Supporting Information

Catalytic enrichment of oligothioalkynes: expanding horizons for functionalized oligotriazole synthesis through IrAAC-mediated post-modification

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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 complexes were 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-*d*6 at 2.54 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm, DMSO-*d*6 at 39.5 ppm).

MS. ESI-MS analyses were measured on Agilent 6540 UHD Accurate-Mass Q-TOF. FTMS (**2-3**, **27-28**) were measured on Bruker Solarix XR Fourier transform ion cyclotron resonance mass spectrometer. MALDI-TOF-MS was measured on a AB Sciex 5800 using α-cyano-4-hydroxycinnamic acid (CHCA) or 2,5-dihydroxybenzoic acid (DHB) as the matrix.

HPLC. High performance liquid chromatography (HPLC) was measured on Shimadzu LC-20AT with a column Shimadzu-GL ODS-3 5um, 4.6*250mm. The conditions of the HPLC method are as follows: 5% acetonitrile - 95%water; Flow rate: 0.3 ml/min; Column temperature of 40ºC; Injection volume of 2 μL. The signal was monitored at 214 nm.

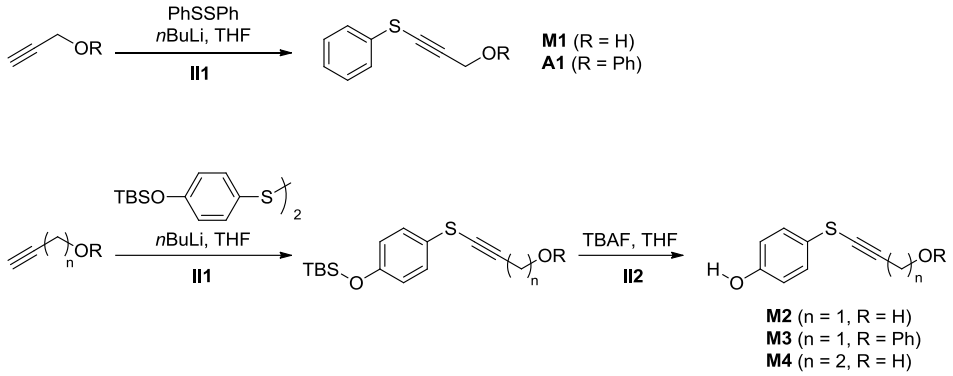
LC-MS. LC-MS analysis was measured on Xevo G2 Qtof with Waters Acquity SDS. The instrument was calibrated in the m/z range 50–1800 with an electrospray source (ESI-MS). The conditions of the reversed phase HPLC method are as follows: initial 5.0% acetonitrile - 95.0%water, 3 min 15.0% acetonitrile - 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 45ºC; 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 ℃ for 40 min. The differential refractive index of each compound was monitored using a WAT038040 (2414) detector.

UV. UV/Vis spectroscopy was performed on a Metash UV-6000PC spectrometer. The spectra were recorded between 200 and 600 nm, with a bandwidth of 1.0 nm, time per point 1 s and two repetitions.

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 500 V and three repetitions.

II. Preparation of Thioalkyne Monomers and Oligothioalkynes



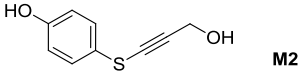
Scheme S1. Preparation of thioalkyne monomers.

General procedure:

II1. At -78 °C, to a solution of alkyne (1.0 eq.) in dry THF (0.25 M) under N_2 atmosphere was slowly added *n*BuLi (R = H, 2.2 eq.; R = Ph, 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.

II2. The TBS-protected thioalkyne was dissolved in THF (0.5 M), TBAF·$3H_2O$ (1.1 eq.) was added at 0 °C and stirred another 20 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 purified by silica gel flash column chromatography to give pure product.

M1 is known compound.[1]



M2

4-((3-hydroxyprop-1-yn-1-yl)thio)phenol (M2)

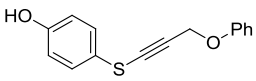
Overall yield = 50%.

Rf = 0.3 (PE/EA = 3/1).

^{1}H NMR (400 MHz, DMSO-d6) δ 9.76 (s, 1 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 6.86 (d, *J* = 8.0 Hz, 2 H), 5.34 (s, 1 H), 4.31 (s, 2 H).

^{13}C NMR (100 MHz, DMSO-d6) δ 157.7, 129.7, 119.8, 117.2, 98.5, 71.9, 50.4.

HRMS *m/z* (ESI) calcd. for $C_9H_{12}O_2SN$ $(M+NH_4)^+$ 198.0589, found 198.0900.



M3

4-((3-phenoxyprop-1-yn-1-yl)thio)phenol (M3)

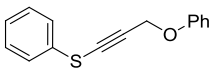
Overall yield = 72%.

Rf = 0.4 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.30 (m, 2 H), 7.28-7.25 (m, 2 H), 7.05-6.99 (m, 3 H), 6.82-6.78 (m, 2 H), 4.89 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 155.1, 129.6, 129.5, 122.2, 121.6, 116.5, 115.0, 92.3, 76.8, 56.9.

HRMS *m/z* (ESI) calcd. for $C_{15}H_{12}O_2SNa$ $(M+Na)^+$ 279.0546, found 279.0855.



A1

(3-phenoxyprop-1-yn-1-yl)(phenyl)sulfane (A1)

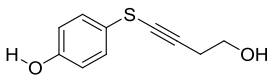
Yield = 86%.

Rf = 0.5 (PE/EA = 50/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.42 (m, 2 H), 7.39-7.34 (m, 4 H), 7.29-7.25 (m, 1 H), 7.08-7.05 (m, 3 H), 4.96 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 132.0, 129.4, 129.24, 129.18, 126.7, 126.5, 121.5, 115.0, 94.0, 74.9, 56.7.

HRMS *m/z* (ESI) calcd. for $C_{15}H_{12}OSNa$ $(M+Na)^+$ 263.0507, found 263.1959.



M4

4-((4-hydroxybut-1-yn-1-yl)thio)phenol (M4)

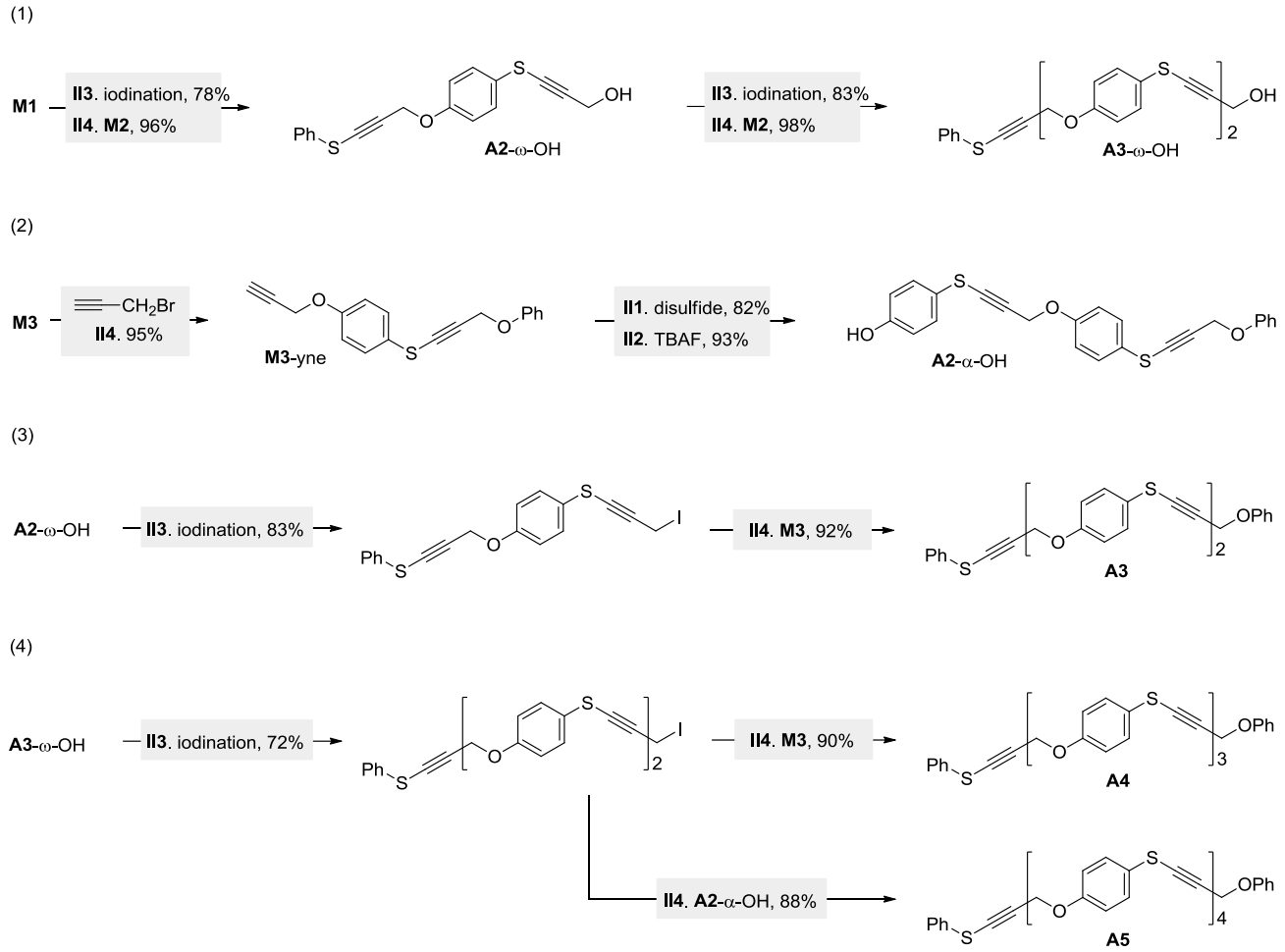
Overall yield = 78%.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.29 (m, 2 H), 6.83-6.80 (m, 2 H), 3.78 (t, *J* = 8.0 Hz, 2 H), 2.69 (t, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 129.1, 123.0, 116.5, 94.1, 69.2, 61.0, 24.6.

HRMS *m/z* (ESI) calcd. for $C_{10}H_9O_2S$ $(M-H)^-$ 193.0323, found 193.0381.

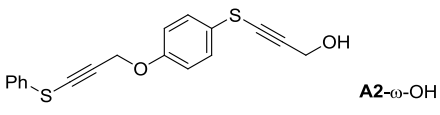


Scheme S2. Preparation of "capped" oligothioalkynes.

General procedure:

II3. To a round bottom flask was added the aliphatic hydroxyl group-involved thioalkyne (1.0 eq.), PPh_3 (1.2 eq.), imidazole (1.2 eq.), iodine (1.2 eq.) into DCM at 0 °C and stirred for 20 minutes. Upon completion indicated by TLC, sodium thiosulfate aqueous solution was added. The aqueous layer was separated and the organic layer was dried over $MgSO_4$ and purified by silica gel flash column chromatography to give pure product.

II4. To a round bottom flask was added phenolic hydroxyl group-involved thioalkyne (1.0 eq.), K_2CO_3 (2.0 eq.) and MeCN (0.5 M). To the stirring solution was added iodo- or bromo-substrates (1.0 eq.) and the reaction was stirred for 4 hours at 70 °C. The mixture was filtered and the solvent was removed by rotary evaporation. The organic layer was dried over Na_2SO_4. **A3** was obtained by purification through silica gel flash column chromatography. Products **A4** and **A5** were obtained by recrystallization with EA/hexane.



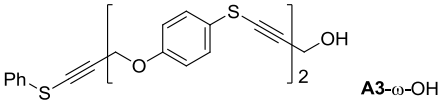
A2-ω-OH

Overall yield = 75%.

Rf = 0.3 (PE/EA = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.30 (m, 4 H), 7.29-7.23 (m, 2 H), 7.20-7.16 (m, 1 H), 6.95-6.90 (m, 2 H), 4.82 (s, 2 H), 4.41 (s, 2 H), 3.27 (1 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 131.4, 129.0, 128.6, 126.6, 123.3, 115.9, 96.0, 93.4, 75.2, 73.6, 56.7, 51.3.



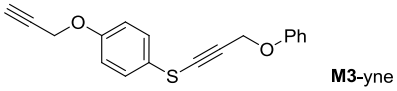
A3-ω-OH

Overall yield = 81%.

Rf = 0.3 (PE/EA = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.31 (m, 4 H), 7.30-7.24 (m, 4 H), 7.21-7.14 (m, 1 H), 6.94-6.88 (m, 4 H), 4.86 (s, 2 H), 4.81 (s, 2 H), 4.41 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.92, 156.85, 131.7, 129.2, 129.16, 128.9, 126.8, 126.5, 123.5, 123.2, 116.2, 116.15, 96.0, 93.4, 92.1, 75.6, 74.2, 56.98, 56.95, 51.8.



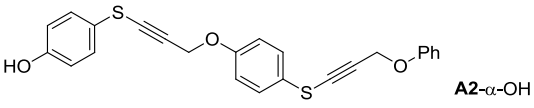
M3-yne

Yield = 95%.

Rf = 0.4 (PE/EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.30 (m, 4 H), 7.05-6.94 (m, 5 H), 4.89 (s, 2 H), 4.69 (d, *J* = 4.0 Hz, 2 H), 2.55 (t, *J* = 4.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 156.95, 129.4, 129.1, 123.4, 121.5, 115.96, 115.0, 92.7, 78.1, 76.2, 75.8, 56.7, 55.9.



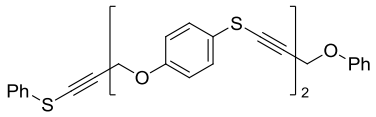
A2-α-OH

Overall yield = 76%.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.29 (m, 4 H), 7.23-7.20 (m, 2 H), 7.04-6.99 (m, 3 H), 6.97-6.93 (m, 2 H), 6.83-6.78 (m, 2 H), 4.92 (s, 2 H), 4.86 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 156.8, 155.4, 129.7, 129.5, 129.0, 123.2, 121.8, 116.4, 116.3, 115.0, 92.5, 91.7, 77.4, 77.2, 57.0, 56.9.



A3

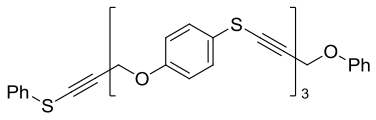
Yield = 92%.

Rf = 0.4 (PE/EA = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 10 H), 7.25-7.21 (m, 1 H), 7.02-6.93 (m, 7 H), 4.90 (s, 2 H), 4.89 (s, 2 H), 4.87 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 157.1, 157.0, 131.8, 129.4, 129.2, 129.0, 126.9, 126.6, 123.4, 123.2, 121.5, 116.2, 115.0, 93.4, 92.8, 92.1, 76.9, 76.2, 75.6, 57.01, 56.98, 56.8.

HRMS *m/z* (ESI) calcd. for $C_{33}H_{24}O_3S_3K$ $(M+K)^+$ 603.0525, found 603.0517.



A4

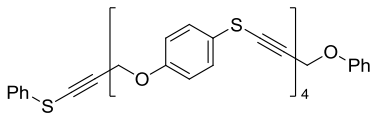
Yield = 90%.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.30 (m, 12 H), 7.26-7.22 (m, 1 H), 7.04-6.94 (m, 9 H), 4.91 (s, 2 H), 4.90 (s, 2 H), 4.88 (s, 2 H), 4.87 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 157.0, 156.9, 131.7, 129.4, 129.2, 129.13, 129.09, 128.9, 126.8, 126.5, 123.2, 123.1, 123.0, 121.4, 116.14, 116.11, 114.9, 93.4, 92.8, 92.13, 92.08, 76.1, 75.5, 56.9, 56.7.

HRMS *m/z* (ESI) calcd. for $C_{42}H_{30}O_4S_4K$ $(M+K)^+$ 765.0659, found 765.0674.



A5

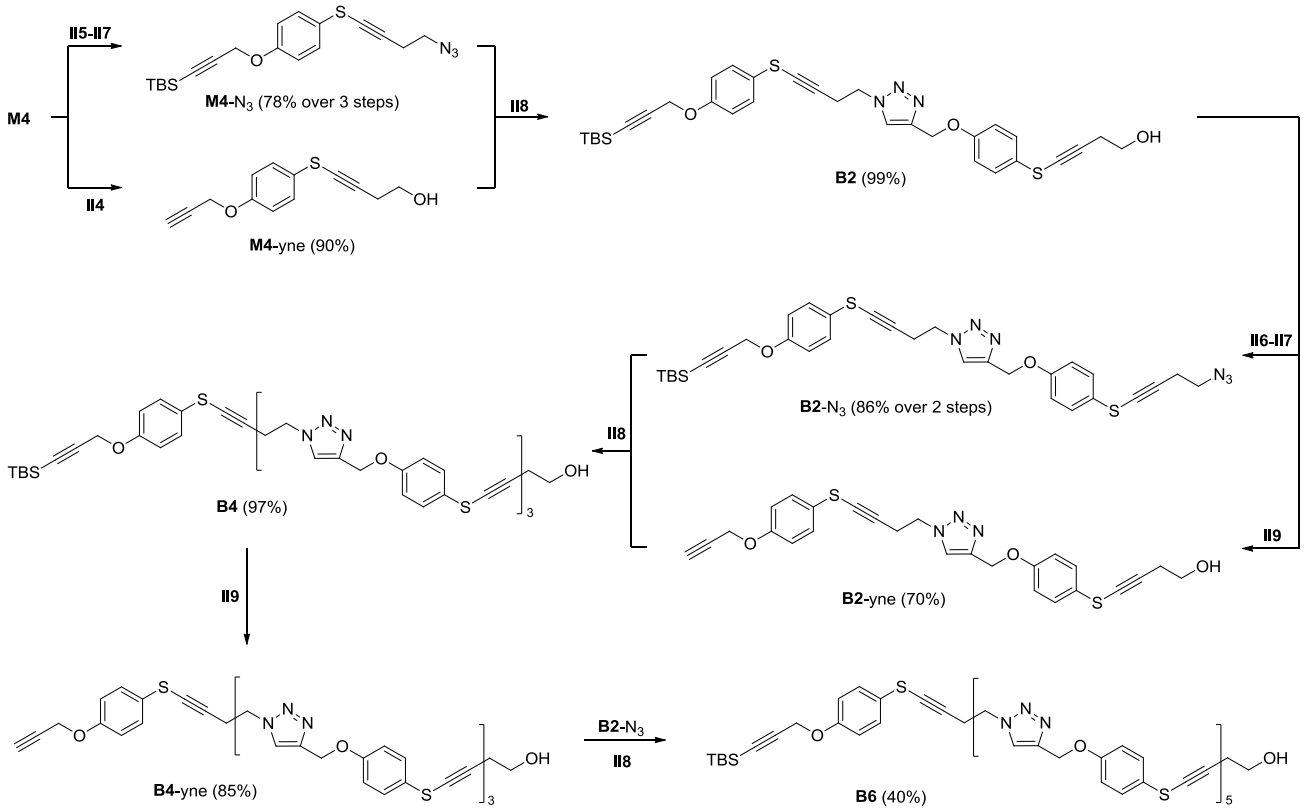
Yield = 88%.

Rf = 0.3 (PE/EA = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.28 (m, 16 H), 7.06-6.98 (m, 10 H), 4.95 (s, 2 H), 4.94 (s, 2 H), 4.93-4.90 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 157.03, 156.95, 131.8, 131.18, 130.21, 129.4, 129.23, 129.22, 129.17, 129.0, 126.9, 126.6, 123.3, 123.2, 123.11, 123.09, 121.5, 116.21, 116.18, 116.0, 115.0, 93.4, 92.8, 92.12, 92.06, 77.2, 76.88, 76.85, 76.2, 75.6, 57.01, 56.98, 56.7.

HRMS *m/z* (ESI) calcd. for $C_{51}H_{37}O_5S_5$ $(M+H)^+$ 889.1245, found 889.1237.



Scheme S3. Preparation of extensible oligothioalkynes.

General procedure：

II5. To a round bottom flask was added **M4** (1.0 eq.), K_2CO_3 (2.0 eq.), TBAI (0.01 eq.) and MeCN (0.5 M). To the stirring solution was added 1-bromo-3-*tert*-butyldimethylsilyl-2-propyne (1.0 eq.) and the reaction was left to stir for 2 hours at 80 °C. The solvent was removed by rotary evaporation and the crude product was extracted with EA. The organic layer was dried over Na_2SO_4 and concentrated. The residual was purified by flash chromatography to afford the desired product.

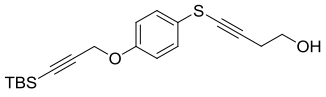
II6. Product from step II5 was dissolved in DCM (0.5 M). Et_3N (2.0 eq.), 4-dimethylaminopyridine (DMAP, 0.01 eq.) and 4-toluenesulfonyl chloride (TsCl, 1.5 eq.) were added under 0 °C. The reaction mixture was stirred at room temperature until completed indicated by TLC, and then washed with brine

(three times), dried over Na_2SO_4. The mixture was filtered and the organic layer was concentrated before being purified by flash chromatography with EA and hexanes to afford the **-OTs** product.

II7. To an oven dried round bottom flask was added the **-OTs** product (1.0 eq.), NaN_3 (1.5 eq.) and DMF. The reaction mixture was then stirred at 80 °C for 2 hours. The mixture was then cooled to room temperature, diluted with ethyl acetate. The organic layer was washed with brine (three times) and dried over Na_2SO_4. The mixture was filtered and the organic layer was concentrated before being purified by flash chromatography with EA and hexanes to afford the azide product.

II8. To a solution of **azide** (1.05 eq.) in DMF (0.5 M), sodium ascorbate (0.5 eq.), PMDETA (0.2 eq.), CuBr (0.2 eq.) and **alkyne** (1.0 eq.) were added. The mixture was stirred until the reaction went to completion (monitored by TLC), then water was added and the mixture was extracted with EA. The combined organic layer was washed with brine and dried over Na_2SO_4. Evaporation of the solvent under vacuum gave a yellow oily residue which was purified by column chromatography to afford the desired coupling product.

II9. The TBS-protected product was dissolved in THF (0.5 M), $TBAF{\cdot}3H_2O$ (1.1 eq.) was added at 0 °C and stirred for 20 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 purified by silica gel flash column chromatography to give the desired product.



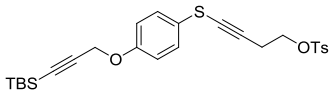
M4-OH

Yield = 93%.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.33 (m, 2 H),6.97-6.95 (m, 2 H), 4.67 (s, 2 H), 3.76 (t, *J* = 8.0 Hz, 2 H),2.68 (t, *J* = 8.0 Hz, 2 H), 1.99 (s, 1 H), 0.89 (s, 9 H), 0.1 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 128.4, 124.1, 116.2, 100.3, 94.5, 91.5, 68.6, 60.9, 56.9, 25.9, 24.6, 16.4, -4.9.



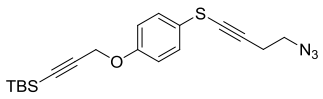
M4-OTs

Yield = 96%.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 2 H), 7.34-7.30 (m, 4 H), 6.98-6.96 (m, 2 H), 4.69 (s, 2 H), 4.15 (t, *J* = 8.0 Hz, 2 H), 2.79 (t, *J* = 8.0 Hz, 2 H), 2.43 (s, 3 H), 0.92 (s, 9 H), 0.12 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 144.9, 132.6, 129.8, 128.3, 127.8, 123.5, 116.1, 100.3, 91.9, 91.4, 69.5, 67.4, 56.8, 25.9, 21.5, 21.1, 16.4, -4.9.



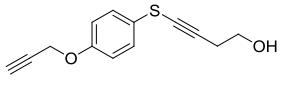
M4-N_3

Yield = 88%.

Rf = 0.7 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.34 (m, 2 H), 6.98-6.96 (m, 2 H), 4.68 (s, 2 H), 3.45 (t, *J* = 8.0 Hz, 2 H), 2.70 (t, *J* = 8.0 Hz, 2 H), 0.90 (s, 9 H), 0.10 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 128.6, 123.8, 116.2, 100.3, 93.6, 91.5, 69.4, 56.9, 49.9, 26.0, 21.3, 16.5, -4.8.



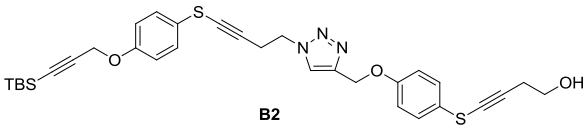
M4-yne

Yield = 90%.

Rf = 0.3 (PE/EA = 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.35 (m, 2 H),6.97-6.95 (m, 2 H), 4.68-4.67 (d, *J* = 4.0 Hz, 2 H), 3.77 (t, *J* = 8.0 Hz, 2 H), 2.68 (t, *J* = 8.0 Hz, 2 H), 2.53 (t, *J* = 4.0 Hz, 1 H),1.92 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 128.4, 124.4, 116.0, 94.7, 78.2, 75.8, 68.5, 61.0, 55.9, 24.6.



B2

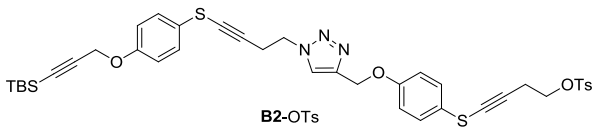
Yield = 99%.

Rf = 0.2 (PE/EA = 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1 H), 7.36-7.34 (m, 2 H), 7.30-7.28 (m, 2 H), 6.98-6.95 (m, 4 H), 5.18 (s, 2 H), 4.66 (s, 2 H), 4.55 (t, *J* = 8.0 Hz, 2 H), 3.79 (t, *J* = 8.0 Hz, 2 H), 3.04 (t, *J* = 8.0 Hz, 2 H), 2.70 (t, *J* = 8.0 Hz, 2 H), 2.04 (s, 1 H), 0.91 (s, 9 H), 0.11 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 157.2, 143.8, 128.9, 128.5, 124.0, 123.3, 116.2, 115.8, 100.2, 94.7, 92.3, 91.5, 70.9, 68.5, 62.0, 60.9, 56.8, 49.0, 29.6, 25.9, 24.6, 22.3, 16.4, -4.9.

HRMS *m/z* (ESI) calcd. for $C_{32}H_{38}N_3O_3S_2Si$ $(M+H)^+$ 604.2124, found 604.2100.



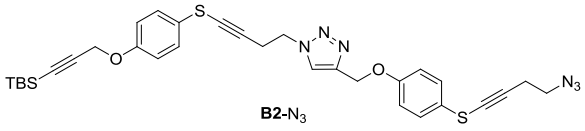
B2-OTs

Yield = 94%.

Rf = 0.3 (PE/EA = 1/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2 H), 7.72 (s, 1 H), 7.34-7.27 (m, 6 H), 6.97-6.94 (m, 4 H), 5.17 (s, 2 H), 4.66 (s, 2 H), 4.54 (t, *J* = 8.0 Hz, 2 H), 4.14 (t, *J* = 8.0 Hz, 2 H), 3.03 (t, *J* = 8.0 Hz, 2 H), 2.78 (t, *J* = 8.0 Hz, 2 H), 2.43 (s, 3 H), 0.91 (s, 9 H), 0.11 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 157.1, 144.9, 143.6, 132.6, 129.8, 128.8, 128.6, 127.8, 123.4, 123.2, 116.2, 115.8, 100.2, 92.3, 91.9, 91.5, 70.8, 69.5, 67.4, 61.9, 56.8, 48.9, 25.9, 22.2, 21.6, 21.1, 16.4, -4.9.



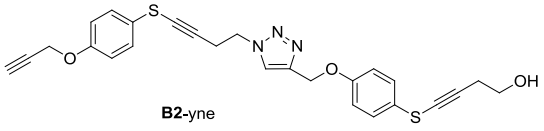
B2-N_3

Yield = 91%.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1 H), 7.38-7.36 (m, 2 H), 7.31-7.29 (m, 2 H), 6.99-6.96 (m, 4 H), 5.19 (s, 2 H), 4.67 (s, 2 H), 4.56 (t, *J* = 8.0 Hz, 2 H), 3.47 (t, *J* = 8.0 Hz, 2 H), 3.05 (t, *J* = 8.0 Hz, 2 H), 2.72 (t, *J* = 8.0 Hz, 2 H), 0.92 (s, 9 H), 0.12 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 157.2, 143.7, 128.9, 128.8, 123.7, 123.3, 123.2, 116.2, 115.9, 100.2, 93.7, 92.3, 91.6, 70.9, 69.3, 62.1, 56.9, 49.8, 48.9, 25.9, 22.3, 21.2, 16.4, -4.9.



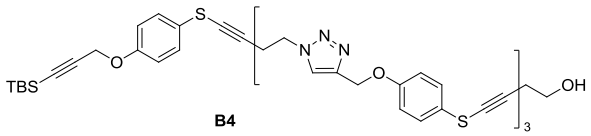
B2-yne

Yield = 70%.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1 H), 7.35-7.33 (m, 2 H), 7.29-7.27 (m, 2 H), 6.96-6.93 (m, 4 H), 5.17 (s, 2 H), 4.64 (d, *J* = 2.4 Hz, 2 H), 4.54 (t, *J* = 8.0 Hz, 2 H), 3.77 (t, *J* = 8.0 Hz, 2 H), 3.03 (t, *J* = 8.0 Hz, 2 H), 2.69 (t, *J* = 8.0 Hz, 2 H), 2.53 (t, *J* = 4.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 156.9, 143.8, 128.9, 128.6, 124.0, 123.6, 123.2, 116.0, 115.9, 94.7, 92.4, 78.1, 77.2, 76.7, 75.9, 70.9, 68.6, 62.1, 60.9, 55.9, 49.0, 24.6, 22.3.



B4

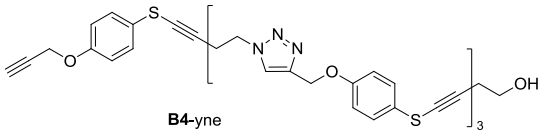
Yield = 97%.

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

^{1}H NMR (400 MHz, DMSO-d6) δ 8.27 (d, *J* = 8.0 Hz, 3 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 7.27-7.24 (m, 6 H), 7.08-6.99 (m, 8 H), 5.15-5.13 (m, 6 H), 4.92 (t, *J* = 4.0 Hz, 1 H), 4.81 (s, 2 H), 4.59 (t, *J* = 8.0 Hz, 6 H), 3.58-3.53 (m, 2 H), 3.09 (t, *J* = 8.0 Hz, 6 H), 2.58 (t, *J* = 8.0 Hz, 2 H), 0.85 (s, 9 H), 0.06 (s, 6 H).

^{13}C NMR (100 MHz, DMSO-d6) δ 157.3, 157.2, 156.5, 142.4, 128.1, 127.9, 127.8, 124.6, 122.8, 122.7, 122.2, 116.3, 116.0, 101.7, 97.4, 95.04, 94.95, 90.3, 68.0, 67.9, 65.9, 61.3, 59.6, 56.4, 48.1, 25.7, 24.1, 21.4, 16.1, -4.9.

HRMS *m/z* (ESI) calcd. for $C_{58}H_{59}N_9O_5S_4Si$ $(M+COOH)^-$ 1162.3273, found 1162.3290.



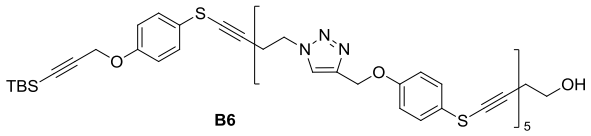
B4-yne

Yield = 85%.

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

^{1}H NMR (400 MHz, DMSO-d6) δ 8.28-8.26 (m, 3 H), 7.36-7.34 (m, 2 H), 7.29-7.22 (m, 6 H), 7.08-6.99 (m, 8 H), 5.15-5.13 (m, 6 H), 4.92 (t, *J* = 4.0 Hz, 1 H), 4.78 (s, 2 H), 4.60-4.56 (m, 6 H), 3.58-3.52 (m, 3 H), 3.11-3.08 (m, 6 H), 2.57 (t, *J* = 12.0 Hz, 2 H).

^{13}C NMR (100 MHz, DMSO-d6) δ 157.3, 157.2, 156.5, 142.5, 128.10, 128.08, 128.0, 127.8, 124.7, 122.8, 122.7, 122.2, 116.2, 116.0, 101.7, 97.4, 95.1, 95.0, 79.0, 78.4, 68.02, 67.99, 67.90, 65.9, 61.3, 59.6, 55.6, 48.1, 25.8, 24.1, 21.4.



B6

Yield = 40%.

Rf = 0.4 (DCM/MeOH = 25/1).

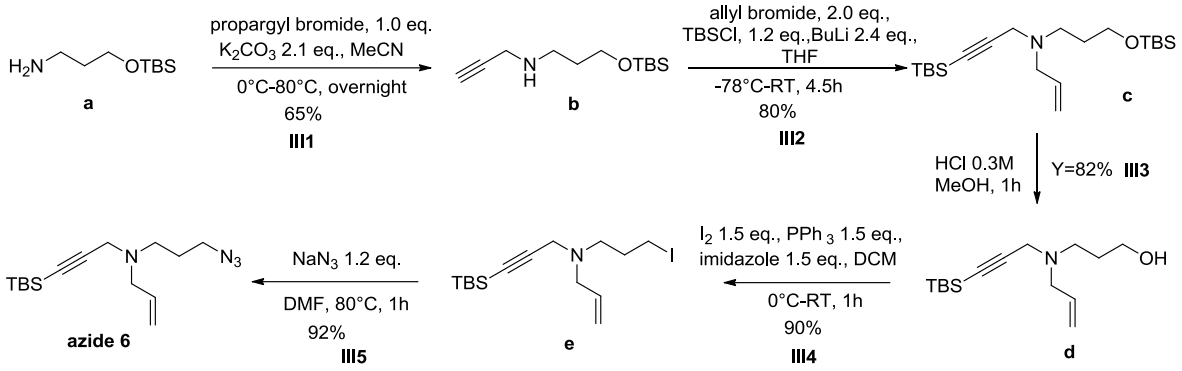
^{1}H NMR (400 MHz, DMSO-d6) δ 8.27 (d, *J* = 4.0 Hz, 5 H), 7.36-7.34 (m, 2 H), 7.27-7.23 (m, 10 H), 7.08-6.99 (m, 12 H), 5.15-5.13 (m, 10 H), 4.91 (t, *J* = 4.0 Hz, 1 H), 4.81 (s, 2 H), 4.58 (t, *J* = 8.0 Hz, 10 H), 3.57-3.53 (m, 2 H), 3.09 (t, *J* = 8.0 Hz, 6 H), 2.57 (t, *J* = 8.0 Hz, 2 H), 0.84 (s, 9 H), 0.06 (s, 6 H).

^{13}C NMR (100 MHz, DMSO-d6) δ 157.3, 157.2, 156.5, 142.4, 128.1, 127.9, 127.8, 124.7, 122.8, 122.7, 122.2, 116.3, 116.1, 116.0, 101.7, 97.4, 95.0, 90.3, 68.0, 67.9, 65.9, 61.3, 59.6, 56.4, 48.1, 25.8, 25.7, 24.0, 21.4, 16.1, -4.9.

HRMS *m/z* (ESI) calcd. for $C_{84}H_{83}N_{15}O_7S_6Si$ $(M+2H)^{2+}$ 816.7347, found 816.7360.

III. Preparation of Organic Azides

Benzyl azide (**azide 1**), 1-(azidomethyl)pyrene (**azide 2**),[2] 1-azido-3-propanol (**azide 3**),[3] (4-azidobutyl)isoindole-1,3-dione (**azide 4**),[4] 4-azido-1-(trimethylsilyl)-1-butyne (**azide 5**),[5] (*S*)-2-(azidomethyl)-1-Boc-pyrrolidine (**azide 7**),[1] 4-bromobenzyl azide (**azide 10**),[5] 4-(azidomethyl)phenol (**azide 11**),[6] 9-anthracenylmethyl azide (**azide 12**),[7] 3-(azidomethyl)furan (**azide 13**),[8] 2,3,4,6-*tetra*-*O*-acetyl-β-*D*-glucopyranosyl azide (**azide 14**)[9] were know compounds.



Scheme S4. Synthesis of **azide 6**.

3-(*tert*-butyldimethylsilanoxy)propylamine (a) was prepared according to literature-known procedure.[10]

III1. To the solution of **a** (2.0 eq.), K_2CO_3 (2.1 eq.) in MeCN (0.5 M) was added propargyl bromide (1.0 eq.) at 0 °C and the reaction was left to stir overnight at 80 °C. The mixture was filtered and the solvent was removed by rotary evaporation. The residual was purified by flash chromatography to give 65% of product **b**.

III2. At -78 °C, to a solution of **b** (1.0 eq.) in dry THF (0.25 M) under N_2 atmosphere was slowly added *n*BuLi (2.4 eq.). The reaction mixture was stirred at the same temperature for 1 hour before TBSCl (1.2 eq.) and allyl bromide (2.0 eq.) were added. Then the reaction mixture was allowed warming to room temperature and stirred for 4.5 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, which was then purified by silica gel flash column chromatography to give 80% of pure product **c**.

III3. A solution of **c** (1.0 eq.) in MeOH (0.2 M) was cooled to 0 ºC, and HCl (0.3 M) was slowly added. The resulting light yellow solution was stirred for 1 h at 0 ºC. It was then quenched by addition of an aqueous $NaHCO_3$ solution and allowed to warm to r.t.. The aqueous layer was separated and extracted

with EA for three times. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated by rotary evaporation. The crude product was purified by flash chromatography to give 82% of pure product **d**.

III4. To a round bottom flask was added **d** (1.0 eq.), DCM, PPh_3 (1.5 eq.), imidazole (1.5 eq.) and iodine (1.5 eq.) at 0 °C and stirred for 1 hour. Upon completion, sodium thiosulfate aqueous solution was added. The aqueous layer was separated and the organic layer was dried over $MgSO_4$ and purified by silica gel flash column chromatography to give 90% of pure product **e**.

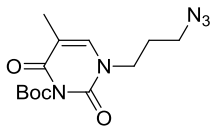
III5. To an oven dried round bottom flask was added **e** (1.0 eq.), NaN_3 (1.2 eq.) and DMF. The reaction mixture was then stirred at 80 °C for 1 hour. The mixture was then cooled to room temperature, diluted with ethyl acetate. The organic layer was washed with brine (three times) and dried over Na_2SO_4. The mixture was filtered and the organic layer was concentrated before being purified by flash chromatography with EA and hexanes to afford 92% of **azide 6**.

Rf = 0.5 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83-5.75 (m, 1 H), 5.24-5.12 (m, 2 H), 3.39 (s, 2 H), 3.32 (t, *J* = 12.0 Hz, 2 H), 3.11 (d, *J* = 4.0 Hz, 2 H), 2.57 (t, *J* = 12.0 Hz, 2 H), 1.72 (qui, *J* = 28.0 Hz, 2 H), 0.94 (s, 9 H), 0.10 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3, 118.0, 101.0, 88.2, 57.0, 49.9, 49.5, 42.5, 26.8, 26.1, 16.4, -4.5.

HRMS *m/z* (ESI) calcd. for $C_{15}H_{29}N_4Si$ $(M+H)^+$ 293.2162, found 293.2177.



azide 8

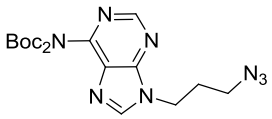
5-Methyl-2,6-dioxo-3,6-dihydro-2*H*-pyrimidine-1-carboxylic acid *tert*-butyl eater (1.0 eq.), 3-azidopropyl 4-methylbenzenesulfonate (1.1 eq.) and K_2CO_3 (1.5 eq.) were dissolved in DMF and stirred at 80 ºC for 3 h. The mixture was cooled to room temperature and washed with water, extracted with ethyl acetate for three times. The combined organic phase was washed with brine, dried over Na_2SO_4 and evaporated under vacuum. Purification of residue by silica gel column chromatography afforded the desired product as pale yellow oil in 80% yield.

Rf = 0.3 (PE/EA = 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 1.6 Hz, 2 H), 3.76 (t, *J* = 16.0 Hz, 2 H), 3.38 (t, *J* = 16.0 Hz, 2 H), 1.94 (quint, *J* = 28.0 Hz, 2 H), 1.89 (d, *J* = 1.6 Hz, 2 H), 1.57 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 151.1, 140.4, 110.8, 48.2, 46.0, 27.9, 12.2.

HRMS *m/z* (ESI) calcd. for $C_{13}H_{19}N_5O_4Na$ $(M+Na)^+$ 332.1335, found 332.1313.



azide 9

tert-Butyl (*tert*-butoxycarbonyl)(9*H*-purin-6-yl)carbamate (1.0 eq.), 3-azidopropyl 4-methylbenzenesulfonate (1.1 eq.) and K_2CO_3 (1.5 eq.) were dissolved in DMF and stirred at 80 ºC for 3 h. The mixture was cooled to room temperature and washed with water, extracted with ethyl acetate for three times. The combined organic phase was washed with brine, dried over Na_2SO_4 and evaporated under vacuum. Purification of residue by silica gel column chromatography afforded the desired product as pale yellow oil in 79% yield.

Rf = 0.3 (PE/EA = 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1 H), 8.06 (s, 1 H), 4.38 (t, *J* = 6.8 Hz, 2 H), 3.36 (t, *J* = 6.2 Hz, 2 H), 2.18 (p, *J* = 6.4 Hz, 2 H), 1.43 (s, 18 H).

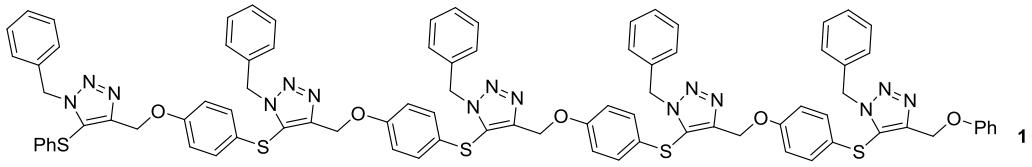
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 152.1, 150.4, 150.3, 144.7, 128.8, 83.7, 77.20, 48.1, 41.3, 28.8, 27.7.

HRMS *m/z* (ESI) calcd. for $C_{18}H_{26}N_8O_4Na$ $(M+Na)^+$ 441.1975, found 441.2018.

IV. Construction of Oligotriazoles by IrAAC-based Click Decoration

General procedure:

In a glove box, to an oven-dried vial was added the building unit involving azide group (1.5 ×(n+1) eq), oligothioalkyne (1.0 eq.), $[Ir(COD)Cl]_2$ (1.5 ×(n+1) mol %) and DMF/DCE 1:10 (0.1 M). The vial was capped and removed from the glove box. The reaction mixture was stirred at room temperature for 2-8 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.



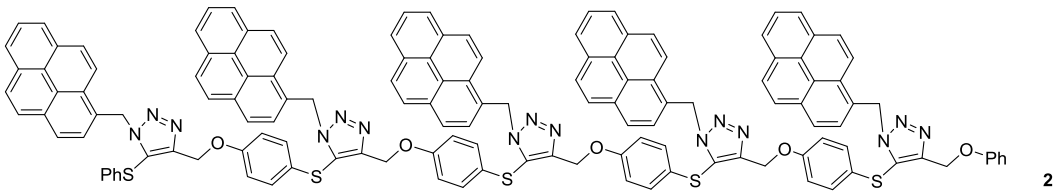
1

1 was prepared as pale yellow solid from benzyl azide (0.28 mmol, 37 mg, 7.0 eq.) and **A5** (0.04 mmol, 36 mg, 1.0 eq.) in 94% yield (58 mg).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.12 (m, 30 H), 6.96-6.90 (m, 13 H), 6.74-6.71 (m, 8 H), 5.52(m, 10 H), 5.11 (s, 2 H), 5.04-5.02 (m, 8 H).

HRMS *m/z* (ESI) calcd. for $C_{86}H_{72}N_{15}O_5S_5$ $(M+H)^+$ 1554.4445, found 1554.4459.



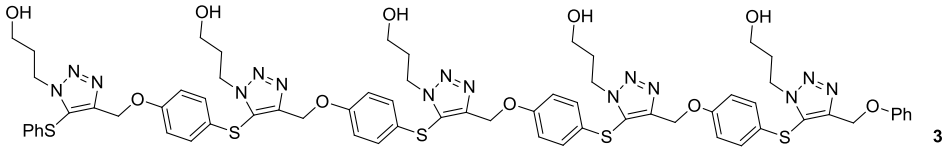
2

2 was prepared as brown solid from 1-(azidomethyl)pyrene (0.28 mmol, 72 mg, 7.0 eq.) and **A5** (0.04 mmol, 36 mg, 1.0 eq.) in 89% yield (77 mg).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27-8.17 (m, 6 H), 8.11-8.05 (m, 10 H), 8.01-7.75 (m, 26 H), 7.61-7.59 (m, 1 H), 7.48-7.41 (m, 4 H), 7.21-7.17 (m, 2 H), 6.93-6.87 (m, 3 H), 6.73-6.50 (m, 13 H), 6.26-6.24 (m, 8 H), 6.14-6.10 (m, 8 H), 5.09 (s, 2 H), 4.65-4.62 (m, 8 H).

FTMS *m/z* calcd. for $C_{136}H_{93}N_{15}O_5S_5$ $(M+2H)^{2+}$ 1088.3, found 1088.3.



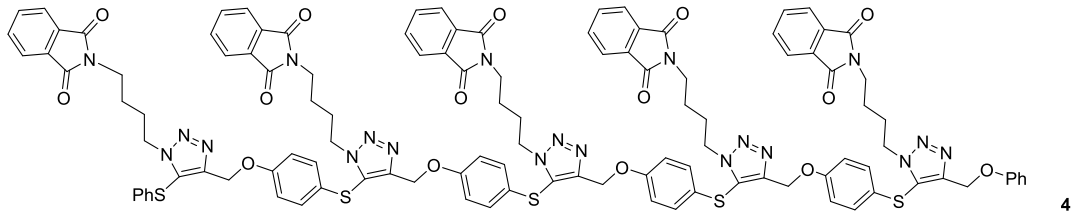
3

3 was prepared as white solid from 1-azido-3-propanol (0.28 mmol, 28 mg, 7.0 eq.) and **A5** (0.04 mmol, 36 mg, 1.0 eq.) in 85% yield (47 mg).

Rf = 0.3 (DCM/MeOH = 15:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.09 (m, 10 H), 7.08-7.02 (m, 4 H), 6.98-6.91 (m, 4 H), 6.85-6.79 (m, 7 H), 6.72 (s, 1 H), 5.15-4.95 (m, 10 H), 4.49-4.34 (m, 10 H), 3.58-3.48 (m, 10 H), 2.01-1.76 (m, 15 H).

FTMS *m/z* calcd. for $C_{66}H_{71}N_{15}O_{10}S_5Na$ $(M+Na)^+$ 1416.4005, found 1416.3999.



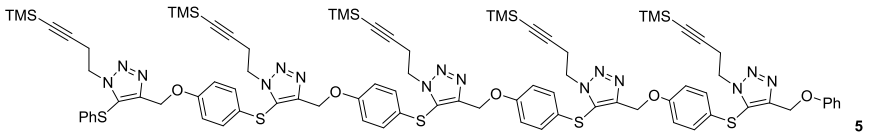
4

4 was prepared as brown solid from 2-(4-azidobutyl)isoindole-1,3-dione (0.28 mmol, 68 mg, 7.0 eq.) and **A5** (0.04 mmol, 36 mg, 1.0 eq.) in 92% yield (77 mg).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.77 (m, 10 H), 7.69-7.66 (m, 10 H), 7.24-7.21 (m, 2 H), 7.15-7.05 (m, 13 H), 5.12 (s, 2 H), 5.09-5.07 (m, 8 H), 4.36-4.32 (m, 10 H), 3.61-3.57 (m, 10 H), 1.77-1.74 (m, 10 H), 1.62-1.69 (m, 10 H).

HRMS *m/z* (ESI) calcd. for $C_{111}H_{98}N_{20}O_{15}S_5$ $(M+2H)^{2+}$ 1055.8080, found 1055.8083.



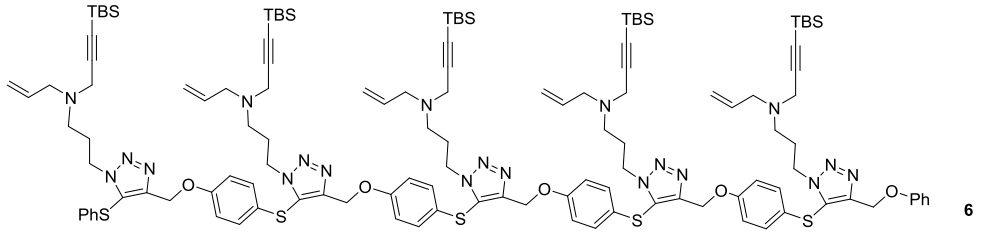
5

5 was prepared as white solid from 4-azido-1-(trimethylsilyl)-1-butyne (0.28 mmol, 46 mg, 7.0 eq.) and **A5** (0.04 mmol, 36 mg, 1.0 eq.) in 88% yield (60 mg).

Rf = 0.7 (PE/EA = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.20 (m, 4 H), 7.15-7.04 (m, 10 H), 6.96-6.93 (m, 4 H), 6.88-6.81 (m, 8 H), 5.12-5.06 (m, 10 H), 4.52-4.48 (m, 10 H), 2.75-2.72 (m, 10 H), 0.13-0.11 (m, 45 H).

HRMS *m/z* (ESI) calcd. for $C_{86}H_{102}N_{15}O_5S_5Si_5$ $(M+H)^+$ 1724.5639, found 1724.5539.



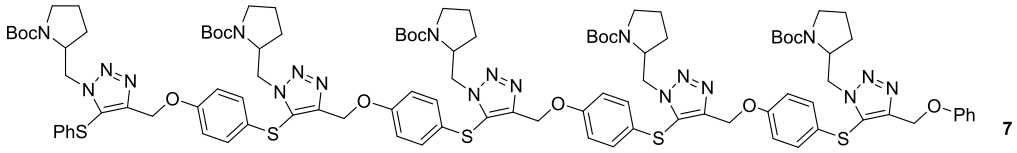
6

6 was prepared as white solid from **azide 6** (0.28 mmol, 81 mg, 7.0 eq.) and **A5** (0.04 mmol, 36 mg, 1.0 eq.) in 73% yield (69 mg).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.04 (m, 16 H), 6.98-6.95 (m, 2 H), 6.90-6.83 (m, 8 H), 5.75-5.72 (m, 5 H), 5.20-5.07 (m, 20 H), 4.39-4.36 (m, 10 H), 3.36-3.35 (m, 8 H), 3.34 (s, 2 H), 3.06-3.04 (m, 10 H), 2.52-2.50 (m, 10 H), 1.96-1.94 (m, 10 H), 0.93 (m, 45 H), 0.09 (m, 30 H).

HRMS *m/z* (ESI) calcd. for $C_{126}H_{178}N_{20}O_5S_5Si_5$ $(M+2H)^{2+}$ 1176.0887, found 1176.0847.



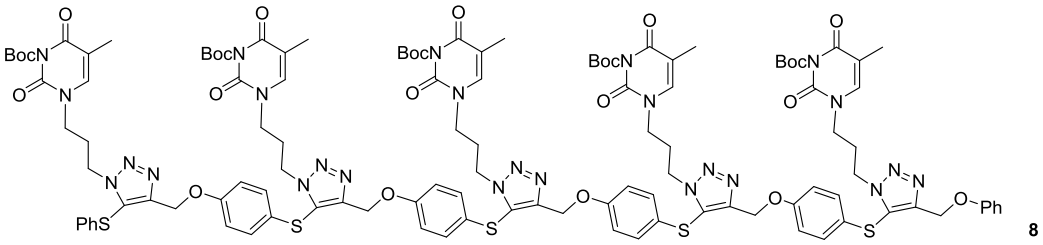
7

7 was prepared as pale yellow solid from (*S*)-2-(azidomethyl)-1-Boc-pyrrolidine (0.28 mmol, 63 mg, 7.0 eq.) and **A5** (0.04 mmol, 36 mg, 1.0 eq.) in 88% yield (71 mg).

Rf = 0.5 (DCM/MeOH = 30:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-6.78 (m, 26 H), 5.08-4.98 (m, 10 H), 4.51-4.25 (m, 15 H), 3.35-3.15 (m, 10 H), 1.80-1.71 (m, 15 H), 1.44-1.40 (m, 45 H), 1.29-1.21 (m, 5 H).

HRMS *m/z* (ESI) calcd. for $C_{101}H_{128}N_{20}O_{15}S_5$ $(M+2H)^{2+}$ 1010.9253, found 1010.9253.



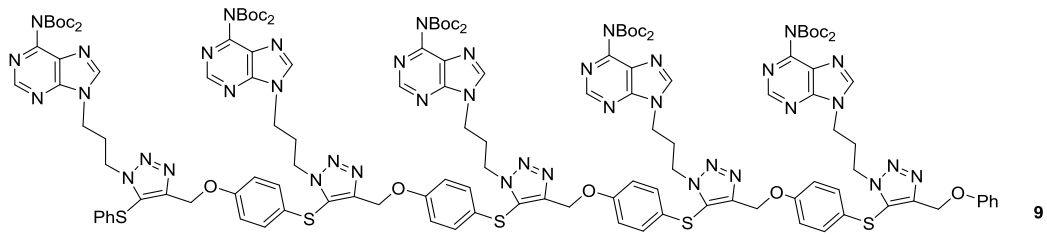
8

8 was prepared as white solid from **azide 8** (0.28 mmol, 86 mg, 7.0 eq.) and **A5** (0.04 mmol, 36 mg, 1.0 eq.) in 85% yield (83 mg).

Rf = 0.3 (DCM/MeOH = 30:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.01 (m, 19 H), 6.97-6.85 (m, 12 H), 5.15-5.09 (m, 10 H), 4.36-4.33 (m, 10 H), 3.73-3.69 (m, 10 H), 2.17-2.12 (m, 10 H), 1.88-1.87 (m, 15 H), 1.58 (m, 45 H).

HRMS *m/z* (ESI) calcd. for $C_{116}H_{133}N_{25}O_{25}S_5$ $(M+2H)^{2+}$ 1218.4272, found 1218.4292.



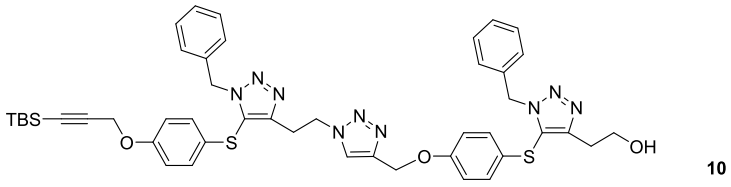
9

9 was prepared as white solid from **azide 9** (0.28 mmol, 110 mg, 7.0 eq.) and **A5** (0.04 mmol, 36 mg, 1.0 eq.) in 77% yield (91 mg).

Rf = 0.2 (DCM/MeOH = 30:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83-8.79 (m, 5 H), 8.19-8.10 (m, 5 H), 7.20-7.19 (m, 3 H), 7.13-6.99 (m, 15 H), 6.89-6.84 (m, 8 H), 5.17-5.11 (m, 10 H), 4.35-4.28 (m, 20 H), 2.38-2.33 (m, 10 H), 1.46-1.45 (m, 90 H).

HRMS *m/z* (ESI) calcd. for $C_{141}H_{168}N_{40}O_{25}S_5$ $(M+2H)^{2+}$ 1513.0691, found 1513.0700.



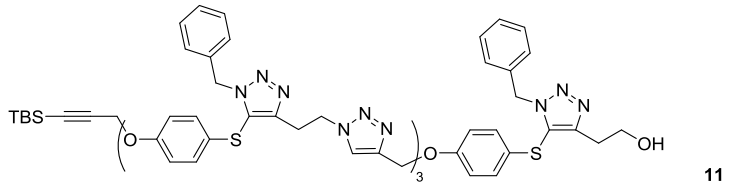
10

10 was prepared as pale yellow solid from benzyl azide (0.15 mmol, 21 mg, 3.0 eq.) and **B2** (0.05 mmol, 30 mg, 1.0 eq.) in 94% yield (44 mg).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1 H), 7.28-7.26 (m, 6 H), 7.23-7.17 (m, 4 H), 6.91-6.89 (m, 2 H), 6.84-6.78 (m, 6 H), 5.56 (s, 2 H), 5.52 (s, 2 H),5.07 (s, 2 H), 4.74 (t, *J* = 8.0 Hz, 2 H), 4.64 (s, 2 H), 3.93 (t, *J* = 8.0 Hz, 2 H), 3.29 (t, *J* = 8.0 Hz, 2 H), 2.91 (t, *J* = 8.0 Hz, 2 H), 0.90 (s, 9 H), 0.11 (s, 6 H).

HRMS *m/z* (ESI) calcd. for $C_{46}H_{52}N_9O_3S_2Si$ $(M+H)^+$ 870.3404, found 870.3392.



11

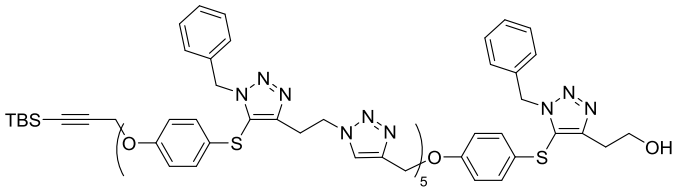
11 was prepared as pale yellow solid from benzyl azide (0.18 mmol, 24 mg, 6.0 eq.) and **B4** (0.03 mmol, 33 mg, 1.0 eq.) in 93% yield (46 mg).

Rf = 0.4 (DCM/MeOH = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 4.0 Hz, 2 H), 7.51 (s, 1 H) 7.23-7.13 (m, 20 H), 6.88-6.86 (m, 2 H), 6.81-6.74 (m, 14 H), 5.50 (d, *J* = 8.0 Hz, 8 H), 5.03 (d, *J* = 4.0 Hz, 6 H), 4.70 (t, *J* = 8.0 Hz,

6 H), 4.61 (s, 2 H), 3.89 (t, *J* = 8.0 Hz, 2 H), 3.25 (t, *J* = 8.0 Hz, 6 H), 2.89 (t, *J* = 8.0 Hz, 2 H), 0.87 (s, 9 H), 0.08 (s, 6 H).

HRMS *m/z* (ESI) calcd. for $C_{86}H_{88}N_{21}O_5S_4Si$ $(M+H)^+$ 1650.5929, found 1650.5916.



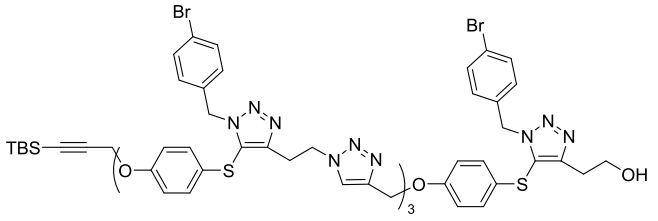
12

12 was prepared as brown solid from benzyl azide (0.27 mmol, 37 mg, 9.0 eq.) and **B6** (0.03 mmol, 40 mg, 1.0 eq.) in 82% yield (59 mg).

Rf = 0.3 (DCM/MeOH = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.51 (m, 5 H), 7.24-7.14 (m, 30 H), 6.88-6.76 (m, 24 H), 5.52-5.49 (m, 12 H), 5.03-5.01 (m, 10 H), 4.72-4.69 (m, 10 H), 4.61 (s, 2 H), 3.90 (t, *J* = 12.0 Hz, 2 H), 3.27-3.24 (m, 10 H), 2.90 (t, *J* = 12.0 Hz, 2 H), 0.87 (s, 9 H), 0.08 (s, 6 H).

HRMS *m/z* (ESI) calcd. for $C_{126}H_{125}N_{33}O_7S_6Si$ $(M+2H)^{2+}$ 1216.4284, found 1216.4294.



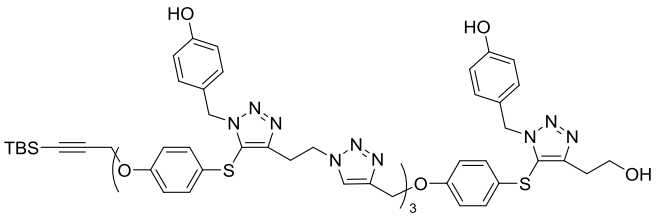
13

13 was prepared as solid from 4-bromobenzyl azide (0.18 mmol, 38 mg, 6.0 eq.) and **B4** (0.03 mmol, 33 mg, 1.0 eq.) in 82% yield (48 mg).

Rf = 0.3 (DCM/MeOH = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.54 (m, 3 H), 7.34-7.29 (m, 8 H), 7.00-6.95 (m, 8 H), 6.85-6.73 (m, 16 H), 5.46-5.43 (m, 8 H), 5.05-5.03 (m, 6 H), 4.75-4.71 (m, 6 H), 4.62 (s, 2 H), 3.92 (t, *J* = 12.0 Hz, 2 H), 3.31-3.27 (m, 6 H), 2.92 (t, *J* = 12.0 Hz, 2 H), 0.87 (s, 9 H), 0.08 (s, 6 H).

HRMS *m/z* (ESI) calcd. for $C_{86}H_{84}Br_4N_{21}O_5S_4Si$ $(M+H)^+$ 1966.2310, found 1966.2293.



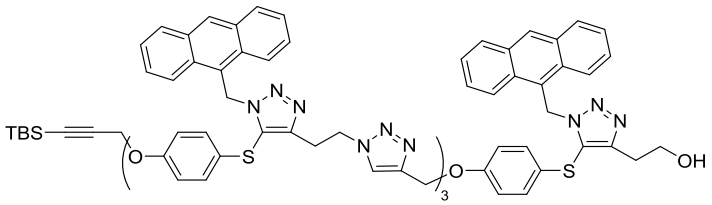
14

14 was prepared as pale yellow solid from 4-(azidomethyl)phenol (0.18 mmol, 27 mg, 6.0 eq.) and **B4** (0.03 mmol, 33 mg, 1.0 eq.) in 91% yield (47 mg).

Rf = 0.4 (DCM/MeOH = 18:1).

^{1}H NMR (400 MHz, DMSO-d6) δ 9.53-9.52 (m, 3 H), 7.13-6.92 (m, 24 H), 6.71-6.69 (m, 8 H), 5.45-5.44 (m, 8 H), 5.10-5.09 (m, 6 H), 4.83 (s, 2 H), 4.77-4.68 (m, 6 H), 3.67-3.63 (m, 2 H), 3.40 (s, 4 H), 3.26-3.22 (m, 6 H), 2.81 (t, *J* = 16.0 Hz, 2 H), 0.85 (s, 9 H), 0.08 (s, 6 H).

HRMS *m/z* (ESI) calcd. for $C_{86}H_{88}N_{21}O_9S_4Si$ $(M+H)^+$ 1714.5727, found 1714.5736.



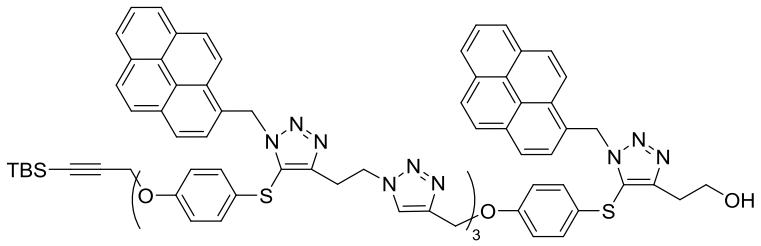
15

15 was prepared as brown solid from 9-anthracenylmethyl azide (0.18 mmol, 42 mg, 6.0 eq.) and **B4** (0.03 mmol, 33 mg, 1.0 eq.) in 67% yield (42 mg).

Rf = 0.3 (DCM/MeOH = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38-8.34 (m, 3 H), 8.16-8.14 (m, 8 H) 7.92-7.91 (m, 8 H), 7.51-7.40 (m, 20 H), 6.70-6.56 (m, 16 H), 6.63-6.30 (m, 8 H), 4.95-4.94 (m, 6 H), 4.70-4.68 (m, 6 H), 4.62-4.61 (m, 2 H), 3.89 (t, *J*=8.0 Hz, 2 H), 3.26-3.25 (m, 6 H), 2.89 (t, *J*=8.0 Hz, 2 H), 0.88 (s, 9 H), 0.09 (s, 6 H).

