Supporting Information

Polymeric Sulfonated Phenylamine as Efficient Solid Catalyst for Photochromic Naphthopyrans Production

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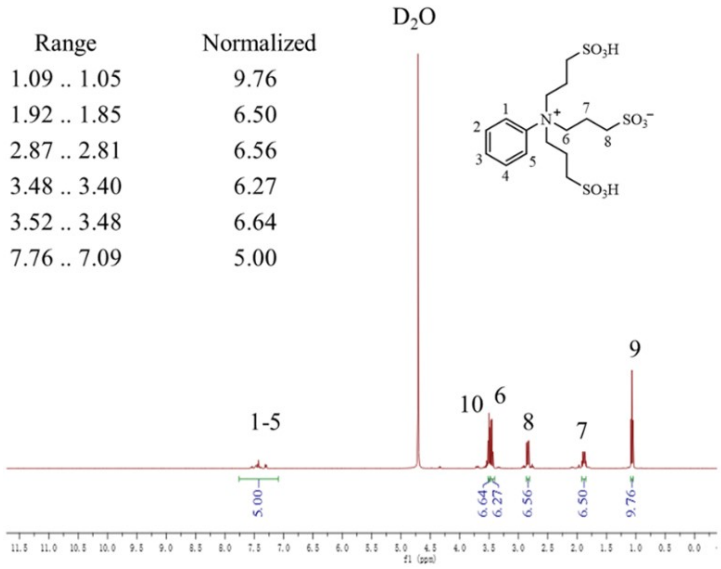

Figure S1. [1]H NMR spectra of SP.[1]

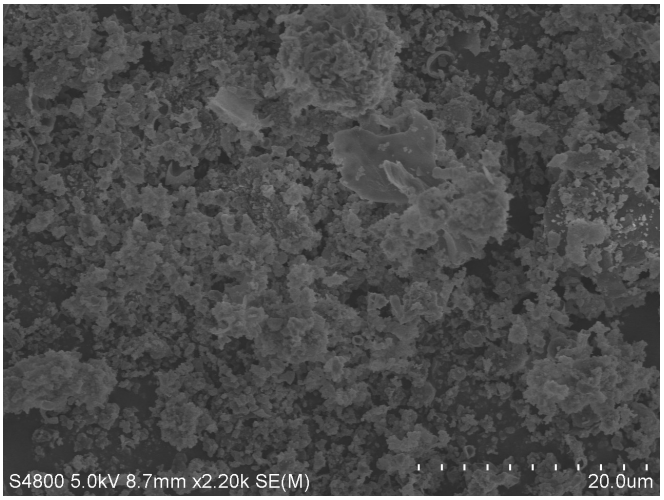

Figure S2. SEM image of PSP.

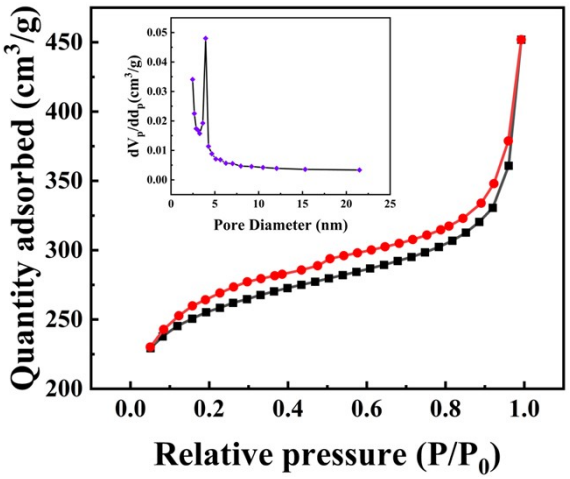

Figure S3. N_2 adsorption-desorption isotherm and pore size distribution of PSP.

