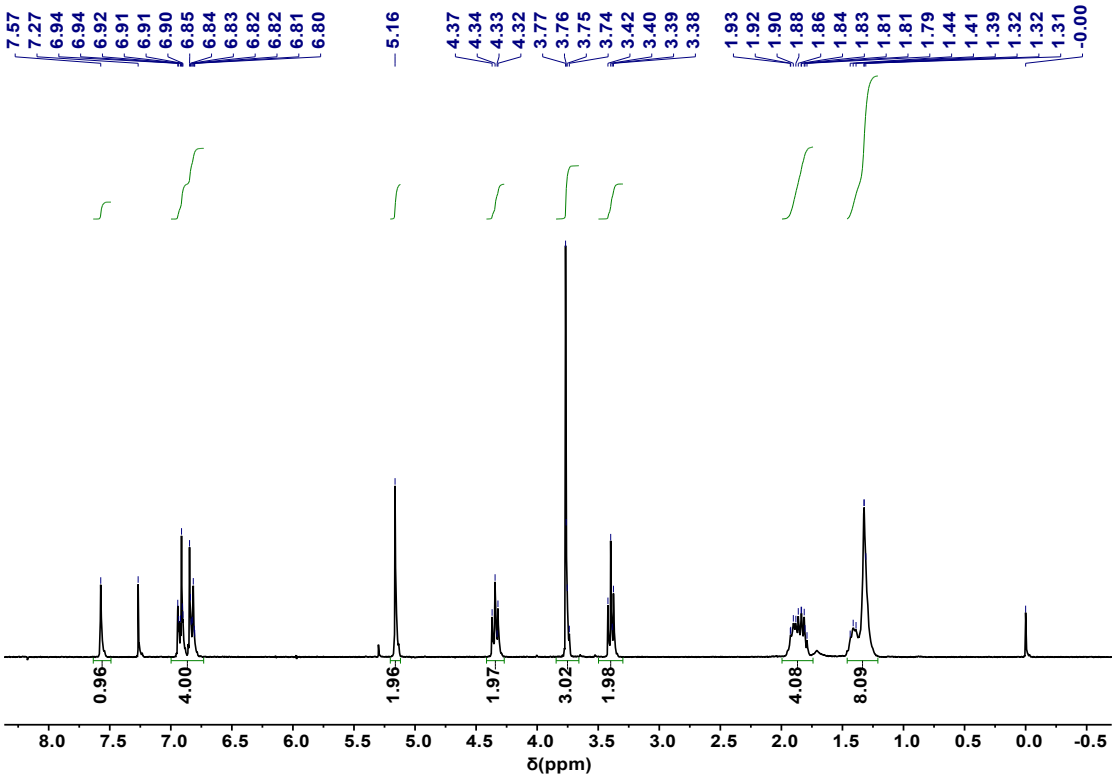



**Fig. S19** $^{1}$H NMR spectroscopy of compound **M4** (300 MHz, $CDCl_3$, 298 K).

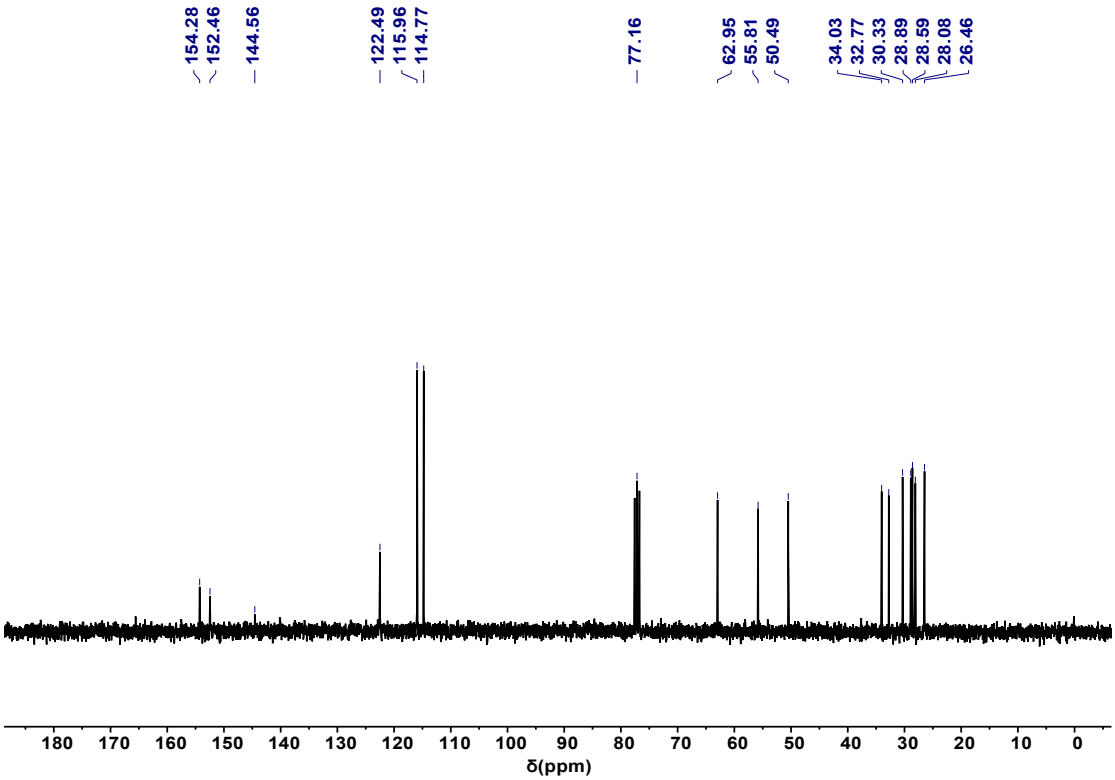



