Supporting information

Exploiting Chemoselectivity for Discrete Oligomer Synthesis through Sequential IrAAC and CuAAC Reactions

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I. General Information

All air or moisture sensitive reactions were conducted in oven-dried glassware under nitrogen atmosphere using dry solvents. Flash column chromatography was performed over silica gel (200-300 mesh) purchased from Qingdao Puke Co., China. Alkynes and common organic chemicals were purchased from commercial suppliers, such as Sigma-Aldrich® and *J*&K® Scientific Ltd., and used as received. Iridium catalyst was purchased from Strem® Chemicals, Inc.

NMR. ^{1}H and ^{13}C spectra were collected on a Bruker AV 400 MHz NMR spectrometer using residue solvent peaks as an internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm, DMSO-*d6* at 2.54 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm, DMSO-*d6* at 39.5 ppm).

MS. ESI-MS analyses were measured on Agilent 6540 UHD Accurate-Mass Q-TOF. FTMS were measured on Bruker Solarix XR Fourier transform ion cyclotron resonance mass spectrometer.

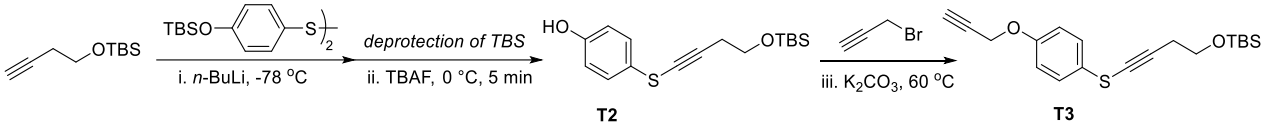
LC-MS. LC-MS analysis was measured on Xevo G2 Qtof with Waters Acquity SDS. The instrument was calibrated in the m/z range 50–1800 with an electrospray source (ESI-MS). The conditions of the reversed phase HPLC method are as follows: initial 5.0% acetonitrile - 95.0% water, 3 min 15.0% acetonitrile - 85.0% water, 9 min 50.0% acetonitrile - 50.0% water, 11 min 100.0% acetonitrile - 0.0% water, 13 min 5.0% acetonitrile - 95.0% water. Flow rate: 0.3 ml/min; Column temperature of 45 °C; Injection volume of 5 μL. The signal was monitored at 214 nm.

SEC. Samples (5 mg) were dissolved in THF (1 mL) and filtered prior to injection. SEC analyses were performed on a Waters 1525 Gel chromatography with three mixed-bed GPC columns in series (three Waters Styragel HT3 THF (7.8*300mm Column)), and THF mobile phase run at 35 °C for 40 min. The differential refractive index of each compound was monitored using a WAT038040 (2414) detector.

Fluorescence. Fluorescence performance was recorded on Hitachi F-7000 FL Spectrophotometer. The spectra were recorded with EX slit 5.0 nm, EM slit 5.0 nm, PMT voltage 300~800 V and three repetitions.

II. Preparation of Substrates

Diazido monomers **A1**,[1] **A2**[2] and **A3**[3] were prepared according to references.

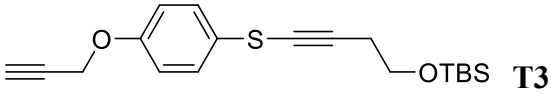


Scheme S1. Synthetic route to **T3**.

Synthesis of 4-((4-((*tert*-butyldimethylsilyl)oxy)but-1-yn-1-yl)thio)phenol (**T2**) (steps i-ii in **Scheme S1)**: (i) At -78 ºC, to a solution of alkyne (30 mmol, 1.0 eq.) in dry THF (0.25 M) under N_2 atmosphere was slowly added *n*-BuLi (1.1 eq.). The mixture was stirred at the same temperature for 1 hour before disulfide (1.0 eq.) and EtI (1.0 eq.) were added. Then the mixture was allowed warming to room temperature and stirred for 2 hours before a saturated aqueous NH_4Cl solution was added. The aqueous phase was separated and extracted with ethyl acetate (EA) for three times. The combined organic phase was washed with brine, dried over Na_2SO_4 and evaporated under vacuum to give the crude product of thioalkyne, which was then purified by silica gel flash column chromatography to give pure thioalkyne. (ii) The TBS-protected thioalkyne was dissolved in THF (0.5 M), TBAF (1.0 eq.) was added at 0 ºC and stirred another 5 minutes. Upon completion indicated by TLC, EA was added and the mixture was washed by water and brine. The organic layer was dried over $MgSO_4$, and evaporated under vacuum to give the crude product of thioalkyne, which was then purified by silica gel flash column chromatography to give pure product **T2** as yellow oil in 71% overall yield (6.56 g). Rf = 0.5 (PE/EA = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.26 (m, 2 H), 6.81-6.78 (m, 2 H), 5.89 (s, 1 H), 3.78 (t, *J* = 8.0 Hz, 2 H), 2.61 (t, *J* = 8.0 Hz, 2 H), 0.89 (s, 9 H), 0.08 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 128.8, 123.3, 116.4, 95.0, 67.7, 61.9, 25.9, 25.6, 24.5, 18.3, 5.3.



T3

Synthesis of *tert*-butyldimethyl((4-((4-(prop-2-yn-1-yloxy)phenyl)thio)but-3-yn-1-yl)oxy)silane

(**T3**) (step iii in **Scheme S1**): **T2** was dissolved in MeCN (0.5 M), K_2CO_3 (2.0 eq.) was added and stirred for 30 minutes, then 3-bromopropyne (1.2 eq.) was added at 0 ºC and stirred over night at 60 ºC. Upon completion indicated by TLC, the reaction solution was filtered under reduced pressure and purified by silica gel flash column chromatography to give pure product **T3** as colorless oil in 83% yield (6.12 g).

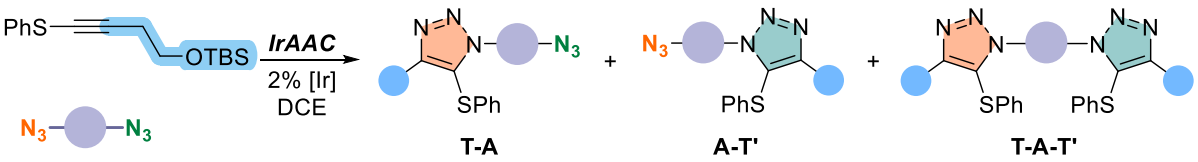
Rf = 0.5 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.35 (m, 2 H), 6.97-6.94 (m, 2 H), 4.68 (d, *J* = 4.0 Hz, 2 H), 3.78 (t, *J* = 8.0 Hz, 2 H), 2.63 (t, *J* = 8.0 Hz, 2 H), 2.52 (t, *J* =4.0 Hz, 1 H), 0.91 (s, 9 H), 0.08 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 128.2, 124.8, 115.9, 95.6, 78.2, 75.7, 67.2, 61.7, 56.0, 25.9, 24.6, 18.3, 5.3.

HRMS *m/z* (ESI) calcd. for $C_{19}H_{27}O_2SSi$ $(M+H)^+$ 347.1496, found 347.1490.

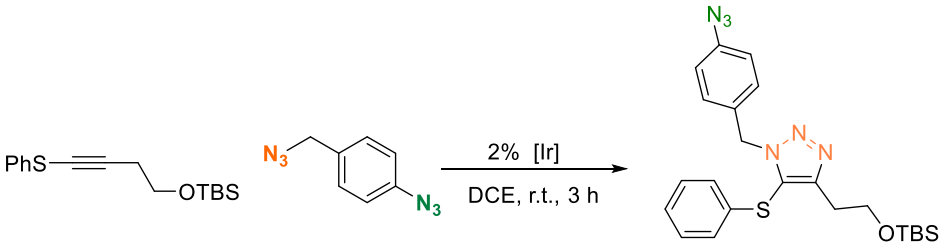
III. Azide Reactivity Study



Scheme S2. IrAAC reaction of bis(azides) with thioalkyne **T1**.

General procedure:

In a glove box, to an oven-dried vial was added the building unit involving bis(azides) (1.2 eq. or 2.0 eq.), **T1** (0.2 mmol, 1.0 eq.), $[Ir(COD)Cl]_2$ (2 mol %) and DCE (0.3 M). The vial was capped and removed from the glove box. The reaction mixture was stirred at room temperature for 3 h until the reaction completed (confirmed by TLC), and then concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to give the mixed product.



T1 0.2 mmol	**A1** 1.2 eq	**T1-A1:A1-T1':T1-A1-T1'** = 91:0:9 Yield (**T1-A1**) = 85%
	A1 2.0 eq	**T1-A1:A1-T1':T1-A1-T1'** > 99:0:1

Scheme S3. Selective reaction of **T1** and **A1**.

The ratio of **T-A**, **A-T'** and **T-A-T'** is determined by ^{1}H NMR analysis. At the completion of the reaction, the reaction solution was concentrated by vacuum and added the internal standard. The ratio of **T1-A1** and **T1-A1-T1'** was determined to be 92:8, by comparing the relative valves of the peak observed at 5.45 ppm (s, 2 H) for **T1-A1** and 5.49 ppm (s, 2 H) for **T1-A1-T1**'. When the **A1** was 2.0 equivalents, the ratio of **T1-A1** and **T1-A1-T1'** was up to 99:1.

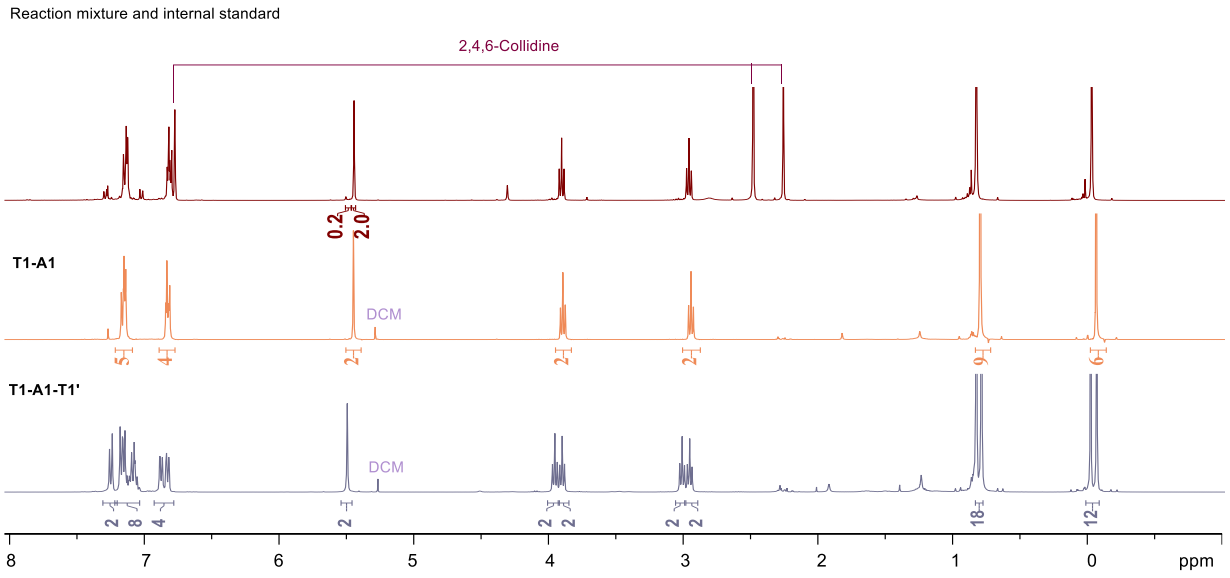
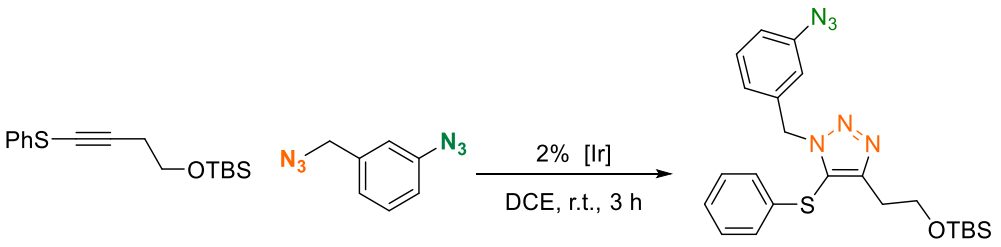


Figure S1. Comparison of ^{1}H NMR for reaction mixture, **T1-A1** and **T1-A1-T1'**.



T1 0.2 mmol	**A2**	1.2 eq	**T1-A2:A2-T1':T1-A2T1'** = 93:0:7 Yield (**T1-A2**) = 86%
	A2	2.0 eq	**T1-A2:A2-T1':T1-A2T1'** > 99:0:1

Scheme S4. Selective reaction of **T1** and **A2**.

The ratio of **T1-A2** and **T1-A2-T1'** was determined to be 93:7, by comparing the relative valves of the peak observed at 5.45 ppm (s, 2 H) for **T1-A2** and 5.44 ppm (s, 2 H) for **T1-A2-T1'**. When the **A2** was 2.0 equivalents, the ratio of **T1-A2** and **T1-A2-T1'** was up to 99:1.

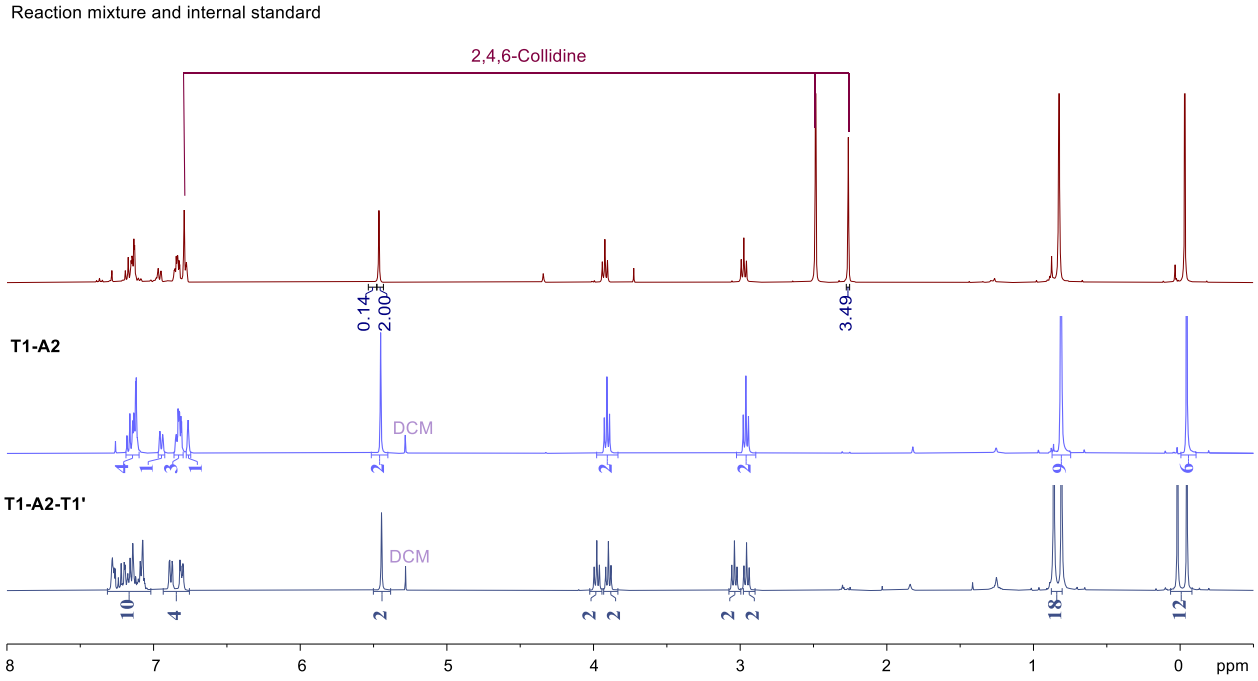
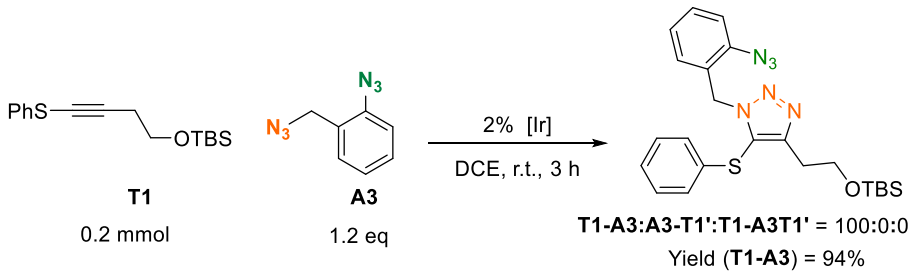
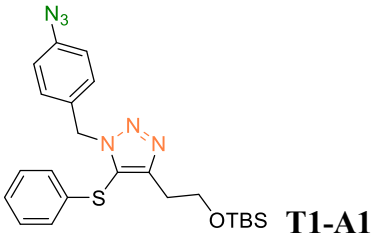


Figure S2. Comparison of ^{1}H NMR for reaction mixture, **T1-A2** and **T1-A2-T1'**.



Scheme S5. Selective reaction of **T1** and **A3**.



T1-A1

1-(4-azidobenzyl)-4-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-5-(phenylthio)-1*H*-1,2,3-triazole (**T1-A1**) was obtained as brown oil in 85% yield (79.2 mg).

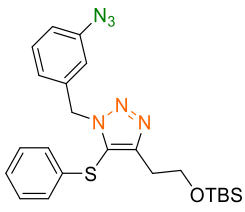
Rf = 0.5 (PE/EA = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.13 (m, 5 H), 6.8-6.80 (m, 4 H), 5.45 (s, 2 H), 3.90 (t, *J* = 8.0 Hz,

2 H), 2.9 (t, *J* = 8.0 Hz, 2 H), 0.81 (s, 9 H), 0.05 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 140.0, 133.8, 131.1, 129.6, 129.3, 126.7, 126.5, 124.3, 119.1, 62.0, 51.7, 29.1, 25.8, 18.2, 5.4.

HRMS *m/z* (ESI) calcd. for $C_{23}H_{31}N_6OSSi$ $(M+H)^+$ 467.2044, found 467.2046.



T1-A2

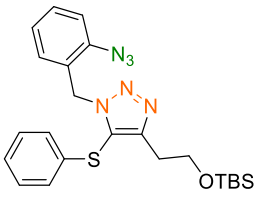
1-(3-azidobenzyl)-4-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-5-(phenylthio)-1*H*-1,2,3-triazole (T1-A2) was obtained as brown oil in 86% yield (80.2 mg).

Rf =0.5 (PE/EA = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.12 (m, 4 H), 6.96 (d, *J* = 8.0 Hz, 1 H), 6.85-6.81 (m, 3 H), 6.76 (s, 1 H), 5.45 (s, 2 H), 3.91 (t, *J* = 8.0 Hz, 2 H), 2.96 (t, *J* = 8.0 Hz, 2 H), 0.81 (s, 9 H), 0.05 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 140.3, 136.3, 133.7, 130.0, 129.2, 126.6, 126.5, 124.4, 118.7, 62.0, 51.8, 29.1, 25.8, 18.2, 5.4.

HRMS *m/z* (ESI) calcd. for $C_{23}H_{31}N_6OSSi$ $(M+H)^+$ 467.2044, found 467.2049.



T1-A3 (1)

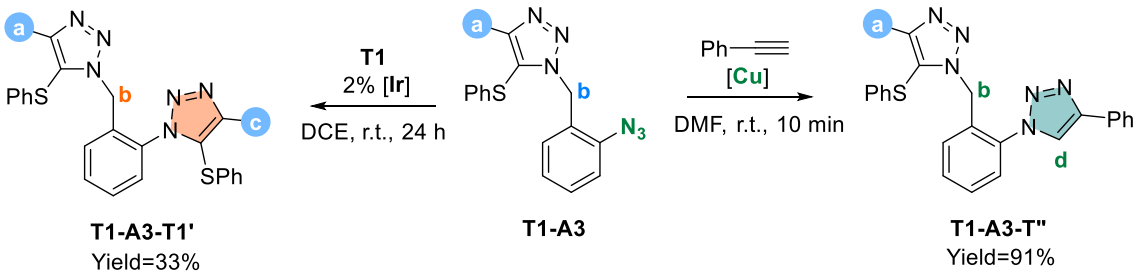
1-(2-azidobenzyl)-4-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-5-(phenylthio)-1*H*-1,2,3-triazole (1) was obtained as brown oil in 94% yield (87.6 mg).

Rf = 0.5 (PE/EA = 3:1).

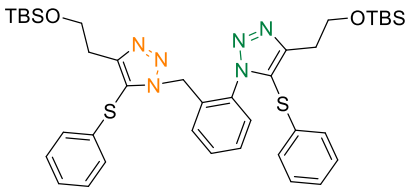
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.21 (m, 1 H), 7.15-7.08 (m, 3 H), 7.00-6.91 (m, 3 H), 6.88-6.86 (m, 2 H), 5.48 (s, 2 H), 3.93 (t, *J* = 8.0 Hz, 2 H), 2.98 (t, *J* = 8.0 Hz, 2 H), 0.83 (s, 9 H), 0.02 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 137.5, 133.7, 129.4, 129.4, 129.1, 126.9, 126.5, 125.8, 124.8, 118.0, 62.1, 47.1, 29.2, 25.9, 18.3, 5.4.

HRMS *m/z* (ESI) calc. for $C_{23}H_{31}N_6OSSi$ $(M+H)^+$ 467.2044, found 467.2046.



Scheme S6. Different reactivity of azido groups in IrAAC and CuAAC.



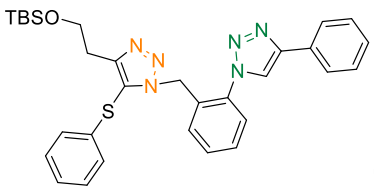
T1-A3-T1'

In a glove box, to an oven-dried vial was added **T1-A3**(0.2 mmol, 1.0 eq.), **T1** (1.2 eq.), $[Ir(COD)Cl]_2$ (2 mol %) and DCE (0.3 M). The vial was capped and removed from the glove box. The reaction mixture was stirred at room temperature for 24 h, then concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to give the pure product **T1-A3-T1'** as brown oil in 33% yield (50.1 mg).

Rf = 0.5 (PE/EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.09 (m, 8 H), 6.94-6.87 (m, 5 H), 6.79-6.76 (m, 1 H), 5.22 (s, 2 H), 4.01 (t, *J* = 8.0 Hz, 2 H), 3.92 (t, *J* = 8.0 Hz, 2 H), 3.06 (t, *J* = 8.0 Hz, 2 H), 2.97 (t, *J* = 8.0 Hz, 2 H), 0.86 (d, *J* = 12.0 Hz, 18 H), 0.03 (d, *J* = 12.0 Hz, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 149.6, 133.7, 133.2, 132.2, 130.3, 129.3, 129.2, 128.8, 128.3, 128.2, 127.9, 127.5, 126.9, 125.7, 62.0, 47.5, 29.1, 25.9, 18.3, 5.4, 5.3.



T1-A3-T"

T1-A3 (0.2 mmol, 1.0 eq.) and phenylacetylene (1.2 eq.) were added into the solution of DMF (0.5 M) involving CuBr (0.2 eq.), PMDETA (0.2 eq.), NaAsc (0.5 eq.). The reaction mixture was stirred for 10 min until the reaction completed (confirmed by TLC). Then diluted with ethyl acetate, washed with

brine (three times), dried over Na_2SO_4, filtered, and evaporated under vacuum. The residue was purified by column chromatography to give **T1-A3-T"** as white solid in 91% yield (103.4 mg).

Rf = 0.5 (PE/EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1 H), 7.90-7.87 (m, 2 H), 7.50-7.32 (m, 6 H), 7.18 (d, *J* = 4.0 Hz, 1 H), 7.09-7.07 (m, 3 H), 6.78-6.76 (m, 2 H), 5.55 (s, 2 H), 3.88 (t, *J* = 8.0 Hz, 2 H), 2.93 (t, *J* = 8.0 Hz, 2 H), 0.81 (s, 9 H), 0.05 (s, 6 H).

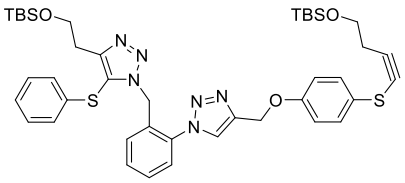
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 149.6, 133.7, 133.2, 132.2, 130.3, 129.3, 129.2, 128.8, 128.3, 128.2, 127.9, 127.5, 126.9, 125.7, 62.0, 47.5, 29.1, 25.9, 18.3, 5.4, 5.3.

IV. Construction of Oligomers via Sequential IrAAC and CuAAC reactions

General procedures:

IrAAC: In a glove box, to an oven-dried vial was added the thioalkyne building unit (first step was **T1**) (1.0 eq.), the building unit **A3** (1.2 eq.), $[Ir(COD)Cl]_2$ (2 mol %) and DCE (0.3 M). The vial was capped and removed from the glove box. The reaction mixture was stirred at room temperature for 2-6 h until the reaction completed (confirmed by TLC), and then concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to give the desired product.

CuAAC: The purified unprotected azide building unit (1.0 eq.) and the thioalkyne building unit **T3** (1.1 eq.) were added into the solution of DMF (0.5 M) involving CuBr (0.2 eq.), PMDETA (0.2 eq.), NaAsc (0.5 eq.). The mixture was stirred at room temperature. The solution was then cooled to room temperature, diluted with ethyl acetate, washed with brine (three times), dried over Na_2SO_4, filtered, and evaporated under vacuum. The residue was purified by column chromatography on silica gel to afford the thioalkyne building unit for next cycle.



2

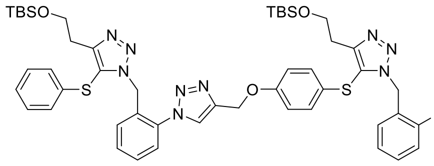
2 was prepared as yellow oil from **1** (4.4 mmol, 2.06 g, 1.0 eq.) and **T3** (4.8 mmol, 1.68 g, 1.1 eq.) in 90% yield (4.12 g).

Rf = 0.5 (PE/EA = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1 H), 7.39-7.33 (m, 4 H), 7.25 (d, *J* = 8.0 Hz, 1 H), 7.10 (m, 4 H), 7.02 (d, *J* = 8.0 Hz, 2 H), 6.76-6.73 (m, 2 H), 5.51 (s, 2 H), 5.25 (s, 2 H), 3.89 (t, *J* = 8.0 Hz, 2 H), 3.78 (t, *J* = 8.0 Hz, 2 H), 2.94 (t, *J* = 8.0 Hz, 2 H), 2.64 (t, *J* = 8.0 Hz, 2 H), 0.89 (s, 9 H), 0.81 (s, 9 H), 0.07 (s, 6 H), 0.04 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 150.5, 144.2, 135.1, 133.3, 130.5, 130.2, 129.6, 129.3, 129.1, 128.3, 126.9, 126.7, 125.5, 124.9, 124.5, 115.7, 62.0, 61.7, 47.3, 29.1, 25.8, 24.6, 18.2, 5.4.

HRMS *m/z* (ESI) calc. for $C_{42}H_{57}N_6O_3S_2Si_2$ $(M+H)^+$ 813.3467, found 813.3459.



3

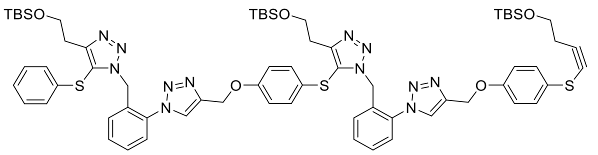
3 was prepared as yellow-brown oil from **2** (4.0 mmol, 3.26 g, 1.0 eq.) and **A3** (4.8 mmol, 0.85 g, 1.2 eq.) in 87% yield (3.43 g).

Rf = 0.4 (PE/EA = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1 H), 7.43-7.35 (m, 2 H), 7.30-7.26 (m, 2 H), 7.13 (t, J = 4.0 Hz, 4 H), 7.08 (d, J = 8.0 Hz, 1 H), 7.00-6.95 (m, 3 H), 6.85-6.78 (m, 5 H), 5.53 (d, J = 12.0 Hz, 4 H), 5.20 (s, 2 H), 3.97 (t, J = 8.0 Hz, 2 H), 3.92 (t, J = 8.0 Hz, 2 H), 3.03 (t, J = 8.0 Hz, 2 H), 2.97 (t, J = 8.0 Hz, 2 H), 0.87 (s, 9 H), 0.83 (s, 9 H), 0.02 (s, 6 H), 0.01 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 150.5, 149.8, 143.9, 137.3, 135.1, 133.3, 130.6, 130.3, 129.7, 129.3, 129.2, 129.1, 127.0, 126.8, 126.2, 126.0, 125.5, 124.9, 124.9, 124.8, 124.6, 118.0, 115.6, 62.1, 61.9, 47.3, 47.1, 29.2, 25.8, 18.3, 5.4.

HRMS *m/z* (ESI) calc. for $C_{49}H_{63}N_{12}O_3S_2Si_2$ $(M+H)^+$ 987.4121, found 987.4124.



