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SYNTHESIS AND CHARACTERIZATION OF HETEROCYCLIC MONOINDENOCORANNULENE

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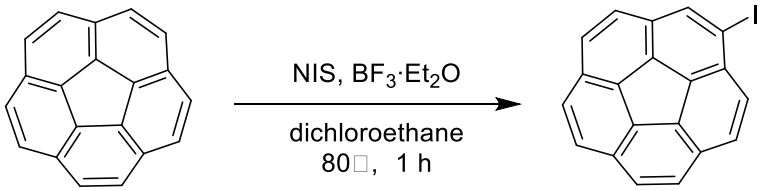
EXPERIMENTAL PROCEDURES

1. Materials and methods

Unless otherwise stated, all solvents were purchased from Concord Technology, Heowns, and Innochem, and solvents were used without further purification or drying. Chemicals, used as received, were purchased from TCI, Innochem, Heowns, Energy, Damas, Alfa, Aladdin, and Yuanli Chemical. All glass vials, including test tubes, flasks, beakers, funnels, flash columns, and sealed tubes, were purchased from Synthware Glass. Nuclear magnetic resonance spectra (NMR) were recorded using a Bruker Avance-600 or Bruker Avance-400 NMR instrument. ^{1}H-NMR data were reported relative to residual solvent: $CHCl_3$ (δ = 7.26 ppm), $C_2H_2Cl_4$ (δ = 6.00 ppm), or $(CH_3)_2CO$ (δ = 2.05 ppm). ^{13}C-NMR data were reported relative to residual solvent: $CHCl_3$ (δ = 77.16 ppm), $C_2H_2Cl_4$ (δ = 73.78 ppm), or $(CH_3)_2CO$ (δ = 29.84 ppm). Data of ^{1}H-NMR were presented in the following format: (instrument, solvent): chemical shift (ppm) (multiplicity, coupling constants (Hz), integration). Multiplicities were reported with following abbreviations: s = singlet, d = doublet, dd = doublet-doublet, t = triplet, m = multiplet, brs = broad singlet. Data of ^{13}C-NMR were presented in the following pattern: (instrument, solvent): chemical shift (ppm). High resolution mass data (HRMS) were collected by the Thermo Scientific Q Exactive HF. MS data were reported in the following pattern: *m/z* experimental data (calculated data). Analytical high performance liquid chromatography (HPLC) investigations were conducted on Shimazu LC-20AT. Preparative HPLC resolution experiments were performed on Shimazu LC-20AP. UV-Vis absorption spectra were obtained on a Hitachi U-3900 spectrometer. The fluorescence excitation and emission spectra were measured on an Edinburgh Instruments FLS980-STM fluorophotometer. Cyclic voltammograms (CV) were collected on Shanghai Chenhua instrument Co. ltd CHI660E Electrochemical Workstation. Electronic circular dichroism (ECD) spectra were acquired on Biologic MOS-500. Single crystals of compounds, appropriate for X-ray diffraction, were chosen and put in inert oil in the cold gas stream. X-ray diffraction intensity data was gathered on a Rigaku XtaLAB FRX diffractometer equipped with the Hypix6000HE detector.

2. Synthetic procedure

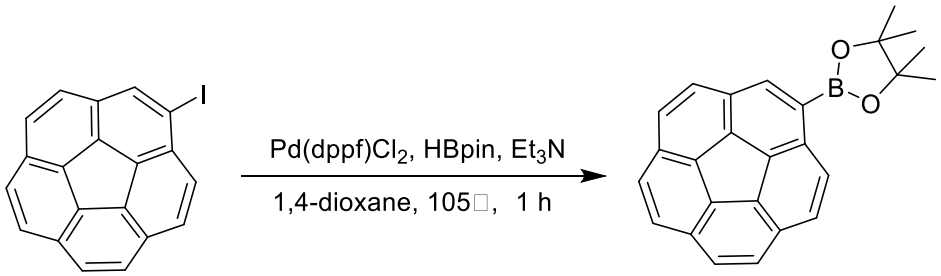
2.1. Synthesis of 1-iodocorannulene (**2**)



1 2

A mixture of **1** (2.4346 g, 9.74 mmol) and *N*-iodosuccinimide (3.5792 g, 14.61 mmol) was added into a 250-mL two-neck round-bottom flask connected with a reflux condenser, into which dichloroethane (50 mL) was injected via a syringe. $BF_3{\cdot}Et_2O$ (1.2 mL, 15.39 mmol) was added via a micropipette. The reaction mixture was stirred and heated in 80℃ oil bath for 1 h until TLC indicated the consumption of **1**. Afterward, the reaction mixture was quenched with saturated $Na_2S_2O_3$ solution and transferred to a separatory funnel. Extraction with dichloromethane was performed three times. The organic layers were combined and dried with Na_2SO_4. The solvent was removed by rotary evaporator, giving a brown crude product. Column chromatography in pure hexane afforded **2** as yellow powders (3.1989 g, 8.50 mmol = 87%).
^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.3277 (s, 1H), 7.8871-7.2597 (m, 9H).

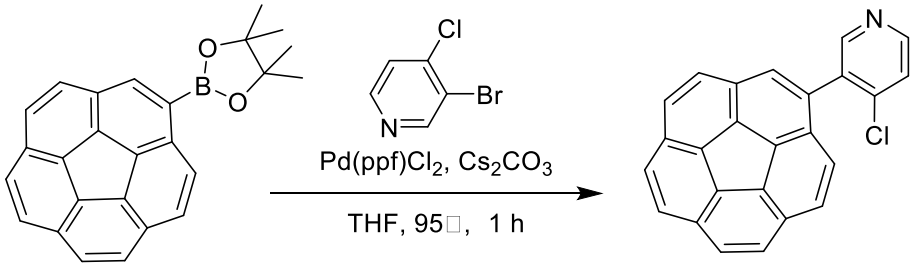
2.2. Synthesis of 1-(Bpin)corannulene (**3**)



2 3

This reaction was set up in the glovebox. A mixture of **2** (376.2 mg, 1.0 mmol) and $Pd(dppf)Cl_2$ (24.5 mg, 0.03 mmol) was transferred into a 15-mL oven-dried sealed tube. Then HBpin (218 μL, 1.5 mmol), anhydrous Et_3N (400 μL, 3 mmol), and anhydrous 1,4-dioxane (4 mL) was added. The sealed tube was taken out from the glove box, then heated and stirred in 105℃ oil bath for 1 h. The reaction mixture was diluted with dichloromethane and washed with H_2O three times. The organic phase was collected, dried with Na_2SO_4, and dichloromethane was removed under vacuo. Column chromatography in hexane/dichloromethane (9:1 to 7:1) finally afforded **3** as yellow powders (269.7 mg, 0.717 mmol = 72%).
^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.4780 (s, 1H), 8.4514 (d, J = 8.82 Hz, 1H), 7.8349-7.7804 (m, 8H), 1.4489 (s, 12H).

2.3. Synthesis of 4-chloro-3-(dibenzo[*ghi*,*mno*]fluoranthen-1-yl)pyridine (**4'**)

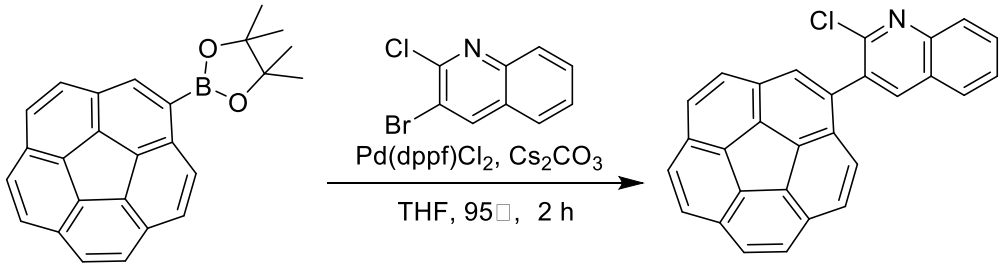


3 **4'**

To a 15-mL oven-dried sealed tube, a mixture of **3** (37.6 mg, 0.1 mmol), 3-bromo-4-chloropyridine (28.9 mg, 0.15 mmol), Pd(dppf)Cl_2 (8.1 mg, 0.01 mmol), and Cs_2CO_3 (130.3 mg, 0.4 mmol) was added. Then anhydrous THF (5 mL) was injected. The mixture was degassed with argon for 10 min, then heated and stirred in 95℃ oil bath for 1 h. The reaction mixture was quenched with dilute HCl solution and extracted with dichloromethane three times. The organic layers were combined and dried with Na_2SO_4. Removing solvent at reduced pressure by rotary evaporator gave a brown crude product. Column chromatography in hexane/ethyl acetate (9:1) afforded **4'** as yellow crystal (21.5 mg, 0.059 mmol = 59%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.6224 (d, *J* = 5.46 Hz, 1H), 8.5837 (br, 1H), 7.8759-7.7671 (m, 8H), 7.5957 (d, *J* = 5.46 Hz, 1H), 7.4568 (d, *J* = 8.82, 1H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 152.32, 149.90, 144.07, 136.41, 136.11, 136.01, 135.81, 135.74, 134.51, 131.40, 131.26, 131.07, 130.33, 129.99, 128.48, 127.74, 127.61, 127.59, 127.38, 127.21, 127.14, 126.02. HRMS (ESI): *m/z* 362.07236 for $[C_{25}H_{13}ClN]^+$ (362.07310 calcd. for $[C_{25}H_{13}ClN]^+$).

2.4. Synthesis of 2-chloro-3-(dibenzo[*ghi*,*mno*]fluoranthen-1-yl)quinoline (**5'**)

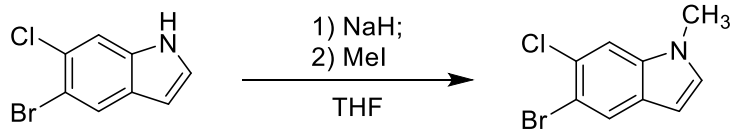


3 **5'**

To a 50-mL oven-dried sealed tube, a mixture of **3** (100.0 mg, 0.27 mmol), 3-bromo-2-chloroquinoline (96.7 mg, 0.40 mmol), Pd(dppf)Cl_2 (21.7 mg, 0.03 mmol), and Cs_2CO_3 (346.7.3 mg, 1.06 mmol) was added. Then anhydrous THF (13 mL) was injected. The mixture was degassed with argon for 10 min, then heated in 95℃ oil bath for 2 h. The reaction mixture was quenched with dilute HCl solution and extracted with dichloromethane three times. The organic layers were combined and dried with Na_2SO_4. Removing solvent at reduced pressure by rotary evaporator gave a brown crude product. Column chromatography in hexane/ethyl acetate (30:1) afforded **5'** as yellow crystal (80.2 mg, 0.195 mmol = 73%).

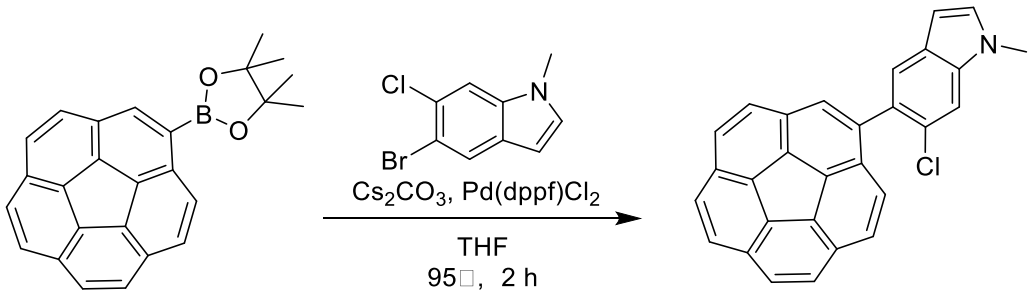
^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.1795 (d, *J* = 8.76 Hz, 1H), 8.1571 (brs, 1H), 7.8778 (d, *J* = 2.52 Hz, 2H), 7.8757 (s, 1H), 7.8549-7.8045 (m, 6H), 7.7600 (d, *J* = 8.76 Hz, 1H), 7.6365-7.7.6095 (td, *J* = 1.20 & 5.16 Hz, 1H), 7.4924 (d, *J* = 8.82 Hz, 1H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 150.75, 147.55, 140.20, 136.68, 136.35, 136.00, 135.95, 135.78, 135.64, 132.94, 131.27, 131.16, 130.96, 130.87, 130.35, 128.65, 128.51, 127.74, 127.66, 127.64, 127.56, 127.50, 127.31, 127.24, 127.18, 127.08, 126.13. HRMS (ESI): *m/z* 412.0884 for $[C_{29}H_{15}ClN]^+$ (412.0888 calcd. for $[C_{29}H_{15}ClN]^+$).

2.5. Synthesis of 5-bromo-6-chloro-*N*-methylindole



To a suspended solution of NaH (260.0 mg, 10.85 mmol) in THF (1 mL), 5-bromo-6-chloro-1*H*-indole (1000.0 mg, 4.34 mmol) in THF (1 mL) was added dropwise at 0℃. The mixture was stirred in ice bath for 15 min, then recovered to room temperature. After stirring for 1 h, the mixture was incubated in ice bath, treated with iodomethane, and warmed to room temperature again. After 30 min, the reaction mixture was quenched with water and extracted with dichloromethane. The organic layers were combined, dried over Na_2SO_4, and then concentrated in vacuo, giving brown crude product. The crude product was purified by a plug with eluent of hexane/dichloromethane = 7:1, yielding white solid as 5-bromo-6-chloro-*N*-methylindole (1051.2 mg, 4.30 mmol = 99%).

2.6. Synthesis of 6-chloro-5-(dibenzo[*ghi*,*mno*]fluoranthen-1-yl)-1-methyl-1*H*-indole (**6'**)

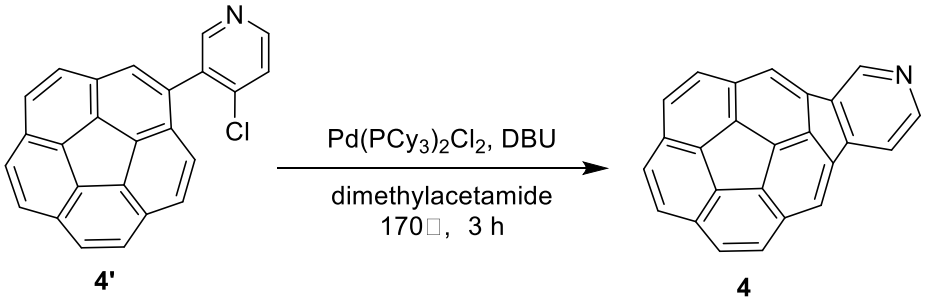


3 **6'**

To an oven-dried sealed tube, a mixture of **3** (66.9 mg, 0.178 mmol), 5-bromo-6-chloro-1-methyl-1*H*-indole (65.3 mg, 0.267 mmol), $Pd(dppf)Cl_2$ (14.7 mg, 0.018 mmol), and Cs_2CO_3 (232.0 mg, 0.712 mmol) was added. Then anhydrous THF (9 mL) was injected. The mixture was degassed with argon for 10 min, then heated and stirred at 95℃ for 2.5 h. Dilute HCl was added to stop the reaction. Extraction with dichloromethane three times followed by removal of solvent gave brown crude product. Flash column with eluent system of hexane/dichloromethane 6:1 afforded **6'** as orange powder (60.6 mg, 0.146 mmol = 82%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.8454 (s, 2H), 8.8285-8.8229 (m, 2H), 7.8086-7.7776 (m, 3H), 7.7040 (d, *J* = 8.76 Hz, 1H), 7.5968 (s, 1H), 7.5631 (br, 1H), 7.4955 (d, *J* = 8.76 Hz, 1H), 7.1217 (d, *J* = 3.12 Hz, 1H), 6.4728 (d, *J* = 3.06 Hz, 1H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 150.75, 147.55, 140.20, 136.68, 136.35, 136.00, 135.95, 135.78, 135.64, 132.94, 131.27, 131.16, 130.96, 130.87, 130.35, 128.65, 128.51, 127.74, 127.66, 127.64, 127.56, 127.50, 127.31, 127.24, 127.18, 127.08, 126.13. HRMS (ESI): *m/z* 414.1040 for $[C_{29}H_{17}ClN]^+$ (414.1044 calcd. for $[C_{29}H_{17}ClN]^+$).

