

Supporting Information

for

A facile synthesis of functionalized 7,8-diaza[5]helicenes through an oxidative ring-closure of 1,1'-binaphthalene-2,2'-diamines (BINAMs)

Youhei Takeda*^{1,2}, Masato Okazaki², Yoshiaki Maruoka², and Satoshi Minakata*²

Address: ¹Frontier Research Base for Global Young Researchers, Graduate School of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565-0871, Japan and ²Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565-0871, Japan

Email: Youhei Takeda - takeda@chem.eng.osaka-u.ac.jp; Satoshi Minakata - minakata@chem.eng.osaka-u.ac.jp

*Corresponding author

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General remarks

All reactions were carried out under an atmosphere of nitrogen unless otherwise noted. Melting points were determined on a Stanford Research Systems MPA100 OptiMelt Automated Melting Point System. ^1H and ^{13}C NMR spectra were recorded on a JEOL JMTC-400/54/SS spectrometer (^1H NMR, 400 MHz; ^{13}C NMR, 100 MHz) using tetramethylsilane as an internal standard. Infrared spectra were acquired on a SHIMADZU IRAffinity-1 FT-IR Spectrometer. Mass spectra were obtained on a JEOL JMS-DX303HF mass spectrometer. High-resolution mass spectra were obtained on a JEOL JMS-DX303HF mass spectrometer. UV/vis spectra were recorded on a Shimadzu UV-2550 spectrophotometer. Emission spectra were recorded on a HAMAMATSU C11347-01 spectrometer with an integrating sphere. Cyclic voltammetry (CV) was performed with ALS-600 (BAS Inc.) system. Thermogravimetric analysis (TGA) was performed with TG/DTA-7200 (SII) system. Products were purified by chromatography on silica gel BW-300 and Chromatorex NH (Fuji Silysia Chemical Ltd.). Analytical thin-layer chromatography (TLC) was performed on pre-coated silica gel glass plates (Merck silica gel 60 F₂₅₄ and Fuji Silysia Chromatorex NH, 0.25 mm thickness). Compounds were visualized with UV lamp. Optical rotations were measured in a thermostated conventional 10 cm cell on a JASCO P-2200 polarimeter using the sodium-D line (589 nm).

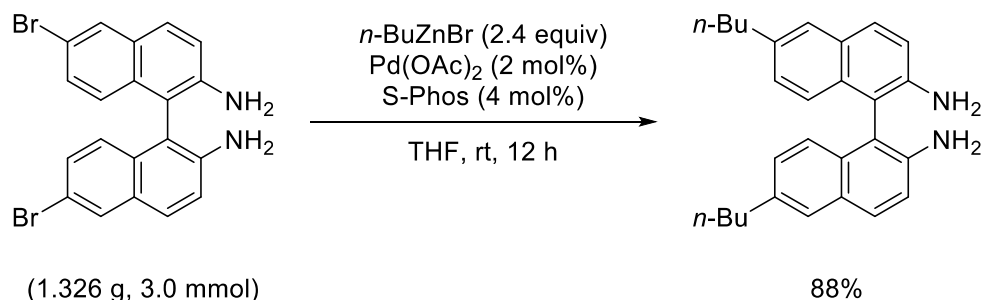
Materials

1,1'-Binaphthalene-2,2'-diamine (BINAM) was purchased from Sigma-Aldrich and used as received. DBU, triethylamine, and 2,6-lutidine were distilled with Kugelrohr apparatus, and other commercial reagents were purchased from Sigma-Aldrich, TCI, or Wako Pure Chemical Industries, Ltd. and used as received. Alcohol solvents were dried over activated molecular sieves 3A. THF, CH₃CN, and Et₂O were purchased as dehydrated grade and dried by passing through a glass contour solvent dispensing system (Nikko Hansen & Co., Ltd.). Dehydrated CH₂Cl₂ and toluene were purchased from Kanto Chemical Co., Inc. and used as received. DMF was distilled using CaSO₄ as a dehydrating agent. CH₂Cl₂ (fluorescence spectroscopic grade) was purchased from Kanto Chemical Co., Inc. for the measurement of UV-vis and emission spectra. Biaryldiamines **1b**^{S1} [360779-01-7], **1c**^{S2} [1051425-55-8, (*R*)-enantiomer], **1d**^{S3} [1229013-43-7], **1e**^{S4} [155855-47-3], **1g**^{S5} [861890-12-2], and **3**^{S6} [1454-80-4] were prepared according to the procedures in literature.

Preparation of 6,6'-di-*n*-butyl-1,1'-binaphthalene-2,2'-diamine (**1f**)

Biaryldiamine **1f** was prepared by modified cross-coupling method^{S7} from biaryldiamine **1g** as follows (Scheme S1): THF was degassed through freeze-pump-thaw cycling for three times before used. To a round-bottomed flask (50 mL) equipped with a