**Fig. S20** $^{13}$C NMR spectroscopy of compound **M4** (75 MHz, $CDCl_3$, 298 K).

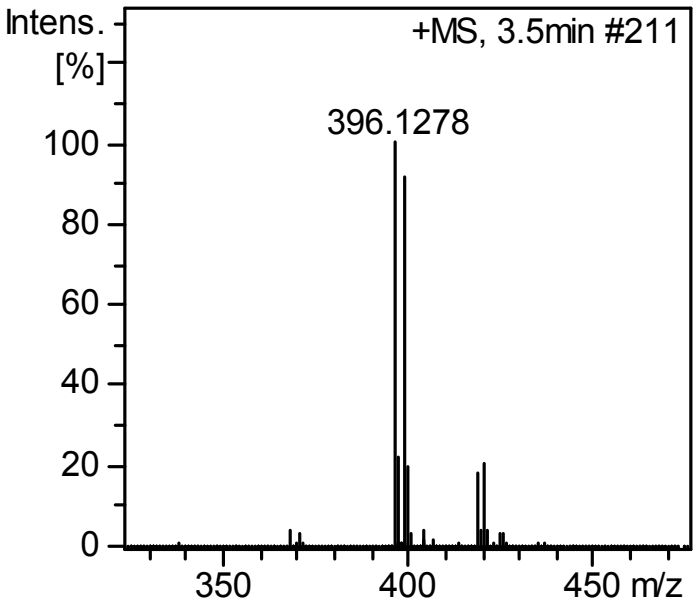
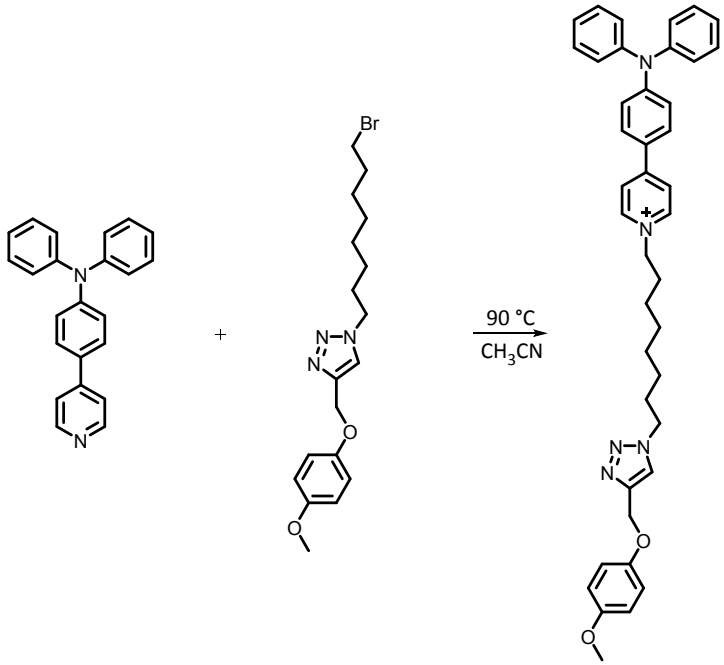



