

Supporting Information

Intrinsically Photosensitive Polyimide Photoresist and Its Double Cross-linking Mechanism

Peng Yang,^{Δ*}a Haiping Yu,^{Δa} Yuting Zhu,^a Xiaonuo Liu,^a Pin Liu,^b Xu Wang,^{*a} and Bo Tang^{*a}

^aShandong Provincial Key Laboratory of Photoresistors, College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan 250014, China.

^bSuntific Materials, Ltd. Weifang, 261061, China.

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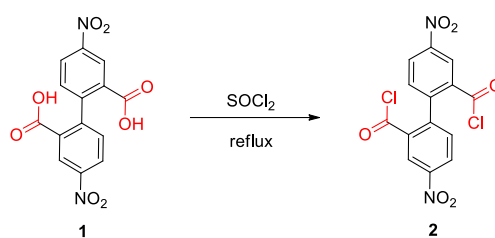
1. General information

All NMR spectra were acquired on Bruker AV 400 MHz NMR spectrometers. ¹H NMR chemical shifts were recorded relative to SiMe₄ (δ 0.00). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets) and m (multiplet). The number of protons (n) for a given resonance was indicated by nH. Coupling constants were reported as a *J* value in Hz. ¹³C NMR chemical shifts were recorded relative to solvent resonance (CDCl₃: δ 77.00). High-resolution mass spectrometry (HRMS) were recorded on a Bruker micro-TOF mass spectrometer using electrospray ionization (ESI), positive ion mode. Fourier transform infrared (FT-IR) Spectra were recorded on the Bruker ALPHA FT-IR Spectrometer, ranging from 500 to 4000 cm⁻¹. Thermogravimetric analysis/differential scanning calorimeter (TGA/DSC) was carried out on TA/Q600 in N₂ atmosphere at 10°C min⁻¹ from 30°C to 800°C. Ultraviolet-visible (UV-Vis) spectra were performed on a Shimadzu UV-6100 spectrophotometer. Gel permeation chromatography (GPC) analysis was performed on Agilent 1260 equipped PLgel MIXED-C using DMA (HPLC grade) as the eluent at 35°C with a flow rate of 1 mL·min⁻¹. Scanning electron microscope (SEM) images were recorded on a SU8010 instrument. Electrical properties were measured on a Keysight Agilent E4980A precision LCR meter.

Reagents 4,4'-dinitro-[1,1'-biphenyl]-2,2'-dicarboxylic acid, 2-hydroxyethyl methacrylate (HEMA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) were purchased from Bide Pharmaceutical Technology Co. Ltd. (China) and stored in a N₂-filled glove-box before use. N-methyl pyrrolidone (NMP) were dried over 4 Å molecular sieves. Unless noted otherwise, commercially available chemicals were used as received without purification. Flash column chromatographies were performed using the indicated solvent system on silica gel (200-300 mesh).

2. Synthesis of monomer

Synthesis of 4,4'-dinitro-[1,1'-biphenyl]-2,2'-dicarbonyl dichloride (**2**)¹



Under nitrogen atmosphere, a suspension of 4,4'-dinitro-[1,1'-biphenyl]-2,2'-dicarboxylic acid **1** (5.0 g, 15 mmol) in excess SOCl_2 (150 mL) were heated to reflux until the disappearance of diacid **1**. The reaction mixture was cooled and concentrated under reduced pressure until all the SOCl_2 had been removed to obtain crude product **2** as a white solid. Yield: 99 %. The product was directly used for the next step.

^1H NMR (400 MHz, DMSO-d_6) δ 8.68 (d, $J = 2.5$ Hz, 2H), 8.45 (dd, $J = 8.4, 2.5$ Hz, 2H), 7.54 (d, $J = 8.4$ Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 165.4, 148.0, 146.9, 131.6, 131.2, 126.0, 124.4

HRMS (ESI): calculated for $\text{C}_{14}\text{H}_6\text{Cl}_2\text{N}_2\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$: 390.9501, found: 390.9506.

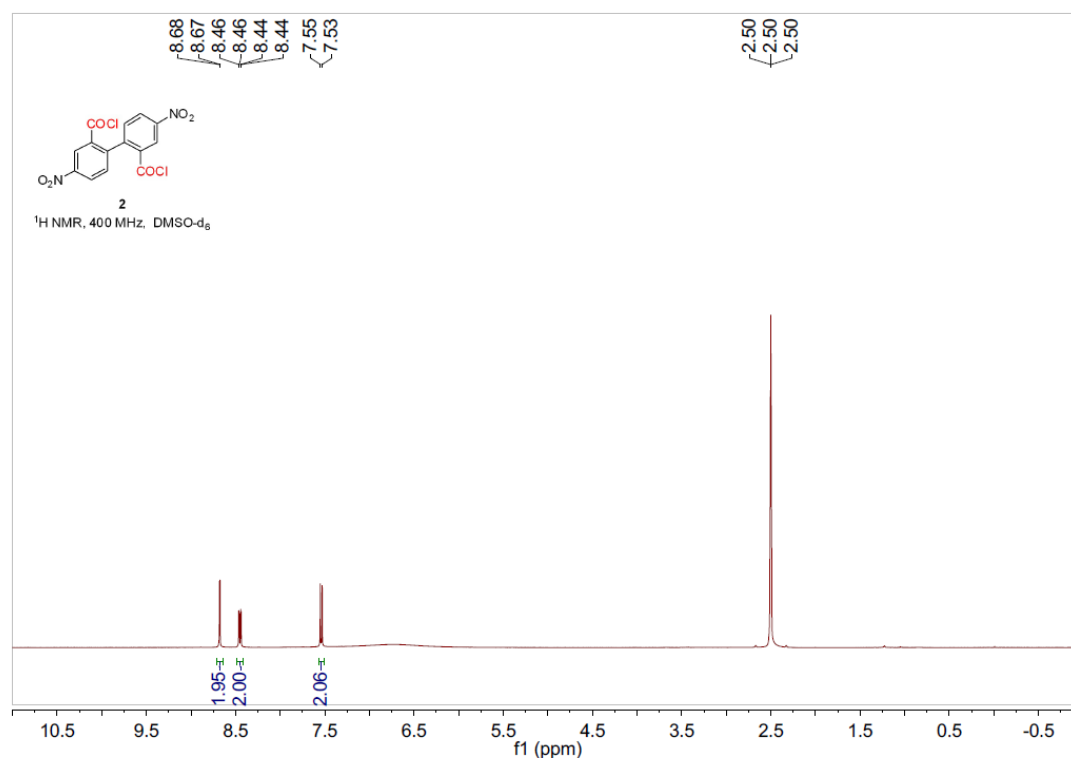


Figure S1. ^1H NMR spectrum of compound **2**.

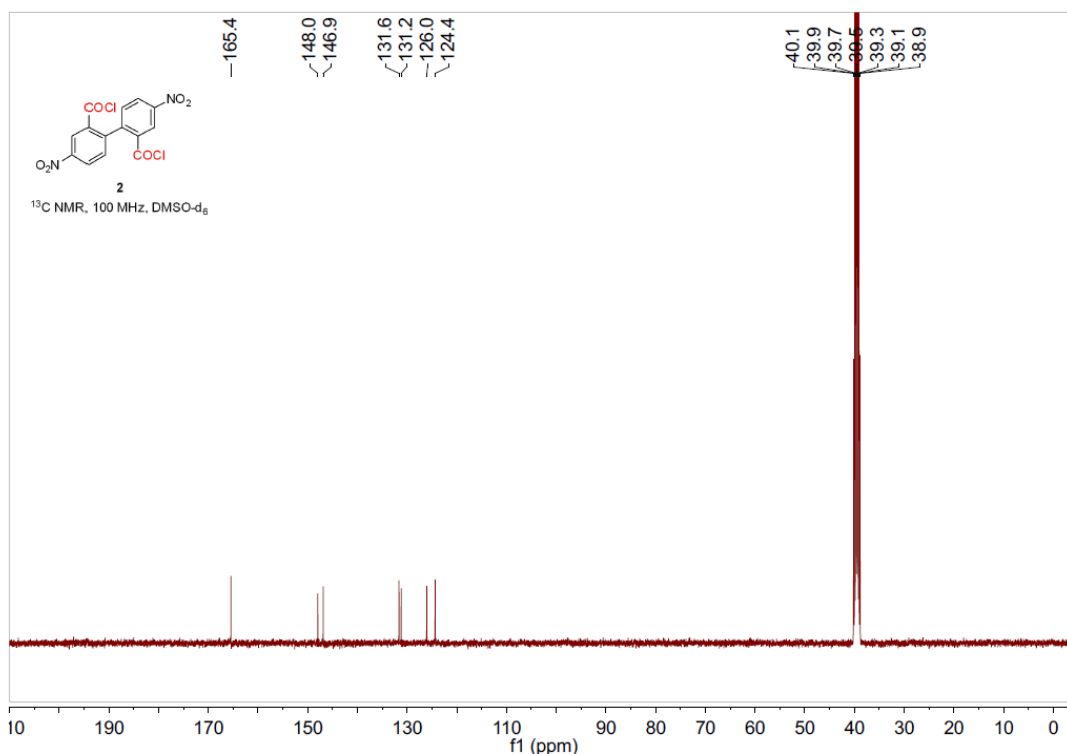
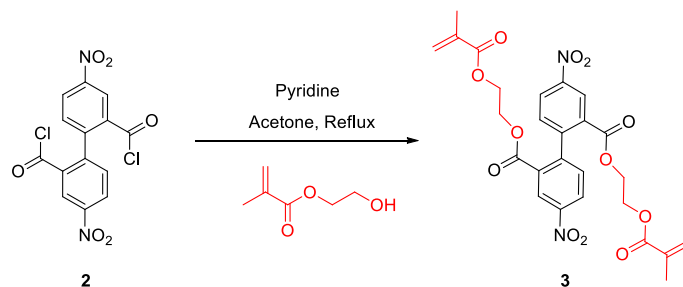


Figure S2. ¹³C NMR spectrum of compound **2**.

