Supporting Information for

Facile synthesis of pyrrole-fused dibenzo[*a*,*e*]pentalene and application as a new extended, ladder-type fused aromatic system

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1. Materials and Methods:

^{1}H NMR and ^{13}C NMR spectra were recorded in deuterated solvents on a Bruker ADVANCE 400 NMR Spectrometer. ^{1}H NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. Mass spectra (MALDI-TOF-MS) were determined on a Bruker BIFLEX III Mass Spectrometer. Absorption spectra were measured with Hitachi (model U-3010) UV-Vis spectrophotometer in a 1-cm quartz cell. Cyclic voltammetry (CV) was performed with a Zahner IM6e electrochemical workstation using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode. 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) dissolved in CH_2Cl_2 was employed as the supporting electrolyte. The plot includes the signal of the ferrocene as an internal potential marker. CH_2Cl_2 was freshly distilled prior to use.
All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified.
The detailed device fabrication method: the transistors based on single-crystal microribbons of **9** were fabricated with "top contact" geometry. SiO_2/Si substrate was treated with octadecyltrichlorosilane (OTS). Single-crystal microribbons of 9 were grown by a simple slowly solvent evaporation process. A saturated solution of 9 in toluene was prepared and poured over the OTS-treated SiO_2/Si substrates directly. After the solvent evaporation, long, thin microribbons of 9 were obtained on the OTS-treated SiO_2/Si substrates. Au was used as the source and drain electrodes based on the fact that the HOMO level of compound 9 (5.3 eV) was very close to the work function of gold (5.1 eV) via "organic nanowires mask" technique.
The detailed method of "organic nanowires mask" technique: Firstly, Si/SiO_2/OTS substrates with patterned ribbons of 9 were prepared by slow solvent evaporation process. Then, an individual ribbon of the "H"-type anthracene derivative (see Ref. 1) was picked up by a mechanical probe and crossed over the patterned ribbon of 9 as an "organic ribbon mask". After that, gold source and drain electrodes were vacuum deposited on the crossed-ribbon structure. Finally, the "organic ribbon mask" was peeled off, and a device fabricated by this "organic ribbon mask" technique was obtained. [1]

2. Synthesis and characterization of compounds 5, 6, 7, 8, 9 and 10.

The starting material **4**[2] and 1-iodo-2-(phenylethynyl)benzene[3] were synthesized according to literature procedures.

Compound 5:

In an oven dried flask, sodium hydride (923 mg, 60% in mineral oil, 23.1 mmol) was added carefully to a solution of compound **4** (5.0 g, 15.4 mmol) in 40 ml anhydrous DMF under nitrogen. The solution was stirred at room temperature for half an hour. Then 2-ethylhexyl bromide (5.9 g, 30.6 mmol) was added dropwise and the reaction mixture was stirred over night at 90 °C. After cooling down, the reaction was quenched by adding 5 ml water dropwise and extracted with CH_2Cl_2. The organic phase was washed with water and dried over $MgSO_4$. After removal of the solvent, the residue was purified by silica gel chromatography (petroether) to afford compound **5** (6.3 g, 93.6%) as a white solid.
^{1}H NMR (400 MHz, 298 K, $CDCl_3$, ppm) δ= 7.89 (d, 2H), 7.50 (d, 2H), 7.34 (dd, 2H), 4.08-4.05 (m,

2H), 2.08-1.96 (m, 1H), 1.43-1.22 (m, 8H), 0.96-0.84 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ= 141.9, 122.6, 121.5, 121.3, 119.8, 112.4, 47.8, 39.3, 30.9, 28.7, 24.5, 23.2, 14.2, 11.0. MS (EI): m/z (M^+) = 437 (calcd for $C_{20}H_{23}Br_2N$: 437.0). HRMS (EI) m/z calcd for $C_{20}H_{23}Br_2N$ (M^+) = 437.0177, found 437.0175

Compound 6:

Compound **5** (6.3 g, 14.4 mmol) in AcOH (120 mL) was heated to 80 °C, and then KI (6.5 g, 39.2 mmol) and KIO_3 (4.1 g, 19.2 mmol) were added in one portion. The mixture was stirred at 80 °C for 6 h, and then poured into 10% sodium thiosulfate solution and extracted with CH_2Cl_2. The combined organic layers were washed with water and dried over $MgSO_4$. After removal of the solvent, the residue was purified by silica gel chromatography (petroether) to afford compound **6** (7.8 g, 78.6%) as a white solid.

^{1}H NMR (400 MHz, 298 K, CD_2Cl_2, ppm) δ= 8.49 (s, 2H), 7.72 (s, 2H), 4.08-3.99 (m, 2H), 2.02-1.93 (m, 1H), 1.39-1.20 (m, 8H), 0.93-0.83 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ= 141.6, 131.5, 126.8, 122.3, 113.4, 89.0, 47.9, 39.2, 30.8, 28.6, 24.4, 23.1, 14.2, 11.0. MS (EI): m/z (M^+) = 689 (calcd for $C_{20}H_{21}Br_2I_2N$: 688.8). HRMS (EI) m/z calcd for $C_{20}H_{21}Br_2I_2N$ (M^+) = 688.8110, found 688.8112.

Compound 7:

Compound **6** (7.6 g, 11.0 mmol), $Pd(PPh_3)_2Cl_2$ (155 mg, 0.22 mmol) and CuI (84 mg, 0.44 mmol) were added into a two necked flask in nitrogen atmosphere. Then Et_3N (50 mL) and THF (50 mL) were added by injection. After addition of phenylacetylene (2.4 g, 23.1 mmol) dropwise, the mixture was stirred at room temperature for 36 h. The reaction mixture was added into 200 ml saturated aqueous ammonium chloride and extracted with CH_2Cl_2. After removal of the solvent, the residue was purified by silica gel chromatography (dichloromethane: petroether =1:3) to afford compound **7** (6.3 g, 89.9%) as a white solid.

^{1}H NMR (400 MHz, 298 K, $CDCl_3$, ppm) δ= 8.20 (s, 2H), 7.65-7.59 (m, 6H), 7.40-7.26 (m, 6H), 4.07-4.04 (m, 2H), 2.06-1.94 (m, 1H), 1.43-1.22 (m, 8H), 0.96-0.85 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ= 141.5, 131.7, 128.5, 128.4, 125.0, 123.5, 121.4, 116.5, 113.4, 92.4, 89.1, 48.0, 39.3, 30.9, 28.6, 24.5, 23.1, 14.1, 11.0. MS (EI): m/z (M^+) = 637 (calcd for $C_{36}H_{31}Br_2N$: 637.1). HRMS (EI) m/z calcd for $C_{36}H_{31}Br_2N$ (M^+) = 637.0803, found 637.0792.

Compound 8

n-BuLi (1.6 M hexane solution, 8.8 ml, 14.1 mmol) was added dropwise into a solution of compound **7** (3.0 g, 4.7 mmol) in 30 ml of dry THF at -78 °C. The mixture was maintained at this temperature for 1h, and then I_2 (4.8 g, 18.9 mmol) in 10 ml dry THF was added dropwise. After warmed to room temperature for another 30 minutes, the mixture was poured into 10% sodium thiosulfate solution and extracted with CH_2Cl_2. After removal of the solvent, the residue was purified by silica gel chromatography (dichloromethane: petroether =1:3) to afford compound **8** (2.8 g, 81.5%) as a white solid.

