

## Electronic Supplementary Information

### **Reversible photochromic properties of 4,5,6-triaryl-4*H*-pyran derivatives in solid state**

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## Contents:

### 1. Experimental

#### 1.1 Measurements and materials

<sup>1</sup>H and <sup>13</sup>C NMR spectra were conducted on a Bruker DRX 500 NMR spectrometer. Melting points were determined using a WRS-1B digital melting point meter (uncorrected). HRMS-ESI mass spectra were conducted on a Hitachi Nano Frontier LD spectrometer. FT-IR spectra were conducted on a Nexus 870 FTIR spectrometer. Fluorescence spectra were conducted on a HITACHI F-7000 fluorometer. Absorption spectra were conducted on a UV-3600 Shimadzu spectrophotometer. XRD curves were recorded using an Empyrean X-ray diffraction instrument. The X-ray crystallographic analyses were conducted on a Bruker SMART II CCD area detector.  $\alpha$ -Phenyl chalcones **1a-1c** could be synthesized according to our previous report.<sup>1</sup> Malononitrile (**2**), piperidine, *tert*-butyl nitrite, and iodic acid were obtained from commercial suppliers.

#### 1.2 Synthesis of NPR-Bf, NPR-Bt, and NPR-Ph

General procedure: The mixture of **1a/1b/1c** (2.5 mmol, 1 equiv), malononitrile (5 mmol, 2 equiv), piperidine (2.5 mmol, 1 equiv), and ethyl alcohol (10 mL) was stirred at 80 °C for 1.5 h. After being cooled to the room temperature, a large amount of solids separated from the mixture. After vacuum filtration, the crude product was washed with ethyl alcohol three times and then gave pure NPR derivative. Characterization data of these compounds are listed as follows.

**2-Amino-6-(benzofuran-2-yl)-4,5-diphenyl-4H-pyran-3-carbonitrile (NPR-Bf)**. White solid (0.63 g, 65% yield). M. p. 238.8-239.6 °C. <sup>1</sup>HNMR (DMSO-*d*<sub>6</sub>, 500MHz):  $\delta$  7.55 (d, *J* = 8.0 Hz, 1H), 7.31-7.26 (m, 4H), 7.21-7.16 (m, 7H), 7.02-7.00 (m, 4H), 6.61 (s, 1H), 4.41 (s, 1H) ppm. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125 MHz):  $\delta$  159.6, 153.6, 148.1, 143.2, 136.5, 135.6, 128.8, 128.5, 128.0, 127.7, 127.6, 127.03, 126.98, 125.3, 123.2, 121.4, 119.9, 110.9, 107.4, 57.1, 45.0 ppm. FT-IR (KBr, cm<sup>-1</sup>): 3451, 3069, 3027, 2197, 1674, 1603, 1449, 1408, 1321, 967, 884, 829, 706. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calculated for C<sub>26</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>, 391.1441; found, 391.1442.

**2-Amino-6-(benzo[*b*]thiophen-2-yl)-4,5-diphenyl-4H-pyran-3-carbonitrile (NPR-Bt)**. White solid (0.68 g, 67% yield). M. p. 243.4-243.8 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz):  $\delta$  7.74 (t, *J* = 7.5 Hz, 2H), 7.55 (s, 1H), 7.34-7.25 (m, 7H), 7.21 (t, *J* = 7.0 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 2H), 7.03 (s, 2H), 6.98 (d, *J* = 7.0 Hz, 2H), 4.29 (s, 1H) ppm. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125 MHz):  $\delta$  159.7, 143.2, 139.5, 138.6, 137.8, 136.1, 134.5, 129.7, 128.6, 128.5, 128.3, 127.8, 127.0, 125.2, 124.6, 124.3, 123.7, 121.9, 119.9, 118.5, 57.0, 45.7 ppm. FT-IR (KBr, cm<sup>-1</sup>): 3451, 3051, 3023, 2194, 1674, 1559, 1454, 1405, 1228, 971, 856, 827, 700. HRMS (ESI) *m/z*: [M+Na]<sup>+</sup> calculated for C<sub>26</sub>H<sub>18</sub>N<sub>2</sub>OSNa, 429.1038; found, 429.1035.

**2-Amino-4,5,6-triphenyl-4H-pyran-3-carbonitrile (NPR-Ph)**. White solid (0.56 g, 64% yield). M. p. 251.2-251.5 °C. <sup>1</sup>HNMR (DMSO-*d*<sub>6</sub>, 500 MHz):  $\delta$  7.30-7.17 (m, 10H), 7.08-7.07 (m,

3H), 6.90-6.88 (m, 2H), 6.85 (s, 2H), 4.38 (s, 1H) ppm.  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 125 MHz):  $\delta$  159.9, 144.3, 144.0, 137.4, 133.1, 129.3, 128.9, 128.48, 128.45, 128.0, 127.8, 127.5, 126.9, 126.7, 120.1, 116.2, 57.3, 44.6 ppm. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3451, 3057, 3021, 2193, 1674, 1641, 1596, 1453, 1414, 1228, 976, 773, 697. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{24}\text{H}_{19}\text{N}_2\text{O}$ , 351.1492; found, 351.1492.

### 1.3 Synthesis of PR-Bf and PR-Bt

General procedure: The mixture of the NPR derivative (2.5 mmol), *tert*-butyl nitrite (3 mmol), and tetrahydrofuran (5 mL) was stirred at room temperature for 12 h. The crude product was obtained by vacuum filtration and then purified by a silica gel column chromatography using ethyl acetate/petroleum ether (v:v = 1:20) as the eluent to give pure PR derivative. Characterization data of these compounds are listed as follows.

**6-(Benzofuran-2-yl)-4,5-diphenyl-4H-pyran-3-carbonitrile (PR-Bf).** White solid (0.48 g, 51% yield). M. p. 180.8-181.2 °C.  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  7.97 (s, 1H), 7.52 (d,  $J = 8.0$  Hz, 1H), 7.36-7.33 (m, 3H), 7.29-7.18 (m, 8H), 7.00 (d,  $J = 7.5$  Hz, 2H), 6.44 (s, 1H), 4.66 (s, 1H) ppm.  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 125 MHz):  $\delta$  153.5, 151.5, 147.5, 140.9, 136.2, 136.1, 128.72, 128.66, 128.4, 128.2, 127.9, 127.7, 127.0, 125.4, 123.3, 121.5, 116.9, 111.0, 107.5, 92.9, 43.0 ppm. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3077, 3029, 2218, 1658, 1629, 1452, 1325, 1250, 1215, 985, 889, 819, 769, 697. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{26}\text{H}_{17}\text{NO}_2\text{Na}$ , 398.1157; found, 398.1153.

**6-(Benzo[*b*]thiophen-2-yl)-4,5-diphenyl-4H-pyran-3-carbonitrile (PR-Bt).** White solid (0.51 g, 52% yield). M. p. 189.7-190.5 °C.  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  7.99 (s, 1H), 7.77-7.22 (m, 2H), 7.35-7.23 (m, 11H), 7.00-6.98 (m, 2H), 4.56 (s, 1H) ppm.  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 125 MHz):  $\delta$  151.7, 140.9, 130.4, 139.1, 138.0, 135.9, 134.2, 129.6, 128.73, 128.67, 128.53, 128.47, 127.7, 125.3, 124.61, 124.5, 124.0, 121.9, 117.0, 116.9, 92.9, 42.7 ppm. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3074, 3030, 2215, 1665, 1627, 1454, 1317, 1217, 980, 883, 841, 749, 669. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{26}\text{H}_{17}\text{NOSNa}$ , 414.0929; found, 414.0925.

