

## Supporting Information

### Polyphosphazene-based nanocarriers for diosgenin and agrochemicals release

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#### 1. Supporting Tables

**Table SI-1.** Linear fitting parameters of *in vitro* release profiles of polymers **P1-P5** up to 8 h (intercept 0, slope k, adjusted R-Square) in PBS (pH 6.0) at 25 °C

Samples	k	Adjusted R-Square
<b>P1</b>	1.34 ± 0.09	0.9786
<b>P2</b>	2.5 ± 0.1	0.9833
<b>P3</b>	(1.72 ± 0.06) <sup>a</sup>	0.9978
<b>P4</b>	(1.65 ± 0.07) <sup>a</sup>	0.9899
<b>P5</b>	3.7 ± 0.5	0.9132

#### 2. Synthesis of materials, monomer and polymers

Synthesis of diosgenin-glycine-NH<sub>2</sub> (**1**). Boc-protected amino acid Boc-Gly-OH (0.13 g, 0.72 mmol), 4-(dimethylamino)pyridine (0.09 g, 0.72 mmol) and *N,N'*-dicyclohexylcarbodiimide (0.19 g, 0.72 mmol) were dissolved in 20 mL CH<sub>2</sub>Cl<sub>2</sub> and stirred at room temperature for 2 h. The reaction mixture was added to a solution of diosgenin (0.30 g, 0.72 mmol) in 10 mL CH<sub>2</sub>Cl<sub>2</sub> and stirred for 48 h. The precipitated *N,N'*-dicyclohexylurea was removed by filtration and the filtrate was extracted with 10% NH<sub>4</sub>Cl aqueous solution (2 × 15 mL), with 5% NaHCO<sub>3</sub> aqueous solution (2 × 15 mL) and saturated NaCl solution (1 × 15 mL). The organic phase was dried over MgSO<sub>4</sub>, filtered and removed under reduced pressure to yield diosgenin-glycine-Boc as a white solid (0.27 g, yield 65%). Then, diosgenin-glycine-Boc (0.27 g, 0.47 mmol) was dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. CF<sub>3</sub>COOH (1 mL, 13.10 mmol) was added dropwise to the diosgenin-glycine-Boc solution and stirred at room temperature overnight. The excess of CF<sub>3</sub>COOH and the solvent were removed under reduced pressure, CH<sub>2</sub>Cl<sub>2</sub> was added and

removed under reduced pressure twice. The remnant solid was dissolved again in 30 mL of  $\text{CH}_2\text{Cl}_2$  and washed with 5%  $\text{NaHCO}_3$  aqueous solution ( $2 \times 15$  mL), saturated  $\text{NaCl}$  solution ( $1 \times 15$  mL) and dried over  $\text{MgSO}_4$ . The  $\text{CH}_2\text{Cl}_2$  was removed under reduced pressure, to obtain diosgenin-glycine- $\text{NH}_2$  (**1**) as a white powder (0.19 g, yield 85%).

Synthesis of monomer trichlorophosphoranimine ( $\text{Cl}_3\text{P}=\text{N}-\text{Si}(\text{CH}_3)_3$ ). Lithium bis(trimethylsilyl)amide ( $\text{LiN}(\text{Si}(\text{CH}_3)_3)_2$ ) (25.00 g, 149.41 mmol) was dissolved in 500 mL of anhydrous  $\text{Et}_2\text{O}$  under Ar atmosphere, cooled to 0-4 °C with ice bath and stirred for 0.5 h. 13.07 mL of  $\text{PCl}_3$  (20.52 g, 149.41 mmol) were slowly added dropwise with a 20 mL syringe, while reaction mixture was stirred at 0-4 °C. Then, the reaction mixture was stirred at room temperature for 1 h. The solution was cooled to 0-4 °C with ice bath for a second time, 12.1 mL of  $\text{SO}_2\text{Cl}_2$  (20.17 g, 149.41 mmol) were added dropwise and the mixture was stirred for 1 h at 0-4 °C. Then, the reaction mixture was fast filtered over Celite and  $\text{Et}_2\text{O}$  was removed under reduced pressure at room temperature. The purification of the product was carried out *via* vacuum distillation with a Büchi glass oven (Büchi Labortechnik, Switzerland) at 40 °C under reduced pressure of 4 mbar to obtain  $\text{Cl}_3\text{P}=\text{N}-\text{Si}(\text{CH}_3)_3$  as a colourless liquid. The monomer was stored under Ar atmosphere at -35 °C in the glovebox (18.00 g, yield 54%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.16 (s, 9H) ppm;  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -54.2 ppm.

Synthesis of the polymer **P1**.  $(\text{C}_6\text{H}_5)_3\text{PCl}_2$  (2.08 mg, 0.006 mmol) and  $\text{Cl}_3\text{P}=\text{N}-\text{Si}(\text{CH}_3)_3$  (35.00 mg, 0.15 mmol) were dissolved in 1 mL of anhydrous  $\text{CH}_2\text{Cl}_2$  and stirred at room temperature overnight. Then, the obtained poly(dichloro)phosphazene (yield quantitative) was transferred to another flask with diosgenin-glycine- $\text{NH}_2$  (**1**) (73.60 mg, 0.16 mmol) and an excess of  $\text{Et}_3\text{N}$  (72.6 mg, 0.72 mmol) in 10 mL of anhydrous THF, and stirred at room temperature for 24 h. Afterwards, the second post-polymerisation functionalisation was carried out with Jeffamine M1000. An excess of Jeffamine M1000 (0.22 g, 0.22 mmol) and  $\text{Et}_3\text{N}$  (108.9 mg, 1.08 mmol) were added to the mixture and allowed to react another 24 h. Once the reaction was completed, the solvent was removed under reduced pressure and the product was purified by dialysis against deionised water (3 L, 1 time, 10 hours) and  $\text{EtOH}$  (750 mL, 10 times, 5 days). The  $\text{EtOH}$  was removed with  $\text{N}_2$  flow and the polymer was further dried under vacuum to give the polymer **P1** as a colorless waxy solid (101.3 mg, yield 36%).

### 3. Characterisation data for materials and polymers **P1-P6**

Diosgenin-glycine- $\text{NH}_2$  (**1**): ATR-FTIR (solid)  $\nu$  max: 2943 (C-H), 1726 (C=O), 1602 (N-H bending), 1557 (N-H bending), 1453 (C-H bending), 1212 (C-O-C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz, 298 K,  $\text{CDCl}_3$ ):  $\delta$  = 0.79 (t, 6H,  $J$  = 3.1 Hz, H18 + H27), 0.97 (d, 3H,  $J$  = 6.9 Hz, H21), 1.03 (s, 3H, H19), 3.37 (t, 1H,  $J$  = 10.8 Hz, H26ax), 3.42 (s, 2H,  $\text{NH}_2-\text{CH}_2-\text{COO}-$ ), 3.47 (m, 1H, H26eq), 4.41 (q, 1H,  $J$  = 7.4 Hz, H16 $\alpha$ ), 4.66 (m, 1H, H3 $\alpha$ ), 5.38 (d, 1H,  $J$  = 4.7 Hz, H6) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 14.7 (C21), 16.4 (C18), 17.3 (C27), 19.5 (C19), 21.0 (C11), 27.9 (C2), 29.0 (C24), 30.4 (C8 + C25), 32.0 (C23), 32.2 (C7), 34.1 (C15), 36.9 (C10), 37.1 (C1), 38.2 (C4), 39.9 (C12), 40.4 (C13), 41.8 (C20), 44.1 ( $\text{NH}_2-\text{CH}_2-\text{COO}-$ ), 50.1 (C9), 56.6 (C14), 62.2 (C17), 67.0 (C26),

74.8 (C3), 80.9 (C16), 109.4 (C22), 122.7 (C6), 139.6 (C5), 156.8 (CF<sub>3</sub>COO<sup>-</sup>), 173.4 (C=O) ppm.<sup>40</sup> It must be noted the presence of characteristic <sup>13</sup>C chemical shifts of CF<sub>3</sub>COO<sup>-</sup> related to obtaining steroid-glycine-NH<sub>2</sub> compounds as [steroid-glycine-NH<sub>3</sub><sup>+</sup>][CF<sub>3</sub>COO<sup>-</sup>].

DI31-glycine-NH<sub>2</sub> (**2**): ATR-FTIR (solid)  $\nu$  max: 3325 (N-H), 2929 (C-H), 1736 (C=O), 1713 (C=O, ketone C6 of DI31), 1627 (N-H bend), 1578 (N-H bend), 1454 (C-H bend), 1216 (C-O-C) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, 298 K, CDCl<sub>3</sub>):  $\delta$  = 0.75 (s, 3H, H18), 0.78 (d, 3H, *J* = 6.4 Hz, H27), 0.82 (s, 3H, H19), 0.96 (d, 3H, *J* = 6.7 Hz, H21), 2.77 (t, 1H, *J* = 12.1 Hz, H7 $\alpha$ ), 3.35 (t, 1H, *J* = 10.7 Hz, H26 ax), 3.45 (m, 3H, H26 eq + NH<sub>2</sub>-CH<sub>2</sub>-COO<sup>-</sup>), 4.40 (m, 1H, H16 $\alpha$ ), 5.09 (m, 1H, H3 $\alpha$ ) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 14.1 (C19), 14.6 (C21), 16.5 (C18), 17.3 (C27), 21.3 (C11), 26.4 (C2), 28.9 (C24), 29.6 (C1), 30.4 (C25), 31.5 (C23), 31.7 (C15), 32.5 (C4), 36.9 (C8), 39.7 (C12), 41.2 (C13), 41.7 (C20), 41.9 (C7), 42.6 (C10), 44.0 (NH<sub>2</sub>-CH<sub>2</sub>-COO<sup>-</sup>), 44.4 (C9), 56.2 (C14), 62.2 (C17), 67.0 (C26), 71.6 (C3), 80.2 (C5), 80.6 (C16), 109.4 (C22), 157.1 (CF<sub>3</sub>COO<sup>-</sup>), 172.8 (C=O, glycine), 212.2 (C=O, C6) ppm.

S7-glycine-NH<sub>2</sub> (**3**): ATR-FTIR (solid)  $\nu$  max: 3321 (N-H), 2934 (C-H), 1711 (C=O, ketone C6 of S7), 1625 (N-H bend), 1574 (N-H bend), 1448 (C-H bend), 1212 (C-O-C) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, 298 K, CDCl<sub>3</sub>):  $\delta$  = 0.64 (s, 3H, H18), 0.80 (s, 3H, H19), 0.93 (m, 6H, H26 + H27), 0.98 (t, 3H, *J* = 6.6 Hz, H29), 1.00 (m, 3H, H21), 2.50 (m, 1H, H22), 2.73 (m, 1H, H23), 3.40 (s, 2H, NH<sub>2</sub>-CH<sub>2</sub>-COO<sup>-</sup>), 5.10 (m, 1H, H3 $\alpha$ ) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 12.2 (C18), 12.6 (C29), 14.1 (C19), 16.5 (C21), 19.2 (C27), 19.4 (C26), 21.5 (C11 + C28), 25.8 (C15), 26.4 (C2), 29.3 (C25), 29.4 (C16), 29.7 (C1), 32.6 (C4), 37.5 (C8), 39.7 (C12), 39.9 (C20), 41.9 (C7), 42.6 (C10), 43.3 (C13), 44.0 (NH<sub>2</sub>-CH<sub>2</sub>-COO<sup>-</sup>), 44.4 (C9), 49.3 (C24), 56.0 (C17), 56.5 (C14), 62.6 (C22 + C23), 71.8 (C3), 80.3 (C5), 156.9 (CF<sub>3</sub>COO<sup>-</sup>), 173.8 (C=O, glycine), 212.5 (C=O, C6) ppm.

Polymer **P1**: ATR-FTIR (solid)  $\nu$  max: 3339 (N-H), 2870 (C-H), 1741 (C=O), 1452 (C-H bending), 1100 (C-O-C), 1050 (P=N) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.77 (s, 6H, H18 + H27), 0.95 (d, 3H, *J* = 6.5 Hz, H21), 0.99 (s, 3H, H19), 1.10 (br, 6H, -O-CH<sub>2</sub>-CH(CH<sub>3</sub>)- of Jeffamine M1000), 3.36 (s, 3H, CH<sub>3</sub>O- end groups of Jeffamine M1000), 3.62 (m, 35H, polyalkylene oxide -CH<sub>2</sub>- of Jeffamine M1000), 4.39 (m, 1H, H16 $\alpha$ ), 4.53 (m, 1H, H3 $\alpha$ ), 5.32 (s, 1H, H6), 7.60 (d, 0.65H, protons of (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P=N- end group) ppm; <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.6 ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 14.7 (C21), 16.4 (C18), 17.3 (C27), 19.5 (C19), 20.9 (C11), 27.8 (C2), 28.9 (C24), 30.4 (C8 + C25), 32.0 (C23), 32.2 (C7), 33.8 (C15), 36.8 (C10), 38.1 (C4), 39.9 (C12), 40.4 (C13), 41.7 (C20), 45.2 (-NH-CH<sub>2</sub>-COO<sup>-</sup>), 50.1 (C9), 56.7 (C14), 59.1 (-O-CH<sub>2</sub>-CH(CH<sub>3</sub>)- of Jeffamine M1000), 62.3 (C17), 66.9 (C26), 70.7 (-O-CH<sub>2</sub>-CH<sub>2</sub>-O- of Jeffamine M1000), 72.0 (-O-CH<sub>2</sub>-CH(CH<sub>3</sub>)- of Jeffamine M1000), 74.3 (C3), 80.8 (C16), 109.3 (C22), 122.4 (C6), 139.8 (C5), 171.7 (C=O) ppm. GPC (g mol<sup>-1</sup>) M<sub>n</sub> = 9586, M<sub>w</sub> = 13134. Glass transition temperature (*T*<sub>g</sub>) = -17.2 °C.

Polymer **P2**: ATR-FTIR (solid)  $\nu$  max: 3312 (N-H), 2867 (C-H), 1740 (C=O), 1453 (C-H bend), 1100 (C-O-C), 1052 (P=N) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, 298 K, CDCl<sub>3</sub>):  $\delta$  = 0.77 (s, 6H, H18 + H27), 0.95 (d, 3H, *J* = 6.3 Hz, H21), 1.00 (s, 3H, H19), 1.11 (br, 14H, CH<sub>3</sub>- of PPO groups of Jeffamine

M-1000), 3.36 (s, 6H, CH<sub>3</sub>O– end groups of Jeffamine M-1000), 3.63 (m, 119H, polyalkylene oxide –CH<sub>2</sub>–), 4.40 (m, 1H, H16 $\alpha$ ), 5.33 (s, 1H, H6), 7.61 (d, 0.68H, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P=N– end group) ppm; <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.8 ppm. GPC (g mol<sup>-1</sup>) M<sub>n</sub> = 15048, Mw = 22121. (*T*<sub>g</sub>) = -13.5 °C, melting temperature (*T*<sub>m</sub>) = 17.9 °C.