magnetic stir bar, were added biaryldiamine **1g** (1.326 g, 3.0 mmol), Pd(OAc)₂ (13.4 mg, 0.06 mmol), and SPhos (49.2 mg, 0.12 mmol) under the air. The tube was capped with a rubber septum, evacuated, and then refilled with N₂ gas for three times. THF (2 mL) and 0.5 M THF solution of *n*-BuZnBr (14.4 mL, 7.2 mmol) were added to the tube through the septum, and the mixture was stirred under N₂ atmosphere at room temperature for 12 h. To the reaction mixture, was added saturated aqueous NH₄Cl solution (10 mL), and the resulting mixture was extracted with EtOAc (20 mL × 3). The organic extract was dried over Na₂SO₄ and concentrated under vacuum to give the crude product. Purification by flash column chromatography on silica gel (eluent: hexane/EtOAc 8:2) gave biaryldiamine **1f** as pale brown solid (1.051 g, 88%). mp 130 °C (dec.); *R*_f 0.13 (hexane/EtOAc 8:2); ¹H NMR (400 MHz, CDCl₃) δ 0.92 (t, *J* = 7.2 Hz, 6H), 1.37 (tq, *J* = 7.2, 7.6 Hz, 4H), 1.63 (tt, *J* = 7.6, 7.6 Hz, 4H), 2.68 (t, *J* = 7.6 Hz, 4H), 3.60 (br, 4 H), 7.01 (d, *J* = 8.8 Hz, 2H), 7.05 (dd, *J* = 1.6, 8.8 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 1.6 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 22.4, 33.5, 35.4, 112.9, 118.3, 123.9, 126.6, 128.3, 128.6, 128.8, 132.0, 136.8, 141.9; IR (ATR) ν 2929, 1606, 1500, 1382, 1282, 824, 810 cm⁻¹; MS (EI): *m/z* (relative intensity, %) 396 (M⁺, 100), 353 ([C₂₅H₂₅N₂]⁺, 45); HRMS (EI): *m/z* calcd for C₂₈H₃₂N₂ (M) 396.2565, found 396.2568.



Scheme S1. Preparation of **1f**.

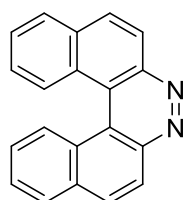
Optimization studies of reaction conditions

A typical procedure for the optimization studies using **1a** as substrate

To a two-necked reaction tube (20 mL, entry 2 in Table S1) or a two-necked round-bottomed flask (50 mL, entries 1 and 3–11 in Table S1, Table S2, and Table S3) equipped with a magnetic stir bar, was added 1,1'-binaphthalene-2,2'-diamine (**1a**) (0.2 mmol) under the air. The vessel was capped with a rubber septum and evacuated and refilled with N₂ gas for three times, and an appropriate solvent was added through the septum. To the mixture, were added an additive and an appropriate oxidant under a stream of N₂ gas at the indicated temperature. The resulting solution was stirred for indicated time before quenched with aqueous Na₂S₂O₃ solution (1.0 M, 20 mL), and the resulting mixture was extracted with

CH₂Cl₂ (20 mL × 3). The combined organic extracts were dried over Na₂SO₄ and concentrated under vacuum to give the crude product. The yields of products were calculated by the integration of ¹H NMR signals of the crude product. Separation by flash column chromatography on silica gel gave product **2a**.

7,8-Diaza[5]helicene (**2a**) [188-55-6]

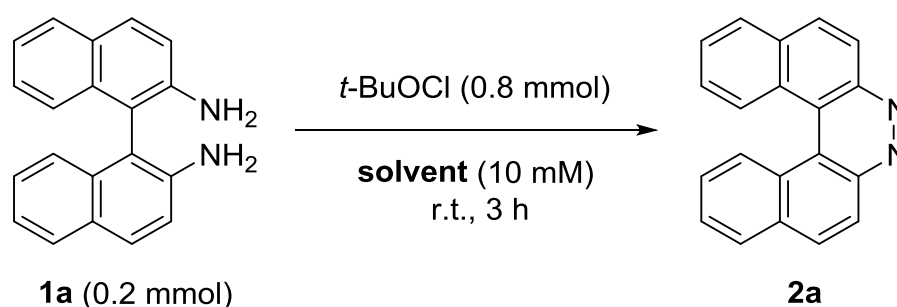


Spectroscopic data were in good agreement with those previously reported.^{S8}

The spectroscopic data are also available in our previous paper.^{S9} Purified by flash column chromatography on silica gel (eluent: hexane/EtOAc, 99:1 to 5:5) and recrystallization from CHCl₃; Yellow solid; *R_f* 0.15 (hexane/EtOAc 8:2); MS (EI): *m/z* (relative intensity, %) 280 (M⁺, 70), 252 ([C₂₀H₁₂]⁺, 100);

HRMS (EI): *m/z* calcd for C₂₀H₁₂N₂ (M) 280.1000, found 280.1002.

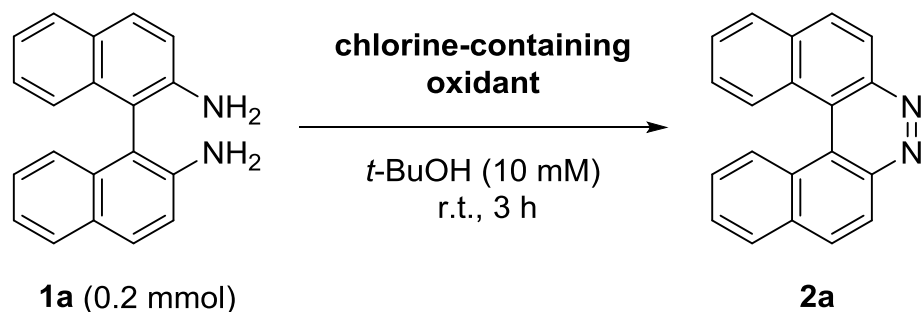
Table S1. The effect of solvents.



entry	solvent	yield (%) ^a	recovery of 1a (%) ^a
1	<i>t</i> -BuOH	89 ^b	0
2	<i>t</i> -BuOH ^c	54	0
3	THF	30	0
4	CH ₃ CN	22	0
5	CH ₂ Cl ₂	52	0
6	toluene	68	0
7	DMF	62	0
8	Et ₂ O	37	0
9	2-propanol	47	48
10	EtOH	61	0
11	MeOH	58	0

^a ¹H NMR yields. ^b isolated yield. ^c 40 mM.

Table S2. The effect of chlorine-containing oxidants.



entry	chlorine-containing oxidant (mmol)	yield (%) ^a	recovery of 1a (%) ^a
1	NCS (0.8)	0	63
2	DCH (0.4)	24 ^b	0
3	DCH (0.8)	57	0
4	NCPH (0.8)	0	95
5	TCCA (0.27)	20	0

^a ¹H NMR yields. ^b isolated yield.