HRMS *m/z* (ESI) calcd. for $C_{118}H_{111}N_{23}O_5S_4Si$ $(M+2NH_4)^{2+}$ 1042.3912, found 1042.3566.



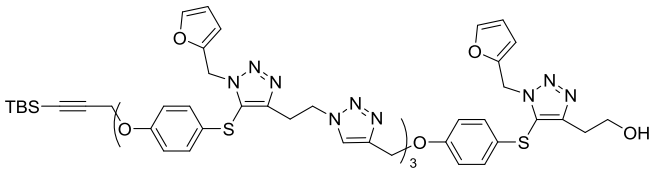
16

16 was prepared as brown solid from 1-(azidomethyl)pyrene (0.18 mmol, 46 mg, 6.0 eq.) and **B4** (0.03 mmol, 33 mg, 1.0 eq.) in 73% yield (47 mg).

Rf = 0.3 (DCM/MeOH = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28-8.23 (m, 4 H), 8.13-7.87 (m, 30 H), 7.59-7.51 (m, 4 H), 7.42-7.41 (m, 3 H), 6.55-6.50 (m, 4 H), 6.46-6.44 (m, 4 H), 6.34-6.32 (m, 2 H), 6.25-6.17 (m, 12 H), 4.75-4.72 (m, 6 H), 4.54-4.50 (m, 6 H), 4.21 (s, 2 H), 3.94 (t, *J*=12.0 Hz, 2 H), 3.30-3.28 (m, 6 H), 2.93 (t, *J*=12.0 Hz, 2 H), 0.87 (s, 9 H), 0.07 (s, 6 H).

HRMS *m/z* (ESI) calcd. for $C_{126}H_{103}N_{21}O_5S_4Si$ $(M)^{2+}$ 1073.3569, found 1073.8589.



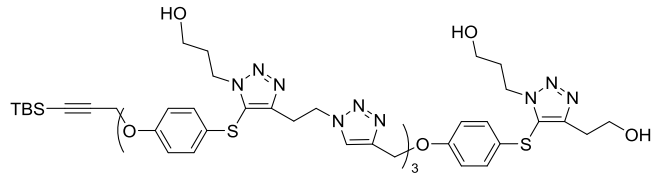
17

17 was prepared as brown oil from 3-(azidomethyl)furan (0.18 mmol, 22 mg, 6.0 eq.) and **B4** (0.03 mmol, 33 mg, 1.0 eq.) in 79% yield (39 mg).

Rf = 0.2 (DCM/MeOH = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.52(m, 3 H), 7.29-7.28 (m, 4 H), 7.00-6.98 (m, 2 H), 6.93-6.88 (m, 6 H), 6.85-6.82 (m, 8 H), 6.25-6.24 (m, 8 H), 5.52-5.50 (m, 8 H), 5.08-5.06 (m, 6 H), 4.72-4.69 (m, 6 H), 4.64 (s, 2 H), 3.90 (t, *J* = 12.0 Hz, 2 H), 3.28-3.26 (m, 6 H), 2.90 (t, *J* = 12.0 Hz, 2 H), 0.87 (s, 9 H), 0.08 (s, 6 H).

HRMS *m/z* (ESI) calcd. for $C_{78}H_{80}N_{21}O_9S_4Si$ $(M+H)^+$ 1610.5101, found 1610.5129.



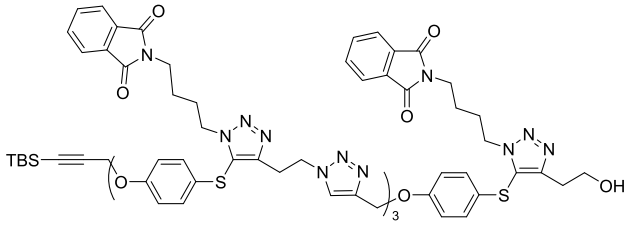
18

18 was prepared as colorless oil from 1-azido-3-propanol (0.18 mmol, 18 mg, 6.0 eq.) and **B4** (0.03 mmol, 33 mg, 1.0 eq.) in 76% yield (35 mg).

Rf = 0.2 (DCM/MeOH = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.52 (m, 3 H), 7.07-7.05 (m, 2 H), 6.98-6.96 (m, 2 H), 6.91-6.83 (m, 12 H), 5.06-5.04 (m, 6 H), 4.73-4.72 (m, 6 H), 4.63 (s, 2 H), 4.43-4.39 (m, 8 H), 3.91 (t, *J* = 12.0 Hz, 2 H), 3.56-3.52 (m, 8 H), 3.30-3.26 (m, 6 H), 2.94 (t, *J* = 12.0 Hz, 2 H), 1.96-1.92 (m, 8 H), 0.86 (s, 9 H), 0.07 (s, 6 H).

HRMS *m/z* (ESI) calcd. for $C_{70}H_{87}N_{21}O_9S_4SiNa$ $(M+Na)^+$ 1544.5513, found 1544.5546.



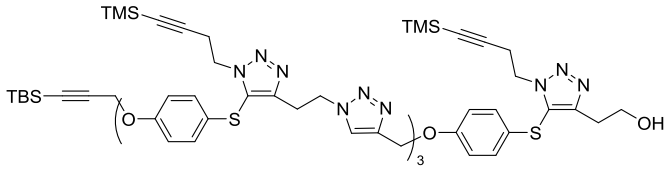
19

19 was prepared as pale yellow solid from 2-(4-azidobutyl)isoindole-1,3-dione (0.18 mmol, 44 mg, 6.0 eq.) and **B4** (0.03 mmol, 33 mg, 1.0 eq.) in 96% yield (60 mg).

Rf = 0.2 (DCM/MeOH = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.77 (m, 8 H), 7.69-7.66 (m, 8 H), 7.58-7.55 (m, 3 H), 7.03-7.01 (m, 2 H), 6.94-6.82 (m, 14 H), 5.07-.06 (m, 6 H), 4.74-4.71 (m, 6 H), 4.61 (s, 2 H), 4.34-4.29 (m, 8 H), 3.92 (t, *J* = 12.0 Hz, 2 H), 3.61-3.59 (m, 8 H), 3.31-3.26 (m, 6 H), 2.92 (t, *J* = 12.0 Hz, 2 H), 1.80-1.76 (m, 8 H), 1.61-1.56 (m, 8 H), 0.84 (s, 9 H), 0.05 (s, 6 H).

HRMS *m/z* (ESI) calcd. for $C_{106}H_{107}N_{25}O_{13}S_4Si$ $(M)^{2+}$ 1047.3583, found 1047.8616.



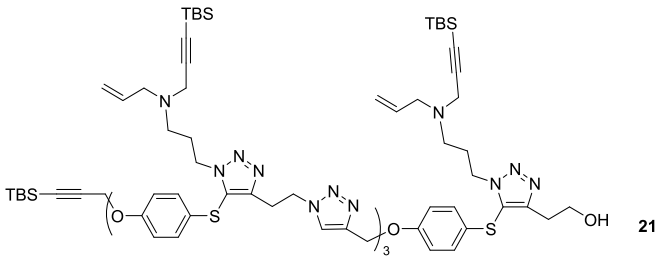
20

20 was prepared as brown oil from 4-azido-1-(trimethylsilyl)-1-butyne (0.18 mmol, 52 mg, 6.0 eq.) and **B4** (0.03 mmol, 33 mg, 1.0 eq.) in 90% yield (48 mg).

Rf = 0.3 (DCM/MeOH = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.55 (m, 3 H), 7.07-7.05 (m, 2 H), 7.00-6.95 (m, 6 H), 6.89-6.86 (m, 8 H), 5.09-5.08 (m, 6 H), 4.73-4.69 (m, 6 H), 4.63 (s, 2 H), 4.50-4.45 (m, 8 H), 3.91 (t, *J* = 12.0 Hz, 2 H), 3.30-3.26 (m, 6 H), 2.91 (t, *J* = 12.0 Hz, 2 H), 2.75-2.69 (m, 8 H), 0.86 (s, 9 H), 0.12-0.11 (m, 36 H), 0.06 (s, 6 H).

HRMS *m/z* (ESI) calcd. for $C_{86}H_{112}N_{21}O_5S_4Si_5$ $(M+H)^+$ 1786.6885, found 1787.6901.



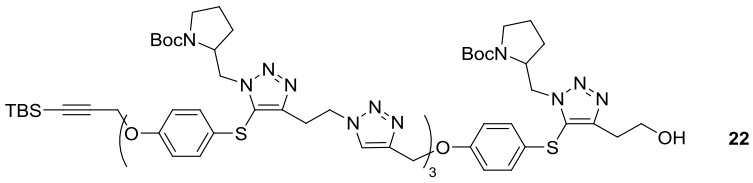
21

21 was prepared as brown solid from **azide 6** (0.18 mmol, 52 mg, 6.0 eq.) and **B4** (0.03 mmol, 33 mg, 1.0 eq.) in 82% yield (56 mg).

Rf = 0.3 (DCM/MeOH = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 2 H), 7.57 (s, 1 H), 7.05-7.03 (m, 2 H), 6.98-6.93 (m, 6 H), 6.88-6.85 (m, 8 H), 5.76-5.69 (m, 4 H), 5.20-5.11 (m, 6 H), 5.09-5.07 (m, 8 H), 4.74-4.62 (m, 6 H), 4.62 (s, 2 H), 4.37-4.33 (m, 8 H), 3.92 (t, *J* = 12.0 Hz, 2 H), 3.35-3.33 (m, 8 H), 3.30-3.29 (m, 6 H), 3.05-3.04 (m, 8 H), 2.92 (t, *J* = 12.0 Hz, 2 H), 2.51-2.49 (m, 8 H), 1.96-1.92 (m, 8 H), 0.91 (m, 36 H), 0.85 (s, 9 H), 0.08 (m, 24 H), 0.06 (s, 6 H).

HRMS *m/z* (ESI) calcd. for $C_{118}H_{173}N_{25}O_5S_4Si_5$ $(M+2H)^{2+}$ 1144.5908, found 1144.5853.



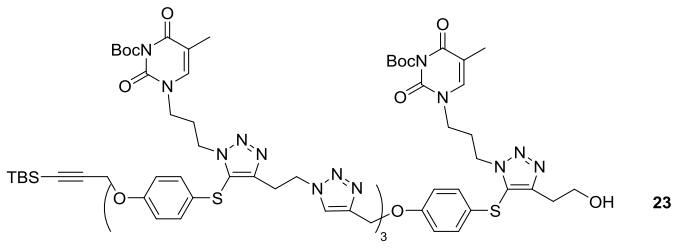
22

22 was prepared as brown solid from (*S*)-2-(azidomethyl)-1-Boc-pyrrolidine (0.18 mmol, 40 mg, 6.0 eq.) and **B4** (0.03 mmol, 33 mg, 1.0 eq.) in 85% yield (51 mg).

Rf = 0.3 (DCM/MeOH = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.60 (m, 3 H), 7.13-6.85 (m, 16 H), 5.08-5.07 (m, 6 H), 4.71-4.69 (m, 6 H), 4.63 (s, 2 H), 4.48-4.47 (m, 6 H), 4.28-4.25 (m, 4 H), 3.88 (t, *J* = 12.0 Hz, 2 H), 3.34-3.23 (m, 16 H), 2.90-2.87 (m, 2 H), 1.90-1.70 (m, 16 H), 1.43-1.41 (m, 36 H), 0.85 (s, 9 H), 0.06 (s, 6 H).

HRMS *m/z* (ESI) calcd. for $C_{98}H_{133}N_{25}O_{13}S_4Si$ $(M+2H)^{2+}$ 1012.4600, found 1012.4569.



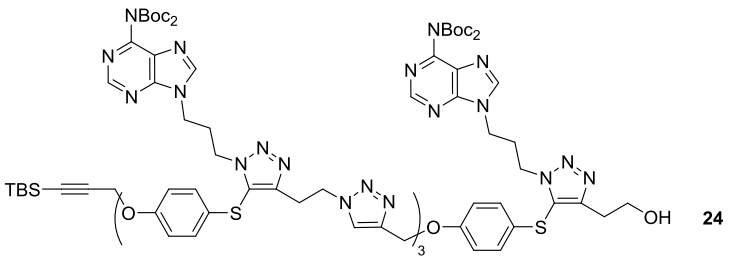
23

23 was prepared as white solid from **azide 8** (0.18 mmol, 55 mg, 6.0 eq.) and **B4** (0.03 mmol, 33 mg, 1.0 eq.) in 82% yield (58 mg).

Rf = 0.2 (DCM/MeOH = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.60 (m, 3 H), 7.10-7.04 (m, 6 H), 6.98-6.96 (m, 2 H), 6.93-6.82 (m, 12 H), 5.06-5.04 (m, 6 H), 4.78-4.73 (m, 6 H), 4.63 (s, 2 H), 4.34-4.28 (m, 8 H), 3.94 (t, *J* = 12.0 Hz, 2 H), 3.69 (t, *J* = 16.0 Hz, 2 H), 3.65-3.61 (m, 6 H), 3.35-3.31 (m, 6 H), 2.97 (t, *J* = 12.0 Hz, 2 H), 2.14-2.11 (m, 8 H), 1.86 (m, 12 H), 1.58-1.57 (m, 36 H), 0.85 (s, 9 H), 0.06 (s, 6 H).

HRMS *m/z* (ESI) calcd. for $C_{110}H_{137}N_{29}O_{21}S_4Si$ $(M+2H)^{2+}$ 1178.4614, found 1178.4623.



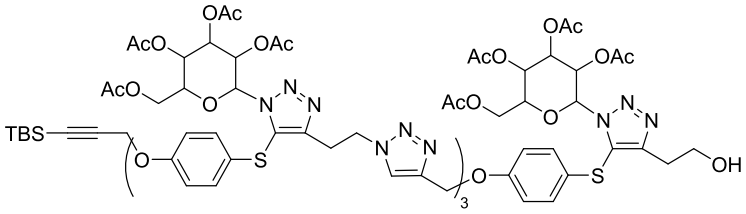
24

24 was prepared as white solid from **azide 9** (0.18 mmol, 75 mg, 6.0 eq.) and **B4** (0.03 mmol, 33 mg, 1.0 eq.) in 79% yield (66 mg).

Rf = 0.2 (DCM/MeOH = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80-8.79 (m, 4 H), 8.16-8.13 (m, 4 H), 7.67-7.64 (m, 3 H), 7.00-6.98 (m, 2 H), 6.90-6.83 (m, 14 H), 5.06-5.05 (m, 6 H), 4.77-4.73 (m, 6 H), 4.62 (s, 2 H), 4.31-4.24 (m, 16 H), 3.94 (t, *J* = 12.0 Hz, 2 H), 3.34-3.32 (m, 6 H), 2.96 (t, *J* = 12.0 Hz, 2 H), 2.37-2.34 (m, 8 H), 1.44-1.43 (m, 72 H), 0.84 (s, 9 H), 0.05 (s, 6 H).

HRMS *m/z* (ESI) calcd. for $C_{130}H_{163}N_{41}O_{21}S_4SiNa_2$ $(M+2Na)^{2+}$ 1418.5714, found 1418.5763.



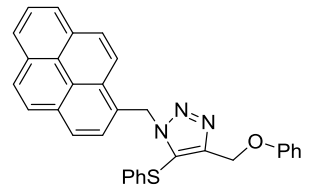
25

25 was prepared as white solid from 2,3,4,6-tetra-*O*-acetyl-*β*-*D*-glucopyranosyl azide (0.18 mmol, 67 mg, 6.0 eq.) and **B4** (0.03 mmol, 33 mg, 1.0 eq.) in 78% yield (61 mg).

Rf = 0.3 (DCM/MeOH = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (m, 2 H), 7.56 (s, 1 H), 7.17-7.07 (m, 8 H), 6.88-6.86 (m, 8 H), 6.06-6.00 (m, 4 H), 5.93-5.87 (m, 4 H), 5.39-5.35 (m, 4 H), 5.27-5.22 (m, 4 H), 5.08 (s, 6 H), 4.63 (m, 8 H), 4.10-4.03 (m, 4 H), 4.00-3.91 (m, 4 H), 3.85-3.81 (m, 6 H), 3.20-3.19 (m, 6 H), 2.86-2.85 (m, 2 H), 2.03-2.01 (m, 24 H), 1.96-1.95 (m, 12 H), 1.80-1.79 (m, 12 H), 0.86 (s, 9 H), 0.06 (s, 6 H).

HRMS *m/z* (ESI) calcd. for $C_{114}H_{137}N_{21}O_{41}S_4Si$ $(M+2H)^{2+}$ 1306.3983, found 1306.3997.



29

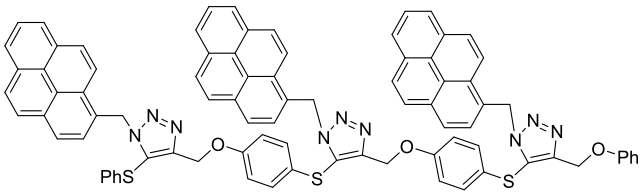
29 was prepared as brown solid from 1-(azidomethyl)pyrene (0.3 mmol, 77 mg, 1.5 eq.) and **A1** (0.2 mmol, 48 mg, 1.0 eq.) in 89% yield (89 mg).

Rf = 0.5 (DCM/MeOH = 80:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.0 Hz, 1 H), 8.18 (d, *J* = 8.0 Hz, 2 H), 8.10 (d, *J* = 8.0 Hz, 1 H), 8.04-8.01 (m, 2 H), 7.94-7.90 (m, 2 H), 7.68 (m, 1 H), 7.27-7.23 (m, 2 H), 6.97-6.93 (m, 3 H), 6.83-6.73 (m, 5 H), 6.23 (s, 2 H), 5.16 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 148.7, 132.3, 131.4, 131.0, 130.4, 129.3, 128.7, 128.7, 128.3, 127.7, 127.3, 127.2, 127.1, 126.9, 126.8, 126.5, 126.0, 125.5, 125.4, 124.6, 124.5, 124.4, 122.1, 121.1, 114.8, 60.7, 50.6.

HRMS *m/z* (ESI) calcd. for $C_{32}H_{24}N_3OS$ $(M+H)^+$ 498.1641, found 498.1624.



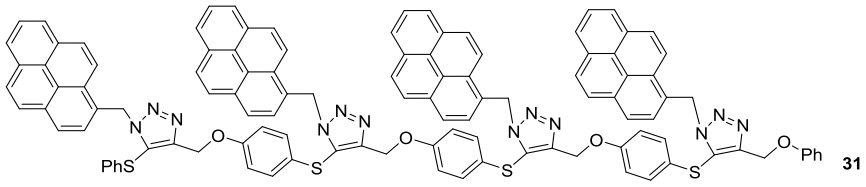
30

30 was prepared as brown solid from 1-(azidomethyl)pyrene (0.45 mmol, 115 mg, 4.5 eq.) and **A3** (0.1 mmol, 56 mg, 1.0 eq.) in 82% yield (109 mg).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32-8.22 (m, 3 H), 8.15-7.81 (m, 22 H), 7.54 (d, *J* = 8.0 Hz, 1 H), 7.51-7.46 (m, 2 H), 7.24-7.20 (m, 2 H), 6.96-6.91 (m, 3 H), 6.76-6.73 (m, 3 H), 6.72-6.62 (m, 3 H), 6.57-6.55 (m, 2 H), 6.28-6.23 (m, 4 H), 6.17 (s, 4 H), 6.16 (s, 2 H), 5.12 (s, 2 H), 4.68 (m, 2 H), 4.67 (s, 2 H).

HRMS *m/z* (ESI) calcd. for $C_{84}H_{58}N_9O_3S_3$ $(M+H)^+$ 1336.3825, found 1336.3827.



31

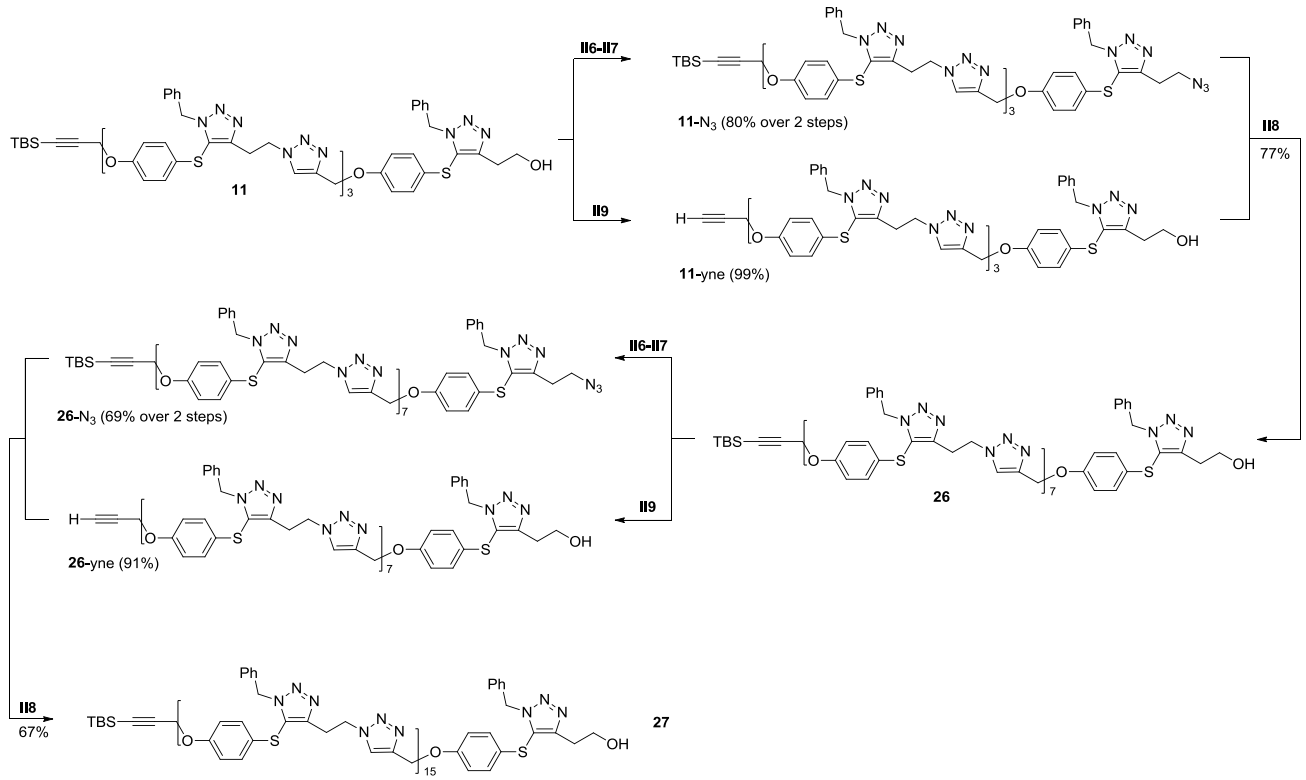
31 was prepared as brown solid from 1-(azidomethyl)pyrene (0.6 mmol, 154 mg, 6.0 eq.) and **A4 (**0.1 mmol, 72 mg, 1.0 eq.) in 86% yield (151 mg).

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

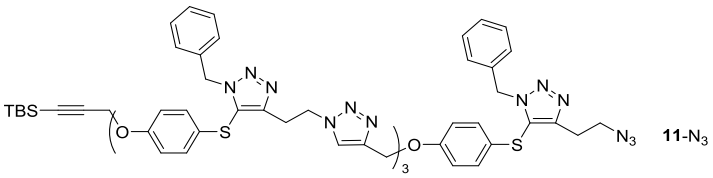
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30-8.20 (m, 4 H), 8.13-8.09 (m, 5 H), 8.07-8.05 (m, 4 H), 8.03-8.01 (m, 3 H), 7.97-7.78 (m, 17 H), 7.62 (d, *J* = 8.0 Hz, 1 H), 7.51-7.44 (m, 3 H), 7.21-7.19 (m, 2 H), 6.95-6.87 (m, 3 H), 6.74-6.52 (m, 10 H), 6.28-6.20 (m, 6 H), 6.17-6.13 (m, 8 H), 5.10 (s, 2 H), 4.67 (s, 2 H), 4.66-4.65 (m, 4 H).

HRMS *m/z* (ESI) calcd. for $C_{110}H_{75}N_{12}O_4S_4$ $(M+H)^+$ 1756.4951, found 1756.0633.

V. Elongation of Oligotriazoles through CuAAC-based Strategy

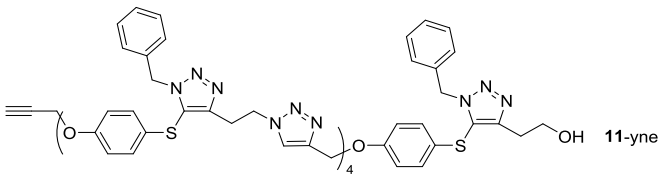


Scheme S5. Elongation of oligotriazole **11** through CuAAC-based IEG strategy.



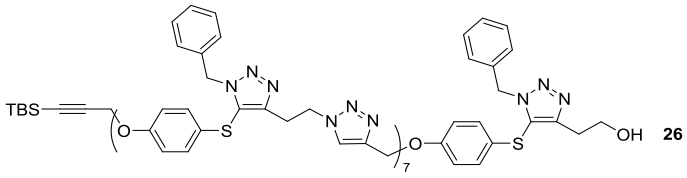
Rf = 0.3 (DCM/MeOH = 30:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.52 (m, 3 H), 7.23-7.15 (m, 21 H), 6.88-6.76 (m, 16 H), 5.52 (s, 2 H), 5.49 (m, 6 H), 5.04-5.02 (m, 6 H), 4.71 (t, *J* = 12.0 Hz, 6 H), 4.61 (s, 2 H), 3.54 (t, *J* = 16.0 Hz, 2 H), 3.26 (t, *J* = 16.0 Hz, 6 H), 2.94 (t, *J* = 16.0 Hz, 2 H), 0.87 (s, 9 H), 0.08 (s, 6 H).



Rf = 0.3 (DCM/MeOH = 25:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.51 (m, 3 H), 7.23-7.12 (m, 20 H), 6.88-6.73 (m, 16 H), 5.51 (s, 2 H), 5.48 (m, 6 H), 5.03-5.00 (m, 6 H), 4.72-4.67 (m, 6 H), 4.61-4.58 (m, 2 H), 3.89 (m, 2 H), 3.28-3.23 (m, 6 H), 2.89 (t, *J* = 12.0 Hz, 2 H), 2.51 (t, *J* = 8.0 Hz, 1 H).

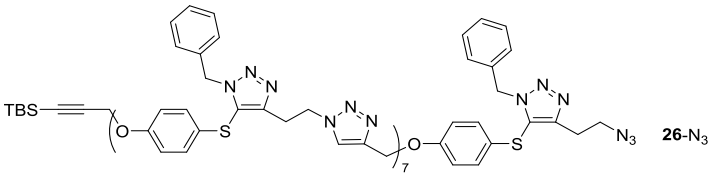


26

Rf = 0.3 (DCM/MeOH = 18:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.51 (m, 7 H), 7.21-7.13 (m, 40 H), 6.88-6.85 (m, 2 H), 6.78-6.73 (m, 30 H), 5.50-5.48 (m, 16 H), 5.01 (m, 14 H), 4.71-4.67 (m, 14 H), 4.60 (s, 2 H), 3.91-3.87 (m, 2 H), 3.27-3.23 (m, 14 H), 2.89 (t, *J* = 12.0 Hz, 2 H), 0.87 (s, 9 H), 0.07 (s, 6 H).

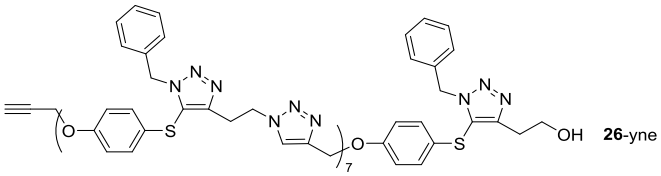
HRMS *m/z* (ESI) calcd. for $C_{166}H_{162}N_{45}O_9S_8Si$ $(M+3H)^{3+}$ 1071.3724, found 1071.3735.



26-N_3

Rf = 0.4 (DCM/MeOH = 18:1).

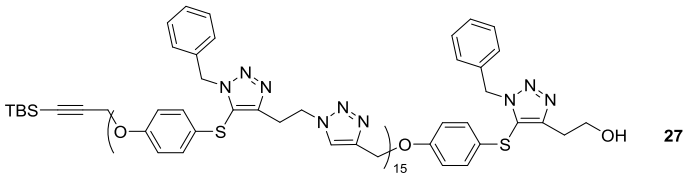
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.47 (m, 5 H), 7.17-7.02 (m, 32 H), 6.82-6.65 (m, 26 H), 5.44-5.41 (m, 12 H), 4.95 (m, 10 H), 4.65-4.53 (m, 12 H), 3.20-3.3.16 (m, 10 H), 0.79 (s, 9 H), 0.00 (s, 6 H).



26-yne

Rf = 0.3 (DCM/MeOH = 18:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.51 (m, 7 H), 7.21-7.13 (m, 40 H), 6.88-6.85 (m, 2 H), 6.77-6.71 (m, 30 H), 5.50-5.48 (m, 16 H), 5.02-5.00 (m, 14 H), 4.71-4.67 (m, 14 H), 4.60 (s, 2 H), 3.89 (t, *J* = 12.0 Hz, 2 H), 3.26-3.22 (m, 14 H), 2.89 (t, *J* = 12.0 Hz, 2 H), 2.51 (t, *J* = 8.0 Hz, 1 H).

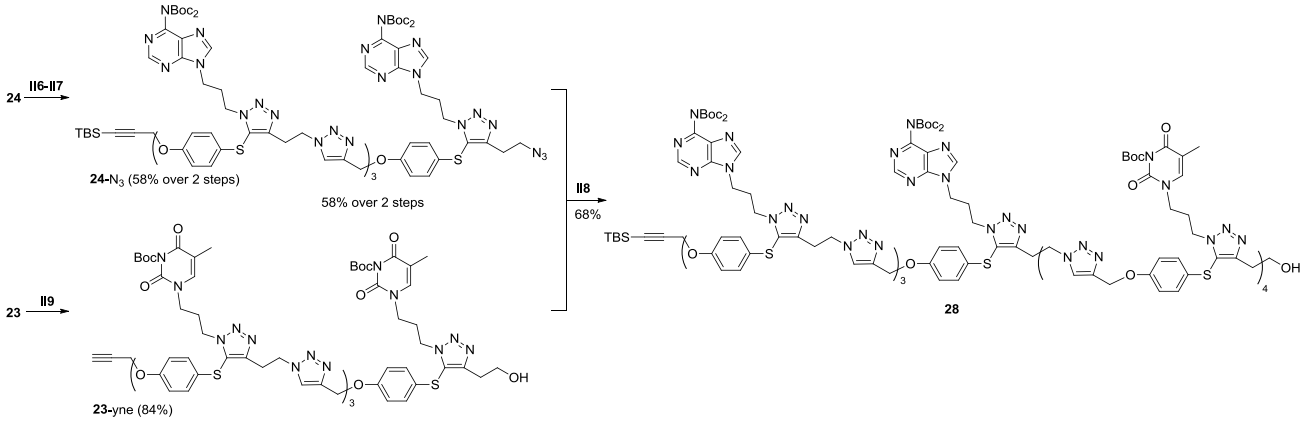


27

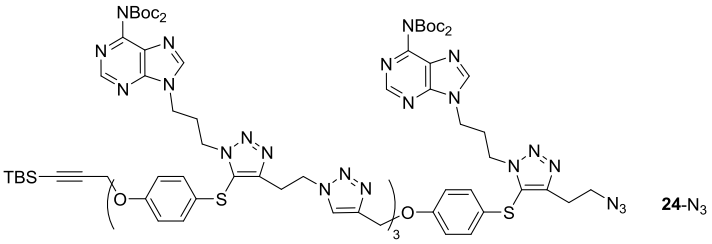
Rf = 0.2 (DCM/MeOH = 18:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.50 (m, 15 H), 7.22-7.21 (m, 48 H), 7.14-7.13 (m, 32 H), 6.88-6.86 (m, 2 H), 6.69-6.76 (m, 62 H), 5.51-5.48 (m, 32 H), 5.01 (m, 30 H), 4.72-4.68 (m, 30 H), 4.61 (s, 2 H), 3.90 (t, *J* = 12.0 Hz, 2 H), 3.27-3.23 (m, 30 H), 2.90 (t, *J* = 12.0 Hz, 2 H), 0.87 (s, 9 H), 0.08 (s, 6 H).

FTMS *m/z* calcd. for $C_{326}H_{306}N_{93}O_{17}S_{16}Si$ $(M+3H)^{3+}$ 2112.4, found 2113.0.



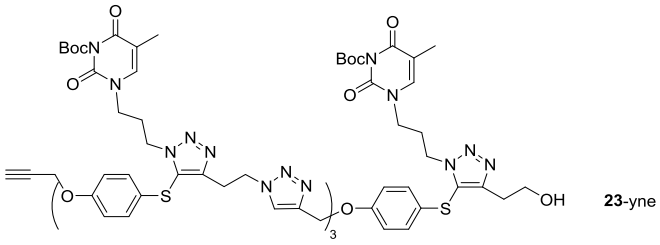
Scheme S6. Synthesis of 8-mer **28** through CuAAC-based coupling.



24-N_3

Rf = 0.3 (DCM/MeOH = 20:1).

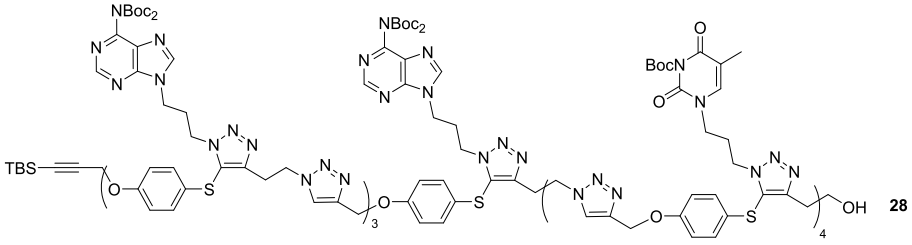
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80-8.79 (m, 4 H), 8.16-8.14 (m, 4 H), 7.67-7.65 (m, 3 H), 7.02-6.99 (m, 2 H), 6.92-6.83 (m, 14 H), 5.08-5.05 (m, 6 H), 4.78-4.73 (m, 6 H), 4.62 (s, 2 H), 4.31-4.22 (m, 16 H), 3.63 (t, *J* = 12.0 Hz, 2 H), 3.35-3.32 (m, 6 H), 3.02 (t, *J* = 12.0 Hz, 2 H), 2.37-2.34 (m, 8 H), 1.44-1.43 (m, 72 H), 0.85 (s, 9 H), 0.05 (s, 6 H).



23-yne

Rf = 0.2 (DCM/MeOH = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.60 (m, 3 H), 7.10-7.04 (m, 6 H), 6.98-6.82 (m, 14 H), 5.06-5.04 (m, 6 H), 4.77-4.74 (m, 6 H), 4.63 (s, 2 H), 4.34-4.29 (m, 8 H), 3.96-3.94 (m, 2 H), 3.69 (t, *J* = 12.0 Hz, 2 H), 3.65-3.61 (m, 6 H), 3.35-3.31 (m, 6 H), 2.97 (t, *J* = 12.0 Hz, 2 H), 2.52(t, *J* = 8.0 Hz, 1 H), 2.14-2.11 (m, 8 H), 1.88-1.86 (m, 12 H), 1.58-1.57 (m, 36 H).



28

Rf = 0.3 (DCM/MeOH = 15:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (m, 4 H), 8.17-8.16 (m, 4 H), 7.67-7.66 (m, 4 H), 7.62-7.60 (m, 3 H), 7.10-7.04 (m, 6 H), 6.93-6.82 (m, 30 H), 5.06-5.04 (m, 14 H), 4.76-4.73 (m, 14 H), 4.62 (s, 2 H), 4.31-4.29 (m, 16 H), 4.26-4.22(m, 8 H), 3.94 (t, *J* = 12.0 Hz, 2 H), 3.69 (t, *J* = 12.0 Hz, 2 H), 3.64-3.61 (m, 6 H), 3.36-3.31 (m, 14 H), 2.96 (t, *J* = 12.0 Hz, 2 H), 2.39-2.34 (m, 8 H), 2.15-2.08 (m, 8 H), 1.87-1.85 (m, 12 H), 1.57-1.56 (m, 36 H), 1.44-1.43 (m, 72 H), 0.84 (s, 9 H), 0.05 (s, 6 H).

FTMS *m/z* calcd. for $C_{234}H_{286}N_{73}O_{41}S_8Si$ $(M+3H)^{3+}$ 1686.7, found 1687.0.

VI. Photophysical Behaviors of Pyrene-Involved Oligomers

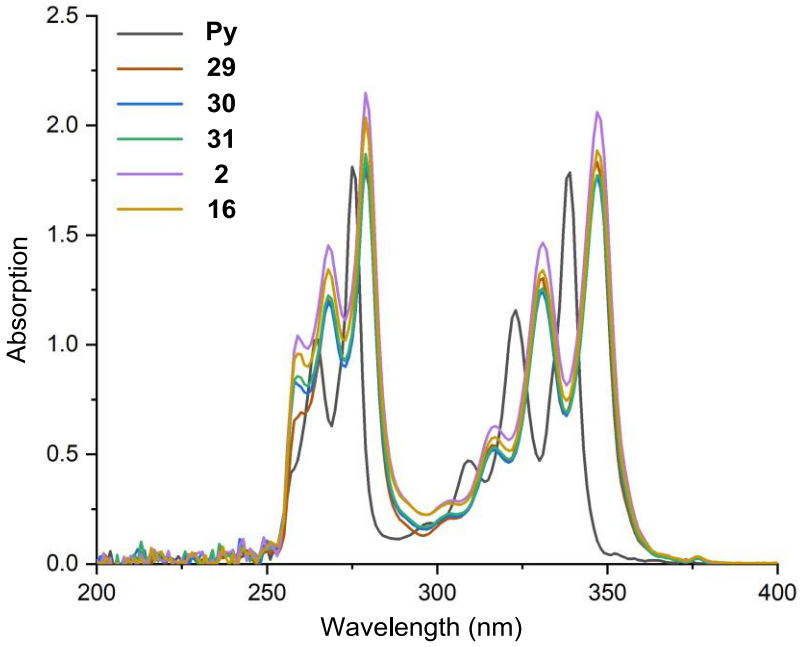


Figure S1. UV-Vis absorption spectra of **Py**, **29-31**, **2** and **16** measured in DMSO. Concentration: 50.0 μmol/L (**Py**, **29**), 16.7 μmol/L (**30**), 12.5 μmol/L (**31** and **16**), 10.0 μmol/L (**2**).

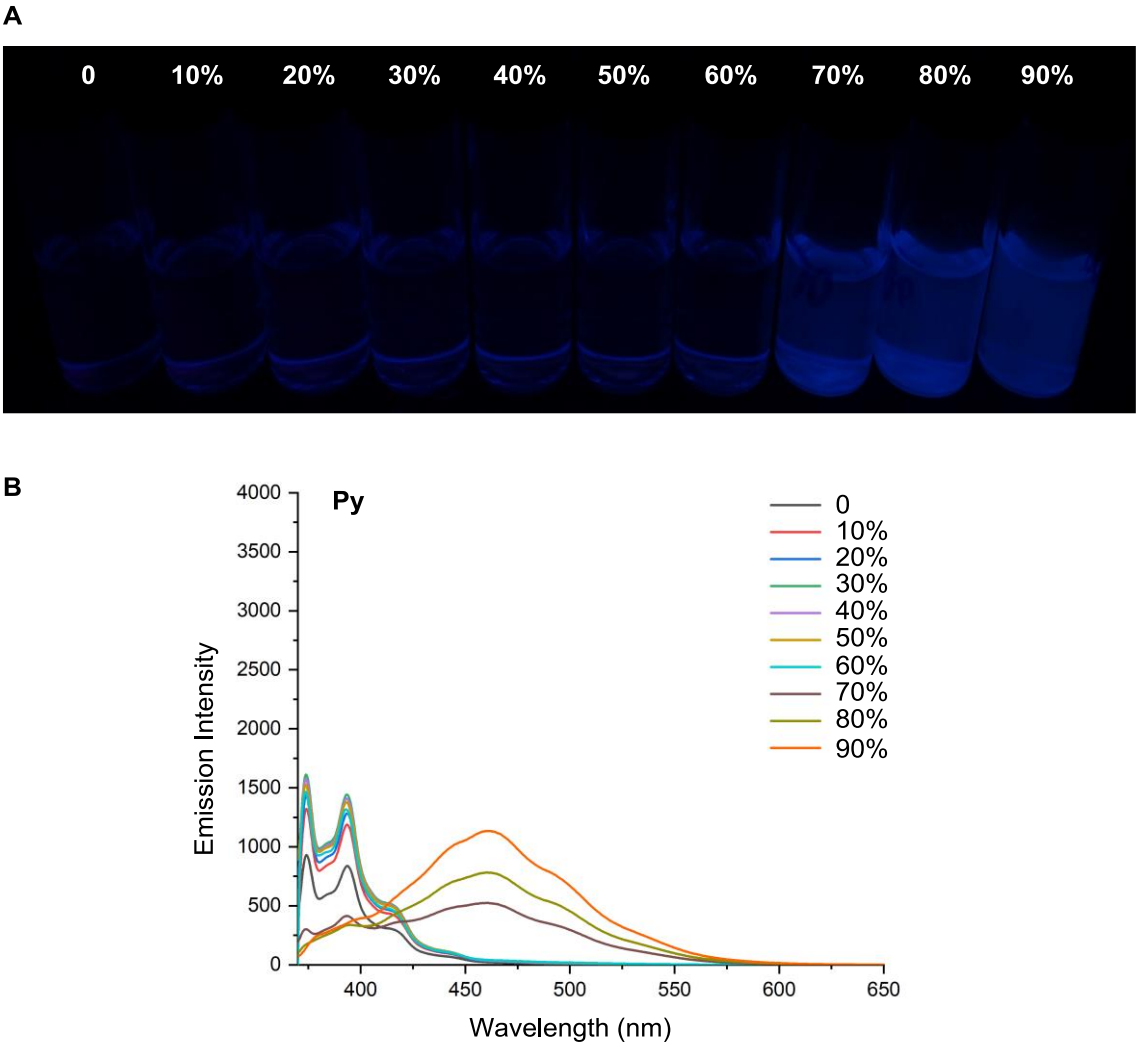


Figure S2. Photograph (λ_{ex}: 365 nm) and photoluminescence spectra (λ_{ex}: 360 nm) of **Py** in DMSO/water mixtures. Concentration: 50 μmol/L.

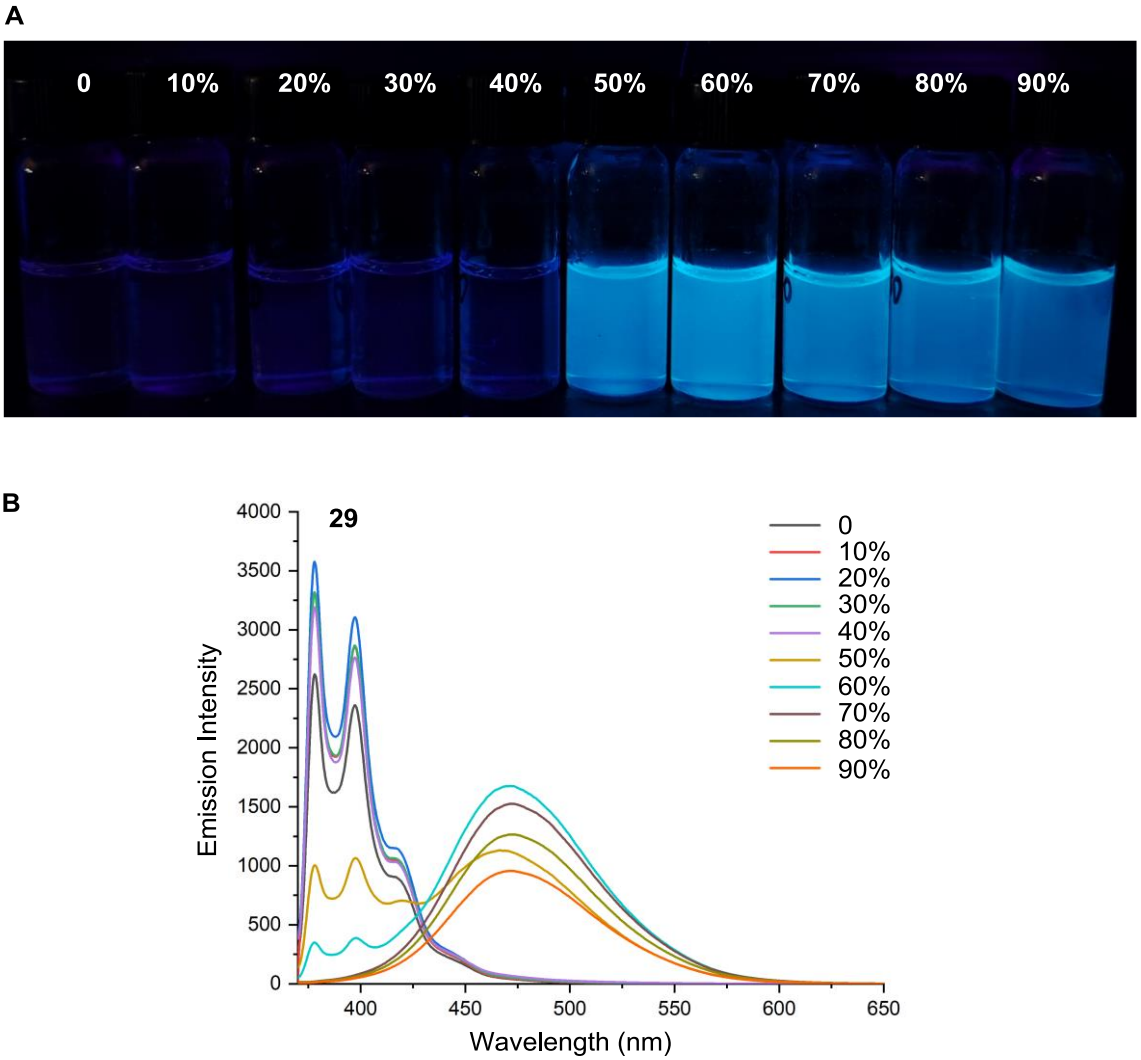


Figure S3. Photograph (λ_{ex}: 365 nm) and photoluminescence spectra (λ_{ex}: 360 nm) of **29** in DMSO/water mixtures. Concentration: 50 μmol/L.

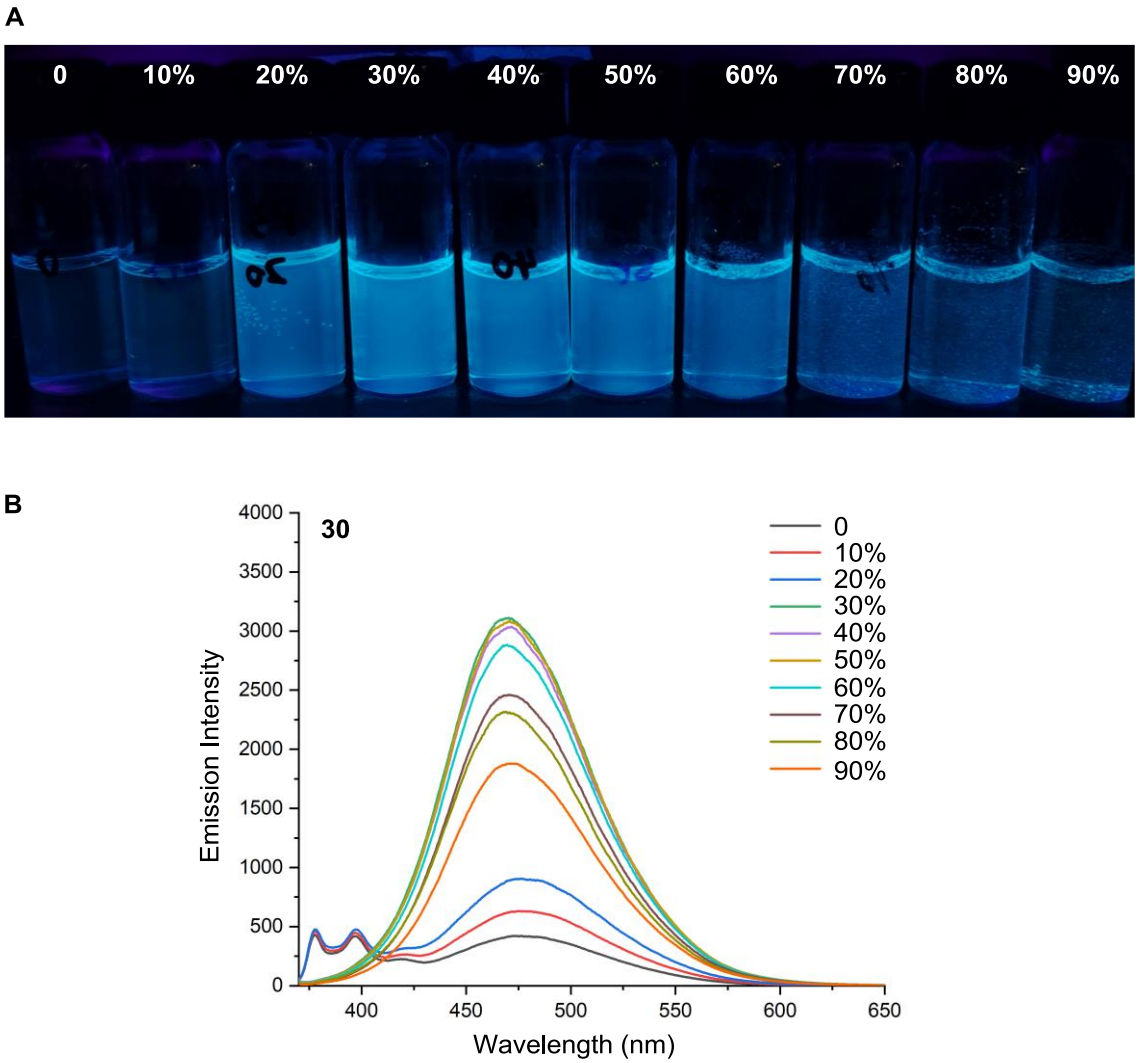


Figure S4. Photograph (λ_{ex}: 365 nm) and photoluminescence spectra (λ_{ex}: 360 nm) of **30** in DMSO/water mixtures. Concentration: 16.7 μmol/L.

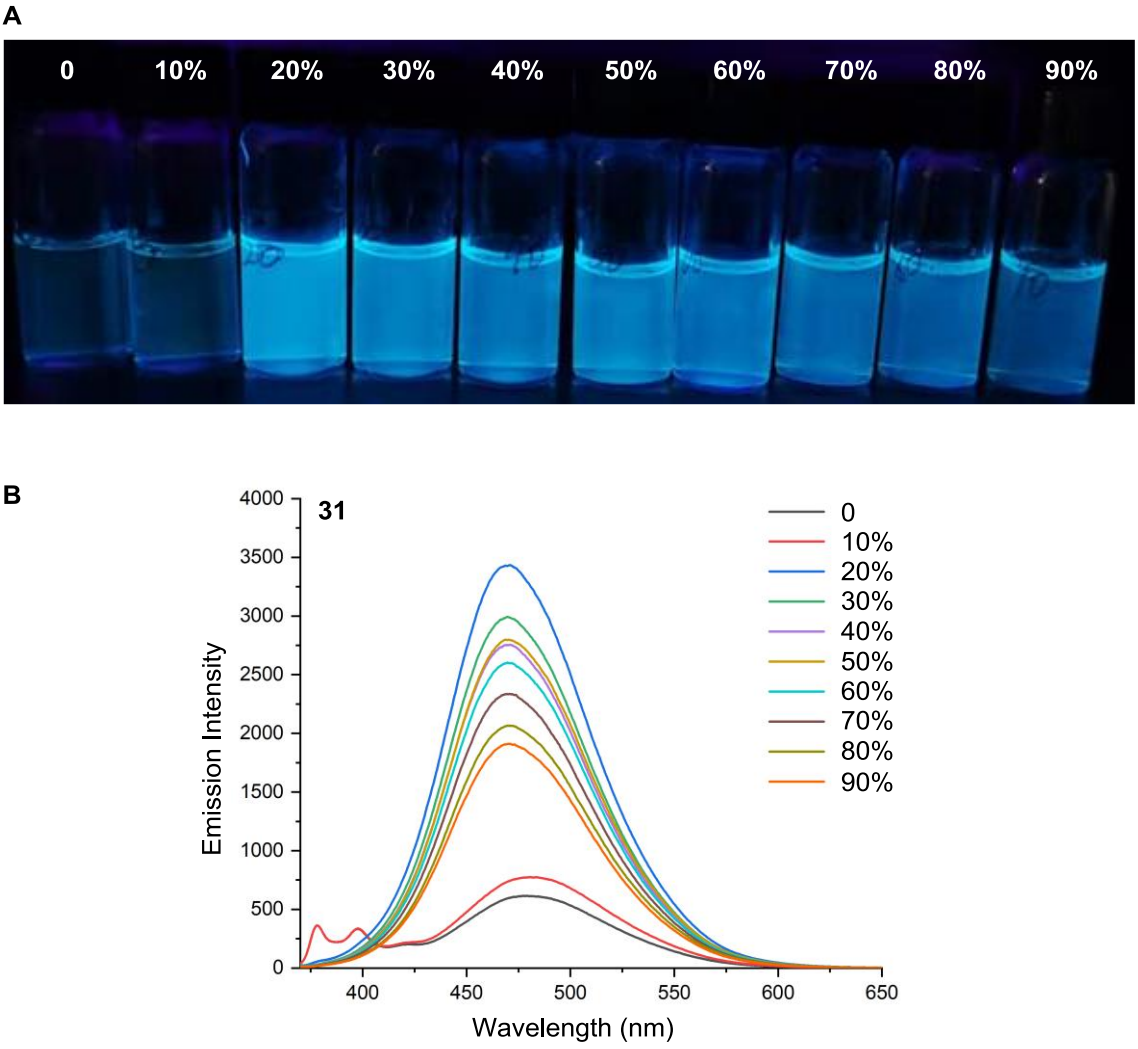


Figure S5. Photograph (λ_{ex}: 365 nm) and photoluminescence spectra (λ_{ex}: 360 nm) of **31** in DMSO/water mixtures. Concentration: 12.5 μmol/L.

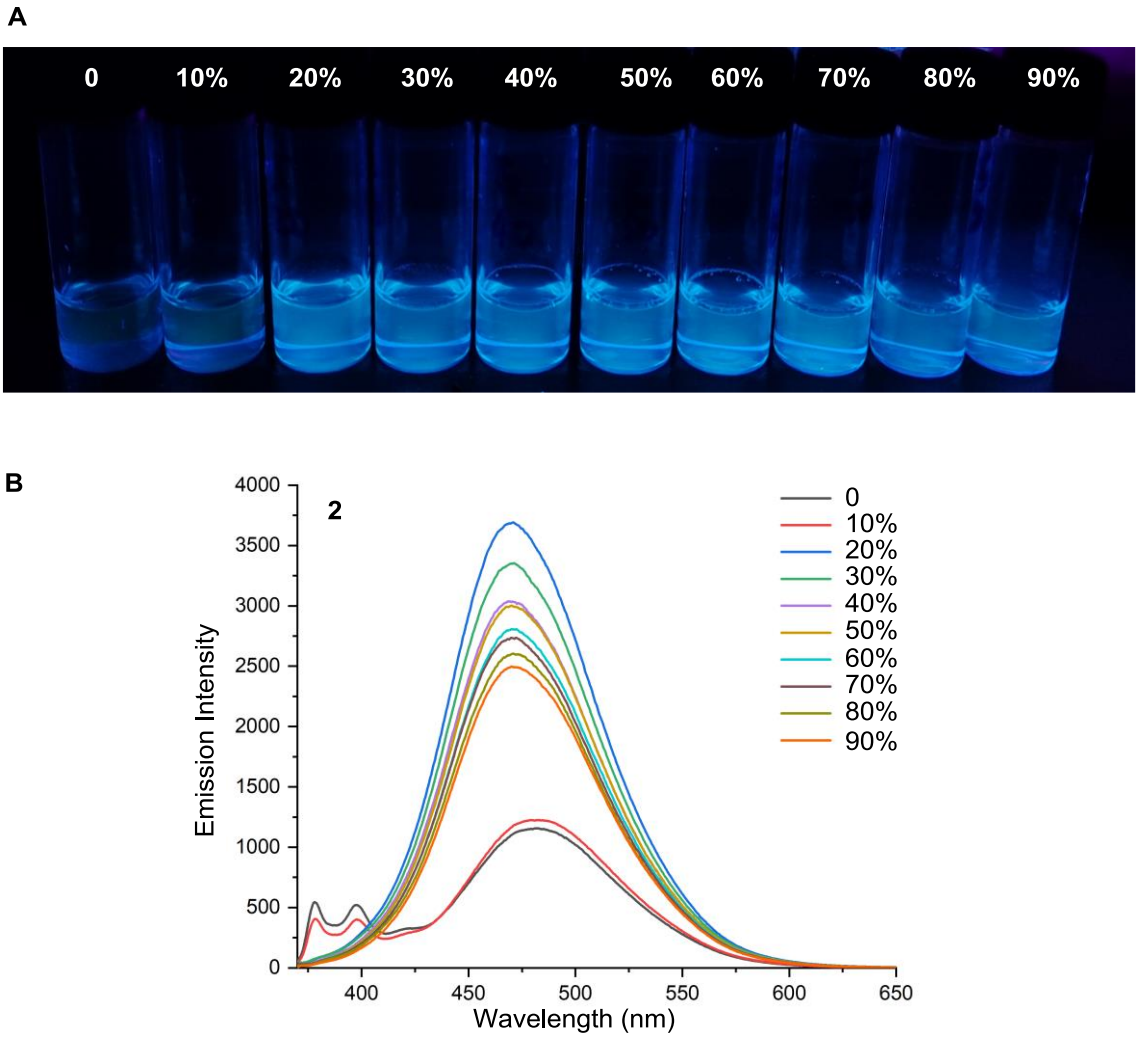


Figure S6. Photograph (λ_{ex}: 365 nm) and photoluminescence spectra (λ_{ex}: 360 nm) of **2** in DMSO/water mixtures. Concentration: 10 μmol/L.

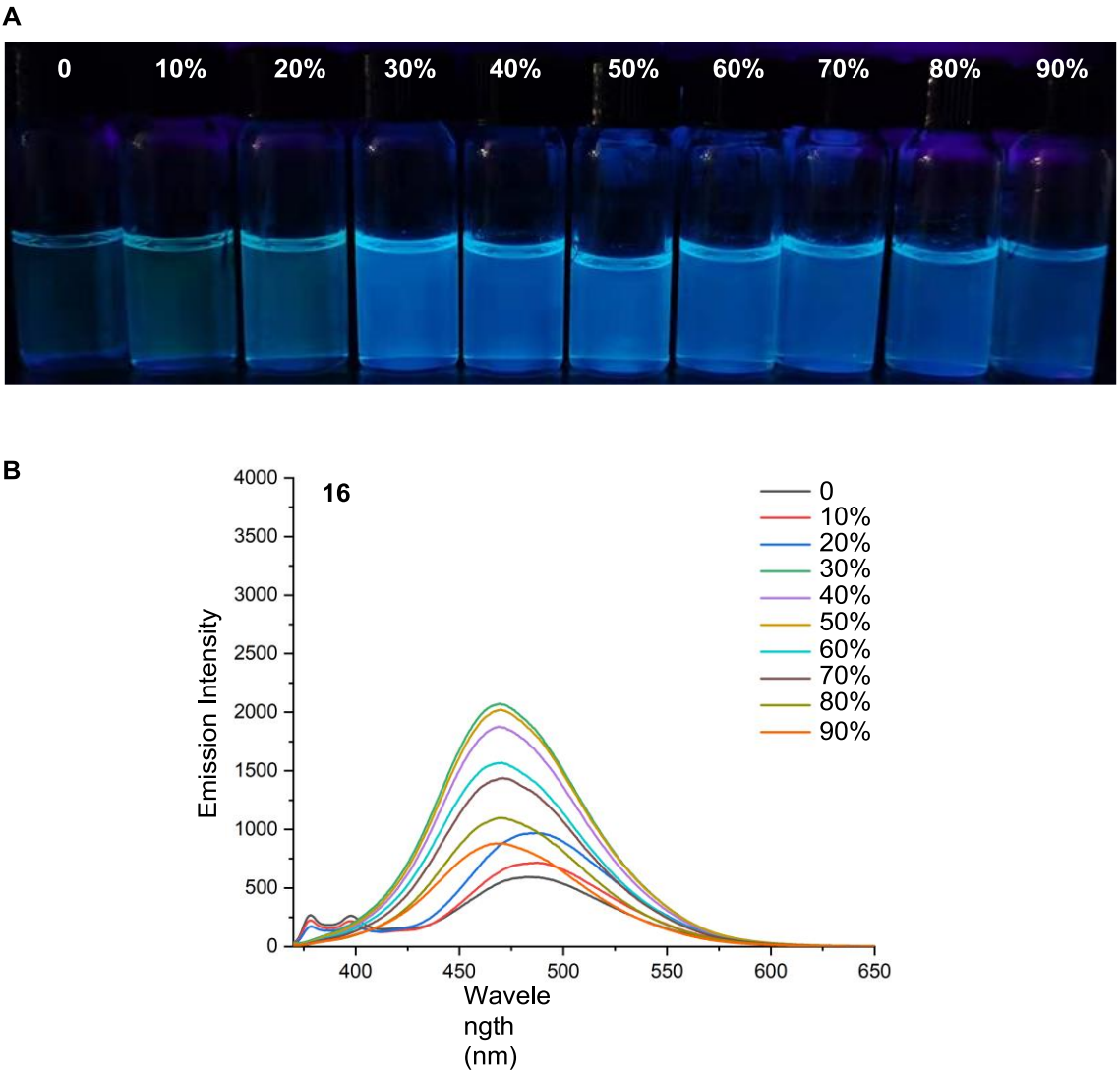


Figure S7. Photograph (λ_{ex}: 365 nm) and photoluminescence spectra (λ_{ex}: 360 nm) of **16** in DMSO/water mixtures. Concentration: 12.5 μmol/L.

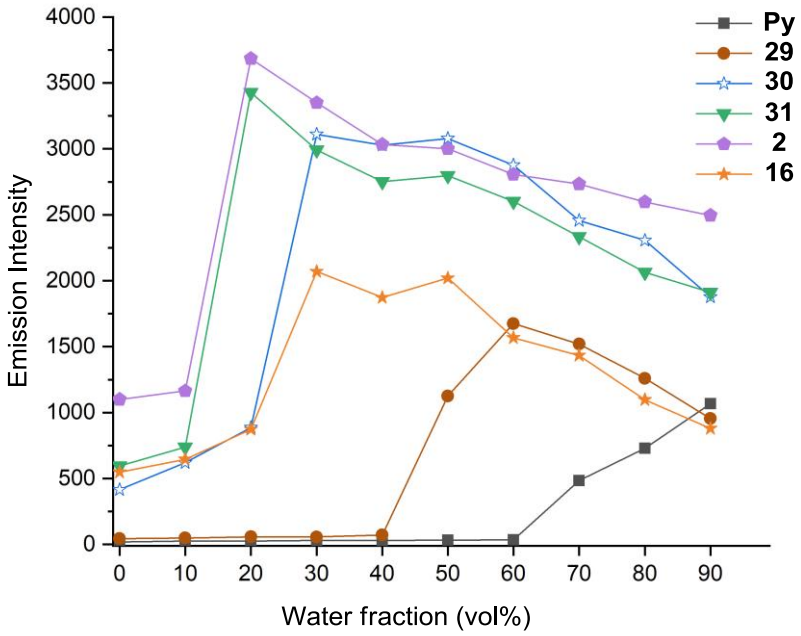


Figure S8. Plots of emission peak intensity at 470 nm of **Py**, **29**-**31**, **2** and **16** versus water fraction of their DMSO/water mixtures.

