

## ***Supporting Information***

# One-Pot Multicomponent Tandem Reactions and Polymerizations for Step-Economic Synthesis of Structure-Controlled Pyrimidine Derivatives and Poly(pyrimidine)s

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**Materials and Instruments.** Phenylacetylene **1** was purchased from TCI; guanidine hydrochloride **3**, *N, N, N', N'*-tetramethylethylenediamine (TMEDA), Cs<sub>2</sub>CO<sub>3</sub>, dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and 1,2-dichlorobenzene (*o*-DCB) were purchased from Energy Chemical; CuCl was purchased from J&K Scientific Ltd; Tetraphenylethene-containing diyne **6** and monoyne **7** were prepared according to the reported procedures.<sup>1</sup> All the commercial available reactants and reagents were used as received without further purification.

All NMR spectra were measured on a Bruker Avance 500 MHz spectrometer using DMSO-*d*<sub>6</sub> as solvent and tetramethylsilane (TMS,  $\delta = 0$ ) as internal reference. FT-IR spectra were collected on a Bruker Vector 33 FT-IR spectrometer. For the ReactIR kinetic experiments, the reaction spectra were recorded using an IC 15 from Mettler-Toledo AutoChem. Data processing was carried out using the iC IR software, version 7.0. The weight-average molecular weights ( $M_w$ ) were determined by a Gel Permeation Chromatography (GPC) with Waters 1515 system, using PMMA as standards and DMF as the eluent in a flow rate of 1.0 mL/min. High resolution mass spectra (HRMS) were measured on a Bruker maxis impact mass spectrometer. Thermogravimetric analysis (TGA) was carried out on a Netzsch TG 209 F3 at a heating rate of 10 °C/min in a nitrogen flow. The static water contact angle was measured by a sessile drop method using POWEREACH JC2000D1. UV-vis absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. Fluorescence spectra were measured on a Horiba Fluoromax-4 fluorescence spectrophotometer. Fluorescence quantum yields were recorded using a Hamamatsu absolute photoluminescence quantum yield spectrometer C113747 Quantaaurus-QY.

**Synthetic procedure of compound 4.** Into a 50 mL Schlenk tube equipped with a magnetic stirrer were placed CuCl (2 mg, 0.02 mmol) and TMEDA (7 mg, 0.06 mmol) in 2 mL of DMSO. The mixture was bubbled with a slow stream of oxygen and stirred at 50 °C for 15 min. Monoyne **1** (102 mg, 1.0 mmol) was dissolved in 3 mL of DMSO, which was then added into the catalyst. The resulting solution was stirred for 4 h at room temperature. Afterward, guanidine hydrochloride **3** (115 mg, 1.2 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (652 mg, 2.0 mmol) were added. The reaction mixture was stirred at 120 °C in air for 12 h. After the reaction mixture was cooled to room temperature, 150 mL of

NaCl solution (5 M) was added and ethyl acetate was used to extract the product for three times ( $3 \times 50$  mL). The organic phases were combined and dried with  $\text{MgSO}_4$ . After the solvent was removed under reduced pressure, the crude product was obtained and purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to obtain compound **4** as a yellow powder in 94% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ )  $\delta$  (TMS, ppm): 8.16-8.14 (m, 2H), 7.99-7.97 (m, 2H), 7.72-7.69 (t, 1H), 7.58-7.52 (m, 5H), 7.46 (s, 1H), 7.07 (s, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO}-d_6$ )  $\delta$  (ppm): 193.63, 165.68, 164.23, 163.30, 136.63, 135.12, 133.86, 131.05, 130.43, 128.89, 127.03, 103.77.

**Synthetic procedure of compound 5.** Into a 50 mL Schlenk tube equipped with a magnetic stirrer were placed  $\text{CuCl}$  (2 mg, 0.02 mmol) and TMEDA (7 mg, 0.06 mmol) in 2 mL of DMSO. The mixture was bubbled with a slow stream of oxygen and stirred at 50 °C for 15 min. Monoyne **1** (102 mg, 1.0 mmol) was dissolved in 3 mL of DMSO which was then added into the catalyst. The resulting solution was stirred for 4 h at room temperature. Afterward, guanidine hydrochloride **3** (115 mg, 1.2 mmol) and  $\text{Cs}_2\text{CO}_3$  (652 mg, 2.0 mmol) were added. The reaction mixture was stirred at 120 °C under nitrogen for 12 h. After the reaction mixture was cooled to room temperature, 150 mL of NaCl solution (5 M) was added and ethyl acetate was used to extract the product for three times ( $3 \times 50$  mL). The organic phases were combined and dried with  $\text{MgSO}_4$ . After the solvent was removed under reduced pressure, the crude product was obtained and purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to obtain compound **5** as a white powder in 88% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ )  $\delta$  (TMS, ppm): 8.02-8.00 (m, 2H), 7.49-7.48 (m, 3H), 7.34-7.29 (m, 4H), 7.23-7.20 (t, 1H), 6.64 (s, 2H), 3.89 (s, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO}-d_6$ )  $\delta$  (ppm): 171.02, 164.48, 164.31, 139.24, 137.65, 130.81, 129.48, 129.12, 128.90, 127.12, 126.80, 105.44, 43.93.

**Experimental procedure of *in situ* IR measurements.** ConcIRT spectra of **3** (4.8 mg, 0.05 mmol), **6** (38 mg, 0.10 mmol), **8** (39 mg, 0.05 mmol), **9** (38 mg, 0.05 mmol), **P1** (23 mg, 0.05 mmol), and **P2** (22 mg, 0.05 mmol) in 0.5 mL of DMSO were recorded by *in situ* IR spectroscopy, respectively, for comparison. Into a 20 mL Schlenk tube equipped with a magnetic stirrer were placed  $\text{CuCl}$  (0.8

mg, 0.008 mmol) and TMEDA (2.8 mg, 0.024 mmol) in 2 mL of *o*-DCB. The mixture was bubbled with a slow stream of oxygen and stirred at 50 °C for 15 min. Diyne **6** (152 mg, 0.40 mmol) was dissolved in 2 mL of *o*-DCB which was then added into the catalyst. The resulting solution was stirred for 2 h at room temperature. Afterward, guanidine hydrochloride **3** (46 mg, 0.48 mmol), Cs<sub>2</sub>CO<sub>3</sub> (261 mg, 0.80 mmol), and 4 mL of DMSO were added. Then the probe of in situ IR was inserted into the polymerization solution. The polymerization was monitored at 120 °C in air or under nitrogen for 12 h. Relative absorbance was calculated based on the height to the baseline.

**Table S1. Solvent optimization for the first step of the multicomponent tandem reaction<sup>a</sup>**

entry	solvent	CuCl	yield (%)
1	CH <sub>2</sub> Cl <sub>2</sub>	5%	54
2	THF	5%	66
3	DMF	5%	75
4	<i>o</i> -DCB	5%	85
5	DMSO	5%	83
6	DMSO	2%	94

<sup>a</sup>The MCTR using **1** as the reactant was carried out in different solvents in the presence of CuCl and TMEDA in air at 50 °C for 4 h, prior to the addition of DMSO, Cs<sub>2</sub>CO<sub>3</sub>, and guanidine hydrochloride **3**, which was then reacted at 120 °C for 12 h. [**1**] = 0.1 M, [CuCl] = 2%[**6**], [TMEDA] = 6%[**6**], [**1**]/[**3**]/[Cs<sub>2</sub>CO<sub>3</sub>] = 1.0/1.2/2.0.

**Table S2. Solvent optimization of the multicomponent tandem polymerization<sup>a</sup>**

entry	solvent	ratio(v/v)	<i>S</i> <sup>b</sup>	yield	<i>M</i> <sub>w</sub> <sup>c</sup>	<i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub> <sup>c</sup>
1	DMSO	--	precipitate	--	--	--
2	DMF/DMSO	1:1	precipitate	--	--	--
3	<i>o</i> -DCB/DMSO	1:1	√	87%	25 300	1.90
4	<i>o</i> -DCB/DMSO	1:2	√	65%	8 600	1.36
5	<i>o</i> -DCB/DMSO	2:1	√	81%	20 500	1.92

<sup>a</sup>The MCTP using **6** as the monomer was carried out in the presence of CuCl and TMEDA in air at 50 °C for 2 h, prior to the addition of DMSO, Cs<sub>2</sub>CO<sub>3</sub>, and guanidine hydrochloride **3**, which was then reacted at 120 °C for 12 h. [**6**] = 0.1 M, [CuCl] = 2%[**6**], [TMEDA] = 6%[**6**], [**6**]/[**3**]/[Cs<sub>2</sub>CO<sub>3</sub>] = 1.0/1.2/2.0. <sup>b</sup>Solubility (*S*) tested in reaction solvent. <sup>c</sup>Estimated by GPC in DMF on the basis of poly(methyl methacrylate) standard samples.

**Table S3. Monomer concentration effect of the MCTP<sup>a</sup>**

entry	[ <b>6</b> ] (M)	yield (%)	$M_w^b$	$M_w/M_n^b$
1	0.05	43	5 500	1.46
2	0.05 <sup>c</sup>	76	12 900	1.85
3	0.10	87	25 300	1.90
4	0.20	gel	--	--

<sup>a</sup>The MCTP using **6** as the monomer was carried out in *o*-DCB in the presence of CuCl and TMEDA in air at 50 °C for 2 h, prior to the addition of DMSO, Cs<sub>2</sub>CO<sub>3</sub>, and guanidine hydrochloride **3**, which was then reacted in air at 120 °C for 12 h. [CuCl] = 2%[**6**], [TMEDA] = 6%[**6**], [**6**]/[**3**]/[Cs<sub>2</sub>CO<sub>3</sub>] = 1.0/1.2/2.0. <sup>b</sup>Estimated by GPC in DMF on the basis of poly(methyl methacrylate) standard samples. <sup>c</sup>Reacted for 6 h for the first step.