Table S1. H_0 values of different catalysts. $H_0=pK(I_{aq})+\log([I]/[IH^+])$

Sample	Absorbance	[I] (%)	$[IH^+]$ (%)	H_0
Blank	1.290	100	0	—
PSP	1.208	93.64	6.36	2.16
SP	0.855	66.28	33.72	1.28
H_2SO_4	0.660	49.61	50.39	1.01
TsOH	0.792	61.40	38.60	1.19
acidic Al_2O_3	1.283	99.46	0.54	3.25

$pK(I_{aq})$ is the pKa value of p-nitroaniline solution (0.99), [I] represents the concentration of unreacted p-nitroaniline in the test reaction solution, and $[IH^+]$ represents the concentration of reacted p-nitroaniline in the test reaction solution.

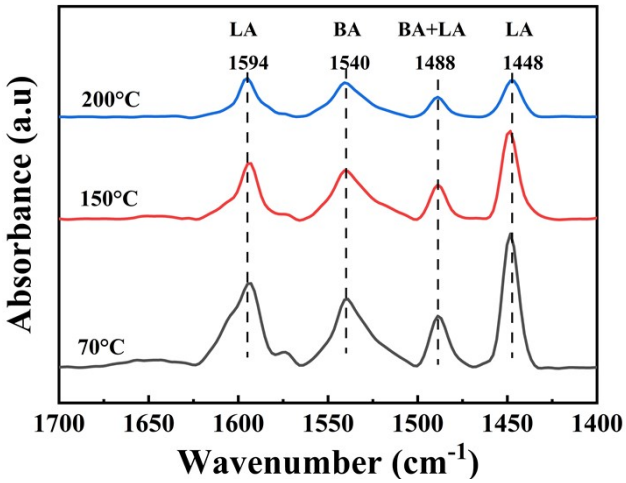

Figure S4. Pyridine-adsorbed FT-IR spectra of PSP.

Table S2. Amounts of acidic sites of PSP at different temperatures.

Temperature	Bronsted sites (C_B μmol/g)	Lewis sites (C_L μmol/g)	B/L ratio
70°C	16.23	11.61	1.40
150°C	12.42	8.02	1.55
200°C	7.80	3.57	2.18

Based on the following equations, the concentration of Brønsted (C_B (μmol g^{-1})) and Lewis acid (C_L (μmol g^{-1})) sites were calculated.

$$C_B\ (\mu mol\ g^{-1}) = (1.88 \times IA_B \times R^2)/W$$

$$C_L\ (\mu mol\ g^{-1}) = (1.42 \times IA_L \times R^2)/W$$

where IA_B and IA_L stand for the absorbance peak area at 1540 cm^{-1} for Brønsted acid sites and peak area at 1448 cm^{-1} for Lewis acid sites, respectively; R stands for the radius of the self-supported disk; W stands for the sample weight.

