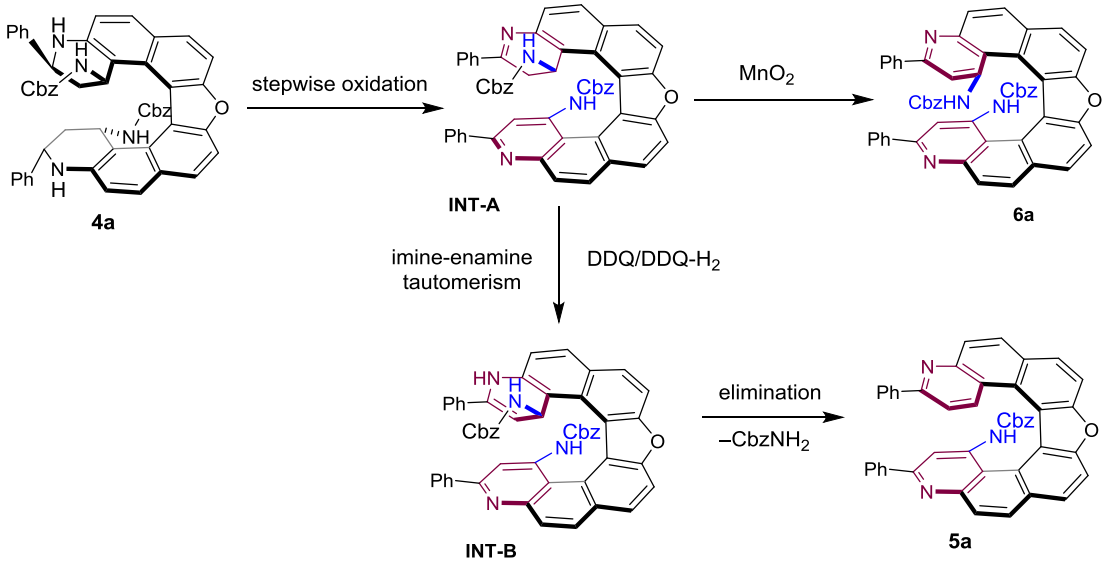
Table of contents

General Information

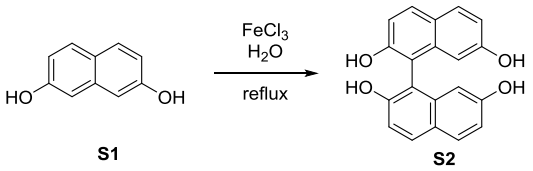
Unless otherwise noted, all commercial reagents were used without further purification. Dichloromethane, toluene, ether, THF were purified by passage through an activated alumina column under argon. Thin-layer chromatography (TLC) analysis of reaction mixtures was performed using Huanghai silica gel HSGF254 TLC plates, and visualized under UV or by staining with ceric ammonium molybdate or potassium permanganate. Flash column chromatography was carried out on Huanghai Silica Gel HHGJ-300, 300-400 mesh. Nuclear magnetic resonance (NMR) spectra were recorded using Bruker Avance III HD spectrometer (FT, 500 MHz for ^{1}H, 126 MHz for ^{13}C, or 400 MHz for ^{1}H, 101 MHz for ^{13}C, $(CD_3)_2SO$, δH= 2.50 and δC = 39.52). ^{1}H and ^{13}C chemical shifts are reported in ppm downfield of tetramethylsilane and referenced to residual solvent peak ($CDCl_3$, δH = 7.26 and δC = 77.16). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad resonance. FT-IR spectra were recorded on ThermoFisher Scientific Nicolet iS7 Spectrometer, and absorption frequencies are reported in reciprocal centimeters (cm−1). Mass spectral data were obtained from the Agilent Technologies 6230 TOF LC/MS spectrometer in electrospray ionization (ESI^+) mode. Optical rotations were measured with an Autopol V Plus/VI digital polarimeter. Enantiomeric excesses were determined on an Agilent 1260 Chiral HPLC using IA, IB, IC columns. Absorbance analysis was performed on Agilengt Cary 5000 UV-Vis Spectrophotometer using PbSmart detector. Fluorescence analysis was performed on Fluorolog-3 from Horiba Jobin Yvon. The circularly polarized luminescence (CPL) spectra were recorded with a JASCO CPL-300 spectrometer at room temperature. Circular dichroism spectra (CD) were recorded on Chirascan Circular Dichroism Spectrometer from Applied Photophysics. Unless otherwise noted, CD analysis, absorbance analysis and fluorescence analysis were performed at 20 ℃ with 1.0 cm x 1.0 cm quartz cell. The racemic products were synthesized using the same procedure for the chiral products, unless the racemic CPA catalyst (±)-**A9** was used instead.

Proposed mechanism



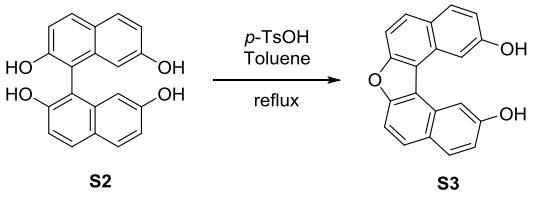
Scheme S1. Proposed reaction mechanism for the formation of diverse azahelicenes under varied conditions

Synthesis of the starting materials



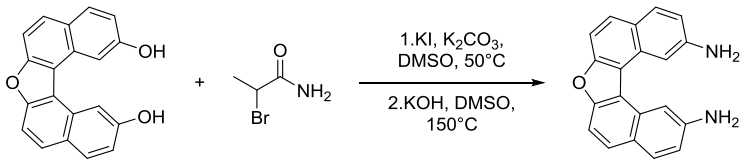
This procedure was adopted from the literature.[1]

To a solution of **S1** (62.4 mmol, 10.0 g, 1.0 equiv.) in water (200 mL) was added a solution of $FeCl_3$ (94 mmol, 15.2 g, 1.5 equiv.) in water (200 mL) at rt, and the mixture was warmed to 100 ℃. After stirring overnight at this temperature, the reaction was cooled to rt and then extracted with ethyl acetate for three times. The organic layers were combined, dried over Na_2SO_4 and concentrated under vacuum to give a residue, which was purified by column chromatography (Petroleum ether: EtOAc = 3:1) to give **S2** (7.8 g, yield = 78%) as a yellow solid.



This procedure was adopted from the literature.[1]

S2 (18.8 mmol, 6.0 g ,1.0 equiv.) was dissolved in toluene (60 mL), and the solution was heated to reflux after added *p*-TsOH (18.8 mmol, 3.60 g, 1.0 equiv.). After stirring overnight, the mixture was cooled to ambient temperature. After diluting with ethyl acetate, the mixture was filtered through Celite and then washed by saturated aqueous $NaHCO_3$ solution for 3 times. The organic layers were combined, dried over Na_2SO_4 and concentrated under vacuum to give a residue, which was purified by column chromatography (DCM: EtOAc = 10:1) to give the corresponding **S3** as a white solid (4.1 g, yield = 73%).

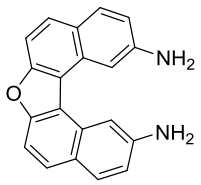


S3 **S4** **1**

This procedure was adopted from the literature.[2]

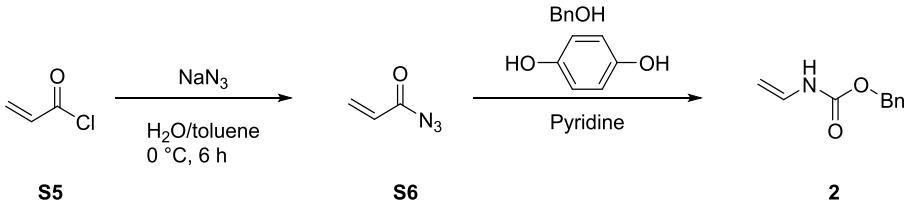
To a solution of **S3** (4.9 mmol, 1.47 g, 1.0 equiv.) in DMSO (10 mL/mmol) was added amide **S4** (14.7 mmol, 2.2 g, 3.0 equiv.), K_2CO_3 (14.7 mmol, 2.0 g, 3.0 equiv.) and KI (1.0 mmol, 166 mg, 20 mol%) sequentially at r.t.. The resulting solution was stirred for 12 h at 50 ℃ until complete consumption of **S3** (monitored by TLC analysis). The reaction mixture was cooled to r.t., and KOH (49 mmol, 2.75 mmol, 10.0 equiv.) was added in one portion. The reaction was warmed to 150 ℃ and stirred for another 8 h. After cooling to room temperature, water was added and the mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated under vacuum to give a residue, which was purified by column chromatography (Petroleum ether: EtOAc = 1:1) to give the corresponding polycyclic arylamine **1a** as a brown solid (950 mg, yield = 65%).

dinaphtho[2,1-b:1',2'-d]furan-2,12-diamine (**1a**)



^{1}H NMR (400 MHz, DMSO) δ 8.10 (d, *J* = 2.1 Hz, 1H), 7.80 (dd, *J* = 17.8, 8.7 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 1H), 7.01 (dd, *J* = 8.6, 2.0 Hz, 1H), 5.84 (s, 2H). ^{13}C NMR (126 MHz, DMSO) δ 154.4, 148.0, 131.2, 130.6, 128.6, 124.1, 117.5, 116.2, 107.7, 106.5.

benzyl vinylcarbamate (**2**)

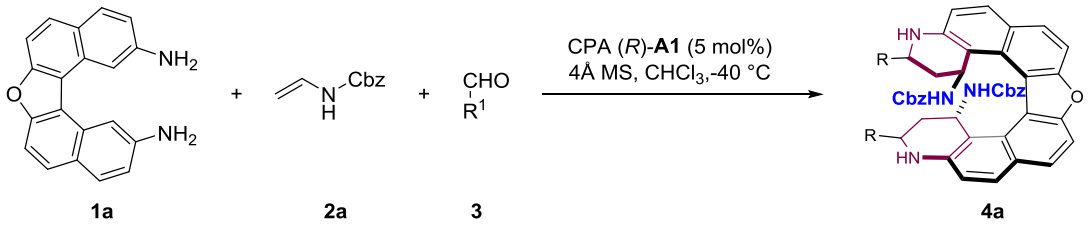


This procedure was adopted from the literature, and the ^{1}H NMR data matched with the literature.[3] To a solution of NaN_3 (1.95 g, 30 mmol, 1.0 eq.) in H_2O (14 mL) was added a solution of acryloyl chloride **S5** (2.4 mL, 30 mmol) in toluene (18 mL) dropwisely at 0 ℃. After stirring for 6 h at this temperature, toluene (ca. 20 mL) was added to dilute the reaction mixture and the mixture was washed by saturated aqueous $NaHCO_3$ solution. The organic layers were combined, dried over Na_2SO_4 and filtered to give a solution of **S6**, which was used directly for next step without further purification.

To the solution of **S6** was successively added BnOH (3.7 mL, 36 mmol, 1.2 eq.), pyridine (1.2 mL, 15 mmol, 0.5 eq.) and hydroquinone (165 mg, 5 mol%) at rt. After stirring for 3 h, this reaction mixture was concentrated under vacuum to give a residue, which was purified by column chromatography (petroleum ether: EtOAc = 8:1) to give benzyl vinylcarbamate (**2**) as a white solid (3.0 g, 56% yield for 2 steps).

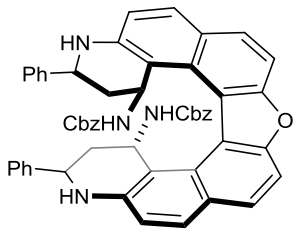
1H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 6H), 6.71 (dt, J = 16.1, 10.0 Hz, 1H), 6.57 – 6.30 (m, 1H), 5.15 (s, 2H), 4.48 (d, J = 15.7 Hz, 1H), 4.30 (d, J = 8.7 Hz, 1H).

Enantioselective synthesis of helicenoid 4a



Diamine **1a** (0.1 mmol), CPA (*R*)-**A1** (0.005 mmol, 5 mol%) and activated 4Å molecular sieves (ca. 50 mg) were placed in a reaction tube and chloroform (1.5 mL) was added into this reaction mixture via syringe, which was followed by adding the corresponding aldehyde **3** (0.4 mmol, 4.0 equiv.). After stirring at rt for about 0.5 h., this reaction mixture was cooled to -40 ℃, and a solution of

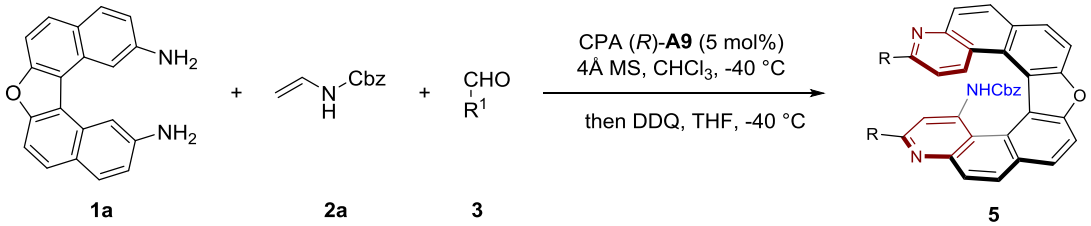
enamide **2a** (0.4 mmol, 4.0 equiv.) in $CHCl_3$ (0.5 mL) was added slowly into the reaction mixture via syringe and the mixture was stirred at the same temperature for additional 12 h. After the completion of the cycloaddition step as monitored by TLC analysis, the mixture was concentrated under vacuum to give a residue, which was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford the corresponding **4a**.



Starting from 0.1 mmol of **1a**, **4a** was afforded as a light yellow solid (77 mg, 94% yield). Column chromatography eluent : petroleum ether : EtOAc = 5:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.71 (m, 1H), 7.70 – 7.62 (m, 1H), 7.59 – 7.40 (m, 3H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.26 – 7.19 (m, 3H), 7.12 – 6.88 (m, 3H), 6.03 – 5.84 (m, 1H), 4.85 – 4.77 (m, 1H), 4.46 (d, *J* = 12.1 Hz, 1H), 4.18 (d, *J* = 12.0 Hz, 1H), 3.82 – 3.70 (m, 1H), 2.89 – 2.67 (m, 1H), 1.87 – 1.67 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 154.1, 145.0, 142.7, 136.5, 130.2, 129.4, 128.9, 128.3, 127.9, 127.8, 127.0, 126.7, 126.6, 118.3, 116.3, 113.2, 107.7, 66.0, 55.4, 48.3, 39.2. HPLC: Chiralpak IA column, 60:40 hexanes/ isopropanol, 1 ml/min, t_R = 9.5 min (major), 13.9 min (minor), 99% ee. m/z HRMS (ESI) found $[M+H]^+$ 829.3379, $C_{54}H_{45}N_4O_5^+$ requires 829.3384.

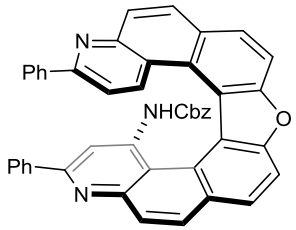
Enantioselective synthesis of heterohelicenes 5



Diamine **1a** (0.1 mmol), CPA (*R*)-**A1** (0.005 mmol, 5 mol%) and activated 4Å molecular sieves (ca. 50 mg) were placed in a reaction tube and chloroform (1.5 mL) was added into this reaction mixture via syringe, which was followed by adding the corresponding aldehyde **3** (0.4 mmol, 4.0 equiv.). After stirring at rt for about 0.5 h., this reaction mixture was cooled to -40 ℃, and a

solution of enamide **2a** (0.4 mmol, 4.0 equiv.) in $CHCl_3$ (0.5 mL) was added slowly into the reaction mixture via syringe and the mixture was stirred at the same temperature for additional 12 h ~ 24 h. After the completion of the cycloaddition step as monitored by TLC analysis, the mixture was concentrated under vacuum to give a residue. The residue was dissolved in THF (3 mL) and then cooled to -40 ^{o}C, which was followed by adding a solution of 1,2-dichloro-4,5-dicyanobenzoquinone (DDQ, 0.6 mmol, 6.0 equiv.) in THF (1 mL). After stirring at −40 °C for another 12 h, the mixture was warmed to room temperature, washed with saturated aqueous $NaHCO_3$ and extracted with EtOAc for 3 times. The combine organic layers were dried over Na_2SO_4 and concentrated under vacuum to give a residue, which was purified by column chromatography on silica gel using petroleum ether/ethyl acetate or dichloromethane as eluent to afford the corresponding **5**.

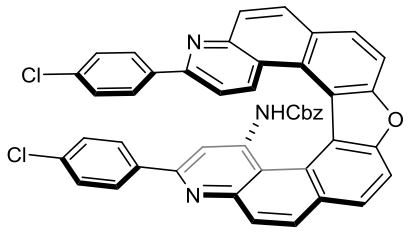
Heterohelicene 5a



Starting from 0.1 mmol of **1a**, **5a** was afforded as a light yellow solid (47.6 mg, 71% yield). Column chromatography eluent: petroleum ether : EtOAc = 5:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.7 Hz, 1H), 7.99 (d, *J* = 8.6 Hz, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.91 – 7.87 (m, 2H), 7.81 (dt, *J* = 15.8, 8.3 Hz, 3H), 7.70 (d, *J* = 7.2 Hz, 4H), 7.46 (s, 1H), 7.27 (d, *J* = 6.3 Hz, 3H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.14 (dt, *J* = 19.0, 7.4 Hz, 3H), 7.07 (t, *J* = 7.5 Hz, 2H), 6.95 (d, *J* = 6.7 Hz, 2H), 6.59 (d, *J* = 8.4 Hz, 1H), 6.22 (d, *J* = 8.4 Hz, 1H), 5.73 (s, 1H), 4.49 (d, *J* = 11.8 Hz, 1H), 4.28 (d, *J* = 11.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 156.6, 155.5, 155.2, 150.4, 148.7, 148.0, 142.6, 138.2, 135.0, 134.0, 130.9, 130.1, 129.2, 128.9, 128.8, 128.7, 128.5, 128.4, 128.4, 128.3, 128.2, 128.0, 127.9, 127.6, 127.5, 127.3, 127.0, 122.1, 120.5, 118.3, 115.4, 113.2, 111.8, 111.4, 104.5, 66.9. HPLC: Chiralpak IA column, 80:20 hexanes/ isopropanol, 1 ml/min, t_R = 7.6 min (major), 10.9 min (minor), 99% ee. $[\alpha]_D^{25}$ = 719 (c = 1.0, $CHCl_3$). m/z HRMS (ESI) found $[M+H]^+$ 672.2283, $C_{46}H_{30}N_3O_3^+$ requires 672.2282.

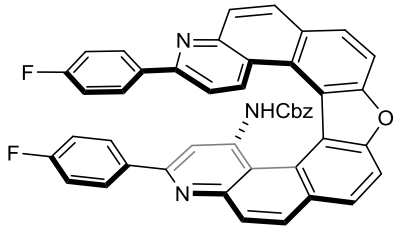
Heterohelicene 5b



Starting from 0.125 mmol of **1**, **5b** was afforded as a yellow solid (49 mg, 51% yield). Column chromatography eluent : petroleum ether : EtOAc = 5:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.4 Hz, 1H), 8.16 (dd, *J* = 8.8, 3.5 Hz, 2H), 8.00 (s, 3H), 7.96 (t, *J* = 1.9 Hz, 3H), 7.53 (s, 1H), 7.51 – 7.43 (m, 2H), 7.37 – 7.31 (m, 3H), 7.20 (ddd, *J* = 17.7, 7.8, 2.1 Hz, 2H), 7.07 (t, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 7.1 Hz, 3H), 6.82 (d, *J* = 8.5 Hz, 1H), 6.35 (d, *J* = 8.4 Hz, 1H), 5.87 (s, 1H), 4.59 (d, *J* = 11.9 Hz, 1H), 4.37 (d, *J* = 11.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8, 155.8, 155.5, 154.8, 150.4, 148.8, 148.0, 142.8, 139.9, 139.8, 134.8, 134.7, 134.6, 134.2, 131.2, 130.4, 129.4, 129.4, 129.2, 129.1, 129.0, 128.9, 128.5, 128.2, 127.8, 127.6, 127.1, 127.1, 126.9, 125.4, 125.0, 122.4, 120.5, 118.5, 115.6, 112.9, 112.2, 111.8, 103.8, 67.1. HPLC: Chiralpak IA column, 80:20 hexanes/ isopropanol, 1 ml/min, t_R = 8.1 min (major), 11.0 min (minor), 99% ee. $[\alpha]_D^{25}$ = 1016 (c = 1.0, $CHCl_3$). m/z HRMS (ESI) found $[M+H]^+$ 740.1522, $C_{46}H_{28}Cl_2N_3O_3^+$ requires 740.1502.

Heterohelicene 5c

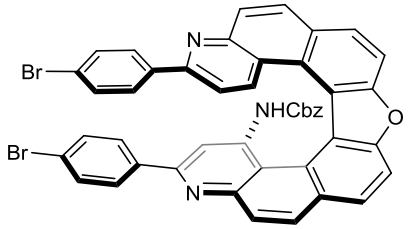


Starting from 0.1 mmol of **1**, **5c** was afforded as a yellow solid (65 mg, 92% yield). Column chromatography eluent : petroleum ether : EtOAc = 5:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 – 8.05 (m, 6H), 8.01 (s, 2H), 7.78 (ddd, *J* = 8.6, 5.5, 2.7 Hz, 4H), 7.53 (s, 1H), 7.33 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.06 – 6.99 (m, 2H), 6.92 – 6.78 (m, 5H), 6.39 (d, *J* = 8.6 Hz, 1H), 5.92 (s, 1H), 4.59 (d, *J* = 11.9 Hz, 1H), 4.37 (d, *J* = 11.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$_new) δ 164.9, 162.9, 156.6, 155.8, 155.5, 155.4, 150.5, 148.8, 148.0, 142.8, 134.9, 134.3, 131.1, 130.3, 129.4, 129.3, 129.1, 129.0, 129.0, 128.9, 128.5, 128.5, 128.1, 127.8, 127.7, 127.1, 122.1, 120.7, 118.6, 118.5, 115.4, 115.2, 115.0, 112.7, 112.1, 111.6, 103.9, 67.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ

-112.55, -112.86. HPLC: Chiralpak IA column, 80:20 hexanes/ isopropanol, 1 ml/min, t_R = 8.7 min (major), 12.1 min (minor), 98% ee. $[\alpha]_D^{25}$ = 671 (c = 1.0, $CHCl_3$). m/z HRMS (ESI) found $[M+H]^+$ 708.2112, $C_{46}H_{28}F_2N_3O_3^+$ requires 708.2093.

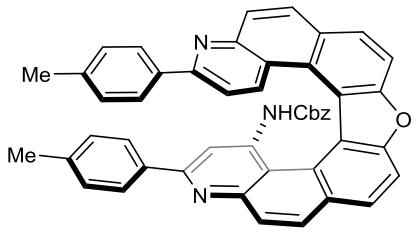
Heterohelicene 5d



Starting from 0.1 mmol of **1a**, **5d** was afforded as a yellow solid (65 mg, 78% yield). Column chromatography eluent : petroleum ether : EtOAc = 5:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 – 8.06 (m, 3H), 8.03 (dt, *J* = 8.8, 2.3 Hz, 3H), 7.95 (s, 2H), 7.58 (dd, *J* = 8.6, 2.2 Hz, 4H), 7.44 (s, 1H), 7.35 – 7.31 (m, 2H), 7.30 – 7.27 (m, 2H), 7.25 – 7.21 (m, 2H), 7.02 – 6.97 (m, 2H), 6.67 (d, *J* = 8.5 Hz, 1H), 6.24 (d, *J* = 8.6 Hz, 1H), 5.79 (s, 1H), 4.55 (d, *J* = 11.8 Hz, 1H), 4.33 (d, *J* = 11.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 155.7, 155.4, 155.0, 150.4, 148.7, 147.9, 142.6, 136.8, 134.8, 134.1, 131.3, 131.3, 131.1, 130.3, 129.1, 128.9, 128.8, 128.5, 128.1, 127.8, 127.5, 126.8, 124.2, 123.9, 122.1, 120.4, 118.4, 118.4, 115.4, 112.4, 112.1, 111.6, 103.5, 67.0. HPLC: Chiralpak IA column, 80:20 hexanes/ isopropanol, 1 ml/min, t_R = 10.4 min (major), 14.5 min (minor), 99% ee. $[\alpha]_D^{25}$ = 939 (c = 1.0, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 828.0517, $C_{46}H_{28}Br_2N_3O_3^+$requires 828.0492.

Heterohelicene 5e

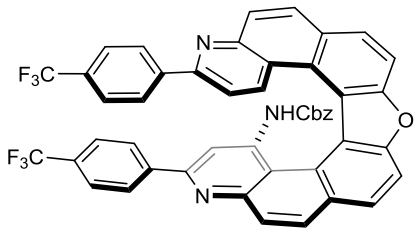


Starting from 0.1 mmol of **1a**, **5e** was afforded as a yellow solid (58.4 mg, 83% yield). Column chromatography eluent : petroleum ether : EtOAc = 5:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 14.7, 8.7 Hz, 2H), 8.11 (s, 2H), 8.04 (dd, *J* = 9.9, 8.7 Hz, 2H), 8.00 – 7.91 (m, 2H), 7.65 (dd, *J* = 8.2, 1.8 Hz, 4H), 7.54 (s, 1H), 7.37 – 7.29 (m, 3H), 7.05 – 6.98

(m, 2H), 6.92 (dd, *J* = 15.3, 7.9 Hz, 4H), 6.83 (d, *J* = 8.5 Hz, 1H), 6.39 (d, *J* = 8.6 Hz, 1H), 5.89 (s, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.35 (d, *J* = 12.0 Hz, 1H), 2.33 (d, *J* = 15.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 156.7, 155.7, 155.4, 150.5, 148.8, 148.0, 142.6, 139.1, 138.7, 135.4, 135.4, 135.0, 134.0, 130.8, 130.0, 129.0, 128.9, 128.8, 128.8, 128.6, 128.5, 128.4, 128.4, 128.0, 127.9, 127.7, 127.4, 127.1, 122.1, 120.8, 118.6, 118.5, 115.4, 113.0, 111.8, 111.3, 104.0, 66.9, 21.3. HPLC: Chiralpak IA column, 80:20 hexanes/ isopropanol, 1 ml/min, t_R = 7.8 min (major), 11.0 min (minor), 98% ee. $[\alpha]_D^{25}$ = 1035 (c = 1.0, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 700.2615, $C_{48}H_{34}N_3O_3^+$requires 700.2595.

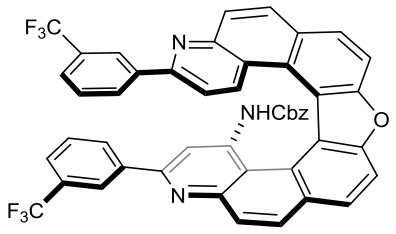
Heterohelicene 5f



Starting from 0.1 mmol of **1a**, **5f** was afforded as a yellow solid (57 mg, 71% yield). Column chromatography eluent : petroleum ether : EtOAc = 5:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.5 Hz, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 8.21 – 8.16 (m, 2H), 8.13 (dd, *J* = 20.0, 8.8 Hz, 2H), 8.05 (t, *J* = 6.4 Hz, 2H), 7.87 (dd, *J* = 13.1, 8.0 Hz, 4H), 7.61 (s, 1H), 7.40 – 7.29 (m, 6H), 7.05 – 7.00 (m, 2H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.45 (d, *J* = 8.5 Hz, 1H), 5.93 (s, 1H), 4.61 (d, *J* = 11.9 Hz, 1H), 4.39 (d, *J* = 11.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 155.6, 154.7, 150.4, 148.9, 148.1, 142.9, 141.3, 134.8, 134.4, 131.3, 130.5, 129.3, 129.0, 129.0, 128.5, 128.5, 128.3, 127.9, 127.7, 127.6, 127.2, 126.9, 125.1, 122.6, 120.5, 118.6, 118.6, 115.7, 113.0, 112.4, 111.9, 104.1, 67.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.91, -62.92. Chiralpak IA column, 80:20 hexanes/ isopropanol, 1 ml/min, t_R = 9.5 min (major), 13.3 min (minor), 99% ee. $[\alpha]_D^{25}$ = 957 (c = 1.0, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 808.2051, $C_{48}H_{28}F_6N_3O_3^+$ requires 808.2029.

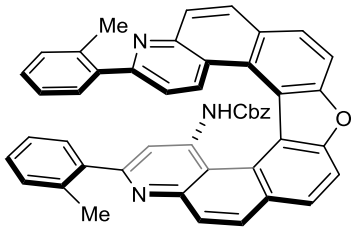
Heterohelicene 5g



Starting from 0.1 mmol of **1a**, **5g** was afforded as a yellow solid (58 mg, 72% yield). Column chromatography eluent : petroleum ether : EtOAc = 5:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 2.0 Hz, 1H), 8.40 (d, *J* = 1.9 Hz, 1H), 8.20 – 8.04 (m, 6H), 7.99 (s, 2H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 19.7 Hz, 2H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 6.6 Hz, 1H), 7.34 (dd, *J* = 5.0, 2.0 Hz, 3H), 7.13 (t, *J* = 7.7 Hz, 1H), 7.08 – 6.99 (m, 3H), 6.77 (d, *J* = 8.5 Hz, 1H), 6.36 (d, *J* = 8.5 Hz, 1H), 5.84 (s, 1H), 4.59 (d, *J* = 11.8 Hz, 1H), 4.36 (d, *J* = 11.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 155.5, 155.4, 154.3, 150.4, 148.8, 148.0, 142.8, 138.7, 134.8, 134.2, 131.2, 130.9, 130.8, 130.7, 130.6, 130.4, 129.8, 129.2, 129.0, 128.9, 128.7, 128.5, 128.5, 128.2, 127.9, 127.7, 126.8, 125.8, 125.6, 125.3, 123.7, 123.1, 122.4, 120.4, 118.5, 115.7, 112.5, 112.2, 111.8, 103.6, 67.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.42, -62.42. HPLC: Chiralpak IA column, 90:10 hexanes/ isopropanol, 1 ml/min, t_R = 9.5 min (major), > 99% ee. $[\alpha]_D^{25}$ = 1046 (c = 1.0, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 808.2050, $C_{48}H_{28}F_6N_3O_3^+$requires 808.2029.

Heterohelicene 5h

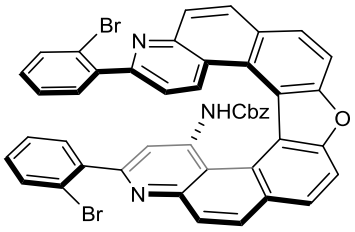


Starting from 0.1 mmol of **1a**, **5h** was afforded as a yellow solid (58 mg, 83% yield). Column chromatography eluent : petroleum ether : EtOAc = 5:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.4 Hz, 1H), 8.21 – 8.14 (m, 2H), 8.14 – 8.06 (m, 3H), 8.05 – 7.96 (m, 2H), 7.66 (s, 1H), 7.35 – 7.30 (m, 4H), 7.24 (qd, *J* = 7.0, 1.4 Hz, 2H), 7.20 – 7.13 (m, 2H), 7.09 (dt, *J* = 10.7, 7.6 Hz, 3H), 7.04 – 6.99 (m, 3H), 6.51 (d, *J* = 8.4 Hz, 1H), 6.18 (s, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.40 (d, *J* = 12.0 Hz, 1H), 2.11 (s, 3H), 2.03 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 160.5, 159.8, 155.9, 155.5, 150.6, 148.9, 147.8, 142.3, 139.6, 139.3, 136.9, 136.4, 135.0, 134.0, 131.3, 131.2, 131.0, 130.2, 130.1, 129.9, 129.4, 129.2, 129.1, 128.6, 128.5, 128.4, 128.3, 128.2, 128.2, 128.0, 128.0, 127.6, 125.9, 125.7, 122.0, 121.2, 118.9, 118.8, 117.8, 115.1, 112.2, 111.6, 108.1, 67.0, 20.4, 20.1. HPLC: Chiralpak IA column, 80:20 hexanes/ isopropanol, 1 ml/min, t_R = 6.9 min (major), 11.5

min (minor), 99% ee. $[\alpha]_D^{25}$ = 306 (c = 2.0, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 700.2612, $C_{48}H_{34}N_3O_3^+$requires 700.2595.

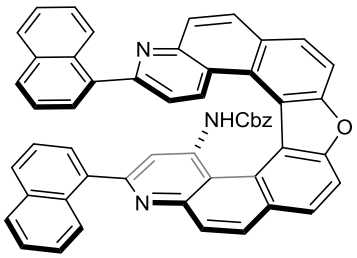
Heterohelicene 5i



Starting from 0.125 mmol of **1a**, **5g** was afforded as a yellow solid (44 mg, 44% yield). Column chromatography eluent : petroleum ether : EtOAc = 4:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.5 Hz, 1H), 8.25 – 8.18 (m, 2H), 8.15 (d, *J* = 8.6 Hz, 2H), 8.09 (d, *J* = 8.9 Hz, 1H), 8.02 (q, *J* = 8.5 Hz, 2H), 7.83 (s, 1H), 7.55 (dd, *J* = 15.5, 7.9 Hz, 2H), 7.34 (tt, *J* = 7.1, 4.4 Hz, 5H), 7.18 (dddd, *J* = 19.0, 8.9, 5.3, 1.6 Hz, 4H), 7.07 – 7.00 (m, 3H), 6.82 (d, *J* = 8.5 Hz, 1H), 6.19 (s, 1H), 4.63 (d, *J* = 11.9 Hz, 1H), 4.42 (d, *J* = 12.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 157.7, 156.0, 155.5, 150.5, 148.9, 148.2, 142.2, 140.7, 140.3, 134.9, 133.7, 133.4, 133.4, 132.2, 131.7, 131.3, 130.5, 129.6, 129.5, 129.3, 129.3, 128.5, 128.0, 127.8, 127.7, 127.4, 122.6, 121.9, 121.1, 119.0, 118.8, 118.3, 115.5, 112.5, 111.9, 108.2, 67.1. HPLC: Chiralpak IA column, 80:20 hexanes/ isopropanol, 1 ml/min, t_R = 10.4 min (major), > 99% ee. $[\alpha]_D^{25}$ = 772 (c = 1.0, $CHCl_3$). m/z HRMS (ESI) found $[M+H]^+$ 828.0511, $C_{46}H_{28}Br_2N_3O_3^+$ requires 828.0492.

Heterohelicene 5j

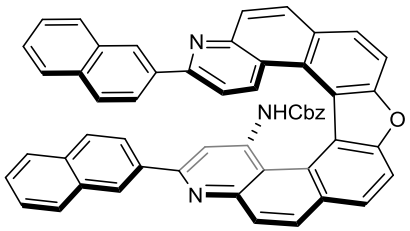


Starting from 0.1 mmol of **1a**, **5j** was afforded as a yellow solid (69 mg, 89% yield). Column chromatography eluent : petroleum ether : EtOAc = 4:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.5 Hz, 1H), 8.26 – 8.10 (m, 6H), 8.09 – 8.01 (m, 3H), 7.89 (s, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.47 (d, *J* = 8.4 Hz,

1H), 7.38 – 7.33 (m, 3H), 7.30 (ddd, *J* = 8.1, 6.7, 1.2 Hz, 1H), 7.26 – 7.20 (m, 3H), 7.12 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.09 – 6.98 (m, 4H), 6.91 (dd, *J* = 8.2, 7.0 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.27 (s, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2, 159.2, 156.0, 155.6, 150.6, 148.9, 148.1, 142.8, 137.4, 137.0, 135.0, 134.5, 133.9, 133.8, 131.2, 130.8, 130.6, 130.3, 129.4, 129.2, 128.5, 128.5, 128.4, 128.4, 128.2, 128.1, 127.8, 127.6, 126.4, 126.1, 125.5, 125.4, 125.4, 124.7, 122.3, 121.2, 119.0, 118.8, 118.7, 115.4, 112.3, 111.8, 108.9, 67.0. HPLC: Chiralpak IA column, 80:20 hexanes/ isopropanol, 1 ml/min, t_R = 10.5 min (major), > 99% ee. $[\alpha]_D^{25}$ = 215 (c = 1.0, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 772.2593, $C_{54}H_{34}N_3O_3^+$requires 772.2595.

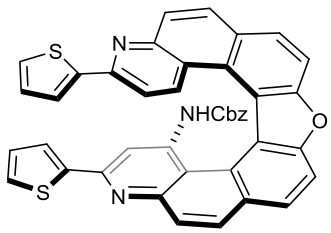
Heterohelicene 5k



Starting from 0.1 mmol of **1a**, **5k** was afforded as a yellow solid (54 mg, 70% yield). Column chromatography eluent : petroleum ether : EtOAc = 5:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 – 8.24 (m, 4H), 8.22 (s, 1H), 8.20 – 8.13 (m, 3H), 8.05 (s, 2H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.86 – 7.77 (m, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.37 – 7.31 (m, 4H), 7.30 – 7.13 (m, 6H), 7.04 (t, *J* = 6.4 Hz, 3H), 6.66 (d, *J* = 8.5 Hz, 1H), 6.02 (s, 1H), 4.66 (d, *J* = 11.9 Hz, 1H), 4.41 (d, *J* = 11.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.6, 156.6, 155.9, 155.6, 150.6, 148.2, 142.9, 135.3, 135.0, 134.3, 133.7, 133.4, 133.0, 132.9, 131.2, 130.2, 129.3, 129.0, 128.5, 128.5, 128.4, 128.2, 128.1, 127.8, 127.6, 127.2, 127.1, 126.8, 126.2, 126.0, 125.4, 124.4, 124.2, 122.4, 120.9, 118.8, 118.7, 115.6, 113.4, 112.1, 111.6, 104.2, 67.0. HPLC: Chiralpak IA column, 80:20 hexanes/ isopropanol, 1 ml/min, t_R = 11.3 min (major), 14.2 min (minor), 94% ee. $[\alpha]_D^{25}$ = 792 (c = 0.5, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 772.2591, $C_{54}H_{34}N_3O_3^+$requires 772.2595.

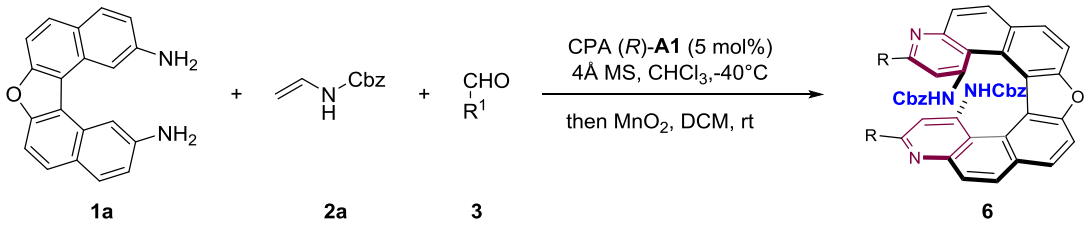
Heterohelicene 5l



Starting from 0.1 mmol of **1a**, **5l** was afforded as a yellow solid (28.3 mg, 41% yield). Column chromatography eluent : petroleum ether : EtOAc = 5:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.4 Hz, 1H), 8.21 (d, *J* = 8.8 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 8.13 – 8.05 (m, 3H), 8.02 (s, 2H), 7.54 (s, 1H), 7.36 – 7.31 (m, 3H), 7.29 – 7.22 (m, 2H), 7.13 (s, 1H), 7.08 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.02 (s, 2H), 6.86 (d, *J* = 8.5 Hz, 1H), 6.75 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.70 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.42 (d, *J* = 8.6 Hz, 1H), 5.92 (s, 1H), 4.59 (d, *J* = 11.9 Hz, 1H), 4.37 (d, *J* = 11.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 155.6, 152.4, 150.4, 144.6, 142.4, 134.0, 131.1, 130.3, 129.1, 129.0, 128.5, 128.1, 128.0, 127.8, 127.6, 127.1, 126.8, 125.9, 125.5, 122.2, 118.5, 112.1, 111.9, 111.4, 107.3, 102.4, 67.0.Chiralpak IA column, 80:20 hexanes/ isopropanol, 1 ml/min, t_R = 11.7 min (major), > 99% ee. $[\alpha]_D^{25}$ = 870 (c = 0.2, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 684.1401, $C_{42}H_{26}N_3O_3S_2^+$requires 684.1410.

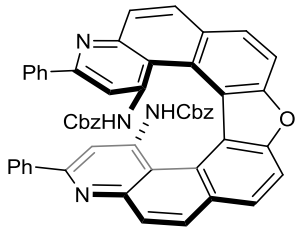
Enantioselective synthesis of heterohelicenes 6



Diamine **1a** (0.1 mmol), CPA (*R*)-**A1** (0.005 mmol, 5 mol%) and activated 4Å molecular sieves (ca. 50 mg) were placed in a reaction tube and chloroform (1.5 mL) was added into this reaction mixture via syringe, which was followed by adding the corresponding aldehyde **3** (0.4 mmol, 4.0 equiv.). After stirring at rt for about 0.5 h., this reaction mixture was cooled to -40 ℃, and a solution of enamide **2a** (0.4 mmol, 4.0 equiv.) in $CHCl_3$ (0.5 mL) was added slowly into the reaction mixture via syringe and the mixture was stirred at the same temperature for additional 12 h ~ 24 h. After the completion of the cycloaddition step as monitored by TLC analysis, the mixture was concentrated under vacuum to give a residue. The residue was then dissolved in DCM (10 mL), and added MnO_2

(10 mmol, 100 equiv.) at rt. After stirring for 48 h, the mixture was filtered through Celite and concentrated under vacuum to give a residue, which was purified by column chromatography on silica gel using petroleum ether/ethyl acetate or dichloromethane as eluent to afford the corresponding product **6**.

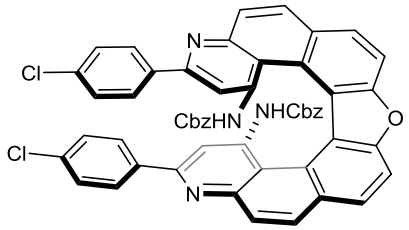
Heterohelicene 6a



Starting from 0.1 mmol of **1a**, **6a** was afforded as a light yellow solid (61.6 mg, 75% yield). Column chromatography eluent : petroleum ether : EtOAc = 5:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.7 Hz, 1H), 8.00 (s, 2H), 7.91 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 7.5 Hz, 2H), 7.68 (s, 1H), 7.35 (q, *J* = 4.4 Hz, 3H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.07 (q, *J* = 7.5 Hz, 4H), 5.69 (s, 1H), 4.61 (d, *J* = 11.9 Hz, 1H), 4.44 (d, *J* = 11.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.6, 154.9, 150.2, 149.7, 142.0, 137.9, 135.0, 129.7, 129.3, 129.1, 128.8, 128.6, 128.5, 128.4, 128.2, 128.2, 128.0, 127.5, 127.4, 122.1, 118.9, 113.9, 111.2, 103.3, 66.9. HPLC: Chiralpak IA column, 80:20 hexanes/ isopropanol, 1 ml/min, t_R = 10.7 min (major), 16.4 min (minor), 99% ee. $[\alpha]_D^{25}$ = 900 (c = 1.0, $CHCl_3$). m/z HRMS (ESI) found $[M+H]^+$ 821.2755, $C_{54}H_{37}N_4O_5^+$ requires 821.2758.

Heterohelicene 6b

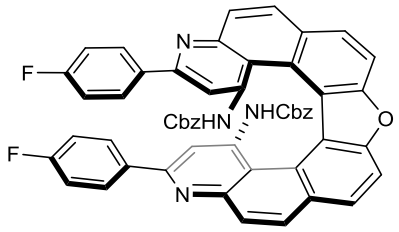


Starting from 0.125 mmol of **1a**, **6b** was afforded as a yellow solid (77 mg, 69% yield). Column chromatography eluent : petroleum ether : EtOAc = 5:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.7 Hz, 1H), 8.12 – 8.05 (m, 3H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.67 (s, 1H), 7.57 (s, 1H), 7.39 – 7.34 (m, 3H), 7.17 (dd, *J* = 7.8, 2.1 Hz, 1H), 7.03 (dd, *J* = 17.5, 9.7 Hz, 3H), 5.71 (s, 1H), 4.64 (d, *J* = 11.8 Hz, 1H), 4.46 (d, *J* = 11.9 Hz, 1H). ^{13}C NMR (126 MHz,

$CDCl_3$_new) δ 160.4, 155.6, 155.0, 150.3, 149.6, 142.1, 139.6, 134.9, 134.5, 130.0, 129.4, 129.3, 129.0, 128.6, 128.5, 128.5, 127.0, 125.2, 121.9, 118.8, 114.1, 111.5, 102.5, 67.0. HPLC: Chiralpak IA column, 80:20 hexanes/ isopropanol, 1 ml/min, t_R = 11.8 min (major), > 99% ee. $[\alpha]_D^{25}$ = 703 (c = 0.5, $CHCl_3$). m/z HRMS (ESI) found $[M+H]^+$ 889.1979, $C_{54}H_{35}Cl_2N_4O_5^+$ requires 889.1979.

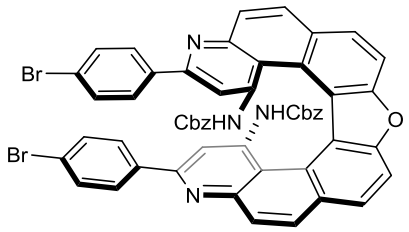
Heterohelicene 6c



Starting from 0.1 mmol of **1a**, **6c** was afforded as a yellow solid (60 mg, 70% yield). Column chromatography eluent : petroleum ether : EtOAc = 4:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 – 8.03 (m, 3H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.84 (t, *J* = 6.8 Hz, 2H), 7.61 (s, 1H), 7.37 – 7.30 (m, 3H), 7.05 (s, 2H), 6.83 – 6.75 (m, 2H), 5.71 (s, 1H), 4.62 (d, *J* = 11.9 Hz, 1H), 4.44 (d, *J* = 11.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.9, 162.9, 156.3, 155.0, 150.3, 149.7, 142.0, 134.9, 134.1, 129.8, 129.3, 129.2, 129.2, 128.9, 128.8, 128.6, 128.5, 122.0, 118.8, 115.0, 114.8, 113.8, 111.3, 102.6, 66.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.95. m/z. HPLC: Chiralpak IA column, 70:30 hexanes/ isopropanol, 1 ml/min, t_R = 9.3 min (major), > 99% ee. $[\alpha]_D^{25}$ = 757 (c = 1.0, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 857.2567, $C_{54}H_{35}F_2N_4O_5^+$requires 857.2570.

Heterohelicene 6d

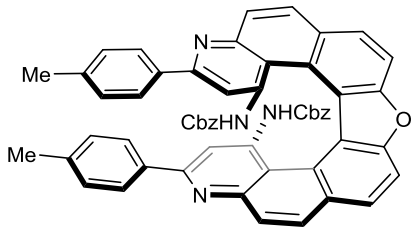


Starting from 0.1 mmol of **1a**, **6d** was afforded as a yellow solid (75 mg, 77% yield). Column chromatography eluent : petroleum ether : EtOAc = 4:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 – 8.02 (m, 3H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.60 (s, 1H), 7.39 – 7.31 (m, 3H), 7.28 – 7.19 (m, 2H), 7.04 (d, *J* = 6.8 Hz, 2H), 5.67 (d, *J* = 9.0 Hz, 1H), 4.61 (d, *J* = 11.9 Hz, 1H), 4.44 (d, *J* = 11.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.1, 155.0, 150.2, 149.7, 142.0, 136.8, 134.9, 131.1, 129.9, 129.3, 128.9, 128.8, 128.6, 128.5, 128.5, 124.2, 121.9,

118.8, 114.0, 111.4, 102.4, 66.9. HPLC: Chiralpak IA column, 70:30 hexanes/ isopropanol, 1 ml/min, t_R = 11.5 min (major), > 99% ee. $[\alpha]_D^{25}$ = 1253 (c = 0.5, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 977.0994, $C_{54}H_{35}Br_2N_4O_5^+$requires 977.0969.

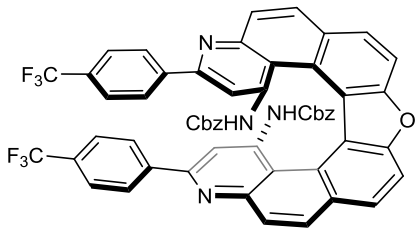
Heterohelicene 6e



Starting from 0.1 mmol of **1a**, **6e** was afforded as a yellow solid (70.8 mg, 83% yield). Column chromatography eluent : petroleum ether : EtOAc = 4 : 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.8 Hz, 1H), 8.05 (s, 2H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.66 (s, 1H), 7.39 – 7.29 (m, 3H), 7.05 (s, 2H), 6.86 (d, *J* = 7.9 Hz, 2H), 5.72 (s, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.44 (d, *J* = 12.0 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$_new) δ 157.7, 154.9, 150.3, 149.7, 141.9, 138.9, 135.2, 135.1, 129.6, 129.2, 128.9, 128.8, 128.7, 128.5, 128.4, 128.4, 127.3, 122.2, 118.9, 113.9, 111.1, 102.8, 66.8, 21.4. Chiralpak IA column, 70:30 hexanes/ isopropanol, 1 ml/min, t_R = 8.3 min (major), 15.5 min (minor), 98% ee. $[\alpha]_D^{25}$ = 876 (c = 1.0, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 849.3084, $C_{56}H_{41}N_4O_5^+$requires 849.3071.

Heterohelicene 6f

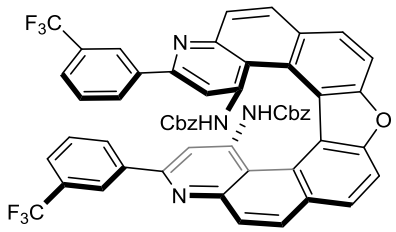


Starting from 0.1 mmol of **1a**, **5f** was afforded as a yellow solid (62 mg, 65% yield). Column chromatography eluent : petroleum ether : EtOAc = 4 : 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.05 (m, 3H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.71 (s, 1H), 7.36 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.08 – 7.02 (m, 2H), 5.72 (s, 1H), 4.63 (d, *J* = 11.9 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 155.0, 150.2, 149.8, 142.2, 141.2, 134.8, 130.0, 129.4, 129.0, 128.9, 128.6, 128.6, 128.5, 127.5, 124.8, 121.9, 118.9, 114.2, 111.7, 103.1, 67.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.89. Chiralpak IA column, 70:30 hexanes/

ethanol, 1 ml/min, t_R = 10.0 min (major), > 99% ee. $[\alpha]_D^{25}$ = 727.2 (c = 0.5, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 957.2535, $C_{56}H_{35}F_6N_4O_5^+$requires 957.2506.

