Supporting Information

Carbohydrate-lectin recognition of well-defined heterogeneous dendronized glycopolymers: systematic studies on heterogeneity in glycopolymer-lectin binding

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1. Experimental Section

1.1 Synthesis of azide-sugars

2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl azide (βGlu-OAc-N_3)[1]

A white solid (βGlu-OAc-N_3) was obtained by using procedures known in the literature.[1] ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.20 (t, *J* = 9.5 Hz, 1H), 5.09 (t, *J* = 10.0 Hz, 1H), 4.94 (dd, *J* = 9.5, 9.0 Hz, 1H), 4.64 (d, *J* = 9.0 Hz, 1H), 4.26 (dd, *J* = 12.5, 5.0 Hz, 1H), 4.15 (dd, *J* = 12.5, 2.0 Hz, 1H), 3.78 (ddd, *J* = 10.0, 5.0, 2.5 Hz, 1H), 2.09 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H).

2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl azide (βGal-OAc-N_3)[2]

A white solid (βGal-OAc-N_3) was obtained by using procedures known in the literature.[2] ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.39 (d, *J* = 2.5 Hz, 1H), 5.13 (t, *J* = 10.0 Hz, 1H), 5.01 (dd, *J* = 10.5, 3.5 Hz, 1H), 4.58 (d, *J* = 8.5 Hz, 1H), 4.14 (t, *J* = 6.5 Hz, 2H), 4.00 (t, *J* = 6.0 Hz, 1H), 2.05 (dd, *J* = 54.5, 38.5 Hz, 12H).

2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl azide (αMan-OAc-N_3)[2]

A colorless oil (αMan-OAc-N_3) was obtained by using procedures known in the literature.[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.39 (d, *J* = 1.5 Hz, 1H), 5.31 – 5.23 (m, 2H), 5.15 (d, *J* = 1.0 Hz, 1H), 4.30 (dd, *J* = 12.5, 5.5 Hz, 1H), 4.18 – 4.13 (m, 2H), 2.17 (s, 3H), 2.11 (s, 3H), 2.05 (s, 3H), 1.99 (s, 3H).

1.2 Experimental details for synthesis and characterization of compounds and glycopolymers

Synthesis of *N*-(*tert*-Butyloxycarbonyl)tris(hydroxymethyl)aminomethane [3]

A solution of di-*tert*-butyl dicarbonate (Boc_2O, 23.42 g, 107.31 mmol) in *t*-BuOH (100 mL) was added under RT to a suspension of tris(hydroxymethyl)aminomethane (10.00 g, 82.55 mmol) in a mixture of MeOH (75 mL) and *t*-BuOH (75 mL). The mixture was stirred at RT for 18 h, then the solution concentrated under reduced pressure. The residue was purified by precipitation with cold ethyl acetate, and vacuum filtered to afforded the pure compound as a white solid (16.44 g, 90%) .^{1}H NMR (500 MHz, DMSO-d_6): δ = 5.71 (s, 1H), 4.55 (s, 3H, OH), 3.46 (s, 6H), 1.31 (s, 9H).

Synthesis of *N*-(*tert*-Butyloxycarbonyl)tris[(propargyloxy)methyl]aminomethane (1) [3]

N-(*tert*-Butyloxycarbonyl)tris(hydroxymethyl)aminomethane (10.00 g, 45.20 mmol) was dissolved in anhydrous DMF (50 mL) and stirred at 0 °C for 10 min. 3-Bromopropyne (10.97 mL, 140.11 mmol) was added dropwise. Then powdered potassium hydroxide (7.86 g, 140.11 mmol) was added, and keeping stirring for 1 h at 0 °C. The reaction was allowed to warm to RT and stirred for 18 h. At the end of the reaction, the reaction mixture was diluted with 100 mL of ethyl acetate and was washed with water (3 × 50 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate 9 : 1) to give the product as a yellow oil **1**

(petroleum ether/ethyl acetate 6 : 1, R_f = 0.55) (9.85 g, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.89 (s, 1H), 4.11 (d, *J* = 2.0 Hz, 6H), 3.74 (s, 6H), 2.41 (t, *J* = 2.0 Hz, 3H), 1.39 (s, 9H).

Synthesis of Boc-βGal-βGal-βGal-OAc (11, BBB)

Compound **1** (0.48 g, 1.43 mmol), 2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl azide (1.60 g, 4.29 mmol) were dissolved in a 8 mL mixture of t-BuOH/H2O (1 : 1 v/v). Then copper(II) sulfate pentahydrate (0.18 g, 0.72 mmol) and sodium ascorbate (0.28 g, 1.43 mmol) were added successively. After stirring for 3 hours at room temperature TLC (petroleum ether/ethyl acetate 1 : 4, compound **11**, Rf = 0.41) showed the reaction was completed. The reaction solution was mixed with 50 mL dichloromethane (DCM) and washed with water (3 × 25 mL). The separated organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to give the residue which was purified by flash column chromatography (petroleum ether/ethyl acetate 1:3) to afford the desired product Boc-βGal-βGal-βGal-OAc (**11**, BBB) (1.77 g, 90%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.86 (s, 3H), 5.92 (d, *J* = 9.0 Hz, 3H), 5.60 (t, *J* = 9.5 Hz, 6H), 5.54 (d, *J* = 3.0 Hz, 3H), 5.29 (s, 6H), 5.00 (s, 1H), 4.63 (d, *J* = 5.0 Hz, 6H), 4.28 (t, *J* = 6.5 Hz, 3H), 4.17 (d, *J* = 6.0 Hz, 7H), 3.74 (dd, *J* = 27.3, 9.0 Hz, 6H), 2.21 (s, 10H), 2.03 (s, 21H), 2.00 (s, 9H), 1.80 (s, 10H), 1.40 (s, 10H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.53, 170.15, 169.10, 145.62, 121.83, 86.19, 74.01, 71.03, 69.67 , 68.09, 67.04, 64.88, 61.25, 53.63, 28.56, 21.03, 20.34, 0.16. HRMS (ESI): *m/z* calc. for $C_{60}H_{82}N_{10}O_{32}Na$ $[M+Na]^+$: 1477.49888; found: 1477.49886.

Synthesis of Boc-βGlu-βGlu-βGlu-OAc (12, CCC)

Compound **1** (0.48 g, 1.43 mmol), 2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl azide (1.60 g, 4.29 mmol) were dissolved in a 8 mL mixture of t-BuOH/H2O (1 : 1 v/v). Then copper(II) sulfate pentahydrate (0.18 g, 0.72 mmol) and sodium ascorbate (0.28 g, 1.43 mmol) were added successively. After stirring for 3 hours at room temperature TLC (petroleum ether/ethyl acetate 1 : 4, compound **12**, Rf = 0.39) showed the reaction was completed. The reaction solution was mixed with 50 mL dichloromethane (DCM) and washed with water (3 × 25 mL). The separated organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to give the residue, which was purified by flash column chromatography (petroleum ether/ethyl acetate 1:3) to afford the desired product Boc-βGlu-βGlu-βGlu-OAc (**12**, CCC) (1.75 g, 89%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96 (s, 3H), 5.97 (d, *J* = 9.0 Hz, 4H), 5.52 (t, *J* = 9.0 Hz, 5H), 5.42 (t, *J* = 9.5 Hz, 3H), 5.31 (t, *J* = 9.5 Hz, 5H), 4.95 (s, 1H), 4.62 (s, 8H), 4.31 – 4.25 (m, 4H), 4.11 (dd, *J* = 15.5, 8.0 Hz, 12H), 3.75 – 3.68 (m, 11H), 2.05 (d, *J* = 2.0 Hz, 41H), 2.01 (s, 18H), 1.79 (s, 11H), 1.37 (s, 14H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.17, 170.56, 170.01, 169.48, 168.86, 154.84, 85.68, 79.22, 75.01, 72.82 , 70.29, 69.62, 67.79, 64.79, 61.65, 60.40, 58.42, 28.37, 21.05, 20.89 – 20.38, 20.11. HRMS (ESI): *m/z* calc. for $C_{60}H_{82}N_{10}O_{32}Na$ $[M+Na]^+$: 1477.49888; found: 1477.49885.

Deprotection of the Boc-Protected compound Boc-αMan-αMan-αMan-OAc (2, AAA)

Compound **2** (0.40 g, 0.27 mmol) was dissolved in 1 mL DCM and trifluoroacetic acid (0.55 mL) dissolved in 0.55 mL DCM was added dropwise at 0 °C. After stirring at 0 °C for 1 hour, the reaction mixture was stirred at room temperature for 3 hours. After the reaction was completed, the mixture was concentrated to dryness. The residue was re-dissolved in CH_2Cl_2 (20 mL) and washed successively with H_2O (2 x 20 mL), followed by saturated aq. $NaHCO_3$ solution (20 mL).

The organic layer was collected and dried over anhydrous Na_2SO_4, the solvent was evaporated to give a product **NH_2-αMan-αMan-αMan-OAc 13** (0.35 g, 94%) which was used directly without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.80 (s, 3H), 6.06 (d, *J* = 2.5 Hz, 3H), 5.95 – 5.89 (m, 6H), 5.38 (t, *J* = 9.0 Hz, 3H), 4.63 (d, *J* = 3.0 Hz, 6H), 4.36 (dd, *J* = 12.5, 5.0 Hz, 3H), 4.06 (dd, *J* = 12.5, 2.5 Hz, 3H), 3.93 – 3.89 (m, 3H), 3.47 (s, 6H), 2.18 (s, 9H), 2.08 (s, 9H), 2.06 (s, 9H), 2.03 (s, 9H), 1.83 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.59, 169.75, 169.51, 145.61, 123.25, 83.71 , 72.12, 68.93, 68.30, 66.06, 64.60, 61.68, 56.26, 20.76, 20.63. HRMS (ESI): *m/z* calc. for $C_{55}H_{74}N_{10}O_{30}Na$ $[M+Na]^+$: 1377.44645; found: 1377.44642.

Deprotection of the Boc-Protected compound Boc-αMan-αMan-yne-OAc (3, AAX)

Compound **3** (0.43 g, 0.39 mmol) was dissolved in 1 mL DCM and trifluoroacetic acid (0.79 mL) dissolved in 0.79 mL DCM was added dropwise at 0 °C. After stirring at 0 °C for 1 hour, the reaction mixture was stirred at room temperature for 3 hours. After the reaction was completed, the mixture was concentrated to dryness. The residue was re-dissolved in CH_2Cl_2 (20 mL) and washed successively with H_2O (2 x 20 mL), followed by saturated aq. $NaHCO_3$ solution (20 mL). The organic layer was collected and dried over anhydrous Na_2SO_4, the solvent was evaporated to give a product **NH_2-αMan-αMan-yne-OAc 19** (0.38 g, 98%) which was used directly without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 2.0 Hz, 2H), 6.03 (s, 2H), 5.95 – 5.88 (m, 4H), 5.37 (t, *J* = 9.0 Hz, 2H), 4.66 (d, *J* = 1.5 Hz, 4H), 4.35 (dd, *J* = 12.5, 5.0 Hz, 2H), 4.12 (d, *J* = 2.0 Hz, 2H), 4.05 (dd, *J* = 12.5, 2.5 Hz, 2H), 3.90 (s, 2H), 3.46 (d, *J* = 5.0 Hz, 6H), 2.45 (s, 1H), 2.17 (s, 6H), 2.08 – 2.03 (m, 18H), 1.97 (d, *J* = 3.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.58, 169.76, 169.73, 169.47, 145.80, 123.10, 83.64, 79.78, 74.90, 72.28, 72.15, 71.69, 68.88, 68.34, 66.07, 64.73, 61.64, 58.67, 56.06, 20.75, 20.63. HRMS (ESI): *m/z* calc. for $C_{41}H_{55}N_7O_{21}Na$ $[M+Na]^+$: 1004.33432; found: 1004.33429.

Deprotection of the Boc-Protected compound Boc-αMan-yne-yne-OAc (4, AXX)

Compound **4** (0.31 g, 0.43 mmol) was dissolved in 1 mL DCM and trifluoroacetic acid (0.87 mL) dissolved in 0.87 mL DCM was added dropwise at 0 °C. After stirring at 0 °C for 1 hour, the reaction mixture was stirred at room temperature for 3 hours. After the reaction was completed, the mixture was concentrated to dryness. The residue was re-dissolved in CH_2Cl_2 (20 mL) and washed successively with H_2O (2 x 20 mL), followed by saturated aq. $NaHCO_3$ solution (20 mL). The organic layer was collected and dried over anhydrous Na_2SO_4, the solvent was evaporated to give a product **NH_2-αMan-yne-yne-OAc 20** (0.25 g, 96%) which was used directly without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.78 (s, 1H), 6.00 (d, *J* = 2.0 Hz, 1H), 5.93 (d, *J* = 7.0 Hz, 2H), 5.37 (t, *J* = 9.0 Hz, 1H), 4.69 (s, 2H), 4.35 (dd, *J* = 12.5, 5.5 Hz, 1H), 4.14 (d, *J* = 2.0 Hz, 4H), 4.05 (dd, *J* = 12.5, 2.5 Hz, 1H), 3.93 – 3.89 (m, 1H), 3.47 (d, *J* = 6.0 Hz, 6H), 2.44 (t, *J* = 2.0 Hz, 2H), 2.29 (s, 2H), 2.18 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.62, 169.81, 169.74, 169.50, 145.91, 123.09, 83.61, 79.69, 74.88, 72.16, 71.99, 71.41, 68.88 , 68.38, 66.08, 64.82, 61.63, 58.71, 56.13, 29.71 , 20.74, 20.63. HRMS (ESI): *m/z* calc. for $C_{27}H_{36}N_4O_{12}Na$ $[M+Na]^+$: 631.22219; found: 631.22212.

Deprotection of the Boc-Protected compound Boc-αMan-αMan-βGal-OAc (5, AAB)

Compound **5** (0.32 g, 0.22 mmol) was dissolved in 1 mL DCM and trifluoroacetic acid (0.44 mL) dissolved in 0.44 mL DCM was added dropwise at 0 °C. After stirring at 0 °C for 1 hour, the

reaction mixture was stirred at room temperature for 3 hours. After the reaction was completed, the mixture was concentrated to dryness. The residue was re-dissolved in CH_2Cl_2 (20 mL) and washed successively with H_2O (2 x 20 mL), followed by saturated aq. $NaHCO_3$ solution (20 mL). The organic layer was collected and dried over anhydrous Na_2SO_4, the solvent was evaporated to give a product **NH_2-αMan-αMan-βGal-OAc 14** (0.28 g, 96%) which was used directly without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.87 (s, 1H), 7.82 (d, *J* = 3.5 Hz, 2H), 6.11 – 6.08 (m, 2H), 5.96 – 5.91 (m, 4H), 5.89 (d, *J* = 9.5 Hz, 1H), 5.59 – 5.54 (m, 2H), 5.40 (t, *J* = 9.0 Hz, 2H), 5.29 (dd, *J* = 10.5, 3.5 Hz, 1H), 4.67 – 4.60 (m, 6H), 4.35 (dd, *J* = 12.5, 5.0 Hz, 2H), 4.28 (s, 1H), 4.15 (dd, *J* = 8.5, 6.5 Hz, 2H), 4.07 (d, *J* = 12.0 Hz, 2H), 3.93 (s, 2H), 3.45 (s, 4H), 3.38 (s, 2H), 2.20 (d, *J* = 12.0 Hz, 9H), 2.09 – 2.00 (m, 27H), 1.81 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.71, 170.54, 170.26, 169.93, 169.85, 169.64, 169.41, 145.82, 145.43, 123.37, 121.76, 83.86, 74.08, 72.22, 71.87, 70.95, 69.06, 68.52, 67.14, 66.12, 64.82, 64.44, 61.81, 61.35, 56.19, 20.92, 20.85, 20.74, 20.66, 20.33. HRMS (ESI): *m/z* calc. for $C_{55}H_{74}N_{10}O_{30}Na$ $[M+Na]^+$: 1377.44645; found: 1377.44636.

Deprotection of the Boc-Protected compound Boc-αMan-αMan-βGlu-OAc (6, AAC)

Compound **6** (0.39 g, 0.27 mmol) was dissolved in 1 mL DCM and trifluoroacetic acid (0.54 mL) dissolved in 0.54 mL DCM was added dropwise at 0 °C. After stirring at 0 °C for 1 hour, the reaction mixture was stirred at room temperature for 3 hours. After the reaction was completed, the mixture was concentrated to dryness. The residue was re-dissolved in CH_2Cl_2 (20 mL) and washed successively with H_2O (2 x 20 mL), followed by saturated aq. $NaHCO_3$ solution (20 mL). The organic layer was collected and dried over anhydrous Na_2SO_4, the solvent was evaporated to give a product **NH_2-αMan-αMan-βGlu-OAc 15** (0.36 g, 98%) which was used directly without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84 (s, 1H), 7.81 (d, *J* = 2.5 Hz, 2H), 6.09 (d, *J* = 2.0 Hz, 2H), 5.96 – 5.90 (m, 5H), 5.47 (dd, *J* = 16.5, 9.0 Hz, 2H), 5.39 (t, *J* = 9.0 Hz, 2H), 5.25 (t, *J* = 9.5 Hz, 1H), 4.69 – 4.59 (m, 6H), 4.35 (dd, *J* = 12.5, 5.0 Hz, 2H), 4.30 (dd, *J* = 12.5, 5.0 Hz, 1H), 4.15 (d, *J* = 10.5 Hz, 1H), 4.07 (dd, *J* = 12.5, 2.0 Hz, 3H), 3.94 – 3.90 (m, 2H), 3.45 (s, 4H), 3.39 (s, 2H), 2.19 (s, 6H), 2.09 – 2.01 (m, 30H), 1.87 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.56, 169.94, 169.77, 169.70, 169.52, 169.43, 169.09, 145.63, 145.60, 145.39, 123.23, 121.59, 85.48, 83.72, 74.95, 72.66, 72.24, 72.06, 71.73, 70.25, 68.92, 68.34, 67.80, 65.96, 64.61, 64.45, 61.67, 56.12, 20.78, 20.70, 20.59, 20.53, 20.10. HRMS (ESI): *m/z* calc. for $C_{55}H_{74}N_{10}O_{30}Na$ $[M+Na]^+$: 1377.44645; found: 1377.44638.

Deprotection of the Boc-Protected compound Boc-αMan-βGal-βGal-OAc (9, ABB)

Compound **9** (0.25 g, 0.17 mmol) was dissolved in 1 mL DCM and trifluoroacetic acid (0.34 mL) dissolved in 0.34 mL DCM was added dropwise at 0 °C. After stirring at 0 °C for 1 hour, the reaction mixture was stirred at room temperature for 3 hours. After the reaction was completed, the mixture was concentrated to dryness. The residue was re-dissolved in CH_2Cl_2 (20 mL) and washed successively with H_2O (2 x 20 mL), followed by saturated aq. $NaHCO_3$ solution (20 mL). The organic layer was collected and dried over anhydrous Na_2SO_4, the solvent was evaporated to give a product **NH_2-αMan-βGal-βGal-OAc 16** (0.22 g, 97%) which was used directly without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 3.5 Hz, 2H), 7.85 (s, 1H), 6.13 (d, *J* = 1.5 Hz, 1H), 5.95 (dd, *J* = 4.5, 2.0 Hz, 2H), 5.90 (dd, *J* = 9.5, 2.0 Hz, 2H), 5.62 – 5.56 (m, 2H), 5.55 (d, *J* = 3.5 Hz, 2H), 5.42 (t, *J* = 9.5 Hz, 1H), 5.28 (dd, *J* = 10.5, 3.5 Hz, 2H), 4.66 – 4.58

(m, 6H), 4.37 – 4.33 (m, 1H), 4.28 (t, *J* = 6.5 Hz, 2H), 4.16 (dd, *J* = 11.5, 5.0 Hz, 4H), 4.08 – 4.05 (m, 1H), 3.96 – 3.92 (m, 1H), 3.47 – 3.40 (m, 6H), 2.21 (d, *J* = 7.5 Hz, 9H), 2.09 – 2.00 (m, 27H), 1.96 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.66, 170.48, 170.20, 169.95, 169.79, 169.67, 169.27, 145.67, 145.44, 123.51, 121.72, 86.11, 83.85, 74.00, 72.31, 72.11, 71.79, 70.89, 69.06, 68.52, 68.04, 67.07, 65.98, 64.73, 64.56, 61.78, 61.28, 56.25, 29.76, 20.76, 20.59, 20.28. HRMS (ESI): *m/z* calc. for $C_{55}H_{74}N_{10}O_{30}Na$ $[M+Na]^+$: 1377.44645; found: 1377.44640.

Deprotection of the Boc-Protected compound Boc-αMan-βGlu-βGlu-OAc (10, ACC)

Compound **10** (0.37 g, 0.25 mmol) was dissolved in 1 mL DCM and trifluoroacetic acid (0.50 mL) dissolved in 0.50 mL DCM was added dropwise at 0 °C. After stirring at 0 °C for 1 hour, the reaction mixture was stirred at room temperature for 3 hours. After the reaction was completed, the mixture was concentrated to dryness. The residue was re-dissolved in CH_2Cl_2 (20 mL) and washed successively with H_2O (2 x 20 mL), followed by saturated aq. $NaHCO_3$ solution (20 mL). The organic layer was collected and dried over anhydrous Na_2SO_4, the solvent was evaporated to give a product **NH_2-αMan-βGlu-βGlu-OAc 17** (0.32 g, 93%) which was used directly without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 4.0 Hz, 2H), 7.81 (s, 1H), 6.11 (d, *J* = 2.0 Hz, 1H), 5.97 – 5.92 (m, 4H), 5.51 (td, *J* = 9.5, 3.5 Hz, 2H), 5.43 (dd, *J* = 18.0, 8.5 Hz, 3H), 5.30 (t, *J* = 10.0 Hz, 2H), 4.66 – 4.60 (m, 6H), 4.37 – 4.29 (m, 3H), 4.16 (d, *J* = 12.5 Hz, 2H), 4.09 – 4.05 (m, 3H), 3.96 – 3.92 (m, 1H), 3.46 – 3.40 (m, 6H), 2.20 (s, 3H), 2.13 – 1.98 (m, 33H), 1.75 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.63, 170.04, 169.87, 169.76, 169.54 , 169.07, 145.77, 145.68, 123.26, 121.51, 85.62, 83.81, 75.07, 72.80, 72.55, 72.14, 70.37, 68.98, 68.47, 67.88, 66.03, 64.74, 64.65, 61.70, 56.11, 20.75, 20.65, 20.60, 20.17. HRMS (ESI): *m/z* calc. for $C_{55}H_{74}N_{10}O_{30}Na$ $[M+Na]^+$: 1377.44645; found: 1377.44628.

Deprotection of the Boc-Protected compound Boc-βGal-βGal-βGal-OAc (11, BBB)

Compound **11** (0.25 g, 0.17 mmol) was dissolved in 1 mL DCM and trifluoroacetic acid (0.34 mL) dissolved in 0.34 mL DCM was added dropwise at 0 °C. After stirring at 0 °C for 1 hour, the reaction mixture was stirred at room temperature for 3 hours. After the reaction was completed, the mixture was concentrated to dryness. The residue was re-dissolved in CH_2Cl_2 (20 mL) and washed successively with H_2O (2 x 20 mL), followed by saturated aq. $NaHCO_3$ solution (20 mL). The organic layer was collected and dried over anhydrous Na_2SO_4, the solvent was evaporated to give a product **NH_2-βGal-βGal-βGal-OAc 21** (0.22 g, 97%) which was used directly without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85 (s, 3H), 5.91 (d, *J* = 9.0 Hz, 3H), 5.61 – 5.51 (m, 6H), 5.28 (d, *J* = 1.5 Hz, 8H), 4.62 (d, *J* = 3.5 Hz, 7H), 4.27 (t, *J* = 6.5 Hz, 3H), 4.16 (d, *J* = 6.5 Hz, 6H), 3.39 (d, *J* = 10.0 Hz, 6H), 2.19 (d, *J* = 1.5 Hz, 10H), 2.01 (d, *J* = 2.0 Hz, 21H), 1.98 (d, *J* = 1.5 Hz, 9H), 1.79 (d, *J* = 1.5 Hz, 10H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.49, 170.11, 169.10, 145.68 (s, 2H), 121.71 (s, 3H), 86.13 (s, 3H), 73.99 (s, 3H), 72.37, 70.94, 68.10, 67.03, 64.81, 61.25, 53.61, 21.05, 20.34. HRMS (ESI): *m/z* calc. for $C_{55}H_{74}N_{10}O_{30}Na$ $[M+Na]^+$: 1377.44645; found: 1377.44642.

Deprotection of the Boc-Protected compound Boc-βGlu-βGlu-βGlu-OAc (12, CCC)

Compound **12** (0.37 g, 0.25 mmol) was dissolved in 1 mL DCM and trifluoroacetic acid (0.50 mL) dissolved in 0.50 mL DCM was added dropwise at 0 °C. After stirring at 0 °C for 1 hour, the reaction mixture was stirred at room temperature for 3 hours. After the reaction was completed,

the mixture was concentrated to dryness. The residue was re-dissolved in CH_2Cl_2 (20 mL) and washed successively with H_2O (2 x 20 mL), followed by saturated aq. $NaHCO_3$ solution (20 mL). The organic layer was collected and dried over anhydrous Na_2SO_4, the solvent was evaporated to give a product **NH_2-βGlu-βGlu-βGlu-OAc 22** (0.32 g, 93%) which was used directly without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92 (s, 3H), 5.96 (d, *J* = 9.5 Hz, 3H), 5.50 (t, *J* = 9.5 Hz, 7H), 5.41 (t, *J* = 9.5 Hz, 3H), 5.30 (t, *J* = 9.5 Hz, 6H), 5.26 (d, *J* = 0.5 Hz, 2H), 4.60 (s, 7H), 4.28 (dd, *J* = 12.5, 5.0 Hz, 4H), 4.12 (d, *J* = 12.0 Hz, 7H), 3.69 – 3.62 (m, 3H), 3.40 (d, *J* = 5.5 Hz, 7H), 2.04 (s, 34H), 2.00 (d, *J* = 3.0 Hz, 18H), 1.78 (s, 10H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.68, 170.11, 169.59, 168.99, 145.86, 121.48, 85.66, 75.09, 72.87, 72.38, 70.40, 67.88, 64.85, 61.72, 58.28, 53.60, 20.99, 20.21. HRMS (ESI): *m/z* calc. for $C_{55}H_{74}N_{10}O_{30}Na$ $[M+Na]^+$: 1377.44645; found: 1377.44644.

Synthesis of Pentafluorophenyl acrylate (PFPA)

PFPA was synthesized according to the general procedure published recently.[4] To the solution of pentafluorophenol (0.62 g, 3.37 mmol) in anhydrous DCM (6 mL) at 0 °C was added dropwise freshly distilled trimethylamine (0.55 mL, 3.97 mmol). The mixture was stirred at 0 °C for 15 min, and then acryloyl chloride (0.32 mL, 3.97 mmol) was added dropwise. After stirred at 0 °C for further 30 min, the reaction mixture was allowed to stir at room temperature for 2 h. After completion of the reaction, the reaction mixture was diluted with DCM, filtered, and washed with DCM. The filtrate was extracted twice with brine. The organic phase was dried over anhydrous Na_2SO_4, filtered, concentrated. The residue was purified by SGC chromatography (100% petroleum ether) to give the product PFPA as a colorless oil (0.56 g, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.72 (d, *J* = 17.0 Hz, 1H), 6.37 (dd, *J* = 17.5, 10.5 Hz, 1H), 6.18 (d, *J* = 10.5 Hz, 1H). ^{19}F NMR (470 MHz, $CDCl_3$): δ = -152.52 (m, 2F, *ortho*), -158.08 (t, 1F, *para*), -162.26 (m, 2F, *meta*).

Synthesis of P(αMan-αMan-αMan-OAc)

Into a solution of pPFPA (30 mg, 0.13 mmol) and NH_2-αMan-αMan-αMan-OAc **13** (239.1 mg, 0.18 mmol) in dry DMF (2 mL) was added dimethylaminopyridine (DMAP) (7.7 mg, 0.06 mmol) under nitrogen atmosphere. The reaction mixture was allowed to stir at 65 °C for 24 hours in nitrogen-filled glove box. After the completion of the reaction, the reaction solution was precipitated in diethyl ether, centrifuged to obtain the crude glycopolymer, then redissolved in THF, precipitated again twice into diethyl ether, centrifuged, and finally dried in a vacuum oven at 40 °C. The product **P(αMan-αMan-αMan-OAc)** was obtained as light yellow powder (99.5 mg, 56%). There was no fluorine signal in the ^{19}F NMR of the product. FT-IR (KBr, cm^{-1}): 1754 (C=O stretching of OAc ester), 1652 (C=O stretching of carbonyl in amide bond).

Synthesis of P(αMan-αMan-βGal-OAc)

Into a solution of pPFPA (30 mg, 0.13 mmol) and NH_2-αMan-αMan-βGal-OAc **14** (239.1 mg, 0.18 mmol) in dry DMF (2 mL) was added dimethylaminopyridine (DMAP) (7.7 mg, 0.06 mmol) under nitrogen atmosphere. The reaction mixture was allowed to stir at 65 °C for 24 hours in nitrogen-filled glove box. After the completion of the reaction, the reaction solution was precipitated in diethyl ether, centrifuged to obtain the crude glycopolymer, then redissolved in THF, precipitated again twice into diethyl ether, centrifuged, and finally dried in a vacuum oven at

40 °C. The product **P(αMan-αMan-βGal-OAc)** was obtained as light yellow powder (97.7 mg, 55%). There was no fluorine signal in the ^{19}F NMR of the product. FT-IR (KBr, cm^{-1}): 1754 (C=O stretching of OAc ester), 1652 (C=O stretching of carbonyl in amide bond).

Synthesis of P(αMan-αMan-βGlu-OAc)

Into a solution of pPFPA (30 mg, 0.13 mmol) and NH_2-αMan-αMan-βGlu-OAc **15** (239.1 mg, 0.18 mmol) in dry DMF (2 mL) was added dimethylaminopyridine (DMAP) (7.7 mg, 0.06 mmol) under nitrogen atmosphere. The reaction mixture was allowed to stir at 65 °C for 24 hours in nitrogen-filled glove box. After the completion of the reaction, the reaction solution was precipitated in diethyl ether, centrifuged to obtain the crude glycopolymer, then redissolved in THF, precipitated again twice into diethyl ether, centrifuged, and finally dried in a vacuum oven at 40 °C. The product **P(αMan-αMan-βGlu-OAc)** was obtained as light yellow powder (103.0 mg, 58%). There was no fluorine signal in the ^{19}F NMR of the product. FT-IR (KBr, cm^{-1}): 1753 (C=O stretching of OAc ester), 1652 (C=O stretching of carbonyl in amide bond).