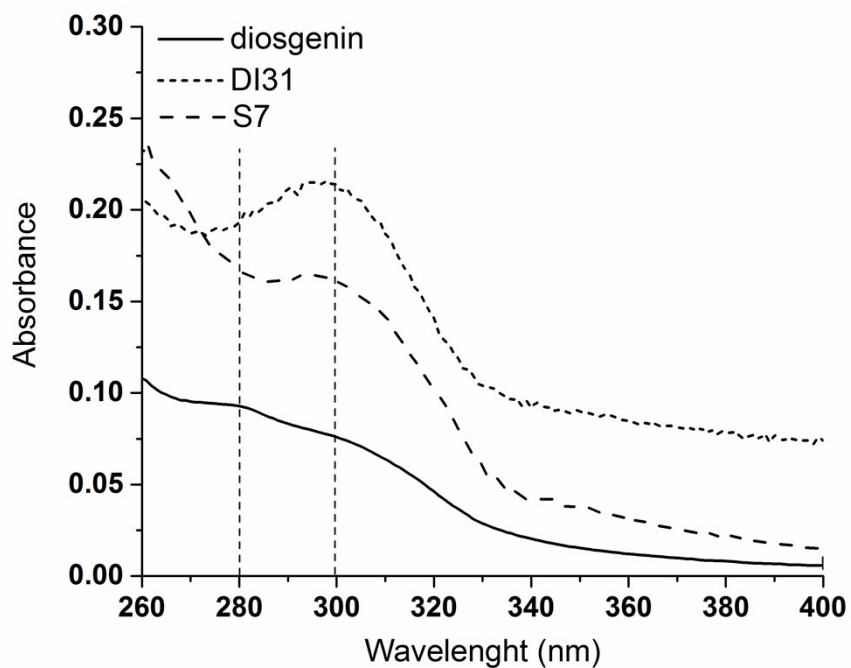
Polymer **P3**: ATR-FTIR (solid)  $\nu$  max: 3327 (N–H), 2869 (C–H), 1741 (C=O), 1453 (C–H bend), 1098 (C–O–C), 1051 (P=N) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.77 (s, 6H, H18 + H27), 0.95 (d, 3H, *J* = 6.3 Hz, H21), 0.99 (s, 3H, H19), 1.11 (br, 6H, CH<sub>3</sub>– of PPO groups of Jeffamine M-1000), 3.36 (s, 3H, CH<sub>3</sub>O– end groups of Jeffamine M-1000), 3.62 (m, 32H, polyalkylene oxide –CH<sub>2</sub>–), 4.39 (m, 1H, H16 $\alpha$ ), 4.53 (m, 1H, H3 $\alpha$ ), 5.32 (s, 1H, H6), 7.61 (d, 0.44H, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P=N– end group) ppm; <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.8 ppm. GPC (g mol<sup>-1</sup>) M<sub>n</sub> = 11926, Mw = 15624. *T*<sub>g</sub> = -60.8 °C.

Polymer **P4**: ATR-FTIR (solid)  $\nu$  max: 3518 (O–H), 3316 (N–H), 2868 (C–H), 1734 (C=O), 1714 (C=O of ketone), 1454 (C–H bend), 1104 (C–O–C), 1040 (P=N) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.78 (s, 9H, H18 + H19 + H27), 0.94 (s, 3H, H21), 1.11 (br, 14H, CH<sub>3</sub>– of PPO groups of Jeffamine M-1000), 3.36 (s, 6H, CH<sub>3</sub>O– end groups of Jeffamine M-1000), 3.63 (m, 108H, polyalkylene oxide –CH<sub>2</sub>–), 4.38 (m, 1H, H16 $\alpha$ ), 7.60 (d, 0.75H, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P=N– end group) ppm; <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.8 ppm. GPC (g mol<sup>-1</sup>) M<sub>n</sub> = 14108, Mw = 19046. *T*<sub>g</sub> = -14.1 °C, *T*<sub>m</sub> = 20.9 °C.

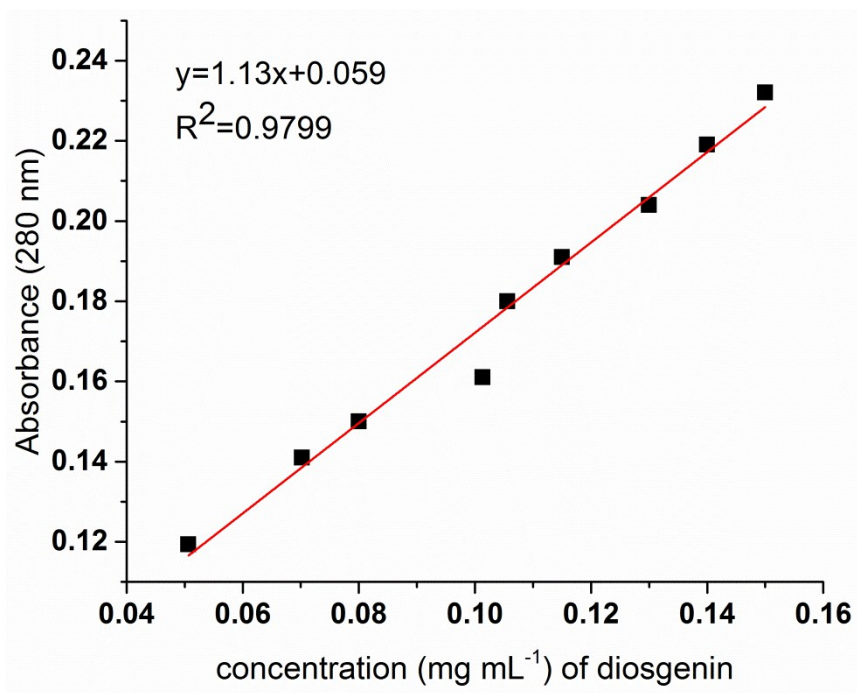
Polymer **P5**: ATR-FTIR (solid)  $\nu$  max: 3303 (N–H), 2867 (C–H), 1734 (C=O), 1713 (C=O of ketone), 1455 (C–H bend), 1103 (C–O–C), 1038 (P=N) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.62 (s, 3H, H18), 0.77 (s, 3H, H19), 0.81 (d, 3H, *J* = 6.6 Hz, H21), 0.91 (m, 9H, H26 + H27 + H29), 1.11 (br, 15H, CH<sub>3</sub>– of PPO groups of Jeffamine M-1000), 3.35 (s, 6H, CH<sub>3</sub>O– end groups of Jeffamine M-1000), 3.62 (m, 137H, polyalkylene oxide –CH<sub>2</sub>–), 5.06 (s, 1H, H3 $\alpha$ ), 7.60 (d, 0.67H, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P=N– end group) ppm; <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.8 ppm. GPC (g mol<sup>-1</sup>) M<sub>n</sub> = 13016, Mw = 19524. *T*<sub>g</sub> = -13.6 °C, *T*<sub>m</sub> = 17.6 °C.

Polymer **P6**: ATR-FTIR (solid)  $\nu$  max: 3300 (N–H), 2883 (C–H), 1459 (C–H bend), 1108 (C–O–C), 1041 (P=N) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.12 (br, 14H, CH<sub>3</sub>– of PPO groups of Jeffamine M-1000), 3.36 (s, 6H, CH<sub>3</sub>O– end groups of Jeffamine M-1000), 3.63 (m, 148H, polyalkylene oxide –CH<sub>2</sub>–), 7.60 (d, 0.66H, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P=N– end group) ppm; <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.0 ppm. GPC (g mol<sup>-1</sup>) M<sub>n</sub> = 10783, Mw = 15489. *T*<sub>g</sub> = -18.1 °C, *T*<sub>m</sub> = 27.9 °C.

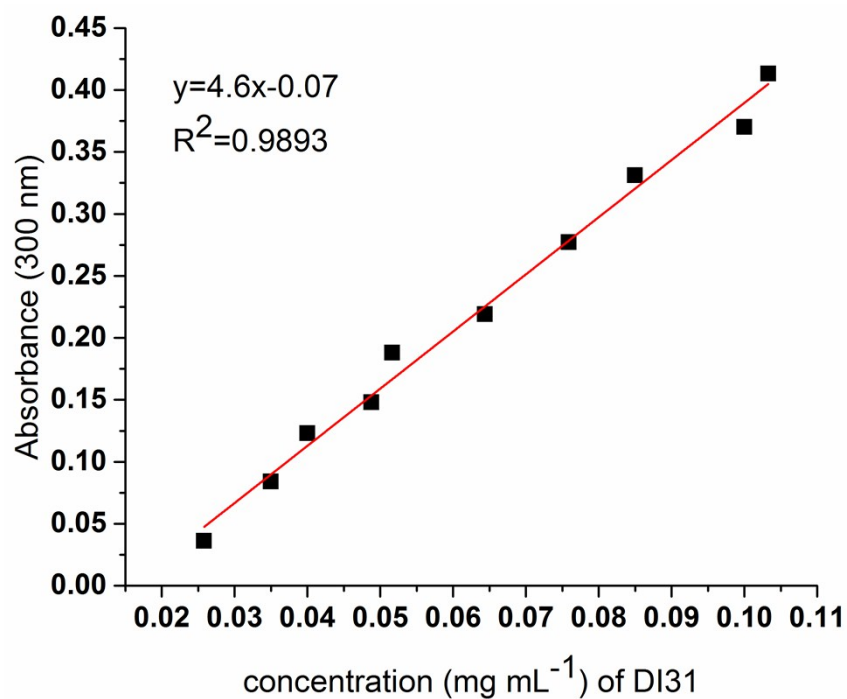
#### 4. Supporting Figures



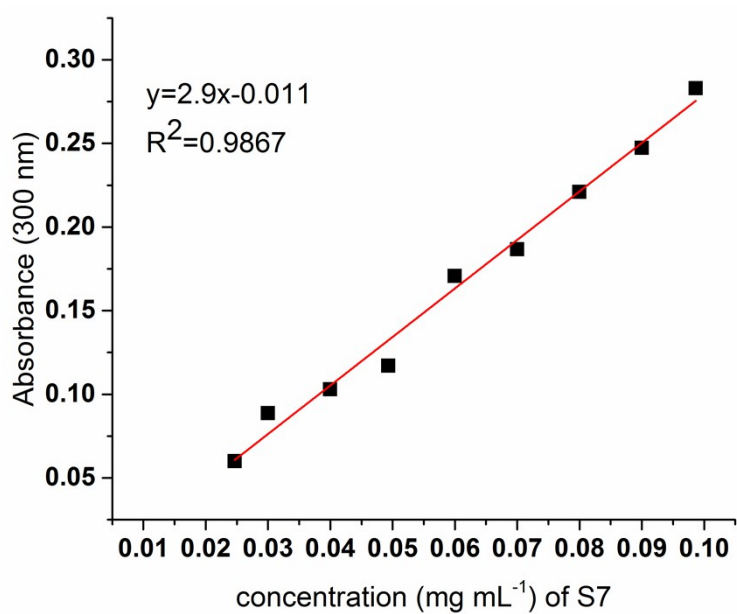
**Figure SI-1** UV spectra of: (a) diosgenin at  $0.056 \text{ mg mL}^{-1}$ , (b) DI31 at  $0.057 \text{ mg mL}^{-1}$ , S7 at  $0.058 \text{ mg mL}^{-1}$  in PBS (pH 6.0).



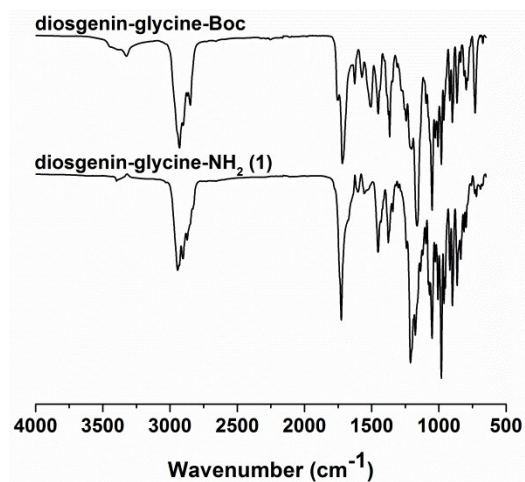
**Figure SI-2** Calibration curve of diosgenin in PBS (pH 6.0).



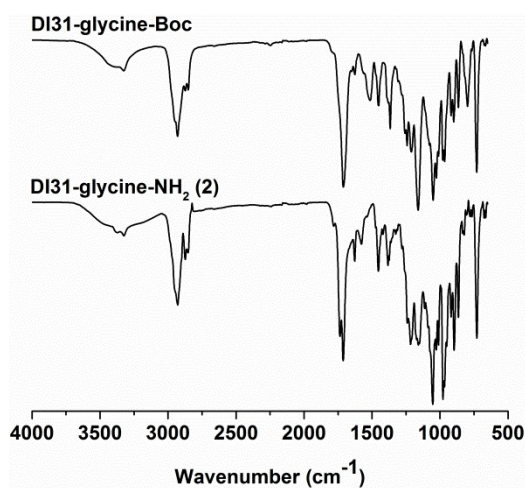
**Figure SI-3** Calibration curve of DI31 in PBS (pH 6.0).



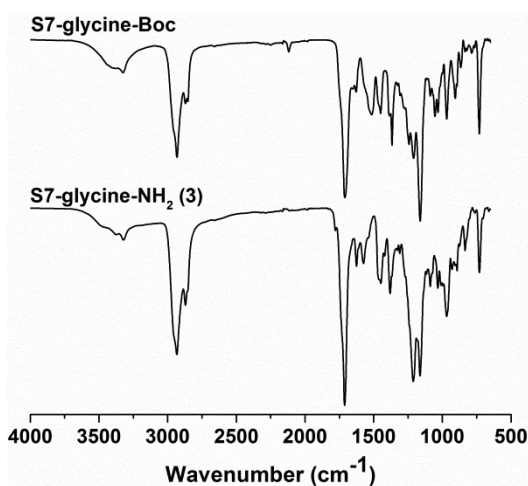
**Figure SI-4** Calibration curve of S7 in PBS (pH 6.0) .



**Figure SI-5** FT-IR spectra of diosgenin-glycine-Boc and diosgenin-glycine-NH<sub>2</sub> (**1**).



**Figure SI-6** FT-IR spectra of DI31-glycine-Boc and DI31-glycine-NH<sub>2</sub> (**2**).



**Figure SI-7** FT-IR spectra of S7-glycine-Boc and S7-glycine-NH<sub>2</sub> (**3**).

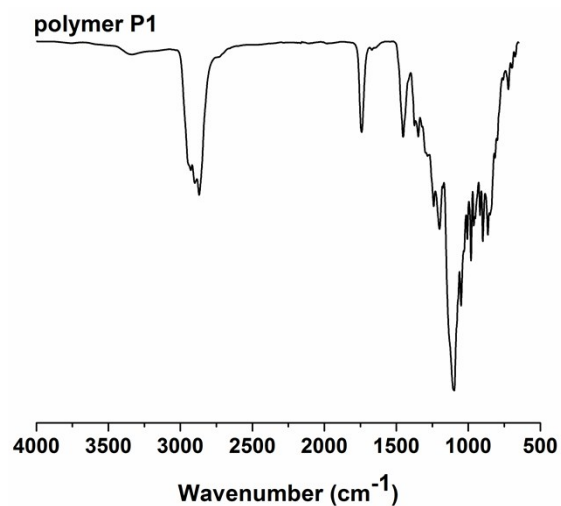


Figure SI-8 FT-IR spectra of polymer P1.

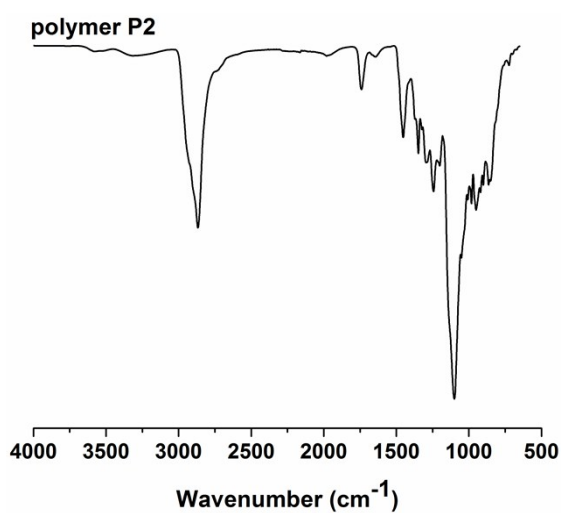


Figure SI-9 FT-IR spectra of polymer P2.

