Supplementary Information

Organogelators derived from the bisphenol A scaffold

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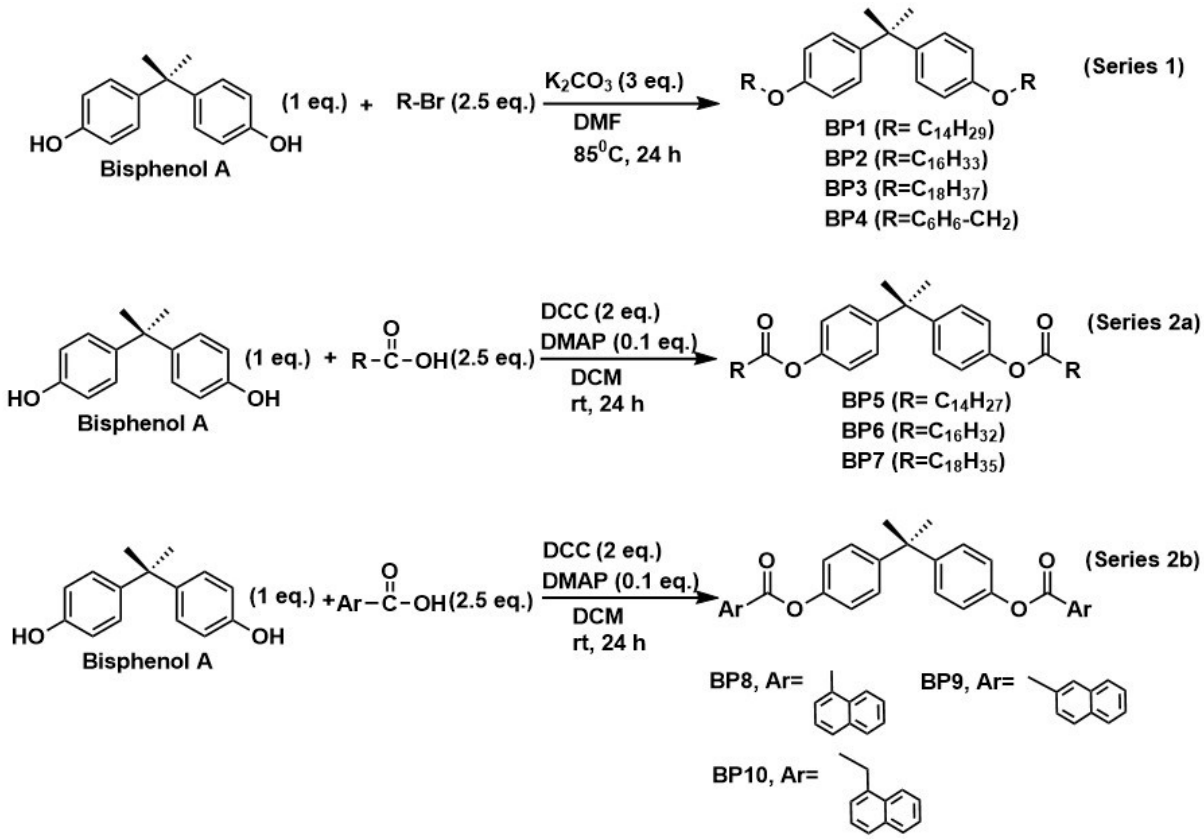


Scheme S1. Synthesis of **BP1**–**BP10**.

1.1. General synthetic procedure for compounds BP1–BP4:

As a representative example, the detailed synthetic procedure for **BP1** is described here. The remaining compounds (**BP2**–**BP4**) were synthesized using a similar procedure. In a 100 mL two-necked round bottom flask, bisphenol A (1 g, 4.38 mmol) and anhydrous potassium carbonate (K_2CO_3) (1.74 g, 12.60 mmol) were taken together and dissolved in 10 mL of dry DMF under a nitrogen atmosphere. The resulting solution was heated at 85 ^{0}C with stirring for 1 hour. Next, 1-bromotetradecane (1.46g, 10.50 mmol) was added dropwise to the stirred solution. The reaction was continued for a further 24 h at 85 ^{0}C. After that, the reaction mixture was cooled down to room temperature. 30 mL of DCM was added to the reaction mixture, and the organic solution was washed three times with water (3 x 20 mL). The organic layer was further washed twice with an aqueous 0.5N HCl solution (2 x 20 mL). Finally, it was washed three times with water (3 x 20 mL). The organic extract was dried over anhydrous sodium sulfate and concentrated by rotary evaporation. The crude product was purified by column chromatography over silica gel 60–120 mesh using petroleum ether:ethyl

acetate (95:5) as the eluent to provide compound **BP1** {*4,4′-(propane-2,2-diyl)bis((tetradecyloxy)benzene)*} as a white solid (1g, 37 %). M.p.: 46–48 ^{0}C. ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.12 (4 H, d, *J* 8.8), 6.78 (4 H, d, *J* 8.8), 3.91 (4 H, t, *J* 6.6), 1.81 – 1.70 (4 H, m), 1.63 (6 H, s), 1.43 (4 H, td, *J* 9.3, 4.6), 1.26 (40 H, s), 0.88 (6 H, t, *J* 6.7). ^{13}C-NMR (101 MHz, $CDCl_3$, δ ppm): 157.03, 143.03, 127.77, 113.85, 67.97, 41.72, 32.04, 31.18, 29.78, 29.70, 29.53, 29.47, 26.20, 22.81, 14.24. Elemental analysis: calculated for $C_{43}H_{72}O_2$: C, 83.2; H, 11.7; Found: C, 82.8; H, 12.3. TOF MS (ES^+) *m/z*: Calc. for $C_{43}H_{72}O_2$ $[M+ACN+H]^+$ 663.07; found 663.40.

4,4′-(propane-2,2-diyl)bis((hexadecyloxy)benzene) (**BP2**). White solid (1.01 g, 34 %). M.p.: 55–57 ^{0}C. ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.12 (4 H, d, *J* 8.8), 6.78 (4 H, d, *J* 8.8), 3.91 (4 H, t, *J* 6.6), 1.81 – 1.70 (4 H, m), 1.63 (6 H, s), 1.49 – 1.38 (4 H, m), 1.26 (48 H, s), 0.88 (6 H, t, *J* 6.7). ^{13}C-NMR (101 MHz, $CDCl_3$, δ ppm): 156.93, 142.94, 127.67, 113.76, 67.89, 41.63, 31.94, 31.08, 29.71, 29.69, 29.67, 29.61, 29.43, 29.37, 26.10, 22.71, 14.14. TOF MS (ES^+) *m/z*: Calc. for $C_{47}H_{80}O_2$ $[M+2Na-H]^+$ 722.12; found 722.50.

4,4′-(propane-2,2-diyl)bis((octadecyloxy)benzene) (**BP3**). White solid (960 mg, 30 %). M.p.: 52–55 ^{0}C. ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.11 (4 H, d, *J* 8.8), 6.78 (4 H, d, *J* 8.8), 3.91 (4 H, t, *J* 6.5), 1.78 – 1.70 (4 H, m), 1.62 (6 H, s), 1.42 (4 H, q, *J* 7.4), 1.25 (56 H, s), 0.87 (6 H, t, *J* 6.7). ^{13}C-NMR (101 MHz, $CDCl_3$, δ ppm): 156.95, 142.93, 127.66, 113.77, 67.88, 41.63, 31.95, 31.08, 29.72, 29.70, 29.68, 29.65, 29.63, 29.61, 29.57, 29.54, 29.52, 29.44, 29.39, 29.21, 28.52, 26.11, 25.84, 22.71, 14.14.

4,4′-(propane-2,2-diyl)bis((benzyloxy)benzene) (**BP4**). White solid (680 mg, 37 %). M.p.: 105–107 ^{0}C. ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.46 – 7.27 (8 H, m), 7.18 – 7.11 (6 H, m), 6.91 – 6.84 (4 H, m), 5.03 (4 H, s), 1.64 (6 H, s). ^{13}C-NMR (101 MHz, $CDCl_3$, δ ppm): 156.19, 142.89, 136.72, 128.10, 127.45, 127.29, 127.07, 113.66, 69.50, 41.24, 30.59. TOF MS (ES^+) *m/z*: Calc. for $C_{29}H_{28}O_2$ $[M+NH_4]^+$ 426.57; found 426.24.

1.2. General synthetic procedure for compounds BP5–BP10:

As a representative example, the detailed synthetic procedure for **BP5** is described here. The remaining compounds (**BP6**–**BP10**) were synthesized using a similar procedure. In a 100 mL two-necked round bottom flask, myristic acid (2.5 g, 10.95 mmol), *N*,*N*′-dicyclohexylcarbodiimide (DCC) (1.77 g, 8.6 mmol), and 4-dimethylaminopyridine (DMAP) (52.53 mg, 0.43 mmol) were dissolved in 10 mL of dry DCM at room temperature under a

nitrogen atmosphere. It was stirred for one hour to dissolve all the reactants completely. To this mixture, bisphenol A (1 g, 4.38 mmol) dissolved in 1 mL of THF was added dropwise, and stirring was continued for 24 h at room temperature. 40 mL of DCM was added to the final reaction mixture and filtered through a filter paper to collect the filtrate. This filtrate was washed three times (3 x 20mL) with water and dried over anhydrous sodium sulfate, and concentrated by rotary evaporation. The crude product was purified by column chromatography over silica gel 60–120 mesh using petroleum ether:ethyl acetate mixture (95:5) as the eluent to give compound **BP5** {*(propane-2,2-diylbis(4,1-phenylene) ditetradecanoate)*} as a white solid (1.05 g, 38 %). M.p.: 58–60 ^{0}C. ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.21 (4 H, d, *J* 8.7), 6.97 (4 H, d, *J* 8.7), 2.53 (4 H, t, *J* 7.5), 1.80 – 1.68 (4 H, m), 1.66 (6 H, s), 1.46 – 1.34 (4 H, m), 1.37 – 1.26 (36 H, m), 0.88 (6 H, t, *J* 6.7). ^{13}C-NMR (101 MHz, $CDCl_3$, δ ppm): 172.54, 148.72, 147.85, 127.89, 121.03, 42.55, 34.52, 32.02, 31.04, 29.78, 29.74, 29.69, 29.57, 29.46, 29.36, 29.20, 25.06, 22.79, 14.23. TOF MS (ES^+) *m/z*: Calc. for $C_{43}H_{68}O_4$ $[M+NH_4]^+$ 667.05; found 667.55.

(**BP6**) *propane-2,2-diylbis(4,1-phenylene) dipalmitate*. White solid (1.32 g, 47 %). M.p.: 57–59 ^{0}C. ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.21 (4 H, d, *J* 8.6), 6.97 (4 H, d), 2.53 (4 H, t, *J* 7.5), 1.80 – 1.68 (4 H, m), 1.66 (6 H, s), 1.46 – 1.34 (4 H, m), 1.28 – 1.23 (44 H, m), 0.88 (6 H, t, *J* 6.7). ^{13}C-NMR (101 MHz, $CDCl_3$, δ ppm): 172.47, 148.62, 147.76, 127.80, 120.94, 42.46, 34.43, 31.95, 30.96, 29.72, 29.70, 29.69, 29.67, 29.63, 29.49, 29.40, 29.29, 29.13, 24.98, 22.72, 14.16. TOF MS (ES^+) *m/z*: Calc. for $C_{47}H_{76}O_4$ $[M+H+Na]^{2+}$ 364.55; found 364.24.

(**BP7**) *propane-2,2-diylbis(4,1-phenylene)distearate*. White solid (1.30 g, 47 %). M.p.: 47–49 ^{0}C. ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.21 (4 H, d, *J* 8.7), 6.97 (4 H, d, *J* 8.7), 2.53 (4 H, t, *J* 7.5), 1.80 – 1.68 (4 H, m), 1.66 (6 H, s), 1.42 – 1.38 (4 H, m), 1.26 (52 H, s), 0.88 (6 H, t, *J* 6.7). ^{13}C-NMR (101 MHz, $CDCl_3$, δ ppm): 172.41, 148.64, 147.75, 127.78, 120.93, 42.46, 34.43, 31.93, 30.95, 29.71, 29.69, 29.67, 29.65, 29.61, 29.48, 29.37, 29.27, 29.12, 24.97, 22.70, 14.13.

