Supporting Information

Combining Hydroxyl-Yne and Thiol-Ene Click Reactions to Facilely Access Sequence-Defined Macromolecules for High-Density Data Storage

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Contents

Materials and instruments

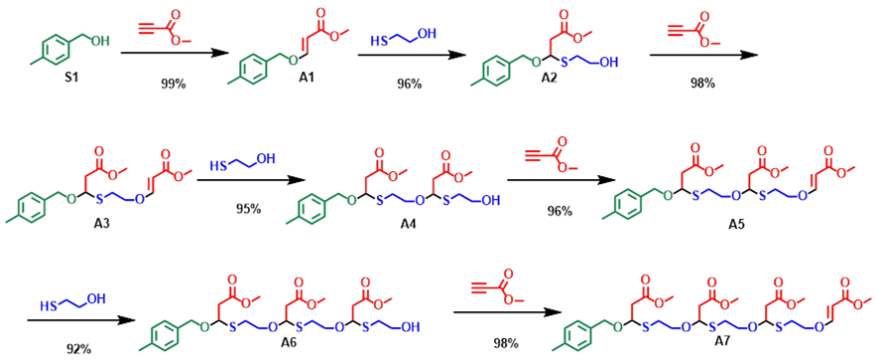
All manipulations involving air- and/or water-sensitive compounds were carried out in a glove box or with the standard Schlenk techniques. **M5, M7** and **S3** was prepared according to our previous procedures.[1] **M1**-**M4**, **M6**, **M8**, **S1**, **S2**, γ-terpinene (1-isopropyl-4-methylcyclohexa-1,4-diene), 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), triethylamine (TEA), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) were purchased from Energy Chemical, Sigma-Aldrich, TCI, and Aladdin, and used without further purification.

^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance 400 MHz NMR spectrometer using deuterated DMSO as solvent and tetramethylsilane (TMS, δ = 0) as internal reference. The gel permeation chromatography (GPC) data of sequence-defined macromolecules were estimated by GPC system, and tetrahydrofuran (THF) was used as eluent at a flow rate of 0.5 mL/min.

High-resolution ESI-MS and MS/MS measurements were performed using Agilent1290/Bruker maXis impact (Bruker, Germany) equipped with an ESI source operated in the positive mode. The capillary voltage was set at +4500 V. In this hybrid instrument, ions were measured using an orthogonal acceleration time-of-flight mass analyzer. In the MS mode, accurate mass measurements were performed using reference ions from Tuning Mix internal standard. In the MS/MS mode, a quadrupole was used for selection of precursor ions to be further submitted to collision-induced dissociation in a collision cell. The precursor ion was used as the reference for

accurate measurements of product ions in MS/MS spectra. Instrument control, data acquisition and data processing were achieved using the Compass Data Analysis provided by Bruker. Macromolecules solutions were prepared in MeOH/THF and introduced in the ionization source with a syringe pump (flow rate: 5 mL min^{-1}).

Synthetic procedure and characterization data for A1-A7



Scheme S1. Synthetic routes to **A1**-**A7**.

A1: *p*-Tolylmethanol **S1** (12.9 g, 105 mmol), methyl propiolate **M1** (8.9 mL, 100 mmol), DABCO (560 mg, 5 mmol), and 50 mL THF were placed into a 250 mL round-bottom flask equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 3 h in air. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (20:1, v/v) as eluent. The product **A1** (20.4 g) was obtained in 99% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.68 (d, J = 12.5 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 7.9 Hz, 2H), 5.35 (d, J = 12.5 Hz, 1H), 4.97 (s, 2H), 3.60 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 167.68, 163.04, 138.20, 133.20, 129.57, 128.66, 97.12, 73.16, 51.24, 21.24. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{12}H_{14}NaO_3$: 229.0841, found 229.0837.

A2: **A1** (10.3 g, 50 mmol), 2-mercaptoethanol **M2** (5.3 mL, 75 mmol), 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (972 mg, 2.5 mmol), and 20 mL DMSO were placed into a 50 mL Schlenk tube equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 5 h under nitrogen, and then extracted three times with ethyl acetate. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (4:1, v/v) as eluent. The product **A2** (13.7 g) was obtained in 96% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.17 (d, J = 2.6 Hz, 4H), 4.95 (m, 1H), 4.83 (t, J = 5.5 Hz, 1H), 4.66 (d, J = 11.5 Hz, 1H), 4.43 (d, J = 11.5 Hz, 1H), 3.59 (s, 3H), 3.56 – 3.47 (m, 2H), 2.88 (m, 2H), 2.66 (m, 2H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 170.23, 137.31, 134.82, 129.30, 128.38, 81.13, 69.25, 61.69, 51.97, 42.11, 30.90, 21.22. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{14}H_{20}NaO_4S$: 307.0980, found 307.0975.

A3: **A2** (11.4 g, 40 mmol), methyl propiolate **M1** (3.9 mL, 44 mmol), DABCO (224 mg, 2 mmol), and 20 mL THF were placed into a 100 mL round-bottom flask equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 3 h in air. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (10:1, v/v) as eluent. The product **A3** (14.4 g) was obtained in 98% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.61 (d, J = 12.5 Hz, 1H), 7.17 (d, J = 6.9 Hz, 4H), 5.25 (d, J = 12.5 Hz, 1H), 5.00 (m, 1H), 4.66 (d, J = 11.5 Hz, 1H), 4.45 (d, J = 11.5 Hz, 1H), 4.07 (t, J = 6.4 Hz, 2H), 3.60 (d, J = 5.0 Hz, 6H), 2.91 (m, 4H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 170.17, 167.63, 163.01, 137.37, 134.68, 129.31, 128.43, 96.82, 81.30, 71.43, 69.43,

52.00, 51.24, 41.92, 27.20, 21.22. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{18}H_{24}NaO_6S$: 391.1191, found 391.1193.

A4: **A3** (11.0 g, 30 mmol), 2-mercaptoethanol **M2** (3.2 mL, 45 mmol), 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (583 mg, 1.5 mmol), and 15 mL DMSO were placed into a 50 mL Schlenk tube equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 5 h under nitrogen, and then extracted three times with ethyl acetate. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (4:1, v/v) as eluent. The product **A4** (12.7 g) was obtained in 95% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.25 – 7.10 (m, 4H), 4.99 – 4.89 (m, 2H), 4.85 – 4.76 (m, 1H), 4.66 (d, J = 11.5 Hz, 1H), 4.44 (d, J = 11.5 Hz, 1H), 3.86 – 3.71 (m, 1H), 3.65 – 3.57 (m, 6H), 3.57 – 3.46 (m, 3H), 2.97 – 2.59 (m, 8H), 2.35 – 2.23 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 170.20, 137.34, 134.76, 129.30, 128.42, 81.70, 81.19, 69.37, 67.68, 61.67, 52.00, 51.99, 42.02, 41.92, 31.00, 30.96, 27.49, 21.22. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{20}H_{30}NaO_7S_2$: 469.1331, found 469.1342.

A5: **A4** (8.9 g, 20 mmol), methyl propiolate **M1** (2.0 mL, 22 mmol), DABCO (112 mg, 1 mmol), and 10 mL THF were placed into a 50 mL round-bottom flask equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 3 h in air. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (10:1, v/v) as eluent. The product **A5** (10.2 g) was obtained in 96% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.61 (d, J = 12.5 Hz, 1H), 7.20 – 7.10 (m, 4H), 5.28 (d, J = 12.5, 1H), 5.03 – 4.92 (m, 2H), 4.66 (d, J = 11.5 Hz, 1H),

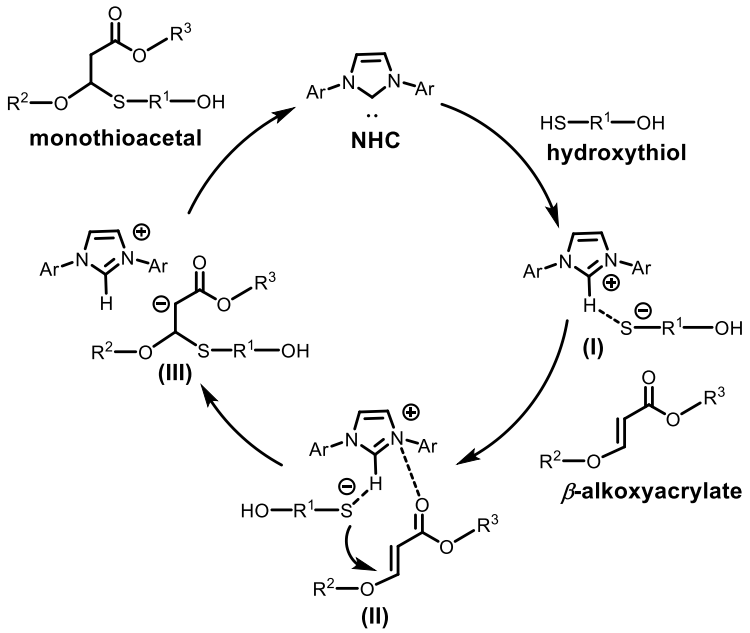
4.43 (d, *J* = 11.5 Hz, 1H), 4.14 – 3.99 (m, 2H), 3.86 – 3.73 (m, 1H), 3.64 – 3.55 (m, 10H), 2.98 – 2.71 (m, 8H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 170.19, 170.12, 167.63, 163.02, 137.33, 134.75, 129.29, 128.40, 96.83, 81.73, 81.20, 71.48, 69.37, 67.78, 52.04, 51.23, 42.00, 41.73, 27.48, 27.27, 27.21, 21.21. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{24}H_{34}NaO_9S_2$: 553.1542, found 553.1559.

A6: **A5** (5.3 g, 10 mmol), 2-mercaptoethanol **M2** (1.1 mL, 15 mmol), 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (196 mg, 0.5 mmol), and 5 mL DMSO were placed into a 50 mL Schlenk tube equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 5 h under nitrogen, and then extracted three times with ethyl acetate. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (4:1, v/v) as eluent. The product **A6** (5.6 g) was obtained in 92% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.23 – 7.11 (m, 4H), 5.01 – 4.87 (m, 3H), 4.81 (m, 1H), 4.66 (d, *J* = 11.5 Hz, 1H), 4.44 (d, *J* = 11.5 Hz, 1H), 3.86 – 3.69 (m, 2H), 3.64 – 3.57 (m, 9H), 3.57 – 3.45 (m, 4H), 2.97 – 2.57 (m, 12H), 2.35 – 2.25 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 170.20, 137.33, 134.77, 129.31, 128.42, 128.40, 81.67, 81.52, 81.20, 69.34, 67.68, 61.66, 52.01, 42.02, 41.93, 41.82, 30.96, 27.50, 21.23. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{26}H_{40}NaO_{10}S_3$: 631.1681, found 631.1687.

A7: **A6** (1.2 g, 2 mmol), methyl propiolate **M1** (0.2 mL, 2.2 mmol), DABCO (11.2 mg, 0.1 mmol), and 2 mL THF were placed into a 10 mL Schlenk tube equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 3 h in air. After solvent evaporation, the crude product was purified by a silica gel column using petroleum

ether/ethyl acetate (10:1, v/v) as eluent. The product **A7** (1.36 g) was obtained in 98% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm):δ 7.61 (d, J = 12.5 Hz, 1H), 7.17 (m, 4H), 5.28 (d, J = 12.5 Hz, 1H), 4.98 – 4.90 (m, 3H), 4.66 (d, J = 11.5 Hz, 1H), 4.43 (d, J = 11.5 Hz, 1H), 4.07 (m, 2H), 3.83 – 3.72 (m, 2H), 3.60 (m, 14H), 2.95 – 2.73 (m, 12H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 170.20, 170.16, 170.11, 167.63, 163.03, 137.33, 134.76, 129.30, 128.40, 96.83, 81.70, 81.20, 71.48, 69.33, 67.73, 52.04, 51.99, 51.24, 42.02, 41.79, 41.72, 27.48, 27.24, 21.22. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{30}H_{44}NaO_{12}S_3$: 715.1893, found 715.1887.

Proposed mechanism



Scheme S2. Proposed mechanism of NHC-catalyzed thiol-ene click reaction.

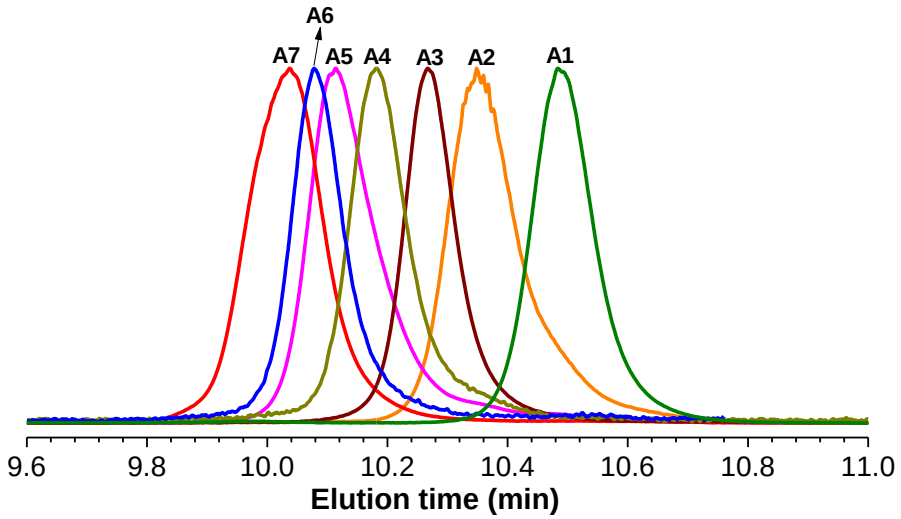
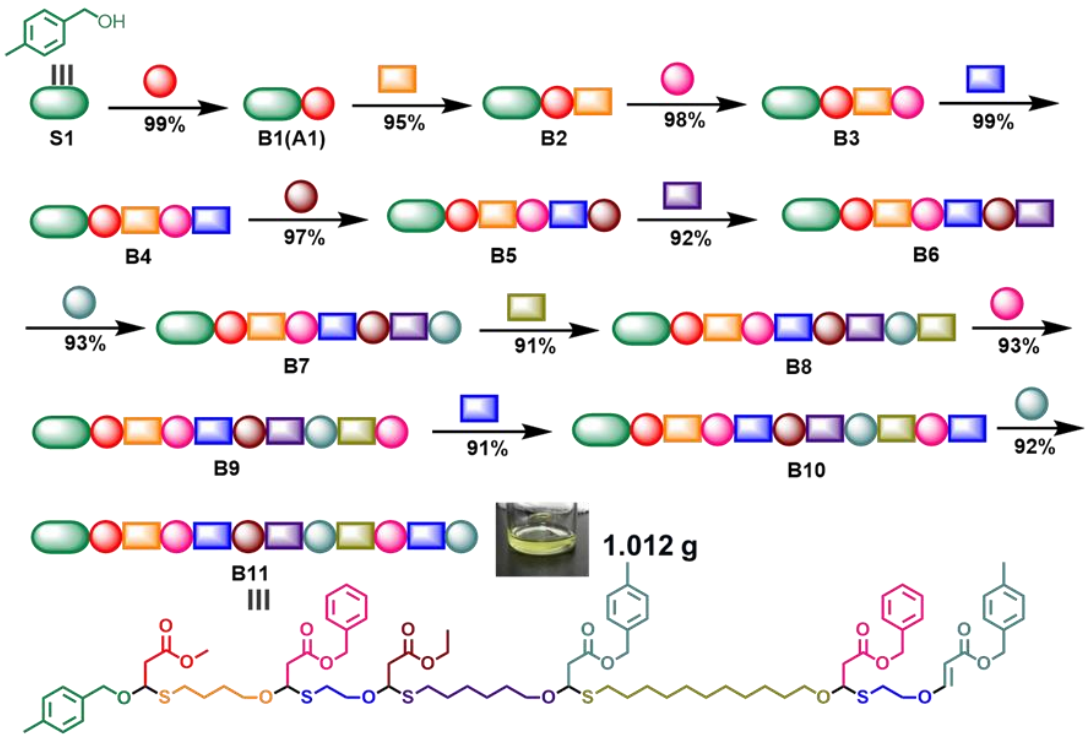


Figure S1. GPC traces of **A1**-**A7**.

Synthetic procedure and characterization data for B2-B11



Scheme S3. Synthetic routes to **B2**-**B11**.

B2: B1(A1) (4.12 g, 20 mmol), 4-mercapto-1-butanol **M4** (3.1 mL, 30 mmol), 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (389 mg, 1 mmol), and 20 mL DMSO were placed into a 50 mL Schlenk tube equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 5 h under nitrogen, and then extracted three times

with ethyl acetate. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (5:1, v/v) as eluent. The product **B2** (5.9 g) was obtained in 95% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.16 (d, J = 3.1 Hz, 4H), 4.92 (m, 1H), 4.65 (d, J = 11.5 Hz, 1H), 4.44 (d, J = 11.5 Hz, 1H), 4.40 (t, J = 5.2 Hz, 1H), 3.59 (s, 3H), 3.39 (d, J = 5.3 Hz, 3H), 2.88 (m, 2H), 2.59 (t, J = 7.3 Hz, 2H), 2.29 (s, 3H), 1.63 – 1.44 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 170.24, 137.30, 134.85, 129.30, 128.39, 81.06, 69.25, 60.66, 51.98, 41.98, 32.22, 27.94, 26.77, 21.22. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{16}H_{24}NaO_4S$: 335.1293, found 335.1295.

B3: **B2** (3.1 g, 10 mmol), **M5** (1.8 g, 11 mmol), DABCO (56 mg, 0.5 mmol), and 10 mL THF were placed into a 50 mL Schlenk tube equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 3 h in air. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (10:1, v/v) as eluent. The product **B3** (4.6 g) was obtained in 98% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.64 (d, J = 12.6 Hz, 1H), 7.40 – 7.28 (m, 5H), 7.15 (d, J = 5.0 Hz, 4H), 5.31 (d, J = 12.5 Hz, 1H), 5.12 (s, 2H), 4.93 (m, 1H), 4.64 (d, J = 11.5 Hz, 1H), 4.44 (d, J = 11.5 Hz, 1H), 3.92 (t, J = 6.3 Hz, 2H), 3.58 (s, 3H), 2.88 (m, 2H), 2.61 (t, J = 7.3 Hz, 2H), 2.27 (s, 3H), 1.81 – 1.54 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 170.23, 167.21, 163.62, 137.30, 137.08, 134.81, 129.29, 128.88, 128.37, 128.34, 96.37, 81.10, 71.14, 69.29, 65.20, 51.98, 41.90, 28.10, 27.57, 26.48, 21.21. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{26}H_{32}NaO_6S$: 495.1817, found 495.1815.

B4: **B3** (3.3 g, 7 mmol), 2-mercaptoethanol **M2** (0.74 mL, 10.5 mmol), 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (136 mg, 0.35 mmol), and 10 mL DMSO were placed into a 50 mL Schlenk tube equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 5 h under nitrogen, and then extracted three times with ethyl acetate. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (3:1, v/v) as eluent. The product **B4** (3.8 g) was obtained in 99% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.36 (m, 5H), 7.16 (d, J = 2.0 Hz, 4H), 5.11 (s, 2H), 4.90 (m, 2H), 4.81 (t, J = 5.5 Hz, 1H), 4.64 (d, J = 11.5 Hz, 1H), 4.43 (d, J = 11.5 Hz, 1H), 3.69 – 3.46 (m, 6H), 3.34 (s, 1H), 2.98 – 2.78 (m, 4H), 2.67 – 2.53 (m, 4H), 2.28 (s, 3H), 1.52 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 170.81, 170.23, 169.75, 137.30, 136.46, 134.83, 129.30, 128.86, 128.48, 128.37, 81.72, 81.08, 69.26, 67.27, 66.09, 61.75, 60.23, 51.98, 30.95, 30.89, 28.46, 27.73, 26.86, 26.84, 25.60, 21.23, 21.22, 14.56. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{28}H_{38}NaO_7S_2$: 573.1957, found 573.1965.

B5: **B4** (2.75 g, 5 mmol), ethyl propriolate **M3** (0.56 mL, 5.5 mmol), DABCO (28 mg, 0.25 mmol), and 5 mL THF were placed into a 50 mL Schlenk tube equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 3 h in air. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (8:1, v/v) as eluent. The product **B5** (3.14 g) was obtained in 97% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.58 (d, J = 12.5 Hz, 1H), 7.44 – 7.26 (m, 5H), 7.15 (d, J = 2.3 Hz, 4H), 5.24 (d, J = 12.5 Hz, 1H), 5.11 (s, 2H), 4.98 – 4.86 (m, 2H), 4.64 (d, J = 11.5 Hz, 1H), 4.43 (d, J = 11.5 Hz, 1H), 4.12 – 4.00 (m,

4H), 3.58 (m, 4H), 3.40 – 3.32 (m, 1H), 2.99 – 2.80 (m, 6H), 2.56 (m, 2H), 2.28 (s, 3H), 1.53 (m, 4H), 1.18 (t, J = 7.1, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 170.22, 169.68, 167.19, 162.88, 137.29, 136.42, 134.82, 129.29, 128.86, 128.49, 128.40, 128.35, 97.08, 81.85, 81.07, 71.50, 69.25, 67.49, 67.39, 66.14, 60.23, 59.64, 51.97, 42.18, 41.95, 28.44, 27.70, 27.21, 26.86, 26.84, 25.60, 21.23, 21.21, 14.73, 14.55. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{33}H_{44}NaO_9S_2$: 671.2324, found 671.2337.

B6: B5 (1.95 g, 3 mmol), 6-mercapto-1-hexanol **M6** (0.62 mL, 4.5 mmol), 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (58.3 mg, 0.15 mmol), and 10 mL DMSO were placed into a 50 mL Schlenk tube equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 5 h under nitrogen, and then extracted three times with ethyl acetate. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (3:1, v/v) as eluent. The product **B6** (2.16 g) was obtained in 92% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.44 – 7.27 (m, 5H), 7.22 – 7.09 (m, 4H), 5.11 (s, 2H), 4.96 – 4.83 (m, 3H), 4.64 (d, J = 11.5 Hz, 1H), 4.43 (d, J = 11.5 Hz, 1H), 4.31 (t, J = 5.1 Hz, 1H), 4.13 – 3.96 (m, 2H), 3.75 (m, 1H), 3.66 – 3.48 (m, 5H), 3.41 – 3.33 (m, 3H), 2.97 – 2.65 (m, 8H), 2.60 – 2.51 (m, 4H), 2.28 (s, 3H), 1.59 – 1.22 (m, 12H), 1.20 – 1.14 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 170.21, 169.69, 169.66, 137.29, 136.44, 134.82, 129.29, 128.85, 128.48, 128.36, 128.35, 81.80, 81.67, 81.63, 81.06, 69.25, 67.74, 67.70, 67.35, 66.11, 61.11, 60.61, 51.98, 42.23, 41.95, 32.90, 30.89, 30.09, 28.74, 28.47, 27.94, 27.88, 27.71, 27.55, 26.87, 26.85, 25.55, 21.22, 14.51 ESI-MS:

m/z calculated for $[M+Na]^+$ $C_{39}H_{58}NaO_{10}S_3$: 805.3090, found 805.3099.

B7: **B6** (1.96 g, 2.5 mmol), **M7** (479 mg, 2.75 mmol), DABCO (14 mg, 0.125 mmol), and 2 mL THF were placed into a 50 mL Schlenk tube equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 3 h in air. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (5:1, v/v) as eluent. The product **B7** (2.23 g) was obtained in 93% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.62 (d, J = 12.6 Hz, 1H), 7.39 – 7.28 (m, 5H), 7.28 – 7.11 (m, 8H), 5.28 (d, J = 12.5 Hz, 1H), 5.10 (s, 2H), 5.05 (s, 2H), 4.94 – 4.82 (m, 3H), 4.64 (d, J = 11.5 Hz, 1H), 4.43 (d, J = 11.5 Hz, 1H), 4.11 – 4.00 (m, 2H), 3.88 (t, J = 6.5 Hz, 2H), 3.75 (m, 1H), 3.67 – 3.48 (m, 5H), 3.34 (m, 1H), 2.98 – 2.66 (m, 8H), 2.60 – 2.51 (m, 4H), 2.28 (d, J = 5.1 Hz, 6H), 1.63 – 1.44 (m, 8H), 1.34 – 1.25 (m, 4H), 1.16 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 170.20, 169.68, 169.65, 167.23, 163.58, 137.64, 137.29, 136.43, 134.81, 134.05, 129.40, 129.29, 128.84, 128.49, 128.34, 96.32, 81.78, 81.62, 81.06, 71.55, 69.25, 67.33, 66.10, 65.10, 60.61, 51.97, 42.21, 41.94, 41.91, 34.86, 30.89, 29.90, 28.74, 28.47, 28.36, 27.70, 27.52, 26.86, 25.21, 21.22, 14.50. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{50}H_{68}NaO_{12}S_3$: 979.3771, found 979.3770.

B8: B7 (1.91 g, 2 mmol), 11-mercapto-1-undecanol **M8** (612 mL, 3 mmol), 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (39 mg, 0.1 mmol), and 5 mL DMSO were placed into a 50 mL Schlenk tube equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 7 h under nitrogen, and then extracted three times with ethyl acetate. After solvent evaporation, the crude product was purified by a

silica gel column using petroleum ether/ethyl acetate (3:1, v/v) as eluent. The product **B8** (2.11 g) was obtained in 91% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.35 (m, 5H), 7.27 – 7.08 (m, 8H), 5.10 (s, 2H), 5.05 (s, 2H), 4.94 – 4.79 (m, 4H), 4.64 (d, J = 11.5 Hz, 1H), 4.43 (d, J = 11.5 Hz, 1H), 4.30 (t, J = 4.9 Hz, 1H), 4.06 (d, J = 7.1 Hz, 2H), 3.75 (m, 1H), 3.58 (m, 6H), 3.36 (m, 4H), 2.97 – 2.66 (m, 10H), 2.60 – 2.52 (m, 6H), 2.28 (d, J = 4.2 Hz, 6H), 1.45 (m, 12H), 1.25 (m, 18H), 1.16 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 170.19, 169.71, 169.66, 169.62, 137.77, 137.28, 136.42, 134.81, 133.44, 129.37, 129.28, 128.84, 128.50, 128.47, 128.33, 81.63, 81.05, 69.25, 67.60, 67.34, 66.10, 65.98, 61.19, 60.60, 51.97, 42.18, 41.95, 41.92, 33.03, 30.07, 29.98, 29.58, 29.45, 29.43, 29.11, 29.04, 28.77, 28.54, 28.47, 27.85, 27.69, 27.52, 25.99, 25.69, 21.22, 14.49. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{61}H_{92}NaO_{13}S_4$: 1183.5318, found 1183.5375.

B9: **B8** (1.74 g, 1.5 mmol), **M5** (264 mg, 1.65 mmol), DABCO (8.4 mg, 0.075 mmol), and 2 mL THF were placed into a 50 mL Schlenk tube equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 5 h in air. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (5:1, v/v) as eluent. The product **B9** (1.84 g) was obtained in 93% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.64 (d, J = 12.5 Hz, 1H), 7.43 – 7.27 (m, 10H), 7.27 – 7.06 (m, 8H), 5.30 (d, J = 12.5 Hz, 1H), 5.10 (d, J = 1.8 Hz, 4H), 5.05 (s, 2H), 4.93 – 4.79 (m, 4H), 4.64 (d, J = 11.5 Hz, 1H), 4.42 (d, J = 11.5 Hz, 1H), 4.04 (m, 2H), 3.90 (t, J = 6.5 Hz, 2H), 3.75 (m, 1H), 3.57 (m, 7H), 3.27 (m, 1H), 2.96 – 2.65 (m, 10H), 2.54 (m, 6H), 2.28 (d, J = 4.0 Hz, 6H), 1.52 (m, 12H), 1.24 (m, 20H), 1.16

(t, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 170.81, 170.18, 169.70, 169.65, 169.60, 167.22, 163.71, 137.77, 137.27, 137.09, 136.42, 134.81, 133.44, 129.36, 129.27, 128.86, 128.83, 128.49, 128.47, 128.34, 128.32, 96.23, 81.62, 81.05, 71.67, 69.25, 67.59, 67.49, 67.33, 66.10, 65.97, 65.17, 60.60, 60.23, 51.96, 42.17, 41.95, 41.91, 30.89, 30.05, 29.98, 29.37, 29.11, 29.08, 29.00, 28.86, 28.74, 28.54, 28.47, 27.83, 27.69, 27.50, 26.86, 25.69, 25.64, 25.60, 21.24, 21.22, 14.56, 14.48. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{71}H_{100}NaO_{15}S_4$: 1343.5843, found 1343.5838.

B10: **B9** (1.32 g, 1 mmol), 2-mercaptoethanol **M2** (105 μL, 1.5 mmol), 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (19 mg, 0.05 mmol), and 2 mL DMSO were placed into a 50 mL Schlenk tube equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 10 h under nitrogen, and then extracted three times with ethyl acetate. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (3:1, v/v) as eluent. The product **B10** (1.27 g) was obtained in 91% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.35 (m, 10H), 7.19 (m, 8H), 5.10 (s, 4H), 5.05 (s, 2H), 4.94 – 4.73 (m, 6H), 4.64 (d, J = 11.5 Hz, 1H), 4.42 (d, J = 11.5 Hz, 1H), 4.05 (m, 2H), 3.74 (m, 1H), 3.67 – 3.42 (m, 10H), 3.30 – 3.23 (m, 2H), 2.80 (m, 20H), 2.28 (d, J = 4.0 Hz, 6H), 1.55 – 1.19 (m, 32H), 1.16 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 170.20, 169.72, 169.66, 169.63, 169.62, 139.67, 137.78, 137.29, 136.42, 134.80, 133.44, 129.37, 129.28, 128.84, 128.50, 128.34, 125.39, 81.63, 81.05, 69.25, 67.60, 67.34, 66.10, 65.98, 61.19, 60.61, 51.97, 42.18, 41.95, 34.86, 33.02, 30.89, 30.06, 29.98, 29.57, 29.45, 29.42, 29.10, 29.04, 28.98, 28.76, 28.53, 28.47, 28.17, 27.85,

27.69, 25.98, 25.68, 21.22, 14.49. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{73}H_{106}NaO_{16}S_5$: 1421.5982, found 1421.6075.

B11: **B10** (0.98 g, 0.7 mmol), **M7** (134 mg, 0.77 mmol), DABCO (4 mg, 0.035 mmol), and 2 mL THF were placed into a 50 mL Schlenk tube equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 6 h in air. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (4:1, v/v) as eluent. The product **B11** (1.012 g) was obtained in 92% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.62 (d, J = 12.5 Hz, 1H), 7.38 – 7.27 (m, 10H), 7.27 – 7.08 (m, 12H), 5.28 (d, J = 12.5 Hz, 1H), 5.10 (s, 4H), 5.05 (s, 4H), 4.97 – 4.76 (m, 5H), 4.64 (d, J = 11.5 Hz, 1H), 4.42 (d, J = 11.5 Hz, 1H), 4.11 – 4.00 (m, 4H), 3.75 (m, 1H), 3.57 (m, 7H), 3.27 (m, 3H), 2.97 – 2.53 (m, 20H), 2.28 (m, 9H), 1.59 – 1.18 (m, 32H), 1.15 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 169.60, 169.12, 169.07, 166.47, 162.68, 137.18, 137.04, 136.69, 135.84, 134.22, 133.41, 132.85, 128.80, 128.78, 128.69, 128.25, 127.91, 127.86, 127.73, 96.25, 81.24, 81.04, 80.46, 70.97, 68.66, 67.33, 67.01, 66.75, 65.51, 65.49, 65.39, 64.56, 60.02, 51.38, 41.62, 41.36, 41.33, 30.31, 29.48, 29.40, 28.85, 28.83, 28.65, 28.60, 28.52, 28.44, 28.19, 27.96, 27.89, 27.26, 27.11, 26.92, 26.58, 26.28, 25.49, 25.10, 20.64, 13.90. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{84}H_{116}NaO_{18}S_5$: 1595.6663, found 1595.6664.

ESI-MS and NMR spectra of B2-B11

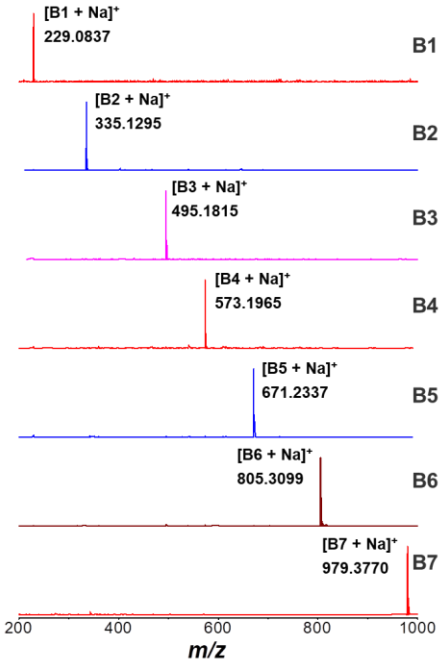


Figure S2. ESI mass spectra of **B1**-**B7**.

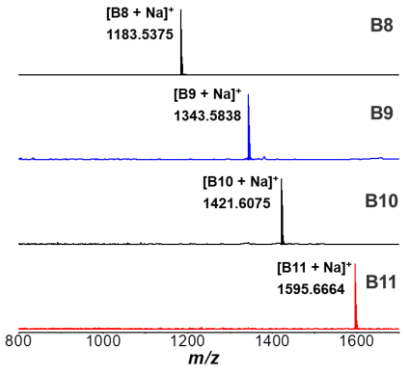


Figure S3. ESI mass spectra of **B8**-**B11**.

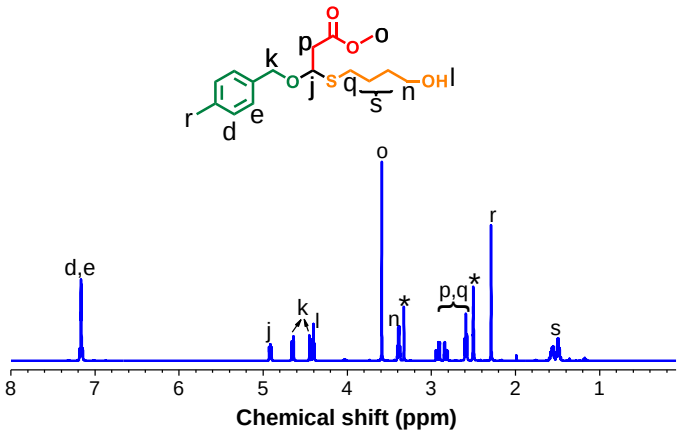


Figure S4. ^{1}H NMR spectrum of **B2** in DMSO-d_6. The solvent peaks are marked with asterisks.

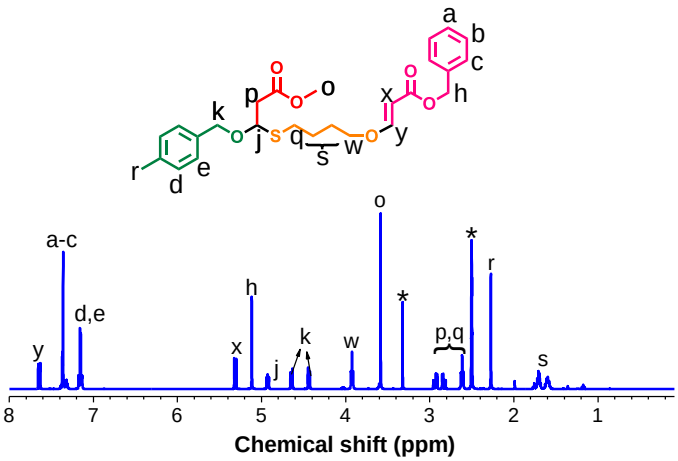


Figure S5. ^{1}H NMR spectrum of **B3** in DMSO-d_6. The solvent peaks are marked with asterisks.

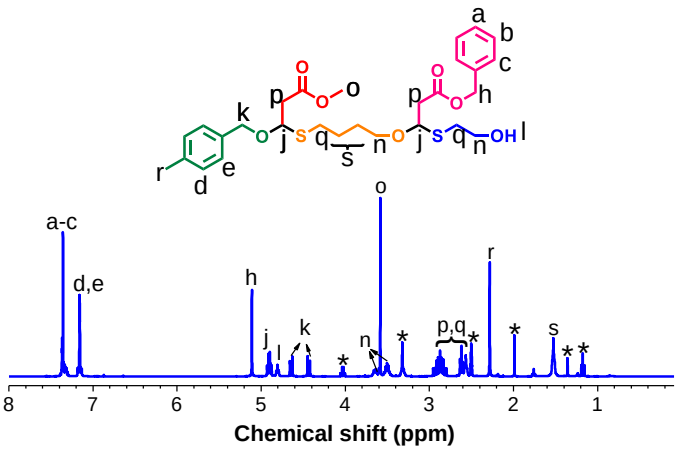


Figure S6. ^{1}H NMR spectrum of **B4** in DMSO-d_6. The solvent peaks are marked with asterisks.

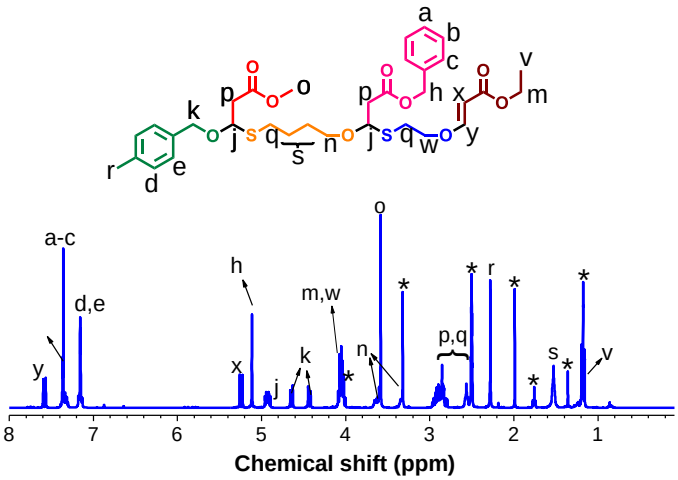


Figure S7. ^{1}H NMR spectrum of **B5** in DMSO-d_6. The solvent peaks are marked with asterisks.

