

Supporting Information

Tuning Photochromism of Indeno-Fused 2*H*-Naphthopyrans by Steric Spirocyclic Groups

Ruiqi Wei¹, Ruiyuan Zhou², Ripei Shen,² Jie Han*,^{1,2}

¹*College of Chemistry and Environmental Science, Kashi University, Kashi
844008, P. R. China*

²*Key Laboratory of Advanced Energy Material Chemistry, College of Chemistry,
Nankai University, 94 Weijin Road, Tianjin 300071, P. R. Chin*

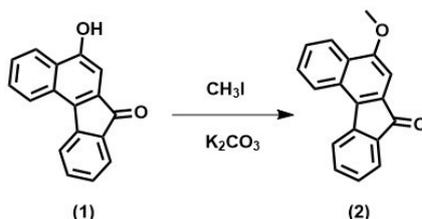
CONTENTS:

1. Synthesis of compounds NPs	S2
2. NMR Spectra	S7
3. MS Spectra	S16
4. Optical Properties of NPs in the solution	S19
5. Optical Properties of PMMA Film Doped with NP-b	S21
6. X-ray Crystallographic Analysis	S22
7. References	S22

1. Synthesis of compounds NPs

5-hydroxy-7H-benzo[c]fluoren-7-one (**1**) and 1,1-bis(4-methoxyphenyl)-2-propyn-1-ol were prepared according to the procedures in the literature.^{1,2}

Synthesis of 5-methoxy-benzofluoren-7(H)-one (**2**)

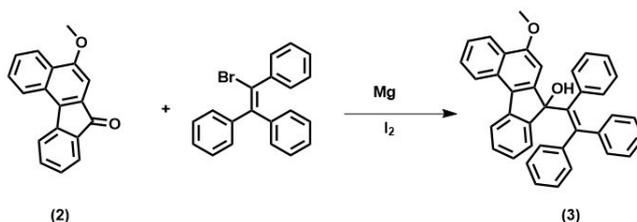


A mixture of 5-hydroxy-7H-benzo[c]fluoren-7-one (2.60 g, 10.65 mmol), K_2CO_3 (5.84 g, 42.223 mmol) and CH_3I (2.25 g, 15.84 mmol) in acetonitrile (30 mL) was stirred at room temperature for 4 h. The reaction mixture was poured into H_2O (100 mL) and extracted with ethyl acetate (50 mL \times 3). The organic extracts were combined, washed with brine and water, dried with anhydrous MgSO_4 , filtered, and the solvent was then removed under reduced pressure. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (v/v = 20:1) as an eluent affording 5-methoxy-benzofluoren-7(H)-one (**2**) was obtained as a reddish-brown solid (2.43 g, 9.34 mmol) in 88% yield. m.p. 142.6 - 143.8°C.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.32 (d, J = 8.3 Hz, 1H), 8.27 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 7.5 Hz, 1H), 7.61 – 7.50 (m, 3H), 7.42 (t, J = 7.5 Hz, 1H), 7.18 (t, J = 7.4 Hz, 1H), 7.03 (s, 1H), 4.03 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.84, 156.78, 145.52, 135.16, 134.50, 134.48, 132.47, 129.53, 129.28, 128.09, 127.46, 127.44, 124.49, 123.82, 123.72, 122.22, 98.05, 77.38, 77.06, 76.74, 55.91.

Synthesis of 5-methoxy-7-(1,2,2-triphenylvinyl)-7H-benzo[c]fluoren-7-ol (**3**)



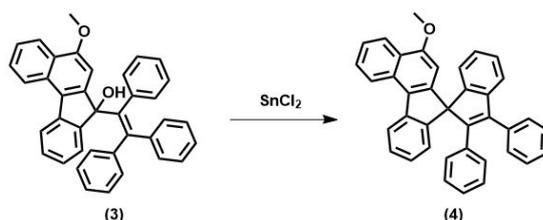
To a flame-dried 250 mL Schlenk flask, bromotriphenylethylene (1.90 g, 5.76 mmol), magnesium powder (158.74 mg, 6.53 mmol), small amounts of I_2 (9.75 mg, 38.42 μmol) and dry THF (80 mL) were added under argon atmosphere. The mixture was stirred for 5 hours at 60°C, then cooled to 0°C. Subsequently, 5-methoxy-benzofluoren-7(H)-one (**2**) (1.0 g, 3.84 mmol) was slowly added using a syringe and the mixture was heated to reflux. After allowing it to react overnight and cool to room temperature, a solution of ammonium chloride was added and the mixture was extracted with ethyl acetate (50 mL \times 3). The organic extracts were combined and washed with brine and water, then dried with anhydrous MgSO_4 , filtered and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (v/v = 50:1) as an eluent affording 5-methoxy-7-(1,2,2-triphenylvinyl)-7H-benzo[c]fluoren-7-ol (**3**) as a pale-yellow solid (365 mg, 0.689 mmol) in 18% yield. m.p. 183.5 - 184.5 °C

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.32 – 8.22 (m, 2H), 7.78 – 7.74 (m, 1H), 7.74 – 7.70 (m, 1H), 7.61 – 7.56 (m, 1H), 7.53 – 7.47 (m, 1H), 7.30 – 7.22 (m, 5H), 7.05 (t, *J* = 7.4 Hz, 2H), 7.00 – 6.95 (m, 1H), 6.94 – 6.85 (m, 4H), 6.84 – 6.79 (m, 1H), 6.65 – 6.59 (m, 1H), 6.54 (t, *J* = 7.2 Hz, 2H), 6.44 (d, *J* = 7.4 Hz, 2H), 5.42 (s, 1H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 155.86, 152.65, 151.16, 144.61, 143.16, 142.49, 141.76, 141.44, 140.59, 132.14, 129.73, 129.57, 128.59, 128.35, 127.71, 127.64, 127.25, 126.85, 126.70, 126.09, 126.05, 125.70, 125.66, 125.30, 125.17, 124.60, 124.16, 122.95, 122.04, 101.94, 82.94, 56.31, 40.64, 40.43, 40.22, 40.01, 39.80, 39.59, 39.38.

HRMS (ESI) calcd. for C₃₈H₂₈O₂ [M+Na]⁺ 539.1982 ; found 539.1984.

Synthesis of 5-methoxy-2',3'-diphenylspiro[benzo[*c*]fluorene-7,1'-indene] (4)



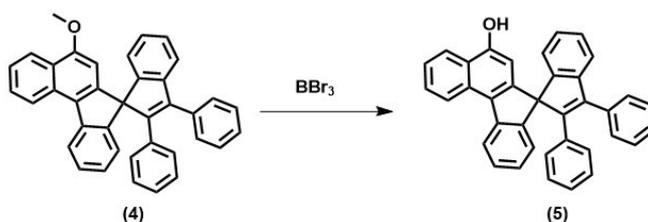
Under an argon atmosphere, anhydrous SnCl₂ (175 mg, 0.39 mmol) was added into a solution of 5-methoxy-7-(1,2,2-triphenylvinyl)-7H-benzo[*c*]fluorene-7-ol (3) (0.46 mmol) in dry CH₂Cl₂ (20 mL). The mixture was stirred for 3 h at room temperature. The reaction mixture was extracted by ethyl acetate twice (50 mL × 2). The organic extracts were combined, washed with brine and water, dried with anhydrous MgSO₄, filtered, and the solvent was then removed under reduced pressure. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (v/v = 50:1) as an eluent affording 5-methoxy-2',3'-diphenylspiro[benzo[*c*]fluorene-7,1'-indene] (4) was obtained as a pale-yellow solid (144 mg, 0.29 mmol) in 85% yield. m.p. 186.5 - 187.5 °C

¹H NMR (400 MHz, Chloroform-*d*) δ 8.71 (d, *J* = 8.4 Hz, 1H), 8.34 (dd, *J* = 8.4, 1.3 Hz, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.73 – 7.64 (m, 1H), 7.57 – 7.49 (m, 3H), 7.48 – 7.32 (m, 5H), 7.30 – 7.22 (m, 1H), 7.15 – 7.05 (m, 2H), 7.03 – 6.97 (m, 1H), 6.88 – 6.81 (m, 1H), 6.79 – 6.71 (m, 2H), 6.67 – 6.58 (m, 3H), 6.47 (s, 1H), 3.82 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 156.18, 148.56, 146.27, 145.90, 145.52, 145.49, 143.65, 143.41, 135.54, 134.98, 130.41, 129.92, 129.78, 128.75, 128.68, 127.86, 127.69, 127.66, 127.38, 127.22, 126.93, 126.48, 126.15, 125.76, 124.88, 123.66, 123.35, 123.26, 122.55, 122.11, 120.82, 99.89, 77.44, 77.33, 77.13, 76.81, 70.86, 55.79.

HRMS (ESI) calcd. for C₃₈H₂₈O₂ [M+Na]⁺ 521.1876; found 521.1878

Synthesis of 2',3'-diphenylspiro[benzo[*c*]fluorene-7,1'-indene]-5-ol (5)



Under an argon atmosphere, 30 mL of dry dichloroethane was added to a dry Schlenk flask (100 mL), followed by the appropriate stoichiometric amount of 5-methoxy-2',3'-diphenylspiro[benzo[*c*]fluorene-7,1'-indene] (4) (260 mg, 0.52 mmol). A solution of boron

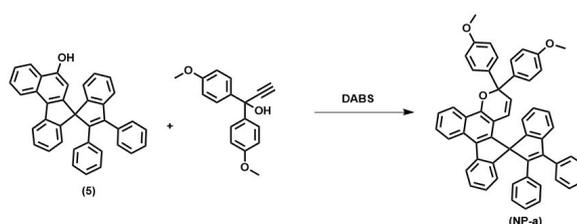
tribromide (653 mg, 2.16 mmol) was then added in an ice bath. The reaction was allowed to proceed for 5 hours at room temperature, followed by the addition of water at 0 °C. The reaction mixture was extracted by ethyl acetate twice (50 mL × 2). The organic extracts were combined, washed with brine and water, dried with anhydrous MgSO₄, filtered, and the solvent was then removed under reduced pressure. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (v/v = 50:1) as an eluent affording 2',3'-diphenylspiro[benzo[*c*]fluorene-7,1'-inden]-5-ol (**5**) was obtained as a white solid (220 mg, 0.29 mmol) in 87% yield. m.p. 197.5 - 198.6 °C

¹H NMR (400 MHz, Chloroform-*d*) δ 8.77 (d, *J* = 8.5 Hz, 1H), 8.30 (d, *J* = 8.2 Hz, 2H), 7.72 (t, *J* = 7.7 Hz, 1H), 7.60 – 7.53 (m, 3H), 7.51 – 7.37 (m, 5H), 7.32 – 7.27 (m, 1H), 7.19 – 7.11 (m, 2H), 7.06 – 6.99 (m, 1H), 6.90 – 6.84 (m, 1H), 6.83 – 6.76 (m, 2H), 6.72 – 6.59 (m, 3H), 6.51 (s, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 152.02, 148.49, 146.03, 145.48, 145.22, 143.56, 143.42, 135.51, 134.84, 130.60, 130.30, 129.70, 128.77, 128.65, 127.90, 127.69, 127.64, 127.45, 127.26, 126.94, 126.45, 125.88, 124.87, 123.80, 123.39, 123.11, 122.52, 122.10, 120.77, 104.57, 77.42, 77.10, 76.78, 70.45.