4

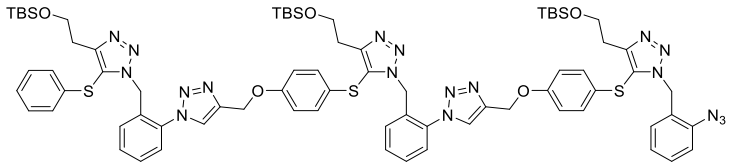
4 was prepared as light brown oil from **3** (3.1 mmol, 3.06 g, 1.0 eq.) and **T3** (3.4 mmol, 1.18 g, 1.1 eq.) in 90% yield (3.72 g).

Rf = 0.2 (PE/EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1 H), 7.80 (s, 1 H), 7.41-7.24 (m, 8 H), 7.11-7.08 (m, 4 H), 7.02-6.96 (m, 3 H), 6.90 (d, J = 8.0 Hz, 2 H), 6.81-6.76 (m, 4 H), 5.53 (d, J = 8.0 Hz, 4 H), 5.28 (s, 2 H), 5.15 (s, 2 H), 3.95-3.87 (m, 4 H), 3.77 (t, J = 8.0 Hz, 2 H), 3.00-2.92 (m, 4 H), 2.62 (t, J = 8.0 Hz, 2 H), 0.89 (s, 9 H), 0.83 (d, J = 4.0 Hz, 18 H), 0.07 (s, 6 H), 0.01 (d , J = 16.0 Hz, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 157.2, 150.5, 149.7, 144.2, 143.8, 135.1, 135.0, 133.3, 130.7, 130.6, 130.3, 130.2, 129.7, 129.4, 129.3, 129.2, 129.1, 128.3, 127.0, 126.8, 126.6, 125.5, 125.0, 124.7, 124.6, 124.3, 115.8, 62.0, 61.9, 61.7, 47.3, 29.1, 25.8, 24.6, 18.3, 18.3, 5.4, 5.3.

HRMS *m/z* (ESI) calc. for $C_{68}H_{89}N_{12}O_5S_3Si_3$ $(M+H)^+$ 1333.5543, found 1333.5546.



5

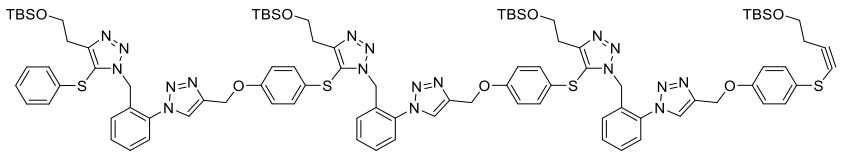
5 was prepared as white solid from **4** (2.6 mmol, 3.47 g, 1.0 eq.) and **A3** (3.2 mmol, 0.55 g, 1.2 eq.) in 87% yield (3.41 g).

Rf = 0.1 (DCM/MeOH = 100:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1 H), 7.83 (s, 1 H), 7.41-7.26 (m, 7 H), 7.12-7.04 (m, 5 H), 6.98-6.92 (m, 6 H), 6.84-6.80 (m, 7 H), 5.52 (t, *J* = 12.0 Hz, 6 H), 5.22 (d, *J* = 16.0 Hz, 4 H), 3.95-3.89 (m, 6 H), 3.01-2.94 (m, 6 H), 0.85-0.82 (m, 27 H), 0.03-0.00 (m, 18 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 157.6, 150.4, 149.7, 149.6, 143.9, 143.7, 137.2, 135.1, 135.0, 133.3, 130.6, 130.5, 130.2, 129.7, 129.3, 129.2, 129.0, 127.0, 126.8, 126.6, 126.2, 126.0, 125.5, 124.9, 124.8, 124.6, 124.2, 117.9, 115.8, 115.6, 62.1, 62.0, 61.9, 47.3, 47.3, 47.0, 29.1, 29.1, 25.8, 18.2, 5.5, 5.4.

HRMS *m/z* (ESI) calcd. for $C_{75}H_{95}N_{18}O_5S_3Si_3$ $(M+H)^+$ 1507.6197, found 1507.6188.



6

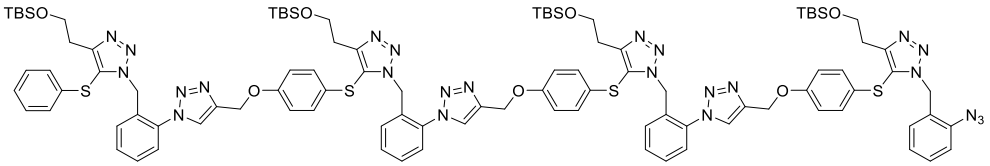
6 was prepared as white solid from **5** (2.2 mmol, 3.31 g, 1.0 eq.) and **T3** (2.42 mmol, 0.84 g, 1.1 eq.) in 86% yield (3.51 g).

Rf = 0.2 (DCM/MeOH = 80:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.92 (d, *J* = 8.0 Hz, 2 H), 7.83 (s, 1 H), 7.40-7.26 (m, 11 H), 7.24-7.09 (m, 4 H), 7.03-6.88 (m, 8 H), 6.83-6.77 (m, 6 H), 5.55 (t, *J* = 4.0 Hz, 6 H), 5.28 (s, 2 H), 5.20 (d, *J* = 12.0 Hz, 4 H), 3.96-3.89 (m, 6 H), 3.78 (t, *J* = 8.0 Hz, 2 H), 3.01-2.93 (m, 6 H), 2.62 (t, *J* = 8.0 Hz, 2 H), 0.90 (s, 9 H), 0.84 (d, *J* = 8.0 Hz, 27 H), 0.08 (s, 6 H), 0.00 (d, *J* = 16.0 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 157.1, 150.4, 149.6, 144.1, 143.7, 143.7, 135.1, 134.9, 133.2, 130.6, 130.6, 130.4, 130.2, 129.6, 129.3, 129.2, 129.0, 128.2, 127.0, 126.8, 126.5, 125.5, 124.9, 124.6, 124.6, 124.5, 124.2, 115.8, 115.7, 62.0, 61.9, 61.6, 47.3, 47.3, 29.1, 25.8, 24.6, 18.2, 5.5, 5.4.

HRMS *m/z* (ESI) calcd. for $C_{94}H_{120}N_{18}NaO_7S_4Si_4$ $(M+Na)^+$ 1875.7444, found 1875.7716.



7

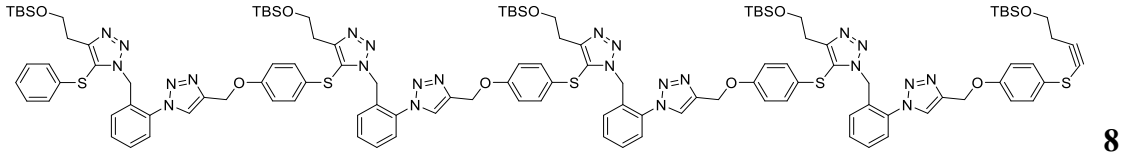
7 was prepared as white solid from **6** (1.8 mmol, 3.33 g, 1.0 eq.) and **A3** (2.2 mmol, 0.38 g, 1.2 eq.) in 96% yield (3.43 g).

Rf = 0.3 (DCM/MeOH = 70:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 4.0 Hz, 2 H), 7.82 (s, 1 H), 7.41-7.23 (m, 10 H), 7.11-7.08 (m, 4 H), 7.04 (d, *J* = 8.0 Hz, 1 H), 6.97-6.90 (m, 9 H), 6.83-6.76 (m, 9 H), 5.53-5.50 (m, 8 H), 5.20-5.16 (m, 6 H), 3.96-3.87 (m, 8 H), 3.01-2.92 (m, 8 H), 0.83-0.80 (m, 36 H), 0.05-0.01 (m, 24 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 157.6, 150.4, 149.7, 143.7, 135.0, 133.3, 129.3, 129.1, 127.0, 126.8, 126.6, 126.3, 125.6, 125.0, 124.9, 124.7, 124.3, 118.0, 115.8, 115.6, 62.1, 62.0, 61.9, 47.4, 47.1, 29.1, 25.9, 18.3, 5.4.

HRMS *m/z* (ESI) calcd. for $C_{101}H_{127}N_{24}O_7S_4Si_4$ $(M+H)^+$ 2027.8274, found 2027.8277.



8

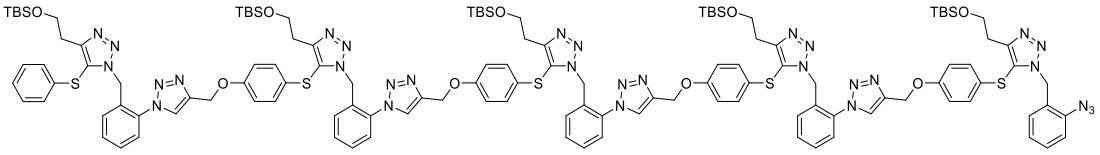
8 was prepared as white solid from **7** (1.6 mmol, 3.23 g, 1.0 eq.) and **T3** (1.76 mmol, 0.61 g, 1.1 eq.) in 88% yield (3.34 g).

Rf = 0.5 (DCM/MeOH = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.90 (m, 3 H), 7.81 (s, 1 H), 7.35-7.26 (m, 13 H), 7.21 (d, *J* = 8.0 Hz, 1 H) 7.08-7.06 (m, 4 H), 7.00 (d, *J* = 8.0 Hz, 2 H), 6.93-6.89 (m, 9 H), 6.85-6.75 (m, 8 H), 5.52-5.49 (m, 8 H), 5.25 (s, 2 H), 5.17 (d, *J* = 12 Hz, 6 H), 3.93-3.86 (m, 8 H), 3.75 (t, *J* = 8.0 Hz, 2 H), 2.98-2.90 (m, 8 H), 2.59 (t, *J* = 8.0 Hz, 2 H), 0.87 (s, 9 H), 0.87-0.79 (m, 36 H), 0.79 (s, 6 H), 0.07-0.01 (m, 24 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 157.1, 150.4, 149.6, 144.1, 143.7, 135.0, 134.9, 133.2, 130.6, 130.6, 130.4, 130.2, 129.6, 129.4, 129.2, 129.1, 129.0, 128.2, 127.0, 126.8, 126.6, 125.5, 124.9, 124.7, 124.5, 124.1, 115.8, 115.7, 61.9, 61.8, 61.6, 47.3, 47.2, 29.0, 25.8, 25.8, 24.5, 18.2, 5.4.

HRMS *m/z* (ESI) calcd. for $C_{120}H_{153}N_{24}O_9S_5Si_5$ $(M+H)^+$ 2373.9697, found 2373.9707.



9

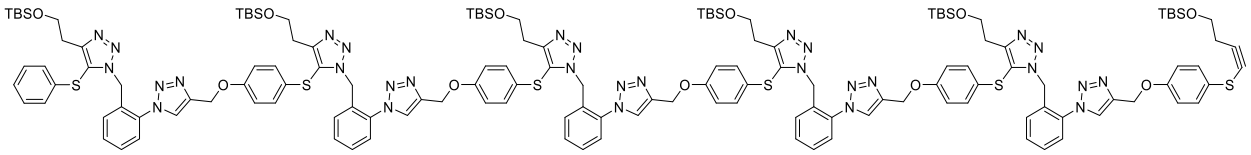
9 was prepared as white solid from **8** (1.4 mmol, 3.31 g, 1.0 eq.) and **A3** (1.68 mmol, 0.30 g, 1.2 eq.) in 90% yield (3.42 g).

Rf = 0.5 (DCM/MeOH = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 4.0 Hz, 3 H), 7.81 (s, 1 H), 7.40-7.23 (m, 13 H), 7.10-7.07 (m, 4 H), 7.03 (d, *J* = 8.0 Hz, 1 H), 6.96-6.89 (m, 12 H), 6.82-6.76 (m, 11 H), 5.52-5.46 (m, 10 H), 5.19-5.15 (m, 8 H), 3.95-3.86 (m, 10 H), 3.01-2.91 (m, 10 H), 0.83-0.80 (m, 45 H), 0.06-0.02 (m, 30 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 149.6, 143.7, 135.0, 130.7, 130.2, 129.7, 129.4, 129.3, 129.1, 127.0, 126.8, 126.6, 126.0, 125.5, 124.7, 124.2, 117.9, 115.8, 115.6, 62.1, 62.0, 61.9, 47.4, 47.1, 29.6, 29.1, 25.9, 25.8, 18.2, 5.4.

HRMS *m/z* (ESI) calcd. for $C_{127}H_{159}N_{30}O_9S_5Si_5$ $(M+H)^+$ 2548.0351, found 2548.0357.



10

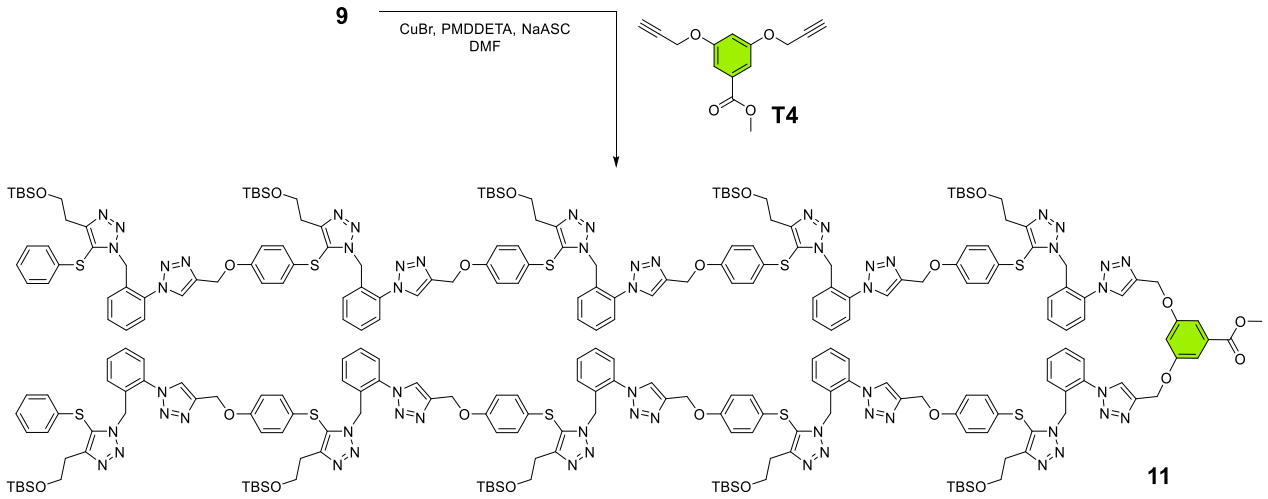
10 was prepared as white solid from **9** (1.1 mmol, 2.80 g, 1.0 eq.) and **T3** (1.4 mmol, 0.49 g, 1.1 eq.) in 93% yield (2.89 g).

Rf = 0.4 (DCM/MeOH = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.92 (m, 4 H), 7.90 (s, 1 H), 7.8-7.25 (m, 18 H), 7.10-7.09 (m, 4 H), 7.01 (s, 1 H), 6.99 (s, 1 H), 6.93-6.86 (m, 12 H), 6.82-6.76 (m, 10 H), 5.52-5.49 (m, 10 H), 5.26 (s, 2 H), 5.18-5.15 (m, 8 H), 3.93-3.86 (m, 10 H), 3.76 (t, *J* = 8.0 Hz, 2 H), 2.99-2.93 (m, 10 H), 2.60 (t, *J* = 8.0 Hz, 2 H), 0.88 (s, 9 H), 0.82-0.07 (d, *J* = 8.0 Hz, 45 H), 0.06 (s, 6 H), 0.04 (d, *J* = 12.0 Hz, 30 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 149.6, 143.7, 143.7, 135.0, 130.7, 130.6, 130.2, 129.4, 129.3, 129.2, 129.1, 128.3, 127.0, 126.8, 126.6, 125.5, 124.7, 124.2, 115.8, 62.0, 61.9, 47.4, 29.1, 25.9, 25.8, 18.2, 5.4.

HRMS *m/z* (ESI) calcd. for $C_{146}H_{184}N_{30}NaO_{11}S_6Si_6$ $(M+Na)^+$ 2916.1593, found 2916.5479.



Scheme S7. Synthesis of **11**.

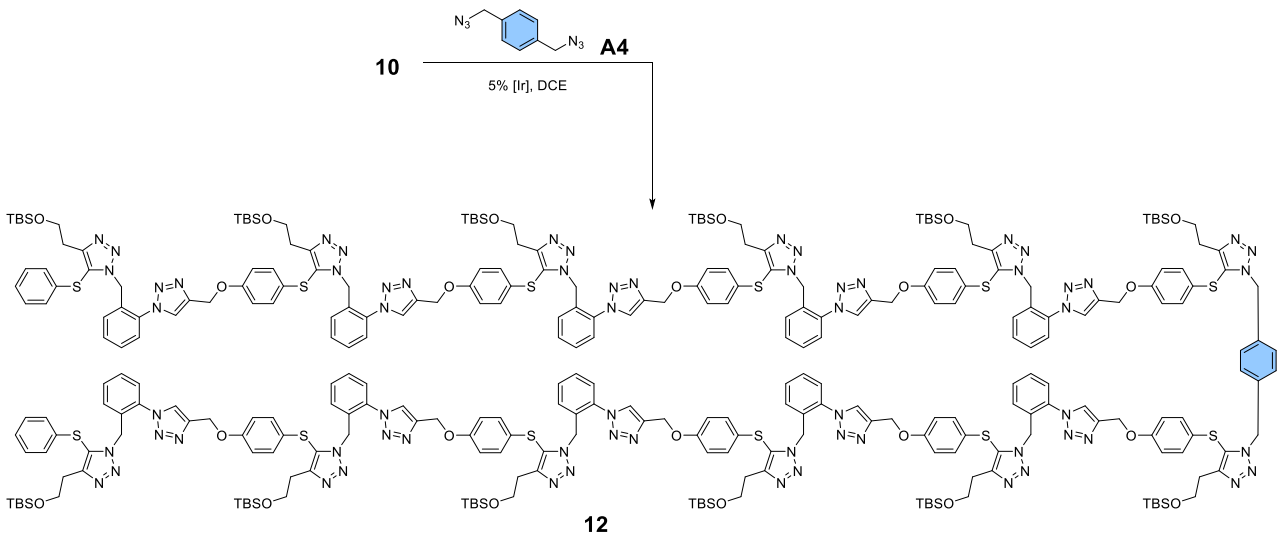
Synthesis of 11: T4 (0.02 mmol, 4.8 mg, 1.0 eq.) and **9** (0.048 mmol, 122.4 mg, 2.2 eq.) were added into the solution of DMF (0.5 M) involving CuBr (0.4 eq.), PMDETA (0.4 eq.), NaAsc (1.0 eq.). The mixture was stirred for 25 min at room temperature. The solution was then cooled to room temperature, diluted with ethyl acetate, washed with brine (three times), dried over Na_2SO_4, filtered, and evaporated under vacuum. The residue was purified by column chromatography on silica gel to get **11** as white solid in 81% yield (86.5 mg).

Rf = 0.2 (DCM/MeOH = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.83 (d, 10 H), 7.39-7.23 (m, 35 H), 7.11-7.07 (m, 8 H), 6.91-6.89 (m, 22 H), 6.82-6.76 (m, 20 H), 5.53 (d, *J* = 12.0 Hz, 20 H), 5.31-5.16 (m, 20 H), 3.92 (s, 20 H), 3.87 (s, 3 H), 2.97 (s, 20 H), 0.82-0.80 (m, 90 H), 0.05-0.02 (m, 60 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 135.1, 135.1, 133.3, 130.8, 130.6, 130.3, 129.3, 129.1, 127.1, 126.8, 125.6, 124.1, 115.8, 61.9, 47.5, 29.1, 25.9, 18.3, 5.4.

FTMS *m/z* (ESI) calcd. for $C_{268}H_{328}N_{60}O_{22}S_{10}Si_{10}$ (M) 5338.13, found 1336.60 $(M+4H)^{4+}$, 1782.18 $(M+3H)^{3+}$.



Scheme S8. Synthesis of **12**.

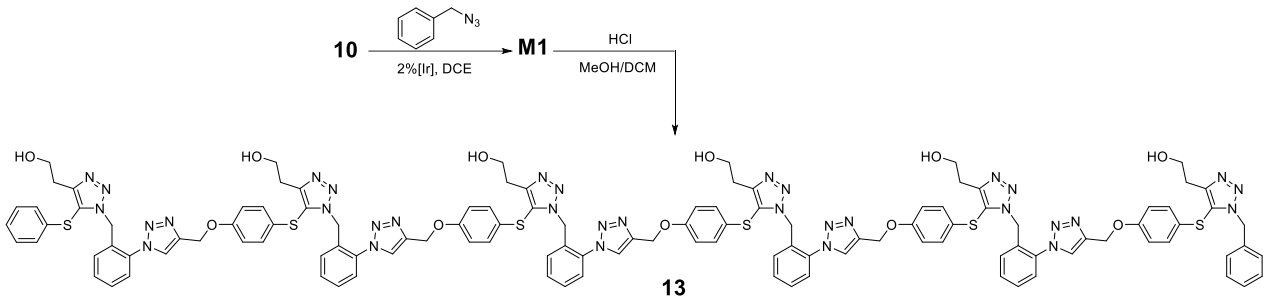
Synthesis of 12: In a glove box, to an oven-dried vial was added **A4** (0.02 mmol, 3.7 mg, 1.0 eq.), **10** (0.048 mmol, 139.1 mg, 2.2 eq.), $[Ir(COD)Cl]_2$ (4 mol %) and DCE (0.1 M). The vial was capped and removed from the glove box. The reaction mixture was stirred at room temperature for 2 h until the reaction completed (confirmed by TLC), and then concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to give the desired product **12** as white solid in 70% yield (83.0 mg).

Rf = 0.3 (DCM/MeOH = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 2 H), 7.94 (s, 6 H), 7.81 (s, 2 H), 7.38-7.35 (m, 10 H), 7.33-7.30 (m, 17 H), 7.28-7.23 (m, 3 H), 7.10-7.07 (m, 8 H), 7.01 (s, 4 H), 6.93-6.76 (m, 52 H), 5.53 (d, *J* = 12.0 Hz, 20 H), 5.43 (s, 4 H), 5.22-5.15 (m, 20 H), 3.90-3.86 (m, 24 H), 2.99-2.91 (m, 24 H), 0.82-0.80 (m, 108 H), 0.06-0.02 (m, 72 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 157.7, 153.2, 152.8, 151.9, 150.4, 149.8, 149.6, 143.7, 143.7, 135.1, 135.0, 133.3, 130.7, 130.6, 130.2, 130.1, 129.4, 129.3, 129.1, 128.0, 127.0, 126.7, 125.5, 124.9, 124.8, 124.7, 124.2, 115.8, 62.0, 61.9, 47.4, 47.3, 29.1, 25.9, 18.3, 5.4.

FTMS *m/z* calcd. for $C_{300}H_{376}N_{66}O_{22}S_{12}Si_{12}$ (M) 5974.42, found 998.68 $(M+6H)^{6+}$, 1994.50 $(M+3H)^{3+}$.



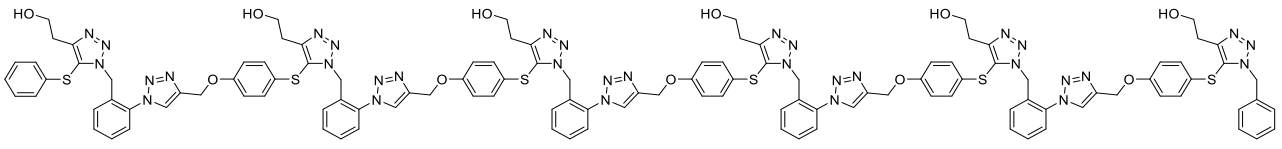
Scheme S9. Synthesis of **13**.

Synthesis of M1: In a glove box, to an oven-dried vial was added **10** (0.6 mmol, 1.73 g, 1.0 eq.), BnN_3 (0.72 mmol, 0.09 g, 1.2 eq.), $[Ir(COD)Cl]_2$ (2 mol %) and DCE (0.1 M). The vial was capped and removed from the glove box. The reaction mixture was stirred at room temperature for 3 h until the reaction completed (confirmed by TLC), and then concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to give the desired product **M1** as white solid in 95% yield (1.58 g).

Rf = 0.4 (DCM/MeOH = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.0 Hz, 4 H), 7.81 (s, 1 H), 7.40-7.27 (m, 14 H), 7.25-7.19 (m, 4 H), 7.15-7.13 (m, 2 H), 7.10-7.07 (m, 4 H), 6.93-6.89 (m, 14 H), 6.84-6.76 (m, 12 H), 5.52-5.47 (m, 12 H), 5.20-5.15 (m, 10 H), 3.93-3.86 (m, 12 H), 2.98-2.91 (m, 12 H), 0.82-0.80 (m, 54 H), 0.03 (d, J = 12.0 Hz, 36 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 157.6, 150.4, 149.6, 143.9, 143.7, 143.7, 135.0, 130.7, 130.6, 130.0, 129.4, 129.1, 128.6, 128.0, 127.8, 127.0, 126.8, 126.6, 125.5, 124.8, 124.7, 124.2, 115.8, 62.0, 61.9, 47.4, 47.3, 29.1, 25.8, 18.2, 5.4.



13

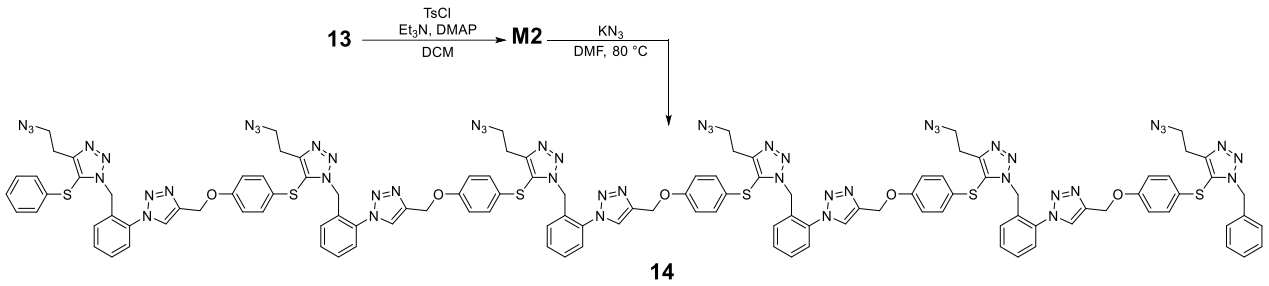
Synthesis of 13: the **M1** was dissolved in MeOH/DCM (2:1, v/v), added the HCl (12 M, 2.0 eq.) at 0 ºC stirred 10 min. After the reaction completed, then concentrated under reduced pressure, diluted with DCM, washed with $NaHCO_3$ aqueous solution, dried over Na_2SO_4, filtered, and evaporated under vacuum. The residue was purified by column chromatography on silica gel to get **13** as white solid in 94% yield (1.17 g).

Rf = 0.5 (DCM/MeOH = 10:1).

^{1}H NMR (400 MHz, DMSO) δ 8.64 (s, 4 H), 8.54 (s, 1 H), 7.50-7.39 (m, 15 H), 7.26-7.24 (m, 3 H), 7.24-7.15 (m, 3 H), 7.11-7.08 (m, 5 H), 7.0-6.93 (m, 22 H), 6.88 (d, *J* = 8.0 Hz, 2 H), 5.56-5.53 (m, 12 H), 5.22-5.16 (m, 10 H), 4.75-4.70 (m, 6 H), 3.65-3.59 (m, 12 H), 2.82-2.74 (m, 12 H).

^{13}C NMR (100 MHz, DMSO) δ 157.7, 149.7, 149.1, 149.0, 142.9, 142.8, 135.4, 134.9, 134.8, 132.9, 130.9, 130.7, 130.2, 130.1, 129.4, 129.3, 129.2, 129.0, 128.5, 127.8, 127.5, 127.1, 126.9, 126.3, 126.1, 126.0, 125.6, 124.3, 123.8, 123.3, 115.9, 61.1, 59.9, 59.8, 51.3, 47.2, 28.9.

ESI-MS *m/z* calcd. for $C_{117}H_{107}N_{33}O_{11}S_6$ (M) 2341.7152, found 2342.1785 $(M+H)^+$, 2365.1450 $(M+Na)^+$.



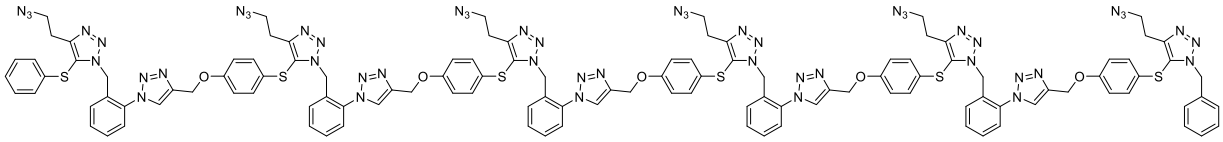
Scheme S10. Synthesis of **14**.

Synthesis of M2: TsCl (9.0 eq.), Et_3N (12.0 eq.), and DMAP (0.12 eq.) were added in the solution of DCM and **13** (0.4 mmol, 0.94g, 1.0 eq.), stirred about 3 h, the reaction was completed, then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to get **M2** as white solid in 89% yield.