**Fig. S21** Mass spectroscopy of compound **M4**. HR-MS: calculated for $[M+H]^+$ $C_{18}H_{27}BrN_3O_2^+$ 396.1281; found 396.1278.

*11. Synthesis of compound **M5***




In a 25 mL sealed tube, compound **M4** (24.5 mg, 0.06 mmol) and compound **M2** (20.0 mg, 0.06 mmol) were dissolved in 1 mL of $CH_3CN$ and kept it at 90 $^oC$ for 24 hours. After the reaction was completed by TLC, the solvent was removed by rotary evaporation and the pure compound was collected by column chromatography purification ($SiO_2$, DCM/MeOH = 60/1) as an orange solid (32.2 mg, 84 %). Melting point 63-67.8 $^oC$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 9.23 (d, *J* = 6.6 Hz, 2H), 8.04 (d, *J*= 6.6 Hz, 2H), 7.69 – 7.58 (m, 3H), 7.41 – 7.29 (m, 4H), 7.23 –7.14 (m, 6H), 7.06 (d, *J* = 8.4 Hz,

2H), 6.95 – 6.87 (m, 2H), 6.81 (d, *J*= 9.2 Hz, 2H), 5.14 (s, 2H), 4.80 (t, *J* = 7.5 Hz, 2H) 4.35 (t, *J* =6.9 Hz, 2H), 3.75 (s, 3H), 2.05 – 1.94 (m, 2H), 1.88 (q, *J* = 6.3,5.7 Hz, 2H), 1.30 (t, *J* = 14.5 Hz, 8H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 155.04,154.38, 152.59, 152.35, 145.97, 144.46, 129.95, 129.13, 126.40, 125.50, 124.17,123.01, 122.88, 120.46, 116.13, 114.86, 77.16, 62.97, 60.44, 55.84, 50.33, 31.59, 30.09,28.54, 28.31, 26.03, 25.72. MS (m/z): HRMS (ESI) calculated for $[M]^+$ $C_{41}H_{44}N_5O_2^+$ 638.3490; found 638.3471.