VII. NMR Spectra

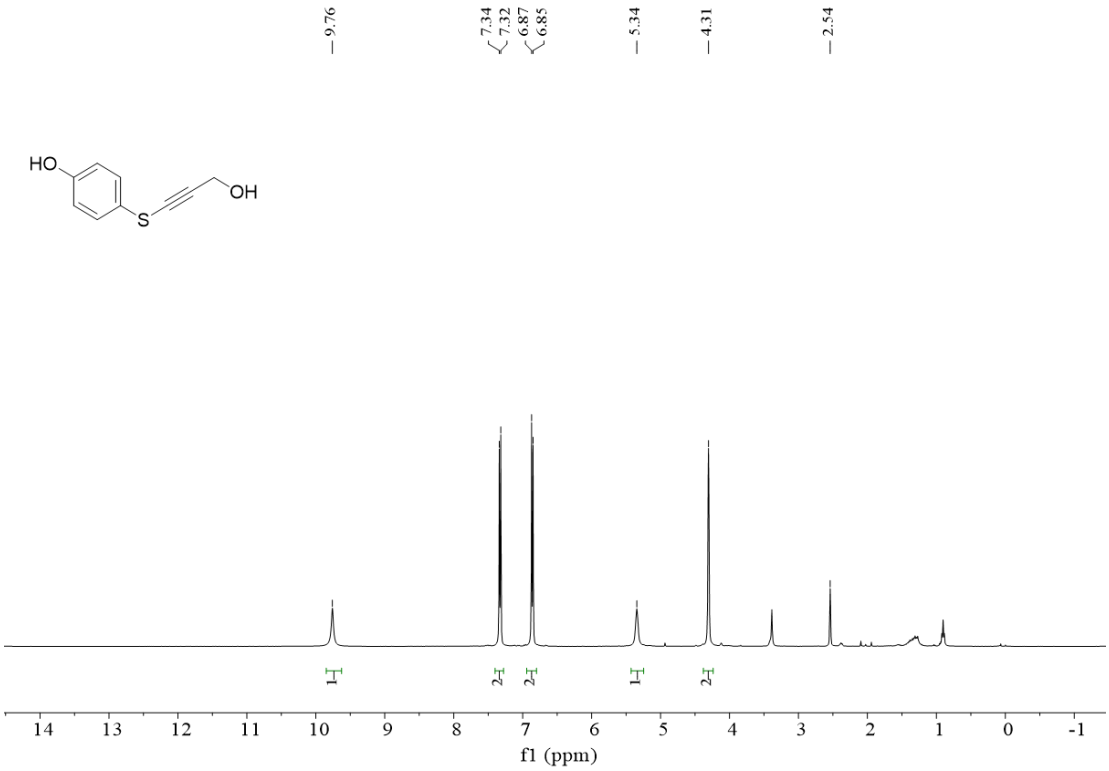


Figure S9. ^{1}H NMR spectra of **M2**.

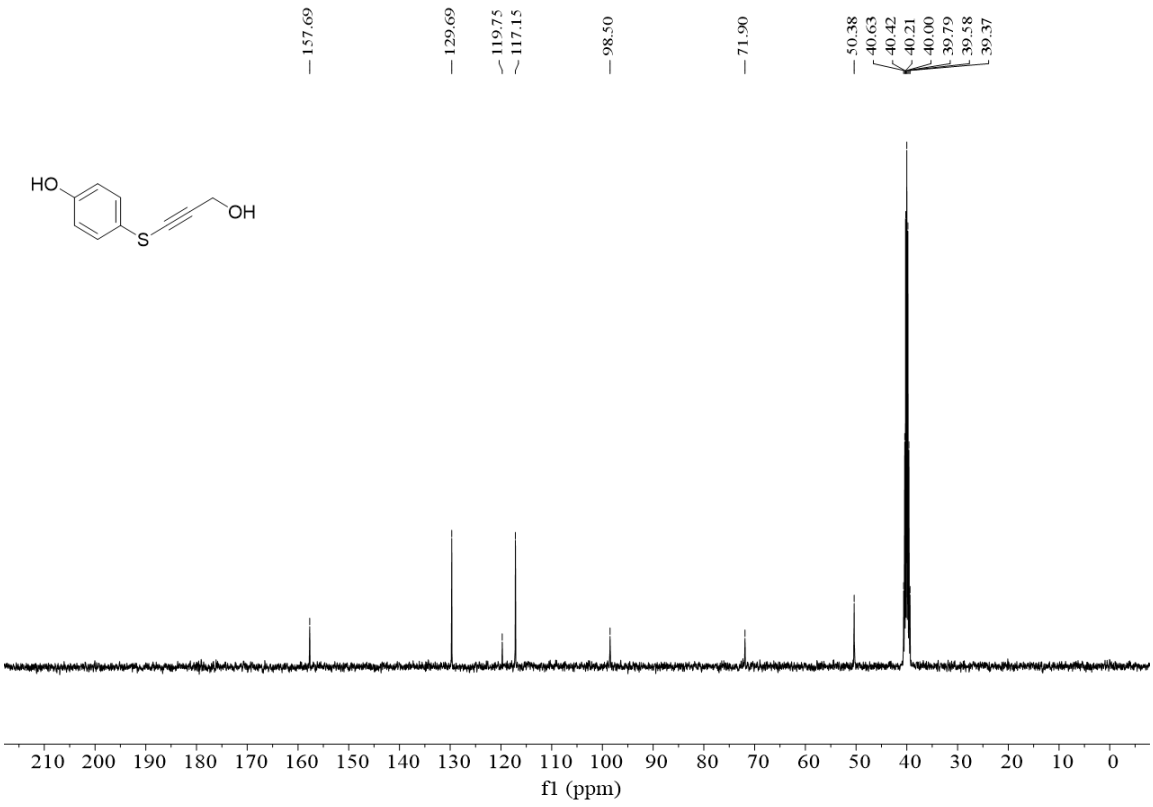


Figure S10. ^{13}C NMR spectra of **M2**.

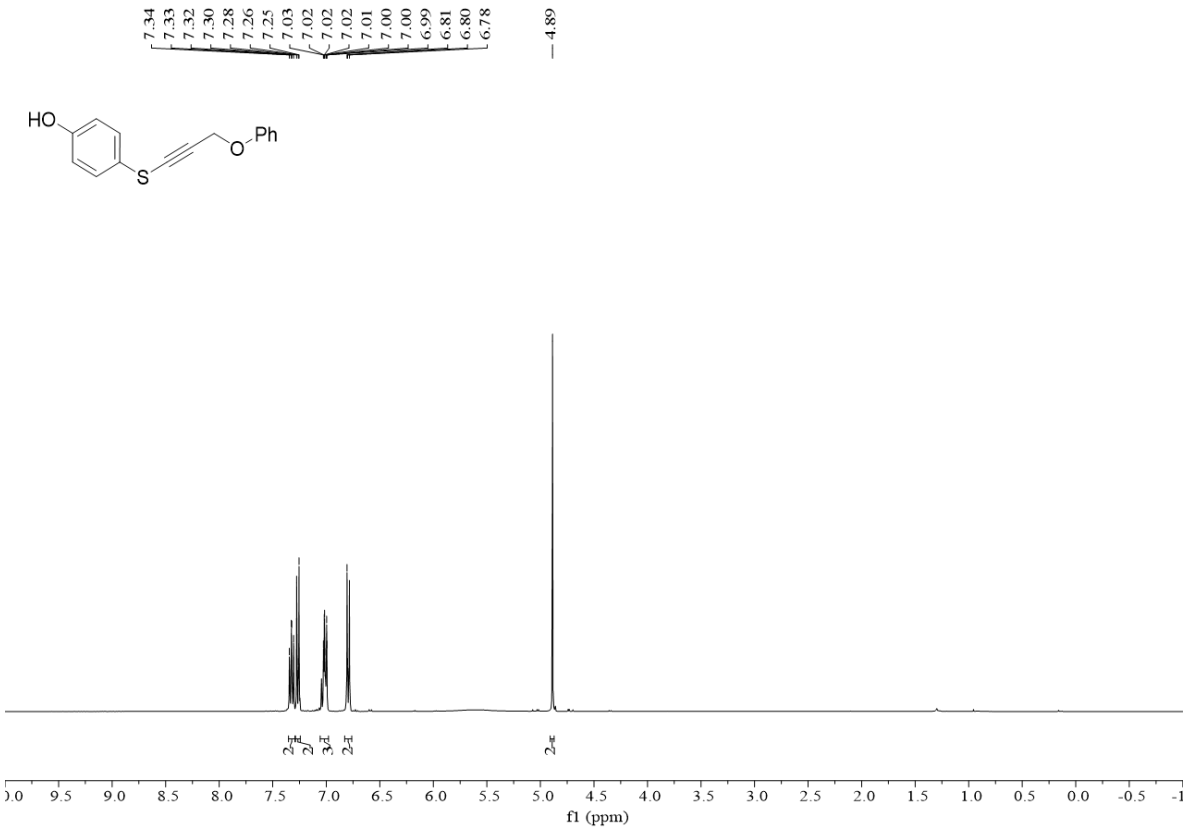


Figure S11. ^{1}H NMR spectra of **M3**.

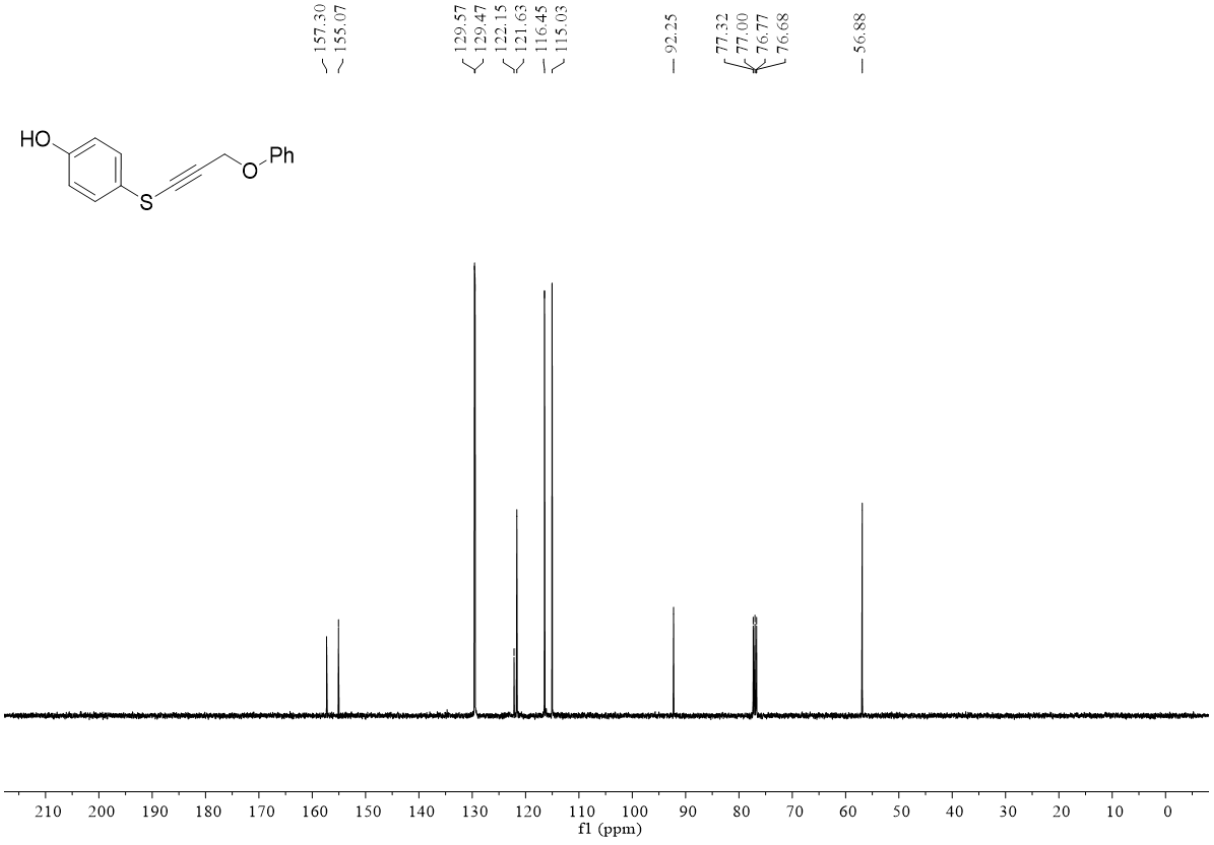


Figure S12. ^{13}C NMR spectra of **M3**.

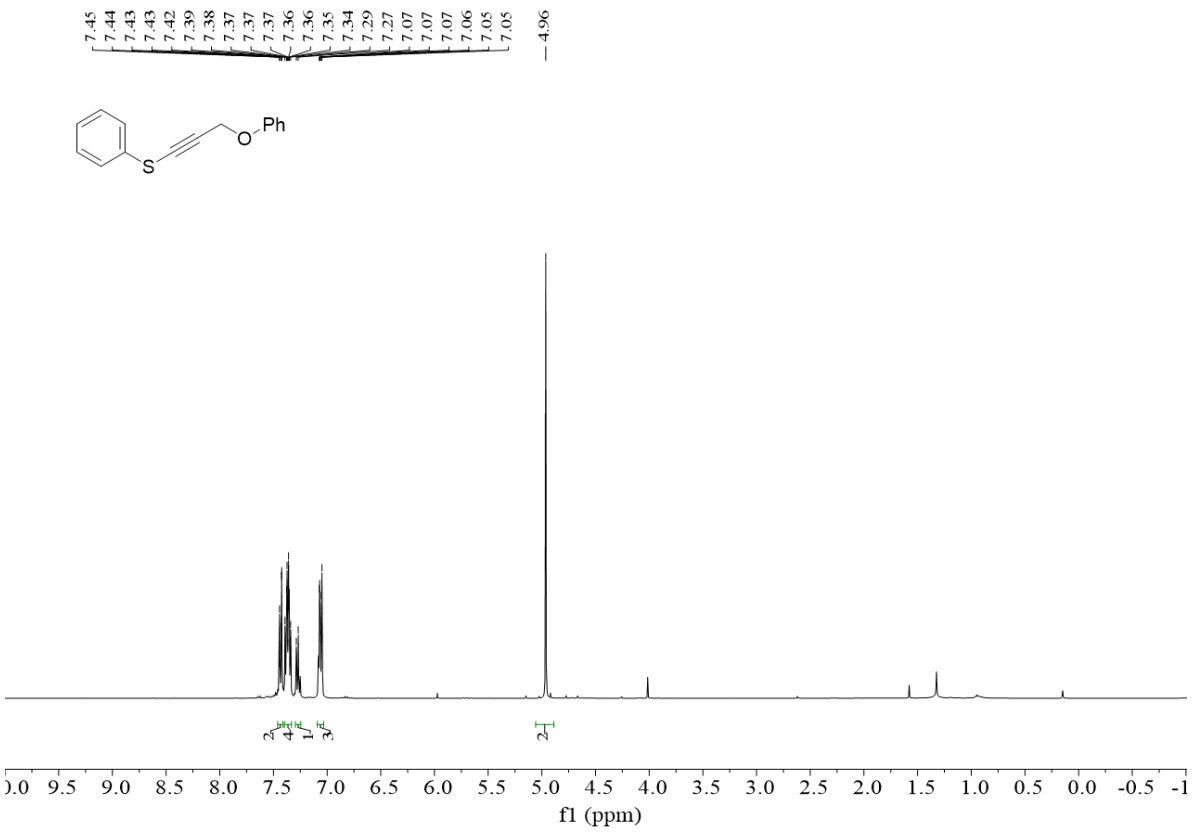


Figure S13. ^{1}H NMR spectra of **A1**.

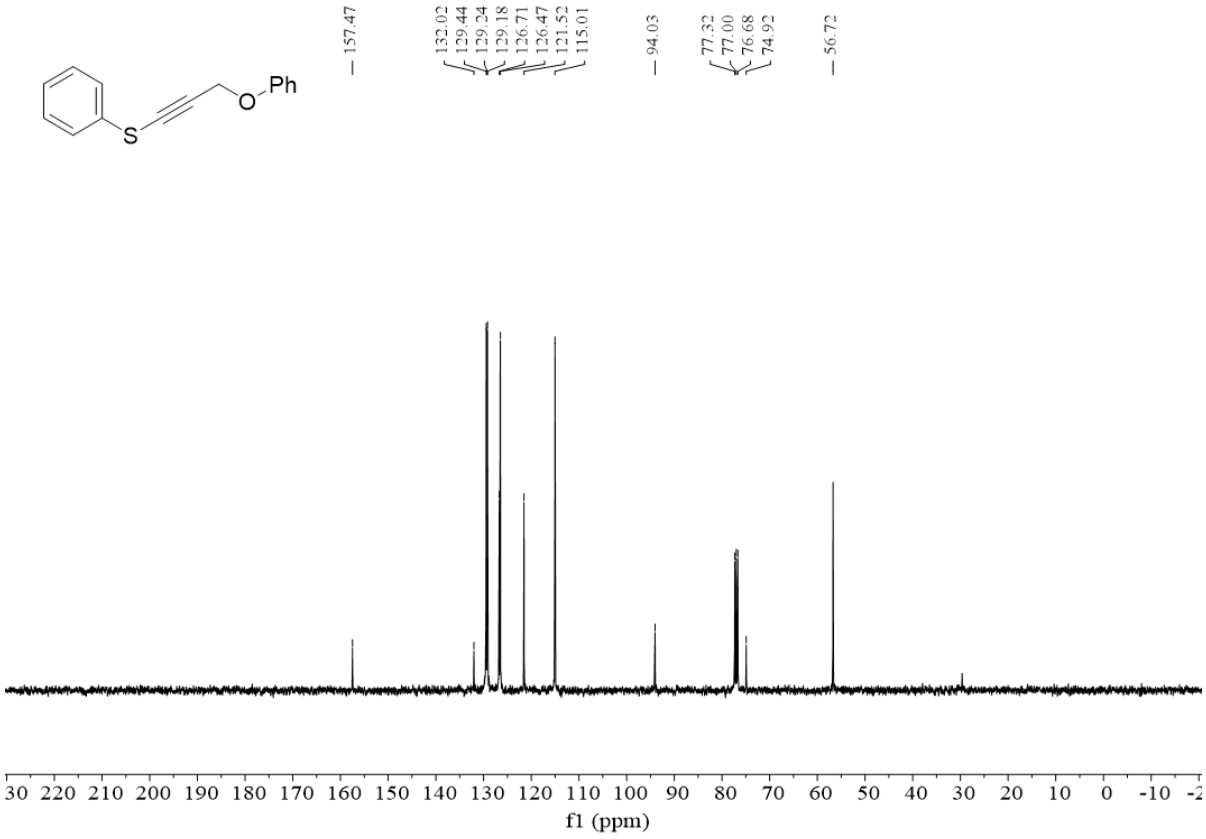


Figure S14. ^{13}C NMR spectra of **A1**.

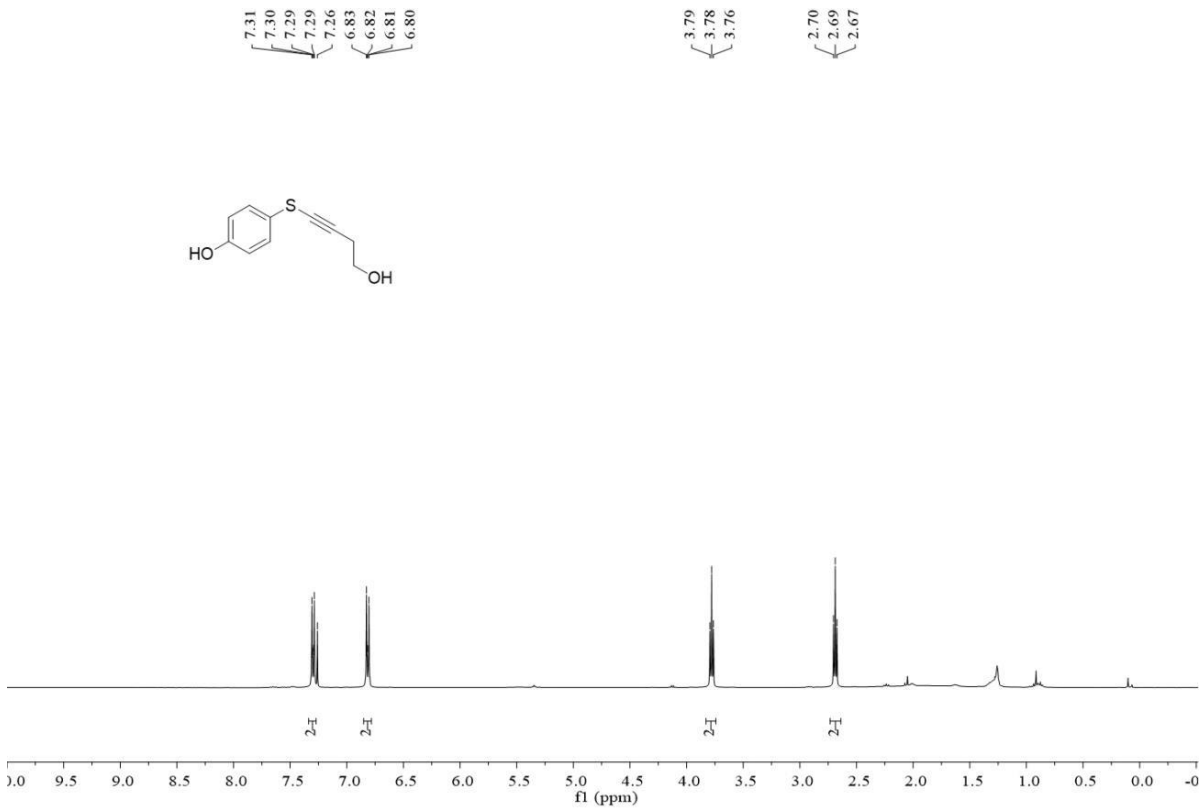


Figure S15. ^{1}H NMR spectra of **M4**.

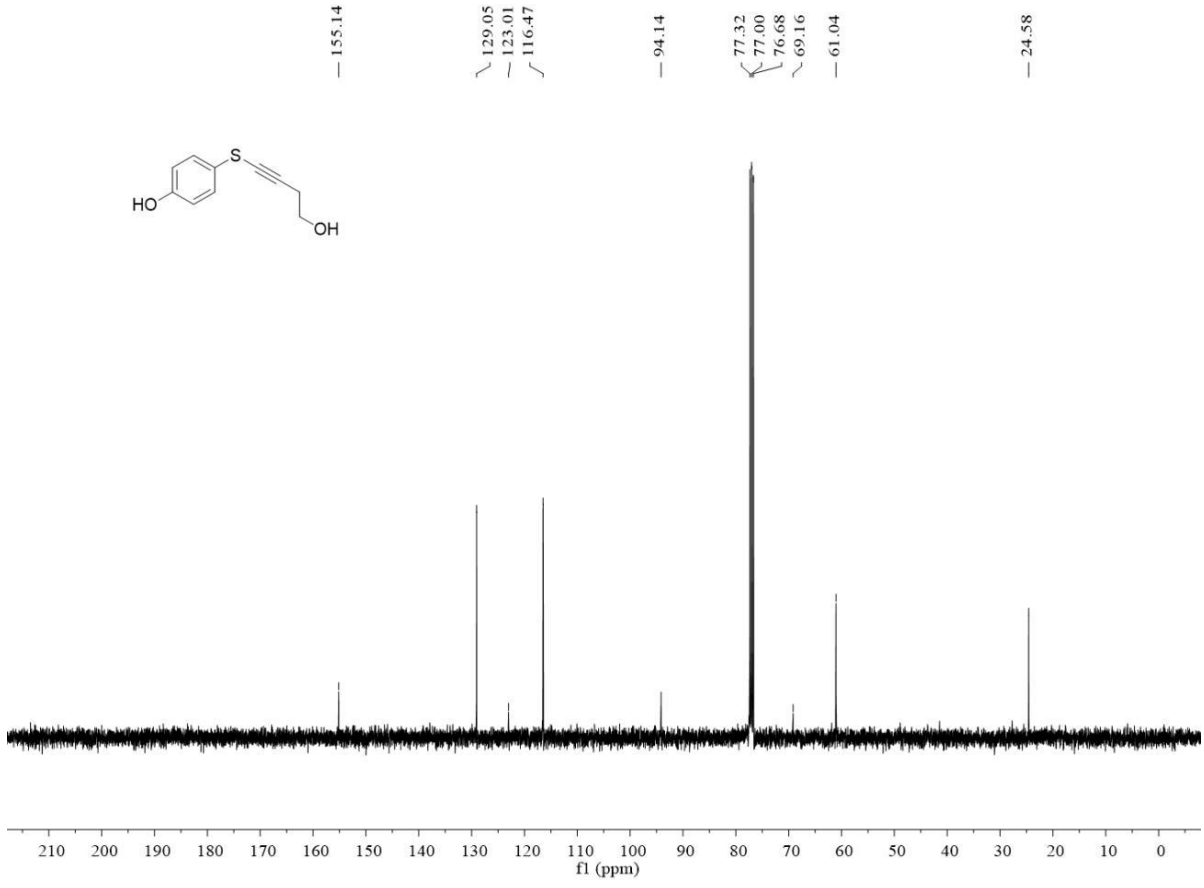


Figure S16. ^{13}C NMR spectra of **M4**.

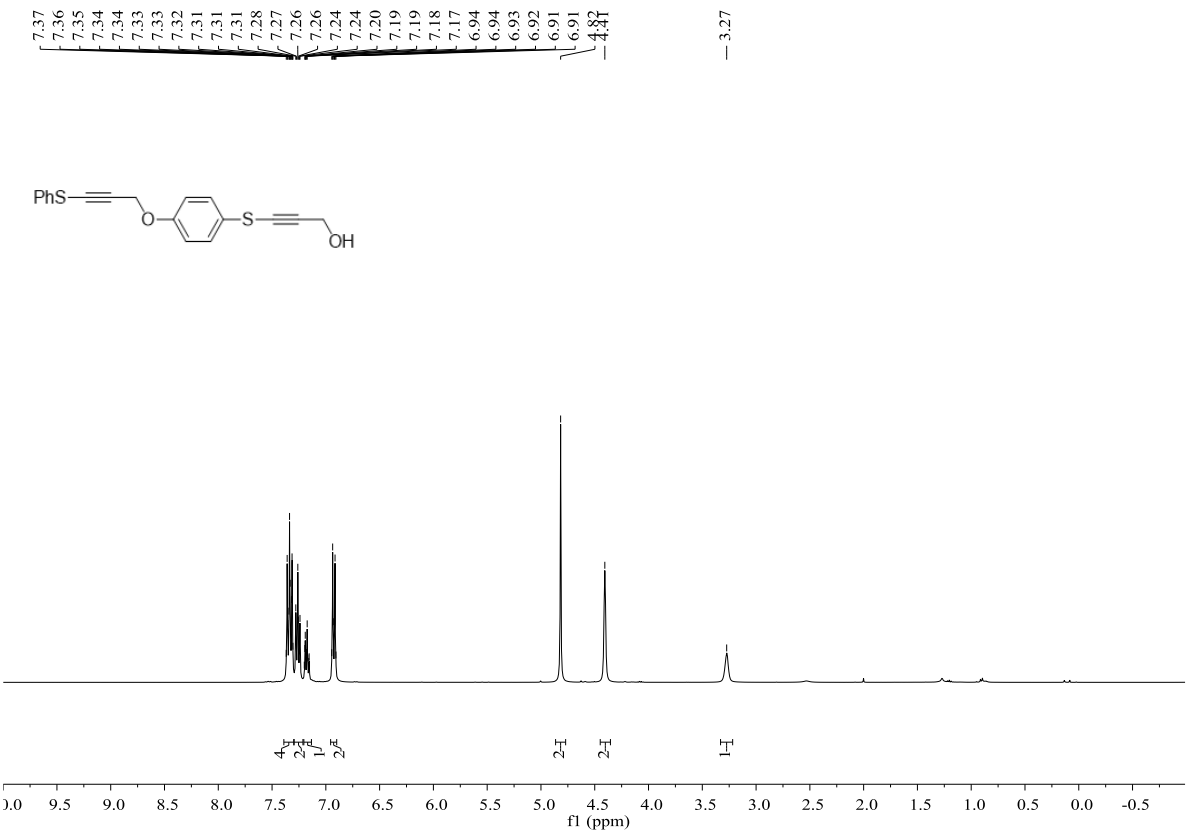


Figure S17. ^{1}H NMR spectra of **A2-ω-OH**.

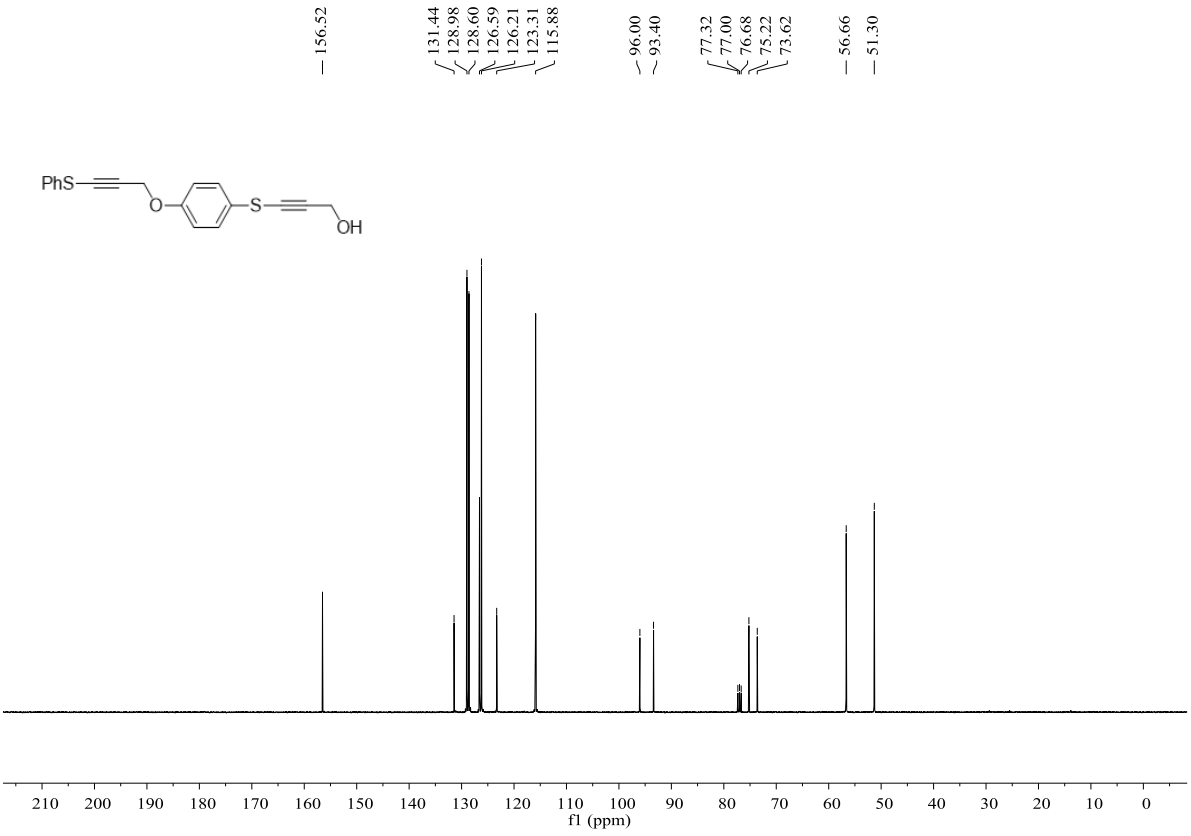


Figure S18. ^{13}C NMR spectra of **A2-ω-OH**.

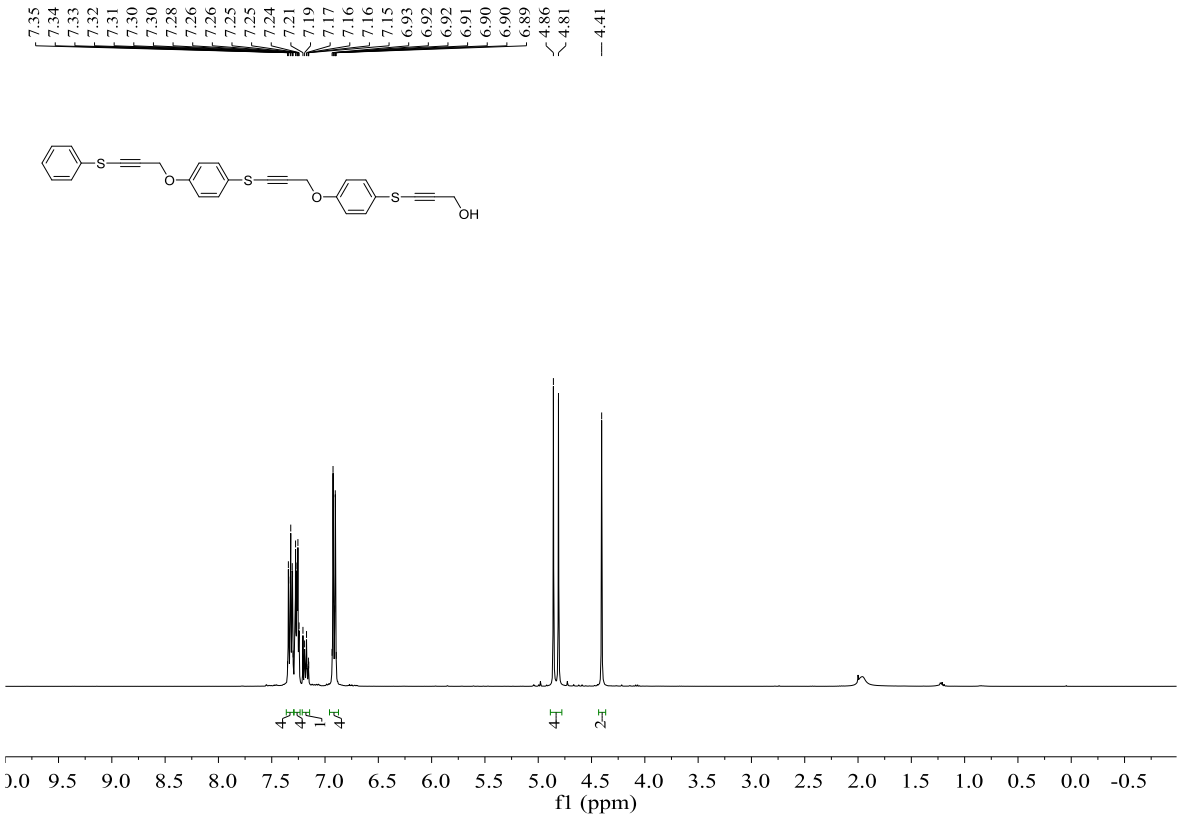


Figure S19. ^{1}H NMR spectra of **A3-ω-OH**.

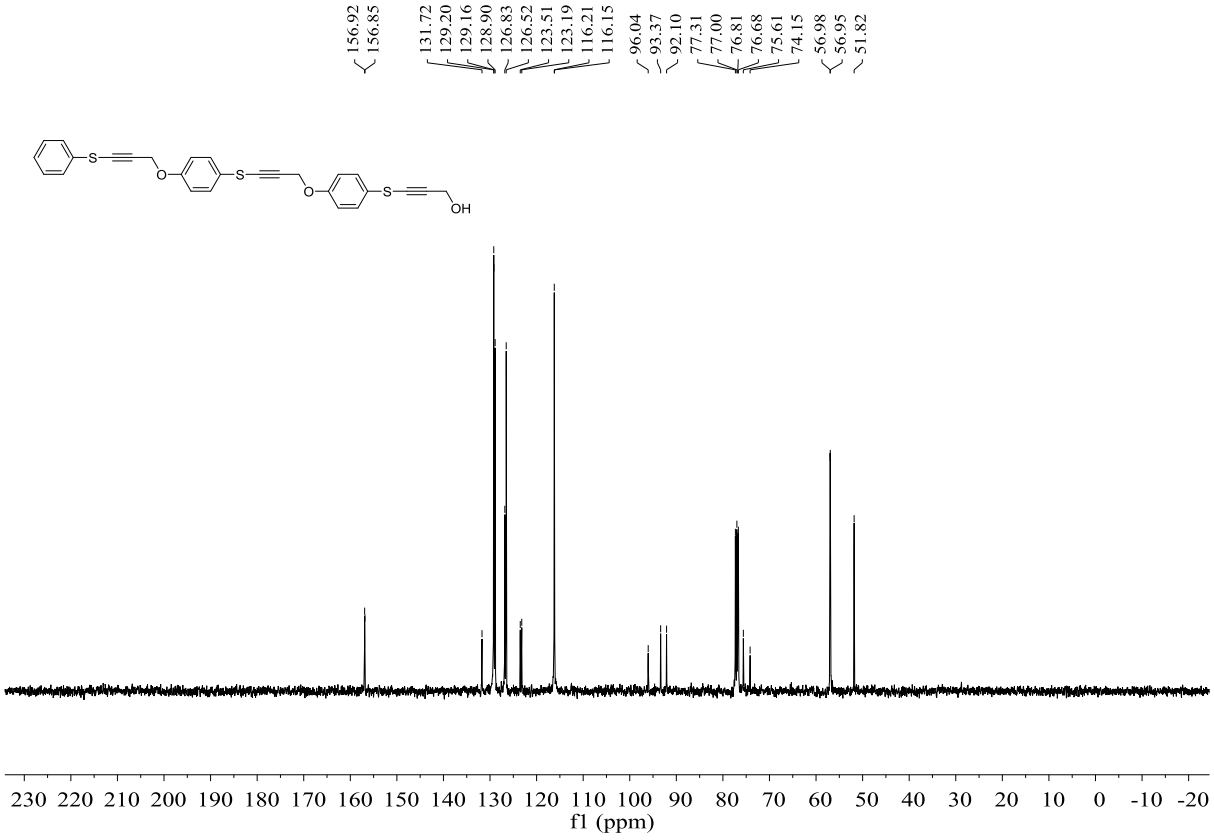


Figure S20. ^{13}C NMR spectra of **A3-ω-OH**.

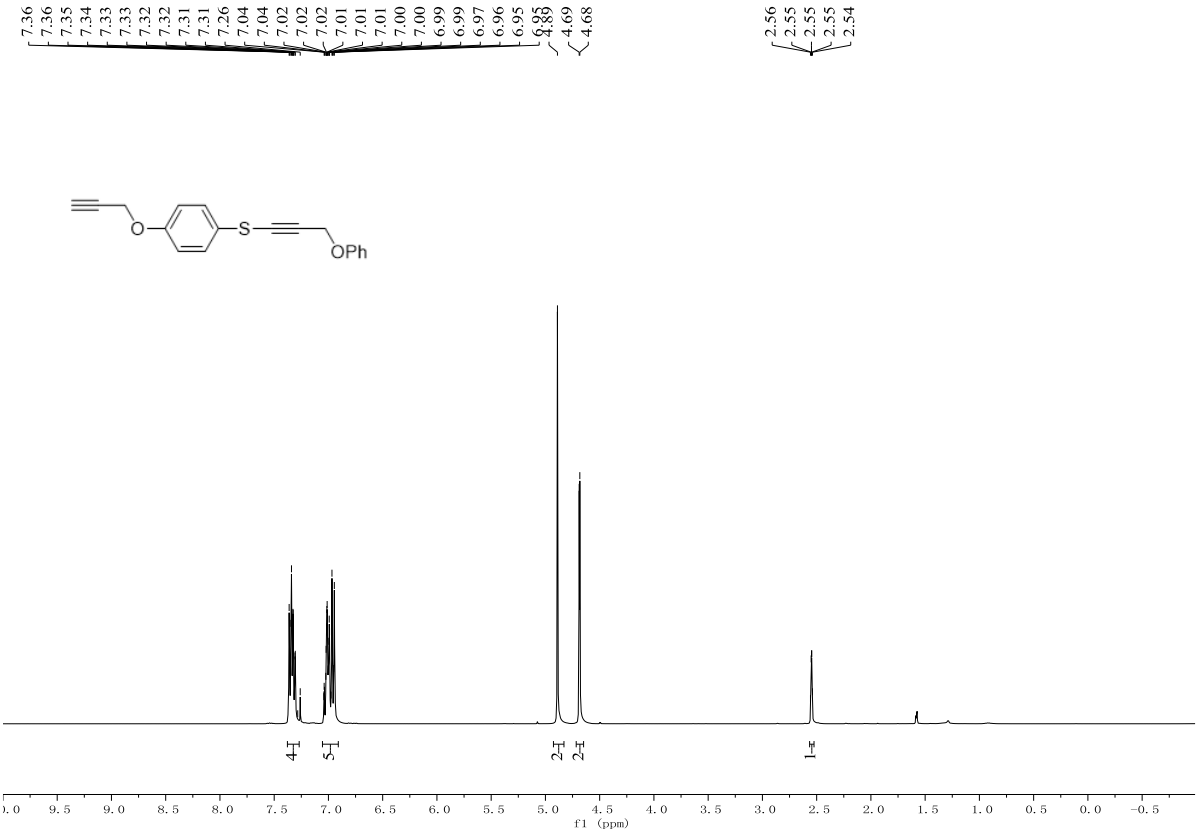


Figure S21. ^{1}H NMR spectra of **M3**-yne.

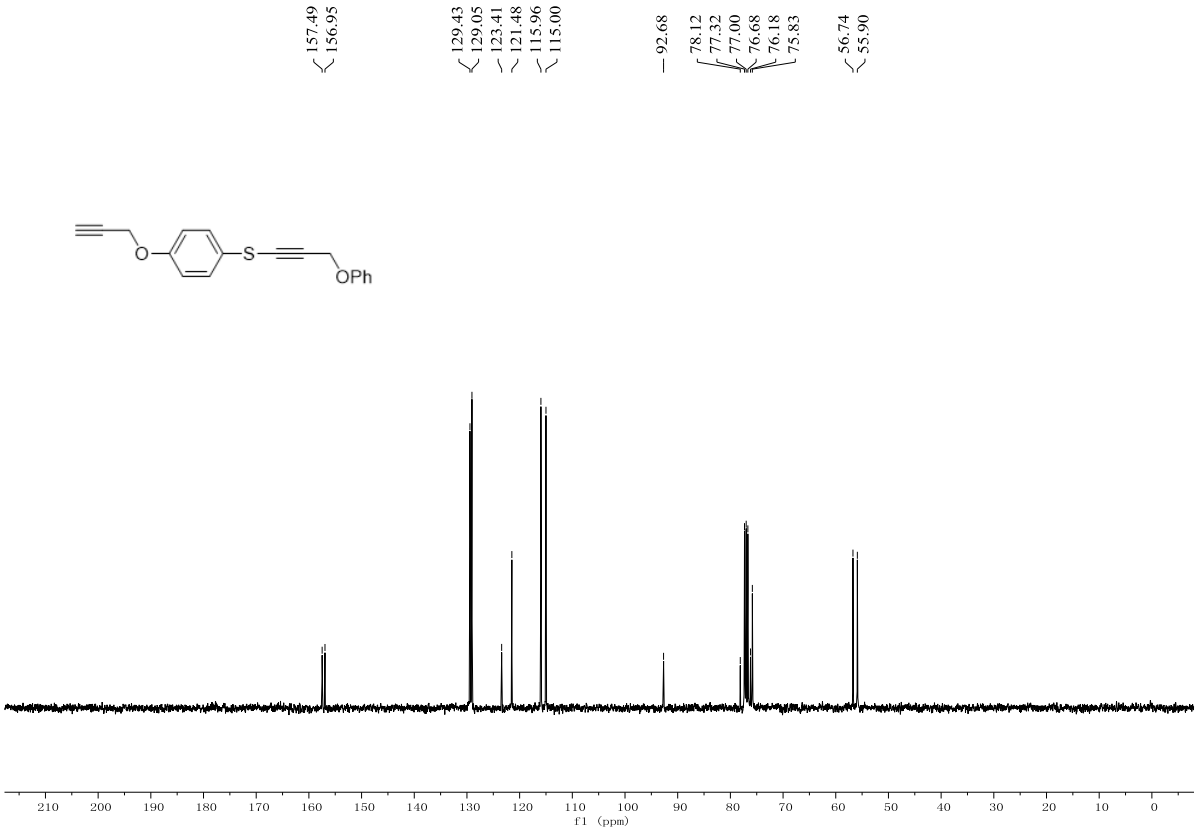


Figure S22. ^{13}C NMR spectra of **M3**-yne.

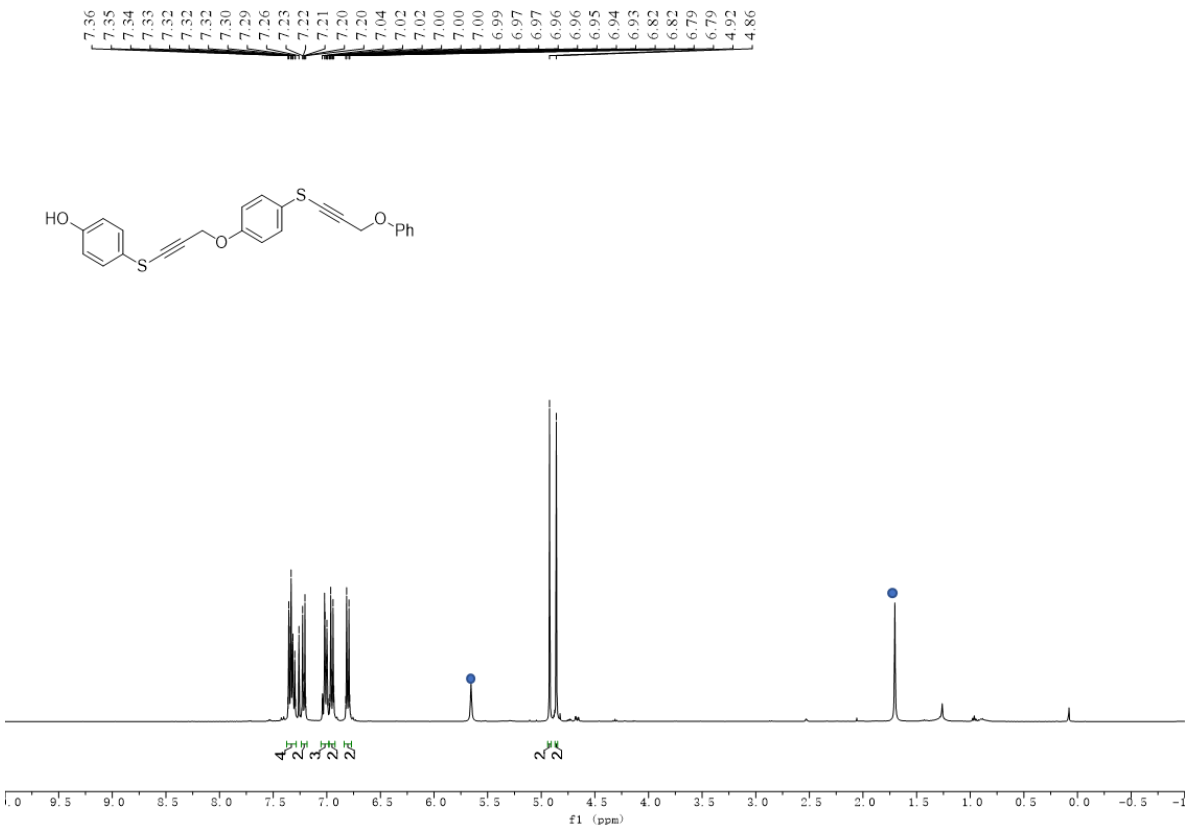


Figure S23. ^{1}H NMR spectra of **A2-α-OH**.

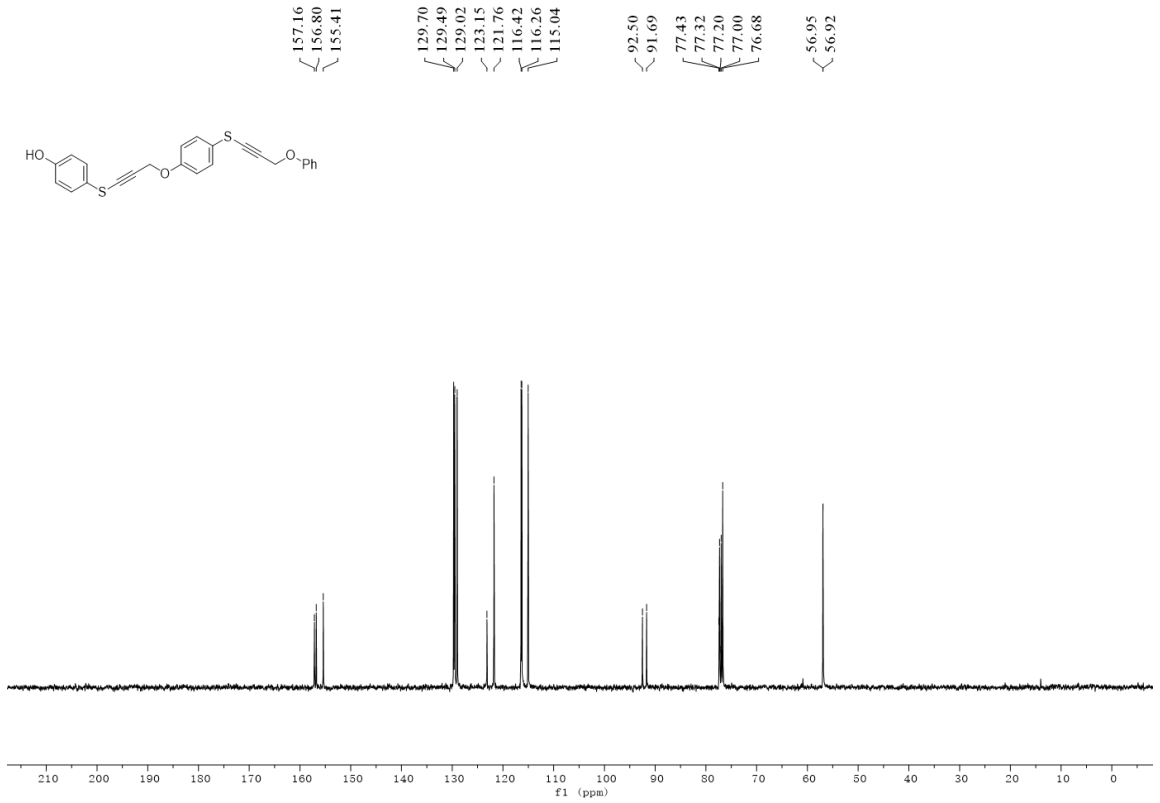


Figure S24. ^{13}C NMR spectra of **A2-α-OH**.

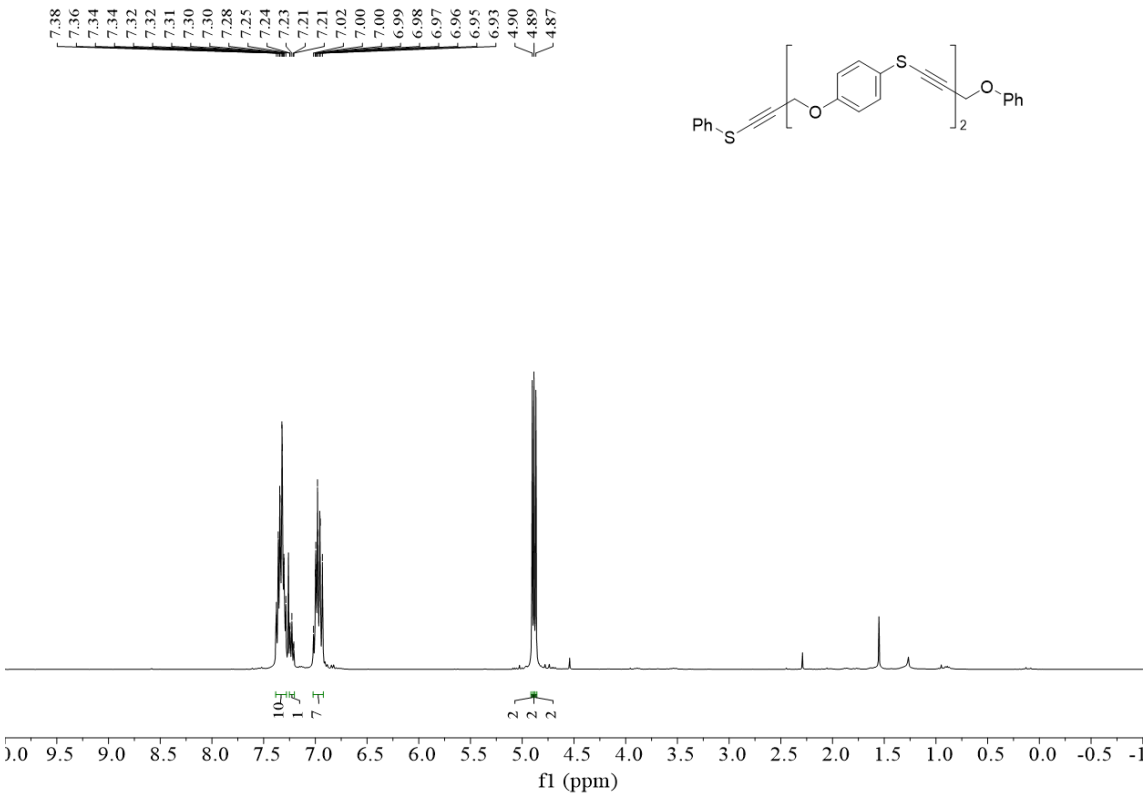


Figure S25. ^{1}H NMR spectra of **A3**.

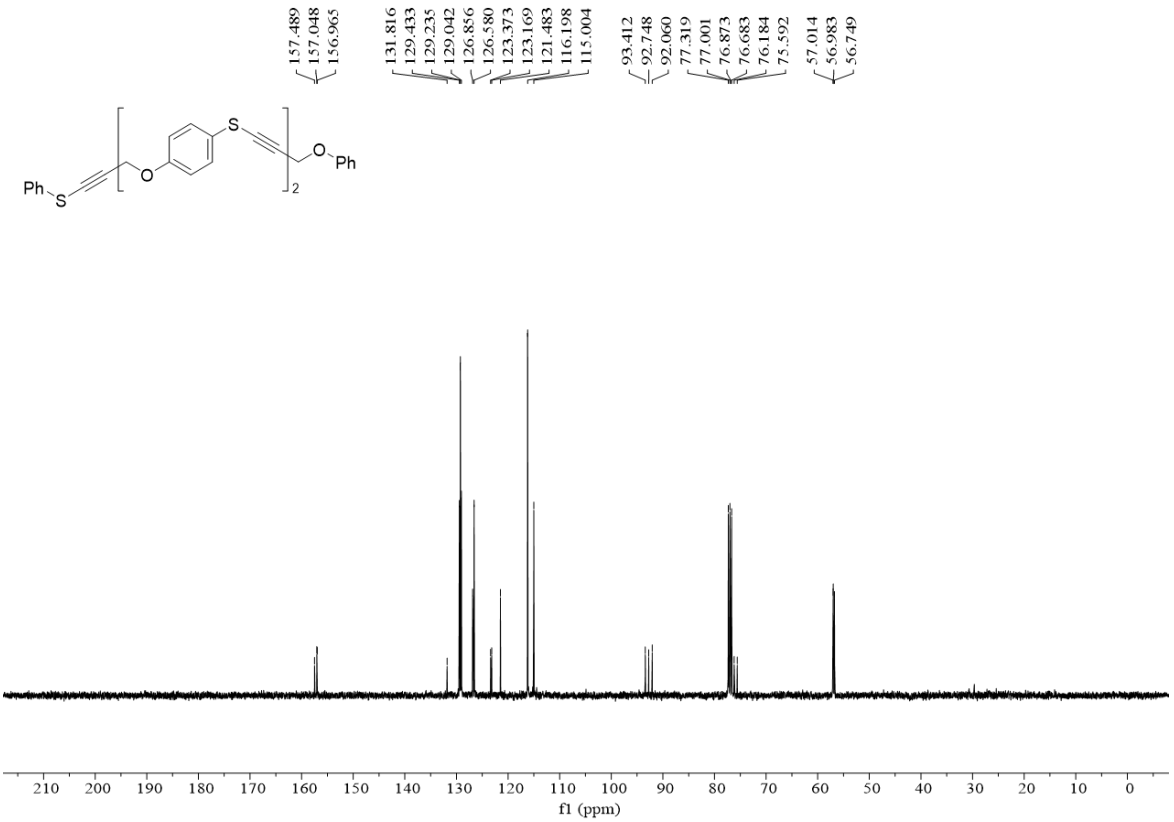


Figure S26. ^{13}C NMR spectra of **A3**.

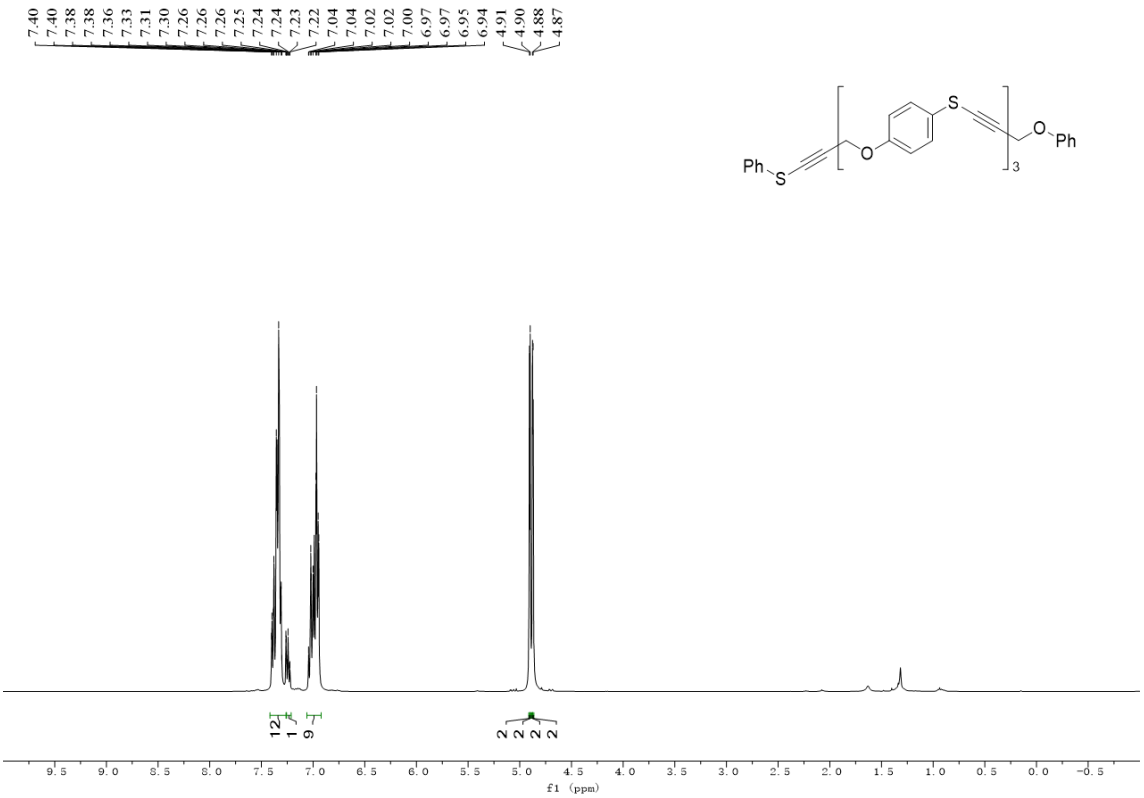


Figure S27. ^{1}H NMR spectra of **A4**.

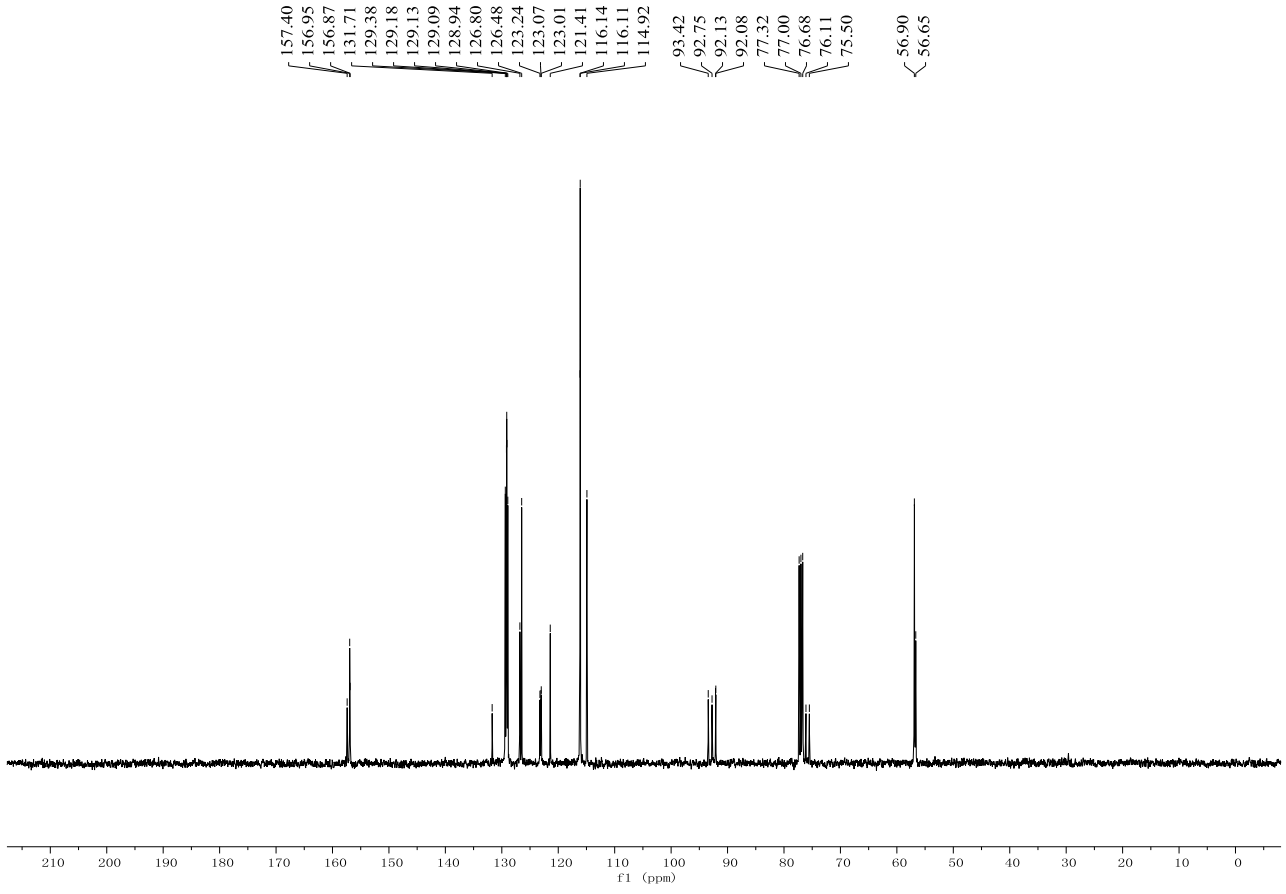


Figure S28. ^{13}C NMR spectra of **A4** .

