Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

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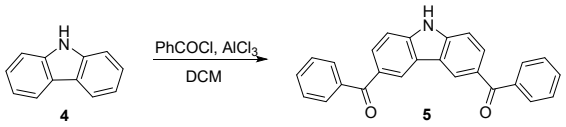
Instrumentation and Materials

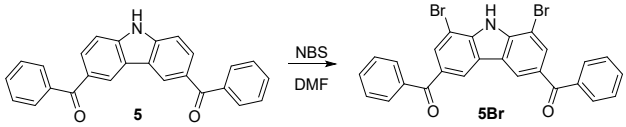
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were taken on a Bruker AVANCE-500 spectrometer. Chemical shifts were reported as the delta scale in ppm relative to the internal standards for $CHCl_3$ (δ = 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR). UV/Vis absorption spectra were recorded on a Shimadzu UV-3600 spectrometer. MALDI-TOF mass spectra were obtained with a Bruker ultrafleXtreme MALDI-TOF/TOF spectrometer with matrix. X-ray data were taken on an Agilent Super Nova X-ray diffractometer equipped with a large area CCD detector.

Synthetic Procedures



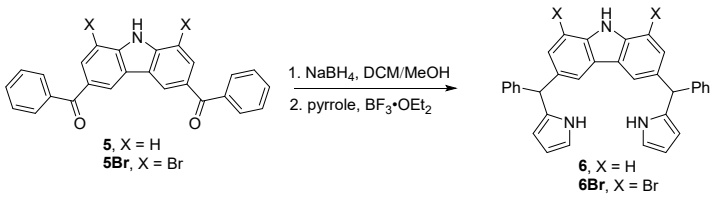
Synthesis of 5: In a 500 mL round-bottomed flask equipped with a magnetic stirring bar, immersed in ice-water bath, aluminum chloride (4.7 g, 35 mmol) and benzoyl chloride (2.8 ml, 24.5 mmol) were dissolved in dichloromethane (200 ml). After complete dissolution of reactants, **4** (1.6 g, 9.7 mmol) was added in one portion, ice-water bath was removed and the setup was fitted with a reflux condenser protected from moisture and then the mixture was stirring for 24 hours. After this time the reaction mixture was poured on ice and stirring for another hour. The organic phase was separated in a separatory funnel, washed with water and saturated $NaHCO_3$ solution and dried over anhydrous magnesium sulfate. After evaporation of the solvent the crude product was recrystallized from dichloromethane-methanol. Yield of yellowish solids: 2.6 g (75%).

5: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 8.65 (s, 1H, N-H), 8.58 (s, 2H, carbazole-H), 8.04 (d, *J* = 8.5 Hz, 2H, carbazole-H), 7.84 (d, *J* = 8.0 Hz, 4H, Ph-*o*-H), 7.62 (t, *J* = 8.0 Hz, 2H, Ph-*p*-H), 7.55 (d, *J* = 8.5 Hz, 2H, carbazole-H), 7.52 (t, *J* = 8.0 Hz, 4H, Ph-*p*-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.6, 142.7, 138.5, 132.1, 130.1, 130.0, 129.3, 128.4, 124.2, 123.1, 110.8 ppm.



Synthesis of 5Br: In a 250 mL round-bottomed flask equipped with a reflux condenser and magnetic stirring, **5** (250.8 mg, 1.8 mmol) was dissolved in 100 mL $CHCl_3$ and NBS (673 mg, 3.8 mmol) was added, the mixture was stirred at 60 ºC for 3.5 h. The reaction mixture was washed with water, dried over anhydrous sodium sulfate, evaporation of the solvent and recrystallization with *n*-hexane. Yield of white solids: 671.8 mg (70 %).

5Br: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 8.77 (s, 1H, N-H), 8.47(s, 2H, carbazole-H), 8.22 (s, 2H, carbazole-H), 7.82 (d, *J* = 8 Hz, 4H, Ph-*o*-H), 7.63-7.66 (t, *J* = 8 Hz, 2H, Ph-*p*-H), 7.53-7.56 (t, *J* = 8 Hz, 4H, Ph-*m*-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 195.0, 140.7, 137.7, 132.5, 132.1, 131.5, 130.0, 128.6, 124.4, 123.3, 104.8 ppm.



5, X = H
5Br, X = Br

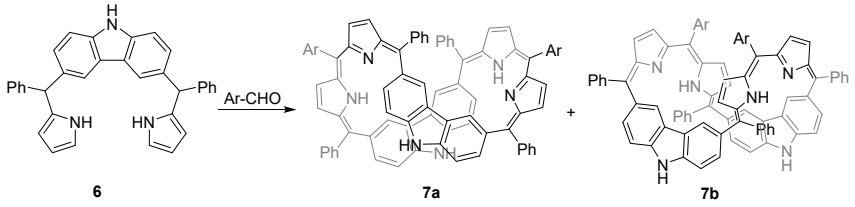
6, X = H
6Br, X = Br

Synthesis of 6 and 6Br: In a 500 mL round-bottomed flask equipped with a magnetic stirring, **5** (2.2 g, 6 mmol) was dissolved in a mixture of DCM (200 mL) and MeOH (100 mL). Sodium borohydride (490 mg, 13 mmol) was added in small portions and the setup was fitted with a nitrogen gas adapter and the mixture was stirring for 2 hours. After this time the reaction was quenched by an addition of water (20 mL) and stirring for another 30 minutes and then placed in a separatory funnel. Organic phase was washed with water couple times and dried over anhydrous sodium sulfate. After evaporation of the solvents the crude, orange oil was obtained. After most of the solvent was removed on a rotary evaporator the mixture was left for crystallization in a refrigerator. Then, in a 250 mL round-bottomed flask equipped with a reflux condenser and magnetic stirring, the solid obtained in the previous step was dissolved in dry pyrrole (30 mL, 145 mmol). The solution was purged with nitrogen for 20 minutes. Subsequently, boron trifluoride diethyl etherate (200 µL) was added, the setup was fitted with a reflux condenser and the solution was refluxed for 10 h in the nitrogen atmosphere. The solution was neutralized by addition of triethylamine (1.5 mL). Most of the pyrrole was removed using a rotary evaporator and the crude residue was chromatographed on silica gel (100–200 mesh) using the mixture of dichloromethane/*n*-hexane as eluent. The desired product eluted as the first fraction. The solvent was removed under reduced pressure. Yield of white solids **6**: 1.5 g (53%),

6Br: 3.8 g (57%).

6: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.96 (s, 1H, carbazole-NH), 7.82 (s, 2H, pyrrole-NH), 7.80 (s, 2H, carbazole-H), 7.30 (t, *J* = 8.5 Hz, 6H, Ph-H), 7.28-7.20 (m, 8H, Ph-H+carbazole-H), 6.78 (s, 2H, pyrrole-H), 6.17 (s, 2H, pyrrole-H) 5.85 (s, 2H, pyrrole-H), 5.56 (s, 2H, CH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 143.8, 138.8, 138.8, 134.4, 134.4, 134.3, 134.3, 128.9, 128.5, 128.5, 127.1, 126.6, 123.4, 123.4, 120.5, 117.1, 117.0, 110.7, 108.2, 108.2, 107.9, 50.6 ppm.

6Br: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 8.26 (s, 1H, NH), 7.84 (s, 2H, NH), 7.72 (s, 2H, carbazole-H), 7.44 (s, 2H, carbazole-H), 7.32 (t, *J* = 7.5 Hz, 4H, Ph-*m*-H), 7.25 (t, *J* = 7.5 Hz, 2H, Ph-*p*-H), 7.21 (d, J = 7.5 Hz, 4H, Ph-*o*-H), 6.73 (s, 2H, pyrrole-H) 6.18-6.16 (m, 2H, pyrrole-H), 5.81 (s, 2H, pyrrole-H), 5.59 (s, 2H, CH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 142.9, 137.1, 136.7, 133.5, 129.6, 128.8, 128.7, 126.9, 124.8, 120.1, 117.4, 108.4, 108.2, 104.5, 50.4 ppm.

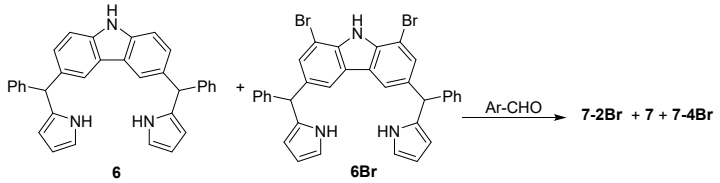


Synthesis of 7a and **7b**: **4** (477.6 mg, 1.0 mmol) and pentafluorobenzaldehyde (196.1 mg, 1.0 mmol) were added to dry dichloromethane (900 mL) under argon. Boron trifluoride-etherate (100 μL) was then added and the reaction mixture was protected from light and stirred for two hours. 2,3-Dichloro-5,6-dicyano1,4-benzoquinone (DDQ; 454 mg, 2.0 mmol) was subsequently added and the reaction mixture was stirring for another 4 hours. After that time solvent was evaporated under reduced pressure and the dark residue was subjected to chromatography (deactivated alumina (4 mL of water for 100 g of basic alumina), dichloromethane). **7a** and **7b** were eluted as the first green fraction. After a second column chromatography (silica gel 100–200 mesh, dichloromethane/*n*-hexane), the first green fraction **7a** and the second green fraction **7b** were collected. After evaporation of solvent and recrystallized from DCM/MeOH, green solids **7a** 104.3 mg (16%) and blue-green solids **7b** 32.6 mg (5%) were obtained respectively.

7a: ^{1}H NMR (500 MHz, DMSO-d_6, 298 K) δ = 13.46 (s, 2H, pyrrole-NH), 10.78 (s, 2H, carbazole-NH), 9.50 (br, 2H, carbazole-H), 8.64 (br, 2H, carbazole-H), 7.40-7.22

(m, 24H), 6.97 (br, 2H), 6.80 (br, 2H), 6.55-6.31 (m, 8H) ppm; UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon[M^{-1}cm^{-1}])$ = 288 (58000), 376 (68800), 442 (55900), 650 (29700) nm; HR-MS (MALDI-TOF-MS): m/z = 1303.3552, calcd for ($C_{82}H_{45}F_{10}N_6$) = 1303.3541 ([*M*+*H*]$^+$).

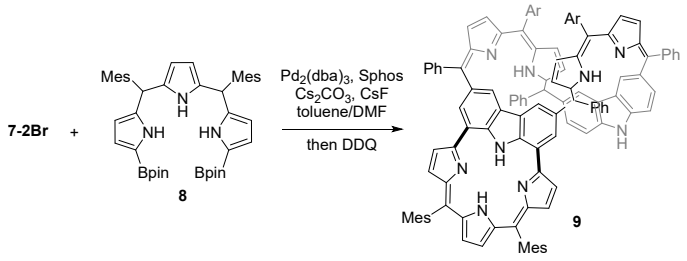
7b (**7b-1** and **7b-2**): ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ = 14.00 (s, 2H, pyrrole-NH), 11.70 (s, 2H, arbazole-NH), 9.18 (s, 2H, carbazole-H), 7.93 (s, 2H, carbazole-H), 7.44-7.40 (m, 8H, Ph-H+carbazole-H), 7.25-7.21 (m, 6H, Ph-H+carbazole-H), 6.79-6.76 (m, 10H, Ph-H+pyrrole-H), 6.56 (d, *J* = 5.0 Hz, 2H, pyrrole-H), 6.49-6.44 (m, 8H, Ph-H+pyrrole-H), 6.36 (t, *J* = 7.0 Hz, 2H, Ph-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 161.5, 159.5, 148.6, 148.2, 142.6, 140.0, 139.5, 138.1, 135.8, 135.4, 135.0, 132.6, 132.0, 131.3, 131.3, 131.2, 130.6, 130.5, 129.5, 129.5, 128.1, 127.8, 127.7, 126.3, 126.3, 125.9, 125.8, 124.4, 124.2, 124.2, 123.5, 123.5, 110.6, 109.6; UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon[M^{-1}cm^{-1}])$ = 288 (66900), 317 (54500), 378 (61500), 655 (37900) nm; HR-MS (MALDI-TOF-MS): m/z = 1303.3552, calcd for ($C_{82}H_{45}F_{10}N_6$) = 1303.3541 ([*M*+*H*]$^+$).



Synthesis of **7-2Br** (**7-2Br-1** and **7-2Br-2**): **6** (238.8 mg, 0.5 mmol), **6Br** (317.7 mg, 0.5 mmol) and pentafluorobenzaldehyde (196.1 mg, 1.0 mmol) were added to dry dichloromethane (900 mL) under argon. Boron trifluoride-etherate (100 μL) was then added and the reaction mixture was protected from light and stirred for two hours. DDQ (454 mg, 2.0 mmol) was subsequently added and the reaction mixture was stirring for another 4 hours. After that time solvent was evaporated under reduced pressure and the dark residue was subjected to chromatography (alumina, dichloromethane). The desired product was eluted as the first, green band. After the second chromatography (silica gel 100–200 mesh, dichloromethane) the crude product was recrystallized from dichloromethane/n-hexane solvents mixture. Yield of blue-green solids **7-2Br** (7-2Br-1 and 7-2Br-2): 43.8 mg (6%), **7**: 45.6 mg (7 %), **7-4Br**: 72.8 mg (9 %).

7-2Br (**7-2Br-1** and **7-2Br-2**): ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 14.37 (s, 1H, NH), 14.34 (s, 1H, NH), 9.30 (s, 1H, carbazole-H), 9.26 (s, 1H, carbazole-H), 8.37 (s, 1H, N-H), 8.22 (s, 1H, N-H), 8.03 (s, 1H, carbazole-H), 7.99 (s, 1H, carbazole-H), 7.42-7.38 (m, 6H, Ph-H), 7.28 (s, 5H, Ph-H+carbazole-H), 7.16 (s, 1H, carbazole-H), 7.09-

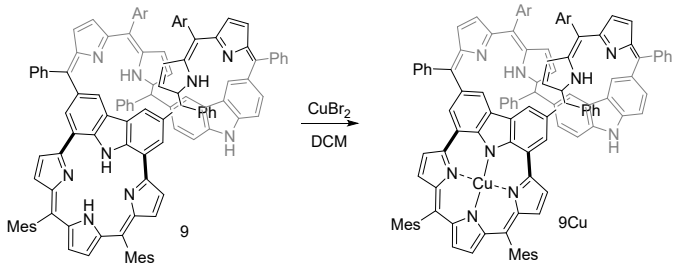
7.07 (m, 2H, carbazole-H), 6.95 (d, *J* = 8.5 Hz, 1H, carbazole-H), 6.89 (d, *J* = 8.5 Hz, 1H, carbazole-H), 6.73 (t, *J* = 5.0 Hz, 2H, pyrrole-H), 6.67 (d, *J* = 5.0 Hz, 2H, pyrrole-H), 6.52 (t, *J* = 8.0 Hz, 4H, Ph-H), 6.37 (d, *J* = 8.0 Hz, 1H, Ph-H), 6.36 (d, *J* = 5.0 Hz, 1H, pyrrole-H), 6.31 (d, *J* = 5.0 Hz, 1H, pyrrole-H), 6.29 (d, *J* = 5.0 Hz, 1H, pyrrole-H), 6.27 (d, *J* = 5.0 Hz, 1H, pyrrole-H) ppm; UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon[M^{-1}cm^{-1}])$ = 289 (57300), 322 (42600), 378 (51200), 652 (29200) nm; HR-MS (MALDI-TOF-MS): m/z = 1458.1726, calcd for ($C_{82}H_{42}Br_2F_{10}N_6$) = 1458.1673 ([*M*]$^+$).



Synthesis of 9: A toluene-DMF solution (2 mL/1 mL) of **7-2Br** (146.2 mg, 0.1 mmol), **8**[1] (71.4 mg, 0.1 mmol), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol), Sphos (16.4 mg, 0.04 mmol), Cs_2CO_3 (65.2 mg, 0.2 mmol) and CsF (30.2 mg, 0.2 mmol) was degassed through three freeze-pump-thaw cycles, and the reaction flask was purged with argon. The resulting mixture was stirred at reflux for 48 h. The reaction mixture was diluted with $CHCl_3$, washed with water, and dried over anhydrous sodium sulfate. A round-bottomed 50-mL flask containing the resulting mixture and excess DDQ, dichloromethane (10 mL) was added. After being stirred for 2 h, the mixture was passed through a short silica-gel column. The solvent was evaporated in vacuo, the product was purified by column chromatography on silica-gel (dichloromethane/*n*-hexane as an eluent) and recrystallization with dichloromethane/n-hexane, **9** was obtained as green solids (11.1 mg, 7% yield).

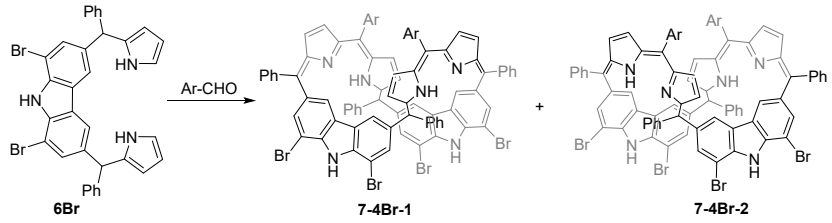
9: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 14.67 (s, 1H, NH), 14.46 (s, 1H, NH), 10.07 (s, 1H, carbazole-H), 9.43 (s, 2H, carbazole-H+NH), 9.27 (s, 1H, NH), 8.71 (s, 1H, carbazole-H), 8.16-8.11 (m, 4H, carbazole-H+NH), 7.47-7.39 (m, 7H, Ph-H+ carbazole-H), 7.30 (s, 2H, Ph-H), 7.19 (d, *J* = 4.5 Hz, 1H, pyrrole-H), 7.15 (d, *J* = 8.5 Hz, 1H, Ph-H), 7.11 (d, *J* = 5.0 Hz, 1H, pyrrole-H), 7.04 (d, *J* = 8.0 Hz, 2H, Ph-H), 7.01 (d, J = 4.5 Hz, 2H, pyrrole-H), 6.98 (s, 1H, Ph-H), 6.91 (s, 1H, Ph-H) 6.88 (d, *J* = 5.0 Hz, 1H, pyrrole-H), 6.84 (d, *J* = 8.0 Hz, 1H, Ph-H), 6.78 (d, *J* = 5.0 Hz, 2H, pyrrole-H), 6.68 (d, *J* = 5.0 Hz, 1H, pyrrole-H), 6.64 (s, 2H, pyrrole-H), 6.52 (s, 2H, Ph-H),

6.41 (d, J = 5.0 Hz, 1H, pyrrole-H), 6.36-6.33 (m, 3H, Ph-H+pyrrole-H) , 6.29 (d, J = 5.0 Hz, 1H, pyrrole-H), 6.01 (br, 4H, Ph-H), 5.59 (t, J = 7.5 Hz, 2H, Ph-H), 2.44 (s, 3H, -CH_3), 2.40 (s, 3H, -CH_3), 2.19 (s, 3H, -CH_3), 2.09 (s, 3H, -CH_3), 2.01 (d, J = 7.5 Hz, 6H, -CH_3); UV/Vis (CH_2Cl_2): λ_{max}(ε[$M^{-1}cm^{-1}$]) = 290 (74700), 320 (69700), 394 (110700), 631 (47200) nm; HR-MS (MALDI-TOF-MS): m/z = 1755.5682, calcd for ($C_{114}H_{71}F_{10}N_9$) = 1755.5667 ([M]$^+$).



Synthesis of 9Cu: 9 (17.6 mg, 0.01 mmol) was added to a round-bottomed 50 mL flask containing a magnetic bar, and dissolved in dichloromethane (20 mL). $CuBr_2$ (22.3 mg,0.1 mmol) was added, after being stirred for 6 h, the solvent was evaporated in vacuo. The product was purified by column chromatography on silica-gel (dichloromethane /*n*-hexane as an eluent) and recrystallization with *n*-hexane, **9Cu** was obtained as green solids (15.1 mg 83% yield).