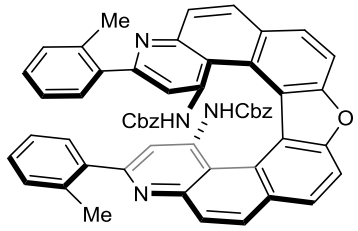
Heterohelicene 6g



Starting from 0.1 mmol of **1a**, **6g** was afforded as a yellow solid (67 mg, 70% yield). Column chromatography eluent : petroleum ether : EtOAc = 5 : 1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.16 (d, *J* = 8.8 Hz, 1H), 8.12 – 8.05 (m, 2H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.69 (s, 1H), 7.62 (s, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.38 – 7.32 (m, 3H), 7.06 (s, 2H), 7.00 (t, *J* = 7.8 Hz, 1H), 5.71 (s, 1H), 4.64 (d, *J* = 11.8 Hz, 1H), 4.46 (d, *J* = 11.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$_new) δ 155.2, 155.0, 150.3, 149.7, 142.1, 138.6, 134.8, 130.9, 130.7, 130.4, 130.2, 130.0, 129.4, 129.0, 128.9, 128.6, 128.5, 125.7, 125.4, 123.8, 123.2, 121.8, 118.8, 114.2, 111.6, 102.5, 67.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.31. HPLC: Chiralpak IA column, 80:20 hexanes/ ethanol, 1 ml/min, t_R = 9.4 min (major), 10.8 min (minor), 99% ee. $[\alpha]_D^{25}$ = 682 (c = 1.0, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 957.2530, $C_{56}H_{35}F_6N_4O_5^+$requires 957.2506.

Heterohelicene 6h

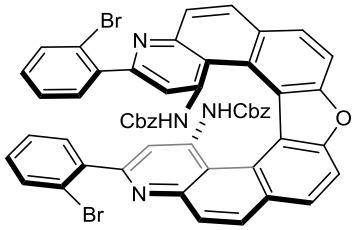


Starting from 0.1 mmol of **1a**, **6h** was afforded as a yellow solid (61.3 mg, 72% yield). Column chromatography eluent : petroleum ether : EtOAc = 4 : 1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.01 (m, 3H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.77 (s, 1H), 7.35 (dp, *J* = 6.0, 2.0 Hz, 3H), 7.21 (t, *J* = 7.3 Hz, 2H), 7.02 (dq, *J* = 10.4, 3.1 Hz, 4H), 5.97 (s, 1H), 4.68 (s, 1H), 4.49 (d, *J* = 12.0 Hz, 1H), 2.09 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.5, 155.0, 150.3, 149.6, 141.6, 139.2, 136.9, 134.9, 131.4, 130.1, 129.9, 129.5, 129.0, 128.6, 128.5, 128.4, 128.4, 128.1, 125.6,

122.6, 119.1, 113.2, 111.4, 106.9, 66.9, 20.4. HPLC: Chiralpak IA column, 70:30 hexanes/ isopropanol, 1 ml/min, t_R = 6.5 min (major), > 99% ee. $[\alpha]_D^{25}$ = 402(c = 1.0, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 849.3093, $C_{56}H_{41}N_4O_5^+$requires 849.3071.

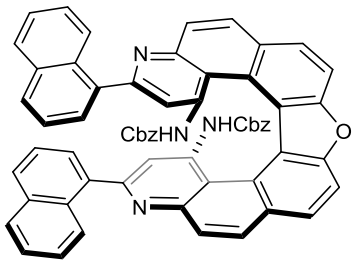
Heterohelicene 6i



Starting from 0.1 mmol of **1a**, **6i** was afforded as a yellow solid (62 mg, 51% yield). Column chromatography eluent : petroleum ether : EtOAc = 3 : 1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 – 8.00 (m, 4H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.50 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.40 – 7.30 (m, 3H), 7.28 – 7.22 (m, 1H), 7.11 (td, *J* = 7.7, 1.7 Hz, 1H), 7.06 – 6.99 (m, 2H), 6.95 (td, *J* = 7.5, 1.2 Hz, 1H), 5.96 (s, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 155.0, 150.2, 149.8, 141.3, 140.3, 134.9, 133.6, 132.1, 130.2, 129.7, 129.4, 129.2, 128.7, 128.5, 128.5, 127.4, 122.4, 121.8, 119.2, 113.8, 111.6, 107.0, 67.0. HPLC: Chiralpak IA column, 80:20 hexanes/ isopropanol, 1 ml/min, t_R = 9.3 min (major),> 99% ee. $[\alpha]_D^{25}$ = 517 (c = 1.0, $CHCl_3$). m/z HRMS (ESI) found $[M+H]^+$ 977.0994, $C_{54}H_{35}Br_2N_4O_5^+$ requires 977.0969.

Heterohelicene 6j

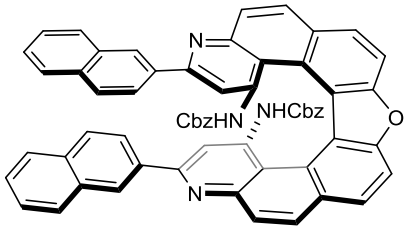


Starting from 0.1 mmol of **1a**, **6j** was afforded as a yellow solid (47 mg, 51% yield). Column chromatography eluent : petroleum ether : EtOAc = 4 : 1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 – 8.03 (m, 5H), 7.98 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.41 – 7.32 (m, 3H), 7.27 – 7.22 (m, 1H), 7.17 (ddd, *J* = 8.1, 6.6, 1.1 Hz, 1H), 7.06 (p, *J* = 3.2 Hz, 2H), 6.99 – 6.90 (m, 2H), 6.07 (s, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 12.0

Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.0, 155.1, 150.4, 149.8, 142.1, 137.2, 135.0, 133.6, 130.3, 130.0, 129.6, 129.2, 129.1, 128.5, 128.5, 128.4, 128.2, 127.5, 126.1, 125.4, 125.2, 124.4, 122.6, 119.2, 113.5, 111.5, 107.6, 66.9. HPLC: Chiralpak IA column, 70:30 hexanes/ isopropanol, 1 ml/min, t_R = 8.9 min (major), > 99% ee. $[\alpha]_D^{25}$ = 253 (c = 1.0, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 921.3093, $C_{62}H_{41}N_4O_5^+$requires 921.3071.

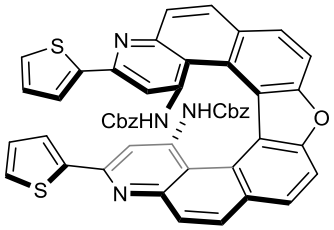
Heterohelicene 6k



Starting from 0.1 mmol of **1a**, **6k** was afforded as a yellow solid (51 mg, 55% yield). Column chromatography eluent : petroleum ether : EtOAc = 5 : 1.

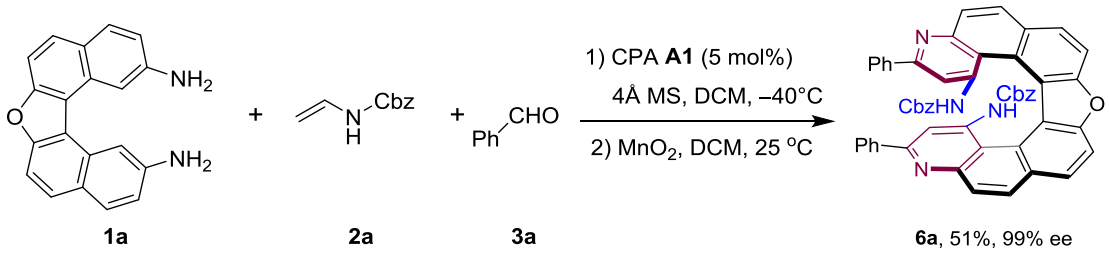
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 1.8 Hz, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 8.10 (s, 2H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.57 – 7.52 (m, 1H), 7.39 – 7.33 (m, 3H), 7.29 – 7.26 (m, 1H), 7.25 – 7.17 (m, 2H), 7.06 (d, *J* = 8.5 Hz, 3H), 5.79 (s, 1H), 4.69 (d, *J* = 11.9 Hz, 1H), 4.48 (d, *J* = 11.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 155.0, 150.4, 149.9, 141.9, 135.2, 135.0, 133.6, 132.8, 129.8, 129.3, 129.0, 128.6, 128.5, 128.5, 128.1, 127.4, 127.1, 126.9, 126.0, 125.2, 124.3, 122.2, 118.9, 114.0, 111.2, 102.9, 66.9. HPLC: Chiralpak IA column, 70:30 hexanes/ isopropanol, 1 ml/min, t_R = 12.1 min (major), 19.9 min (minor), 93% ee. $[\alpha]_D^{25}$ = 386 (c = 0.5, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 921.3090, $C_{62}H_{41}N_4O_5^+$requires 921.3071.

Heterohelicene 6l



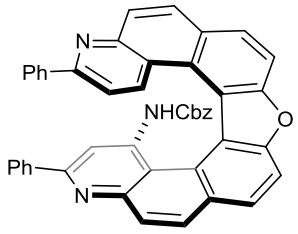
Starting from 0.1 mmol of **1a**, **6l** was afforded as a yellow solid (29 mg, 35% yield). Column chromatography eluent : petroleum ether : EtOAc = 4 : 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.01 (m, 3H), 7.96 (d, *J* = 8.9 Hz, 1H), 7.58 (s, 1H), 7.35 (p, *J* = 3.2 Hz, 3H), 7.23 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.18 – 7.13 (m, 1H), 7.04 (s, 2H), 6.68 (dd, *J* = 5.0, 3.7 Hz, 1H), 5.70 (s, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.43 (d, *J* = 12.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.0, 153.3, 150.2, 149.5, 144.6, 141.6, 135.0, 129.9, 129.3, 128.8, 128.5, 128.4, 128.1, 127.8, 126.5, 122.0, 118.7, 114.0, 111.1, 101.5, 66.9. Chiralpak IA column, 70:30 hexanes/ isopropanol, 1 ml/min, t_R = 13.2 min (major), > 99% ee. $[\alpha]_D^{25}$ = 751 (c = 0.5, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 833.1909, $C_{50}H_{33}N_4O_5S_2^+$requires 833.1887.



Scheme S2. One-pot asymmetric synthesis of azahelicene 6a via sequential bis-Povarov reaction and oxidative aromatization.

Thermal racemization study of helicene product 5a and 6a

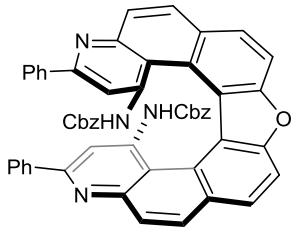


5a

Thermal racemization of **5a** at 150°C (in mesitylene)

Time/s	ee (%) of **5a**
0	99.2
1800	99.3
3600	99.5
7200	99.0
21600	98.7
43200	99.2
86400	99.0
172800	99.5

259200	98.6
432000	98.9

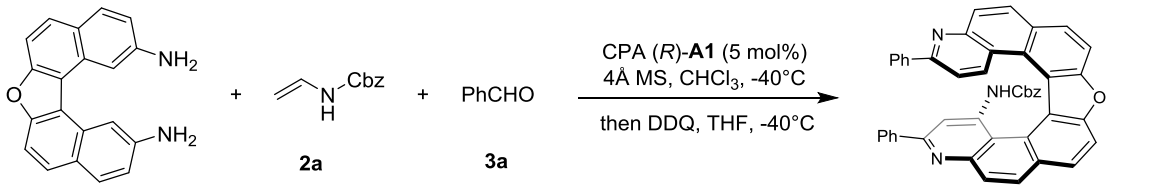


6a

Thermal racemization of **6a** at 150°C (in mesitylene)

Time/s	ee (%) of **6a**
0	98.5
1800	98.4
3600	98.7
7200	98.5
21600	98.4
43200	98.5
86400	98.3
172800	98.6
259200	98.1
432000	98.2

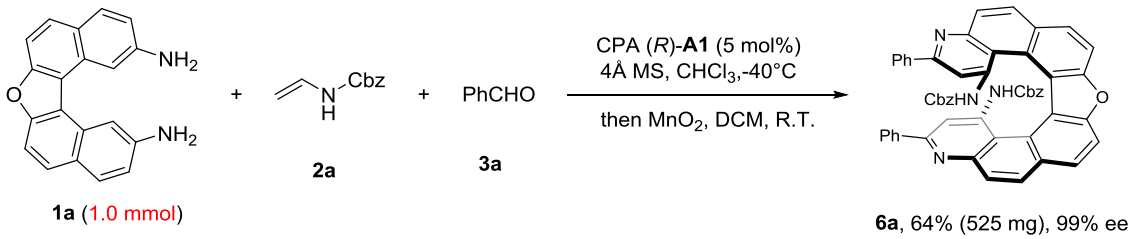
Large-scale asymmetric synthesis of 5a and 6a



1a (1.0 mmol) **2a** **3a** **5a**, 77% (517 mg), 99% ee

Diamine **1a** (1 mmol), CPA (*R*)-**A9** (0.05 mmol, 5 mol%) and activated 4Å molecular sieves (ca. 500 mg) were placed in a reaction tube and $CHCl_3$ (15 mL) was added into this reaction mixture via syringe, which was followed by adding benzaldehyde **3a** (4 mmol, 4.0 equiv.) at rt. After stirring at rt for about 0.5 h, the reaction mixture was cooled to -40 ℃, and a solution of enamide **2** (4 mmol, 4.0 equiv.) in $CHCl_3$ (5 mL) was added slowly into the reaction mixture via syringe. After stirring at the same temperature for additional 24 h, the mixture was concentrated under vacuum to give a residue. The residue was dissolved in THF (15 mL) and then cooled to -40 °C. Then a solution of

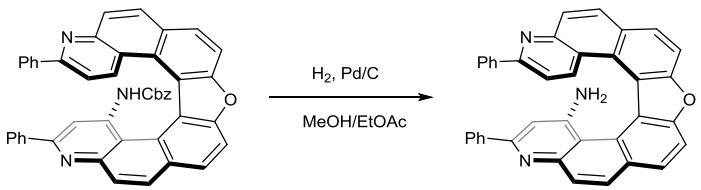
1,2-dichloro-4,5-dicyanobenzoquinone (DDQ, 6 mmol, 6.0 equiv.) in THF (5 mL) was added and the mixture was allowed to stir at −40 °C for another 24 h. After that, this mixture was warmed to room temperature and washed with saturated aqueous $NaHCO_3$ and extracted with EtOAc for 3 times. The combine organic layers were then, dried over Na_2SO_4 and concentrated under vacuum to give a residue, which was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to afford the *(P)*-**5a** as a yellow solid (517 mg, 77% yield, 99% ee).



1a (1.0 mmol) **2a** **3a** **6a**, 64% (525 mg), 99% ee

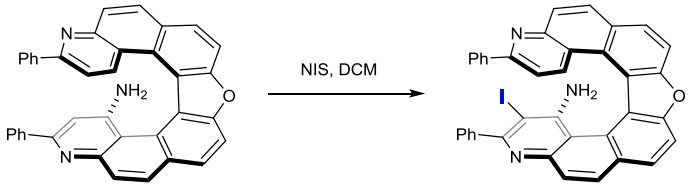
Diamine **1a** (1 mmol), CPA (*R*)-**A9** (0.05 mmol, 5 mol%) and activated 4Å molecular sieves (ca. 500 mg) were placed in a reaction tube and $CHCl_3$ (15 mL) was added into this reaction mixture via syringe, which was followed by adding benzaldehyde **3a** (4 mmol, 4.0 equiv.) at rt. After stirring at rt for about 0.5 h, the reaction mixture was cooled to -40 ℃, and a solution of enamide **2a** (4 mmol, 4.0 equiv.) in $CHCl_3$ (5 mL) was added slowly into the reaction mixture via syringe. After stirring at the same temperature for additional 24 h, the mixture was concentrated under vacuum to give a residue. The residue was dissolved in DCM (50 mL), and added MnO_2 (100 mmol, 100 equiv.) at rt. After stirring for another 48 h at rt, the mixture was filtered through Celite and concentrated under vacuum to give a residue, which was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1) to afford the *(P)*-**6a** as a yellow solid (525 mg, 64% yield, 99% ee).

Derivatizations of the chiral azahelicene products



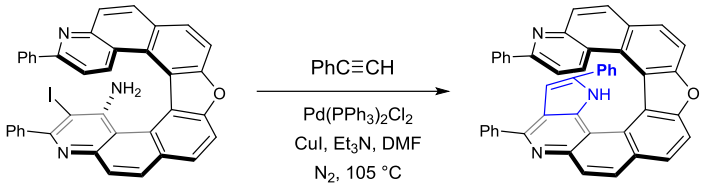
5a, 99% ee **7a,** 90% yield, 99% ee

To a solution of **5a** (50 mg, 0.0745 mmol) in MeOH/EtOAc (5 mL/1 mL) was added Pd/C (ca. 10 mg, 10% Pd, 55 wt% H_2O) at rt. After stirring under H_2 atmosphere (1.0 atm, balloon) for 18 h at rt, the mixture was filtered through Celite. The filtrate was concentrated under vacuum to give a residue, which was purified by column chromatography on silica gel using petroleum ether/ethyl acetate = 3:1 as eluent to afford **7a** as a yellow solid (36 mg, 90% yield, 99% ee). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 – 8.06 (m, 8H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.18 – 7.03 (m, 6H), 6.61 (d, *J* = 8.4 Hz, 1H), 5.89 (s, 1H), 3.45 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0, 155.9, 155.3, 151.3, 147.5, 138.5, 134.6, 130.9, 130.8, 128.9, 128.8, 128.6, 128.3, 128.2, 127.6, 127.4, 127.4, 127.3, 123.5, 122.6, 119.0, 118.3, 114.6, 113.9, 111.4, 110.9, 101.1.Chiralpak IA column, 70:30 hexanes/ isopropanol, 1 ml/min, t_R = 5.7 min (major), 9.8 min (minor), 99% ee. $[\alpha]_D^{25}$ = 1396 (c = 1.0, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 538.1918, $C_{38}H_{24}N_3O^+$requires 538.1914.



7a, 99% ee **8a,** 62% yield, 99% ee

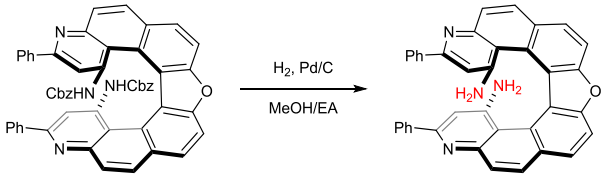
To a solution of **7a** (97 mg, 0.18 mmol) in DCM (10 mL) was added NIS (45 mg, 0.2 mmol, 1.1 equiv.) at rt. After stirring at rt for 15 h, the mixture was concentrated under vacuum to give a residue, which was purified by column chromatography on silica gel using dichloromethane/ethyl acetate = 50/1 as eluent to afford **8a** as a brown solid (74 mg, 62% yield, 99% ee).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 – 8.16 (m, 5H), 8.11 (d, *J* = 8.4 Hz, 1H), 8.07 (td, *J* = 5.4, 3.1 Hz, 4H), 7.47 – 7.37 (m, 3H), 7.23 – 7.14 (m, 4H), 7.01 (dd, *J* = 8.5, 6.7 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 1H), 4.26 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5, 156.6, 156.1, 155.3, 150.5, 148.5, 147.6, 142.2, 138.9, 134.6, 131.3, 131.0, 129.5, 129.4, 128.9, 128.8, 128.2, 127.8, 127.7, 127.5, 127.3, 123.2, 122.1, 118.7, 118.3, 113.8, 113.0, 111.5. Chiralpak IA column, 70:30 hexanes/ isopropanol, 1 ml/min, t_R = 8.3 min (major), 9.7 min (minor), 99% ee. $[\alpha]_D^{25}$ = 1601 (c = 1.0, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 664.0881, $C_{38}H_{23}IN_3O^+$requires 664.0880.



8a, 99% ee

9a, 61% yield, 99% ee

Under N_2 atmosphere, **8a** (20 mg, 0.03 mmol), phenylacetylene (8 μL, 0.075 mmol, 2.5 equiv.), $Pd(PPh_3)_2Cl_2$ (4.2 mg, 20 mol%), CuI (2.3 mg, 40 mol%) and Et_3N (12.5 μL, 0.09 mmol, 3.0 equiv.) were dissolved in DMF (1 mL), and the mixture was placed into 105℃ oil bath and was allowed to stirred for 12 h. After the completion of this reaction, the mixture was cooled to rt and diluted with EtOAc, washed by brine, dried over Na_2SO_4 and concentrated under vacuum to give a residue, which was purified by column chromatography on silica gel using petroleum ether/ethyl acetate = 3/1 as eluent to afford **9a** as a yellow solid (12 mg, 61% yield, 99% ee). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.36 (d, *J* = 8.5 Hz, 1H), 8.32 – 8.19 (m, 4H), 7.85 – 7.71 (m, 8H), 7.50 (s, 1H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.22 (dt, *J* = 11.8, 7.8 Hz, 5H), 7.17 – 7.06 (m, 3H), 6.54 – 6.48 (m, 2H), 6.45 – 6.39 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.8, 156.6, 155.7, 147.5, 138.6, 136.7, 135.4, 134.5, 130.3, 130.0, 129.3, 129.1, 129.0, 128.8, 128.5, 128.3, 128.2, 128.1, 127.7, 127.4, 124.2, 122.0, 121.6, 119.5, 118.0, 117.7, 113.7, 113.3, 112.0, 111.7, 99.6. Chiralpak IB column, 80:20 hexanes/ isopropanol, 1 ml/min, t_R = 27.0 min (major), 20.4 min (minor), 99% ee. $[\alpha]_D^{25}$ = 1516 (c = 0.5, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 638.2230, $C_{46}H_{28}N_3O^+$requires 638.2227.

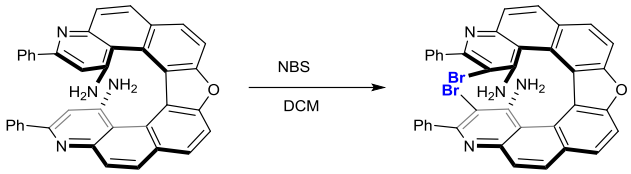


6a, 99% ee

10a, 98% yield, 99% ee

To a solution of **6a** (200 mg, 0.244 mmol) in MeOH/EA (10 mL/5 mL) was added Pd/C (ca. 30 mg, 10% Pd, 55 wt% H_2O) at rt. After stirring under H_2 atmosphere (1.0 atm, balloon) for 12 h at rt, the mixture was filtered through Celite. The filtrate was concentrated under vacuum to give a residue, which was triturated with DCM and filtered to afford **10a** as a light yellow solid (132 mg, 98% yield, 99% ee). ^{1}H NMR (500 MHz, MeOD) δ 8.28 (d, *J* = 8.5 Hz, 1H), 8.18 (d, *J* = 8.9 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.9 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.21 – 7.14 (m, 1H), 7.11 – 7.06 (m, 2H), 6.11 (s, 1H), 5.49 (s, 2H). ***Due to the compound's poor solubility in various deuterated solvents, its ^{13}C NMR***

spectrum was not recorded. Chiralpak IA column, 70:30 hexanes/ isopropanol, 1 ml/min, t_R = 5.6 min (major), > 99% ee. $[\alpha]_D^{25}$ = 859 (c = 0.1, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 553.2028, $C_{38}H_{25}N_4O^+$requires 553.2023.



10a, 99% ee **11a**, 61% yield, 99% ee

To a solution of **10a** (20 mg, 0.036 mmol) in DCM (2 mL) was added NBS (14 mg, 0.0792 mmol, 2.2 equiv.) at rt. After stirring at rt for 5.5 h, the mixture was concentrated under vacuum to give a residue, which was purified by column chromatography on silica gel using petroleum ether/ethyl acetate = 3/1 as eluent to afford **11a** as an orange solid (15.5 mg, 61% yield, 99% ee).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 8.8 Hz, 1H), 8.11 (dd, *J* = 8.6, 7.1 Hz, 2H), 7.65 – 7.58 (m, 2H), 7.37 – 7.30 (m, 1H), 7.24 – 7.15 (m, 2H), 3.97 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0, 154.9, 148.1, 147.6, 139.6, 130.7, 130.6, 128.9, 128.5, 128.2, 128.1, 127.5, 124.5, 118.7, 112.6, 110.7, 100.6. Chiralpak IA column, 80:20 hexanes/ isopropanol, 1 ml/min, t_R = 11.7 min (major), 18.0 min (minor), 99% ee. $[\alpha]_D^{25}$ = 1581 (c = 1, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 709.0232, $C_{38}H_{23}Br_2N_4O^+$requires 709.0233.

Optical properties of the products

Unless otherwise noted, CD analysis, absorbance analysis and fluorescence analysis were performed at 20 ℃ with 1.0 cm x 1.0 cm quartz cell.

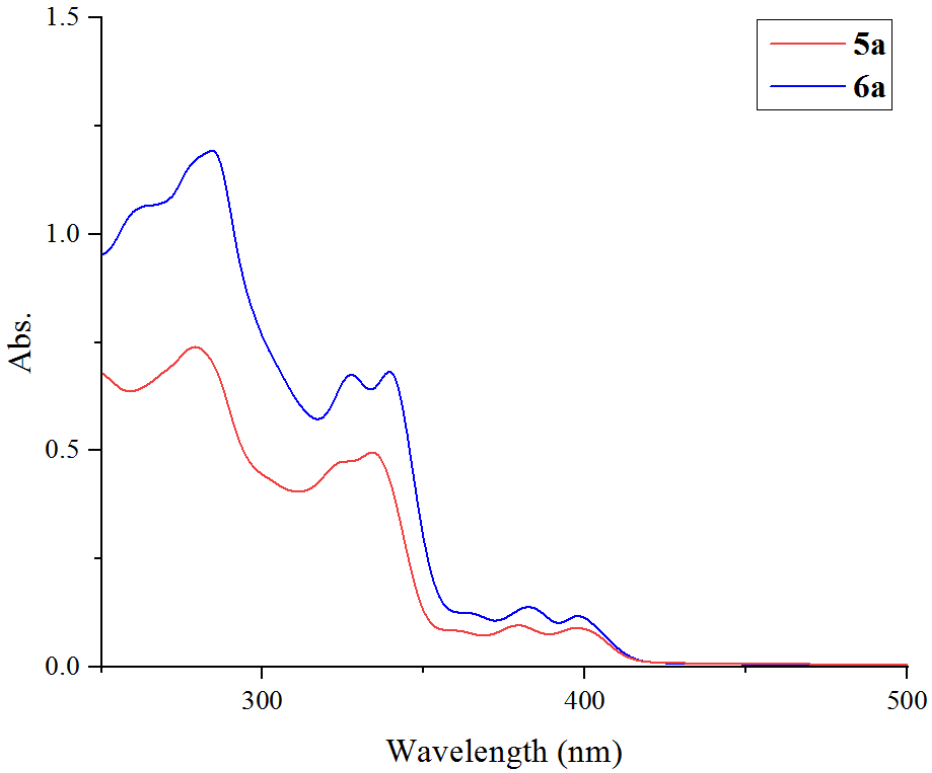


Figure S1. UV/vis absorbance spectra for **5a** and **6a** measured in DCM (1.0×10^{-4} M).

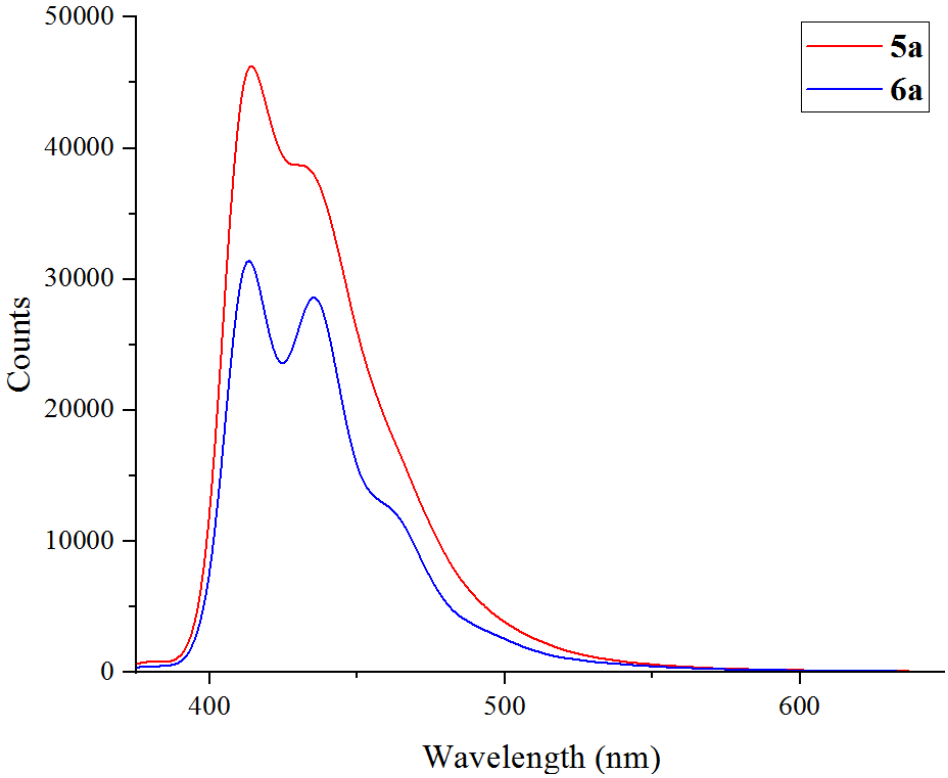


Figure S2. Fluorescence spectra for **5a** and **6a** measured at in dichloromethane (1.0×10^{-4} M , excited by 350nm).

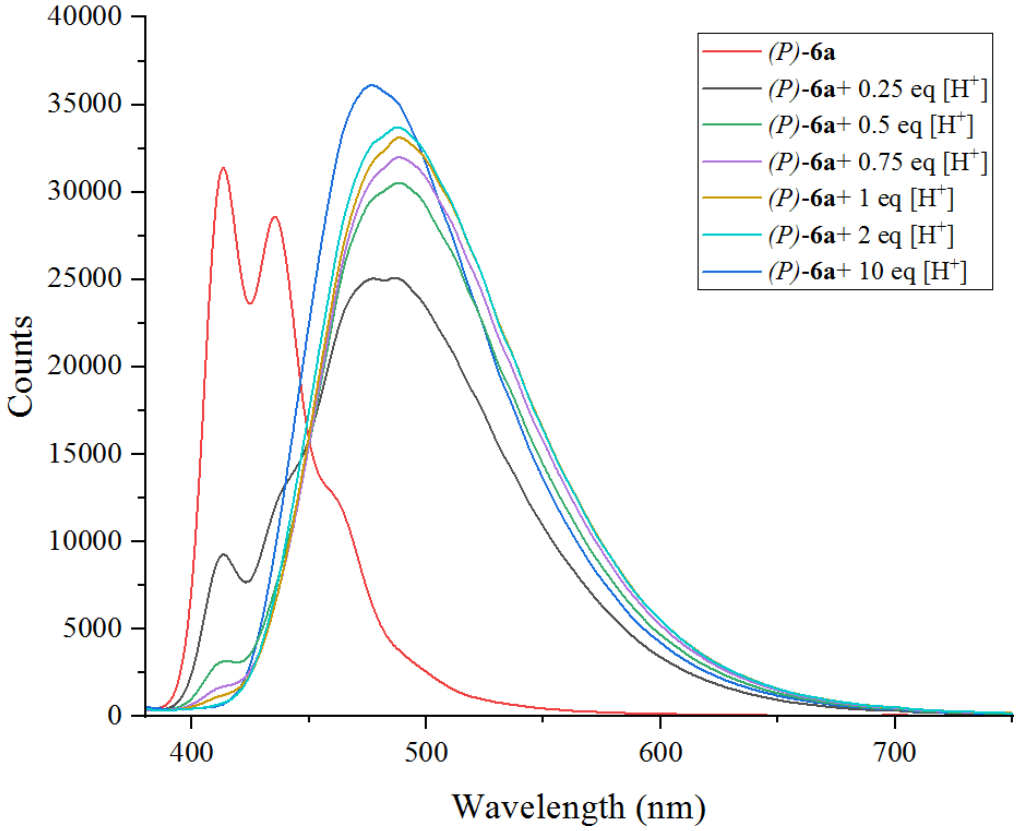


Figure S3. Fluorescence spectra for **5a** and *(P)*-**5a**+[H^+] measured at in dichloromethane (1.0×10^{-4} M , excited by 350nm).

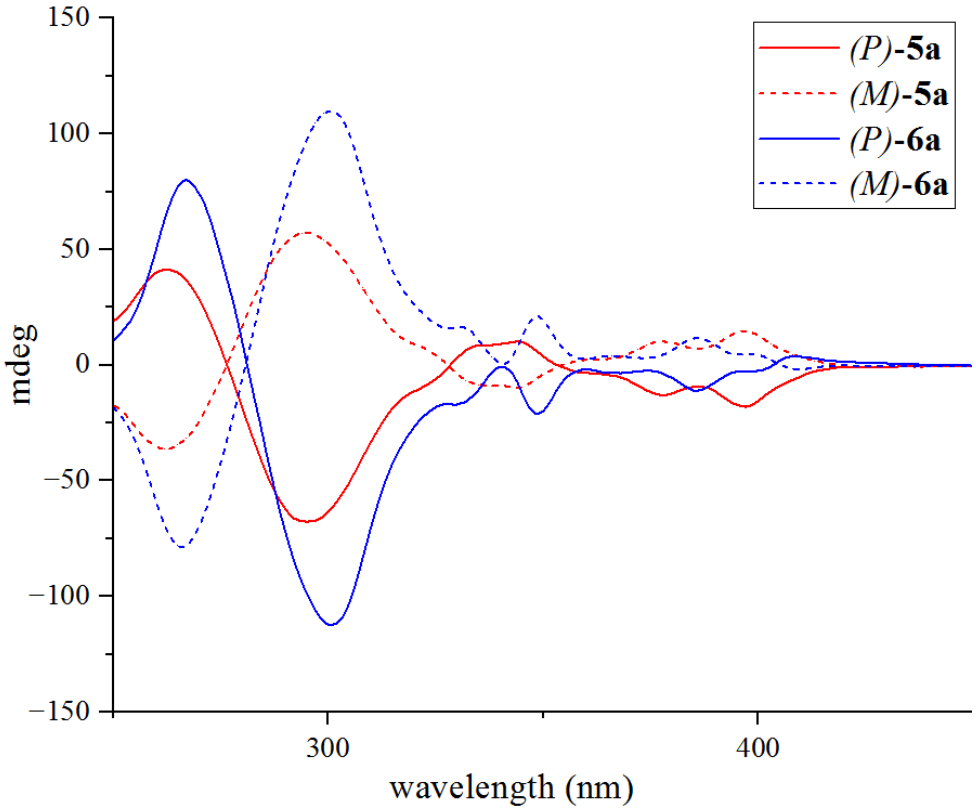


Figure S4. CD spectra of *(P)*/*(M)*-**5a** and *(P)*/*(M)*-**6a** in dichloromethane (1.0×10^{-4} M).

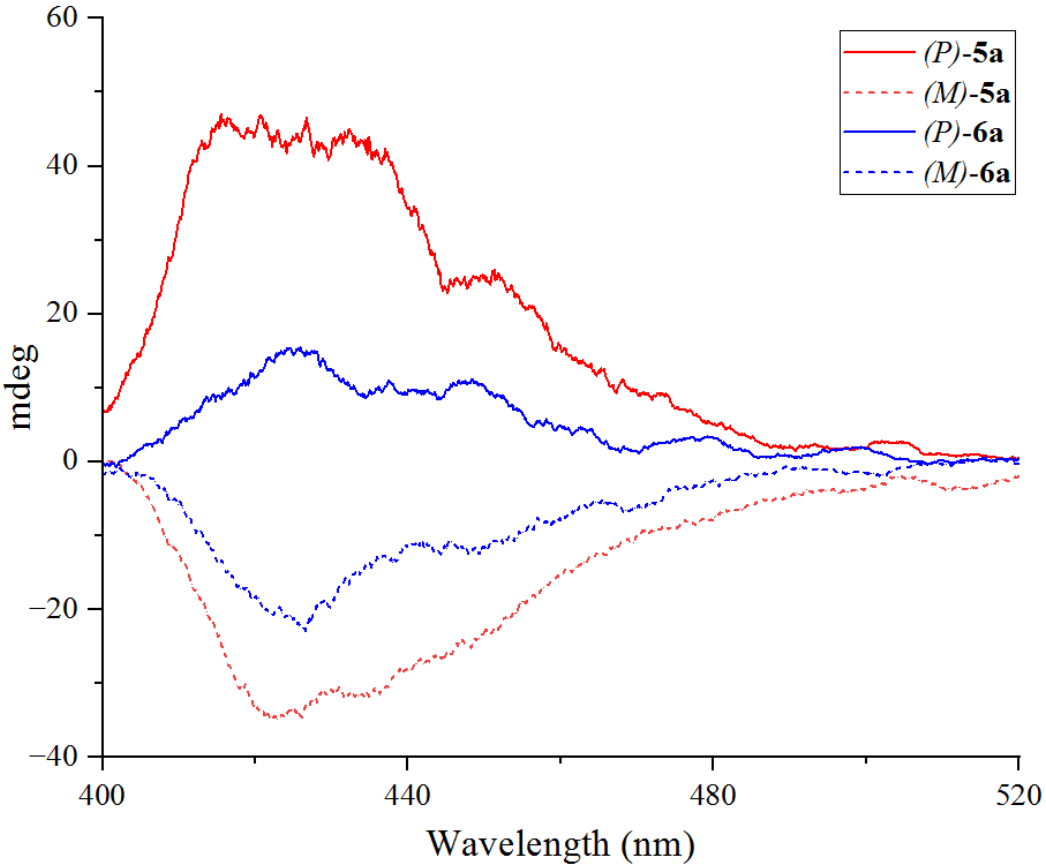


Figure S5. CPL spectra of *(P)/(M)*-**5a** and *(P)/(M)*-**6a** in DCM (1.0×10^{-4} M).

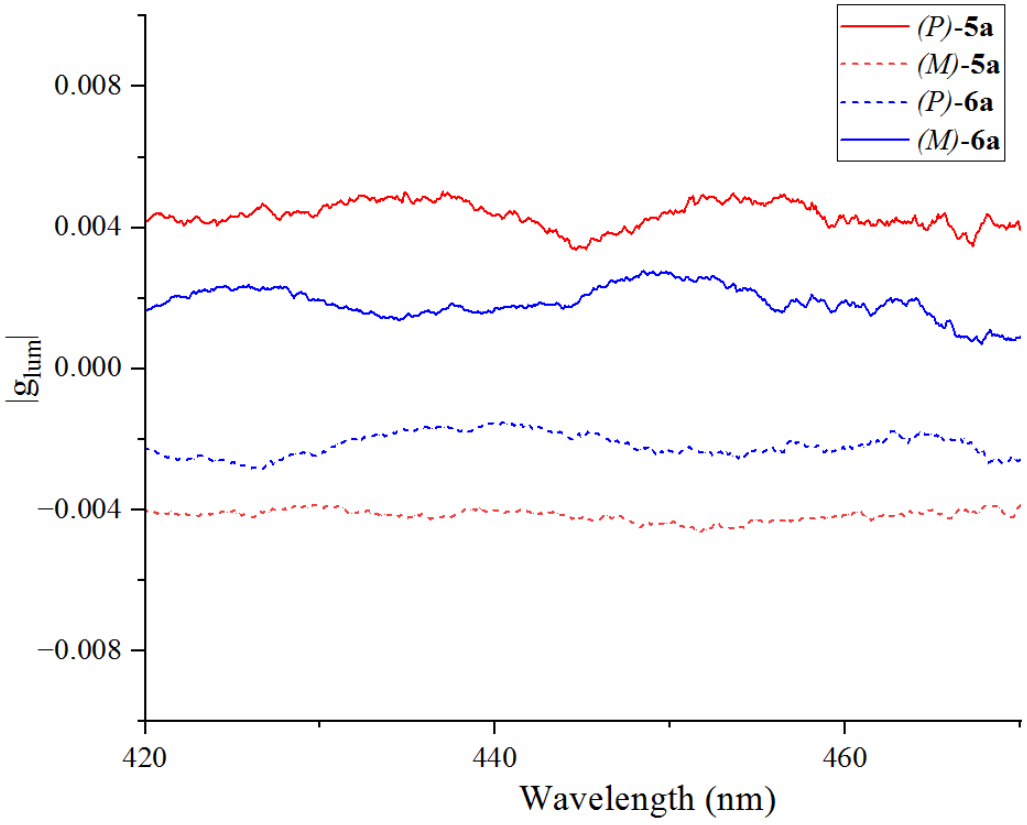


Figure S6. Dissymmetry values of azahelicenes *(P)/(M)*-**5a** and *(P)/(M)*-**6a**

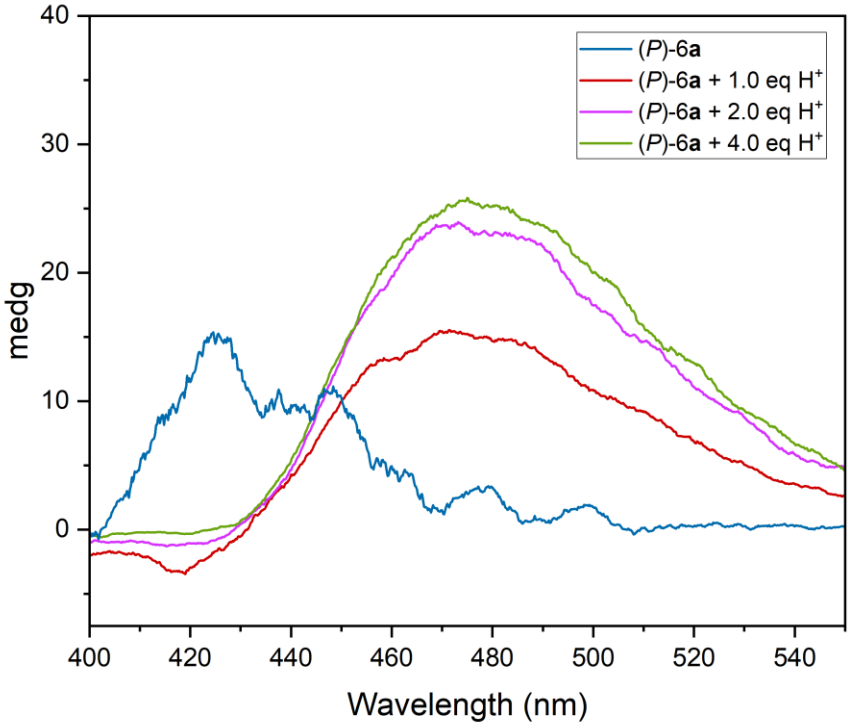


Figure S7. CPL spectra of *(P* **-6a** in DCM (1.0×10^{-4} M) with addition of TFA.

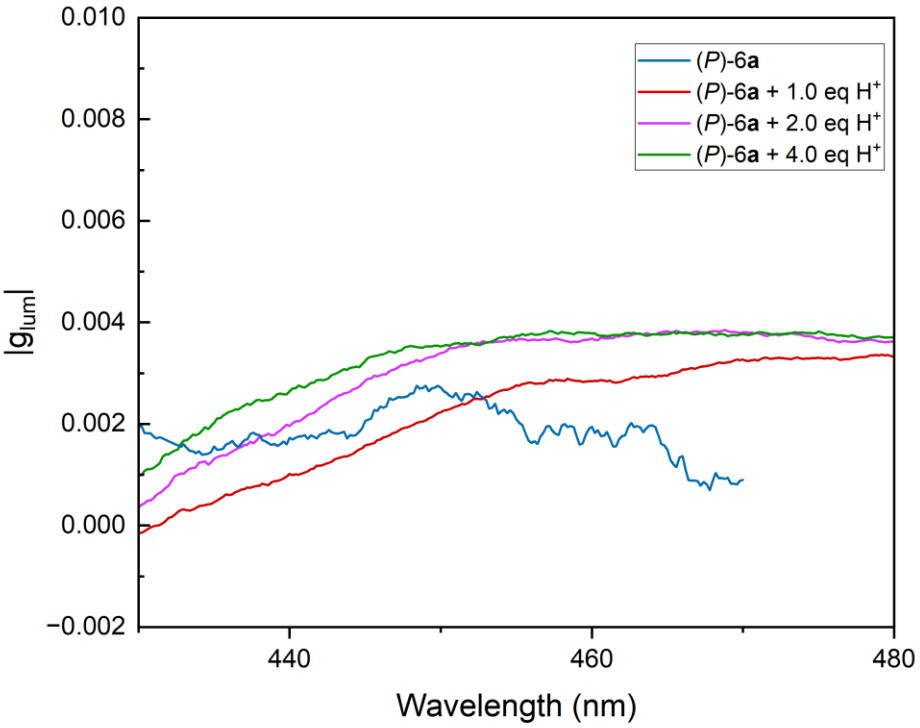


Figure S8. Dissymmetry values of azahelicenes *(P)* **6a** with addition of TFA.

Reference

1. Areephong, J.; Ruangsupapichart, N.; Thongpanchang, T., A concise synthesis of functionalized 7-oxa-[5]-helicenes. *Tetrahedron Letters* **2004,** *45* (15), 3067-3070.

2. Chang, X.; Zhang, Q.; Guo, C., Switchable Smiles Rearrangement for Enantioselective O-Aryl Amination. *Org Lett* **2019,** *21* (12), 4915-4918.

3. Hoang, T. T.; Smith, T. P.; Raines, R. T., A Boronic Acid Conjugate of Angiogenin that Shows ROS-Responsive Neuroprotective Activity. *Angew Chem Int Ed* **2017,** *56* (10), 2619-2622.

X-ray structure

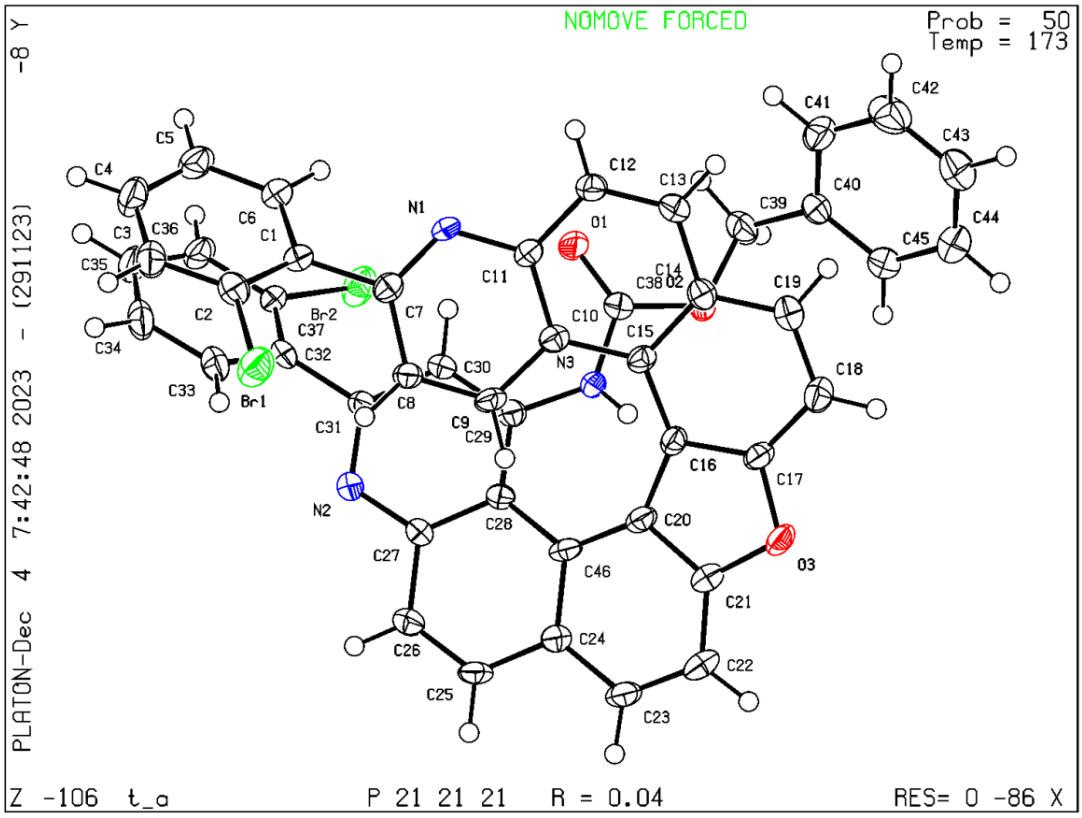


Figure S9. X-ray structure of (*P*)-**5i** (CCDC number 2401332)

Table S1 Crystal data and structure refinement for *(P)*-5i.

