Supplementary Information

Construction of sequence-defined polytriazoles using IrAAC and CuAAC reactions

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I. General information

All air or moisture sensitive reactions were conducted in oven-dried glassware under nitrogen atmosphere using dry solvents. Flash column chromatography was performed over silica gel (200-300 mesh) purchased from Qingdao Puke Co., China. Alkyne 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, ^{13}C, and 2D NMR spectrum 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, ^{13}C NMR: $CDCl_3$ at 77.0 ppm).

MS. ESI-MS was measured on a Waters Xevo G2 Qtof mass spectrometer. MALDI-TOF-MS was measured on a AB Sciex 5800 MALDI–TOF/TOF mass spectrometer using α-cyano-4-hydroxycinnamic acid (CHCA) or 1,5-dihydroxybenzoic acid (DHB) as the matrix. FTIRC-MS was measured on a Bruker Solarix XR FIICR mass spectrometer.

MS/MS. The MS/MS experiments for the resulting sequence-defined polytriazole 6b was conducted using nano-electrospray ionization on a AB Sciex 5800 MALDI–TOF/TOF with an Advion TriVersa NanoMate as the nano-electrospray ionization source. The sample was dissolved in MeOH containing 10 mM NH_4OAc. Optimization of the signal intensity was performed for the doubly charged ammonium adduct. MS/MS spectra was acquired using collision-induced dissociation fragmentation.

SEC. All polymer 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.

II. Synthesis of thioalkyne substrates

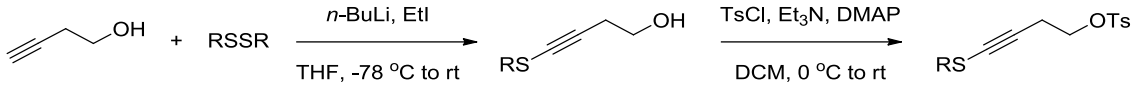
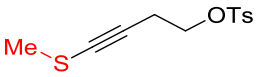


Figure S1. Synthesis of thioalkynes **S1-S6**.

General procedure for the synthesis of thioalkynes S1-S6. At -78 °C, to solution of 3-butyn-1-ol (1.0 eq.) in THF (0.25 M) under N_2 atmosphere was slowly added *n*-BuLi (2.0 eq.). The reaction mixture was stirred at the same temperature for 1 h before disulfide (1.0 eq.) and ethyl iodide (EtI, 1.0 eq.) were added. Then the reaction mixture was allowed to warm to room temperature and stirred for 2 h before a saturated aqueous NH_4Cl solution was added. The aqueous phase was separated and extracted with ethyl acetate 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 involving hydroxyl group. Without purification, the residue was dissolved in DCM (0.5 M) with subsequent addition of Et_3N (2.0 eq.) and 4-dimethylaminopyridine (DMAP, 1 mol %). Then the solution of 4-toluenesulfonyl chloride (TsCl, 1.5 eq.) in DCM (1.0 M) was slowly added into the previous mixture. The reaction mixture was stirred at room temperature until the reaction completed (confirmed by TLC), and then washed with brine (three times), dried over Na_2SO_4, filtered, and evaporated under vacuum to give the residue of thioalkyne involving OTs group, which was then purified by silica gel flash column chromatography to give the pure desired product.



S1

4-(Methylthio)but-3-yn-1-yl 4-methylbenzenesulfonate (S1).

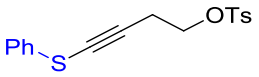
75% overall yield.

Rf = 0.2 (PE/EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 2 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 4.06 (t, *J* = 8.0 Hz, 2 H), 2.64 (t, *J* = 8.0 Hz, 2 H), 2.44 (s, 3 H), 2.30 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 132.8, 129.8, 127.9, 86.8, 73.3, 67.6, 21.6, 20.9, 18.9.

HRMS *m/z* (ESI) calcd. for $C_{12}H_{15}O_3S_2$ $(M+H)^+$ 271.0463, found 271.0462.



S2

4-(Phenylthio)but-3-yn-1-yl 4-methylbenzenesulfonate (S2).

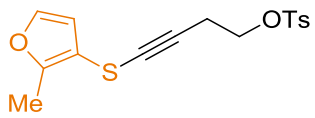
80% overall yield.

Rf = 0.2 (PE/EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2 H), 7.22-7.08 (m, 5 H), 7.05 (t, *J* = 8.0 Hz, 2 H), 4.01 (t, *J* = 8.0 Hz, 2 H), 2.66 (t, *J* = 8.0 Hz, 2 H), 2.24 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ144.8, 132.3, 129.7, 129.0, 127.7, 126.3, 125.8, 93.6, 93.5, 68.0, 67.4, 21.4, 21.0.

HRMS *m/z* (ESI) calcd. for $C_{17}H_{17}O_3S_2$ $(M+H)^+$ 333.0620, found 333.0622.



S3

4-((2-Methylfuran-3-yl)thio)but-3-yn-1-yl 4-methylbenzenesulfonate (S3).

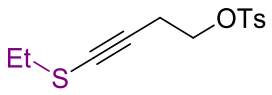
74% overall yield.

Rf = 0.2 (PE/EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2 H), 7.24 (d, *J* = 8.0 Hz, 2 H), 7.17 (d, *J* = 4.0 Hz ,1 H), 6.28 (d, *J* = 4.0 Hz, 1 H), 3.96 (t, *J* = 8.0 Hz, 2 H), 2.54 (t, *J* = 8.0 Hz, 2 H), 2.34 (s, 3 H), 2.21 (s, 3 H).

^{13}C NMR (100 MHz, CDCl3) δ 153.6, 144.9, 140.9, 132.8, 129.9, 127.9, 113.5, 106.9, 86.0, 70.6, 67.4, 21.6, 20.8, 11.8.

HRMS *m/z* (ESI) calcd. for $C_{16}H_{17}O_4S_2$ $(M+H)^+$ 337.0569, found 337.0661.



S4

4-(Ethylthio)but-3-yn-1-yl 4-methylbenzenesulfonate (S4).

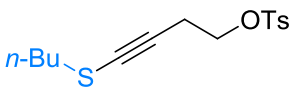
69% overall yield.

Rf = 0.2 (PE/EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 4.07 (t, *J* = 8.0 Hz, 2 H), 2.69-2.60 (m, 4 H), 2.44 (s, 3 H), 1.32 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 132.8, 129.8, 127.9, 88.2, 71.6, 67.7, 29.4, 21.6, 21.0, 14.6.

HRMS *m/z* (ESI) calcd. for $C_{13}H_{17}O_3S_2$ $(M+H)^+$ 285.0620, found 285.0639.



S5

4-(Butylthio)but-3-yn-1-yl 4-methylbenzenesulfonate (S5).

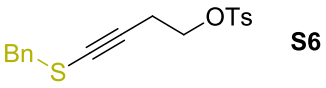
68% overall yield.

Rf = 0.2 (PE/EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 2 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 4.07 (t, *J* = 8.0 Hz, 2 H), 2.67 (t, *J* = 8.0 Hz, 2 H), 2.64 (t, *J* = 8.0 Hz, 2 H), 2.45 (s, 3 H), 1.68-1.62 (m, 2 H), 1.44-1.38 (m, 2 H), 0.92 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 132.8, 129.9, 127.9, 87.6, 72.1, 67.7, 35.0, 31.2, 21.6, 21.3, 21.0, 13.5.

HRMS *m/z* (ESI) calcd. for $C_{15}H_{21}O_3S_2$ $(M+H)^+$ 313.0933, found 313.0946.



S6

4-(Benzylthio)but-3-yn-1-yl 4-methylbenzenesulfonate (S6).

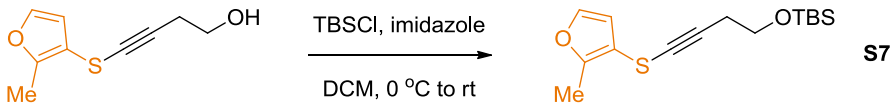
65% overall yield.

Rf = 0.2 (PE/EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 2 H), 7.39-7.25 (m, 7 H), 4.04 (t, *J* = 8.0 Hz, 2 H), 3.89 (s, 2 H), 2.66 (t, *J* = 8.0 Hz, 2 H), 2.48 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 136.5, 132.7, 129.8, 128.9, 128.5, 127.9, 127.6, 89.5, 71.6, 67.5, 39.8, 21.6, 20.9.

HRMS *m/z* (ESI) calcd. for $C_{18}H_{19}O_3S_2$ $(M+H)^+$ 347.0776, found 347.0765.



S7

Figure S2. Synthesis of thioalkyne **S7**.

General procedure for the synthesis of *tert*-Butyldimethyl((4-((2-methylfuran-3-yl)thio)but-3-yn-1-yl)oxy)silane (S7). The crude product of thioalkyne involving hydroxyl group was dissolved in DCM (0.5 M) with subsequent addition of imidazole (1.5 eq.). Then *tert*-butyldimethylsilyl chloride (TBSCl, 1.5 eq.) was slowly added into the previous mixture. The reaction mixture was stirred at room temperature until the reaction completed (confirmed by TLC), and then washed with brine (three times), dried over Na_2SO_4, filtered, and evaporated under vacuum to give the residue of thioalkyne involving OTBS group, which was then purified by silica gel flash column chromatography to give the pure desired product **S7** in 77% overall yield

Rf = 0.2 (PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 4.0 Hz, 1 H), 6.47 (d, *J* = 4.0 Hz, 1 H), 3.73 (t, *J* = 8.0, 2 H), 2.52 (t, *J* = 8.0, 2 H), 2.37 (s, 3 H), 0.91 (s, 9 H), 0.09 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 140.8, 113.7, 107.6, 89.3, 68.6, 61.7, 25.8, 24.3, 18.3, 11.8, -5.3.

HRMS *m/z* (ESI) calcd. for $C_{15}H_{25}O_2SSi$ $(M+H)^+$ 297.1345, found 297.1373.

III. Synthesis of azide substrates

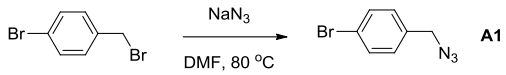


Figure S3. Synthesis of azide **A1**.

General procedure for the synthesis of 1-(azidomethyl)-4-bromobenzene (A1).[2] 1-Bromo-4-(bromomethyl)benzene (1.0 eq.) and NaN_3 (1.5 eq.) were added to DMF. The reaction mixture was then heated to 80 °C for 6 h. The solution was then cooled to room temperature, diluted with ethyl acetate, washed with brine (three times), dried over Na_2SO_4, filtered, and evaporated under vacuum. The crude product was purified by column chromatography on silica gel to afford the related pure product **A1** in 95% yield.

Rf = 0.1 (PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* =8.0 Hz, 2 H), 7.20 (d, *J* =8.0 Hz, 2 H), 4.30 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 134.3, 131.9, 129.8, 122.3, 54.0.

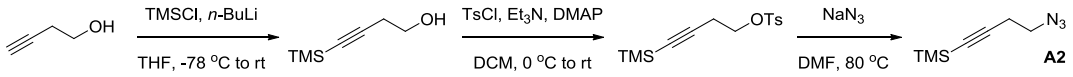


Figure S4. Synthesis of thioalkyne **A2**.

General procedure for the synthesis of (4-azidobut-1-yn-1-yl)trimethylsilane (A2).[3] At -78 °C, to solution of 3-butyn-1-ol (1.0 eq.) in THF (0.25 M) under N_2 atmosphere was slowly added *n*-BuLi (2.0 eq.). The reaction mixture was stirred at the same temperature for 1 h before chlorotrimethylsilane (TMSCl, 2.1 eq.) was added. The reaction mixture was then allowed to warm to room temperature and stirred for 2 h before a saturated aqueous NH_4Cl solution was added. The aqueous phase was separated and extracted with ethyl acetate 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 1-silylalkyne involving hydroxyl group. Without purification, the residue was dissolved in DCM (0.5 M) with subsequent addition of Et_3N (2.0 eq.) and 4-dimethylaminopyridine (DMAP, 1 mol %). Then the solution of 4-toluenesulfonyl chloride (TsCl, 1.5 eq.) in DCM (1.0 M) was slowly added into the previous mixture. The reaction mixture was stirred at room temperature until the reaction completed (confirmed by TLC), and then washed with brine (three times), dried over Na_2SO_4, filtered, and evaporated under vacuum to give the residue of 1-silylalkyne involving OTs group, which was then purified by silica gel flash column chromatography to give the pure desired product. Then the purified building block involving OTs group (1.0 eq.) and NaN_3 (1.5 eq.) were added to DMF (0.5 M). The reaction mixture was then

heated to 80 ^{o}C and stirred until the reaction completed (confirmed by TLC). The solution was then cooled to room temperature, diluted with ethyl acetate, washed with brine (three times), dried over Na_2SO_4, filtered, and evaporated under vacuum. The crude product was purified by column chromatography on silica gel to afford the desired product **A2** in 73% overall yield

Rf = 0.1 (PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.37 (t, *J* = 8.0 Hz, 2 H), 2.52 (t, *J* = 8.0 Hz, 2 H), 0.15 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 102.6, 87.2, 49.7, 21.0, -0.2.

IV. ISG synthesis and characterization of sequence-defined polytriazoles

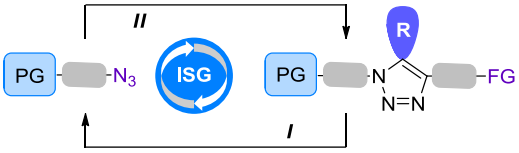
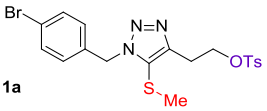


Figure S5. Synthesis of polytriazoles *via* ISG strategy.

General procedure for the two steps of ISG strategy. ***I***. The building unit involving OTs or OTBS group (1.0 eq.) and NaN_3 (1.5 eq.) were added to DMF. The reaction mixture was then heated to 80 ^oC for 3-12 h until the reaction completed, which was confirmed by thin-layer chromatography (TLC). The solution was then cooled to room temperature, diluted with ethyl acetate, washed with brine (three times), dried over Na_2SO_4, filtered, and evaporated under vacuum. The crude product was purified by column chromatography on silica gel to afford the related pure building unit involving azide group.

II. In a glove box, to an oven-dried vial was added the building unit involving azide group (1.0 eq.), the thioalkyne involving OTs or OTBS group (1.05~1.5 eq.), $[Ir(COD)Cl]_2$ (2-4 mol %) and THF (0.5 M). The vial was capped and removed from the glove box. The reaction mixture was stirred at room temperature for 2-6 h until the reaction completed (confirmed by TLC), and then concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to give the desired product.



1a

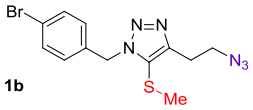
1a (α-Br-**A**-ω-OTs) was prepared as yellow oil from **A1** (15.0 mmol, 3.17 g, 1.5 eq.) and **S1** (10.0 mmol, 2.70 g, 1.0 eq.) in 93% yield (4.49 g).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.07 (d, *J* = 8.0 Hz, 2 H), 5.44 (s, 2 H), 4.26 (t, *J* = 8.0 Hz, 2 H), 3.01 (t, *J* = 8.0 Hz, 2 H), 2.34 (s, 3 H), 1.90 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 144.7, 134.0, 132.5, 131.8, 129.7, 129.3, 128.7, 127.7, 122.3, 68.4, 51.2, 25.4, 21.5, 19.2.

ESI-MS *m/z* (ESI) calcd. for $C_{19}H_{21}BrN_3O_3S_2$ $(M+H)^+$ 484.0188, found 484.0125.



1b

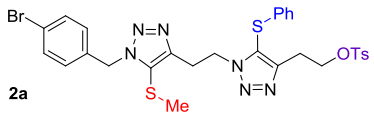
1b (α-Br-**A**-ω-N_3) was prepared as colorless oil from **1a** (9.3 mmol, 4.49 g, 1.0 eq.) in 92% yield (3.04 g).

Rf = 0.2 (PE/EA = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 2 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 5.52 (s, 2 H), 3.63 (t, *J* = 8.0 Hz, 2 H), 2.96 (t, *J* = 8.0 Hz, 2 H), 1.96 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 134.0, 131.8, 129.3, 128.3, 122.2, 51.2, 50.0, 25.3, 19.1.

ESI-MS *m/z* (ESI) calcd. for $C_{12}H_{14}BrN_6S$ $(M+H)^+$ 355.0164, found 355.0165.



2a

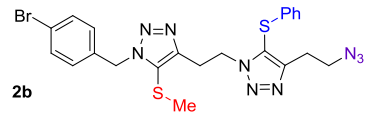
2a (α-Br-**AB**-ω-OTs) was prepared as pale yellow oil from **1b** (8.4 mmol, 2.97 g, 1.0 eq.) and **S2** (13.5 mmol, 4.34 g, 1.5 eq.) in 91% yield (5.24 g).

Rf = 0.1 (PE/EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* =8.0 Hz, 2 H), 7.36 (d, *J* =8.0 Hz, 2 H), 7.21-7.05 (m, 7 H), 6.91 (d, *J* =8.0 Hz, 2 H), 5.43 (s, 2 H), 4.59 (t, *J*=8.0 Hz, 2 H), 4.23 (t, *J* =8.0 Hz, 2 H), 3.14 (t, *J* =8.0 Hz, 2 H), 2.94 (t, *J* =8.0 Hz, 2 H), 2.33 (s, 3 H), 1.79 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 144.6, 134.0, 133.0, 132.6, 131.8, 129.7, 129.5, 129.4, 128.4, 127.7, 127.3, 127.0, 125.2, 122.3, 68.0, 51.3, 47.2, 26.0, 25.2, 21.5, 18.9.

ESI-MS *m/z* (ESI) calcd. for $C_{29}H_{30}BrN_6O_3S_3$ $(M+H)^+$ 687.0705, found 687.0716.



2b

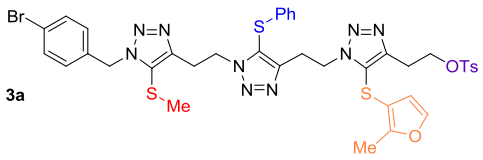
2b (α-Br-**AB**-ω-N_3) was prepared as colorless oil from **2a** (7.0 mmol, 4.81 g, 1.0 eq.) in 97% yield (3.78 g).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2 H), 7.18-7.05 (m, 5 H), 6.92 (d, *J* = 8.0 Hz, 2 H), 5.43 (s, 2 H), 4.63 (t, *J* = 8.0 Hz, 2 H), 3.49 (t, *J* = 8.0 Hz, 2 H), 3.19 (t, *J* = 8.0 Hz, 2 H), 2.87 (t, *J* = 8.0 Hz, 2 H), 1.80 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 147.3, 133.9, 133.3, 131.8, 129.4, 129.3, 128.3, 127.0, 126.9, 124.9, 122.3, 51.2, 49.7, 47.2, 26.0, 25.1, 18.9.

ESI-MS *m/z* (ESI) calcd. for $C_{22}H_{23}BrN_9S_2$ $(M+H)^+$ 558.0681, found 558.1094.



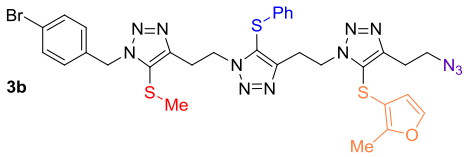
3a (α-Br-**ABC**-ω-OTs) was prepared as pale yellow oil from **2b** (6.0 mmol, 3.33 g, 1.0 eq.) and **S3** (9.0 mmol, 3.02 g, 1.5 eq.) in 90% yield (4.82 g).

Rf = 0.1 (PE/EA = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 7.21-7.06 (m, 6 H), 6.86 (d, *J* = 8.0 Hz, 2 H), 6.05 (d, *J* = 4.0 Hz, 1 H), 5.44 (s, 2 H), 4.62 (t, *J* =8.0 Hz, 2 H), 4.59 (t, *J* =8.0 Hz, 2 H), 4.21 (t, *J* = 8.0 Hz, 2 H), 3.18 (t, *J* = 8.0 Hz, 2 H), 3.12 (t, *J* = 8.0 Hz, 2 H), 2.99 (t, *J* = 8.0 Hz, 2 H), 2.33 (s, 3 H), 2.28 (s, 3 H), 1.81 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 147.9, 147.2, 145.3, 144.6, 141.3, 133.9, 133.0, 132.5, 131.8, 129.6, 129.4, 129.3, 128.3, 127.7, 127.0, 126.9, 124.9, 122.3, 113.3, 107.3, 68.2, 51.3, 47.2, 46.9, 26.0, 25.8, 25.2, 21.4, 18.9, 11.8.

ESI-MS *m/z* (ESI) calcd. for $C_{38}H_{39}BrN_9O_4S_4$ $(M+H)^+$ 894.1171, found 894.2150.



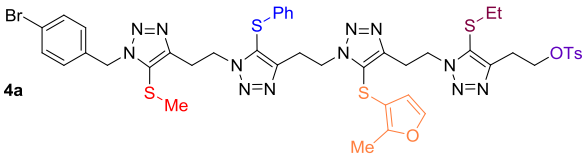
3b (α-Br-**ABC**-ω-N_3) was prepared as colorless oil from **3a** (4.8 mmol, 4.32 g, 1.0 eq.) in 95% yield (3.48 g).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2 H), 7.16-7.06 (m, 6 H), 6.87 (d, *J* = 8.0 Hz, 2 H), 6.07 (d, *J* = 4.0 Hz, 1 H), 5.44 (s, 2 H), 4.63 (t, *J* = 8.0 Hz, 2 H), 4.62 (t, *J* = 8.0 Hz, 2 H), 3.52 (t, *J* = 8.0 Hz, 2 H), 3.18 (t, *J* = 8.0 Hz, 2 H), 3.15 (t, *J* = 8.0 Hz, 2 H), 2.90 (t, *J* = 8.0 Hz, 2 H), 2.30 (s, 3 H), 1.81 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 147.9, 147.2, 146.9, 141.3, 133.9, 133.0, 131.8, 129.4, 129.3, 128.2, 127.0, 126.9, 126.5, 124.9, 122.2, 113.2, 107.6, 51.2, 49.8, 47.16, 46.9, 26.0, 25.8, 25.3, 18.9, 11.8.

ESI-MS *m/z* (ESI) calcd. for $C_{31}H_{32}BrN_{12}OS_3$ $(M+H)^+$ 765.1148, found 765.1322.



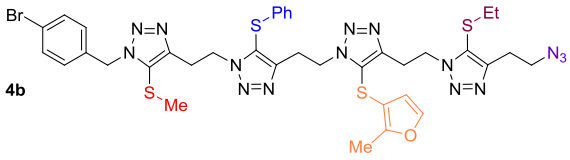
4a (α-Br-**ABCD**-ω-OTs) was prepared as pale yellow oil from **3b** (4.0 mmol, 3.11 g, 1.0 eq.) and **S4** (6.0 mmol, 1.72 g, 1.5 eq.) in 90% yield (3.77 g).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2 H), 7.40 (d, *J* = 8.0 Hz, 2 H), 7.25 (d, *J* = 8.0 Hz, 2 H), 7.20-7.08 (m, 6 H), 6.88 (d, *J* = 8.0 Hz, 2 H), 6.06 (d, *J* = 4.0 Hz, 1 H), 5.46 (s, 2 H), 4.67-4.59 (m, 6 H), 4.28 (t, *J* = 8.0 Hz, 2 H), 3.27-3.15 (m, 6 H), 3.03 (t, *J* = 8.0 Hz, 2 H), 2.56 (q, *J* = 8.0 Hz, 2 H), 2.37 (s, 3 H), 2.30 (s, 3 H), 1.82 (s, 3 H), 1.07 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 148.1, 147.5, 146.8, 146.4, 144.8, 141.5, 134.0, 133.2, 132.8, 132.0, 129.8, 129.6, 129.5, 128.4, 127.9, 127.2, 127.1, 126.9, 125.1, 122.5, 113.5, 107.6, 68.5, 51.5, 47.4, 47.1, 46.9, 30.7, 26.3, 26.2, 26.0, 25.5, 21.6, 19.1, 14.8, 12.1.

MALDI-TOF-MS *m/z* (MALDI) calcd. for $C_{44}H_{48}BrN_{12}O_4S_5$ $(M+H)^+$ 1049.16, found 1049.04.



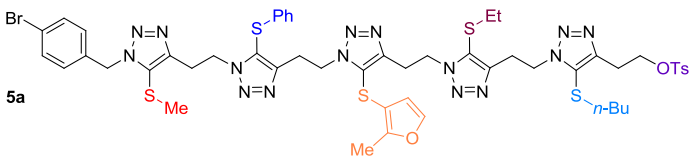
4b (α-Br-**ABCD**-ω-N_3) was prepared as colorless oil from **4a** (3.0 mmol, 3.22 g, 1.0 eq.) in 95% yield (2.62 g).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2 H), 7.27-7.14 (m, 6 H), 6.96 (d, *J* = 8.0 Hz, 2 H), 6.15 (d, *J* = 4.0 Hz, 1 H), 5.54 (s, 2 H), 4.76-4.69 (m, 6 H), 3.69 (t, *J* = 8.0 Hz, 2 H), 3.37 (t, *J* = 8.0 Hz, 2 H), 3.28 (t, *J* = 8.0 Hz, 2 H),3.24 (t, *J* = 8.0 Hz, 2 H), 3.03 (t, *J* = 8.0 Hz, 2 H), 2.69 (q, *J* = 8.0 Hz, 2 H), 2.38 (s, 3 H), 1.91 (s, 3 H), 1.18 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 148.3, 148.0, 147.4, 146.4, 141.4, 134.0, 133.1, 131.9, 129.5, 129.4, 128.3, 127.1, 127.0, 126.84, 126.78, 125.0, 122.4, 113.4, 107.5, 51.4, 50.1, 47.3, 47.0, 46.9, 30.6, 26.3, 26.1, 26.0, 25.4, 19.0, 14.7, 12.0.

ESI-MS *m/z* (ESI) calcd. for $C_{37}H_{41}BrN_{15}OS_4$ $(M+H)^+$ 920.1665, found 920.1677.



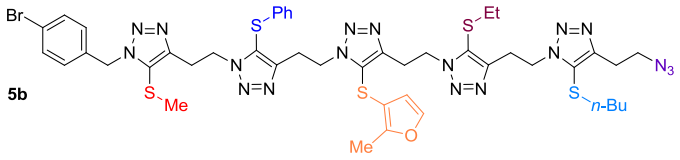
5a (α-Br-**ABCDE**-ω-OTs) was prepared as pale yellow oil from **4b** (2.3 mmol, 2.17 g, 1.0 eq.) and **S5** (3.5 mmol, 1.07 g, 1.5 eq.) in 85% yield (2.40 g).

Rf = 0.2 (DCM/Methanol = 40:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2 H), 7.46 (d, *J* = 8.0 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 7.25-7.15 (m, 6 H), 6.97 (d, *J* = 8.0 Hz, 2 H), 6.17 (d, *J* = 4.0 Hz, 1 H), 5.54 (s, 2 H), 4.80-4.70 (m, 8 H), 4.36 (t, *J* = 8.0 Hz, 2 H), 3.38 (t, *J* = 8.0 Hz, 2 H), 3.36 (t, *J* = 8.0 Hz, 2 H), 3.28 (t, *J* = 8.0 Hz, 2 H), 3.25 (t, *J* = 8.0 Hz, 2 H), 3.10 (t, *J* = 8.0 Hz, 2 H), 2.65 (t, *J* = 8.0 Hz, 2 H), 2.63 (t, *J* = 8.0 Hz, 2 H), 2.44 (s, 3 H), 2.39 (s, 3 H), 1.91 (s, 3 H), 1.50-1.33 (m, 4 H), 1.14 (t, *J* = 8.0 Hz, 3 H), 0.89 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 148.0, 147.4, 147.3, 146.4, 146.3, 144.6, 141.3, 133.9, 133.1, 132.6, 131.8, 129.7, 129.5, 129.4, 128.3, 127.7, 127.5, 127.1, 127.0, 126.7, 124.9, 122.3, 113.4, 107.4, 68.4, 51.3, 47.2, 46.93, 46.88, 46.8, 36.1, 31.5, 30.3, 26.3, 26.2, 26.1, 25.9, 25.4, 21.5, 18.9, 14.6, 13.4, 12.0.

MALDI-TOF-MS *m/z* (MALDI) calcd. for $C_{52}H_{60}BrN_{15}O_4S_6K$ $(M+K)^+$ 1270.34, found 1270.05.



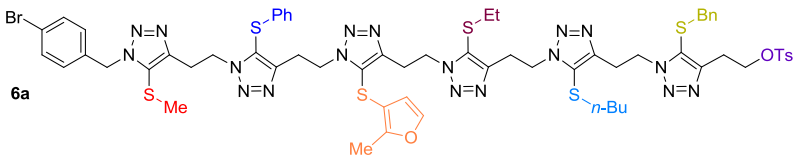
5b (α-Br-**ABCDE**-ω-N_3) was prepared as pale yellow oil from **5a** (1.5 mmol, 1.92 g, 1.0 eq.) in 88% yield (1.45 g).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2 H), 7.27-7.15 (m, 6 H), 6.97 (d, *J* = 8.0 Hz, 2 H), 6.17 (d, *J* = 4.0 Hz, 1 H), 5.54 (s, 2 H), 4.80 (t, *J* = 8.0 Hz, 2 H), 4.79-4.70 (m, 6 H), 3.69 (t, *J* = 8.0 Hz, 2 H), 3.39 (t, *J* = 8.0 Hz, 2 H), 3.37 (t, *J* = 8.0 Hz, 2 H), 3.28 (t, *J* = 8.0 Hz, 2 H), 3.27 (t, *J* = 8.0 Hz, 2 H), 3.02 (t, *J* = 8.0 Hz, 2 H), 2.69 (t, *J* = 8.0 Hz, 2 H), 2.65 (t, *J* = 8.0 Hz, 2 H), 2.40 (s, 3 H), 1.91 (s, 3 H), 1.53-1.35 (m, 4 H), 1.13 (t, *J* = 8.0 Hz, 3 H), 0.88 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 148.0, 147.5, 147.3, 146.3, 141.3, 133.9, 133.1, 131.9, 129.5, 129.3, 128.3, 127.2, 127.1, 127.0, 126.7, 124.9, 122.3, 113.4, 107.4, 51.3, 50.0, 47.2, 46.9, 46.8, 36.1, 31.5, 30.3, 26.3, 26.2, 26.1, 25.9, 25.3, 21.5, 18.9, 14.6, 13.4, 12.0.

MALDI-TOF-MS *m/z* (MALDI) calcd. for $C_{45}H_{53}BrN_{18}OS_5Na$ $(M+Na)^+$ 1125.23, found 1125.07.



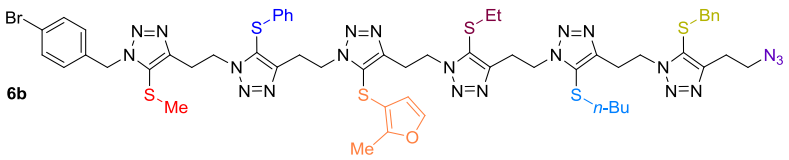
6a (α-Br-**ABCDEF**-ω-OTs) was prepared as yellow oil from **5b** (0.3 mmol, 0.55 g, 1.0 eq.) and **S6** (0.45 mmol, 0.16 g, 1.5 eq.) in 90% yield (0.39 g).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2 H), 7.47 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.27-7.15 (m, 9 H), 6.99-6.94 (m, 4 H), 6.16 (d, *J* = 4.0 Hz, 1 H), 5.53 (s, 2 H), 4.82-4.69 (m, 8 H), 4.40 (t, *J* = 8.0 Hz, 2 H), 4.21 (t, *J* = 8.0 Hz, 2 H), 3.77 (s, 2 H), 3.40 (t, *J* = 8.0 Hz, 2 H), 3.37 (t, *J* = 8.0 Hz, 2 H), 3.33-3.19 (m, 6 H), 2.76 (t, *J* = 8.0 Hz, 2 H), 2.62 (t, *J* = 8.0 Hz, 2 H), 2.60 (t, *J* = 8.0 Hz, 2 H),, 2.44 (s, 3 H), 2.37 (s, 3 H), 1.88 (s, 3 H), 1.49-1.31 (m, 4 H), 1.12 (t, *J* = 8.0 Hz, 3 H), 0.85 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 148.1, 147.6, 147.48, 147.45, 147.4, 146.4, 144.8, 141.5, 136.4, 134.0, 133.2, 132.8, 132.0, 129.8, 129.6, 129.5, 128.8, 128.7, 128.4, 127.9, 127.8, 127.3, 127.2, 127.1, 126.9, 126.8, 126.3, 125.1, 122.5, 113.5, 107.6, 68.5, 51.5, 47.4, 47.1, 47.0, 46.9, 46.6, 40.8, 36.1, 31.6, 30.4, 26.4, 26.3, 26.20, 26.15, 26.0, 25.1, 21.6, 19.1, 14.8, 13.5, 12.1.

MALDI-TOF-MS *m/z* (MALDI) calcd. for $C_{63}H_{72}BrN_{18}O_4S_7$ $(M+H)^+$ 1449.32, found 1449.13.



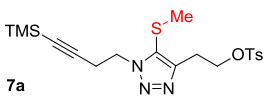
6b (α-Br-**ABCDEF**-ω-N_3) was prepared as yellow oil from **6a** (0.2 mmol, 0.29 g, 1.0 eq.) in 90% yield (0.23 g).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2 H), 7.27-7.15 (m, 9 H), 6.99-6.94 (m, 4 H), 6.16 (d, *J* = 4.0 Hz, 1 H), 5.53 (s, 2 H), 4.80-4.69 (m, 8 H), 4.48 (t, *J* = 8.0 Hz, 2 H), 3.80 (s, 2 H), 3.46 (t, *J* = 8.0 Hz, 2 H), 3.37-3.33 (m, 4 H), 3.30-3.22 (m, 6 H), 2.68-2.59 (m, 6 H), 2.39 (s, 3 H), 1.90 (s, 3 H), 1.45-1.32 (m, 4 H), 1.14 (t, *J* = 8.0 Hz, 3 H), 0.87 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 154.5, 149.0, 148.1, 147.6, 147.4, 146.4, 141.4, 136.6, 136.3, 134.0, 133.2, 132.0, 129.6, 129.5, 128.8, 128.7, 128.4, 127.8, 127.4, 127.1, 126.9, 126.8, 125.9, 125.1, 122.5, 113.5, 107.5, 76.7, 51.4, 49.9, 47.3, 47.0, 46.9, 46.8, 46.7, 46.5, 40.7, 40.5, 36.0, 31.6, 30.4, 26.4, 26.2, 26.0, 25.8, 24.9, 21.6, 19.0, 14.8, 13.5, 12.1.

MALDI-TOF-MS *m/z* (MALDI) calcd. for $C_{56}H_{64}BrN_{21}OS_6Na$ $(M+Na)^+$ 1342.30, found 1342.24.



7a (α-TMS-**A**-ω-OTs) was prepared as yellow oil from **A2** (10 mmol, 1.68 g, 1.0 eq.) and **S1** (15 mmol, 4.06 g, 1.5 eq.) in 92% yield (4.02 g).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 4.41 (t, *J* = 8.0 Hz, 2 H), 4.24 (t, *J* = 8.0 Hz, 2 H), 3.01 (t, *J* = 8.0 Hz, 2 H), 2.76 (t, *J* = 8.0 Hz, 2 H), 2.33 (s, 3 H), 2.19 (s, 3 H), 0.00 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 144.7, 132.6, 129.8, 129.3, 127.8, 101.3, 87.8, 68.5, 46.5, 25.5, 21.6, 21.5, 19.7, -0.3.

ESI-MS *m/z* (ESI) calcd. for $C_{19}H_{28}N_3O_3S_2Si$ $(M+H)^+$ 438.1341, found 438.1373.

7b

7b (α-TMS-**A**-ω-N_3) was prepared from **7a** (9.2 mmol, 4.02 g, 1.0 eq.) as colorless oil in 95% yield (2.69 g).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.53 (t, *J* = 8.0 Hz, 2 H), 3.67 (t, *J* = 8.0 Hz, 2 H), 3.00 (t, *J* = 8.0 Hz, 2 H), 2.86 (t, *J* = 8.0 Hz, 2 H), 2.29 (s, 3 H), 0.08 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 128.8, 101.3, 87.8, 50.2, 46.5, 25.4, 21.7, 19.8, 0.2.

ESI-MS *m/z* (ESI) calcd. for $C_{12}H_{21}N_6SSi$ $(M+H)^+$ 309.1318, found 309.1329.

8a

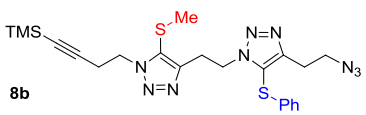
8a (α-TMS-**AB**-ω-OTs) was prepared from **7b** (8.6 mmol, 2.64 g, 1.0 eq.) and **S2** (12.0 mmol, 4.04 g, 1.5 eq.) as pale yellow oil in 91% yield (5.02 g).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2 H), 7.21-7.10 (m, 5 H), 6.91 (d, *J* = 8.0 Hz, 2 H), 4.59 (t, *J* = 8.0 Hz, 2 H), 4.41 (t, *J* = 8.0 Hz, 2 H), 4.23 (t, *J* = 8.0 Hz, 2 H), 3.15 (t, *J* = 8.0 Hz, 2 H), 2.96 (t, *J* = 8.0 Hz, 2 H), 2.76 (t, *J* = 8.0 Hz, 2 H), 2.33 (s, 3 H), 2.08 (s, 3 H), 0.00 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 146.4, 144.6, 133.0, 132.6, 129.6, 129.5, 128.7, 127.7, 127.2, 127.0, 125.2, 101.3, 87.7, 68.0, 47.2, 46.4, 26.0, 25.2, 21.5, 21.4, 19.3, -0.3.

ESI-MS *m/z* (ESI) calcd. for $C_{29}H_{37}N_6O_3S_3Si$ $(M+H)^+$ 641.1859, found 641.1887.



8b

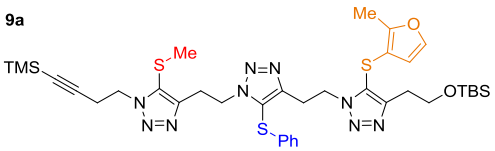
8b (α-TMS-**AB**-ω-N_3) was prepared from **8a** (7.8 mmol, 5.02 g, 1.0 eq.) as colorless oil in 93% yield (3.71 g).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.09 (m, 3 H), 6.92 (d, *J* = 8.0 Hz, 2 H), 4.63 (t, *J* = 8.0 Hz, 2 H), 4.40 (t, *J* = 8.0 Hz, 2 H), 3.50 (t, *J* = 8.0 Hz, 2 H), 3.20 (t, *J* = 8.0 Hz, 2 H), 2.88 (t, *J* = 8.0 Hz, 2 H), 2.75 (t, *J* = 8.0 Hz, 2 H), 2.09 (s, 3 H), 0.00 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 146.6, 133.5, 129.5, 128.8, 127.1, 127.0, 125.0, 101.3, 87.8, 49.9, 47.3, 46.5, 26.2, 25.3, 21.7, 19.5, -0.2.

ESI-MS *m/z* (ESI) calcd. for $C_{22}H_{30}N_9S_2Si$ $(M+H)^+$ 512.1835, found 512.1831.



9a (α-TMS-**ABC**-ω-OTBS) was prepared from **8b** (7.3 mmol, 3.70 g, 1.0 eq.) and **S7** (11.0 mmol, 3.30 g, 1.5 eq.) as pale yellow oil in 95% yield (5.60 g).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.05 (m, 4 H), 6.87 (d, *J* = 8.0 Hz, 2 H), 6.05 (s, 1 H), 4.63 (t, *J* = 8.0 Hz, 2 H), 4.61 (t, *J* = 8.0 Hz, 2 H), 4.41 (t, *J* = 8.0 Hz, 2 H), 3.78 (t, *J* = 8.0 Hz, 2 H), 3.19 (t, *J* = 8.0 Hz, 2 H), 3.15 (t, *J* = 8.0 Hz, 2 H), 2.88 (t, *J* = 8.0 Hz, 2 H), 2.76 (t, *J* = 8.0 Hz, 2 H), 2.28 (s, 3 H), 2.10 (s, 3 H), 0.75 (s, 9 H), 0.00 (s, 9 H), -0.10 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 148.3, 148.1, 146.6, 141.2, 133.3, 129.6, 128.8, 127.3, 127.1, 126.5, 125.1, 113.6, 108.2, 101.3, 87.9, 62.2, 47.3, 47.0, 46.6, 29.1, 26.2, 26.1, 25.9, 21.7, 19.5, 18.3, 12.0, -0.2, -5.4.

MALDI-TOF-MS *m/z* (MALDI) calcd. for $C_{37}H_{53}N_9O_2S_3Si_2K$ $(M+K)^+$ 846.40, found 846.27.

V. IEG synthesis and characterization of sequence-defined polytriazoles

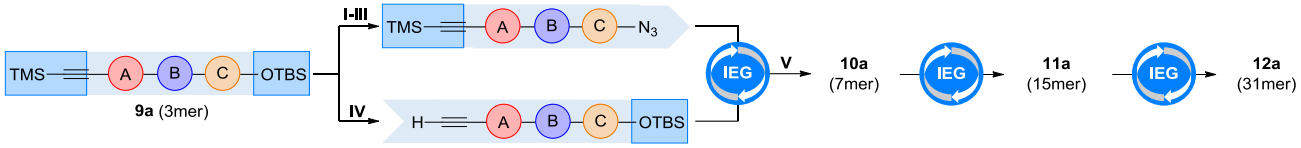


Figure S6. Synthesis of polytriazoles *via* IEG strategy.

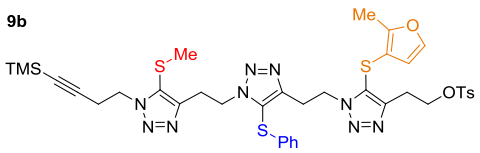
General procedure for the four steps of IEG strategy. The diprotected building unit (**9a**, **10a**, **11a**) was split equally into two parts.

*Preparation of the monoprotected azide building unit (**I-III**).* To an oven-dried flask was added the diprotected building unit (1.0 eq.) and MeOH (0.5 M). The solution was cooled to 0 ^{o}C, and then acetyl chloride (2.0 eq.) was added slowly. The reaction mixture was stirred at room temperature until the reaction completed (confirmed by TLC), and then diluted with ethyl acetate, washed with brine (three times), dried over Na_2SO_4, filtered, and evaporated under vacuum to give the crude product monoprotected -OH building block. Without purification, the residue was dissolved in DCM (0.5 M) with subsequent addition of Et_3N (2.0 eq.) and 4-dimethylaminopyridine (DMAP, 1 mol %). Then the solution of TsCl (1.5 eq.) in DCM (1.0 M) was slowly added into the previous mixture. The reaction mixture was stirred at room temperature until he reaction completed (confirmed by TLC), and then diluted with ethyl acetate, washed with brine (three times), dried over Na_2SO_4, filtered, and evaporated under vacuum to give the residue of monoprotected -OTs building block, which was then purified by silica gel flash column chromatography. Then the purified building block involving OTs group (1.0 eq.) and NaN_3 (1.5 eq.) were added to DMF (0.5 M). The reaction mixture was then heated to 80 ^{o}C and stirred until the reaction completed (confirmed by TLC). The solution was then cooled to room temperature, diluted with ethyl acetate, washed with brine (three times), dried over Na_2SO_4, filtered, and evaporated under vacuum. The crude product was purified by column chromatography on silica gel to afford the monoprotected azide building unit.

*Preparation of the monoprotected alkyne building unit (**IV**).* The diprotected building unit (1.0 eq.) and K_2CO_3 (3.0 eq.) were dissolved in MeOH (0.5 M). The solution was stirred for 2-4 h until the reaction completed. Then the reaction mixture was diluted with ethyl acetate, washed with brine (three times), dried over Na_2SO_4, filtered, and evaporated under vacuum to give the crude product, which then was purified by column chromatography on silica gel to afford the monoprotected alkyne building unit.

*Preparation of the diprotected building unit for next cycle (**V**).* In a glove box, the purified monoprotected azide building unit (1.0 eq.) and the monoprotected alkyne building unit (1.05 eq.) were added into the solution of DMF (0.5 M) involving CuBr (10 mol %) and PMDETA (20 mol %).

The reaction mixture was heated to 50 °C and stirred for 4 h. The solution was then cooled to room temperature, diluted with ethyl acetate, washed with brine (three times), dried over Na_2SO_4, filtered, and evaporated under vacuum. The residue was purified by column chromatography on silica gel to afford the diprotected building unit for next cycle.



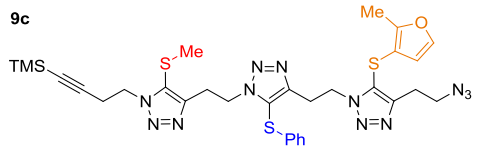
9b (α-TMS-**ABC**-ω-OTs) was prepared from **9a** (2.7 mmol, 2.18 g, 1.0 eq.) as pale yellow oil in 90% yield (2.06 g).

Rf = 0.1 (PE/EA = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2 H), 7.22-7.06 (m, 6 H), 6.86 (d, *J* = 8.0 Hz, 2 H), 6.03 (d, *J* = 4.0 Hz, 1 H), 4.62 (t, *J* = 8.0 Hz, 2 H), 4.59 (t, *J* = 8.0 Hz, 2 H), 4.41 (t, *J* = 8.0 Hz, 2 H), 4.19 (t, *J* = 8.0 Hz, 2 H), 3.19 (t, *J* = 8.0 Hz, 2 H), 3.13 (t, *J* = 8.0 Hz, 2 H), 2.98 (t, *J* = 8.0 Hz, 2 H), 2.76 (t, *J* = 8.0 Hz, 2 H), 2.32 (s, 3 H), 2.27 (s, 3 H), 2.10 (s, 3 H), 0.00 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 148.1, 146.6, 145.5, 144.8, 141.5, 133.2, 132.8, 129.8, 129.6, 128.9, 127.9, 127.3, 127.20, 127.15, 125.2, 113.5, 107.5, 101.3, 87.9, 68.3, 47.4, 47.1, 46.6, 26.2, 26.0, 25.4, 21.7, 21.6, 19.6, 12.0, -0.2.

ESI-MS *m/z* (ESI) calcd. for $C_{38}H_{46}N_9O_4S_4Si$ $(M+H)^+$ 848.2325, found 848.2297.



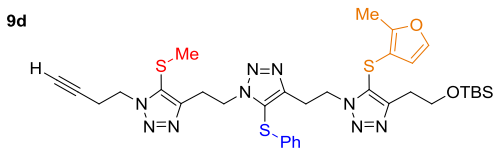
9c (α-TMS-**ABC**-ω-N_3) was prepared from **9b** (2.43 mmol, 2.06 g, 1.0 eq.) as colorless oil in 92% yield (1.61 g).

Rf = 0.25 (PE/EA = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.09 (m, 4 H), 6.88 (d, *J* = 8.0 Hz, 2 H), 6.07 (d, *J* = 4.0 Hz, 1 H), 4.65 (t, *J* = 8.0 Hz, 2 H), 4.64 (t, *J* = 8.0 Hz, 2 H), 4.43 (t, *J* = 8.0 Hz, 2 H), 3.51 (t, *J* = 8.0 Hz, 2 H), 3.19 (t, *J* = 8.0 Hz, 2 H), 3.18 (t, *J* = 8.0 Hz, 2 H), 2.91 (t, *J* = 8.0 Hz, 2 H), 2.78 (t, *J* = 8.0 Hz, 2 H), 2.31 (s, 3 H), 2.12 (s, 3 H), 0.02 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 148.1, 147.0, 146.5, 141.4, 133.2, 129.6, 128.8, 127.3, 127.1, 125.1, 113.6, 108.2, 101.3, 87.9, 62.2, 47.3, 47.0, 46.6, 29.1, 26.2, 26.1, 25.9, 21.7, 19.5, 18.3, 12.0, -0.2.

ESI-MS *m/z* (ESI) calcd. for $C_{31}H_{39}N_{12}OS_3Si$ $(M+H)^+$ 719.2302, found 719.2304.



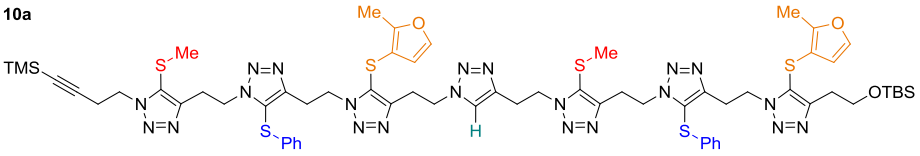
9d (α-H-**ABC**-ω-OTBS) was prepared from **9a** (2.7 mmol, 2.18 g, 1.0 eq.) as colorless oil in 97% yield (1.93 g).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.15 (m, 4 H), 6.97 (d, *J* = 8.0 Hz, 2 H), 6.15 (d, *J* = 4.0 Hz, 1 H), 4.72 (t, *J* = 8.0 Hz, 2 H), 4.70 (t, *J* = 8.0 Hz, 2 H), 4.52 (t, *J* = 8.0 Hz, 2 H), 3.88 (t, *J* = 8.0 Hz, 2 H), 3.29 (t, *J* = 8.0 Hz, 2 H), 3.22 (t, *J* = 8.0 Hz, 2 H), 2.97 (t, *J* = 8.0 Hz, 2 H), 2.84 (t, *J* = 8.0 Hz, 2 H), 2.38 (s, 3 H), 2.19 (s, 3 H), 2.02 (t, *J* = 4.0 Hz, 1 H), 0.85 (s, 9 H), 0.00 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 148.3, 148.1, 146.8, 141.2, 133.2, 129.6, 128.7, 127.3, 127.1, 126.4, 125.1, 113.6, 108.2, 79.2, 71.2, 62.2, 47.3, 46.9, 46.5, 29.1, 26.2, 26.1, 25.9, 20.2, 19.5, 18.2, 12.0, -5.4.

ESI-MS *m/z* (ESI) calcd. for $C_{34}H_{46}N_9O_2S_3Si$ $(M+H)^+$ 736.2706, found 736.2704.



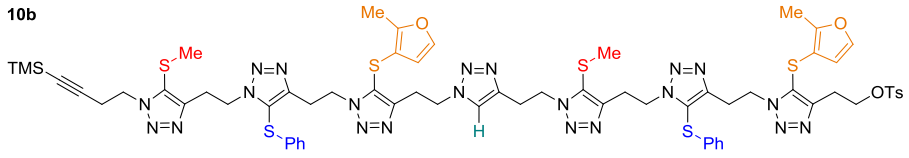
10a (α-TMS-**ABCHABC**-ω-OTBS) was prepared from **9c** (2.2 mmol, 1.58 g, 1.0 eq.) and **9d** (2.2 mmol, 1.62 g, 1.0 eq.) as colorless oil in 77% yield (2.46 g).

Rf = 0.2 (DCM/Methanol = 40:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.10 (m, 9 H), 6.94 (d, *J* = 8.0 Hz, 4 H), 6.11 (d, *J* = 4.0 Hz, 1 H), 6.01 (d, *J* = 4.0 Hz, 1 H), 4.70-4.60 (m, 12 H), 4.47 (t, *J* = 8.0 Hz, 2 H), 3.84 (t, *J* = 8.0 Hz, 2 H), 3.23 (t, *J* = 8.0 Hz, 2 H), 3.21-3.16 (m, 10 H), 2.93 (t, *J* = 8.0 Hz, 2 H), 2.82 (t, *J* = 8.0 Hz, 2 H), 2.33 (s, 3 H), 2.31 (s, 3 H), 2.16 (s, 3 H), 2.04 (s, 3 H), 0.81 (s, 9 H), 0.06 (s, 9 H), -0.04 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 154.1, 148.3, 148.1, 148.0, 146.7, 146.5, 146.3, 142.8, 141.5, 141.2, 133.2, 129.58, 129.56, 128.7, 128.6, 127.2, 127.1, 127.0, 126.4, 125.0, 124.9, 122.5, 113.5, 113.4, 108.1, 107.4, 101.3, 87.8, 62.2, 48.5, 47.5, 47.4, 47.3, 47.1, 46.9, 46.5, 29.1, 26.5, 26.3, 26.1, 26.0, 25.9, 25.8, 21.7, 19.5, 19.1, 18.2, 12.0, -0.2, -5.4.

MALDI-TOF-MS *m/z* (MALDI) calcd. for $C_{65}H_{84}N_{21}O_3S_6Si_2$ $(M+H)^+$ 1454.49, found 1454.57.



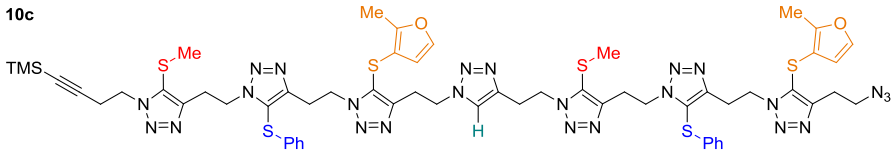
10b (α-TMS-**ABCHABC**-ω-OTs) was prepared from **10a** (0.8 mmol, 1.16 g, 1.0 eq.) as colorless oil in 88% yield (1.05 g).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2 H), 7.33-7.16 (m, 11 H), 7.01-6.97 (m, 4 H), 6.14 (s, 1 H), 6.07 (s, 1 H), 4.75-4.68 (m, 12 H), 4.52 (t, *J* = 8.0 Hz, 2 H), 4.30 (t, *J* = 8.0 Hz, 2 H), 3.31-3.21 (m, 12 H), 3.08 (t, *J* = 8.0 Hz, 2 H), 2.88 (t, *J* = 8.0 Hz, 2 H), 2.43 (s, 3 H), 2.40 (s, 3 H), 2.37 (s, 3 H), 2.21 (s, 3 H), 2.09 (s, 3 H), 0.11 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 148.1, 146.5, 145.4, 144.7, 142.8, 141.47, 141.45, 133.2, 132.7, 129.8, 129.60, 129.58, 128.8, 127.8, 127.2, 127.13, 127.06, 125.0, 122.7, 113.5, 113.4, 107.5, 107.4, 101.3, 87.8, 68.3, 48.6, 47.51, 47.45, 47.3, 47.2, 47.0, 46.6, 26.5, 26.3, 26.1, 26.0, 25.4, 21.7, 21.6, 19.5, 19.1, 11.98, 11.95, -0.2.

MALDI-TOF-MS *m/z* (MALDI) calcd. for $C_{66}H_{75}N_{21}O_5S_7SiNa$ $(M+Na)^+$ 1516.40, found 1516.31.



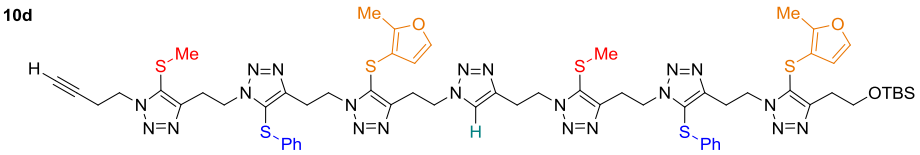
10c (α-TMS-**ABCHABC**-ω-N_3) was prepared from **10b** (0.7 mmol, 1.05 g, 1.0 eq.) as colorless oil in 98% yield (0.94 g).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.06 (m, 9 H), 6.89-6.86 (m, 4 H), 6.05 (d, *J* = 4.0 Hz, 1 H), 5.96 (d, *J* = 4.0 Hz, 1 H), 4.66-4.54 (m, 12 H), 4.41 (t, *J* = 8.0 Hz, 2 H), 3.50 (t, *J* = 8.0 Hz, 2 H), 3.19 (t, *J* = 8.0 Hz, 2 H), 3.17-3.13 (m, 10 H), 2.88 (t, *J* = 8.0 Hz, 2 H), 2.76 (t, *J* = 8.0 Hz, 2 H), 2.28 (s, 3 H), 2.25 (s, 3 H), 2.10 (s, 3 H), 1.98 (s, 3 H), 0.00 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 154.3, 148.12, 148.05, 147.0, 146.6, 146.5, 146.2, 142.7, 141.4, 141.4, 133.2, 129.5, 128.7, 128.6, 127.2, 127.1, 127.0, 126.7, 124.5, 122.6, 113.4, 107.7, 107.4, 101.3, 87.8, 49.2, 48.5, 47.5, 47.4, 47.3, 47.2, 47.0, 46.5, 26.5, 26.2, 26.1, 26.0, 25.9, 25.3, 21.6, 19.5, 19.1, 11.9, -0.2.

MALDI-TOF-MS *m/z* (MALDI) calcd. for $C_{59}H_{69}N_{24}O_2S_6Si$ $(M+H)^+$ 1365.41, found 1365.29.



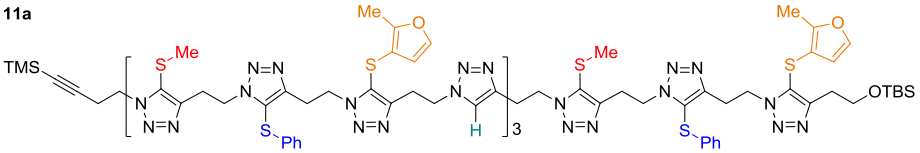
10d (α-H-**ABCHABC**-ω-OTBS) was prepared from **10a** (0.8 mmol, 1.16 g, 1.0 eq.) as colorless oil in 98% yield (1.07 g).

Rf = 0.2 (DCM/Methanol = 40:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.15 (m, 9 H), 6.99 (d, *J* = 8.0 Hz, 4 H), 6.16 (d, *J* = 4.0 Hz, 1 H), 6.07 (d, *J* = 4.0 Hz, 1 H), 4.77-4.65 (m, 12 H), 4.53 (t, *J* = 8.0 Hz, 2 H), 3.89 (t, *J* = 8.0 Hz, 2 H), 3.30 (t, *J* = 8.0 Hz, 2 H), 3.29-3.21 (m, 10 H), 2.99 (t, *J* = 8.0 Hz, 2 H), 2.86 (t, *J* = 8.0 Hz, 2 H), 2.39 (s, 3 H), 2.36 (s, 3 H), 2.21 (s, 3 H), 2.10 (s, 3 H), 2.04 (t, *J* = 4.0 Hz, 1 H), 0.86 (s, 9 H), 0.02 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 154.3, 148.3, 148.1, 147.0, 146.6, 146.5, 146.2, 142.7, 141.5, 141.2, 133.2, 129.5, 128.7, 128.6, 127.2, 127.1, 127.0, 126.7, 125.0, 122.6, 113.4, 107.7, 107.4, 101.3, 87.8, 49.9, 48.5, 47.5, 47.4, 47.3, 47.1, 47.0, 46.5, 26.5, 26.2, 26.1, 26.0, 25.9, 25.3, 21.6, 19.5, 19.1, 11.9, -0.24.

MALDI-TOF-MS *m/z* (MALDI) calcd. for $C_{62}H_{75}N_{21}O_3S_6SiNa$ $(M+Na)^+$ 1404.44, found 1404.34.



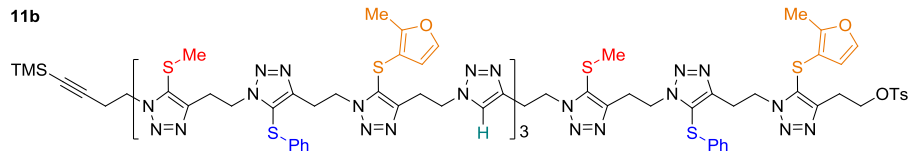
11a (α-TMS-**(ABCH)$_3$ABC**-ω-OTBS) was prepared from **10c** (0.6 mmol, 0.82 g, 1.0 eq.) and **10d** (0.6 mmol, 0.83 g, 1.0 eq.) as colorless oil in 72% yield (1.19 g).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.03 (m, 19 H), 6.90-6.86 (m, 8 H), 6.05 (d, *J* = 4.0 Hz, 1 H), 5.95 (d, *J* = 4.0 Hz, 3 H), 4.66-4.53 (m, 28 H), 4.41 (t, *J* = 8.0 Hz, 2 H), 3.78 (t, *J* = 8.0 Hz, 2 H), 3.26-3.10 (m, 28 H), 2.88 (t, *J* = 8.0 Hz, 2 H), 2.76 (t, *J* = 8.0 Hz, 2 H), 2.27 (s, 3 H), 2.26 (s, 9 H), 2.10 (s, 3 H), 1.98 (s, 9 H), 0.75 (s, 9 H), 0.00 (s, 9 H), -0.01 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 154.0, 148.1, 147.9, 146.5, 146.4, 146.1, 142.7, 141.3, 141.1, 133.0, 129.4, 128.6, 128.4, 127.1, 127.0, 126.9, 126.2, 124.8, 122.4, 113.4, 113.2, 108.0, 107.3, 101.2, 87.7, 77.3, 62.0, 48.3, 47.4, 47.3, 47.2, 47.0, 46.7, 46.4, 29.4, 28.9, 26.4, 26.2, 26.0, 25.9, 25.8, 25.7, 21.5, 19.4, 19.0, 18.1, 11.8, -0.3, -5.6.