**Table S4. Temperature effect of the MCTP<sup>a</sup>**

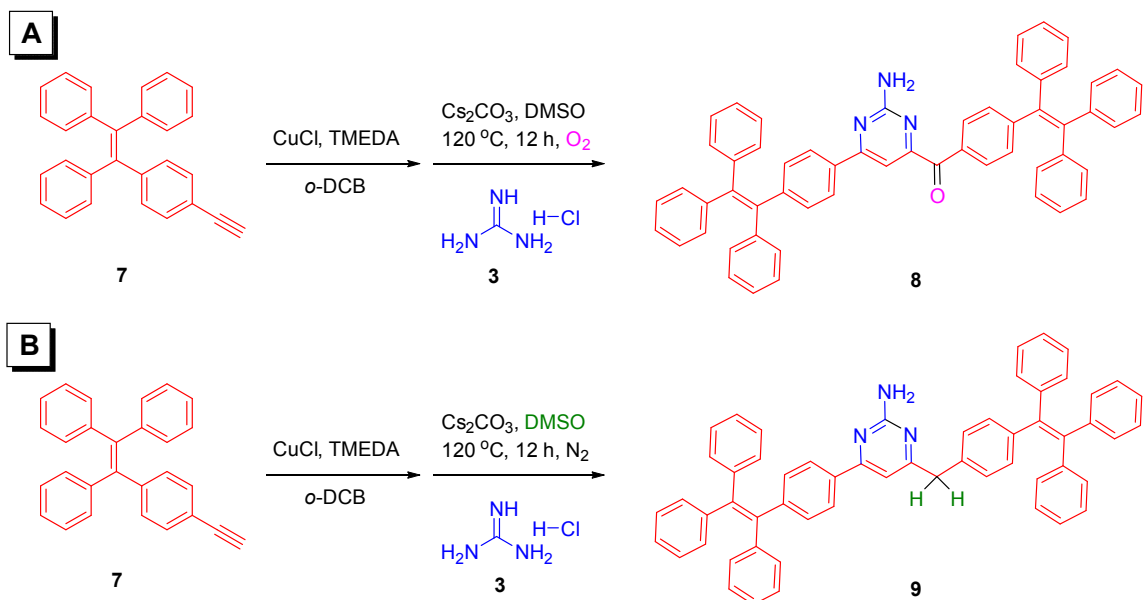
entry	T (°C)	yield (%)	$M_w^b$	$M_w/M_n^b$
1	120	87	25 300	1.90
2	130	87	21 100	1.67
3	140	78	17 800	1.66
4	160	67	13 500	1.63

<sup>a</sup>The MCTP using **6** as the monomer was carried out in *o*-DCB in the presence of CuCl and TMEDA in air at 50 °C for 2 h, prior to the addition of DMSO, Cs<sub>2</sub>CO<sub>3</sub>, and guanidine hydrochloride **3**, which was then reacted in air for 12 h at different temperatures. [**6**] = 0.1 M, [CuCl] = 2%[**6**], [TMEDA] = 6%[**6**], [**6**]/[**3**]/[Cs<sub>2</sub>CO<sub>3</sub>] = 1.0/1.2/2.0. <sup>b</sup>Estimated by GPC in DMF on the basis of poly(methyl methacrylate) standard samples.

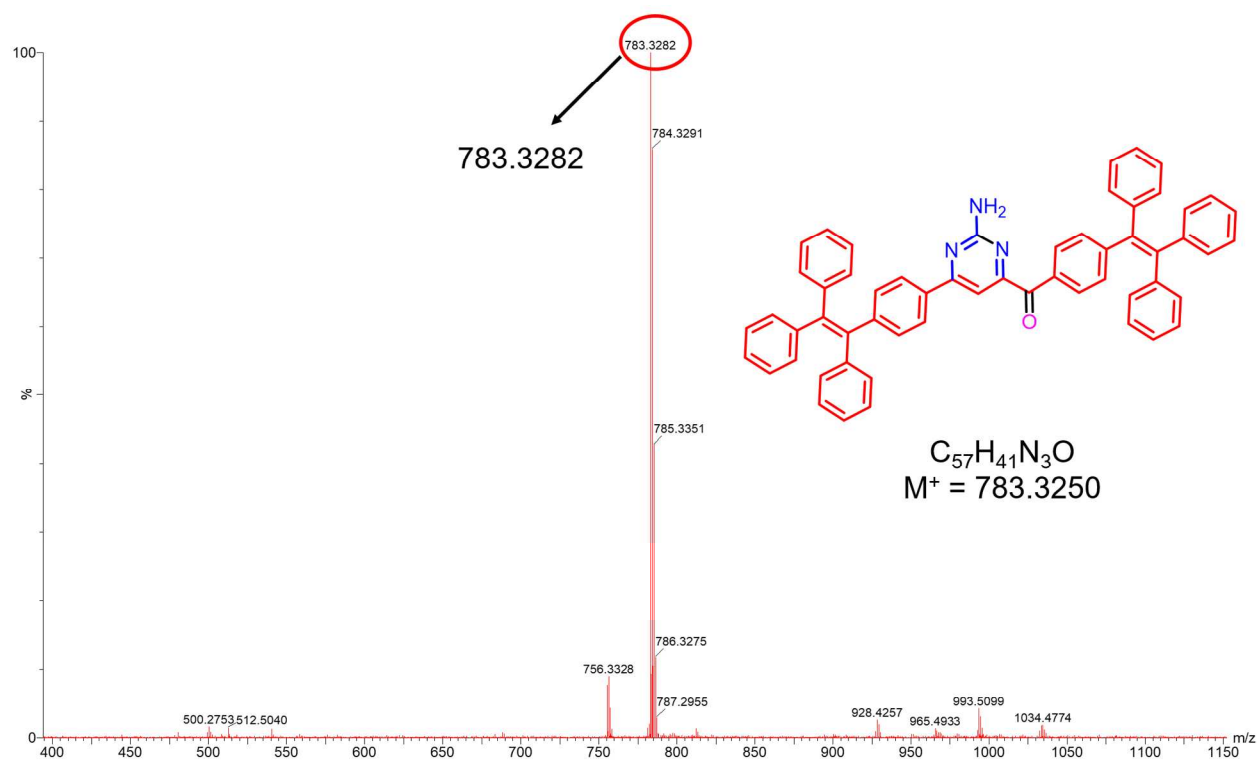
**Table S5. Time course of the polymerization after the addition of **3**<sup>a</sup>**

entry	time (h)	yield (%)	$M_w^b$	$M_w/M_n^b$
1	8	82	23 500	1.77
2	10	85	25 700	1.82
3	12	87	25 300	1.90
4	14	83	26 600	1.98

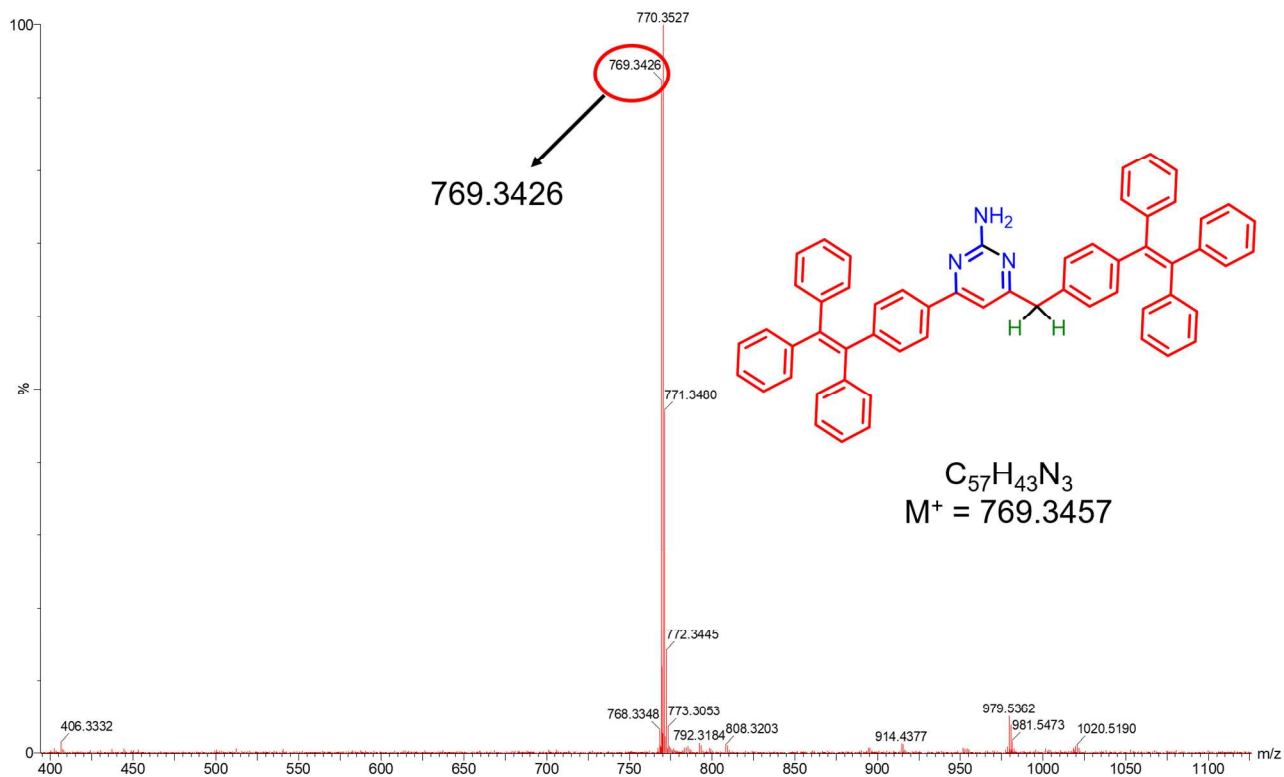
<sup>a</sup>The MCTP using **6** as the monomer was carried out in *o*-DCB in the presence of CuCl and TMEDA in air at 50 °C for 2 h, prior to the addition of DMSO, Cs<sub>2</sub>CO<sub>3</sub>, and guanidine hydrochloride **3**, which was then reacted in air at 120 °C for different time. [**6**] = 0.1 M, [CuCl] = 2%[**6**], [TMEDA] = 6%[**6**], [**6**]/[**3**]/[Cs<sub>2</sub>CO<sub>3</sub>] = 1.0/1.2/2.0. <sup>b</sup>Estimated by GPC in DMF on the basis of poly(methyl methacrylate) standard samples.