Identification code	t_a
Empirical formula	$C_{46}H_{27}Br_2N_3O_3$
Formula weight	829.52
Temperature/K	173(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.1539(4)
b/Å	11.8063(5)
c/Å	29.1718(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3497.1(2)
Z	4
ρ_{calc}g/cm^3	1.576
μ/mm^{-1}	3.338
F(000)	1672.0
Crystal size/mm^3	0.160 × 0.150 × 0.120
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.078 to 137.714
Index ranges	$-12 \le h \le 12$, $-13 \le k \le 14$, $-35 \le l \le 34$
Reflections collected	43860
Independent reflections	6434 [R_{int} = 0.0695, R_{sigma} = 0.0421]
Data/restraints/parameters	6434/0/490
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0441, wR_2 = 0.1085
Final R indexes [all data]	R_1 = 0.0478, wR_2 = 0.1110
Largest diff. peak/hole / e Å^{-3}	0.40/-0.86
Flack parameter	0.065(8)

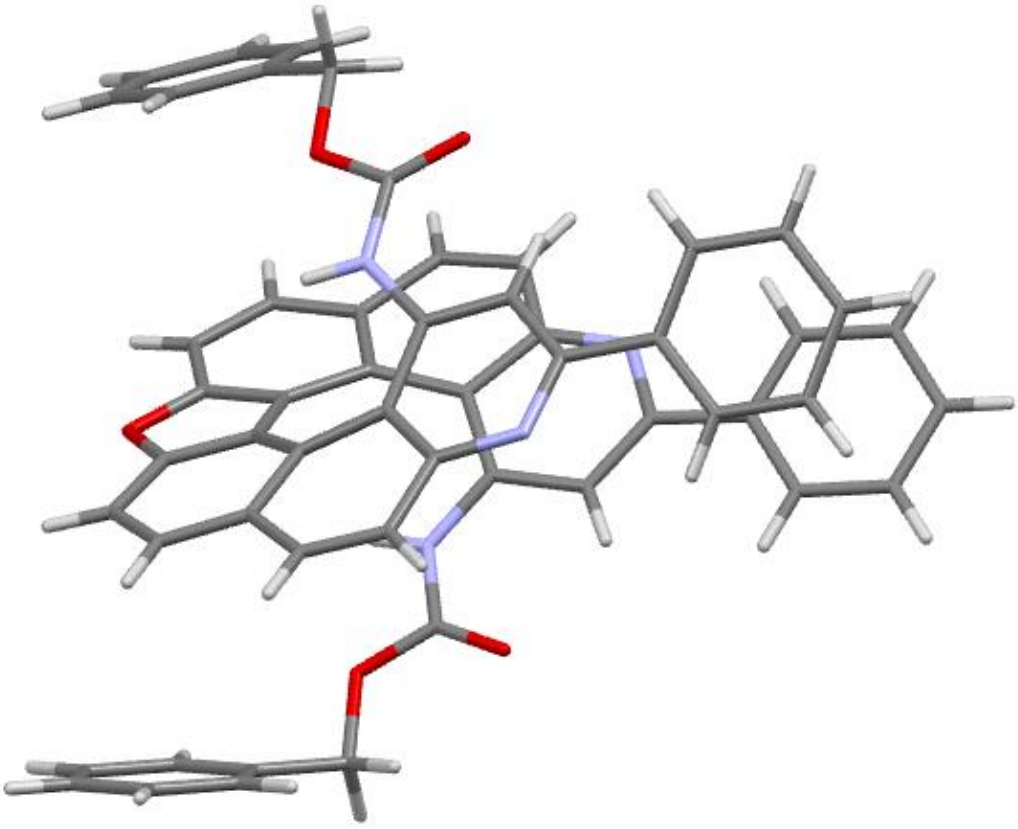


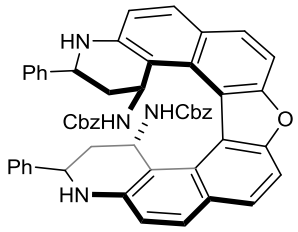
Figure S10. X-ray structure of **6a** (CCDC number 2401205)

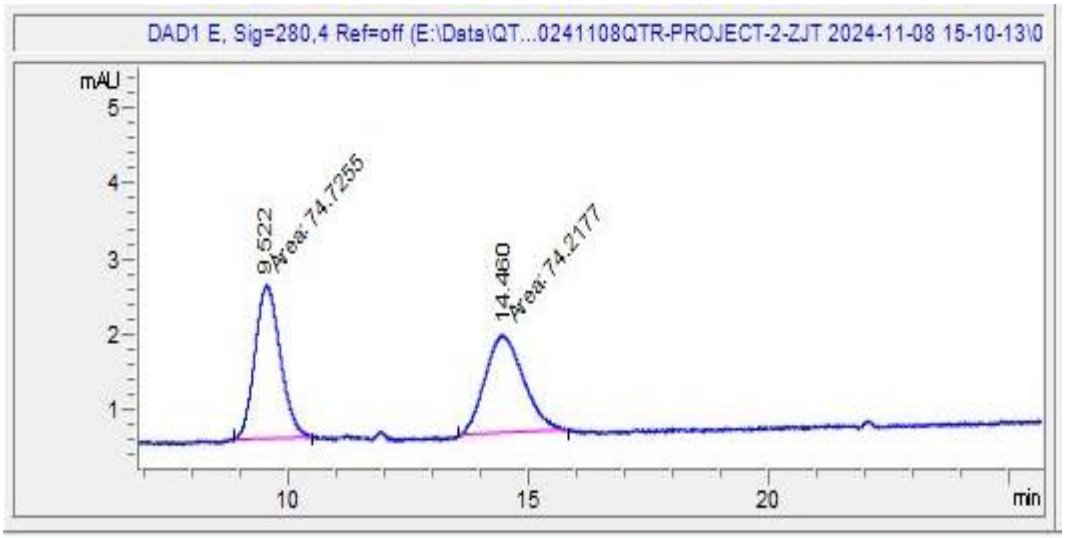
Table S2. Crystal data and structure refinement for 6a

Identification code	t
Empirical formula	$C_{54}H_{36}N_4O_5$
Formula weight	820.87
Temperature/K	173.00
Crystal system	orthorhombic
Space group	$P2_12_12$
a/Å	21.7158(6)
b/Å	40.9507(11)
c/Å	14.8230(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	13181.8(6)
Z	12
ρ_{calc}g/cm^3	1.241
μ/mm^{-1}	0.645
F(000)	5136.0
Crystal size/mm^3	0.14 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.316 to 137.11
Index ranges	-25 ≤ h ≤ 26, -49 ≤ k ≤ 49, -17 ≤ l ≤ 17
Reflections collected	147661
Independent reflections	24194 [R_{int} = 0.0874, R_{sigma} = 0.0552]
Data/restraints/parameters	24194/711/1788
Goodness-of-fit on F^2	1.008
Final R indexes [I>=2σ (I)]	R_1 = 0.0789, wR_2 = 0.2109
Final R indexes [all data]	R_1 = 0.1110, wR_2 = 0.2423
Largest diff. peak/hole / e Å^{-3}	0.76/-0.44
Flack parameter	2.19(9)

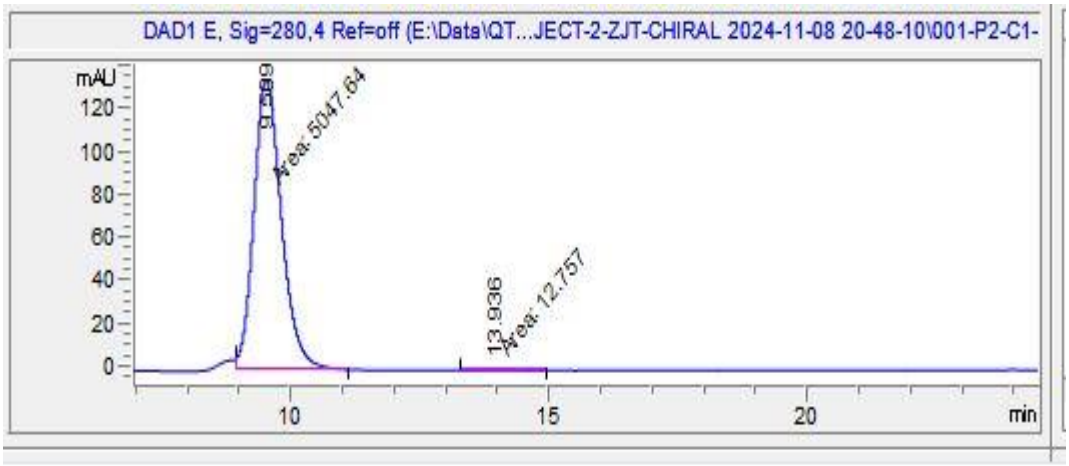
HPLC traces

Helicenoid 4a



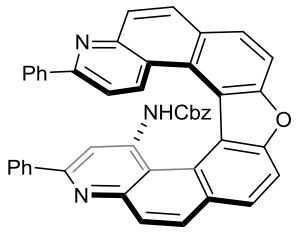


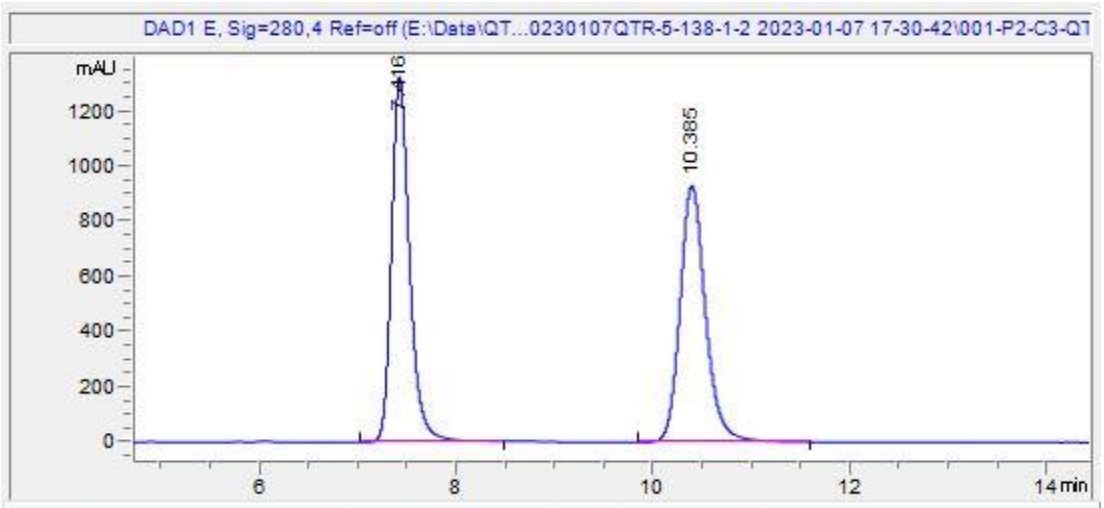
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.522	MM	74.7	2	0.6103	50.170	0.766
2	14.46	MM	74.2	1.3	0.9416	49.830	0.885



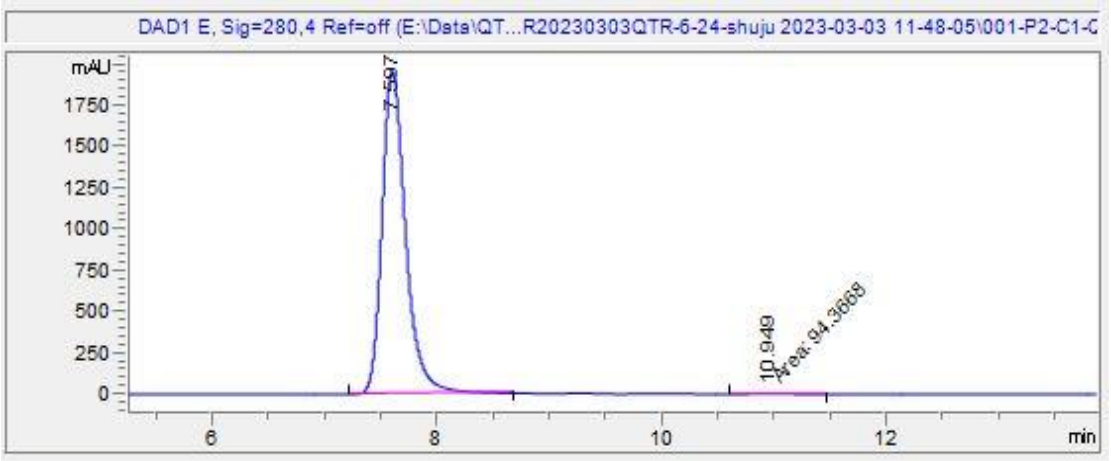
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.509	FM	5047.6	135.3	0.6218	99.748	0.791
2	13.936	MM	12.8	2.8E-1	0.7553	0.252	1.081

Heterohelicene 5a



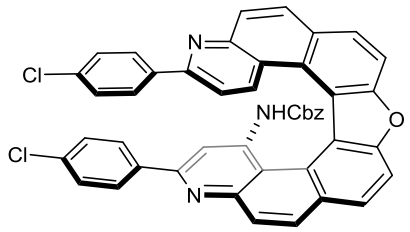


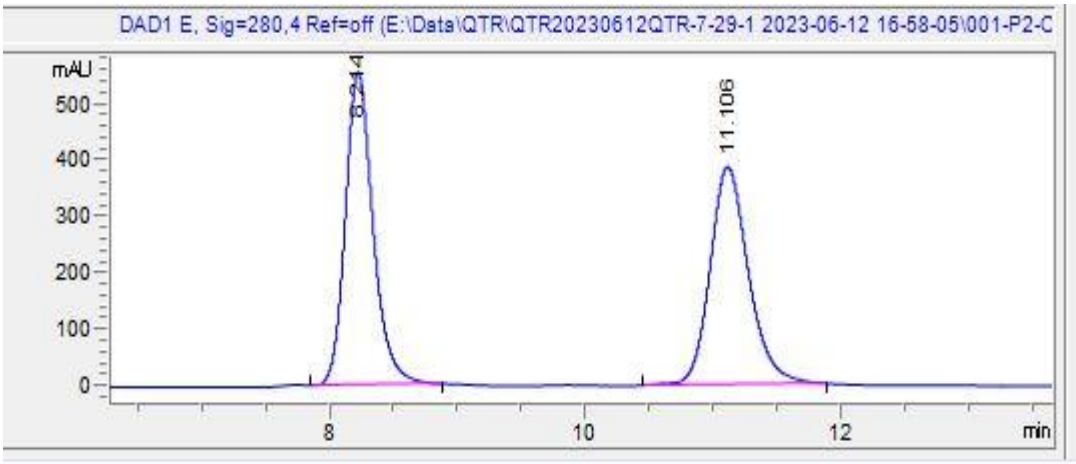
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.416	VVR	16840.4	1327.8	0.1823	50.059	0.748
2	10.385	BVR	16800.7	932.9	0.2461	49.941	0.809



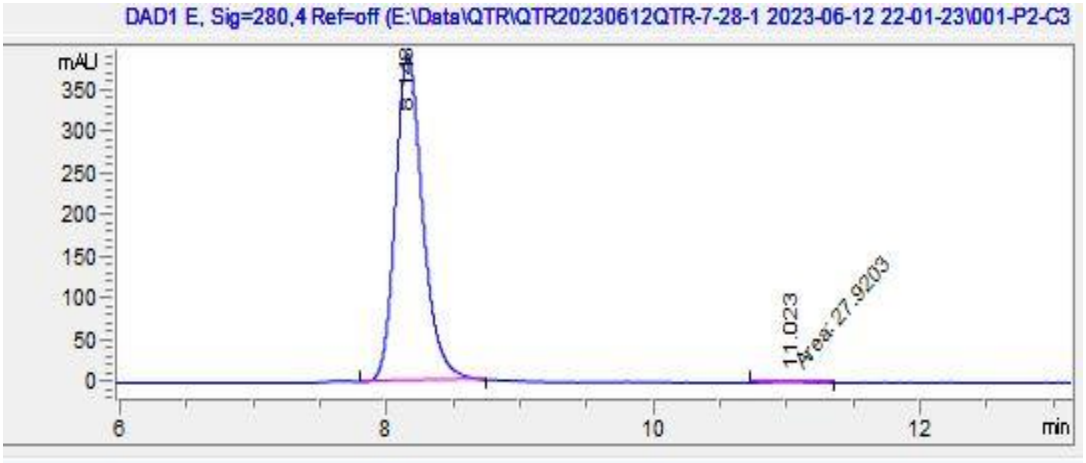
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.597	BVR	28681	1951.2	0.177	99.672	0.704
2	10.949	MM	94.4	4.5	0.3506	0.328	0.787

Heterohelicene 5b



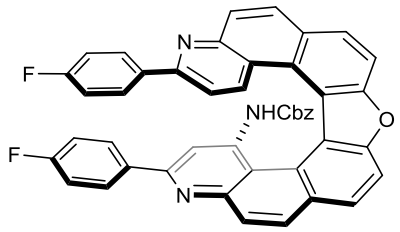


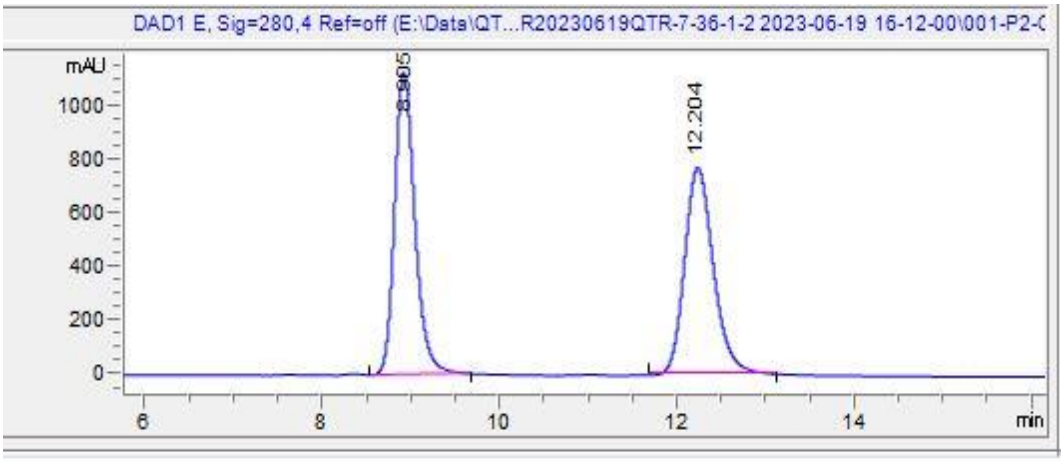
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.214	BV R	8363	553.1	0.1799	50.875	0.805
2	11.106	VV R	8075.3	385.6	0.2464	49.125	0.817



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.148	BV R	5577.1	390.6	0.1686	99.502	0.791
2	11.023	MM	27.9	1.5	0.3035	0.498	1.131

Heterohelicene 5c





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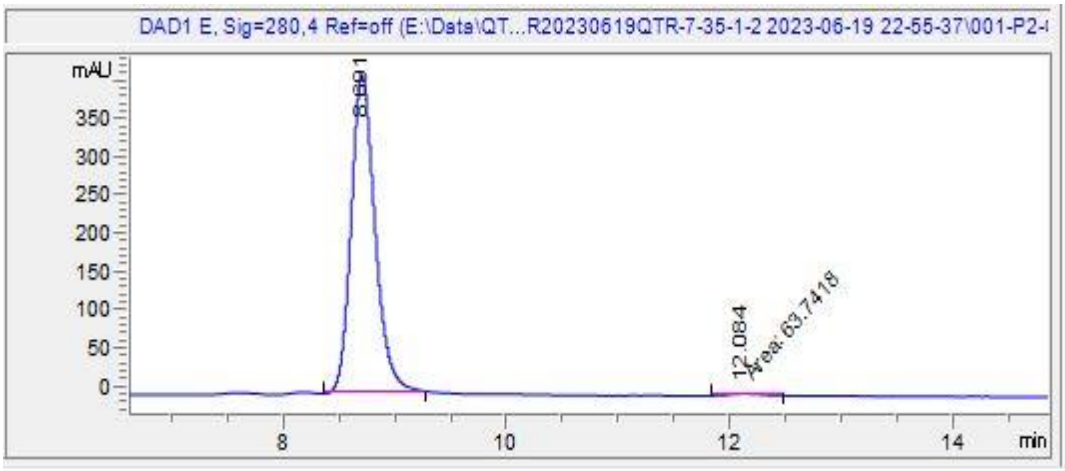
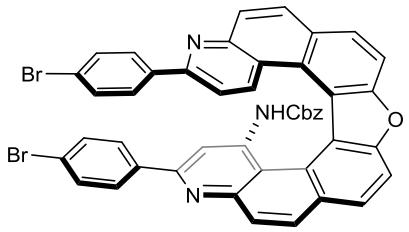
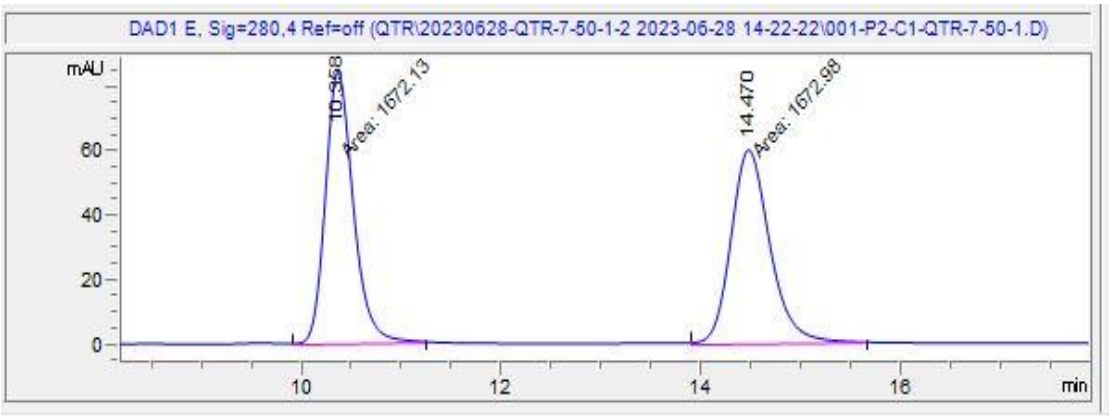
1	8.905	BV R	17992.7	1133.3	0.1887	50.576	0.845
2	12.204	BV R	17582.8	776.2	0.2663	49.424	0.777



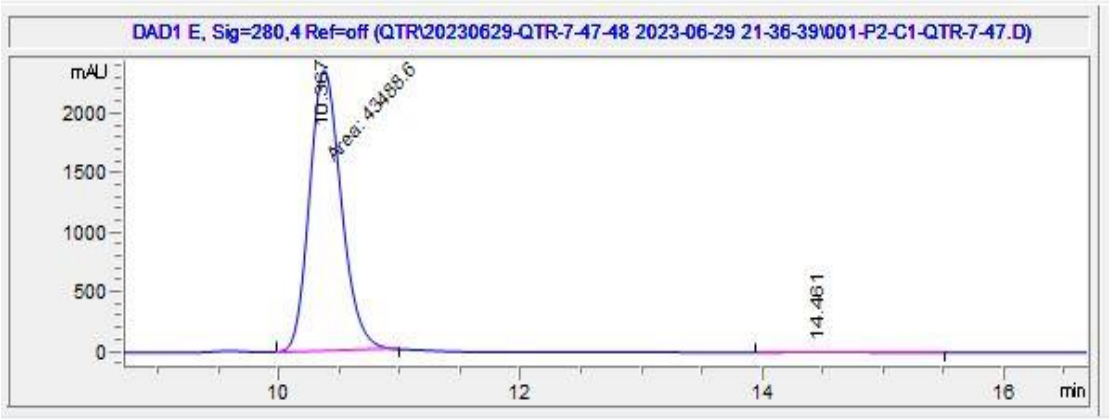
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.691	BV R	6249.4	416.7	0.1805	98.990	0.82
2	12.084	MM	63.7	3.6	0.2981	1.010	0.649

Heterohelicene 5d



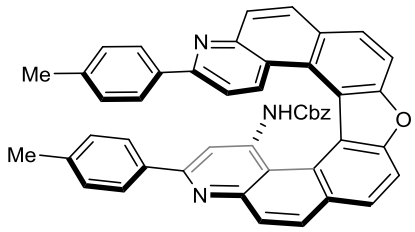


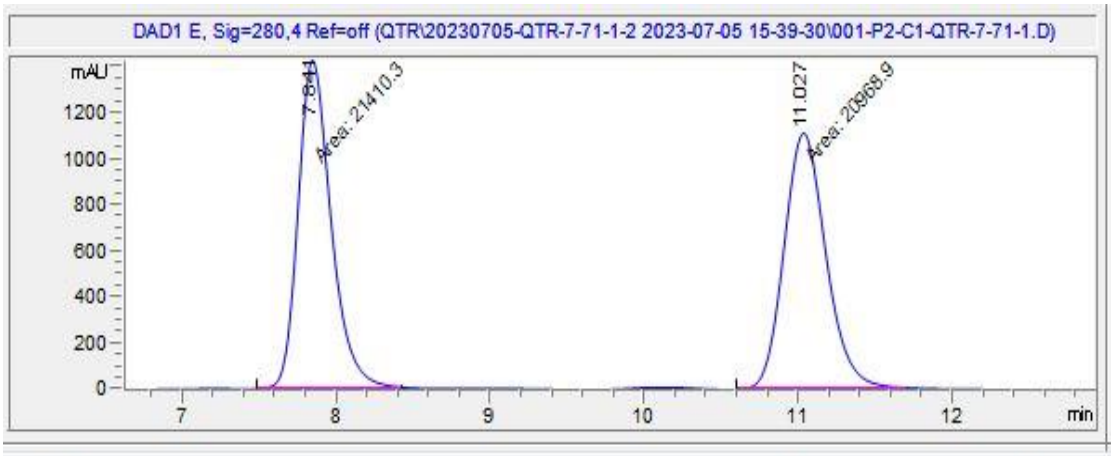
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	10.358	1672.1	84.9	0.3284	49.987	0.781	MM	MM
2	14.47	1673	60.5	0.4606	50.013	0.795	MM	MM



#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	10.367	43488.6	2358.6	0.3073	99.760	0.833	MM	MM
2	14.461	104.8	3.6	0.4338	0.240	0.671	BB	BB

Heterohelicene 5e





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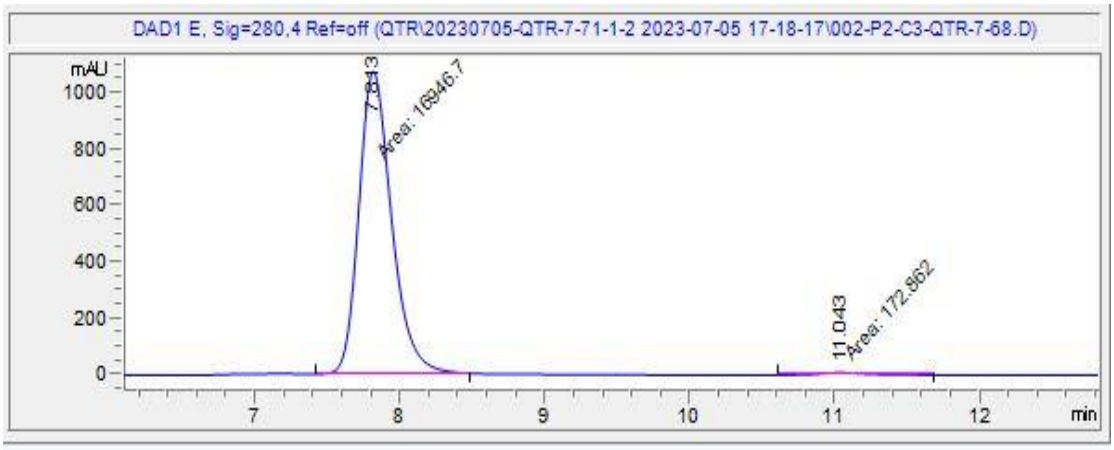
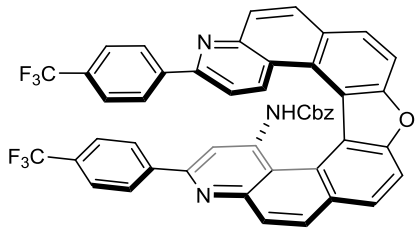
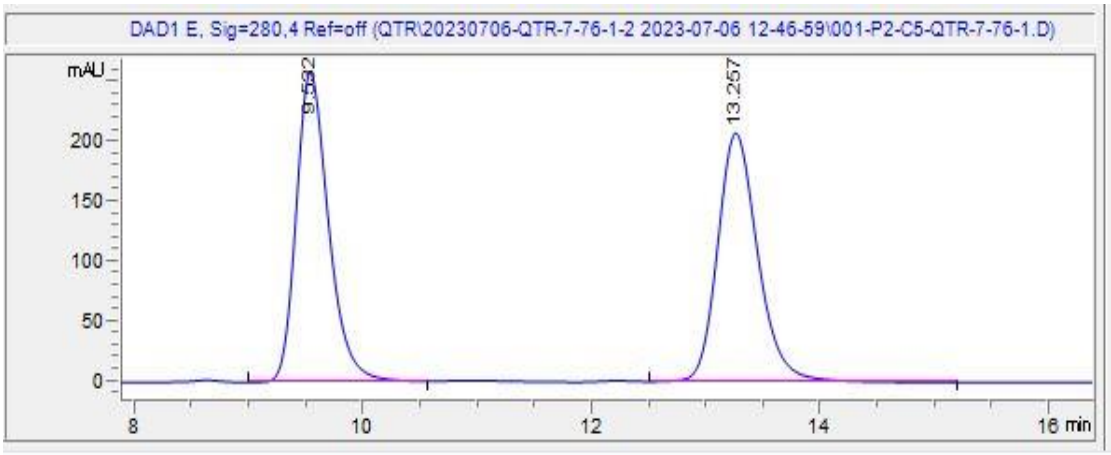
1	7.841	21410.3	1426.4	0.2502	50.521	0.746	MM	MM
2	11.027	20968.9	1109.1	0.3151	49.479	0.845	MM	MM



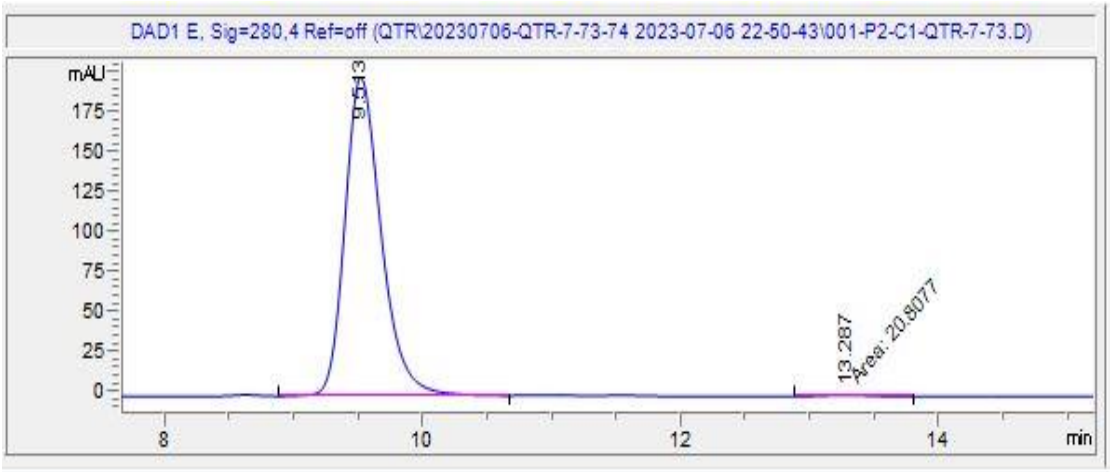
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	7.813	16946.7	1070.1	0.2639	98.990	0.757	MM	MM
2	11.043	172.9	8.1	0.354	1.010	0.768	MM	MM

Heterohelicene 5f



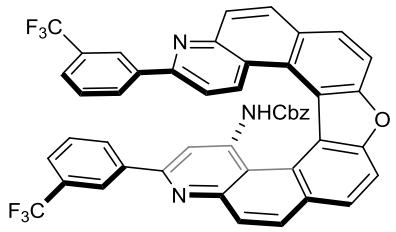


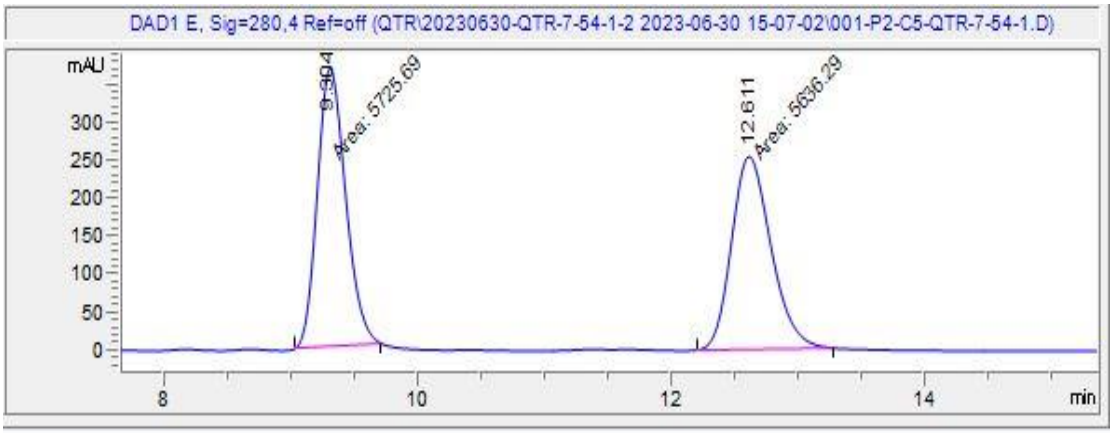
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	9.532	5067.7	257.2	0.3019	49.995	0.728	BB	BB
2	13.257	5068.6	206.8	0.374	50.005	0.779	BB	BB



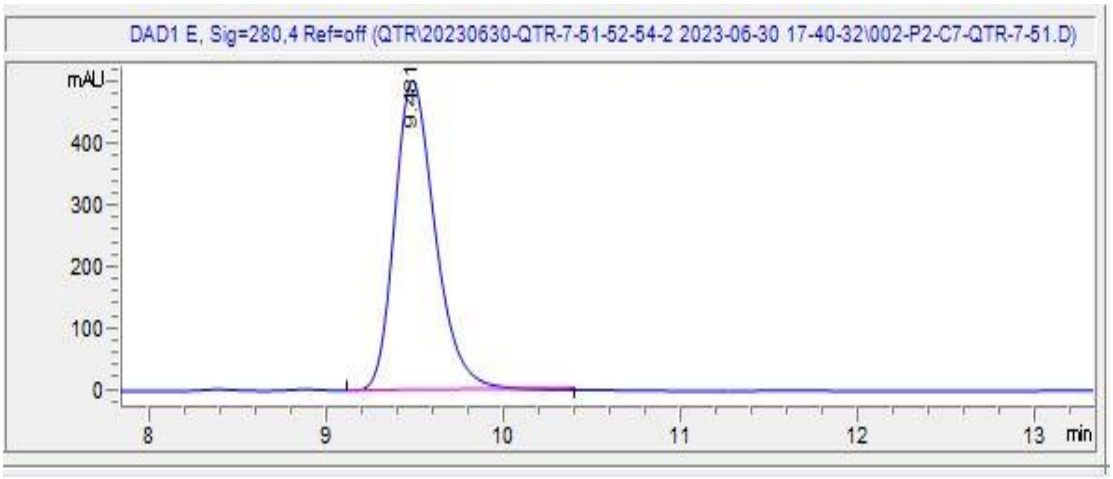
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	9.513	3917.6	199.4	0.2992	99.472	0.733	BB	BB
2	13.287	20.8	9E-1	0.385	0.528	0.835	MM	MM

Heterohelicene 5g



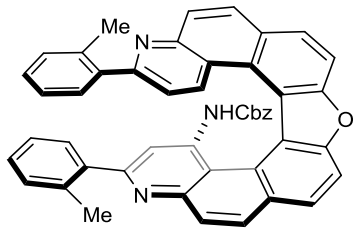


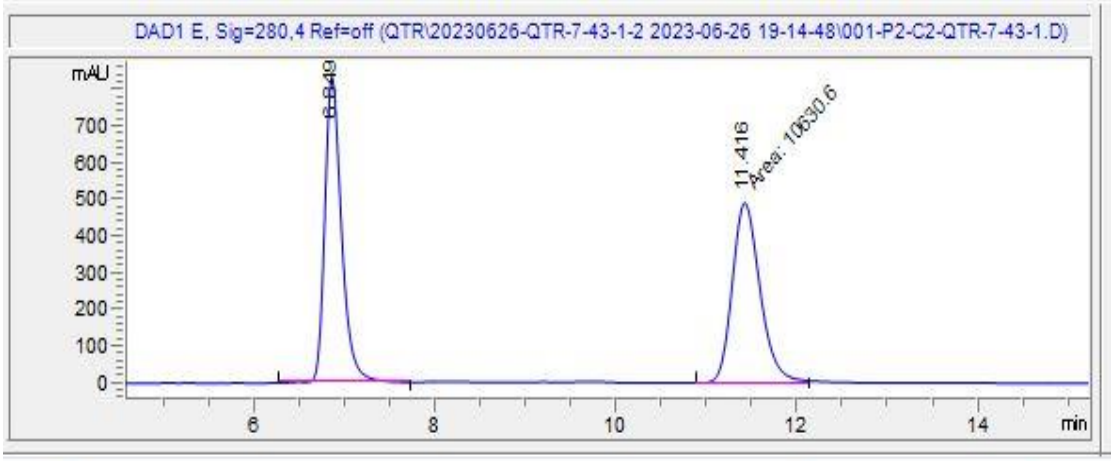
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	9.304	5725.7	367.1	0.2599	50.393	0.796	MM	MM
2	12.611	5636.3	255.9	0.3671	49.607	0.774	MM	MM



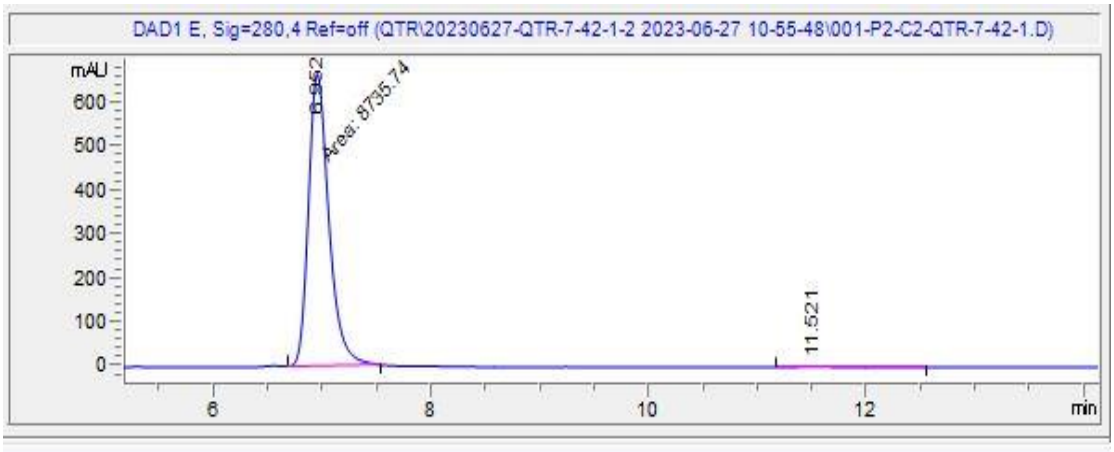
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	9.481	8036.5	501.6	0.2449	100.000	0.721	BB	BB

Heterohelicene 5h



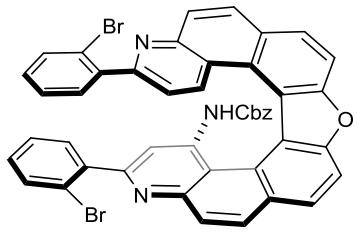


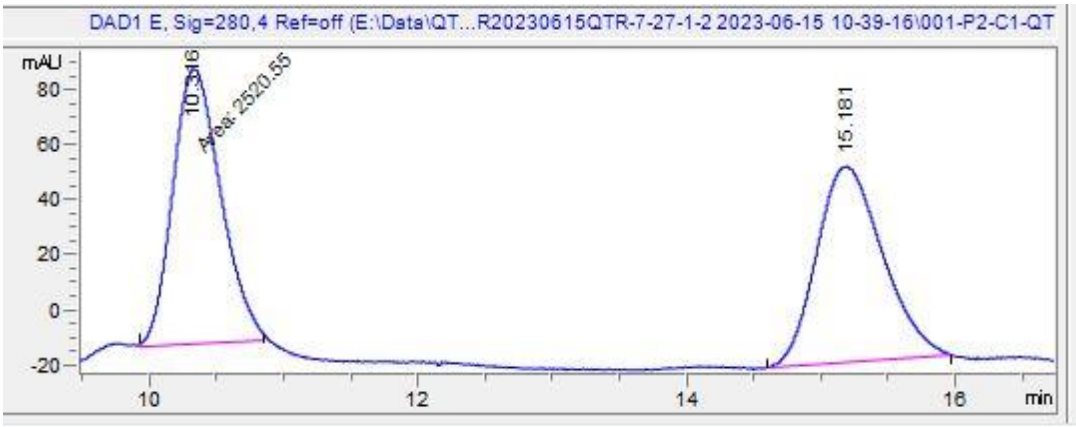
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	6.849	10803.4	834.2	0.1967	50.403	0.706	BB R	BB R
2	11.416	10630.6	493.6	0.3589	49.597	0.782	MM	



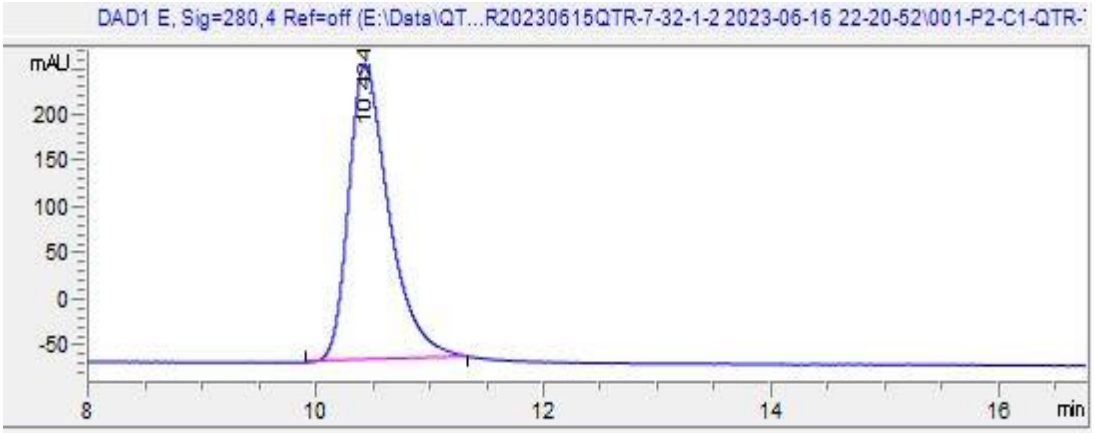
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	6.952	8735.7	667	0.2183	99.714	0.719	MM	MM
2	11.521	25	1.2	0.3067	0.286	0.736	BB	BB

Heterohelicene 5i



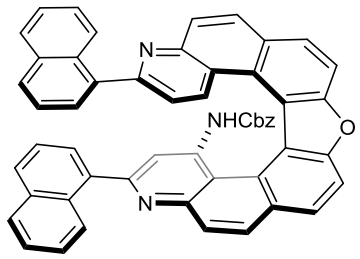


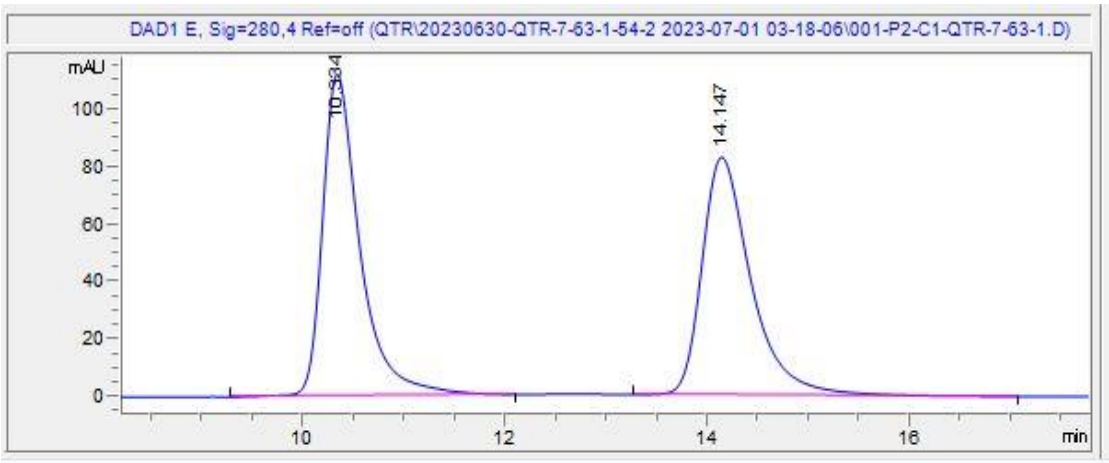
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.316	MM	2520.6	101.2	0.415	50.509	0.716
2	**15.181**	**WR**	**2469.8**	**72.1**	**0.4018**	**49.491**	**0.74**



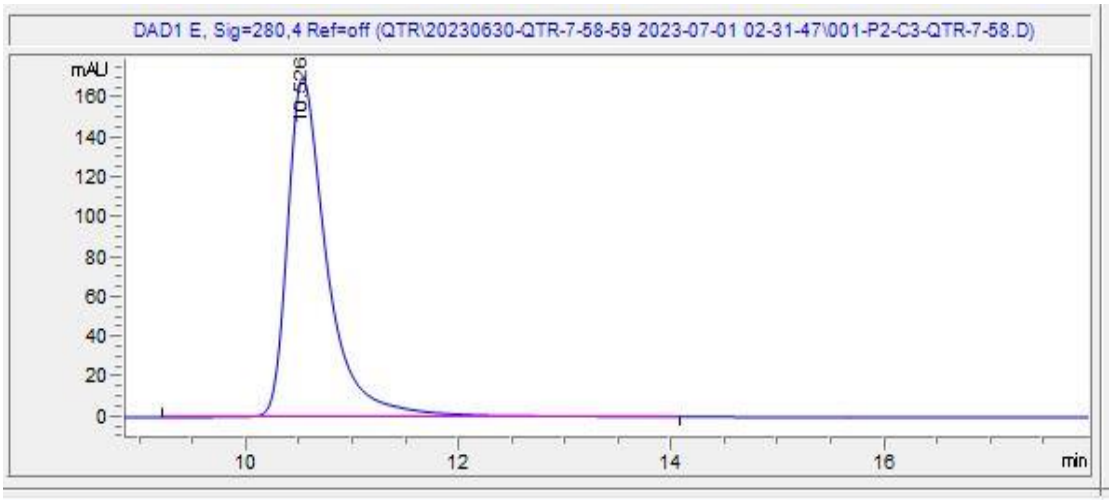
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.424	WR	7905.3	319.4	0.2897	100.000	0.645

Heterohelicene 5j



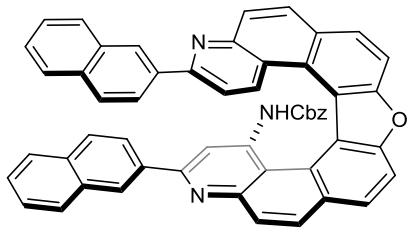


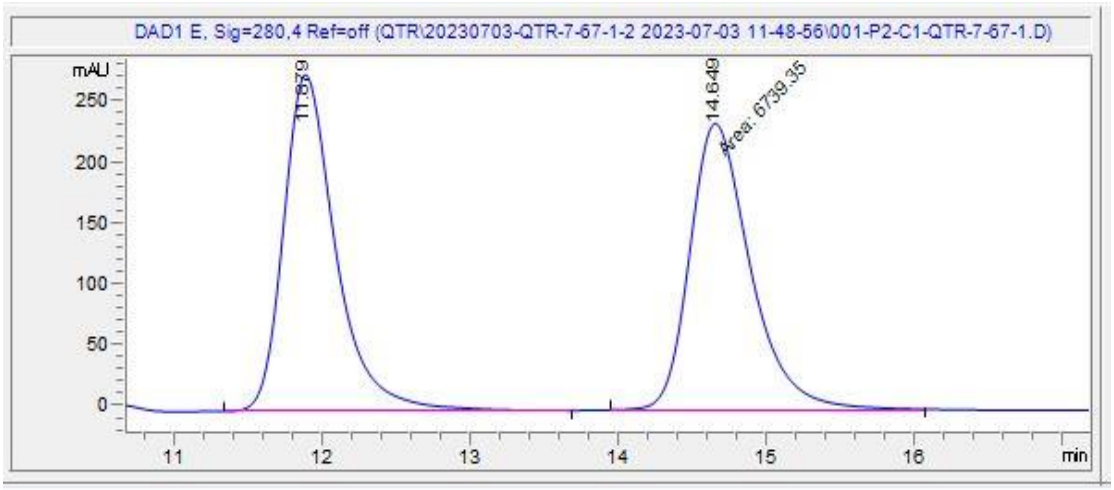
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	10.334	2888.2	112.2	0.3844	50.715	0.594	BB	BB
2	14.147	2806.8	82.8	0.5113	49.285	0.619	BB	BB



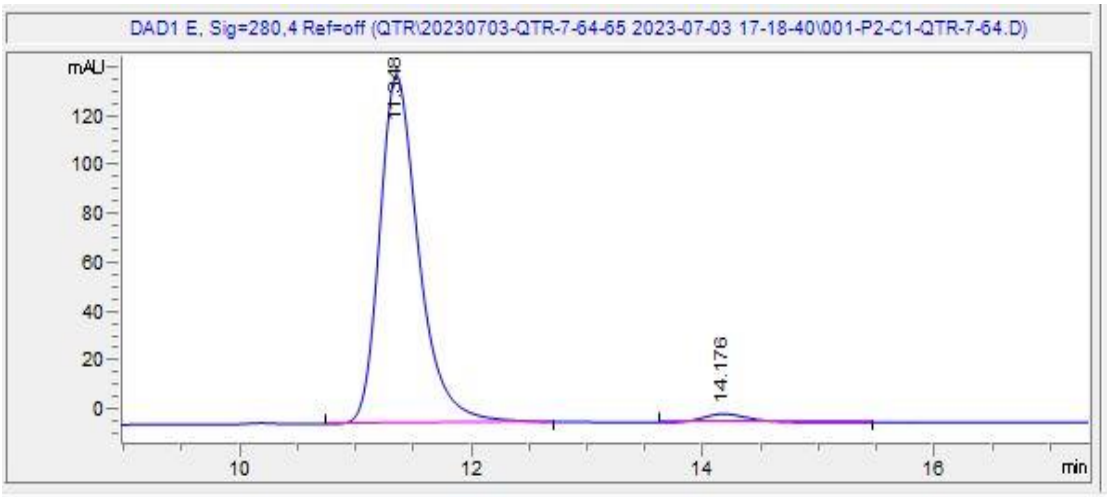
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	10.526	4476	171.1	0.3892	100.000	0.558	BB	BB

Heterohelicene 5k



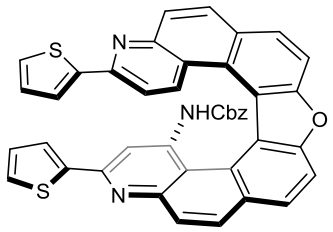


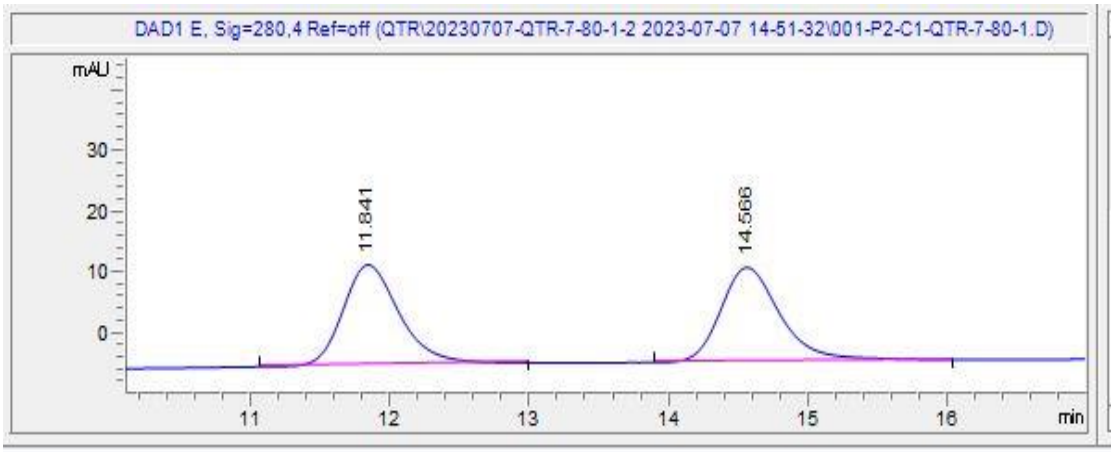
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	11.879	6733.2	274.3	0.3703	49.977	0.677	BB	BB
2	14.649	6739.4	234.4	0.4792	50.023	0.7	MM	