(**BP8**) *propane-2,2-diylbis(4,1-phenylene) bis(1-naphthoate)*. White solid (800 mg, 37 %). M.p.: 140–143 ^{0}C. ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 9.04 (2 H, d, *J* 1.0), 8.47 (2 H, dd, *J* 7.3, 1.3), 8.11 (4 H, dt, *J* 8.2, 1.1), 7.96 – 7.85 (2 H, m), 7.61 (4 H, td), 7.37 (4 H, d), 7.22 (4 H, d), 1.76 (6 H, s). ^{13}C-NMR (101 MHz, $CDCl_3$, δ ppm): 165.99, 148.89, 148.11, 134.35, 133.94, 131.71,

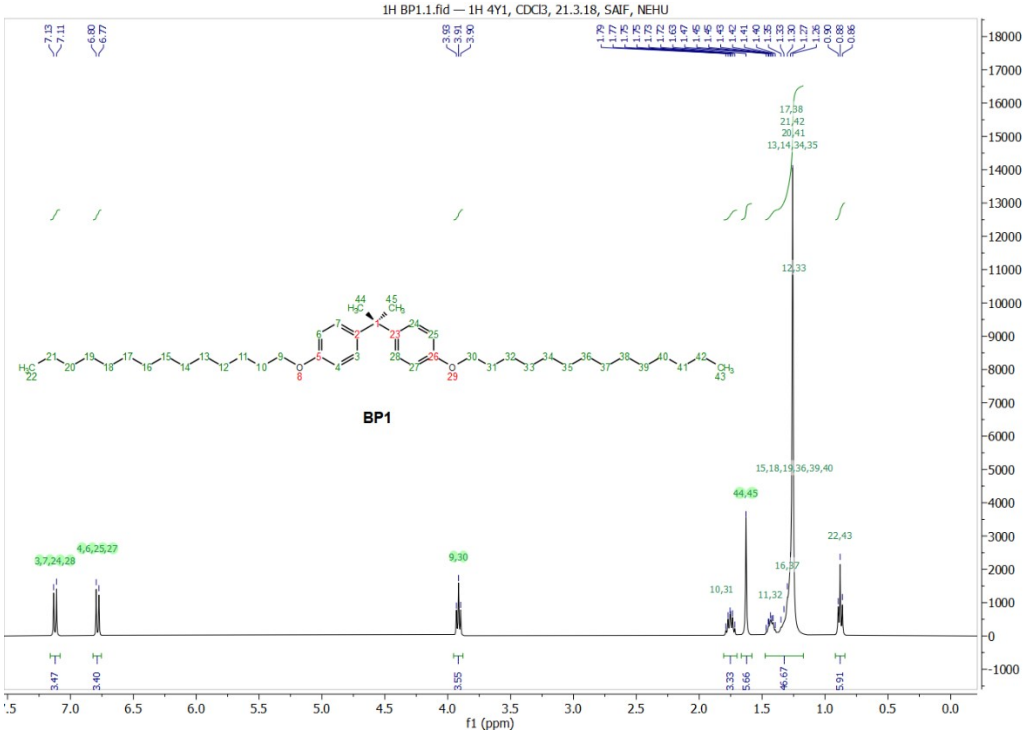
131.27, 128.73, 128.20, 128.06, 126.44, 125.93, 125.80, 124.58, 121.35, 42.66, 31.08. TOF MS (ES^+) *m/z*: Calc. for $C_{37}H_{28}O_4$ $[M+NH_4]^+$ 554.66; found 554.18.

(**BP9**) *propane-2,2-diylbis(4,1-phenylene) bis(2-naphthoate)*. White solid (566 mg, 49 %). M.p.: 153–155 ^{0}C. ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 8.81 – 8.76 (2 H, m), 8.20 (2 H, dd, *J* 8.6, 1.7), 8.04 – 7.89 (6 H, m), 7.68 – 7.54 (4 H, m), 7.38 – 7.31 (4 H, m), 7.24 – 7.16 (4 H, m), 1.75 (6 H, s). ^{13}C-NMR (101 MHz, $CDCl_3$, δ ppm): 165.47, 148.96, 148.07, 135.84, 132.51, 131.95, 129.53, 128.42, 128.03, 127.87, 126.86, 126.83, 125.51, 121.20, 42.63, 31.07. TOF MS (ES^+) *m/z*: Calc. for $C_{37}H_{28}O_4$ $[M+NH_4]^+$ 554.66; found 554.23.

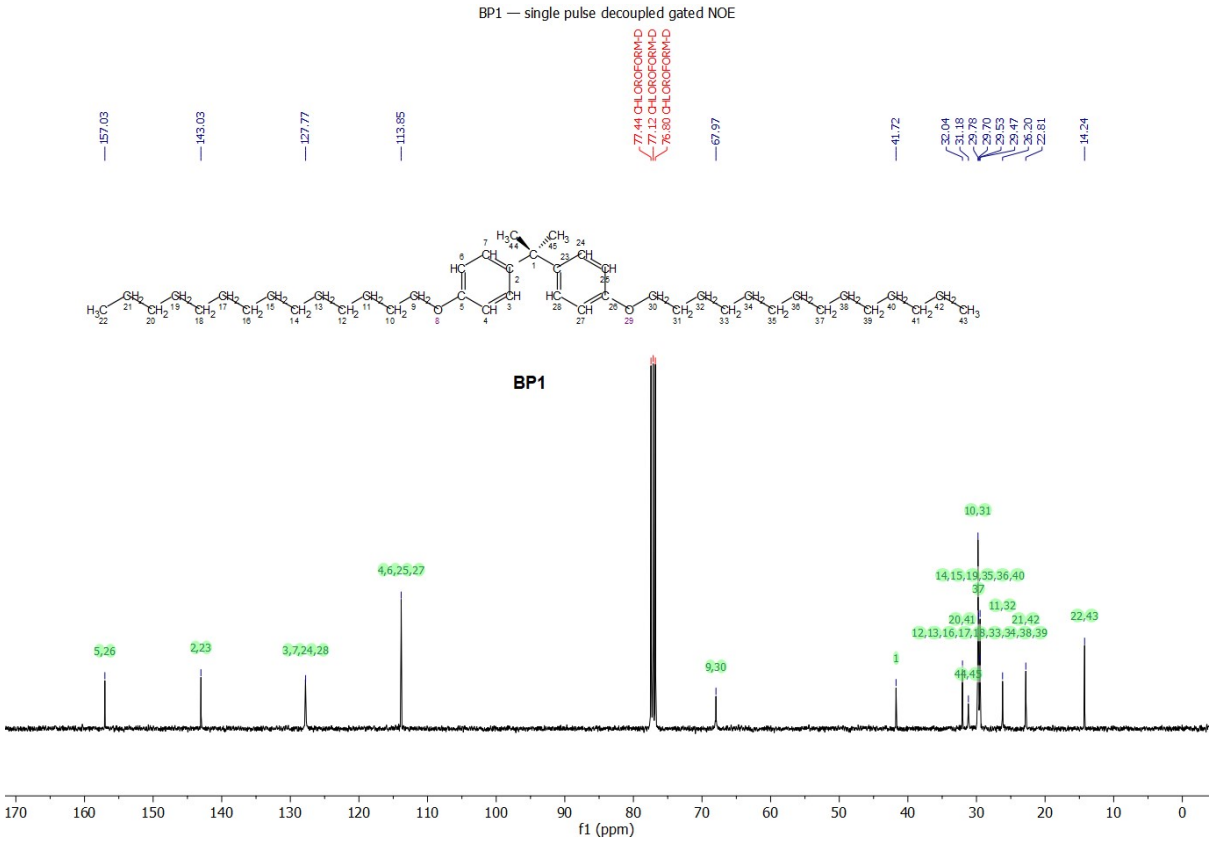
(**BP10**) *propane-2,2-diylbis(4,1-phenylene)bis(2-(naphthalen-1-yl)acetate)*. White solid (1.06g, 48 %). M.p.: 83–85 ^{0}C. ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 8.12 – 8.05 (2 H, m), 7.91 – 7.84 (2 H, m), 7.81 (4 H, dt, *J* 8.1, 1.2), 7.60 – 7.40 (6 H, m), 7.17 – 7.06 (4 H, m), 6.94 – 6.83 (4 H, m), 4.27 (4 H, s), 1.58 (6 H, s). ^{13}C-NMR (101 MHz, $CDCl_3$, δ ppm): 170.22, 148.64, 147.94, 133.91, 132.12, 130.14, 128.87, 128.37, 128.21, 127.82, 127.76, 126.58, 125.94, 125.58, 120.81, 42.46, 39.43, 30.90. TOF MS (ES^+) *m/z*: Calc. for $C_{39}H_{32}O_4$ $[M+NH_4]^+$ 582.71; found 582.26.

2. NMR and MS spectra.

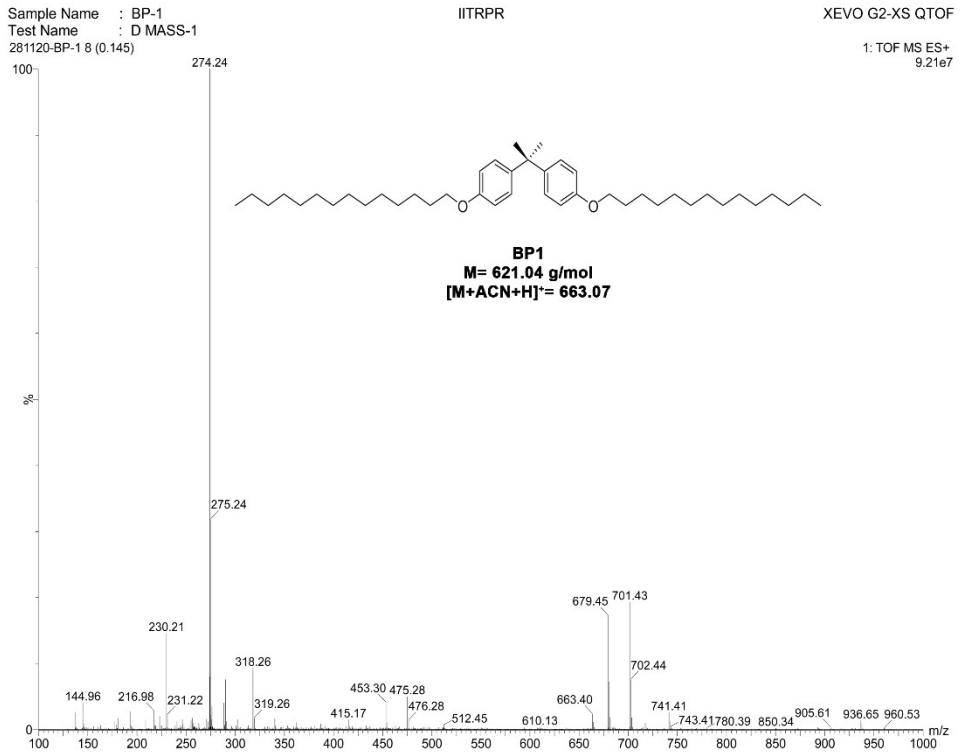
(1) ^{1}H NMR ($CDCl_3$) spectrum of **BP1**.



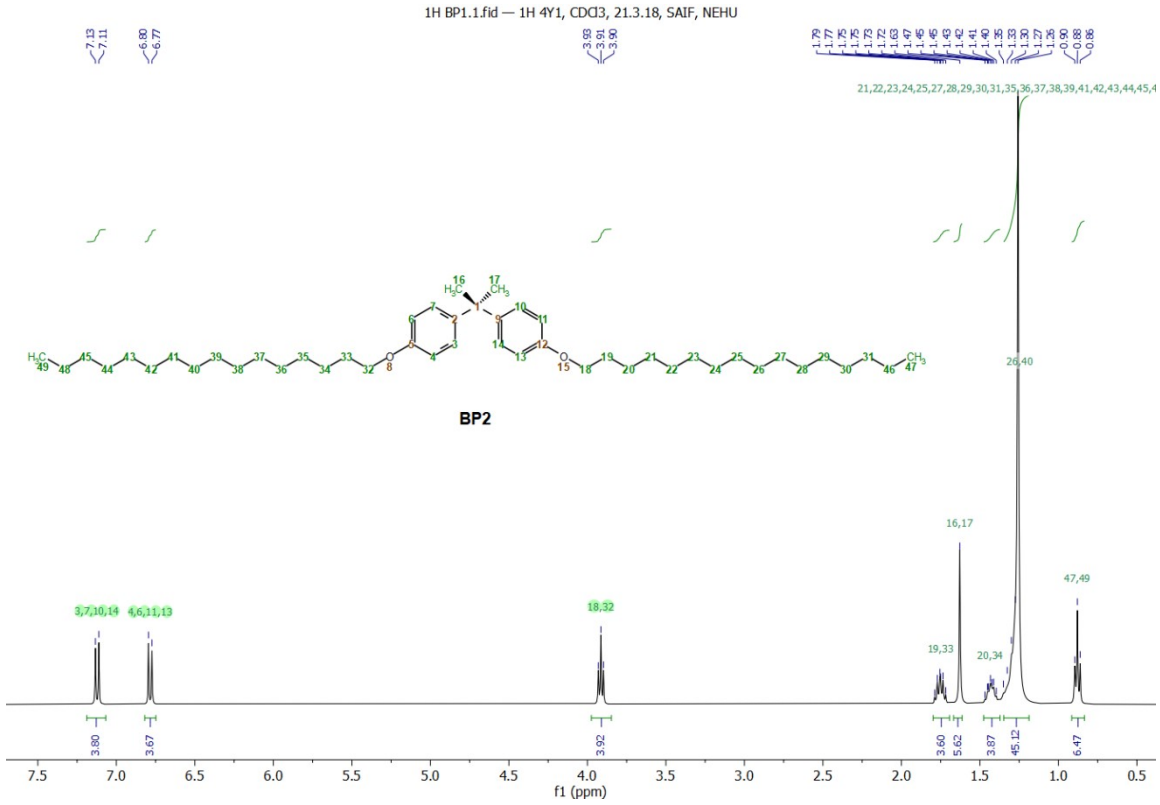
(2) ^{13}C NMR ($CDCl_3$) spectrum of **BP1**.