### 1.4 Synthesis of 4-phenyl-4H-benzo[*f*]benzofuro[3,2-*h*]chromene-3-carbonitrile (PR-Bf-Ox)

The mixture of **PR-Bf** (100 mg, 0.27 mmol), iodic acid (54 mg, 0.33 mmol), and acetonitrile (5 mL) was stirred for 3 h under the irradiation (365 nm, 10 W) in a light reactor, and thus a large amount of solids separated from the mixture. After vacuum filtration, the crude product was washed with acetonitrile three times and then gave pure **PR-Bf-Ox** (83 mg, 83%) as a white solid. Due to the very poor solubility of **PR-Bf-Ox** in common organic solvents, the NMR spectra of this compound could not be obtained. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{26}\text{H}_{15}\text{NO}_2\text{Na}$ , 396.1001; found, 396.0995.

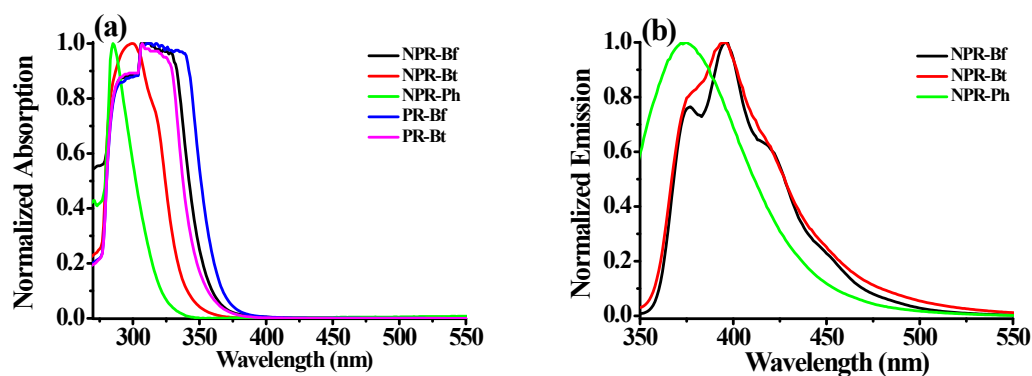
### 1.5 Synthesis of 4-phenyl-4H-benzo[*f*]benzo[4,5]thieno[3,2-*h*]chromene-3-carbonitrile (PR-Bt-Ox)

The mixture of **PR-Bt** (100 mg, 0.25 mmol), iodic acid (53 mg, 0.3 mmol), and acetonitrile (5 mL) was stirred for 3 h under the irradiation (365 nm, 10 W) in a light reactor, and thus a large amount of solids separated from the mixture. The crude product was obtained by vacuum filtration and then purified by a silica gel column chromatography using ethyl acetate/petroleum ether) (v:v = 1:80) as the eluent to give pure **PR-Bt-Ox** (72 mg, 74%) as a white solid. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz): δ 9.05 (d, *J* = 8.5 Hz, 1H), 8.97 (d, *J* = 8.5 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.11 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.71-7.63 (m, 3H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.35-7.30 (m, 4H), 7.24-7.21 (m, 1H), 5.66 (s, 1H) ppm. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125 MHz): δ 150.6, 142.9, 141.7, 139.0, 135.5, 130.4, 129.04, 128.99, 128.1, 127.9, 127.5, 126.6, 126.4, 126.0, 125.8, 125.1, 125.0, 123.8, 123.7, 117.1, 112.1, 95.1, 54.9, 37.3 ppm. HRMS (ESI) *m/z*: [M+Na]<sup>+</sup> calculated for C<sub>26</sub>H<sub>15</sub>NOSNa, 412.0772; found, 412.0770.

## References

1. L. Shan, G. Wu, M. Liu, W. Gao, J. Ding, X. Huang and H. Wu, *Org. Chem. Front.* 2018, **5**, 1651–1654.

## 2. Figures and tables

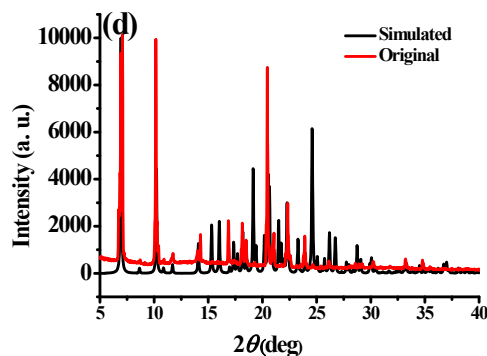
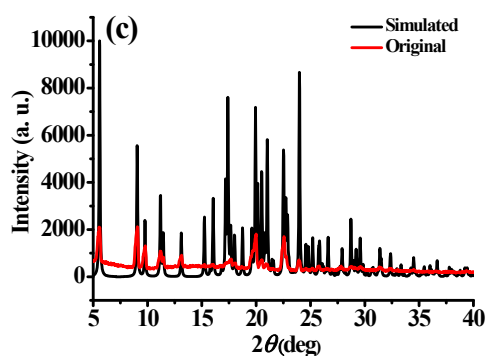
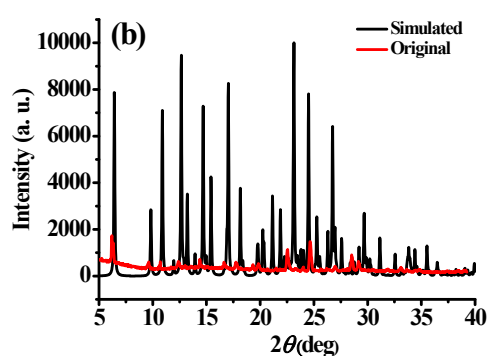
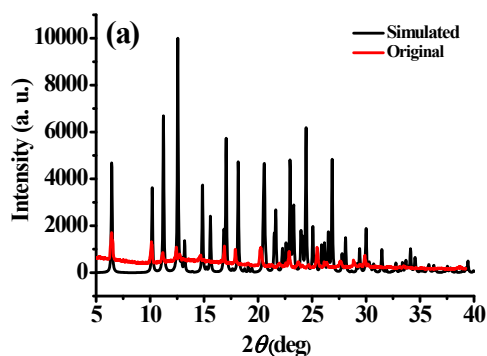


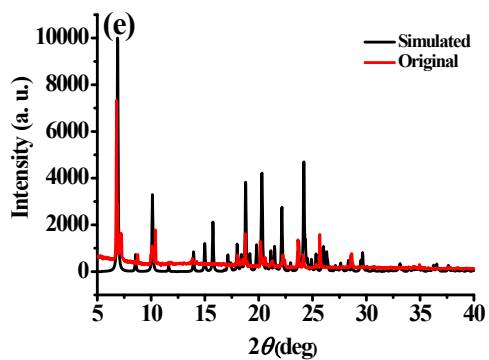
**Fig. S1** Normalized absorption (a) and fluorescence (b) spectra of the NPR and PR derivatives in toluene ( $1 \times 10^{-3}$  mol/L).

**Table S1** Crystallographic data and details of collection and refinement for single crystals of the NPR derivatives, PR derivatives, and **PR-Bt-Ox**.

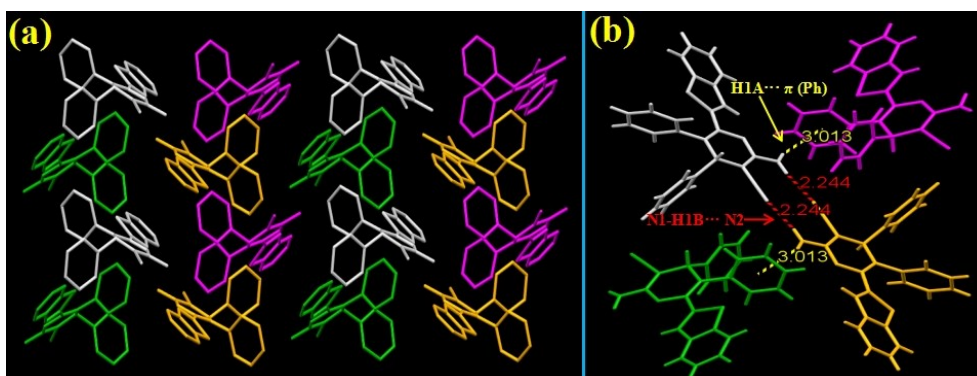
	<b>NPR-Bf</b>	<b>NPR-Bt</b>	<b>NPR-Ph</b>	<b>PR-Bf</b>	<b>PR-Bt</b>	<b>PR-Bt-Ox</b>
CCDC (No.)	2010048	2010049	2010051	2010050	2010052	2058996
Empirical formula	C <sub>26</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub>	C <sub>26</sub> H <sub>18</sub> N <sub>2</sub> OS	C <sub>24</sub> H <sub>18</sub> N <sub>2</sub> O	C <sub>26</sub> H <sub>17</sub> NO <sub>2</sub>	C <sub>26</sub> H <sub>17</sub> NOS	C <sub>26</sub> H <sub>15</sub> NOS
Formula weight	390.42	406.48	350.40	375.40	391.46	389.45
Temperature (K)	296(2)	293(2)	296(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>
<i>Z</i>	4	4	8	4	4	4