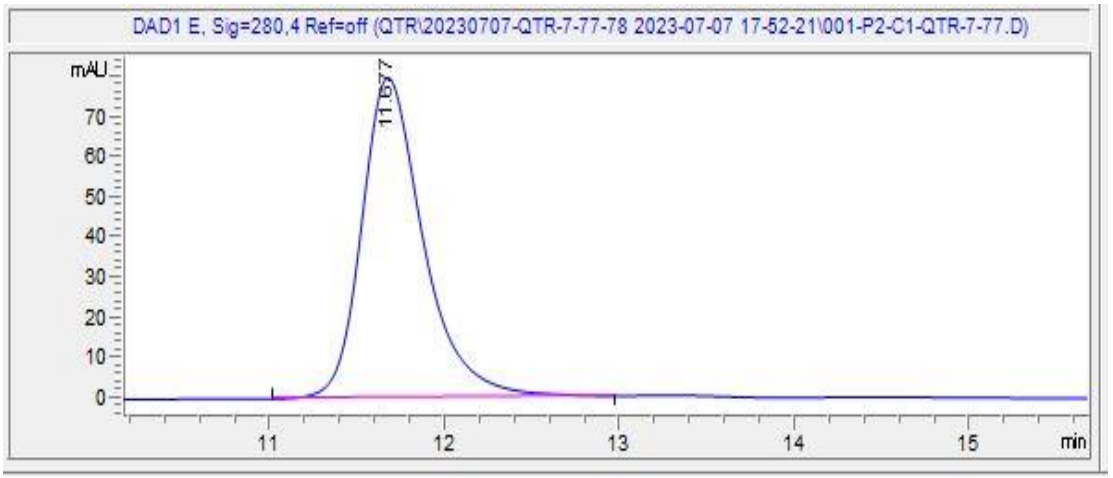
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	11.348	3355.3	142.8	0.3562	97.100	0.705	BB	BB
2	14.176	100.2	3.5	0.4332	2.900	0.744	BB	BB

Heterohelicene 5l



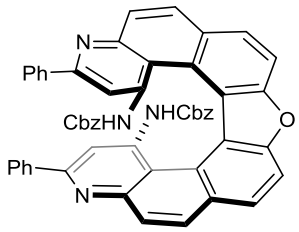


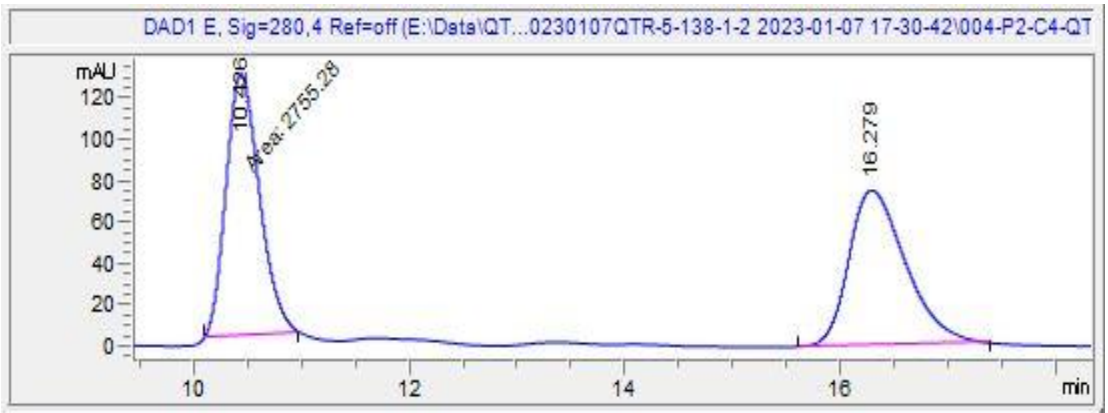
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	11.841	475.7	16.7	0.4296	50.281	0.756	BB	BB
2	14.566	470.3	15.7	0.4534	49.719	0.73	BB	BB



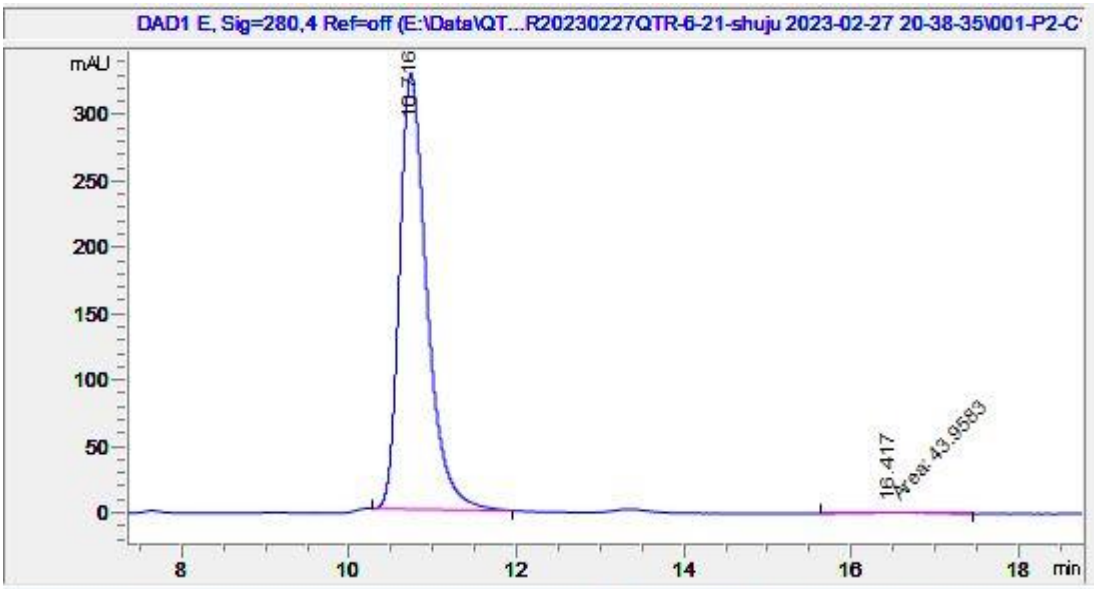
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	11.677	1961.9	79.8	0.3707	100.000	0.697	BB	BB

Heterohelicene 6a



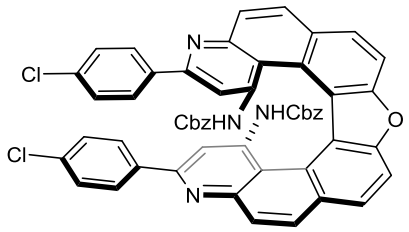


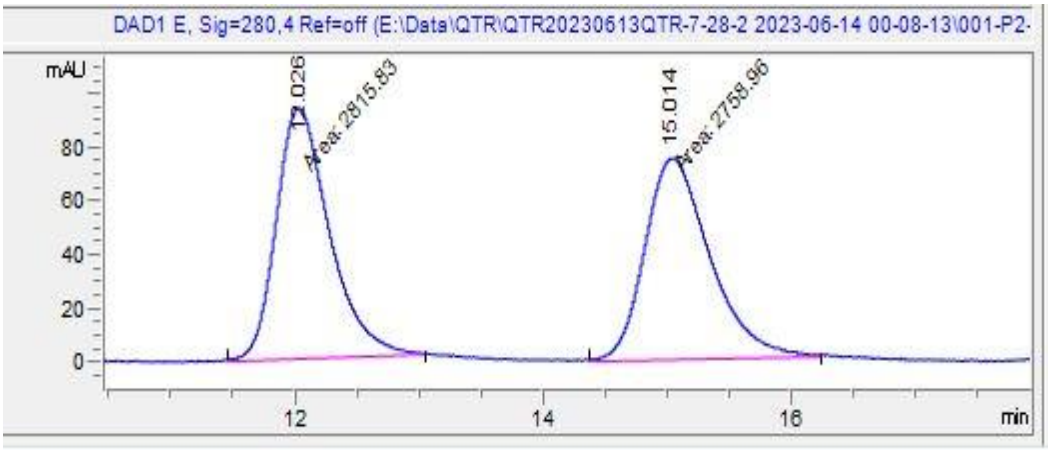
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.426	MM	2755.3	127	0.3616	50.005	0.768
2	16.279	VV R	2754.7	75	0.4307	49.995	0.662



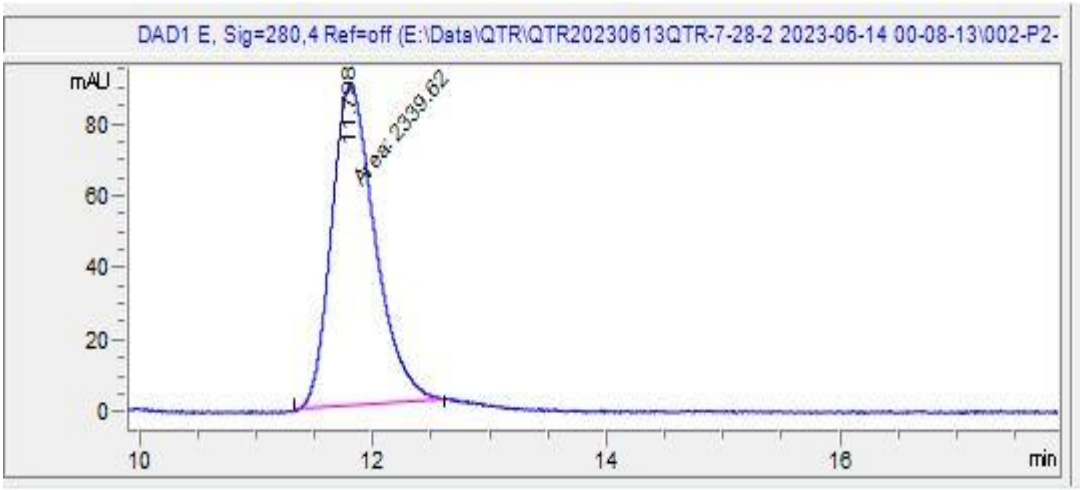
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.716	VV R	7406.1	327.2	0.2726	99.410	0.68
2	16.417	MM	44	7.8E-1	0.9362	0.590	0.667

Heterohelicene 6b



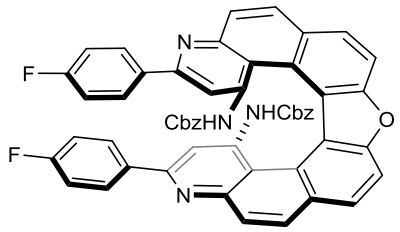


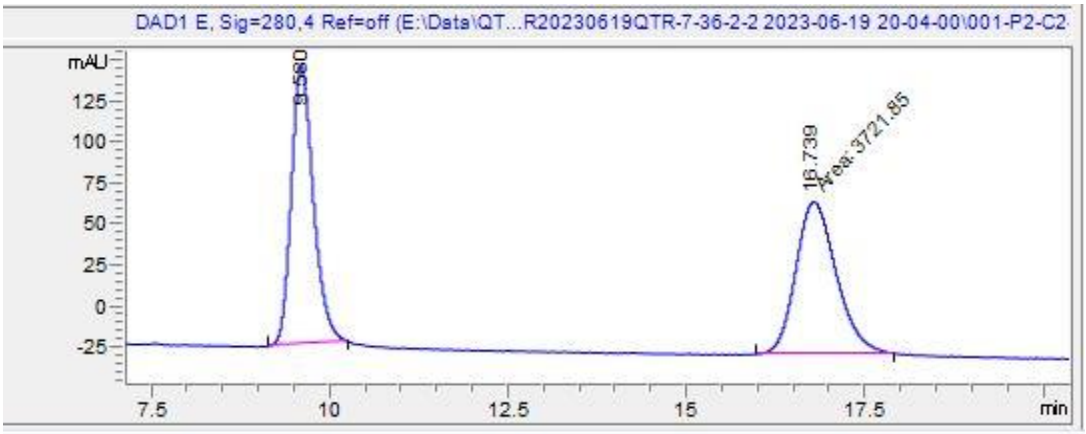
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.026	MM	2815.8	93.5	0.5018	50.510	0.721
2	15.014	MM	2759	75	0.613	49.490	0.621



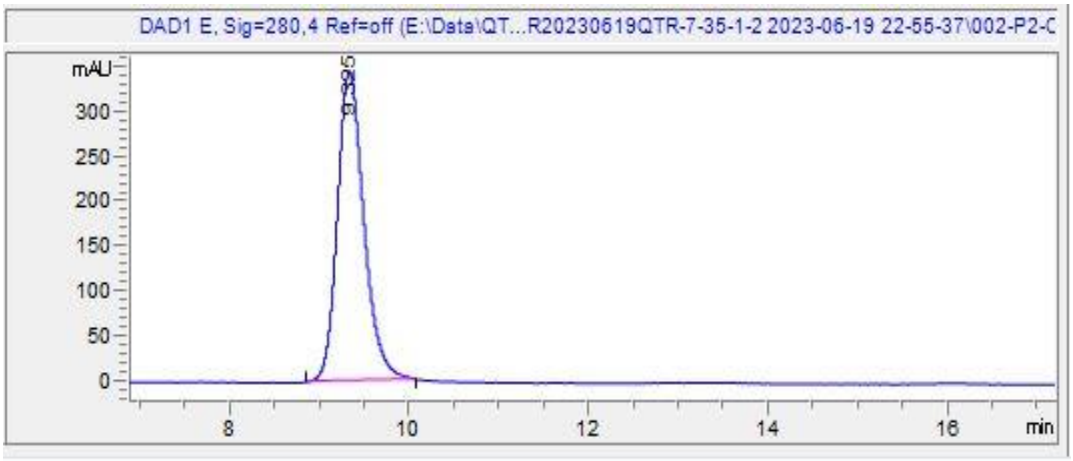
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.798	MM	2339.6	89.3	0.4367	100.000	0.721

Heterohelicene 6c



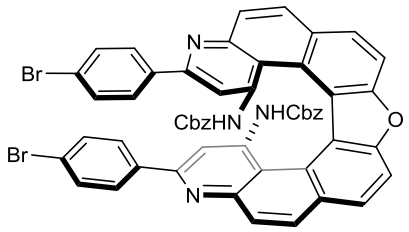


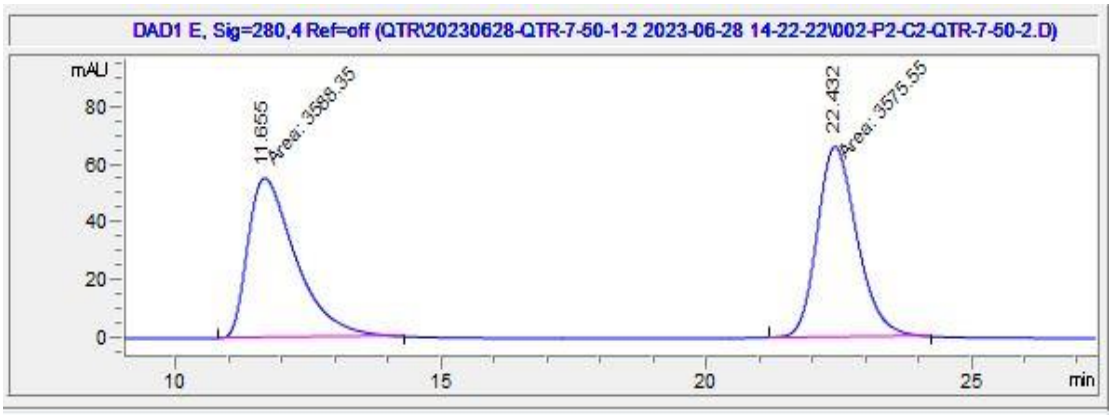
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.58	VV R	3685.6	170.2	0.2552	49.755	0.758
2	16.739	MM	3721.9	93.3	0.6649	50.245	0.708



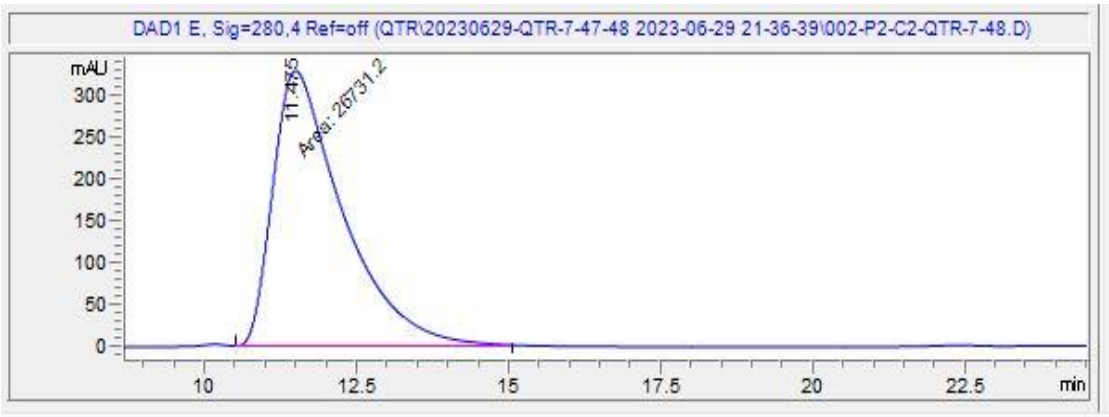
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.325	VV R	7051.1	343.3	0.2432	100.000	0.766

Heterohelicene 6d



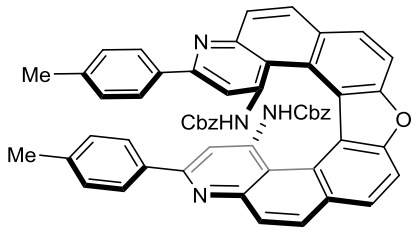


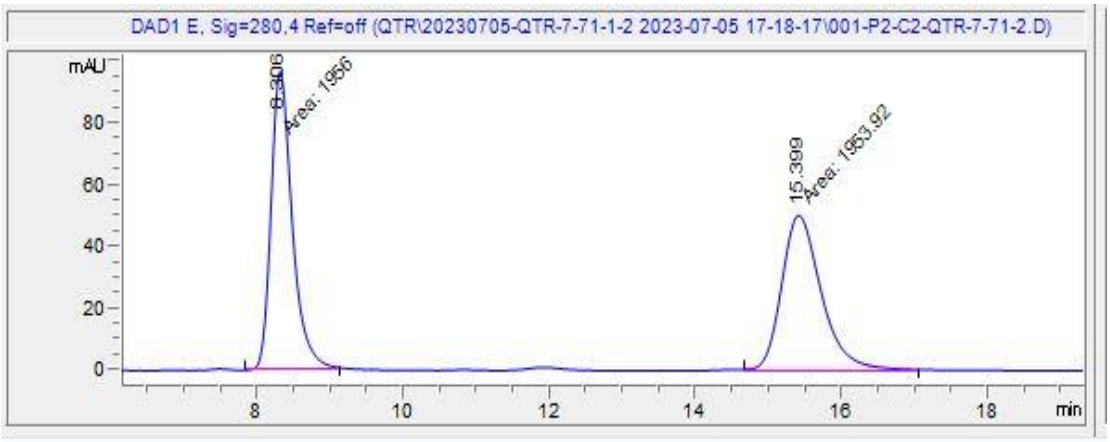
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	11.655	3588.4	56.1	1.0664	50.089	0.517	MM	MM
2	22.432	3575.6	67.2	0.8873	49.911	0.777	MM	MM



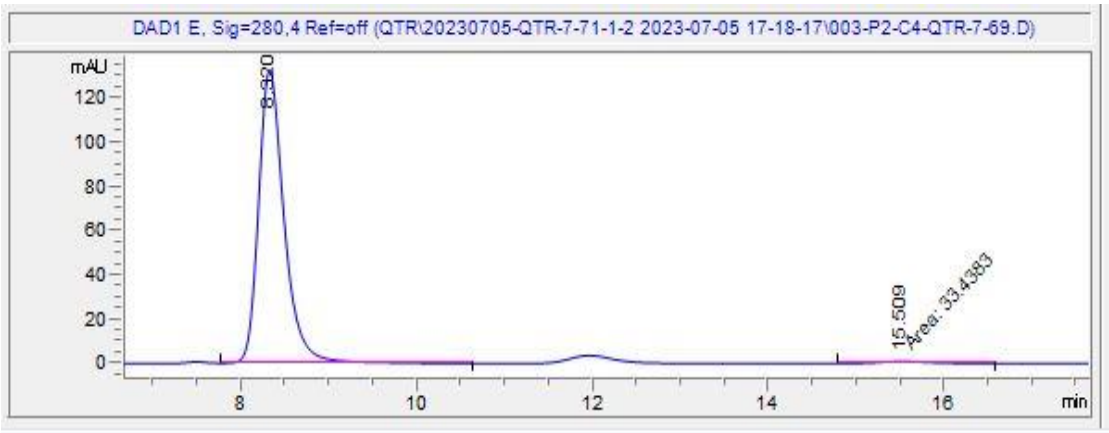
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	11.475	26731.2	330.9	1.3463	100.000	0.462	MM	MM

Heterohelicene 6e



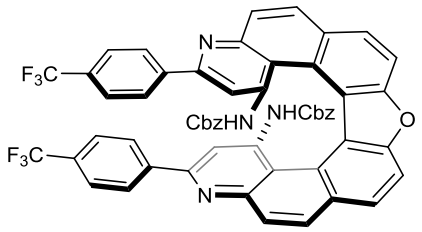


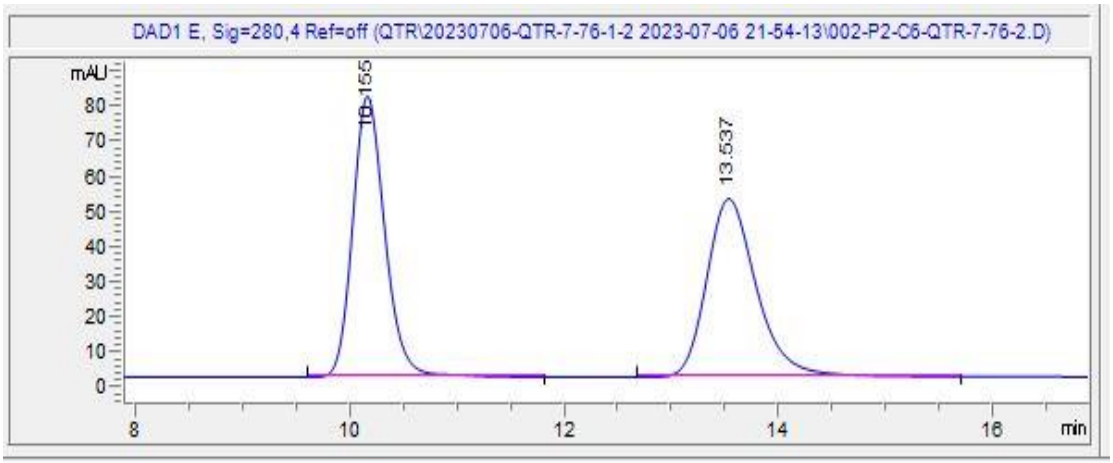
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	8.306	1956	96.9	0.3363	50.027	0.718	MM	MM
2	15.399	1953.9	50.7	0.6421	49.973	0.722	MM	MM



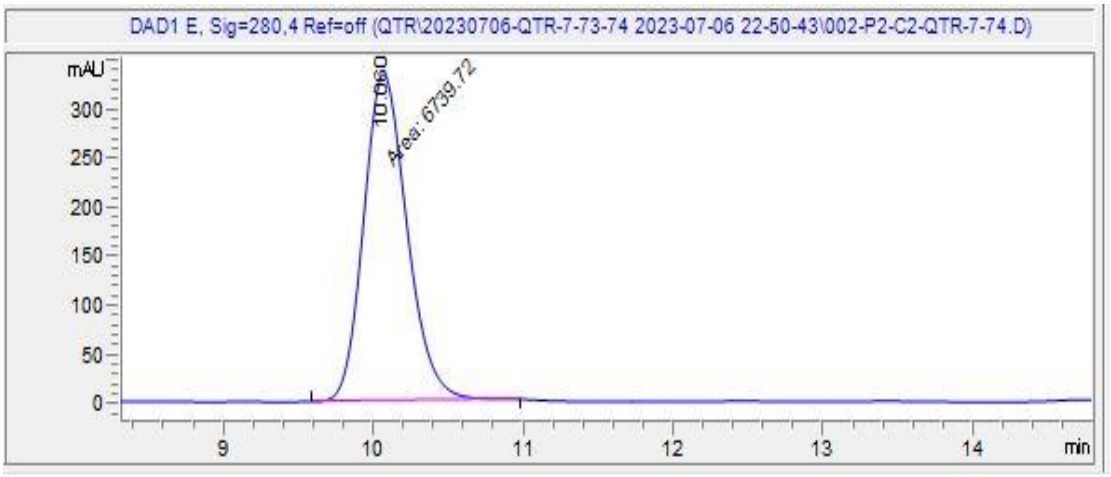
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	8.32	2669	132.3	0.3074	98.763	0.696	BB	BB
2	15.509	33.4	8.9E-1	0.6275	1.237	0.811	MM	MM

Heterohelicene 6f



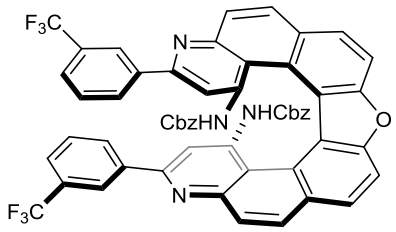


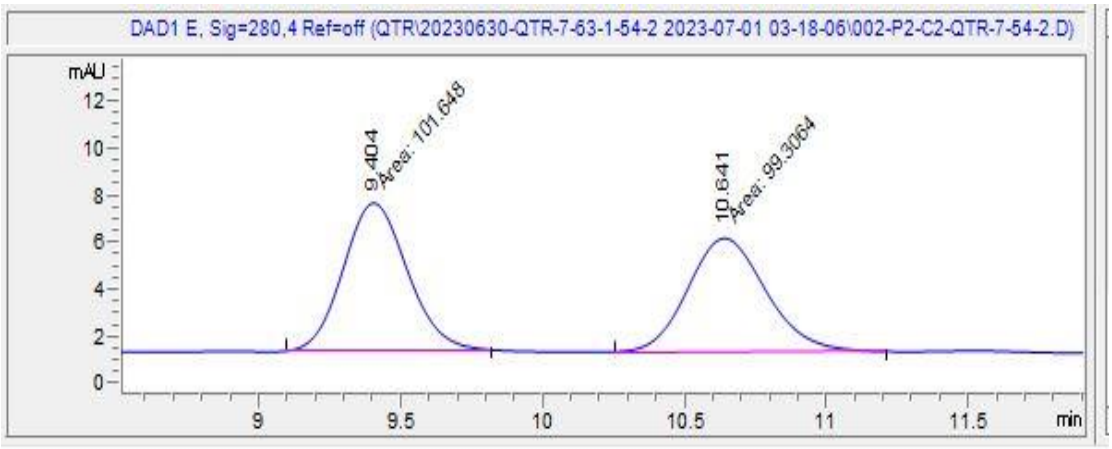
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	10.155	1691.1	80.7	0.3226	50.407	0.791	BB	BB
2	13.537	1663.8	51.2	0.4953	49.593	0.742	BB	BB



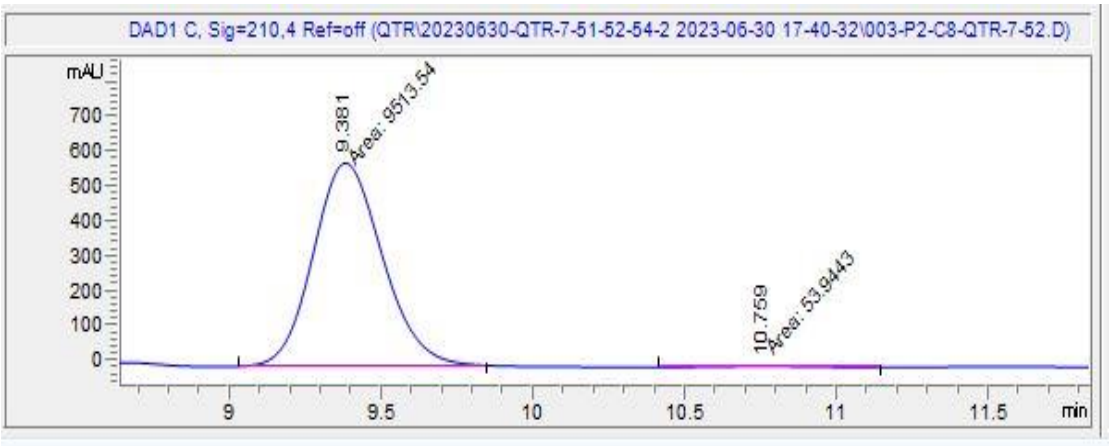
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	10.06	6739.7	333.5	0.3368	100.000	0.808	MM	MM

Heterohelicene 6g



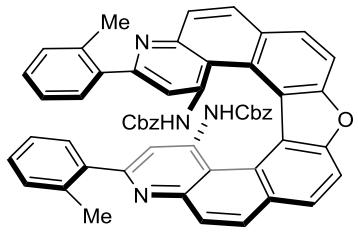


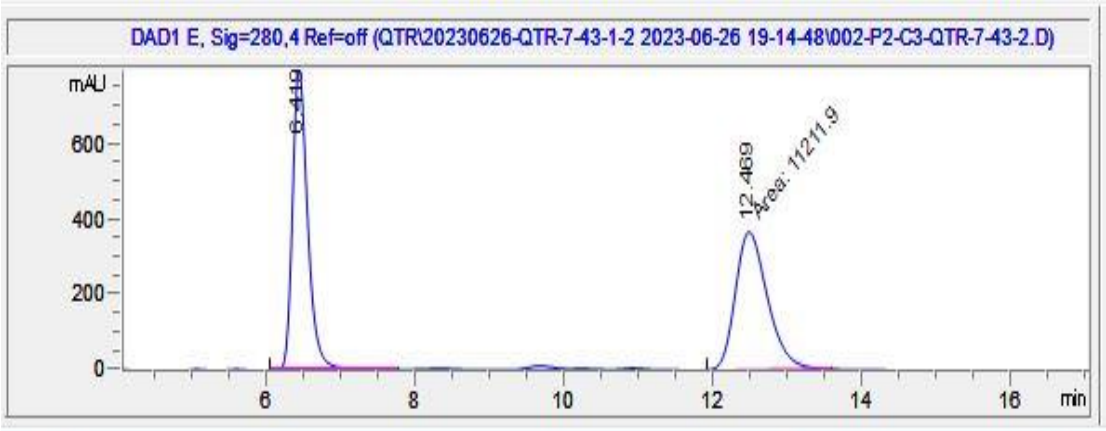
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	9.404	101.6	6.4	0.2654	50.583	0.875	MM	MM
2	10.641	99.3	5	0.3322	49.417	0.863	MM	MM



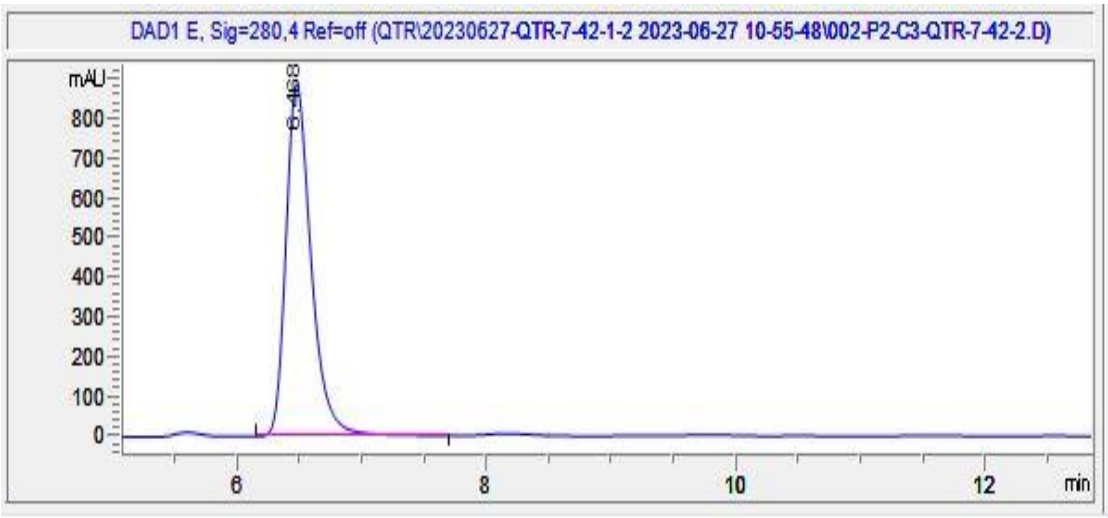
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	9.381	9513.5	589.6	0.2689	99.436	0.844	MM	MM
2	10.759	53.9	2.8	0.3227	0.564	0.937	MM	

Heterohelicene 6h



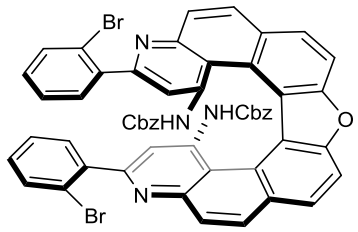


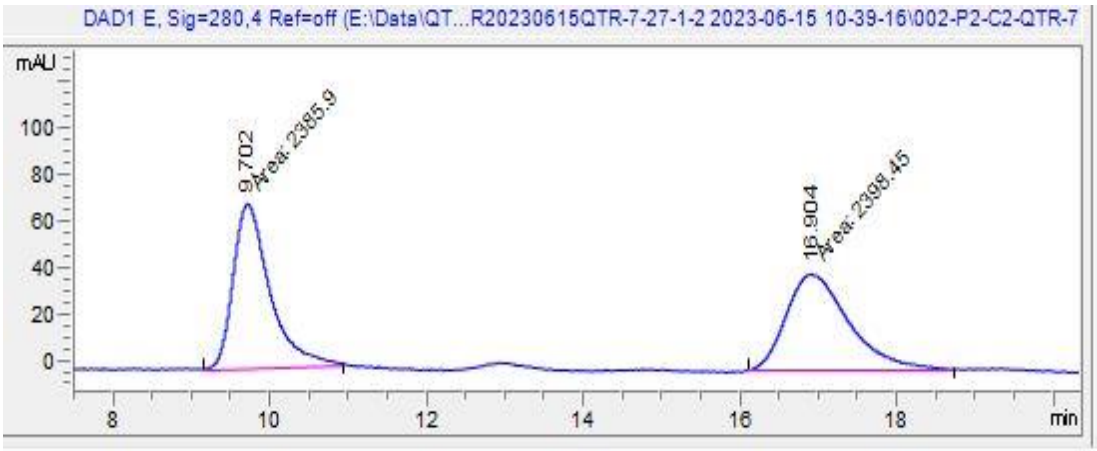
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	6.419	11286.6	794.3	0.2158	50.166	0.688	BB	BB
2	12.469	11211.9	365.9	0.5107	49.834	0.717	MM	MM



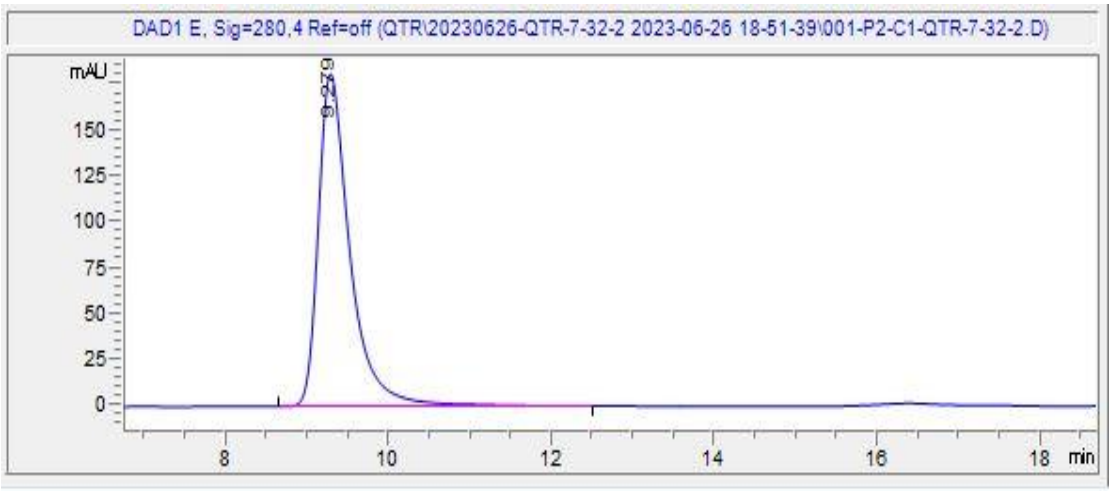
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	6.468	12497.3	889.3	0.2139	100.000	0.674	VB	VB

Heterohelicene 6i



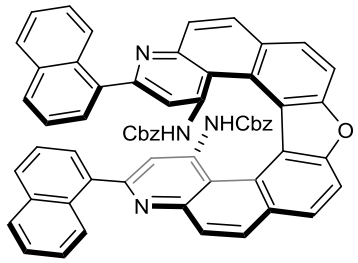


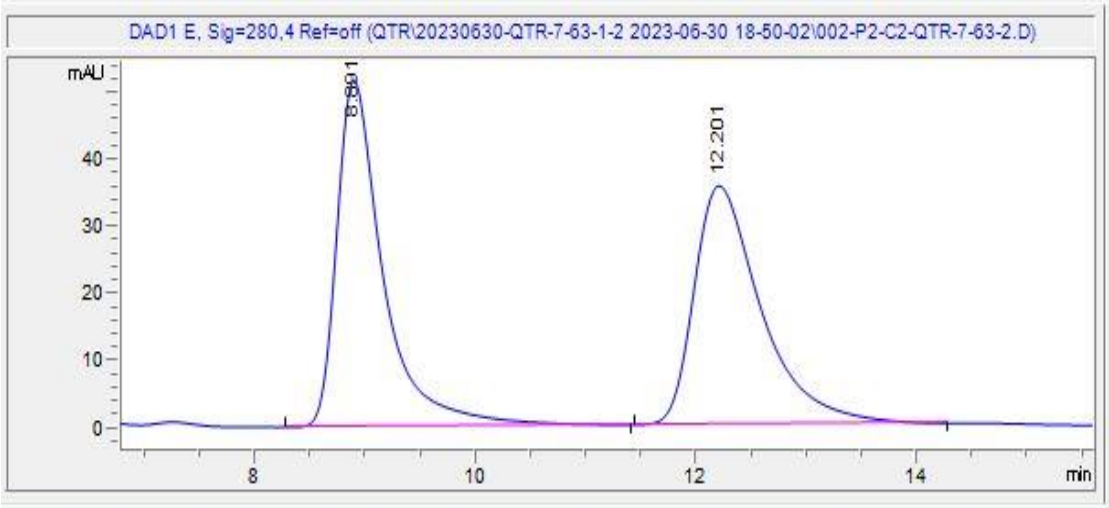
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.702	MM	2385.9	71.8	0.5538	49.869	0.605
2	16.904	MM	2398.5	42.2	0.9475	50.131	0.651



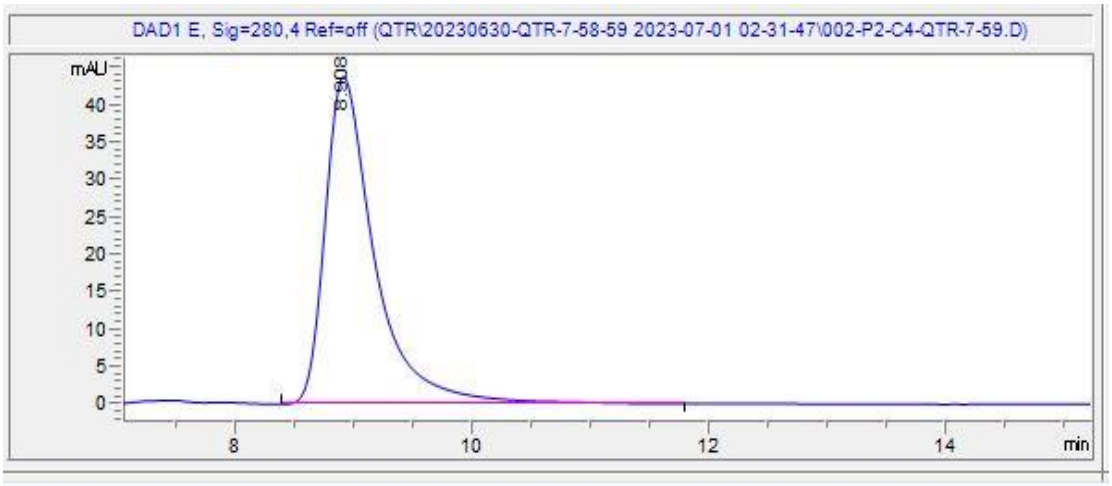
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	9.279	4865.6	179.9	0.4015	100.000	0.57	BB	BB

Heterohelicene 6j



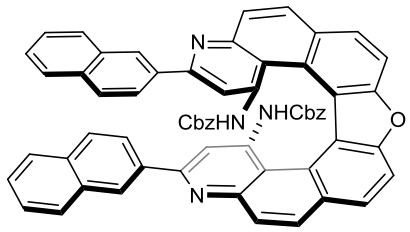


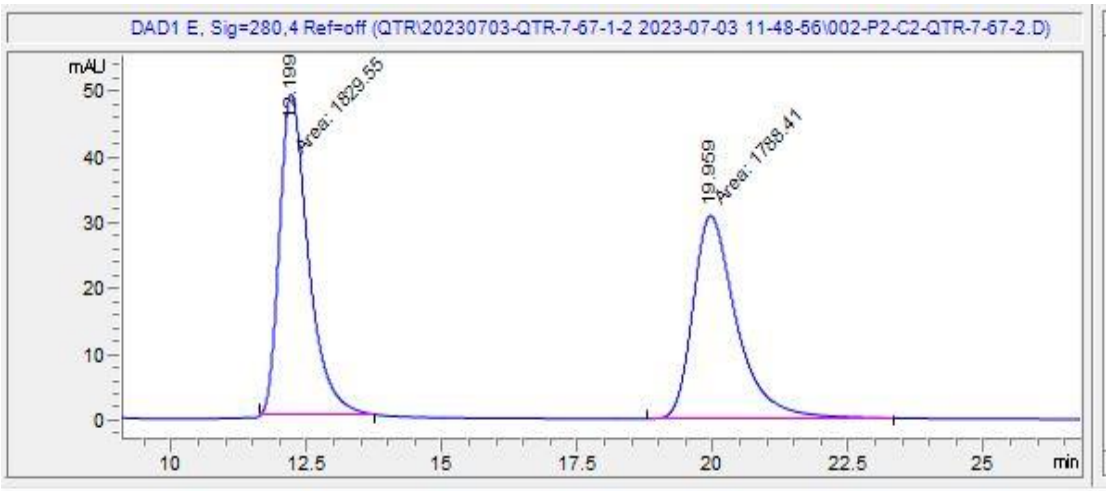
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	8.891	1515.9	51.7	0.4338	50.140	0.529	BB	BB
2	12.201	1507.4	35.6	0.6314	49.860	0.55	BB	BB



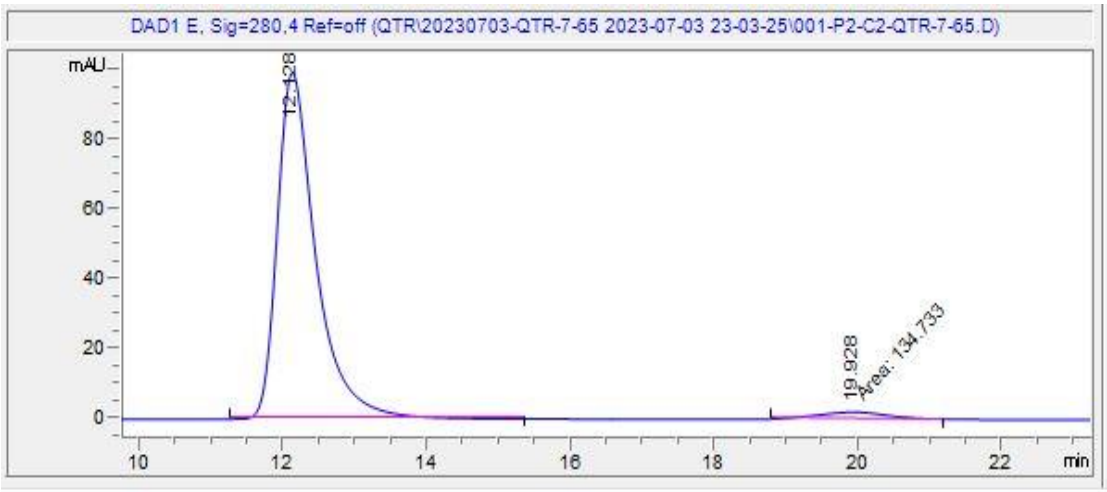
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	8.908	1288.7	44	0.4317	100.000	0.535	BB	BB

Heterohelicene 6k



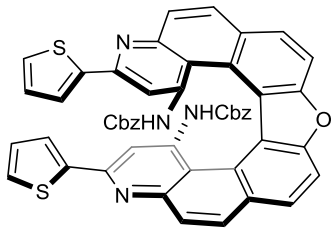


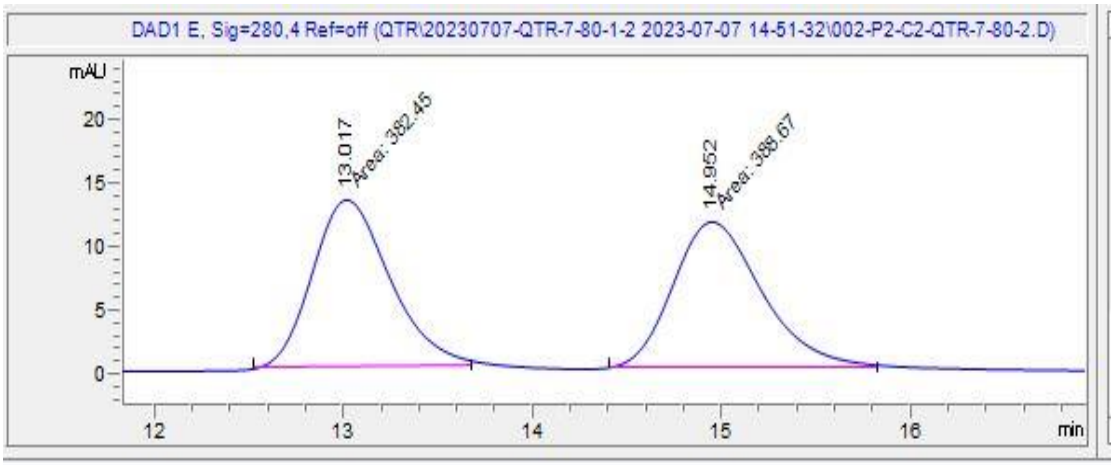
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	12.199	1829.6	48.9	0.6235	50.569	0.654	MM	MM
2	19.959	1788.4	31	0.9611	49.431	0.64	MM	MM



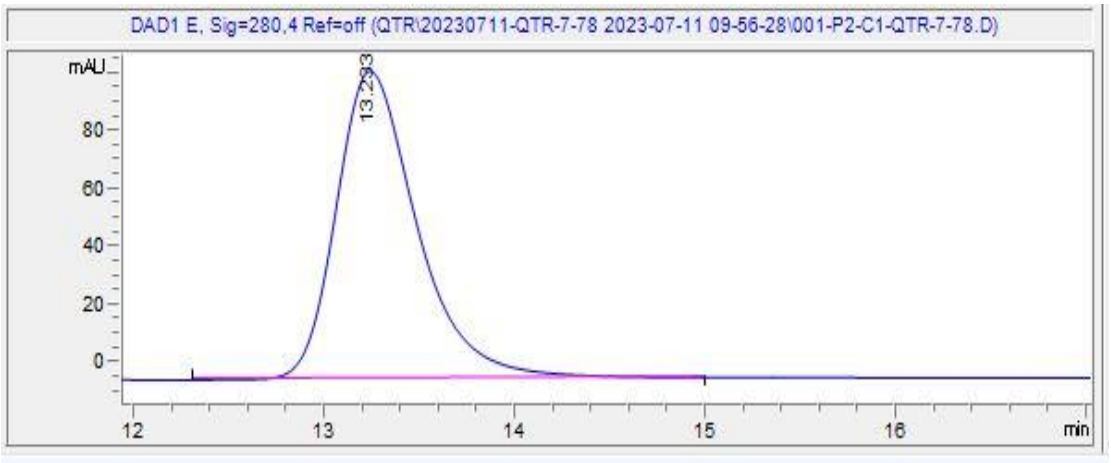
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	12.128	3730.8	99.7	0.5584	96.514	0.585	BB	BB
2	19.928	134.7	2	1.1173	3.486	1.063	MM	MM

Heterohelicene 6l



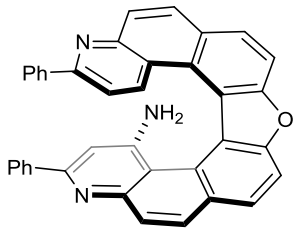


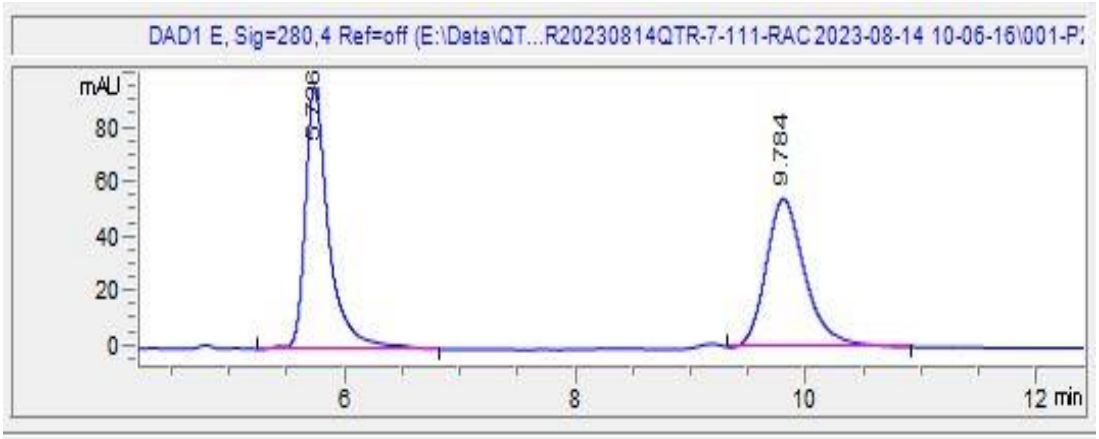
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	13.017	382.4	13.3	0.4797	49.597	0.785	MM	MM
2	14.952	388.7	11.7	0.556	50.403	0.758	MM	