2.7. Synthesis of acenaphtho[3',2',1',8':9,10,1,2]acephenanthryleno[4,5-c]pyridine (**4**)

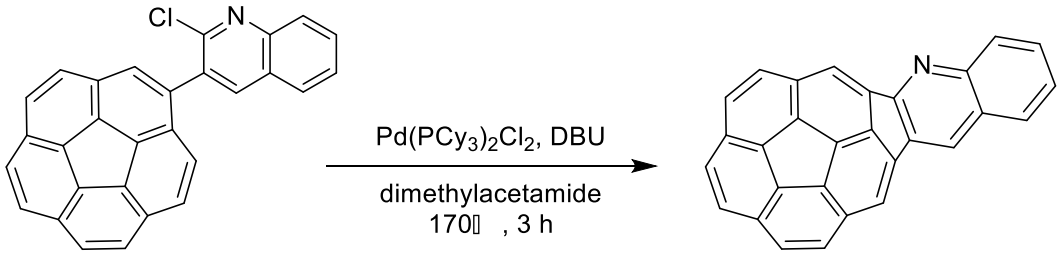


4' **4**

A mixture of **4'** (40.0 mg, 0.11 mmol) and $Pd(PCy_3)_2Cl_2$ (16.0 mg, 0.022 mmol) was added to a 15-mL oven-dried sealed tube. Then dimethylacetamide (3 mL) was injected via a syringe, and DBU (168 μL, 1.1 mmol) was added via a micropipette. The mixture was degassed with argon for 10 min, then heated and stirred in 170℃ oil bath for 3 h. Next, dimethylacetamide was removed at reduced pressure by rotary evaporator. Then the dark residue was diluted with HCl solution, and extracted with dichloromethane three times. The organic layers were combined and dried with Na_2SO_4. Removing solvent at reduced pressure by rotary evaporator gave a brown crude product. After column chromatography in dichloromethane/methanol (80:1) and recrystallization in hexane/dichloromethane, final product **4** was afforded as light yellow solid (10.6 mg, 0.033 mmol = 30%).

^{1}H-NMR (600 MHz, $C_2D_2Cl_4$): δ 8.8863 (s, 1H), 8.4772 (d, *J* = 4.98 Hz, 1H), 7.8326 (s, 1H), 7.7721 (s, 1H), 7.6956 (t, *J* = 8.82 Hz, 2H), 7.425-7.6197 (dd, *J* = 4.86 & 3.96 Hz, 2H), 7.591-7.5795 (dd, *J* = 4.80 & 4.20 Hz, 3H). ^{13}C-NMR (151 MHz, $C_2D_2Cl_4$): δ 149.80, 146.45, 143.87, 142.60, 139.42, 139.32, 138.57, 138.44, 137.41, 137.30, 137.20, 136.87, 134.31, 130.40, 130.16, 128.37, 128.35, 127.74, 127.42, 127.28, 127.25, 124.67, 123.21, 116.60. HRMS (ESI): *m/z* 326.09615 for $[C_{25}H_{12}N]^+$ (326.09643 calcd. for $[C_{25}H_{12}N]^+$).

2.8. Synthesis of acenaphtho[3',2',1',8':9,10,1,2]acephenanthryleno[4,5-b]quinoline (**5**)

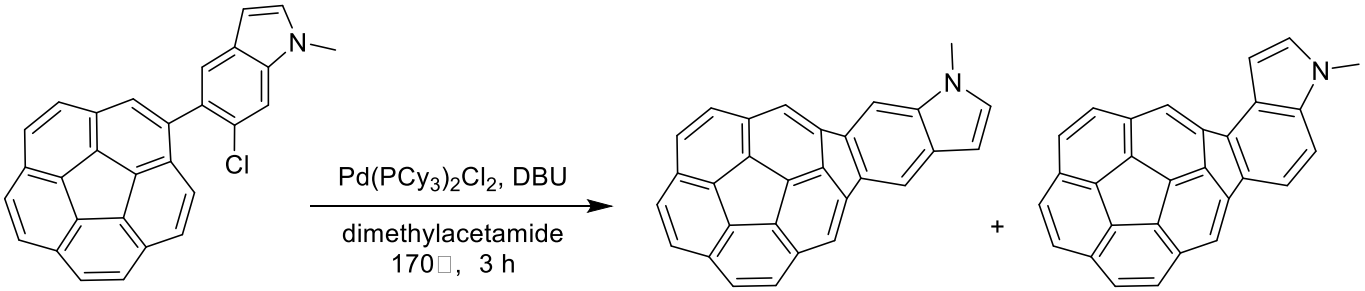


5' **5**

To a 15-mL oven-dried sealed tube, a mixture of **5'** (15.0 mg, 0.036 mmol) and $Pd(PCy_3)_2Cl_2$ (5.3 mg, 0.007 mmol) was added. Then dimethylacetamide (2 mL) was injected, and DBU (54 μL, 0.36 mmol) was pipetted to the system. The reaction mixture was degassed with argon for 10 min, then heated and stirred in 170℃ oil bath. The reaction mixture was allowed to cool down to room temperature, and dimethylacetamide was removed under vacuo by rotary evaporator, giving dark brown residue. Then the residue was diluted with dichloromethane, neutralized with dilute HCl solution, and extracted with dichloromethane three times. The organic layers were combined, dried with Na_2SO_4, and concentrated under vacuo. The crude was purified by flash chromatography in hexane/dichloromethane (1:1), rendering **5** as yellow crystal (4.1 mg, 0.011 mmol = 31%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.2756 (s, 1H), 8.2376 (s, 1H), 8.0905 (d, *J* = 8.34 Hz, 1H), 7.8111 (s, 1H), 7.7997-7.7805 (dd, *J* = 2.52 & 7.50 Hz, 2H), 7.7240 (d, *J* = 8.82 Hz, 1H), 7.6795-7.6311 (m, 5H), 7.4888 (t, *J* = 7.68 Hz, 1H). ^{13}C-NMR (151 MHz, $C_2D_2Cl_4$): δ 159.79, 145.53, 139.78, 139.14, 139.06, 137.81, 137.59, 137.52, 137.50, 137.16, 132.87, 130.86, 130.49, 129.65, 128.97, 128.73, 128.55, 127.89, 127.78, 127.64, 127.59, 127.54, 127.38, 126.98, 124.13, 122.45. HRMS (ESI): *m/z* 376.1117 for $[C_{29}H_{14}N]^+$ (376.1121 calcd. for $[C_{29}H_{14}N]^+$).

2.9. Synthesis of 9-methyl-9*H*-acenaphtho[3',2',1',8':9,10,1,2]acephenanthryleno[4,5-f]indole (**6**) and 10-methyl-10*H*-acenaphtho[3',2',1',8':9,10,1,2]acephenanthryleno[4,5-e]indole (**7**)



6' **6** **7**

To a 15-mL oven-dried sealed tube, a mixture of **6'** (82.8 mg, 0.2 mmol) and $Pd(PCy_3)_2Cl_2$ (29.4 mg, 0.04 mmol) was added. Then dimethylacetamide (10 mL) was injected, and DBU (300 μL, 2 mmol) was pipetted to the system. The reaction mixture was degassed with argon for 10 min, then heated and stirred in 170℃

oil bath. The reaction mixture was allowed to cool down to room temperature, and dimethylacetamide was removed under vacuo by rotary evaporator, giving dark brown residue. Then the residue was diluted with dichloromethane, neutralized with dilute HCl solution, and extracted with dichloromethane three times. The organic layers were combined, dried with Na_2SO_4, and concentrated under vacuo. The crude was purified by flash chromatography in hexane/ethyl acetate (20:1), giving orange solid, a mixture of **6** and **7**. Preparative HPLC rendered **6** as yellow crystal (18.1 mg, 0.05 mmol = 24%) and **7** as yellow crystal (6.0 mg, 0.02 mmol = 8%).

Preparative HPLC parameters: run time is 25 min; sample solvent is isopropanol (HPLC grade); sample concentration is 2 mg/mL; column is Chiralpak®-IF (10 mm φ × 250 mmL, 5 μm); sample volume is 1 mL; mobile phase is hexane and isopropanol; gradient is 80:20 for first 10 minutes, then 90:10 for next 15 min; flow rate is 5 mL/min; column temperature is 25°C; signals are detected at 365 nm.

Compound **6**:

^{1}H-NMR (600 MHz, $(CD_3)_2CO$): δ 7.8978 (s, 1H), 7.8291 (s, 1H), 7.7975 (s, 1H), 7.7748 (s, 1H), 7.7564 (d, *J* = 3.9 Hz, 2H), 7.7051-7.7678 (dd, *J* = 3.06 Hz, 2H), 7.1851 (d, *J* = 3.06 Hz, 2H), 7.4207 (d, *J* = 3.00 Hz, 2H), 3.8595 (s, 3H, CH3). ^{13}C-NMR (151 MHz, $(CD_3)_2CO$): δ 146.26, 143.66, 143.53, 139.88, 139.14, 138.95, 138.78, 138.40, 138.25, 135.66, 133.52, 131.38, 131.13, 131.07, 130.27, 129.30, 129.26, 127.93, 127.92, 127.82, 121.31, 120.98, 115.29, 105.07, 103.14, 33.12. HRMS (ESI): *m/z* 378.1274 for $[C_{29}H_{16}N]^+$ (378.1277 calcd. for $[C_{29}H_{16}N]^+$).

Compound **7**:

^{1}H-NMR (600 MHz, $(CD_3)_2CO$): δ 7.9423 (s, 1H), 7.7632 (d, *J* = 8.88 Hz, 1H), 7.7148 (d, *J* = 8.88 Hz, 1H), 7.6907 (s, 1H), 7.6679-7.6337 (dd, *J* = 8.76 & 11.7 Hz, 2H), 7.5910 (d, *J* = 1.02 Hz, 2H), 7.5695 (d, *J* = 8.28 Hz, 1H), 7.3411 (d, *J* = 3.18 Hz, 1H), 7.2746-7.2592 (dd, *J* = 0.9 & 8.4 Hz, 1H), 6.8669-8.8601 (dd, *J* = 0.96 & 3.24 Hz, 1H), 4.8254 (s, 3H, CH3). ^{13}C-NMR (151 MHz, $(CD_3)_2CO$): δ 146.21, 144.30, 143.15, 139.90, 139.86, 139.14, 138.96, 138.86, 138.67, 138.48, 138.18, 132.75, 132.39, 131.83, 131.08, 130.94, 130.63, 129.36, 129.27, 128.11, 127.90, 127.83, 127.75, 125.33, 123.78, 121.75, 116.36, 110.46, 100.15, 33.26. HRMS (ESI): m/z 378.12720 for $[C_{29}H_{16}N]^+$ (378.12773 calcd. for $[C_{29}H_{16}N]^+$).

RESULTS AND DISCUSSION

1. Chiral resolution

Resolution of **4**:

Analytical HPLC parameters: run time is 30 min; sample solvent is dichloromethane (HPLC grade); sample concentration is 1 mg/mL; column is Chiralpak®-IC (4.6 mm φ × 250 mmL, 5 μm); sample volume is 5 μL; mobile phase is heptane/dichloromethane/isopropanol/triethylamine (58:30:12:1); flow rate is 1 mL/min; column temperature is 25℃; signals are detected at 365 nm.

Preparative HPLC parameters: run time is 30 min; sample solvent is dichloromethane (HPLC grade); sample concentration is 2 mg/mL; column is Chiralpak®-IC (10 mm φ × 250 mmL, 5 μm); sample volume is 1 mL; mobile phase is heptane/dichloromethane/isopropanol/triethylamine (58:30:12:1); flow rate is 5 mL/min; column temperature is 25℃; signals are detected at 365 nm.

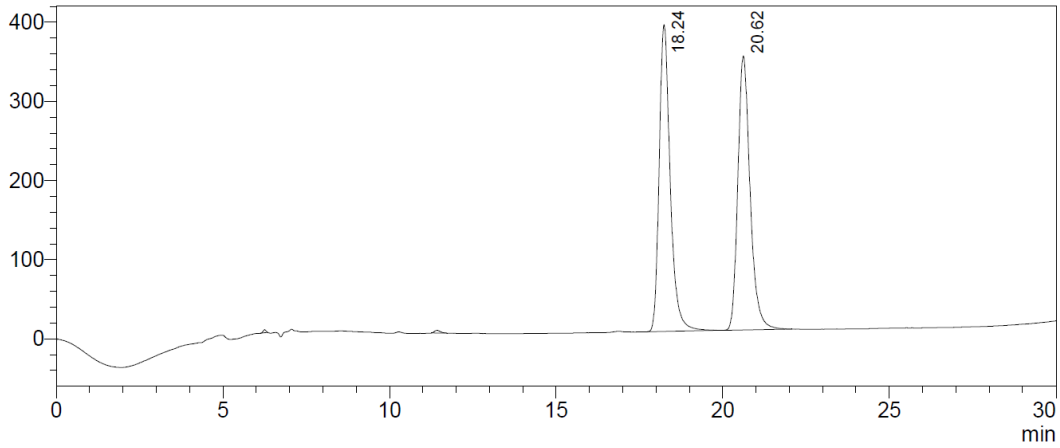


Figure S1. Analytical HPLC of **4** on Chiralpak®-IC

Resolution of **5**

Analytical HPLC parameters: run time is 10 min; sample solvent is dichloromethane (HPLC grade); sample concentration is 1 mg/mL; column is Chiralpak®-IF (4.6 mm φ × 250 mmL, 5 μm); sample volume is 5 μL; mobile phase is hexane/dichloromethane (45:55); flow rate is 1 mL/min; column temperature is 25℃; signals are detected at 365 nm.

Preparative HPLC parameters: run time is 30 min; sample solvent is dichloromethane (HPLC grade); sample concentration is 2 mg/mL; column is Chiralpak®-IF (10 mm φ × 250 mmL, 5 μm); sample volume is 1 mL; mobile phase is hexane/dichloromethane (45:55); flow rate is 5 mL/min; column temperature is 25℃; signals are detected at 365 nm.

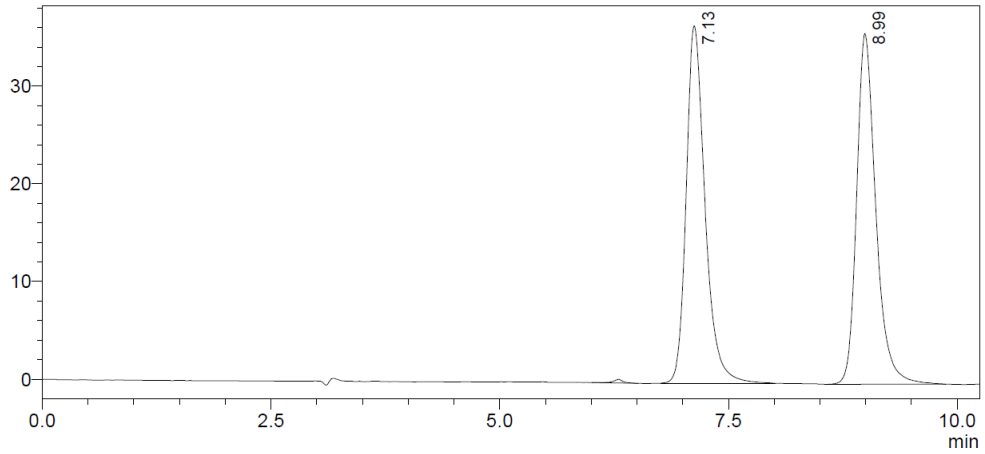


Figure S2. Analytical HPLC of **5** on Chiralpak®-IF

Resolution of **6** and **7**

Analytical HPLC parameters: run time is 30 min; sample solvent is isopropanol (HPLC grade); sample concentration is 1 mg/mL; column is Chiralpak®-IE (4.6 mm φ × 250 mmL, 5 μm); sample volume is 5 μL; mobile phase is hexane and isopropanol; gradient is 80:20 for first 10 minutes, then 90:10 for next 15 min; flow rate is 5 mL/min; column temperature is 25°C; signals are detected at 365 nm.

Preparative HPLC parameters: run time is 30 min; sample solvent is isopropanol (HPLC grade); sample concentration is 2 mg/mL; column is Chiralpak®-IE (10 mm φ × 250 mmL, 5 μm); sample volume is 0.5 mL; mobile phase is hexane and isopropanol; gradient is 80:20 for first 10 minutes, then 90:10 for the next 15 min; flow rate is 5 mL/min; column temperature is 25°C; signals are detected at 365 nm.