Rf = 0.5(DCM/MeOH = 50:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 4 H), 7.80 (s, 1 H), 7.67-7.65 (m, 12 H), 7.40-7.22 (m, 30 H), 7.15-7.04 (m, 6 H), 6.95-6.82 (m, 24 H), 6.76-6.74 (m, 2 H), 5.53-5.48 (m, 12 H), 5.20 (t, *J* = 12.0 Hz, 10 H), 4.31-4.24 (m, 12 H), 3.07-3.01 (m, 12 H), 2.40 (s, 18 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 147.8, 146.9, 144.8, 143.8, 135.0, 132.6, 131.3, 130.8, 130.3, 129.8, 129.5, 129.3, 128.7, 127.8, 125.6, 124.8, 123.2, 116.0, 52.3, 47.7, 47.7, 25.4, 21.6.



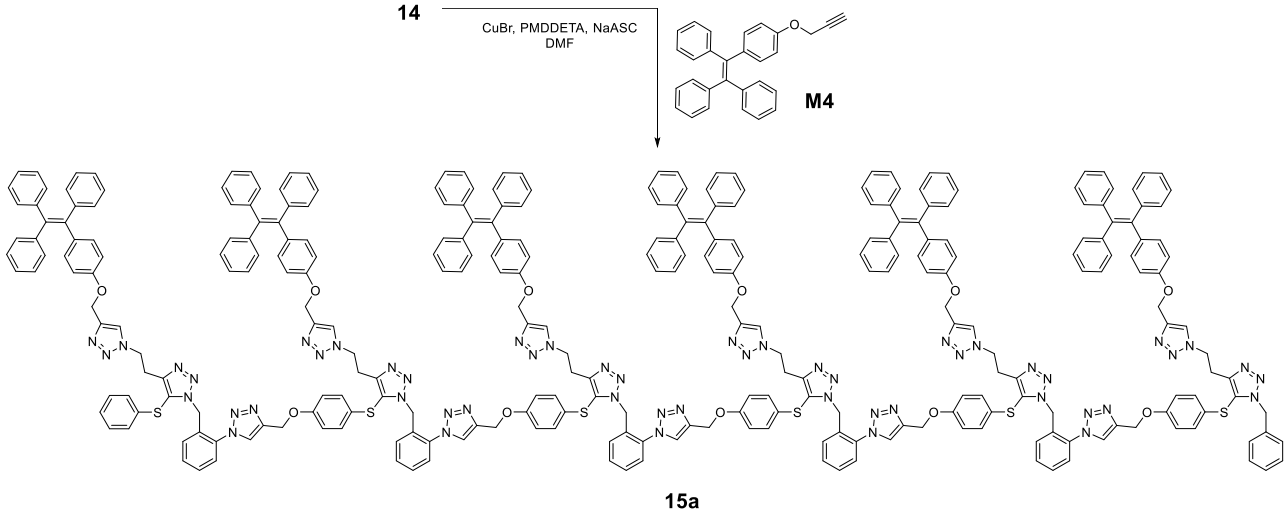
14

Synthesis of 14: Added potassium azide (9.0 eq.) to the solution of **M2** in DMF, heat 80 ºC, stirred 3 h before a saturated aqueous NaCl solution was added. The aqueous phase was separated and extracted with ethyl acetate (EA) for three times. The combined organic phase was washed with brine, dried over Na_2SO_4 and evaporated under vacuum to give the which was then purified by silica gel flash column chromatography to give pure product **14** as white solid in 80% yield (642.7 mg).

Rf = 0.5 (DCM/MeOH = 50:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 4 H), 7.79 (s, 1 H), 7.44-7.35 (m, 10 H), 7.31 (d, *J* = 4.0 Hz, 4 H) , 7.25-7.23 (m, 3 H), 7.19-7.13 (m, 6 H), 7.04 (d, *J* = 8.0 Hz, 4 H), 6.93-6.83 (m, 21 H), 6.79-6.77 (m, 2 H), 5.56 (s, 8 H), 5.53 (d, *J* = 4.0 Hz, 4 H), 5.20 (t, *J* = 8.0 Hz, 10 H), 3.60-3.54 (m, 12 H), 2.99-2.94 (m, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 148.5, 143.8, 135.1, 130.9, 130.4, 129.7, 129.5, 128.7, 128.3, 127.9, 127.1, 127.0, 125.7, 124.8, 124.7, 123.7, 116.0, 116.0, 61.9, 49.9, 47.7, 25.5.



Scheme S11. Synthesis of **15a**.

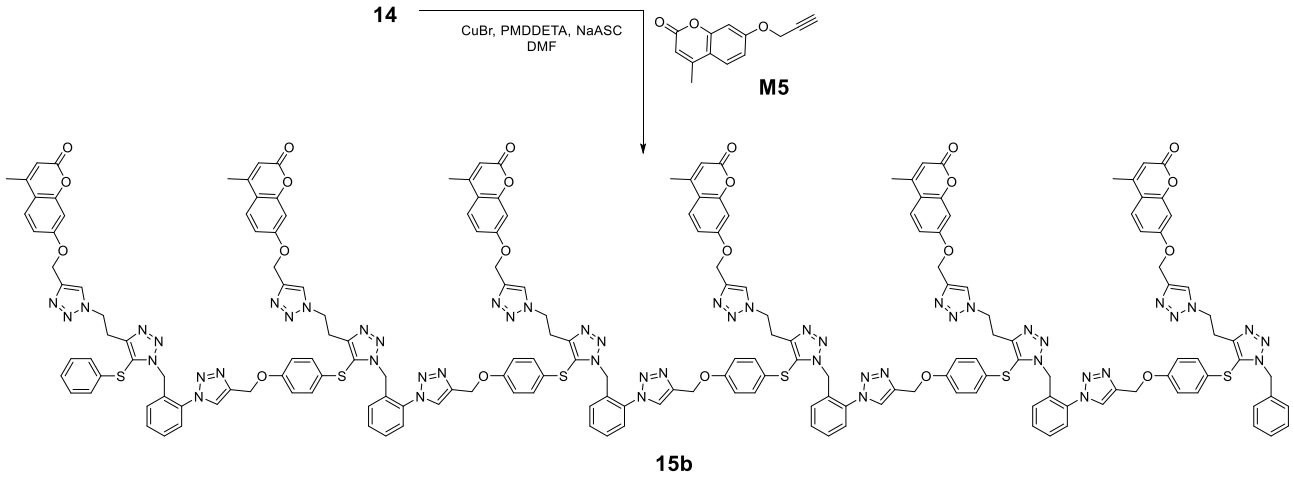
Synthesis of 15a: M4 (0.29 mmol, 111.2 mg, 7.2 eq.) and **14** (0.04 mmol, 100 mg, 1.0 eq.) were added into the solution of DMF (0.1 M) involving CuBr (1.2 eq.), PMDETA (1.2 eq.), NaAsc (6.0 eq.). The

reaction mixture was stirred for 25 min at room temperature. The solution was then cooled to room temperature, diluted with ethyl acetate, washed with brine (three times), dried over Na_2SO_4, filtered, and evaporated under vacuum. The residue was purified by column chromatography on silica gel to get **15a** as white solid in 51% yield (96.2 mg).

Rf = 0.4 (DCM/MeOH = 40:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 4 H), 7.77 (s, 1 H), 7.52-7.51 (m, 5 H), 7.46 (s, 1 H), 7.34-7.30 (m, 11 H), 7.21-7.16 (m, 16 H), 7.09-6.91 (m, 103 H), 6.81-6.75 (m, 20 H), 6.67-6.65 (m, 14 H), 5.52 (t, *J* = 8.0 Hz, 12 H), 5.16 (t, *J* = 12.0 Hz, 10 H), 5.00 (t, *J* = 4.0 Hz, 12 H), 4.73-4.68 (m, 12 H), 3.29-3.23 (m, 12 H).

FTMS *m/z* calcd. for $C_{291}H_{233}N_{51}O_{11}S_6$ (M) 4808.76, found 1604.97 $(M+3H)^{3+}$, 2407.45 $(M+2H)^{2+}$.



Scheme S12. Synthesis of **15b**.

Synthesis of 15b: M5 (0.29 mmol, 62.1 mg, 7.2 eq.) and **14** (0.04 mmol, 100 mg, 1.0 eq.) were added into the solution of DMF (0.1 M) involving CuBr (1.2 eq.), PMDETA (1.2 eq.), NaAsc (6.0 eq.). The reaction mixture was stirred at room temperature. The solution was then cooled to room temperature, diluted with ethyl acetate, washed with brine (three times), dried over Na_2SO_4, filtered, and evaporated under vacuum. The residue was purified by column chromatography on silica gel to get **15b** as white solid in 73% yield (105.7 mg).

Rf = 0.3 (DCM/MeOH = 40:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 4.0 Hz, 4 H), 7.82 (s, 1 H), 7.65 (t, *J* = 4.0 Hz, 5 H) 7.58 (s, 1 H), 7.48-7.45 (m, 6 H), 7.41-7.29 (m, 14 H), 7.24-7.10 (m, 3 H), 7.09-7.04 (m, 6 H), 6.93-6.71 (m, 37 H), 6.64-6.61 (m, 2 H), 6.11-6.08 (m, 6 H), 5.52-5.49 (m, 12 H), 5.20-5.13 (m, 22 H), 4.77-4.73

(m, 12 H), 3.32,-3.24 (m, 12 H), 2.37-2.35 (m, 18 H).

FTMS *m/z* calcd. for $C_{195}H_{161}N_{51}O_{23}S_6$ (M) 3776.13, found 1260.45 $(M+3H)^{3+}$, 1891.31 $(M+2H)^{2+}$.

V. SEC Traces

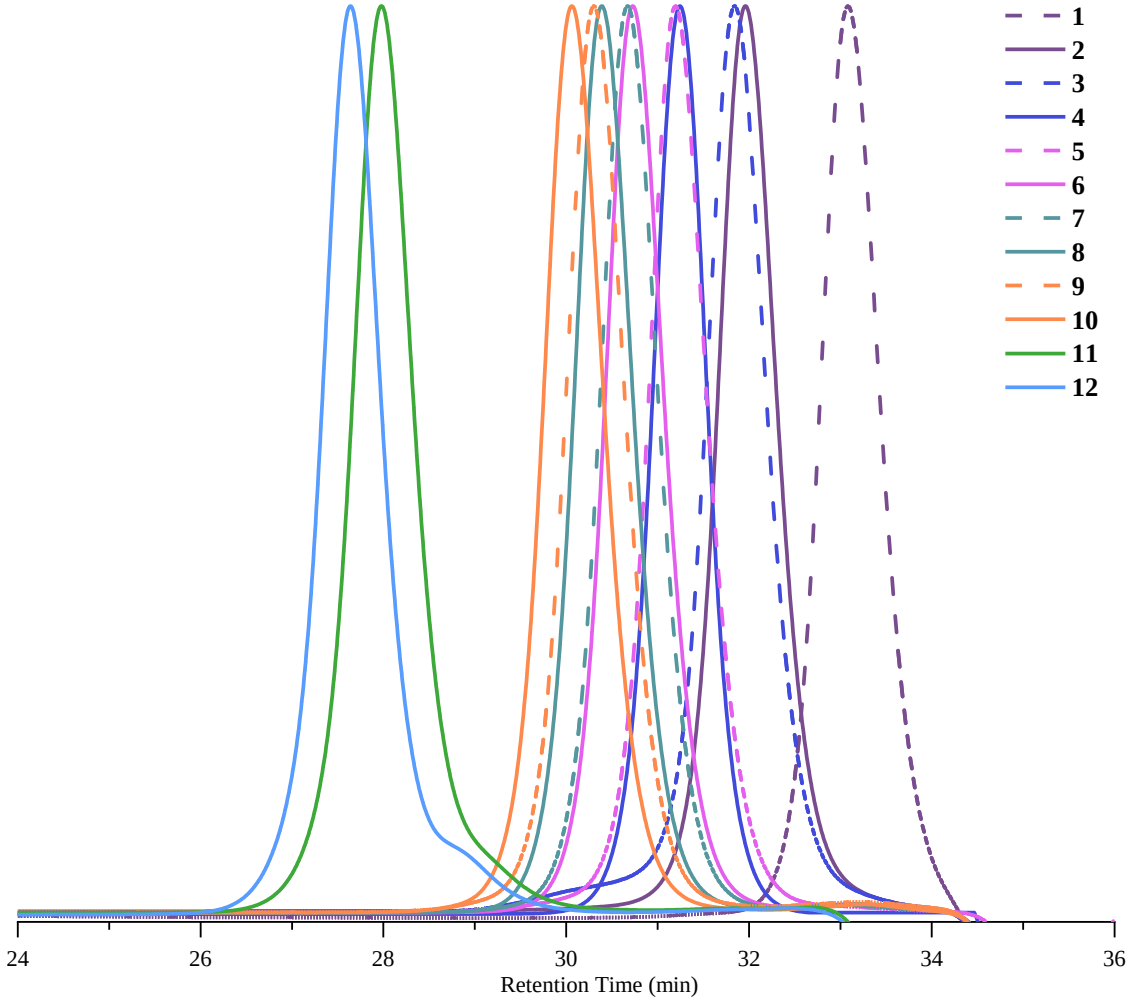


Figure S3. GPC traces of **1**~**12**.

VI. NMR Spectra

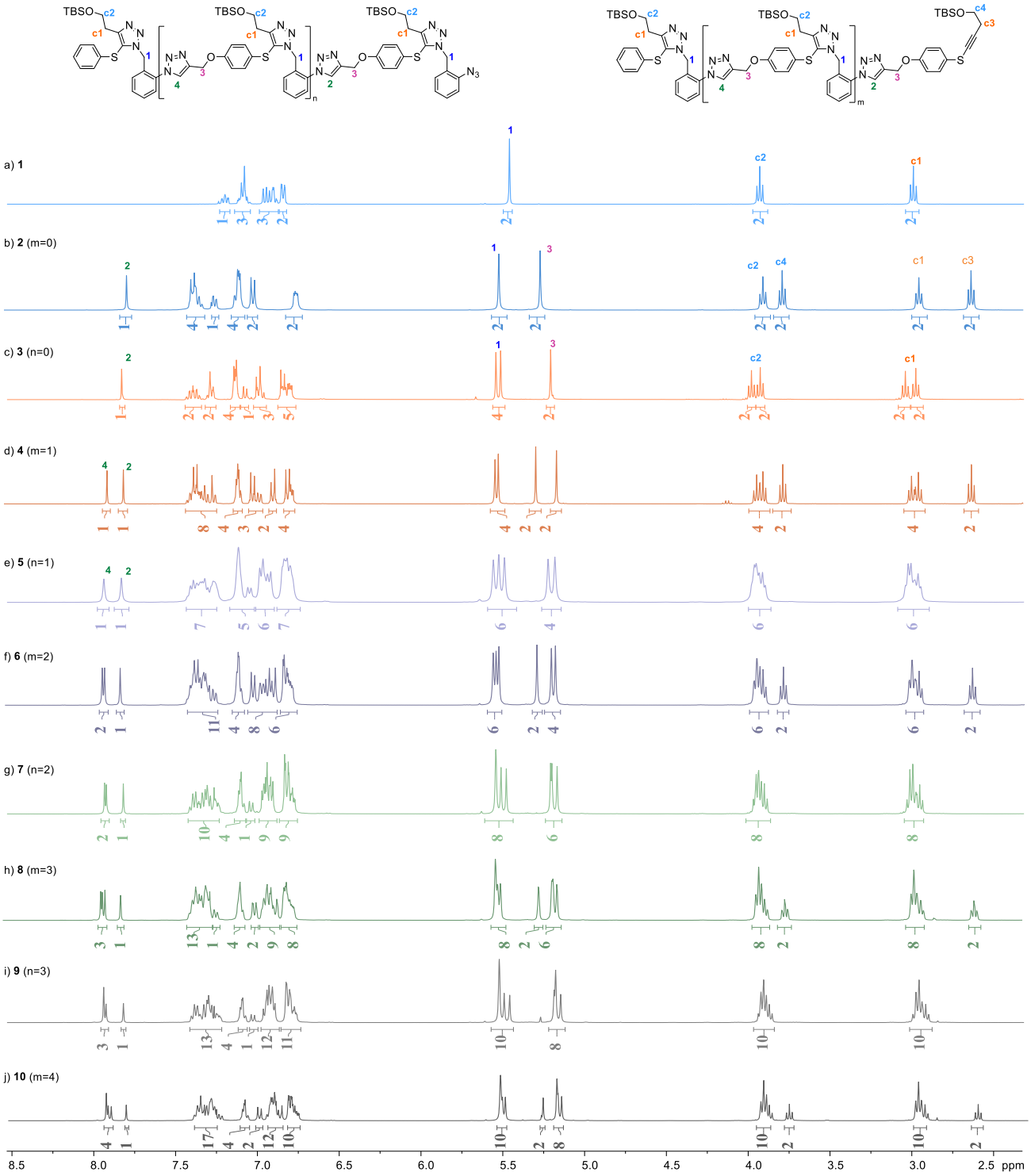


Figure S4. Comparison of ^{1}H NMR for **1-12**.

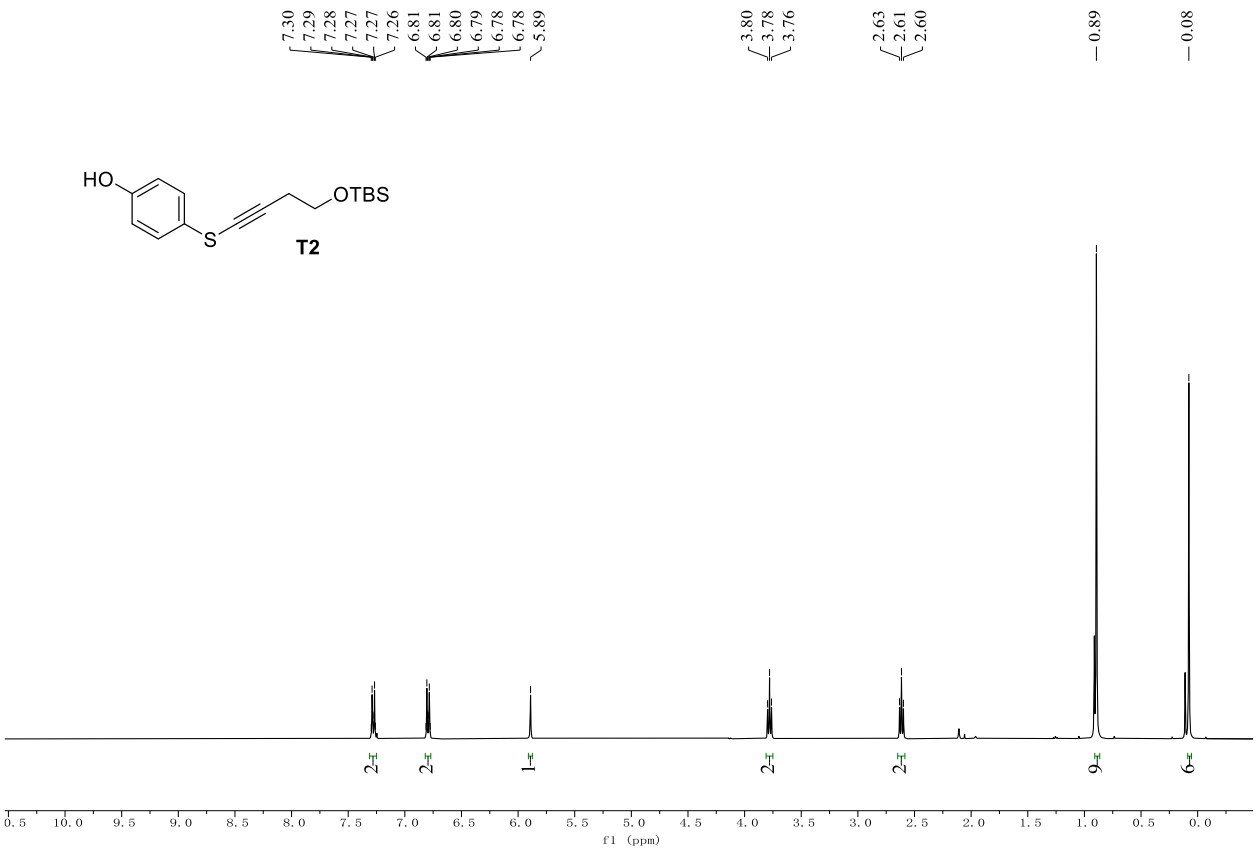


Figure S5. ^{1}H NMR spectra of **T2** ($CDCl_3$, 400 MHz).

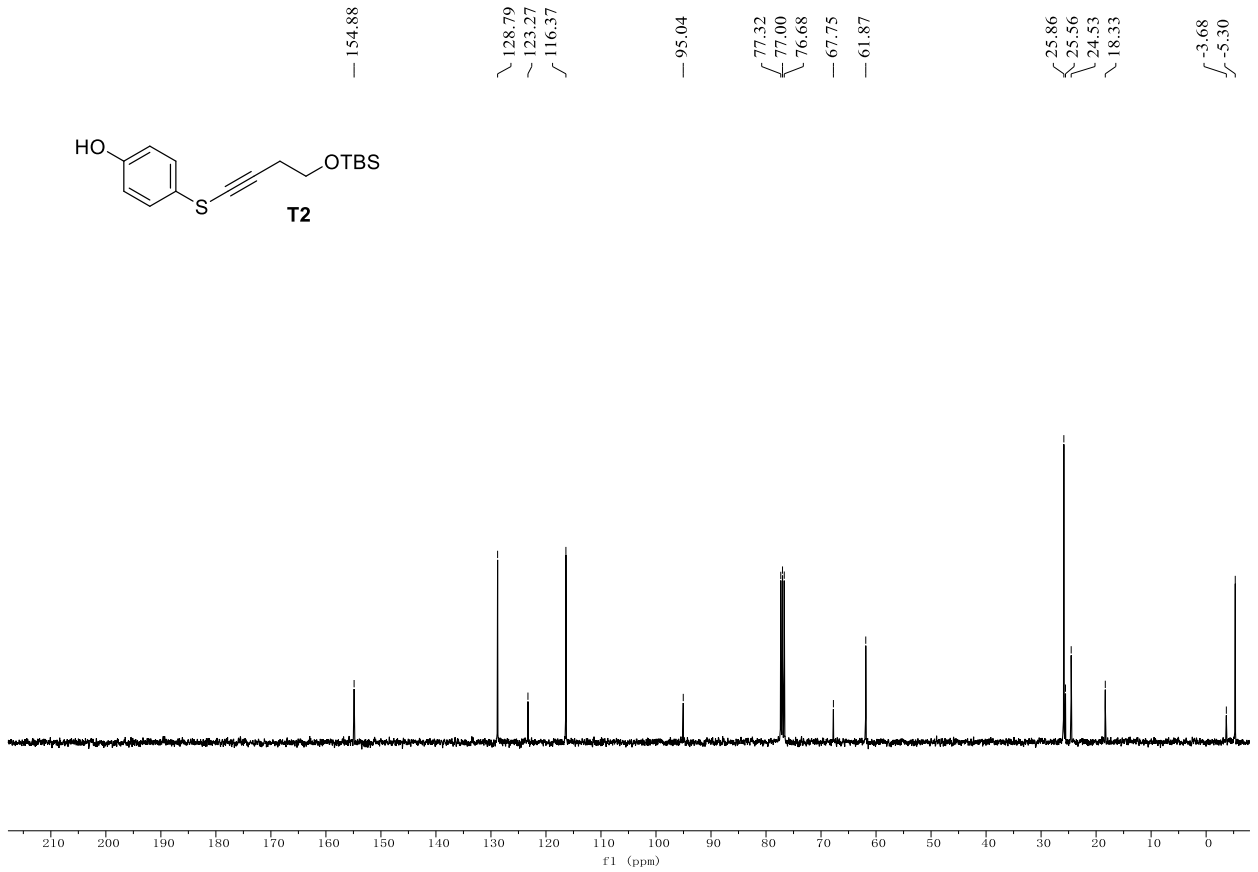


Figure S6. ^{13}C NMR spectra of **T2** ($CDCl_3$, 100 MHz).

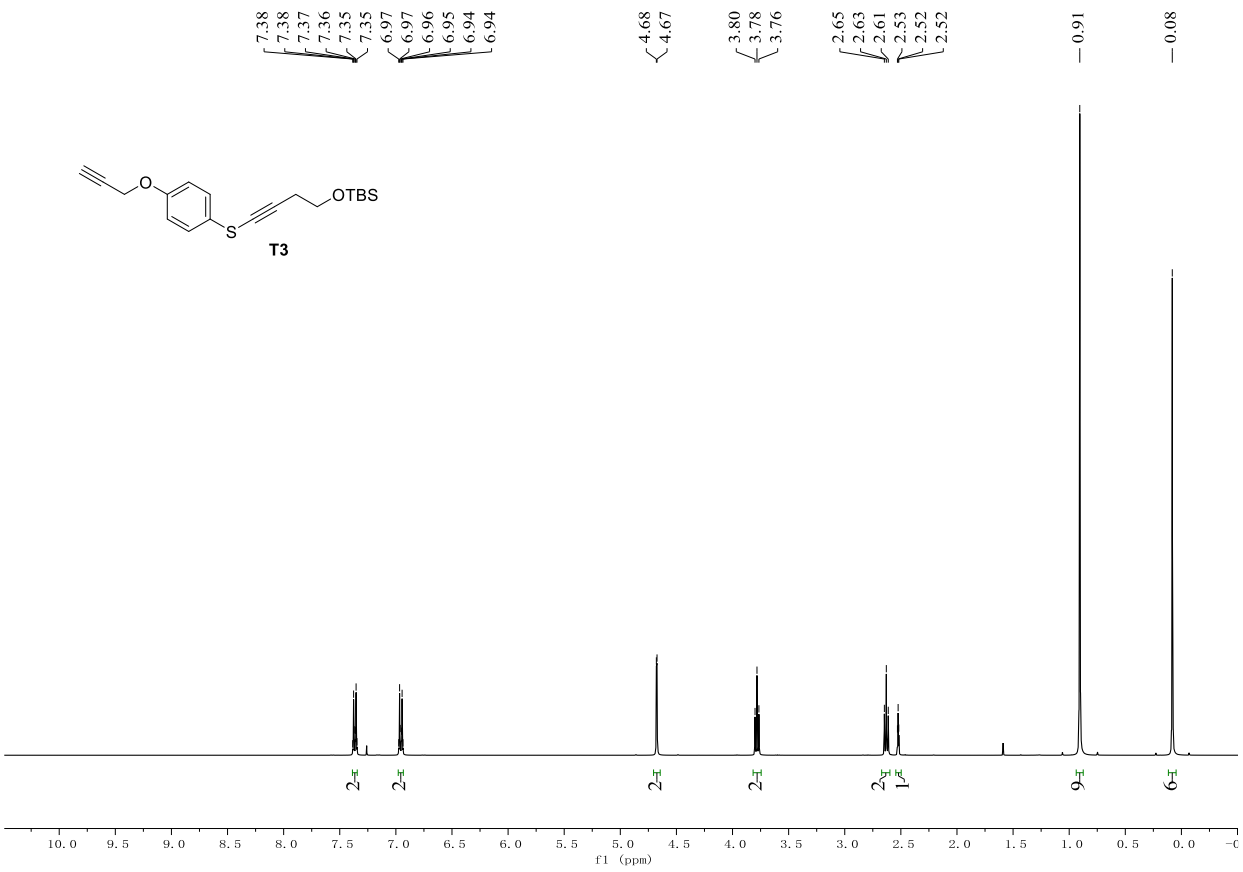


Figure S7. ^{1}H NMR spectra of **T3** ($CDCl_3$, 400 MHz).