^{1}H NMR (400 MHz, 298 K, CD_2Cl_2, ppm) δ= 8.25 (s, 2H), 7.93 (s, 2H), 7.65-7.63 (m, 4H), 7.41-7.39 (m, 6H), 4.09-4.08 (m, 2H), 2.02 (s, 1H), 1.43-1.21 (m, 8H), 0.97-0.82 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ= 141.3, 131.6, 128.5, 128.4, 124.2, 123.6, 122.2, 120.5, 119.7, 98.5, 92.6, 91.6, 47.9, 39.3, 30.8, 28.6, 24.5, 23.1, 14.2, 11.0. MS (EI): m/z (M^+) = 731 (calcd for $C_{36}H_{31}I_2N$: 731.1). HRMS (EI) m/z calcd for $C_{36}H_{31}I_2N$ (M^+) = 731.0546, found. 731.0535

Compound 9 and 10:

For this reaction, 50 mL heavy-walled pressure vessels were used. A 50 mL oven dried glass

pressure vessel was equipped with a teflon-coated magnetic stirring bar and was purged with dry nitrogen. The vessel was then charged with hydroquinone (1.2 g, 10.9 mmol), Cs_2CO_3 (3.6 g, 11.0 mmol), CsF (1.8 g, 11.8 mmol), P^tBu_3 (10 wt% in hexane, 663 mg, 0.3 mmol), $Pd_2(dba)_3$ (75.2 mg, 0.08 mmol), compound **8** (2.0 g, 2.7 mmol) and 1-iodo-2-(phenylethynyl)benzene (3.3 g, 10.9 mmol), After adding 15 ml dry 1,4-dioxane by injection , the vessel was sealed and immediately heated to 140 °C. During the reaction a dark red solution formed. After heating for 30 h, the mixture was removed from the oil bath, cooled, opened to the air, and immediately diluted with 100 ml CH_2Cl_2. The combined organic layers were washed with water and dried over $MgSO_4$. After removal of the solvent, the residue was purified by silica gel chromatography (gradient elution from pure petroether to petroether: CH_2Cl_2=1:2) to afford the pure sample of compound **1** (98.0 mg, 5.1%, calculated from 1-iodo-2-(phenylethynyl)benzene) as a brown solid, the crud product of compound **9** as a red solid. The pure sample of compound **9** (272.2 mg, 12.0%, calculated from compound **8**) was obtained by recrystallization from the mixture solvent of CH_2Cl_2 and n-hexane. And trace of compound **10** as a dark red solid was also obtained in this reaction.

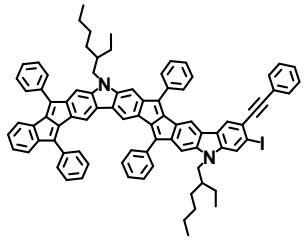


Figure S1. The chemical structure of compound **10**.

Compound 1

Spectroscopic data match those previously reported.[4]

^{1}H NMR (400 MHz, $CDCl_3$, 298K, ppm) δ= 7.67 (d, 4H), 7.52 (t, 4H), 7.45 (t, 2H), 7.21 (d, 2H), 7.03 (d, 2H), 6.91 (t, 2H), 6.85 (t, 2H).^{13}C NMR (101 MHz, $CDCl_3$, 298K, ppm) δ= 149.8, 143.3, 140.8, 135.3, 134.0, 128.9, 128.8, 128.7, 127.9, 127.6, 122.6, 122.1. MS (EI): m/z (M^+) = 354 (calcd for $C_{28}H_{18}$: 354.1). HRMS (EI) m/z calcd for $C_{28}H_{18}$ (M^+) = 354.1409, found. 354.1412

Compound 9

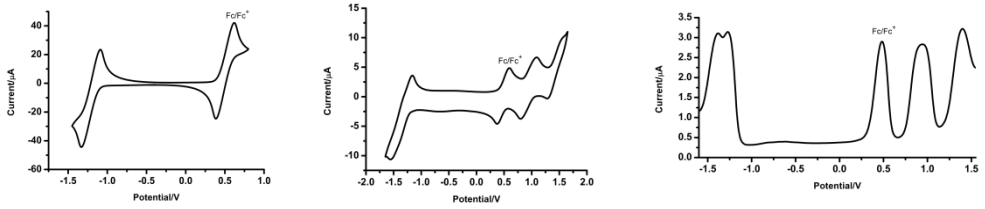
^{1}H NMR (400 MHz, 298 K, C_6D_6:CS_2 (V/V=2:3), ppm) δ = 7.66-7.56 (m, 10H), 7.36-7.32 (m, 10H), 7.25 (t, 2H), 7.10 (d, 2H), 6.92 (d, 2H), 6.78-6.70 (m, 4H), 6.64 (t, 2H), 3.62- 3.51 (m, 2H), 1.70 (m, 1H), 1.21-1.03 (m, 8H), 0.87-0.72 (m, 6H). ^{13}C NMR (100 MHz, 298 K, C_6D_6:CS_2 (V/V=2:3), ppm) δ = 150.7, 148.6, 145.4, 143.7, 141.7, 141.4, 137.7, 135.6, 135.0, 134.8, 129.1, 129.03, 128.99, 128.95, 128.5, 128.2, 128.0, 127.1, 123.1, 122.4, 122.3, 114.4, 105.4, 46.7, 40.1, 31.5, 29.3, 24.9, 23.6, 14.5, 11.2.MS (MALDI-TOF): m/z (M^+) = 831.6 (calcd for $C_{64}H_{49}N$: 831.4). HRMS (MALDI-TOF): m/z calcd for $C_{64}H_{49}N$ $[M]^+$: 831.3865, found. 831.3869

Compound 10

^{1}H NMR (400 MHz, 298 K, CD_2Cl_2:CS_2 (V/V=2:3), ppm) δ = 7.90 (s, 1H), 7.82-7.69 (m, 8H), 7.69-7.43 (m, 18H), 7.37-7.35 (m, 3H), 7.12 (d, 1H), 6.98 (d, 1H), 6.94 (s, 1H), 6.87 (t, 1H), 6.81-6.73 (m, 3H), 3.99 (m, 2H), 3.85 (m, 2H), 1.95 (m, 1H), 1.84 (m 1H), 1.42-1.22 (m, 16H), 0.99-0.87 (m, 12H).^{13}C NMR (100 MHz, 298 K, C_6D_6:CS_2 (V/V=2:3), ppm) δ = 150.7, 150.6, 149.2, 148.3, 146.1, 145.1, 144.7, 143.7, 142.0, 141.8, 141.7, 141.6, 141.4, 138.8, 137.5, 137.2, 135.5, 135.0, 134.9, 134.6, 131.8, 129.2, 129.1, 129.1, 129.01, 128.96, 128.6, 127.1, 124.4, 124.0, 123.9, 123.0, 122.5, 122.3,

122.2, 120.6, 120.4, 119.6, 114.7, 114.4, 114.2, 105.4, 104.8, 104.4, 97.3, 94.0, 91.8, 47.3, 46.8, 40.2, 39.9, 31.6, 31.5, 29.5, 29.2, 25.0, 23.73, 23.71, 14.63, 14.60, 11.34, 11.31.MS (MALDI-TOF): m/z (M^+) = 1258.1 (calcd for $C_{86}H_{71}IN_2$: 1258.5). HRMS (MALDI-TOF): m/z calcd for $C_{86}H_{71}IN_2$ $[M]^+$: 1258.4662, found 1258.4625.

3. Cyclic voltammograms



CV of **1** CV of **9** DPV of **9**

Figure S2. Cyclic voltammograms of **1** and **9,** and the DPV plot of **9** (vs Ag/AgCl).