Synthesis of P(αMan-βGal-βGal-OAc)

Into a solution of pPFPA (30 mg, 0.13 mmol) and NH_2-αMan-βGal-βGal-OAc **16** (239.1 mg, 0.18 mmol) in dry DMF (2 mL) was added dimethylaminopyridine (DMAP) (7.7 mg, 0.06 mmol) under nitrogen atmosphere. The reaction mixture was allowed to stir at 65 °C for 24 hours in nitrogen-filled glove box. After the completion of the reaction, the reaction solution was precipitated in diethyl ether, centrifuged to obtain the crude glycopolymer, then redissolved in THF, precipitated again twice into diethyl ether, centrifuged, and finally dried in a vacuum oven at 40 °C. The product **P(αMan-βGal-βGal-OAc)** was obtained as light yellow powder (99.4 mg, 56%). There was no fluorine signal in the ^{19}F NMR of the product. FT-IR (KBr, cm^{-1}): 1754 (C=O stretching of OAc ester), 1652 (C=O stretching of carbonyl in amide bond).

Synthesis of P(αMan-βGlu-βGlu-OAc)

Into a solution of pPFPA (30 mg, 0.13 mmol) and NH_2-αMan-βGlu-βGlu-OAc **17** (239.1 mg, 0.18 mmol) in dry DMF (2 mL) was added dimethylaminopyridine (DMAP) (7.7 mg, 0.06 mmol) under nitrogen atmosphere. The reaction mixture was allowed to stir at 65 °C for 24 hours in nitrogen-filled glove box. After the completion of the reaction, the reaction solution was precipitated in diethyl ether, centrifuged to obtain the crude glycopolymer, then redissolved in THF, precipitated again twice into diethyl ether, centrifuged, and finally dried in a vacuum oven at 40 °C. The product **P(αMan-βGlu-βGlu-OAc)** was obtained as light yellow powder (103.0 mg, 58%). There was no fluorine signal in the ^{19}F NMR of the product. FT-IR (KBr, cm^{-1}): 1754 (C=O stretching of OAc ester), 1651 (C=O stretching of carbonyl in amide bond).

Synthesis of P(αMan-αMan-yne-OAc)

Into a solution of pPFPA (50 mg, 0.21 mmol) and NH_2-αMan-αMan-yne-OAc **19** (288.7 mg, 0.29 mmol) in dry DMF (4 mL) was added dimethylaminopyridine (DMAP) (12.8 mg, 0.10 mmol) under nitrogen atmosphere. The reaction mixture was allowed to stir at 65 °C for 24 hours in nitrogen-filled glove box. After the completion of the reaction, the reaction solution was precipitated in diethyl ether, centrifuged to obtain the crude glycopolymer, then redissolved in

THF, precipitated again twice into diethyl ether, centrifuged, and finally dried in a vacuum oven at 40 °C. The product **P(αMan-αMan-yne-OAc)** was obtained as light yellow powder (119.7 mg, 55%). There was no fluorine signal in the ^{19}F NMR of the product. FT-IR (KBr, cm^{-1}): 1754 (C=O stretching of OAc ester), 1651 (C=O stretching of carbonyl in amide bond).

Synthesis of P(αMan-yne-yne-OAc)

Into a solution of pPFPA (50 mg, 0.21 mmol) and NH_2-αMan-yne-yne-OAc **20** (179.9 mg, 0.29 mmol) in dry DMF (4 mL) was added dimethylaminopyridine (DMAP) (12.8 mg, 0.10 mmol) under nitrogen atmosphere. The reaction mixture was allowed to stir at 65 °C for 24 hours in nitrogen-filled glove box. After the completion of the reaction, the reaction solution was precipitated in diethyl ether, centrifuged to obtain the crude glycopolymer, then redissolved in THF, precipitated again twice into diethyl ether, centrifuged, and finally dried in a vacuum oven at 40 °C. The product **P(αMan-yne-yne-OAc)** was obtained as light yellow powder (77.9 mg, 56%). There was no fluorine signal in the ^{19}F NMR of the product. FT-IR (KBr, cm^{-1}): 1755 (C=O stretching of OAc ester), 1651 (C=O stretching of carbonyl in amide bond).

Synthesis of P(βGal-βGal-βGal-OAc)

Into a solution of pPFPA (30 mg, 0.13 mmol) and NH_2-βGal-βGal-βGal-OAc **21** (239.1 mg, 0.18 mmol) in dry DMF (2 mL) was added dimethylaminopyridine (DMAP) (7.7 mg, 0.06 mmol) under nitrogen atmosphere. The reaction mixture was allowed to stir at 65 °C for 24 hours in nitrogen-filled glove box. After the completion of the reaction, the reaction solution was precipitated in diethyl ether, centrifuged to obtain the crude glycopolymer. then redissolved in THF, precipitated again twice into diethyl ether, centrifuged, and finally dried in a vacuum oven at 40 °C. The product **P(βGal-βGal-βGal-OAc)** was obtained as light yellow powder (99.3 mg, 56%). There was no fluorine signal in the ^{19}F NMR of the product. FT-IR (KBr, cm^{-1}): 1754 (C=O stretching of OAc ester), 1652 (C=O stretching of carbonyl in amide bond).

Synthesis of P(βGlu-βGlu-βGlu-OAc)

Into a solution of pPFPA (30 mg, 0.13 mmol) and NH_2-βGlu-βGlu-βGlu-OAc **22** (239.1 mg, 0.18 mmol) in dry DMF (2 mL) was added dimethylaminopyridine (DMAP) (7.7 mg, 0.06 mmol) under nitrogen atmosphere. The reaction mixture was allowed to stir at 65 °C for 24 hours in nitrogen-filled glove box. After the completion of the reaction, the reaction solution was precipitated in diethyl ether, centrifuged to obtain the crude glycopolymer, then redissolved in THF, precipitated again twice into diethyl ether, centrifuged, and finally dried in a vacuum oven at 40 °C. The product **P(βGlu-βGlu-βGlu-OAc)** was obtained as light yellow powder (103.0 mg, 58%). There was no fluorine signal in the ^{19}F NMR of the product. FT-IR (KBr, cm^{-1}): 1754 (C=O stretching of OAc ester), 1651 (C=O stretching of carbonyl in amide bond).

Synthesis of deacetylated glycopolymer P(αMan-αMan-αMan) (P1)

OAc-Protected glycopolymer P(αMan-αMan-αMan-OAc) (50 mg, 0.04 mmol) was dissolved in MeOH/DCM (2 mL, 1: 1 v/v) and sodium methoxide (23 mg) in MeOH (0.5 mL) was added at room temperature. The reaction mixture was stirred at room temperature for 1 hour. Subsequently the solvent was evaporated, the residue was redissolved in H_2O, and then the Dowex H^+ resin was

added to neutralize to pH = 7. The aqueous solution was filtered and purified by dialysis against methyl alcohol (MWCO 3500 Da). The final glycopolymer **P1** P(αMan-αMan-αMan) was obtained after lyophilisation as a pale brown powder (31.5 mg, 98%). FT-IR (KBr, cm^{-1}): 3430 (O-H stretching in carbohydrate), 1645 (C=O stretching of carbonyl in amide bond).

Synthesis of deacetylated glycopolymer P(αMan-αMan-βGal) (P2)

OAc-Protected glycopolymer P(αMan-αMan-βGal-OAc) (50 mg, 0.04 mmol) was dissolved in MeOH/DCM (2 mL, 1: 1 v/v) and sodium methoxide (23 mg) in MeOH (0.5 mL) was added at room temperature. The reaction mixture was stirred at room temperature for 1 hour. Subsequently the solvent was evaporated, the residue was redissolved in H_2O, and then the Dowex H^+ resin was added to neutralize to pH = 7. The aqueous solution was filtered and purified by dialysis against methyl alcohol (MWCO 3500 Da). The final glycopolymer **P2** P(αMan-αMan-βGal) was obtained after lyophilisation as a pale brown powder (30.5 mg, 95%). FT-IR (KBr, cm^{-1}): 3433 (O-H stretching in carbohydrate), 1640 (C=O stretching of carbonyl in amide bond).

Synthesis of deacetylated glycopolymer P(αMan-αMan-βGlu) (P3)

OAc-Protected glycopolymer P(αMan-αMan-βGlu-OAc) (50 mg, 0.04 mmol) was dissolved in MeOH/DCM (2 mL, 1: 1 v/v) and sodium methoxide (23 mg) in MeOH (0.5 mL) was added at room temperature. The reaction mixture was stirred at room temperature for 1 hour. Subsequently the solvent was evaporated, the residue was redissolved in H_2O, and then the Dowex H^+ resin was added to neutralize to pH = 7. The aqueous solution was filtered and purified by dialysis against methyl alcohol (MWCO 3500 Da). The final glycopolymer **P3** P(αMan-αMan-βGlu) was obtained after lyophilisation as a pale brown powder (31.1 mg, 97%). FT-IR (KBr, cm^{-1}): 3438 (O-H stretching in carbohydrate), 1644 (C=O stretching of carbonyl in amide bond).

Synthesis of deacetylated glycopolymer P(αMan-αMan-yne) (P4)

OAc-Protected glycopolymer P(αMan-αMan-yne-OAc) (50 mg, 0.05 mmol) was dissolved in MeOH/DCM (2 mL, 1: 1 v/v) and sodium methoxide (21 mg) in MeOH (0.5 mL) was added at room temperature. The reaction mixture was stirred at room temperature for 1 hour. Subsequently the solvent was evaporated, the residue was redissolved in H_2O, and then the Dowex H^+ resin was added to neutralize to pH = 7. The aqueous solution was filtered and purified by dialysis against methyl alcohol (MWCO 3500 Da). The final glycopolymer **P4** P(αMan-αMan-yne) was obtained after lyophilisation as a pale brown powder (32.4 mg, 97%). FT-IR (KBr, cm^{-1}): 3435 (O-H stretching in carbohydrate), 1646 (C=O stretching of carbonyl in amide bond).

Synthesis of deacetylated glycopolymer P(αMan-βGal-βGal) (P6)

OAc-Protected glycopolymer P(αMan-βGal-βGal-OAc) (50 mg, 0.04 mmol) was dissolved in MeOH/DCM (2 mL, 1: 1 v/v) and sodium methoxide (23 mg) in MeOH (0.5 mL) was added at room temperature. The reaction mixture was stirred at room temperature for 1 hour. Subsequently the solvent was evaporated, the residue was redissolved in H_2O, and then the Dowex H^+ resin was added to neutralize to pH = 7. The aqueous solution was filtered and purified by dialysis against methyl alcohol (MWCO 3500 Da). The final glycopolymer **P6** P(αMan-βGal-βGal) was obtained after lyophilisation as a pale brown powder (30.5 mg, 95%). FT-IR (KBr, cm^{-1}): 3422 (O-H

stretching in carbohydrate), 1646 (C=O stretching of carbonyl in amide bond).

Synthesis of deacetylated glycopolymer P(αMan-βGlu-βGlu) (P7)

OAc-Protected glycopolymer P(αMan-βGlu-βGlu-OAc) (50 mg, 0.04 mmol) was dissolved in MeOH/DCM (2 mL, 1: 1 v/v) and sodium methoxide (23 mg) in MeOH (0.5 mL) was added at room temperature. The reaction mixture was stirred at room temperature for 1 hour. Subsequently the solvent was evaporated, the residue was redissolved in H_2O, and then the Dowex H^+ resin was added to neutralize to pH = 7. The aqueous solution was filtered and purified by dialysis against methyl alcohol (MWCO 3500 Da). The final glycopolymer **P7** P(αMan-βGlu-βGlu) was obtained after lyophilisation as a pale brown powder (31.1 mg, 97%). FT-IR (KBr, cm^{-1}): 3432 (O-H stretching in carbohydrate), 1644 (C=O stretching of carbonyl in amide bond).

Synthesis of deacetylated glycopolymer P(αMan-yne-yne) (P8)

OAc-Protected glycopolymer P(αMan-yne-yne-OAc) (50 mg, 0.08 mmol) was dissolved in MeOH/DCM (2 mL, 1: 1 v/v) and sodium methoxide (16 mg) in MeOH (0.5 mL) was added at room temperature. The reaction mixture was stirred at room temperature for 1 hour. Subsequently the solvent was evaporated, the residue was redissolved in H_2O, and then the Dowex H^+ resin was added to neutralize to pH = 7. The aqueous solution was filtered and purified by dialysis against methyl alcohol (MWCO 3500 Da). The final glycopolymer **P8** P(αMan-yne-yne) was obtained after lyophilisation as a pale brown powder (35.8 mg, 96%). FT-IR (KBr, cm^{-1}): 3437 (O-H stretching in carbohydrate), 1649 (C=O stretching of carbonyl in amide bond).

Synthesis of deacetylated glycopolymer P(βGal-βGal-βGal) (P9)

OAc-Protected glycopolymer P(βGal-βGal-βGal-OAc) (50 mg, 0.04 mmol) was dissolved in MeOH/DCM (2 mL, 1: 1 v/v) and sodium methoxide (23 mg) in MeOH (0.5 mL) was added at room temperature. The reaction mixture was stirred at room temperature for 1 hour. Subsequently the solvent was evaporated, the residue was redissolved in H_2O, and then the Dowex H^+ resin was added to neutralize to pH = 7. The aqueous solution was filtered and purified by dialysis against methyl alcohol (MWCO 3500 Da). The final glycopolymer **P9** P(βGal-βGal-βGal) was obtained after lyophilisation as a pale brown powder (30.5 mg, 95%). FT-IR (KBr, cm^{-1}): 3422 (O-H stretching in carbohydrate), 1646 (C=O stretching of carbonyl in amide bond).

Synthesis of deacetylated glycopolymer P(βGlu-βGlu-βGlu) (P10)

OAc-Protected glycopolymer P(βGlu-βGlu-βGlu-OAc) (50 mg, 0.04 mmol) was dissolved in MeOH/DCM (2 mL, 1: 1 v/v) and sodium methoxide (23 mg) in MeOH (0.5 mL) was added at room temperature. The reaction mixture was stirred at room temperature for 1 hour. Subsequently the solvent was evaporated, the residue was redissolved in H_2O, and then the Dowex H^+ resin was added to neutralize to pH = 7. The aqueous solution was filtered and purified by dialysis against methyl alcohol (MWCO 3500 Da). The final glycopolymer **P10** P(βGlu-βGlu-βGlu) was obtained after lyophilisation as a pale brown powder (31.1 mg, 97%). FT-IR (KBr, cm^{-1}): 3432 (O-H stretching in carbohydrate), 1644 (C=O stretching of carbonyl in amide bond).

1.3 References

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2. Copies of NMR spectra of compounds and glycopolymers

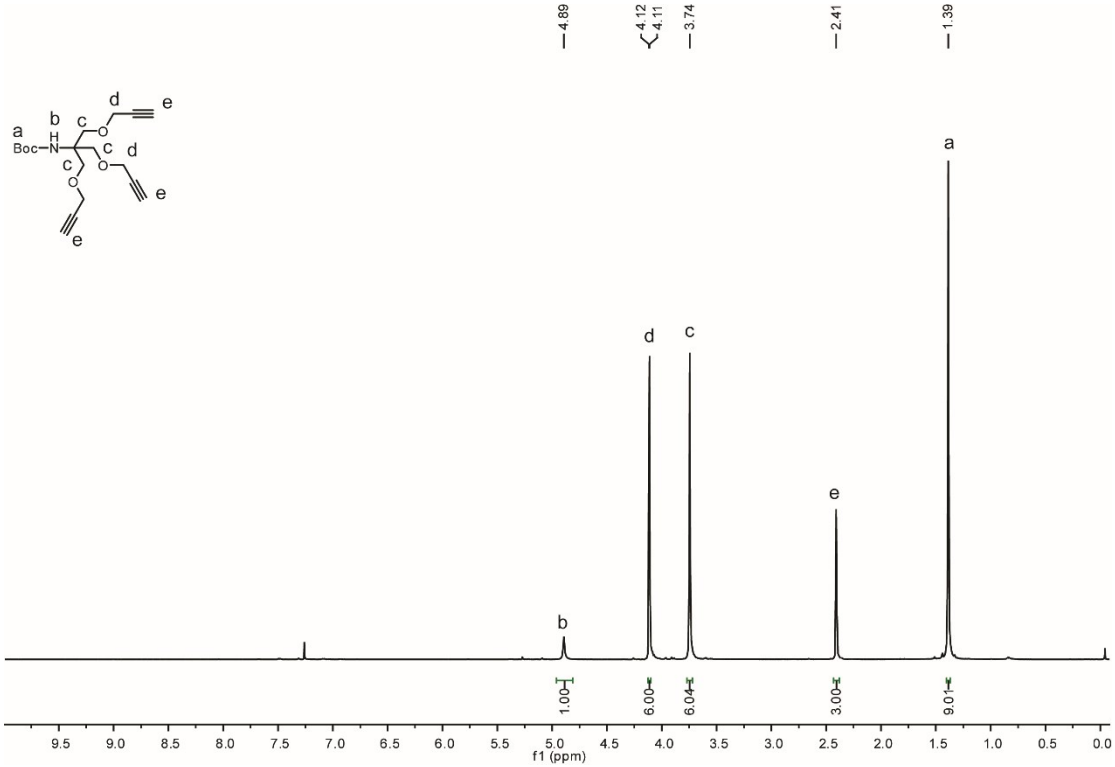

Figure S1. ^{1}H NMR spectrum of Compound **1** in $CDCl_3$.