MALDI-TOF-MS *m/z* (MALDI) calcd. for $C_{121}H_{143}N_{45}O_5S_{12}Si_2Na$ $(M+Na)^+$ 2769.84, found 2770.49.



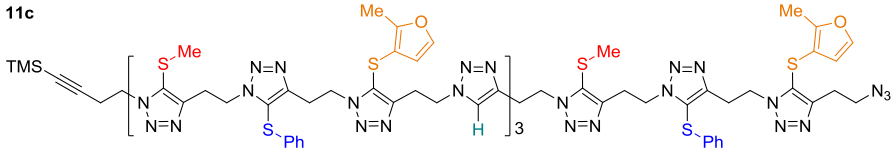
11b (α-TMS-**(ABCH)$_3$ABC**-ω-OTs) was prepared from **11a** (0.21 mmol, 0.58 g, 1.0 eq.) as colorless oil in 87% yield (0.51 g).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2 H), 7.21-7.04 (m, 21 H), 6.90-6.86 (m, 8 H), 6.02 (d, *J* = 4.0 Hz, 1 H), 5.95 (d, *J* = 4.0 Hz, 3 H), 4.67-4.52 (m, 28 H), 4.41 (t, *J* = 8.0 Hz, 2 H), 4.17 (t, *J* = 8.0 Hz, 2 H), 3.29-3.10 (m, 28 H), 2.88 (t, *J* = 8.0 Hz, 2 H), 2.76 (t, *J* = 8.0 Hz, 2 H), 2.32 (s, 3 H), 2.26 (s, 3 H), 2.24 (s, 9 H), 2.10 (s, 3 H), 1.98 (s, 9 H), 0.00 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 148.1, 146.7, 146.6, 146.3, 145.5, 144.8, 142.9, 141.5, 133.2, 129.8, 129.6, 128.6, 127.9, 127.13, 127.07, 125.0, 122.6, 113.45, 113.41, 107.4, 101.3, 87.9, 68.3, 48.5, 47.53, 47.46, 47.3, 47.2, 47.0, 46.6, 26.6, 26.3, 26.1, 26.0, 25.4, 21.7, 21.6, 19.5, 19.2, 12.0, -0.2.

MALDI-TOF-MS *m/z* (MALDI) calcd. for $C_{122}H_{135}N_{45}O_7S_{13}SiK$ $(M+K)^+$ 2825.88, found 2826.37.



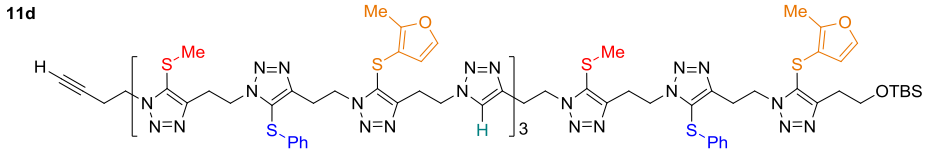
11c (α-TMS-**(ABCH)$_3$ABC**-ω-N_3) was prepared from **11b** (0.18 mmol, 0.5 g, 1.0 eq.) as colorless oil in 92% yield (0.44 g).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.03 (m, 19 H), 6.70-6.86 (m, 8 H), 6.05 (d, *J* = 4.0 Hz, 1 H), 5.95 (d, *J* = 4.0 Hz, 3 H), 4.67-4.52 (m, 28 H), 4.41 (t, *J* = 8.0 Hz, 2 H), 3.50 (t, *J* = 8.0 Hz, 2 H), 3.29-3.10 (m, 28 H), 2.88 (t, *J* = 8.0 Hz, 2 H), 2.76 (t, *J* = 8.0 Hz, 2 H), 2.28 (s, 3 H), 2.25 (s, 9 H), 2.10 (s, 3 H), 1.98 (s, 9 H), 0.00 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 154.3, 148.12, 148.05, 147.0, 146.63, 146.60, 146.5, 146.2, 142.8, 141.44, 141.4, 133.1, 129.6, 129.5, 128.7, 128.6, 127.2, 127.1, 127.0, 126.7, 125.0, 124.9, 122.5, 113.4, 107.7, 107.4, 101.3, 87.8, 49.9, 48.5, 47.5, 47.4, 47.3, 47.1, 47.0, 46.5, 29.6, 29.2, 26.5, 26.3, 26.2, 26.0, 25.9, 25.3, 22.6, 21.6, 19.5, 19.1, 14.0, 11.9, -0.2.

MALDI-TOF-MS *m/z* (MALDI) calcd. for $C_{115}H_{128}N_{48}O_4S_{12}SiNa$ $(M+Na)^+$ 2680.76, found 2681.28.



11d (α-H-**(ABCH)$_3$ABC**-ω-OTBS) was prepared from **11a** (0.21 mmol, 0.58 g, 1.0 eq.) as colorless oil in 90% yield (0.51 g).

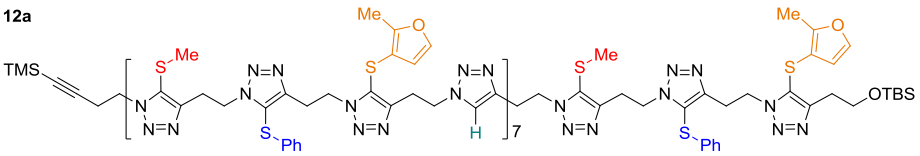
Rf = 0.2 (DCM/Methanol = 30:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.10 (m, 19 H), 6.98-6.93 (m, 8 H), 6.12 (d, *J* = 4.0 Hz, 1 H), 6.03 (d, *J* = 4.0 Hz, 3 H), 4.74-4.60 (m, 28 H), 4.49 (t, *J* = 8.0 Hz, 2 H), 3.85 (t, *J* = 8.0 Hz, 2 H), 3.34-3.20

(m, 28 H), 2.88 (t, *J* = 8.0 Hz, 2 H), 2.76 (t, *J* = 8.0 Hz, 2 H), 2.34 (s, 3 H), 2.32 (s, 9 H), 2.06 (s, 3 H), 2.01 (s, 9 H), 2.00 (t, *J* = 4.0 Hz, 1 H), 0.82 (s, 9 H), -0.03 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 154.1, 148.3, 148.1, 146.64, 146.6, 146.2, 142.8, 141.4, 141.2, 133.2, 129.6, 128.7, 128.5, 127.2, 127.1, 127.0, 126.3, 125.0, 124.9, 122.5, 113.5, 113.4, 108.1, 107.4, 79.2, 71.1, 62.1, 48.5, 47.5, 47.4, 47.3, 47.1, 46.9, 46.4, 29.6, 29.1, 26.5, 26.3, 26.1, 25.9, 25.8, 20.2, 19.4, 19.1, 18.2, 11.9, -5.5.

MALDI-TOF-MS *m/z* (MALDI) calcd. for $C_{115}H_{128}N_{48}O_4S_{12}SiNa$ $(M+Na)^+$ 2715.60, found 2715.34.



12a (α-TMS-**(ABCH)$_7$ABC**-ω-OTBS) was prepared from **11c** (0.026 mmol, 70 mg) and **11d** (0.026 mmol, 70 mg) as colorless oil in 53% yield (74 mg).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.02 (m, 39 H), 6.90-6.86 (m, 16 H), 6.05 (d, *J* = 4.0 Hz, 1 H), 5.95 (d, *J* = 4.0 Hz, 7 H), 4.68-4.51 (m, 60 H), 4.41 (t, *J* = 8.0 Hz, 2 H), 3.78 (t, *J* = 8.0 Hz, 2 H), 3.30-3.09 (m, 60 H), 2.88 (t, *J* = 8.0 Hz, 2 H), 2.76 (t, *J* = 8.0 Hz, 2 H), 2.27 (s, 3 H), 2.25 (s, 21 H), 2.10 (s, 3 H), 1.98 (s, 21 H), 0.75 (s, 9 H), 0.00 (s, 9 H), -0.10 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 148.1, 146.6, 146.2, 142.8, 141.4, 141.2, 133.1, 130.5, 129.6, 128.6, 127.1, 126.4, 125.0, 122.5, 113.4, 107.4, 79.1, 78.5, 78.1, 62.2, 48.4, 47.5, 47.1, 29.5, 29.0, 27.4, 26.5, 26.3, 26.1, 25.9, 25.8, 21.2, 19.4, 19.1, 11.9, -0.2, -5.5.

FTICR-MS *m/z* (ESI) calcd. for $C_{233}H_{264}N_{93}O_9S_{24}Si_2$ $(M+H)^+$5335.5921, found 5335.8539.

VI. Supplementary data

Table S1. MS Characterization and Yield for **1a-6a**.

Com.	Sequence	$m/z_{calc.}$	$m/z_{obs.}$	Yield[a]
1a[b,d]	Br-**A**-OTs	484.0188	484.0125	93%
1b[b,d]	Br-**A**-N_3	355.0164	355.0165	92%
2a[b,d]	Br-**AB**-OTs	687.0705	687.0716	91%
2b[b,d]	Br-**AB**-N_3	558.0681	558.1094	97%
3a[b,d]	Br-**ABC**-OTs	894.1171	894.2150	90%
3b[b,d]	Br-**ABC**-N_3	765.1148	765.1322	95%
4a[c,d]	Br-**ABCD**-OTs	1049.16	1049.04	90%
4b[b,d]	Br-**ABCD**-N_3	920.1665	920.1677	95%
5a[c,f]	Br-**ABCDE**-OTs	1270.34	1270.05	85%
5b[c,e]	Br-**ABCDE**-N_3	1125.23	1125.07	88%
6a[c,d]	Br-**ABCDEF**-OTs	1449.32	1449.13	90%

[a]Isolated yield. [b]ESI-MS. [c]MALDI-TOF-MS. [d][M+H]$^+$. [e][M+Na]$^+$. [f][M+K]$^+$.

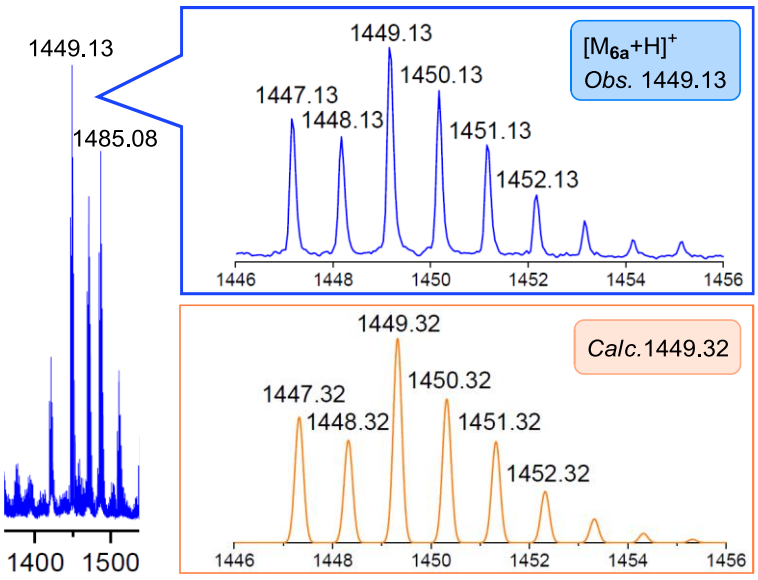


Figure S7. MALDI-TOF-MS of polymer **6a** and monoisotopic mass for the full-length primer product.

Table S2. MS Characterization and Yield for **7a-12a**.

Com.	Sequence	$m/z_{calc.}$	$m/z_{obs.}$	Yield[a]
7a[b,e]	TMS-**A**-OTs	438.1341	438.1373	92%
7b[b,e]	TMS-**A**-N_3	309.1318	309.1329	95%
8a[b,e]	TMS-**AB**-OTs	641.1859	641.1887	91%
8b[b,e]	TMS-**AB**-N_3	512.1835	512.1831	93%
9a[c,g]	TMS-**ABC**-OTBS	846.40	846.27	95%
9b[b,e]	TMS-**ABC**-OTs	848.2325	848.2297	90%
9c[b,e]	TMS-**ABC**-N_3	719.2302	719.2304	92%
9d[b,e]	H-**ABC**-OTBS	736.2706	736.2704	97%
10a[c,e]	TMS-**ABCHABC**-OTBS	1454.49	1454.57	77%
10b[c,f]	TMS-**ABCHABC**-OTs	1516.40	1516.31	88%
10c[c,e]	TMS-**ABCHABC**-N_3	1365.41	1365.29	98%
10d[c,f]	H-**ABCHABC**-OTBS	1404.44	1404.34	98%
11a[c,f]	TMS-(**ABCH**)$_3$**ABC**-OTBS	2769.84	2770.49	72%
11b[c,g]	TMS-(**ABCH**)$_3$**ABC**-OTs	2825.88	2826.37	87%
11c[c,f]	TMS-(**ABCH**)$_3$**ABC**-N_3	2680.76	2681.28	92%
11d[c,g]	H-(**ABCH**)$_3$**ABC**-OTBS	2715.60	2715.34	90%
12a[d,e]	TMS-(**ABCH**)$_7$**ABC**-OTBS	5335.5921	5335.8539	53%

[a]Isolated yield. [b]ESI-MS. [c]MALDI-TOF-MS. [d]FTICR-MS. [e][M+H]$^+$. [f][M+Na]$^+$. [g][M+K]$^+$.

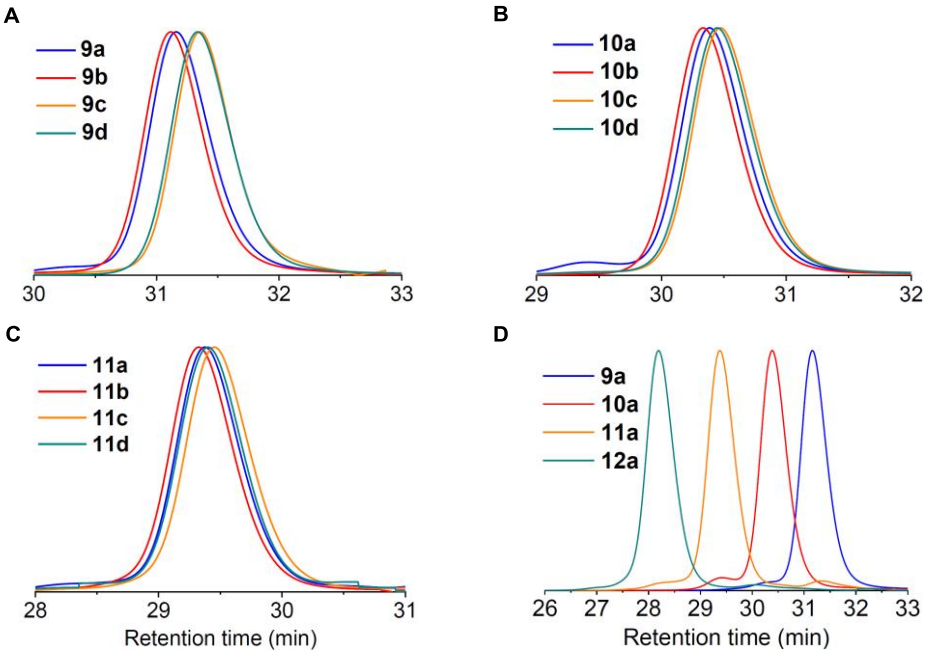


Figure S8. (A) SEC traces of 3-mers. (B) SEC traces of 7-mers. (C) SEC traces of 15-mers. (D) SEC traces of **9a**, **10a**, **11a** and **12a**.

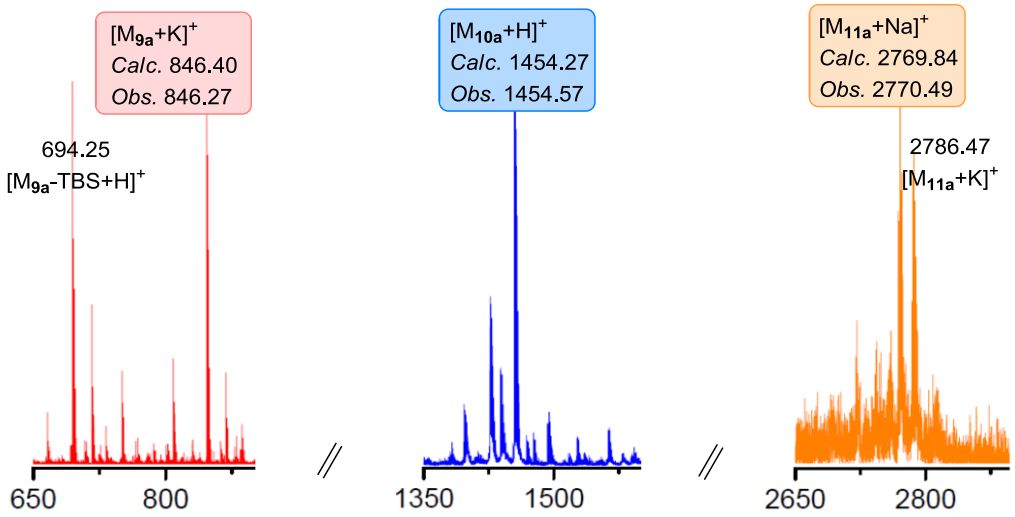
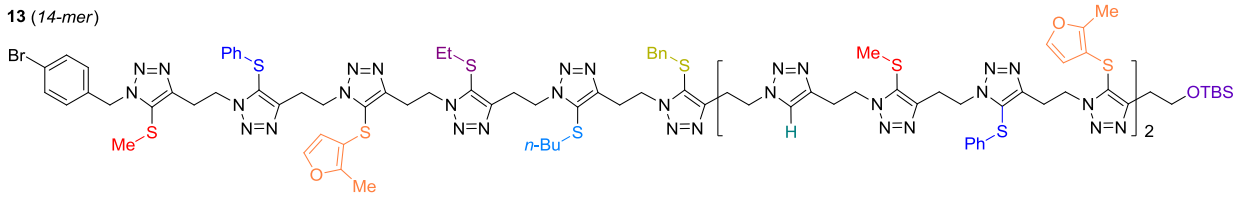


Figure S9. MALDI-TOF-MS of **9a**, **10a** and **11a**.

VII. Construction of sequence-defined polytriazole under CuAAC



13 (α-Br-**ABCDEF(HABC)**$_2$-ω-OTBS). In a glove box, the coupling partner **6b** (0.02 mmol, 26 mg, 1.0 eq.) and **10d** (0.02 mmol, 28 mg, 1.0 eq.) were added into the solution of DMF (0.5 M) involving CuBr (10 mol %) and PMDETA (20 mol %). The reaction mixture was heated to 50 ^{o}C and stirred for 4 h. The solution was then cooled to room temperature, diluted with ethyl acetate, washed with brine (three times), dried over Na_2SO_4, filtered, and evaporated under vacuum. The residue was purified by column chromatography on silica gel to give the desired product as colorless oil in 81% yield (43 mg). Rf = 0.2 (DCM/Methanol = 30:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 2 H), 7.31-7.21 (m, 19 H), 7.19-7.17 (m, 6 H), 6.99 (d, *J* = 8.0 Hz, 2 H), 6.18 (t, *J* = 4.0 Hz, 2 H), 6.08 (d, *J* = 4.0 Hz, 1 H), 5.55 (s, 2 H), 4.79-4.67 (m, 24 H), 4.57 (t, *J* = 8.0 Hz, 2 H), 4.47 (t, *J* = 8.0 Hz, 2 H), 3.90 (t, *J* = 8.0 Hz, 2 H), 3.72 (s, 2 H), 3.42-3.20 (m, 24 H), 2.98 (t, *J* = 8.0 Hz, 2 H), 2.95 (t, *J* = 8.0 Hz, 2 H), 2.67 (t, *J* = 8.0 Hz, 2 H), 2.64 (t, *J* = 8.0 Hz, 2 H), 2.40 (s, 6 H), 2.36 (s, 3 H), 2.10 (s, 6 H), 1.92 (s, 3 H), 1.48-1.32 (m, 4 H), 1.16 (t, *J* = 8.0 Hz, 3 H), 0.89 (t, *J* = 8.0 Hz, 3 H), 0.89 (s, 9 H), 0.02 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 154.2, 148.4, 148.1, 147.6, 147.5, 146.8, 146.4, 146.3, 142.9, 141.5, 141.2, 136.5, 134.0, 133.2, 132.0, 129.6, 129.5, 128.83, 128.78, 128.7, 128.4, 127.8, 127.3, 127.22, 127.18, 127.1, 126.9, 125.1, 125.0, 122.6, 122.5, 113.6, 113.53, 113.45, 108.2, 107.6, 107.5, 62.6, 51.5, 48.6, 47.6, 47.5, 47.4, 47.2, 47.1, 47.02, 46.95, 46.8, 40.6, 36.1, 31.7, 30.5, 29.1, 26.6, 26.4, 26.2, 26.1, 25.9, 21.7, 19.2, 19.1, 18.3, 14.8, 13.6, 12.1, 12.0, 0.0, -5.4.

FTMS *m/z* (ESI) calcd. for $C_{118}H_{140}BrN_{42}O_4S_{12}Si$ $(M+H)^+$ 2702.7658, found 2702.8246.

VIII. Comparison of ^{1}H NMR spectrum

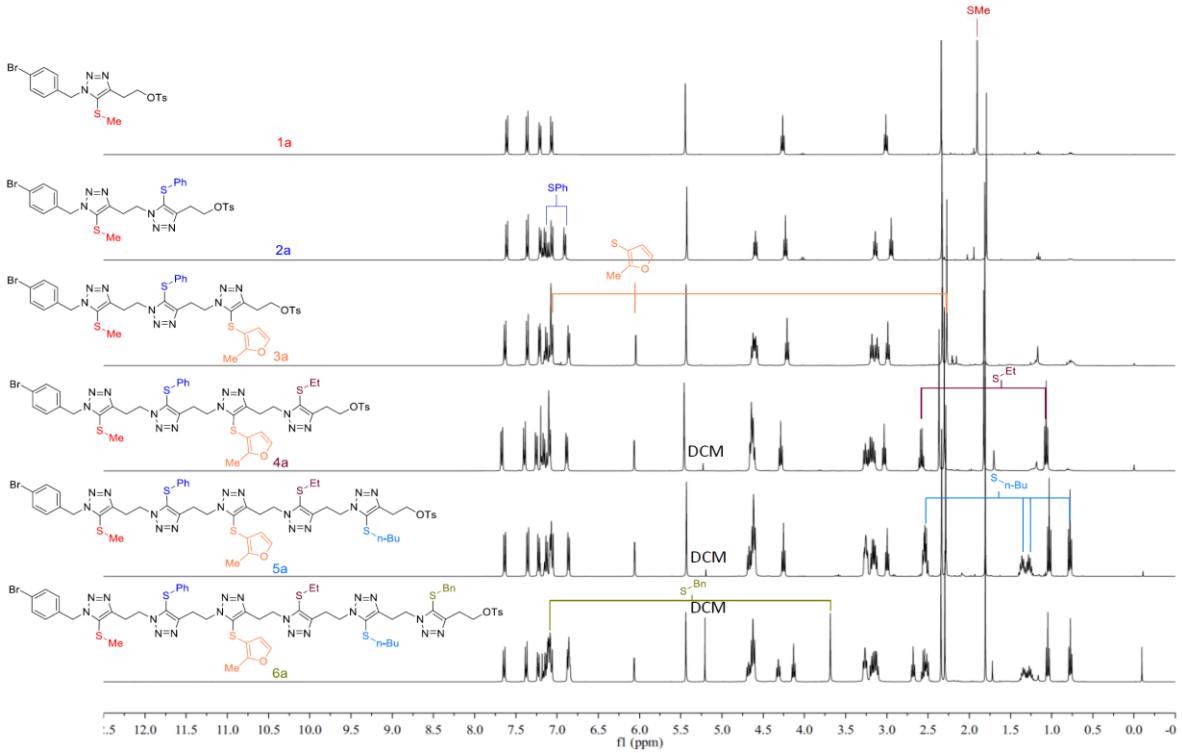


Figure S10. Comparison of ^{1}H NMR spectra for the α-Br-ω-OTs oligomers ($CDCl_3$, 400 MHz).

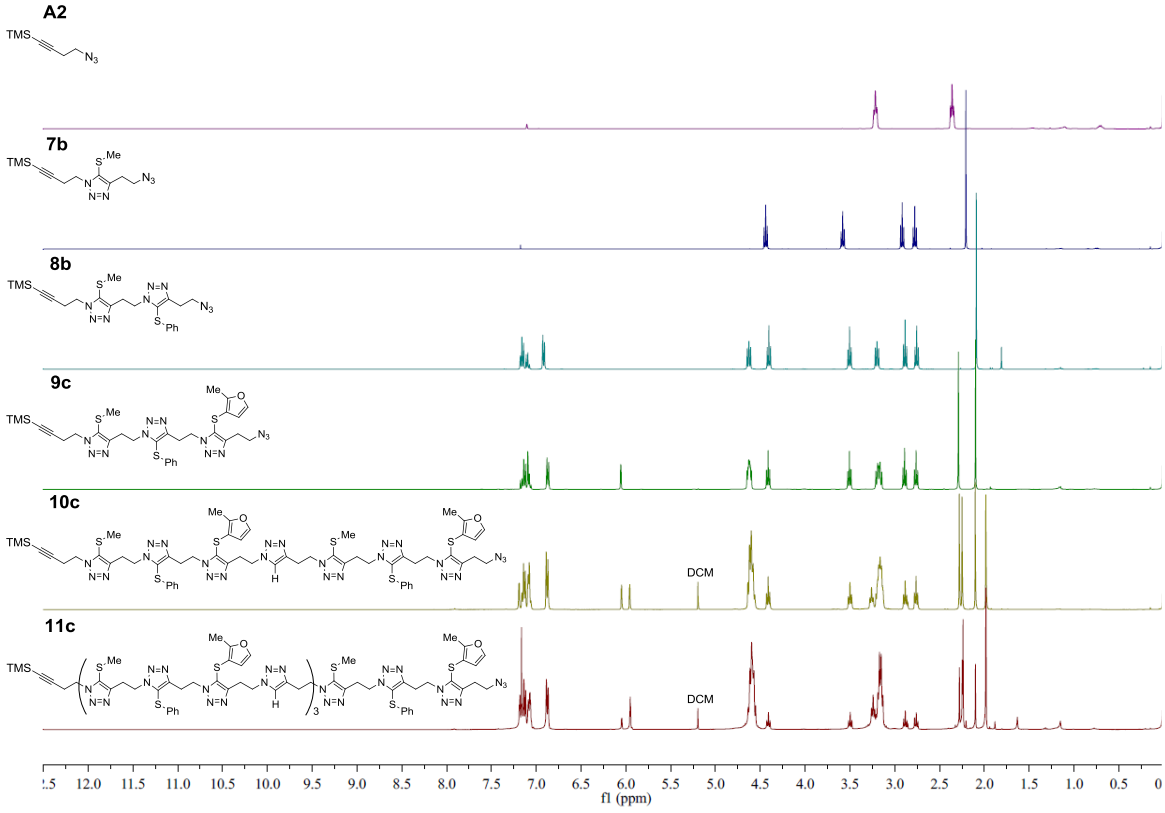


Figure S11. Comparison of ^{1}H NMR spectra for the α-TMS-ω-N_3 oligomers ($CDCl_3$, 400 MHz).

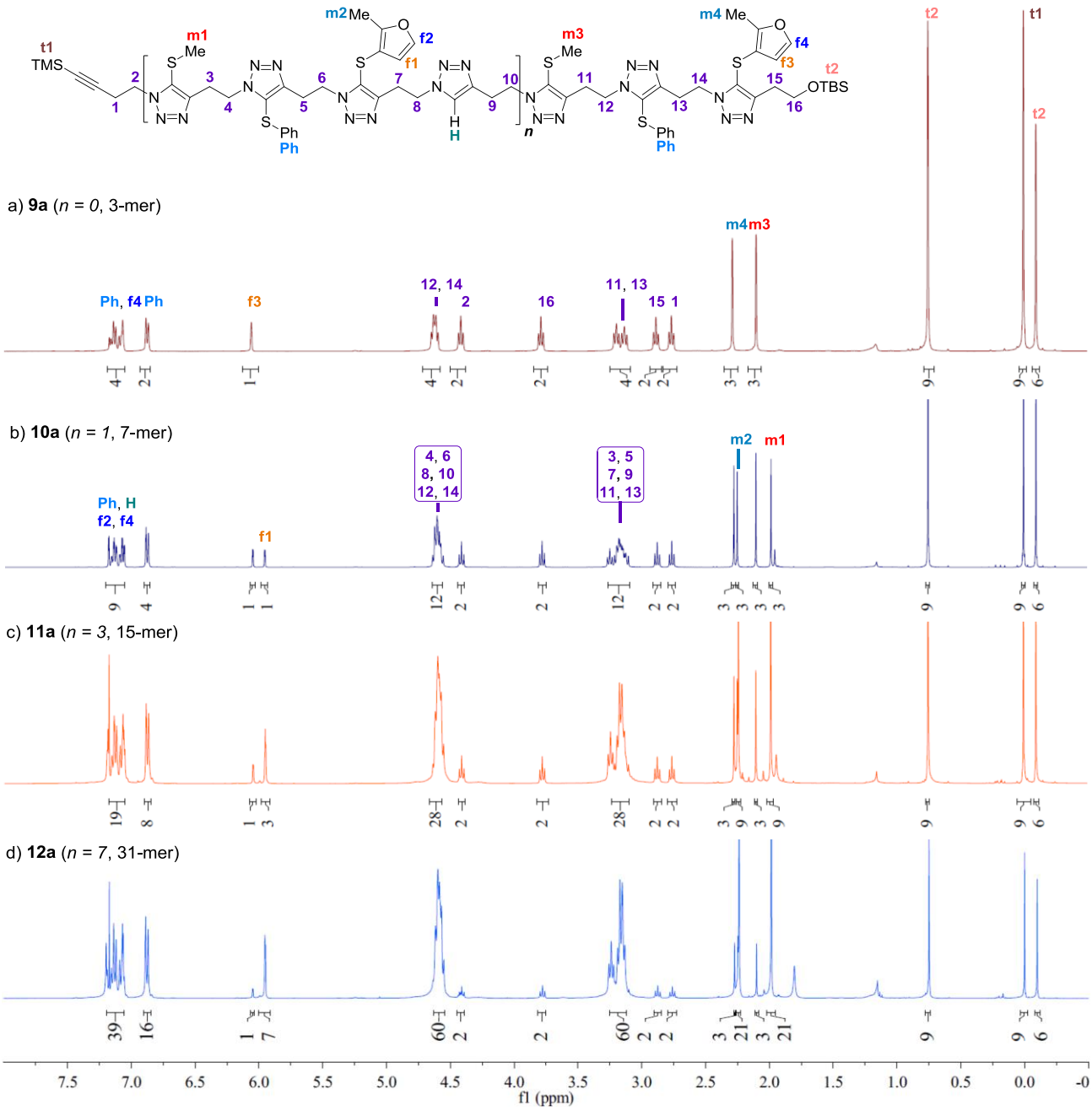


Figure S12. Comparison of ^{1}H NMR spectra for the α-TMS-ω-OTBS oligomers ($CDCl_3$, 400 MHz).

IX. MS/MS Spectra of 6b

The monomer sequence of the final sequence-defined polytriazole **6b** was determined by the tandem mass spectrometry. The charged ion of *m/z* 1342.24 for **6b** was selected for fragmentation.

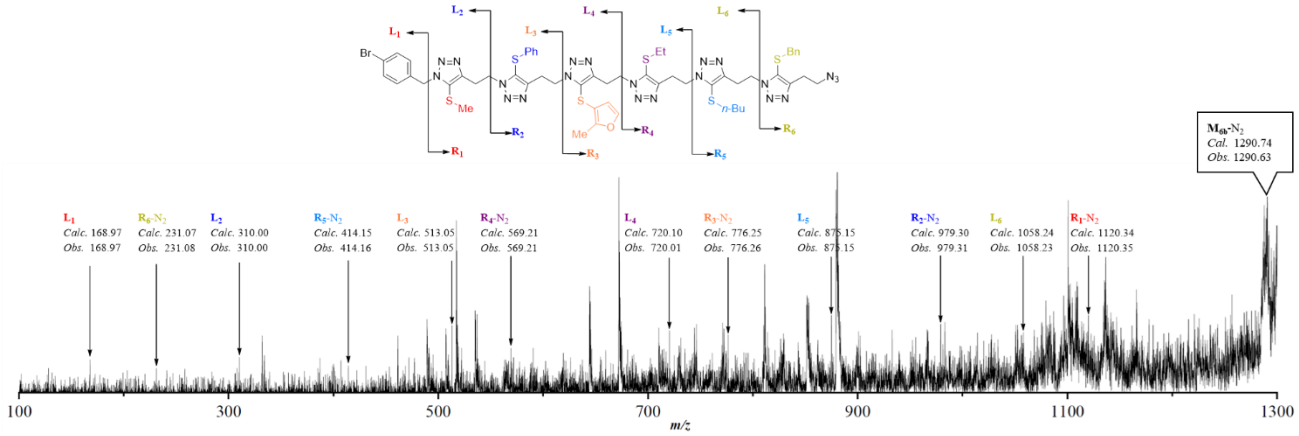


Figure S13. Tandem mass spectra of **6b** with sequence analysis.

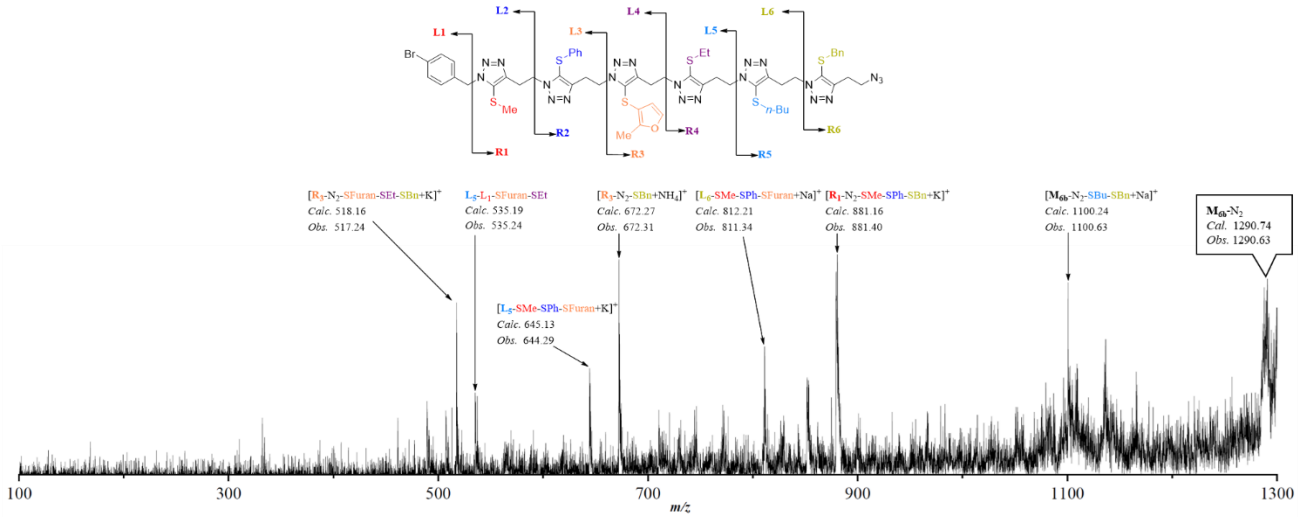


Figure S14. Tandem mass spectra of **6b** with analysis of major peaks.

X. NMR Spectrum

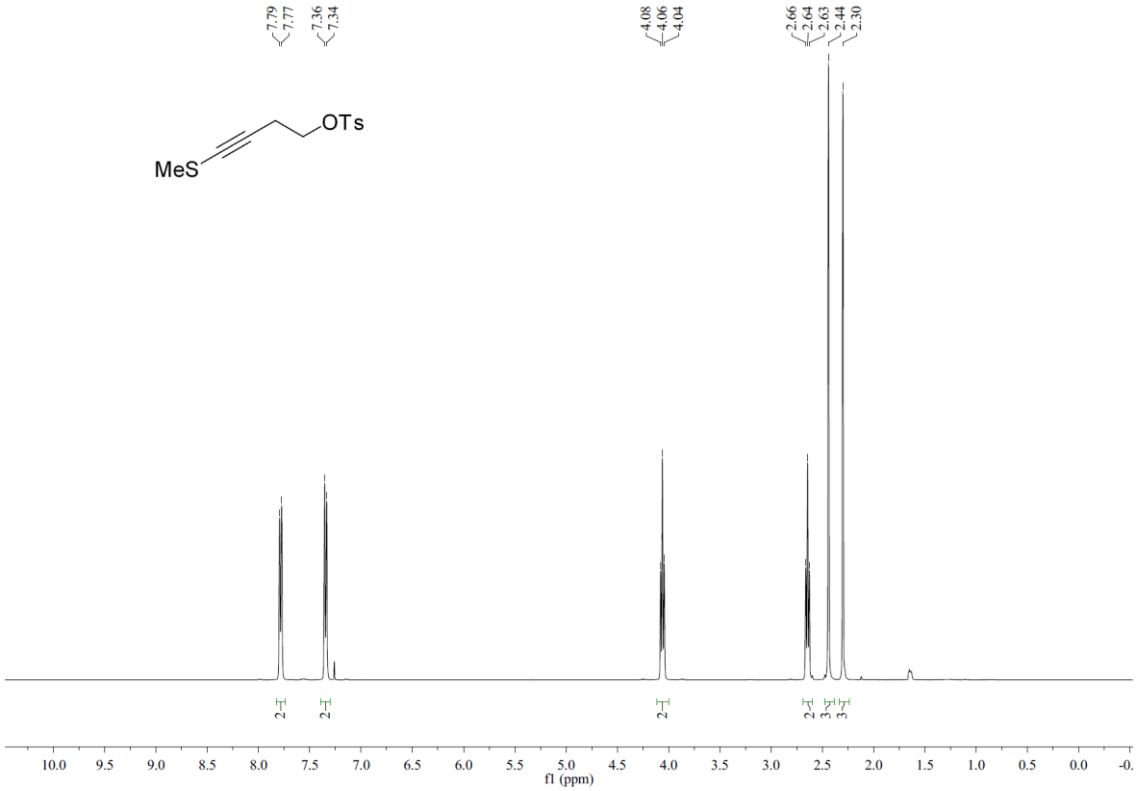


Figure S15. ^{1}H NMR spectra of **S1** ($CDCl_3$, 400 MHz).

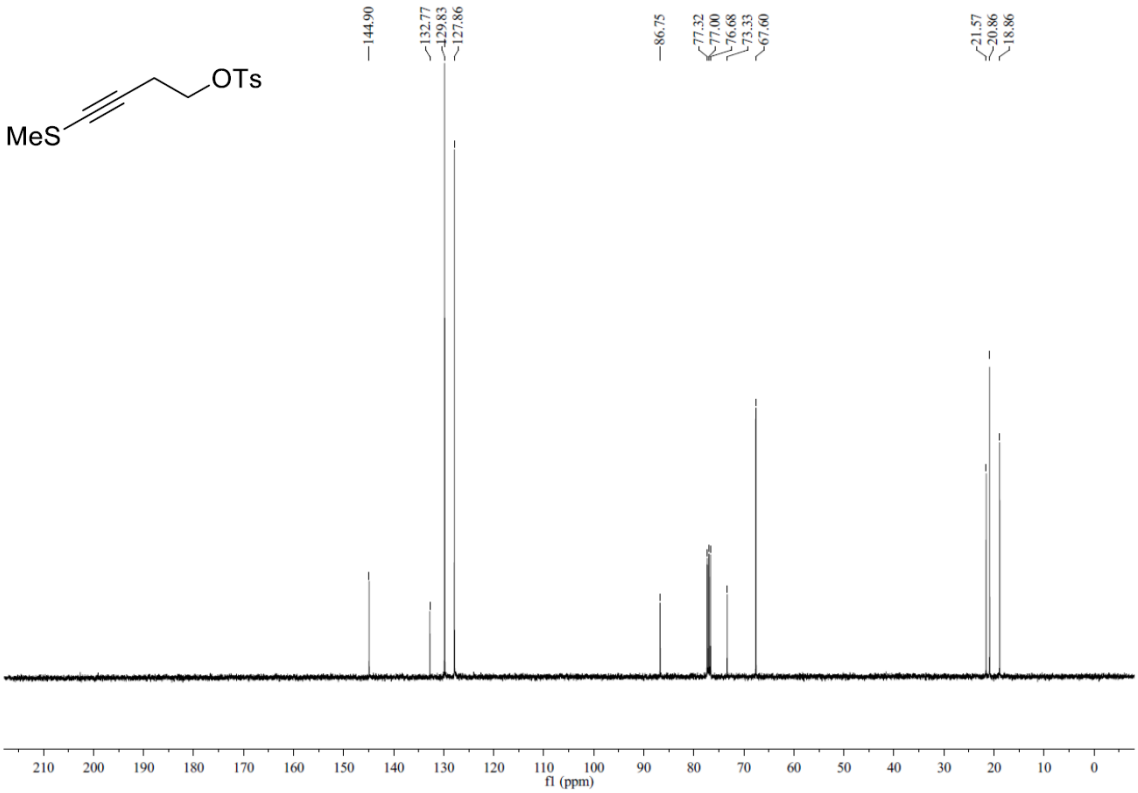


Figure S16. ^{13}C NMR spectra of **S1** ($CDCl_3$, 100 MHz).

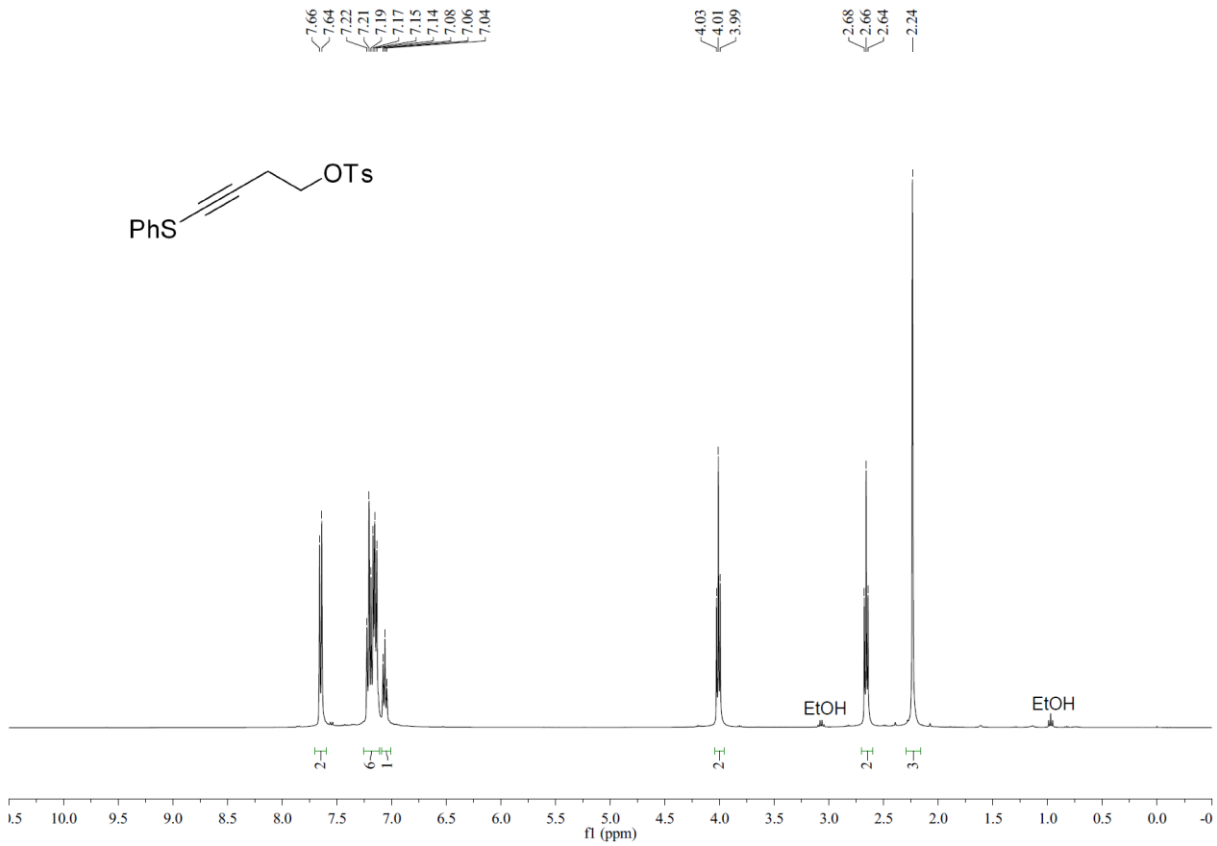


Figure S17. ^{1}H NMR spectra of **S2** ($CDCl_3$, 400 MHz).

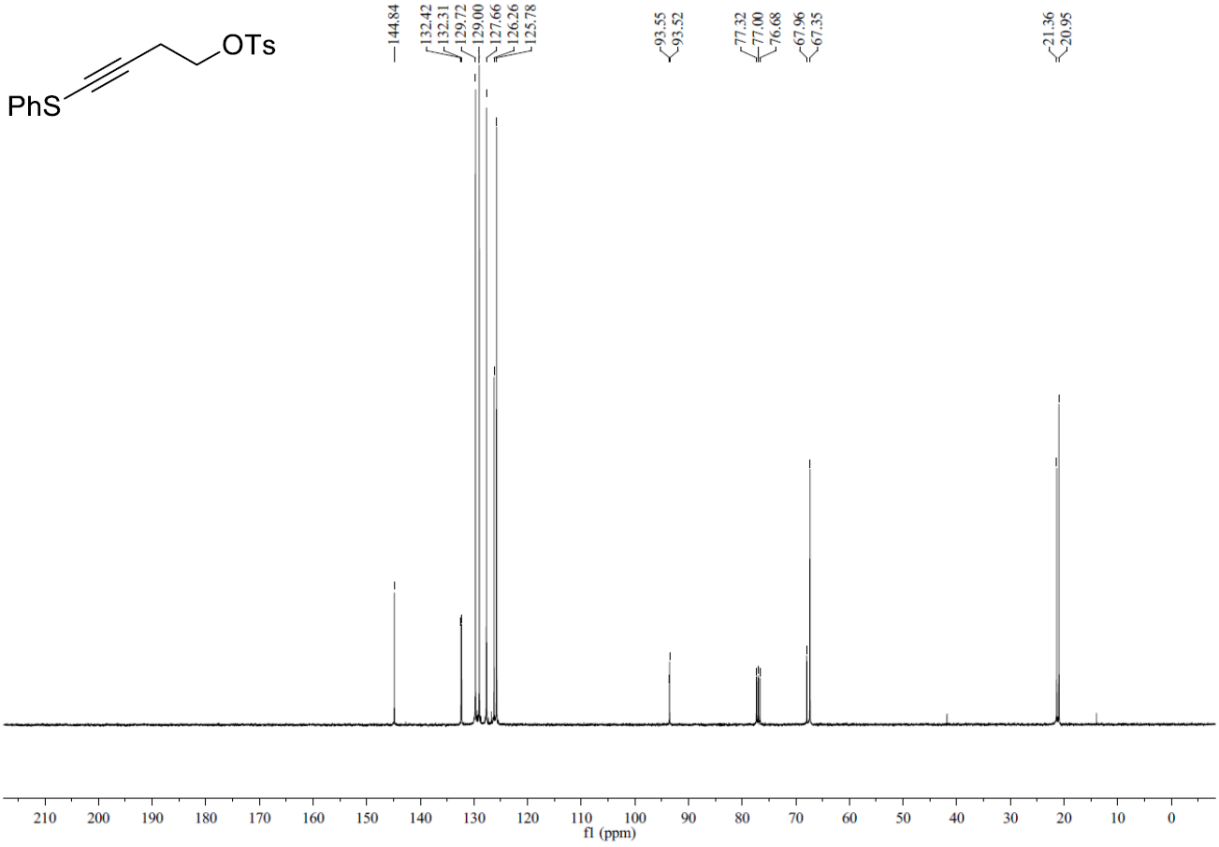


Figure S18. ^{13}C NMR spectra of **S2** ($CDCl_3$, 100 MHz).

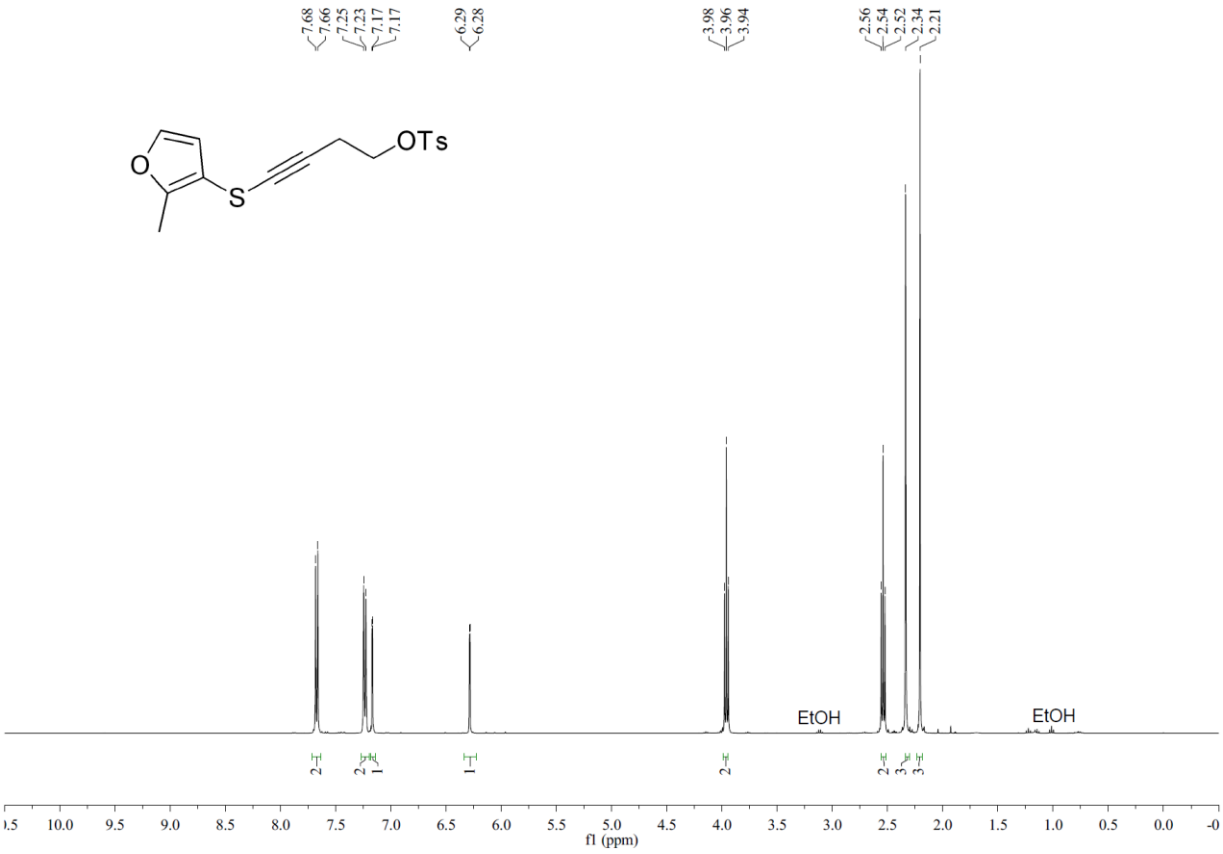


Figure S19. ^{1}H NMR spectra of **S3** ($CDCl_3$, 400 MHz).

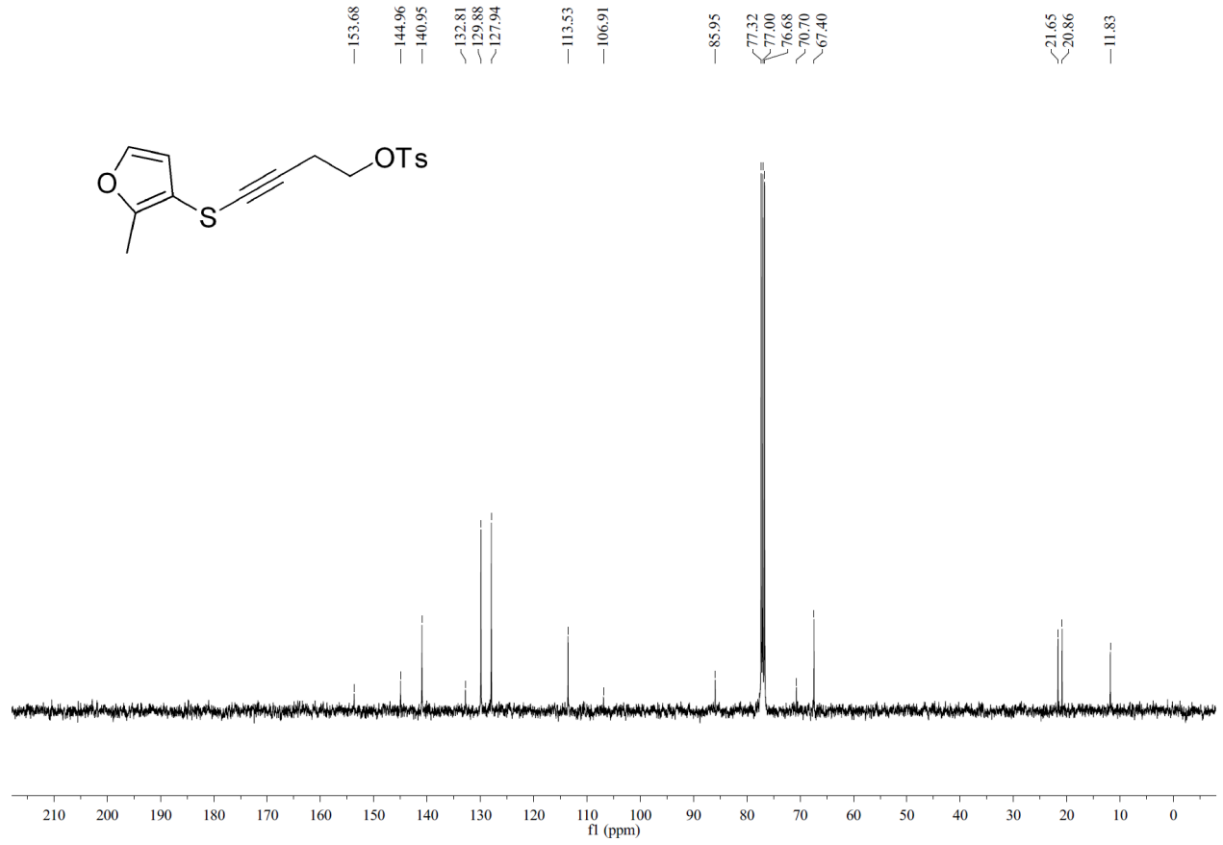


Figure S20. ^{13}C NMR spectra of **S3** ($CDCl_3$, 100 MHz).

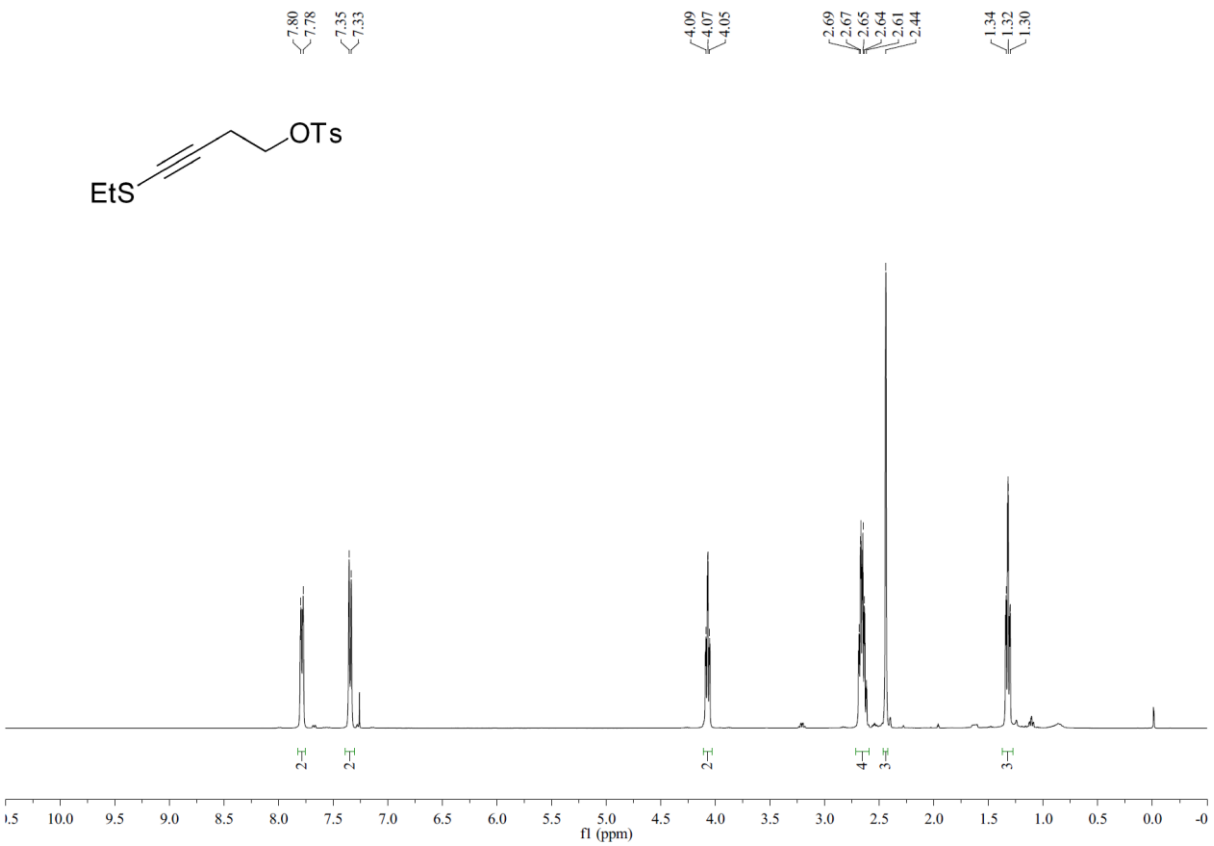


Figure S21. ^{1}H NMR spectra of **S4** ($CDCl_3$, 400 MHz).