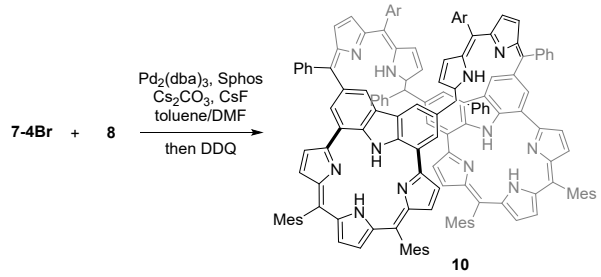
9Cu: UV/Vis (CH_2Cl_2): λ_{max}(ε [$M^{-1}cm^{-1}$]) = 290 (60600), 389 (107100), 658 (58400) nm; HR-MS (MALDI-TOF-MS): m/z = 1816.4826, calcd for ($C_{114}H_{69}CuF_{10}N_9$)$^+$ = 1816.4807 ([M]$^+$).



Synthesis of **7-4Br** (**7-4Br-1** and **7-4Br-2**): **6Br** (635.4 mg, 1.0 mmol) and pentafluorobenzaldehyde (196.1 mg, 1.0 mmol) were added to dry dichloromethane (900 mL) under argon. Boron trifluoride-etherate (100 μL) was then added and the reaction mixture was protected from light and stirred for two hours. DDQ (454 mg, 2.0 mmol) was subsequently added and the reaction mixture was stirring for another 4 hours. After that time solvent was evaporated under reduced pressure and the dark residue was subjected to chromatography (deactivated alumina, dichloromethane). The

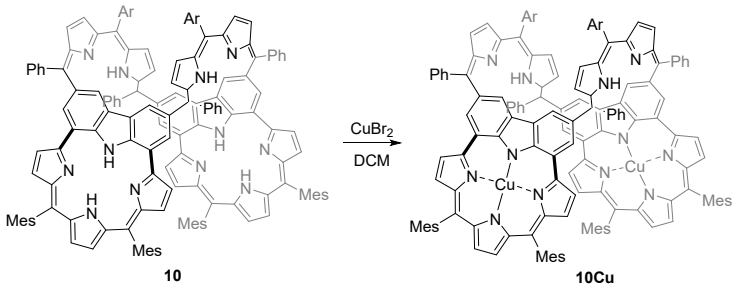
desired product was eluted as the first, green band. After the second chromatography (silica gel 100–200 mesh, dichloromethane) the crude product was recrystallized from dichloromethane/*n*-hexane solvents mixture. Yield of green solids **7-4Br** (**7-4Br-1** and **7-4Br-2**): 145.7 mg (19%).

7-4Br (**7-4Br-1** and **7-4Br-2**): ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 14.30 (s, 2H, pyrrole-NH), 9.22 (s, 2H, carbazole-H), 8.41 (s, 2H, carbazole-H), 7.93 (s, 2H, carbazole-NH), 7.42-7.41 (m, 8H, Ph-H), 7.26 (s, 6H, Ph-H), 7.18 (d, *J* = 2.5 Hz, 2H, carbazole-H), 7.09 (d, *J* = 2.5 Hz, 2H, carbazole-H), 6.69 (d, *J* = 4.5 Hz, 2H, pyrrole-H), 6.67 (d, J = 4.5 Hz, 2H, pyrrole-H), 6.54 (s, 6H, Ph-H), 6.33 (s, 4H, pyrrole-H), 6.28 (s, 4H, pyrrole-H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 161.9, 160.1, 160.1, 149.2, 148.9, 141.7, 137.9, 137.5, 137.5, 135.3, 135.1, 134.5, 134.2, 133.6, 133.5, 133.5, 132.2, 131.9, 131.5, 128.4, 128.0, 127.9, 127.0, 126.7, 126.6, 126.6, 125.6, 125.1, 124.6, 123.6, 104.5, 103.9; UV/Vis (CH_2Cl_2): λ_{max}(ε [$M^{-1}cm^{-1}$]) = 290 (80800), 324 (65000), 378 (90200), 652 (46700) nm; HR-MS (MALDI-TOF-MS): m/z = 1617.9843, calcd for $(C_{82}H_{40}Br_4F_{10}N_6)^+$ = 1617.9861 ([*M*]$^+$).



Synthesis of 10: A toluene-DMF solution (3 mL/1.5 mL) of **7-4Br** (161.9 mg, 0.1 mmol), **8** (142.8 mg, 0.2 mmol), $Pd_2(dba)_3$ (18.3 mg, 0.02 mmol), Sphos (32.8 mg, 0.08 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol) and CsF (60.7 mg, 0.4 mmol) was degassed through three freeze-pump-thaw cycles, and the reaction flask was purged with argon. The resulting mixture was stirred at reflux for 48 h. The reaction mixture was diluted with $CHCl_3$, washed with water, and dried over anhydrous sodium sulfate. A round-bottomed 50-mL flask containing the resulting mixture and excess DDQ, dichloromethane (10 mL) was added. After being stirred for 2 h, the mixture was passed through a short silica-gel column. The solvent was evaporated in vacuo, the product was purified by column chromatography on silica-gel (dichloromethane/*n*-hexane as an eluent) and recrystallization with dichloromethane/*n*-hexane, **10** was obtained as green solids (8.8 mg, 4% yield).

10: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 14.84 (s, 2H, pyrrole-NH), 10.19 (s, 2H, carbazole-H), 9.46 (s, 2H, NH), 9.27 (s, 2H, NH), 8.76 (s, 2H, carbazole-H), 8.19 (s, 2H, carbazole-H), 8.11 (s, 2H, carbazole-H), 7.48 (s, 12H, Ph-H+pyrrole-H), 7.39 (d, *J* = 5.0 Hz, 2H, pyrrole-H), 7.21 (d, *J* = 5.0 Hz, 2H, pyrrole-H), 7.07 (s, 2H, Ph-*m*-H), 7.04 (d, *J* = 5.0 Hz, 2H, pyrrole-H), 7.02 (s, 2H, Ph-*m*-H), 6.96 (s, 4H, Ph-H), 6.90 (d, *J* = 5.0 Hz, 2H, pyrrole-H), 6.82 (d, *J* = 5.0 Hz, 2H, pyrrole-H), 6.67 (s, 2H, pyrrole-H), 6.65 (s, 2H, pyrrole-H), 6.46 (d, *J* = 5.0 Hz, 2H, pyrrole-H), 6.39 (d, *J* = 5.0 Hz, 2H, pyrrole-H), 6.15(br, 4H, Ph-H), 5.64 (t, *J* = 7.5 Hz, 2H, Ph-H), 2.44 (s, 6H, -CH_3), 2.37 (s, 6H, -CH_3), 2.23 (s, 6H, -CH_3), 2.07 (s, 6H, -CH_3), 2.02 (s, 6H, -CH_3), 2.00 (s, 6H, -CH_3) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 166.7, 166.7, 163.4, 159.1, 152.8, 152.6, 150.2, 148.3, 147.0, 145.0, 142.9, 138.2, 138.0, 137.9, 137.9, 137.8, 137.7, 137.4, 136.9, 136.0, 136.0, 135.9, 135.7, 134.6, 133.4, 133.1, 132.8, 132.5, 132.3, 131.9, 131.2, 130.6, 128.8, 128.5, 128.2, 128.2, 128.2, 128.1, 128.1, 127.9, 127.2, 127.0, 126.9, 126.6, 125.9, 125.2, 125.1, 122.8, 122.6, 115.8, 115.0, 88.6, 21.5, 21.5, 21.0, 20.8, 20.7; UV/Vis (CH_2Cl_2): λ_{max}(ε [$M^{-1}cm^{-1}$]) = 259 (88200), 295 (87400), 322 (90700), 394 (173700), 625 (69600) nm; HR-MS (MALDI-TOF-MS): m/z = 2208.7789, calcd for $(C_{146}H_{98}F_{10}N_{12})^+$ = 2208.7872 ([*M*]$^+$)



Synthesis of 10Cu: 10 (22.1 mg, 0.01 mmol) was added to a round-bottomed 50 mL flask containing a magnetic bar, and dissolved in dichloromethane (20 mL). $CuBr_2$ (22.3 mg,0.1 mmol) was added, after being stirred for 6 h, the solvent was evaporated in vacuo. The product was purified by column chromatography on silica-gel (dichloromethane/*n*-hexane as an eluent) and recrystallization with *n*-hexane, **10Cu** was obtained as green solids (14.7 mg 63% yield).

10Cu: UV/Vis (CH_2Cl_2): λ_{max}(ε [$M^{-1}cm^{-1}$]) = 294 (96800), 333 (74400), 420 (157300), 702 (85000) nm; HR-MS (MALDI-TOF-MS): m/z = 2230.6153, calcd for $(C_{146}H_{94}Cu_2F_{10}N_{12})^+$ = 2230.6151 ([*M*]$^+$).

Spectra of Compounds

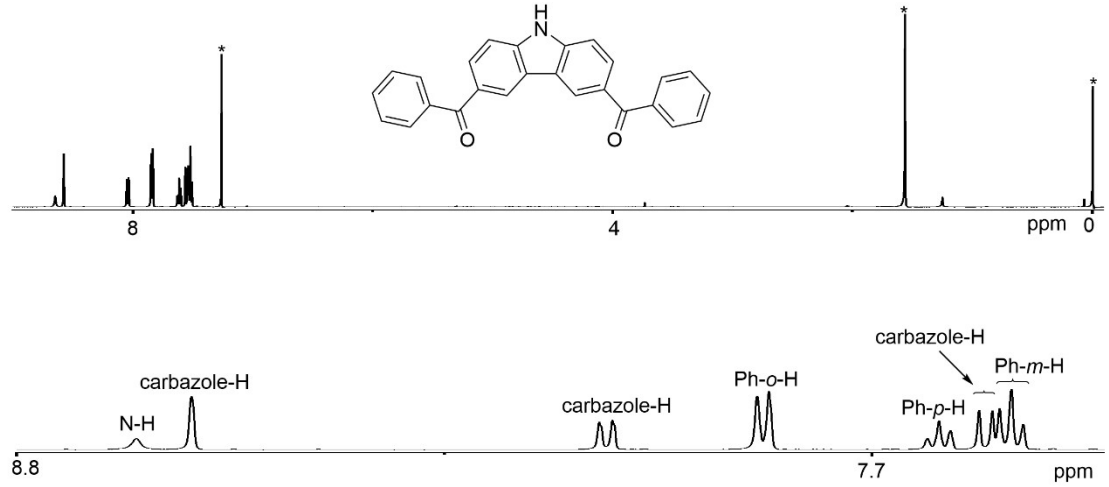


Figure S1. ^{1}H NMR spectrum of **5** in $CDCl_3$ at 25 °C.

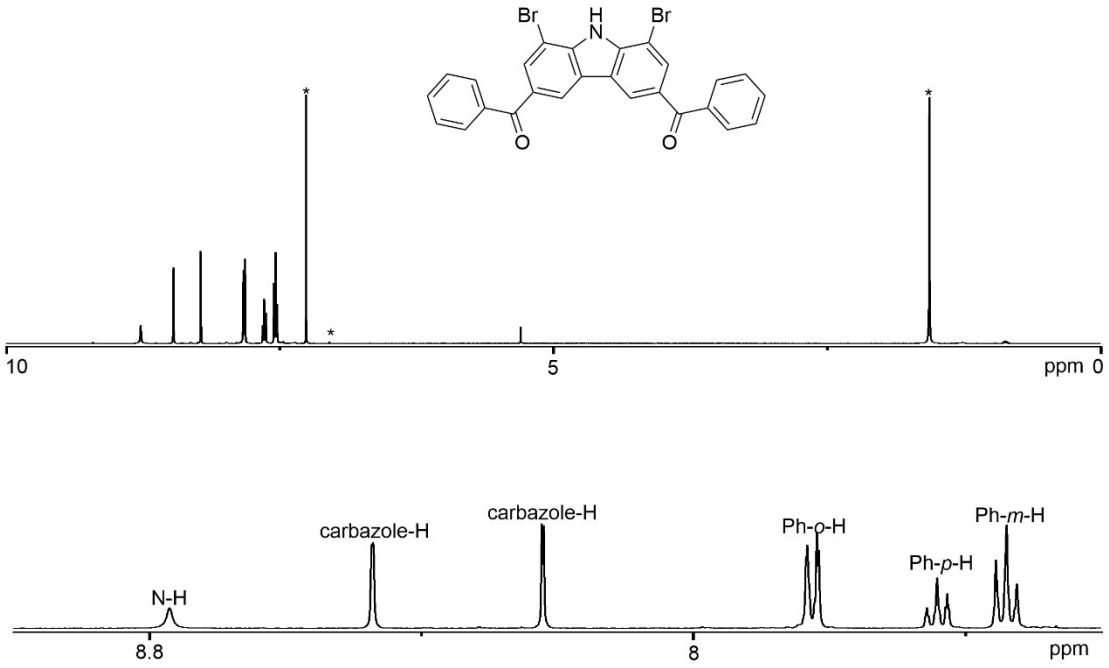


Figure S2. ^{1}H NMR spectrum of **5Br** in $CDCl_3$ at 25 °C.

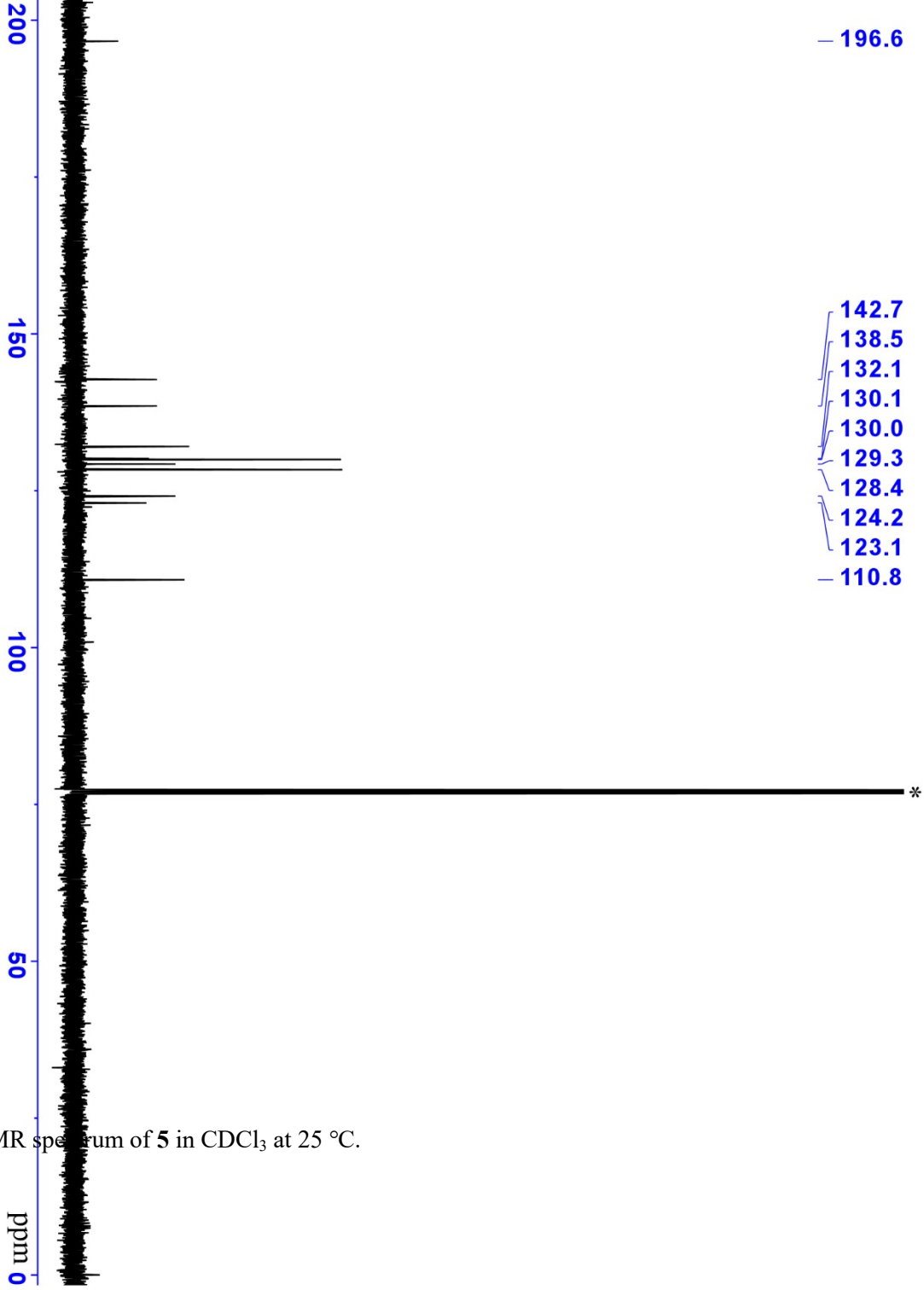


Figure S3. ^{13}C NMR spectrum of **5** in $CDCl_3$ at 25 ℃.

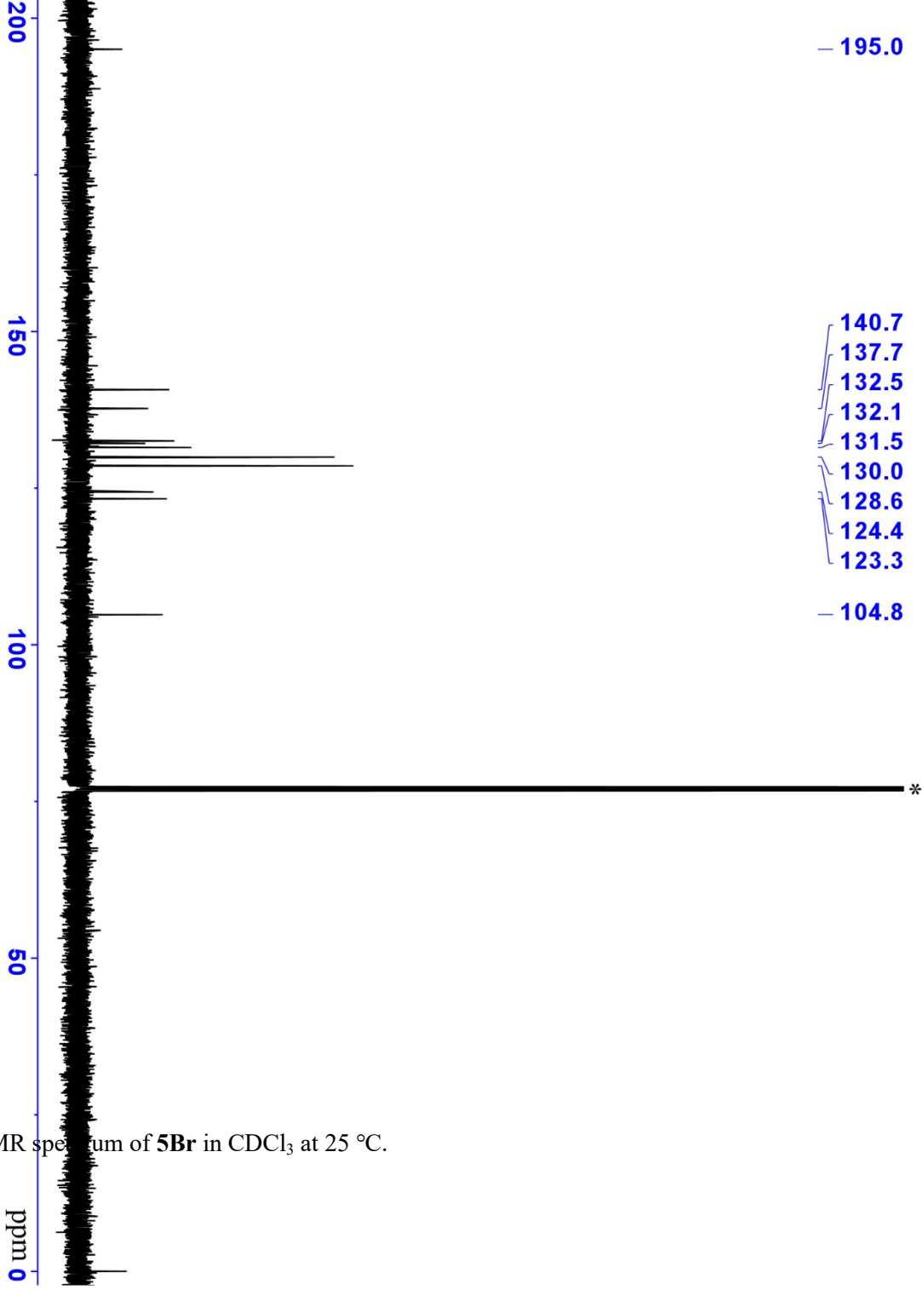


Figure S4. ^{13}C NMR spectrum of **5Br** in $CDCl_3$ at 25 °C.