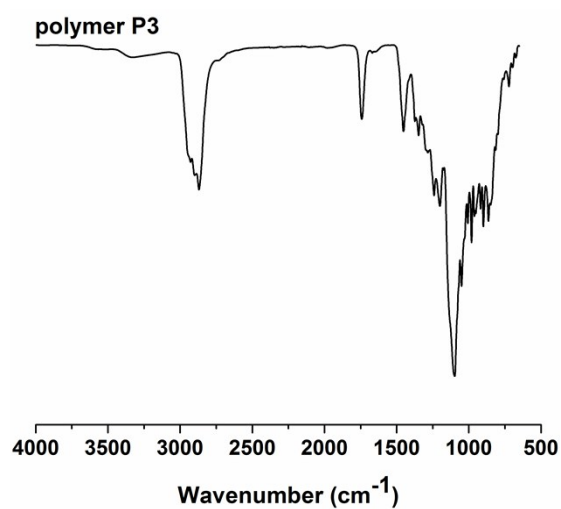


Figure SI-10 FT-IR spectra of polymer P3.



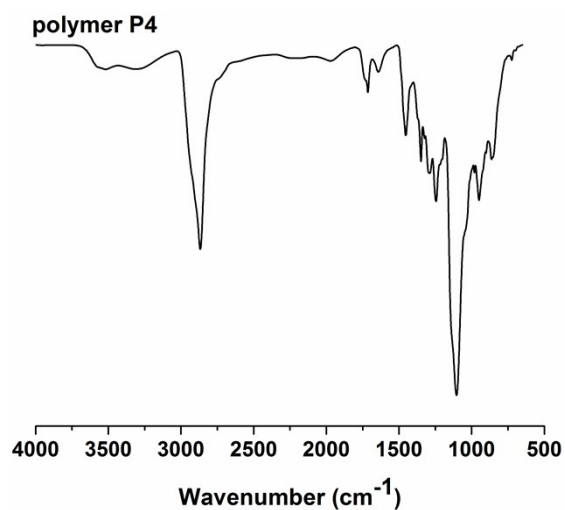


Figure SI-11 FT-IR spectra of polymer P4.

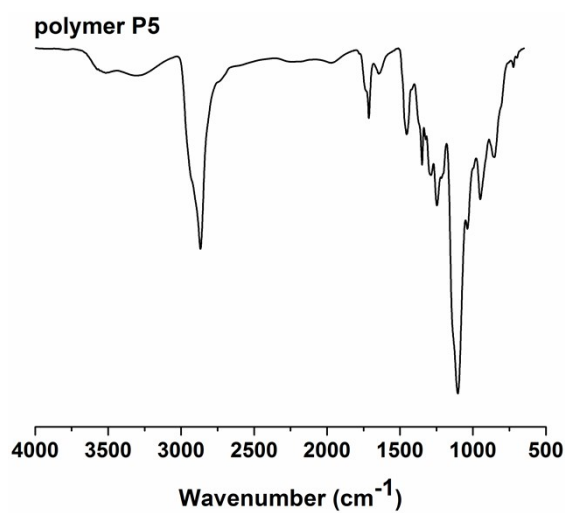


Figure SI-12 FT-IR spectra of polymer P5.

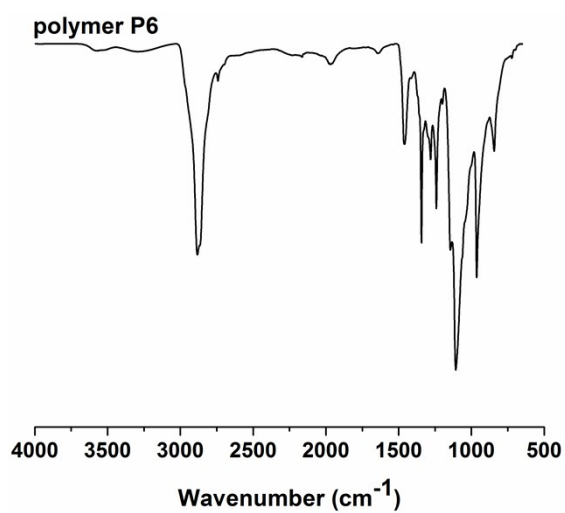


Figure SI-13 FT-IR spectra of polymer P6.

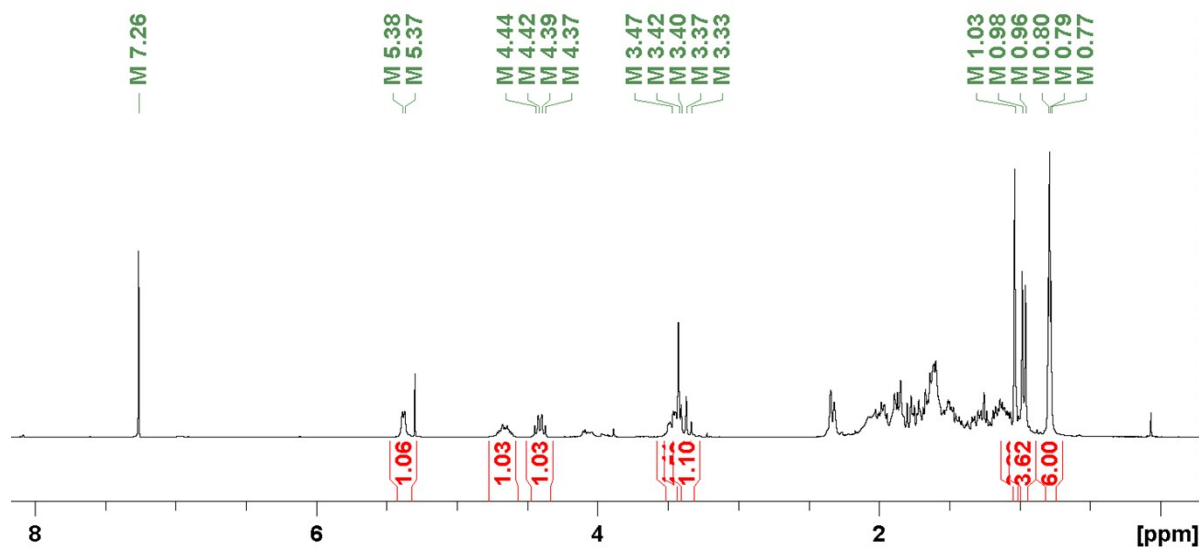


Figure SI-14 Partial  $^1\text{H}$  NMR (300 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of diosgenin-glycine- $\text{NH}_2$  (**1**).

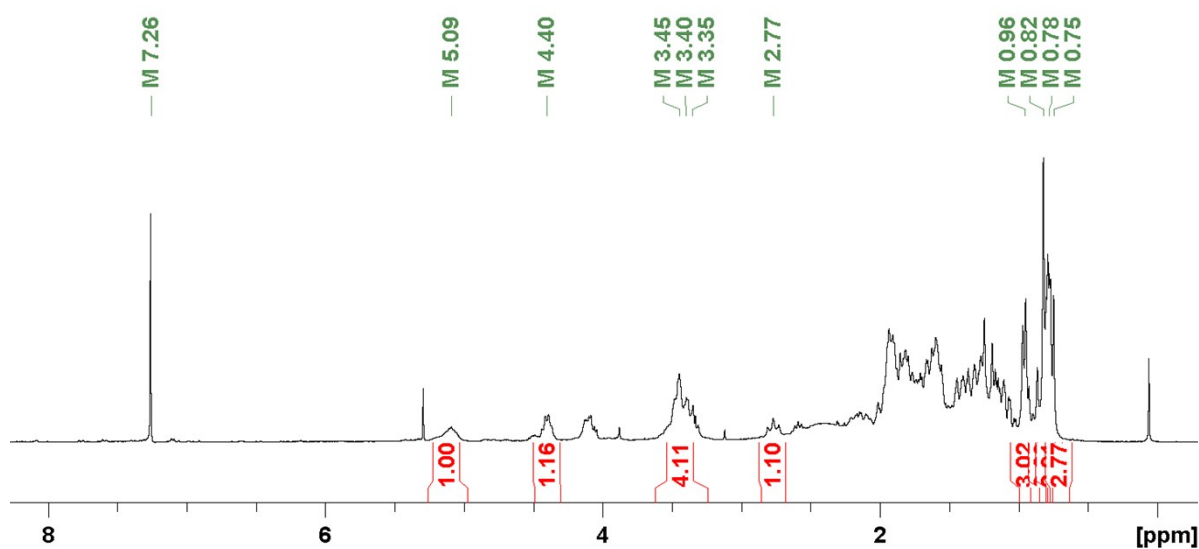
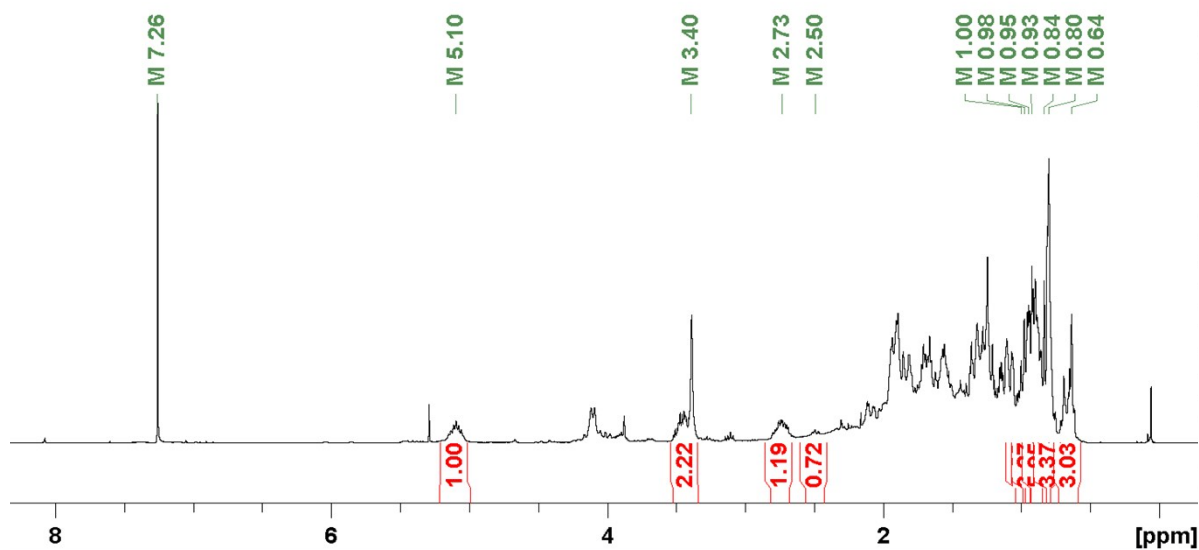
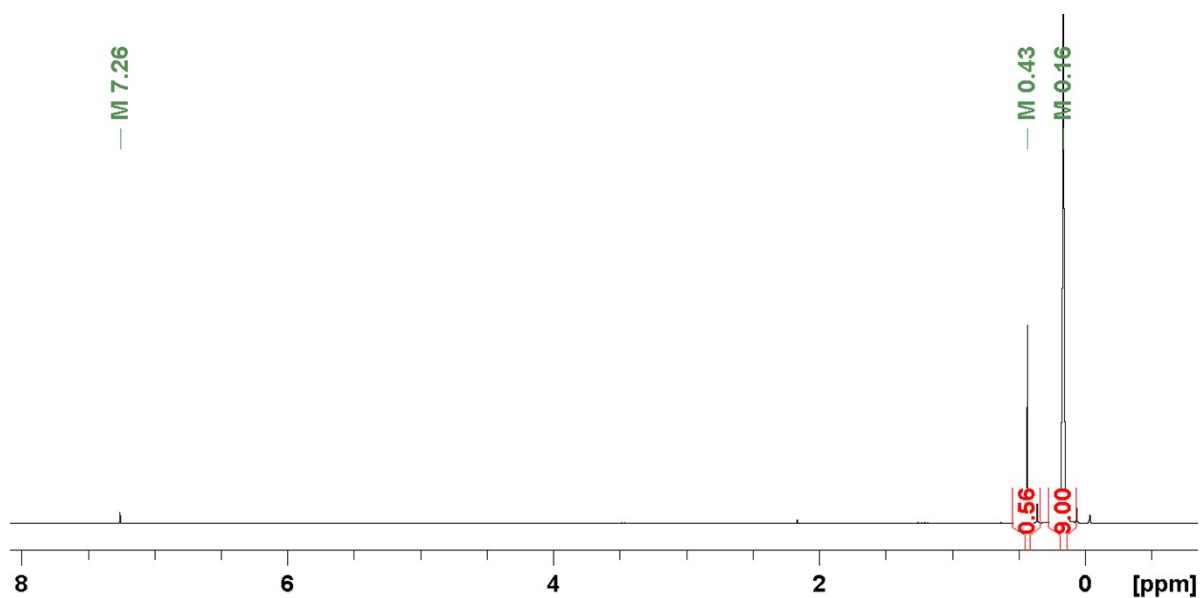


Figure SI-15 Partial  $^1\text{H}$  NMR (300 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of DI31-glycine- $\text{NH}_2$  (**2**).



**Figure SI-16** Partial  $^1\text{H}$  NMR (300 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of S7-glycine- $\text{NH}_2$  (**3**).



**Figure SI-17** Partial  $^1\text{H}$  NMR (300 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of monomer trichlorophosphoranimine ( $\text{Cl}_3\text{P}=\text{N}-\text{Si}(\text{CH}_3)_3$ ).

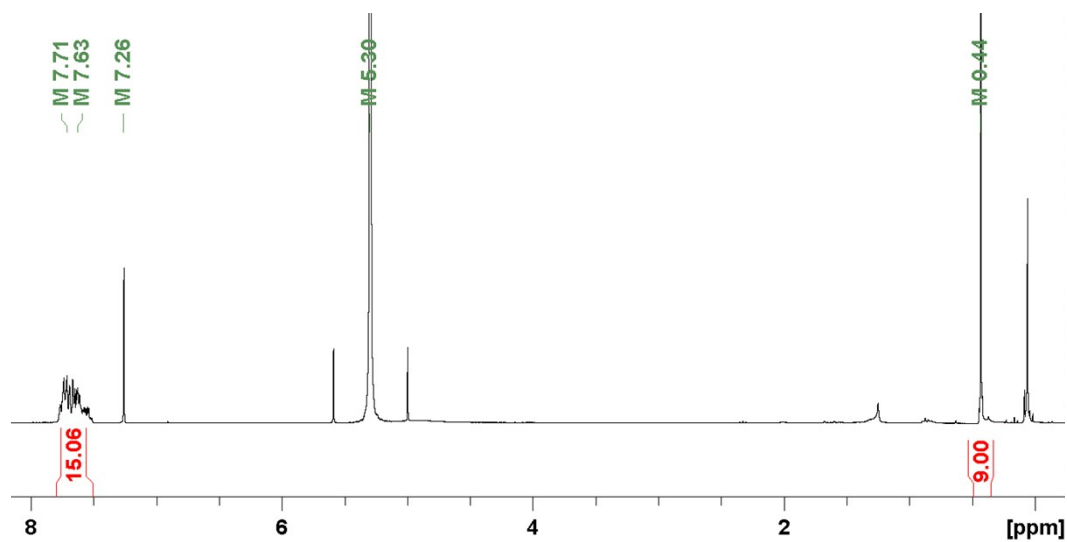


Figure SI-18 Partial  $^1\text{H}$  NMR (300 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of polydichlorophosphazene.

