Electronic Supplementary Material (ESI) for Polymer Chemistry.

Organocatalytic orthogonal ATRP and ring-opening polymerization using a single dual-function photocatalyst

Qiang Ma,[a] *Yu Jiang,*[a] *Junqiang Lin,*[a] *Xun Zhang,*[a] *Hui Shao,*[a] *Saihu Liao*[*,a,b]

[a] Key Laboratory of Molecule Synthesis and Function Discovery (Fujian Province University), State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350108, China.

[b] Beijing National Laboratory for Molecular Science, Beijing 100190, China.

Corresponding Author: shliao@fzu.edu.cn

Materials

Methyl methacrylate (MMA; 99%, TCI), δ-valerolactone (δ-VL; 99%, TCI) and ε-caprolactone (ε-CL; 99%, TCI) were distilled over CaH_2 under reduced pressure and stored under an argon atmosphere at −20 °C. Toluene was purchased from J&K Chemical, distilled over CaH_2 under an argon atmosphere and dried with 4 Å molecular sieves before use. Amberlyst A21 (Alfa Aesar) was used as received. All other chemicals were obtained from Shanghai Chemical Reagents Co., Ltd and used as received unless specified. The dual-functional initiators were synthesized according to literature procedures[1-3] (detailed procedures were shown in synthetic part).

Instruments

The number-average molecular weight ($M_{n,\ GPC}$) and molecular weight distribution (M_w/M_n) values of the obtained polymers determined by a Waters 1515 gel permeation chromatograph (GPC) equipped with a Waters 2414 refractive-index detector, using a Styragel HR 3 THF (7.8 × 300 mm) Column and a Styragel HR 4 THF (7.8 × 300 mm) column with measurable molecular weights ranging from 10^2 to 10^6 g·mol^{-1}. THF was used as eluent at a flow rate of 1.0 mL/min at 35 °C. GPC samples were injected manually and polystyrene standards were used for calibration. ^{1}H NMR spectra were recorded using Bruker AVIII 400 spectrometer spectrometer. Chemical shift values were recorded as parts per million (ppm) relative to tetramethylsilane (TMS), chloroform or dichloromethane as internal standard, and coupling constants (*J*) in Hertz. The ultraviolet−visible (UV−vis) spectra were obtained using a Perkins Elmer Lambda 900 spectrometer equipped with a PTP-1 Peltier temperature controller and the photoluminescence (PL) spectra were recorded at room temperature on an Edinburgh Instruments, FLS980 spectrometer equipped with a 450 W Xe lamp for excitation and detected by a photomultiplier (PMT R928P). Cyclic voltammetry experiments were carried out with a CHI660 D electrochemical workstation (Shanghai Chenhua Instrument Plant, China) using a one compartment electrolysis cell consisting of a typical glassy carbon working electrode (3 mm diameter), a platinum wire counter electrode, and a Ag/AgCl reference electrode. Before performing electrochemical cleaning, the electrode should be sonicated in ethanol and deionized water for 1~3mins respectively to obtain a clean electrode. The measurements were done in 1.0 mM toluene solution with 0.1 M tetrabutylammonium hexafluorophosphate (*n*-Bu_4NPF_6, TCI chemicals) as supporting electrolyte at a scan rate of 50 mV/s. 12 W purple bulbs (Light intensity: ~ 2 mW/cm^2) was purchased from GeAo Chemical.

Polymerization Methods

One-Pot Sequential O-ATRP of MMA and ROP of δ-VL (Route 1)

A typical procedure for one-pot sequential O-ATRP of MMA and ROP of δ-VL was as follow: Dual-initiator (0.047 mmol, 1 eq.), MMA (0.50 mL, 4.7 mmol, 100 eq.), a toluene stock solution (0.25 mL) of Photo-PA (4.7×10^{-3} mmol, 0.1 eq.) and 0.5 mL of toluene were placed into a 10-mL glass vial in glove box. The solution was then irradiated under purple light for 24 h at room temperature. Samples were withdrawn periodically for GPC and ^{1}H NMR analysis. After that, the polymerization was removed from purple light followed by addition of δ-VL (0.24 mL, 2.4 mmol, 50 eq.) and 0.25 mL of toluene. The polymerization was continued to proceed for 8 h. Samples were withdrawn at predetermined time for GPC and ^{1}H NMR analysis. Then, the polymerization was quenched by the addition of Amberlyst A21. The polymer was isolated by precipitation from THF to cold methanol and dried under vacuum.

One-Pot Sequential ROP of δ-VL and O-ATRP of MMA (Route 2)

A typical procedure for one-pot sequential ROP of δ-VL and O-ATRP of MMA was as follow: Dual-initiator (0.047 mmol, 1 eq.), MMA (0.50 mL, 4.7 mmol, 100 eq.), a toluene stock solution (0.5 mL) of Photo-PA (4.7×10^{-3} mmol, 0.1 eq.), δ-VL (0.24 mL, 2.4 mmol, 50 eq.) and 0.5 mL of toluene were placed into a 10-mL glass vial in glove box. The solution was stirred in the absence of light for 8 h to proceed the ring opening polymerization. Samples were withdrawn periodically for GPC and ^{1}H NMR analysis. After that, the polymerization was put under the irradiation of purple light to start the O-ATRP process. Samples were withdrawn periodically for GPC and ^{1}H NMR analysis. The polymerization was quenched by adding Amberlyst A21 and removal from light. The polymer was isolated by precipitation from THF to cold methanol and dried under vacuum.

One-Pot Simultaneous O-ATRP of MMA and ROP of δ-VL (Route 3)

A typical procedure for one-pot simultaneous O-ATRP of MMA and ROP of δ-VL was as follow: Dual-initiator (0.047 mmol, 1 eq.), MMA (0.50 mL, 4.7 mmol, 100 eq.), a toluene stock solution (0.5 mL) of Photo-PA (4.7×10^{-3} mmol, 0.1 eq.), δ-VL (0.24 mL, 2.4 mmol, 50 eq.) and 0.5 mL of toluene were placed into a 10-mL glass vial in glove box. The solution was put under irradiation of purple light. Samples were withdrawn periodically for GPC and ^{1}H NMR analysis. Then, the polymerization was quenched by the addition of Amberlyst A21. The polymer was isolated by

precipitation from THF to cold methanol and dried under vacuum.

UV-Vis Absorption Spectra

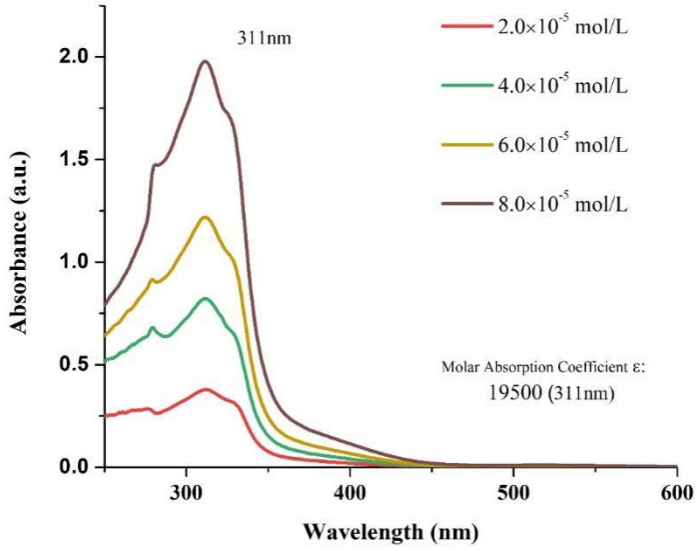


Figure S1. UV-Vis spectra of catalyst Photo-PA at different concentration in toluene.

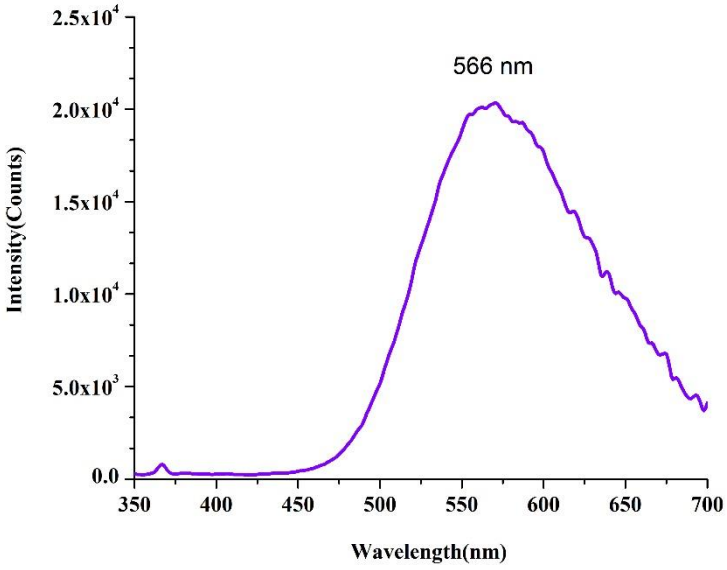


Figure S2. Fluorescence emission spectra of catalyst Photo-PA in toluene.