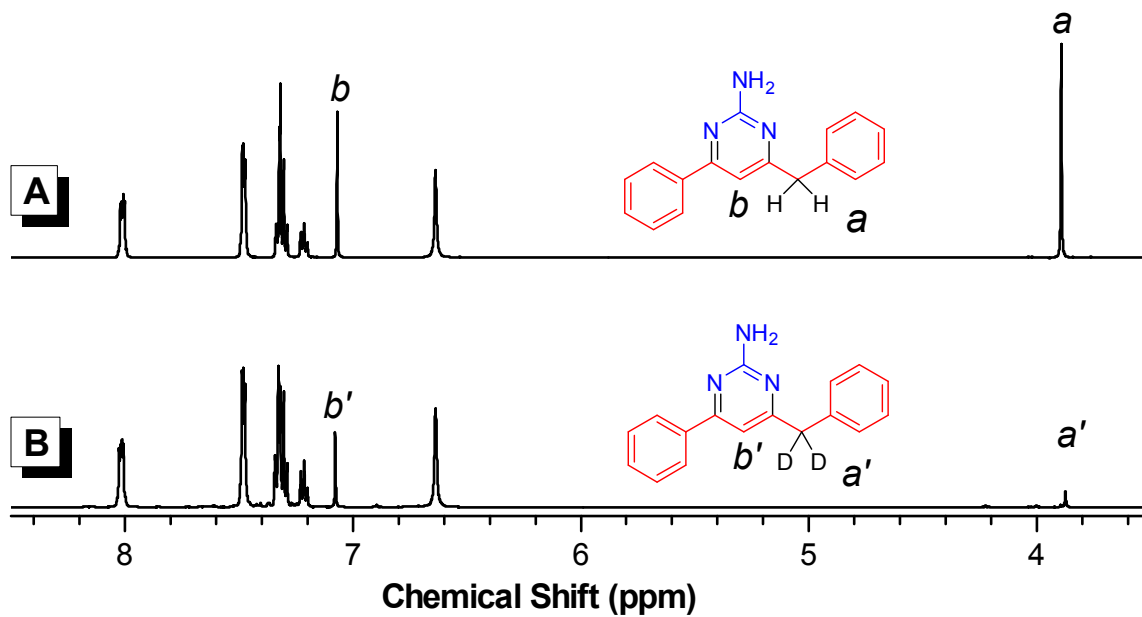
**Scheme S1.** Synthetic routes of model compounds **8** and **9** by the multicomponent tandem reactions.