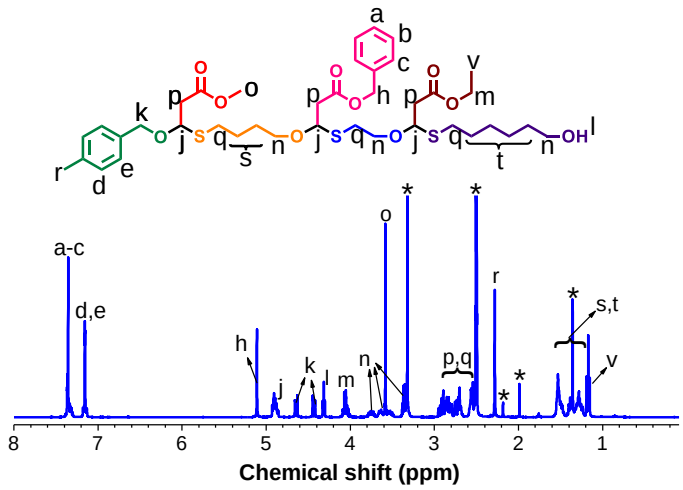


Figure S8. ^{1}H NMR spectrum of **B6** in DMSO-d_6. The solvent peaks are marked with asterisks.

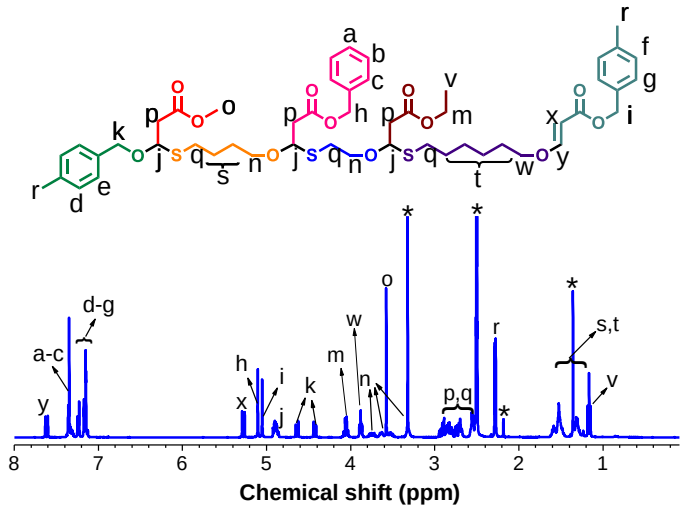


Figure S9. ^{1}H NMR spectrum of **B7** in DMSO-d_6. The solvent peaks are marked with asterisks.

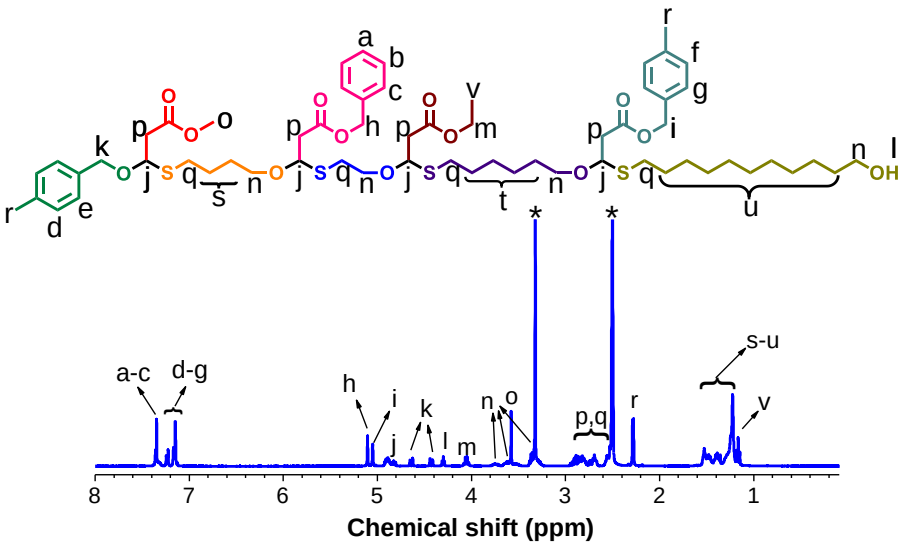


Figure S10. ^{1}H NMR spectrum of **B8** in DMSO-d_6. The solvent peaks are marked with asterisks.

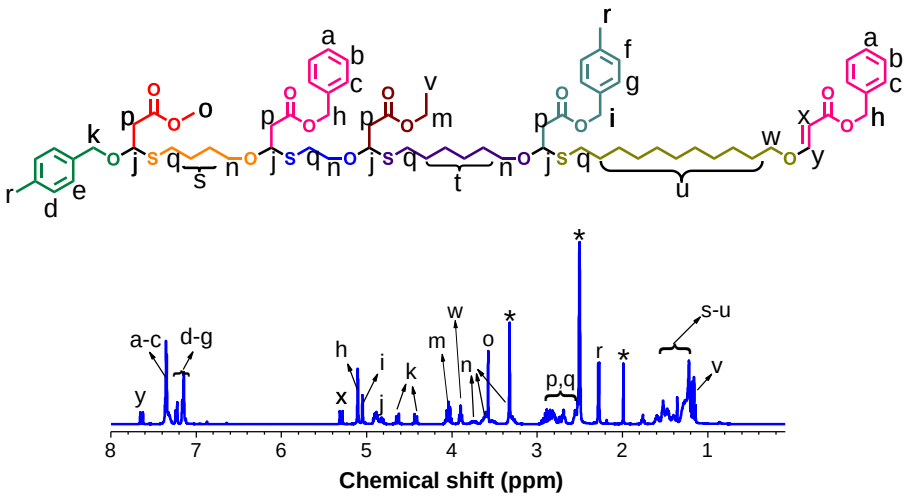


Figure S11. ^{1}H NMR spectrum of **B9** in DMSO-d_6. The solvent peaks are marked with asterisks.

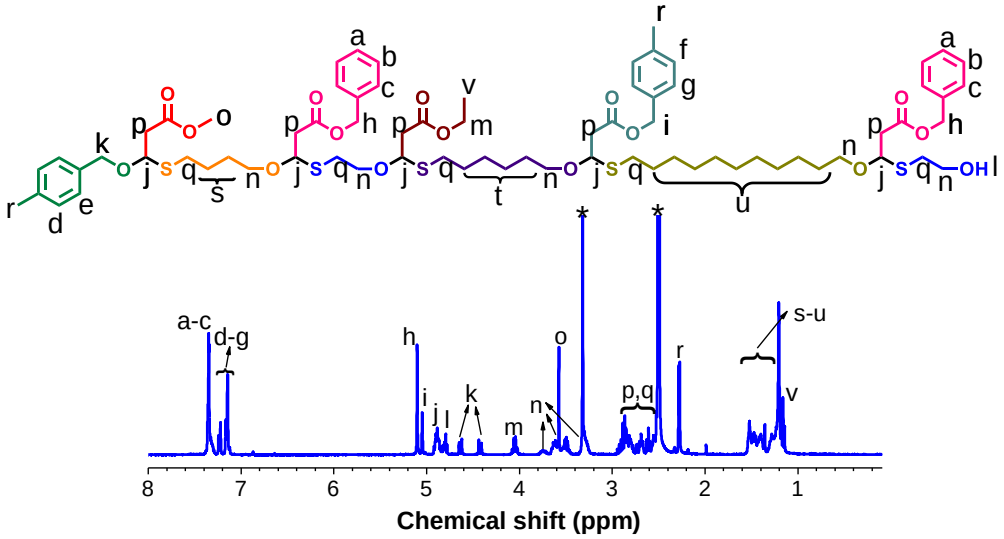


Figure S12. ^{1}H NMR spectrum of **B10** in DMSO-d_6. The solvent peaks are marked with asterisks.

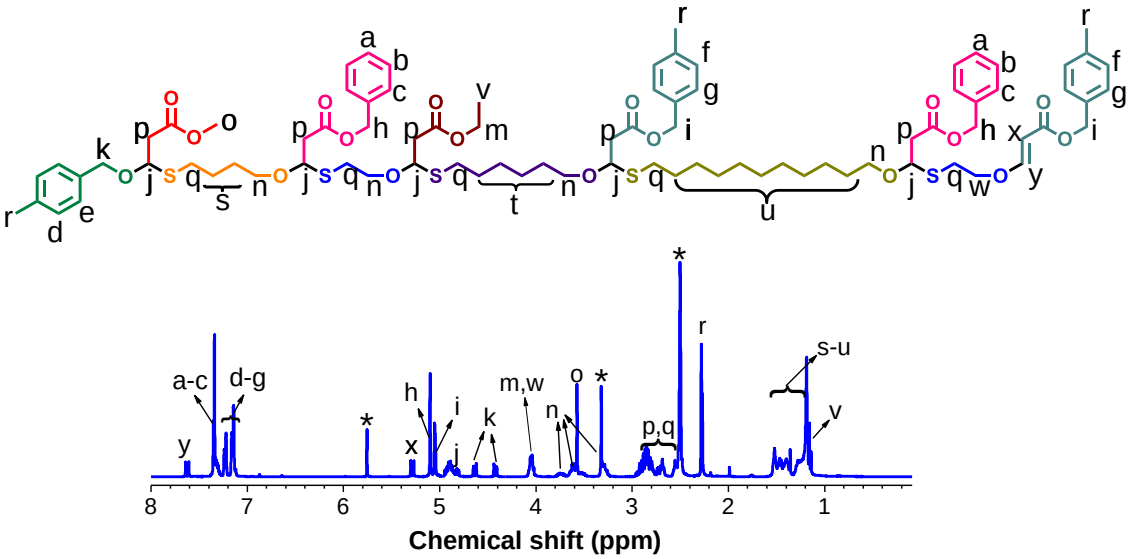


Figure S13. ^{1}H NMR spectrum of **B11** in DMSO-d_6. The solvent peaks are marked with asterisks.

Tandem ESI-MS/MS decoding of oligo(monothioacetal)s

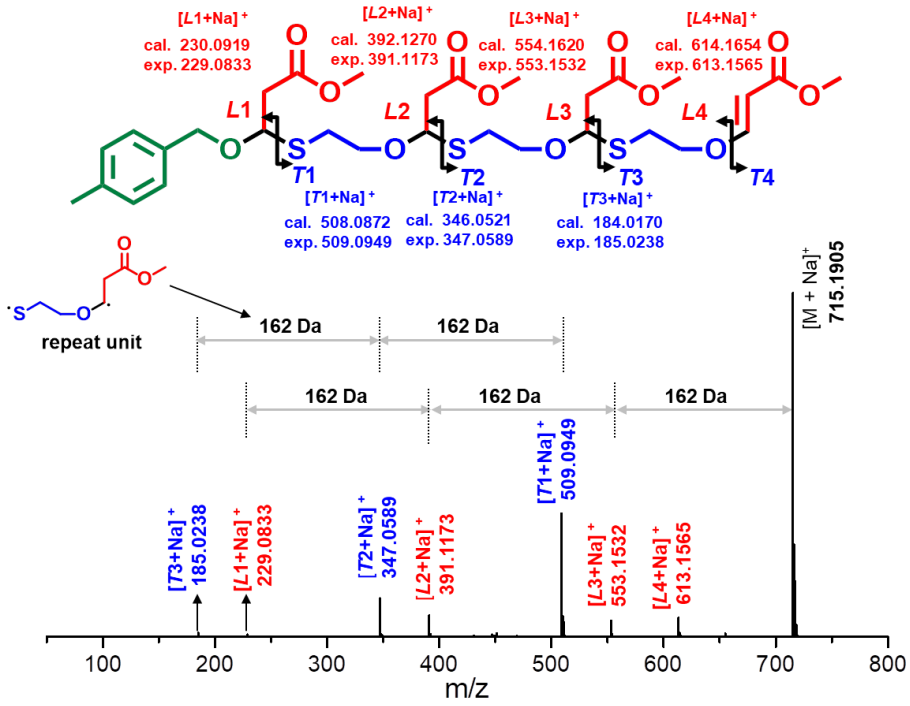


Figure S14. Decoding of sequence-defined **A7** by tandem ESI-MS/MS spectrometry.

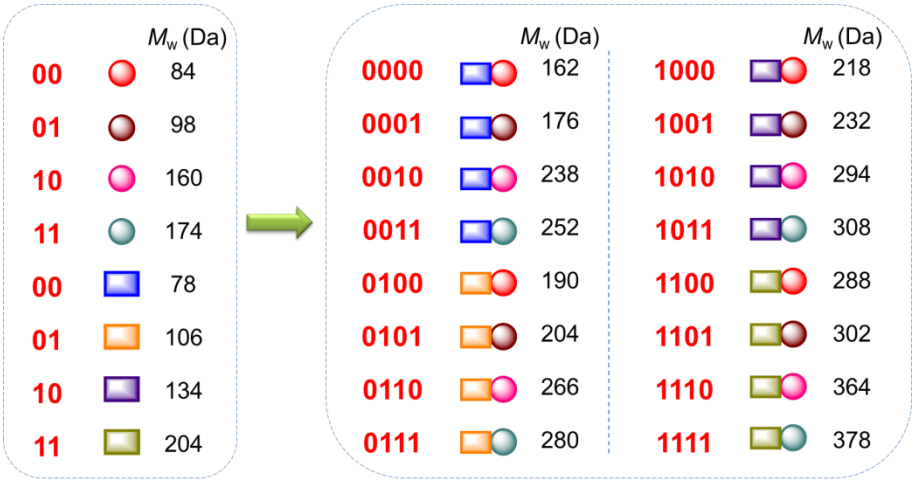


Figure S15. 4 + 4 monomer strategy and 4 × 4 combinations for M-ary encoding.

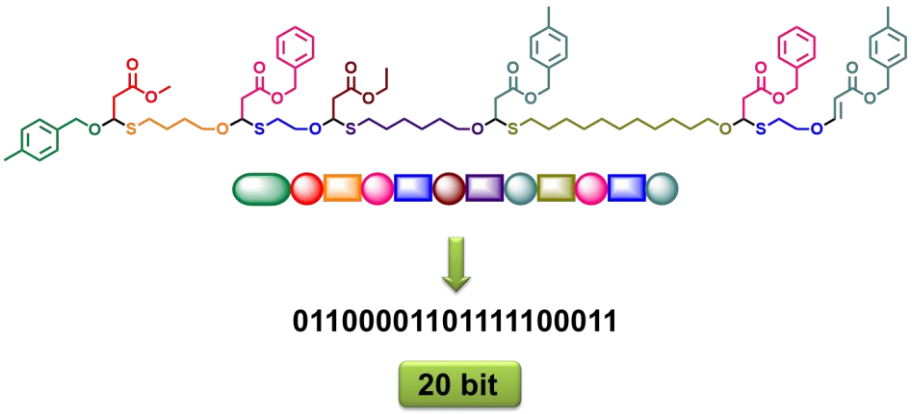


Figure S16. MS/MS translation of **B11.**

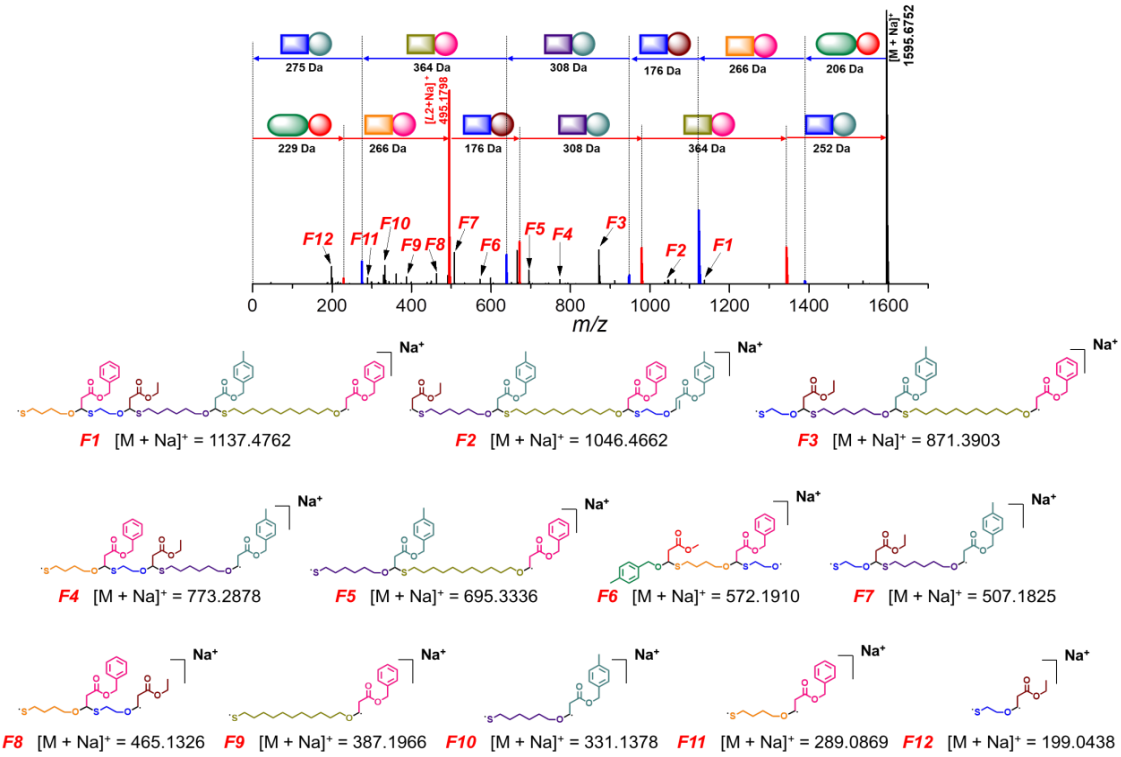
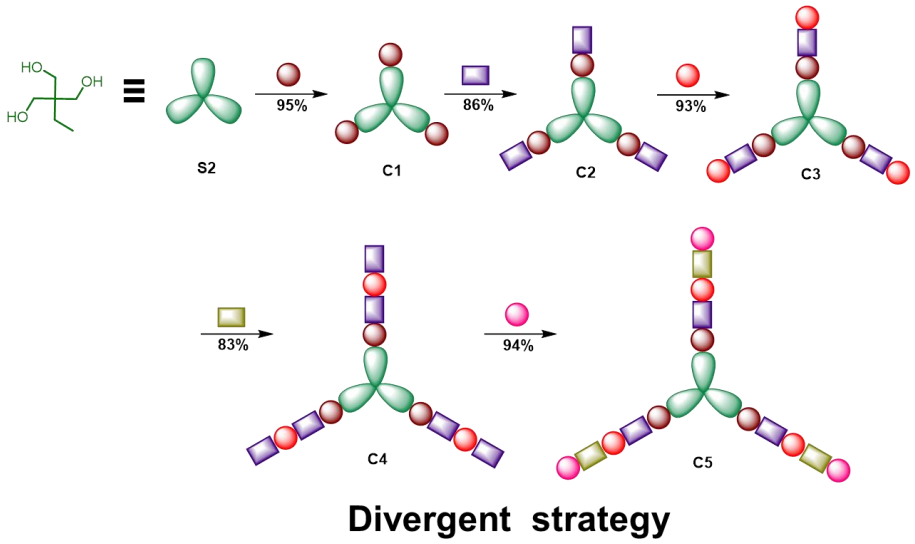
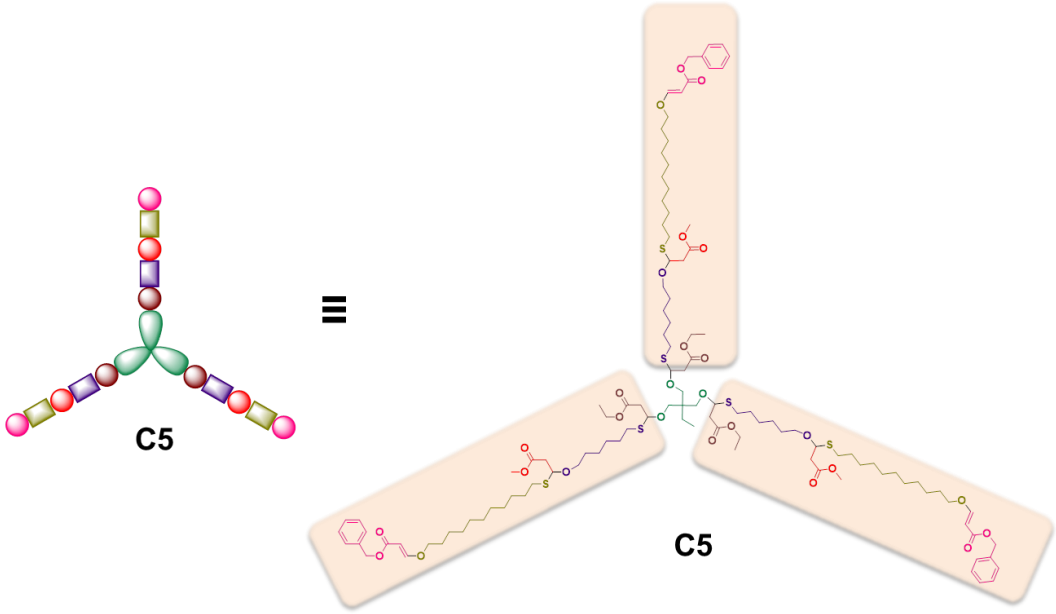


Figure S17. Proposed secondary product ions formed during secondary dissociation reactions in ESI-MS/MS of **B11**.

Synthetic procedure and characterization data for C1-C5, D1, and E1-E3



Scheme S4. Synthetic routes to **C1**-**C5**.



Scheme S5. The molecular structure of **C5**.

C1: 2-Ethyl-2-(hydroxymethyl)propane-1,3-diol (**S2**, 6 g, 50 mmol), ethyl propiolate **M3** (16.7 mL, 165 mmol), DABCO (840 mg, 7.5 mmol), and 50 mL THF were placed into a 250 mL round-bottom flask equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 6 h in air. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (8:1, v/v) as eluent.

The product **C1** (20.3 g) was obtained in 95% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.57 (d, J = 12.5 Hz, 3H), 5.31 (d, J = 12.5 Hz, 3H), 4.06 (m, 6H), 3.86 (s, 6H), 1.50 – 1.37 (m, 2H), 1.18 (t, J = 7.1 Hz, 9H), 0.83 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 167.09, 162.92, 97.19, 70.79, 59.66, 42.30, 22.51, 14.70, 7.50. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{21}H_{32}NaO_9$: 451.1944, found 451.1960.

C2: **C1** (6.4 g, 15 mmol), 6-mercapto-1-hexanol **M6** (9.3 mL, 68 mmol), 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (875 mg, 2.25 mmol), and 20 mL DMSO were placed into a 50 mL Schlenk tube equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 10 h under nitrogen, and then extracted three times with ethyl acetate. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (1:2, v/v) as eluent. The product **C2** (10.7 g) was obtained in 86% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 4.82 – 4.72 (m, 3H), 4.32 (t, J = 5.1 Hz, 3H), 4.13 – 4.00 (m, 6H), 3.52 (d, J = 9.2 Hz, 3H), 3.37 (m, 6H), 3.16 – 3.05 (m, 3H), 2.86 – 2.67 (m, 6H), 2.54 (t, J = 7.1 Hz, 6H), 1.57 – 1.45 (m, 6H), 1.44 – 1.23 (m, 20H), 1.19 (t, J = 7.2 Hz, 9H), 0.76 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 169.76, 82.31, 68.83, 61.11, 60.61, 42.22, 32.92, 30.15, 28.87, 28.85, 27.99, 27.87, 25.61, 14.52, 7.92. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{29}H_{74}NaO_{12}S_3$: 853.4240, found 853.4272.

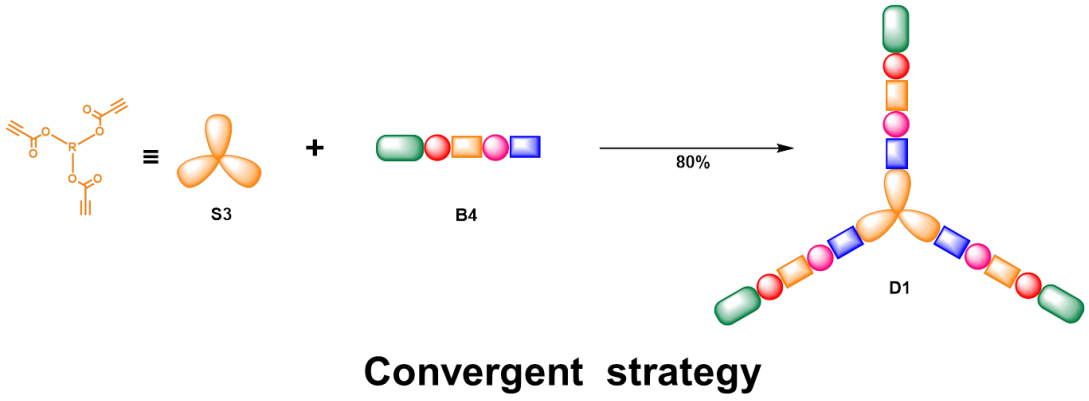
C3: **C2** (9.9 g, 12 mmol), methyl propiolate **M1** (3.6 mL, 40 mmol), DABCO (202 mg, 1.8 mmol), and 10 mL THF were placed into a 50 mL Schlenk tube equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 6 h in air. After solvent

evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (5:1, v/v) as eluent. The product **C3** (12.1 g) was obtained in 93% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.59 (d, J = 12.6 Hz, 3H), 5.24 (d, J = 12.6 Hz, 3H), 4.77 (m, 3H), 4.15 – 4.00 (m, 6H), 3.90 (t, J = 6.5 Hz, 6H), 3.59 (s, 9H), 3.52 (d, J = 8.0 Hz, 3H), 3.12 (m, 3H), 2.77 (m, 6H), 2.52 (m, 6H), 1.68 – 1.48 (m, 12H), 1.32 (m, 14H), 1.21 – 1.16 (m, 9H), 0.76 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 169.76, 82.31, 68.83, 61.11, 60.61, 42.22, 32.92, 30.15, 28.87, 28.85, 27.99, 27.87, 25.61, 14.52, 7.92. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{51}H_{86}NaO_{18}S_3$: 1105.4874, found 1105.4873.

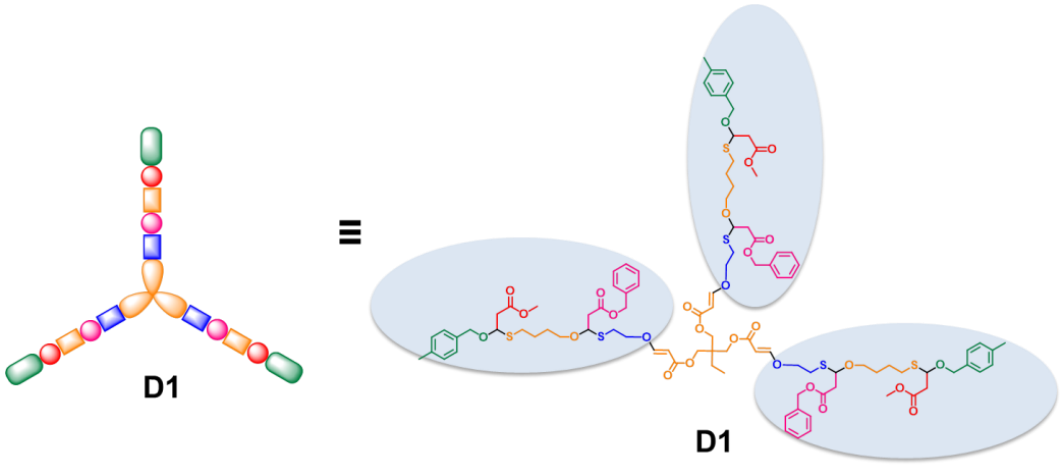
C4: **C3** (1.08 g, 1 mmol), 11-mercapto-1-undecanol **M8** (920 mg, 4.5 mmol), 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (59 mg, 0.15 mmol), and 2 mL DMSO were placed into a 50 mL Schlenk tube equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 10 h under nitrogen, and then extracted three times with ethyl acetate. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (1:2, v/v) as eluent. The product **C4** (1.41 g) was obtained in 83% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 4.87 (m, 3H), 4.81 (m, 3H), 4.14 (m, 6H), 3.77 – 3.67 (m, 12H), 3.62 (m, 9H), 3.38 (d, J = 9.1 Hz, 3H), 3.17 (d, J = 9.3 Hz, 3H), 2.95 – 2.68 (m, 12H), 2.56 (t, J = 7.4 Hz, 12H), 1.61 – 1.51 (m, 24H), 1.40 – 1.24 (m, 65H), 0.82 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 170.58, 81.40, 67.91, 63.05, 60.69, 51.84, 41.97, 32.81, 30.11, 29.57, 29.49, 29.42, 29.25, 29.19, 29.04, 27.89, 25.74, 14.19, 7.50. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{84}H_{158}NaO_{21}S_6$: 1717.9518, found

1717.9592.

C5: **C4** (848 mg, 0.5 mmol), **M5** (264 mg, 1.65 mmol), DABCO (8.4 mg, 0.075 mmol), and 1 mL THF were placed into a 50 mL Schlenk tube equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 6 h in air. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (5:1, v/v) as eluent. The product **C5** (1.023 g) was obtained in 94% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.64 (d, J = 12.6 Hz, 3H), 7.42 – 7.28 (m, 15H), 5.24 (d, J = 12.6 Hz, 3H), 5.16 (s, 6H), 4.90 – 4.75 (m, 6H), 4.15 (m, 6H), 3.83 (t, J = 6.5 Hz, 6H), 3.77 – 3.66 (m, 12H), 3.61 (d, J = 9.5 Hz, 3H), 3.41 – 3.32 (m, 3H), 3.17 (d, J = 8.6 Hz, 3H), 2.98 – 2.62 (m, 12H), 2.55 (t, J = 7.3 Hz, 12H), 1.71 – 1.52 (m, 24H), 1.39 – 1.22 (m, 65H), 0.81 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 170.54, 167.77, 163.06, 136.49, 128.53, 128.13, 128.06, 96.00, 82.23, 81.42, 71.22, 67.95, 65.60, 60.68, 51.83, 42.00, 30.33, 30.14, 30.09, 29.50, 29.23, 29.08, 28.96, 28.86, 27.91, 25.91, 25.75, 14.27, 7.66. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{114}H_{182}NaO_{27}S_6$: 2198.1090, found 2198.1133.



Scheme S6. Synthetic route to **D1**.



Scheme S7. The molecular structure of **D1**.

D1: The triyne **S3** (145 mg, 0.5 mmol), **B4** (880 mg, 1.6 mmol), DABCO (16.8 mg, 0.15 mmol), and 2 mL THF were placed into a 50 mL Schlenk tube equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 6 h in air. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (2:1, v/v) as eluent. The product **D1** (776 mg) was obtained in 80% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.54 (d, J = 12.6 Hz, 3H), 7.41 – 7.30 (m, 15H), 7.17 (m, 12H), 5.18 – 5.09 (m, 9H), 4.98 – 4.86 (m, 6H), 4.72 (d, J = 11.2 Hz, 3H), 4.48 (d, J = 11.3 Hz, 3H), 4.08 (s, 6H), 3.94 (m, 6H), 3.78 – 3.58 (m, 12H), 3.36 (m, 3H), 2.85 (m, 18H), 2.59 (m, 6H), 2.33 (s, 9H), 1.62 (m, 14H), 0.89 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 170.34, 169.49, 167.22, 162.16, 137.59, 135.61, 134.22, 129.26, 129.10, 128.59, 128.48, 128.37, 128.21, 127.13, 125.53, 96.58, 81.44, 80.54, 70.39, 69.48, 67.63, 66.68, 65.31, 63.46, 51.84, 42.13, 41.97, 40.92, 34.23, 30.32, 28.54, 27.25, 26.75, 26.73, 26.28, 21.19, 21.16, 7.49. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{99}H_{128}NaO_{27}S_6$: 1963.6865, found 1963.6896.

E1: **S3** (290 mg, 1 mmol), **A2** (966 mg, 3.4 mmol), DABCO (33.6 mg, 0.3 mmol), and 2 mL THF were placed into a 50 mL Schlenk tube equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 6 h in air. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (2:1, v/v) as eluent. The product **E1** (950 mg) was obtained in 83% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.56 (d, J = 12.7 Hz, 3H), 7.17 (m, 12H), 5.17 (d, J = 12.6 Hz, 3H), 4.99 (m, 3H), 4.72 (d, J = 11.3 Hz, 3H), 4.51 (d, J = 11.3 Hz, 3H), 4.09 (s, 6H), 3.98 (m, 6H), 3.68 (s, 9H), 3.01 – 2.76 (m, 12H), 2.34 (s, 9H), 1.54 – 1.46 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 170.04, 167.25, 162.18, 137.84, 133.78, 129.20, 128.29, 96.59, 80.49, 70.35, 69.75, 63.52, 51.95, 41.92, 40.93, 26.20, 21.21, 7.49. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{57}H_{74}NaO_{18}S_3$: 1165.3935, found 1165.3972.

E2: **E1** (572 mg, 0.5 mmol), 11-mercapto-1-undecanol **M8** (460 mg, 2.25 mmol), 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (29 mg, 0.075 mmol), and 2 mL DMSO were placed into a 50 mL Schlenk tube equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 10 h under nitrogen, and then extracted three times with ethyl acetate. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (1:2, v/v) as eluent. The product **E2** (764 mg) was obtained in 87% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.17 (m, 12H), 4.97 (m, 5.4 Hz, 3H), 4.91 – 4.82 (m, 3H), 4.73 (d, J = 11.3 Hz, 3H), 4.48 (d, J = 11.3 Hz, 3H), 4.06 (m, 6H), 3.89 (m, 3H), 3.71 – 3.51 (m, 18H), 2.94 (m, 6H), 2.80 (m, 12H), 2.56 (m, 6H), 2.33 (s, 9H), 1.62 – 1.52 (m, 12H), 1.39 – 1.19

(m, 44H), 0.88 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 170.25, 169.87, 169.51, 137.62, 134.09, 129.11, 128.28, 81.35, 80.52, 69.62, 67.45, 63.06, 51.86, 42.09, 32.82, 30.01, 29.59, 29.53, 29.43, 29.24, 29.14, 25.75, 21.21, 7.42. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{90}H_{146}NaO_{21}S_6$: 1777.8579, found 1777.8544.

E3: **E2** (176 mg, 0.1 mmol), **M5** (96 mg, 0.6 mmol), DABCO (4 mg, 0.03 mmol), and 2 mL THF were placed into a 50 mL Schlenk tube equipped with a magnetic stir bar. The mixture was stirred at 25 ℃ for 6 h in air. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (2:1, v/v) as eluent. The product **E3** (210 mg) was obtained in 94% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 12.6 Hz, 3H), 7.34 (m, 15H), 7.17 (m, 12H), 5.23 (d, J = 12.6 Hz, 3H), 5.16 (s, 6H), 4.96 (m, 3H), 4.88 (m, 3H), 4.73 (d, J = 11.4 Hz, 3H), 4.47 (d, J = 11.3 Hz, 3H), 4.06 (m, 6H), 3.85 (m, 9H), 3.70 – 3.52 (m, 12H), 2.91 (m, 6H), 2.85 – 2.71 (m, 12H), 2.54 (m, 6H), 2.33 (s, 9H), 1.67 (d, J = 7.2 Hz, 6H), 1.30 (d, J = 33.9 Hz, 50H), 0.88 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 170.21, 169.50, 167.78, 163.06, 137.61, 136.48, 134.09, 129.11, 128.53, 128.27, 128.13, 128.07, 96.00, 81.15, 80.52, 71.21, 69.62, 67.46, 65.61, 51.84, 42.09, 41.75, 30.34, 30.02, 29.55, 29.52, 29.26, 29.18, 28.87, 26.89, 25.77, 21.21, 7.43. ESI-MS: m/z calculated for $[M+Na]^+$ $C_{120}H_{170}NaO_{27}S_6$: 2258.0151, found 2258.0156.

GPC, ESI-MS and NMR spectra of C1-C5, D1, and E1-E3

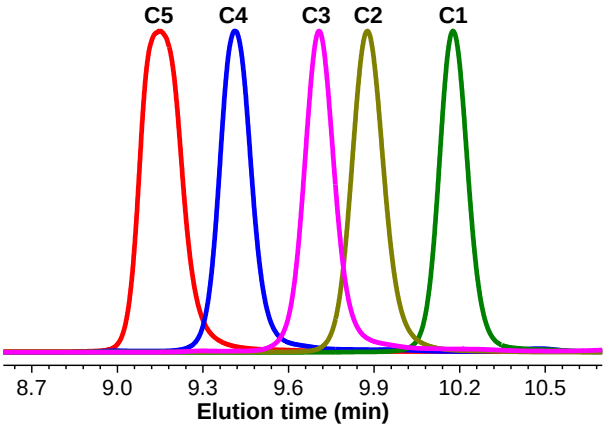


Figure S18. GPC traces of **C1-C5**.

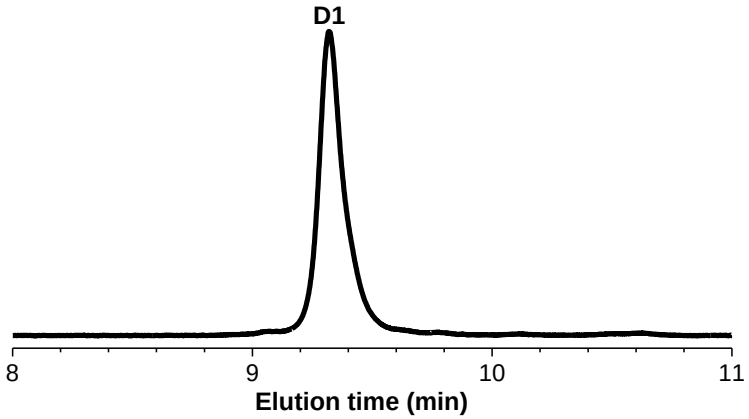


Figure S19. GPC trace of **D1**.