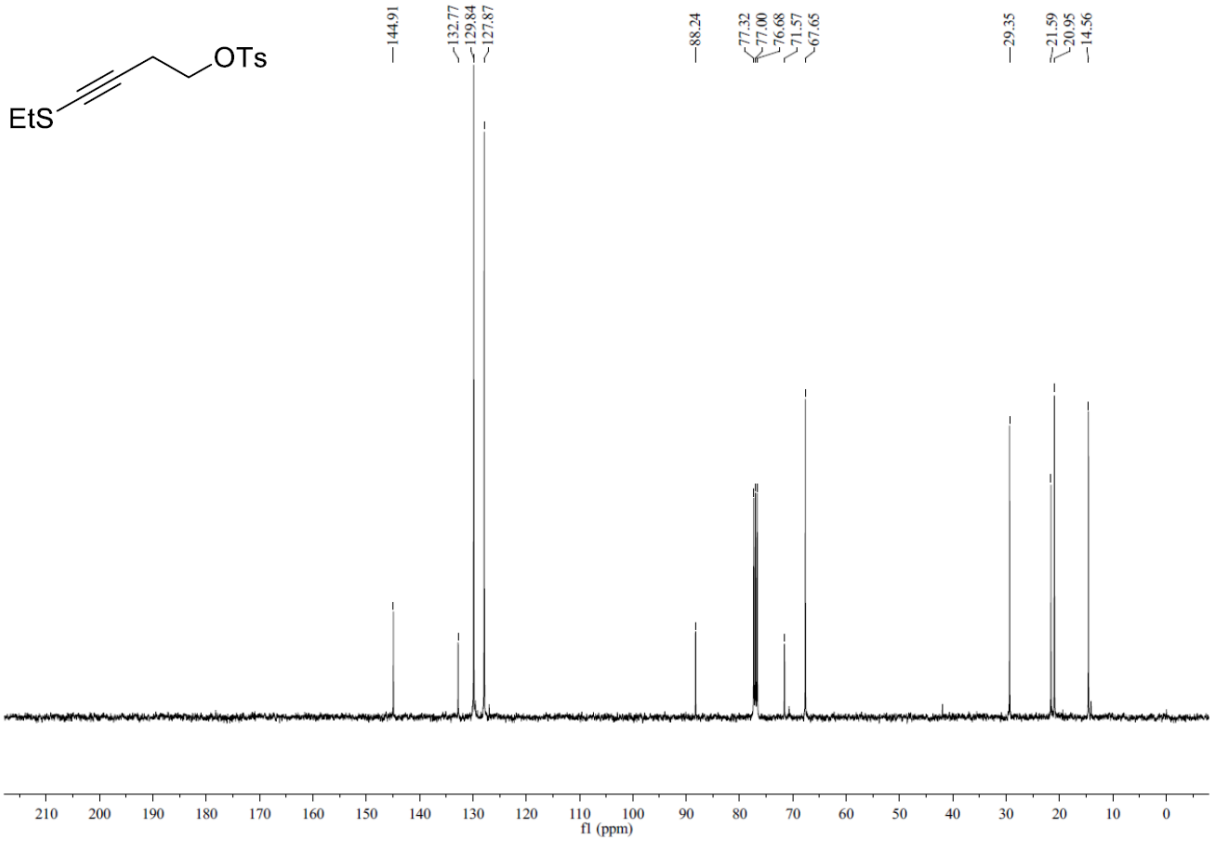


Figure S22. ^{13}C NMR spectra of **S4** ($CDCl_3$, 100 MHz).

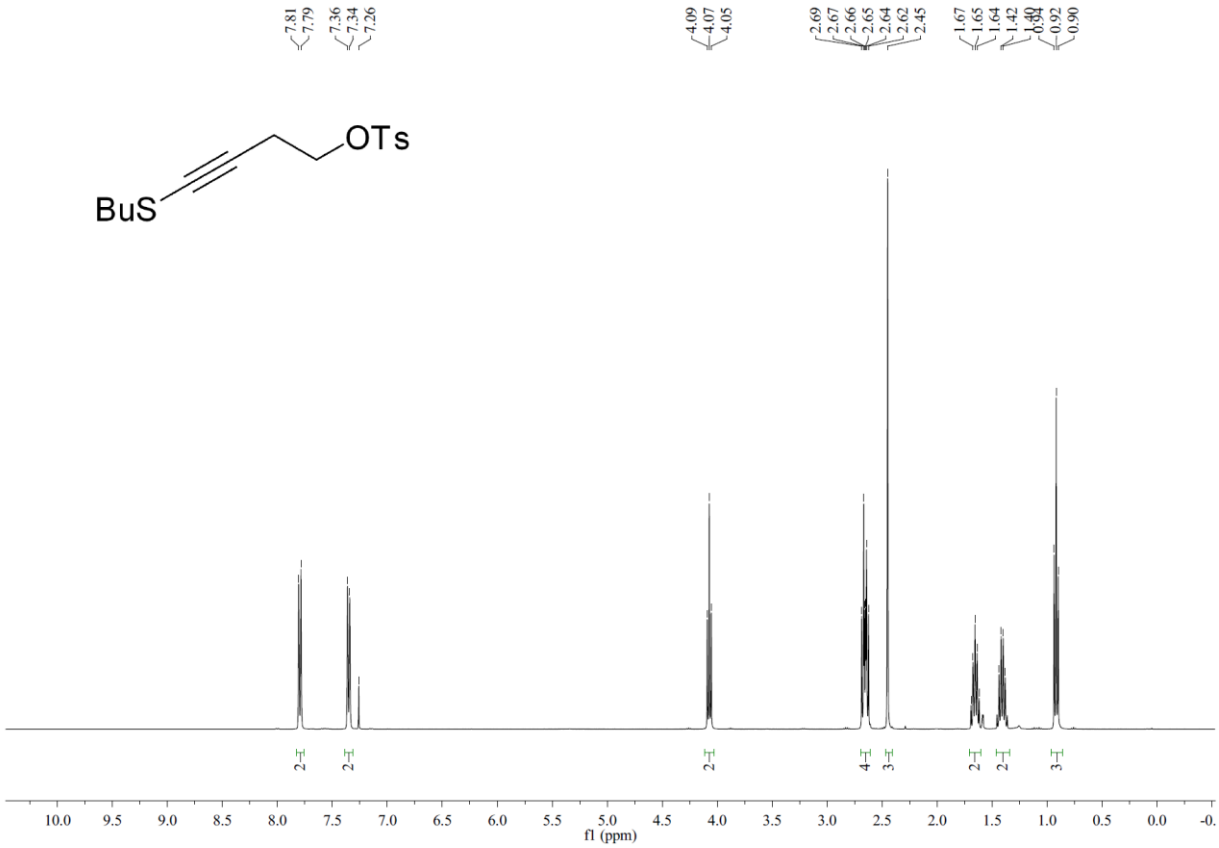


Figure S23. ^{1}H NMR spectra of **S5** ($CDCl_3$, 400 MHz).

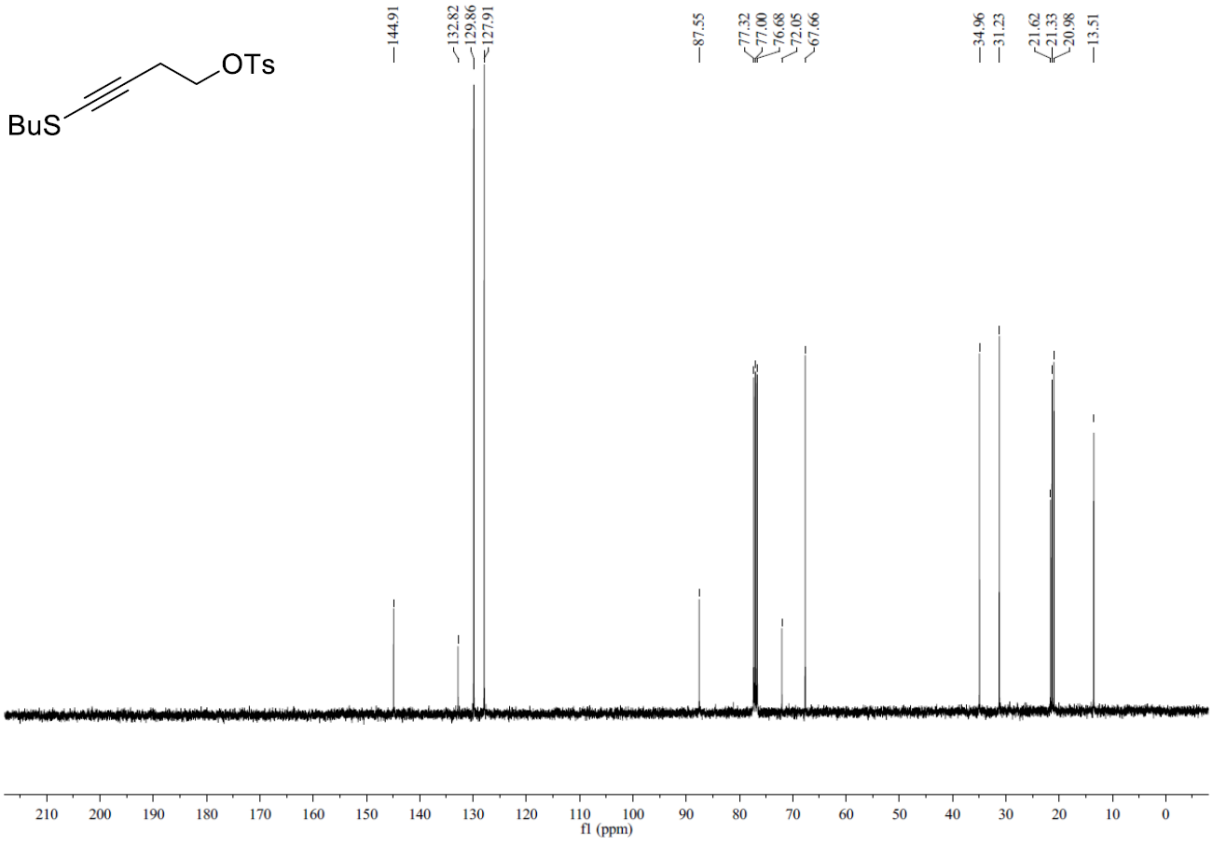


Figure S24. ^{13}C NMR spectra of **S5** ($CDCl_3$, 100 MHz).

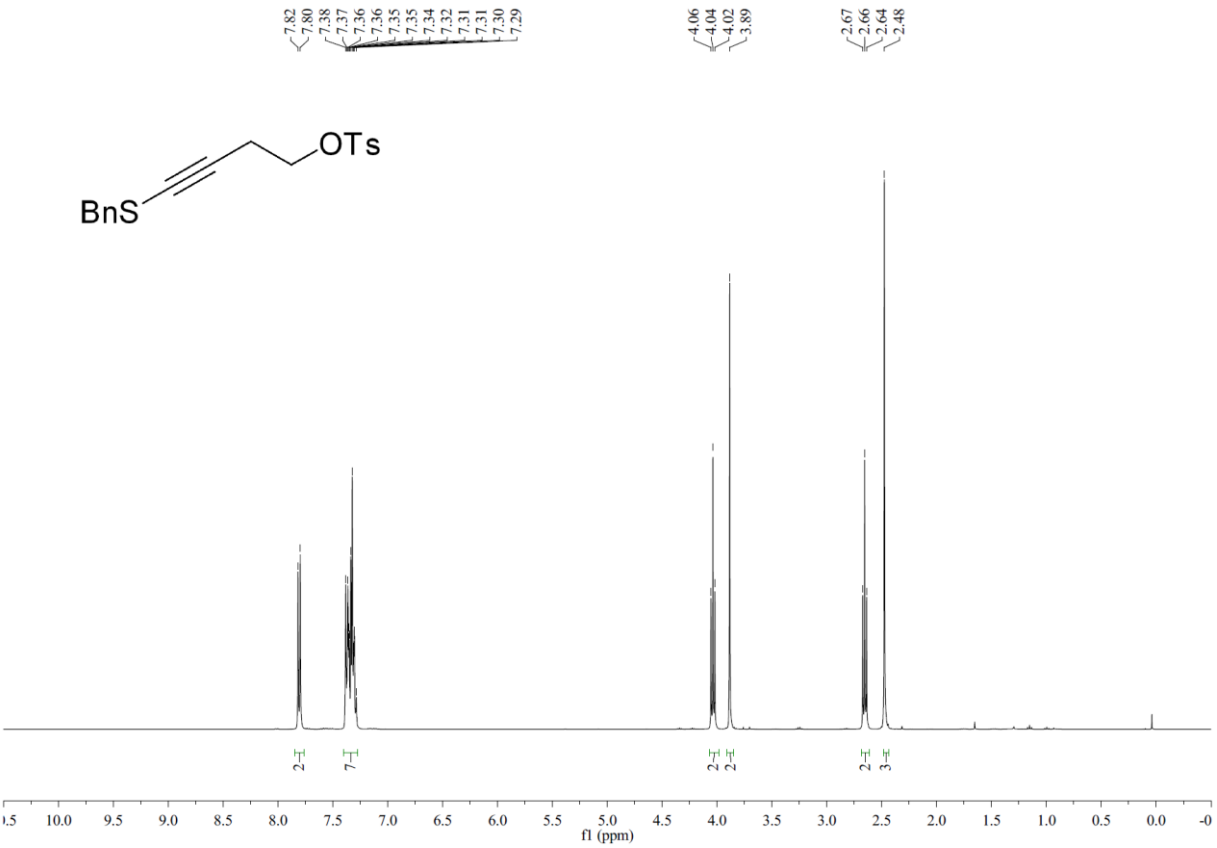


Figure S25. ^{1}H NMR spectra of **S6** ($CDCl_3$, 400 MHz).

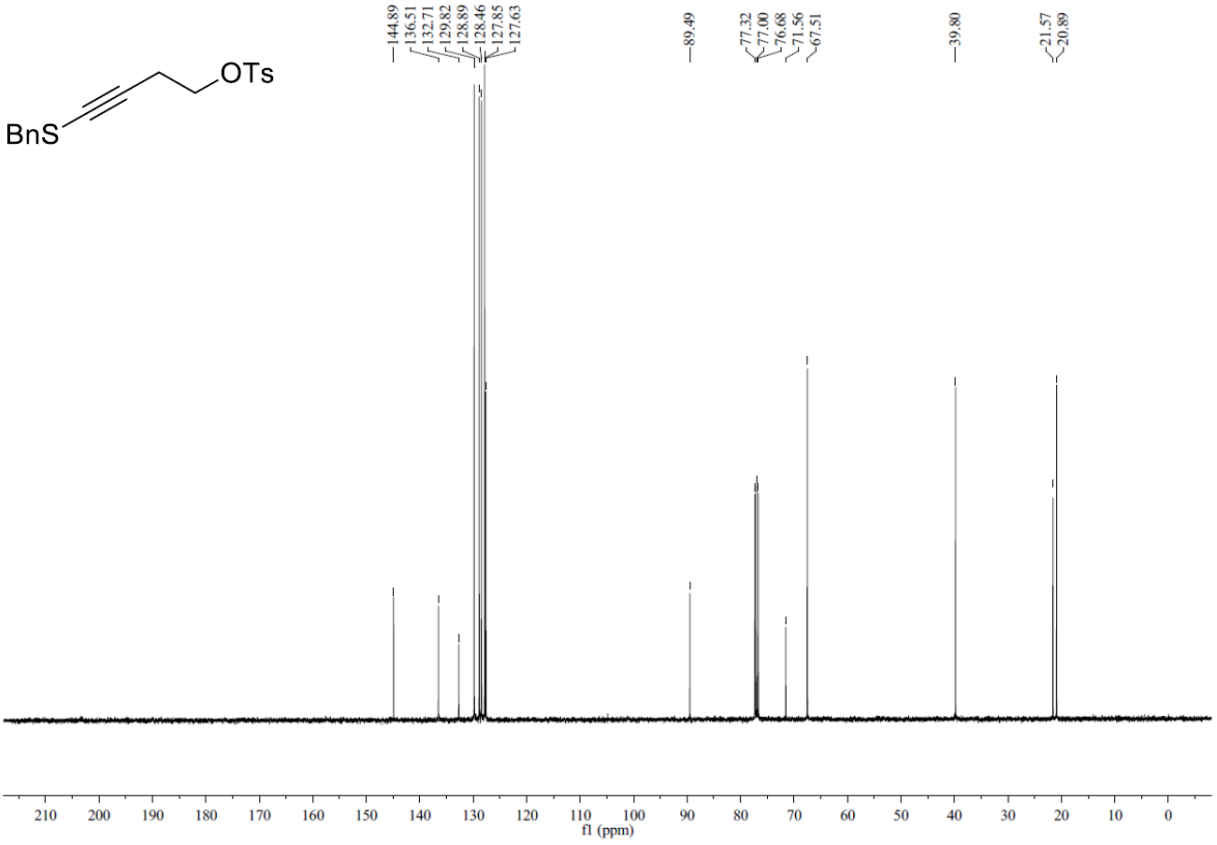


Figure S26. ^{13}C NMR spectra of **S6** ($CDCl_3$, 100 MHz).

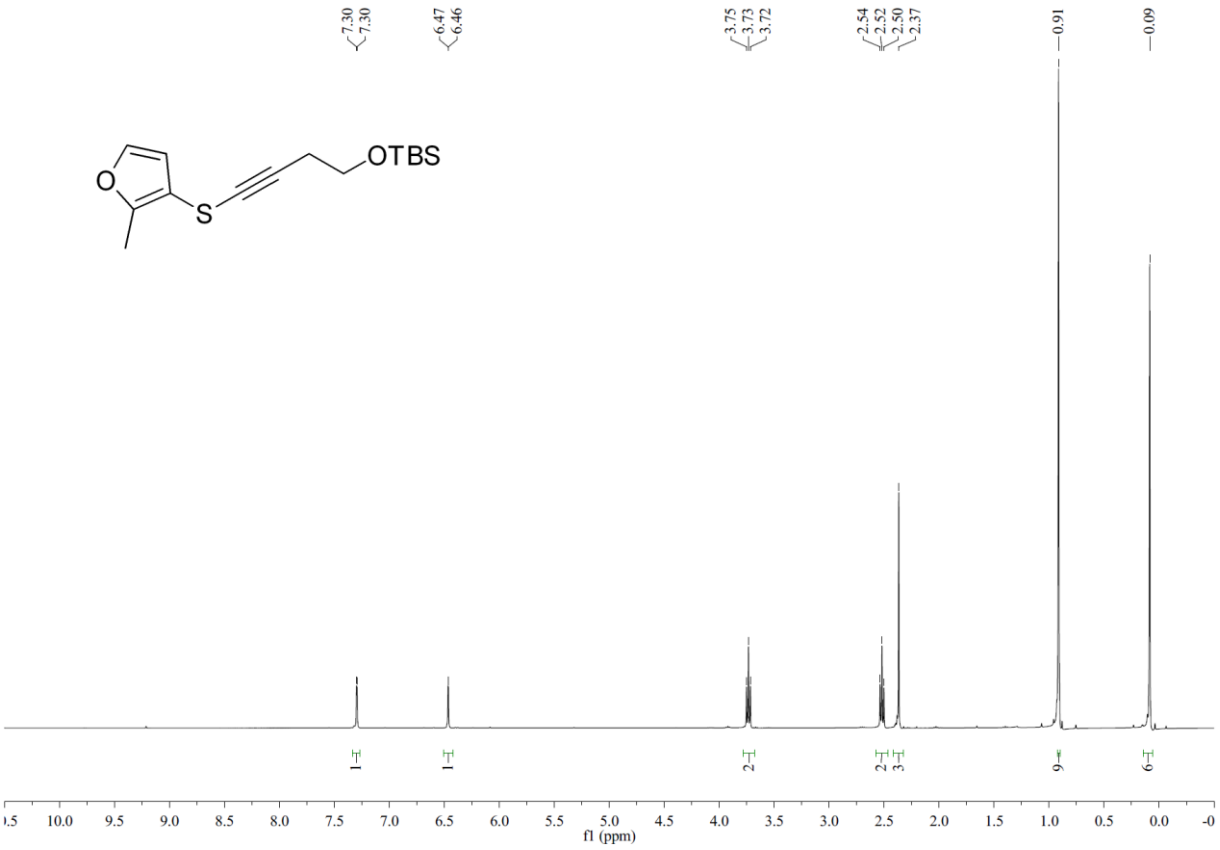


Figure S27. ^{1}H NMR spectra of **S7** ($CDCl_3$, 400 MHz).

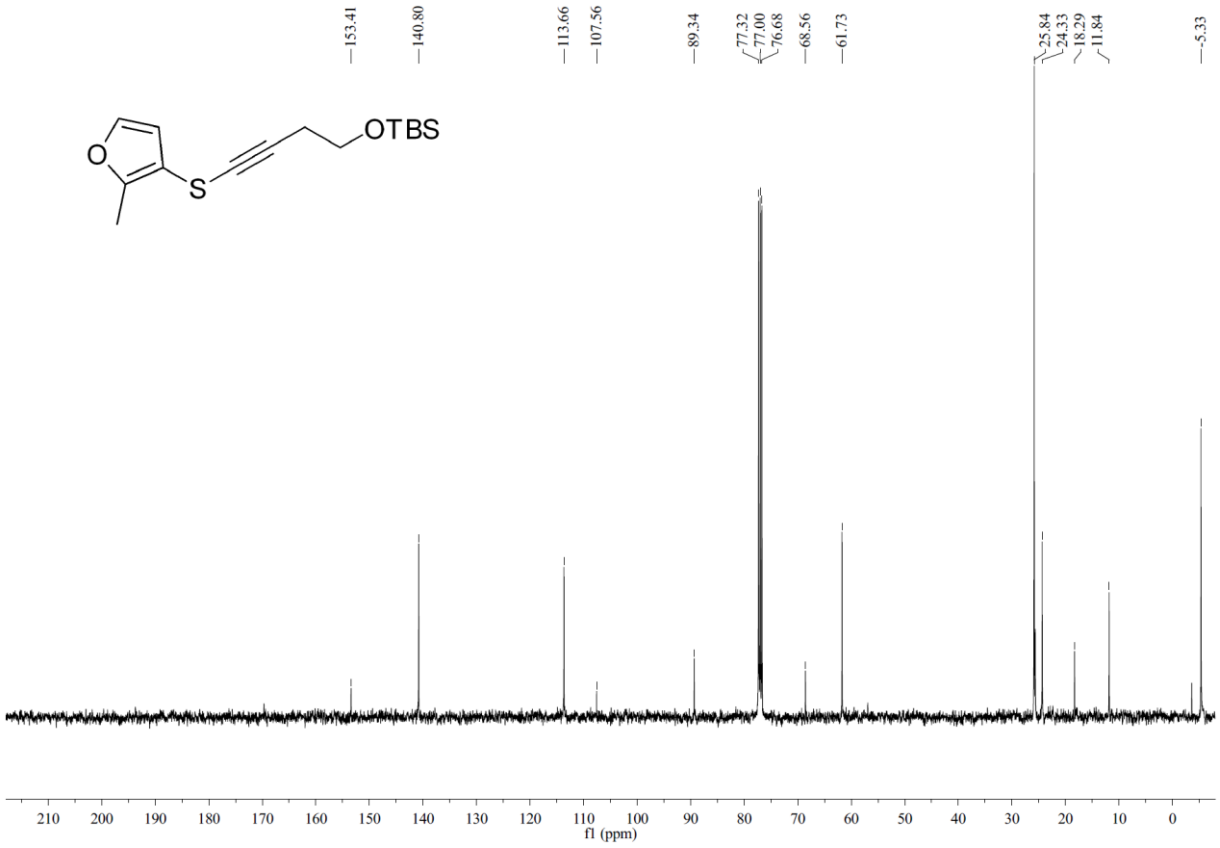


Figure S28. ^{13}C NMR spectra of **S7** ($CDCl_3$, 100 MHz).

Figure S29. ^{1}H NMR spectra of **A1** ($CDCl_3$, 400 MHz).

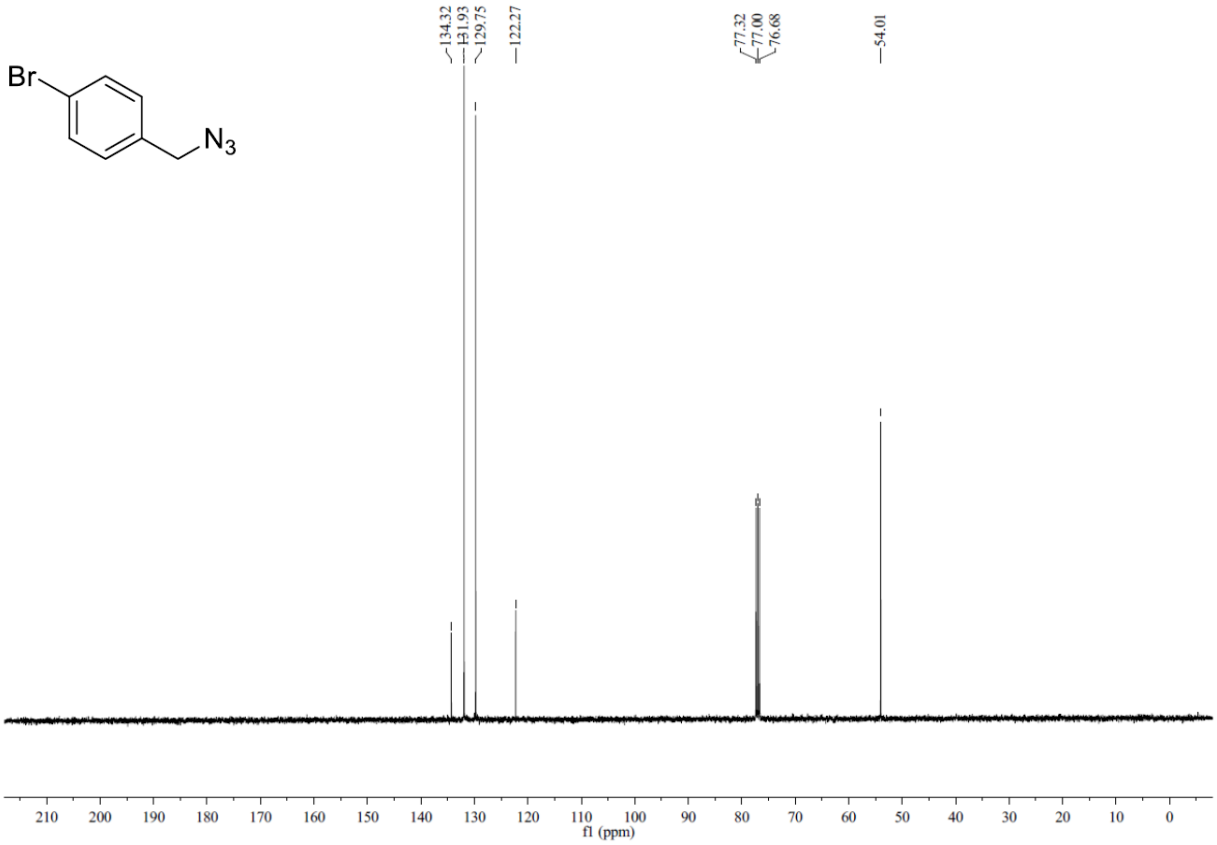


Figure S30. ^{13}C NMR spectra of **A1** ($CDCl_3$, 100 MHz).

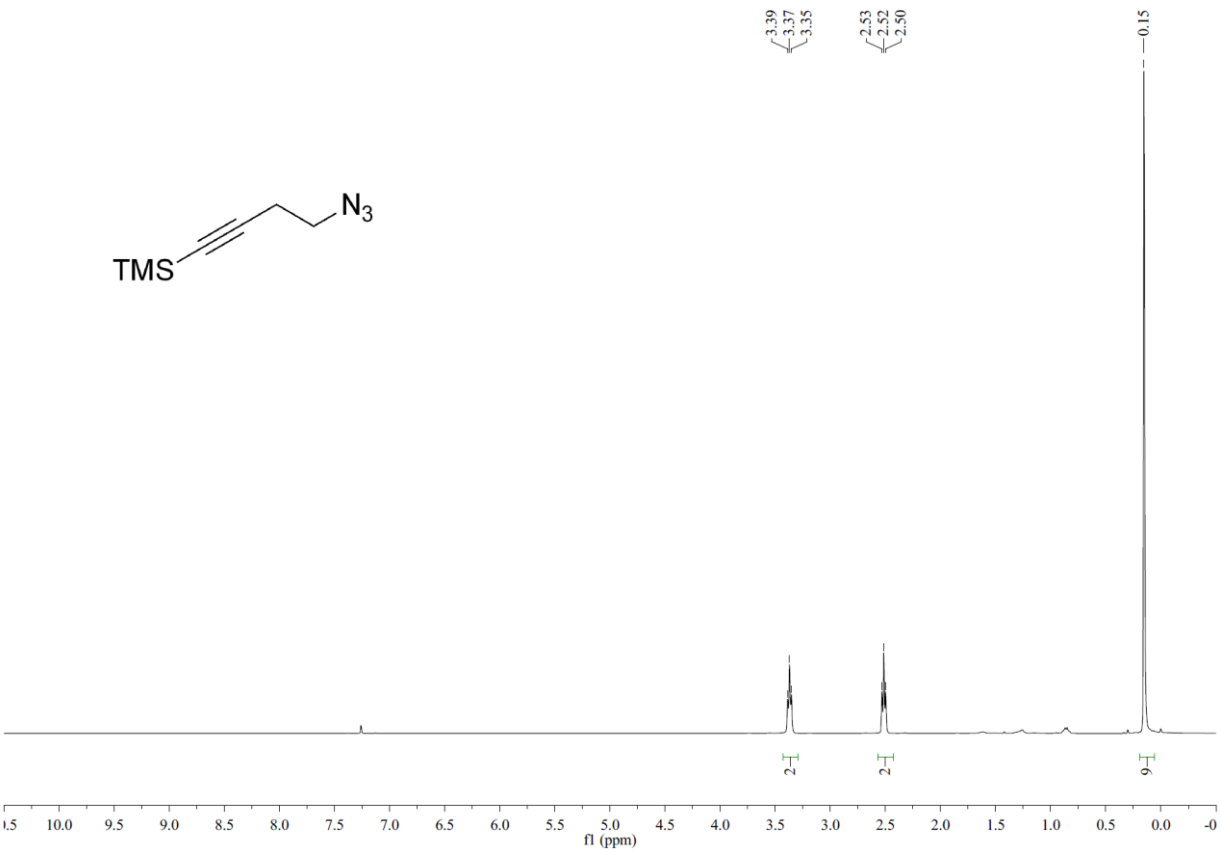


Figure S31. ^{1}H NMR spectra of **A2** ($CDCl_3$, 400 MHz).

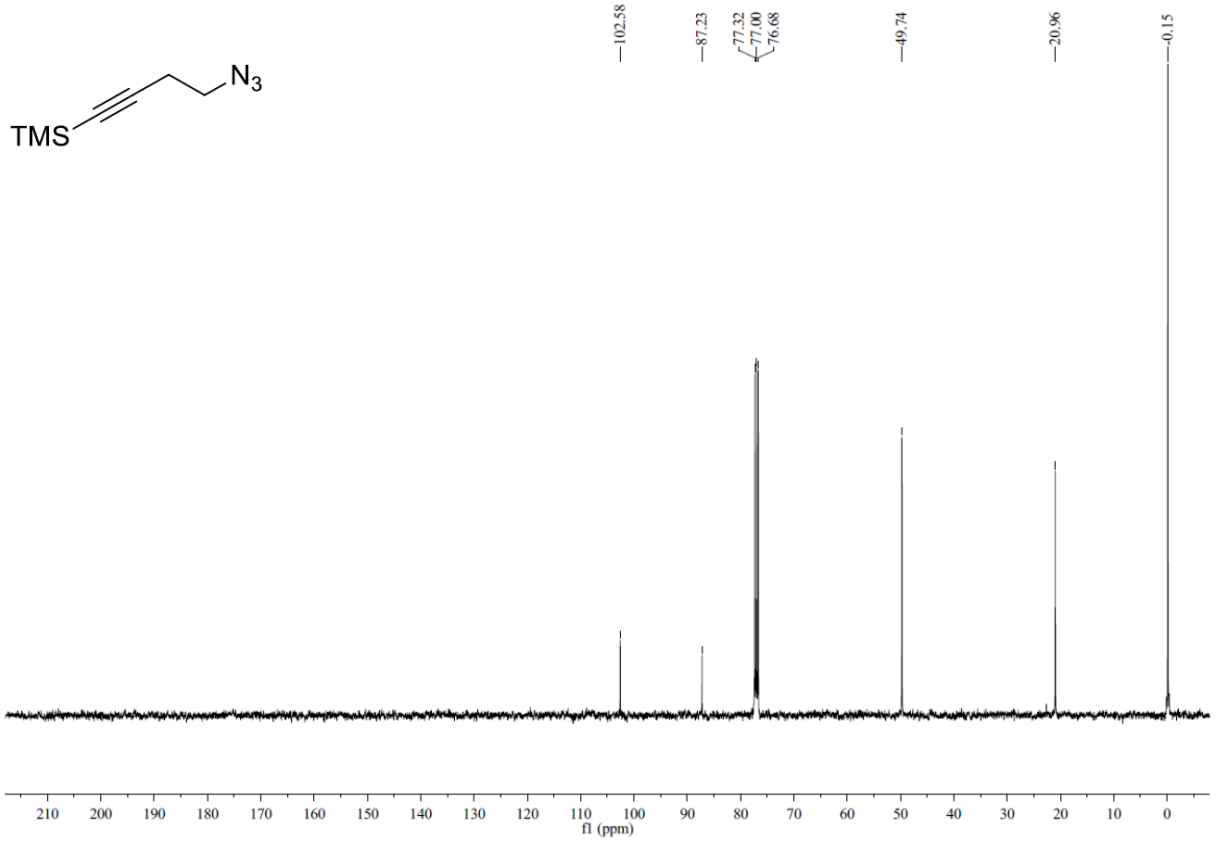


Figure S32. ^{13}C NMR spectra of **A2** ($CDCl_3$, 100 MHz).

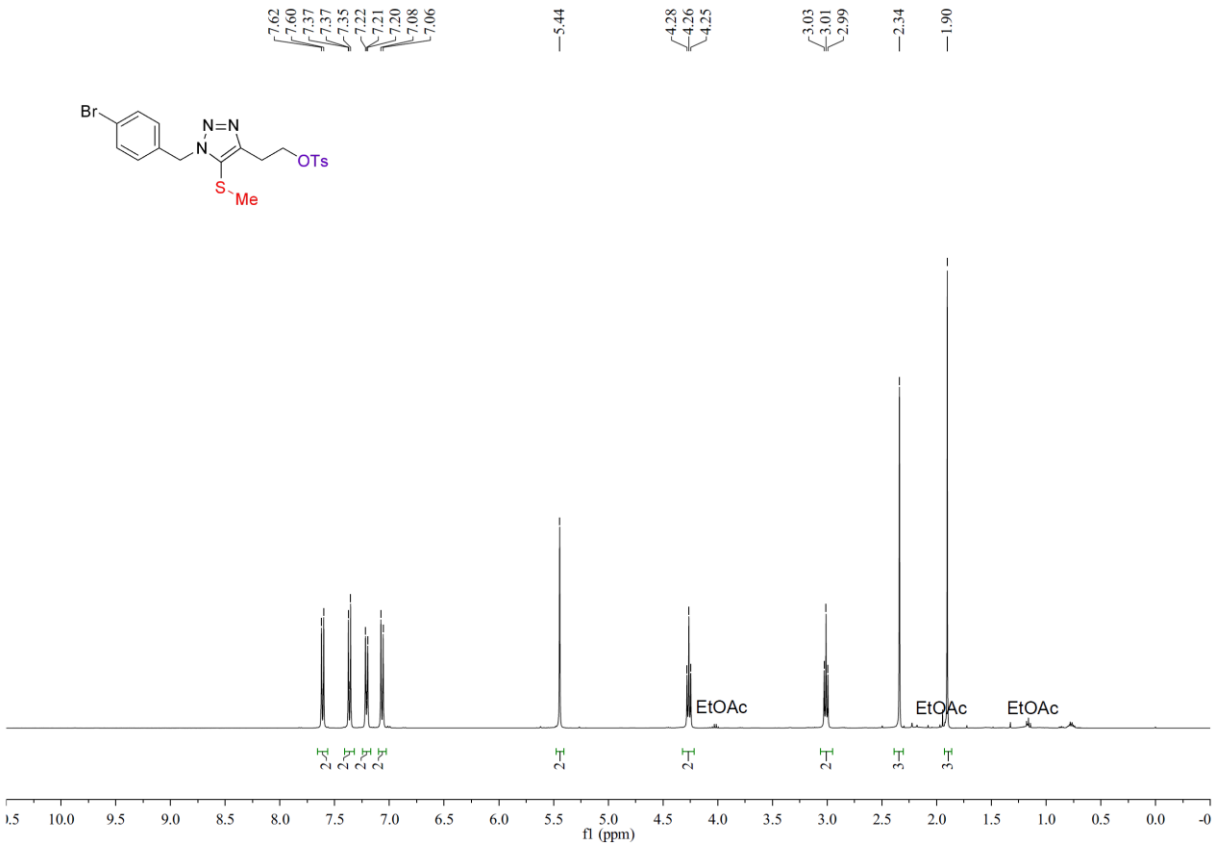


Figure S33. ^{1}H NMR spectra of **1a** ($CDCl_3$, 400 MHz).

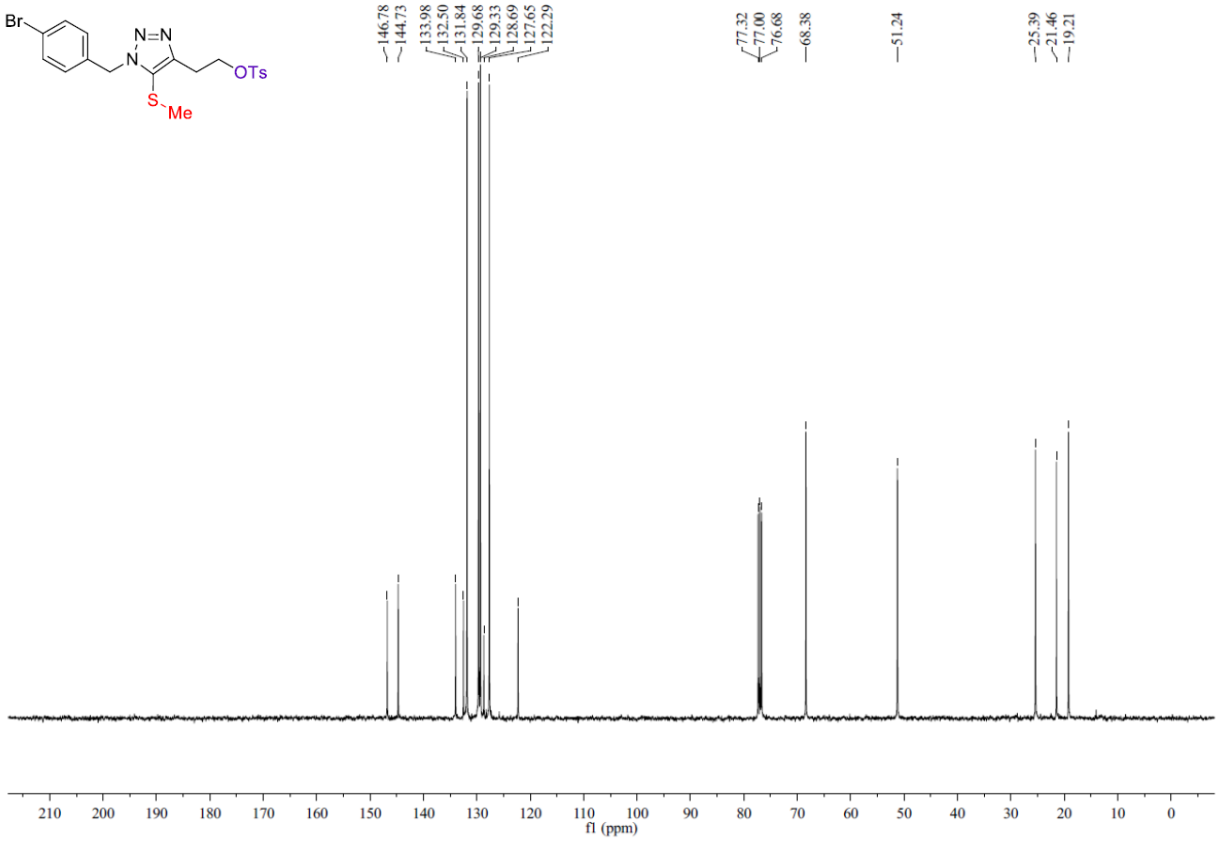


Figure S34. ^{13}C NMR spectra of **1a** ($CDCl_3$, 100 MHz).

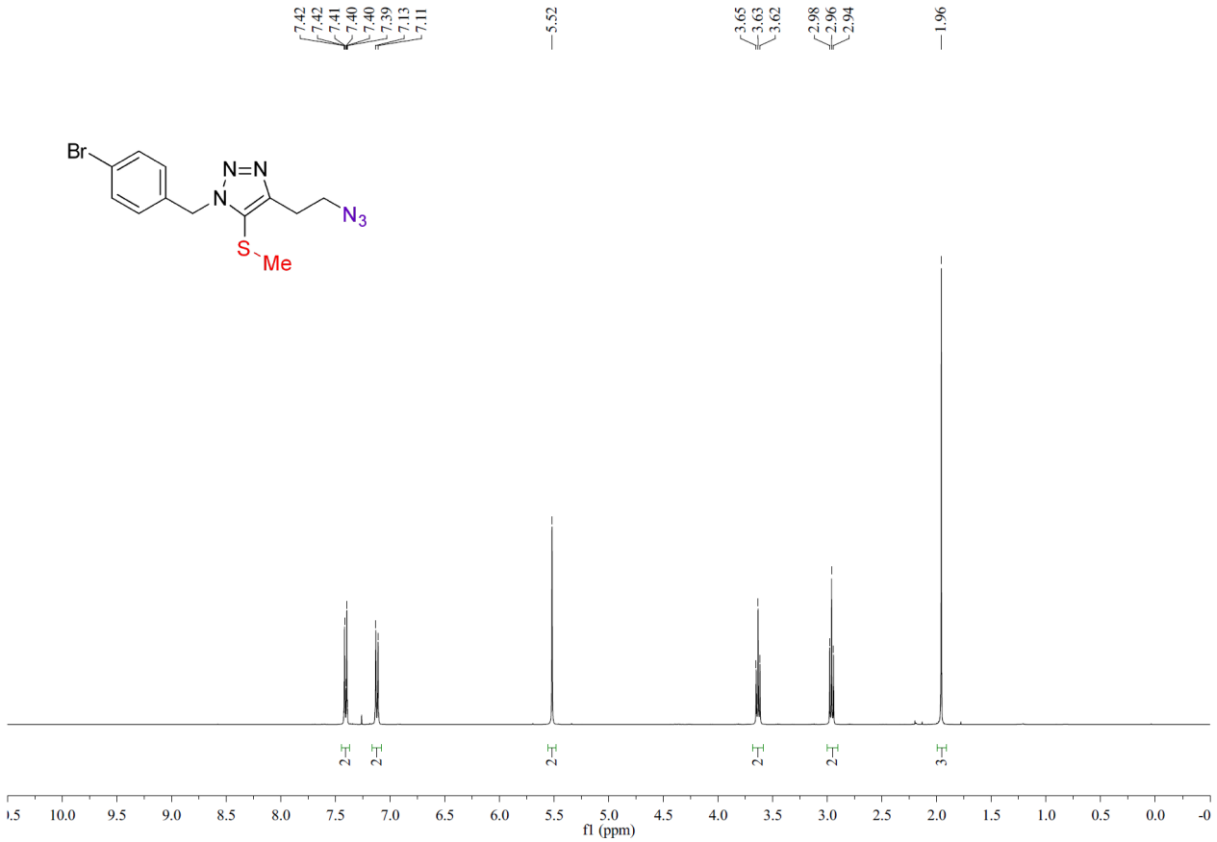


Figure S35. ^{1}H NMR spectra of **1b** ($CDCl_3$, 400 MHz).

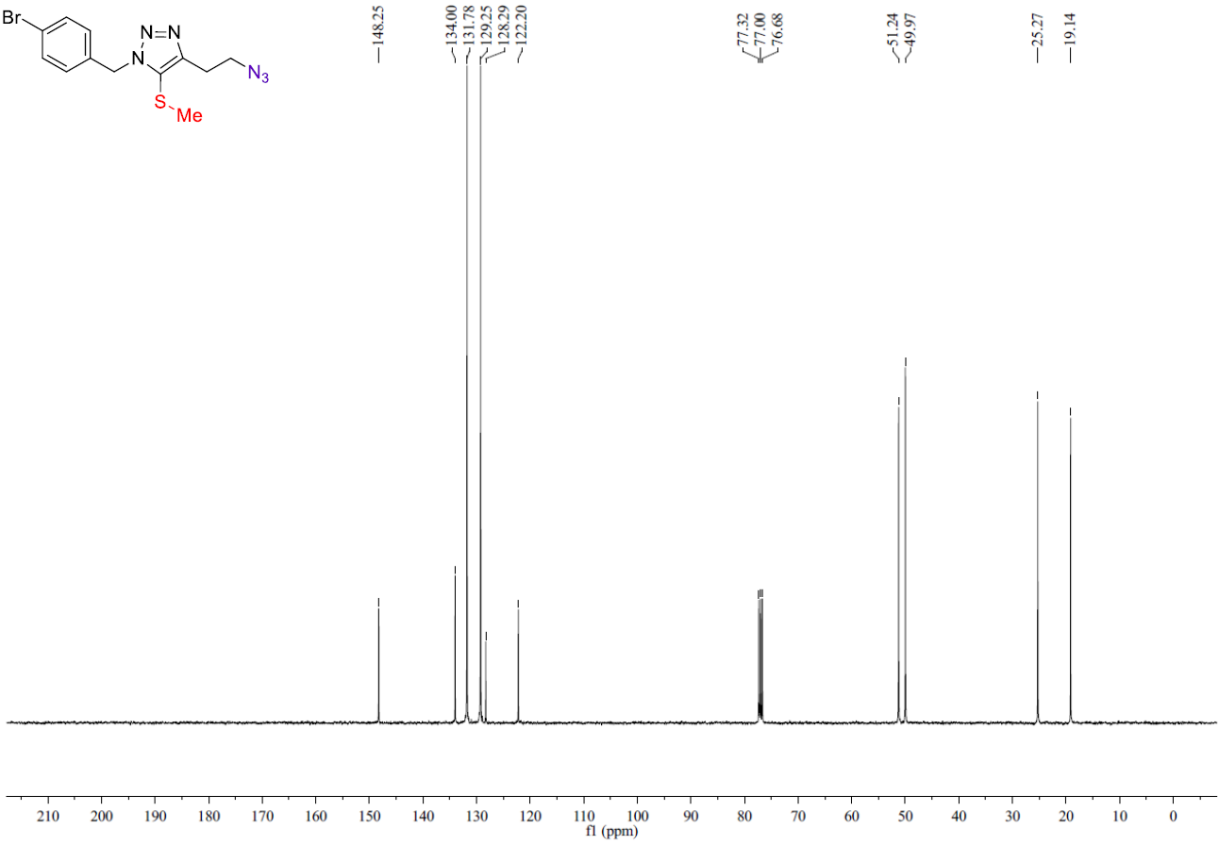


Figure S36. ^{13}C NMR spectra of **1b** ($CDCl_3$, 100 MHz).

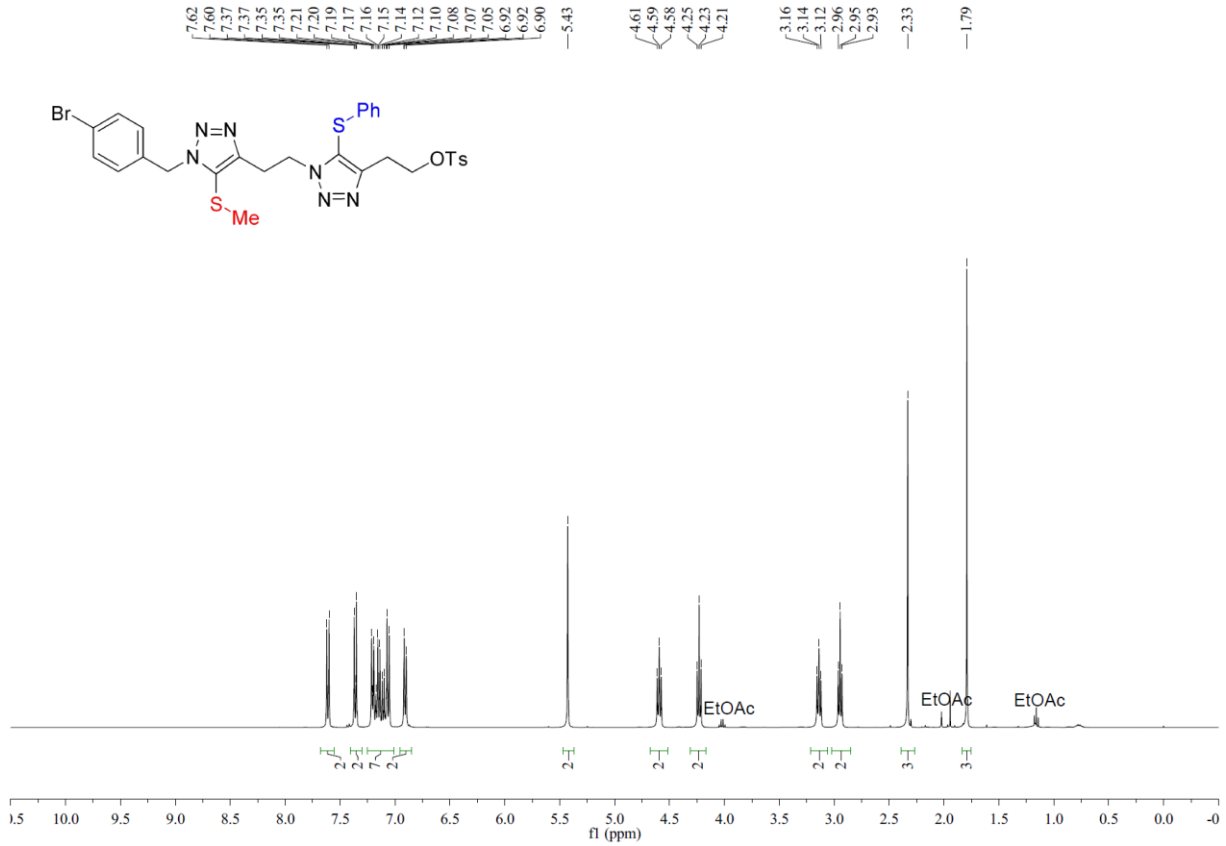


Figure S37. ^{1}H NMR spectra of **2a** ($CDCl_3$, 400 MHz).

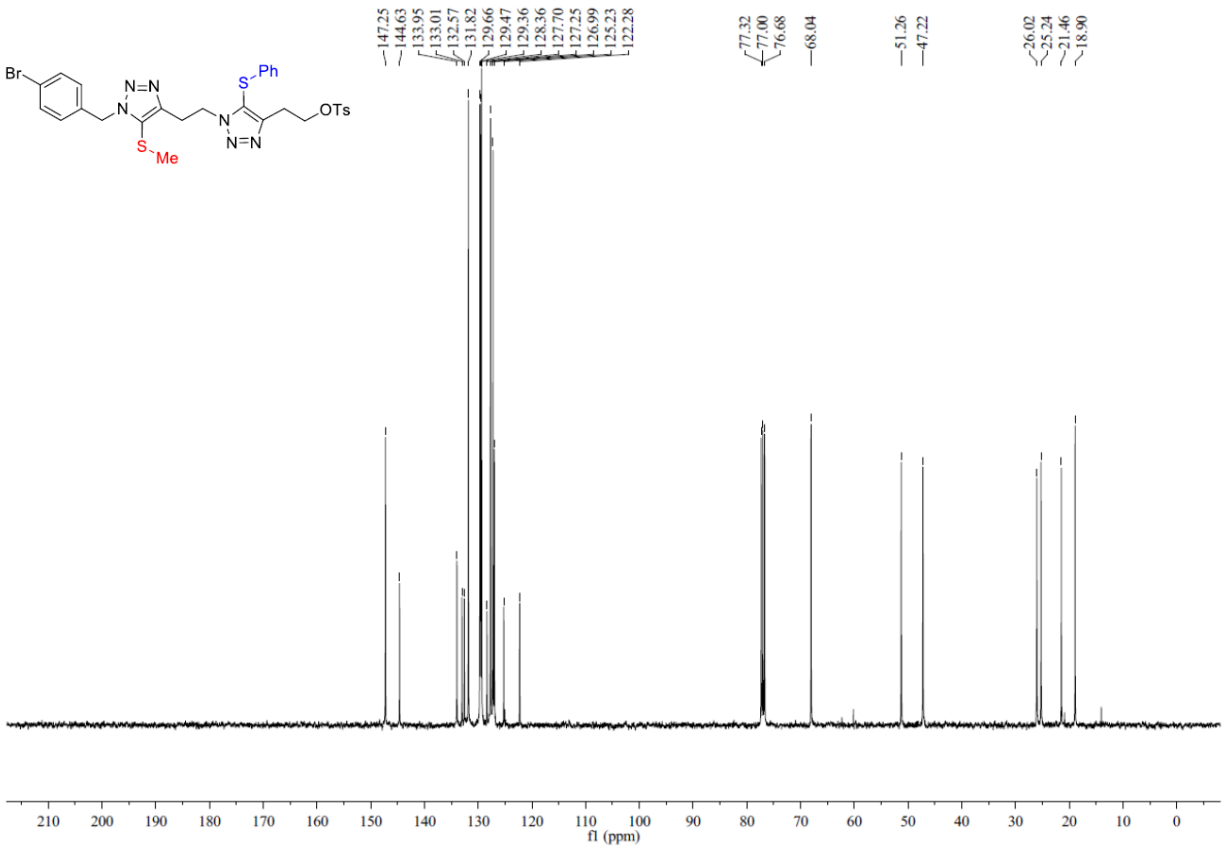


Figure S38. ^{13}C NMR spectra of **2a** ($CDCl_3$, 100 MHz).

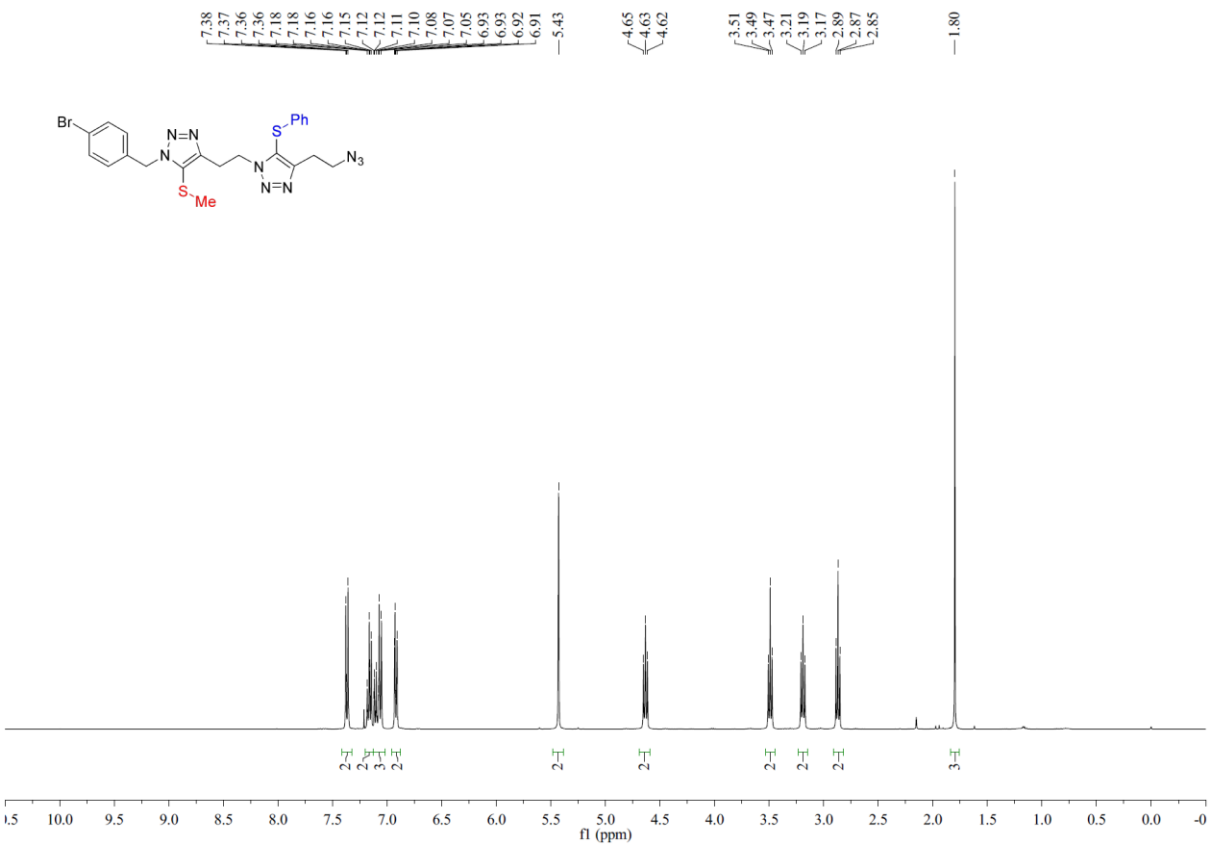


Figure S39. ^{1}H NMR spectra of **2b** ($CDCl_3$, 400 MHz).

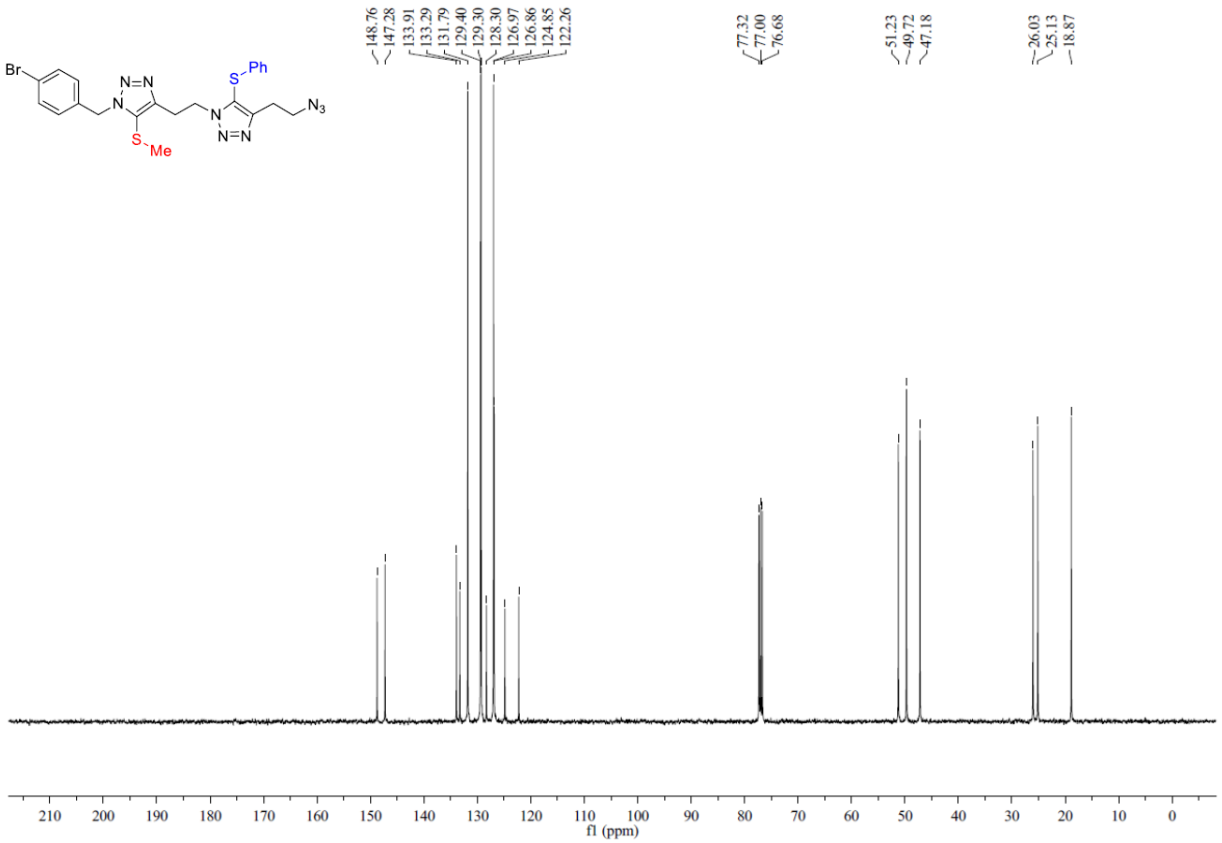


Figure S40. ^{13}C NMR spectra of **2b** ($CDCl_3$, 100 MHz).

