Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Short-step synthesis and chiroptical properties of polyaza[5]–[9]helicenes with blue to green-colour emission

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Contents

1. General Information

1,4-Phenylenediamine was purchased from Tokyo Chemical Industry Co., Ltd. The other reagents were purchased from Wako Pure Chemical Industries, Ltd., Kanto Chemical CO., Inc., and Sigma-Aldrich Co. LLC. Preparative thin-layer chromatography (PTLC) was performed with silica gel-precoated glass plates (Merck 60 GF254) prepared in our laboratory. Silica-gel column chromatography was carried out using Silica Gel 60 N (Kanto Chemical Co., spherical, neutral, 0.040–0.050 mm). All reagents were weighed and handled in air and backfilled under argon at room temperature. All reactions were performed under an argon atmosphere.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with JEOL ECX-500 (500 MHz) spectrometer. Chemical shift values for protons are reported in parts per million (δ) relative to internal standard TMS (0.00 ppm). ^{13}C NMR spectra were obtained by JEOL ECX-500 (125.8 MHz) spectrometers and referenced to the internal solvent signals (central peak is 77.16 ppm in $CDCl_3$ and 39.52 ppm in $(CD_3)_2SO$). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublet, m = multiplet), coupling constant (Hz), and integration.

High-resolution mass spectra (HRMS) were performed on a JMS-SX102A, a JMS-HX110. All melting points were determined on a Yanaco melting point apparatus and are uncorrected.

Ultraviolet spectra were measured on a Shimadzu UV-2400 spectrometer. Fluorescence spectra were measured on a JASCO FP-8300 instrument. Absolute PL quantum yield was measured by Hamamatsu Photonics C9920-02 spectrometer, and quantum yields were determined with an integrating sphere (diameter 10 cm). X-ray structures were obtained by a Rigaku R-AXIS RAPID diffractometer. CD spectra were measured on a JASCO J-820 (420 W Xe) spectropolarimeter. CPL spectra were obtained using a JASCO CPL-200 at room temperature. Optical rotations were measured with a JASCO DIP-1000 polarimeter.

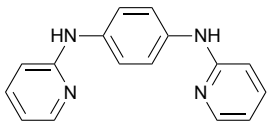
2. Synthesis

General Procedure (I): Preparation of Precursor of Helicene. Helicene precursors were synthesized as follows. A mixture of *p*-phenylenediamine and 2-chloropyridine was heated under reflux conditions. After being cooled to room temperature, the mixture was filtered and rinsed with diethyl ether. To the cake was added aqueous ammonia and the mixture was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The resulting residue was purified by a silica gel column chromatography or preparative TLC to give desire product.

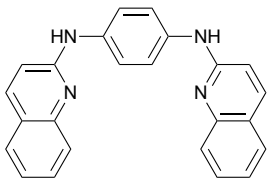
General Procedure (II): Preparation of Precursor of Symmetric Helicene. Helicene precursors were synthesized as follows. A mixture of amine compound, nitrogen-containing heteroaryl chlorides and 1-butanol was heated under reflux conditions. After being cooled to room temperature, the mixture was

filtered and rinsed with diethyl ether. To the cake was added aqueous ammonia and the mixture was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The resulting residue was purified by a silica gel column chromatography or preparative TLC to give desire product.

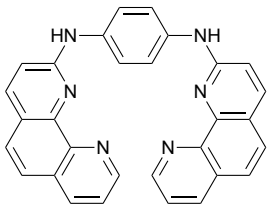
General Procedure (III): Synthesis of Azahelicene. Helicenes were synthesized as follows. To a stirred mixture of helicene precursor (0.1 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol), and HFIP (1.5 mL) was added *m*CPBA (73.8 mg, 0.3 mmol) in six portions every 0.5 h over 2.5 hours under room temperature. The mixture was stirred for another 0.5 h and then aqueous $NaHCO_3$ (20 mL) was added. The mixture was extracted with $CHCl_3$ (20 mL × 3) and the organic layer was condensed under reduced pressure. The residue was purified by preparative TLC (eluent: toluene/ethyl acetate = 1/2, additive: triethylamine 4%) to give desire product.



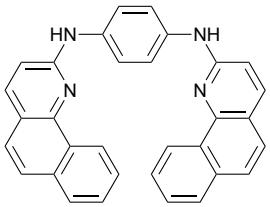
***N*1,*N*4-Di(pyridin-2-yl)benzene-1,4-diamine (6).** The title compound (94 mg, 36%) was synthesized from *p*-phenylenediamine (**4**) (108 mg, 1.0 mmol) and 2-chloropyridine (**5**) (341 mg, 3.0 mmol) according to the general procedure (**I**) (reflux time: 2 h). The resulting residue was purified by recrystallization with CH_3CN; purple solid; Mp: 203–204 ºC; ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.19 (dd, *J* = 5.2, 1.8 Hz, 2H), 7.48 (ddd, *J*=8.5, 7.2, 1.8 Hz, 2H), 7.31(s, 4H), 6.80 (d, *J* = 8.5 Hz, 2H), 6.72 (dd, *J*= 7.2, 5.2 Hz, 2H), 6.53 (brs, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$, δ): 156.6, 148.5, 137.8, 135.9, 122.4, 114.8, 107.9; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{16}H_{15}N_4$: 263.1291, found: 263.1290.



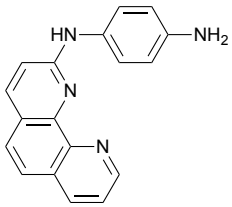
***N*1,*N*4-Di(quinolin-2-yl)benzene-1,4-diamine (8).** The title compound (187 mg, 52%) was synthesized from *p*-phenylenediamine (**4**) (108 g, 1.0 mmol) and 2-chloroquinoline (**7**) (489 mg, 3.0 mmol) according to the general procedure (**II**) (reflux time: 26 h). The resulting residue was purified by recrystallization with CH_3CN; transparent yellowish green solid; Mp 248–250 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.92 (d, *J* = 9.1 Hz, 2H), 7.77 (d, *J* = 8.6 Hz, 2H), 7.64 (d, *J* = 7.9 Hz, 2H), 7.56–7.61 (m, 6H), 7.29 (dd, *J* = 7.9, 6.8 Hz, 2H), 6.96 (d, *J* = 9.1 Hz, 2H), 7.92 (d, *J* = 9.1 Hz, 2H), 6.74 (brs, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$, δ): 154.7, 147.8, 137.9, 135.8, 129.9, 127.5, 126.7, 124.2, 123.1, 122.2, 111.5; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{19}N_4$: 363.1604, found: 363.1603.



***N*1,*N*4-Di(1,10-phenanthrolin-2-yl)benzene-1,4-diamine (11).** The title compound (163 mg, 70%) was synthesized from *p*-phenylenediamine (**4**) (54 mg, 0.5 mmol) and 2-chloro-1,10-phenanthroline (**9**) (322 mg, 1.5 mmol) according to the general procedure (**II**) (reflux time: 48 h); dark yellow solid; Mp: 300 °C over; ^{1}H NMR (500 MHz, $(CD_3)_2SO$, δ): 8.69 (s, 2H), 8.29 (d, *J* = 4.1 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.43 (s, 4H), 7.32 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 4.1 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.39 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (125.8 MHz, $(CD_3)_2SO$, δ): 155.3, 150.0, 145.6, 145.3, 137.6, 136.5, 136.1, 129.5, 127.1, 123.2, 123.1, 122.3, 119.6, 114.4; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{30}H_{21}N_6$: 465.1822, found: 465.1821.

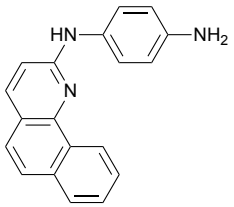


***N*1,*N*4-Bis(benzo[*h*]quinolin-2-yl)benzene-1,4-diamine (12).** The title compound (53 mg, 46%) was synthesized from *p*-phenylenediamine (**4**) (27 mg, 0.25 mmol) and 2-chlorobenzo[*h*]quinolone (**10**) (319 mg, 1.5 mmol) according to the general procedure (**II**) (reflux time: 48 h); indigo solid; Mp: 300 °C over; ^{1}H NMR (500 MHz, $(CD_3)_2SO$, δ): 8.63 (s, 2H), 8.22 (d, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H), 7.20 (s, 4H), 7.11 (d, *J* = 7.5 Hz, 2H), 6.79–8.88 (m, 8H), 6.30 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (125.8 MHz, $(CD_3)_2SO$, δ): 154.8, 145.2, 137.7, 135.8, 134.4, 130.6, 128.4, 128.1, 126.6, 126.1, 124.4, 123.2, 120.4, 119.8, 113.5; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{32}H_{23}N_4$: 463.1917, found: 463.1916.

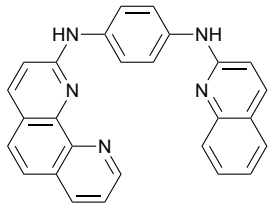


***N*1-(1,10-Phenanthrolin-2-yl)benzene-1,4-diamine (13).** The title compound (110 mg, 77%) was synthesized from *p*-phenylenediamine (**4**) (162 mg, 1.5 mmol) and 2-chloro-1,10-phenanthroline (**9**) (107 mg, 0.5 mmol) according to the general procedure (**II**) (reflux time: 48 h). The residue was purified by preparative TLC (eluent: toluene/ethyl acetate = 1/2, Rf = 0.10); yellowish green solid; Mp 110–114 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.10 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.17 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.93 (d, *J* = 8.9 Hz, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.53 (dd, *J* = 8.1, 4.3 Hz, 1H), 7.50 (d, *J* = 8.7 Hz, 1H), 7.12 (d, *J* = 8.6 Hz, 2H), 7.08 (d, *J* = 8.9 Hz, 1H), 6.71 (d, *J*= 8.6 Hz, 2H), 3.48 (brs, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$, δ): 157.3, 149.6, 144.4, 138.2, 136.0, 130.4, 129.4, 126.5, 126.2, 123.4, 122.9, 122.6, 121.8, 116.8, 116.1,

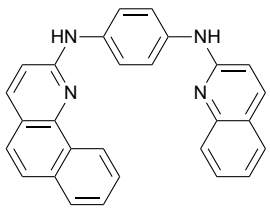
109.9; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{15}N_4$: 287.1291, found: 287.1291.



***N*1-(Benzo[*h*]quinolin-2-yl)benzene-1,4-diamine (14).** The title compound (175 mg, 61%) was synthesized from *p*-phenylenediamine (**4**) (216 mg, 2.0 mmol) and 2-chlorobenzo[*h*]quinolone (**10**) (213 mg, 1.0 mmol) according to the general procedure (**II**) (reflux time: 72 h). The residue was purified by preparative TLC (eluent: toluene/ethyl acetate = 1/1, Rf = 0.47); light black solid; Mp: 52–55 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.15 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.86 (dd, *J* = 8.4, 7.7 Hz, 1H), 7.60–7.69 (m, 2H), 7.57 (d, *J* = 8.6 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 1H), 6.74 (d, *J* = 8.5 Hz, 2H), 6.72 (brs, 1H), 3.58 (brs, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$, δ): 155.6, 145.9, 143.1, 137.8, 134.3, 131.5, 130.6, 127.8, 127.7, 126.1, 125.4, 124.5, 124.2, 123.3, 120.6, 116.0, 109.7; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{19}H_{16}N_3$: 286.1339, found: 286.1337.

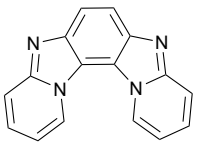


***N*1-(1,10-Phenanthrolin-2-yl)-*N*4-(quinolin-2-yl)benzene-1,4-diamine (15).** The title compound (81 mg, 89%) was synthesized from *N*1-(1,10-phenanthrolin-2-yl)benzene-1,4-diamine (**13**) (62 mg, 0.22 mmol) and 2-chloroquinoline (**7**) (107 mg, 0.66 mmol) according to the general procedure (**II**) (reflux time: 48 h). The residue was purified by preparative TLC (eluent: toluene/ethyl acetate = 1/2, Rf = 0.12); Yellow solid; Mp: 158–164 ºC; ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.10 (d, *J* = 3.8 Hz, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.9 Hz, 1H), 7.91 (d, *J* = 8.9 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.51–7.68 (m, 7H), 7.26–7.40 (m, 5H), 6.96 (d, *J* = 8.9 Hz, 1H), 6.94 (brs, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$, δ): 156.3, 154.5, 149.6, 147.7, 146.0, 145.1, 138.2, 137.9, 136.8, 136.1, 135.2, 129.9, 129.4, 127.5, 126.7, 126.5, 124.2, 123.6, 123.4, 123.2, 122.7, 122.2, 122.0, 111.9, 110.2; HRMS-ESI (*m/z*): $[M+H]^+$calcd for $C_{27}H_{20}N_5$: 414.1713, found:414.1713.

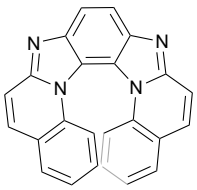


***N*1-(Benzo[*h*]quinolin-2-yl)-*N*4-(quinolin-2-yl)benzene-1,4-diamine (16).** The title compound (192 mg, 77%) was synthesized from *N*1-(benzo[*h*]quinolin-2-yl)benzene-1,4-diamine (**14**) (172 mg, 0.6 mmol) and 2-chloroquinoline (**7**) (293 mg, 1.8 mmol) according to the general procedure (**II**) (reflux time: 48 h). After

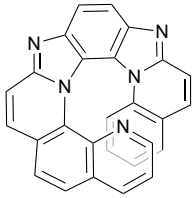
extraction, the resulting residue was not purified; yellow solid; Mp: 213–216 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.14 (d, *J* = 8.1 Hz, 1H), 7.97 (d, *J* = 8.6 Hz, 1H), 7.92 (d, *J* = 8.9 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.56–7.71 (m, 11H), 7.29 (dd, *J* = 7.3, 8.0 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 1H), 6.98 (d, *J* = 8.9 Hz, 1H), 6.85 (brs, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$, δ): 154.9, 154.2, 147.7, 145.8, 138.0, 137.8, 136.3, 135.2, 134.3, 130.7, 130.0, 127.8, 127.6, 126.6, 126.3, 125.3, 124.6, 124.1, 123.8, 123.1, 122.4, 121.5, 121.0, 111.5, 110.7; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{28}H_{21}N_4$: 413.1761, found:413.1760.



Pyrido[2''',1''':2'',3'']imidazo[4'',5'':3',4']benzo[1',2':4,5]imidazo[1,2-*a*]pyridine ([5]H). The title compound (15.2 mg, 59%) was synthesized from *N*^{1},*N*^{4}-di(pyridin-2-yl)benzene-1,4-diamine (**6**) (26.2 mg, 0.1 mmol) according to the general procedure **(III)**. The residue was purified by preparative TLC (eluent: toluene/ethyl acetate = 1/2, additive: triethylamine 4%, Rf = 0.13); deep green solid; Mp: 263–267 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.92 (d, *J* = 7.0 Hz, 2H), 8.03 (s, 2H), 7.77(d, *J* = 9.1 Hz, 2H), 7.38 (dd, *J* = 9.1, 6.9 Hz, 2H), 6.70 (dd, *J*=7.0, 6.9 Hz, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$, δ): 146.9, 141.5, 127.2, 126.7, 119.0, 118.9, 116.0, 111.4; HRMS-ESI (*m/z*):$[M+H]^+$ calcd for $C_{16}H_{11}N_4$: 259.0978, found: 259.0977.

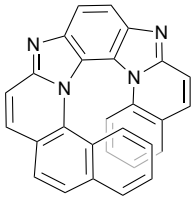


Quinolino[2''',1''':2'',3'']imidazo[4'',5'':3',4']benzo[1',2':4,5]imidazo[1,2-*a*]quinoline ([7]H). The title racemic compound (13.6 mg, 38%) was synthesized from *N*^{1},*N*^{4}-di(quinolin-2-yl)benzene- 1,4-diamine (**8**) (36.2 mg, 0.1 mmol) according to the general procedure **(III)**. The residue was purified by preparative TLC (eluent: toluene/ethyl acetate = 1/2, additive: triethylamine 4%, Rf = 0.22); light brown solid; Mp: 288–291 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.16 (s, 2H), 7.76–7.71(m, 6H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.20 (dd, *J* = 7.7, 7.6 Hz, 2H), 6.73 (dd, *J* = 8.3, 7.7 Hz, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$, δ): 147.5, 142.9, 136.2, 130.3, 128.1, 126.7, 124.6, 123.4, 119.3, 118.4, 117.8, 117.4; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{15}N_4$: 359.1291, found: 359.1289.

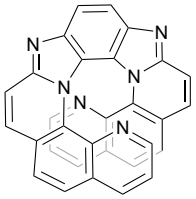


Quinolino[2''',1''':2'',3'']imidazo[4'',5'':3',4']benzo[1',2':4,5]imidazo[1,2-*a*]phenanthoroline ([8]Ha). To a stirred mixture of *N*^{1}-(1,10-phenanthrolin-2-yl)-*N*^{4}-(quinolin-2-yl)benzene-1,4-diamine (**15**) (41.4 mg, 0.1 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol), and HFIP (1.5 mL) was added *m*CPBA (73.8 mg, 0.3 mmol)

in six portions every 0.5 h over 2.5 hours under room temperature. The mixture was stirred for another 0.5 h and then aqueous $NaHCO_3$ (20 mL) was added. The mixture was extracted with $CHCl_3$ (20 mL × 3) and the organic layer was condensed under reduced pressure. The residue was purified by preparative TLC (eluent: toluene/ethyl acetate = 1/2, additive: triethylamine 4%, Rf = 0.16) to give the desire product (4.7 mg, 12%) as a yellow solid; Mp: 235–240 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.27 (d, *J* = 8.7 Hz, 2H), 8.07 (d, *J* = 9.1 Hz, 1H), 7.94 (dd, *J* = 9.1, 2.5 Hz, 2H), 7.72–7.77 (m, 2H), 7.68 (dd, *J* = 9.2, 5.6 Hz, 2H), 7.48 (d, *J* = 9.2 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 6.83–6.89 (m, 3H), 6.32 (ddd, *J* = 8.5, 7.3, 1.6 Hz, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$, δ): 147.4, 146.9, 146.3, 143.3, 141.6, 141.5, 135.1, 134.5, 134.4, 129.1, 128.6, 127.1, 126.6, 125.8, 125.2, 124.4, 123.6, 123.3, 122.8, 121.9, 121.7, 120.9, 119.2, 118.9, 118.1, 117.7; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{27}H_{16}N_4$: 410.1400, found: 410.1400.

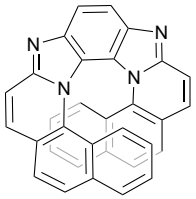


Quinolino[2’’’,1’’’:2’’,3’’]imidazo[4'',5'':3',4']benzo[1',2':4,5]imidazo[1,2-*a*]benzo[h]quinoline ([8]Hb). N^1-(Benzo[*h*]quinolin-2-yl)-N^4-(quinolin-2-yl)benzene-1,4-diamine (**16**) (40.8 mg, 0.1 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol), and HFIP (1.5 mL) was added *m*CPBA (73.8 mg, 0.3 mmol) in six portions every 0.5 h over 2.5 hours under room temperature. The mixture was stirred for another 0.5 h and then aqueous $NaHCO_3$ (20 mL) was added. The mixture was extracted with $CHCl_3$ (20 mL × 3) and the organic layer was condensed under reduced pressure. The residue was purified by preparative TLC (eluent: toluene/ethyl acetate = 1/2, additive: triethylamine 4%, Rf = 0.25) to give desire product (31.5 mg, 77%) as a yellow solid; Mp: 280–283 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.29 (s, 2H), 7.96 (d, *J* = 9.1 Hz, 1H), 7.90 (d, *J* = 9.1 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 9.4 Hz, 1H), 7.42 (d, *J* = 9.4 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 6.96 (dd, *J* = 8.1, 7.2 Hz, 1H), 6.88 (dd, *J* = 8.2, 7.2 Hz, 1H), 6.50 (dd, *J* = 8.3, 7.5 Hz, 1H), 6.42 (d, *J* = 8.2 Hz, 1H), 6.26 (dd, *J* = 8.3, 7.4 Hz, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$, δ): 147.8, 146.9, 142.8, 141.6, 134.7, 133.7, 132.1, 129.8, 129.6, 127.1, 126.8, 126.7, 126.0, 126.0, 125.0, 124.3, 123.9, 123.6, 122.8, 121.6, 120.7, 120.5, 118.7, 118.2, 118.0, 117.7, 117.4, 117.2; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{28}H_{17}N_4$: 409.1448, found: 409.1447.