4. The TGA plot of **9**

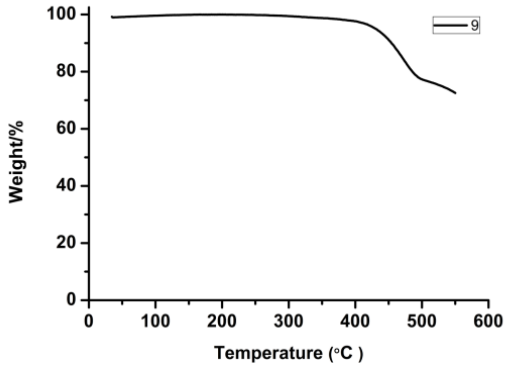


Figure S3. The TGA plot of **9.**

5. The OM image of single crystal microribbons of **9**

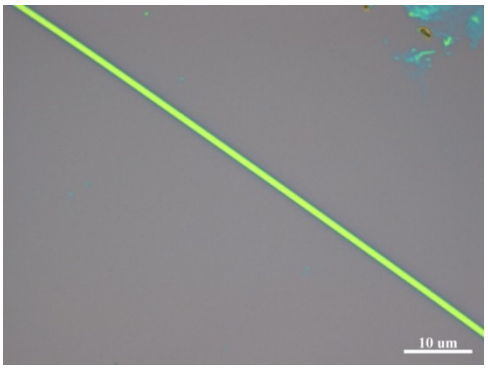


Figure S4. The OM image of single crystal microribbon of **9**

6. The physical properties of **1** and **9** investigated by DFT calculations

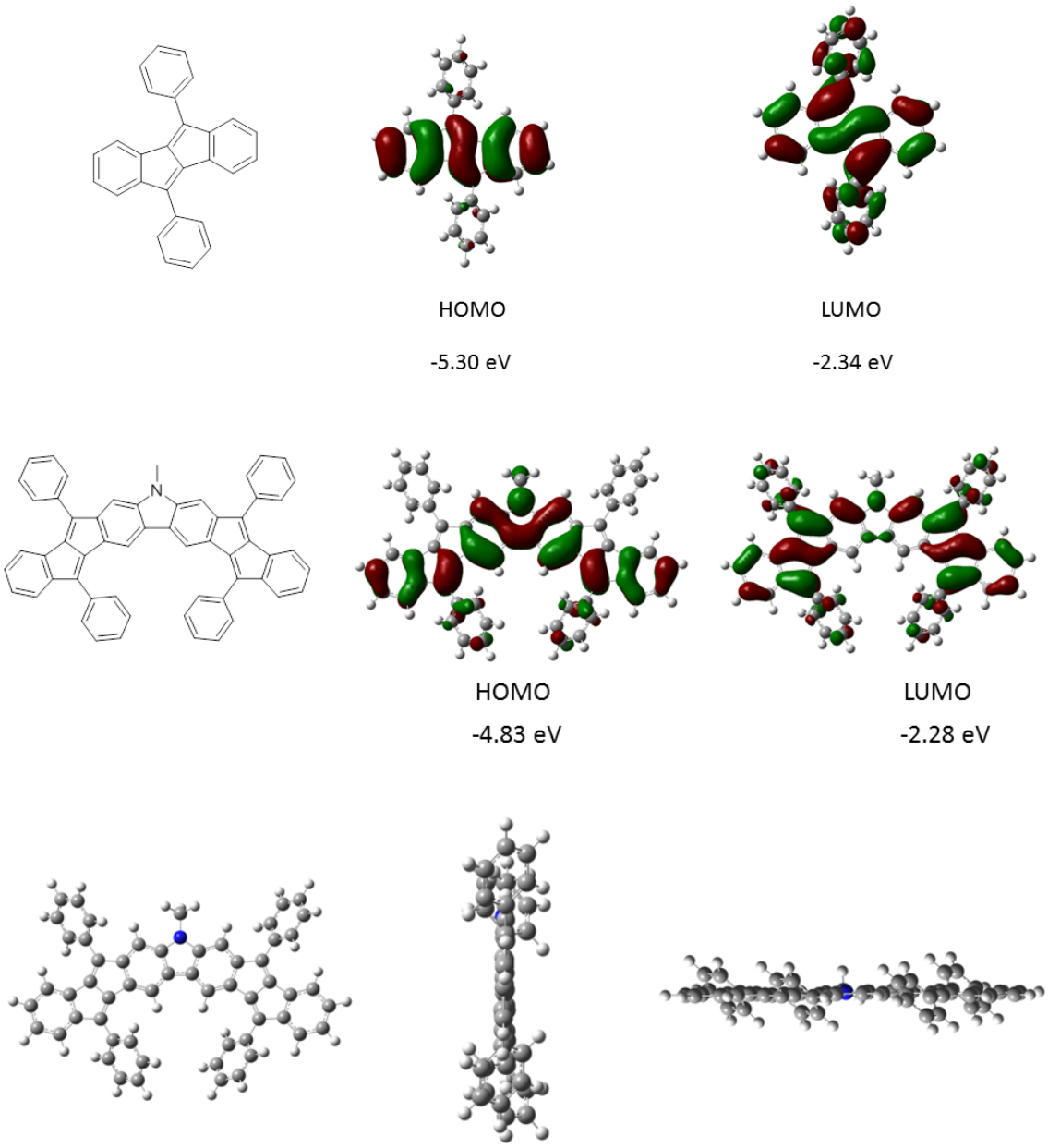


Figure S5. Energies and shapes of B3LYP/6-31G* frontier orbitals (HOMOs and LUMOs) of model **1** and **9**, and the DFT models of **9**.

References:

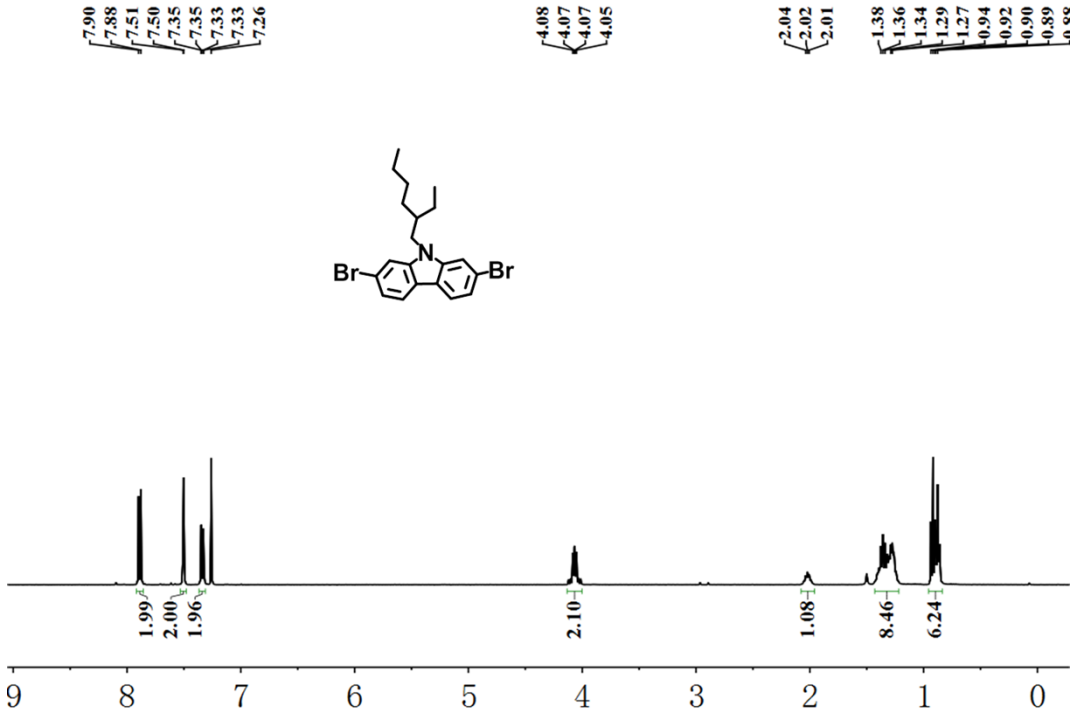
(1) Jiang, L.; Gao, J.; Wang, E.; Li, H.; Wang, Z.; Hu, W.; Jiang, L. *Adv. Mater.* **2008**, *20*, 2735-2740.

(2) Jiang, W.; Duan, L.; Qiao, J.; Dong, G.; Zhang, D.; Wang, L.; Qiu, Y. *J. Mater. Chem.* **2011**, *21*, 4918-4926.

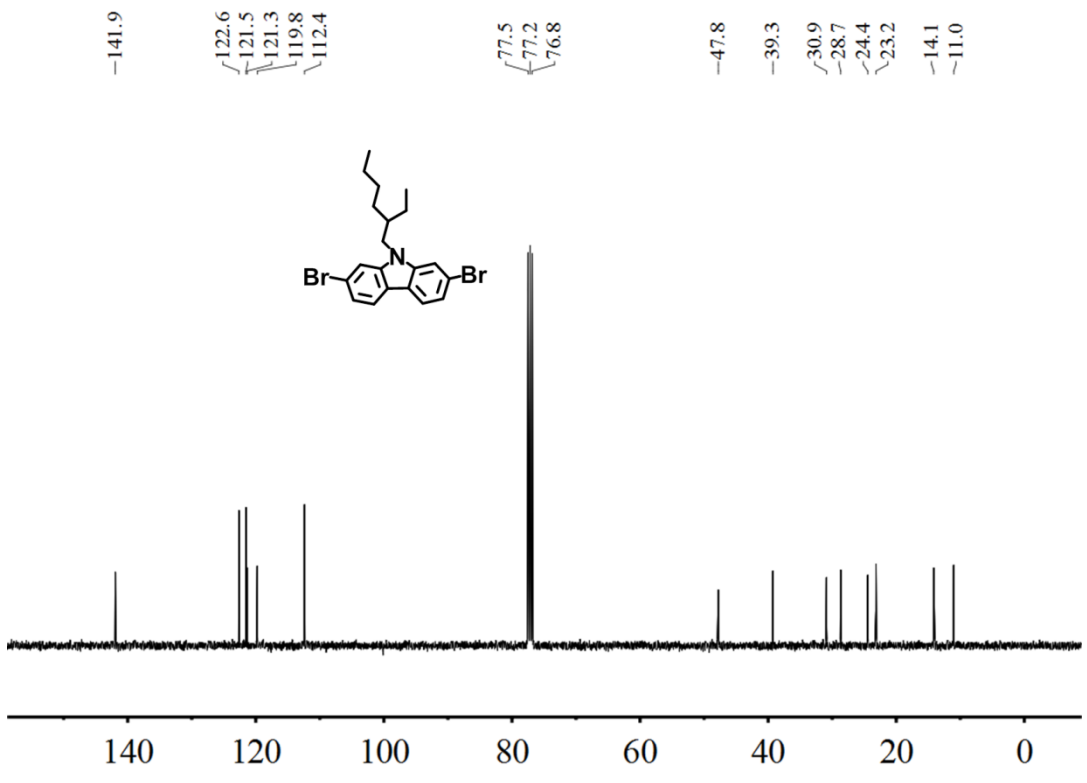
(3) Verma, A. K.; Kesharwani, T.; Singh, J.; Tandon, V.; Larock, R. C. *Angew. Chem., Int. Ed.* **2009**, *48*, 1138-1143.