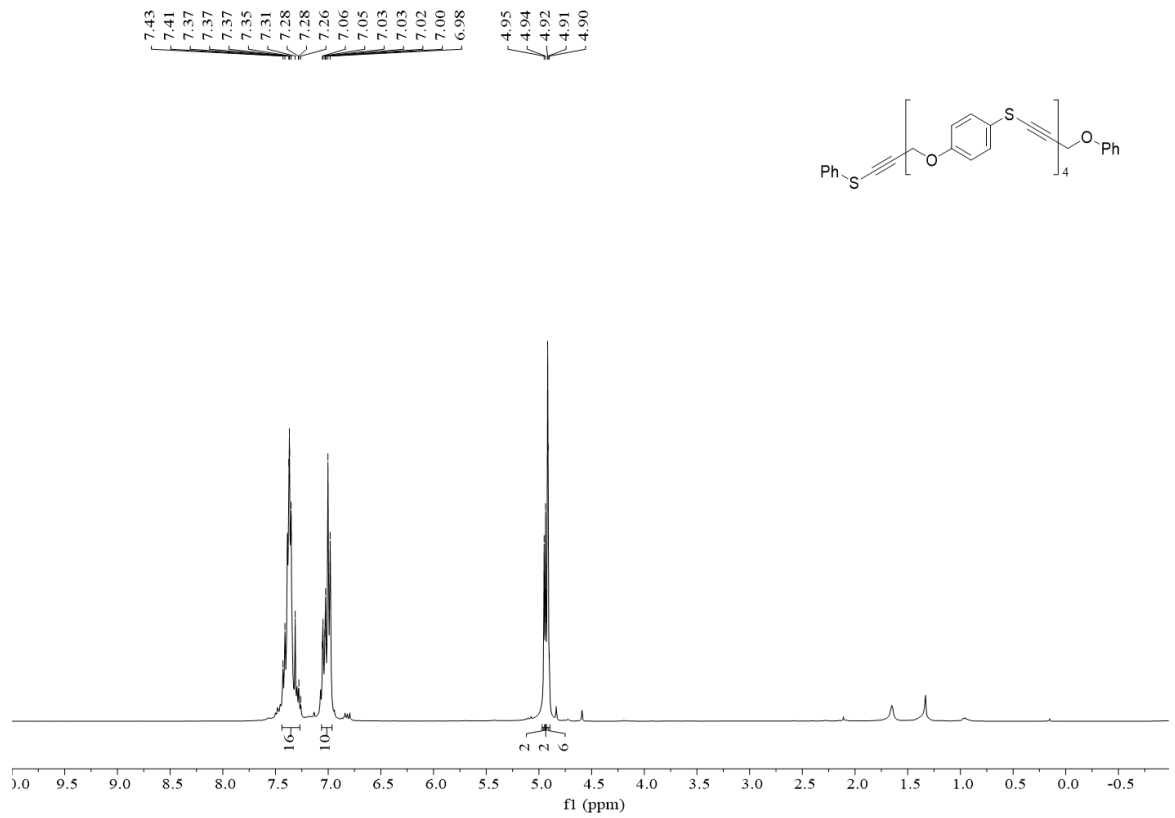


Figure S29. ^{1}H NMR spectra of **A5**.

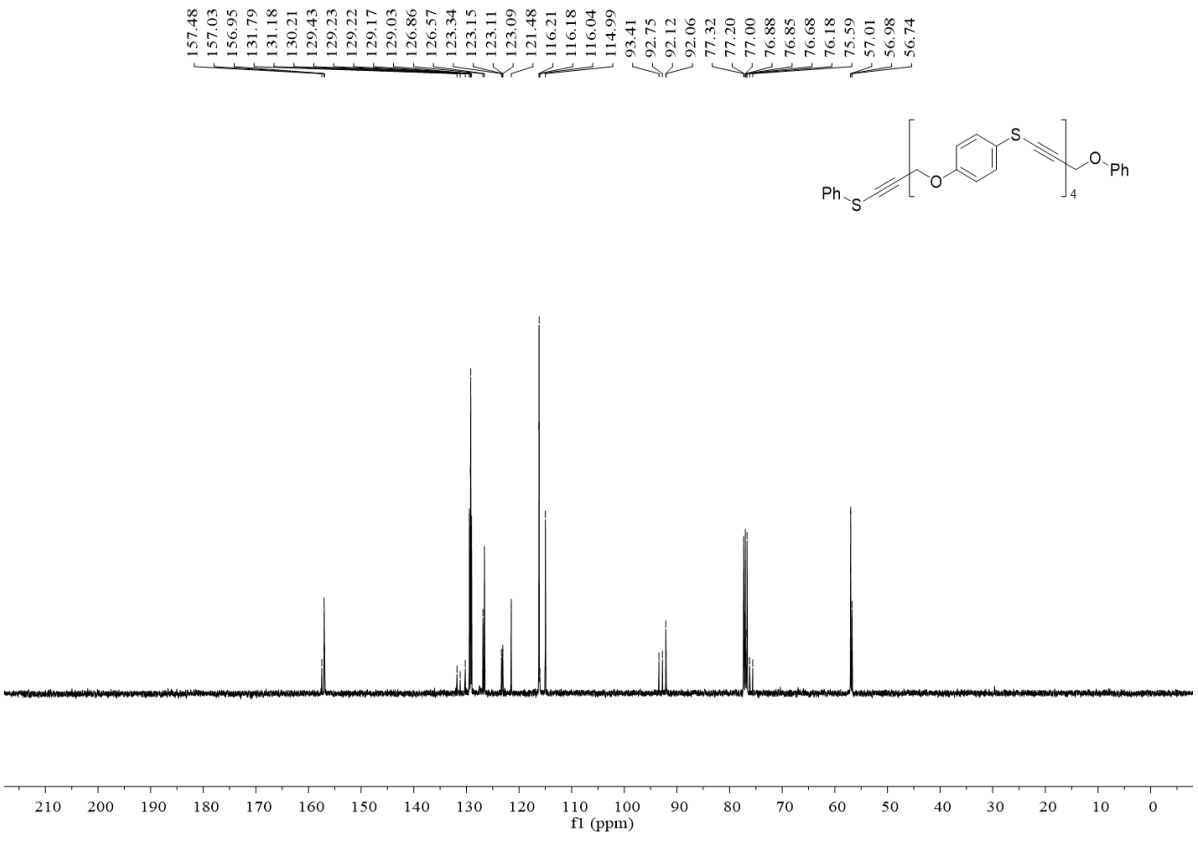


Figure S30. ^{13}C NMR spectra of **A5**.

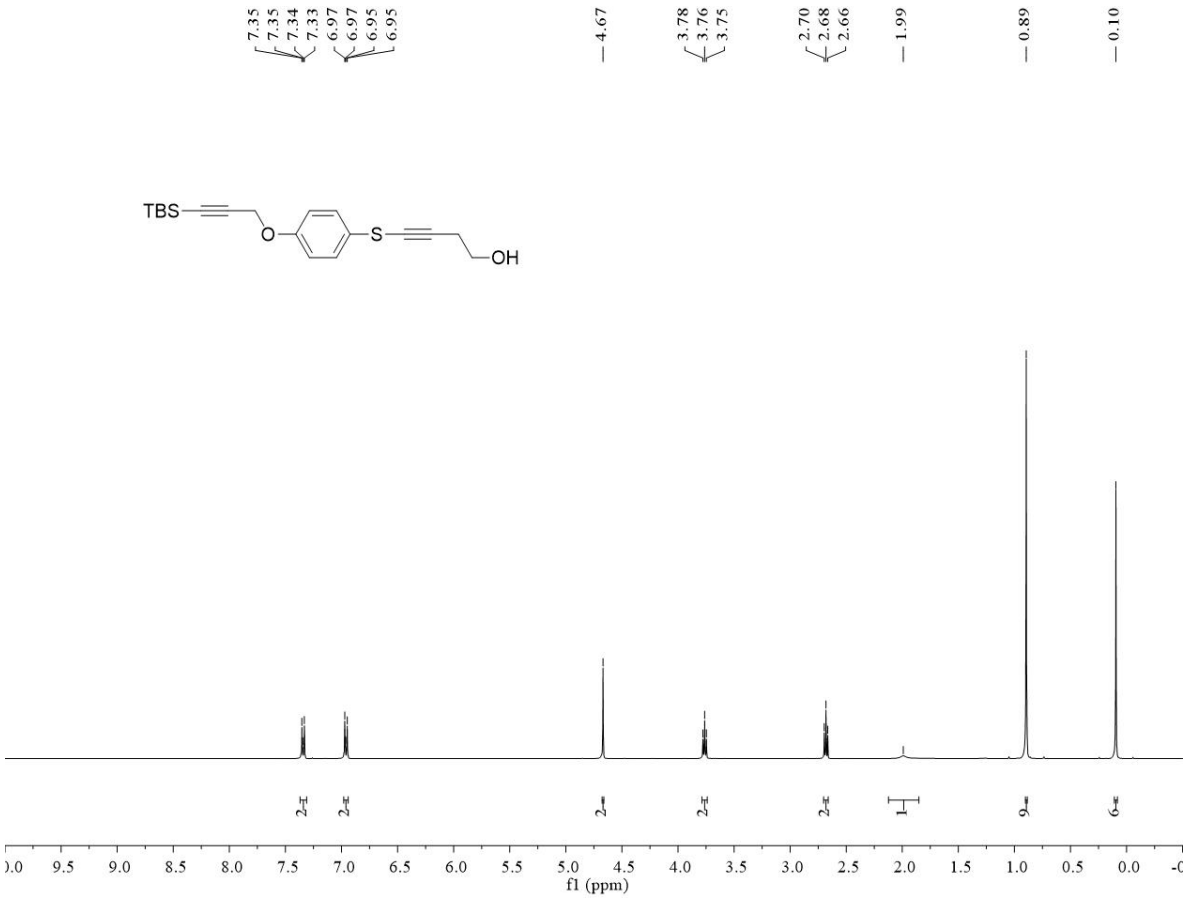


Figure S31. ^{1}H NMR spectra of **M4-OH**.

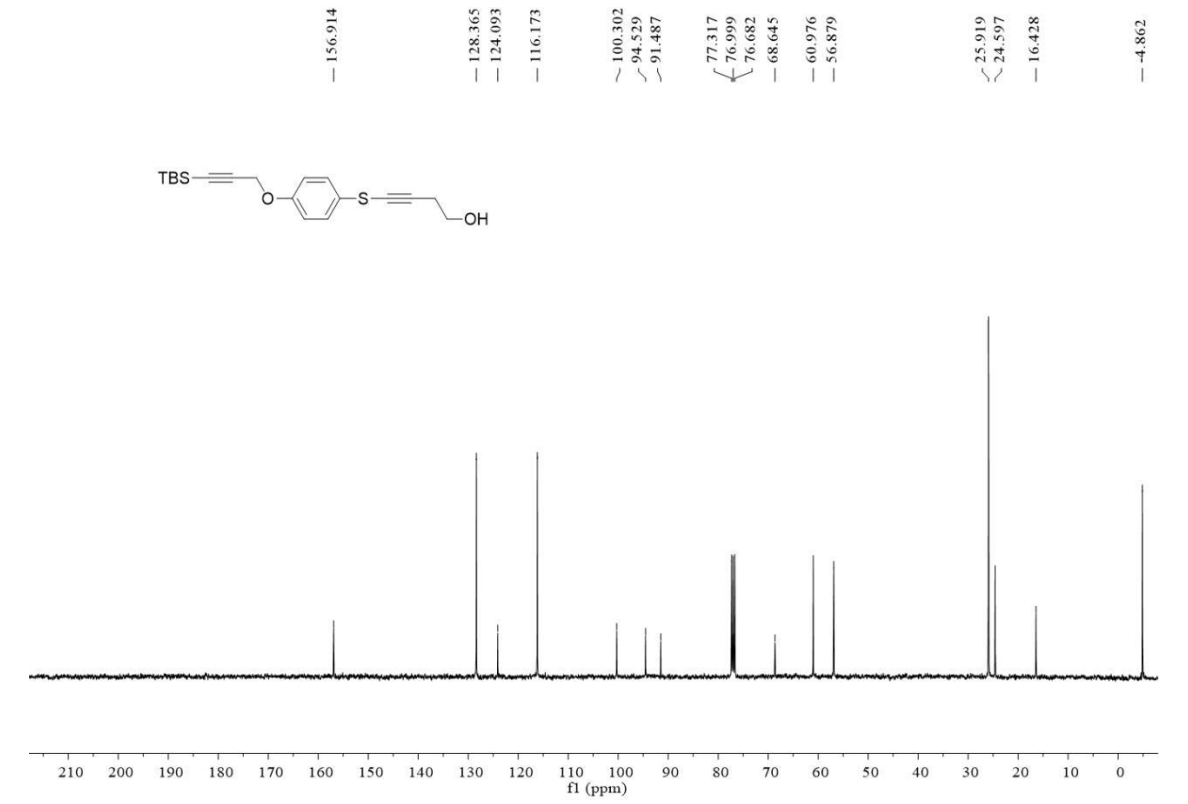


Figure S32. ^{13}C NMR spectra of **M4-OH**.

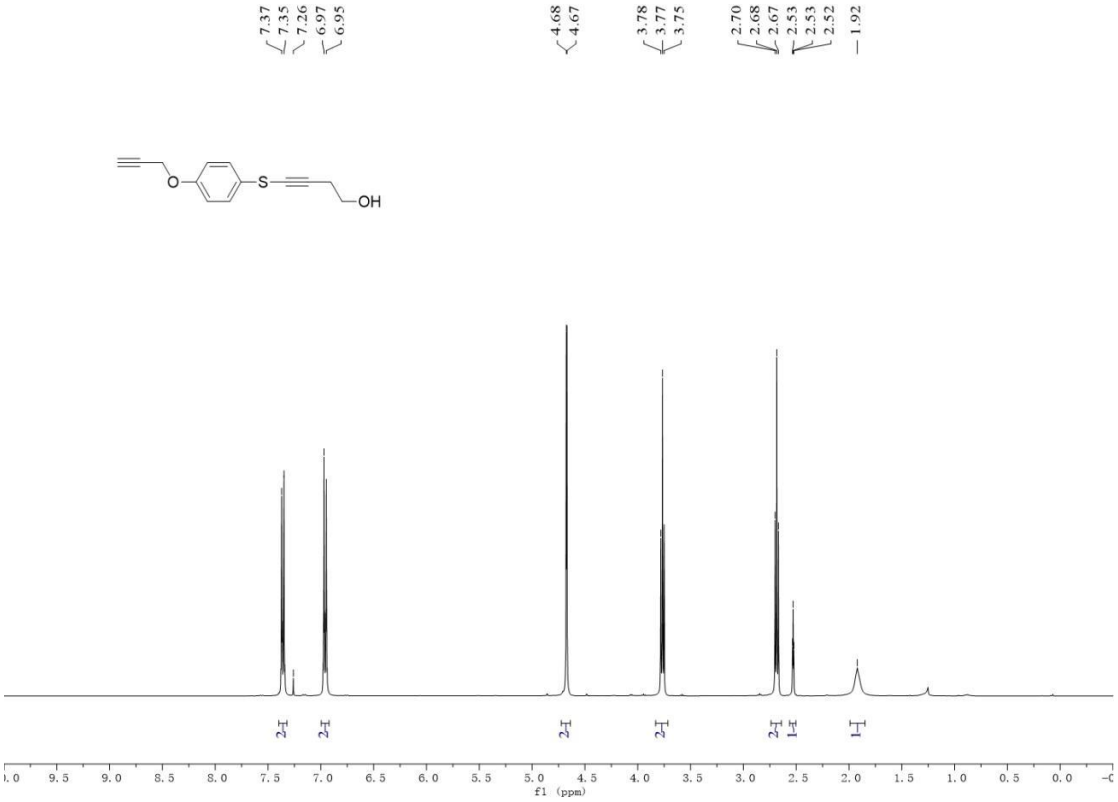


Figure S33. ^{1}H NMR spectra of **M4-yne**.

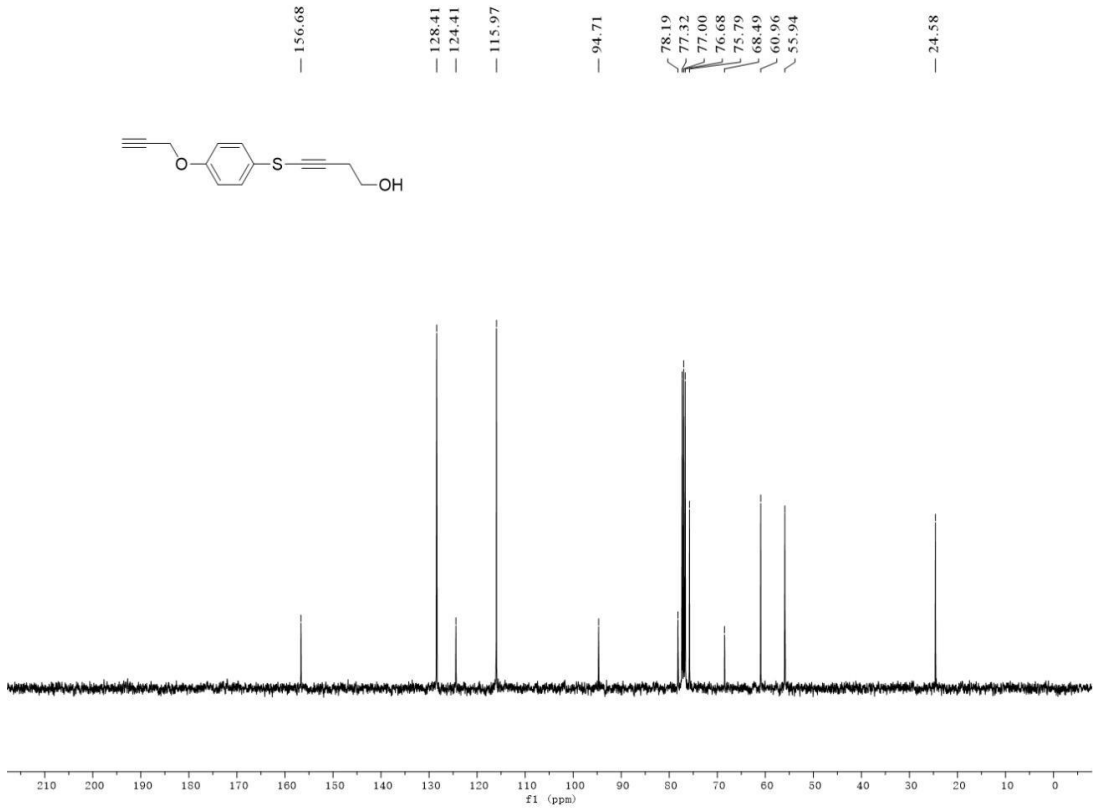


Figure S34. ^{13}C NMR spectra of **M4-yne**.

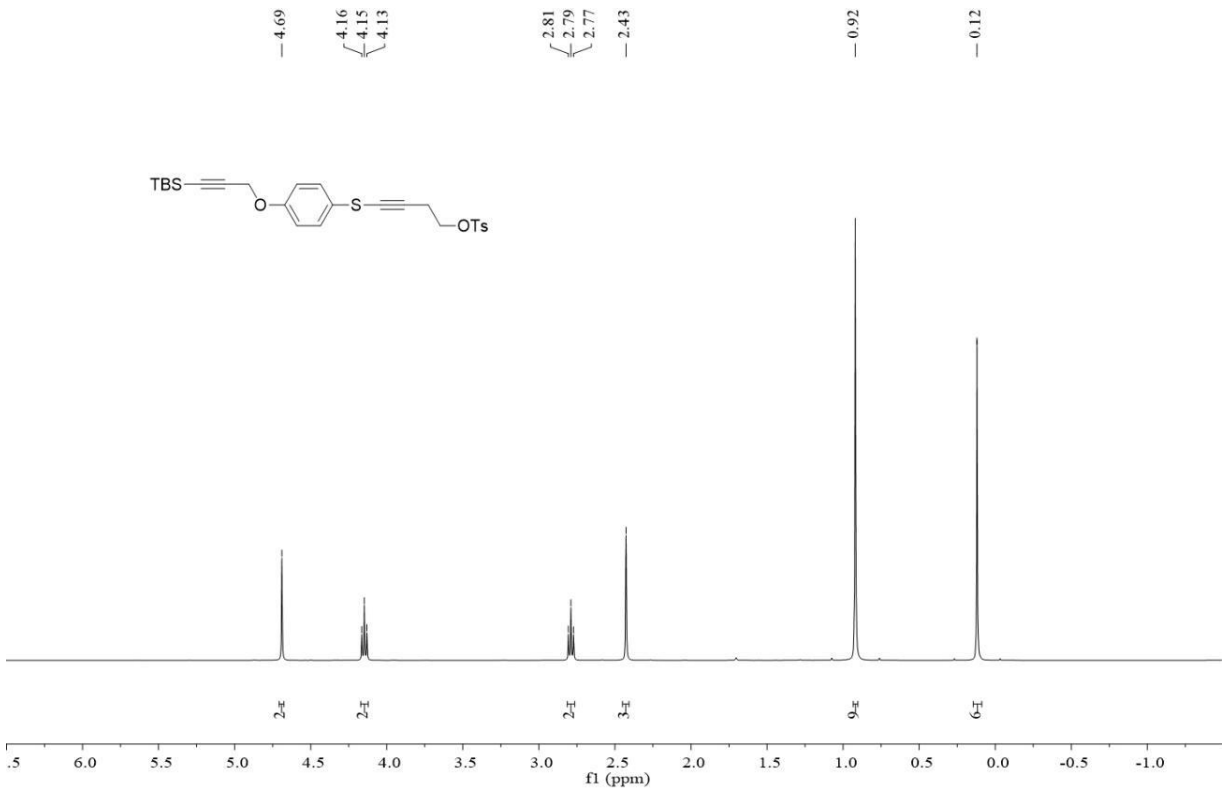


Figure S35. ^{1}H NMR spectra of **M4-OTs**.

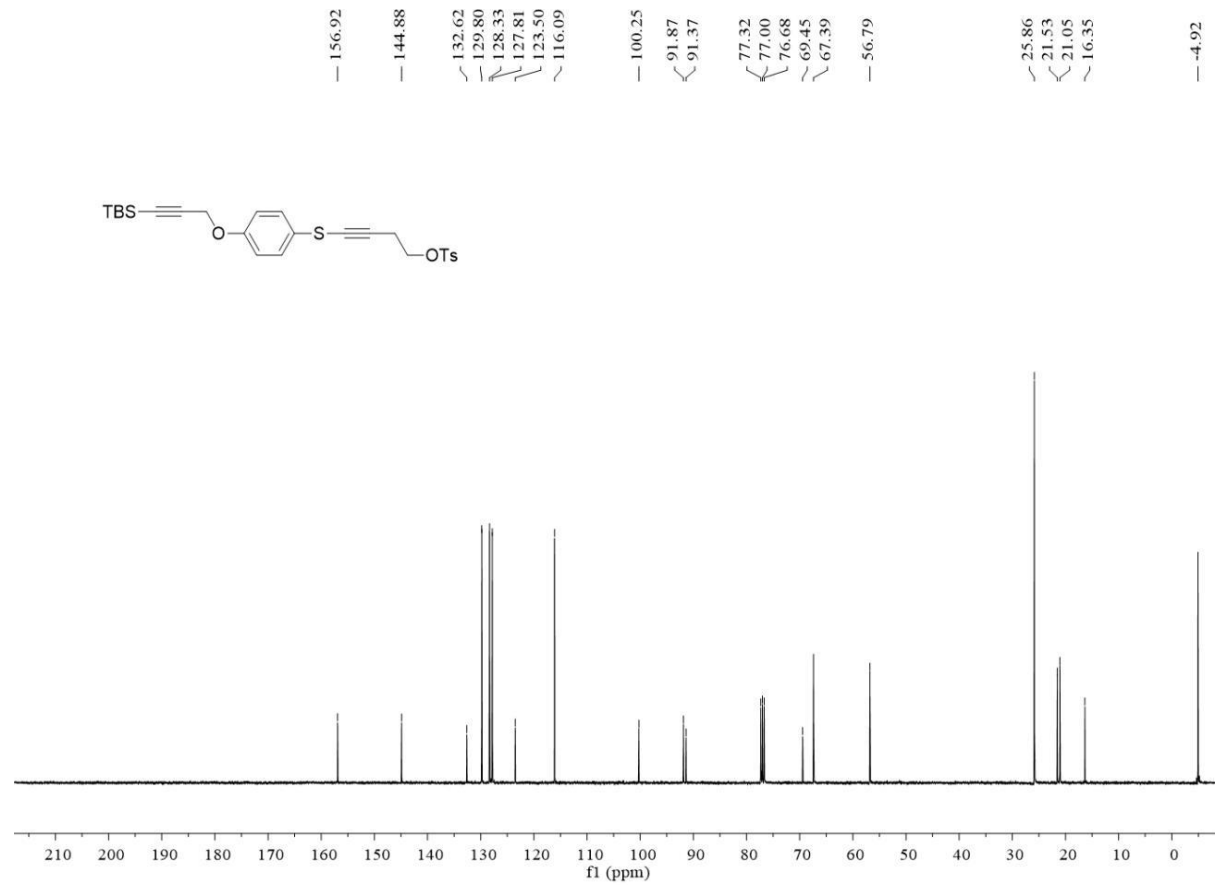


Figure S36. ^{13}C NMR spectra of **M4-OTs**.

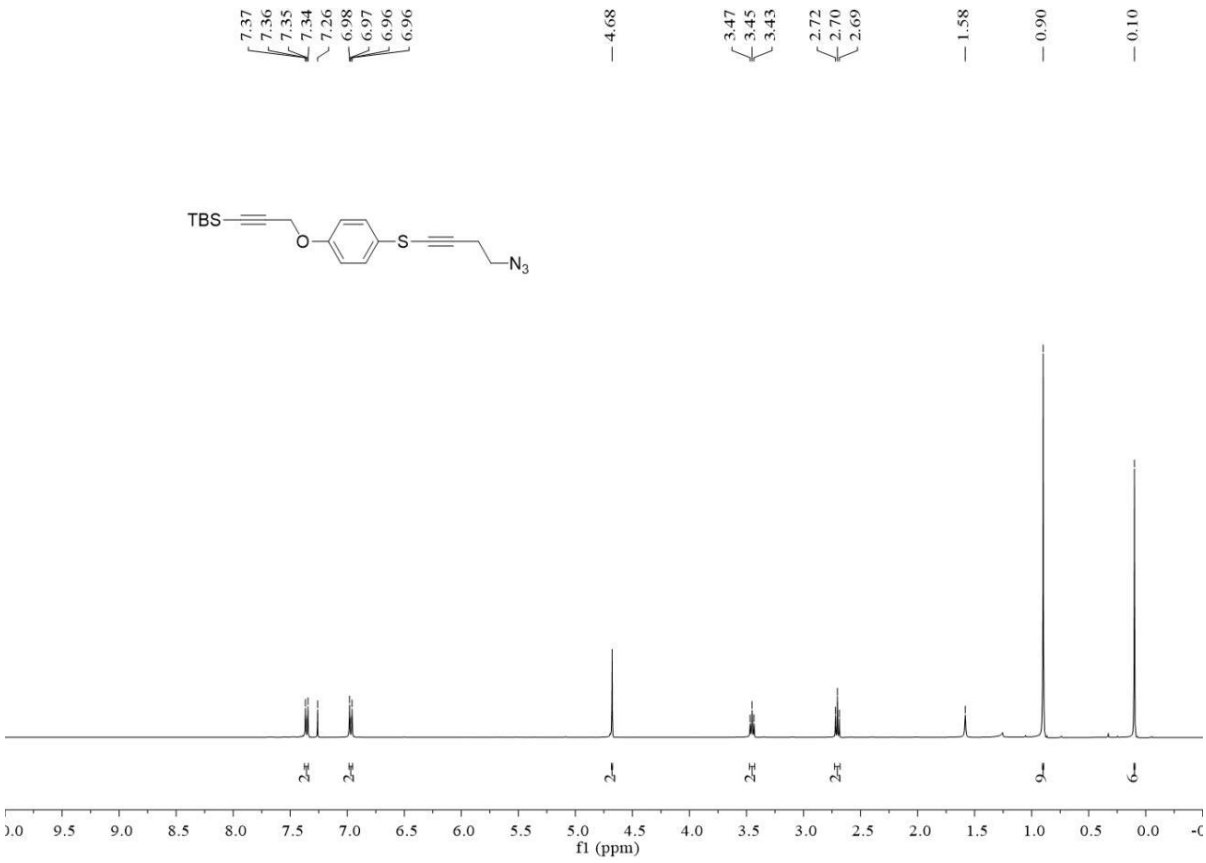


Figure S37. ^{1}H NMR spectra of **M4-N$_3$**.

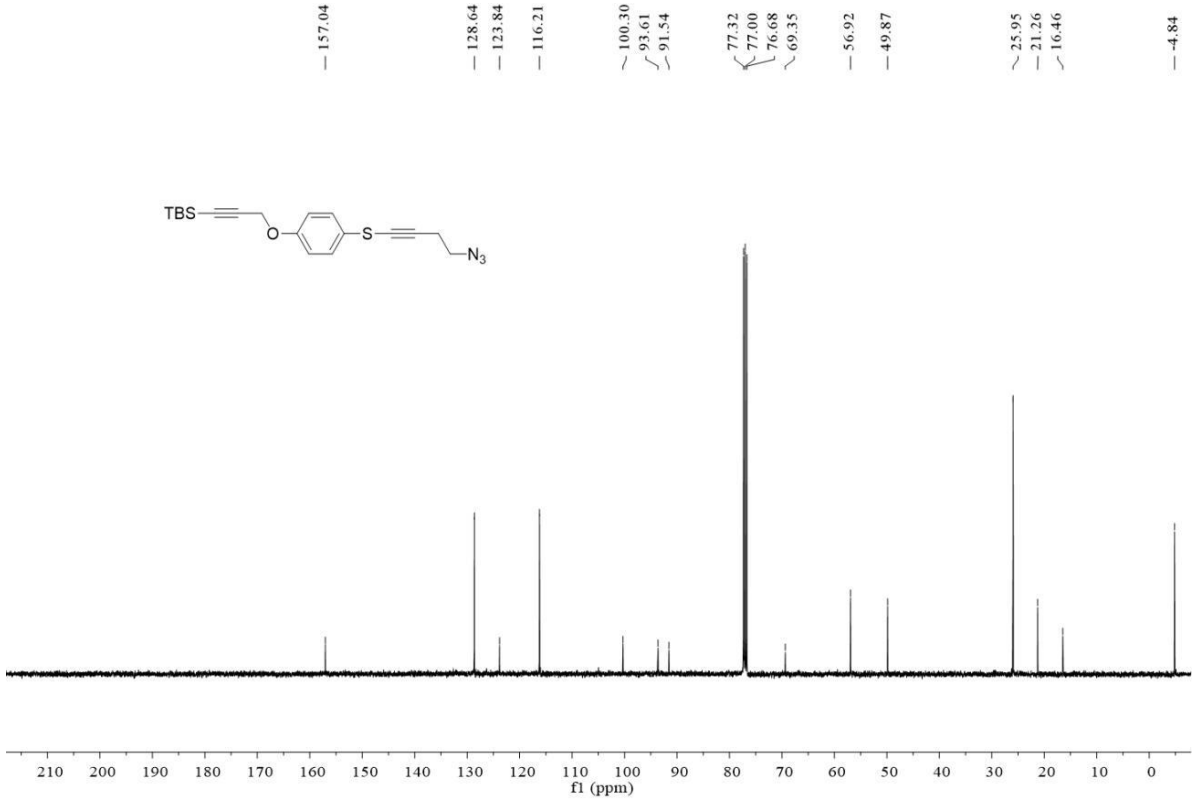


Figure S38. ^{13}C NMR spectra of **M4-N$_3$**.

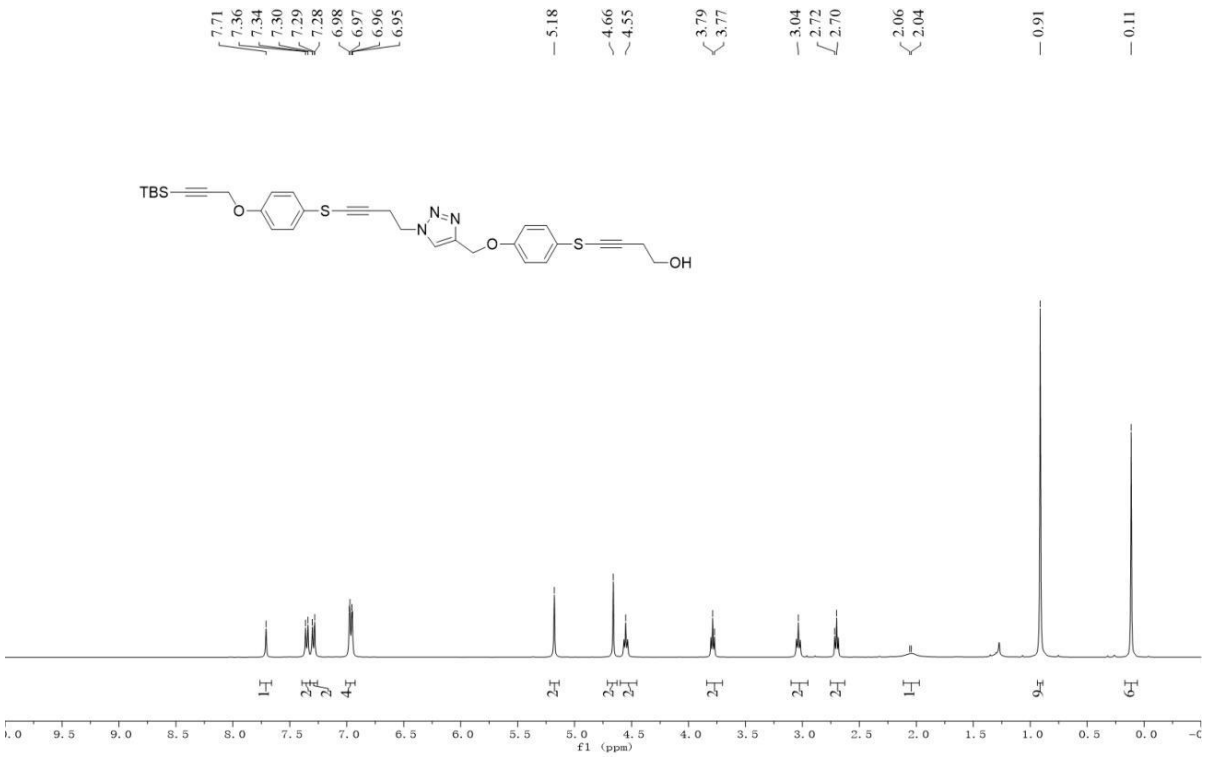


Figure S39. ^{1}H NMR spectra of **B2.**

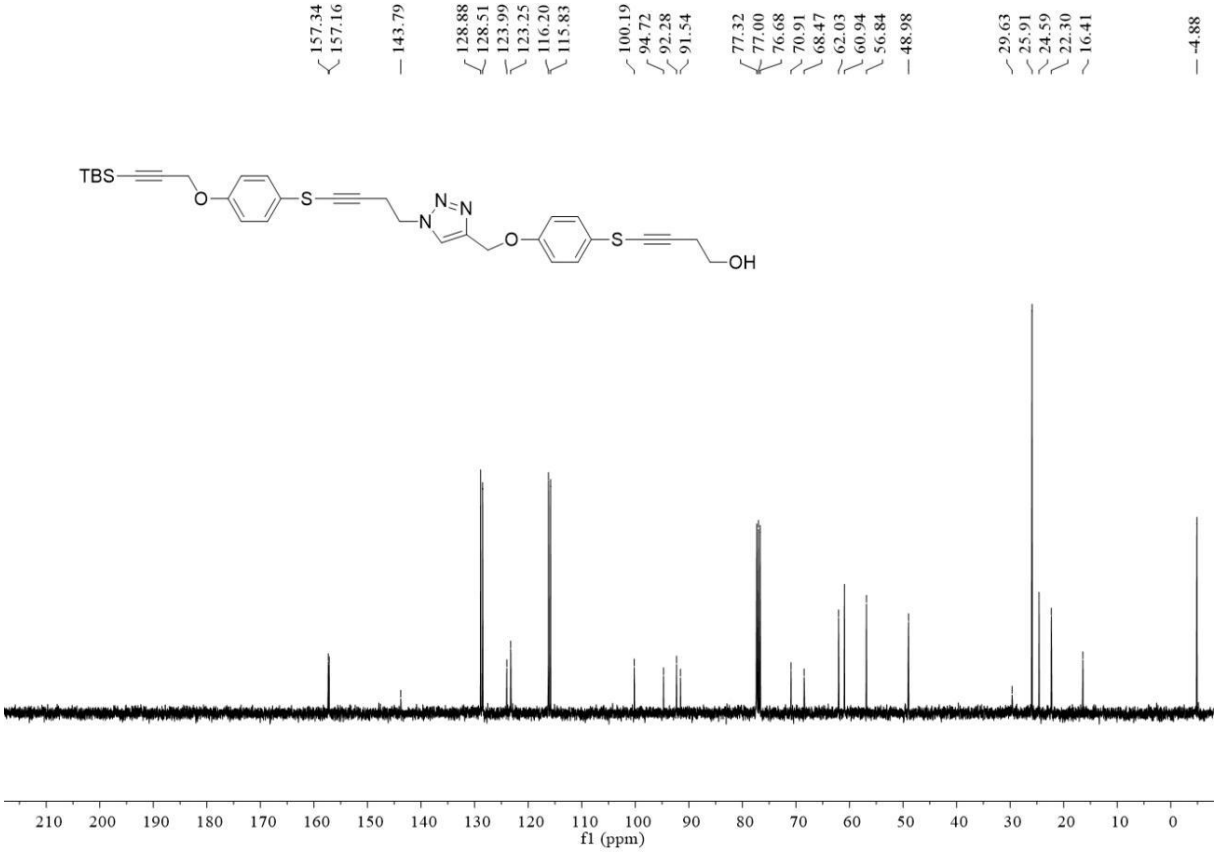


Figure S40. ^{13}C NMR spectra of **B2**.

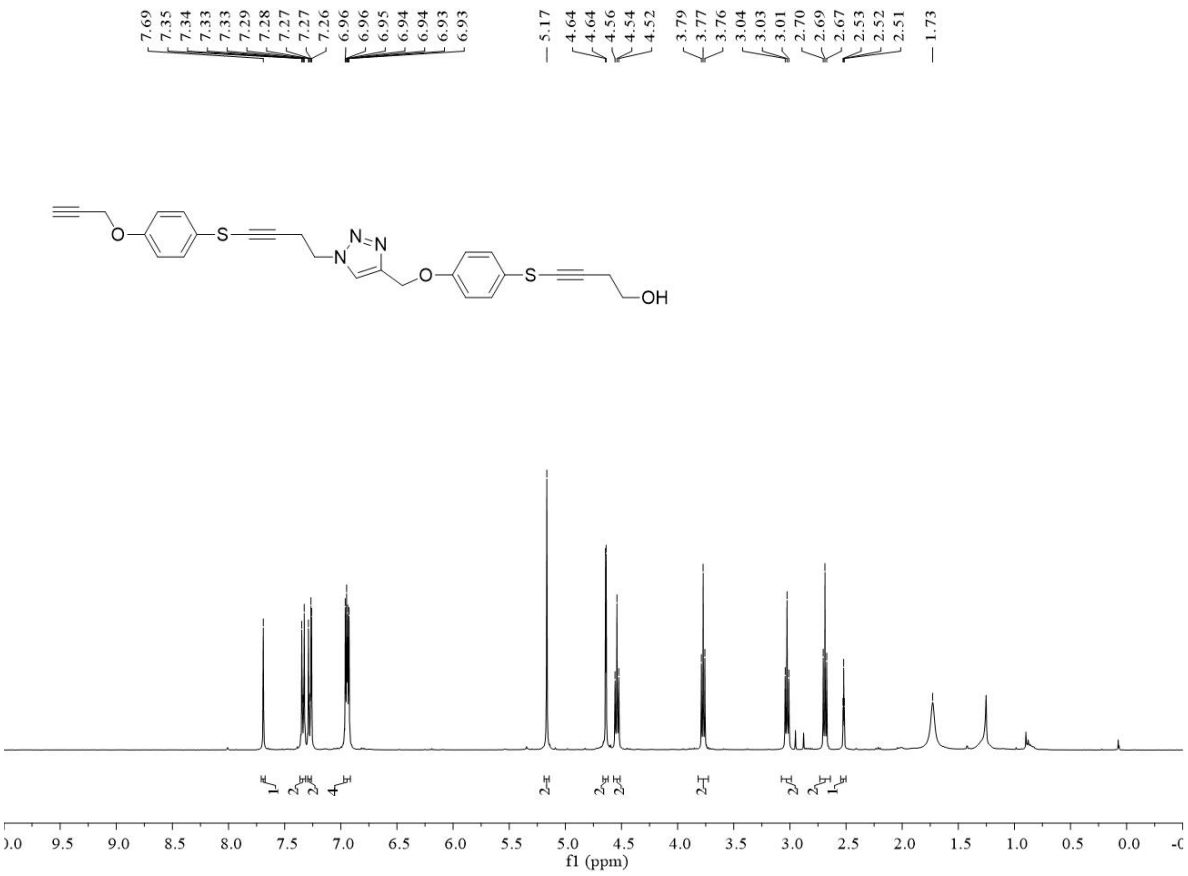


Figure S41. ^{1}H NMR spectra of **B2-yne**.

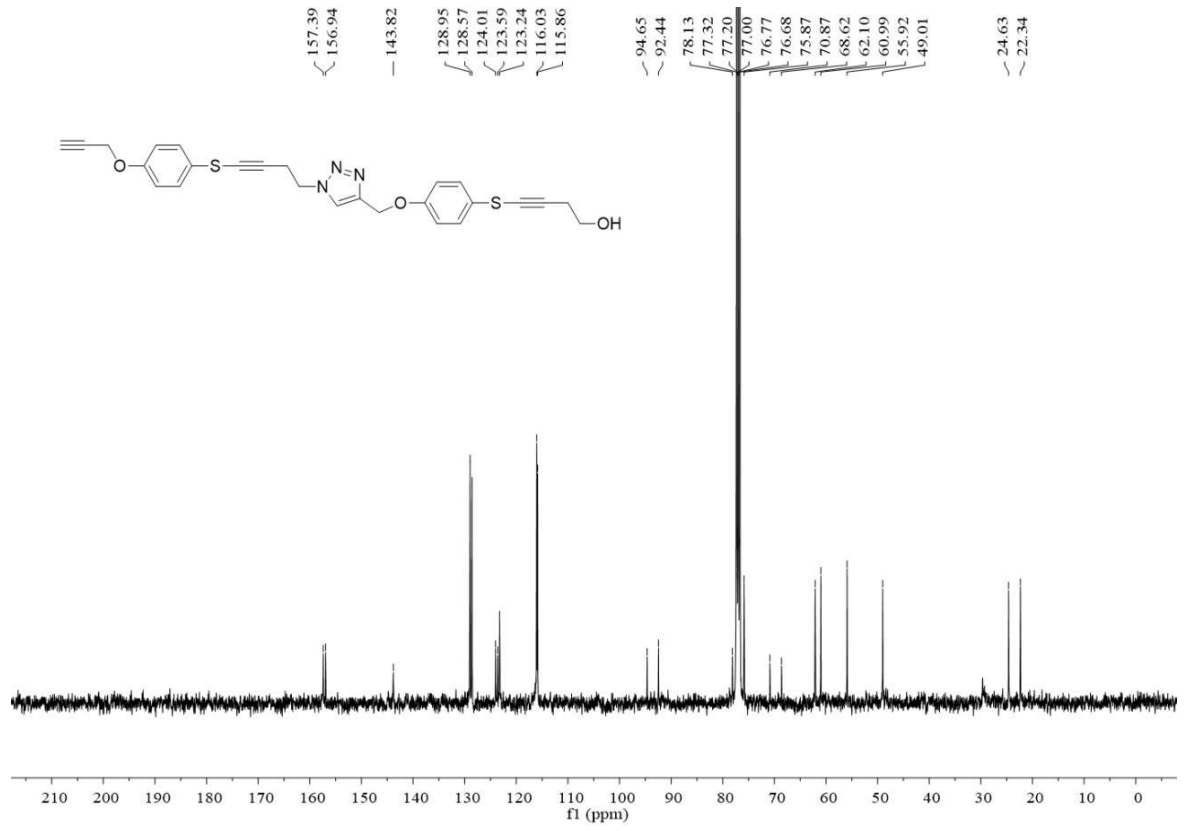


Figure S42. ^{13}C NMR spectra of **B2-yne**.

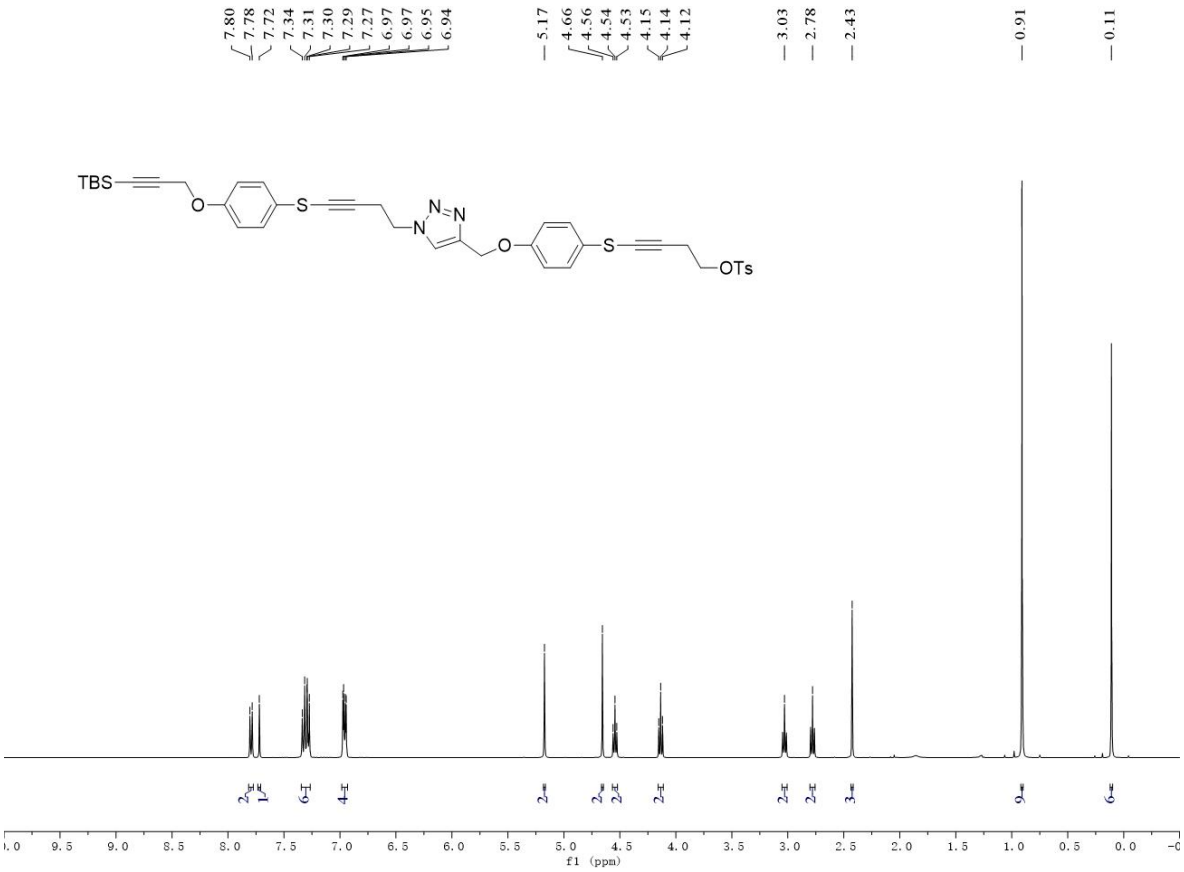


Figure S43. ^{1}H NMR spectra of **B2-OTs**.

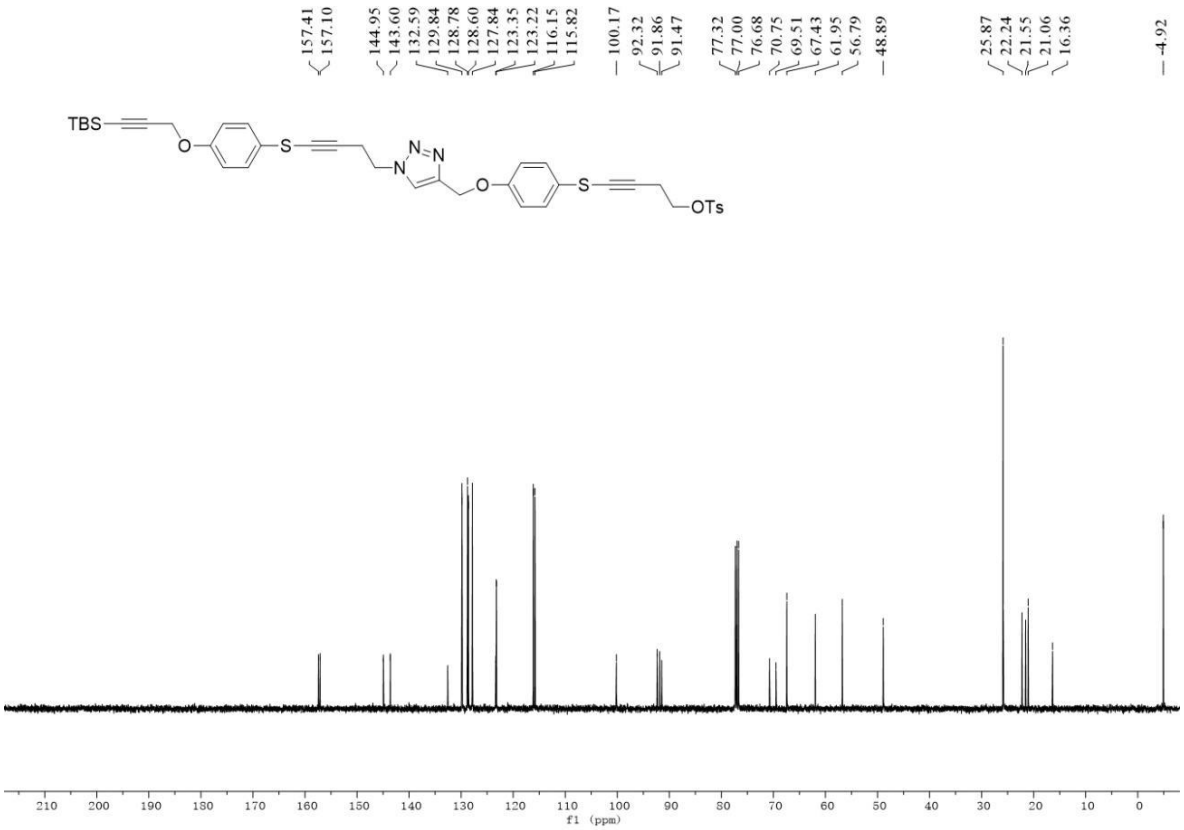


Figure S44. ^{13}C NMR spectra of **B2-OTs**.

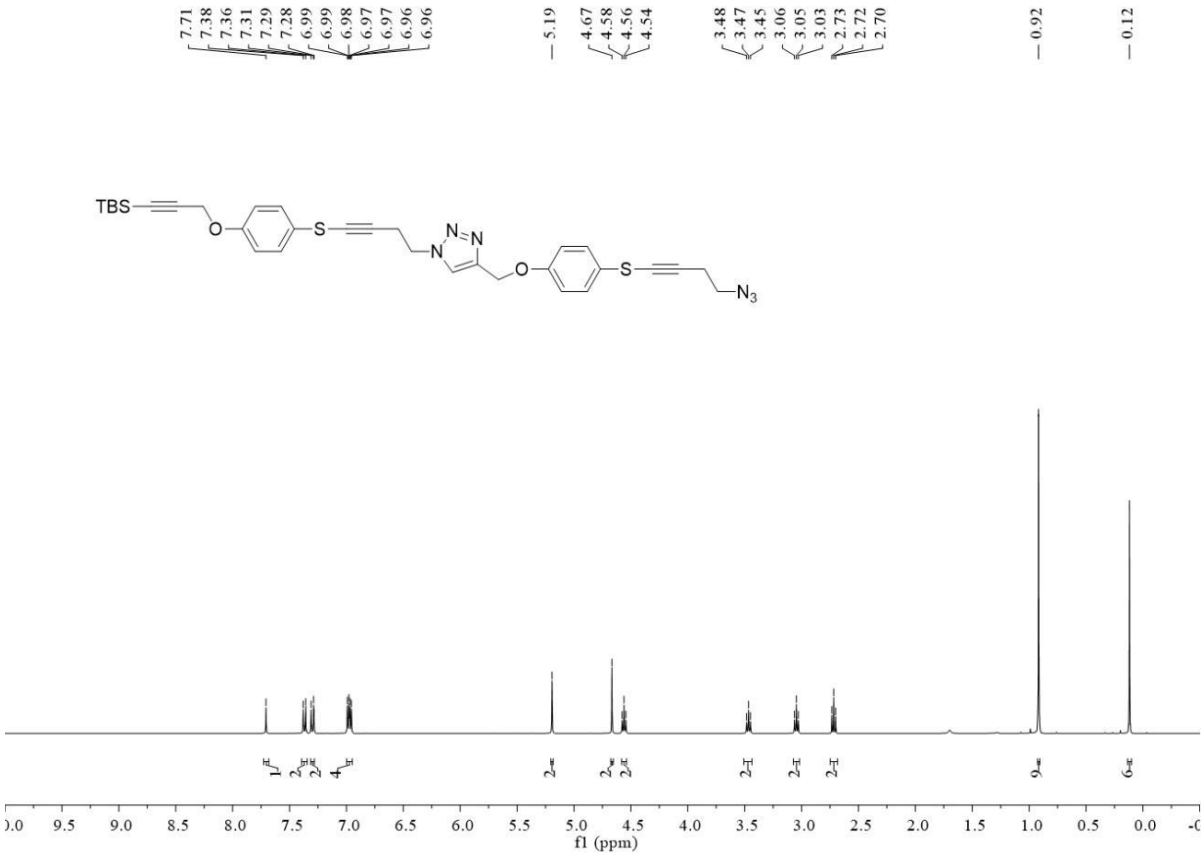


Figure S45. ^{1}H NMR spectra of **B2-N$_3$**.

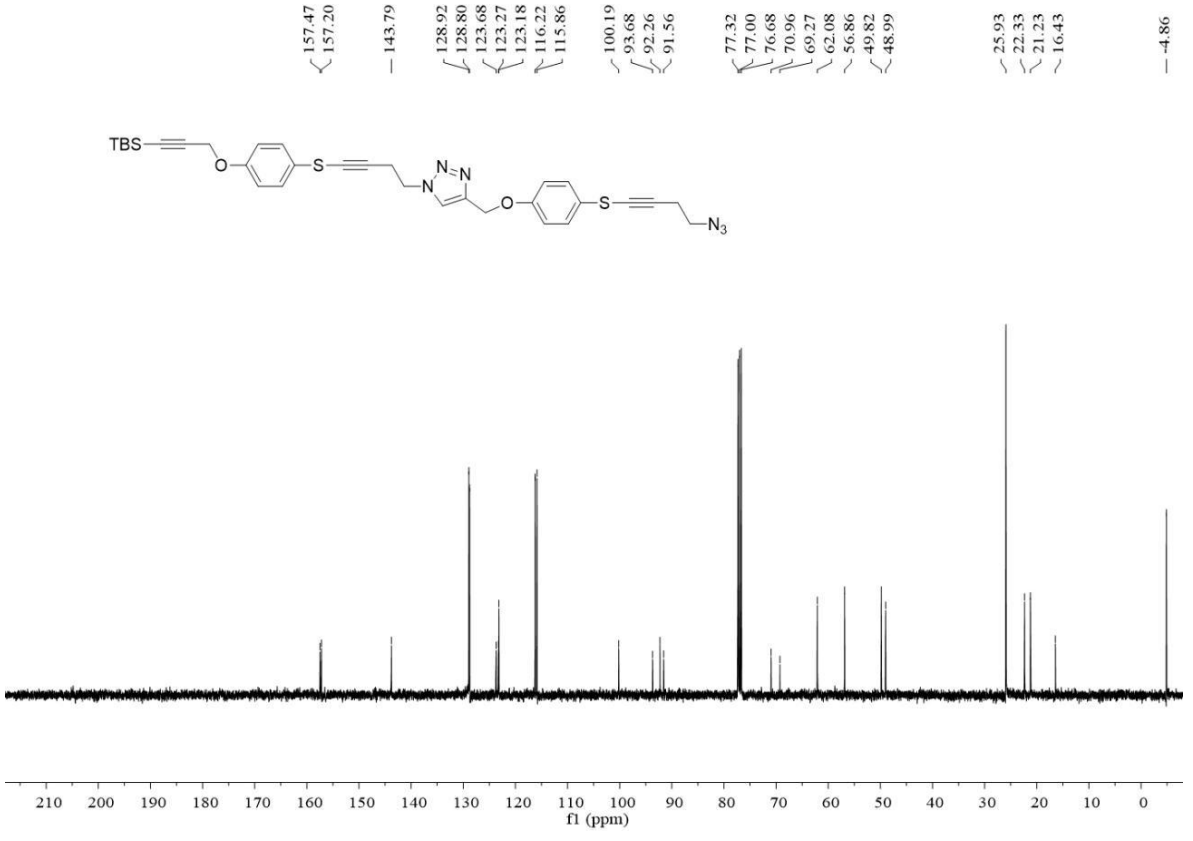


Figure S46. ^{13}C NMR spectra of **B2-N$_3$**.

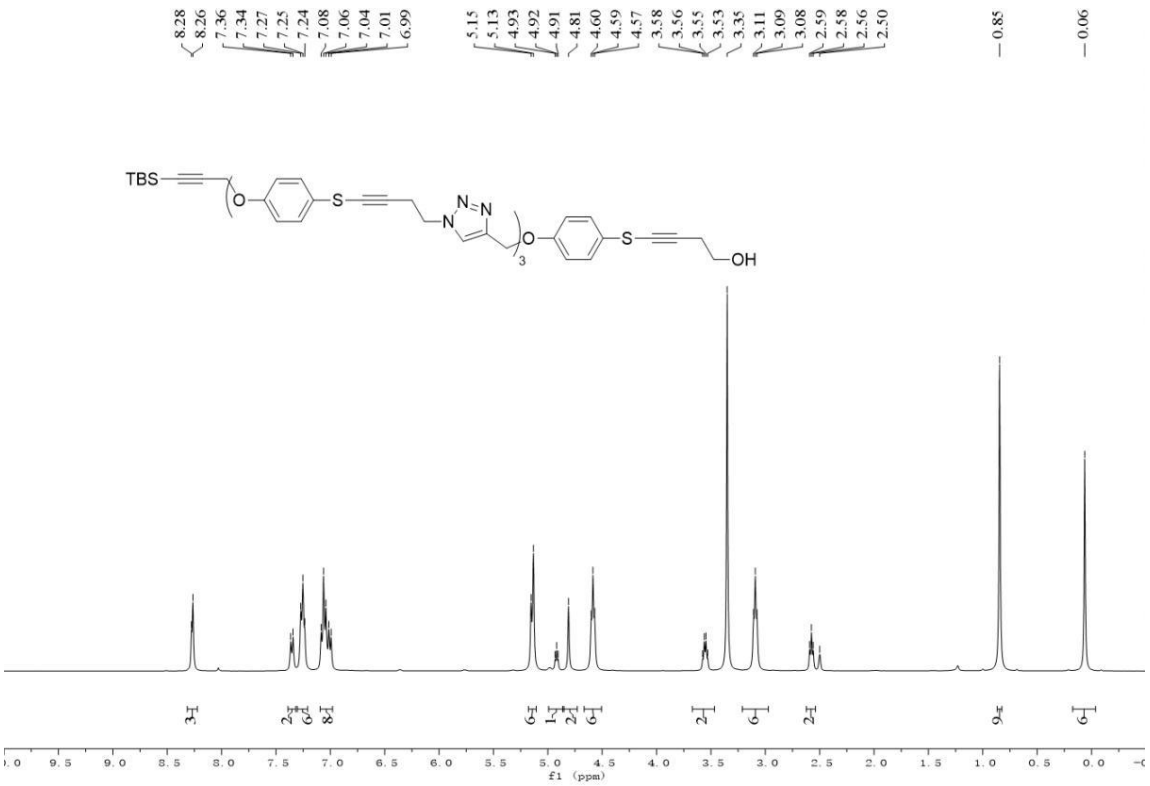


Figure S47. ^{1}H NMR spectra of **B4**.

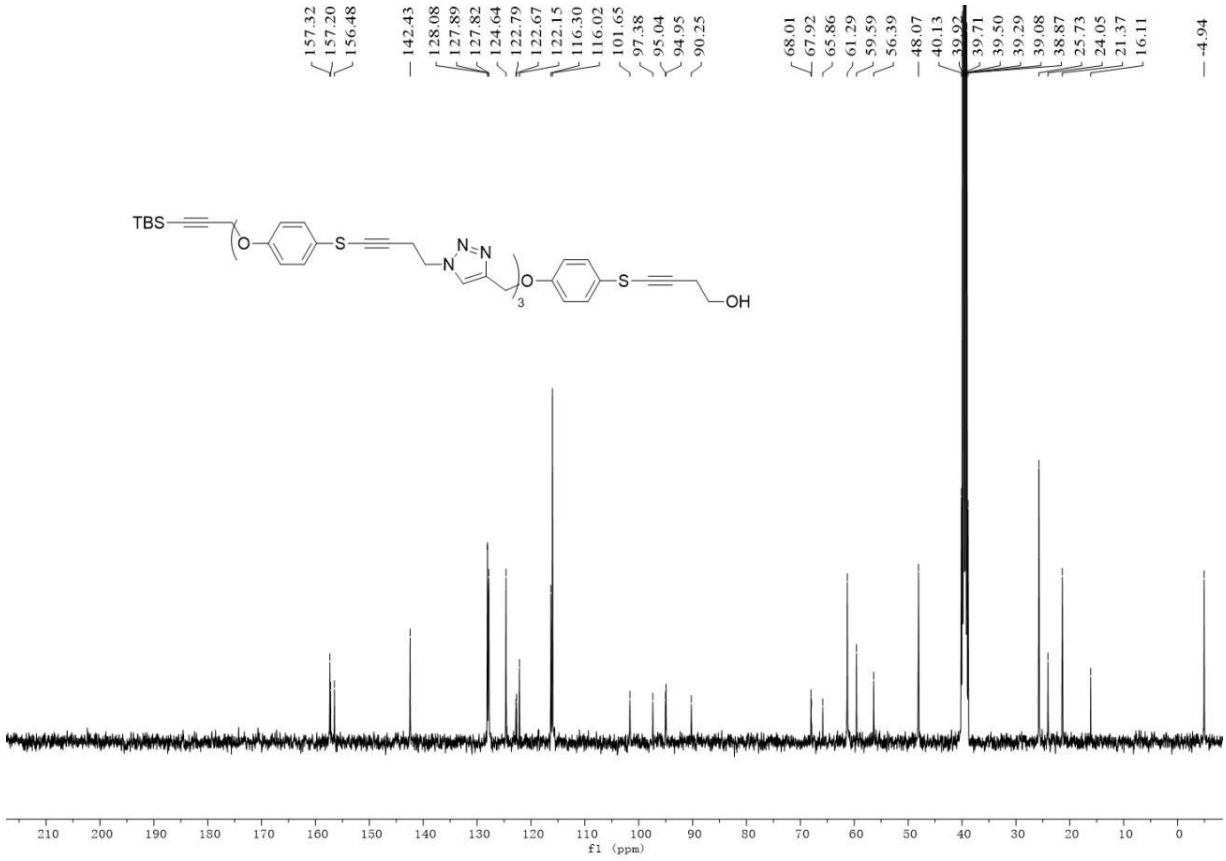


Figure S48. ^{13}C NMR spectra of **B4**.