HRMS (ESI) calcd. for C₃₇H₂₄O [M+Na]⁺ 507.1719; found 507.1723

The synthesis of compounds NP-a:



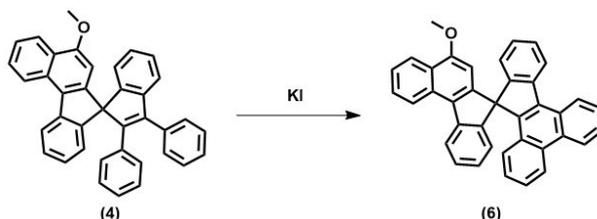
A solution of 2',3'-diphenylspiro[benzo[*c*]fluorene-7,1'-inden]-5-ol (**5**) (3.8 mmol), 1,1-diphenylprop-2-yn-1-ol **5a** (0.11 g, 0.52 mmol), and two drops of dodecylbenzenesulphonic acid in dry toluene (8 mL) was stirred at 40 °C for 3 h. After cooling down to room temperature, the reaction mixture was extracted by ethyl acetate twice (50 mL × 2). The organic extracts were combined, washed with brine and water, dried with anhydrous MgSO₄, filtered, and the solvent was then removed under reduced pressure. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (v/v = 50:1) as an eluent affording **NP-a** as a pale-yellow solid in 43%. m.p. 183.5 - 184.6 °C

¹H NMR (400 MHz, Chloroform-*d*) δ 8.70 (d, *J* = 8.5 Hz, 1H), 8.46 (d, *J* = 8.4 Hz, 1H), 8.24 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 4H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.44 – 7.28 (m, 8H), 7.17 – 7.07 (m, 3H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.78 – 6.68 (m, 5H), 6.59 (d, *J* = 7.7 Hz, 2H), 6.43 (d, *J* = 9.8 Hz, 1H), 5.91 (d, *J* = 9.8 Hz, 1H), 3.80 (s, 3H), 3.75 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 157.72, 147.05, 146.75, 145.40, 145.25, 144.07, 142.05, 141.66, 138.89, 136.00, 135.22, 134.36, 133.68, 129.72, 128.84, 128.44, 127.99, 127.65, 127.63, 127.29, 127.26, 126.61, 126.55, 126.48, 126.24, 126.01, 125.71, 125.51, 124.75, 124.52, 124.00, 122.68, 122.27, 121.56, 121.36, 121.18, 120.04, 119.07, 113.13, 112.30, 81.38, 69.31, 54.17, 54.09.

HRMS (ESI) calcd. for C₅₂H₃₄O₃ [M+Na]⁺ 757.2713; found 757.2718.

Synthesis of 5-methoxyspiro[benzo[*c*]fluorene-7,13'-indeno[1,2-*l*]phenanthrene] (6**)**



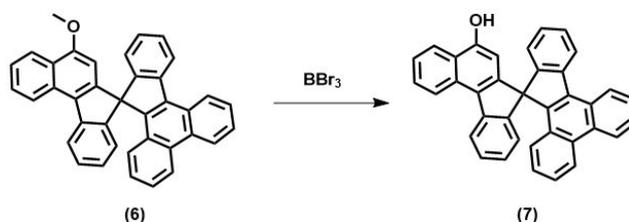
To a flame-dried 50 mL round-bottom flask, Potassium iodide (4.10 mmol) and 5-methoxy-2',3'-diphenylspiro[benzo[c]fluorene-7,1'-indene] (**4**) (0.802 mmol) and cyclohexane (20 mL) were added under air atmosphere. The solution was irradiated with a UV lamp (365 nm, 500 mW) for 4 hours. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (v/v = 50 : 1) as an eluent affording 5-methoxyspiro[benzo[c]fluorene-7,13'-indeno[1,2-l]phenanthrene] as a pale-yellow solid (310 mg, 0.623 mmol) in 77% yield. m.p. 226.5 - 227.5 °C

¹H NMR (400 MHz, Chloroform-*d*) δ 9.13 (d, J = 8.2 Hz, 1H), 8.94 (d, J = 8.5 Hz, 1H), 8.89 (d, J = 8.3 Hz, 1H), 8.70 (d, J = 8.4 Hz, 1H), 8.56 (d, J = 7.9 Hz, 1H), 8.50 (d, J = 7.9 Hz, 1H), 8.37 (d, J = 8.4 Hz, 1H), 7.89 (t, J = 7.5 Hz, 1H), 7.81 (t, J = 7.8 Hz, 2H), 7.59 (t, J = 7.6 Hz, 1H), 7.51 – 7.40 (m, 3H), 7.15 – 7.06 (m, 2H), 7.01 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 8.2 Hz, 1H), 6.78 – 6.67 (m, 2H), 6.13 (s, 1H), 3.58 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 156.32, 150.51, 148.76, 148.63, 142.97, 142.33, 141.65, 136.90, 131.86, 130.71, 130.57, 129.00, 128.94, 128.42, 127.90, 127.56, 127.47, 127.19, 127.10, 126.95, 126.54, 126.26, 126.19, 125.97, 125.04, 124.90, 124.75, 123.76, 123.73, 123.49, 123.31, 123.22, 123.13, 122.90, 122.38, 99.89, 77.37, 77.26, 77.06, 76.74, 67.22, 55.61.

HRMS (ESI) calcd. for C₅₂H₃₄O₃ [M+Na]⁺ 757.2713; found 757.2718.

Synthesis of spiro[benzo[c]fluorene-7,13'-indeno[1,2-l]phenanthren]-5-ol (**7**)



5-methoxyspiro[benzo[c]fluorene-7,13'-indeno[1,2-l]phenanthrene] (**6**) (260 mg, 0.52 mmol) and boron tribromide (653 mg, 2.16 mmol) were combined in a 50 mL round-bottom flask and dissolved in dry dichloroethane (20 mL) under an argon atmosphere. The reaction was allowed to proceed for 5 hours at room temperature, followed by the addition of water at 0°C. The organic phase was combined and washed with brine and water, then dried with anhydrous MgSO₄, filtered and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (v/v = 50 : 1) as an eluent affording spiro[benzo[c]fluorene-7,13'-indeno[1,2-l]phenanthren]-5-ol (**7**) as a pale-yellow solid (185 mg, 0.38 mmol) in 73% yield. m.p. 197.5 - 198.6 °C

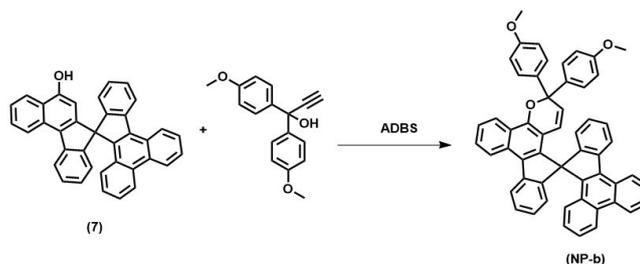
¹H NMR (400 MHz, Chloroform-*d*) δ 9.09 (d, J = 8.2 Hz, 1H), 8.93 (d, J = 8.6 Hz, 1H), 8.86 (d, J = 8.3 Hz, 1H), 8.69 (d, J = 8.4 Hz, 1H), 8.53 (d, J = 7.9 Hz, 1H), 8.49 (d, J = 7.9 Hz, 1H), 8.28 (d, J = 8.4 Hz, 1H), 7.87 (t, J = 7.6 Hz, 1H), 7.83 – 7.75 (m, 2H), 7.58 (t, J = 7.7 Hz, 1H), 7.54 – 7.40 (m, 3H), 7.15 – 6.99 (m, 3H), 6.89 (d, J = 8.2 Hz, 1H), 6.75 (d, J = 7.5 Hz, 1H), 6.70 (d, J = 7.6 Hz, 1H), 6.11 (s, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 156.32, 150.51, 148.76, 148.63, 142.97, 142.33, 141.65, 136.90, 131.86, 130.71, 130.57, 129.00, 128.94, 128.42, 127.90, 127.56, 127.47, 127.19, 127.10, 126.95, 126.54, 126.26, 126.19, 125.97, 125.04, 124.90, 124.75, 123.76, 123.73, 123.49, 123.31, 123.22, 123.13, 122.90, 122.38, 99.89, 77.37, 77.26, 77.06, 76.74, 67.22, 55.61.

HRMS (ESI) calcd. for C₃₇H₂₂O [M+H]⁺ 483.1743; found 483.1705.

Compound NP-b

This compound was prepared according to the same procedure as that of **NP-b**, except that the eluent for column chromatography is petroleum ether/ethyl acetate (v/v = 50 : 1) as an eluent. The product **NP-b** is a pale-yellow solid in 46% yield. m.p. 179.5 - 180.6 °C.



¹H NMR (400 MHz, Chloroform-*d*) δ 9.44 (d, *J* = 8.0 Hz, 1H), 9.06 (d, *J* = 8.2 Hz, 1H), 8.91 (d, *J* = 8.6 Hz, 1H), 8.84 (d, *J* = 8.3 Hz, 1H), 8.66 (d, *J* = 8.3 Hz, 1H), 8.52 – 8.45 (m, 2H), 8.27 (d, *J* = 8.4 Hz, 1H), 7.87 – 7.81 (m, 1H), 7.81 – 7.74 (m, 2H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.42 – 7.38 (m, 2H), 7.28 (d, *J* = 8.5 Hz, 1H), 7.20 (s, 1H), 7.09 – 7.04 (m, 2H), 7.02 – 6.98 (m, 1H), 6.93 (d, *J* = 8.3 Hz, 2H), 6.89 – 6.85 (m, 3H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 6.09 (s, 1H), 3.85 (s, 3H), 3.81 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 193.78, 162.24, 161.70, 160.79, 152.27, 150.38, 148.62, 148.50, 142.96, 142.28, 141.46, 136.81, 132.49, 132.44, 131.79, 130.79, 130.68, 130.60, 129.31, 129.20, 128.90, 128.38, 128.29, 128.11, 127.98, 127.62, 127.55, 127.19, 127.14, 126.93, 126.57, 126.29, 126.09, 125.43, 124.99, 124.96, 124.85, 124.82, 124.68, 123.85, 123.75, 123.48, 123.34, 123.22, 123.11, 122.94, 122.39, 77.38, 77.06, 76.75, 66.86, 55.45, 55.43.

HRMS (ESI) Calcd. for C₅₄H₃₆O₃ [M+H]⁺ 733.2738; found 733.2719.