Phenanthoro[2’’’,1’’’:2’’,3’’]imidazo[4'',5'':3',4']benzo[1',2':4,5]imidazo[1,2-*a*]phenanthroline ([9]Ha). The title compound (6 mg, 12%) was synthesized from N^1,N^4-di(1,10-phenanthrolin-2-yl)benzene-1,4-diamine (**11**) (46.4 mg, 0.1 mmol) according to the general procedure **(III)**. The residue was purified by preparative TLC (eluent: toluene/ethyl acetate = 1/2, additive: triethylamine 4%, Rf = 0.13);

yellow solid; Mp: 283–289 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.38 (s, 2H), 8.00 (d, *J* = 9.1 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 9.1 Hz, 2H), 7.50 (d, *J* = 1.7 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.82 (dd, *J* = 8.1, 1.7 Hz, 2H); ^{13}C NMR (125.8 MHz, $(CD_3)_2SO$ and $CDCl_3$, δ): 146.9, 146.2, 141.3, 140.1, 134.4, 132.9, 128.3, 125.7, 125.4, 123.5, 123.2, 122.0, 118.6, 117.8; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{30}H_{17}N_6$: 461.1509, found: 461.1511.



Benzoquinolino[2’’’,1’’’:2’’,3’’]imidazo[4'',5'':3',4']benzo[1',2':4,5]imidazo[1,2-*a*]benzoquinoline ([9]Hb). The title compound (15.3 mg, 33%) was synthesized from N^1,N^4-bis(benzo[*h*]-quinolin-2-yl)benzene-1,4-diamine (**12**) (46.2 mg, 0.1 mmol) according to the general procedure **(III)**. The residue was purified by preparative TLC (eluent: toluene/ethyl acetate = 1/2, additive: triethylamine 4%, Rf = 0.16); yellow solid; Mp: 293–295 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.42 (s, 2H), 7.82 (d, *J* = 9.1 Hz, 2H), 7.55 (d, *J* = 9.1 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H), 6.98 (dd, *J* = 7.8, 6.9 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.36 (dd, *J* = 8.5, 6.9 Hz, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$, δ): 132.6, 131.1, 129.6, 127.2, 126.5, 125.3, 124.7, 123.9, 123.1, 121.2, 119.9, 118.2, 117.0; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{32}H_{19}N_4$: 459.1604, found: 459.1603.

3. NMR Spectra

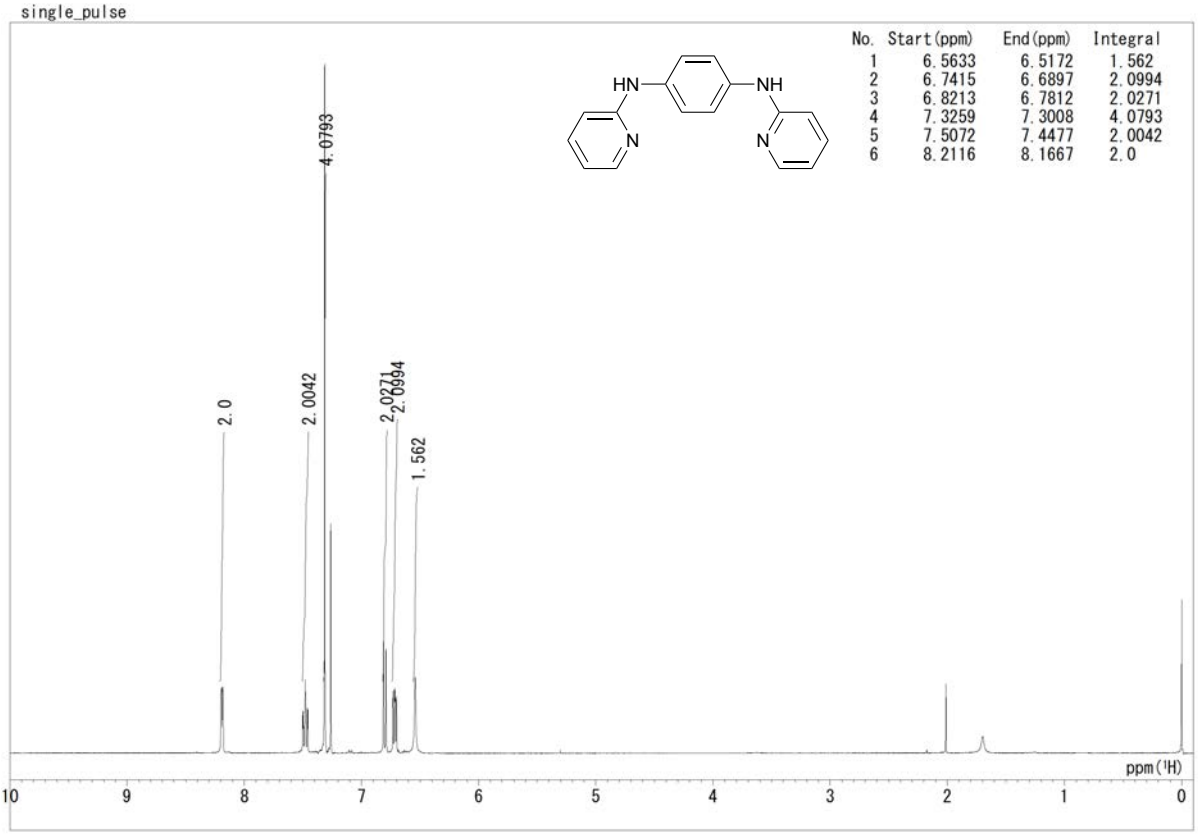


Fig. S1 ^{1}H NMR spectrum of **6** in $CDCl_3$.

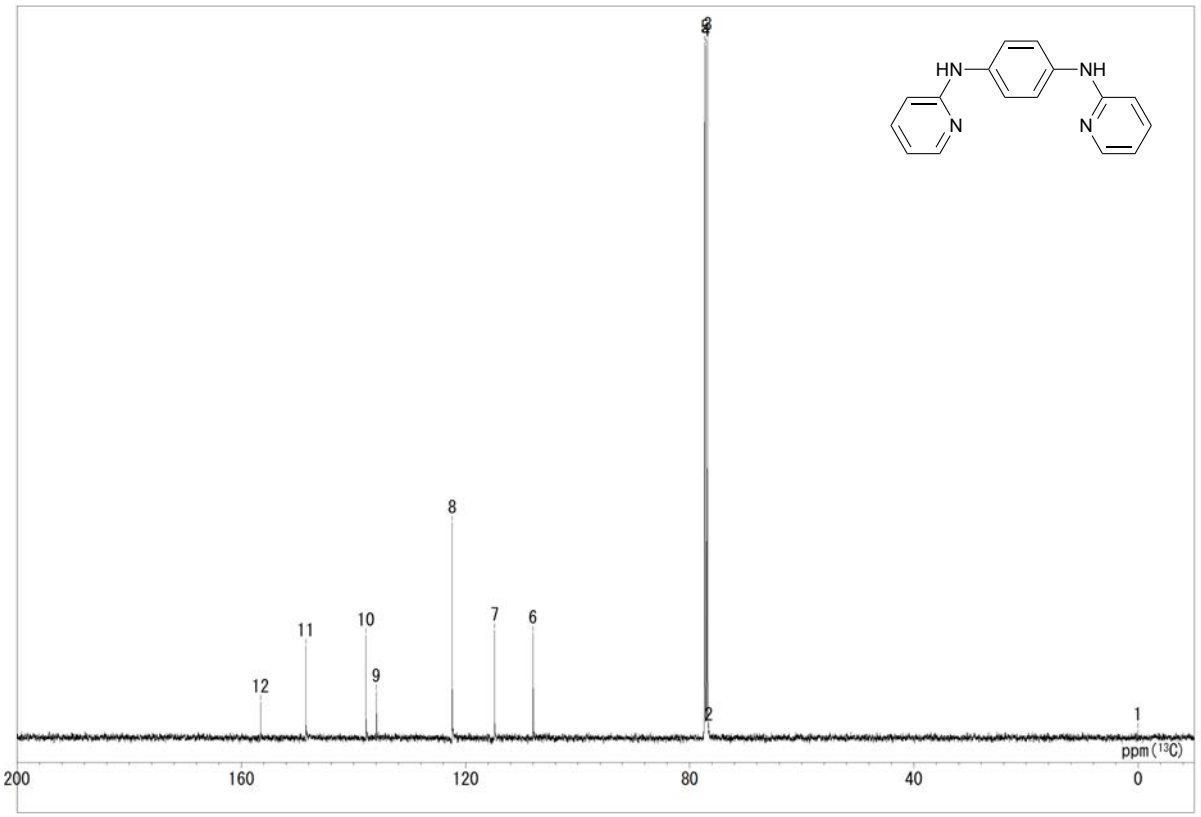


Fig. S2 ^{13}C NMR spectrum of **6** in $CDCl_3$.

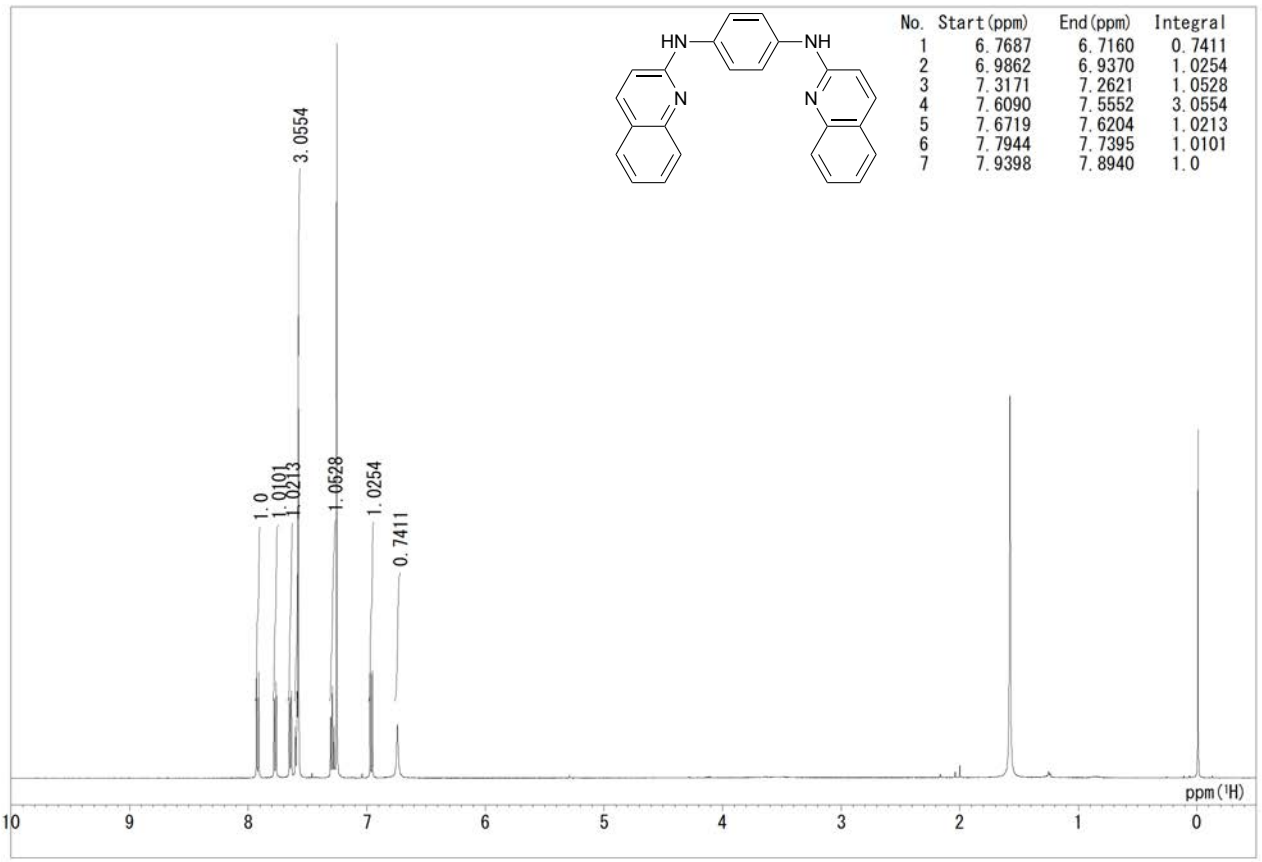


Fig. S3 ^{1}H NMR spectrum of **8** in $CDCl_3$.

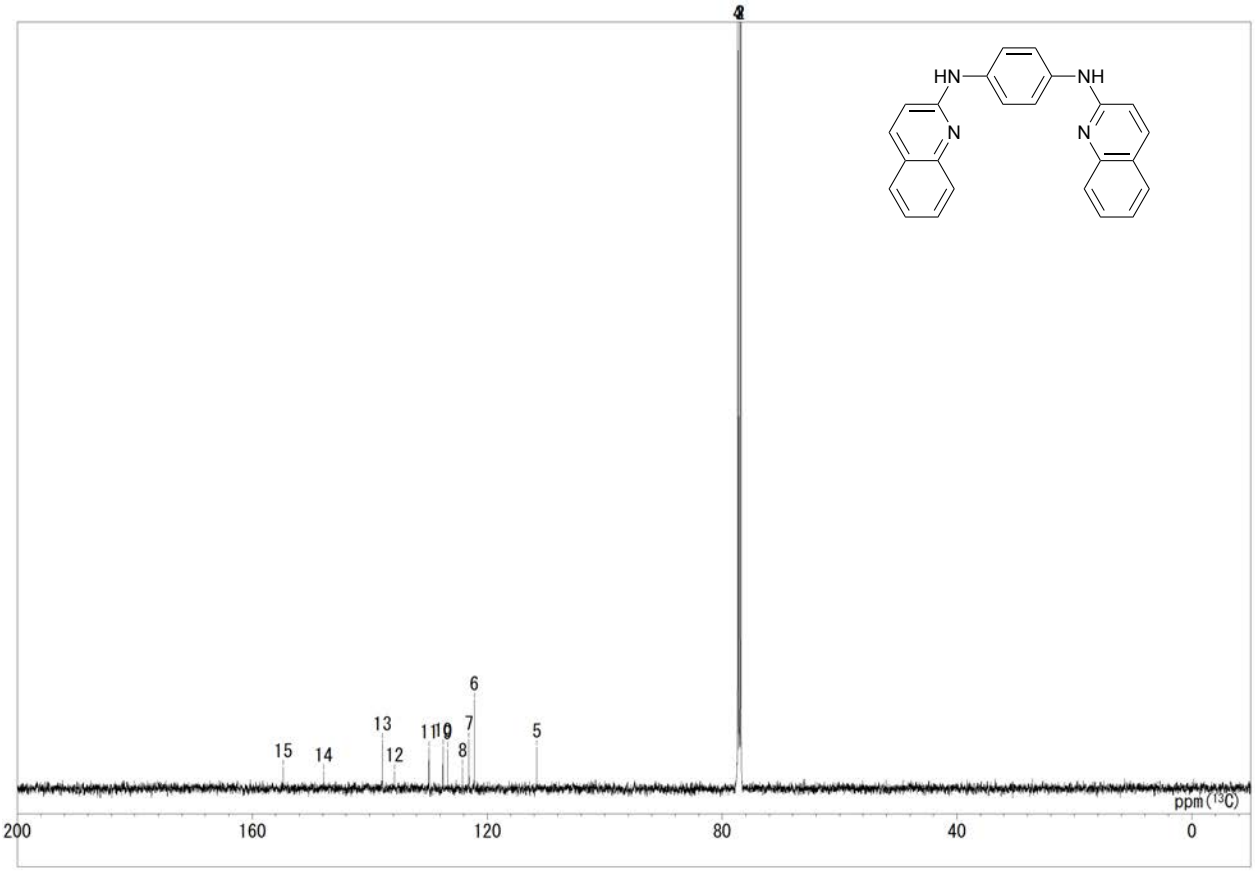


Fig. S4. ^{13}C NMR spectrum of **8** in $CDCl_3$.

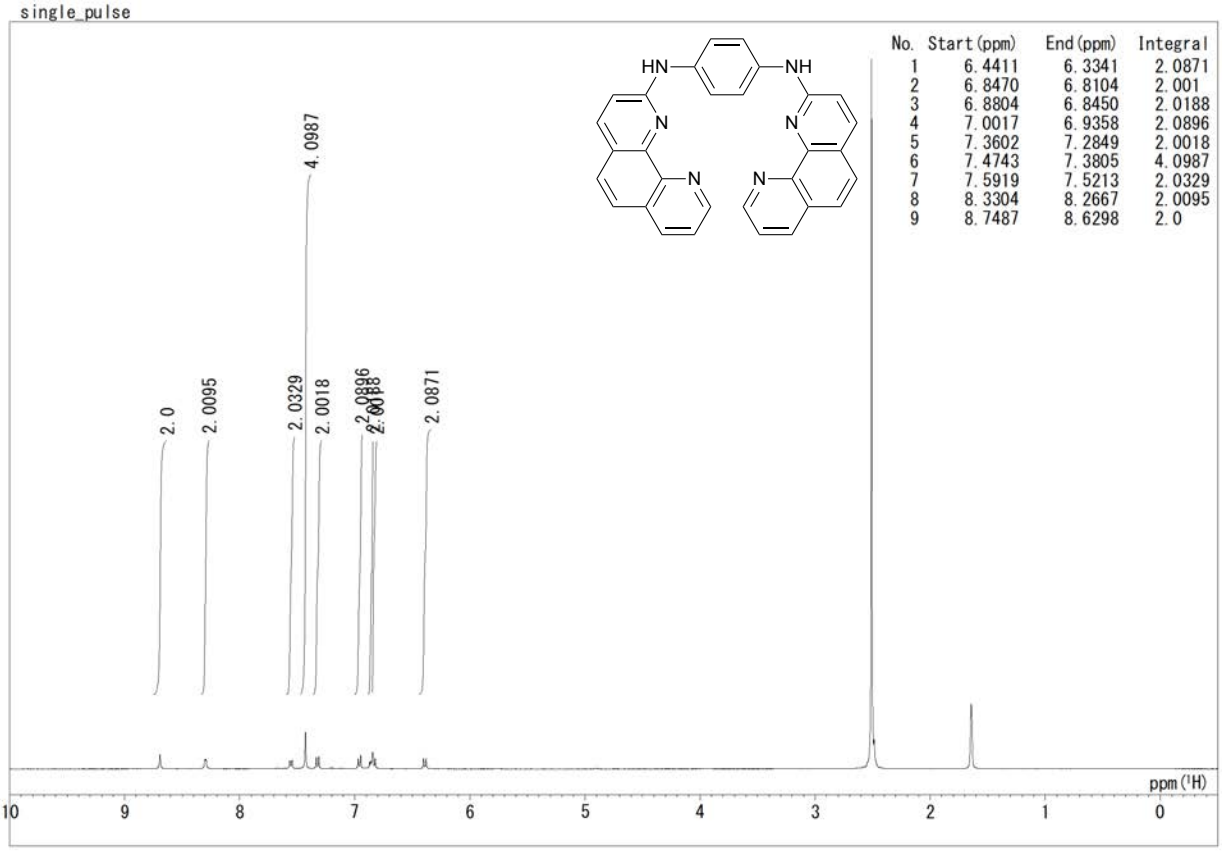


Fig. S5 ^{1}H NMR spectrum of **15** in CDCl3.

