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Electronic Supplementary Information (ESI)

Synthesis of well-defined glycopolymers with highly ordered sugar units in the side chain *via* combining CuAAC reaction and ROMP: lectin interaction study in homo- and hetero- glycopolymers

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Experiments：

1. Synthesis of α-D-mannopyranosyl azide[1].

The α-D-mannopyranosyl azide was synthesized according to the ref. 1. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.33 (d, J = 1.3 Hz, 1H), 5.24–5.15 (m, 2H), 5.10–5.06 (m, 1H), 4.23 (dd, J = 12.6, 5.7 Hz, 1H), 4.08 (dd, J = 10.1, 5.4 Hz, 2H), 2.09 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H), 1.92 (s, 3H).

2. Synthesis of β-D-glucopyranosylazide azide[2].

The β-D-glucopyranosylazidewas synthesized according to the ref. 2. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.22 (t, J = 9.5 Hz, 1H), 5.11 (t, J = 9.7 Hz, 1H), 4.96 (t, J = 9.2 Hz, 1H), 4.66 (d, J = 8.8 Hz, 1H), 4.28 (dd, J = 12.4, 4.7 Hz, 1H), 4.17 (d, J = 12.4 Hz, 1H), 3.8–3.78 (m, 1H), 2.11 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H).

3. Synthesis of α-D-glucopyranosyl azide[3].

The α-D-glucopyranosyl azide was synthesized according to the ref. 3. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.21 (t, J = 9.5 Hz, 1H), 5.09 (t, J = 9.8 Hz, 1H), 4.95 (t, J = 9.2 Hz, 1H), 4.64 (d, J = 8.9 Hz, 1H), 4.26 (dd, J = 12.5, 4.8 Hz, 1H), 4.16 (dd, J = 12.5, 2.3 Hz, 1H), 3.79 (ddd, J = 10.1, 4.8, 2.3 Hz, 1H), 2.09 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H).

4. **Synthesis of β-D-galactopyranosyl azide[4].**

The β-D-galactopyranosyl azide was synthesized according to the ref. 4. ^{1}H NMR (501 MHz, $CDCl_3$): δ 5.19 (t, J = 9.5 Hz, 1H), 5.07 (t, J = 9.7 Hz, 1H), 4.92 (t, J = 9.2 Hz, 1H), 4.63 (d, J = 8.8 Hz, 1H), 4.28–4.08 (m, 2H), 3.77 (d, J = 7.6 Hz, 1H), 2.02 (dd, J = 34.7, 11.7 Hz, 12H).

5. **Synthesis of homo-disaccharide monomer (5A, M(βGlu-βGlu)).**

Compound **3** (0.5 g, 1.5 mmol) and β-D-glucopyranosyl azide (1.2 g, 3.3 mmol) were dissolved in *t*-BuOH/H_2O (8 mL, 1 : 1 *v/v*). Then copper(II) sulfate pentahydrate (0.18 g, 0.75 mmol) and Na ascorbate (0.29 g, 1.5 mmol) were added. The reaction mixture was stirred for 2h at 60 °C. The insoluble salt was filtered off and the filtrate was concentrated to give the crude product, which was purified by column chromatography (ethyl acetate/petroleum ether 3 : 1, R_f = 0.37). **5A** was obtained as a white solid to yield 1.3 g, 83%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, J = 19.5 Hz, 2H), 5.94 (t, J = 10.0 Hz, 4H), 5.50–5.44 (m, 2H), 5.40–5.34 (m, 2H), 5.32–5.23 (m, 2H), 4.53 (d, J = 6.5 Hz, 4H), 4.23–4.21 (m, 2H), 4.08–4.01 (m, 4H), 3.85–3.77 (m, 4H), 3.22 (s, 2H), 3.04 (s,

2H), 2.10–1.94 (m, 18H), 1.76–1.72 (m, 6H), 1.54 (d, J = 8.0 Hz, 1H), 1.36 (d, J = 7.5 Hz, 1H), 1.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.93, 170.49, 169.95, 169.46, 168.81, 168.78, 145.86, 134.43, 121.16, 85.49, 74.90, 72.76, 70.72, 70.54, 70.21, 67.74, 64.50, 64.34, 63.19, 61.57, 51.65, 47.87, 42.84, 20.62, 20.56, 20.51, 20.08, 20.02, 19.15. HRMS (ESI): calc. for $C_{47}H_{59}N_7O_{22}H$ ($M+H^+$):1074.37579; found: 1074.37381.

6. Synthesis of homo-disaccharide monomer (6A, M(αGlu-αGlu)).

Compound **3** (0.5 g, 1.5 mmol) and α-D-glucopyranosyl azide (1.2 g, 3.3 mmol) were dissolved in *t*-BuOH/H_2O (8 mL, 1 : 1 v/v). Then copper(II) sulfate pentahydrate (0.18 g, 0.75 mmol) and Na ascorbate (0.29 g, 1.5 mmol) were added. The reaction mixture was stirred for 2 h at 60 °C. The insoluble salt was filtered off and the filtrate was concentrated to give the crude product, which was purified by column chromatography (ethyl acetate/petroleum ether 3 : 1, R_f = 0.40). **6A** was obtained as a white solid to yield 1.1 g, 74%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (s, 2H), 6.06 (s, 2H), 5.93 (d, J = 9.3 Hz, 2H), 5.57 (s, 4H), 5.29 (s, 2H), 4.63 (d, J = 9.6 Hz, 4H), 4.29 (s, 2H), 4.20 (d, J = 5.7 Hz, 4H), 3.98 (d, J = 9.2 Hz, 1H), 3.94 (d, J = 9.2 Hz, 1H), 3.89–3.82 (m, 2H), 3.34 (s, 2H), 3.16 (s, 2H), 2.25 (s, 6H), 2.04 (d, J = 17.9 Hz, 12H), 1.88 (s, 3H), 1.83 (s, 3H), 1.68 (s, 1H), 1.48 (d, J = 8.7 Hz, 1H), 1.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.98, 170.36, 170.05, 169.85, 168.94, 145.71, 134.47, 121.40, 86.04, 77.32, 77.06, 76.81, 73.87, 70.88, 67.86, 66.93, 64.45, 63.30, 61.12, 51.71, 45.39, 20.66, 20.49, 20.18, 19.29, 14.18. HRMS (ESI): calc. for $C_{47}H_{59}N_7O_{22}H$ ($M+H^+$): 1074.37672; found: 1074.37489.

7. Synthesis of hetero-disaccharide monomer (6B, M(Man-αGlu)).

Compound **4B** (0.30 g, 0.43 mmol) and α-D-glucopyranosyl azide (0.19 g, 0.52 mmol) was dissolved in *t*-BuOH/H_2O (4 mL, 1 : 1 *v/v*). Then copper(II) sulfate pentahydrate (0.05 g, 0.21 mmol) and Na ascorbate (0.08 g, 0.43 mmol) were added. The insoluble salt was filtered off and the filtrate was concentrated to give the crude product, which was purified by column chromatography (ethyl acetate/petroleum ether 3 : 1, R_f = 0.39). **6B** was obtained as a white solid to yield 0.31 g, 73%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (s, 2H), 5.94 (d, J = 7.9 Hz, 2H), 5.86 (d, J = 8.7 Hz, 2H), 5.24 (s, 5H), 5.21–5.15 (m, 1H), 4.56–4.47 (m, 4H), 4.30–4.20 (m, 2H), 4.01 (s, 4H), 3.90–3.84 (m, 2H), 3.75 (s, 2H), 3.23 (s, 2H), 3.06 (s, 2H), 2.12 (d, J = 2.1 Hz, 3H), 1.98 (dd, J = 11.9, 10.5 Hz, 18H), 1.75 (d, J = 11.7 Hz, 3H), 1.56 (d, J = 5.4 Hz, 1H), 1.39 (d, J = 8.4 Hz, 1H), 1.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.93, 170.44, 169.83, 169.66, 169.45, 168.88, 145.70, 145.61, 145.51, 134.40, 123.08, 121.19, 85.38, 83.65, 77.44, 77.18, 76.93, 74.85, 72.61, 71.90, 70.64, 70.57, 70.33, 70.13, 68.86, 68.27, 67.74, 65.91, 64.25, 64.06, 63.20, 61.57, 51.62, 45.30, 20.53, 19.99, 19.17, 14.11. HRMS (ESI): calc. for $C_{47}H_{59}N_7O_{22}H$ ($M+H^+$): 1074.37826; found: 1074.37692.

8. Synthesis of homo-disaccharide monomer (7A, M(βGal-βGal)).

Compound **3** (0.5 g, 1.5 mmol) and β-D-galactopyranosyl azide (1.2 g, 3.3 mmol) were dissolved in *t*-BuOH/H_2O (8 mL, 1 : 1 v/v). Then copper(II) sulfate pentahydrate (0.18 g, 0.75 mmol) and Na ascorbate (0.29 g, 1.5 mmol) were added. The reaction mixture was stirred for 2 h at 60 °C. The insoluble salt was filtered off and the filtrate was concentrated to give the crude product, which was purified by column chromatography (ethyl acetate/petroleum ether 3 : 1, R_f = 0.40). **7A** was obtained as a white solid to yield 1.2 g, 76%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (s, 2H),

6.01 (s, 2H), 5.90 (d, J = 9.3 Hz, 2H), 5.52 (d, J = 2.8 Hz, 4H), 5.30–5.23 (m, 2H), 4.57 (t, J = 6.6 Hz, 4H), 4.27 (s, 2H), 4.18–4.09 (m, 4H), 3.90 (dd, J =23.1, 9.1 Hz, 2H), 3.83–3.76 (m, 2H), 3.28 (s, 2H), 3.11 (s, 2H), 2.19 (s, 6H), 2.0–1.96 (m, 12H), 1.82 (s, 3H), 1.78 (s, 3H), 1.61 (d, J = 8.6 Hz, 1H), 1.43 (d, J = 8.5 Hz, 1H), 1.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.96, 170.52, 169.97, 169.47, 168.84, 145.91, 134.45, 121.13, 85.56, 77.33, 77.08, 76.82, 74.98, 72.80, 70.77, 70.60, 70.20, 67.79, 64.46, 63.24, 61.59, 51.68, 45.36, 20.63, 20.57, 20.52, 20.10, 20.04, 19.17, 14.17. The ^{1}H NMR and ^{13}C spectrum of the desired product was seen in Figures S22-23. HRMS (ESI): calc. for $C_{47}H_{59}N_7O_{22}H$ ($M+H^+$): 1074.37548; found: 1074.37853.

9. Synthesis of hetero-disaccharide monomer (7B, M(αMan-βGal)).

Compound **4B** (0.30 g, 0.43 mmol) and β-D-galactopyranosyl azide (0.19 g, 0.52 mmol) was dissolved in t-BuOH/H_2O (4 mL, 1 : 1 v/v). Then copper(II) sulfate pentahydrate (0.05 g, 0.21 mmol) and Na ascorbate (0.08 g, 0.43 mmol) were added. The insoluble salt was filtered off and the filtrate was concentrated to give the crude product, which was purified by column chromatography (ethyl acetate/petroleum ether 3 : 1, R_f = 0.40). **7B** was obtained as a white solid to yield 0.33 g, 74%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (dd, J = 18.7, 13.1 Hz, 2H), 6.03–5.83 (m, 6H), 5.51 (d, J = 10.1 Hz, 2H), 5.39–5.33 (m, 1H), 5.25 (d, J = 2.3 Hz, 1H), 4.54 (dd, J = 22.7, 12.7 Hz, 4H), 4.24 (s, 2H), 4.17–3.98 (m, 4H), 3.91 (d, J = 8.2 Hz, 2H), 3.81–3.76 (m, 2H), 3.26 (s, 2H), 3.09 (s, 2H), 2.18–2.14 (m, 6H), 2.03 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.97 (s, 3H), 1.94 (s, 3H), 1.78 (d, J = 17.5 Hz, 3H), 1.59 (d, J = 7.9 Hz, 1H), 1.42 (d, J = 8.6 Hz, 1H), 1.35 (d, J = 4.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.95, 170.48, 170.28, 170.01, 169.67, 169.43, 169.10, 145.77, 145.44, 134.45, 123.17, 121.35, 85.91, 83.70, 77.39, 77.14, 76.88, 73.85, 71.91, 70.78, 70.22, 68.93, 68.35, 67.74, 66.98, 65.91, 64.31, 64.02, 63.25, 61.62, 61.18, 51.67, 45.39, 45.32, 45.29, 20.63, 20.58, 20.52, 20.44, 20.16, 20.10, 19.21. The ^{1}H NMR and ^{13}C spectrum of the desired product was seen in Figures S24-25. HRMS (ESI): calc. for $C_{47}H_{59}N_7O_{22}H$ ($M+H^+$): 1074.375712; found: 1074.37252.

10. Synthesis of poly(Man-Man-OAc)

A glass vial was charged with **4A** (100 mg, 0.09 mmol) and Grubbs 3rd (2.7 mg, 0.009 mmol) sealing with rubber stopper and their head space thoroughly sparged with argon for 10 min. Then 1 mL of anhydrous tetrahydrofuran was added for keeping argon. After being dissolved, the mixture was stirred at 50 °C for 12 h and monitored by TLC. Finally, ethylvinyl ether (0.3 mL) was added to quench the reaction and precipitated with an excess of ether for twice. The polymer **poly(Man-Man-OAc)** was isolated by centrifugation to yield 0.091 g, 91% an off white solid.

11. Synthesis of poly(Man-Man)

The **poly(Man-Man-OAc)** (80 mg, 0.01 mmol) dissolved in MeOH/DCM (2 mL, 1 : 1 v/v) and then MeONa (8 mg, 10 wt%) was added. The reaction mixture was stirred at room temperature for 12 h and the solvent was evaporated under reduced pressure. The residue was dissolved water (2 mL) and brought to neutral pH with Dowex H^+ resin. The aqueous solution was filtered and lyophilized to produce **poly(Man-Man)** as a brown solid yield 0.031 g, 76%.

12. Synthesis of poly(βGlu-βGlu-OAc)

A glass vial was charged with **5A** (100 mg, 0.09 mmol) and Grubbs 3rd (2.7 mg, 0.009 mmol) sealing with rubber stopper and their head space thoroughly sparged with argon for 10 min. Then 1 mL of anhydrous tetrahydrofuran was added for keeping argon. After being dissolved, the mixture was stirred at 50 °C for 12 h and monitored by TLC. Finally, ethylvinyl ether (0.3 mL) was added to quench the reaction and precipitated with an excess of ether for twice. The polymer **poly(βGlu-βGlu-OAc)** was isolated by centrifugation to yield 0.092 g, 92% an off white solid.

13. Synthesis of poly(βGlu-βGlu)

The **poly(βGlu-βGlu-OAc)** (80 mg, 0.01 mmol) dissolved in MeOH/DCM (2 mL, 1 : 1 v/v) and then MeONa (8 mg, 10 wt%) was added. The reaction mixture was stirred at room temperature for 12 h and the solvent was evaporated under reduced pressure. The residue was dissolved water (2 mL) and brought to neutral pH with Dowex H^+ resin. The aqueous solution was filtered and lyophilized to produce **poly(βGlu-βGlu)** as a brown solid yield 0.031 g, 76%.

14. Synthesis of poly(Man-Alkyne-OAc)

A glass vial was charged with **4B** (100 mg, 0.09 mmol) and Grubbs 3rd (2.7 mg, 0.009 mmol) sealing with rubber stopper and their head space thoroughly sparged with argon for 10 min. Then 1 mL of anhydrous tetrahydrofuran was added for keeping argon. After being dissolved, the mixture was stirred at 50 °C for 12 h and monitored by TLC. Finally, ethylvinyl ether (0.3 mL) was added to quench the reaction and precipitated with an excess of ether for twice. The polymer **poly((Man-Alkyne-OAc)** was isolated by centrifugation to yield 0.061 g, 61% an off white solid.

15. Synthesis of poly(Man-Alkyne)

The **poly(Man-Alkyne-OAc)** (80 mg, 0.01 mmol) dissolved in MeOH/DCM (2 mL, 1 : 1 v/v) and then MeONa (8 mg, 10 wt%) was added. The reaction mixture was stirred at room temperature for 12 h and the solvent was evaporated under reduced pressure. The residue was dissolved water (2 mL) and brought to neutral pH with Dowex H^+ resin. The aqueous solution was filtered and lyophilized to produce **poly((Man-Alkyne)** as a brown solid yield 0.041 g, 68%.

16. Synthesis of poly(βGlu-Alkyne-OAc)

A glass vial was charged with **4C** (100 mg, 0.09 mmol) and Grubbs 3rd (2.7 mg, 0.009 mmol) sealing with rubber stopper and their head space thoroughly sparged with argon for 10 min. Then 1 mL of anhydrous tetrahydrofuran was added for keeping argon. After being dissolved, the mixture was stirred at 50 °C for 12 h and monitored by TLC. Finally, ethylvinyl ether (0.3 mL) was added to quench the reaction and precipitated with an excess of ether for twice. The polymer **poly((βGlu-Alkyne-OAc)** was isolated by centrifugation to yield 0.058 g, 58% an off white solid.

17. Synthesis of poly((βGlu-Alkyne)

The **poly(βGlu-Alkyne-OAc)** (80 mg, 0.01 mmol) dissolved in MeOH/DCM (2 mL, 1 : 1 v/v) and then MeONa (8 mg, 10 wt%) was added. The reaction mixture was stirred at room temperature for 12 h and the solvent was evaporated under reduced pressure. The residue was dissolved water (2 mL) and brought to neutral pH with Dowex H^+ resin. The aqueous solution was filtered and lyophilized to produce **poly((βGlu-Alkyne)** as a brown solid yield 0.039 g, 65%.

18. Synthesis of poly(Man-βGlu-OAc)

A glass vial was charged with **5B** (100 mg, 0.09 mmol) and Grubbs 3rd (2.7 mg, 0.009 mmol) sealing with rubber stopper and their head space thoroughly sparged with argon for 10 min. Then 1 mL of anhydrous tetrahydrofuran was added for keeping argon. After being dissolved, the mixture was stirred at 50 °C for 12 h and monitored by TLC. Finally, ethylvinyl ether (0.3 mL) was added to quench the reaction and precipitated with an excess of ether for twice. The polymer **poly(Man-βGlu-OAc)** was isolated by centrifugation to yield 0.089 g, 89% an off white solid.