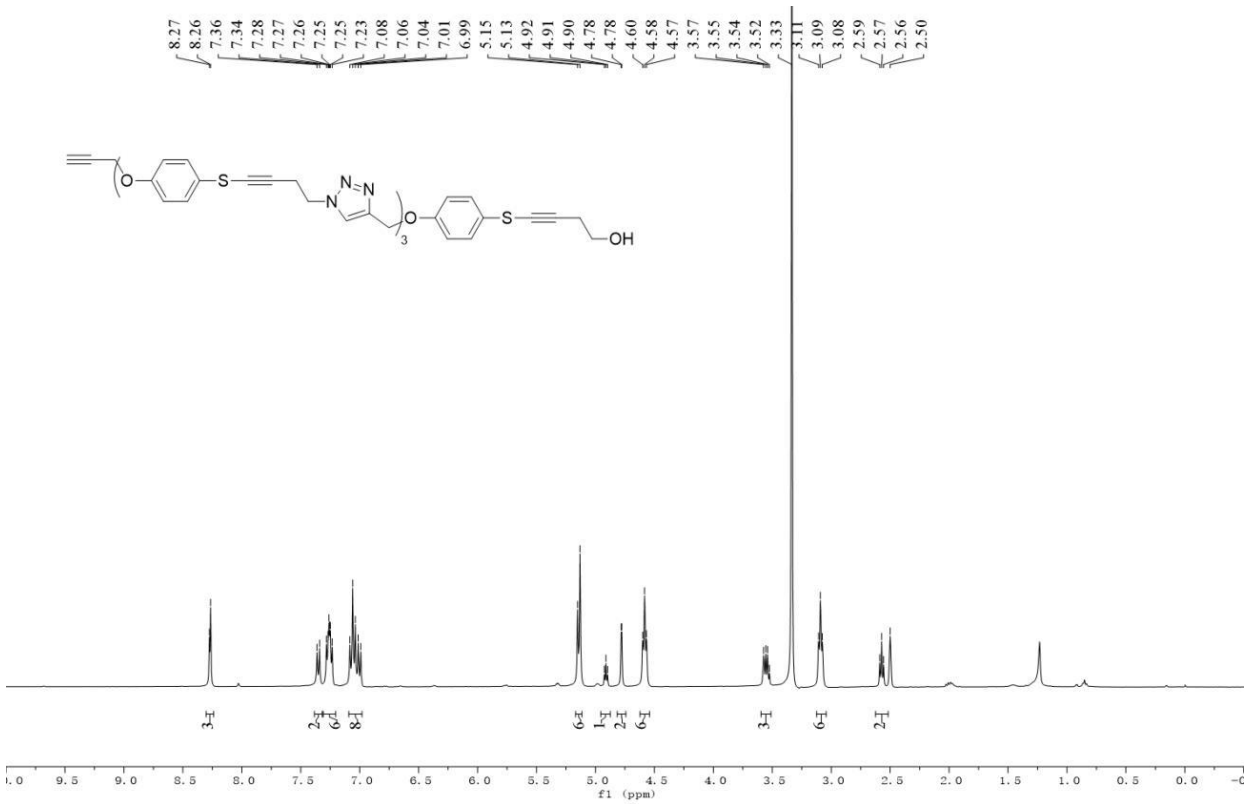


Figure S49. ^{1}H NMR spectra of **B4-yne**.

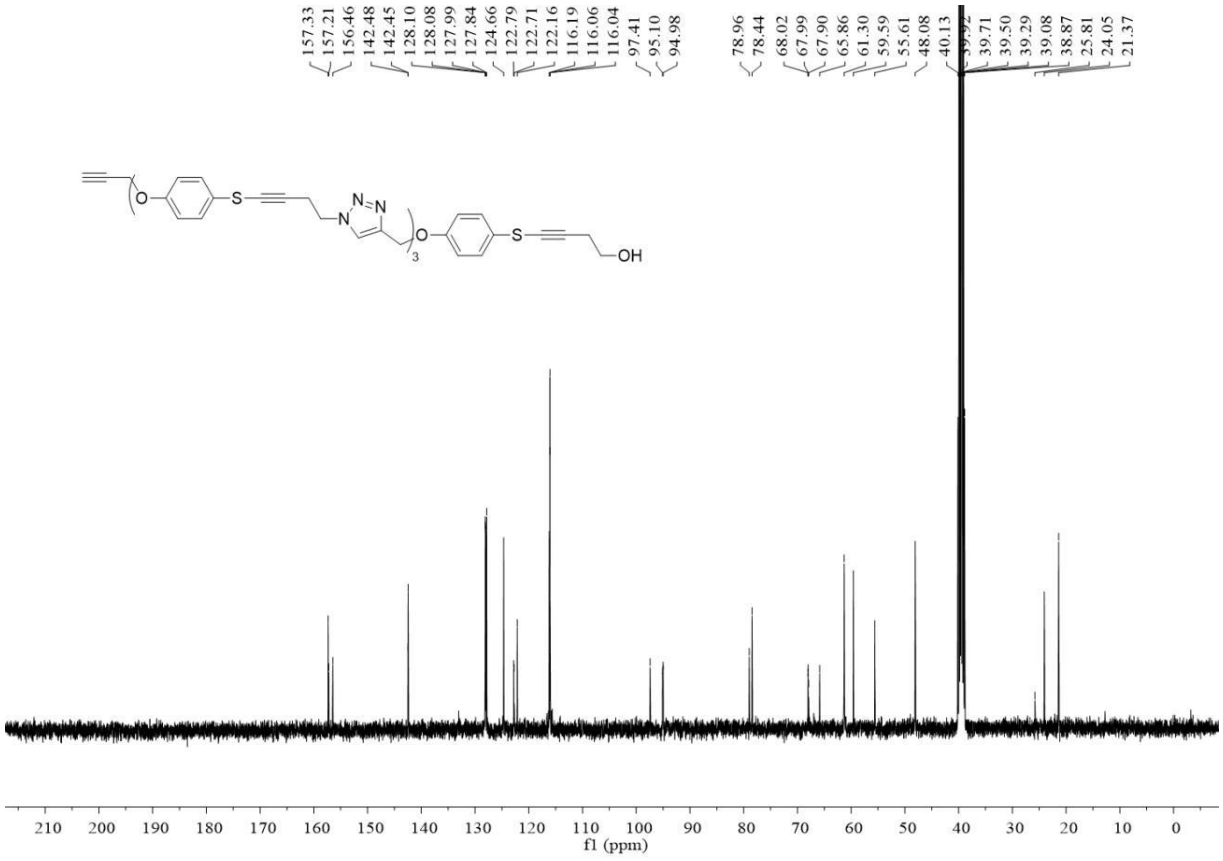


Figure S50. ^{13}C NMR spectra of **B4-yne**.

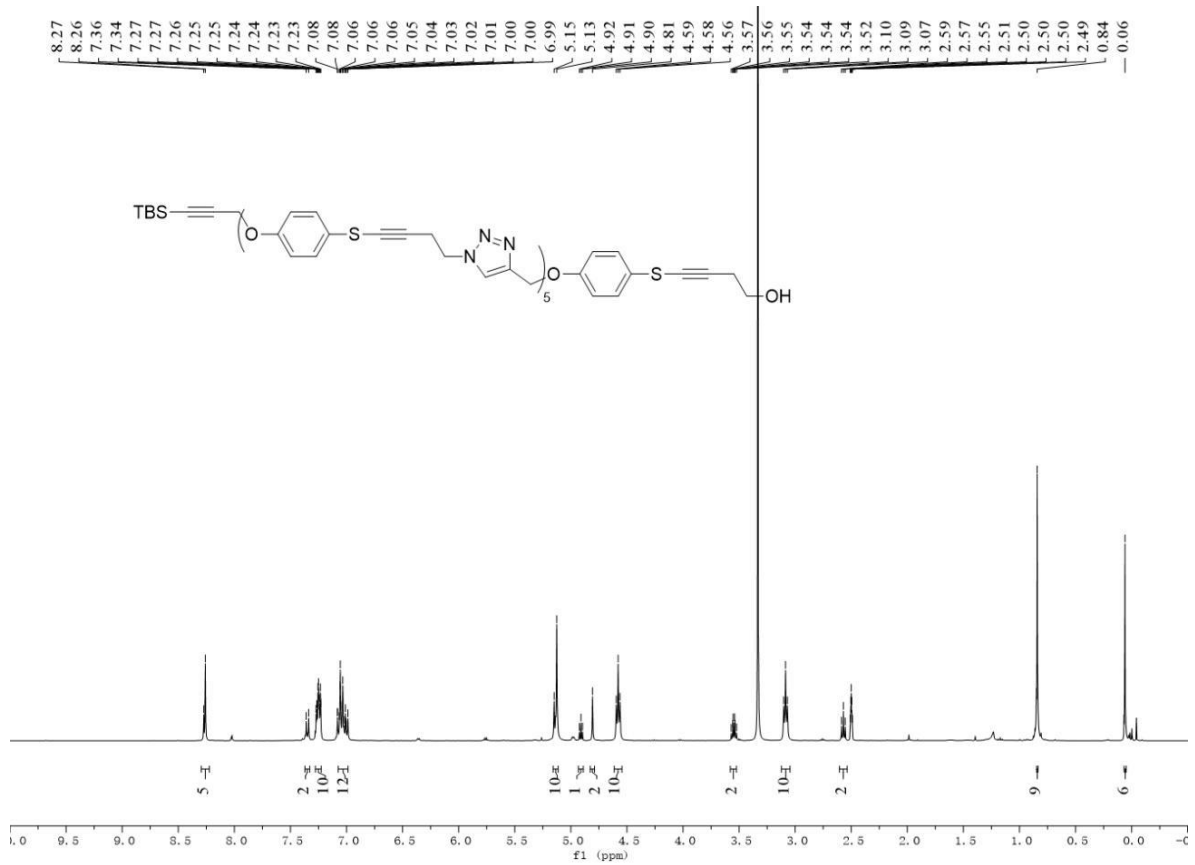


Figure S51. ^{1}H NMR spectra of **B6**.

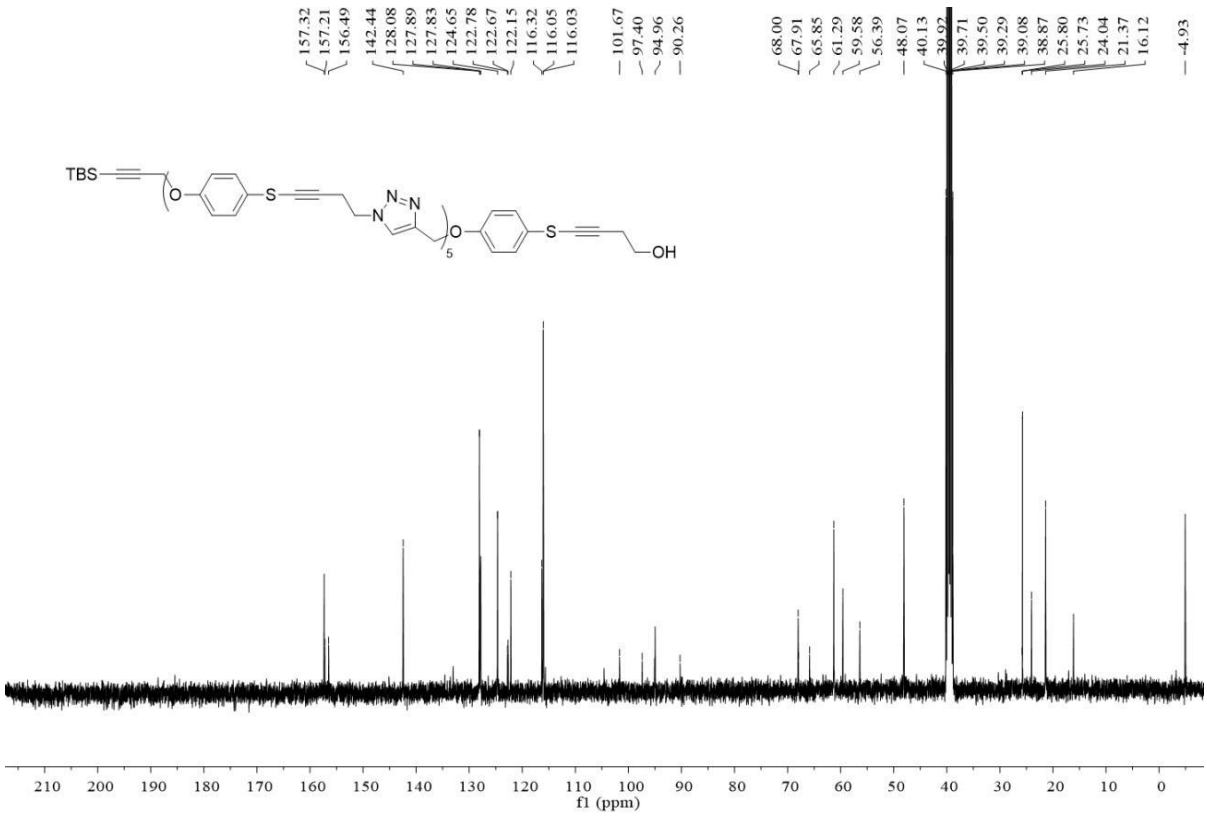


Figure S52. ^{13}C NMR spectra of **B6**.

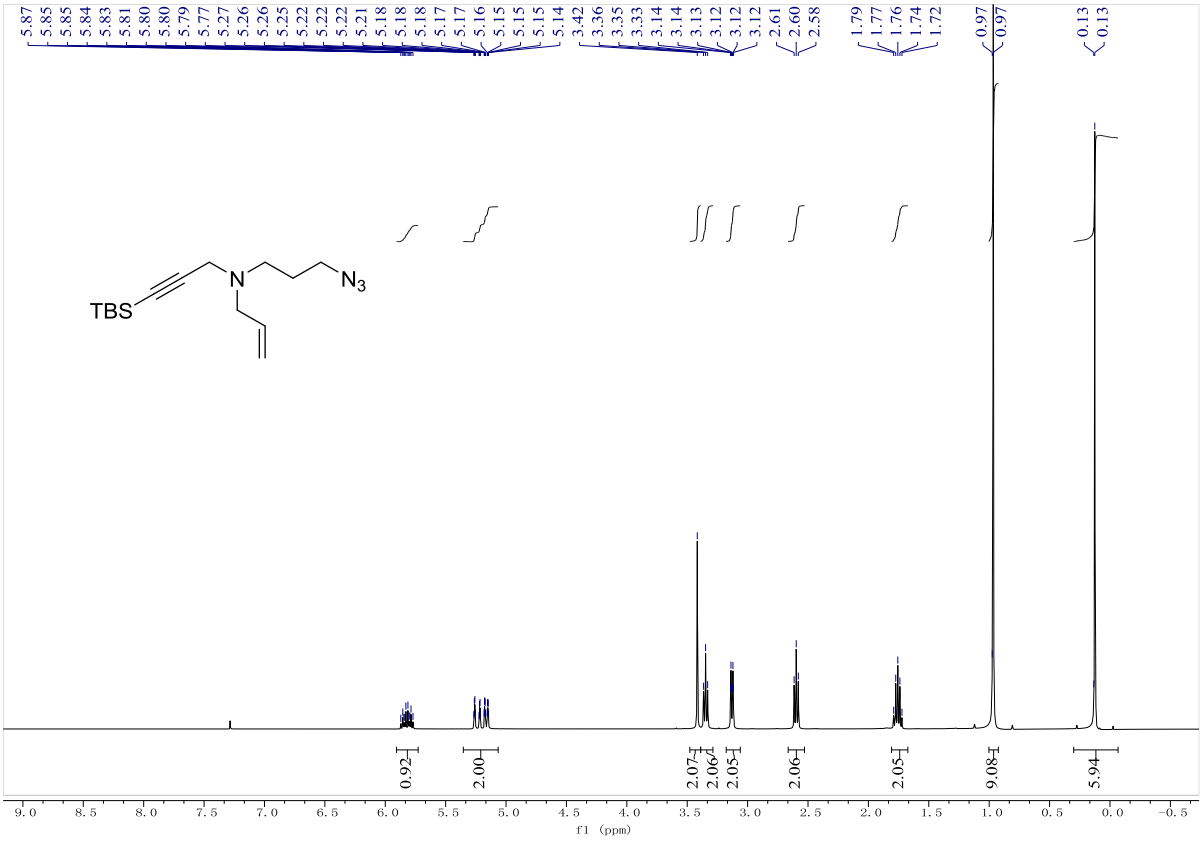


Figure S53. ^{1}H NMR spectra of **azide 6**.

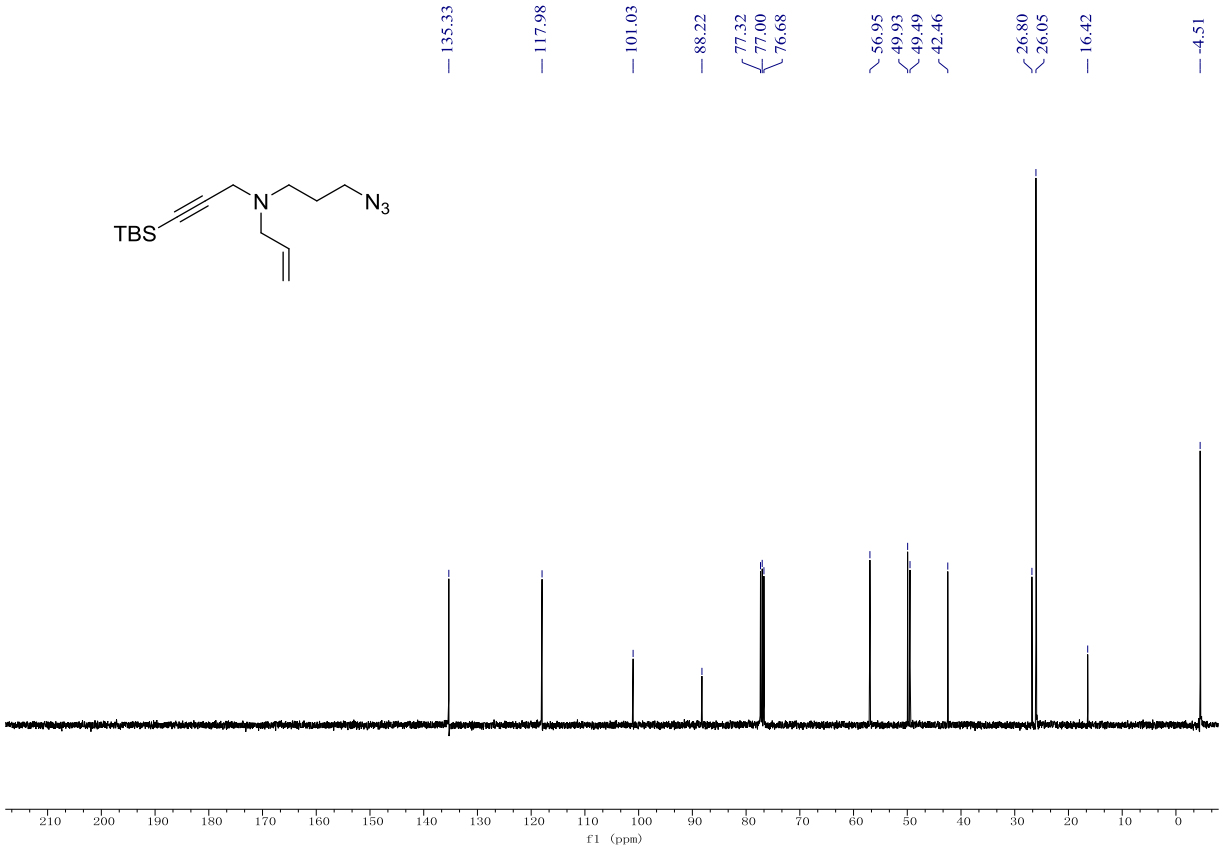


Figure S54. ^{13}C NMR spectra of **azide 6**.

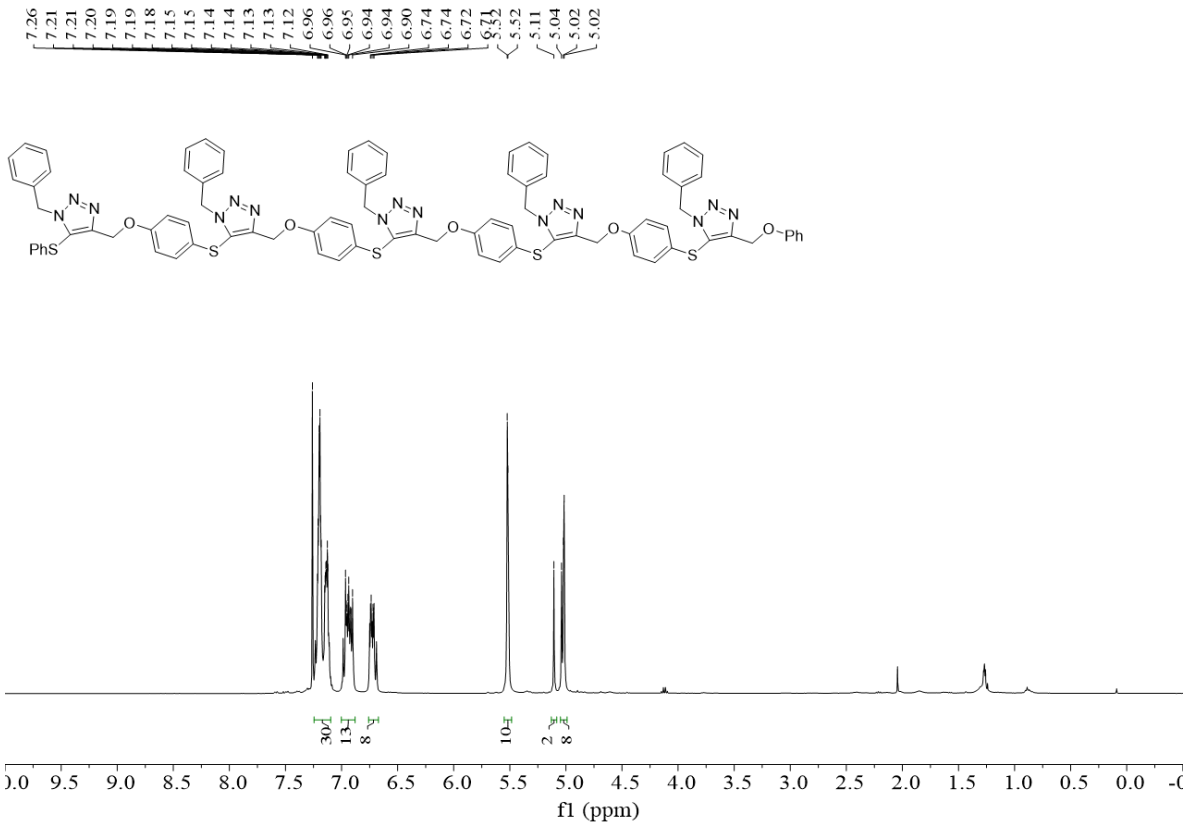


Figure S55. ^{1}H NMR spectra of **1**.

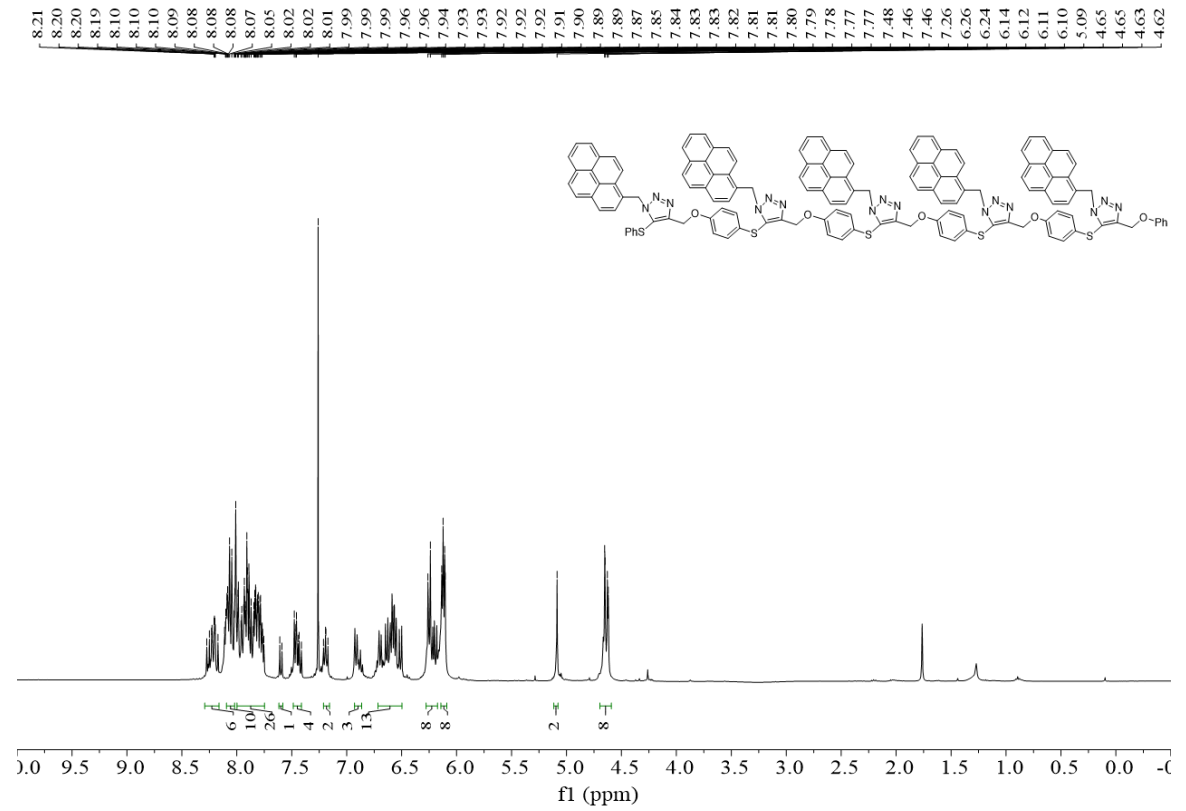


Figure S56. ^{1}H NMR spectra of **2**.

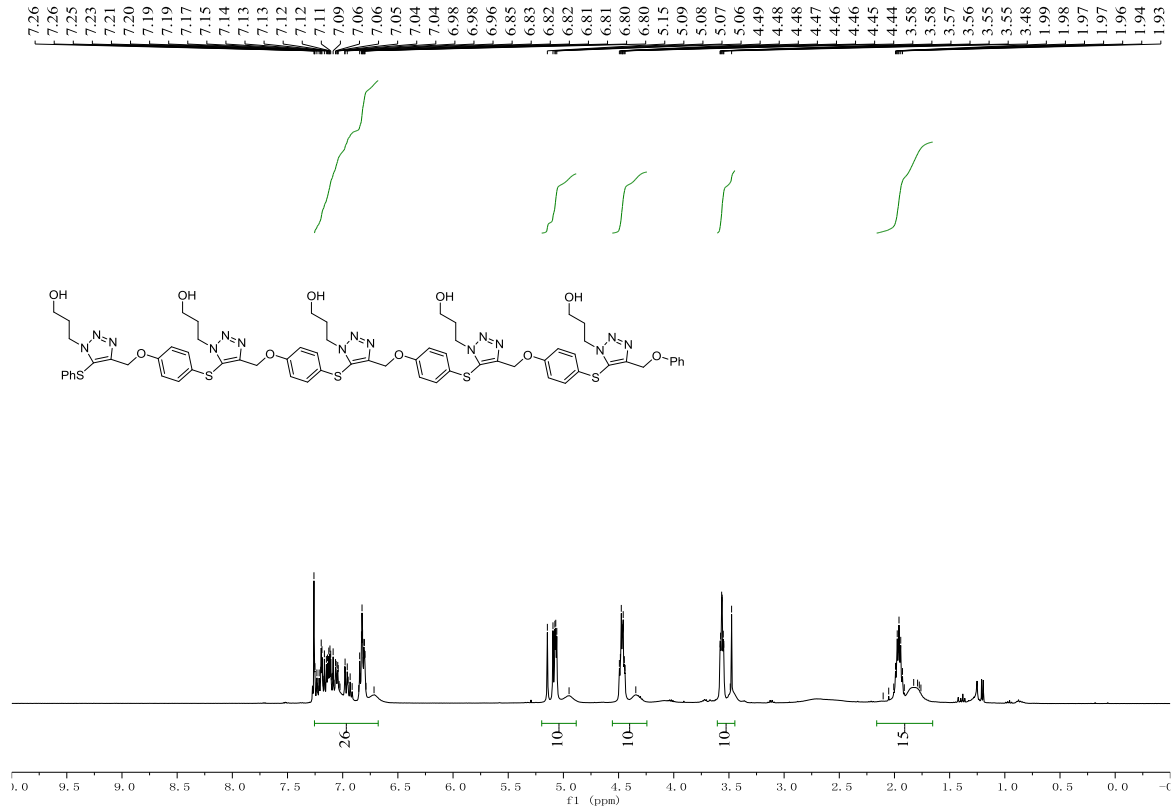


Figure S57. ^{1}H NMR spectra of **3**.

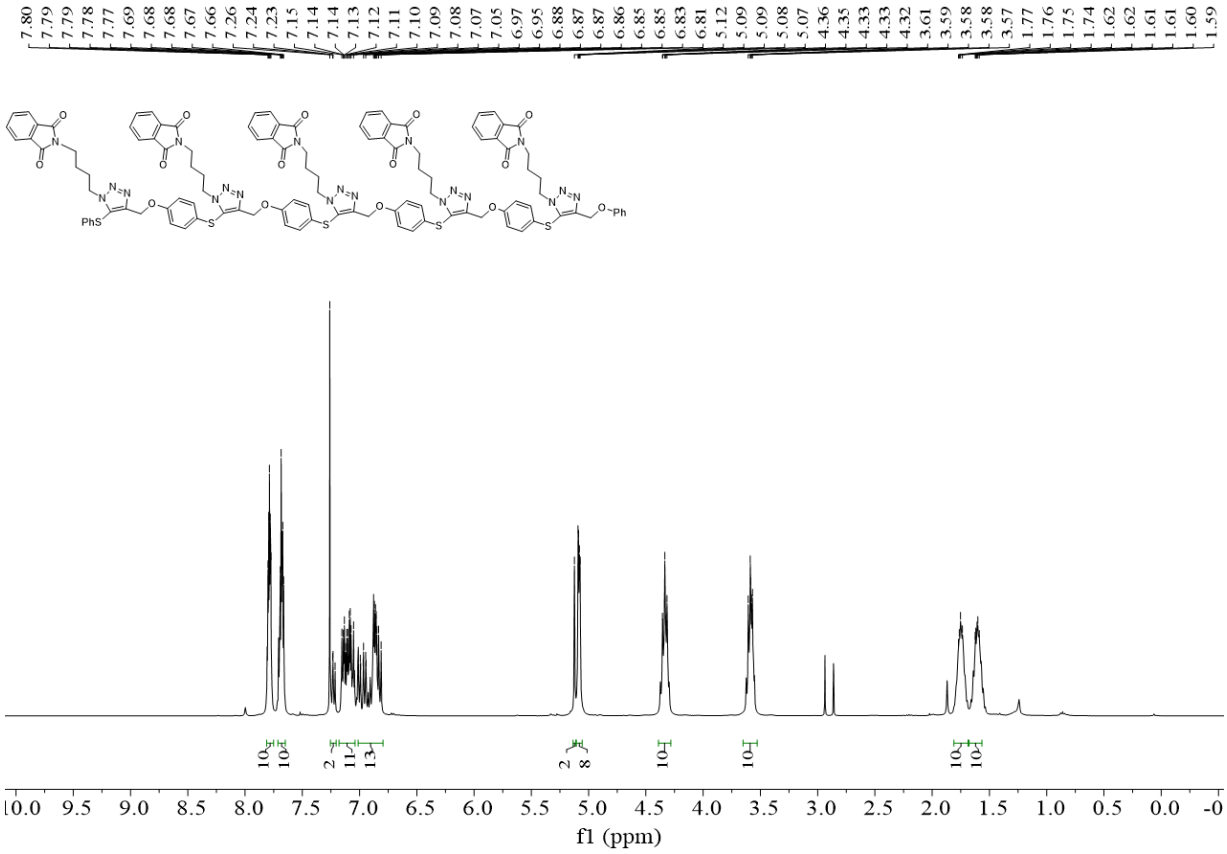


Figure S58. ^{1}H NMR spectra of **4**.

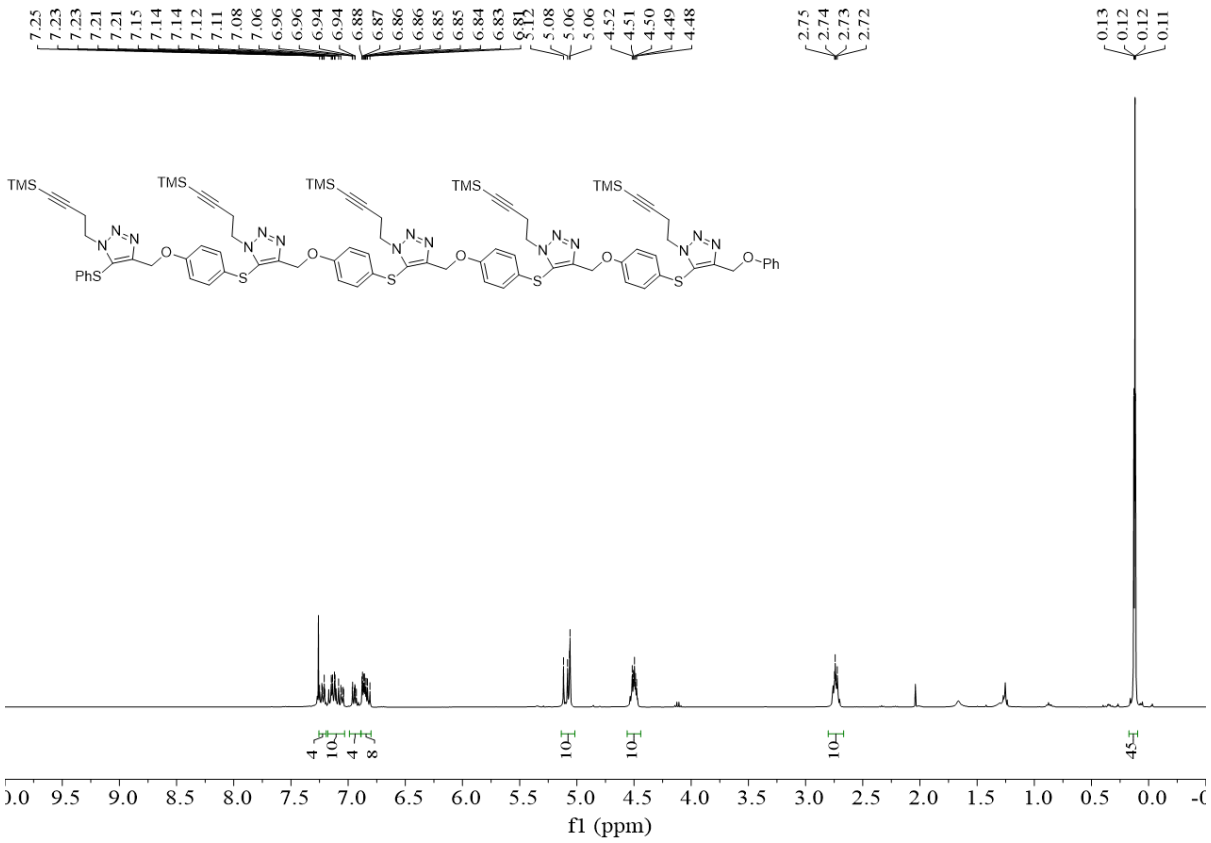


Figure S59. ^{1}H NMR spectra of **5**.

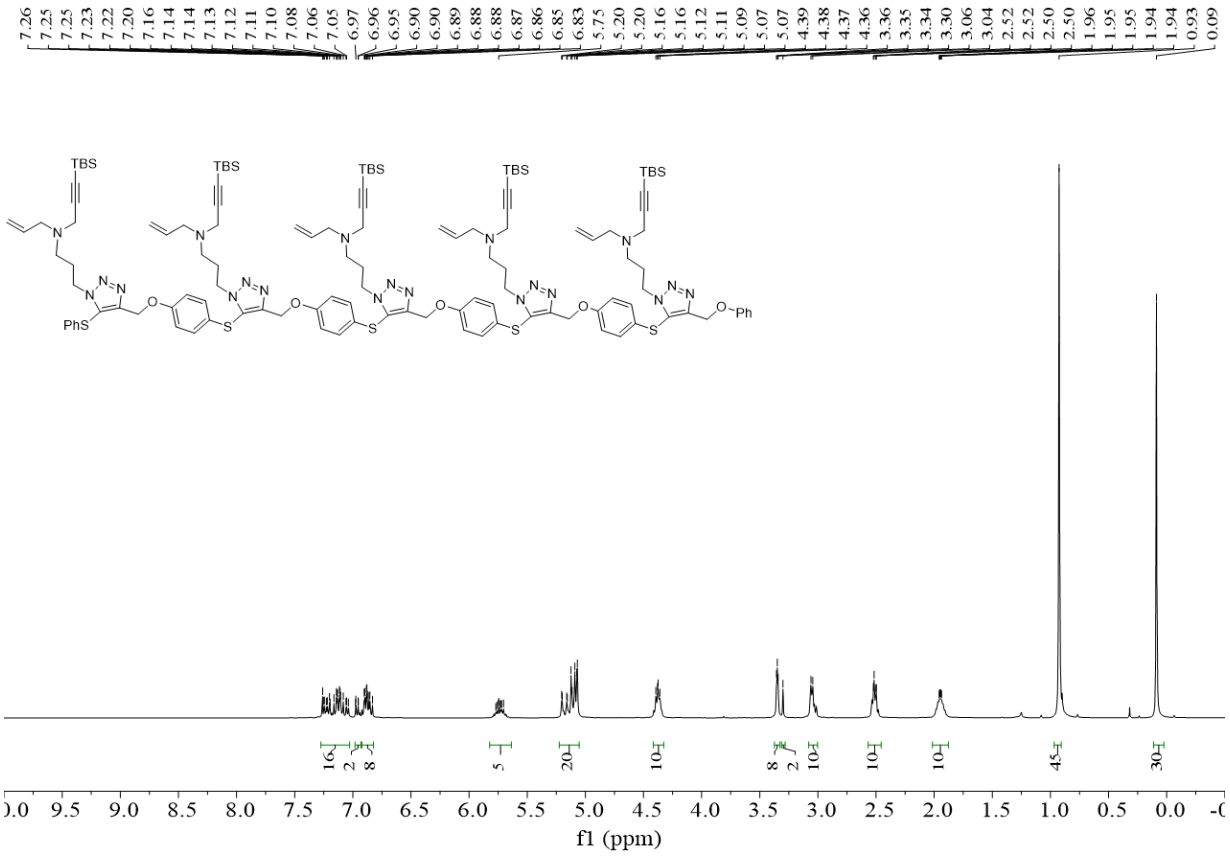


Figure S60. ^{1}H NMR spectra of **6**.

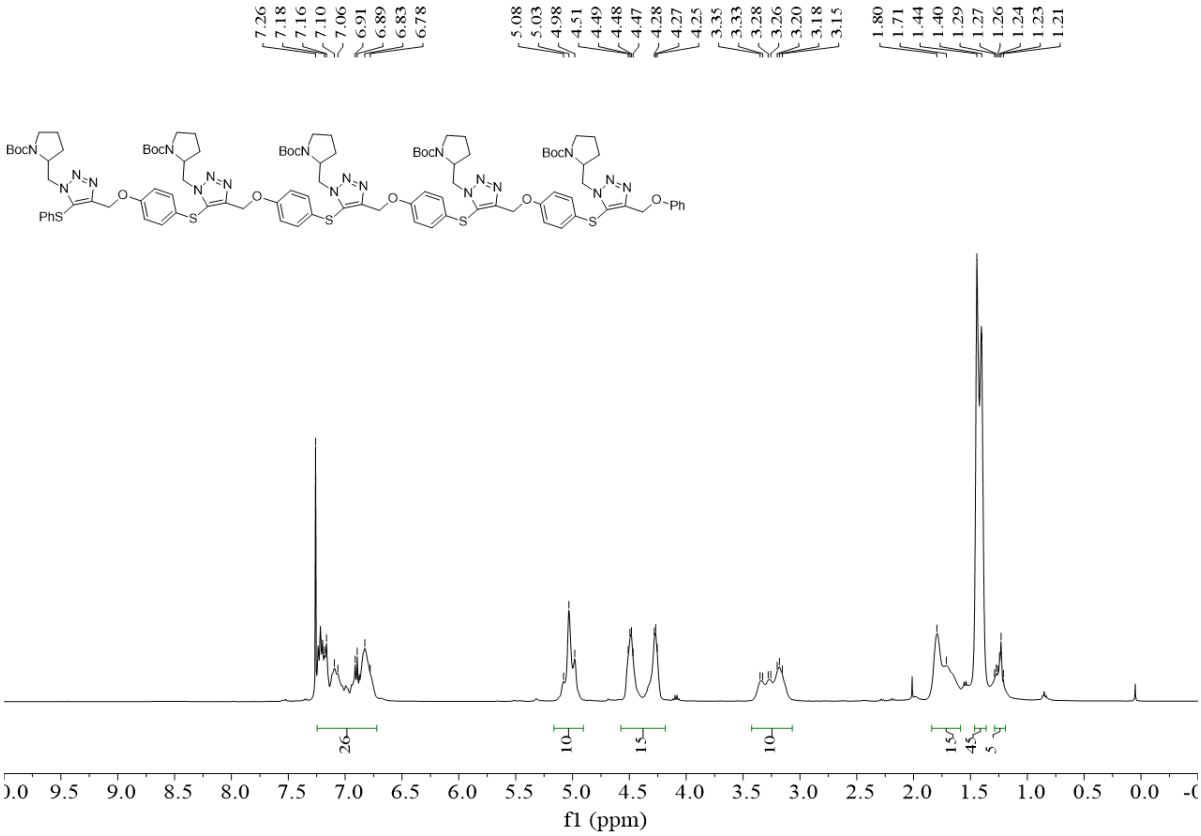


Figure S61. ^{1}H NMR spectra of **7**.

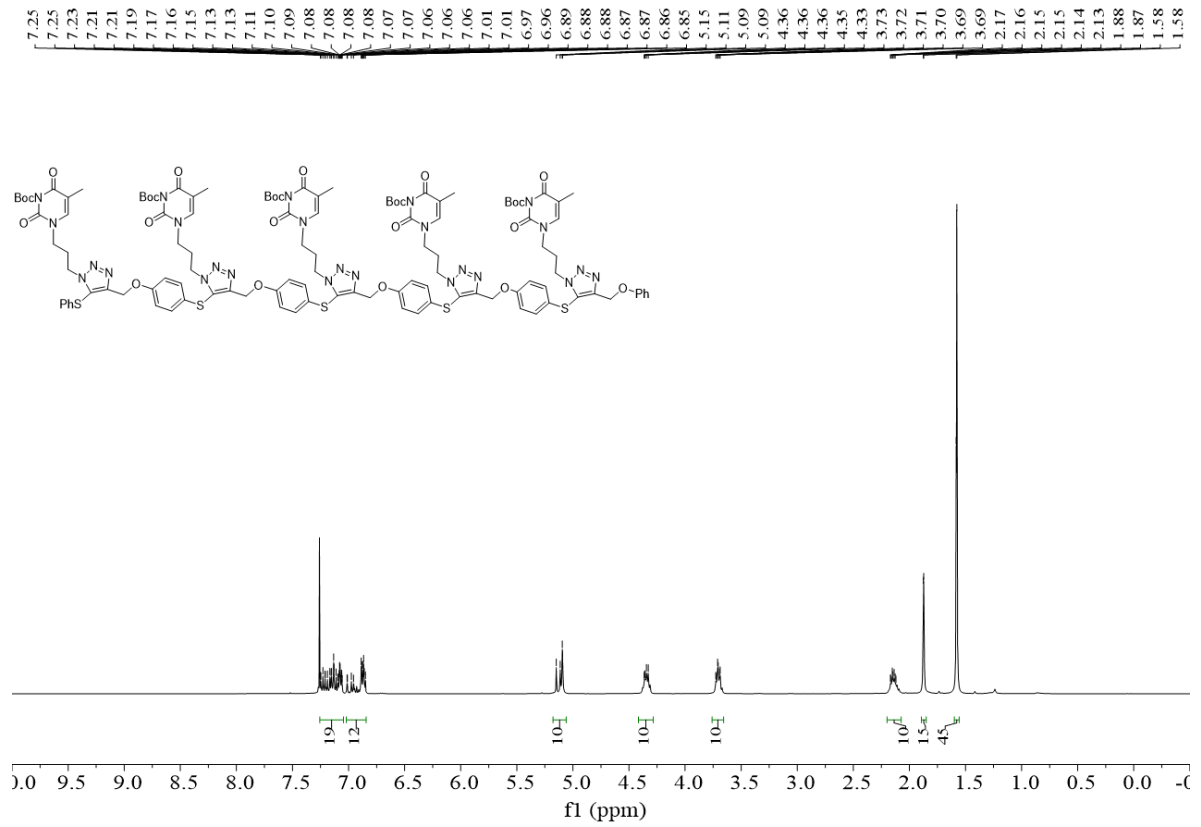


Figure S62. ^{1}H NMR spectra of **8**.

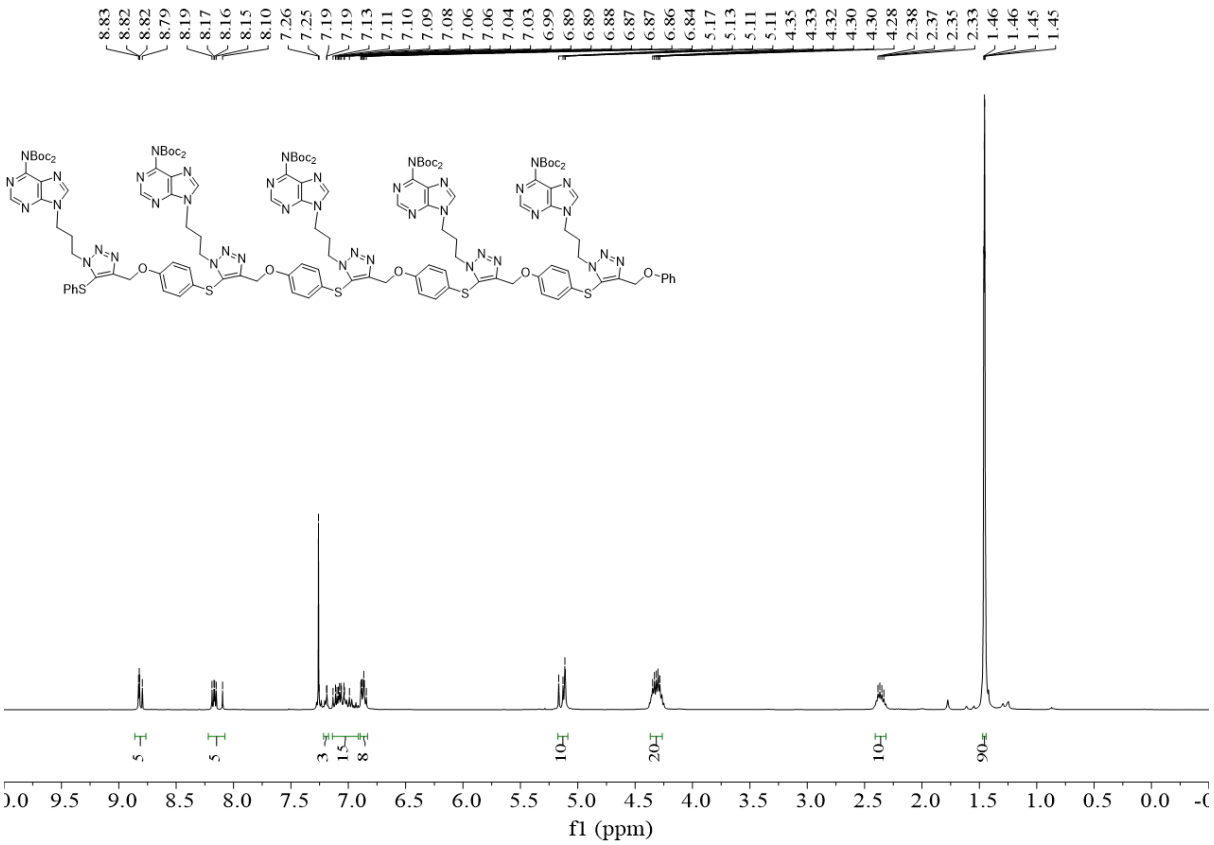


Figure S63. ^{1}H NMR spectra of **9**.

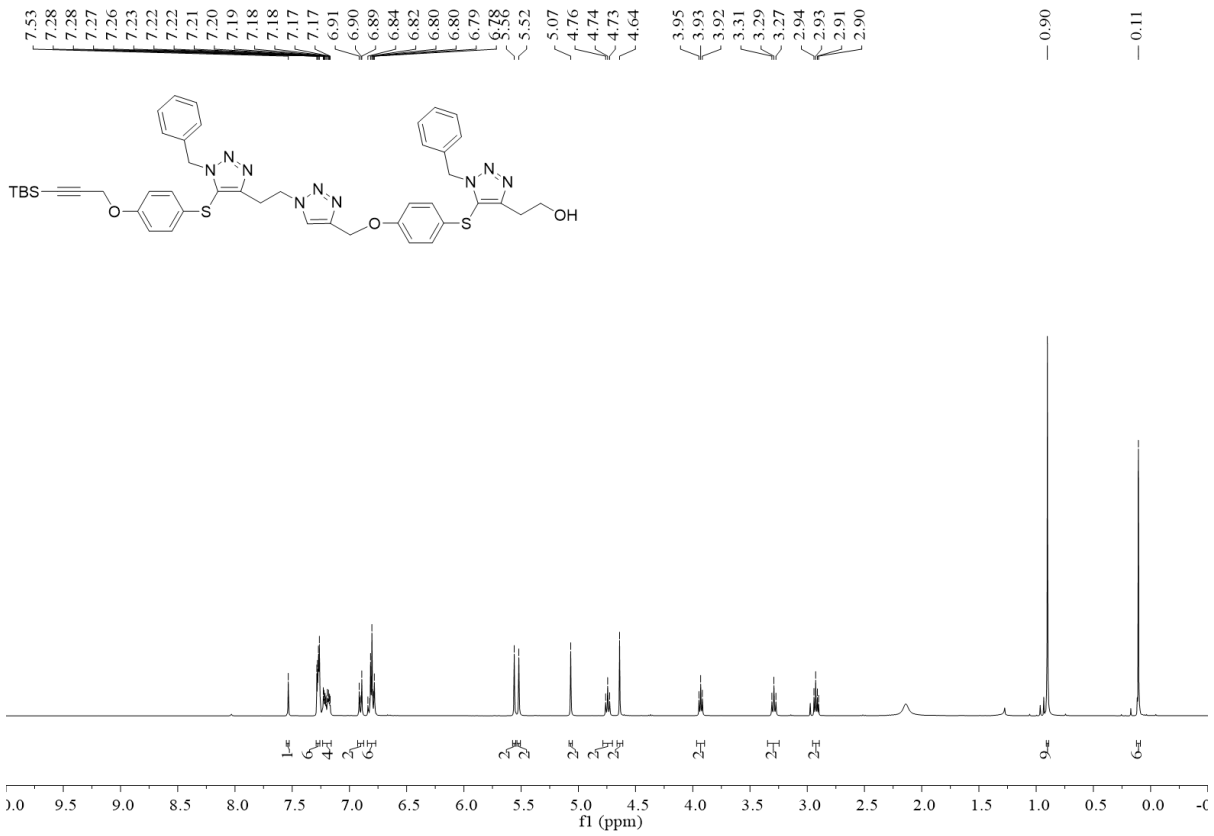


Figure S64. ^{1}H NMR spectra of **10**.

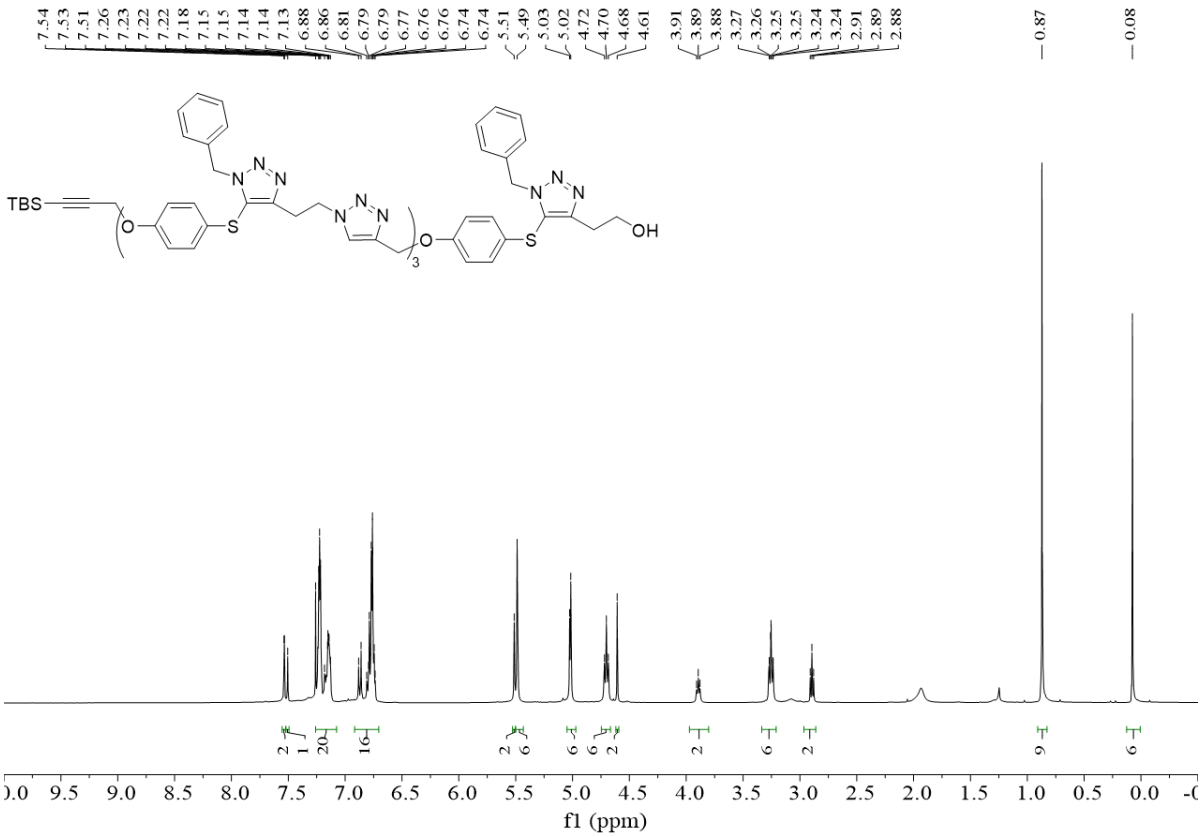


Figure S65. ^{1}H NMR spectra of **11**.

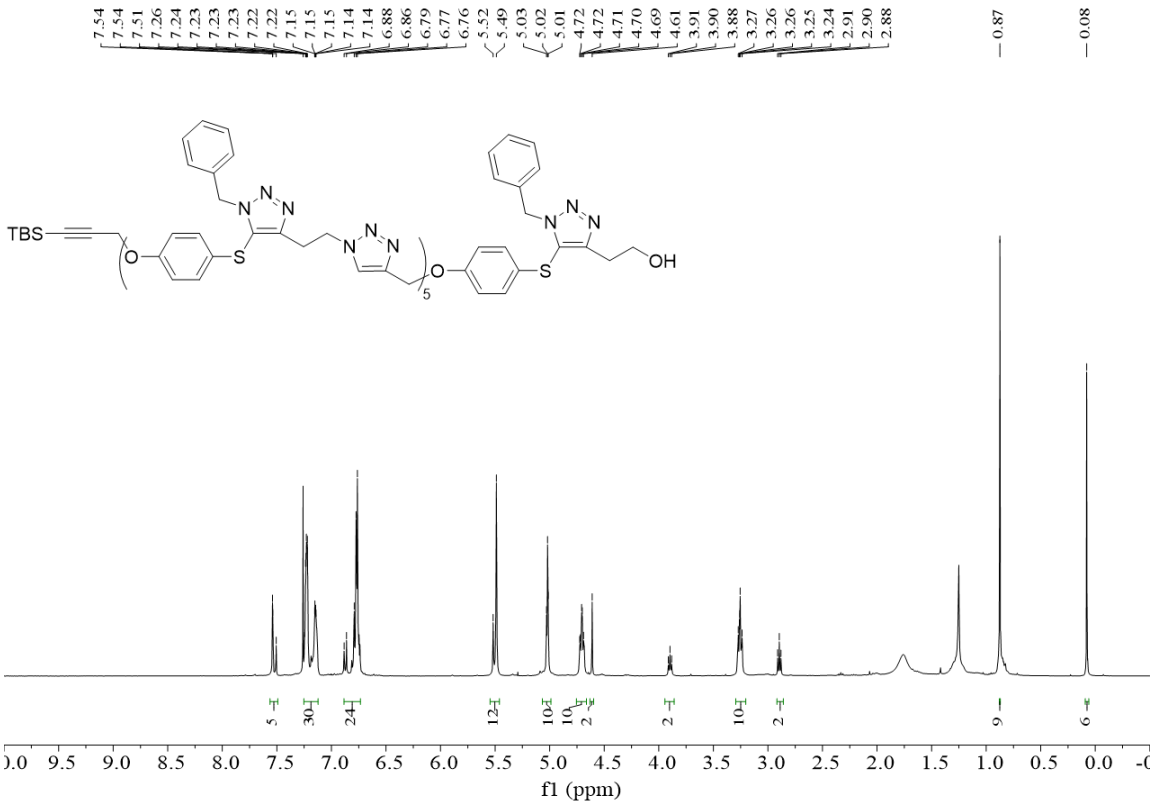


Figure S66. ^{1}H NMR spectra of **12**.

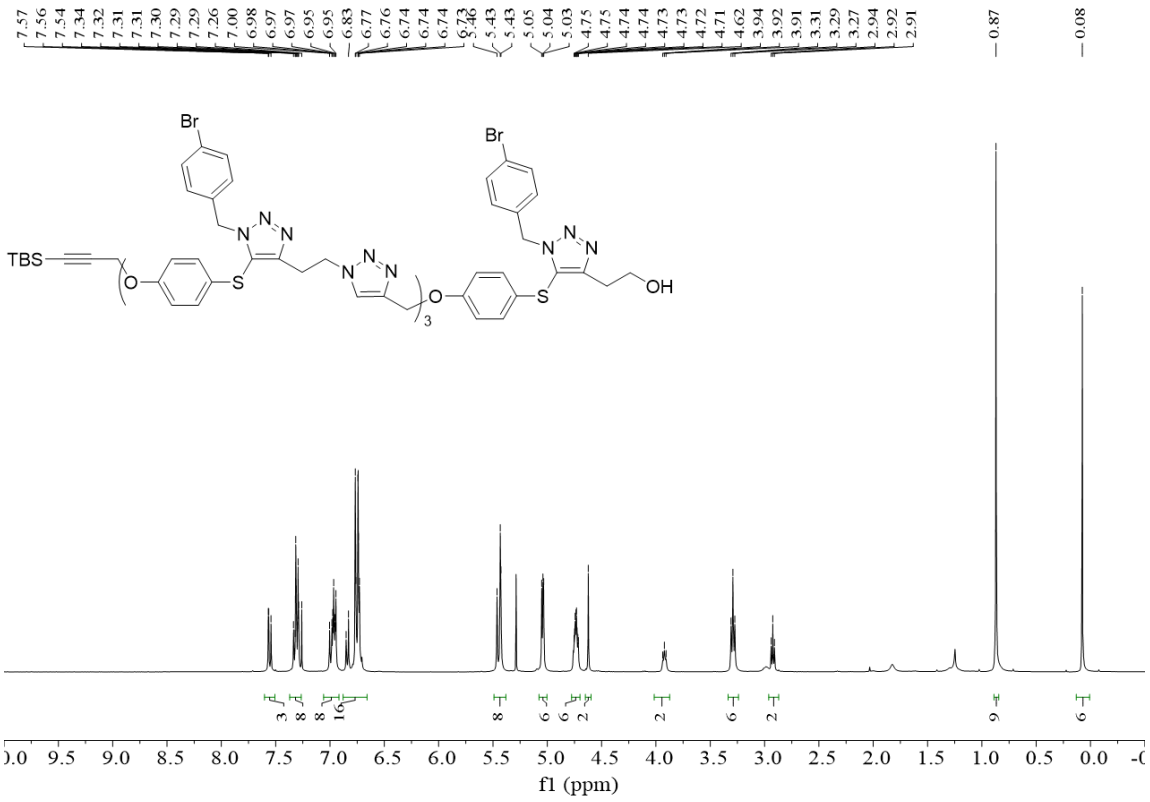


Figure S67. ^{1}H NMR spectra of **13**.

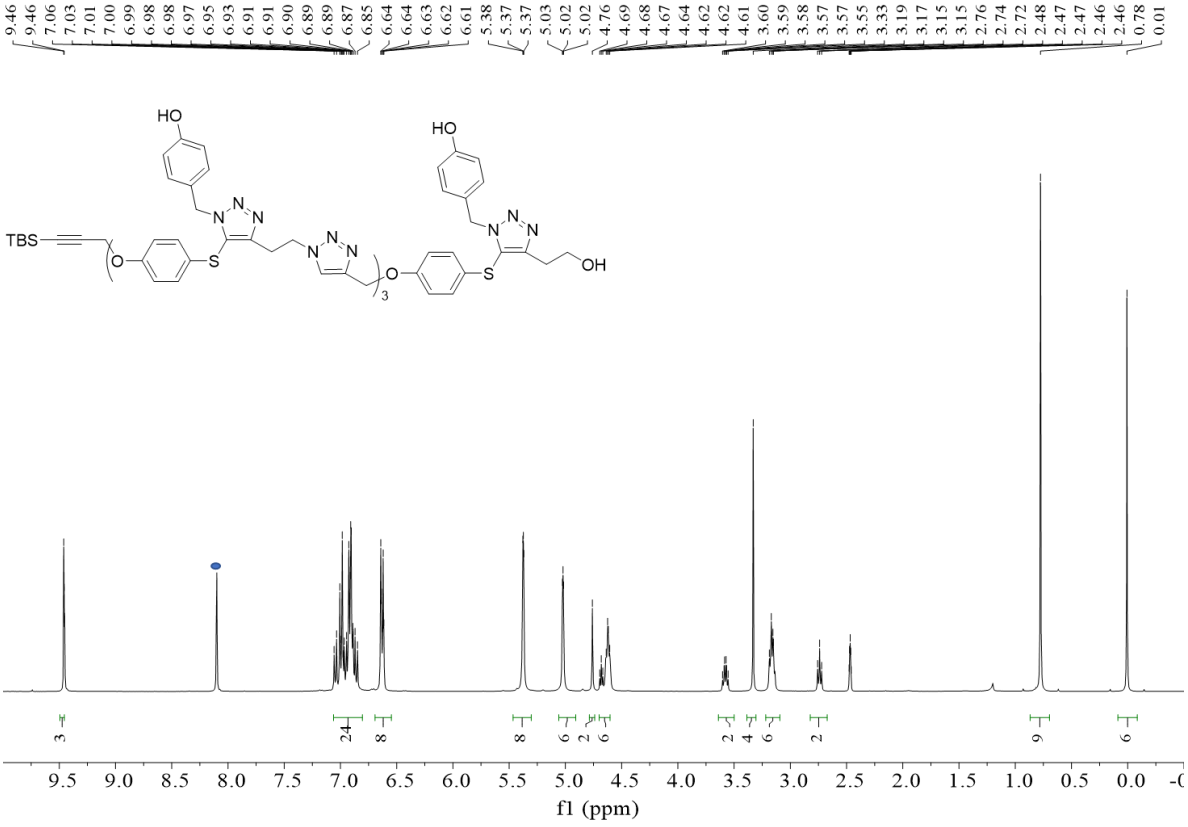


Figure S68. ^{1}H NMR spectra of **14**.