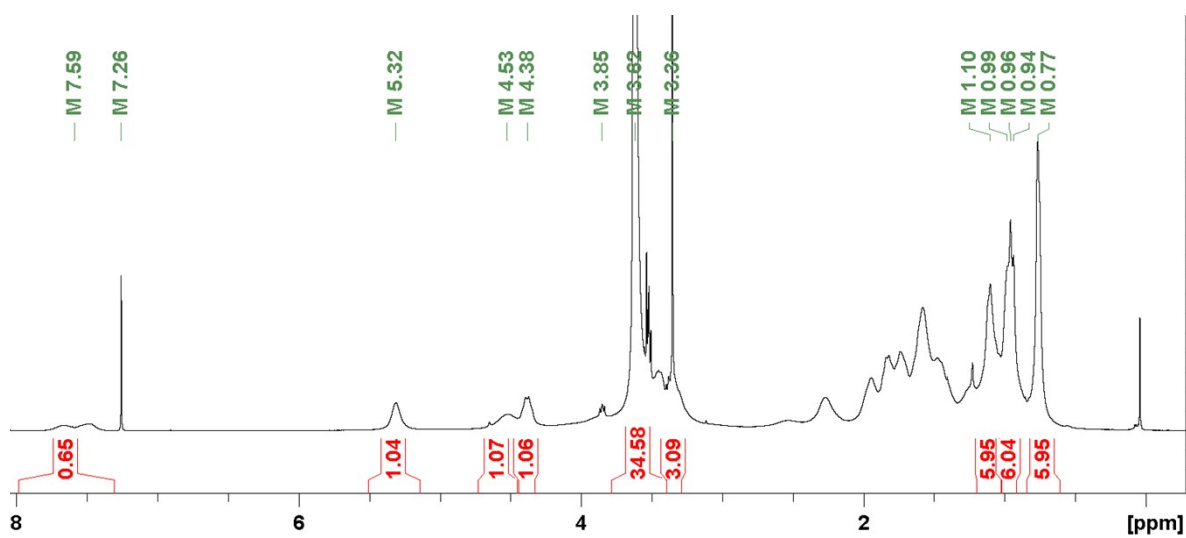


Figure SI-19 Partial  $^1\text{H}$  NMR (300 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of polymer P1.

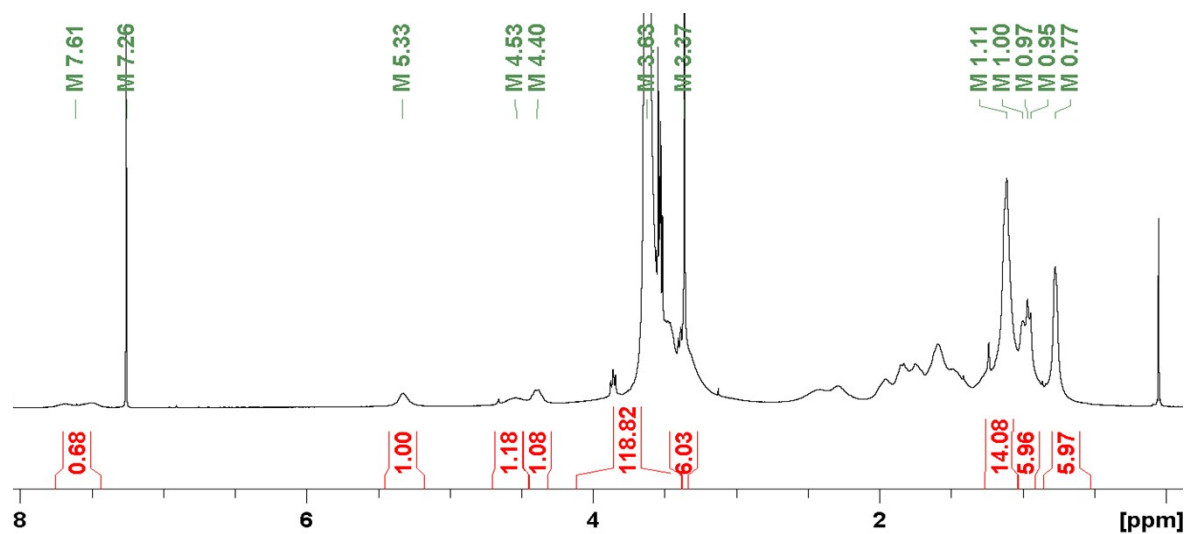


Figure SI-20 Partial  $^1\text{H}$  NMR (300 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of polymer P2.

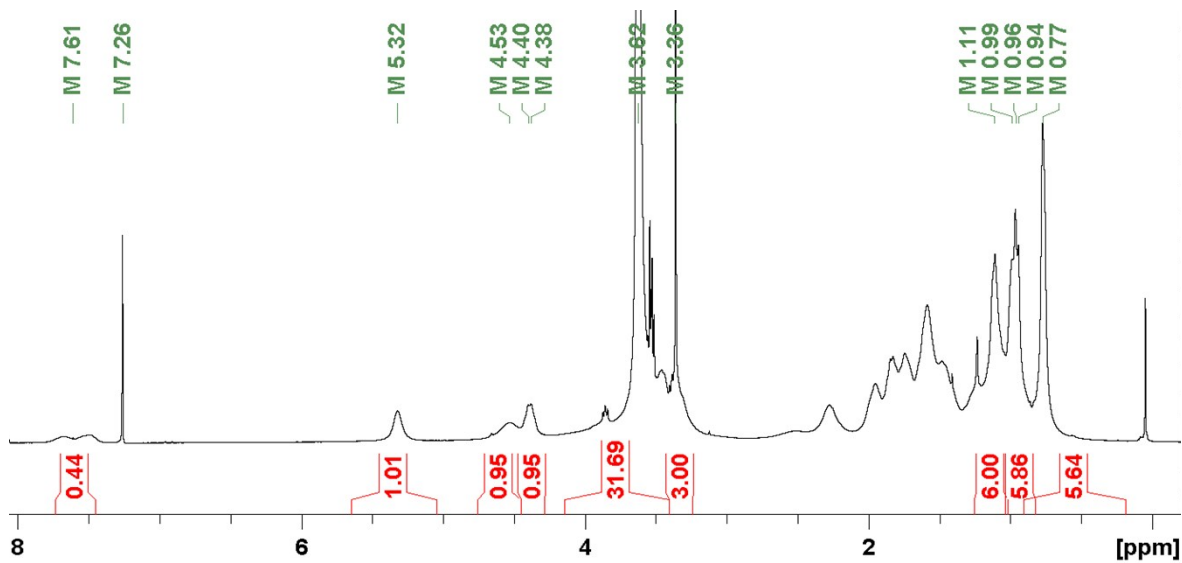


Figure SI-21 Partial  $^1\text{H}$  NMR (300 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of polymer P3.

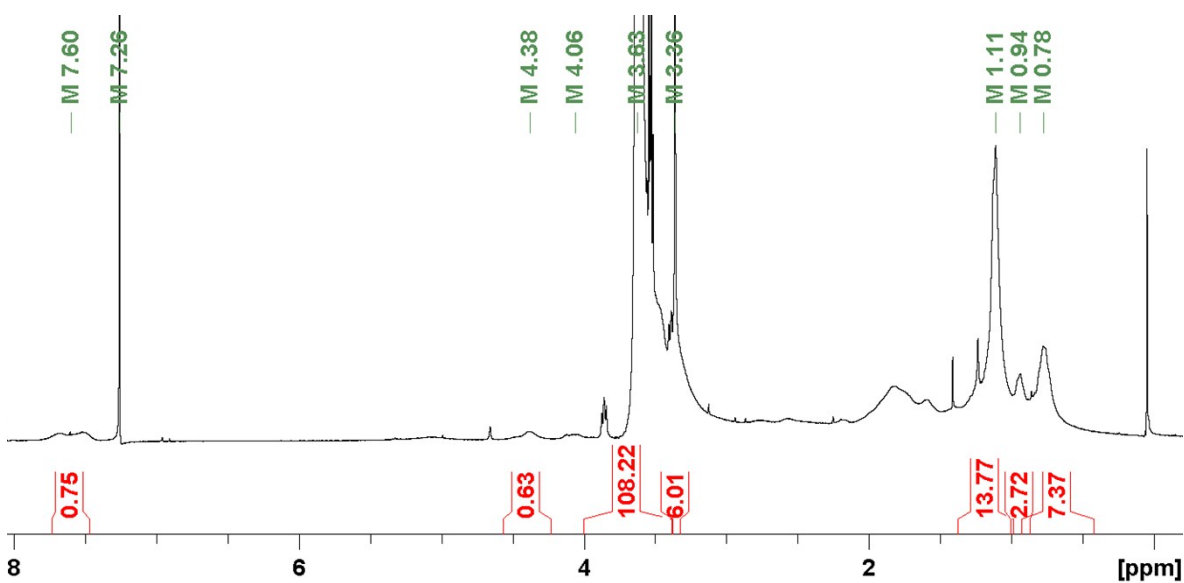


Figure SI-22 Partial  $^1\text{H}$  NMR (300 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of polymer P4.

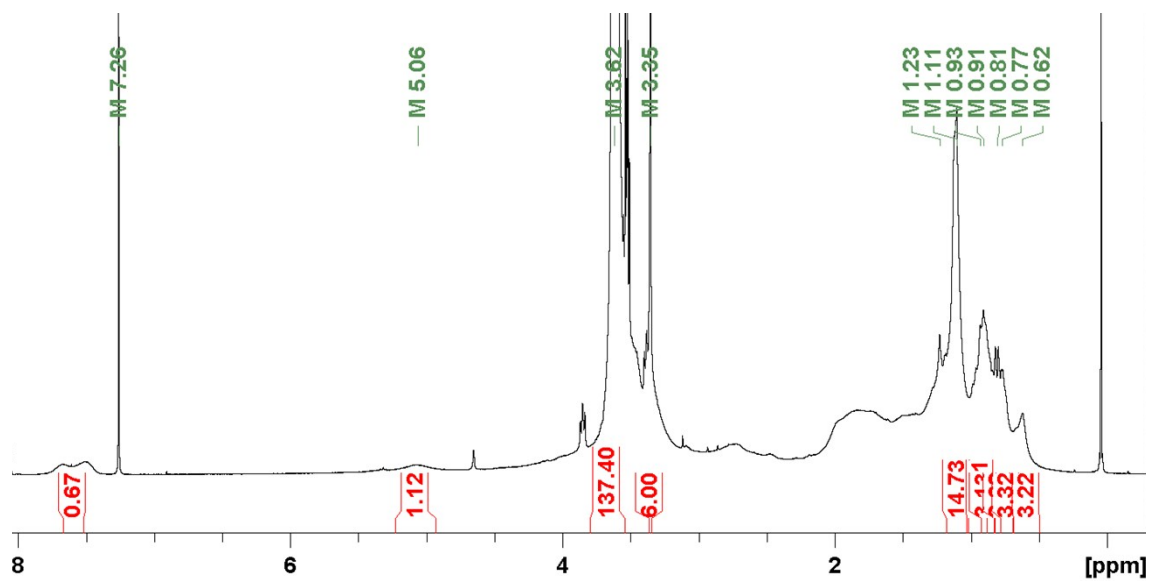


Figure SI-23 Partial  $^1\text{H}$  NMR (300 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of polymer P5.

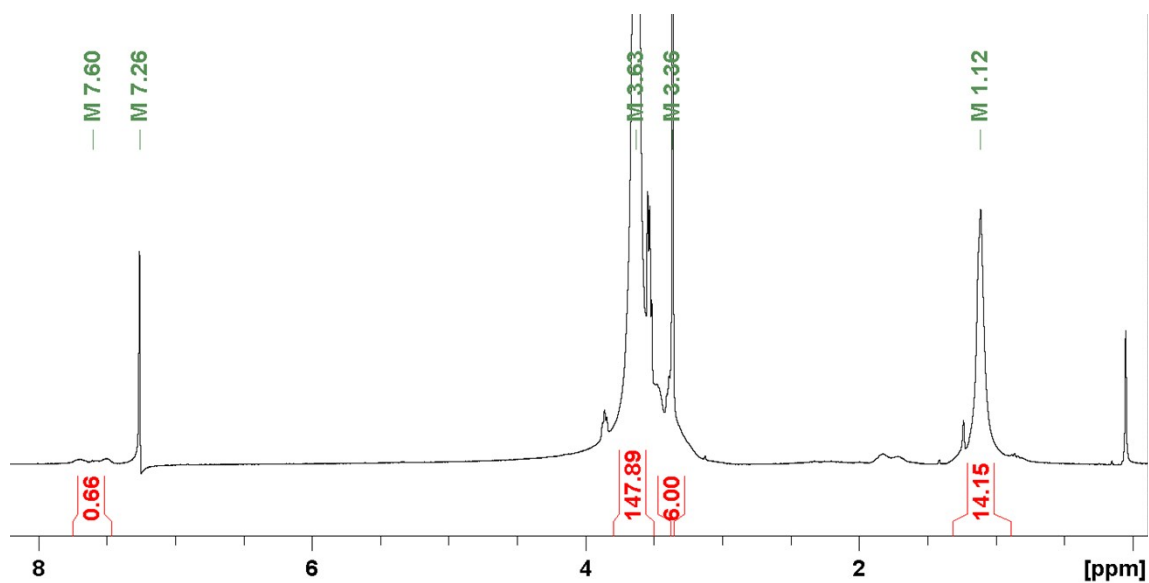


Figure SI-24 Partial  $^1\text{H}$  NMR (300 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of polymer P6.

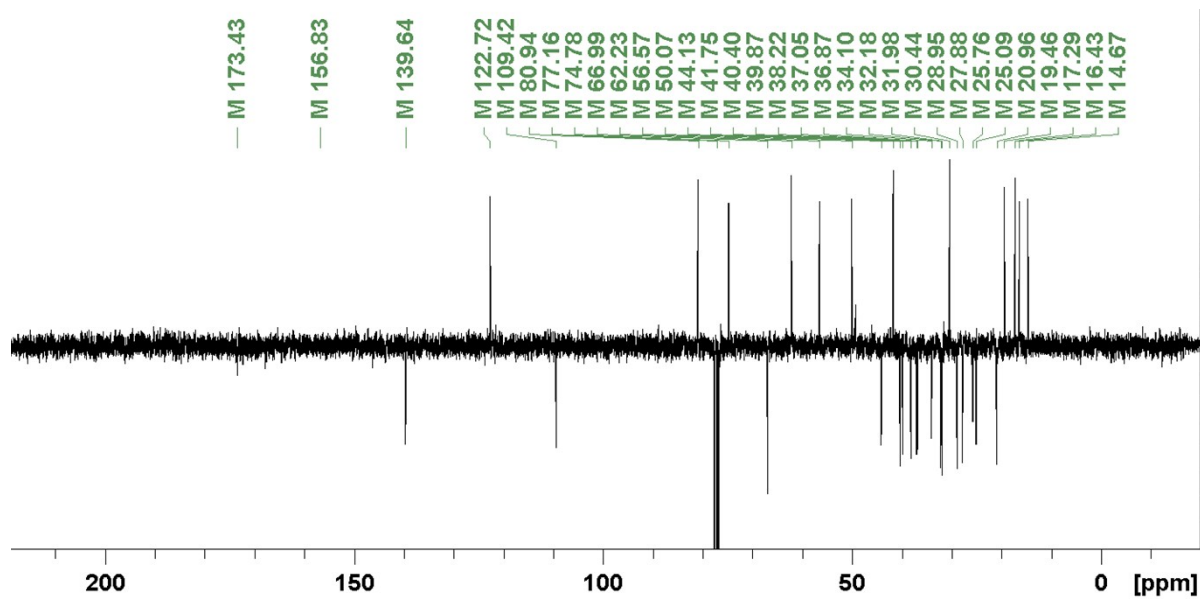


Figure SI-25 Partial APT  $^{13}\text{C}$  NMR (75 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of diosgenin-glycine- $\text{NH}_2$  (**1**).