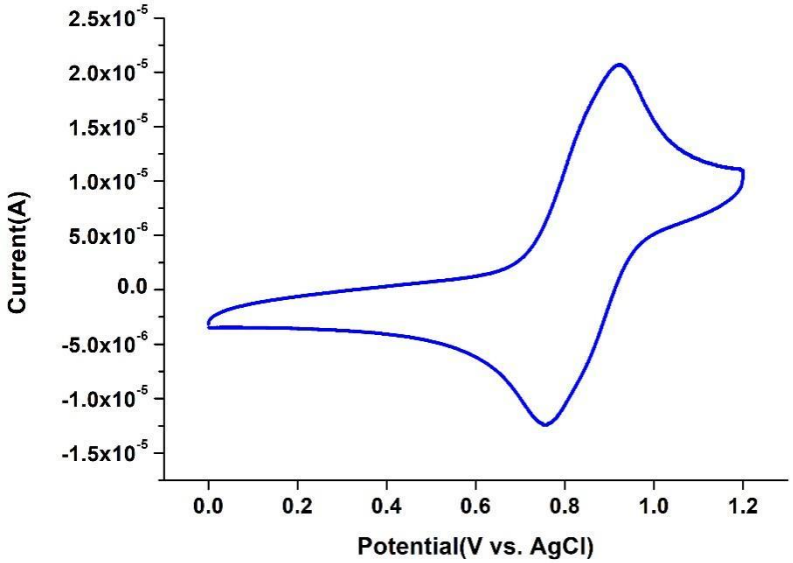


Figure S3. Cyclic voltammogram (vs. Ag/AgCl) of catalyst Photo-PA in toluene.

Experimental Determination of Excited State Reducing Power

Using photoluminescence maximum and E^{ox}, the excited state reduction potential was estimated for the organic photocatalyst (OPC, Photo-PA) (***E*_{1/2} (OPC$^{\bullet+}$/OPC*) = -1.41 V vs SCE**) according to the following equations[4]

$$E_{1/2}\,(\mathrm{OPC}^{\bullet+}/\mathrm{OPC}^{*}) = E^{ox} - E_{0,0}$$

$$\text{where } E_{0,0} = hc/\lambda_{max} = 1240\ \text{nm} / \lambda_{max}$$

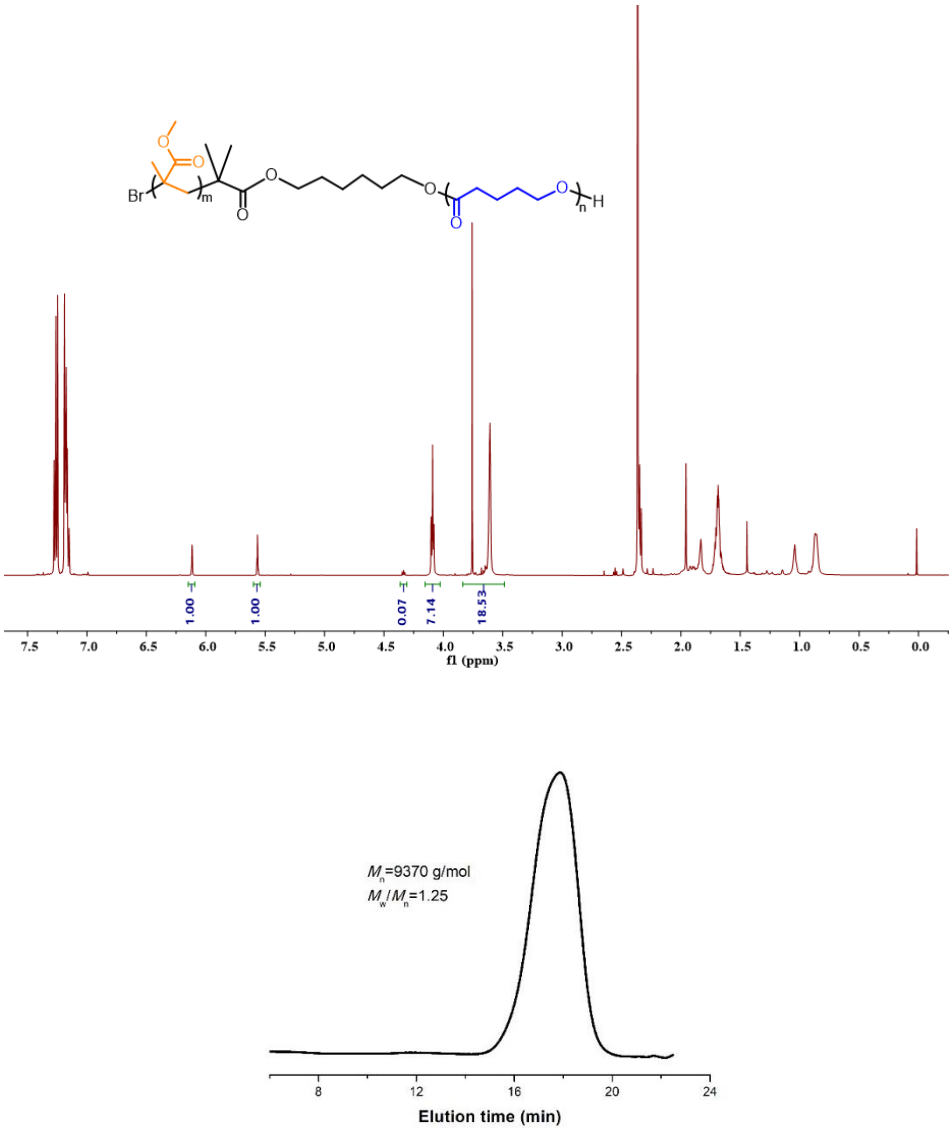


Figure S4. Conversion analysis by ^{1}H NMR ($CDCl_3$) of reaction mixture of one-pot sequential O-ATRP of MMA and ROP of VL, and the GPC trace (Table 2, Entry 1).

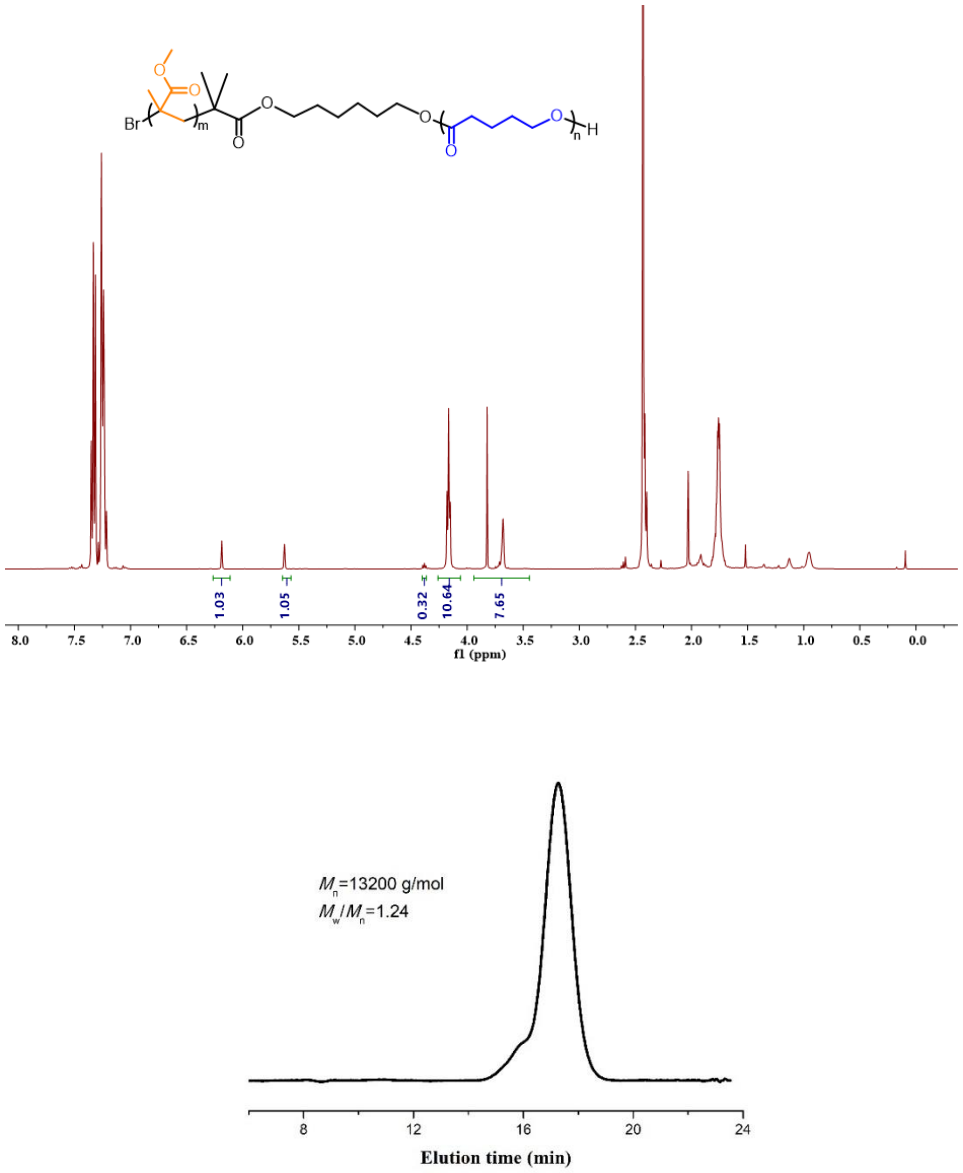


Figure S5. Conversion analysis by ^{1}H NMR spectrum ($CDCl_3$) of reaction mixture of one-pot sequential ROP of VL and O-ATRP of MMA, and the GPC trace (Table 2, entry 3).