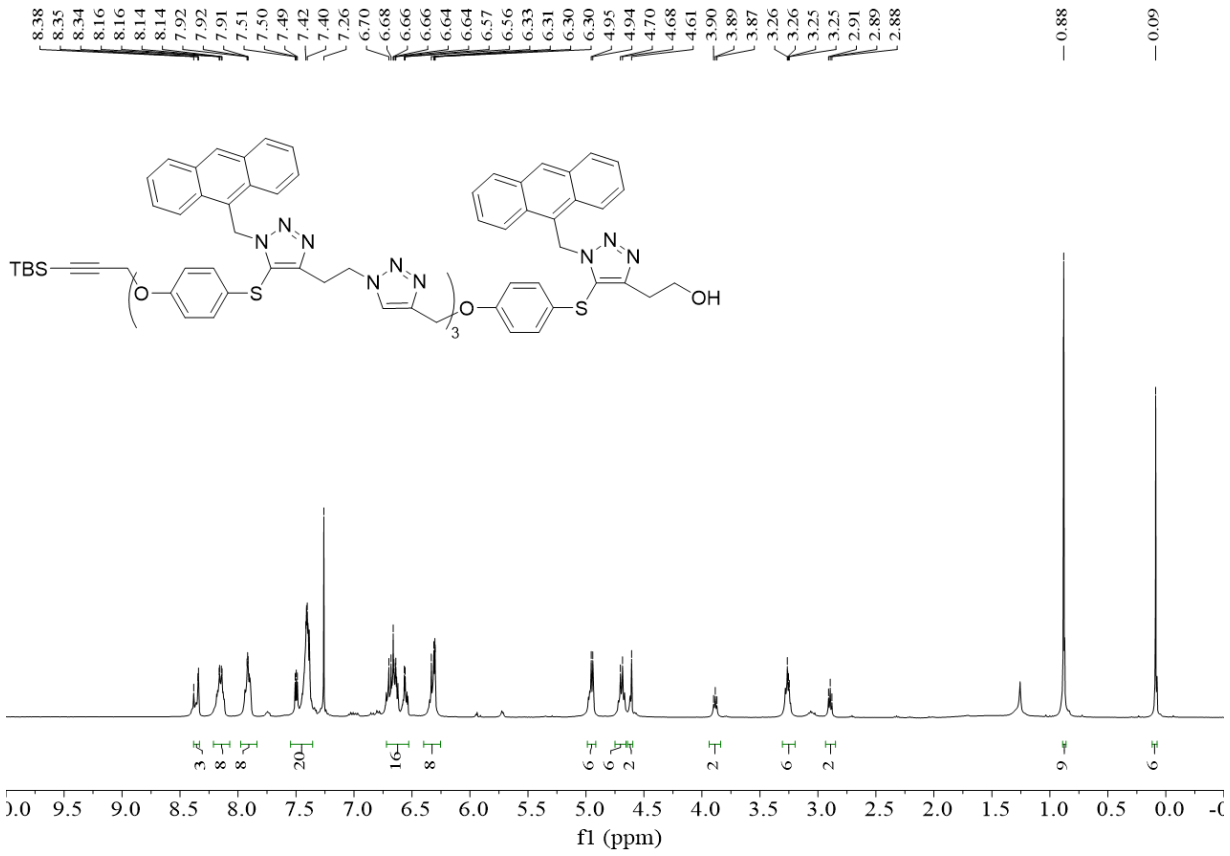


Figure S69. ^{1}H NMR spectra of **15**.

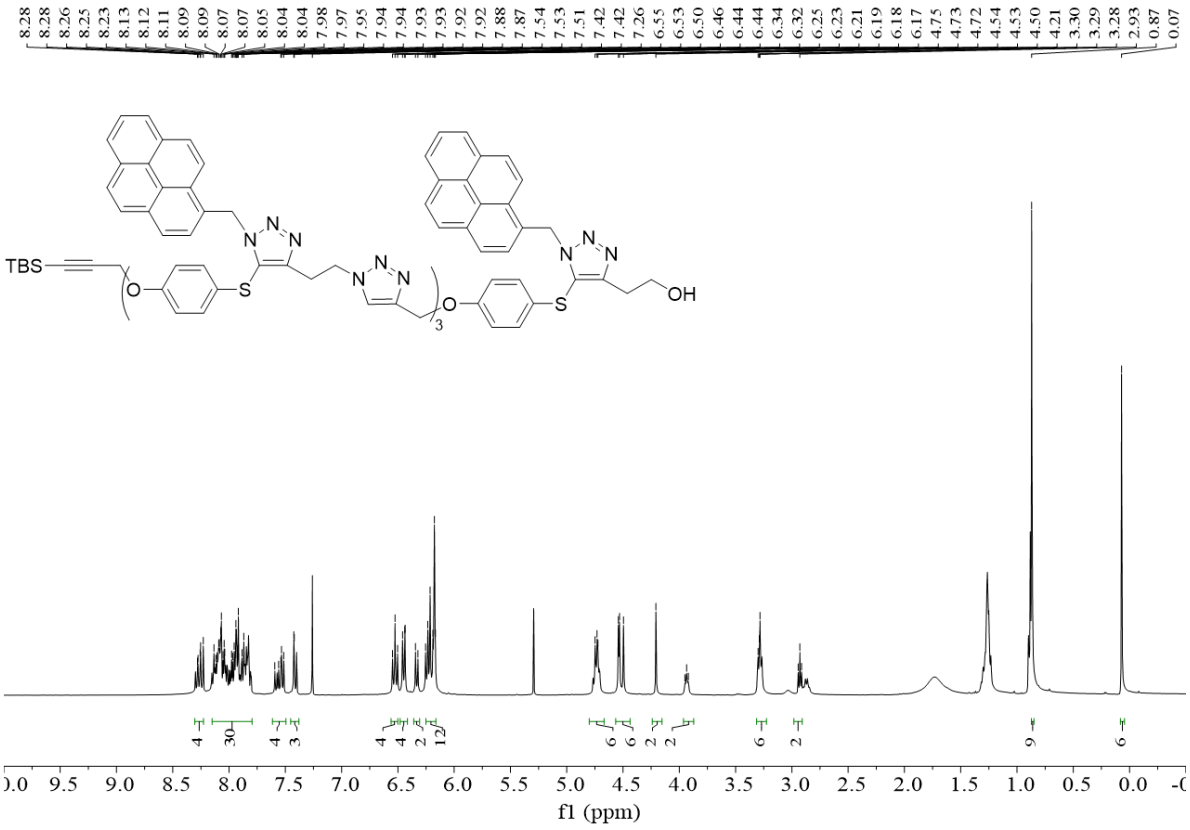


Figure S70. ^{1}H NMR spectra of **16**.

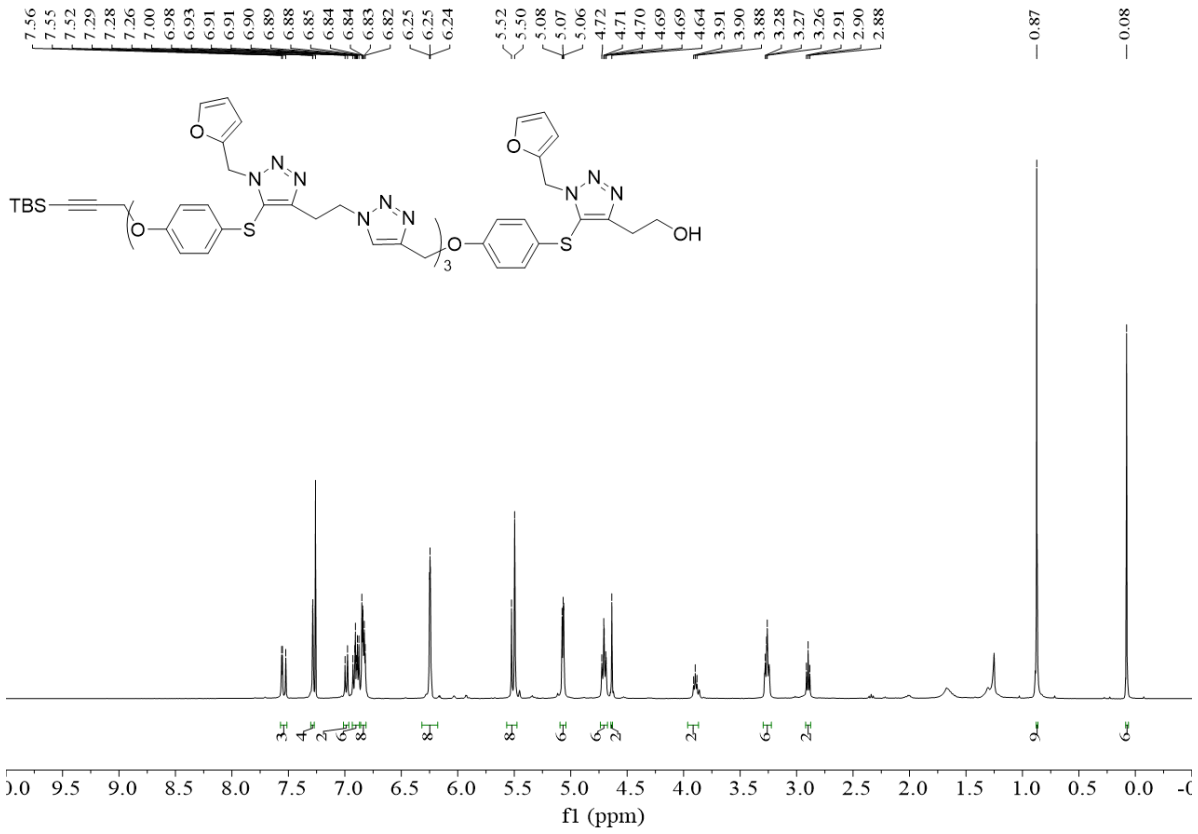


Figure S71. ^{1}H NMR spectra of **17**

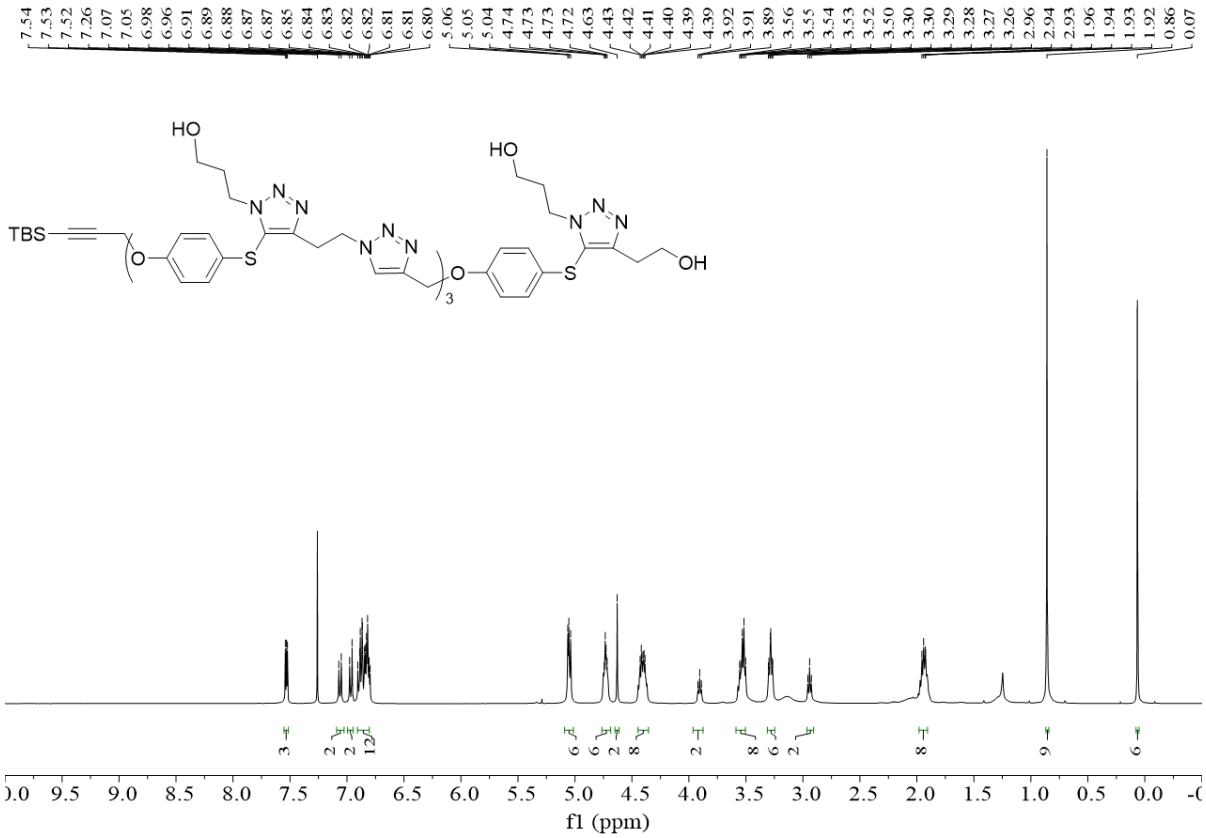


Figure S72. ^{1}H NMR spectra of **18**.

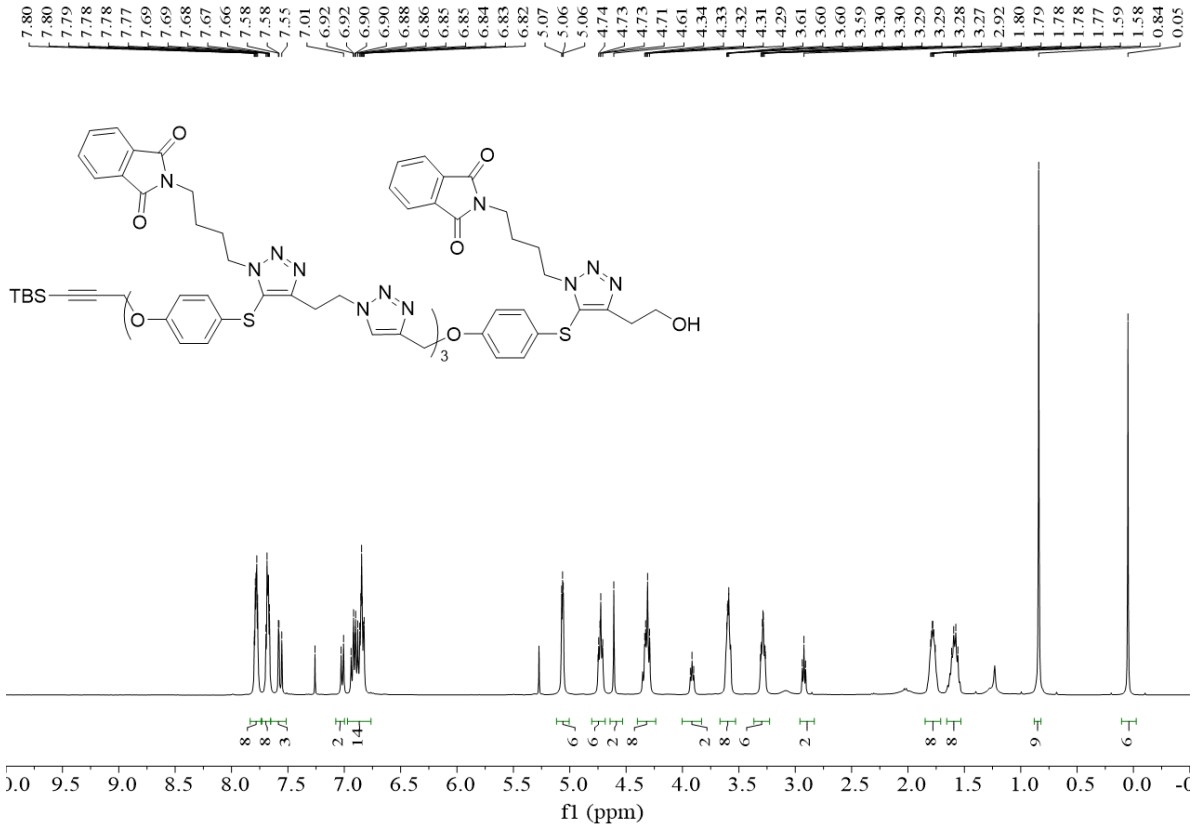


Figure S73. ^{1}H NMR spectra of **19**.

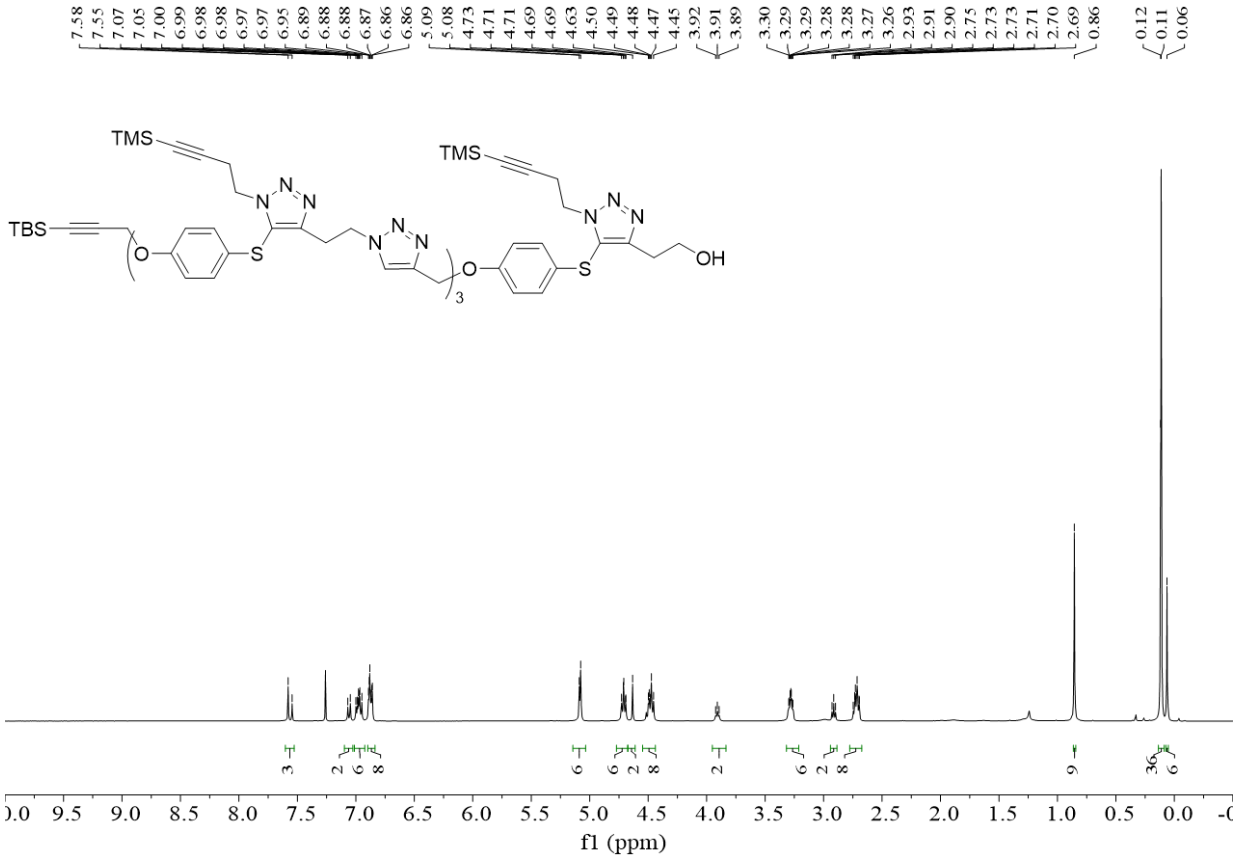


Figure S74. ^{1}H NMR spectra of **20**.

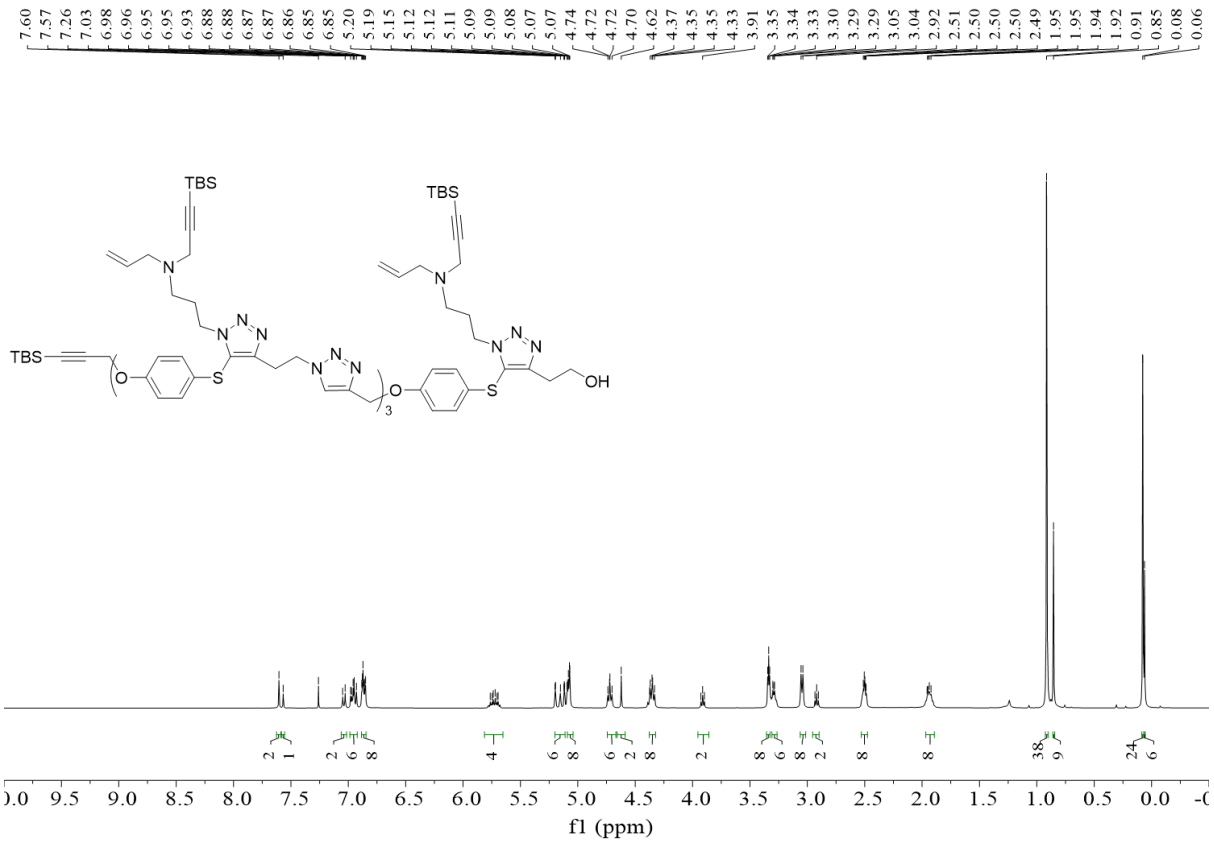


Figure S75. ^{1}H NMR spectra of **21**.

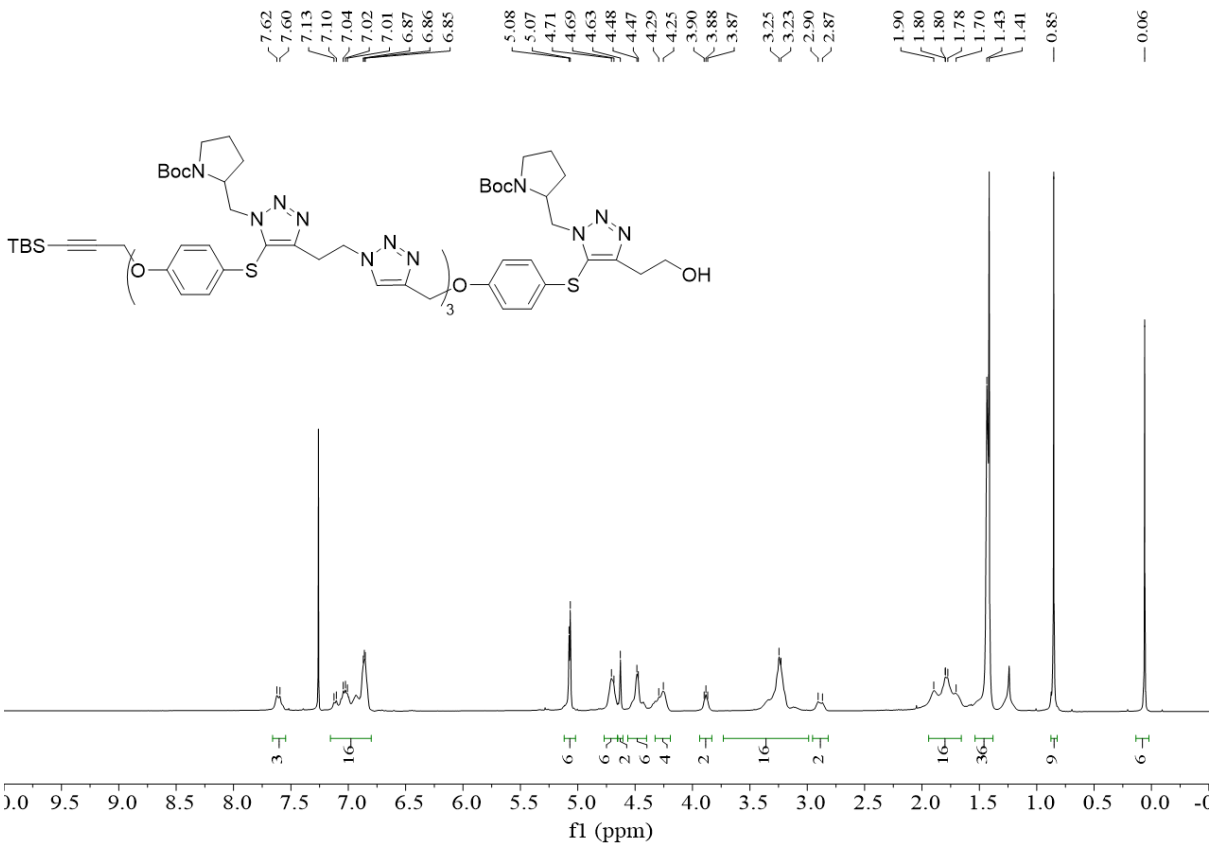


Figure S76. ^{1}H NMR spectra of **22**.

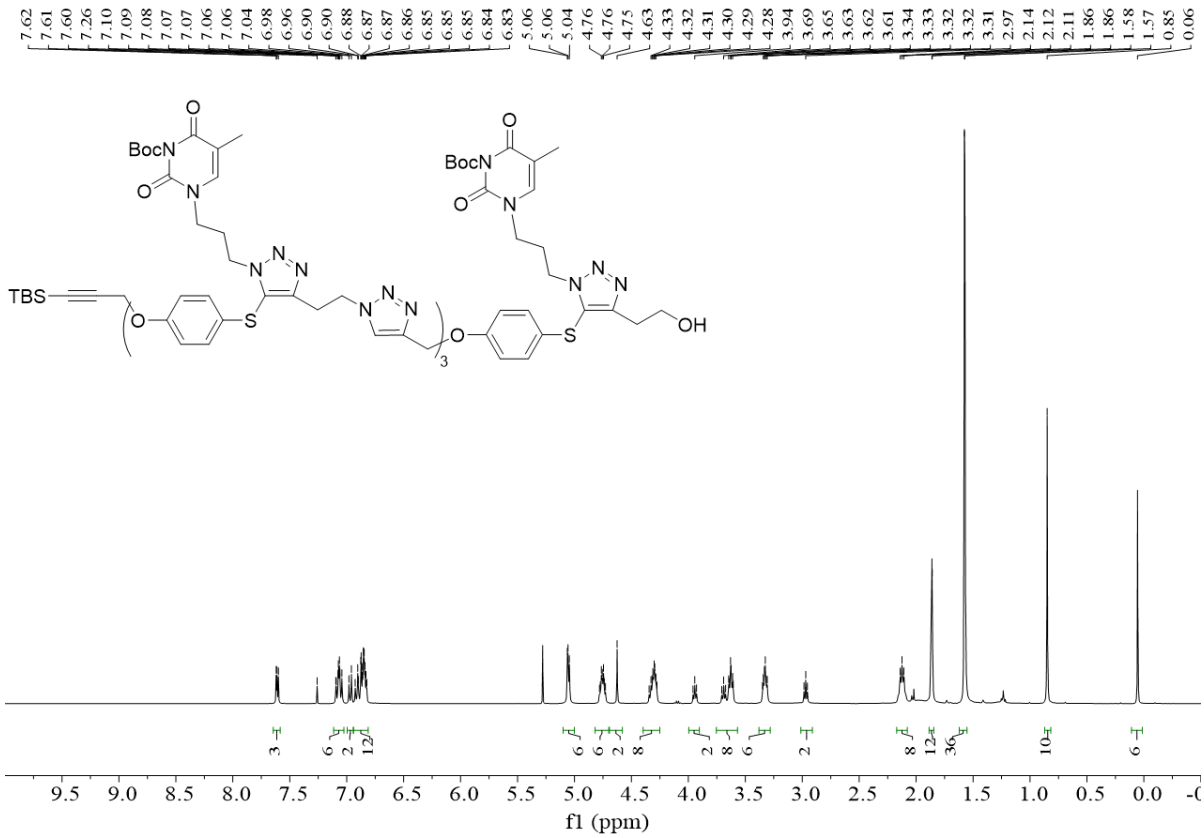


Figure S77. ^{1}H NMR spectra of **23**

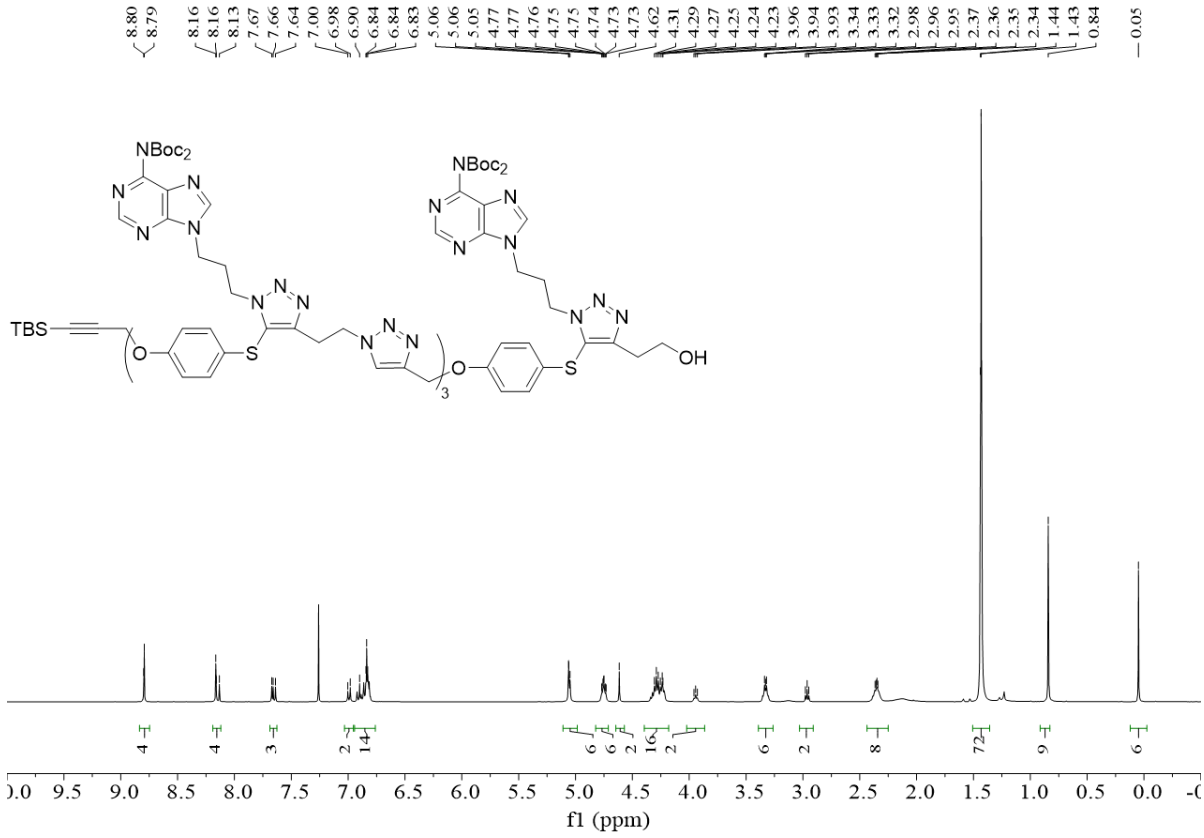


Figure S78. ^{1}H NMR spectra of **24**.

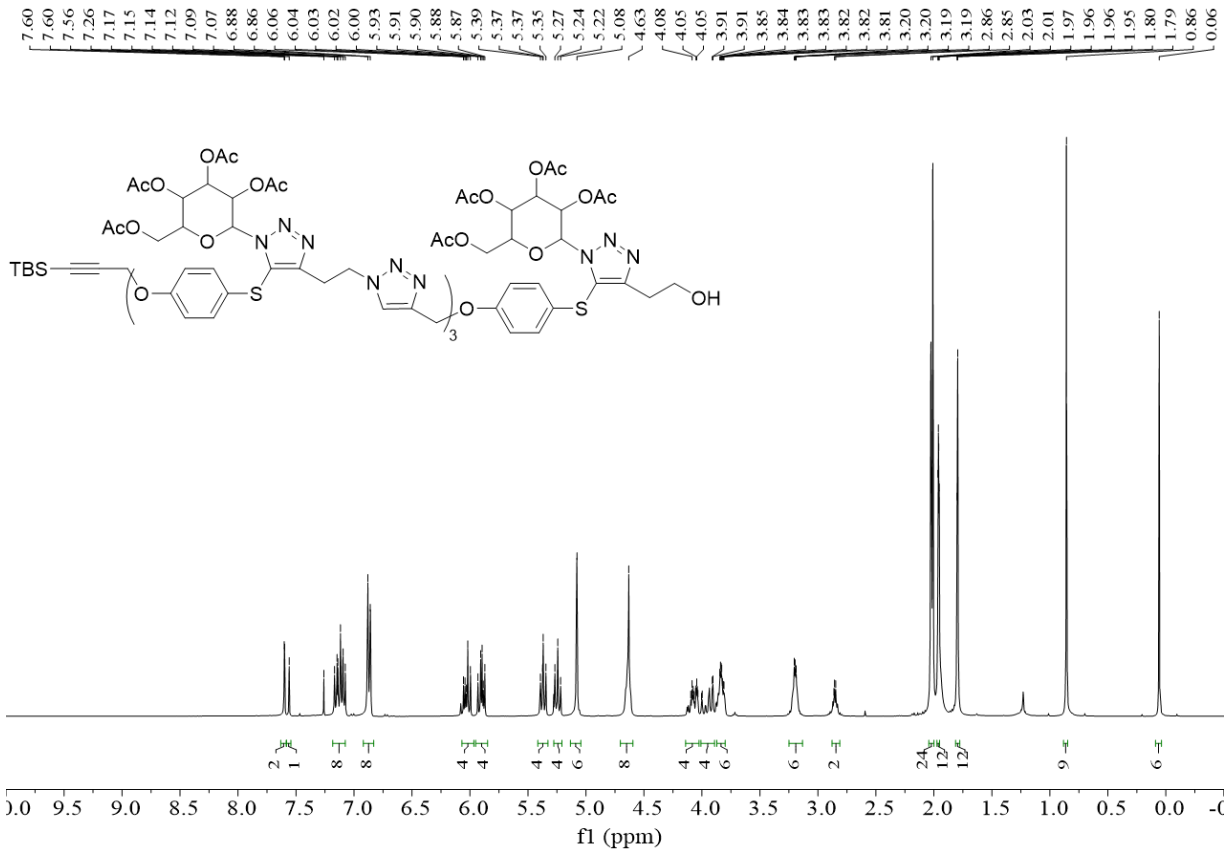


Figure S79. ^{1}H NMR spectra of **25**.

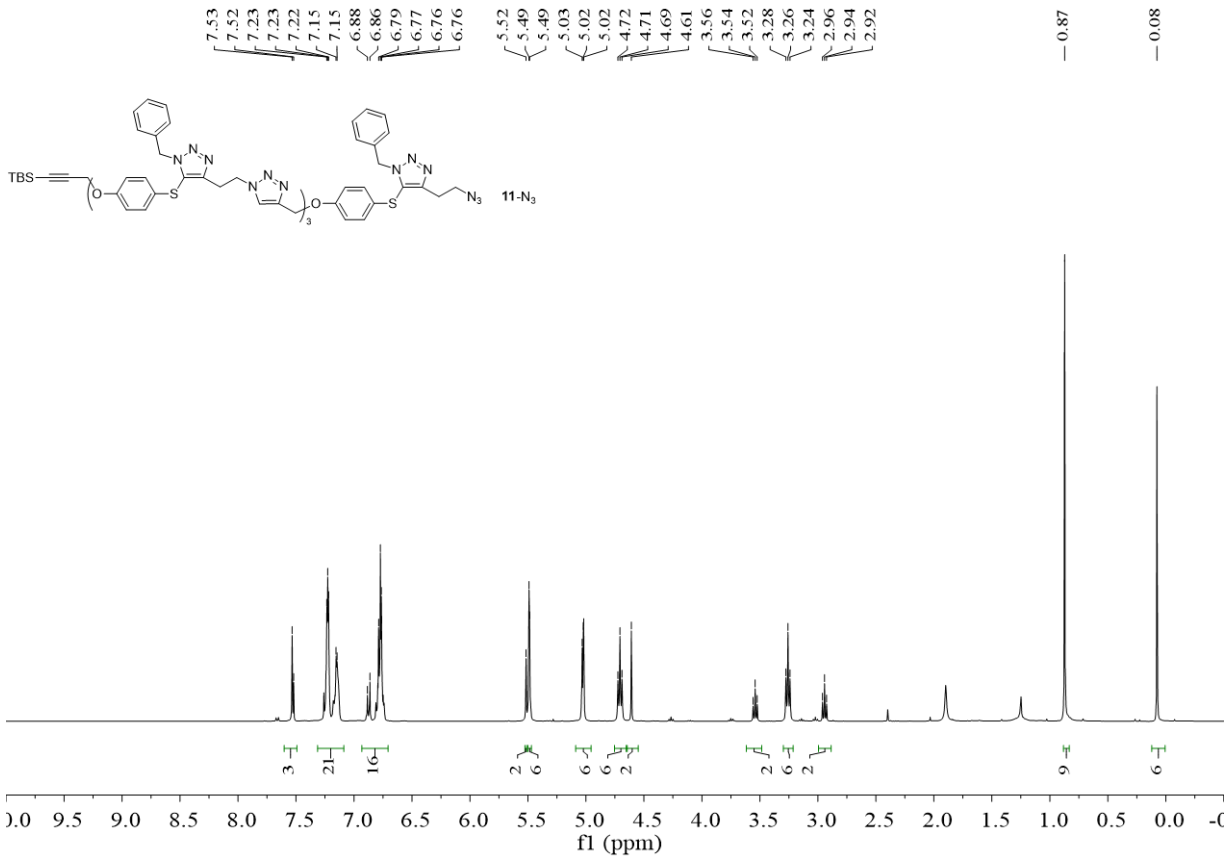


Figure S80. ^{1}H NMR spectra of **11-N$_3$**.

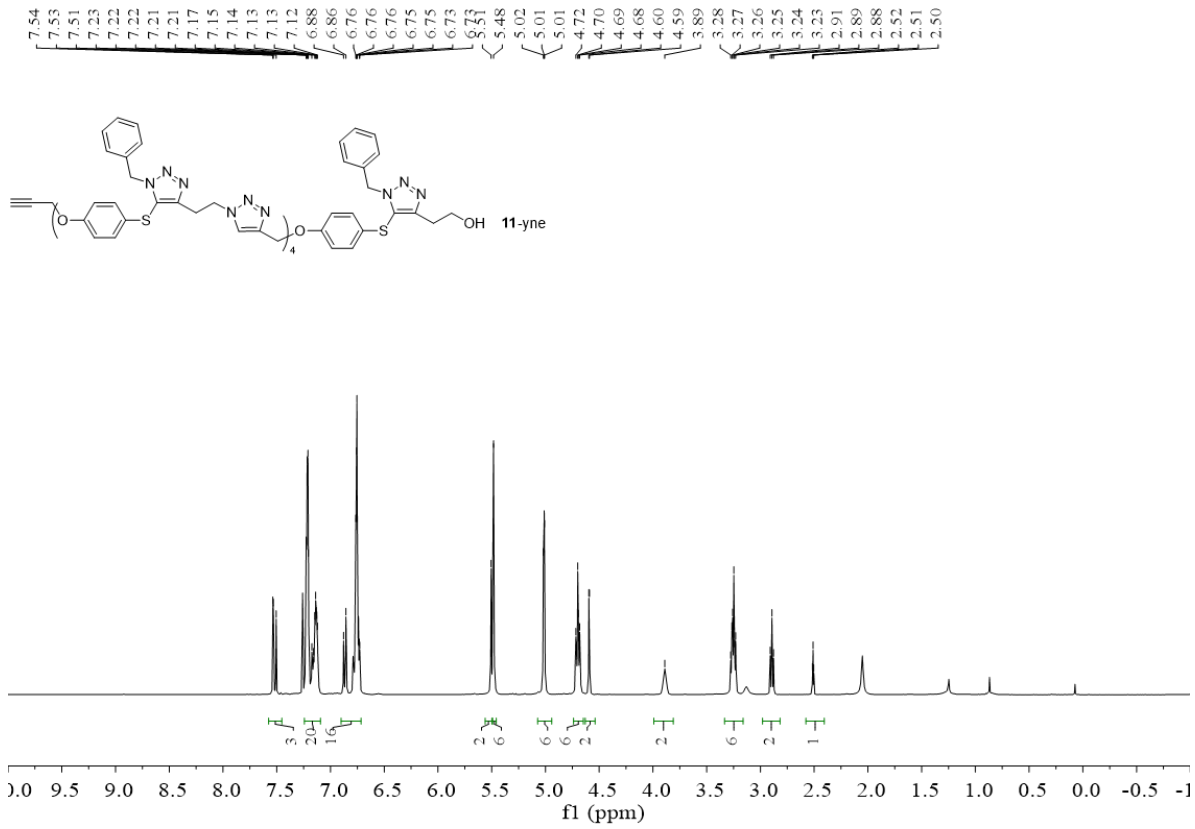


Figure S81. ^{1}H NMR spectra of **11-yne**.

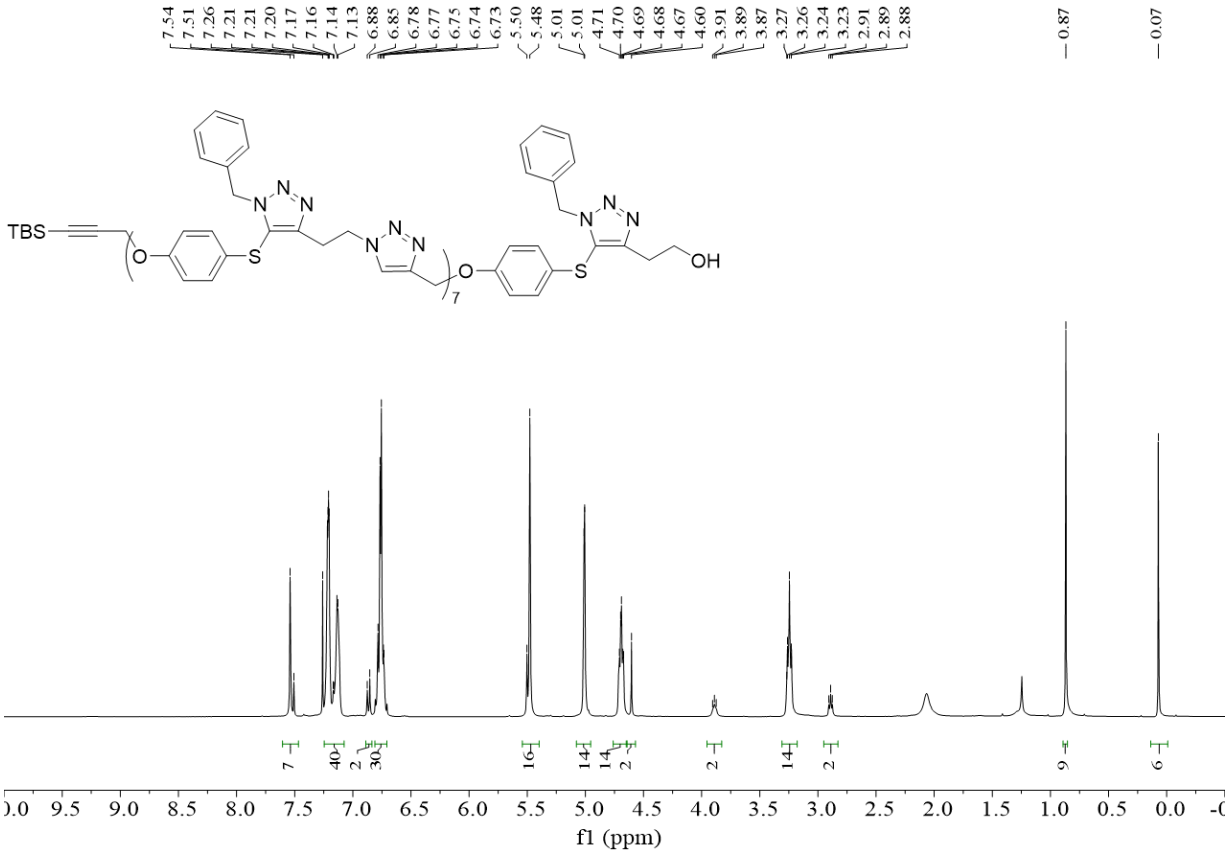


Figure S82. ^{1}H NMR spectra of **26**.

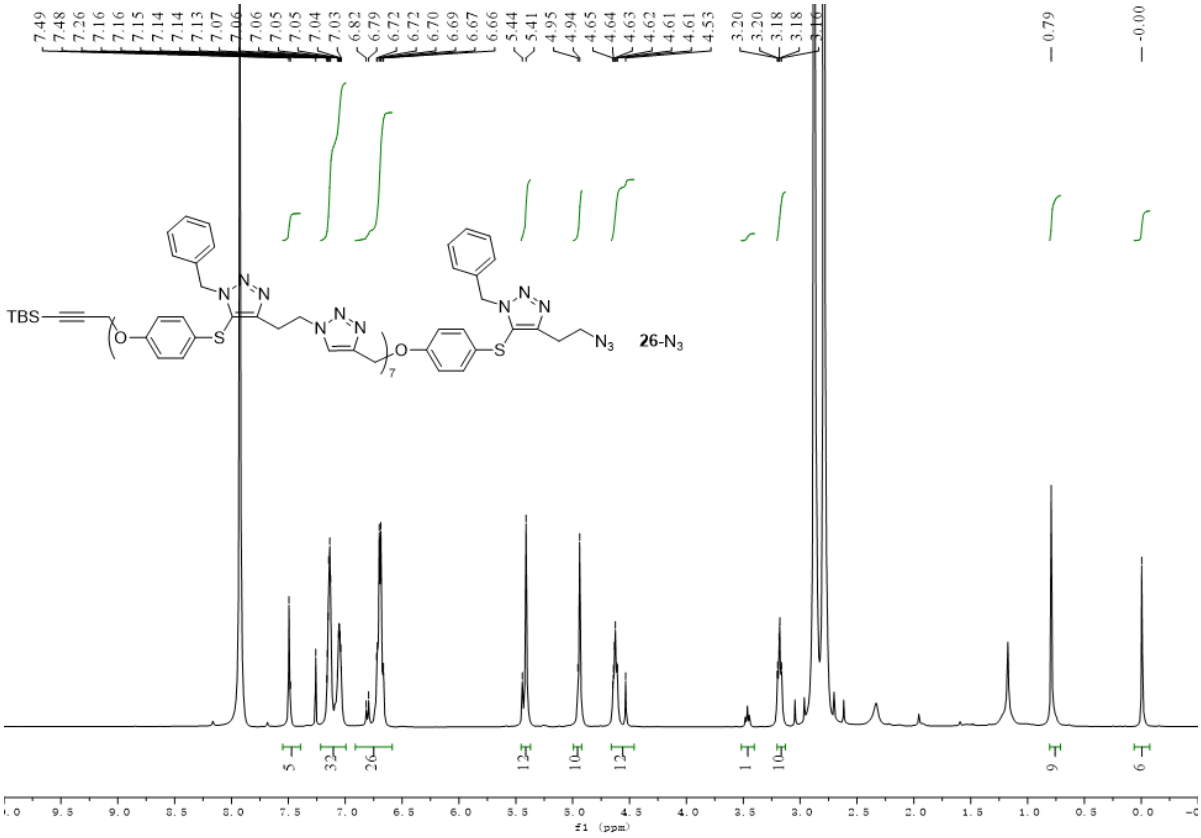


Figure S83. ^{1}H NMR spectra of **26-N$_3$**.

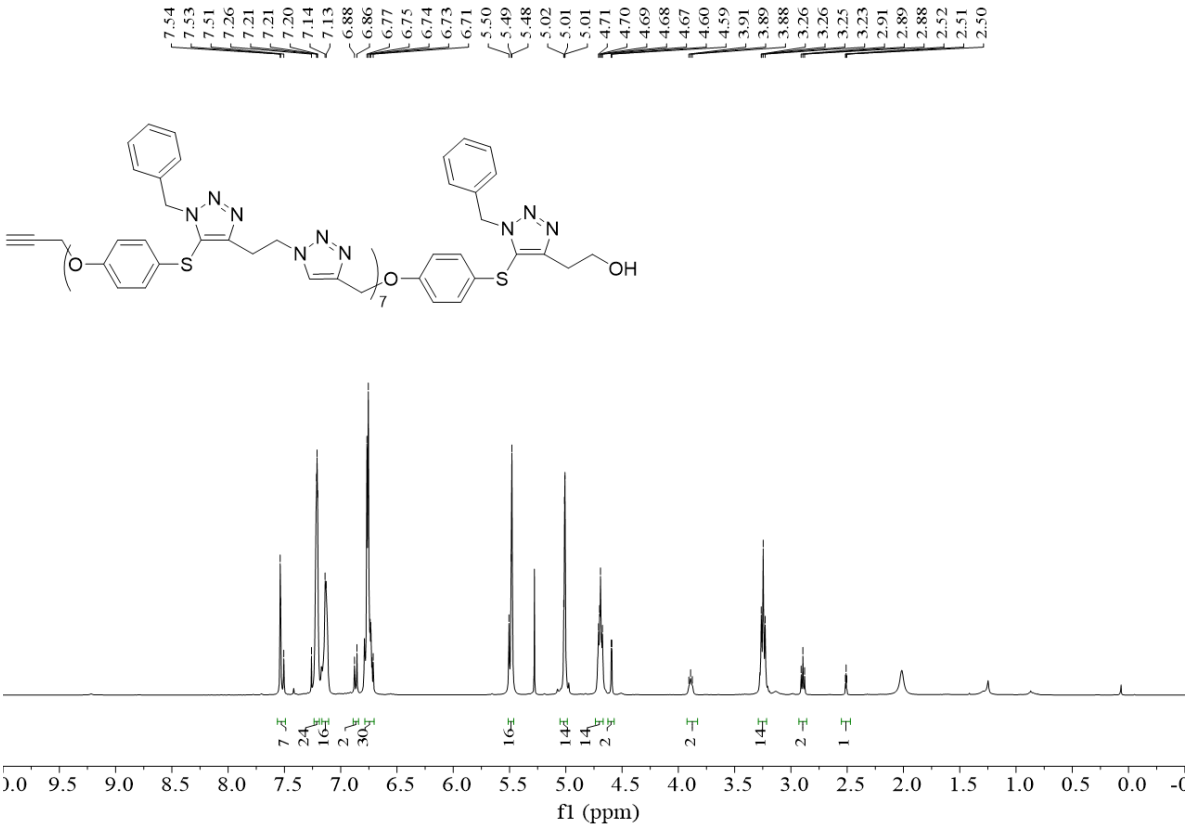


Figure S84. ^{1}H NMR spectra of **26-yne**.

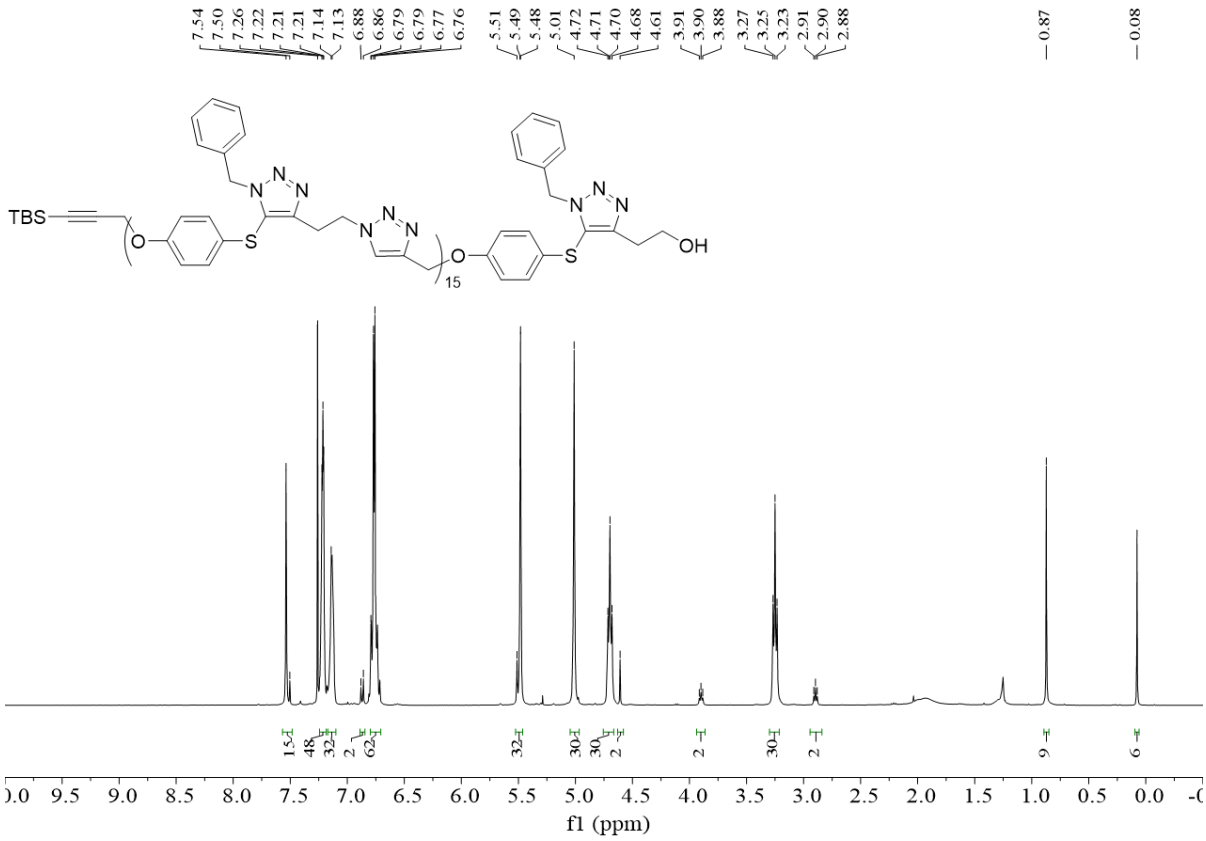


Figure S85. ^{1}H NMR spectra of **27**.

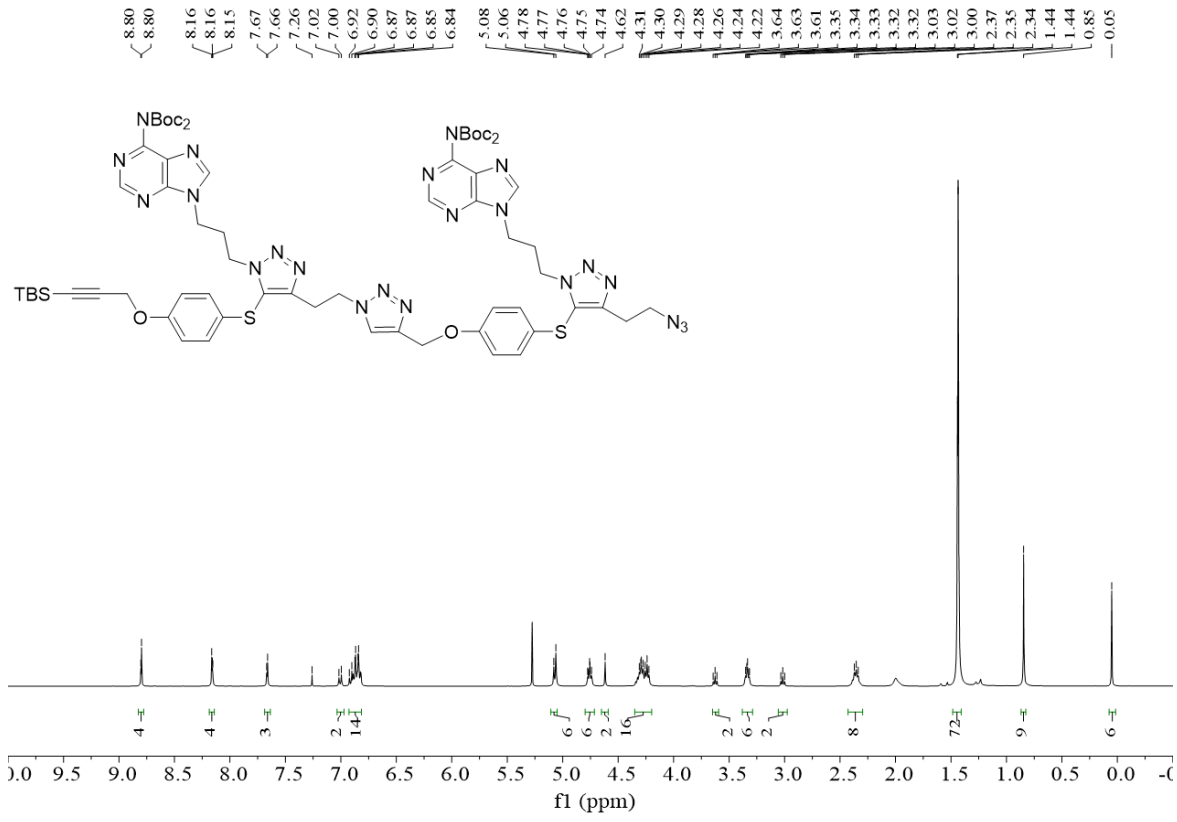


Figure S86. ^{1}H NMR spectra of **24-N$_3$**.

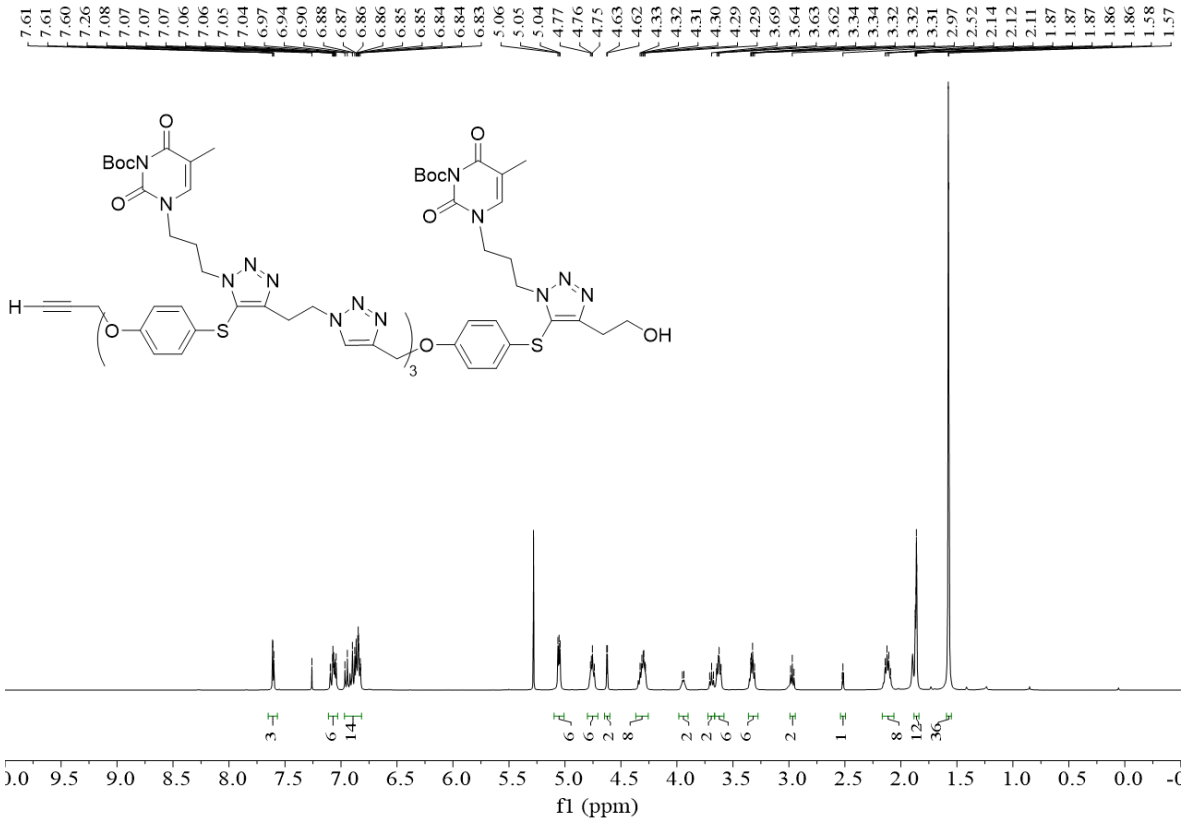


Figure S87. ^{1}H NMR spectra of **23-yne**.