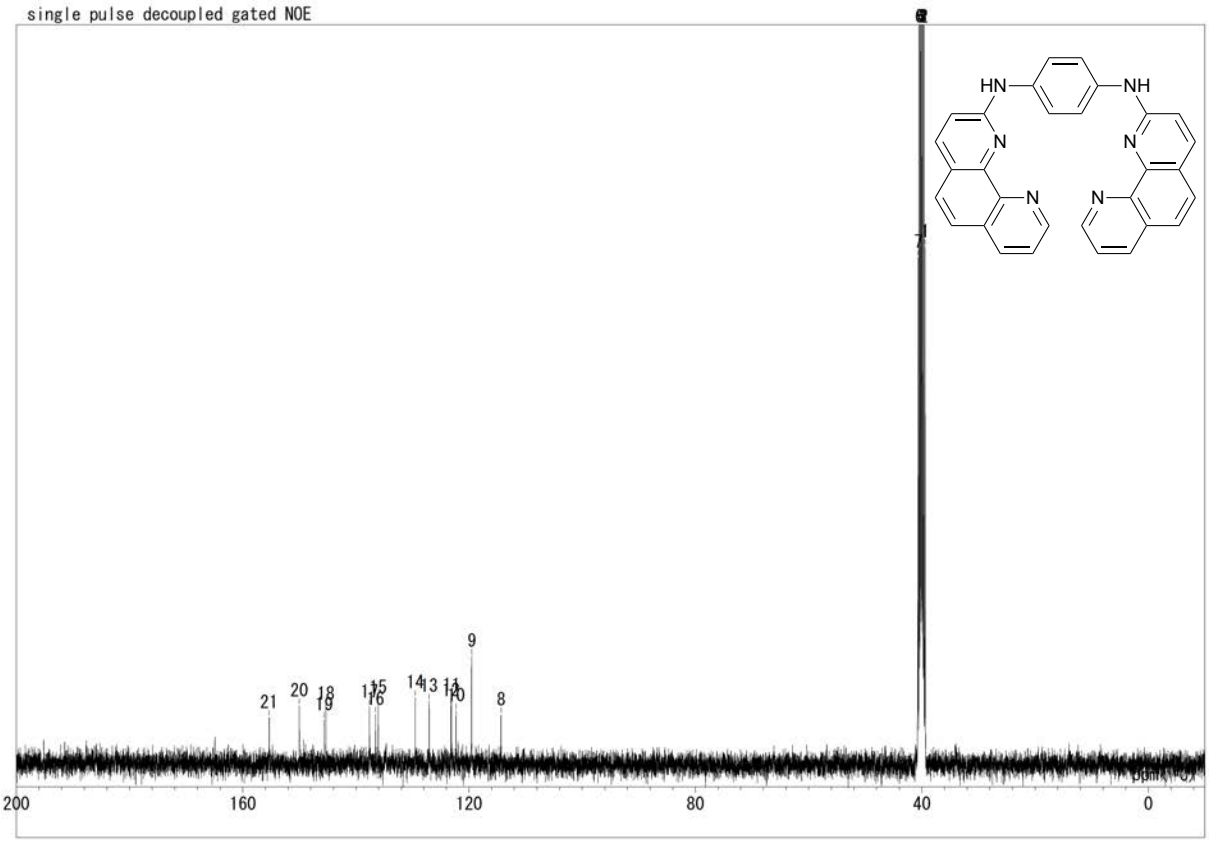


Fig. S6 ^{13}C NMR spectrum of **15** in $CDCl_3$.

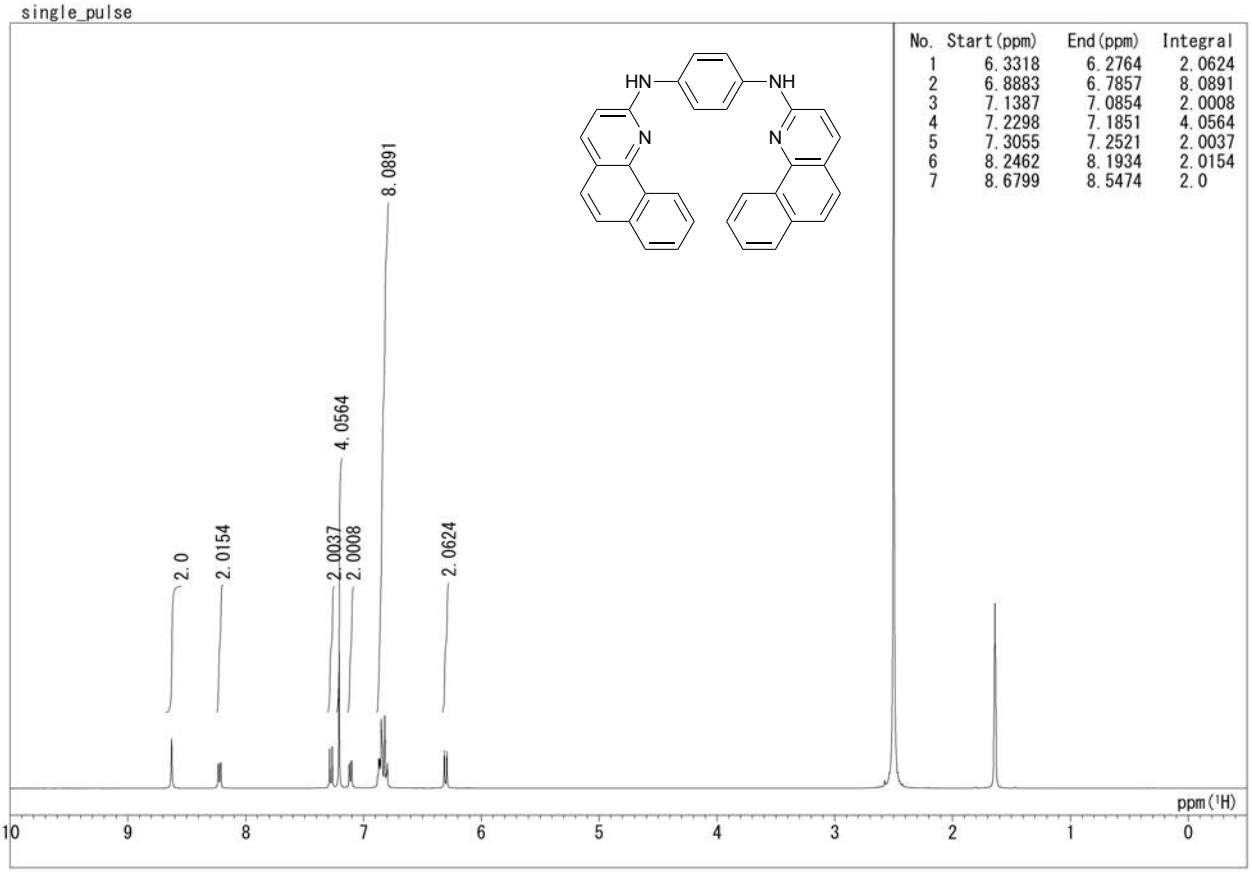


Fig. S7 ^{1}H NMR spectrum of **16** in $(CD_3)_2SO$.

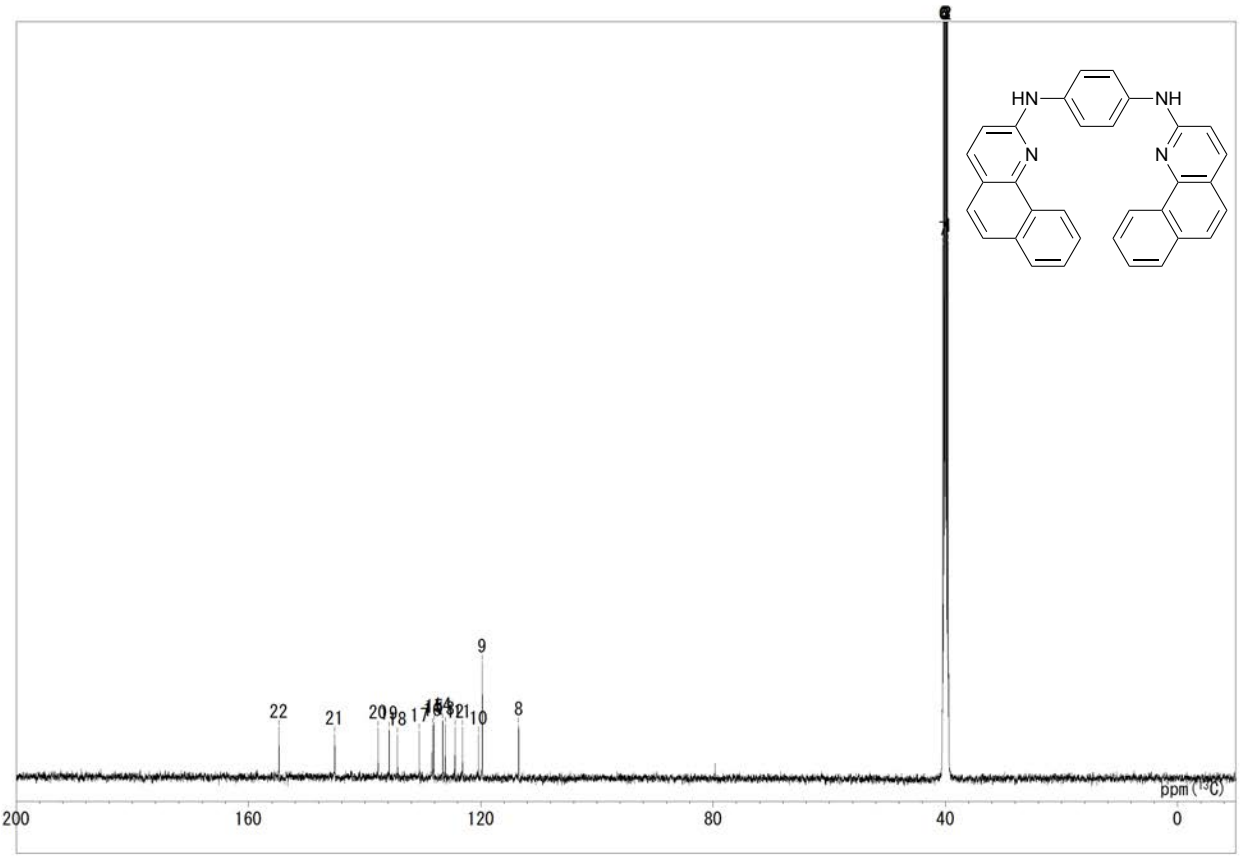


Fig. S8 ^{13}C NMR spectrum of **16** in $(CD_3)_2SO$.

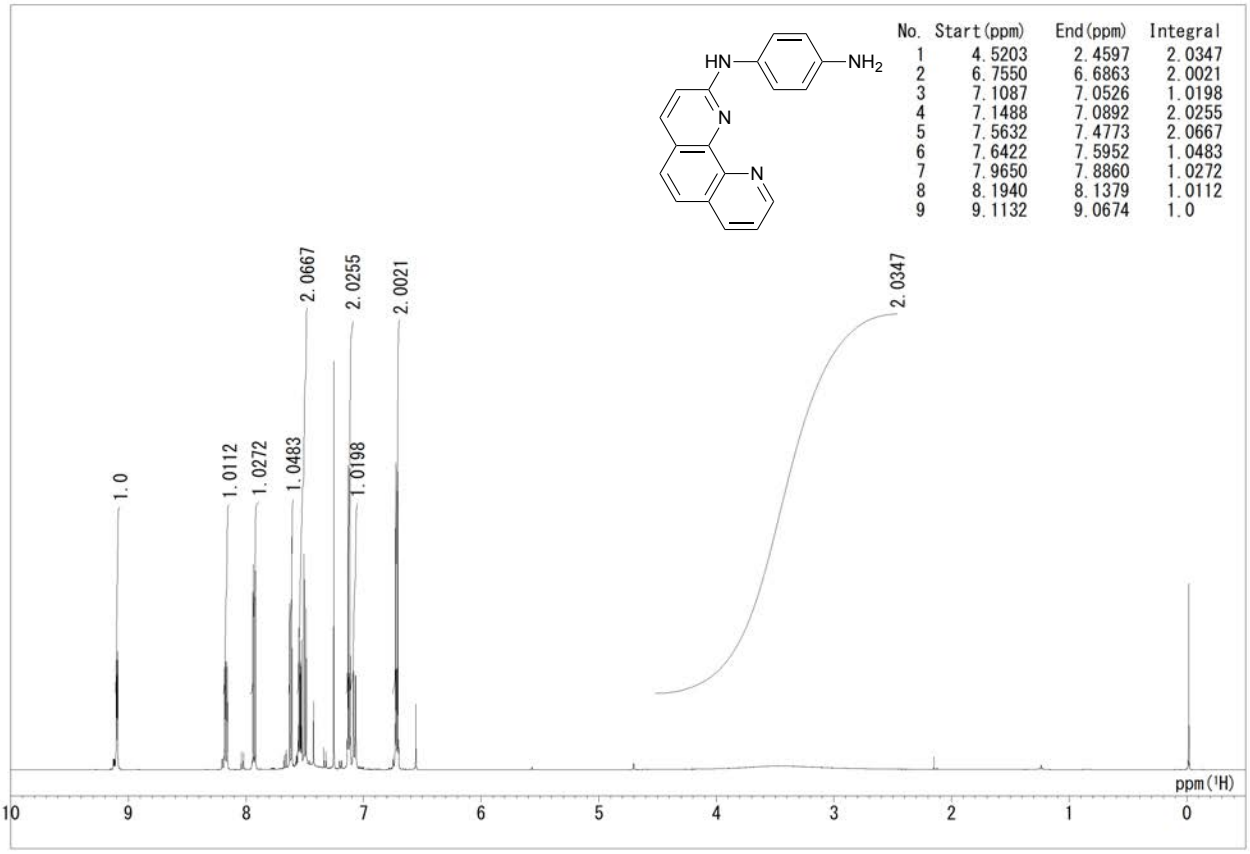


Fig. S9 ^{1}H NMR spectrum of **13** in $CDCl_3$.

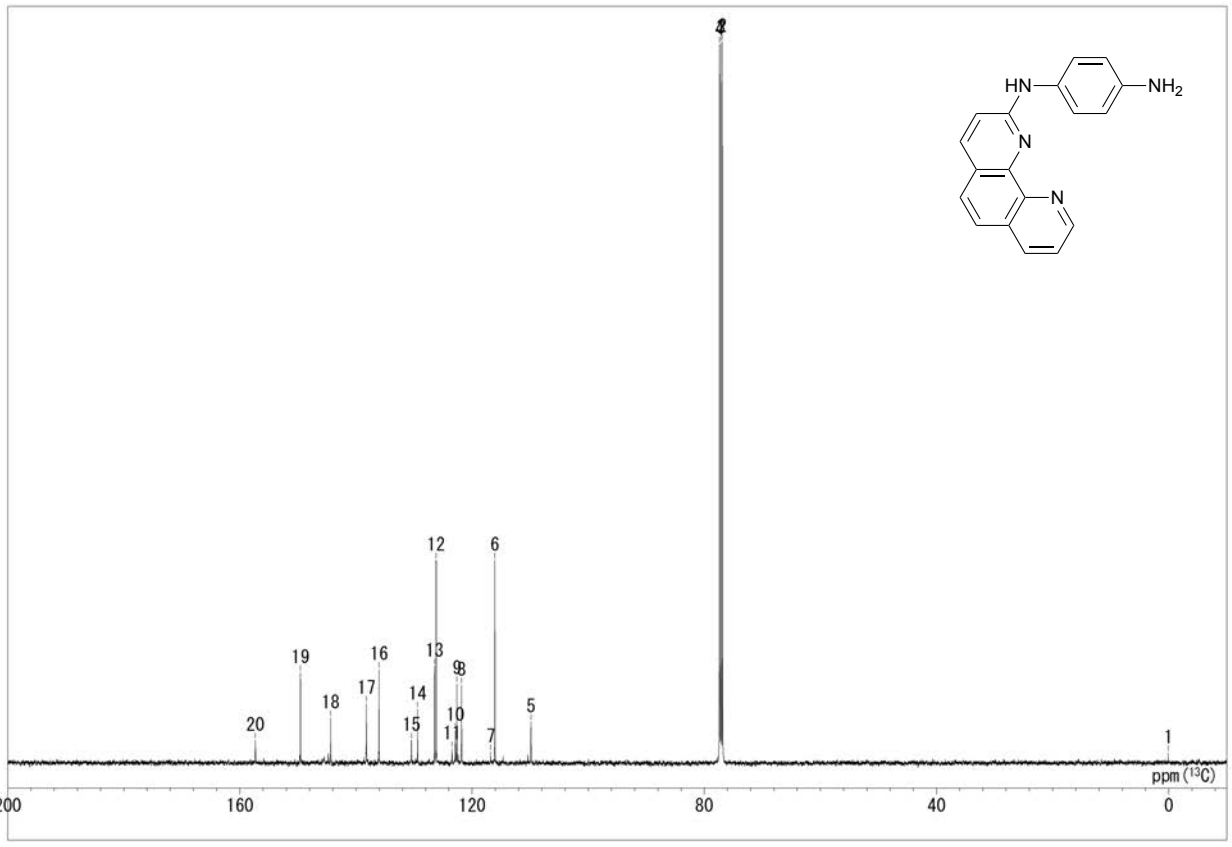


Fig. S10 ^{13}C NMR spectrum of **13** in $CDCl_3$.

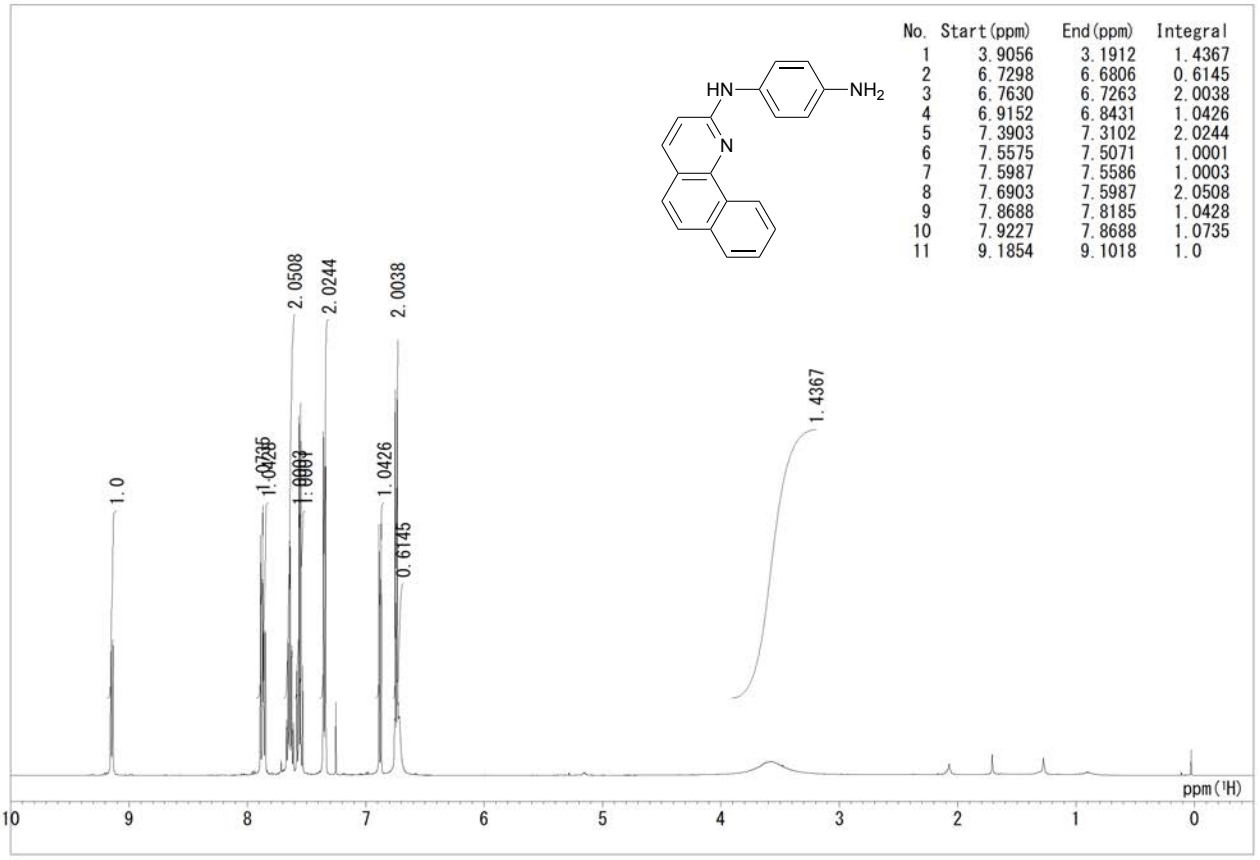


Fig. S11 ^{1}H NMR spectrum of **14** in $CDCl_3$.