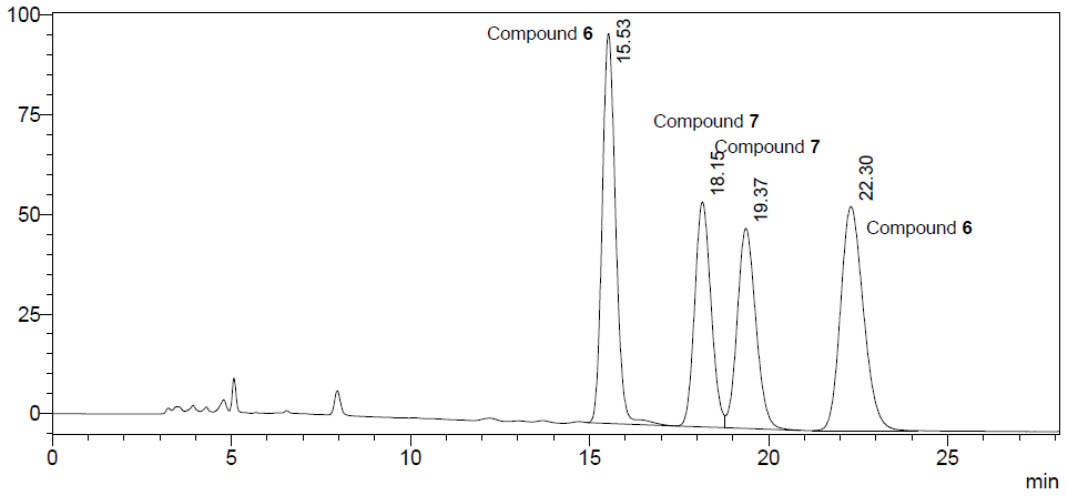


Figure S3. Analytical HPLC of **6** and **7** on Chiralpak®-IE

2. ECD spectra

Enantiomerically pure compounds of **4**-**7** were dissolved in HPLC grade acetonitrile to prepare the samples for ECD measurement. The pure solvent was measured as a blank spectrum, then the enantiomerically pure compound solution was subtracted by blank to record ECD spectra. The specific sample concentrations are labeled in the spectra (Figure S4-S7). The absolute configurations are summarized in Table S1. ECD parameters: slit is 2 nm; begin wavelength is 190 nm; end wavelength is 450 nm; step is 1 nm; repeat is 1; acquisition duration is 1 s.

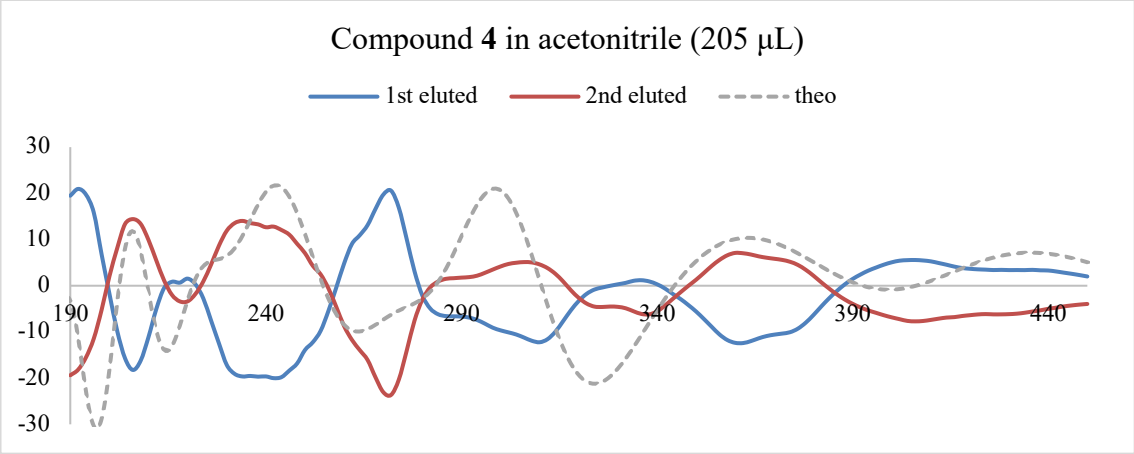


Figure S4. Experimental and calculated ECD spectra of **4**

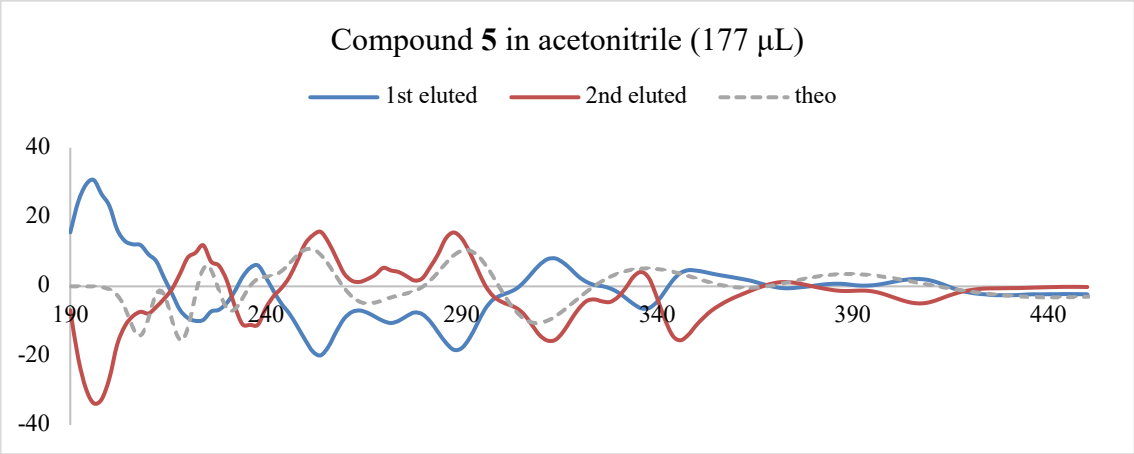


Figure S5. Experimental and calculated ECD spectra of **5**

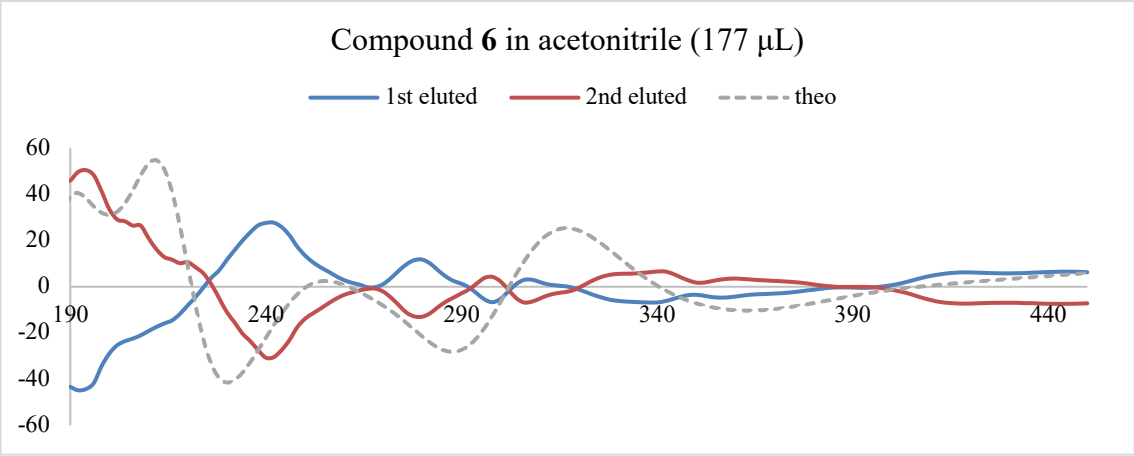


Figure S6. Experimental and calculated ECD spectra of **6**

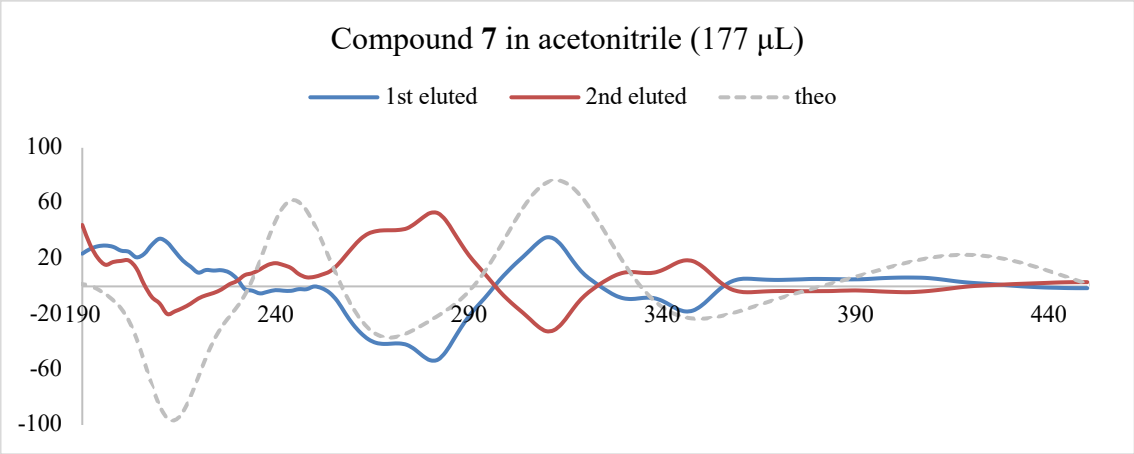


Figure S7. Experimental and calculated ECD spectra of **7**

Table S1. Configuration assignment of **4**-**7**

Compd.	1st eluted	2nd eluted	theo
4	乓	乒	乒
5	乓	乒	乒
6	乓	乒	乒
7	乓	乒	乓

3. UV-Vis and fluorescence spectra

Absorption measurement:

The sample solution for UV-Vis measurement was prepared in HPLC grade solvent. Trifluoromethanesulfonic acid (HOTf) was added to dichloromethane as solvent for protonated

measurement. Two cuvettes were filled with solvent to measure the blank spectrum. Then the cuvette for data measurement was added with 1 mL sample solution to record the absorption spectrum.

Excitation and emission measurement:
The solution from absorption measurement was used directly in the emission and excitation measurement on the fluorophotometer. First, the maximum absorption wavelength of the sample was set up as the excitation wavelength to obtain the emission wavelength. Next, the maximum emission wavelength was used to obtain the actual excitation spectrum. Then the excitation wavelength was chosen from the excitation spectrum to measure the correct emission spectrum.

Individual UV-Vis and fluorescence spectra of **4**-**7** are displayed in Figure S8-S15.

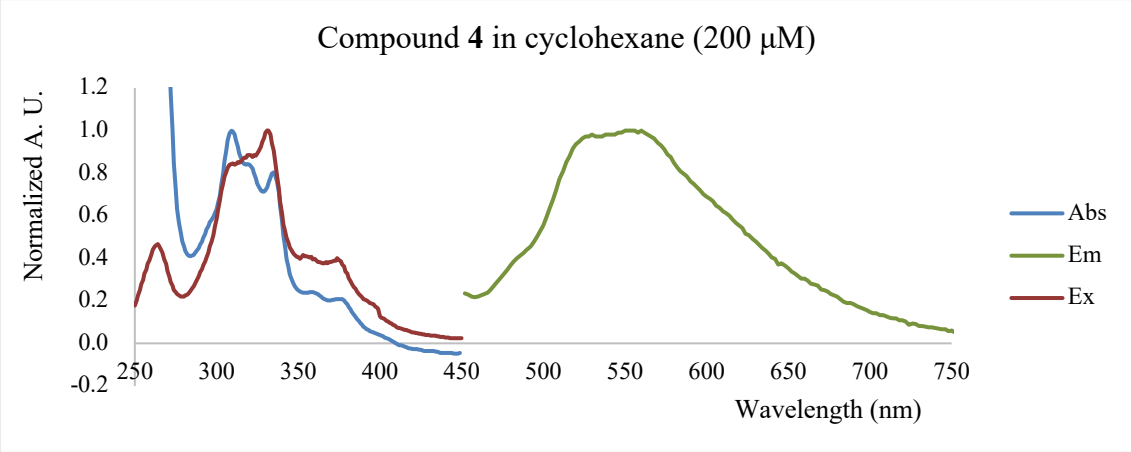


Figure S8. UV-Vis and fluorescence spectra of **4** in cyclohexane, excitation wavelength was 337 nm, emission wavelength was 560 nm

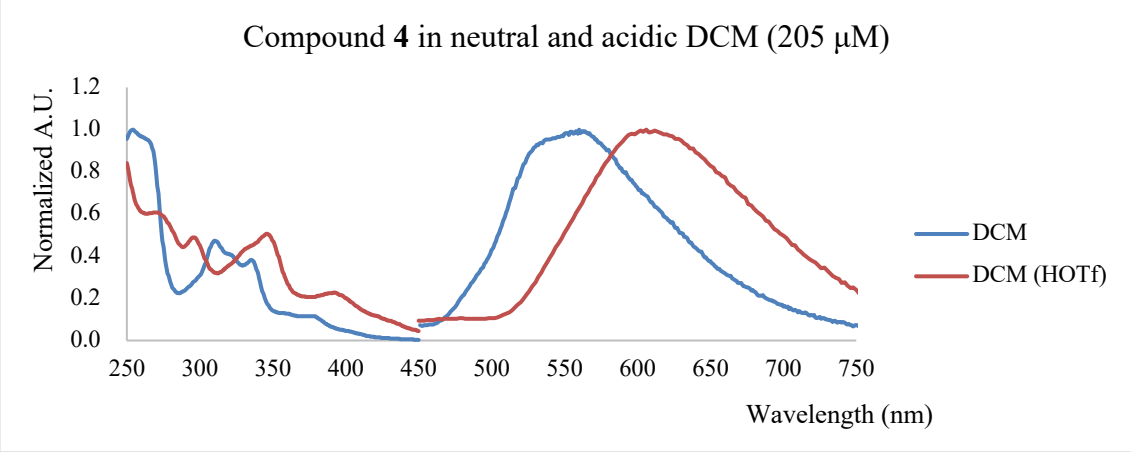


Figure S9. Neutral and acidified UV-Vis and fluorescence spectra of **4**, excitation wavelength in neutral DCM was 331 nm, excitation wavelength in acidified DCM was 346 nm

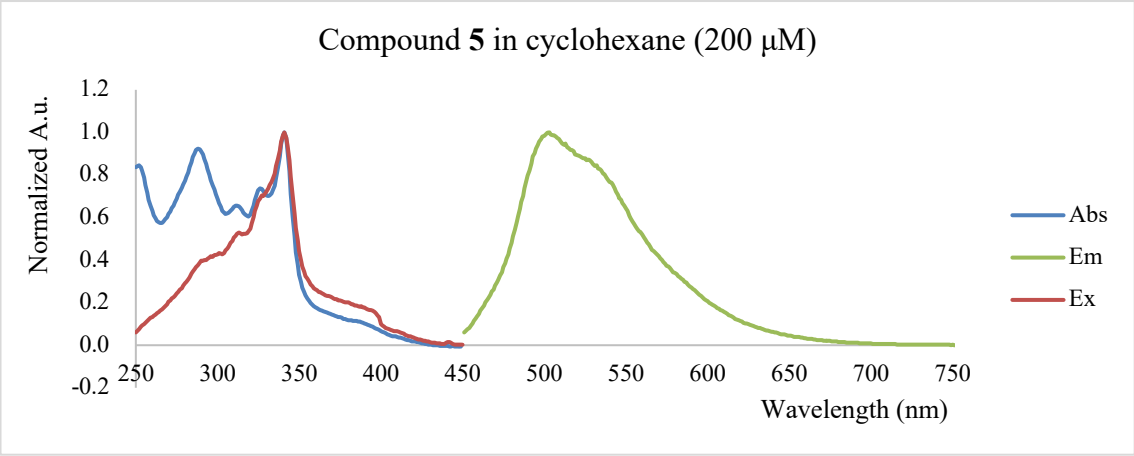


Figure S10. UV-Vis and fluorescence spectra of **5** in cyclohexane, excitation wavelength was 341 nm, emission wavelength was 503 nm

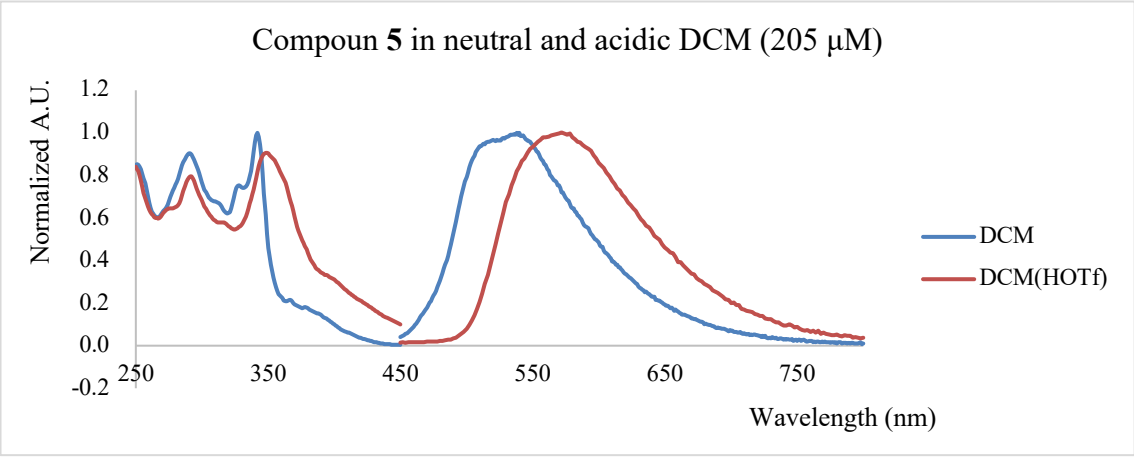


Figure S11. Neutral and acidified UV-Vis and fluorescence spectra of **5**, excitation wavelength in neutral DCM was 340 nm, excitation wavelength in acidified DCM was 360 nm