Structures of chlorine-containing oxidants:

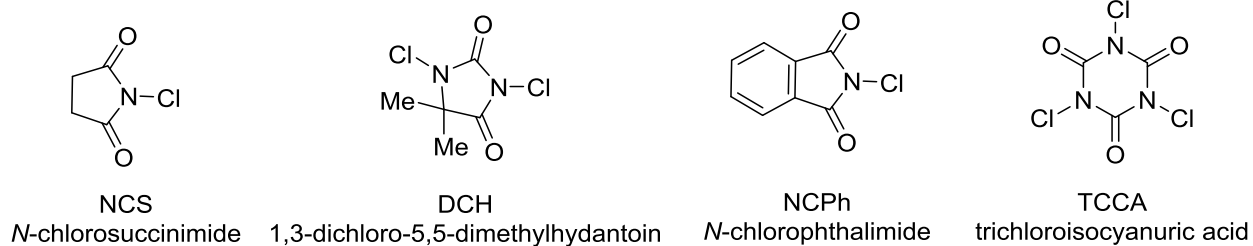
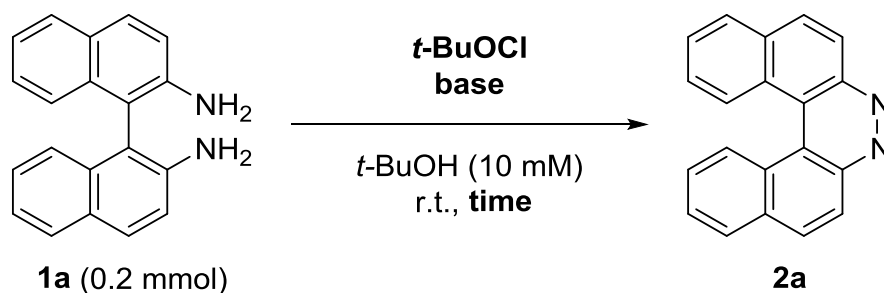


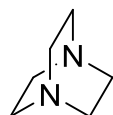
Table S3. The effect of equivalents of *t*-BuOCl and bases.



entry	<i>t</i> -BuOCl (mmol)	base (mmol)	time (h)	yield (%) ^a	recovery of 1a (%) ^a
1	0.6	-	3	93	0
2	0.4	-	3	54	34
3	0.4	-	24	71	19
4	0.4	K ₂ CO ₃ (0.4)	3	69	20
5	0.4	DABCO (0.4)	3	32	45
6	0.4	DBU (0.4)	3	0	34
7	0.4	NEt ₃ (0.4)	3	0	65
8	0.4	pyridine (0.4)	3	33	40
9	0.4	2,6-di- <i>tert</i> -butylpyridine (0.4)	3	77	19
10	0.4	2,6-lutidine (0.4)	3	90	10
11	0.4	2,6-lutidine (0.4)	7	92	8
12	0.44	2,6-lutidine (0.44)	3	97 ^b	0

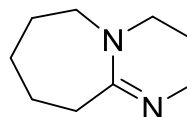
^a ¹H NMR yields. ^b isolated yield.

Structures of bases



DABCO

1,4-diazabicyclo[2.2.2]octane



DBU

1,8-diazabicyclo[5.4.0]undec-7-ene

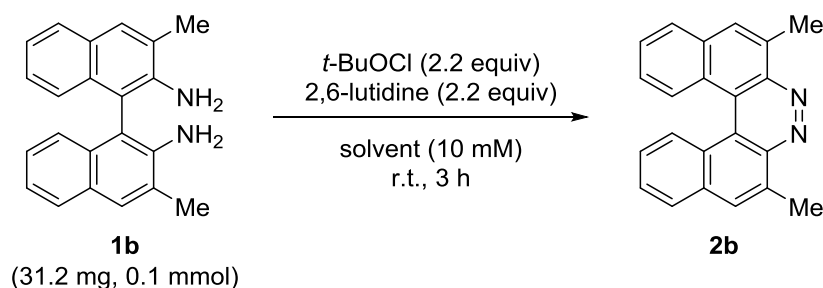
Oxidative ring-closure of biaryldiamines **1** and **3**

A typical procedure for the oxidative ring-closure of biaryldiamines **1** and **3**

To a two-necked round-bottomed flask (50 mL) equipped with a magnetic stir bar, was added biaryldiamine **1** (or **3**) (0.1 mmol) under the air. The flask was capped with a

rubber septum, evacuated, and refilled with N₂ gas for three times. Solvent (10 mL) and 2,6-lutidine (23.5 mg, 0.22 mmol or none) were added to the tube through the septum. To the mixture, was added *t*-BuOCl (23.8 mg, 0.22 mmol or 43.4 mg, 0.40 mmol) through the septum at the indicated temperature. The resulting solution was stirred for the indicated time (Table 2 in the text) before quenched with aqueous Na₂S₂O₃ solution (1.0 M, 20 mL), and the resulting mixture was extracted with CH₂Cl₂ (20 mL × 3). The combined organic extracts were dried over Na₂SO₄ and concentrated under vacuum to give the crude product. Purification by flash column chromatography on silica gel gave the corresponding 7,8-diaza[5]helicene (for example, compound **2a**: 27.2 mg, 97%).

Table S4. The oxidative ring-closure of biaryldiamine **1b**.