19. Synthesis of poly(Man-βGlu)

The **poly(Man-βGlu-OAc)** (80 mg, 0.01 mmol) dissolved in MeOH/DCM (2 mL, 1 : 1 v/v) and then MeONa (8 mg, 10 wt%) was added. The reaction mixture was stirred at room temperature for 12 h and the solvent was evaporated under reduced pressure. The residue was dissolved water (2 mL) and brought to neutral pH with Dowex H^+ resin. The aqueous solution was filtered and lyophilized to produce **poly(Man-βGlu)** as a brown solid yield 0.030 g, 73%.

20. Synthesis of poly((αGlu-αGlu-OAc)

A glass vial was charged with **6A** (100 mg, 0.09 mmol) and Grubbs 3rd (2.7 mg, 0.009 mmol) sealing with rubber stopper and their head space thoroughly sparged with argon for 10 min. Then 1 mL of anhydrous tetrahydrofuran was added for keeping argon. After being dissolved, the mixture was stirred at 50 °C for 12 h and monitored by TLC. Finally, ethylvinyl ether (0.3 mL) was added to quench the reaction and precipitated with an excess of ether for twice. The polymer **poly((αGlu-αGlu-OAc)** was isolated by centrifugation to yield 0.090 g, 90% an off white solid.

21. Synthesis of poly((αGlu-αGlu)

The **poly(αGlu-αGlu-OAc)** (80 mg, 0.01 mmol) dissolved in MeOH/DCM (2 mL, 1 : 1 v/v) and then MeONa (8 mg, 10 wt%) was added. The reaction mixture was stirred at room temperature for 12 h and the solvent was evaporated under reduced pressure. The residue was dissolved water (2 mL) and brought to neutral pH with Dowex H^+ resin. The aqueous solution was filtered and lyophilized to produce **poly((αGlu-αGlu)** as a brown solid yield 0.032 g, 78%.

22. Synthesis of poly(Man-αGlu-OAc)

A glass vial was charged with **6B** (100 mg, 0.09 mmol) and Grubbs 3rd (2.7 mg, 0.009 mmol) sealing with rubber stopper and their head space thoroughly sparged with argon for 10 min. Then 1 mL of anhydrous tetrahydrofuran was added for keeping argon. After being dissolved, the mixture was stirred at 50 °C for 12 h and monitored by TLC. Finally, ethylvinyl ether (0.3 mL) was added to quench the reaction and precipitated with an excess of ether for twice. The polymer **poly(Man-αGlu-OAc)** was isolated by centrifugation to yield 0.092 g, 92% an off white solid.

23. Synthesis of poly(Man-αGlu)

The **poly(Man-αGlu-OAc)** (80 mg, 0.01 mmol) dissolved in MeOH/DCM (2 mL, 1 : 1 v/v) and then MeONa (8 mg, 10 wt%) was added. The reaction mixture was stirred at room temperature for 12 h and the solvent was evaporated under reduced pressure. The residue was dissolved water (2

mL) and brought to neutral pH with Dowex H^+ resin. The aqueous solution was filtered and lyophilized to produce **poly(Man-αGlu)** as a brown solid yield 0.029 g, 72%.

24. Synthesis of poly(βGal-βGal-OAc)

A glass vial was charged with **7A** (100 mg, 0.09 mmol) and Grubbs 3rd (2.7 mg, 0.009 mmol) sealing with rubber stopper and their head space thoroughly sparged with argon for 10 min. Then 1 mL of anhydrous tetrahydrofuran was added for keeping argon. After being dissolved, the mixture was stirred at 50 °C for 12 h and monitored by TLC. Finally, ethylvinyl ether (0.3 mL) was added to quench the reaction and precipitated with an excess of ether for twice. The polymer **poly(βGal-βGal-OAc)** was isolated by centrifugation to yield 0.091 g, 91% an offwhite solid.

25. Synthesis of poly(βGal-βGal)

The **poly(βGal-βGal-OAc)** (80 mg, 0.01 mmol) dissolved in MeOH/DCM (2 mL, 1 : 1 v/v) and then MeONa (8 mg, 10 wt%) was added. The reaction mixture was stirred at room temperature for 12 h and the solvent was evaporated under reduced pressure. The residue was dissolved water (2 mL) and brought to neutral pH with Dowex H^+ resin. The aqueous solution was filtered and lyophilized to produce **poly(βGal-βGal)** as a brown solid yield 0.031 g, 77%.

26. Synthesis of poly(Man-βGal-OAc)

A glass vial was charged with **7B** (100 mg, 0.09 mmol) and Grubbs 3rd (2.7 mg, 0.009 mmol) sealing with rubber stopper and their head space thoroughly sparged with argon for 10 min. Then 1 mL of anhydrous tetrahydrofuran was added for keeping argon. After being dissolved, the mixture was stirred at 50 °C for 12 h and monitored by TLC. Finally, ethylvinyl ether (0.3 mL) was added to quench the reaction and precipitated with an excess of ether for twice. The polymer **poly(Man-βGal-OAc)** was isolated by centrifugation to yield 0.088 g, 88% an off white solid.

27. Synthesis of poly(Man-βGal)

The **poly(Man-βGal-OAc)** (80 mg, 0.01 mmol) dissolved in MeOH/DCM (2 mL, 1 : 1 v/v) and then MeONa (8 mg, 10 wt%) was added. The reaction mixture was stirred at room temperature for 12 h and the solvent was evaporated under reduced pressure. The residue was dissolved water (2 mL) and brought to neutral pH with Dowex H^+ resin. The aqueous solution was filtered and lyophilized to produce **poly(Man-βGal)** as a brown solid yield 0.030 g, 73%.

28. Synthesis of poly(Man-βGlu-OAc)-b-poly(Man-Alkyne-OAc)

A glass vial was charged with **5B** (50 mg, 0.045 mmol) and Grubbs 3rd (2.7 mg, 0.009 mmol) sealing with rubber stopper and their head space thoroughly sparged with argon for 10 min. Then 1 mL of anhydrous tetrahydrofuran was added for keeping argon. After being dissolved, the mixture was stirred at 50 °C for 12 h. Then add **4B** (31.5 mg, 0.045 mmol) to the vial. After being dissolved, the mixture was stirred at 50 °C for 12 h and monitored by TLC.Finally, ethylvinyl ether (0.3 mL) was added to quench the reaction and precipitated with an excess of ether for twice. The polymer **poly(Man-βGlu-OAc)-b-poly(Man-Alkyne-OAc)** was isolated by centrifugation to yield 0. 059 g, 73% an off white solid.

29. Synthesis of poly(Man-βGlu)-b-poly(Man-Alkyne)

The **poly(Man-βGlu-OAc)-b-poly(Man-Alkyne-OAc)** (70 mg, 0.01 mmol) dissolved in MeOH/DCM (2 mL, 1 : 1 v/v) and then MeONa (8 mg, 10 wt%) was added. The reaction mixture was stirred at room temperature for 12 h and the solvent was evaporated under reduced pressure. The residue was dissolved water (2 mL) and brought to neutral pH with Dowex H^+ resin. The aqueous solution was filtered and lyophilized to produce **poly(Man-βGlu)-b-poly(Man-Alkyne)** as a brown solid yield 0.039 g, 77%.

30. Synthesis of poly(Man-Man-OAc)-r-poly(βGlu-βGlu-OAc)

A glass vial was charged with **4A** (50 mg, 0.045 mmol), **5A** (50 mg, 0.045 mmol) and Grubbs 3rd (2.7 mg, 0.009 mmol) sealing with rubber stopper and their head space thoroughly sparged with argon for 10 min. Then 1 mL of anhydrous tetrahydrofuran was added for keeping argon. After being dissolved, the mixture was stirred at 50 °C for 12 h and monitored by TLC. Finally, ethylvinyl ether (0.3 mL) was added to quench the reaction and precipitated with an excess of ether for twice. The polymer **poly(Man-Man-OAc)-r-poly(βGlu-βGlu-OAc)** was isolated by centrifugation to yield 0. 085 g, 85% an off white solid.

31. Synthesis of poly(Man-Man)-r-poly(βGlu-βGlu)

The **poly(Man-Man-OAc)-r-poly(βGlu-βGlu-OAc)** (80 mg, 0.01 mmol) dissolved in MeOH/DCM (2 mL, 1 : 1 v/v) and then MeONa (8 mg, 10 wt%) was added. The reaction mixture was stirred at room temperature for 12 h and the solvent was evaporated under reduced pressure. The residue was dissolved water (2 mL) and brought to neutral pH with Dowex H^+ resin. The aqueous solution was filtered and lyophilized to produce **poly(Man-Man)-r-poly(βGlu-βGlu)** as a brown solid yield 0.030 g, 75%.

32. Synthesis of poly(Man-Man-OAc)-b-poly(βGlu-βGlu-OAc)

A glass vial was charged with **4A** (50 mg, 0.045 mmol) and Grubbs 3rd (2.7 mg, 0.009 mmol) sealing with rubber stopper and their head space thoroughly sparged with argon for 10 min. Then 1 mL of anhydrous tetrahydrofuran was added for keeping argon. After being dissolved, the mixture was stirred at 50 °C for 12 h. Then add **5A** (50 mg, 0.045 mmol) to the vial. After being dissolved, the mixture was stirred at 50 °C for 12 h and monitored by TLC. Finally, ethylvinyl ether (0.3 mL) was added to quench the reaction and precipitated with an excess of ether for twice. The polymer **poly(Man-Man-OAc)-b-poly(βGlu-βGlu-OAc)** was isolated by centrifugation to yield 0.071 g, 71% an off white solid.

33. Synthesis of poly(Man-Man)-b-poly(βGlu-βGlu)

The **poly(Man-Man-OAc)-b-poly(βGlu-βGlu-OAc)** (80 mg, 0.01 mmol) dissolved in MeOH/DCM (2 mL, 1 : 1 v/v) and then MeONa (8 mg, 10 wt%) was added. The reaction mixture was stirred at room temperature for 12 h and the solvent was evaporated under reduced pressure. The residue was dissolved water (2 mL) and brought to neutral pH with Dowex H^+ resin. The aqueous solution was filtered and lyophilized to produce **poly(Man-Man)-b-poly(βGlu-βGlu)** as a brown solid yield 0.031 g, 76%.

References：

1. B. Kang, P. Okwieka, S. Schottler, S. Winzen, J. Langhanki, K. Mohr, T. Opatz, V. Mailander, K. Landfester and F. R. Wurm, *Angew. Chem.*, 2015, **54**, 7436–7440.

2. I. D. S. García-Viñuales, P. Merino and T. Tejero, *Synthesis*, 2016, **48**, 3339–3351.

3. A. Biabchi, and A.Bernardi, *J. Org. Chem*. 2006, **71**, 4565–4577.

4. S. B. S.Salunke, S.Babuz and *C.Cheno, Chem. Commun*, 2011, **47**, 10440–10442.

Tables and Figures：

Table S1. Polymerization of the **5A** M(βGlu-βGlu) glycomonomer under different conditions by ROMP

Entry	Catalyst	Solvent	T(℃)	Time (h)	Conv.[a](%)
1	G1[nd]	DCM	25	6	NR
2	G1[nd]	THF	25	6	5
3	H-G1[nd]	THF	25	6	8
4	G3[rd]	THF	25	6	40
5	G3[rd]	THF	50	6	78
6	G3[rd]	THF	50	12	96

[a]Monomer conversion determined by the ^{1}H NMR integrations of the monomer olefin signals (5.9–6.1 ppm) to the polymer olefin signals (5.3–5.5 ppm).

Table S2. Polymerization of different glycomonomers by ROMP.

Entry	Glycoonomer	Polymer	Conv.[a](%)
1	**4A**	**poly(Man-Man-OAc)**	91
2	**4B**	**poly((Man-Alkyne-OAc)**	61
3	**4C**	**poly(βGlu-Alkyne-OAc)**	58

4	**5A**	**poly(βGlu-βGlu-OAc)**	92
5	**5B**	**poly(Man-βGlu-OAc)**	89
6	**6A**	**poly((αGlu-αGlu-OAc)**	90
7	**6B**	**poly(Man-αGlu)**	92
8	**7A**	**poly(βGal-βGal-OAc)**	91
9	**7B**	**poly(αMan-βGal-OAc)**	88
10	**5B+4B**	**poly(αMan-βGlu)-b-poly(αMan-Alkyne)**	73
11	**4A+5A**	**poly(Man-Man-OAc)-r-poly(βGlu-βGlu-OAc)**	85
12	**4A+5A**	**poly(Man-Man-OAc)-b-poly(βGlu-βGlu-OAc)**	71

[a]Monomer conversion determined by the ^{1}H NMR integrations of the monomer olefin signals (5.9–6.1 ppm) to the polymer olefin signals (5.3–5.5 ppm).

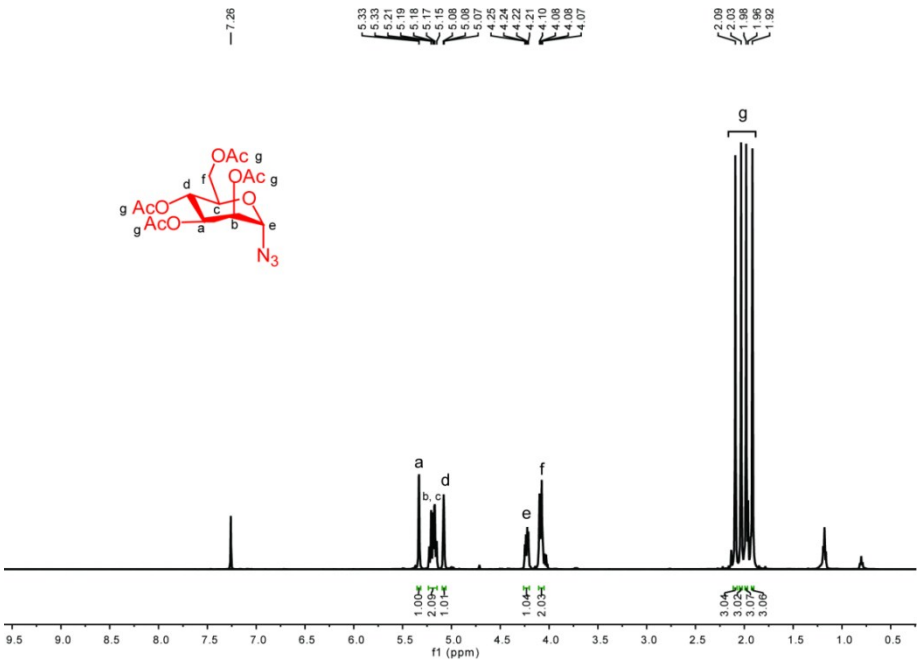

Figure S1. ^{1}H NMR spectrum of α-D-mannopyranosyl azide in $CDCl_3$.

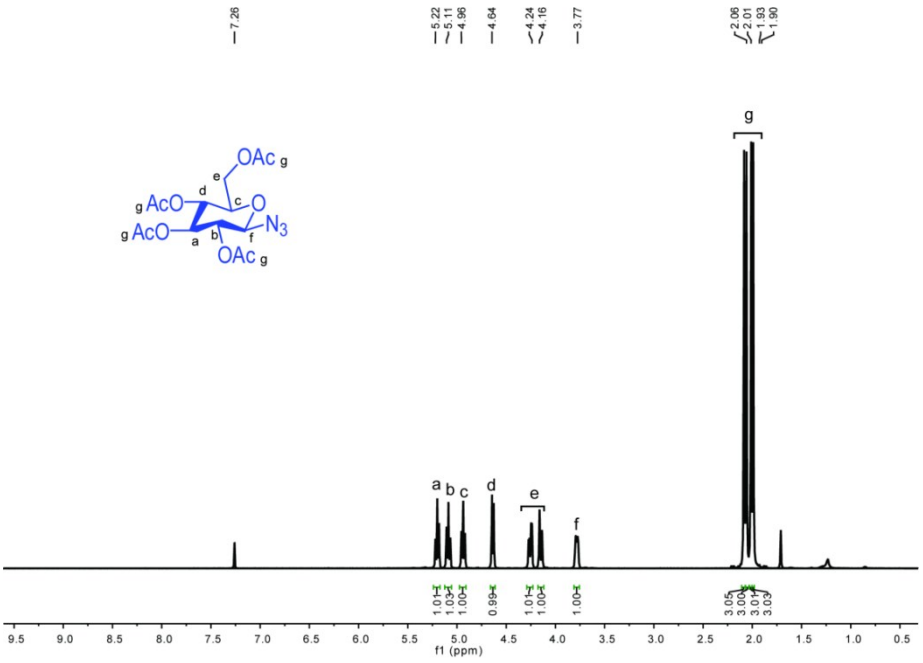

Figure S2. ^{1}H NMR spectrum of β-D-glucopyranosyl azide in $CDCl_3$.

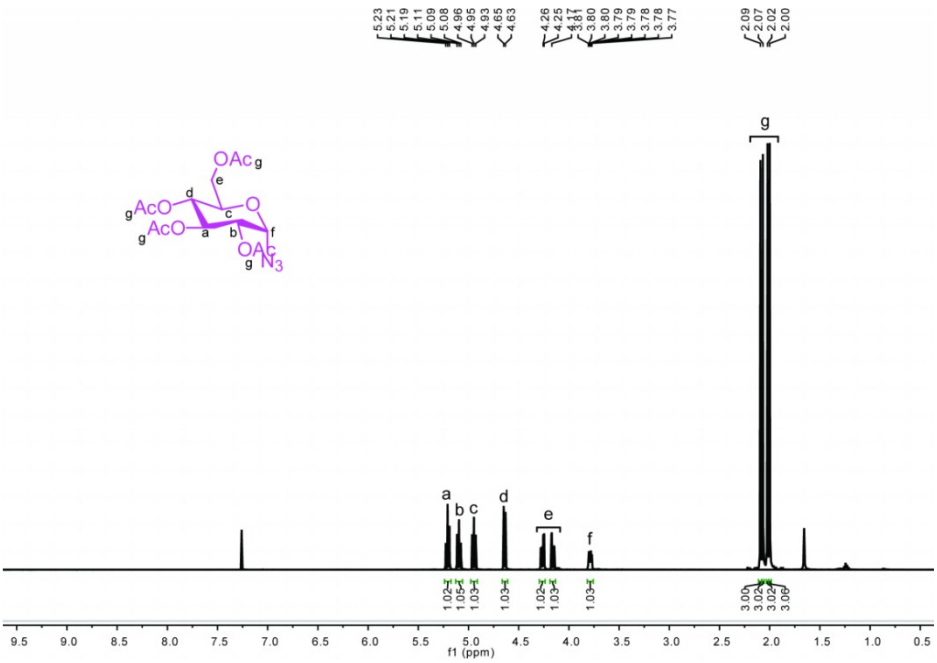

Figure S3. ^{1}H NMR spectrum of α-D-glucopyranosyl azide in $CDCl_3$.