2. NMR Spectra

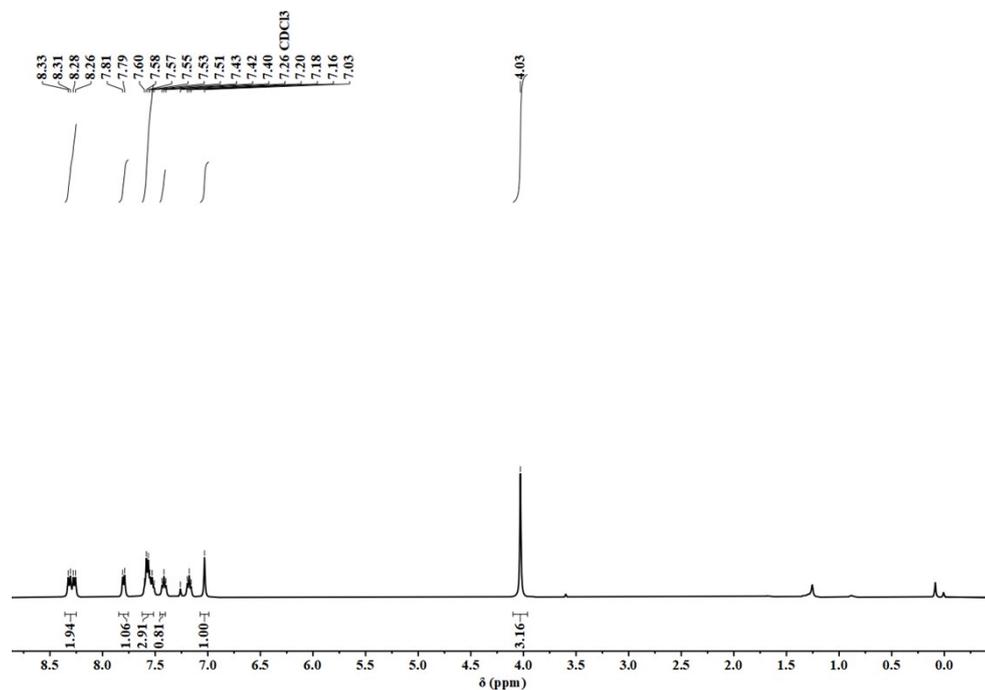


Fig. S1 ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 5-methoxy-benzofluoren-7(*H*)-one

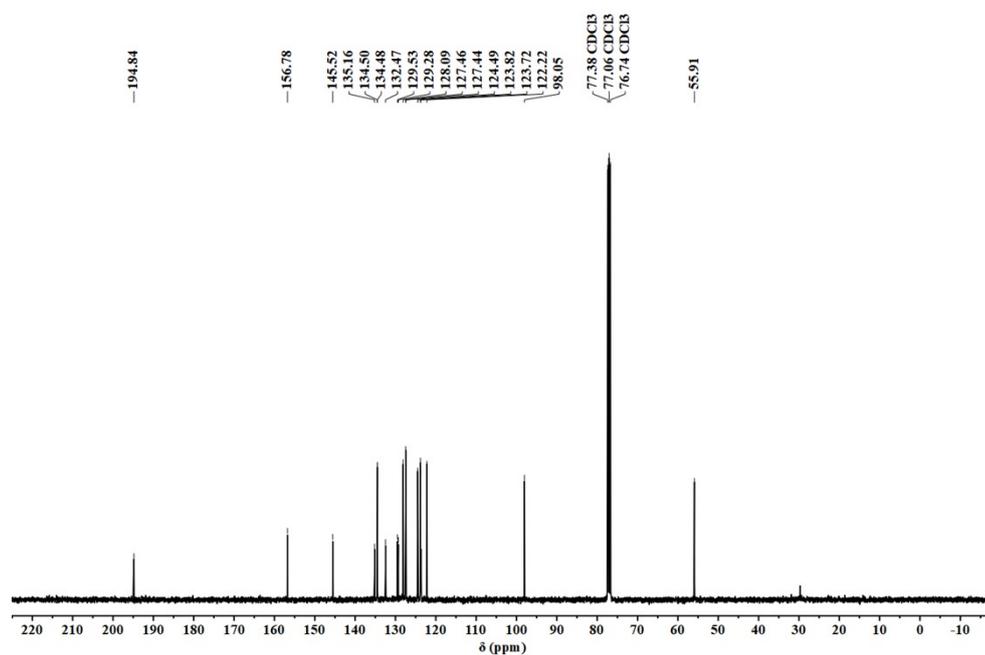


Fig. S2 ¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of 5-methoxy-benzofluoren-7(*H*)-one.

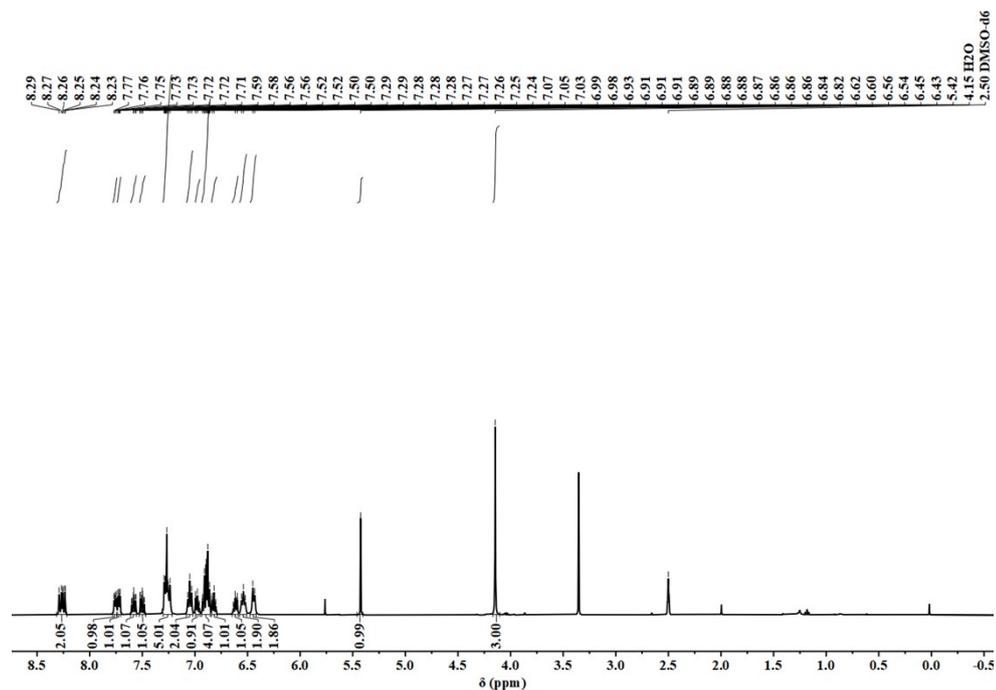


Fig. S3 ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$, 298 K) of 5-methoxy-7-(1,2,2-triphenylvinyl)-7H-benzo[c]fluoren-7-ol

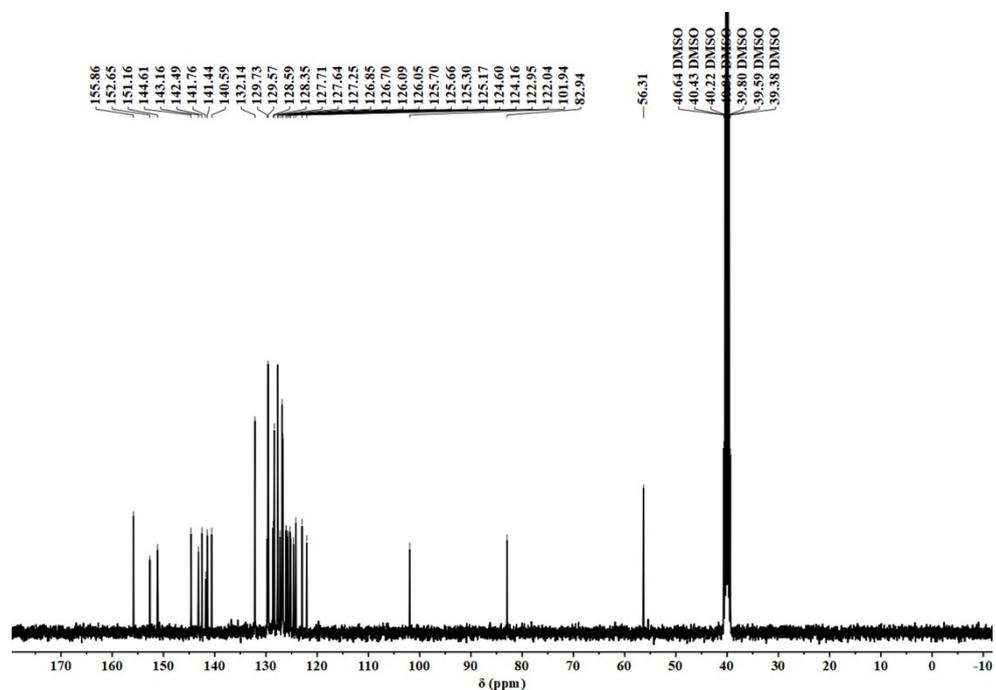


Fig. S4 ^{13}C NMR spectrum (101 MHz, $\text{DMSO-}d_6$, 298 K) of 5-methoxy-7-(1,2,2-triphenylvinyl)-7H-benzo[c]fluoren-7-ol

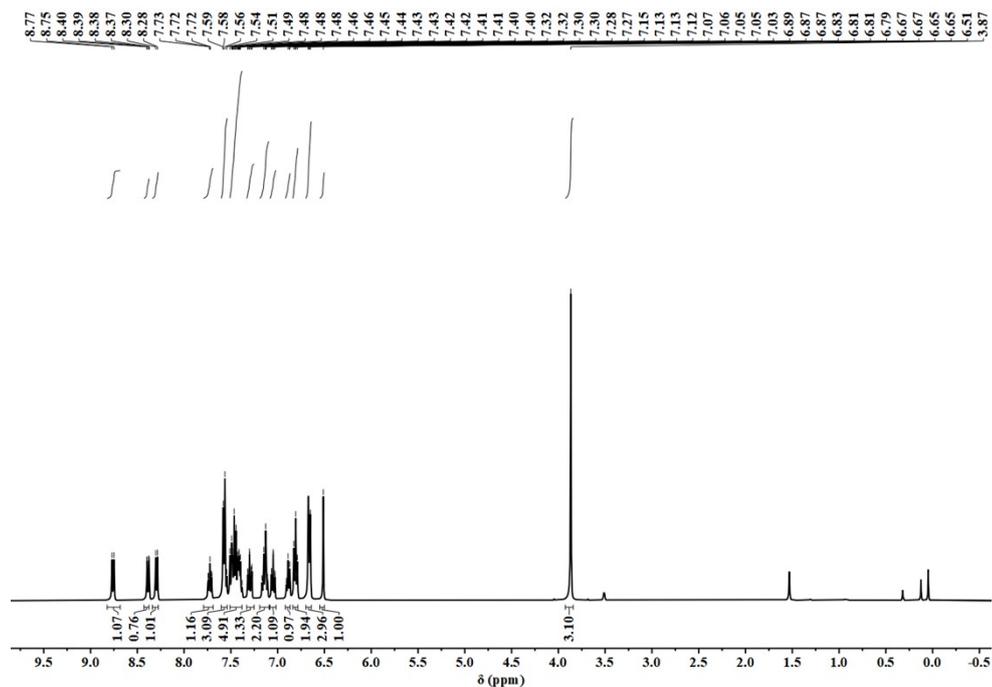


Fig. S5 ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of 5-methoxy-2',3'-diphenylspiro[benzo[c]fluorene-7,1'-indene]