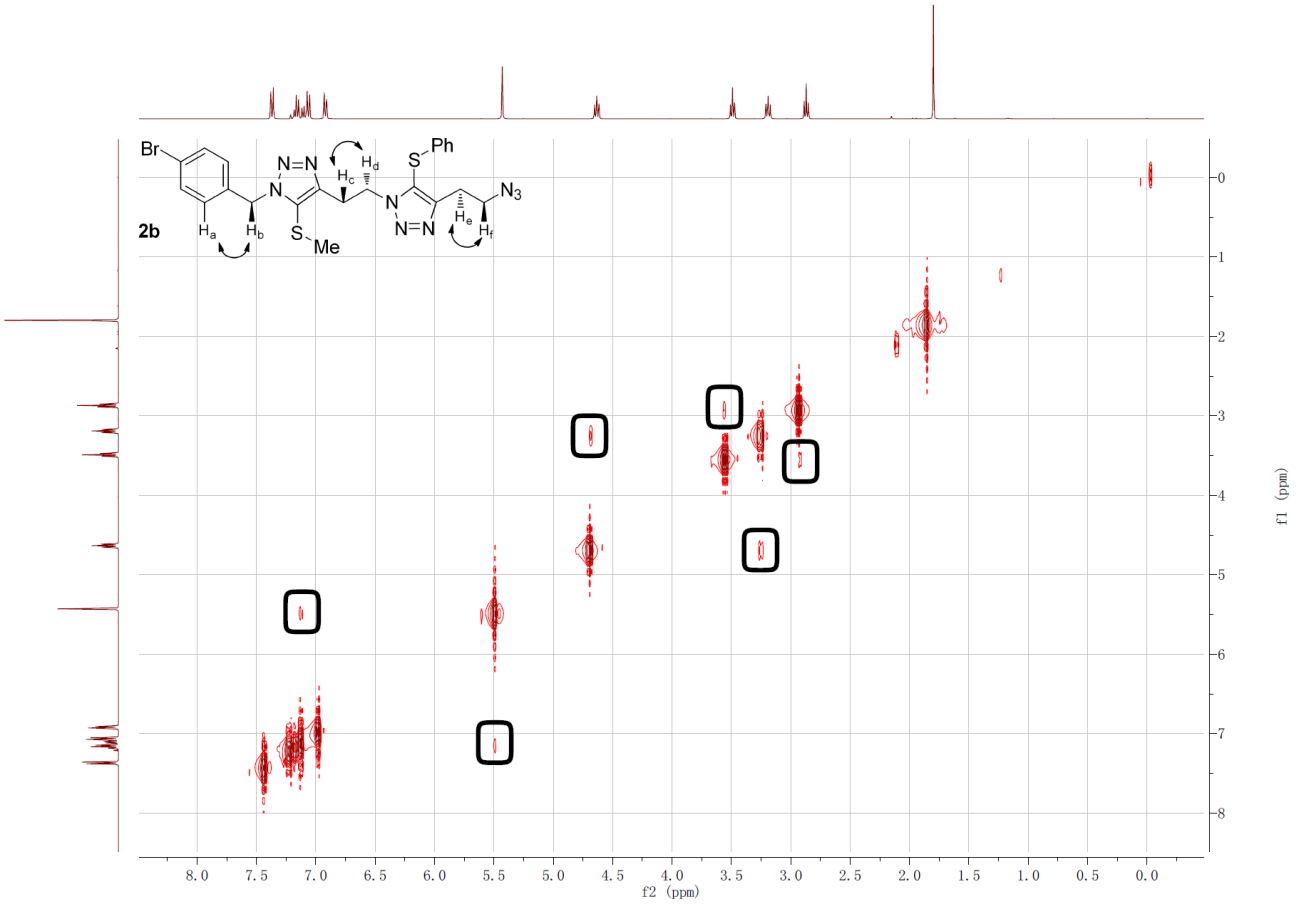


Figure S41. 2D NOESY spectra of **2b** ($CDCl_3$, 400 MHz).

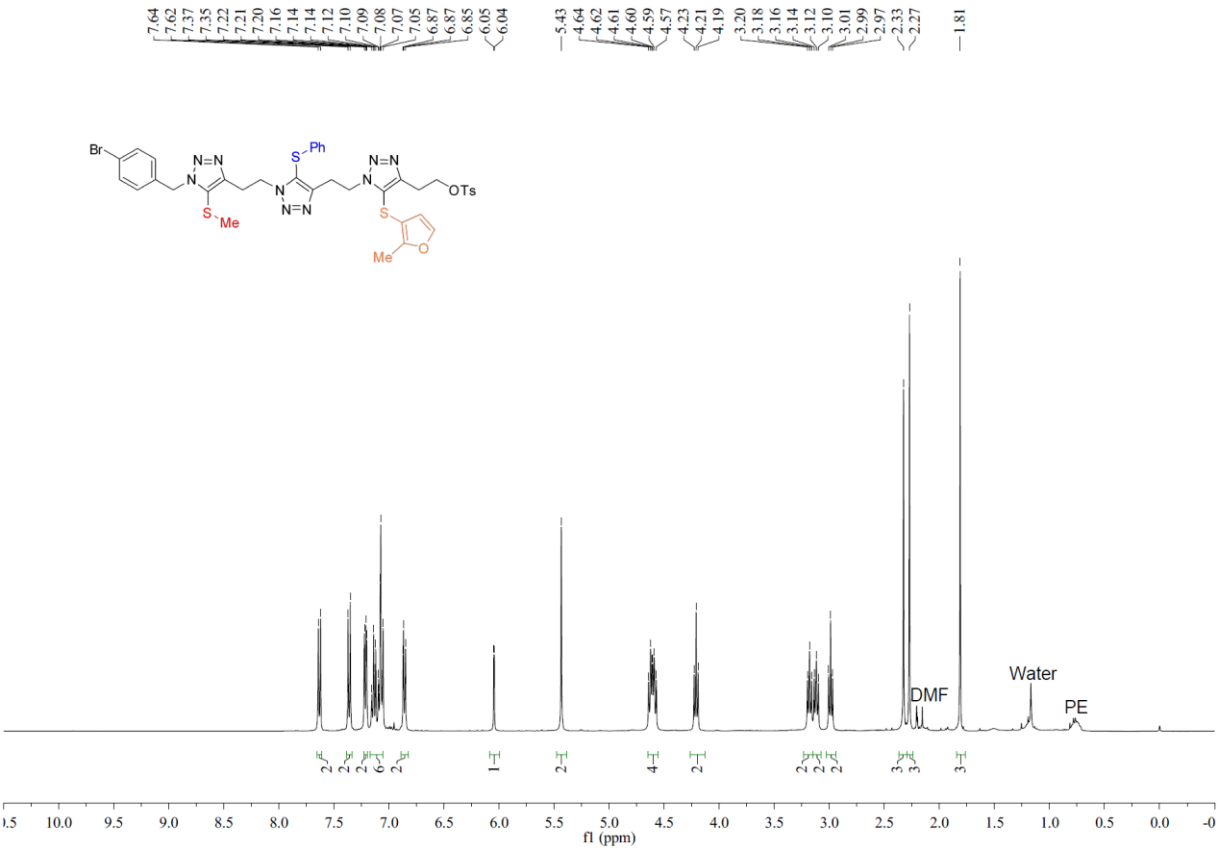


Figure S42. ^{1}H NMR spectra of **3a** ($CDCl_3$, 400 MHz).

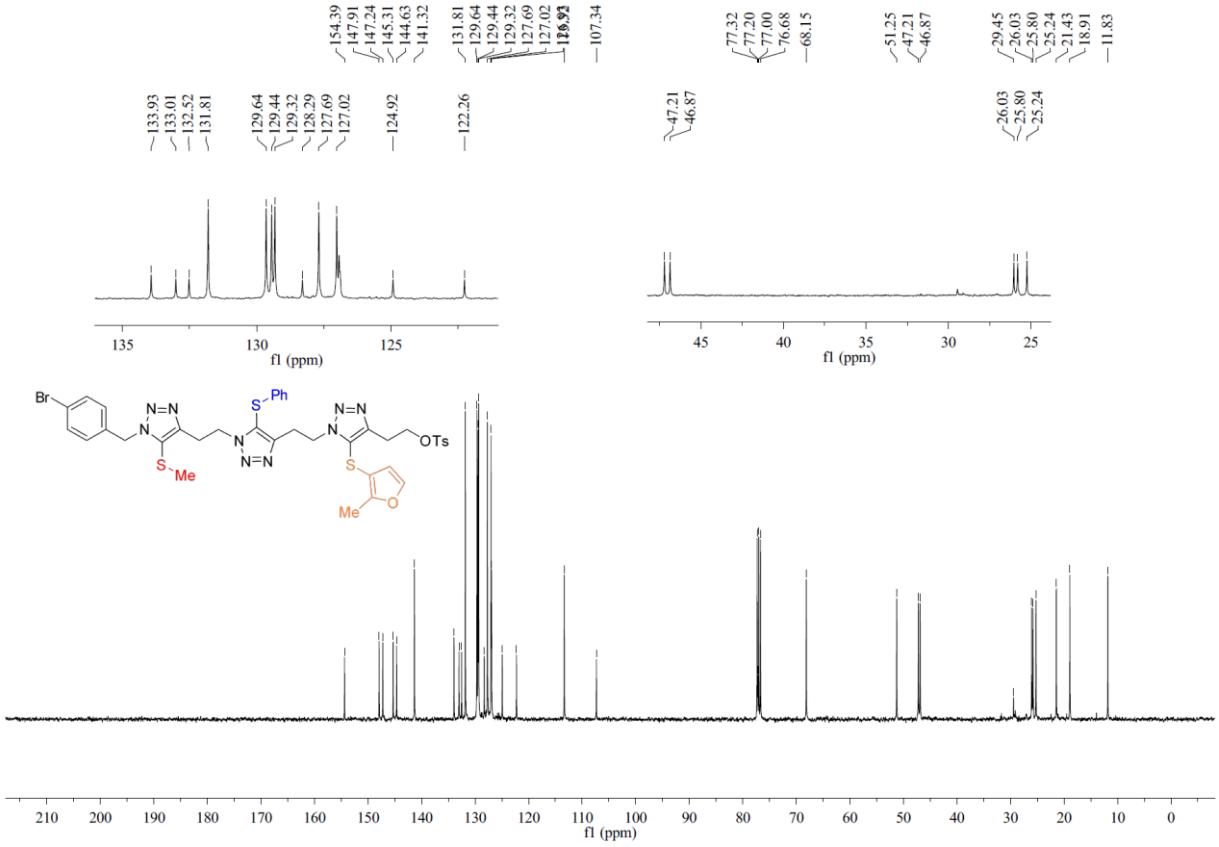


Figure S43. ^{13}C NMR spectra of **3a** ($CDCl_3$, 100 MHz).

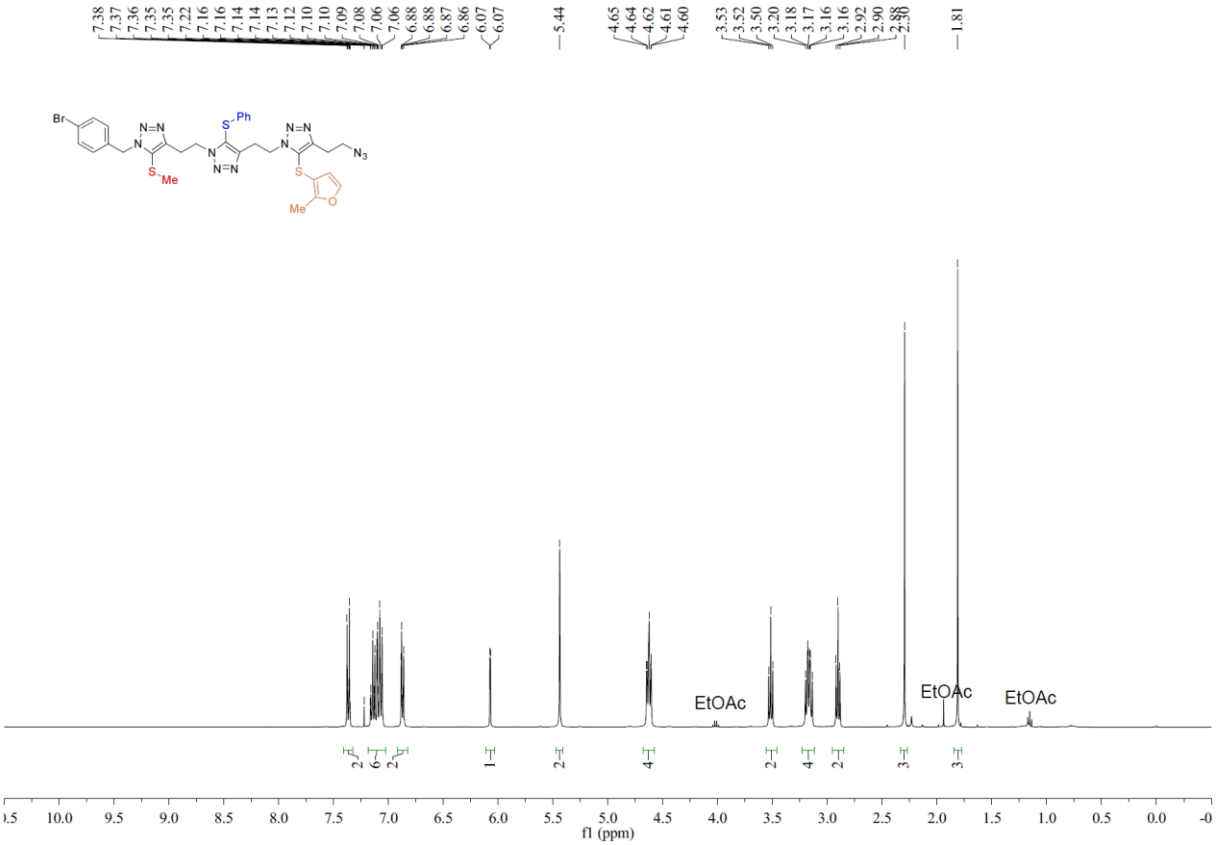


Figure S44. ^{1}H NMR spectra of **3b** ($CDCl_3$, 400 MHz).

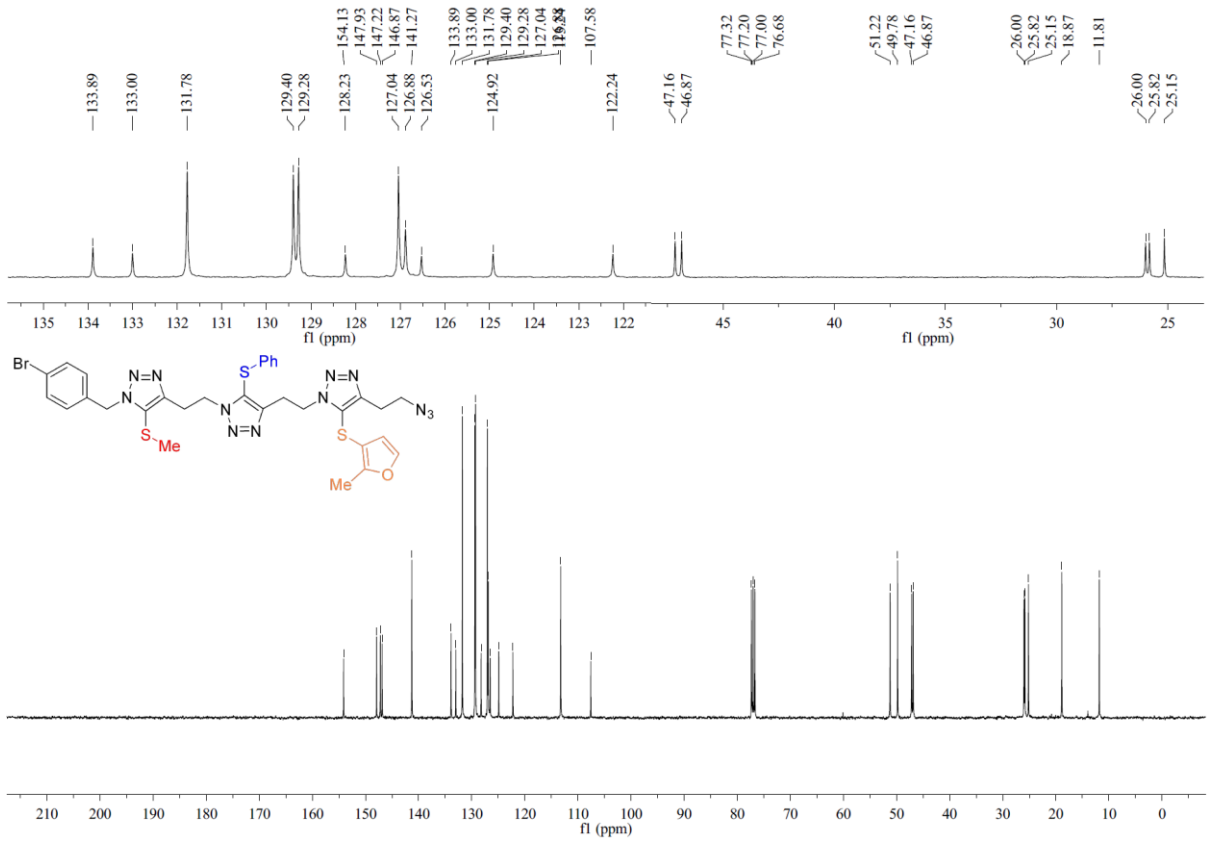


Figure S45. ^{13}C NMR spectra of **3b** ($CDCl_3$, 100 MHz).

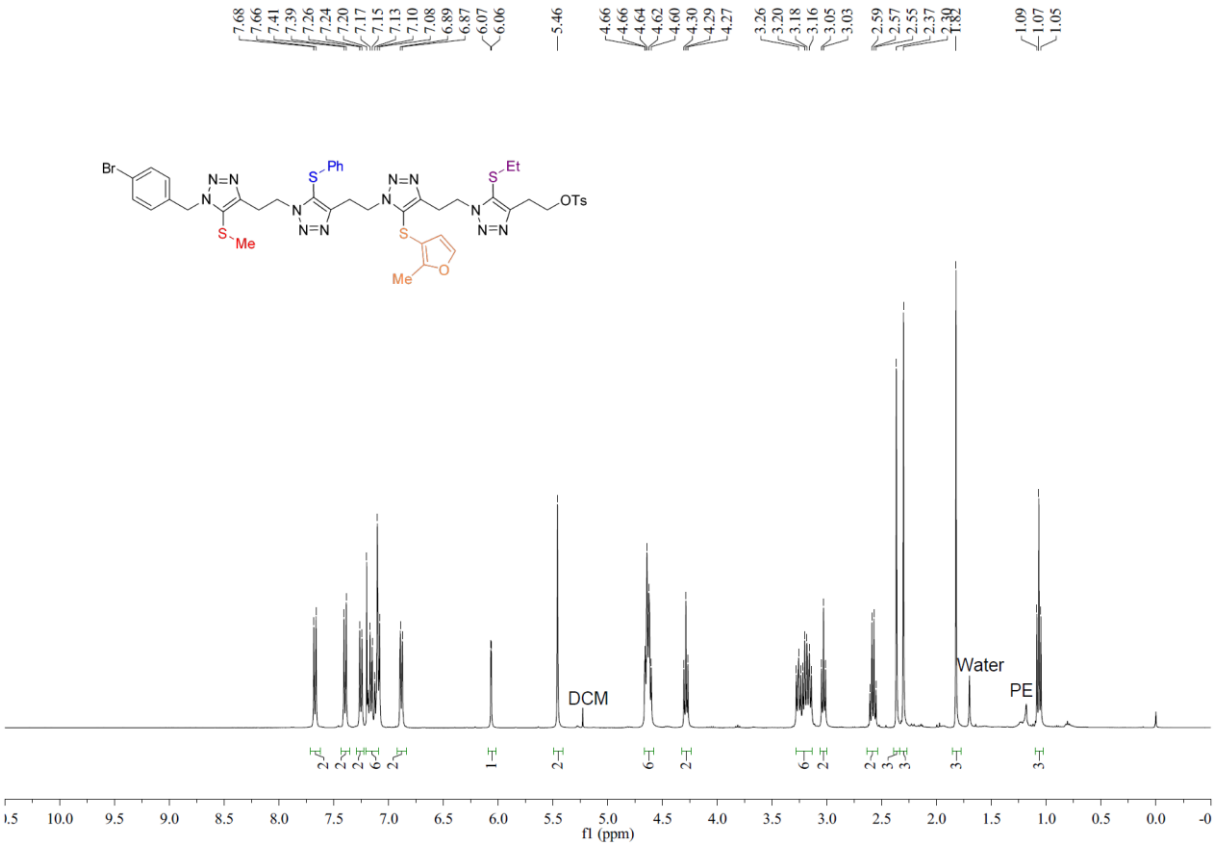


Figure S46. ^{1}H NMR spectra of **4a** ($CDCl_3$, 400 MHz).

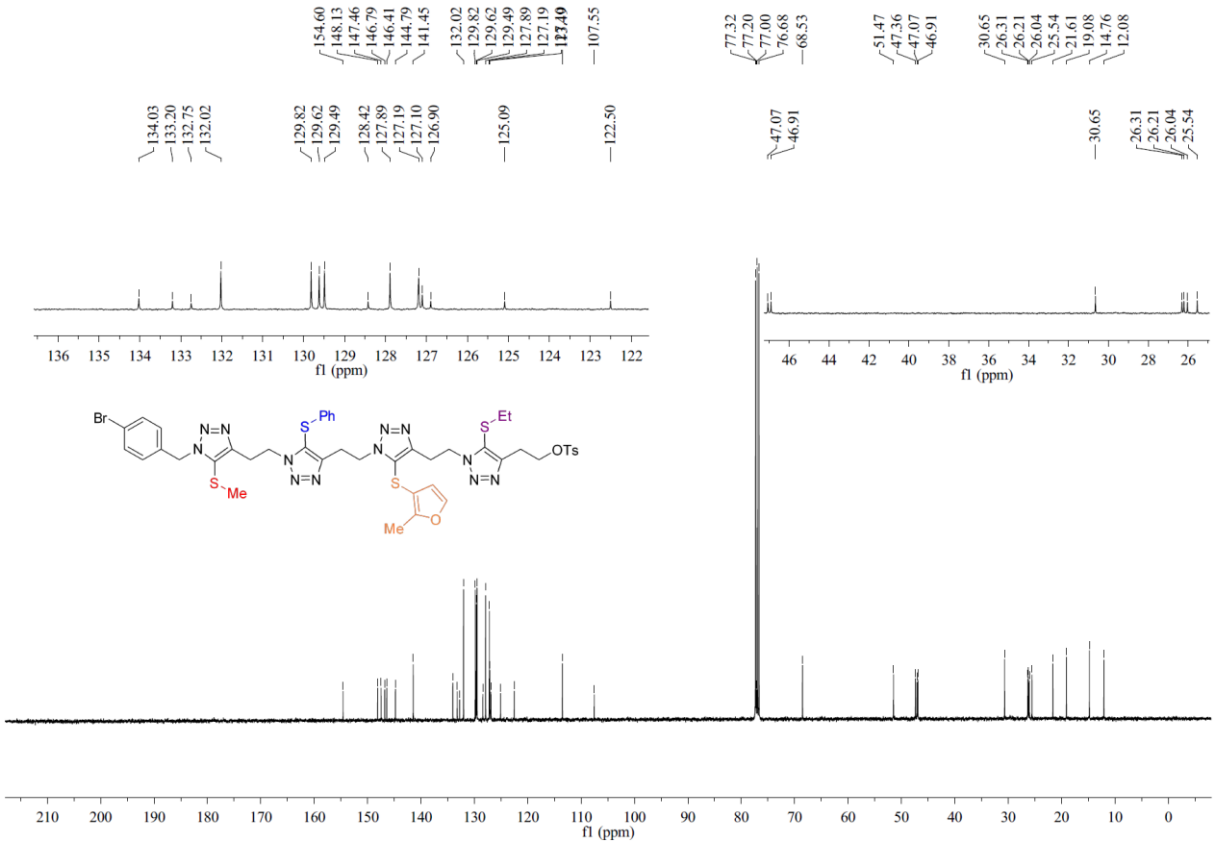


Figure S47. ^{13}C NMR spectra of **4a** ($CDCl_3$, 100 MHz).

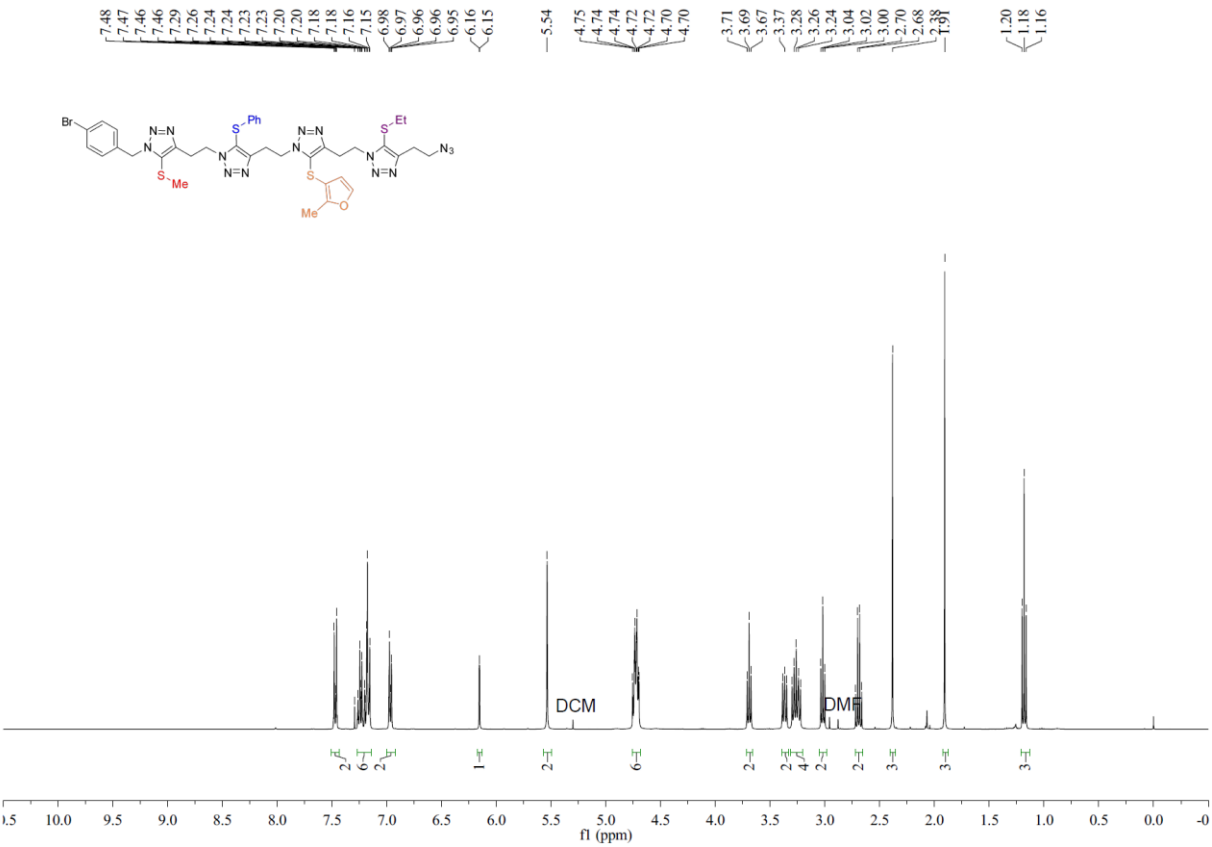


Figure S48. ^{1}H NMR spectra of **4b** ($CDCl_3$, 400 MHz).

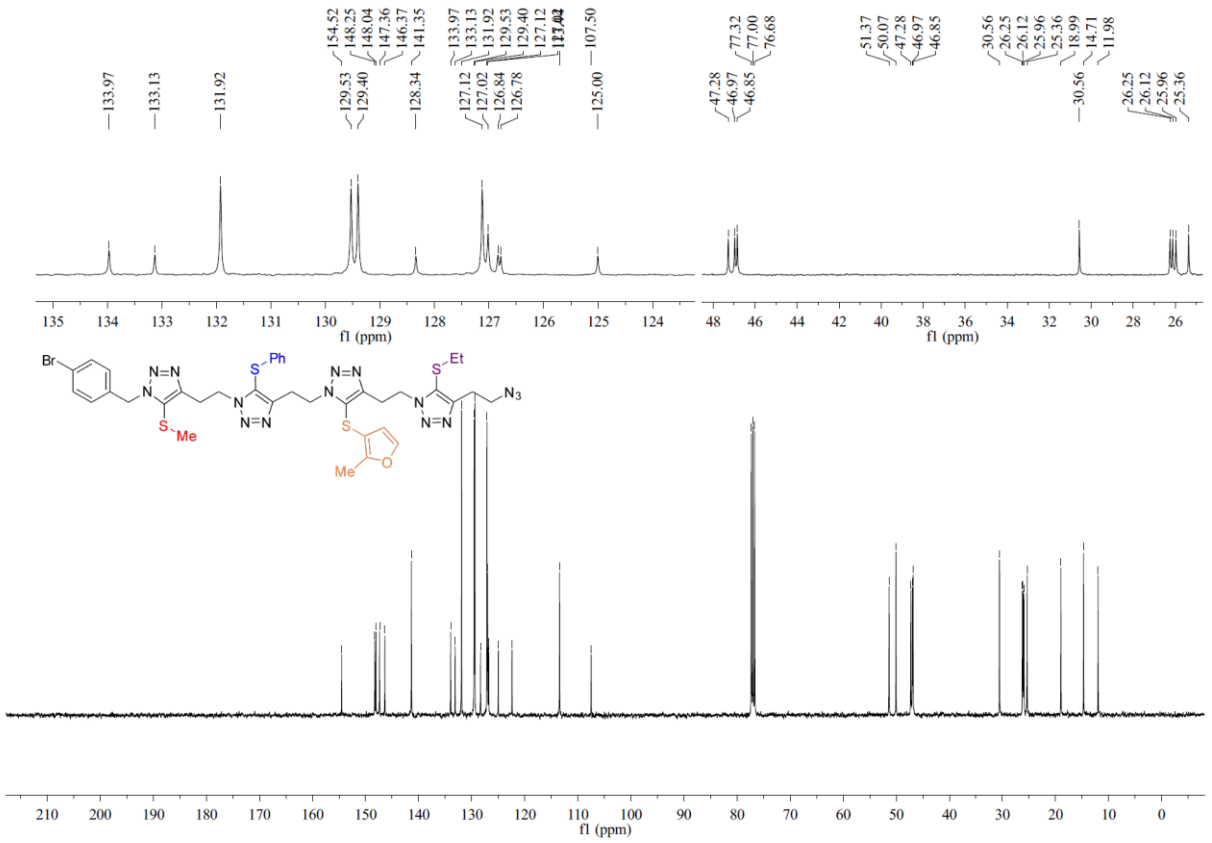


Figure S49. ^{13}C NMR spectra of **4b** ($CDCl_3$, 100 MHz).

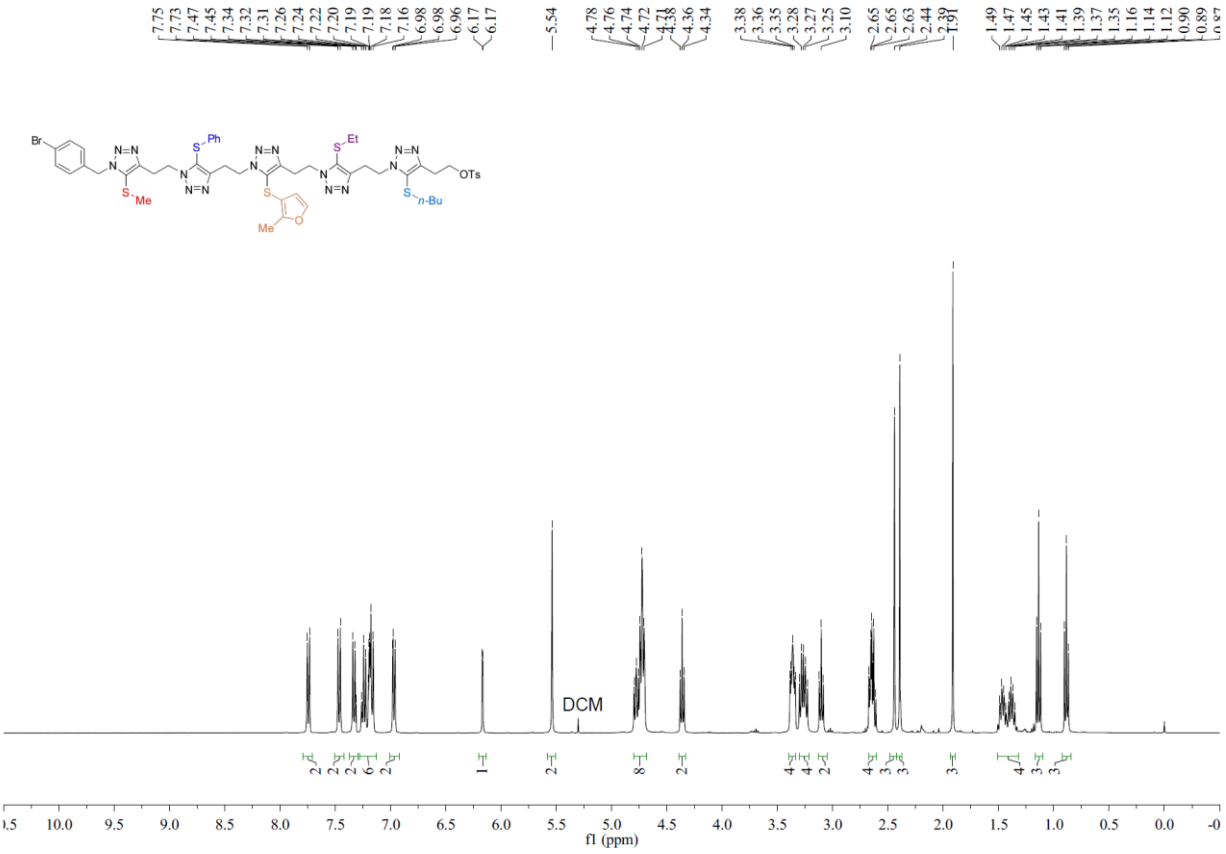


Figure S50. ^{1}H NMR spectra of **5a** ($CDCl_3$, 400 MHz).

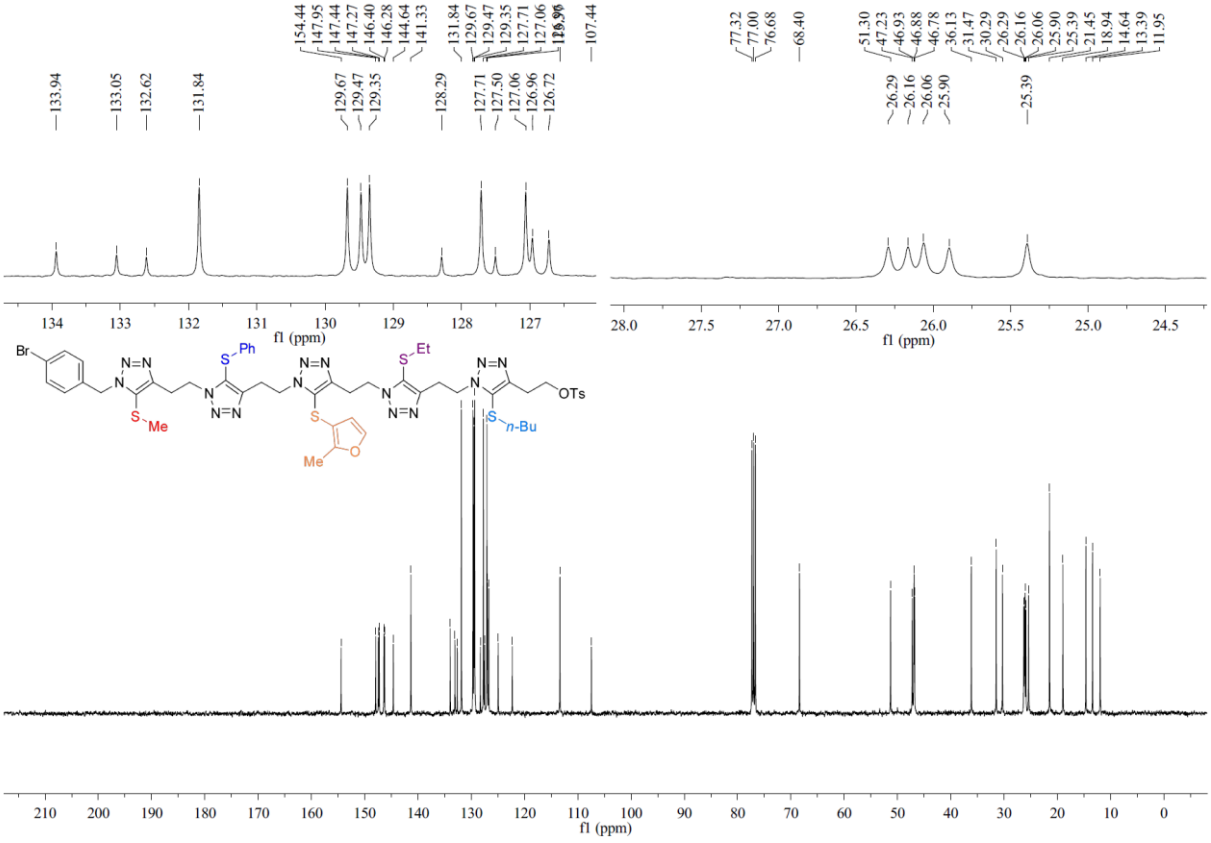


Figure S51. ^{13}C NMR spectra of **5a** ($CDCl_3$, 100 MHz).

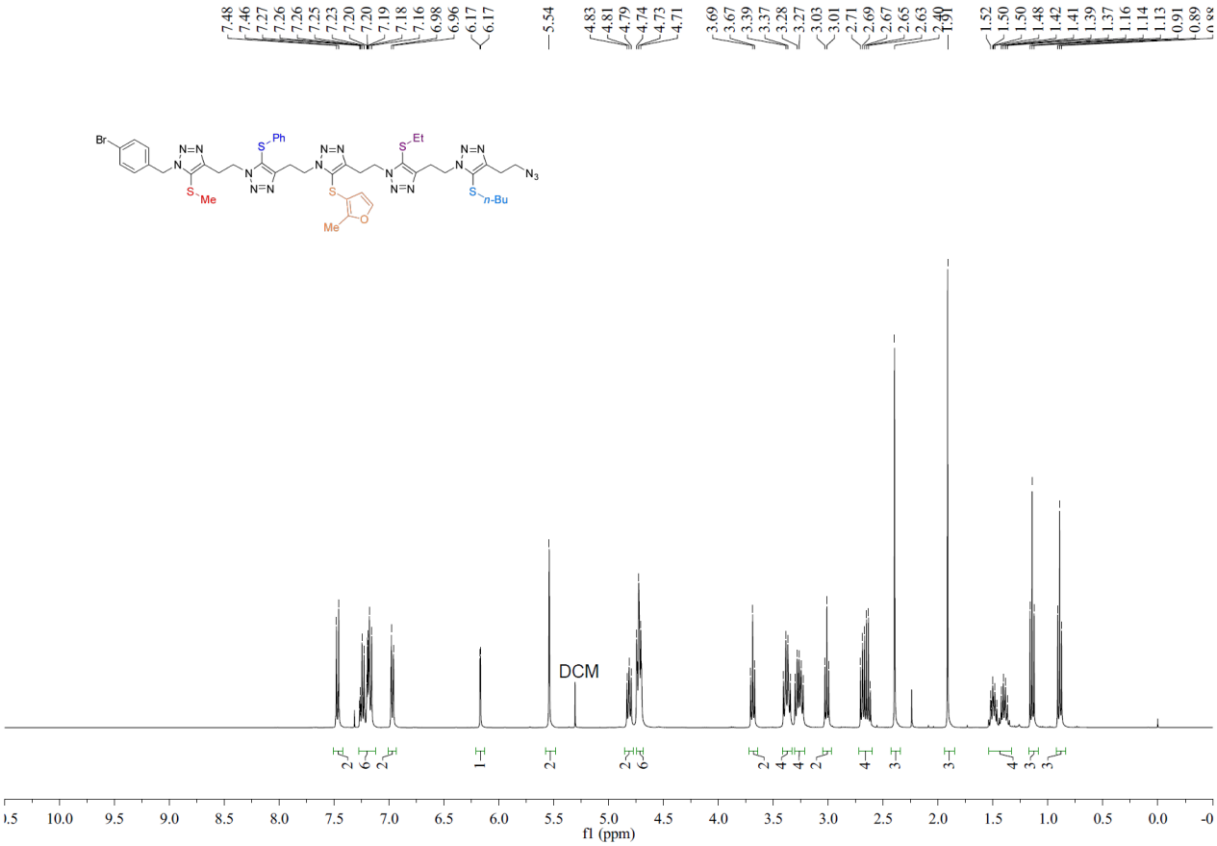


Figure S52. ^{1}H NMR spectra of **5b** ($CDCl_3$, 400 MHz).

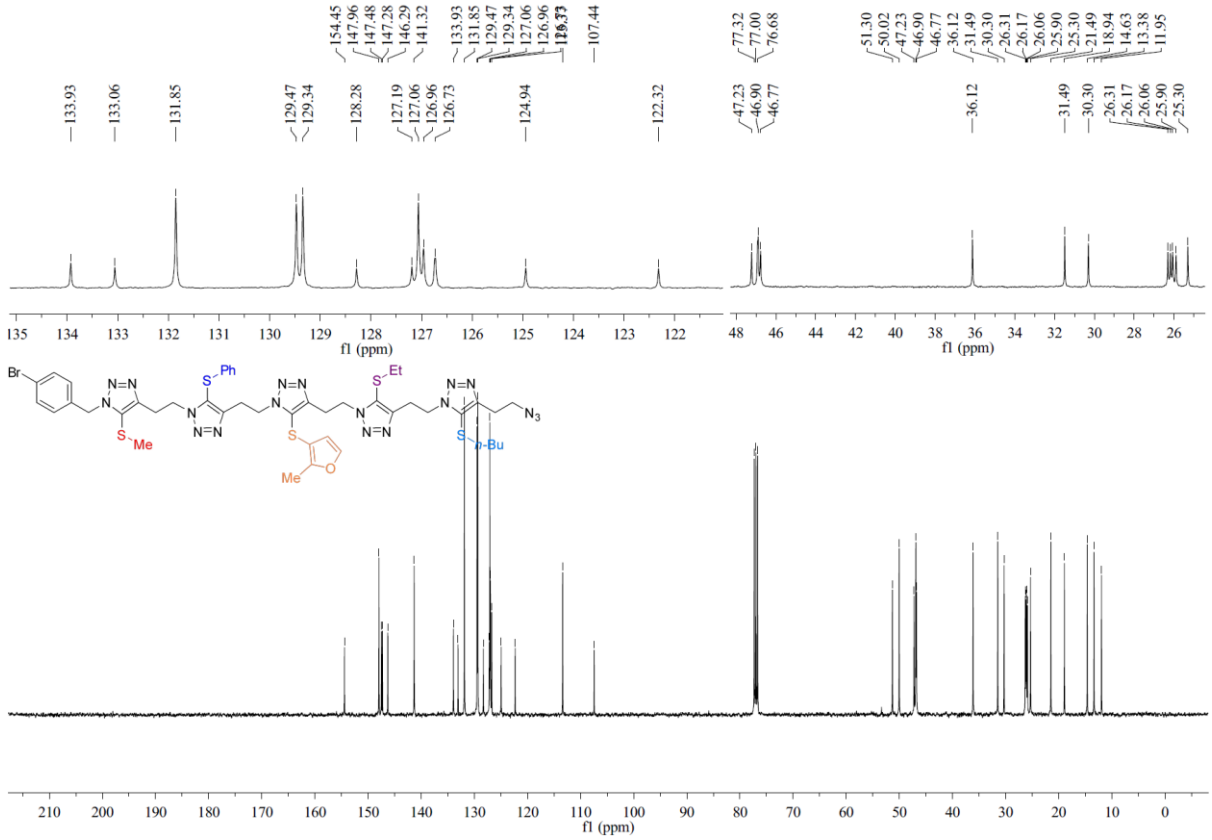


Figure S53. ^{13}C NMR spectra of **5b** ($CDCl_3$, 100 MHz).

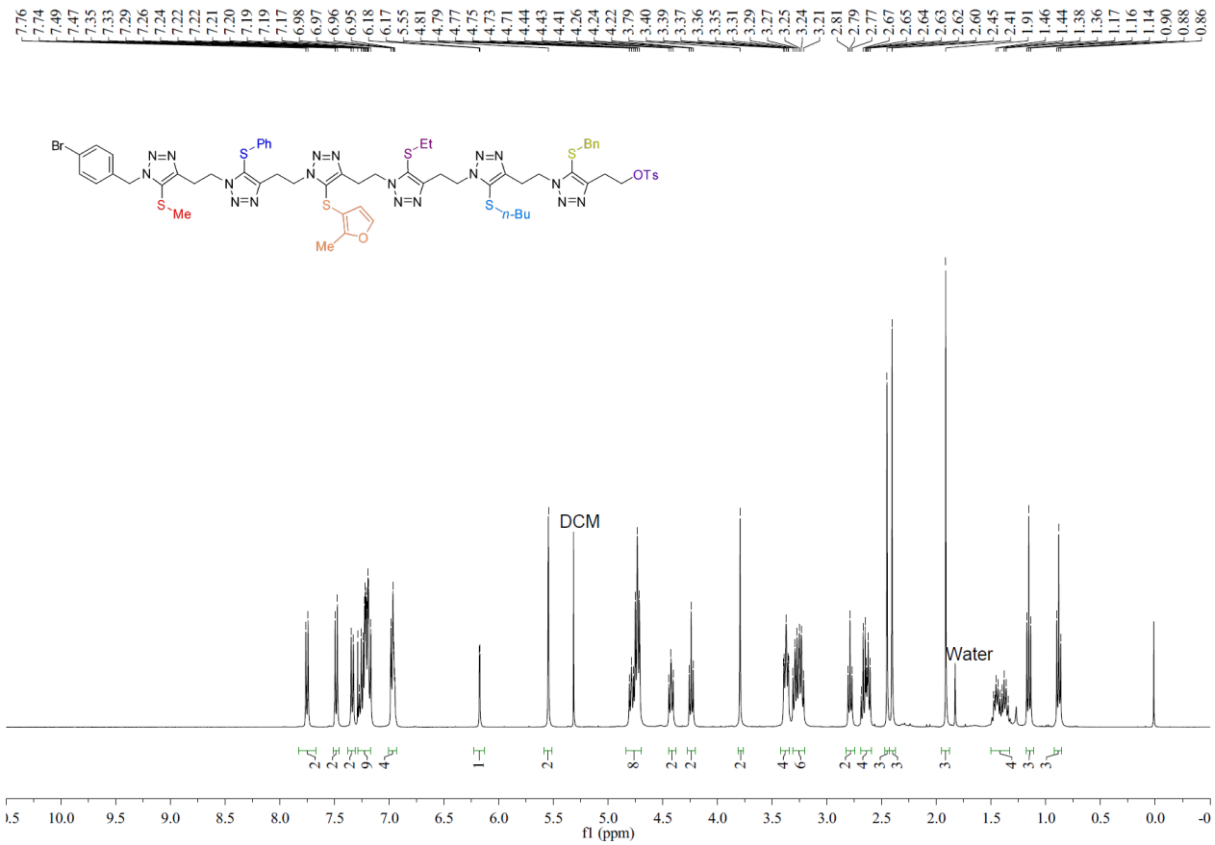


Figure S54. ^{1}H NMR spectra of **6a** ($CDCl_3$, 400 MHz).

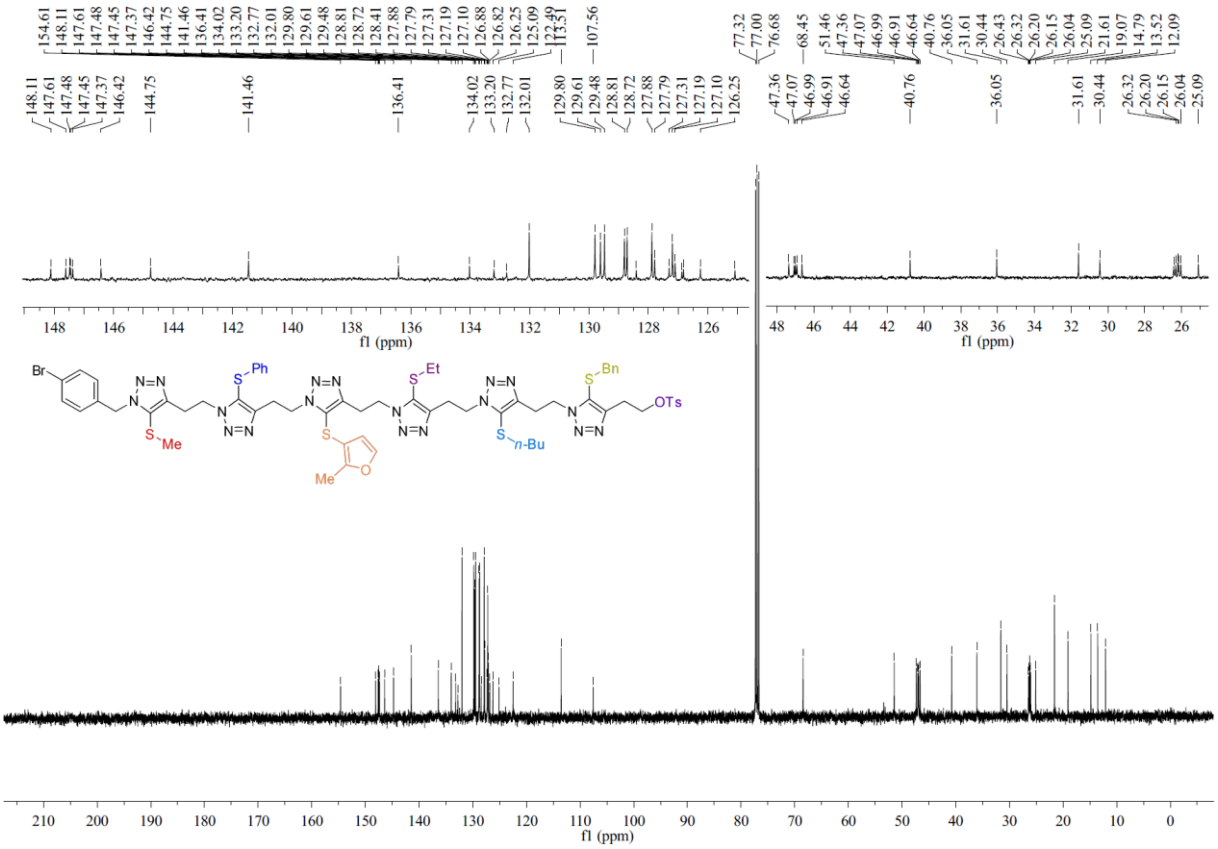


Figure S55. ^{13}C NMR spectra of **6a** ($CDCl_3$, 100 MHz).

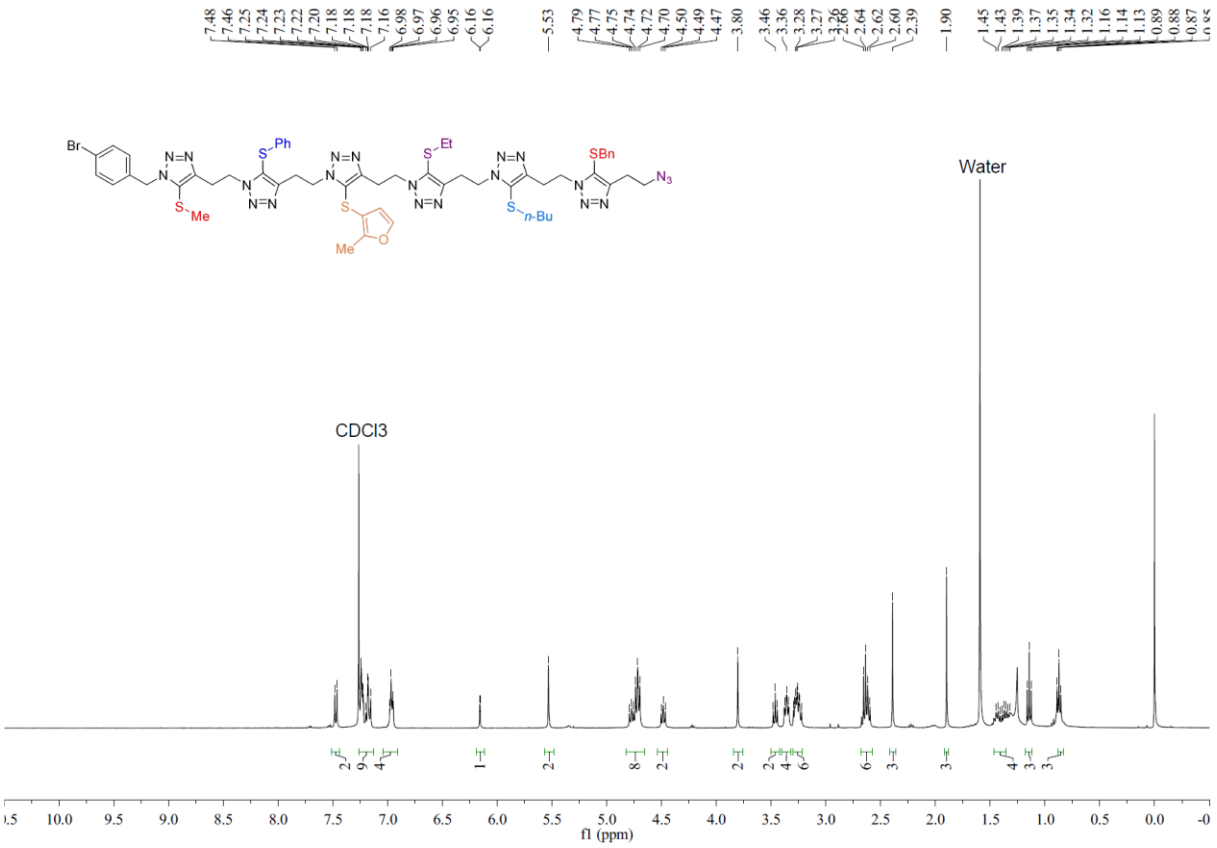


Figure S56. ^{1}H NMR spectra of **6b** ($CDCl_3$, 400 MHz).

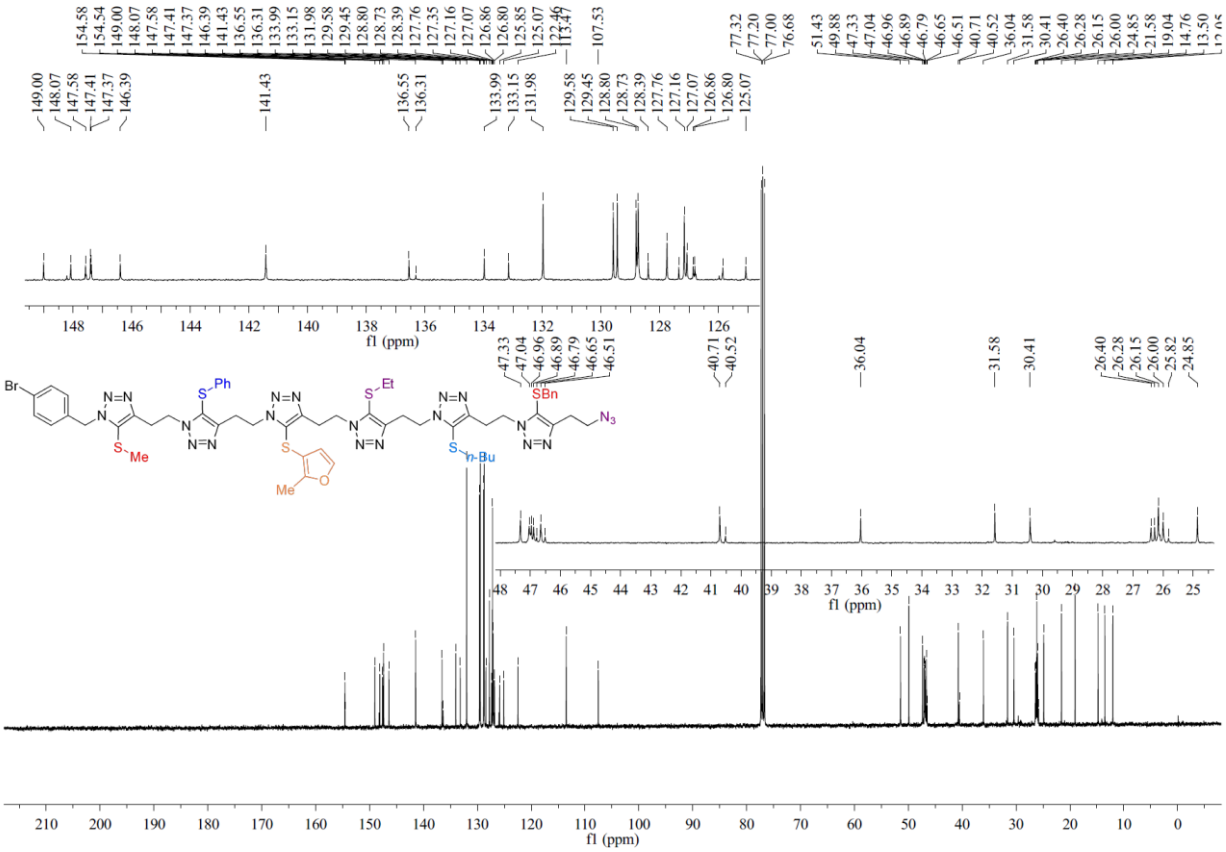


Figure S57. ^{13}C NMR spectra of **6b** ($CDCl_3$, 100 MHz).

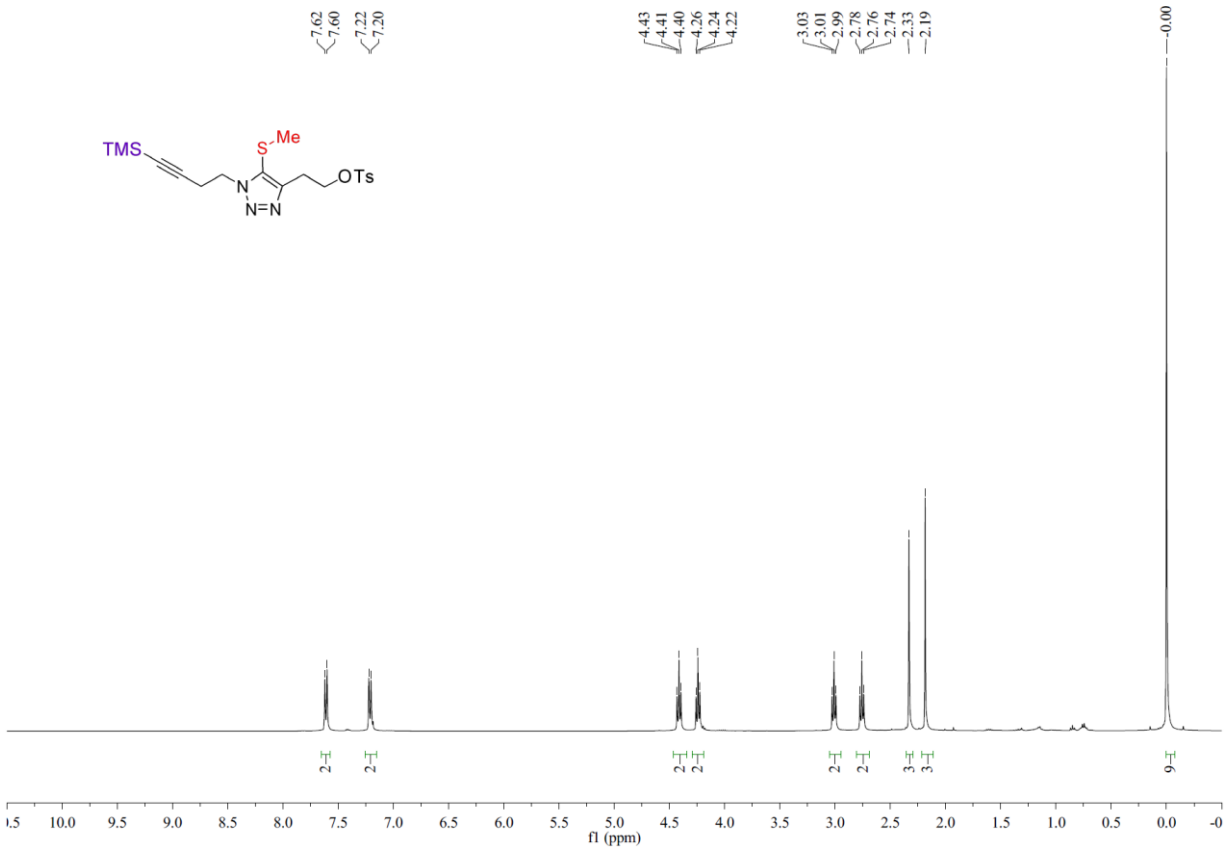


Figure S58. ^{1}H NMR spectra of **7a** ($CDCl_3$, 400 MHz).