Synthesis of bis(2-(methacryloyloxy)ethyl) 4,4'-dinitro-[1,1'-biphenyl]-2,2'-dicarboxylate (**3**)²



4,4'-Dinitro-[1,1'-biphenyl]-2,2'-dicarbonyl dichloride **2** (5.5 g, 15 mmol) and pyridine (1.2 mL, 15 mmol) were added to 7.2 mL of acetone at 0 °C. At the same temperature, 2-hydroxyethyl methacrylate (HEMA, 3.7 mL, 30 mmol) was added in drop-wise. Then the mixture was kept refluxing for 2 hours. After being cooled to room temperature, the reaction was quenched with water. The reaction mixture was extracted 3 times with dichloromethane (DCM) and dried by anhydrous Na₂SO₄. Solvent was removed and the residue was purified by silica gel column chromatography using ethyl acetate/hexane (5/1) as eluent. The product **3** is a yellow viscous liquid. Yield: 80%.

¹H NMR (400 MHz, CDCl₃) δ 8.92 (d, *J* = 2.3 Hz, 2H), 8.43 (dd, *J* = 8.4, 2.3 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 6.08 (s, 2H), 5.61 (s, 2H), 4.41-4.38 (m, 4H), 4.28-4.26 (m, 4H), 1.93 (s, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 166.8, 163.9, 147.7, 147.4, 135.7, 130.8, 129.9, 126.4, 126.2, 125.5, 63.5, 61.9, 18.1.

HRMS (ESI): calculated for $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_{12}\text{Na}$ $[\text{M}+\text{Na}]^+$: 579.1227, found: 579.1226.

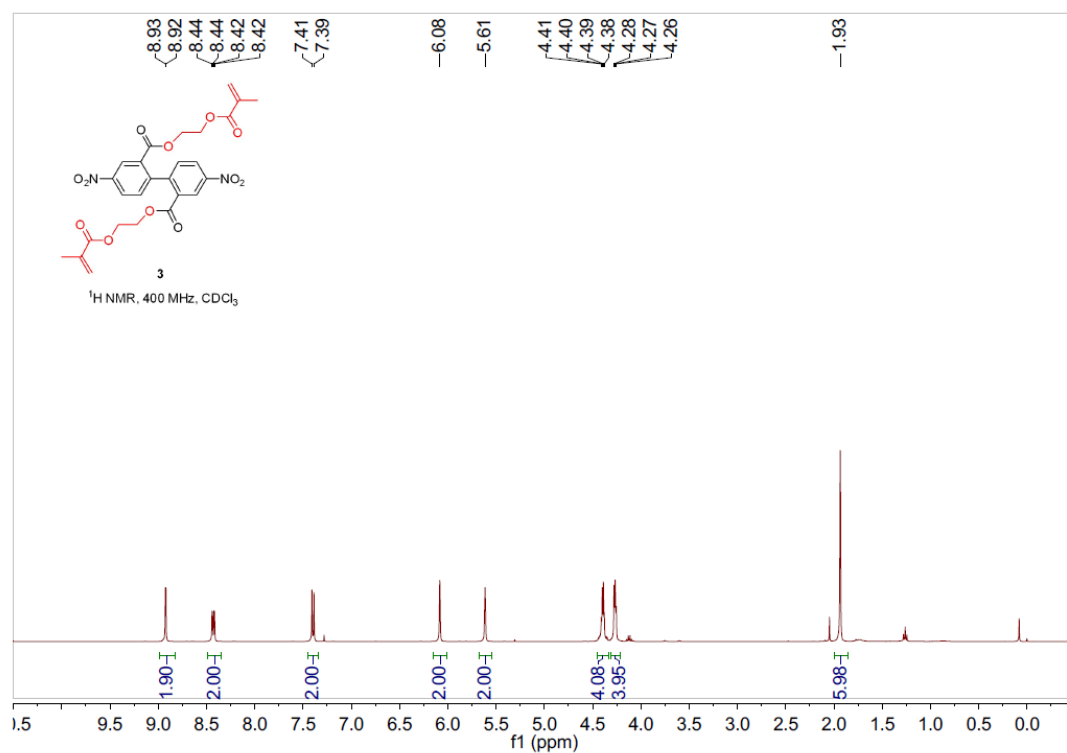


Figure S3. ^1H NMR spectrum of compound 3.

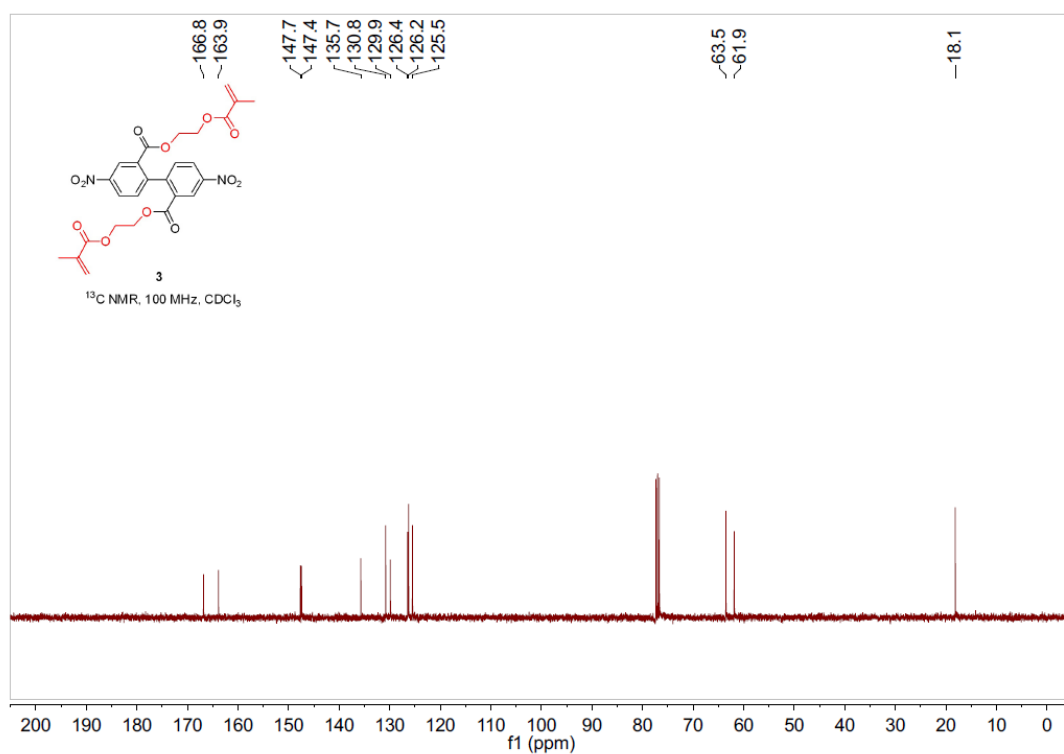
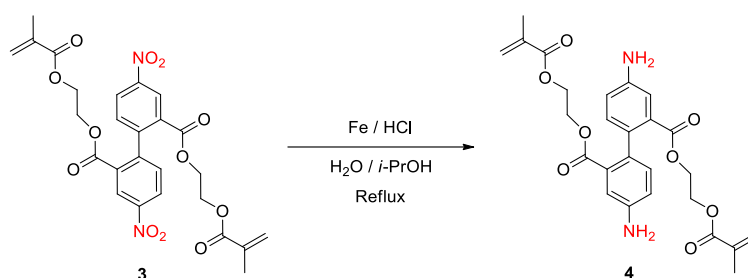


Figure S4. ^{13}C NMR spectrum of compound 3.

Synthesis of BMADA (4)²



Under nitrogen atmosphere, compound **3** (3.9 g, 7 mmol), iron powder (3.9 g, 70 mmol, 100 mesh) and concentrated HCl (70 μ L) were added to *i*-PrOH/water (11.2 mL/2.8 mL) and the mixture was heated to reflux for 15 minutes. After cooled to room temperature, an additional concentrated HCl (70 μ L) and iron powder (3.9g, 70 mmol, 100 mesh) were added to the reaction mixture. The reaction mixture was heated to reflux for one hour. After the full consumption of **3**, the mixture was filtered to remove the excess iron powder. Then the mixture was extracted 3 times with dichloromethane (DCM) and dried by anhydrous Na₂SO₄. Solvent was removed and the residue was purified by silica gel column chromatography using ethyl acetate/hexane (1/1) as eluent. The product **4** is a yellow viscous liquid. Yield: 76%.

¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, J = 2.3 Hz, 2H), 6.95 (d, J = 8.1 Hz, 2H), 6.77 (dd, J = 8.1, 2.4 Hz, 2H), 6.07 (s, 2H), 5.57 (s, 2H), 4.26-4.22 (m, 4H), 4.07-4.03 (m, 4H), 3.78 (s, 4H), 1.92 (s, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 167.1, 167.0, 145.2, 135.9, 133.3, 131.6, 130.2, 125.9, 118.1, 116.1, 62.4, 62.0, 18.2.

HRMS (ESI): calculated for C₂₆H₂₈N₂O₈Na [M+Na]⁺ : 519.1743, found: 519.1741.