(4) Levi, Z. U.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 2796-2797.

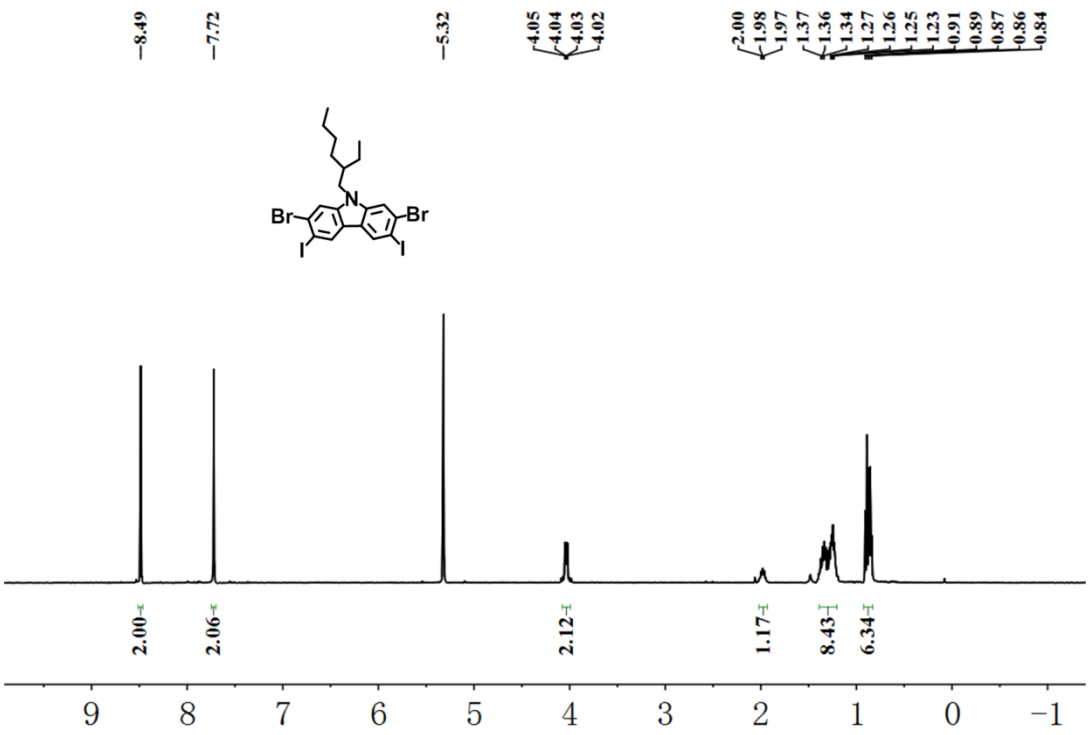
^{1}H NMR spectrum of **5** in $CDCl_3$



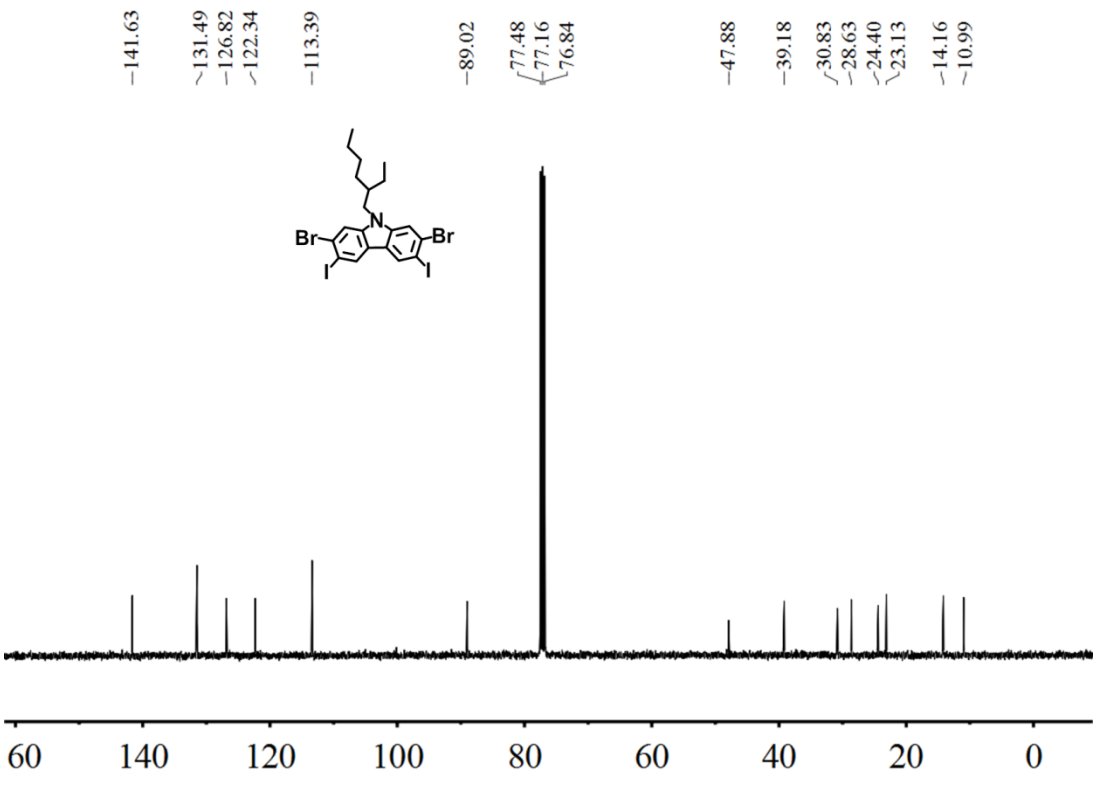
^{13}C NMR spectrum of **5** in $CDCl_3$