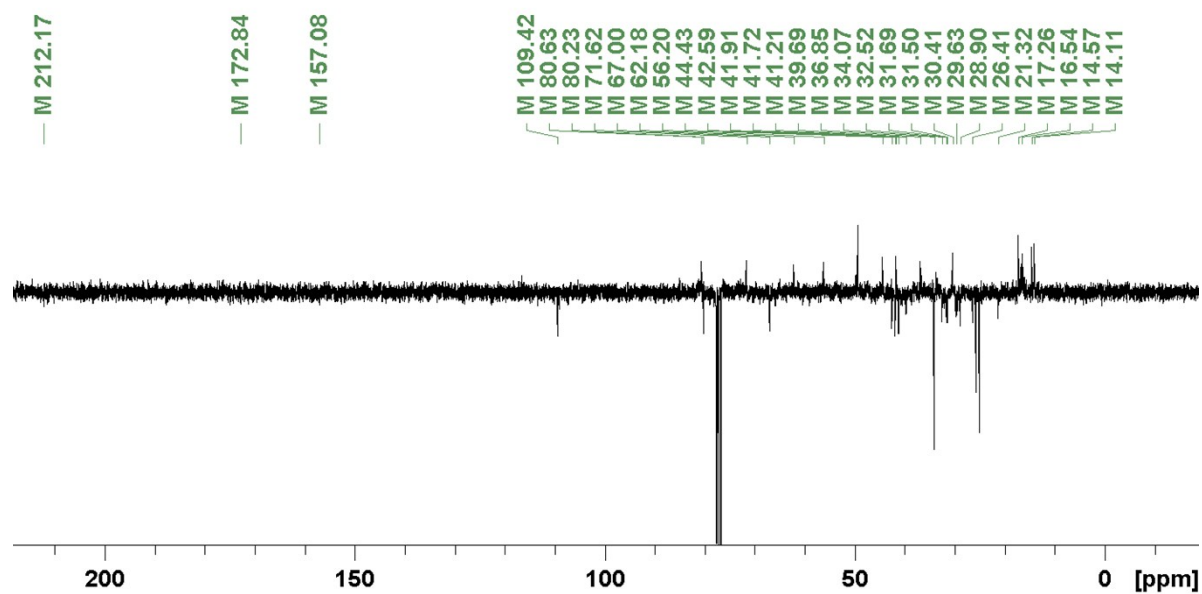


Figure SI-26 Partial APT  $^{13}\text{C}$  NMR (75 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of DI31-glycine- $\text{NH}_2$  (**2**).

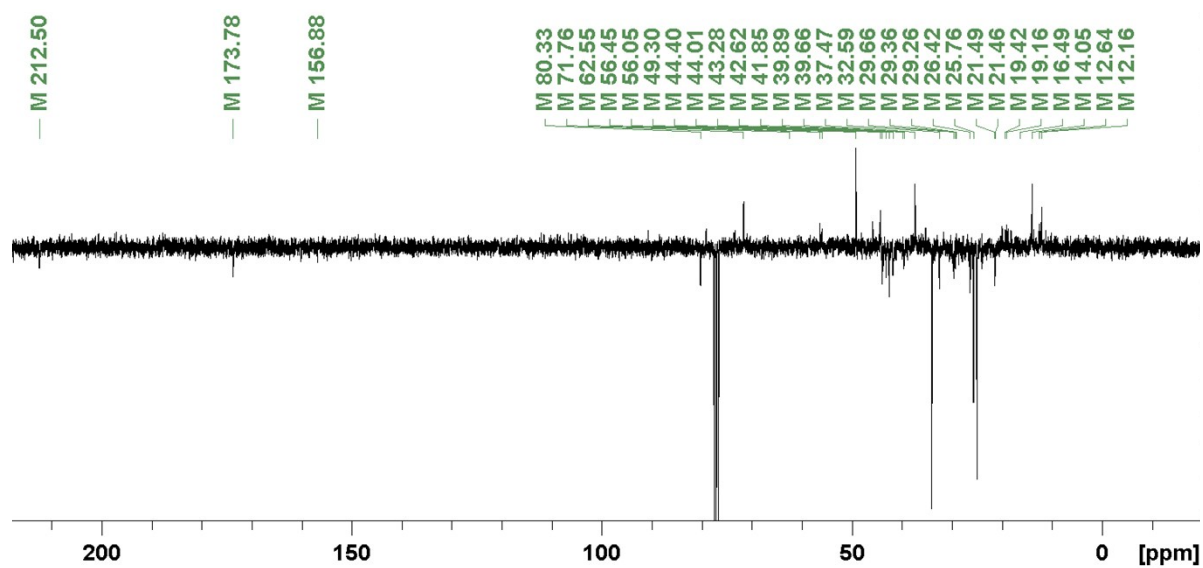


Figure SI-27 Partial APT  $^{13}\text{C}$  NMR (75 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of S7-glycine- $\text{NH}_2$  (**3**).

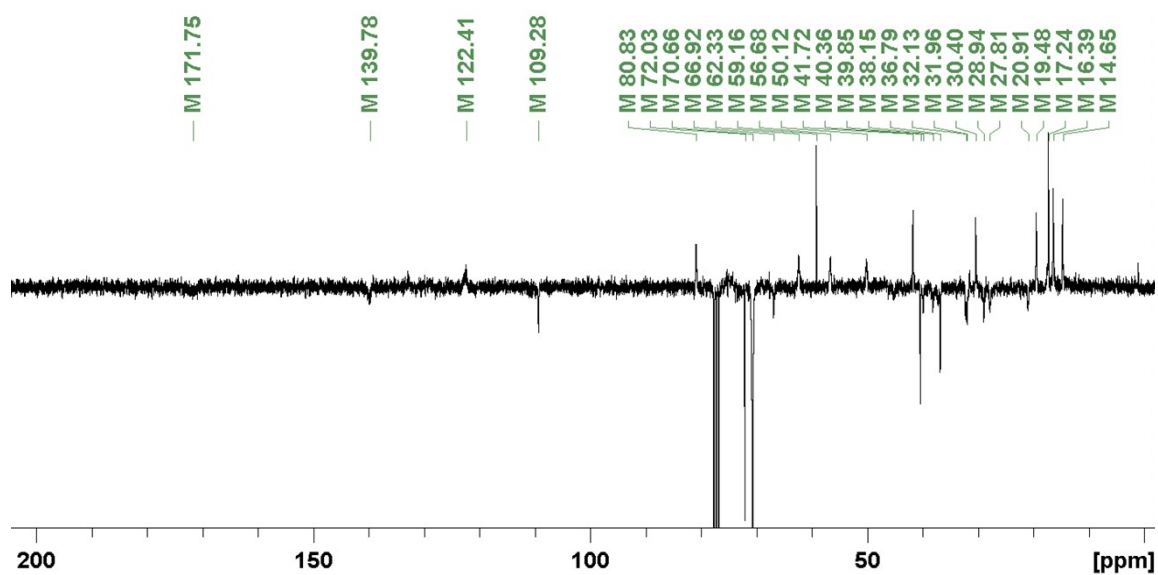
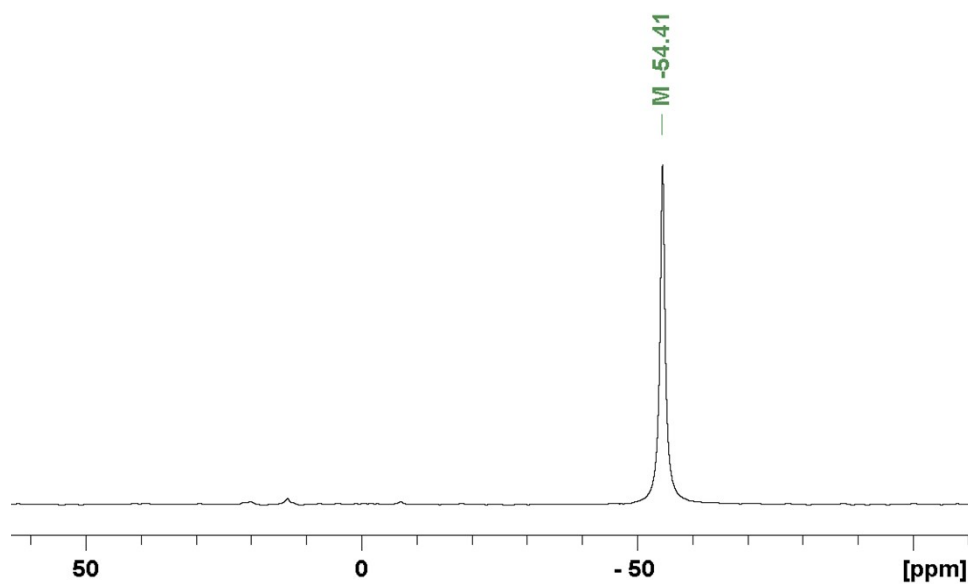
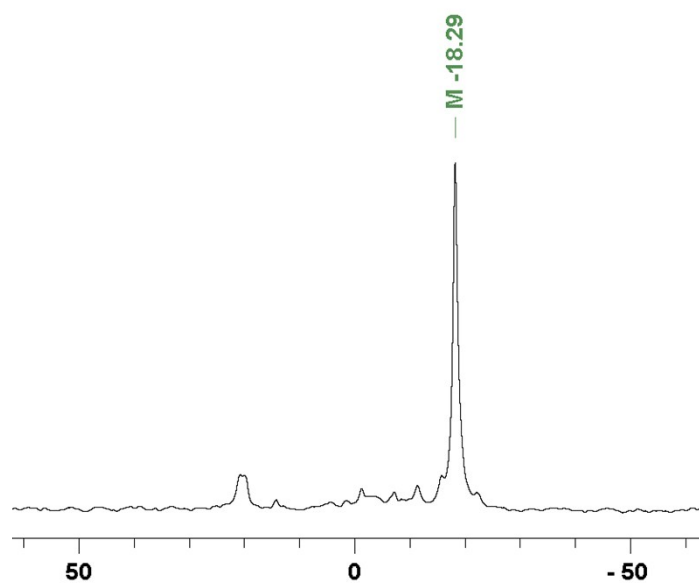


Figure SI-28 Partial APT  $^{13}\text{C}$  NMR (75 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of polymer **P1**.

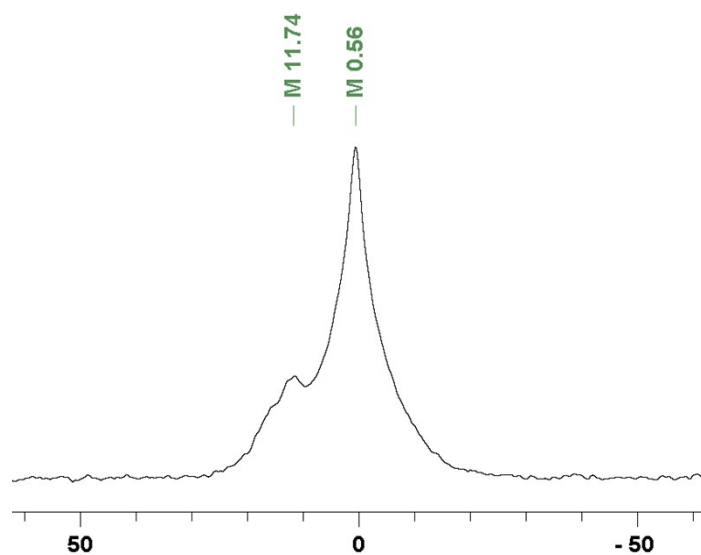




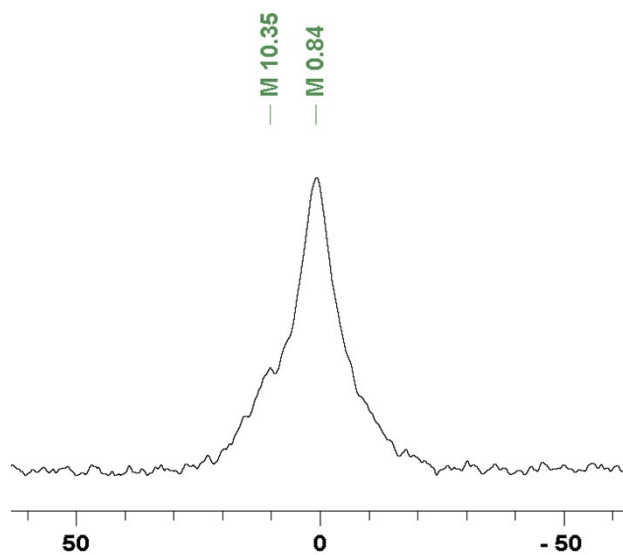
**Figure SI-29** Partial  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of monomer trichlorophosphoranimine ( $\text{Cl}_3\text{P}=\text{N}-\text{Si}(\text{CH}_3)_3$ ).



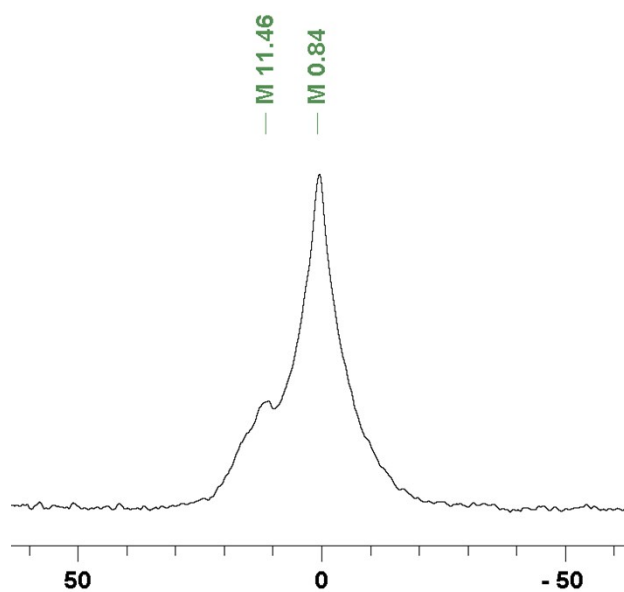
**Figure SI-30** Partial  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of polydichlorophosphazene.



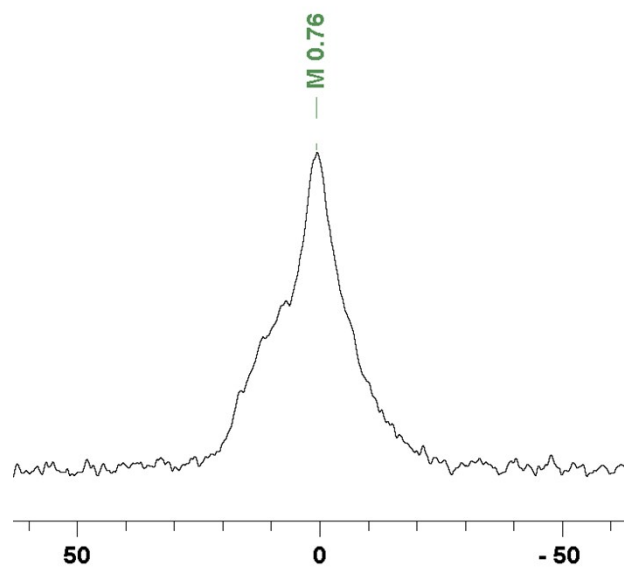
**Figure SI-31** Partial  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of polymer P1.