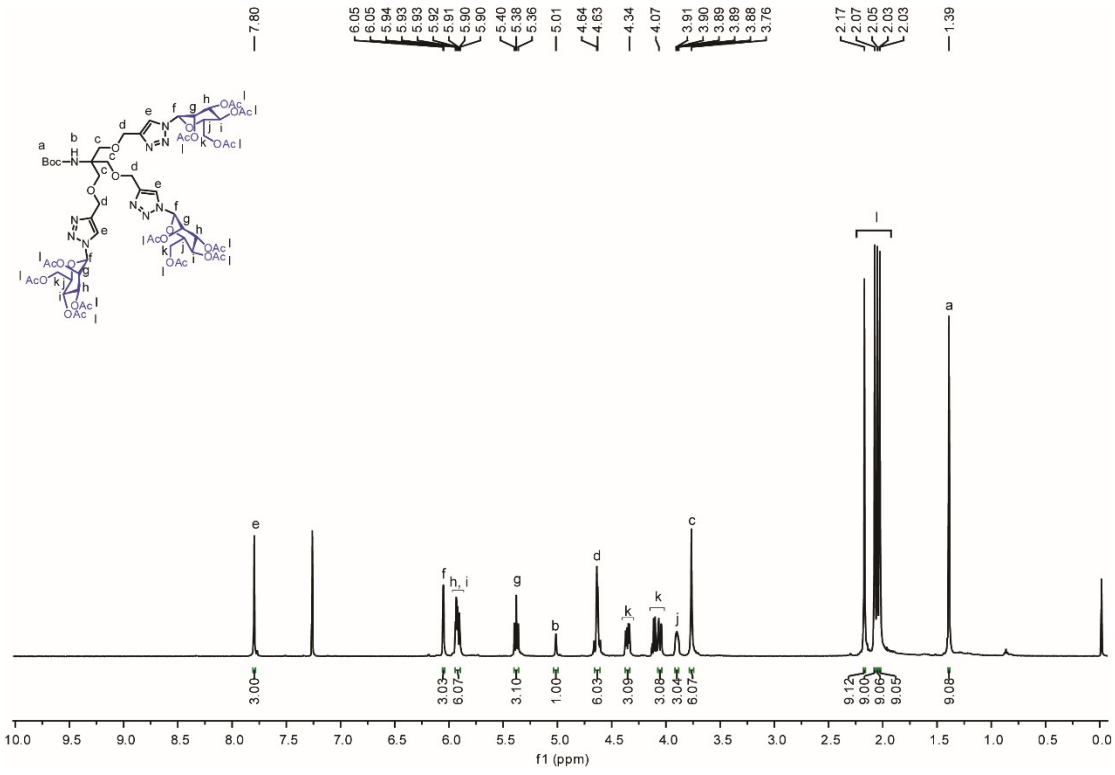

Figure S2. ^{1}H NMR spectrum of Compound **2** in $CDCl_3$

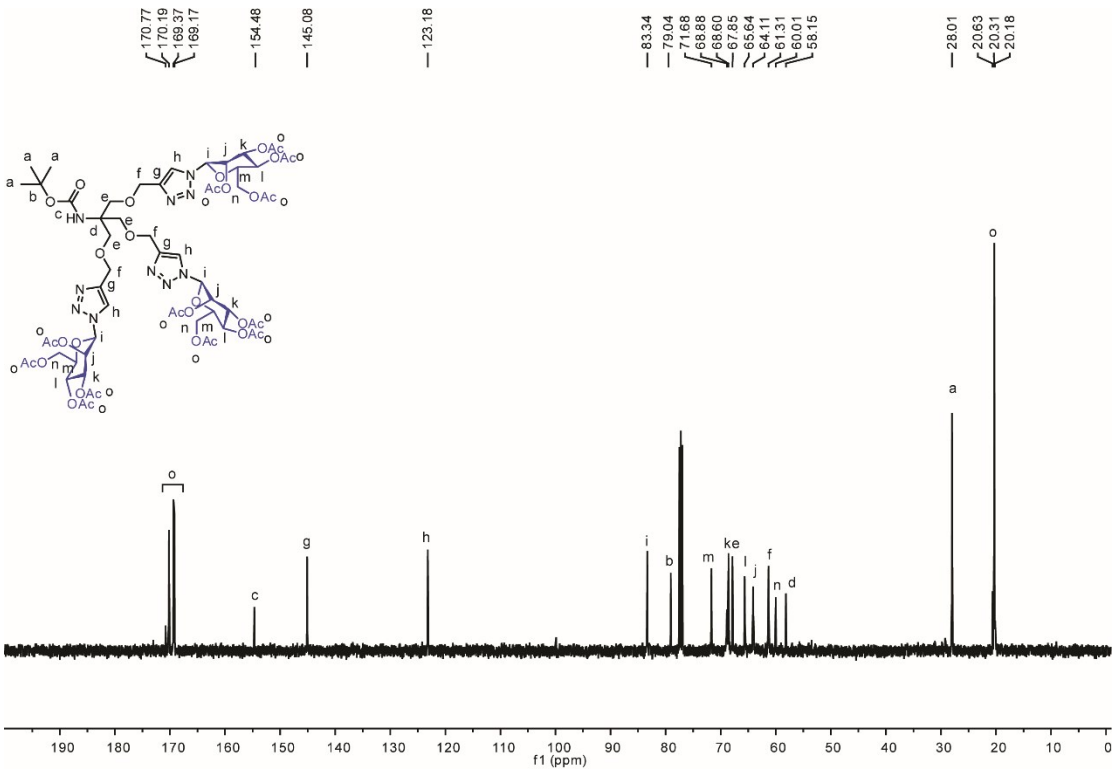

Figure S3. ^{13}C NMR spectrum of compound **2** in $CDCl_3$

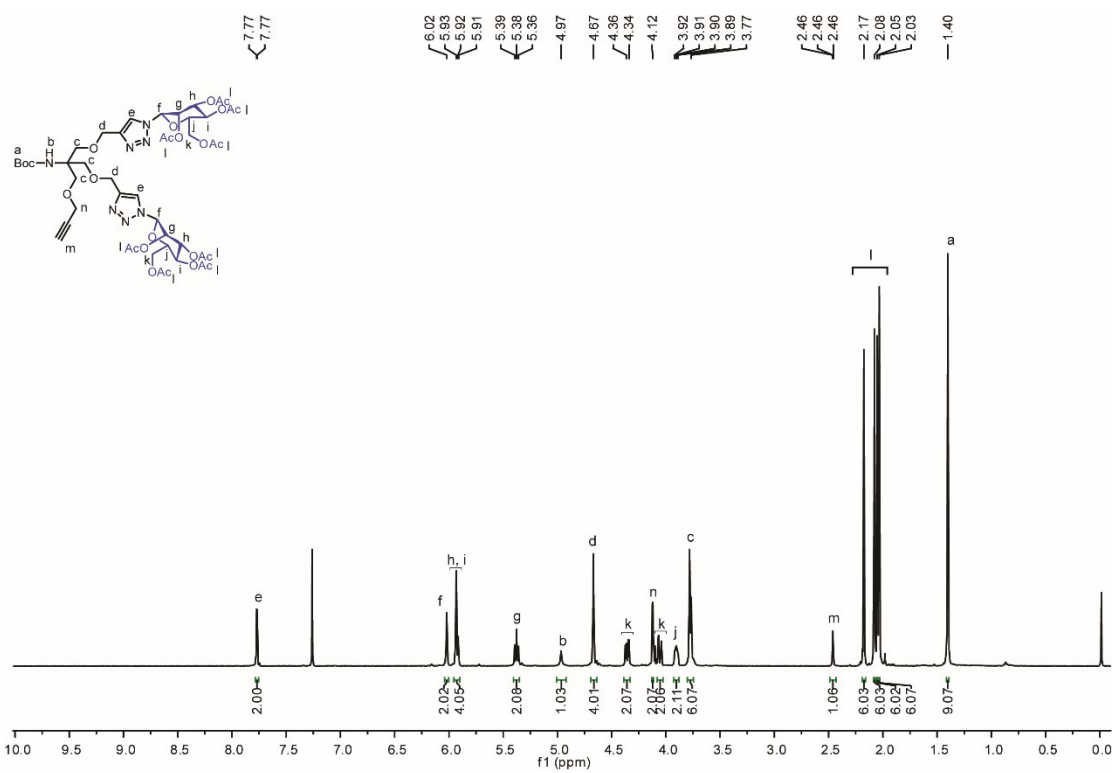

Figure S4. ^{1}H NMR spectrum of Compound **3** in $CDCl_3$

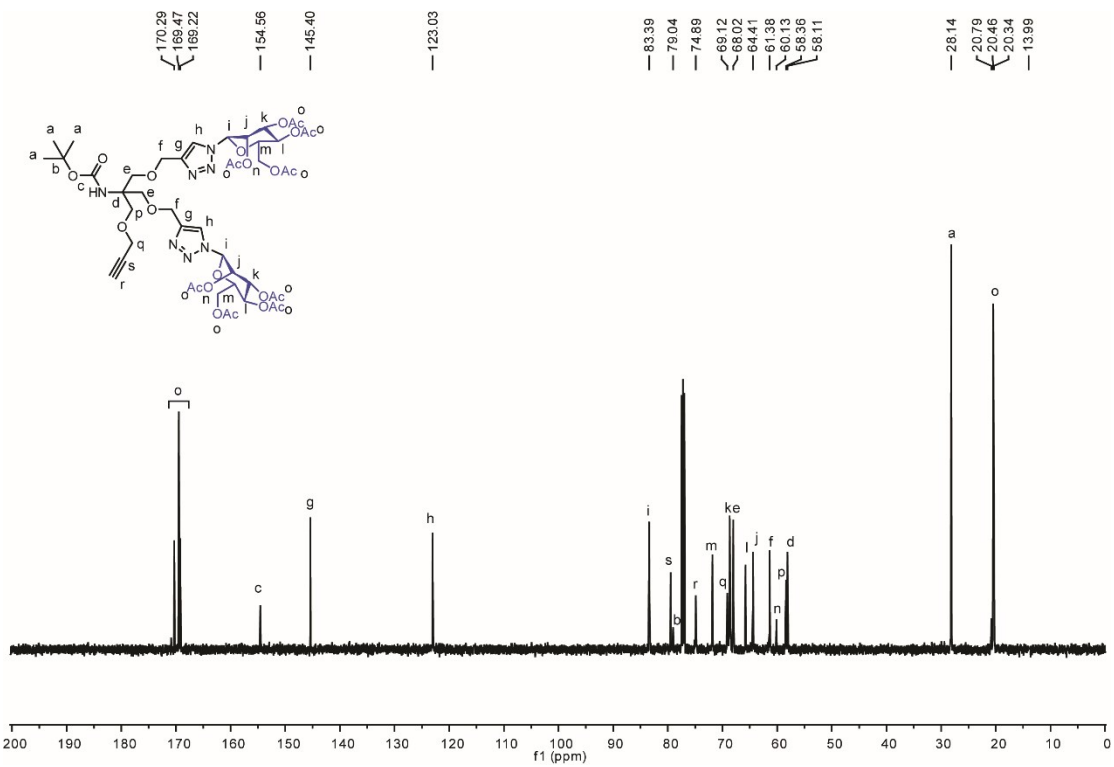

Figure S5. ^{13}C NMR spectrum of compound **3** in $CDCl_3$

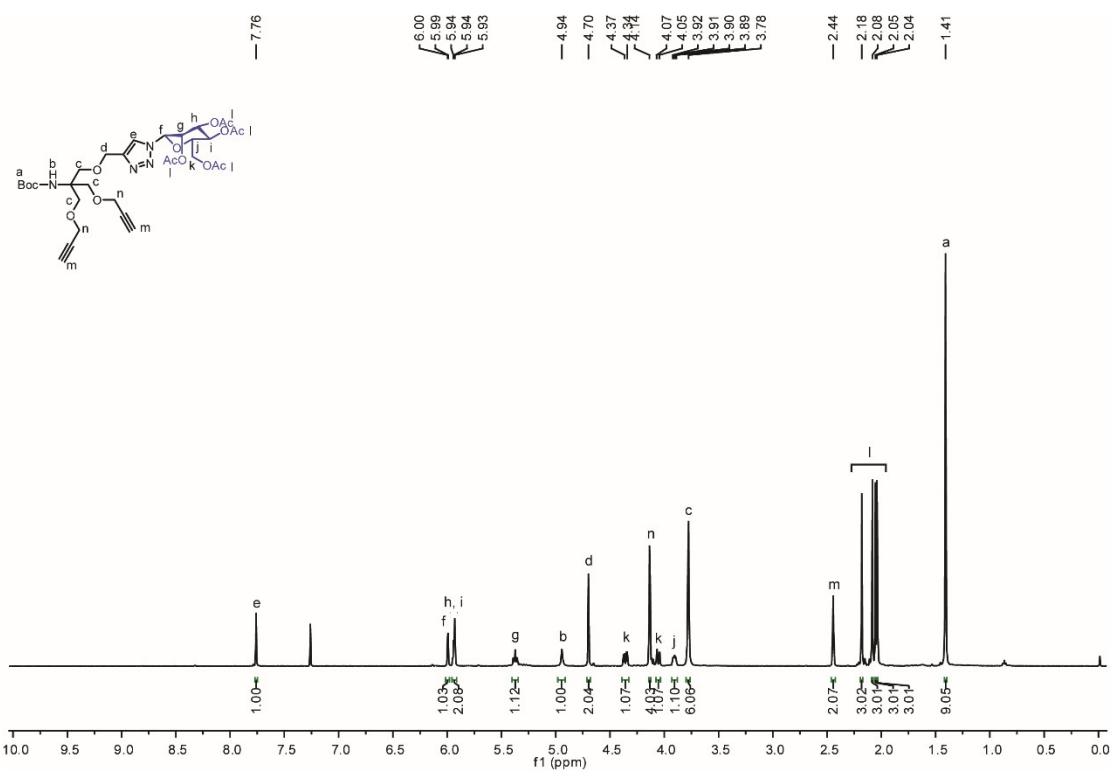

Figure S6. ^{1}H NMR spectrum of Compound **4** in $CDCl_3$

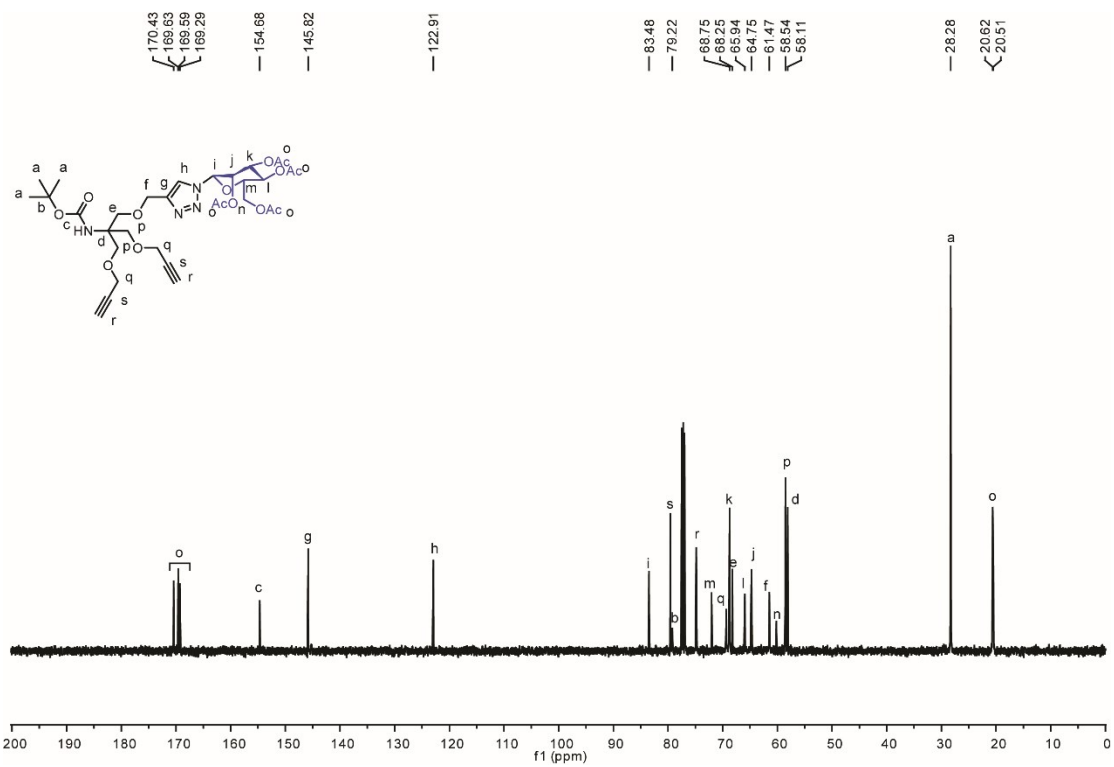

Figure S7. ^{13}C NMR spectrum of compound **4** in $CDCl_3$

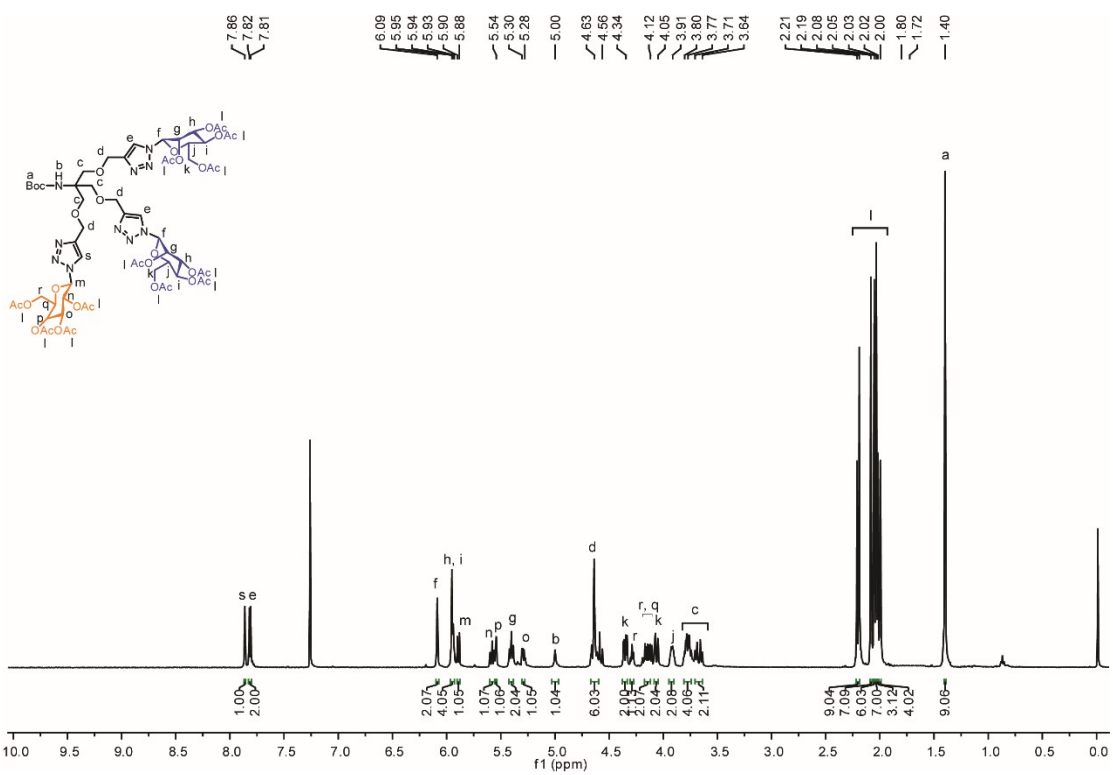

Figure S8. ^{1}H NMR spectrum of Compound **5** in $CDCl_3$

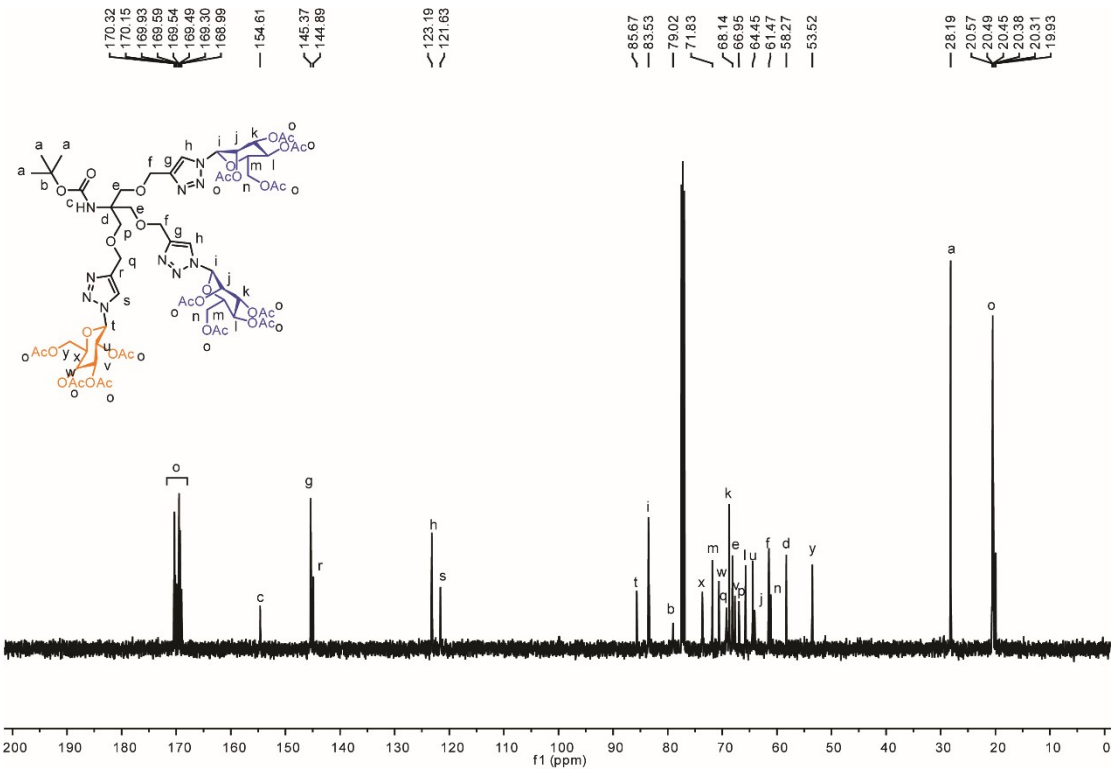

Figure S9. ^{13}C NMR spectrum of compound **5** in $CDCl_3$

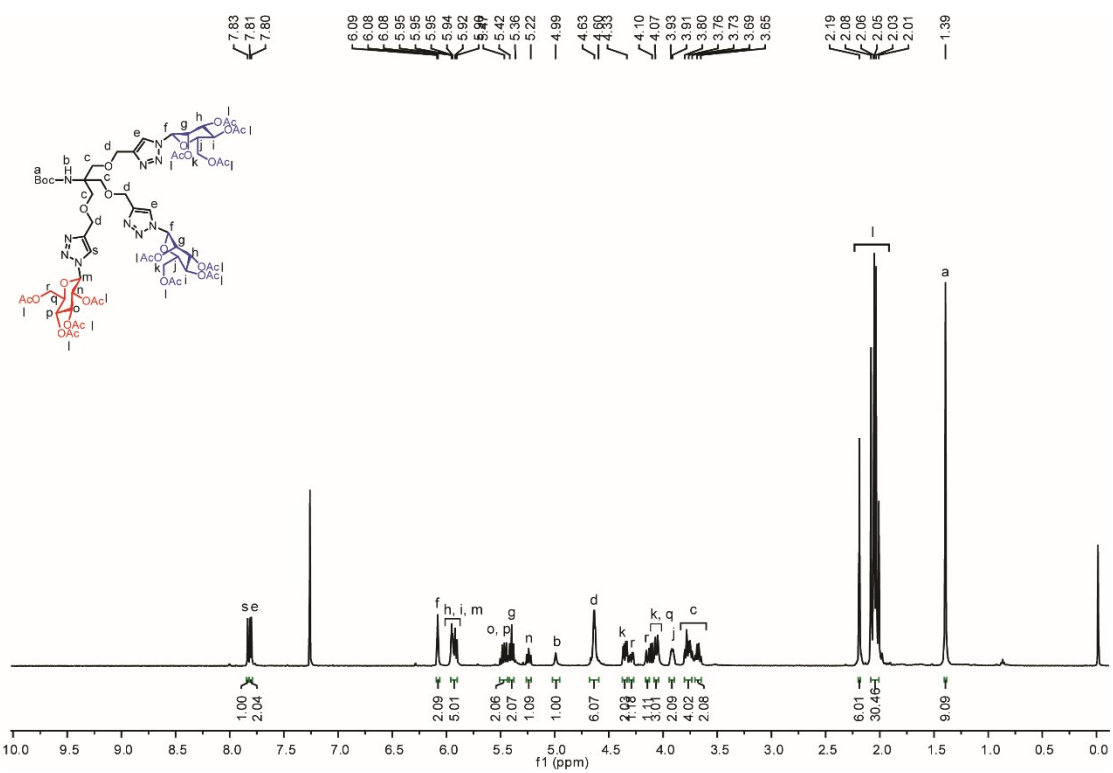

Figure S10. ^{1}H NMR spectrum of Compound **6** in $CDCl_3$

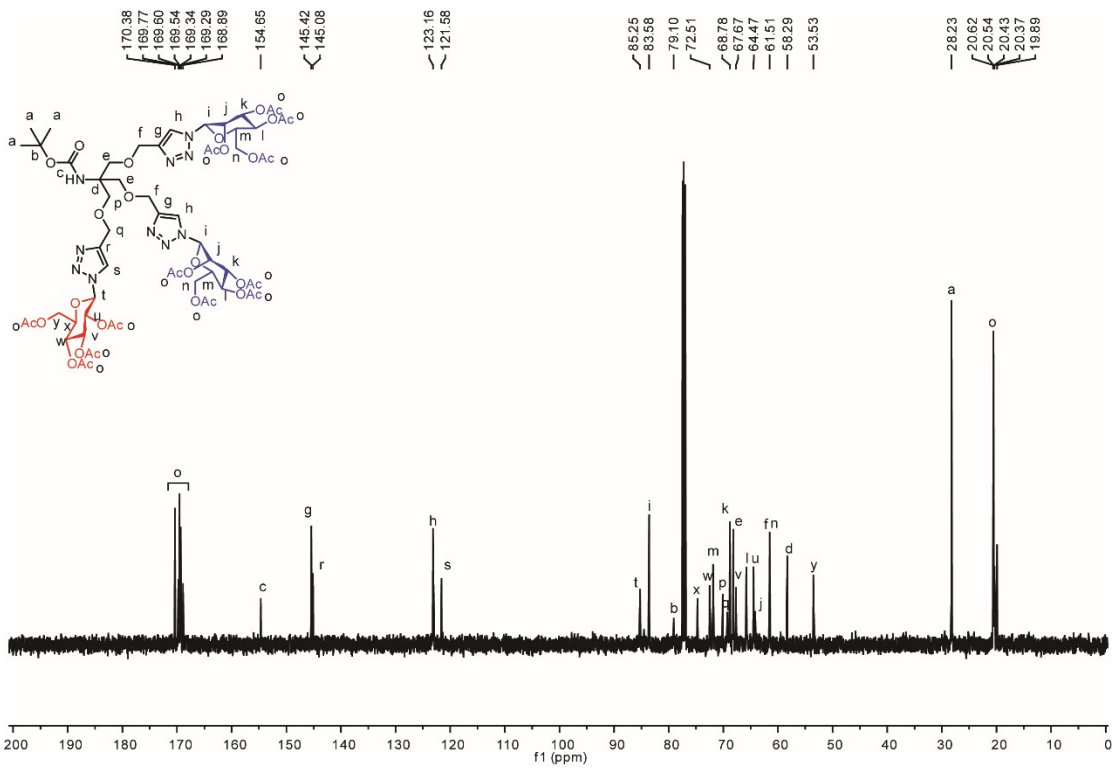

Figure S11. ^{13}C NMR spectrum of compound **6** in $CDCl_3$

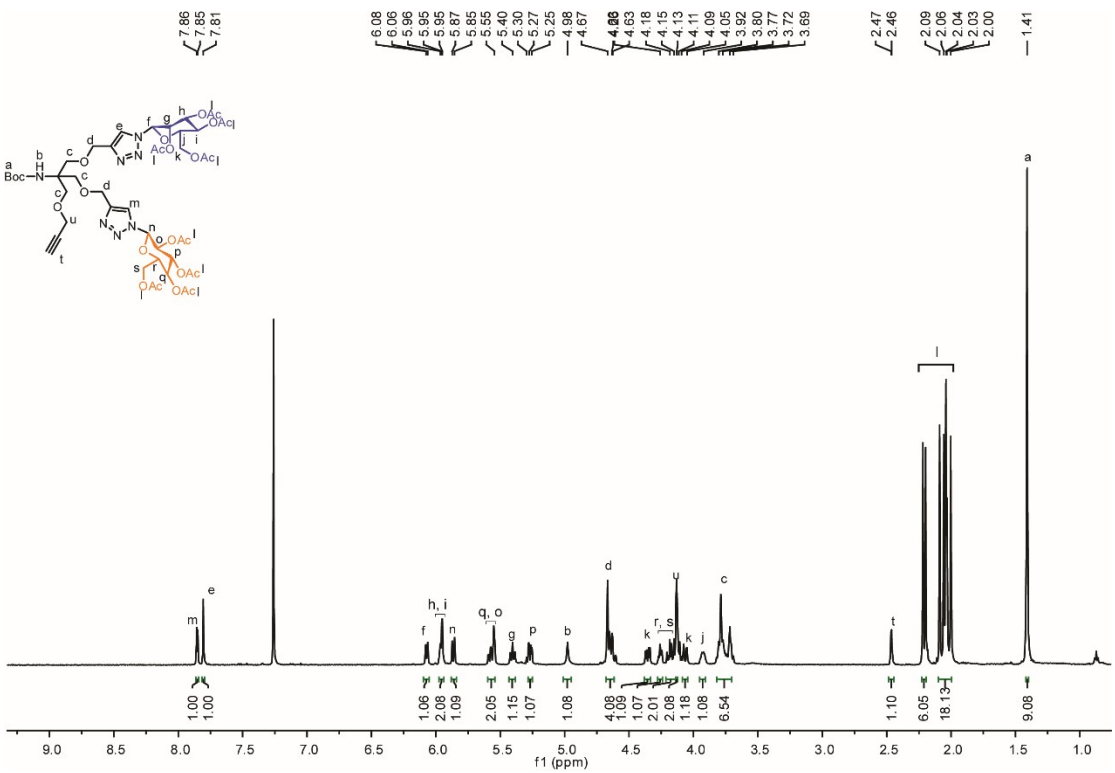

Figure S12. ^{1}H NMR spectrum of Compound **7** in $CDCl_3$

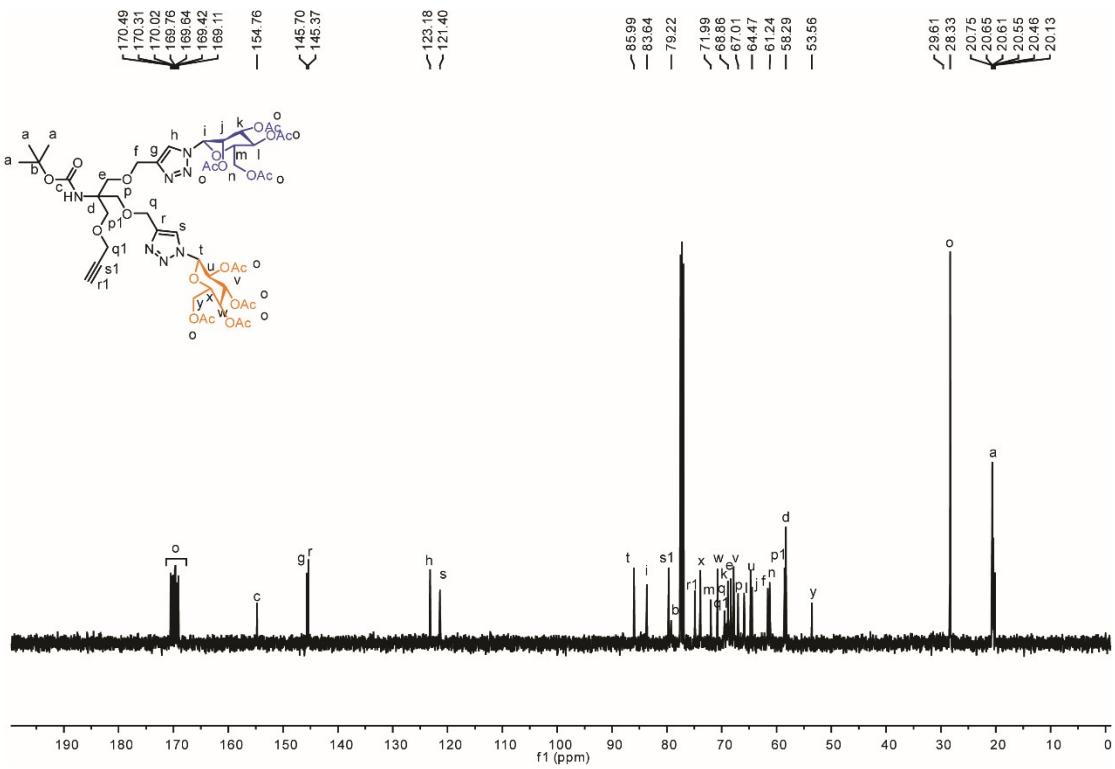

Figure S13. ^{13}C NMR spectrum of compound **7** in $CDCl_3$

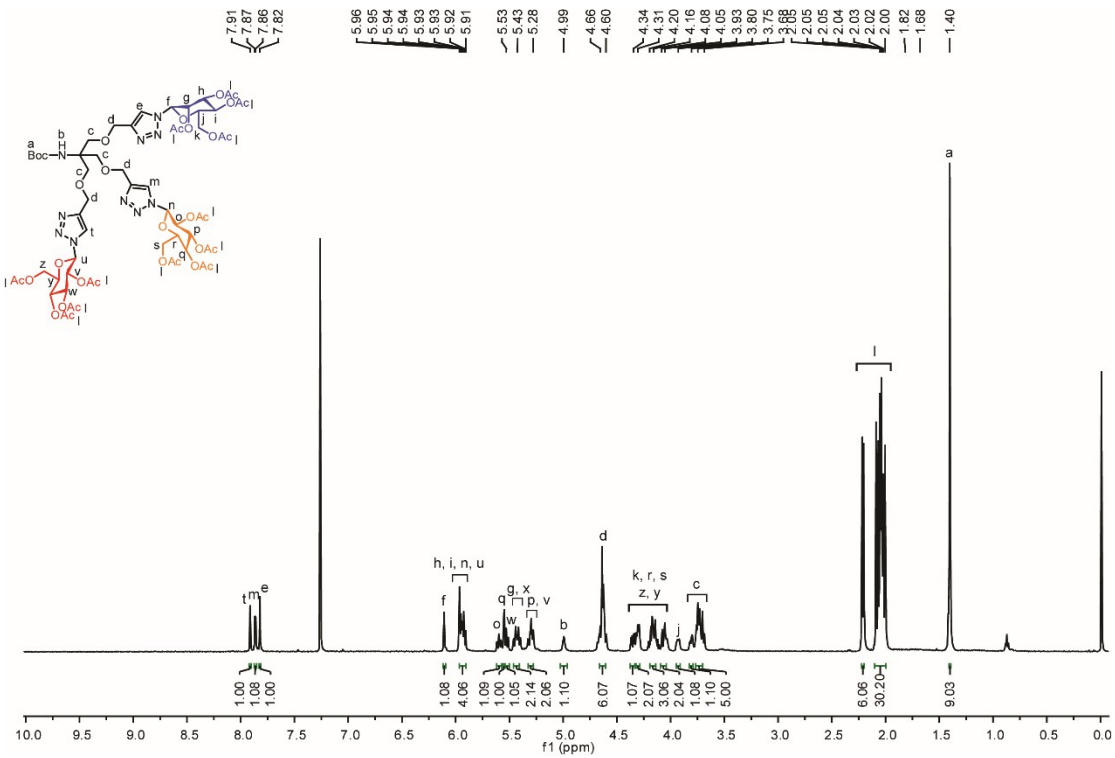

Figure S14. ^{1}H NMR spectrum of Compound **8** in $CDCl_3$

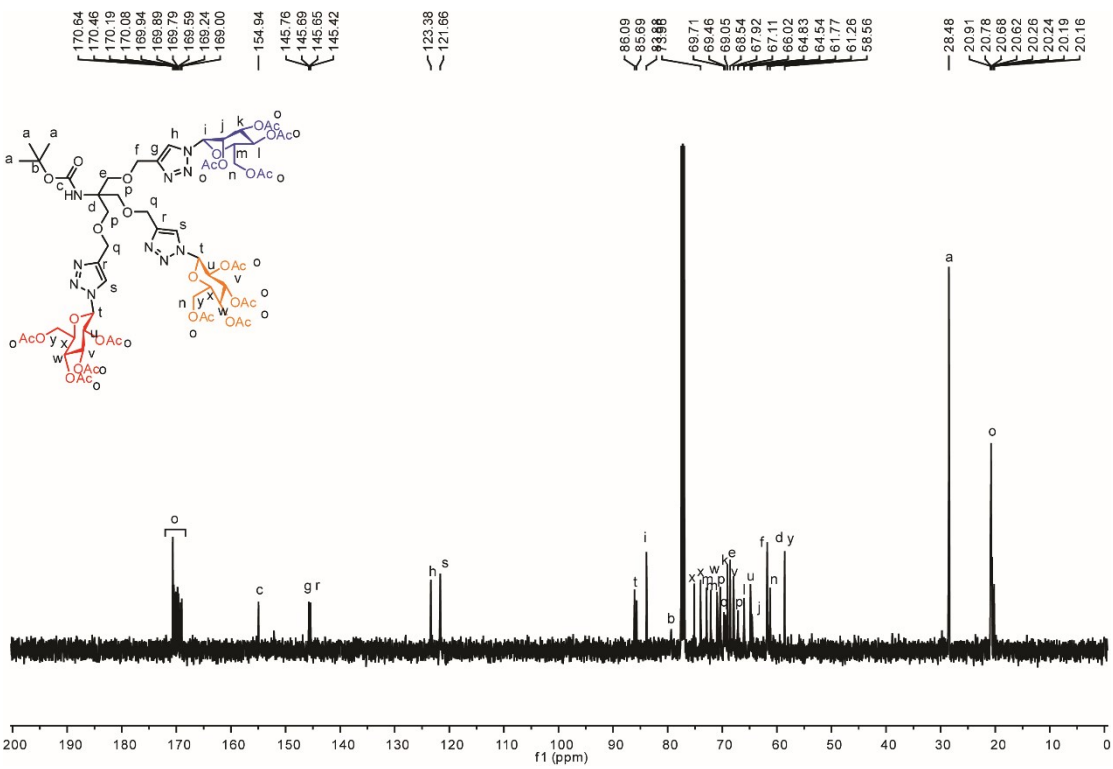

Figure S15. ^{13}C NMR spectrum of compound **8** in $CDCl_3$

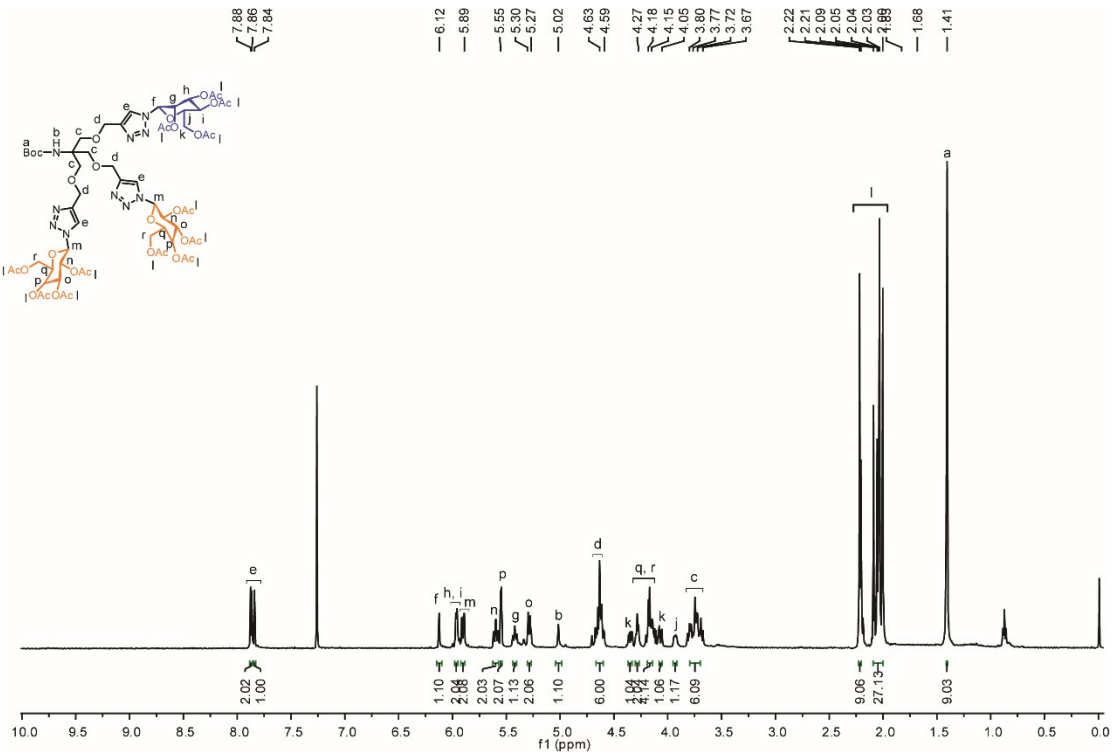