FT-IR (cm⁻¹): 3370, 3461 (H-N-H, NH₂), 1702 (C=O, COOR), 1626 (C=C), 1164 (C-O-C)

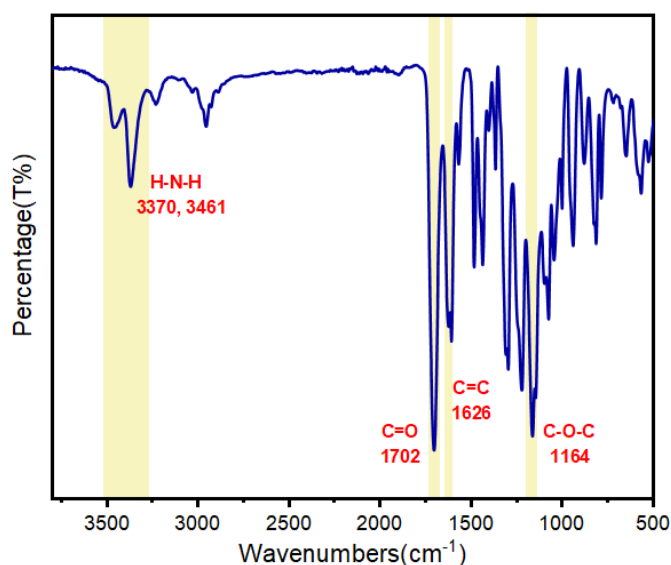


Figure S5. FT-IR spectrum of compound **4** (BMADA).

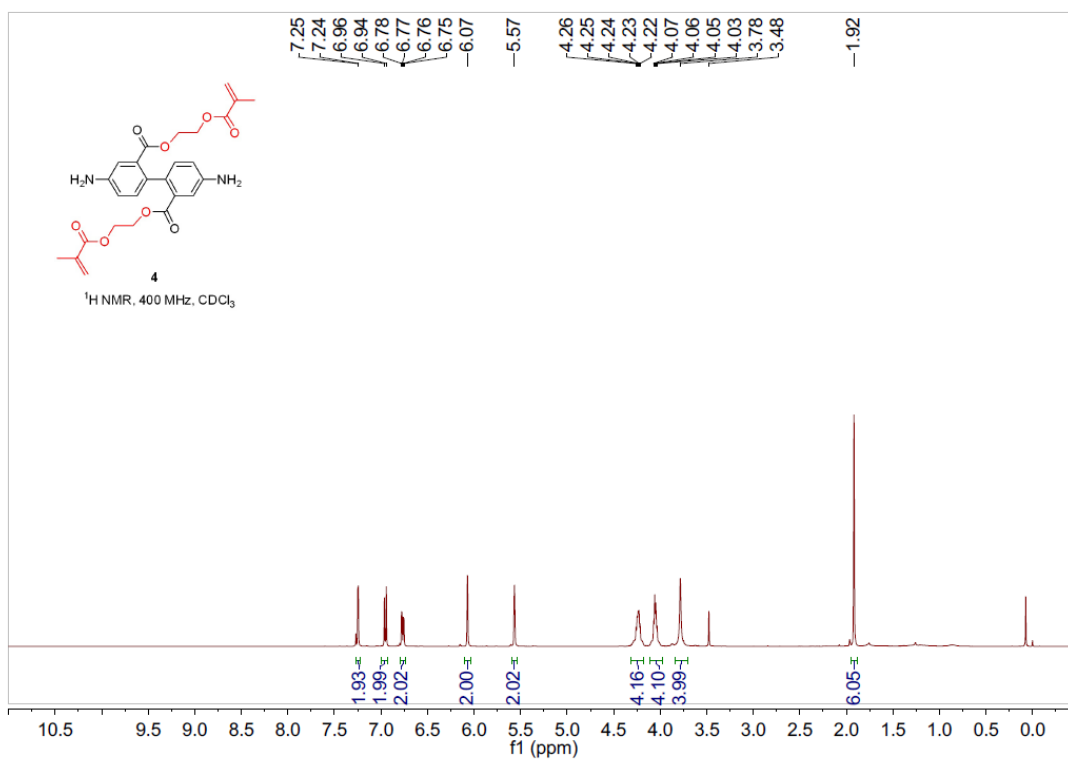


Figure S6. ¹H NMR spectrum of compound 4 (BMADA).

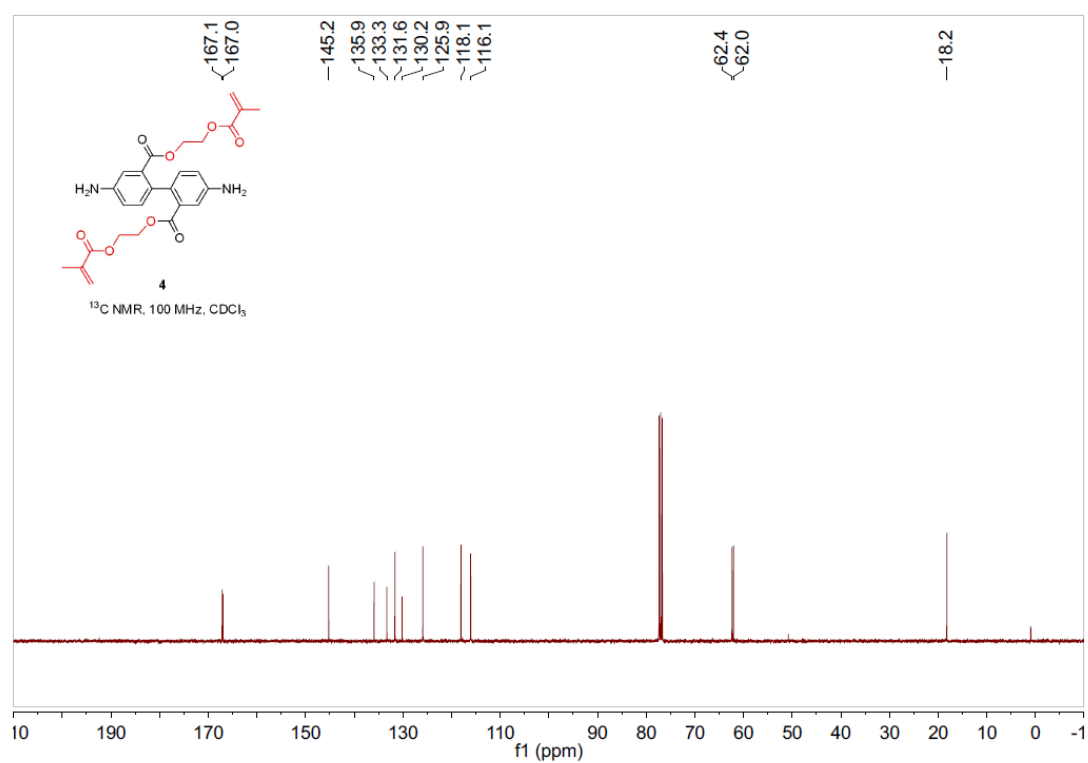
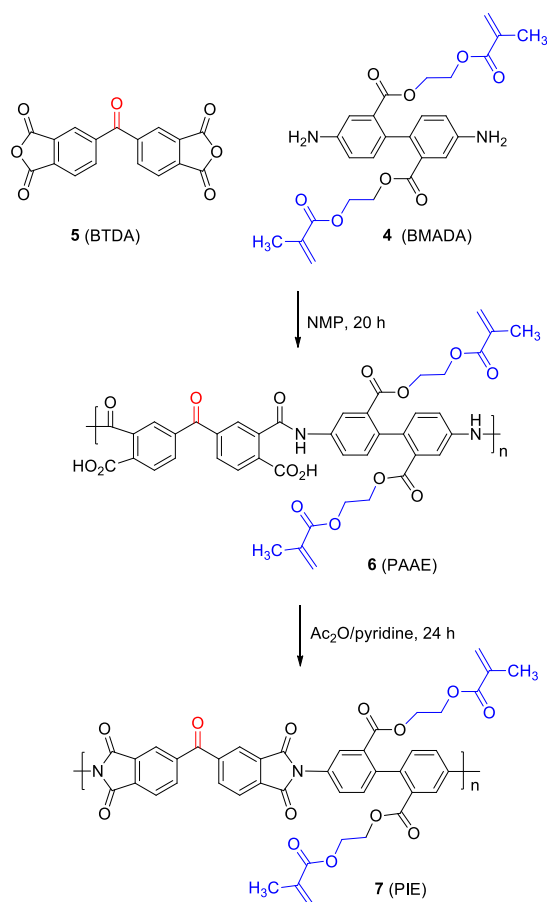


Figure S7. ¹³C NMR spectrum of compound 4 (BMADA).

3. Synthesis of photosensitive polyimide (PSPI)³



Synthesis of poly(amic acid ester) 6 (PAAE)

Under nitrogen atmosphere, BMADA **4** (3.0 g, 6 mmol) was added into a 100 mL flask containing ultra-dry NMP (20 mL). Transparent BMADA **4** solution was then obtained after stirring at 10 °C for 30 minutes. Then BTDA **5** (2.0 g, 6 mmol) was added with an additional NMP (7.6 mL) to give a reaction mixture with 15 wt% solid content. The temperature of the reaction mixture was increased to room temperature (25 °C) and the polymerization system was stirred at such temperature for 20 h to afford a highly viscous solution. The homogeneous PAAE **6** solution was then successively poured into aqueous ethanol solution (200 mL, 75 vol%) to afford the filament resin. The reaction was filtered and washed three times with methanol to obtain a yellow viscous solid. Then the yellow viscous solid was collected and dried at 60°C in vacuum overnight. The product **6** is a yellow solid.