^{1}H NMR spectrum of **6** in CD_2Cl_2



^{13}C NMR spectrum of **6** in $CDCl_3$



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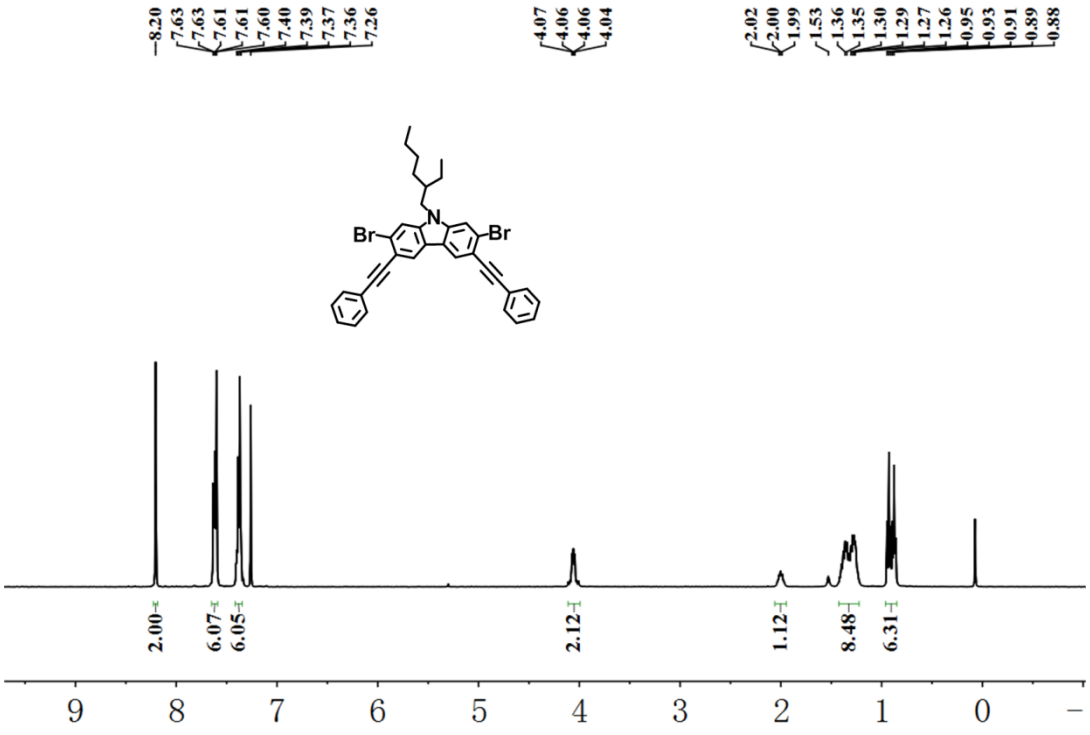
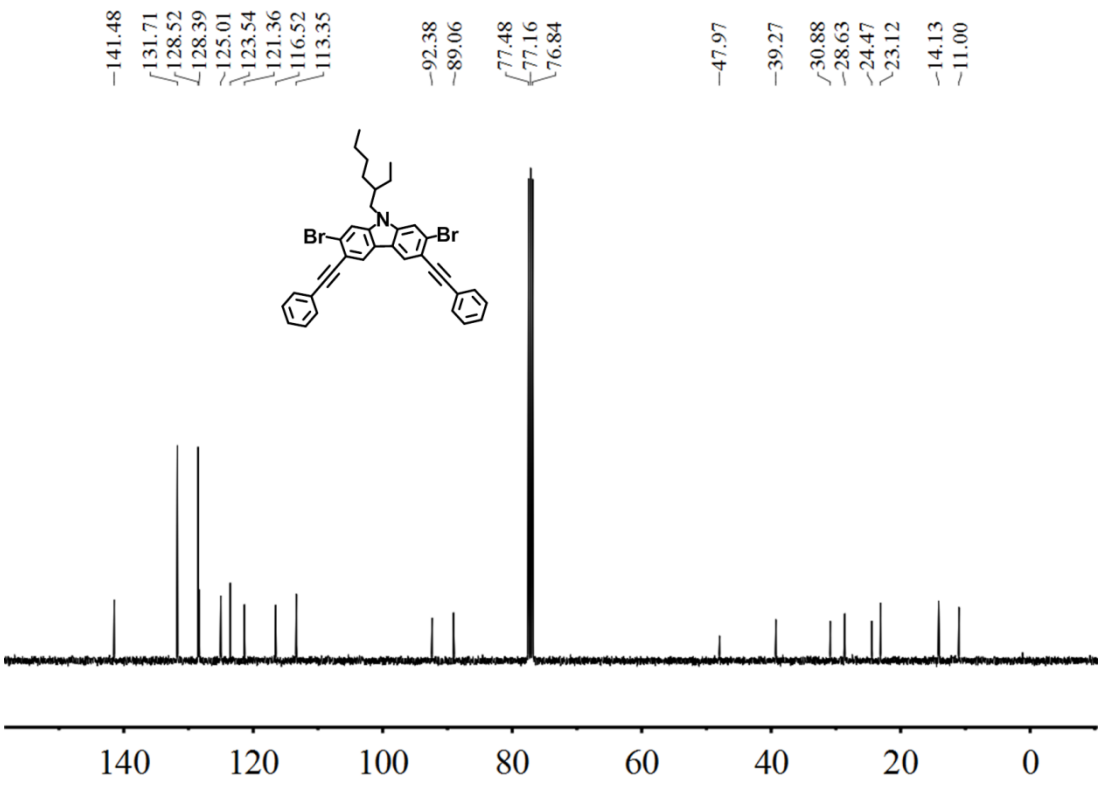
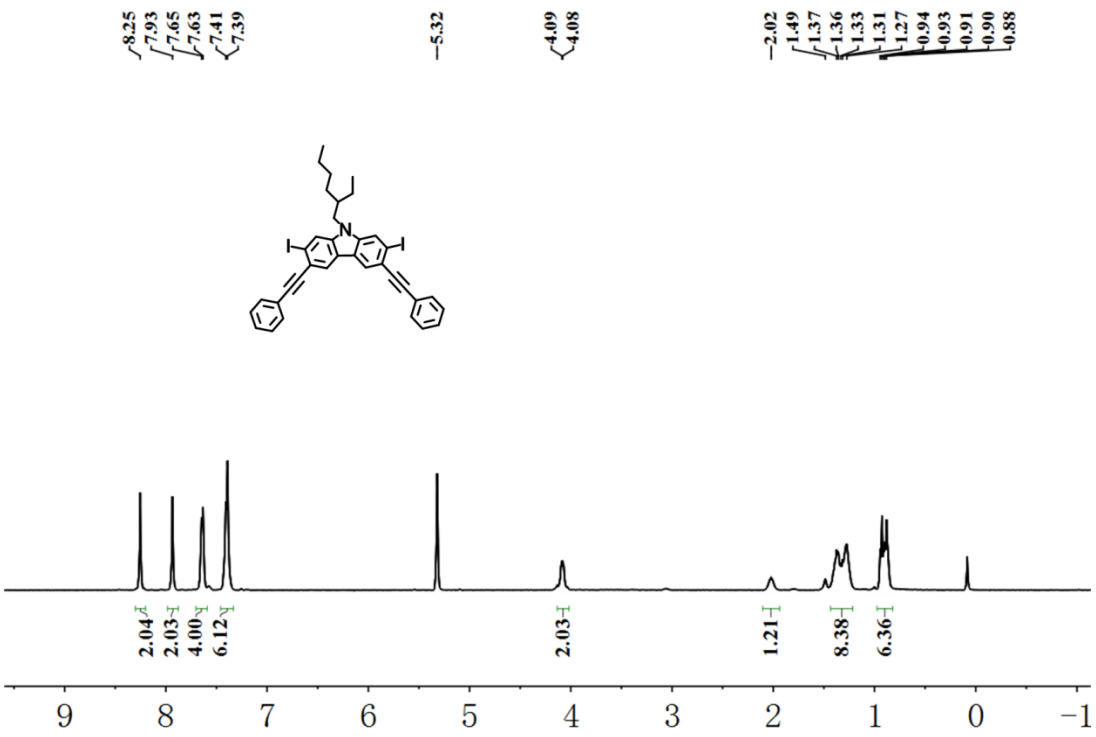


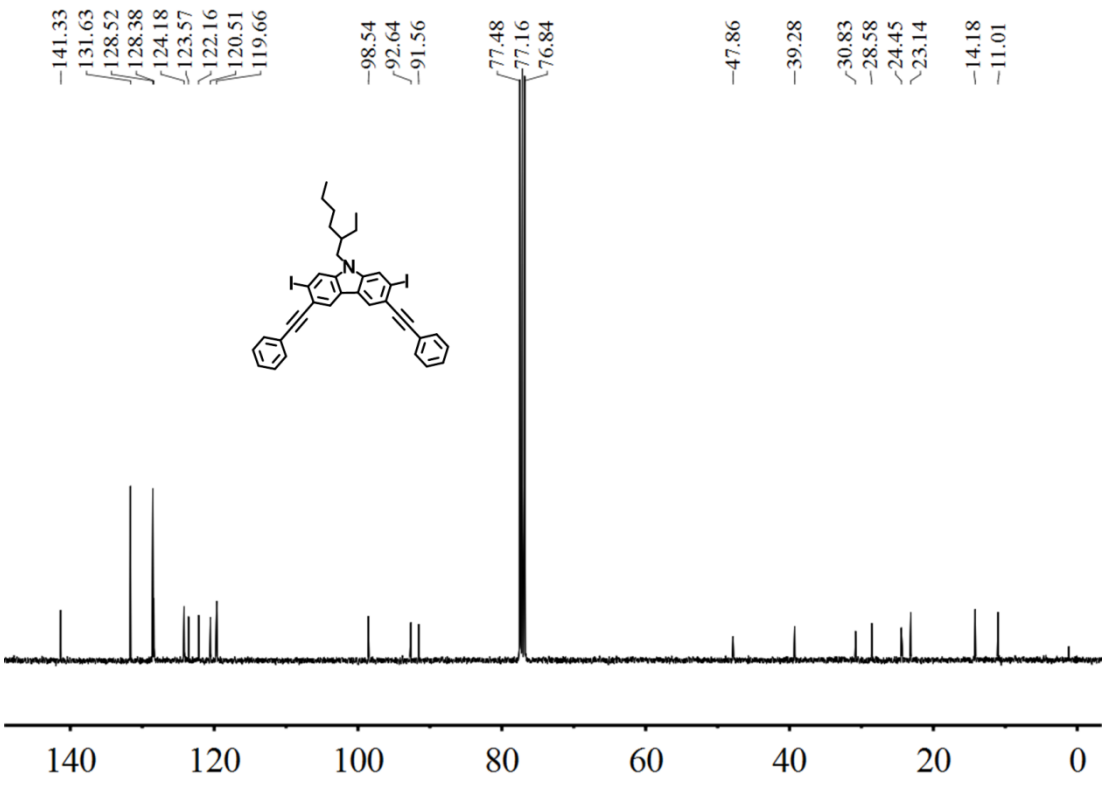
^{13}C NMR spectrum of **7** in $CDCl_3$