**Figure S1.** HR-MS spectrum of **8**.

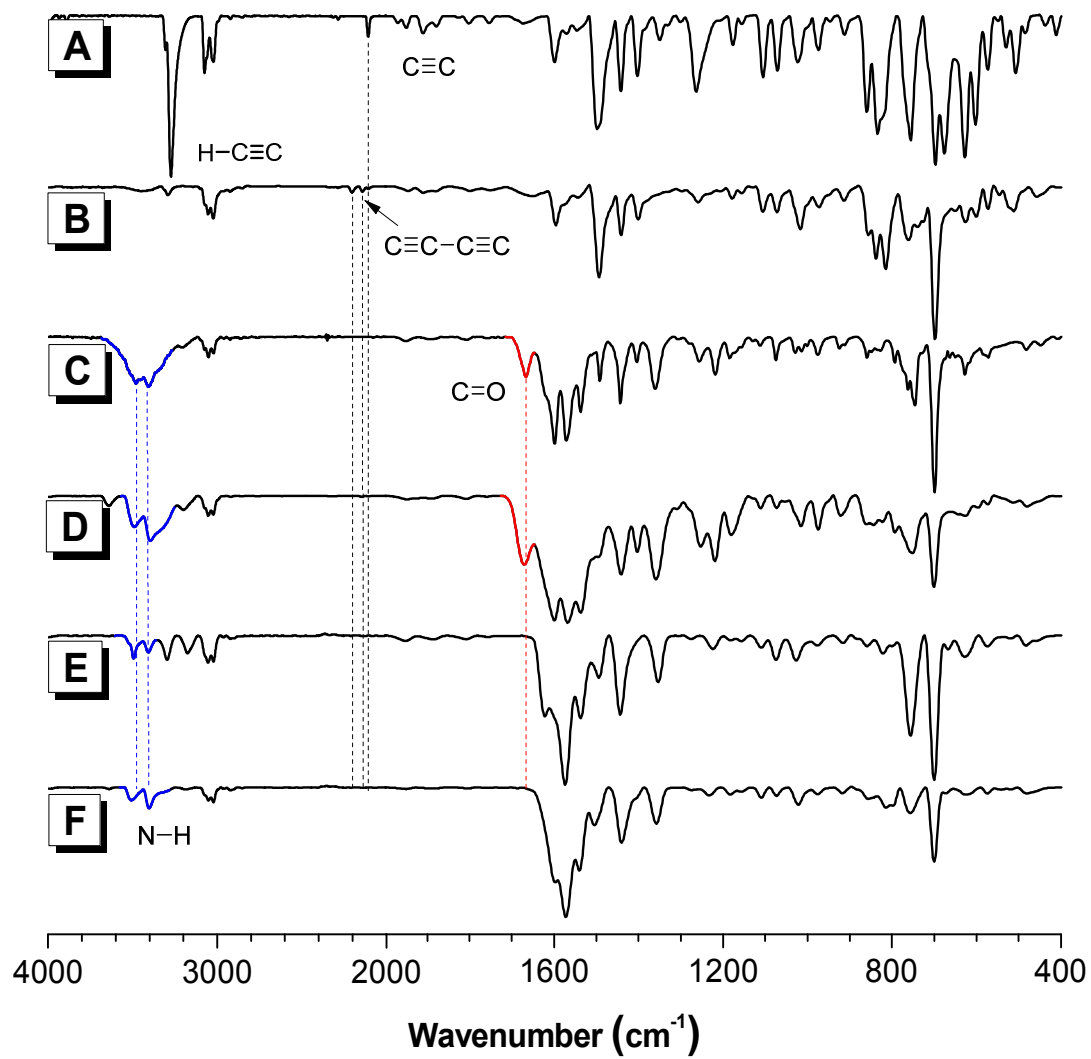


**Figure S2.** HR-MS spectrum of **9**.

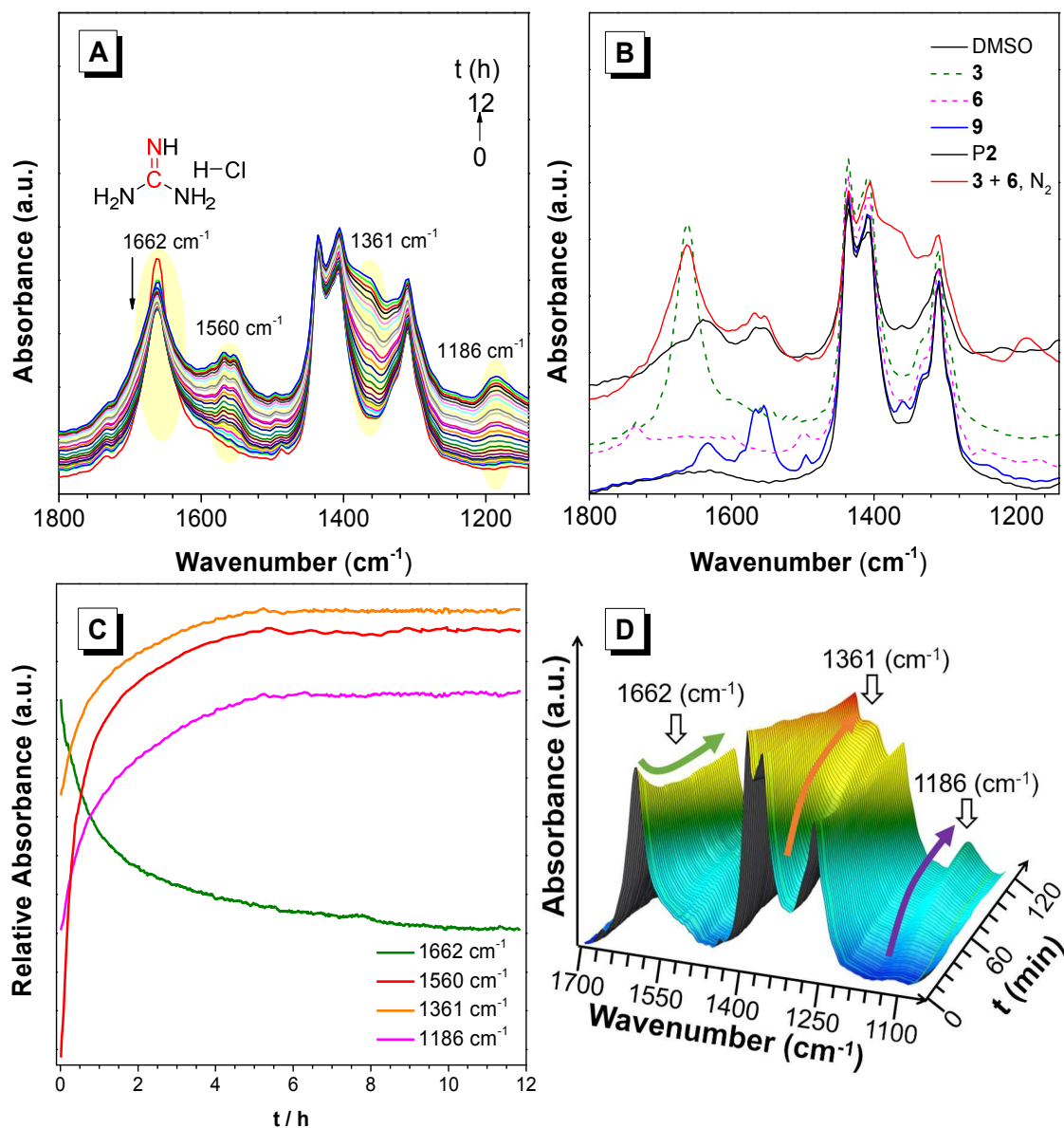


**Figure S3.**  $^1H$  NMR spectra of (A) **5** and (B) **5'** in  $DMSO-d_6$ .





**Figure S4.** IR spectra of (A) **6**, (B) **P1'**, (C) **8**, (D) **P1**, (E) **9**, and (F) **P2**.

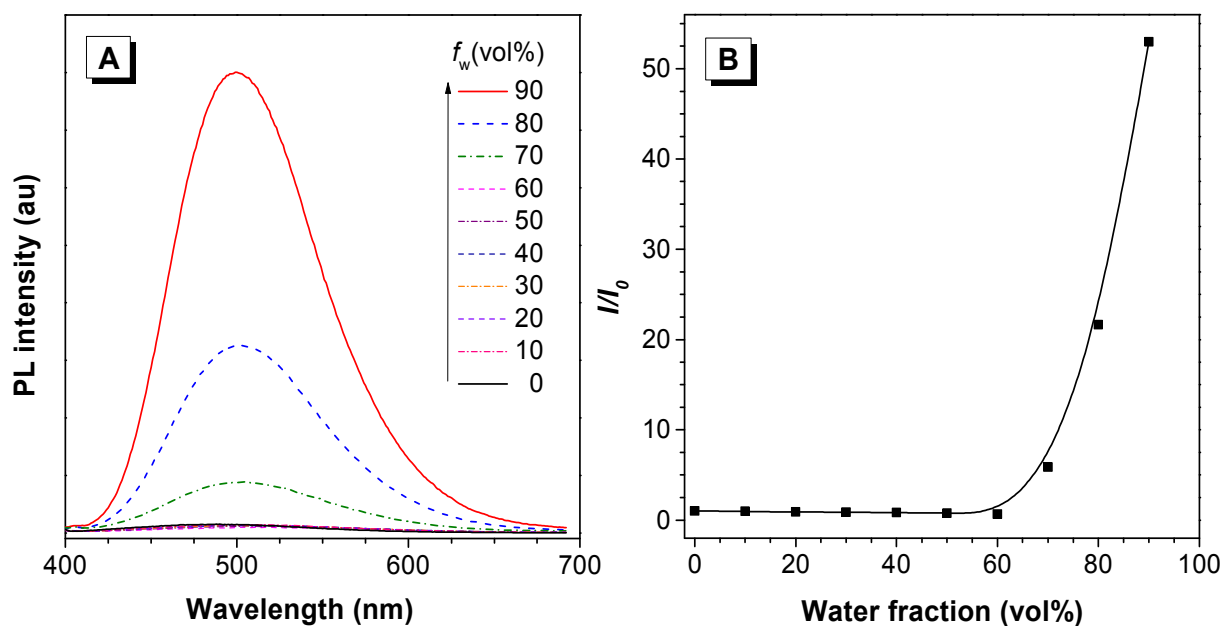


**Figure S5.** (A) Stacked in situ IR profiles collected at different instants of the polymerization solution of **3** and **6** in DMSO under nitrogen. (B) The in situ IR spectra of DMSO, **3**, **6**, **9**, P2, and the polymerization solution of **3** and **6** after reaction under nitrogen for 12 h. (C) The time-dependent peak intensity at 1662, 1560, 1361, and 1186  $\text{cm}^{-1}$ . (D) The 3D-FTIR profile of the polymerization solution of **3** and **6** under nitrogen.

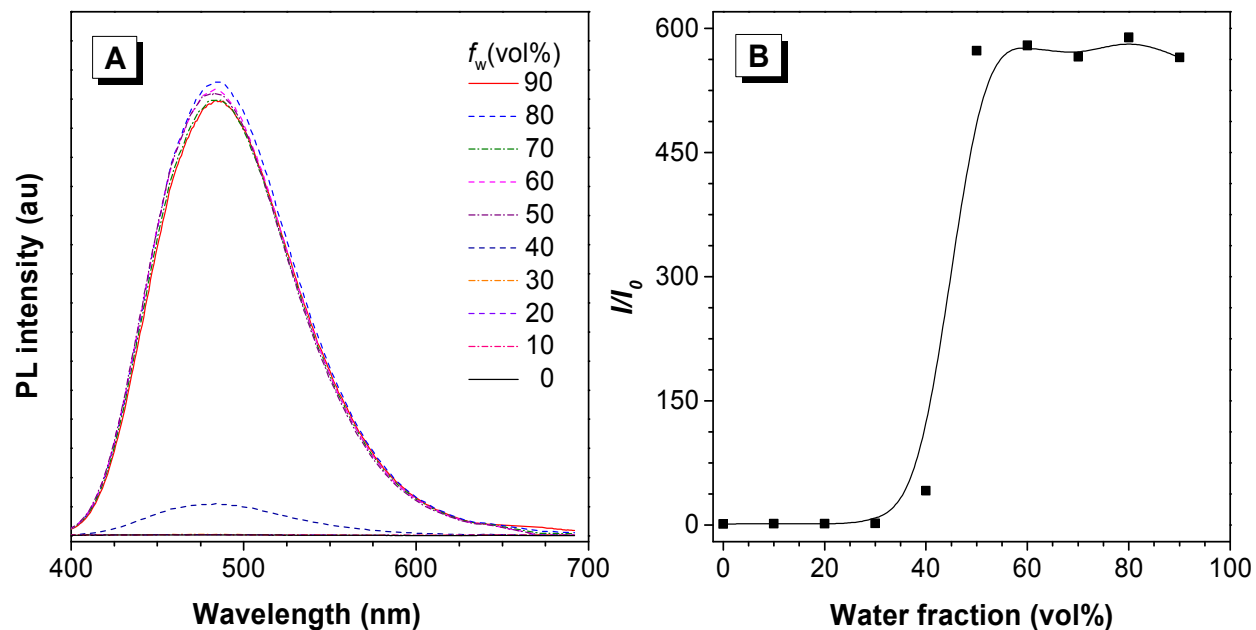
**Table S6. Time course of the polymerization after the addition of 3<sup>a</sup>**

entry	time (h)	yield (%)	$M_w^b$	$M_w/M_n^b$
1	1	92	10 600	1.47
2	2	85	13 200	1.59
3	3	87	16 800	1.71
4	4	89	18 600	1.59
5	6	85	24 000	1.83

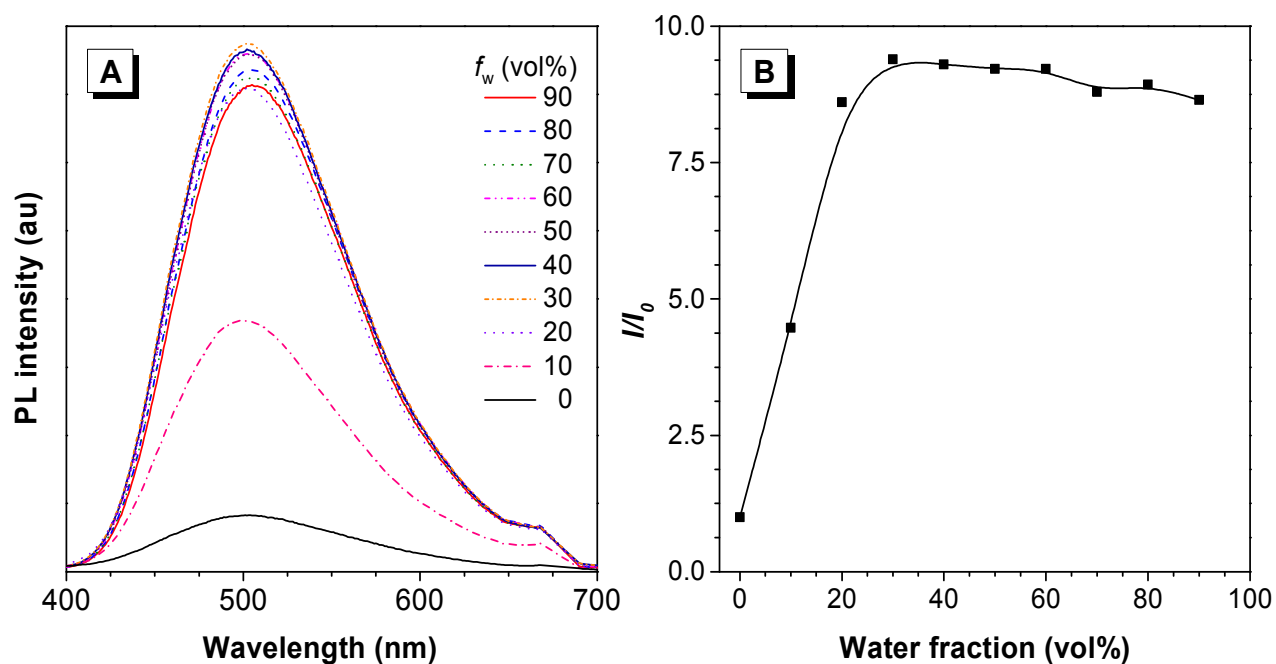
<sup>a</sup>The MCTP using **6** as the monomer was carried out in *o*-DCB in the presence of CuCl and TMEDA in air at 50 °C for 2 h, prior to the addition of DMSO, Cs<sub>2</sub>CO<sub>3</sub>, and guanidine hydrochloride **3**, which was then reacted in air at 120 °C for different time. [**6**] = 0.1 M, [CuCl] = 2%[**6**], [TMEDA] = 6%[**6**], [**6**]/[**3**]/[Cs<sub>2</sub>CO<sub>3</sub>] = 1.0/1.2/2.0. <sup>b</sup>Estimated by GPC in DMF on the basis of poly(methyl methacrylate) standard samples.