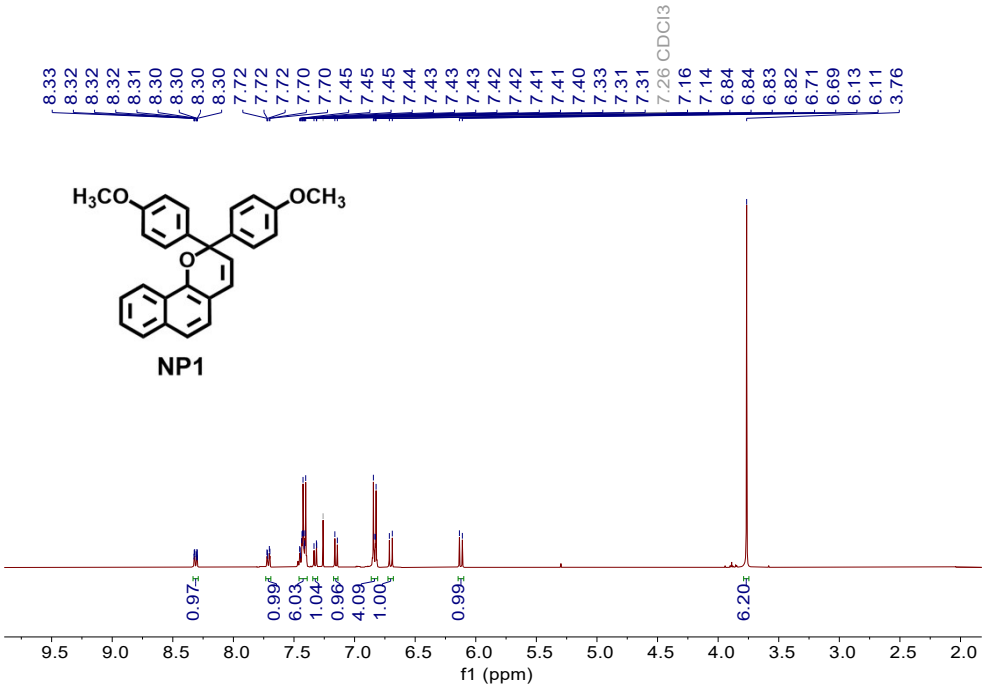

Figure S5. ^{1}H NMR spectra of **NP1** in $CDCl_3$

2,2-bis(4-methoxyphenyl)-2H-benzo[h]chromene **(NP1)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33–8.29 (m, 1H), 7.71 (dd, J = 8.1, 1.5 Hz, 1H), 7.46–7.40 (m, 6H), 7.35–7.30 (m, 1H), 7.15 (d, J = 8.3 Hz, 1H), 6.85–6.82 (m, 4H), 6.70 (d, J = 9.7 Hz, 1H), 6.12 (d, J = 9.7 Hz, 1H), 3.76 (s, 6H).

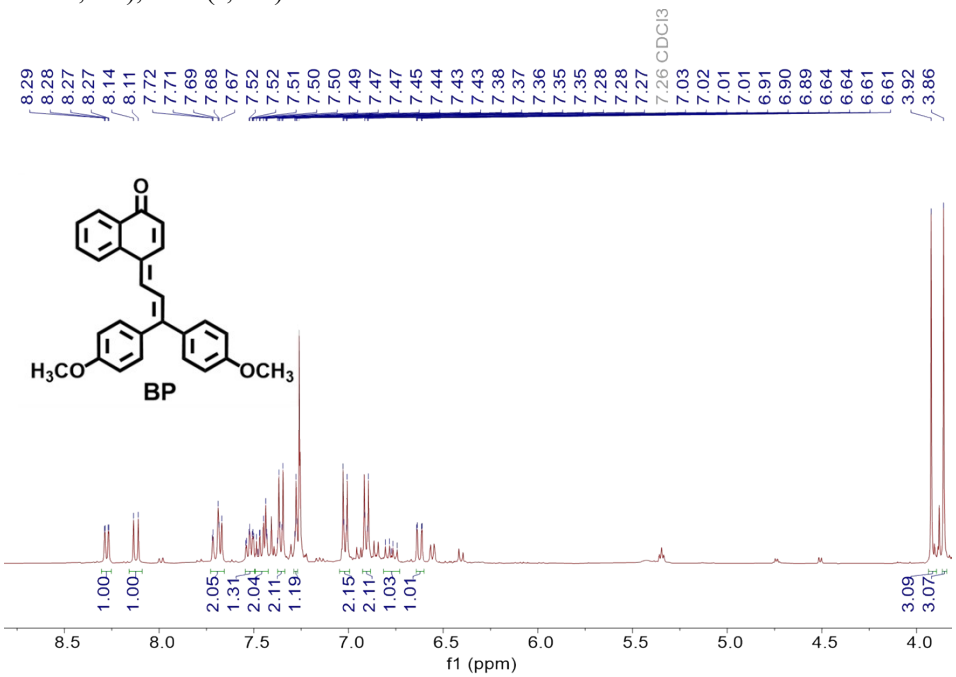

Figure S6. ^{1}H NMR spectra of **BP** in $CDCl_3$

4-(3,3-bis(4-methoxyphenyl)allylidene)naphthalen-1(4H)-one **(BP)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (dd, J = 7.8, 1.6 Hz, 1H), 8.12 (d, J = 10.1 Hz, 1H), 7.73–7.66 (m, 2H), 7.54–7.50 (m, 1H), 7.49–7.42 (m, 2H), 7.38–7.34 (m, 2H), 7.27 (d, J = 2.1 Hz, 1H), 7.03–7.00 (m, 2H), 6.90 (d, J = 7.6 Hz, 2H), 6.77 (dd, J = 16.0, 8.7 Hz, 1H), 6.63 (dd, J = 10.1, 1.6 Hz, 1H), 3.92 (s, 3H), 3.86 (s, 3H).