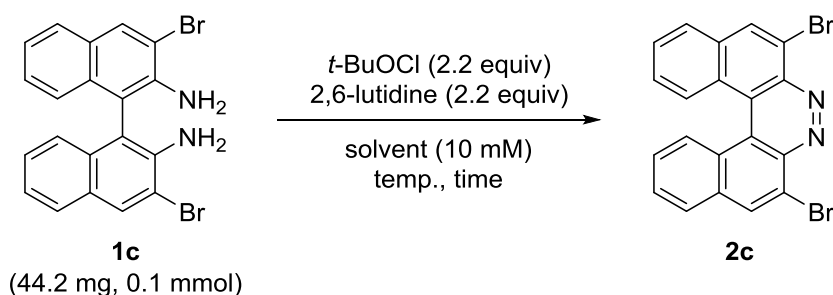


entry	solvent	yield (%) ^a	recovery of 1b (%) ^a
1	<i>t</i> -BuOH	32	22
2	MeOH	17	28
3	CH ₂ Cl ₂	16	trace
4	toluene	44 ^b	11 ^b

^a ¹H NMR yields. ^b isolated yield.

6,9-Dimethyl-7,8-diaza[5]helicene (**2b**)

Purified by flash column chromatography on NH silica gel (eluent: hexane/EtOAc 99:1) and recrystallization from hexane; Yellow solid (13.6 mg, 44%); mp 196 °C (dec.); *R*_f 0.33 (hexane/EtOAc 8:2, NH); ¹H NMR (400 MHz, CDCl₃) δ 3.16 (s, 6H), 7.31 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.64 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.95 (s, 2H), 8.71 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 18.5, 120.0, 124.5, 127.3, 127.5, 129.2, 129.5, 129.8, 134.0, 134.2, 145.9; IR (ATR) ν 2922, 1734, 1457, 1425, 1261, 1160, 1116, 889, 753 cm⁻¹; MS (EI): *m/z* (relative intensity, %) 308 (M⁺, 100), 280 ([C₂₂H₁₆]⁺, 31); HRMS (EI): *m/z* calcd for C₂₂H₁₆N₂ (M) 308.1313, found 308.1312.

Table S5. The oxidative ring-closure of biaryldiamine **1c**

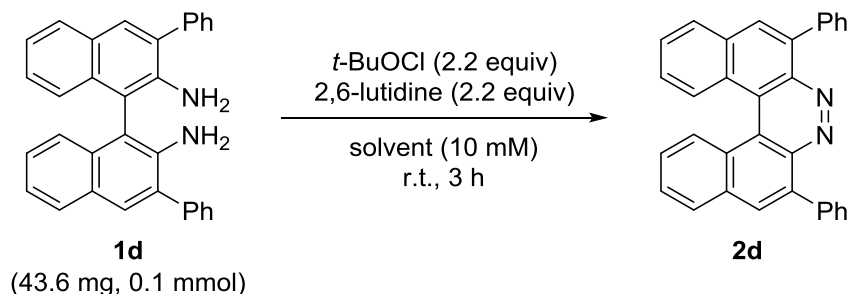
entry	solvent	temp. (°C)	time (h)	yield (%) ^a	recovery of 1c (%) ^a
1	<i>t</i> -BuOH	rt	20	44 ^b	15 ^b
2 ^c	<i>t</i> -BuOH	rt	19	77 ^b	0
3	<i>t</i> -BuOH	60	24	36	12
4	MeOH	rt	9	9	28
5	toluene	rt	24	15	0

^a ¹H NMR yields. ^b isolated yield. ^c *t*-BuOCl (4.0 equiv), 2,6-lutidine (0 equiv)

6,9-Dibromo-7,8-diaza[5]helicene (**2c**)

Parts of spectroscopic data are available in a literature.^{S10} Purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 99:1–95:5) and recrystallization from hexane/CHCl₃; Yellow solid (19.3 mg, 44% or 33.7 mg, 77%); mp 307 °C (dec.); *R*_f 0.40 (hexane/EtOAc 8:2); ¹H NMR (400 MHz, CDCl₃) δ 7.41 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.71 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 2H), 8.51 (s, 2H), 8.64 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 121.3, 121.6, 126.0, 127.4, 127.5, 129.5, 130.3, 134.4, 134.5, 143.6; IR (ATR) ν 3053, 1591, 1383, 1250, 1108, 960, 890, 837, 773, 753 cm⁻¹; MS (EI): *m/z* (relative intensity, %) 438 (M⁺, 50), 357 ([C₂₀H₁₀BrN₂]⁺, 14), 278 ([C₂₀H₁₀N₂]⁺, 23), 250 ([C₂₀H₁₀]⁺, 100); HRMS (EI): *m/z* calcd for C₂₀H₁₀Br₂N₂ (M) 435.9211, found 435.9210.

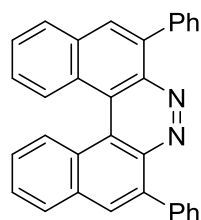
Table S6. The oxidative ring-closure of biaryldiamine **1d**.



entry	solvent	yield (%) ^a	recovery of 1d (%) ^a
1	<i>t</i> -BuOH	33 ^b	18 ^b
2	MeOH	28	24
3	toluene	87 ^b	0

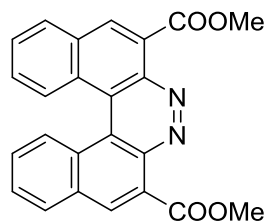
^a ¹H NMR yields. ^b isolated yield.

6,9-Diphenyl-7,8-diaza[5]helicene (**2d**)



Purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 97:3) and recrystallization from hexane/CHCl₃; Yellow solid (37.6 mg, 87%); mp 239 °C (dec.); *R*_f 0.35 (hexane/EtOAc 8:2); ¹H NMR (400 MHz, CDCl₃) δ 7.43–7.45 (m, 4H), 7.50 (dd, *J* = 7.6, 7.6 Hz, 4H), 7.72 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.82 (d, *J* = 6.8 Hz, 4H), 8.06 (d, *J* = 7.6 Hz, 2H), 8.17 (s, 2H), 8.79 (d, *J* = 8.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 120.1, 125.4, 127.7, 128.0, 128.1, 128.3, 129.4, 129.5, 130.9, 131.2, 133.8, 137.8, 138.4, 144.6; IR (ATR) ν 3027, 1494, 1445, 898, 766, 754 cm⁻¹; MS (EI): *m/z* (relative intensity, %) 432 (M⁺, 67), 431 ([C₃₂H₁₉N₂]⁺, 100); HRMS (EI): *m/z* calcd for C₃₂H₂₀N₂ (M) 432.1626, found 432.1624.