Figure S16. ^{1}H NMR spectrum of Compound **9** in $CDCl_3$

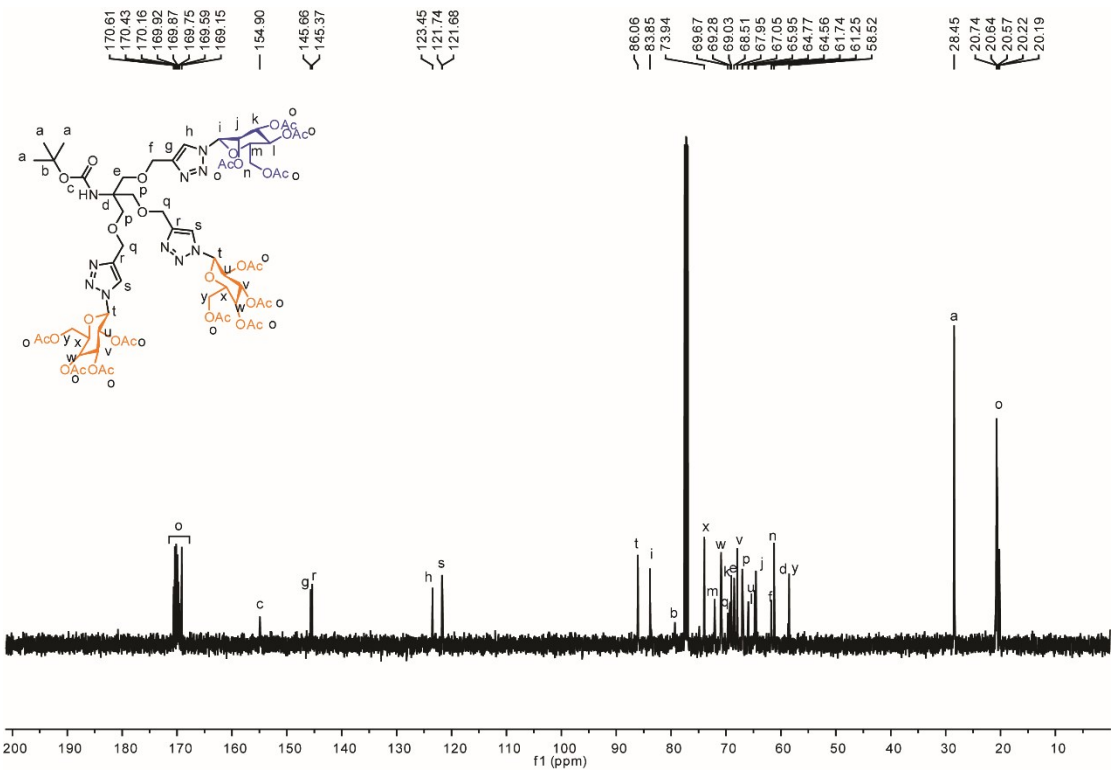

Figure S17. ^{13}C NMR spectrum of compound **9** in $CDCl_3$

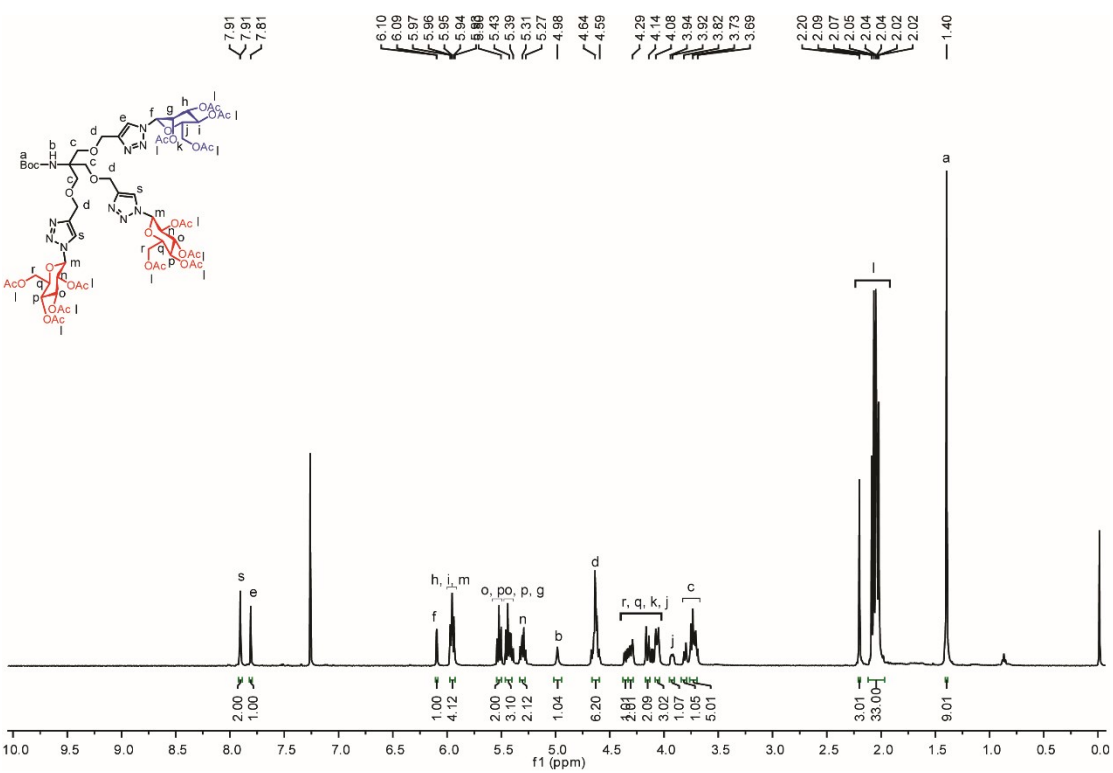

Figure S18. ^{1}H NMR spectrum of Compound **10** in $CDCl_3$

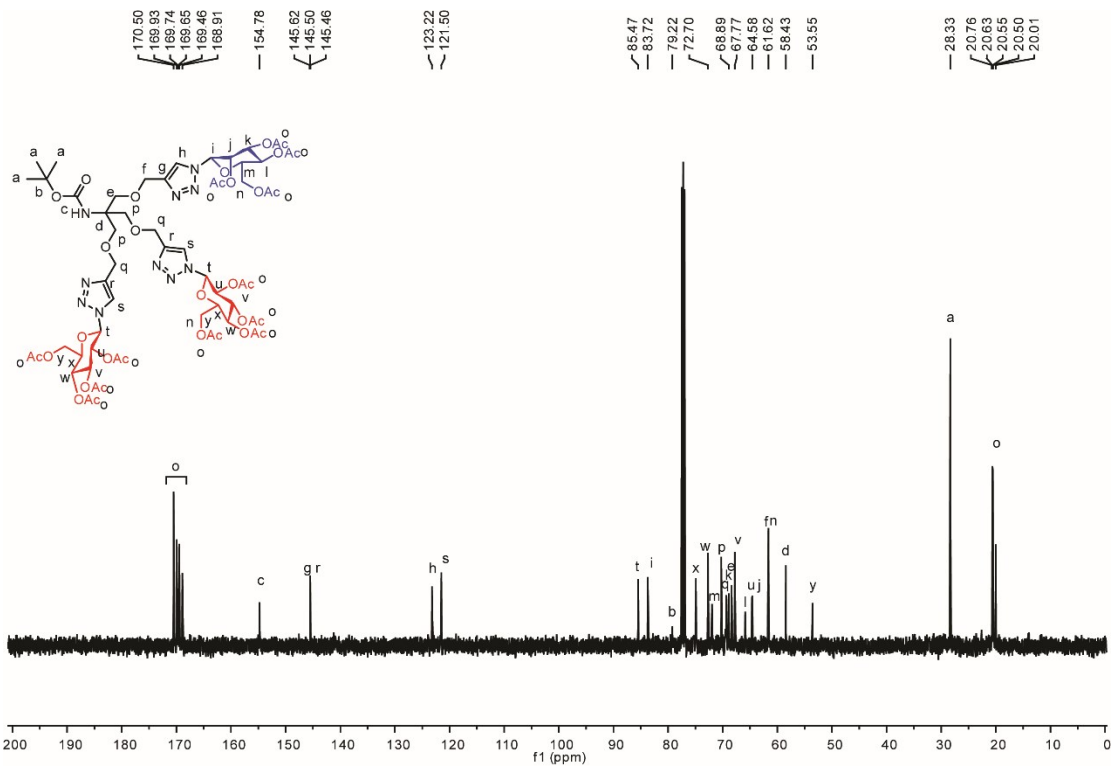

Figure S19. ^{13}C NMR spectrum of compound **10** in $CDCl_3$

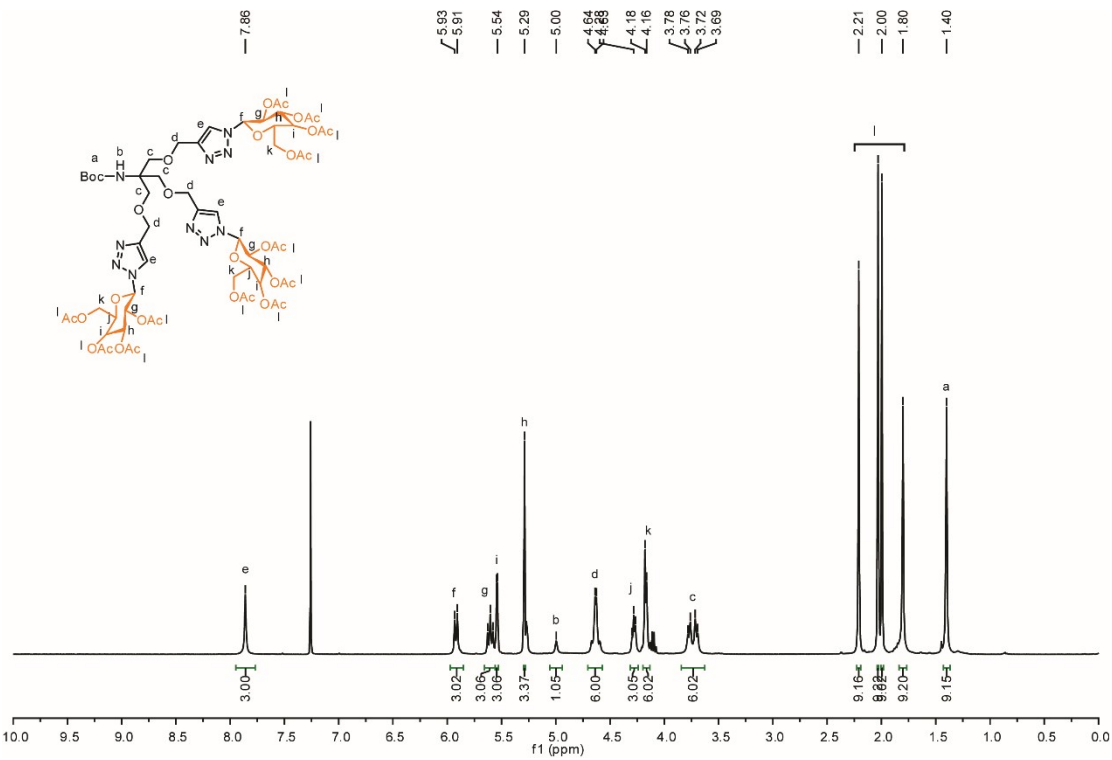

Figure S20. ^{1}H NMR spectrum of Compound **11** in $CDCl_3$

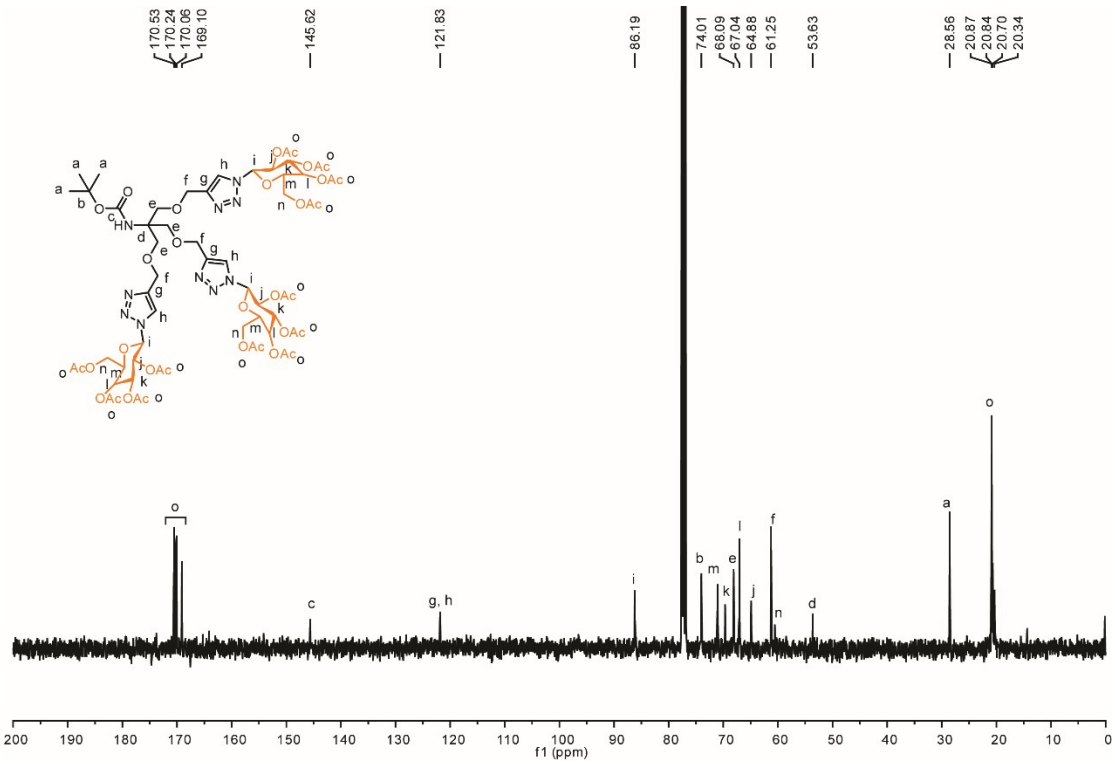

Figure S21. ^{13}C NMR spectrum of compound **11** in $CDCl_3$

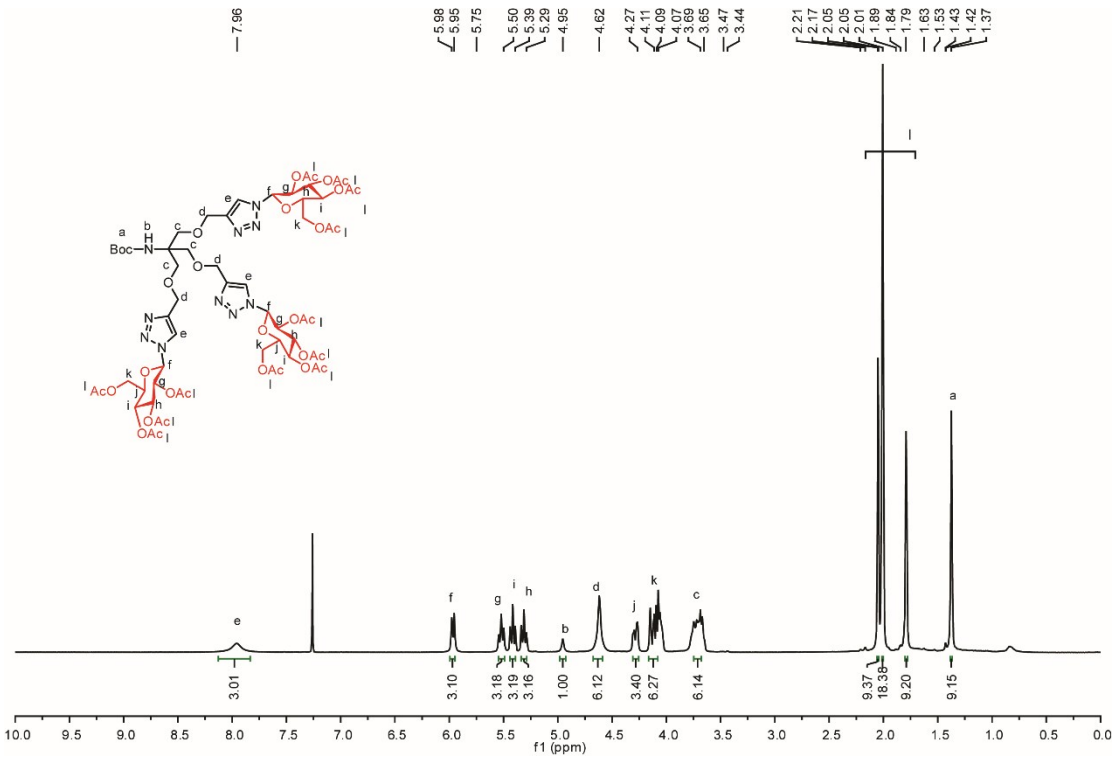

Figure S22. ^{1}H NMR spectrum of Compound **12** in $CDCl_3$

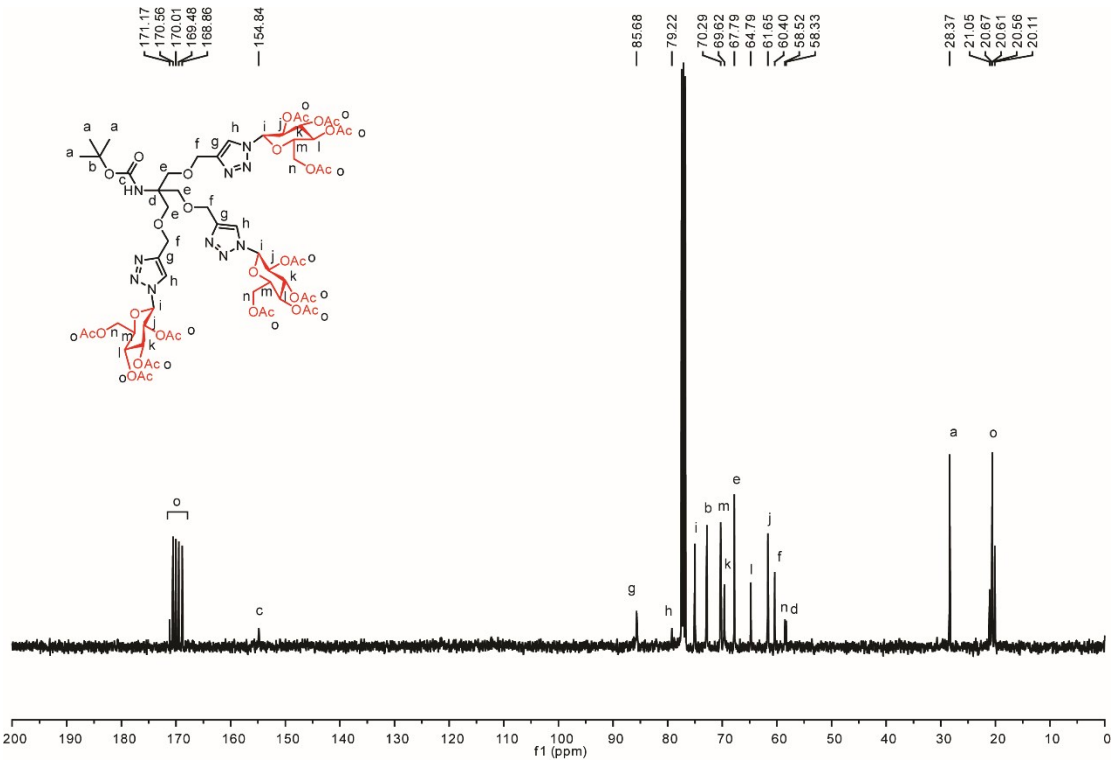

Figure S23. ^{13}C NMR spectrum of compound **12** in $CDCl_3$

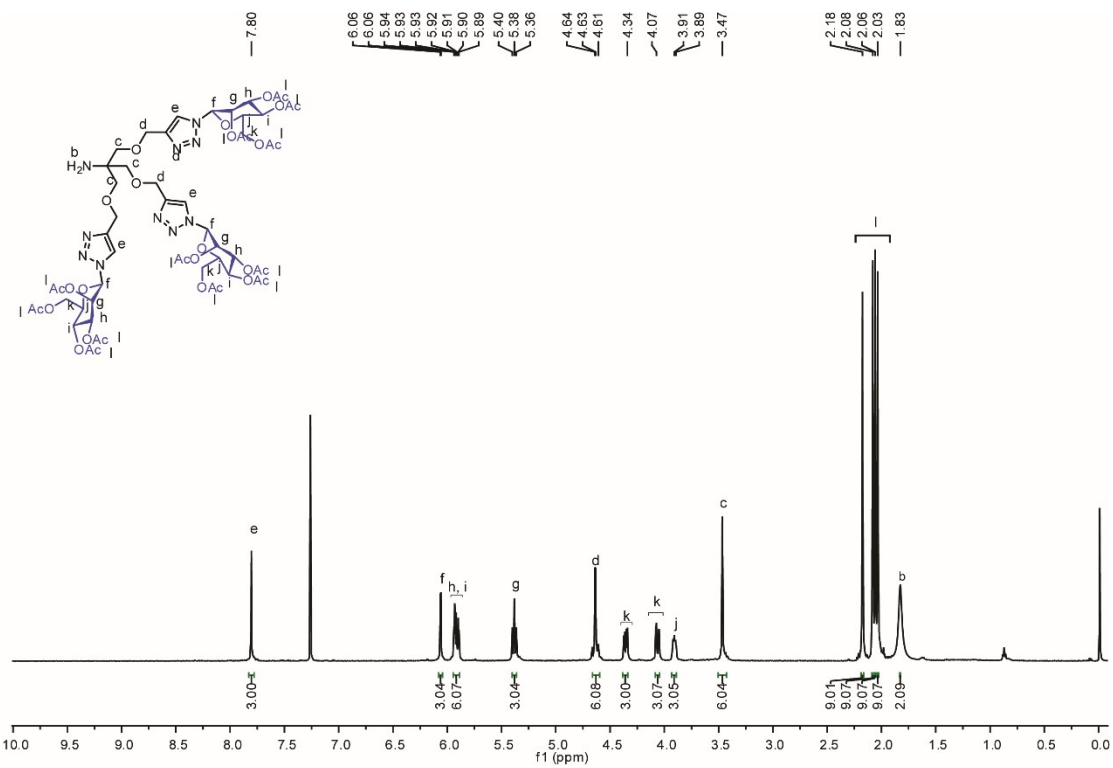

Figure S24. ^{1}H NMR spectrum of Compound **13** in $CDCl_3$

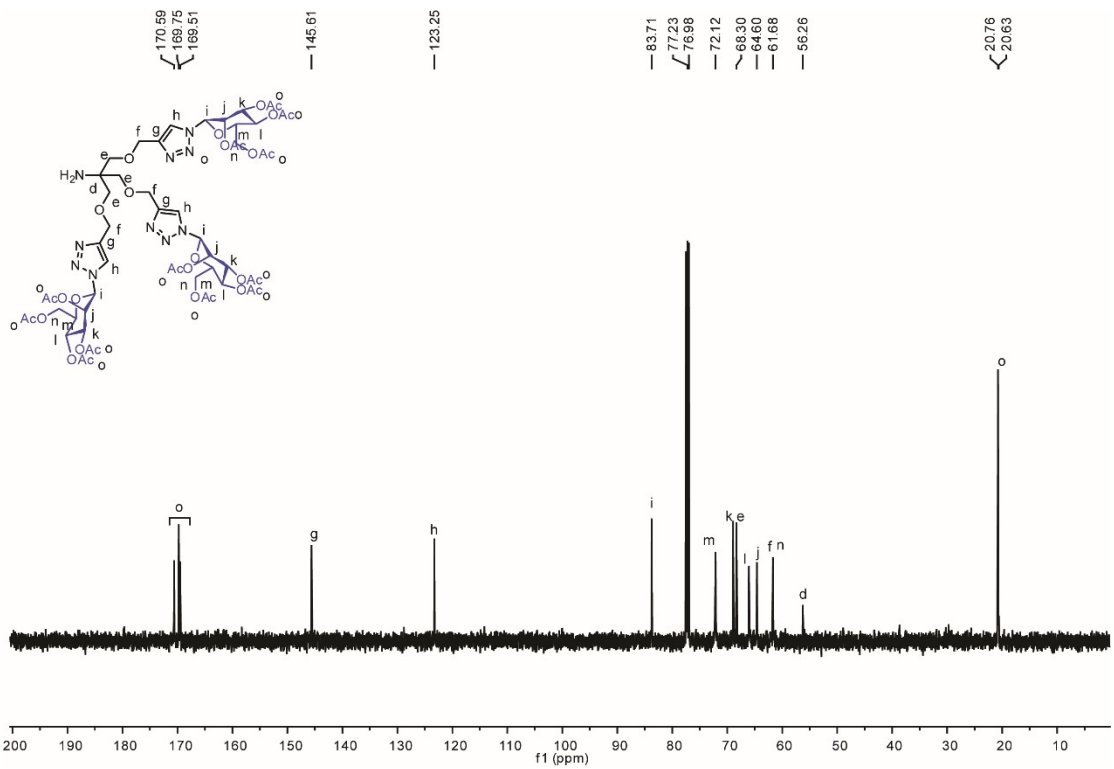

Figure S25. ^{13}C NMR spectrum of compound **13** in $CDCl_3$

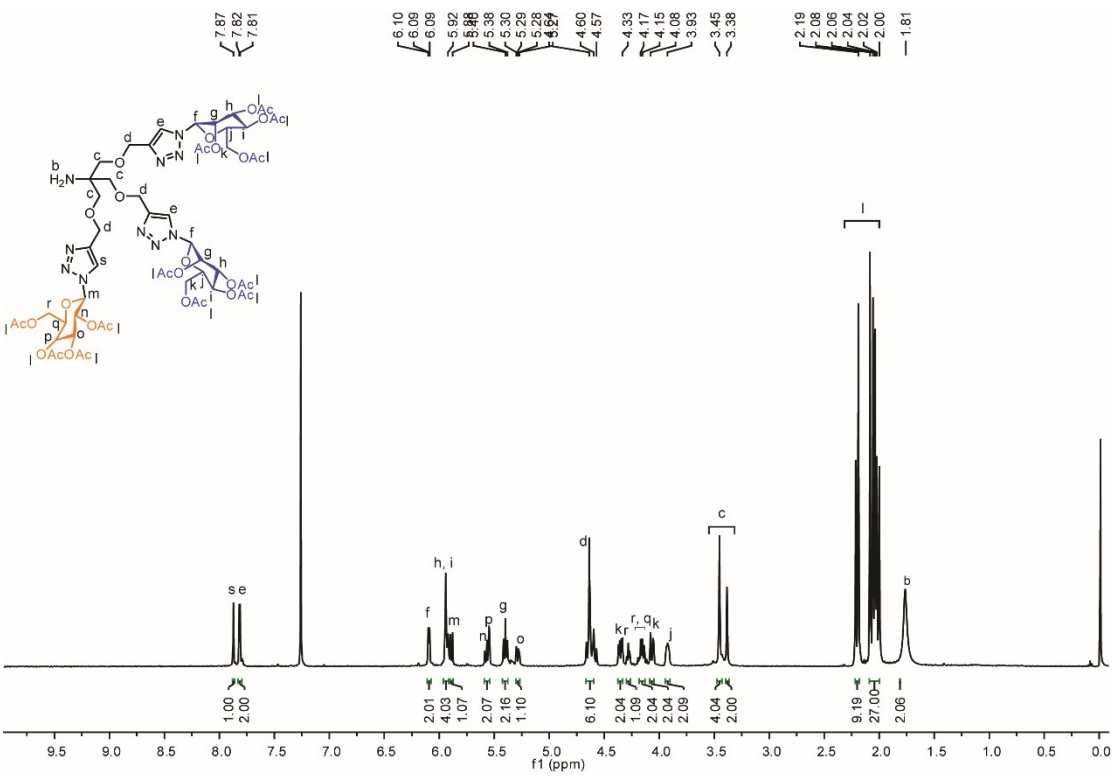

Figure S26. ^{1}H NMR spectrum of Compound **14** in $CDCl_3$

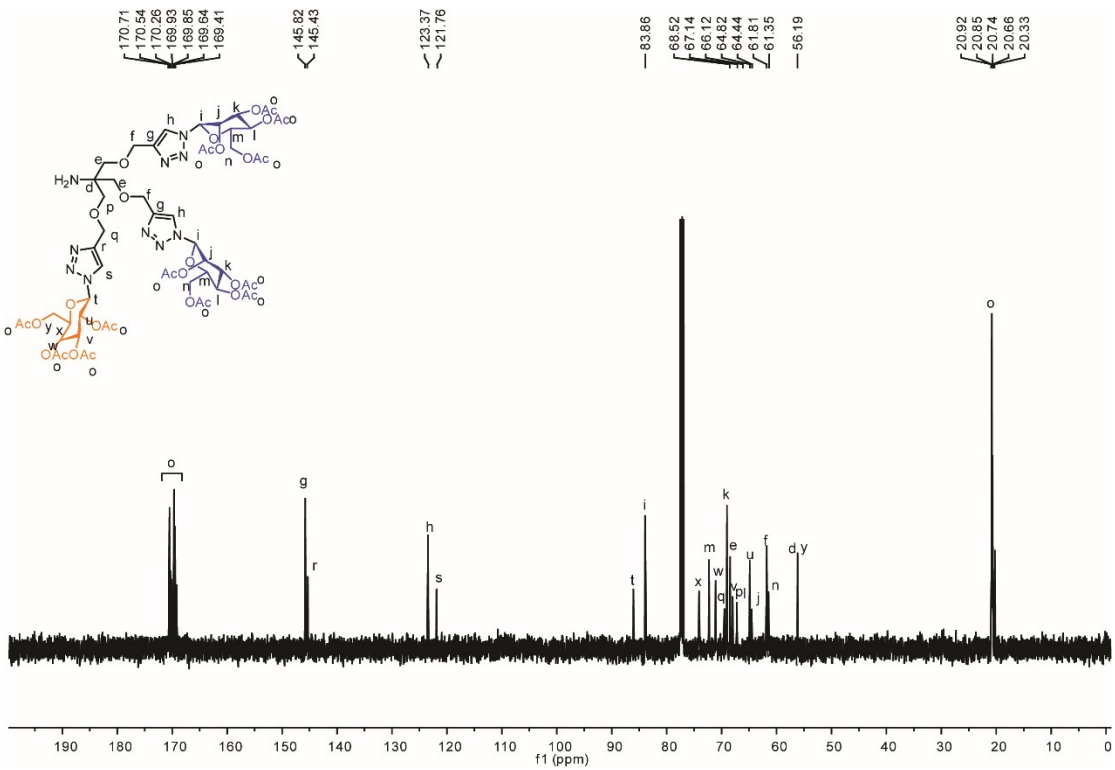

Figure S27. ^{13}C NMR spectrum of compound **14** in $CDCl_3$

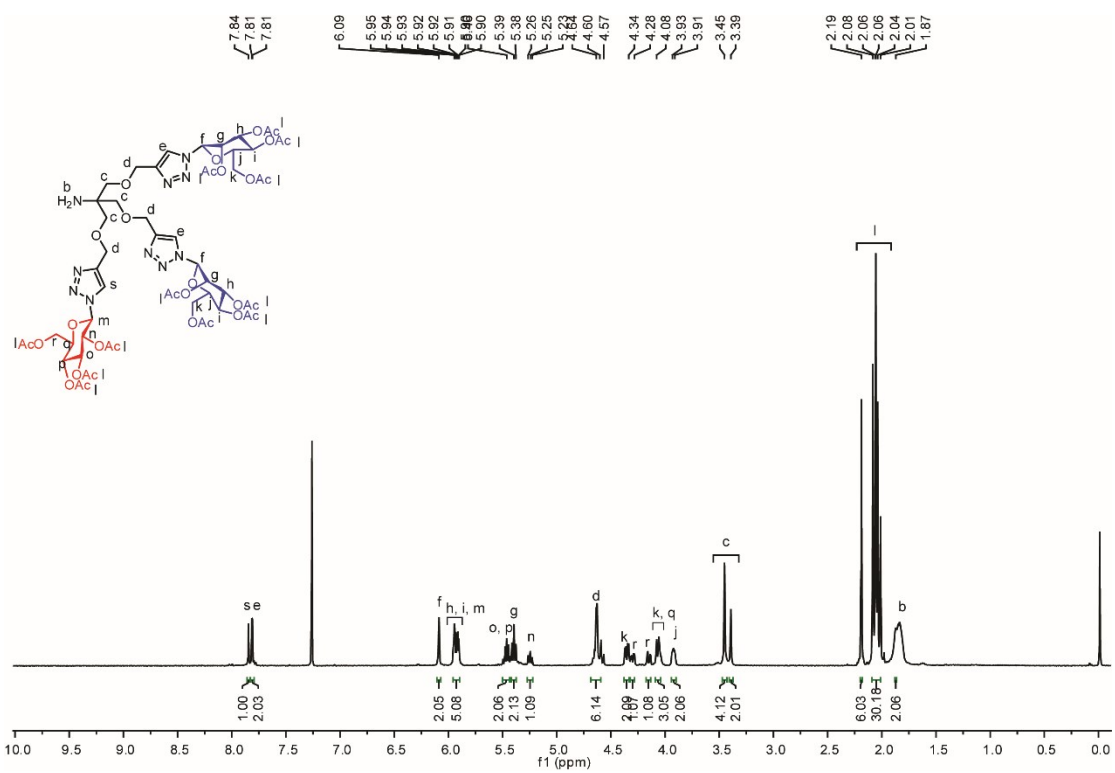

Figure S28 . ^{1}H NMR spectrum of Compound **15** in $CDCl_3$

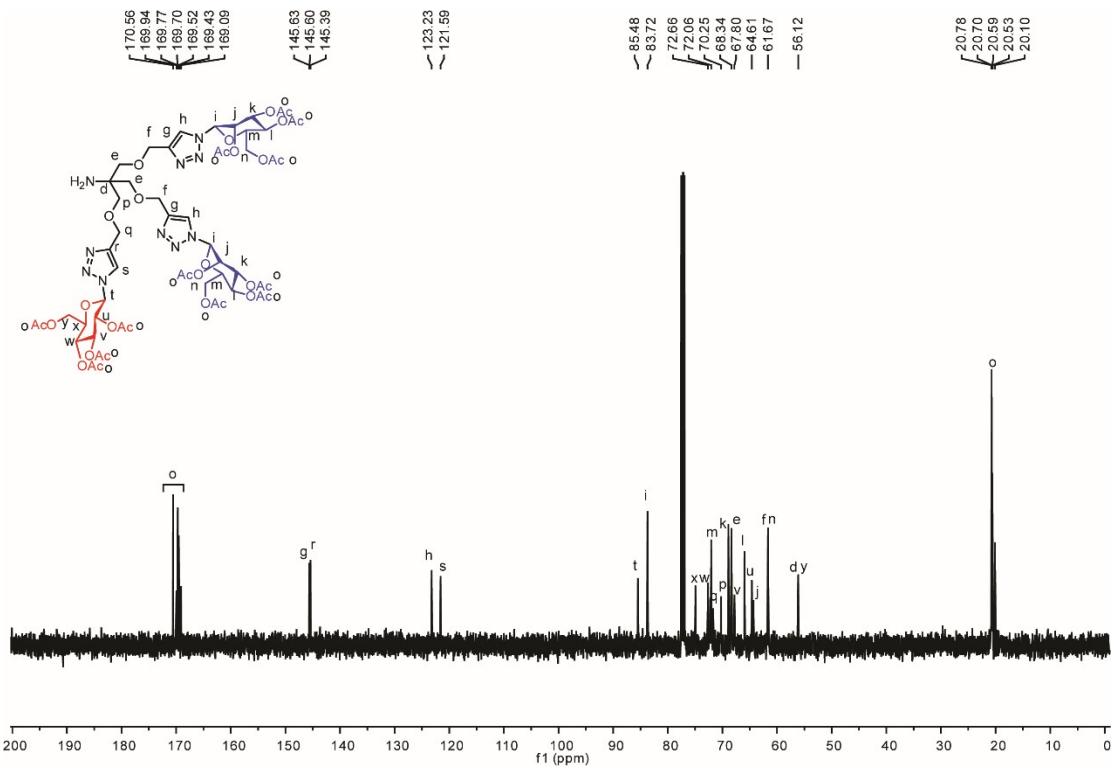

Figure S29. ^{13}C NMR spectrum of compound **15** in $CDCl_3$

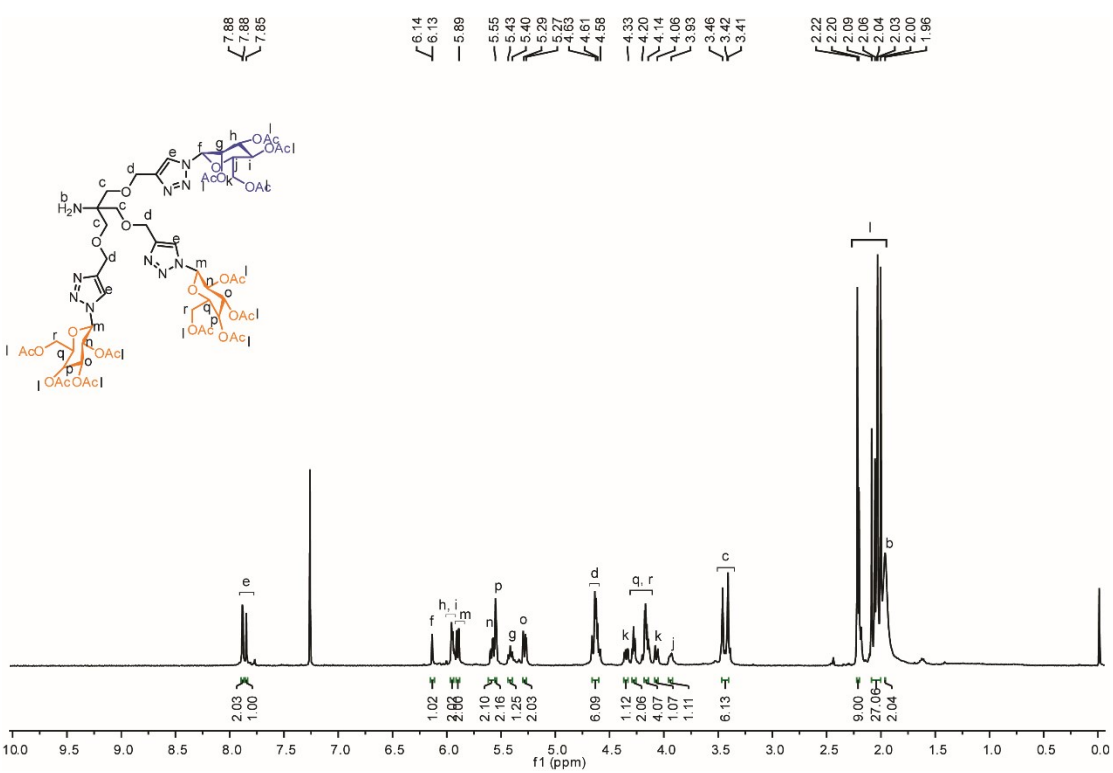

Figure S30. ^{1}H NMR spectrum of Compound **16** in $CDCl_3$