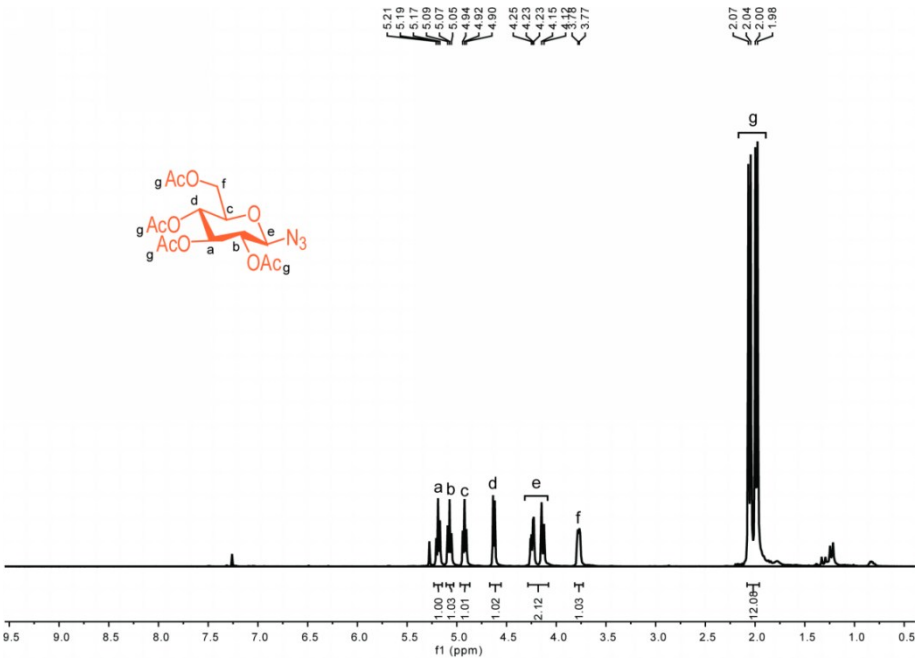

Figure S4. ^{1}H NMR spectrum of β-D-galactopyranosyl azide in $CDCl_3$.

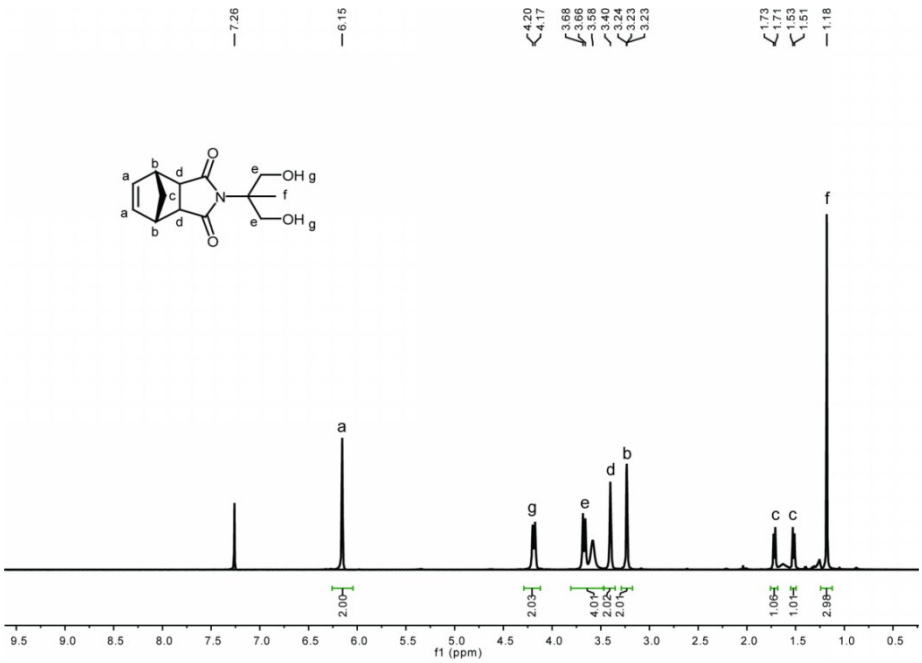

Figure S5. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

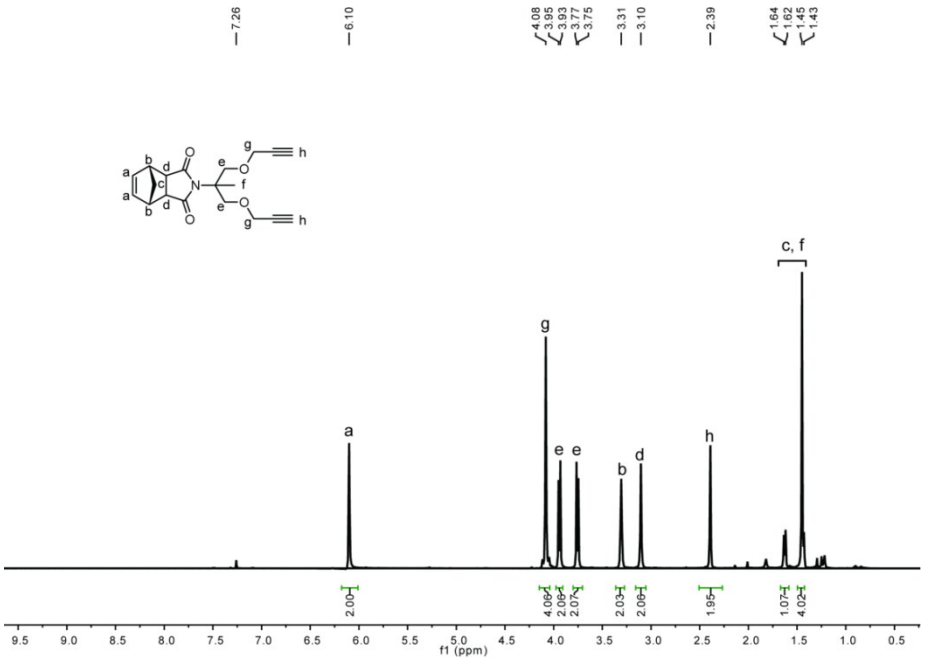

Figure S6. ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

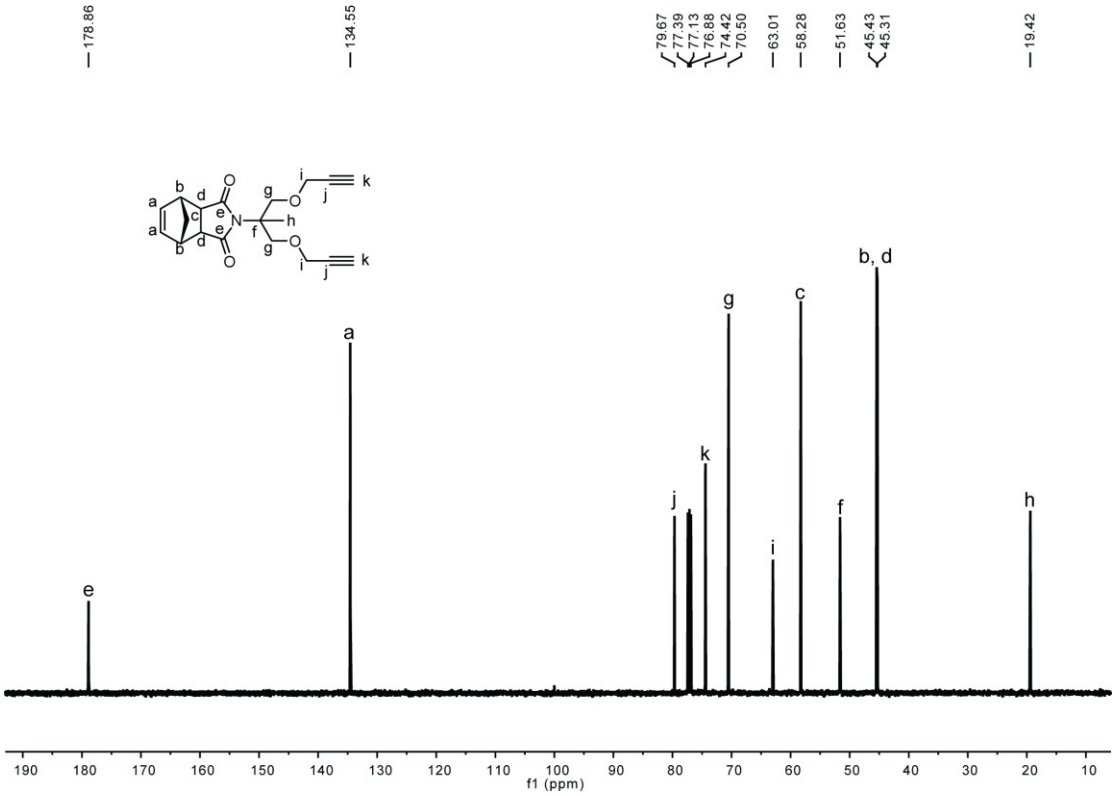

Figure S7. ^{13}C NMR spectrum of compound **3** in $CDCl_3$.

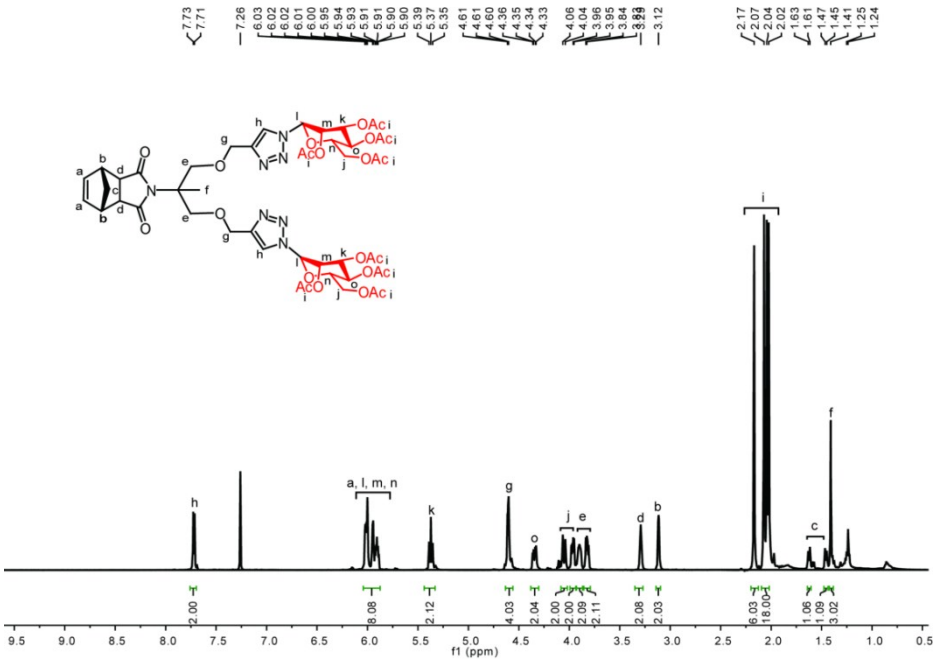

Figure S8. ^{1}H NMR spectrum of compound **4A** in $CDCl_3$.

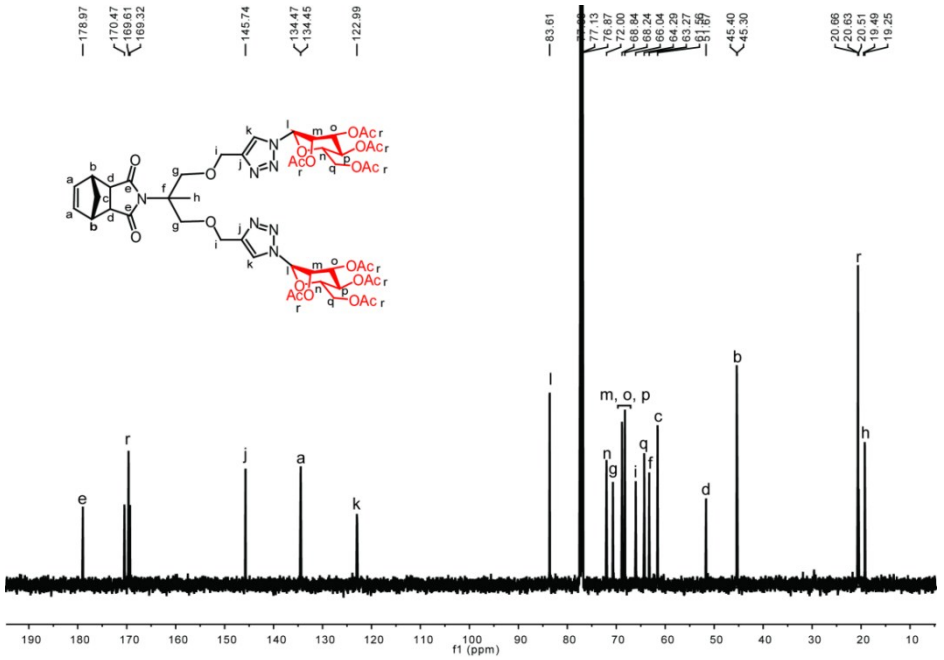

Figure S9. ^{13}C NMR spectrum of compound **4A**in $CDCl_3$.

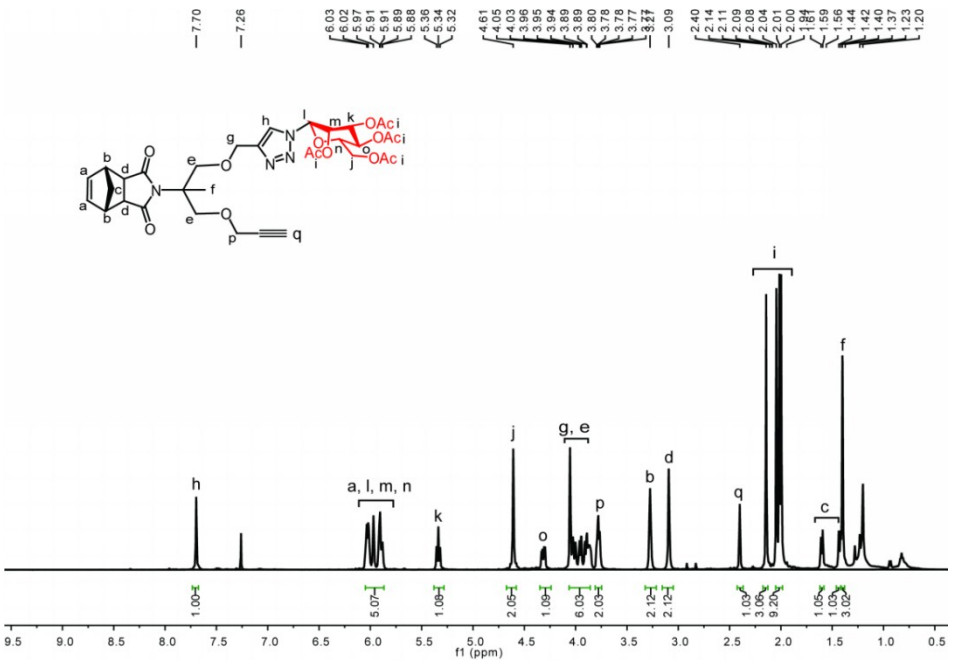

Figure S10. ^{1}H NMR spectrum of compound **4B** in $CDCl_3$.

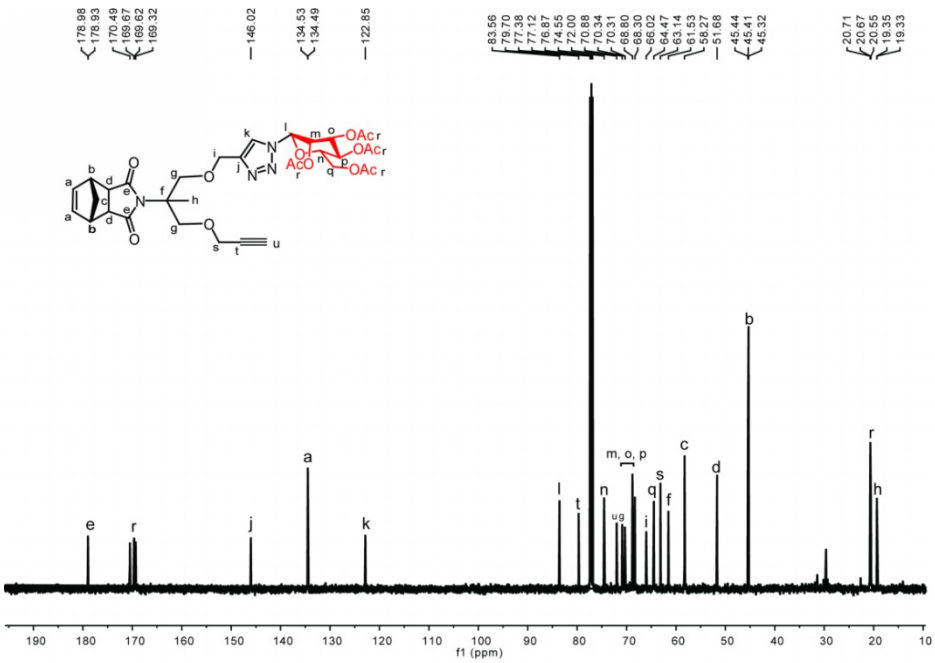

Figure S11. ^{13}C NMR spectrum of compound **4B** in $CDCl_3$.