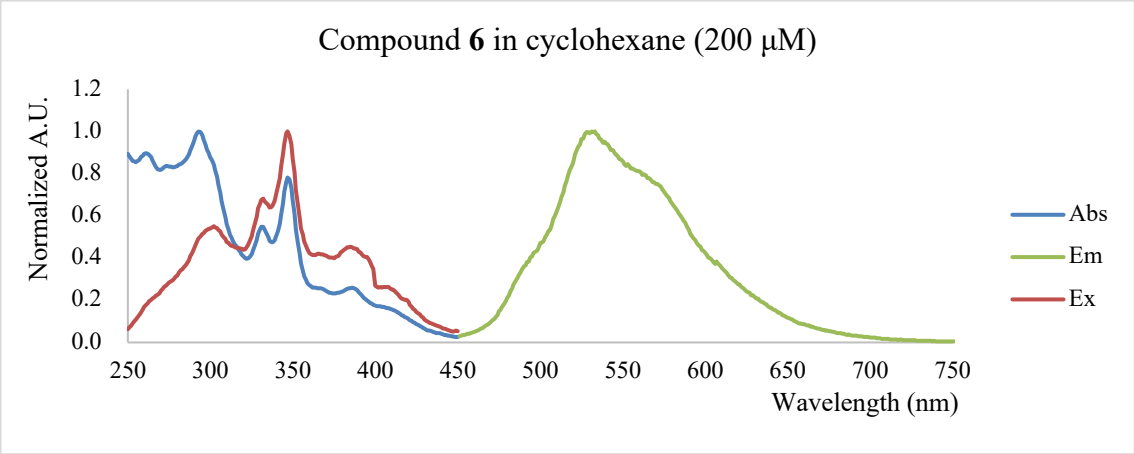


Figure S12. UV-Vis and fluorescence spectra of **6** in cyclohexane, excitation wavelength was 347 nm, emission wavelength was 531 nm

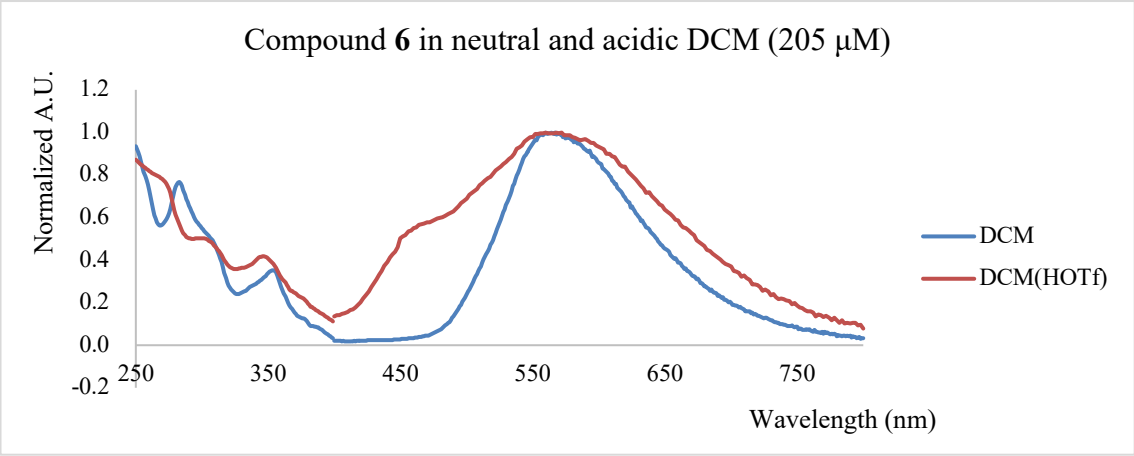


Figure S13. Neutral and acidified UV-Vis and fluorescence spectra of **6**, excitation wavelength in neutral DCM was 348 nm, excitation wavelength in acidified DCM was 346 nm

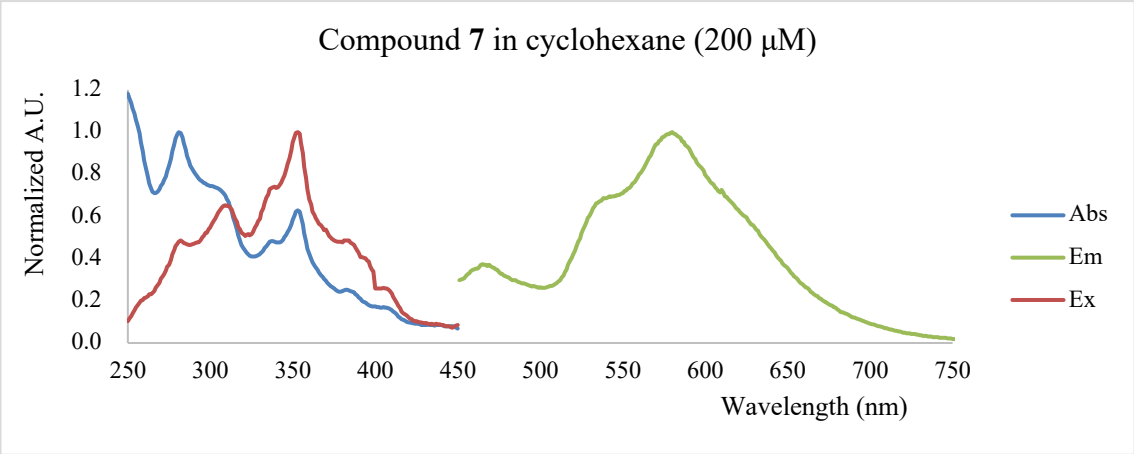


Figure S14. UV-Vis and fluorescence spectra of **7** in cyclohexane, excitation wavelength was 353 nm, emission wavelength was 580 nm

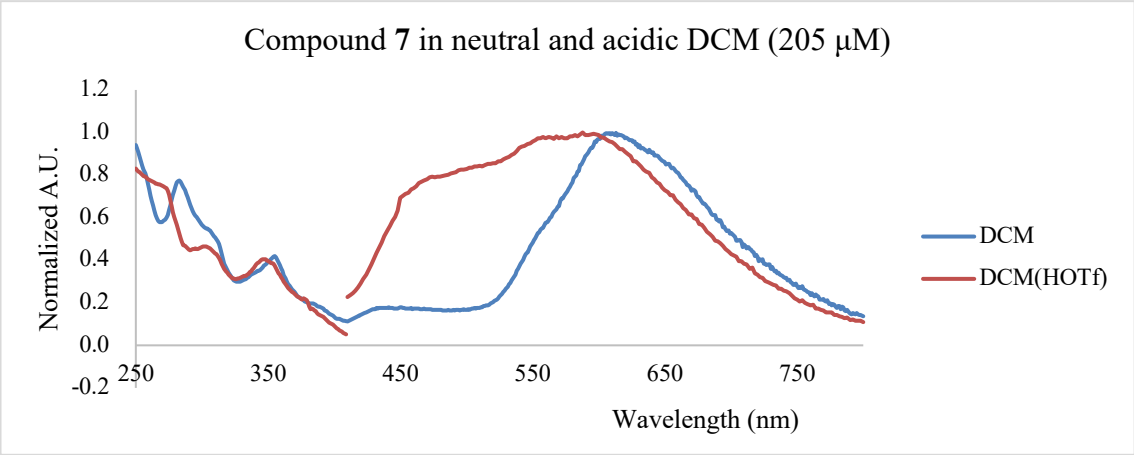


Figure S15. Neutral and acidified UV-Vis and fluorescence spectra of **7**, excitation wavelength in neutral DCM was 353 nm, excitation wavelength in acidified DCM was 350 nm

4. Crystal structures of **4** and **7**

Single crystal of **4**, suitable for X-ray diffraction, was obtained from dichloromethane/hexane via slow evaporation of solvents.

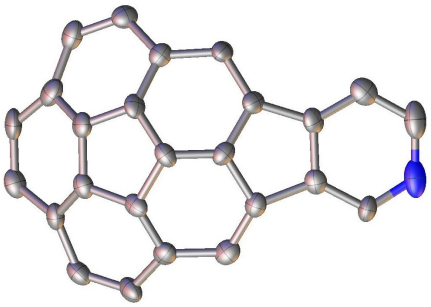


Figure S16. Crystal structure of **4**

Identification code	027437_LAS_c(1)
Empirical formula	$C_{25}H_{11}N$
Formula weight	325.35
Temperature/K	159.99(10)
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	26.2844(4)
b/Å	3.83524(5)
c/Å	14.2305(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1434.53(4)
Z	4
ρ_{calc}g/cm^3	1.506
μ/mm^{-1}	0.677
F(000)	672
Crystal size/mm^3	0.2 × 0.05 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.726 to 154.858
Index ranges	$-31 \leq h \leq 33$, $-4 \leq k \leq 4$, $-18 \leq l \leq 17$

Reflections collected	24754
Independent reflections	2940 [R_{int} = 0.0793, R_{sigma} = 0.0428]
Data/restraints/parameters	2940/6/237
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0439, wR_2 = 0.1145
Final R indexes [all data]	R_1 = 0.0534, wR_2 = 0.1227
Largest diff. peak/hole / e $Å^{-3}$	0.20/-0.19
Flack parameter	1(5)

Single crystal of **7**, suitable for X-ray diffraction, was obtained from dichloromethane via slow evaporation of solvent.

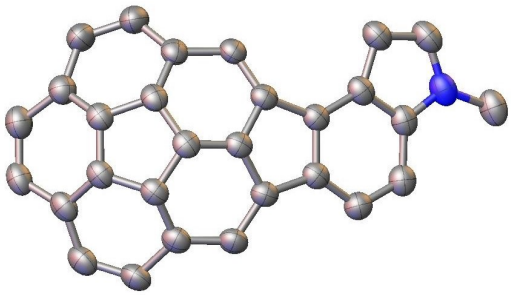


Figure S17. Crystal structure of **7**

Identification code	036884_LAS_5ClP23DCM_b(1)
Empirical formula	$C_{29}H_{15}N$
Formula weight	377.42
Temperature/K	159.98(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.97370(10)
b/Å	15.4309(2)
c/Å	13.5388(2)
α/°	90
β/°	103.4760(10)
γ/°	90
Volume/$Å^3$	1823.13(4)
Z	4

ρ_{calc}g/cm^3	1.375
μ/mm^{-1}	0.612
F(000)	784
Crystal size/mm^3	0.08 × 0.08 × 0.06
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.828 to 145.44
Index ranges	$-11 \leq h \leq 10$, $-18 \leq k \leq 19$, $-16 \leq l \leq 16$
Reflections collected	32576
Independent reflections	3556 [R_{int} = 0.0353, R_{sigma} = 0.0168]
Data/restraints/parameters	3556/688/538
Goodness-of-fit on F^2	1.106
Final R indexes [I>=2σ (I)]	R_1 = 0.0459, wR_2 = 0.1276
Final R indexes [all data]	R_1 = 0.0513, wR_2 = 0.1316
Largest diff. peak/hole / e Å^{-3}	0.59/-0.12

5. CV

Tetrabutylammonium hexafluorophosphate (TBAH) solution (0.07 mmol/mL) was prepared by dissolving TBAH (542.4 mg, 1.4 mmol) in anhydrous THF (20 mL). $AgNO_3$ TBAH solution (0.01 mmol/mL and 0.1 mmol/mL) was prepared by dissolving $AgNO_3$ (8.5 mg, 0.05 mmol) and TBAH (193.7 mg, 0.5 mmol) in anhydrous acetonitrile (5 mL). Ferrocene standard solution was prepared by dissolving ferrocene (0.5 mg, 0.005 mmol) in TBAH solution (5 mL). The sample solution was prepared by dissolving compound (1 mg) in TBAH solution (4 mL). After the solutions were ready, the electrodes and sample vial were washed with anhydrous THF. The carbon electrode was polished over aluminum oxide paste for 10 min. Then 4 mL of ferrocene standard solution was added to the sample container. Then the platinum and carbon electrodes were attached. After 10-minute degassing with nitrogen, the reference electrode was filled with $AgNO_3$ solution and connected to the sample vial. Then the standard voltammogram was recorded. The same procedure was performed on the sample solutions to obtain cyclic voltammograms.