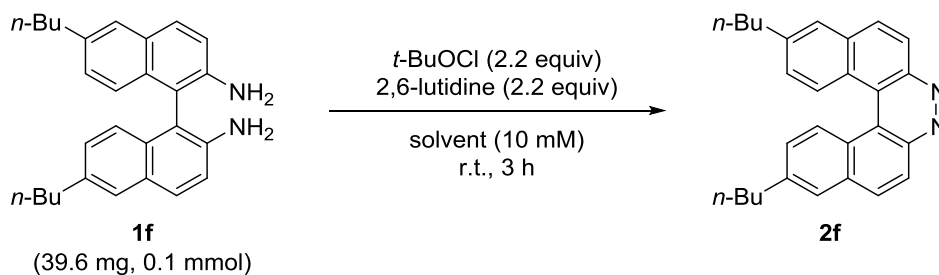
Dimethyl 7,8-diaza[5]helicene-6,9-dicarboxylate (**2e**)



Purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 8:2–5:5) and recrystallization from hexane/CHCl₃; Yellow solid (33.3 mg, 84%); mp 215 °C (dec.); *R*_f 0.35 (hexane/EtOAc 5:5); ¹H NMR (400 MHz, CDCl₃) δ 4.14 (s, 6H), 7.48 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.75 (dd, *J* = 8.0, 8.0 Hz, 2H), 8.07 (d, *J* = 8.0 Hz, 2H), 8.45 (s, 2H), 8.69 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 53.1, 119.7,

127.2, 128.8, 129.1, 129.2, 129.4, 130.1, 132.1, 132.6, 143.3, 168.0; IR (ATR) ν 2942, 1724, 1425, 1269, 1220, 1137, 781, 761 cm^{-1} ; MS (EI): m/z (relative intensity, %) 396 (M^+ , 32), 338 ($[\text{C}_{22}\text{H}_{14}\text{N}_2\text{O}_2]^+$, 100), 250 ($[\text{C}_{20}\text{H}_{10}]^+$, 18); HRMS (EI): m/z calcd for $\text{C}_{24}\text{H}_{16}\text{N}_2\text{O}_4$ (M) 396.1110, found 396.1112.

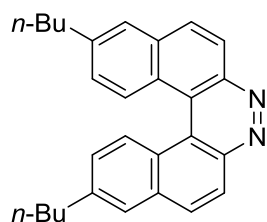
Table S7. The oxidative ring-closure of biaryldiamine **1f**.



entry	solvent	yield (%) ^a	recovery of 1f (%) ^a
1	<i>t</i> -BuOH	49	23
2	MeOH	26	0
3	toluene	72 ^b	0

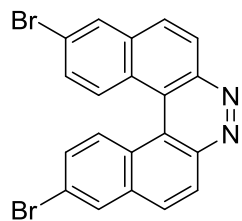
^a ¹H NMR yields. ^b isolated yield.

3,12-Di-*n*-butyl-7,8-diaza[5]helicene (**2f**)



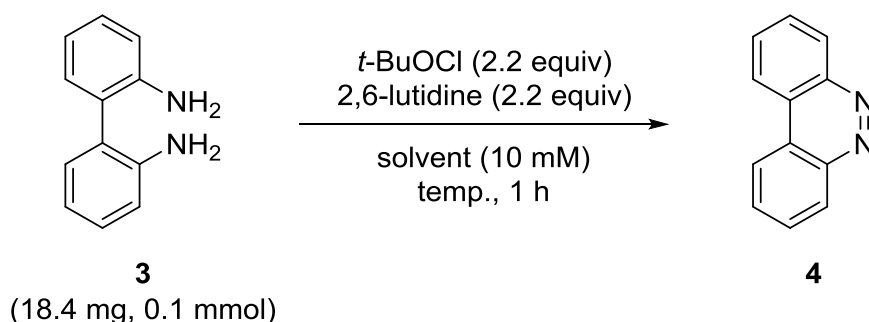
Purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 9:1–8:2) and recrystallization from hexane; Pale yellow solid (28.2 mg, 72%); mp 161 °C (dec.); R_f 0.18 (hexane/EtOAc 8:2); ¹H NMR (400 MHz, CDCl_3) δ 0.99 (t, $J = 7.6$ Hz, 6H), 1.44 (tq, $J = 7.6, 7.6$ Hz, 4H), 1.76 (tt, $J = 7.6, 7.6$ Hz, 4H), 2.86 (t, $J = 7.6$ Hz, 4H), 7.28 (dd, $J = 1.6, 8.4$ Hz, 2H), 7.80 (d, $J = 1.6$ Hz, 2H), 8.09 (d, $J = 8.8$ Hz, 2H), 8.49 (d, $J = 8.8$ Hz, 2H), 8.75 (d, $J = 8.4$ Hz, 2H); ¹³C NMR (100 MHz, CDCl_3) δ 13.9, 22.5, 33.3, 35.7, 120.0, 126.1, 126.5, 126.9, 129.1, 130.5, 134.4, 144.6, 146.6 (one carbon is unsatisfied, probably due to the overlap of signals.); IR (ATR) ν 2930, 1618, 1464, 1259, 1105, 891, 827, 810 cm^{-1} ; MS (EI): m/z (relative intensity, %) 392 (M^+ , 100), 364 ($[\text{C}_{28}\text{H}_{28}]^+$, 15), 349 ($[\text{C}_{27}\text{H}_{25}]^+$, 12), 335 ($[\text{C}_{26}\text{H}_{23}]^+$, 31), 321 ($[\text{C}_{25}\text{H}_{21}]^+$, 17), 307 ($[\text{C}_{24}\text{H}_{19}]^+$, 47); HRMS (EI): m/z calcd for $\text{C}_{28}\text{H}_{28}\text{N}_2$ (M) 392.2252, found 392.2251.