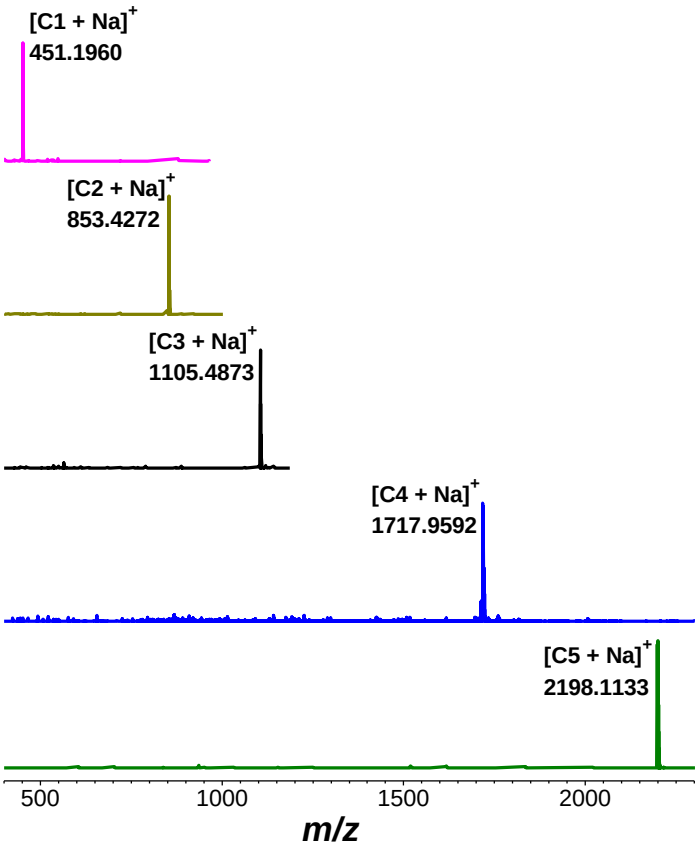


Figure S20. ESI mass spectra of **C1**-**C5**.

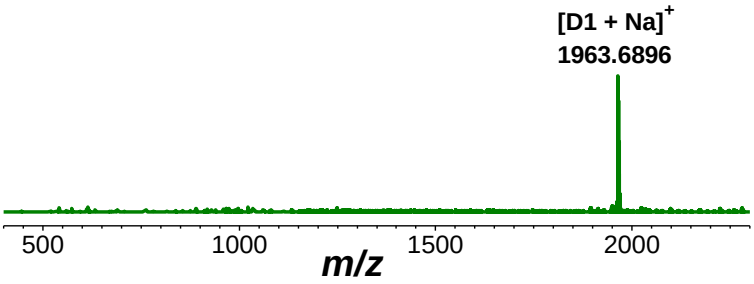


Figure S21. ESI mass spectra of **D1**.

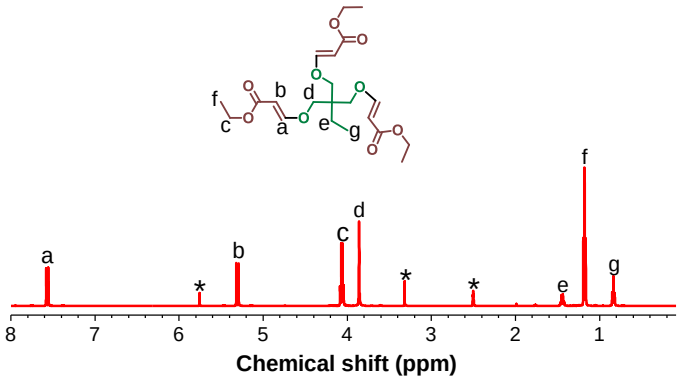


Figure S22. ^{1}H NMR spectrum of **C1** in DMSO-d_6. The solvent peaks are marked with asterisks.

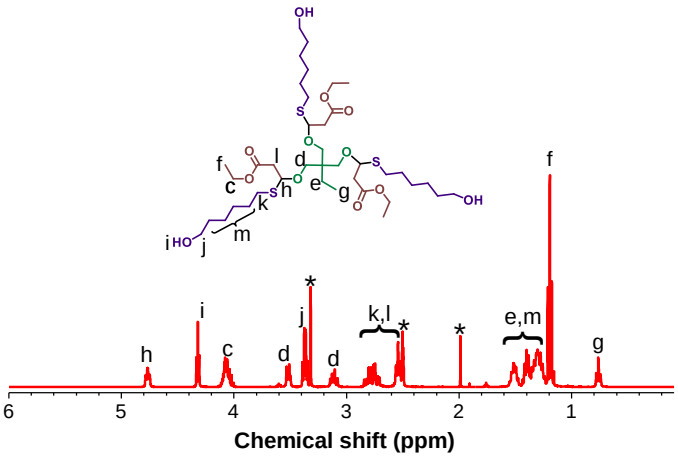


Figure S23. ^{1}H NMR spectrum of **C2** in DMSO-d_6. The solvent peaks are marked with asterisks.

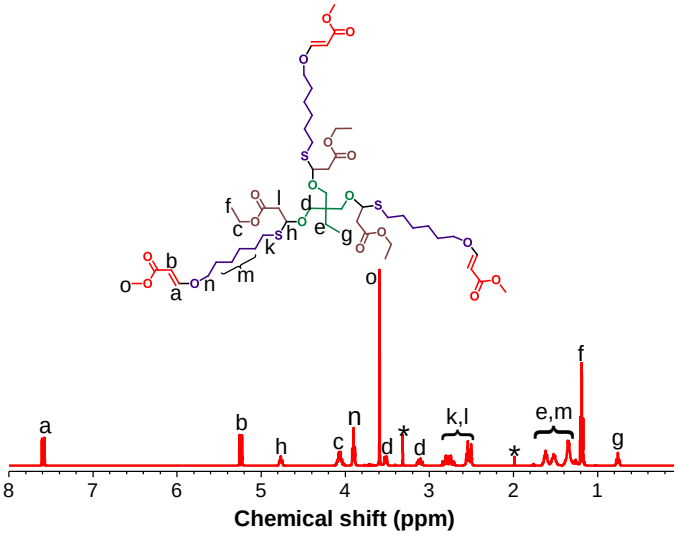


Figure S24. ^{1}H NMR spectrum of **C3** in DMSO-d_6. The solvent peaks are marked with asterisks.

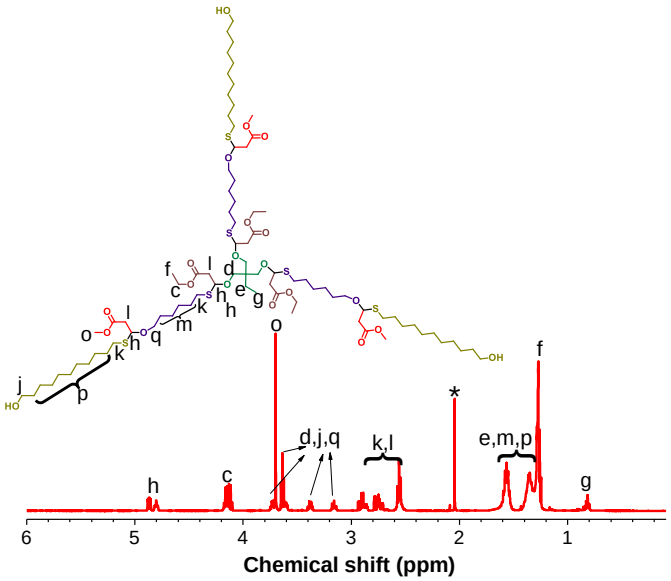


Figure S25. ^{1}H NMR spectrum of **C4** in DMSO-d_6. The solvent peaks are marked with asterisks.

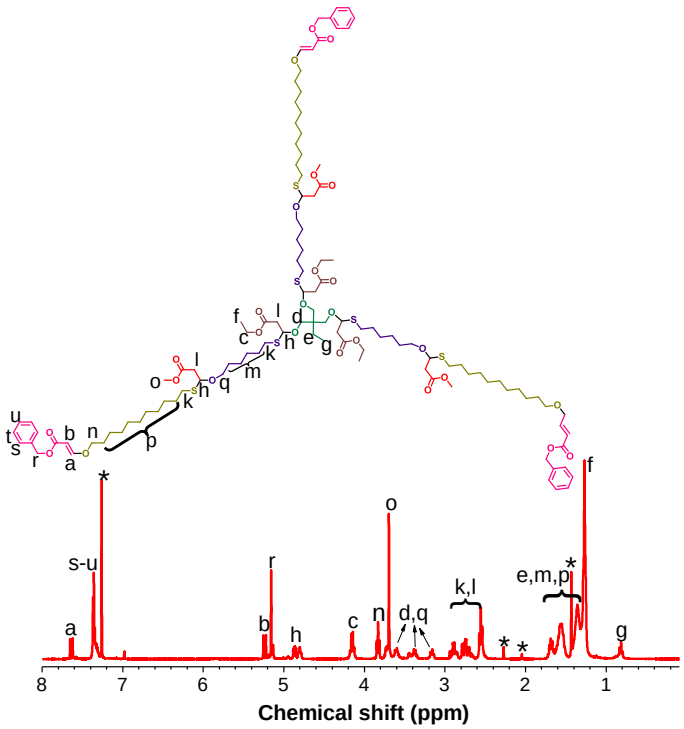


Figure S26. ^{1}H NMR spectrum of **C5** in DMSO-d_6. The solvent peaks are marked with asterisks.

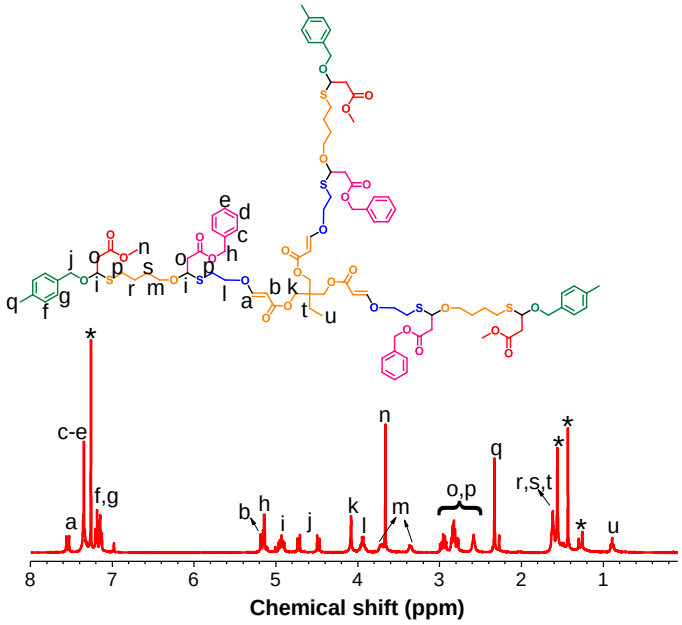


Figure S27. ^{1}H NMR spectrum of **D1** in DMSO-d_6. The solvent peaks are marked with asterisks.

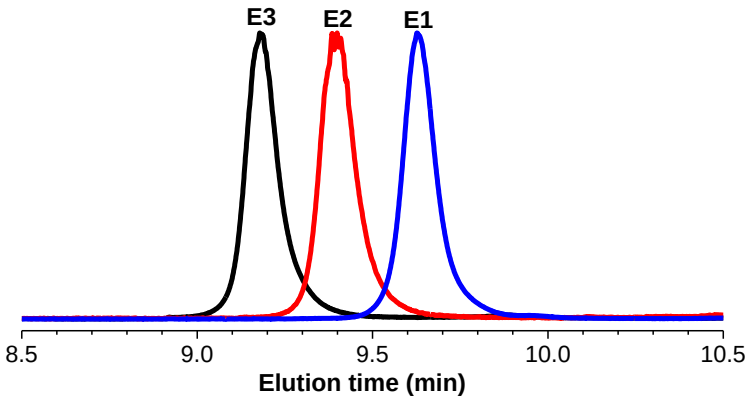


Figure S28. GPC traces of **E1**-**E3**.

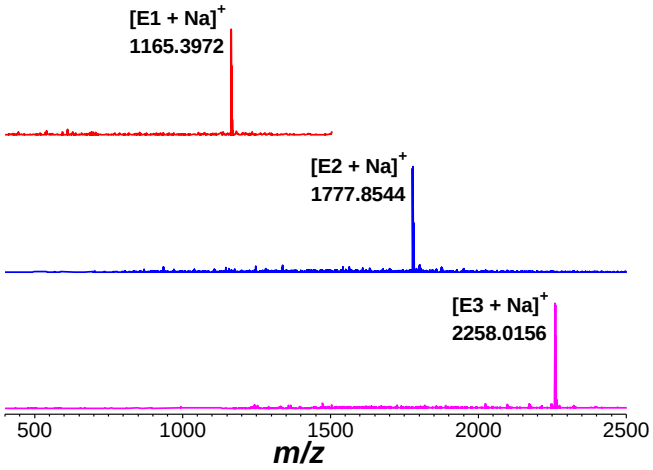


Figure S29. ESI mass spectra of **E1**-**E3**.

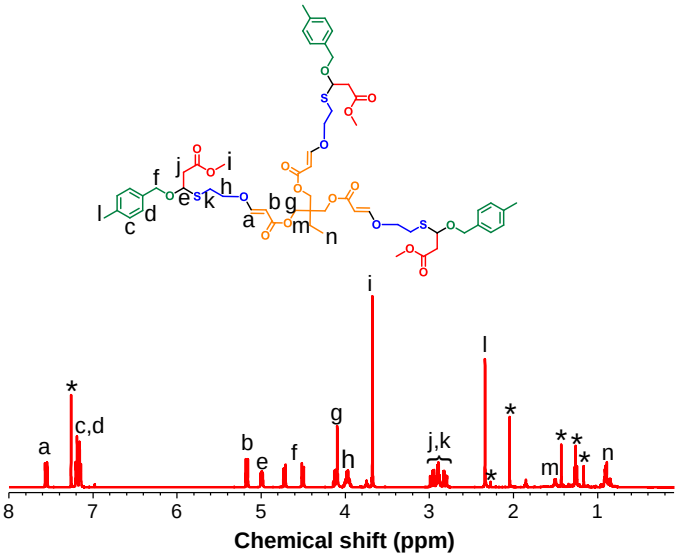


Figure S30. ^{1}H NMR spectrum of **E1** in DMSO-d_6. The solvent peaks are marked with asterisks.

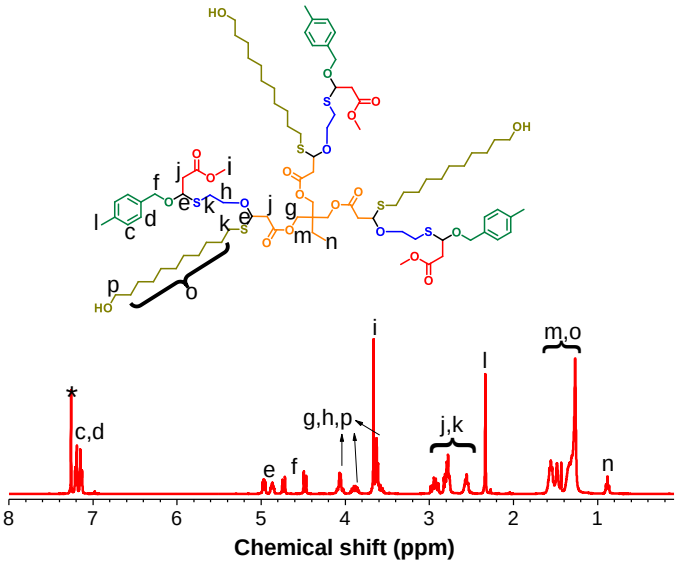


Figure S31. ^{1}H NMR spectrum of **E2** in DMSO-d_6. The solvent peaks are marked with asterisks.

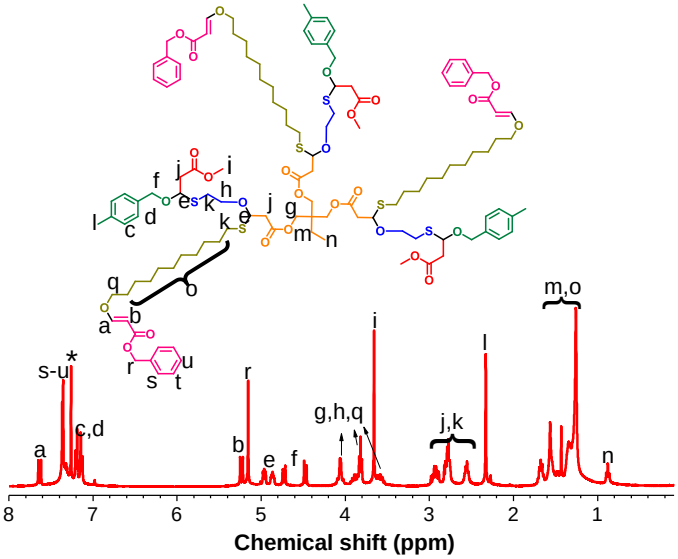


Figure S32. ^{1}H NMR spectrum of **E3** in DMSO-d_6. The solvent peaks are marked with asterisks.

Tandem ESI-MS/MS decoding and translation of the miktoarm star oligo(monothioacetal) E3

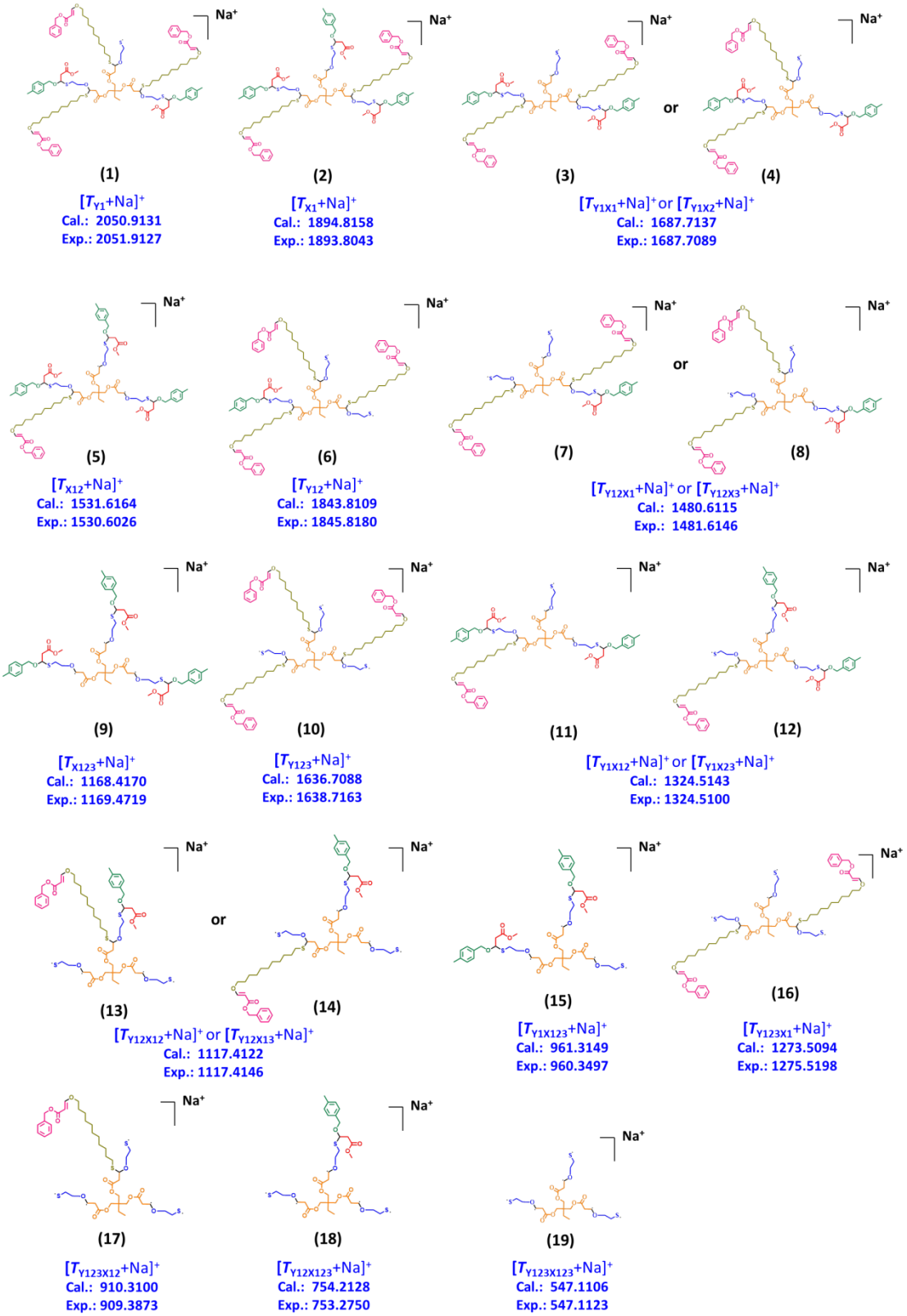
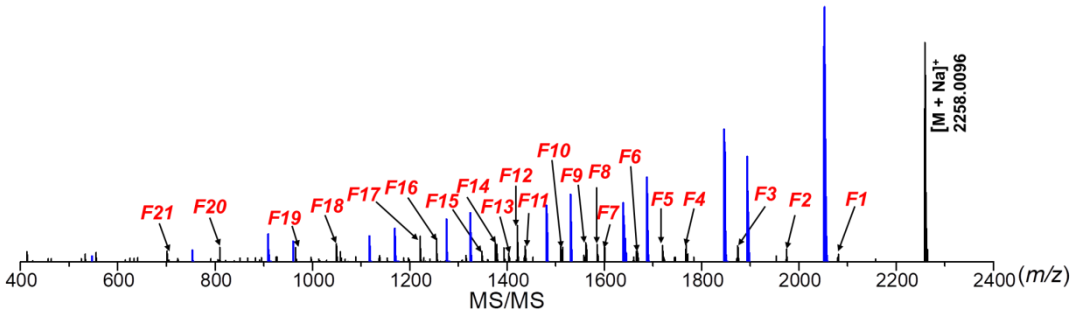
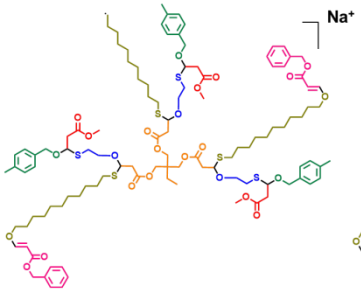
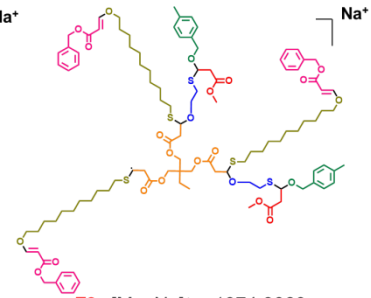


Figure S33. 19 main fragment ions of **E3**.

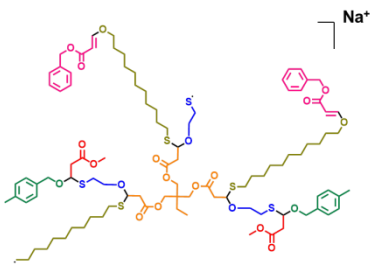




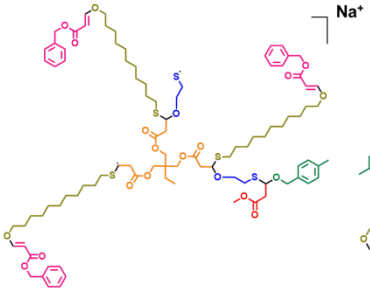
F1 [M + Na]+ = 2080.9489



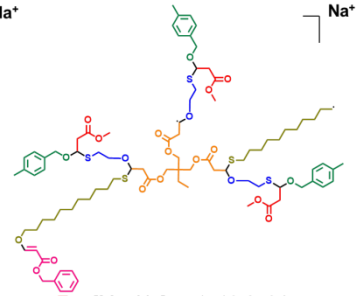
F2 [M + Na]+ = 1974.9060



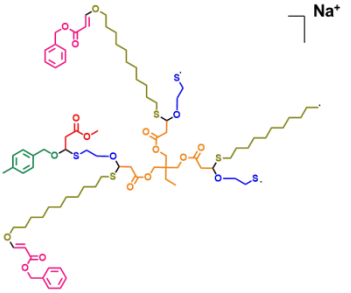
F3 [M + Na]+ = 1873.8586



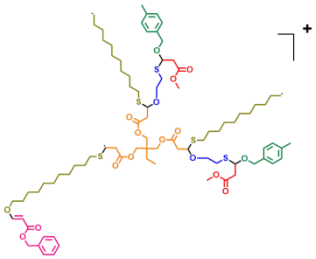
F4 [M + Na]+ = 1767.802 0



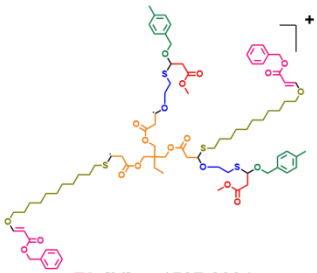
F5 [M + Na]+ = 1719.6794



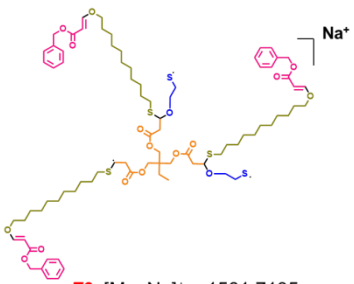
F6 [M + Na]+ = 1666.7777



F7 [M]+ = 1597.8177



F8 [M]+ = 1587.6834



F9 [M + Na]+ = 1561.7135

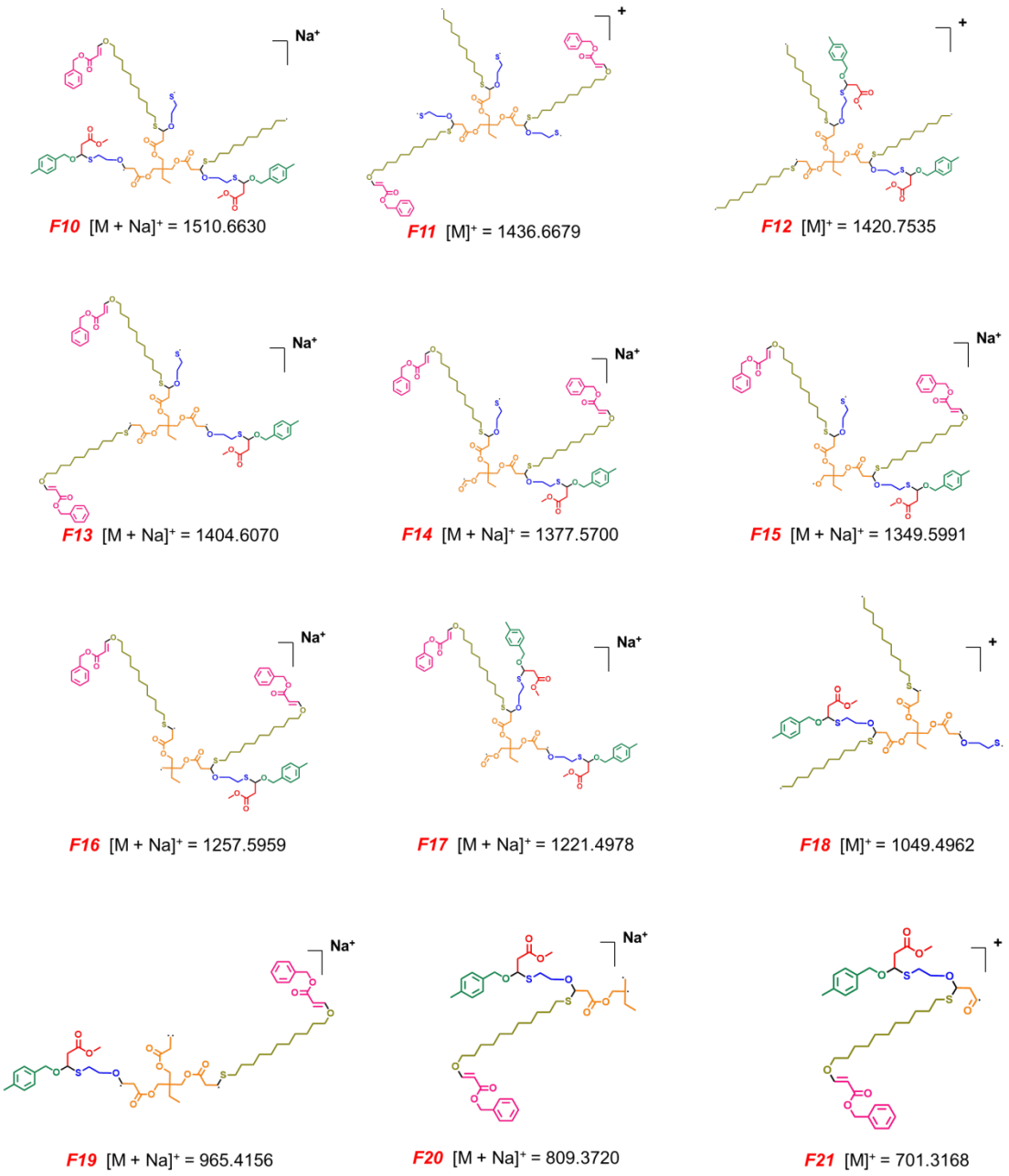


Figure S34. Proposed secondary product ions formed during secondary dissociation reactions in ESI-MS/MS of **E3**.

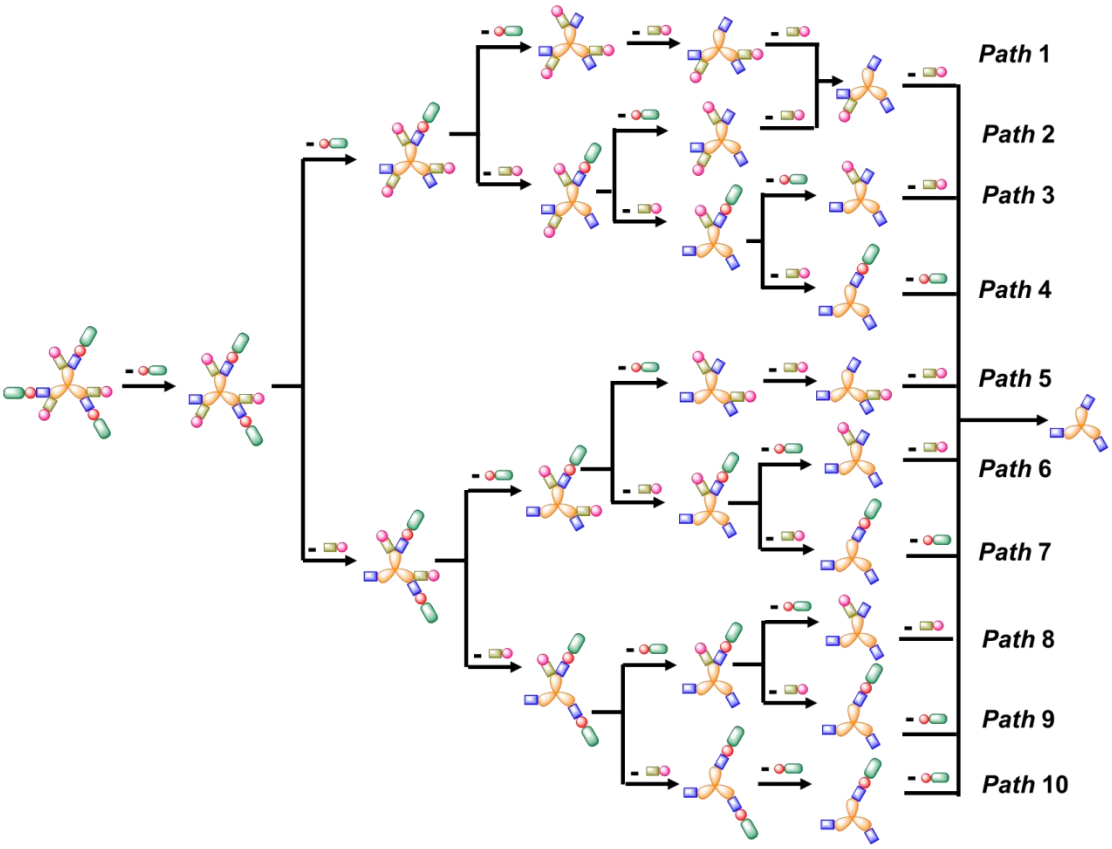


Figure S35. Schematic fragmentation path 1-10.

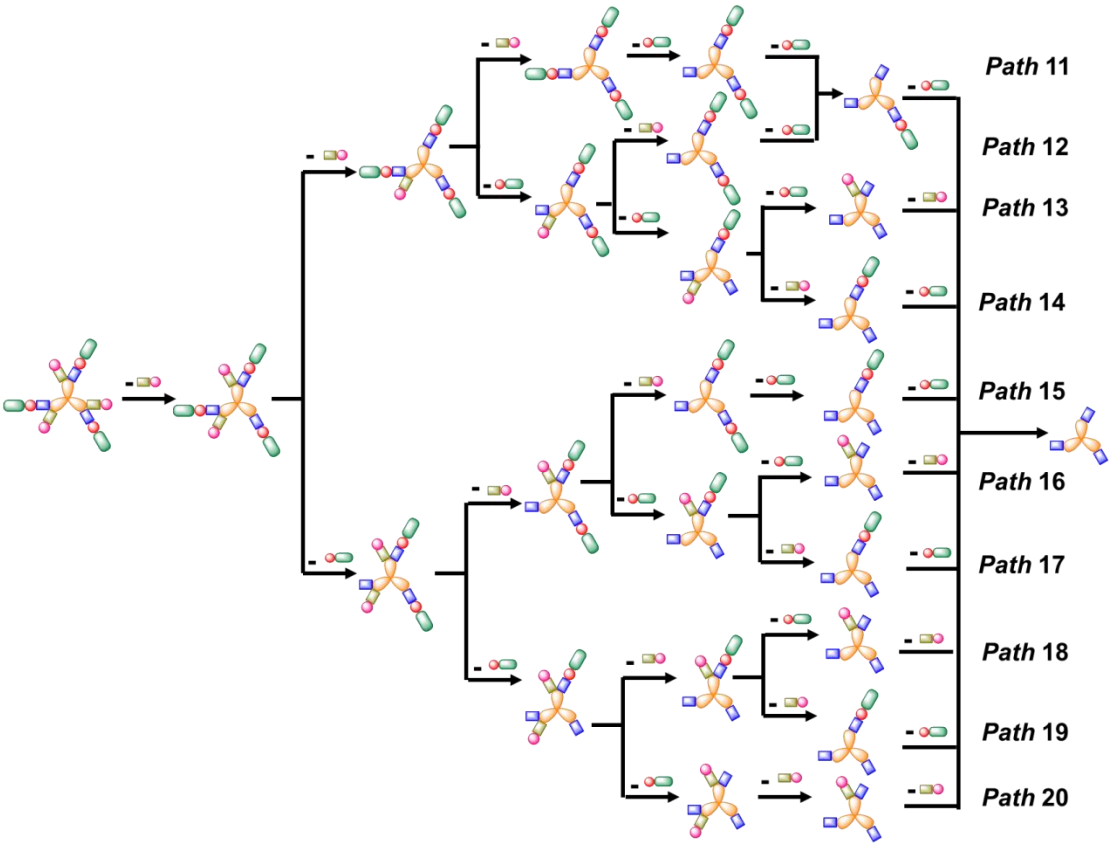


Figure S36. Schematic fragmentation path 11-20.

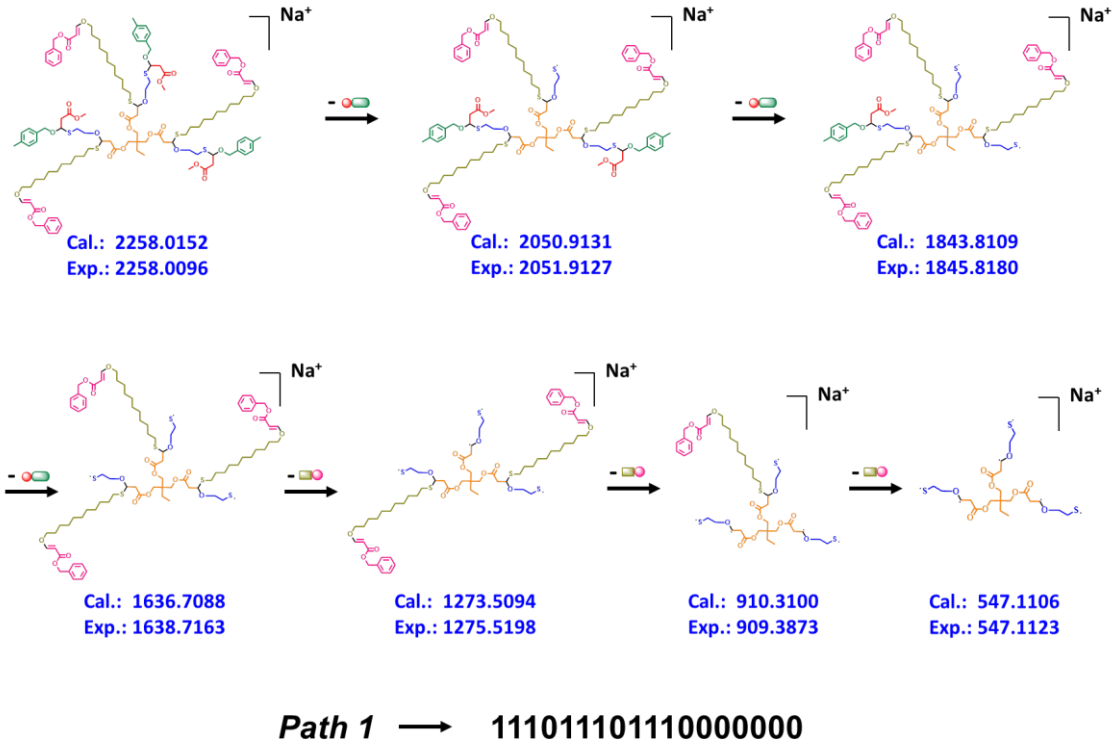


Figure S37. Fragmentation path 1 of **E3**.