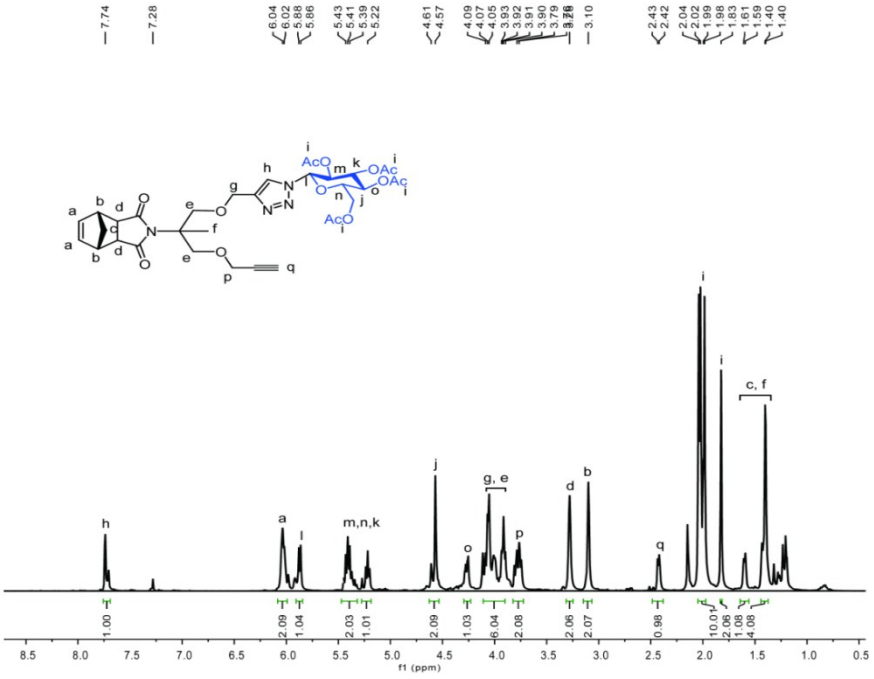

Figure S12. ^{1}H NMR spectrum of compound **4C** in $CDCl_3$

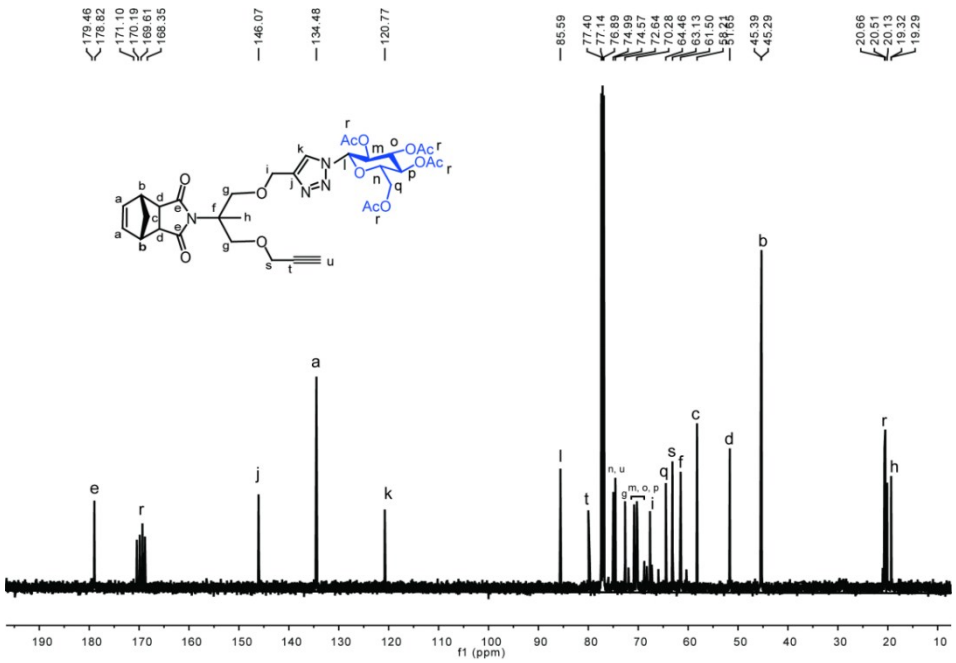

Figure S13. ^{13}C NMR spectrum of compound **4C** in $CDCl_3$.

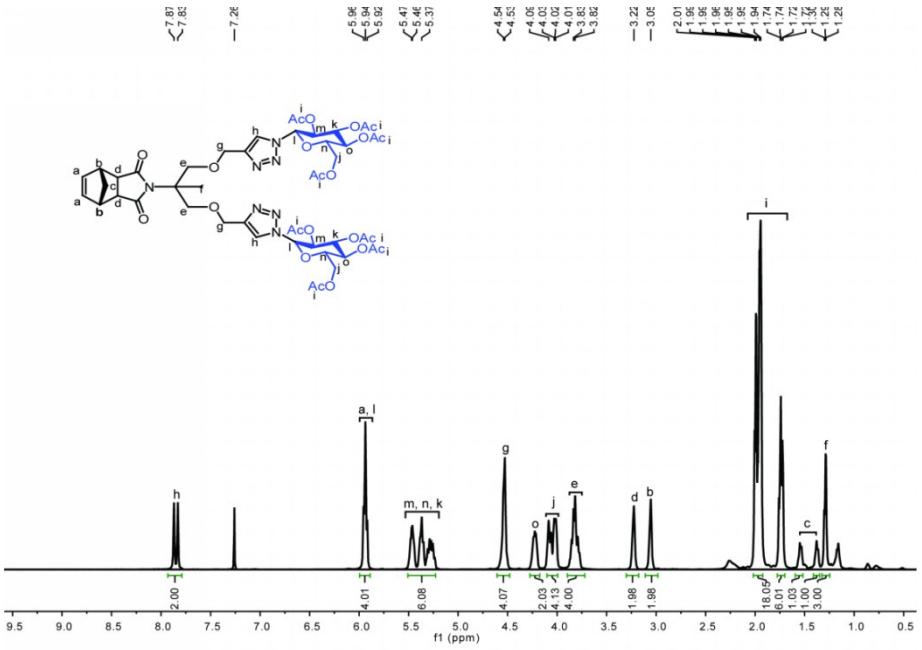

Figure S14. ^{1}H NMR spectrum of compound **5A** in $CDCl_3$.

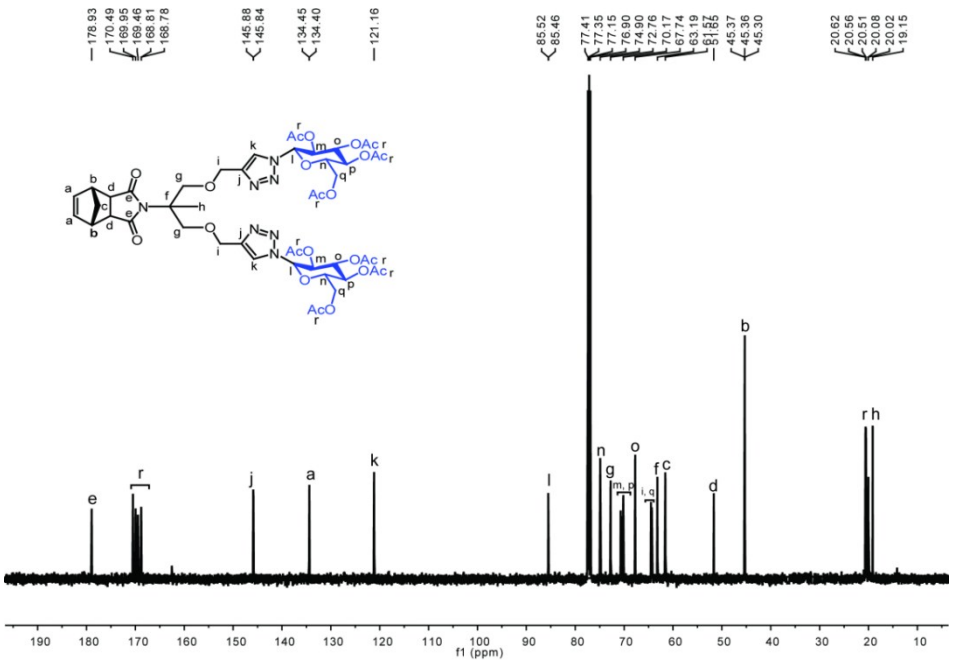

Figure S15. ^{13}C NMR spectrum of compound 5**A** in $CDCl_3$.

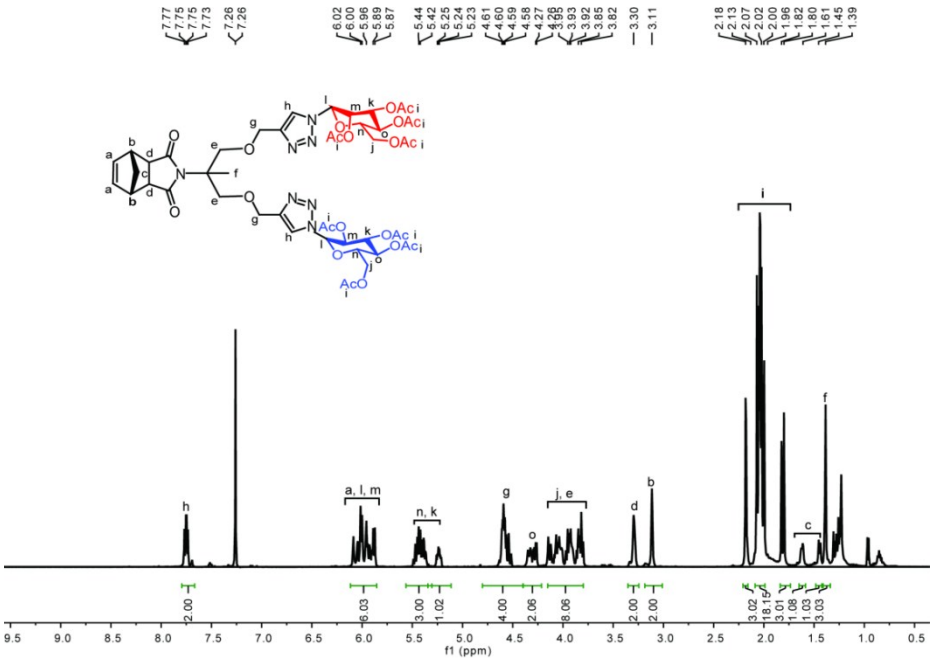

Figure S16. ^{1}H NMR spectrum of compound **5B** in $CDCl_3$.

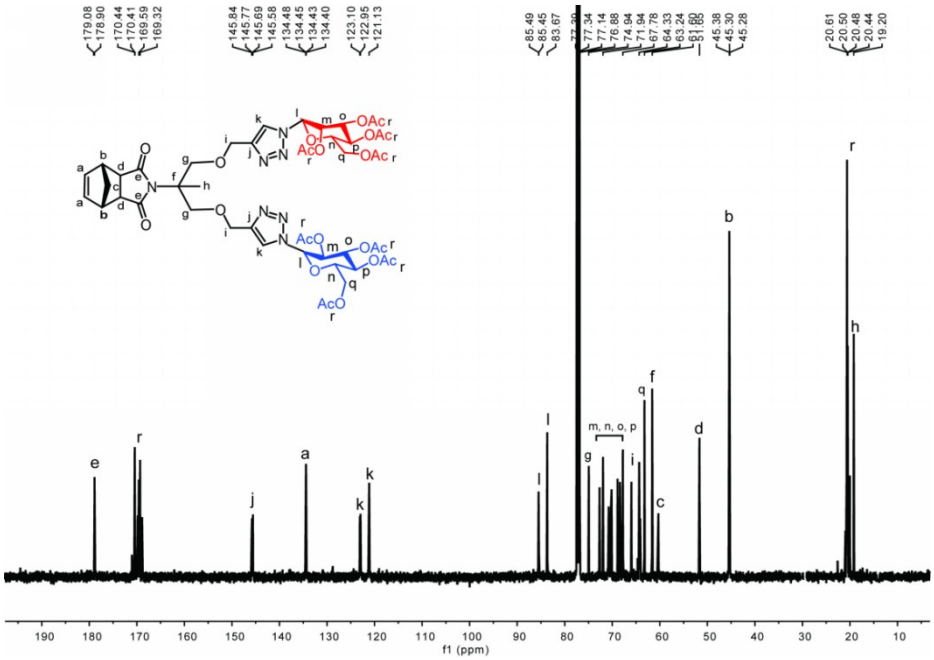

Figure S17. ^{13}C NMR spectrum of compound **5B** in $CDCl_3$.

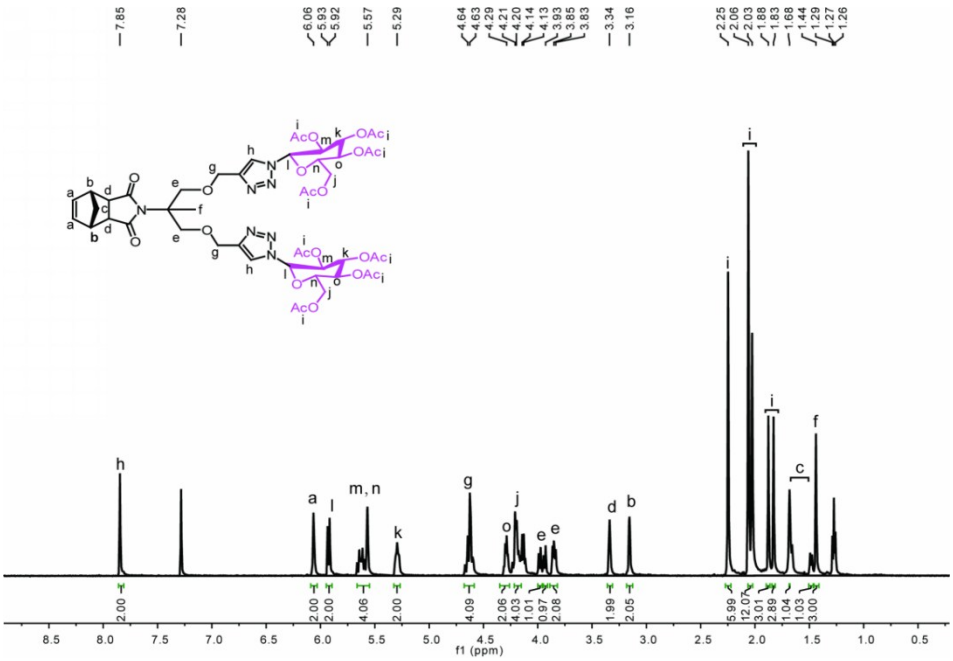

Figure S18. ^{1}H NMR spectrum of compound **6A** in $CDCl_3$.

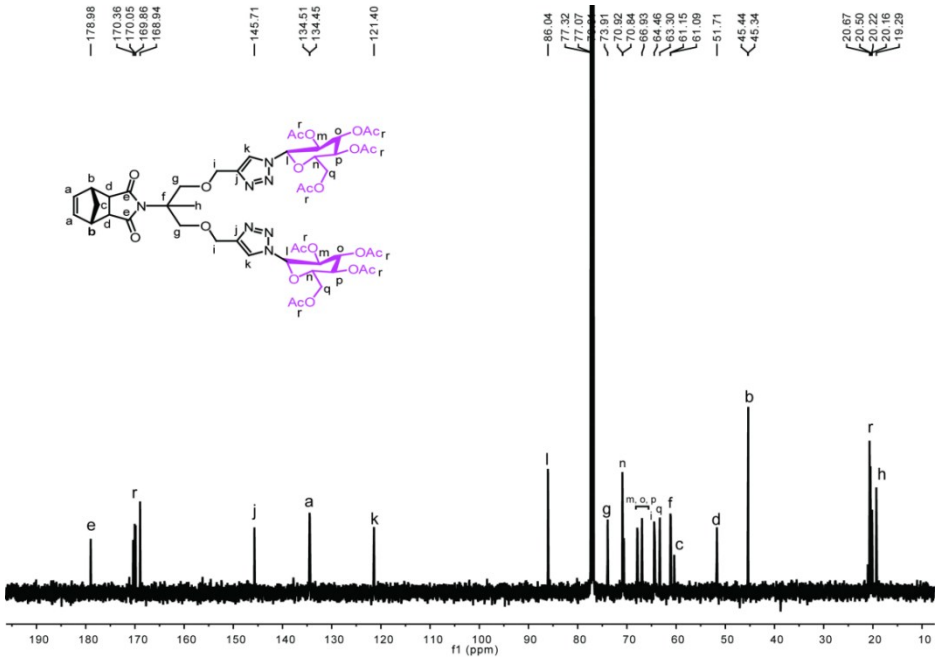

Figure S19. ^{13}C NMR spectrum of compound 6**A** in $CDCl_3$.

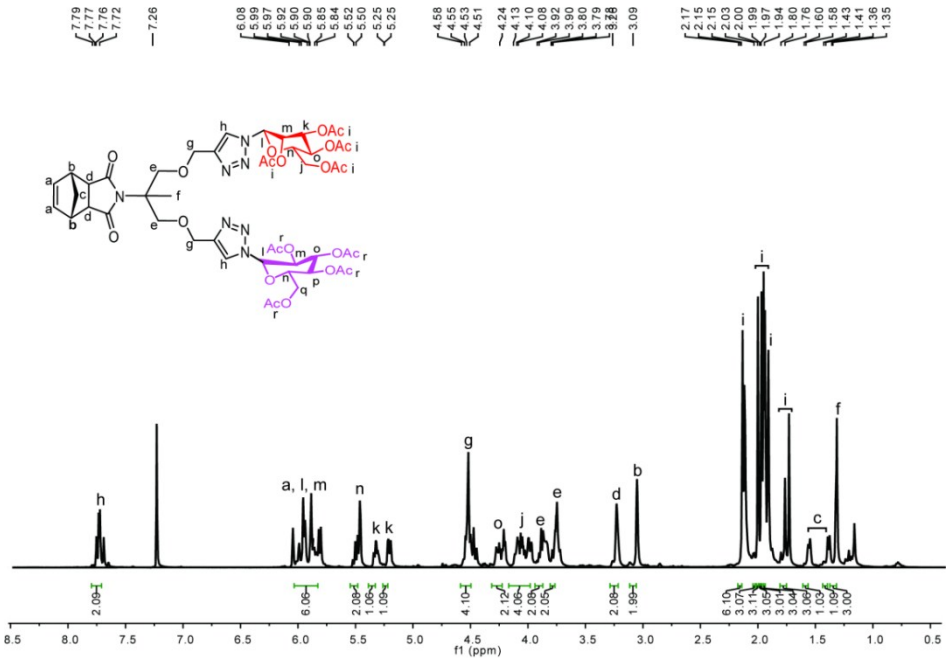

Figure S20. ^{1}H NMR spectrum of compound **6B** in $CDCl_3$.