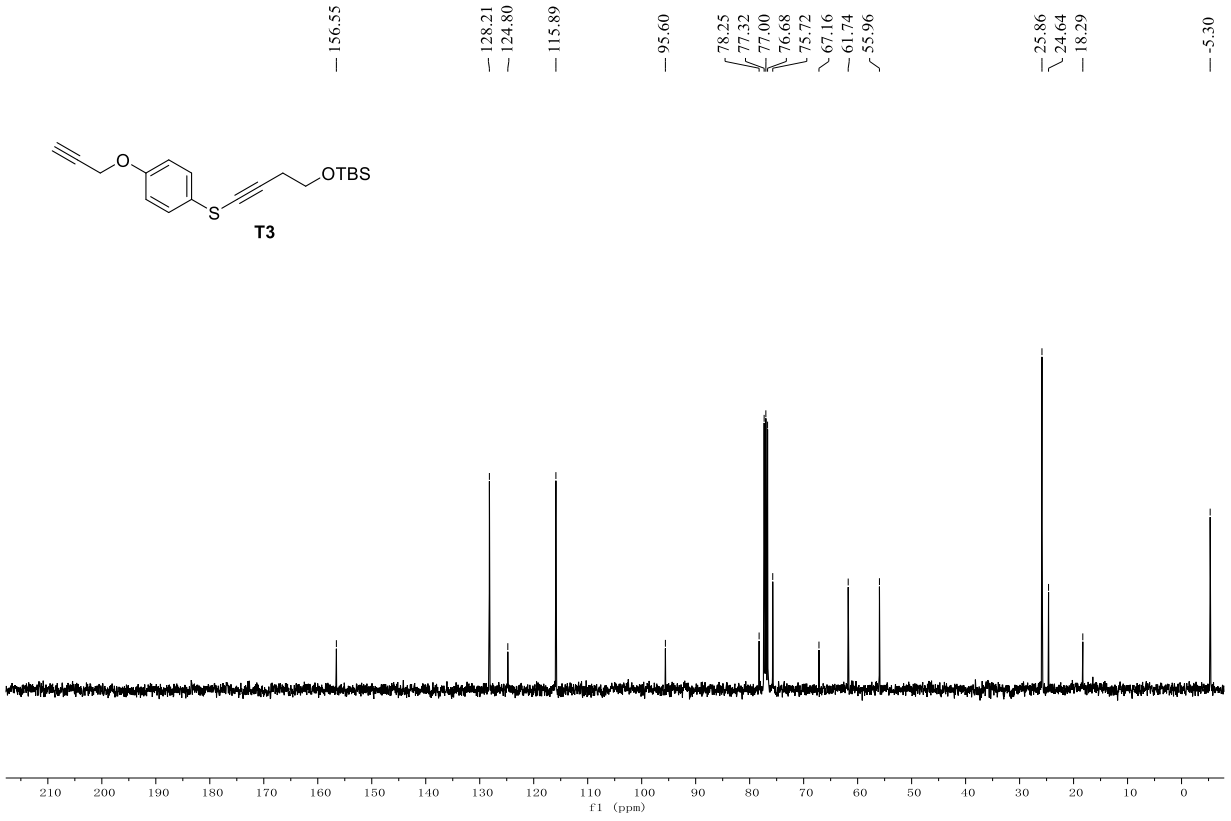


Figure S8. ^{13}C NMR spectra of **T3** ($CDCl_3$, 100 MHz).

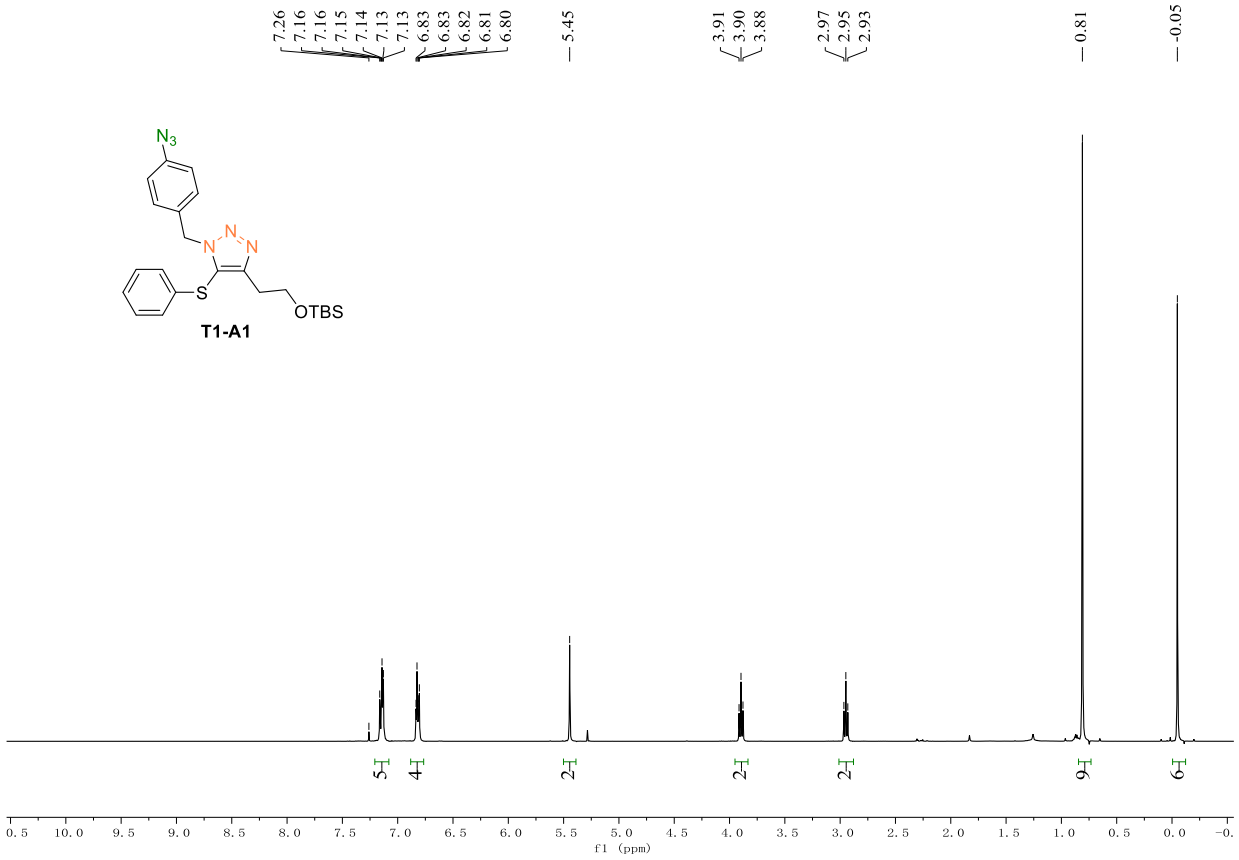


Figure S9. ^{1}H NMR spectra of **T1-A1** ($CDCl_3$, 400 MHz).

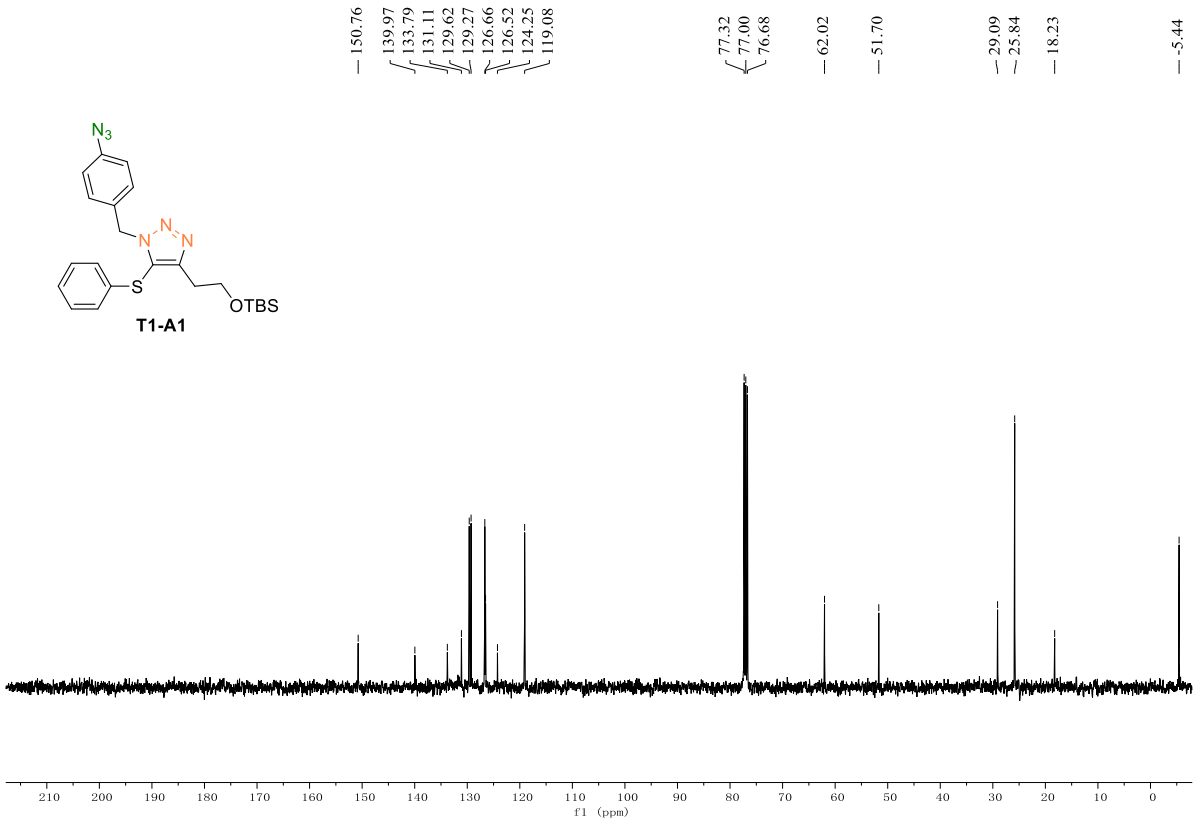


Figure S10. ^{13}C NMR spectra of **T1-A1** ($CDCl_3$, 100 MHz).

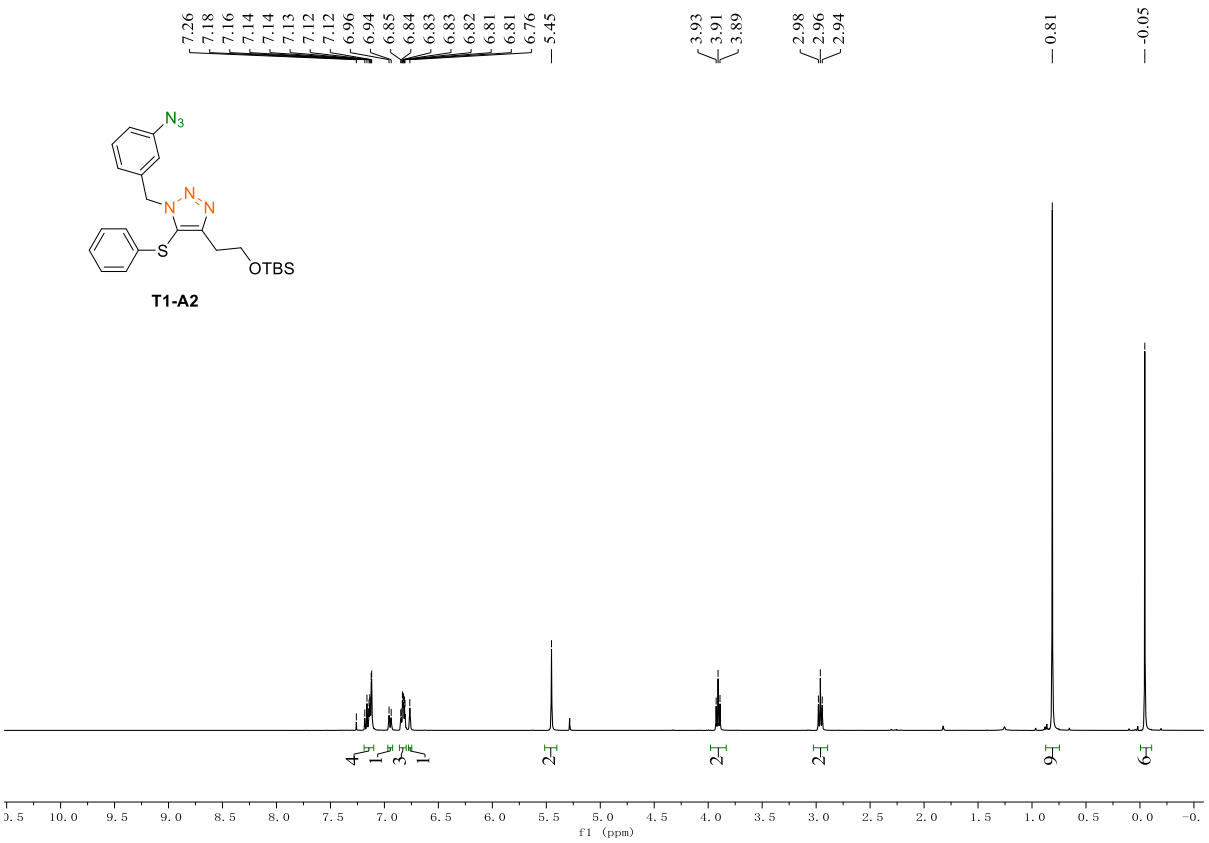


Figure S11. ^{1}H NMR spectra of **T1-A2** ($CDCl_3$, 400 MHz).

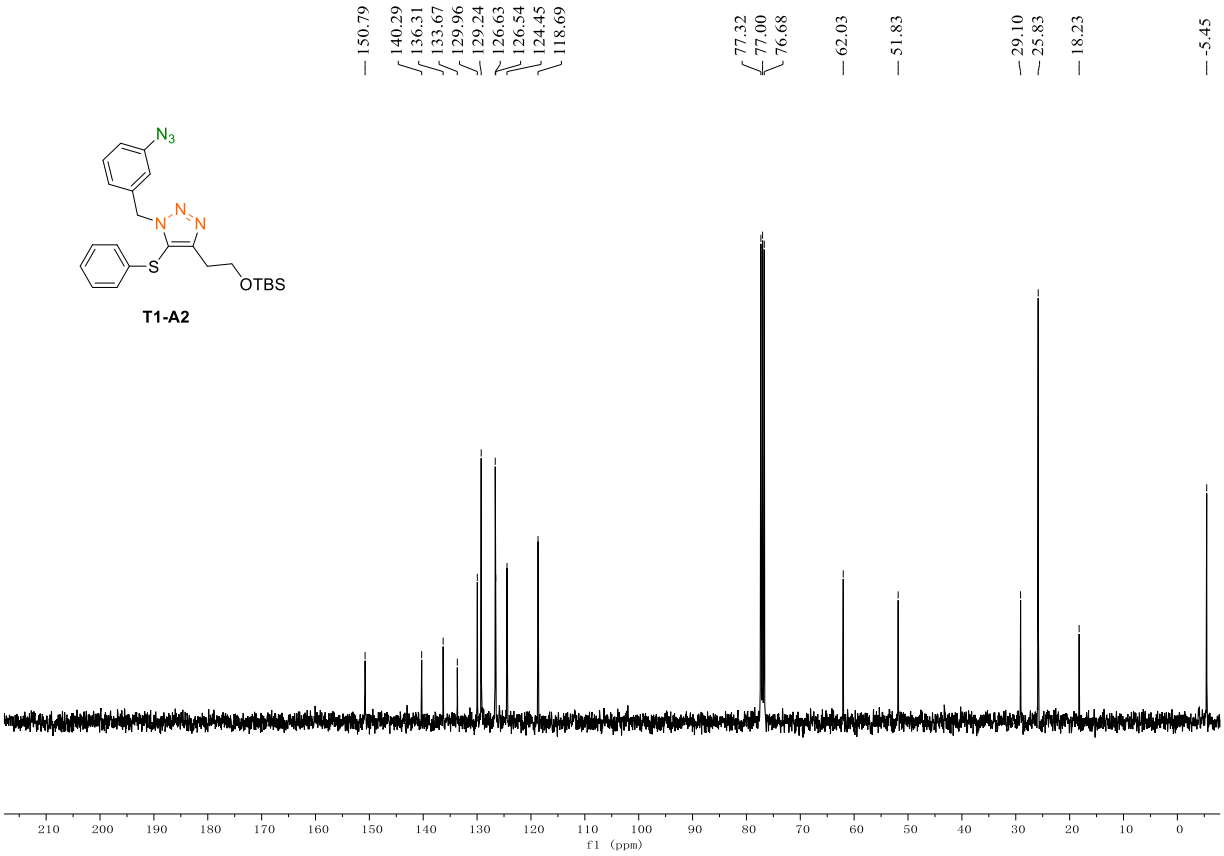


Figure S12. ^{13}C NMR spectra of **T1-A2** ($CDCl_3$, 100 MHz).

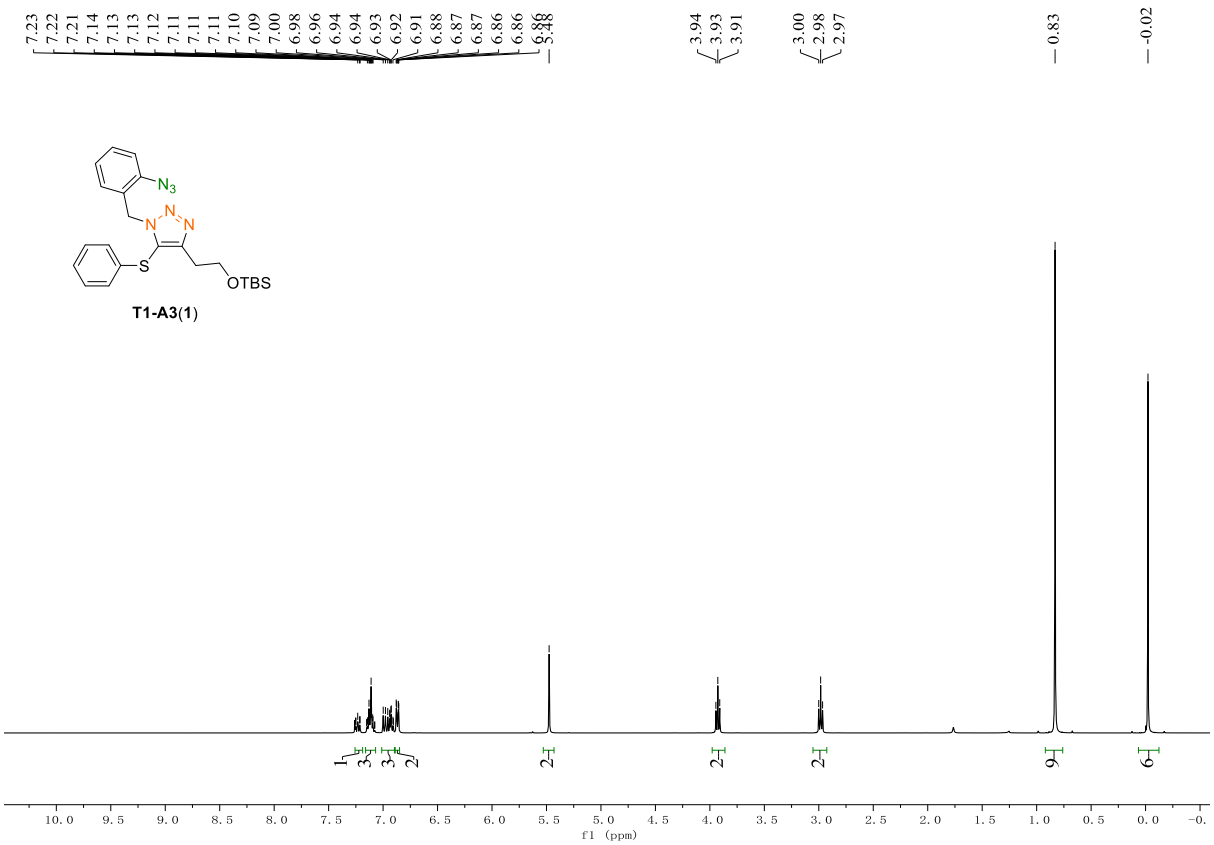


Figure S13. ^{1}H NMR spectra of **1** ($CDCl_3$, 400 MHz).

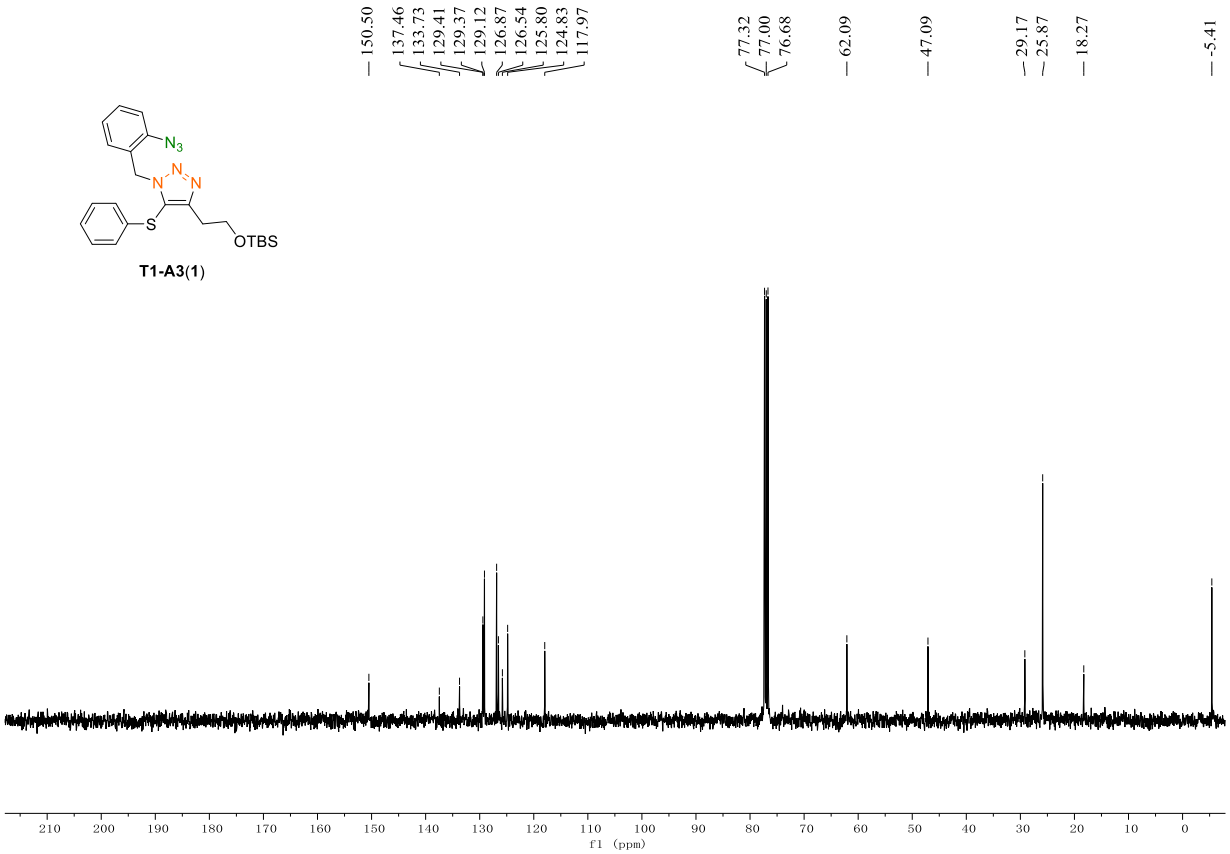


Figure S14. ^{13}C NMR spectra of **1** ($CDCl_3$, 100 MHz).

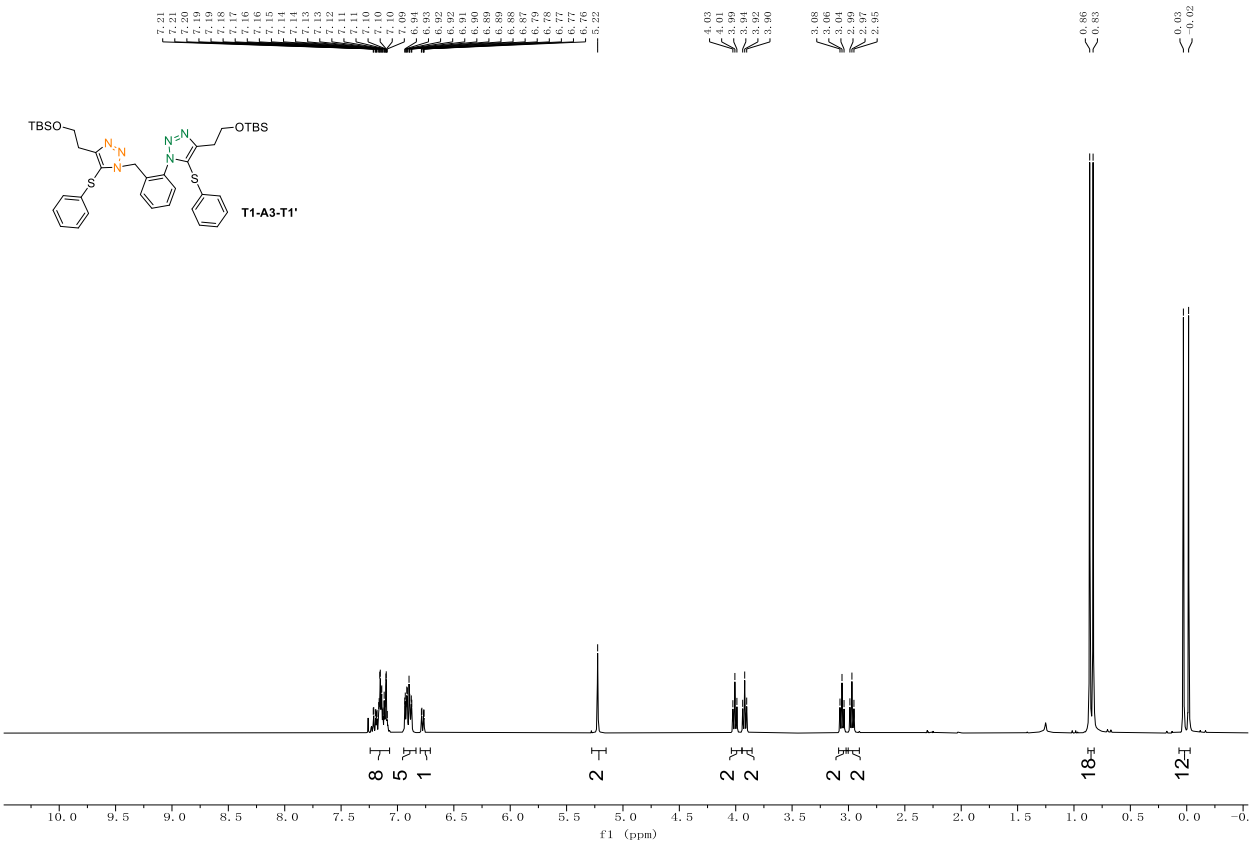


Figure S15. ^{1}H NMR spectra of **T1-A3-T1'** ($CDCl_3$, 400 MHz).

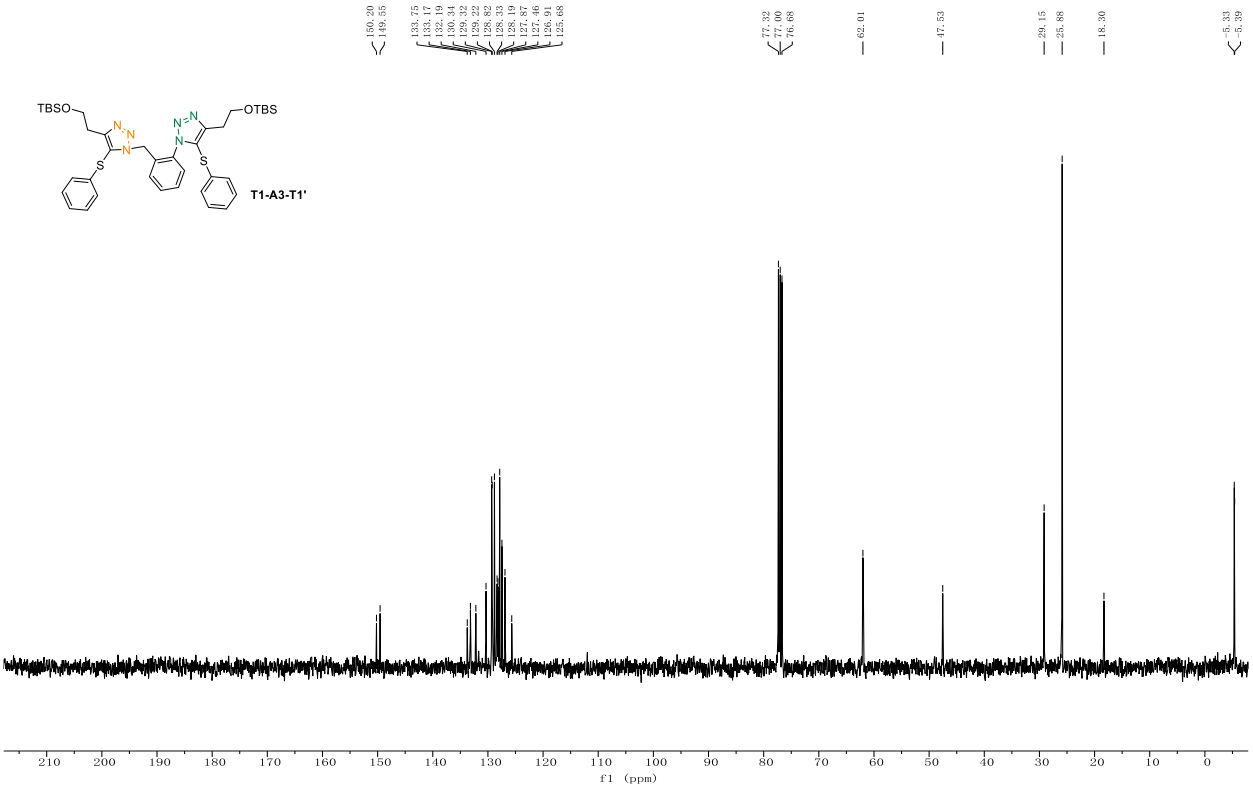


Figure S16. ^{13}C NMR spectra of **T1-A3-T1'** ($CDCl_3$, 100 MHz).