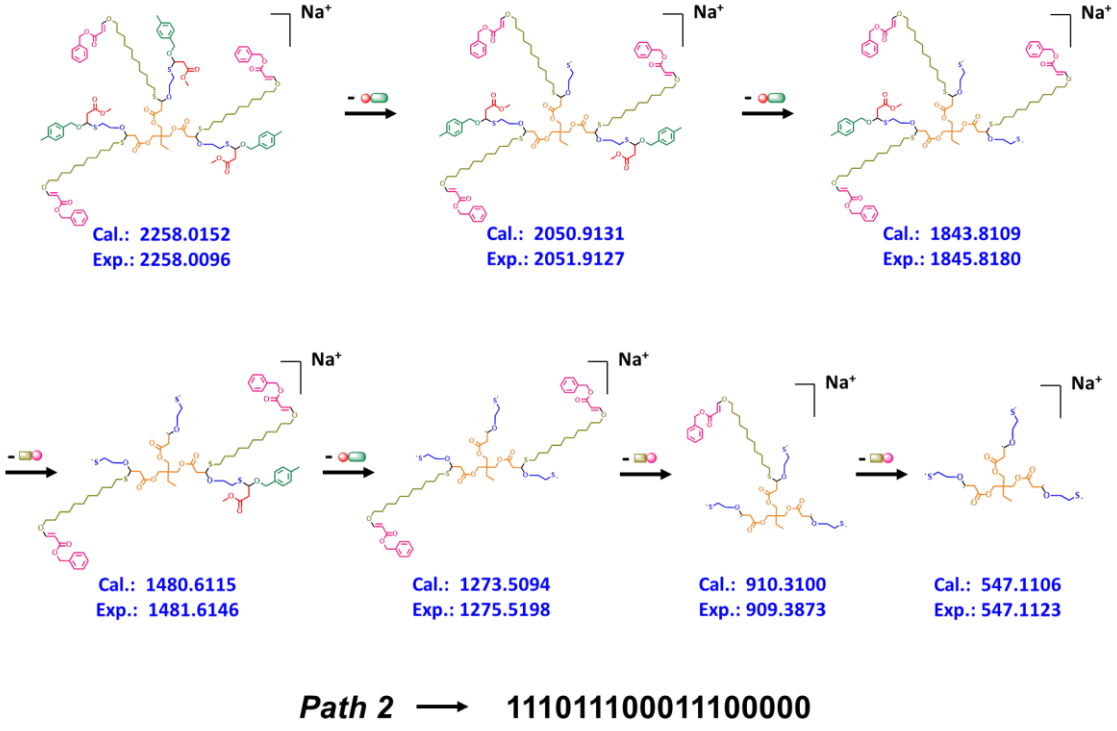


Figure S38. Fragmentation path 2 of **E3**.

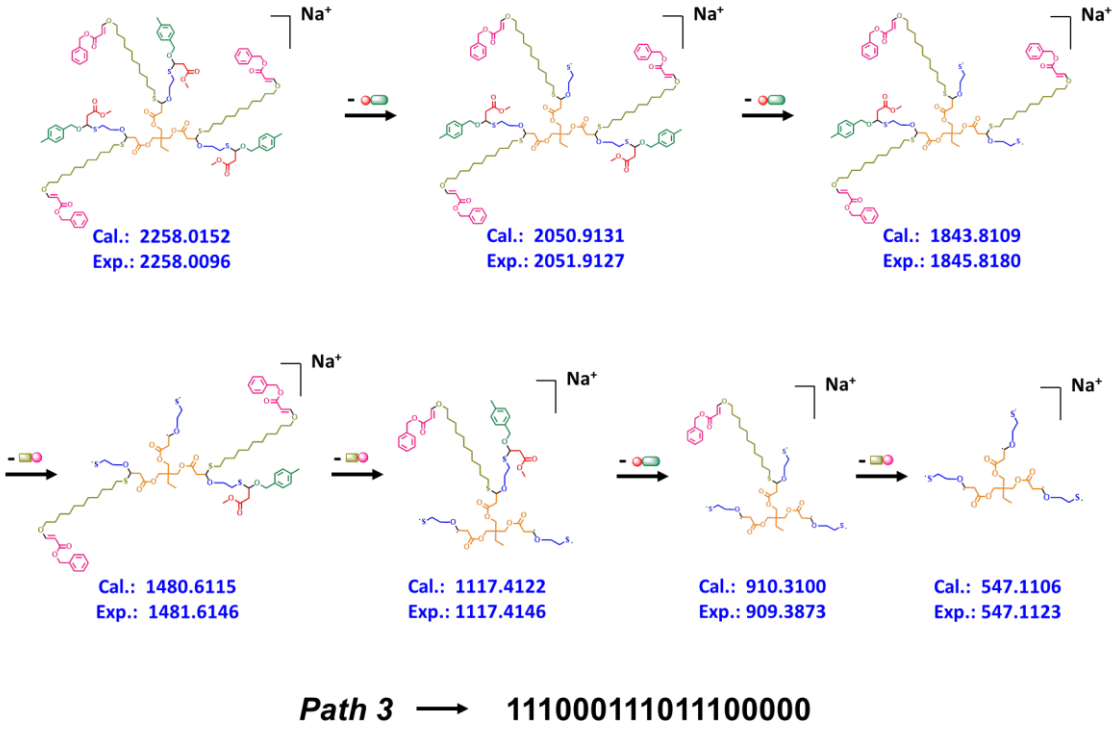


Figure S39. Fragmentation path 3 of **E3**.

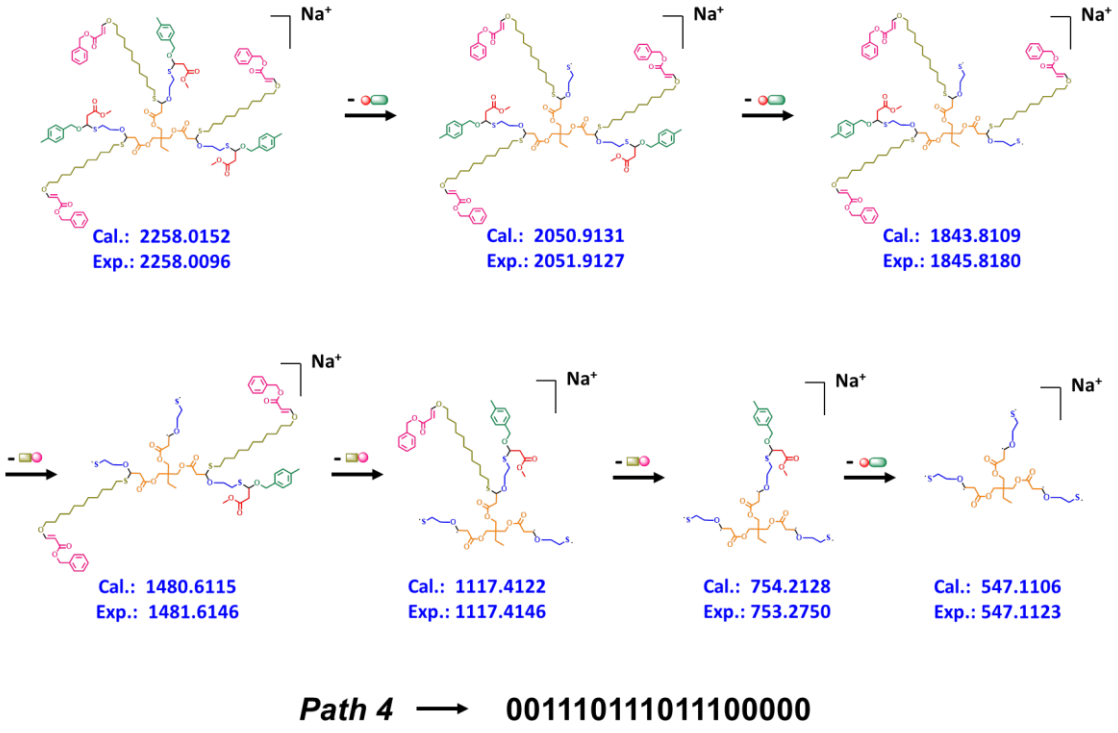


Figure S40. Fragmentation path 4 of **E3**.

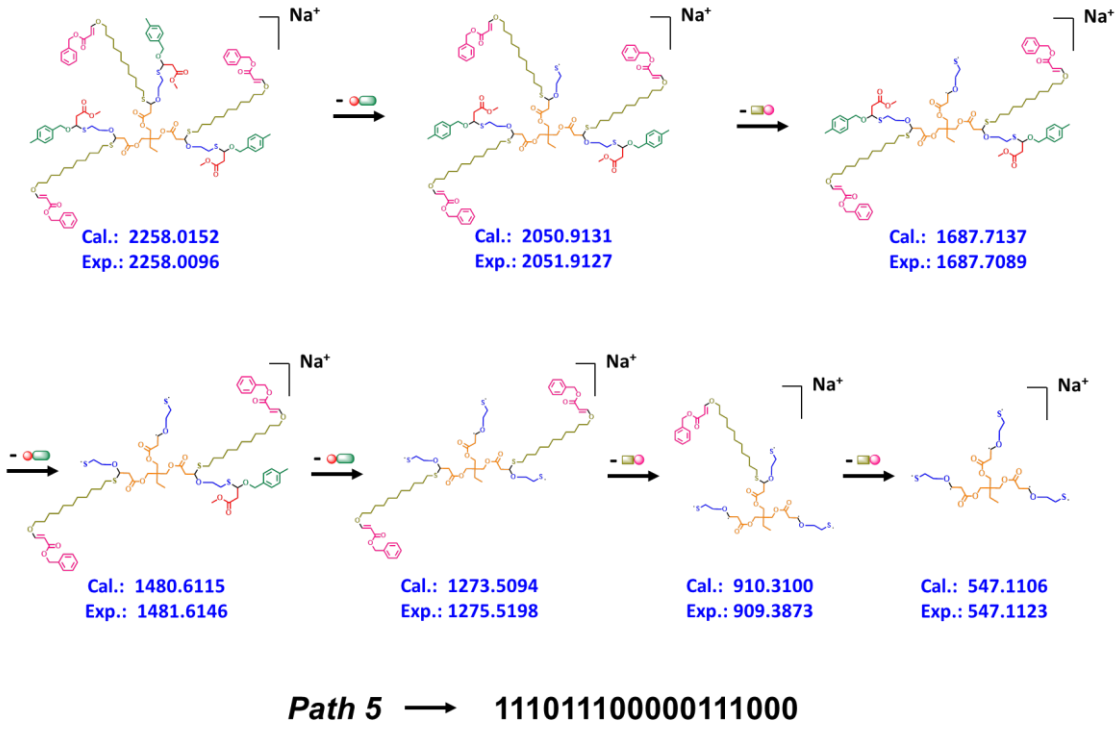


Figure S41. Fragmentation path 5 of **E3**.

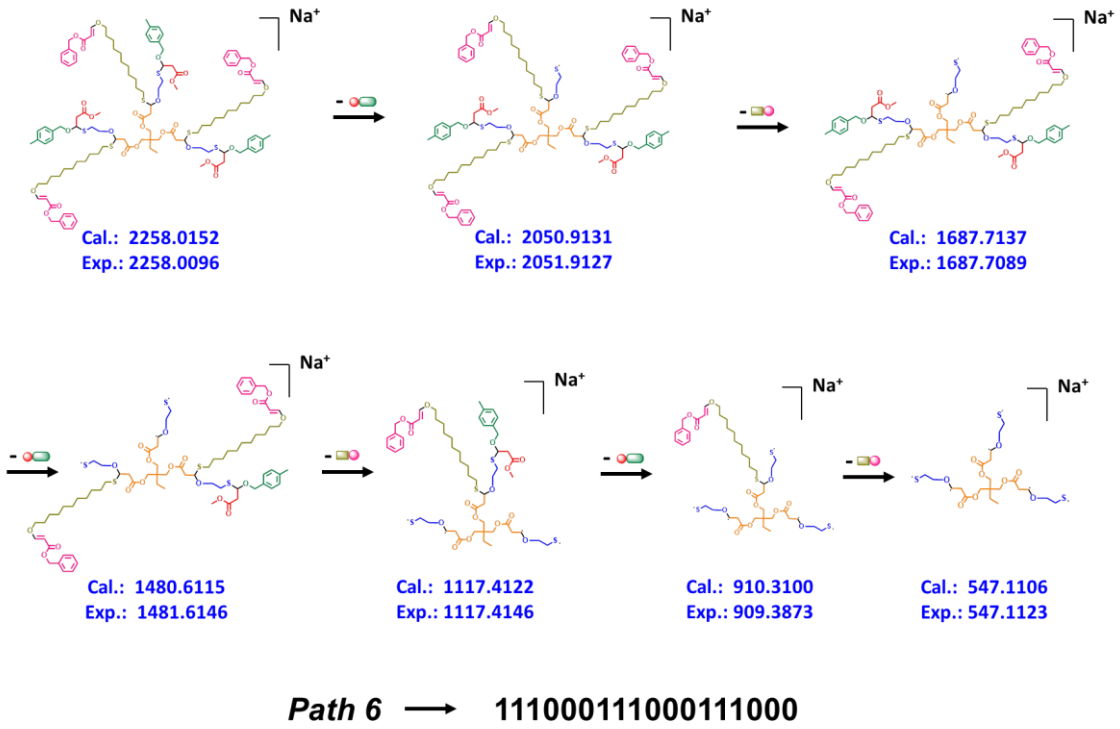


Figure S42. Fragmentation path 6 of **E3**.

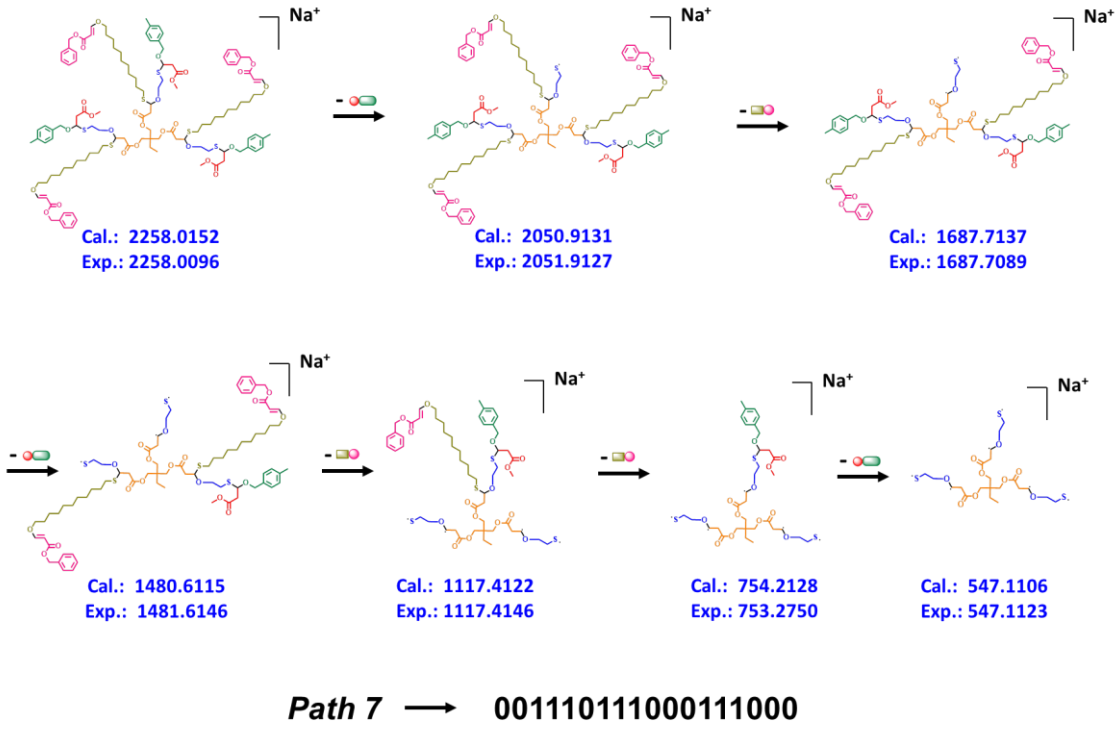


Figure S43. Fragmentation path 7 of **E3**.

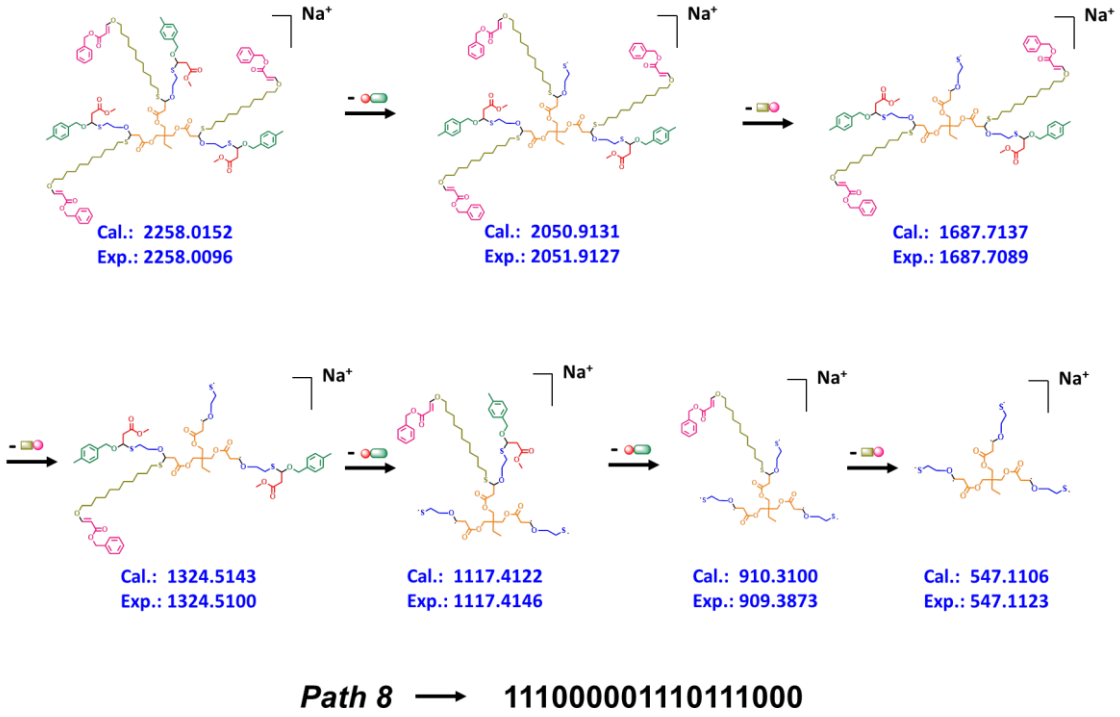


Figure S44. Fragmentation path 8 of **E3**.

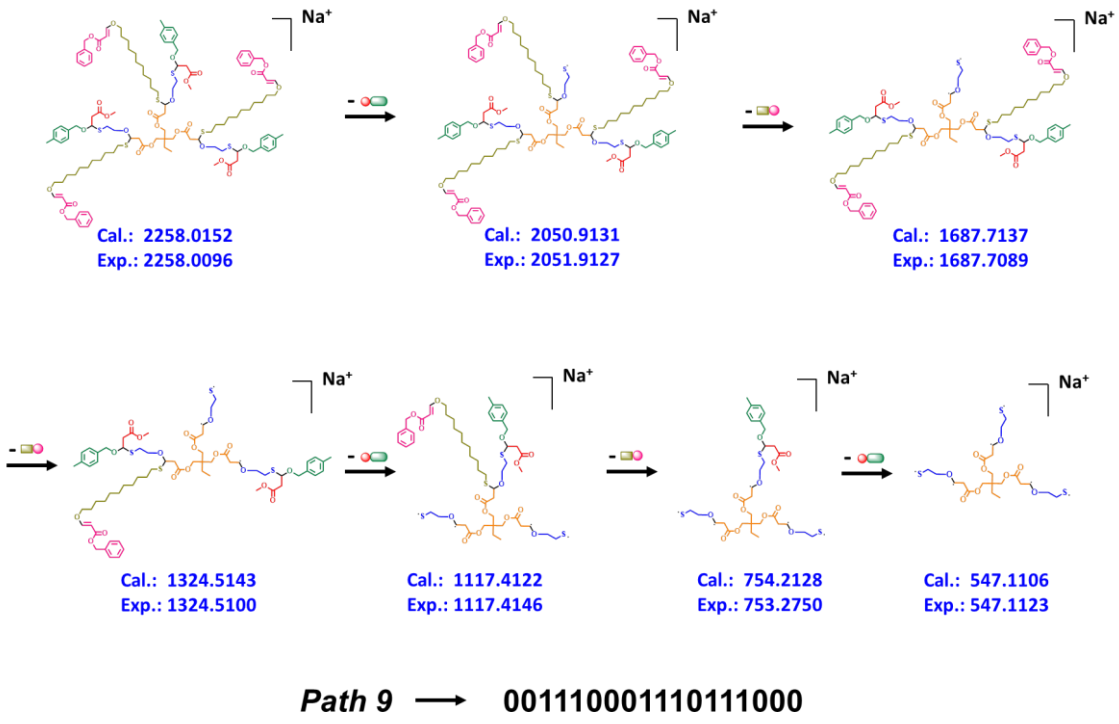


Figure S45. Fragmentation path 9 of **E3**.

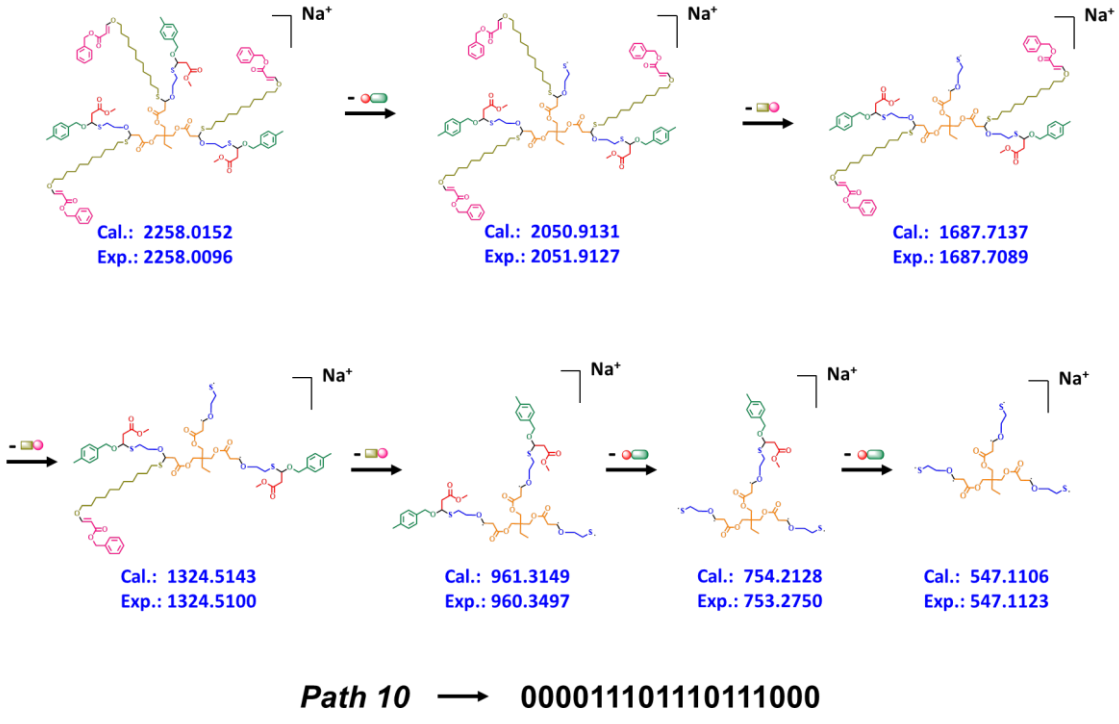


Figure S46. Fragmentation path 10 of **E3**.

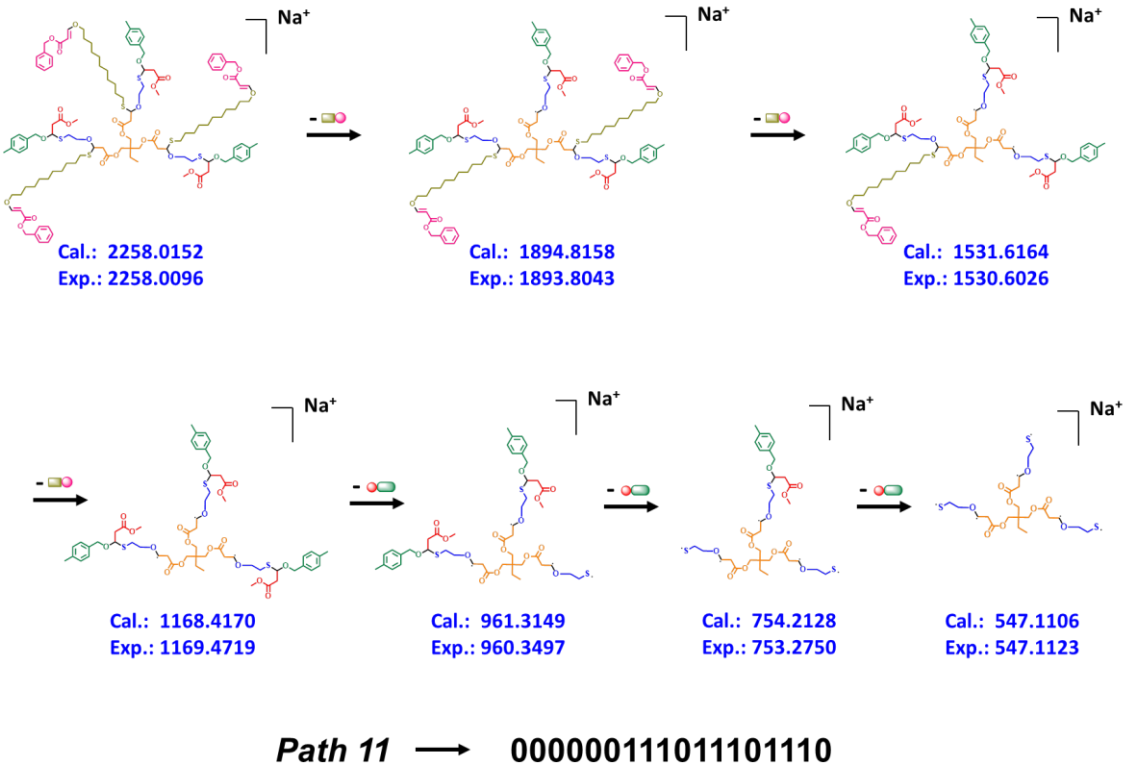


Figure S47. Fragmentation path 11 of **E3**.

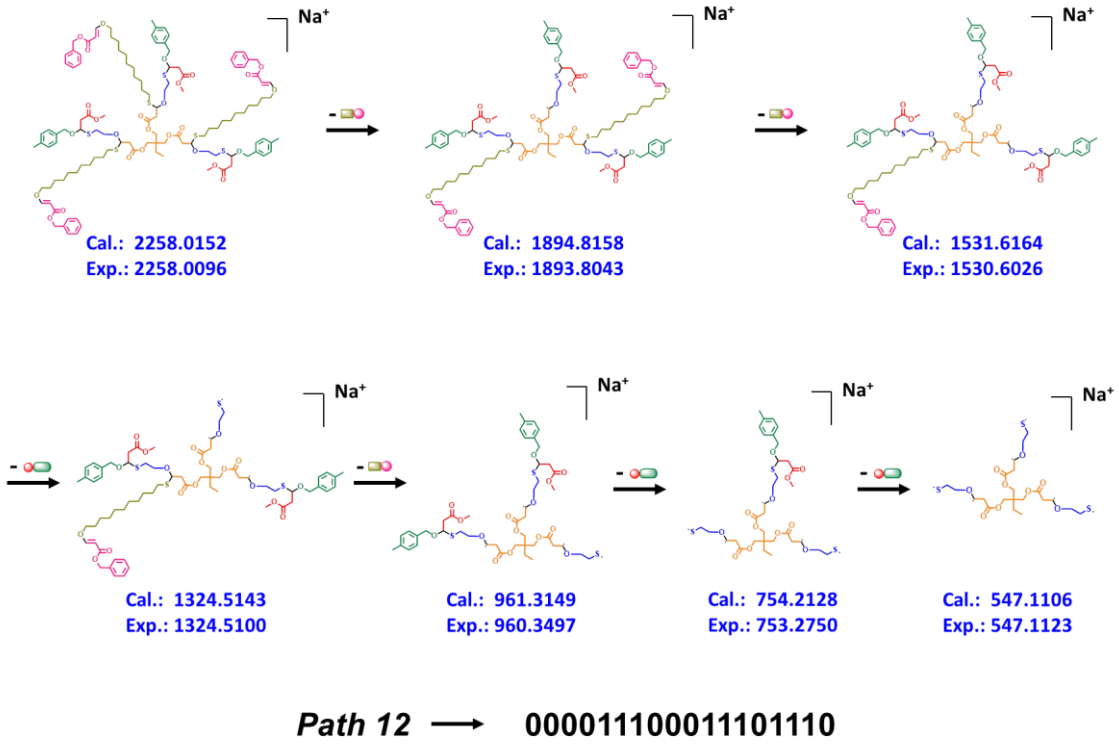


Figure S48. Fragmentation path 12 of **E3**.

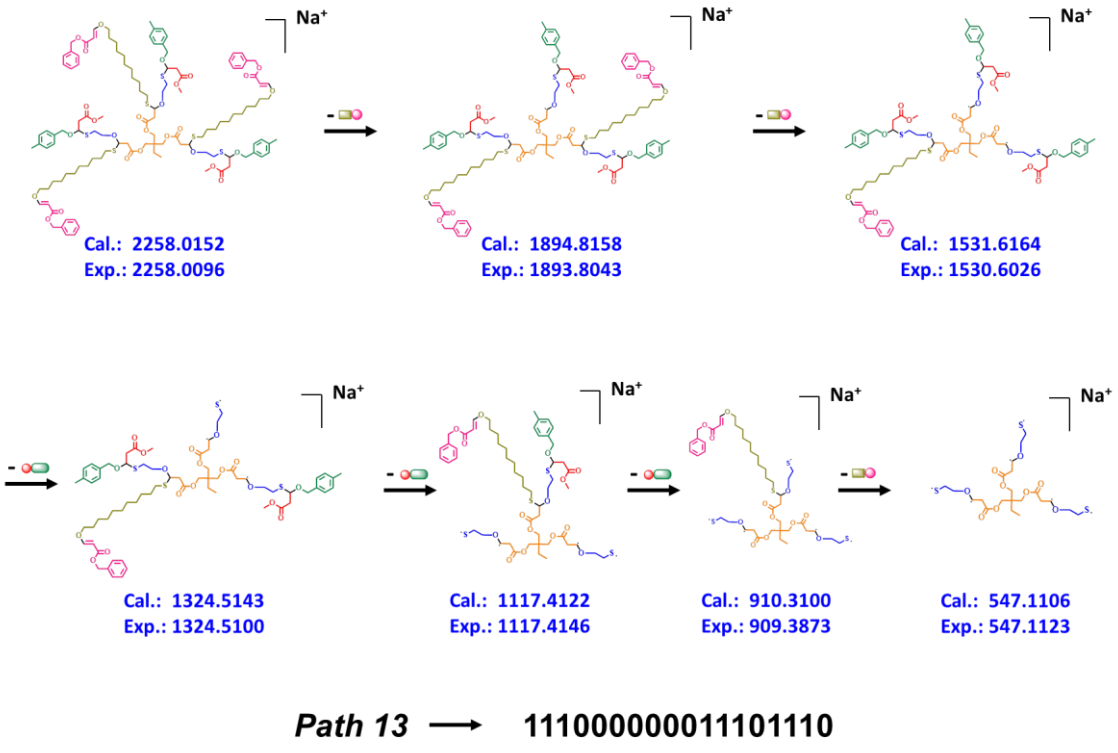


Figure S49. Fragmentation path 13 of **E3**.

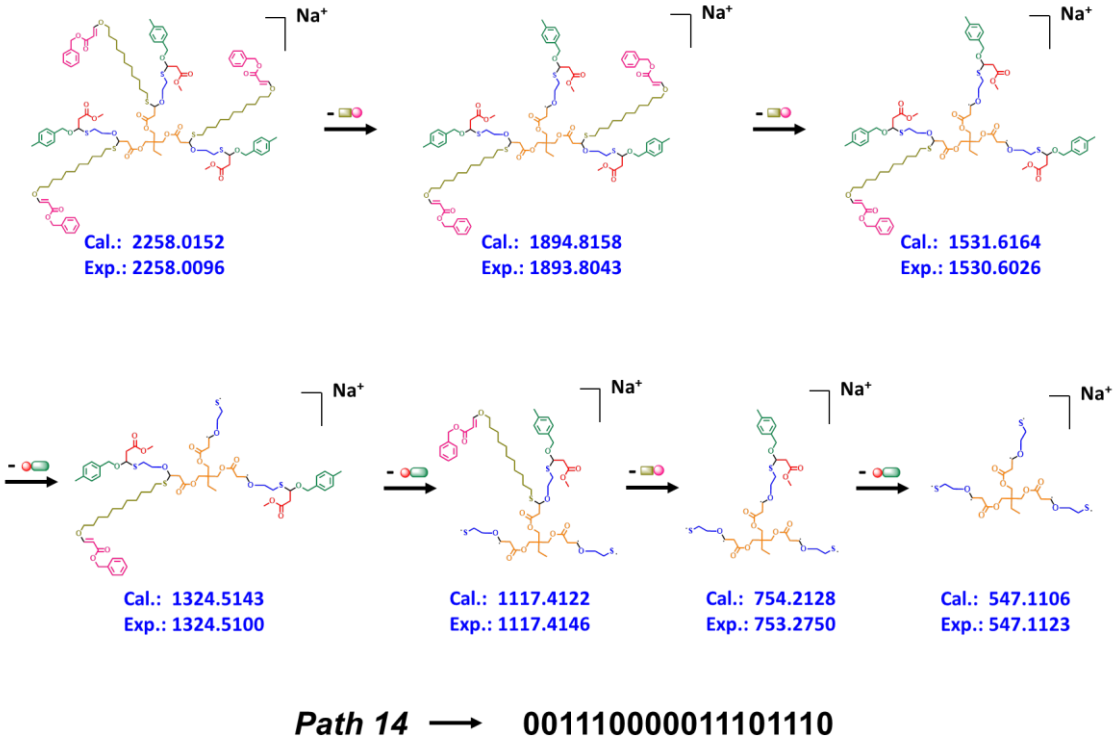


Figure S50. Fragmentation path 14 of **E3**.

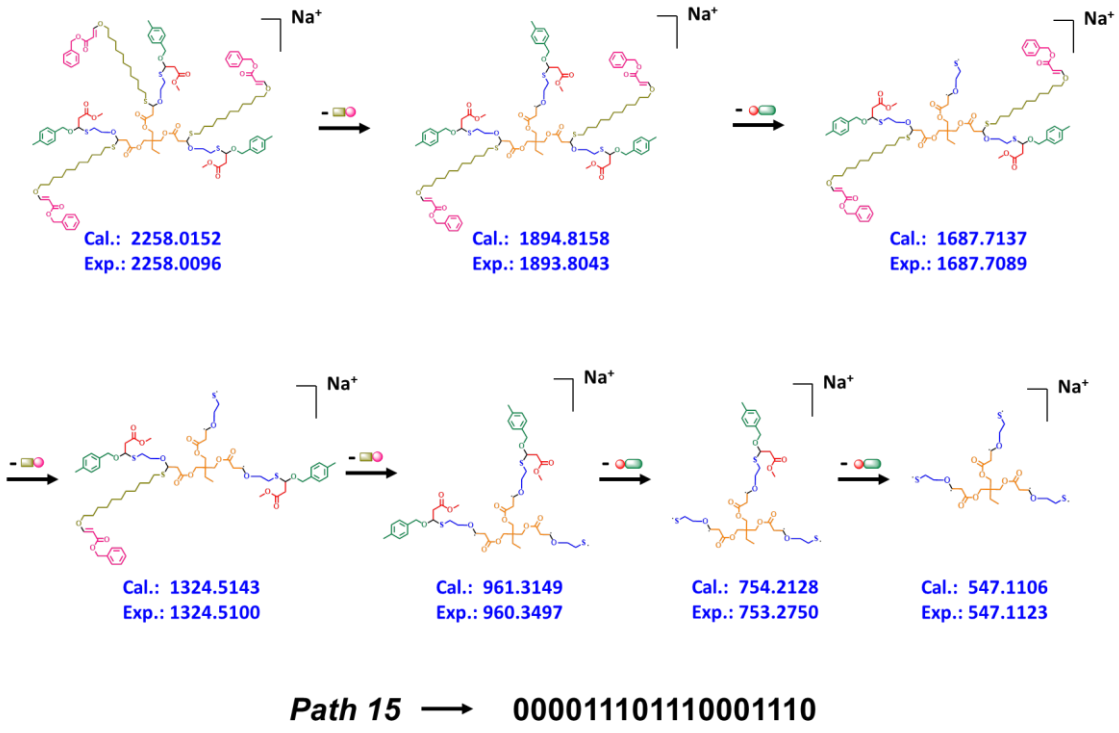


Figure S51. Fragmentation path 15 of **E3**.

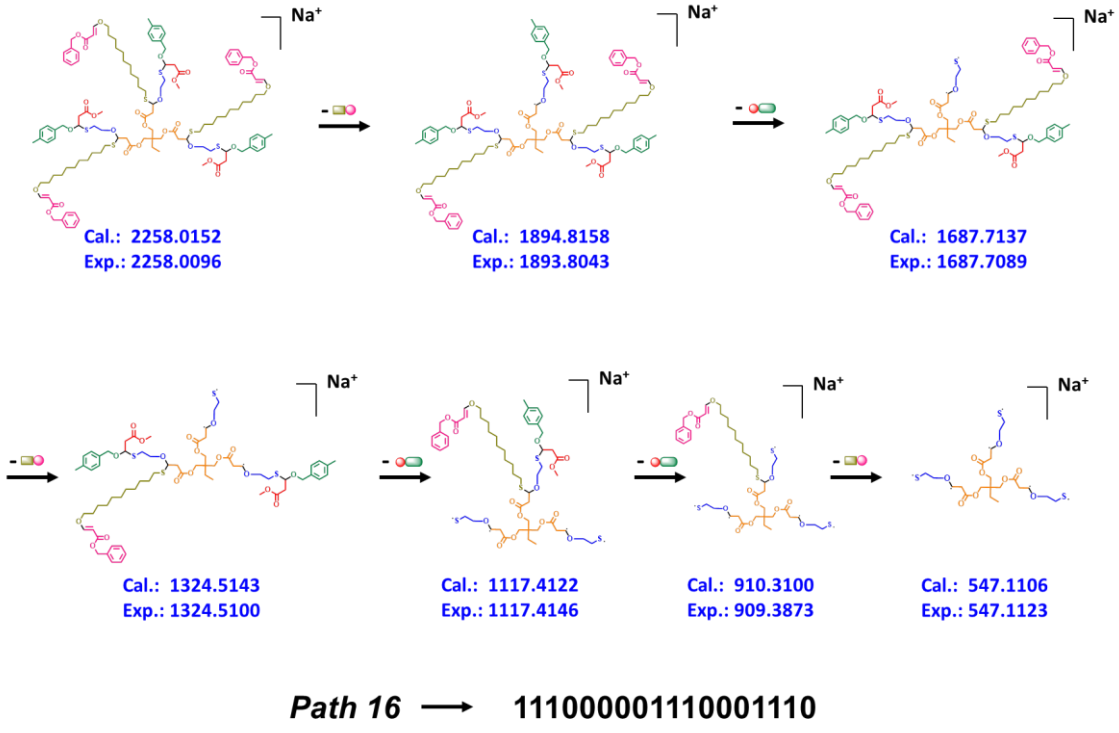


Figure S52. Fragmentation path 16 of **E3**.