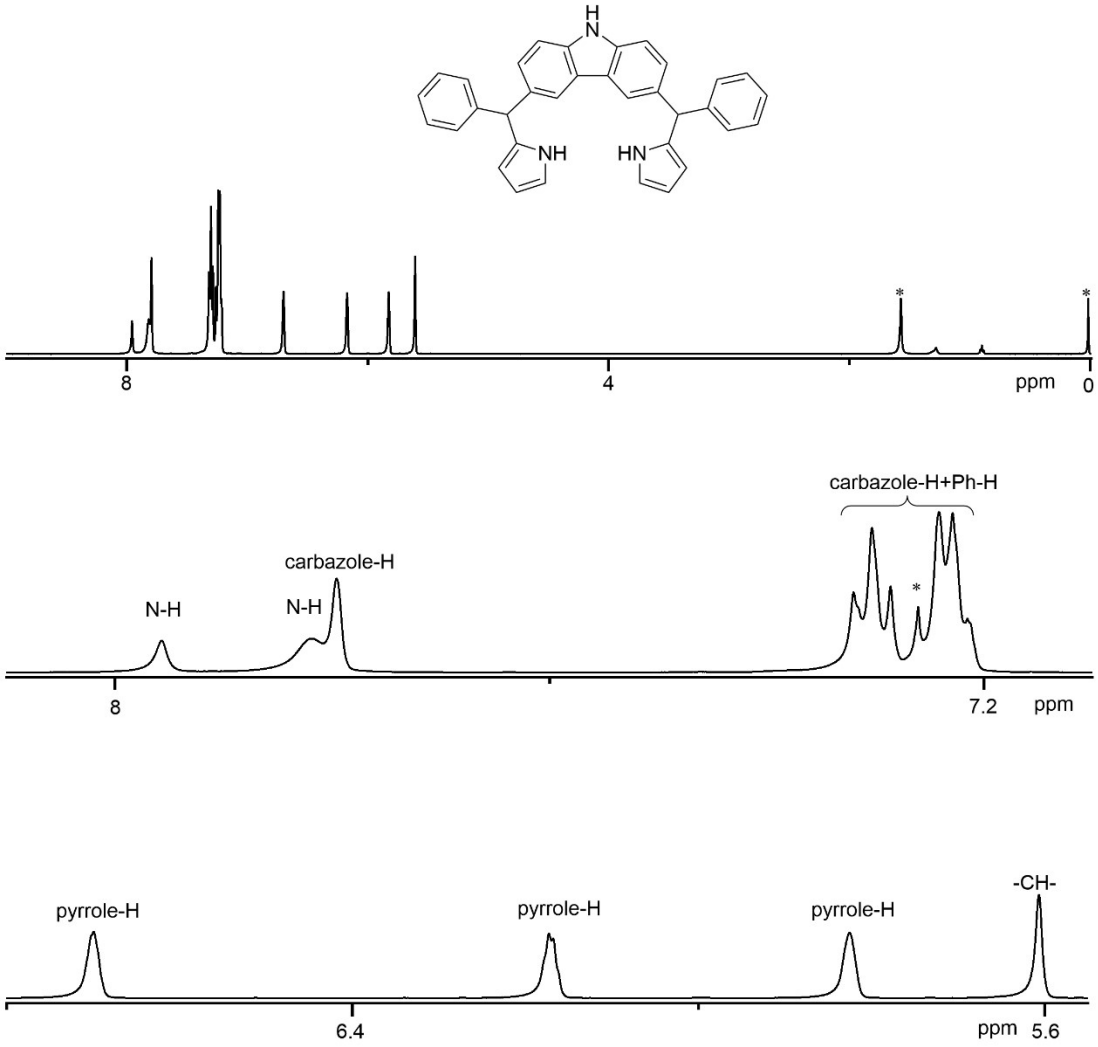


Figure S5. ^{1}H NMR spectrum of **6** in $CDCl_3$ at 25 °C.

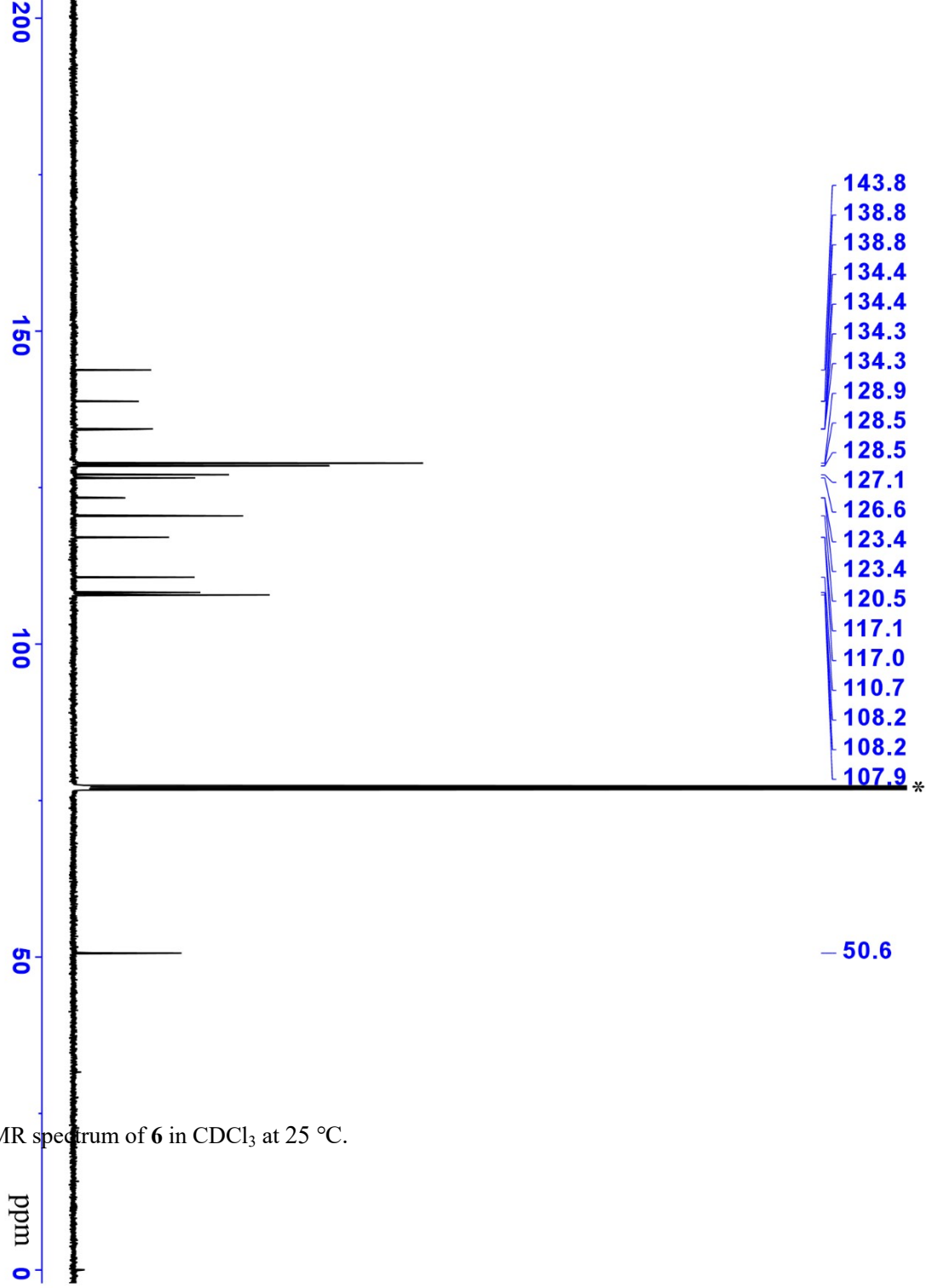


Figure S6. ^{13}C NMR spectrum of **6** in $CDCl_3$ at 25 °C.

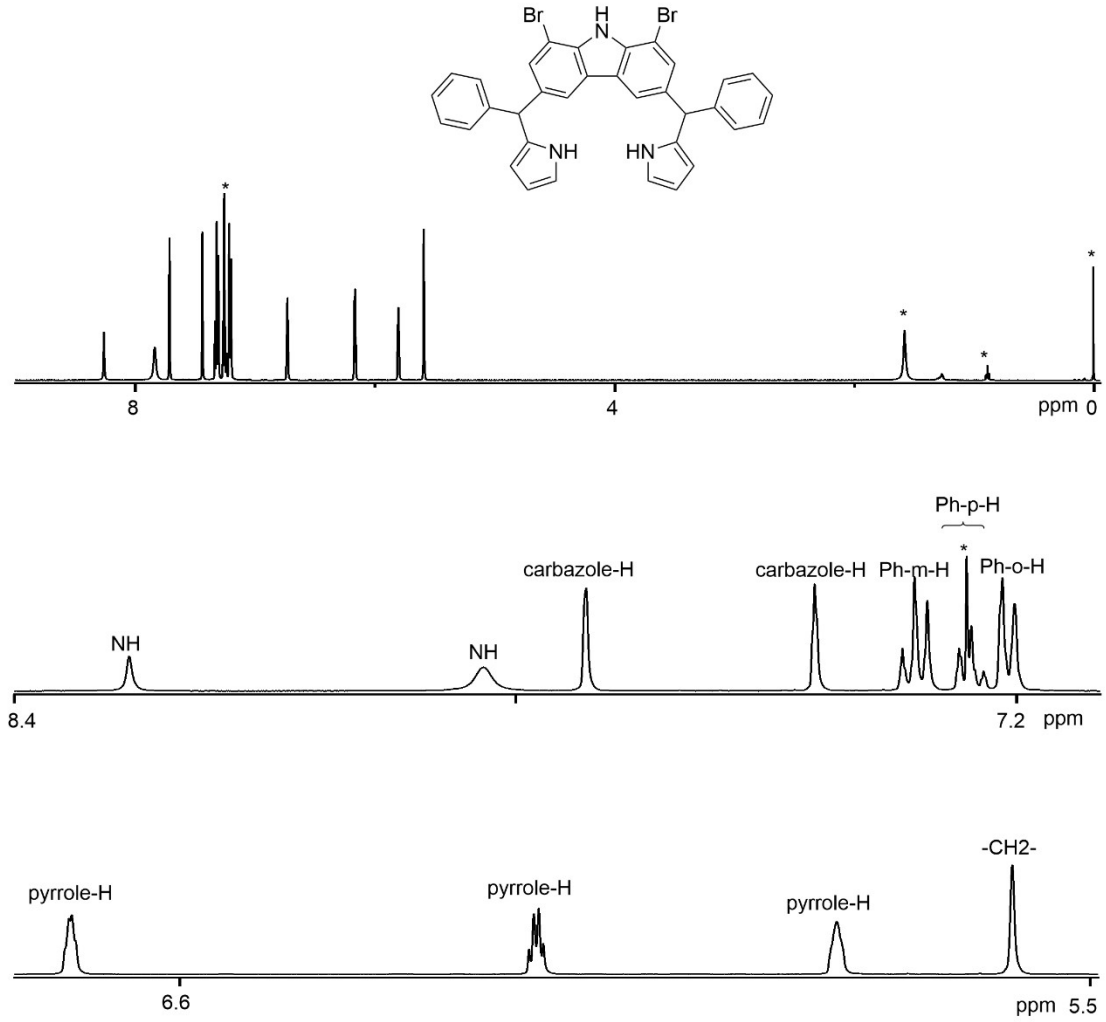


Figure S7. ^{1}H NMR spectrum of **6Br** in $CDCl_3$ at 25 °C.

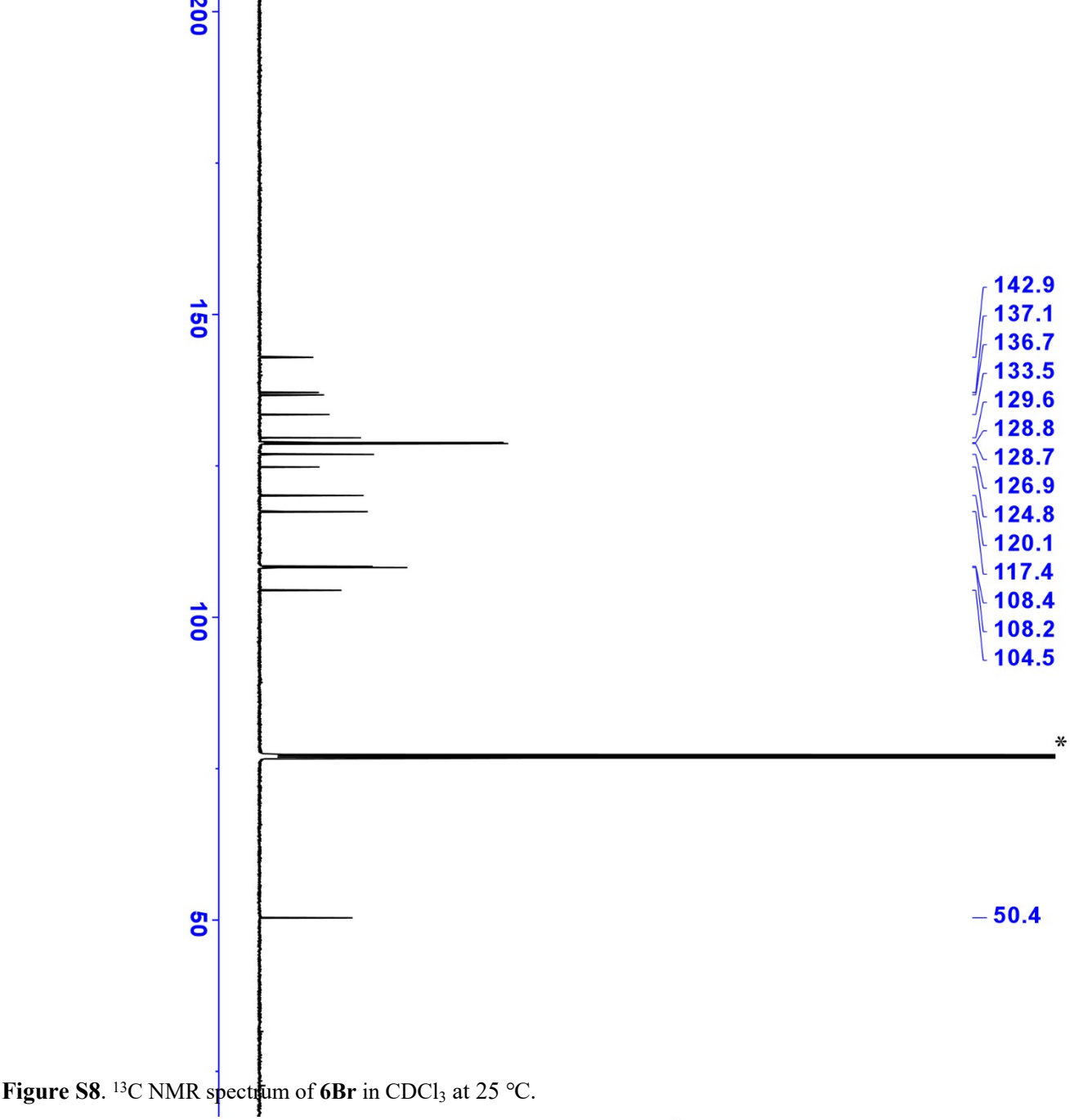


Figure S8. ^{13}C NMR spectrum of **6Br** in $CDCl_3$ at 25 °C.

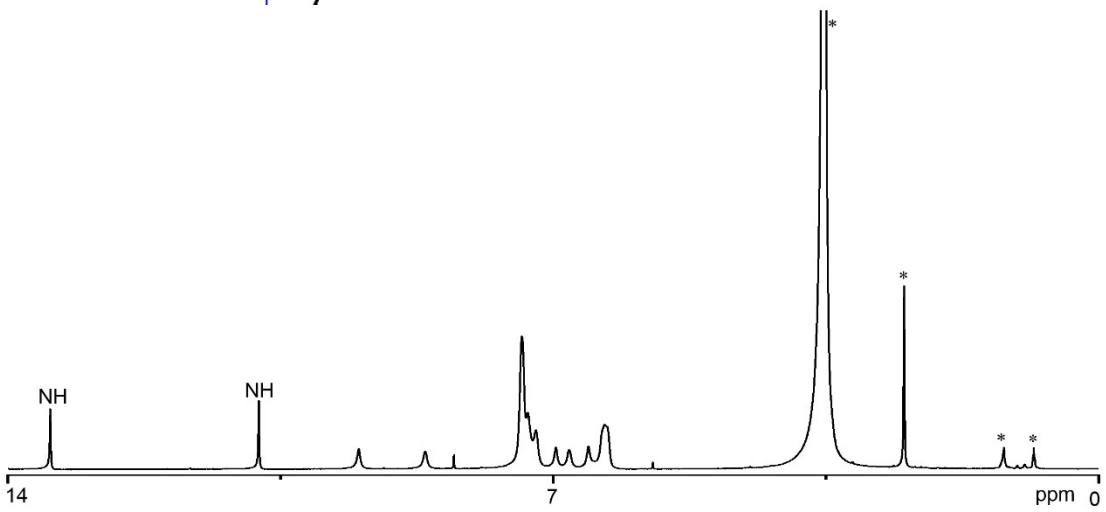


Figure S9. ^{1}H NMR spectrum of **7a** in DMSO-d_6 at 25 °C.

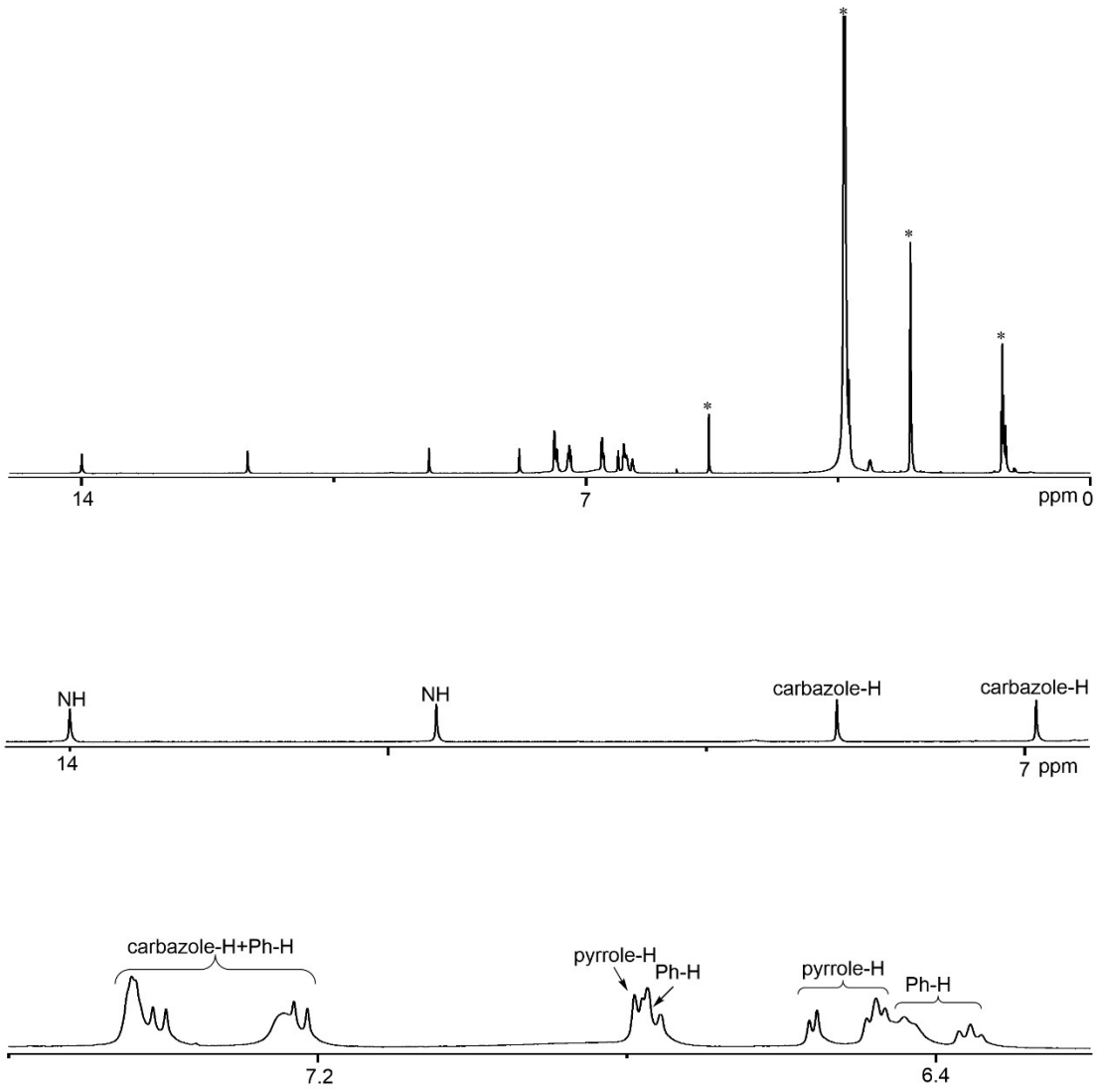


Figure S10. ^{1}H NMR spectrum of **7b** in DMSO-d_6 at 25 ℃.