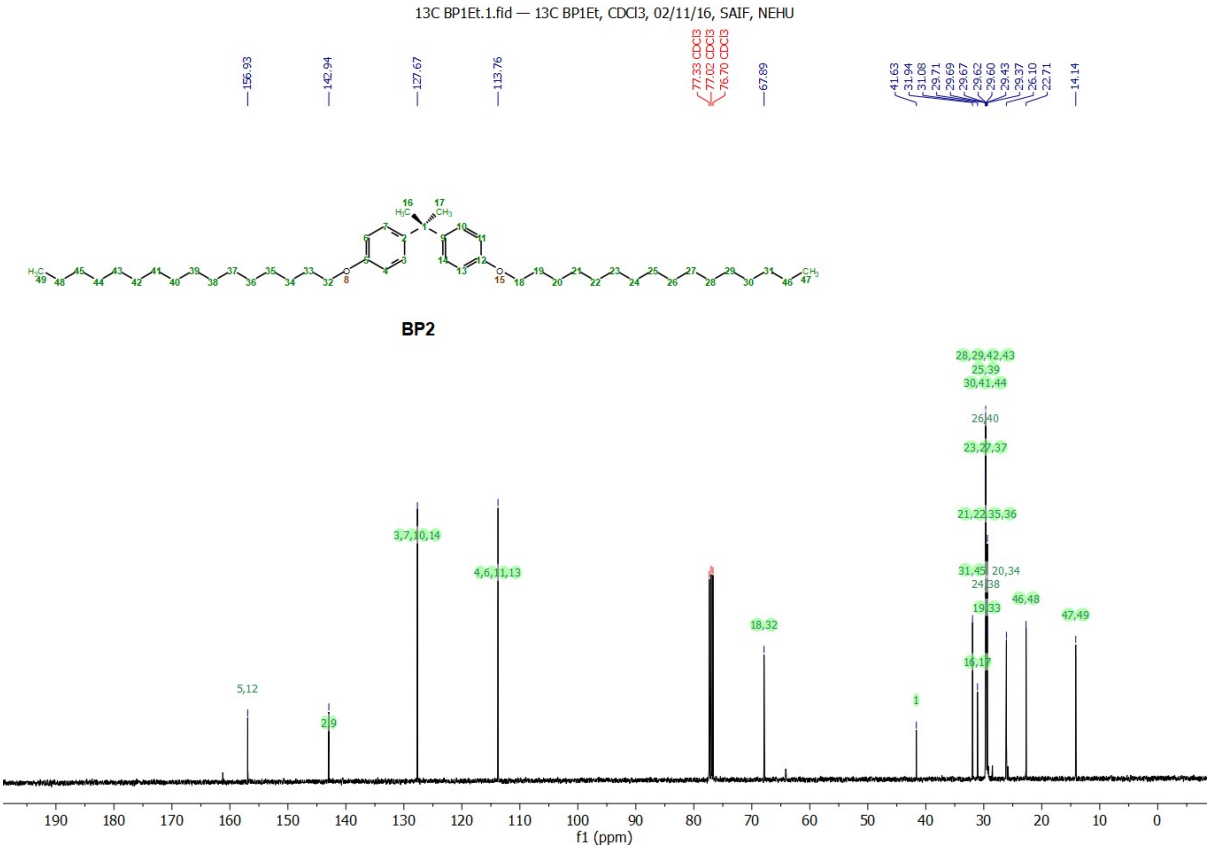
(3) ESI-MS spectrum of **BP1**



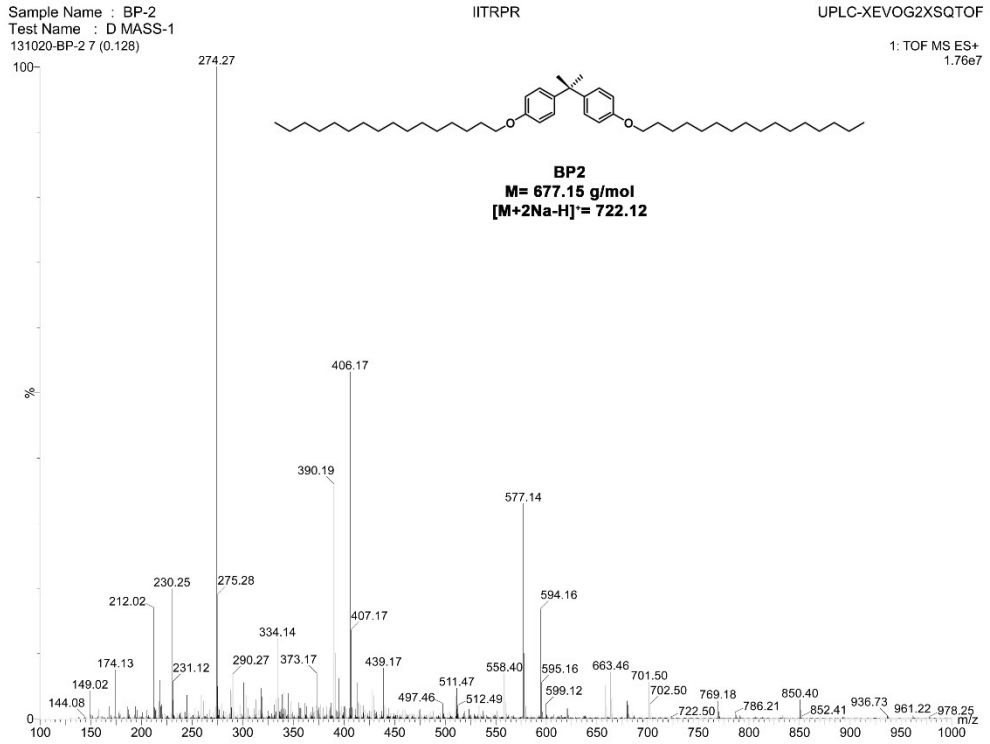
(4) ^{1}H NMR ($CDCl_3$) spectrum of **BP2**.



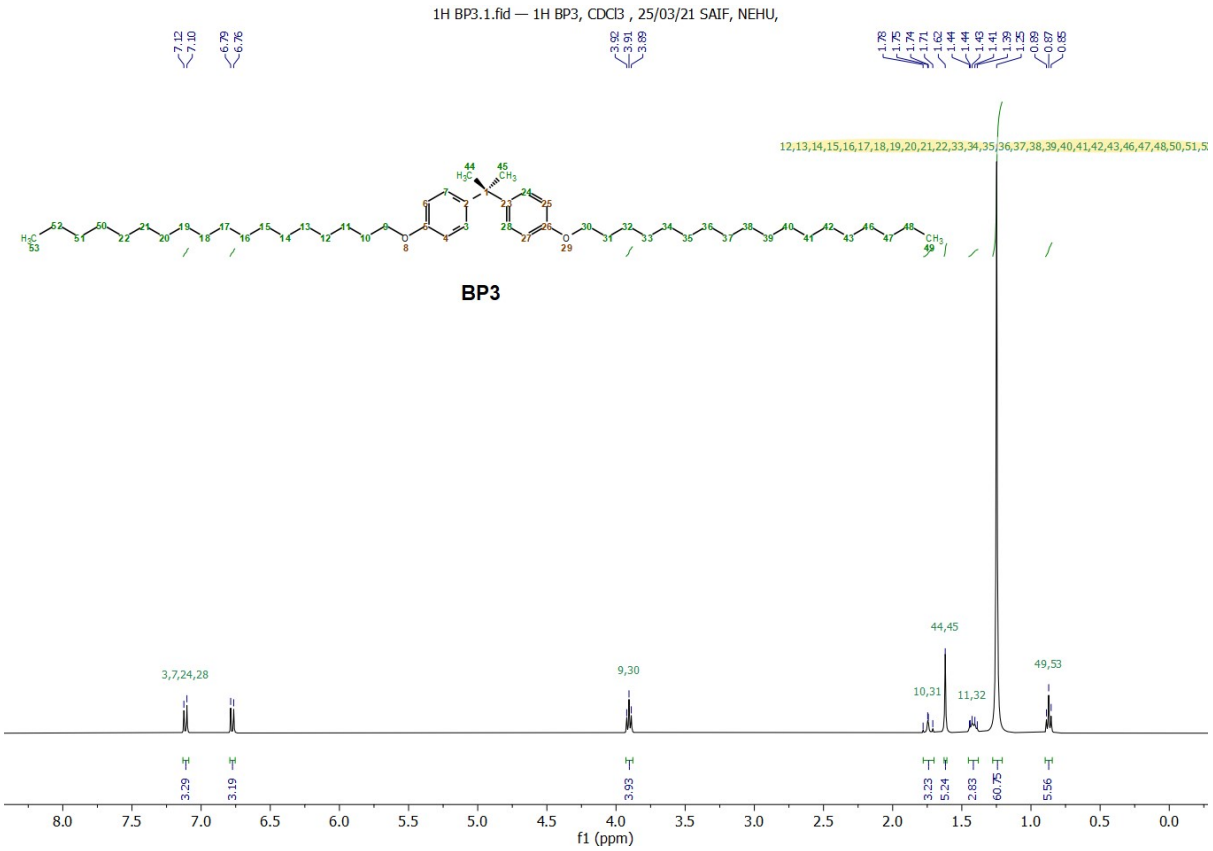
(5) ^{13}C NMR ($CDCl_3$) spectrum of **BP2**.



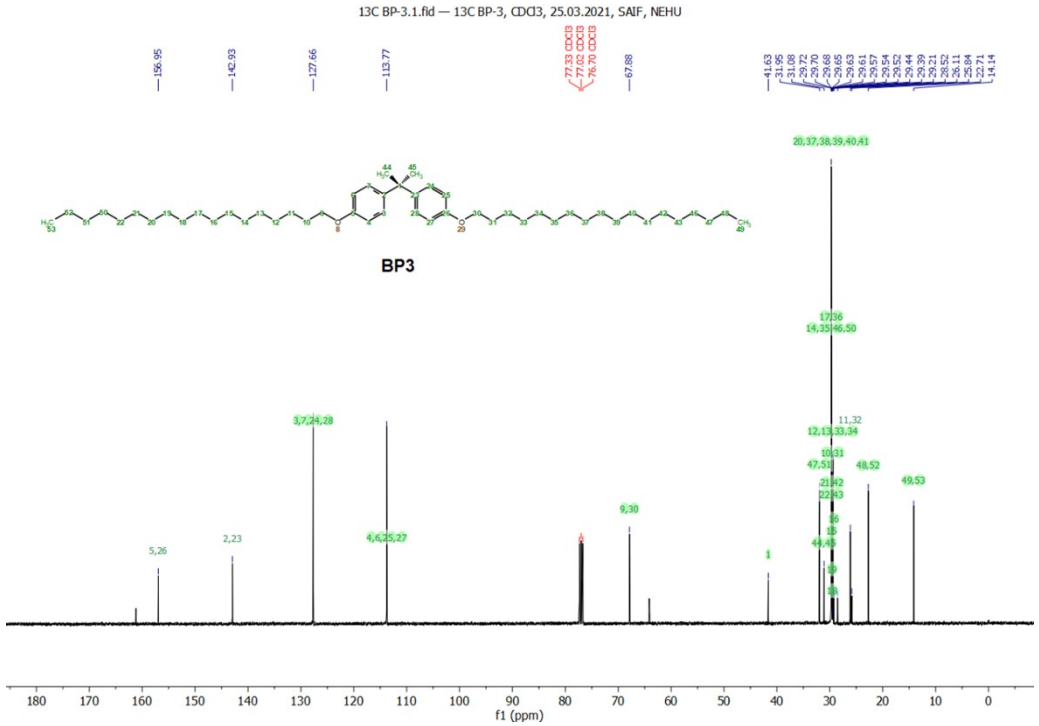
(6) ESI-MS spectrum of **BP2**



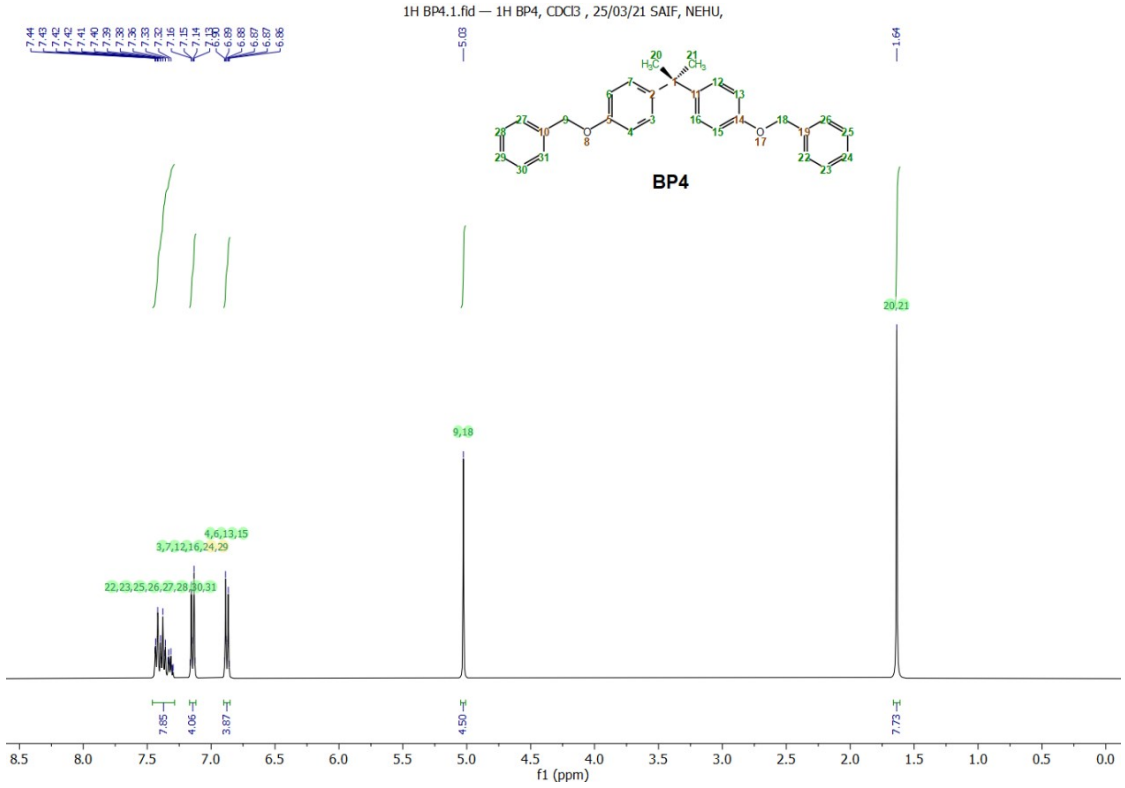
(7) ^{1}H NMR ($CDCl_3$) spectrum of **BP3**.