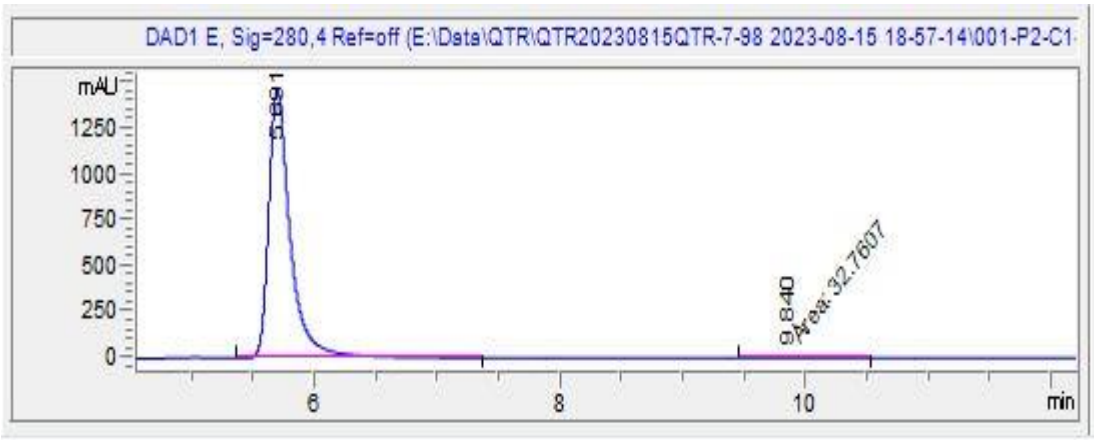
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	13.233	3145.6	106.4	0.451	100.000	0.676	BB	BB

Heterohelicene 7a



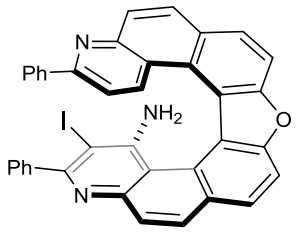


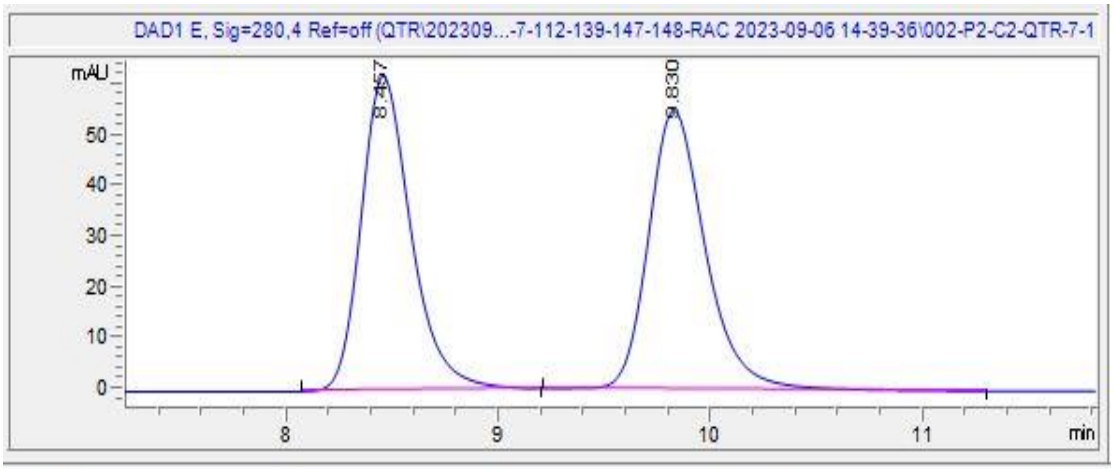
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.726	BB	1371.4	96.8	0.2078	51.667	0.6
2	9.784	BB	1282.9	54.6	0.3141	48.333	0.756



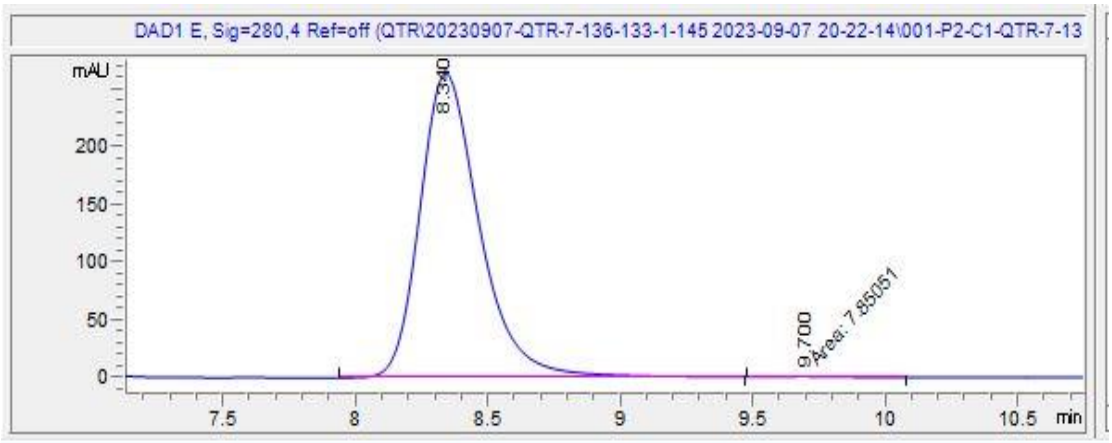
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.691	BB	18105.6	1479.4	0.1818	99.819	0.563
2	9.84	MM	32.8	1.4	0.3792	0.181	0.645

Heterohelicene 8a



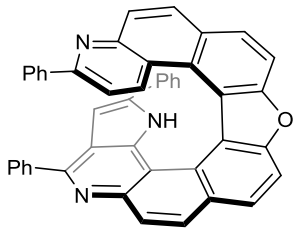


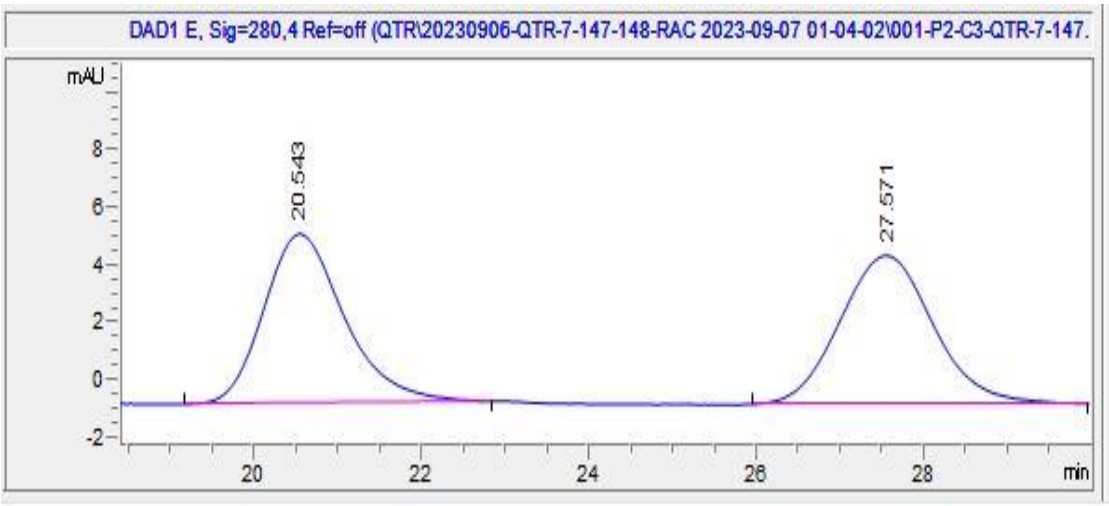
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	8.457	1014.5	61.9	0.2513	49.637	0.741	BB	BB
2	9.83	1029.3	55	0.2865	50.363	0.748	BB	BB



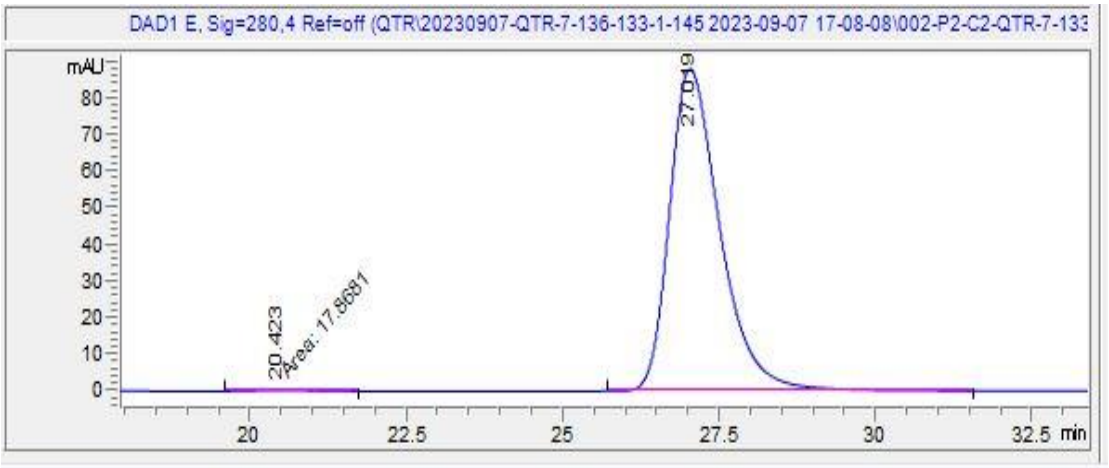
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	8.34	4110.4	262.8	0.2384	99.809	0.711	BB	BB
2	9.7	7.9	5E-1	0.2601	0.191	0.654	MM	MM

Heterohelicene 9a



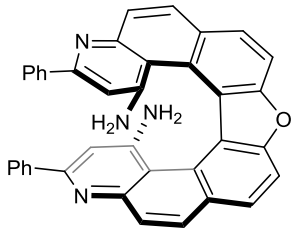


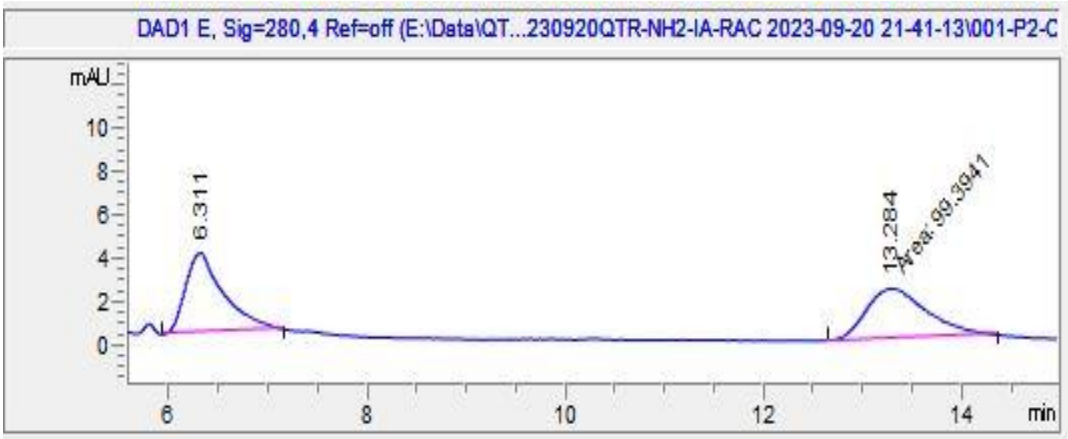
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	20.543	396.7	5.9	0.9119	49.543	0.774	BB	BB
2	27.571	404.1	5.2	0.9414	50.457	0.983	BB	BB



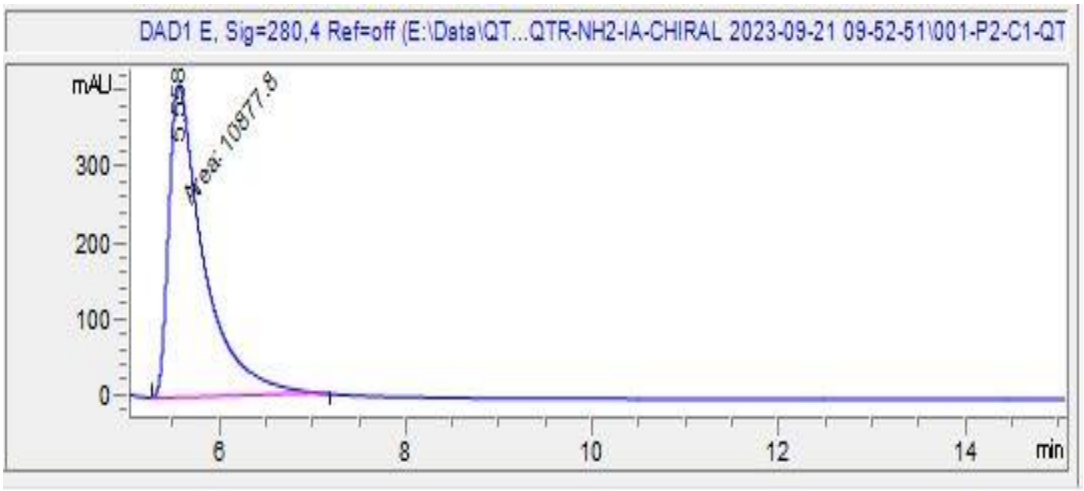
#	时间	峰面积	峰高	峰宽	峰面积 %	对称因子	类型	Type
1	20.423	17.9	2.8E-1	1.0476	0.363	0.655	MM	MM
2	27.019	4900.4	87.4	0.8503	99.637	0.64	BB	BB

Heterohelicene 10a



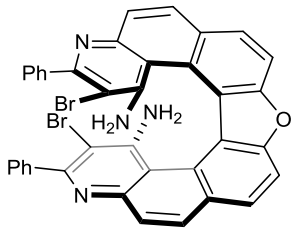


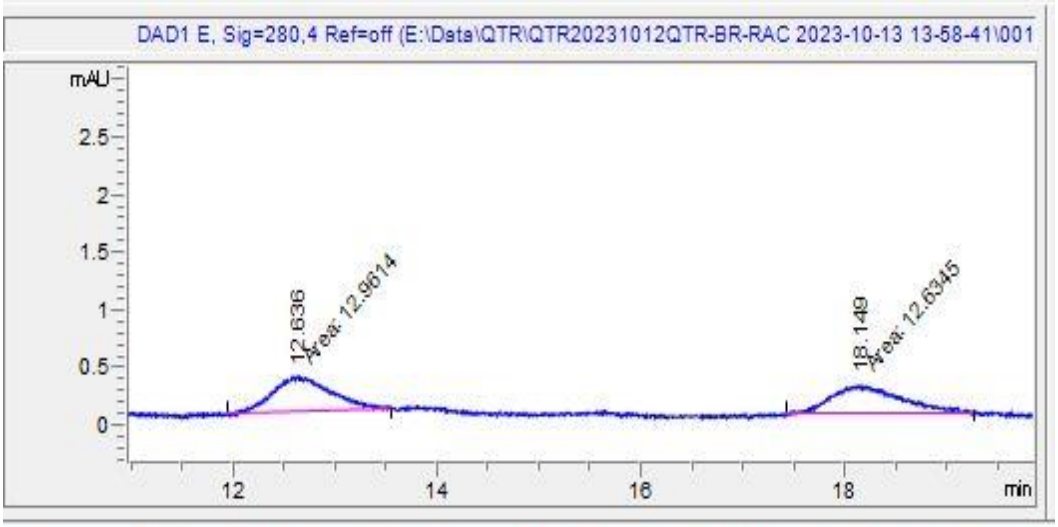
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.311	BB	100.3	3.7	0.3195	50.218	0.626
2	13.284	MM	99.4	2.3	0.711	49.782	0.678



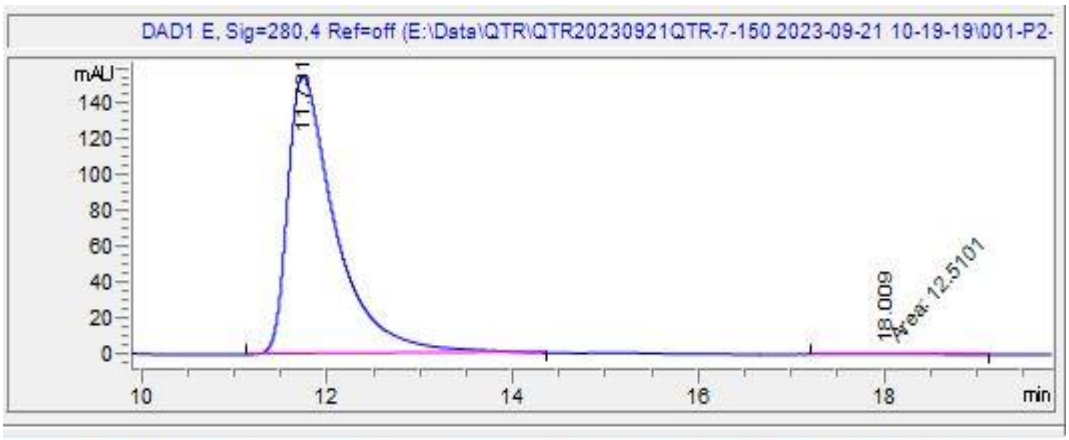
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.558	MM	10877.8	412.1	0.4399	100.000	0.393

Heterohelicene 11a





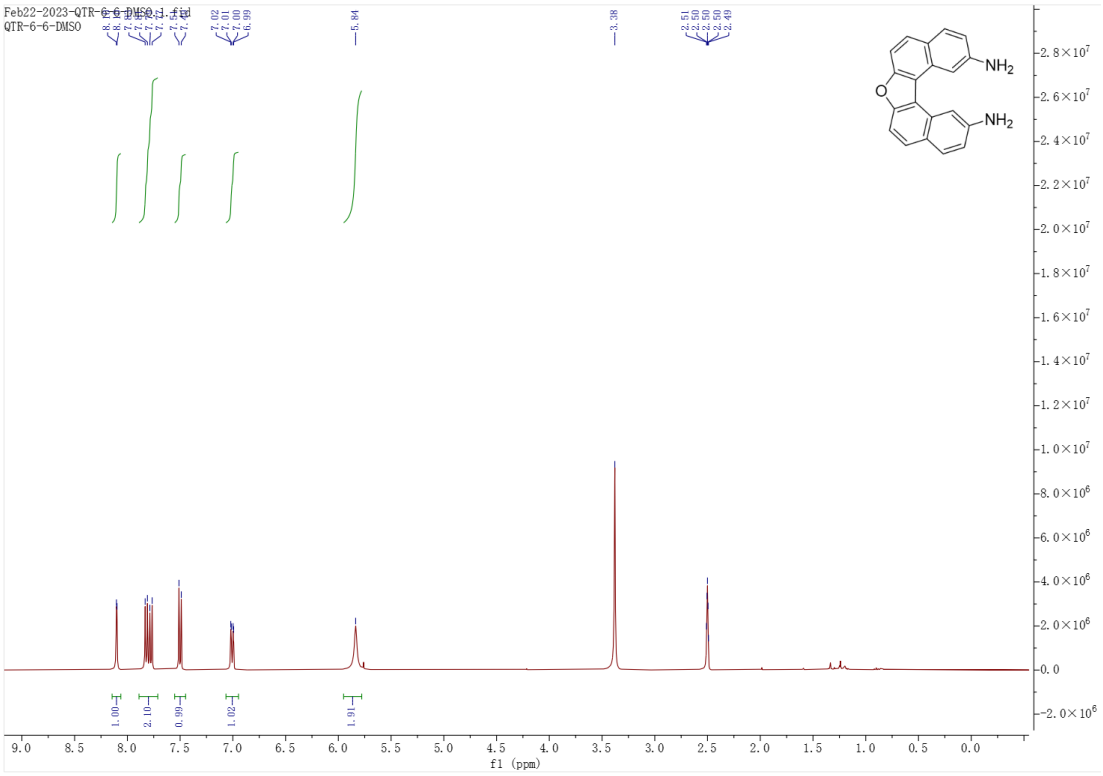
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.636	MM	13	3.2E-1	0.6718	50.639	0.769
2	18.149	MM	12.6	2.6E-1	0.8156	49.361	0.662

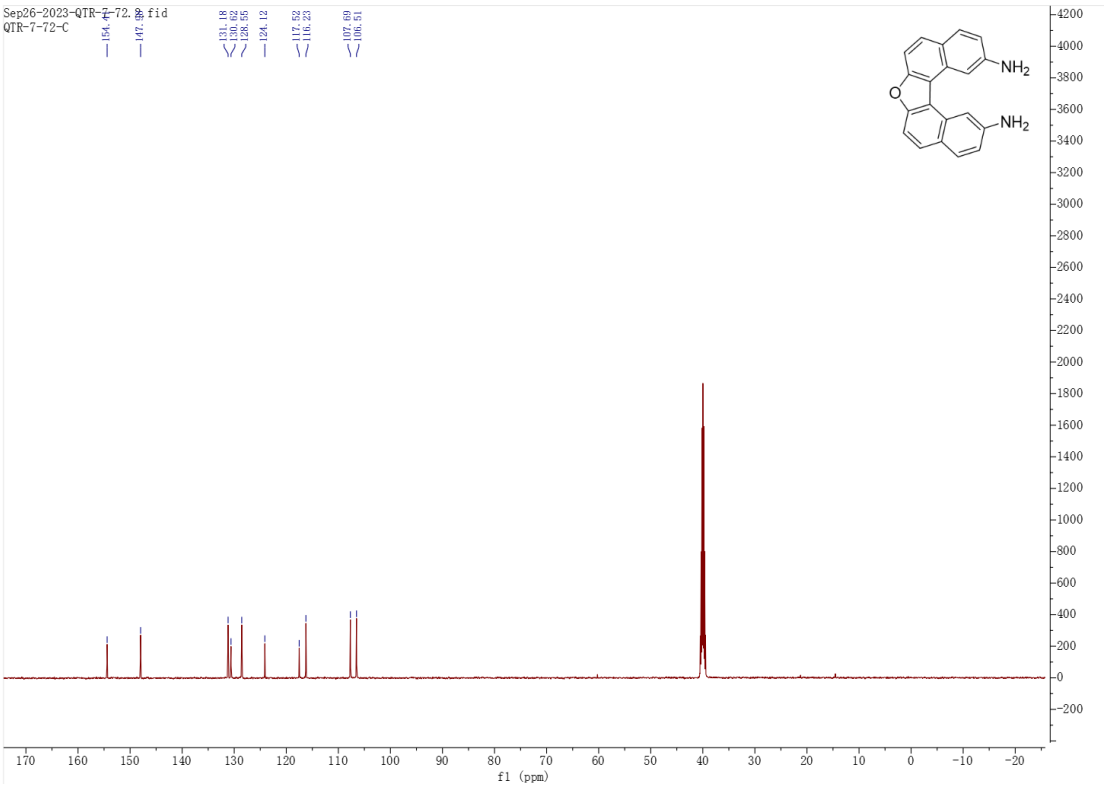


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.731	BB	5590.8	155.3	0.4769	99.777	0.424
2	18.009	MM	12.5	2.2E-1	0.9384	0.223	0.811

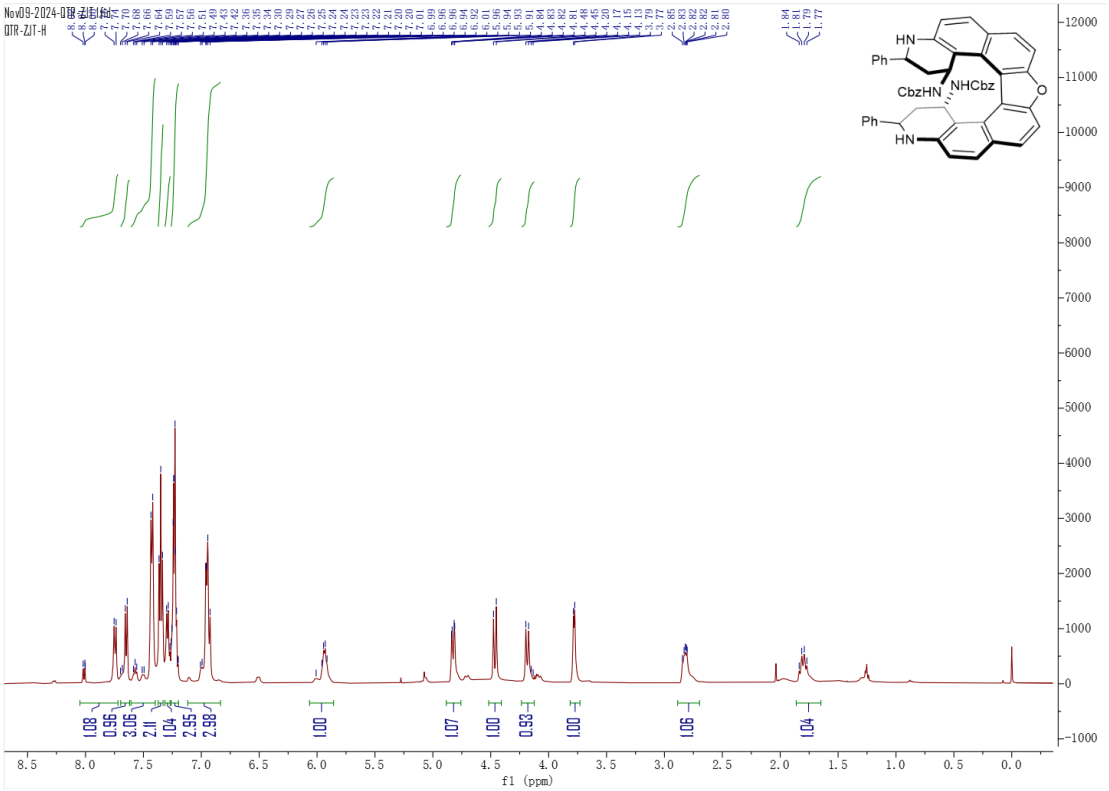
NMR spectra

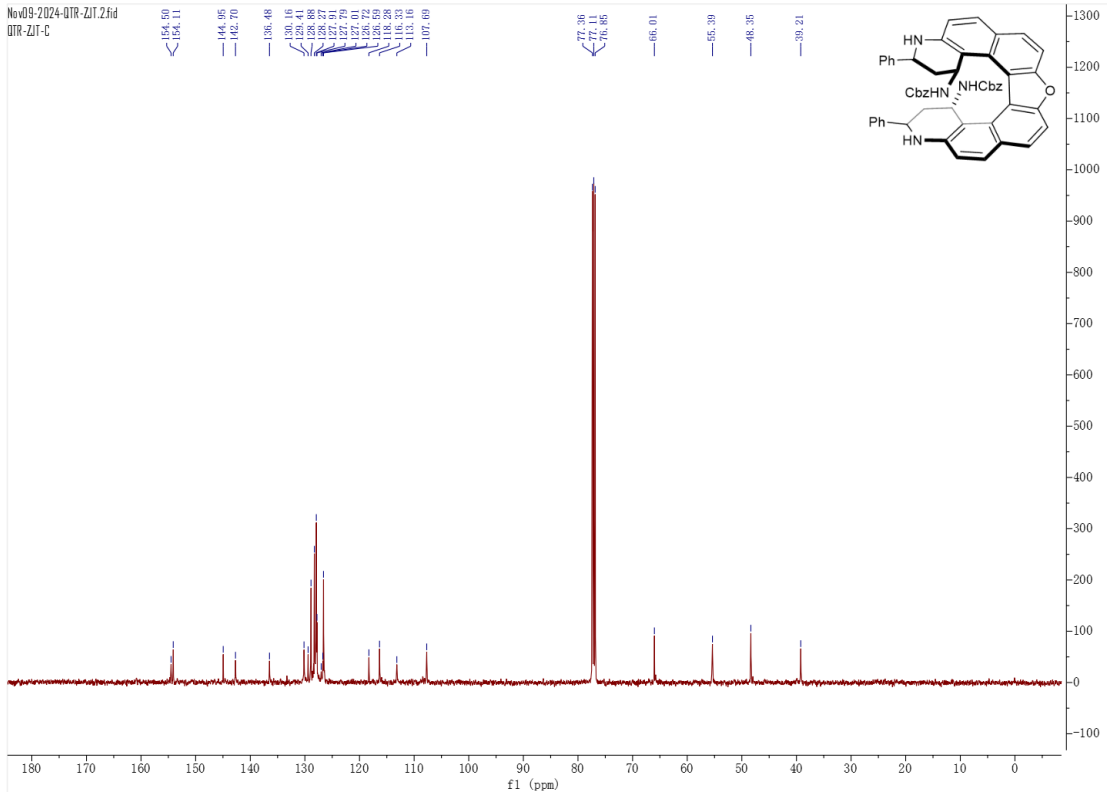
dinaphtho[2,1-b:1',2'-d]furan-2,12-diamine (**1a**)



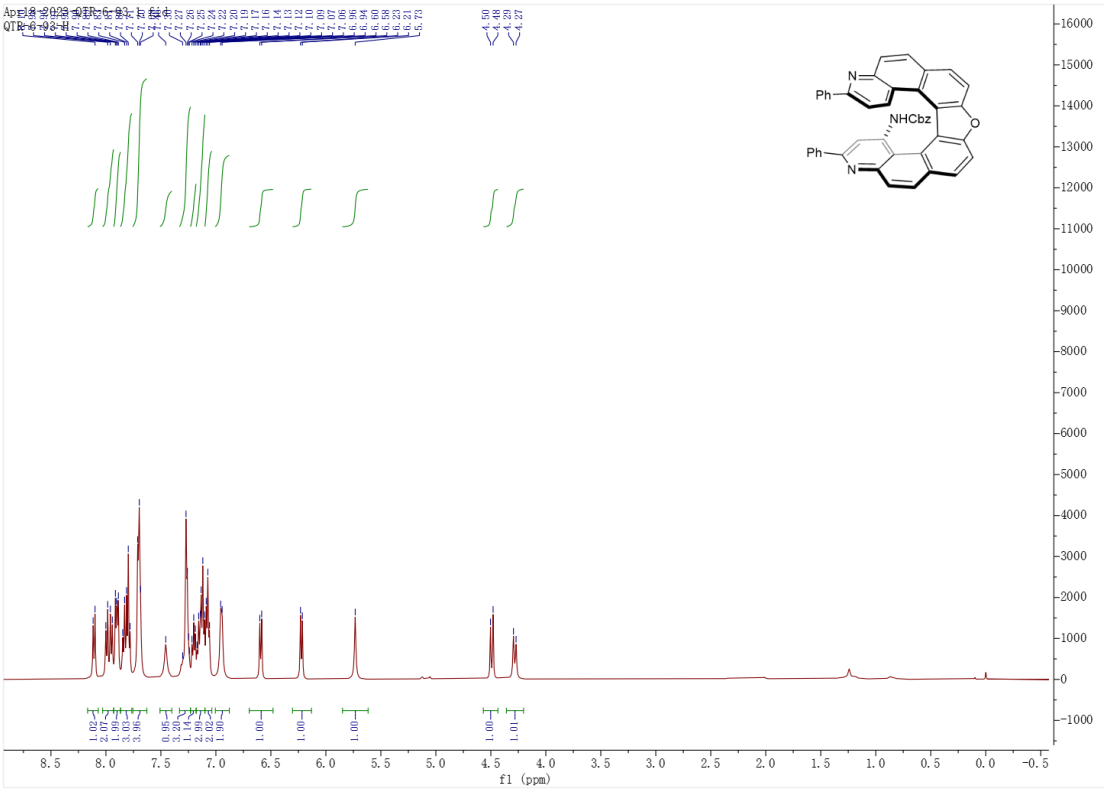


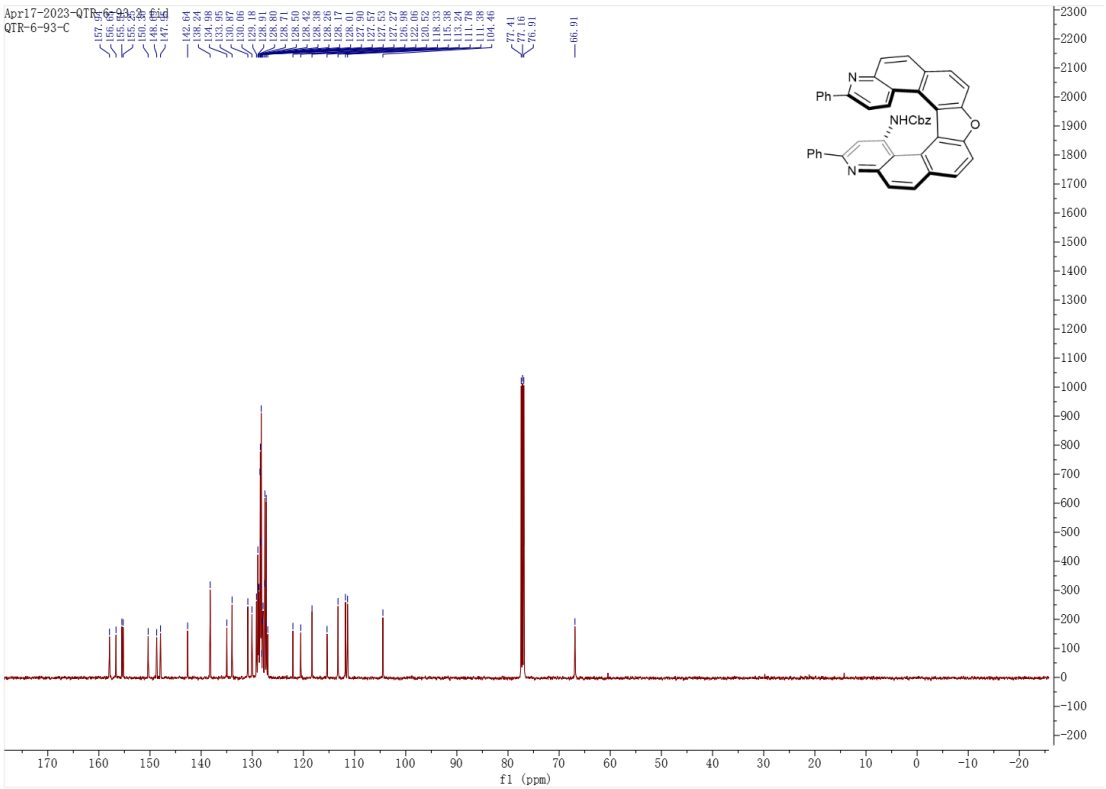
helicenoid 4a



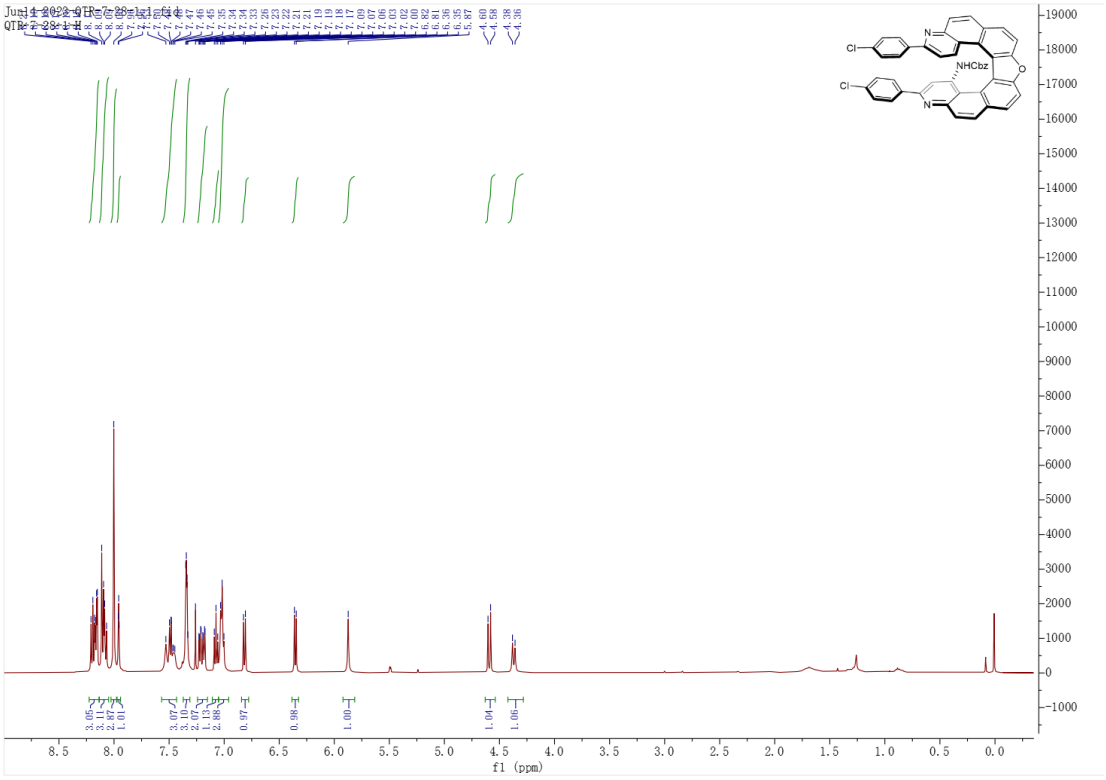


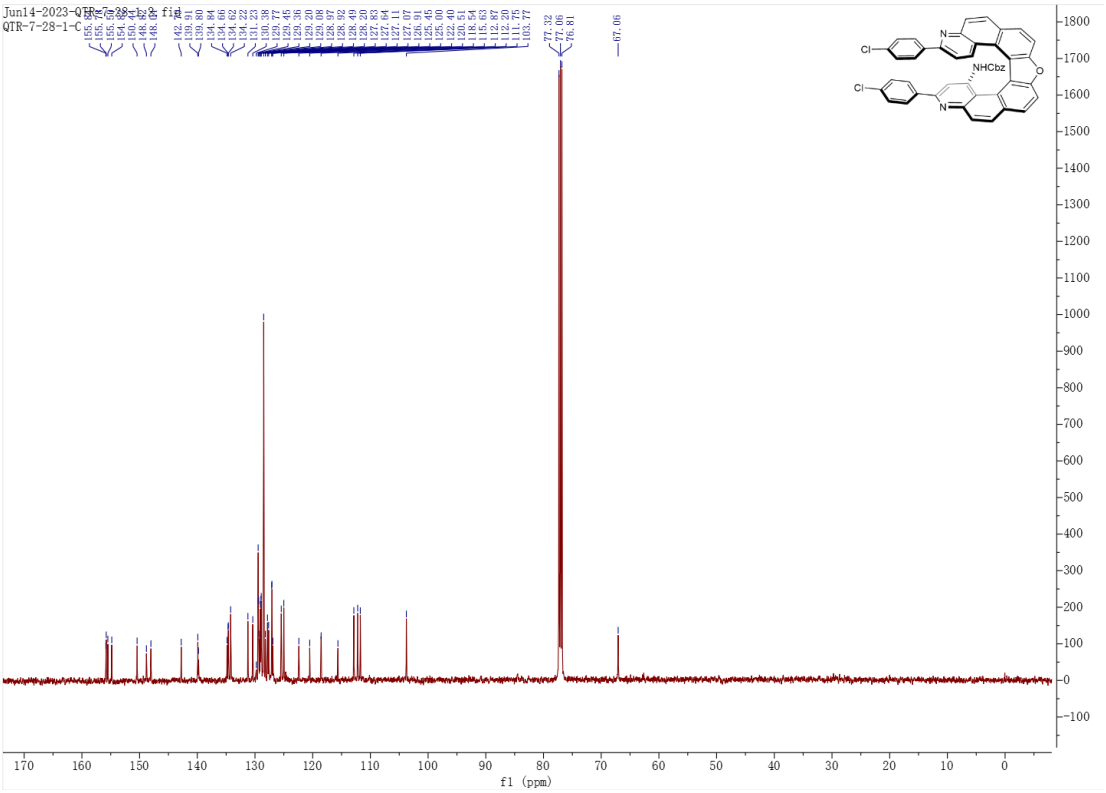
Helicene 5a



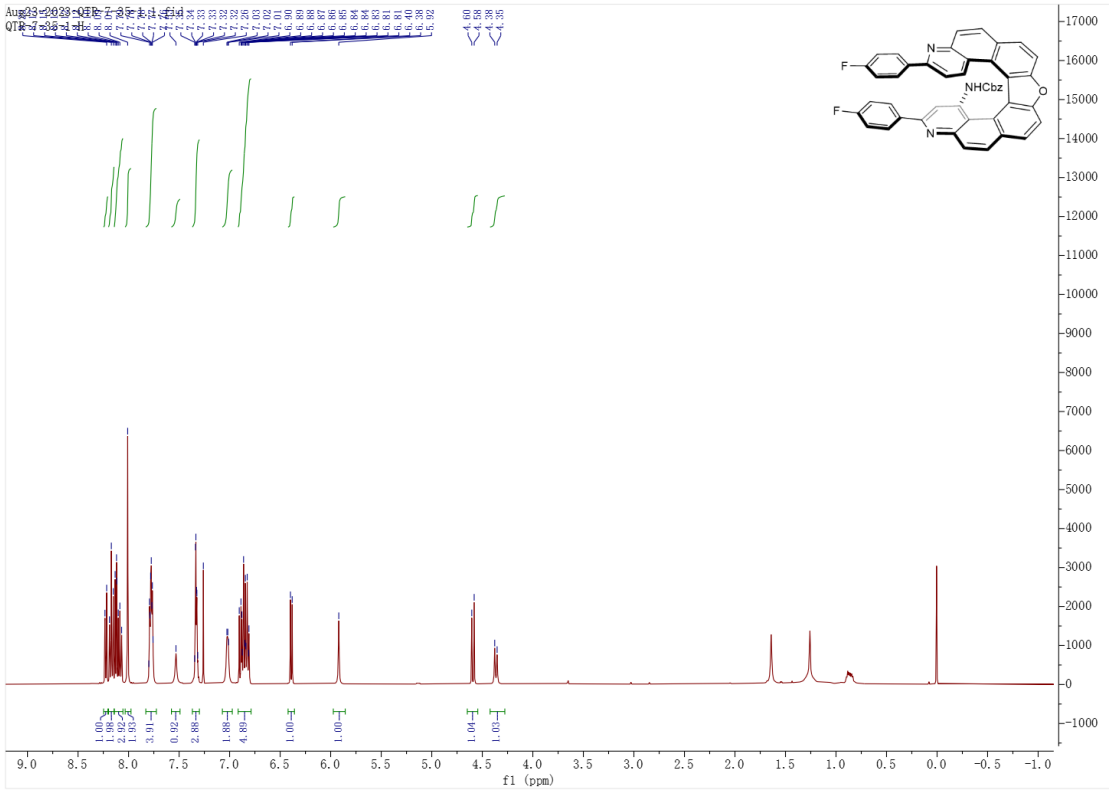


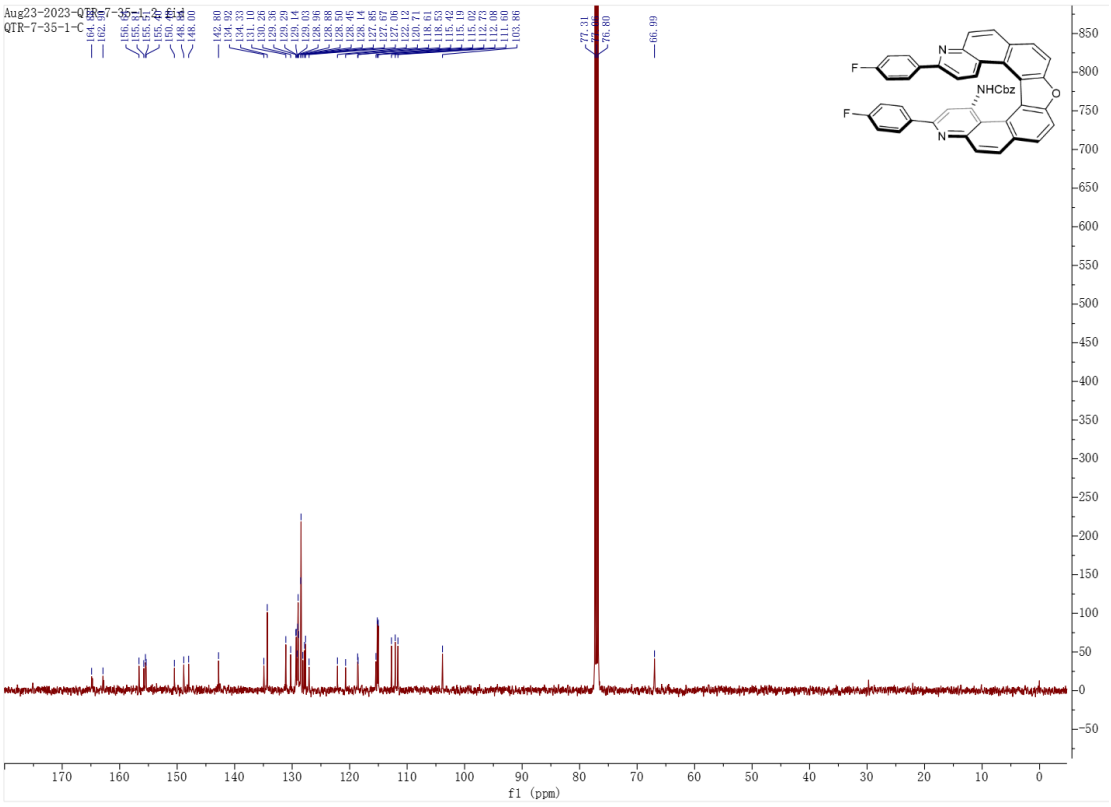
Helicene 5b

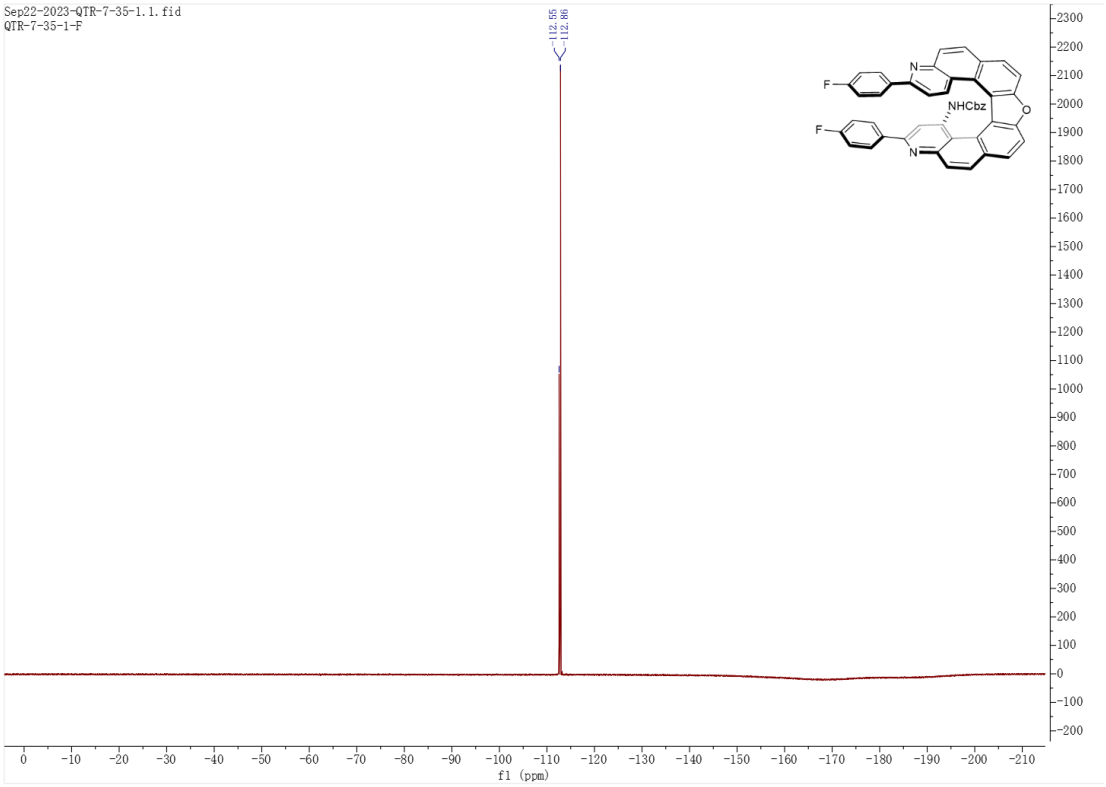




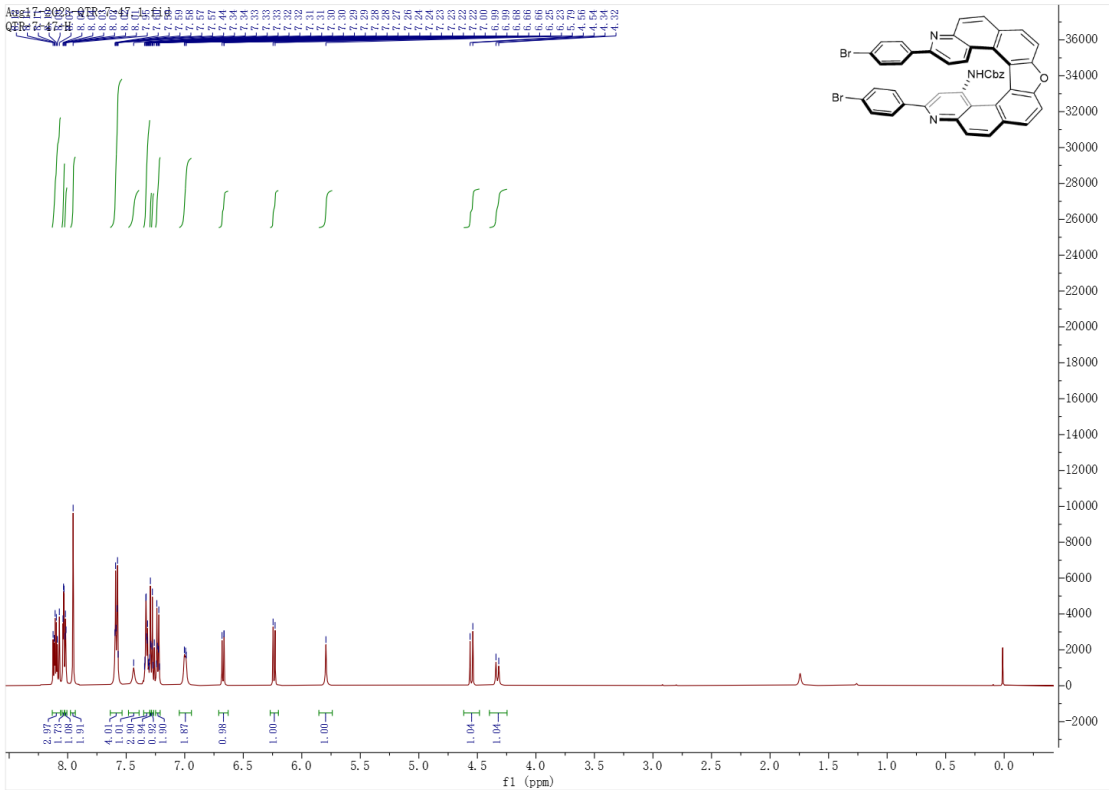
Helicene 5c

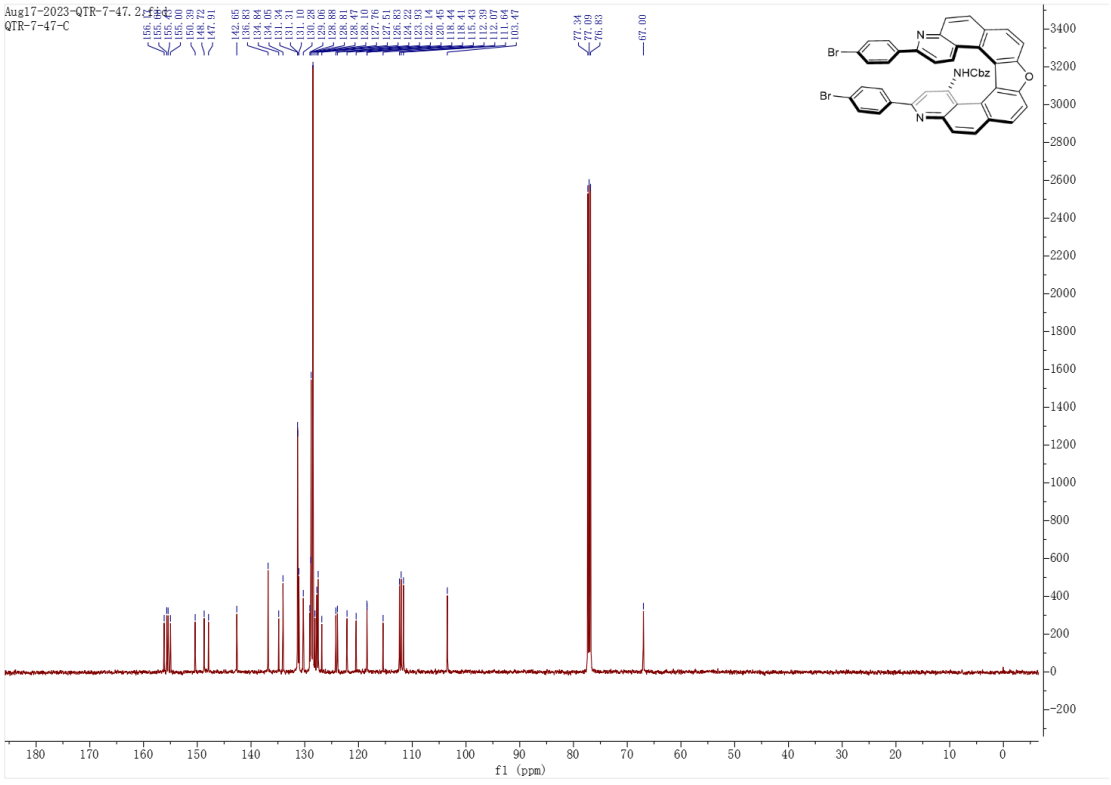




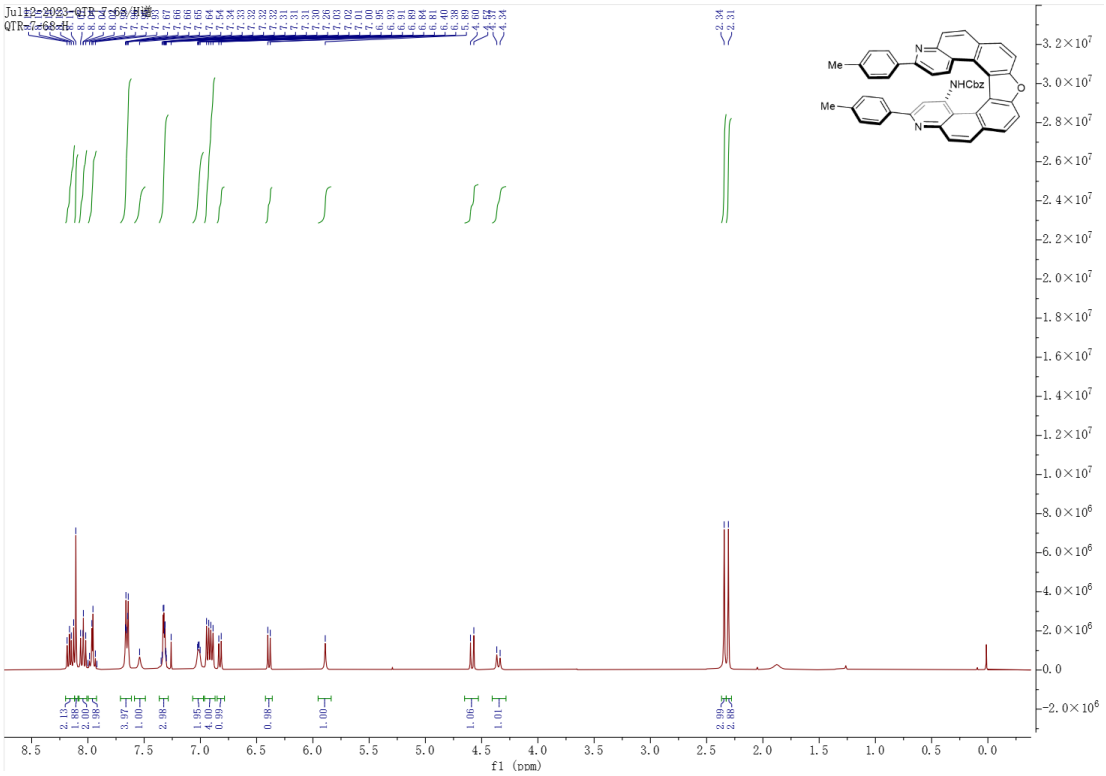

Sep22-2023-QTR-7-35-1.1.fid
QTR-7-35-1-F
-112.55
-112.86
F
F
N
N
O
NHCbz
f1 (ppm)