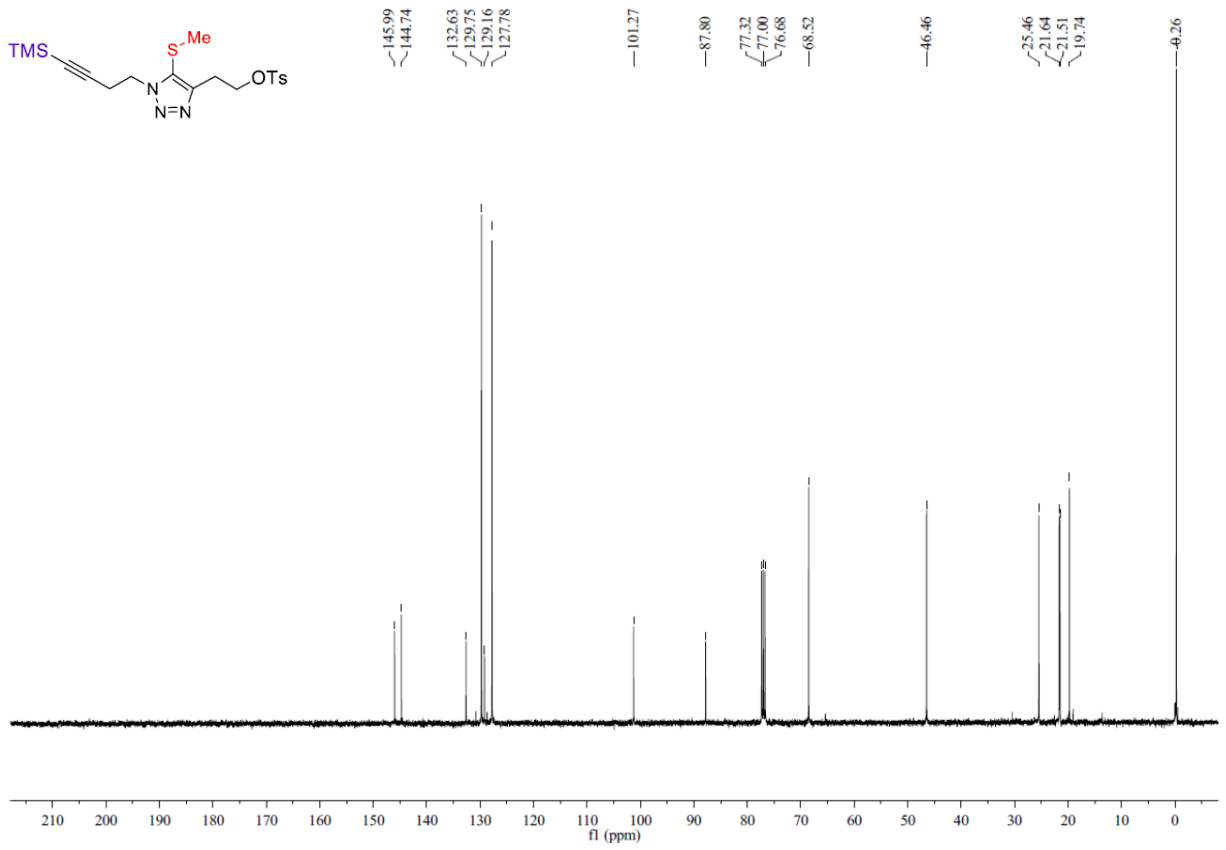


Figure S59. ^{13}C NMR spectra of **7a** ($CDCl_3$, 100 MHz).

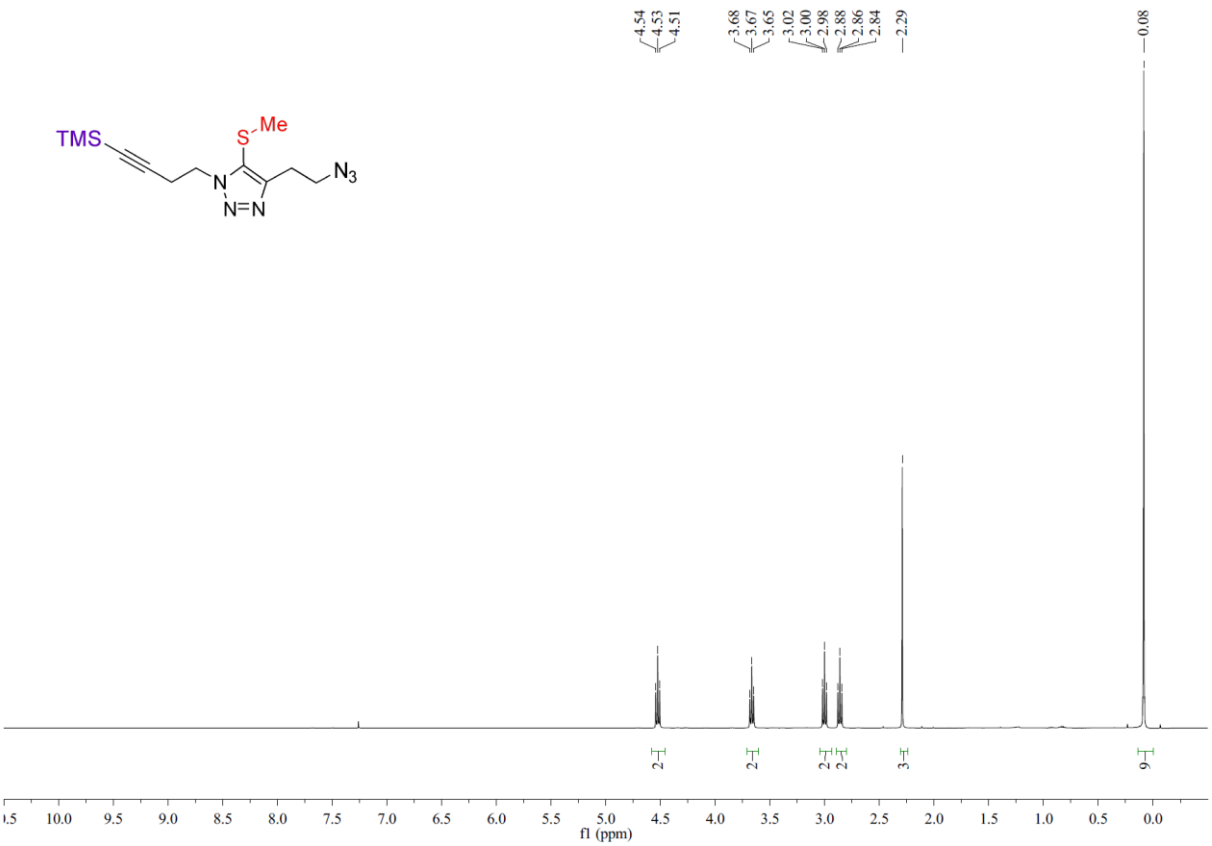


Figure S60. ^{1}H NMR spectra of **7b** ($CDCl_3$, 400 MHz).

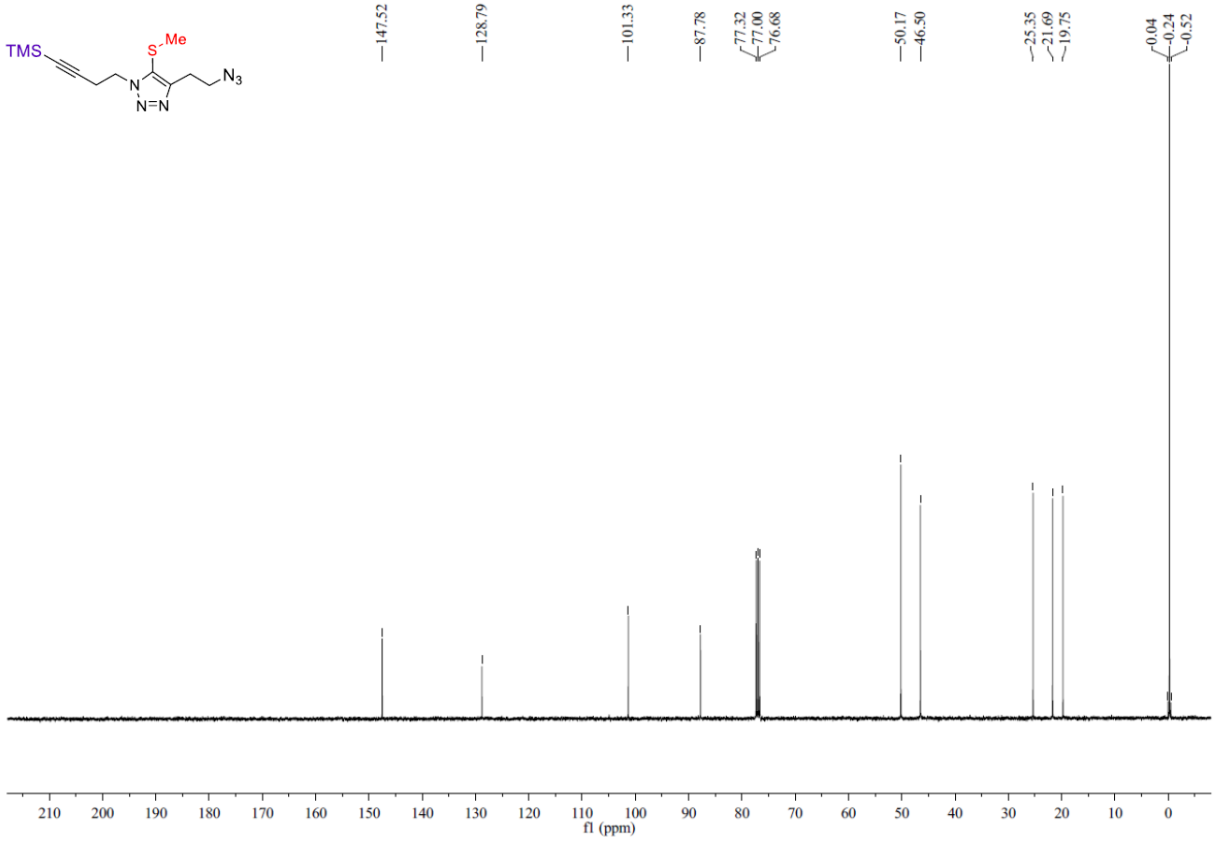


Figure S61. ^{13}C NMR spectra of **7b** ($CDCl_3$, 100 MHz).

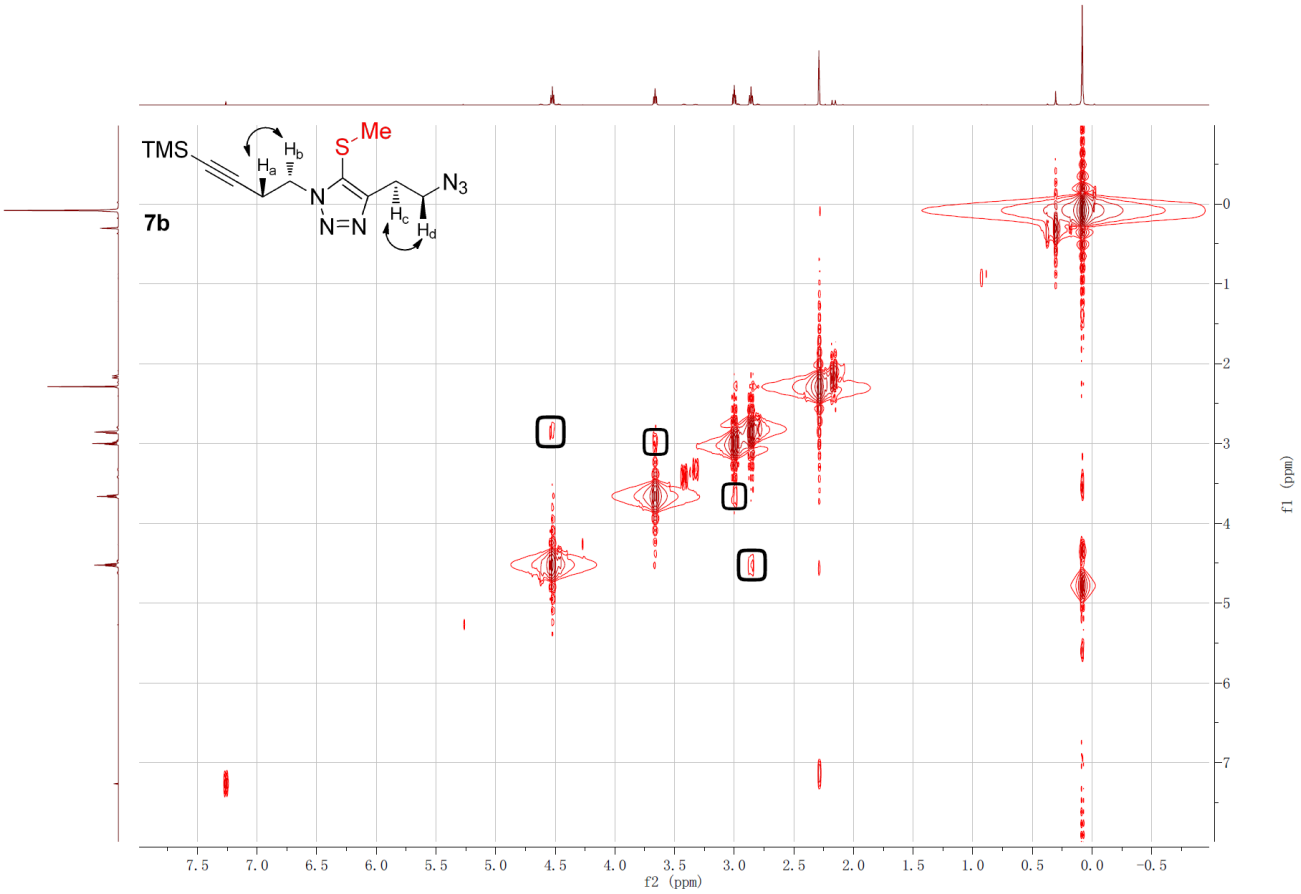


Figure S62. 2D NOESY spectra of **7b** ($CDCl_3$, 400 MHz).

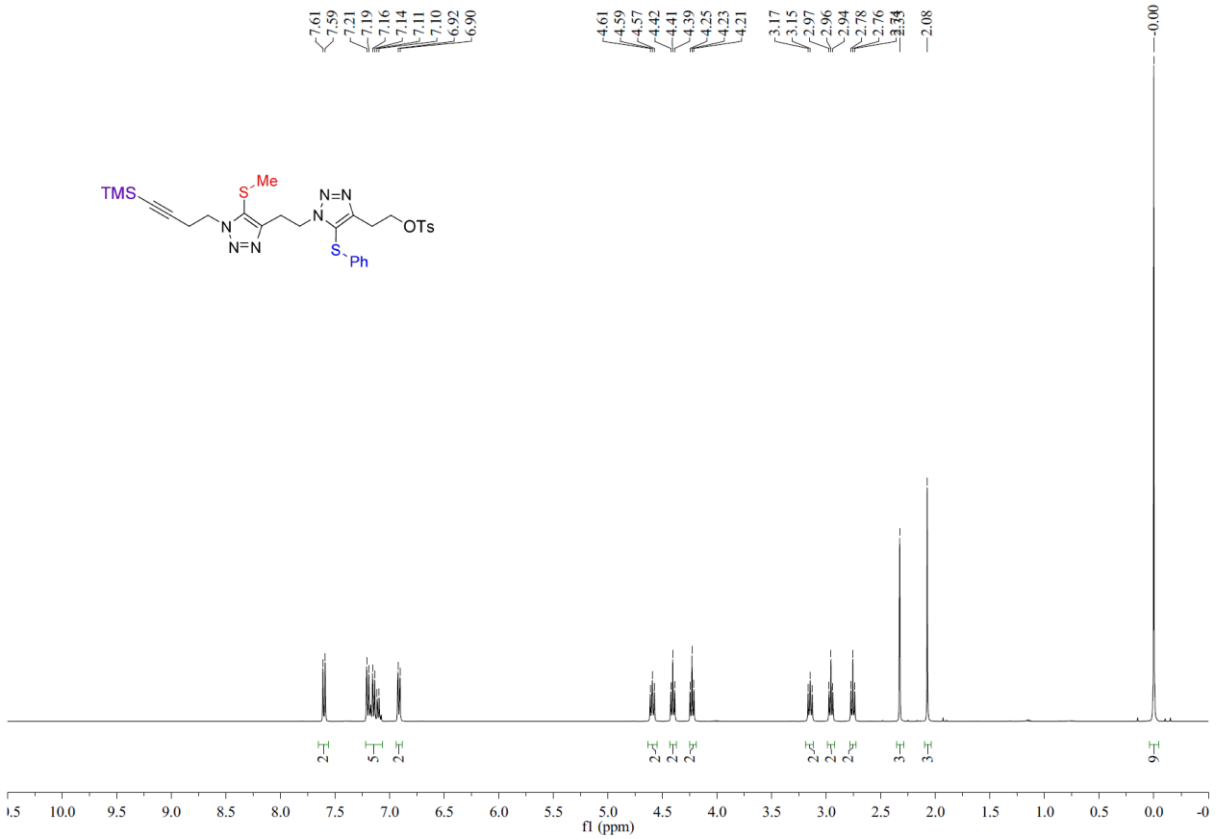


Figure S63. ^{1}H NMR spectra of **8a** ($CDCl_3$, 400 MHz).

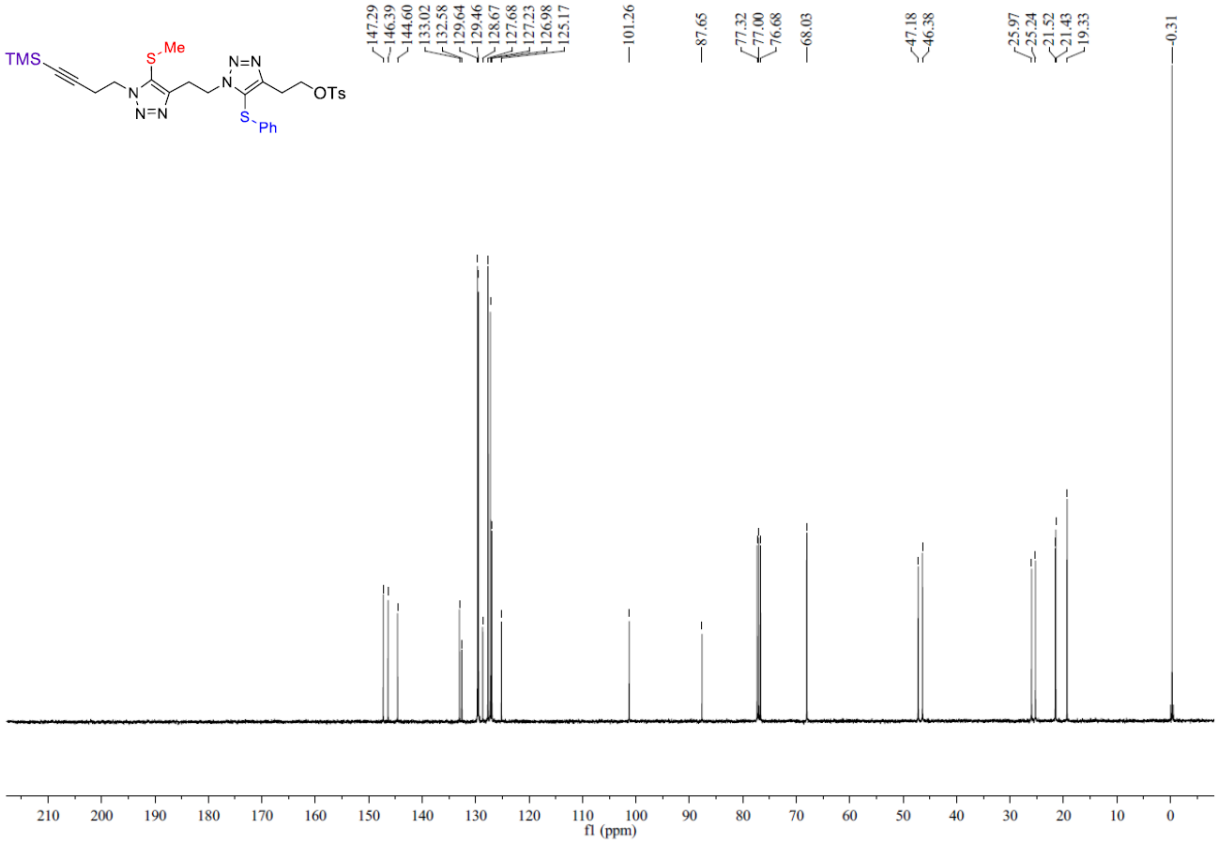


Figure S64. ^{13}C NMR spectra of **8a** ($CDCl_3$, 100 MHz).

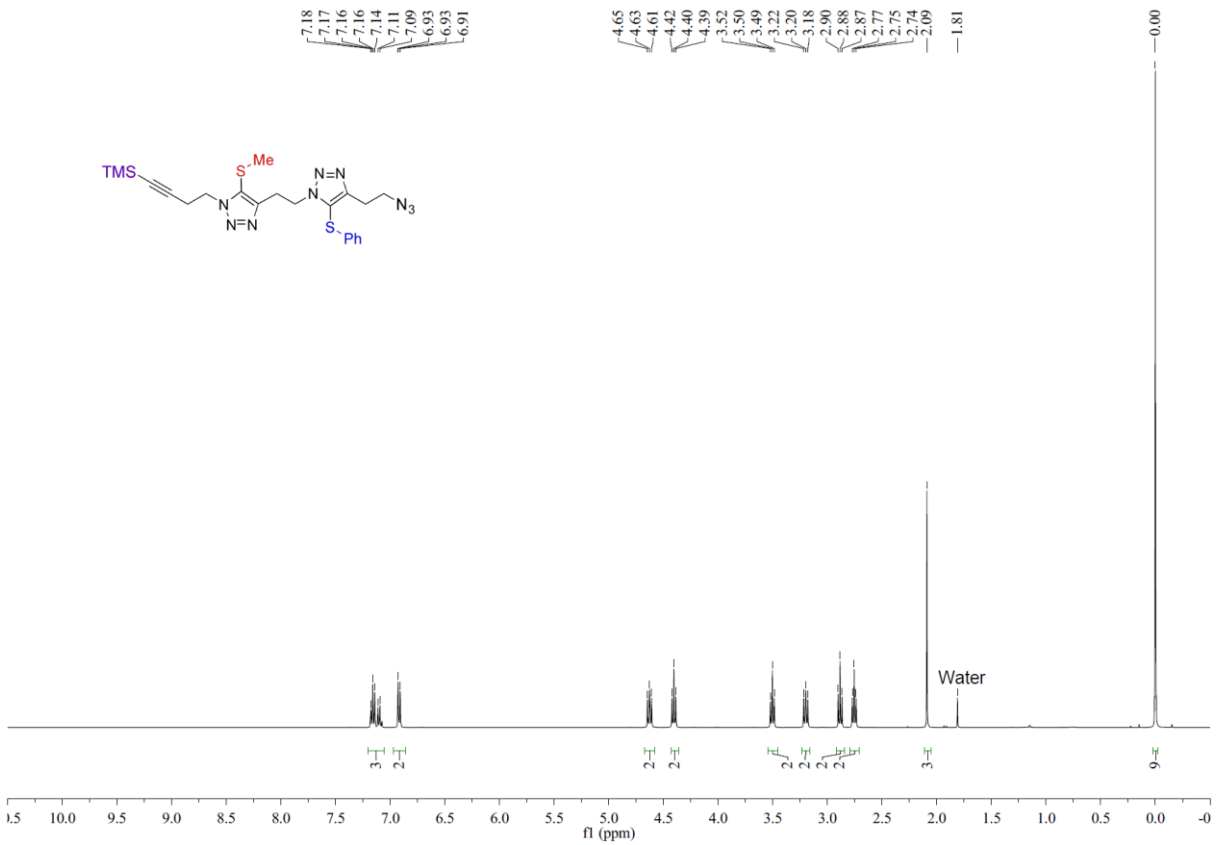


Figure S65. ^{1}H NMR spectra of **8b** ($CDCl_3$, 400 MHz).

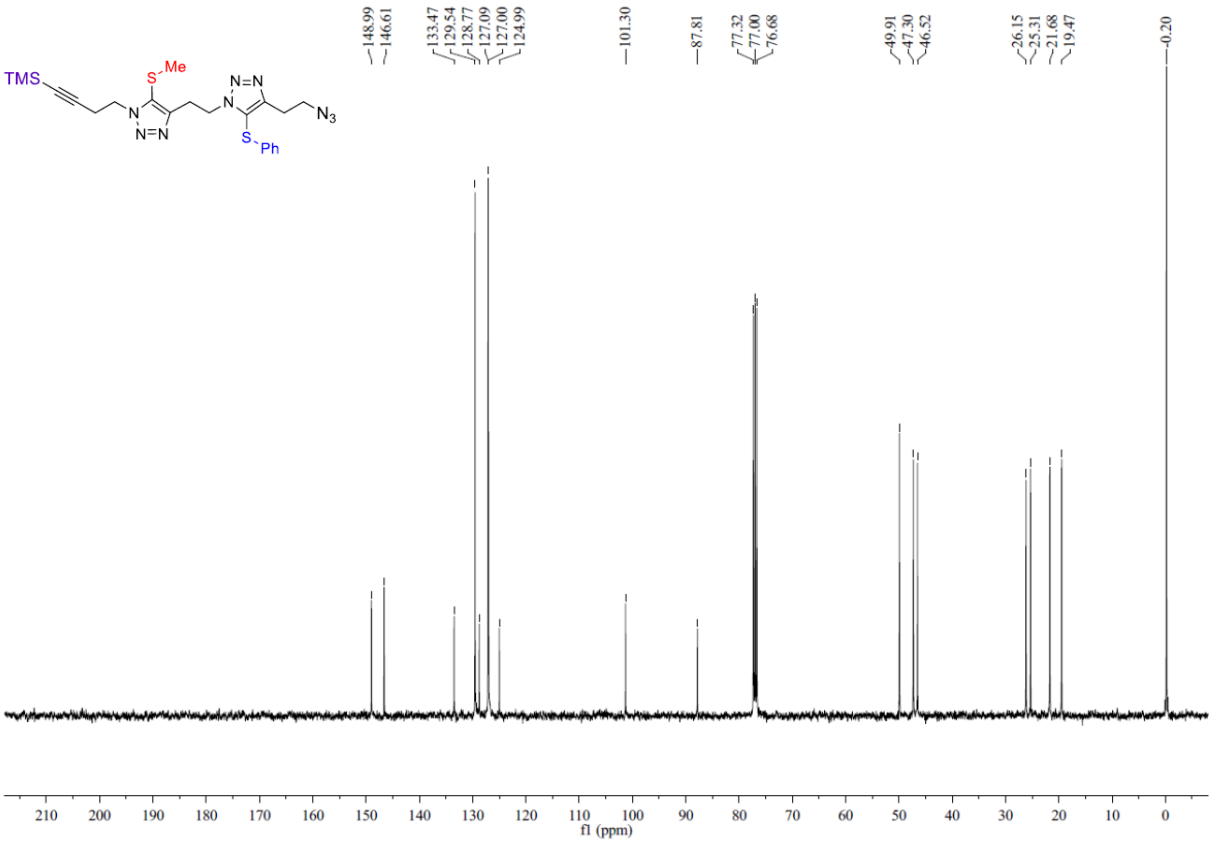


Figure S66. ^{13}C NMR spectra of **8b** ($CDCl_3$, 100 MHz).

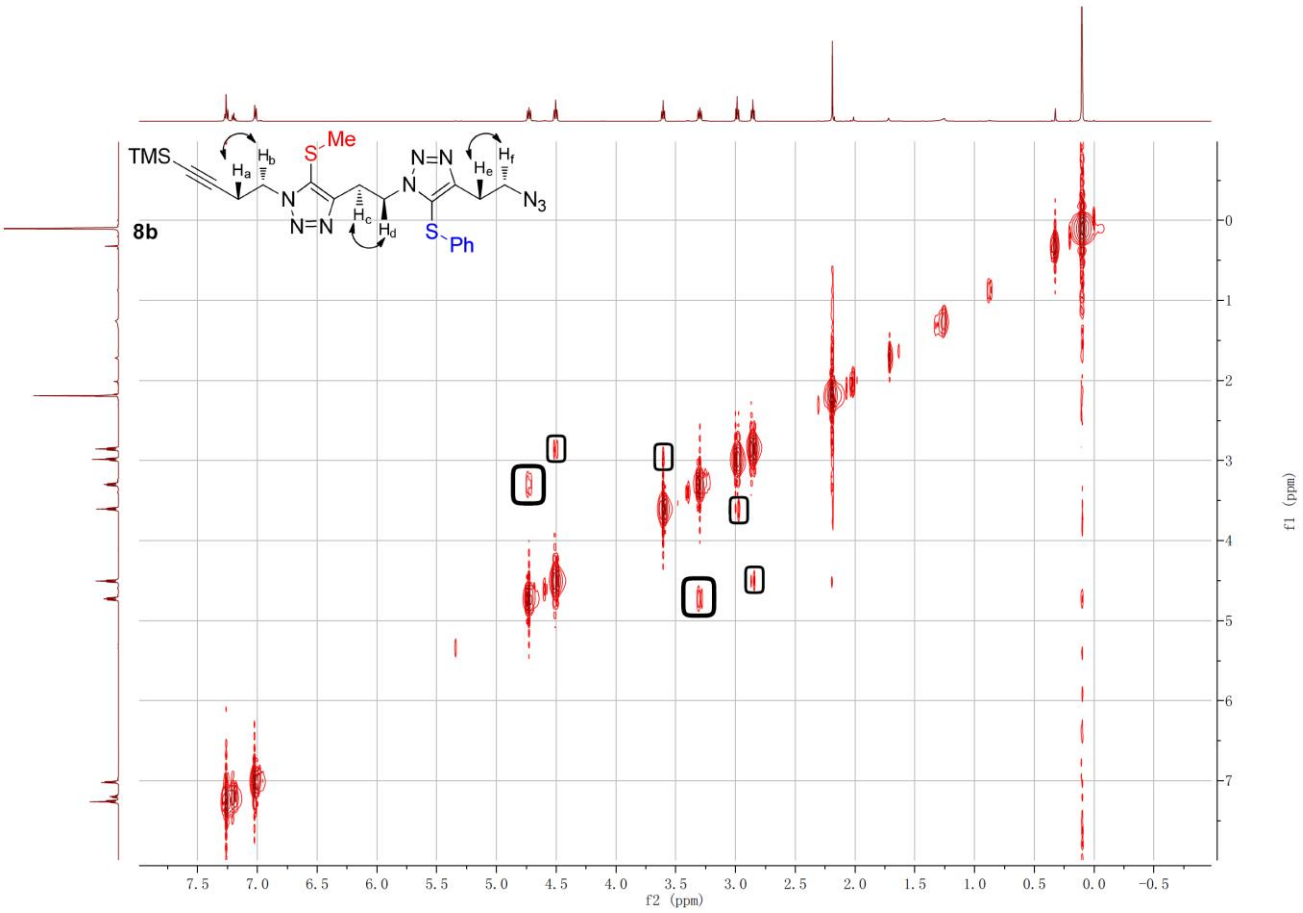


Figure S67. 2D NOESY spectra of **8b** ($CDCl_3$, 400 MHz).

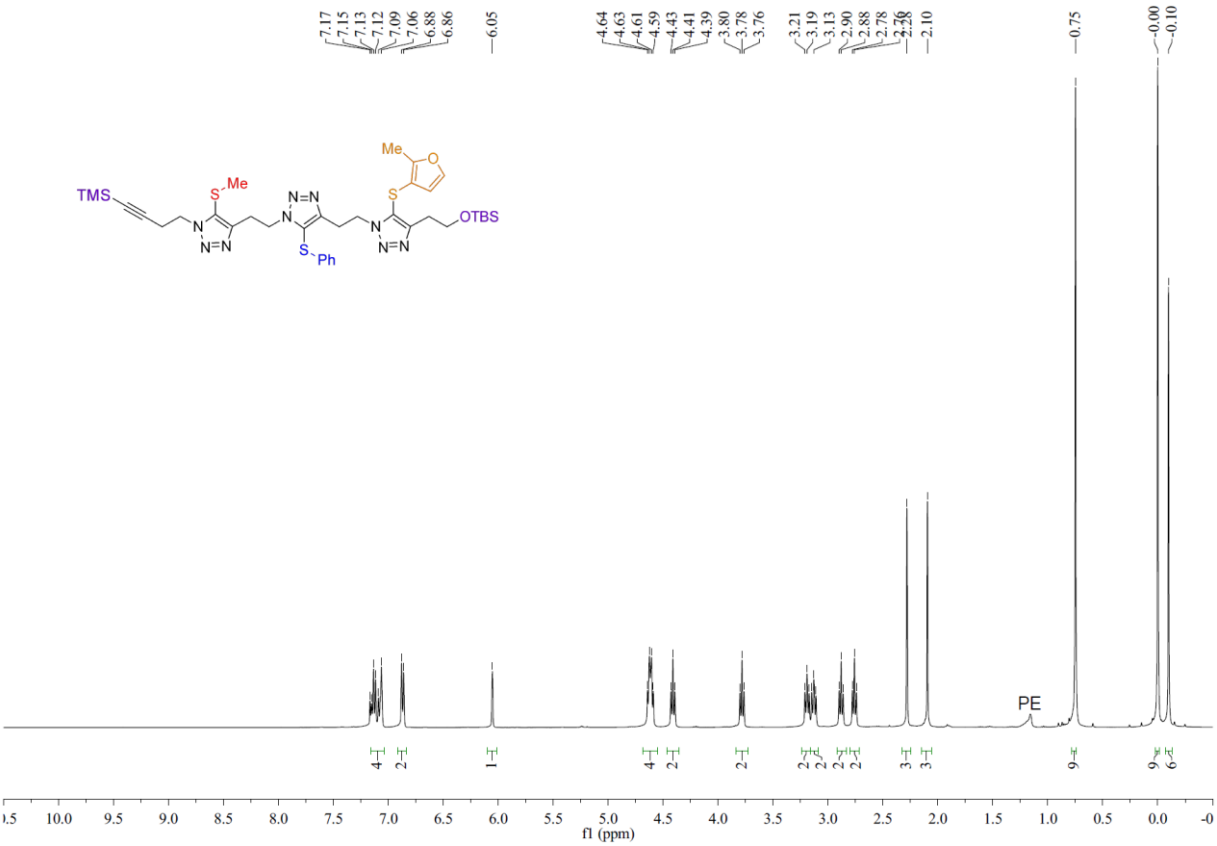


Figure S68. ^{1}H NMR spectra of **9a** ($CDCl_3$, 400 MHz).

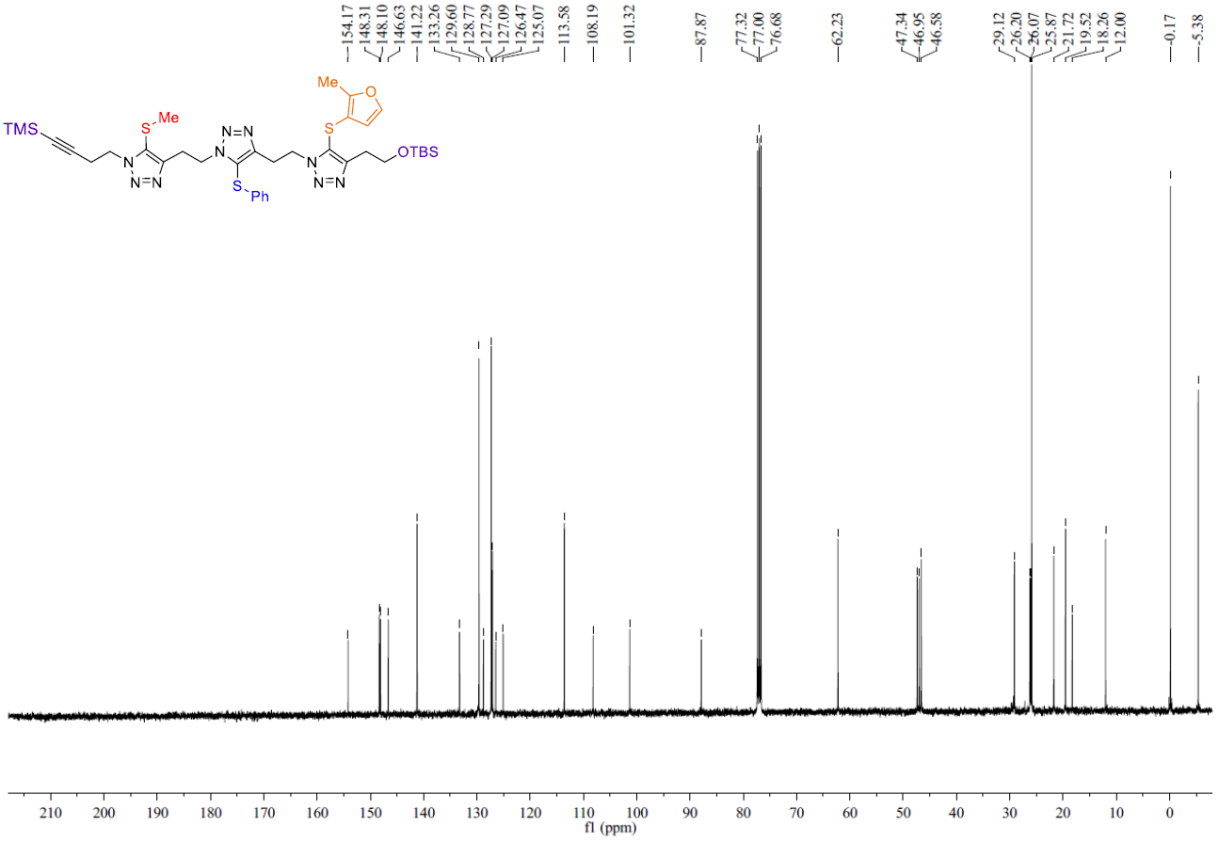


Figure S69. ^{13}C NMR spectra of **9a** ($CDCl_3$, 100 MHz).

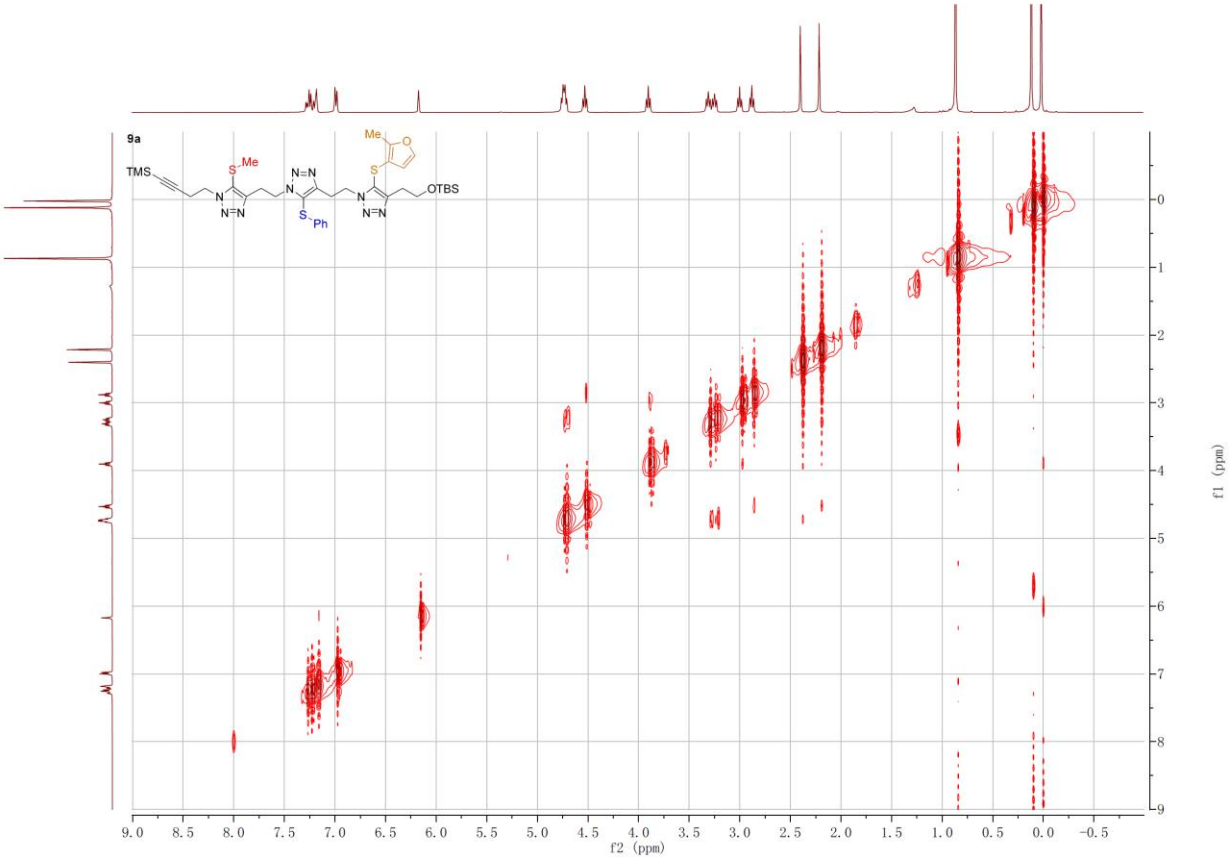


Figure S70. 2D NOESY spectra of **9a** ($CDCl_3$, 400 MHz).

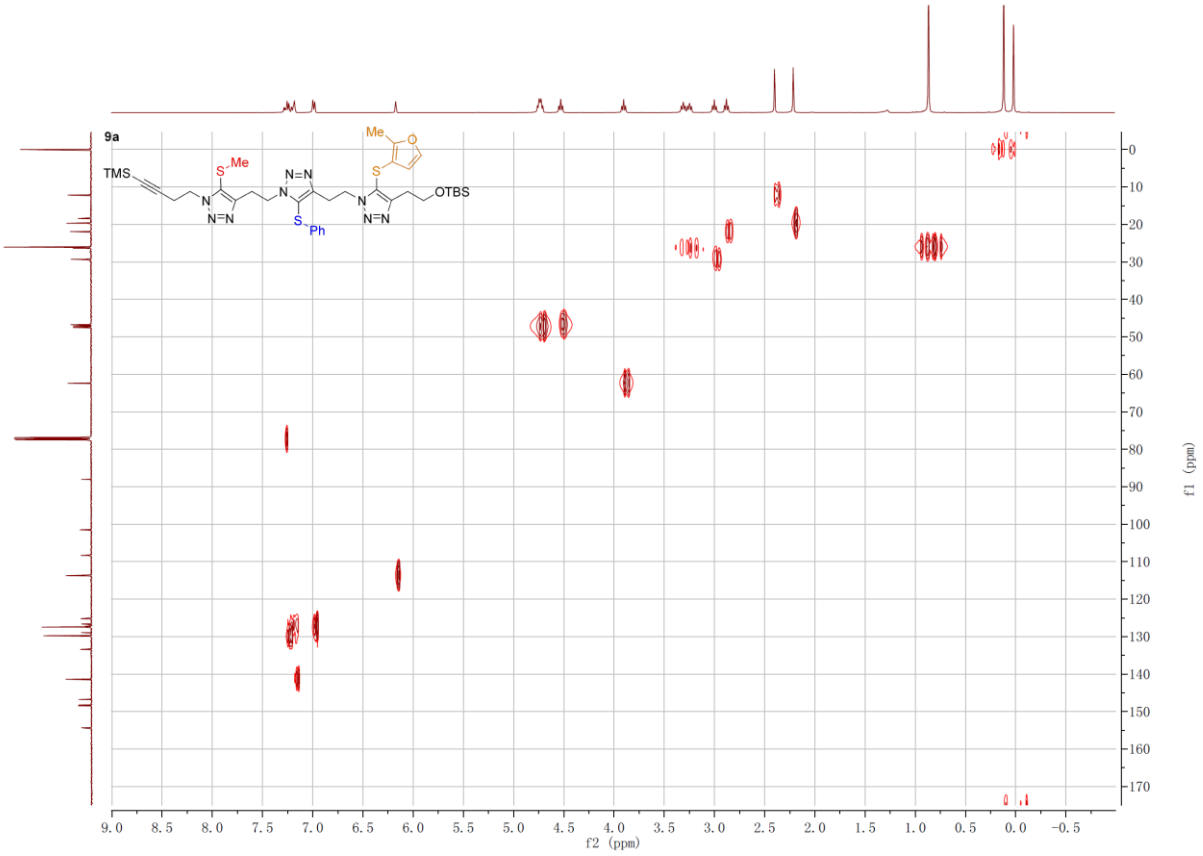


Figure S71. 2D HSQC spectra of **9a** ($CDCl_3$, 400 MHz for ^{1}H, 100 MHz for ^{13}C).

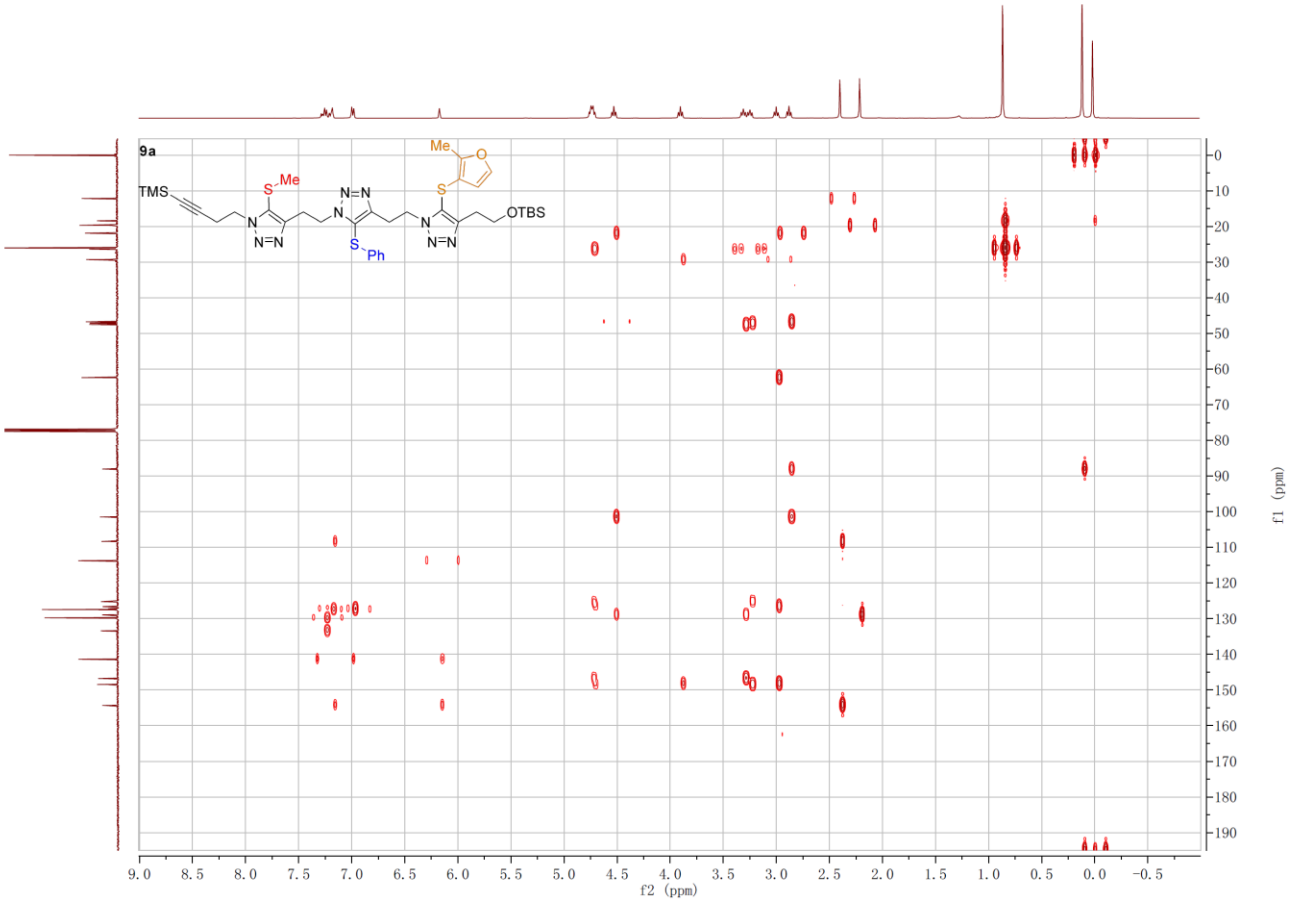


Figure S72. 2D HMBC spectra of **9a** ($CDCl_3$, 400 MHz for ^{1}H, 100 MHz for ^{13}C).

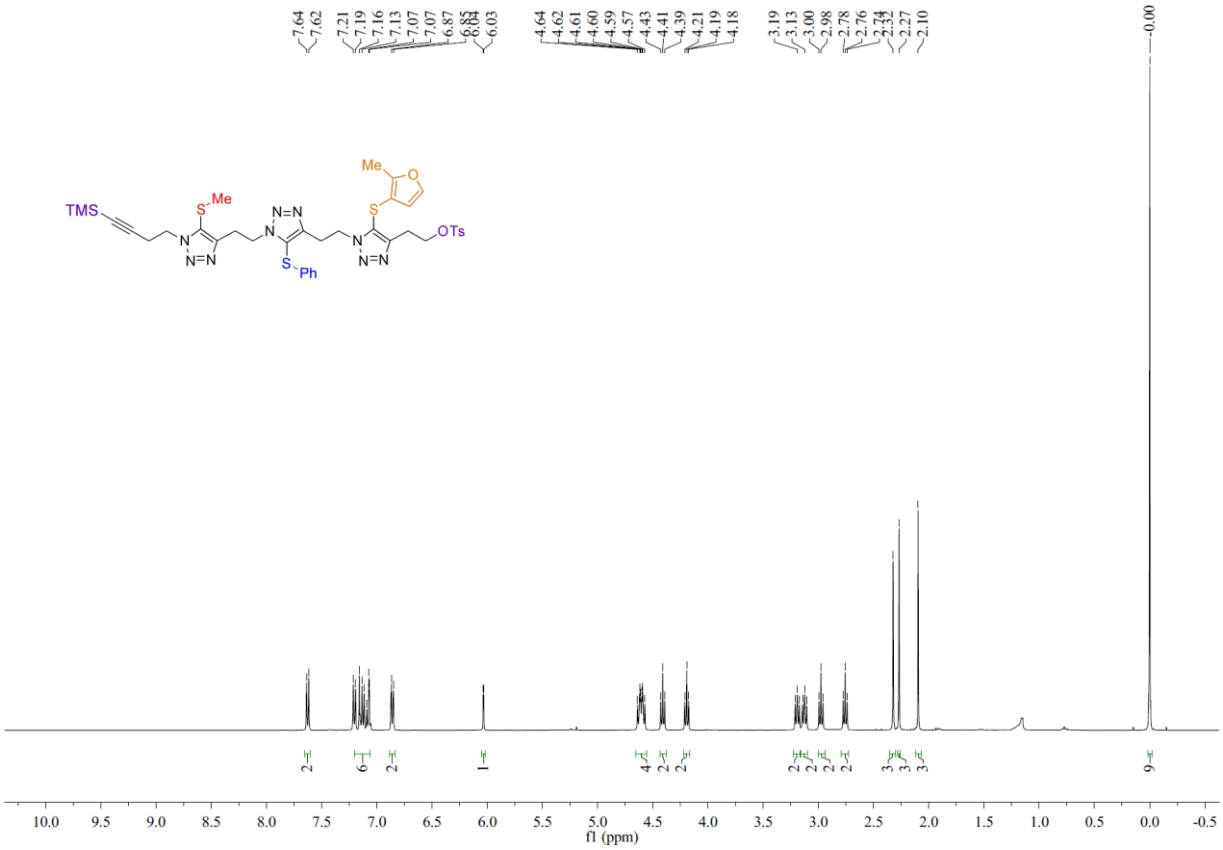


Figure S73. ^{1}H NMR spectra of **9b** ($CDCl_3$, 400 MHz).

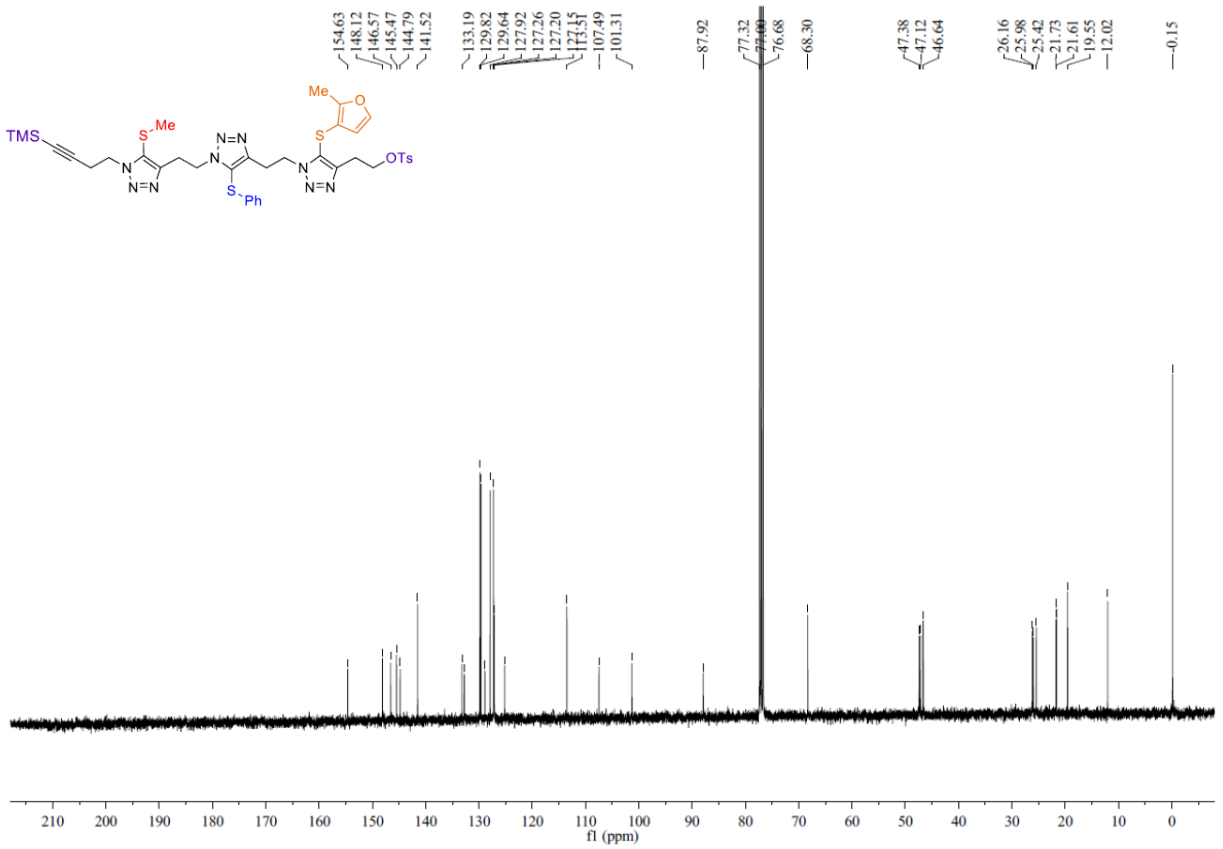


Figure S74. ^{13}C NMR spectra of **9b** ($CDCl_3$, 100 MHz).

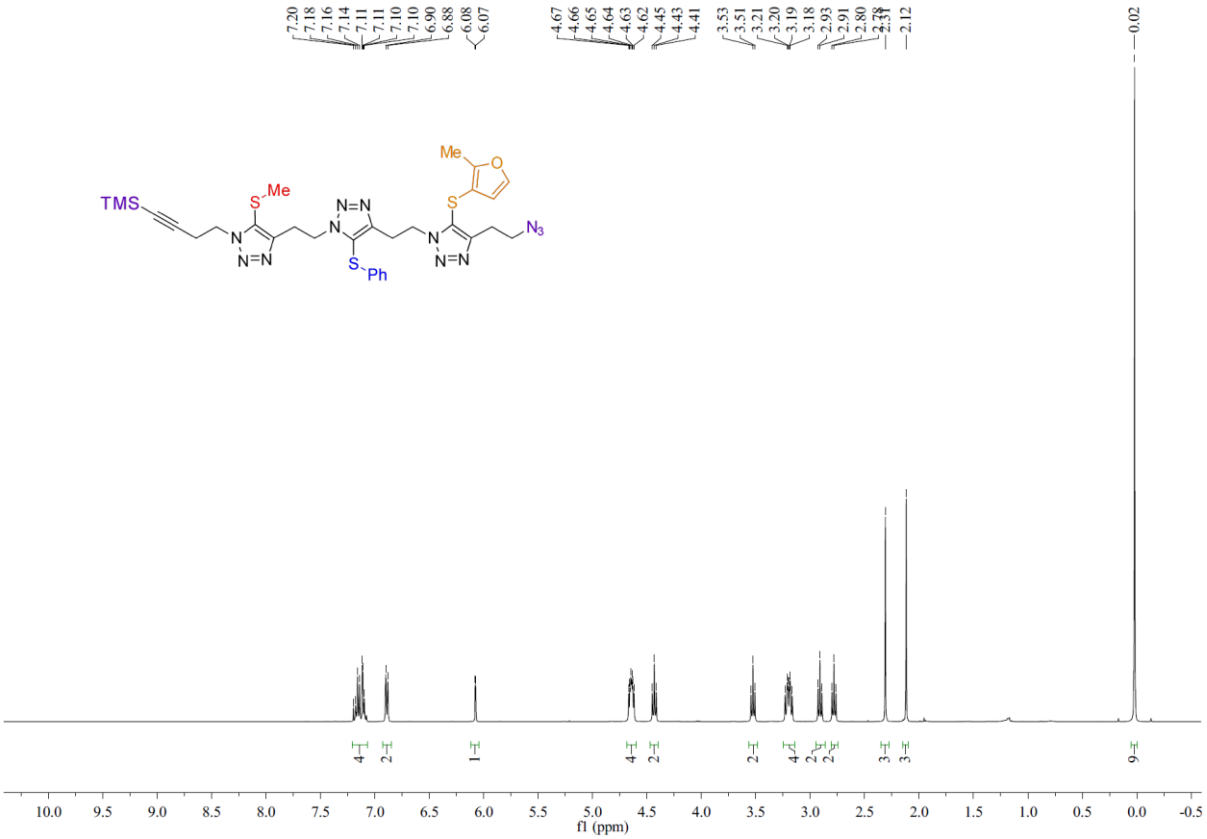


Figure S75. ^{1}H NMR spectra of **9c** ($CDCl_3$, 400 MHz).