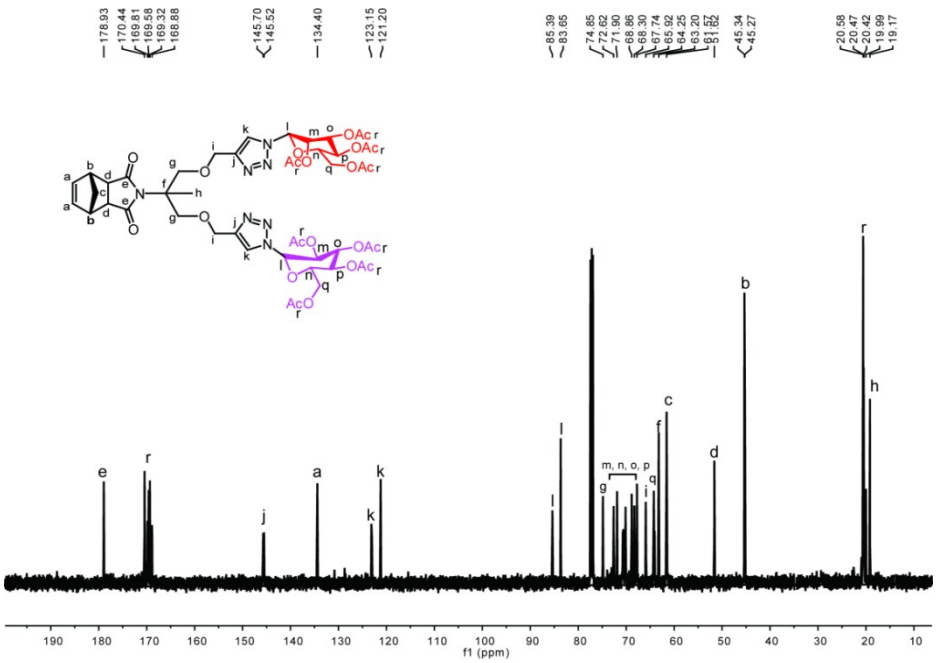

Figure S21. ^{13}C NMR spectrum of compound **6B** in $CDCl_3$.

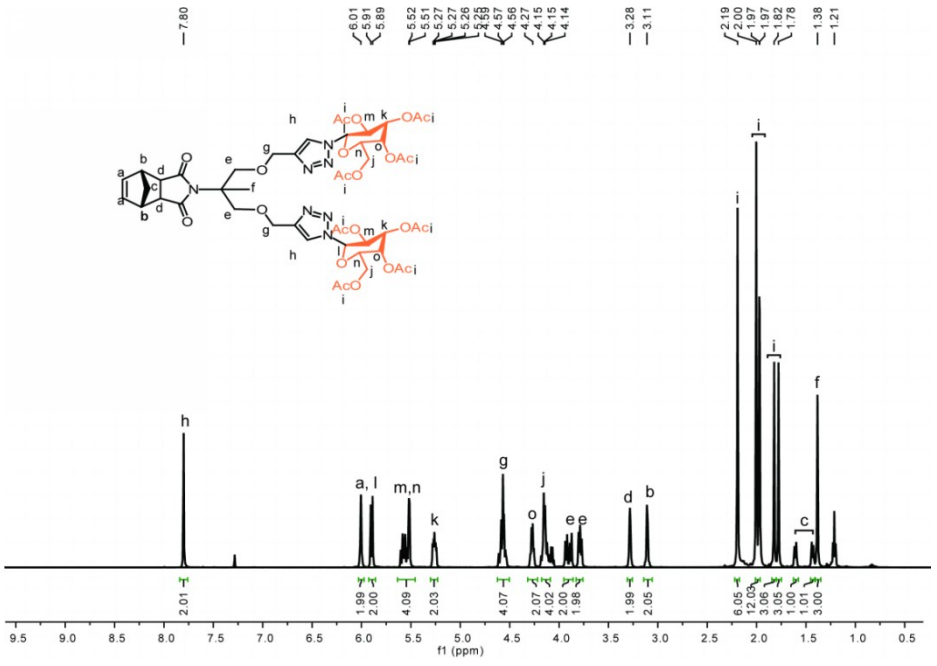

Figure S22. ^{1}H NMR spectrum of compound **7A** in $CDCl_3$.

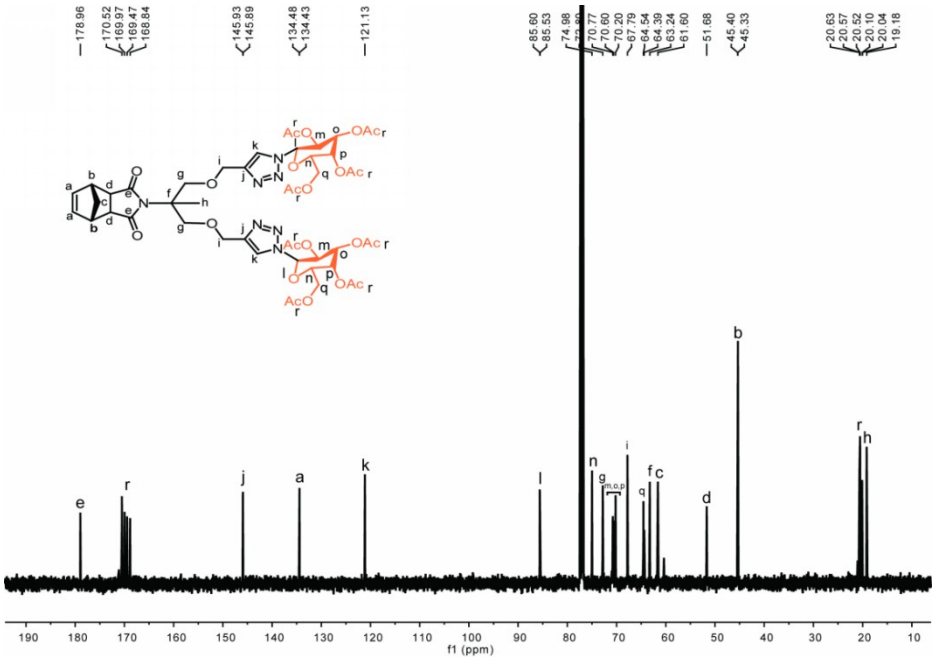

Figure S23. ^{13}C NMR spectrum of compound 7**A** in $CDCl_3$.

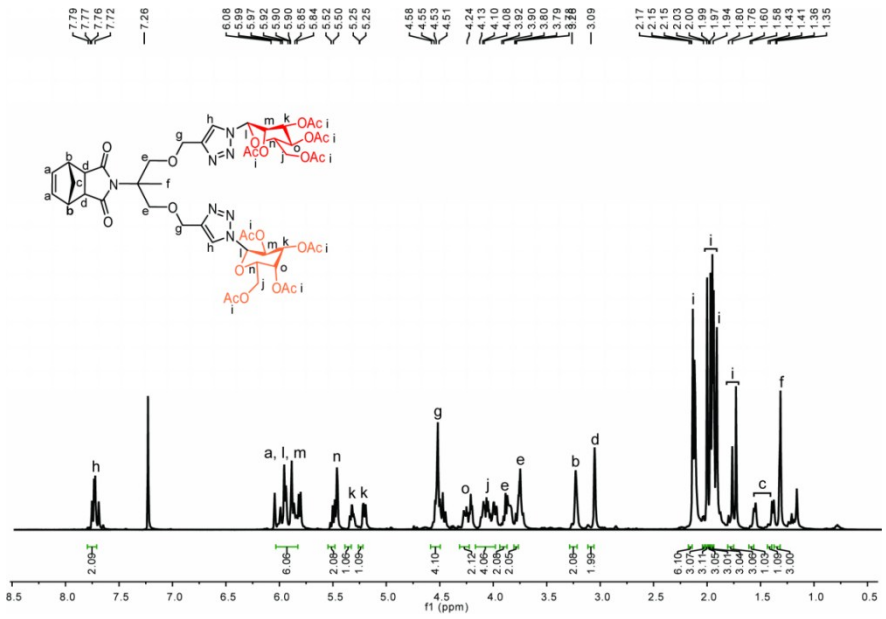

Figure S24. ^{1}H NMR spectrum of compound **7B** in $CDCl_3$.

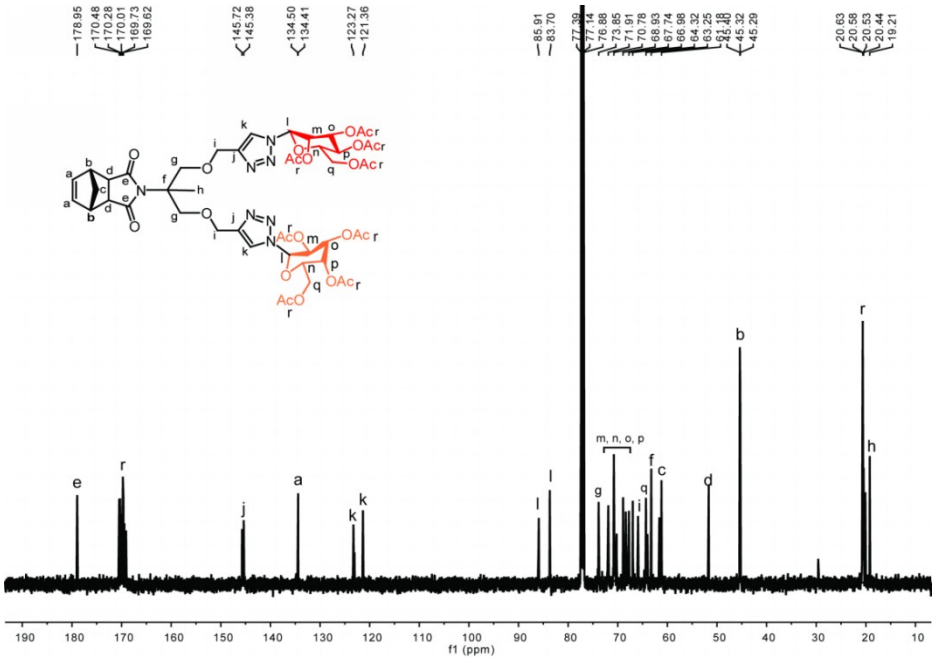

Figure S25. ^{13}C NMR spectrum of compound **7B** in $CDCl_3$.

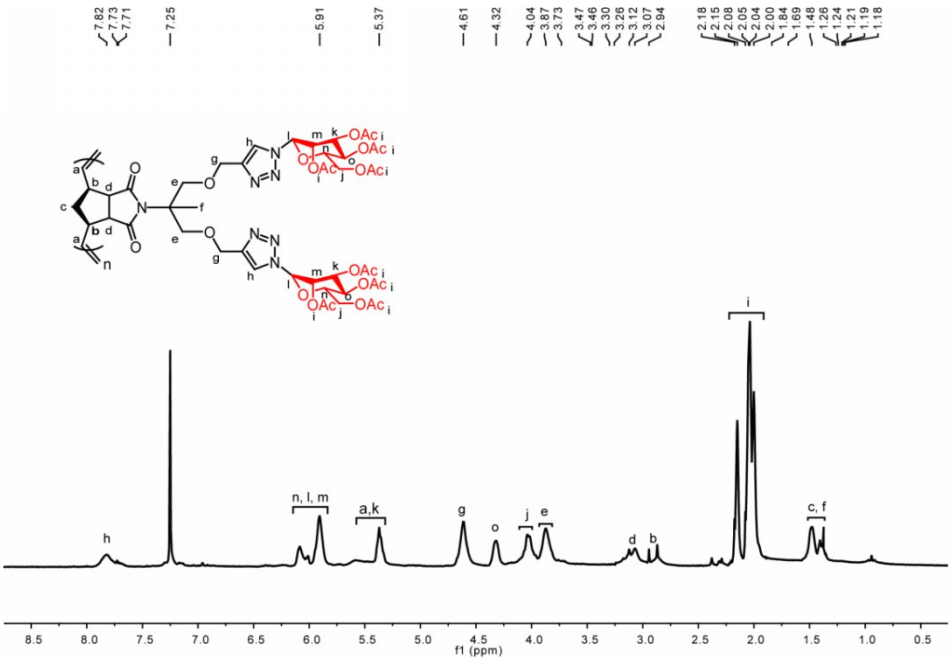

Figure S26. ^{1}H NMR spectrum of poly(Man-Man-OAc) in $CDCl_3$.

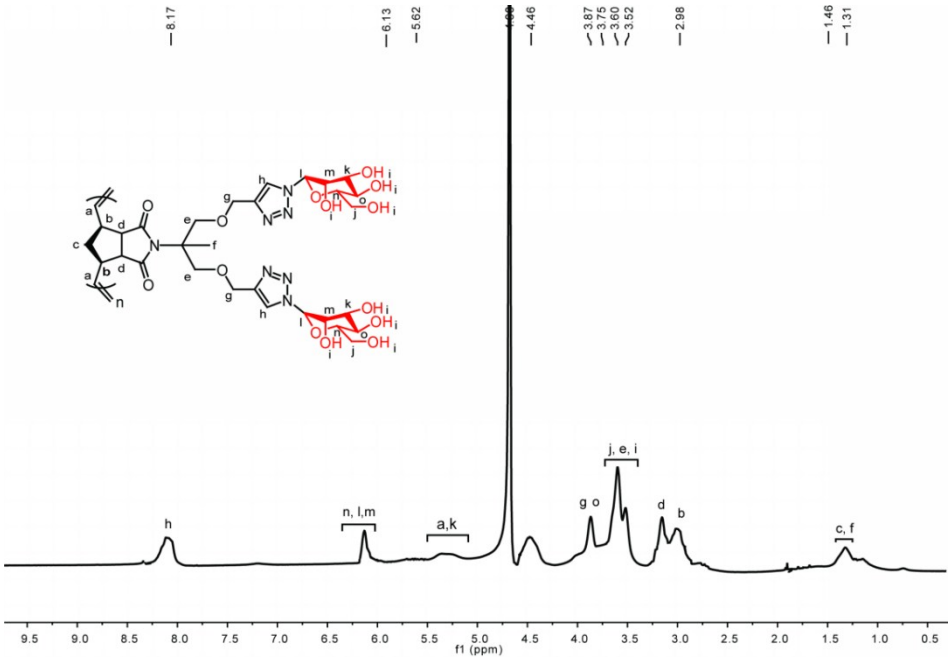

Figure S27. ^{1}H NMR spectrum of poly(Man-Man) in D_2O.

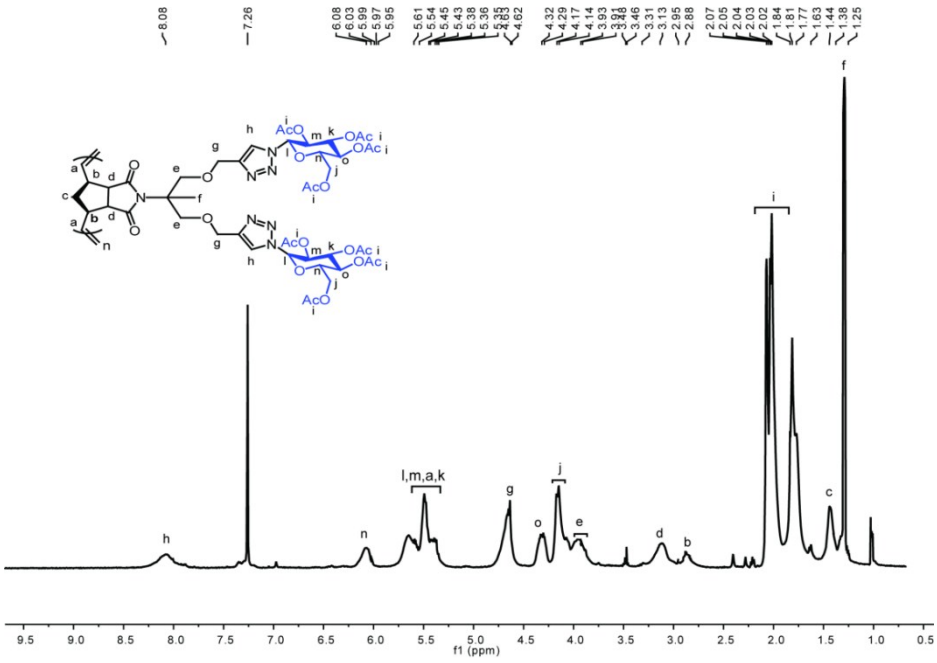

Figure S28. ^{1}H NMR spectrum of poly(βGlu-βGlu-OAc) in $CDCl_3$.

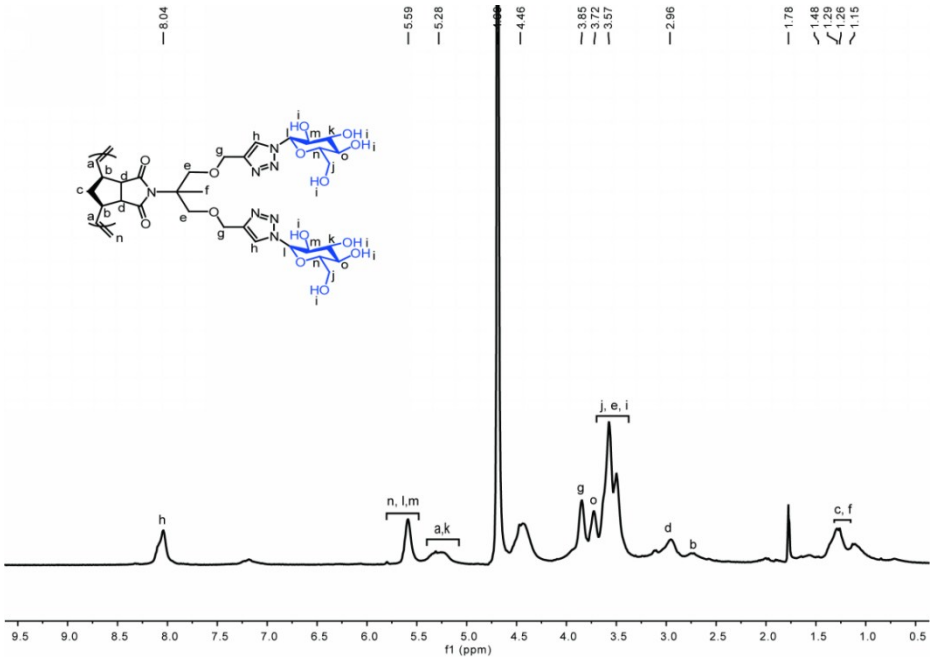

Figure S29. ^{1}H NMR spectrum of poly(βGlu-βGlu) in D_2O.