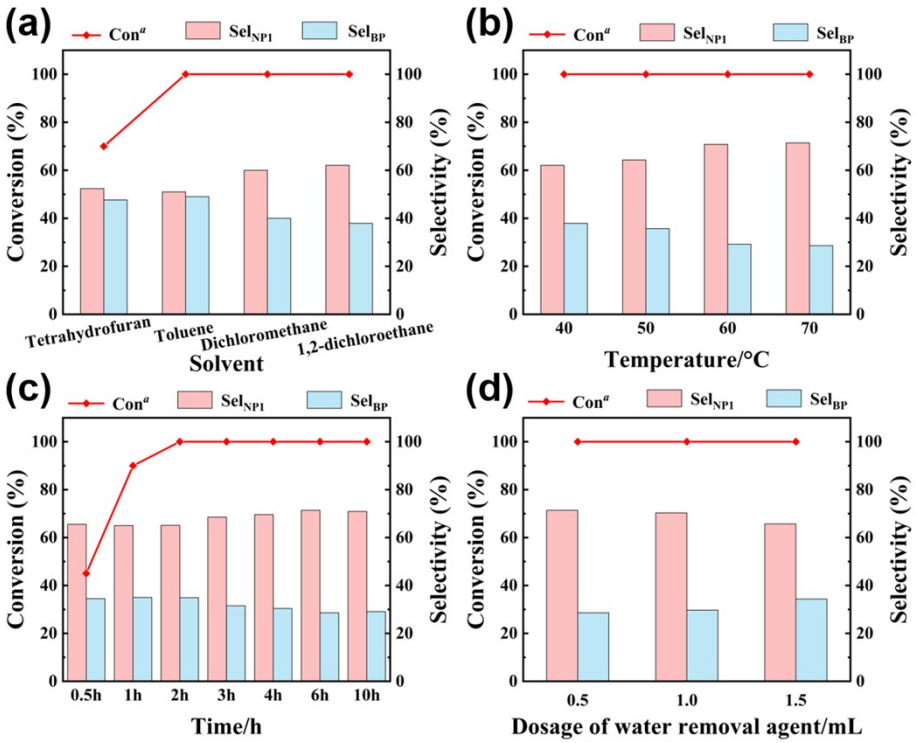

Figure S7. Influence of parameters towards reaction: (a) reaction solvent, (b) reaction temperature, (c) reaction time, (d) dosage of water removal agent. [a] Conversion of 1-naphthol. Reaction conditions of (a)(b)(c)(d): (a) 1-naphthol (0.69 mmol), 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol (0.76 mmol), trimethyl orthoformate (0.5 mL), PSP (0.01 g), different solvents (3 mL), 70°C for 6 h; (b) 1-naphthol (0.69 mmol), 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol (0.76 mmol), trimethyl orthoformate (0.5 mL), PSP (0.01 g), DCE (3 mL), different temperatures for 6 h; (c) 1-naphthol (0.69 mmol), 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol (0.76 mmol), trimethyl orthoformate (0.5 mL), PSP (0.01 g), DCE (3 mL), 70°C for different time; (d) 1-naphthol (0.69 mmol), 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol (0.76 mmol), different dosage of water remover (trimethyl orthoformate), PSP (0.01 g), DCE (3 mL), 70°C for 6h.