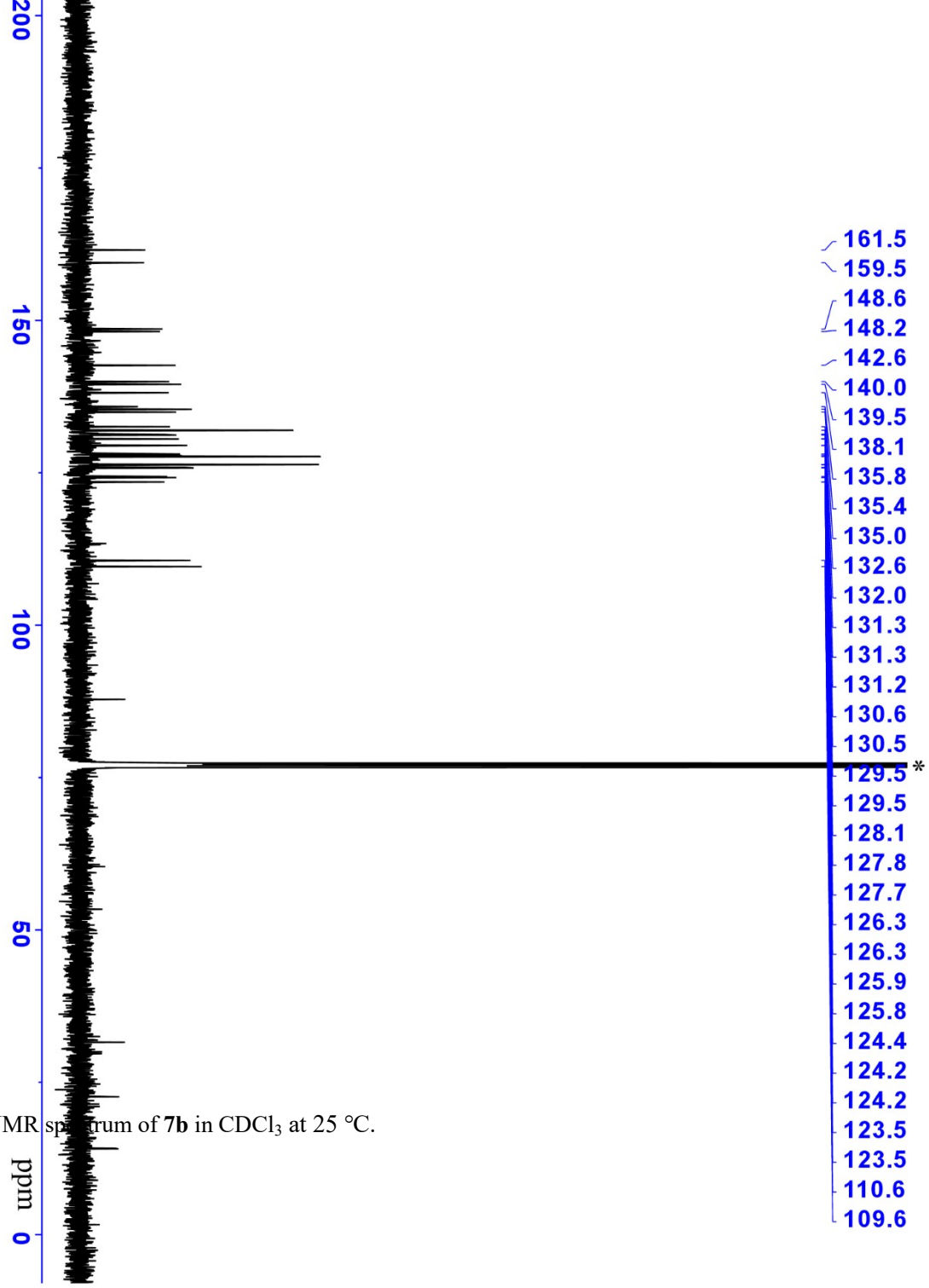


Figure S11. ^{13}C NMR spectrum of **7b** in $CDCl_3$ at 25 ℃.

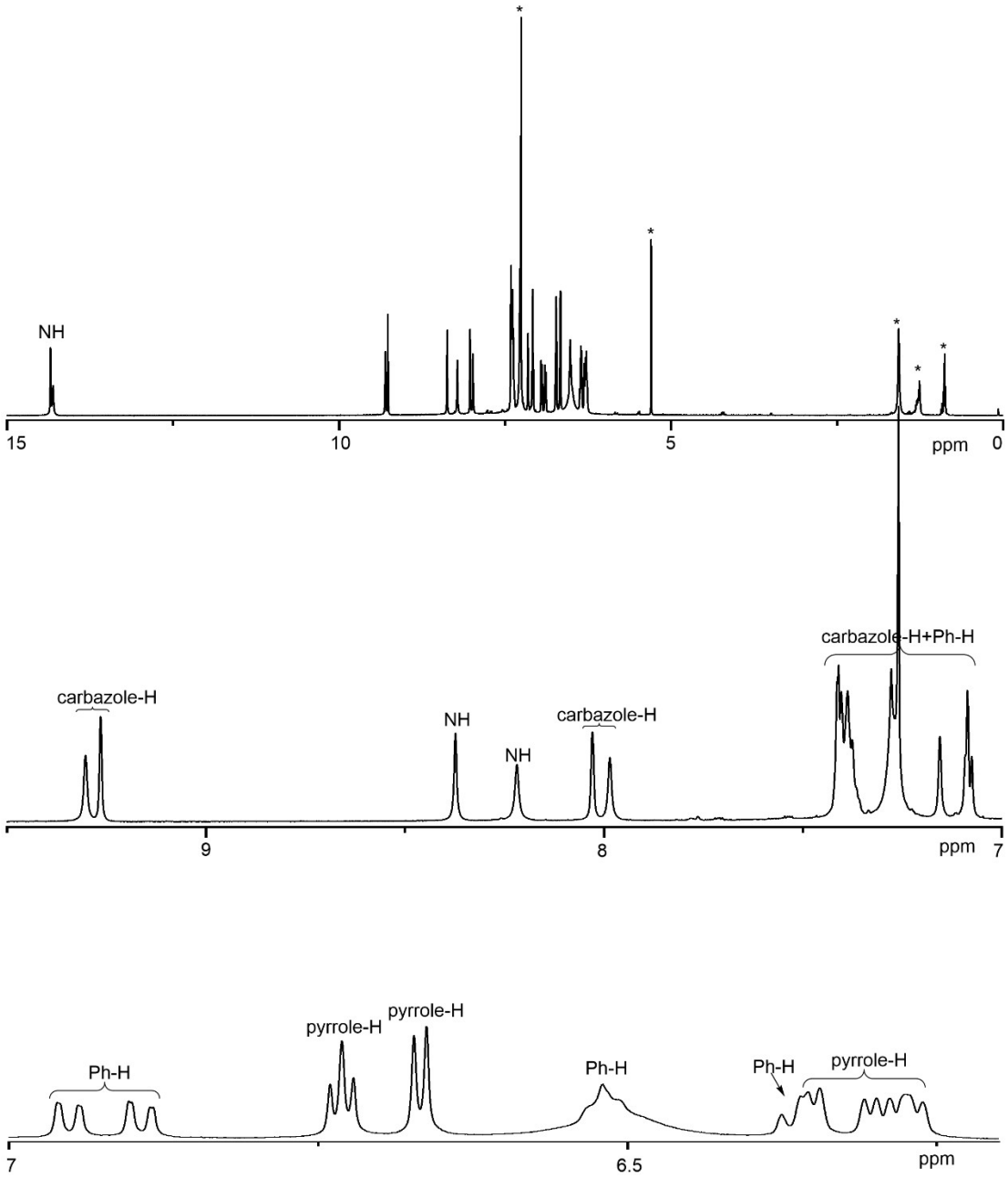


Figure S12. ^{1}H NMR spectrum of **7-2Br** in $CDCl_3$ at 25 ℃.

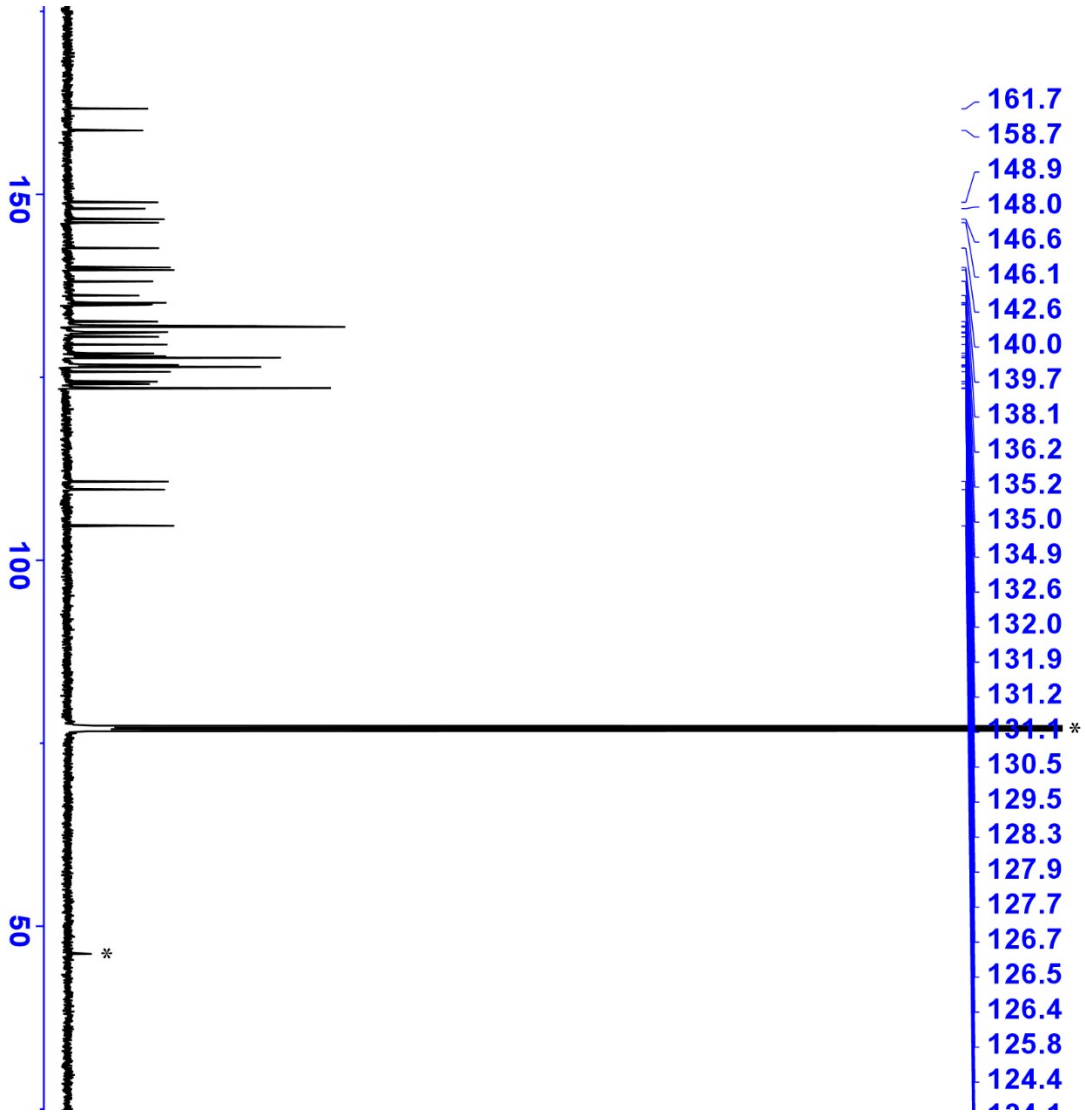


Figure S13. ^{13}C NMR spectrum of **7-2Br** in $CDCl_3$ at 25 °C.

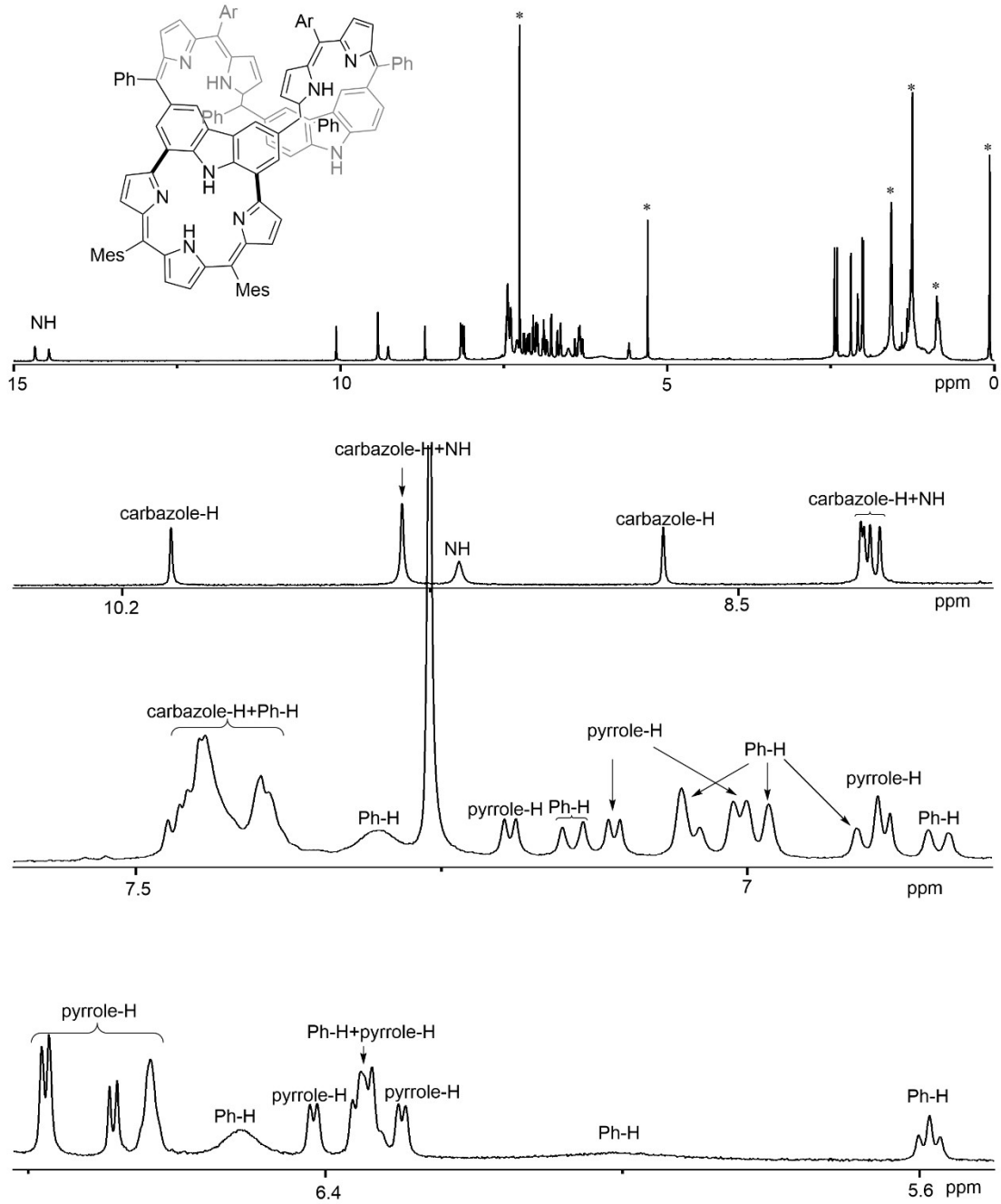


Figure S14. ^{1}H NMR spectrum of **9** in $CDCl_3$ at 25 °C.

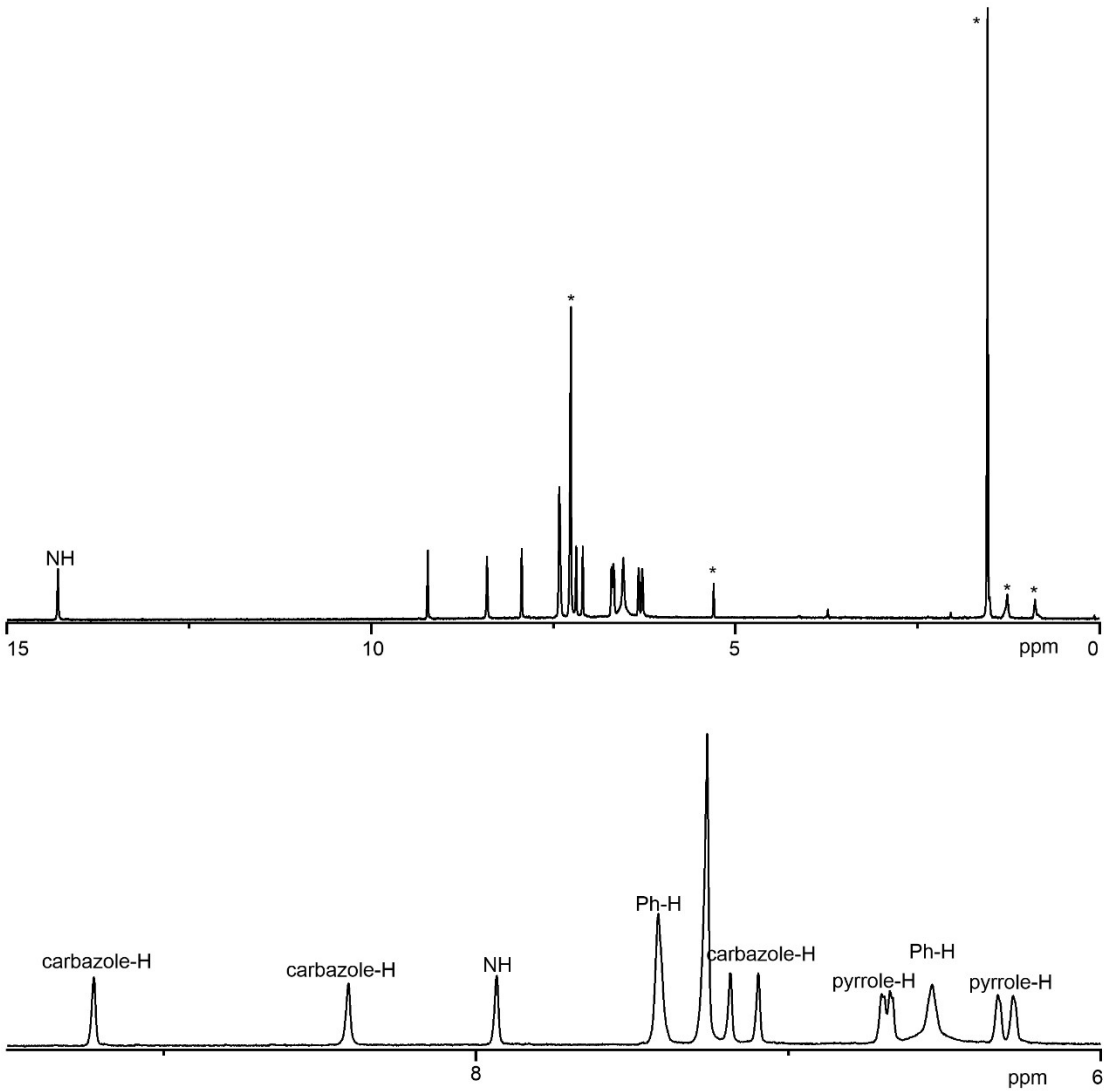


Figure S15. ^{1}H NMR spectrum of **7-4Br** in $CDCl_3$ at 25 ℃.