**Figure S6.** (A) PL spectra of **8** in DMF/water mixtures with different water fractions. (B) Plots of the relative emission peak intensity ( $I/I_0$ ) versus the water fractions. Concentration: 10  $\mu$ M,  $\lambda_{em}$  = 356 nm.



**Figure S7.** (A) PL spectra of **9** in DMF/water mixtures with different water fractions. (B) Plots of the relative emission peak intensity ( $I/I_0$ ) versus the water fractions. Concentration:  $10\ \mu\text{M}$ ,  $\lambda_{\text{em}} = 323\ \text{nm}$ .

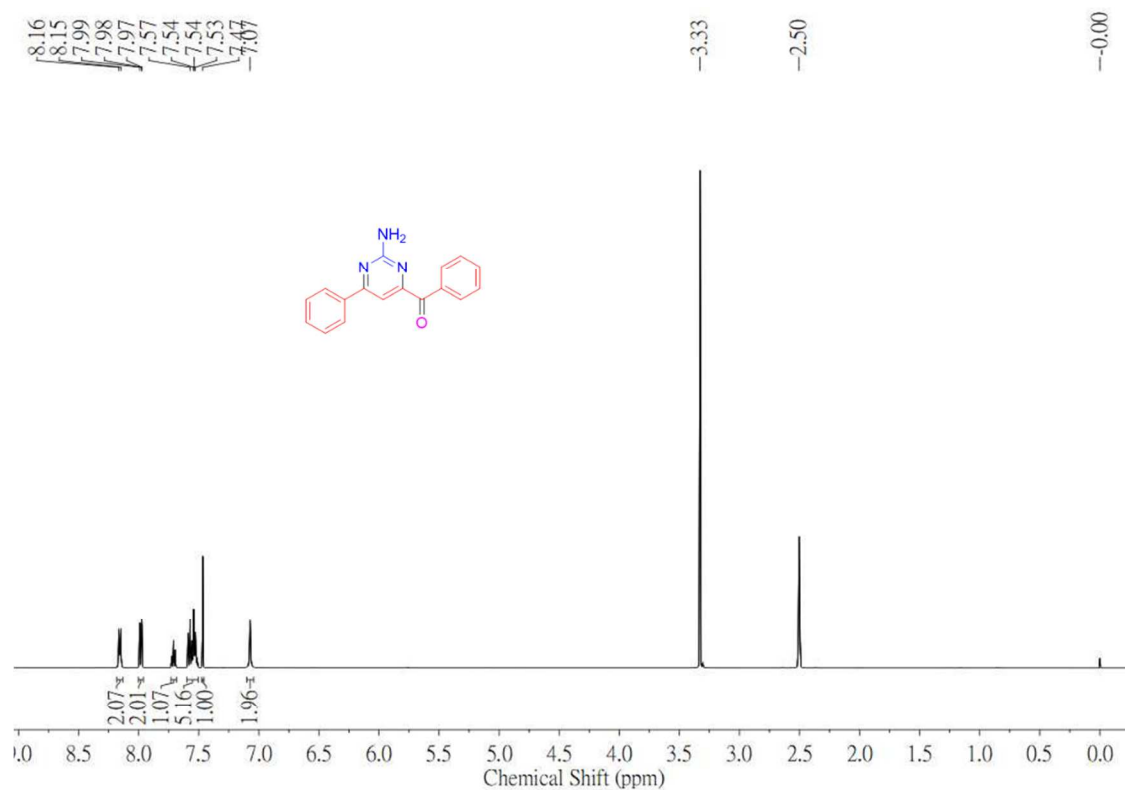


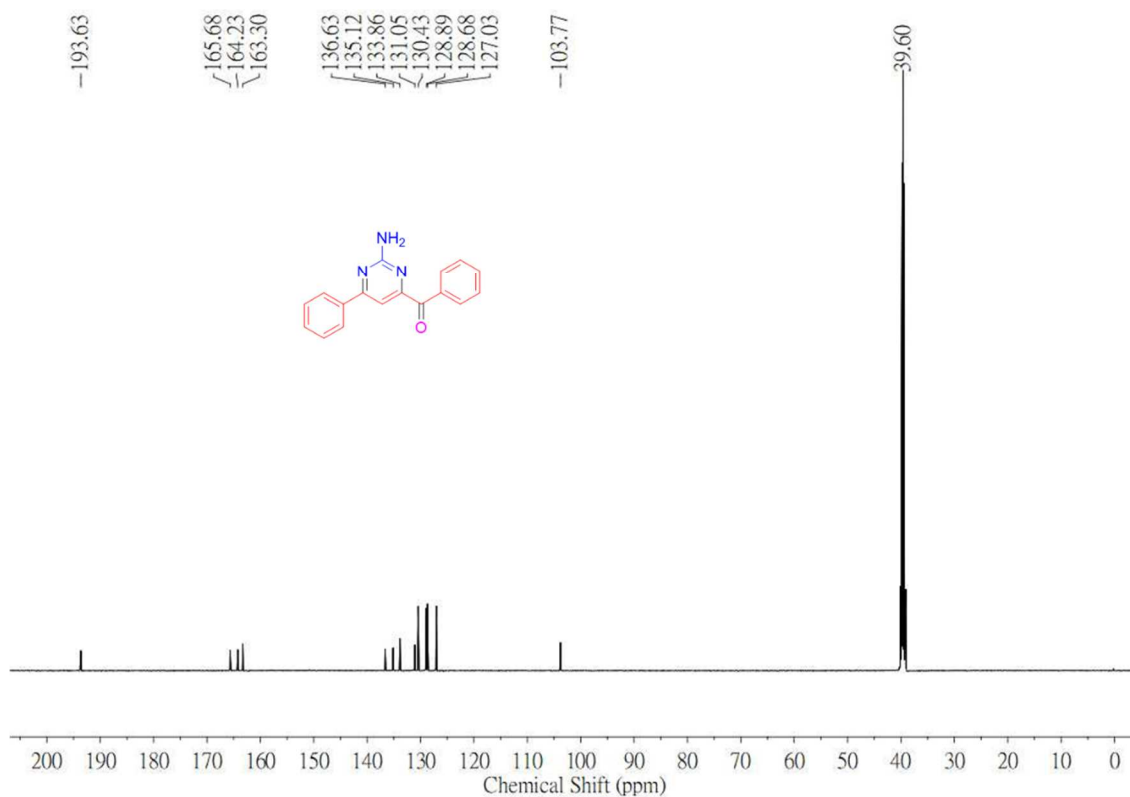
**Figure S8.** (A) PL spectra of **P2** in DMF/water mixtures with different water fractions. (B) Plots of the relative emission peak intensity ( $I/I_0$ ) versus the water fractions. Concentration:  $10\ \mu\text{M}$ ,  $\lambda_{\text{em}} = 339\ \text{nm}$ .

**Table S7. Photophysical properties of the model compounds and polymers<sup>a</sup>**

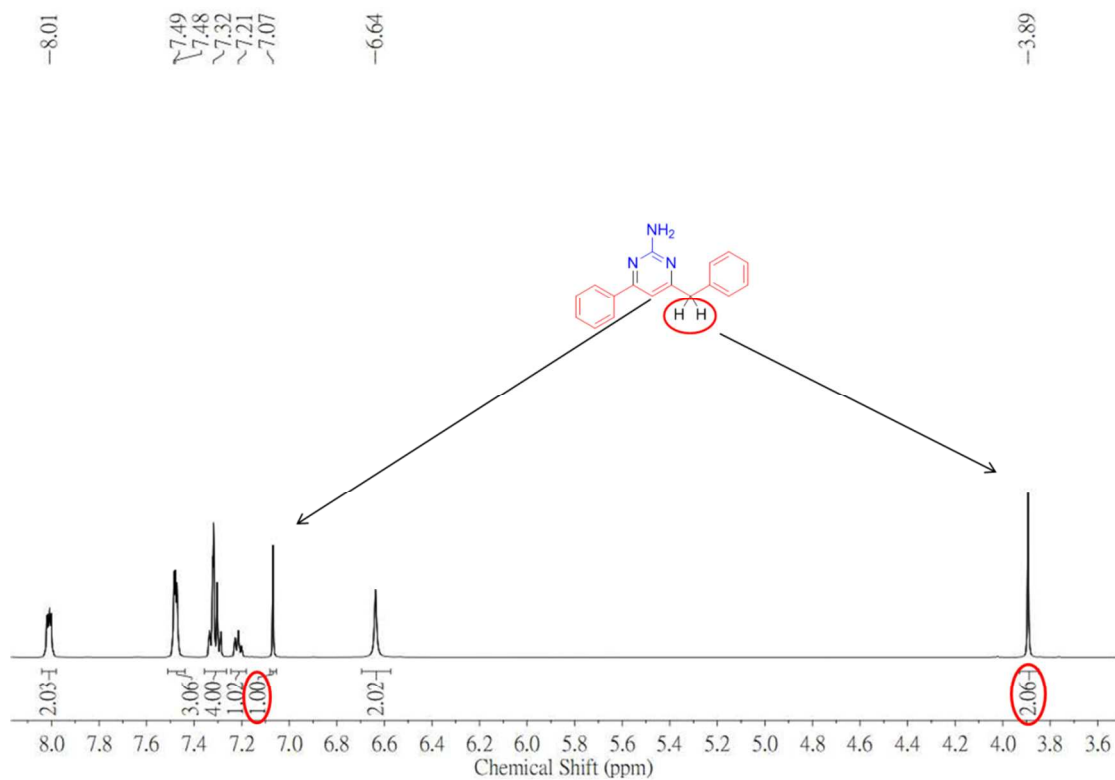
entry	$\lambda_{\text{ab}}$ (nm)	$\varepsilon$ (L mol <sup>-1</sup> cm <sup>-1</sup> )	Solution		Solid	
			$\lambda_{\text{em}}$ (nm)	$\Phi$ (%) <sup>b</sup>	$\lambda_{\text{em}}$ (nm)	$\Phi$ (%) <sup>b</sup>
<b>8</b>	356	27500	490	0.6	512	7.6
<b>9</b>	323	44900	--	--	450	56.0
<b>P1</b>	361	31600	527	0.9	549	6.9
<b>P2</b>	339	61800	--	--	537	4.7

<sup>a</sup>Abbreviations:  $\lambda_{\text{ab}}$  = absorption maximum of DMF solutions,  $\varepsilon$  = molar absorptivity,  $\lambda_{\text{em}}$  = emission maximum,  $\Phi$  = fluorescence quantum yield measured by a calibrated integrating sphere. Concentrations of **8**, **9**, **P1**, and **P2**: 10  $\mu\text{M}$ . <sup>b</sup> $\lambda_{\text{em}} = \lambda_{\text{ab}}$ .