3,12-Dibromo-7,8-diaza[5]helicene (2g)



Purified by flash column chromatography on silica gel (eluent: hexane/EtOAc 9:1–7:3) and recrystallization from CHCl₃; Brown solid (39.9 mg, 91%); mp 205 °C (dec.); *R*_f 0.18 (hexane/EtOAc 8:2); ¹H NMR (400 MHz, CDCl₃) δ 7.55 (dd, *J* = 2.0, 8.8 Hz, 2H), 8.09 (d, *J* = 8.8 Hz, 2H), 8.20 (d, *J* = 2.0 Hz, 2H), 8.58 (d, *J* = 8.8 Hz, 2H), 8.61 (d, *J* = 8.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 119.4, 123.8, 126.4, 127.9, 129.0, 129.8, 130.4, 130.5, 135.6, 146.5; IR (ATR) ν 3061, 1591, 1495, 1436, 1263, 1086, 876, 852, 833, 820, 803 cm⁻¹; MS (EI): *m/z* (relative intensity, %) 438 (M⁺, 69), 278 ([C₂₀H₁₀N₂]⁺, 79), 250 ([C₂₀H₁₀]⁺, 100); HRMS (EI): *m/z* calcd for C₂₀H₁₀N₂Br₂ (M) 435.9211, found 435.9208.

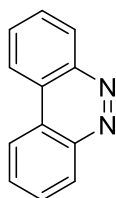
Table S8. The oxidative ring-closure of biaryldiamine **3**.



entry	solvent	temp. (°C)	yield (%) ^a	recovery of 3 (%) ^a
1	<i>t</i> -BuOH	rt	53	trace
2	MeOH	rt	42	0
3	MeOH	0	65 ^b	0
4	MeOH	-40	85 ^b	0

^a ¹H NMR yields. ^b isolated yields.

Benzo[*c*]cinnoline (**4**) [230-17-1]



Spectroscopic data were in agreement with those previously reported.^{S11} The spectroscopic data are also available in our previous paper.^{S9} Purified by flash column chromatography on silica gel (hexane/EtOAc 95:5 to 8:2); Yellow solid; *R*_f 0.18 (hexane/EtOAc 8:2).

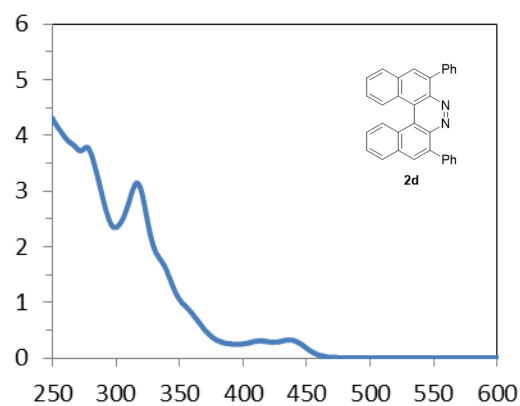
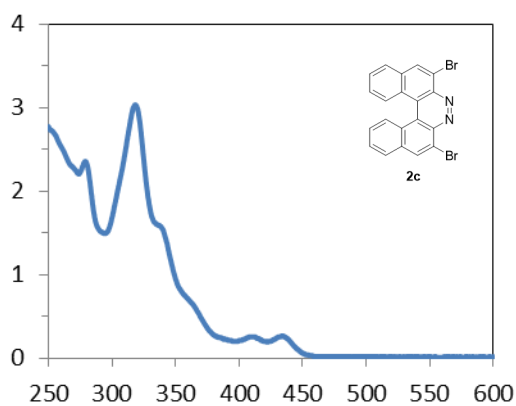
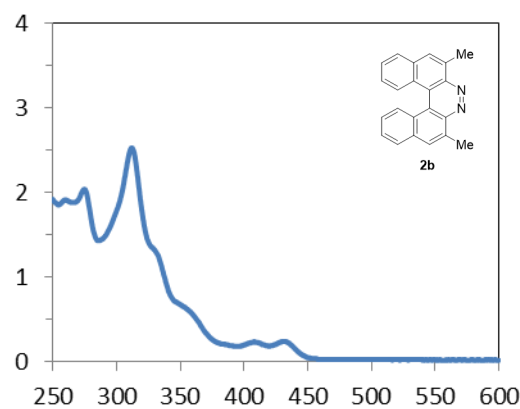
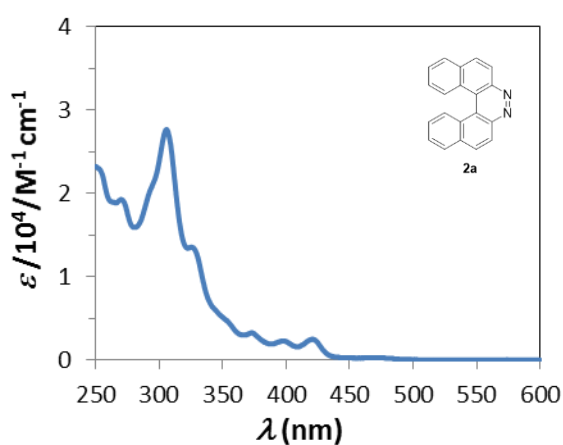
Physicochemical properties