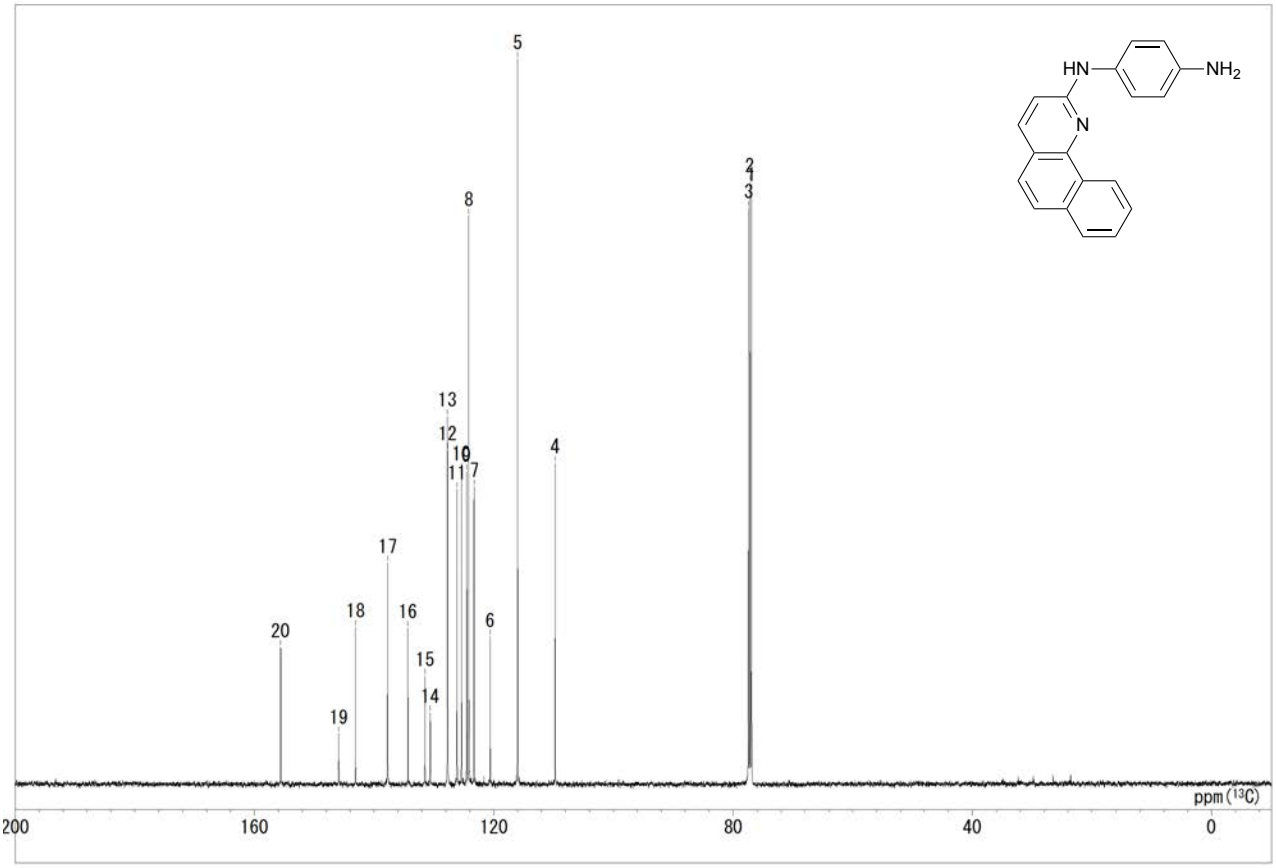


Fig. S12 ^{13}C NMR spectrum of **14** in $CDCl_3$.

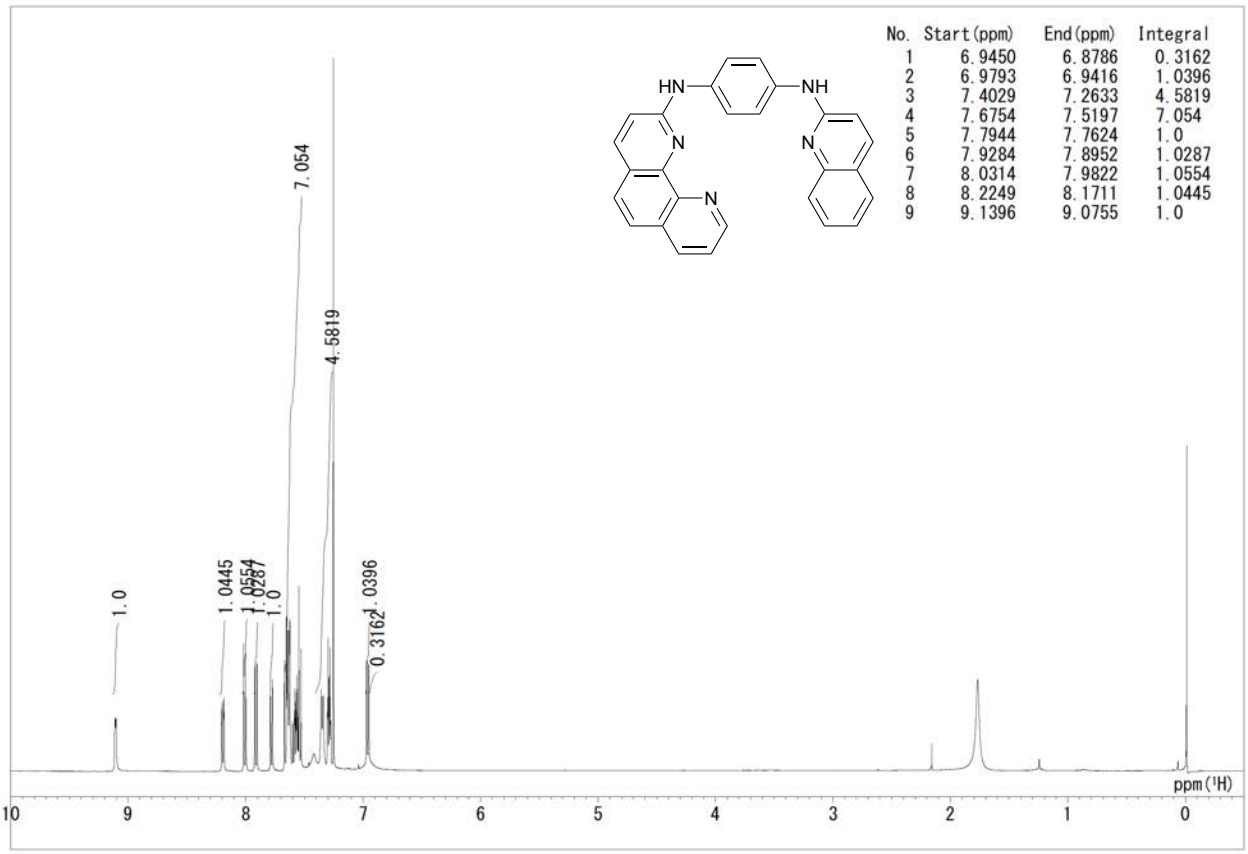


Fig. S13 ^{1}H NMR spectrum of **15** in $CDCl_3$.

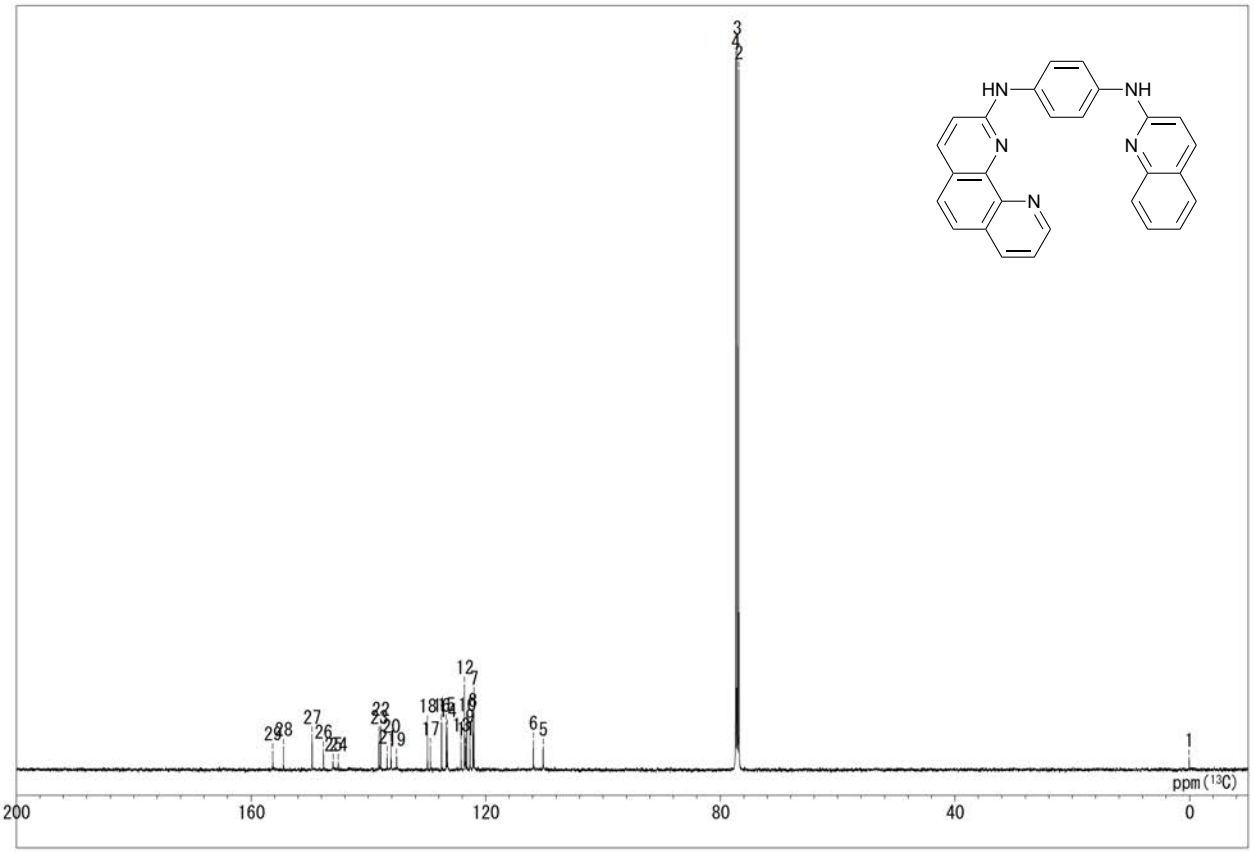


Fig. S14 ^{13}C NMR spectrum of **15** in $CDCl_3$.

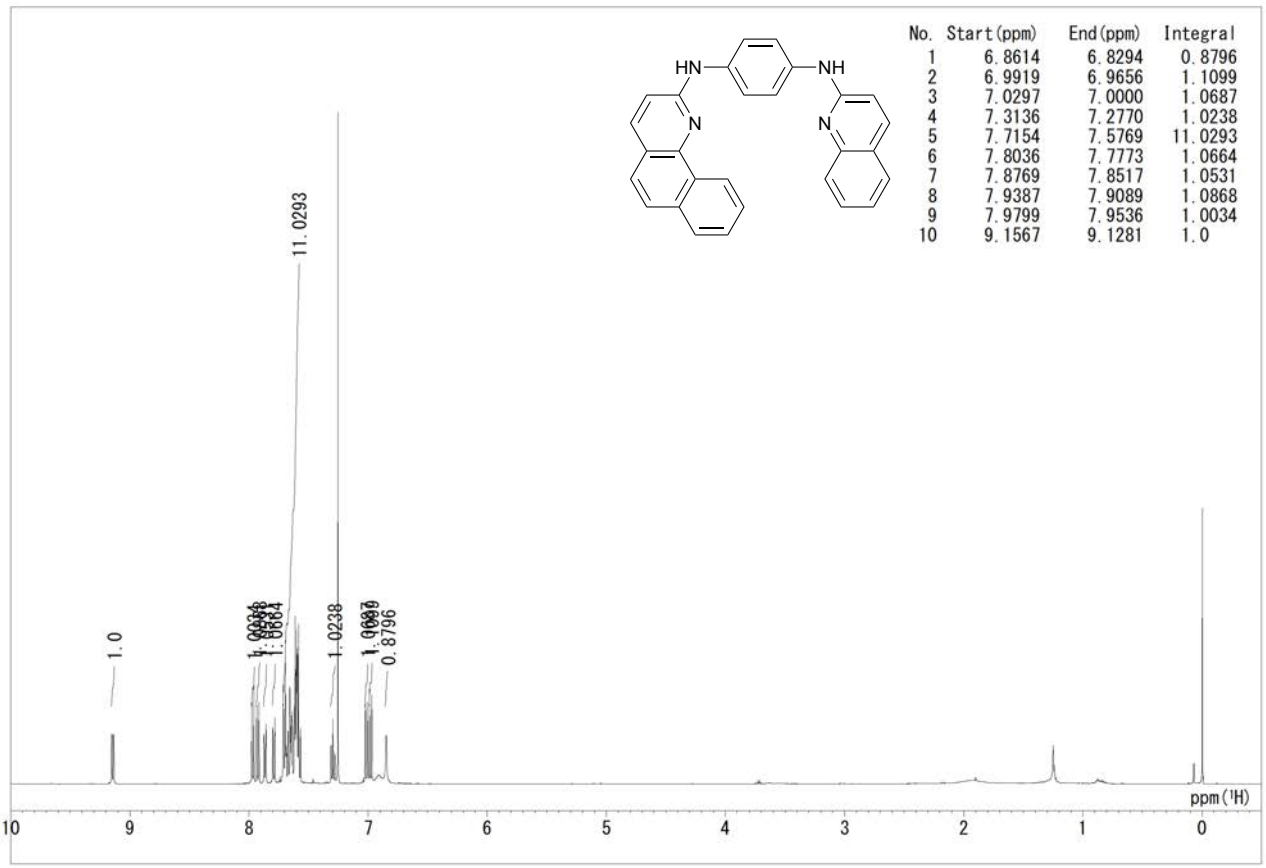


Fig. S15 ^{1}H NMR spectrum of **16** in $CDCl_3$.

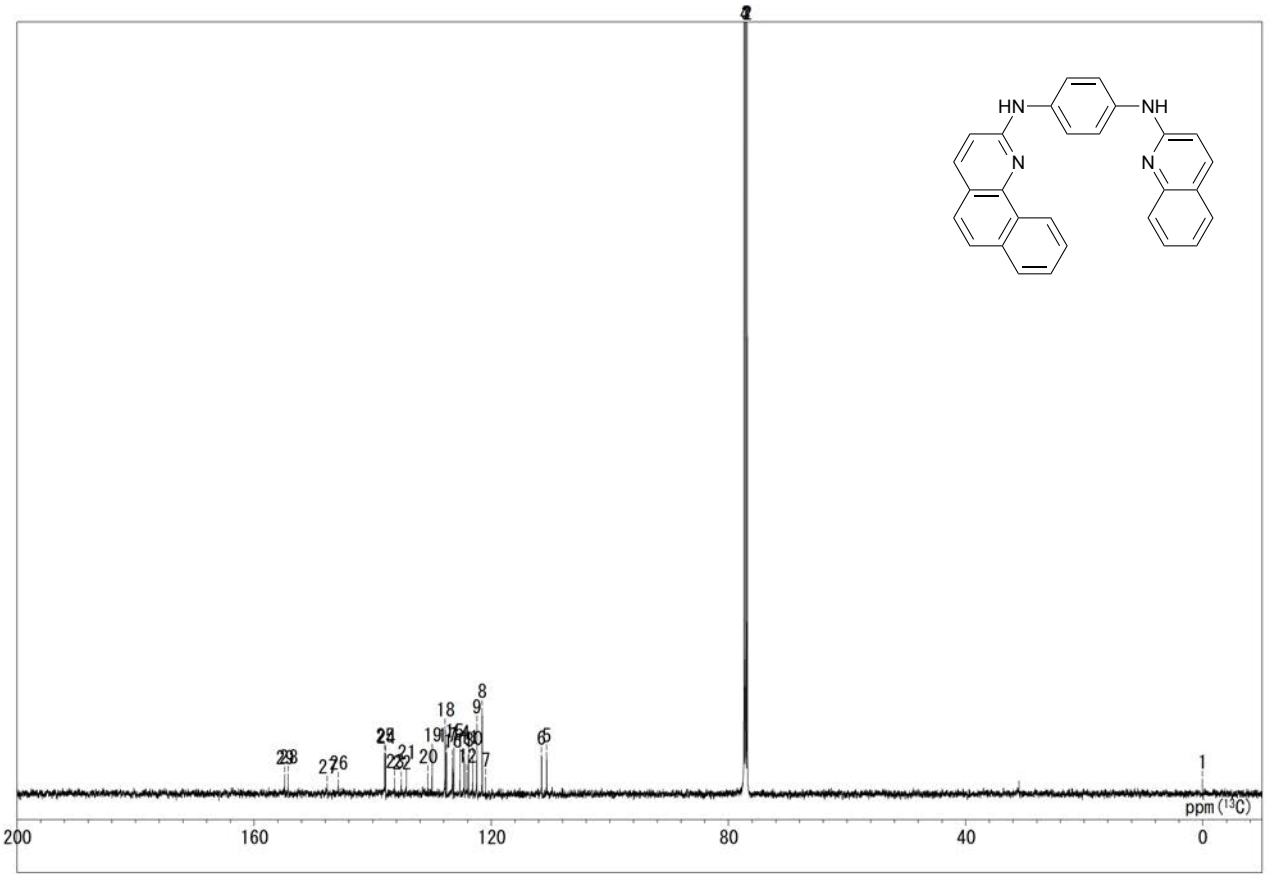


Fig. S16 ^{13}C NMR spectrum of **16** in $CDCl_3$.