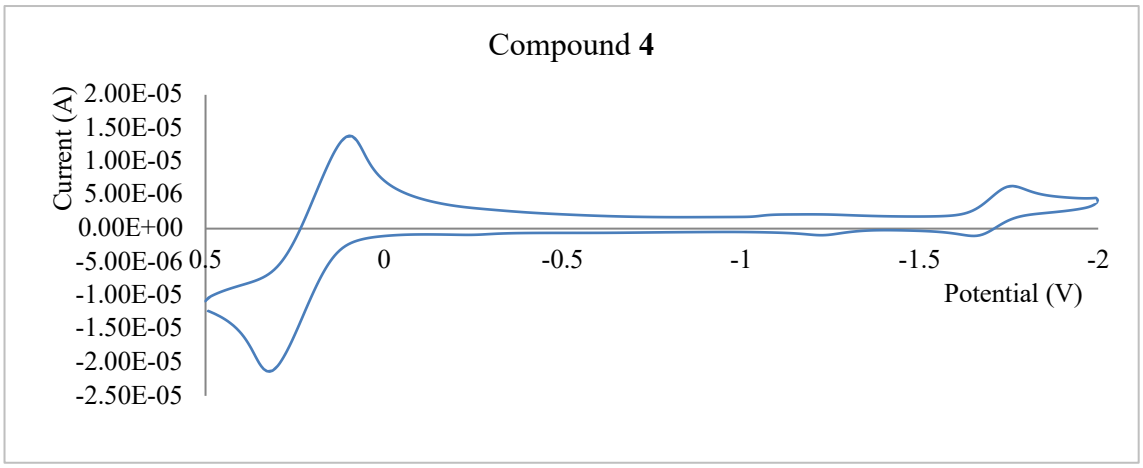


Figure S18. Cyclic voltammogram of **4**

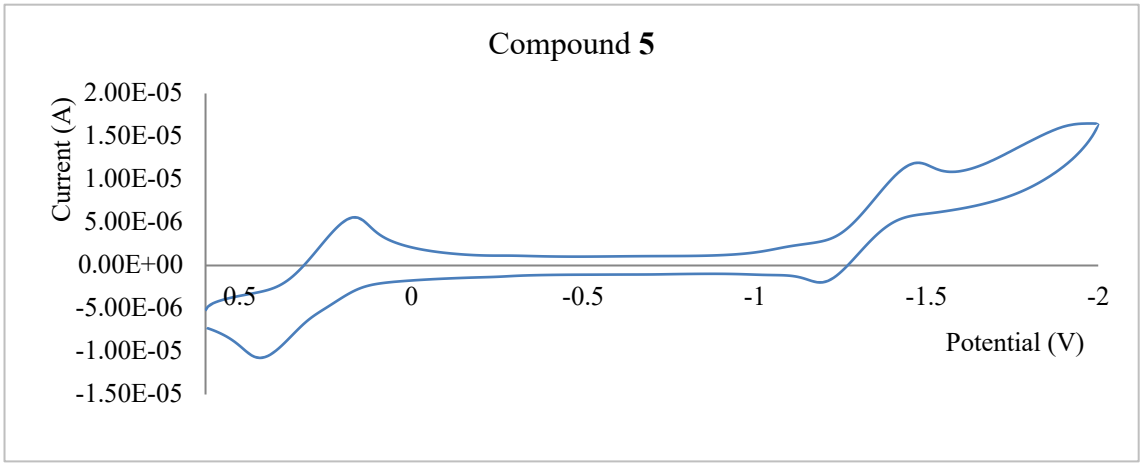


Figure S19. Cyclic voltammogram of **5**

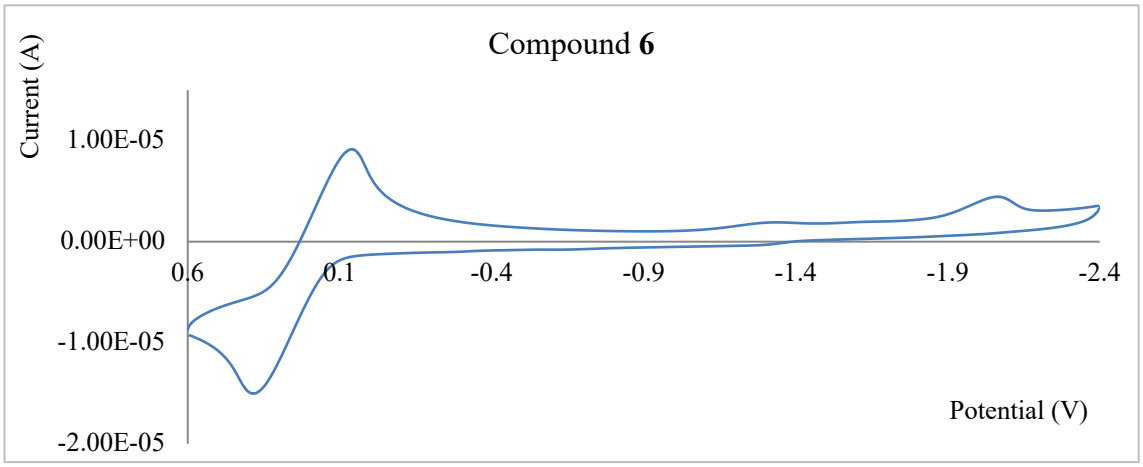


Figure S20. Cyclic voltammogram of **6**

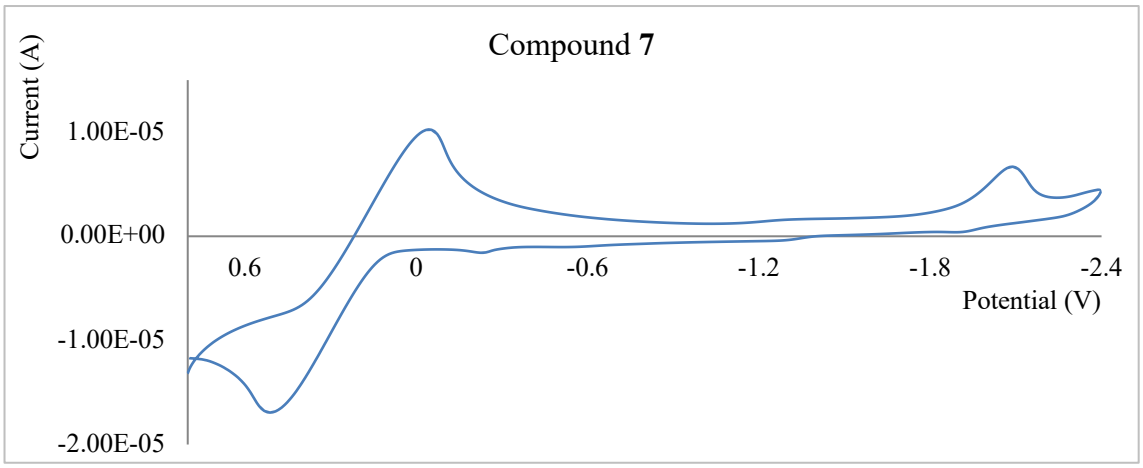
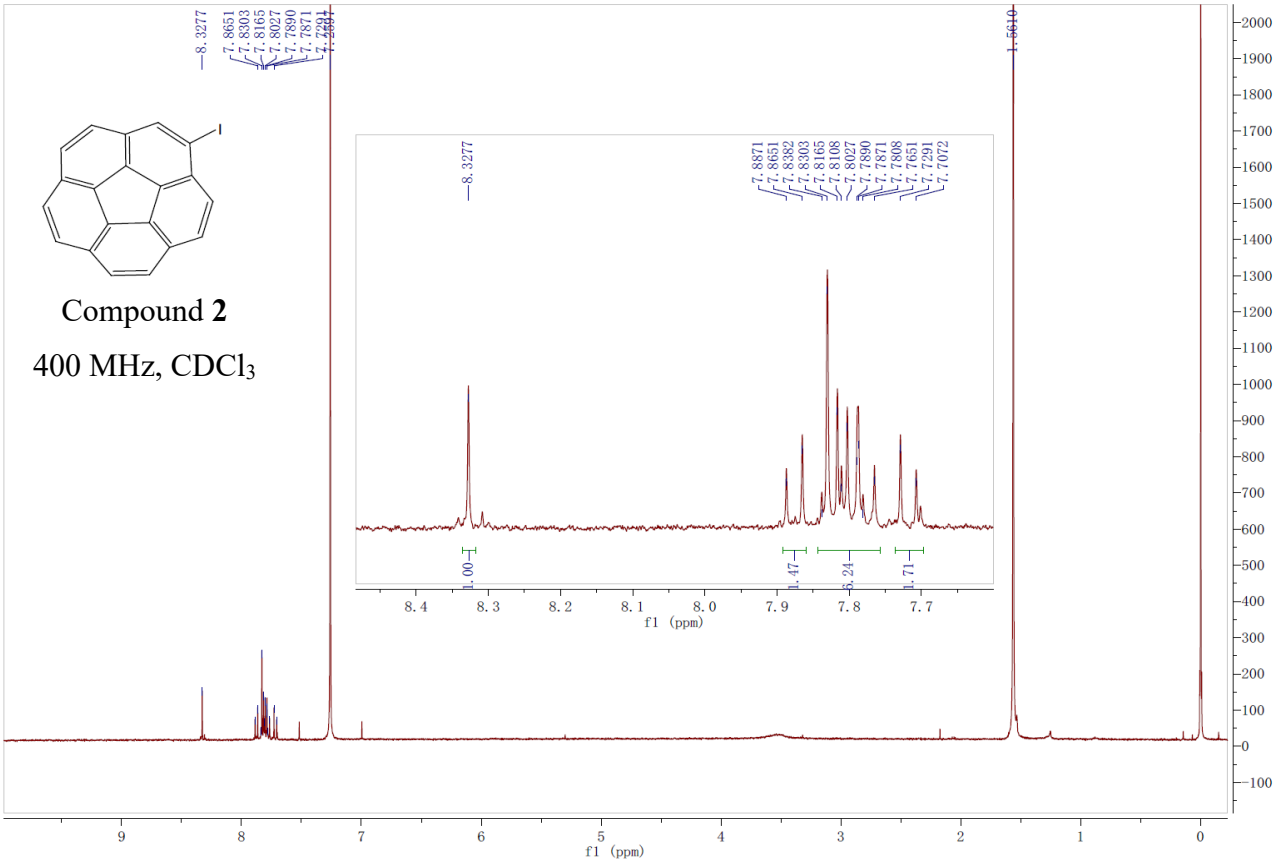


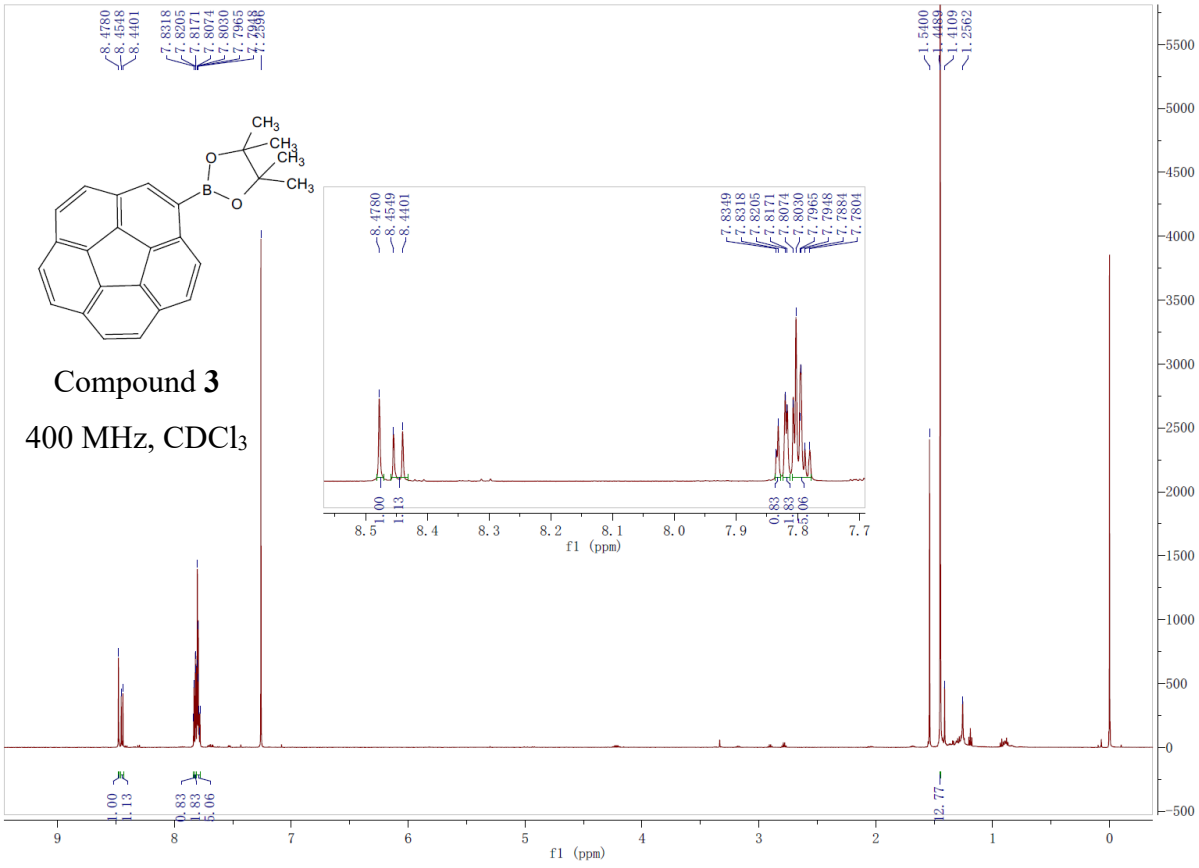
Figure S21. Cyclic voltammogram of **7**

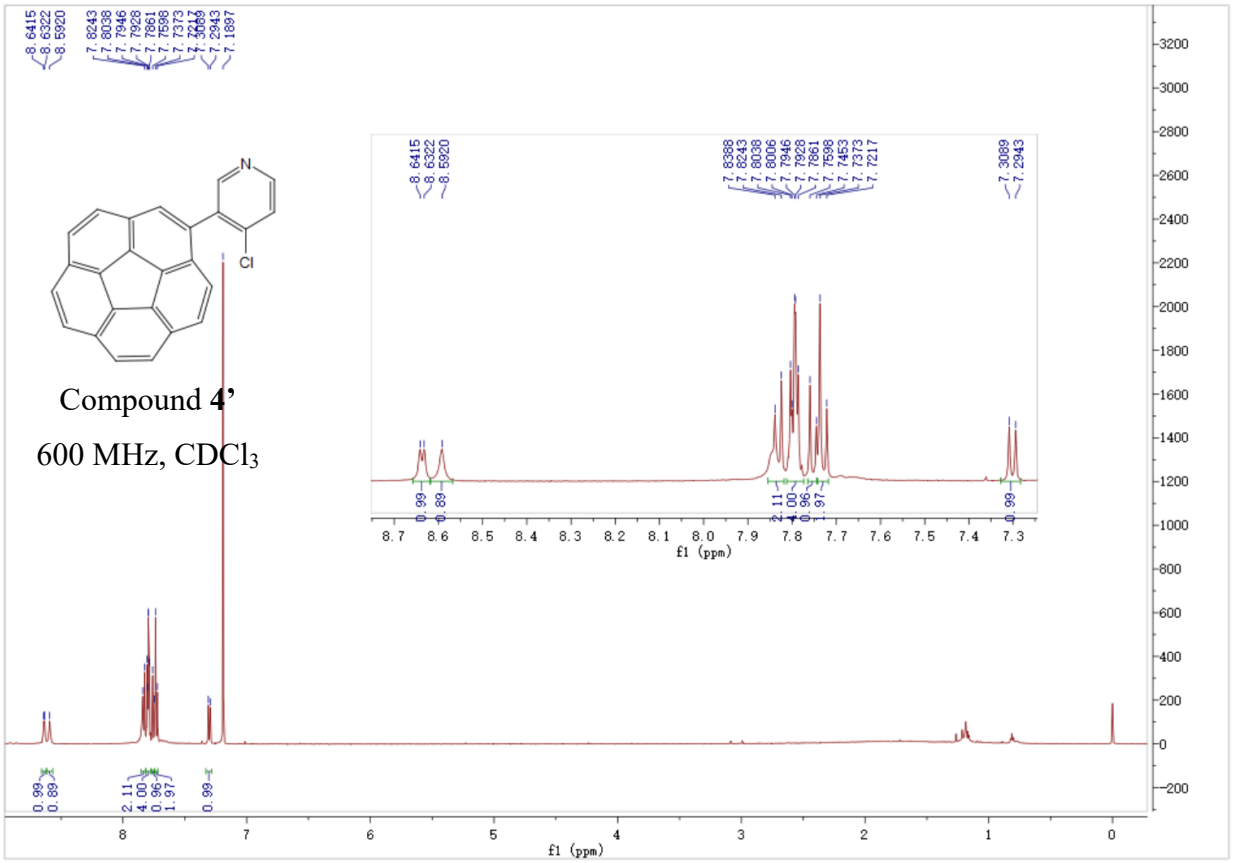
Table 2. Electrochemical properties of **4**-**7** from cyclic voltammetry

Compd.	E_c (V)	$E_{1/2}$ (V)	I_{pa}/I_{pc}
4	-1.88	-1.83	0.53
5	-1.69	-1.55	0.39
6	-2.20	/	/
7	-2.23	/	/