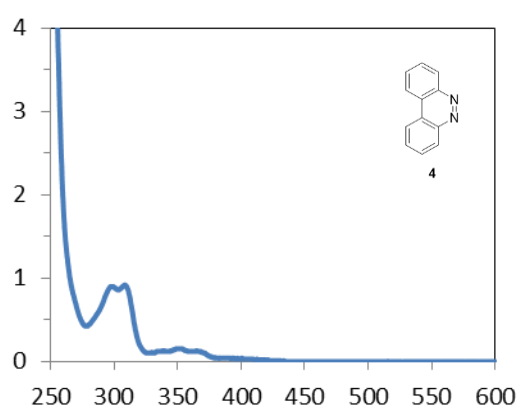
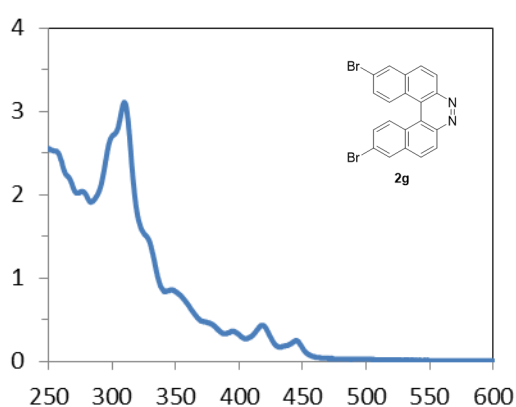
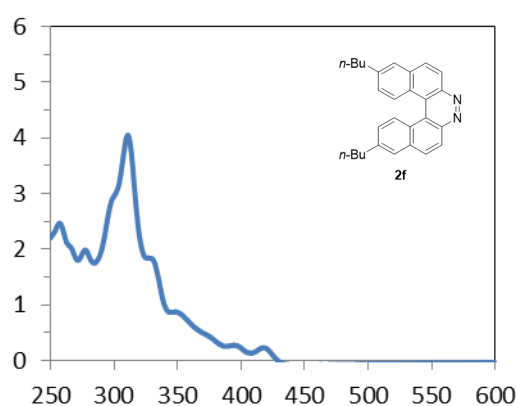
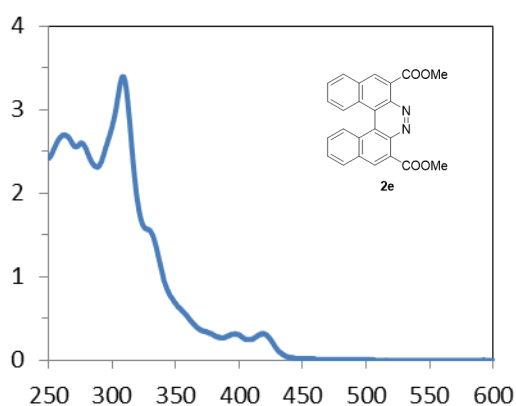
Table S9. Summary of physicochemical properties of diazahelicenes **2** and cinnoline **4**.

	Absorption		Emission (solution)		CV (vs. Fc/Fc ⁺)				TGA
	λ_{max} (nm)	ϵ (M ⁻¹ cm ⁻¹)	λ_{ex} (nm)	Φ_{FL}	$^{\text{red}}E_{\text{pc}}$ (V)	$^{\text{red}}E_{\text{pa}}$ (V)	$^{\text{red}}E_{1/2}$ (V)	LUMO level (eV)	T_{d} (5wt% loss) (°C)
2a	306, 398, 421	27672, 2294, 2509	300	0.02	-1.92	-1.83	-1.88	-2.92	251
2b	312, 408, 431	25282, 2403, 2403	300	<0.01	-	-	-	-	268
2c	318, 410, 434	30326, 2580, 2688	300	<0.01	-1.70	-1.62	-1.66	-3.13	306
2d	316, 413, 436	31470, 3157, 3266	300	<0.01	-1.93	-1.80	-1.86	-2.93	222
2e	309, 397, 419	33950, 3223, 3223	300	<0.01	-1.74	-1.61	-1.67	-3.12	315
2f	311, 392, 418	40513, 2715, 2280	300	<0.01	-	-	-	-	300
2g	310, 395, 418, 445	31106, 3635, 4342, 2524	300	<0.01	-1.80	-1.72	-1.76	-3.03	277
4	298,308,351, 357	8990,9192, 1515, 1313	300	0.15	-	-	-	-	172

UV-vis and emission spectra

CH₂Cl₂ (fluorescence spectroscopic grade) was purged with N₂ for 30 min before the measurements. UV-vis and emission spectra of diazahelicenes **2** and cinnoline **4** were measured at room temperature using CH₂Cl₂ solutions (1.0 × 10⁻⁵ M).