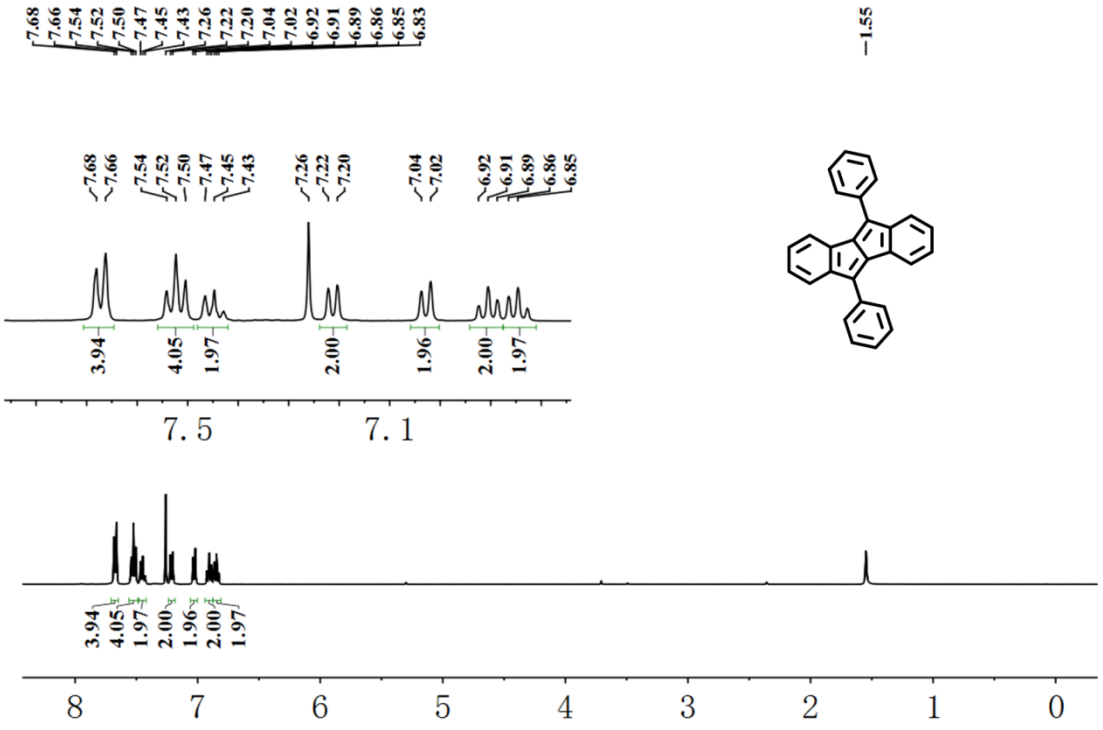
^{1}H NMR spectrum of **8** in CD_2Cl_2



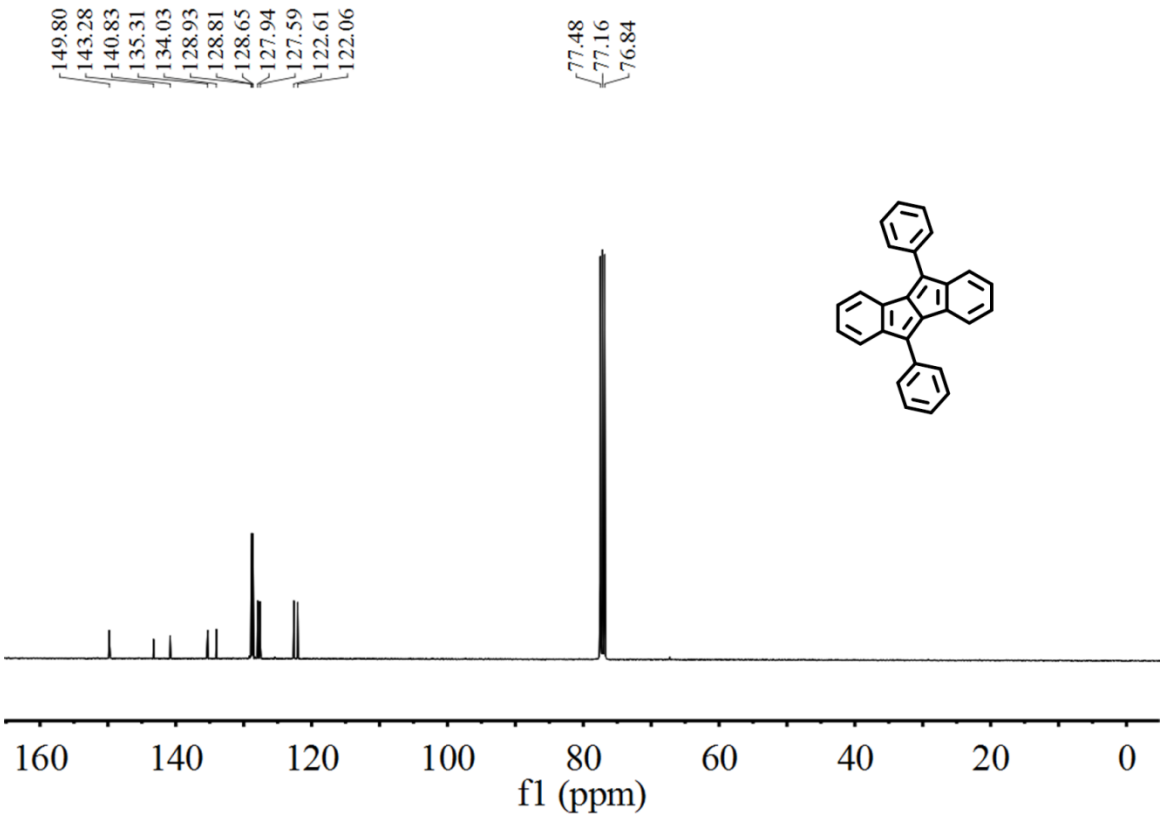
^{13}C NMR spectrum of **8** in $CDCl_3$