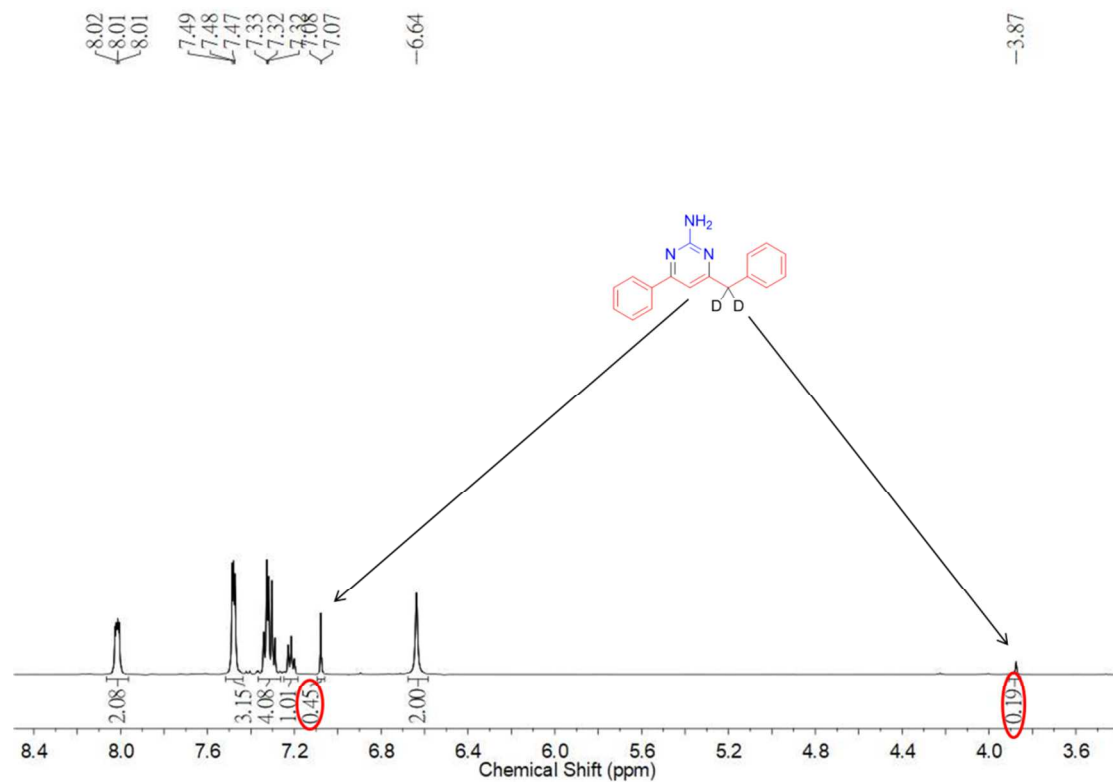
**Figure S9.** <sup>1</sup>H NMR of **4** in DMSO-*d*<sub>6</sub>.



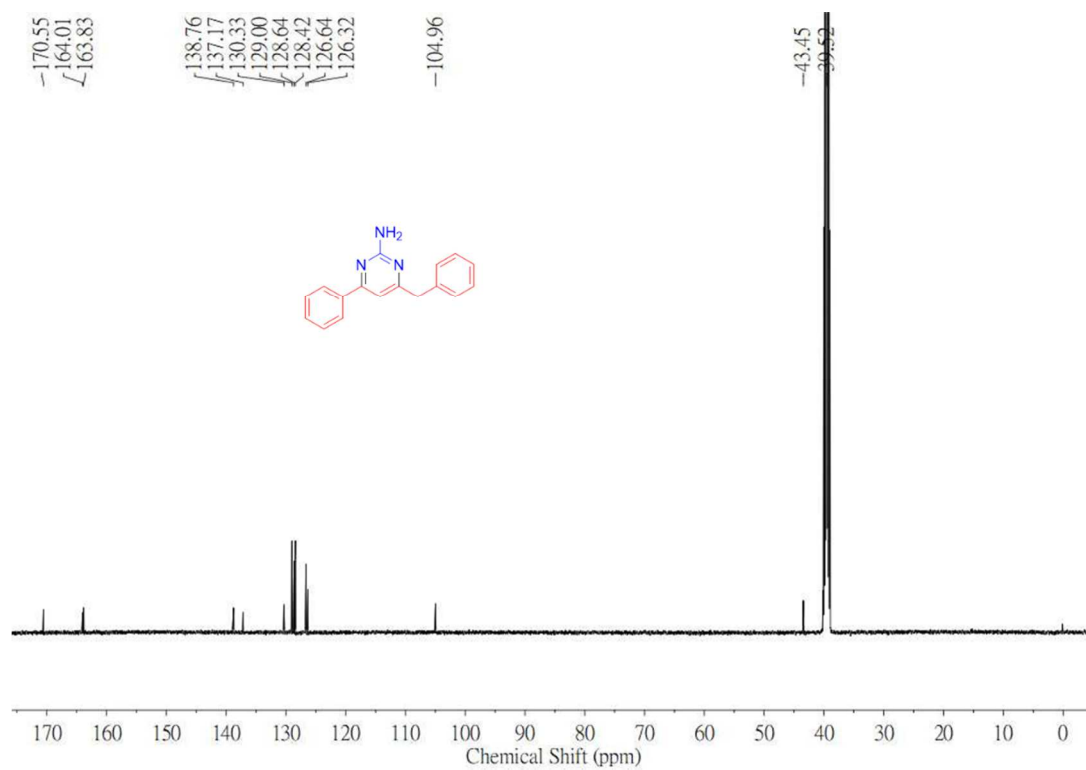
**Figure S10.** <sup>13</sup>C NMR of **4** in DMSO-*d*<sub>6</sub>.



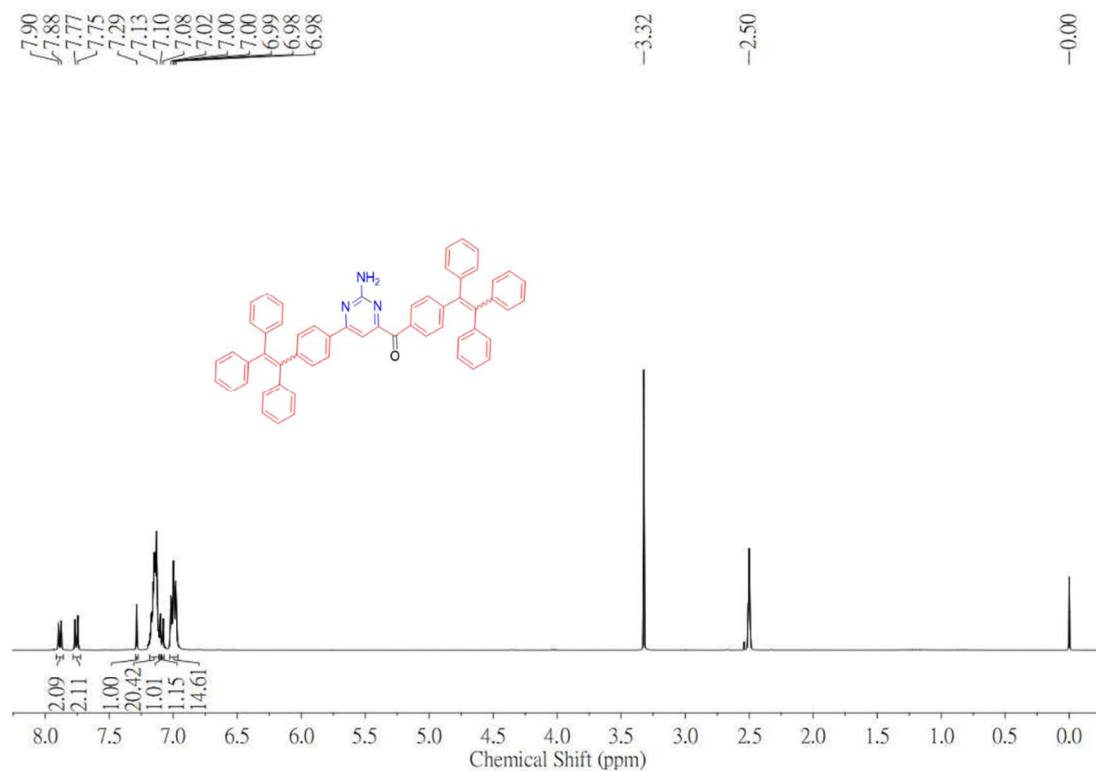
**Figure S11.** <sup>1</sup>H NMR of **5** in DMSO-*d*<sub>6</sub>.