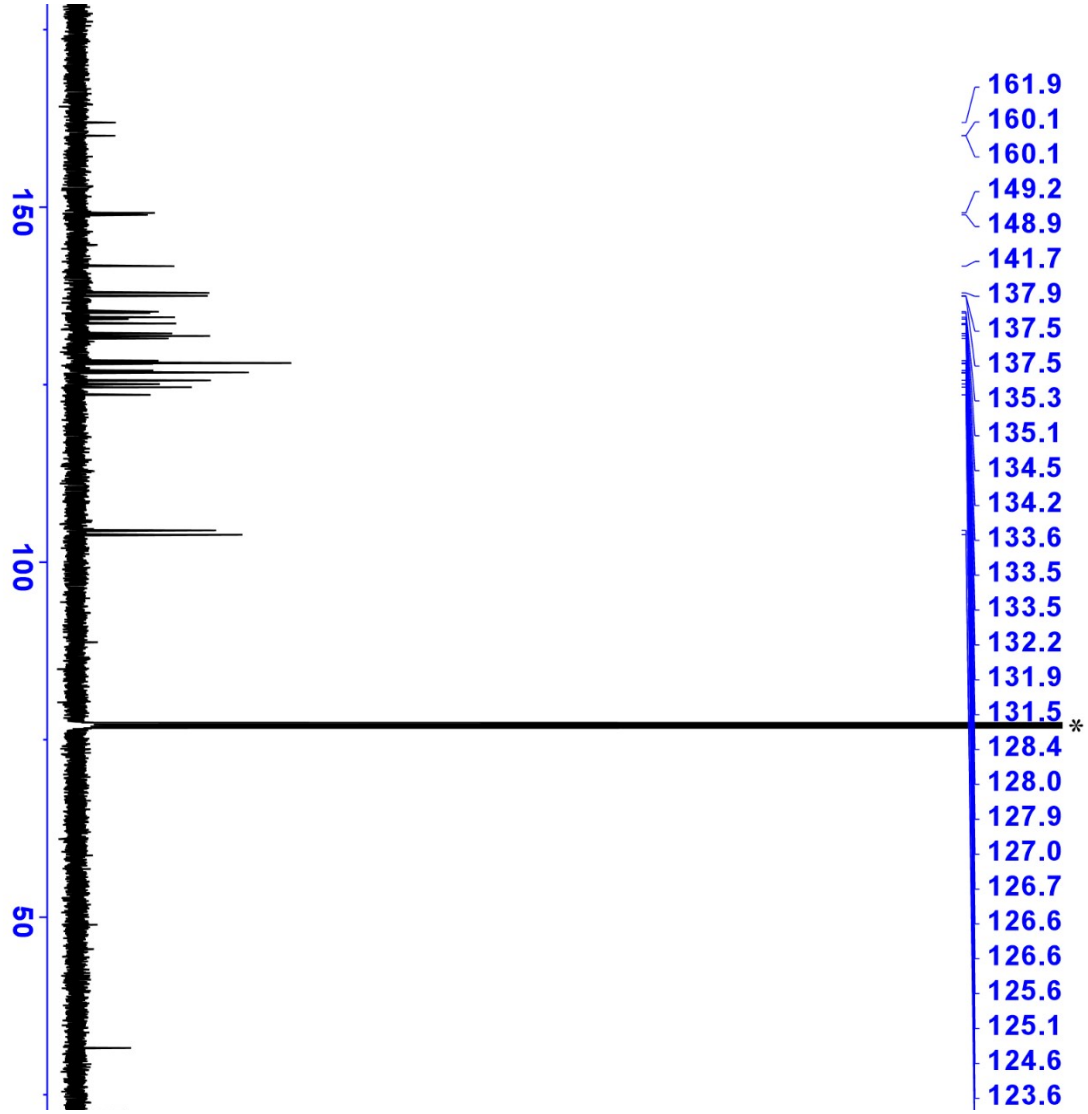


Figure S16. ^{13}C NMR spectrum of **7-4Br** in $CDCl_3$ at 25 °C.

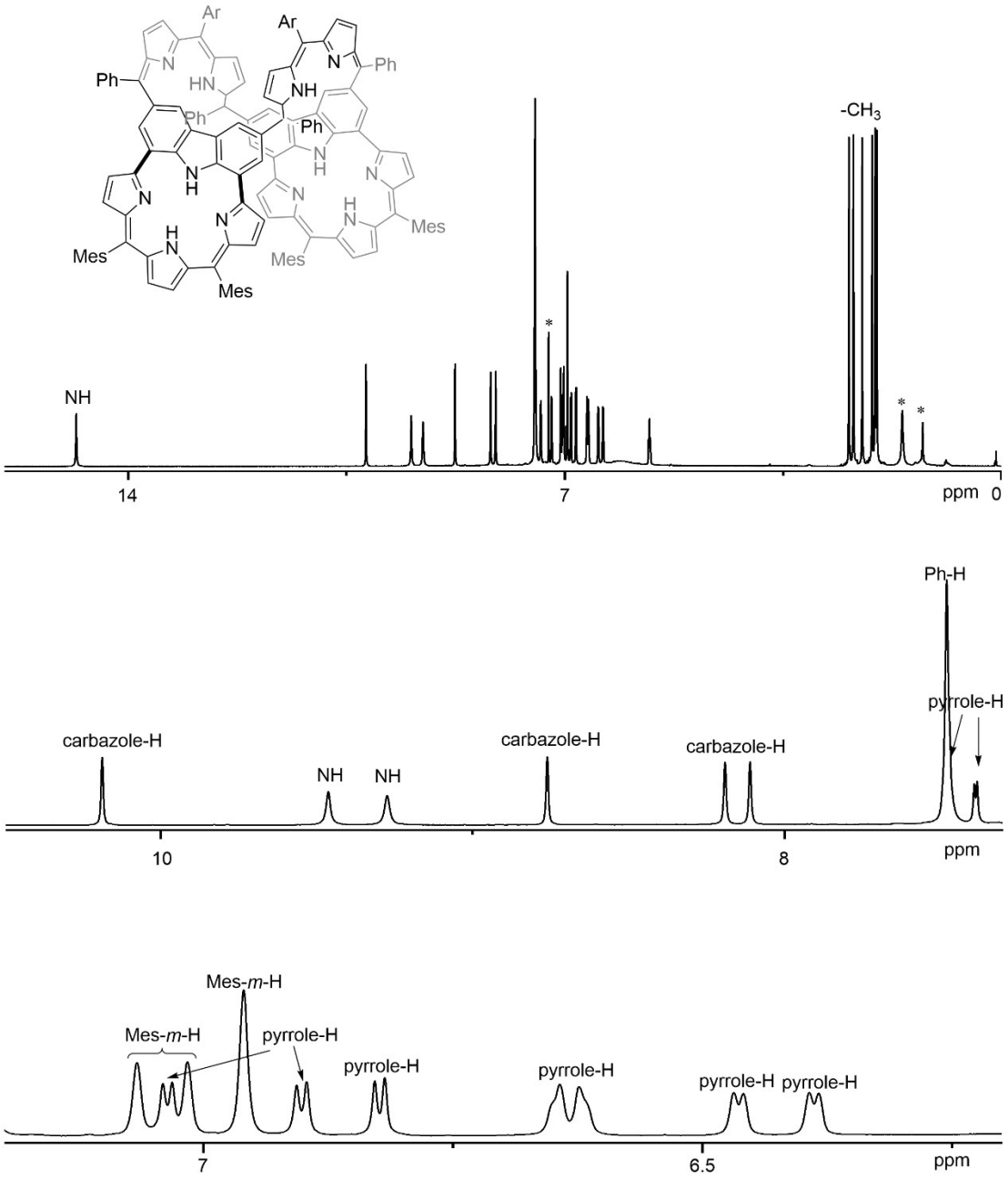


Figure S17. ^{1}H NMR spectrum of **10** in $CDCl_3$ at 25 ℃.

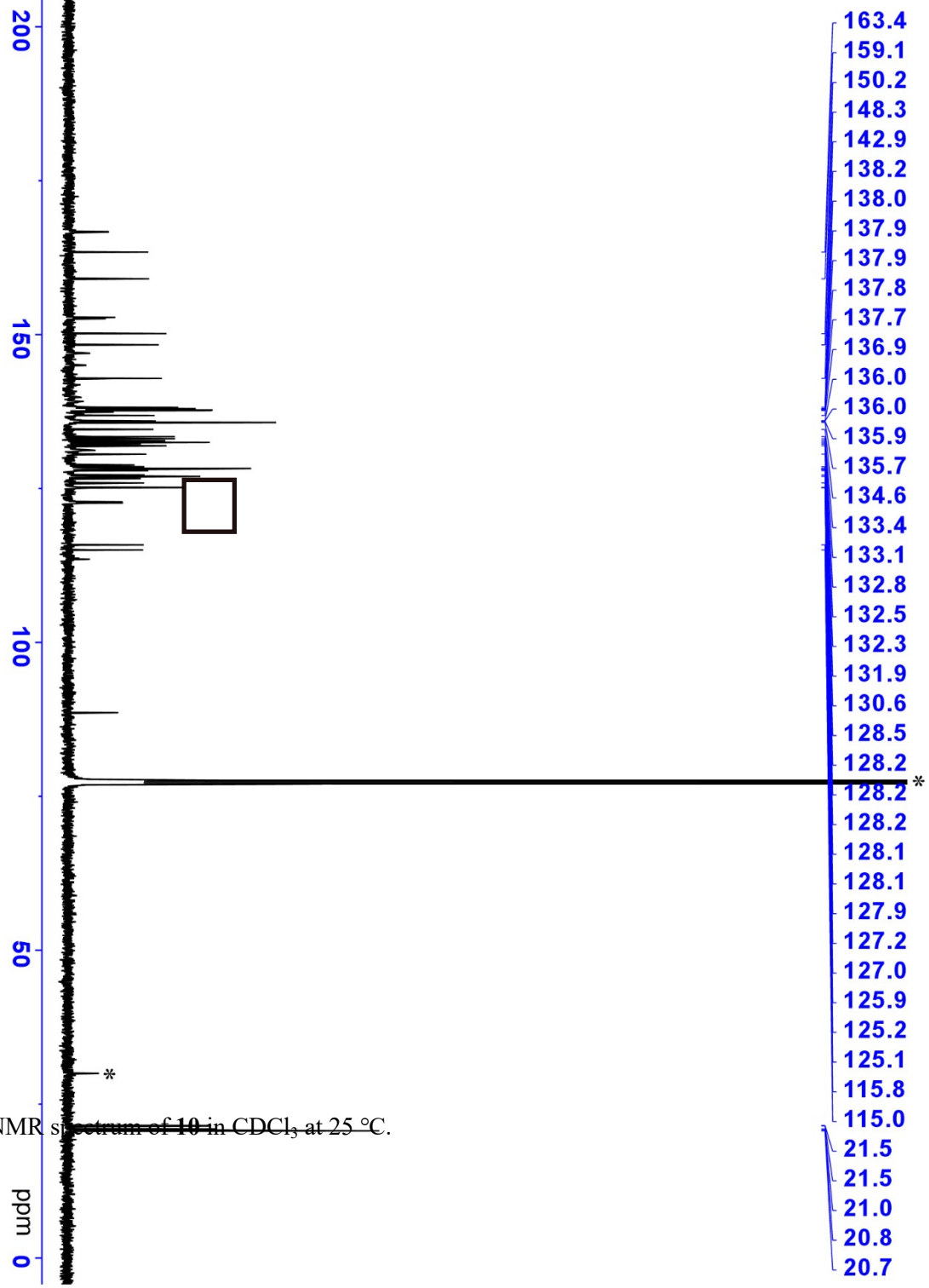


Figure S18. ^{13}C NMR spectrum of ~~**10** in $CDCl_3$ at 25 °C~~.

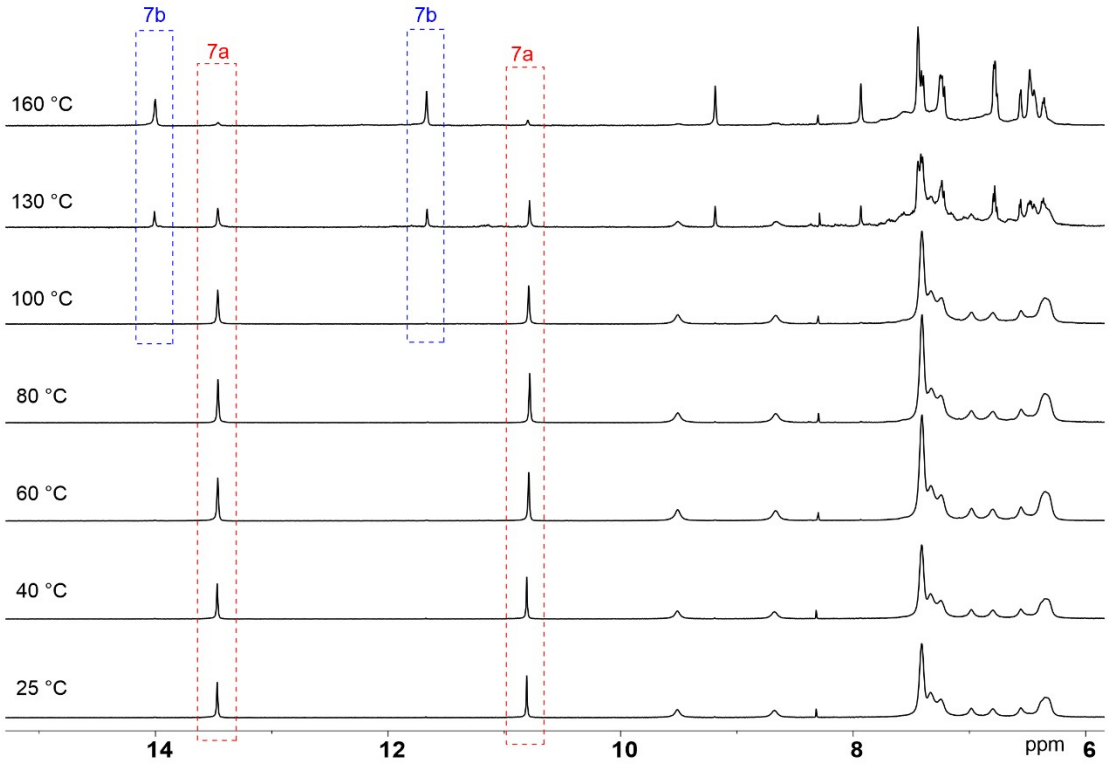


Figure S19. ^{1}H NMR spectra of **7a** recorded in 25 ºC – 160 ºC temperature range after heating with 2 h (500 MHz, DMSO-d_6).

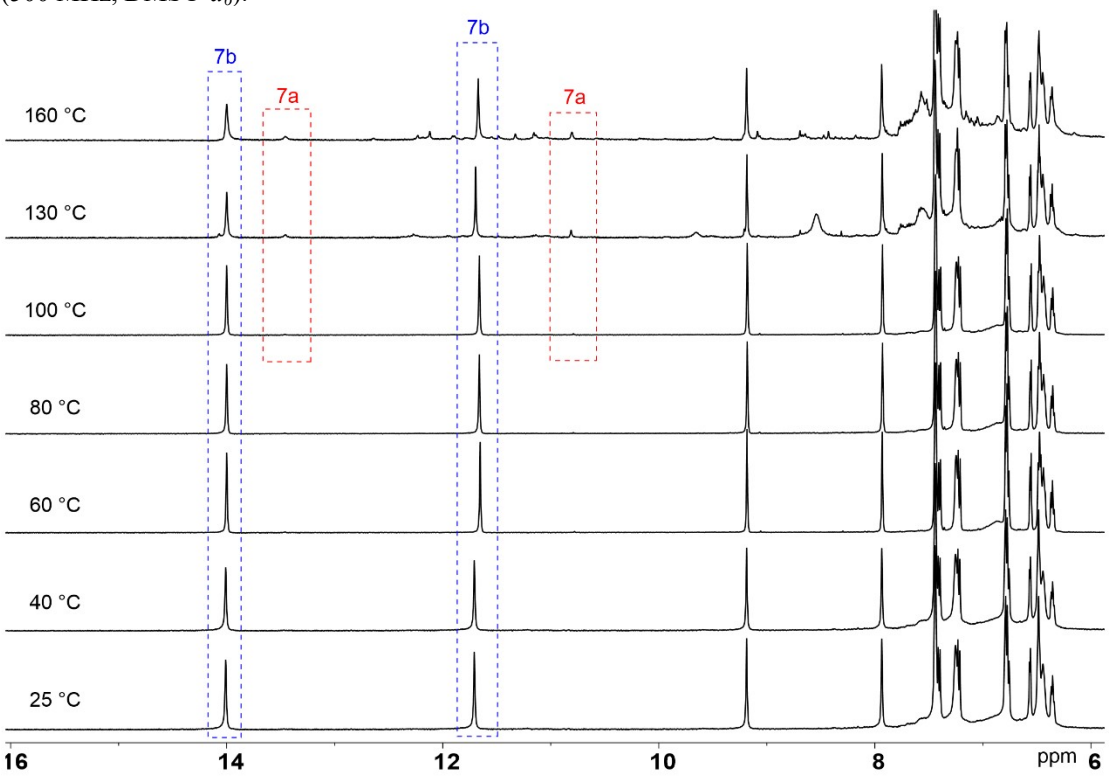


Figure S20. ^{1}H NMR spectra of **7b** recorded in 25 ºC – 160 ºC temperature range after heating with 2 h (500 MHz, DMSO-d_6).