$D_{\text{calcd}}$ [Mg/m <sup>3</sup> ]	1.316	1.330	1.256	1.281	1.289	1.365
$F(000)$	816	848	1472	784	816	808
$\theta$ range [°]	3.226-65.991	2.753-25.500	2.578-26.000	2.504-25.998	2.491-25.992	2.553-25.997
$R_1$ [ $I > 2\sigma(I)$ ]	0.0498	0.0596	0.0403	0.0461	0.0434	0.0433
$wR_2$ [ $I > 2\sigma(I)$ ]	0.1353	0.1190	0.0940	0.1085	0.1016	0.0907
$a$ [Å]	13.8506(3)	13.9040(12)	32.1003(8)	5.8562(2)	5.9742(2)	10.3399(5)
$b$ [Å]	8.2078(2)	8.1180(7)	5.9107(2)	20.4312(6)	20.6532(6)	1.2956(10)
$c$ [Å]	17.5327(4)	18.1962(17)	19.8365(5)	16.4731(5)	16.5404(4)	8.7889(5)
$\alpha$ [deg]	90	90	90	90	90	90
$\beta$ [deg]	98.5150(10)	98.813(3)	100.1180(10)	99.0920(10)	98.6610(10)	101.714(2)
$\gamma$ [deg]	90	90	90	90	90	90
$V$ [Å <sup>3</sup> ]	1971.20(8)	2029.6(3)	3705.15(18)	1946.23(11)	2017.59(10)	1894.96(17)
GOF	1.062	1.085	1.048	1.013	1.026	1.038
$R$ (int)	0.0335	0.0588	0.0453	0.0439	0.0394	0.0606
No. of reflcns collected	12562	15234	39121	23860	20471	18922
No. of unique reflcns	3427	3766	3639	3813	3953	3721
$R_1$ (all data)	0.0512	0.1023	0.0495	0.0708	0.0655	0.0666
$wR_2$ (all data)	0.1366	0.1418	0.1016	0.1272	0.1181	0.1026

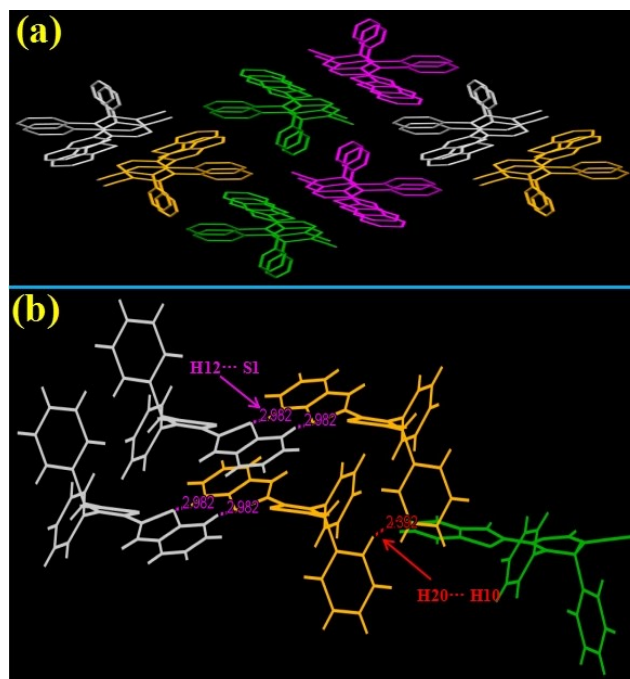




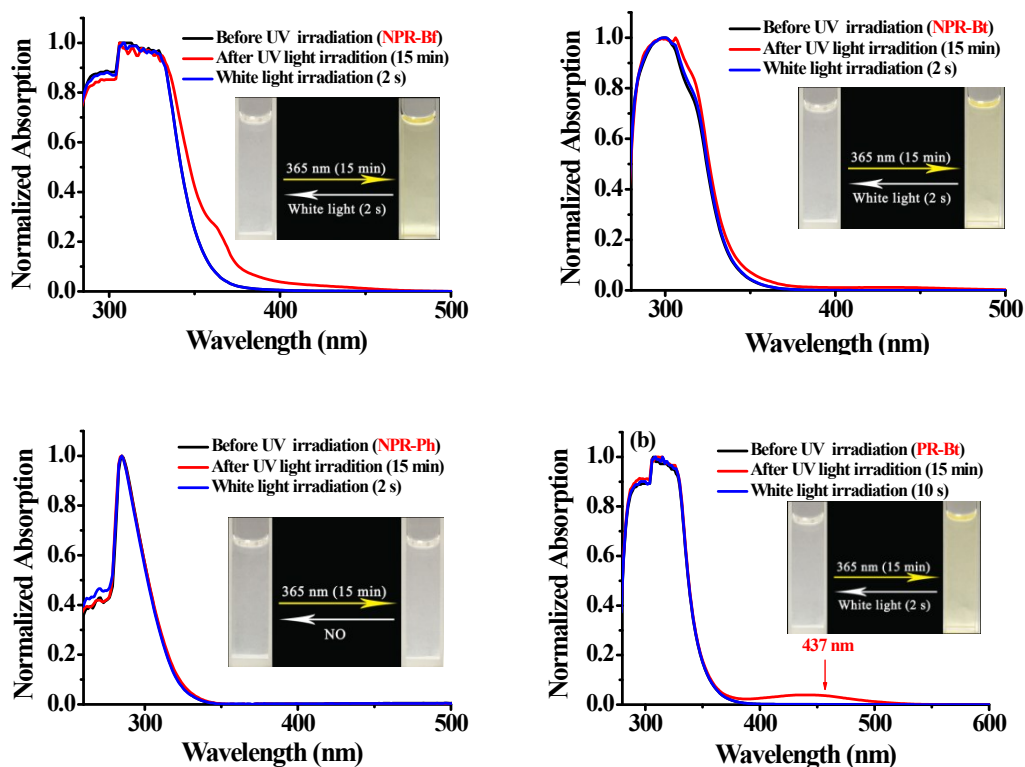
**Fig. S2** Comparison of XRD curves of the original samples of the target compounds and the simulated XRD curves obtained from the corresponding single crystals: **NPR-Bf** (a), **NPR-Bt** (b), **NPR-Ph** (c), **PR-Bf** (d), and **PR-Bt** (e).