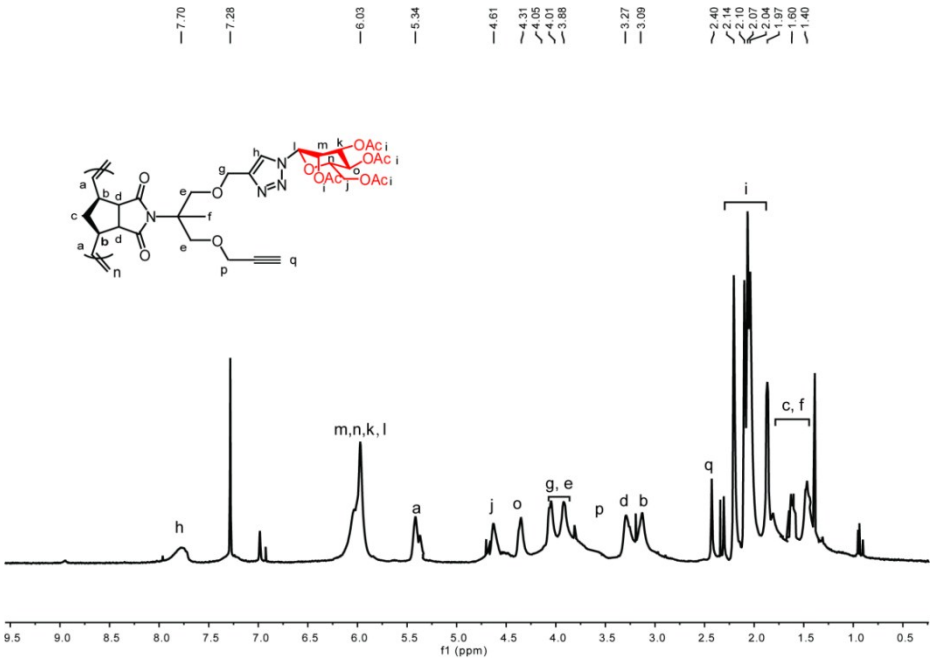

Figure S30. ^{1}H NMR spectrum of poly(Man-Alkyne-OAc) in $CDCl_3$.

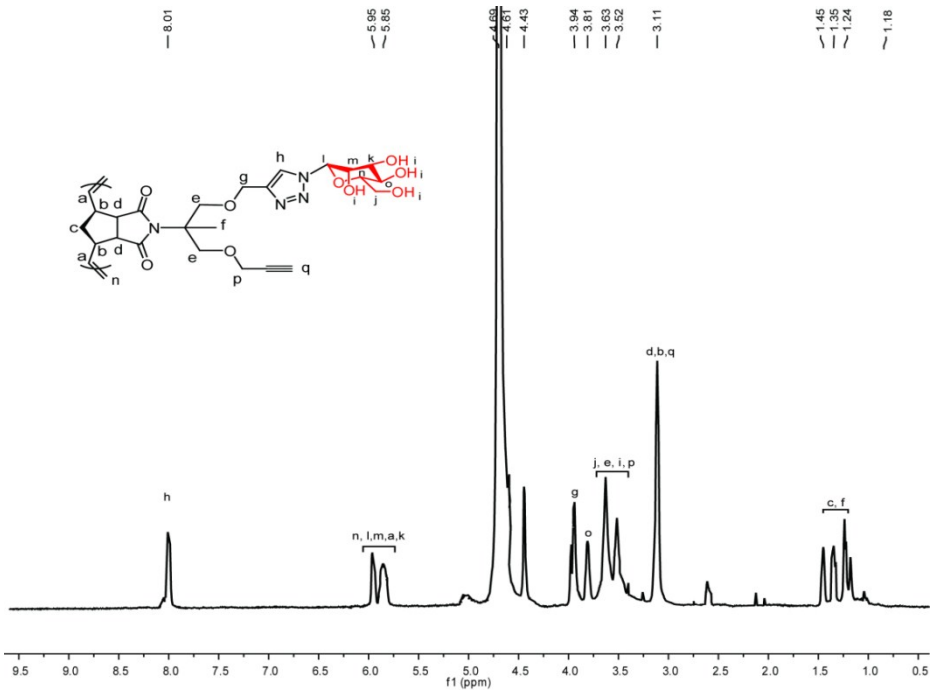

Figure S31. ^{1}H NMR spectrum of poly(Man-Alkyne) in D_2O.

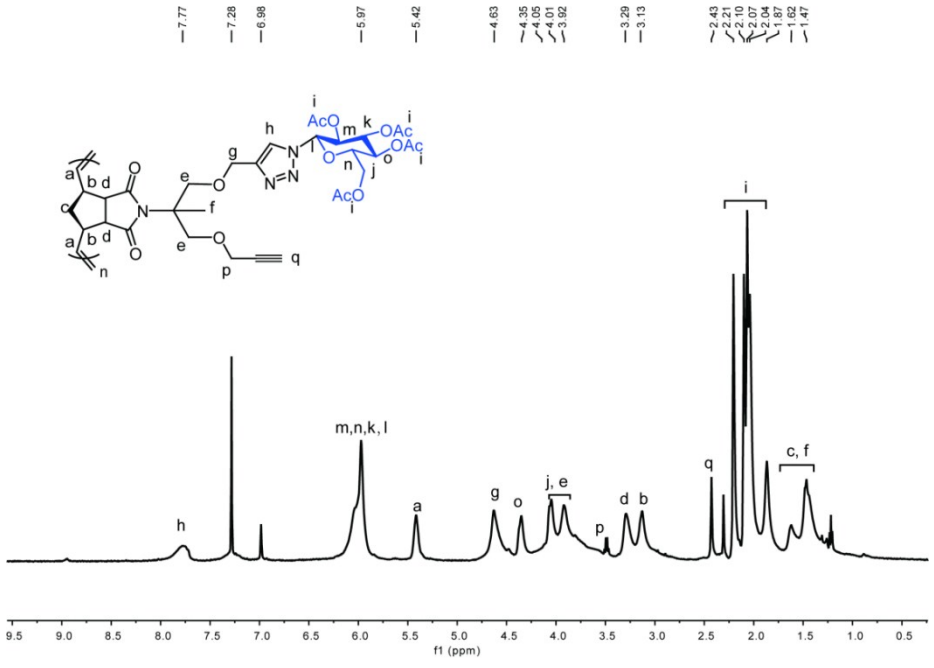

Figure S32. ^{1}H NMR spectrum of poly((βGlu-Alkyne-OAc) in $CDCl_3$.

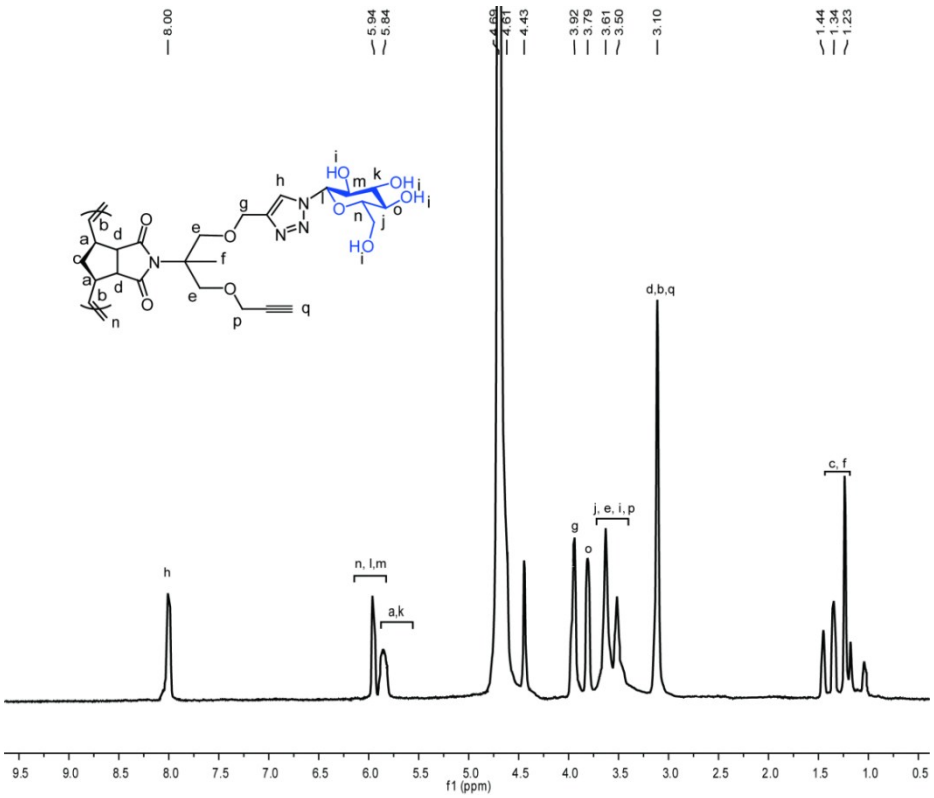

Figure S33. ^{1}H NMR spectrum of poly(βGlu-Alkyne) in D_2O.

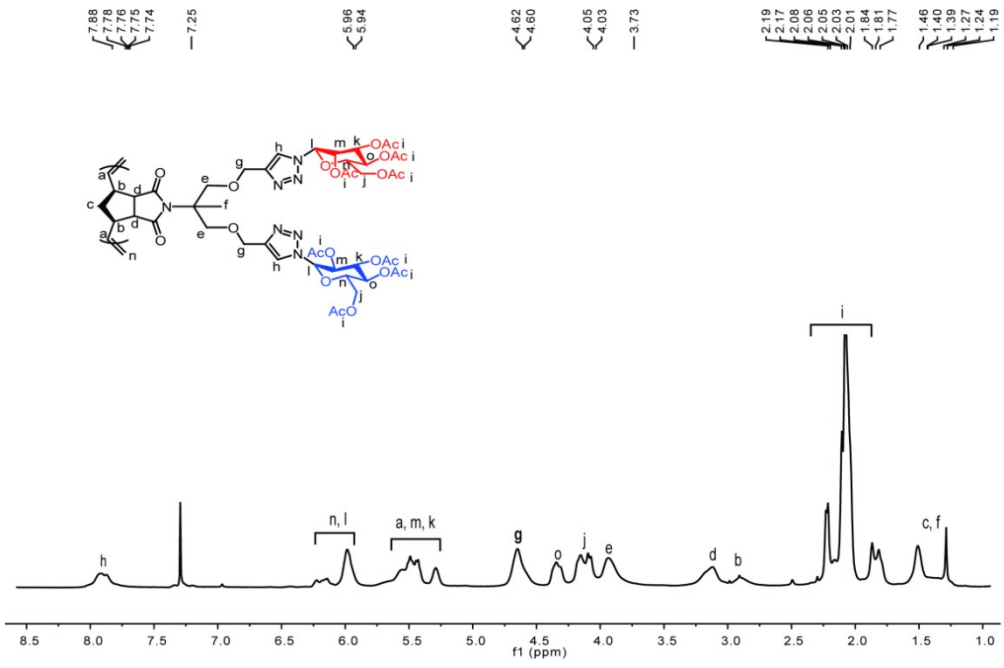

Figure S34. ^{1}H NMR spectrum of poly(Man-βGlu-OAc) in $CDCl_3$.

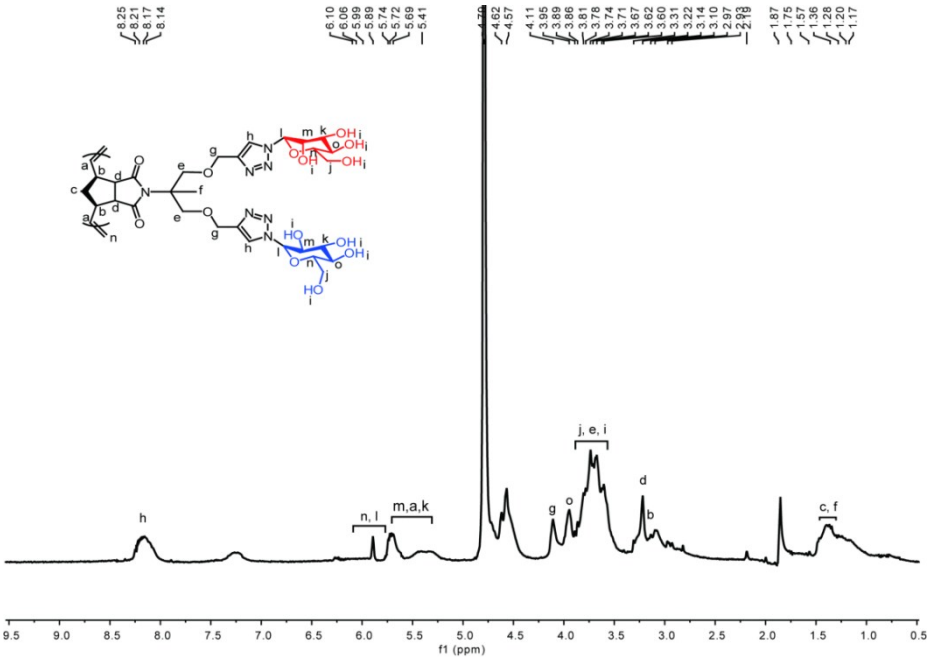

Figure S35. ^{1}H NMR spectrum of poly(Man-βGlu) in D_2O.

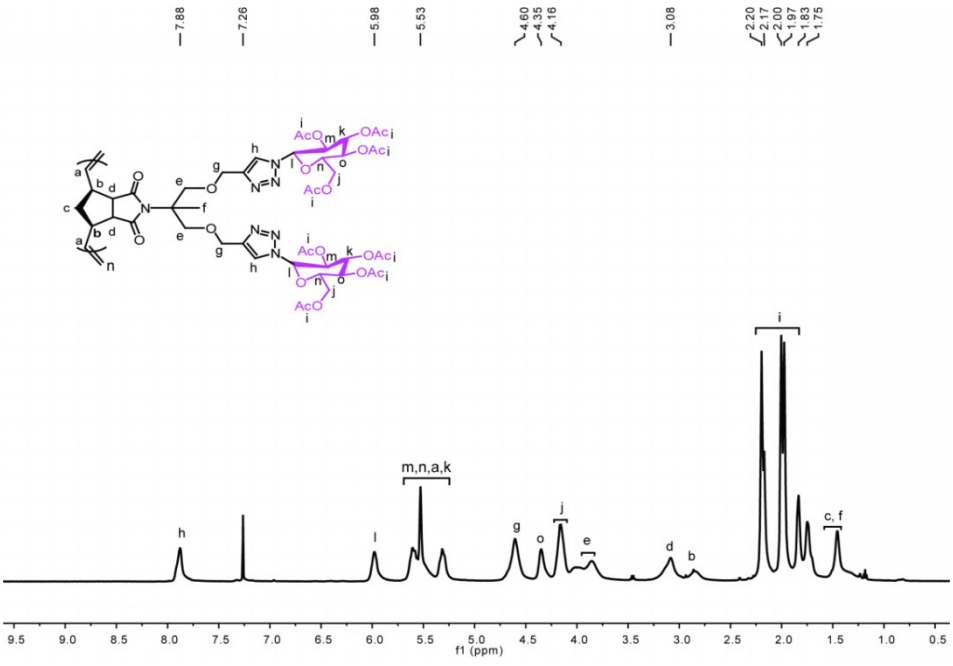

Figure S36. ^{1}H NMR spectrum of poly((αGlu-αGlu-OAc) in $CDCl_3$.

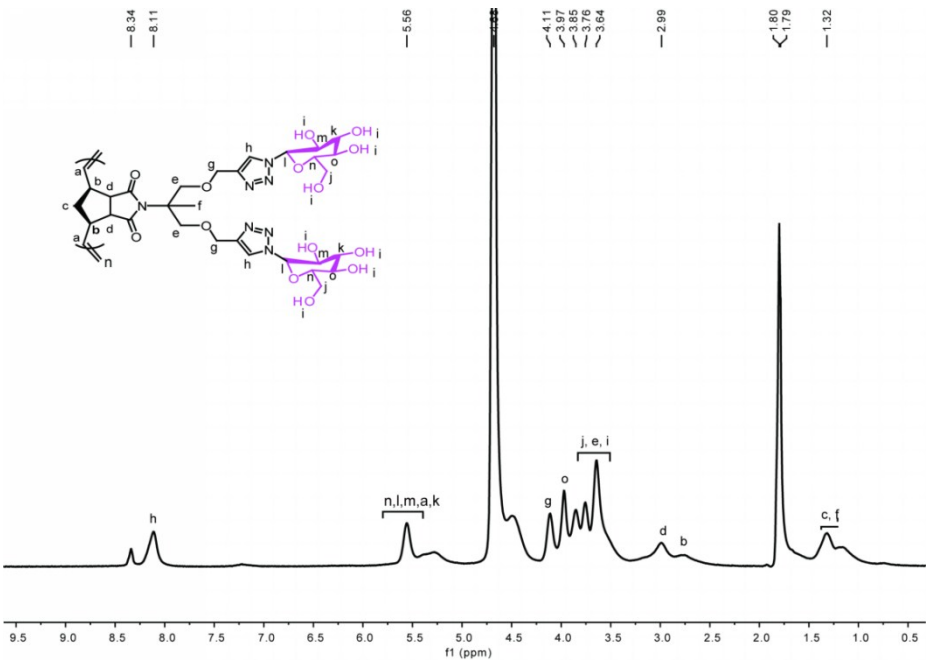

Figure S37. ^{1}H NMR spectrum of poly(αGlu-αGlu) in D_2O.