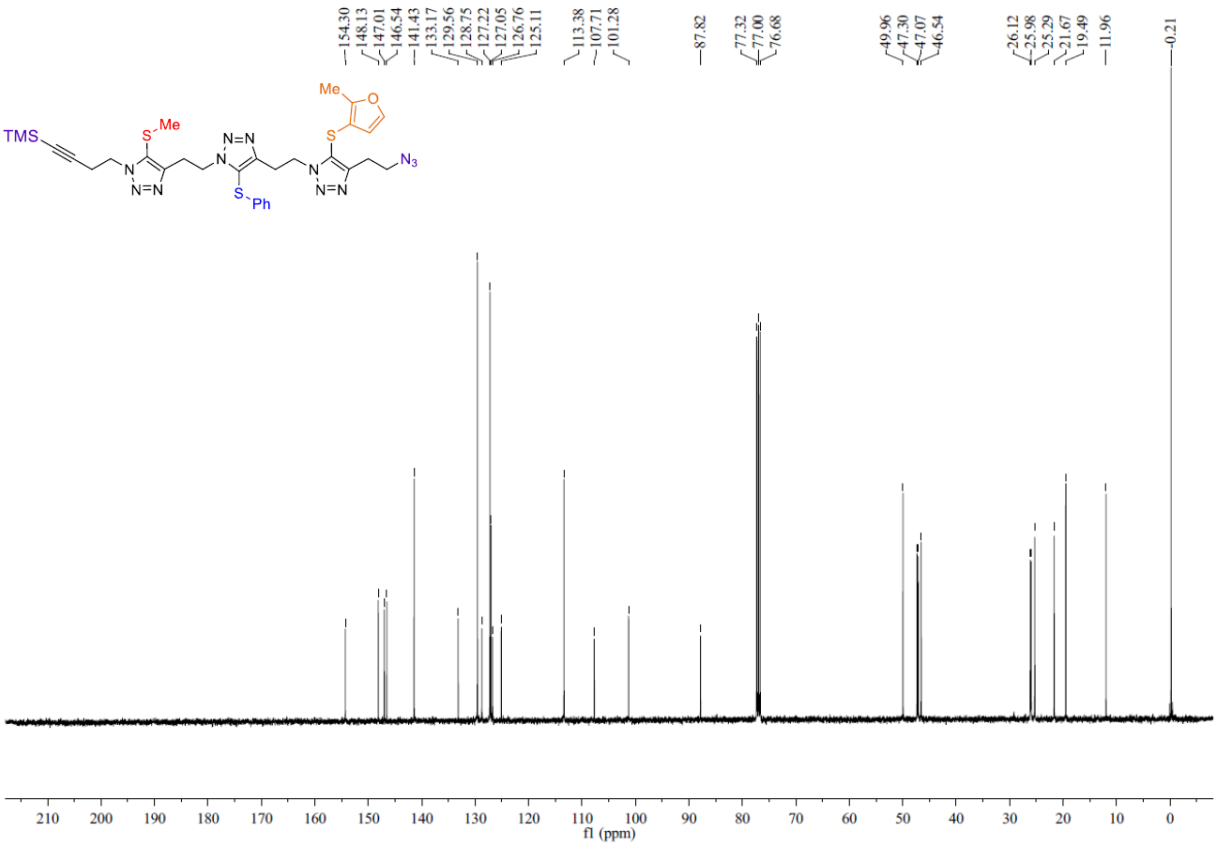


Figure S76. ^{13}C NMR spectra of **9c** ($CDCl_3$, 100 MHz).

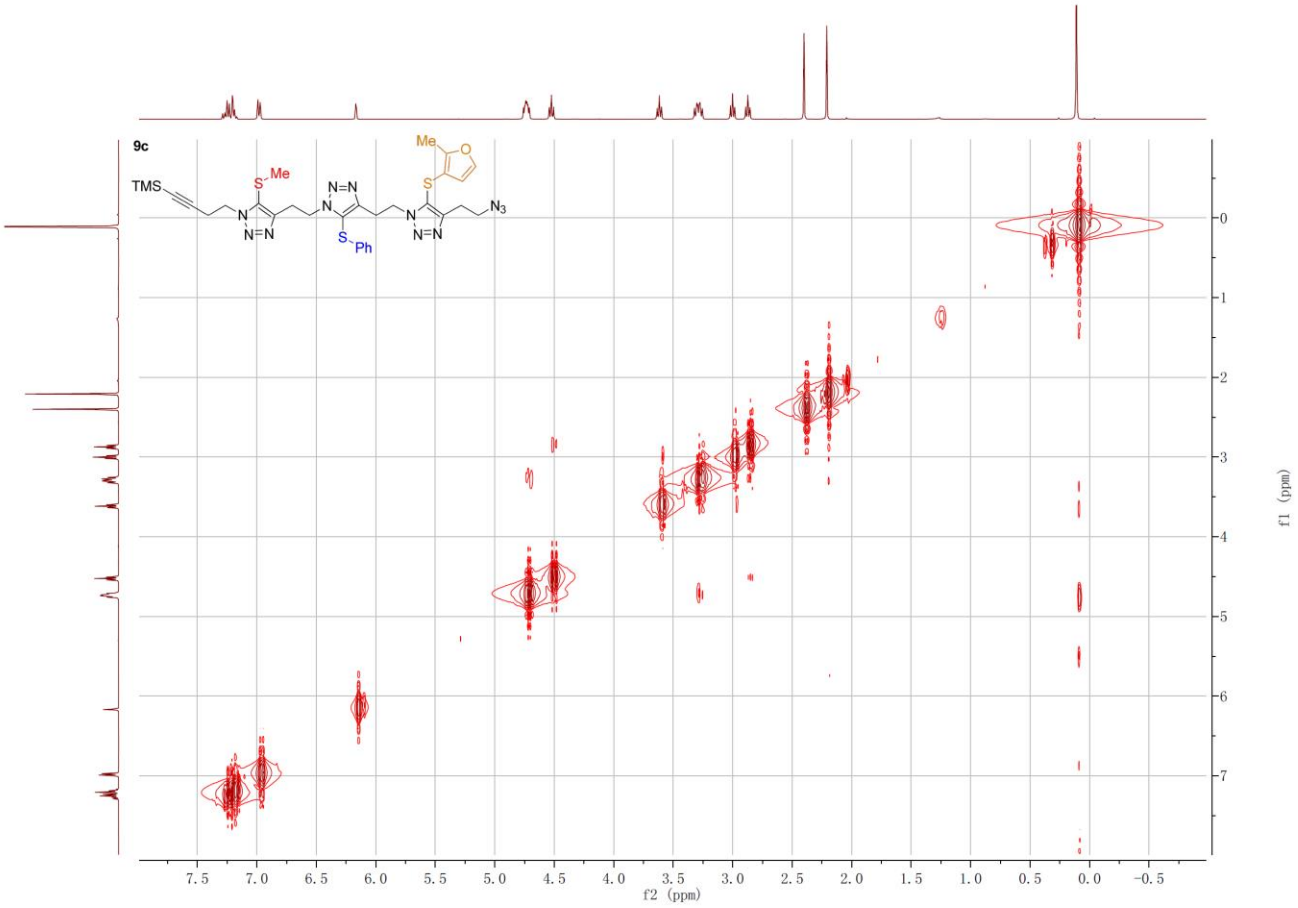


Figure S77. 2D NOESY spectra of **9c** ($CDCl_3$, 400 MHz).

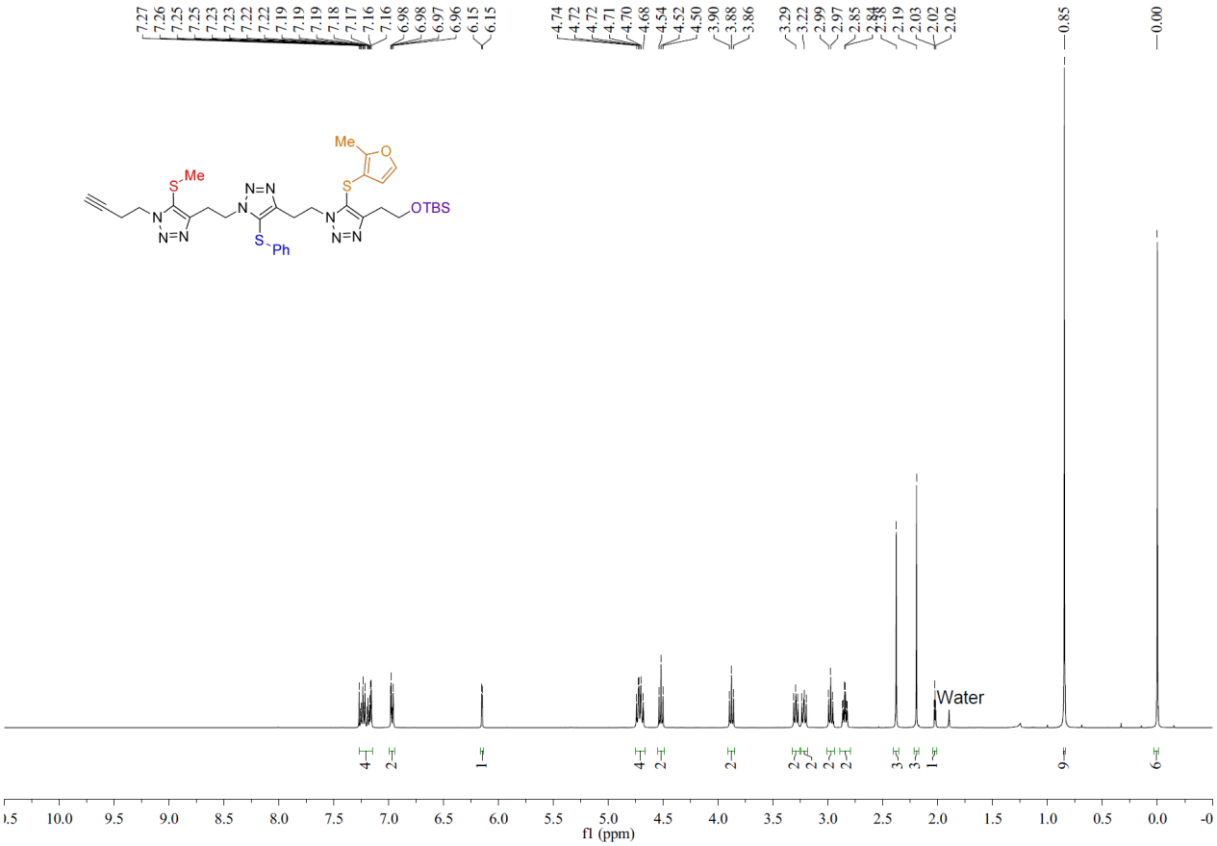


Figure S78. ^{1}H NMR spectra of **9d** ($CDCl_3$, 400 MHz).

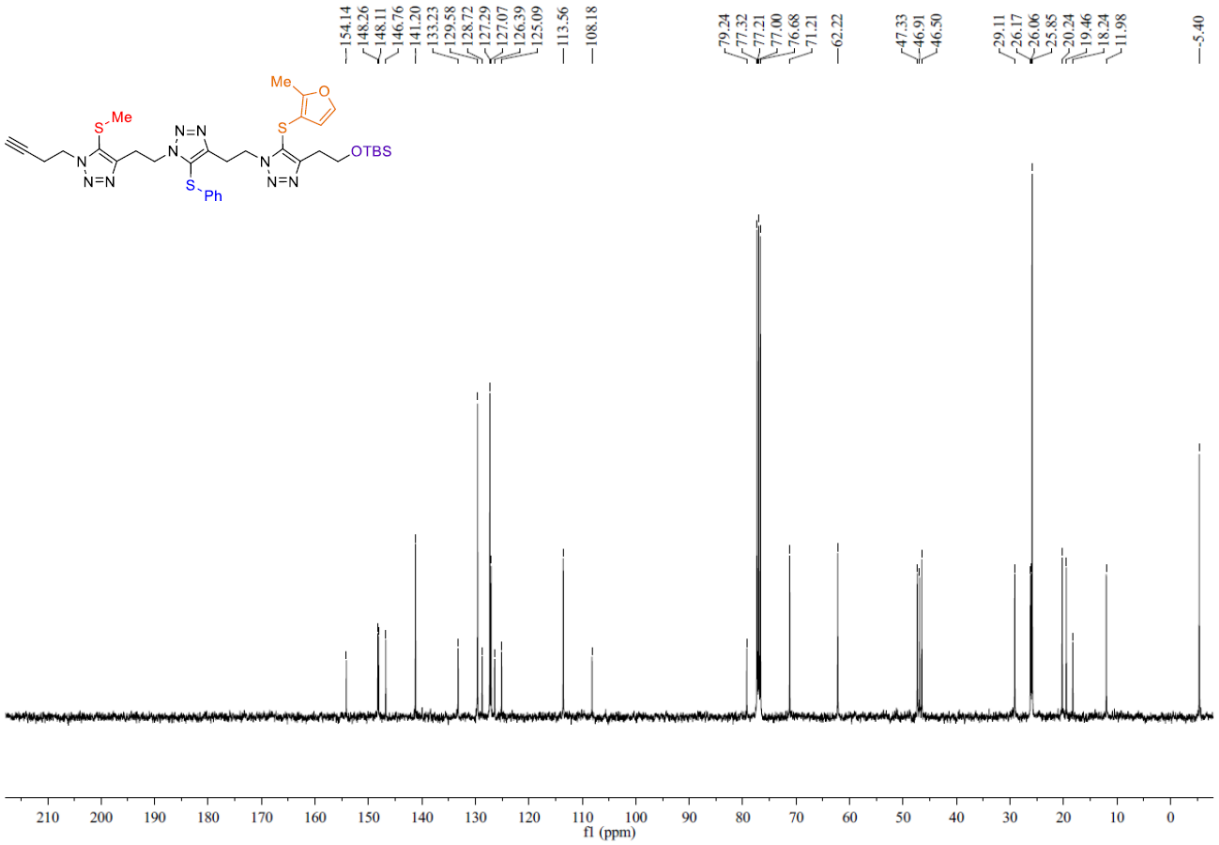


Figure S79. ^{13}C NMR spectra of **9d** ($CDCl_3$, 100 MHz).

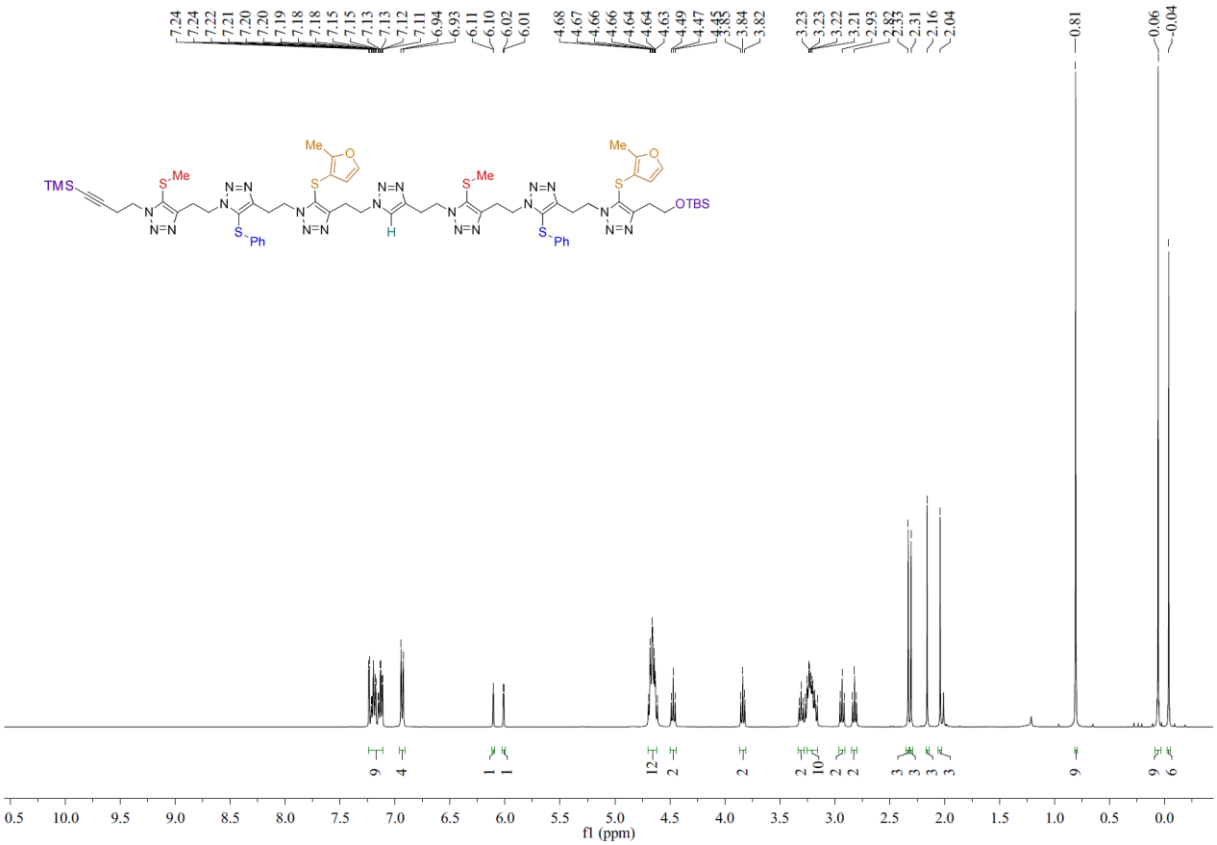


Figure S80. ^{1}H NMR spectra of **10a** ($CDCl_3$, 400 MHz).

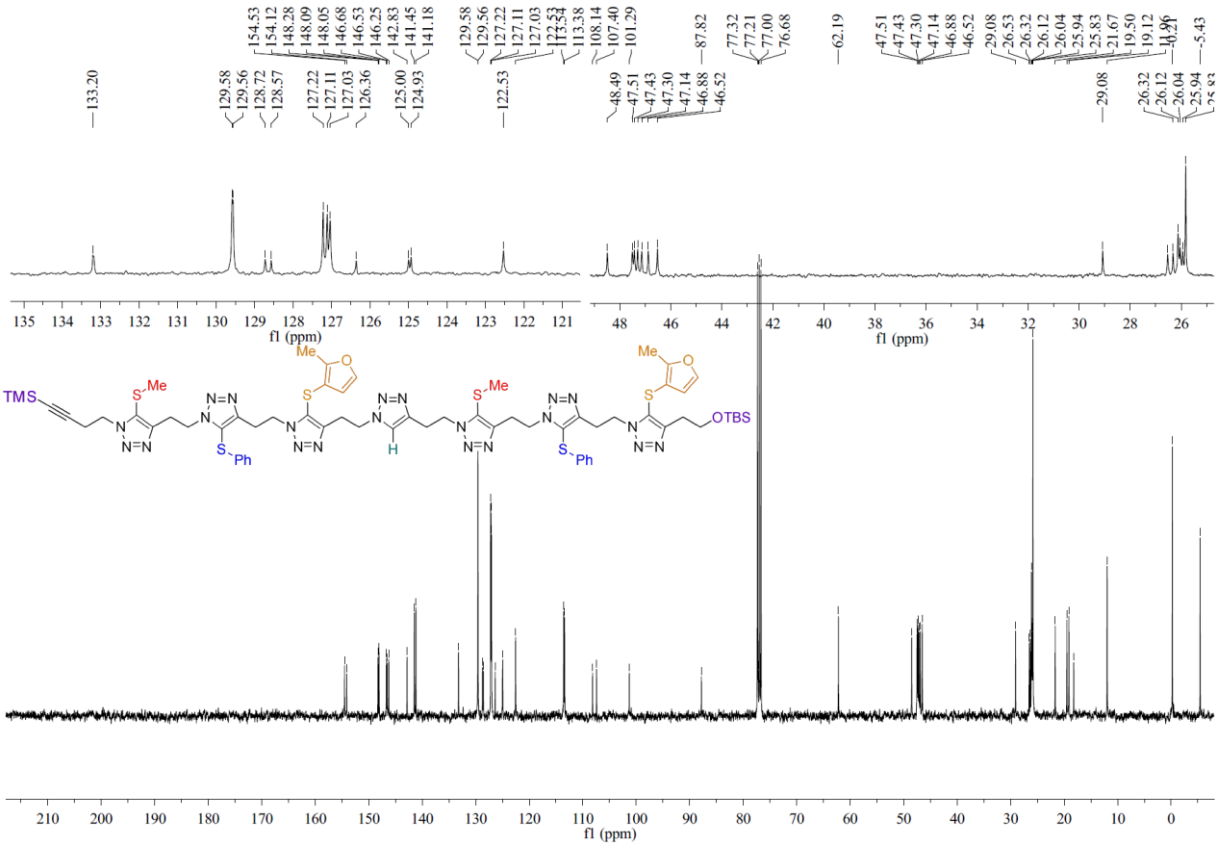


Figure S81. ^{13}C NMR spectra of **10a** ($CDCl_3$, 100 MHz).

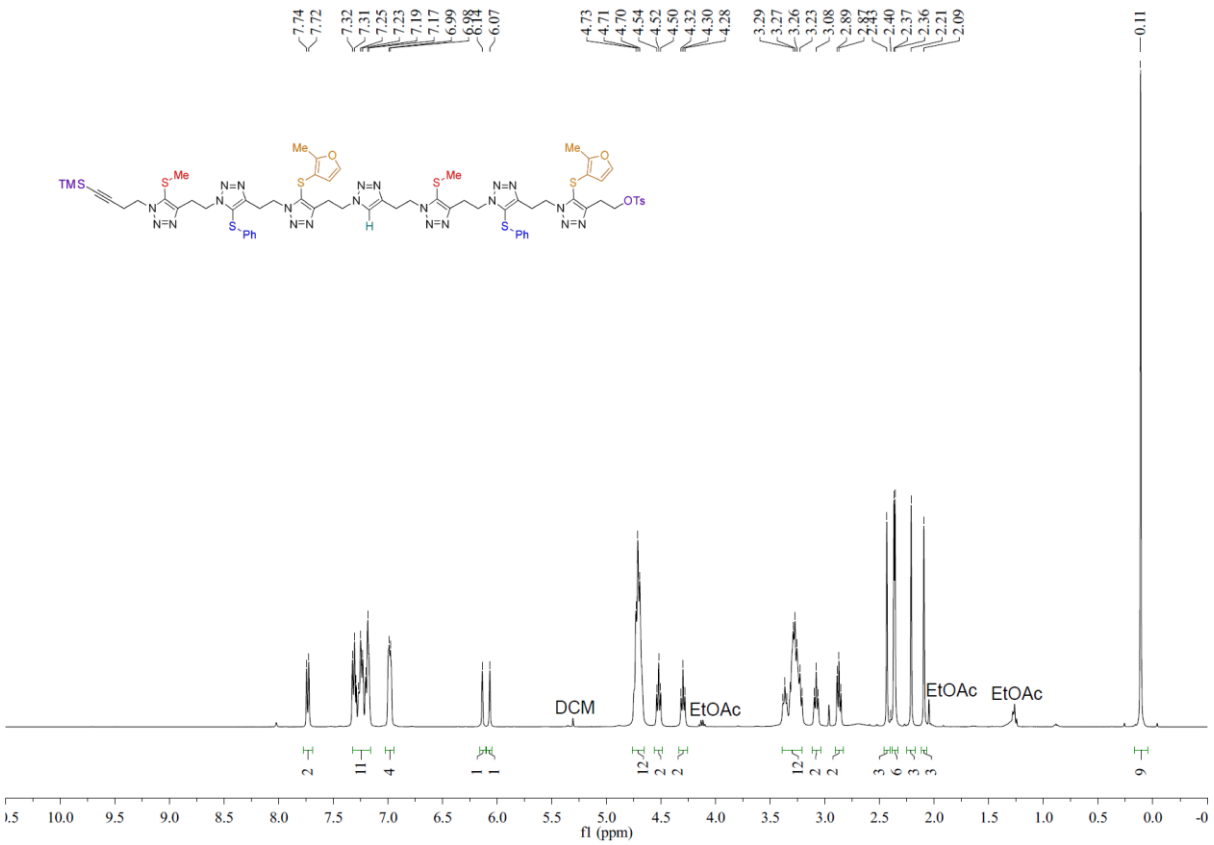


Figure S82. ^{1}H NMR spectra of **10b** ($CDCl_3$, 400 MHz).

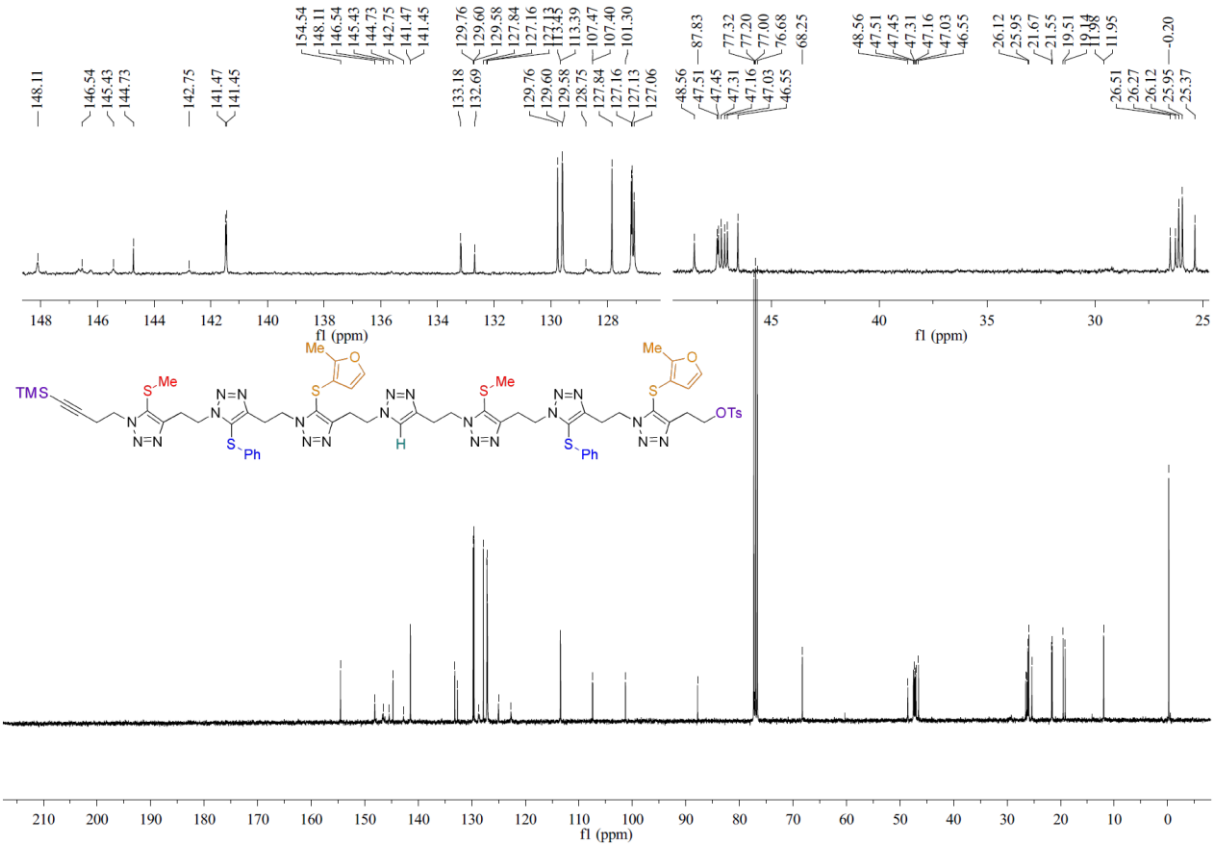


Figure S83. ^{13}C NMR spectra of **10b** ($CDCl_3$, 100 MHz).

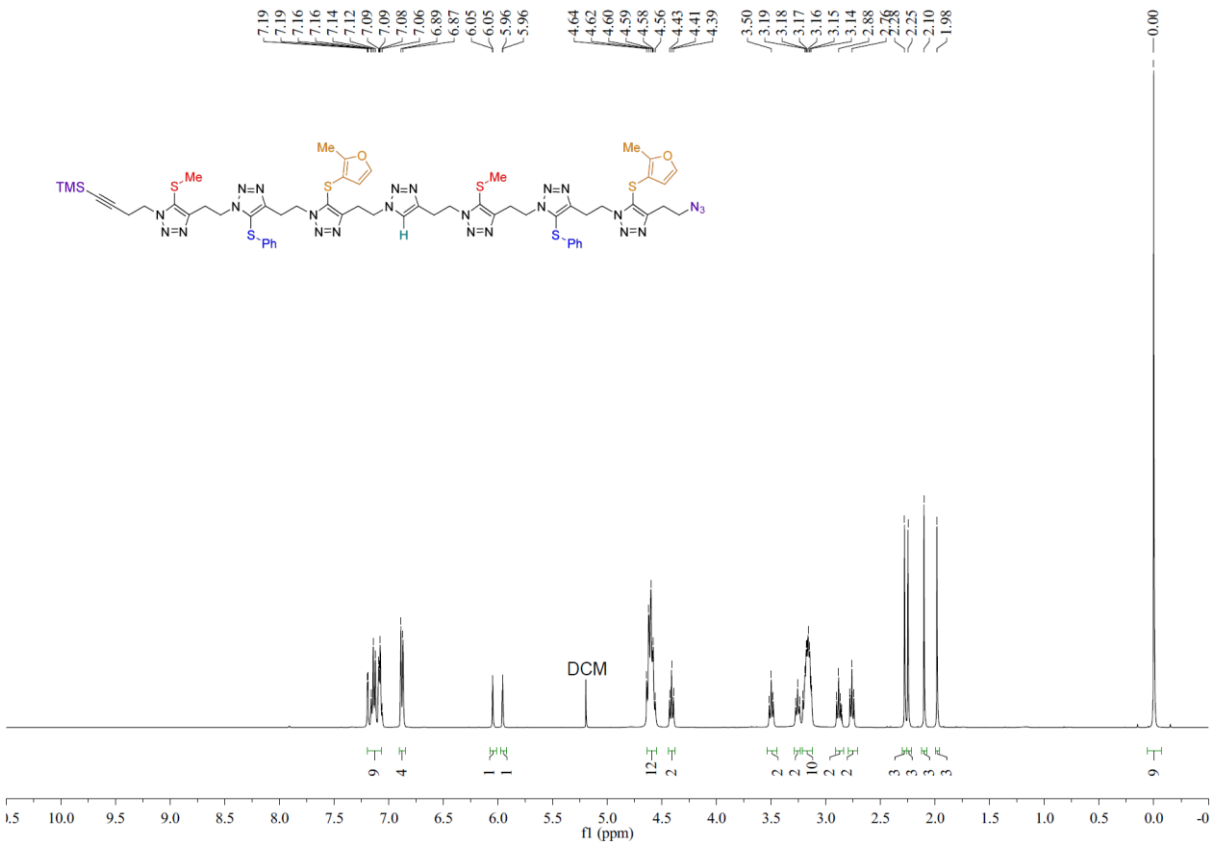


Figure S84. ^{1}H NMR spectra of **10c** ($CDCl_3$, 400 MHz).

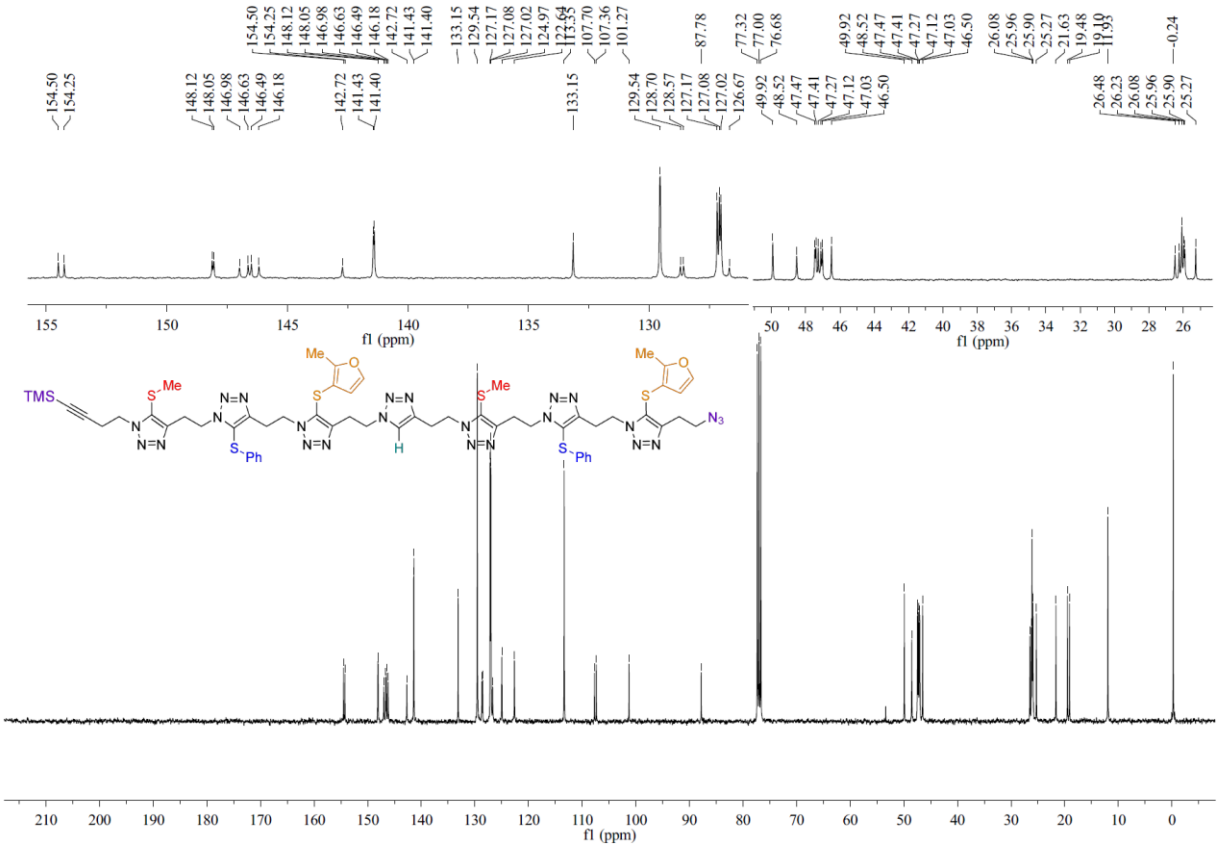


Figure S85. ^{13}C NMR spectra of **10c** ($CDCl_3$, 100 MHz).

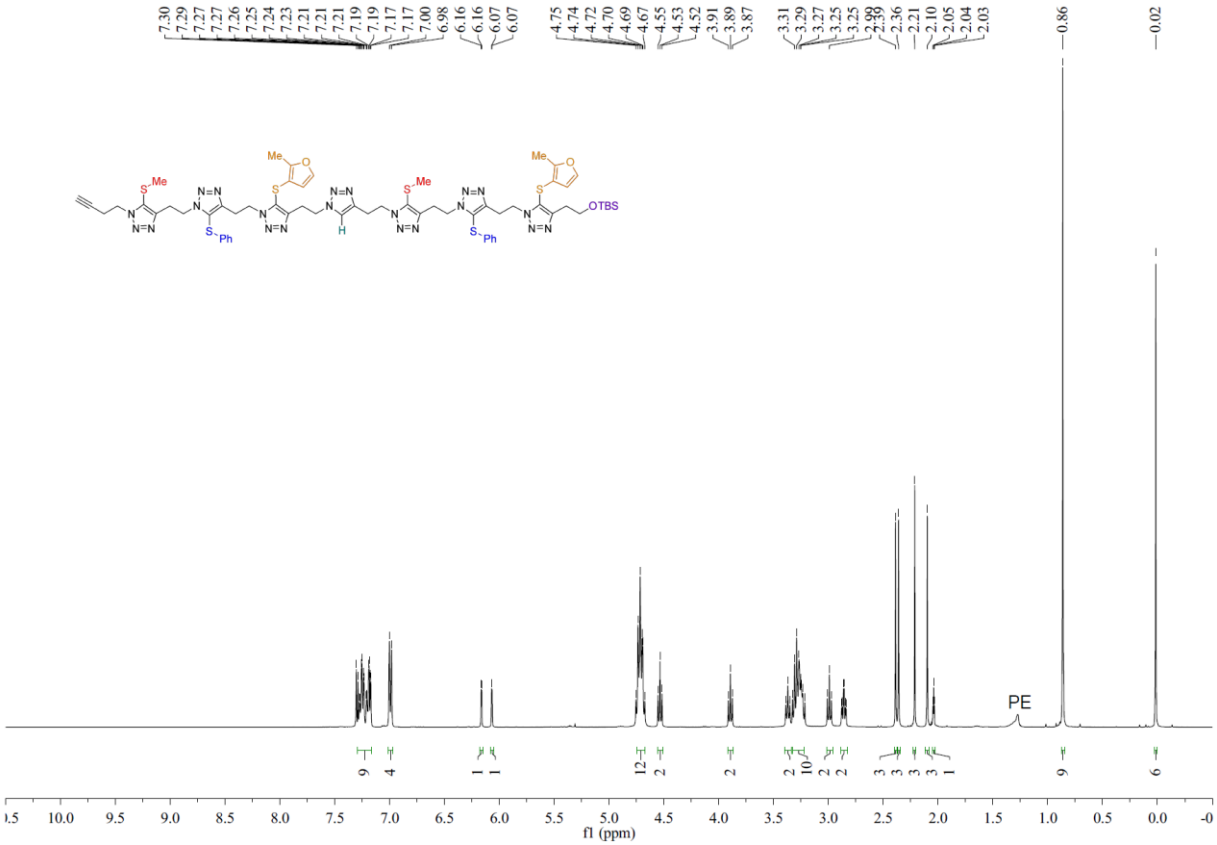


Figure S86. ^{1}H NMR spectra of **10d** ($CDCl_3$, 400 MHz).

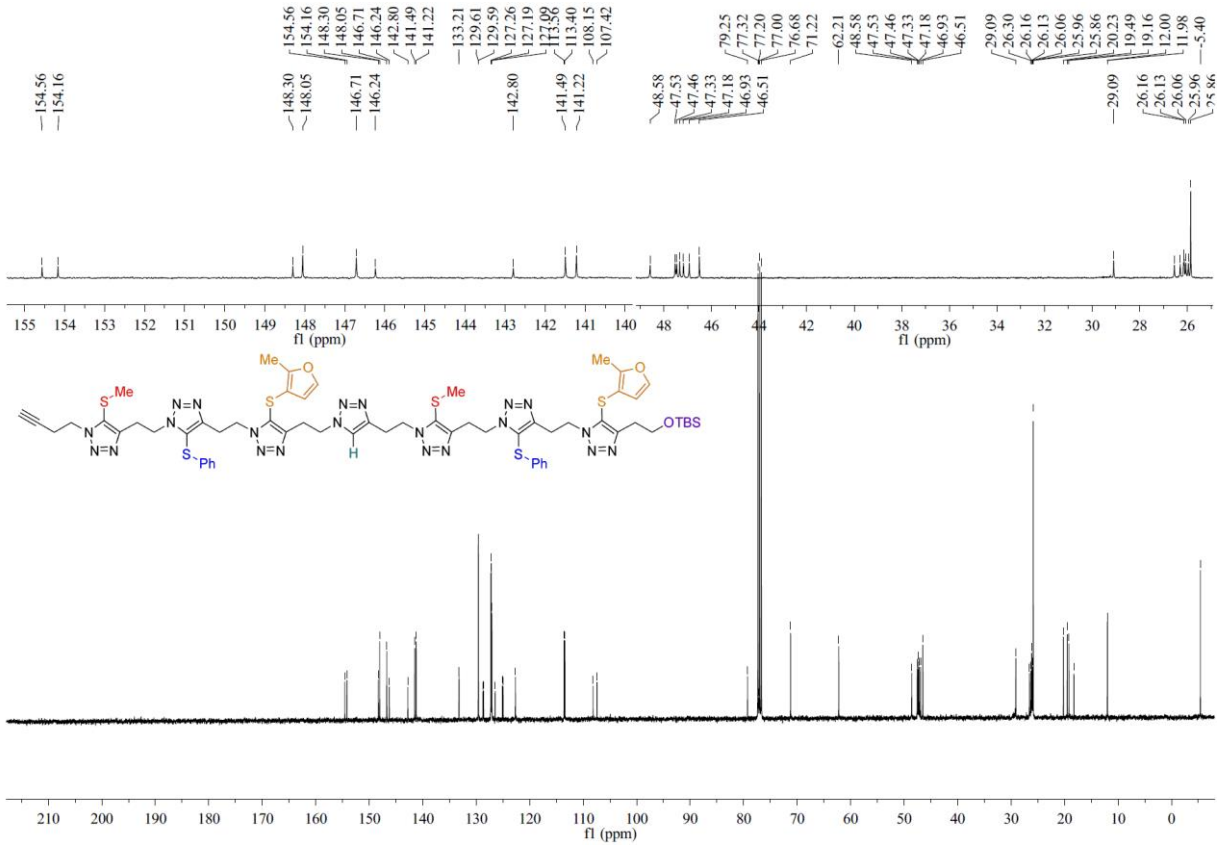


Figure S87. ^{13}C NMR spectra of **10d** ($CDCl_3$, 100 MHz).

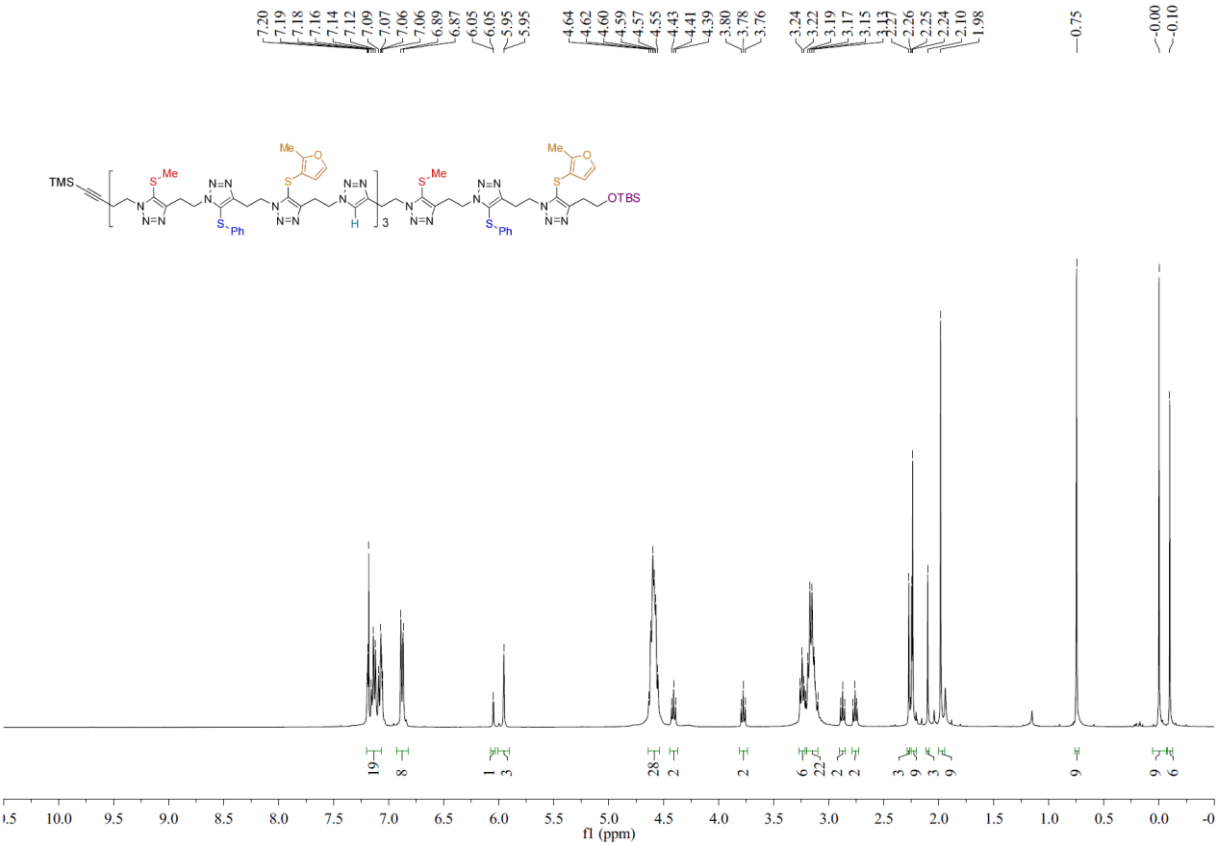


Figure S88. ^{1}H NMR spectra of **11a** ($CDCl_3$, 400 MHz).

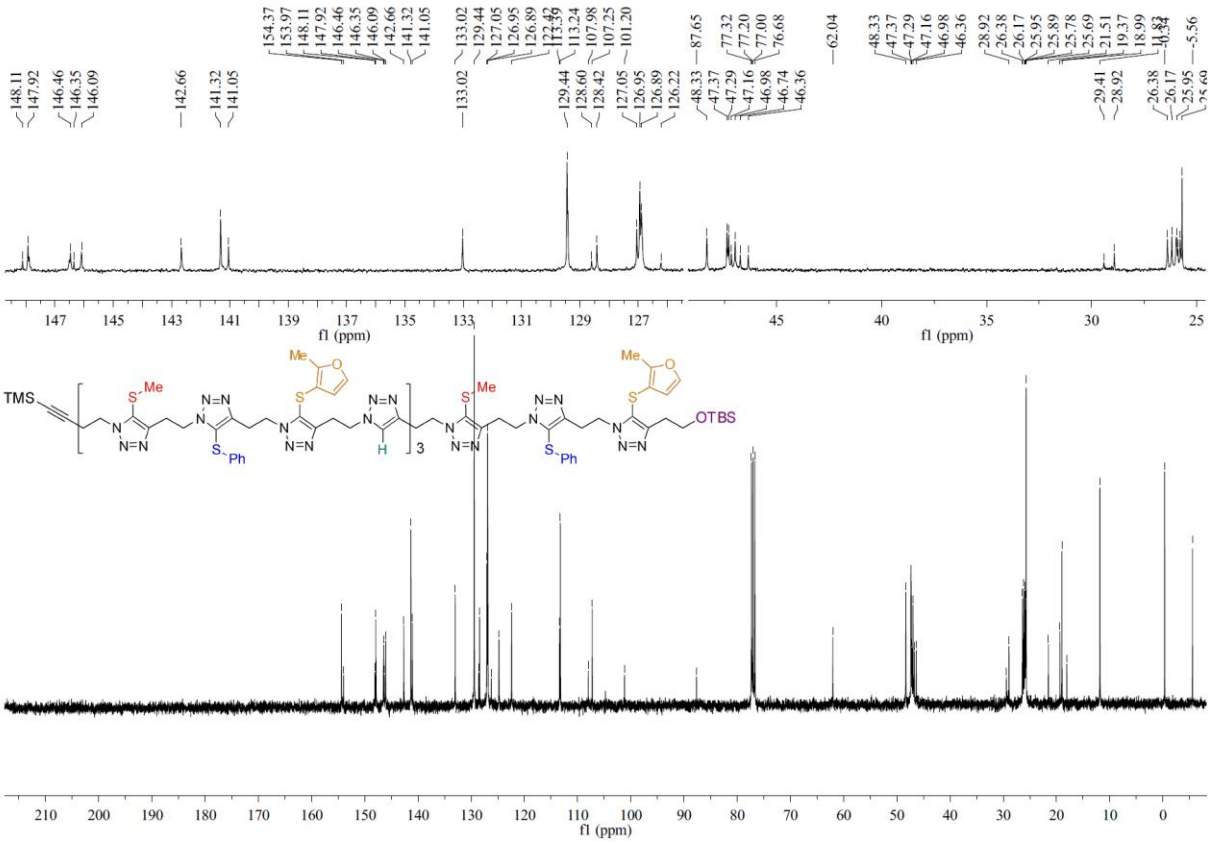


Figure S89. ^{13}C NMR spectra of **11a** ($CDCl_3$, 100 MHz).

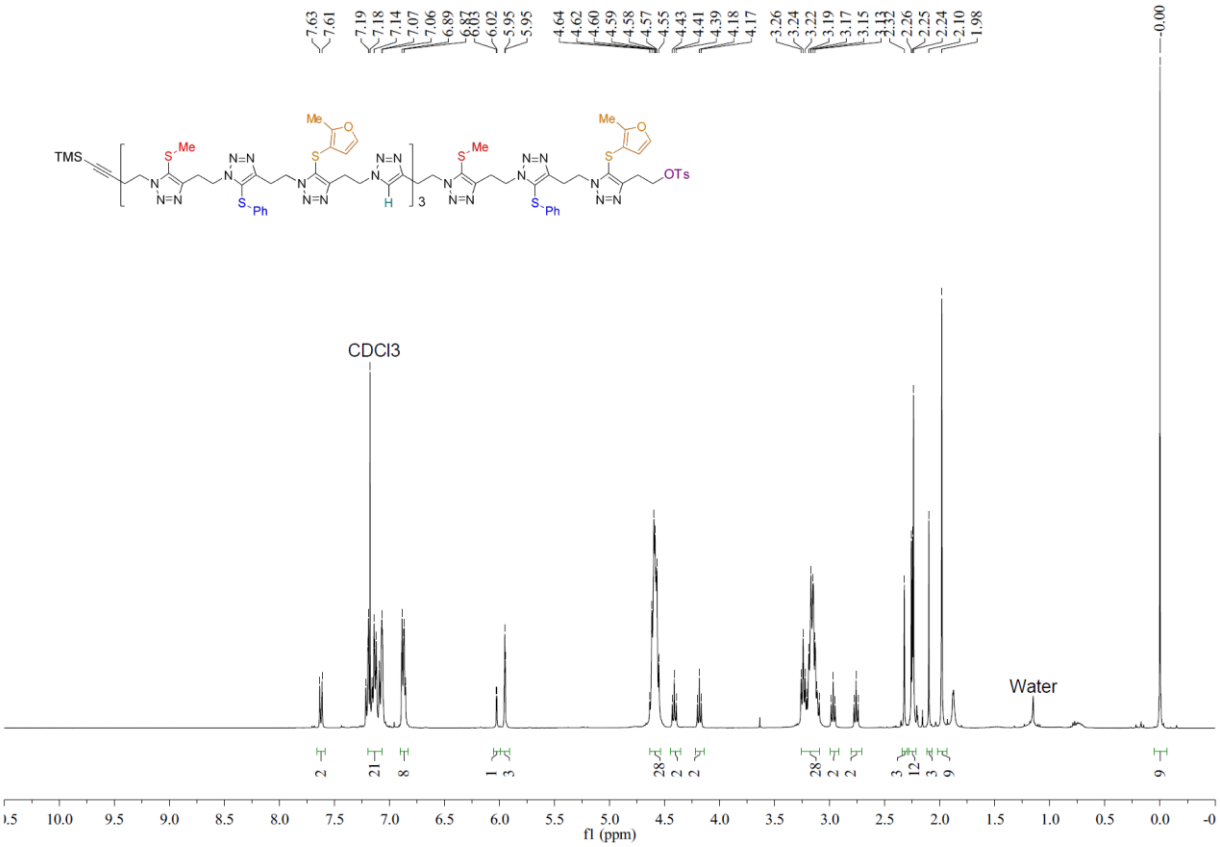


Figure S90. ^{1}H NMR spectra of **11b** ($CDCl_3$, 400 MHz).

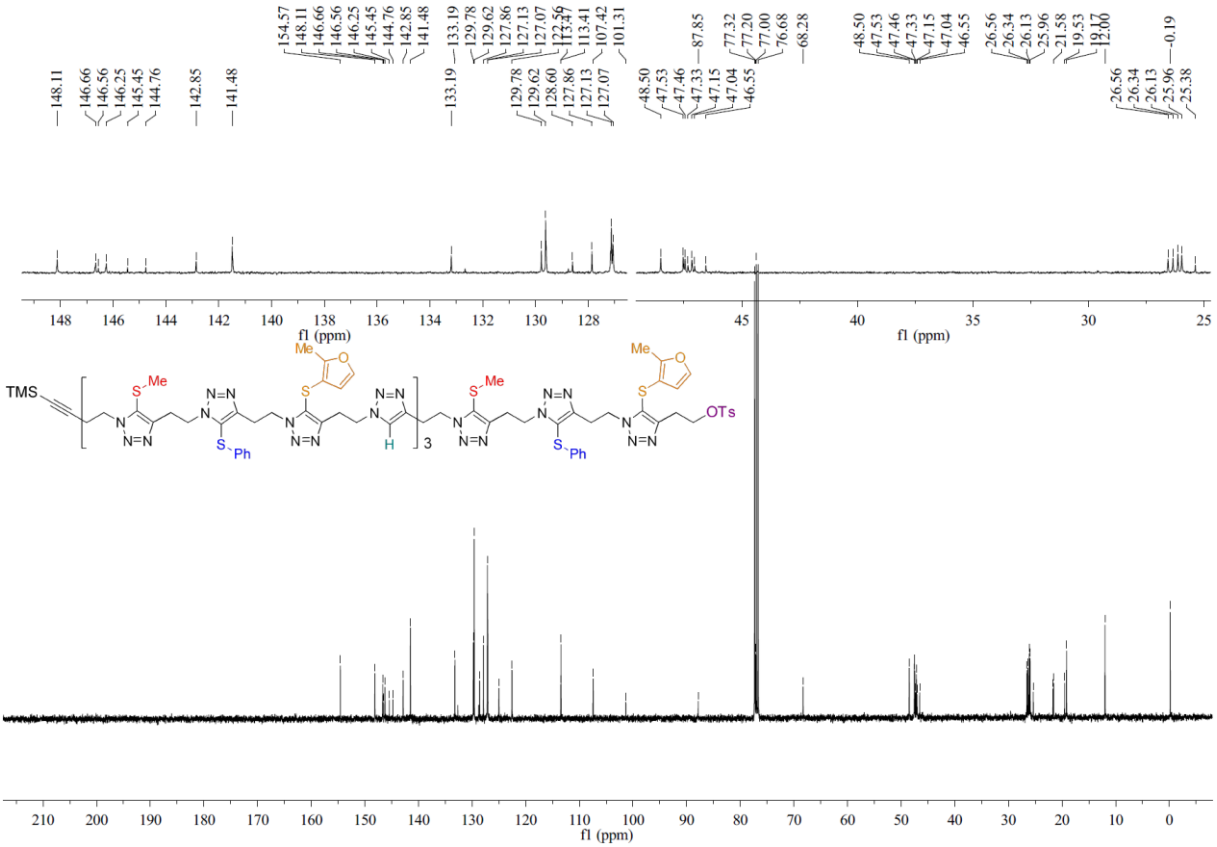


Figure S91. ^{13}C NMR spectra of **11b** ($CDCl_3$, 100 MHz).

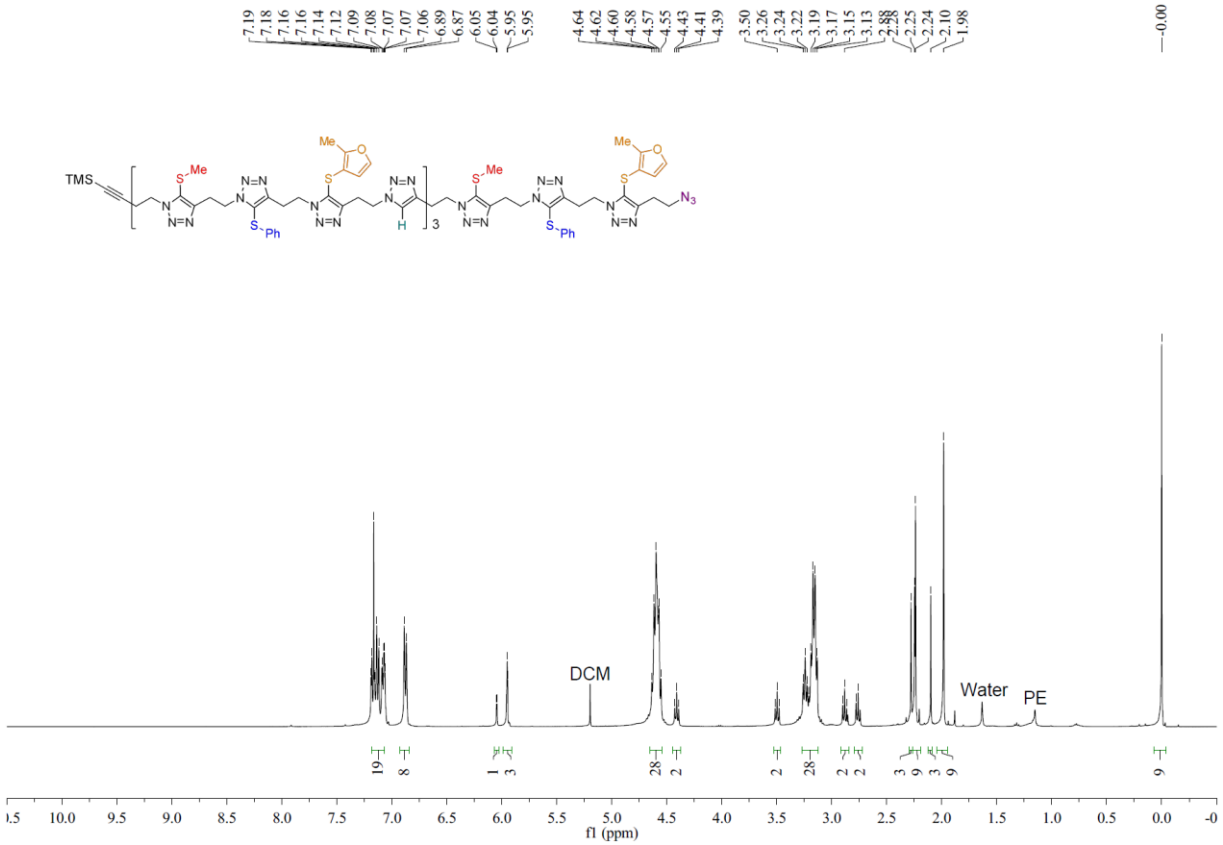


Figure S92. ^{1}H NMR spectra of **11c** ($CDCl_3$, 400 MHz).

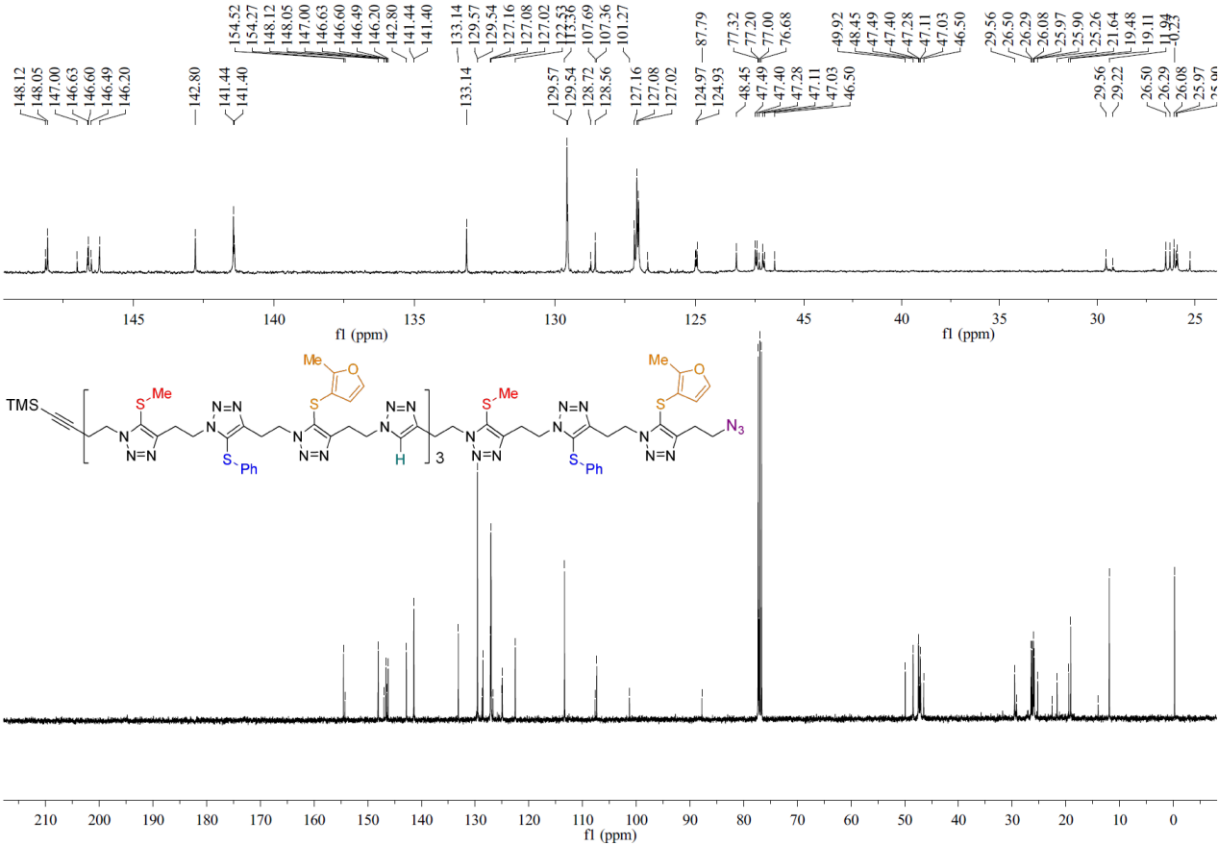


Figure S93. ^{13}C NMR spectra of **11c** ($CDCl_3$, 100 MHz).