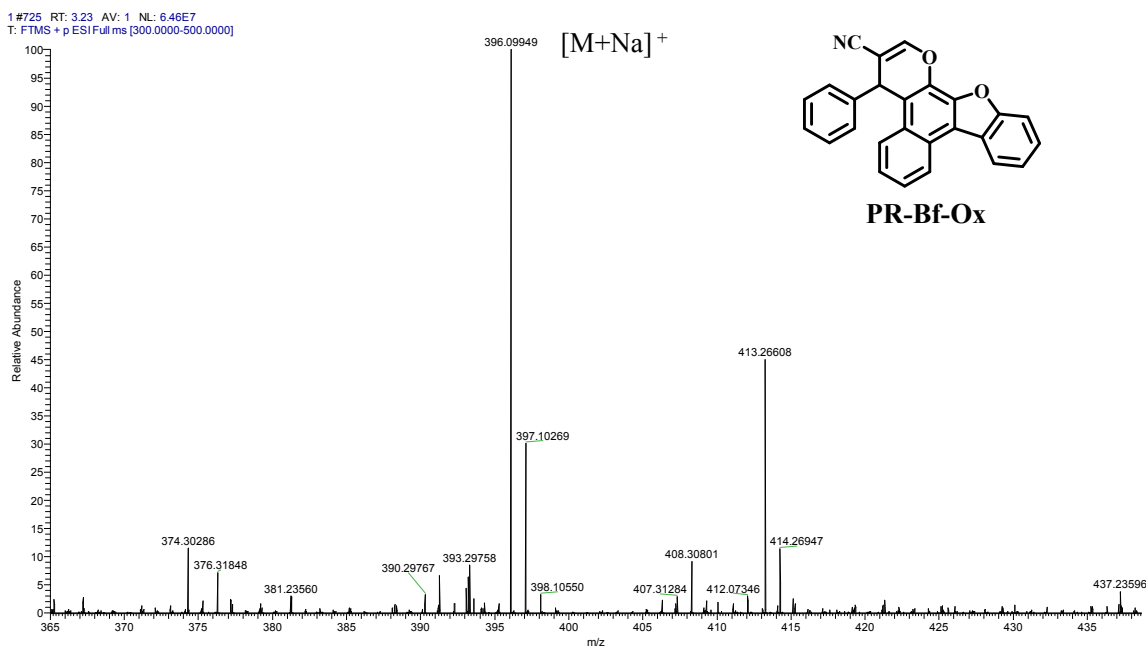
**Fig. S3** Single crystal **NPR-Bt**: (a) molecular stacking arrangement; (b) intermolecular interactions including C-H...N hydrogen bond and C-H... $\pi$  interaction.



**Fig. S4** Single crystal **PR-Bt**: (a) molecular stacking arrangement; (b) intermolecular interactions including C-H...S bond and C-H...H interaction.



**Fig. S5** The photochromic response of the NPR and PR derivatives in toluene solvent ( $1 \times 10^{-3}$  mol/L) under different conditions. Inset: the color pictures of the NPR and PR derivatives after UV-light (right) and then white-light irradiation (left).



**Fig. S6** HRMS-ESI of PR-Bf-Ox.

### 3. Spectra of NMR

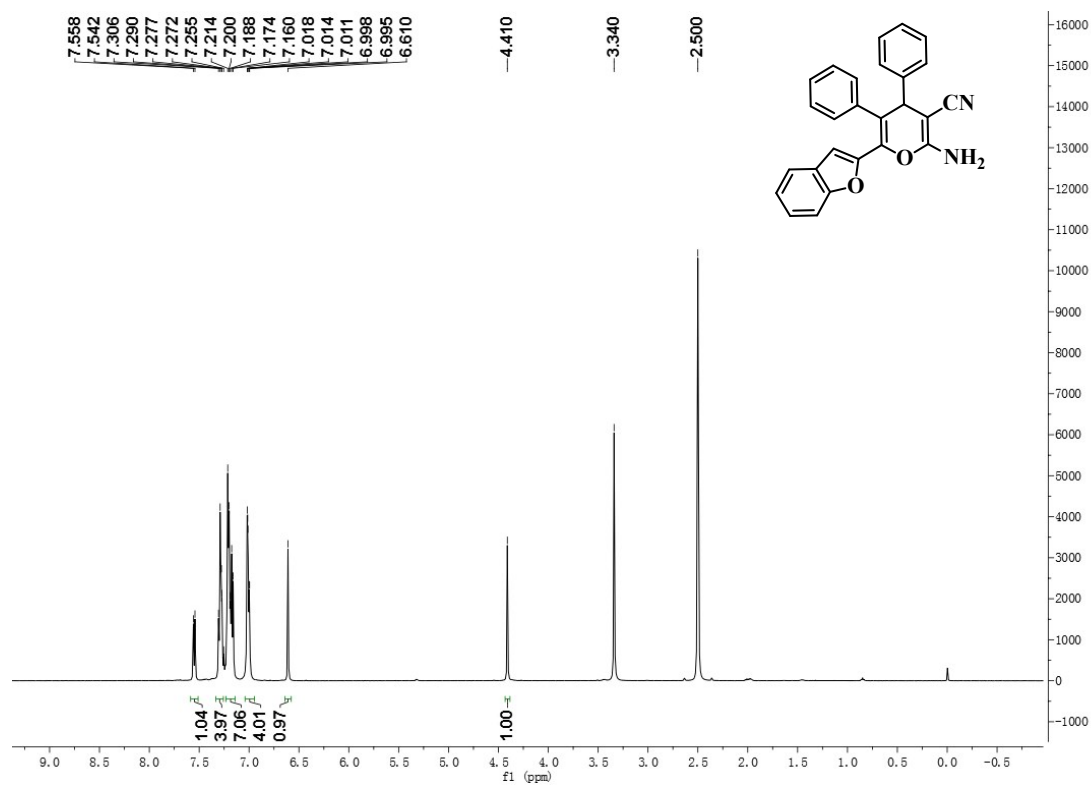


Fig. S7  $^1\text{H}$  NMR of NPR-Bf (DMSO- $d_6$ , 500 MHz).

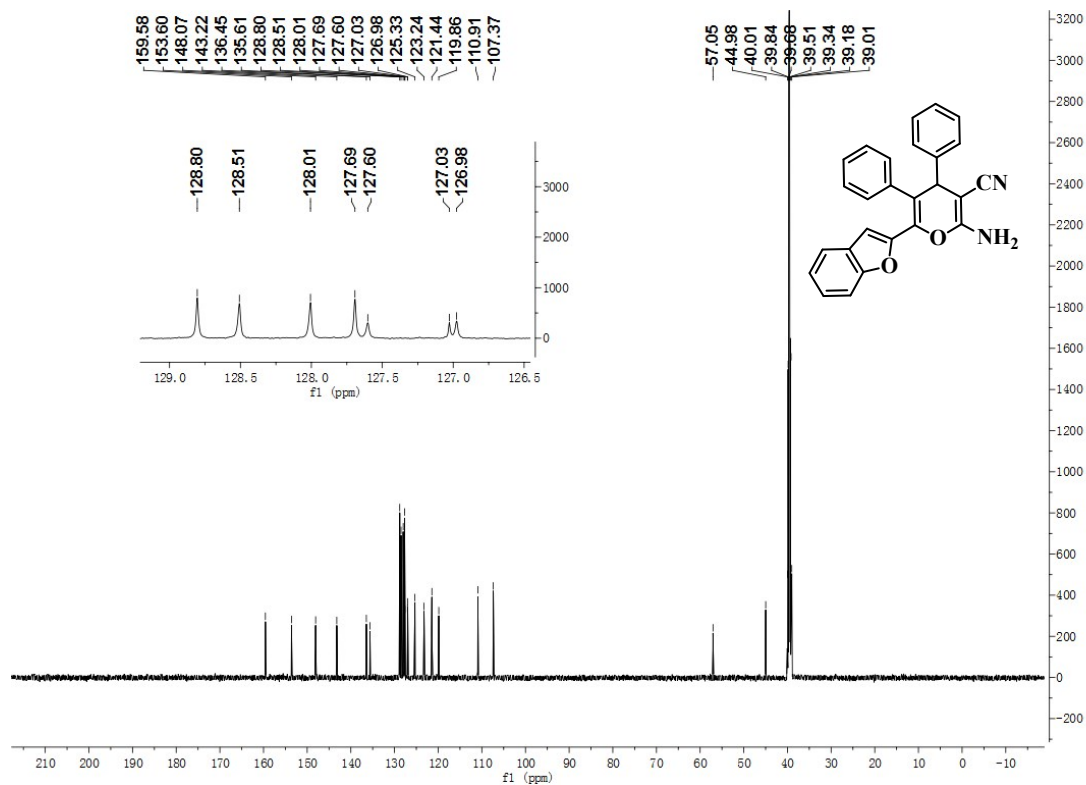


Fig. S8  $^{13}\text{C}$  NMR of NPR-Bf (DMSO- $d_6$ , 125 MHz).