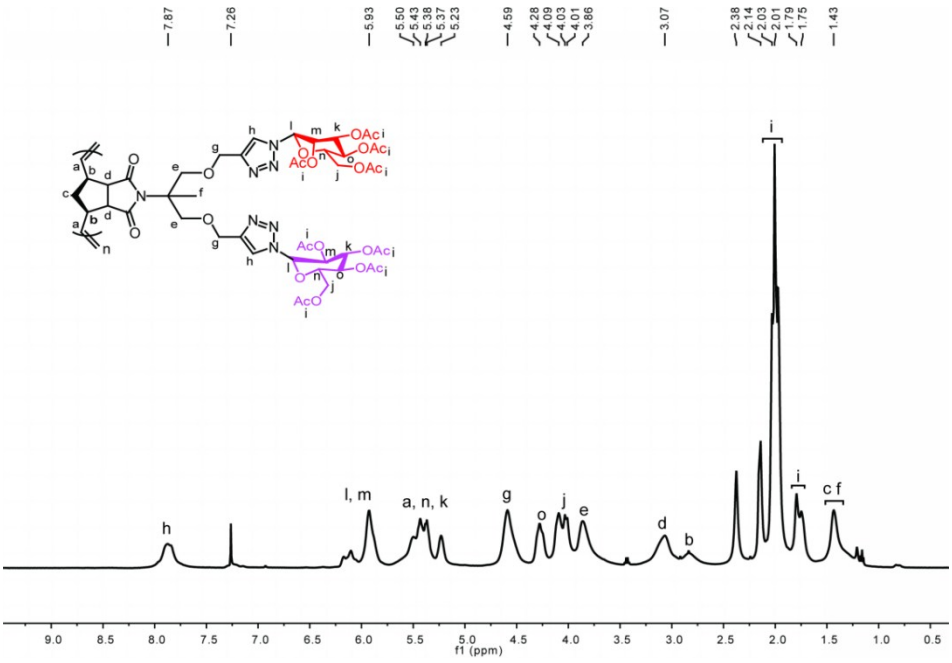

Figure S38. ^{1}H NMR spectrum of poly(Man-αGlu-OAc) in $CDCl_3$.

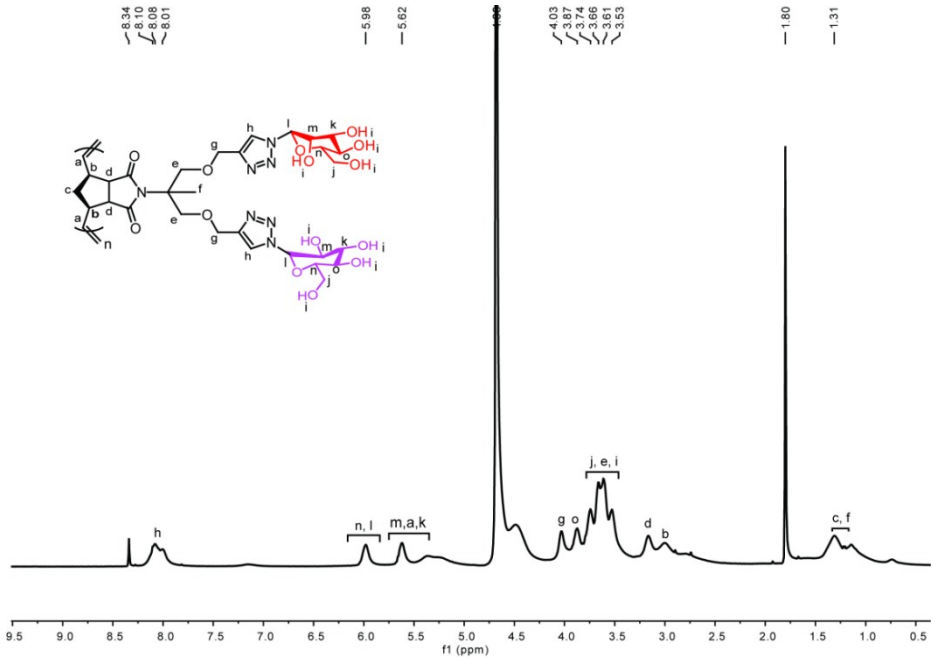

Figure S39. ^{1}H NMR spectrum of poly(Man-αGlu) in D_2O

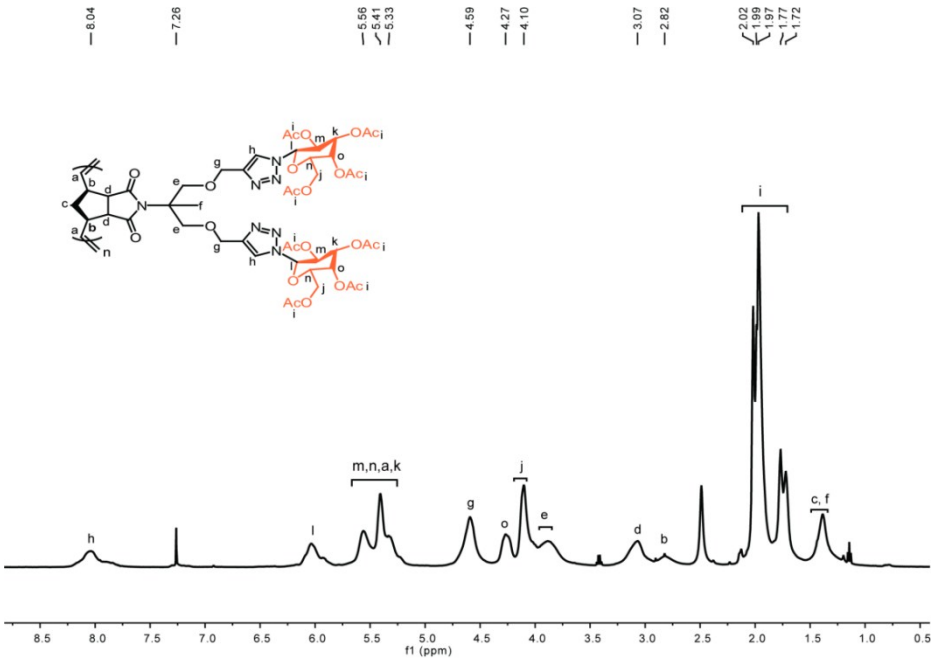

Figure S40. ^{1}H NMR spectrum of poly(βGal-βGal-OAc) in $CDCl_3$.

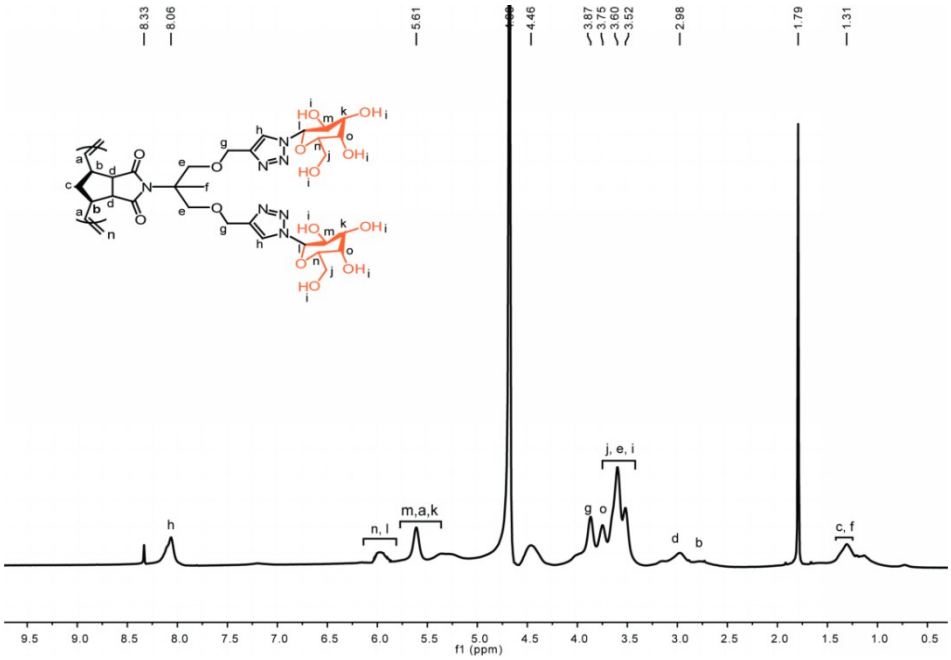

Figure S41. ^{1}H NMR spectrum of poly(βGal-βGal) in D_2O.

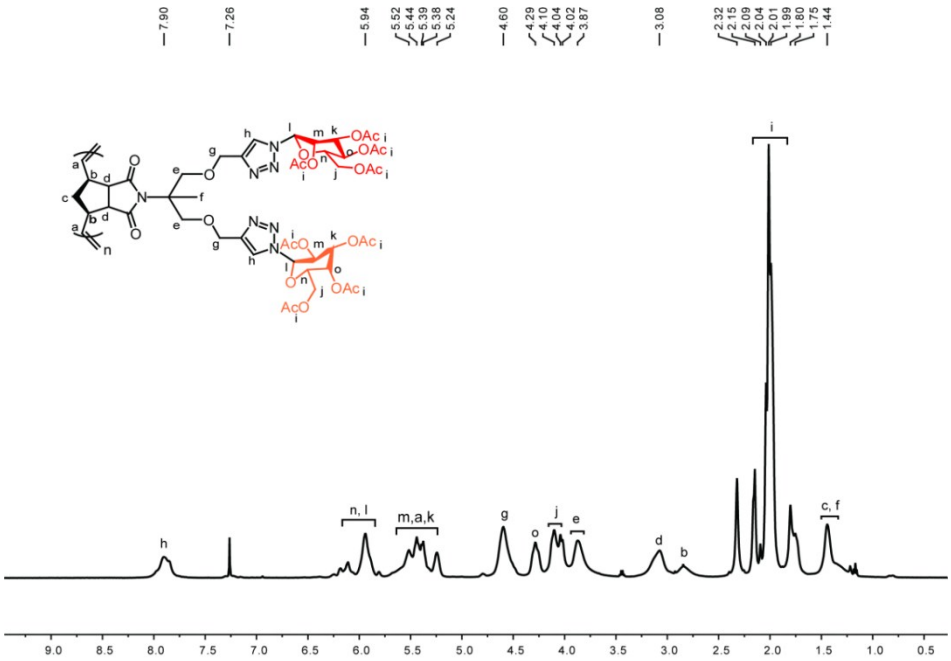

Figure S42. ^{1}H NMR spectrum of poly(Man-βGal-OAc) in $CDCl_3$.

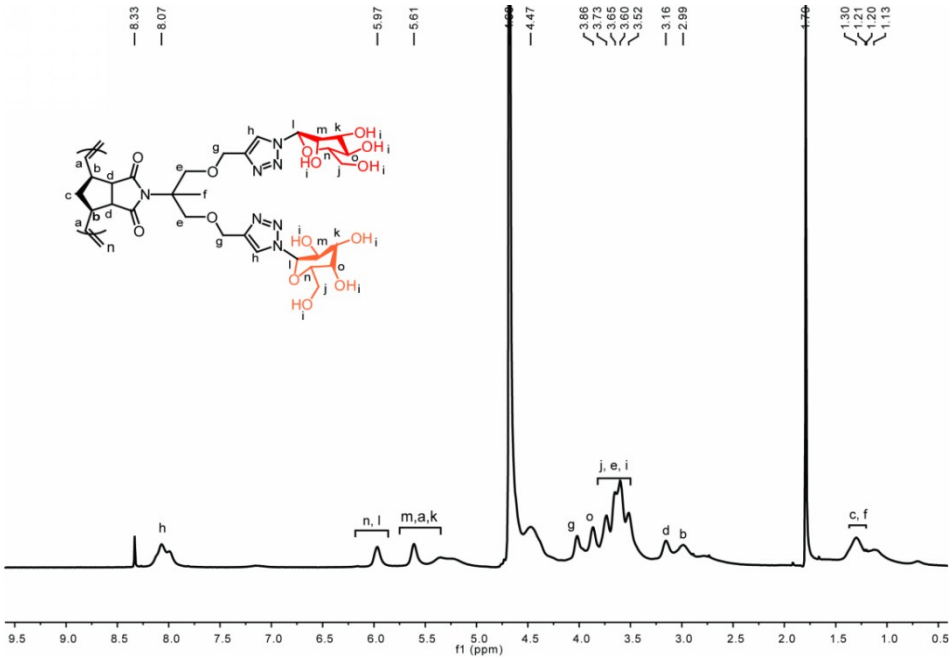

Figure S43. ^{1}H NMR spectrum of poly(Man-βGal) in D_2O.

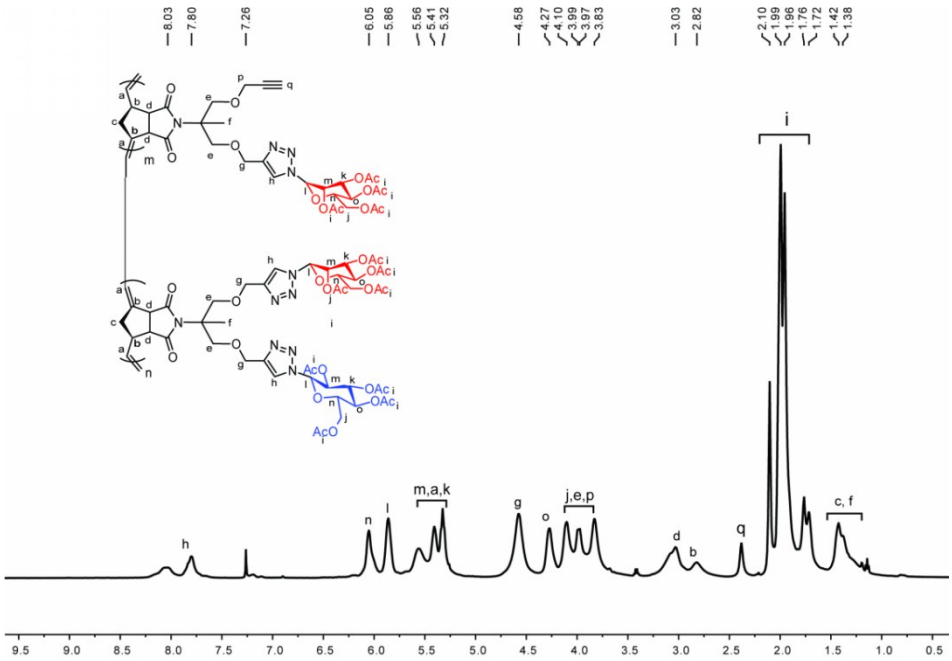

Figure S44. ^{1}H NMR spectrum of block glycopolymers poly(Man-βGlu-OAc)-b-poly(Man-Alkyne-OAc) in $CDCl_3$.

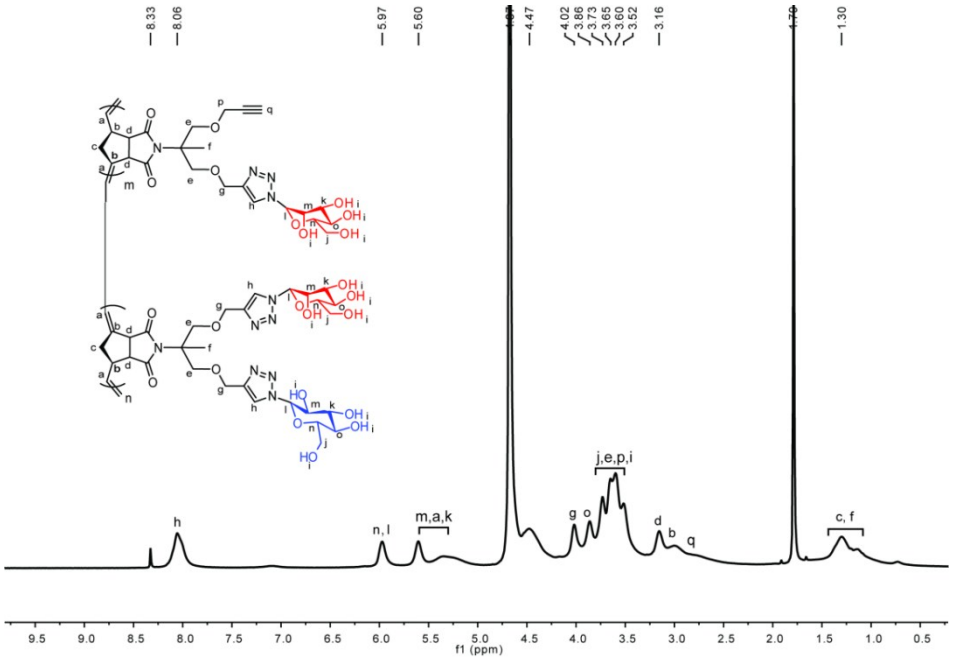

Figure S45. ^{1}H NMR spectrum of block glycopolymers poly(Man-βGlu)-b-poly(Man-Alkyne)in D_2O.