6. NMR spectra

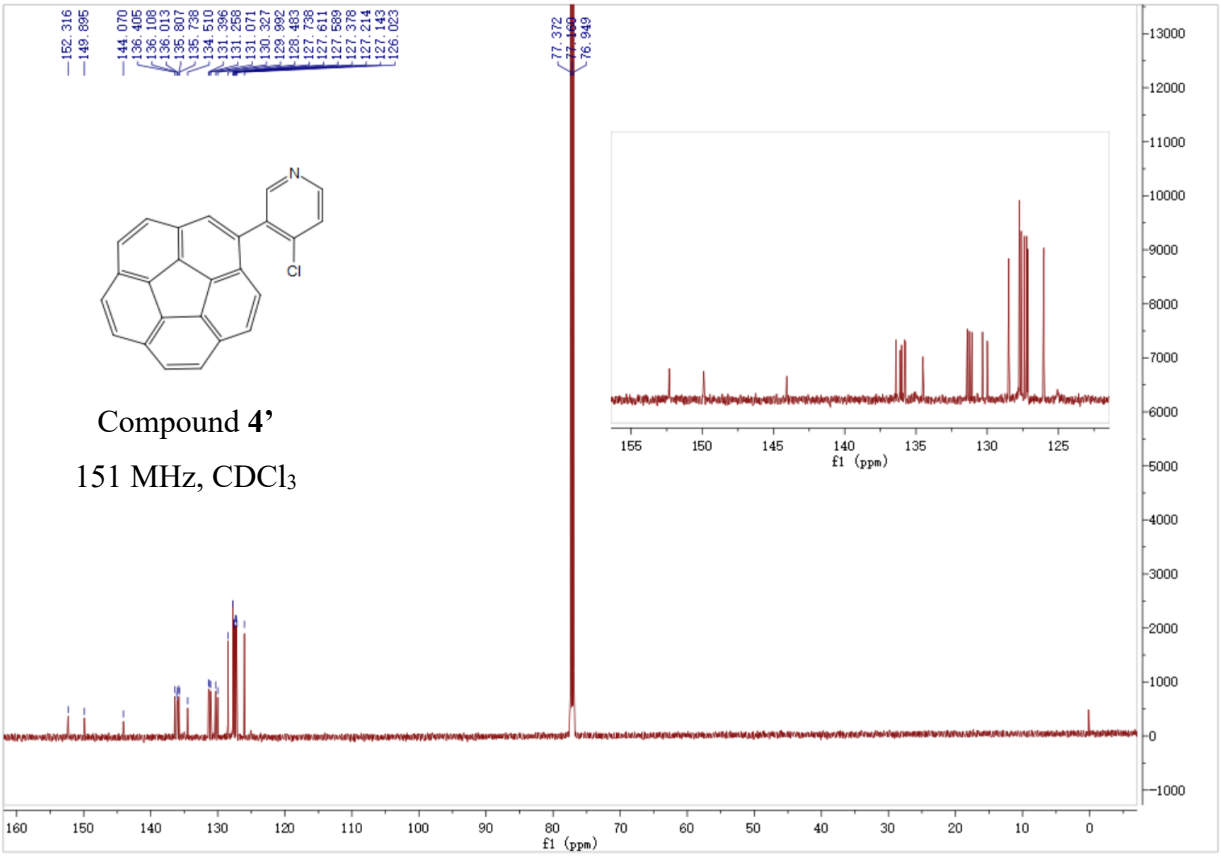






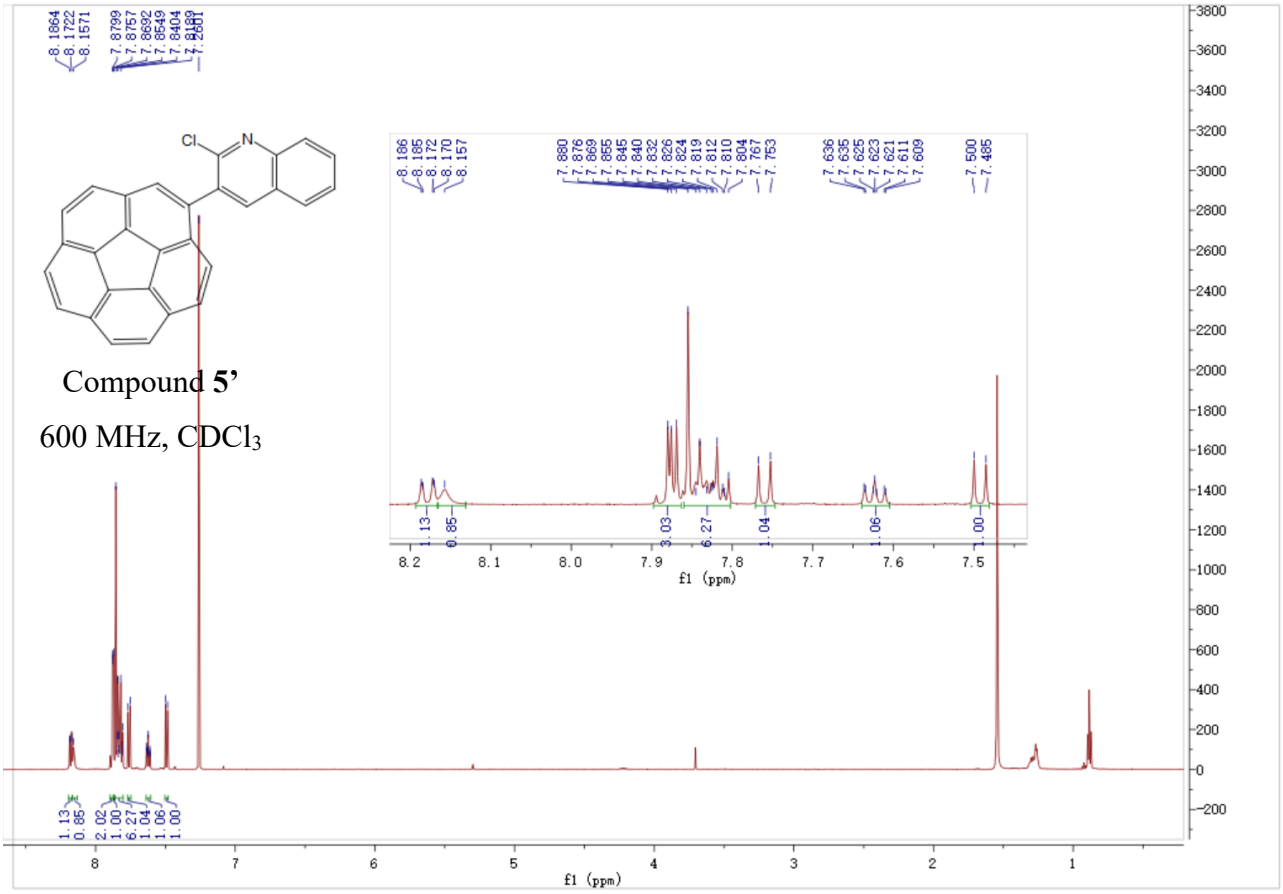
Compound **4'**

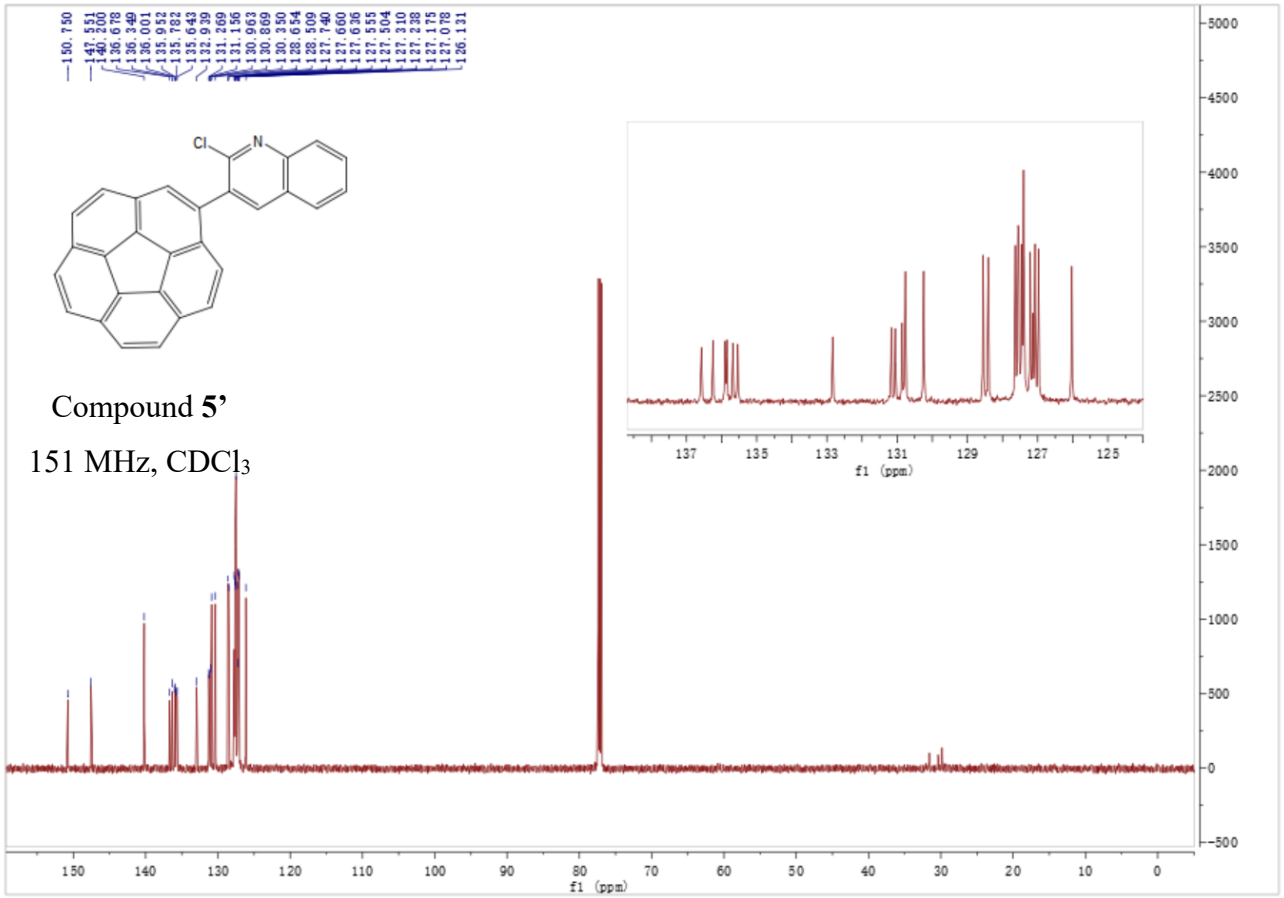
600 MHz, $CDCl_3$

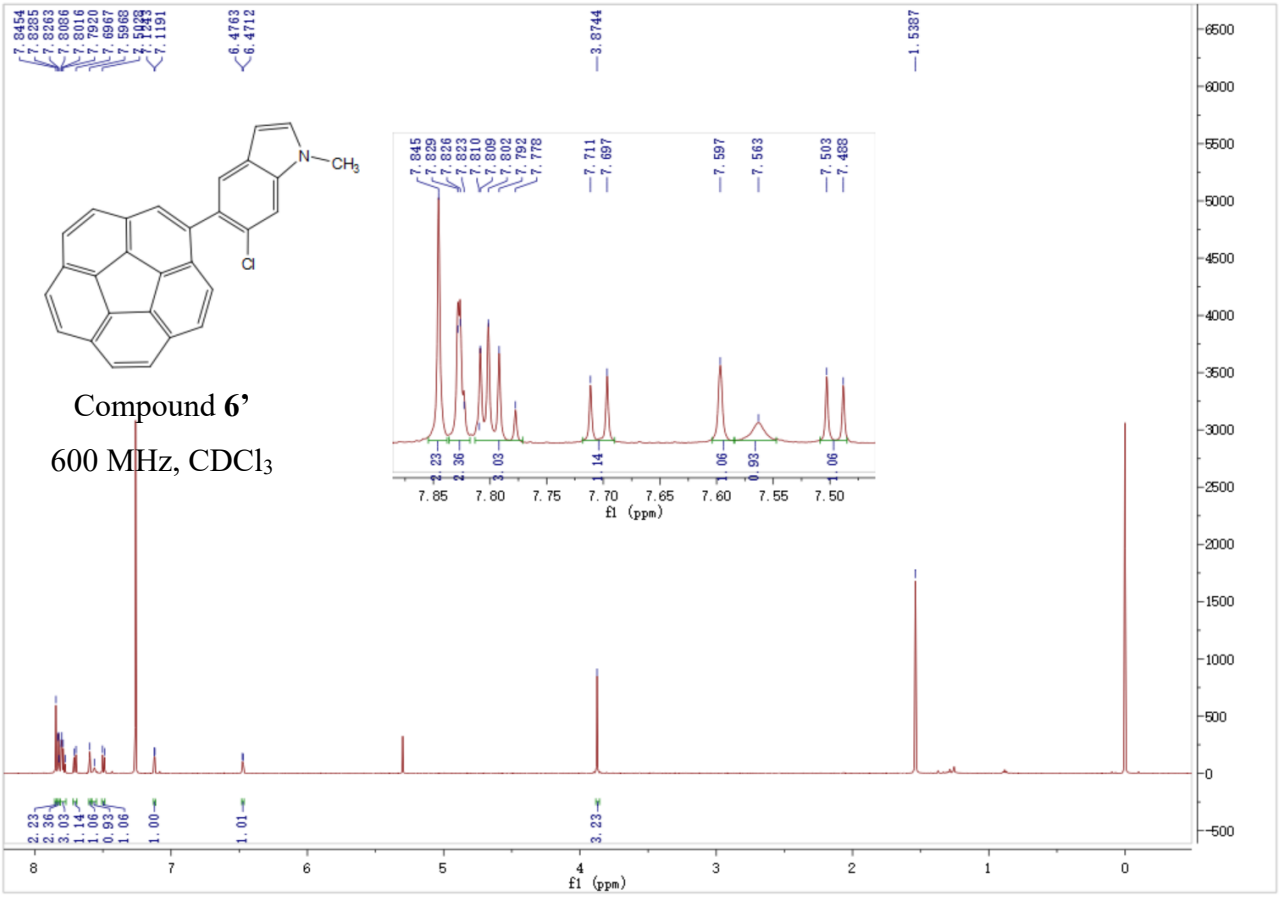


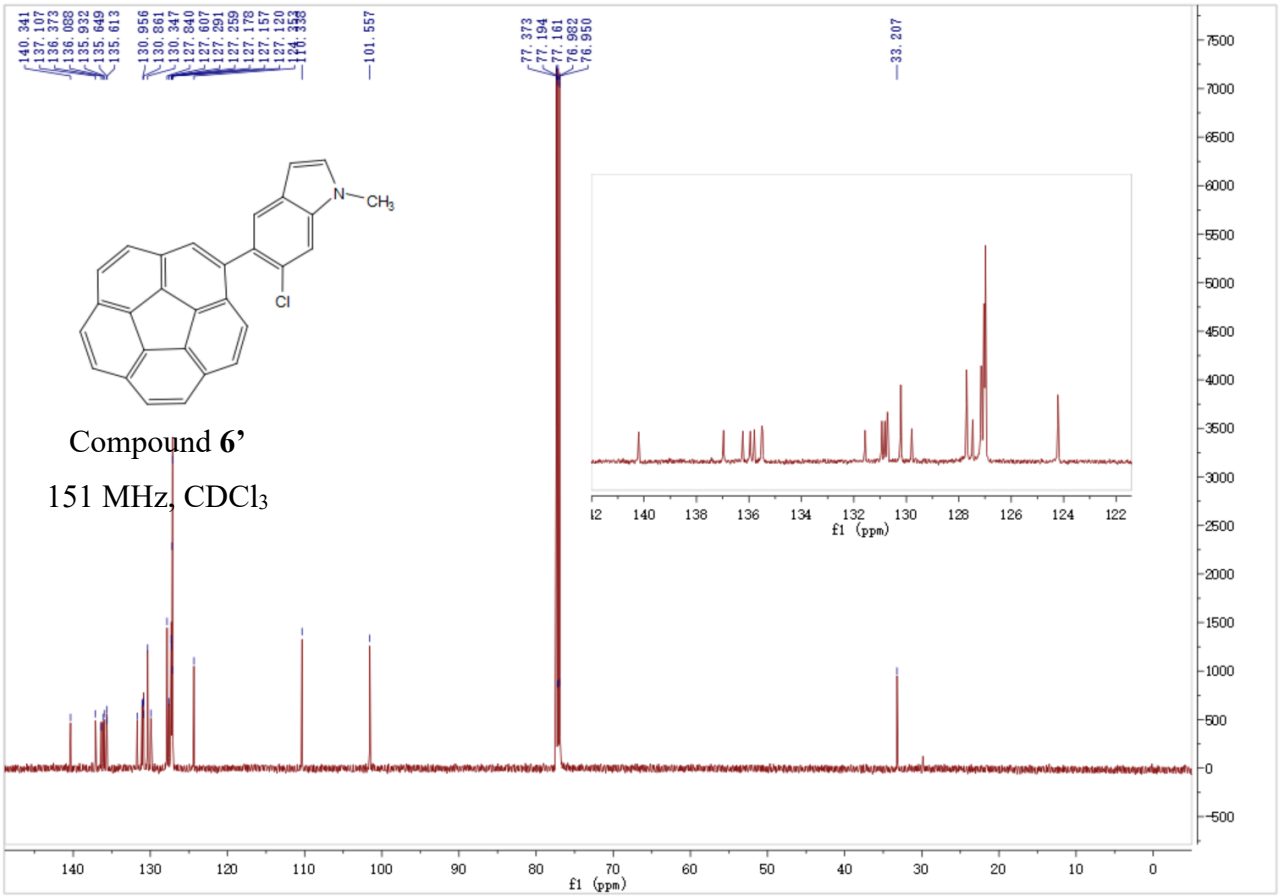
Compound **4'**

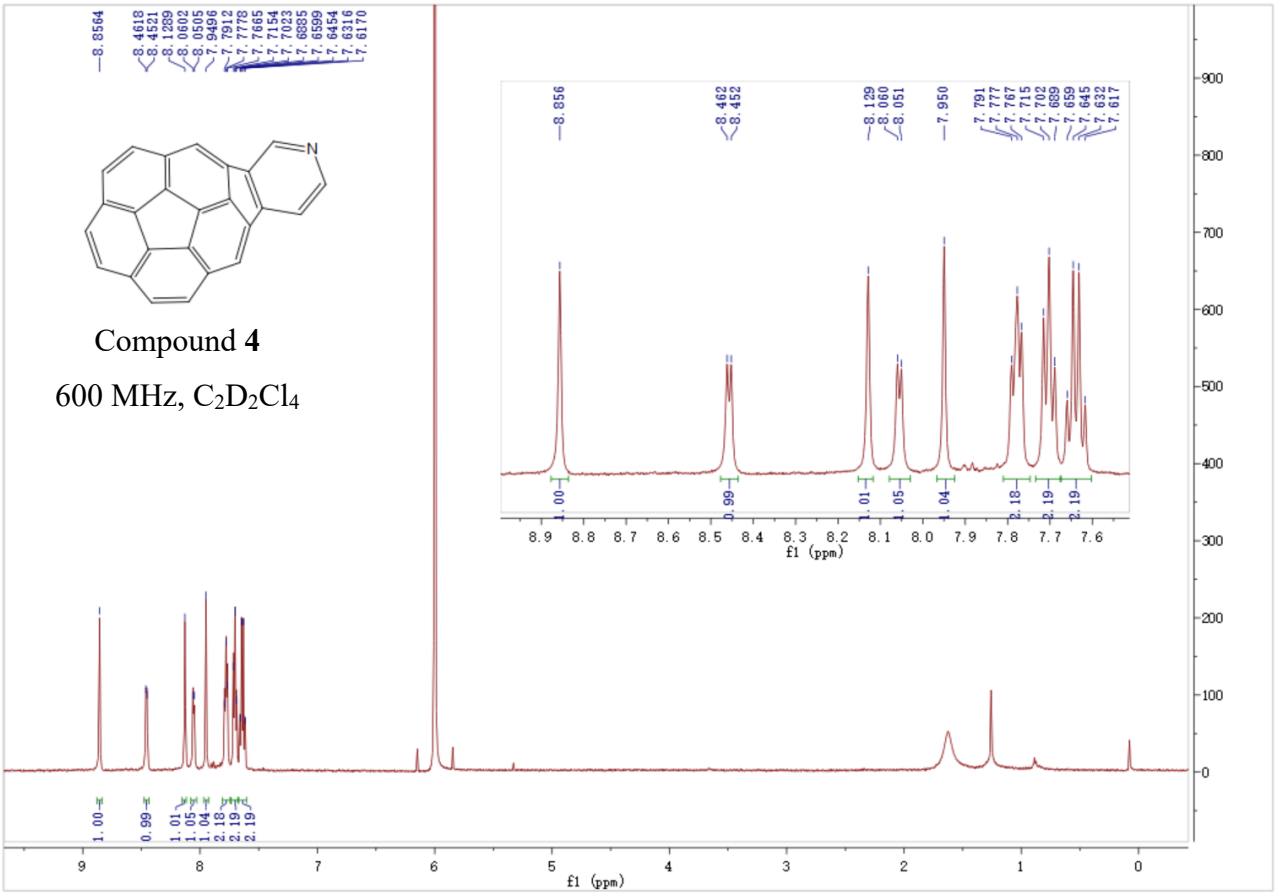
151 MHz, $CDCl_3$


Cl
N
Compound 5'
600 MHz, CDCl3
f1 (ppm)