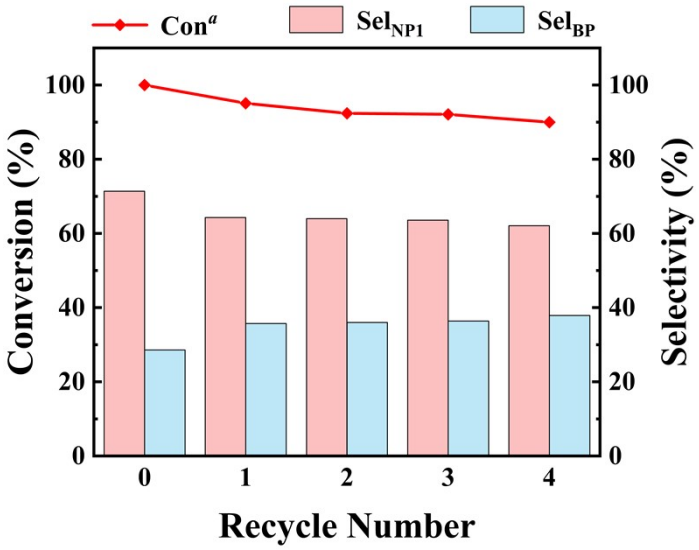

Figure S8. The reusability of PSP. [a] Conversion of 1-naphthol. Reaction condition: 1-naphthol (0.69 mmol), 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol (0.76 mmol), trimethyl orthoformate (0.5 mL), PSP (0.01 g), DCE (3 mL), 70°C for 6 h.

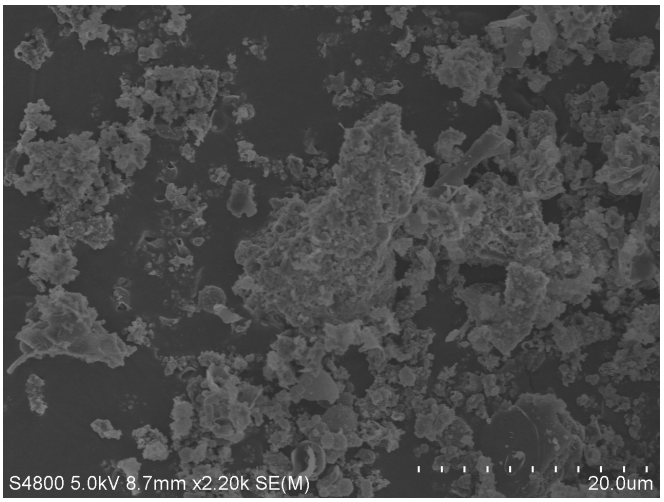

Figure S9. SEM image of recovered PSP.

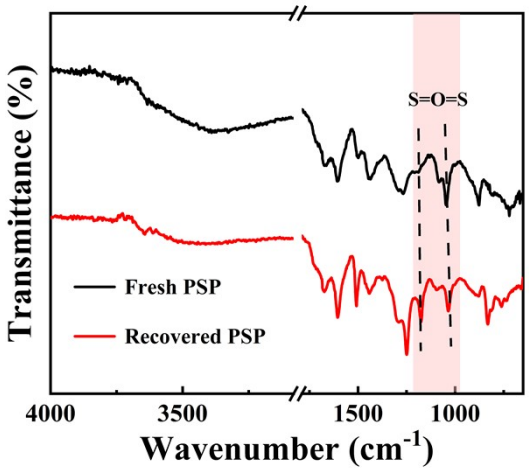

Figure S10. FT-IR spectra for the fresh and recovered PSP.

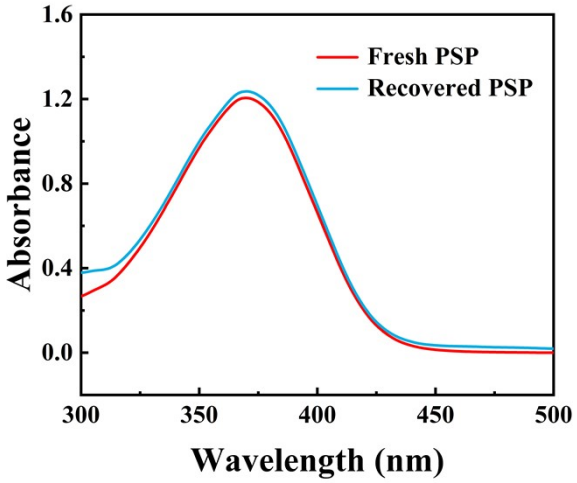

Figure S11. FT-IR spectra for the fresh and recovered PSP.