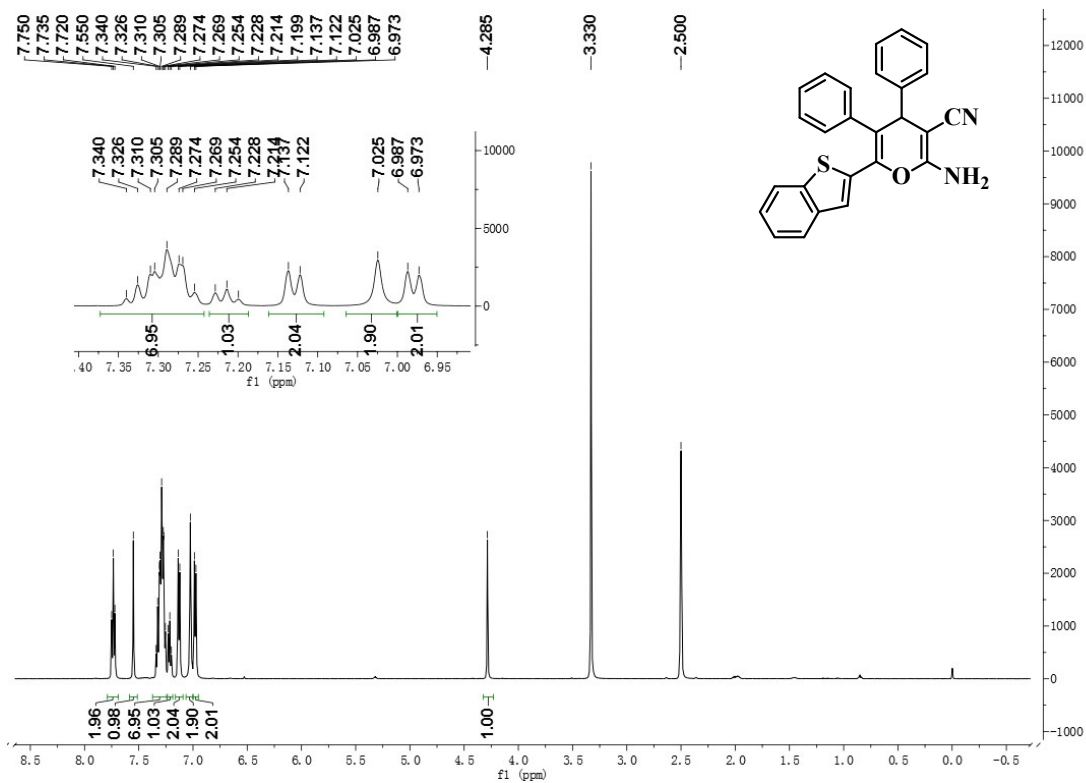


Fig. S9 <sup>1</sup>H NMR of NPR-Bt (DMSO-*d*<sub>6</sub>, 500 MHz).

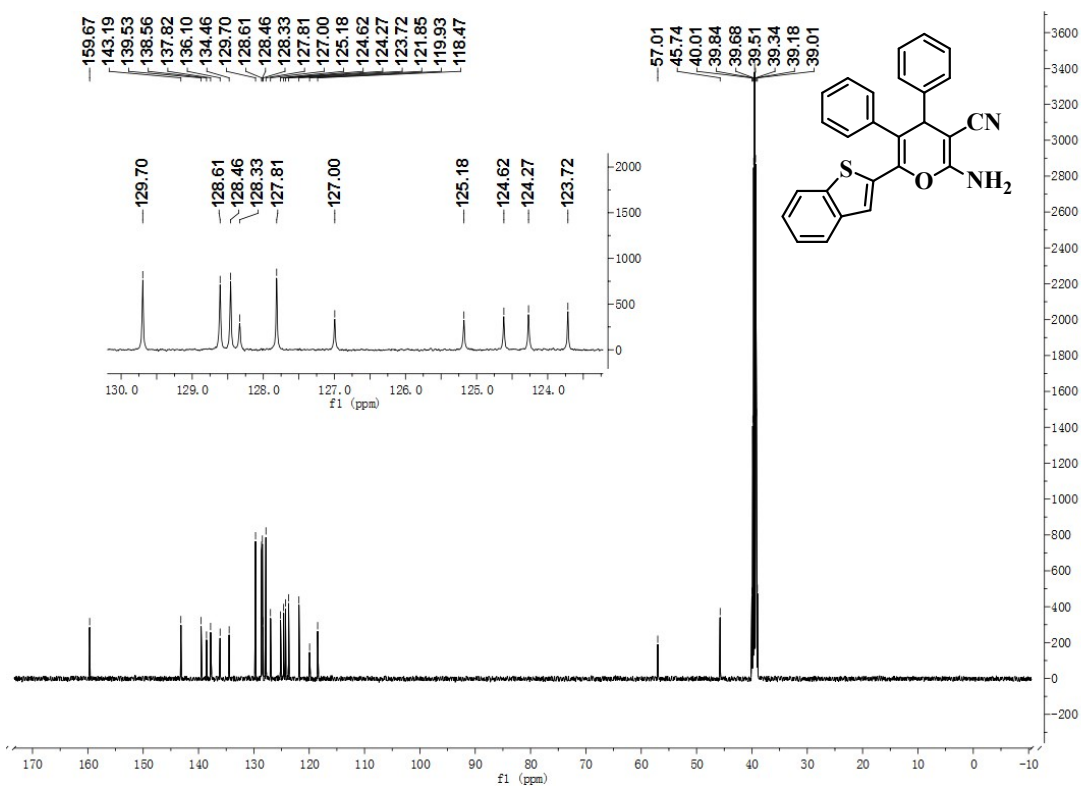


Fig. S10 <sup>13</sup>C NMR of NPR-Bt (DMSO-*d*<sub>6</sub>, 125 MHz).

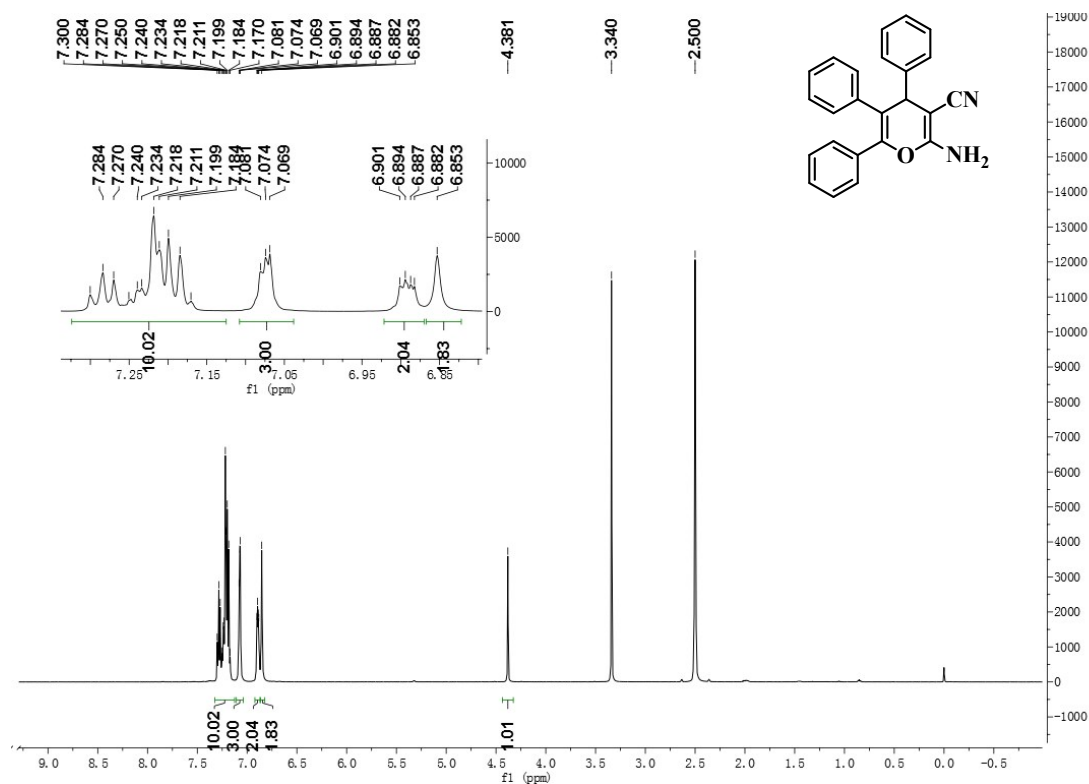


Fig. S11 <sup>1</sup>H NMR of NPR-Ph (DMSO-*d*<sub>6</sub>, 500 MHz).