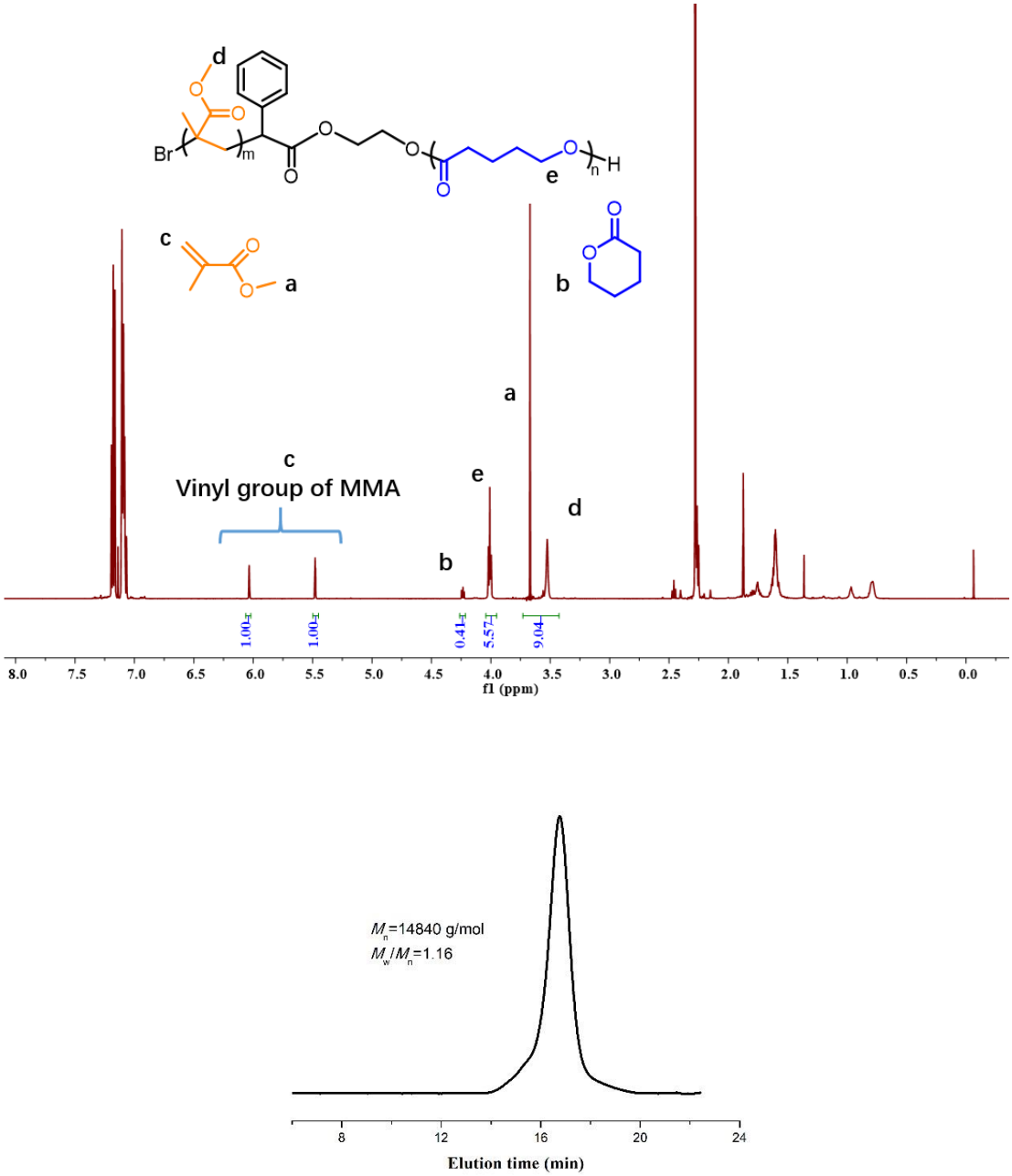


Figure S6. Typical ^{1}H NMR spectrum ($CDCl_3$) of reaction mixture of one-pot simultaneous ROP of VL and O-ATRP of MMA at the time of 15 h, and the GPC trace (Table 1, entry 5).

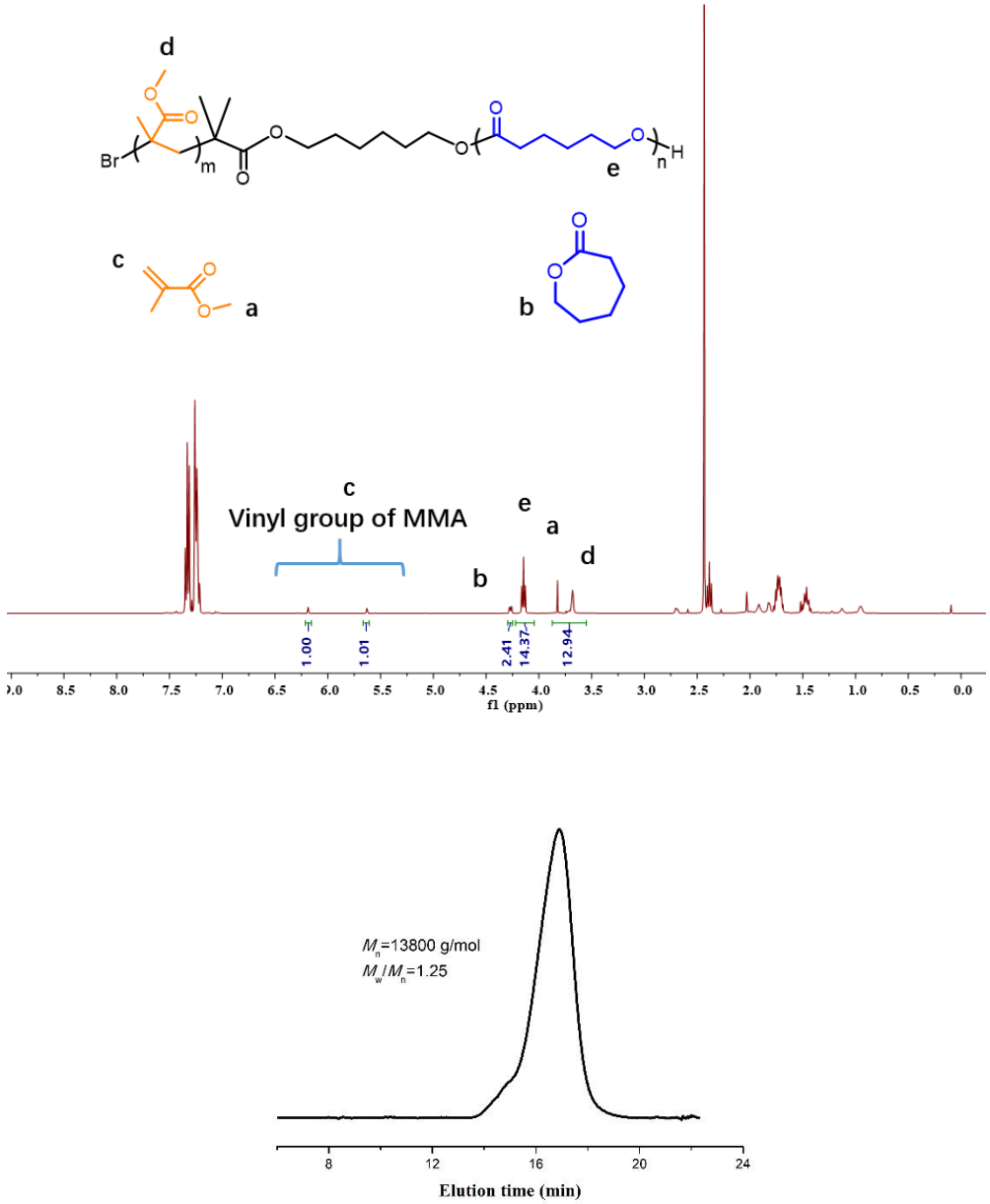


Figure S7. Typical ^{1}H NMR spectrum ($CDCl_3$) of reaction mixture of one-pot simultaneous ROP of CL and O-ATRP of MMA at the time of 28 h (Table 2, entry 9).

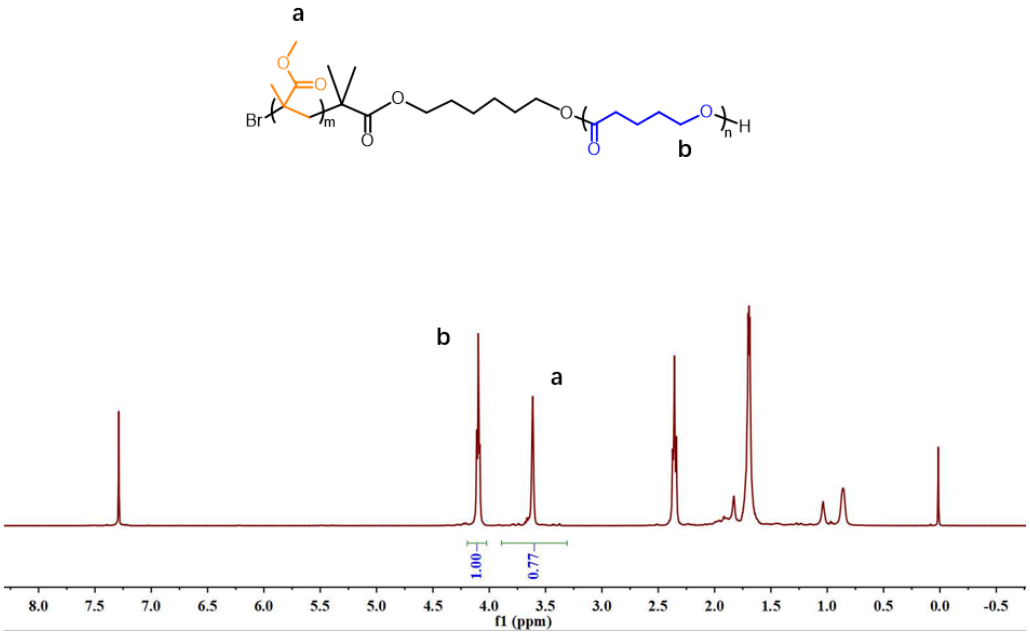


Figure S8. ^{1}H NMR spectrum ($CDCl_3$) of isolated PVL-*b*-PMMA diblock copolymer by simultaneous ROP of VL and O-ATRP of MMA.