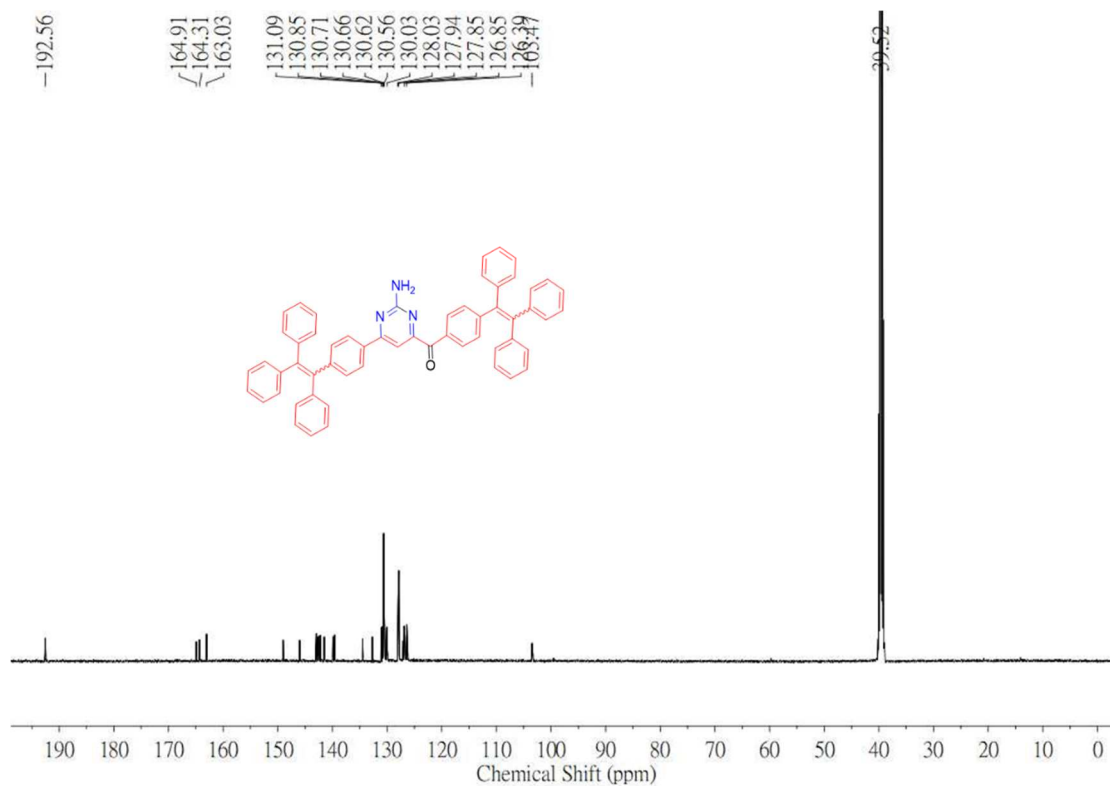
**Figure S12.**  $^1\text{H}$  NMR of **5'** in  $\text{DMSO-}d_6$ .