Table S3. H_0 values of fresh and recovered PSP. $H_0=pK(I_{aq})+\log([I]/[IH^+])$

Sample	Absorbance	[I] (%)	$[IH^+]$ (%)	H_0
Fresh PSP	1.208	93.64	6.36	2.16
Recovered PSP	1.238	95.97	4.03	2.36

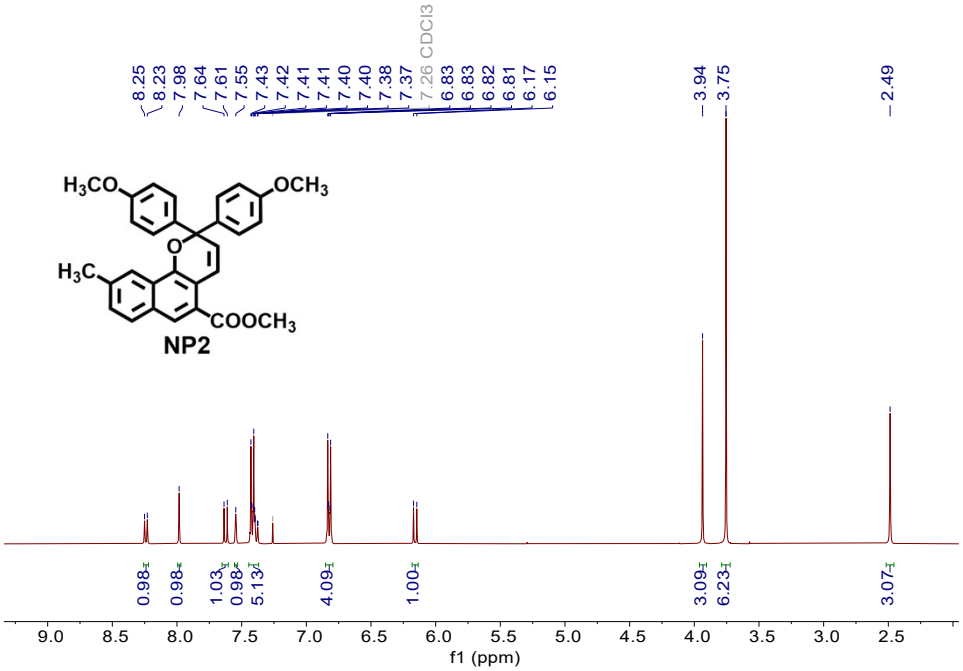

Figure S12. ^{1}H NMR spectra of **NP2** in $CDCl_3$

Methyl 2,2-bis(4-methoxyphenyl)-9-methyl-2H-benzo[h]chromene-5-carboxylate **(NP2)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, J = 8.5 Hz, 1H), 7.98 (s, 1H), 7.62 (d, J = 10.1 Hz, 1H), 7.55 (s, 1H), 7.45–7.35 (m, 5H), 6.88–6.80 (m, 4H), 6.16 (d, J = 10.1 Hz, 1H), 3.94 (s, 3H), 3.75 (s, 6H), 2.49 (s, 3H).