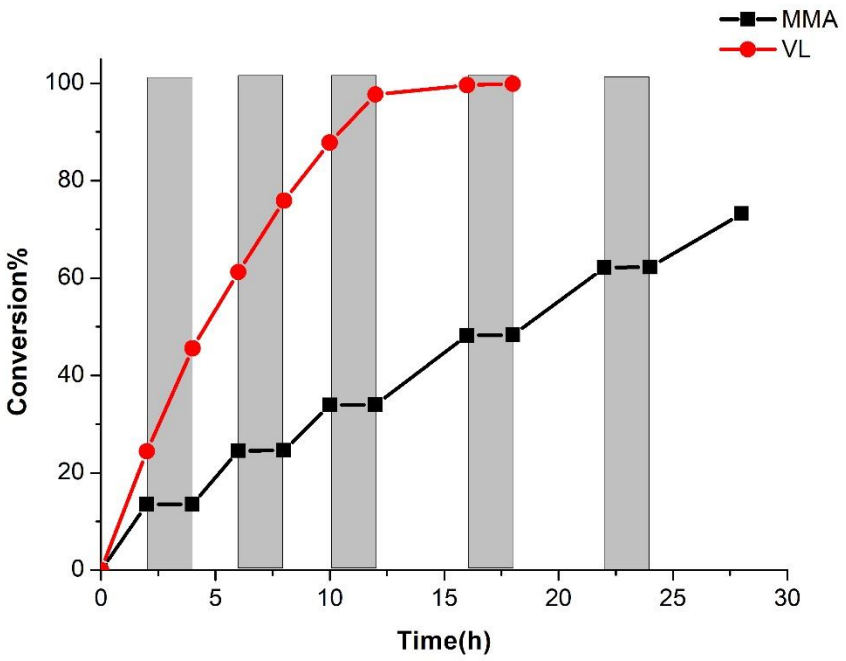


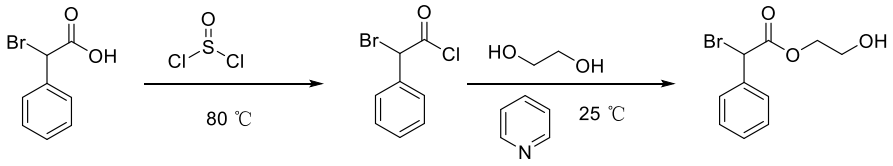
Figure S9. Light "ON/OFF" experiment on the simultaneous O-ATRP and ROP ($[VL]_0/[MMA]_0/[Photo\text{-}PA]_0 = 100/50/0.05$)

General procedure for kinetic study of one-pot simultaneous ROP of VL and O-ATRP of MMA

Kinetic experiments were performed in glovebox using a [δ-VL]: [MMA]: [HH-BrMP]: [Photo-PA] ratio of 100: 50: 1: 0.05 with 1.5 mL of toluene. The mixture was then irradiated by a purple bulb at room temperature. Aliquots were withdrawn by argon-purged syringes from the reaction mixture at predetermined interval times and analyzed by ^{1}H NMR ($CDCl_3$) and GPC (THF) to measure the conversions, number average molecular weights (M_n), and polydispersities (M_n/M_w).

Synthetic of Dual Initiators and Photo-PA

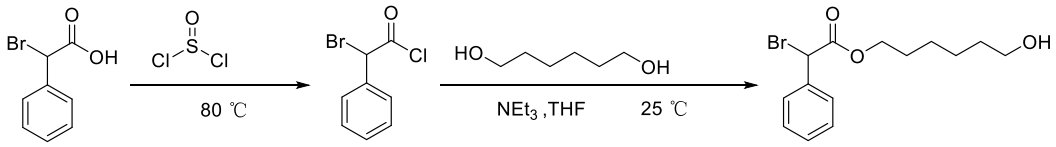
Synthesis of 2-hydroxyethyl 2-bromo-2-phenylacetate(HE-BrPA)[1]



HE-BrPA

A mixture of 2-bromo-2-phenylacetic acid (10.0 g, 46 mmol, 1 eq.) and thionyl chloride (10.9 g, 92 mmol, 2 eq.) was stirred at 80 °C for 1 h. Then, the mixture was evaporated under reduced pressure. The compound was added to a mixture of pyridine (3.8 g, 48 mmol) and ethylene glycol (113.9 g, 1.8 mol) over 30 min at 25 °C, and sequentially stirred for 1 h. The solution was diluted with dichloromethane, extracted with saturated aqueous $NaHSO_3$ and water. Then the mixture was dried on $MgSO_4$ under vacuum to obtain product HE-BrPA (yield: 59%).^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.58 – 7.46 (m, 2H); 7.43-7.32 (m, 3H); 5.41 (s, 1H); 4.36-4.23 (m, 2H); 3.86-3.78 (m, 2H).

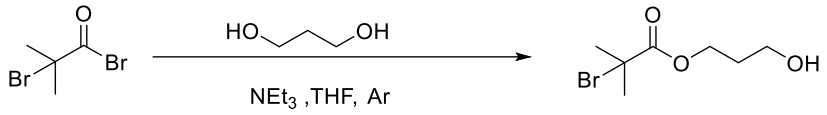
Synthesis of -hydroxyhexyl 2-bromo-2-phenylacetate (HH-BrPA)[1]



HH-BrPA

A mixture of 2-bromo-2-phenylacetic acid (2 g, 9.3 mmol) and thionyl chloride (2.1 g, 18.6 mmol) was stirred at 80 °C for 4 h. Then, the mixture was evaporated under reduced pressure. The compound was added to a mixture of NEt_3 (0.94 g, 9.3 mmol), hexylene glycol (44 g, 0.37mol) and THF (15 mL) over 30 min at 0 °C under argon, and sequentially stirred for 24 h at room temperature. Then the mixture was evaporated under reduced pressure. The solution was extracted with ethyl acetate, washed with 10% (v/v) HCl, brine and water. Then the mixture was dried on $MgSO_4$ under vacuum to obtain product HH-BrPA (yield: 65%).^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.60 – 7.54 (m, 2H); 7.43-7.35 (m, 3H); 5.37 (s, 1H); 4.26-4.14 (m, 2H); 3.70-3.60 (m, 2H); 1.73-1.63 (m, 2H); 1.62-1.51 (m, 2H); 1.43-1.31 (m, 4H).

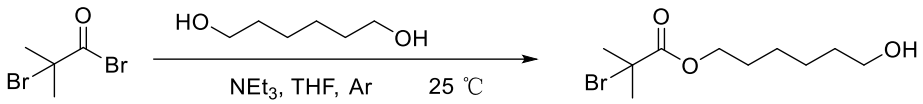
Synthesis of 3-hydroxypropyl 2-bromo-2-methylpropanoate(HP-BrMP)[2]



HP-BrMP

1,3-Propanediol (16.7 g, 0.22 mol) and NEt_3 (1.11 g, 10 mmol) were stirred in THF (30 mL) and cooled in an ice bath. 2-bromoisobutyrylbromide (2.50 g, 10 mmol) in THF (20 mL) was added dropwise under argon and the reaction mixture was stirred overnight at room temperature. The mixture was filtered and the solvent evaporated on a rotary evaporator. The resultant clear oil was taken up in diethyl ether (100 mL) and the organics washed with 10% (v/v) HCl (3*30 mL), brine (3*30 mL) and water (3*30 mL). The organic layer was dried with $MgSO_4$ and the solvent was removed on a rotary evaporator. The product was purified by column chromatography (with 2/3 ethyl ether/hexane as eluting solvent), resulting in a clear oil product (HP-BrMP, yield: 71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 4.31 (t, J = 6.1 Hz, 2H); 3.71 (t, J = 6.1 Hz, 2H); 1.90 (s, 6H); 1.89-1.93 (m, 2H)

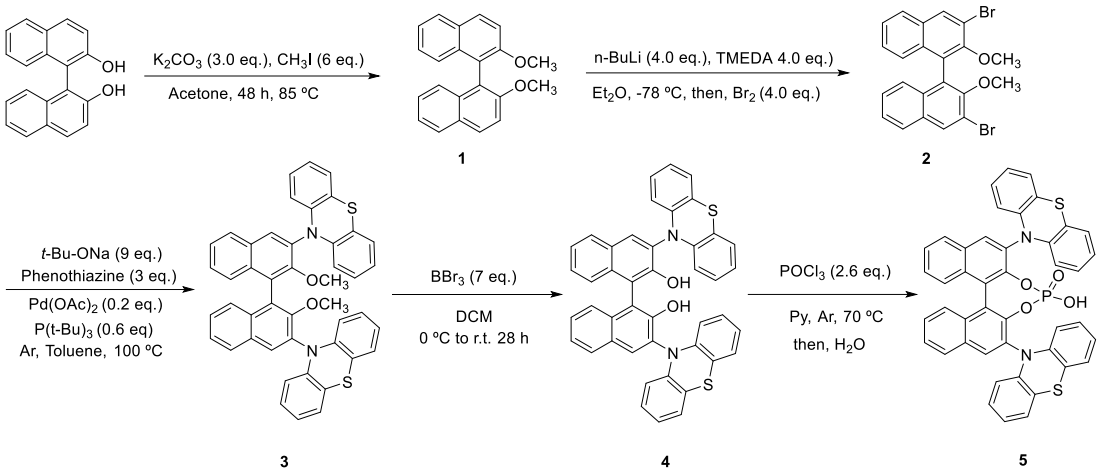
Synthesis of 6-hydroxyhexyl 2-bromo-2-methylpropanoate(HH-BrMP)[2,3]



HH-BrMP

1,6-Hexanediol (47.3 g, 400 mmol) and NEt_3 (2.22 g, 20 mmol) were stirred in THF (60 mL) and cooled in an ice bath. 2-bromoisobutyrylbromide (5.00 g, 20 mmol) in THF (40 mL) was added dropwise under argon and the reaction mixture was stirred overnight at room temperature. The mixture was filtered and the solvent evaporated on a rotary evaporator. The resultant clear oil was taken up in diethyl ether (200 mL) and the organics washed with 10% (v/v) HCl (3*60 mL), brine (3*60 mL) and water (3*60 mL). The organic layer was dried with $MgSO_4$ and the solvent removed on a rotary evaporator. The product was purified by column chromatography (with 2/3 ethyl ether/hexane as eluting solvent), resulting in a clear oil product (HH-BrMP, yield: 75%).^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 4.06 (t, J = 6.3 Hz, 2H); 3.52 (t, J = 6.5 Hz, 2H); 1.81 (s, 6H); 1.60-1.55 (m, 2H); 1.51-1.44 (m, 2H), 1.34-1.26 (m, 4H).