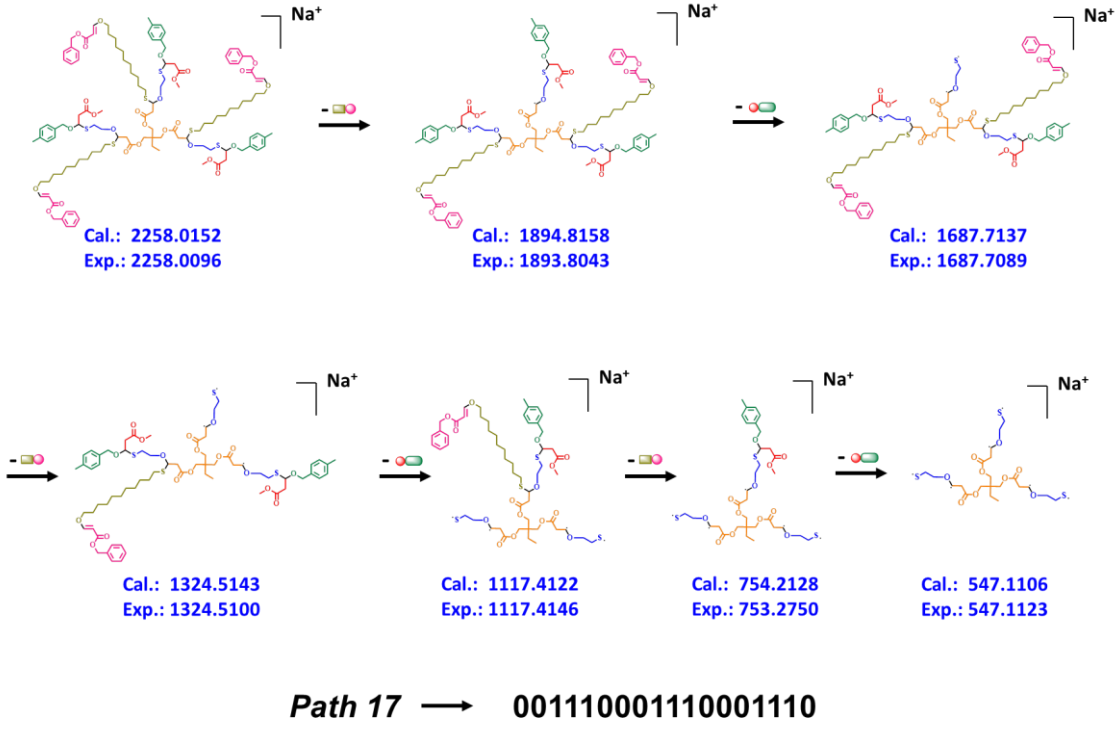


Figure S53. Fragmentation path 17 of **E3**.

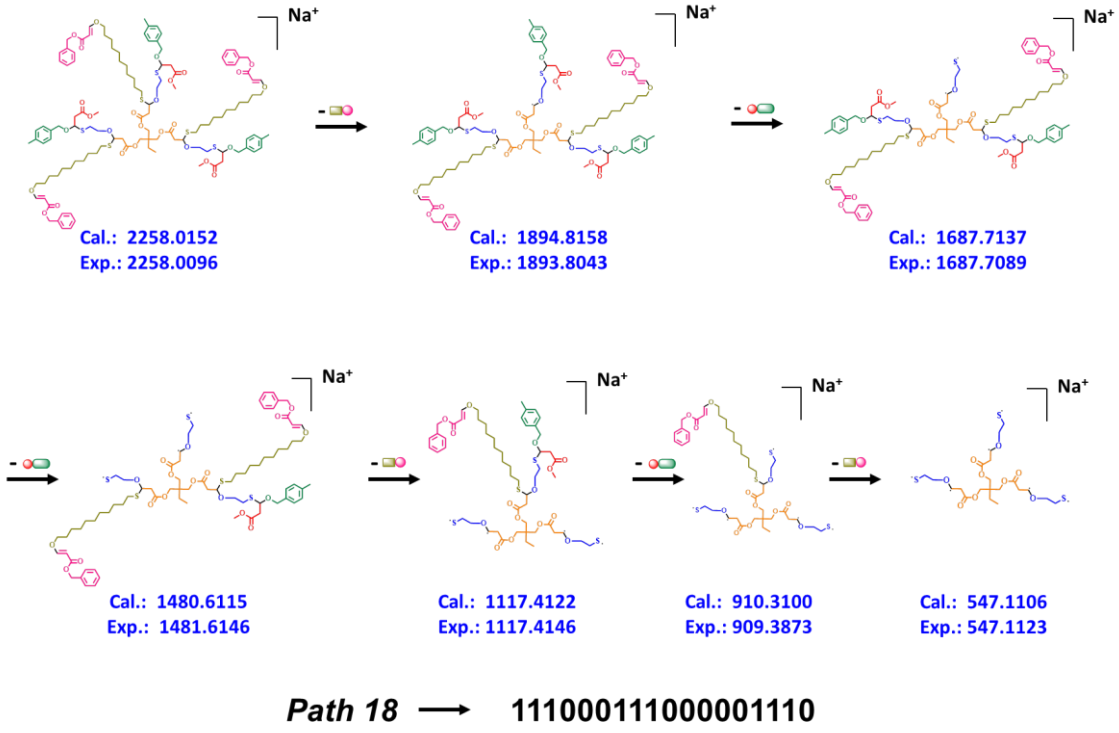


Figure S54. Fragmentation path 18 of **E3**.

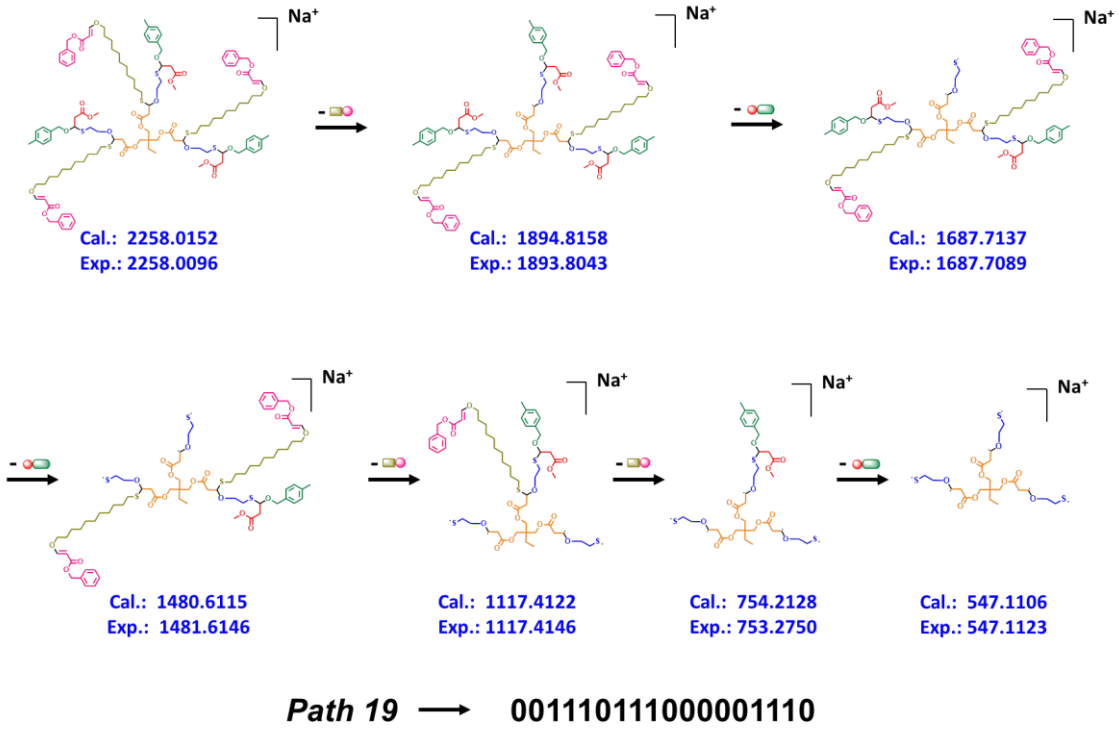


Figure S55. Fragmentation path 19 of **E3**.

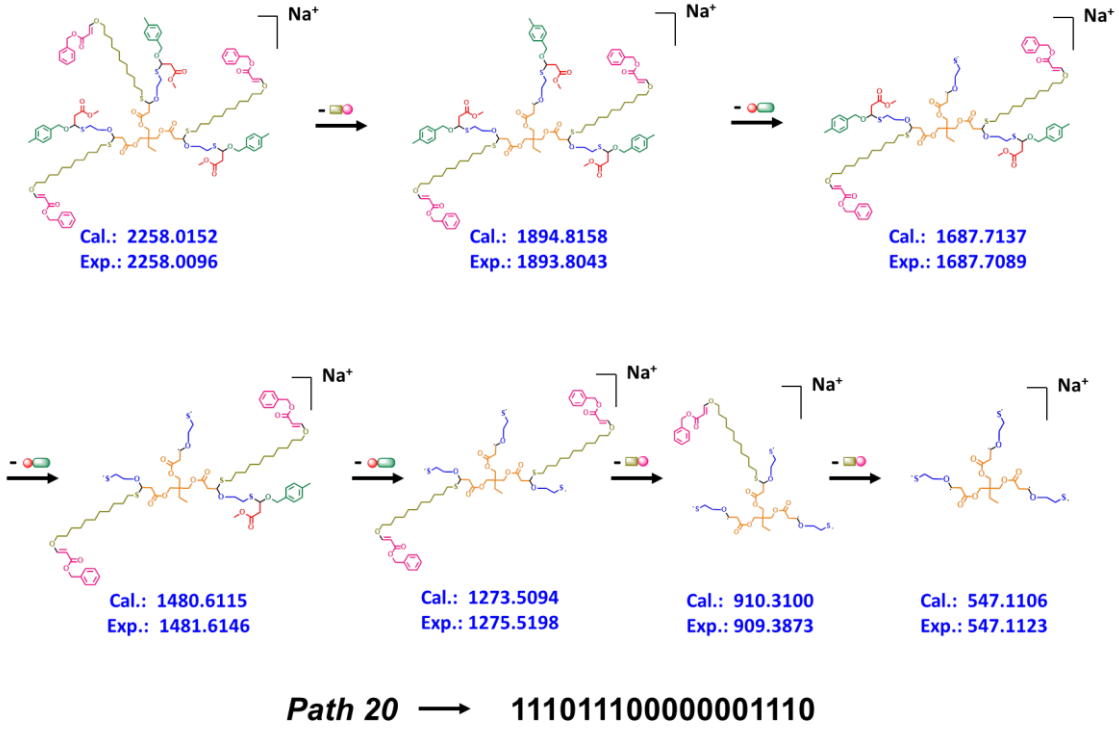


Figure S56. Fragmentation path 20 of **E3**.

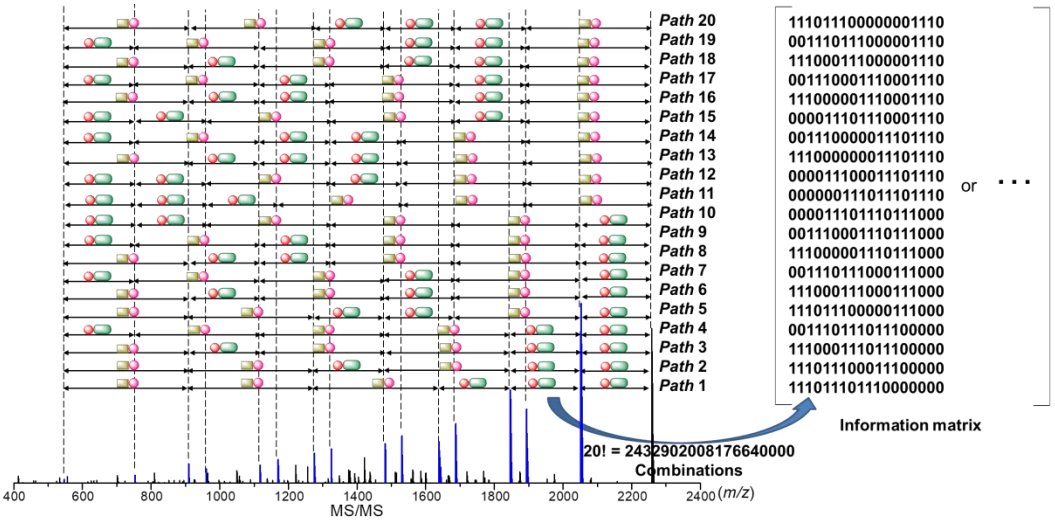


Figure S57. Translation from MS/MS fragmentation paths of **E3** to information matrix.

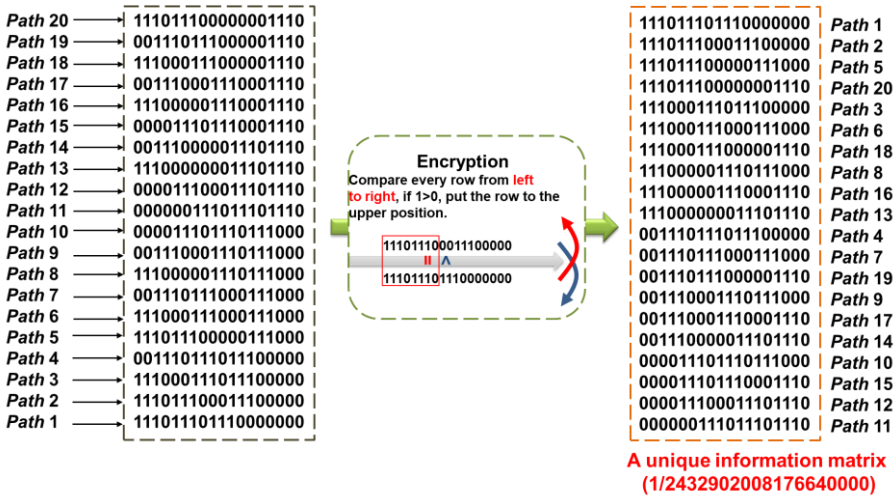


Figure S58. A second encryption with the rule of "comparing every row from left to right, if 1 > 0, put the row to the upper position".

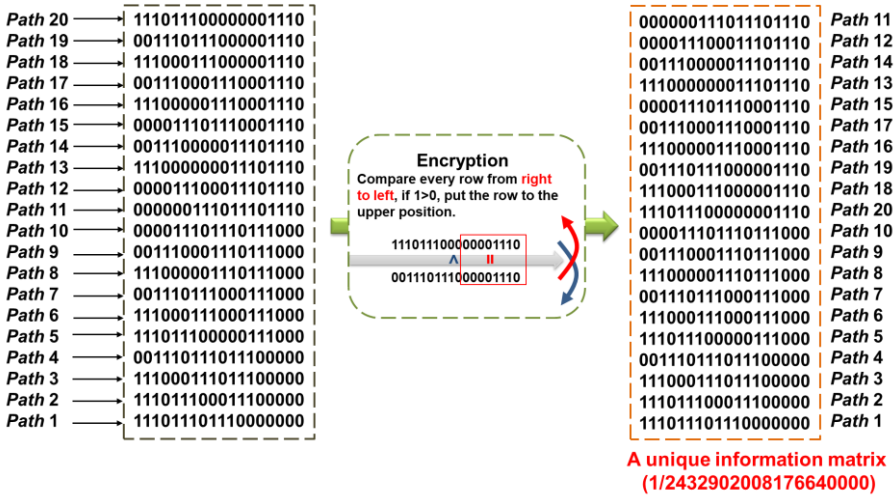


Figure S59. A second encryption with the rule of "comparing every row from right to left, if 1>0, put the row to the upper position".

References

[1] Li, H.; Wang, J.; Sun, J. Z.; Hu, R.; Qin, A.; Tang, B. Z. Metal-Free Click Polymerization of Propiolates and Azides: Facile Synthesis of Functional Poly(aroxycarbonyltriazole) s. *Polym. Chem.* **2012**, *3*, 1075-1083.

Additional Data

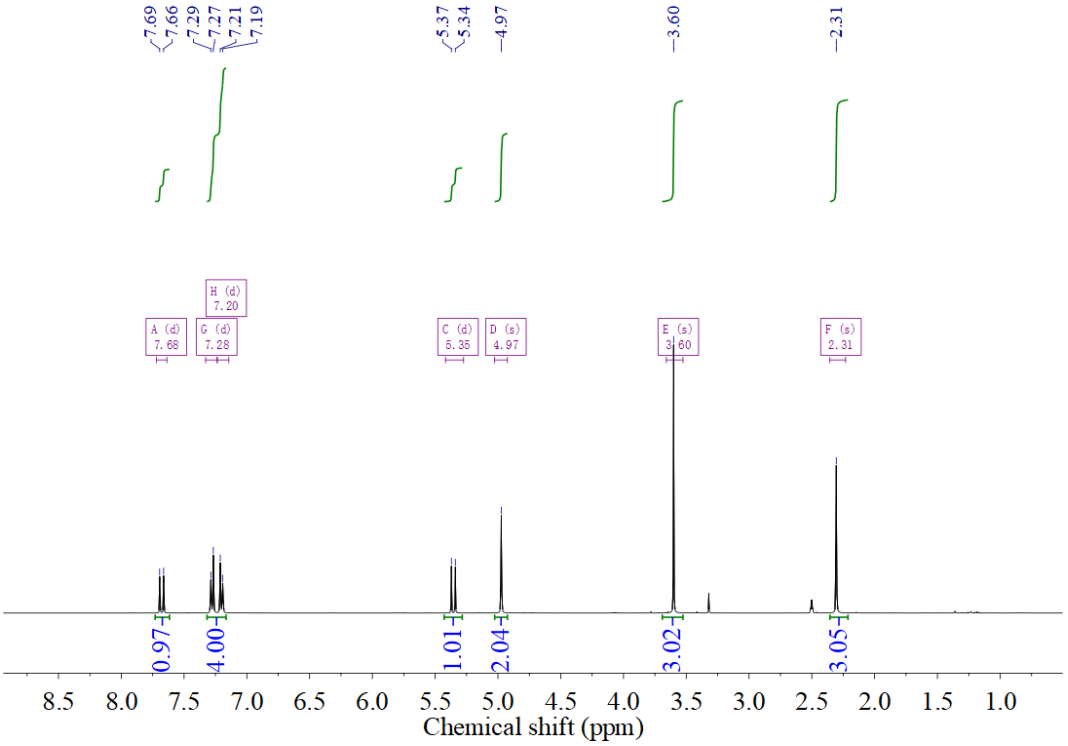


Figure S60. ^{1}H NMR spectrum of **A1** in DMSO-d_6.

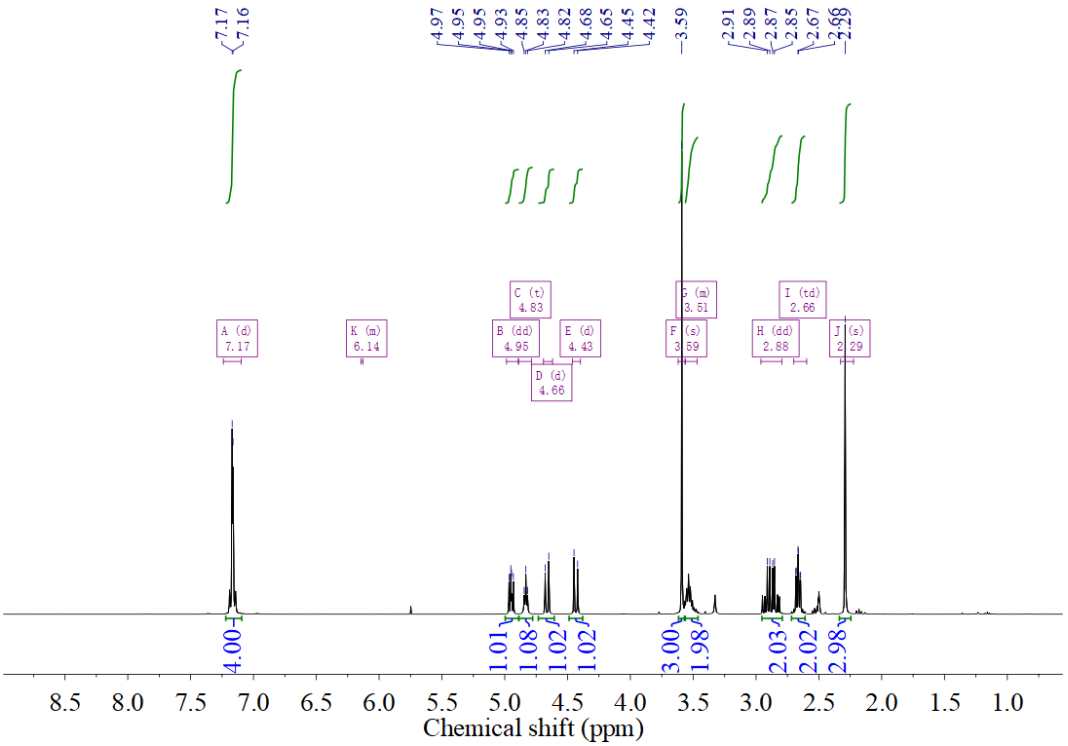


Figure S61. ^{1}H NMR spectrum of **A2** in DMSO-d_6.

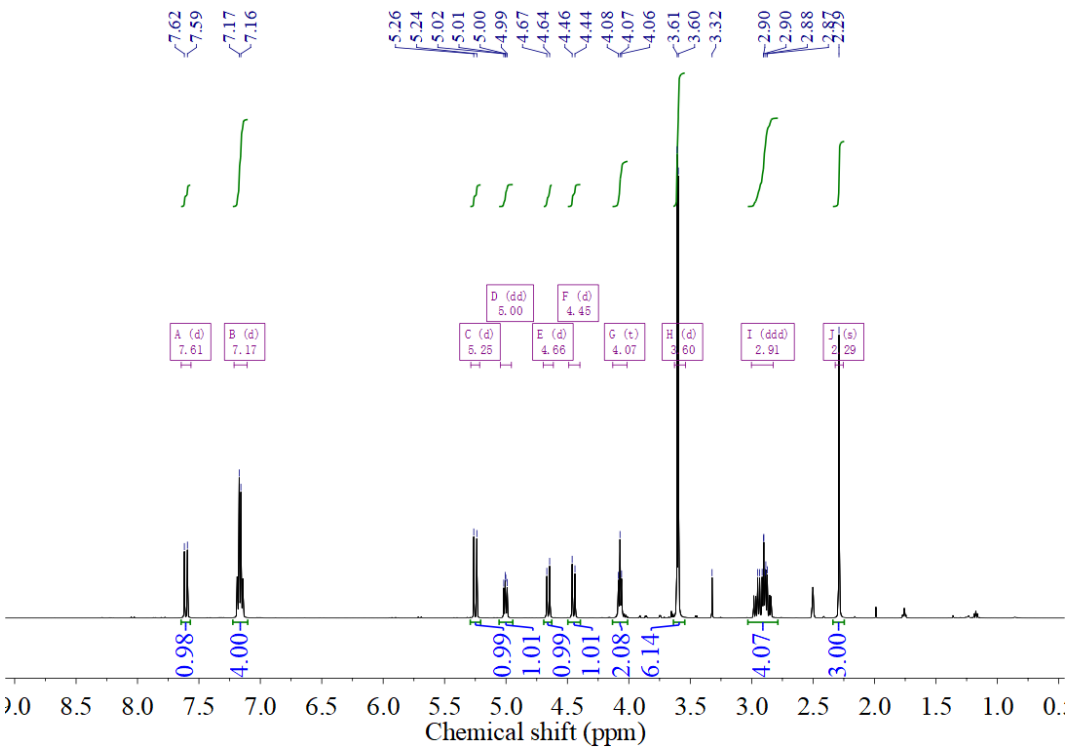


Figure S62. ^{1}H NMR spectrum of **A3** in DMSO-d_6.

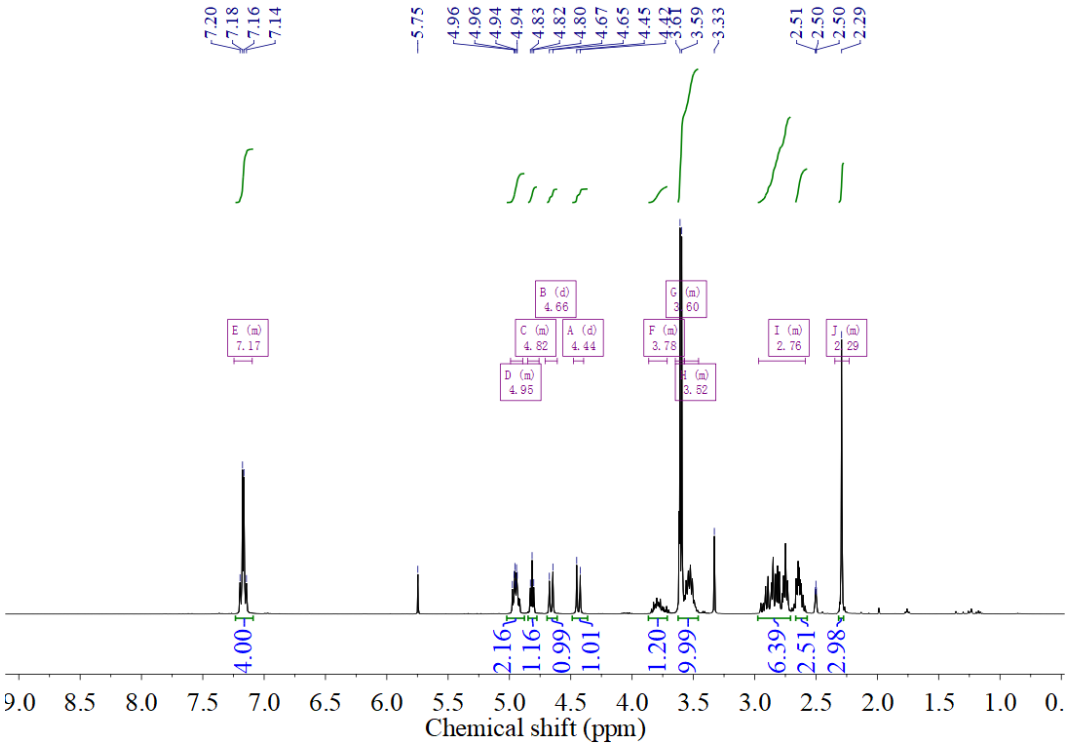


Figure S63. ^{1}H NMR spectrum of **A4** in DMSO-d_6.

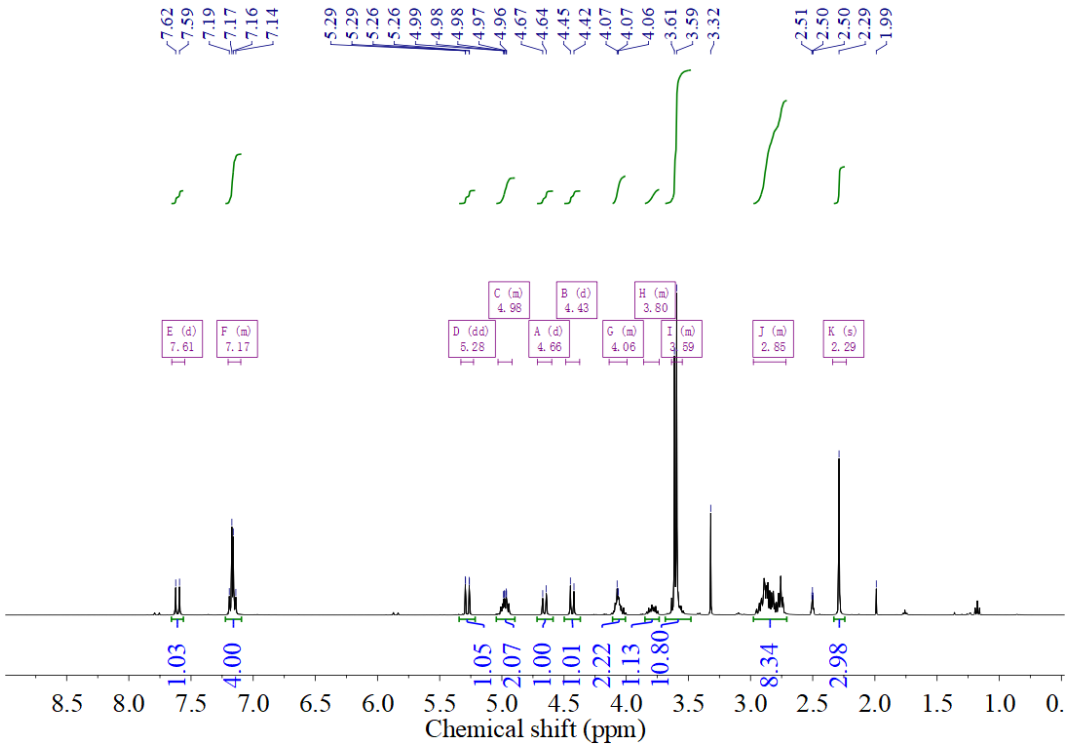


Figure S64. ^{1}H NMR spectrum of **A5** in DMSO-d_6.

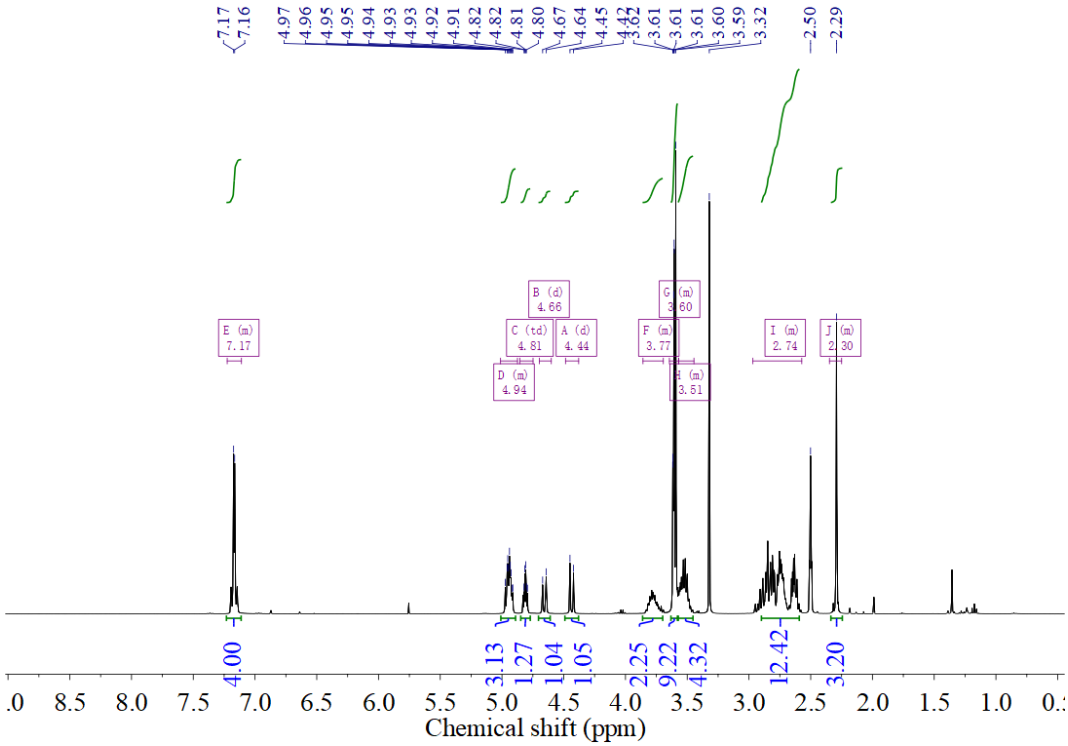


Figure S65. ^{1}H NMR spectrum of **A6** in DMSO-d_6.

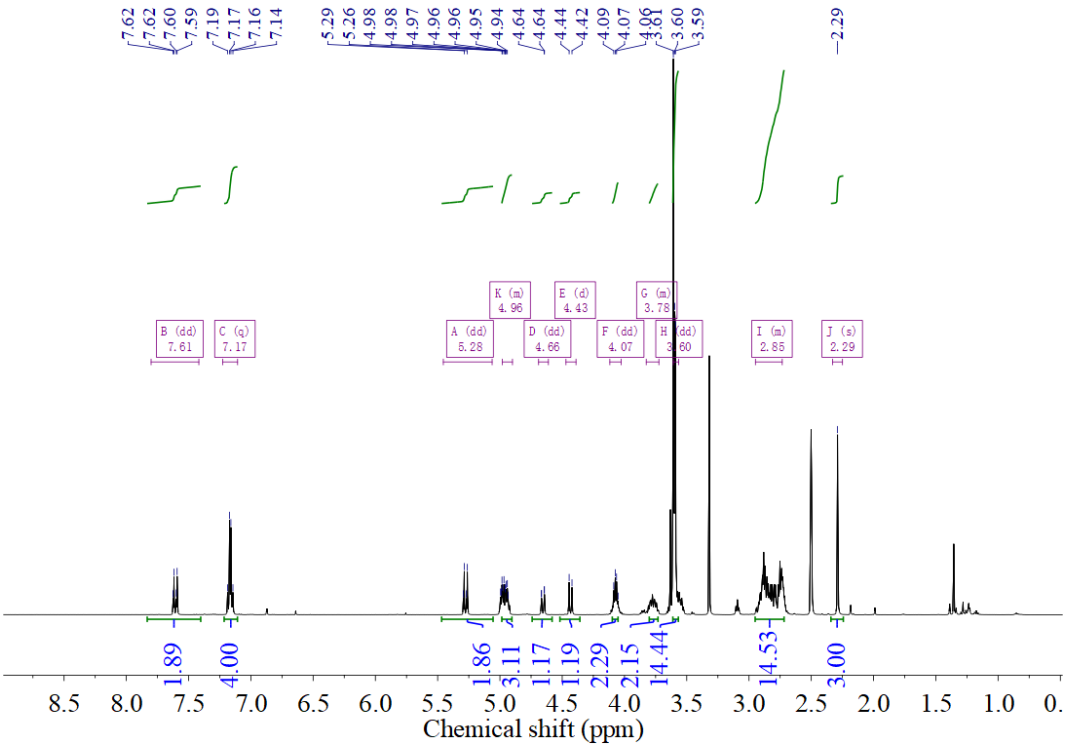


Figure S66. ^{1}H NMR spectrum of **A7** in DMSO-d_6.

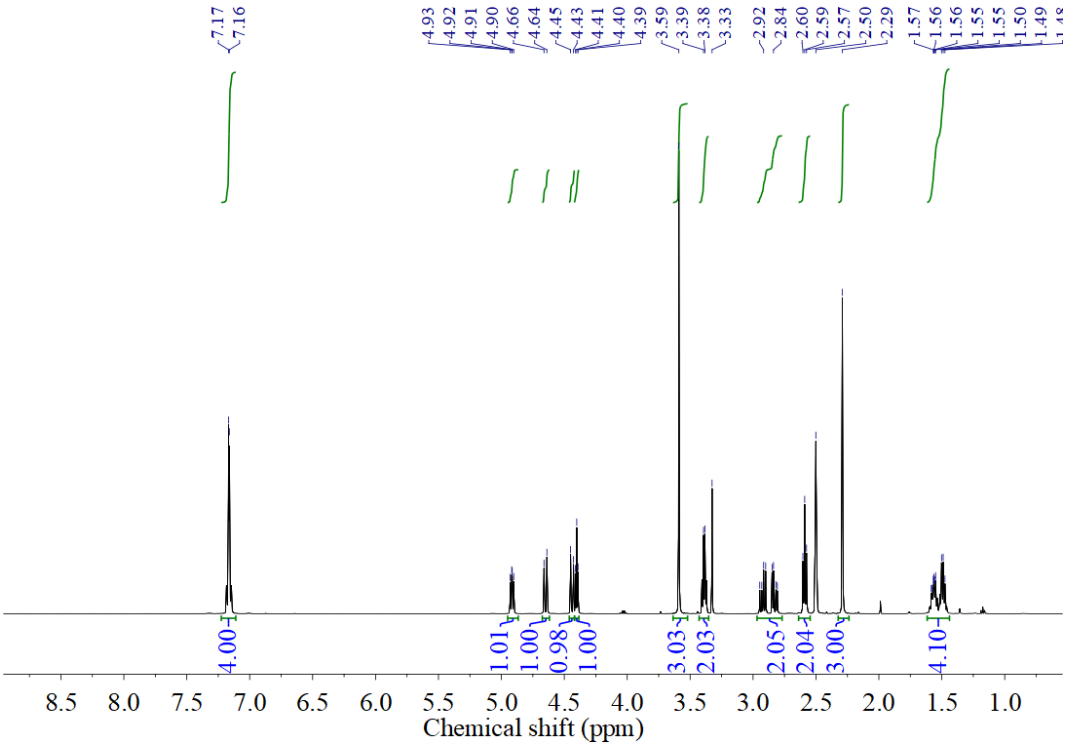


Figure S67. ^{1}H NMR spectrum of **B2** in DMSO-d_6.