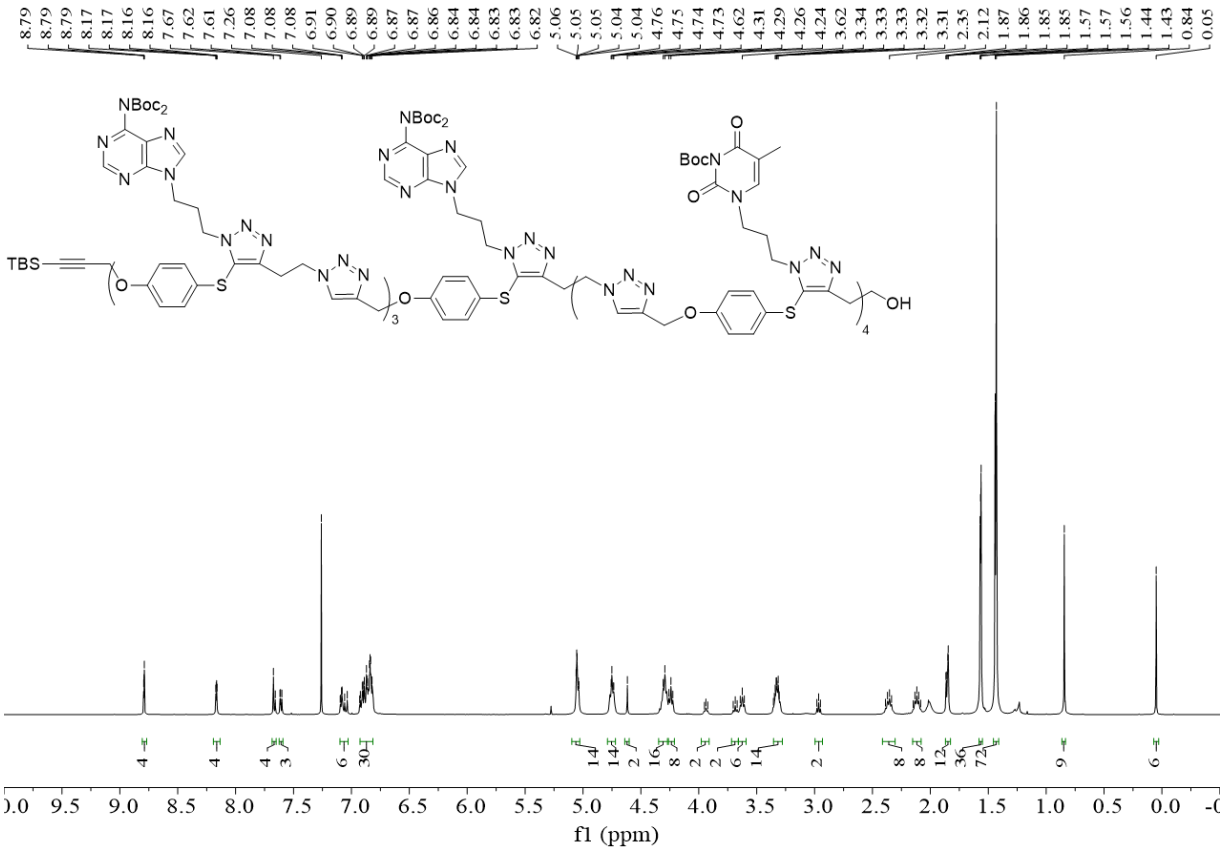


Figure S88. ^{1}H NMR spectra of **28**.

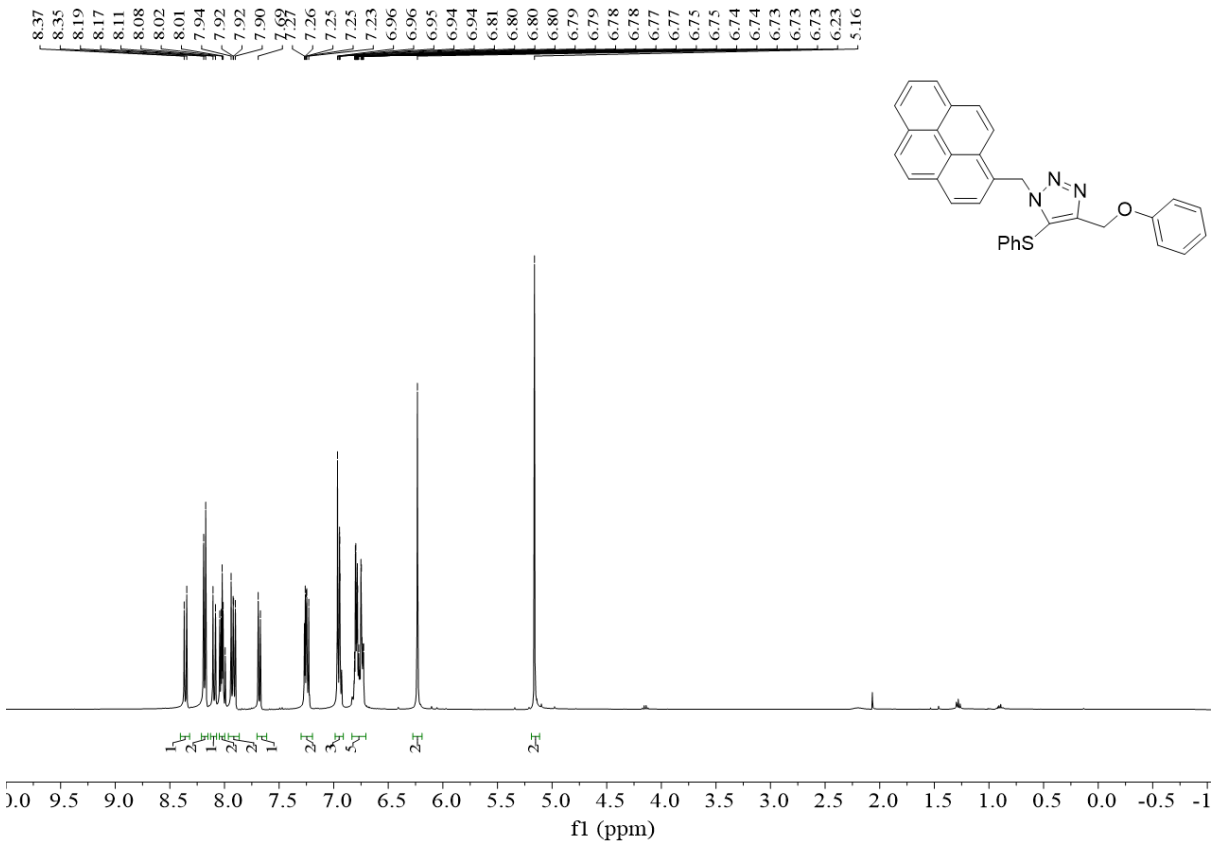


Figure S89. ^{1}H NMR spectra of **29**.

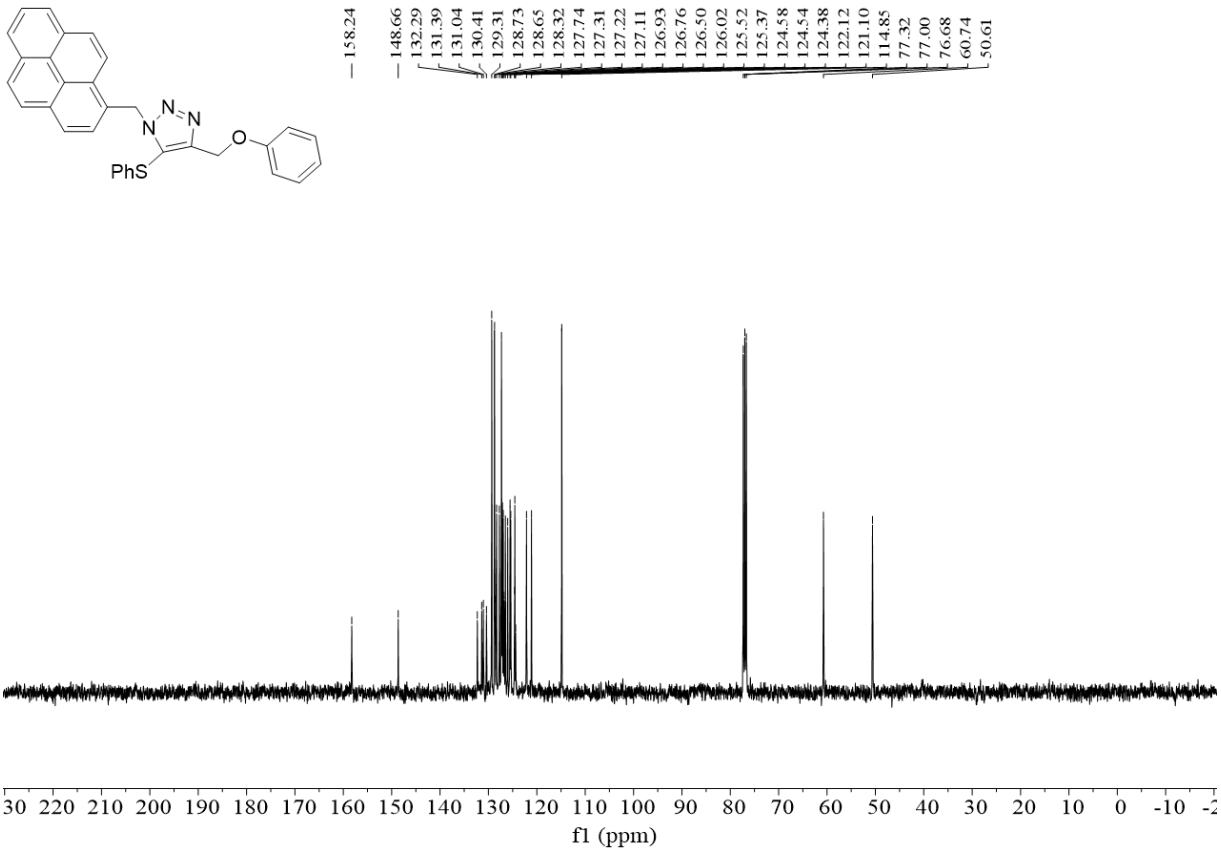


Figure S90. ^{13}C NMR spectra of **29**.

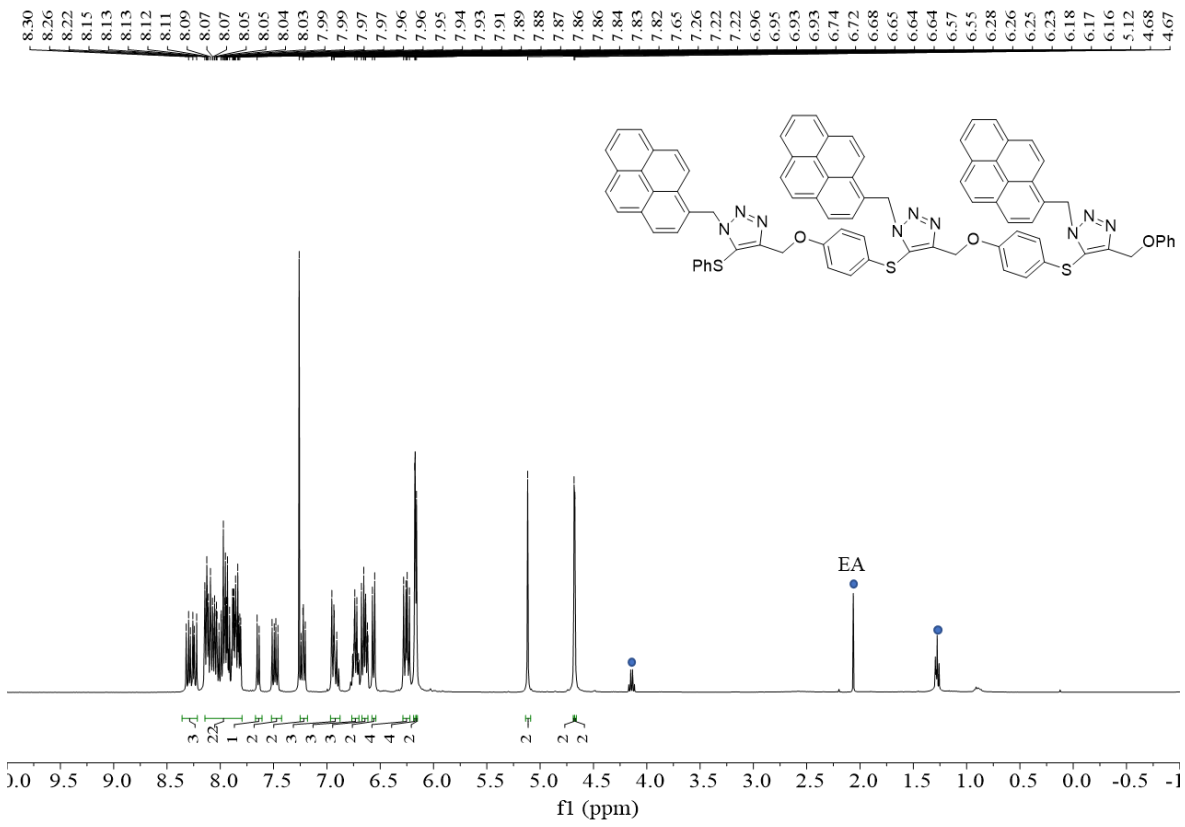


Figure S91. ^{1}H NMR spectra of **30**.

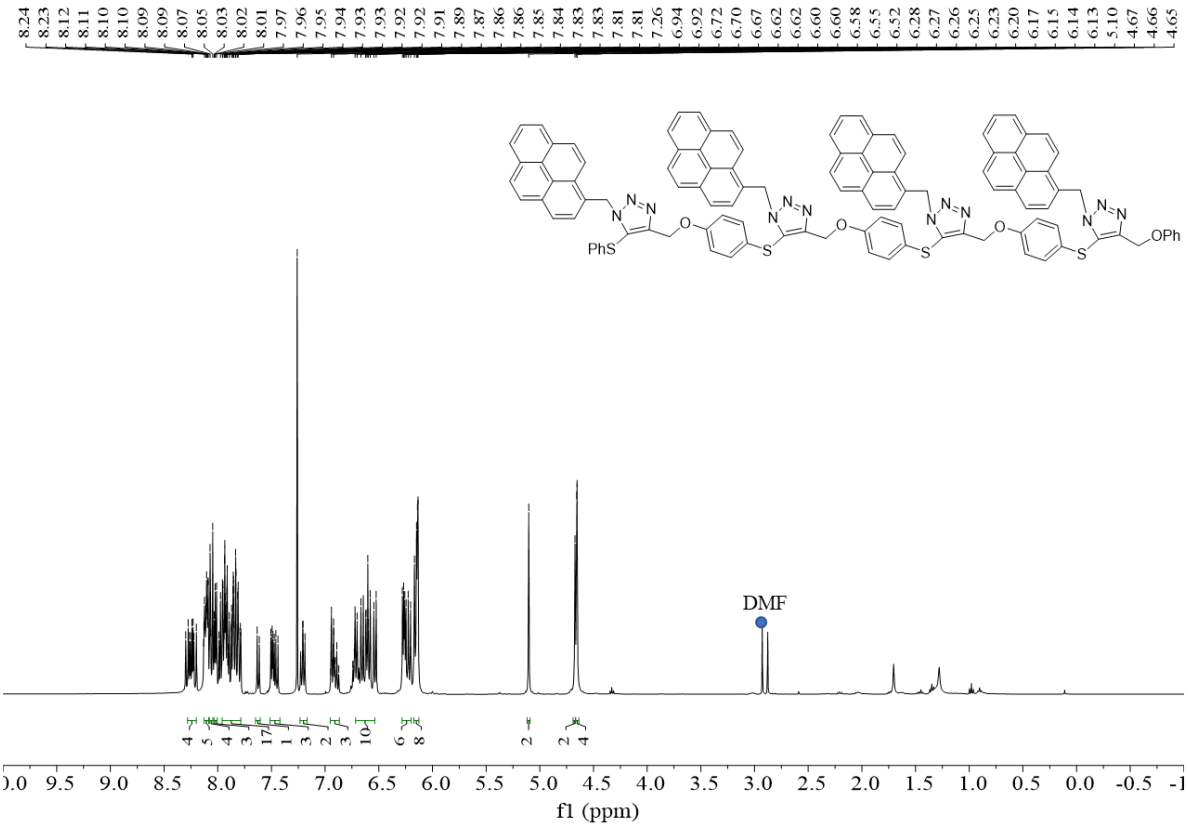


Figure S92. ^{1}H NMR spectra of **31**.

VIII. Mass Spectra of Oligomers

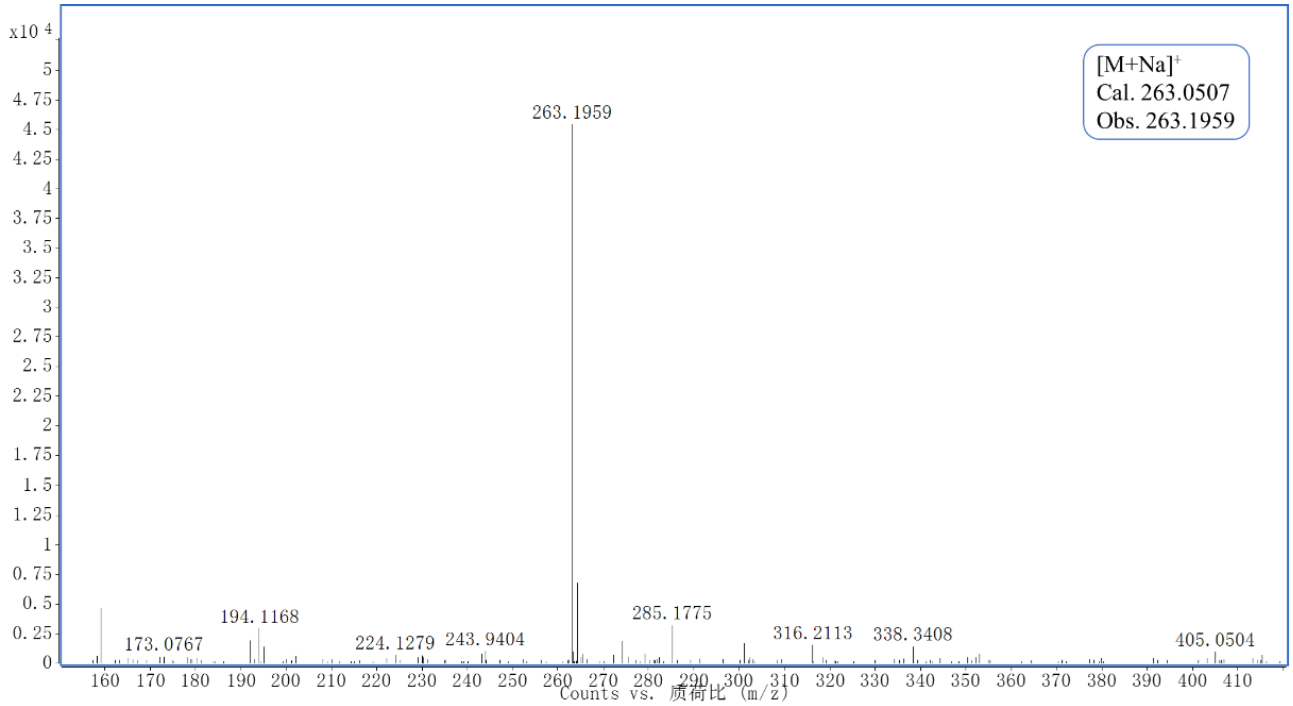


Figure S93. ESI-MS of **A1**.

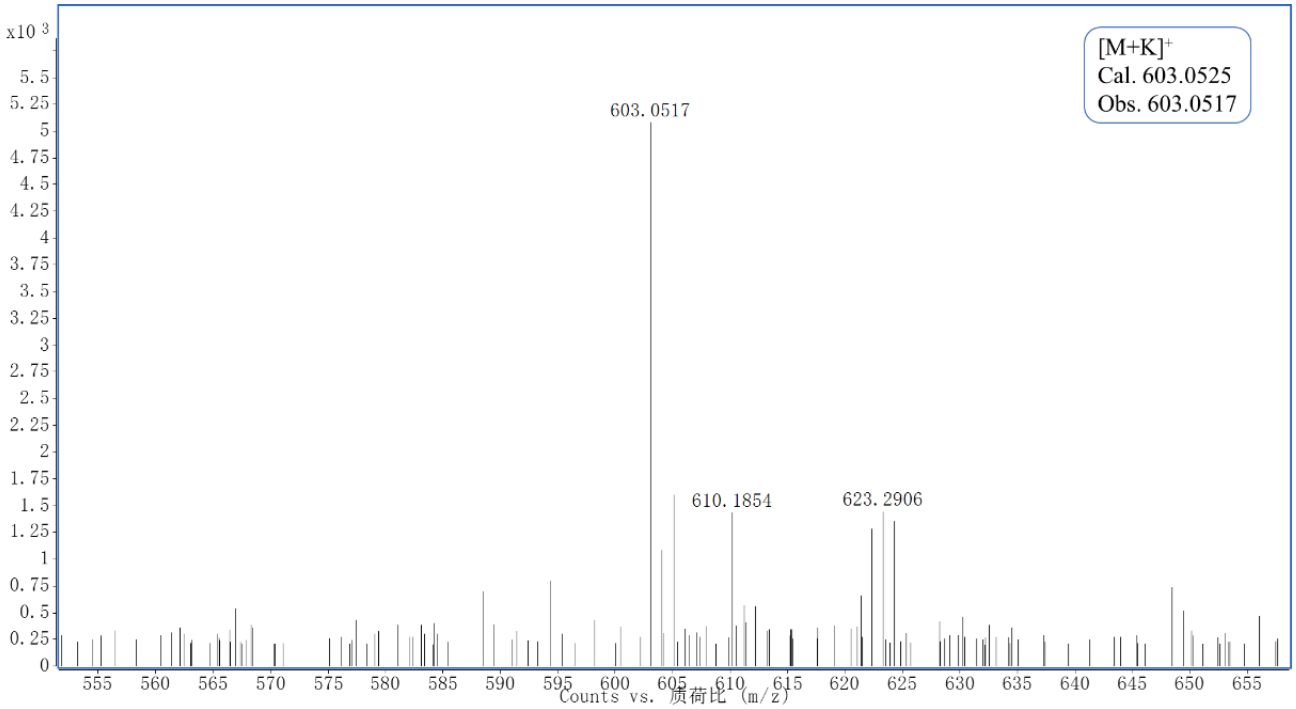


Figure S94. ESI-MS of **A3**.

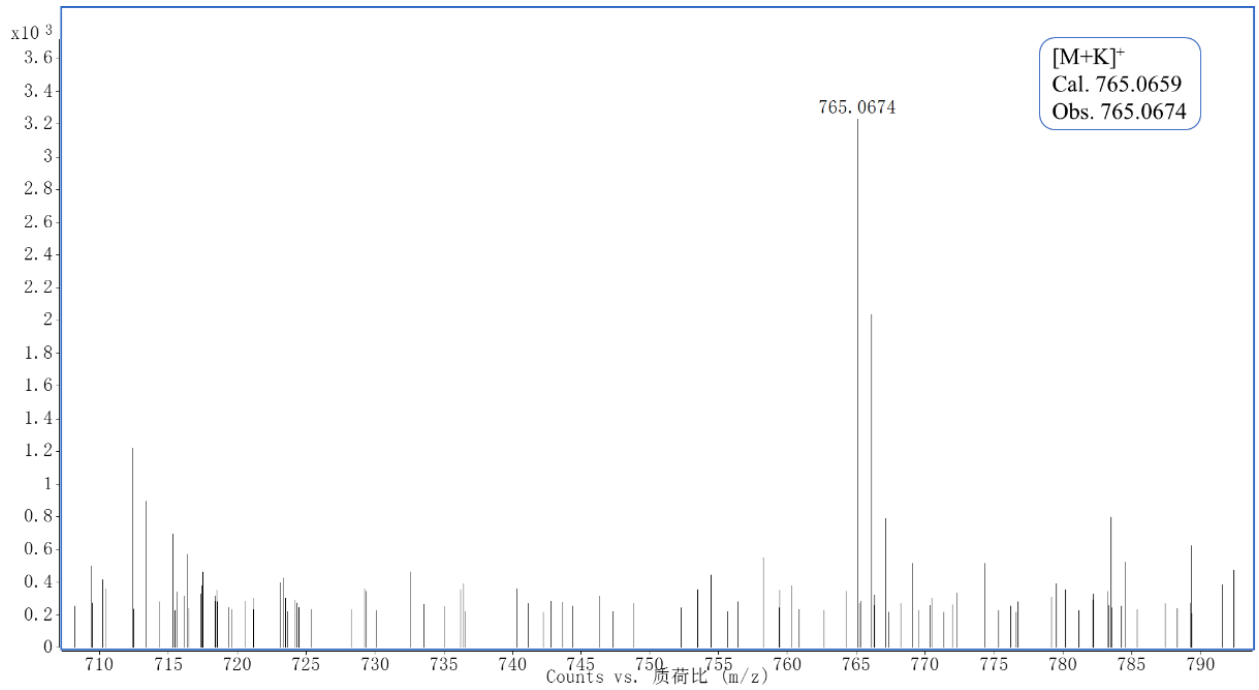


Figure S95. ESI-MS of **A4**.

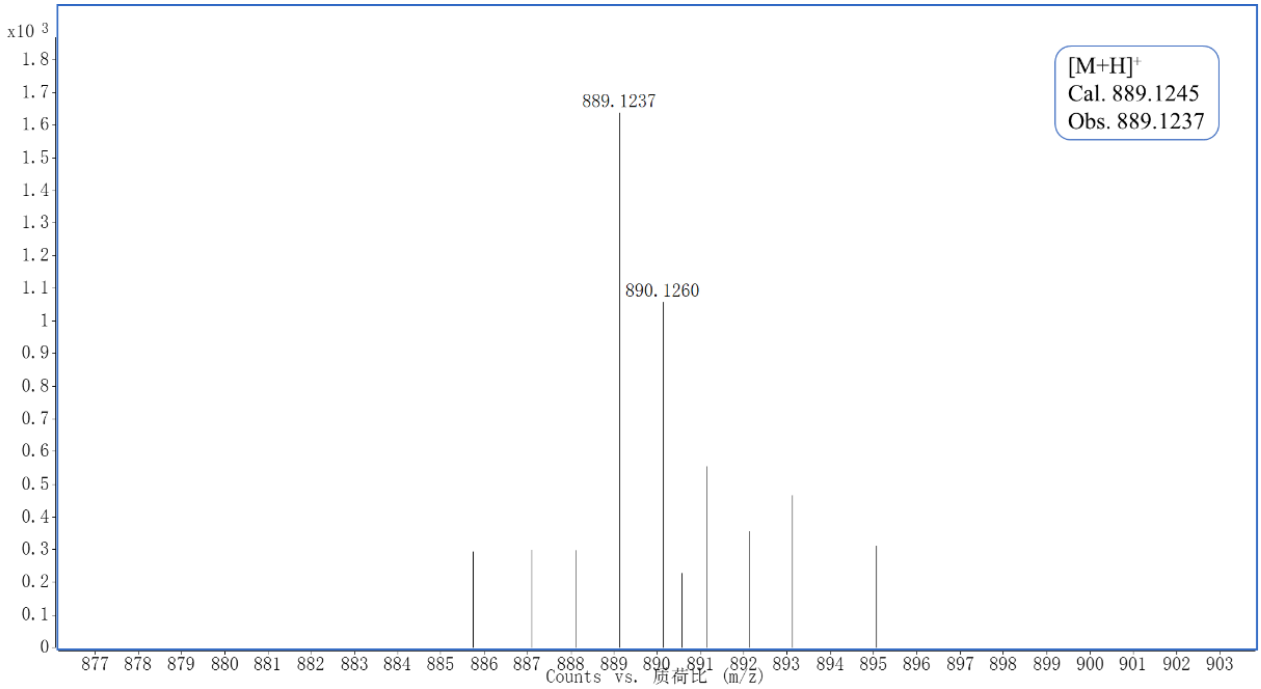


Figure S96. ESI-MS of **A5**.

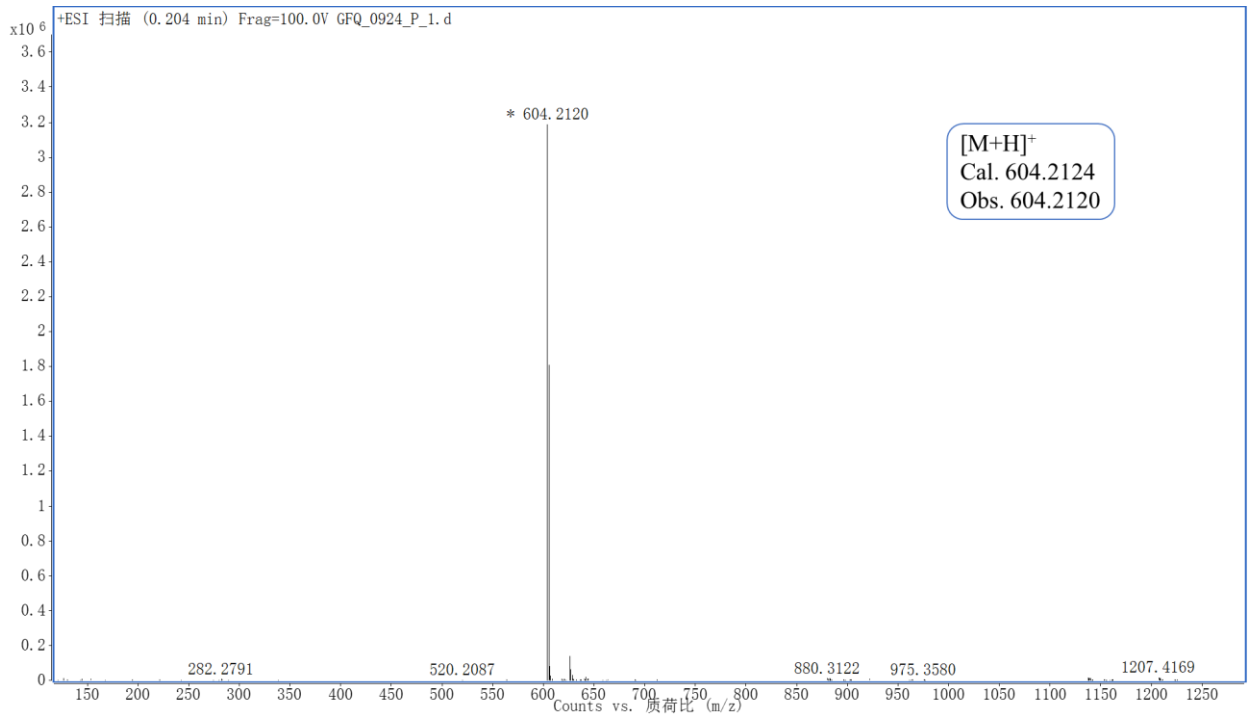


Figure S97. ESI-MS of **B2**.

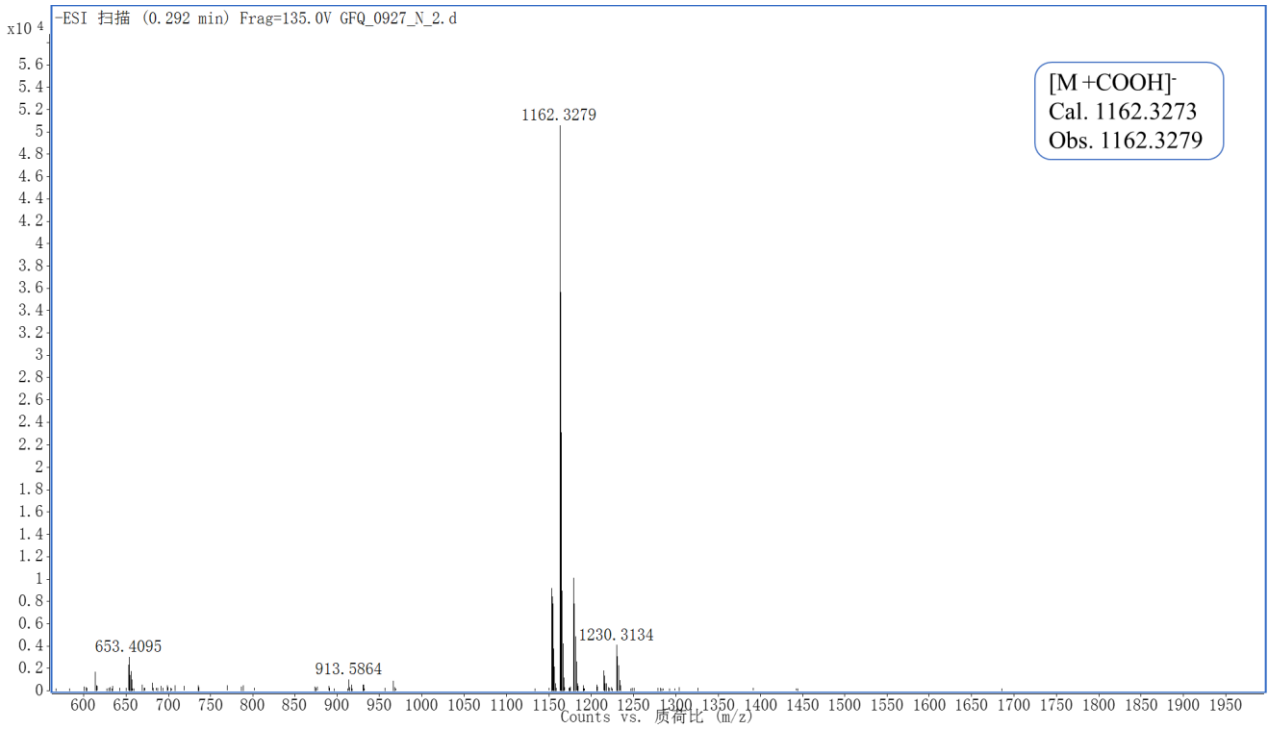


Figure S98. ESI-MS of **B4**.

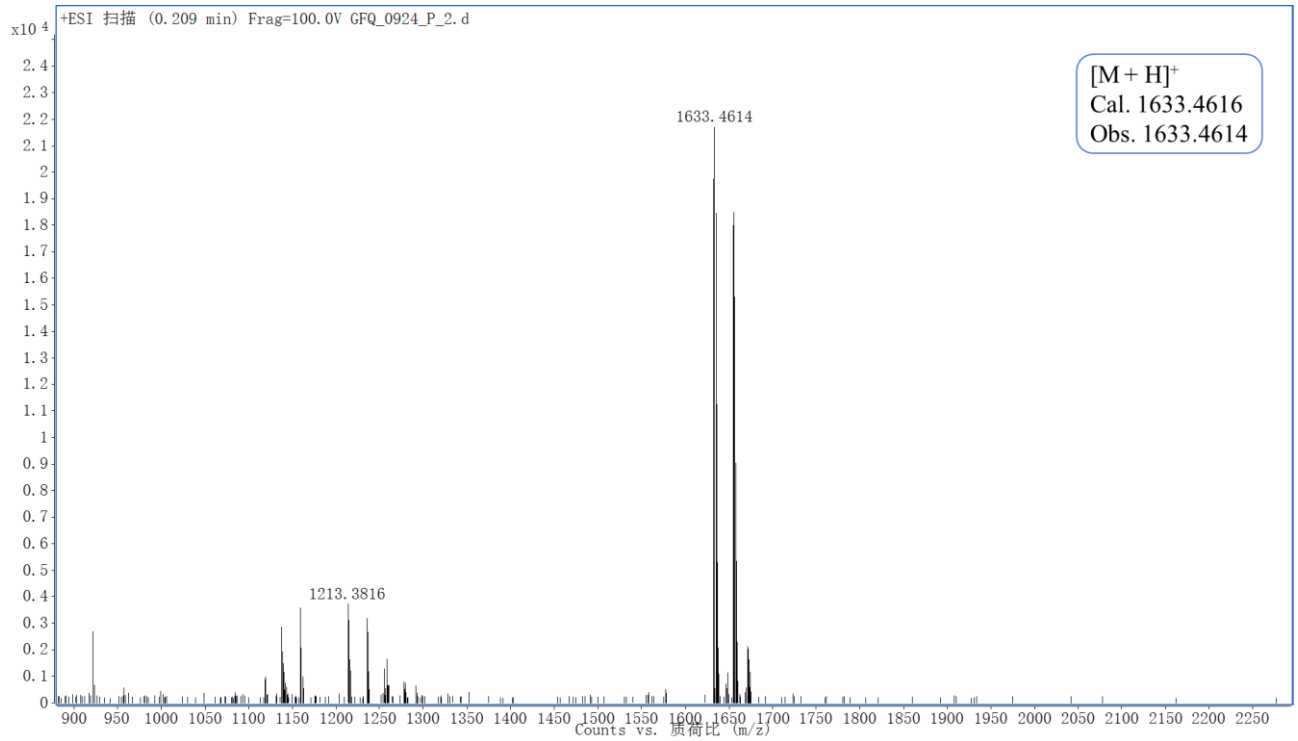


Figure S99. ESI-MS of **B6**.

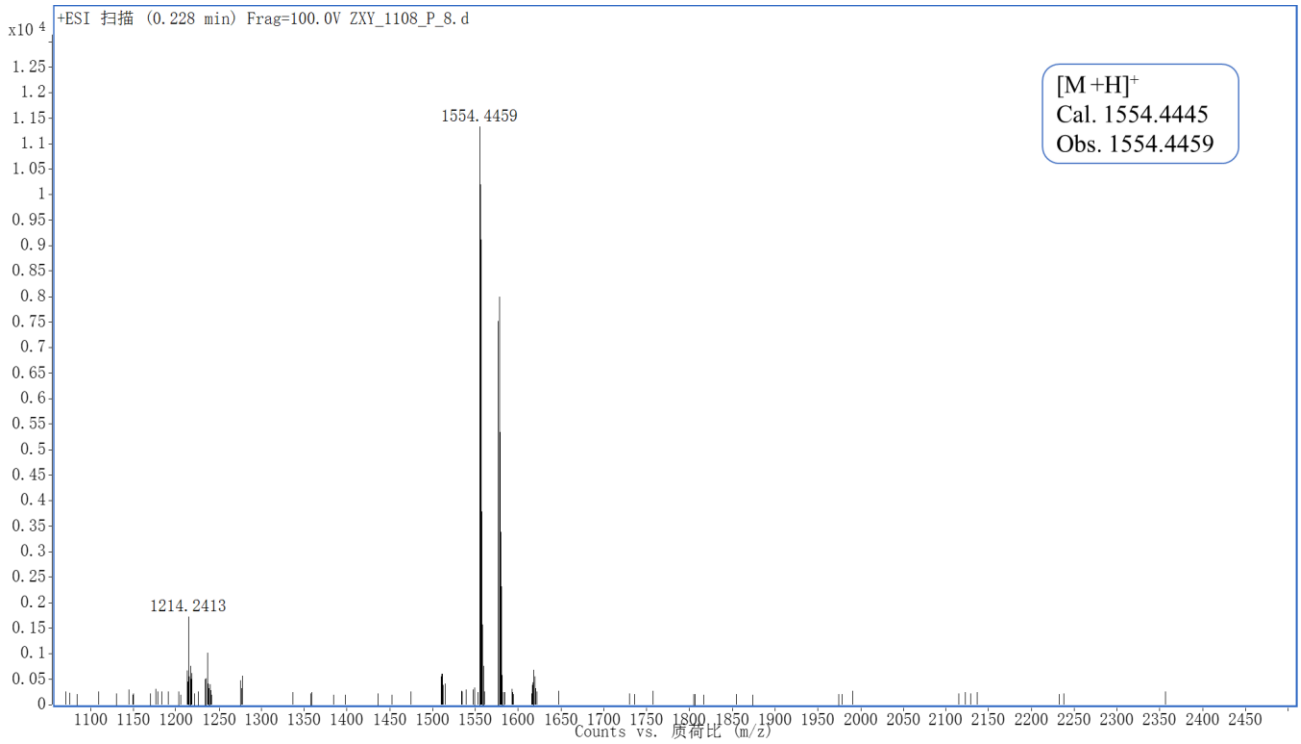


Figure S100. ESI-MS of **1**.

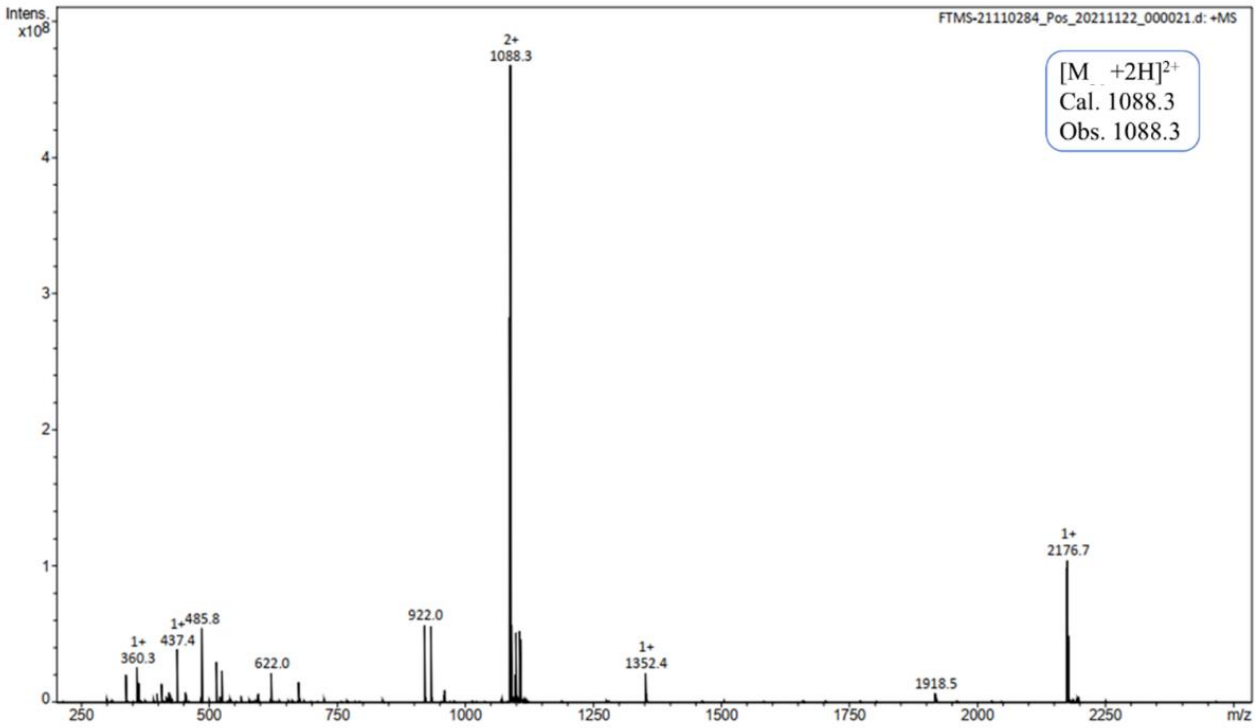


Figure S101. FTMS of **2**.

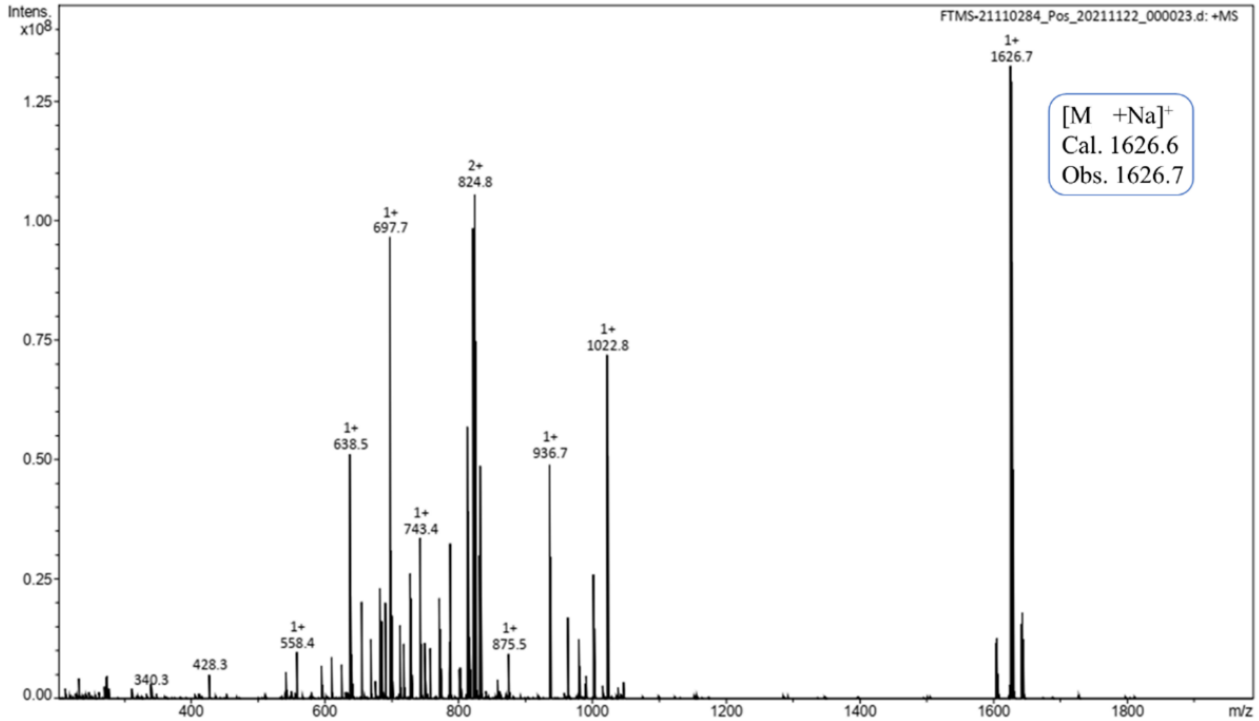


Figure S102. FTMS of **3**.

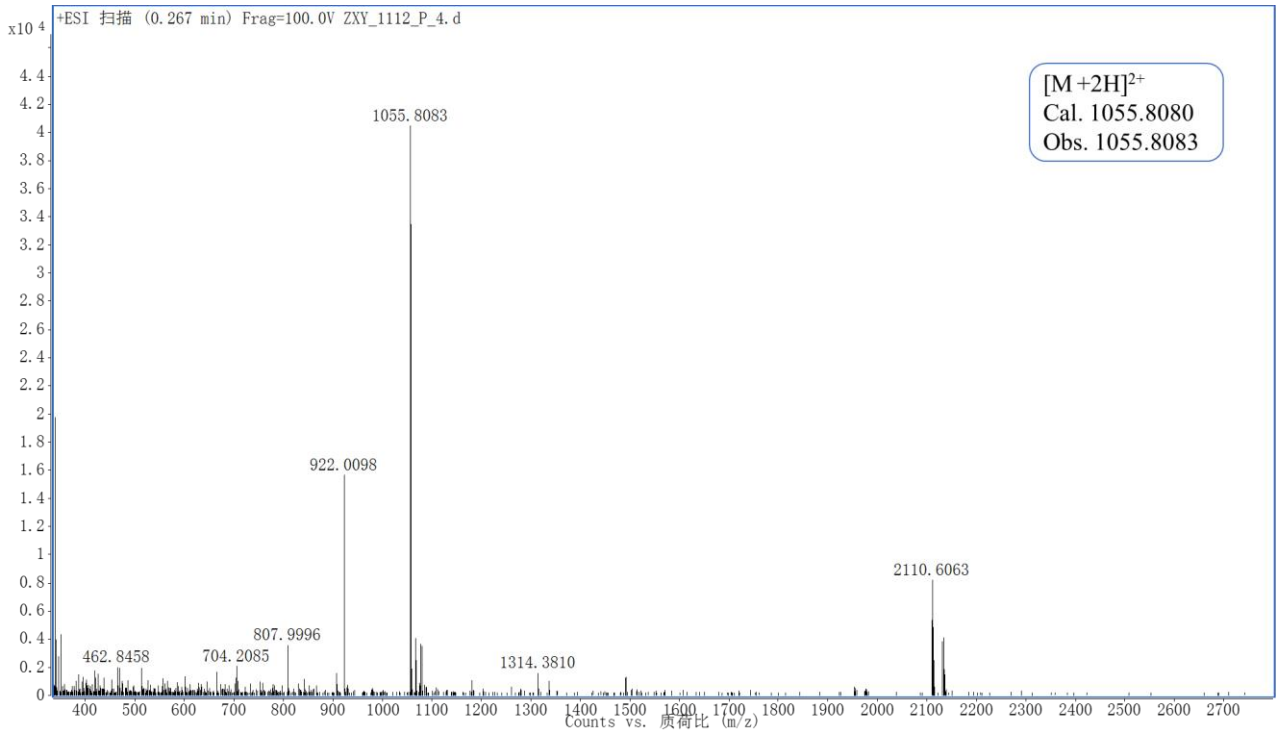


Figure S103. ESI-MS of **4**.

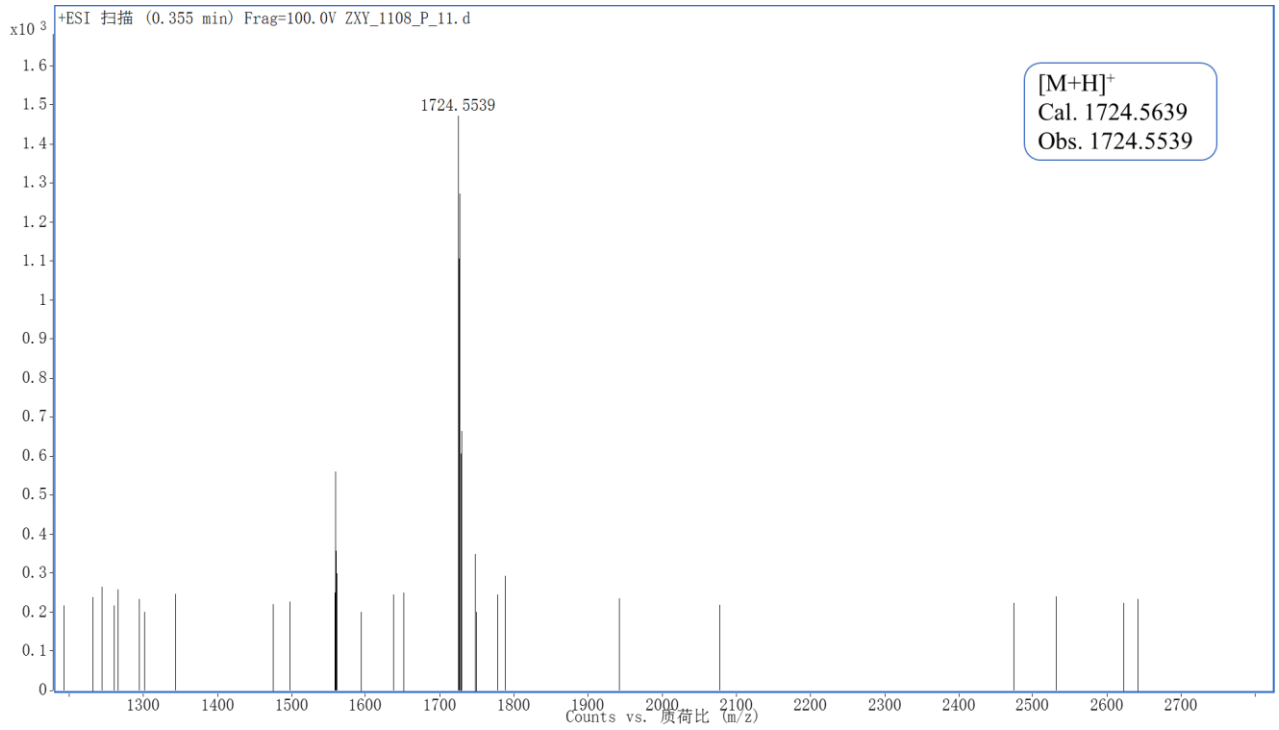


Figure S104. ESI-MS of **5**.

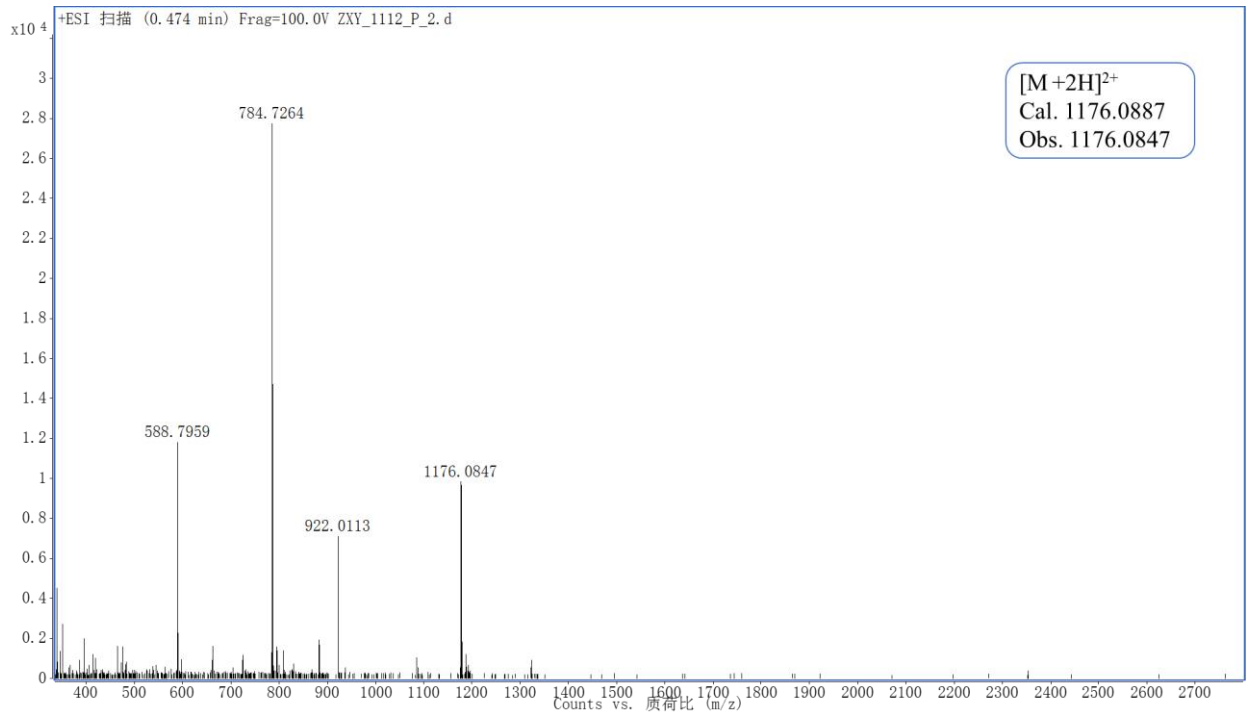


Figure S105. ESI-MS of **6**.

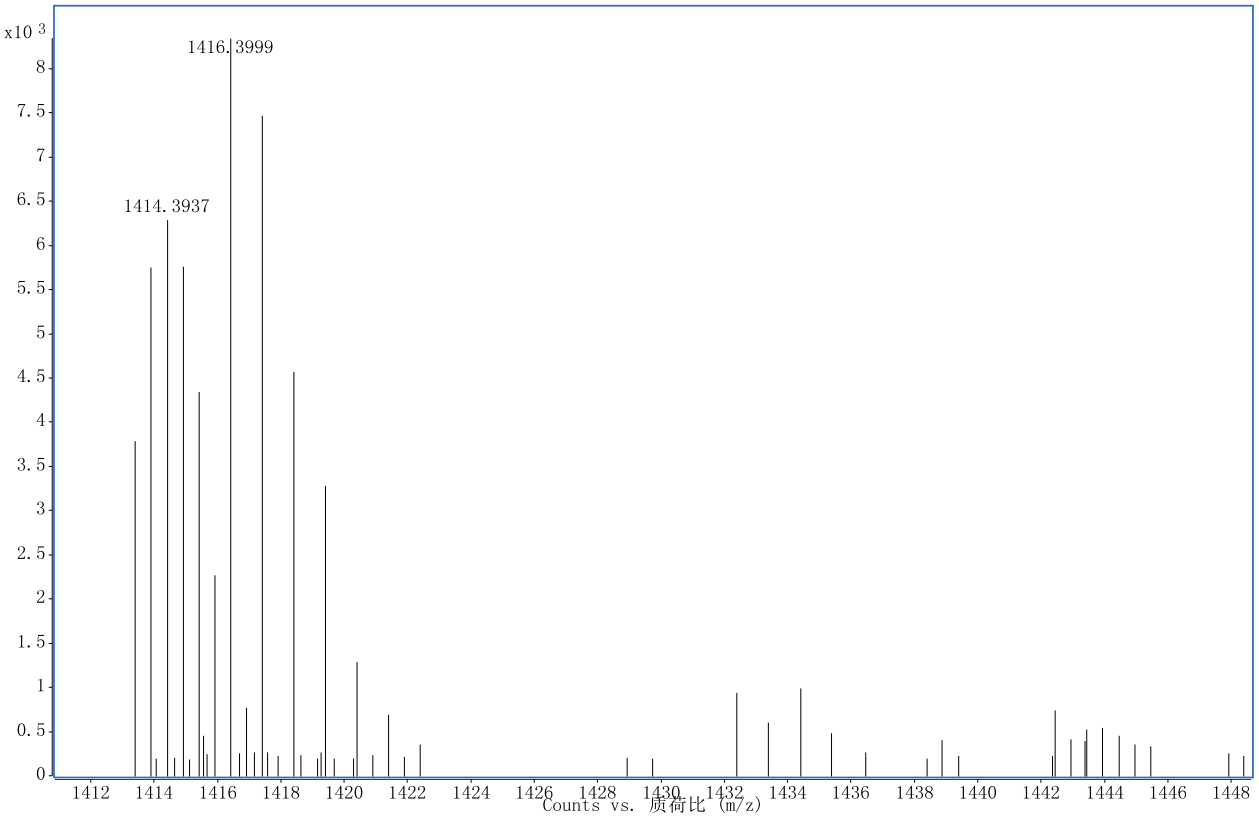


Figure S106. ESI-MS of **7**.

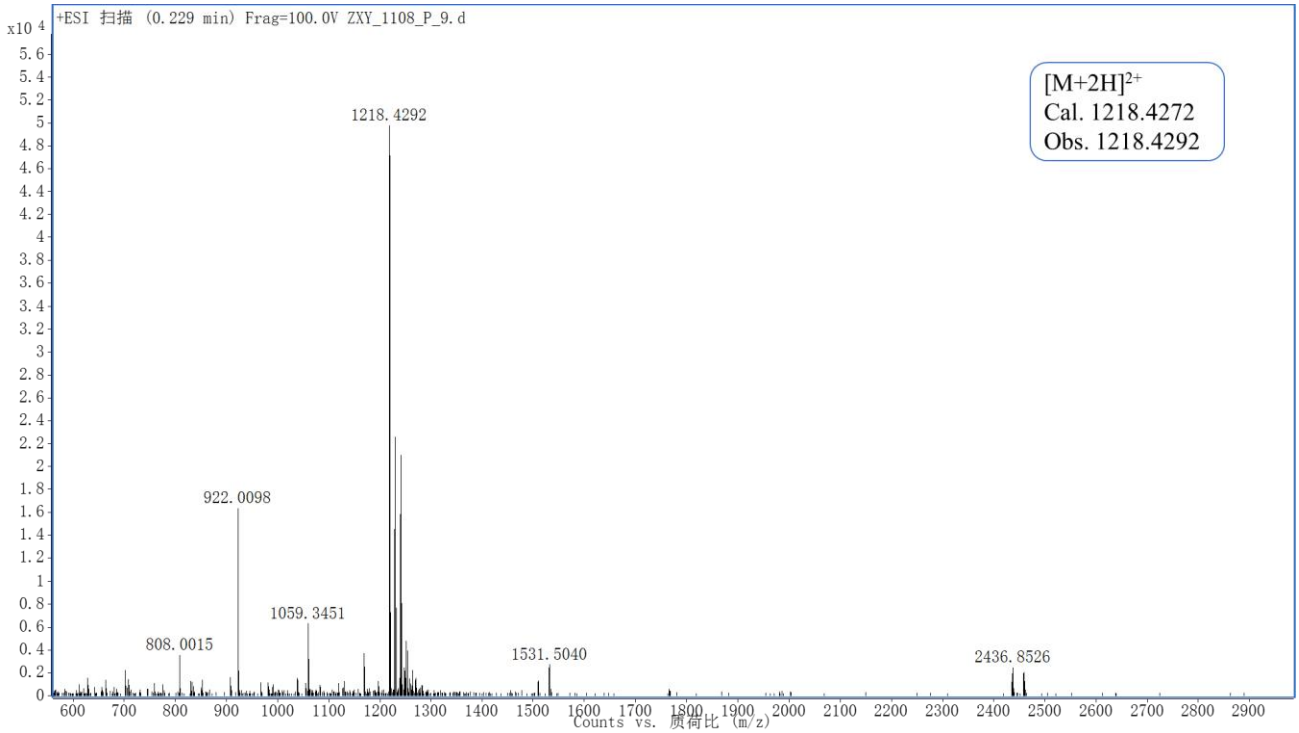


Figure S107. ESI-MS of **8**.

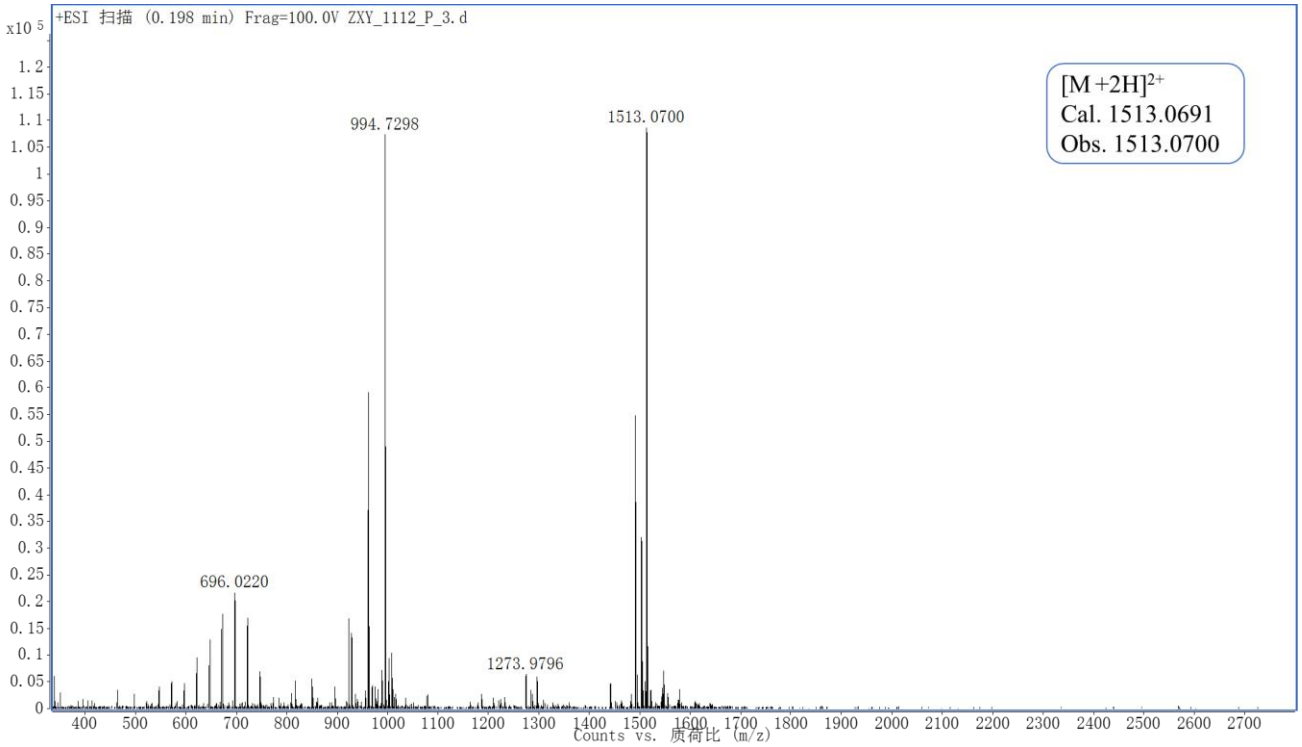


Figure S108. ESI-MS of **9**.