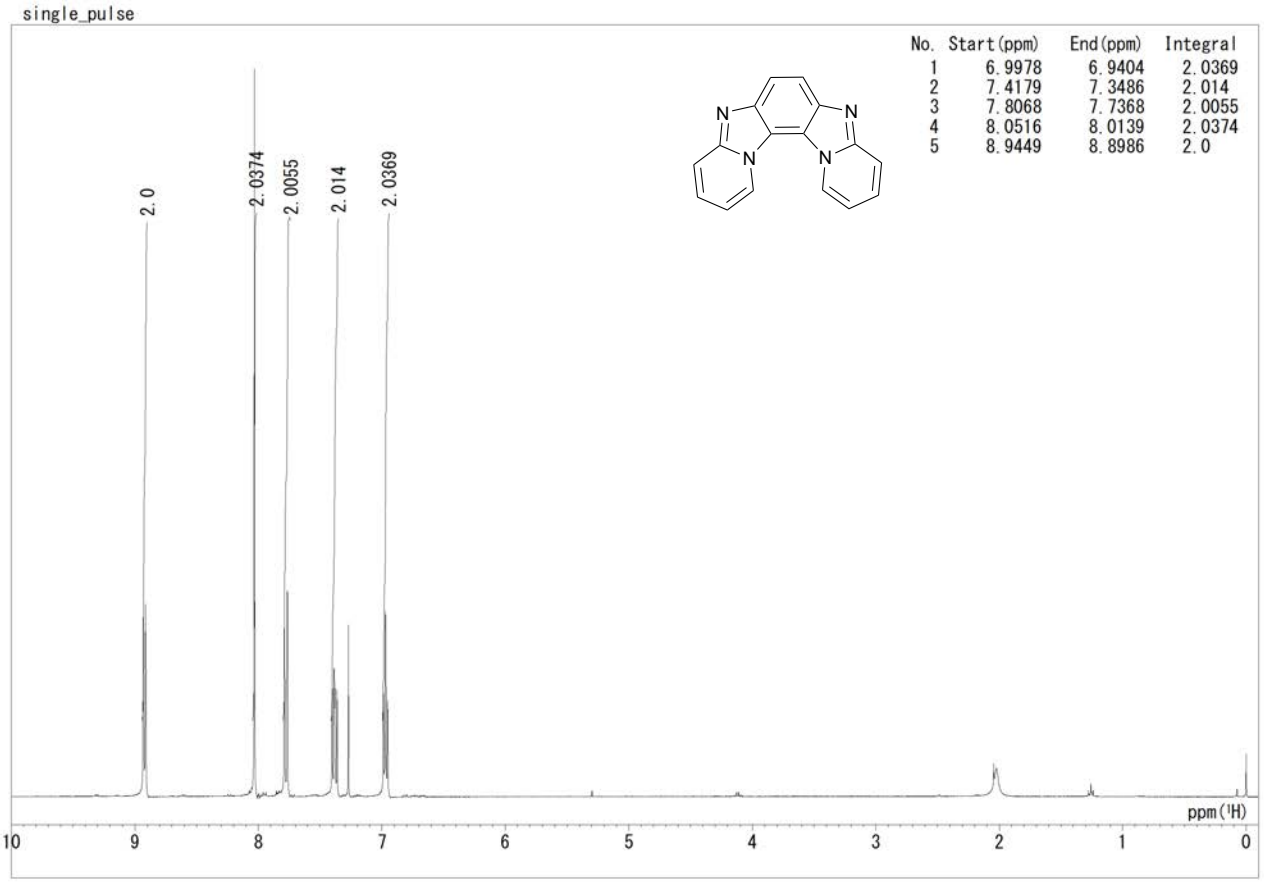


Fig. S17 ^{1}H NMR spectrum of **[5]H** in $CDCl_3$.

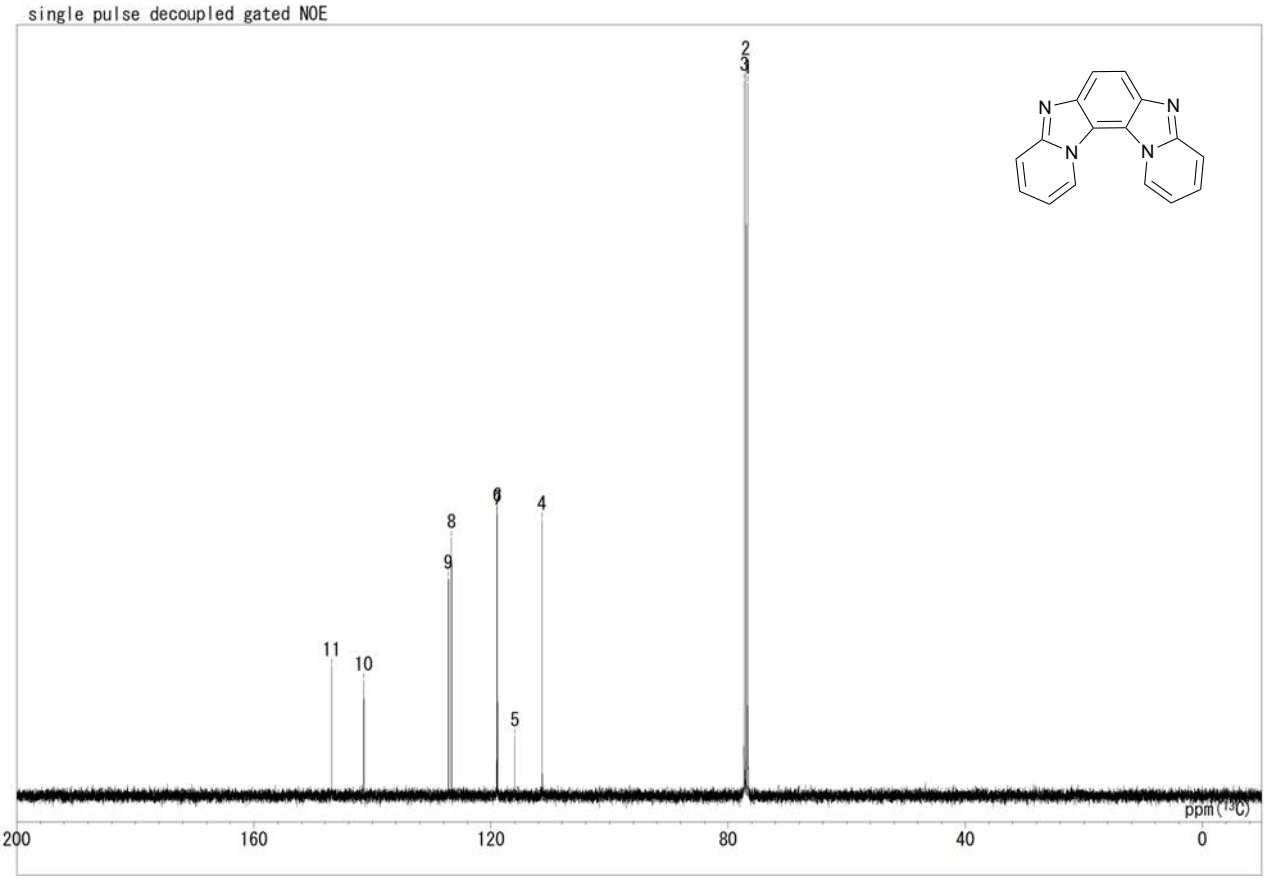


Fig. S18 ^{13}C NMR spectrum of **[5]H** in $CDCl_3$.

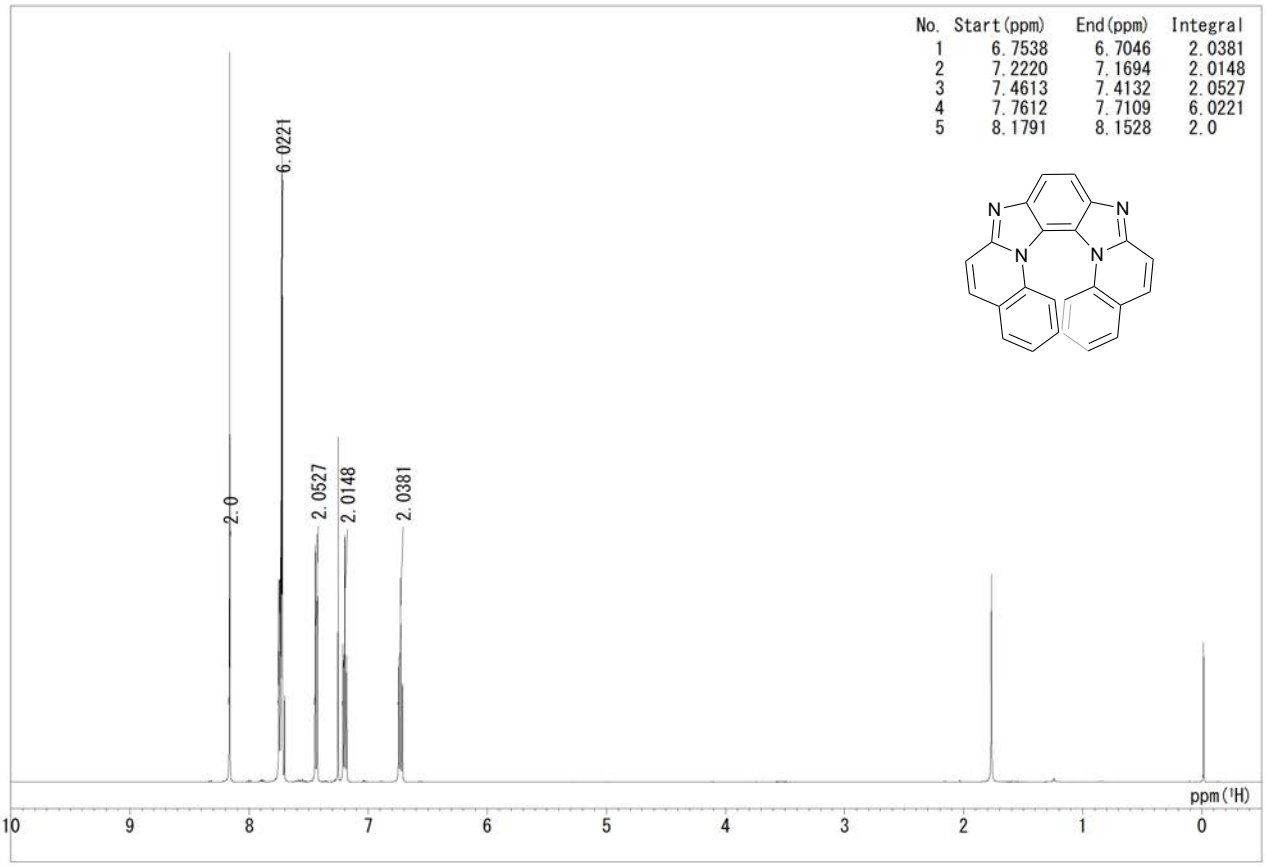


Fig. S19 ^{1}H NMR spectrum of **[7]H** in $CDCl_3$.

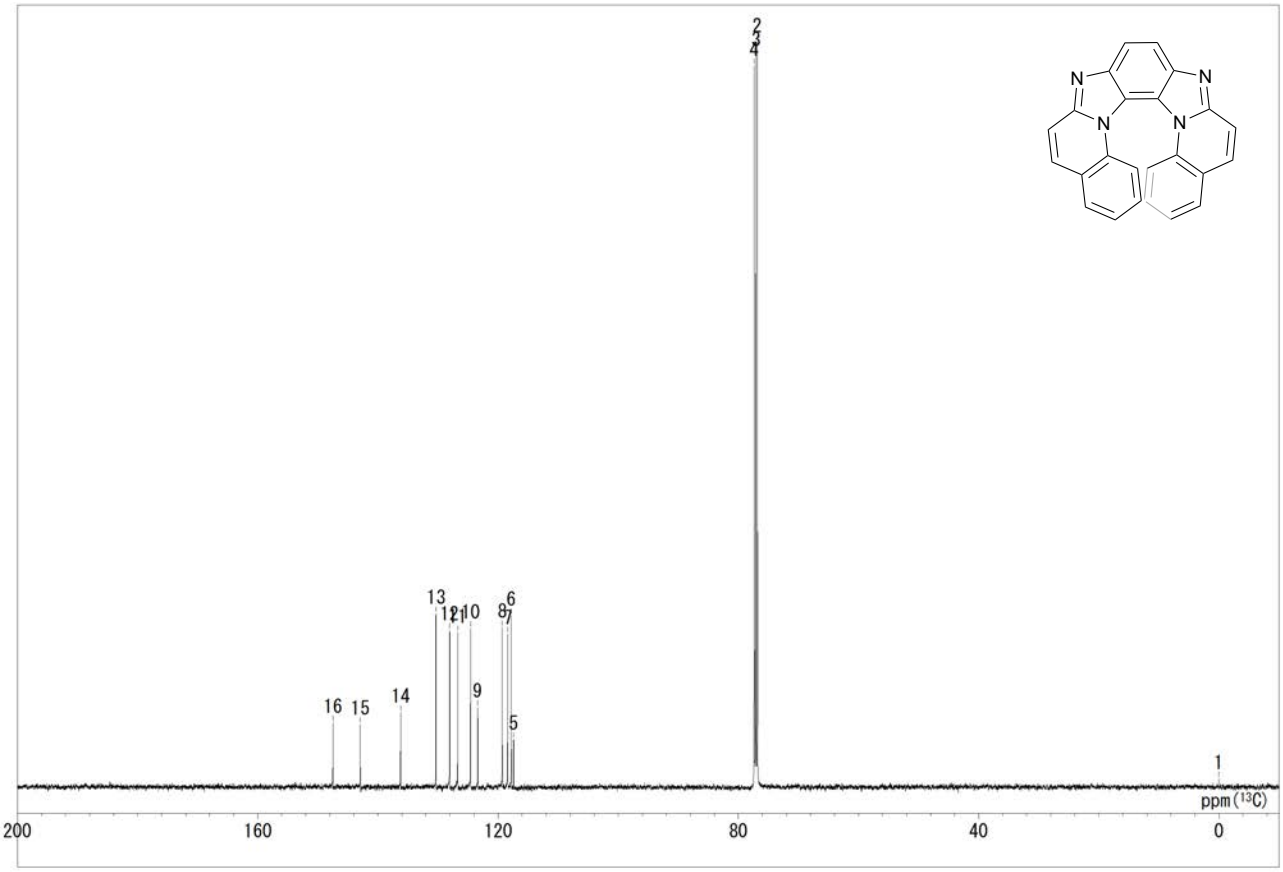


Fig. S20 ^{13}C NMR spectrum of **[7]H** in $CDCl_3$.

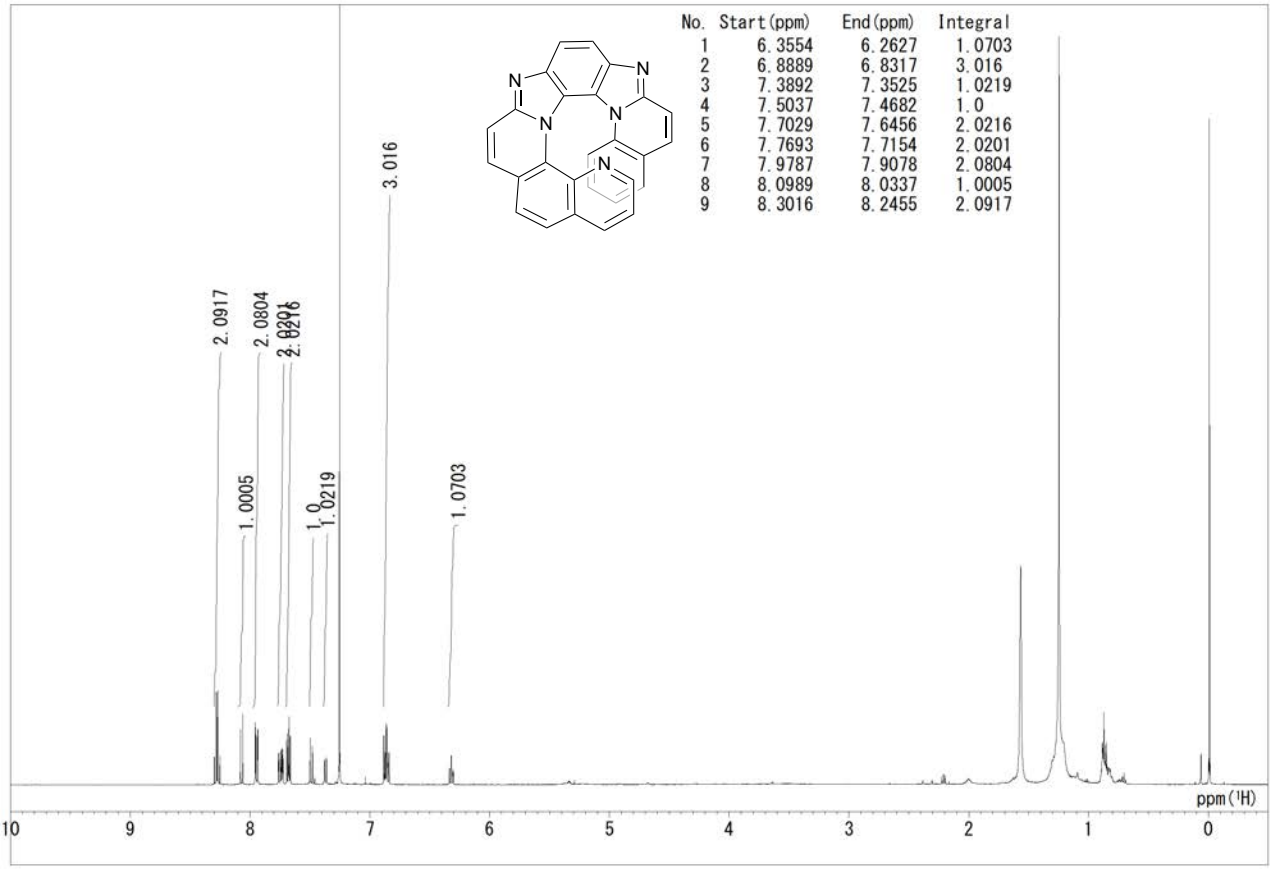


Fig. S21 ^{1}H NMR spectrum of **[8]Ha** in $CDCl_3$.