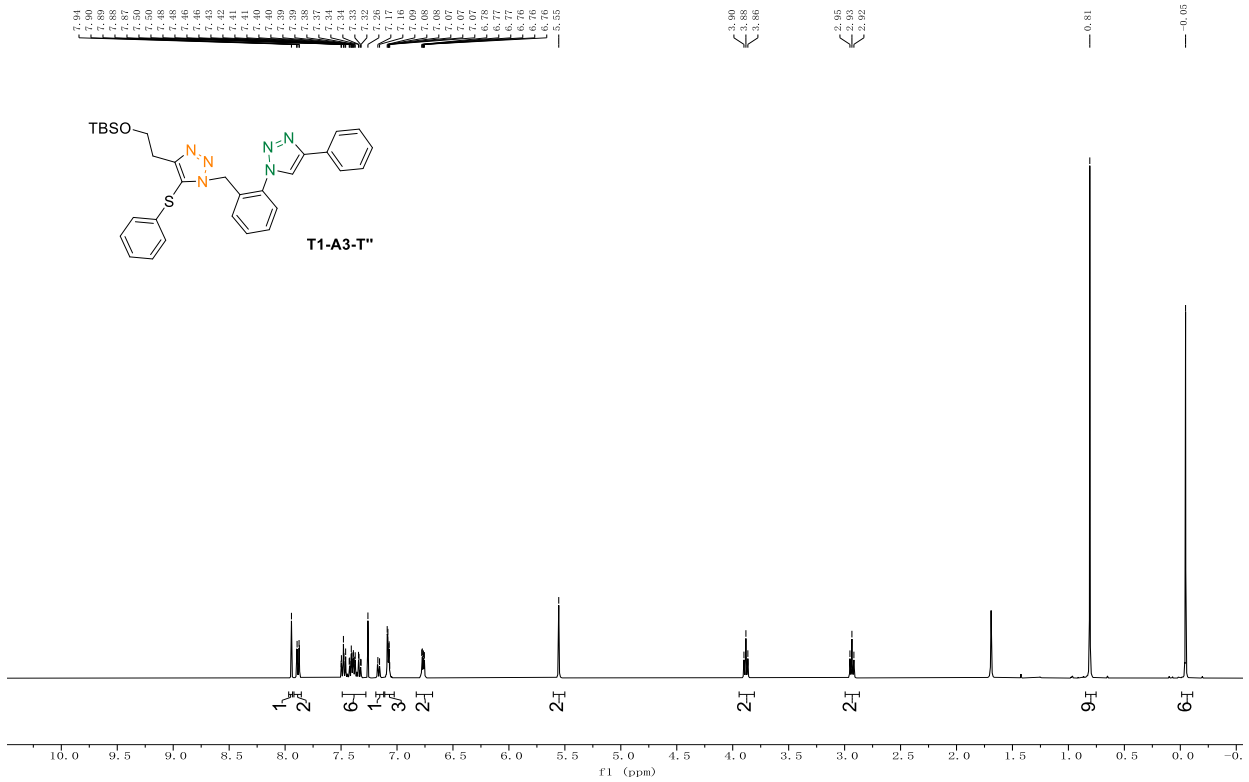


Figure S17. ^{1}H NMR spectra of **T1-A3-T"** ($CDCl_3$, 400 MHz).

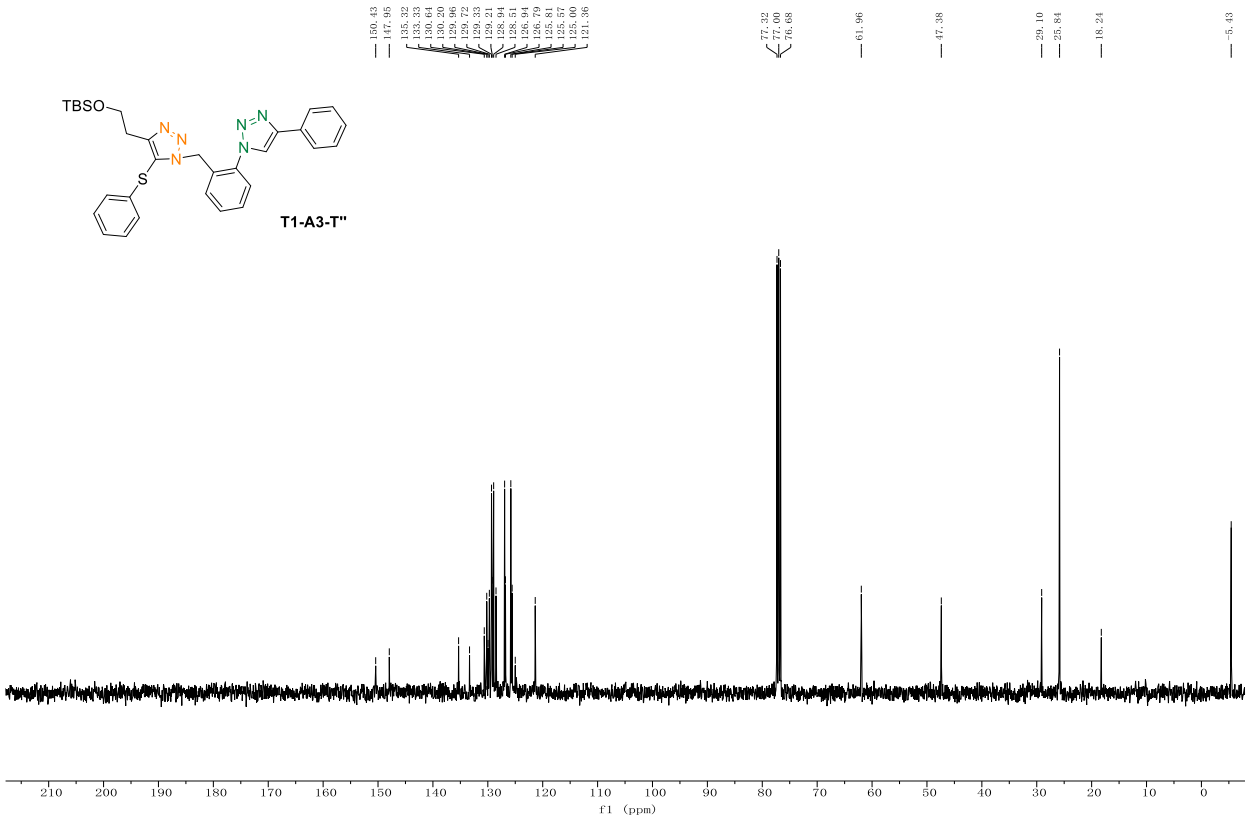


Figure S18. ^{13}C NMR spectra of **T1-A3-T"** ($CDCl_3$, 100 MHz).

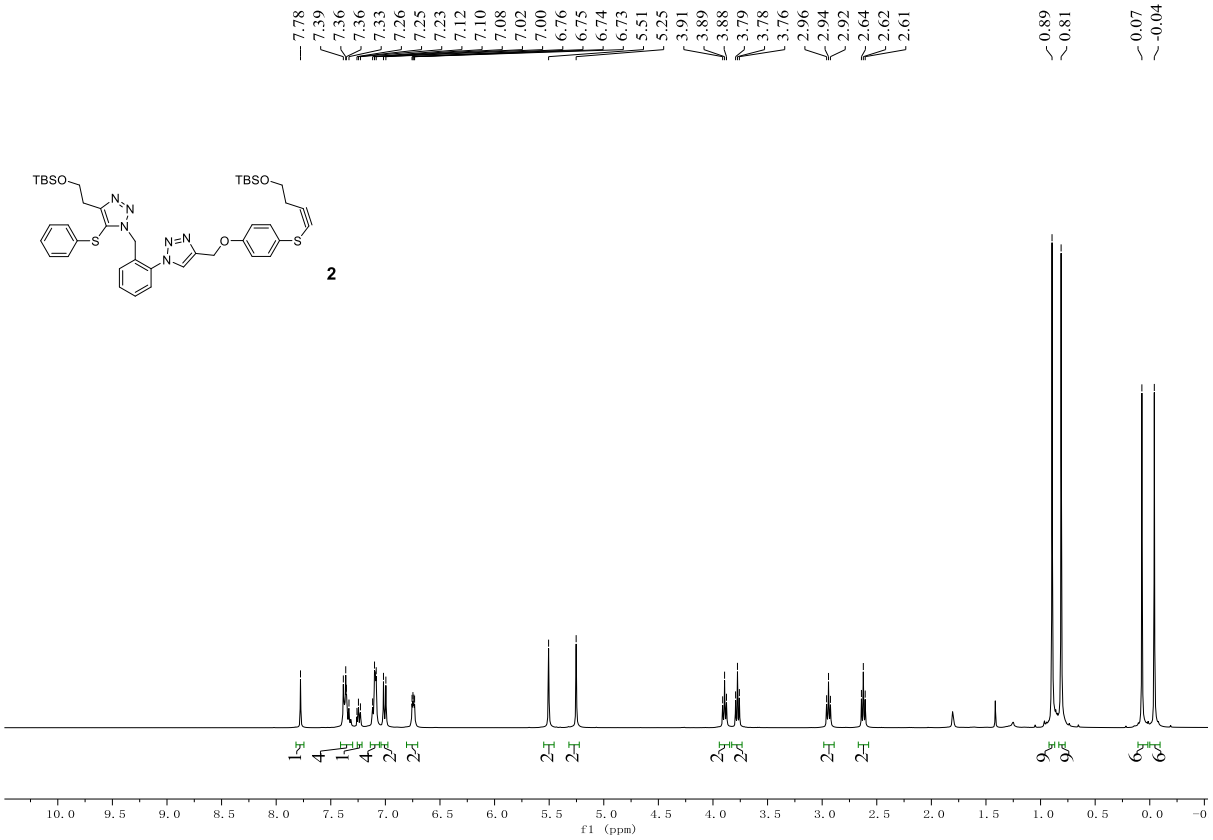


Figure S19. ^{1}H NMR spectra of **2** ($CDCl_3$, 400 MHz).

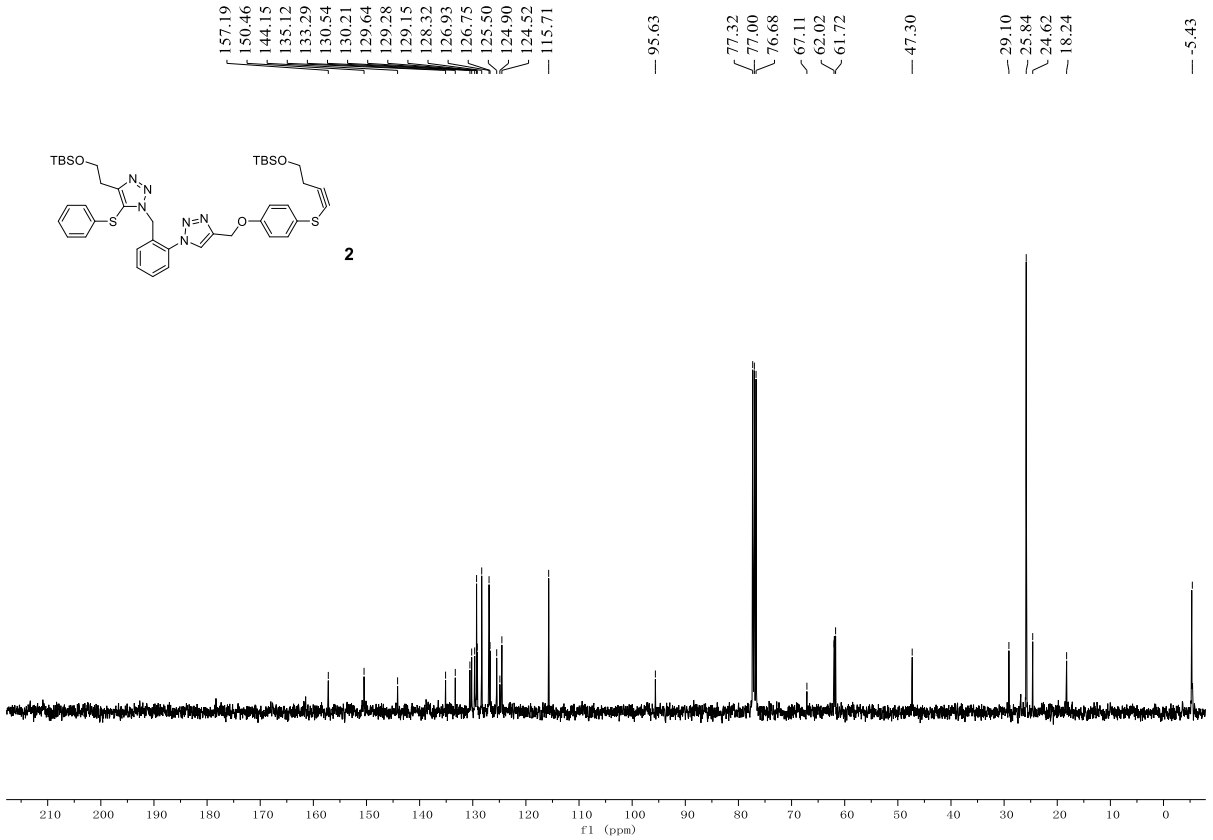


Figure S20. ^{13}C NMR spectra of **2** ($CDCl_3$, 100 MHz).

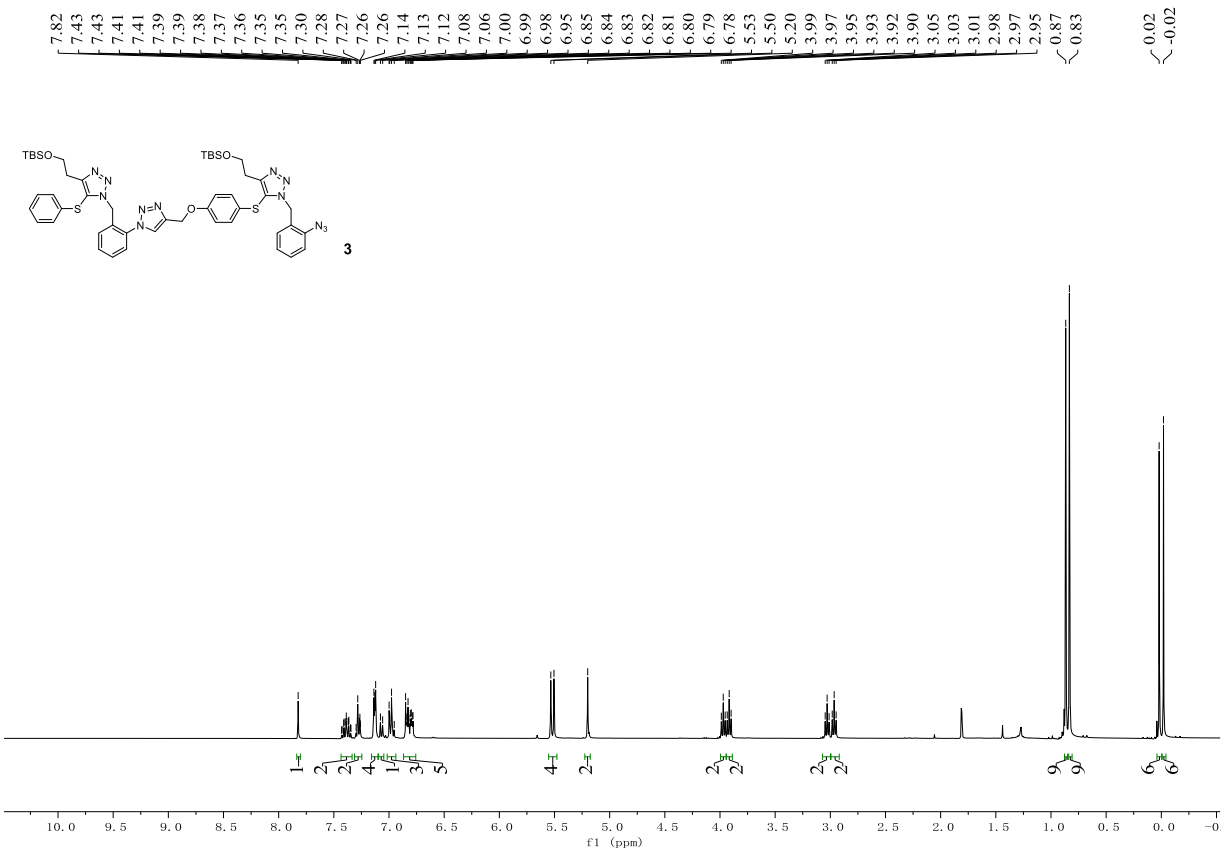


Figure S21. ^{1}H NMR spectra of **3** ($CDCl_3$, 400 MHz).

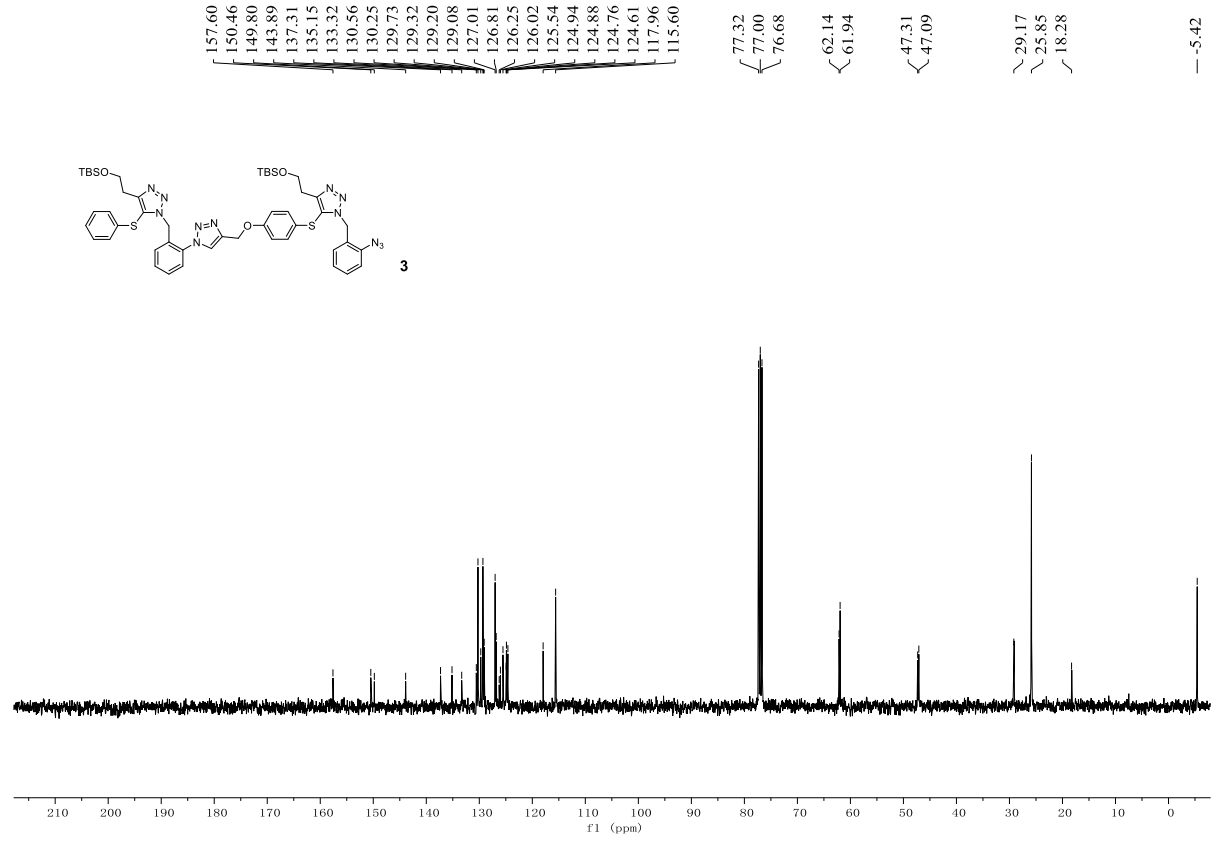


Figure S22. ^{13}C NMR spectra of **3** ($CDCl_3$, 100 MHz).

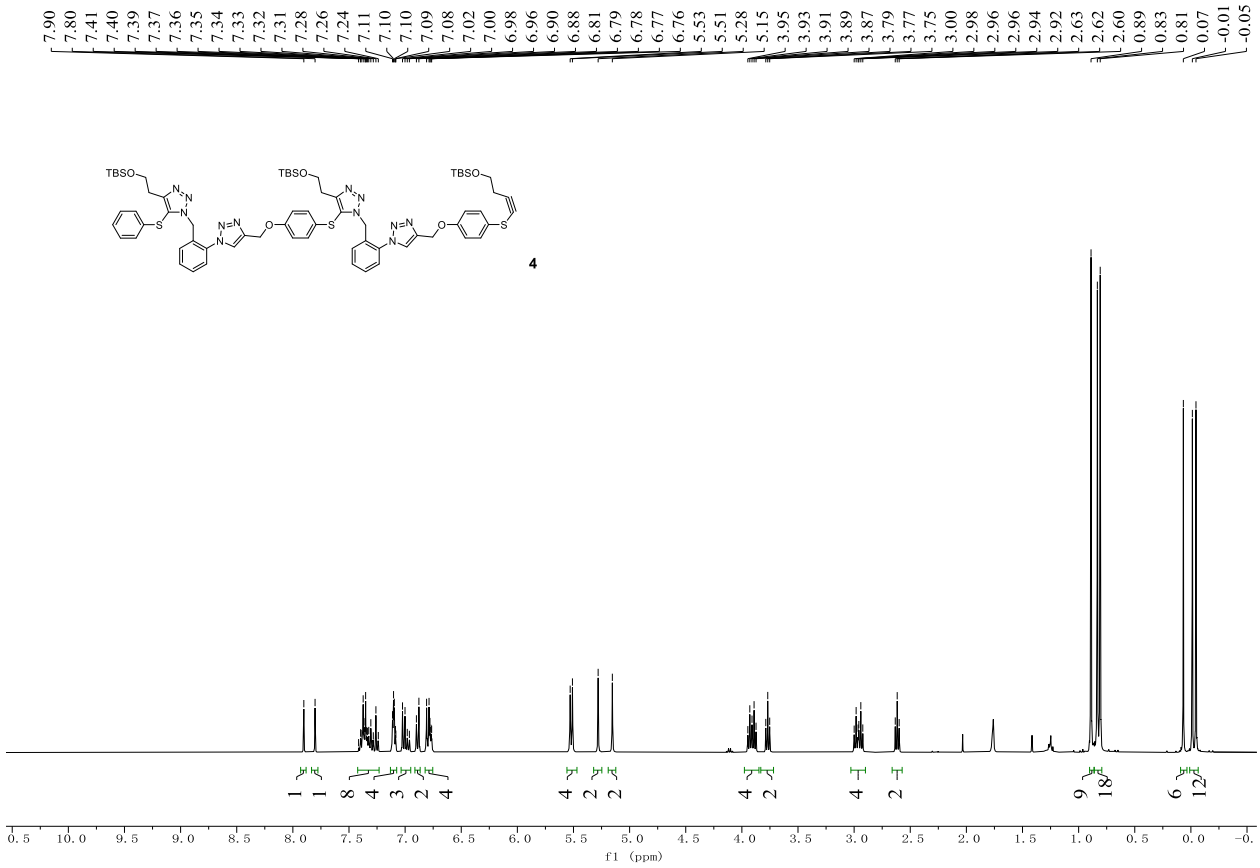


Figure S23. ^{1}H NMR spectra of **4** ($CDCl_3$, 400 MHz).

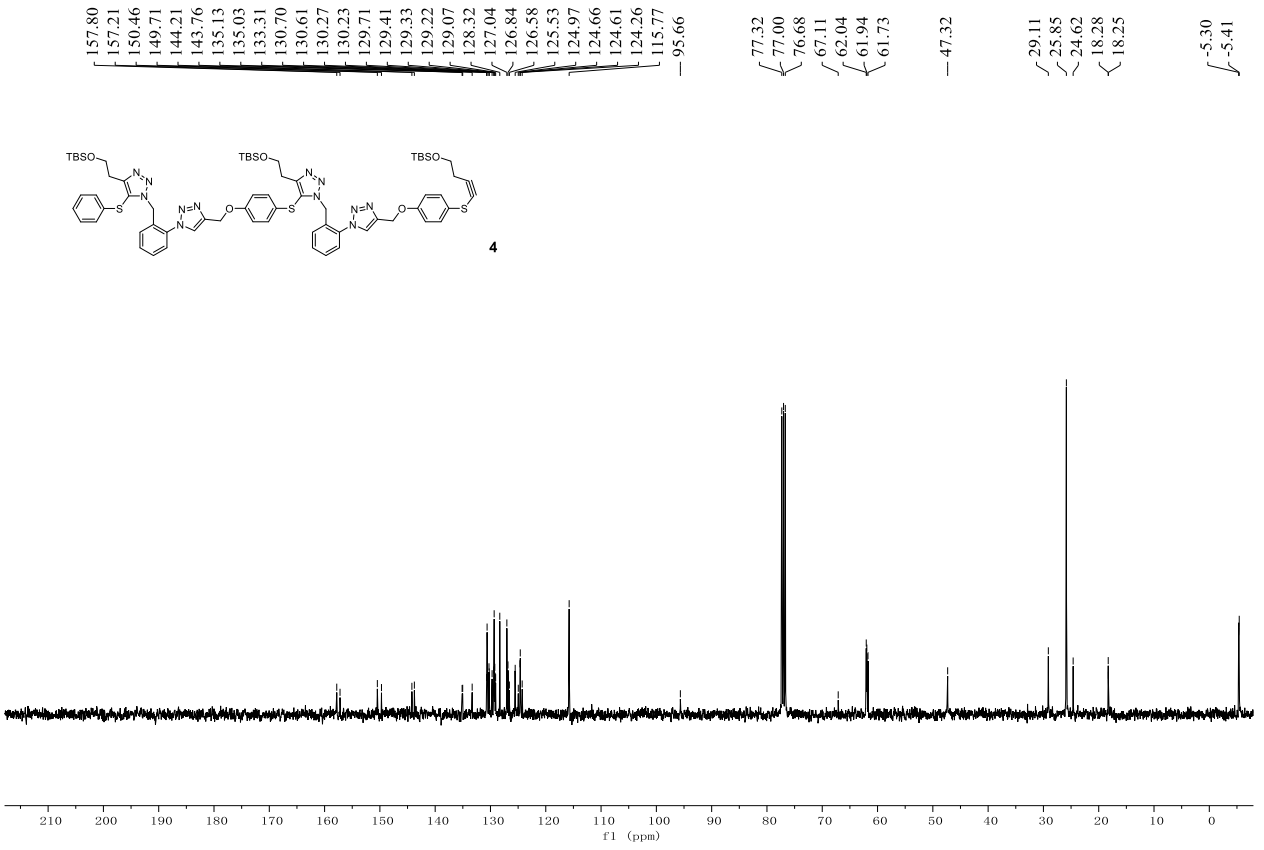


Figure S24. ^{13}C NMR spectra of **4** ($CDCl_3$, 100 MHz).

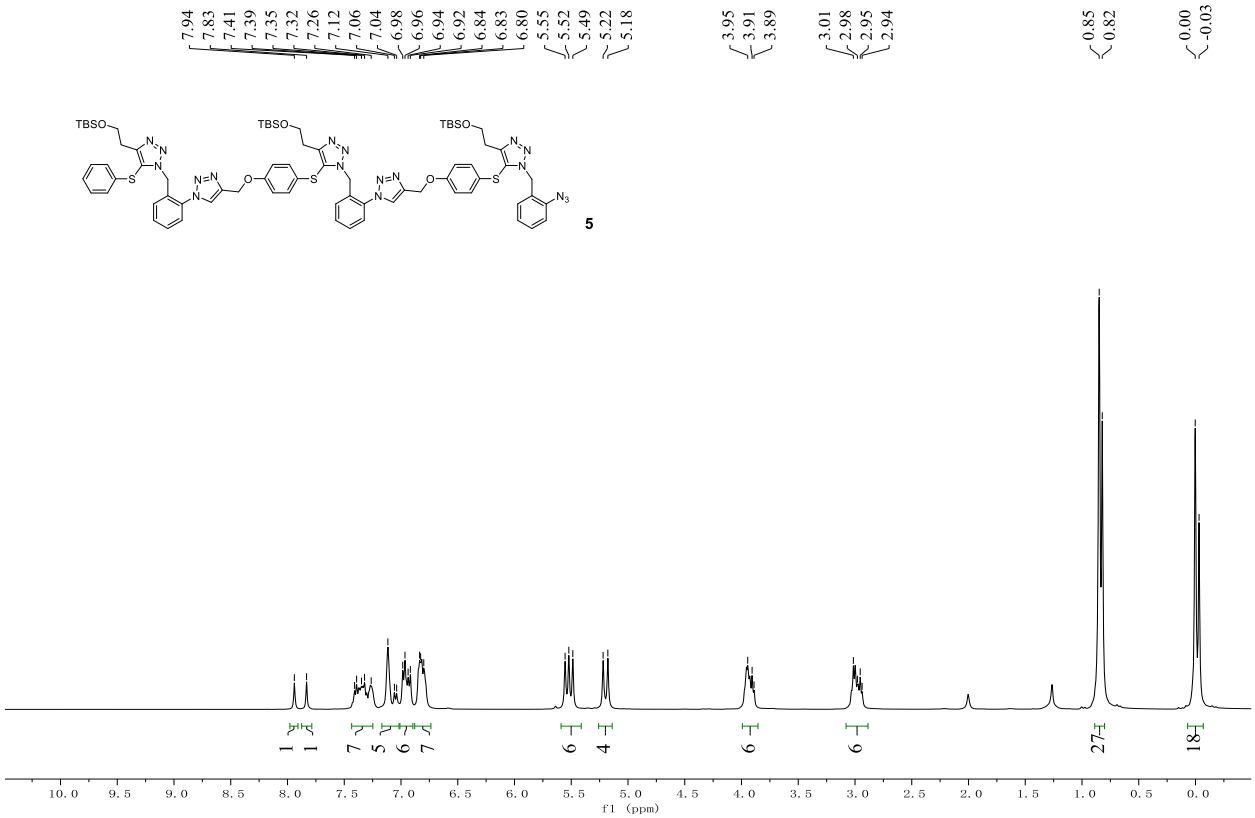


Figure S25. ^{1}H NMR spectra of **5** ($CDCl_3$, 400 MHz).