Synthesis of Bi-functional catalyst (Photo-PA)



Synthesis of compound **1**:

A solution of K_2CO_3 (2.28 g, 16.5 mmol) and 1,1'-bi-2-naphthol (BINOL, 1.81 g, 5.5 mmol) in anhydrous acetone (60 mL) was stirred at room temperature for 1 h under argon. Then 20 mL solution of CH_3I (4.68 g, 33 mmol) was added in one portion and keep refluxing at 85°C for reaction. After reflux under argon for 48 h, the solvent was evaporated. The mixture was then dissolved in DCM, and washed with distilled water for 3 times. The organic phase was dried over anhydrous Na_2SO_4, filtrated and evaporated. After rapid column chromatography over silica gel (DCM as eluent), compound 1 was obtained as a white solid. (yield: 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 8.01 (dd, 2H); 7.90 (d, *J* = 8.0 Hz, 2H); 7.49 (d, *J* = 8.1 Hz, 2H); 7.35 (t, *J* = 7.4 Hz, 2H); 7.24 (t, *J* = 7.6 Hz, 2H); 7.14 (d, *J* = 8.4 Hz, 2H); 3.80 (s, 6H).

Synthesis of compound **2**:

To a solution of compound 1 (3.14 g, 10 mmol) in 80 mL anhydrous THF, *n*-butyllithium (16 mL, 2.5 M in hexane, 40 mmol) and TMEDA (4.65 g, 40 mmol)was added slowly at -78 °C. The reaction mixture stirred at same temperature for 2 hours; then Br_2 (6.32 g, 40 mmol) was added dropwise by drop with a dropping funnel. The stirring was continued at room temperature for 3.5 hours before quenching excess of Br_2 with 50 mL of Na_2SO_3 solution. The crude product was isolated by extraction with EtOAc. The combined organic layers washed with brine; dried over Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica gel using hexane/EtOAc as eluent isolating compound **2** as a pale yellow solid. (yield: 69%) ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 8.29 (s, 2H); 7.84 (d, *J* = 8.4 Hz, 2H);

7.44 (t, *J* = 7.6 Hz, 2H); 7.30-7.24 (m, 2H); 7.10 (d, *J* = 8.4 Hz, 2H); 3.53 (s, 6H).

Synthesis of compound **3**:

A three-neck round bottom flask was charged with compound 2 (0.2 g, 0.43 mmol), Phenothiazine (0.254 g, 1.29 mmol), *t*-BuONa (0.368 g, 3.87 mmol), $Pd(OAc)_2$ (0.242 g, 0.08 mmol) under argon. The flask was vacuumed and refilled with argon for three times. Anhydrous toluene (15 mL) and $P(t\text{-}Bu)_3$ (0.66ml, 0.28mmol) was injected in the flask under stirring and argon. The mixture was heated for further reaction at 101 °C for 12 h. After cooling down to room temperature, quenching the reaction system with water. The mixture was filtrated and the washed with DCM. Then the resulting liquid was extracted with DCM and water. The organic layer was dried with $MgSO_4$ and the solvent removed on a rotary evaporator. And then purified further with column chromatography (20:1, *n*-hexane : ethyl acetate). The compound **3** was obtained as a light green needle solid. (yield: 42%) ^1H NMR (400 MHz, $CDCl_3$): δ (ppm): 8.08 (s, 2H); 7.94 (d, *J* = 8.0 Hz, 2H); 7.48 (t, *J* = 7.4 Hz, 2H); 7.38 (t, *J* = 7.6 Hz, 2H); 7.32 (d, *J* = 8.0 Hz, 2H); 7.00 (d, *J* = 7.8 Hz, 4H); 6.87-6.74 (m, 8H); 6.38 (d, *J* = 8.0 Hz, 4H); 3.54 (s, 6H).

Synthesis of compound **4**:

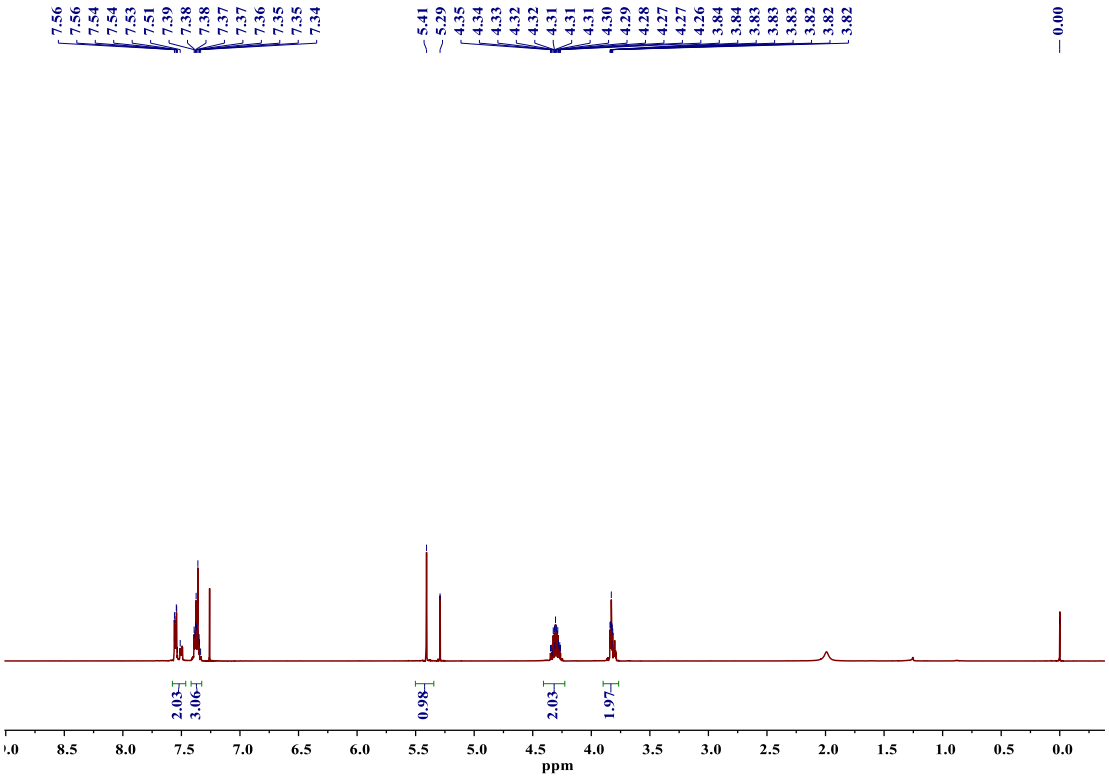
A three-neck round bottom flask was vacuumed and refilled with argon for three times. The flask was charged with compound 3 (0.335 g, 0.47 mmol) and 30 mL anhydrous DCM under argon. The BBr_3 (0.83 g, 3.3 mmol) in 3 mL anhydrous DCM was added dropwise under argon at 0 °C. The reaction mixture was stirred for 24 h till the detection of the disappearance of compound 3 at room temperature. After cooling down to 0 °C, quenching the reaction system with 15 mL water. The mixture was extracted with DCM two times. The organic layer was dried with $MgSO_4$ and the solvent removed on a rotary evaporator. And then purified further with column chromatography(4:1, Petroleum ether : Dichloromethane).The compound **4** was obtained as a light green powder solid. (yield: 86%) ^1H NMR (400 MHz, $CDCl_3$): δ (ppm): 8.21 (s, 2H); 7.98 (d, *J* = 8.0 Hz, 2H); 7.52-7.38 (m, 4H); 7.35 (d, *J* = 8.0 Hz, 2H); 7.15 (d, *J* = 8.0 Hz, 2H); 7.03-6.88 (m, 8H); 6.62 (d, *J* = 7.8 Hz, 4H); 6.11 (s, 2H).