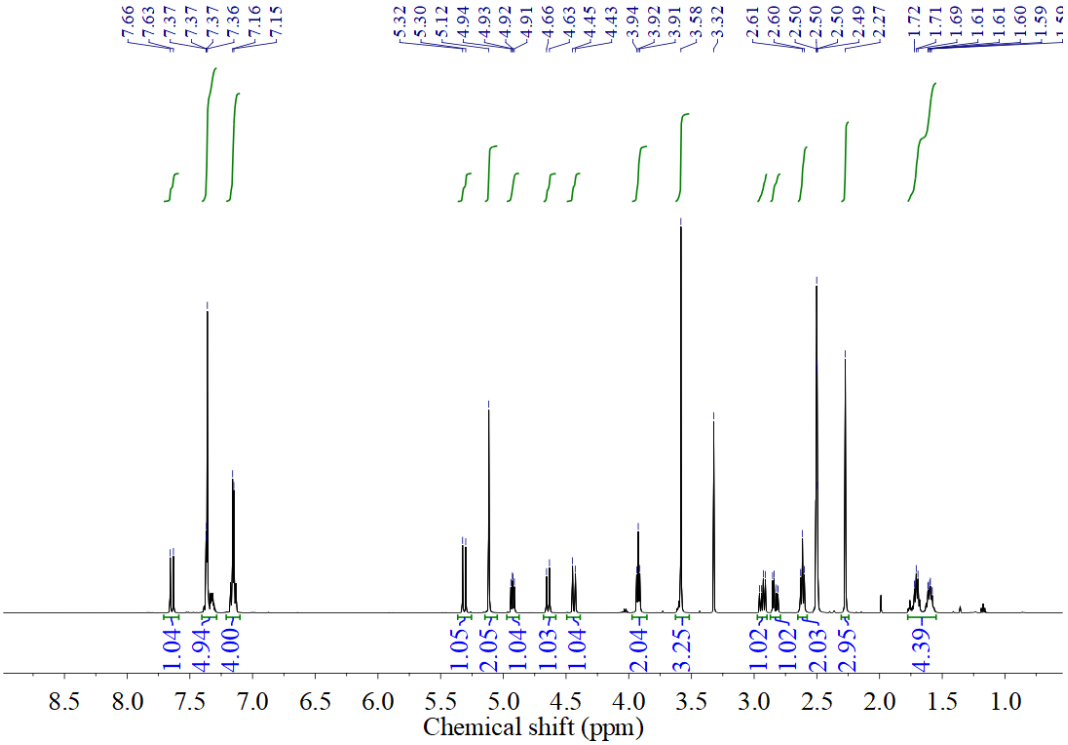


Figure S68. ^{1}H NMR spectrum of **B3** in DMSO-d_6.

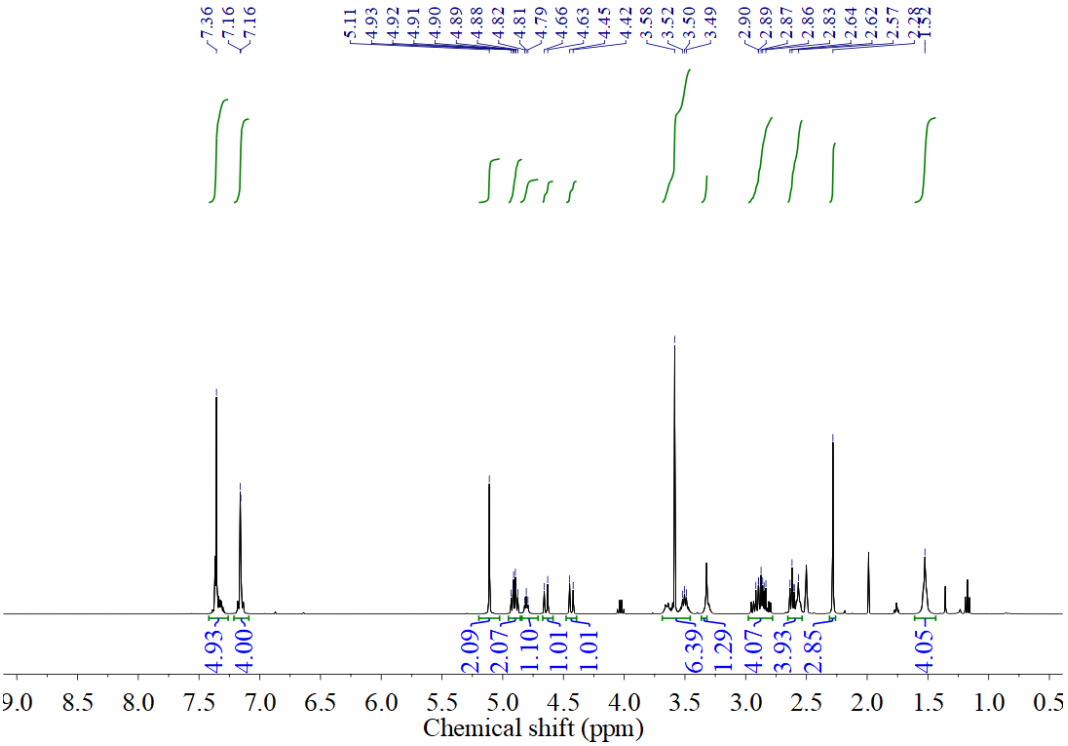


Figure S69. ^{1}H NMR spectrum of **B4** in DMSO-d_6.

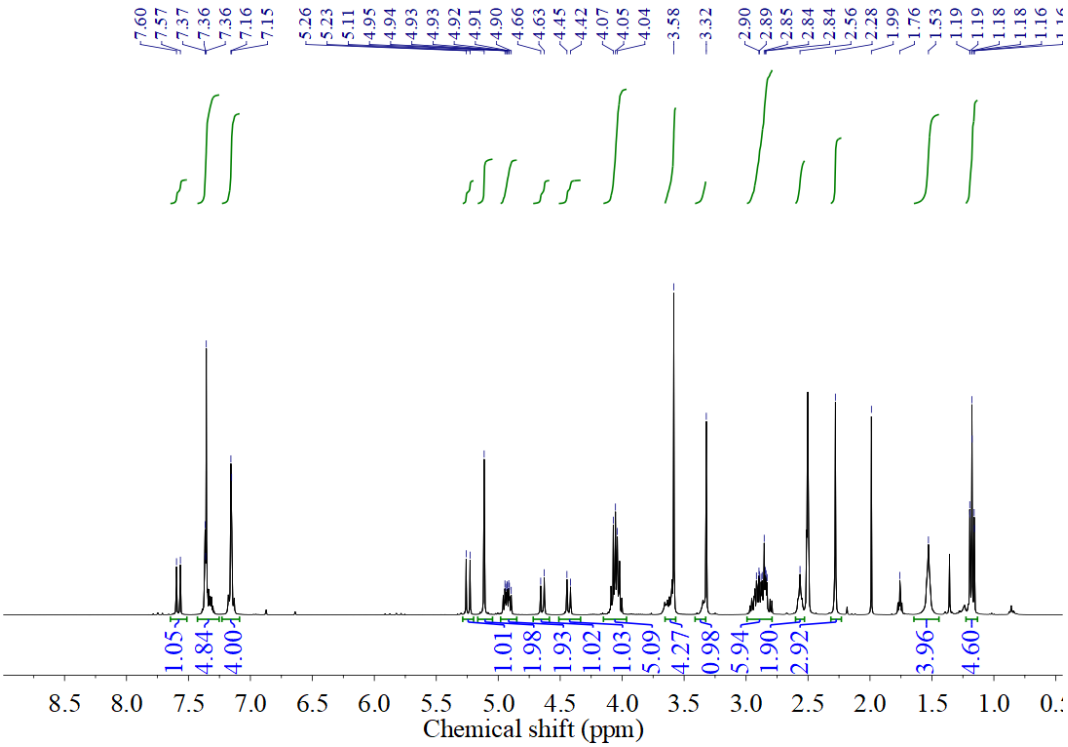


Figure S70. ^{1}H NMR spectrum of **B5** in DMSO-d_6.

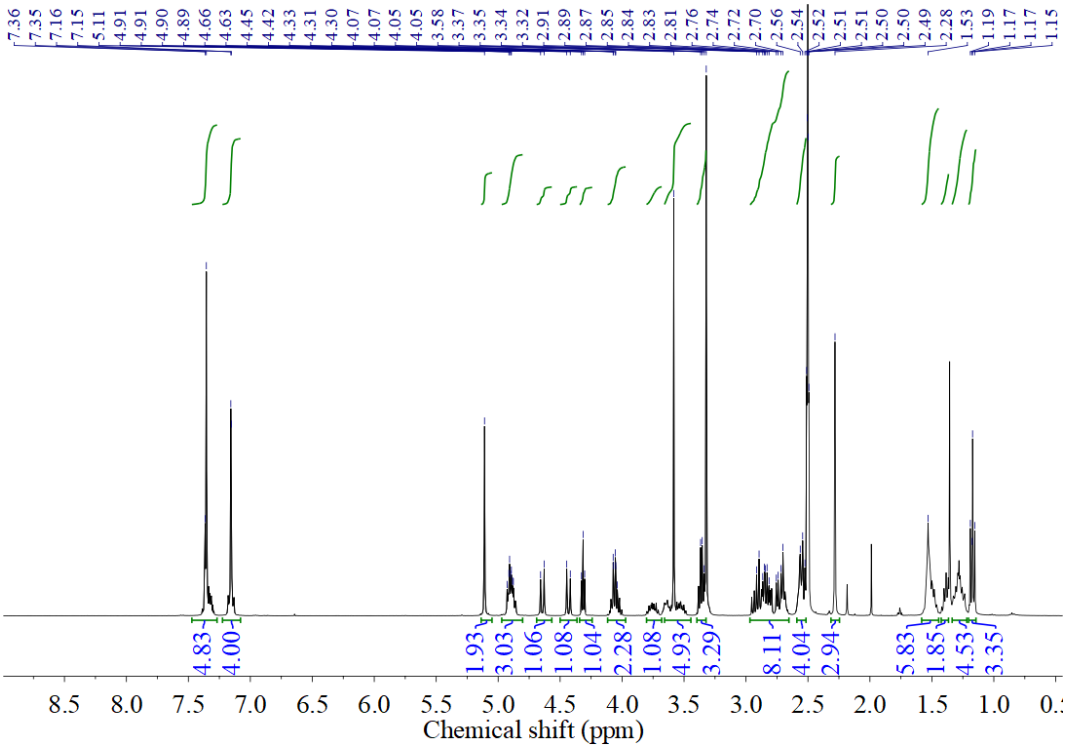


Figure S71. ^{1}H NMR spectrum of **B6** in DMSO-d_6.

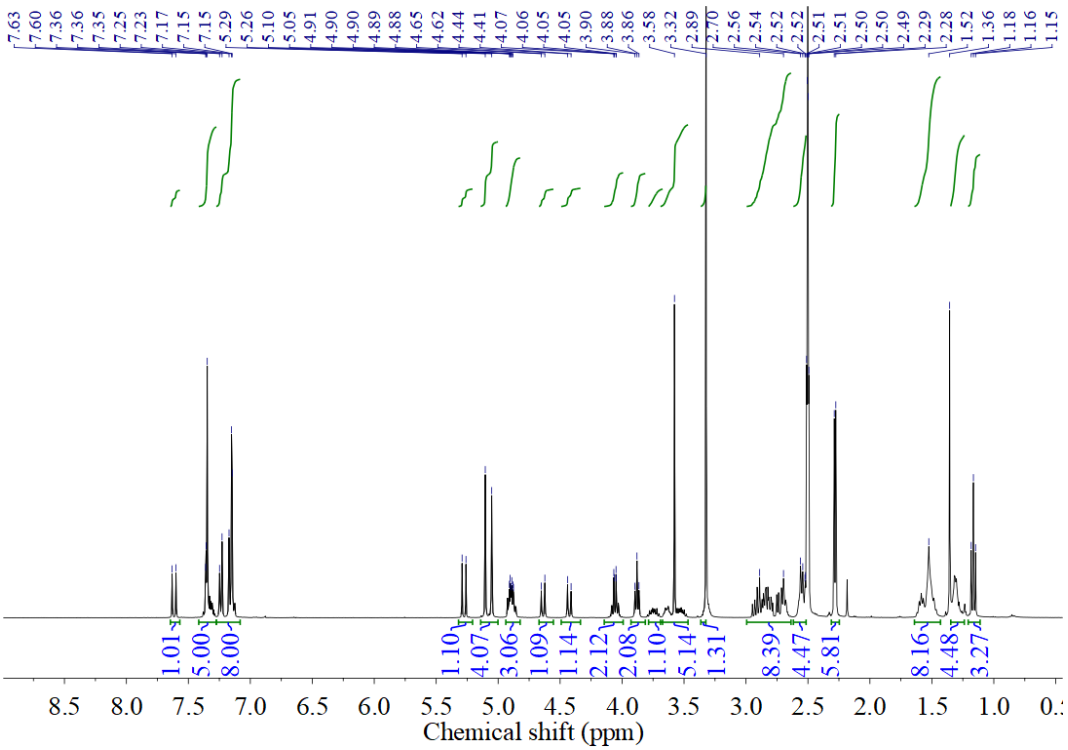


Figure S72. ^{1}H NMR spectrum of **B7** in DMSO-d_6.

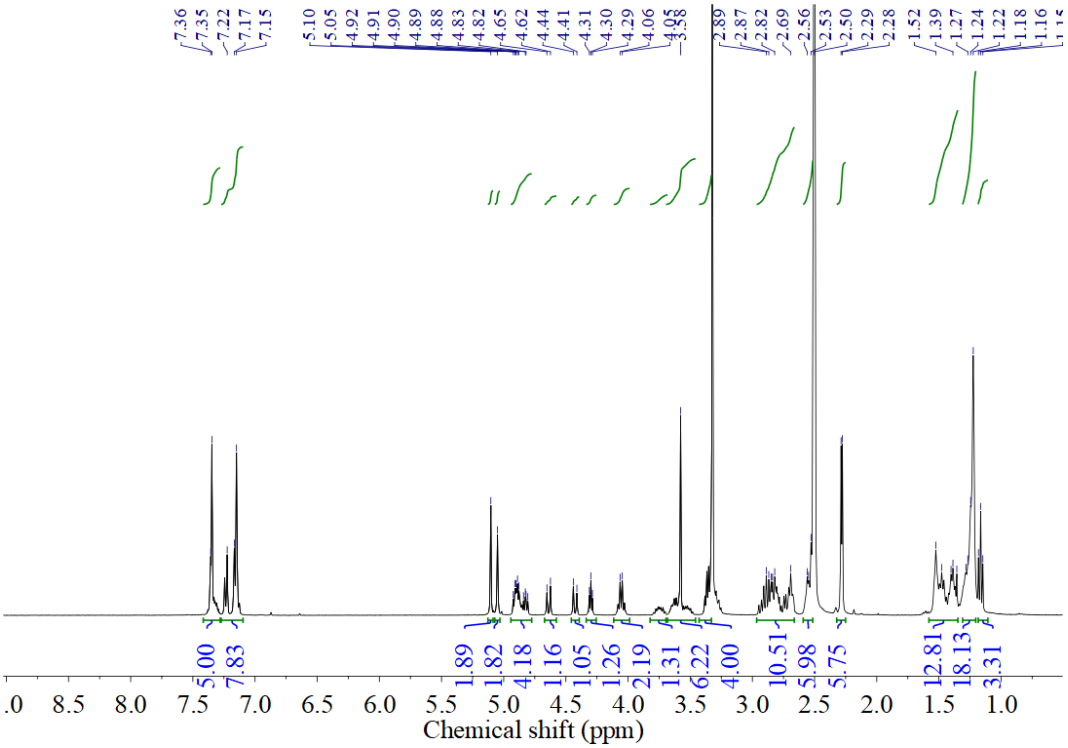


Figure S73. ^{1}H NMR spectrum of **B8** in DMSO-d_6.

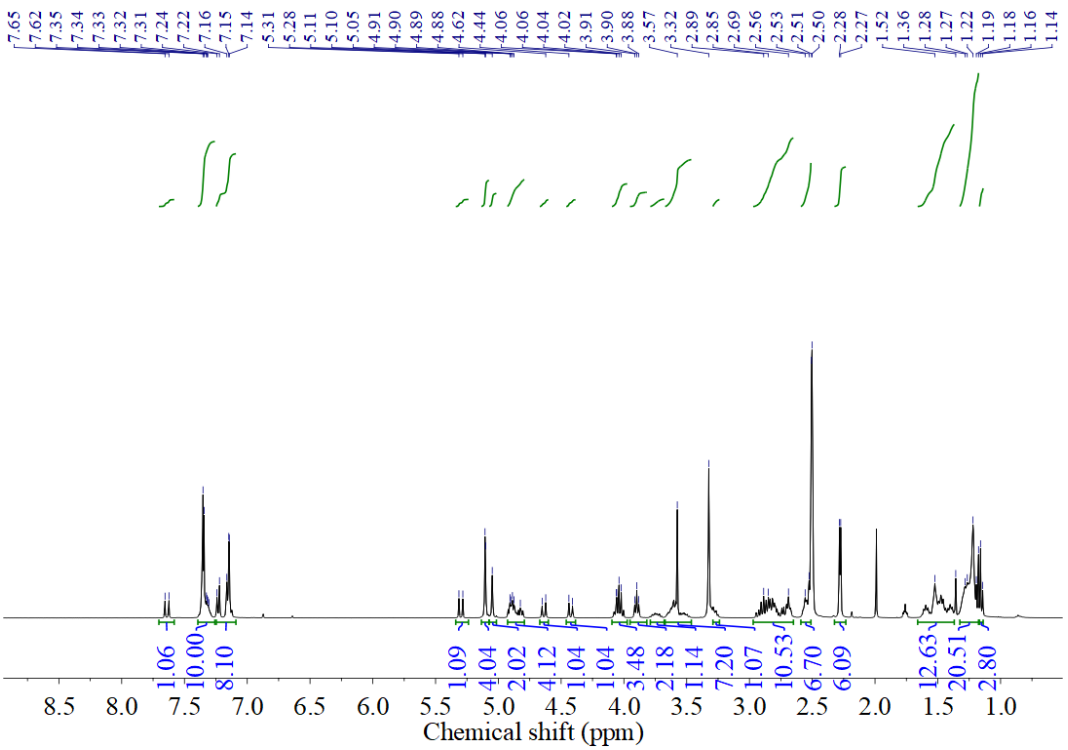


Figure S74. ^{1}H NMR spectrum of **B9** in DMSO-d_6.

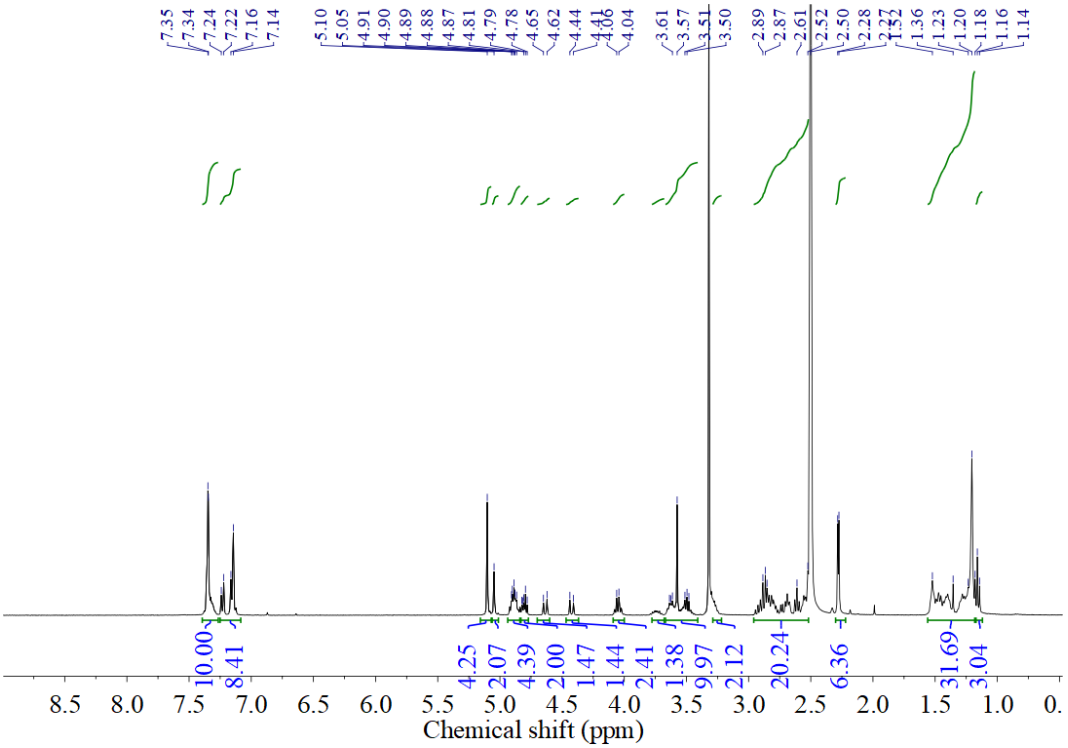


Figure S75. ^{1}H NMR spectrum of **B10** in DMSO-d_6.

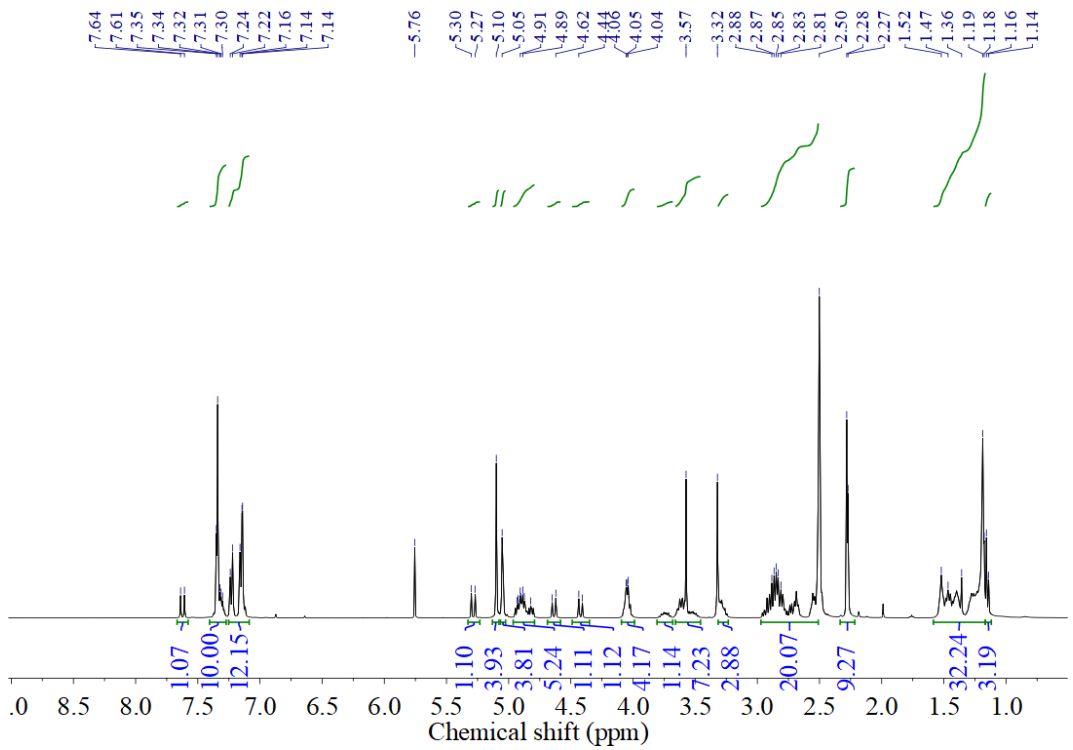


Figure S76. ^{1}H NMR spectrum of **B11** in DMSO-d_6.

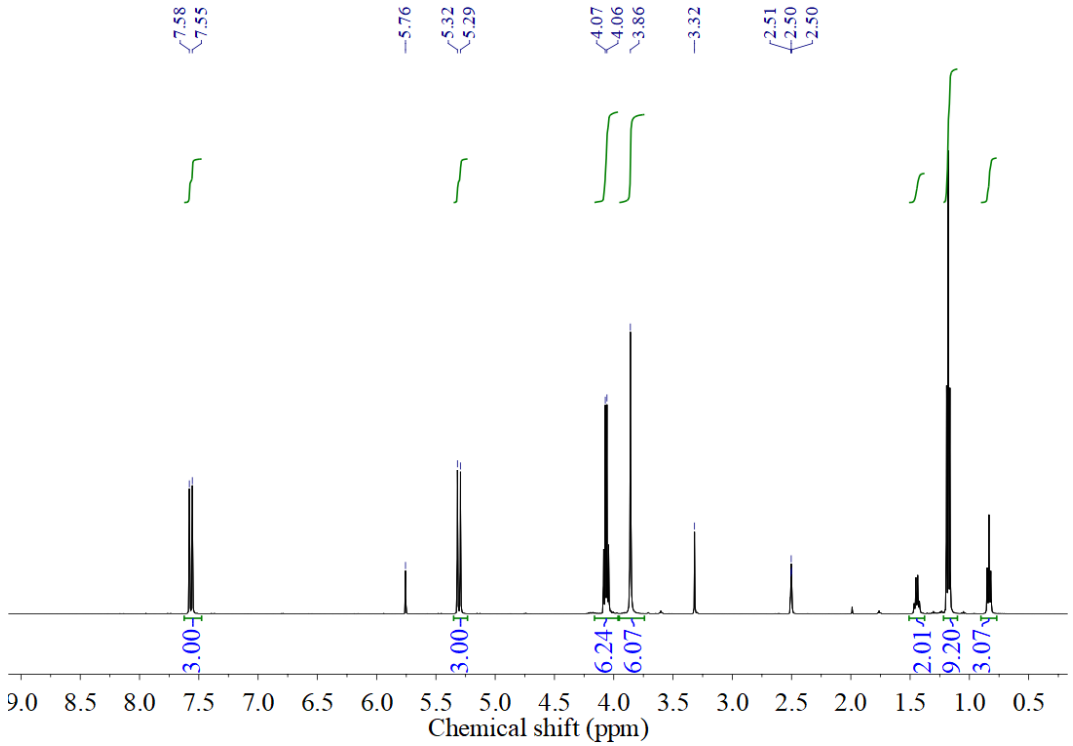


Figure S77. ^{1}H NMR spectrum of **C1** in DMSO-d_6.

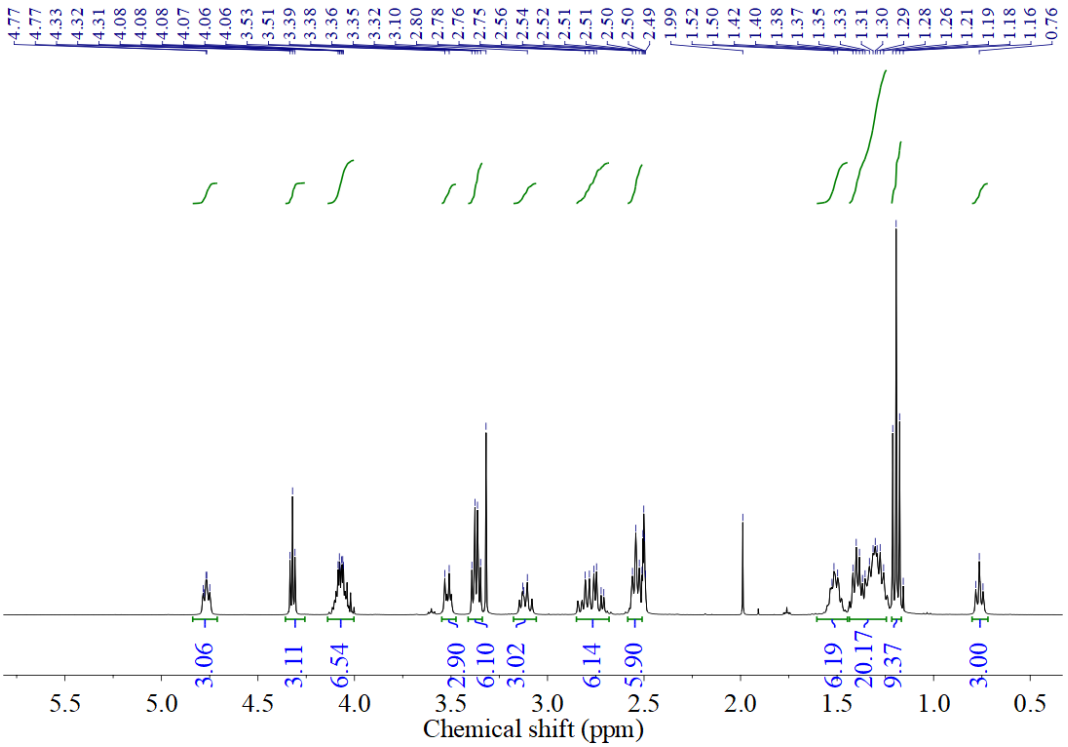


Figure S78. ^{1}H NMR spectrum of **C2** in DMSO-d_6.

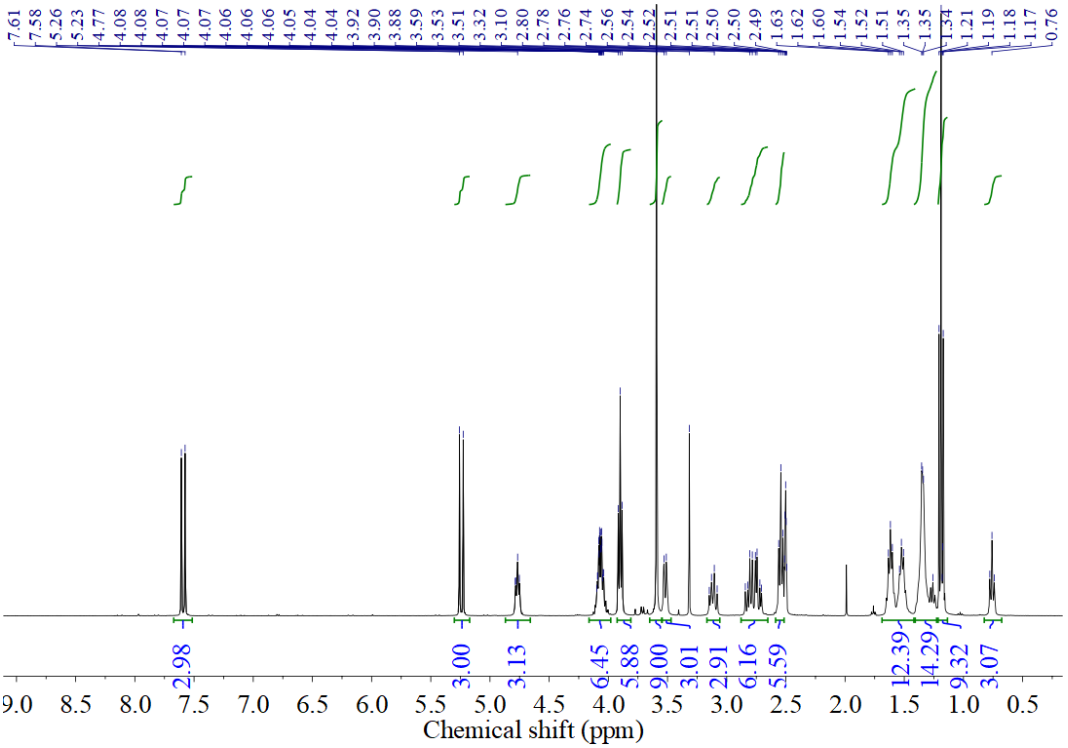


Figure S79. ^{1}H NMR spectrum of **C3** in DMSO-d_6.

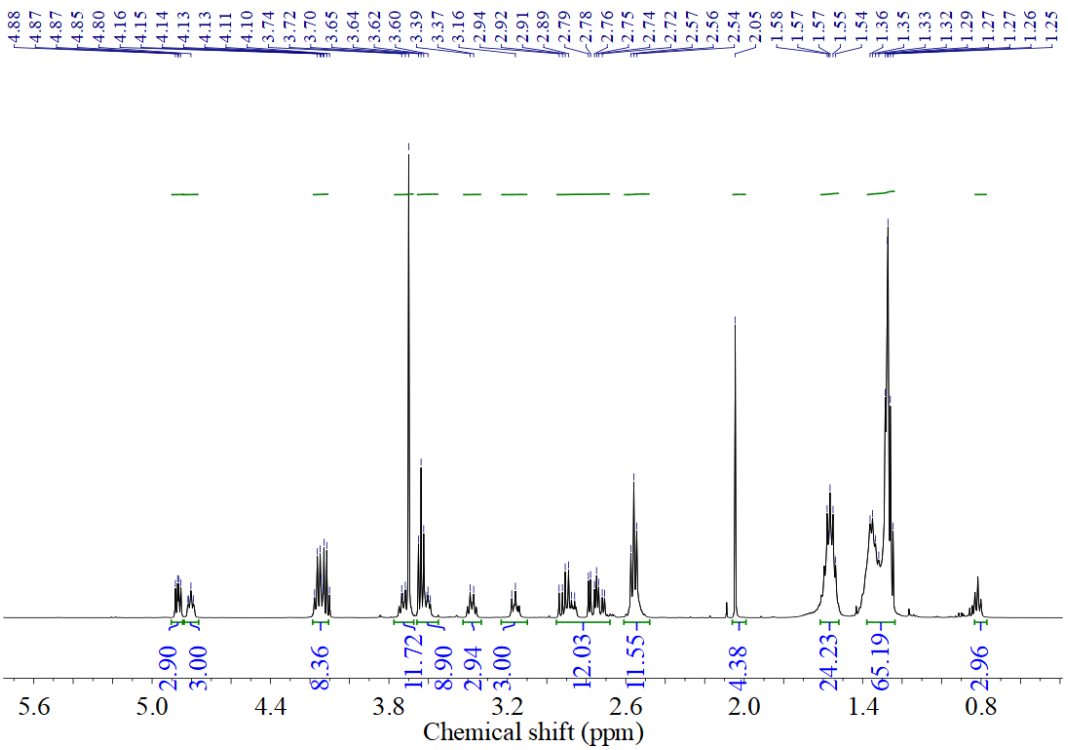


Figure S80. ^{1}H NMR spectrum of **C4** in DMSO-d_6.

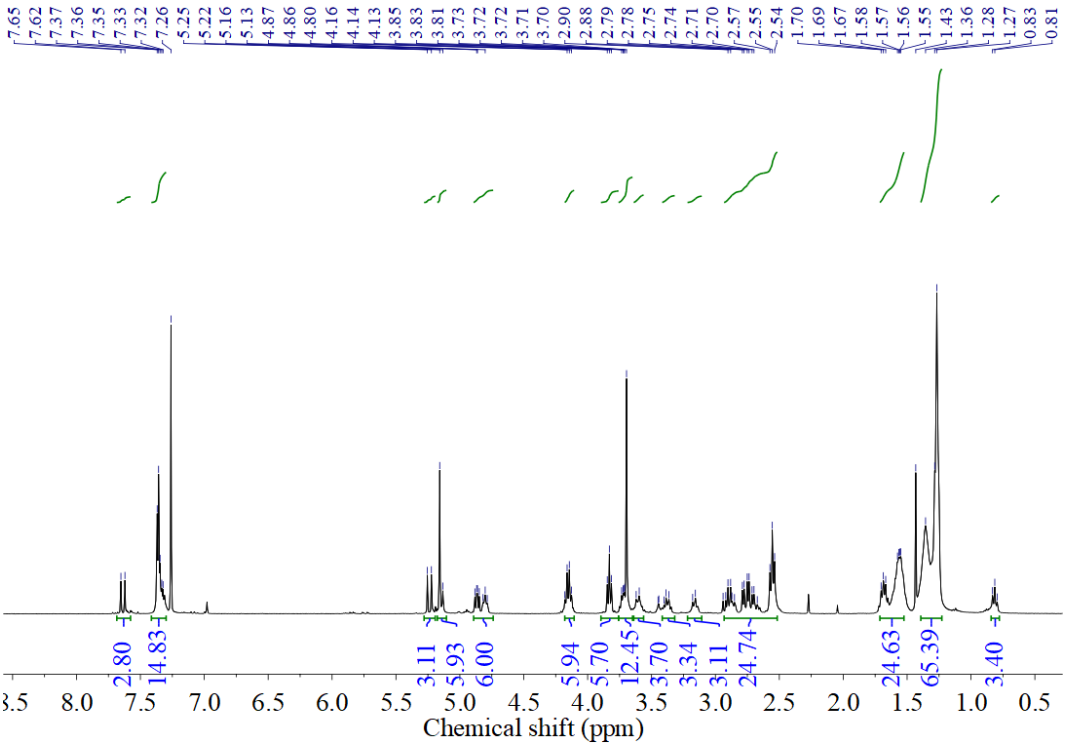


Figure S81. ^{1}H NMR spectrum of **C5** in DMSO-d_6.

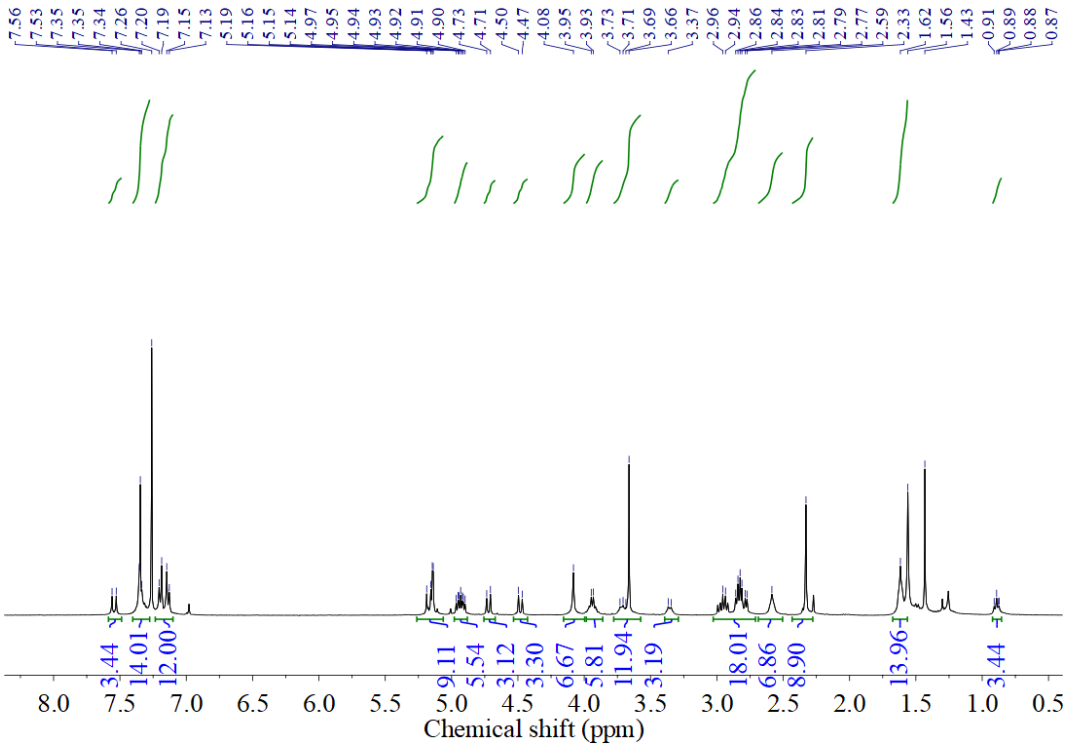


Figure S82. ^{1}H NMR spectrum of **D1** in DMSO-d_6.