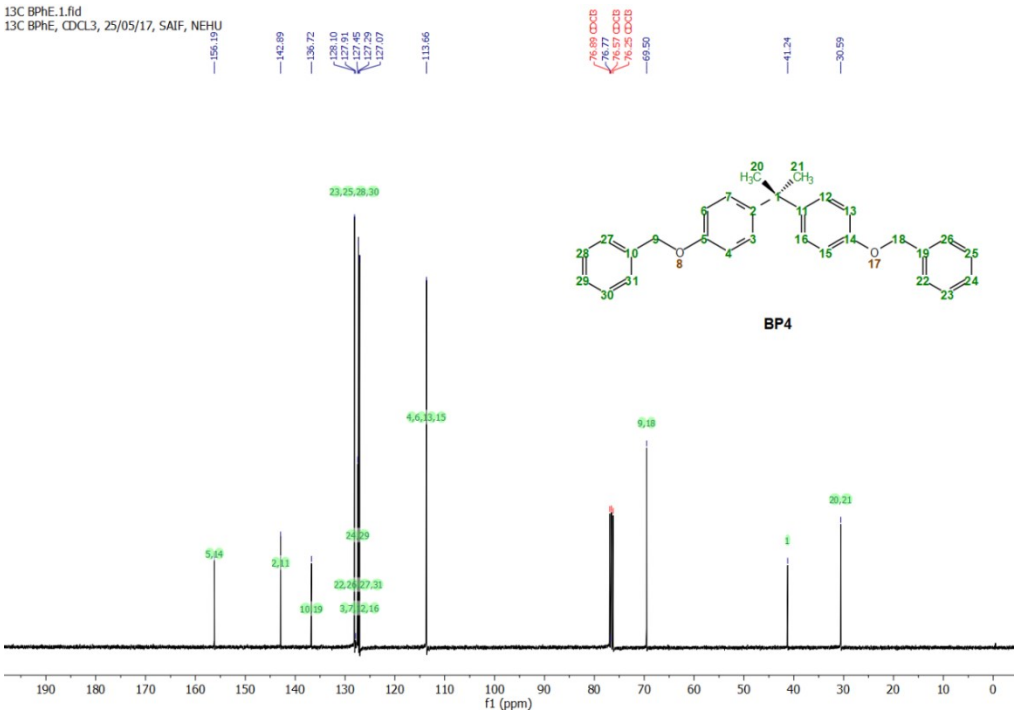
(8) ^{13}C NMR ($CDCl_3$) spectrum of **BP3**.



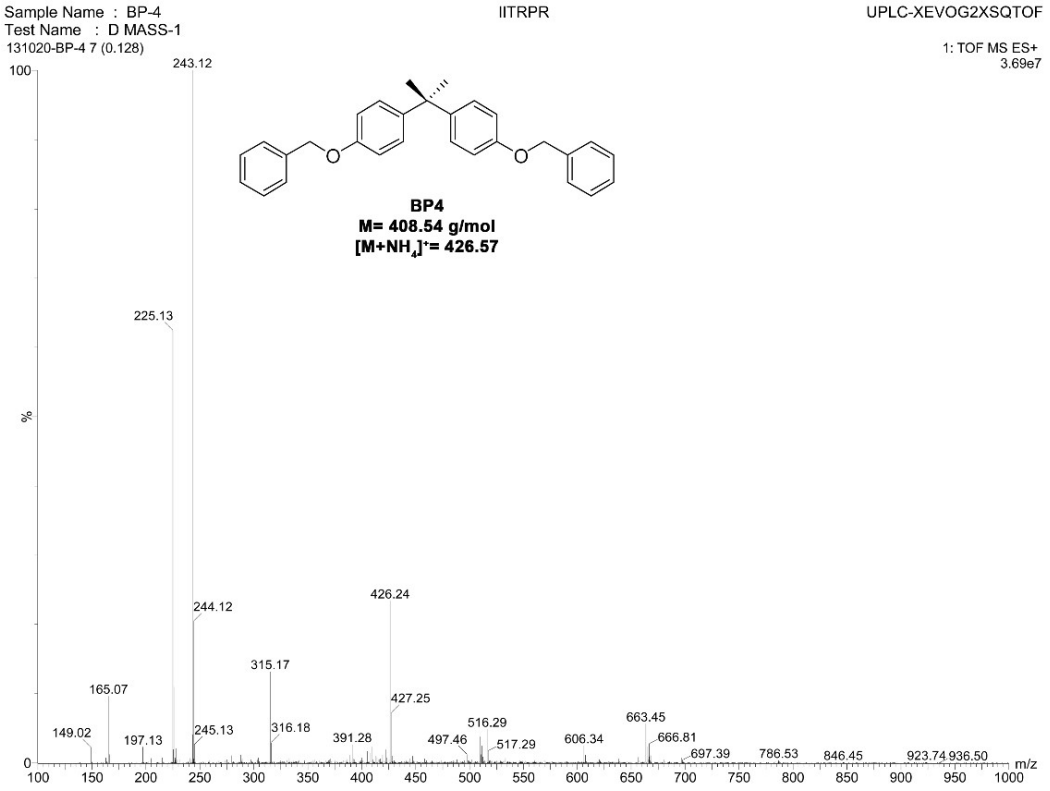
(9) ^{1}H NMR ($CDCl_3$) spectrum of **BP4**.



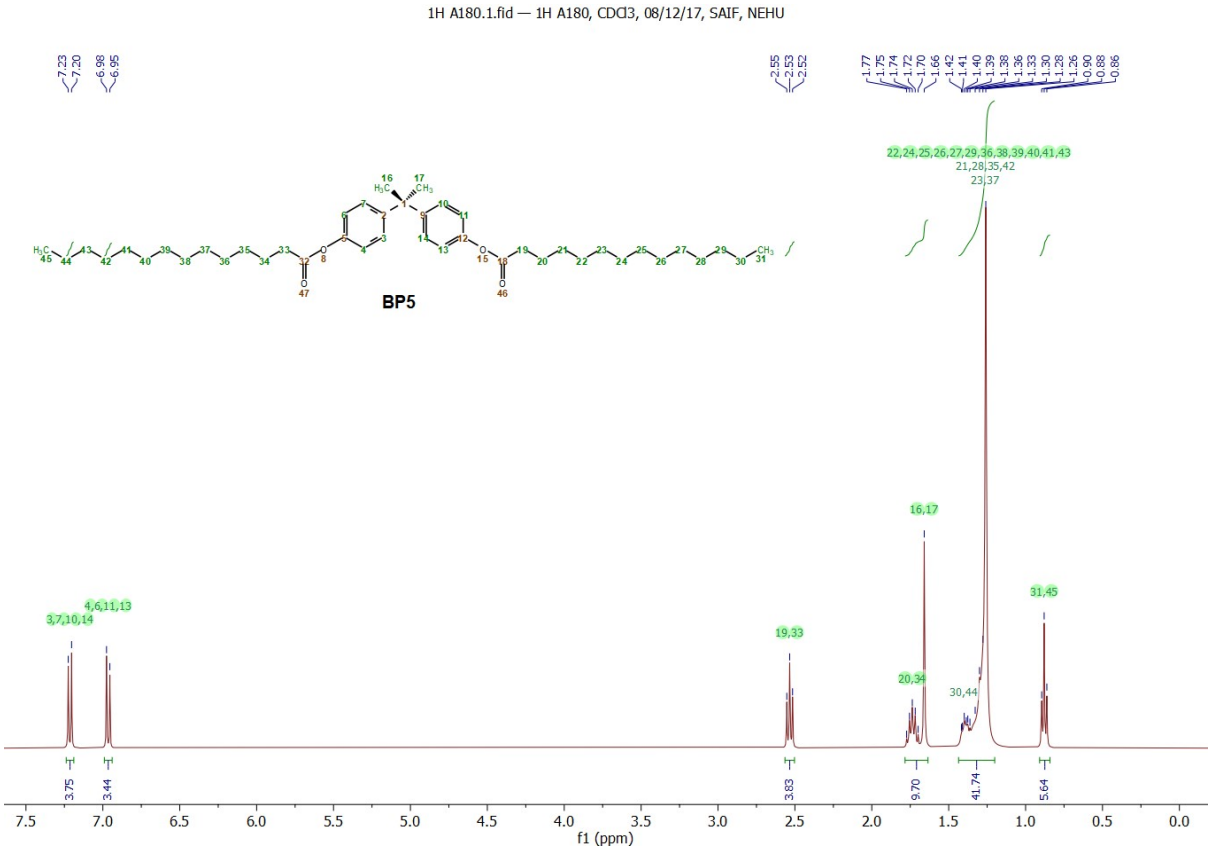
(10) ^{13}C NMR ($CDCl_3$) spectrum of **BP4**.