¹H NMR (400 MHz, DMSO-d₆) δ 13.50 (brs, 2H), 10.78 (s, 2H), 8.30-8.26 (m, 3H), 8.11-8.06 (m, 2H), 8.01-7.94 (m, 2H), 7.87-7.81 (m, 3H), 7.19 (s, 2H), 5.97 (s, 2H), 5.65 (s, 2H), 4.25 (s, 4H), 4.09 (s, 4H), 1.84 (s, 6H).

FT-IR (cm⁻¹): 1707 (C=O, COOH), 1655 (C=O, CONH), 1523 (C-N).

Synthesis of polyimide ester 7(PIE)

Under nitrogen atmosphere, BMADA **4** (3.0 g, 6 mmol) was added into a 100 mL flask containing ultra-dry NMP (20 mL). Transparent diamine **4** solution was then obtained after stirring at 10 °C for 30 minutes. Then BTDA **5** (2.0 g, 6 mmol) was added with an additional NMP (7.6 mL) to give a reaction mixture with 15 wt% solid content. The temperature of the reaction mixture was increased to room temperature (25°C) and the polymerization system was stirred at such temperature for 20 h to afford a highly viscous solution. Then, the dehydration system of acetic anhydride (Ac₂O) (2.8 mL, 30 mmol), pyridine (1.9 mL, 24 mmol) and extra ultra-dry NMP (20 mL) were added to the solution, and the reaction mixture was stirred at 50 °C for another 24 h. The homogeneous PIE **7** solution was then successively poured into aqueous ethanol solution (200 mL, 75 vol%) to afford the filament resin. The resin was filtered and washed three times with methanol to obtain a yellow solid. Then the yellow solid was collected and dried at 60°C in vacuum overnight. The product **7** is a faint yellow solid.

¹H NMR (400 MHz, DMSO-d₆) δ 8.33-8.31 (m, 2H), 8.27-8.21 (m, 4H), 8.13 (s, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 2H), 5.96 (s, 2H), 5.64 (s, 2H), 4.28-4.27 (m, 2H), 4.13 (s, 2H), 1.81 (s, 6H).

FT-IR (cm⁻¹): 1776 (C=O), 1707 (C=O), 1363 (C-N-C), 717 (imide ring).

4. Characterization of photosensitive polyimide (PSPI)

4.1. ¹H NMR spectra

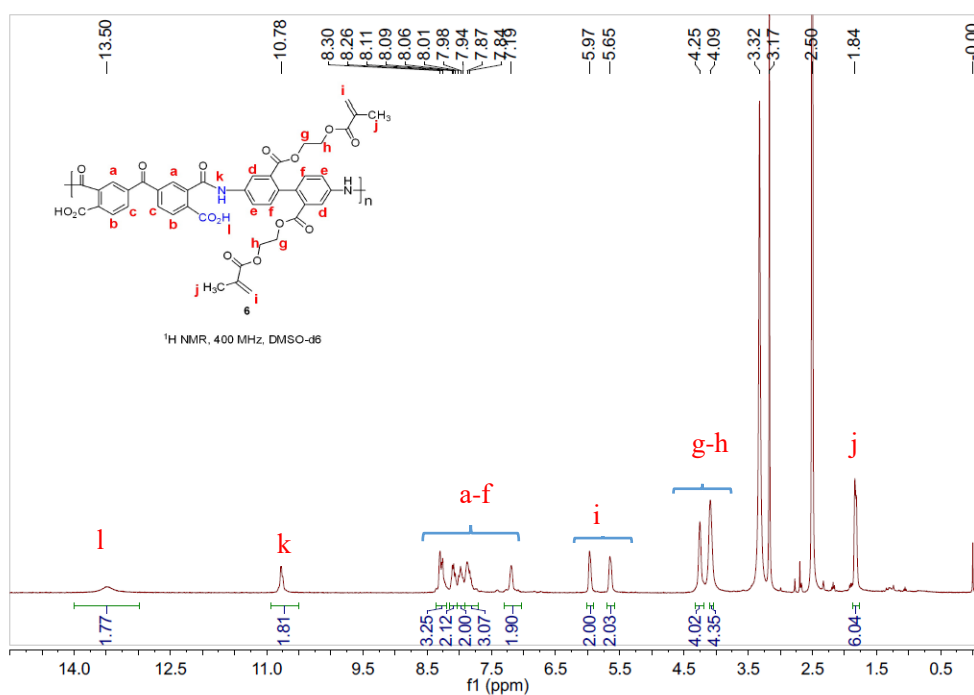


Figure S8. ^1H NMR spectrum of 6.

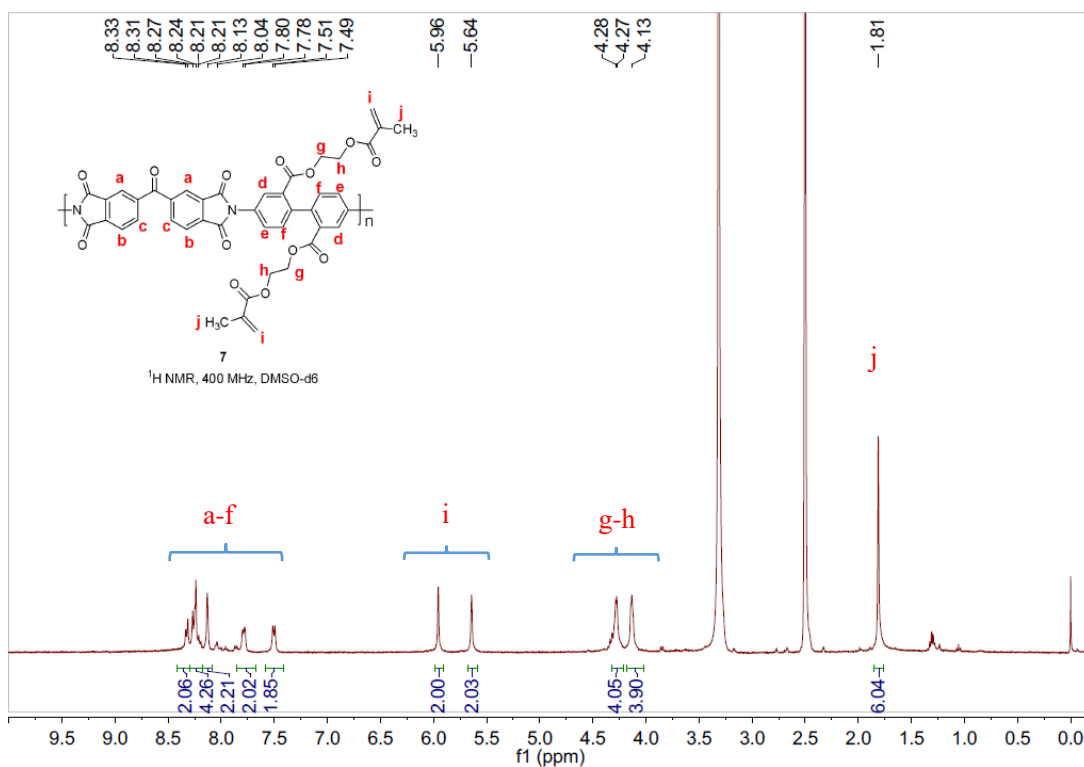


Figure S9. ^1H NMR spectrum of 7 in DMSO- d_6 .

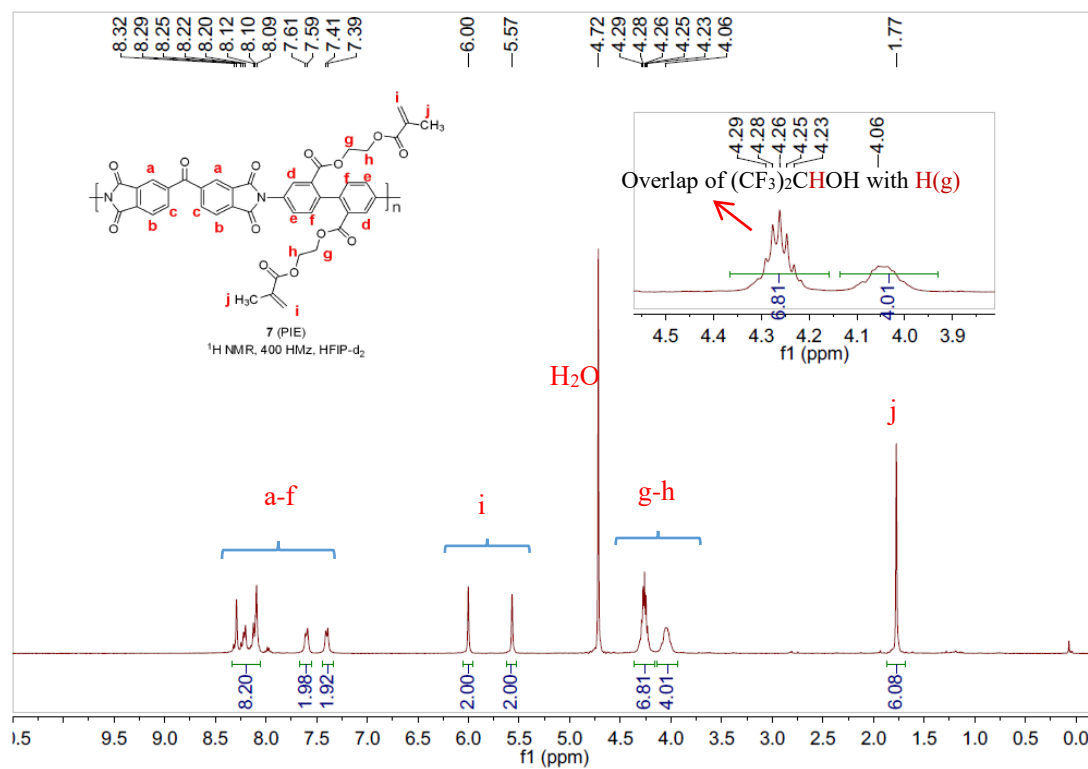


Figure S10. ^1H NMR spectrum of 7 in HFIP- d_2 .