Synthesis of compound **5** (**Photo-PA**):

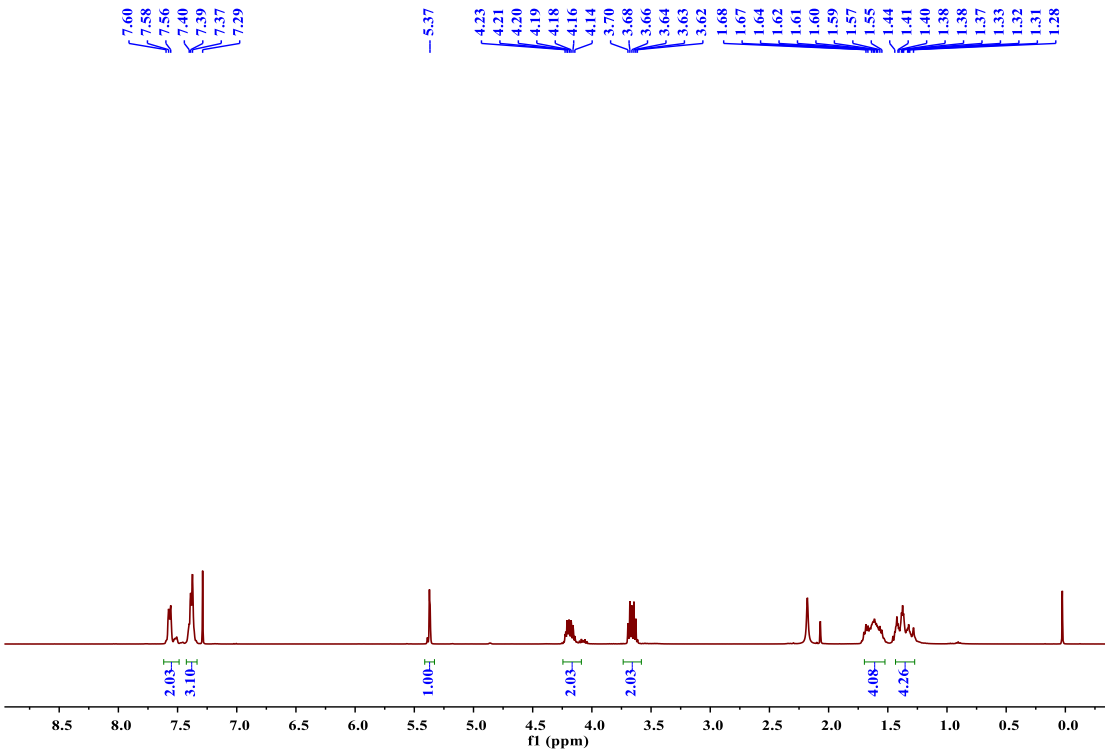
A three-neck round bottom flask was vacuumed and refilled with argon for three times. The flask

was charged with compound 4 (0.095 g, 0.14 mmol), 3 mL anhydrous pyridine, $POCl_3$(0.056 g, 0.36 mmol) under argon and stirred for 6 h at 70 °C. After cooling down to room temperature, water (10 mL) was added and then the mixture was heated at 140 °C to reflux for 3~5 h. After cooling down to room temperature, 8 mL HCl (3 M) was added and stirred for 0.5 h and then 5~8 mL DCM was added. The mixture was extracted with DCM and washed with HCl (4 M) three times. The organic layer was dried with Na_2SO_4 and the solvent removed on a rotary evaporator. And then purified further with column chromatography (50:1, dichloromethane : methanol). The final product (**Photo-PA**) was obtained as a brown yellow solid. (yield: 55%) ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 8.24 (s, 2H); 8.01 (d, *J* = 8.0 Hz, 2H); 7.62-7.52 (m, 2H); 7.46-7.35 (m, 4H); 6.88-6.54 (m, 12H); 6.40 (d, *J* = 7.6 Hz, 4H); 4.6 (s, br). ^{31}P NMR(162 MHz, $CDCl_3$): 2.09 ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm): 147.3, 143.3, 133.8, 132.4, 132.1, 131.4, 128.4, 127.3, 127.1, 127.0, 126.4, 125.9, 124.9, 122.5, 118.9, 116.5. HRMS (ESI): *m/z* calculated for $C_{44}H_{26}N_2O_4PS_2$: 741.1066, found 741.1080.