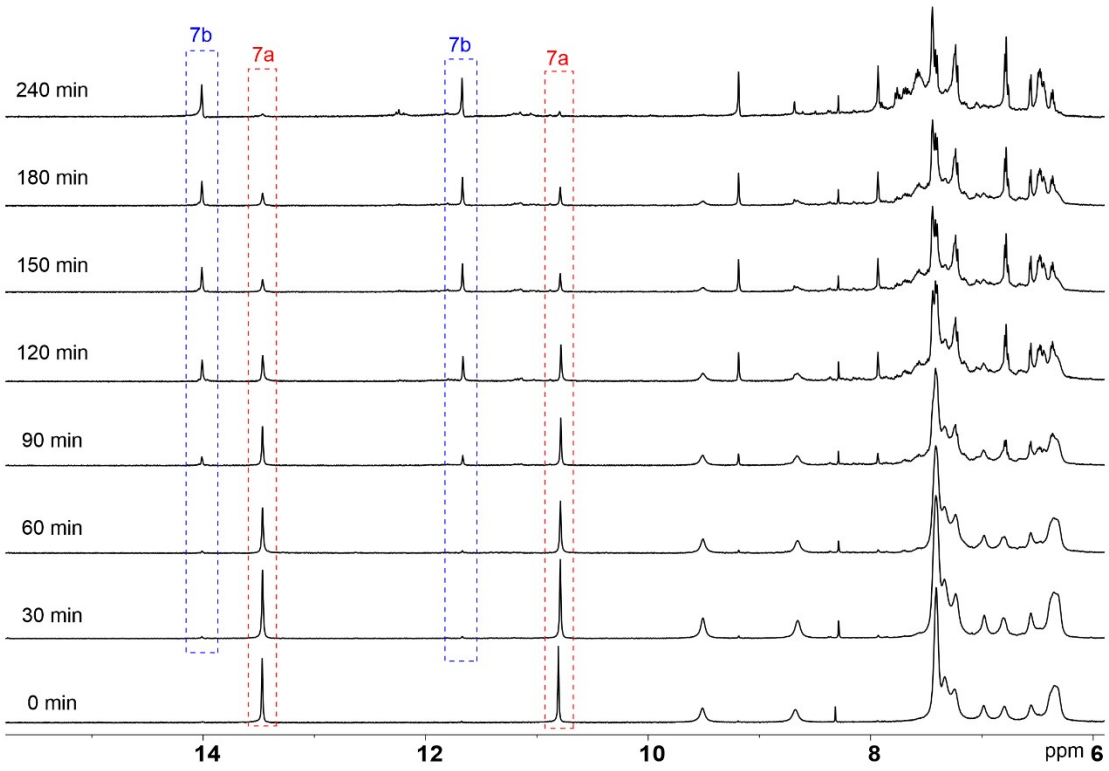


Figure S21. ^{1}H NMR spectra of **7a** recorded in 130 ºC (500 MHz, DMSO-d_6)

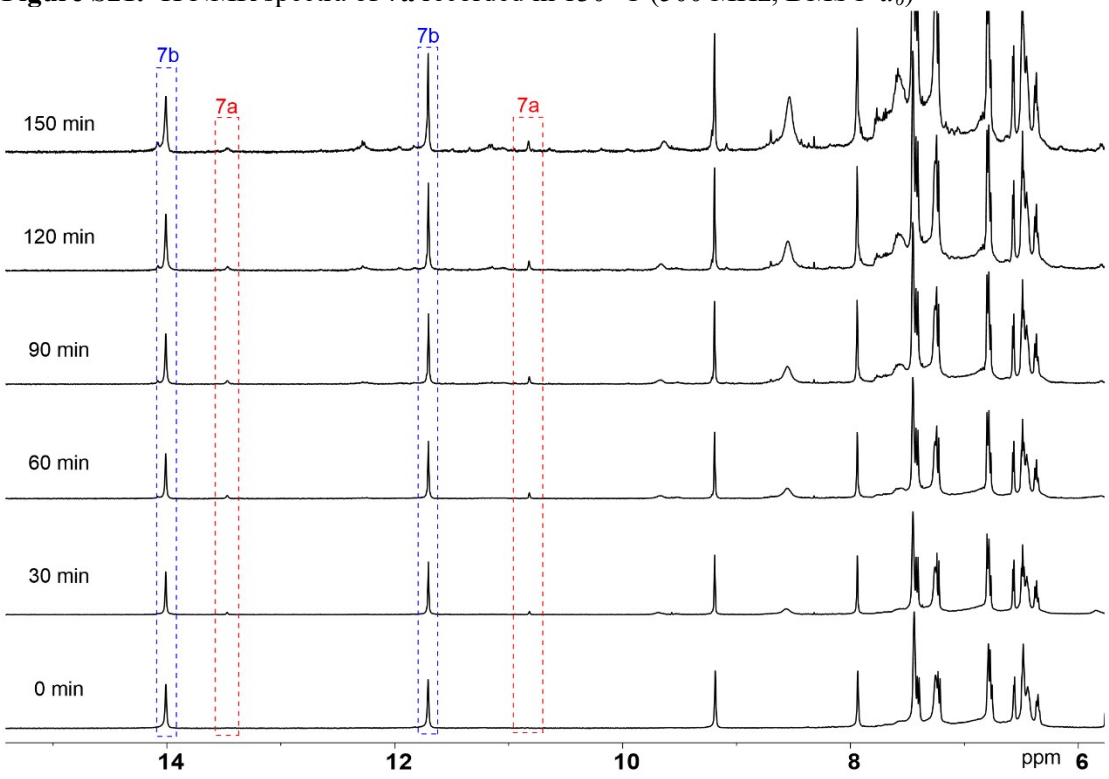


Figure S22. ^{1}H NMR spectra of **7b** recorded in 130 ºC (500 MHz, DMSO-d_6)

UV/vis absorption spectra

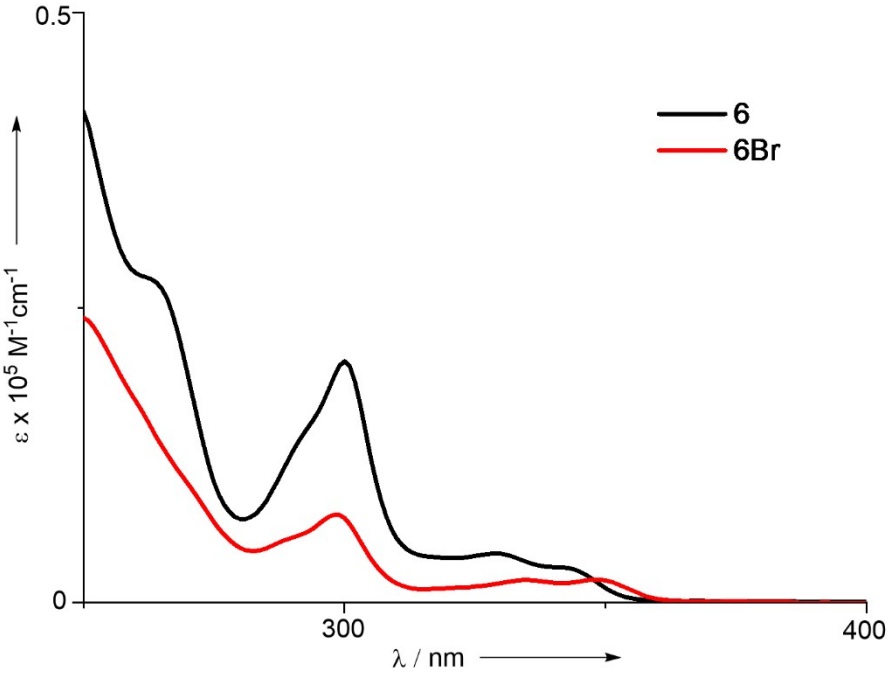


Figure S23. UV/vis absorption spectra of **6** (black line) and **6Br** (red line) in CH_2Cl_2.

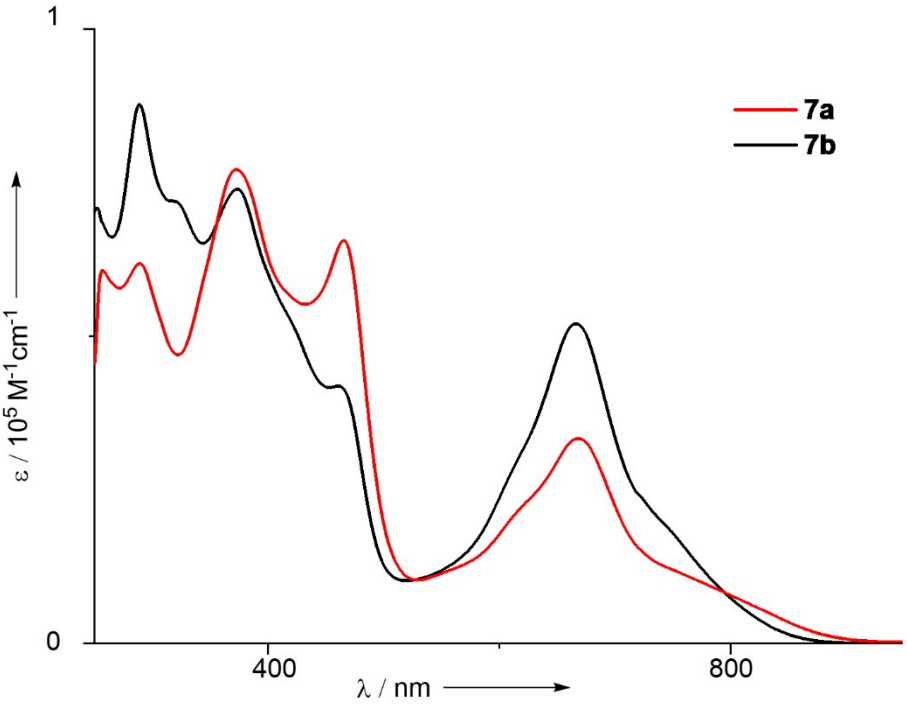


Figure S24. UV/vis absorption spectra of **7a** (red line) and **7b** (black line) in CH_2Cl_2.

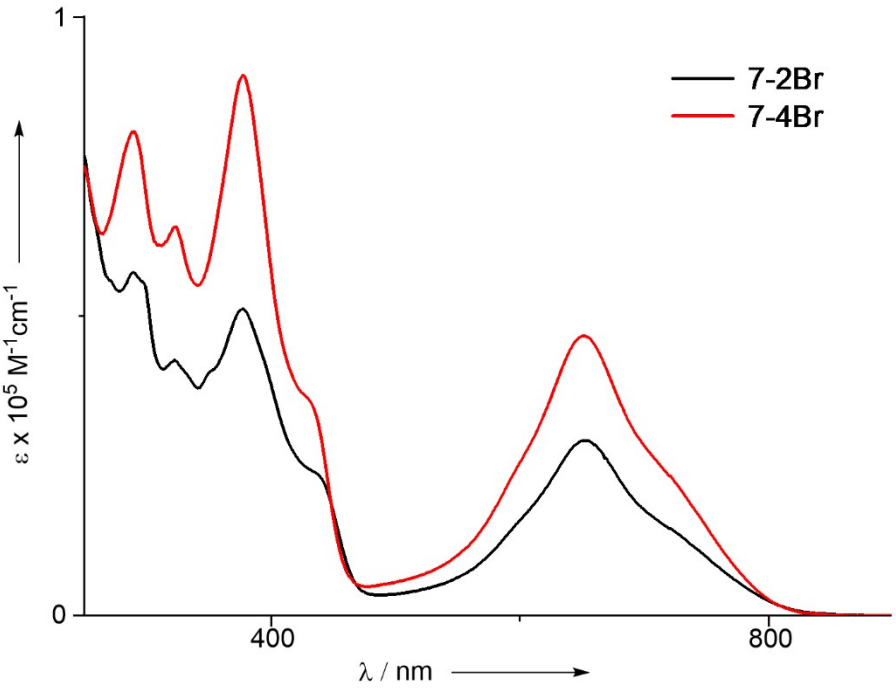


Figure S25. UV/vis absorption spectra of **7-2Br** (black line) and **7-4Br** (red line) in CH_2Cl_2.

High-resolution MS spectra

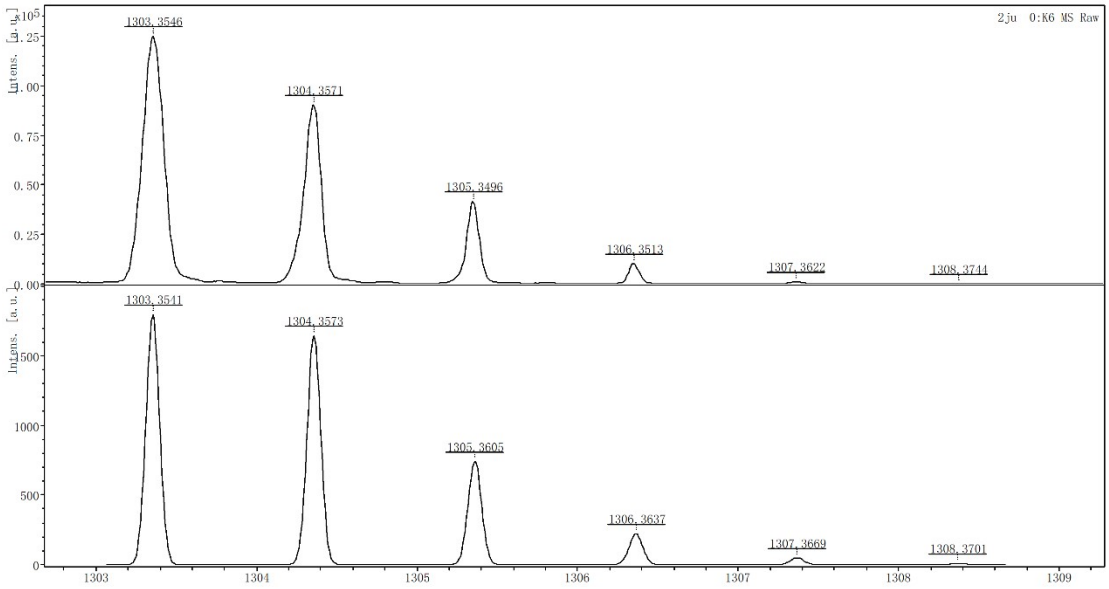


Figure S26. The high-resolution mass spectrum of **7a** ($[M+H]^+$). Top: experimental spectrum, bottom: simulated pattern.

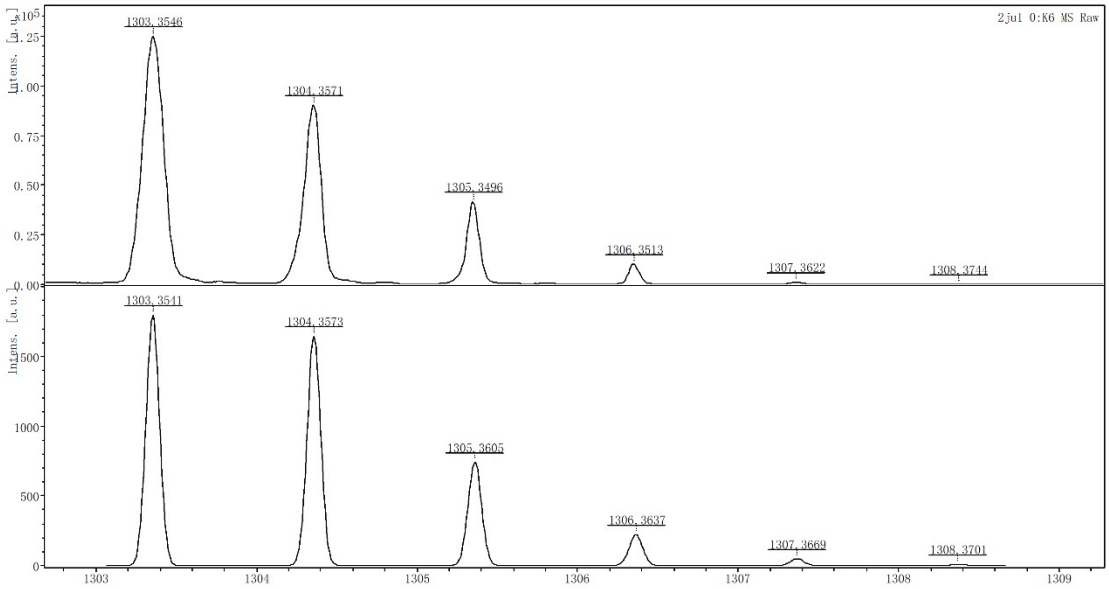


Figure S27. The high-resolution mass spectrum of **7b** ($[M+H]^+$). Top: experimental spectrum, bottom: simulated pattern.

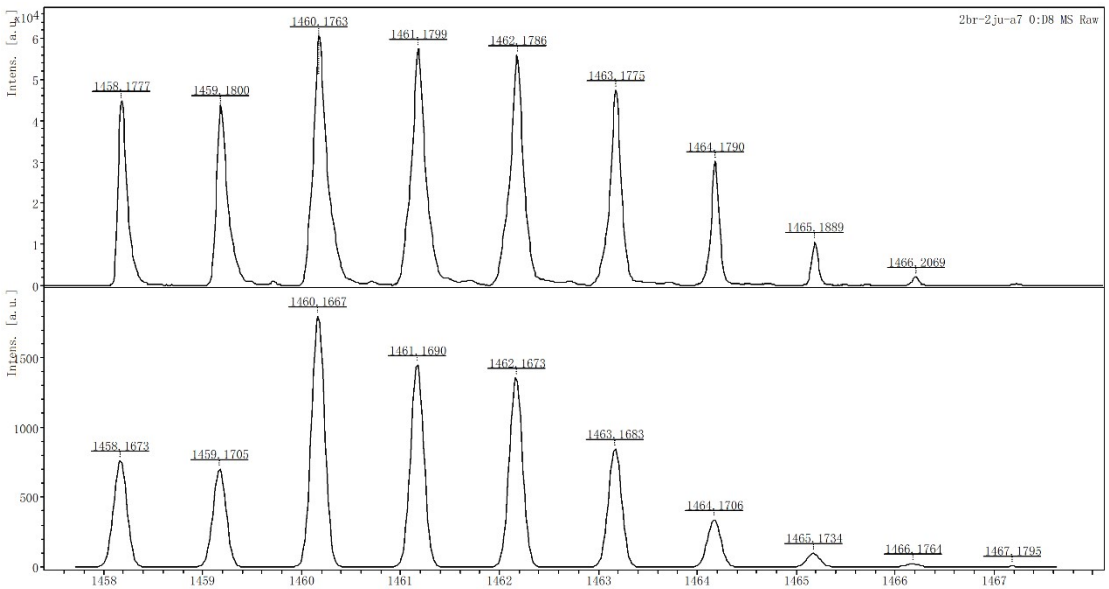


Figure S28. The high-resolution mass spectrum of **7-2Br** ([*M*]$^+$). Top: experimental spectrum, bottom: simulated pattern.

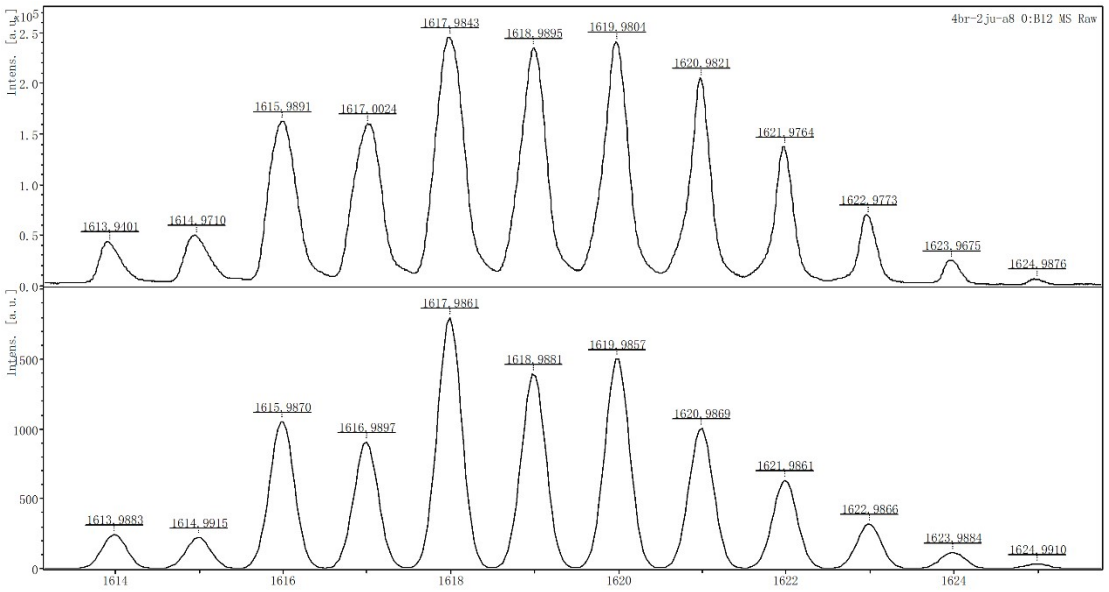


Figure S29. The high-resolution mass spectrum of **7-4Br** ([*M*]$^+$). Top: experimental spectrum, bottom: simulated pattern.