4.2. FT-IR absorption spectra

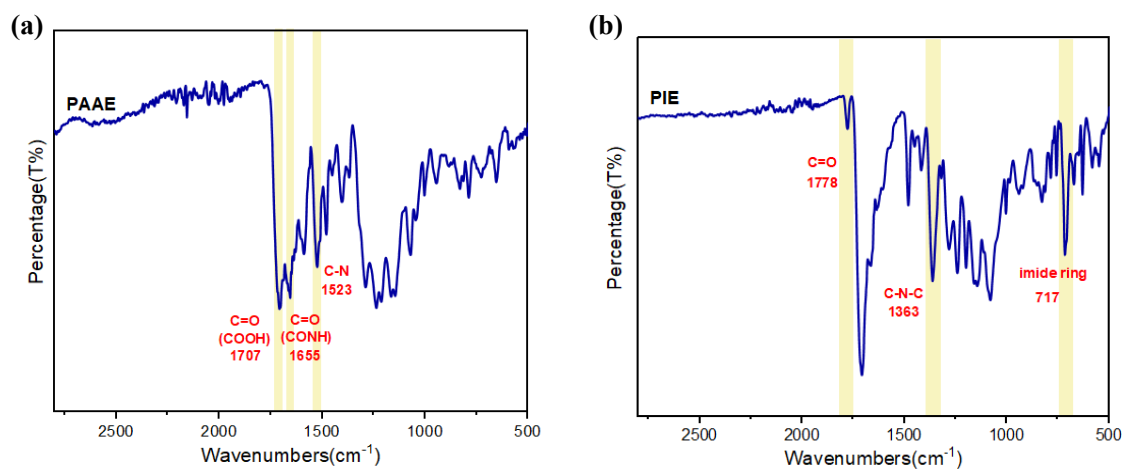


Figure S11. (a) FT-IR spectrum of **6**; (b) FT-IR spectrum of **7**.

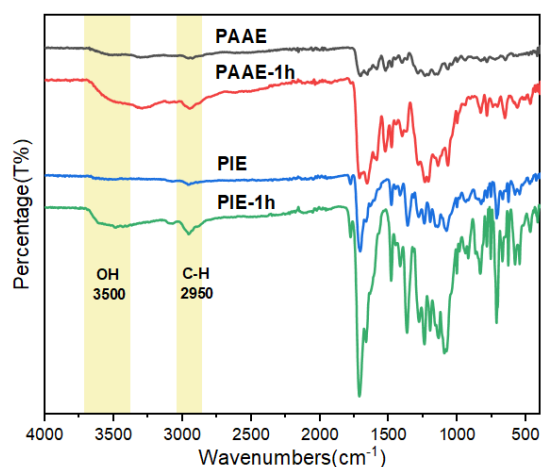


Figure S12. FT-IR spectra of PAAE **6** and PIE **7** films before and after 365 nm UV-light irradiation

4.3. Solubility

Table S1. Dissolution performance of **6** and **7**.

	Solubility							
	NMP	HFIP	DMA	DMF	DMSO	H ₂ O	MeOH	EtOH
PAAE	++	+/-	+/-	+/-	+/-	--	--	--
PIE	++	++	+/-	+/-	+/-	--	--	--

Qualitative solubility was determined with 5 mg of polymer in 0.5 mL of solvent.

++: dissolved completely; +/-: dissolved partly; --: insoluble completely.

NMP: N-methyl-2-pyrrolidone; HFIP: 1,1,1,3,3,3-hexafluoro-2-propanol;

DMA: N,N-dimethylacetamide; DMF: N,N-dimethylformamide; DMSO: dimethyl sulfoxide;

H₂O: primary water; MeOH: methanol; EtOH: ethanol.

4.4. Molecular weight

Table S2. Molecular weight of **6** and **7**.

sample	M_n (g/mol)	M_w (g/mol)	PDI
6	13355	29696	2.22
7	8336	12007	1.44

M_n : Number average molecular weight; M_w : Weight average molecular weight,
PDI: Polydispersity index, $PDI = M_w/M_n$.

4.5. TGA and DSC curves

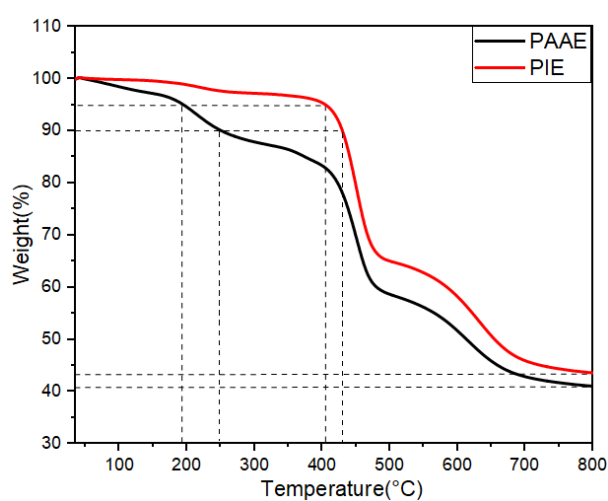


Figure S13. Thermogravimetric analysis (TGA) curves of PAAE **6** and PIE **7**.

(The heating rate is 10 °C/min. PAAE- $T_{5\%}$ = 195 °C, PAAE- $T_{10\%}$ = 250 °C, PAAE- R_{w800} = 41%
PIE- $T_{5\%}$ = 405 °C, PIE- $T_{10\%}$ = 430 °C, PIE- R_{w800} = 44%.)

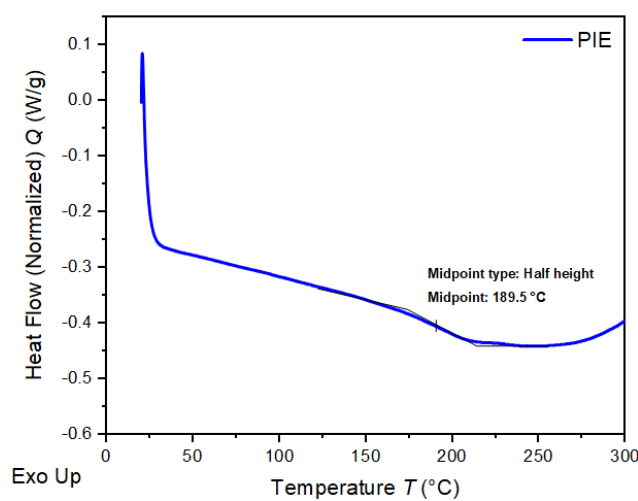


Figure S14. Differential Scanning Calorimetry (DSC) curve of **7**.

(The second round heating. The heating rate is 20 °C/min.)

4.6. UV-Vis absorption spectra

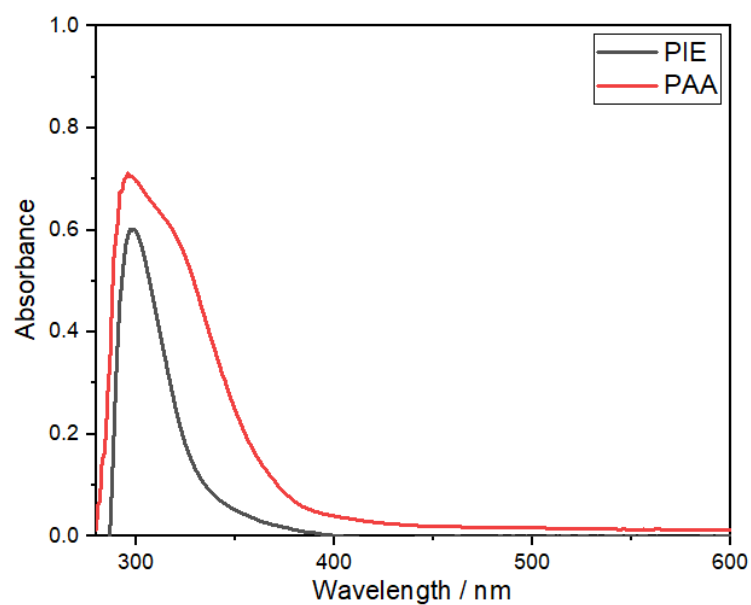


Figure S15. UV-vis absorption spectra of **6** and **7**.

PAAE- λ_{\max} = 296 nm, PIE- λ_{\max} = 299 nm.

4.7. Photosensitivity curve

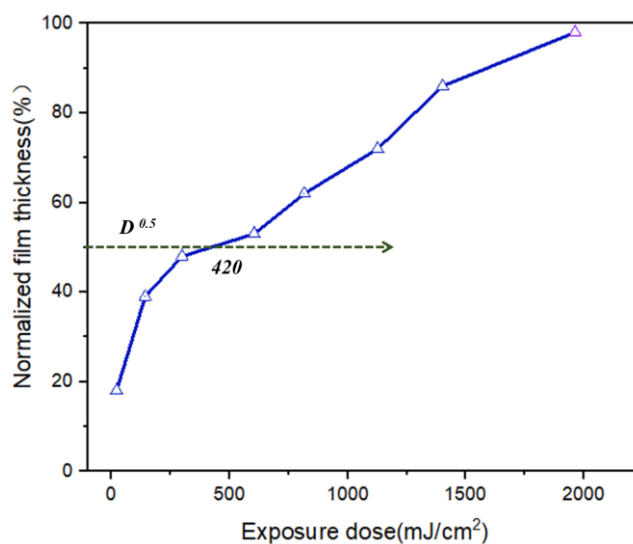


Figure S16. Characteristic UV-exposure curve of **6** (PAAE).