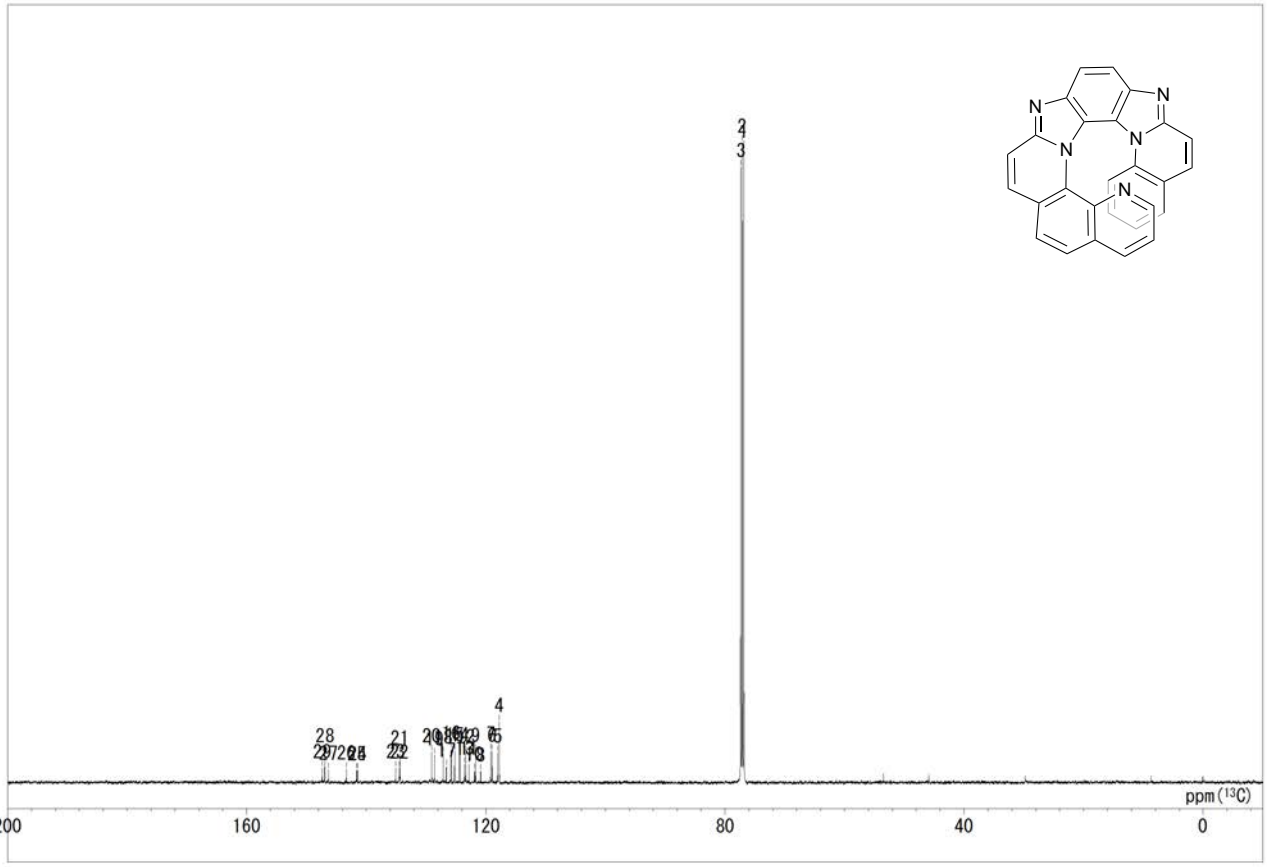


Fig. S22 ^{13}C NMR spectrum of **[8]Ha** in $CDCl_3$.

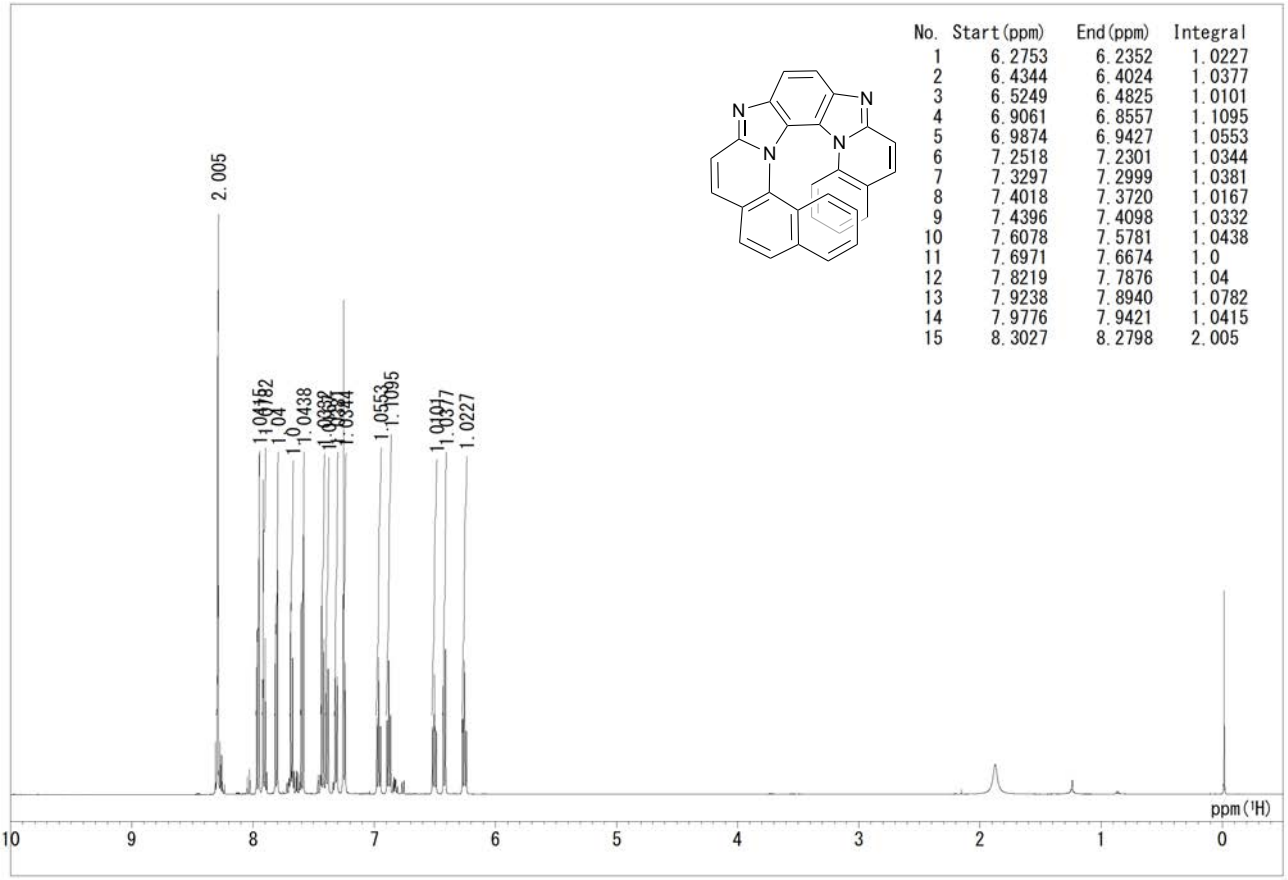


Fig. S23 ^{1}H NMR spectrum of **[8]Hb** in$CDCl_3$.

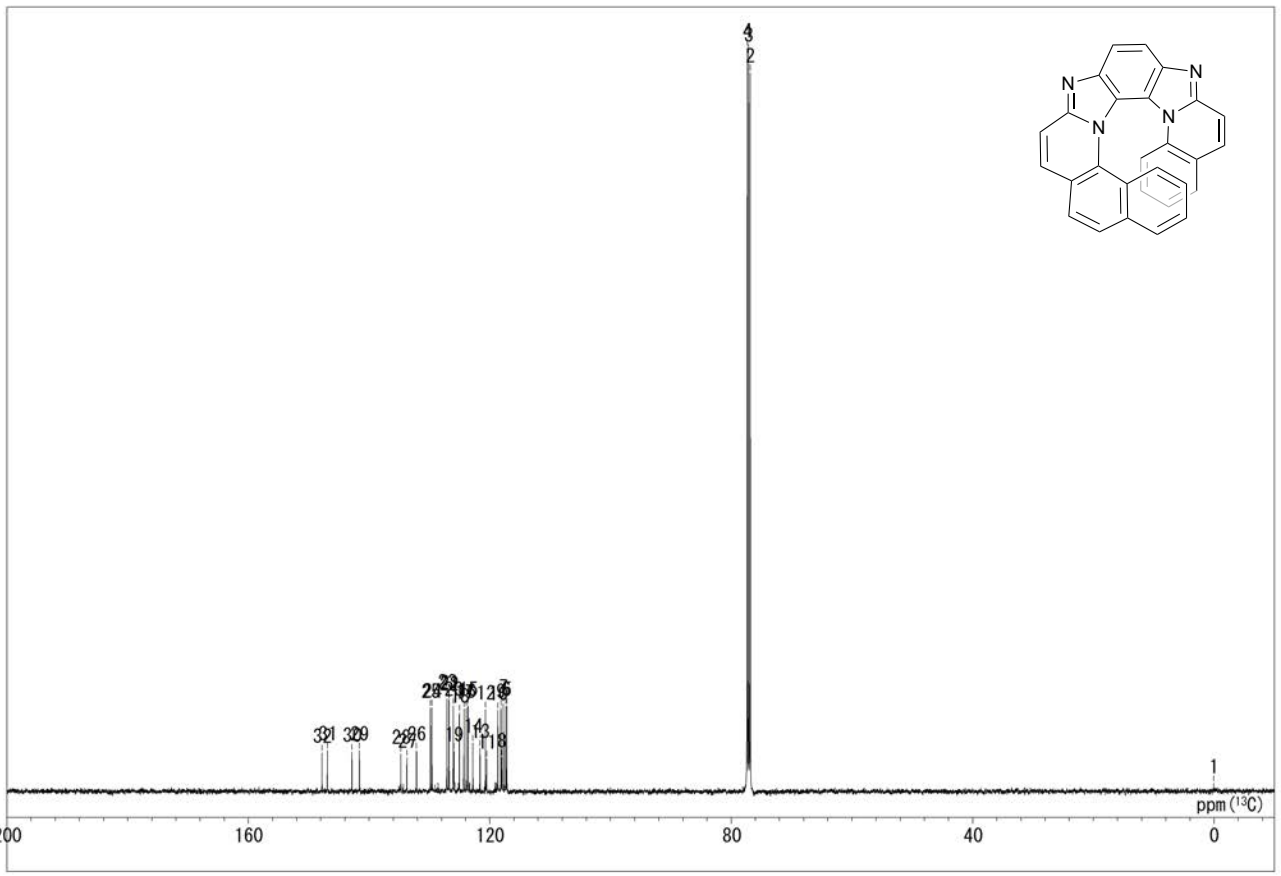


Fig. S24 ^{13}C NMR spectrum of **[8]Hb** in $CDCl_3$.

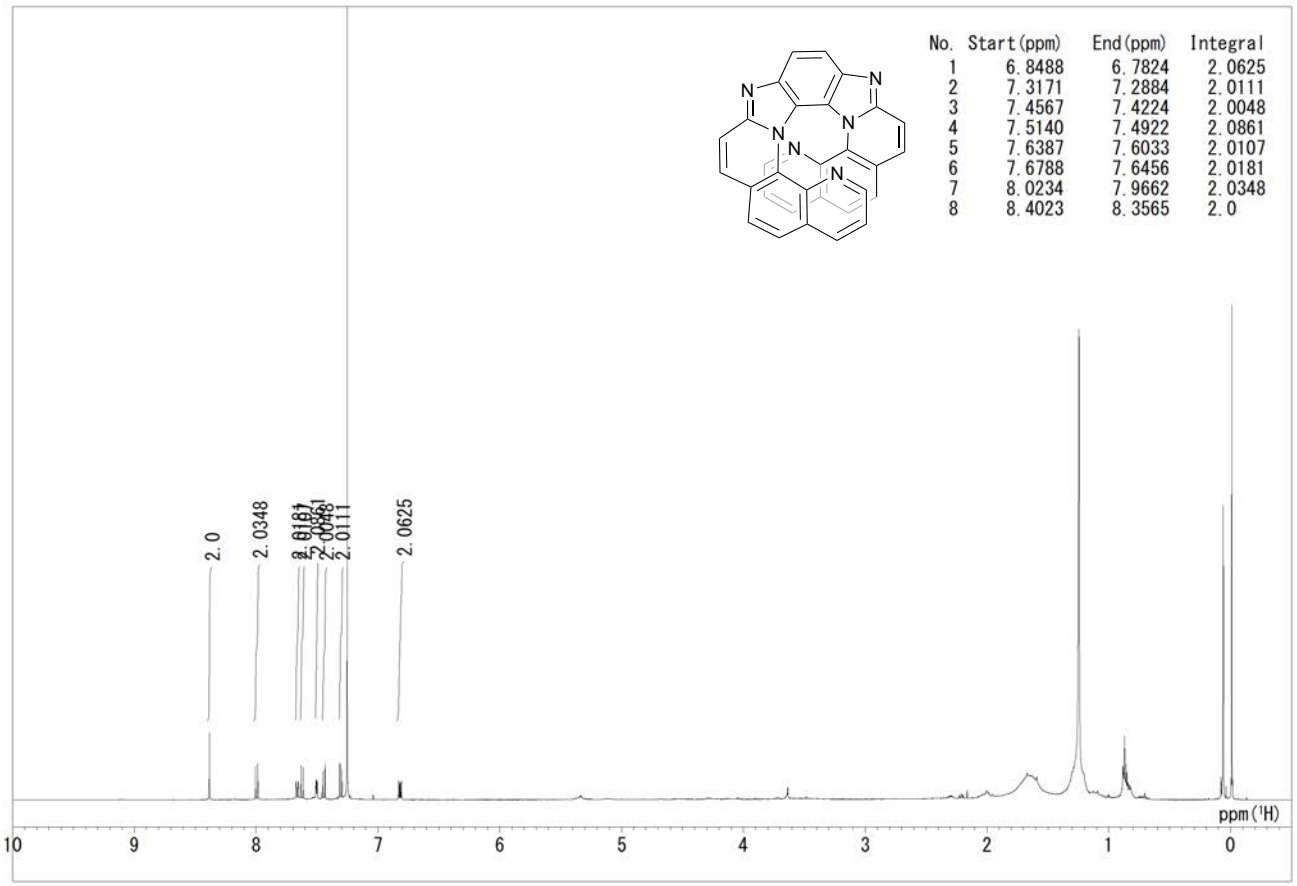


Fig. S25 ^{1}H NMR spectrum of **[9]Ha** in $CDCl_3$.

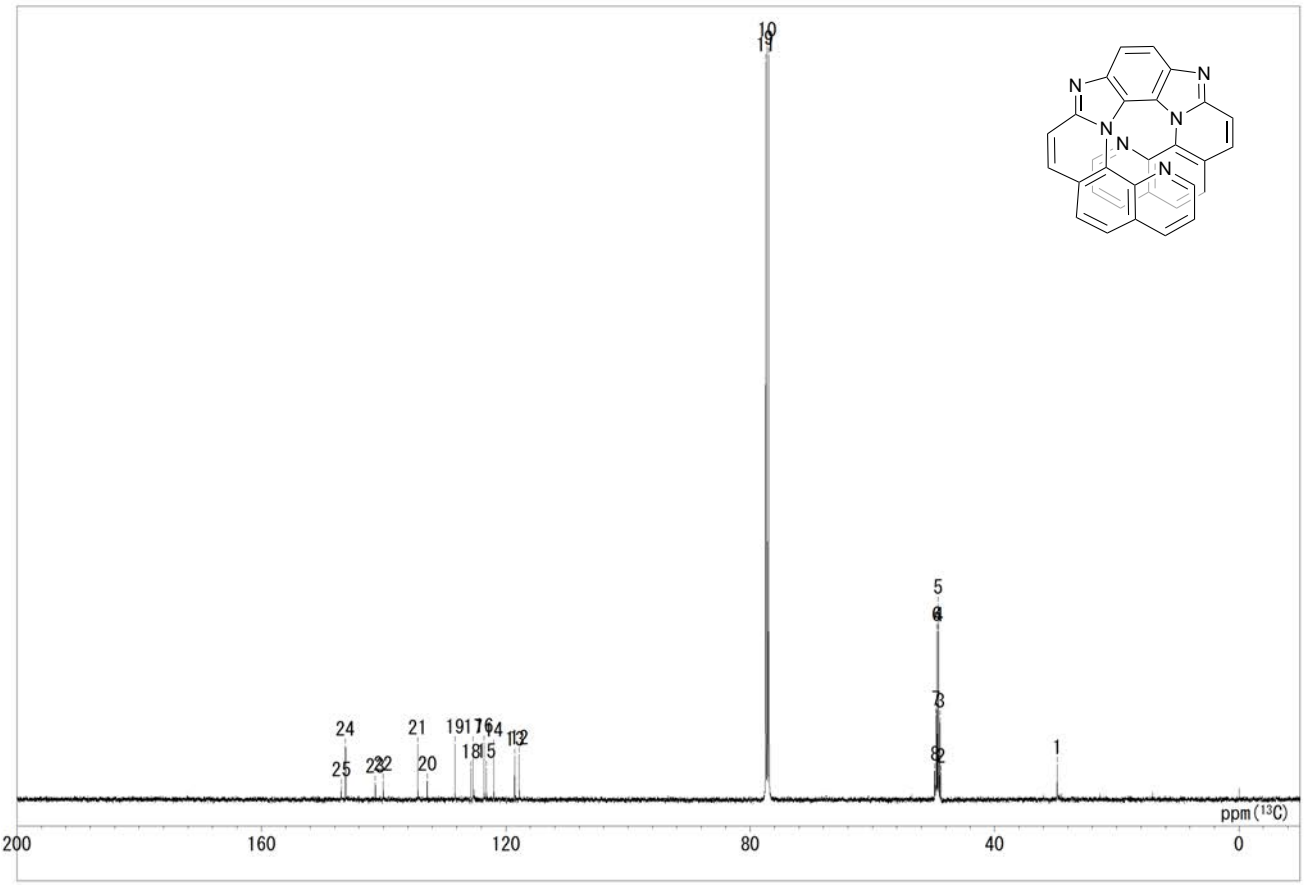


Fig. S26 ^{13}C NMR spectrum of **[9]Ha** in $(CD_3)_2SO$ and $CDCl_3$.

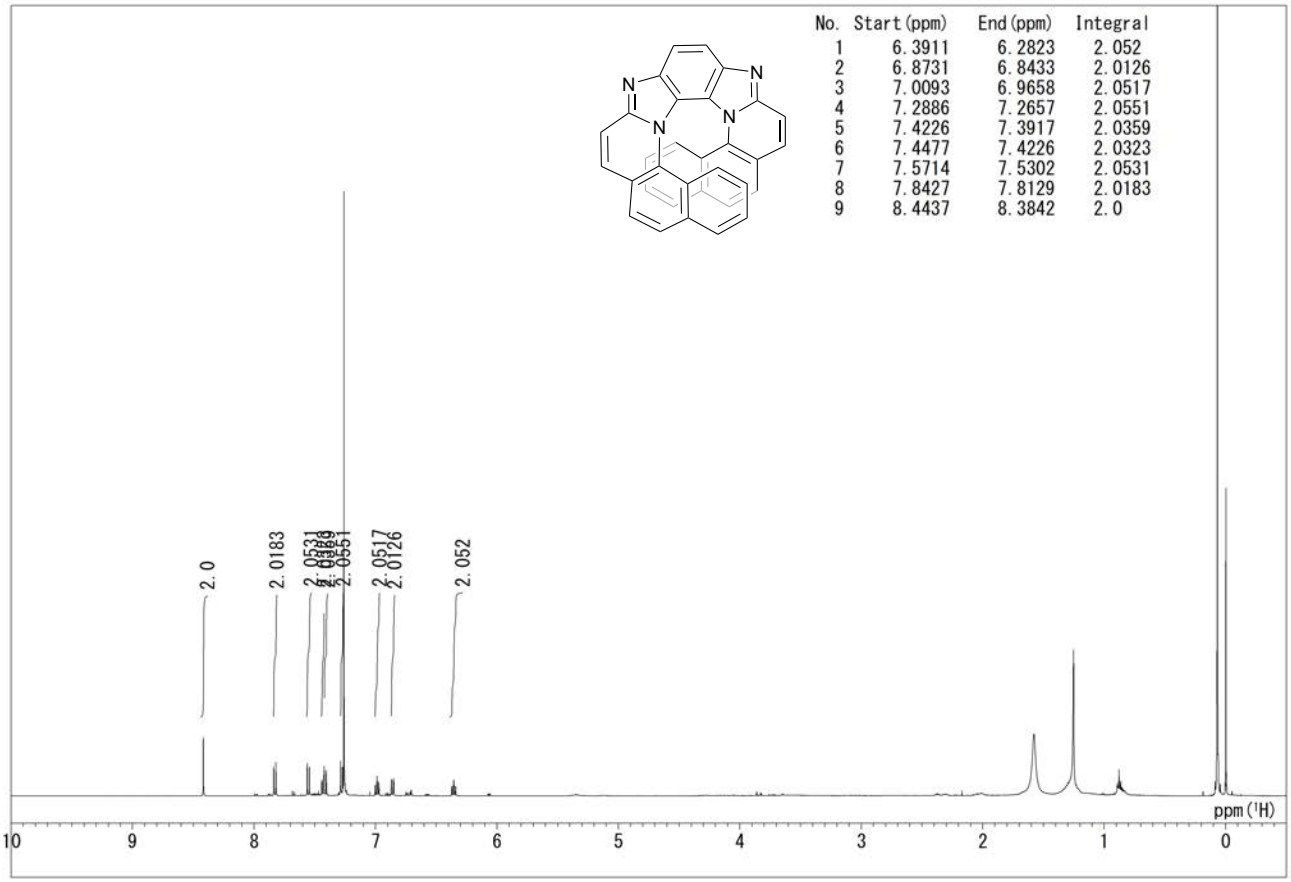


Fig. S27 ^{1}H NMR spectrum of **[9]Hb** in $CDCl_3$.