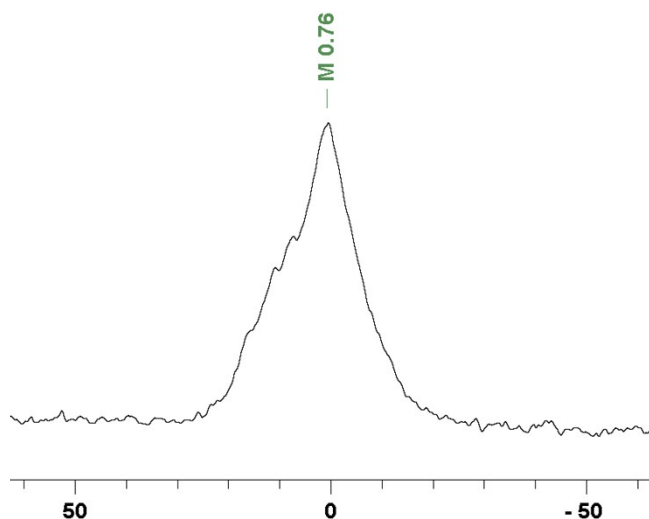
**Figure SI-32** Partial  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of polymer P2.



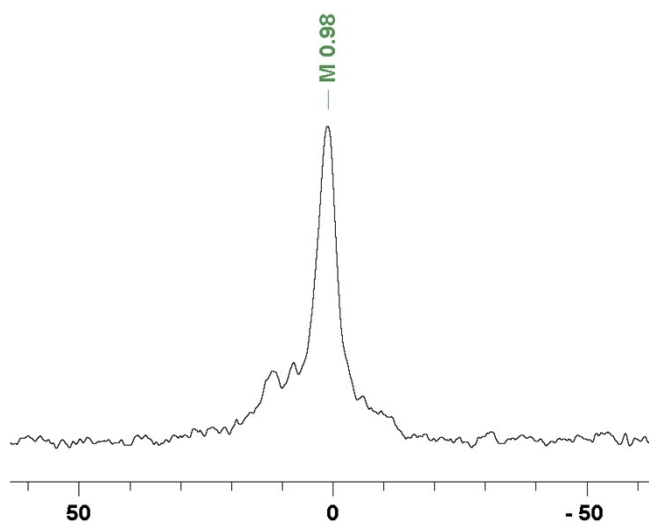
**Figure SI-33** Partial  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of polymer **P3**.



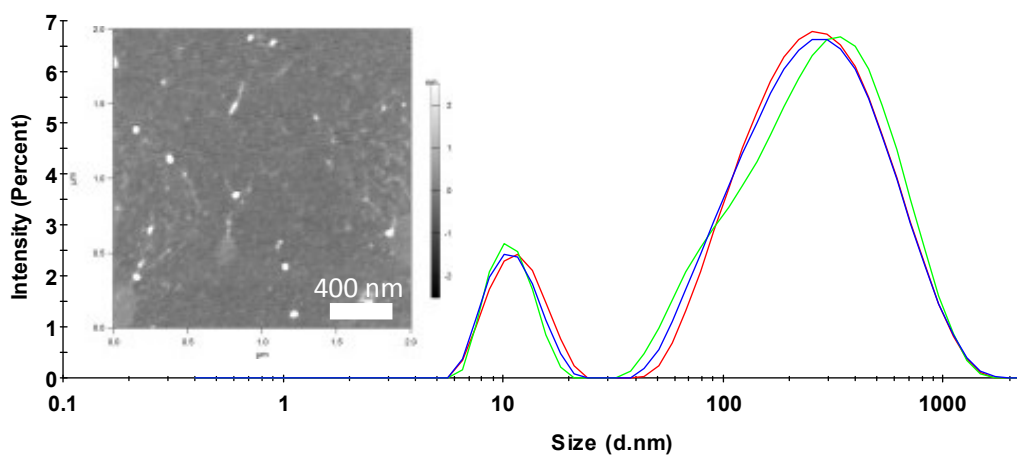
**Figure SI-34** Partial  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of polymer **P4**.



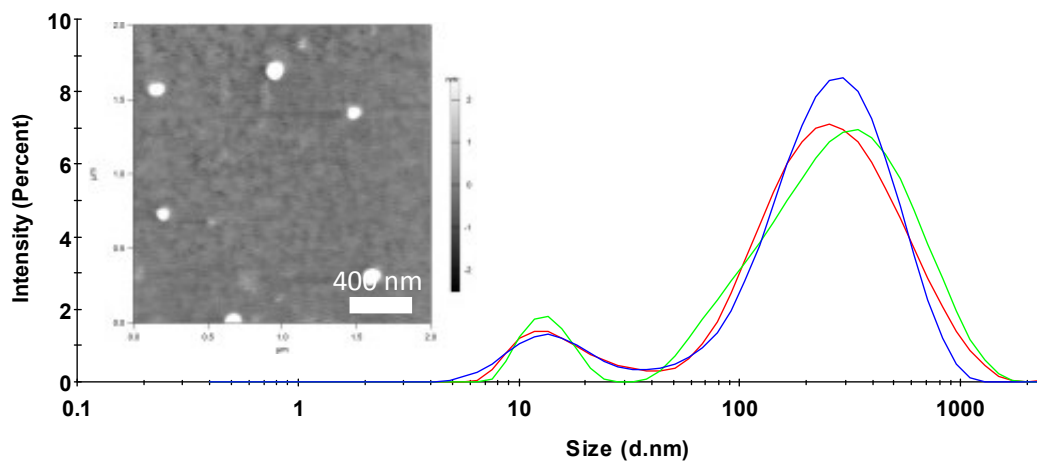
**Figure SI-35** Partial  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of polymer **P5**.



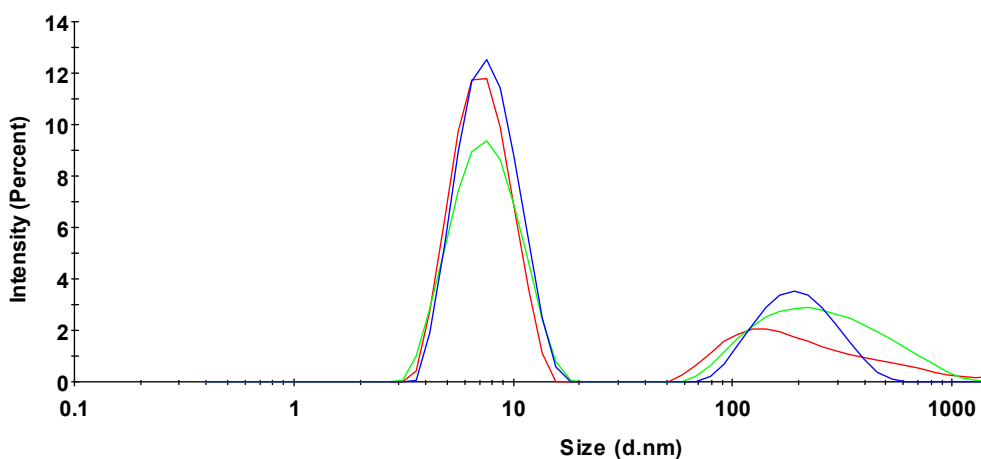
**Figure SI-36** Partial  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of polymer **P6**.



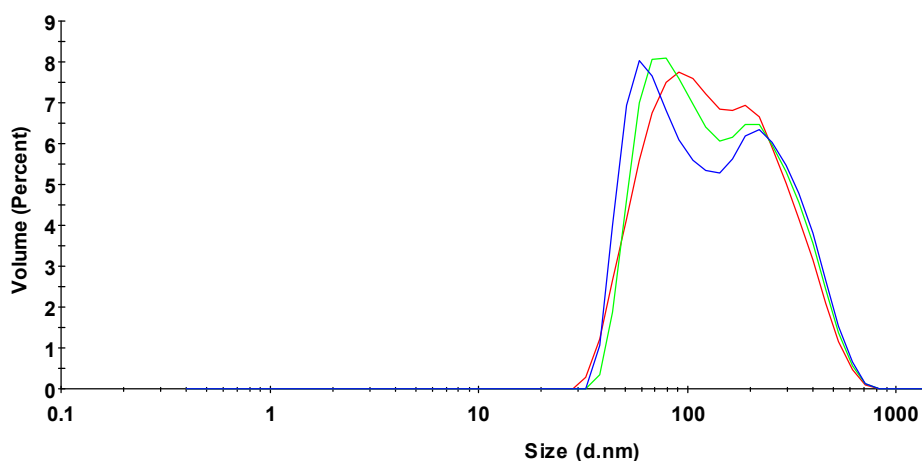
**Figure SI-37** Dynamic light scattering, size distribution by intensity of polymer **P4**. Insert: AFM image of **P4**, scale bar = 400 nm.



**Figure SI-38** Dynamic light scattering, size distribution by intensity of polymer **P5**. Insert: AFM image of **P5**, scale bar = 400 nm.



**Figure SI-39** Dynamic light scattering, size distribution by intensity of polymer **P6**.



**Figure SI-40** Dynamic light scattering, size distribution by volume of polymer **P1**.

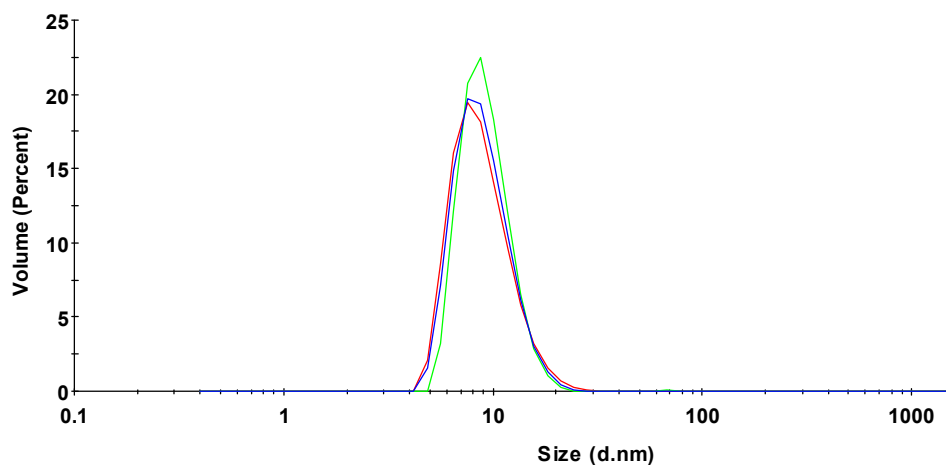


Figure SI-41 Dynamic light scattering, size distribution by volume of polymer **P2**.

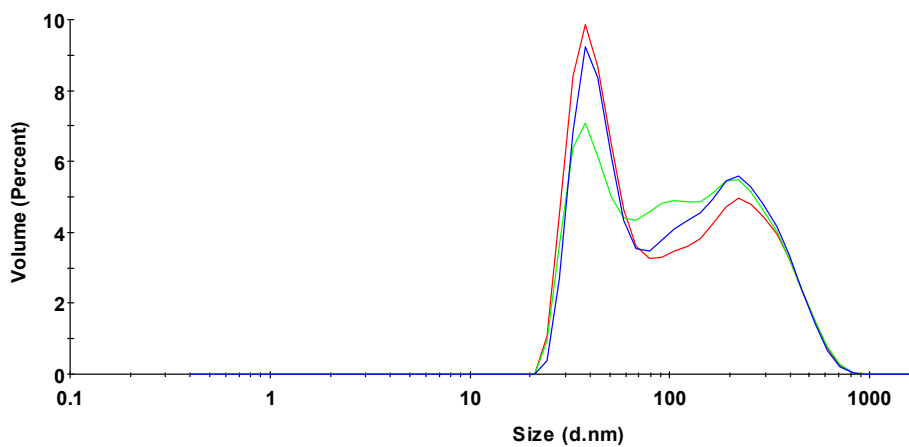


Figure SI-42 Dynamic light scattering, size distribution by volume of polymer **P3**.

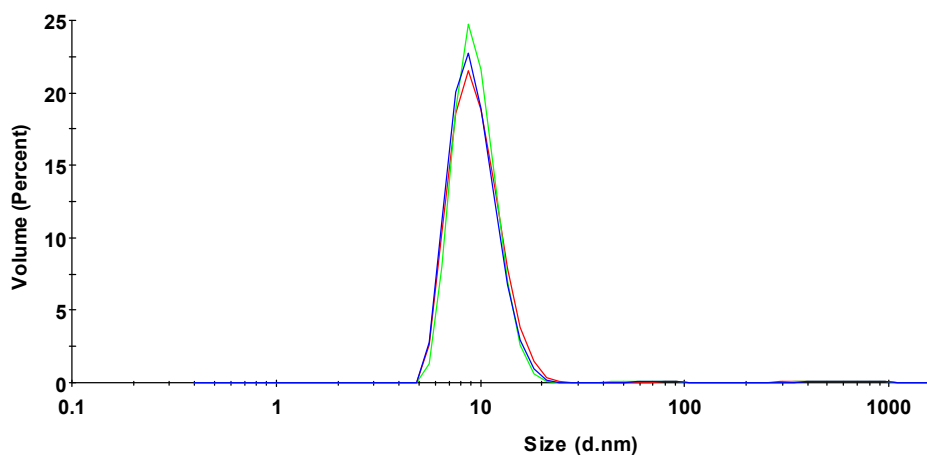


Figure SI-43 Dynamic light scattering, size distribution by volume of polymer **P4**.

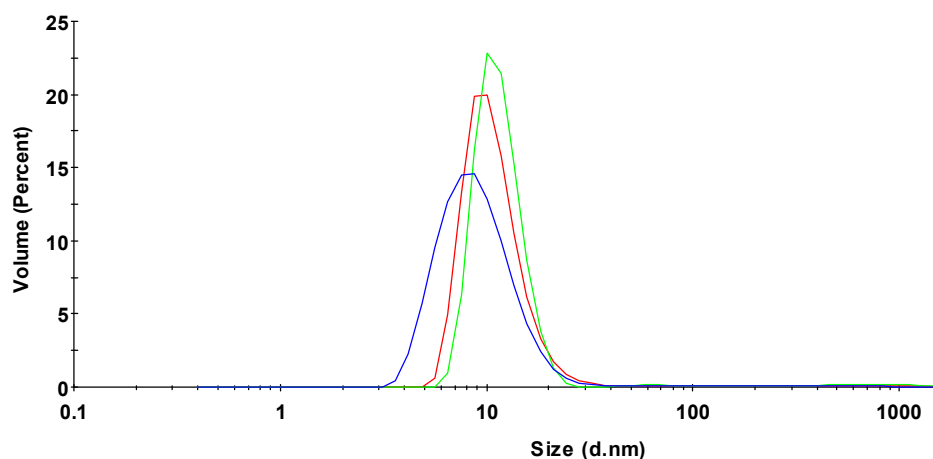


Figure SI-44 Dynamic light scattering, size distribution by volume of polymer P5.

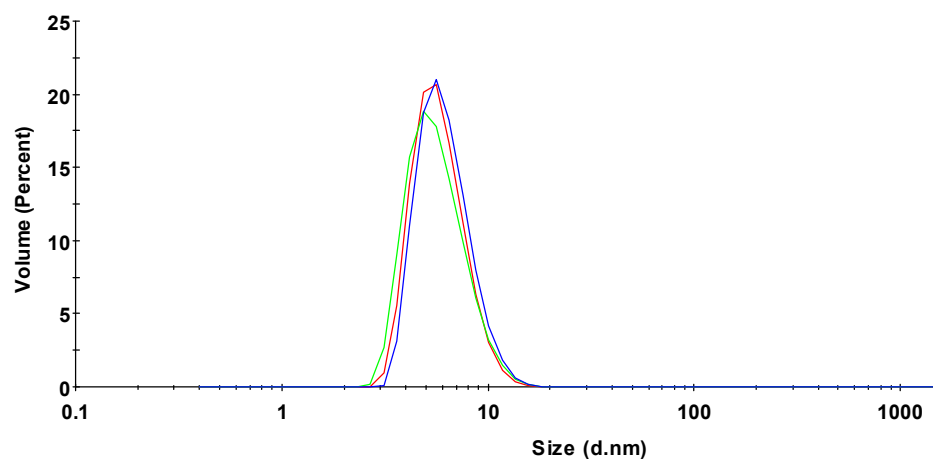


Figure SI-45 Dynamic light scattering, size distribution by volume of polymer P6.