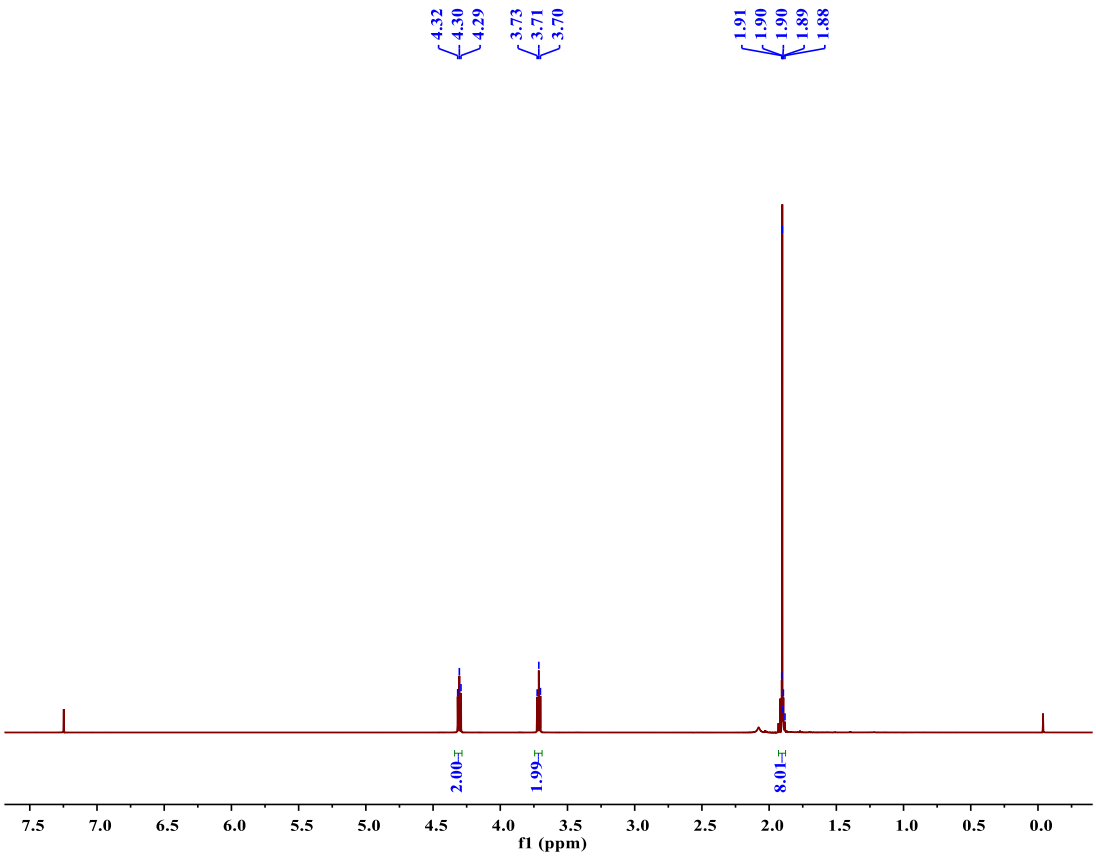
NMR spectra



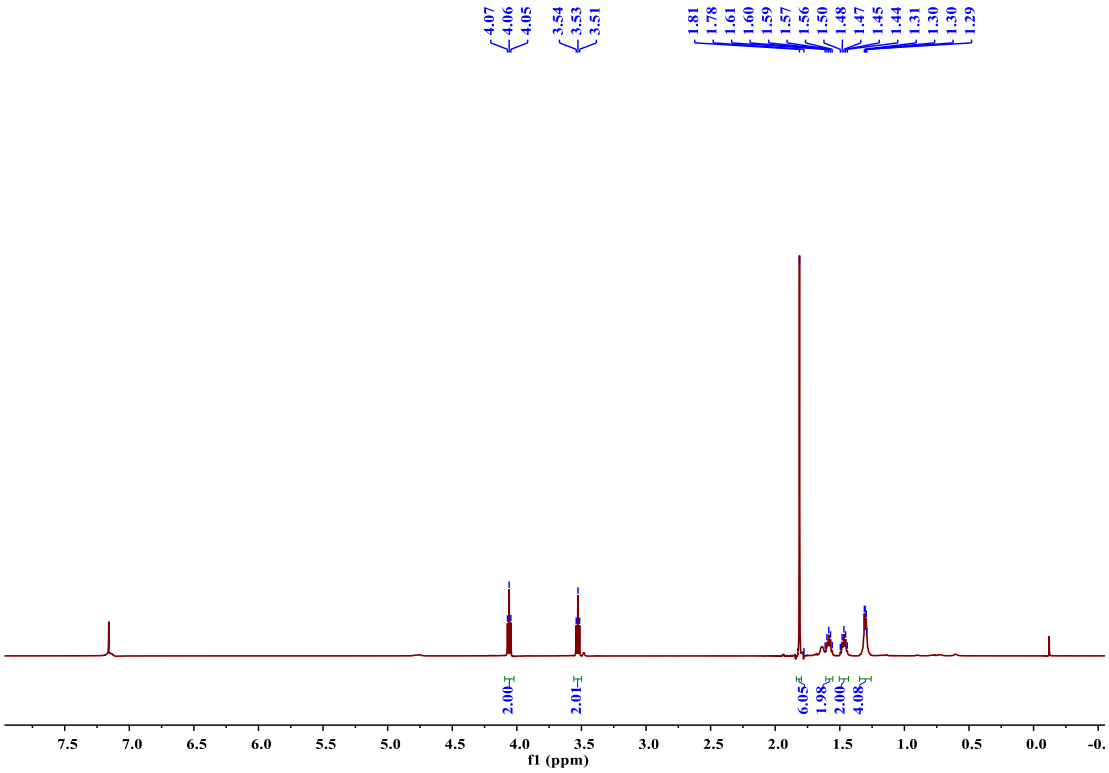
^{1}H NMR Spectrum of HE-BrPA



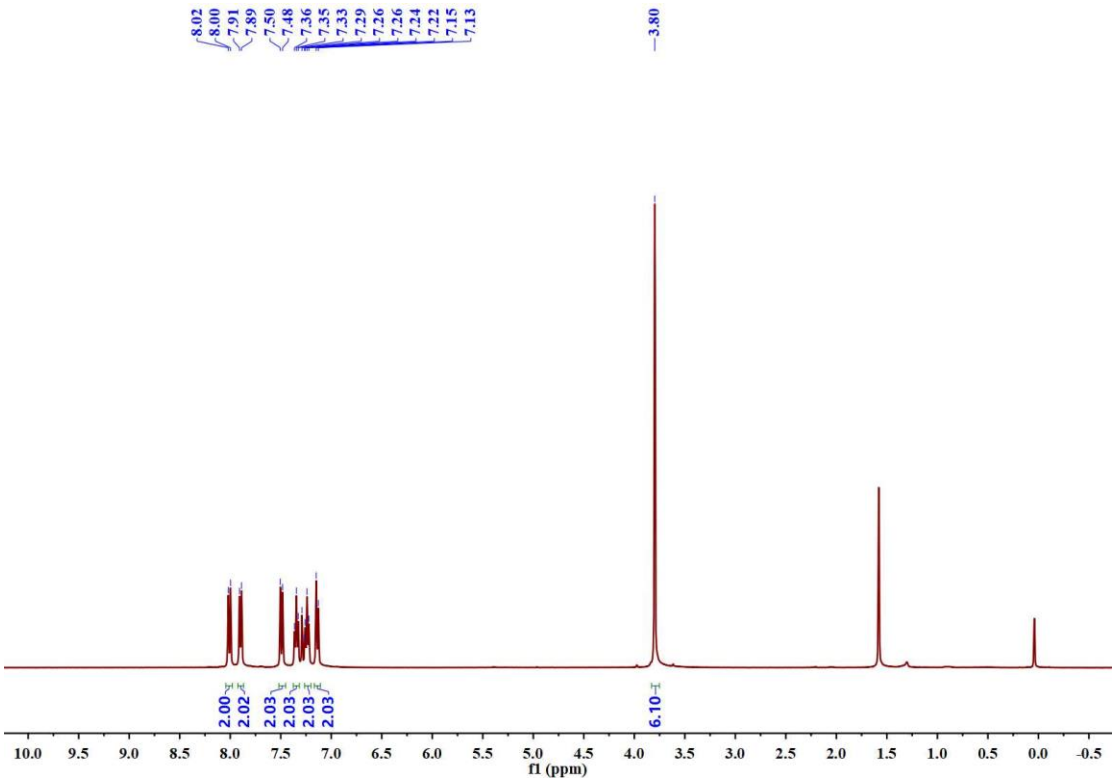
^{1}H NMR Spectrum of HH-BrPA



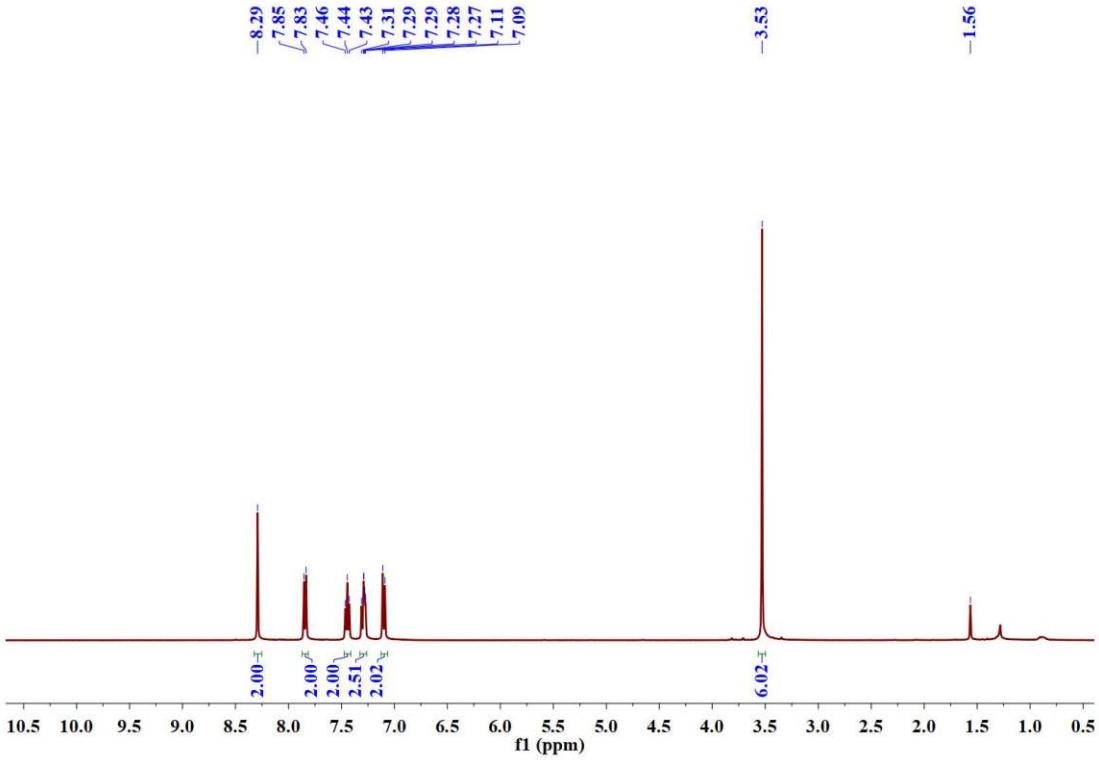
^{1}H NMR Spectrum of HP-BrMP



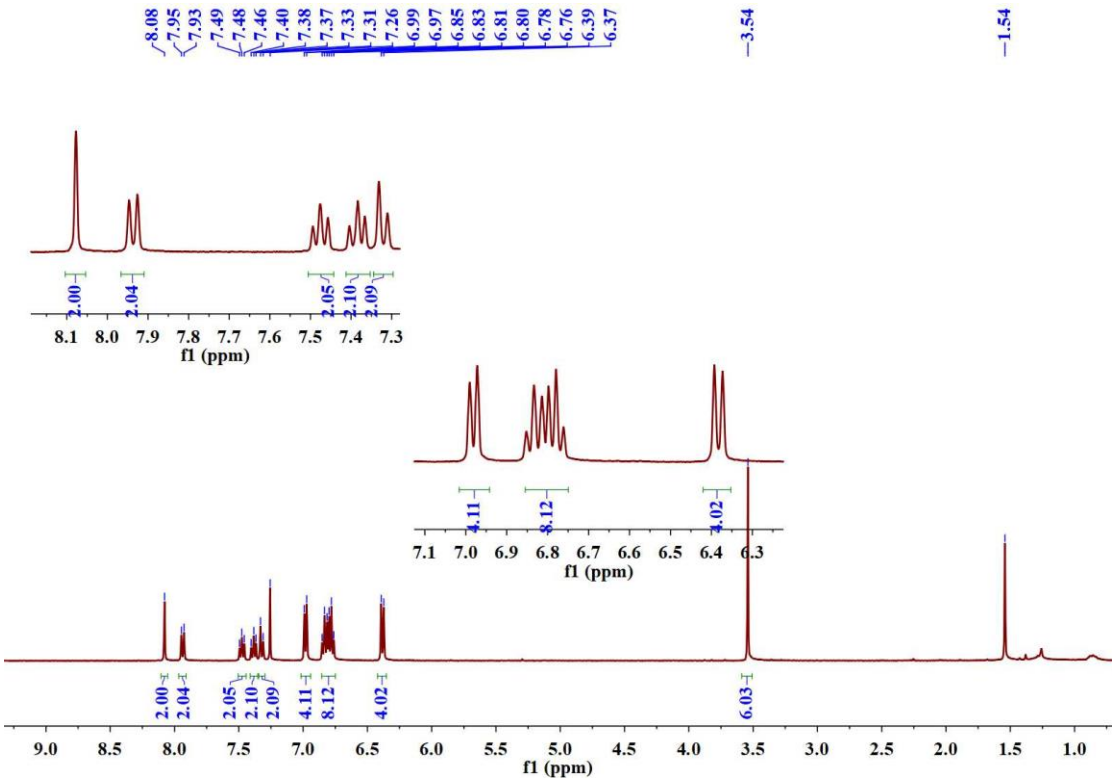
^{1}H NMR Spectrum of HH-BrMP



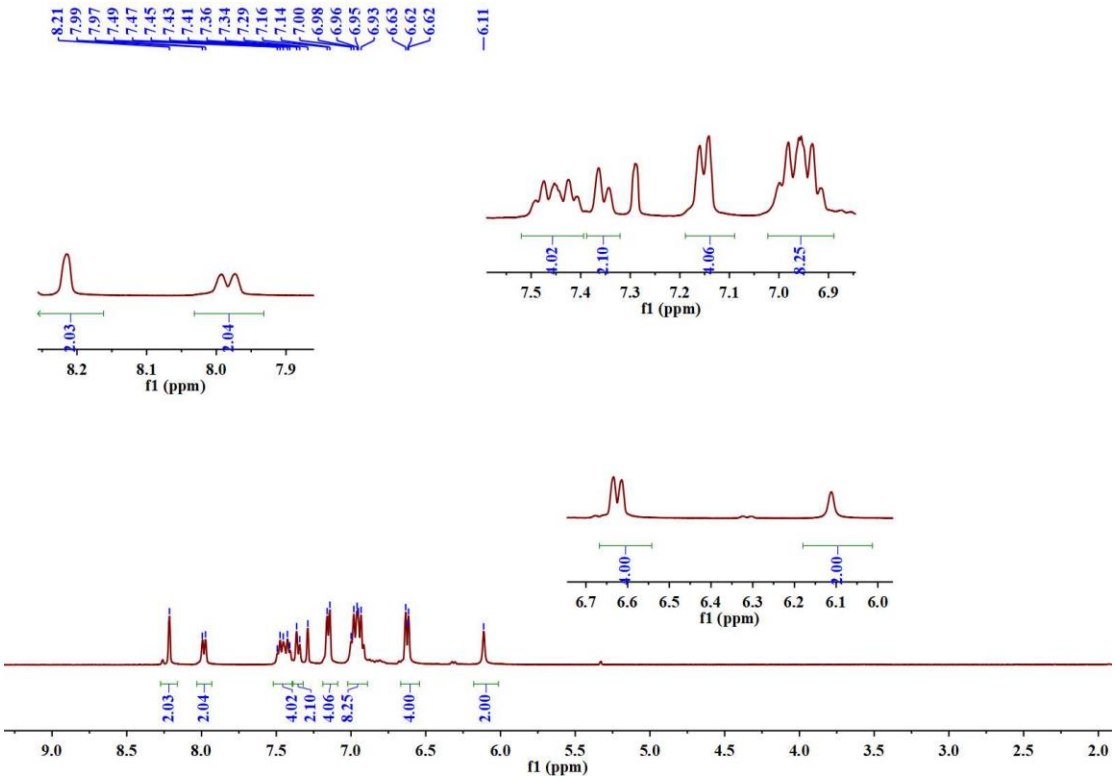
^{1}H NMR Spectrum of Compound 1



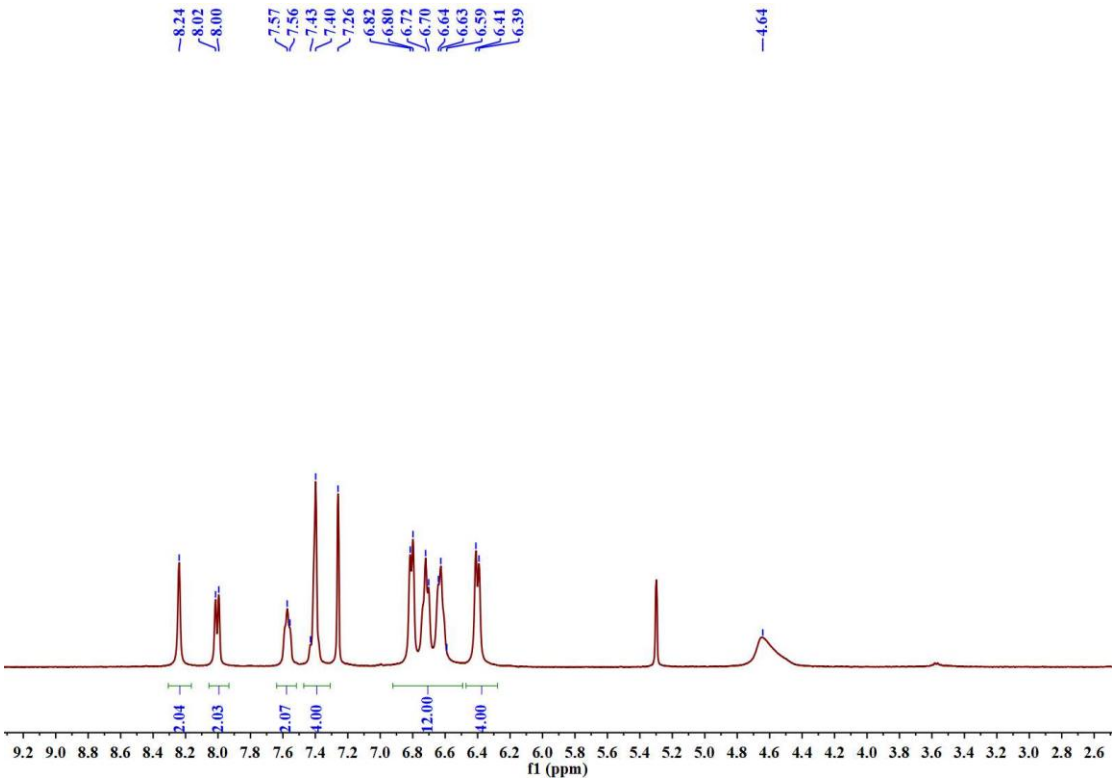
^{1}H NMR Spectrum of Compound 2



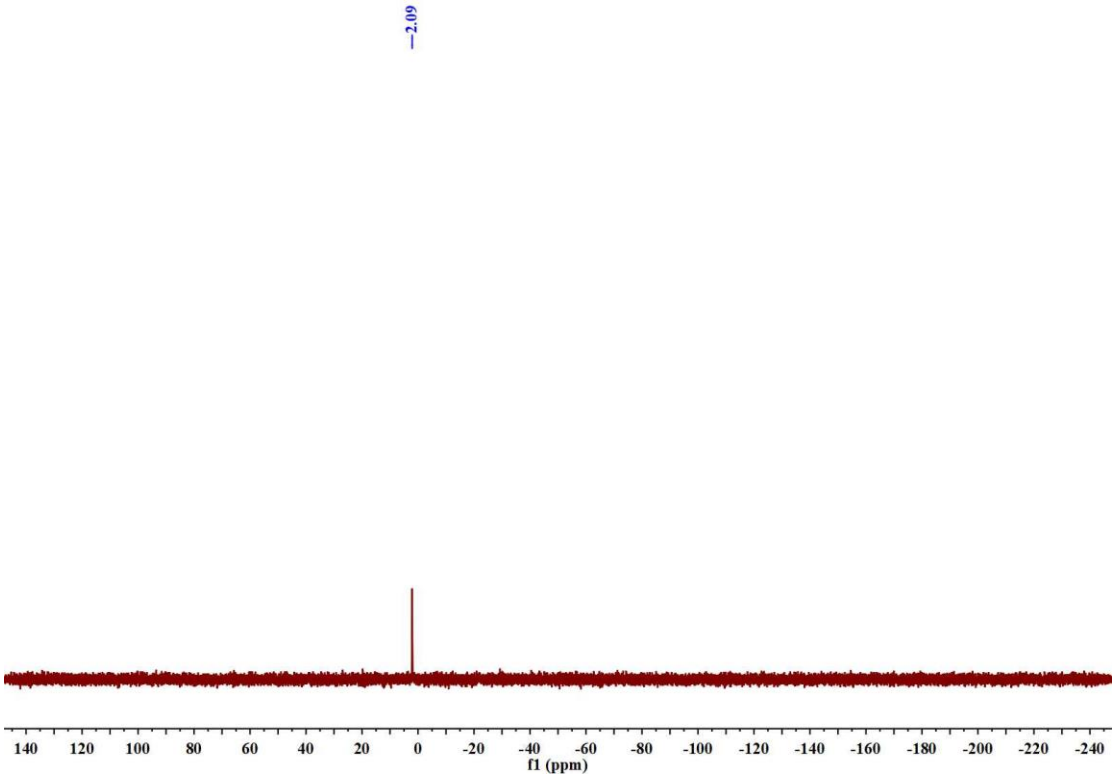
[1]H NMR Spectrum of Compound 3



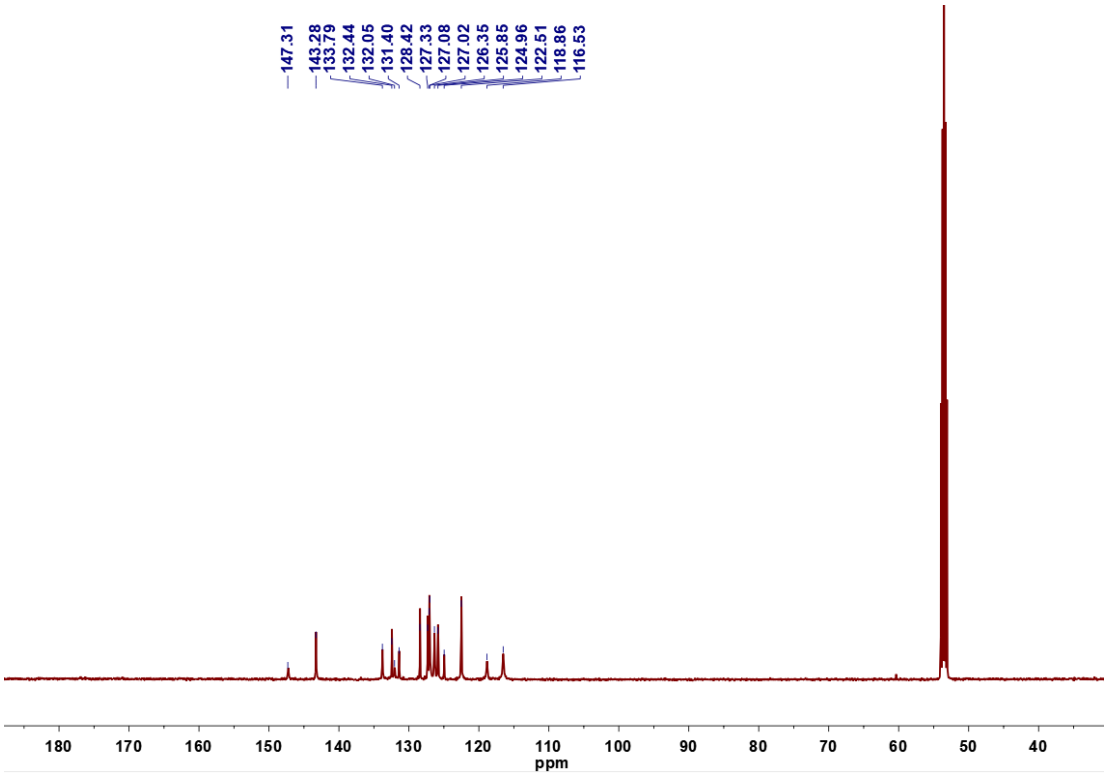
[1]H NMR Spectrum of Compound 4



^{1}H NMR Spectrum of Compound 5 (Photo-PA)



^{31}P NMR Spectrum of Compound 5 (Photo-PA)



^{13}C NMR Spectrum of Compound 5 (Photo-PA)

Reference

1. F. Li, W. Yang, M. Li, L. Lei, *Polym. Chem.* 2019, **10**, 3996-4005.
2. C. Aydogan, C. Kutahya, A. Allushi, G. Yilmaz, Y. Yagci, *Polym. Chem.* 2017, **8**, 2899-2903.
3. C. N. Urbani, C. A. Bell, M. R. Whittaker, M. J. Monteiro, *Macromolecules* 2008, **41**, 1057-1060.
4. N. J. Treat, H. Sprafke, J. W. Kramer, P. G. Clark, B. E. Barton, J. Read de Alaniz; B. P. Fors, C. J. Hawker, *J. Am. Chem. Soc.* 2014, **136**, 16096-101.