The photosensitivity was evaluated by the irradiation of the films with 365 nm UV-light and subsequent determination of the insoluble fraction after development as a function of exposure dose.

The exposure energy to attain a 0.5 gel fraction is about 420 mJ/cm²

4.8. Dielectric properties

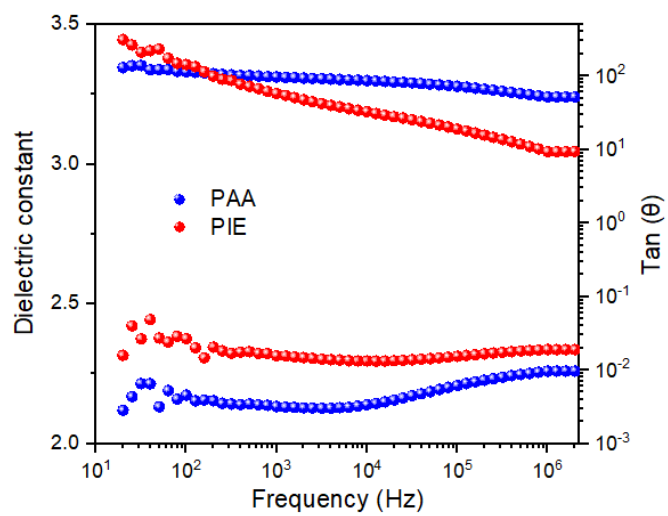


Figure S17. The dielectric constant curves of PAAE **6** and PIE **7**.

4.9. Photolithographic formability properties

Preparation of photoresist

PAAE 6 (1.0 g), OXE-1 (BASF, 0.01 g), dipentaerythritol hexaacrylate (0.03 g) and vinyltrimethoxysilane (0.1 g) were added to 9 g NMP solvent. The solution was sonicated for 1 hour. The photosensitive polymer solution was filtered through a 0.45 μm polytetrafluoroethylene membrane to remove impurities and obtain a completely dissolved homogeneous solution. (note: in our lab, a pure solution of PAAE 6 in NMP without any additives was used to demonstrate its photolithographic formability properties. But in industry, a small amount crosslinker (1%) and photoinitiator (0.1%) were added to the photoresist solution in order to compliant with industrial process/equipment and make better photolithographic patterns. The amount of additives is much lower than that of commercial photoresist.)

Table S3. Photolithographic process and the corresponding parameters.

Process	Parameters
Spin-coating	1000 r/20 s
Soft-bake	100 °C×3 min 480 nm
Exposure	i-line, 600 mj/cm ²
Develop	1% Na ₂ CO ₃ , 14s

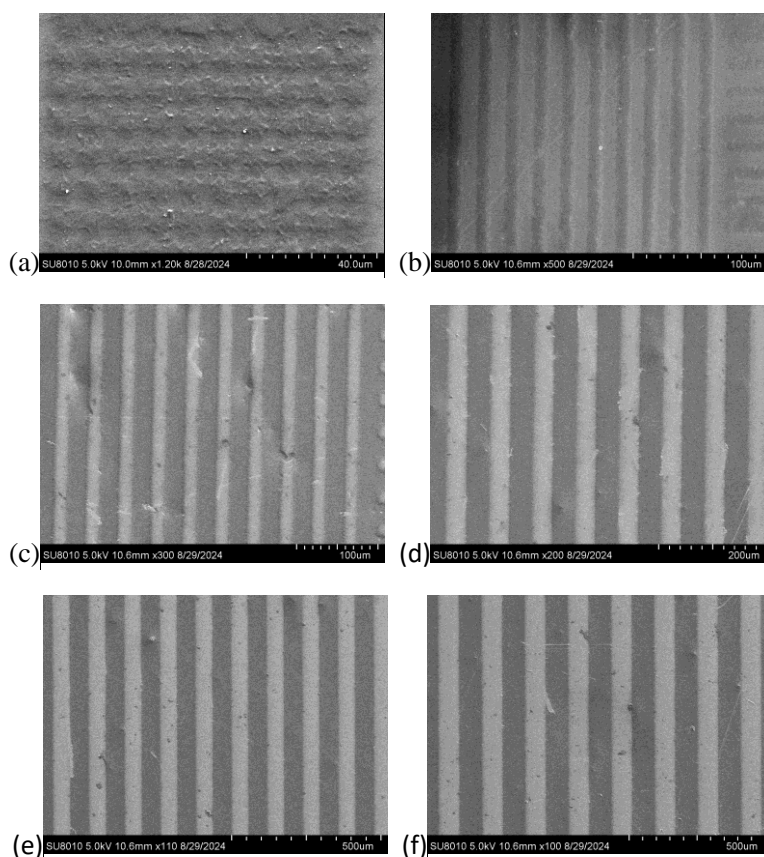
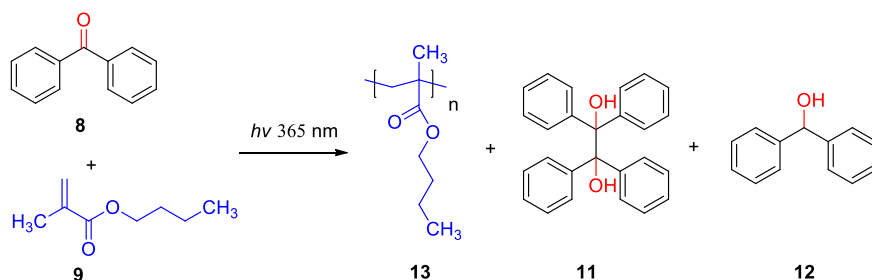


Figure S18. SEM photos of micro-patterns with different line width formed by PAAE 6. (a) 5 μm line width; (b) 10 μm line width; (c) 20 μm line width; (d) 40 μm line width; (e) 60 μm line width; (f) 80 μm line width.

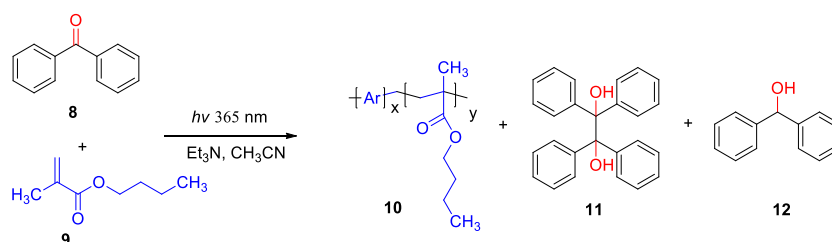
5. Mimic the photoreaction of polyimide with small molecules

(1) neat conditions:



Under nitrogen atmosphere, benzophenone **8** (0.6 mmol, 109.4 mg) was dissolved in butyl methacrylate **9** (1.2 mmol, 191 μ L). The homogeneous solution was exposed to a high-pressure ultraviolet lamp for 1 h. After completion of the reaction, the reaction mixture was diluted with 1 mL of ethyl acetate (EA) and separated by preparative TLC using ethyl acetate/hexane (1/10) as eluent. Three main products including poly(butyl methacrylate) **13** ($R_f = 0.06$, generally on the starting line of the TLC plate), benzopinacol **11** ($R_f = 0.38$), and phenylethanol **12** ($R_f = 0.25$) were obtained. The structures were determined by ^1H and ^{13}C NMR analysis.

(2) diluted conditions:



Under nitrogen atmosphere, benzophenone **8** (0.3 mmol, 54.7 mg), butyl methacrylate **9** (0.6 mmol, 95.4 μ L), Et_3N (0.3 mmol, 41.7 μ L) and acetonitrile (2 mL) were charged in a glass vial. The reaction mixture was exposed to a high-pressure ultraviolet lamp for 1 h. After completion of the reaction, the solvent was partially removed and the residue was purified by preparative TLC using ethyl acetate/hexane (1/10) as eluent. Three main products including benzophenone-methacrylate copolymer **10** ($R_f = 0.01-0.5$, the R_f of unknown polymer **10** varies in different experiment batches), benzopinacol **11** ($R_f = 0.38$), and phenylethanol **12** ($R_f = 0.25$) were obtained.

The poly(butyl methacrylate) **13** is a sticky gel. The NMR data is consistent with the literature reports.⁴

^1H NMR (400 MHz, CDCl_3) δ 3.95-3.94 (m, 2H), 1.91-1.81 (m, 2H), 1.67-1.61 (m, 2H), 1.41-1.39 (m, 2H), 1.03-1.87 (m, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 176.5, 63.7, 53.1, 43.7, 29.2, 18.3, 12.7, 12.7.