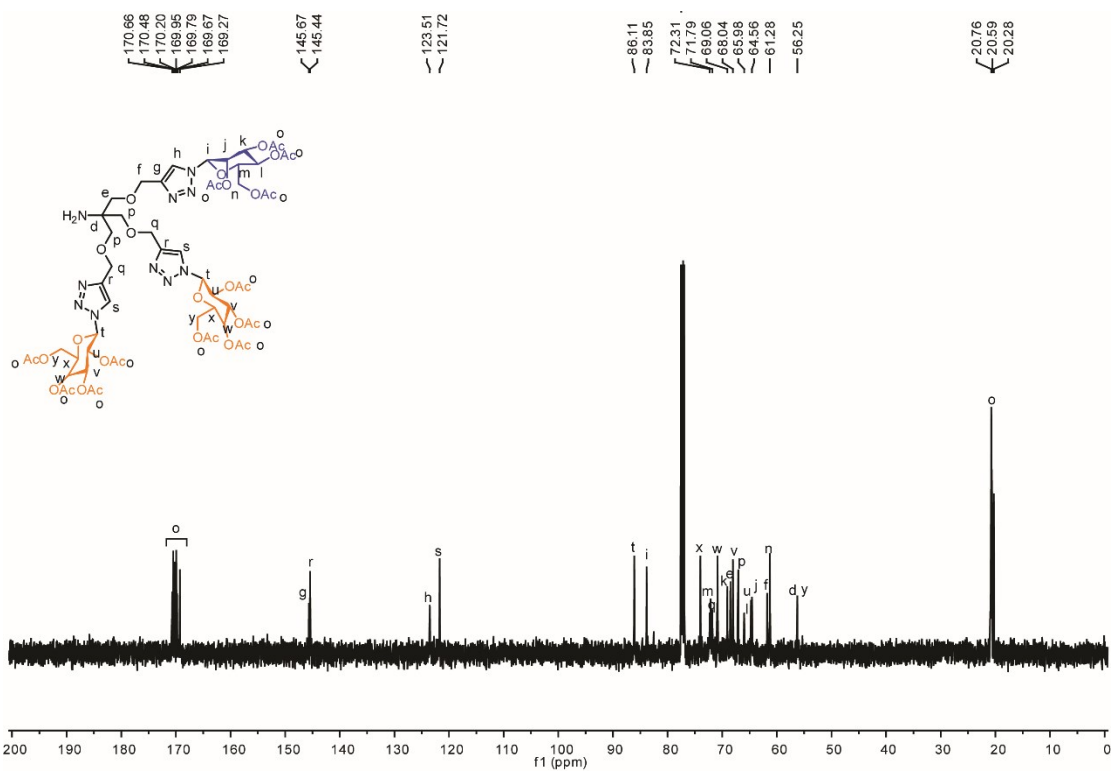

Figure S31. ^{13}C NMR spectrum of compound **16** in $CDCl_3$

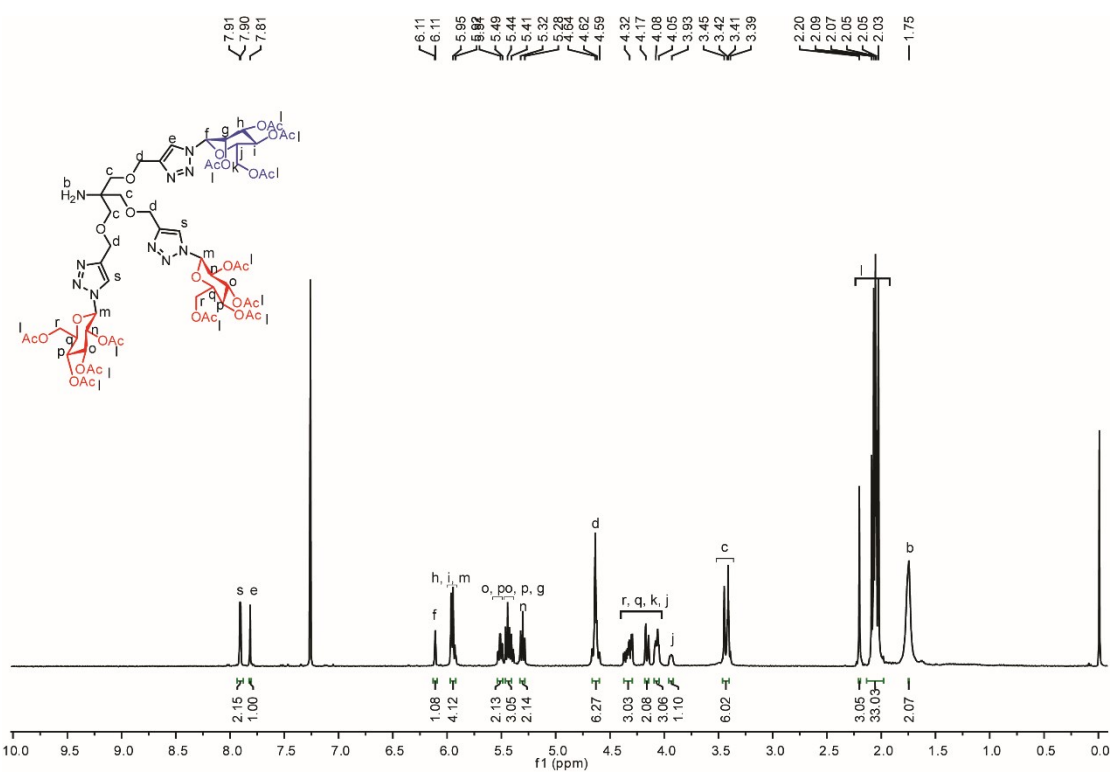

Figure S32. ^{1}H NMR spectrum of compound **17** in $CDCl_3$

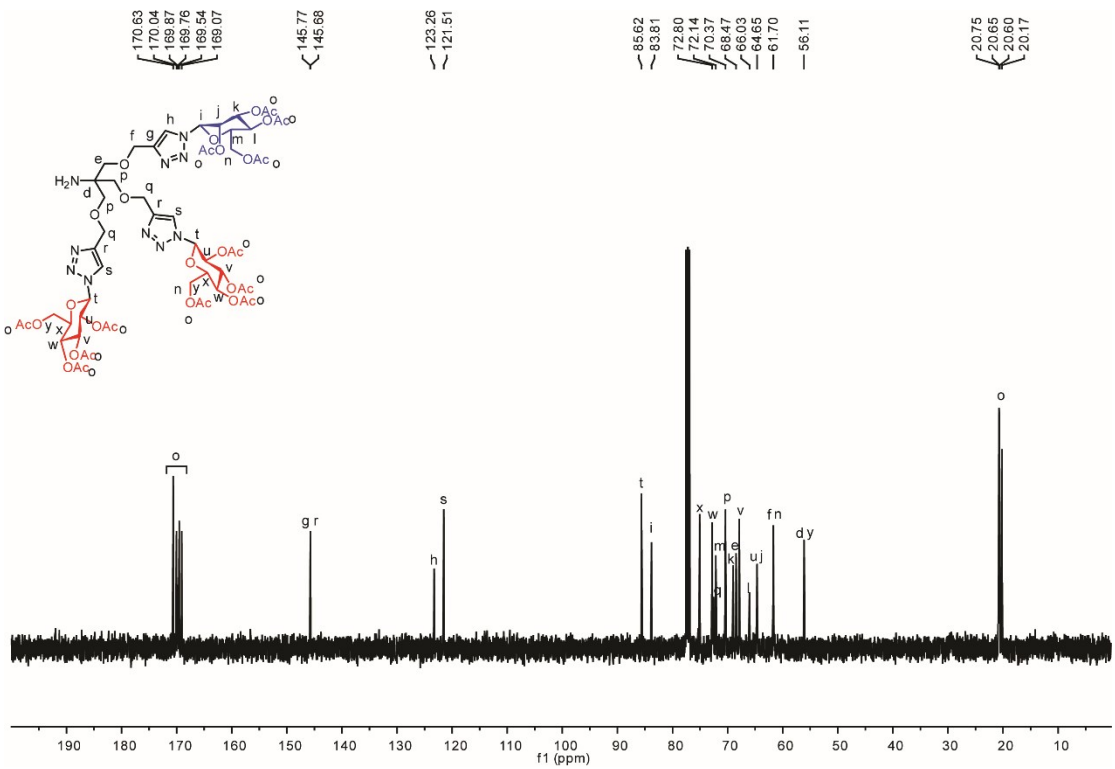

Figure S33. ^{13}C NMR spectrum of compound **17** in $CDCl_3$

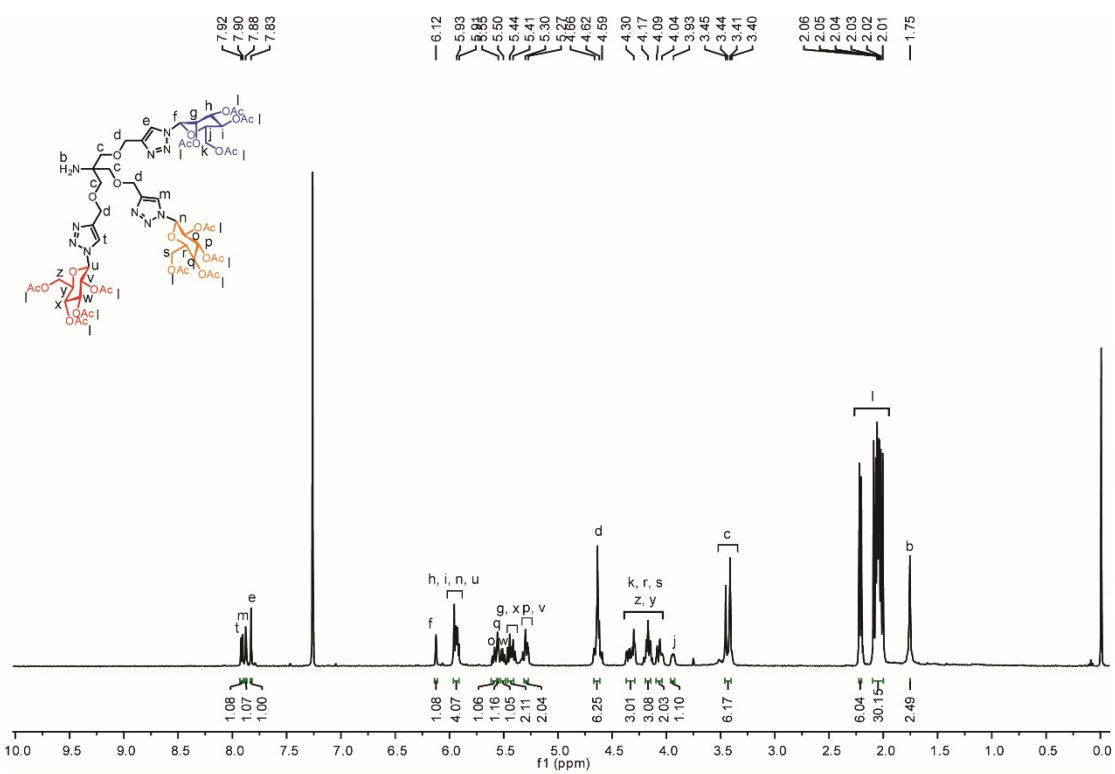

Figure S34. ^{1}H NMR spectrum of compound **18** in $CDCl_3$

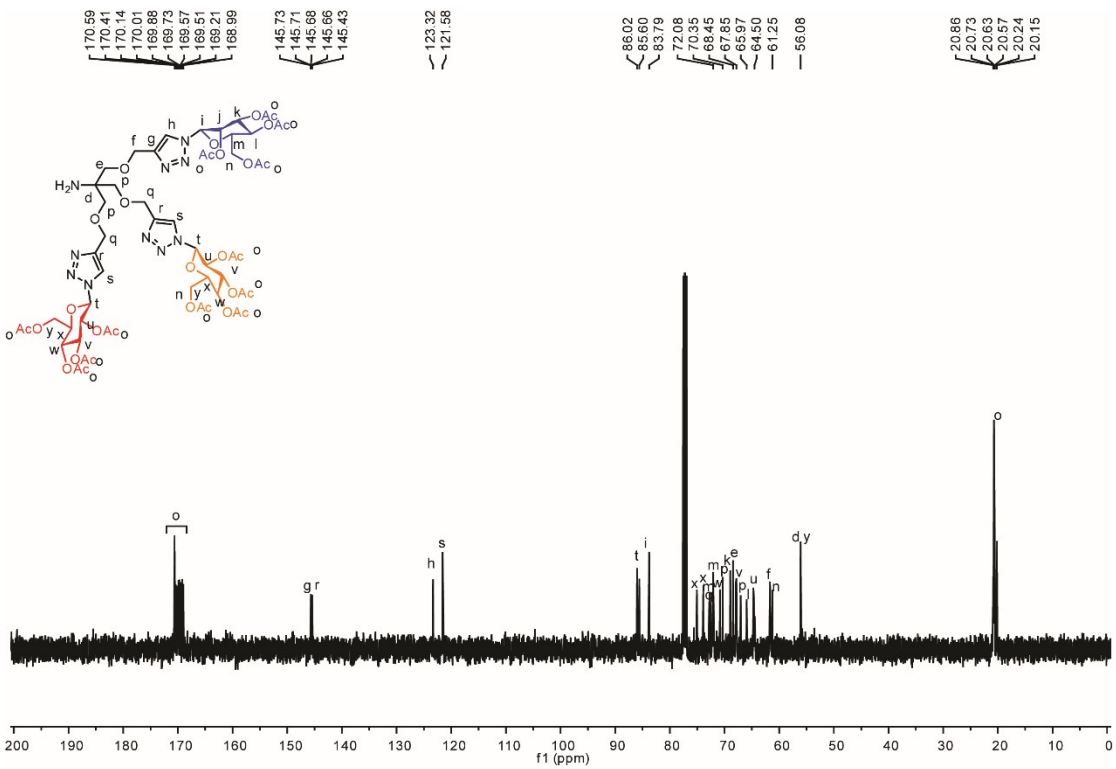

Figure S35. ^{13}C NMR spectrum of compound **18** in $CDCl_3$

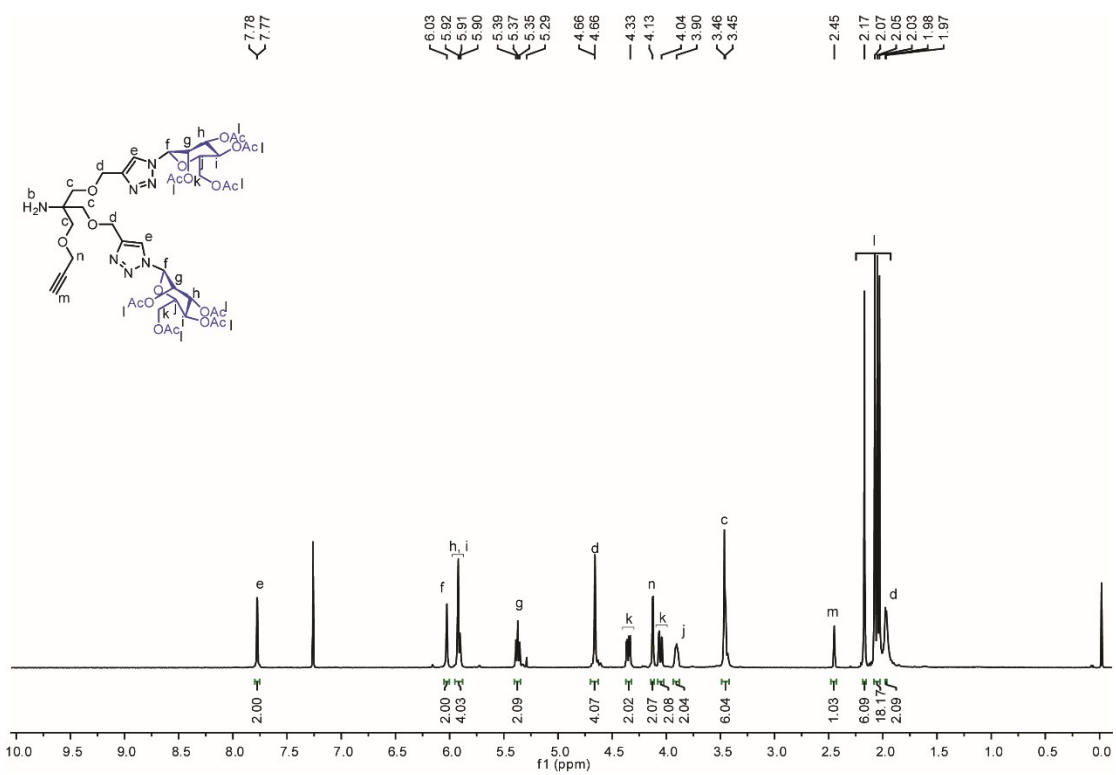

Figure S36. ^{1}H NMR spectrum of compound **19** in $CDCl_3$

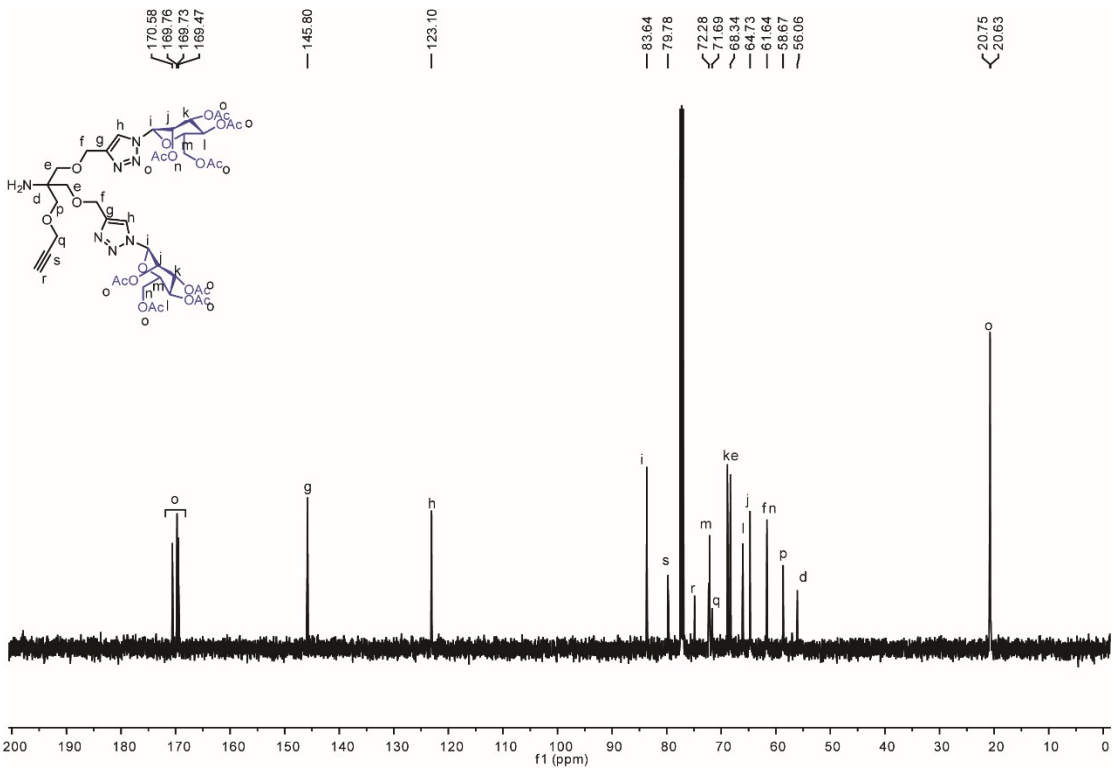

Figure S37. ^{13}C NMR spectrum of compound **19** in $CDCl_3$

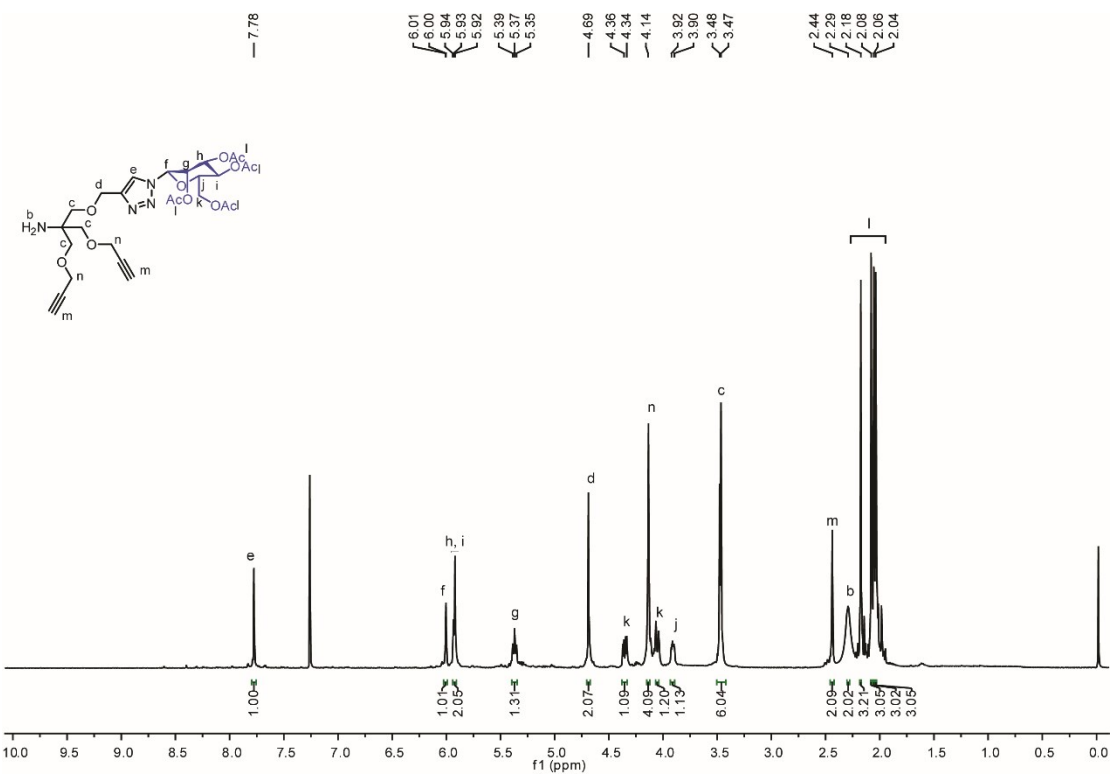

Figure S38. ^{1}H NMR spectrum of compound **20** in $CDCl_3$

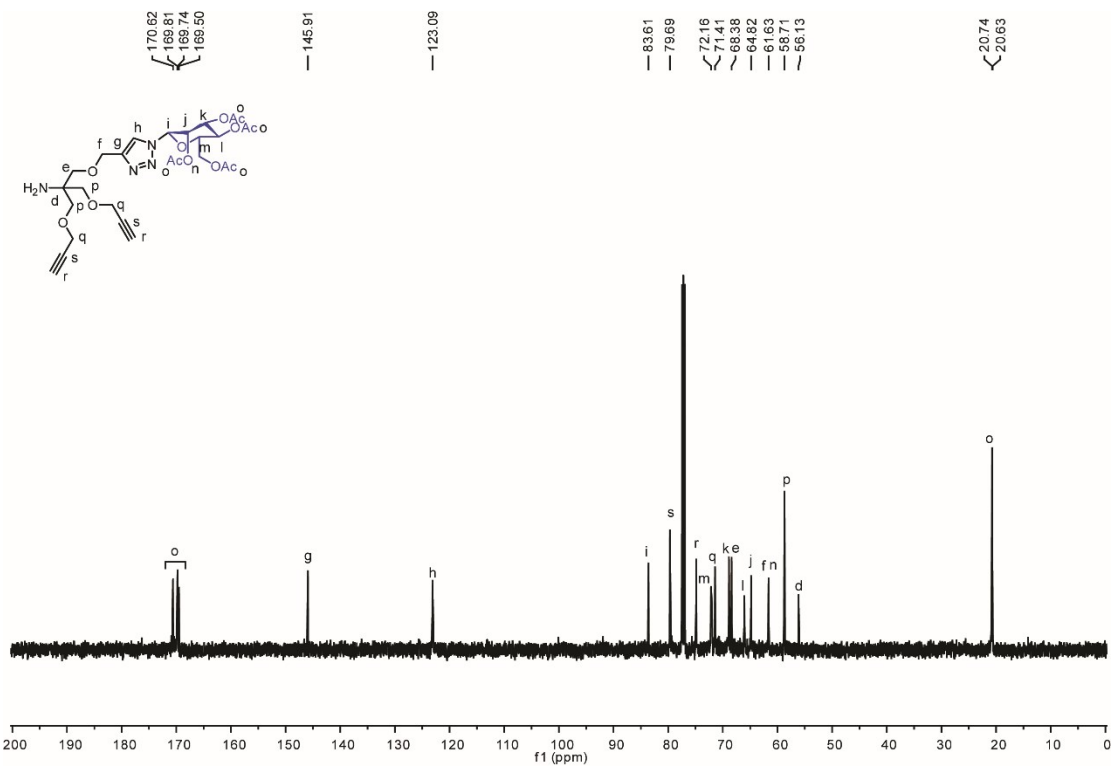

Figure S39. ^{13}C NMR spectrum of compound **20** in $CDCl_3$

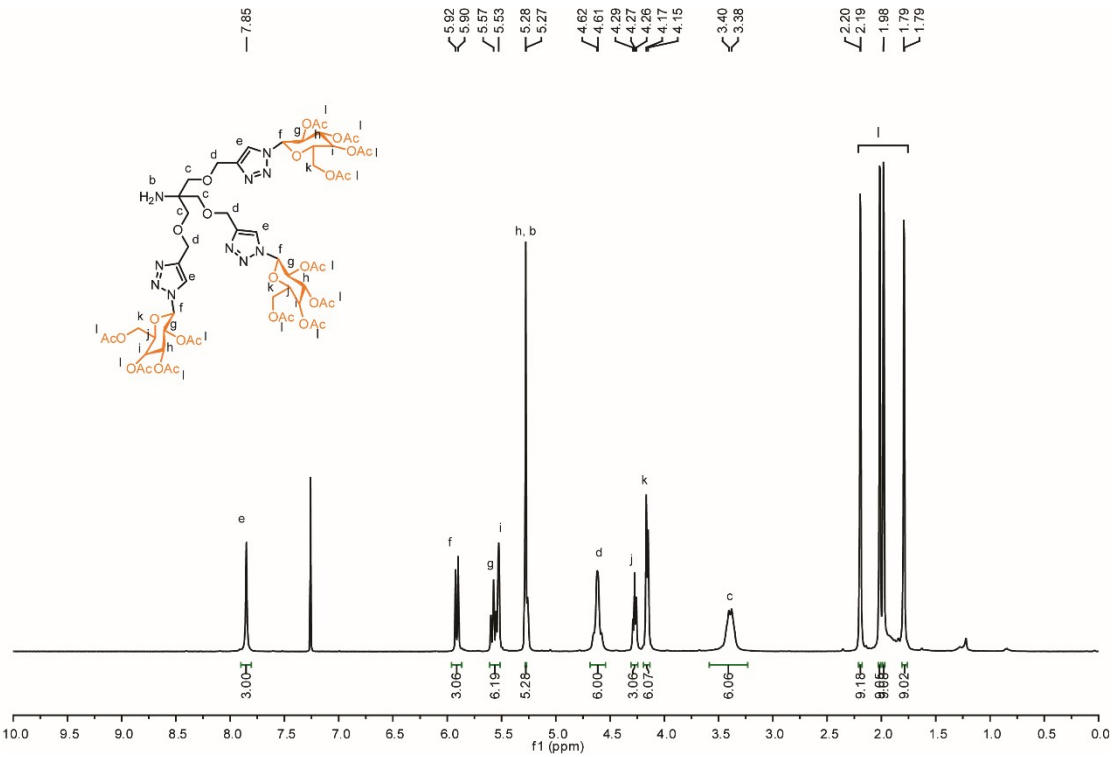

Figure S40. ^{1}H NMR spectrum of compound **21** in $CDCl_3$

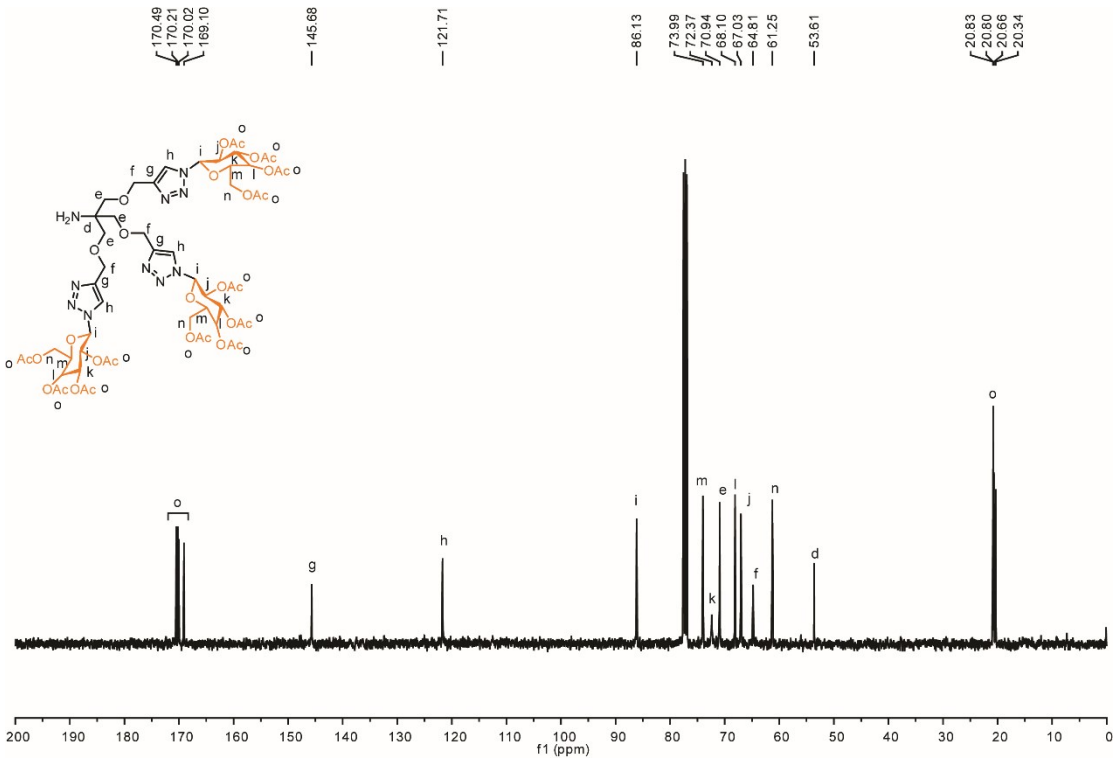

Figure S41. ^{13}C NMR spectrum of compound **21** in $CDCl_3$

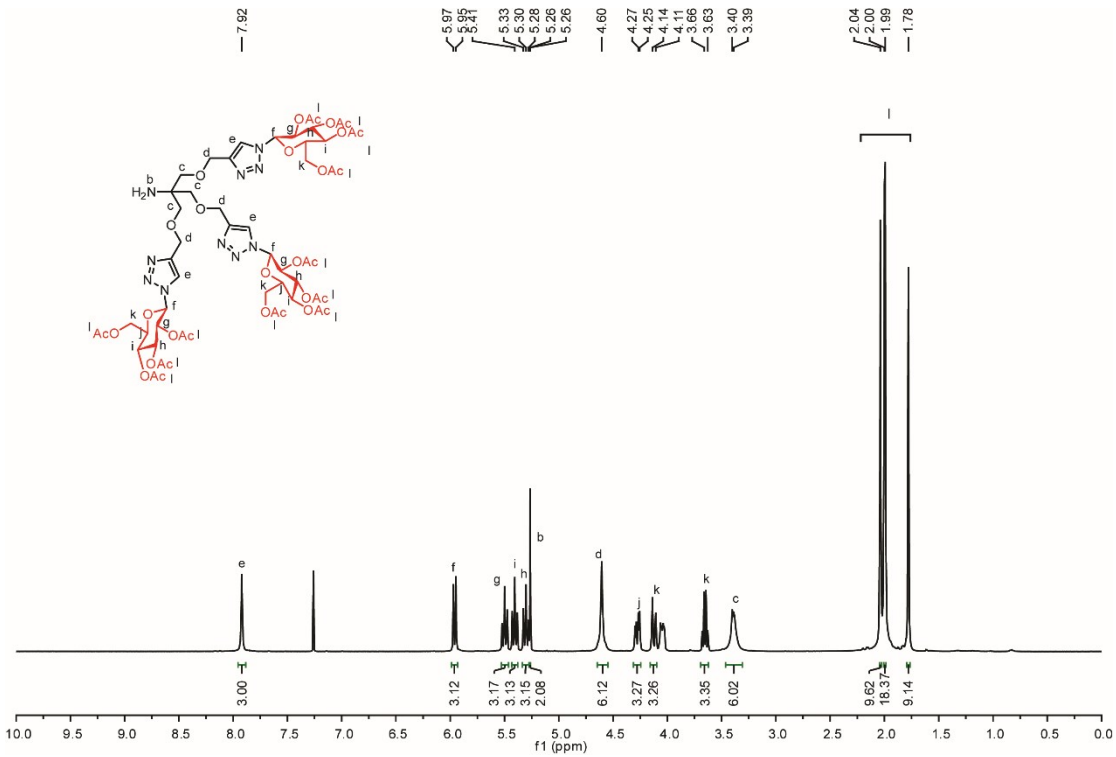

Figure S42. ^{1}H NMR spectrum of compound **22** in $CDCl_3$

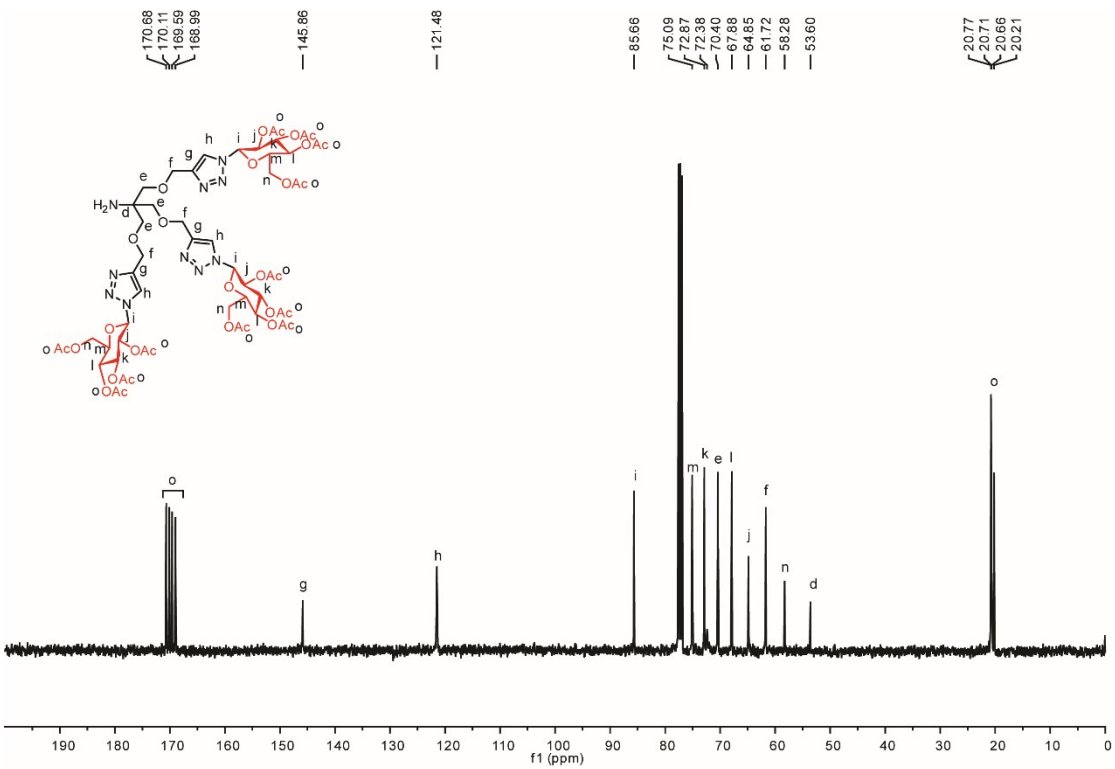

Figure S43. ^{13}C NMR spectrum of compound **22** in $CDCl_3$

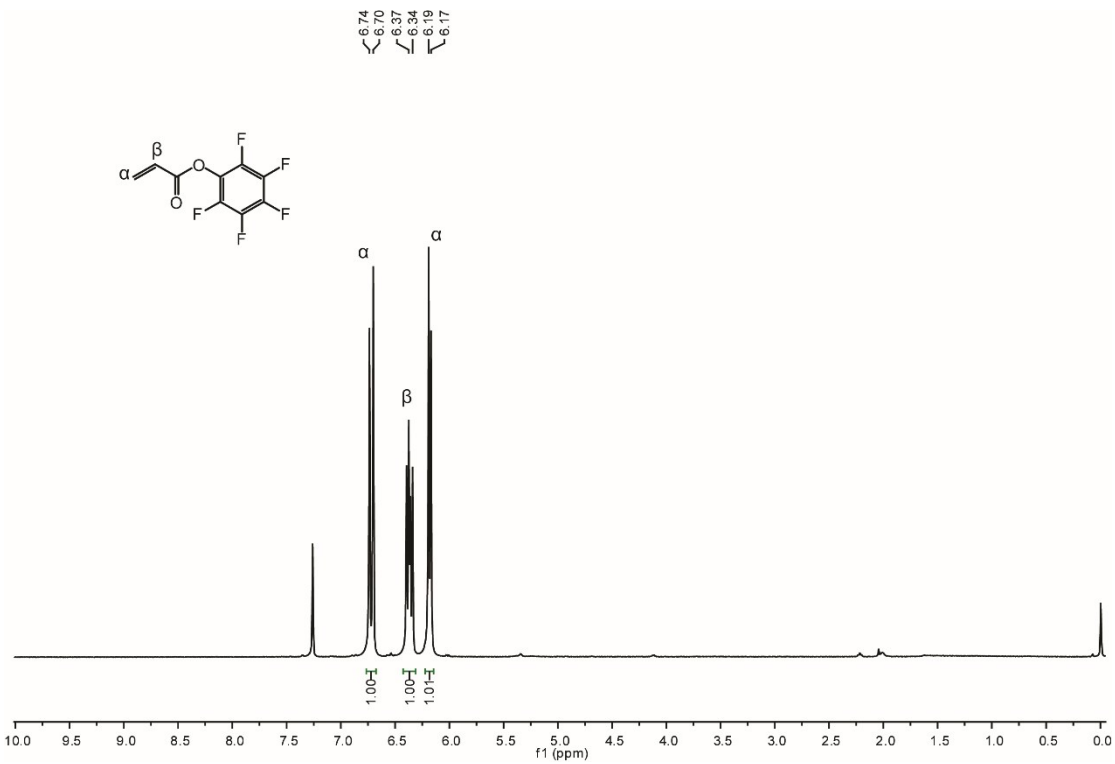

Figure S44. ^{1}H NMR spectrum of **PFPA** in $CDCl_3$