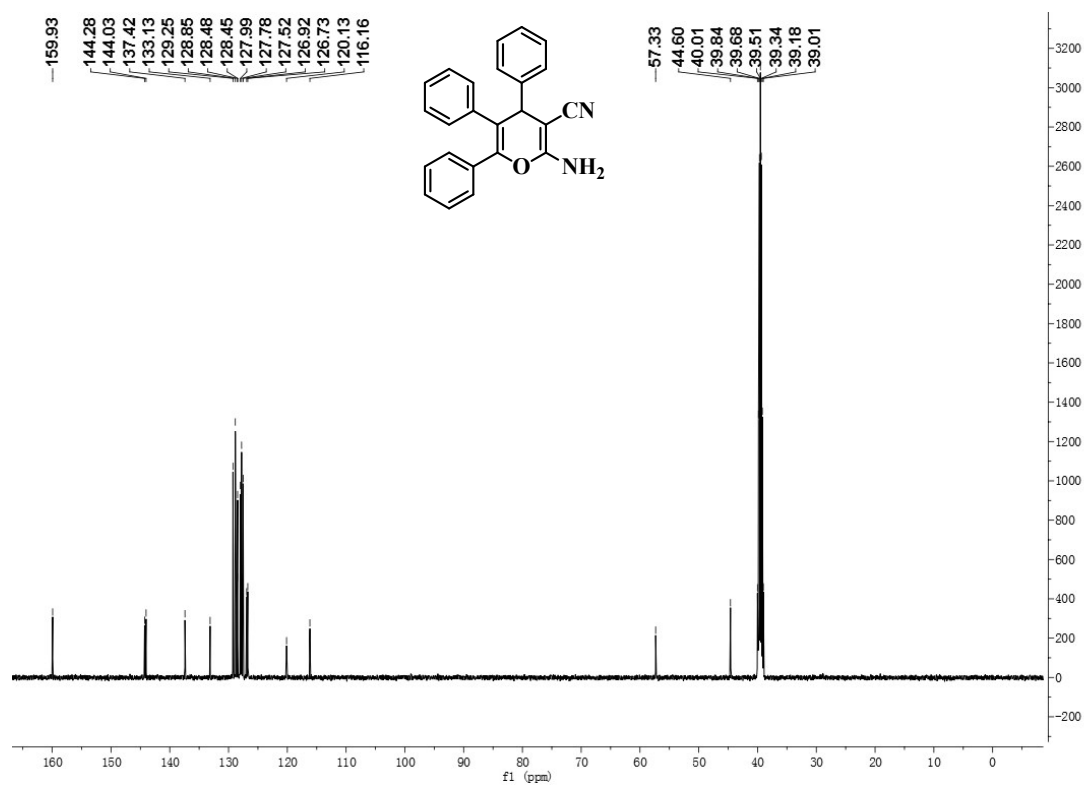


Fig. S12 <sup>13</sup>C NMR of NPR-Ph (DMSO-*d*<sub>6</sub>, 125 MHz).

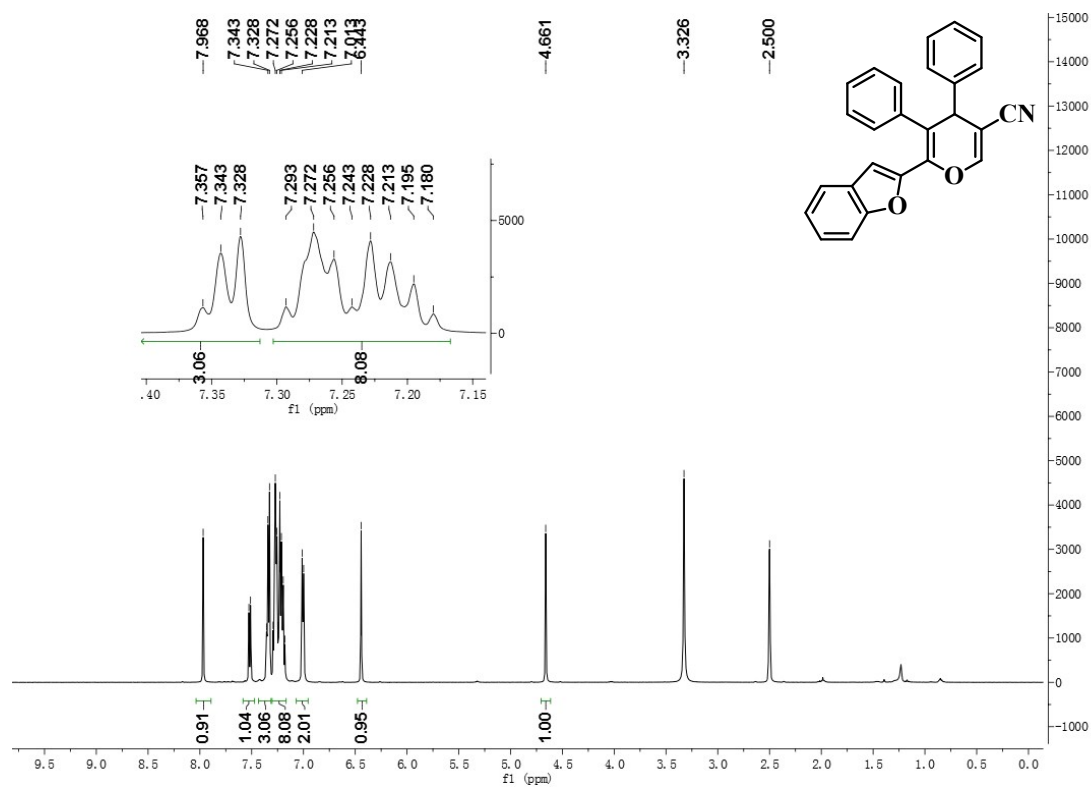


Fig. S13 <sup>1</sup>H NMR of PR-Bf (DMSO-*d*<sub>6</sub>, 500 MHz).