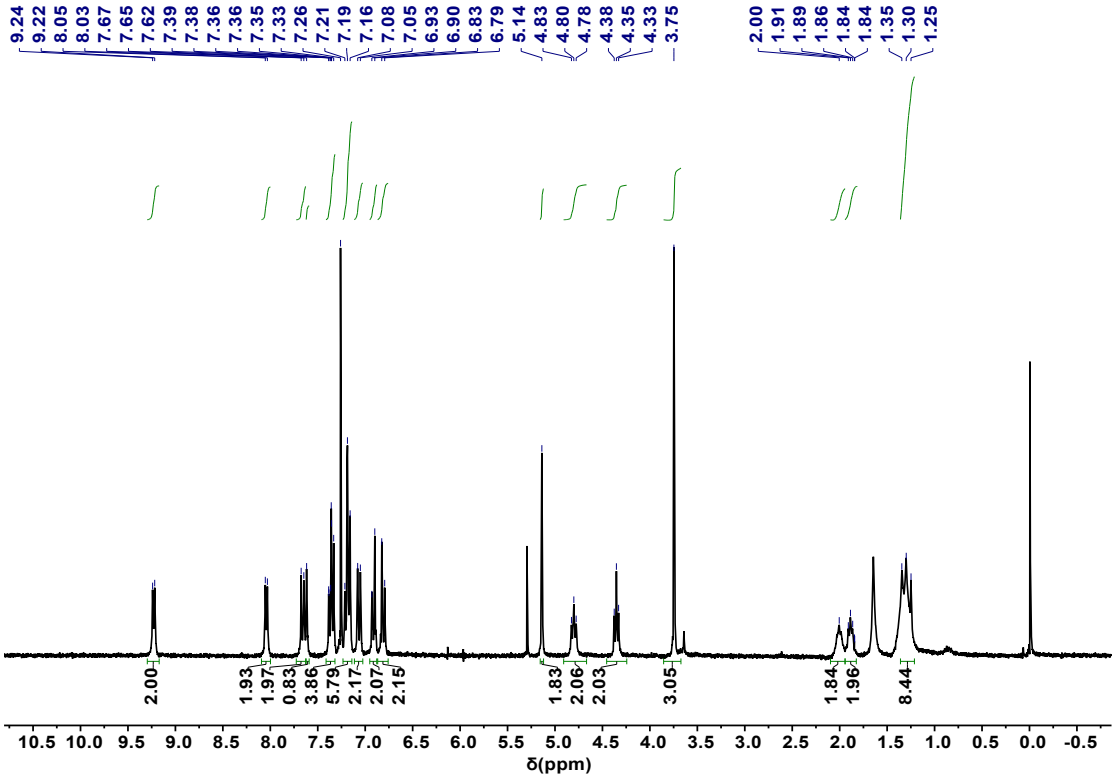



**Fig. S22** $^1$H NMR spectroscopy of compound **M5** (300 MHz, $CDCl_3$, 298 K).

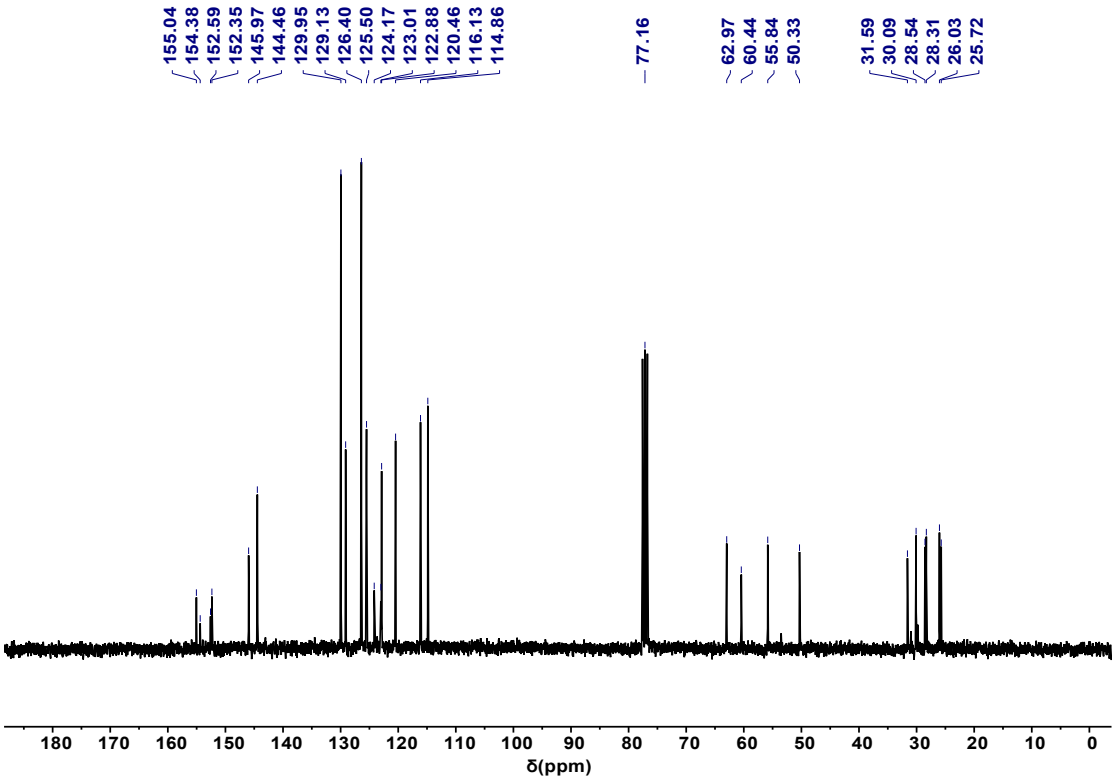



**Fig. S23** $^{13}C$ NMR spectroscopy of