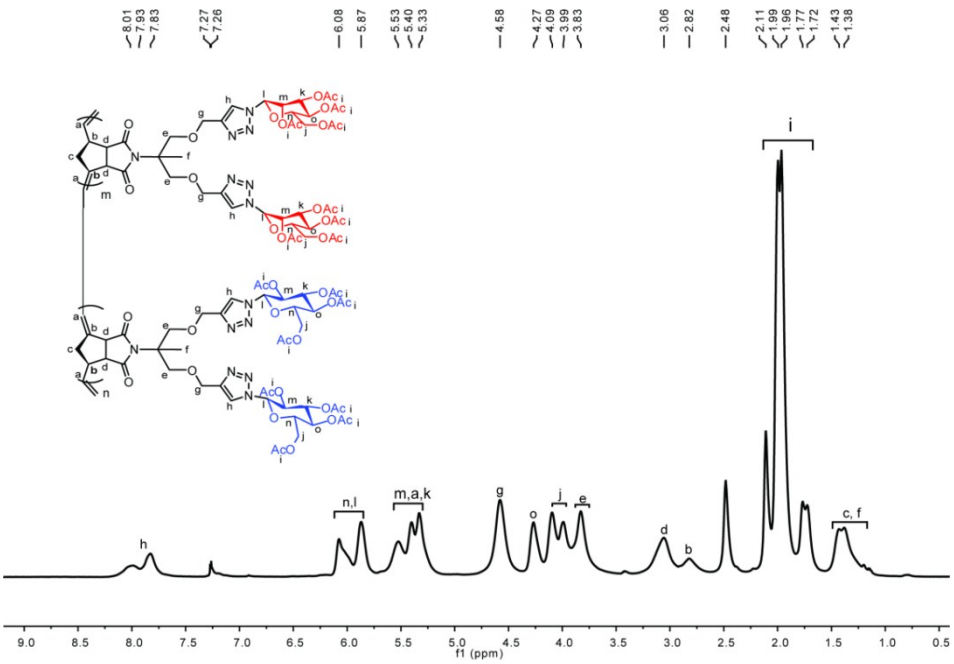

Figure S46. ^{1}H NMR spectrum of random glycopolymers poly(Man-Man-OAc)-r-poly(βGlu-βGlu-OAc) in $CDCl_3$.

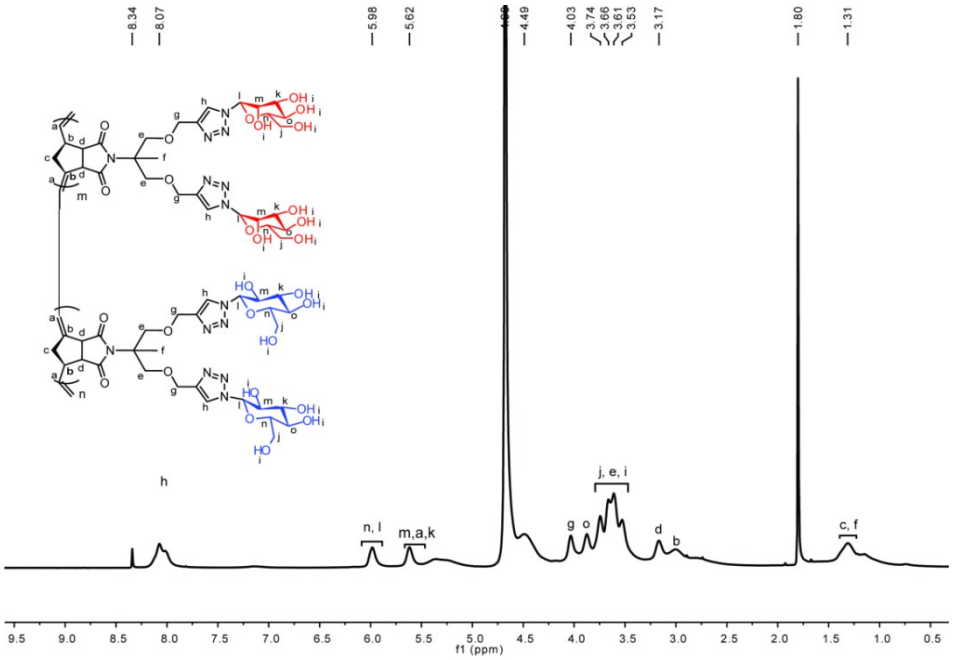

Figure S47. ^{1}H NMR spectrum of random glycopolymers poly(Man-Man)-r-poly(βGlu-βGlu) in D_2O.

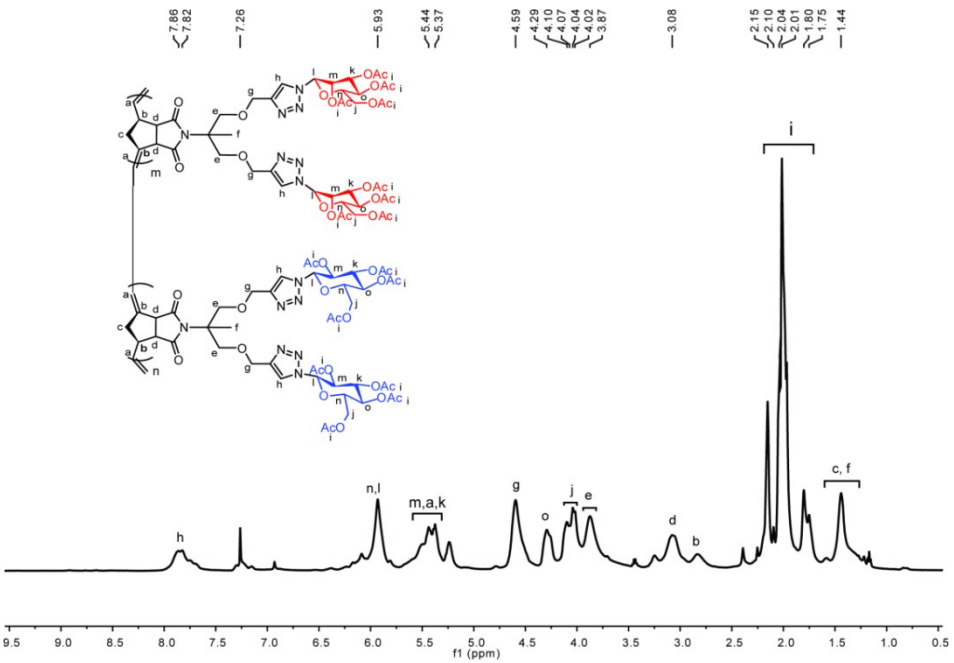

Figure S48. ^{1}H NMR spectrum of block glycopolymers poly(Man-Man-OAc)-b-poly(βGlu-βGlu-OAc) in $CDCl_3$.

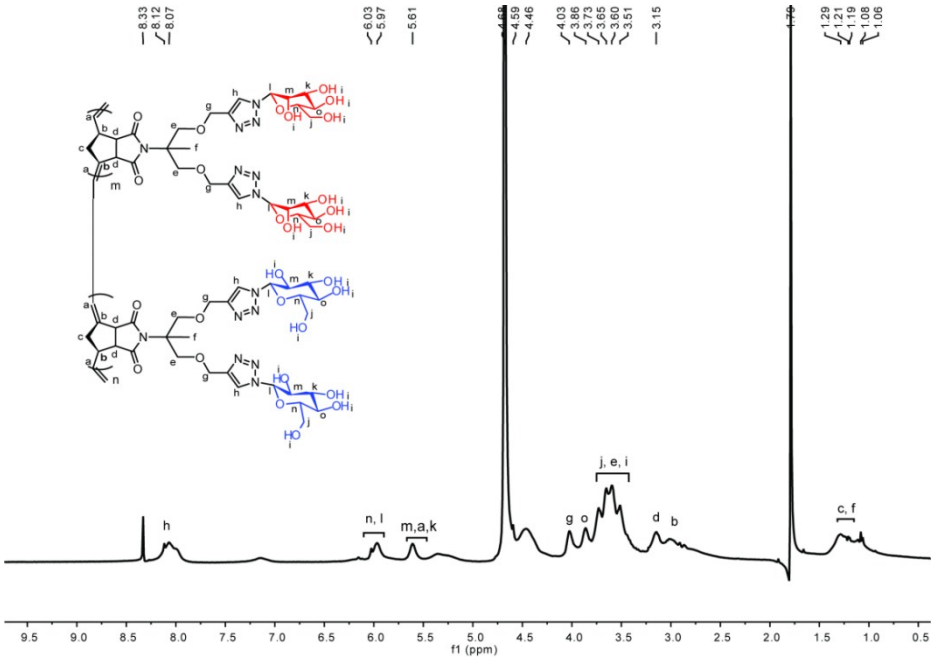

Figure S49. ^{1}H NMR spectrum of block glycopolymers poly(Man-Man)-b-poly(βGlu-βGlu) in D_2O.

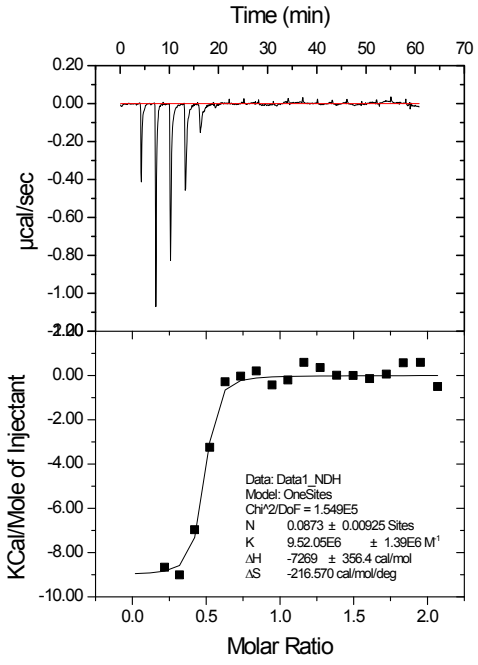

Figure S50. Calorimetric titration for poly($^{\alpha}$Glu-$^{\alpha}$Glu).

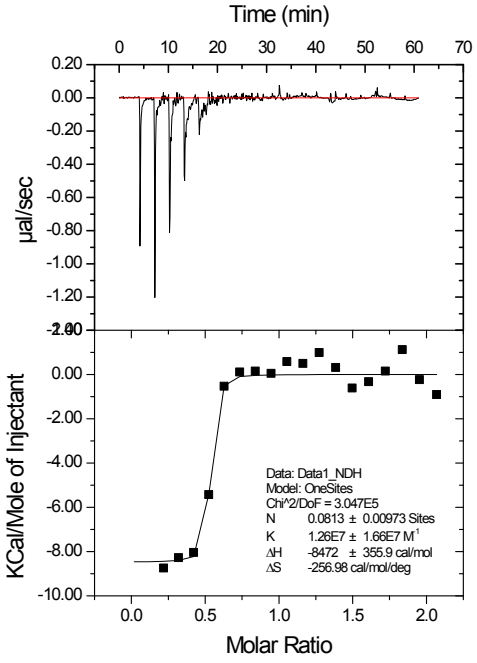

Figure S51. Calorimetric titration for poly(Man-αGlu).

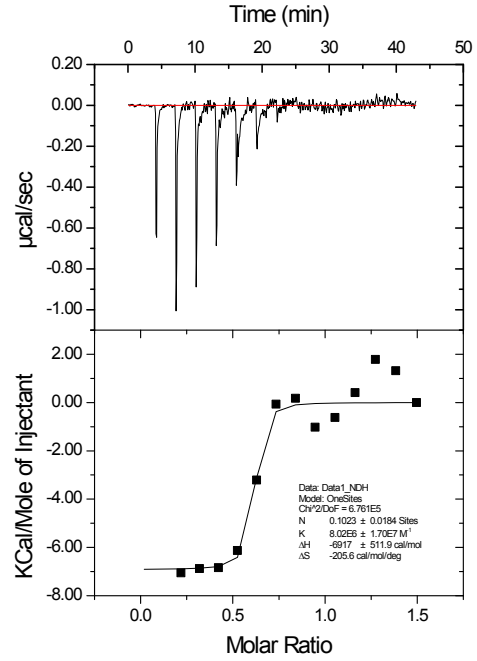

Figure S52. Calorimetric titration for poly(Man-βGal).

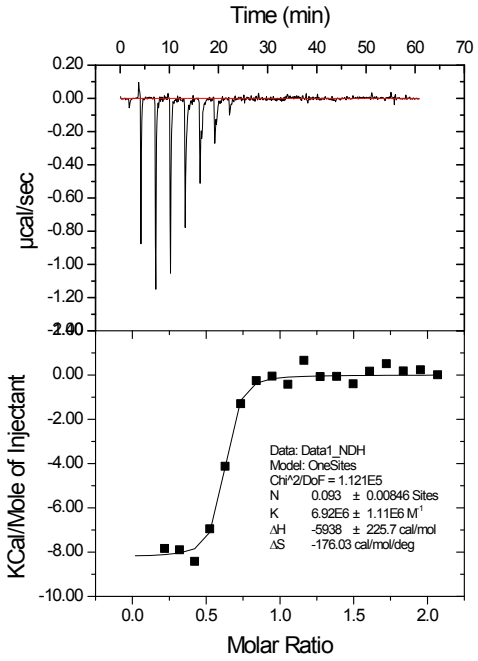

Figure S53. Calorimetric titration for poly(Man-βGlu)-b-poly(Man-Alkyne).

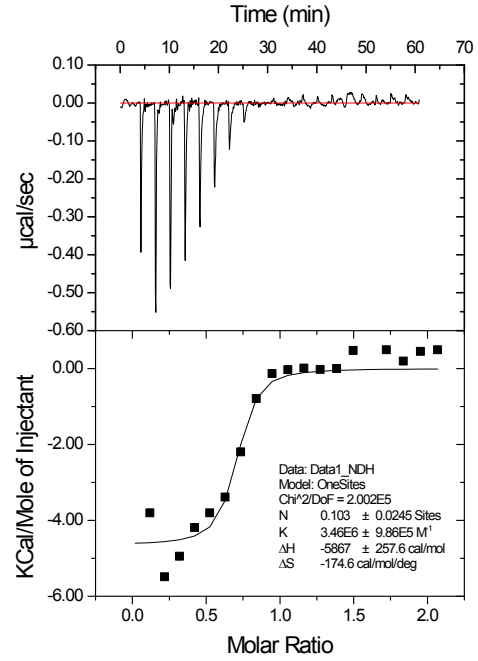

Figure S54. Calorimetric titration for poly(Man-Man)-r-poly(βGlu-βGlu).

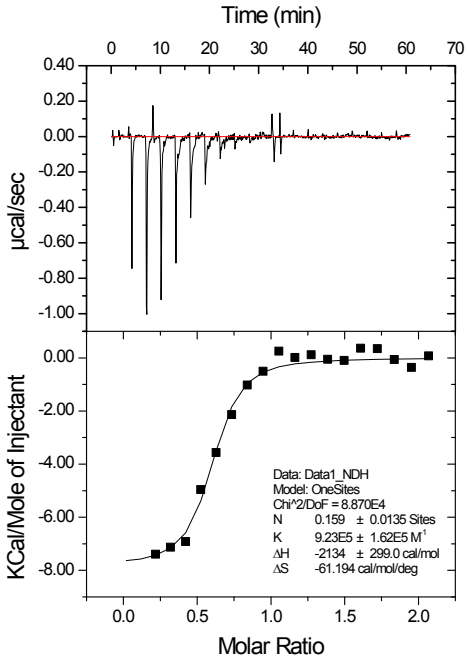

Figure S55. Calorimetric titration for Poly(Man-Man)-b-poly(βGlu-βGlu).

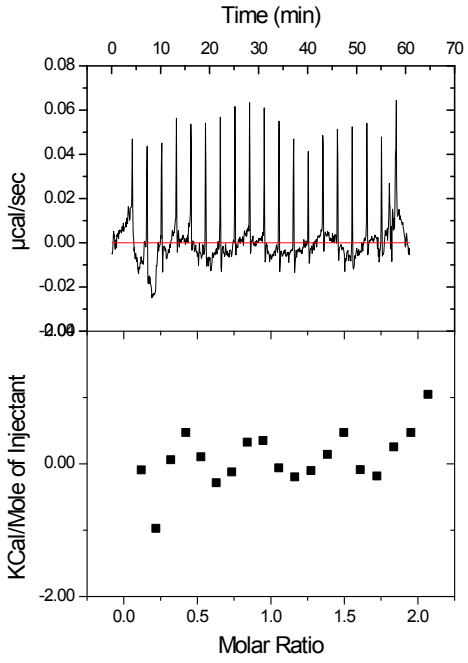

Figure S56. Calorimetric titration for poly(βGal-βGal).

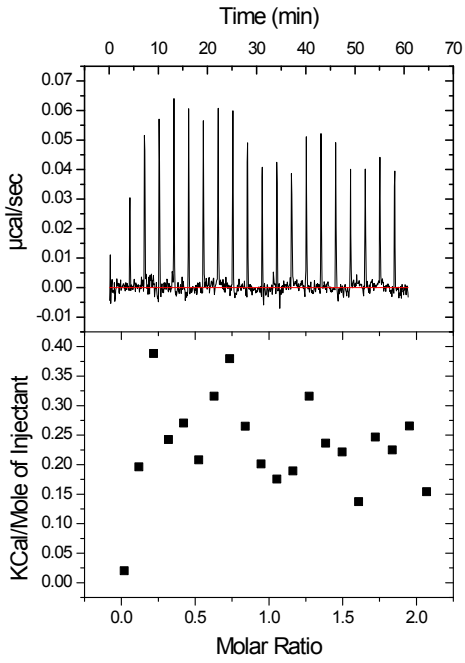

Figure S57. Calorimetric titration for poly(βGlu-Alkyne).

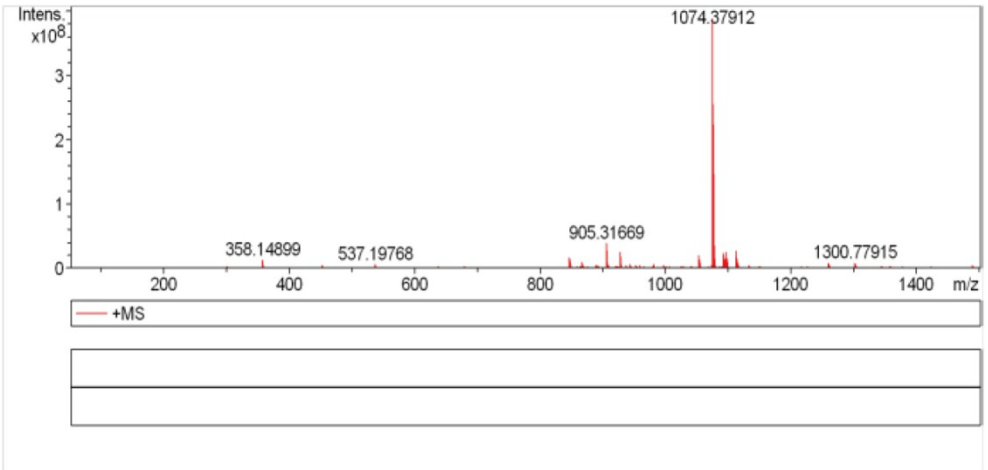

Figure S58. HRMS spectrum of compound **5B**.