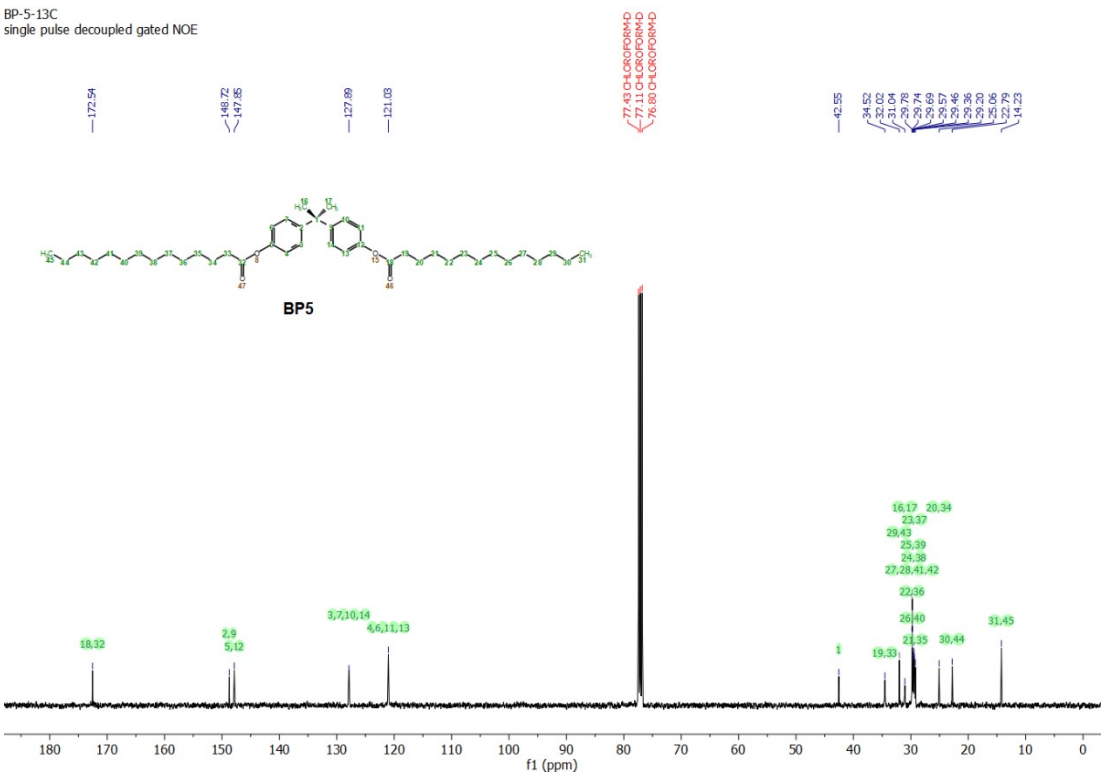
(11) ESI-MS spectrum of **BP4.**



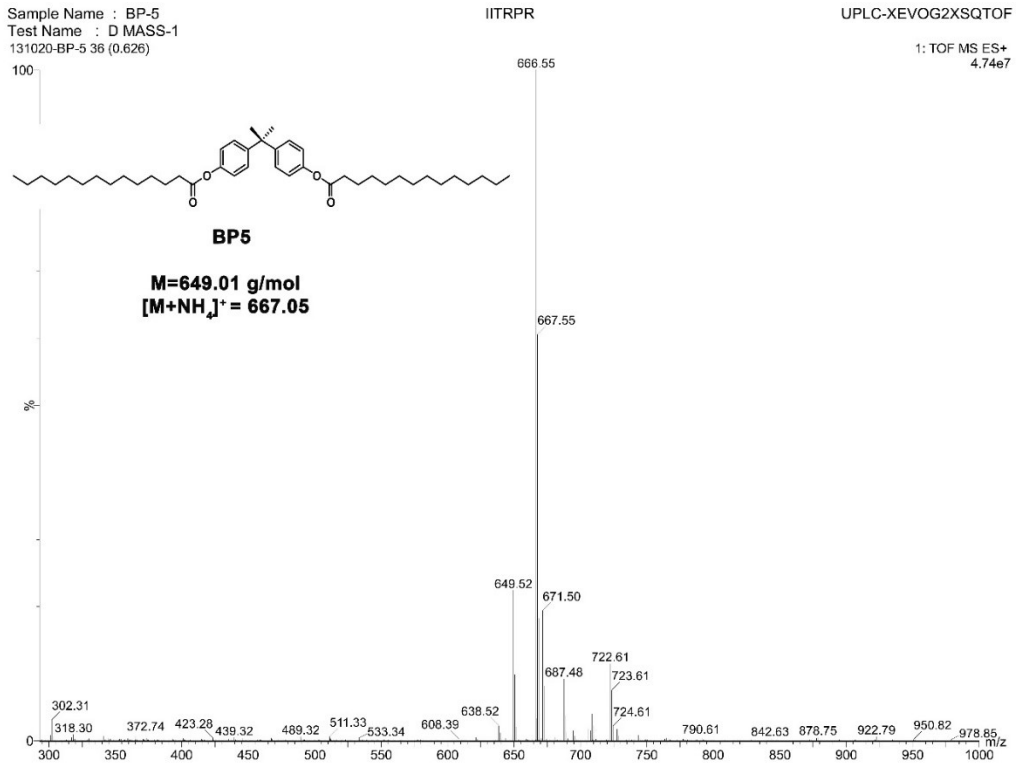
(12) ^{1}H NMR ($CDCl_3$) spectrum of **BP5**.



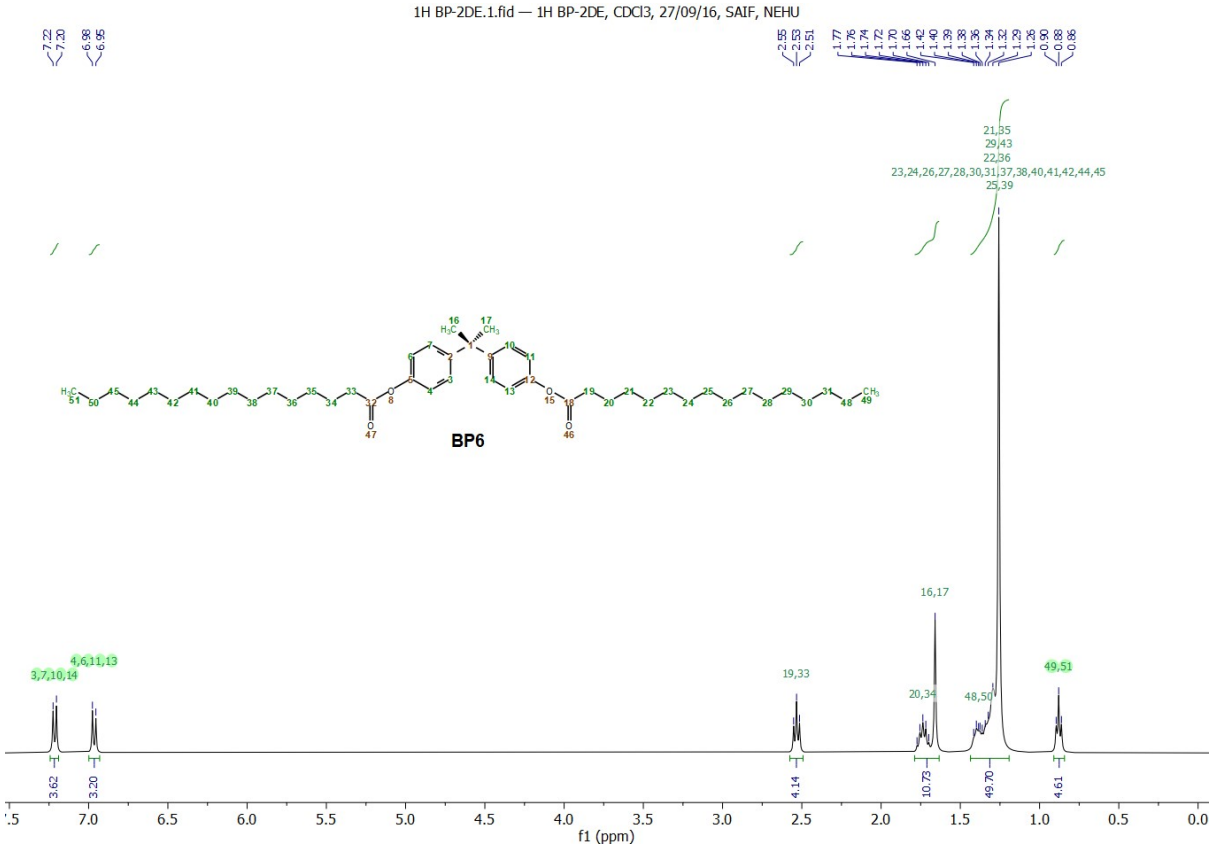
(13) ^{13}C NMR ($CDCl_3$) spectrum of **BP5**.



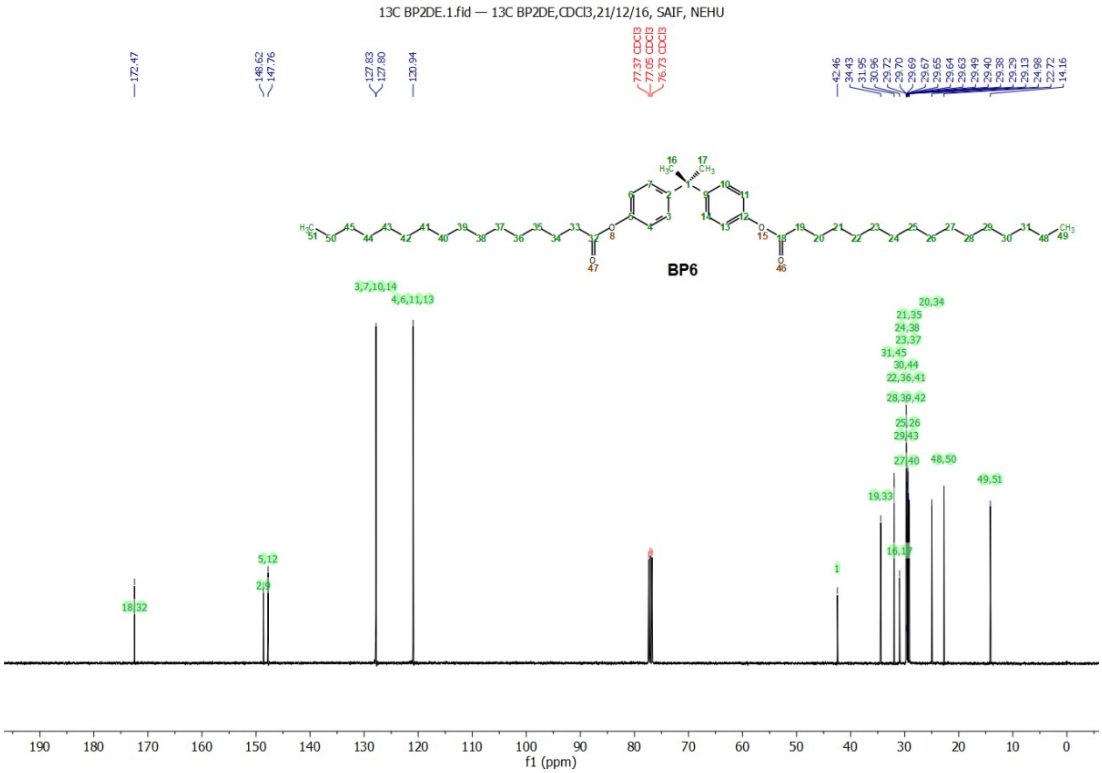
(14) ESI-MS spectrum of **BP5.**



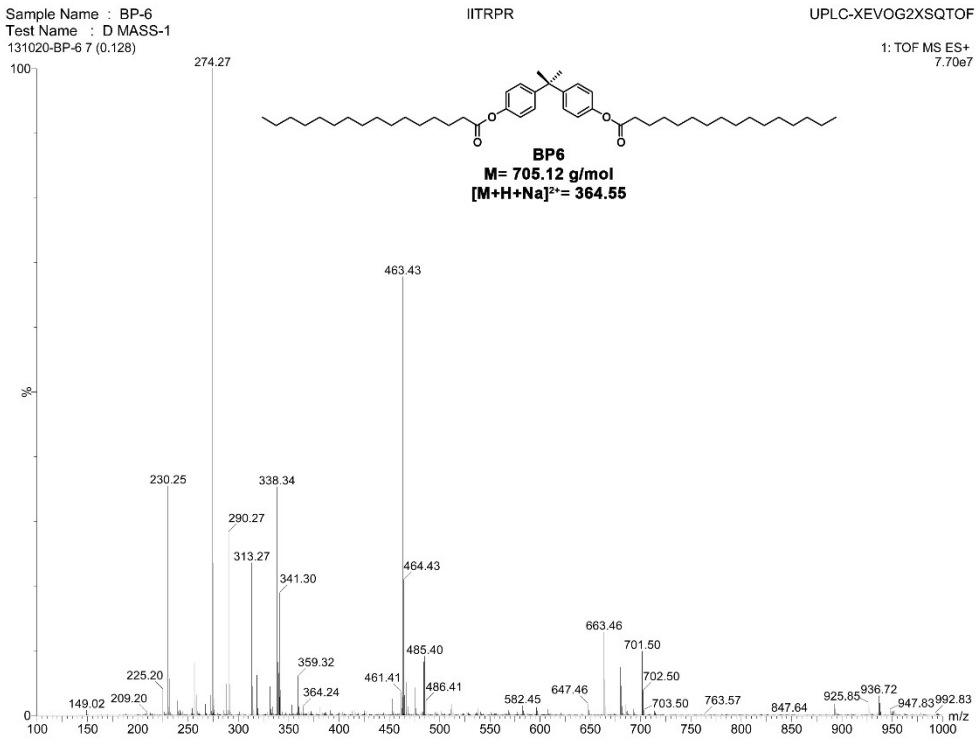
(15) ^{1}H NMR ($CDCl_3$) spectrum of **BP6**.