compound **M5** (75 MHz, $CDCl_3$, 298 K).

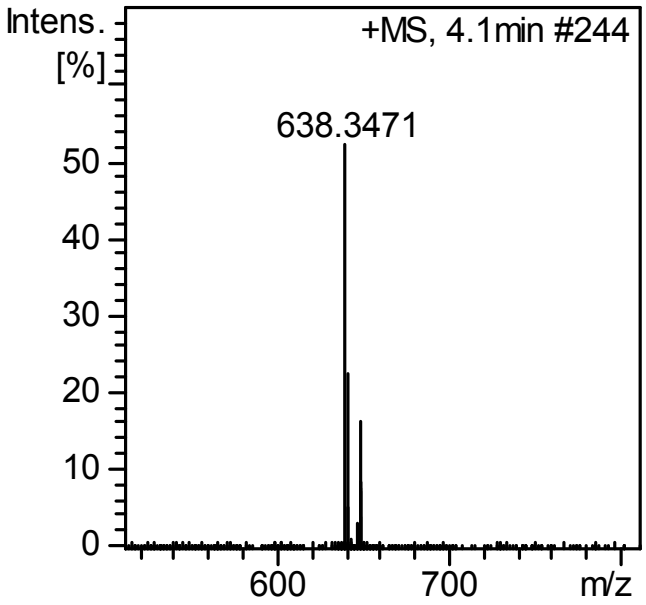



**Fig. S24** Mass spectroscopy of compound **M5**. HR-MS: calculated for $[M]^+$ $C_{41}H_{44}N_5O_2^+$ 638.3490; found 638.3471.