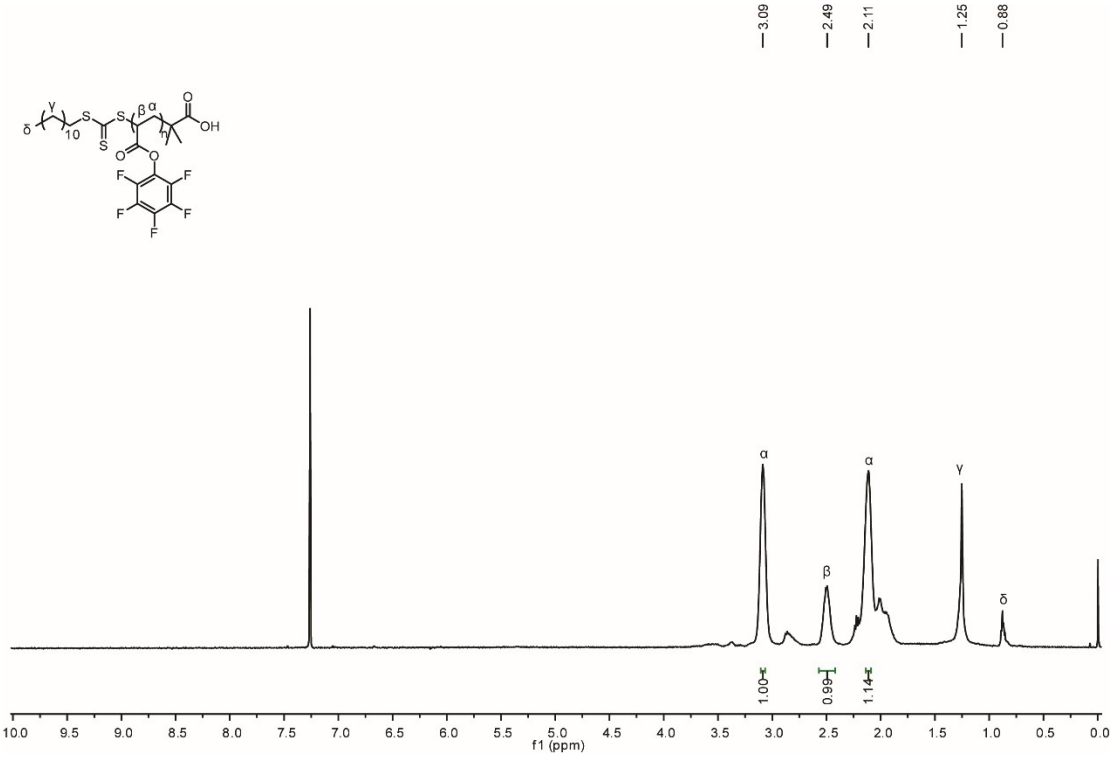

Figure S45. ^{1}H NMR spectrum of **pPFPA** in $CDCl_3$

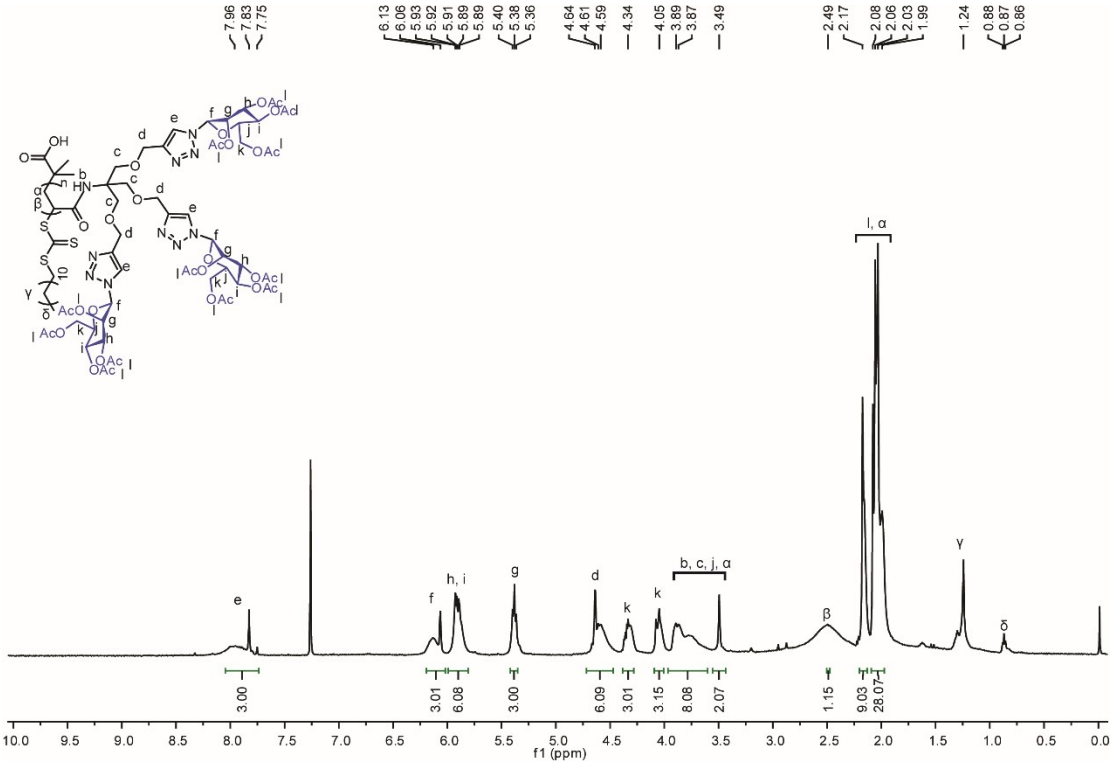

Figure S46. ^{1}H NMR spectrum of **P(αMan-αMan-αMan-OAc)** in $CDCl_3$

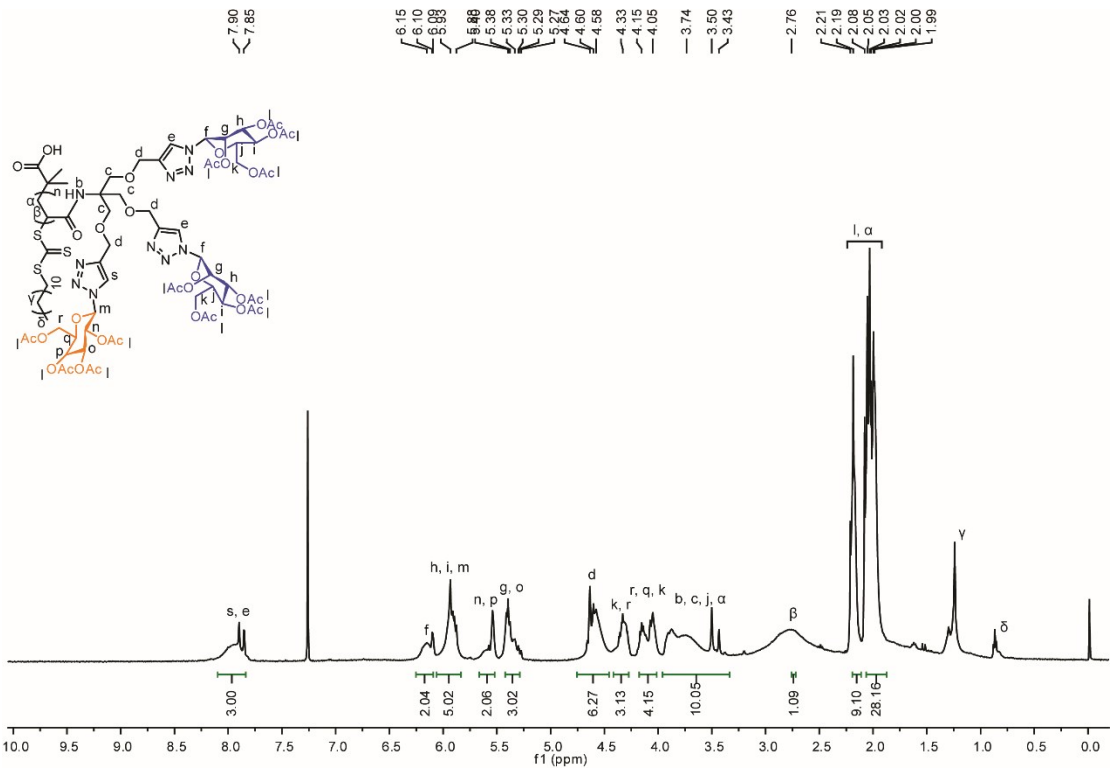

Figure S47. ^{1}H NMR spectrum of **P(αMan-αMan-βGal-OAc)** in $CDCl_3$

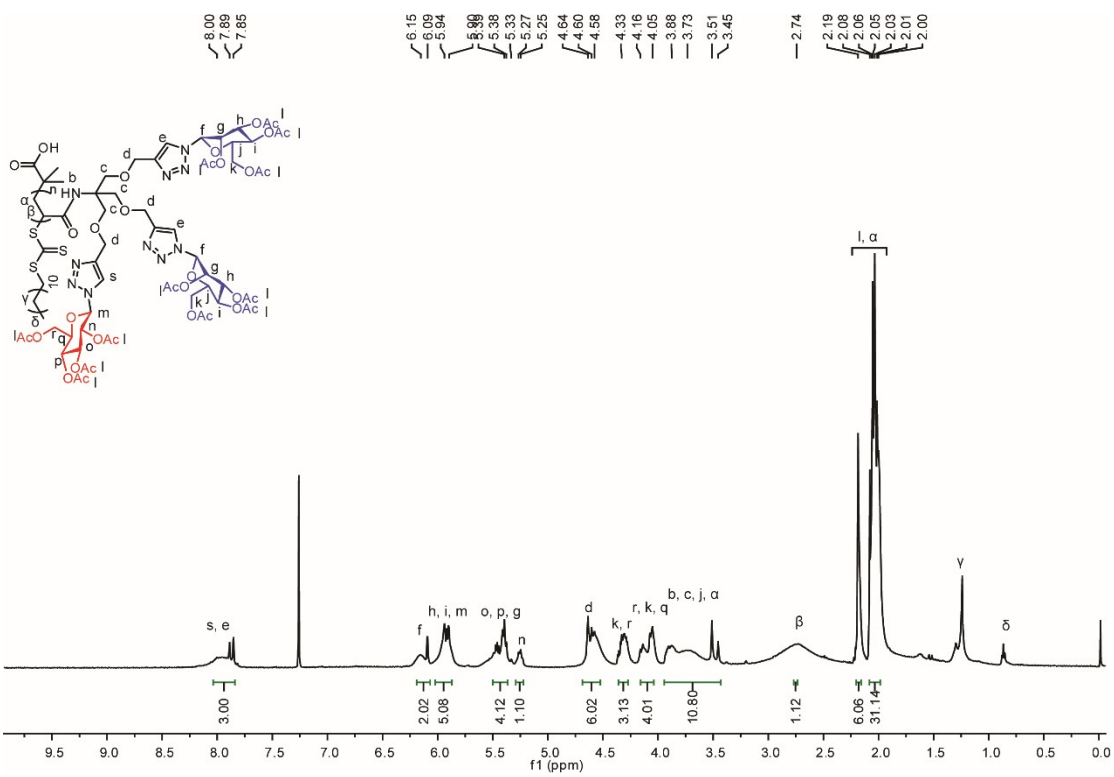

Figure S48. ^{1}H NMR spectrum of **P(αMan-αMan-βGlu-OAc)** in $CDCl_3$

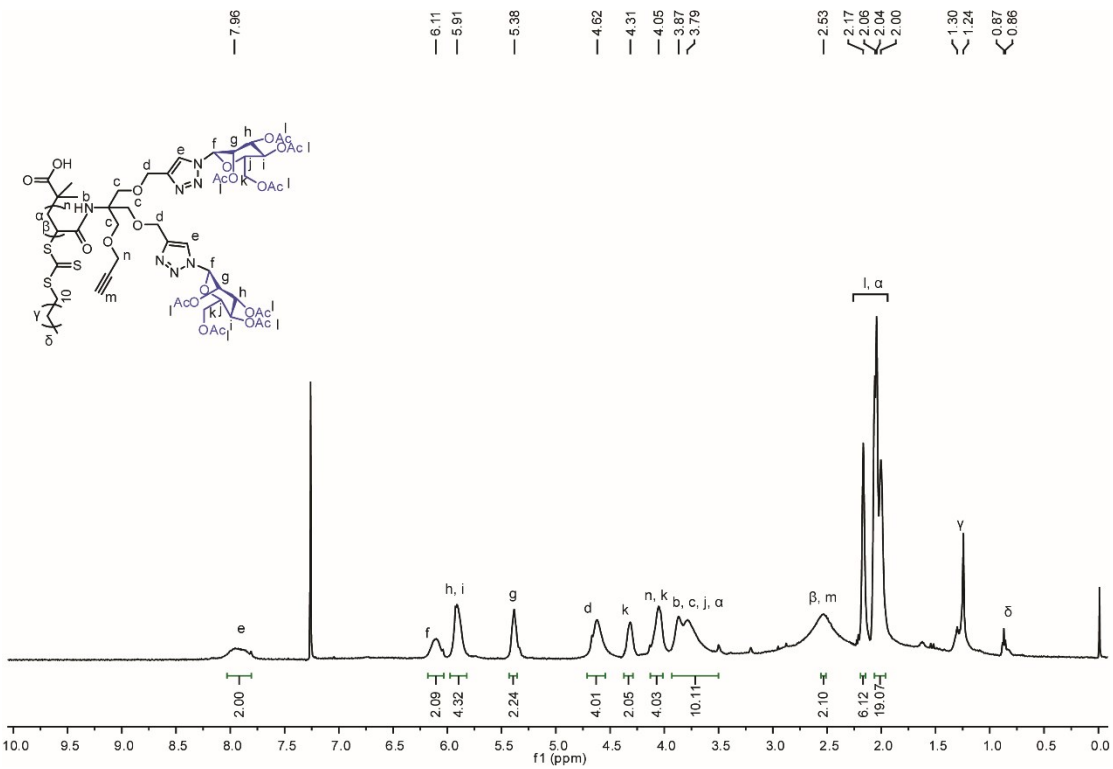

Figure S49. ^{1}H NMR spectrum of **P(αMan-αMan-yne-OAc)** in $CDCl_3$

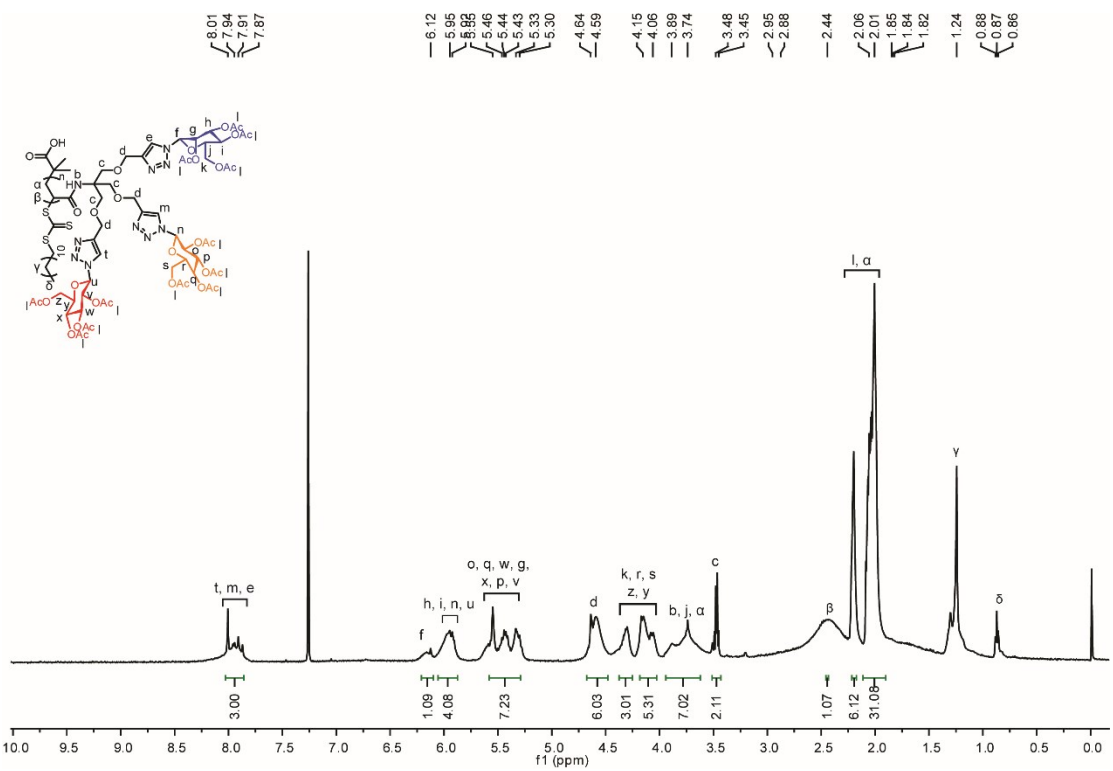

Figure S50. ^{1}H NMR spectrum of **P(αMan-βGal-βGlu-OAc)** in $CDCl_3$

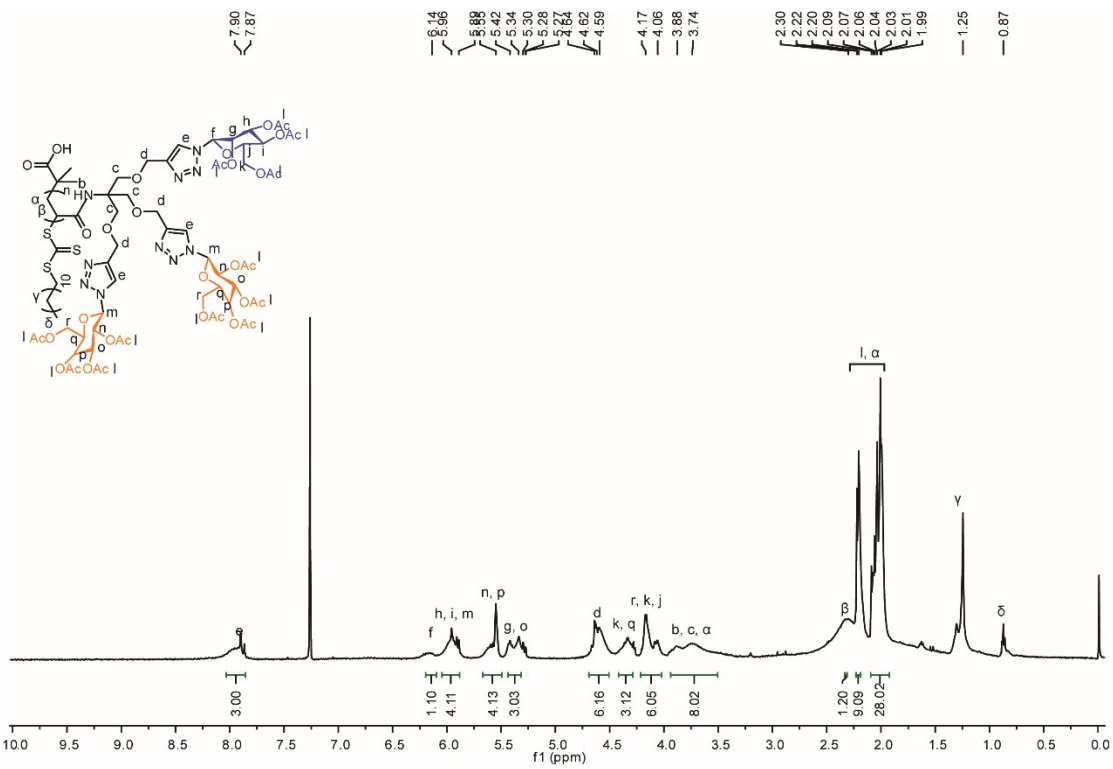

Figure S51. ^{1}H NMR spectrum of **P(αMan-βGal-βGal-OAc)** in $CDCl_3$

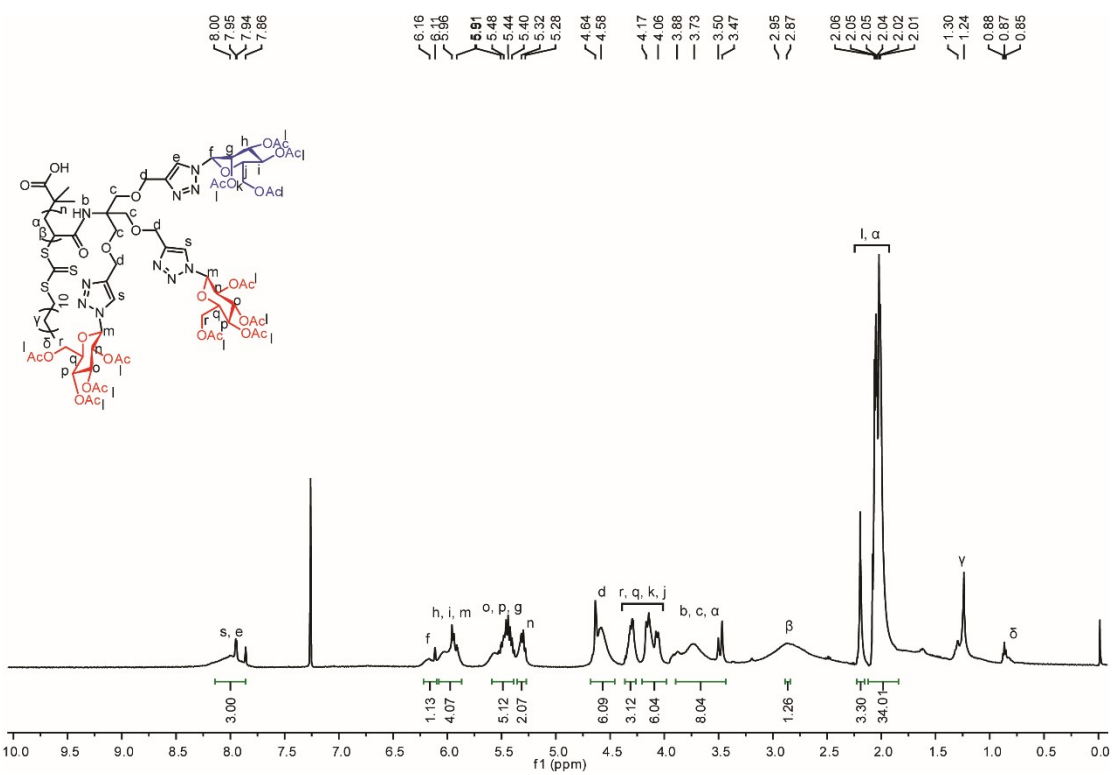

Figure S52. ^{1}H NMR spectrum of **P(αMan-βGlu-βGlu-OAc)** in $CDCl_3$

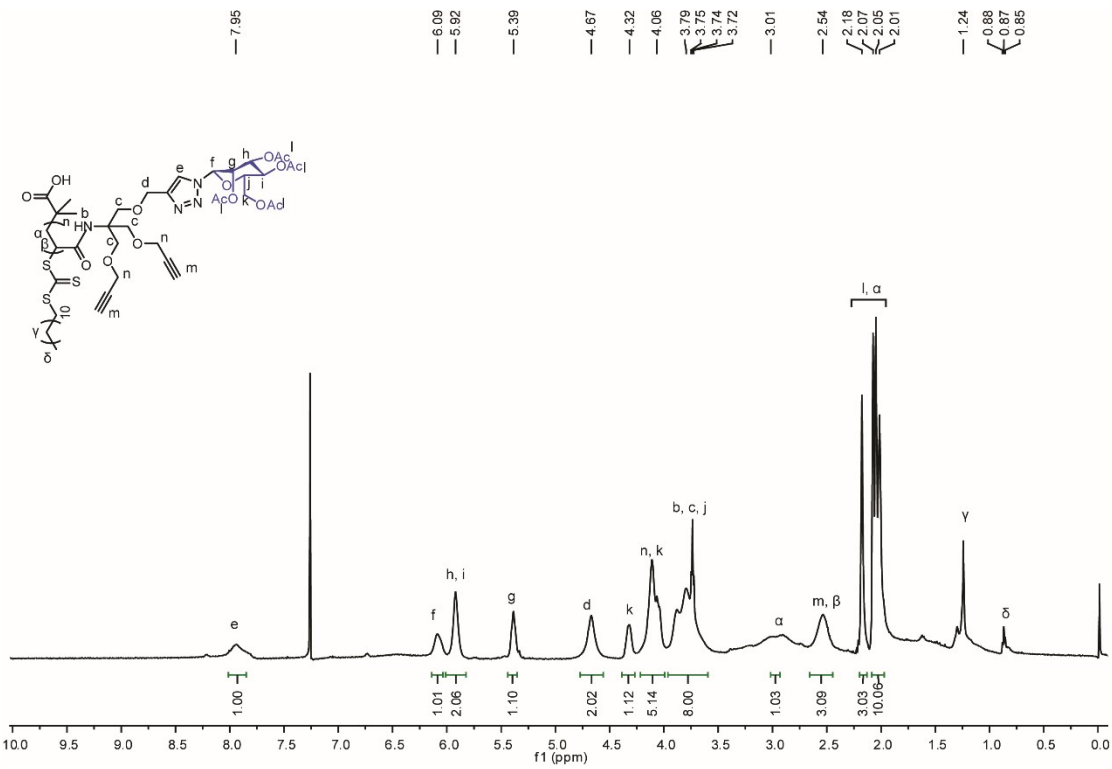

Figure S53. ^{1}H NMR spectrum of **P(*α*Man-yne-yne-OAc)** in $CDCl_3$

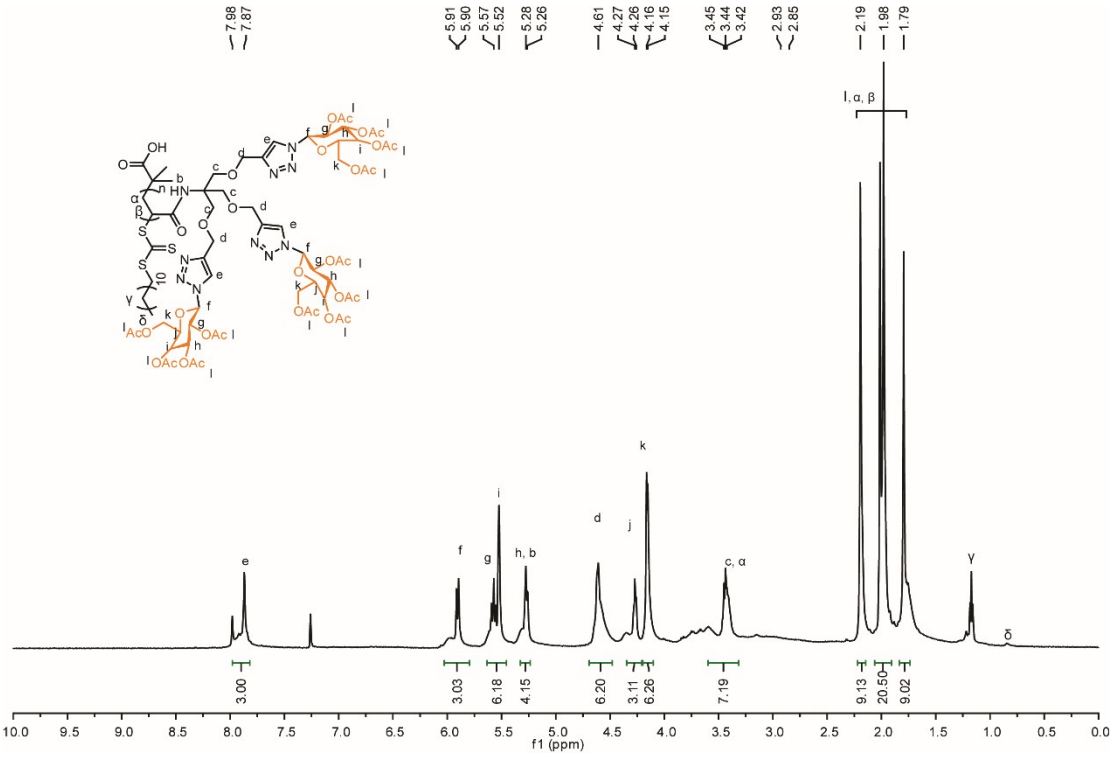

Figure S54. ^{1}H NMR spectrum of **P(βGal-βGal-βGal-OAc)** in $CDCl_3$

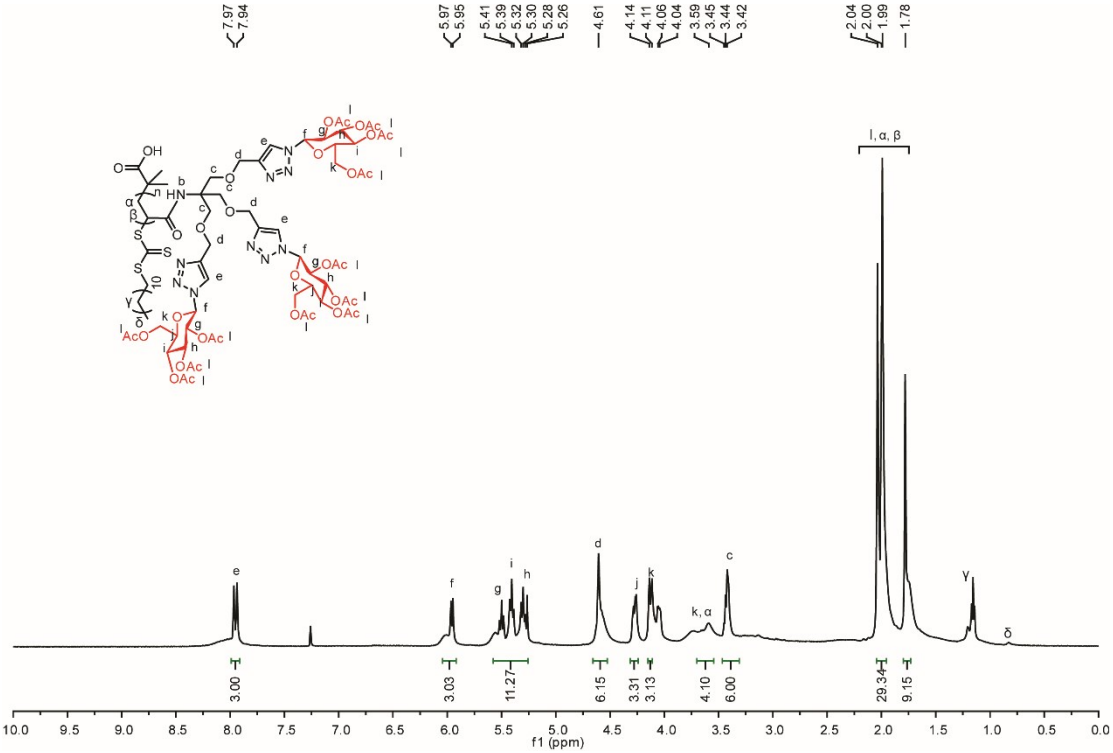

Figure S55. ^{1}H NMR spectrum of **P(βGlu-βGlu-βGlu-OAc)** in $CDCl_3$

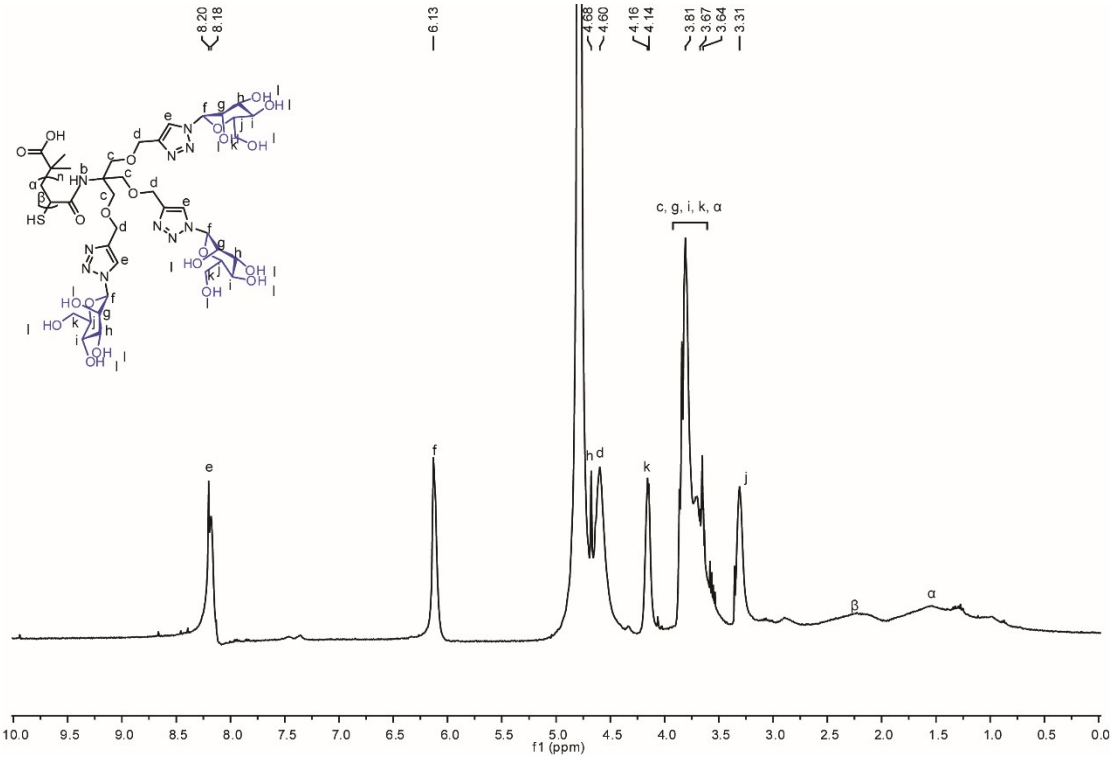

Figure S56. ^{1}H NMR spectrum of **P(αMan-αMan-αMan) (P1)** in $CDCl_3$

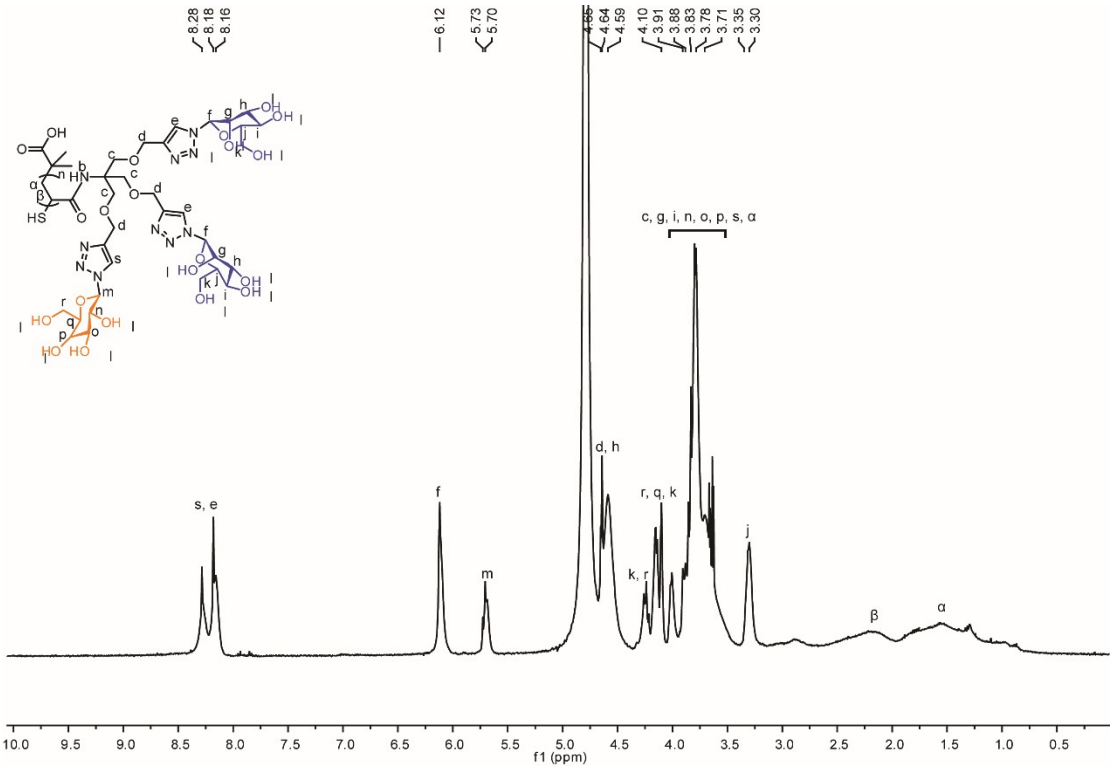

Figure S57. ^{1}H NMR spectrum of **P(αMan-αMan-βGal) (P2)** in $CDCl_3$

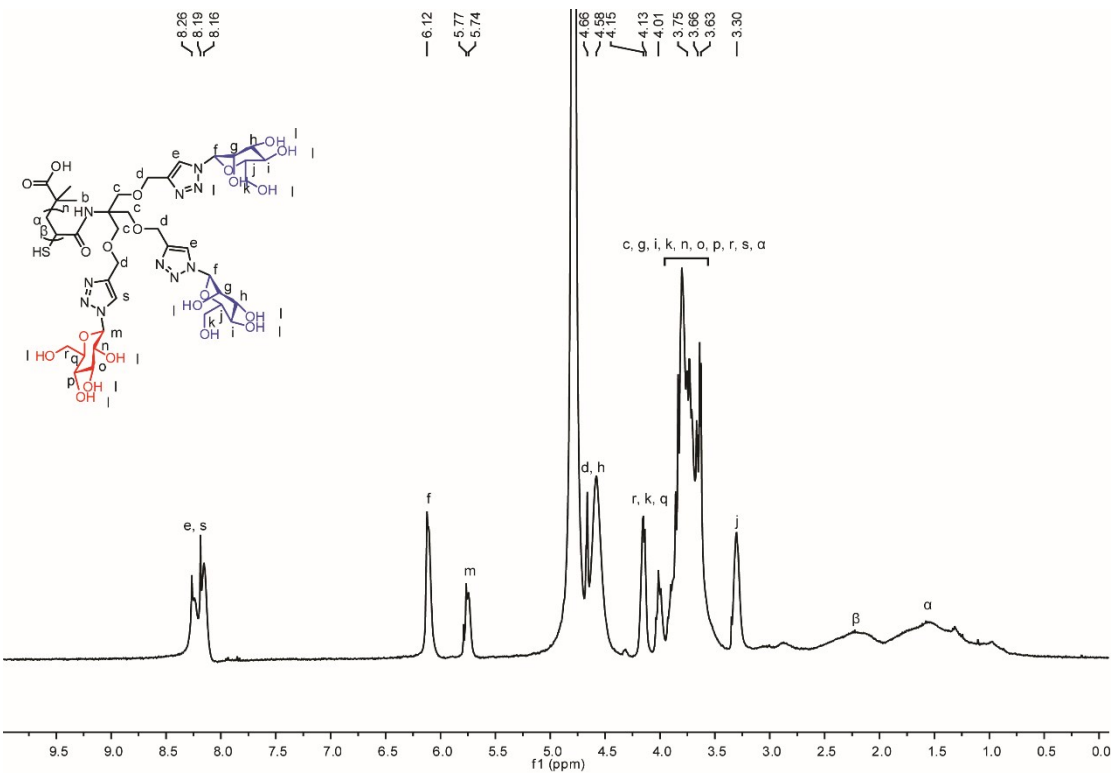