**Figure S13.**  $^{13}\text{C}$  NMR of **5** in  $\text{DMSO-}d_6$ .

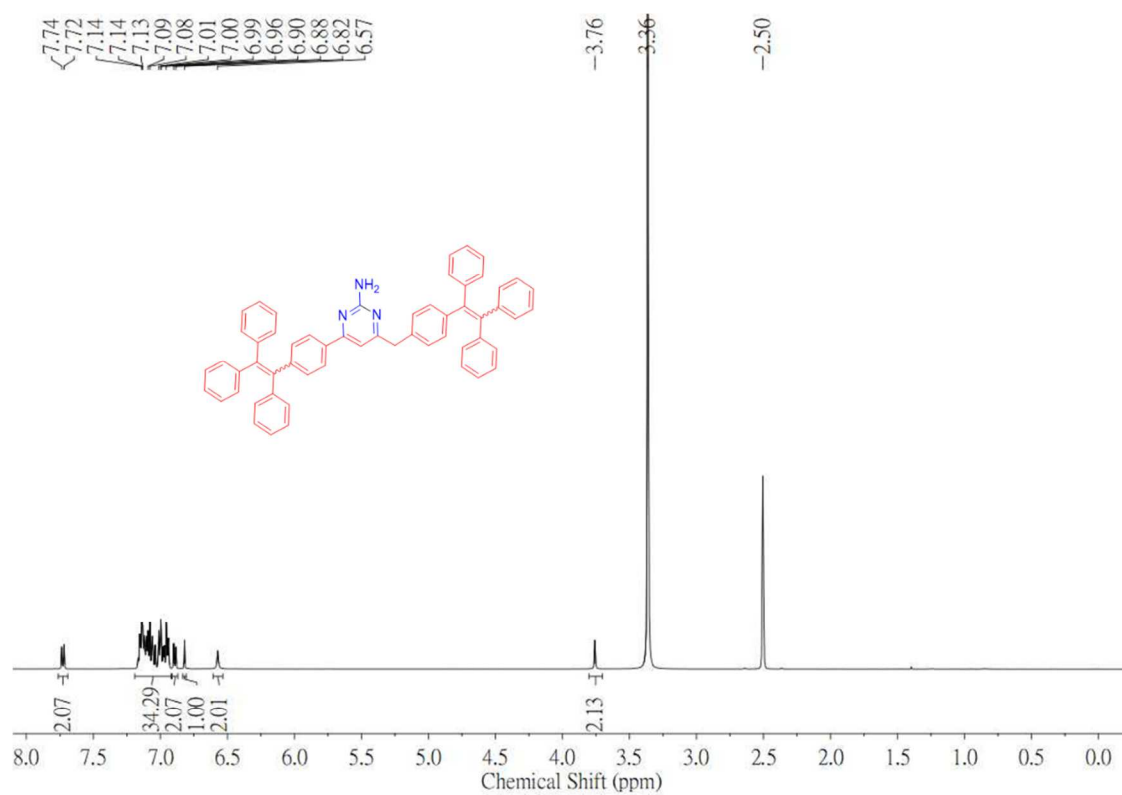


**Figure S14.** <sup>1</sup>H NMR of **8** in DMSO-*d*<sub>6</sub>.

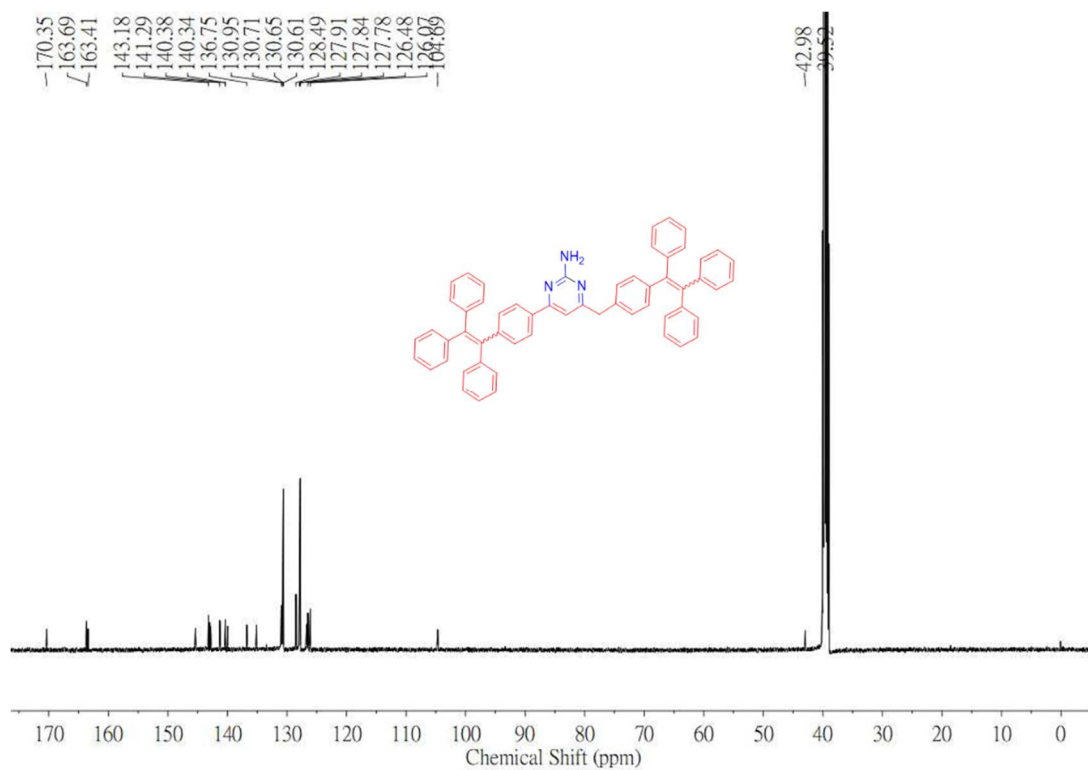


**Figure S15.** <sup>13</sup>C NMR of **8** in DMSO-*d*<sub>6</sub>.

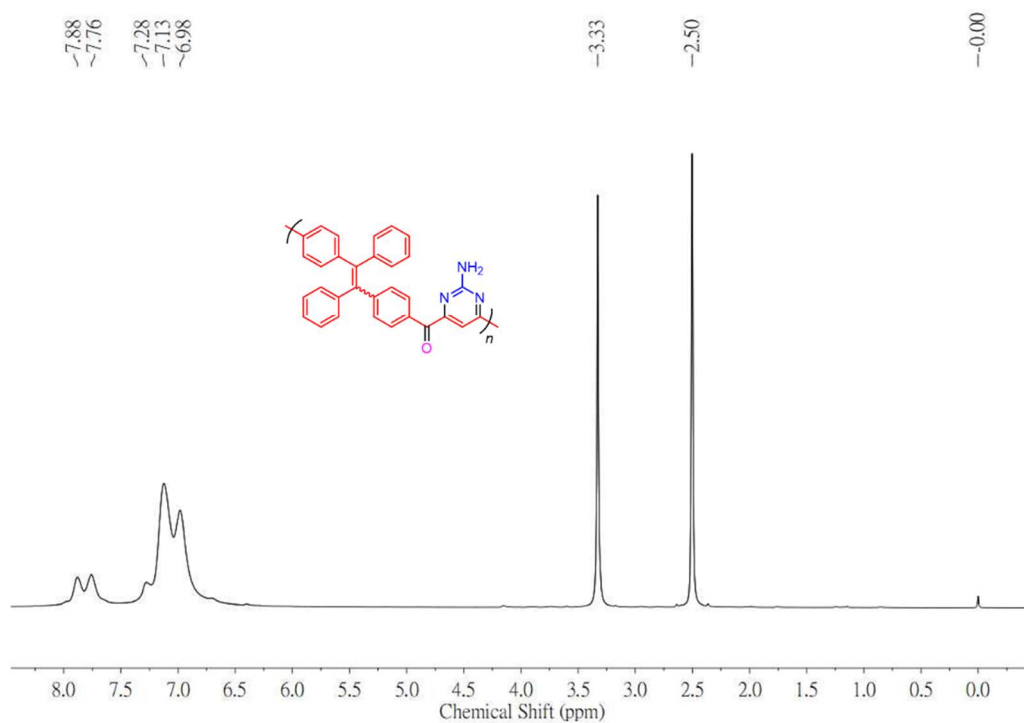




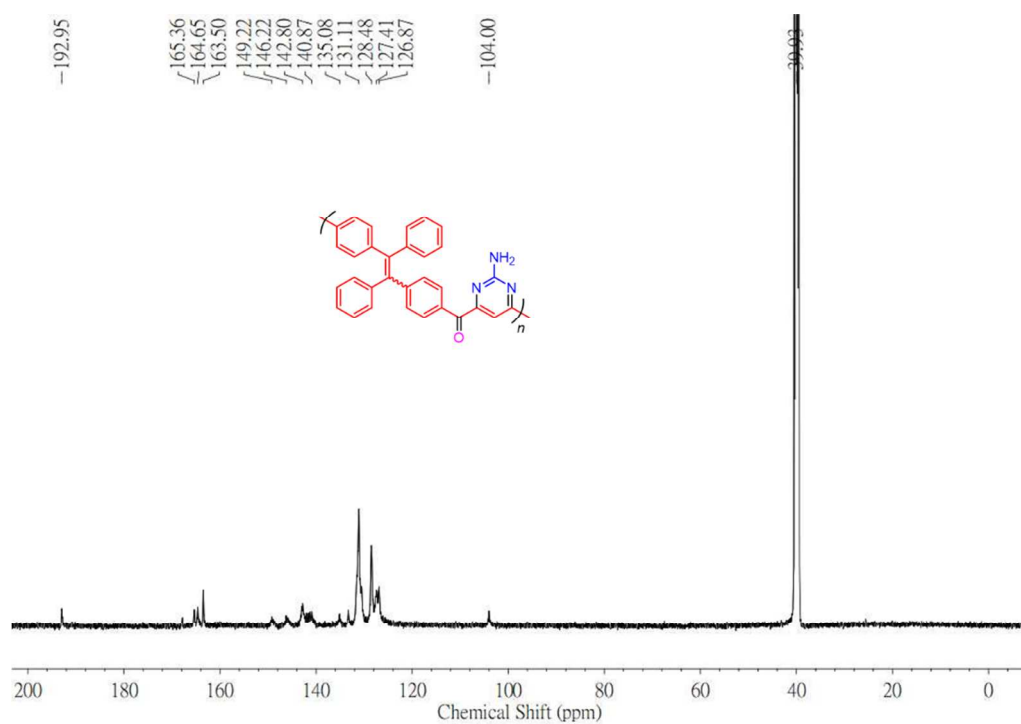
**Figure S16.** <sup>1</sup>H NMR of **9** in DMSO-*d*<sub>6</sub>.



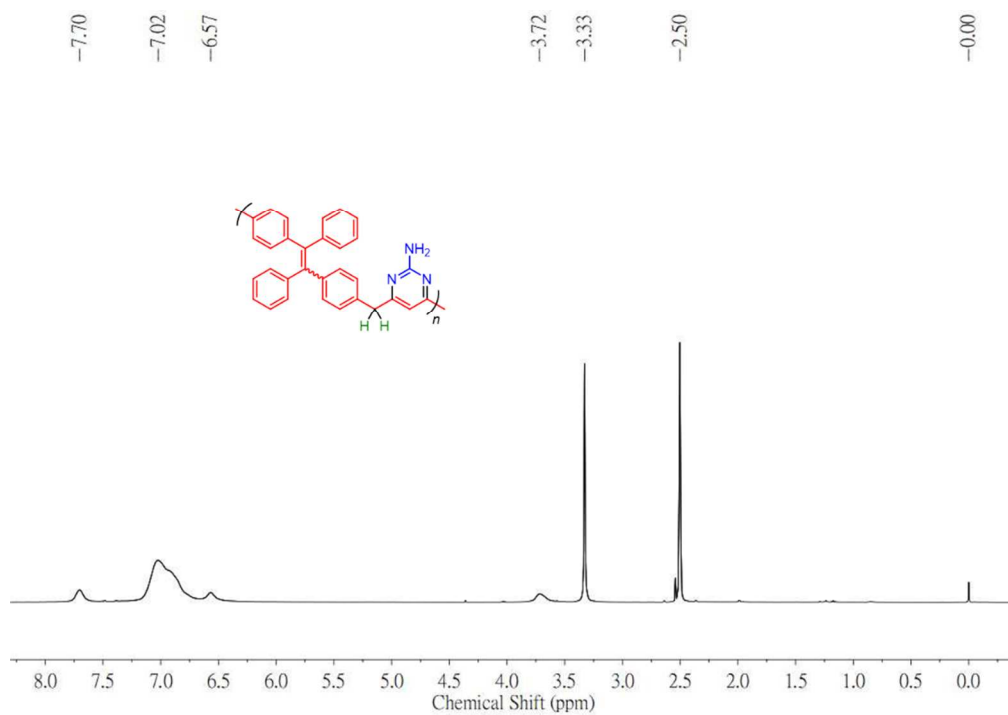
**Figure S17.** <sup>13</sup>C NMR of **9** in DMSO-*d*<sub>6</sub>.



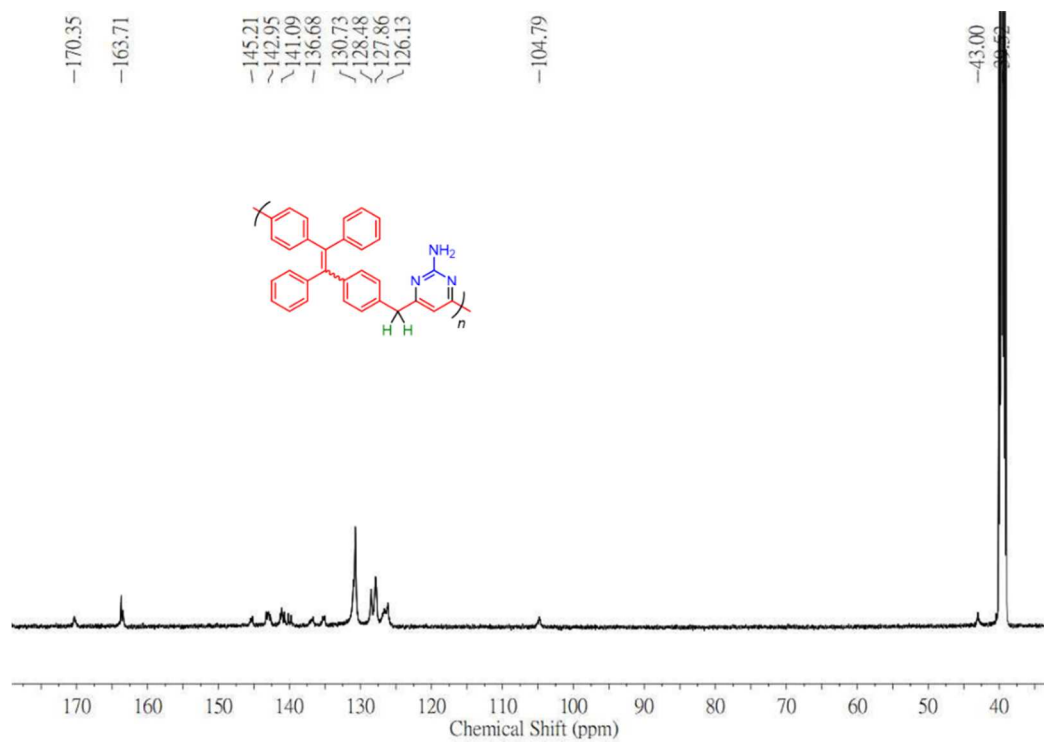
**Figure S18.** <sup>1</sup>H NMR of P1 in DMSO-*d*<sub>6</sub>.



**Figure S19.** <sup>13</sup>C NMR of P1 in DMSO-*d*<sub>6</sub>.



**Figure S20.** <sup>1</sup>H NMR of P2 in DMSO-*d*<sub>6</sub>.



**Figure S21.** <sup>13</sup>C NMR of P2 in DMSO-*d*<sub>6</sub>.

**Reference:**

- (1) Hu, R.; Maldonado, J. L.; Rodriguez, M.; Deng C.; Jim, C. K. W.; Lam, J. W. Y.; Yuen, M. M. F.; Ramos-Ortiz, G.; Tang, B. Z. *J. Mater. Chem.* **2012**, 22, 232-240.