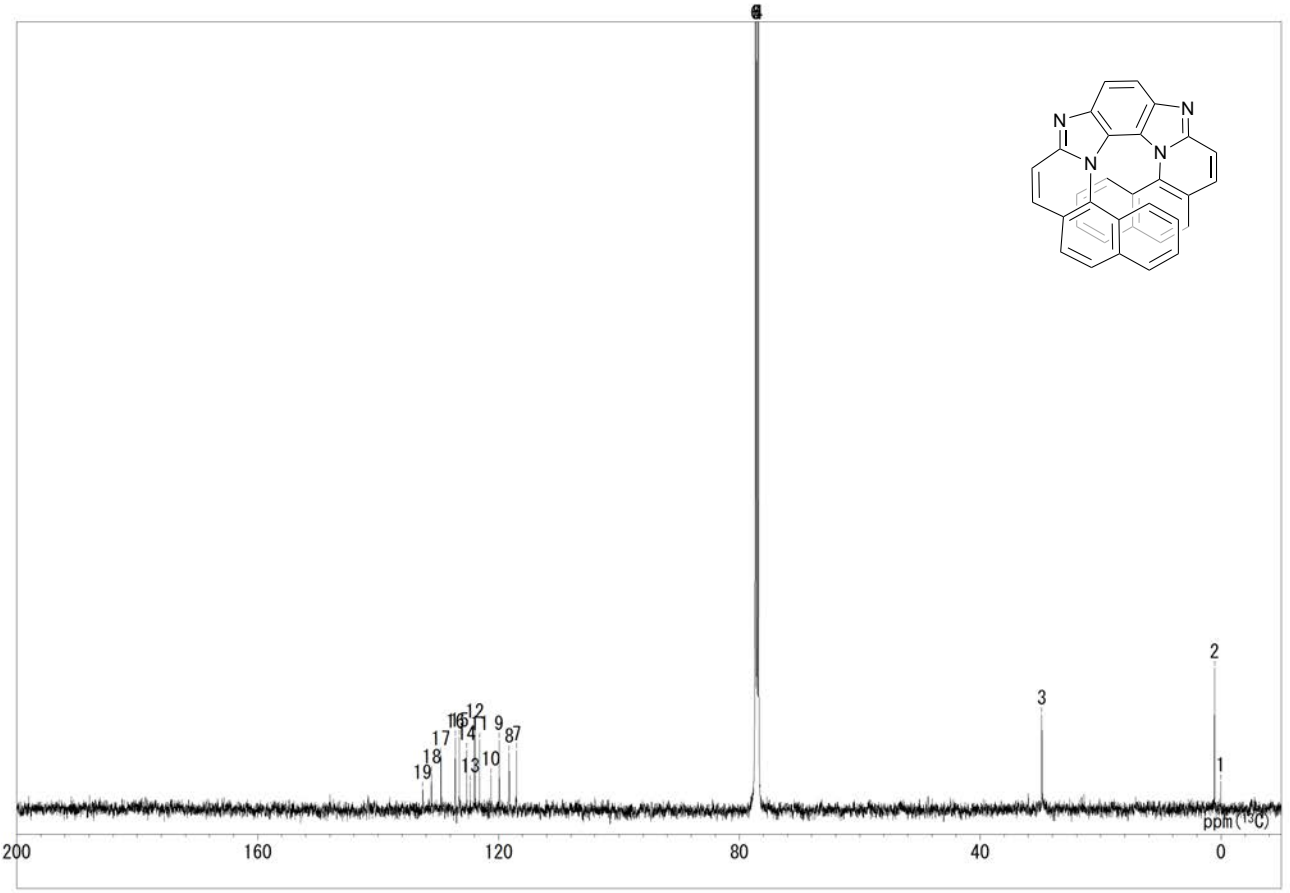
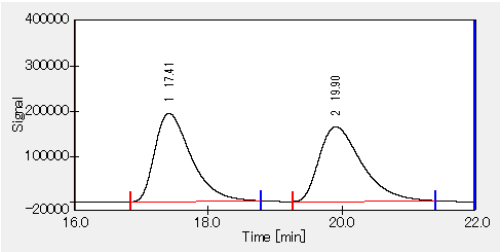


Fig. S28 ^{13}C NMR spectrum of **[9]Hb** in $CDCl_3$.

4. Optical Resolution

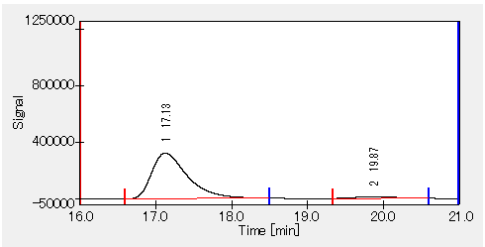
Optical resolution of [7]H. Optical resolution of racemic compound was conducted by MPLC analysis using chiral flash column (CHIRALFLASH® IC: 30 mm ×100 mm, eluent: MeOH / EtOH = 25/75, Flow Rate 20 mL/min). Analytical conditions for HPLC were as follows: Daicel CHIRALPAK IC-3: 4.6×250 mm, 254 nm UV detector, rt, eluent: MeOH / EtOH = 25/75, flow rate: 1.0 mL/min.



No.	Rt	Configuration	Area	Area(%)	Height
1	17.41	(M)	7348476	50.1023	195191
2	19.9	(P)	7318462.1	49.8977	164989
Total			14666938.1	100	360180

Fig. S29 Copy of HPLC chromatogram of racemic **[7]H**.

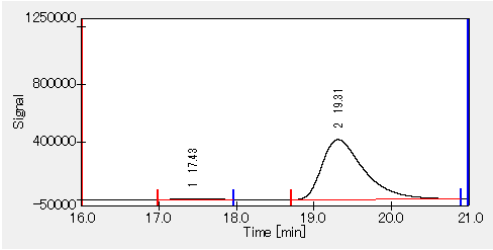
(*M*)-[7]H: $[\alpha]^{25}_{D} = -3611$ (*c* 0.270, $CHCl_3$, 91% ee).



No.	Rt	Configuration	Area	Area(%)	Height
1	17.13	(M)	10612900.4	95.8804	323714
2	19.87	(P)	455994.8	4.1196	12240
Total			11068895.2	100	335954

Fig. S30 Copy of HPLC chromatogram of **(*M*)-[7]H**.

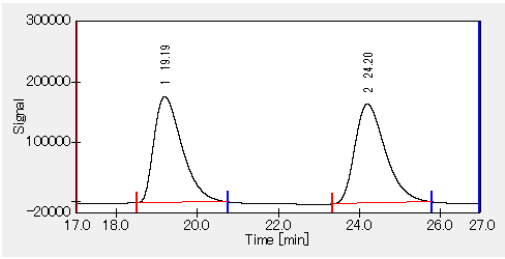
(*P*)-[7]H: $[\alpha]^{25}_{D}$ = +3232 (*c* 0.405, $CHCl_3$, 97% ee)



No.	Rt	Configuration	Area	Area(%)	Height
1	17.43	(M)	258501.6	1.6237	8636
2	19.31	(P)	15662135.2	98.3763	416445
Total			15920636.8	100	425081

Fig. S31 Copy of HPLC chromatogram of (***P***)-**[7]H**.

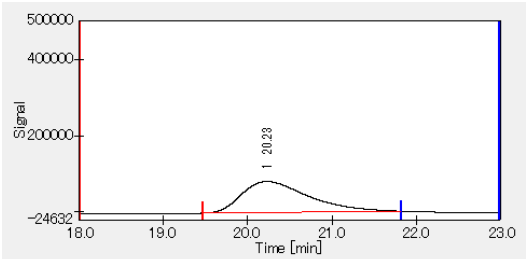
Optical resolution of [8]Ha. Optical resolution of racemic compound was conducted by MPLC analysis using chiral flash column (CHIRALFLASH® IC: 30 mm ×100 mm, eluent: MeOH / EtOH = 25/75, Flow Rate 20 mL/min). Analytical conditions for HPLC were as follows: Daicel CHIRALPAK IC-3: 4.6×250 mm, 254 nm UV detector, rt, eluent: MeOH / EtOH = 25/75, flow rate: 1.0 mL/min.



No.	Rt	Configuration	Area	Area(%)	Height
1	19.19	(P)	8535193.3	49.5928	176751
2	24.2	(M)	8675354.4	50.4072	165607
Total			17210547.7	100	342358

Fig. S32 Copy of HPLC chromatogram of racemic **[8]Ha**.

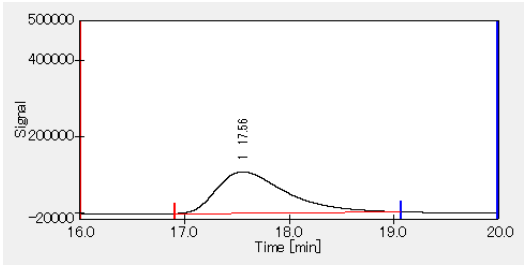
(+)-[8]Ha: $[\alpha]^{25}_{D}$ = +6774 (*c* 0.060, $CHCl_3$, 100% ee).



No.	Rt	Peak Name	Area	Area(%)	Height
1	17.56		4975858	100	108221
Total			4975858	100	108221

Fig. S33 Copy of HPLC chromatogram of (+)-**[8]Ha**.

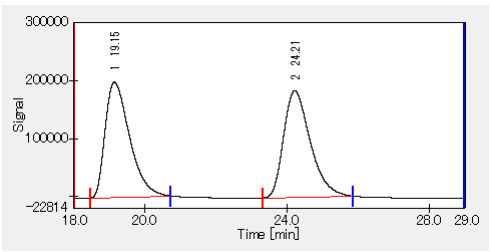
(–)-[8]Ha: $[\alpha]^{25}_{D} = -6103$ (*c* 0.080, $CHCl_3$, 100% ee)



No.	Rt	Peak Name	Area	Area(%)	Height
1	20.23		4492396	100	81647
Total			4492396	100	81647

Fig. S34 Copy of HPLC chromatogram of (–)-**[8]Ha**.

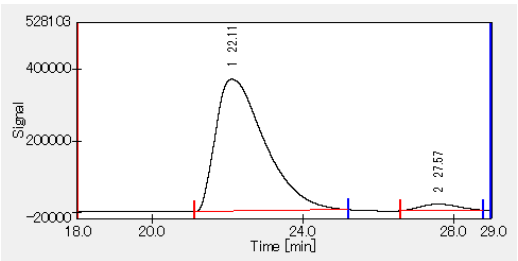
Optical resolution of [8]Hb. Optical resolution of racemic compound was conducted by MPLC analysis using chiral flash column (CHIRALFLASH® IC: 30 mm ×100 mm, eluent: MeOH / EtOH = 25/75, Flow Rate 20 mL/min). Analytical conditions for HPLC were as follows: Daicel CHIRALPAK IC-3: 4.6×250 mm, 254 nm UV detector, rt, eluent: MeOH / EtOH = 25/75, flow rate: 1.0 mL/min.



No.	Rt	Configuration	Area	Area(%)	Height
1	19.15	(P)	9535537.9	49.7509	200099
2	24.21	(M)	9631012.2	50.2491	185014
Total			19166550.1	100	385113

Fig. S35 Copy of HPLC chromatogram of racemic **[8]Hb**.

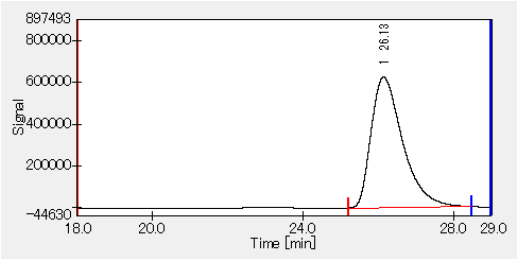
(+)-[8]Hb: $[\alpha]^{25}_{D} = +4471$ (*c* 0.370, $CHCl_3$, 93% ee).



No.	Rt	Peak Name	Area	Area(%)	Height
1	22.11		33335751.3	96.4275	368445
2	27.57		1235035.8	3.5725	17780
			34570787.1	100	386225

Fig. S36 Copy of HPLC chromatogram of (+)-**[8]Hb**.

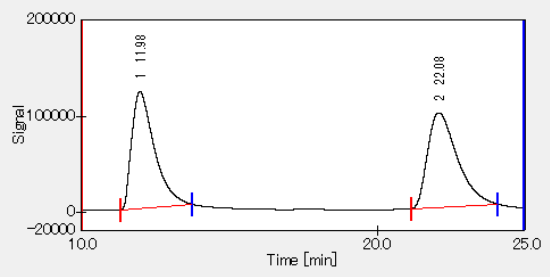
(–)-[8]Hb: $[\alpha]^{25}_{D}$ = -4124 (*c* 0.380, $CHCl_3$, 100% ee).



No.	Rt	Peak Name	Area	Area(%)	Height
1	26.13		36448030.2	100	626054
			36448030.2	100	626054

Fig. S37 Copy of HPLC chromatogram of (–)-**[8]Hb**.

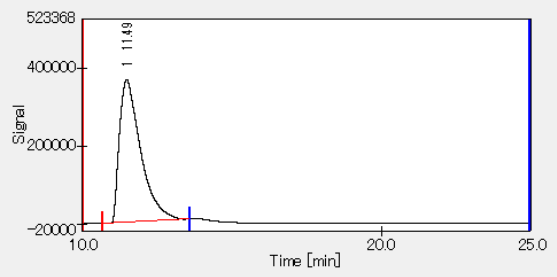
Optical resolution of [9]Ha. Optical resolution of racemic compound was conducted by MPLC analysis using chiral flash column (CHIRALFLASH® IC: 30 mm ×100 mm, eluent: MeOH / EtOH = 50/50, Flow Rate 20 mL/min) Analytical conditions for HPLC were as follows: Daicel CHIRALPAK IC-3: 4.6×250 mm, 254 nm UV detector, rt, eluent: MeOH / EtOH = 50/50, flow rate: 1.0 mL/min.



No.	Rt	Configuration	Area	Area(%)	Height
1	11.98	(P)	6658660.351	49.4037	122611
2	22.08	(M)	6819391.2	50.5963	98749
Total			13478051.55	100	221360

Fig. S38 Copy of HPLC chromatogram of racemic **[9]Ha**.

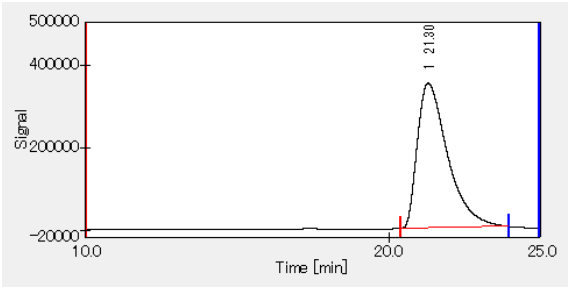
(+)-[9]Ha: $[\alpha]^{25}_{D} = +7055$ (*c* 0.145, $CHCl_3$, 100% ee).



No.	Rt	Peak Name	Area	Area(%)	Height
1	11.49		17998892.24	100	365984
			17998892.24	100	365984

Fig. S39 Copy of HPLC chromatogram of racemic **[9]Ha**.

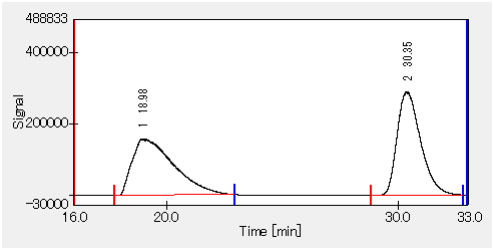
(–)-[9]Ha: $[\alpha]^{25}_{D} = -7207$ (*c* 0.140, $CHCl_3$, 100% ee).



No.	Rt	Peak Name	Area	Area(%)	Height
1	21.3		24338719	100	350359
			24338719	100	350359

Fig. S40 Copy of HPLC chromatogram of racemic **[9]Ha**.

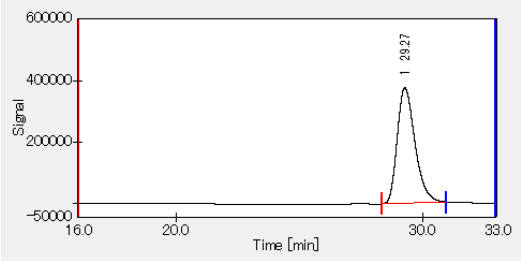
Optical resolution of [9]Hb. Optical resolution of racemic compound was conducted by MPLC analysis using chiral flash column (CHIRALFLASH® IC: 30 mm ×100 mm, eluent: MeOH / EtOH = 50/50, Flow Rate 20 mL/min) Analytical conditions for HPLC were as follows: Daicel CHIRALPAK IC-3: 4.6×250 mm, 254 nm UV detector, rt, eluent: MeOH / EtOH = 50/50, flow rate: 1.0 mL/min.



No.	Rt	Configuration	Area	Area(%)	Height
1	19.74	(P)	19659626.06	49.1159	128814
2	30.35	(M)	20367382.27	50.8841	290345
Total			40027008.33	100	419159

Fig. S41 Copy of HPLC chromatogram of racemic **[9]Hb**.

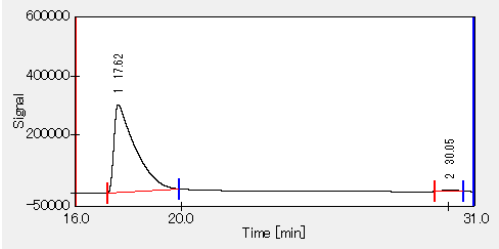
(+)-[9]Hb: $[\alpha]^{25}_{D} = +3768$ (*c* 0.470, $CHCl_3$, 100% ee).



No.	Rt	Peak Name	Area	Area(%)	Height
1	17.62		16489547.8	98.8638	300532
2	30.05		189505.1	1.1362	4689
			16679052.9	100	305221

Fig. S42 Copy of HPLC chromatogram of (+)-**[9]Hb**.

(–)-[9]Hb: $[\alpha]^{25}_{D} = -3946$ (*c* 0.285, $CHCl_3$, 100% ee).



No.	Rt	Peak Name	Area	Area(%)	Height
1	29.27		18588328.6	100	376288
			18588328.6	100	376288

Fig. S43 Copy of HPLC chromatogram of (–)-**[9]Hb**.