Figure S58. ^{1}H NMR spectrum of **P(αMan-αMan-βGlu) (P3)** in $CDCl_3$

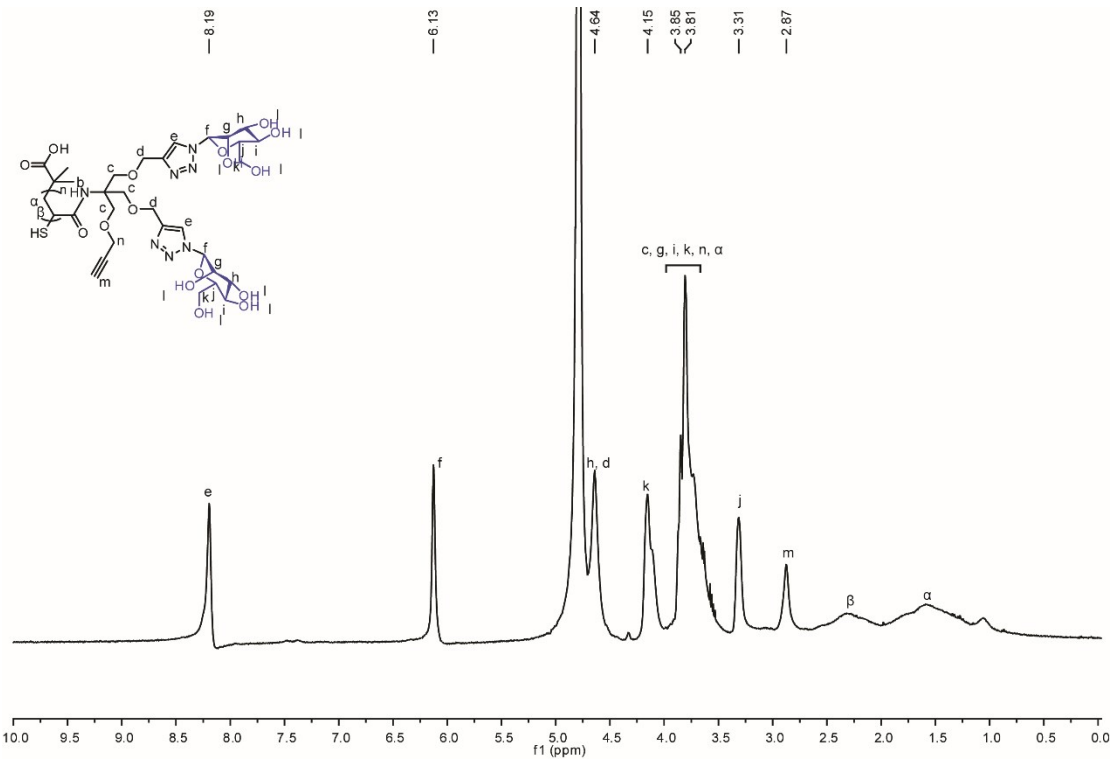

Figure S59. ^{1}H NMR spectrum of **P(αMan-αMan-yne) (P4)** in $CDCl_3$

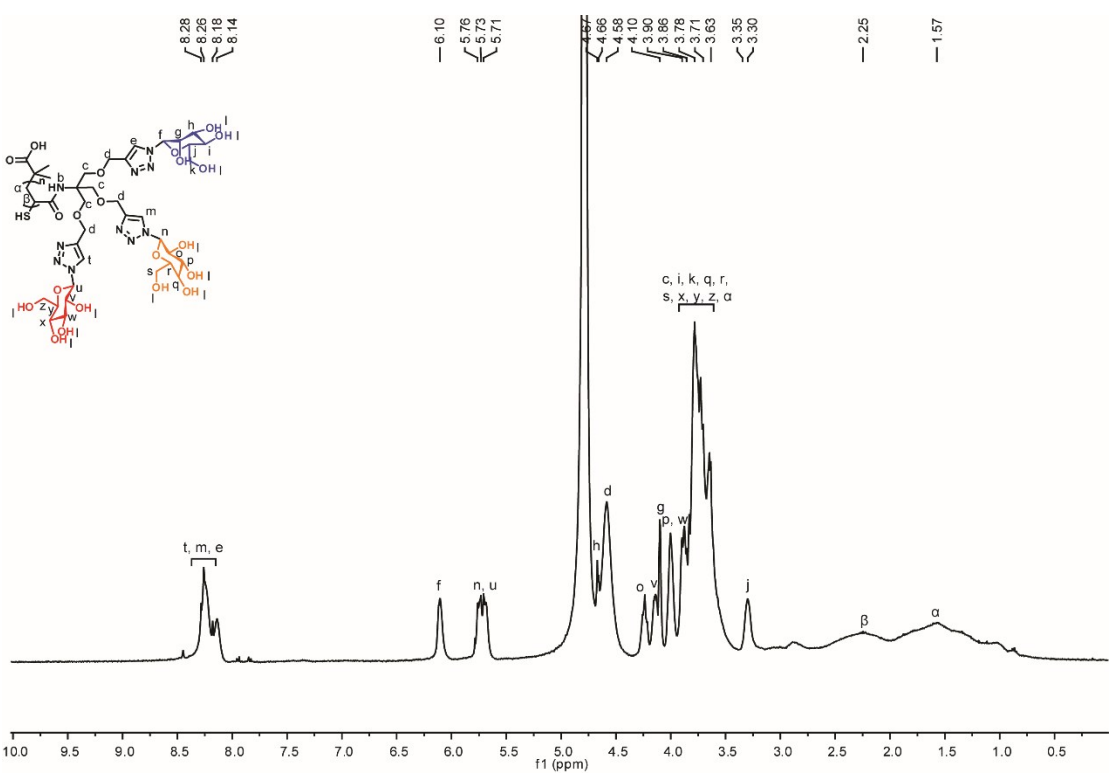

Figure S60. ^{1}H NMR spectrum of **P(αMan-βGal-βGlu) (P5)** in $CDCl_3$

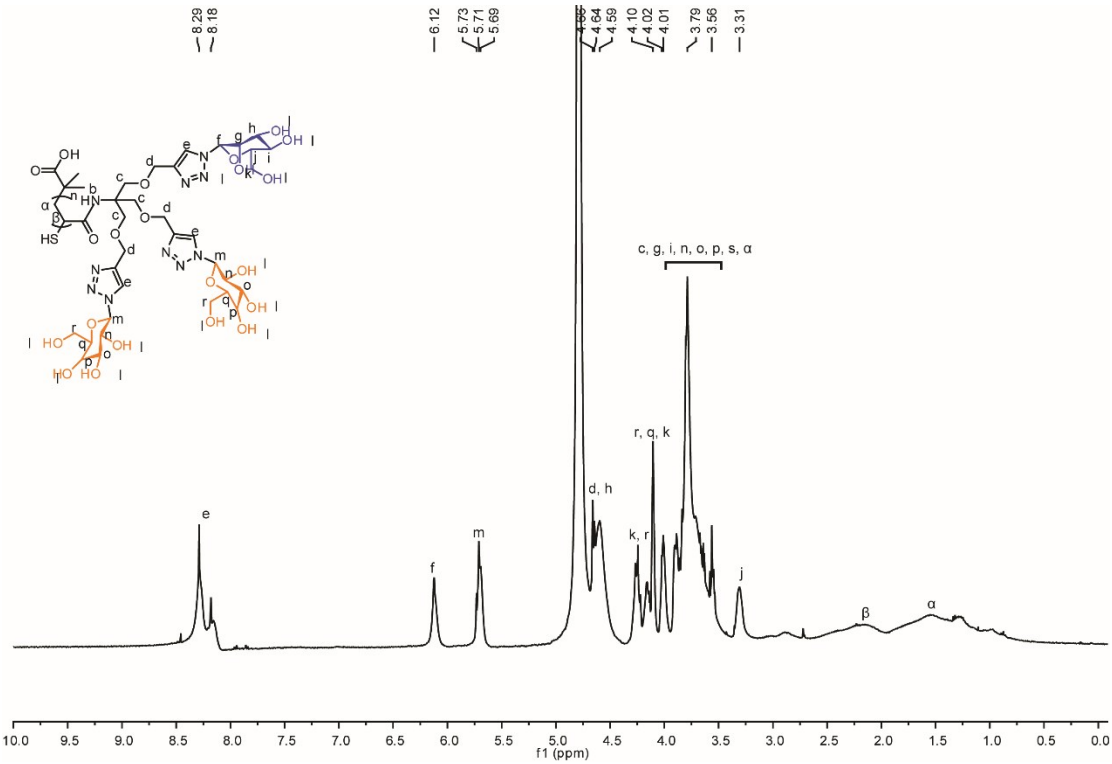

Figure S61. ^{1}H NMR spectrum of **P(αMan-βGal-βGal) (P6)** in $CDCl_3$

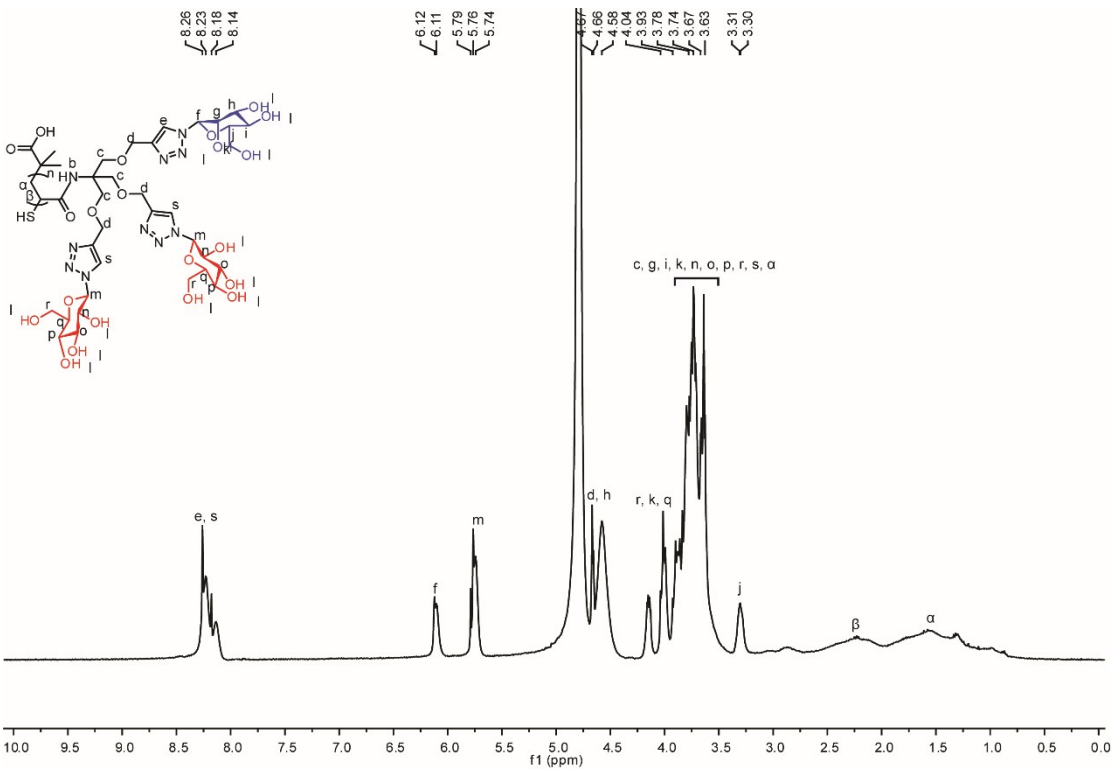

Figure S62. ^{1}H NMR spectrum of **P(αMan-βGlu-βGlu) (P7)** in $CDCl_3$

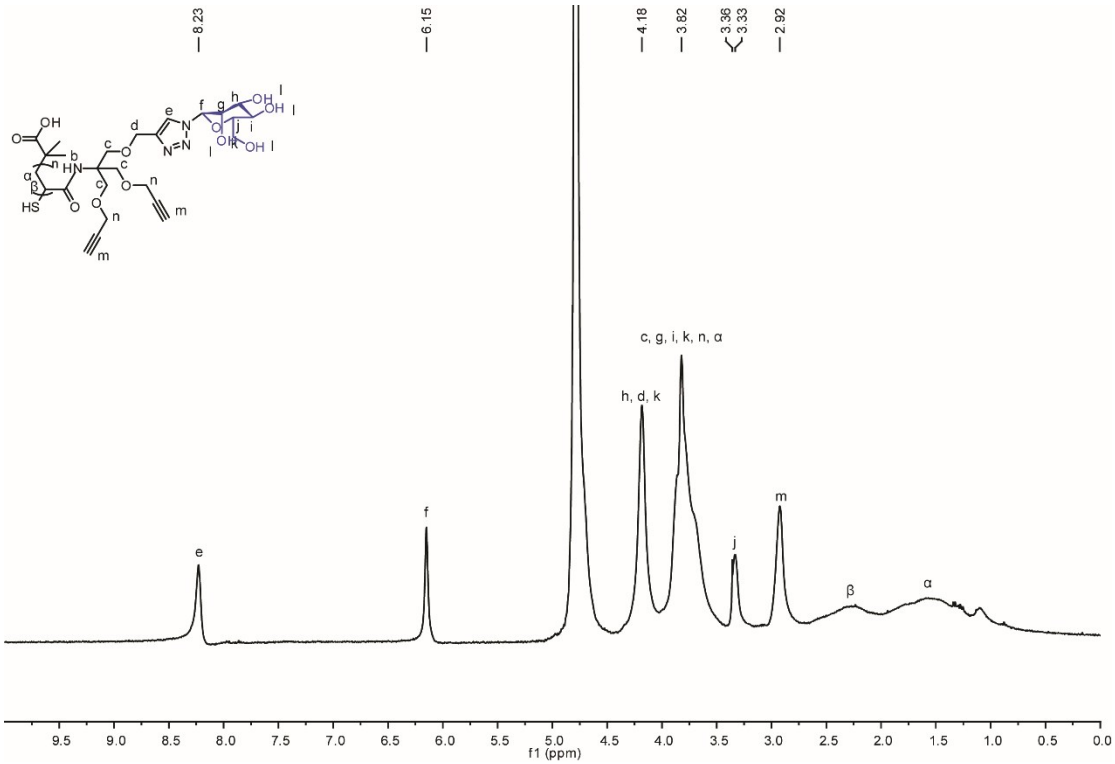

Figure S63. ^{1}H NMR spectrum of **P(αMan-yne-yne) (P8)** in $CDCl_3$

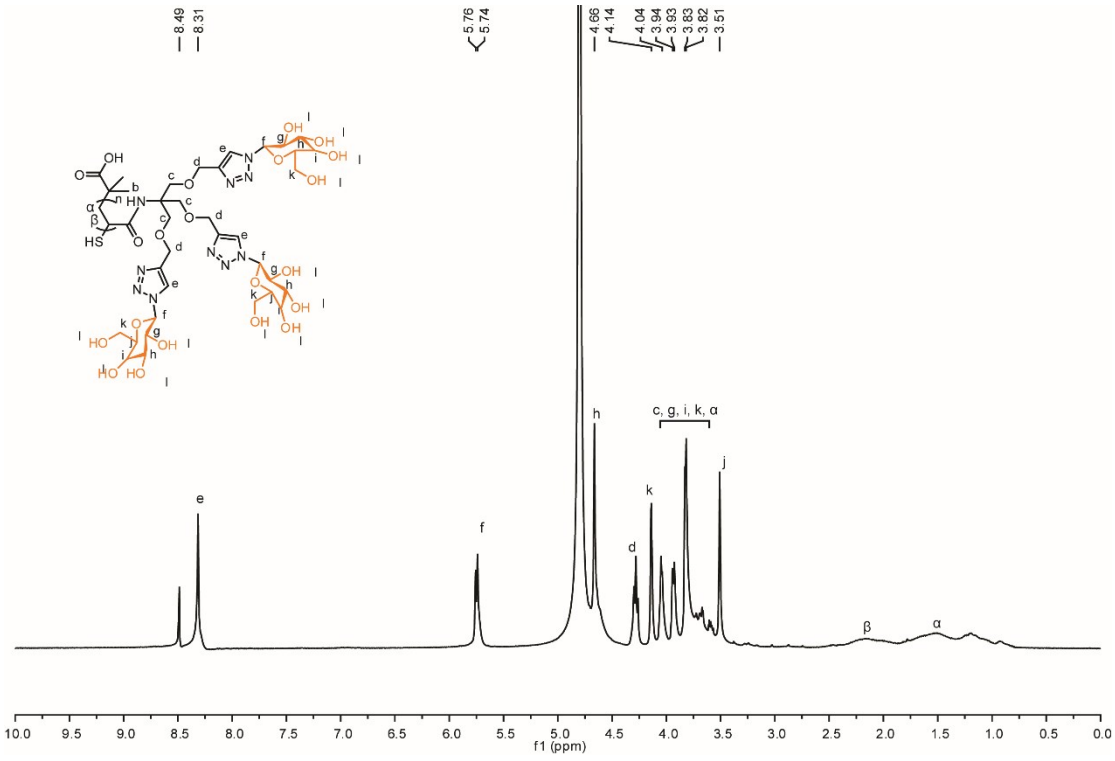

Figure S64. ^{1}H NMR spectrum of **P(βGal-βGal-βGal) (P9)** in $CDCl_3$

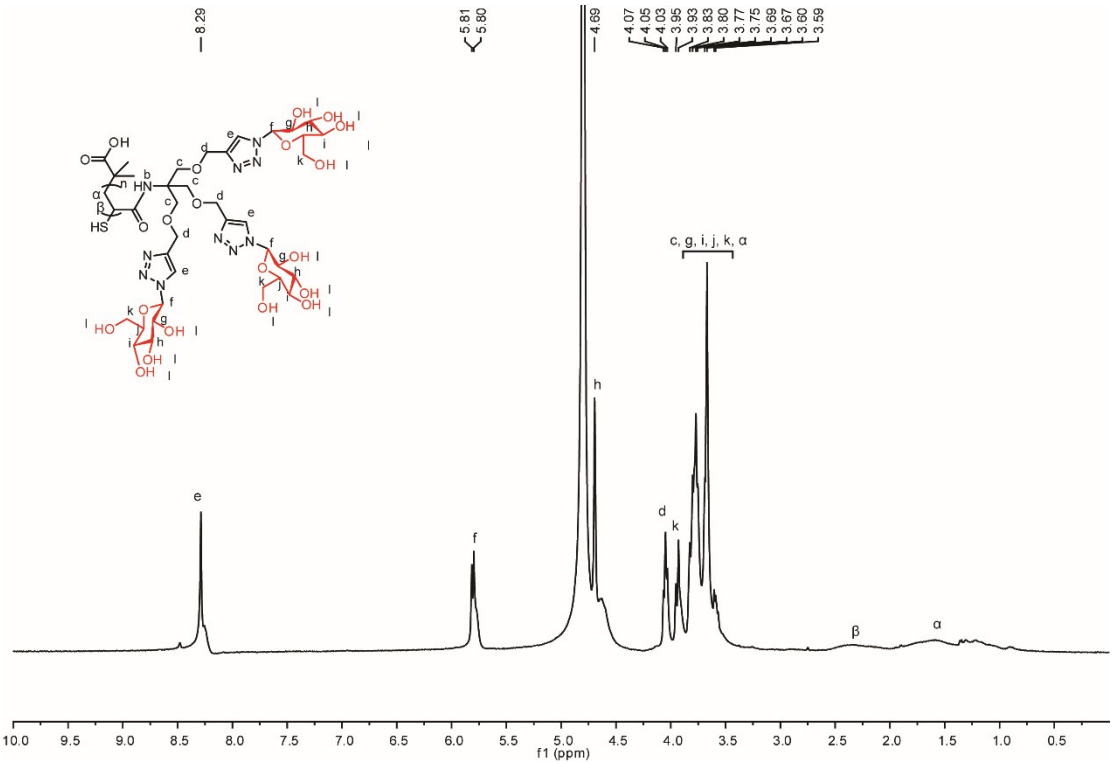

Figure S65. ^{1}H NMR spectrum of **P(βGlu-βGlu-βGlu) (P10)** in $CDCl_3$

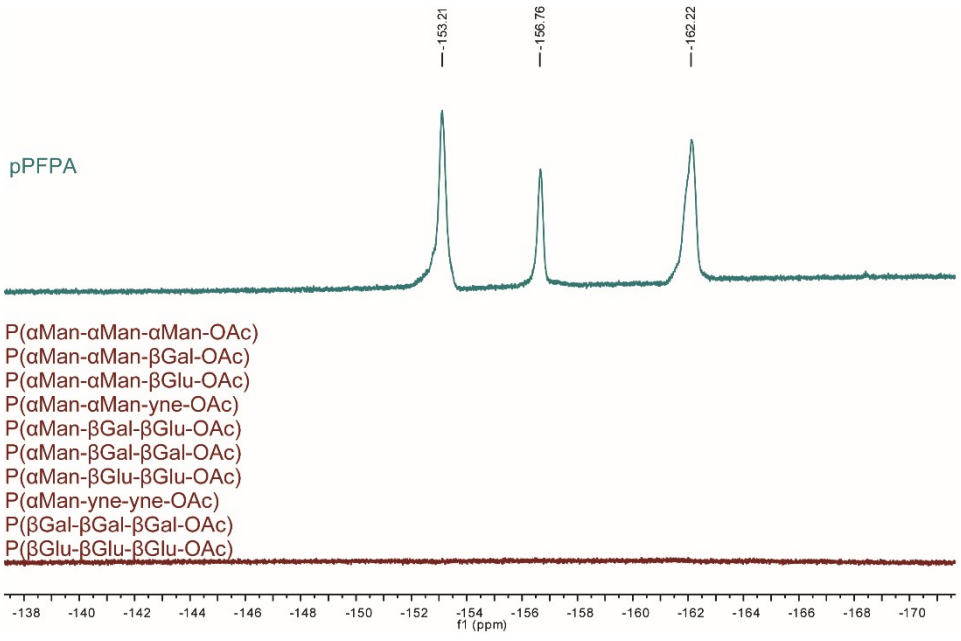

Figure S66. ^{19}F NMR spectrum of pPFPA and OAc-protected glycopolymers in $CDCl_3$

3. FT-IR spectra of glycopolymers

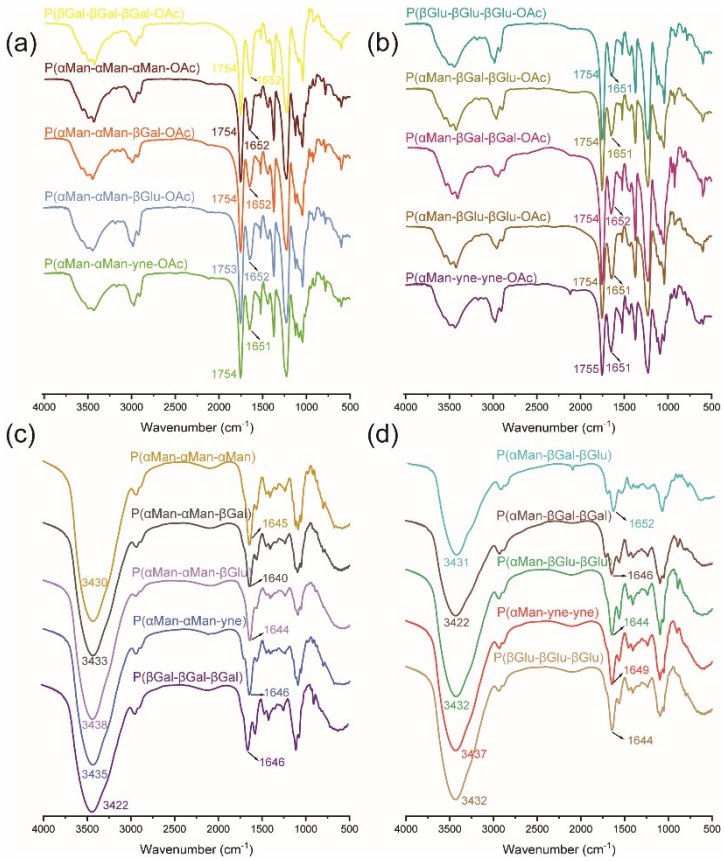

Figure S67. FT-IR spectra of the OAc-protected glycopolymers (a), (b) and deprotected glycopolymers (c), (d).

4. Dynamic light scattering

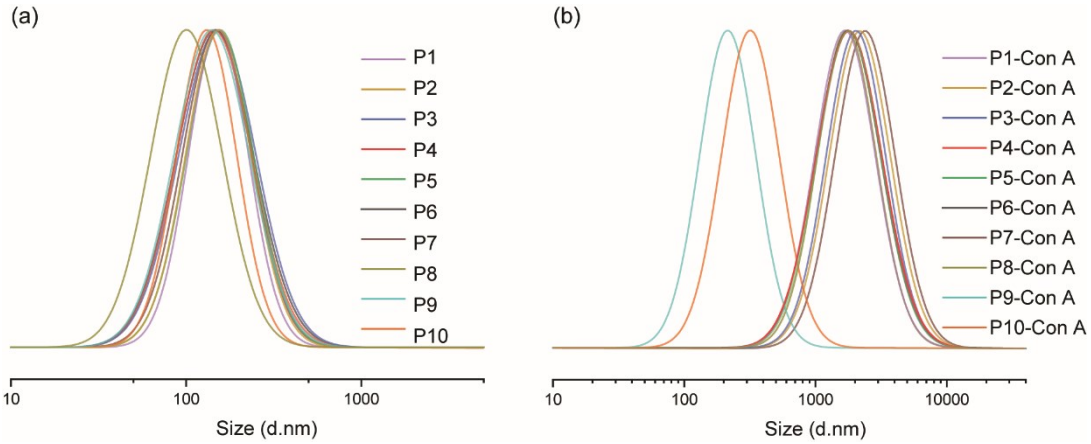

Figure S68. DLS study of interaction behavior between glycopolymers and Con A in HEPES buffer.

5. ITC thermograms

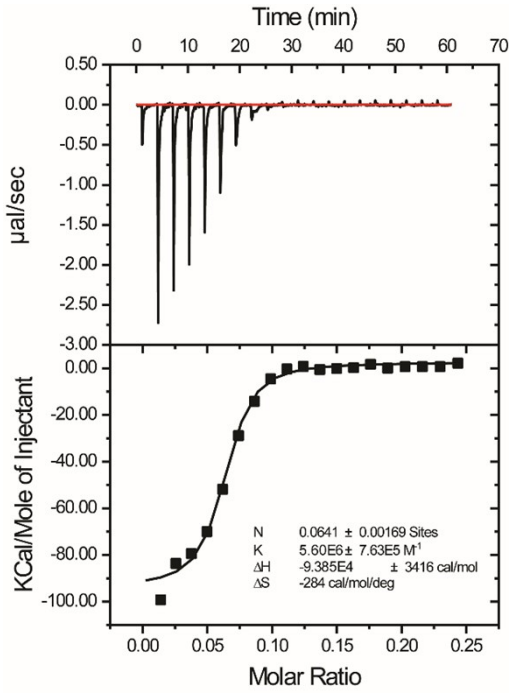

Figure S69. Calorimetric titration for **P(αMan-αMan-αMan)**.