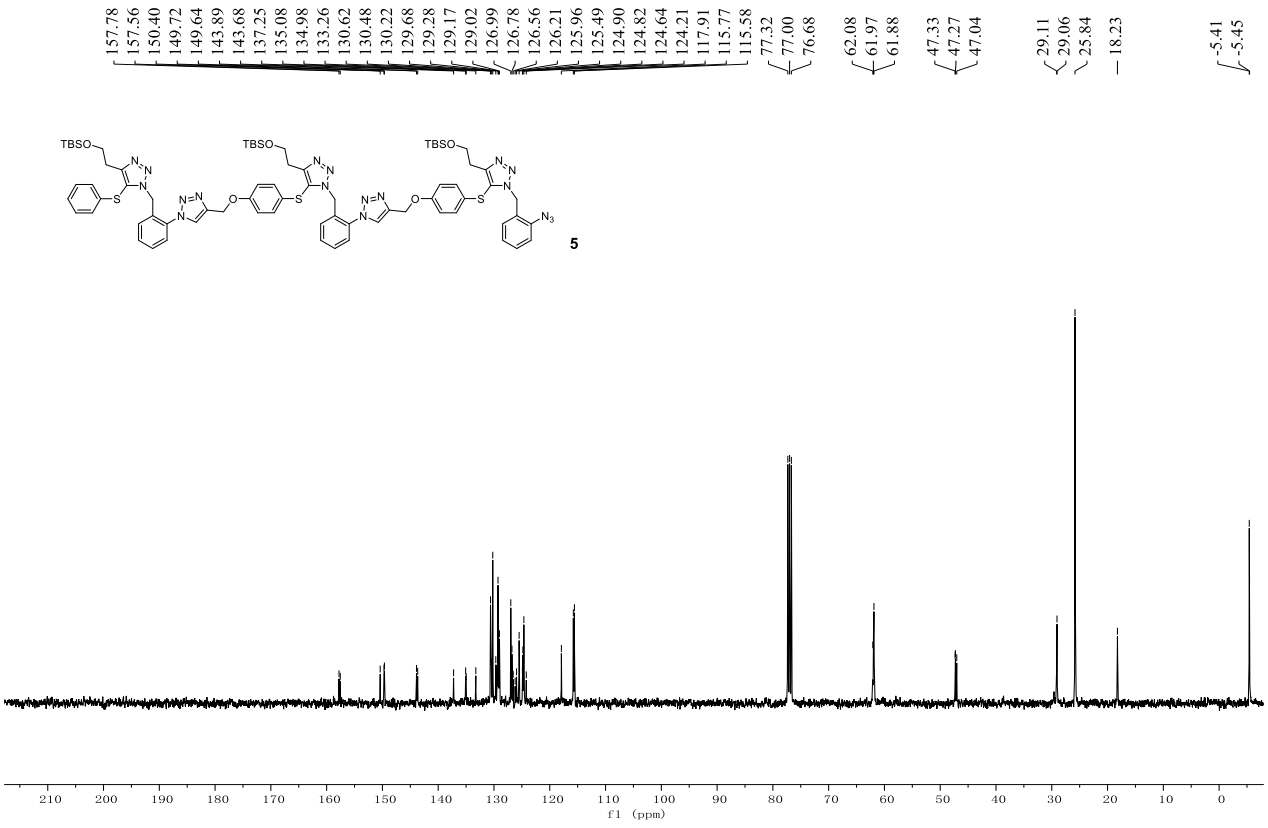


Figure S26. ^{13}C NMR spectra of **5** ($CDCl_3$, 100 MHz).

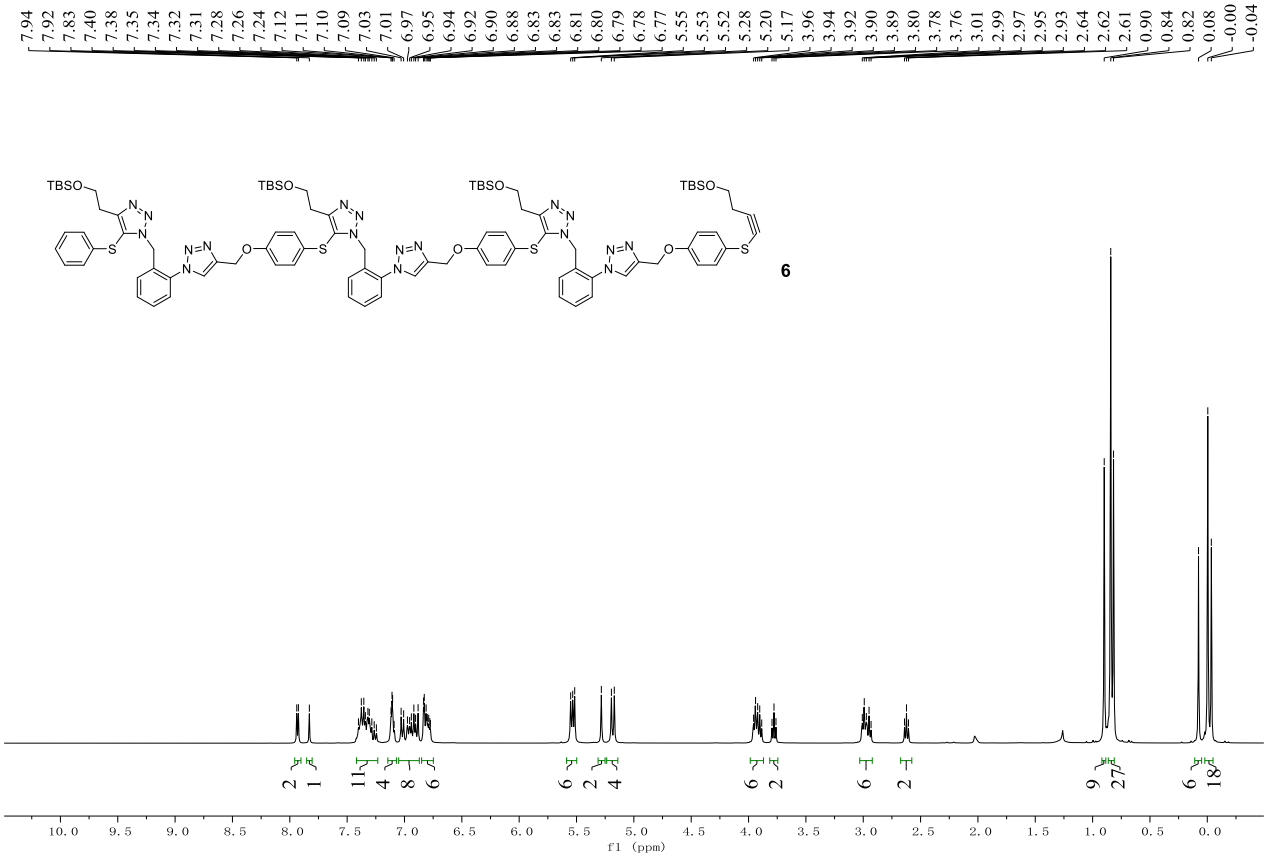


Figure S27. ^{1}H NMR spectra of **6** ($CDCl_3$, 400 MHz).

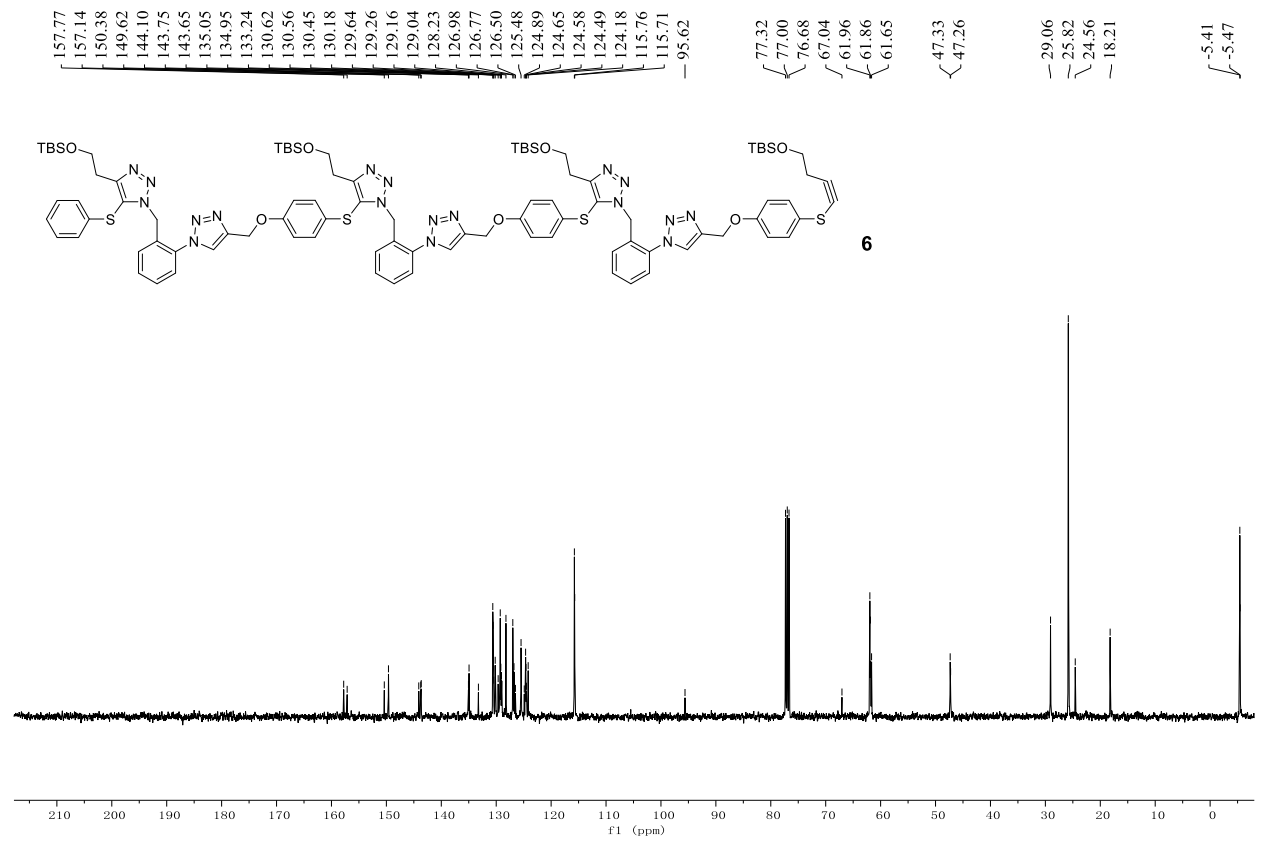


Figure S28. ^{13}C NMR spectra of **6** ($CDCl_3$, 100 MHz).

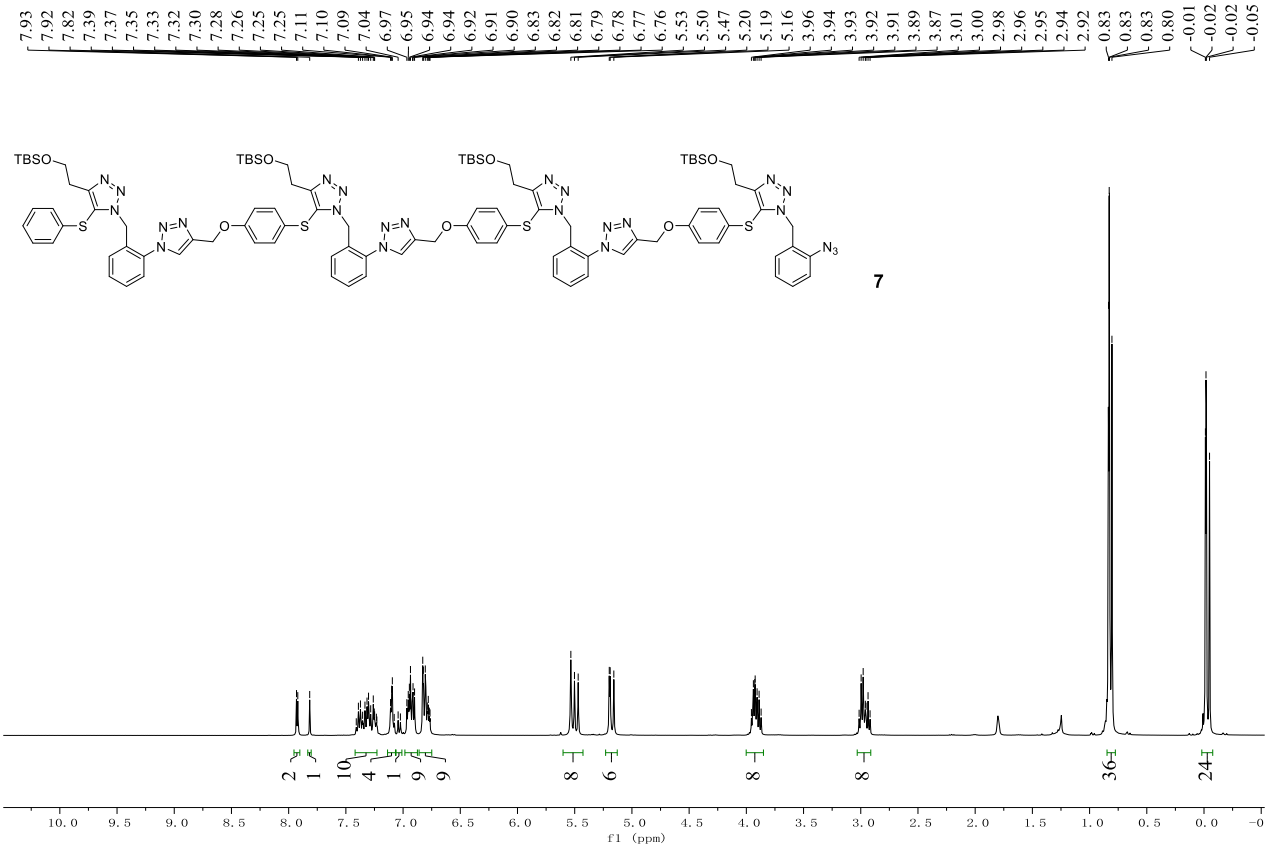


Figure S29. ^{1}H NMR spectra of **7** ($CDCl_3$, 400 MHz).

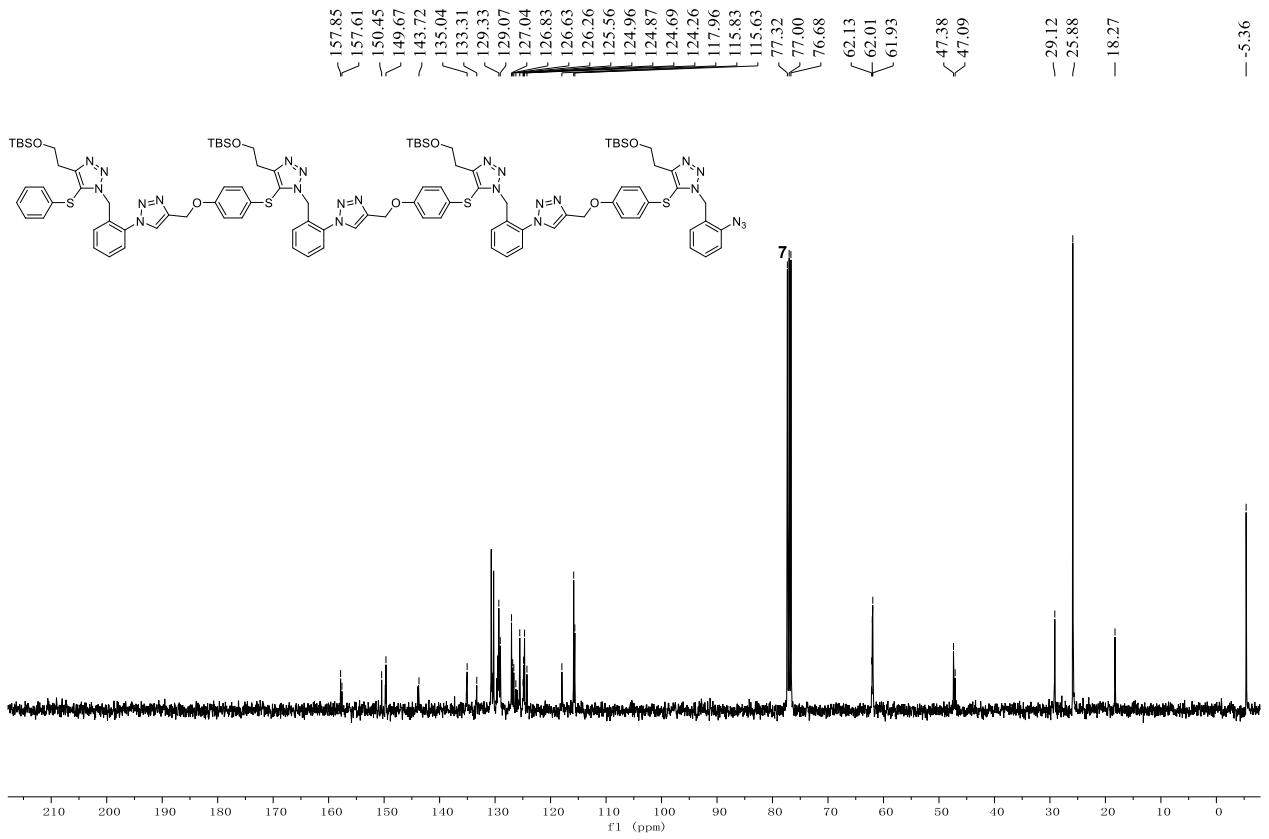


Figure S30. ^{13}C NMR spectra of **7** ($CDCl_3$, 100 MHz).

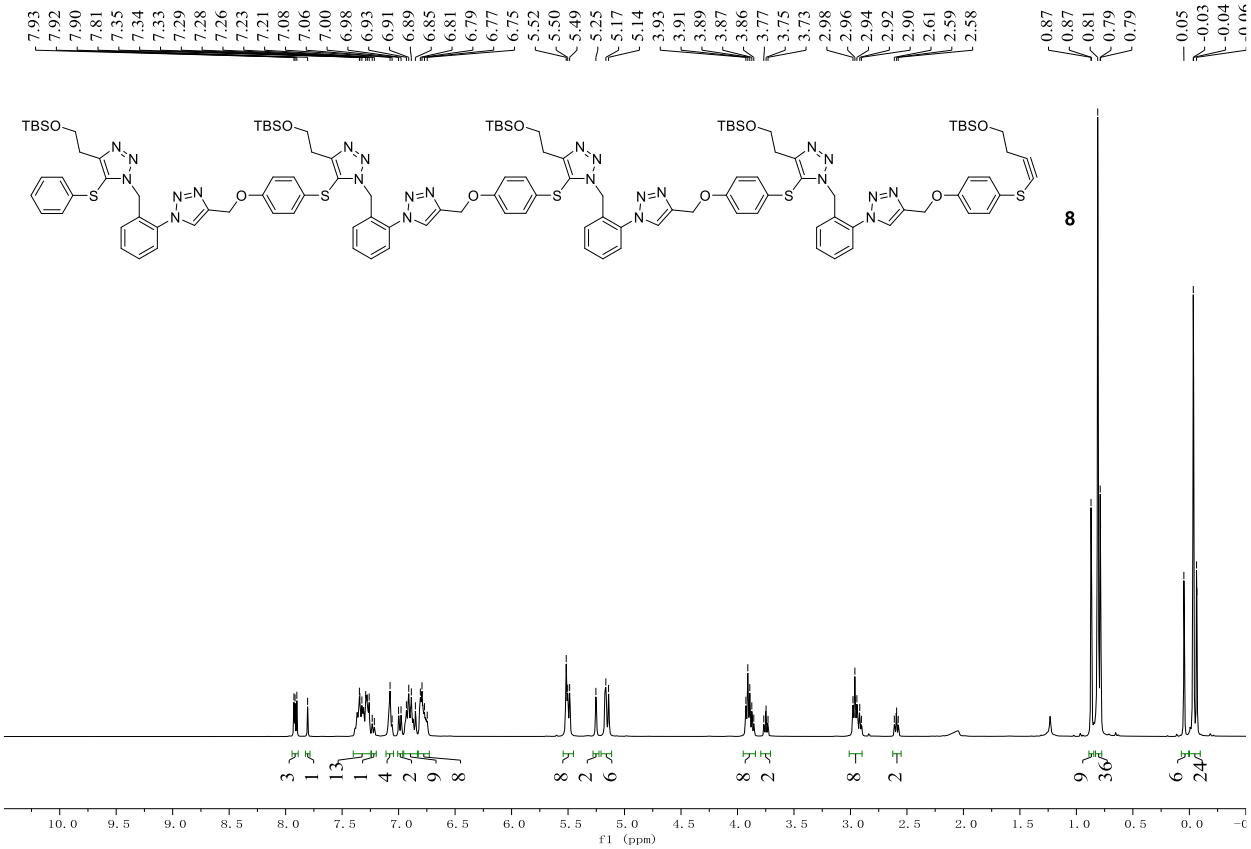


Figure S31. ^{1}H NMR spectra of **8** ($CDCl_3$, 400 MHz).

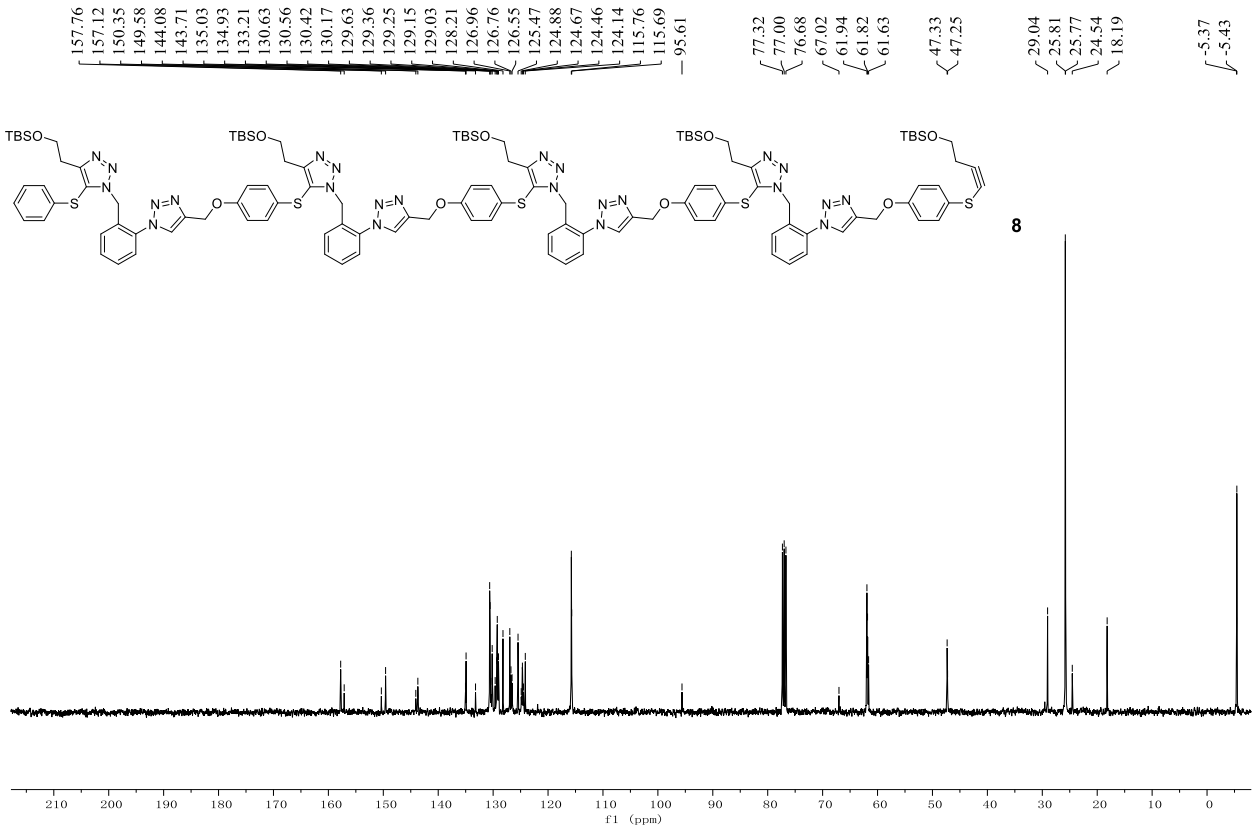


Figure S32. ^{13}C NMR spectra of **8** ($CDCl_3$, 100 MHz).

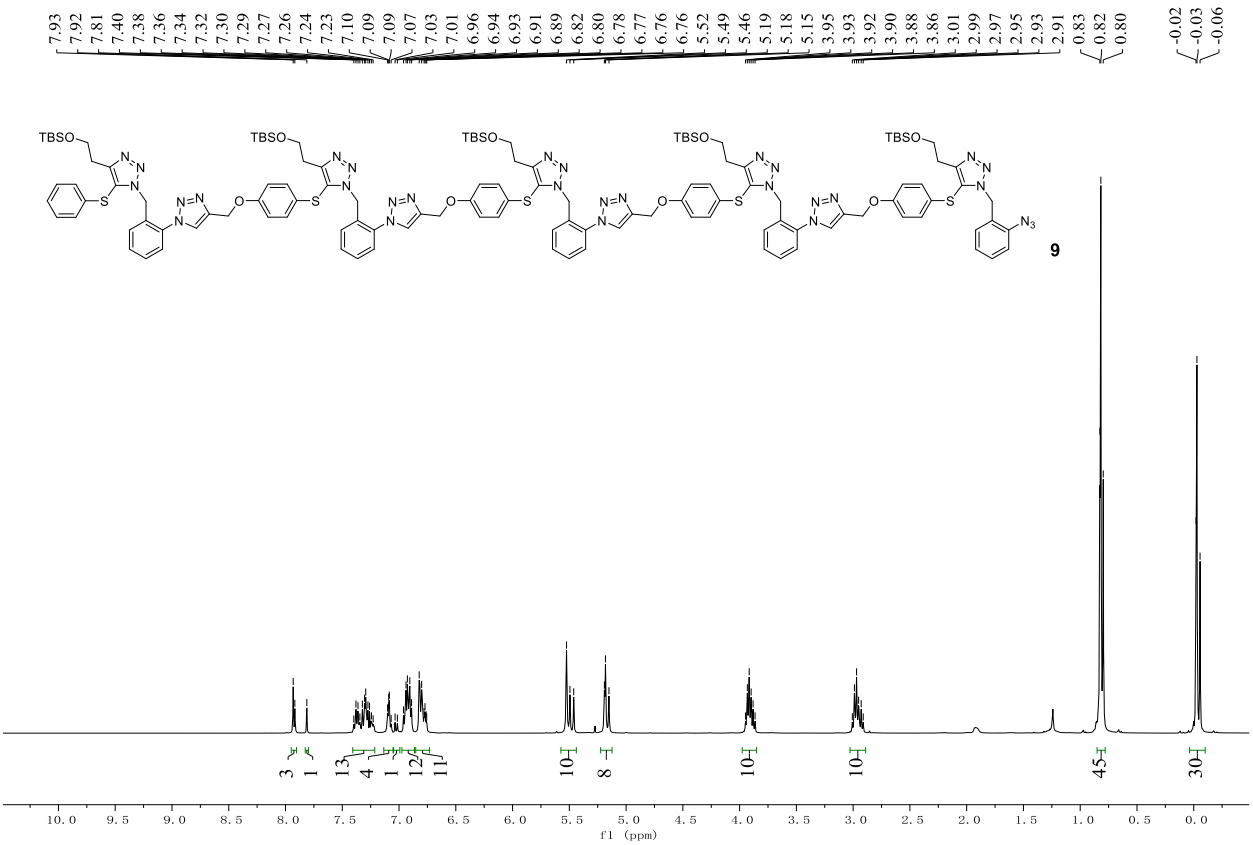


Figure S33. ^{1}H NMR spectra of **9** ($CDCl_3$, 400 MHz).