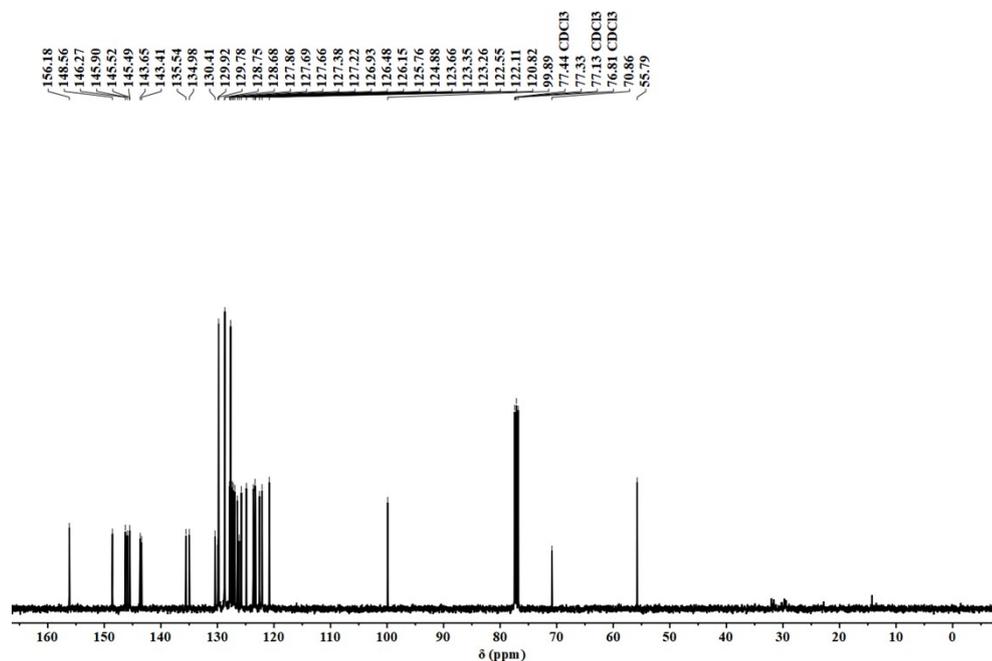


Fig. S6 ^{13}C NMR spectrum (101 MHz, CDCl_3 , 298 K) of 5-methoxy-2',3'-diphenylspiro[benzo[c]fluorene-7,1'-indene]

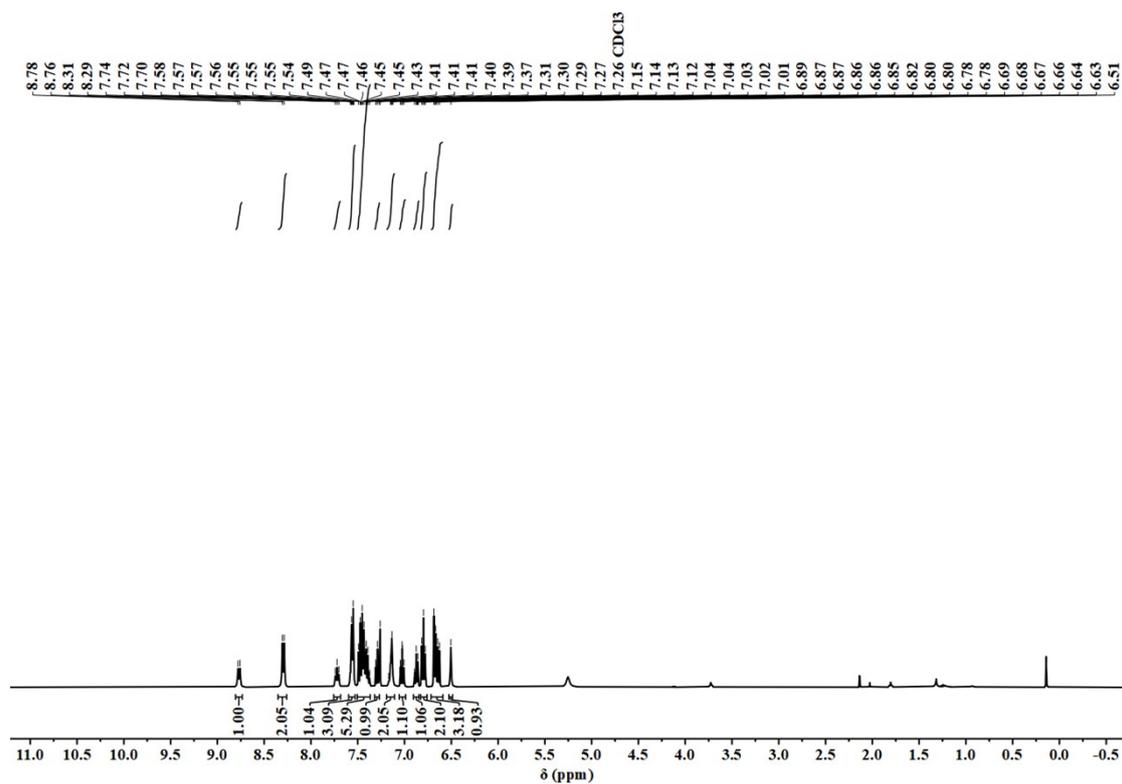


Fig. S7 ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 2',3'-diphenylspiro[benzo[c]fluorene-7,1'-inden]-5-ol

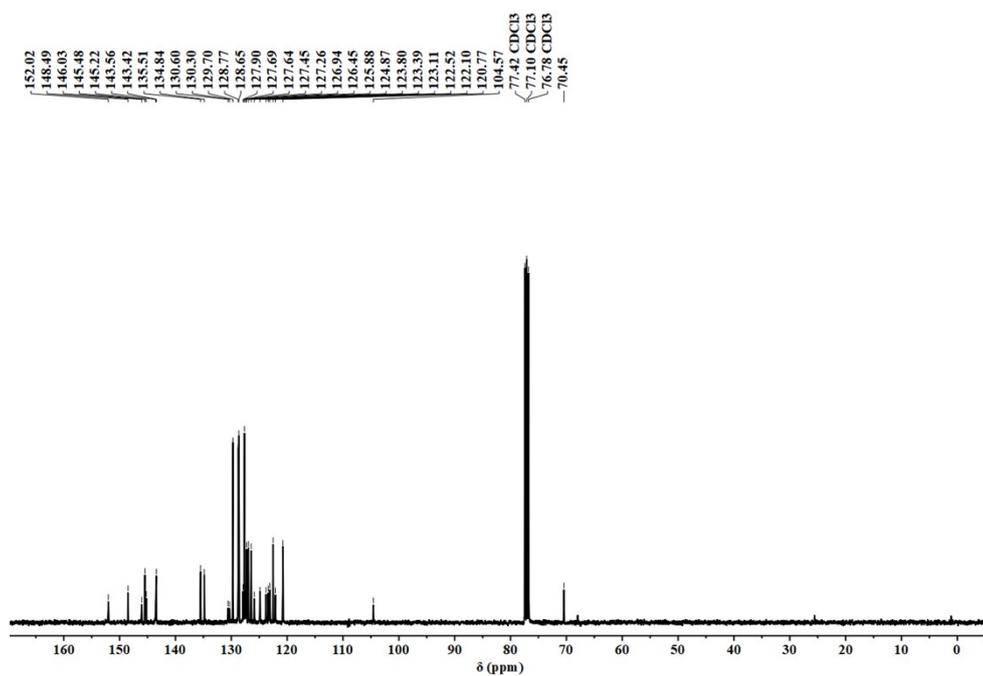


Fig. S8 ¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of 2',3'-diphenylspiro[benzo[c]fluorene-7,1'-inden]-5-ol

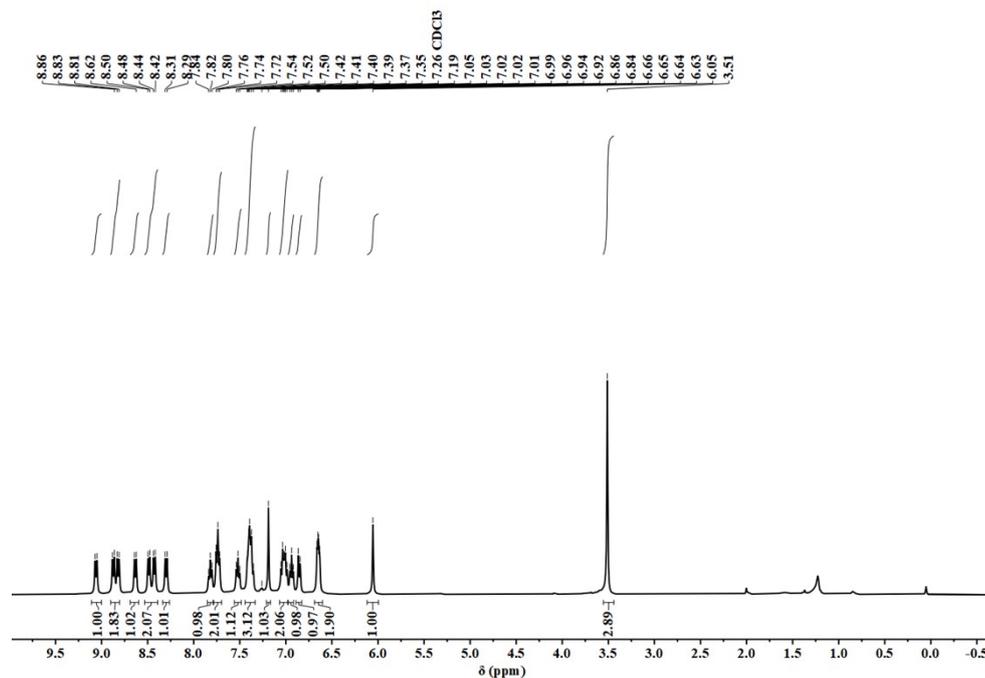


Fig. S9 ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 5-methoxyspiro[benzo[c]fluorene-7,13'-indeno[1,2-l]phenanthrene]

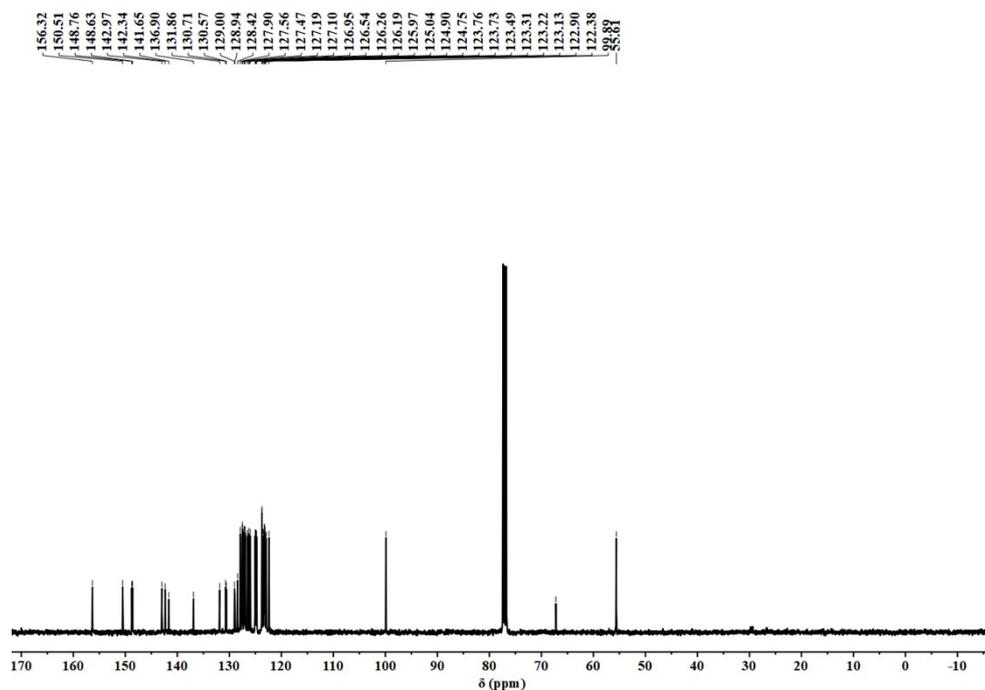


Fig. S10 ¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of 5-methoxyspiro[benzo[c]fluorene-7,13'-indeno[1,2-l]phenanthrene]