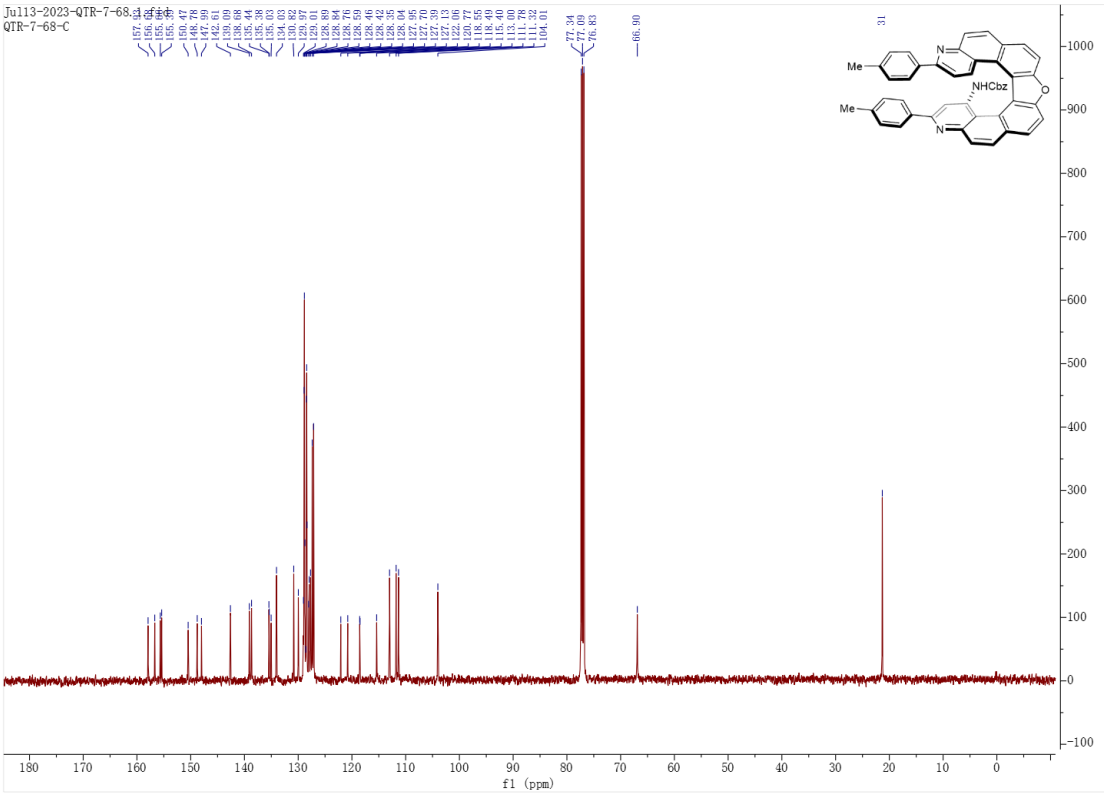
Helicene 5d


Br
N
NHCbz
O
Br
N
f1 (ppm)

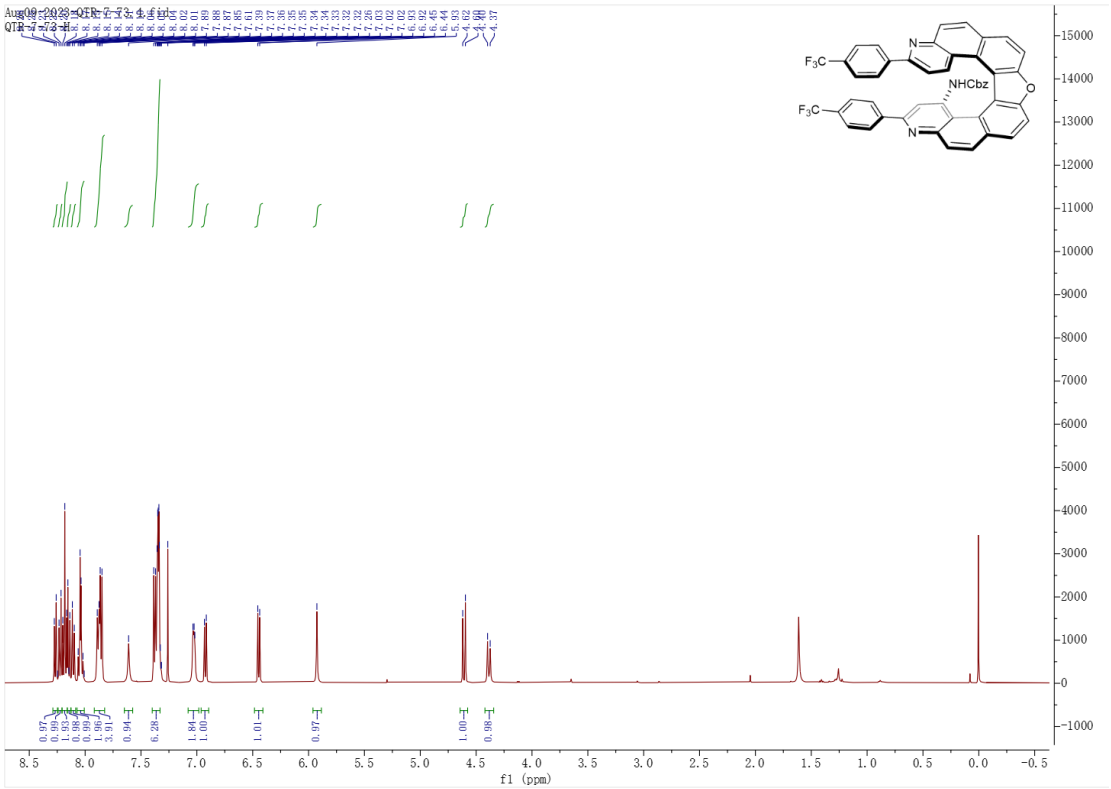

Aug17-2023-QTR-7-47.2.fid
QTR-7-47-C
Br
N
NHCbz
O
Br
N
f1 (ppm)

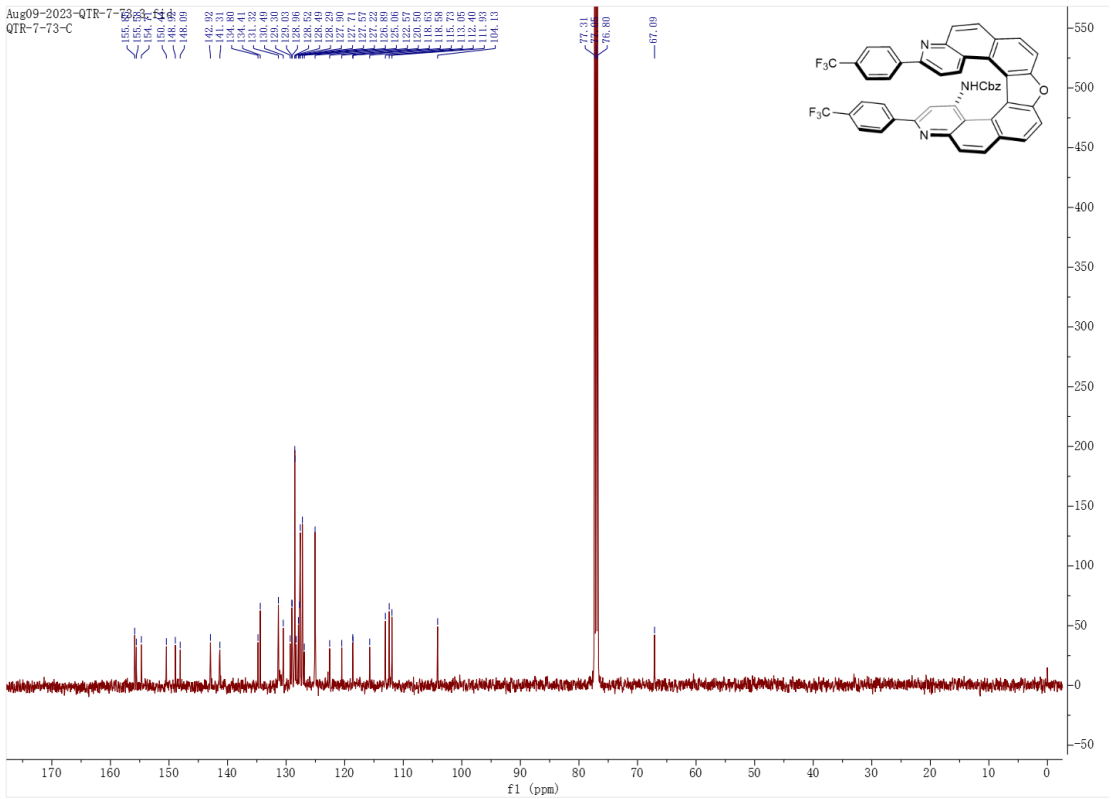
Helicene 5e

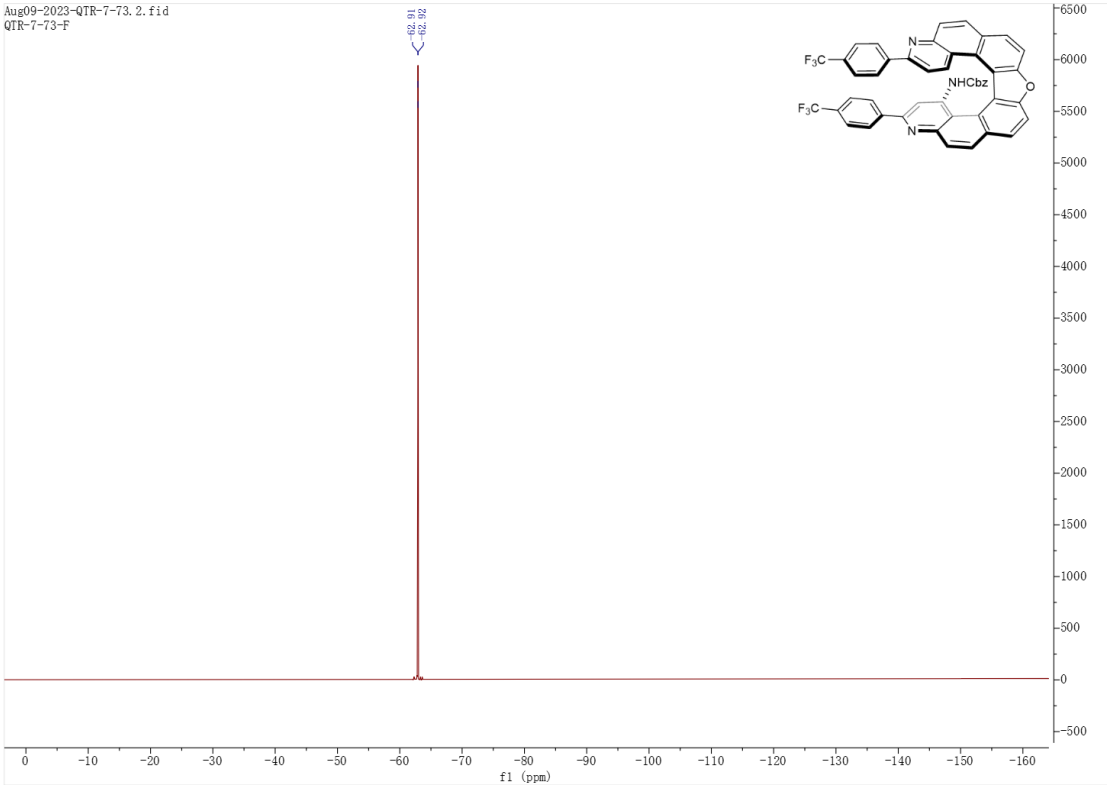




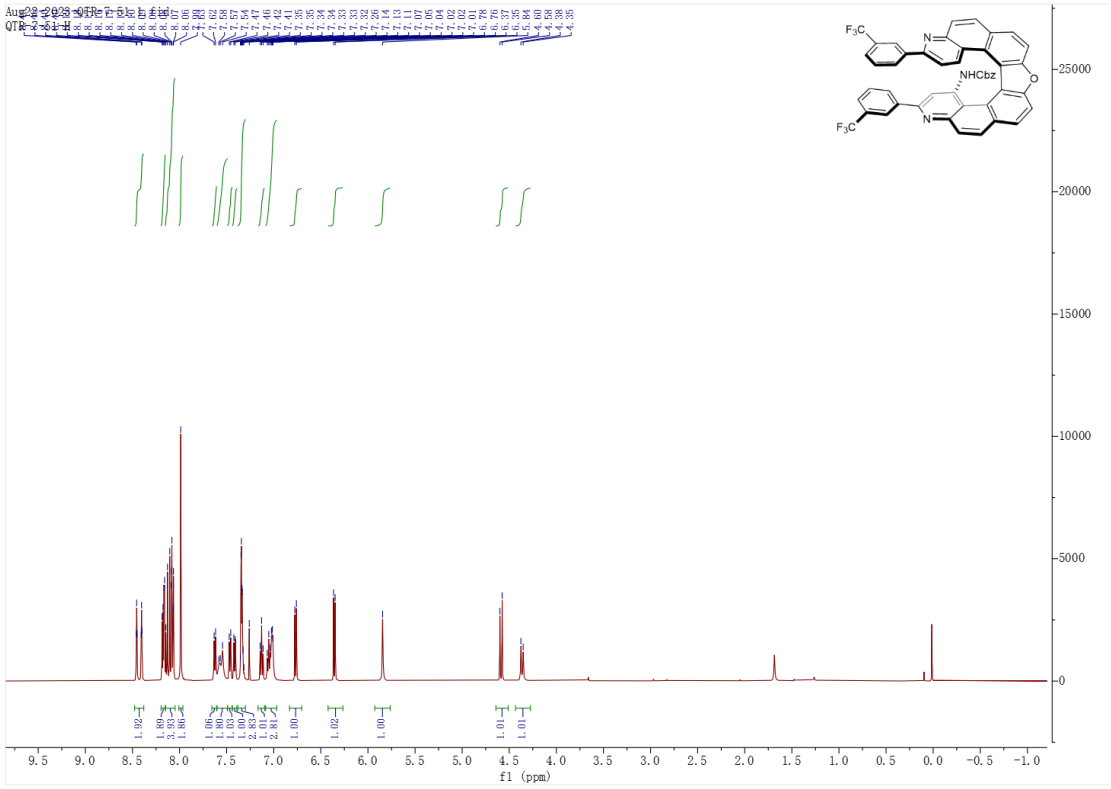
Helicene 5f

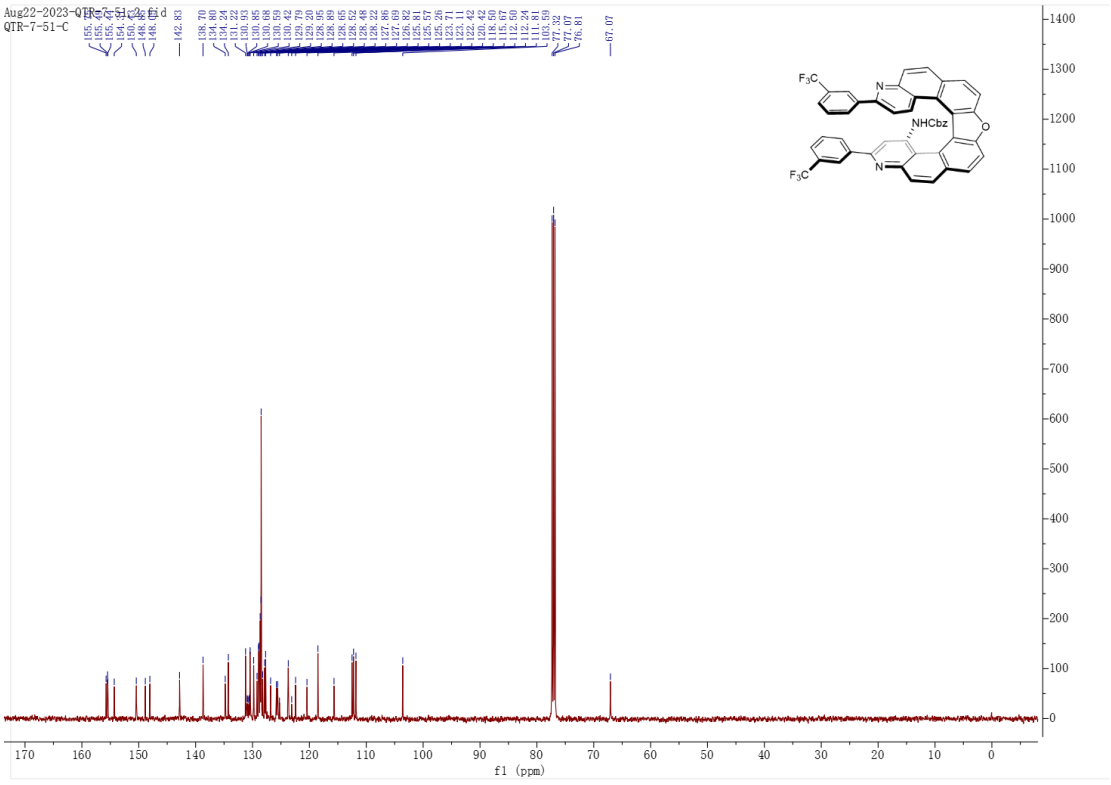

Aug09-2023-QTR-7-73-H.fid
QTR-7-73-H
F3C
NHCbz
F3C
N
N
O
f1 (ppm)

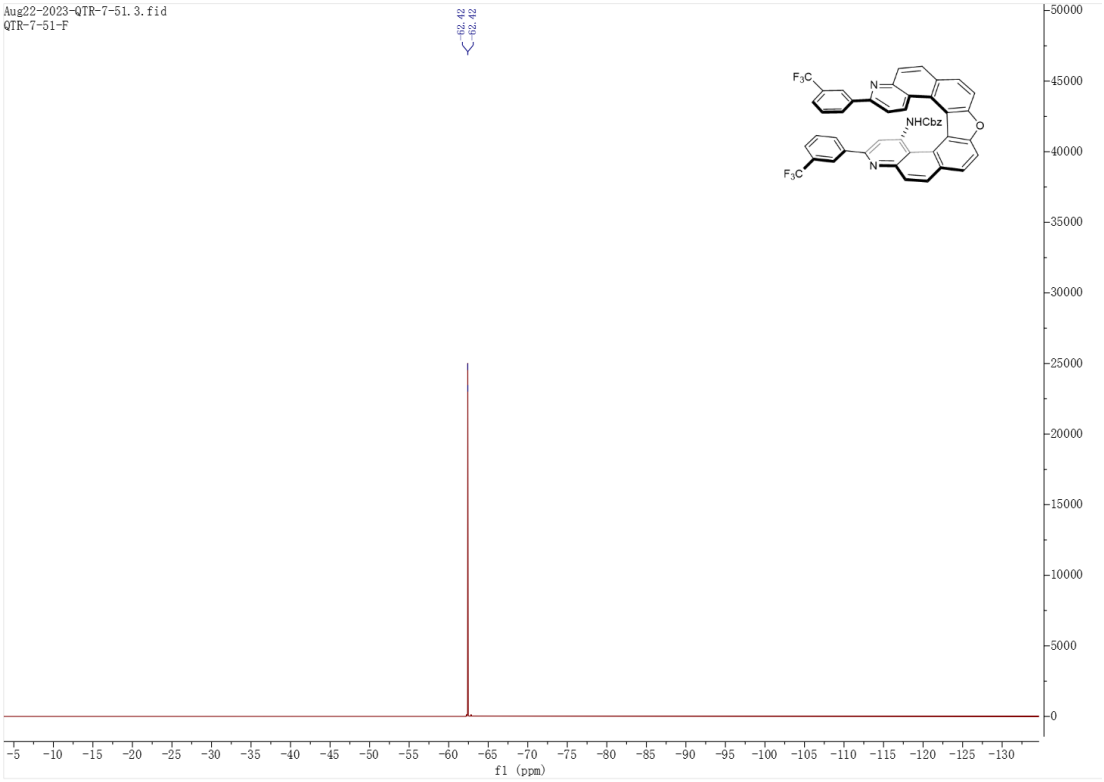

Aug09-2023-QTR-7-73-C.fid
QTR-7-73-C
F3C
NHCbz
F3C
N
N
O
f1 (ppm)


Aug09-2023-QTR-7-73.2.fid
QTR-7-73-F
-62.91
-62.92
F3C
NHCbz
F3C
N
N
O
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

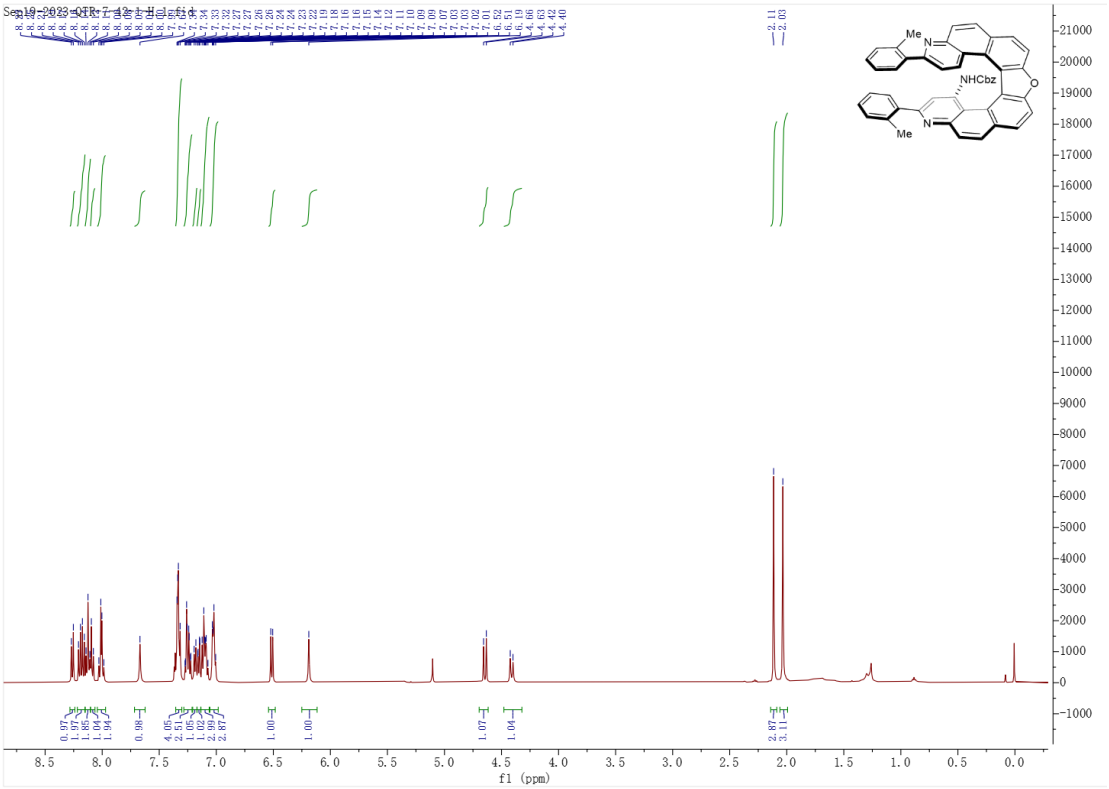
Helicene 5g

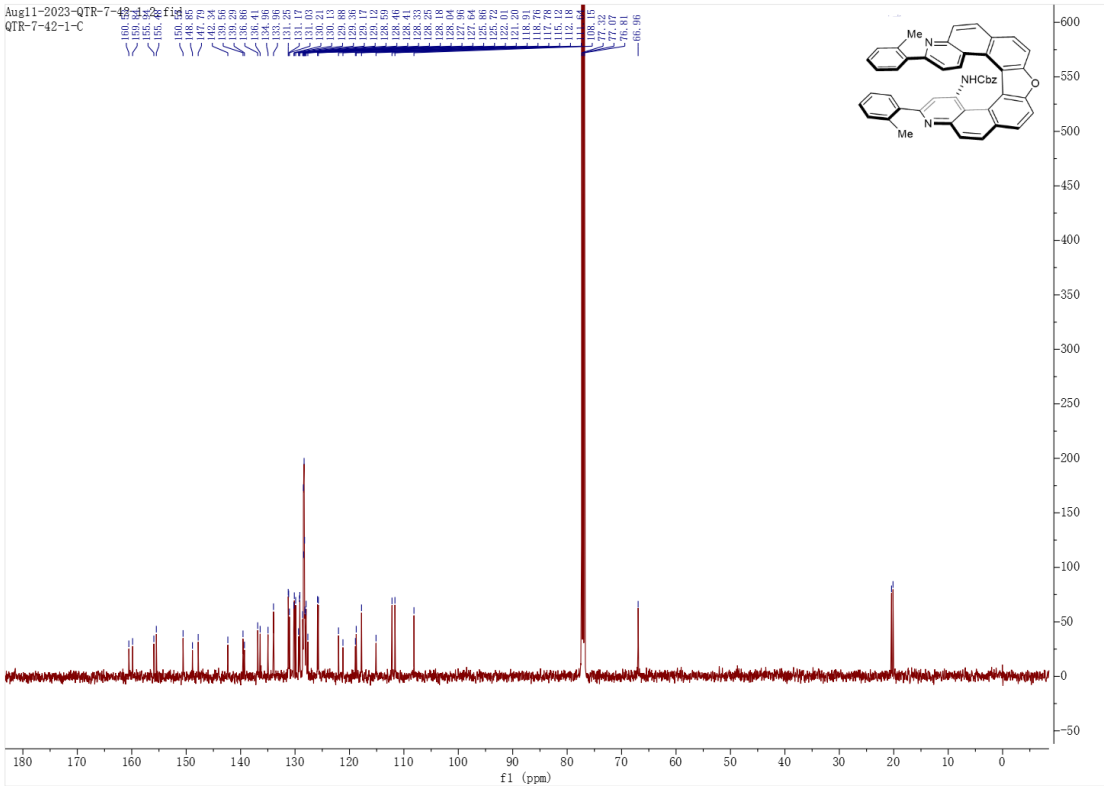




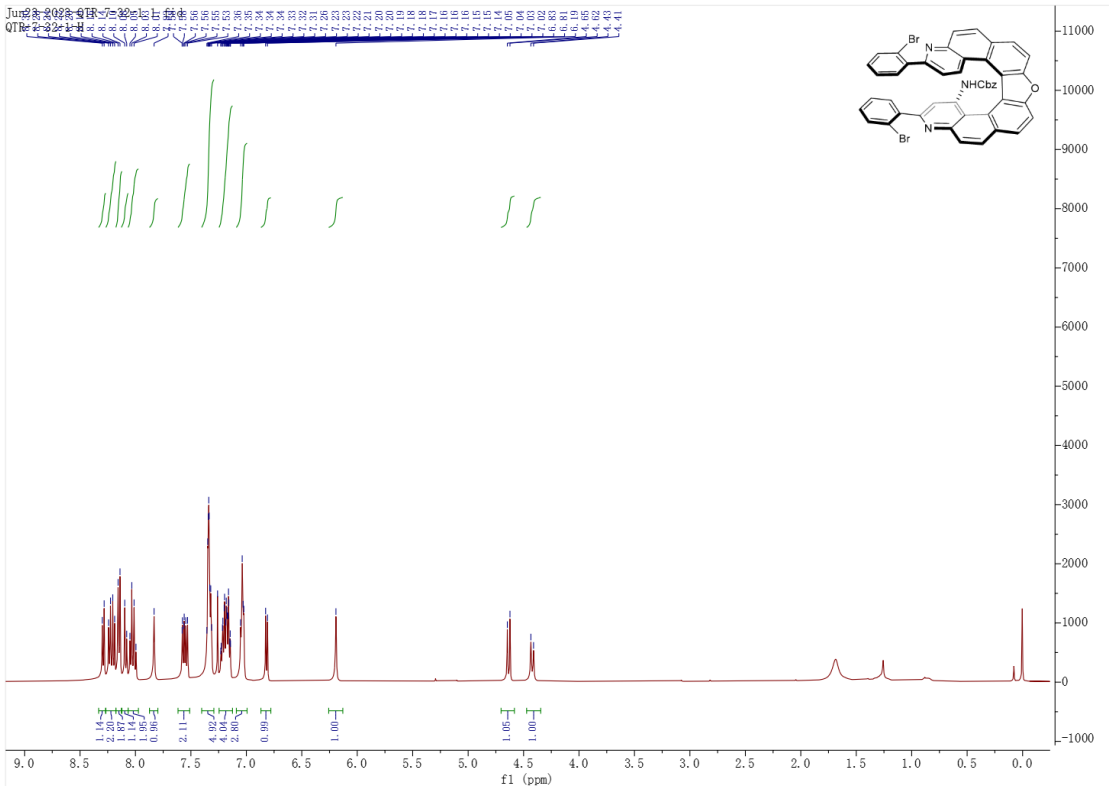

Aug22-2023-QTR-7-51.3.fid
QTR-7-51-F
-62.42
-62.42
F3C
N
NHCbz
O
N
F3C
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)

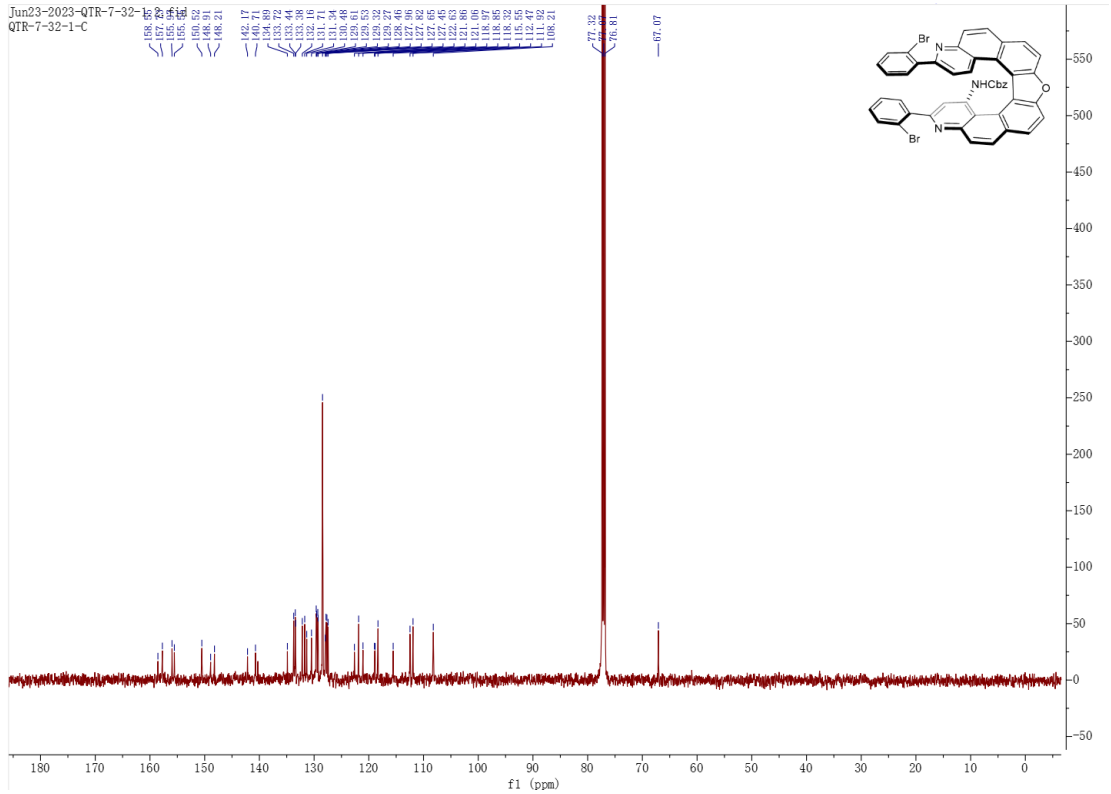
Helicene 5h


Me
N
NHCbz
O
N
Me
f1 (ppm)

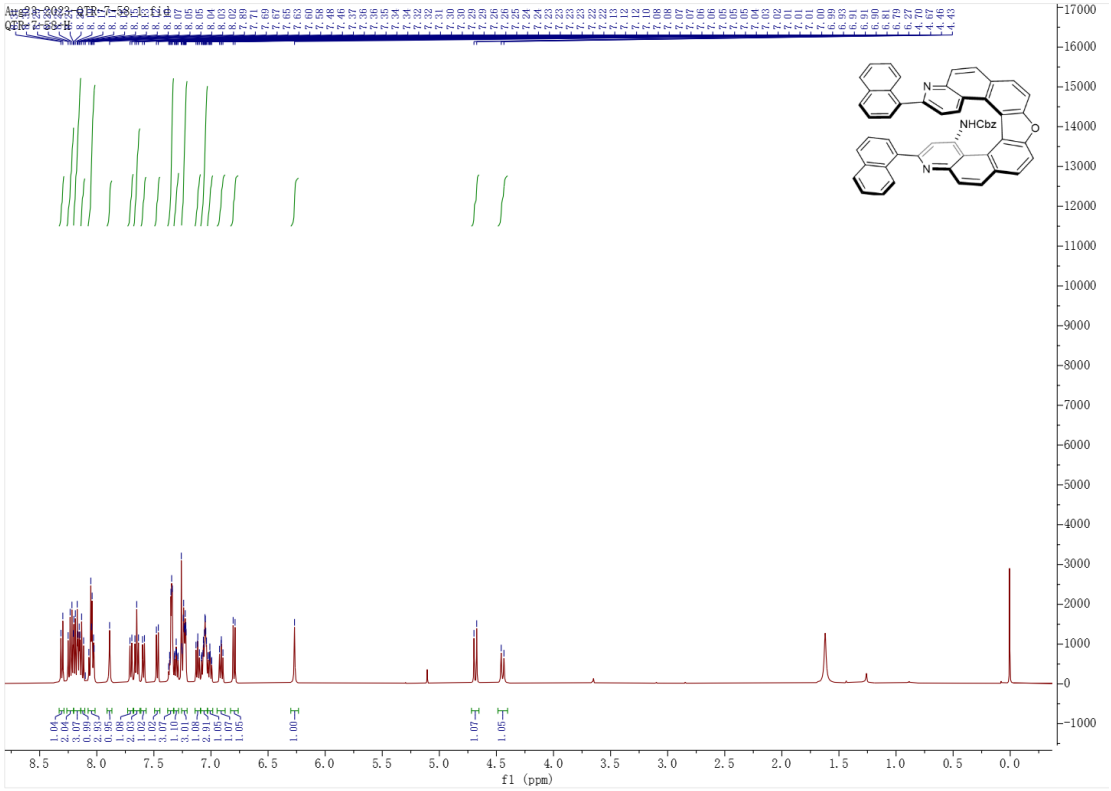

Aug11-2023-QTR-7-42-1-C-2.fid
QTR-7-42-1-C
Me
N
NHCbz
O
N
Me
f1 (ppm)