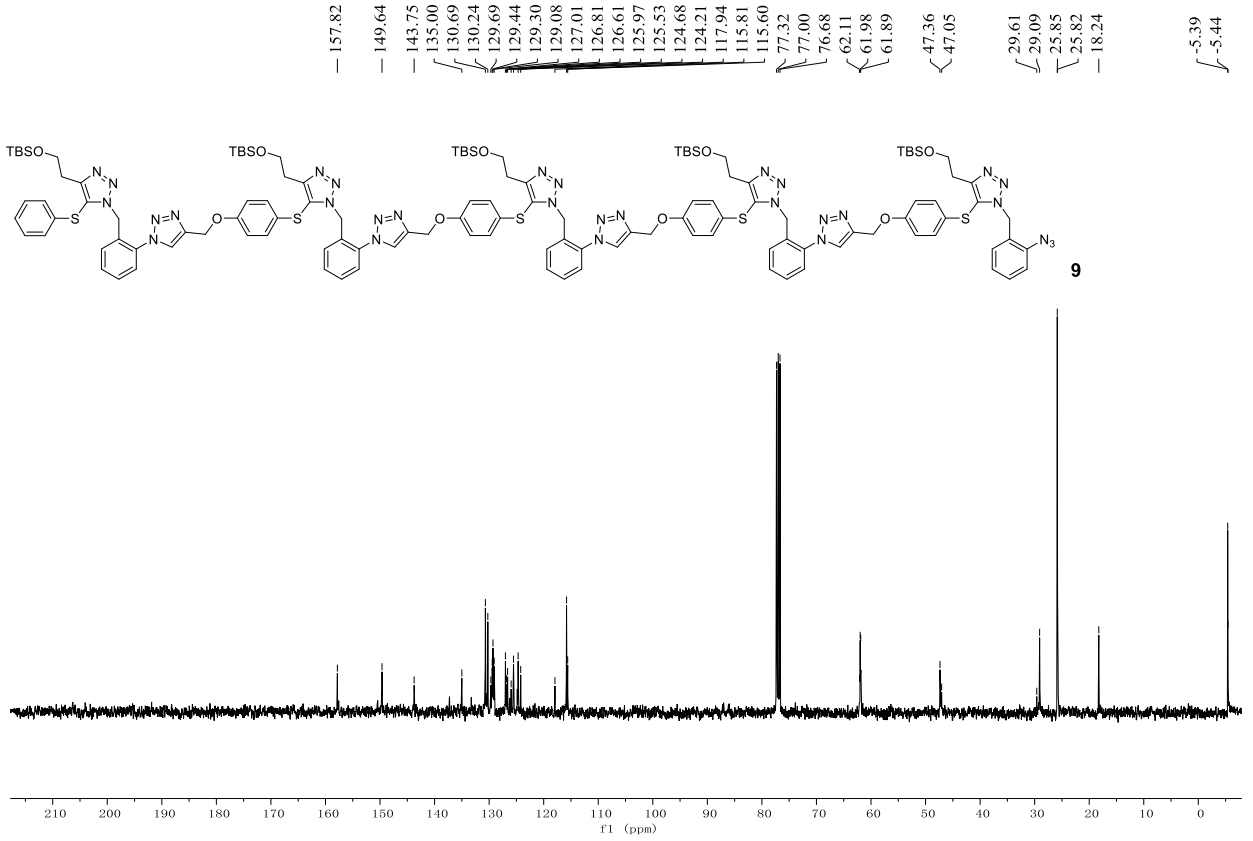


Figure S34. ^{13}C NMR spectra of **9** ($CDCl_3$, 100 MHz).

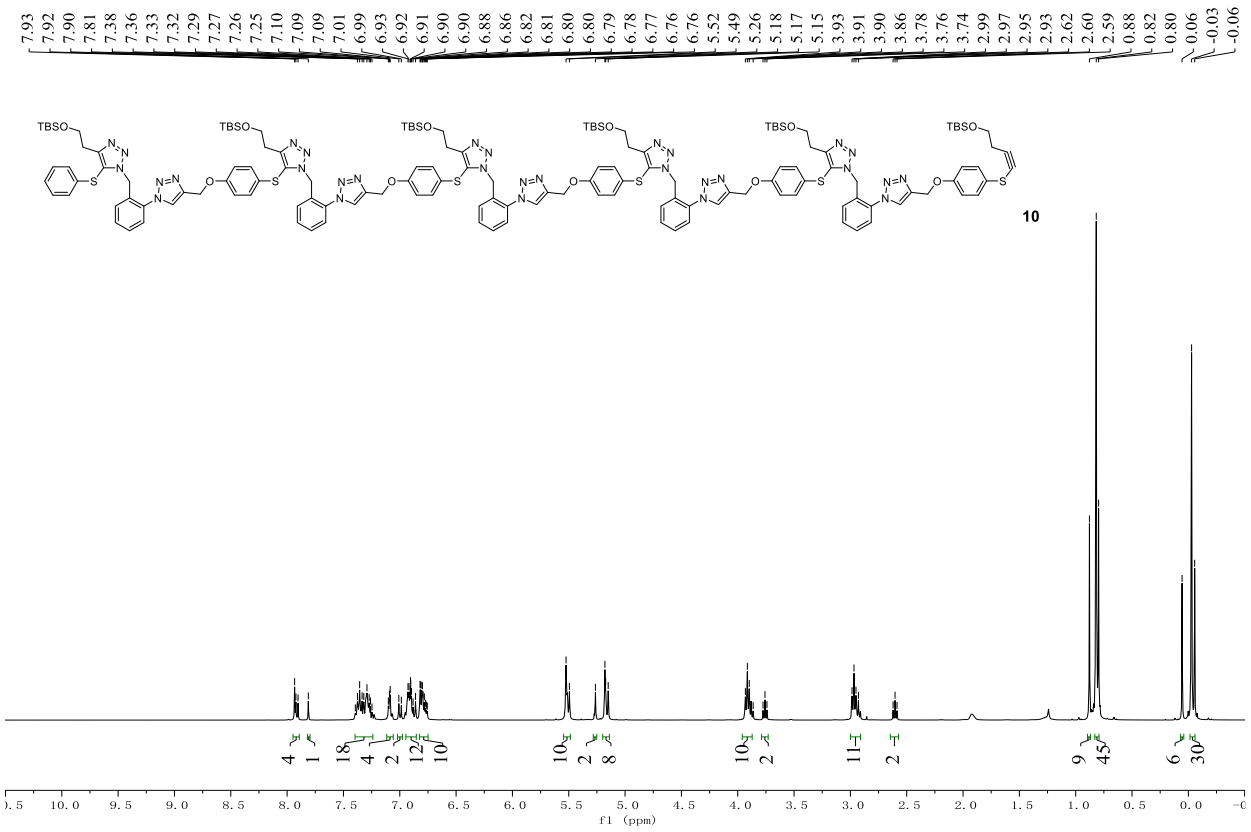


Figure S35. ^{1}H NMR spectra of **10** ($CDCl_3$, 400 MHz).

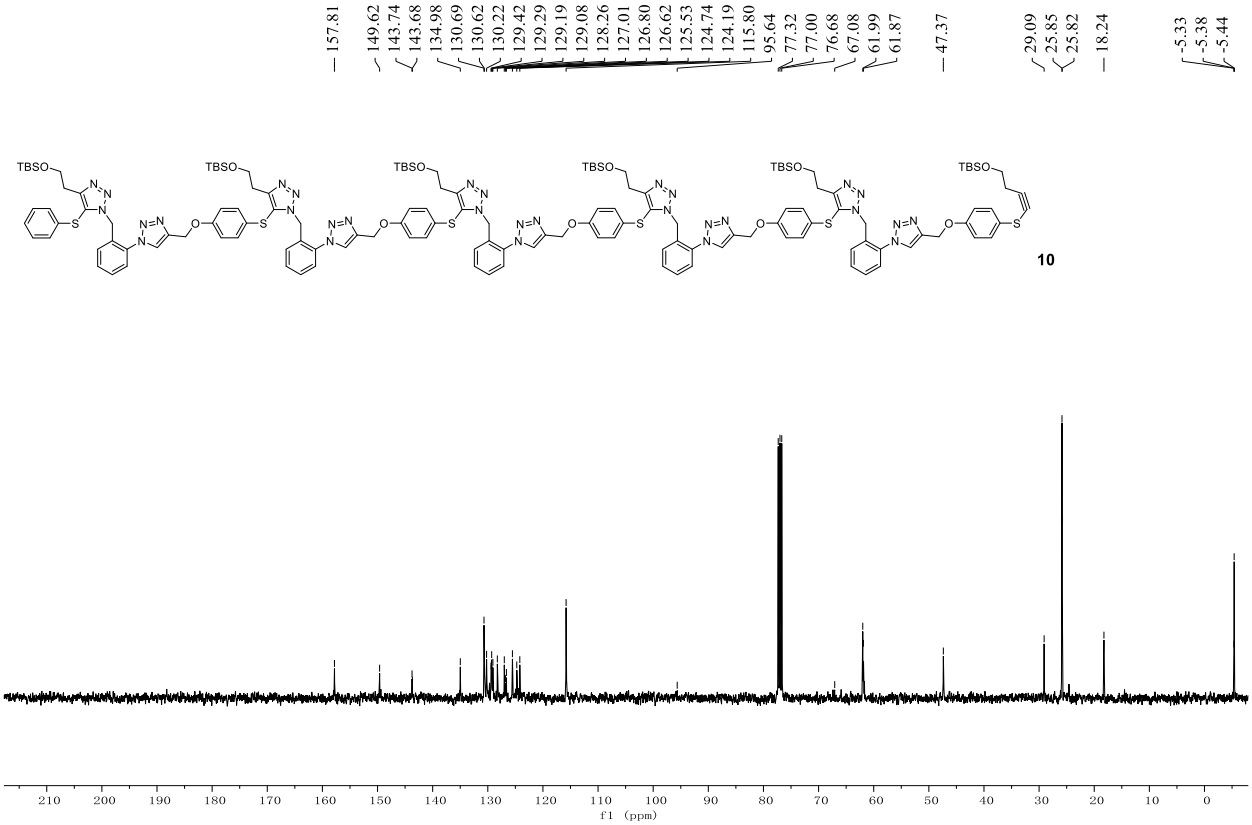


Figure S36. ^{13}C NMR spectra of **10** ($CDCl_3$, 100 MHz).

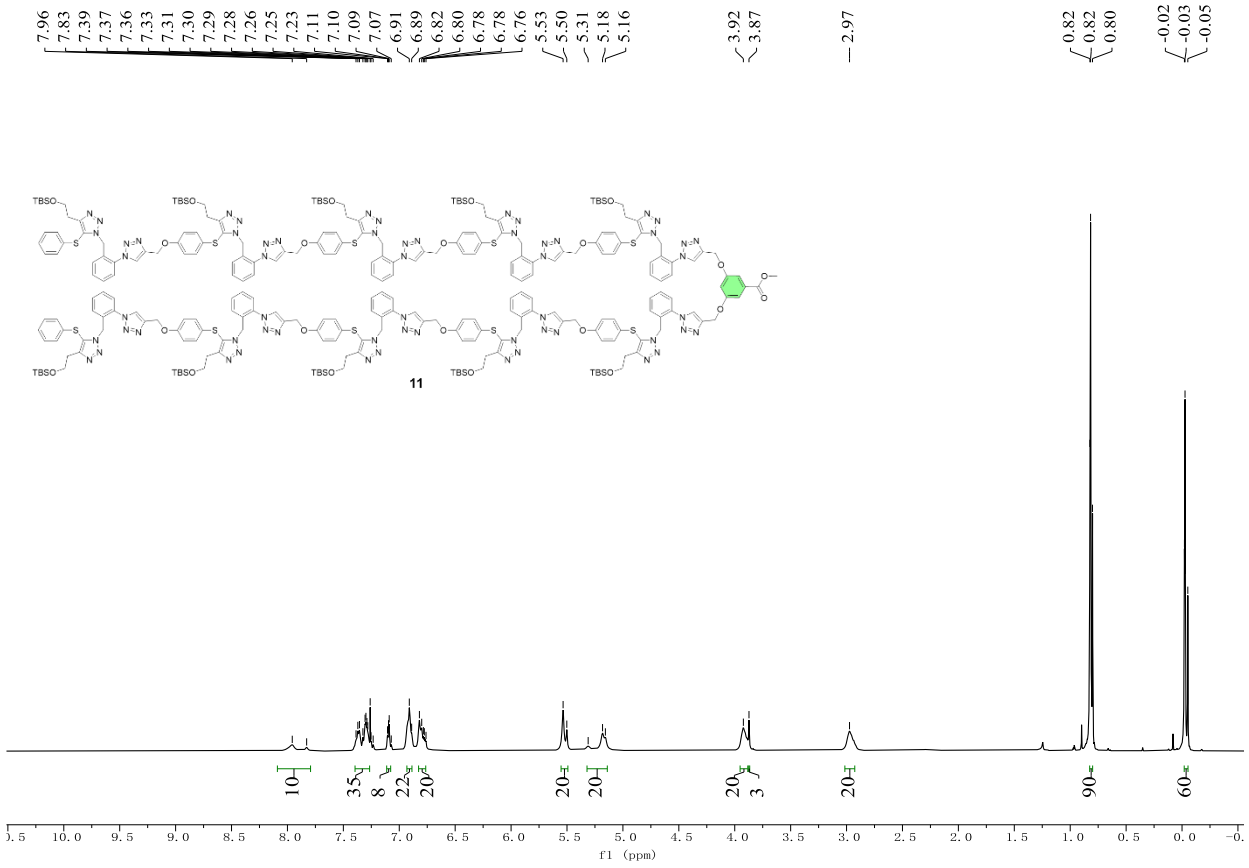


Figure S37. ^{1}H NMR spectra of **11** ($CDCl_3$, 400 MHz).

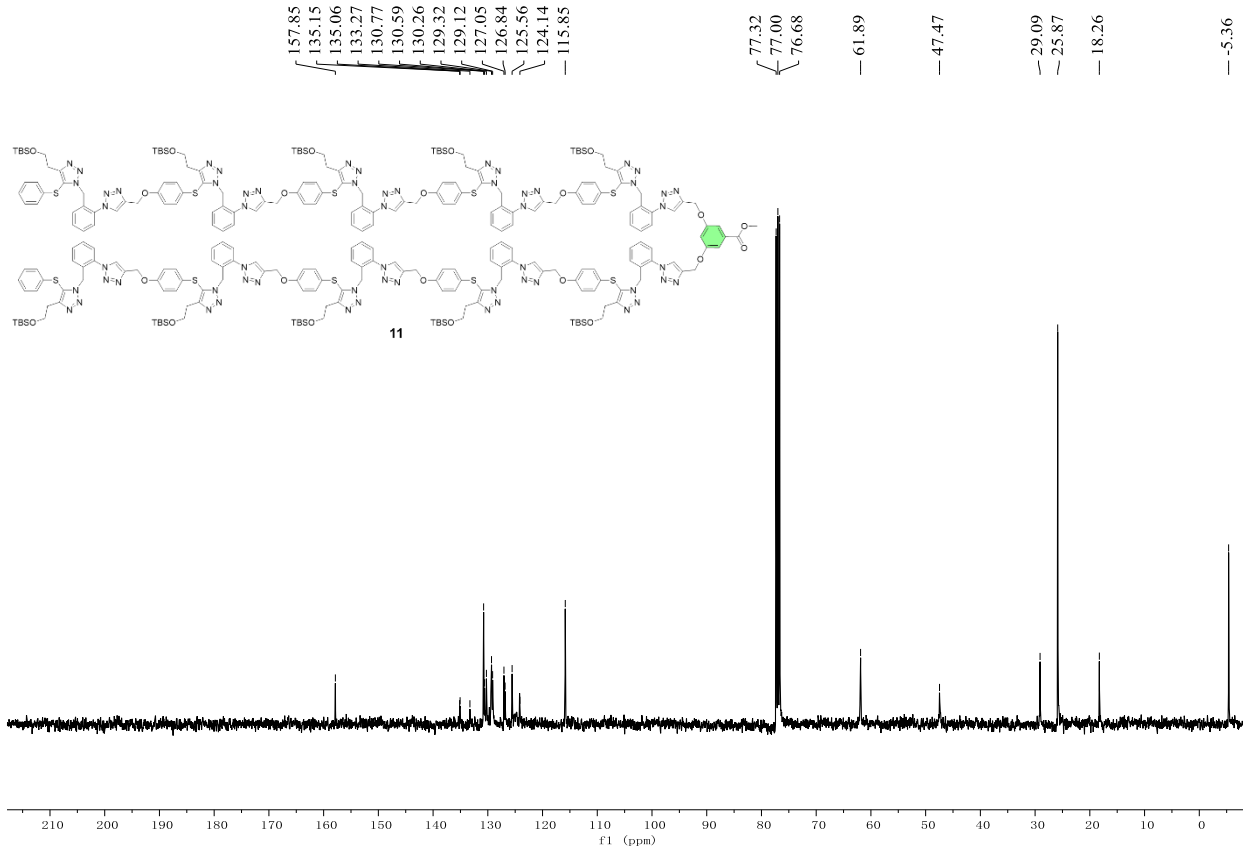


Figure S38. ^{13}C NMR spectra of **11** ($CDCl_3$, 100 MHz).

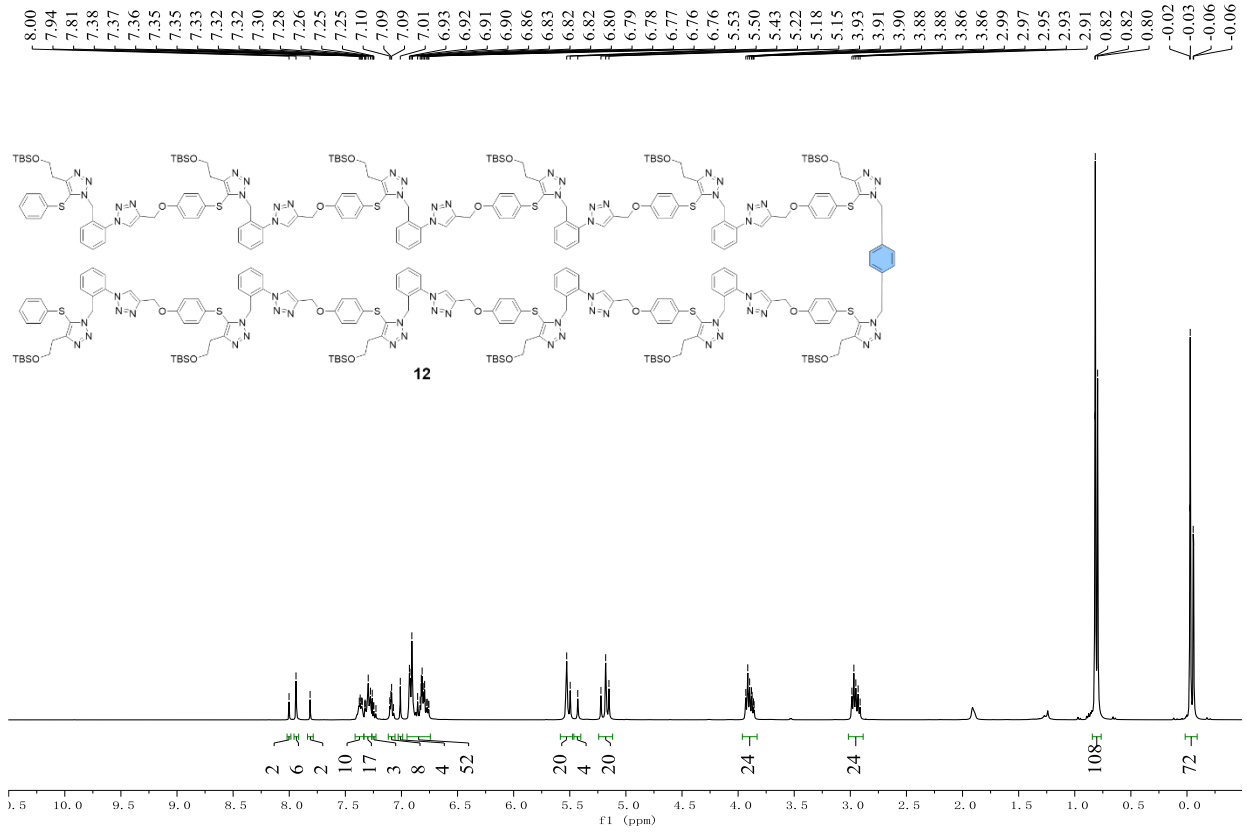


Figure S39. ^{1}H NMR spectra of **12** ($CDCl_3$, 400 MHz).

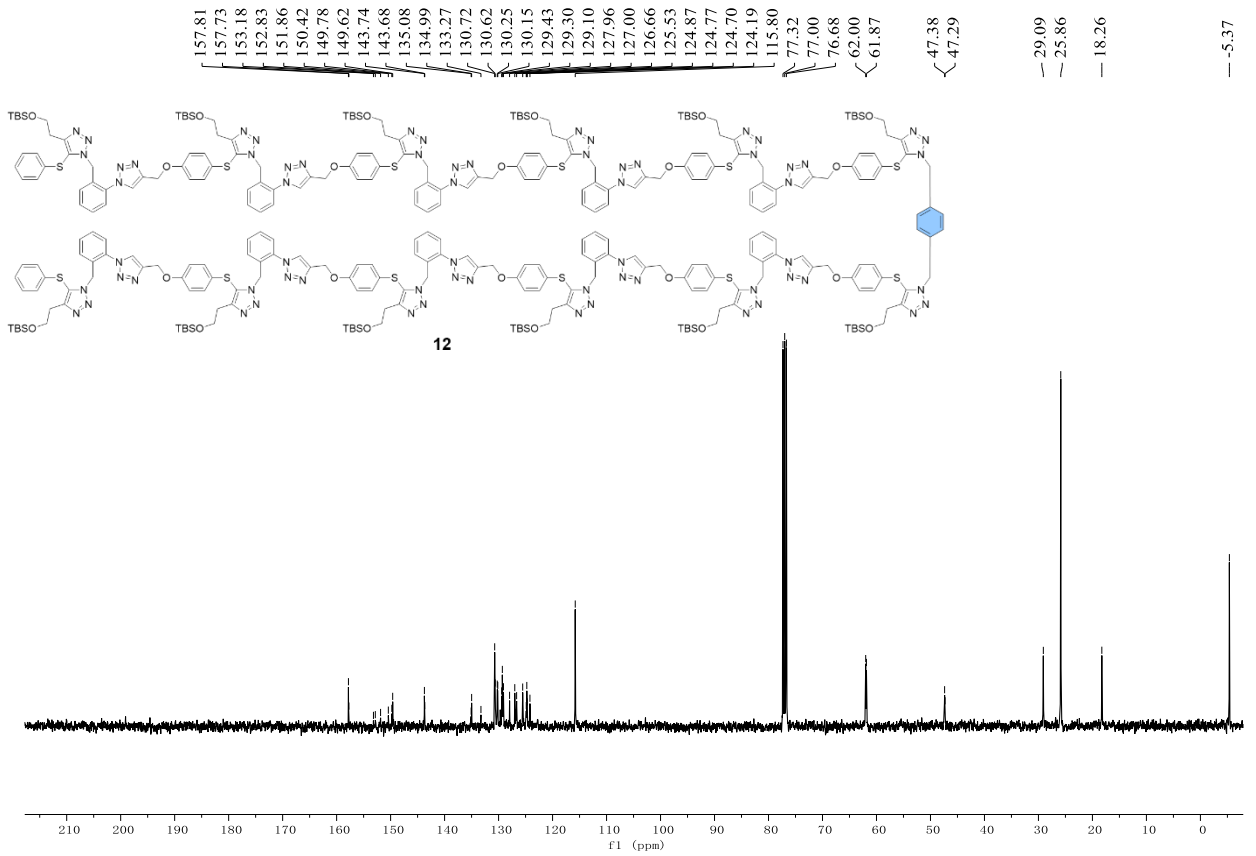


Figure S40. ^{13}C NMR spectra of **12** ($CDCl_3$, 100 MHz).

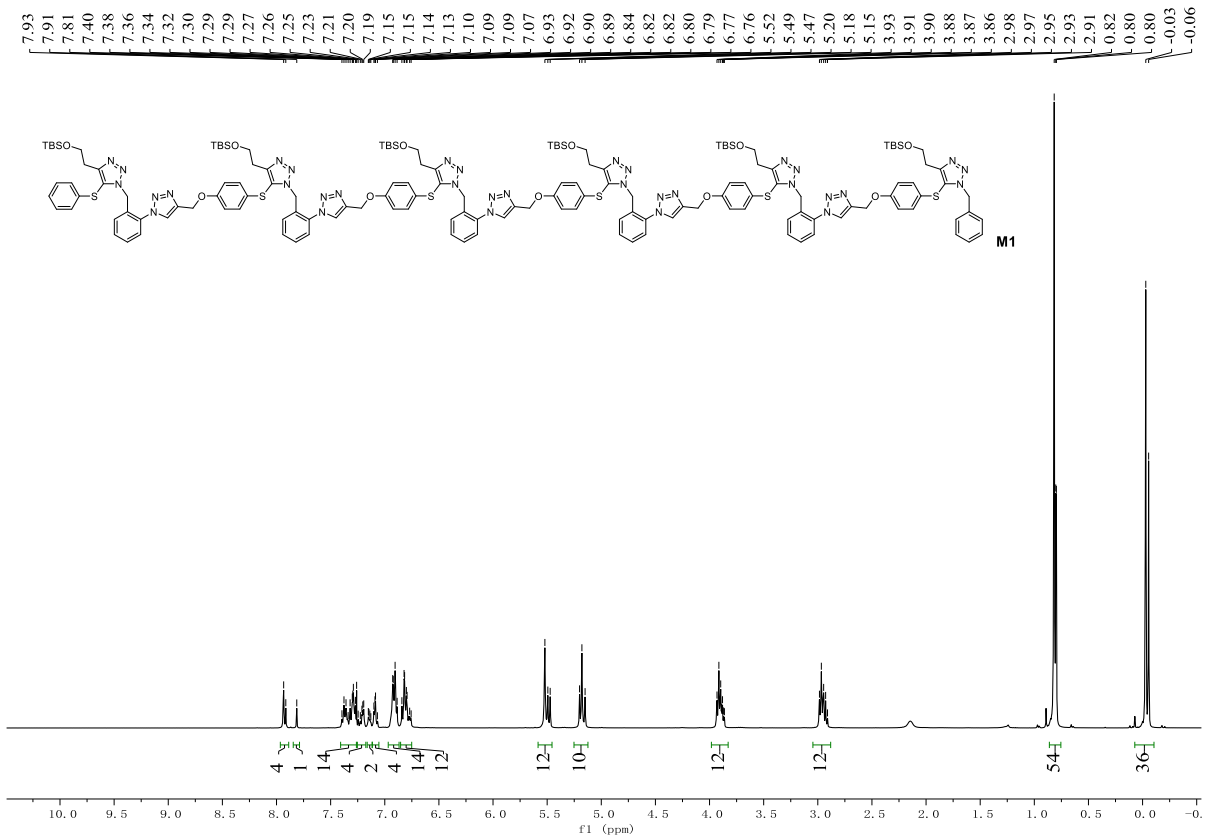


Figure S41. ^{1}H NMR spectra of **M1** ($CDCl_3$, 400 MHz).

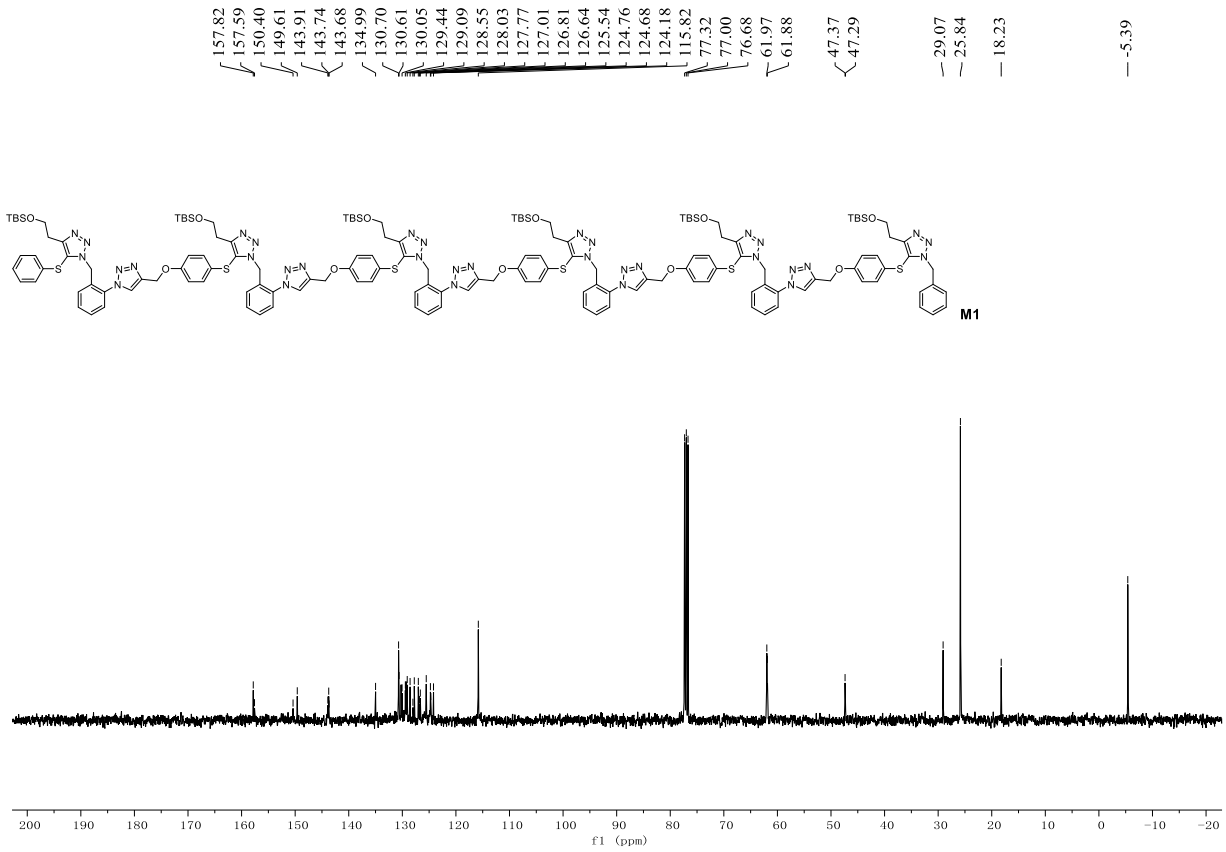


Figure S42. ^{13}C NMR spectra of **M1** ($CDCl_3$, 100 MHz).