Cl
N
Compound 5'
151 MHz, CDCl3
f1 (ppm)

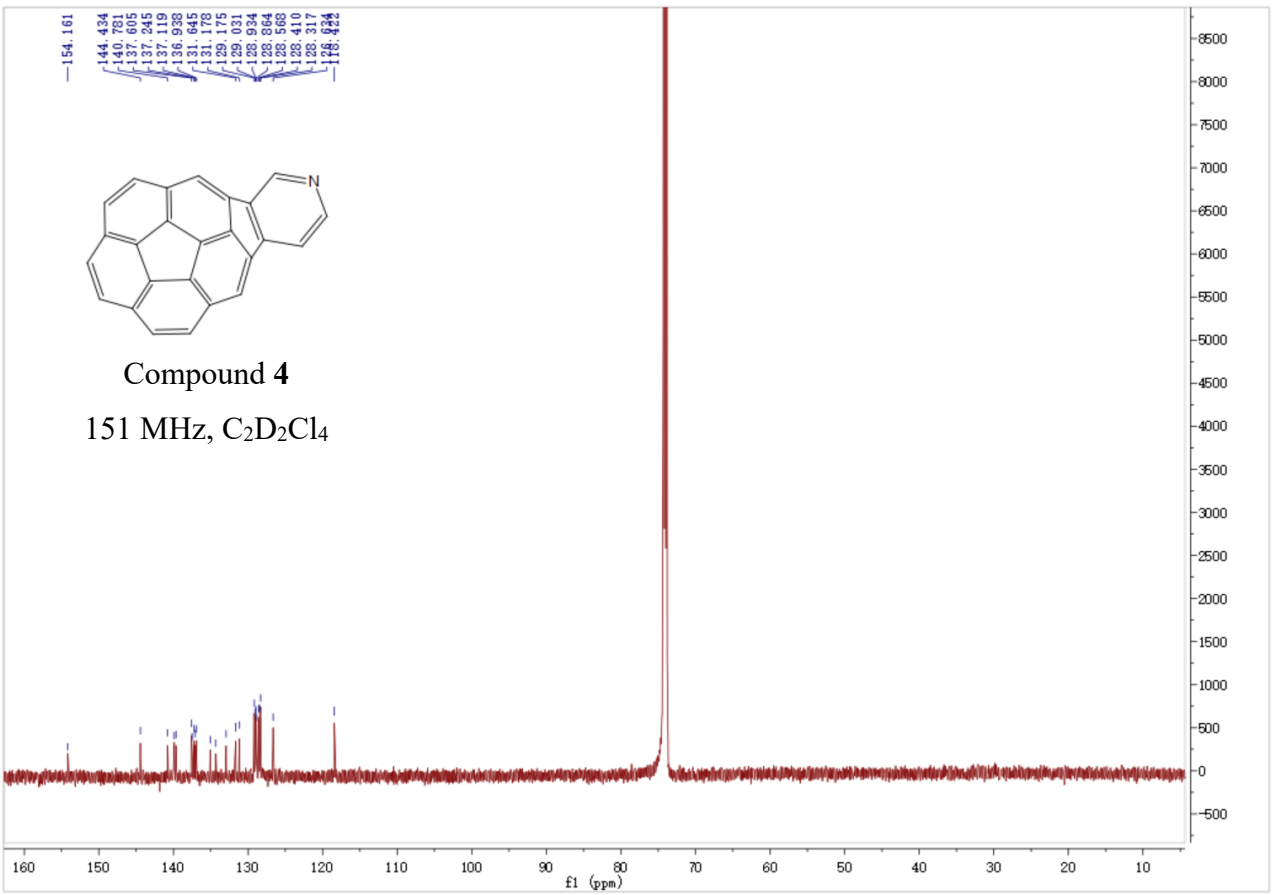

Compound 6'
600 MHz, CDCl3
f1 (ppm)


Compound 6'
151 MHz, CDCl3
f1 (ppm)