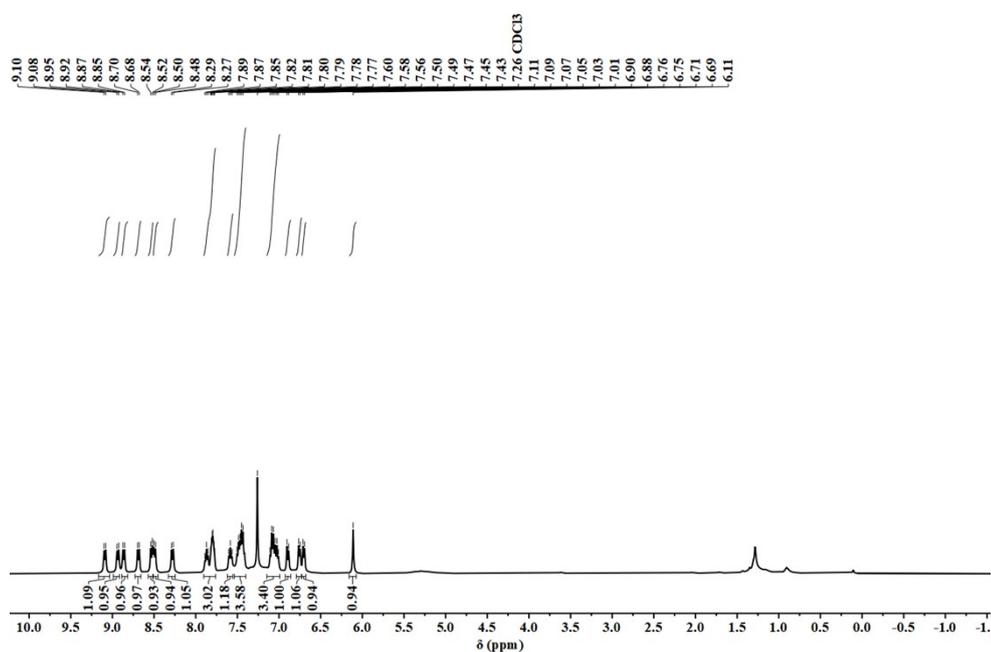


Fig. S11 ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of spiro[benzo[c]fluorene-7,13'-indeno[1,2-l]phenanthren]-5-ol

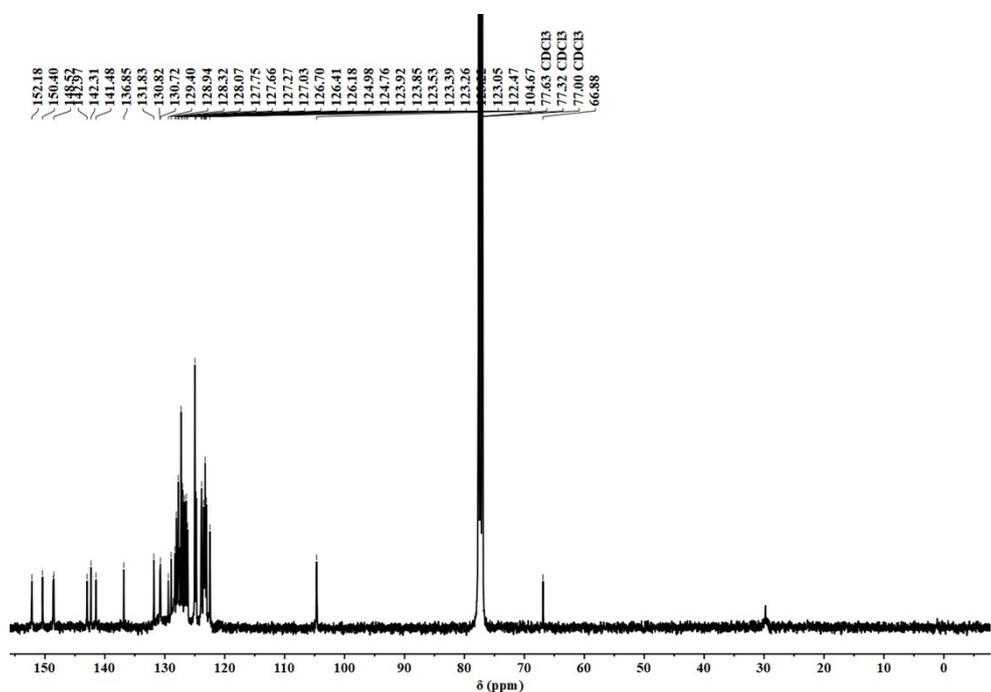


Fig. S12 ¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of spiro[benzo[c]fluorene-7,13'-indeno[1,2-l]phenanthren]-5-ol