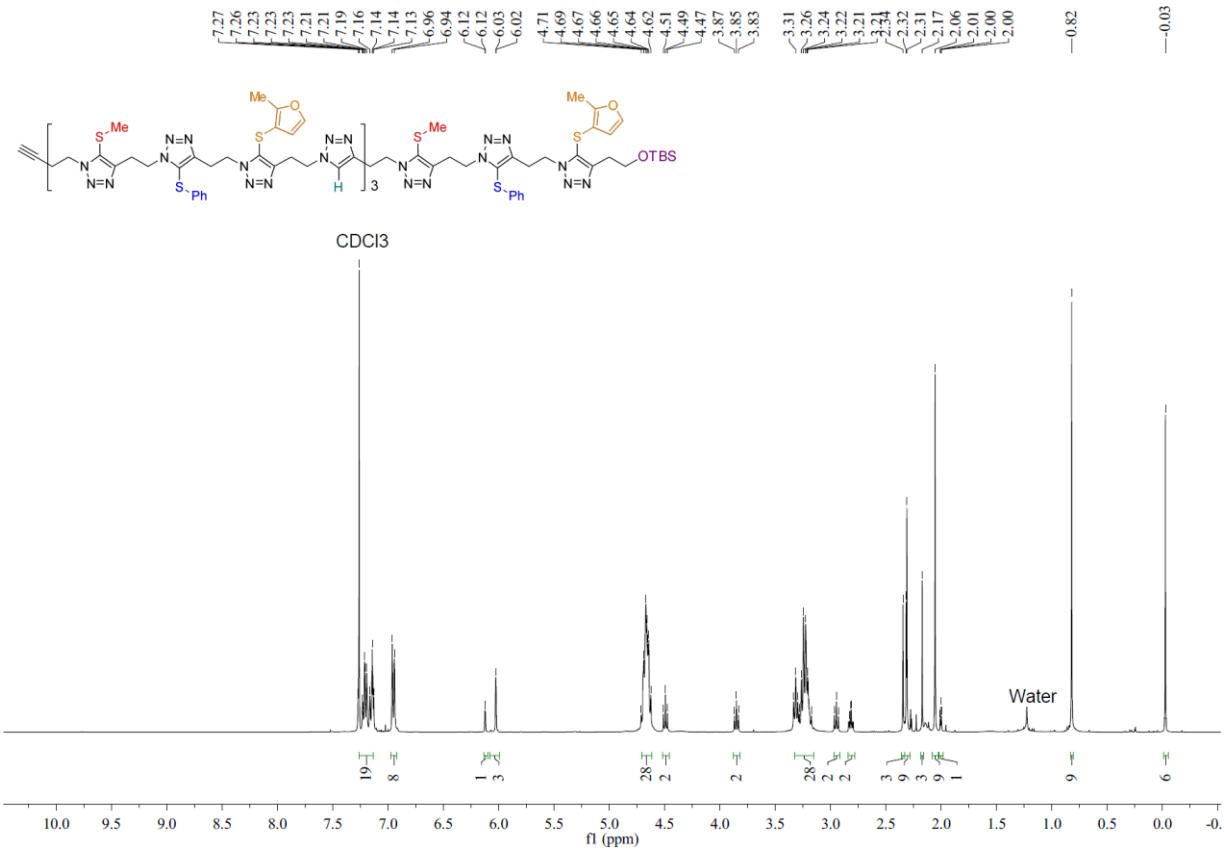


Figure S94. ^{1}H NMR spectra of **11d** ($CDCl_3$, 400 MHz).

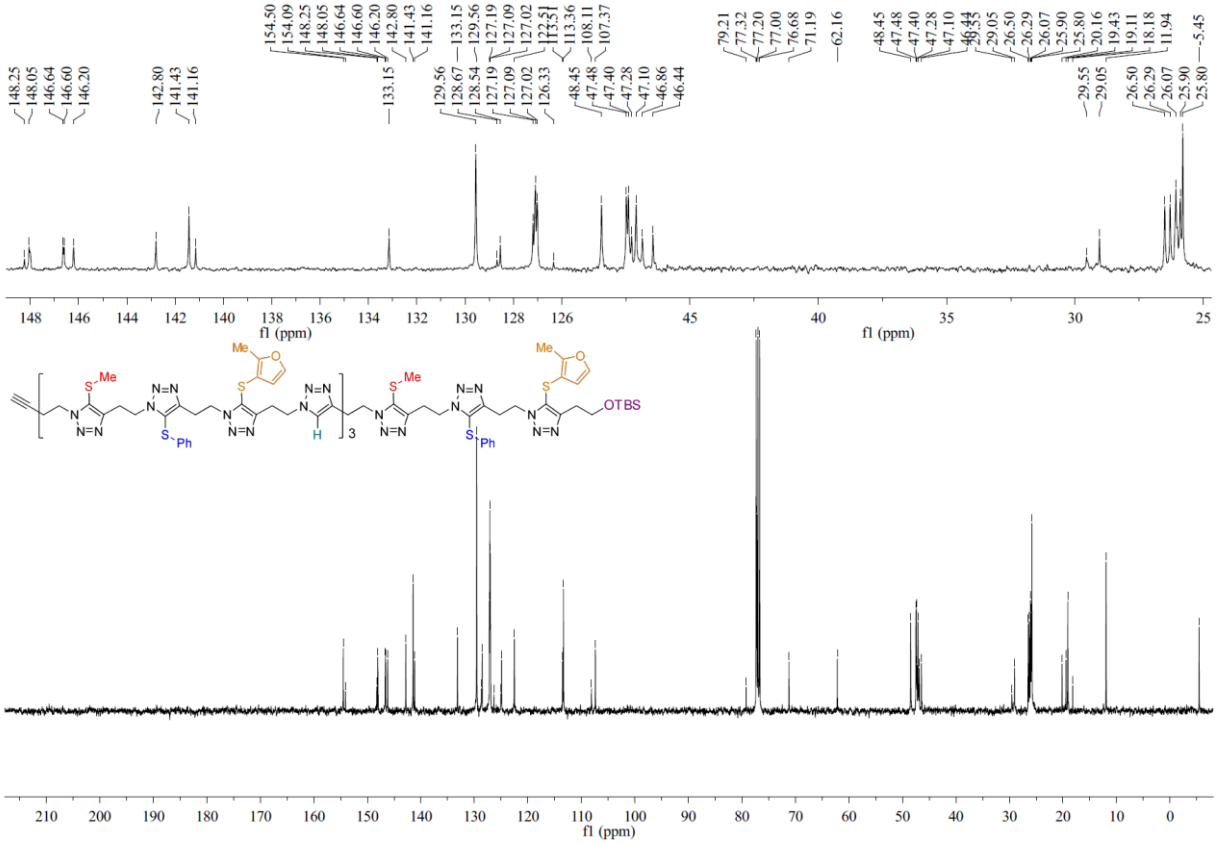


Figure S95. ^{13}C NMR spectra of **11d** ($CDCl_3$, 100 MHz).

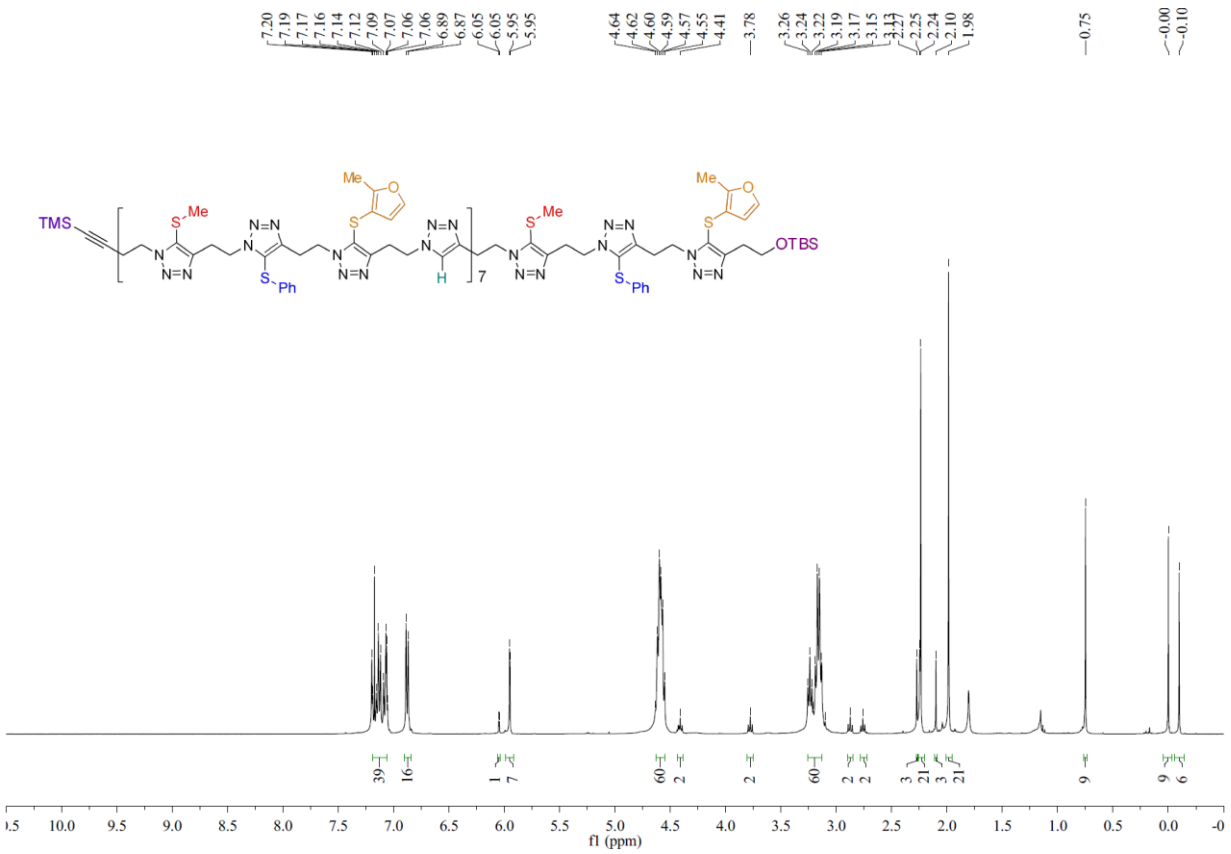


Figure S96. ^{1}H NMR spectra of **12a** ($CDCl_3$, 400 MHz).

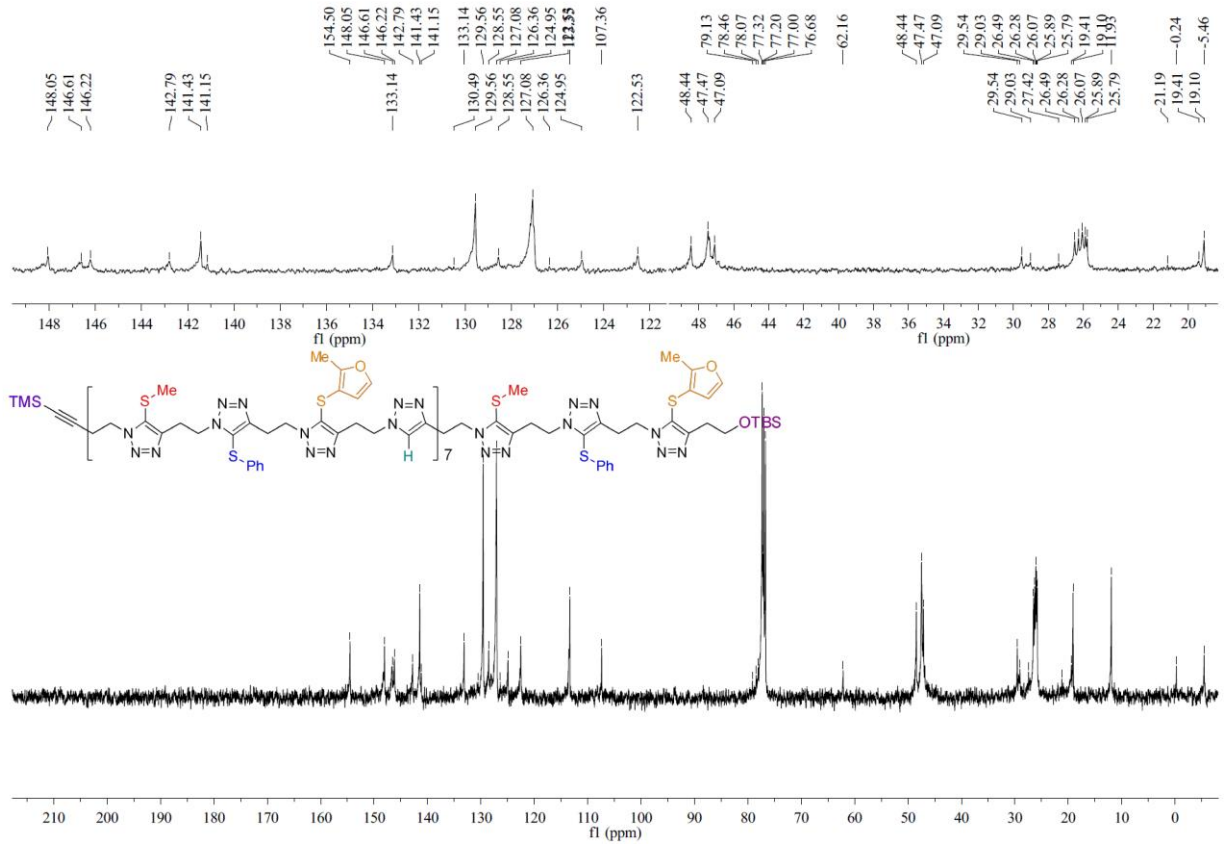


Figure S97. ^{13}C NMR spectra of **12a** ($CDCl_3$, 100 MHz).

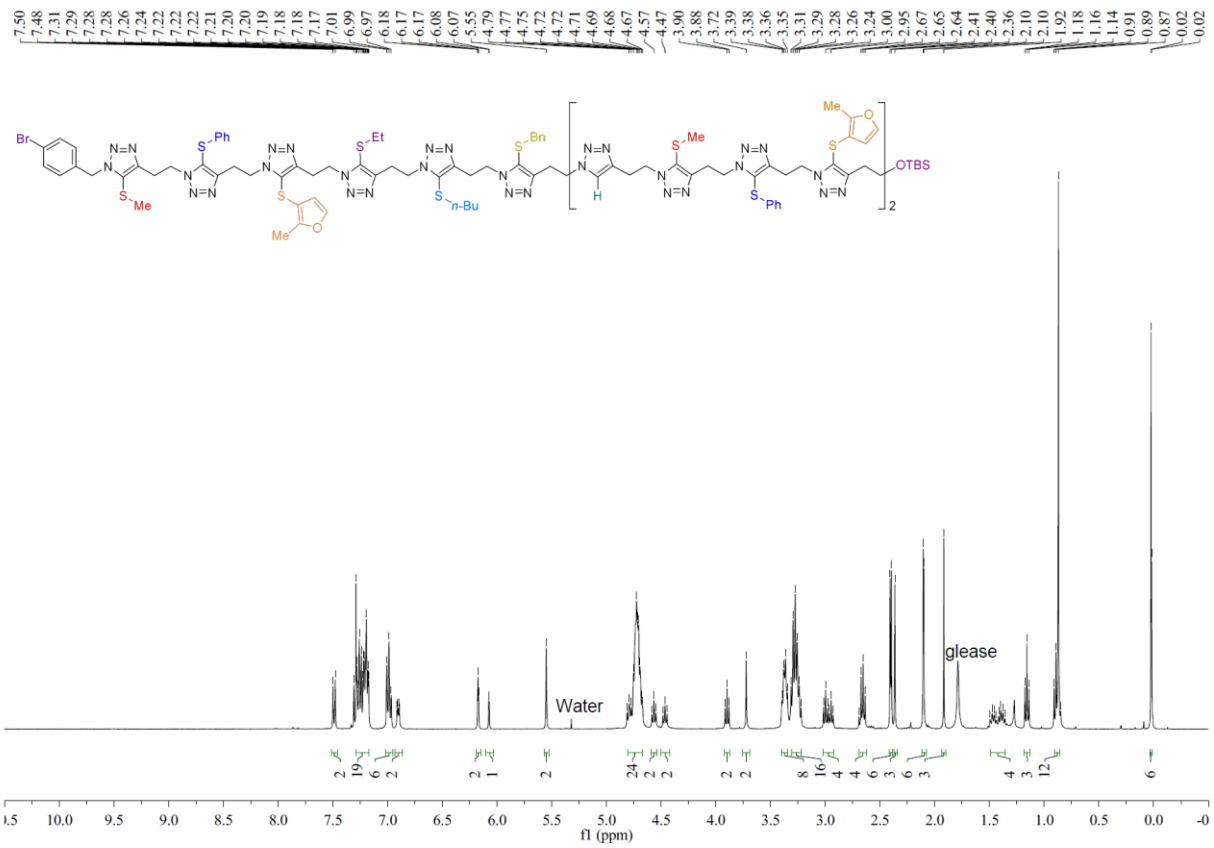


Figure S98. ^{1}H NMR spectra of **13** ($CDCl_3$, 400 MHz).

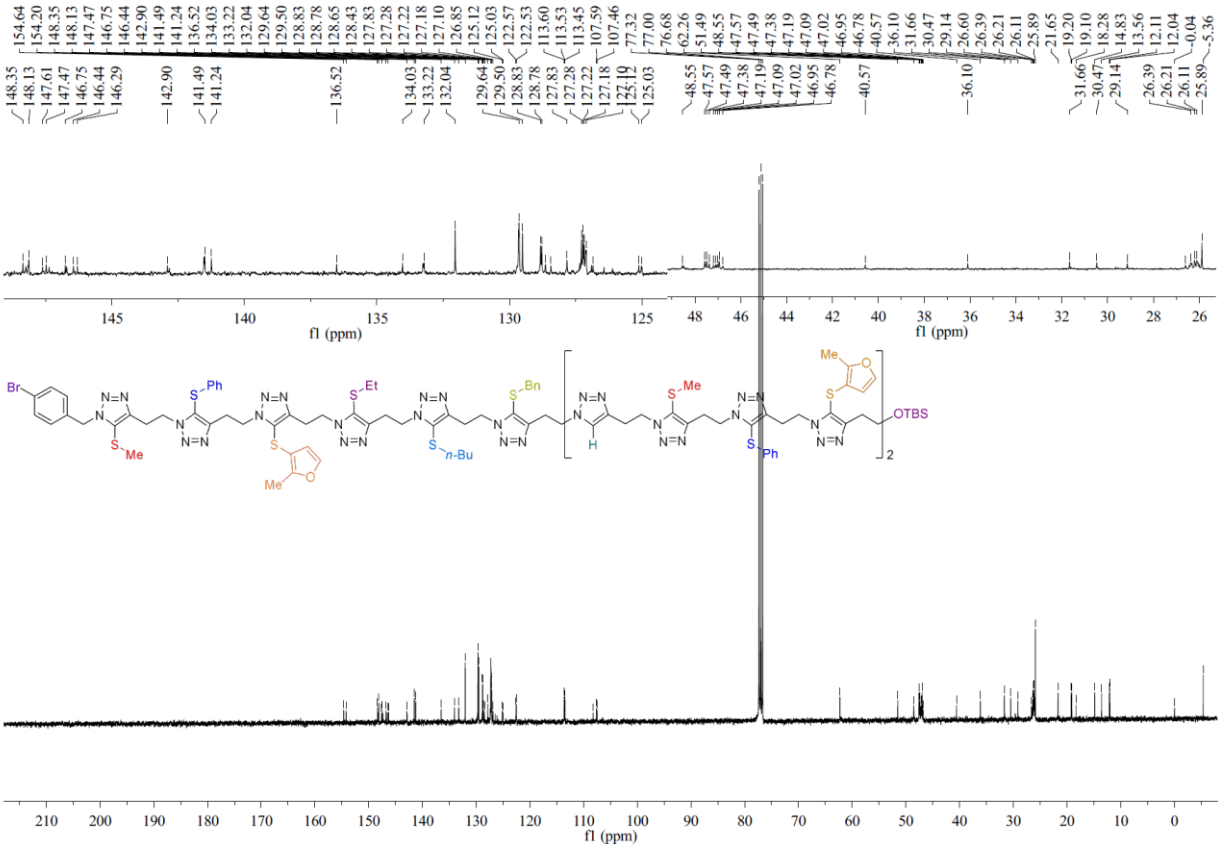


Figure S99. ^{13}C NMR spectra of **13** ($CDCl_3$, 100 MHz).

XI. Mass spectrum

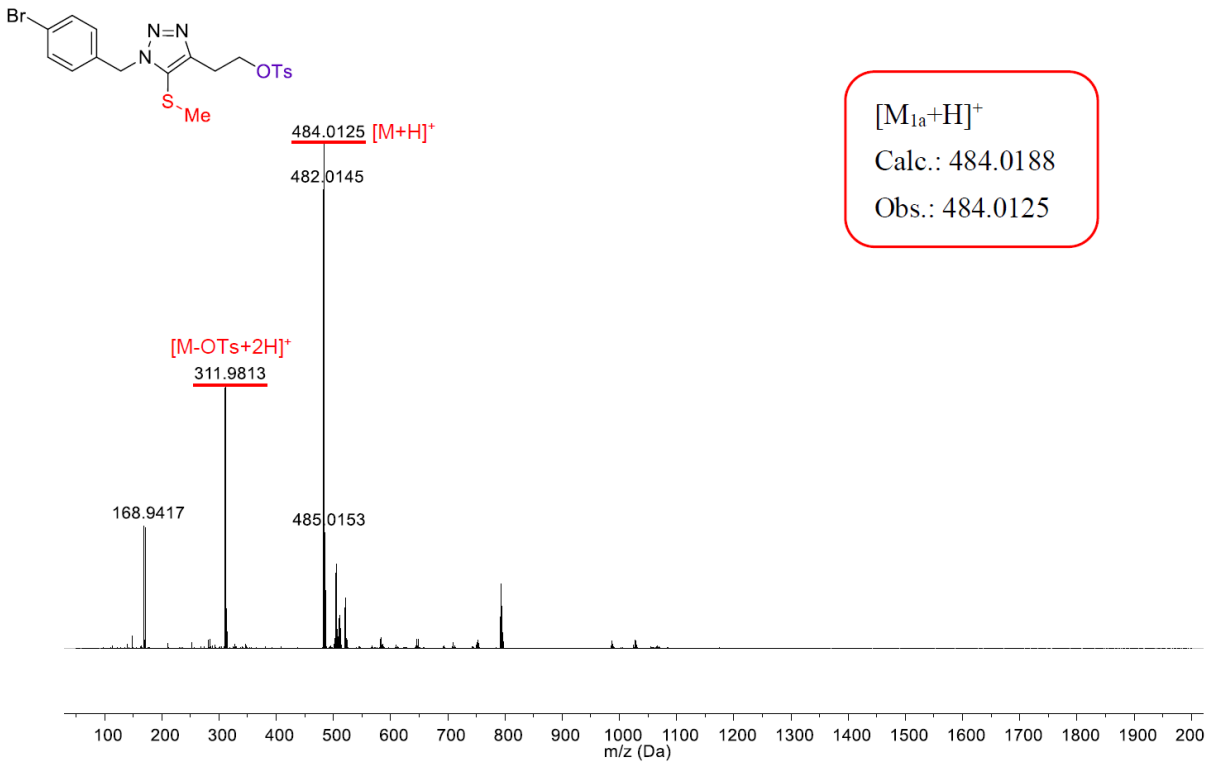


Figure S100. ESI-MS of **1a**.

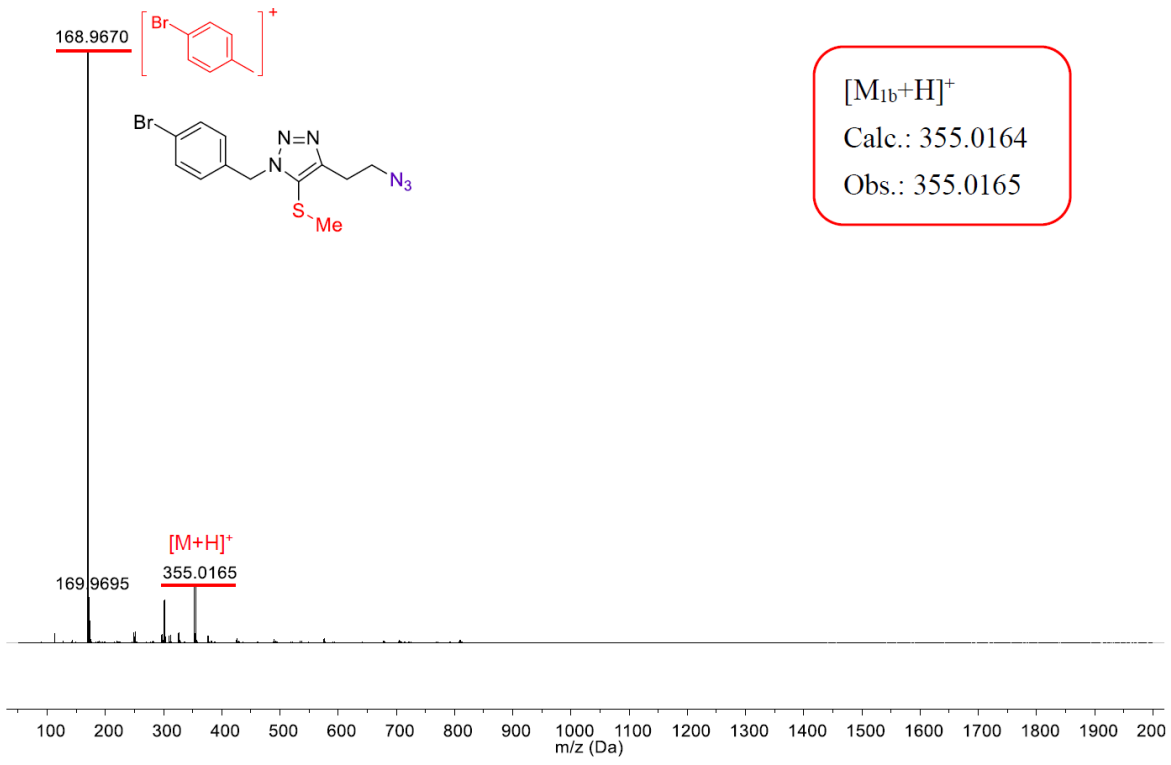


Figure S101. ESI-MS of **1b**.

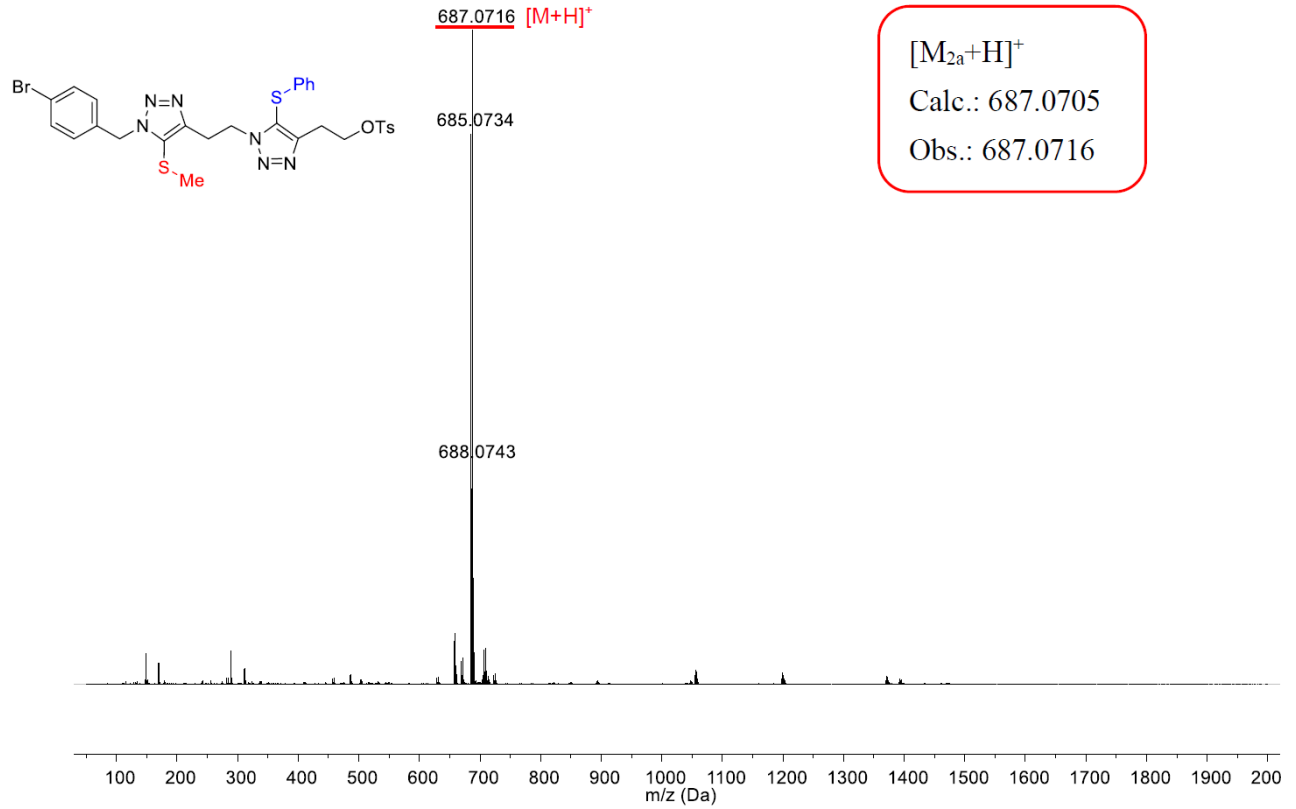


Figure S102. ESI-MS of **2a**.

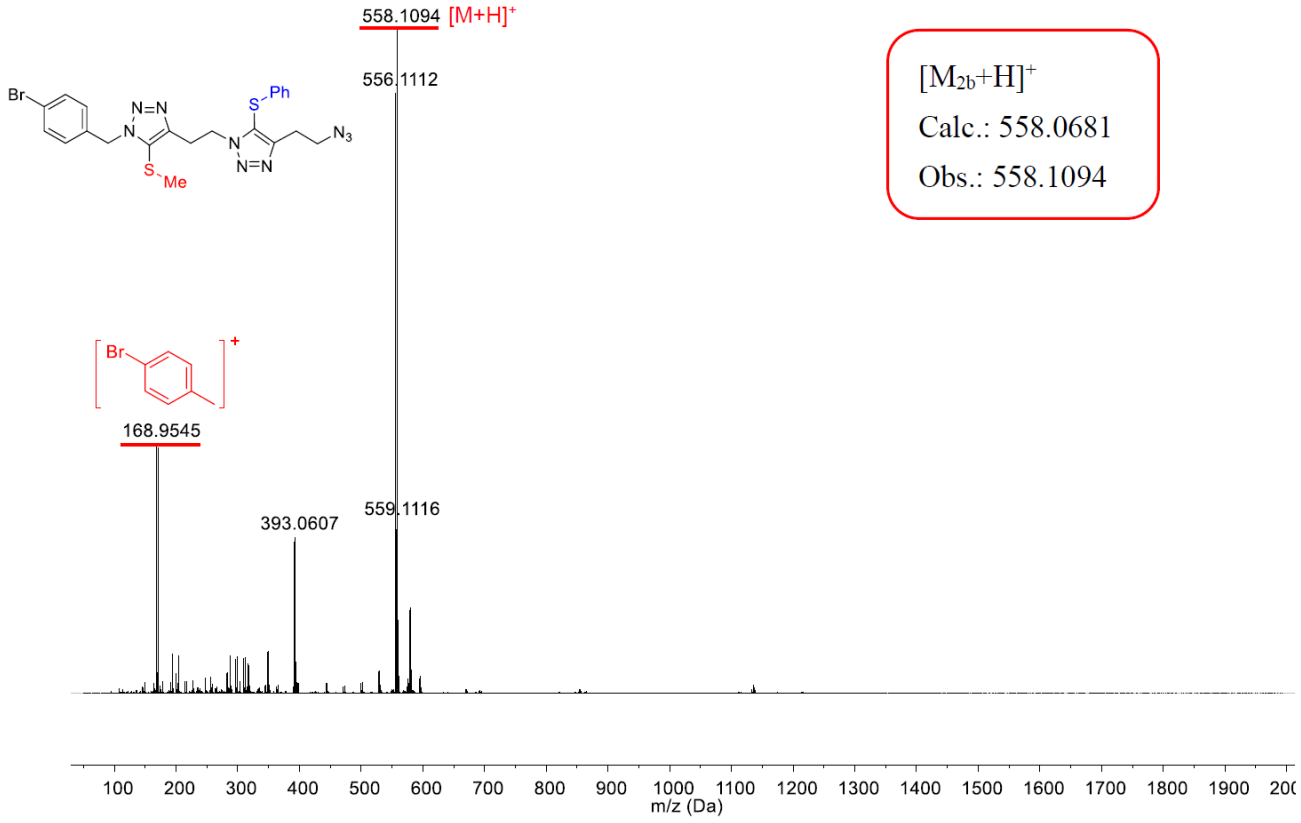


Figure S103. ESI-MS of **2b**.

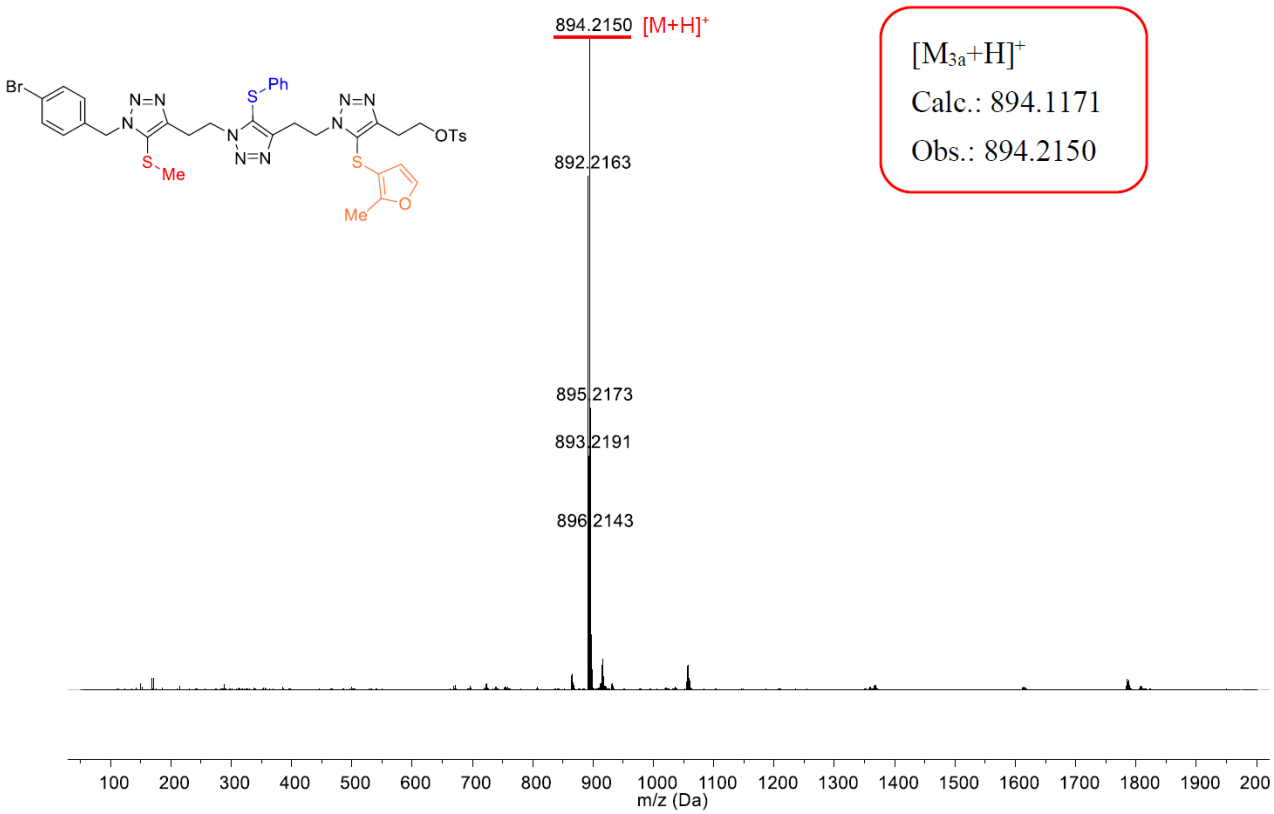


Figure S104. ESI-MS of **3a**.

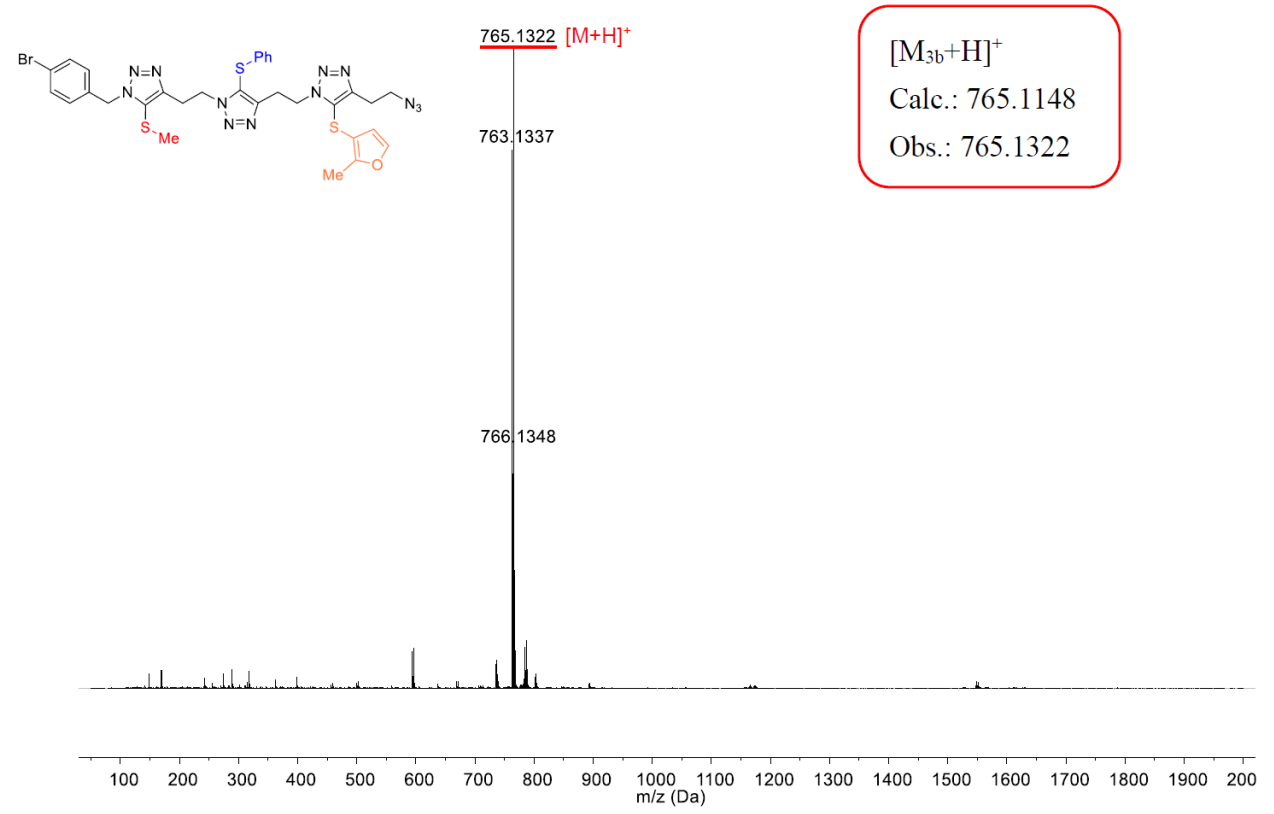


Figure S105. ESI-MS of **3b**.

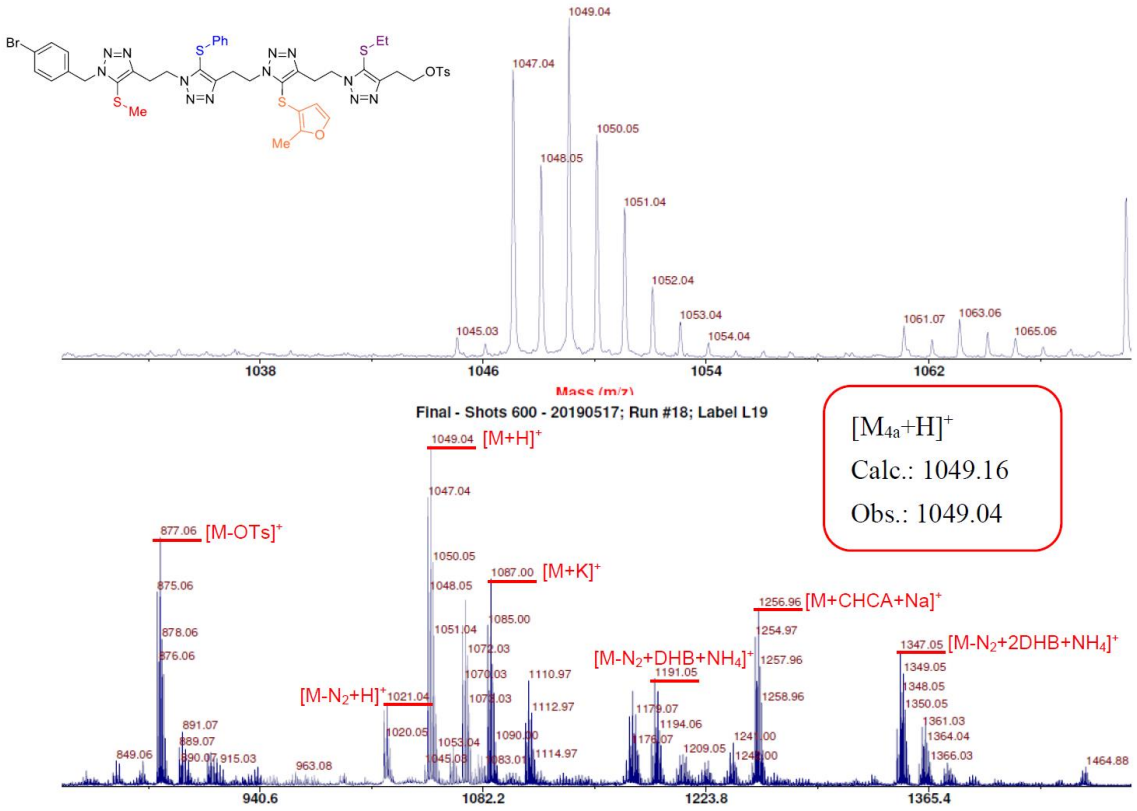


Figure S106. MALDI-TOF-MS of **4a**.

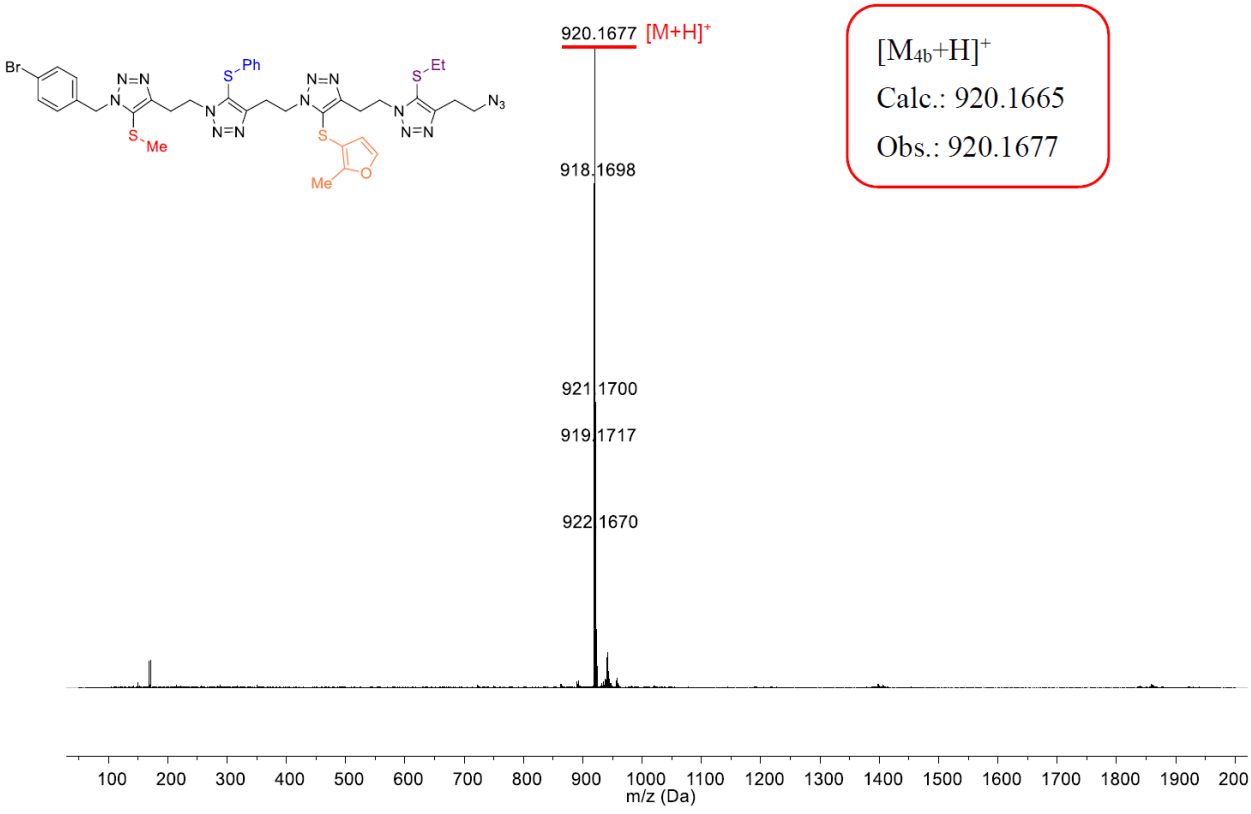


Figure S107. ESI-MS of **4b**.

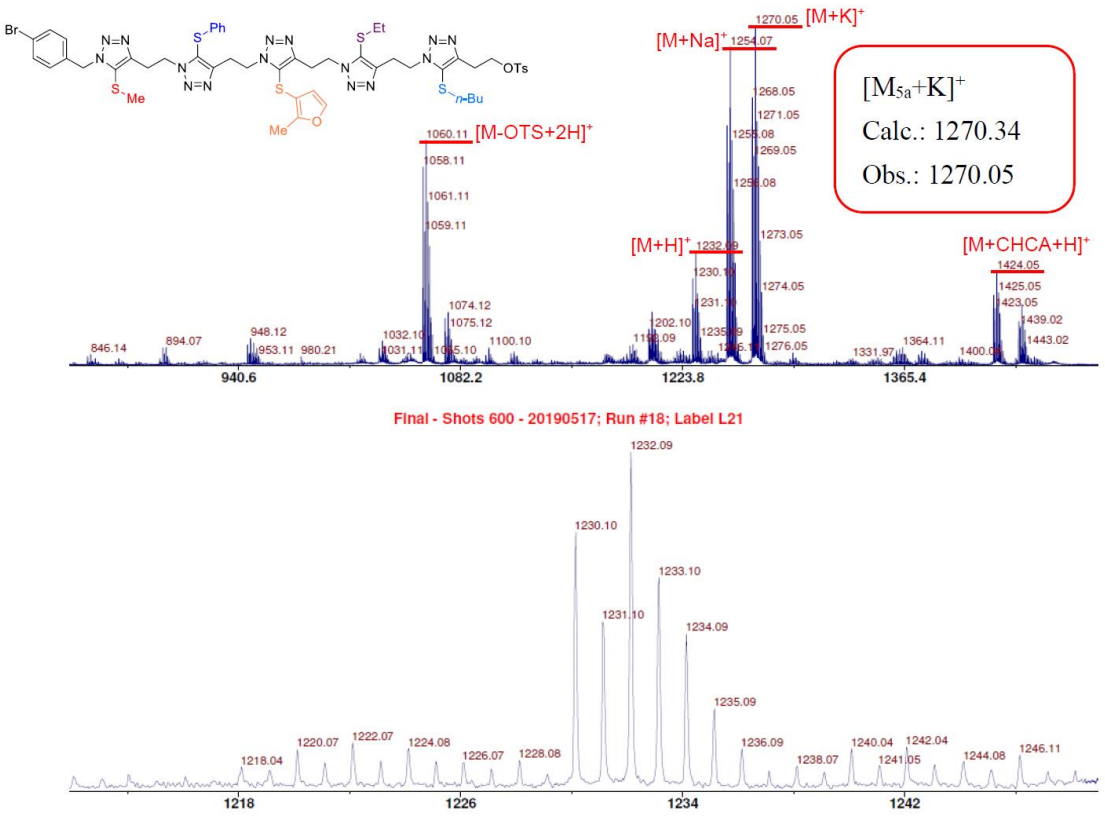


Figure S108. MALDI-TOF-MS of **5a**.

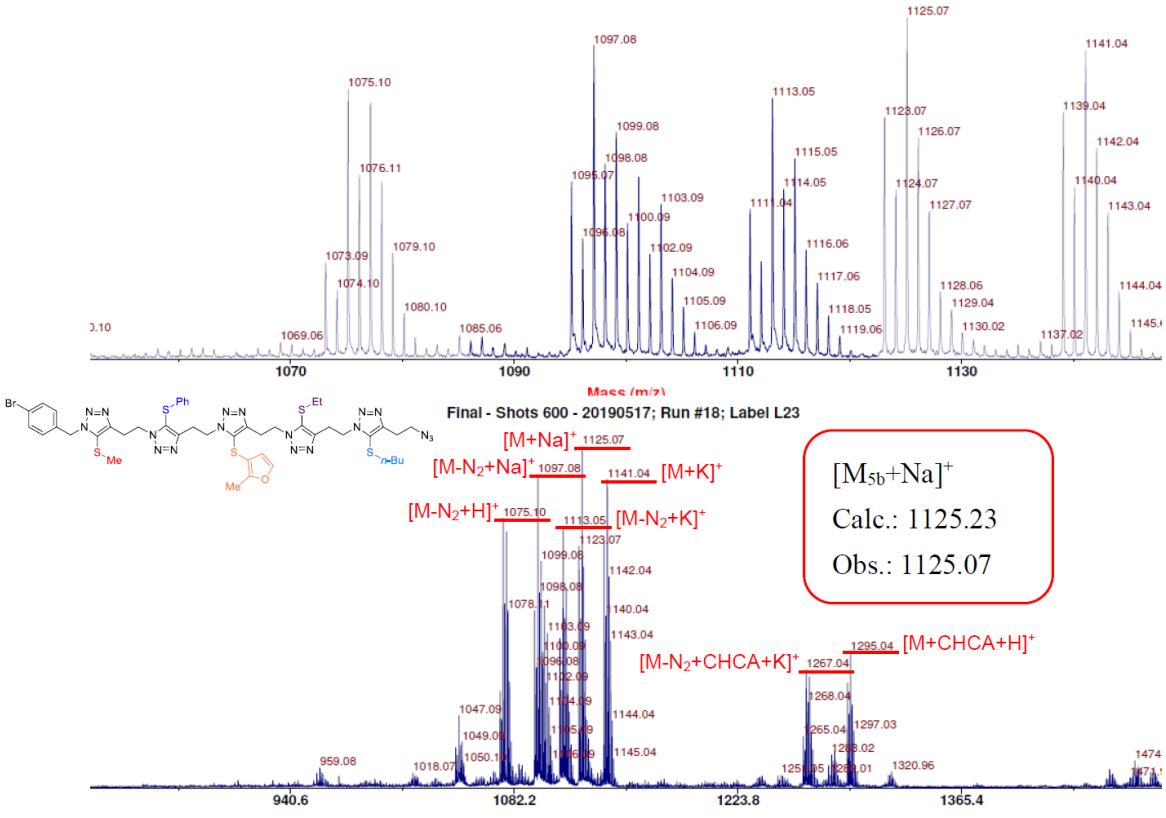


Figure S109. MALDI-TOF-MS of **5b**.

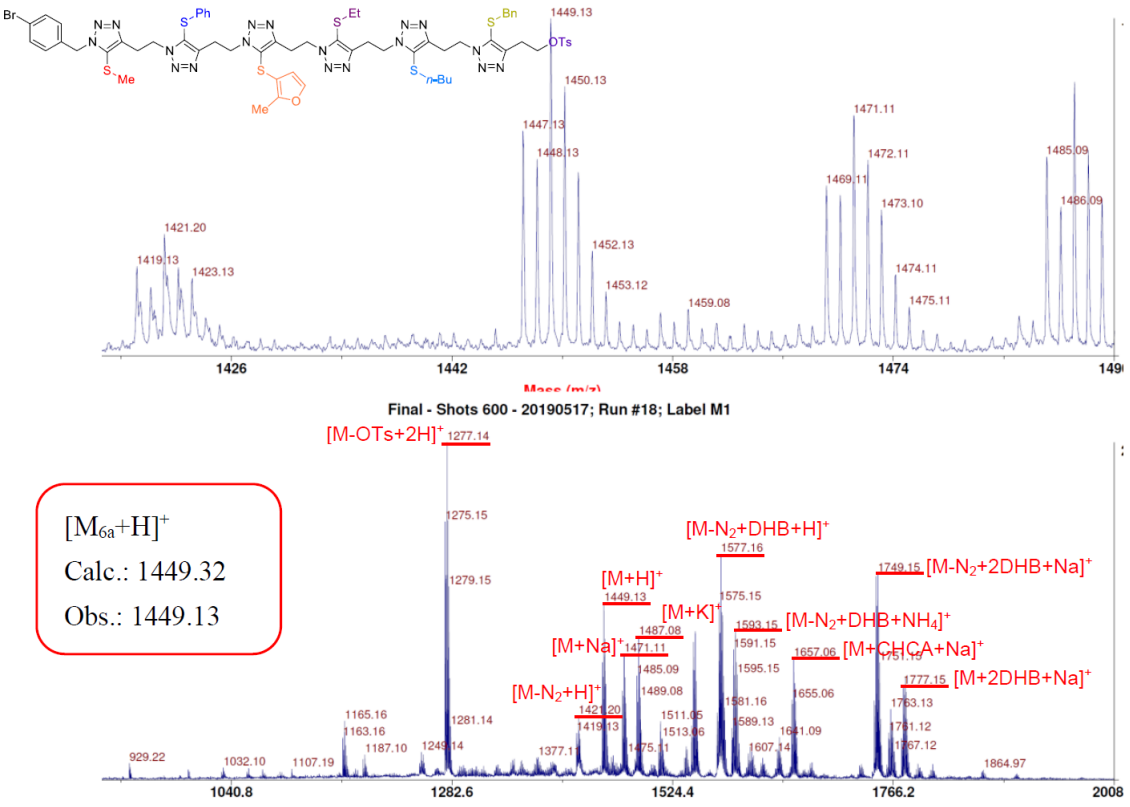


Figure S110. MALDI-TOF-MS of **6a**.

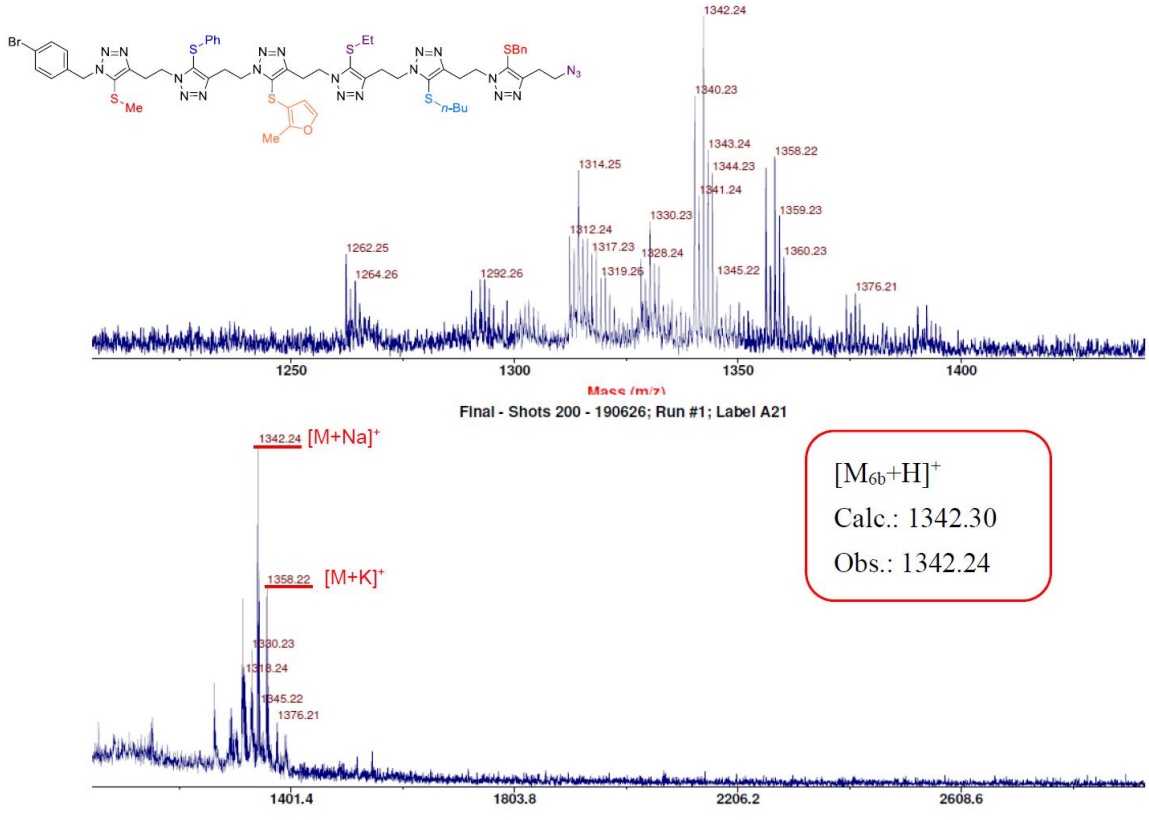


Figure S111. MALDI-TOF-MS of **6b**.