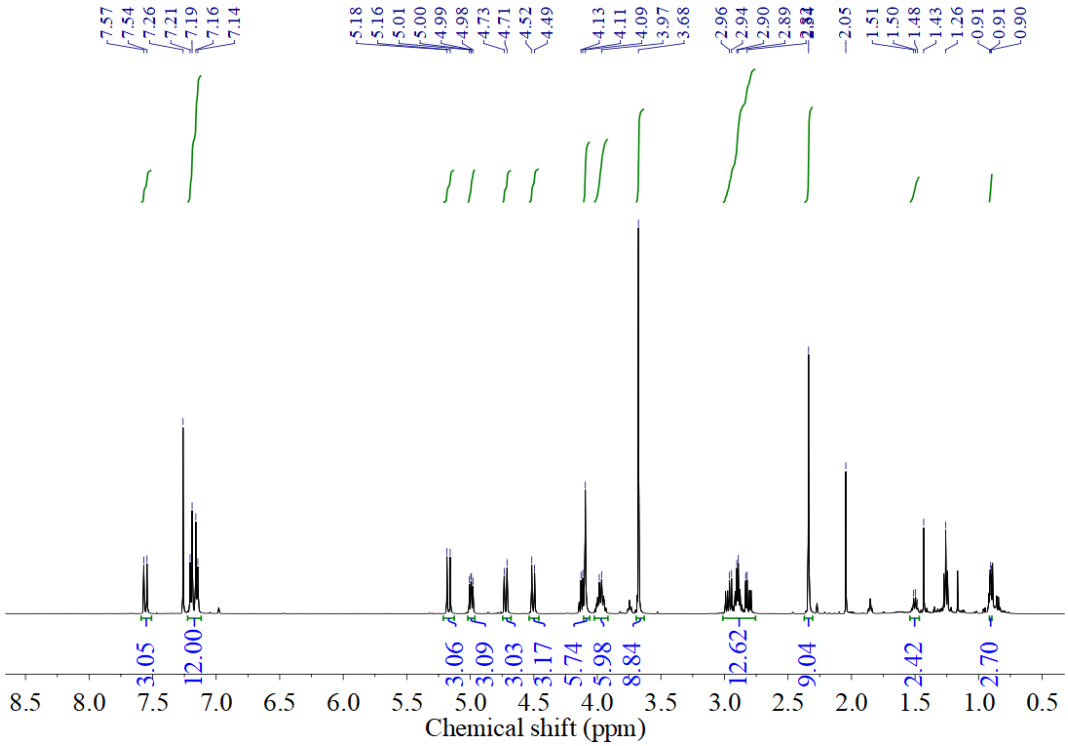


Figure S83. ^{1}H NMR spectrum of **E1** in DMSO-d_6.

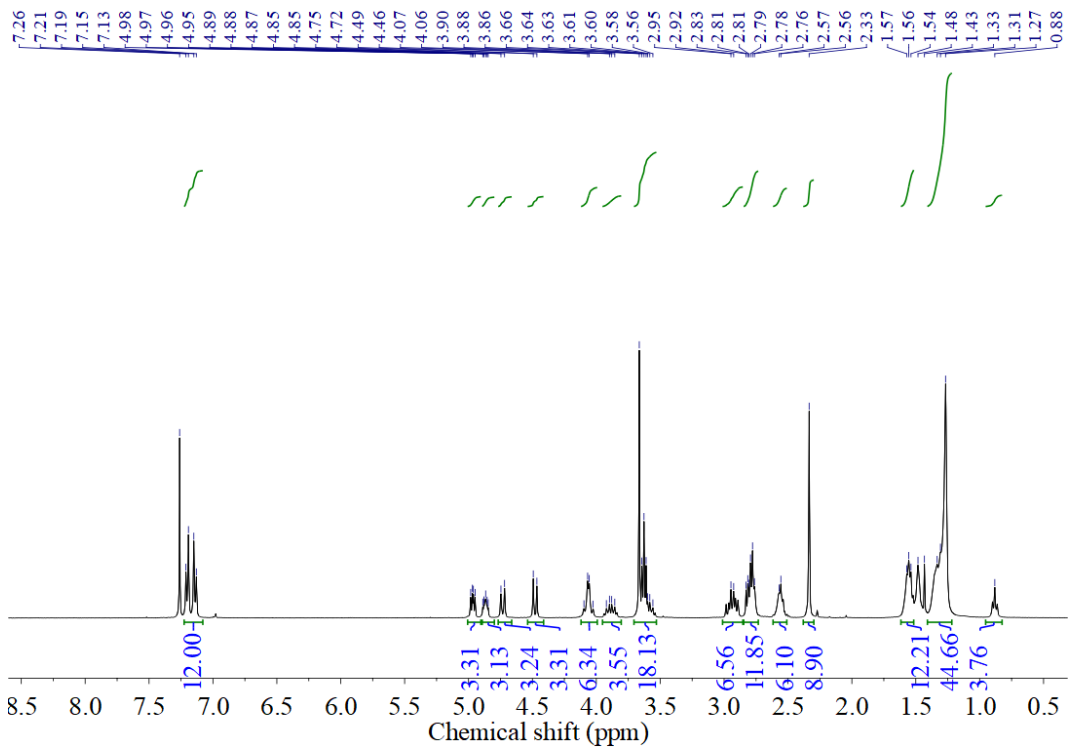


Figure S84. ^{1}H NMR spectrum of **E2** in DMSO-d_6.

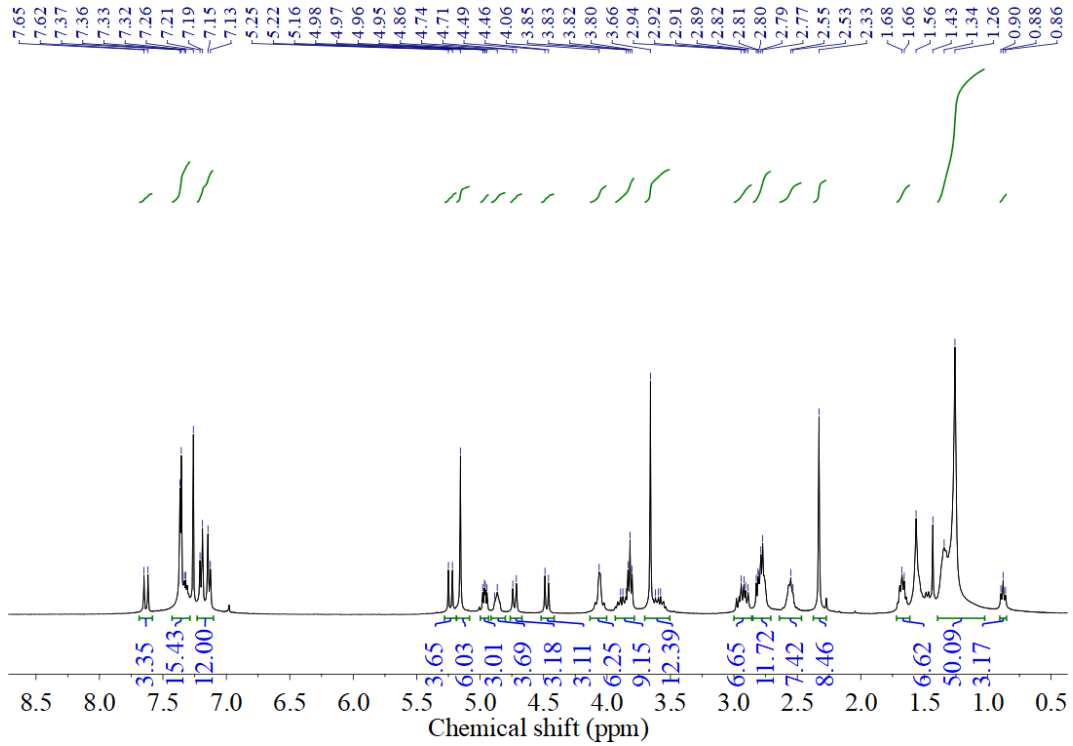


Figure S85. ^{1}H NMR spectrum of **E3** in DMSO-d_6.

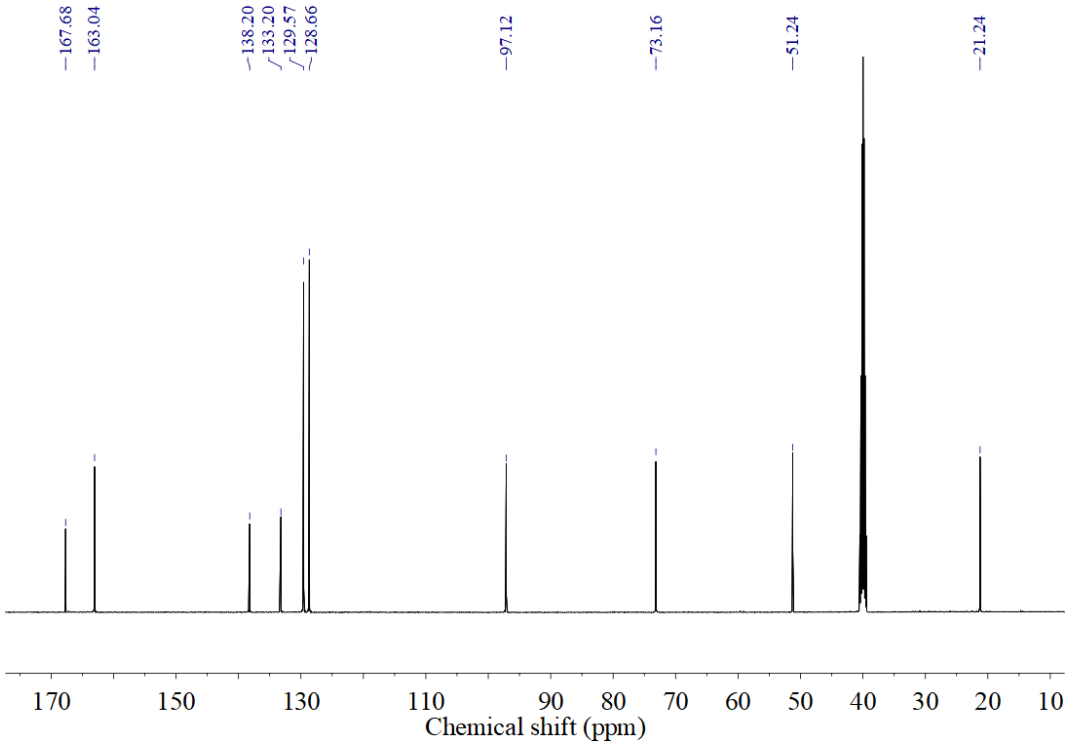


Figure S86. ^{13}C NMR spectrum of **A1** in DMSO-d_6.

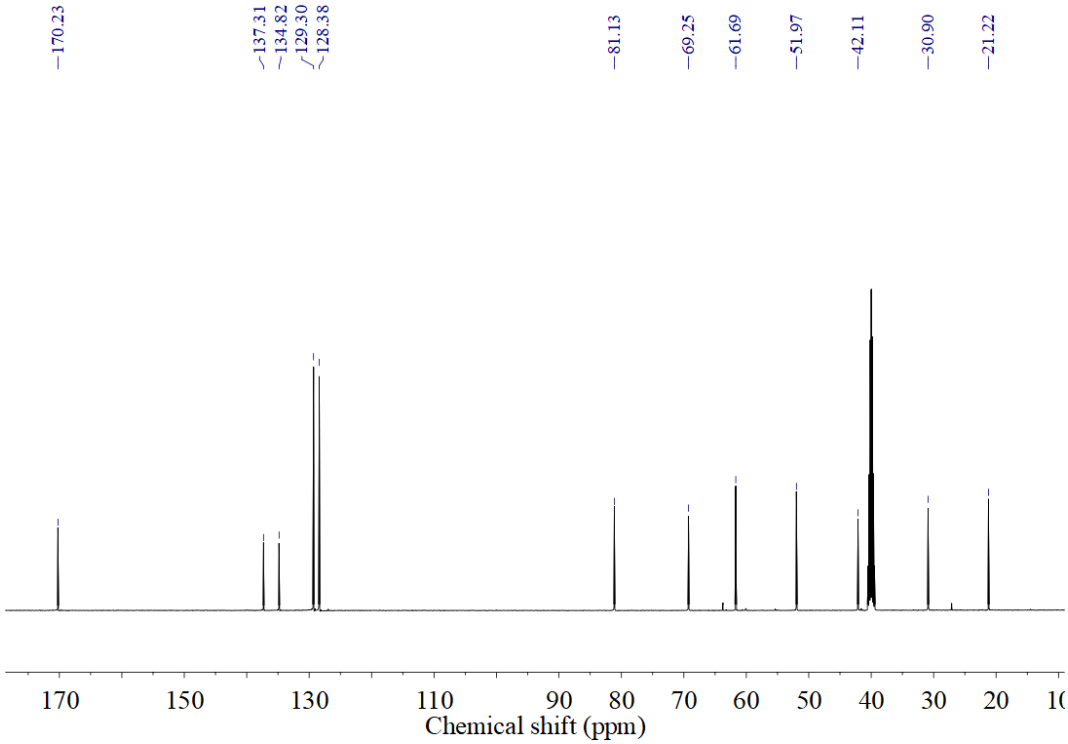


Figure S87. ^{13}C NMR spectrum of **A2** in DMSO-d_6.

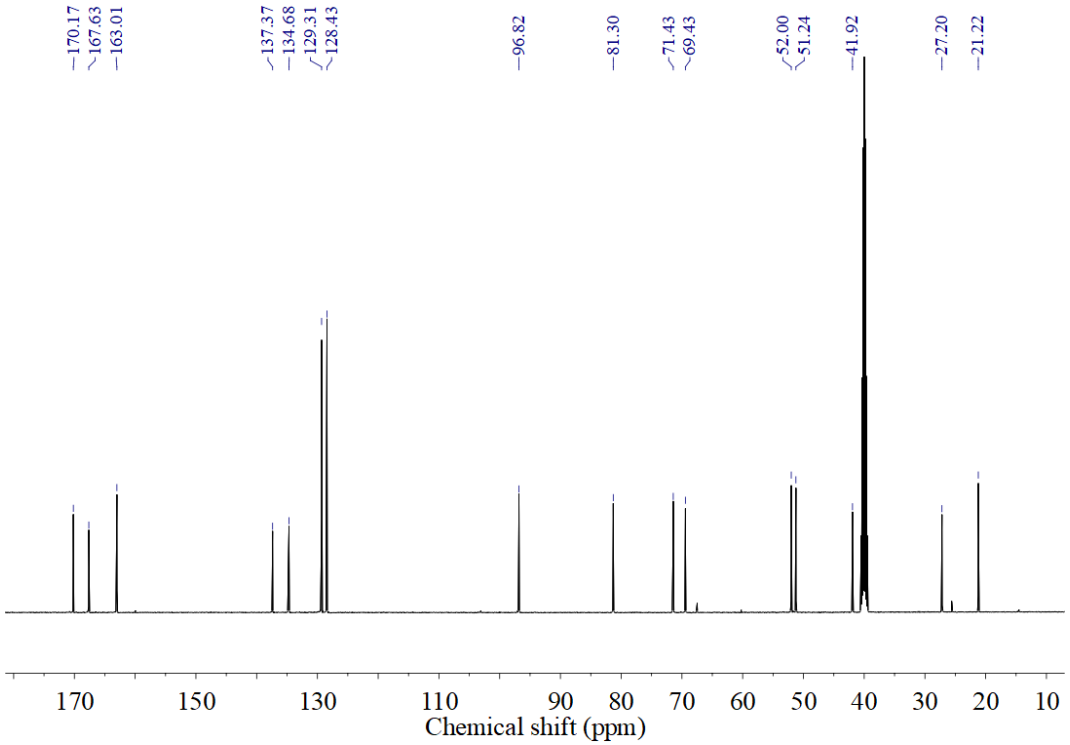


Figure S88. ^{13}C NMR spectrum of **A3** in DMSO-d_6.

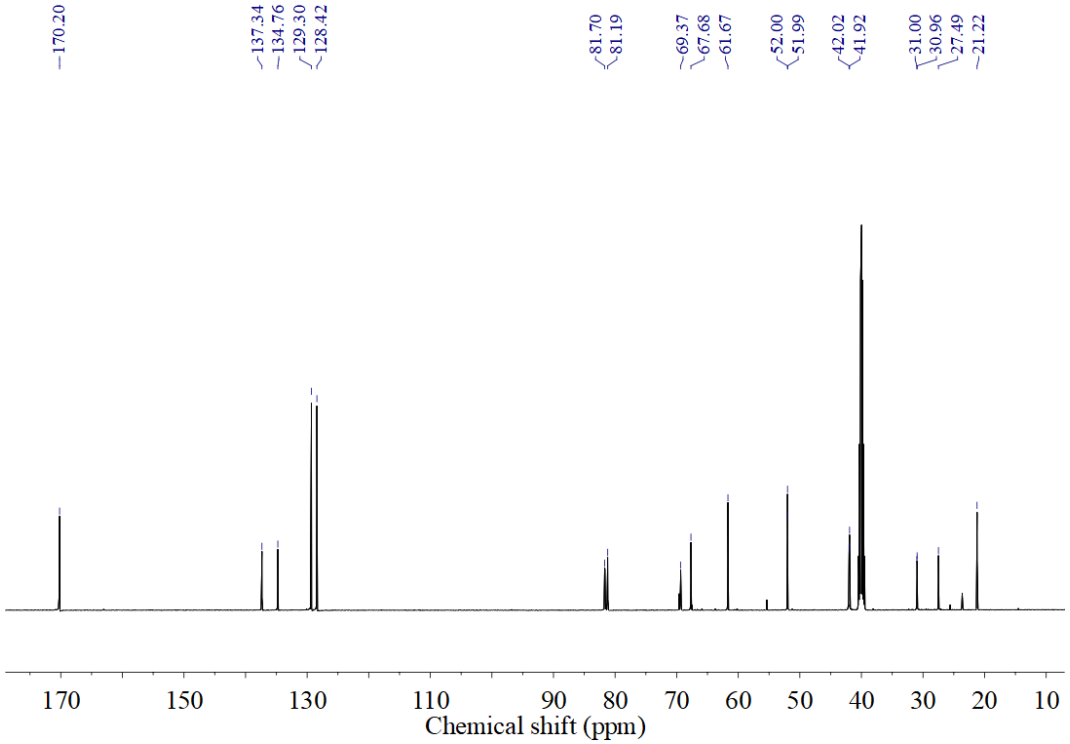


Figure S89. ^{13}C NMR spectrum of **A4** in DMSO-d_6.

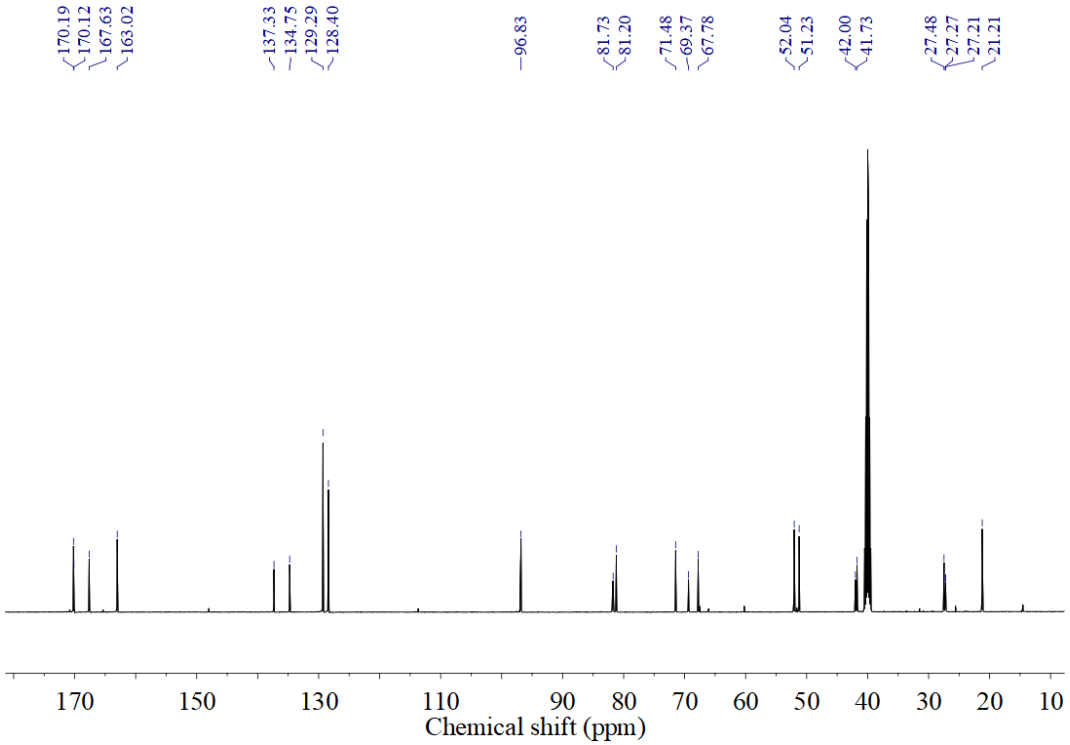


Figure S90. ^{13}C NMR spectrum of **A5** in DMSO-d_6.

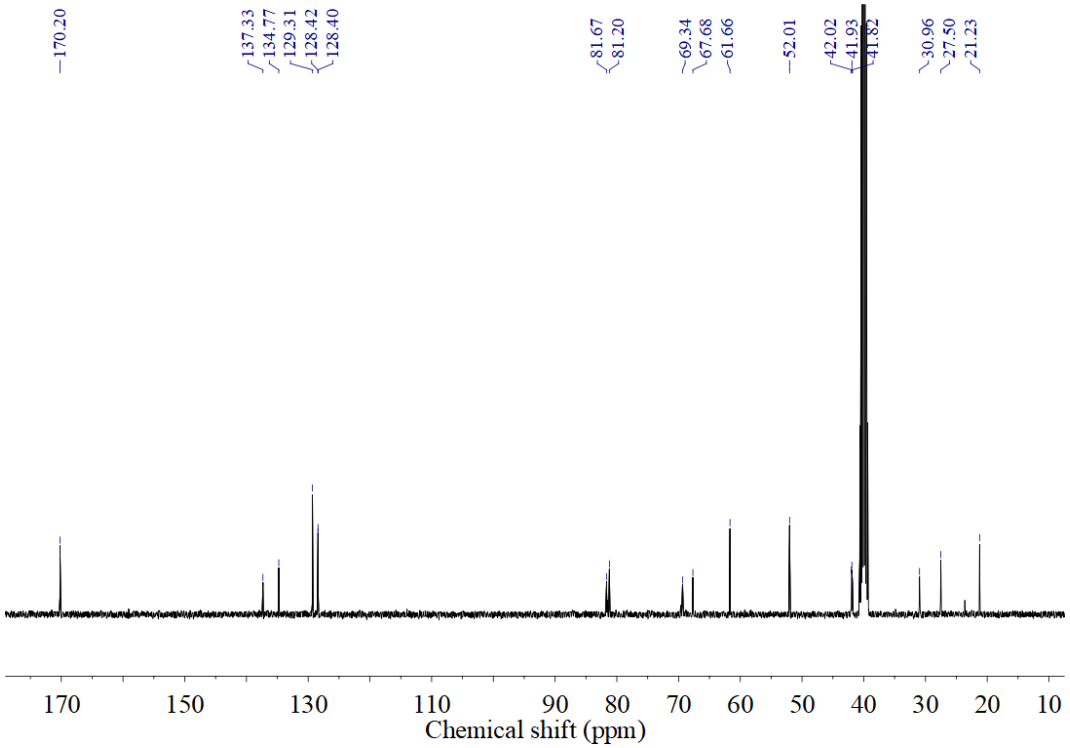


Figure S91. ^{13}C NMR spectrum of **A6** in DMSO-d_6.

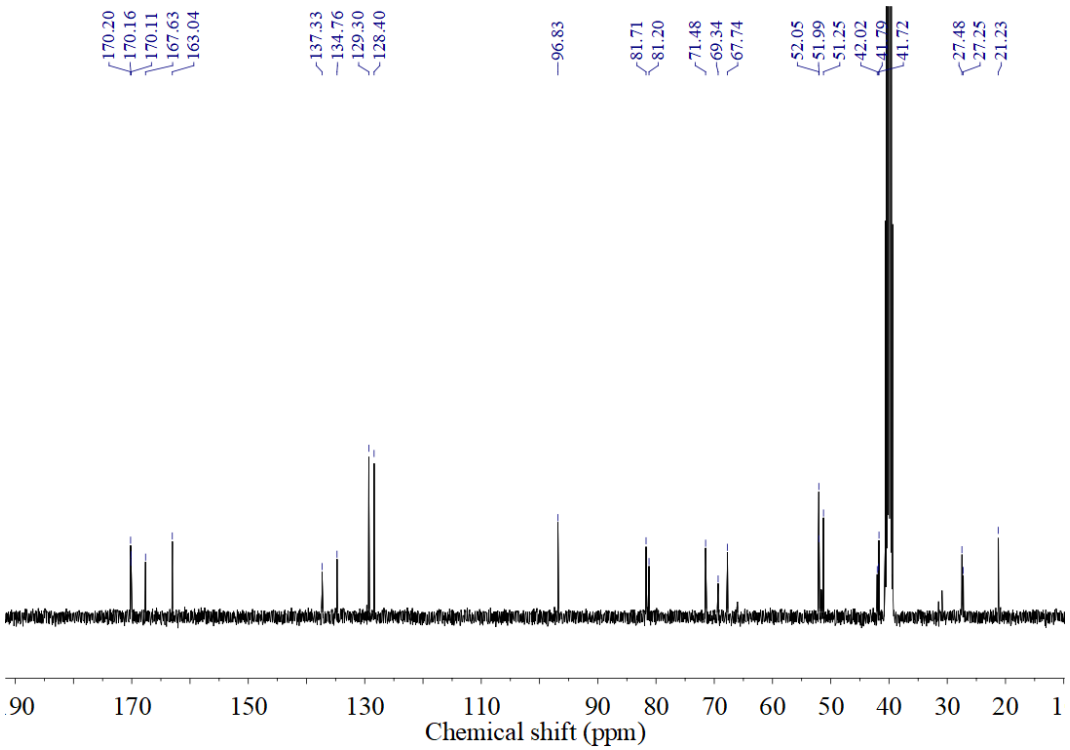


Figure S92. ^{13}C NMR spectrum of **A7** in DMSO-d_6.

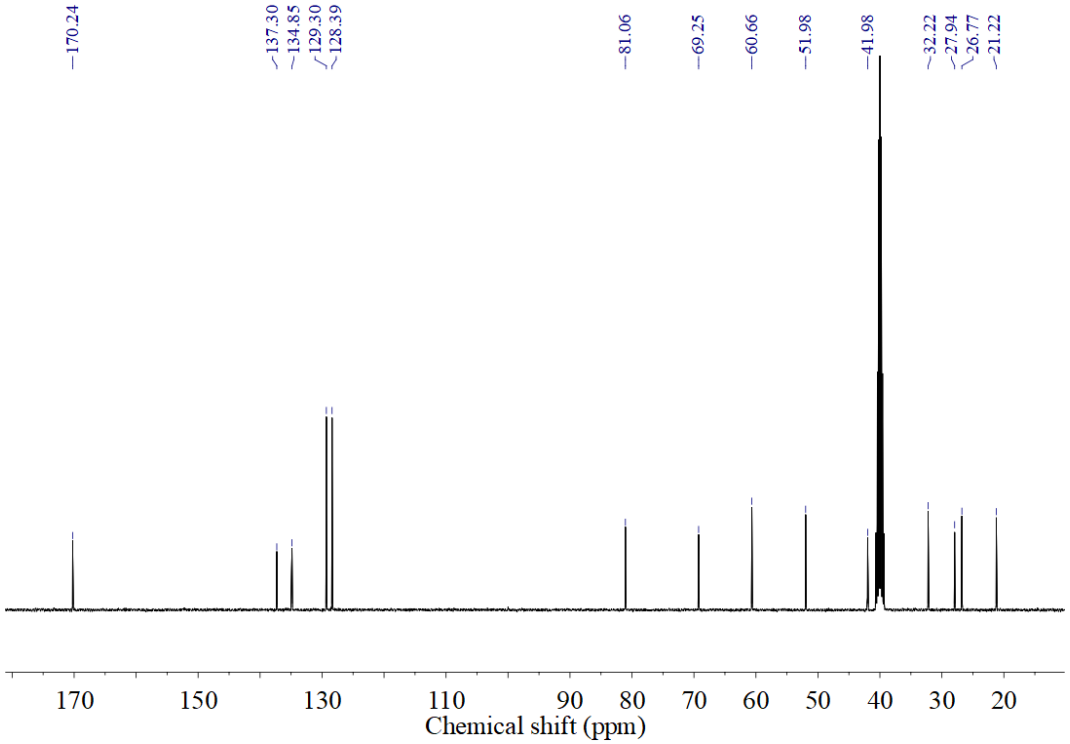


Figure S93. ^{13}C NMR spectrum of **B2** in DMSO-d_6.

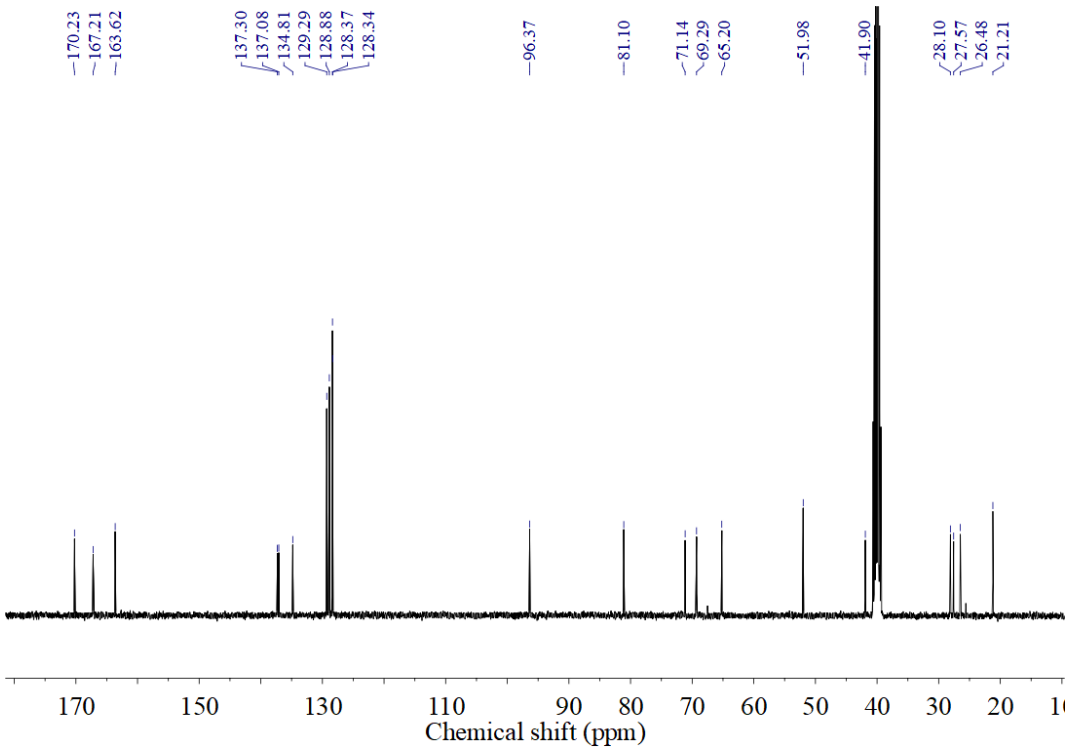


Figure S94. ^{13}C NMR spectrum of **B3** in DMSO-d_6.

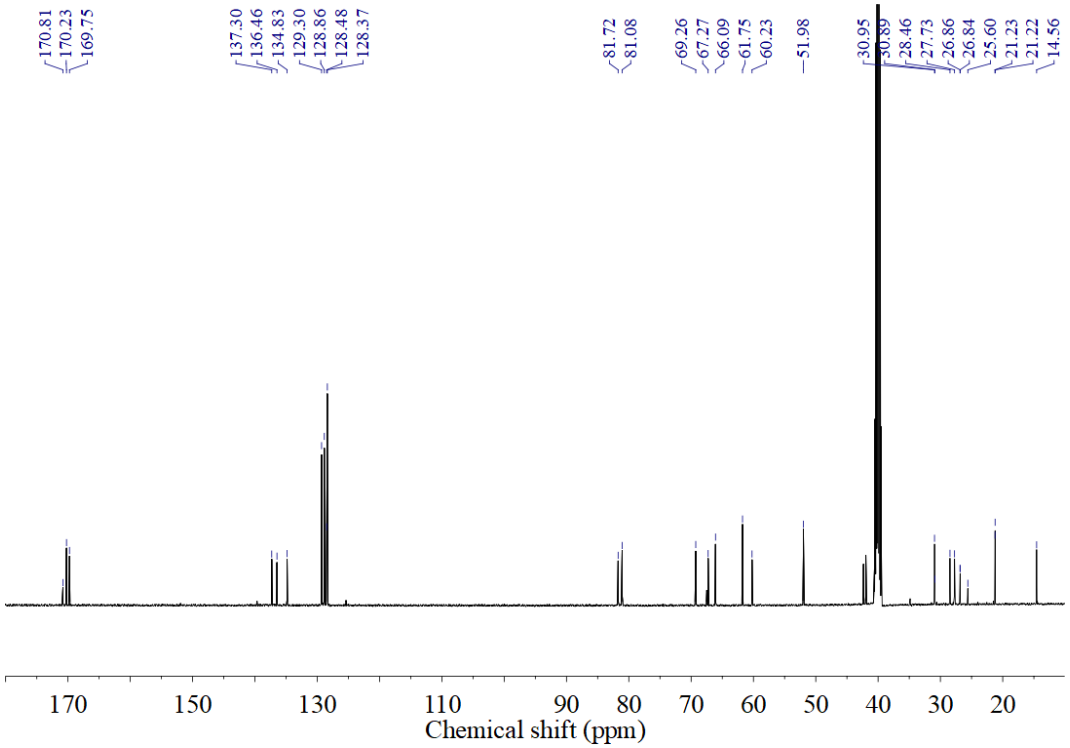


Figure S95. ^{13}C NMR spectrum of **B4** in DMSO-d_6.

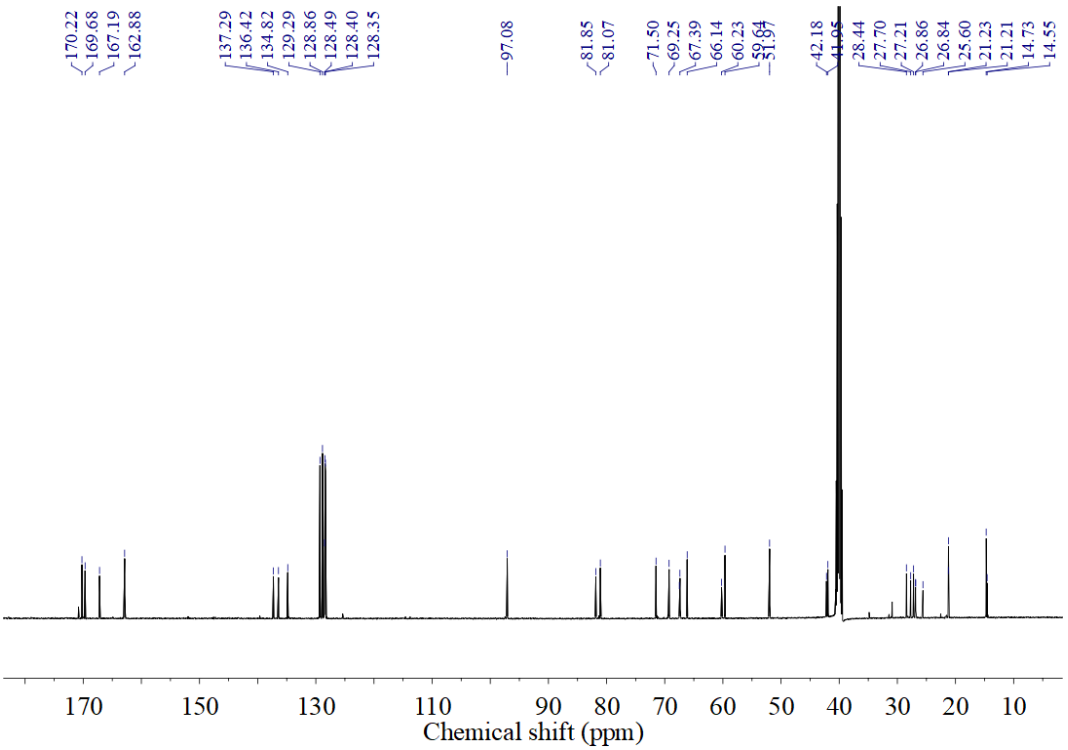


Figure S96. ^{13}C NMR spectrum of **B5** in DMSO-d_6.