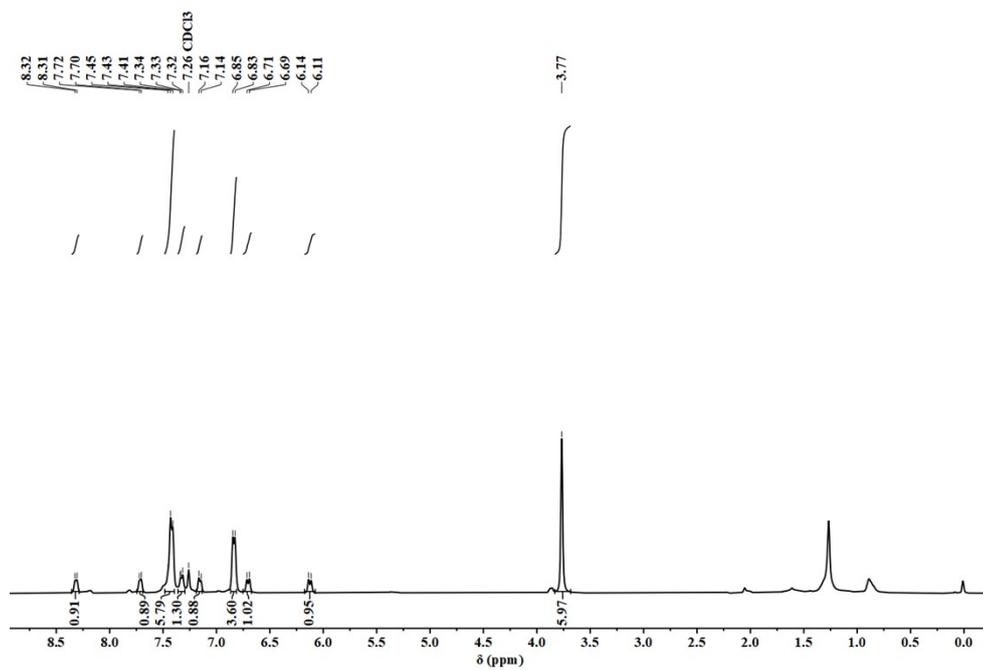


Fig. S13 ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of NP

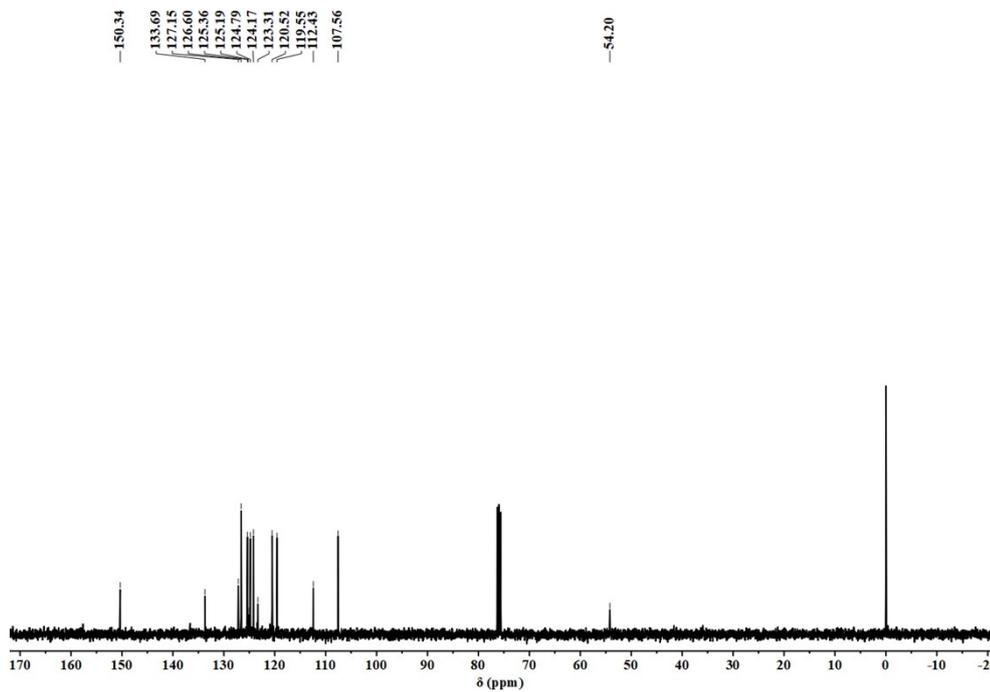


Fig. S14 ¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of NP

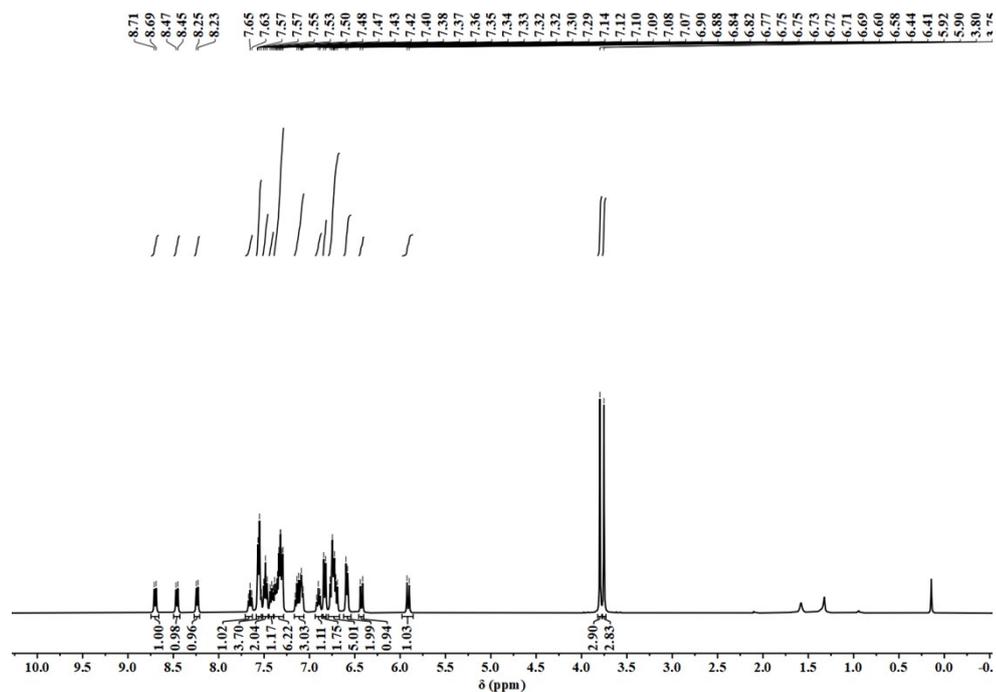


Fig. S15 ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of NP-a

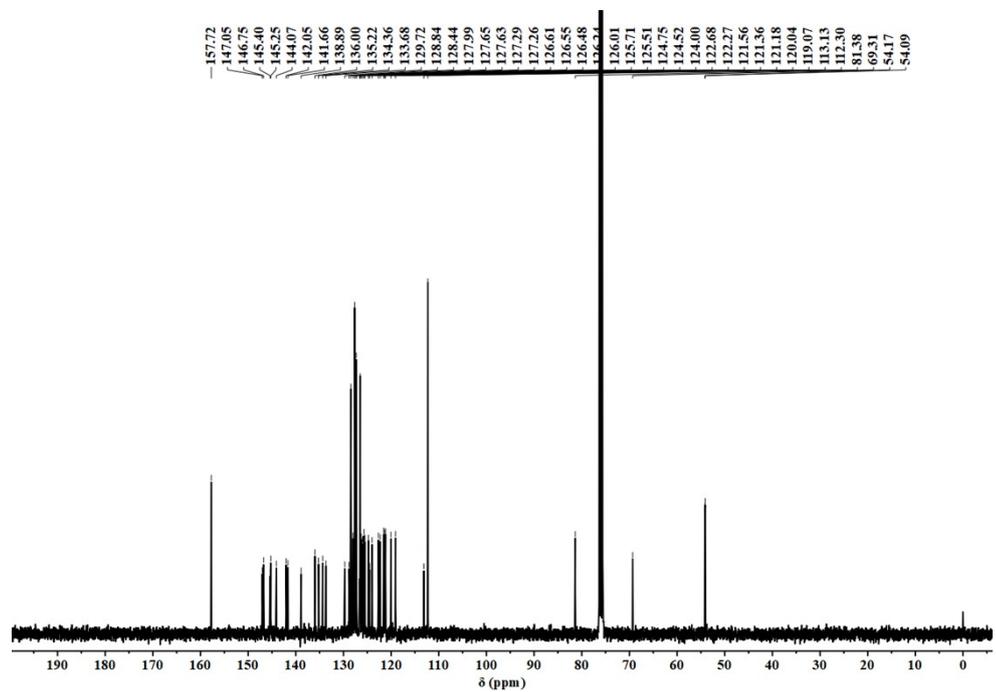


Fig. S16 ¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of NP-a

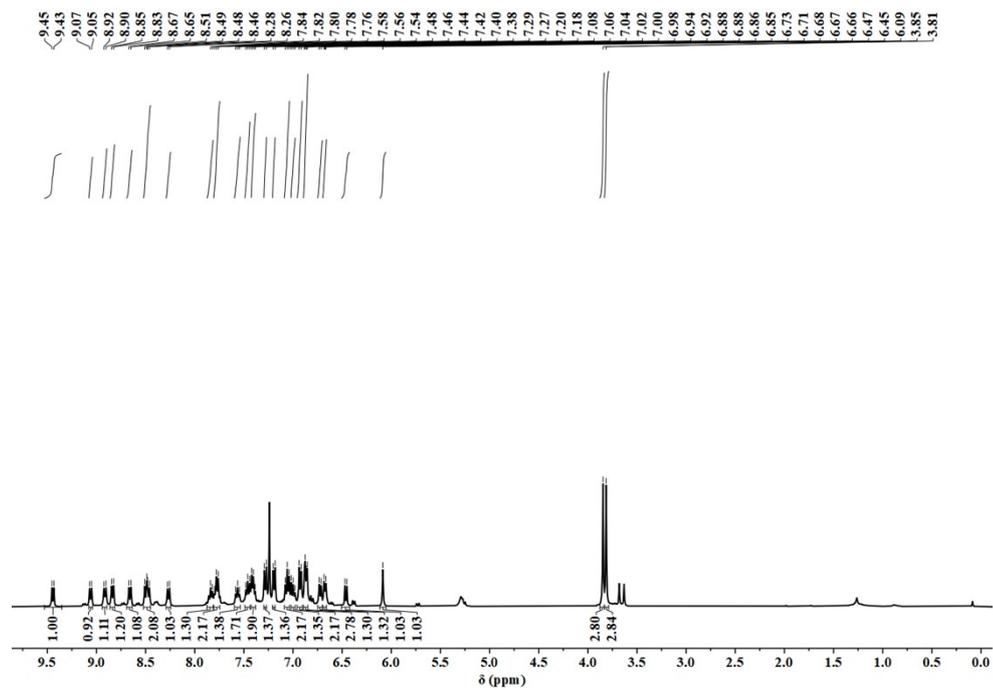


Fig. S17 ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of NP-b

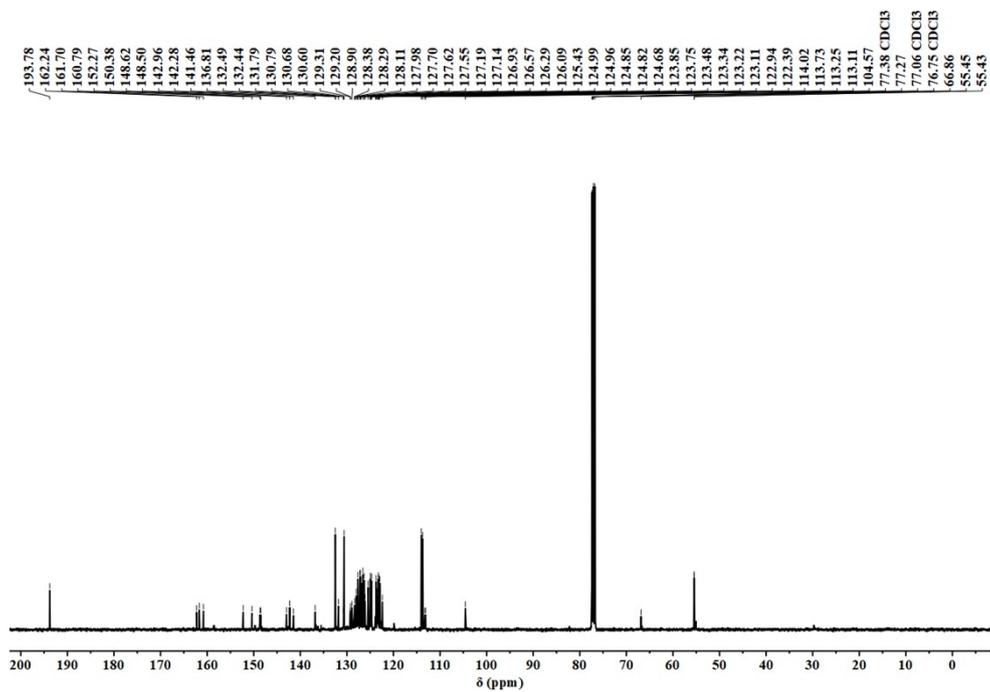


Fig. S18 ¹³C NMR spectrum (101 MHz, CDCl₃, 298 K) of NP-b

3. MS Spectra

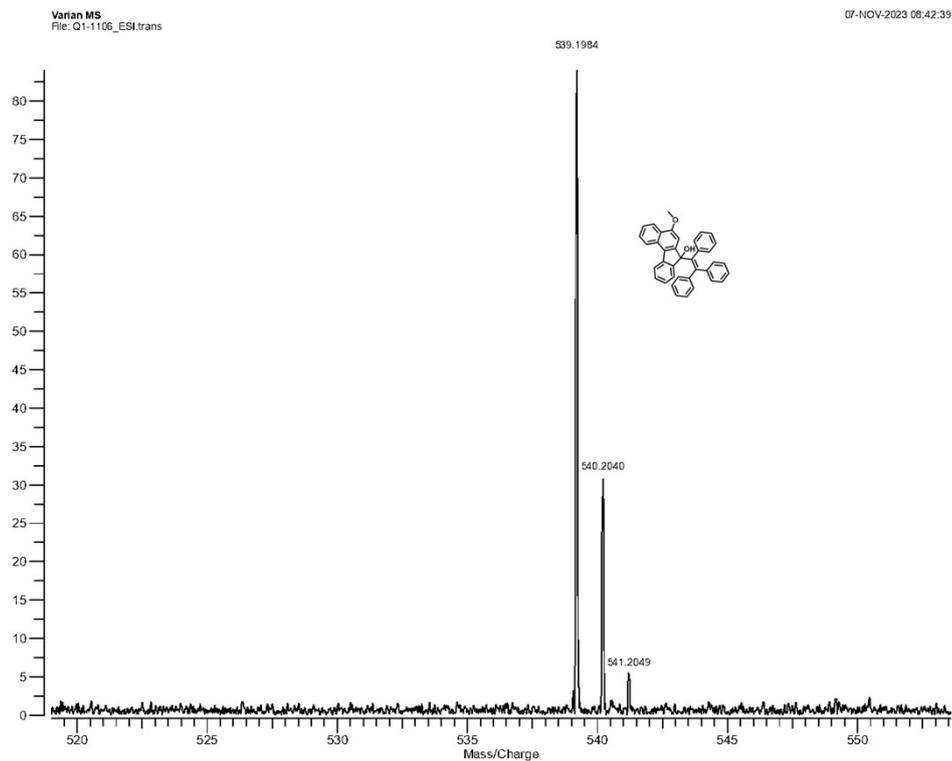


Fig. S19 HR-ESI-TOF-MS of 5-methoxy-7-(1,2,2-triphenylvinyl)-7*H*-benzo[c]fluoren-7-ol

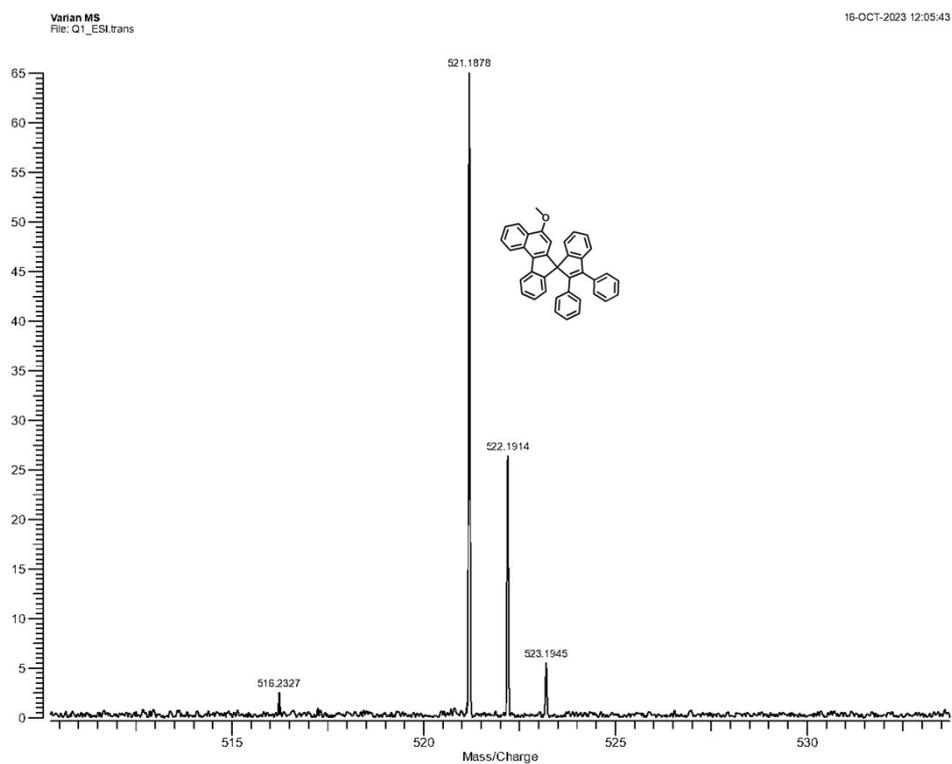


Fig. S20 HR-ESI-TOF-MS of 5-methoxy-2',3'-diphenylspiro[benzo[c]fluorene-7,1'-indene]