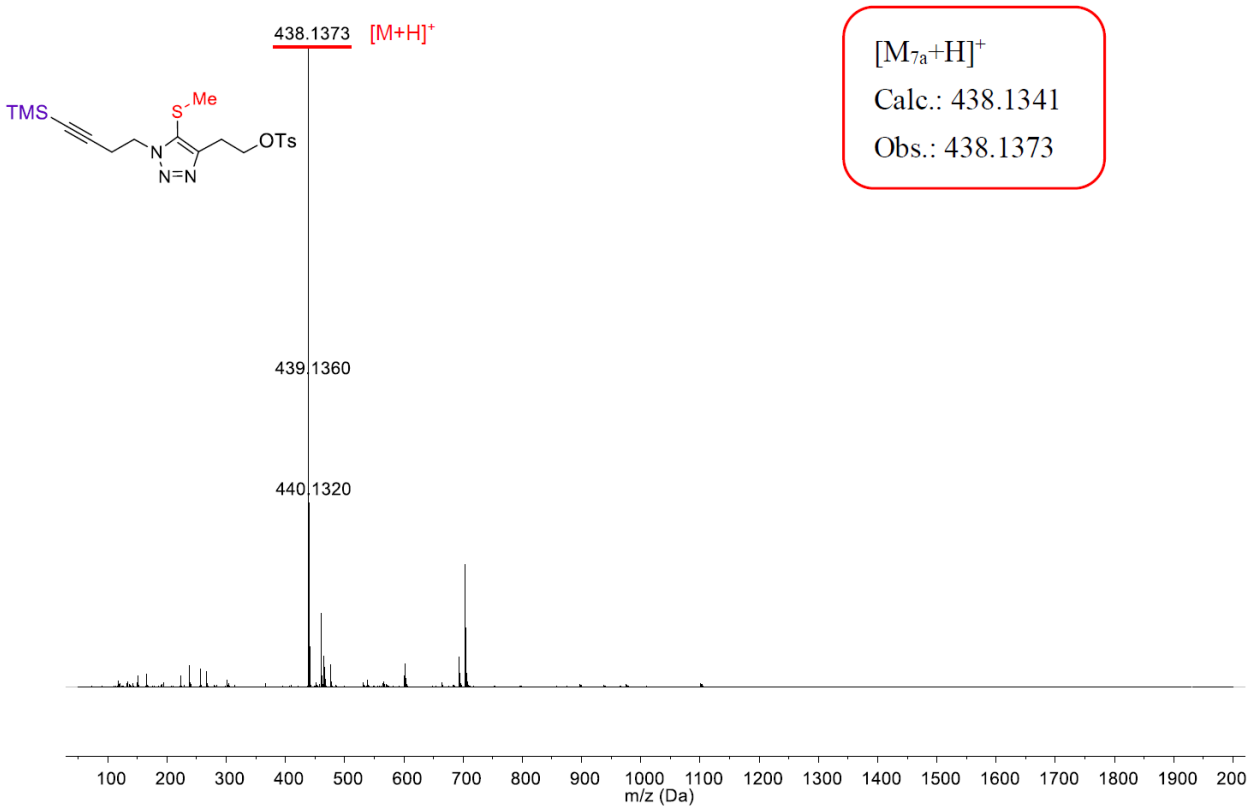


Figure S112. ESI-MS of **7a**.

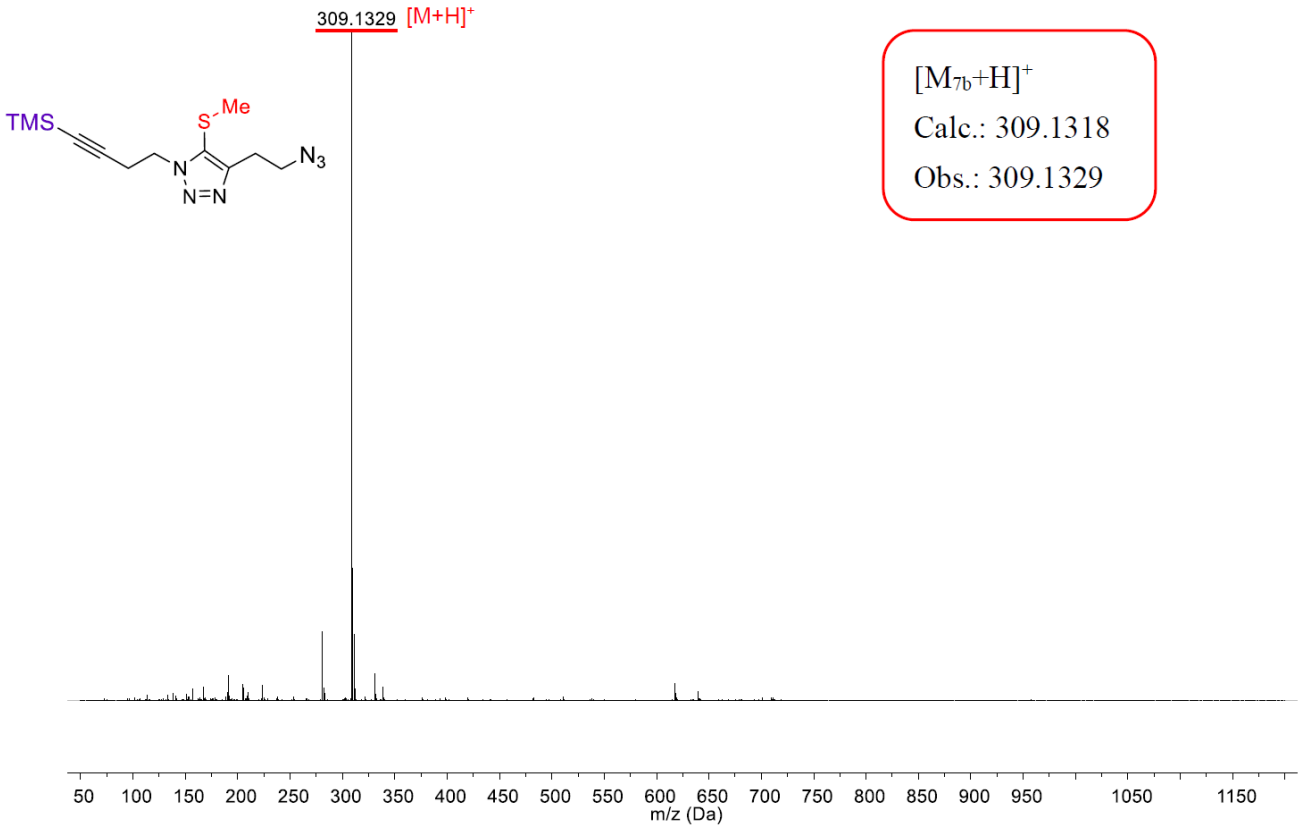


Figure S113. ESI-MS of **7b**.

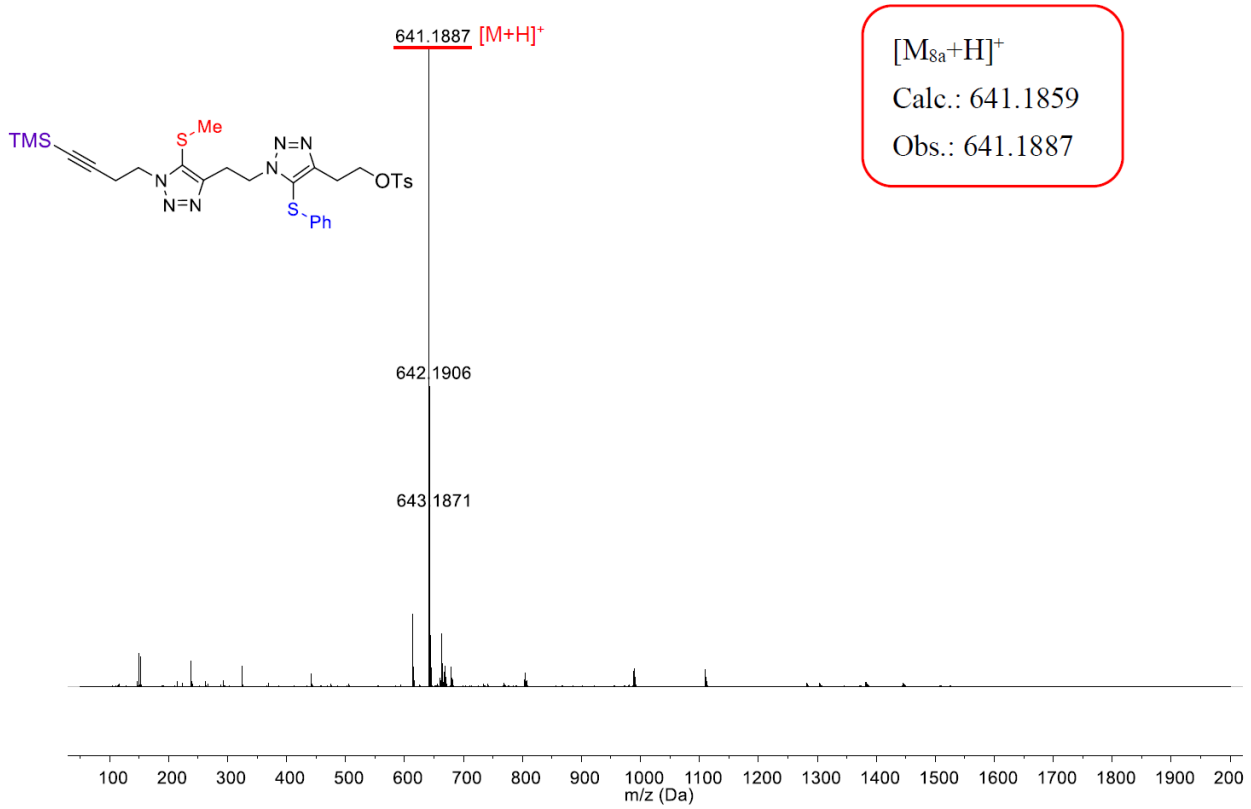


Figure S114. ESI-MS of **8a**.

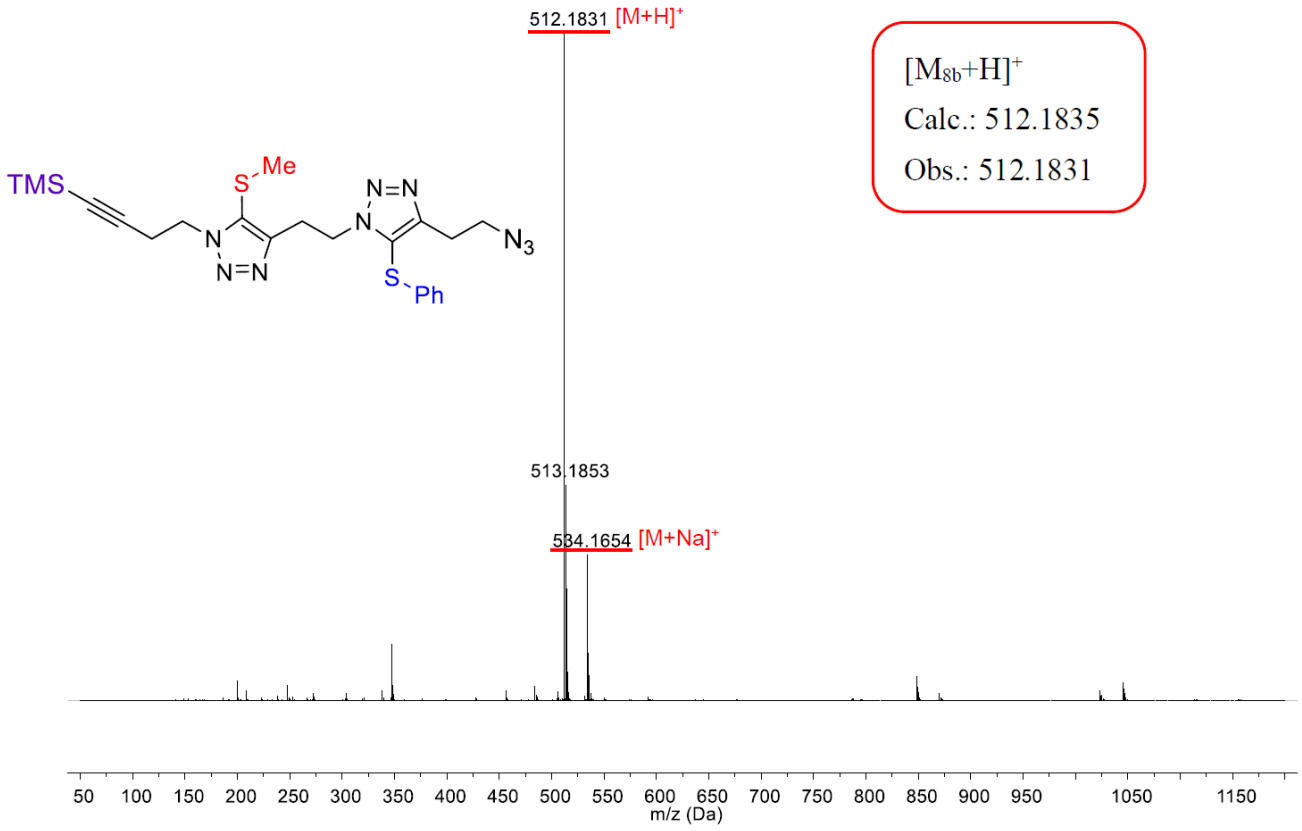


Figure S115. ESI-MS of **8b**.

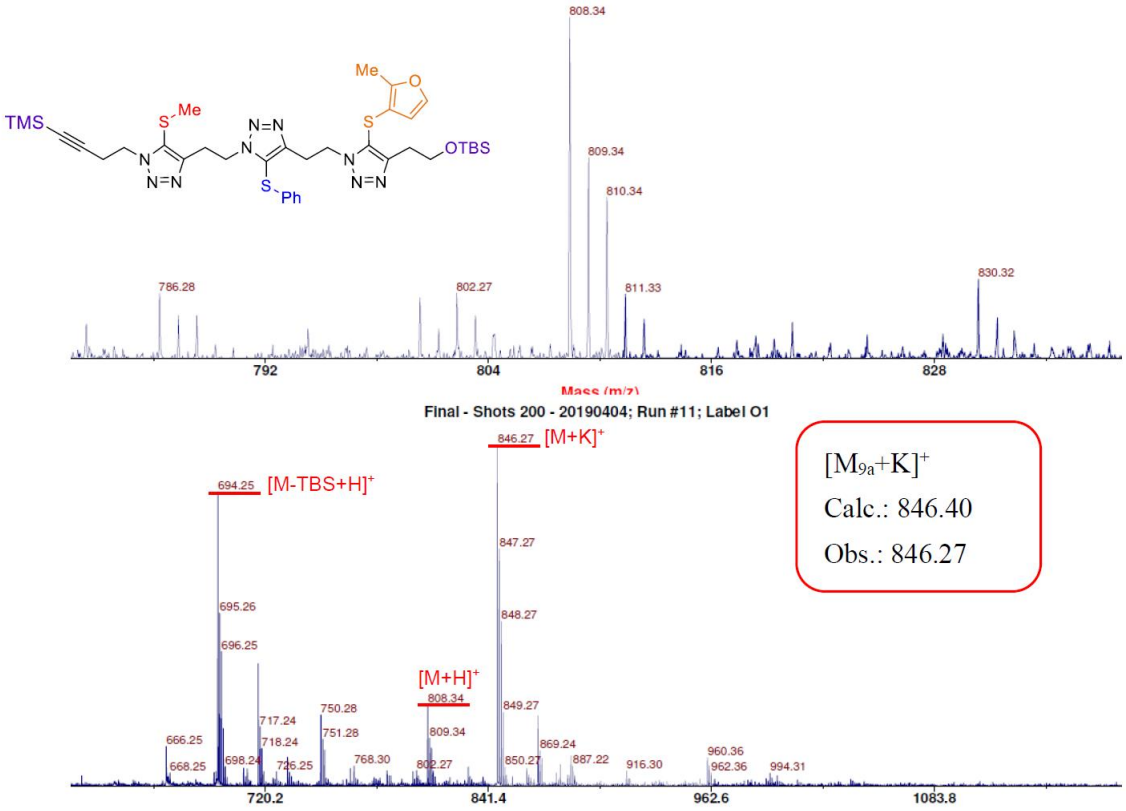


Figure S116. MALDI-TOF-MS of **9a**.

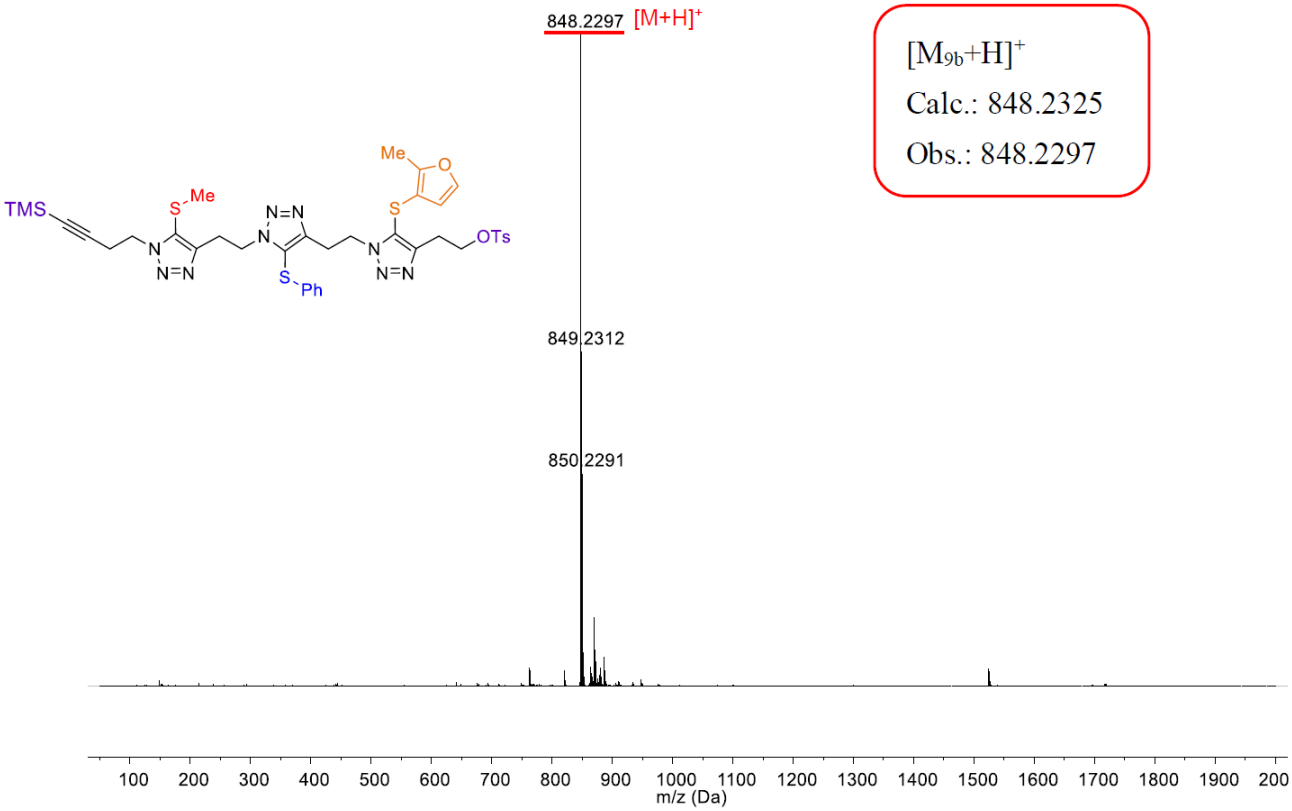


Figure S117. ESI-MS of **9b**.

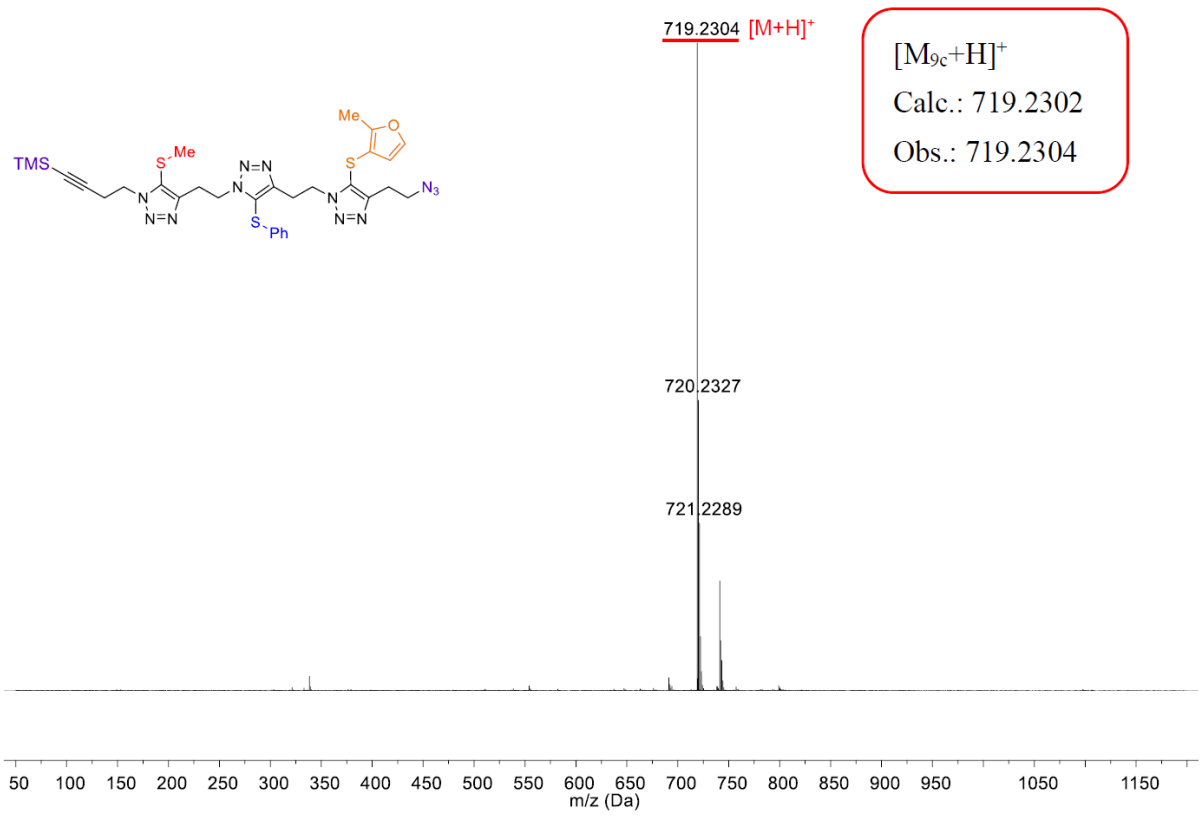


Figure S118. ESI-MS of **9c**.

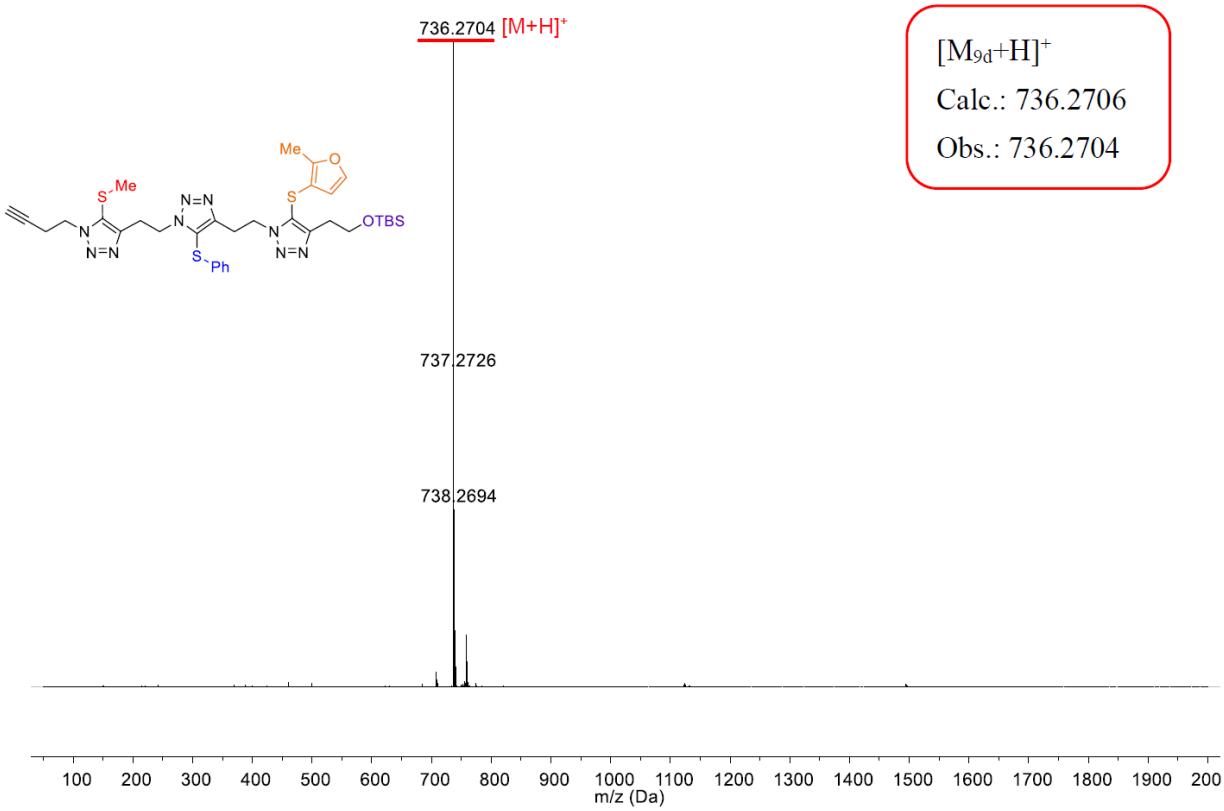


Figure S119. ESI-MS of **9d**.

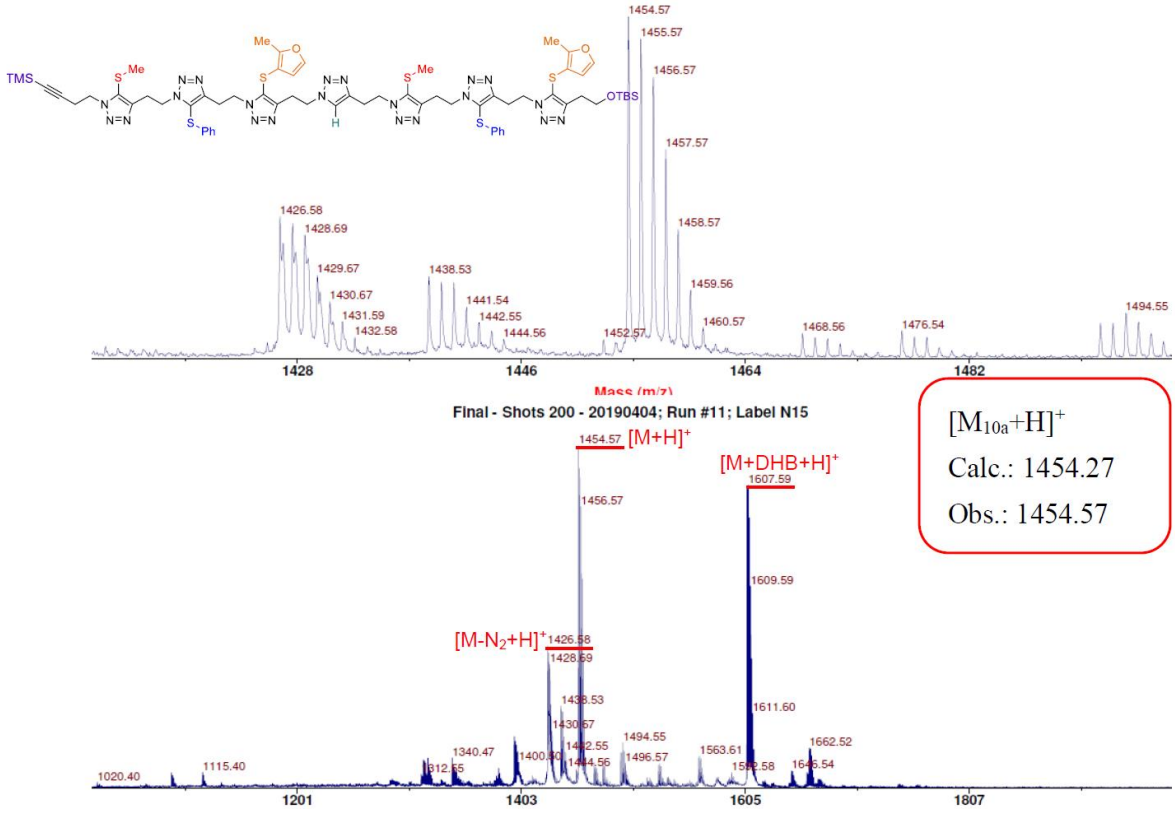


Figure S120. MALDI-TOF-MS of **10a**.

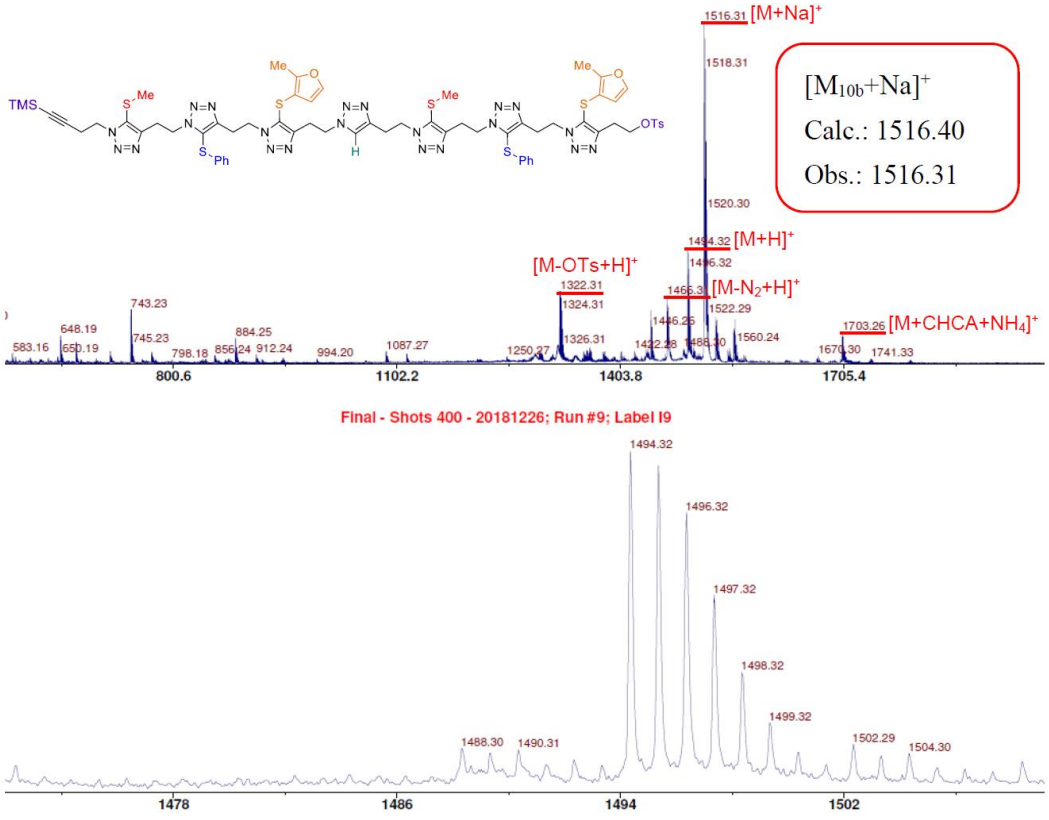


Figure S121. MALDI-TOF-MS of **10b**.

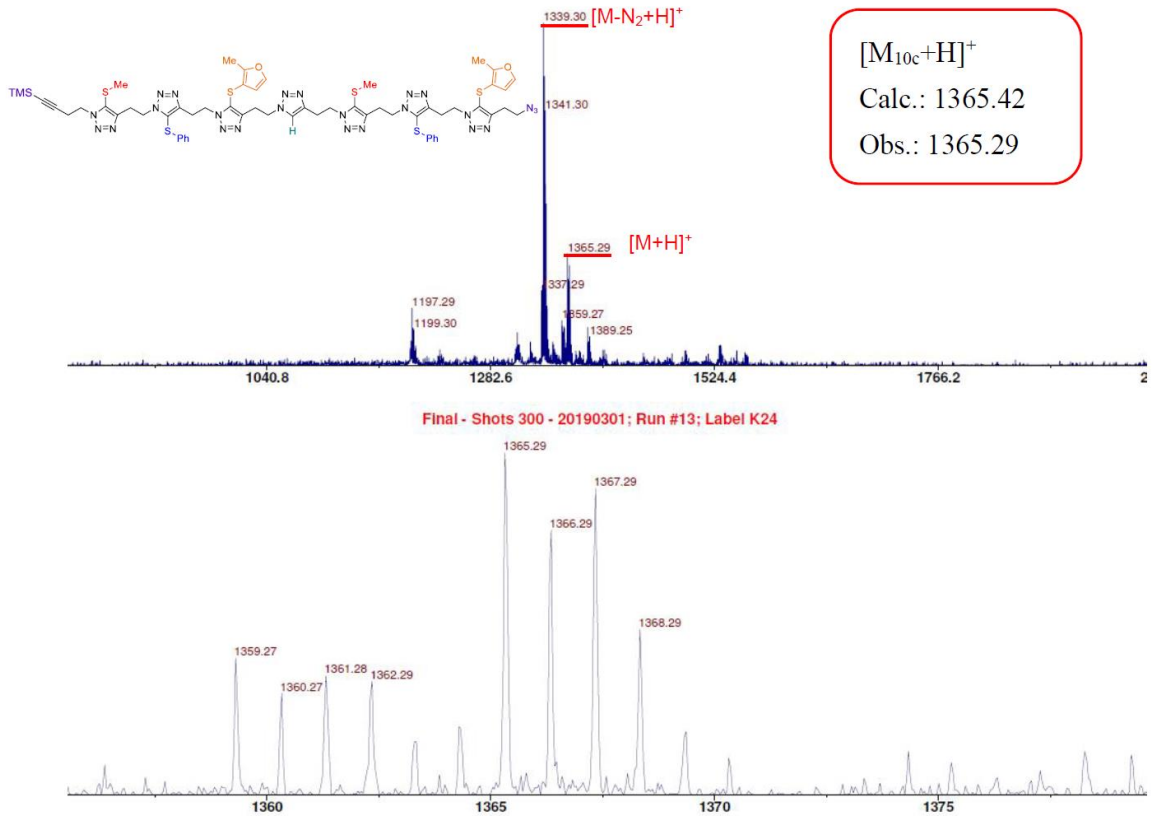


Figure S122. MALDI-TOF-MS of **10c**.

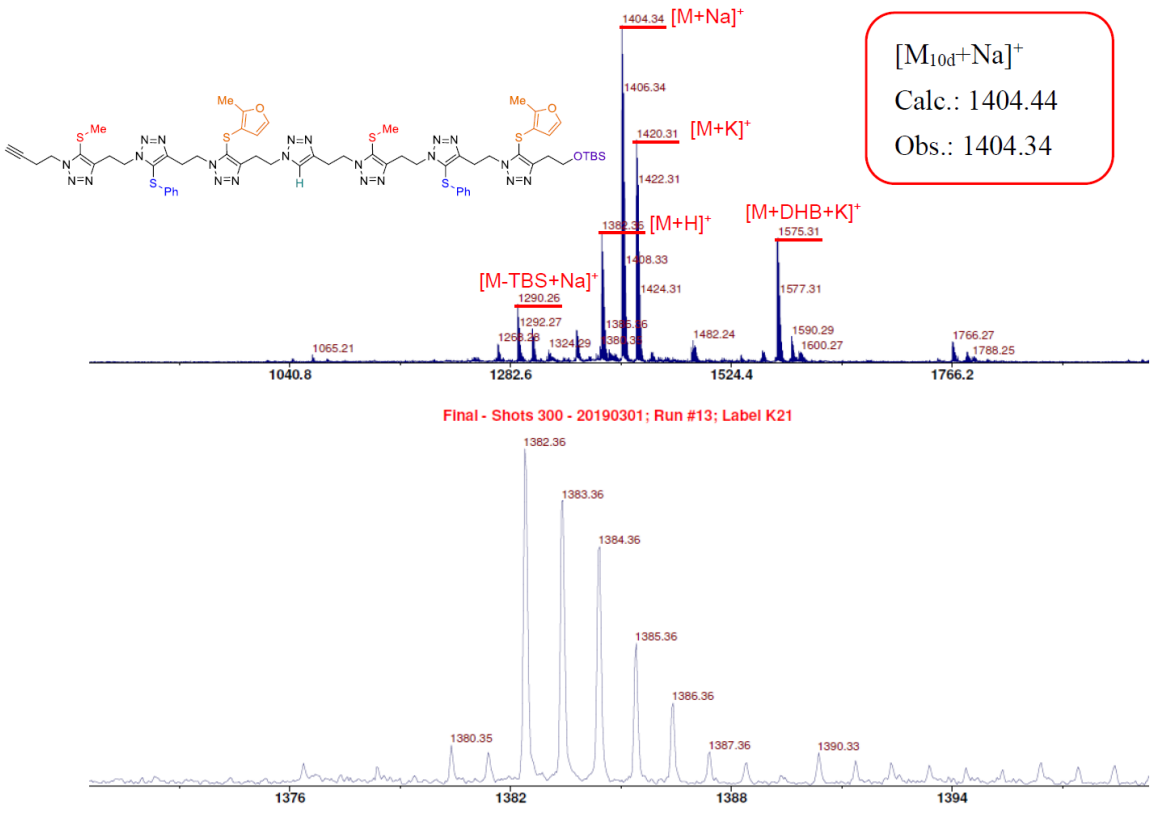


Figure S123. MALDI-TOF-MS of **10d**.

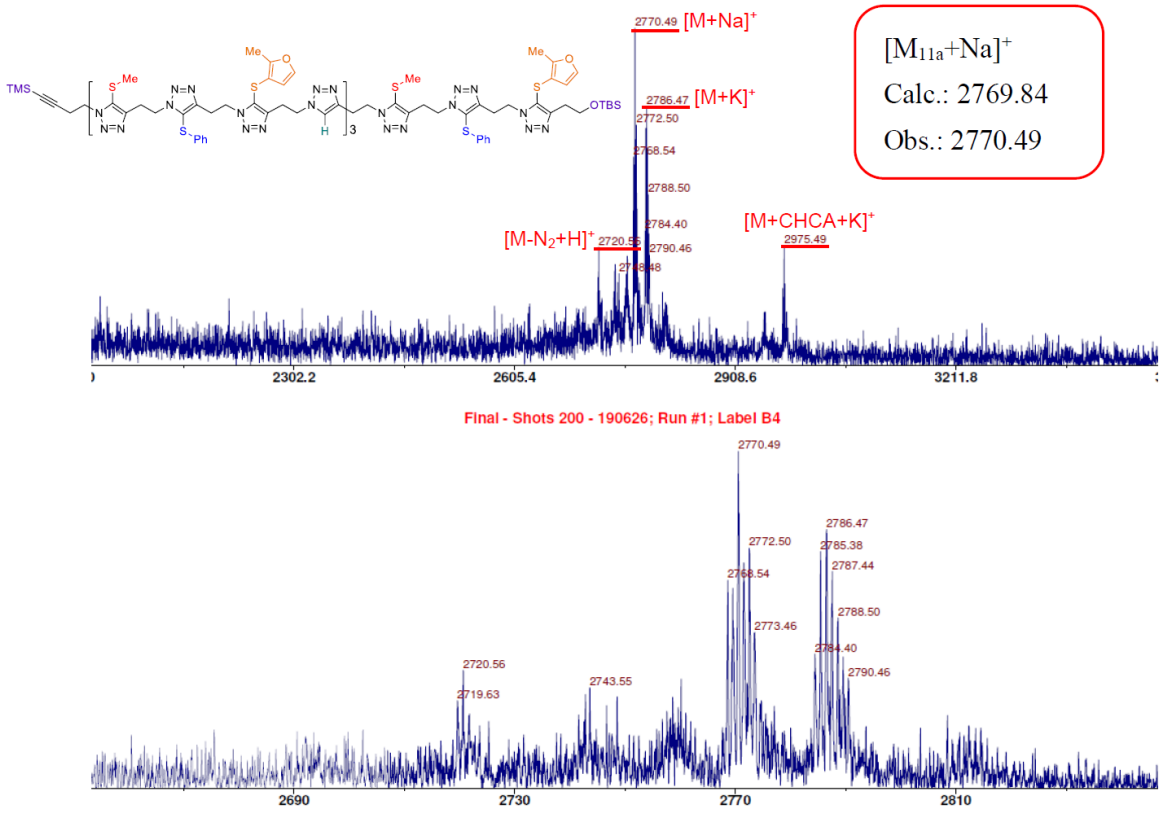


Figure S124. MALDI-TOF-MS of **11a**.

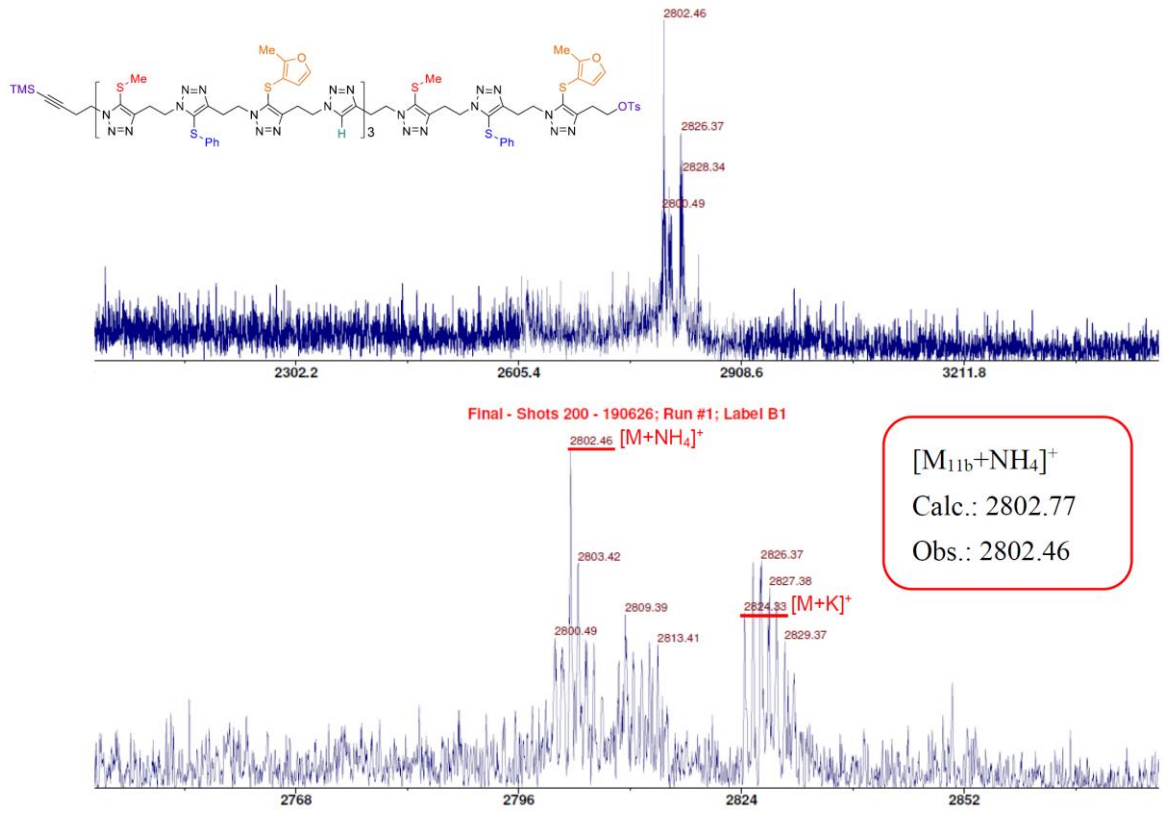


Figure S125. MALDI-TOF-MS of **11b**.

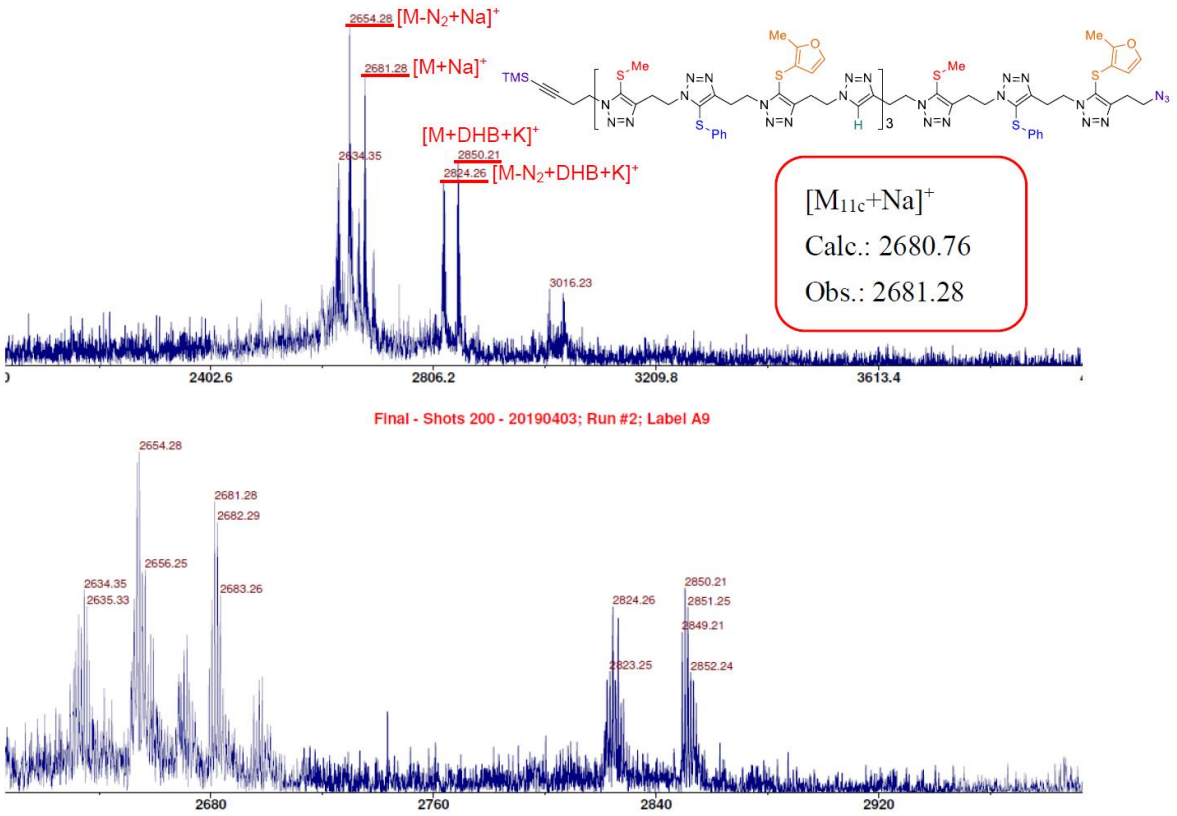


Figure S126. MALDI-TOF-MS of **11c**.

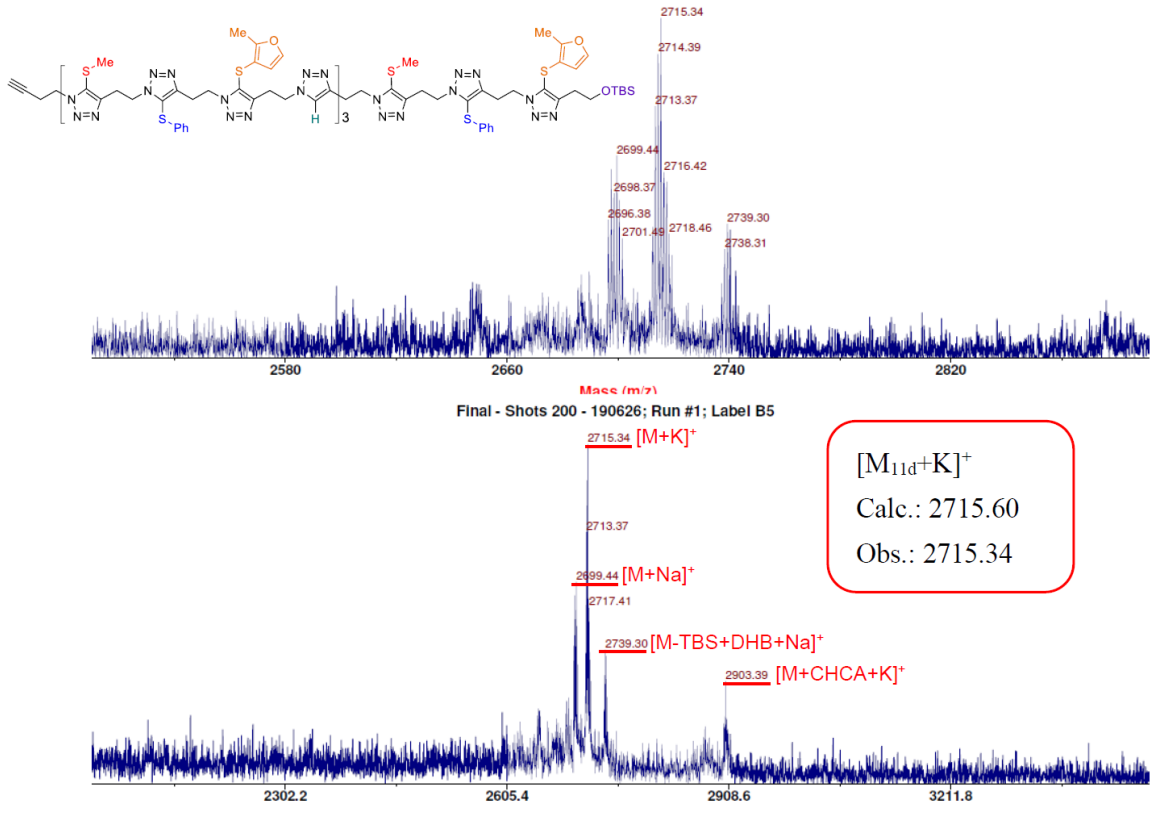


Figure S127. MALDI-TOF-MS of **11d**.

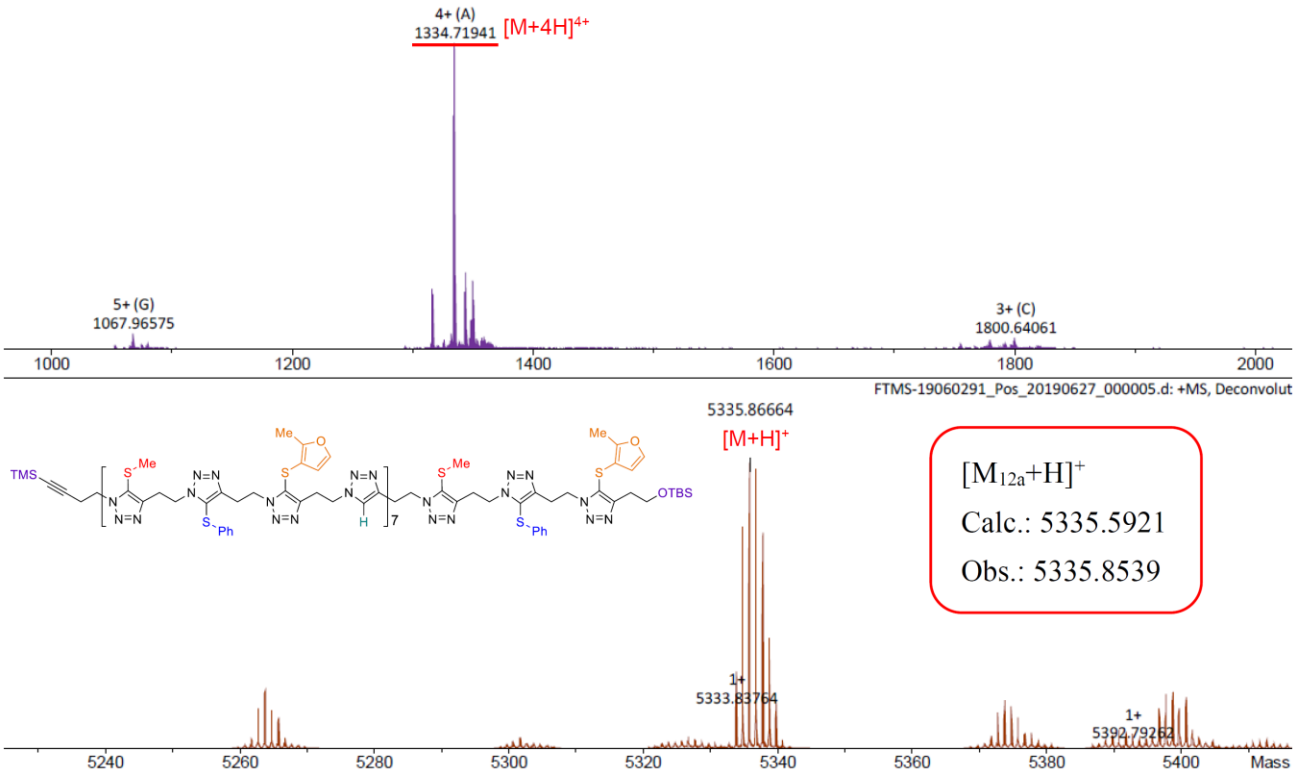


Figure S128. FTICR-MS of **12a**.

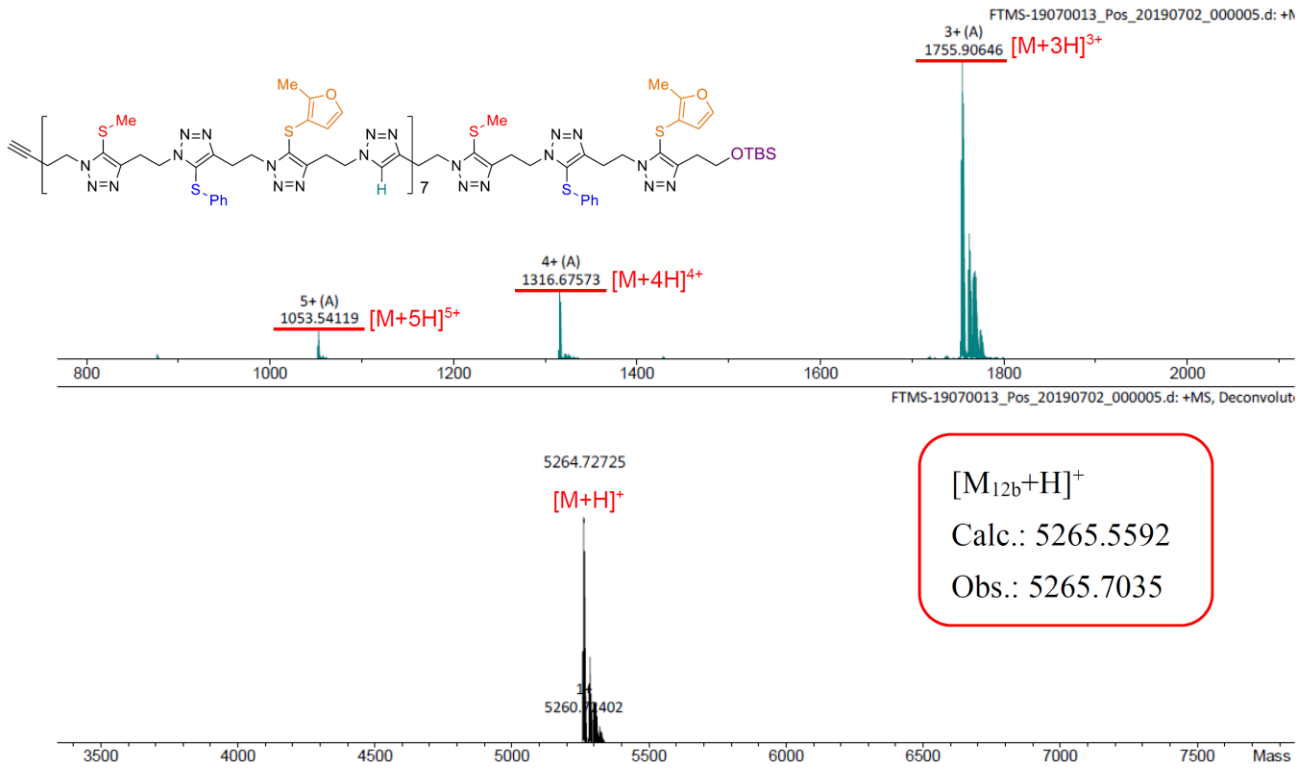


Figure S129. FTICR-MS of **12b**.

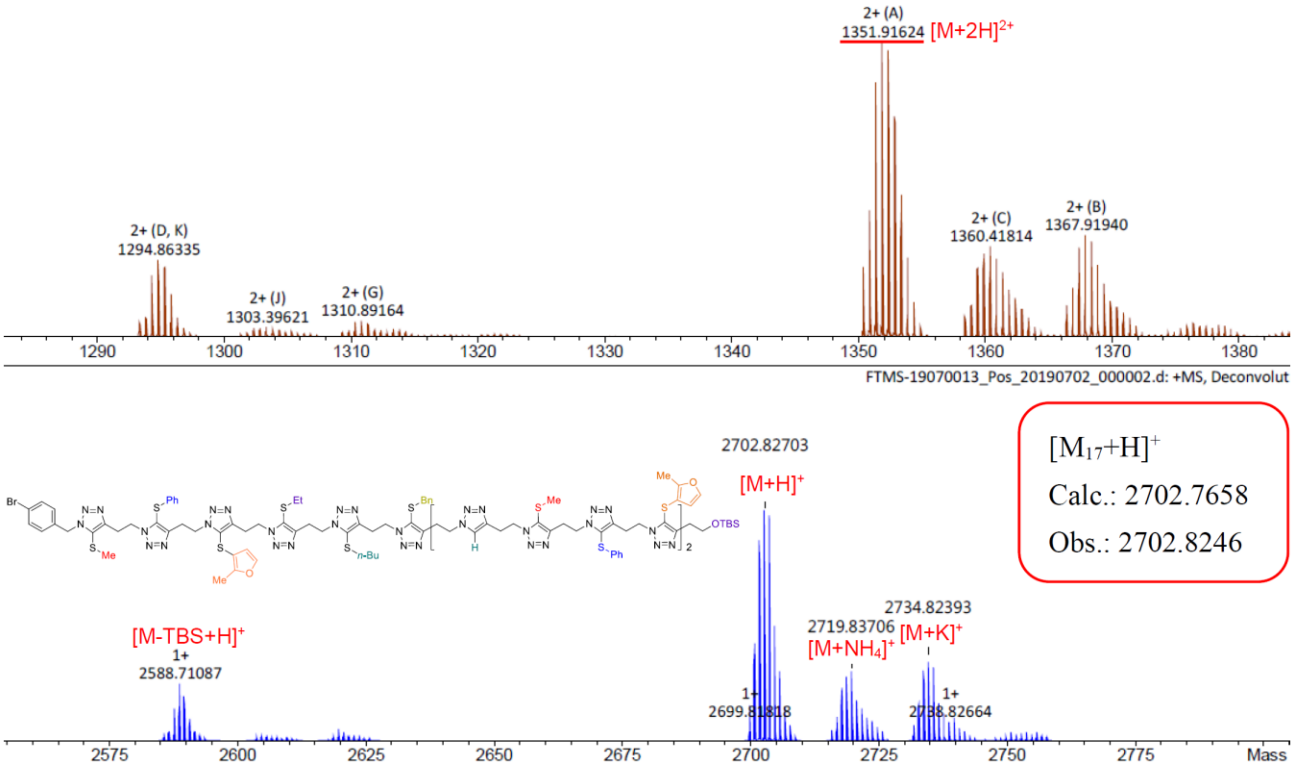


Figure S130. FTICR-MS of **13**.

XII. Supplementary references

1. R. Rintje, R. G. Micetich, *Can. J. Chem.***1968**, *46*, 1057-1063.
2. D. Yadav, N. Singh, T. W. Kim, J. Y. Kim, N.-J. Park, J.-O. Baeg, *Green Chem.* **2019**, *21*, 2677-2685.
3. H. Durga Prasad, W. Jerome, *J. Am. Chem. Soc.* **2016**, *138*, 2190-2193.