*12. NMR titration of compound **P3** in $CDCl_3$*

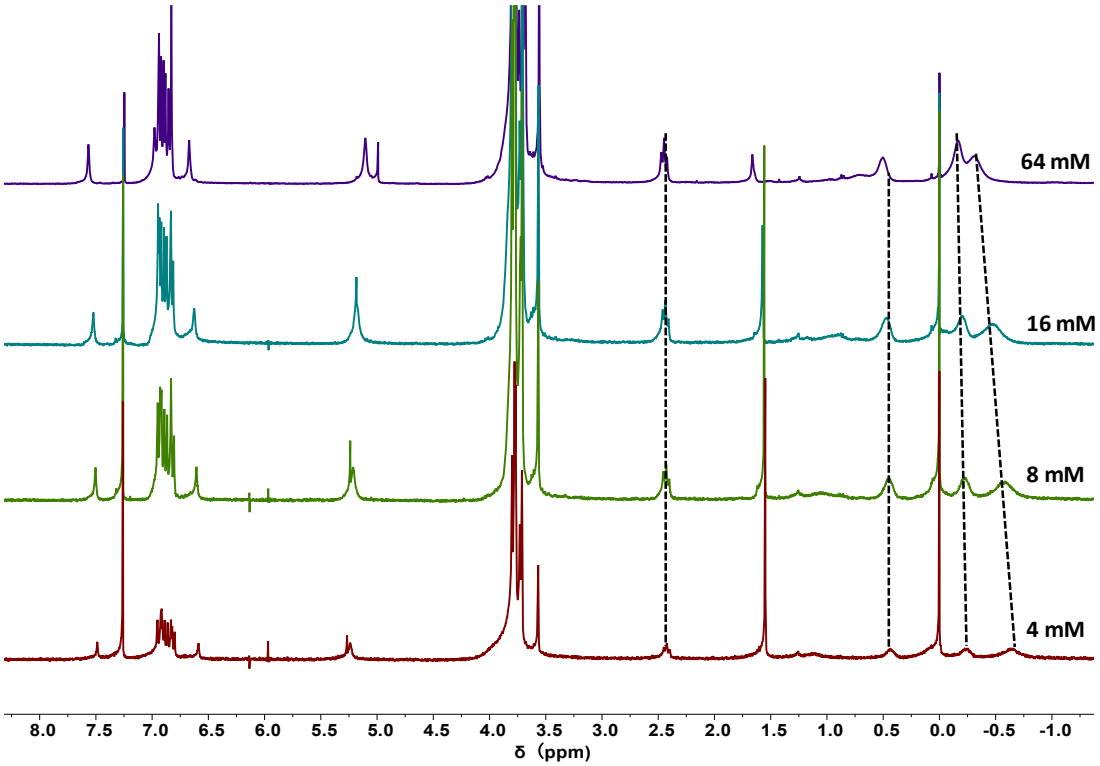



**Fig. S25** NMR titration spectra of compound **P3** (300 MHz, $CDCl_3$, 298 K).

*13. 2D $^1$H-$^1$H NOESY NMR spectrum of compound **P4***

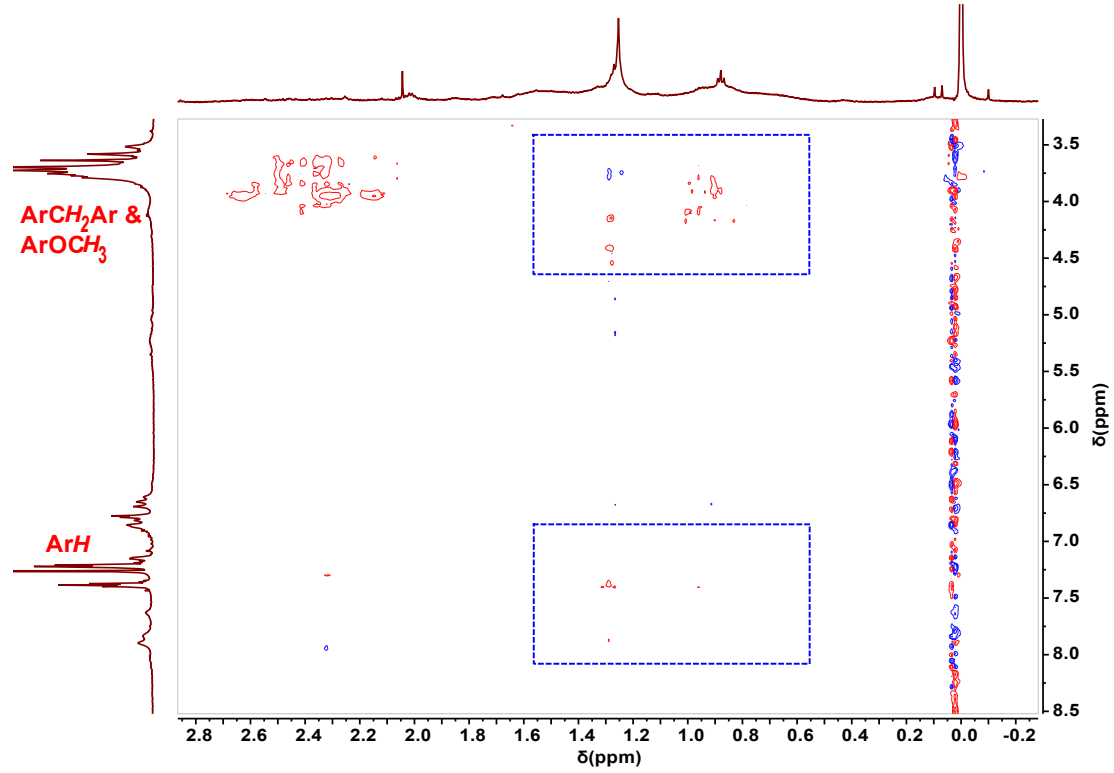