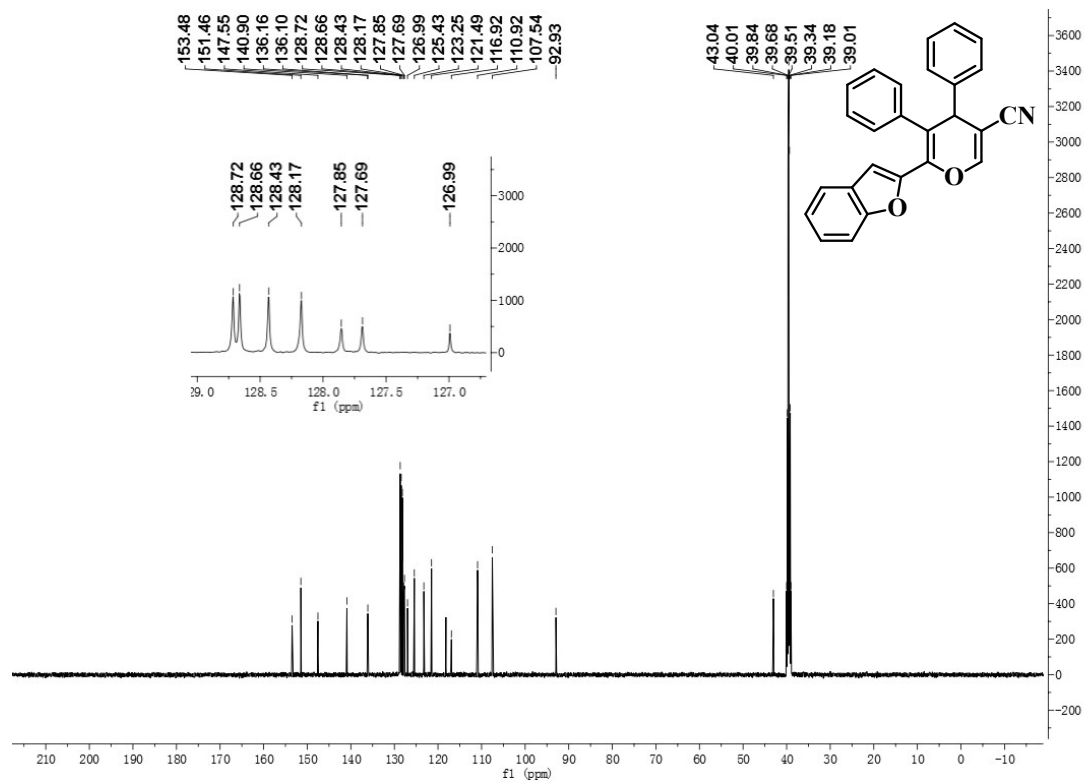


Fig. S14 <sup>13</sup>C NMR of PR-Bf (DMSO-*d*<sub>6</sub>, 125 MHz).

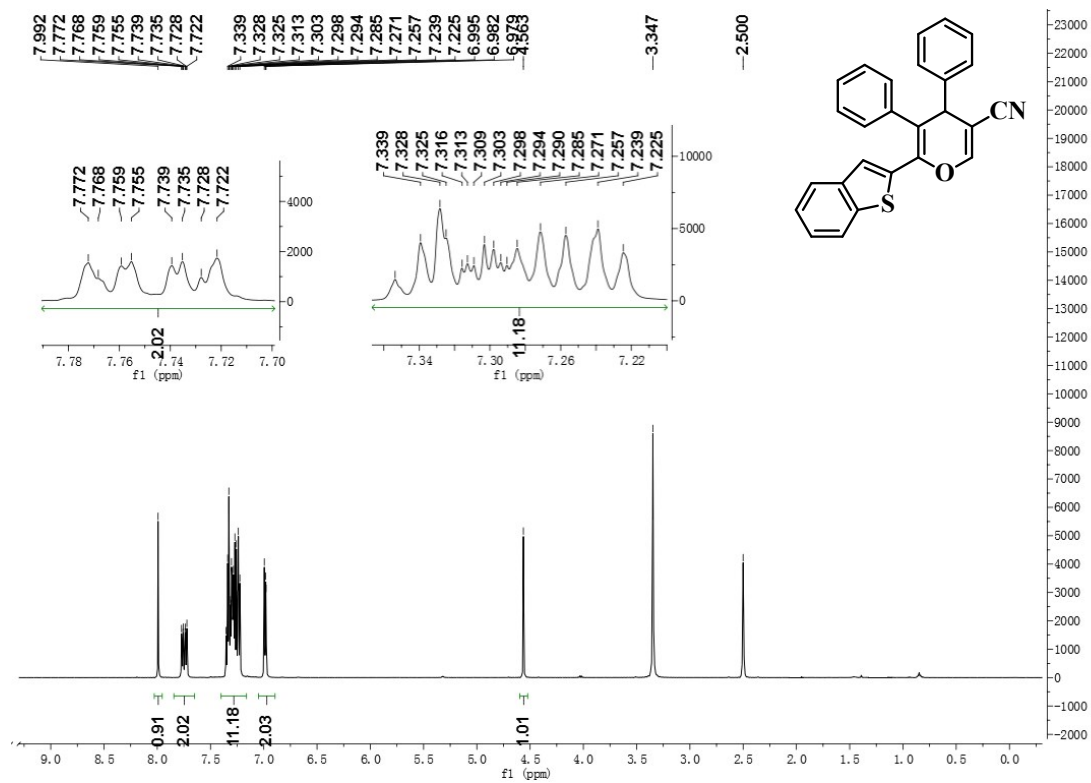


Fig. S15 <sup>1</sup>H NMR of PR-Bt (DMSO-*d*<sub>6</sub>, 500 MHz).

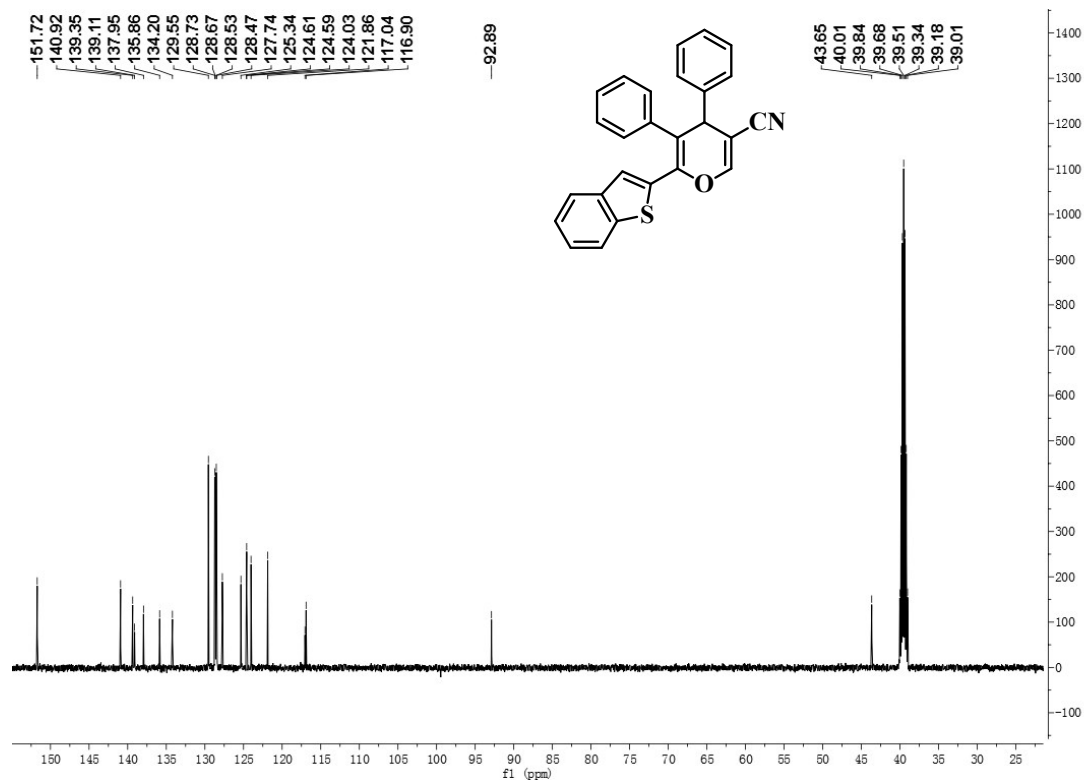


Fig. S16 <sup>13</sup>C NMR of PR-Bt (DMSO-*d*<sub>6</sub>, 125 MHz).