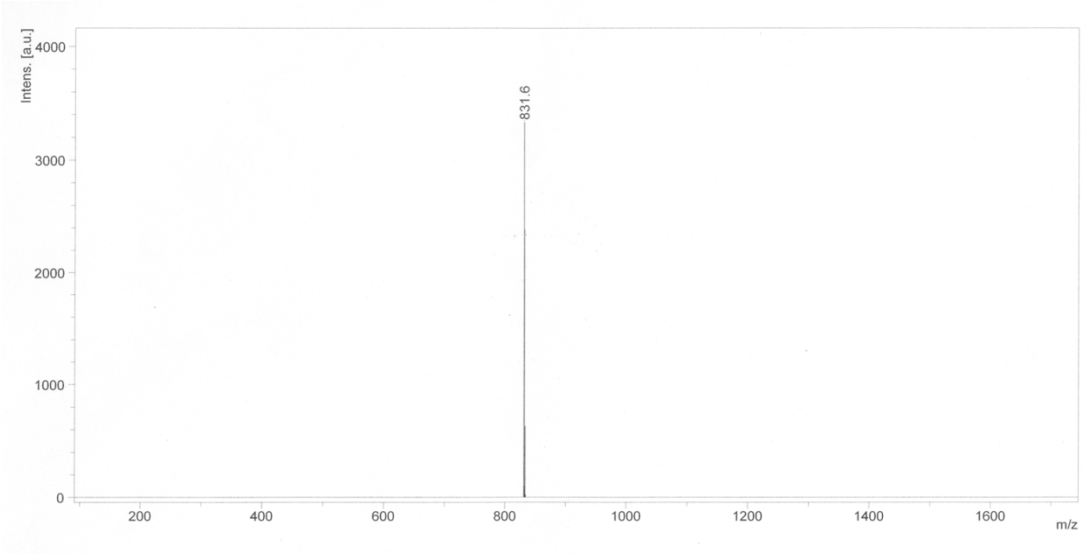
^{1}H NMR spectrum of **1** in $CDCl_3$

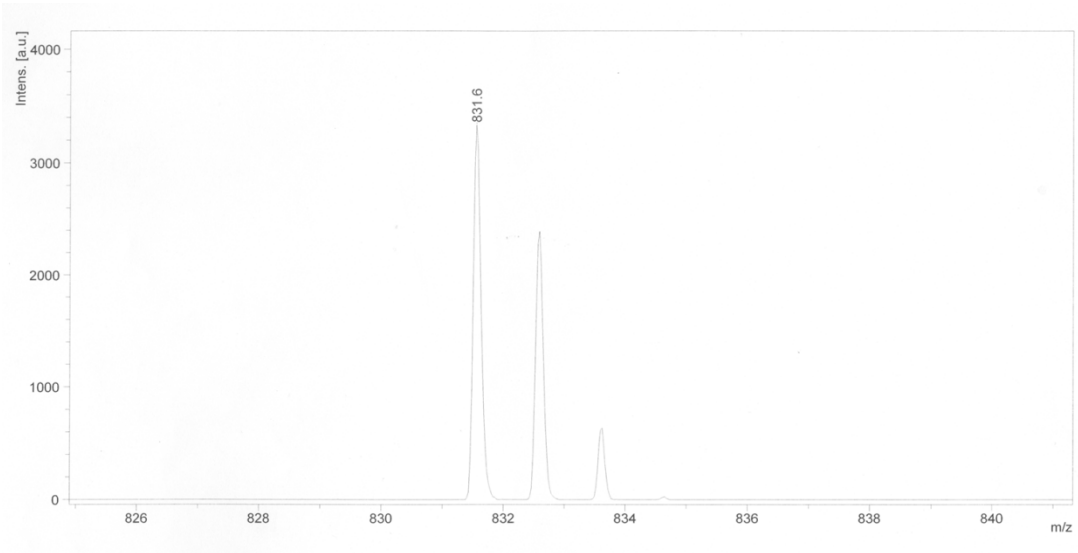


^{13}C NMR spectrum of **1** in $CDCl_3$

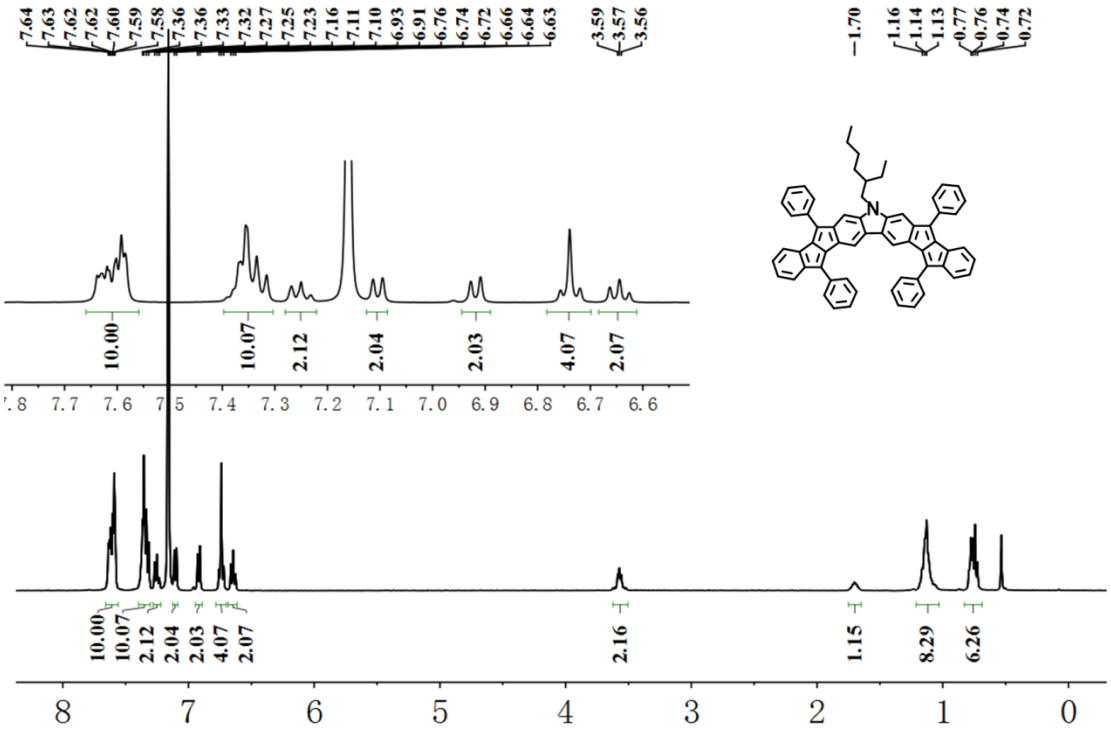


MALDI-TOF mass spectrum of **9**

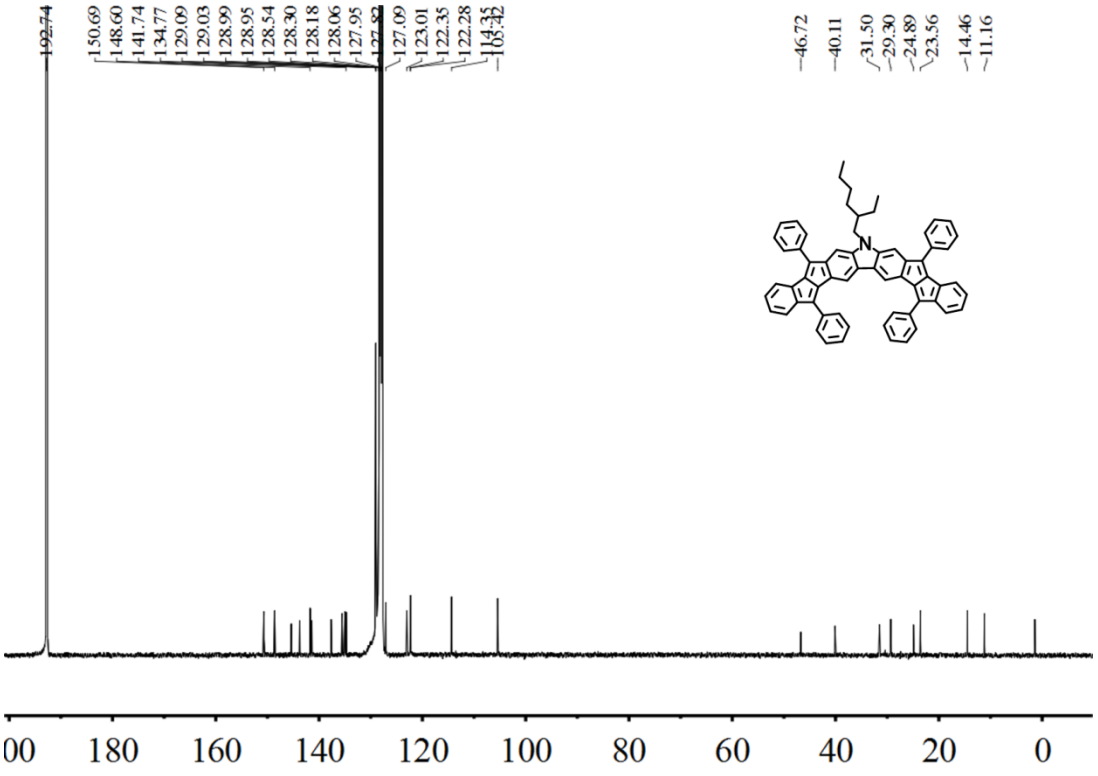




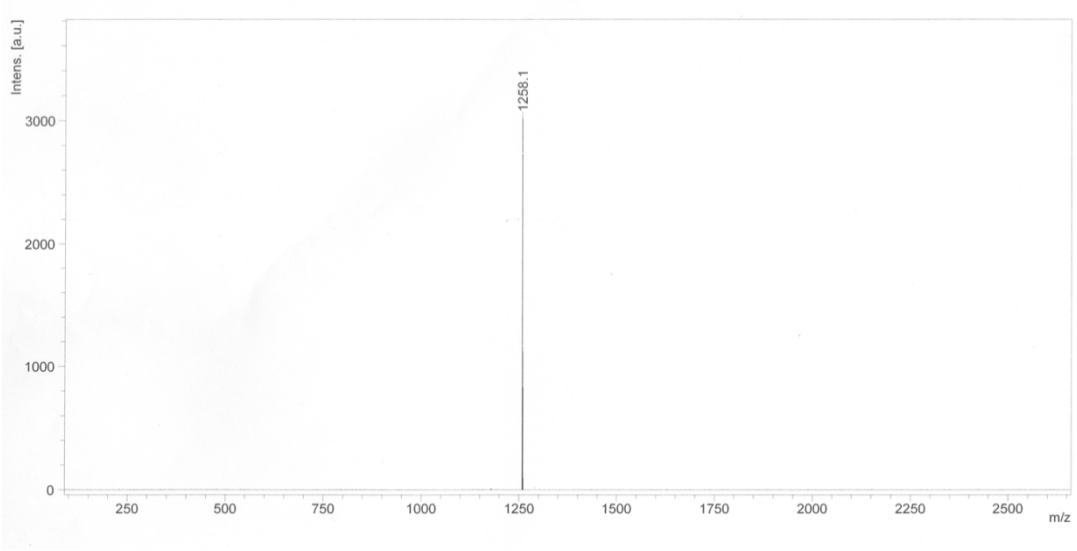
^{1}H NMR spectrum of **9** in C_6D_6/CS_2 (V/V=2:3)