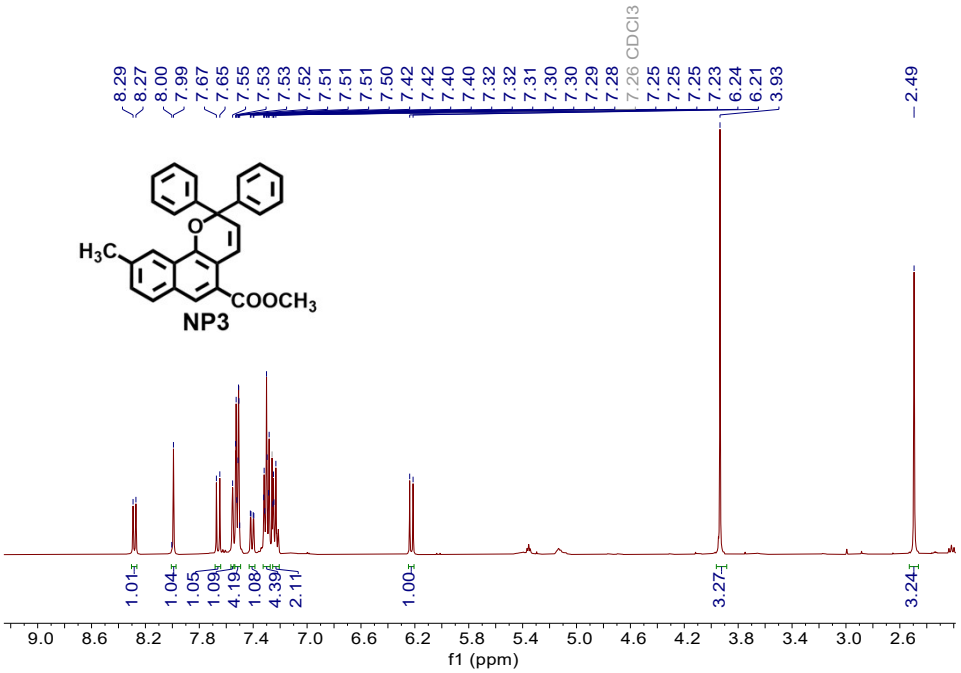

Figure S13. ^{1}H NMR spectra of **NP3** in $CDCl_3$

Methyl 9-methyl-2,2-diphenyl-2H-benzo[h]chromene-5-carboxylate **(NP3)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 8.5 Hz, 1H), 7.99 (s, 1H), 7.66 (d, J = 10.1 Hz, 1H), 7.55 (s, 1H), 7.54–7.50 (m, 4H), 7.41 (dd, J = 8.6, 1.7 Hz, 1H), 7.33–7.27 (m, 4H), 7.26–7.21 (m, 2H), 6.23 (d, J = 10.1 Hz, 1H), 3.93 (s, 3H), 2.49 (s, 3H).