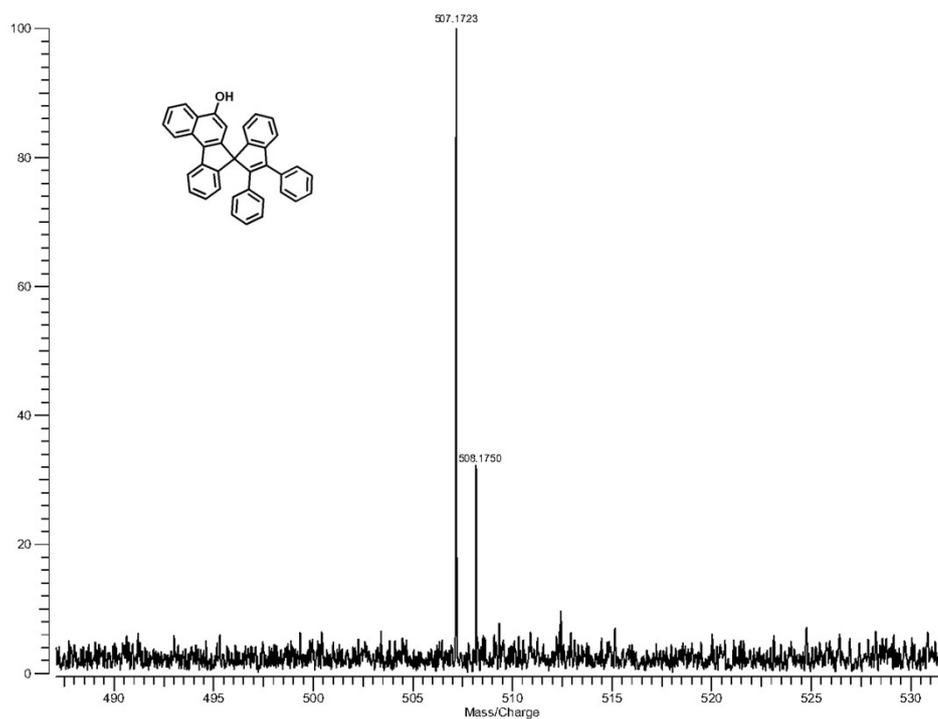


Fig. S21 HR-ESI-TOF-MS of 2',3'-diphenylspiro[benzo[c]fluorene-7,1'-inden]-5-ol

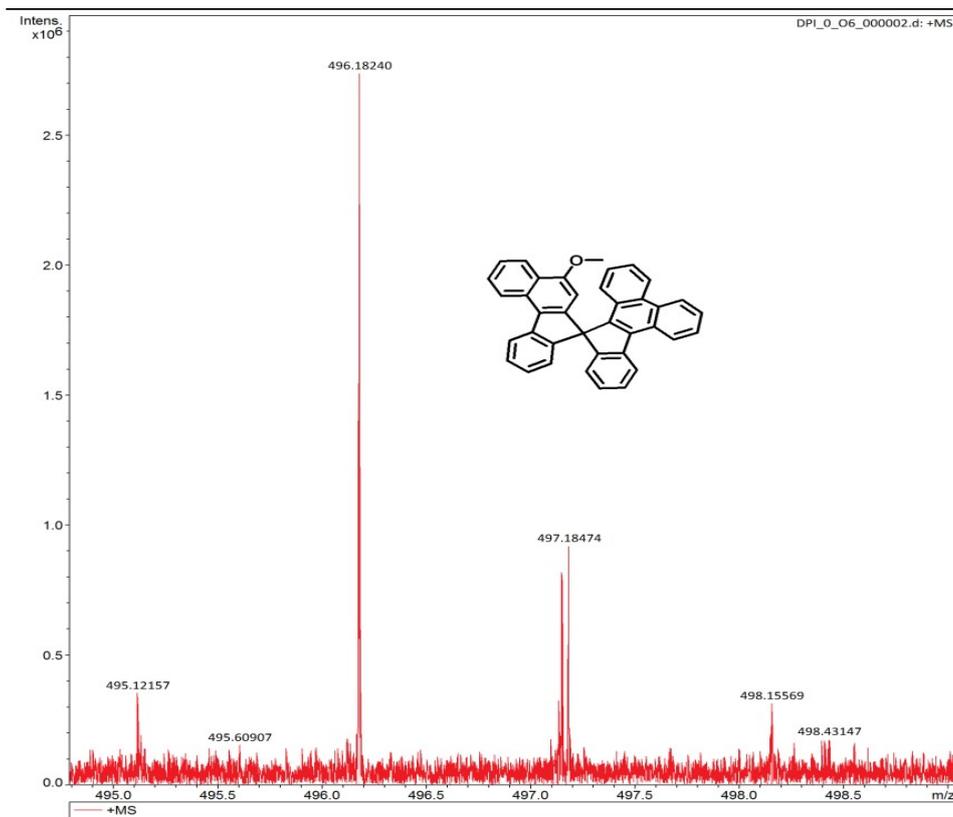


Fig. S22 HR-ESI-TOF-MS of 5-methoxyspiro[benzo[c]fluorene-7,13'-indeno[1,2-l]phenanthrene]

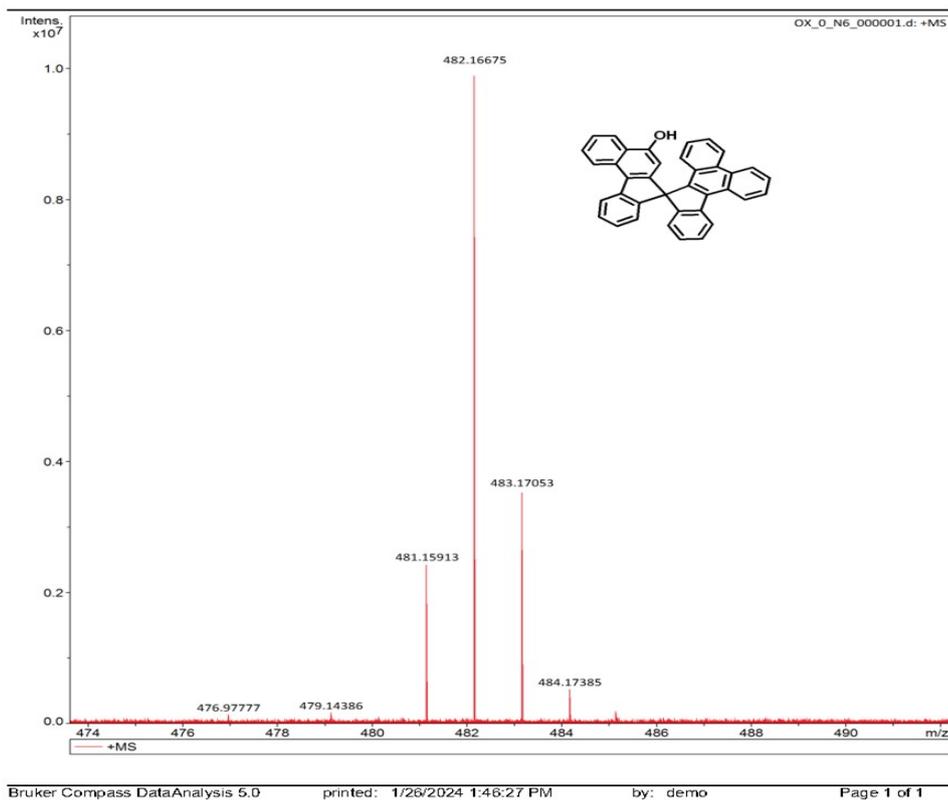


Fig. S23 HR-ESI-TOF-MS of spiro[benzo[c]fluorene-7,13'-indeno[1,2-l]phenanthren]-5-ol

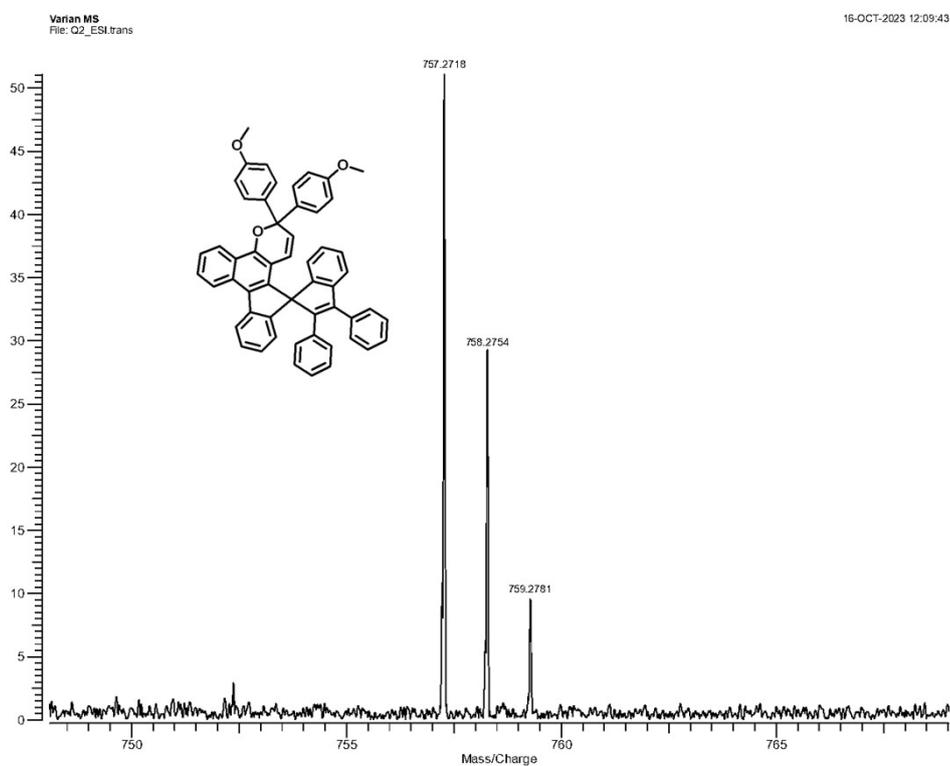
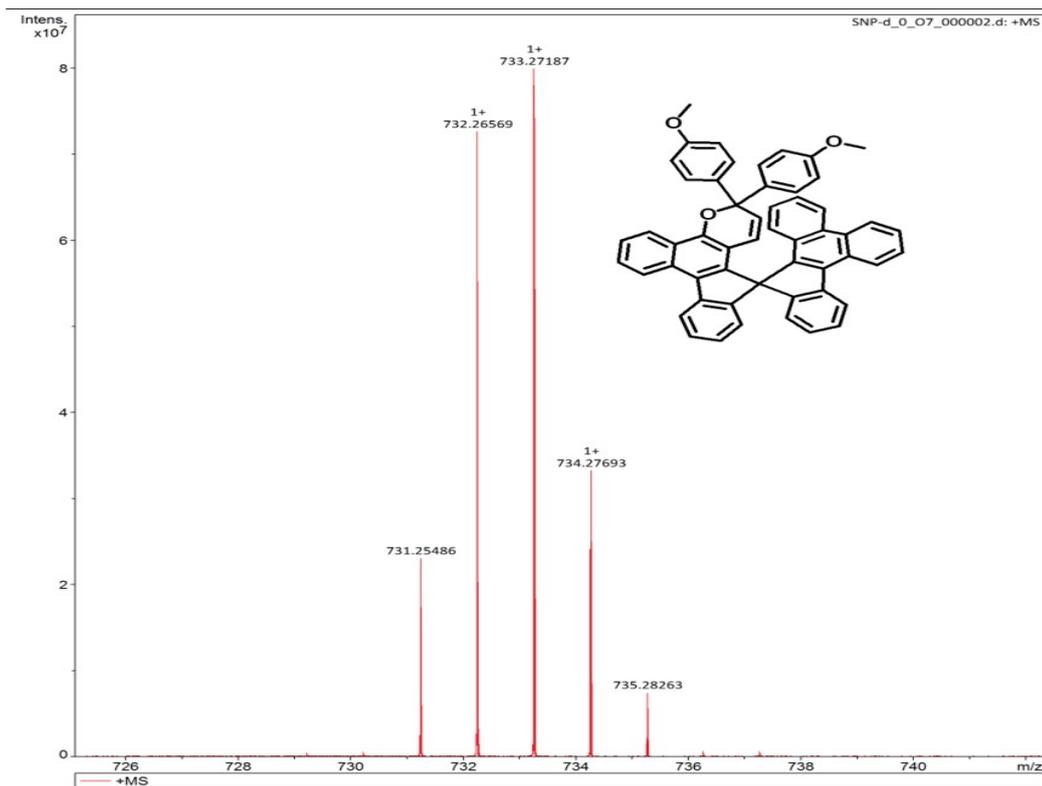