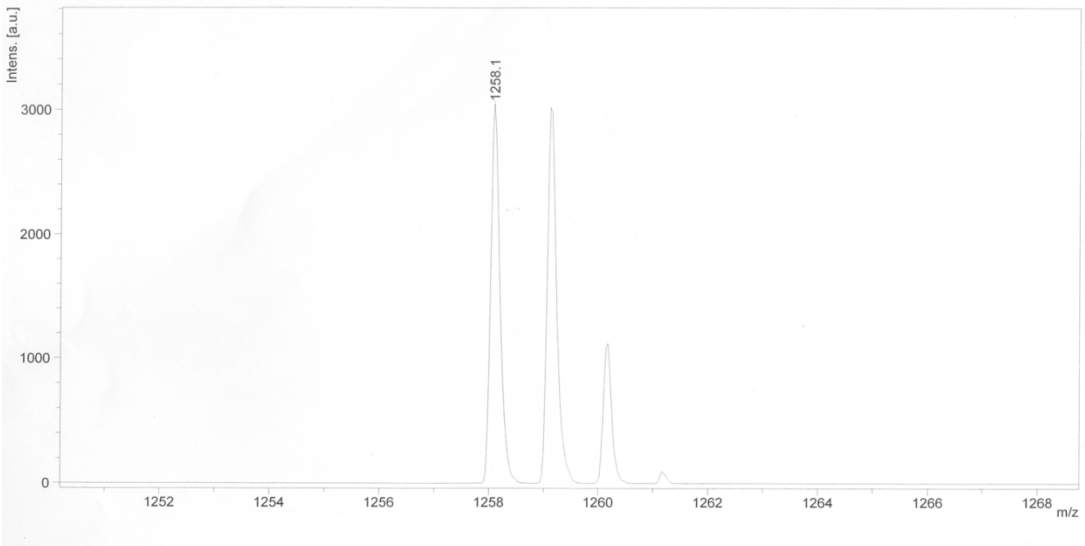


^{13}C NMR spectrum of **9** in C_6D_6/CS_2 (V/V=2:3)

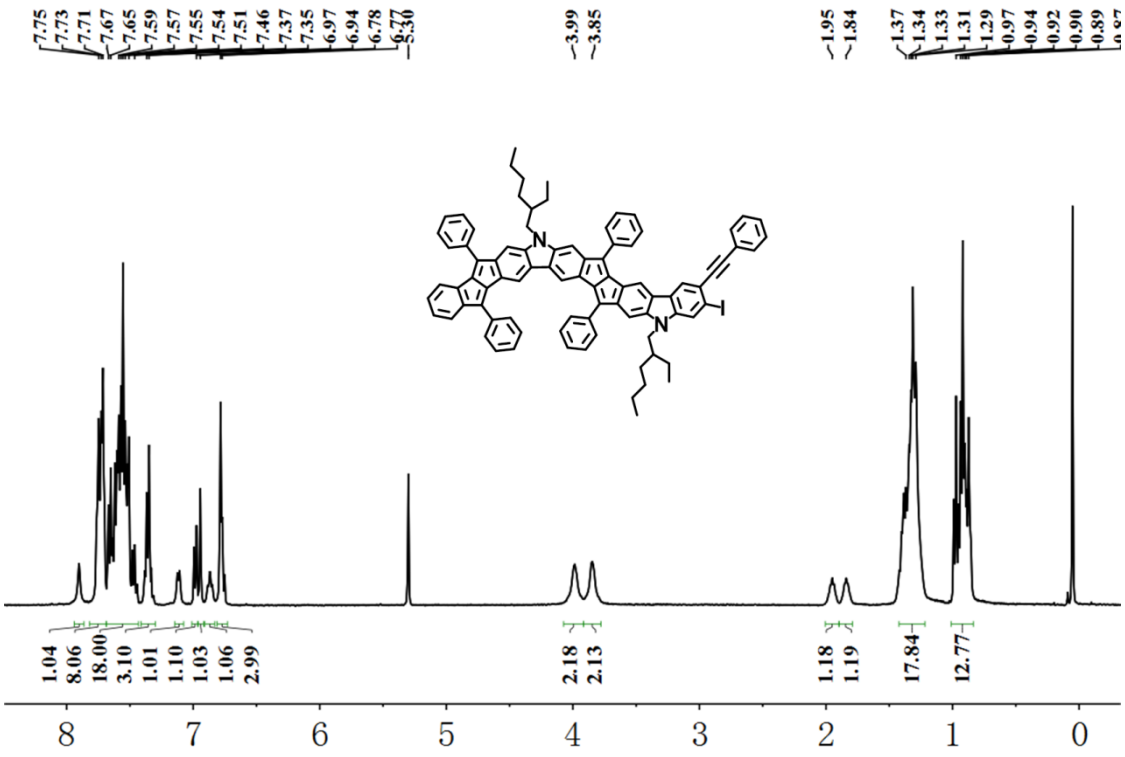


MALDI-TOF mass spectrum of **10**

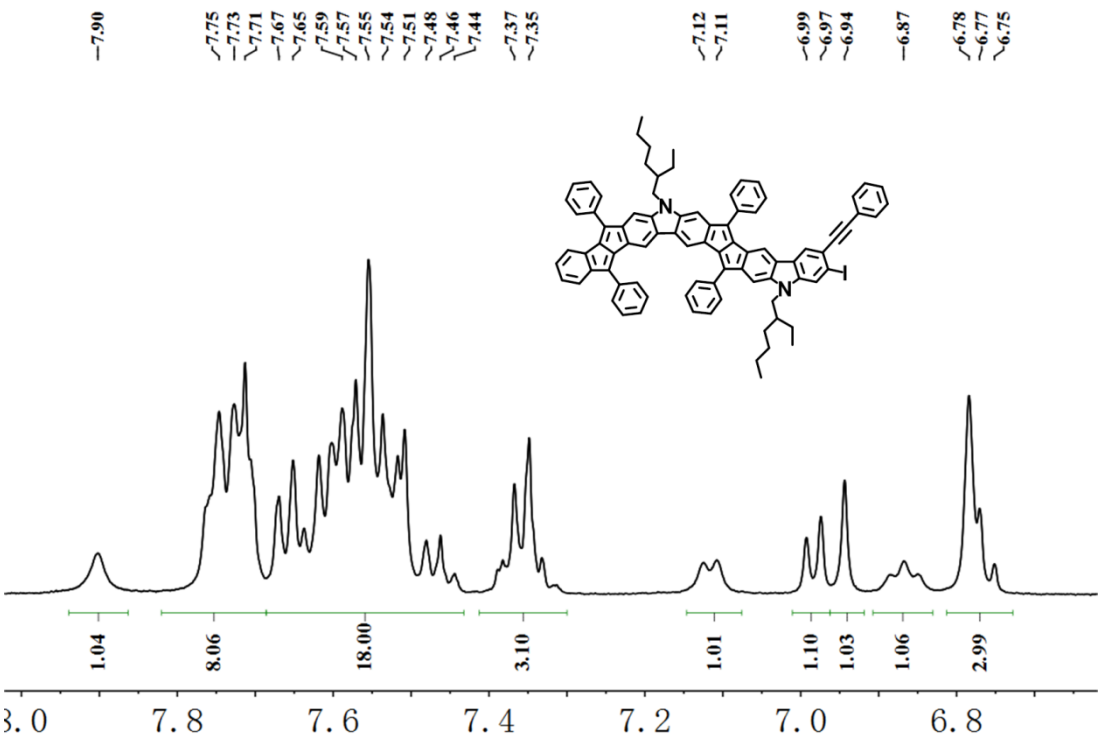




^{1}H NMR spectrum of **10** in CD_2Cl_2/CS_2 (V/V=2:3)



The low-filed section ^{1}H NMR spectra of 10 in CD_2Cl_2/CS_2 (V/V=2:3)



^{13}C NMR spectrum of **10** in C_6D_6/CS_2 (V/V=2:3)