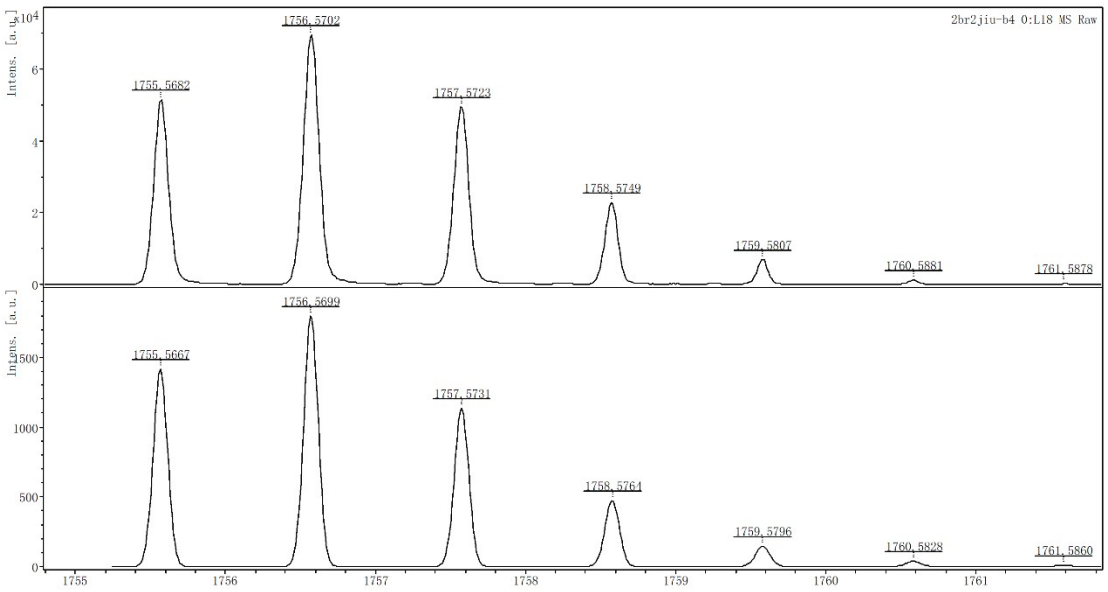


Figure S30. The high-resolution mass spectrum of **9** ([*M*]$^+$). Top: experimental spectrum, bottom: simulated pattern.

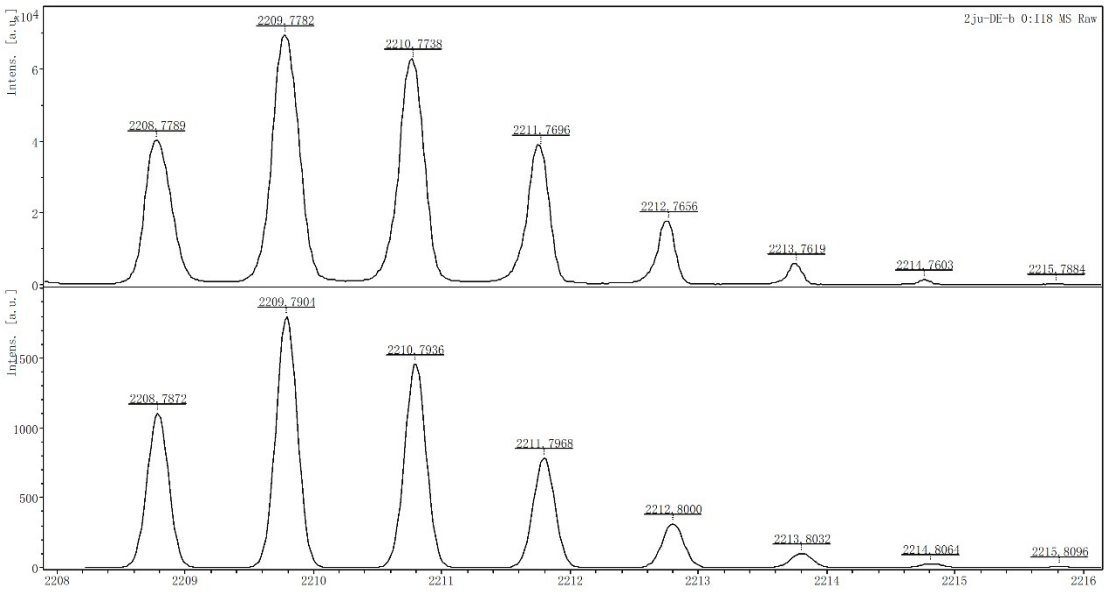


Figure S31. The high-resolution mass spectrum of **10** ([*M*]$^+$). Top: experimental spectrum, bottom: simulated pattern.

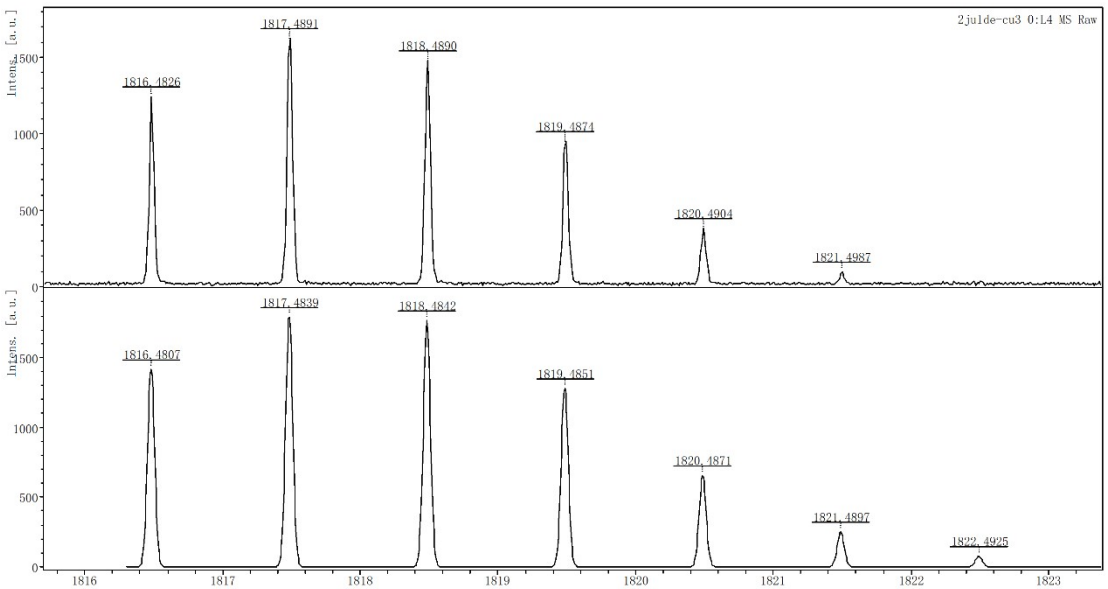


Figure S32. The high-resolution mass spectrum of **9Cu** ([M]$^+$). Top: experimental spectrum, bottom: simulated pattern.

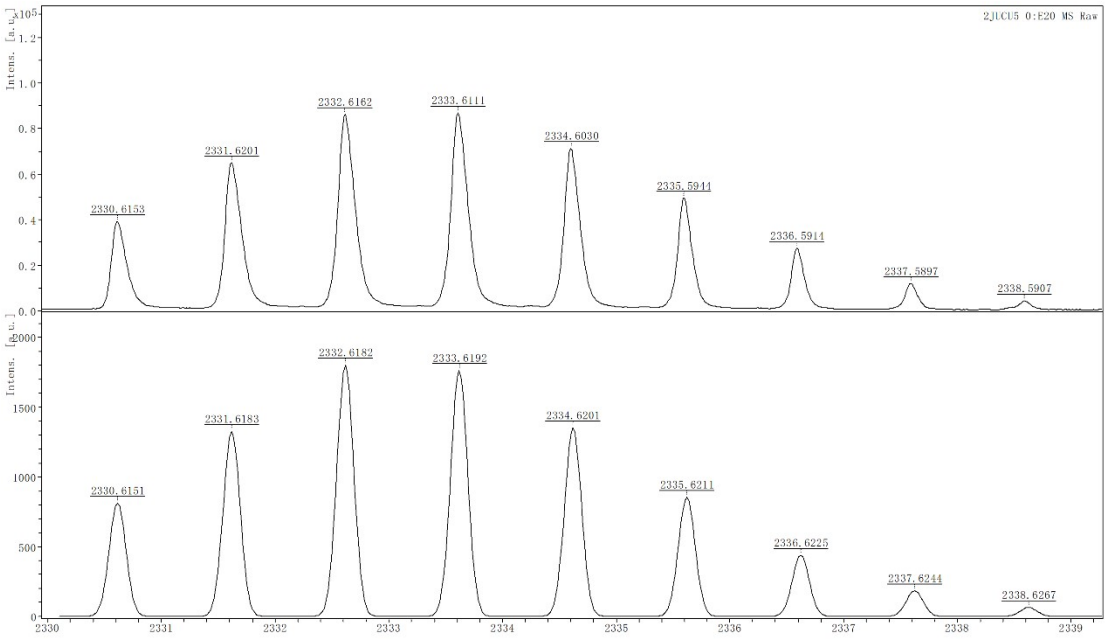


Figure S33. The high-resolution mass spectrum of **10Cu** ([M]$^+$). Top: experimental spectrum, bottom: simulated pattern.

X-Ray Crystal Data

Table S1. Crystal data and structure refinement for **7a**

Empirical formula	$C_{82}H_{44}F_{10}N_6$	
Formula weight	1303.23	
Temperature	100(1) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 17.3154(7) Å	α = 90°.
	b = 11.2554(5) Å	β = 101.158(4)°.
	c = 40.1263(17) Å	γ = 90°.
Volume	7672.5(6) $Å^3$	
Z	4	
Density (calculated)	1.128 Mg/m^3	
Absorption coefficient	0.700 mm^{-1}	
F(000)	2672	
Crystal size	0.2 x 0.1 x 0.02 mm^3	
Theta range for data collection	2.245 to 66.598°.	
Index ranges	-20<=h<=20, -13<=k<=13, -47<=l<=47	
Reflections collected	28118	
Independent reflections	13576 [R(int) = 0.0687]	
Completeness to theta = 66.598°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.38418	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13576 / 0 / 883	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0748, wR2 = 0.1837	
R indices (all data)	R1 = 0.1061, wR2 = 0.2054	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.448 and -0.591 $e.Å^{-3}$	
CCDC No.	2143843	

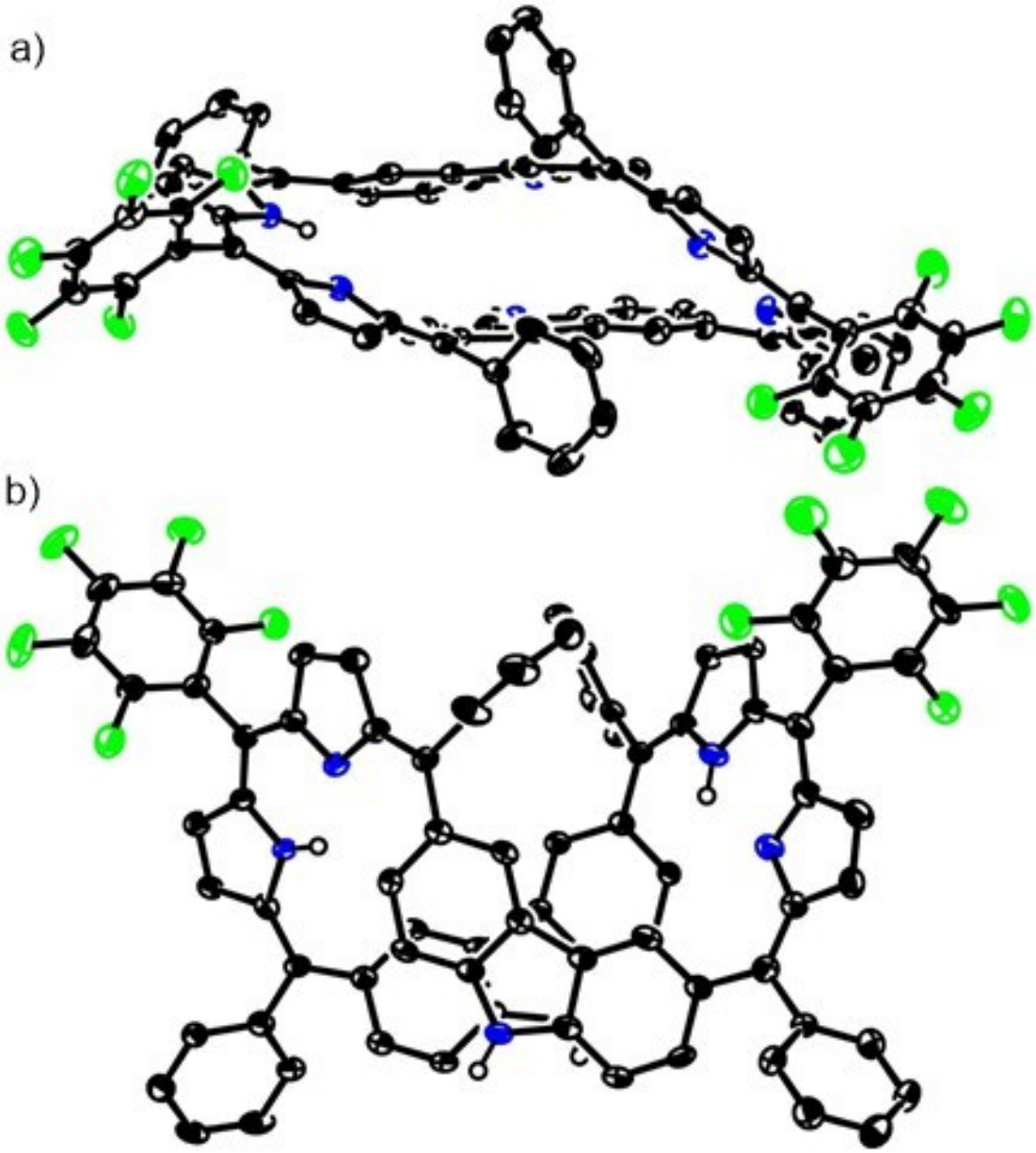


Figure S34. X-ray crystal structure of **7a**. a) Top view, b) side view. The thermal ellipsoids are 50% probability level. Solvent molecules and hydrogens are omitted for clarity.

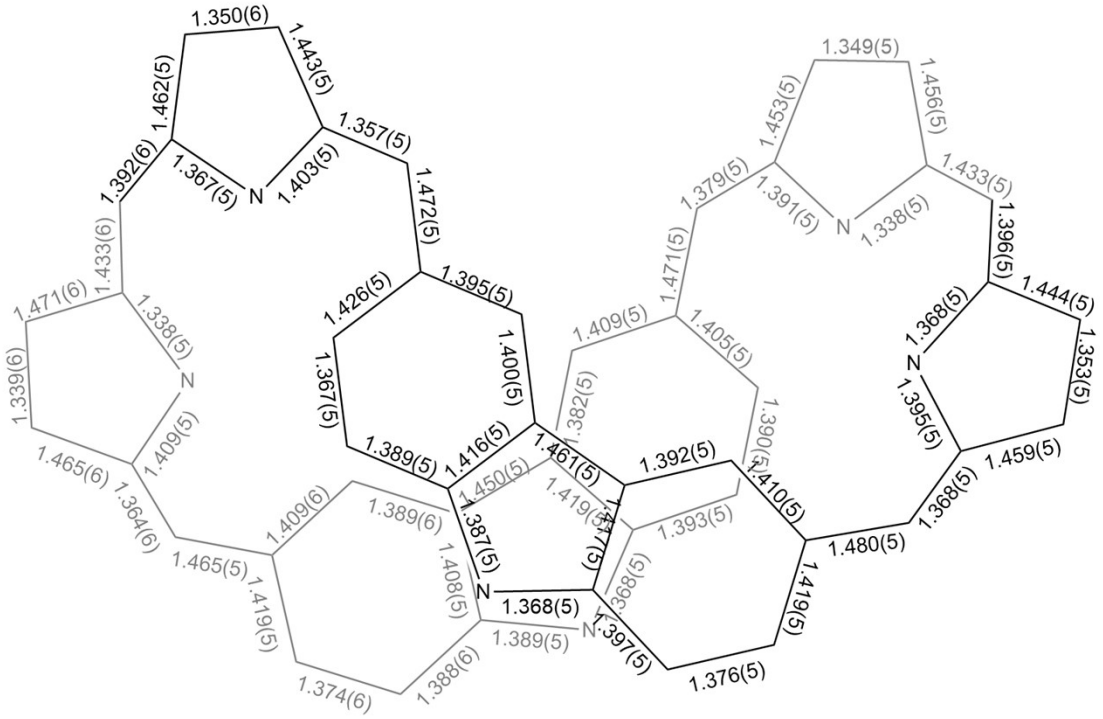


Figure S35. X-ray diffraction analysis of **7a**.

Table S3. Crystal data and structure refinement for **7-4Br**

Empirical formula	$C_{82}H_{40}Br_4F_{10}N_6$	
Formula weight	1618.84	
Temperature	100(1) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	*I*2/a	
Unit cell dimensions	a = 24.5735(4) Å	α = 90°.
	b = 22.5595(4) Å	β = 103.119(2)°.
	c = 49.1675(10) Å	γ = 90°.
Volume	26545.4(9) $Å^3$	
Z	12	
Density (calculated)	1.215 Mg/m^3	
Absorption coefficient	2.740 mm^{-1}	
F(000)	9648	
Crystal size	0.3 x 0.3 x 0.05 mm^3	
Theta range for data collection	3.392 to 66.600°.	
Index ranges	-29<=h<=29, -26<=k<=19, -58<=l<=58	
Reflections collected	89641	
Independent reflections	23413 [R(int) = 0.0648]	
Completeness to theta = 66.600°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.64568	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	23413 / 0 / 1378	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0786, wR2 = 0.2172	
R indices (all data)	R1 = 0.0875, wR2 = 0.2281	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.724 and -2.279 $e.Å^{-3}$	
CCDC No.	2143912	

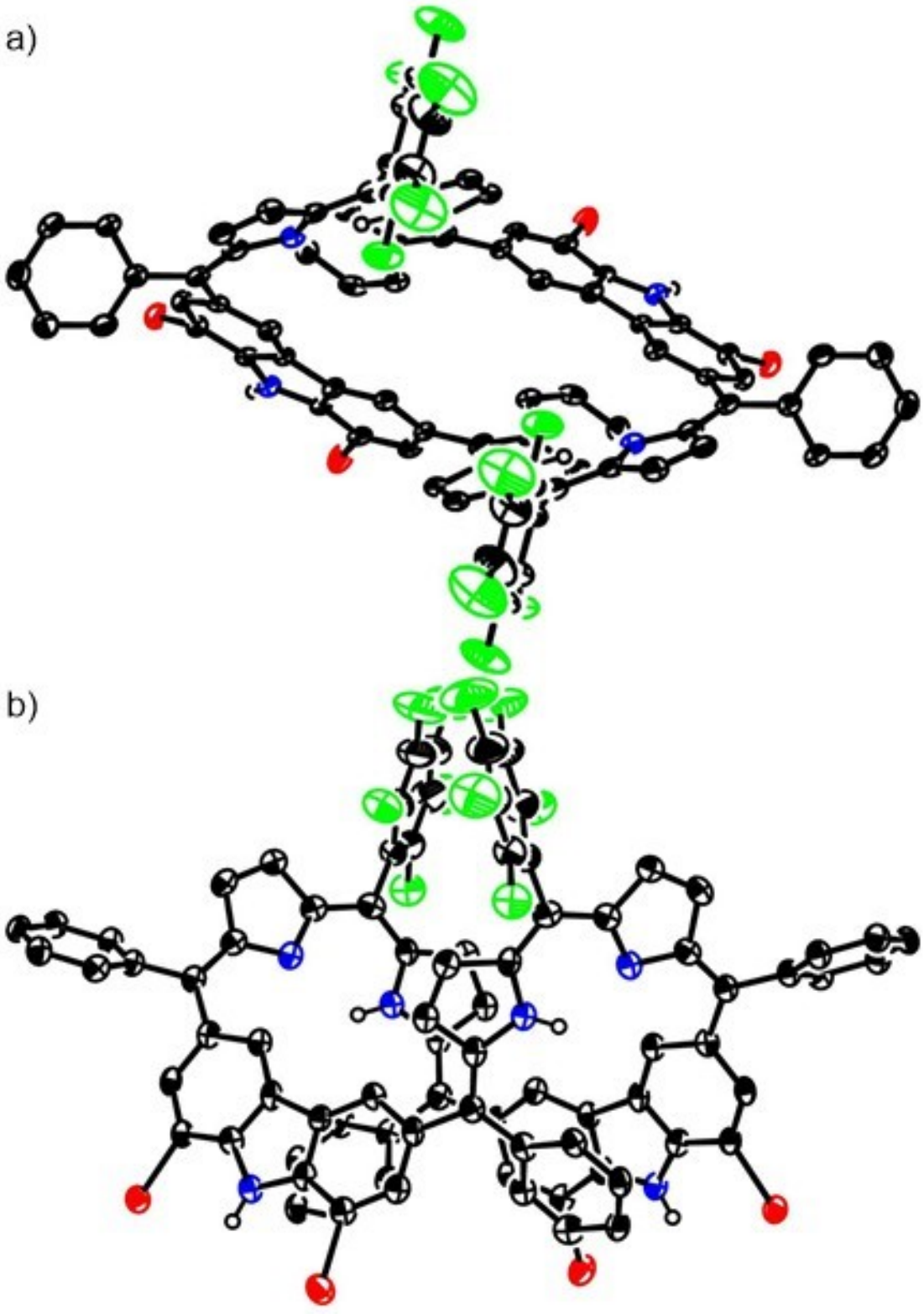


Figure S36. X-ray crystal structure of **7-4Br-1**. a) Top view, b) side view. The thermal ellipsoids are 50% probability level. Solvent molecules and hydrogens are omitted for clarity.