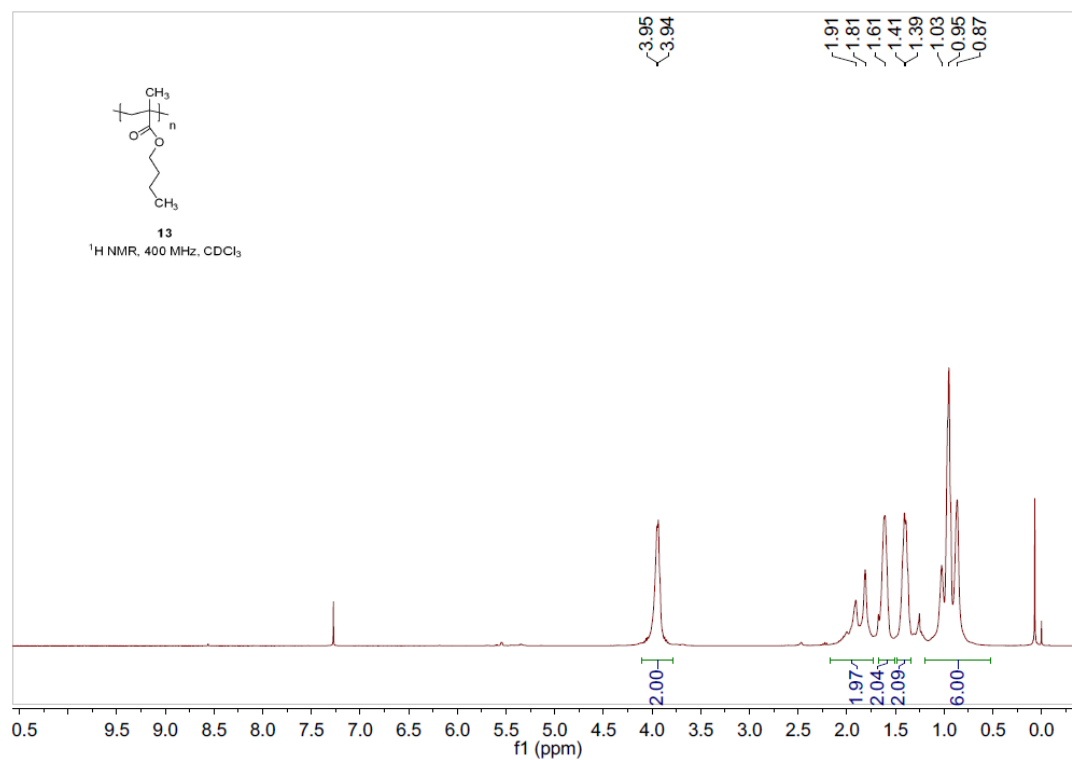


Figure S19. ^1H NMR spectrum of **13**.

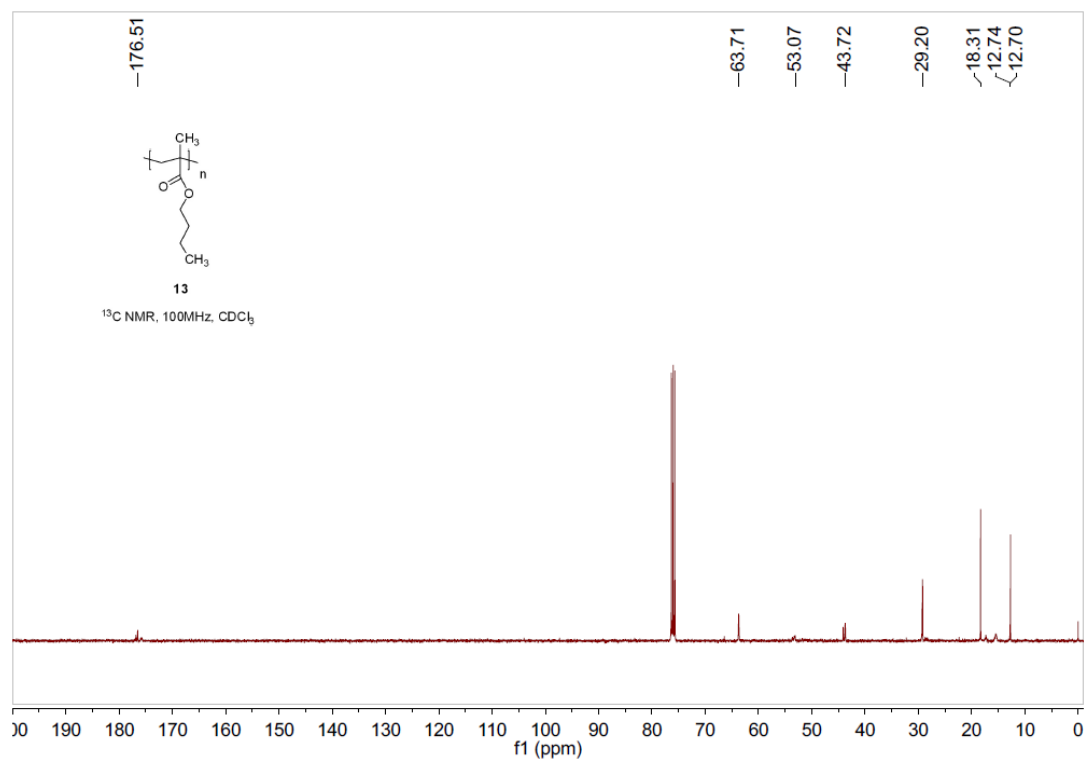


Figure S20. ^{13}C NMR spectrum of **13**.

The polymer **10** is a colorless liquid. We carried out numerous rounds of experiments and discovered that the structure of **10** obtained each time was diverse. In the ^1H NMR spectrum of **10**, the ratio of hydrogen numbers in the aromatic part to those in the aliphatic part varies each time. The molecular weight (M_n) of co-polymer **10** in a batch was measured by GPC to be 2191 g/mol.

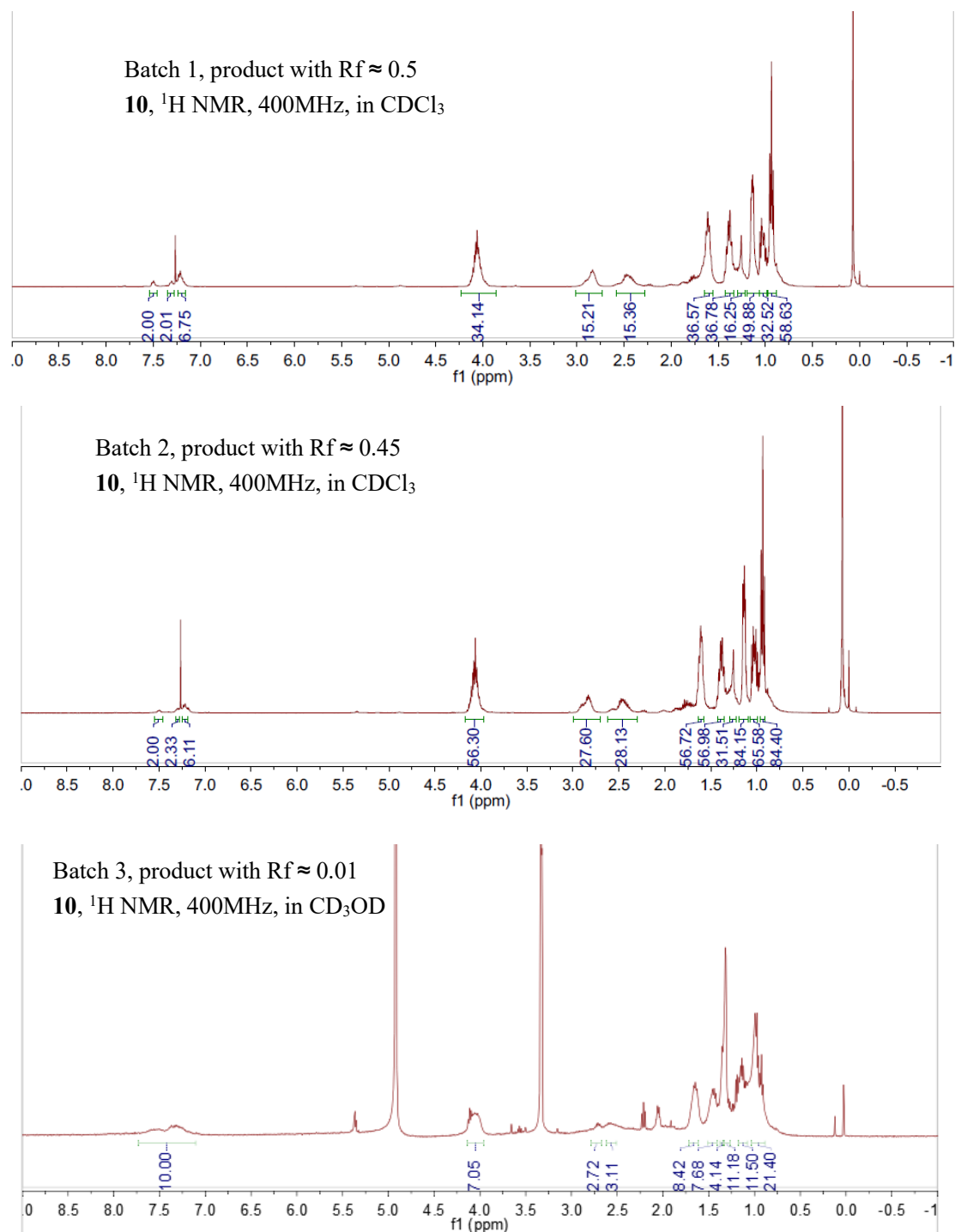


Figure S21. ^1H NMR spectra of **10** obtained from three separate batches.

Benzopinacolone **11** is a white solid. The NMR data is consistent with the literature reports.⁵

¹H NMR (400 MHz, CDCl₃) δ 7.31–7.28 (m, 8H), 7.20–7.15 (m, 12H), 3.03 (s, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 144.1, 128.6, 127.3, 126.9, 83.0.

HRMS (ESI): calculated for C₂₆H₂₂O₂Na [M+Na]⁺ : 389.1517, found: 389.1518.