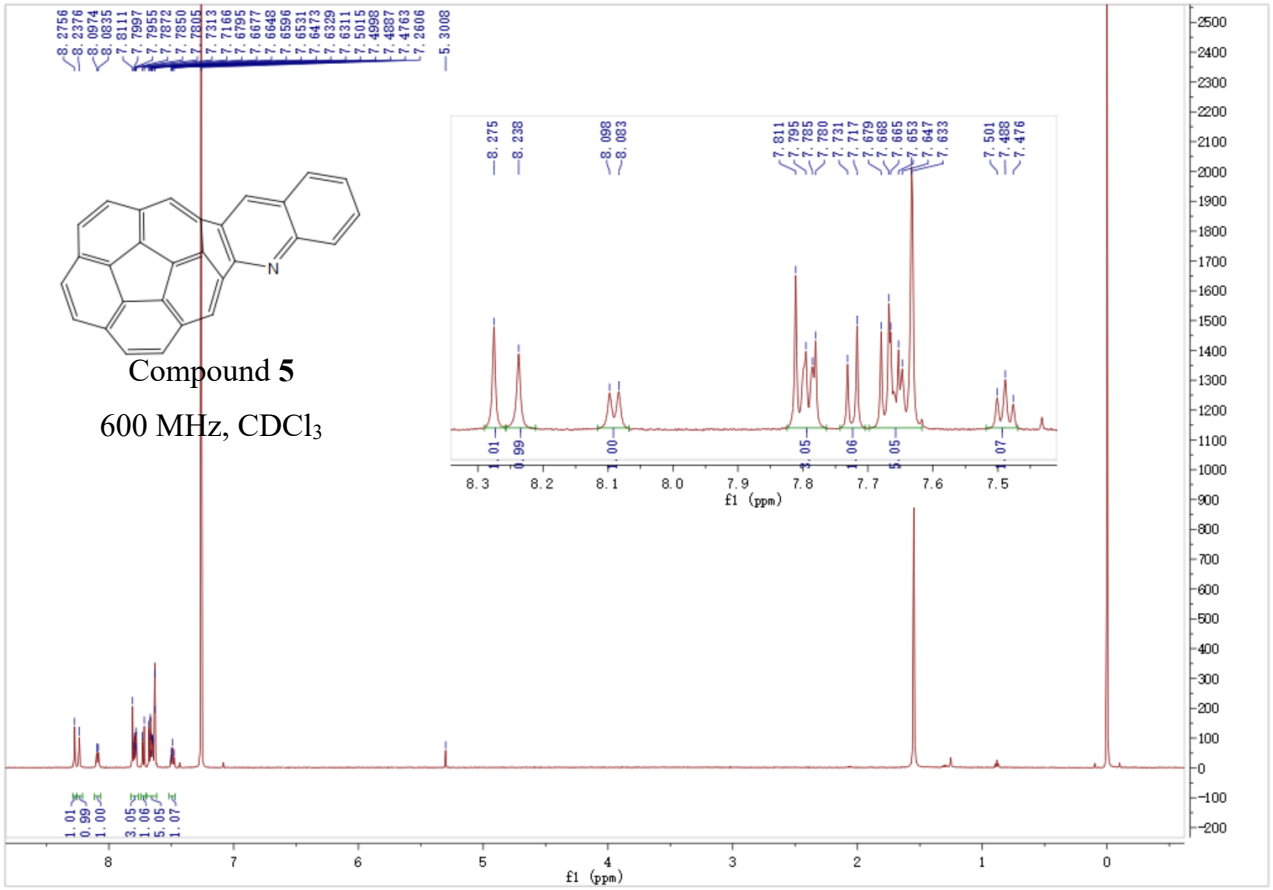
Compound **4**

600 MHz, $C_2D_2Cl_4$



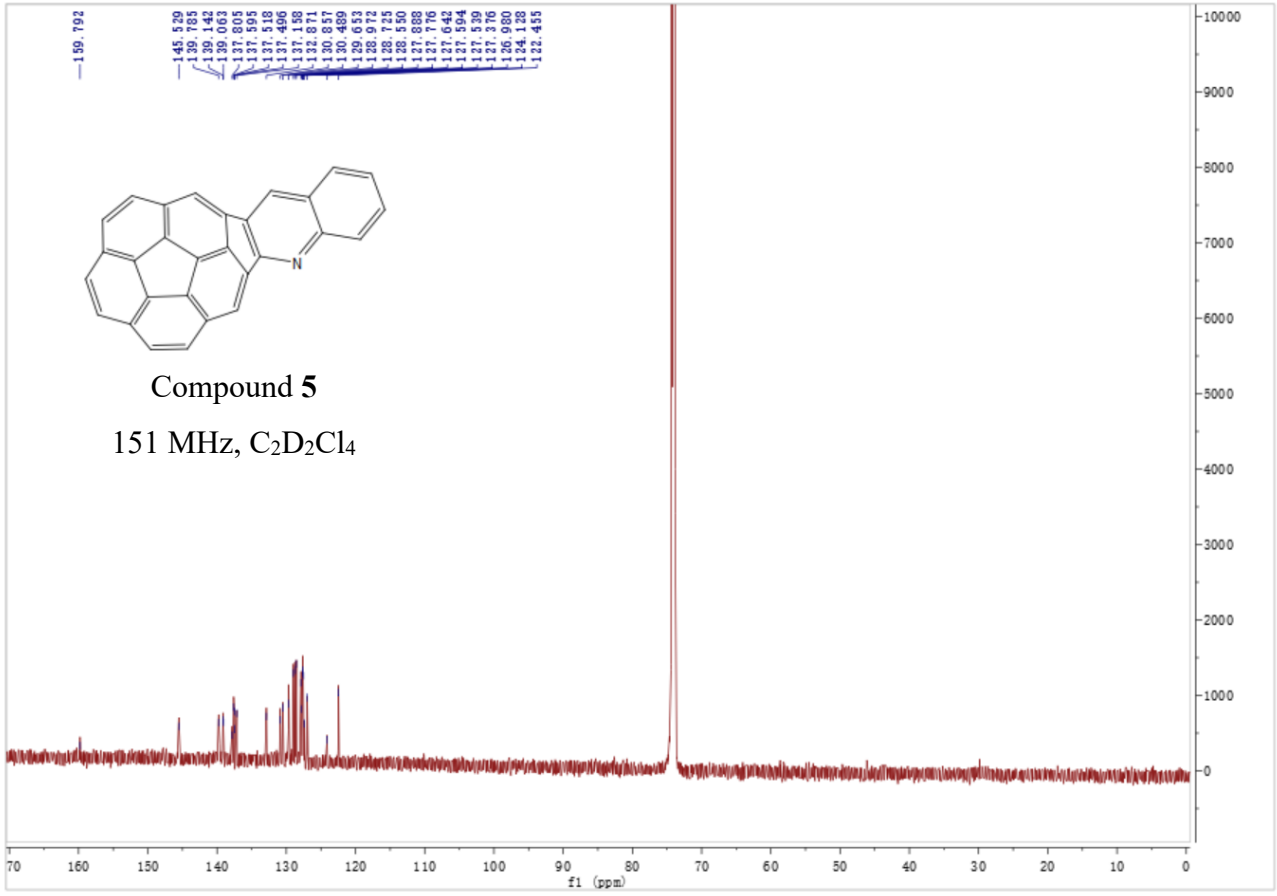
Compound **4**

151 MHz, $C_2D_2Cl_4$



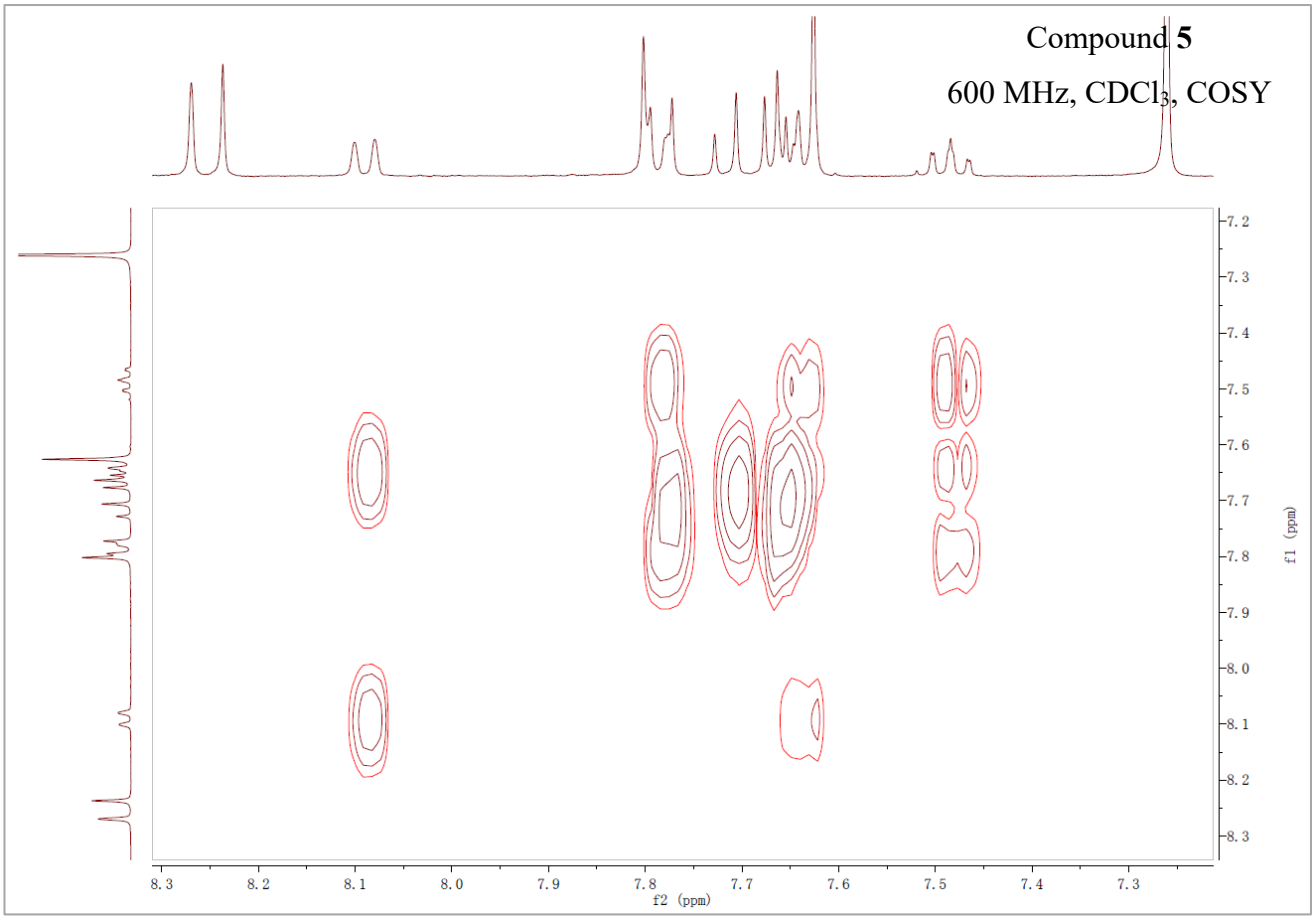
Compound **5**

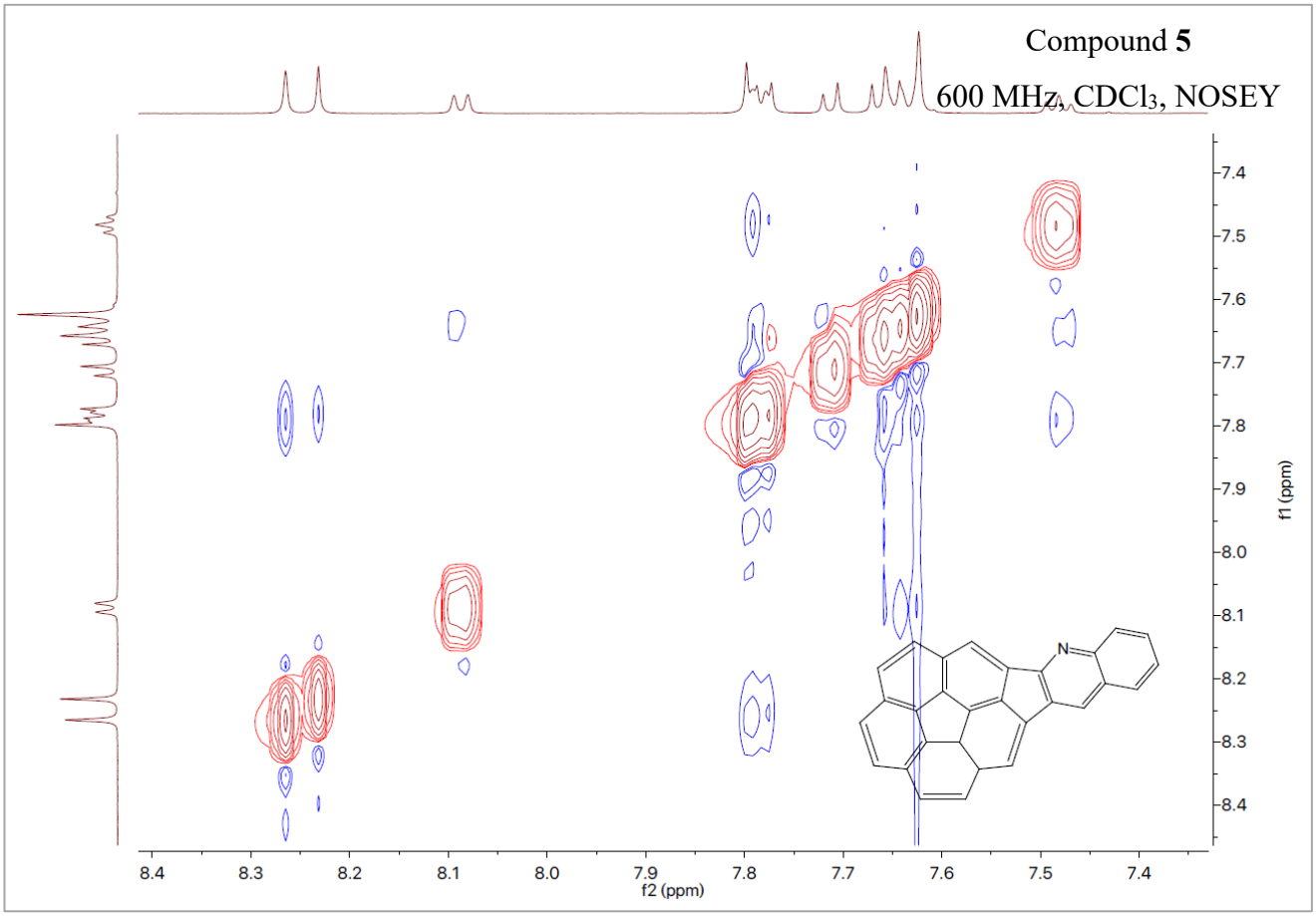
600 MHz, $CDCl_3$

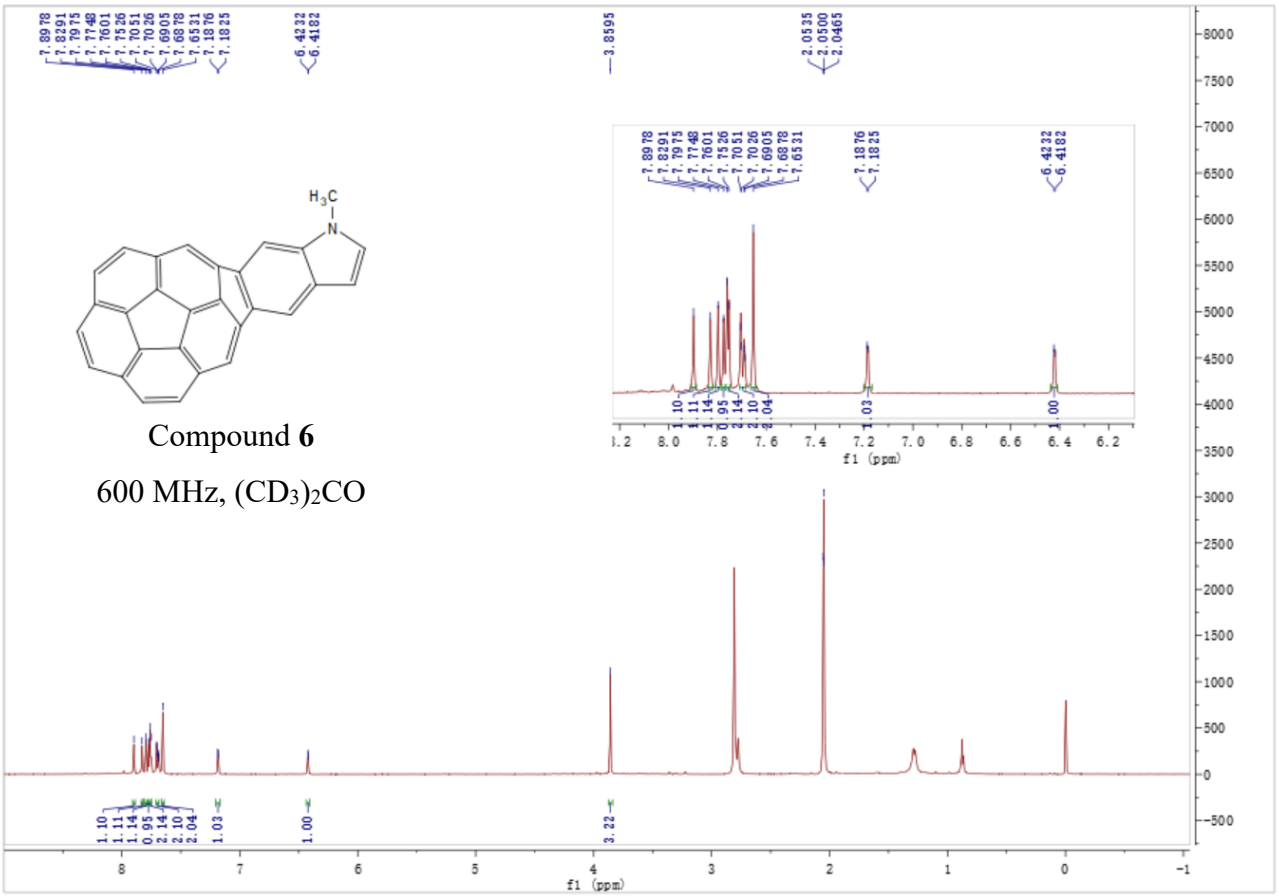


Compound **5**

151 MHz, $C_2D_2Cl_4$

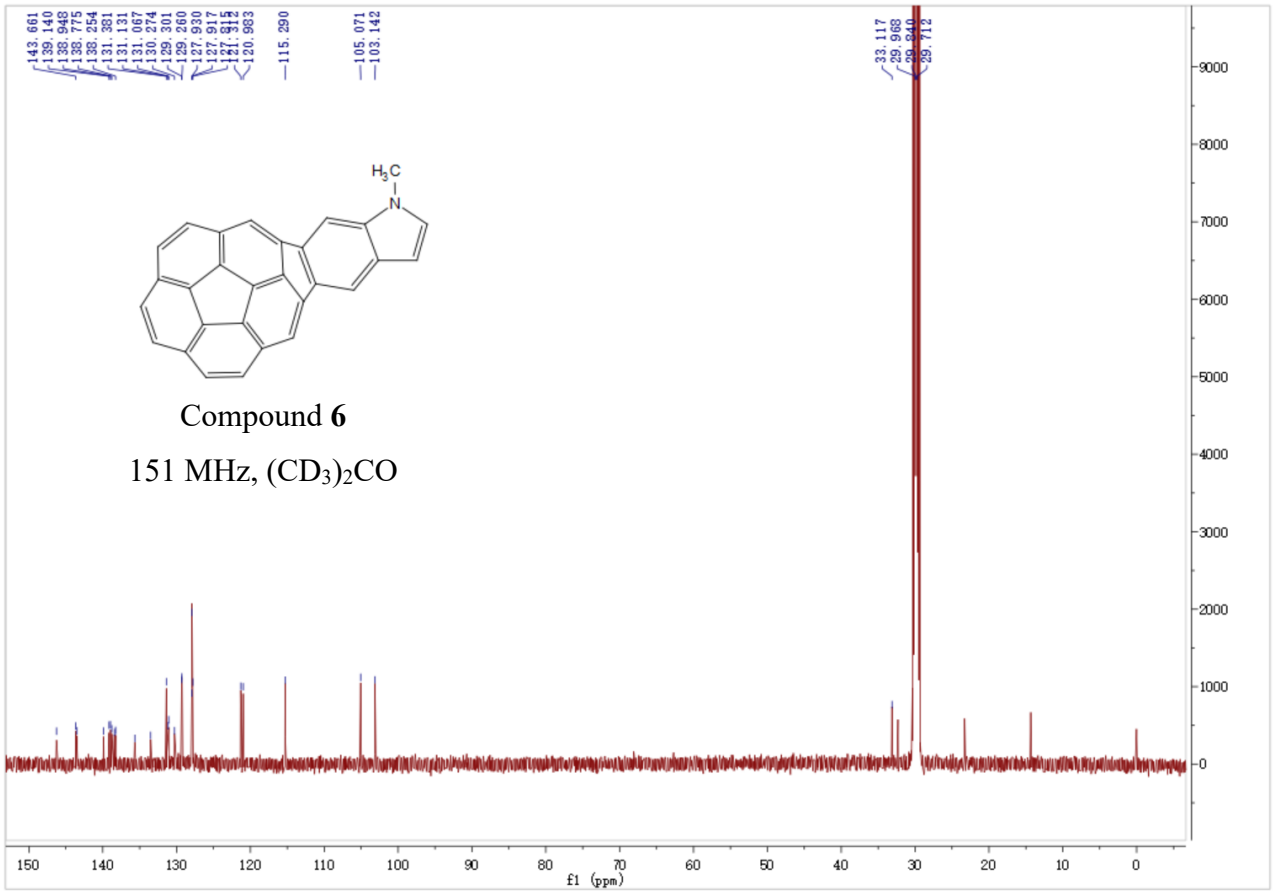

Compound 5
600 MHz, CDCl3, COSY
f2 (ppm)
f1 (ppm)


Compound 5
600 MHz, CDCl3, NOSEY
f2 (ppm)
f1 (ppm)
N



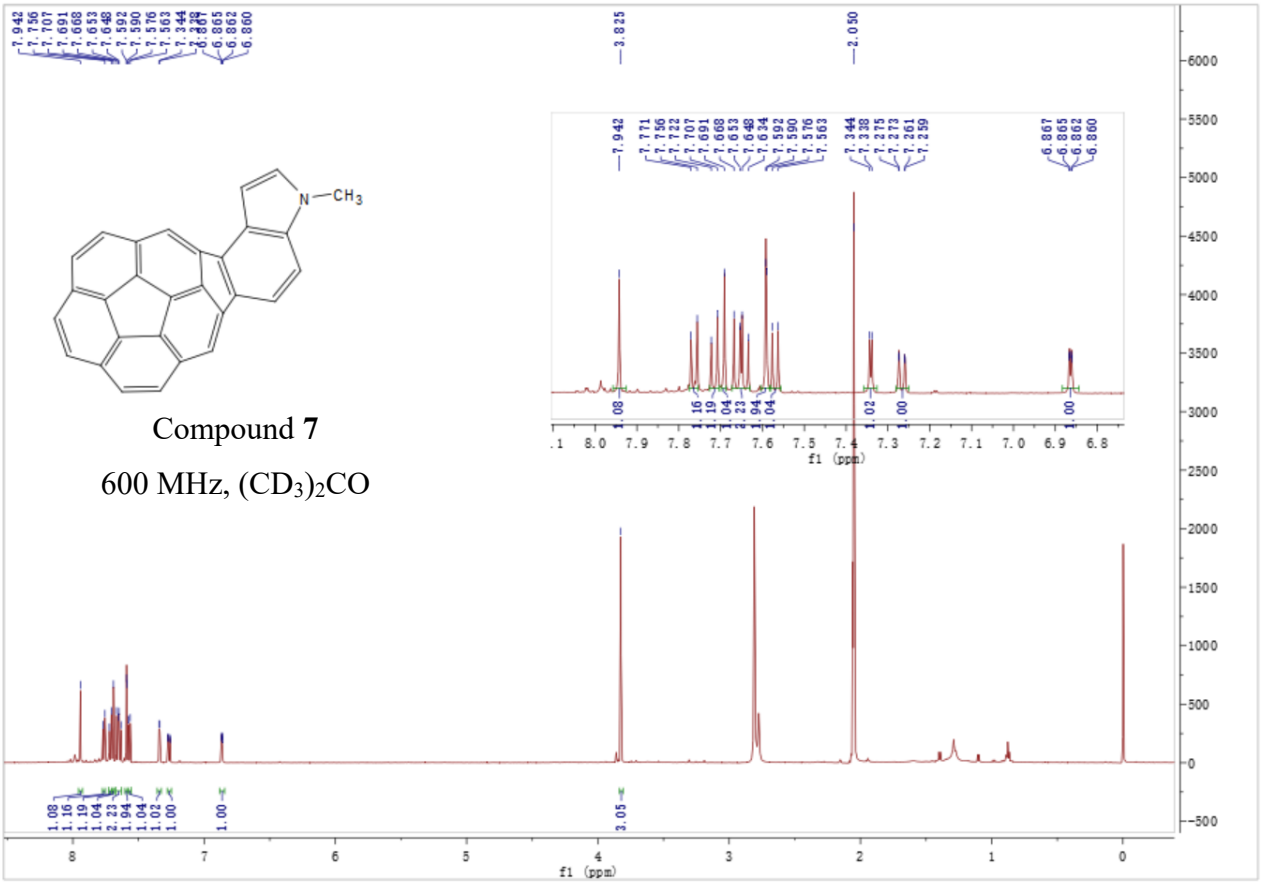
Compound **6**

600 MHz, $(CD_3)_2CO$



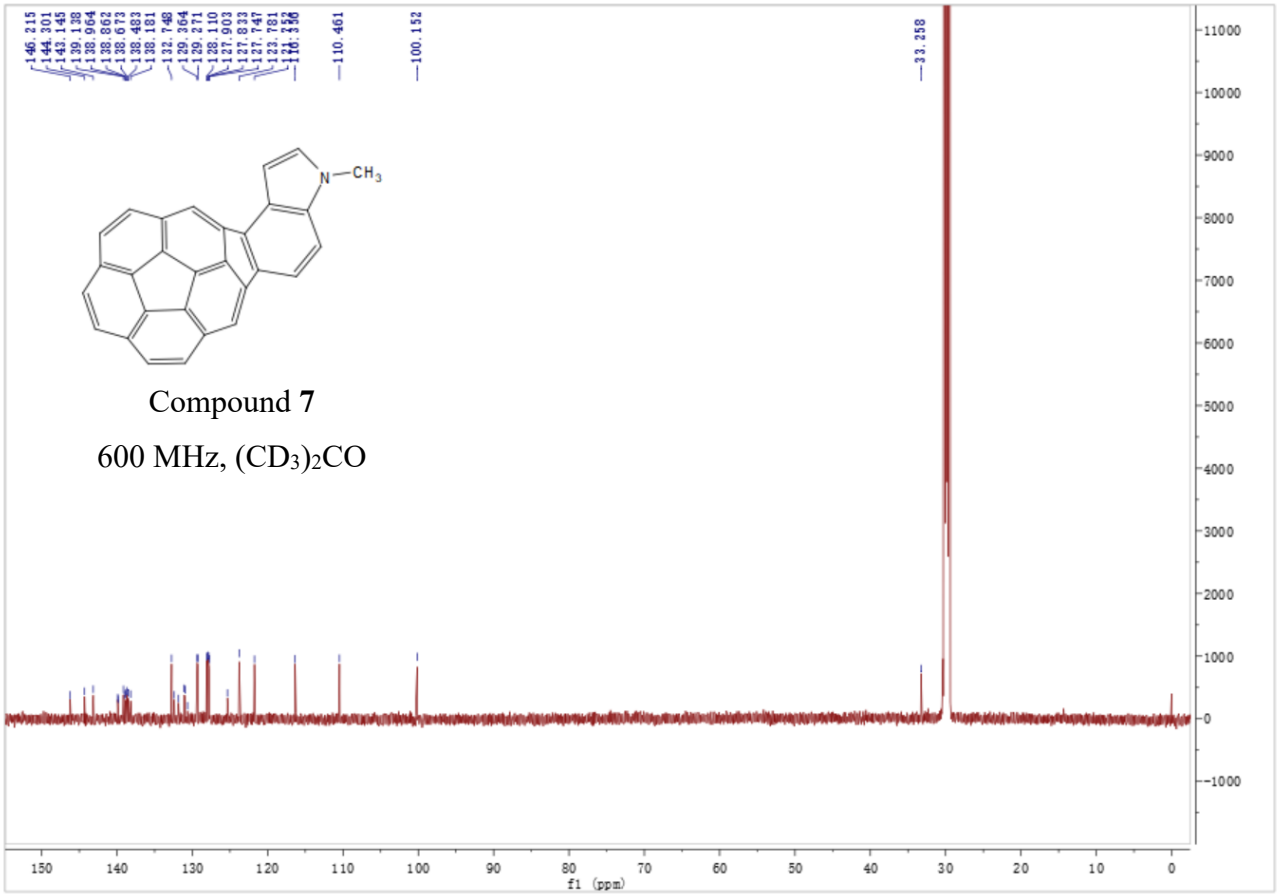
Compound **6**

151 MHz, $(CD_3)_2CO$



Compound **7**

600 MHz, $(CD_3)_2CO$



Compound **7**

600 MHz, $(CD_3)_2CO$