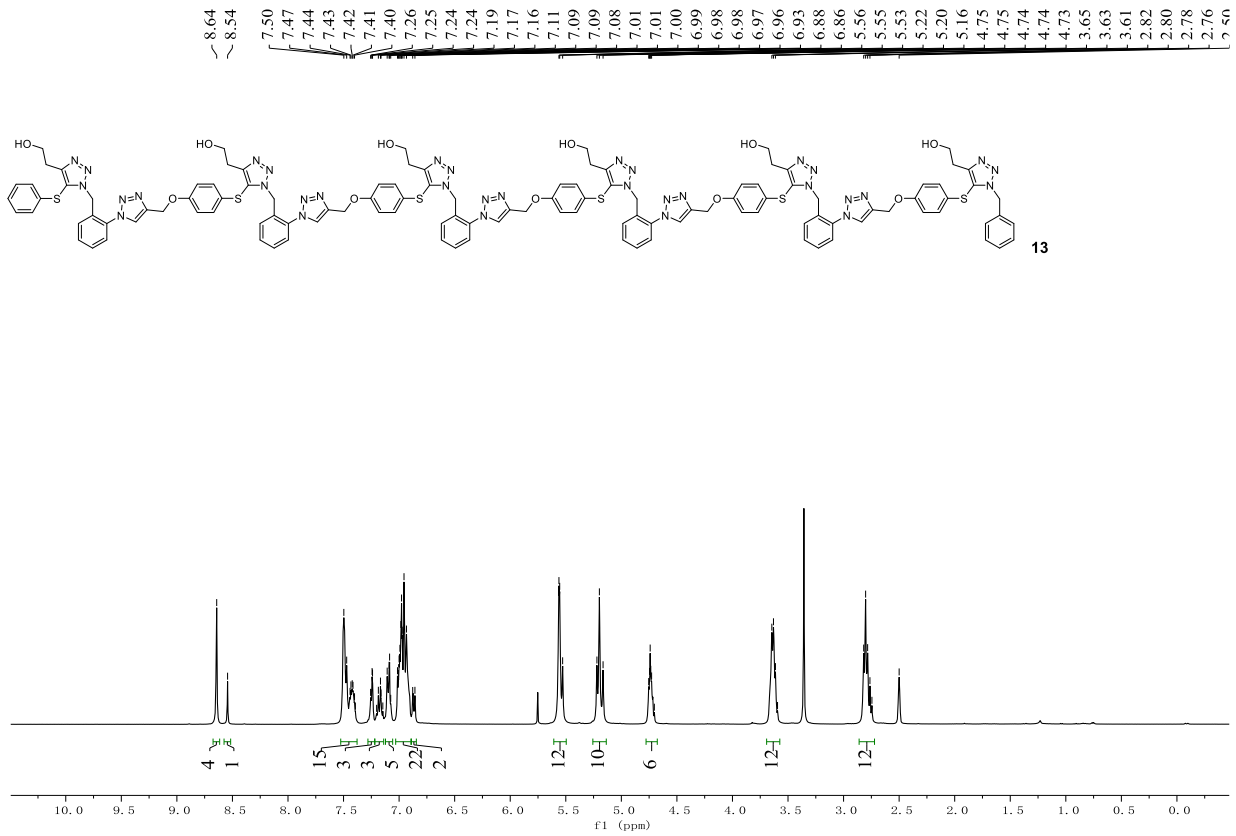


Figure S43. ^{1}H NMR spectra of **13** (DMSO,400 MHz).

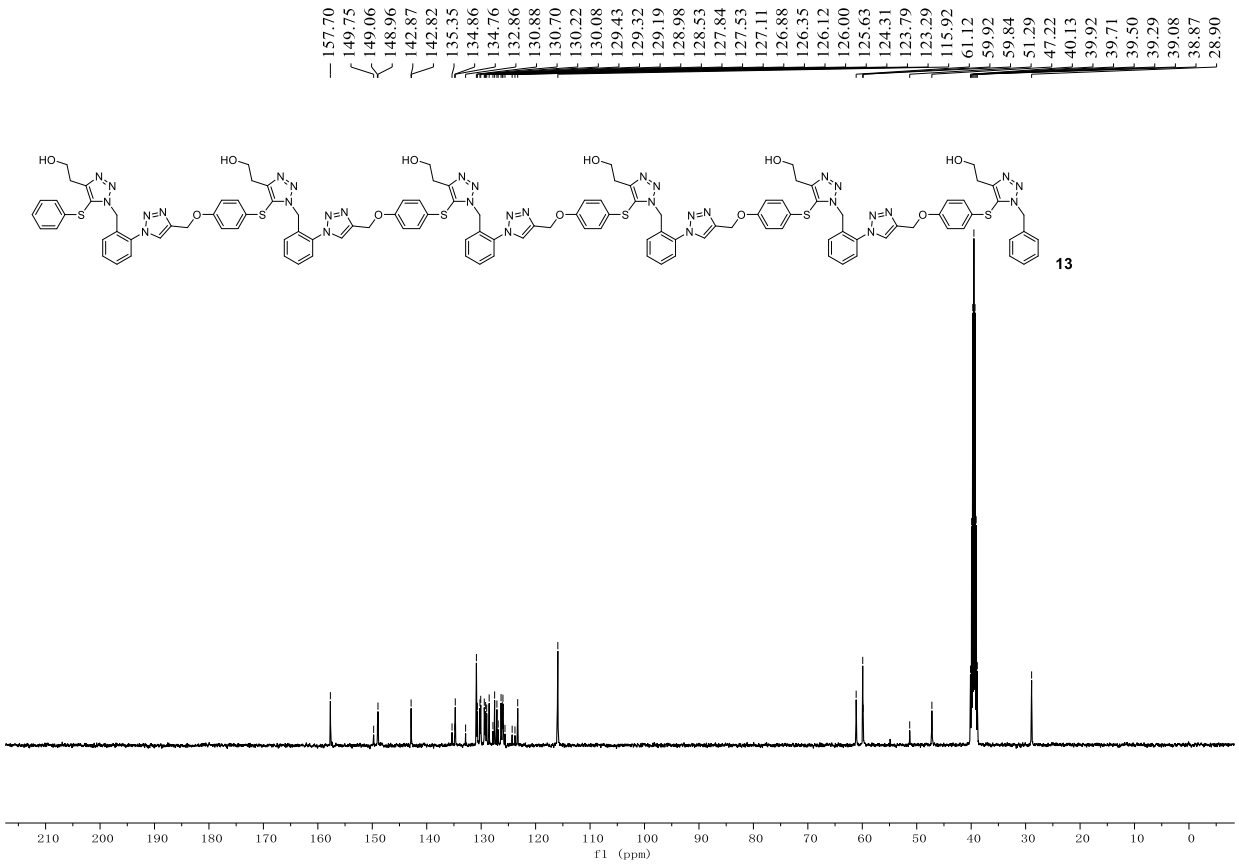


Figure S44. ^{13}C NMR spectra of **13** (DMSO, 100 MHz).

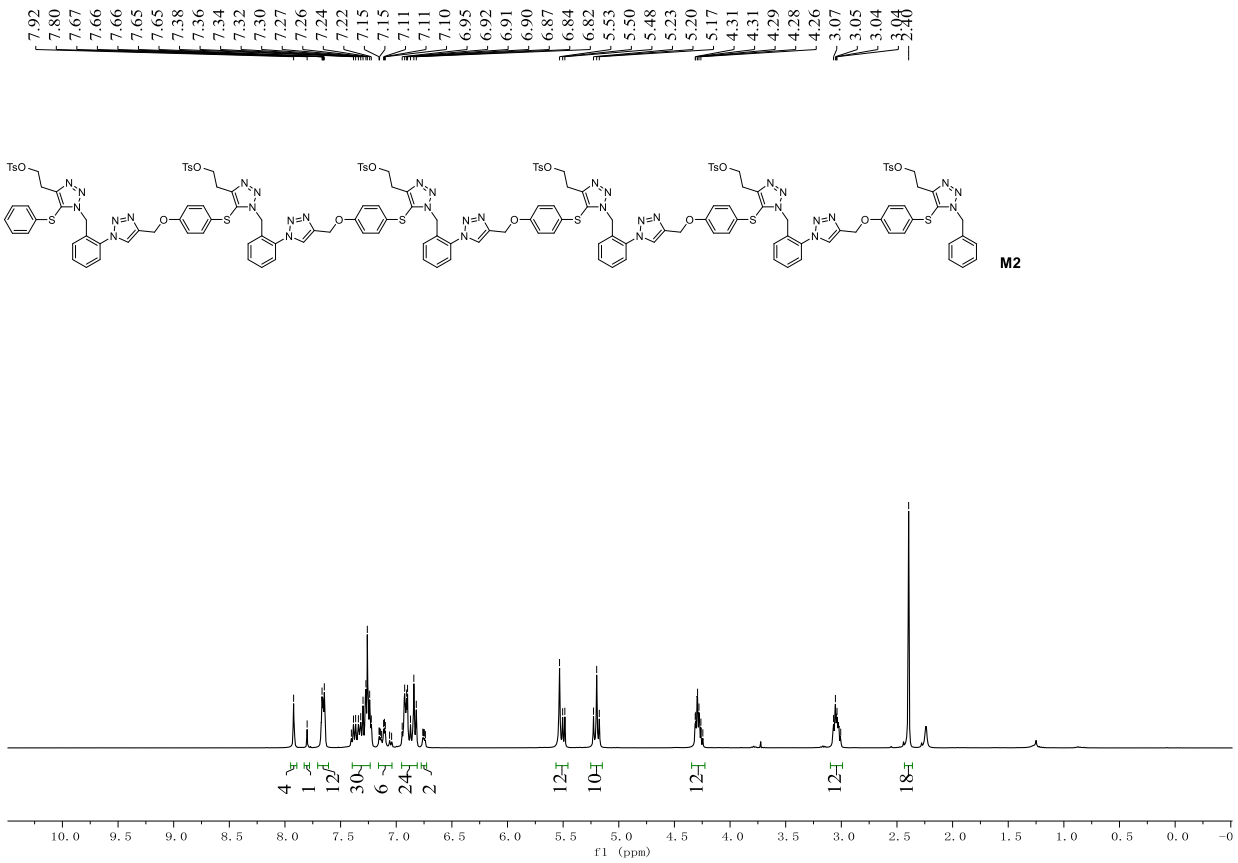


Figure S45. ^{1}H NMR spectra of **M2** ($CDCl_3$,400 MHz).

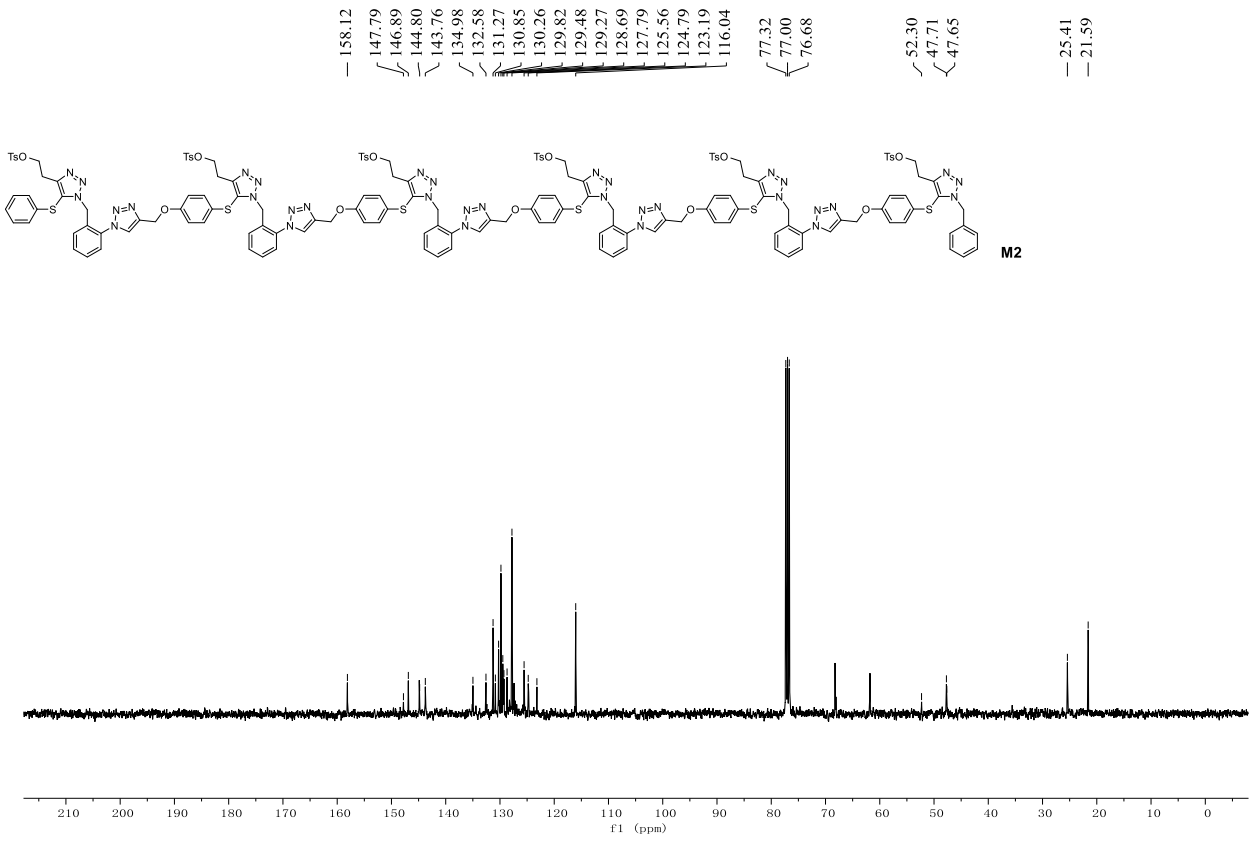


Figure S46. ^{13}C NMR spectra of **M2** ($CDCl_3$, 100 MHz).

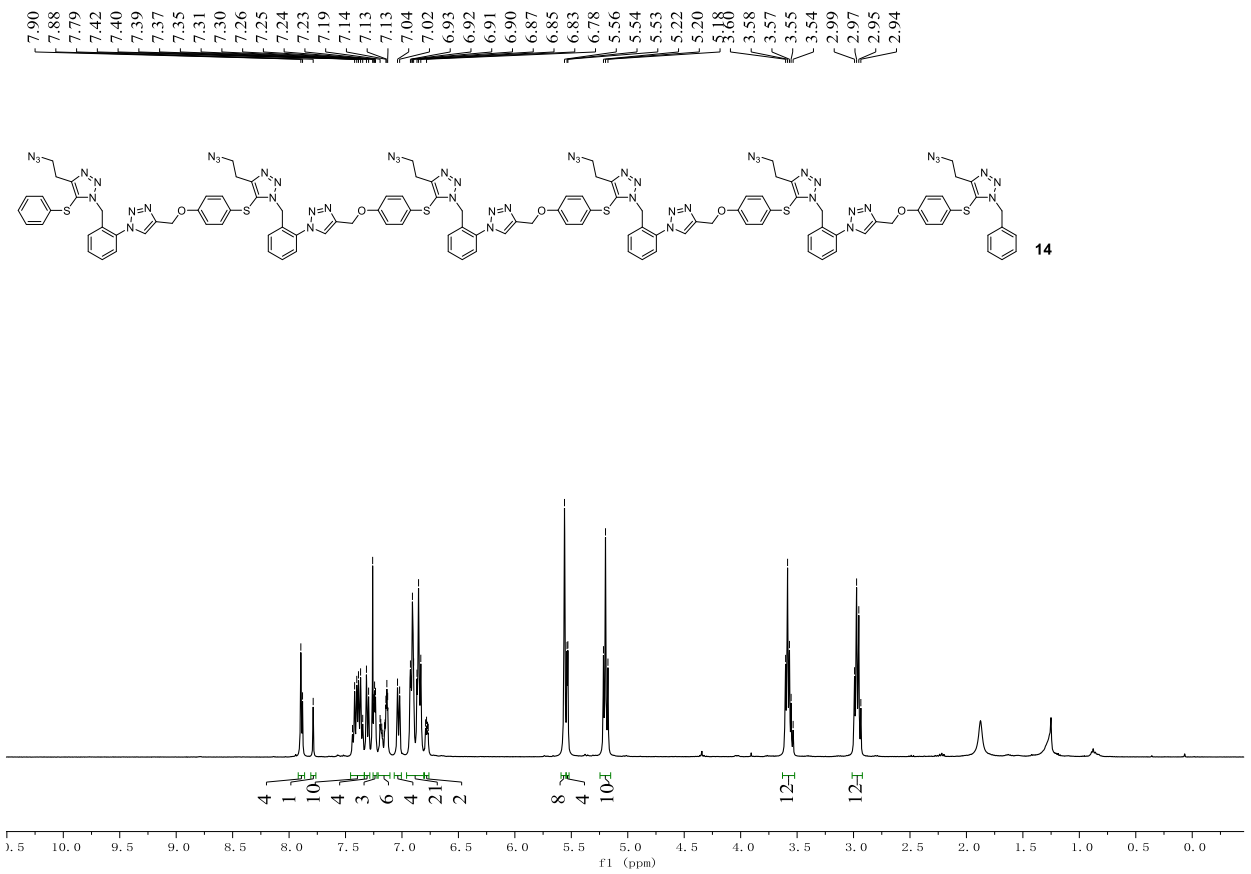


Figure S47. ^{1}H NMR spectra of **14** ($CDCl_3$, 400 MHz).

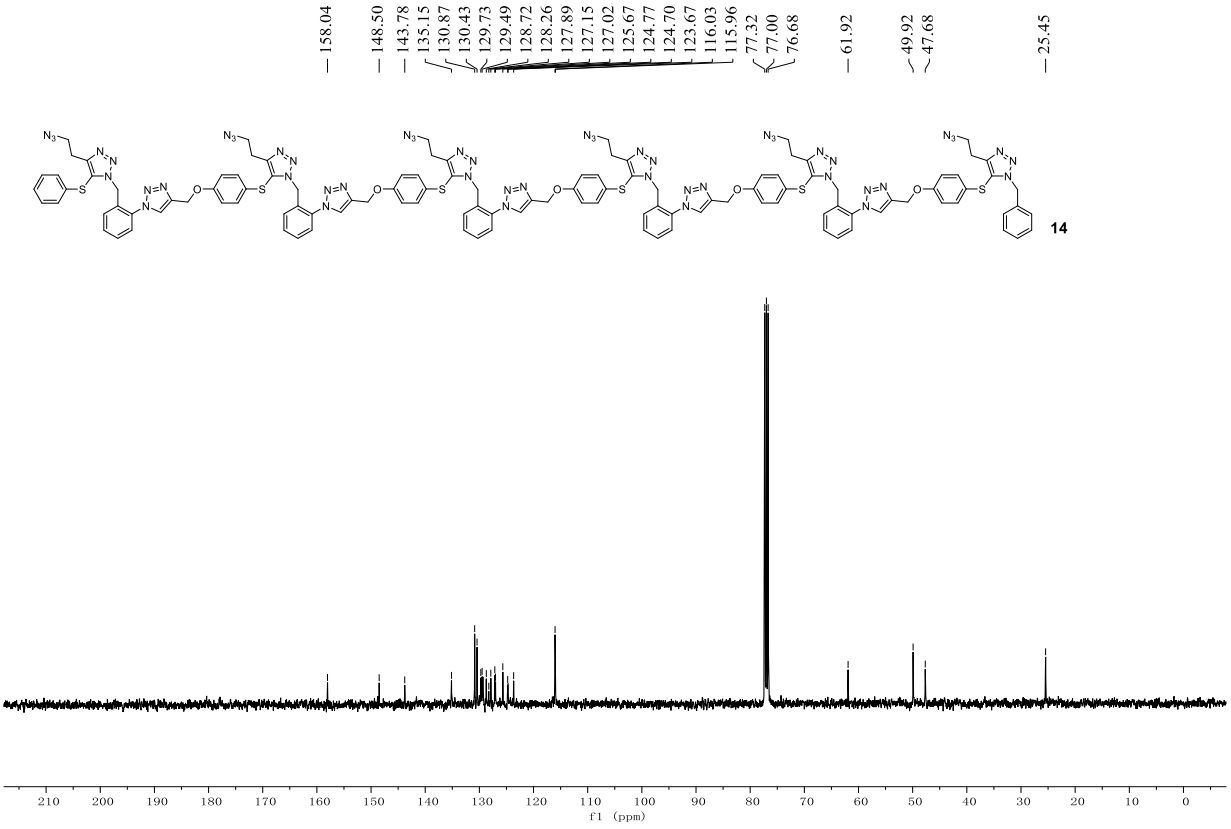


Figure S48. ^{13}C NMR spectra of **14** ($CDCl_3$, 100 MHz).

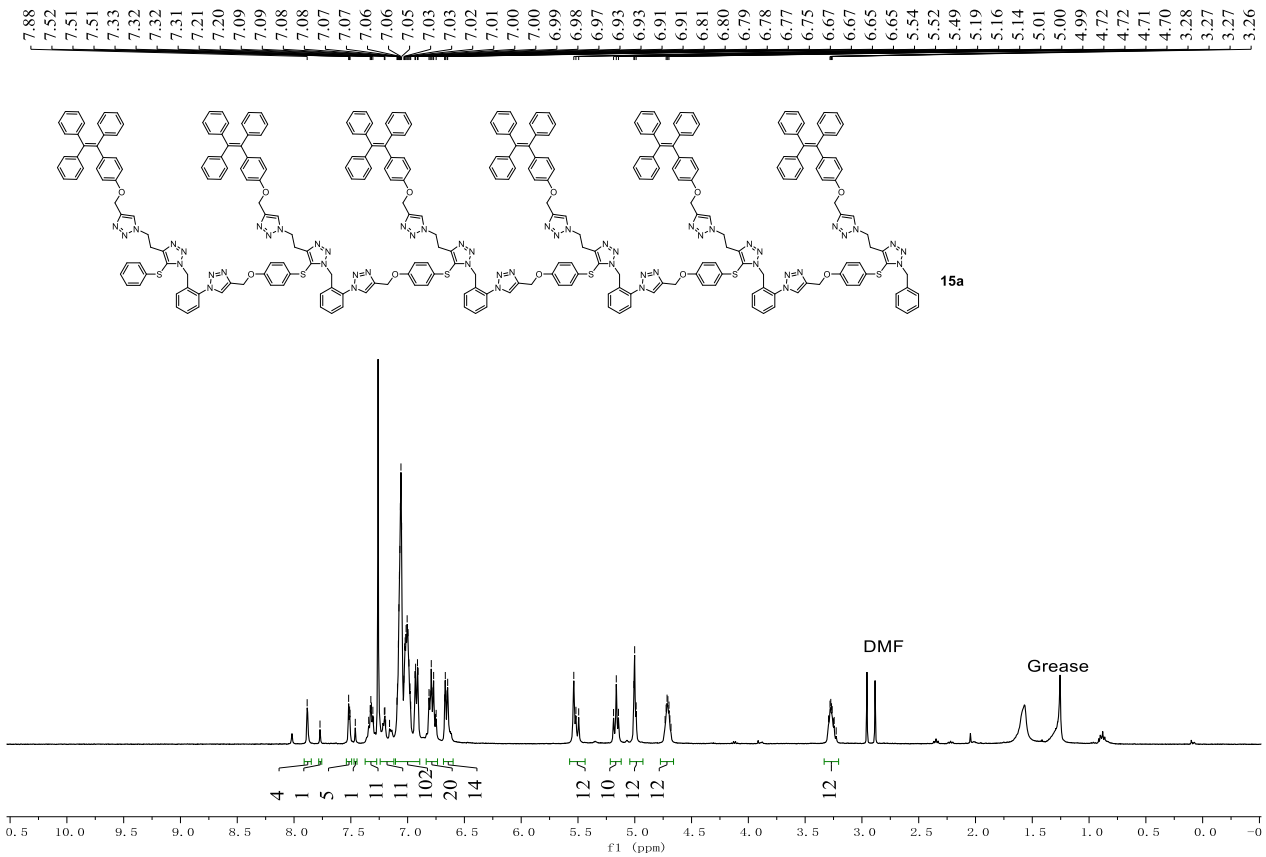


Figure S49. ^{1}H NMR spectra of **15a** ($CDCl_3$, 400 MHz).

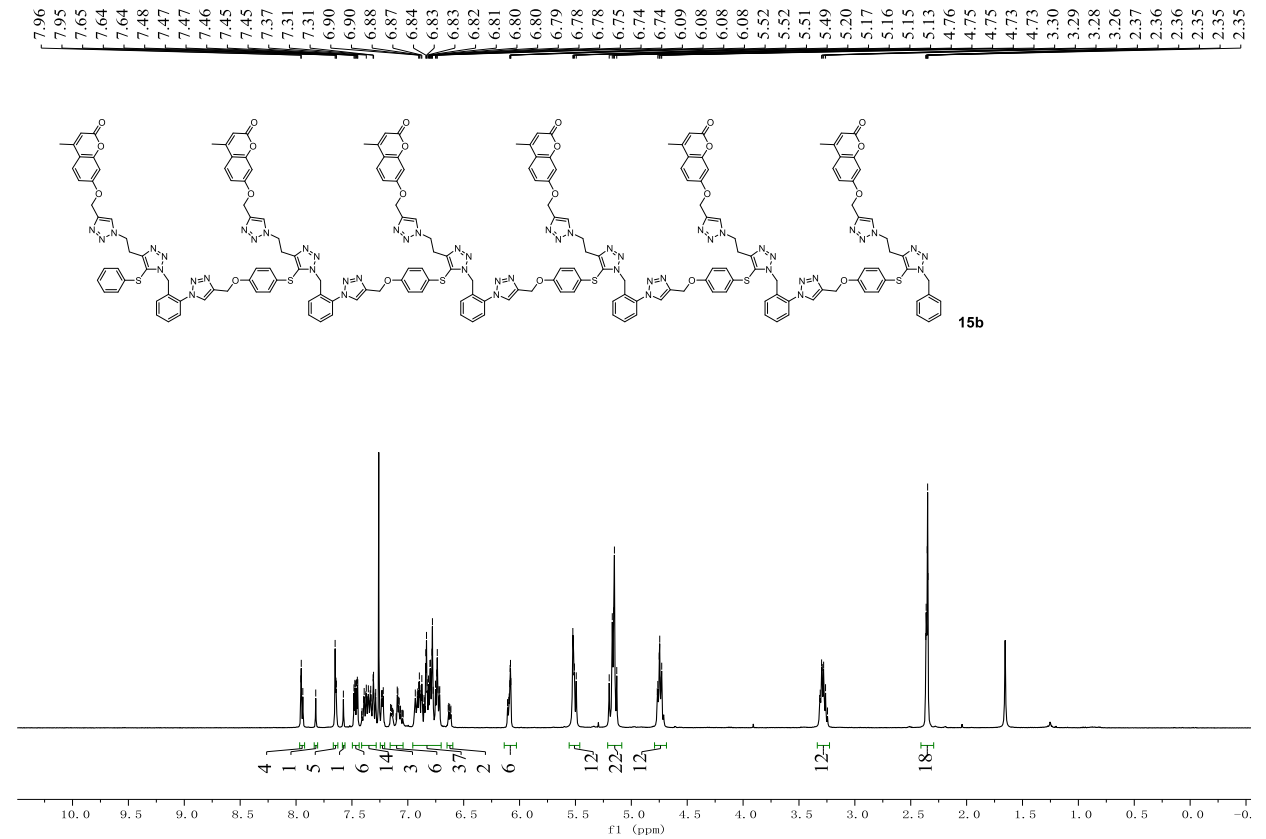


Figure S50. ^{1}H NMR spectra of **15b** ($CDCl_3$, 400 MHz).

VII. References

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