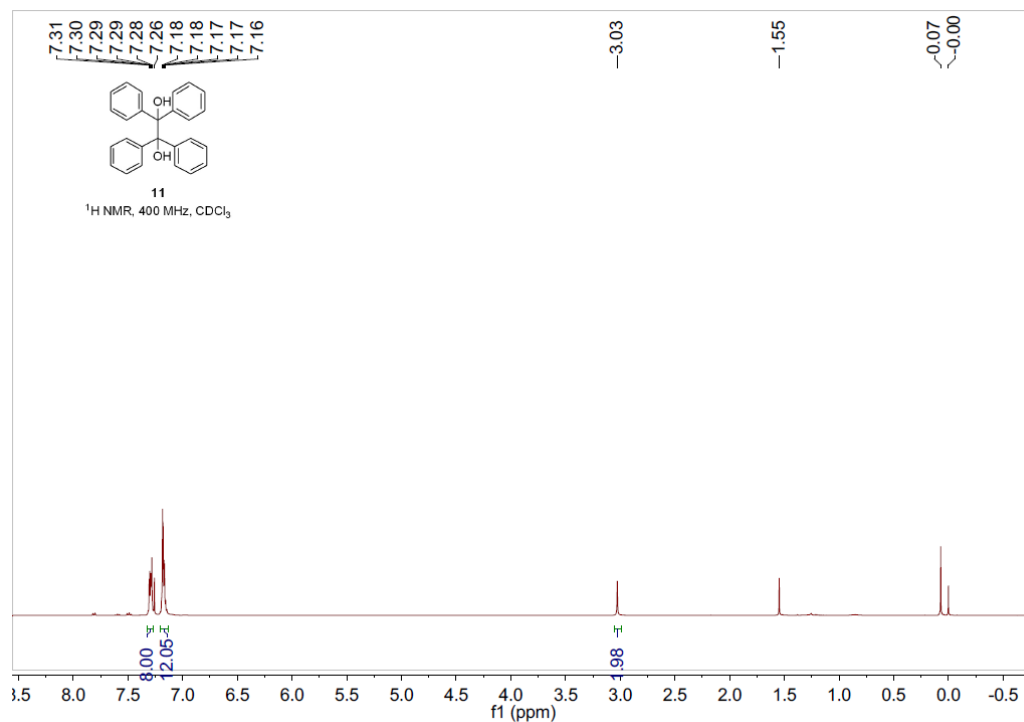


Figure S22. ¹H NMR spectrum of **11**.

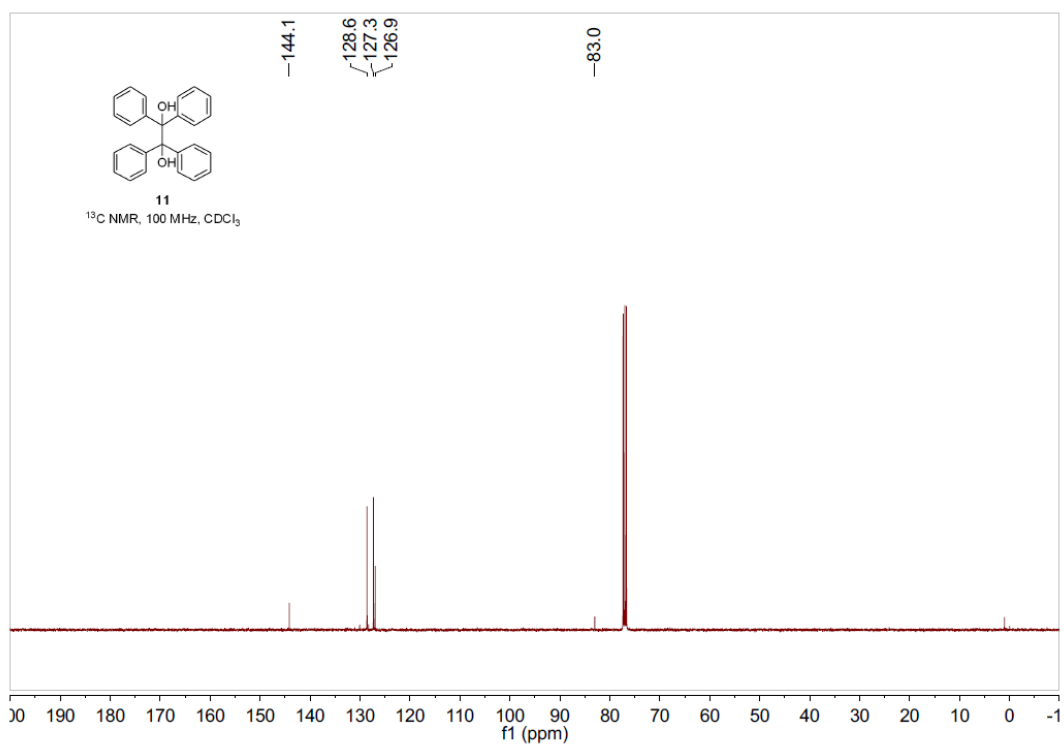


Figure S23. ¹³C NMR spectrum of **11**.

The phenylethanol **12** is a white solid. The NMR data is consistent with the literature reports.⁶
¹H NMR (400 MHz, CDCl₃) δ 7.40–7.32 (m, 8H), 7.29–7.24 (m, 2H), 5.85 (d, *J* = 3.5 Hz, 1H), 2.23 (d, *J* = 3.5 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 143.8, 128.5, 127.6, 126.5, 76.3.

HRMS (ESI): calculated for C₁₃H₁₂ONa [M+Na]⁺ : 207.0786, found: 207.0787.

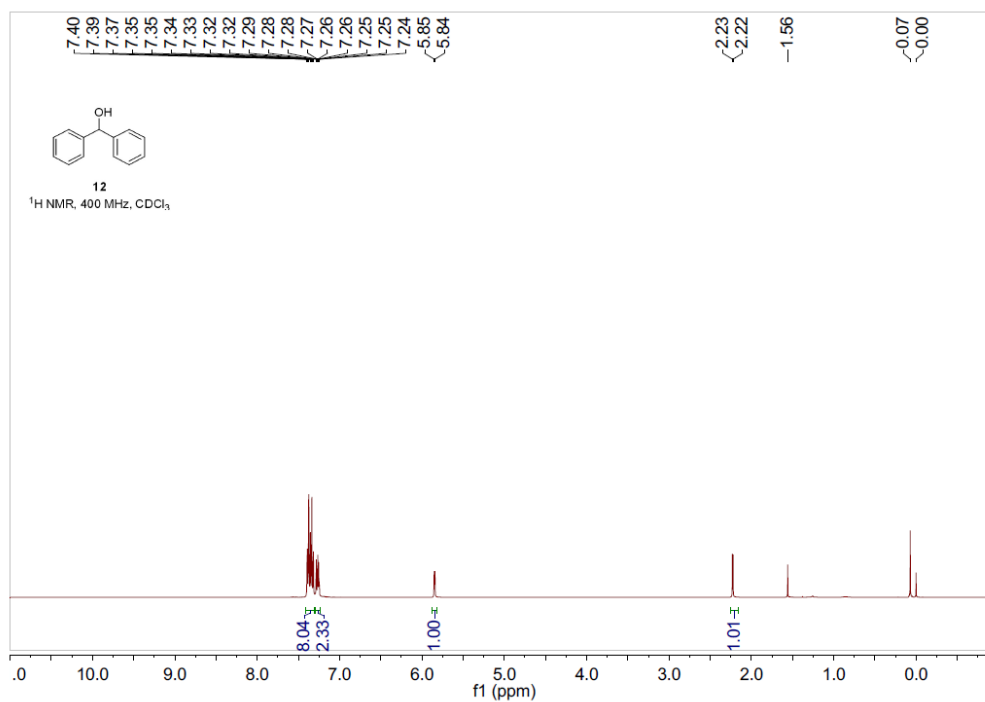


Figure S24. ¹H NMR spectrum of **12**.

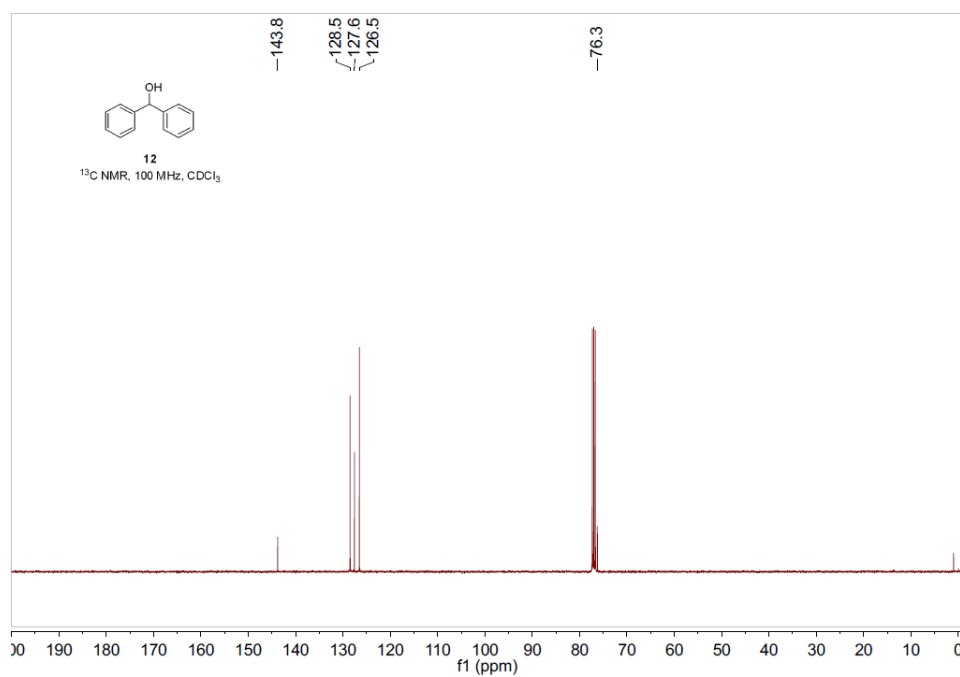


Figure S25. ¹³C NMR spectrum of **12**.

6. References

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