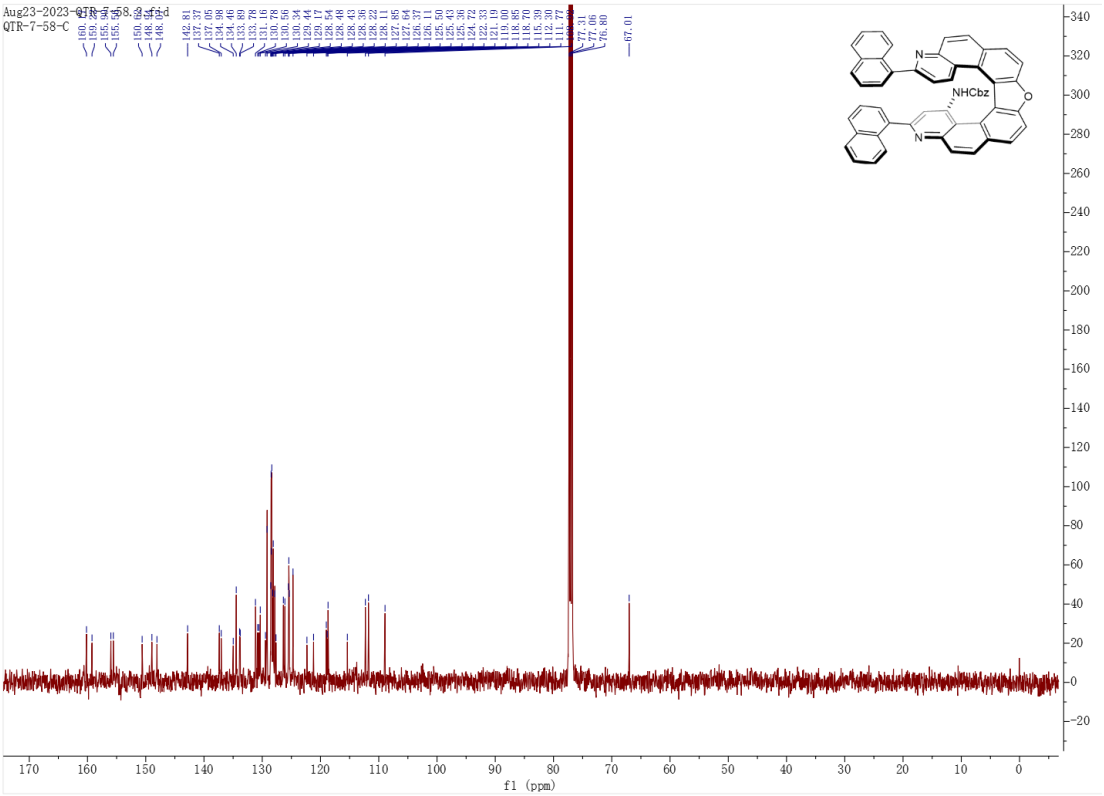
Helicene 5i



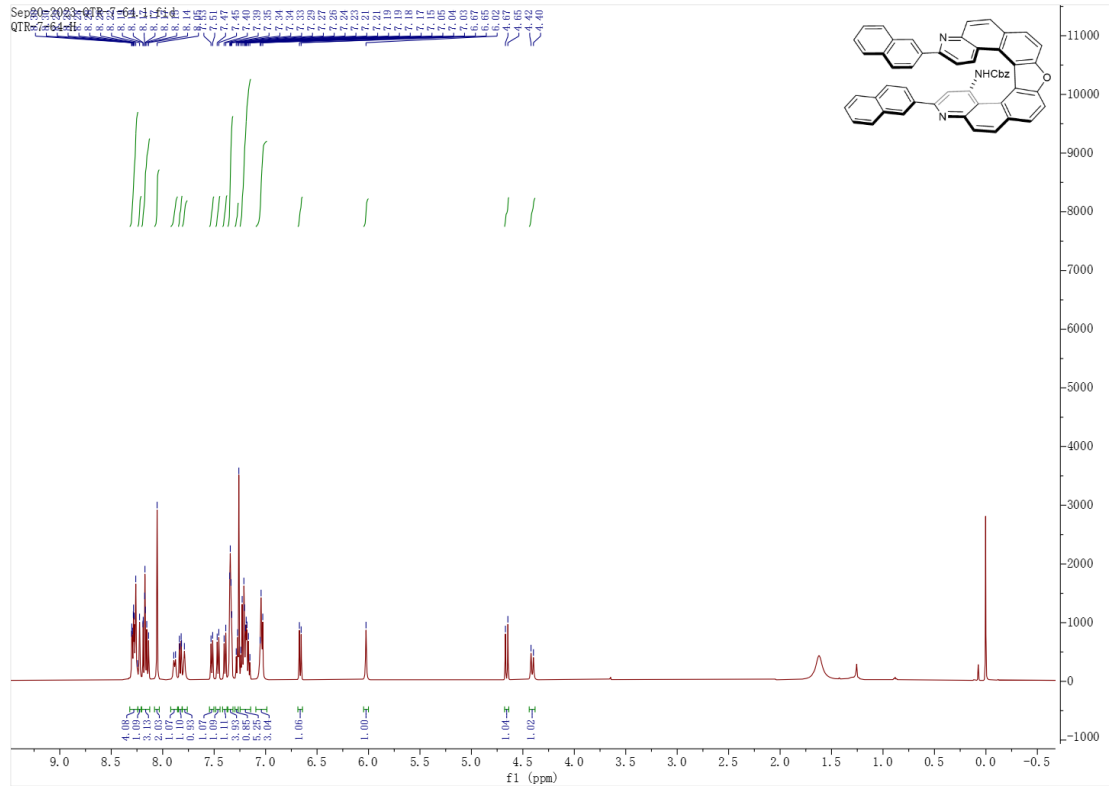


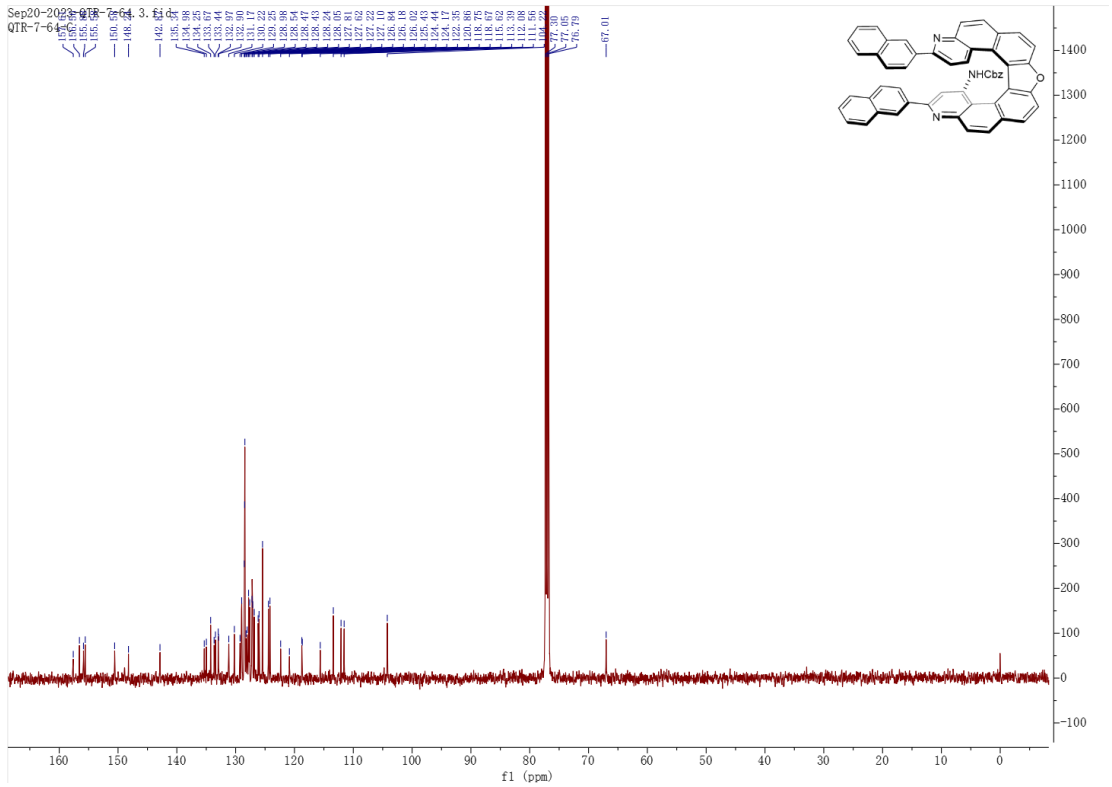
Helicene 5j



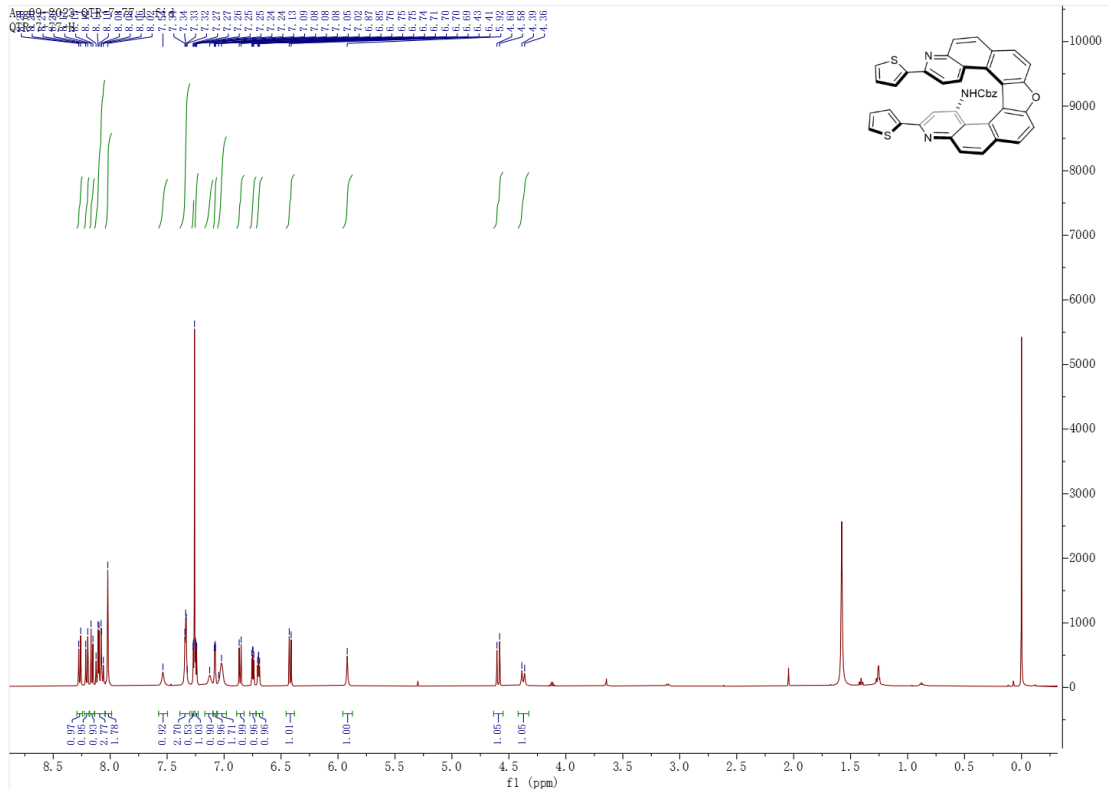


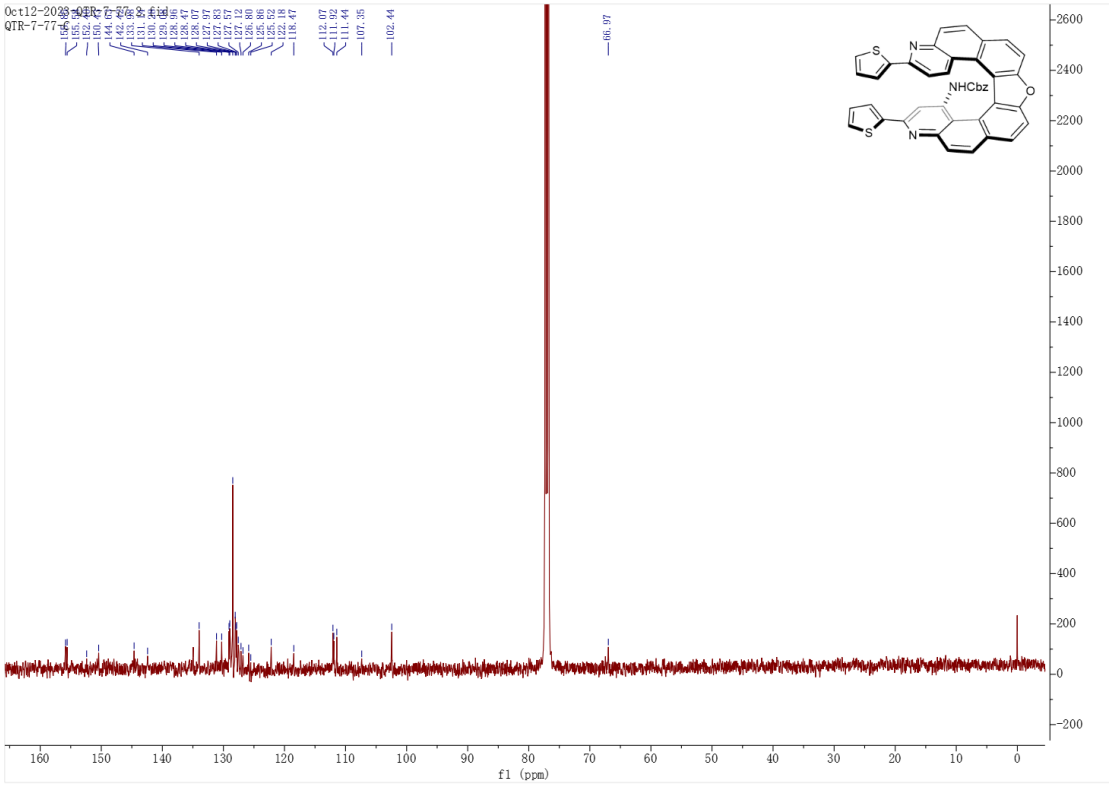
Helicene 5k



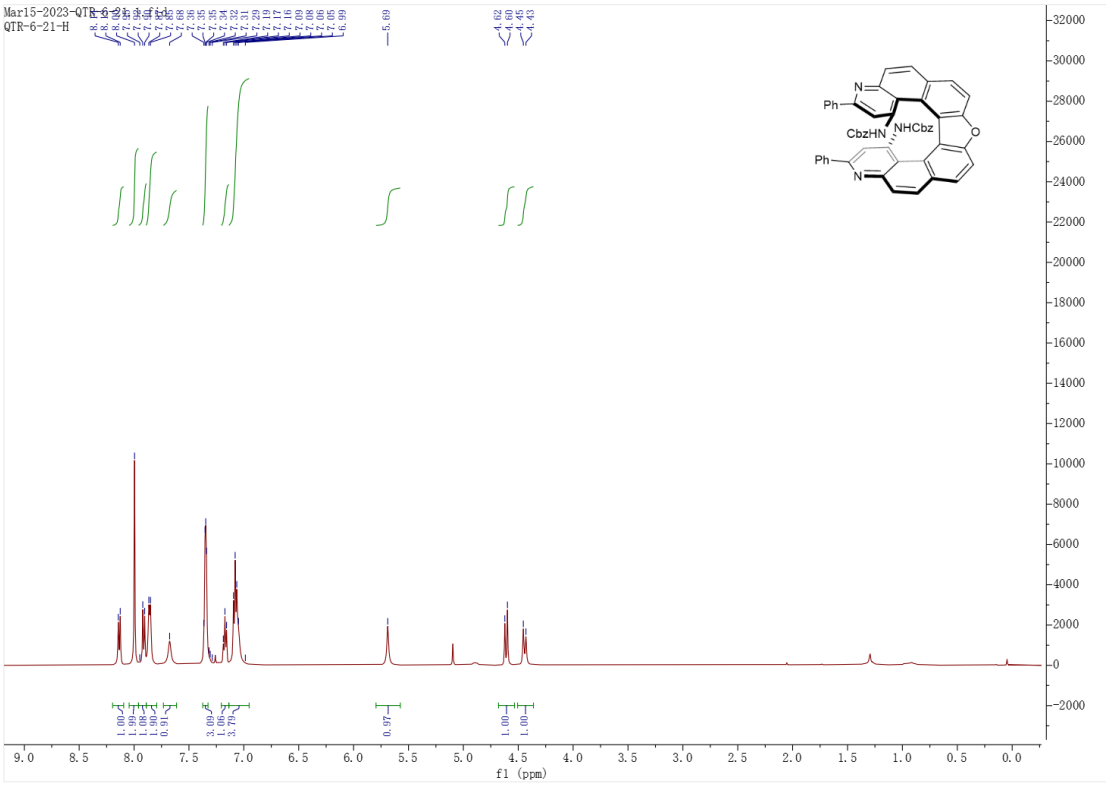


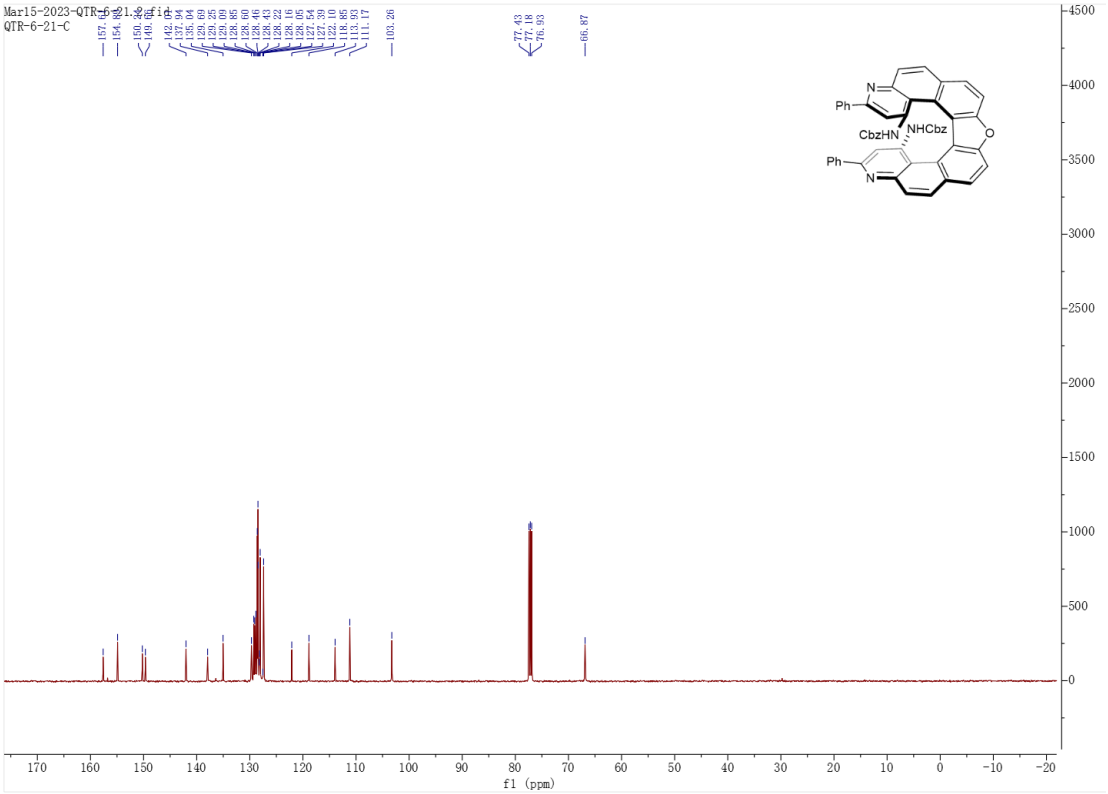
Helicene 5l



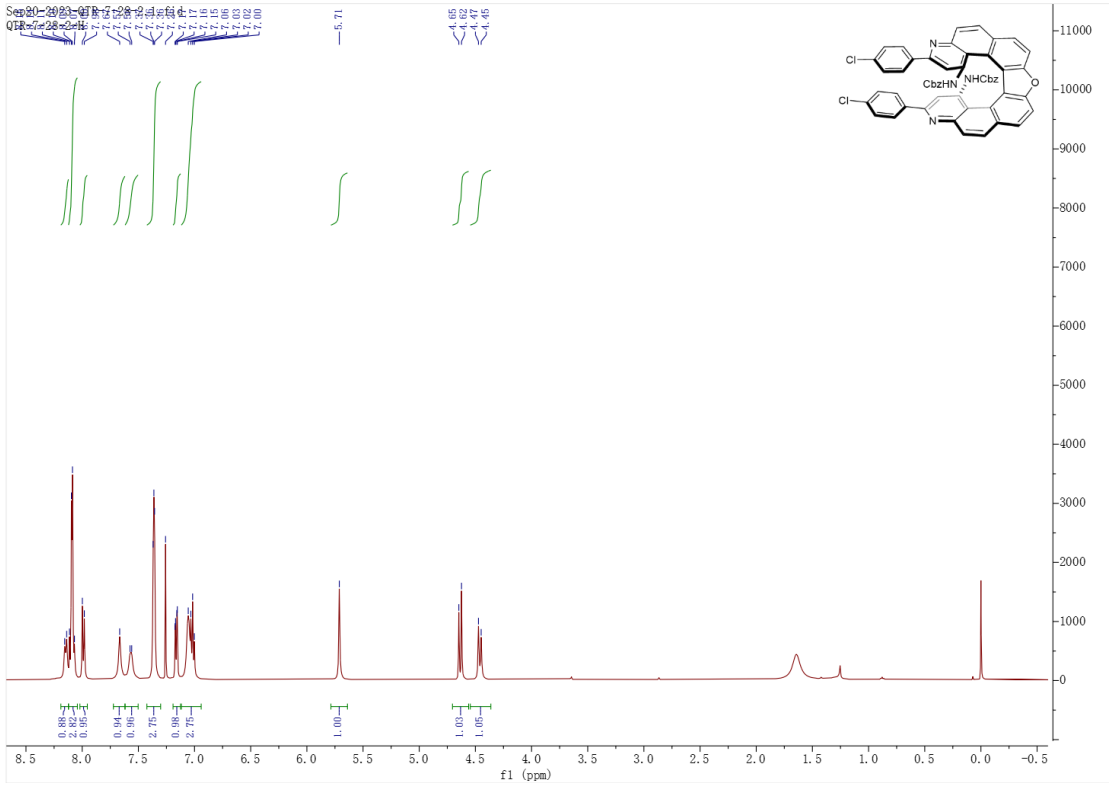


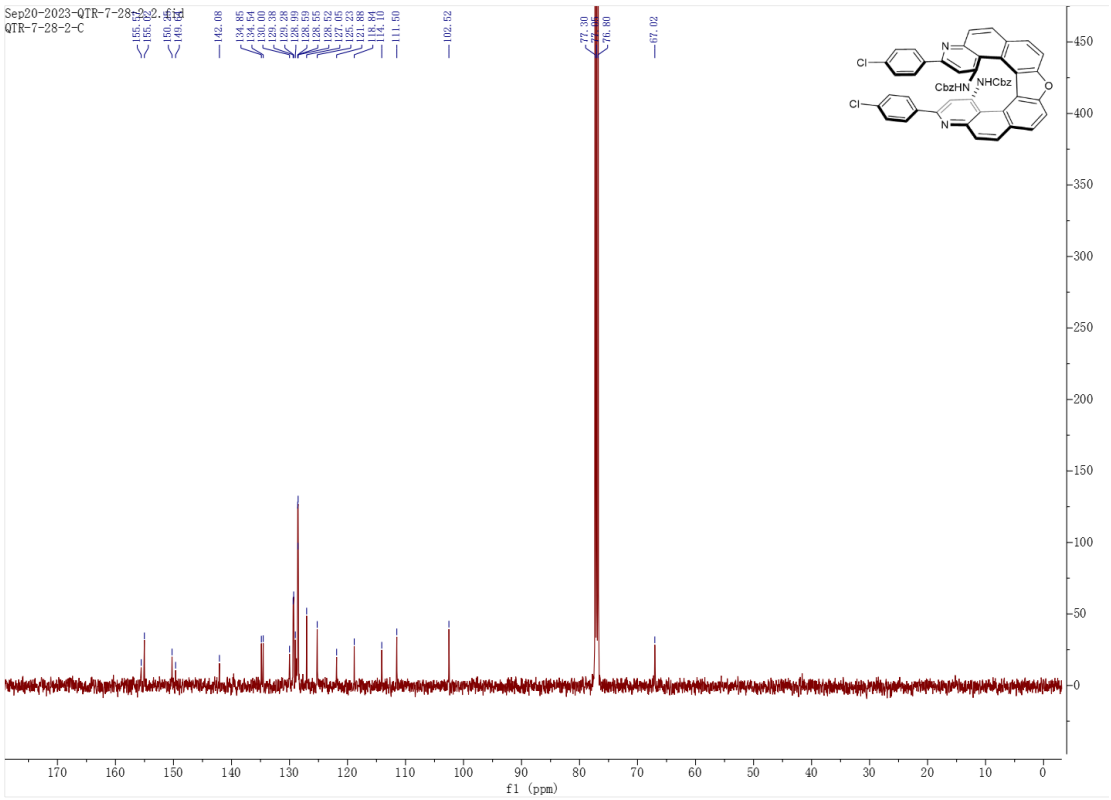
Helicene 6a


Mar15-2023-QTR-6-21-H.esp
QTR-6-21-H
Ph
CbzHN
NHCbz
O
Ph
N
f1 (ppm)

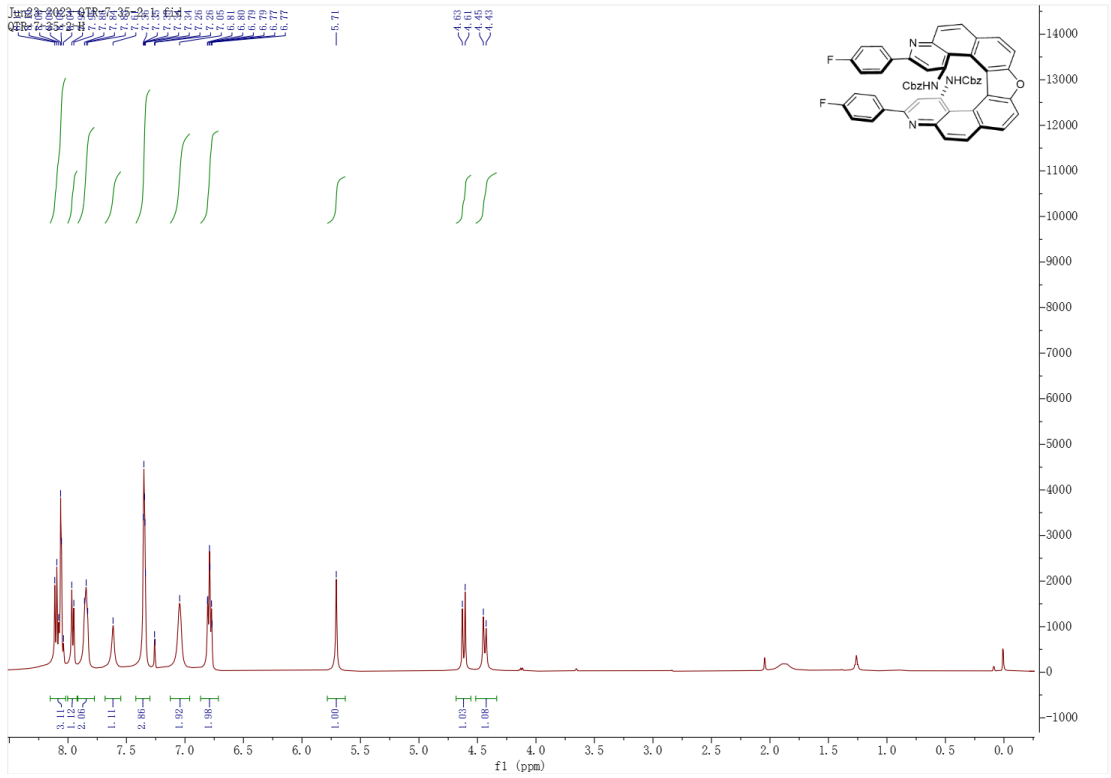

Mar15-2023-QTR-6-21-C.esp
QTR-6-21-C
Ph
CbzHN
NHCbz
O
Ph
N
f1 (ppm)

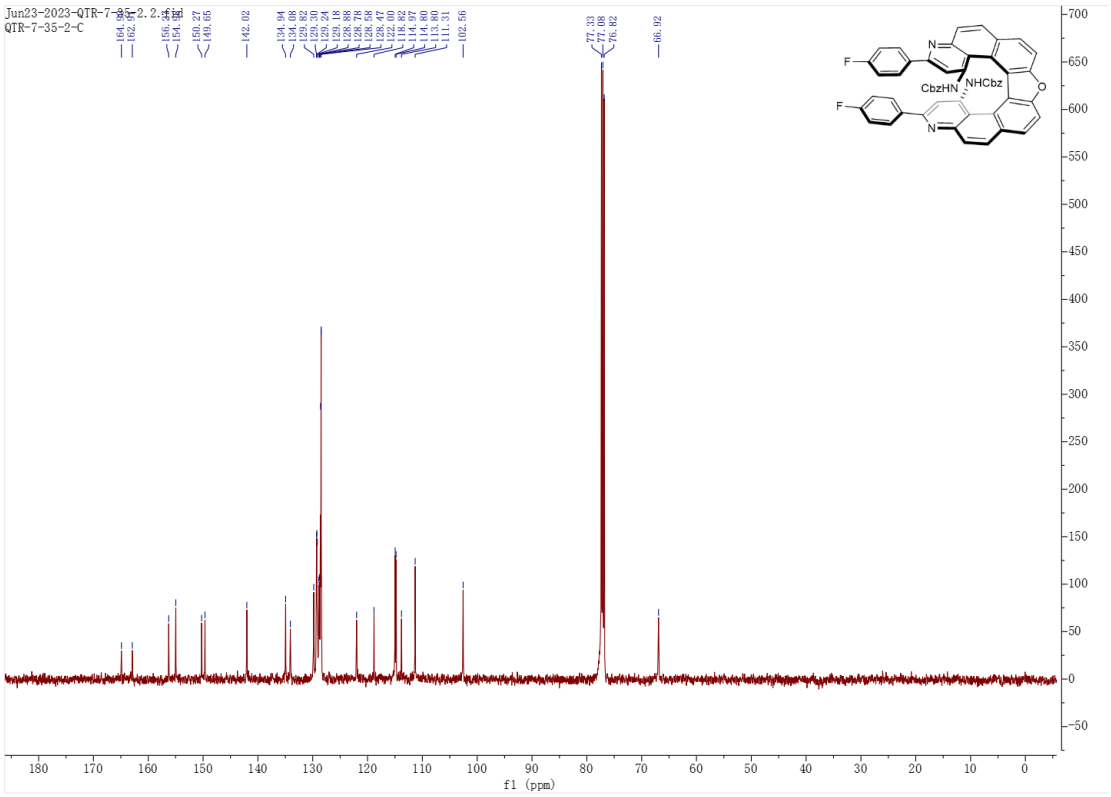
Helicene 6b

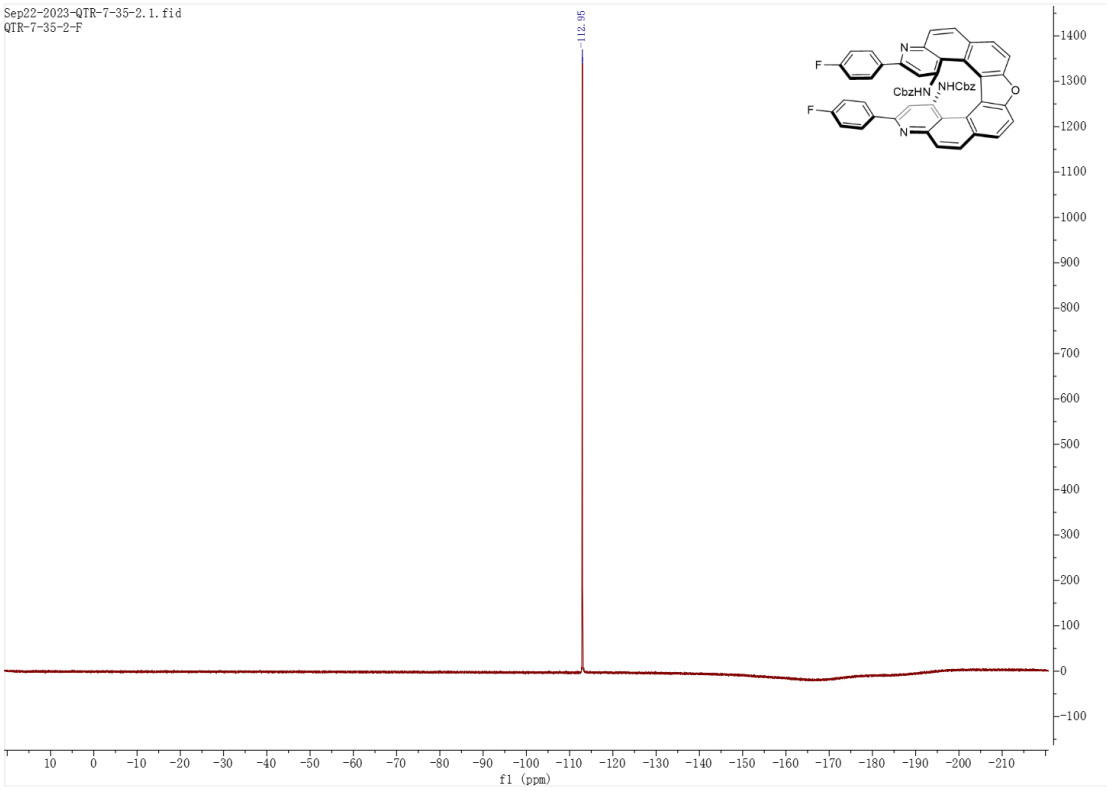




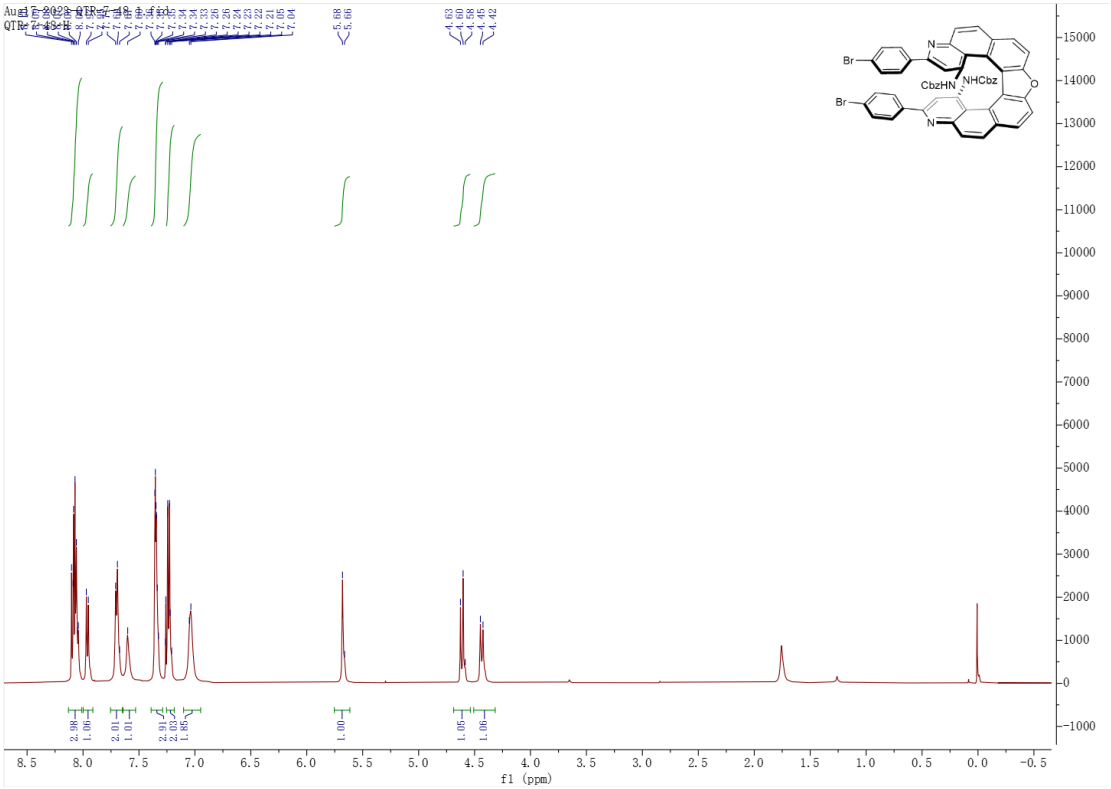
Helicene 6c

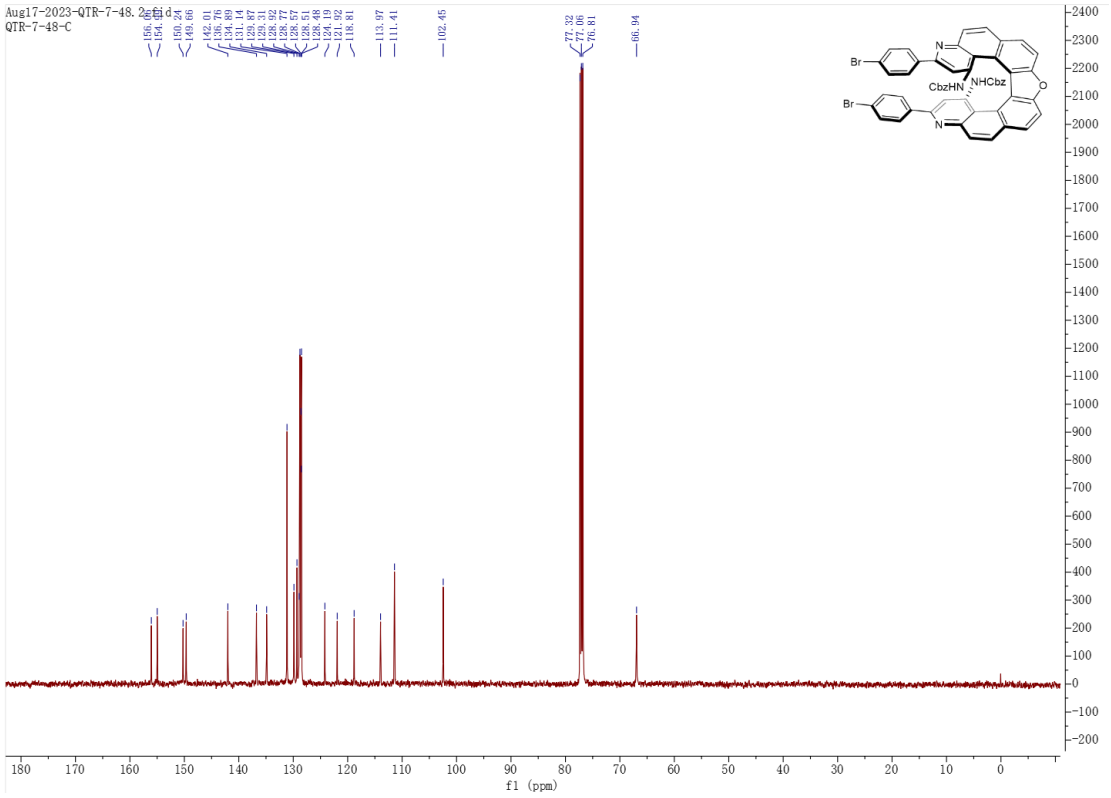




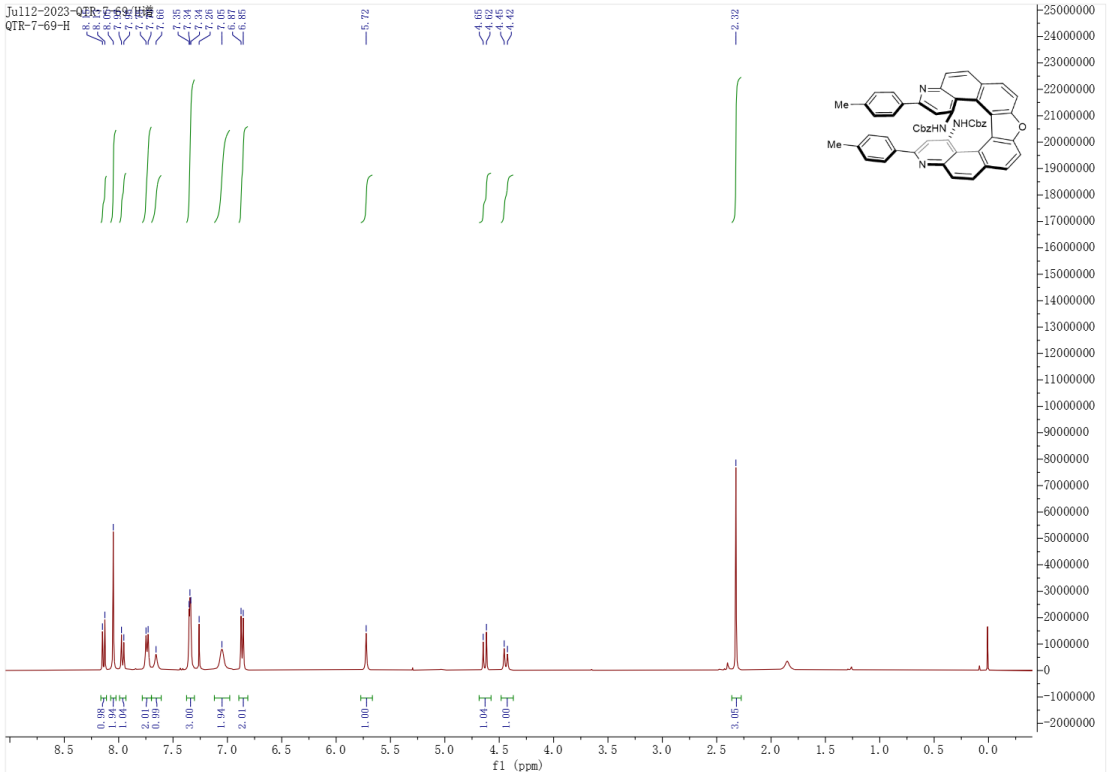

Sep22-2023-QTR-7-35-2.1.fid
QTR-7-35-2-F
-112.95
F
N
CbzHN
NHCbz
O
F
N
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

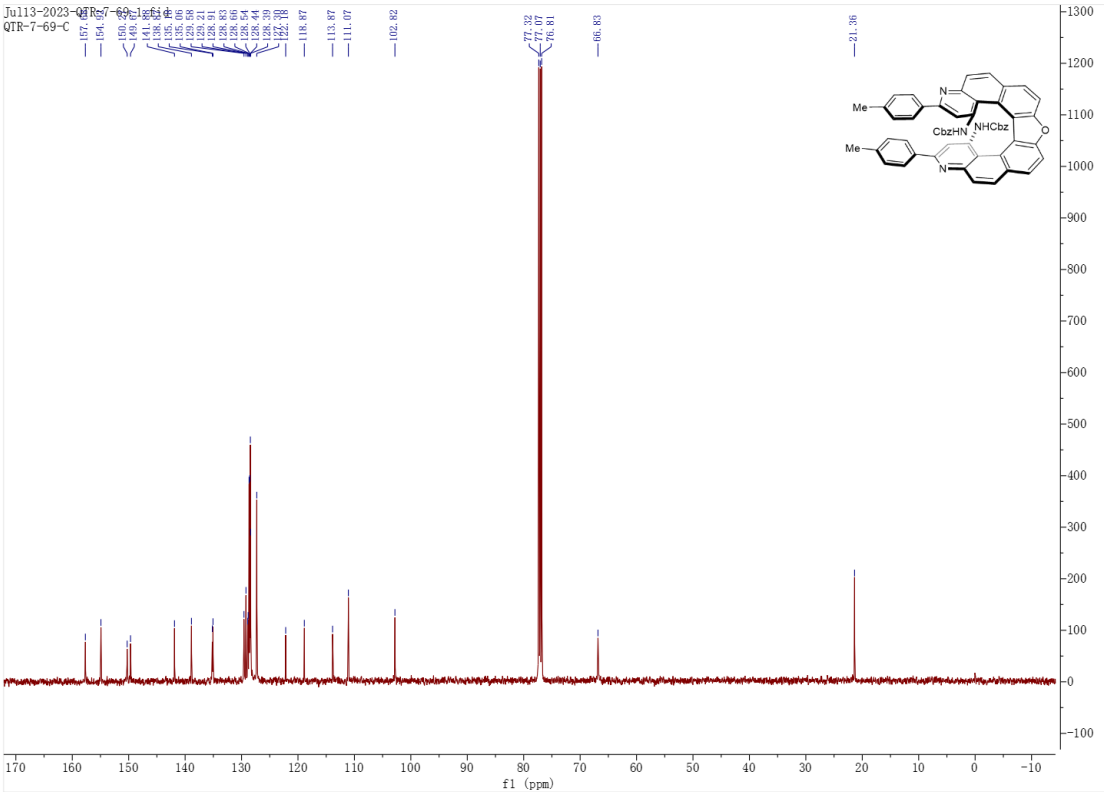
Helicene 6d



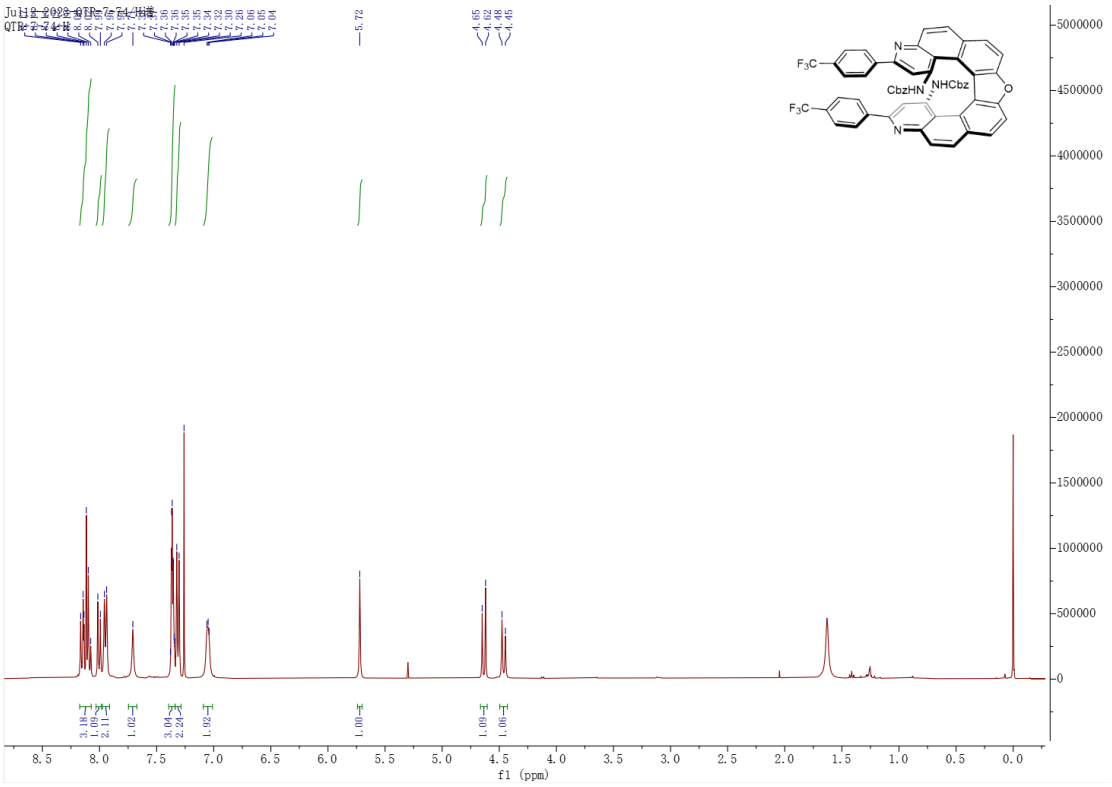


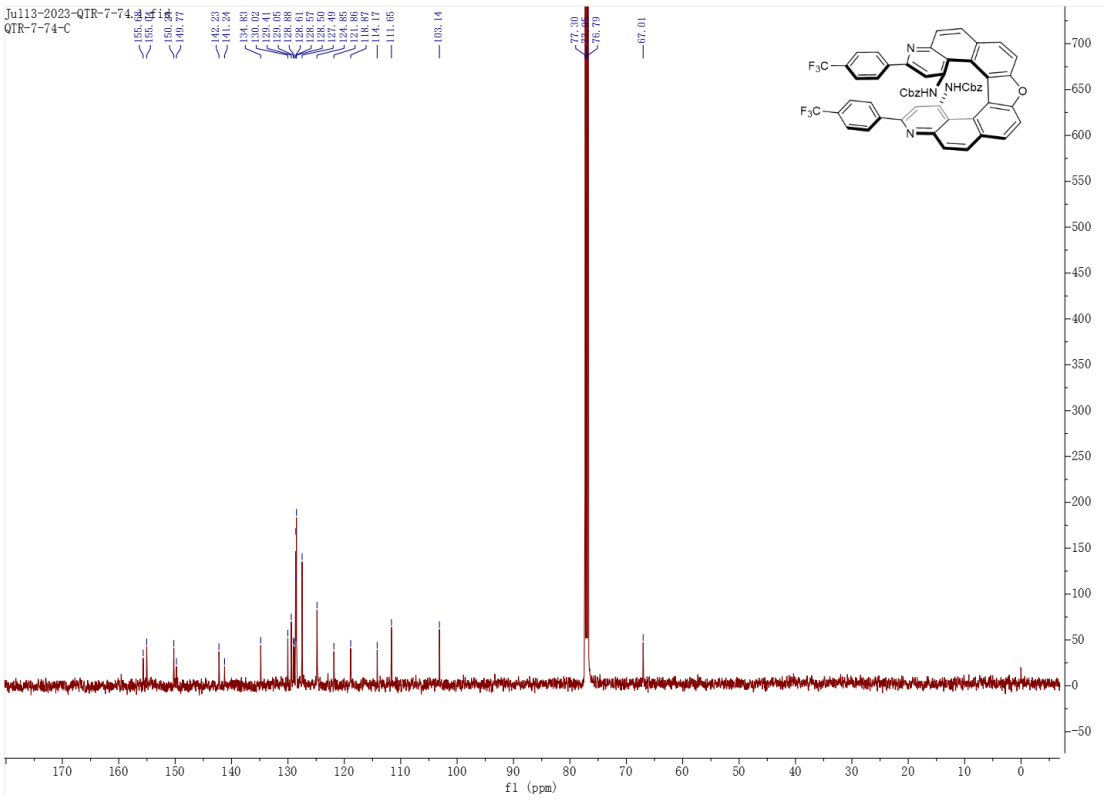
Helicene 6e

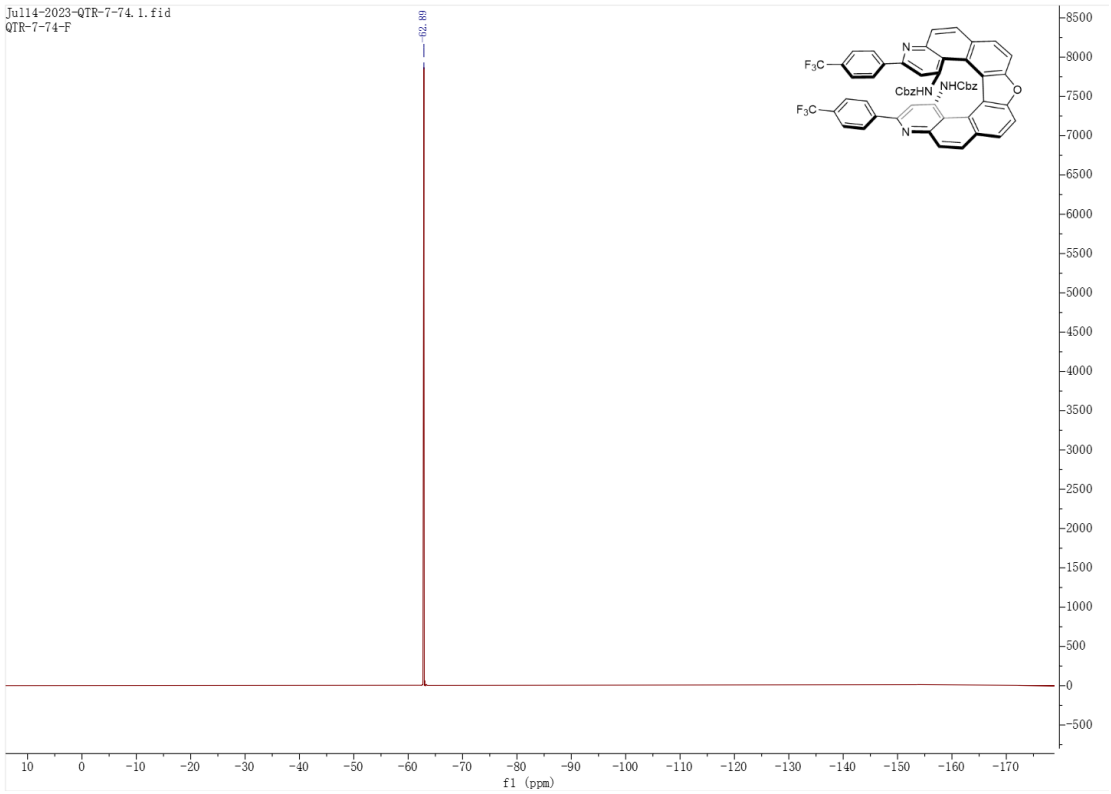

Jul12-2023-QTR-7-69-H
QTR-7-69-H
Me
CbzHN
NHCbz
Me
f1 (ppm)


Jul13-2023-QTR-7-69-1-cf1-1
QTR-7-69-C
Me
CbzHN
NHCbz
Me
f1 (ppm)

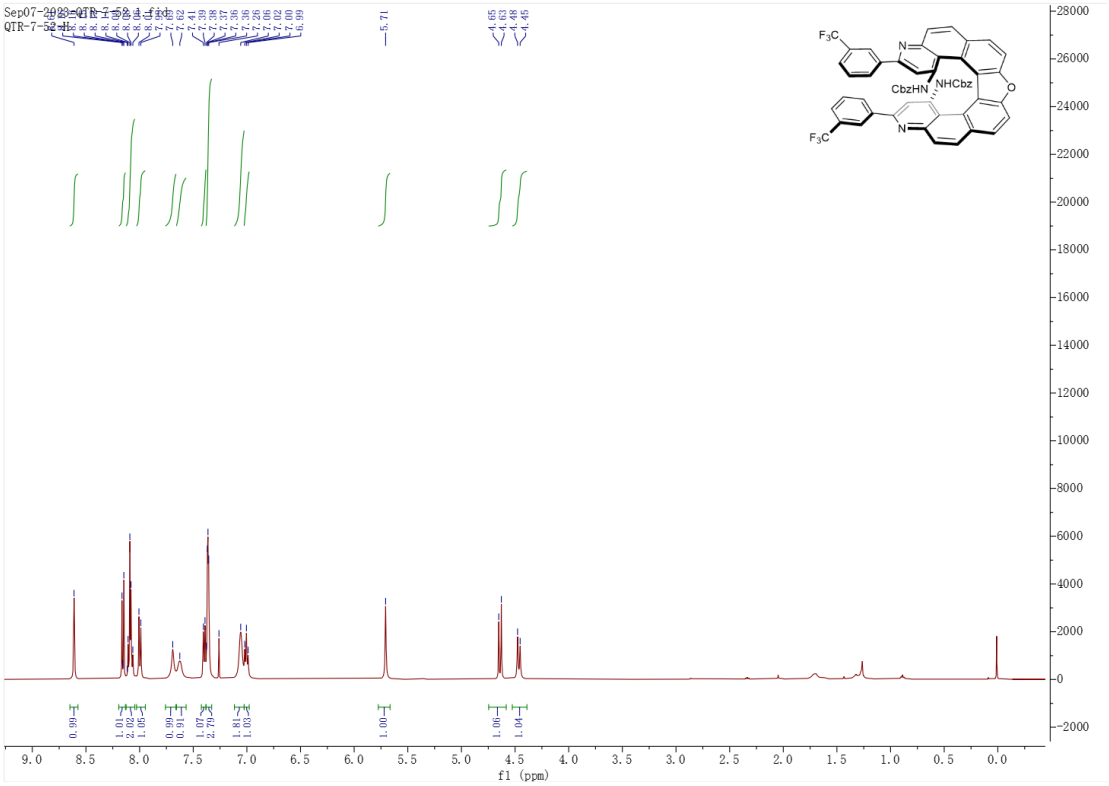
Helicene 6f

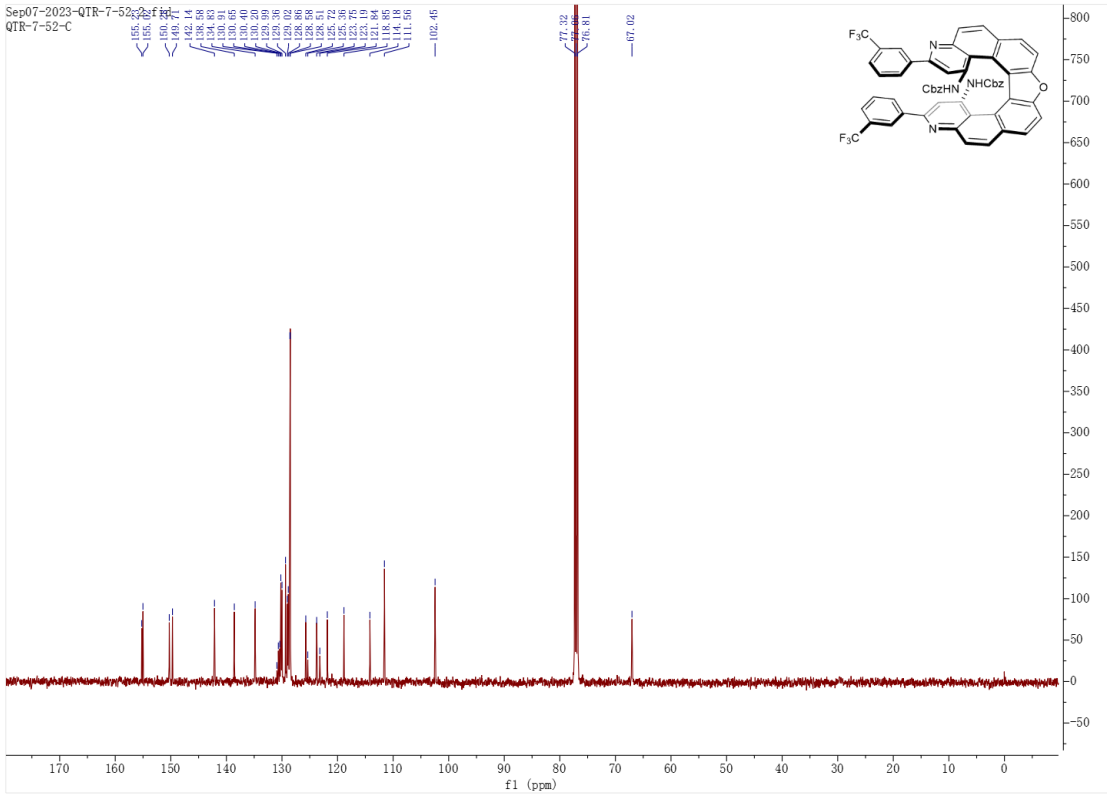


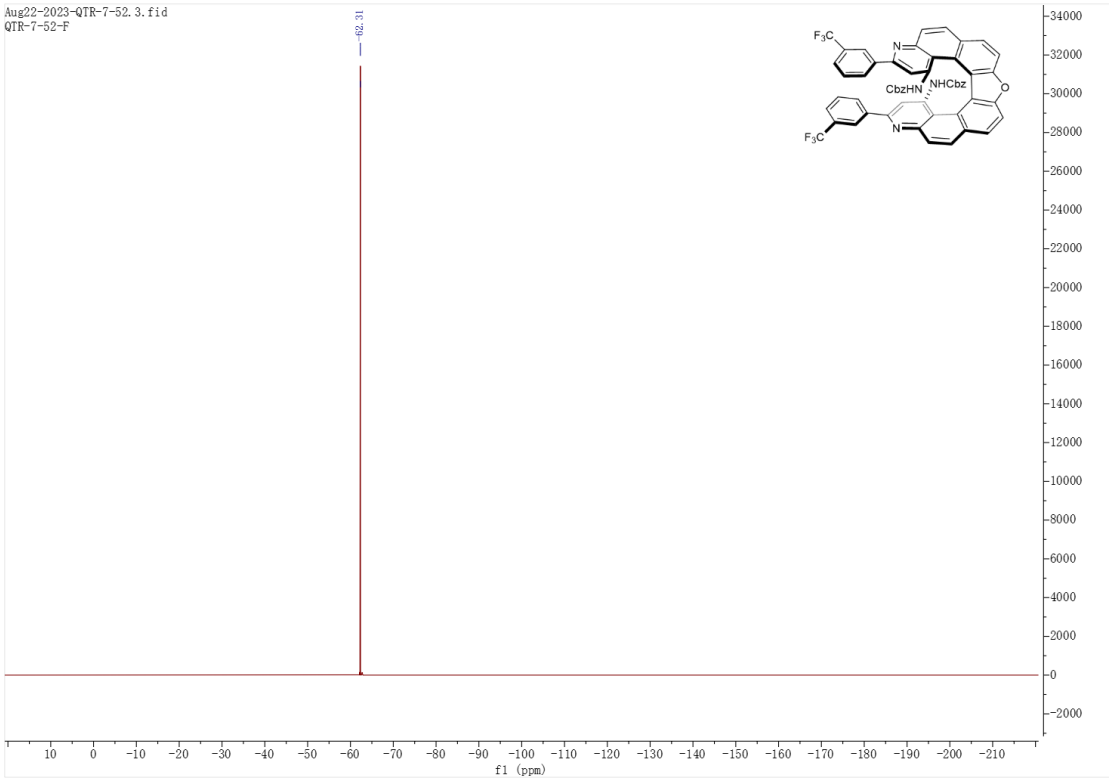



Jul14-2023-QTR-7-74.1.fid
QTR-7-74-F
-62.89
F3C
CbzHN
NHCbz
F3C
N
N
O
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