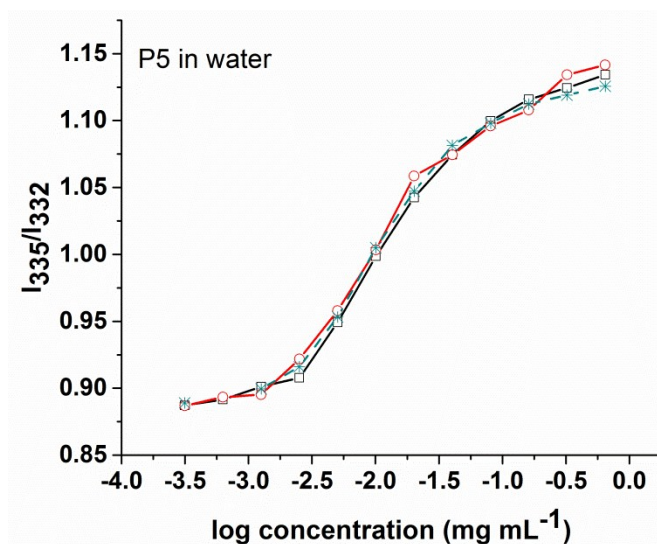


Figure SI-46 Plots of the fluorescence intensity ratio  $I_{335}/I_{332}$  from pyrene excitation spectra as a function of the P5 concentration in water at 25 °C.

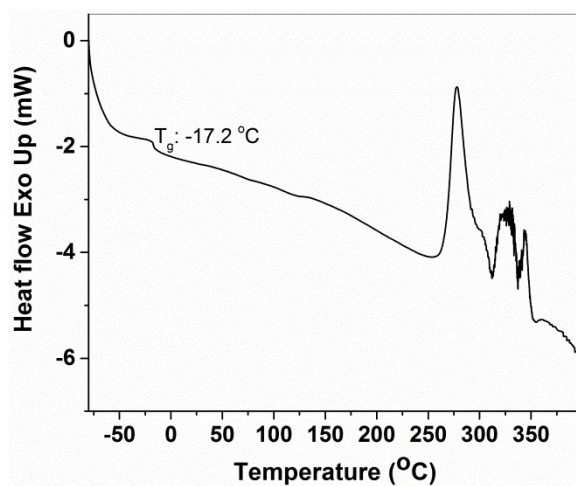


Figure SI-47 Calorimetry differential scanning curve of polymer P1.

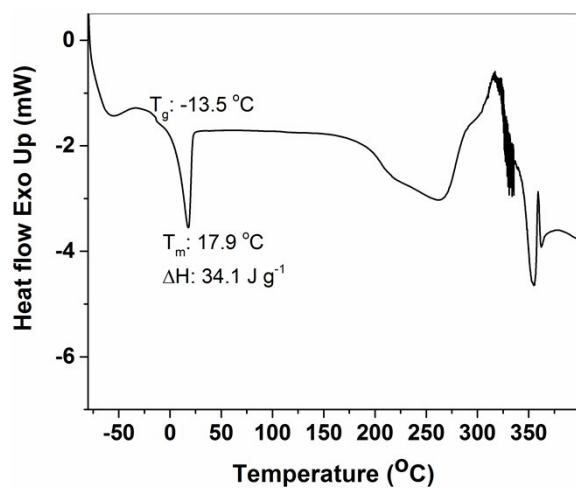


Figure SI-48 Calorimetry differential scanning curve of polymer P2.

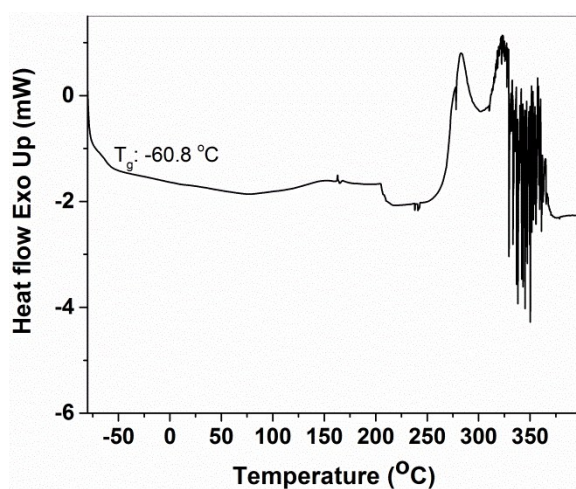


Figure SI-49 Calorimetry differential scanning curve of polymer P3.



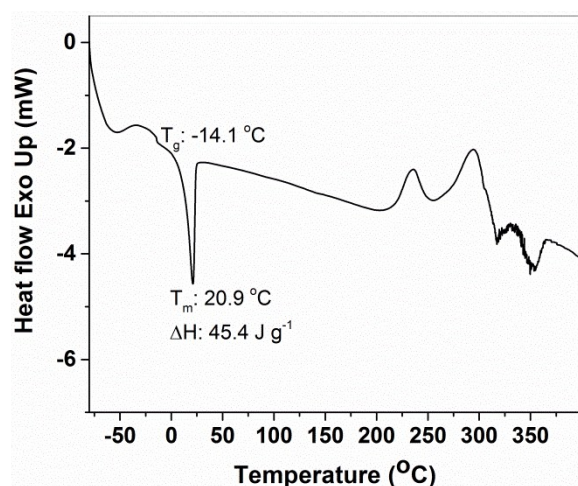


Figure SI-50 Calorimetry differential scanning curve of polymer P4.

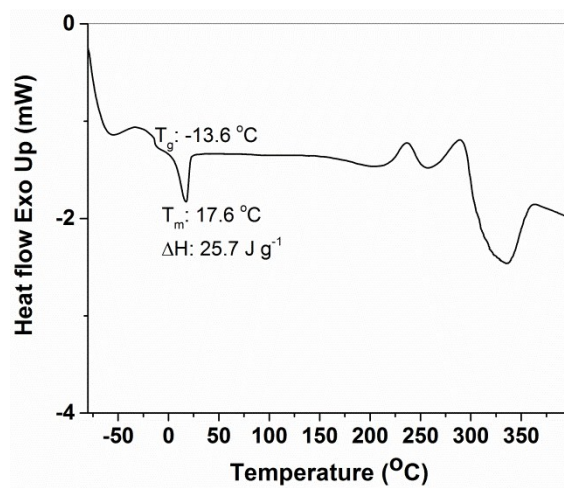


Figure SI-51 Calorimetry differential scanning curve of polymer P5.

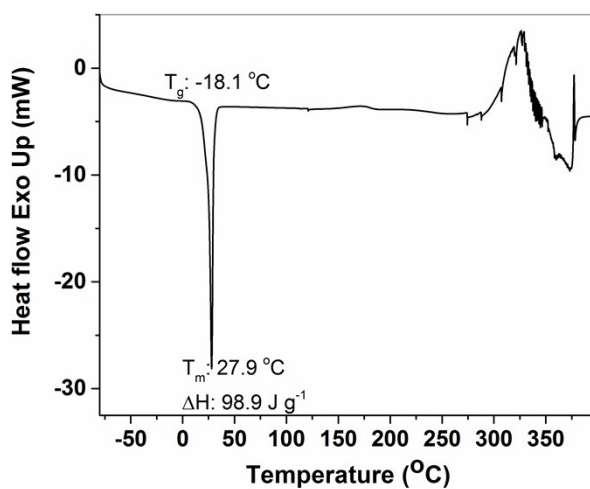
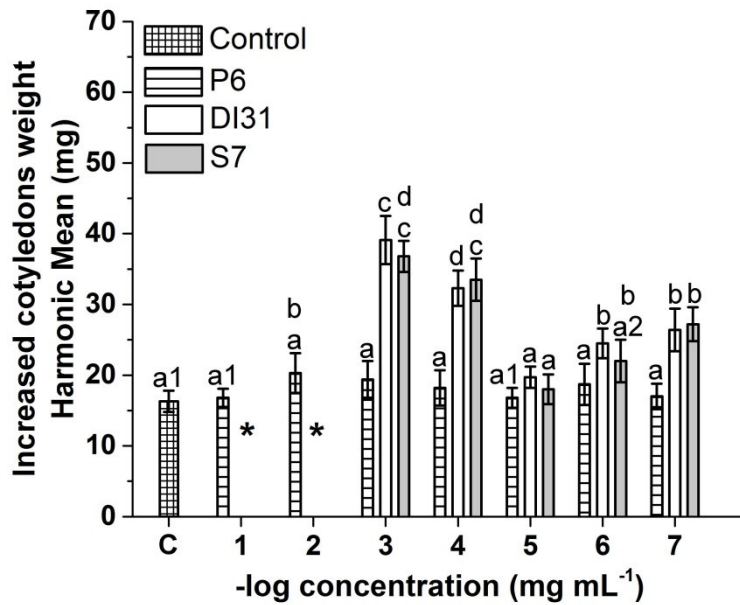
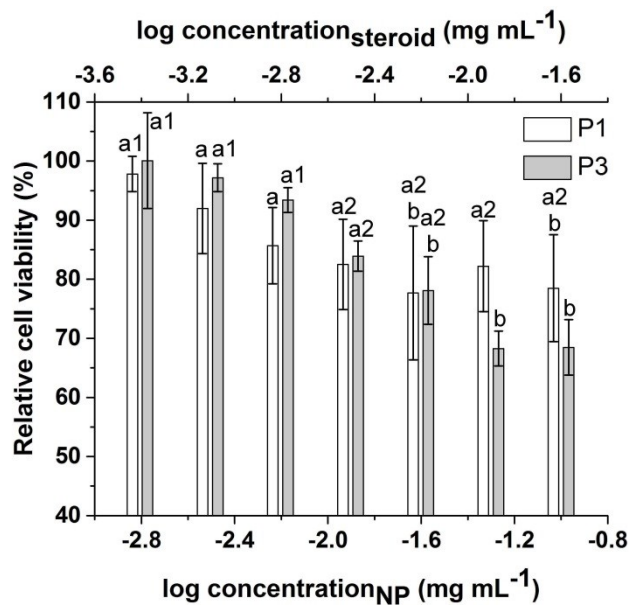


Figure SI-52 Calorimetry differential scanning curve of polymer P6.



**Figure SI-53** *In vitro* agrochemical activity expressed in terms of increased weight of 10 radish cotyledons as a function of concentration of applied polymer **P6**, parent **DI31** and **S7**, C refers to control (radish cotyledons treated with water). \* Data not shown because radish cotyledons died as result of high ethanol content in **DI31** and **S7** solutions at  $10^{-1}$  and  $10^{-2}$  mg mL<sup>-1</sup>.



**Figure SI-54** Relative cell viability of MCF-7 breast cancer cells treated with polymers **P1**, **P3**.

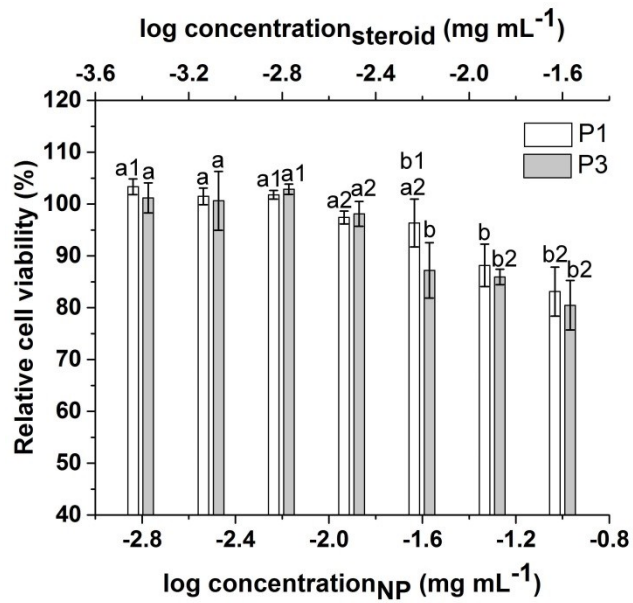


Figure SI-55 Relative cell viability of primary HLF treated with polymers P1, P3.

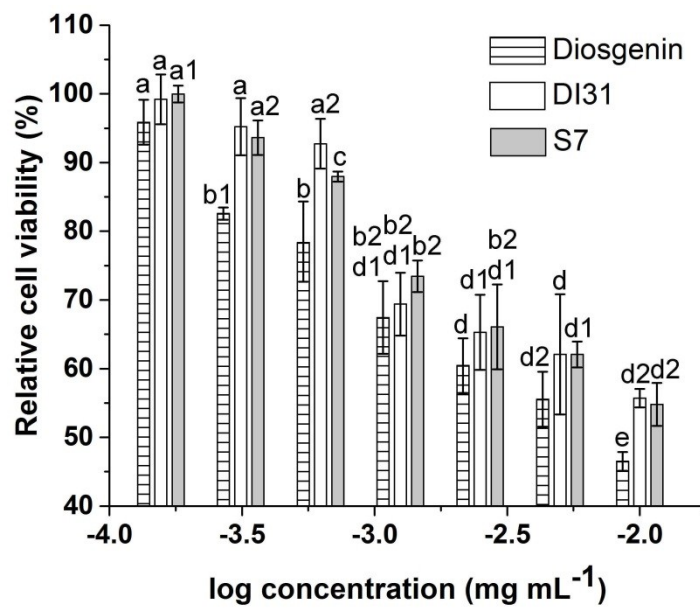


Figure SI-56 Relative cell viability of MCF-7 breast cancer cells treated with parent steroids.

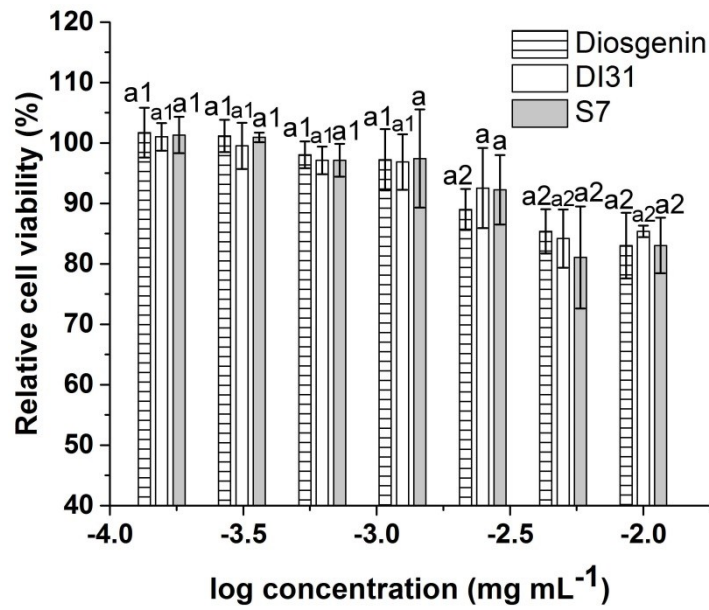


Figure SI-57 Relative cell viability of non-cancer HLF cells treated with parent steroids.