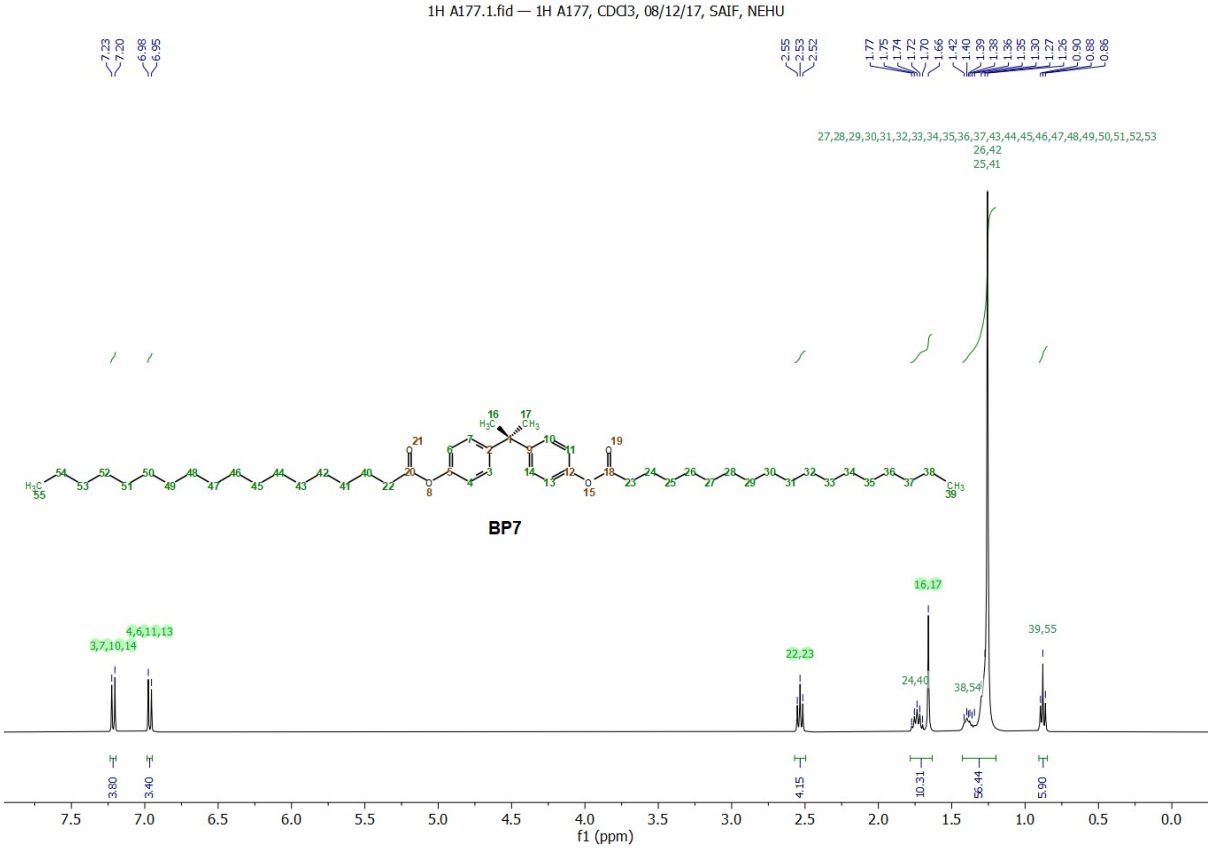
(16) ^{13}C NMR ($CDCl_3$) spectrum of **BP6**.



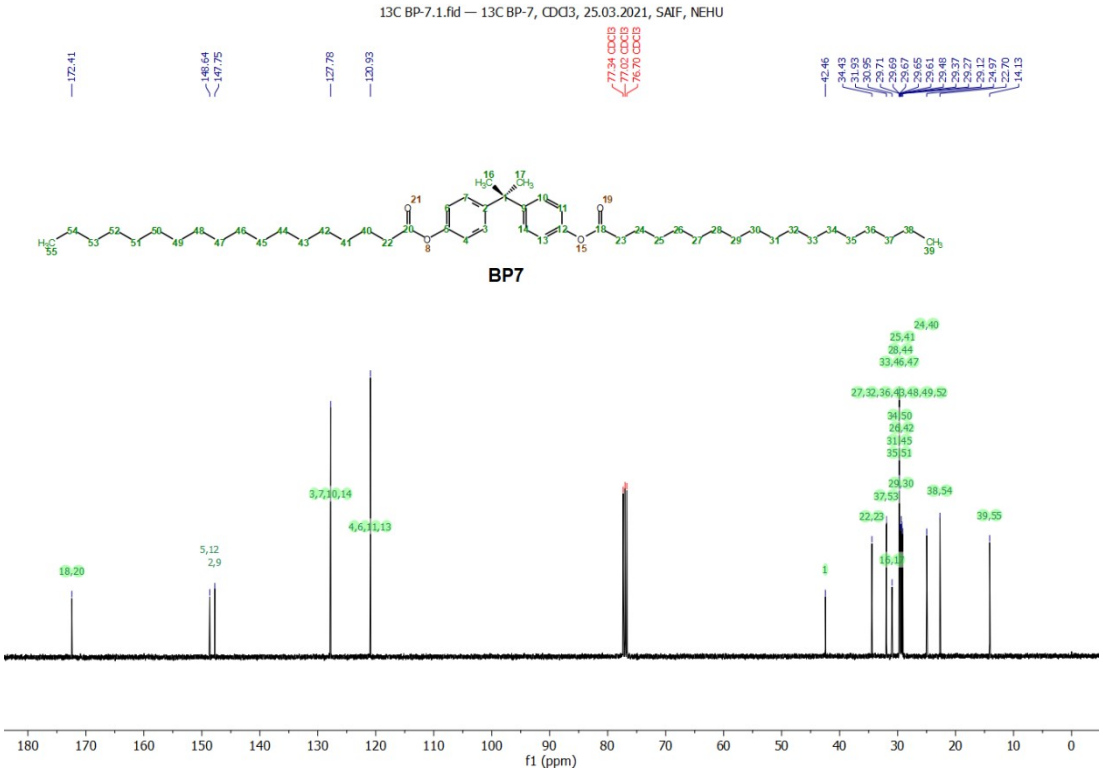
(17) ESI-MS spectrum of **BP6.**



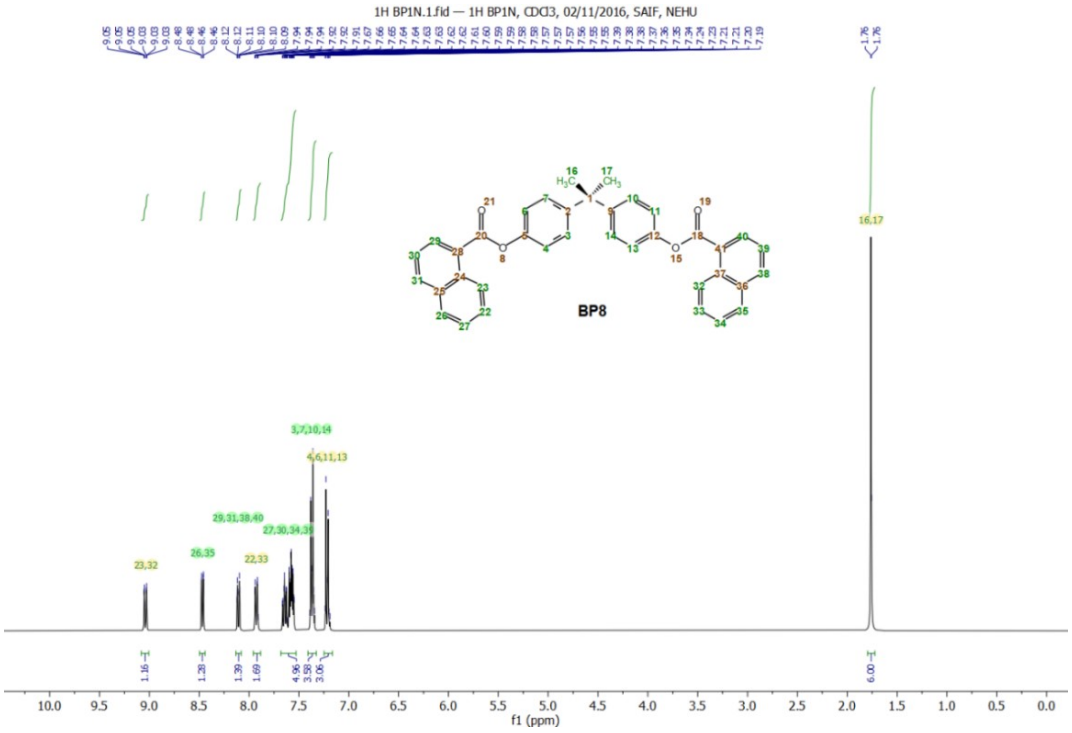
(18) ^{1}H NMR ($CDCl_3$) spectrum of **BP7**.



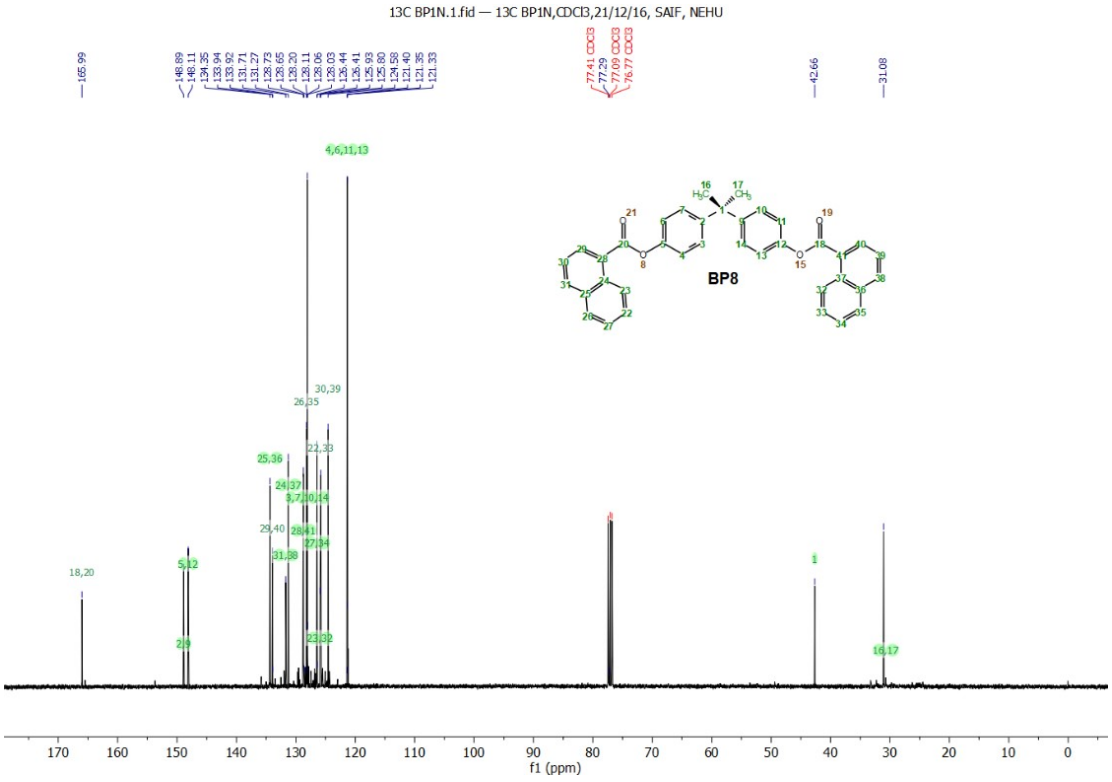
(19) ^{13}C NMR ($CDCl_3$) spectrum of **BP7**.



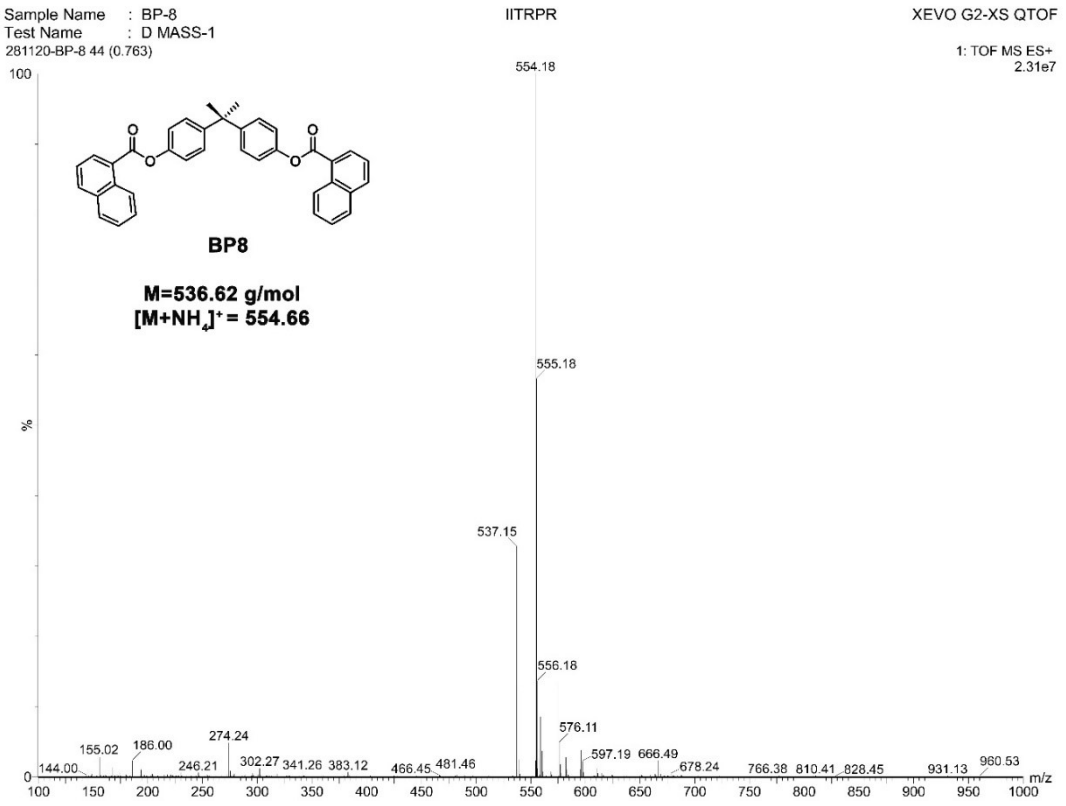
(20) ^{1}H NMR ($CDCl_3$) spectrum of **BP8**.