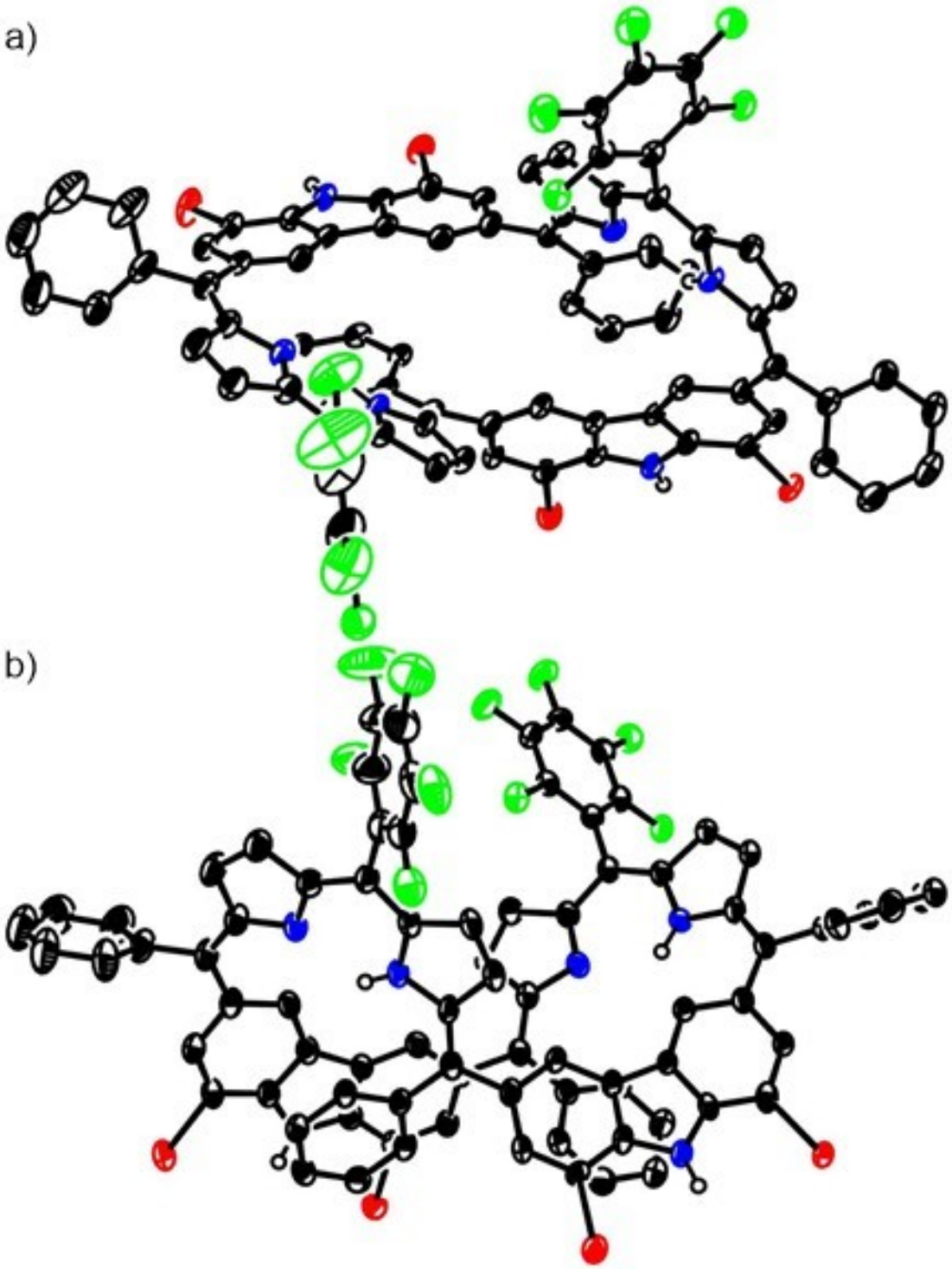


Figure S37. X-ray crystal structure of **7-4Br-2**. a) Top view, b) side view. The thermal ellipsoids are 50% probability level. Solvent molecules and hydrogens are omitted for clarity.

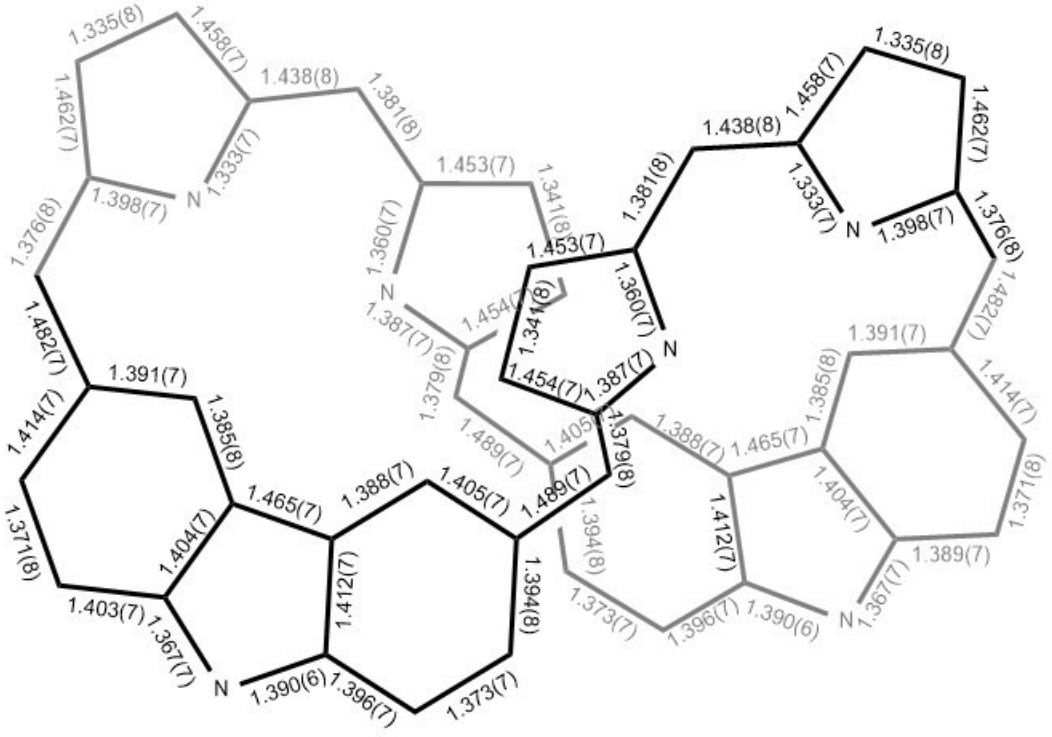


Figure S38. X-ray diffraction analysis of **7-4Br-1**.

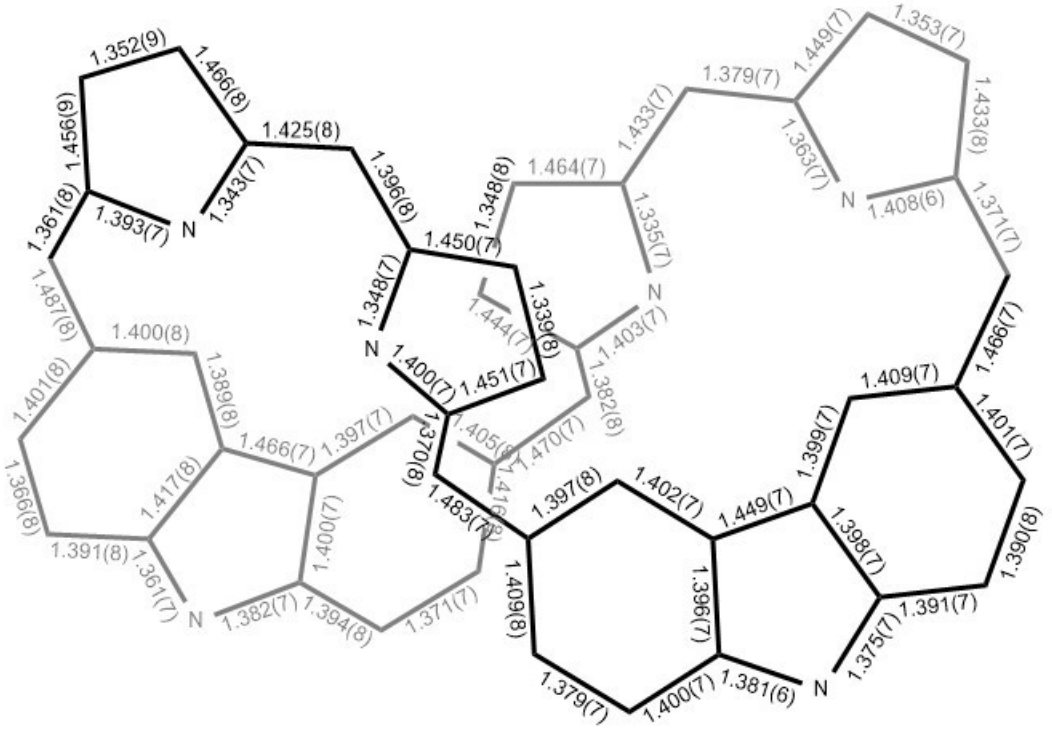


Figure S39. X-ray diffraction analysis of **7-4Br-2**.

Table S4. Crystal data and structure refinement for **10**

Empirical formula	$C_{146}H_{98}F_{10}N_{12}$	
Formula weight	2210.36	
Temperature	100.01(10) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 18.2574(4) Å	α = 69.686(2)°.
	b = 21.7852(6) Å	β = 89.019(2)°.
	c = 22.9344(5) Å	γ = 66.178(2)°.
Volume	7744.8(4) $Å^3$	
Z	2	
Density (calculated)	0.948 Mg/m^3	
Absorption coefficient	0.523 mm^{-1}	
F(000)	2296	
Crystal size	0.3 x 0.3 x 0.2 mm^3	
Theta range for data collection	2.076 to 66.600°.	
Index ranges	-14<=h<=21, -23<=k<=25, -27<=l<=27	
Reflections collected	54157	
Independent reflections	27347 [R(int) = 0.0403]	
Completeness to theta = 66.600°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.76081	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	27347 / 93 / 1525	
Goodness-of-fit on F^2	1.087	
Final R indices [I>2sigma(I)]	R1 = 0.0862, wR2 = 0.2197	
R indices (all data)	R1 = 0.1095, wR2 = 0.2352	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.495 and -0.325 $e.Å^{-3}$	
CCDC No.	2143913	

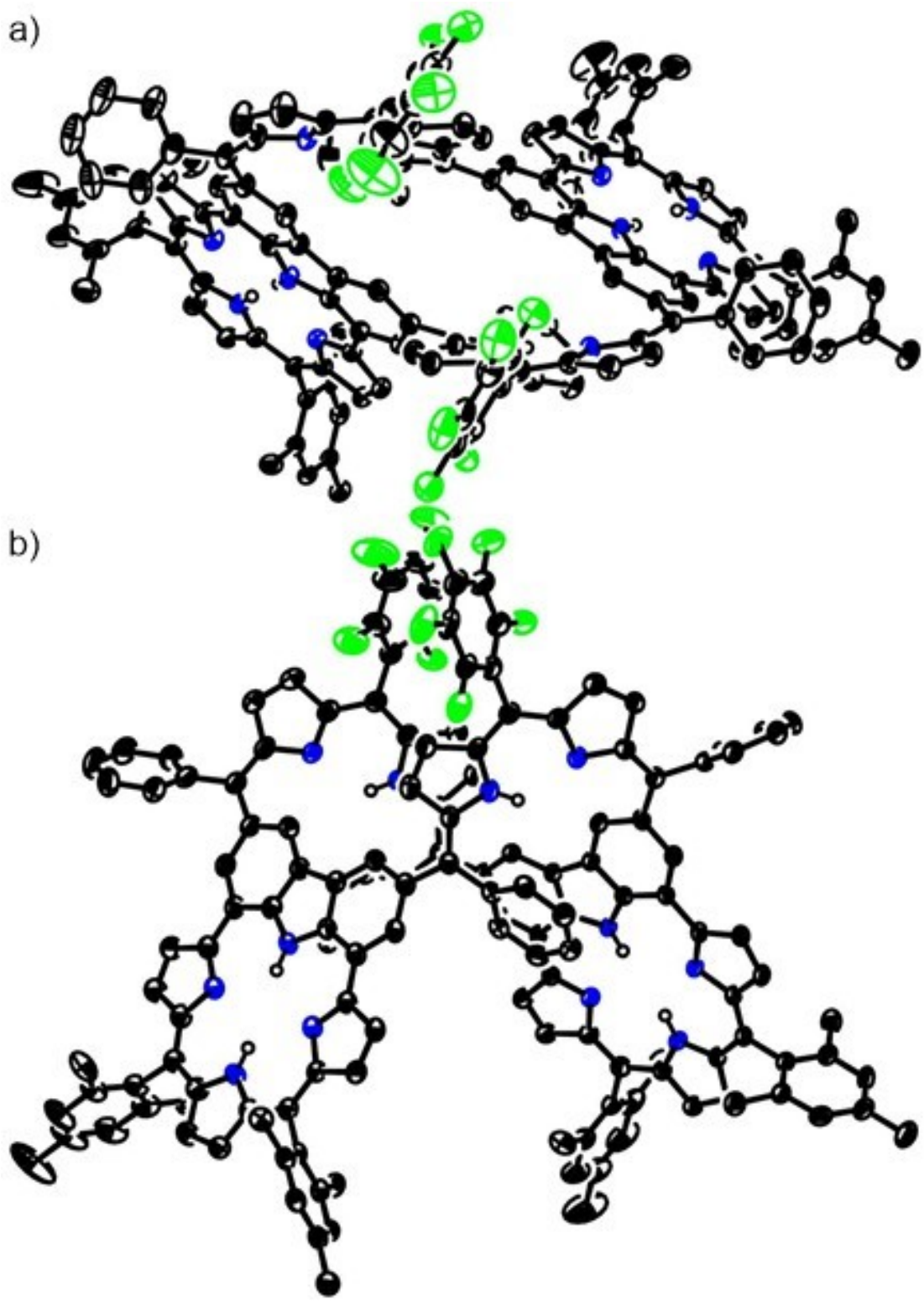


Figure S40. X-ray crystal structure of **10**. a) Top view, b) side view. The thermal ellipsoids are 50% probability level. Solvent molecules and hydrogens are omitted for clarity.

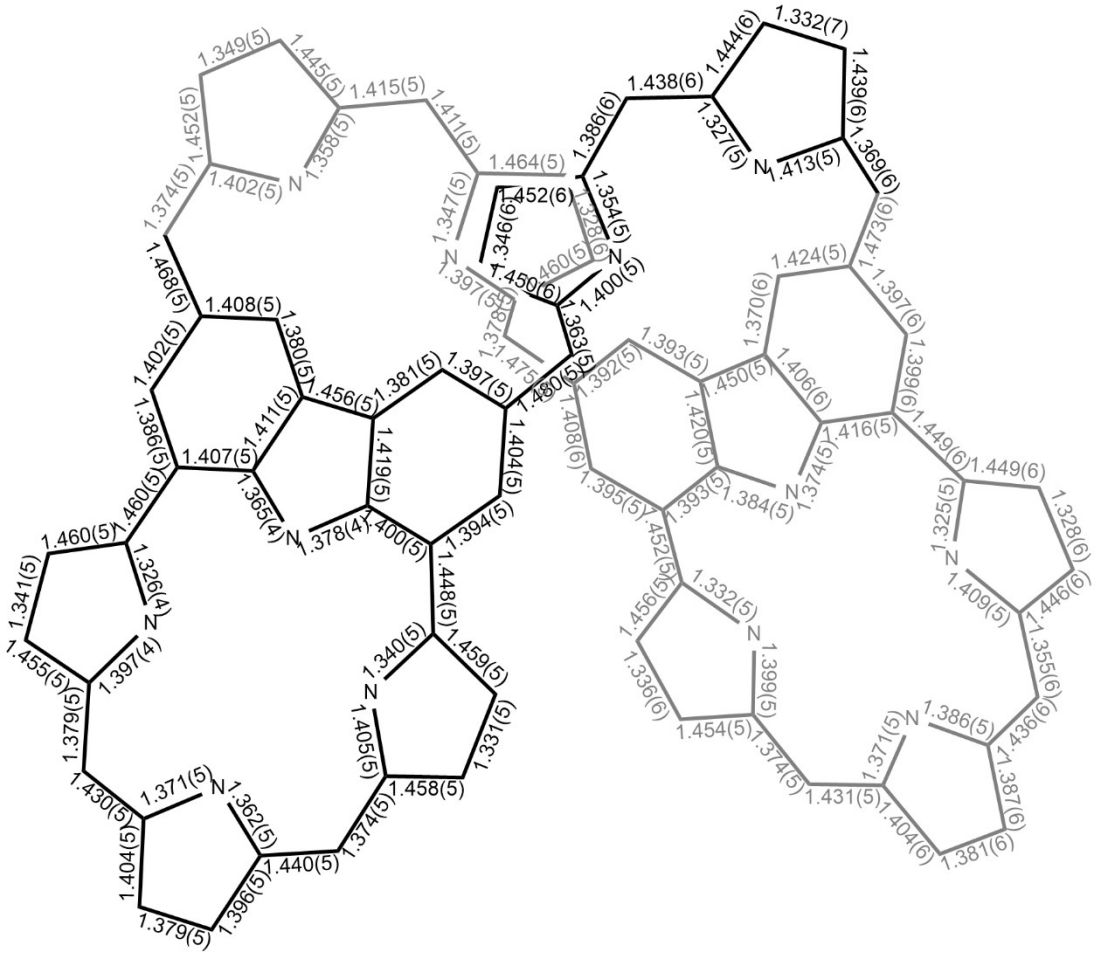


Figure S41. X-ray diffraction analysis of **10**.