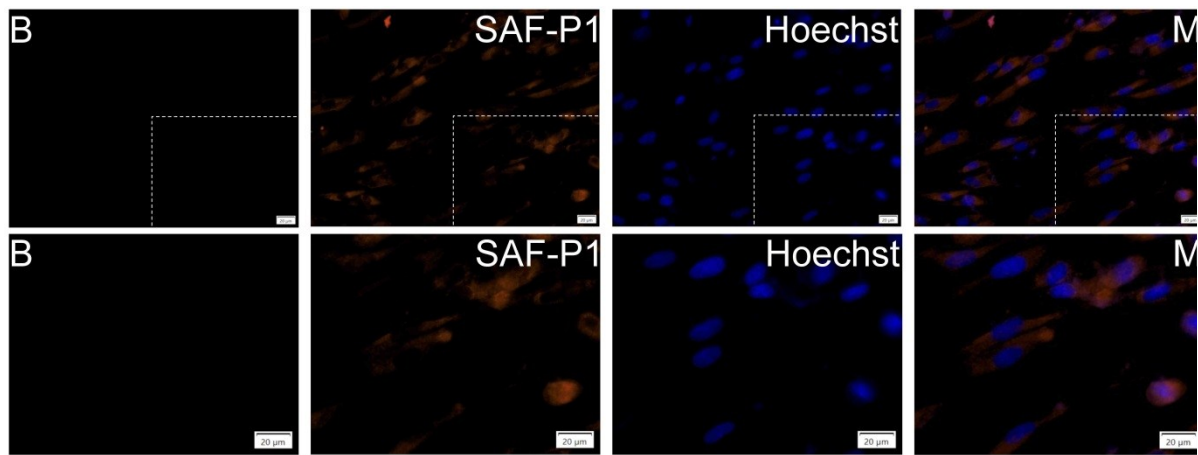


Figure SI-58 Primary HLF cells with 0.1 mg mL<sup>-1</sup> SAF-P1 aggregates, 1 µg mL<sup>-1</sup> of Hoechst 33342 and merged pictures (M), scale bars represents 20 µm.

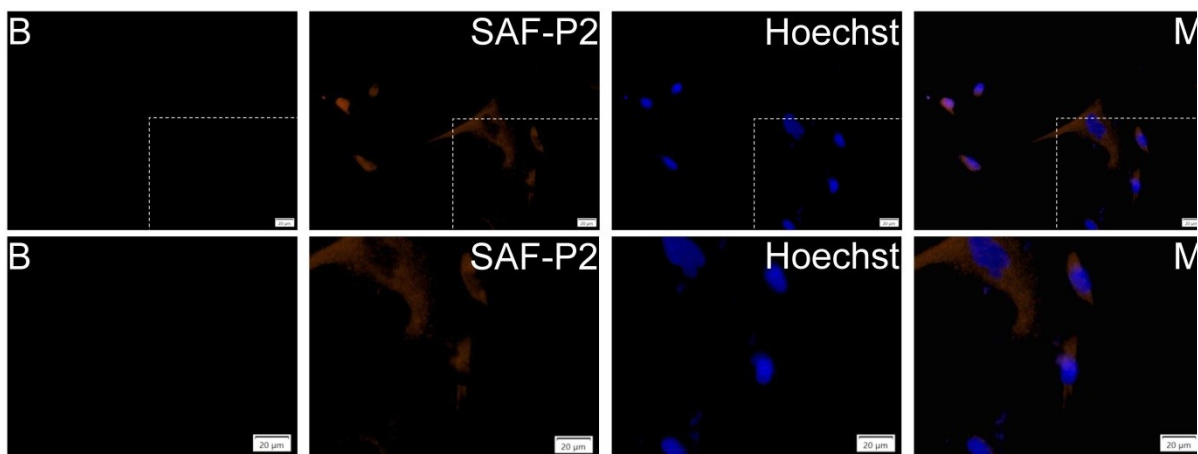
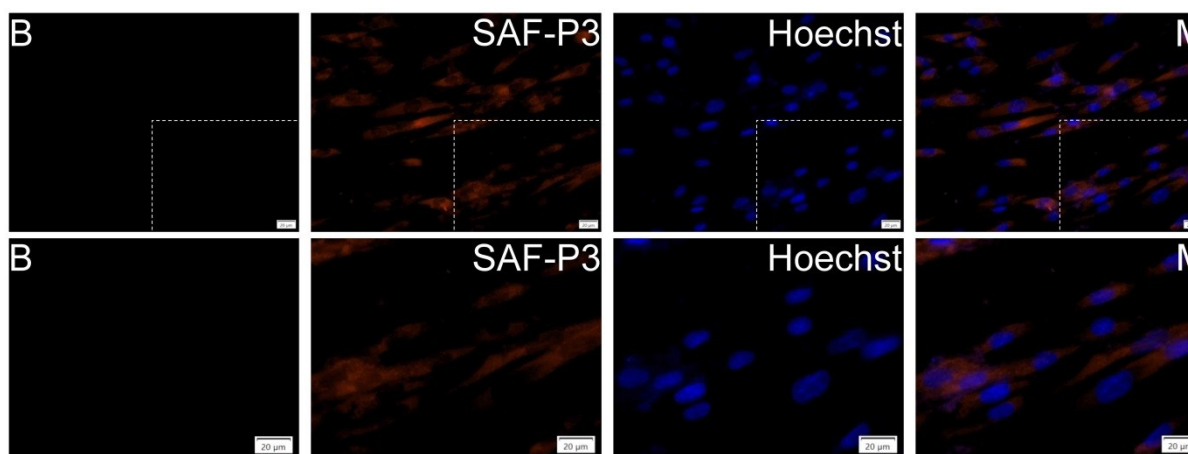
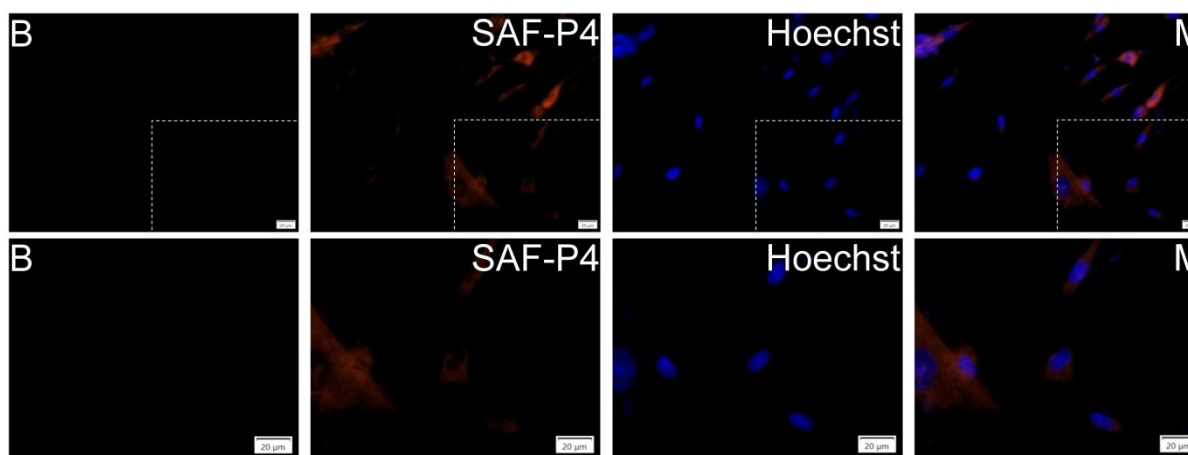


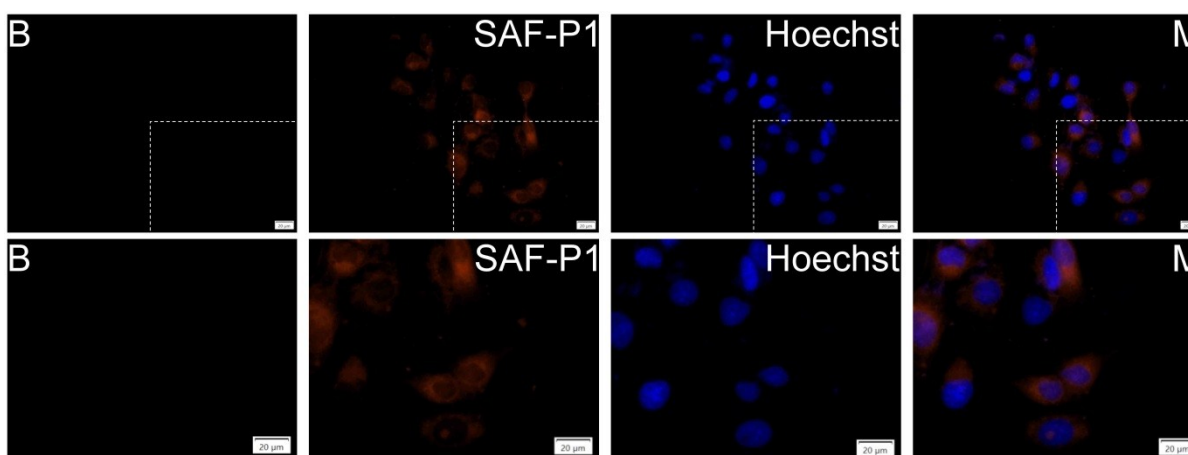
Figure SI-59 Primary HLF cells with 0.1 mg mL<sup>-1</sup> SAF-P2 aggregates, 1 µg mL<sup>-1</sup> of Hoechst 33342 and merged pictures (M), scale bars represents 20 µm.



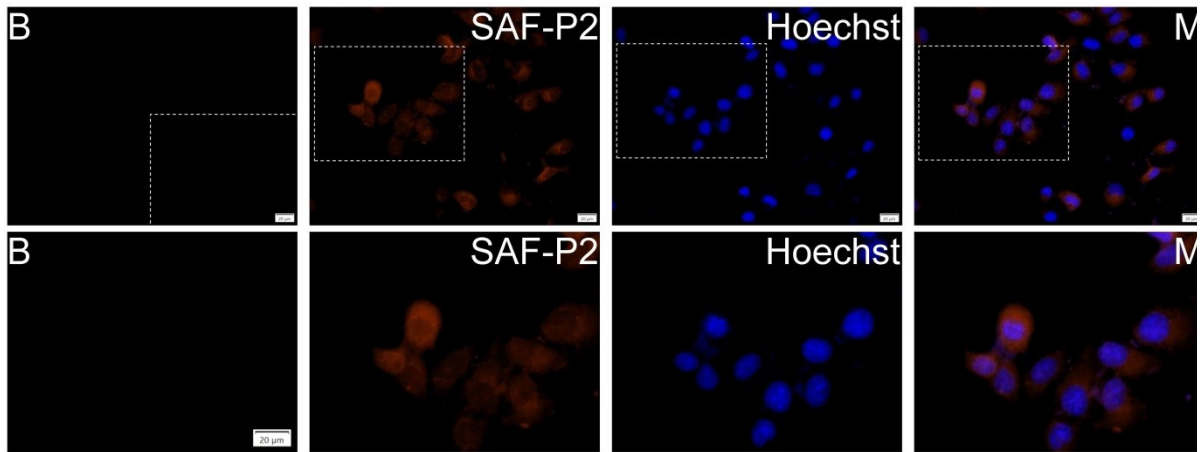
**Figure SI-60** Primary HLF cells with  $0.1 \text{ mg mL}^{-1}$  SAF-P3 aggregates,  $1 \text{ } \mu\text{g mL}^{-1}$  of Hoechst 33342 and merged pictures (M), scale bars represents  $20 \text{ } \mu\text{m}$ .



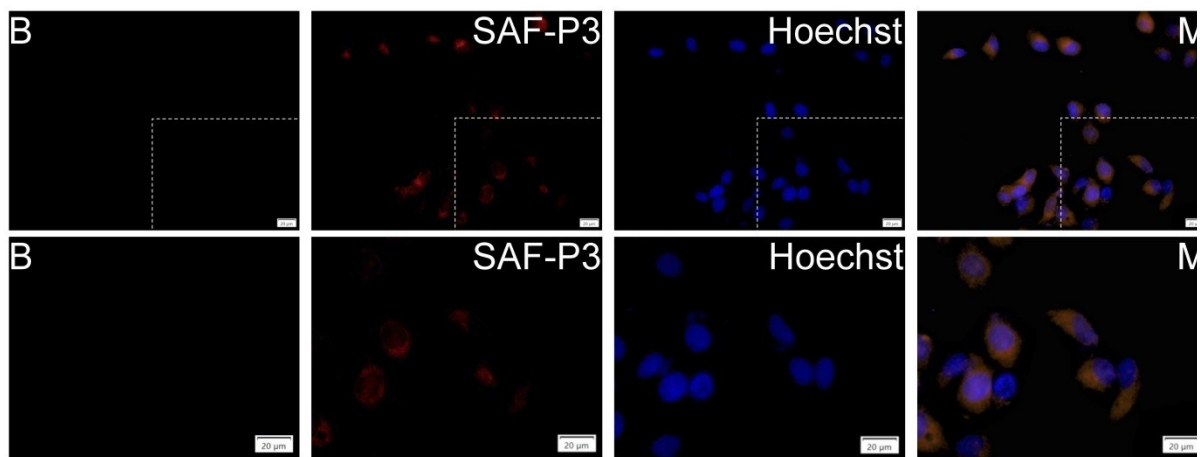
**Figure SI-61** Primary HLF cells with  $0.1 \text{ mg mL}^{-1}$  SAF-P4 aggregates,  $1 \text{ } \mu\text{g mL}^{-1}$  of Hoechst 33342 and merged pictures (M), scale bars represents  $20 \text{ } \mu\text{m}$ .



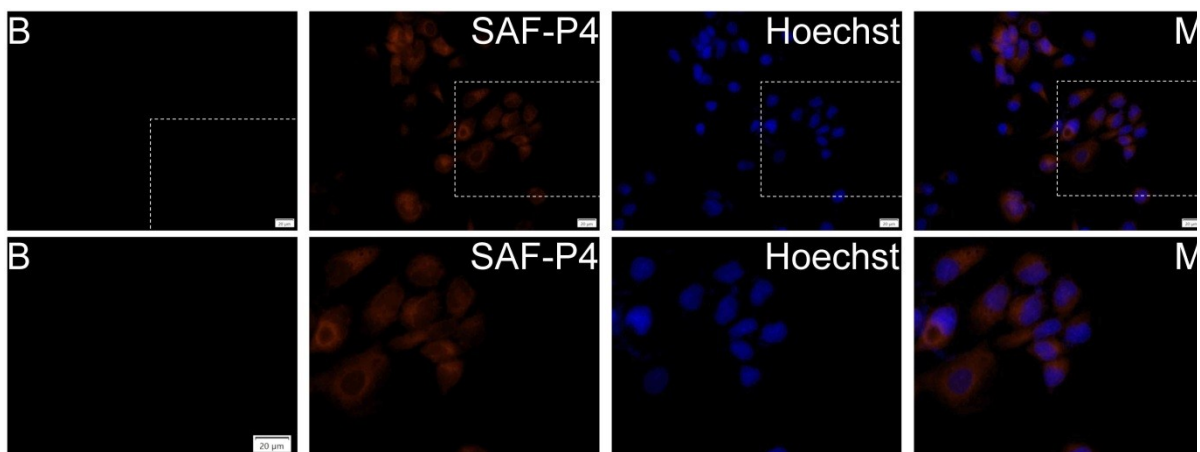
**Figure SI-62** MCF-7 cancer cells with  $0.1 \text{ mg mL}^{-1}$  SAF-P1 aggregates,  $1 \text{ } \mu\text{g mL}^{-1}$  of Hoechst 33342 and merged pictures (M), scale bars represents  $20 \text{ } \mu\text{m}$ .



**Figure SI-63** MCF-7 cancer cells with 0.1 mg mL<sup>-1</sup> SAF-P2 aggregates, 1 µg mL<sup>-1</sup> of Hoechst 33342 and merged pictures (M), scale bars represents 20 µm.



**Figure SI-64** MCF-7 cancer cells with 0.1 mg mL<sup>-1</sup> SAF-P3 aggregates, 1 µg mL<sup>-1</sup> of Hoechst 33342 and merged pictures (M), scale bars represents 20 µm.



**Figure SI-65** MCF-7 cancer cells with 0.1 mg mL<sup>-1</sup> SAF-P4 aggregates, 1 µg mL<sup>-1</sup> of Hoechst 33342 and merged pictures (M), scale bars represents 20 µm.