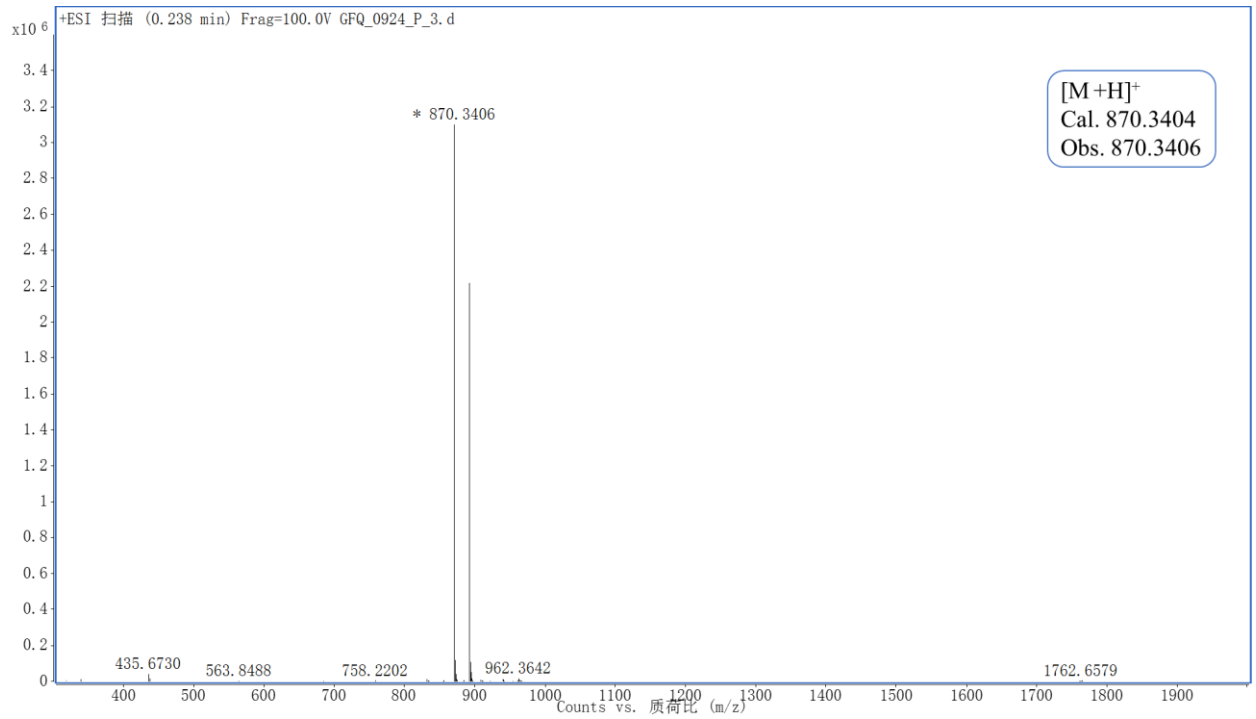


Figure S109. ESI-MS of **10**.

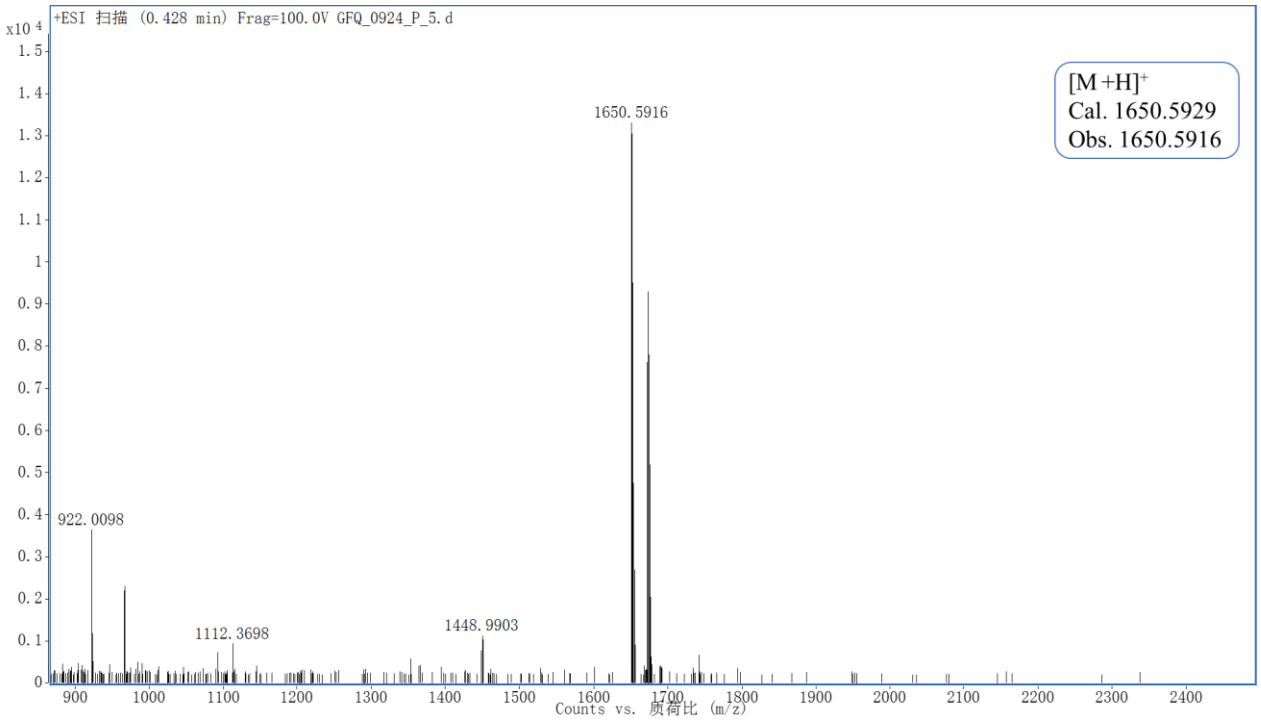


Figure S110. ESI-MS of **11**.

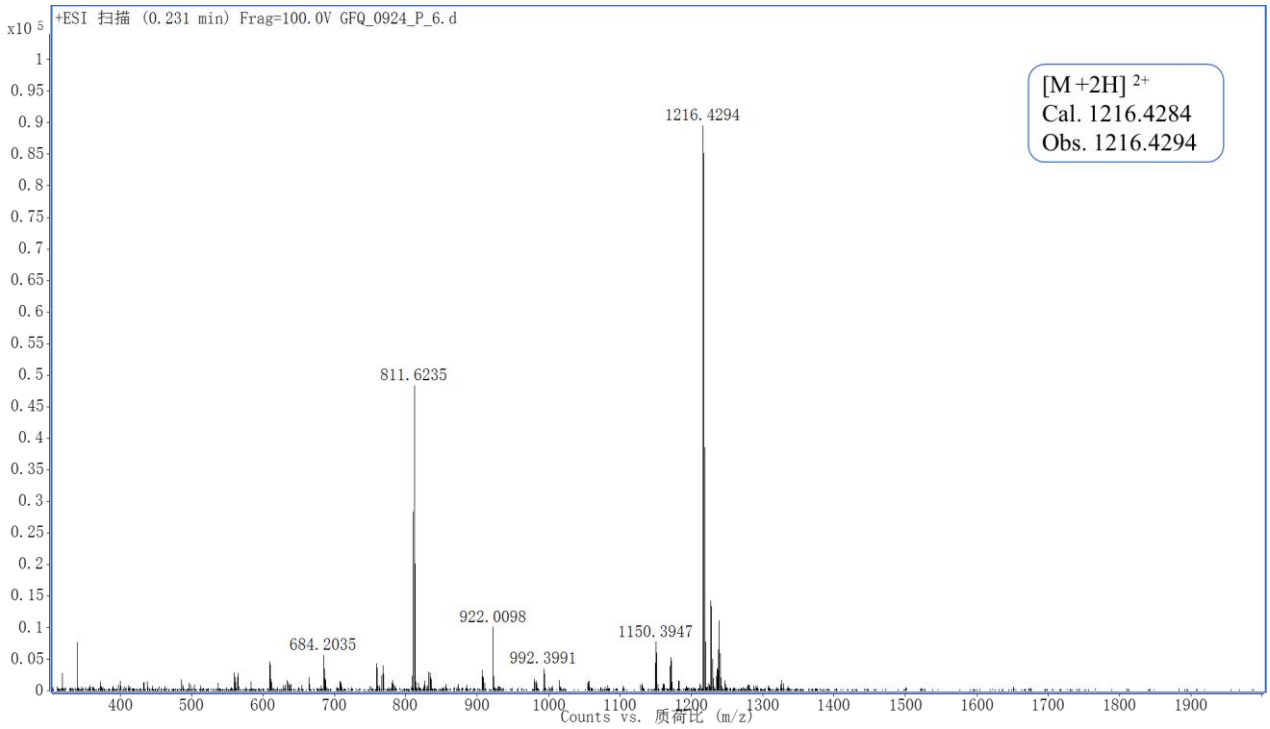


Figure S111. ESI-MS of **12**.

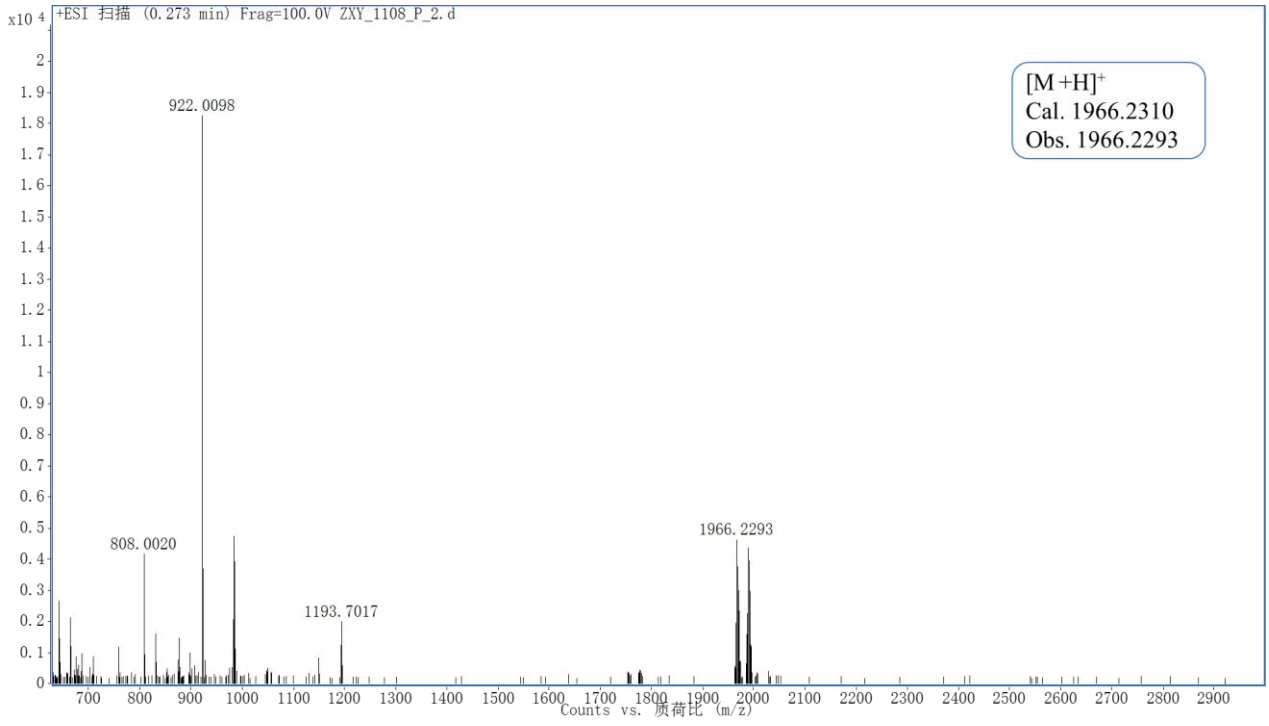


Figure S112. ESI-MS of **13**.

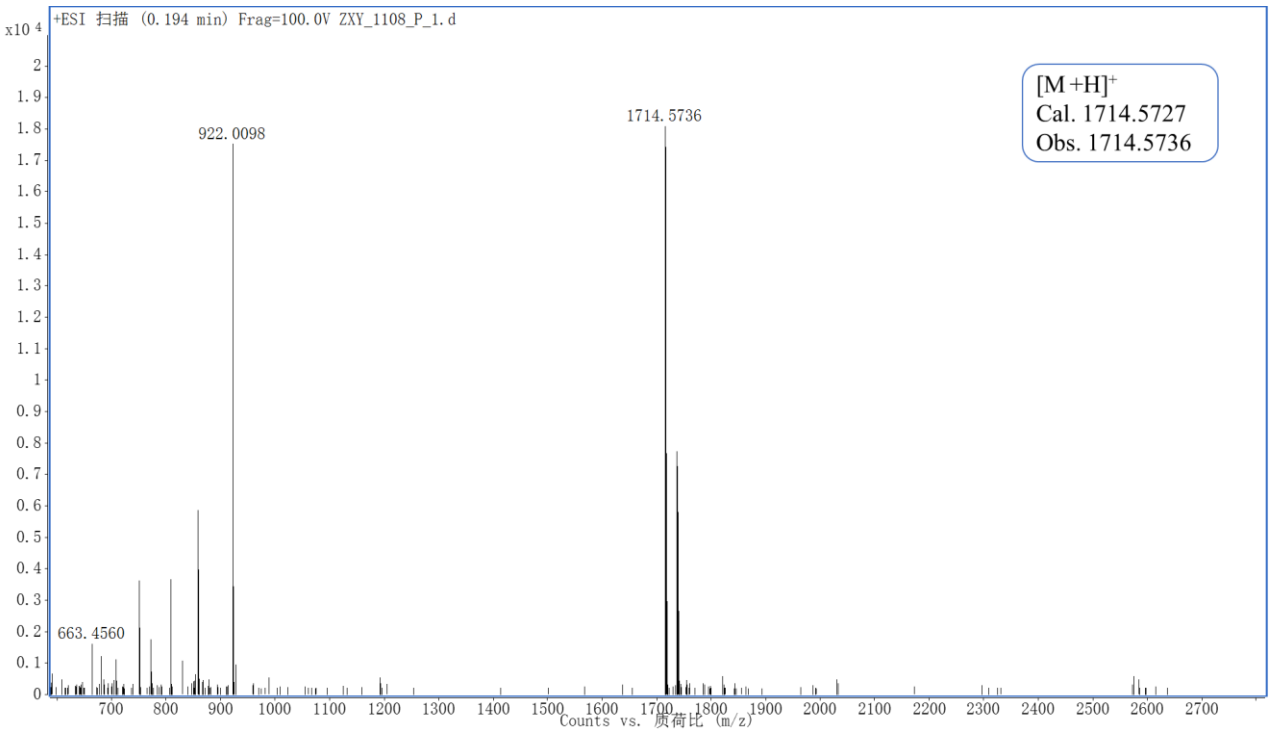


Figure S113. ESI-MS of **14**.

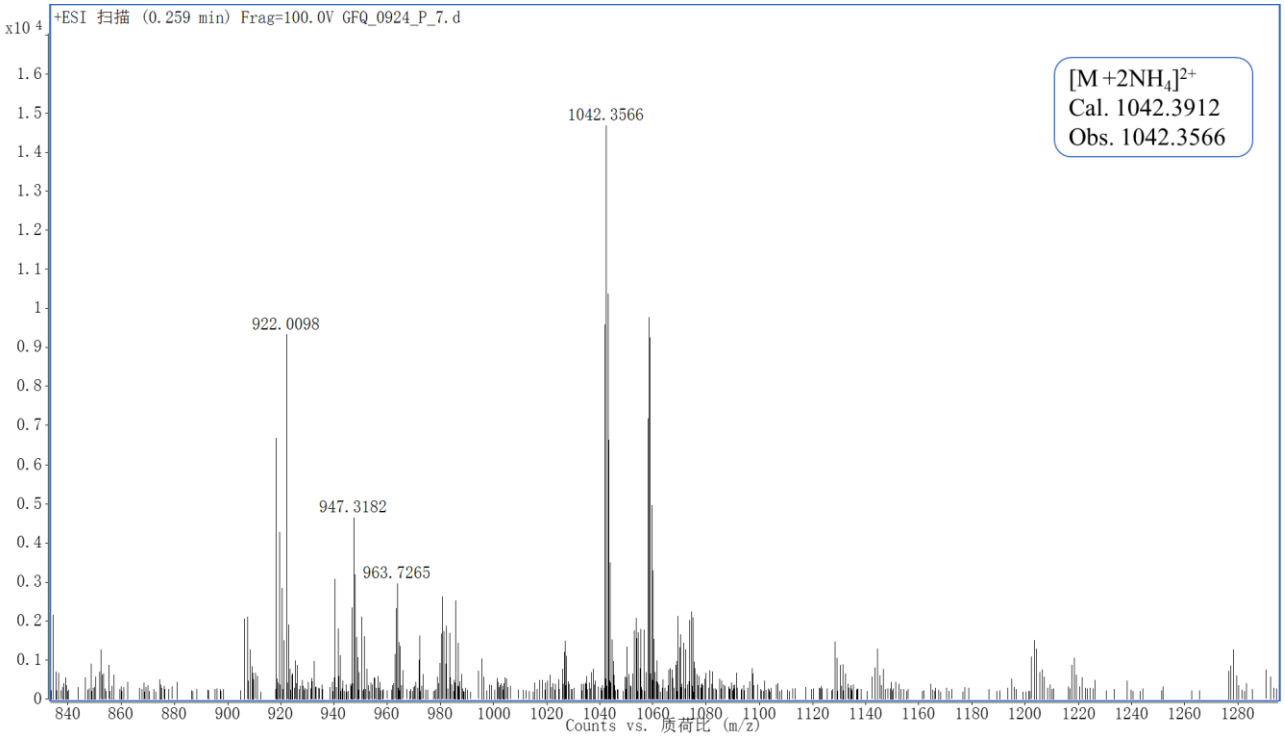


Figure S114. ESI-MS of **15**.

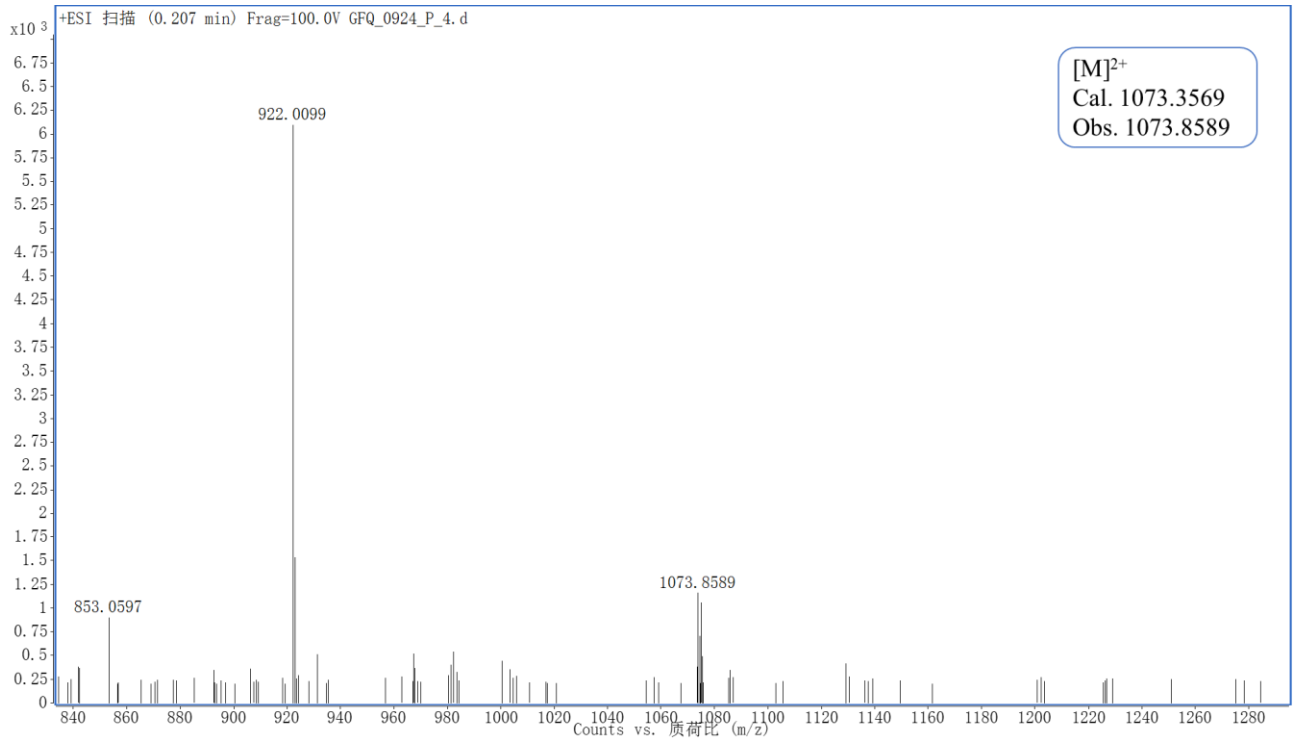


Figure S115. ESI-MS of **16**.

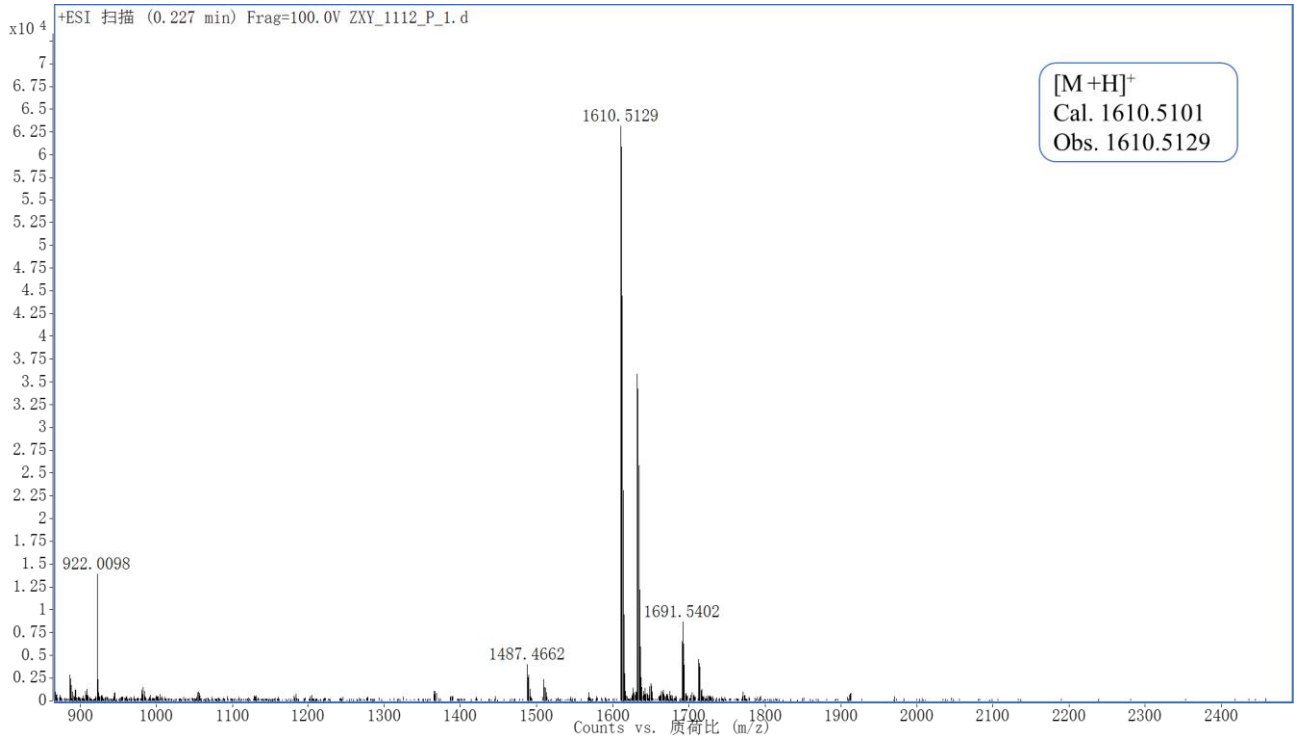


Figure S116. ESI-MS of **17**.

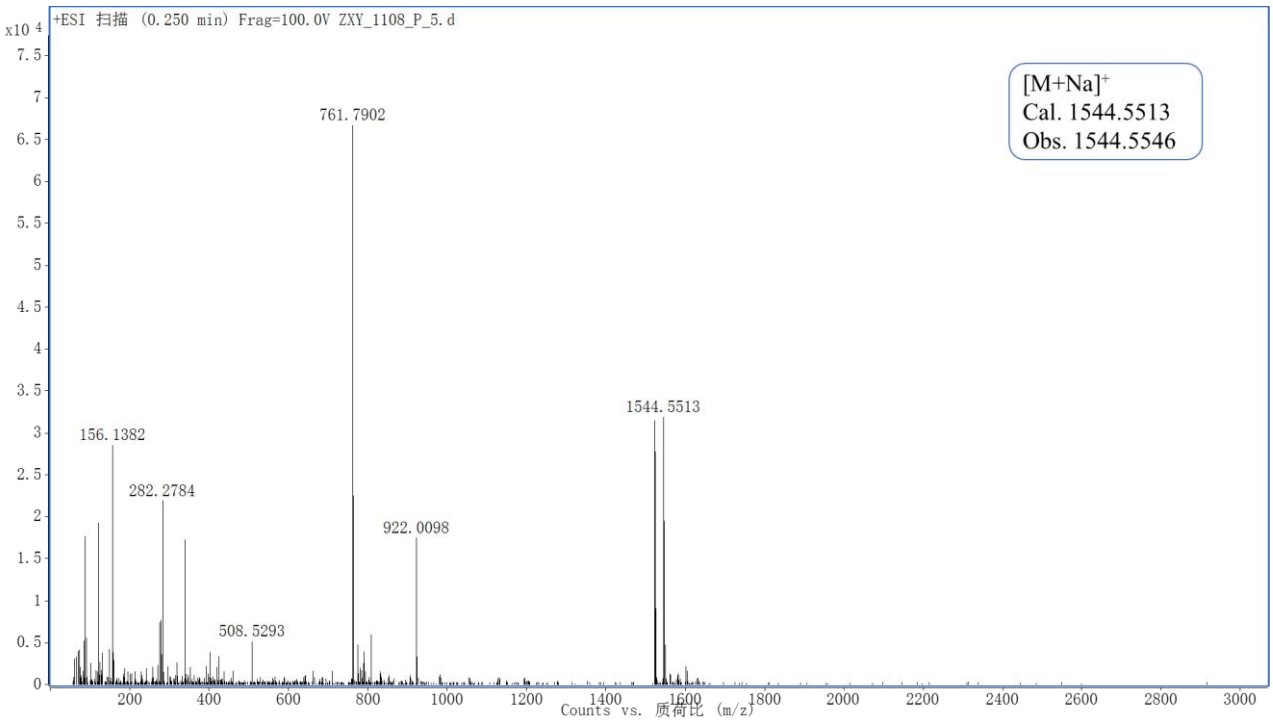


Figure S117. ESI-MS of **18**.

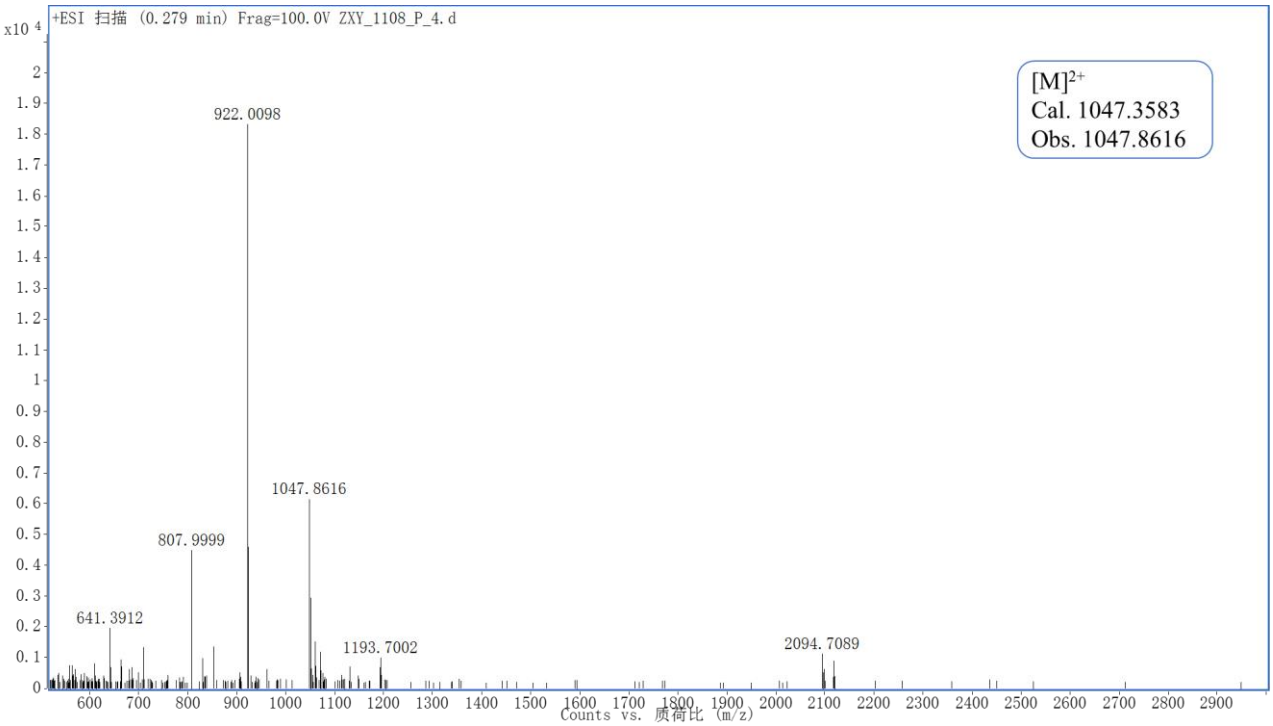


Figure S118. ESI-MS of **19.**

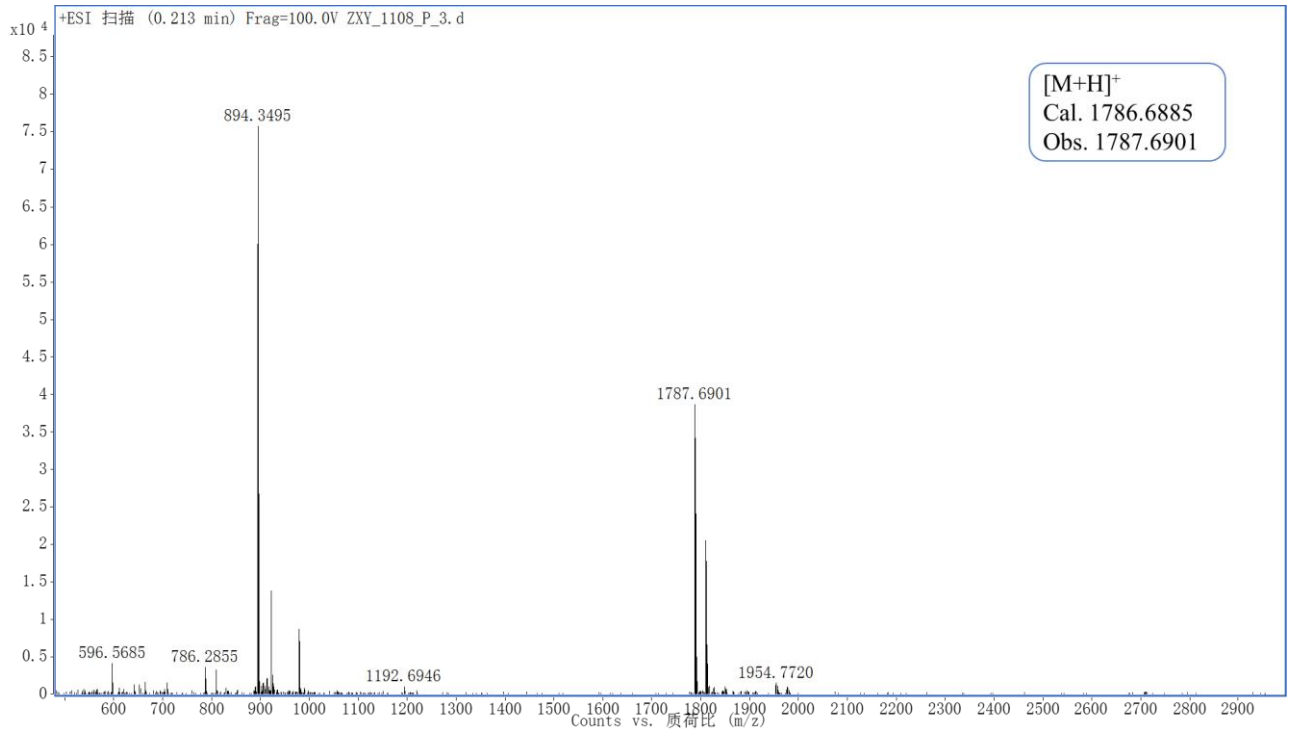


Figure S119. ESI-MS of **20**.

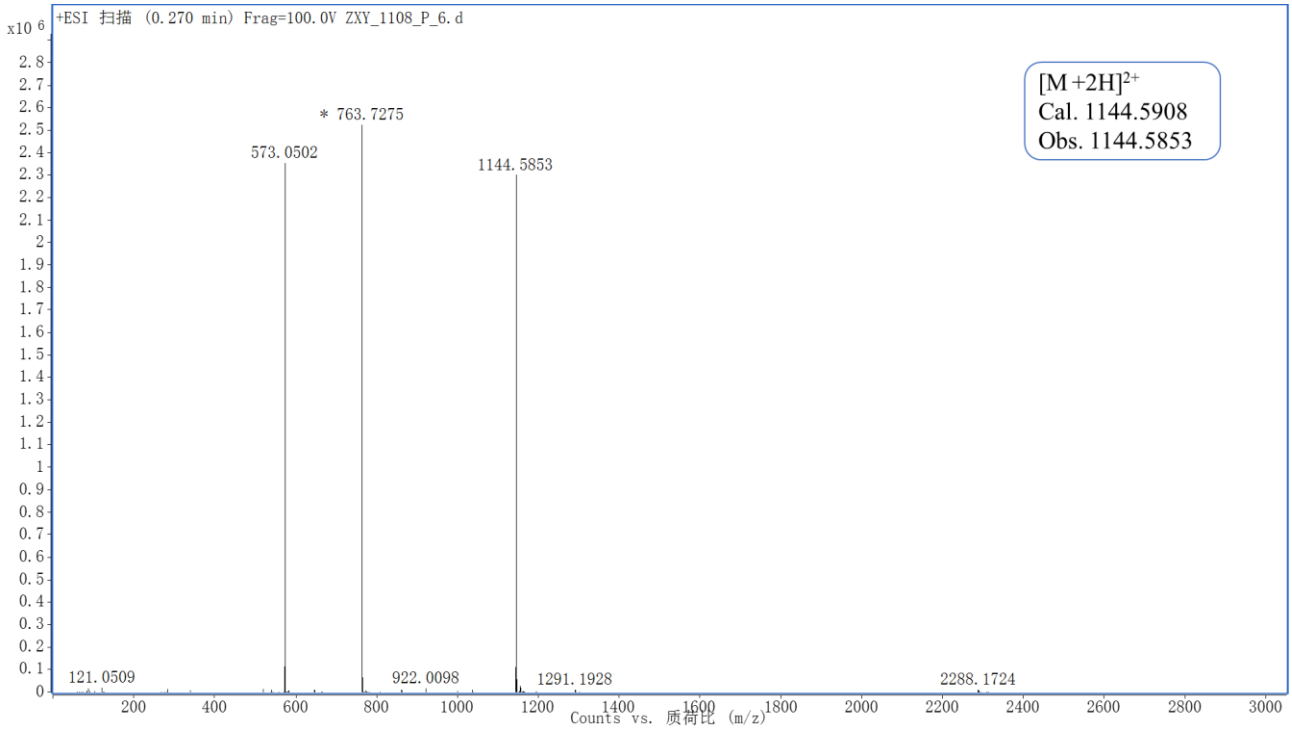


Figure S120. ESI-MS of **21**.

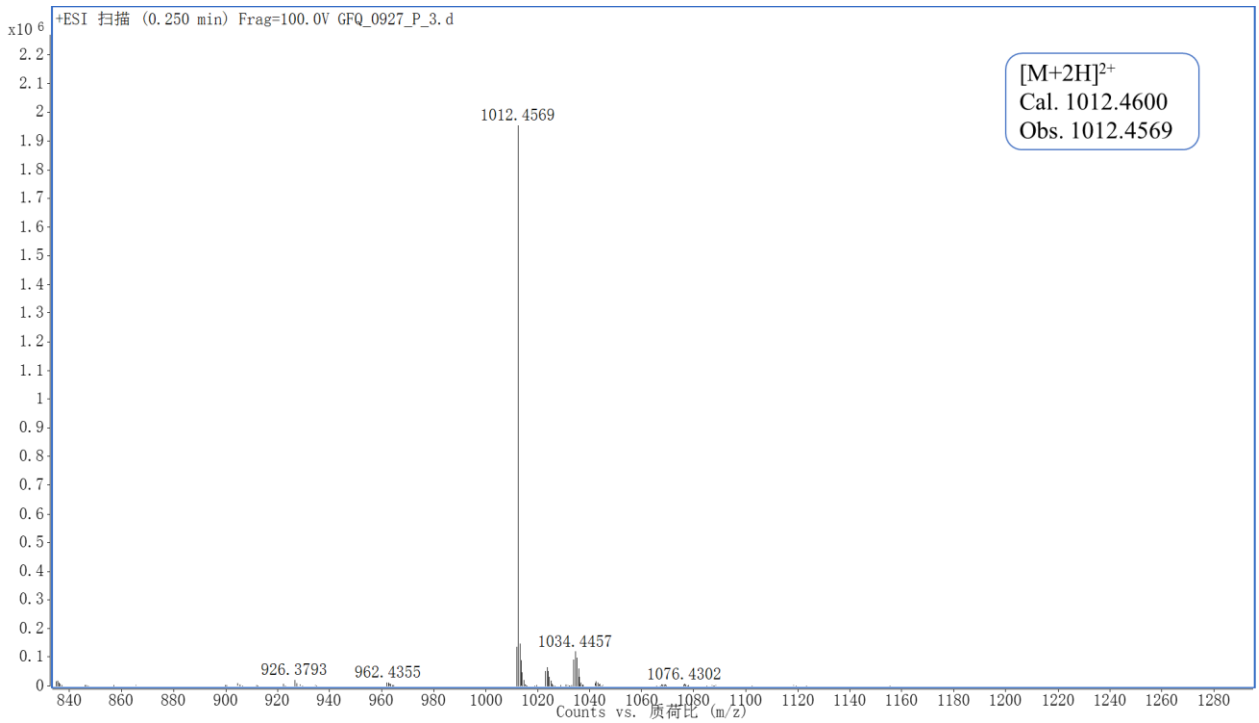


Figure S121. ESI-MS of **22**.

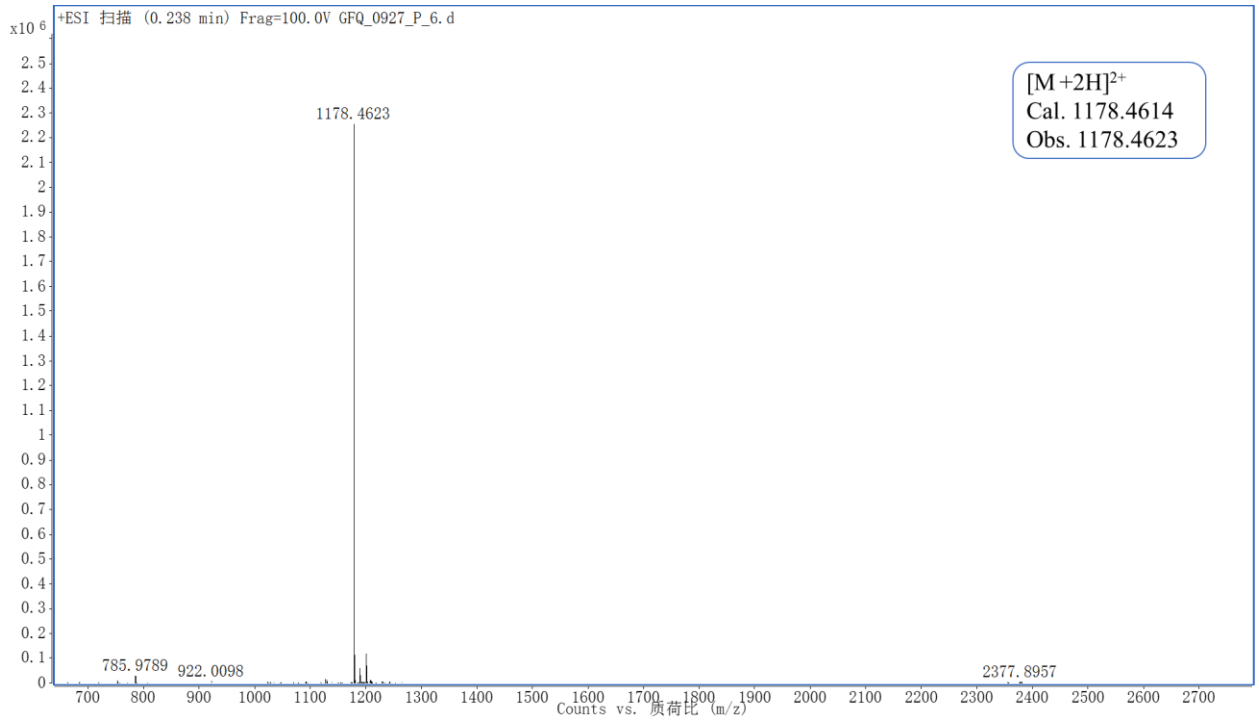


Figure S122. ESI-MS of **23**.

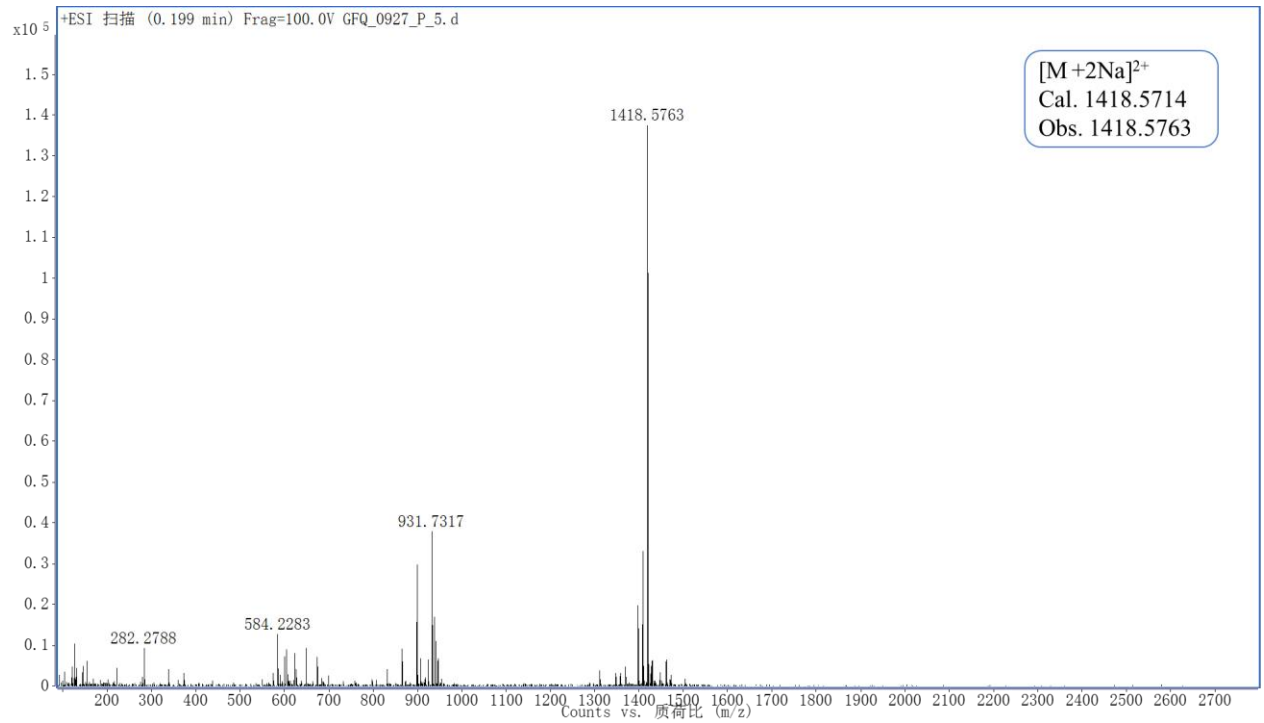


Figure S123. ESI-MS of **24**.

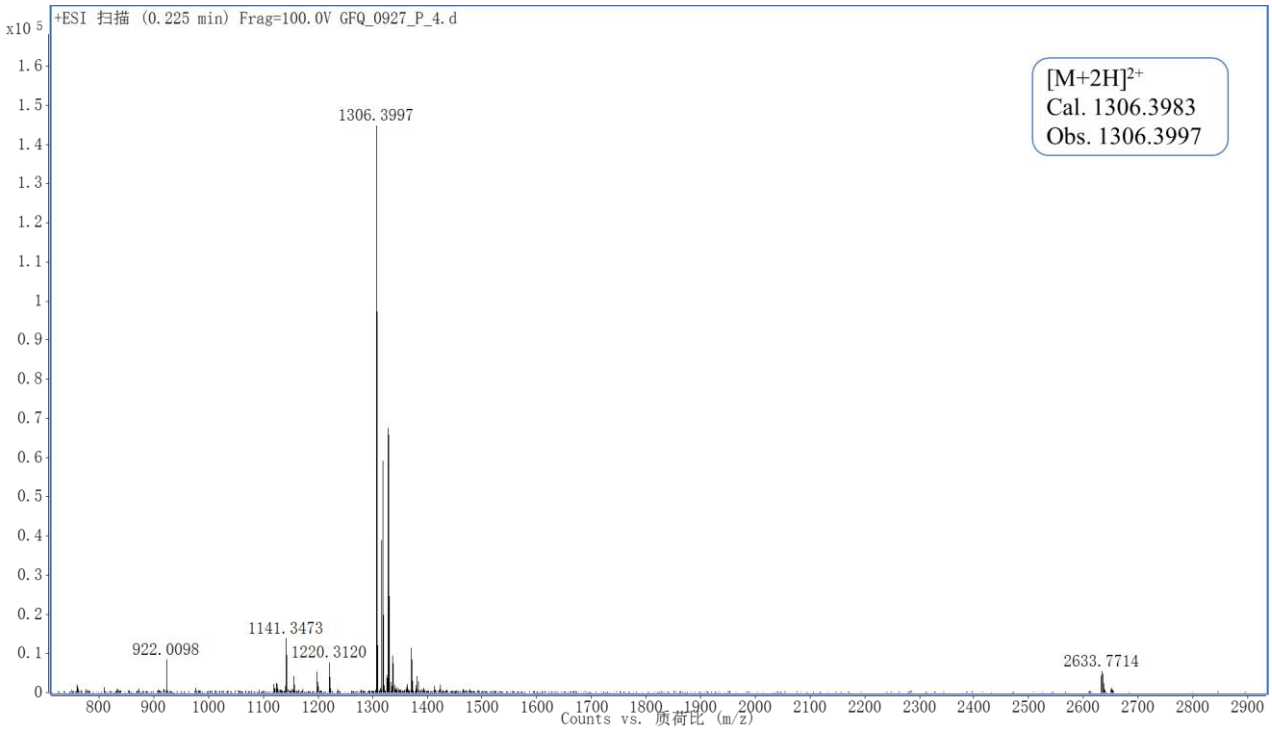


Figure S124. ESI-MS of **25**.

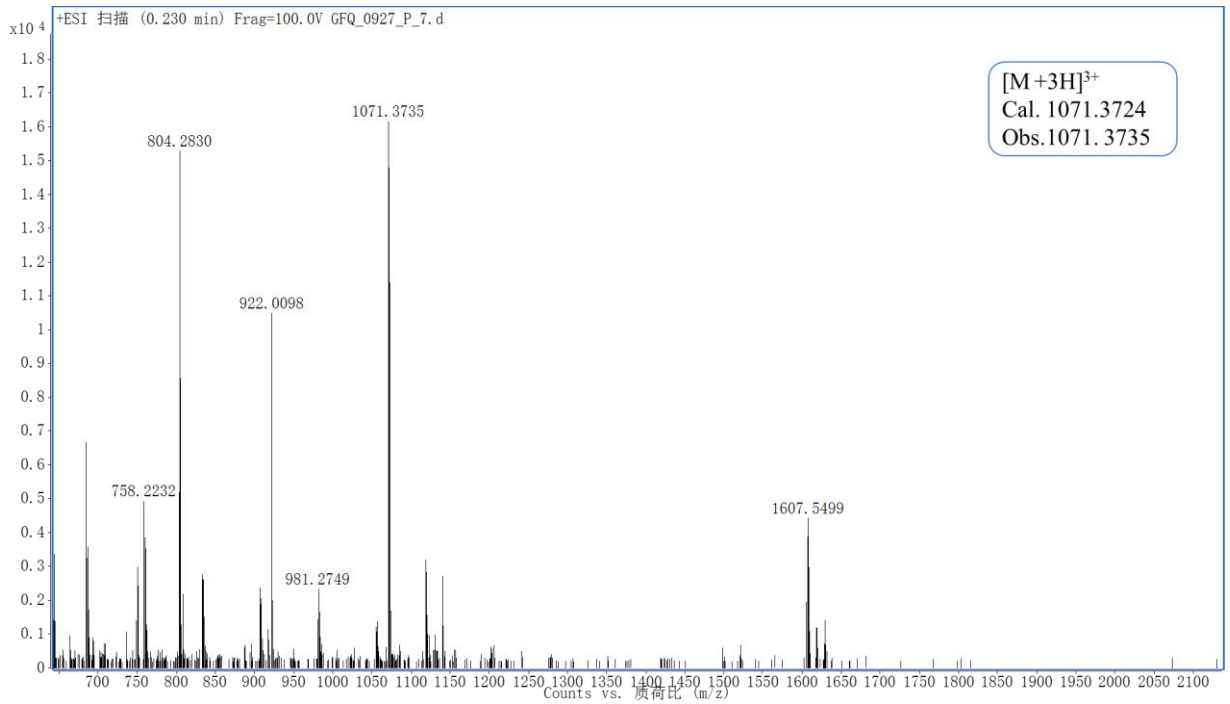


Figure S125. ESI-MS of **26**.

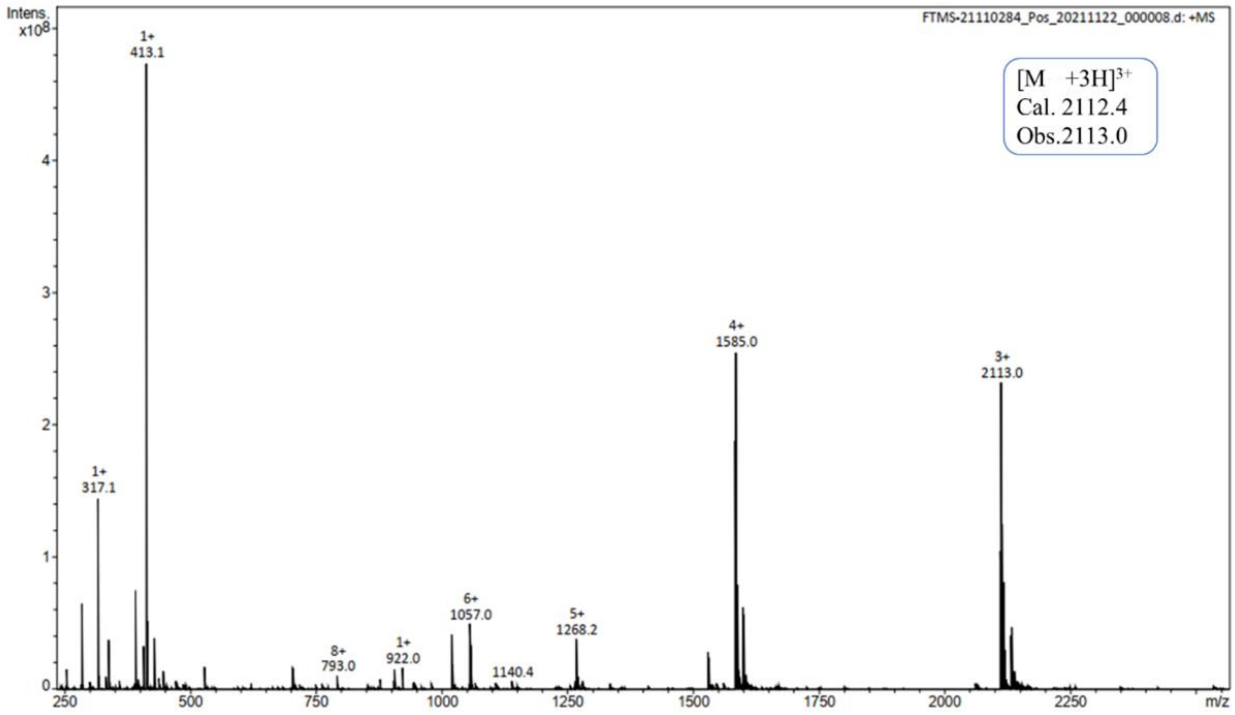


Figure S126. FTMS of **27**.

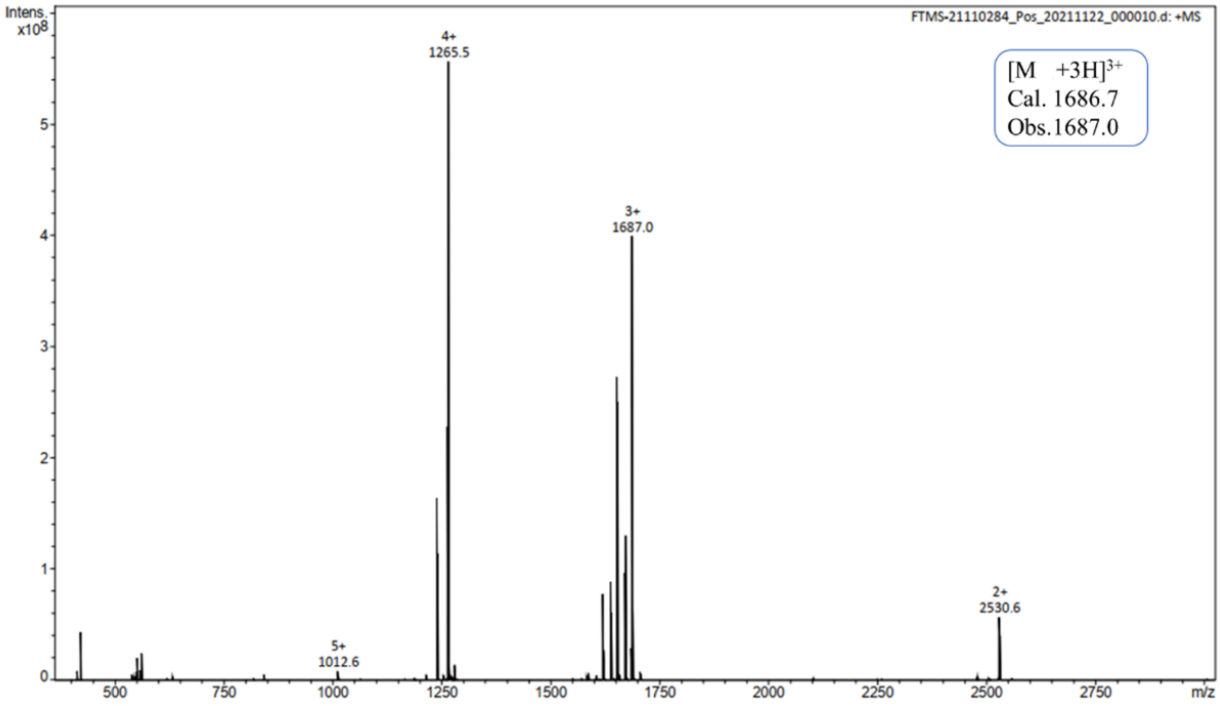


Figure S127. FTMS of **28**.

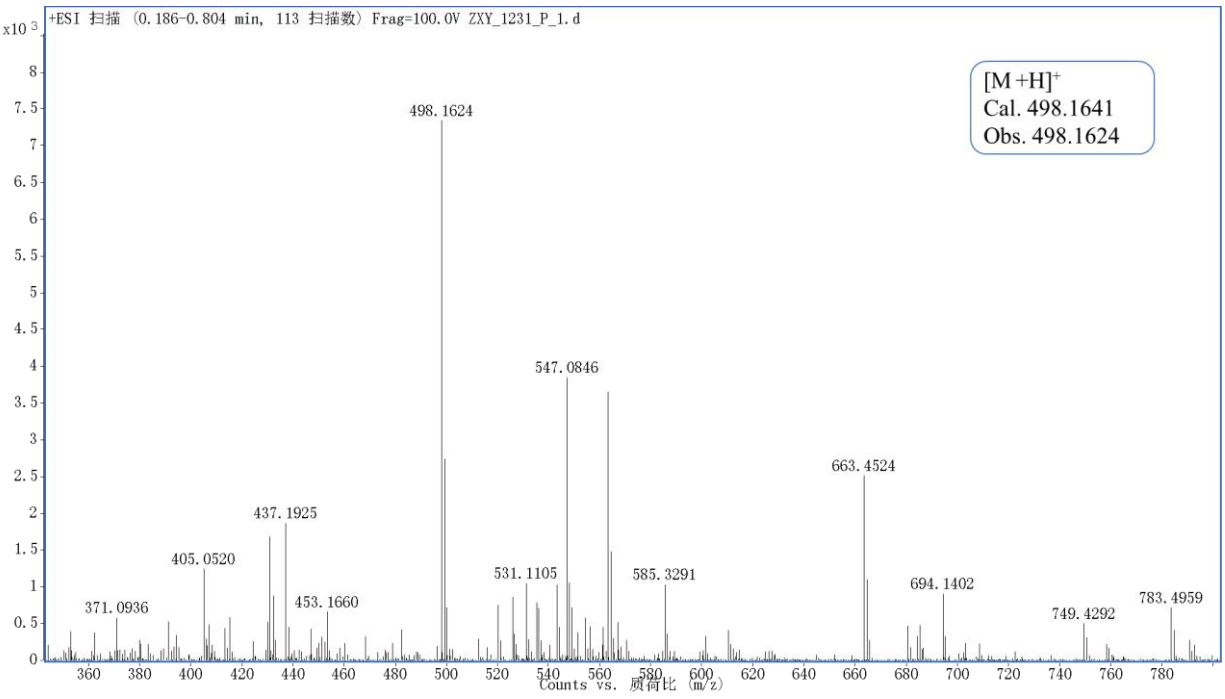


Figure S128. ESI-MS of **29**.

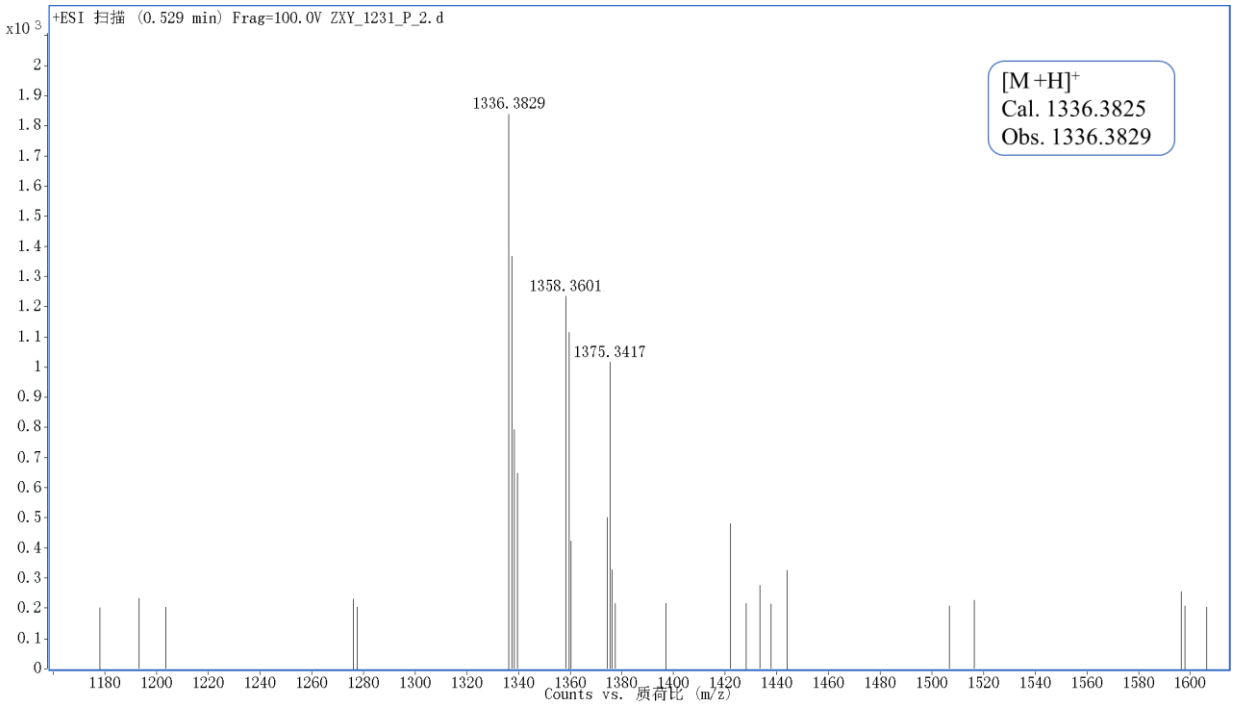


Figure S129. ESI-MS of **30**.

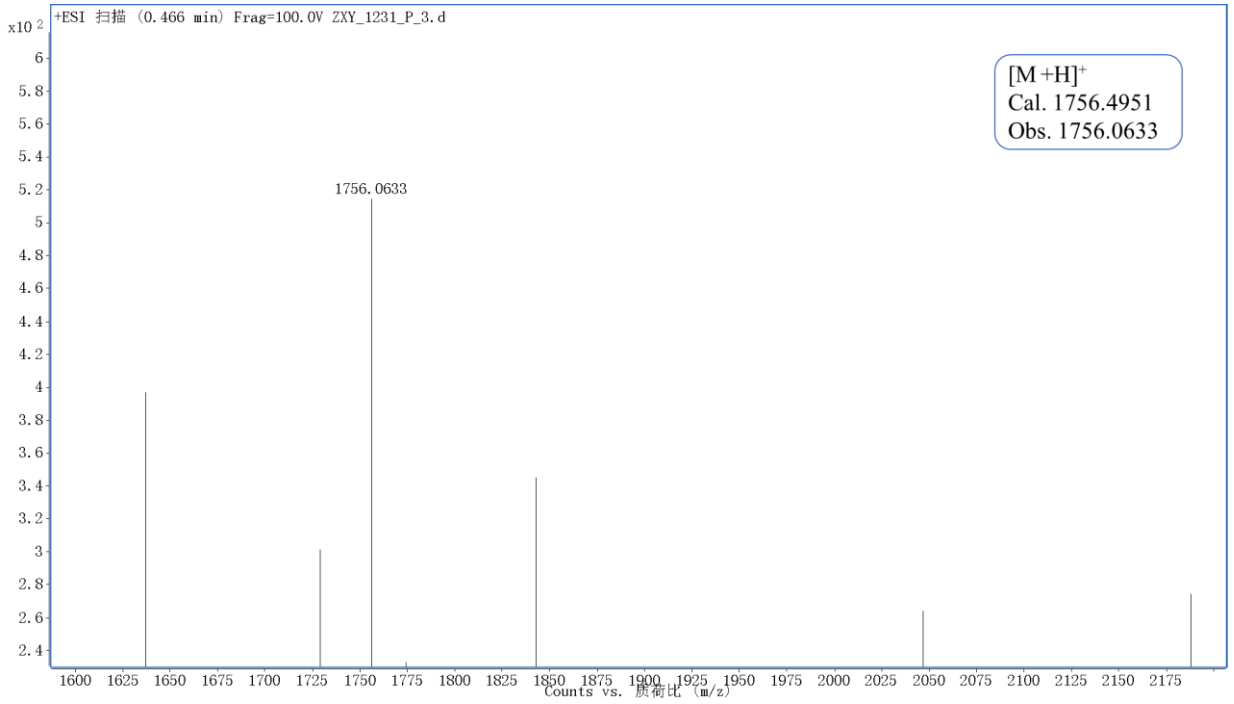


Figure S130. ESI-MS of **31**.

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