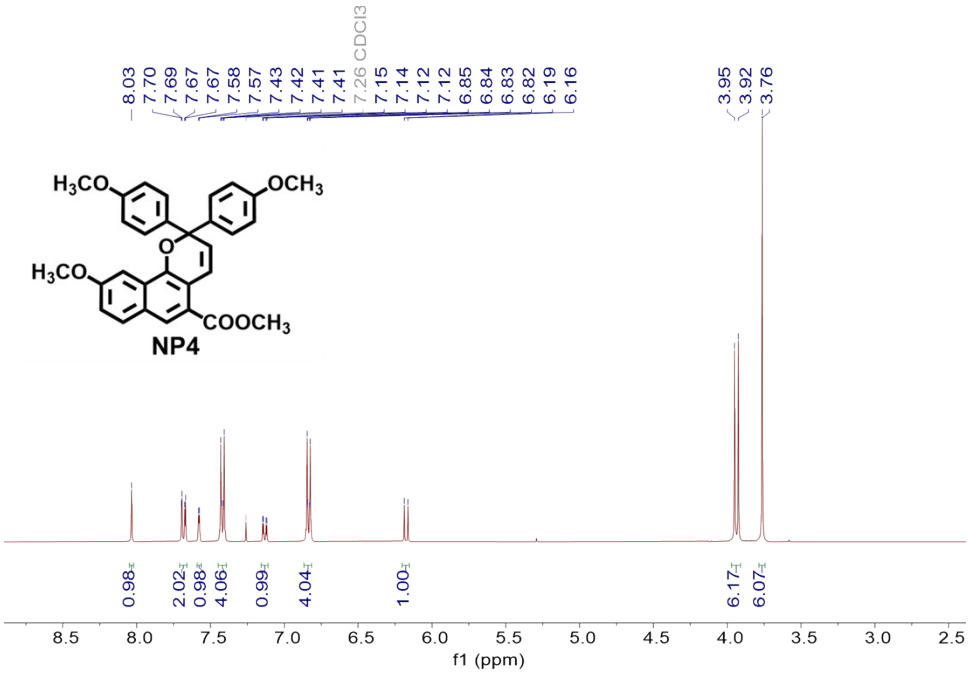

Figure S14. ^{1}H NMR spectra of **NP4** in $CDCl_3$

Methyl 9-methoxy-2,2-bis(4-methoxyphenyl)-2H-benzo[h]chromene-5-carboxylate **(NP4)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.68 (dd, J = 9.5, 1.9 Hz, 2H), 7.58 (d, J = 2.6 Hz, 1H), 7.44–7.40 (m, 4H), 7.13 (dd, J = 8.9, 2.6 Hz, 1H), 6.85–6.82 (m, 4H), 6.18 (d, J = 10.1 Hz, 1H), 3.94 (d, J = 10.3 Hz, 6H), 3.76 (s, 6H).

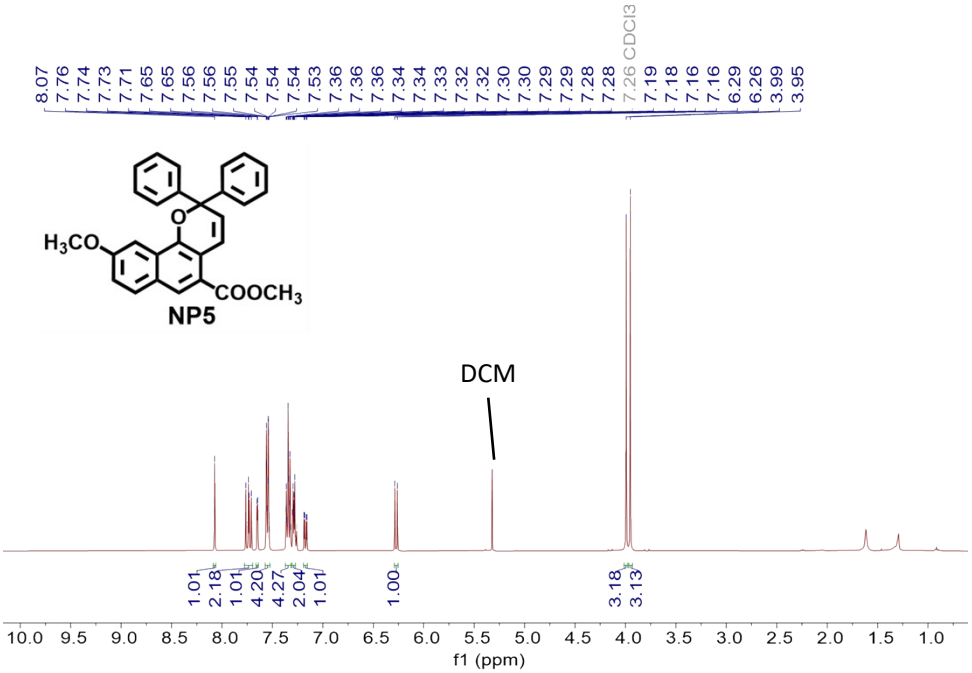

Figure S15. ^{1}H NMR spectra of **NP5** in $CDCl_3$

Methyl 9-methoxy-2,2-diphenyl-2H-benzo[h]chromene-5-carboxylate **(NP5)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.74 (dd, J = 12.5, 9.5 Hz, 2H), 7.65 (d, J = 2.6 Hz, 1H), 7.57–7.52 (m, 4H), 7.37–7.32 (m, 4H), 7.30–7.28 (m, 2H), 7.17 (dd, J = 8.9, 2.6 Hz, 1H), 6.27 (d, J = 10.1 Hz, 1H), 3.99 (s, 3H), 3.95 (s, 3H).

Notes and references

1. M. Zhang, S. Li, P. Zhang and Y. Leng, *New J. Chem.*, 2023, **47**, 13789-13796.