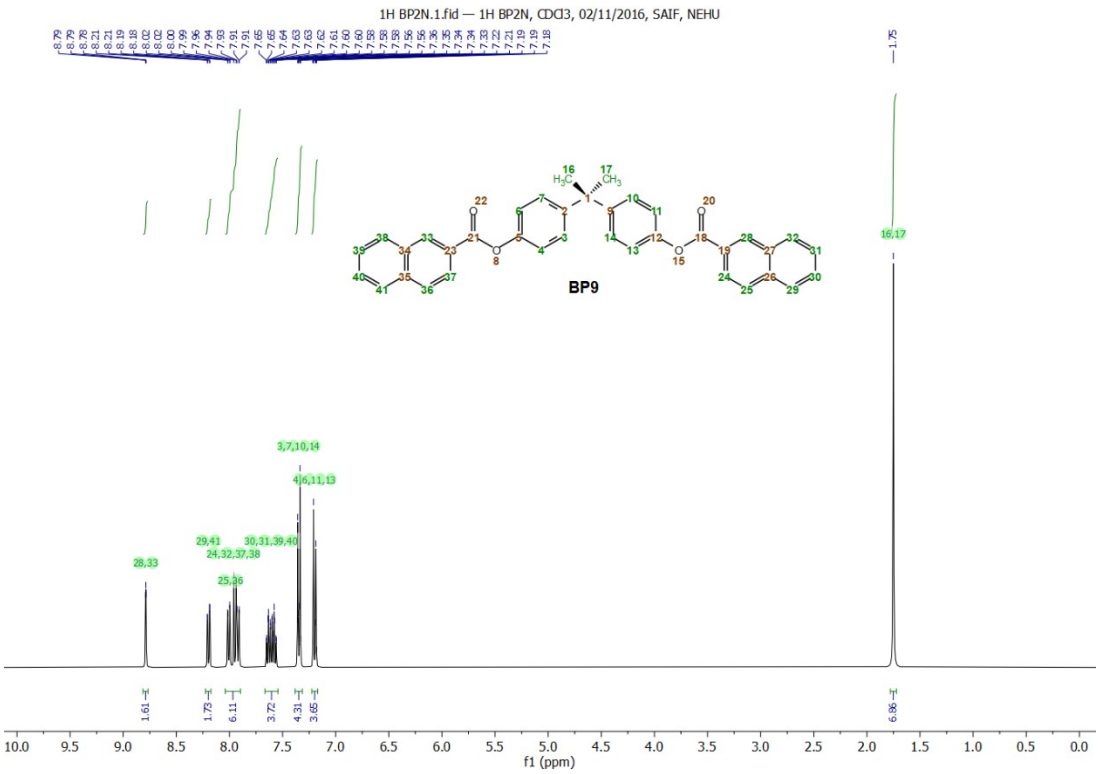
(21) ^{13}C NMR ($CDCl_3$) spectrum of **BP8**.



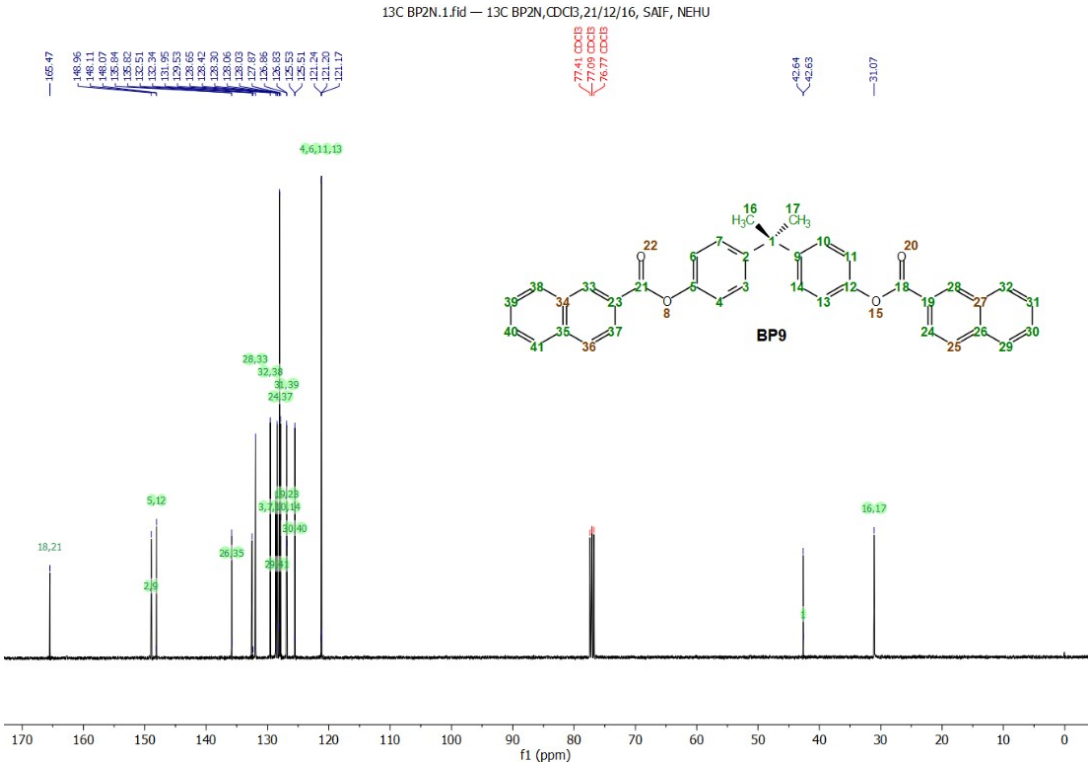
(22) ESI-MS spectrum of **BP8.**



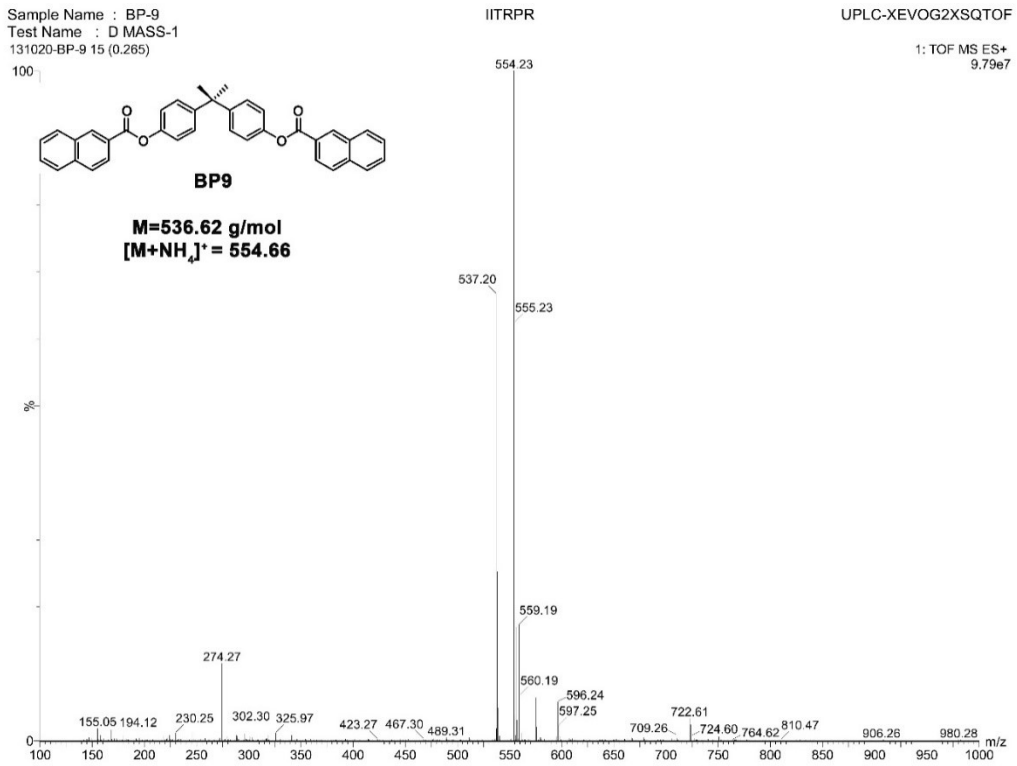
(23) ^{1}H NMR ($CDCl_3$) spectrum of **BP9**.



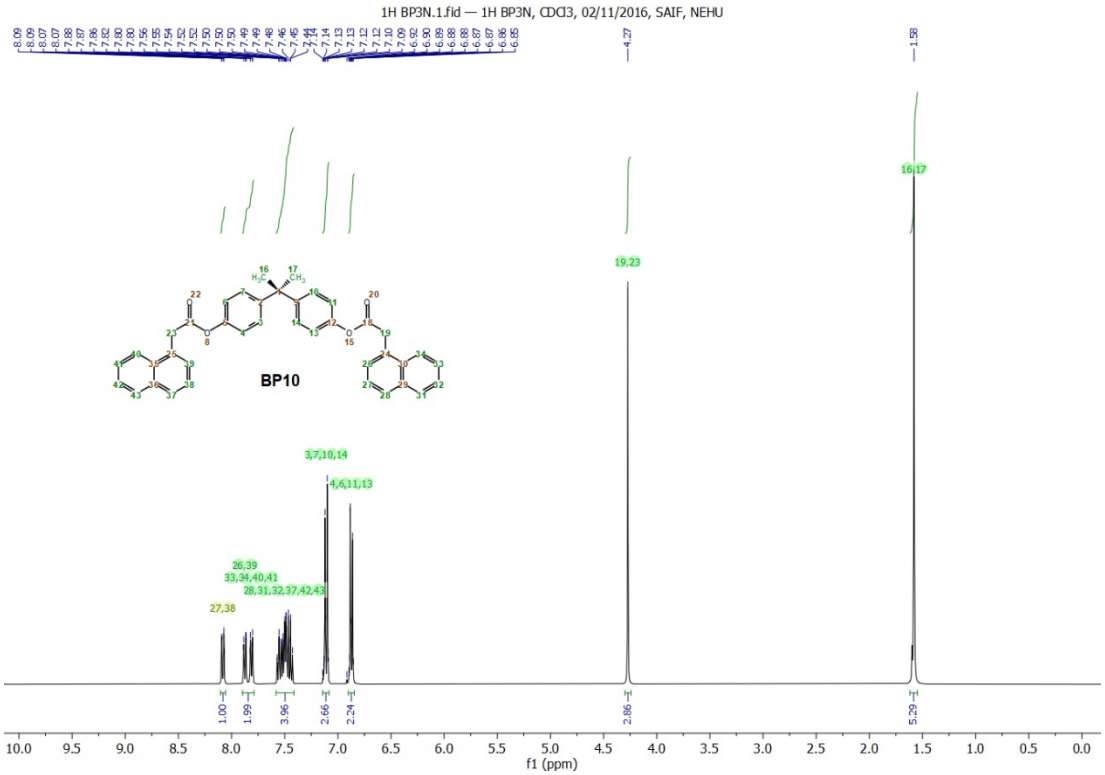
(24) ^{13}C NMR ($CDCl_3$) spectrum of **BP9**.