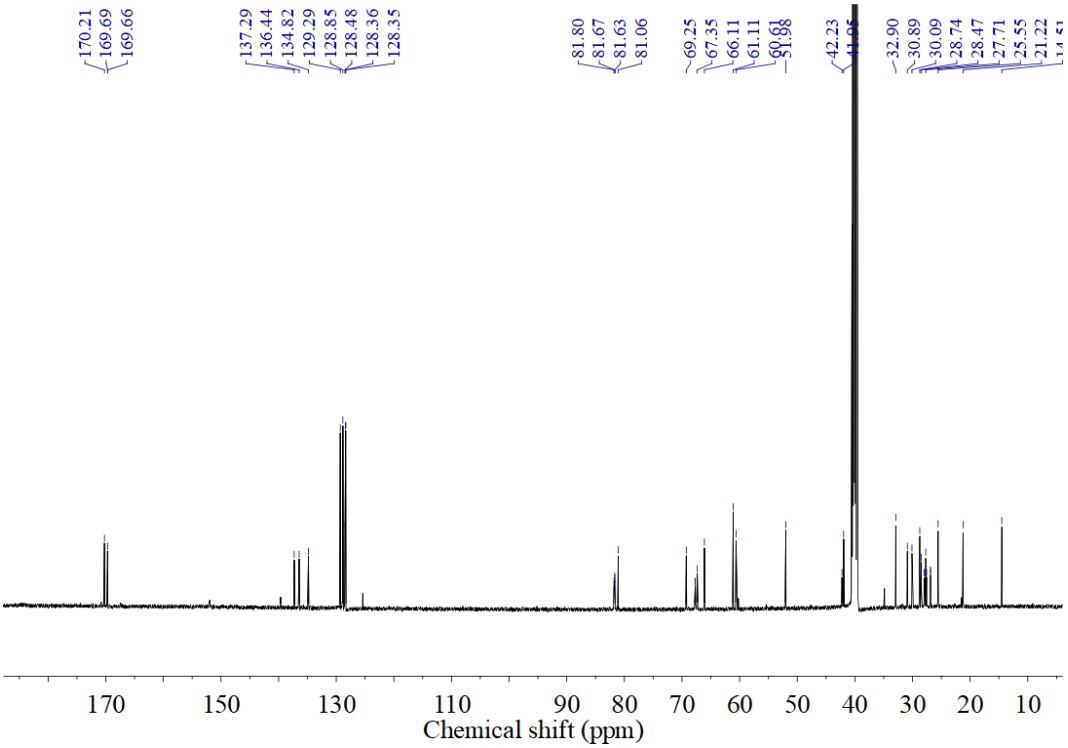


Figure S97. ^{13}C NMR spectrum of **B6** in DMSO-d_6.

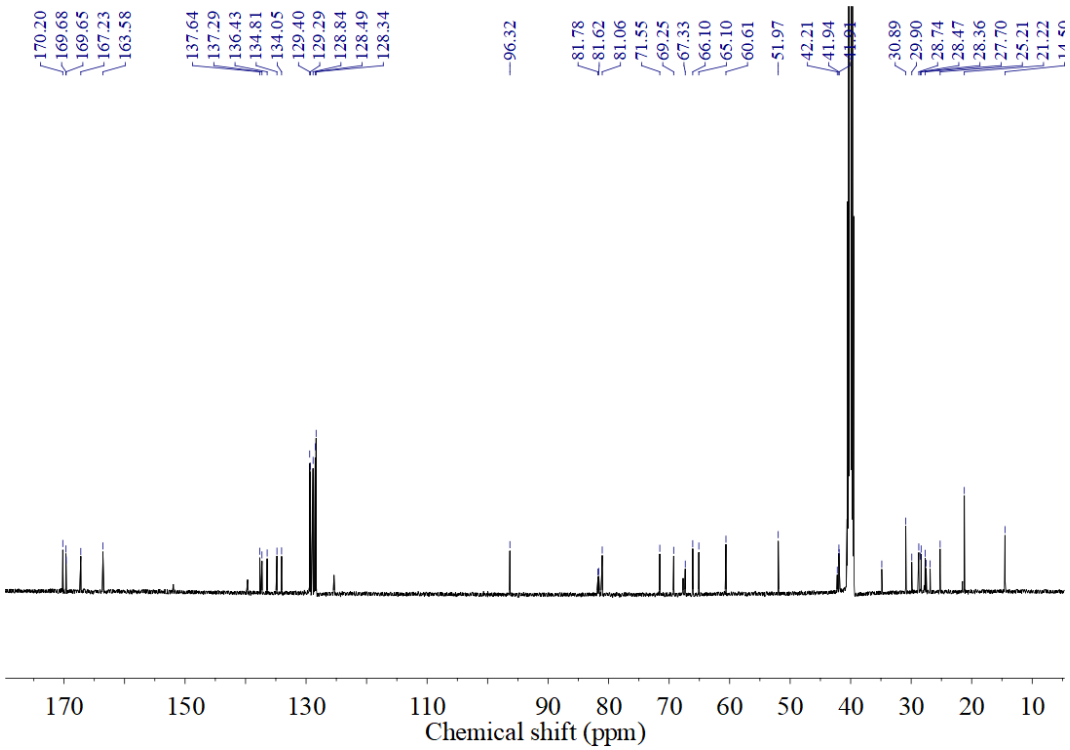


Figure S98. ^{13}C NMR spectrum of **B7** in DMSO-d_6.

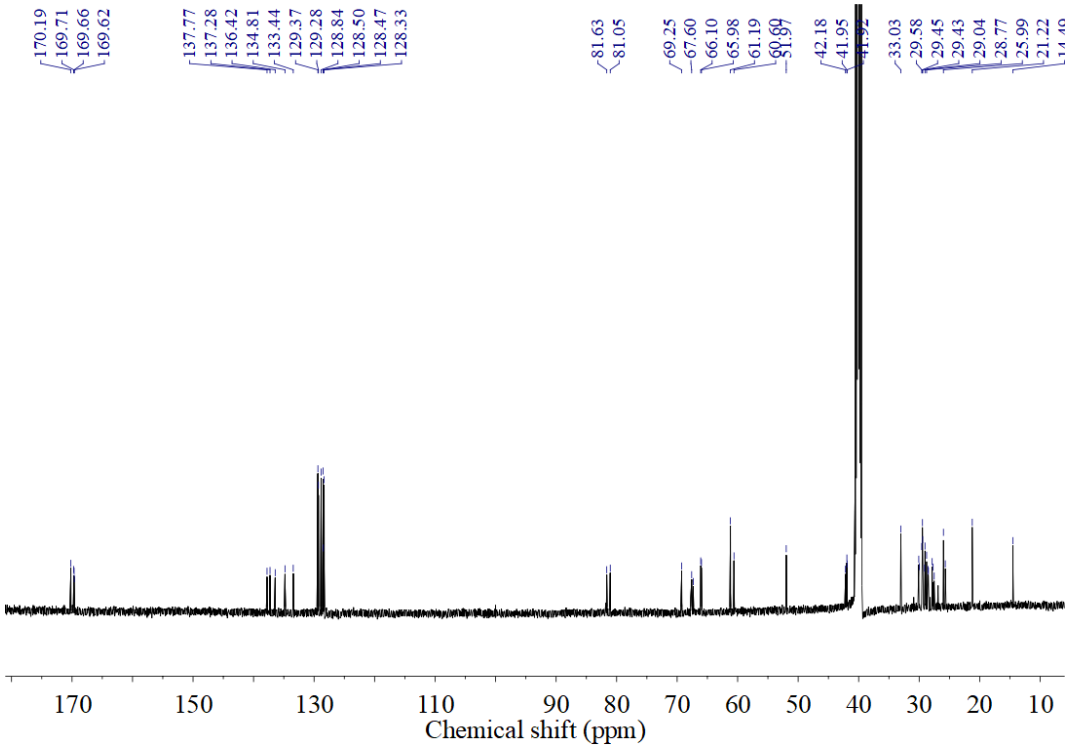


Figure S99. ^{13}C NMR spectrum of **B8** in DMSO-d_6.

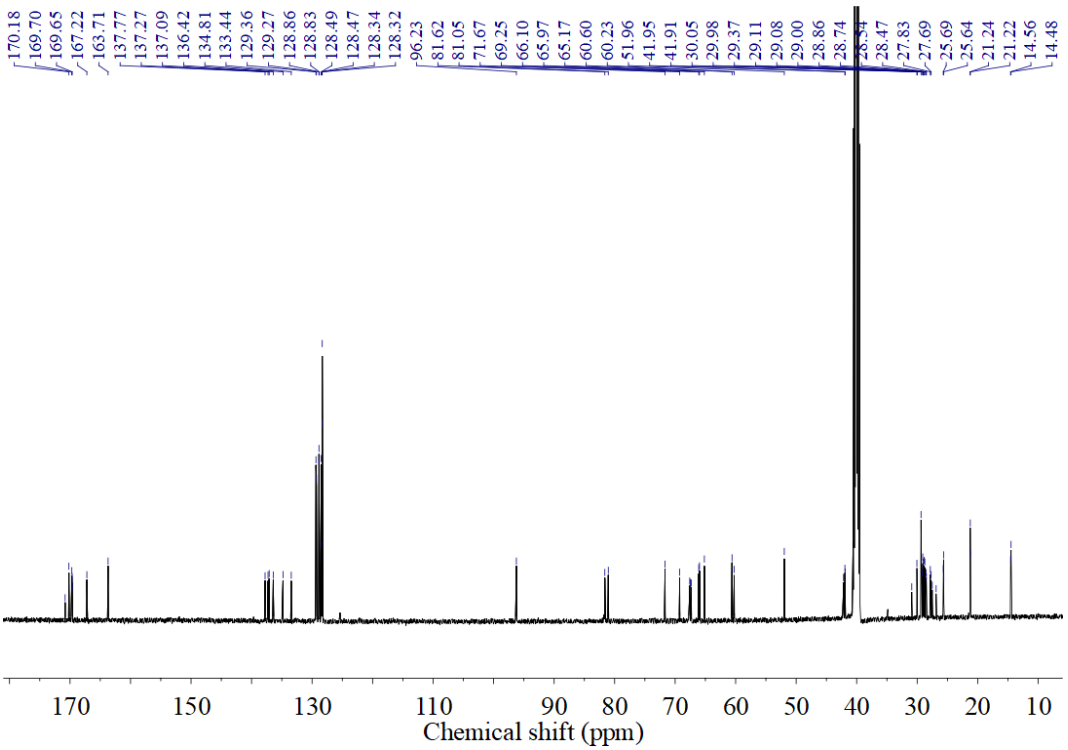


Figure S100. ^{13}C NMR spectrum of **B9** in DMSO-d_6.

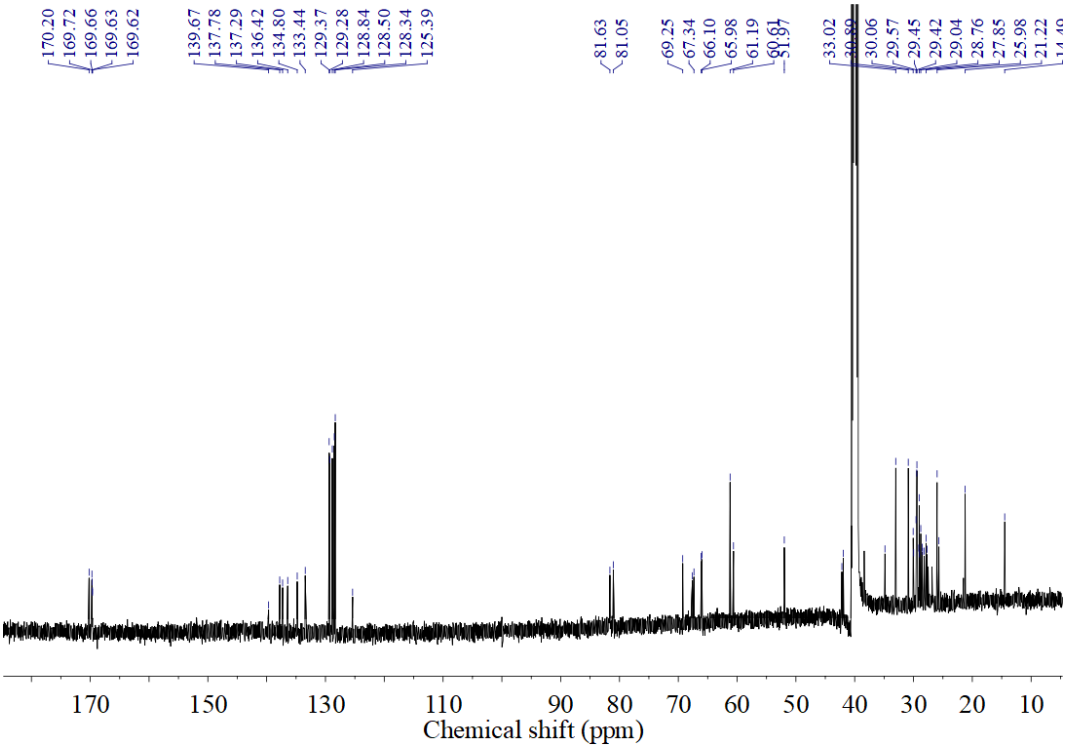


Figure S101. ^{13}C NMR spectrum of **B10** in DMSO-d_6.

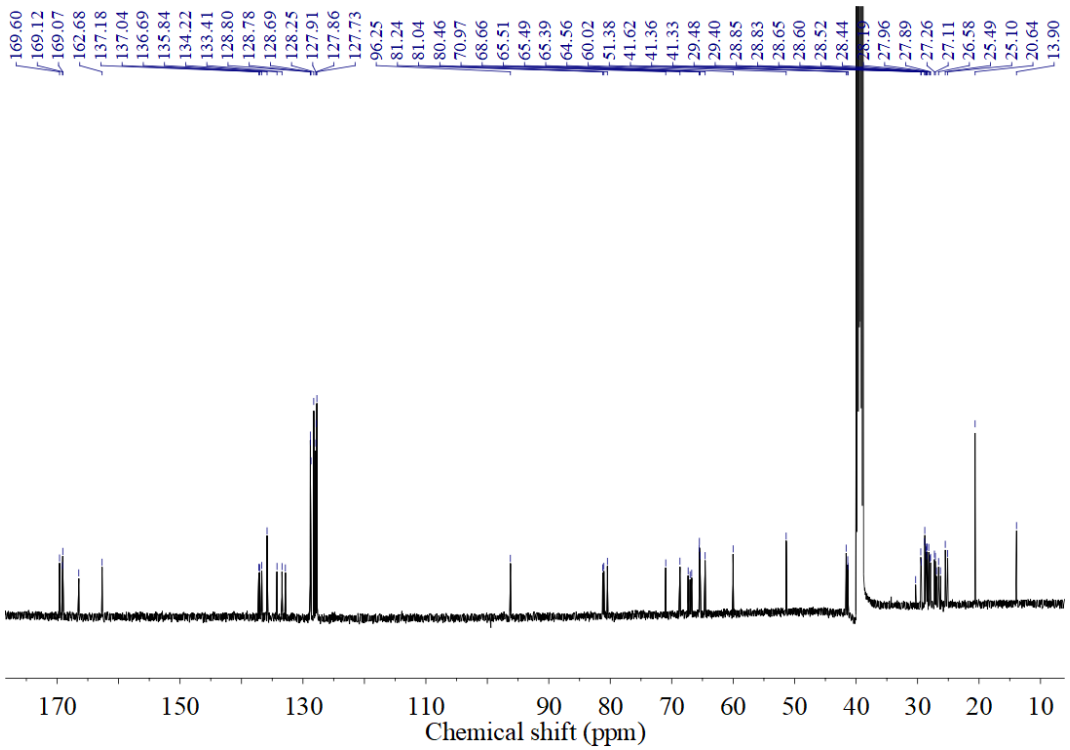


Figure S102. ^{13}C NMR spectrum of **B11** in DMSO-d_6.

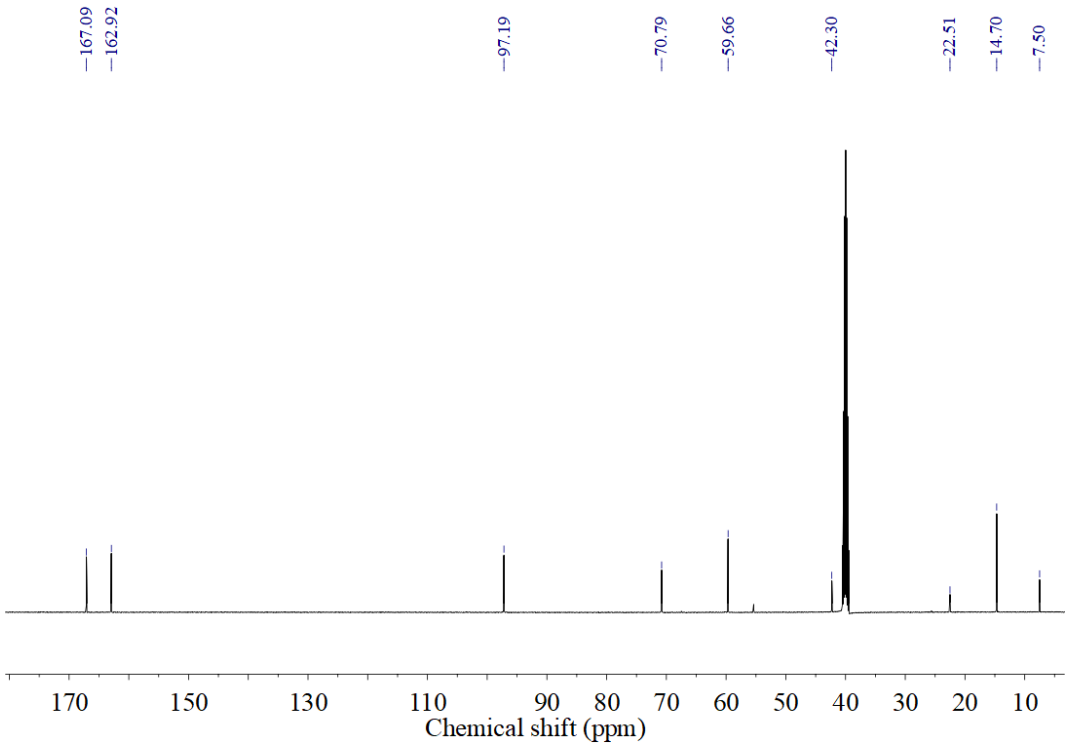


Figure S103. ^{13}C NMR spectrum of **C1** in DMSO-d_6.

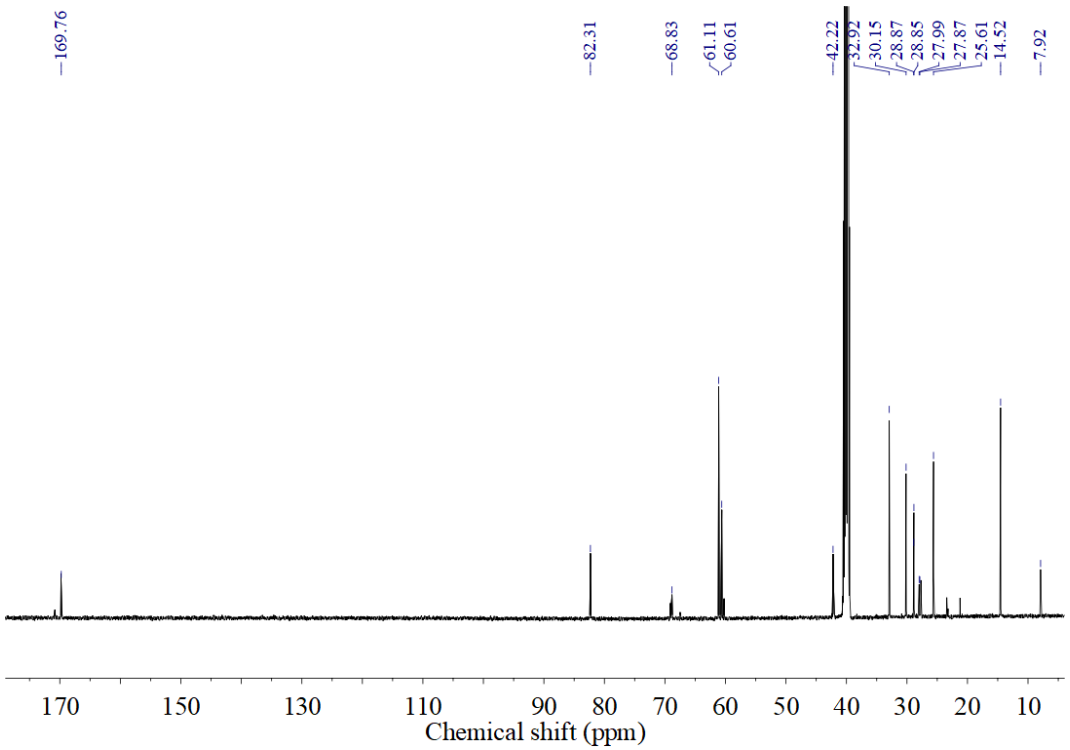


Figure S104. ^{13}C NMR spectrum of **C2** in DMSO-d_6.

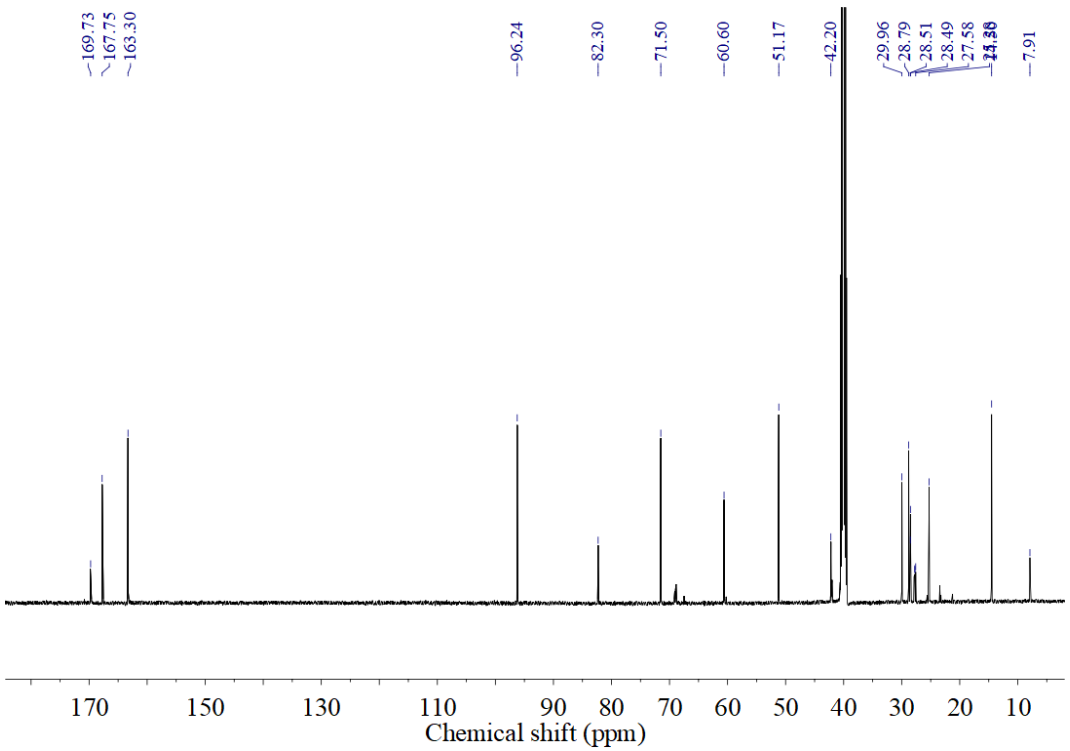


Figure S105. ^{13}C NMR spectrum of **C3** in DMSO-d_6.

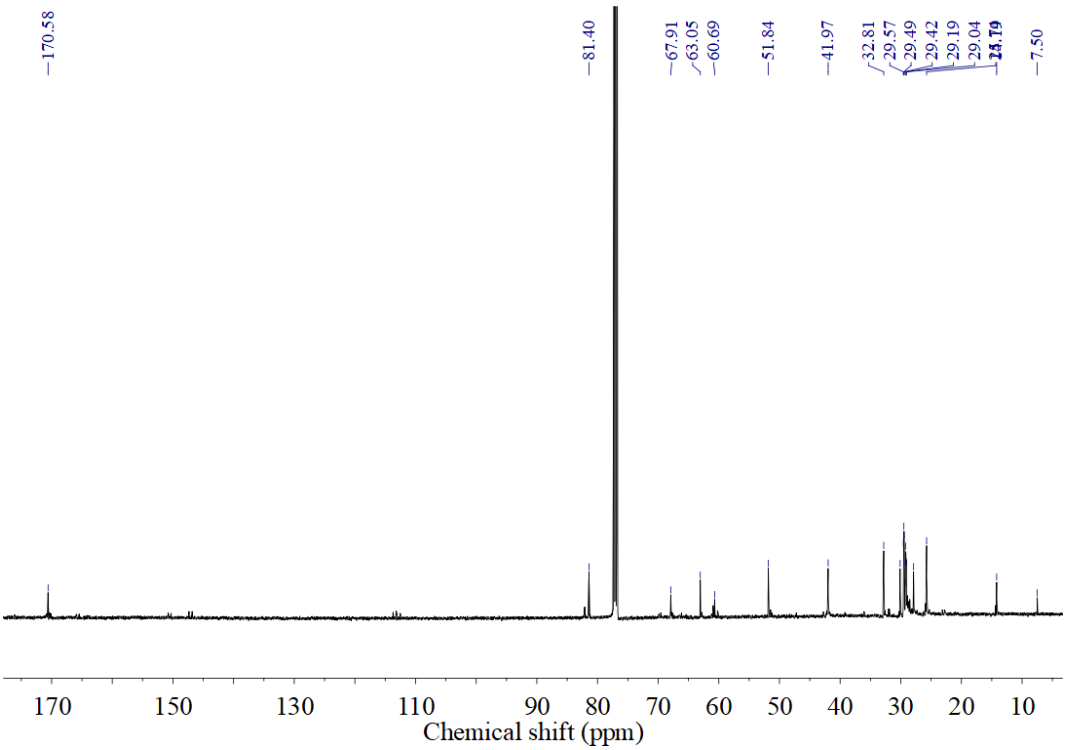


Figure S106. ^{13}C NMR spectrum of **C4** in DMSO-d_6.

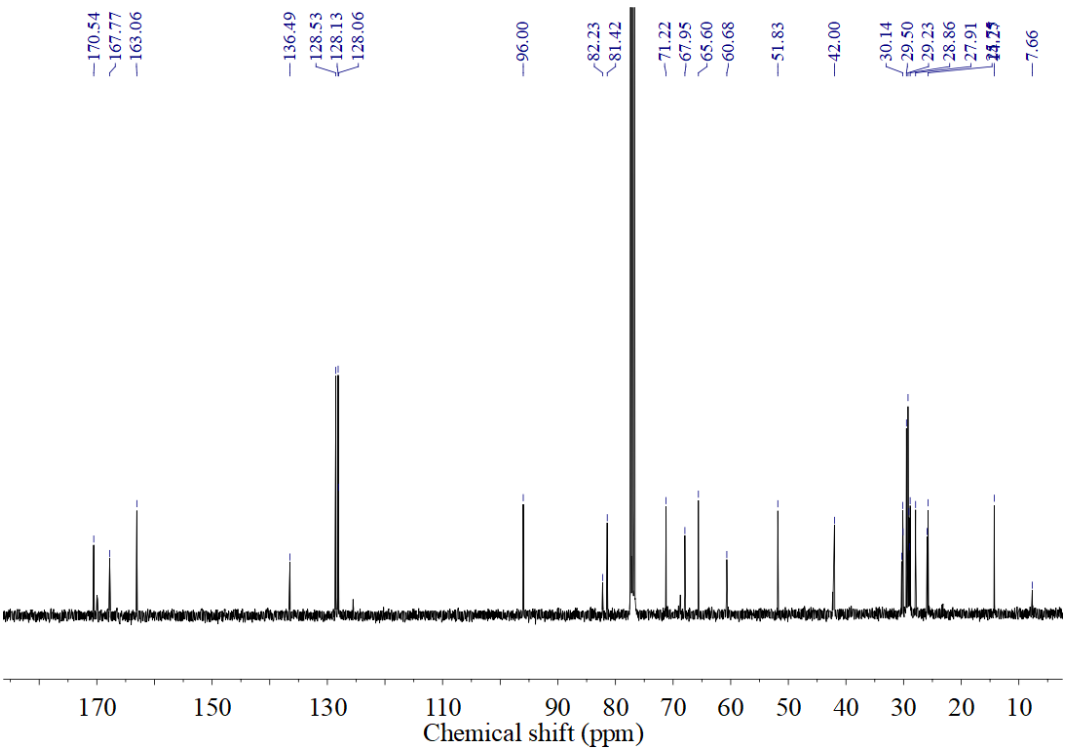


Figure S107. ^{13}C NMR spectrum of **C5** in DMSO-d_6.

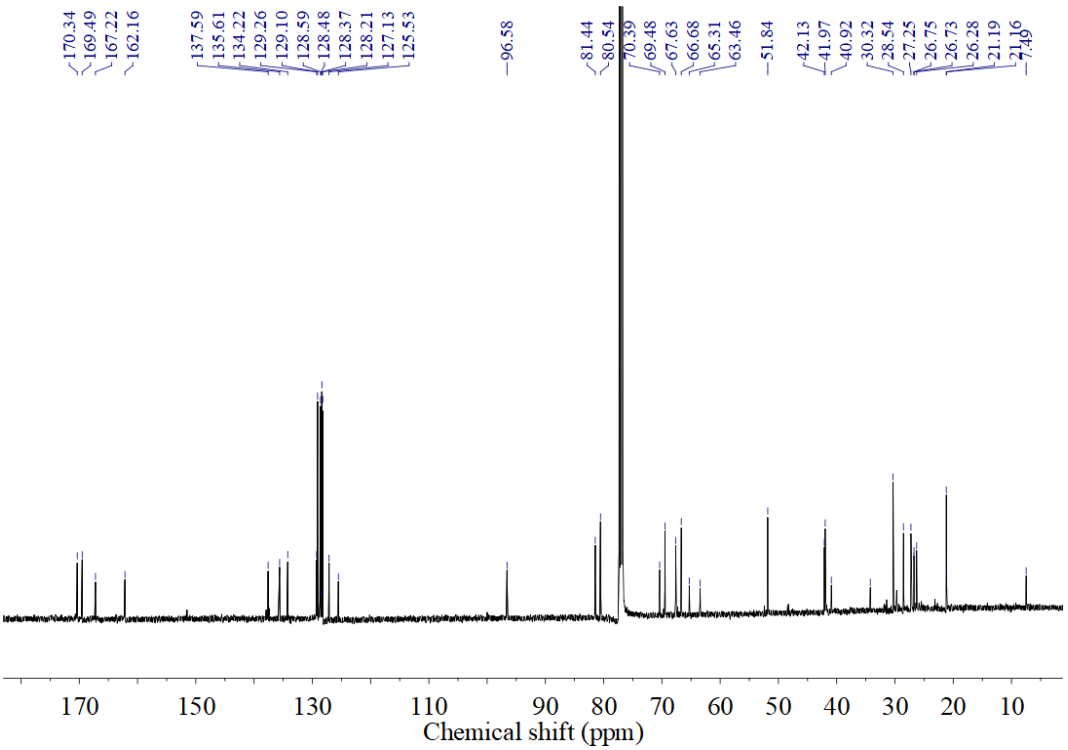


Figure S108. ^{13}C NMR spectrum of **D1** in DMSO-d_6.

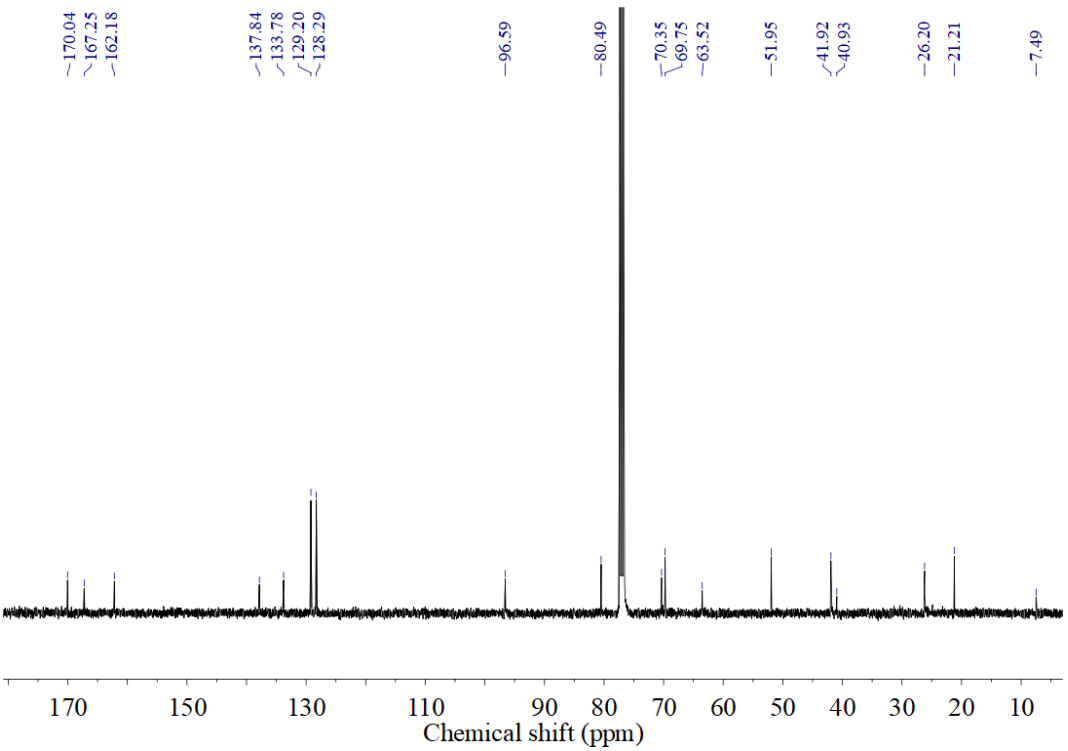


Figure S109. ^{13}C NMR spectrum of **E1** in DMSO-d_6.

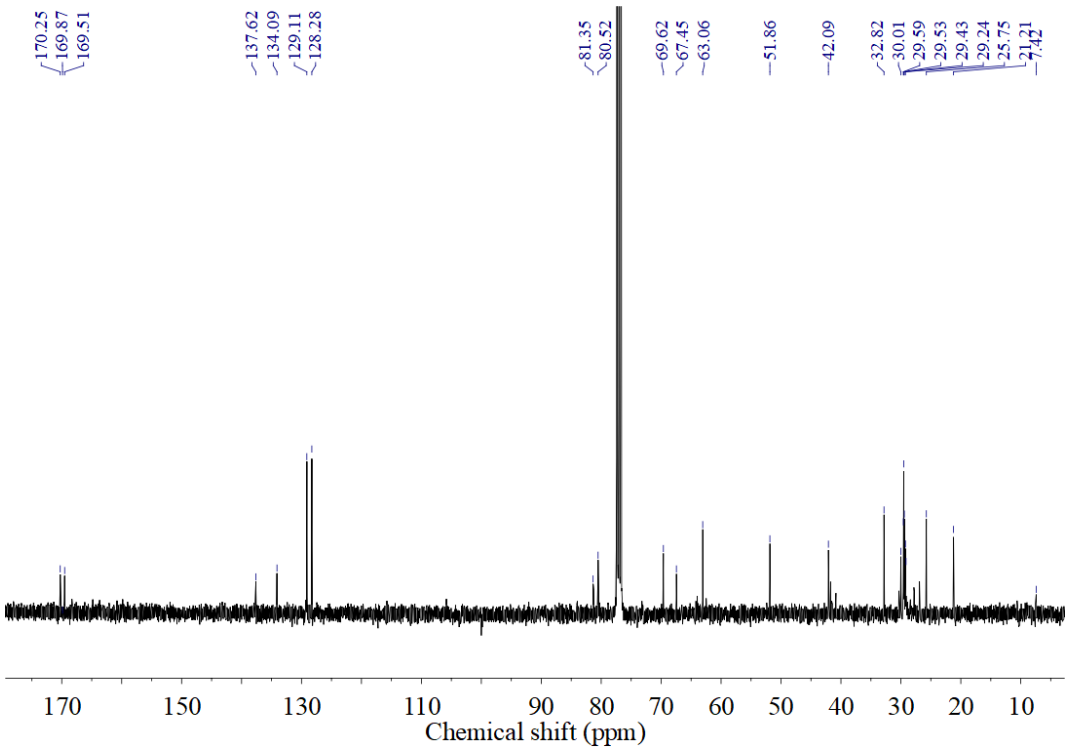


Figure S110. ^{13}C NMR spectrum of **E2** in DMSO-d_6.

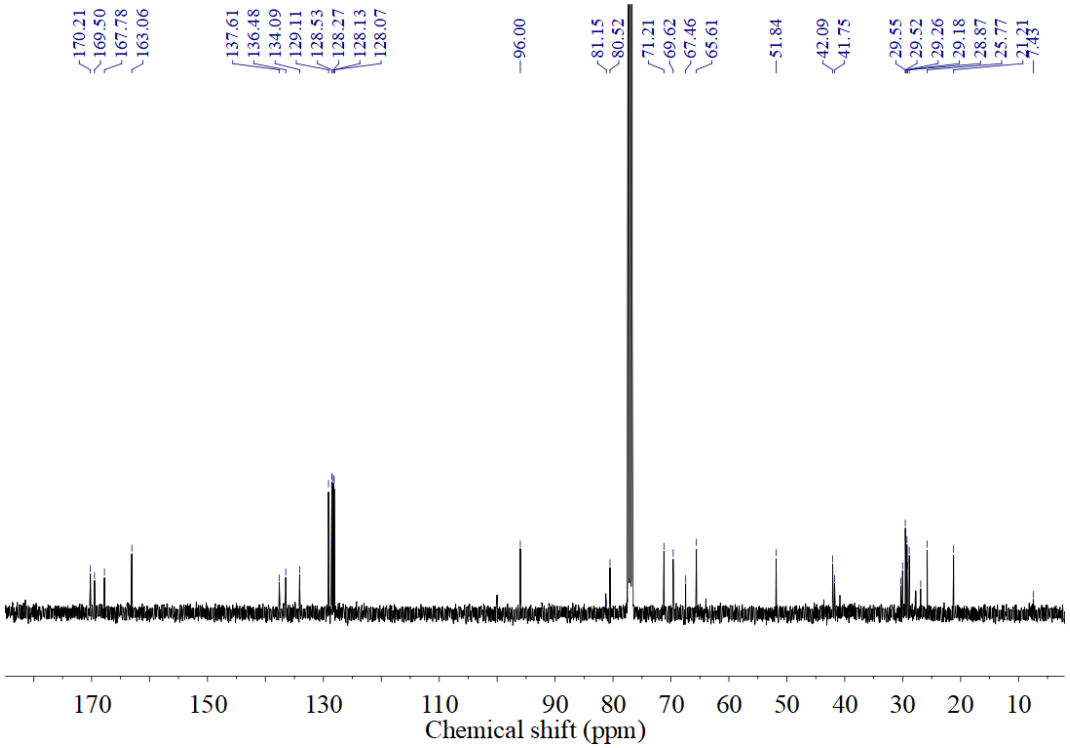


Figure S111. ^{13}C NMR spectrum of **E3** in DMSO-d_6.