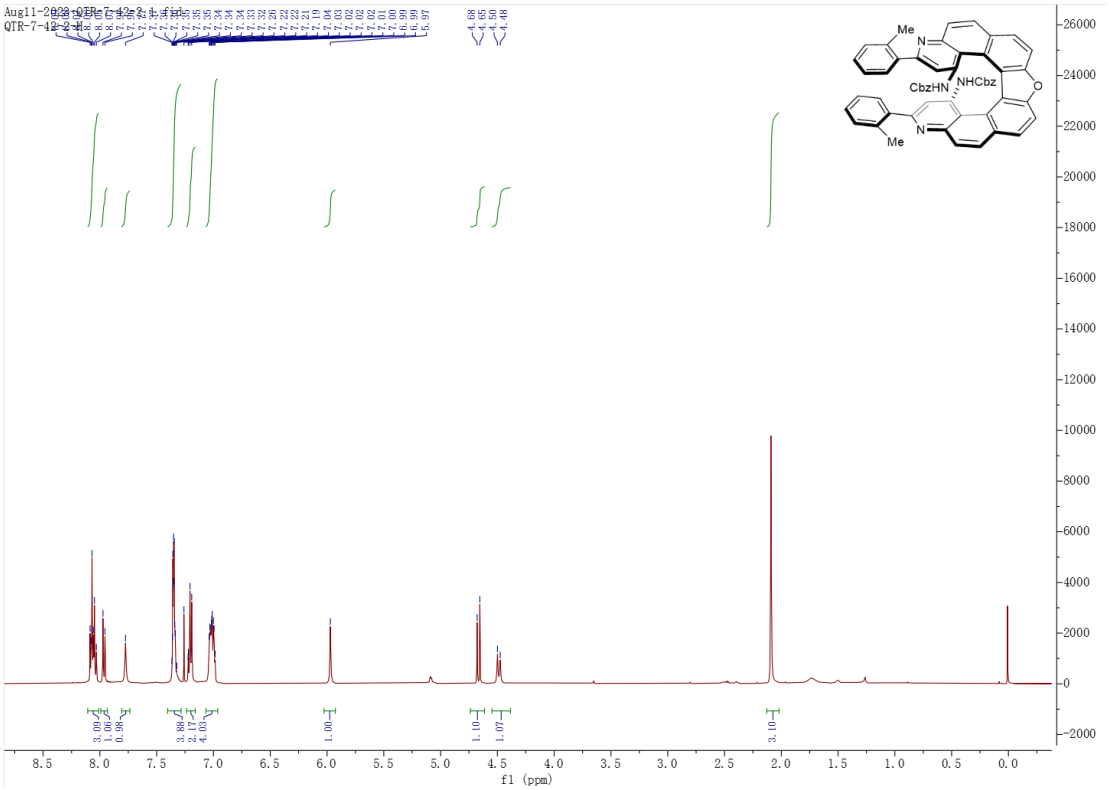
Helicene 6g

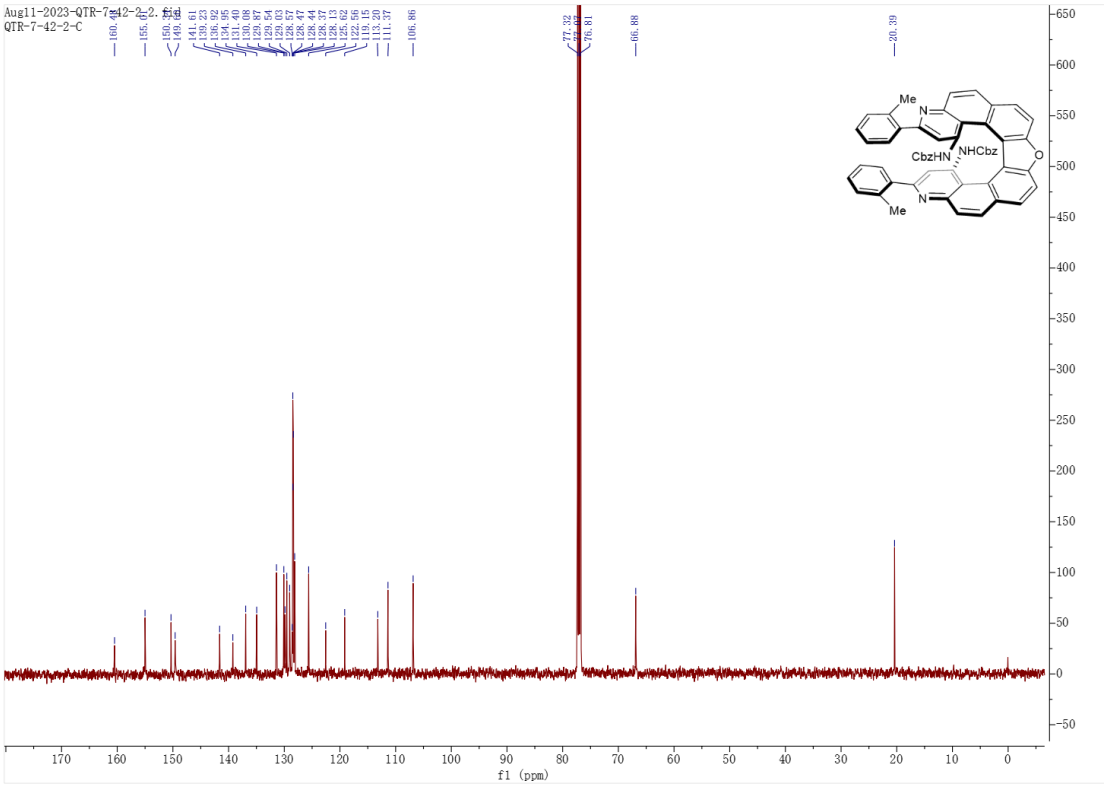

Sep07-2023-QTR-7-52-1.fid
QTR-7-52-H
5.71
4.65
4.63
4.48
4.45
F3C
N
CbzHN
NHCbz
O
F3C
N
0.99
1.01
2.02
1.05
0.99
0.91
1.07
2.79
1.81
1.03
1.00
1.00
1.04
f1 (ppm)


Sep07-2023-QTR-7-52-2.fid
QTR-7-52-C
155.32
155.10
150.87
149.71
142.14
138.58
134.83
130.91
130.65
130.40
130.20
129.99
129.36
129.02
128.86
128.58
128.51
128.22
125.36
123.75
123.19
121.84
118.85
114.18
111.56
102.45
77.32
77.06
76.81
67.02
F3C
N
CbzHN
NHCbz
O
F3C
N
f1 (ppm)

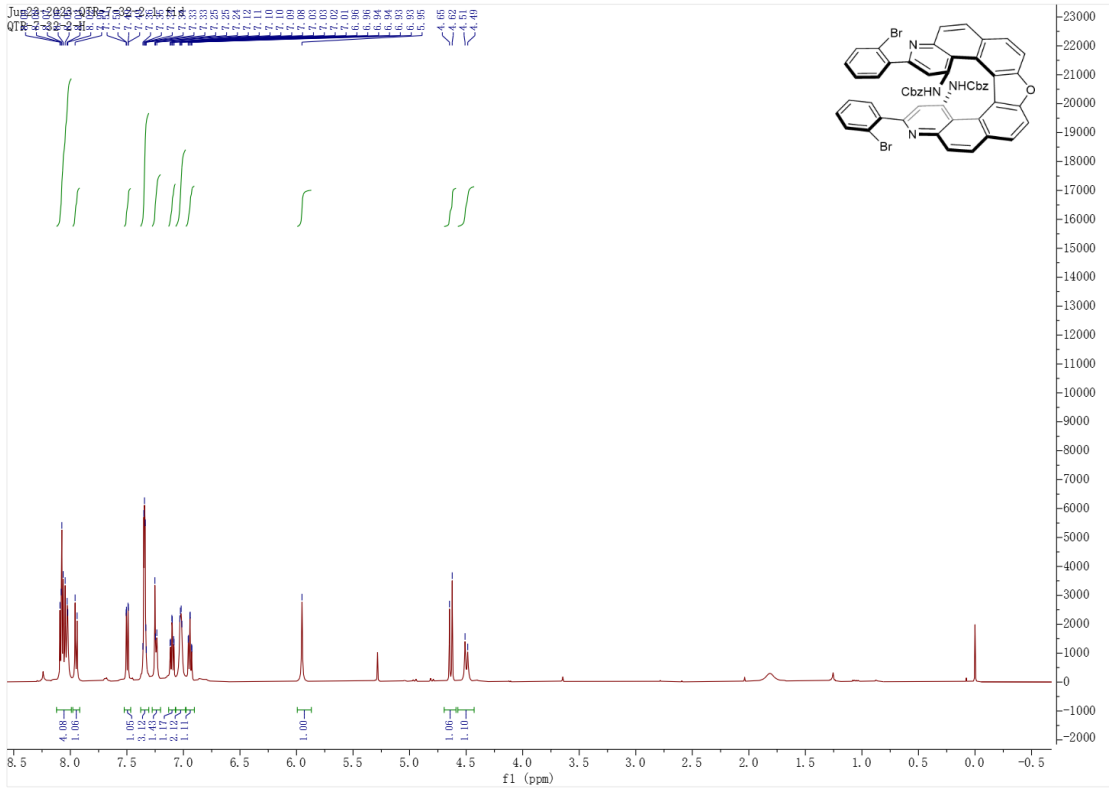

Aug22-2023-QTR-7-52.3.fid
QTR-7-52-F
-62.31
F3C
N
CbzHN
NHCbz
O
N
F3C
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

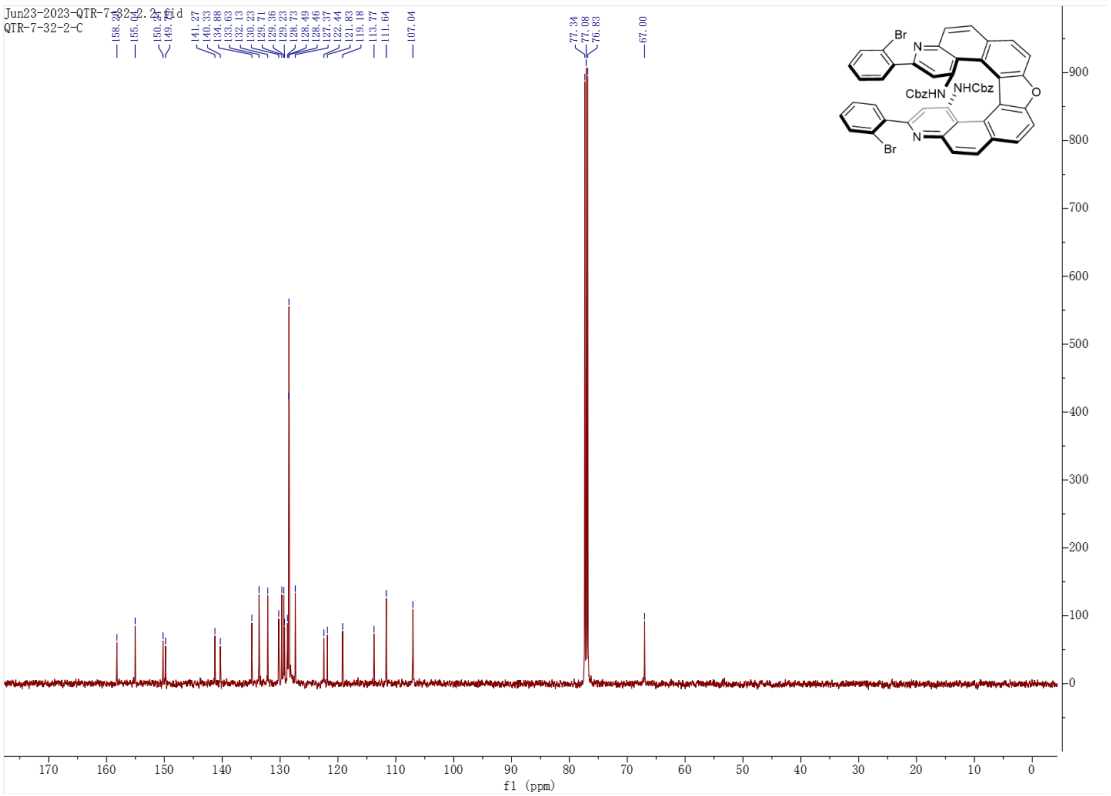
Helicene 6h



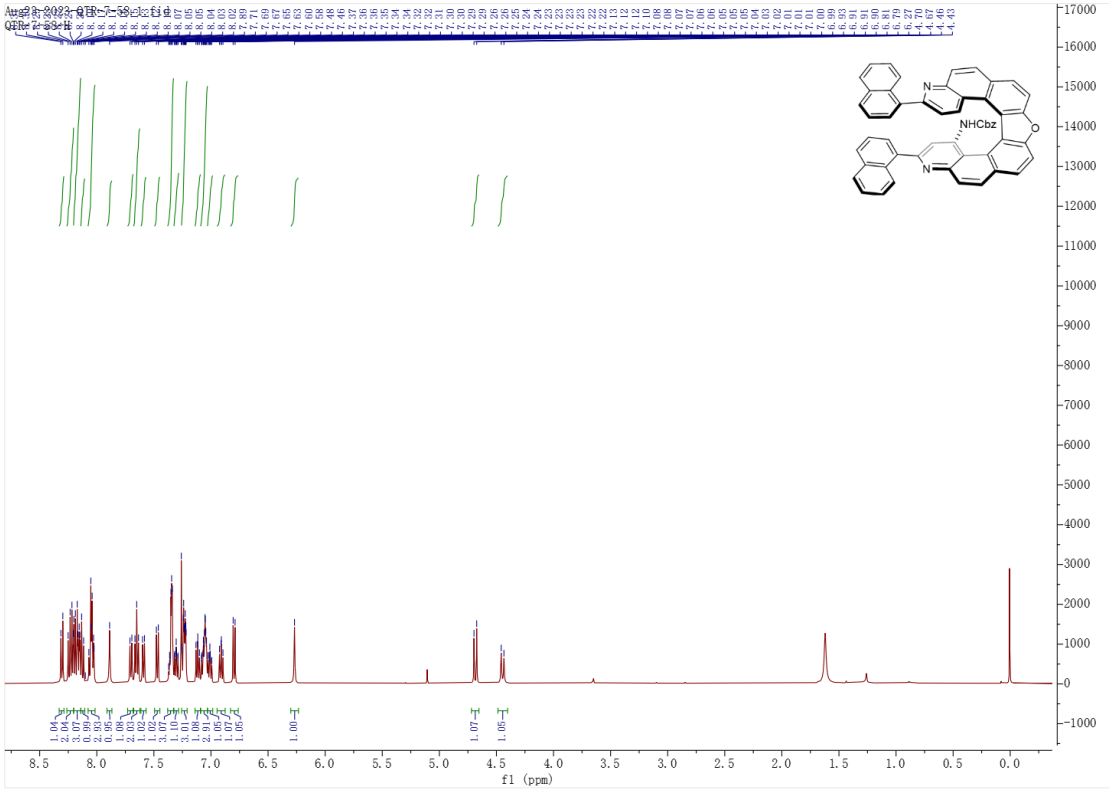


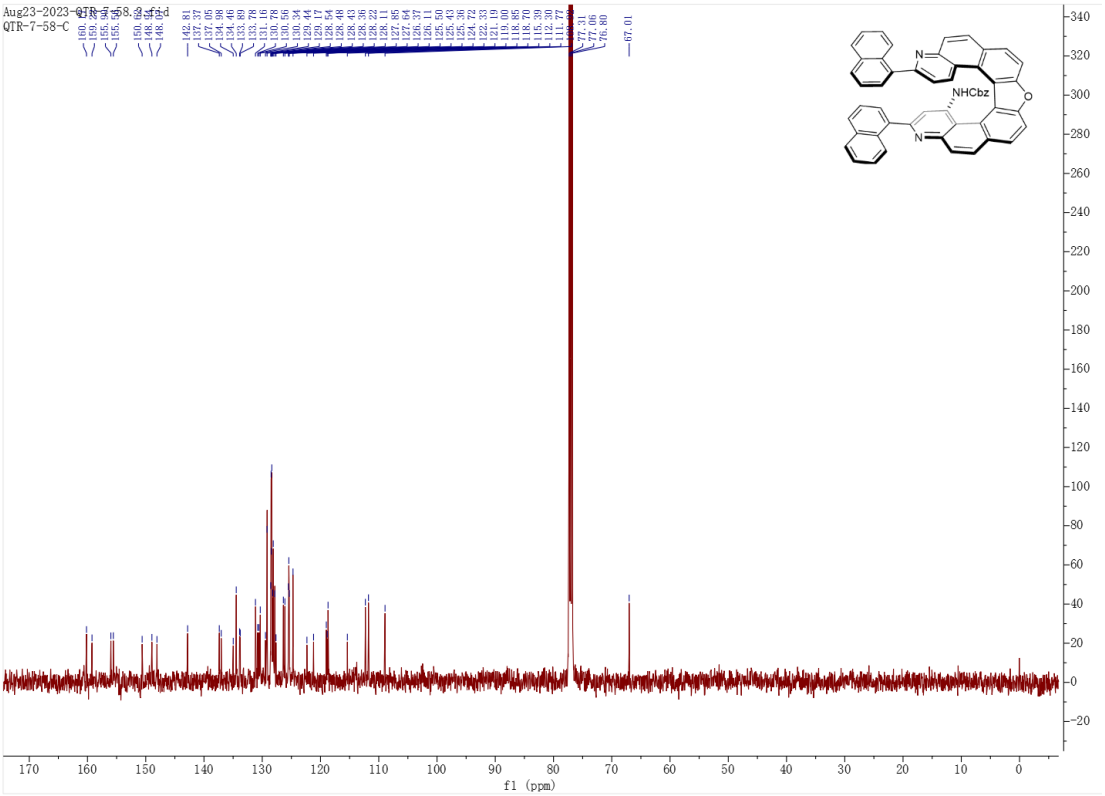
Helicene 6i



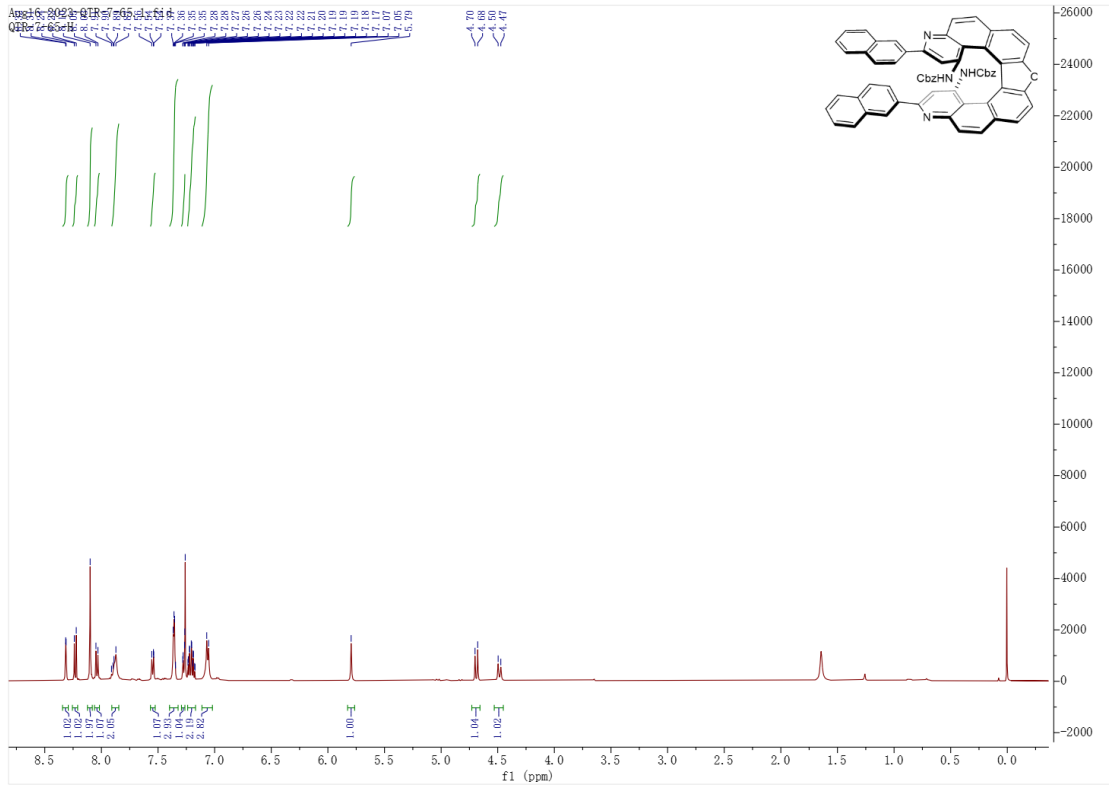


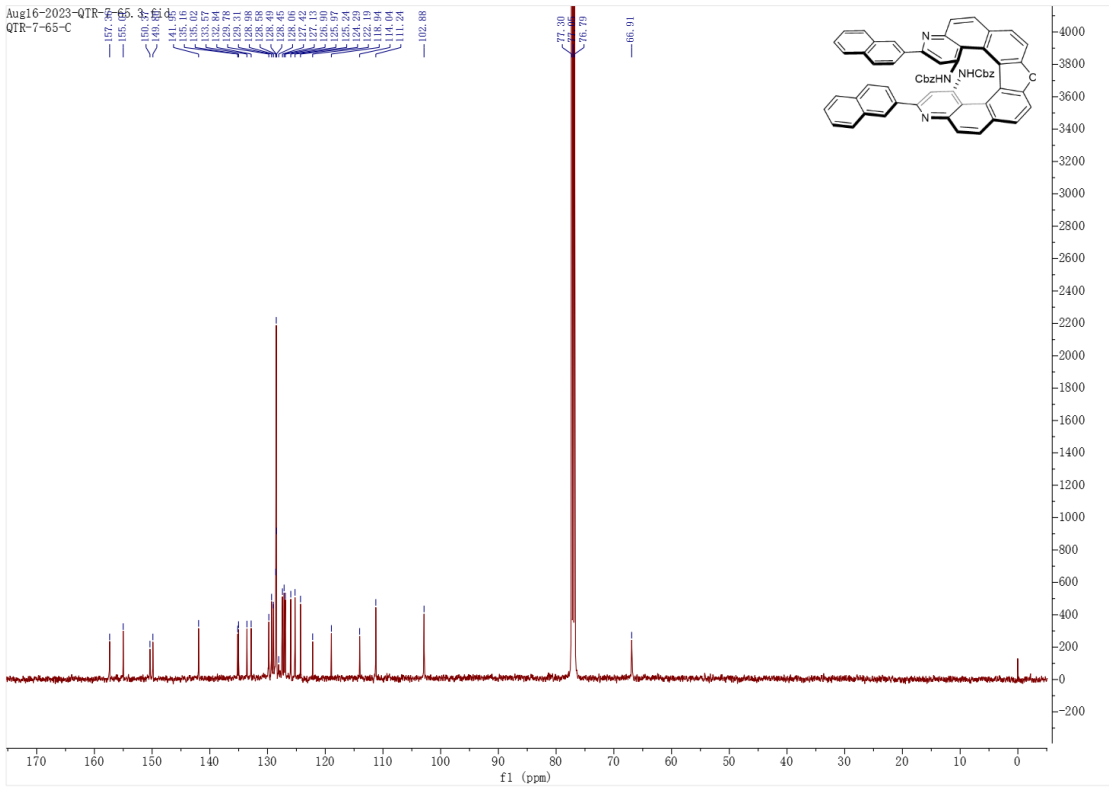
Helicene 6j



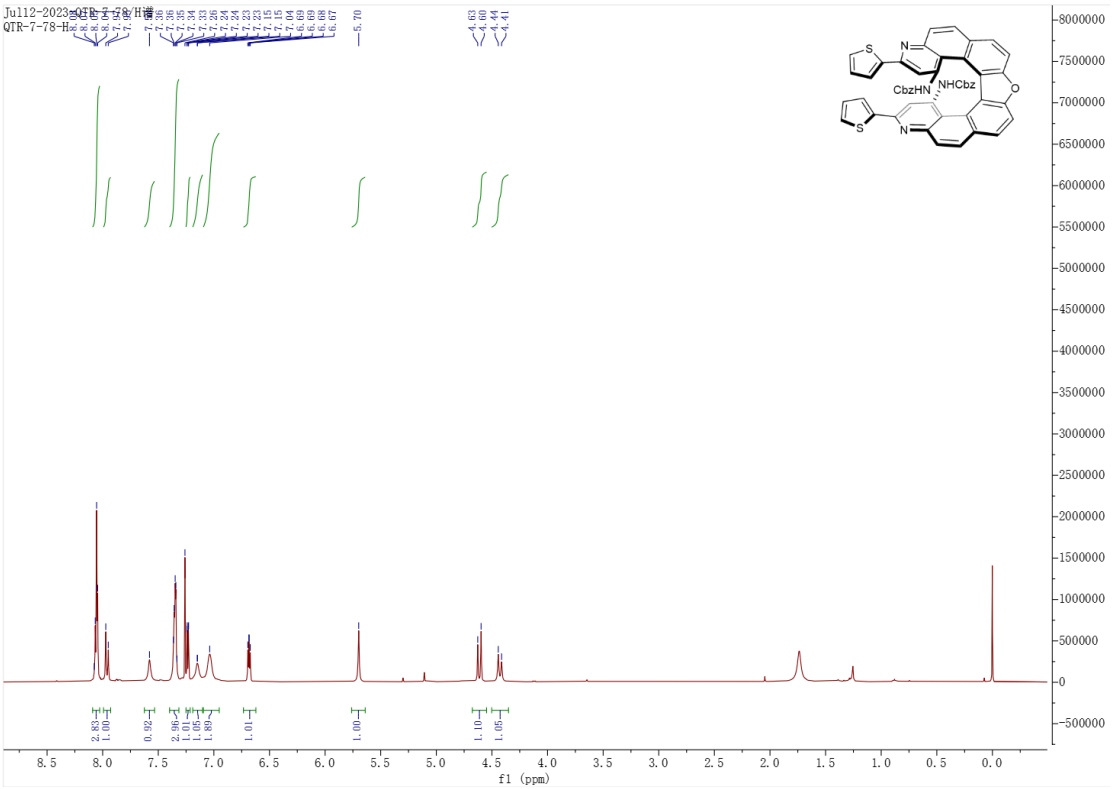


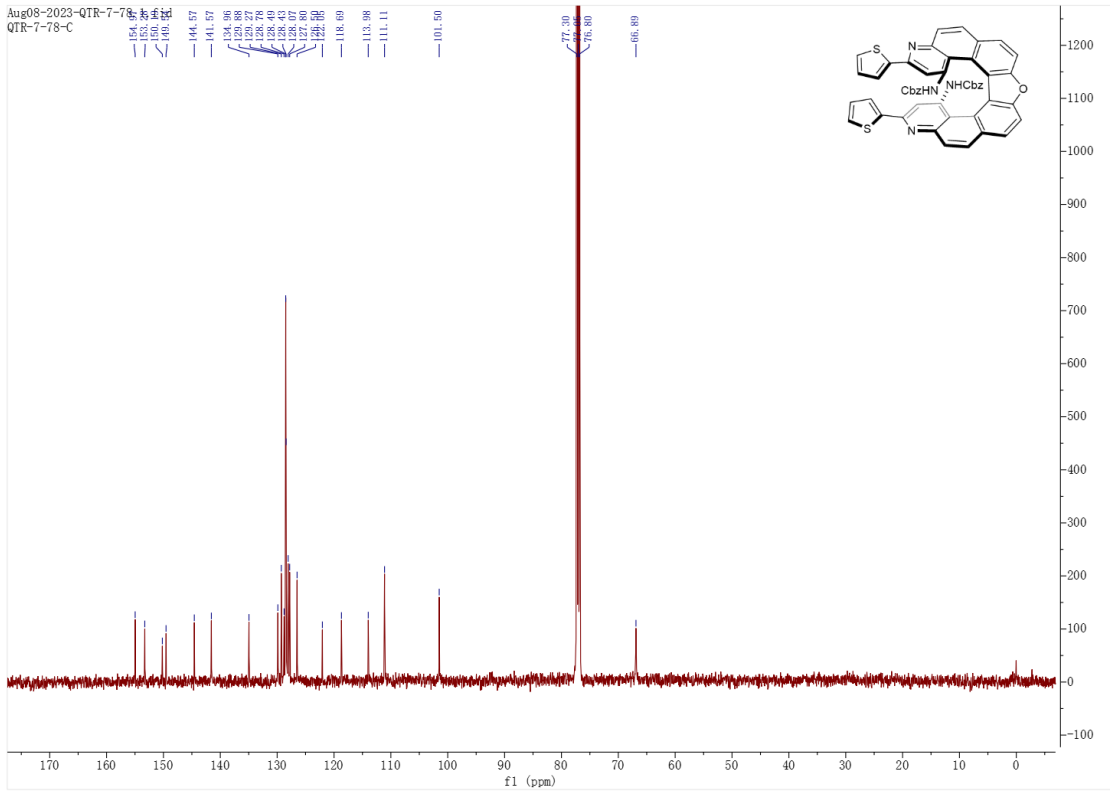
Helicene 6k



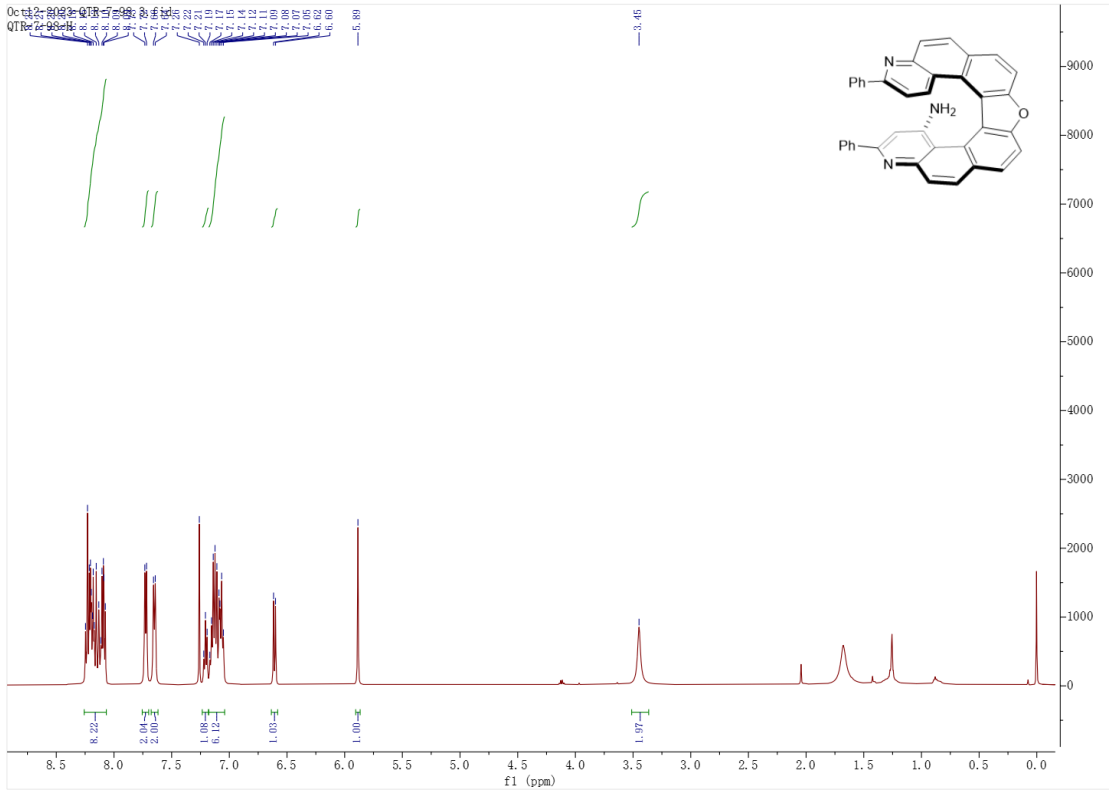


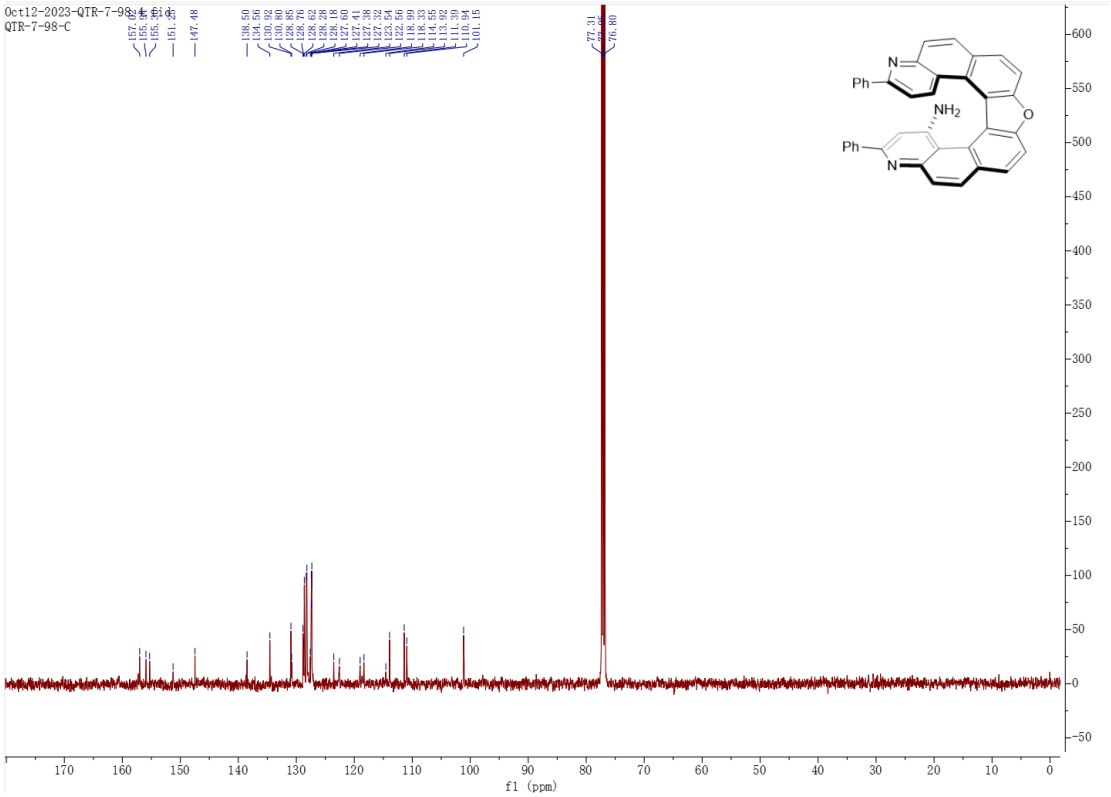
Helicene 6l



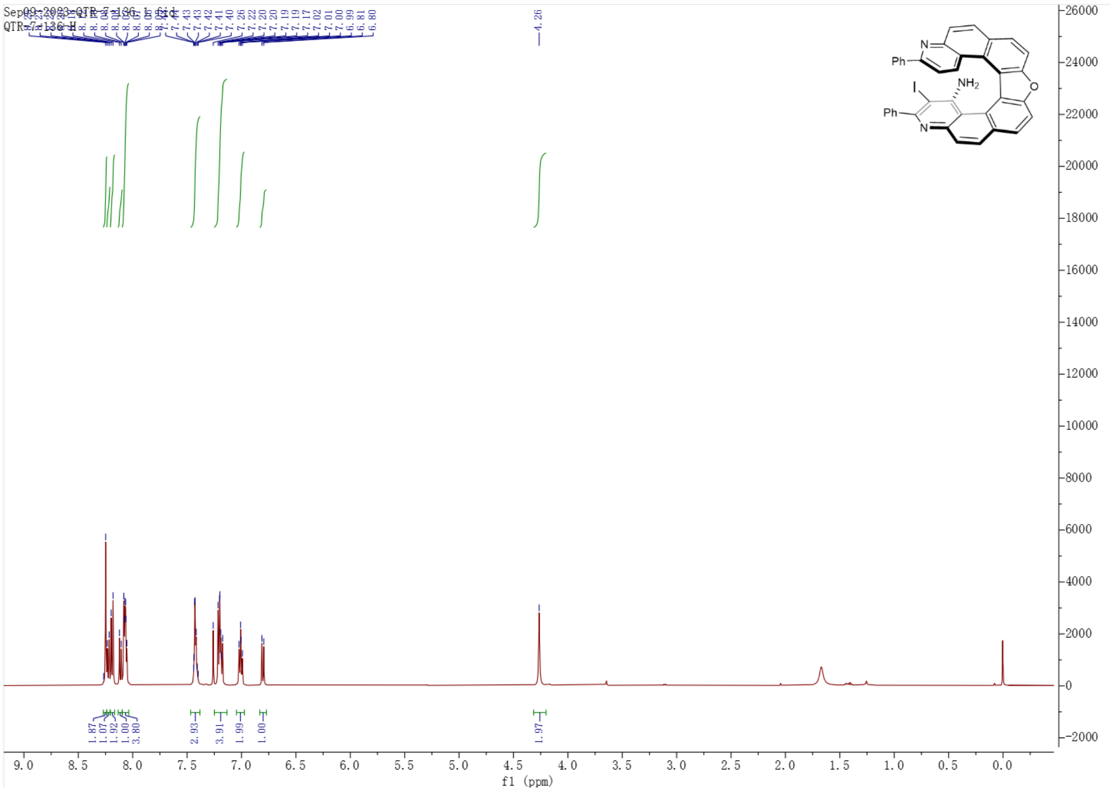


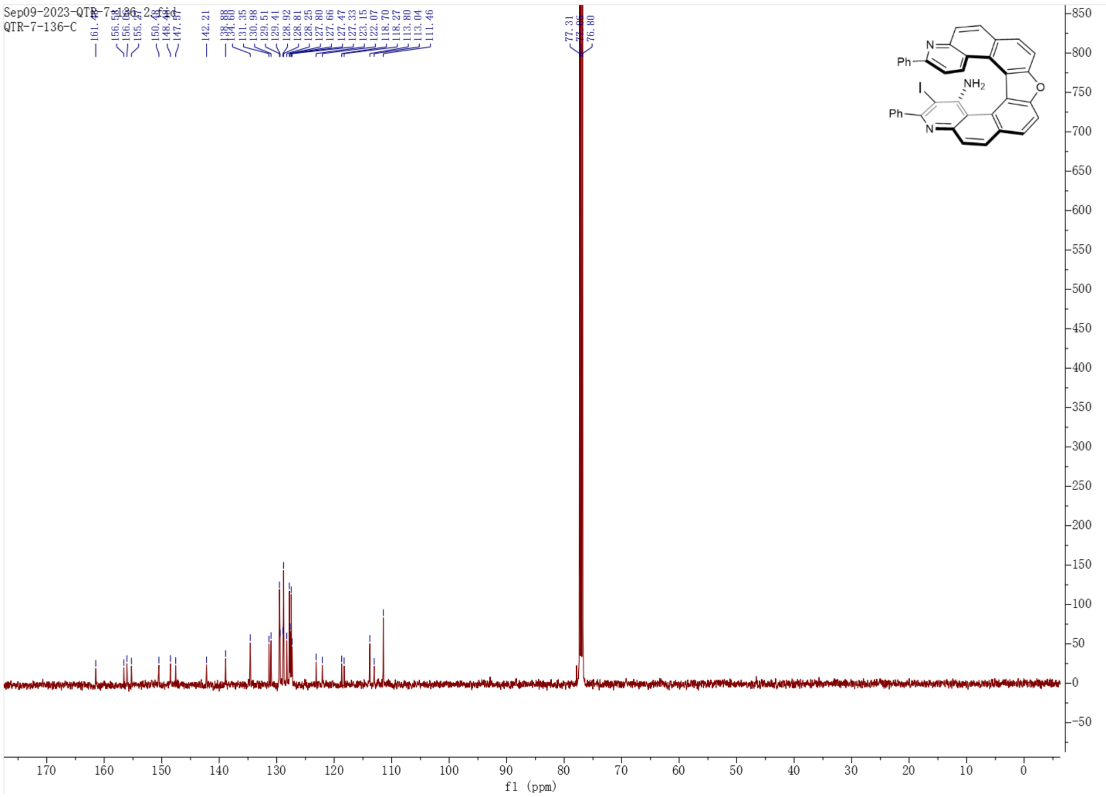
Helicene 7a



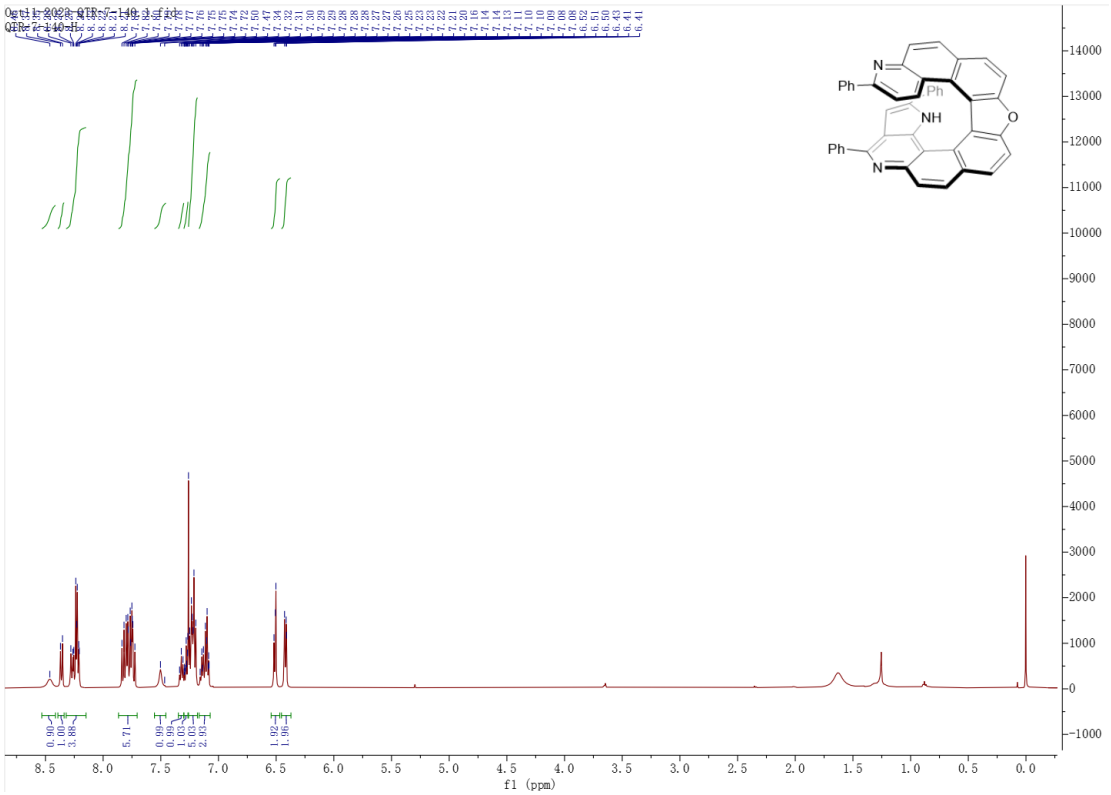


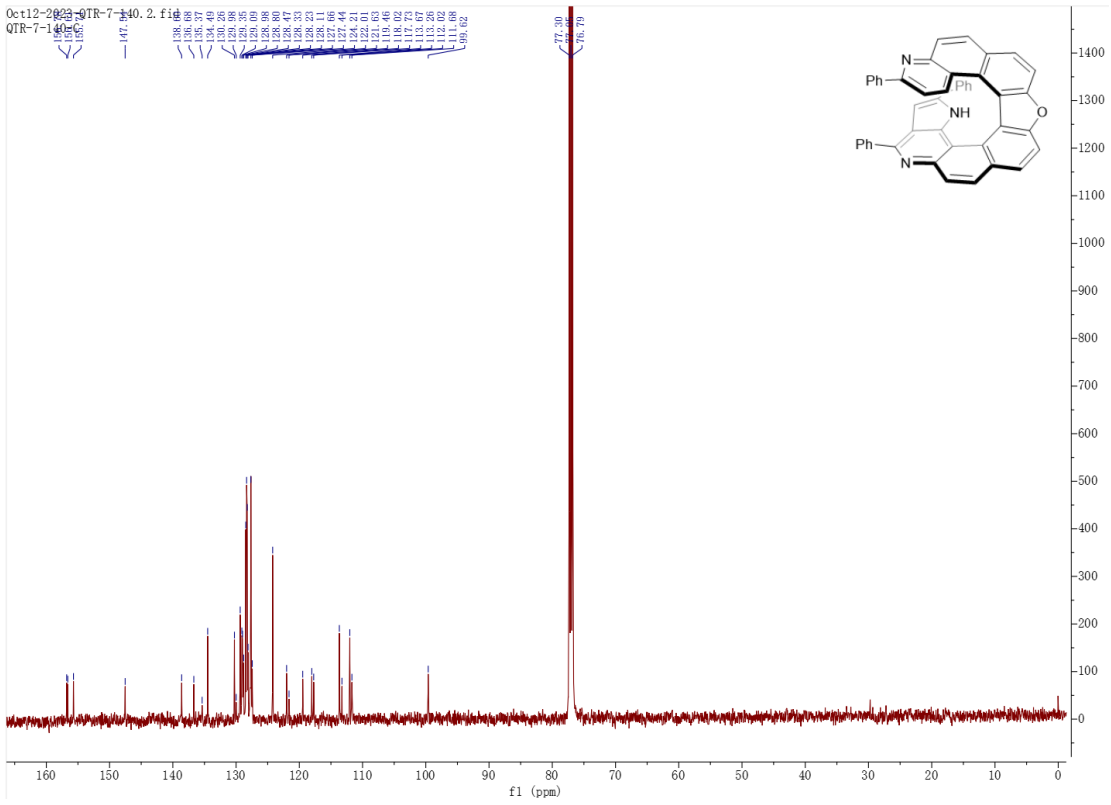
Helicene 8a



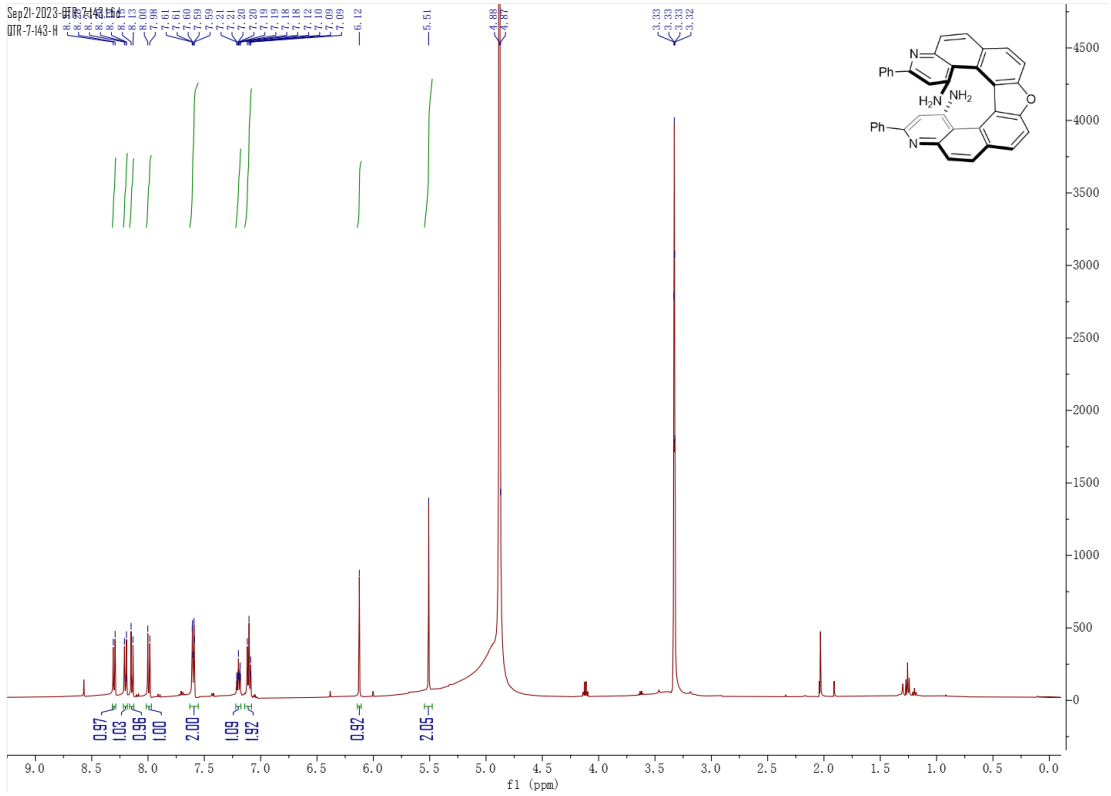


Helicene 9a


Oct11-2023-QTR-7-140-1.fid
QTR-7-140-H
Ph
N
NH
O
f1 (ppm)


Oct12-2023-QTR-7-140-2.fid
QTR-7-140-C
Ph
N
NH
O
f1 (ppm)

Helicene 10a



Helicene 11a