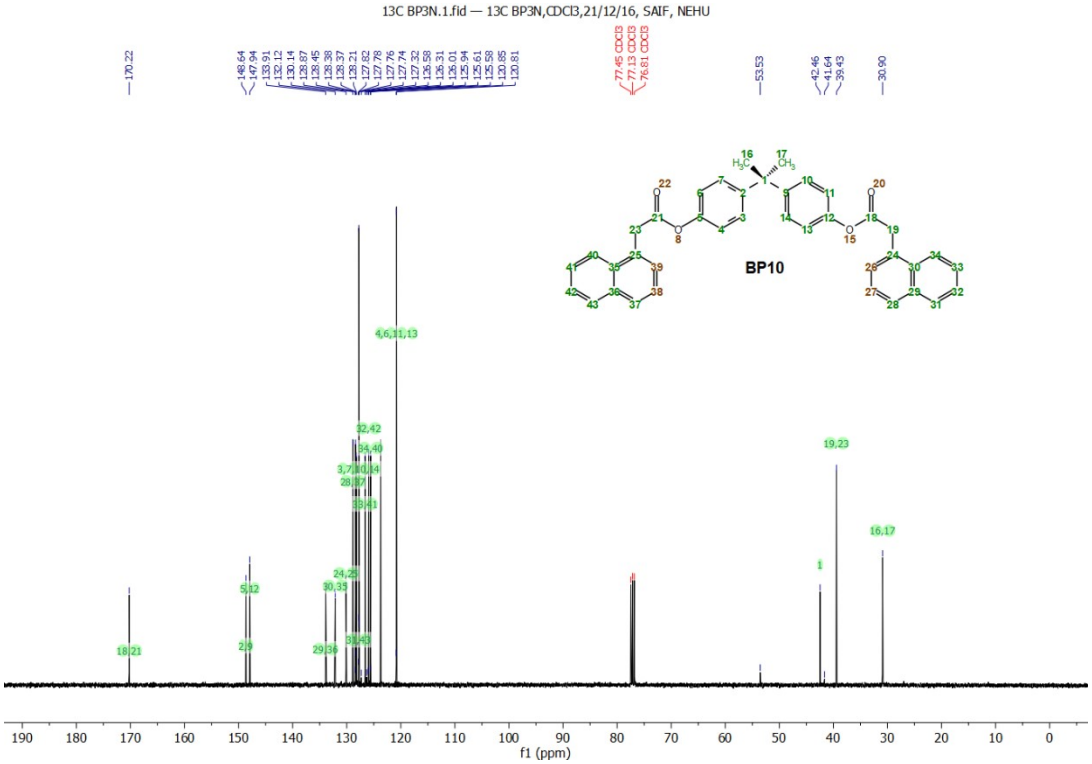
(25) ESI-MS spectrum of **BP9.**



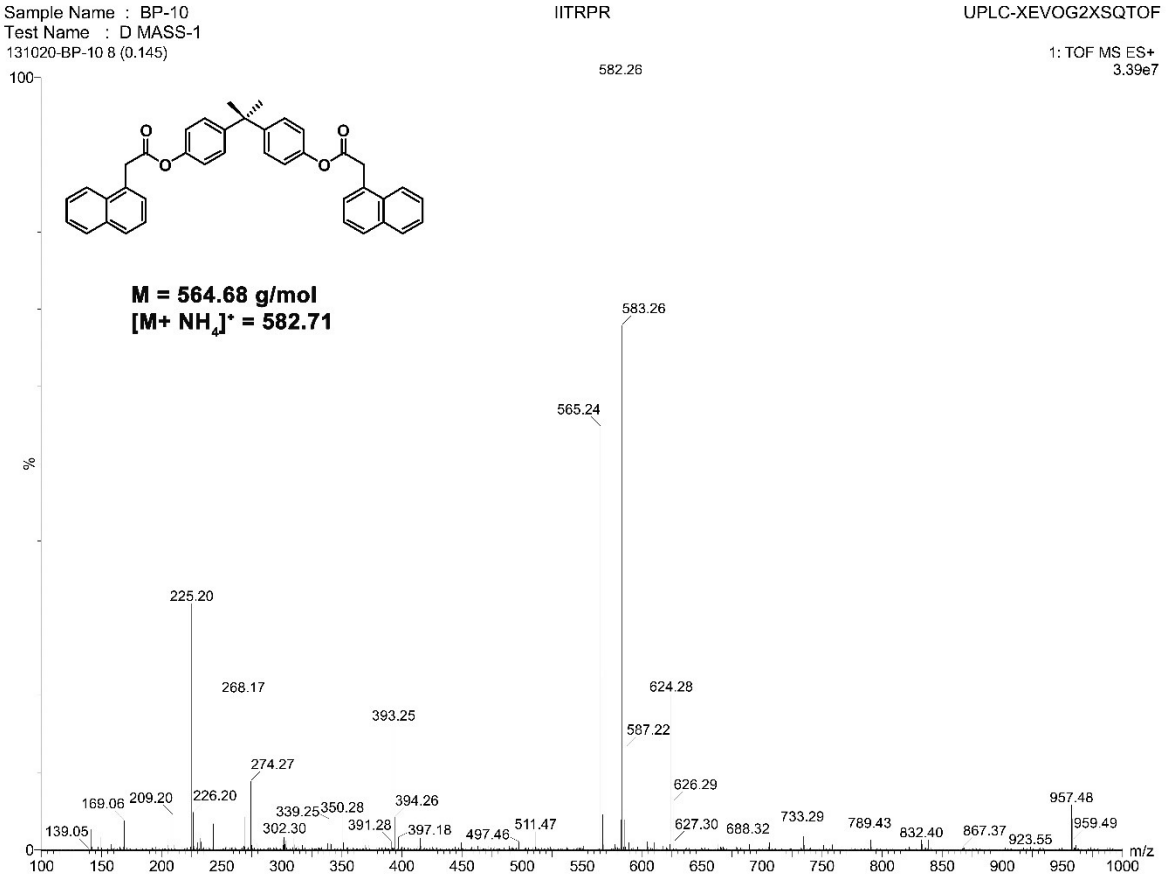
(26) ^{1}H NMR ($CDCl_3$) spectrum of **BP10**.



(27) ^{13}C NMR ($CDCl_3$) spectrum of **BP10**.



(28) ESI-MS spectrum of **BP10.**



3. Dye absorption studies:

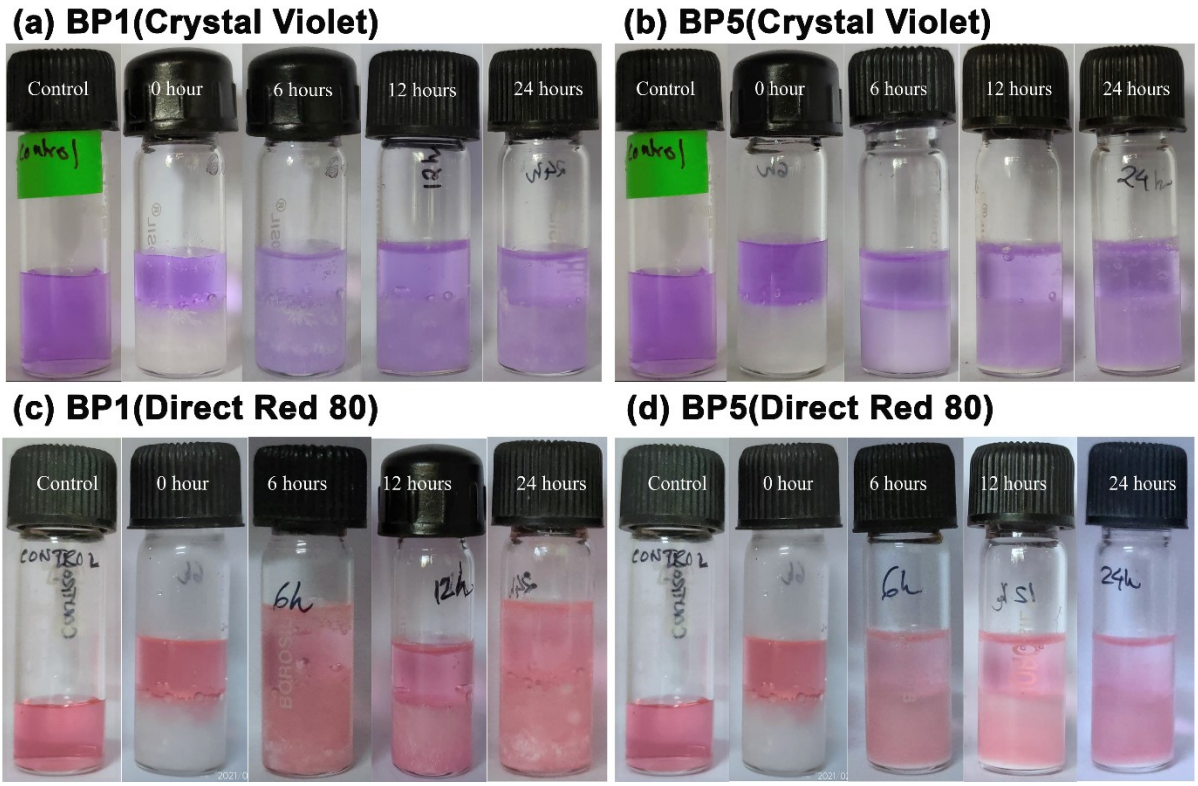


Figure S1. Images for time-dependent absorption of aqueous crystal violet solution (0.02 mM) by (a) **BP1** (b) **BP5** gels (3% w/v in propan-1-ol) and aqueous direct red 80 solution (0.02 mM) by (c) **BP1** (d) **BP5** gels (3% w/v in propan-1-ol).

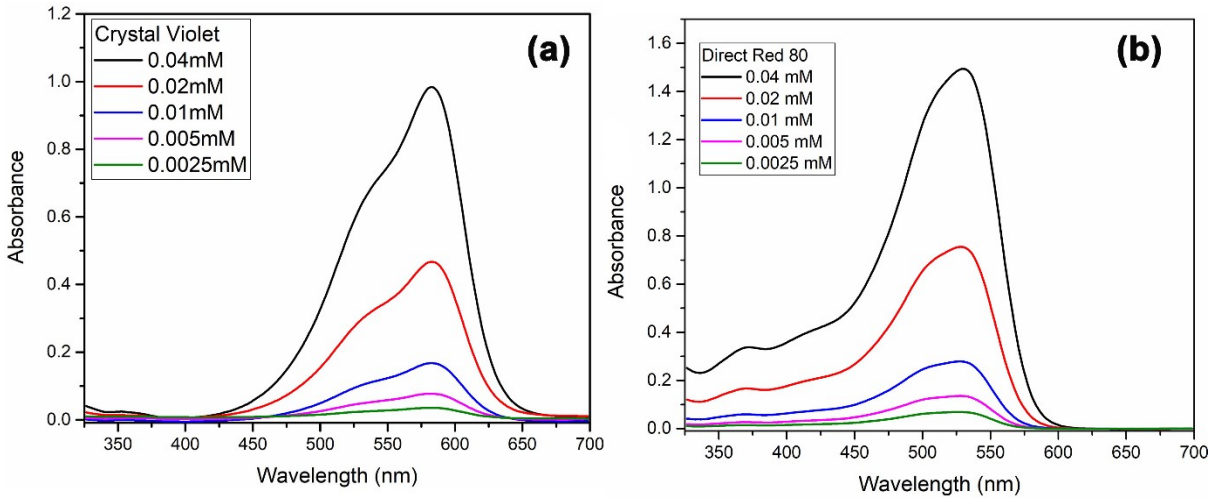


Figure S2: UV–vis absorption profiles of standard aqueous solutions of (a) Crystal Violet (b) Direct Red 80 at different concentrations.

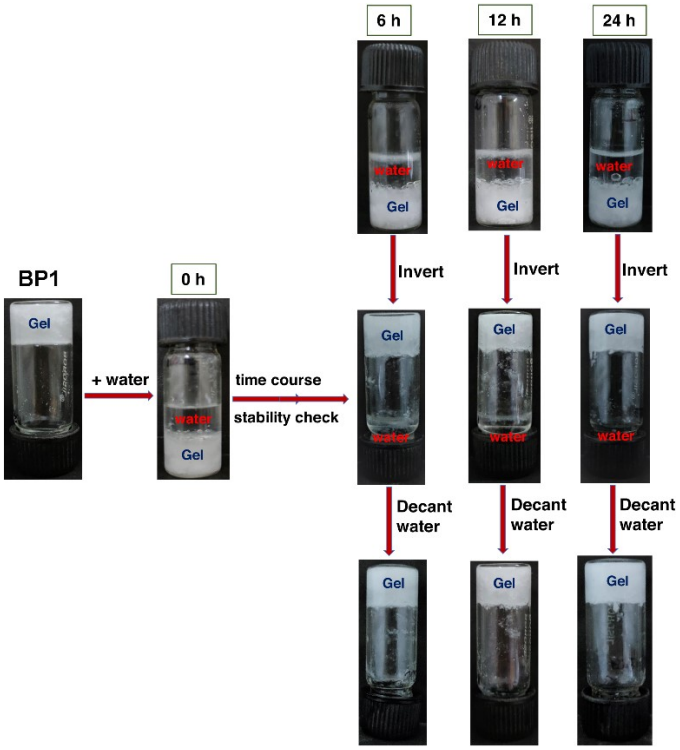


Figure S3. Stability of **BP1** propan-1-ol gels (3% w/v) at room temperature in the presence of water at different time points.

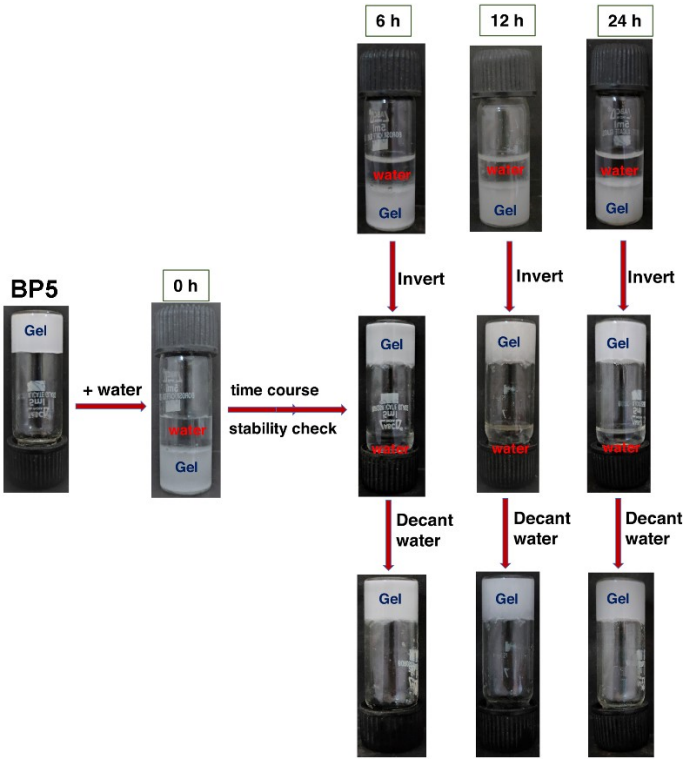


Figure S4. Stability of **BP5** propan-1-ol gels (3% w/v) at room temperature in the presence of water at different time points.