Fig. S24 HR-ESI-TOF-MS of NP-a



Bruker Compass DataAnalysis 5.0 printed: 2/2/2024 3:48:31 PM by: demo Page 1 of 1

Fig. S25 HR-ESI-TOF-MS of NP-b

4. Optical Properties of NPs in the solution

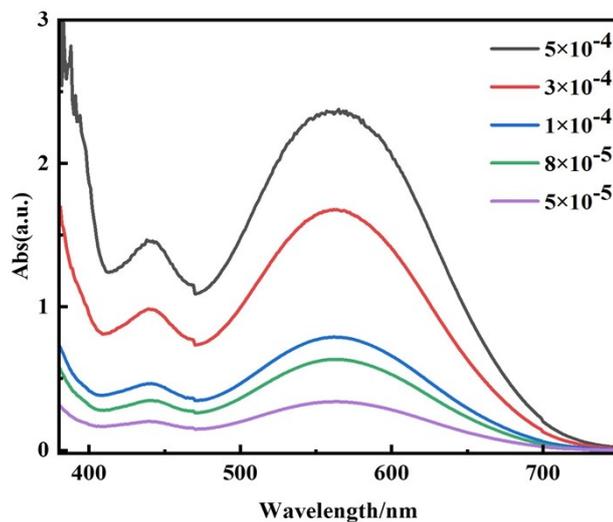


Fig. S26 UV-Vis absorption spectra of NP-a in chloroform with various concentrations upon irradiation with UV light (365 nm, 200 mW) for 50 seconds

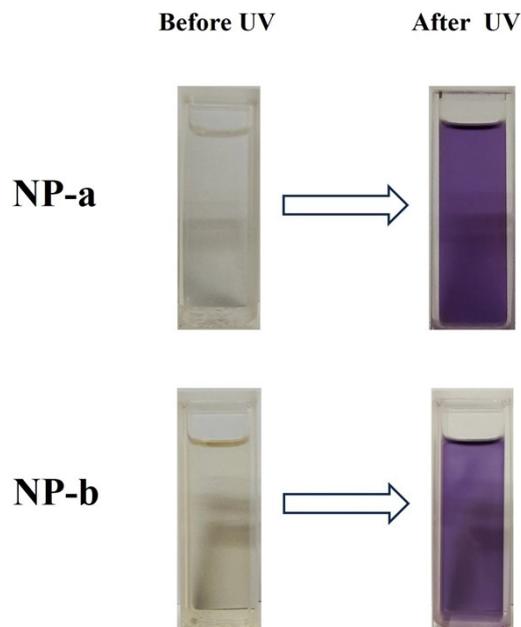


Fig. S27 Color change of **NP-a** and **NP-b** in chloroform (8.0×10^{-5} M) upon UV irradiation (365nm, 260mW /cm²) to PSS

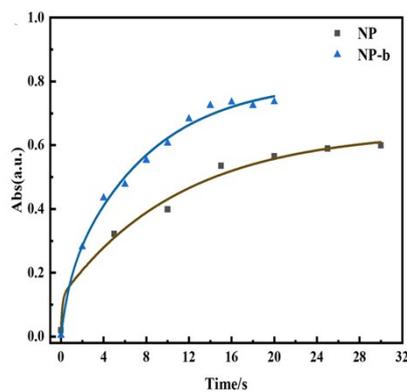


Fig. S28 Photochromic curves over time at λ_{max} of **NP-b** and **NP** in chloroform (8×10^{-5} mol/L) upon UV irradiation(365nm, 260mW /cm²); (b) Thermal fading curves of **NP-a**, **NP-b** and **NP** in chloroform (8×10^{-5} mol/L) at 298 K

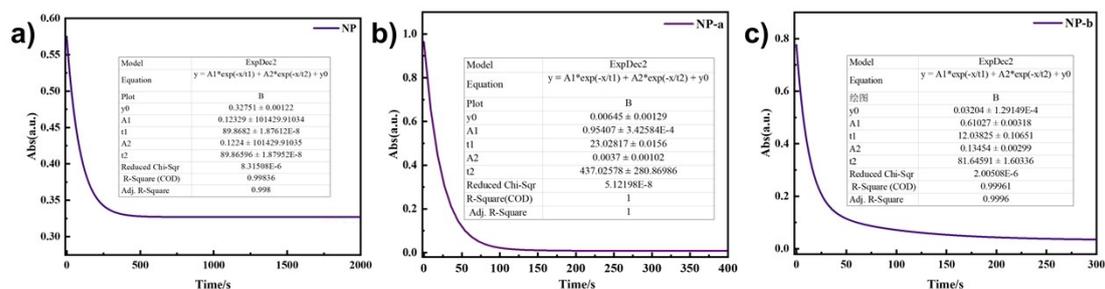


Fig. S29 Thermal fading curves with kinetics parameters of (a) **NP-a**, (b) **NP-b** and (c) **NP** in chloroform (8×10^{-5} mol/L) at 298 K

Table S1 Photophysical data of **NP-a** in various solvents (5×10^{-5} mol/L) upon irradiation with UV light (365 nm, 200 mW) for 50 s

Solvent	λ_{\max} (nm)	A_{\max}	$\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$
Toluene	551	0.1694	3.39×10^3
Acetone	553	0.2937	5.87×10^3
MeCN	553	0.2405	4.81×10^3
Chloroform	562	0.4505	9.01×10^3
m			
THF	551	0.3863	7.73×10^3

5. Optical Properties of PMMA Film Doped with NP-b

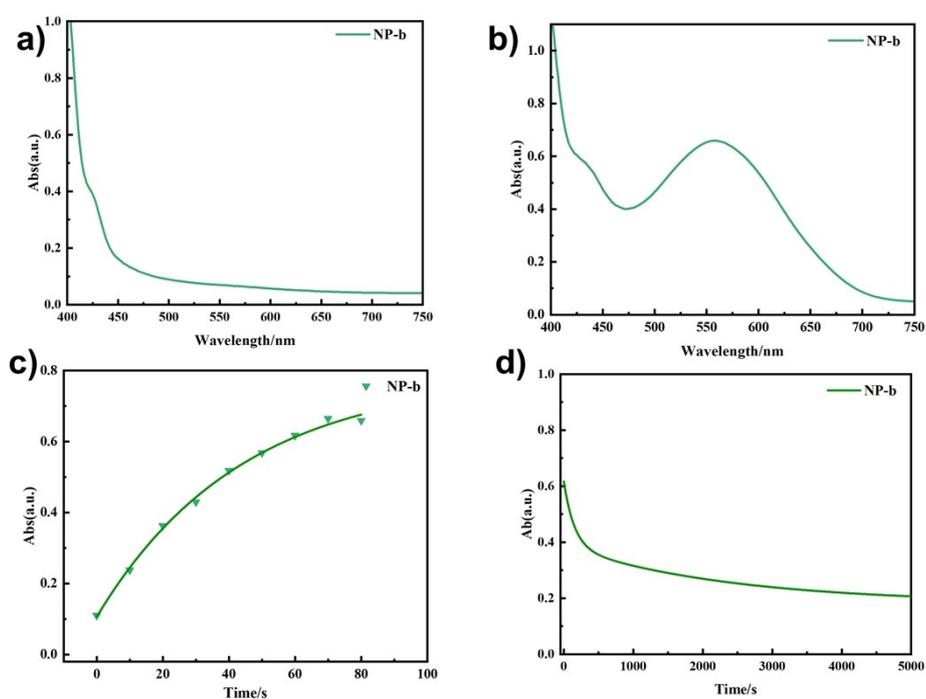


Fig. S30 (a) UV-Vis absorption spectra of the PMMA doped with **NP-b** without UV irradiation; (b) UV-Vis absorption spectra of the PMMA doped with **NP-b** upon UV irradiation (365nm, 260mW/cm²) to PSS; (c) Photochromic curve over time at λ_{\max} of the PMMA doped with **NP-b**; (d) Thermal fading curve of the PMMA doped with **NP-b** at 298 K.

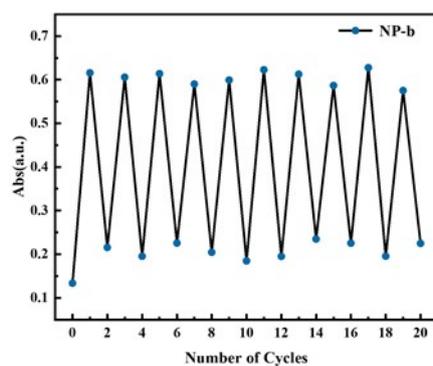


Fig. S31 Absorbance values at λ_{\max} of the process of color generation and decoloration of the PMMA film doped with **NP-b** at room temperature

6. X-ray Crystallographic Analysis.

Single crystals of **NP-a** were grown by slowly diffusing *n*-hexane into the chloroform solution.

Table S2 X-ray crystal structure refinement data for **NP-a**.

Identification code	NP-a
Empirical formula	C ₅₄ H ₃₈ O ₃
Formula weight	734.84
Temperature/K	302(2)
Crystal system	triclinic
Space group	P-1
a/Å	11.6774(3)
b/Å	12.0992(3)
c/Å	14.8445(4)
α /°	88.277(2)
β /°	72.382(2)
γ /°	71.540(2)
Volume/Å ³	1891.08(9)
Z	2
Pcalc g/cm ³	1.291
μ /mm-1	0.613
F(000)	772.0
Radiation	CuK α (λ = 1.54184)
2 θ range for data collection/°	7.724 to 153.356
Index ranges	-14 \leq h \leq 14, -15 \leq k \leq 15, -18 \leq l \leq 15
Reflections collected	24115
Independent reflections	7655 [R _{int} = 0.0264, R _{sigma} = 0.0253]
Data/restraints/parameters	7655/0/517
Goodness-of-fit on F ²	1.059
Final R indexes [I \geq 2 σ (I)]	R ₁ = 0.0383, wR ₂ = 0.1023
Final R indexes [all data]	R ₁ = 0.0416, wR ₂ = 0.1049
Largest diff. peak/hole / e Å ⁻³	0.43/-0.28

7. References

1. J. Momoda, S. Izumi and Y. Yokoyama, *Dyes Pigments*, 2015, **119**, 95–107.
2. M.-H. Kim, M. Saleem, J.-S. Seo, C.-S. Choi and K. H. Lee, *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.*, 2015, **136**, 1291–1297.