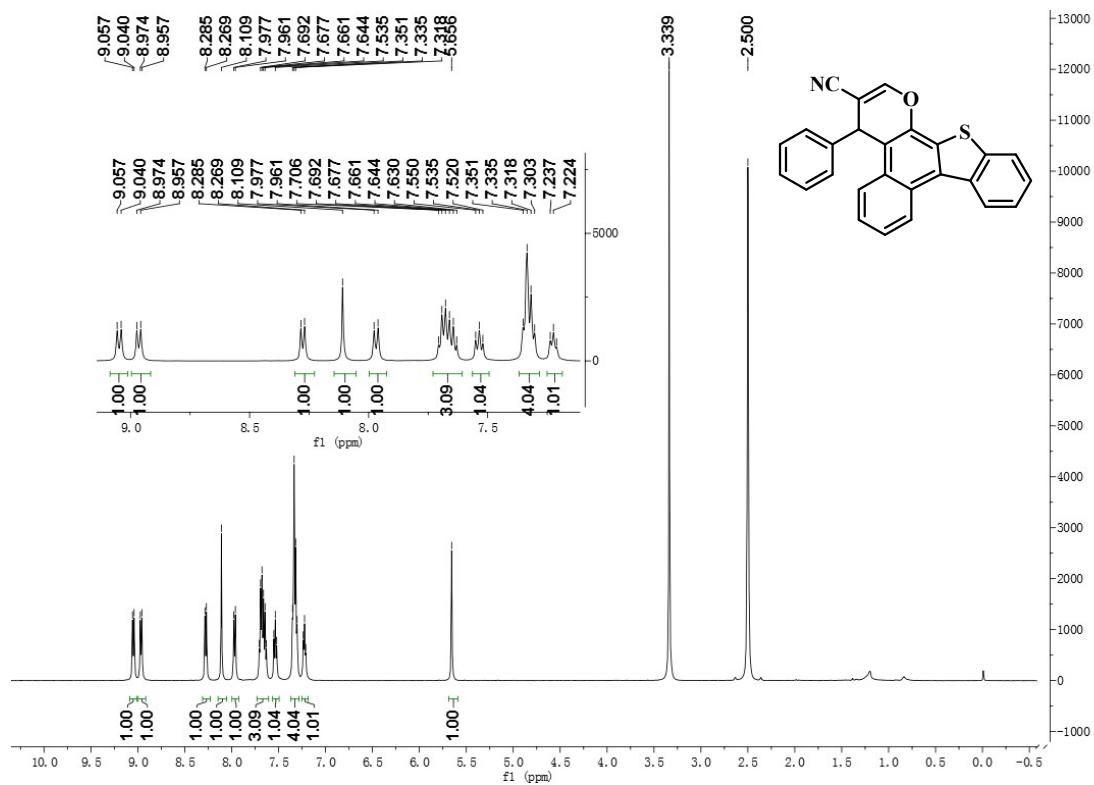


Fig. S17  $^1\text{H}$  NMR of PR-Bt-Ox (DMSO- $d_6$ , 500 MHz).

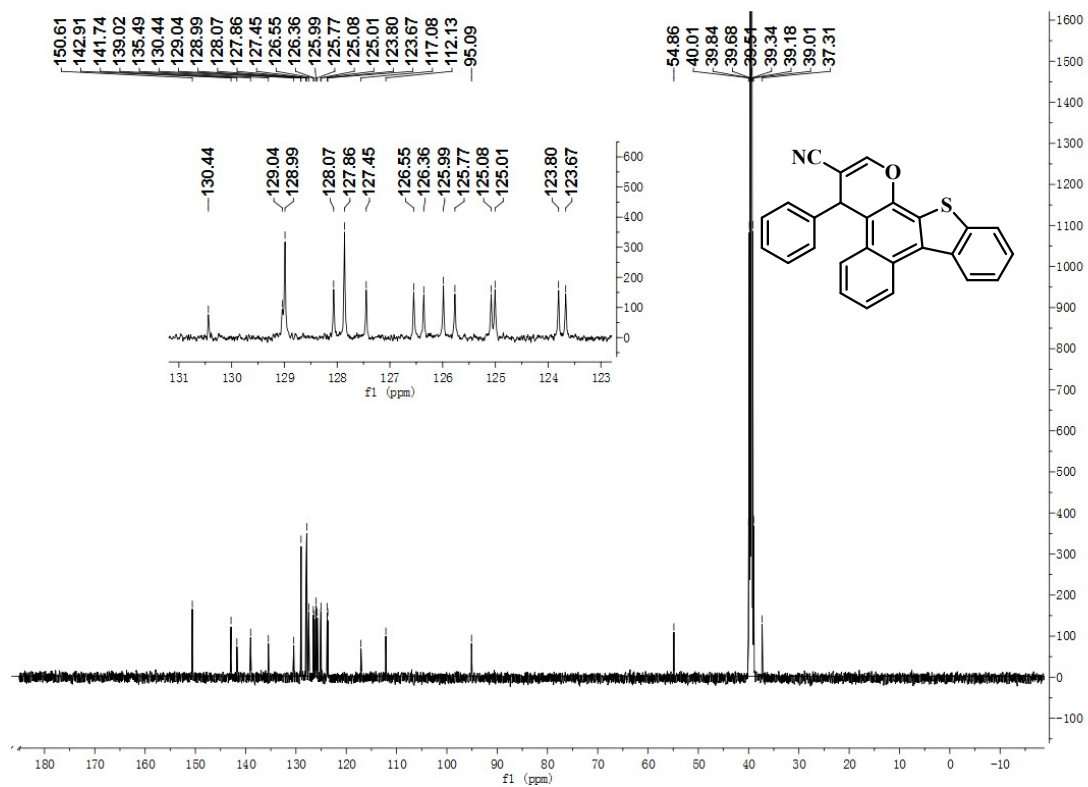
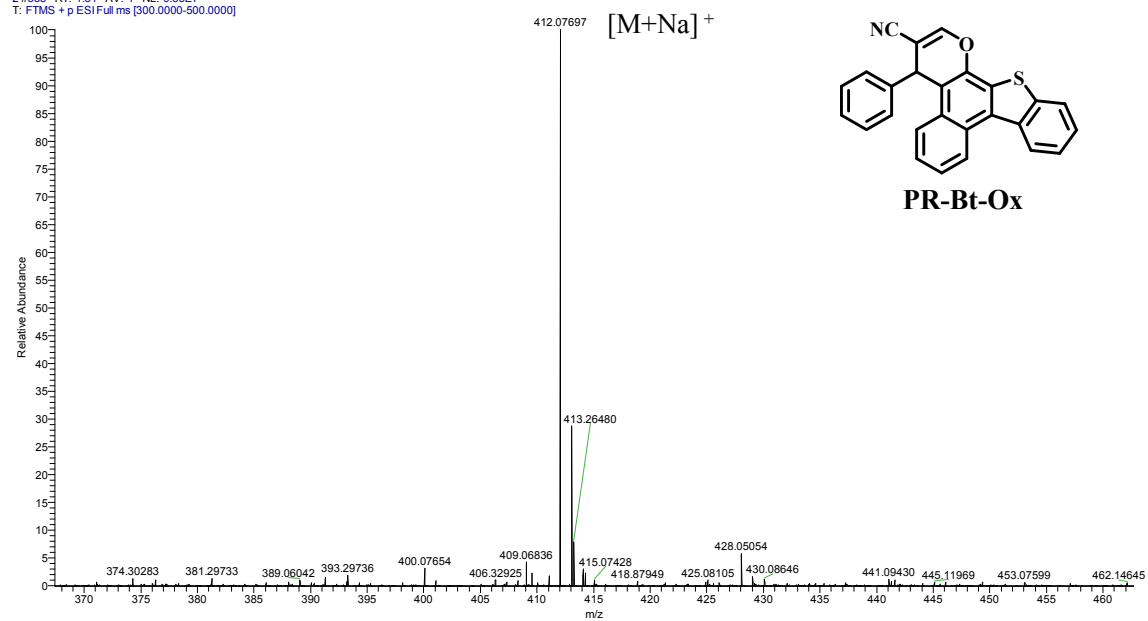


Fig. S18  $^{13}\text{C}$  NMR of PR-Bt-Ox (DMSO- $d_6$ , 125 MHz).

2 #338 RT: 1.51 AV: 1 NL: 9.86E7  
T: FTMS + p ESI Full ms [300.0000-500.0000]



**Fig. S19** HRMS-ESI of PR-Bt-Ox.