**Fig. S26** 2D $^1$H-$^1$H NOESY NMR spectroscopy of compound **P4** (600 MHz, $CDCl_3$, 298 K).

*14. $^1$H NMR spectra displaying a descriptive comparison of compounds **P4** and **M5** in*

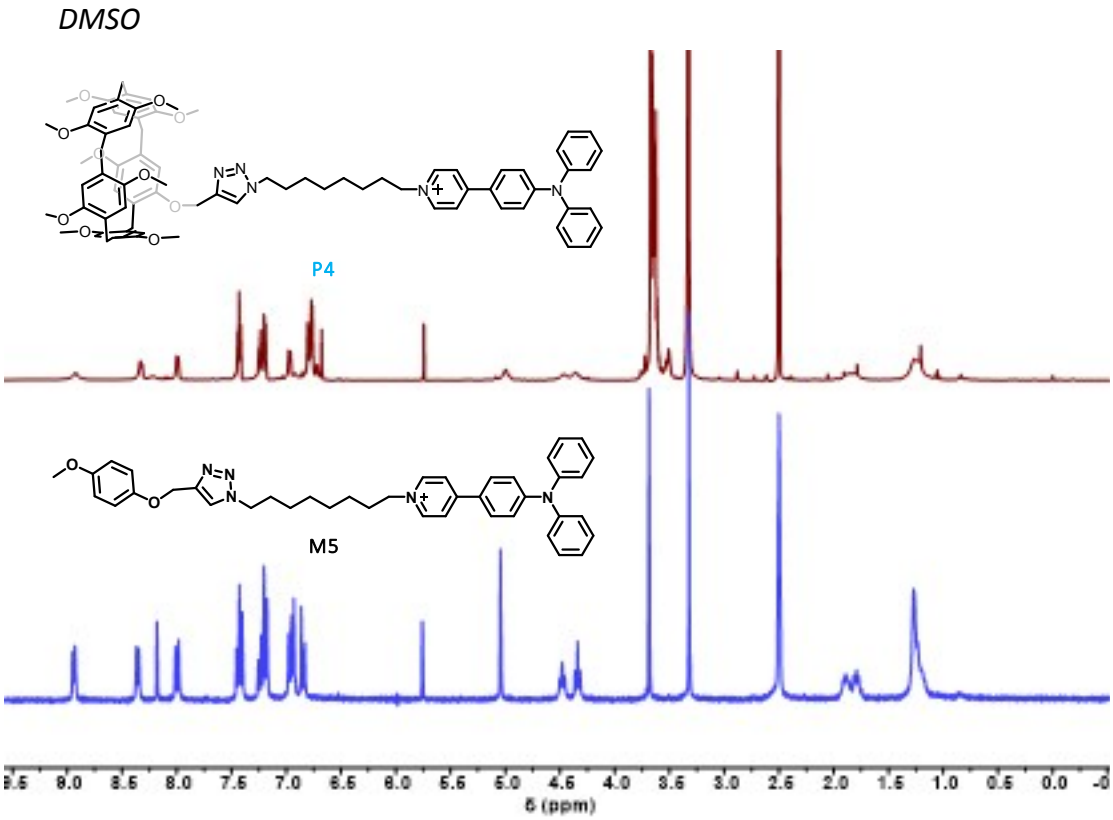



**Fig. S27** $^{1}$H NMR spectra of compounds **P4** and **M5** in DMSO.