5. X-ray Analysis

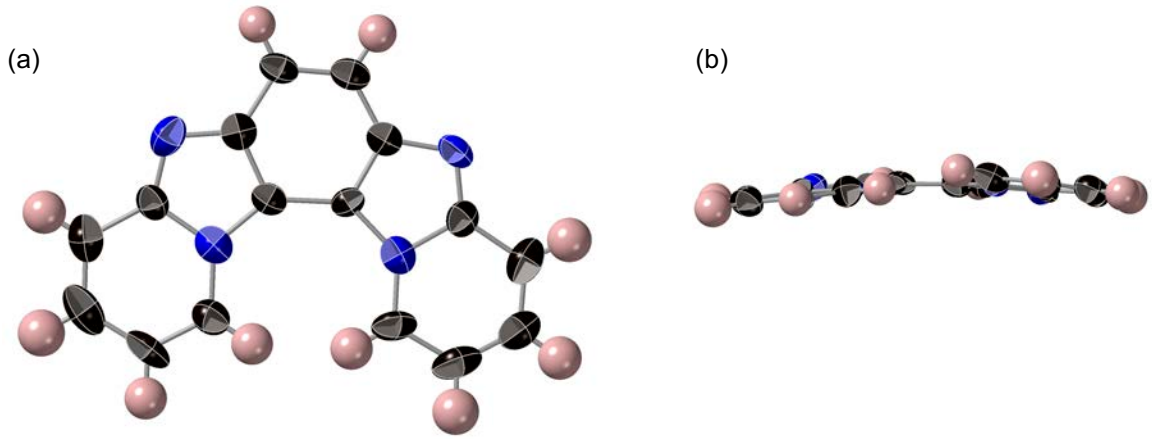


Fig. S44 ORTEP diagram of **[5]H**: (a) Top and (b) side view. Ellipsoids are set at 50% probability.

Table S1 Crystal data and structural refinement parameters for **[5]H, (*M*)-[7]H** and **[9]Ha**

Component		**[5]H**	(*M*)-**[7]H**	**[9]Ha**
Data deposition		1979567	1979582	1569975
Empirical formula		$C_{16}H_{10}N_4$	$C_{24}H_{14}N_4 \cdot (CHCl_3)$	$C_{30}H_{16}N_6$
Formula weight		258.28	477.78	460.5
Temperature		296 K	296 K	296 K
Wavelength		1.54187 Å	1.54187 Å	1.54187 Å
Crystal system		monoclinic	orthorhombic	tetragonal
Space group		*P*1*n*1	$P2_12_12_1$	*I*-42*d*
Unit cell dimensions	*a*	11.6524(7) Å	11.2100 Å	22.3365(5) Å
	b	4.0000(2) Å	17.1917 Å	22.3365(5) Å
	c	14.3571(8) Å	19.6180 Å	9.9167(2) Å
	α	90.0000 °	90.0000 °	90.0000 °
	β	92.273(7) °	90.0000 °	90.0000 °
	γ	90.0000 °	90.0000 °	90.0000 °
Volume		668.66 $Å^3$	3780.7647 $Å^3$	4947.62(18) $Å^3$
Z		4	8	16
Density (calculated)		2.565 g/m^3	1.679 g/m^3	2.473 g/m^3
Absorption coefficient Mu		1.279 mm^{-1}	4.585 mm^{-1}	1.212 mm^{-1}
F(000)		536	1952	3808
Crystal size		0.200 × 0.100 × 0.100 mm^3	0.500 × 0.500 × 0.100 mm^3	0.700 × 0.200 × 0.200 mm^3
Theta range for data collection		3.08 to 68.05 °	3.418 to 68.226 °	3.96 to 68.22 °
Index ranges		–14<=h<=13	–13<=h<=13	–26<=h<=26
		–4<=k<=4	–19<=k<=20	–26<=k<=26
		–17<=l<=17	–23<=l<=23	–11<=l<=11
Reflections collected		6812	43243	28498
Refinement method		Full-matrix least-squares refinement^2 on F^2	Full-matrix least-squares refinement^2 on F^2	Full-matrix least-squares refinement^2 on F^2
Data/restraints/parameters		2366/2/181	6904/0/532	2257/0/163
Goodness-of-fit on F^2		1.892	1.021	1.051
Final *R* indices [$I>2\sigma(I)$]		$R_1 = 0.1609$, $wR_2 = 0.4010$	$R_1 = 0.1660$, $wR_2 = 0.0628$	$R_1 = 0.0623$, $wR_2 = 0.1996$
R indices (all data)		$R_1 = 0.1641$, $wR_2 = 0.4065$	$R_1 = 0.0667$, $wR_2 = 0.1696$	$R_1 = 0.0626$, $wR_2 = 0.2002$

6. Photophysical Properties

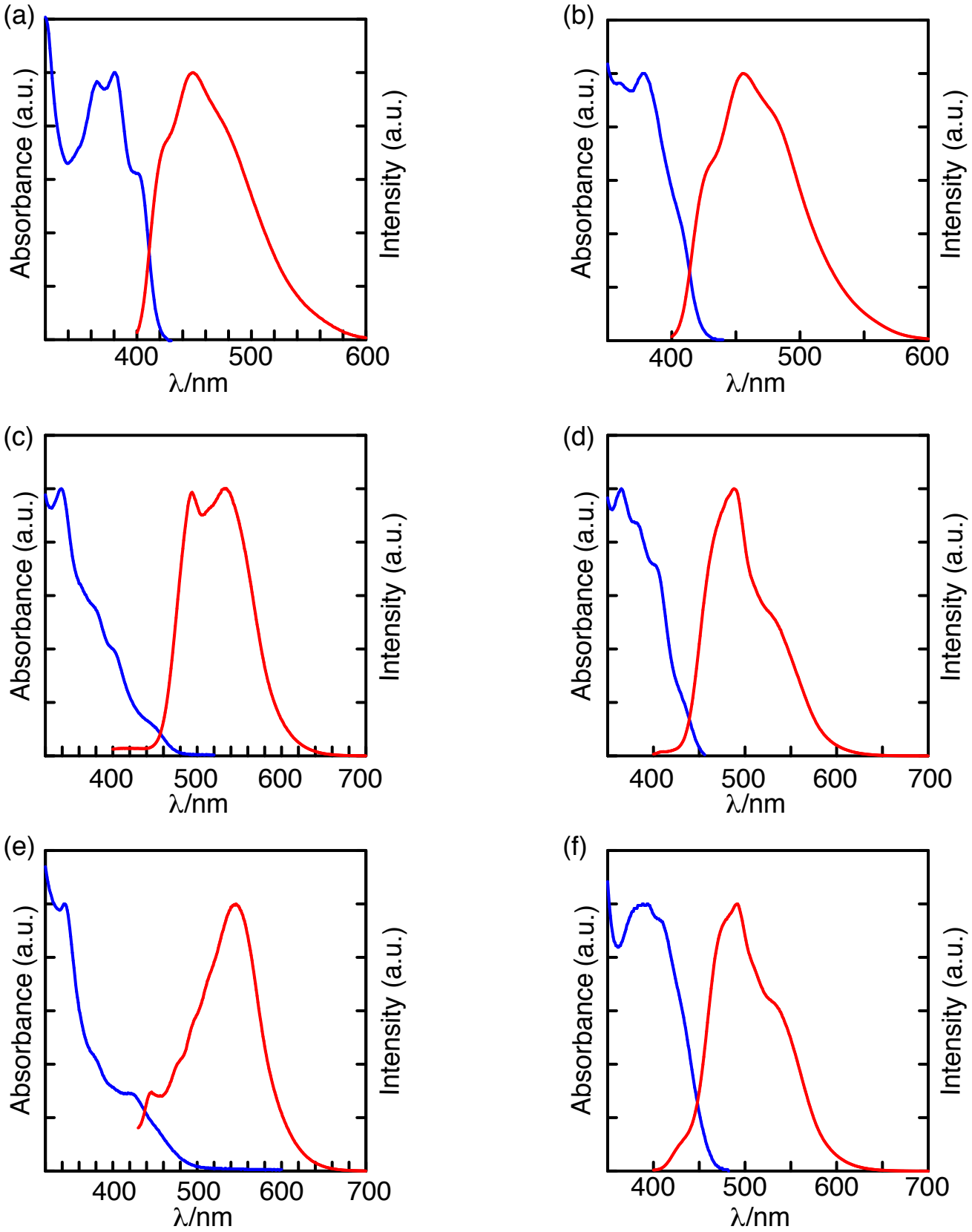
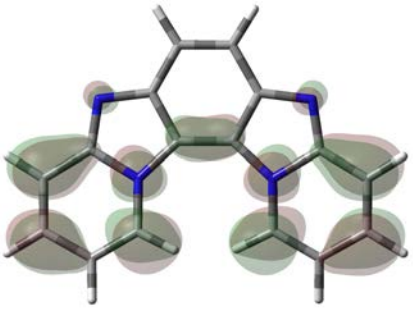
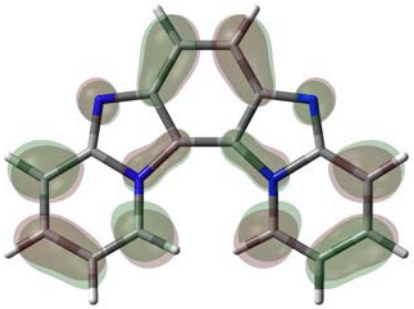


Fig. S45 Absorption and fluorescence spectra of (a) **[5]H**, (b) **[7]H**, (c) **[8]Ha**, (d) **[8]Hb**, (e) **[9]Ha** and (f) **[9]Hb**.

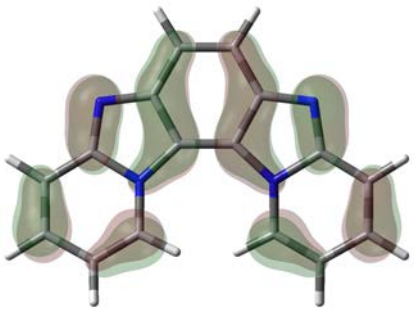
7. DFT Calculations



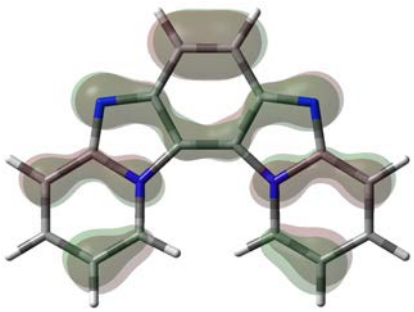
LUMO+1 (–1.25 eV)



LUMO (–1.50 eV)

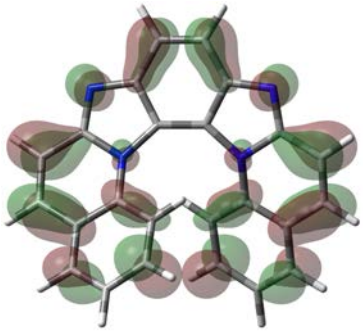


HOMO (–5.18 eV)

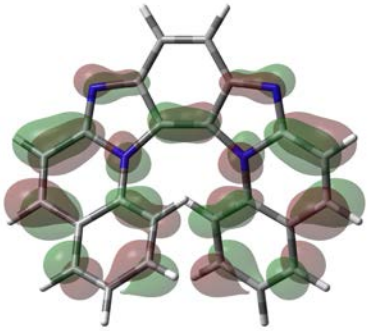


HOMO–1 (–5.85 eV)

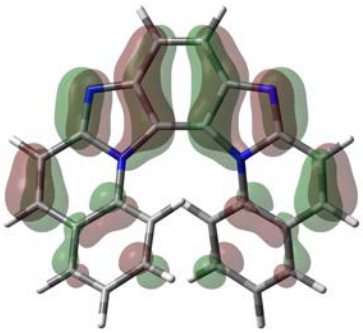
Fig. S46 The LUMO+1, LUMO, HOMO and HOMO–1 of **[5]H** calculated by DFT method [B3LYP/6-31G(d,p)].



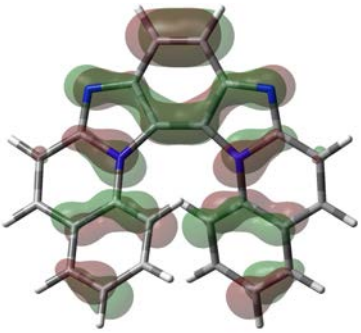
LUMO+1 (–1.54 eV)



LUMO (–1.61 eV)

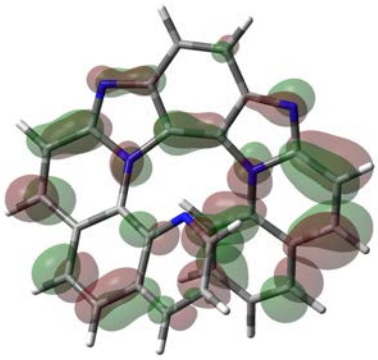


HOMO (–5.23 eV)

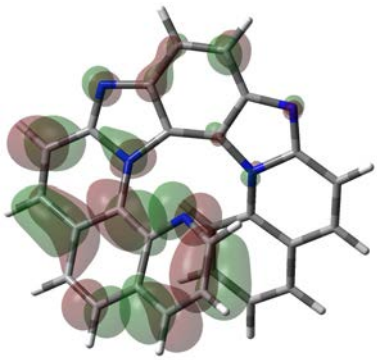


HOMO–1 (–5.73 eV)

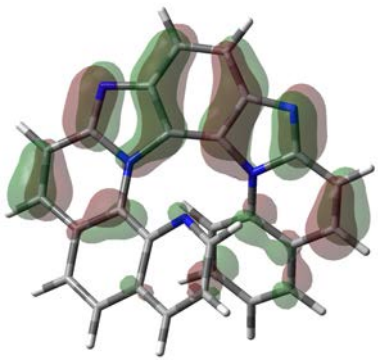
Fig. S47 The LUMO+1, LUMO, HOMO and HOMO–1 of **[7]H** calculated by DFT method [B3LYP/6-31G(d,p)].



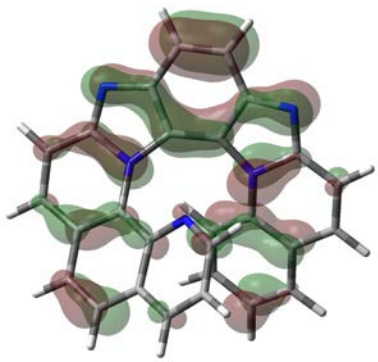
LUMO+1 (–1.47 eV)



LUMO (–1.88 eV)

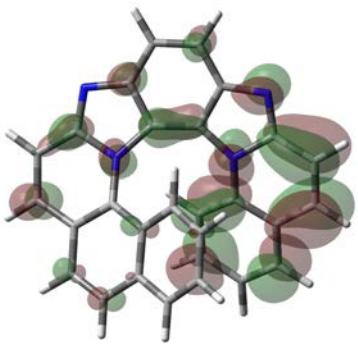


HOMO (–5.08 eV)

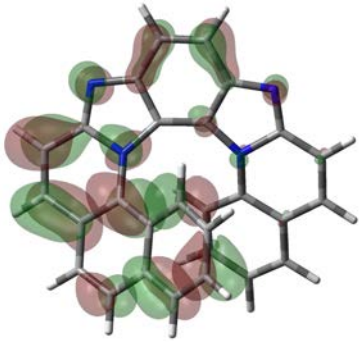


HOMO–1 (–5.52 eV)

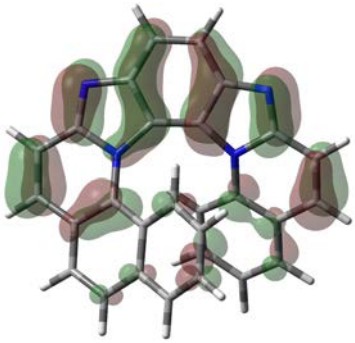
Fig. S48 The LUMO+1, LUMO, HOMO and HOMO–1 of **[8]Ha** calculated by DFT method [B3LYP/6-31G(d,p)].



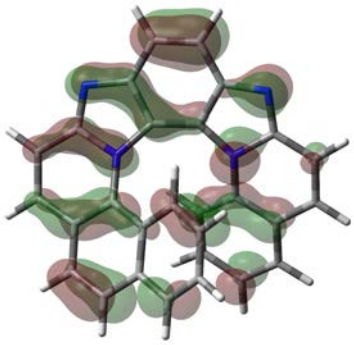
LUMO+1 (–1.52 eV)



LUMO (–1.71 eV)

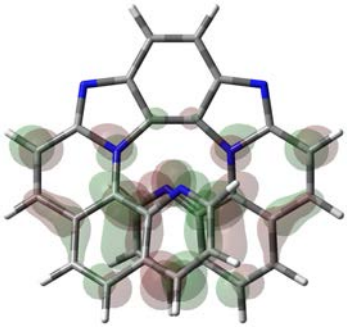


HOMO (–5.16 eV)

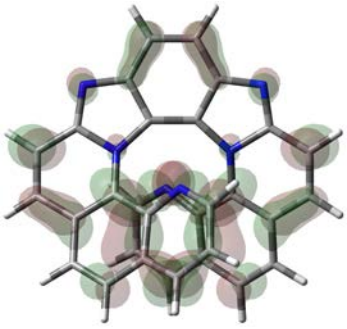


HOMO–1 (–5.60 eV)

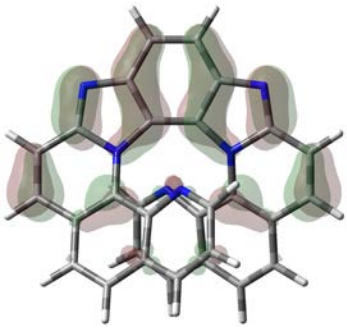
Fig. S49 The LUMO+1, LUMO, HOMO and HOMO–1 of **[8]Hb** calculated by DFT method [B3LYP/6-31G(d,p)].



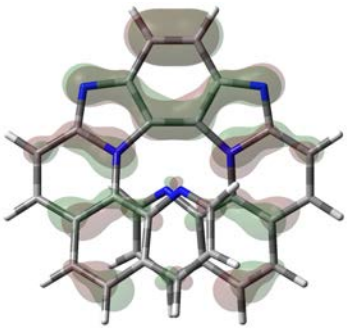
LUMO+1 (–1.76 eV)



LUMO (–1.77 eV)

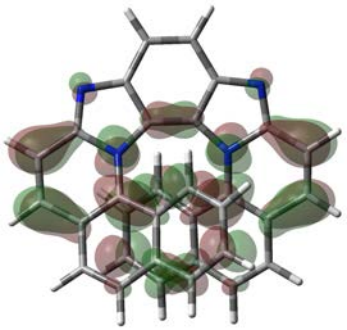


HOMO (–4.95 eV)

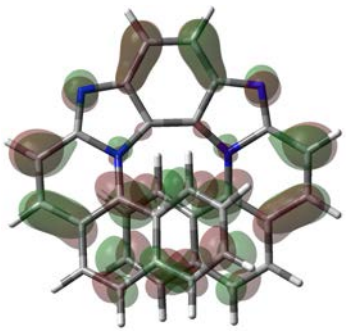


HOMO–1 (–5.43 eV)

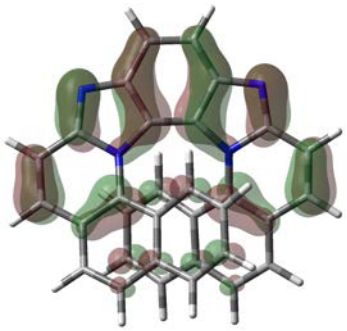
Fig. S50 The LUMO+1, LUMO, HOMO and HOMO–1 of **[9]Ha** calculated by DFT method [B3LYP/6-31G(d,p)].



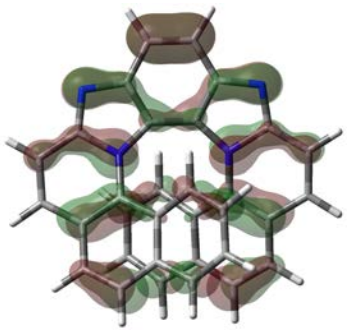
LUMO+1 (–1.60 eV)



LUMO (–1.68 eV)



HOMO (–5.09 eV)



HOMO–1 (–5.52 eV)

Fig. S51 The LUMO+1, LUMO, HOMO and HOMO–1 of **[9]Hb** calculated by DFT method [B3LYP/6-31G(d,p)].