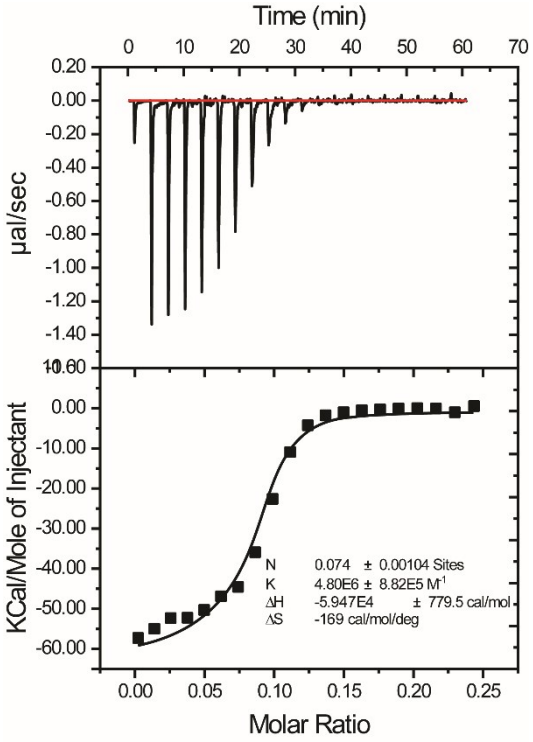

Figure S70. Calorimetric titration for **P(αMan-αMan-βGal)**.

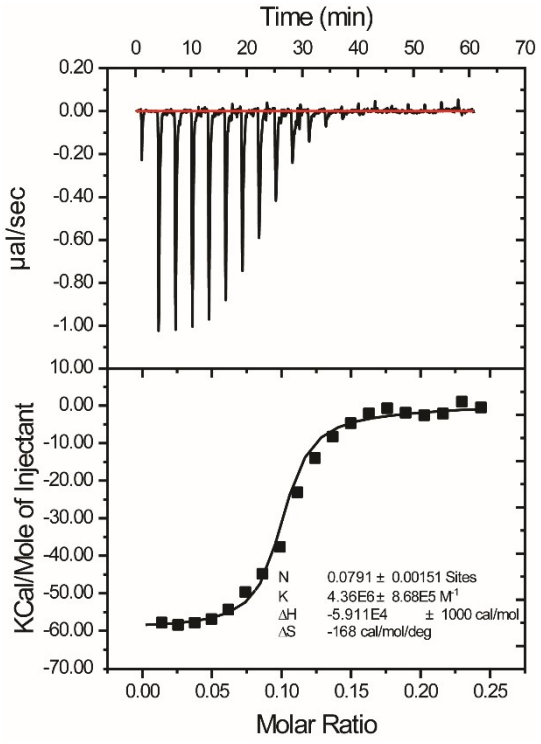

Figure S71. Calorimetric titration for **P(αMan-αMan-βGlu)**.

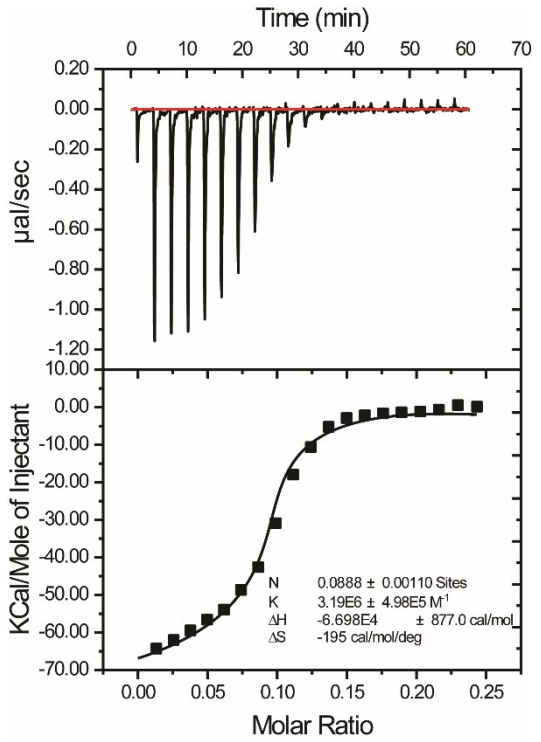

Figure S72. Calorimetric titration for **P(αMan-αMan-yne)**.

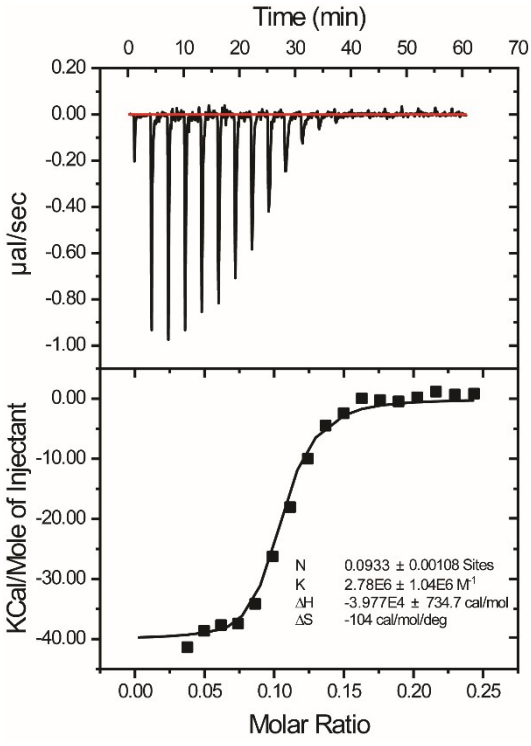

Figure S73. Calorimetric titration for **P(αMan-βGal-βGlu)**.

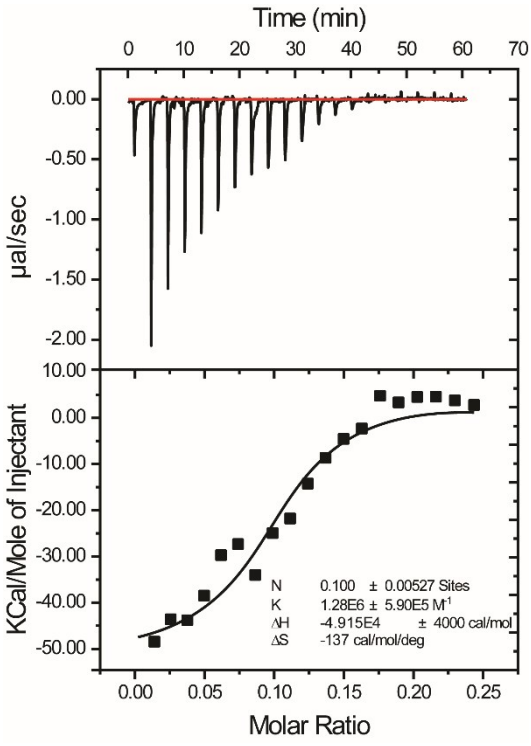

Figure S74. Calorimetric titration for **P(αMan-βGal-βGal)**.

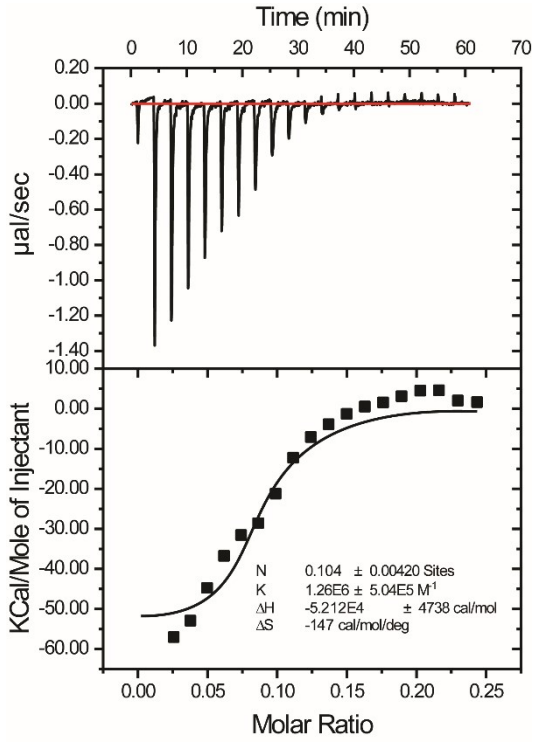

Figure S75. Calorimetric titration for **P(αMan-βGlu-βGlu)**.

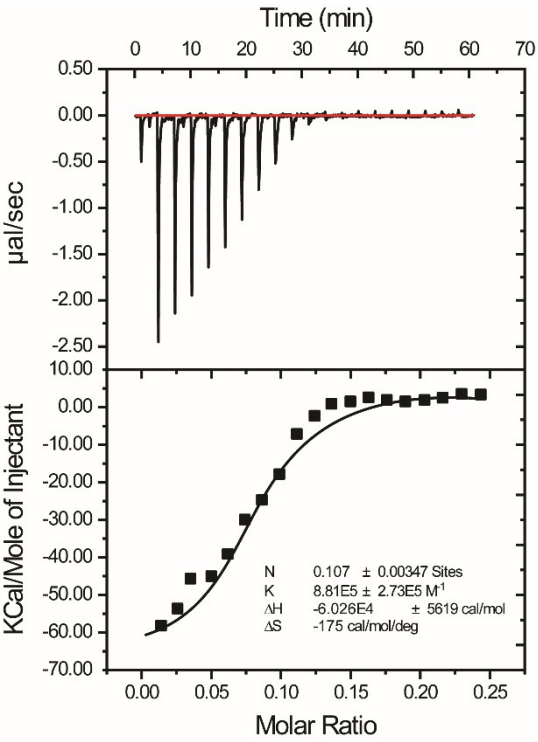

Figure S76. Calorimetric titration for **P(αMan-yne-yne)**.

6. Characterization of OAc-protected glycopolymers

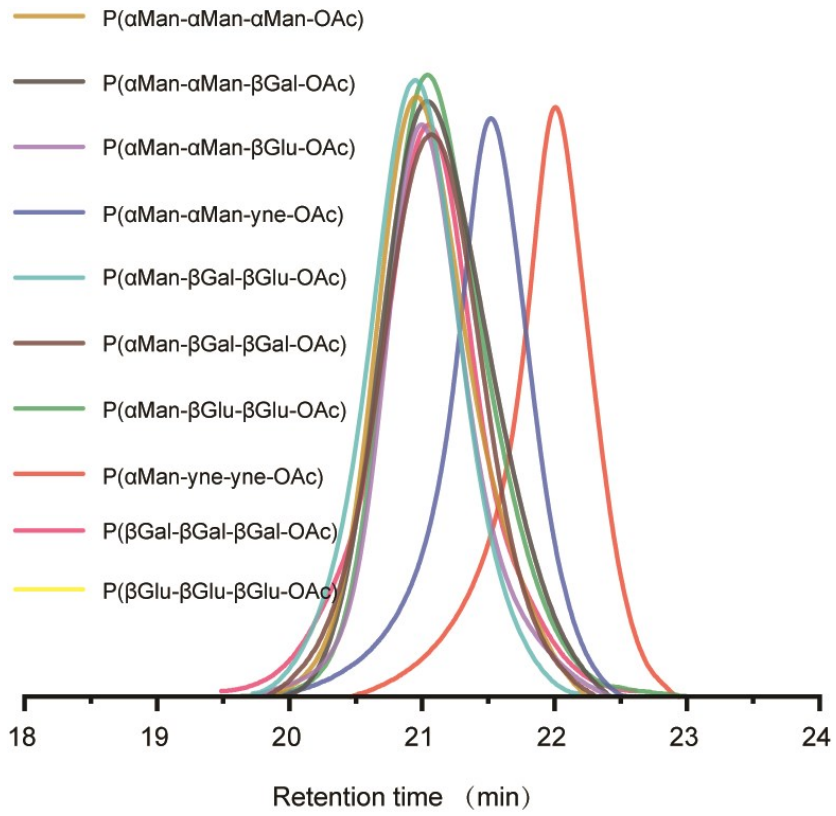

Figure S77. GPC chromatogram of OAc-protected glycopolymers

Table S1 Characterization of the pPFPA and OAc-protected glycopolymers

OAc-protected glycopolymer and pPFPA	Yield [a] [%]	M_n [b] [KDa]	M_w [b] [KDa]	$Đ$ [b]
P(αMan-αMan-αMan-OAc)	56	15.5	19.2	1.24
P(αMan-αMan-βGal-OAc)	55	15.3	19.0	1.24
P(αMan-αMan-βGlu-OAc)	58	15.5	18.9	1.22
P(αMan-αMan-yne-OAc)	55	11.4	14.2	1.25
P(αMan-βGal-βGlu-OAc)	55	15.5	19.0	1.23
P(αMan-βGal-βGal-OAc)	56	15.1	18.8	1.25
P(αMan-βGlu-βGlu-OAc)	58	15.3	18.7	1.23
P(αMan-yne-yne-OAc)	56	6.8	8.4	1.24
P(βGal-βGal-βGal-OAc)	56	15.3	18.8	1.23
P(βGlu-βGlu-βGlu-OAc)	58	15.5	19.1	1.23
pPFPA	65	3.8	4.3	1.14

[a] Isolated yield. [b] Obtained by GPC (DMF).