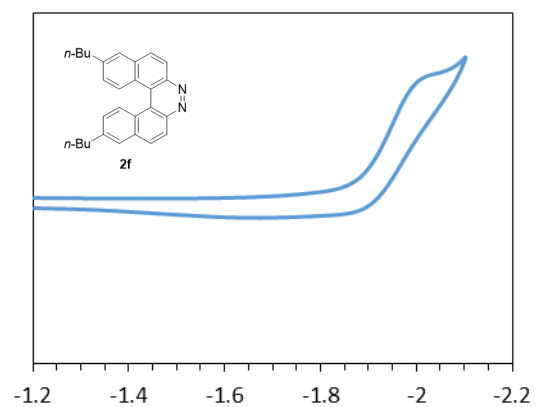
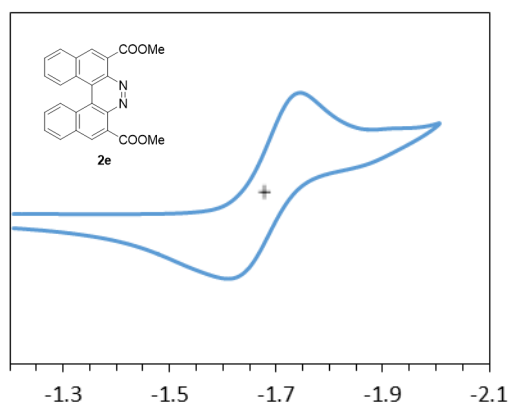
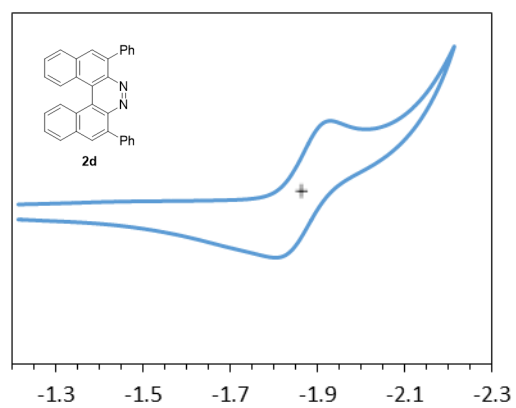
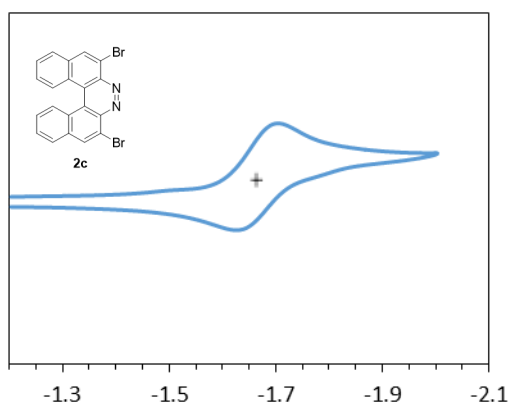
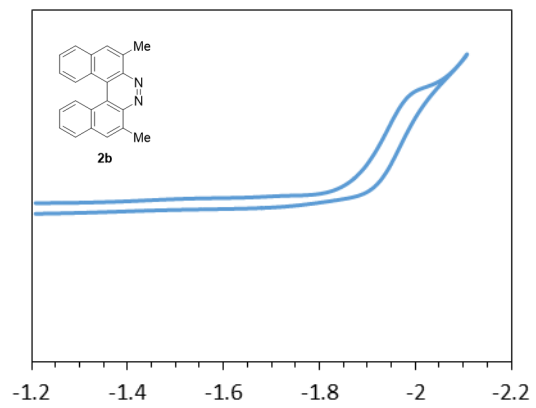
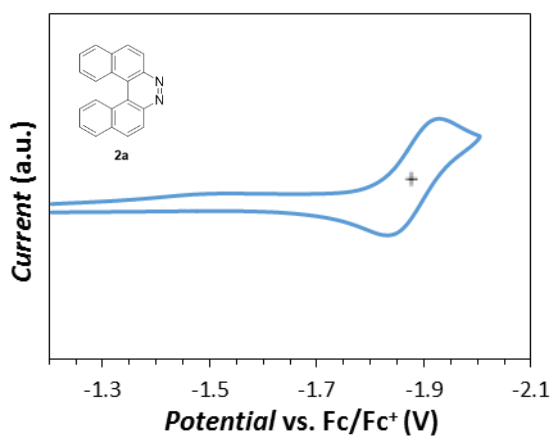


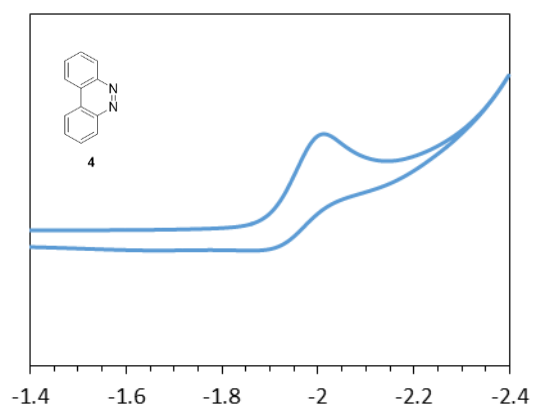
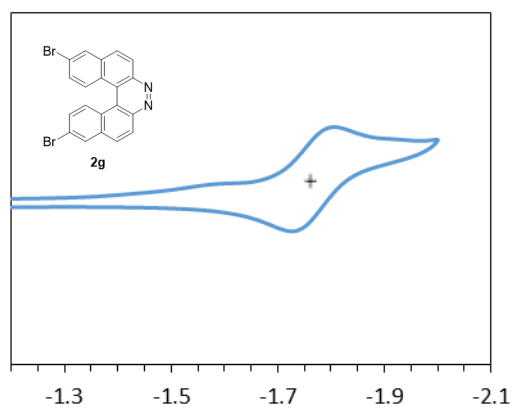


Cyclic voltammetry

Cyclic voltammetry experiments were conducted at room temperature with CH_2Cl_2 solutions of diazahelicenes **2** and cinnoline **4** (5.0×10^{-4} M) containing 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte in a cell equipped with a Pt as the working electrode (scanning rate: 100 m/V). A Pt wire and an Ag wire were applied as the counter and the reference electrode, respectively. All the potentials were corrected against the Fc/Fc^+ (Fc = ferrocene) couple and the values of LUMO levels were calculated with the equation S1.

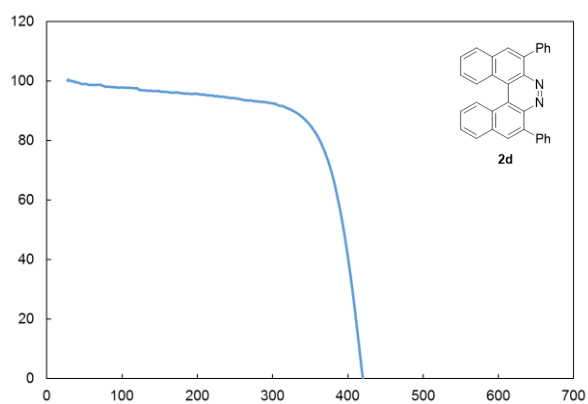
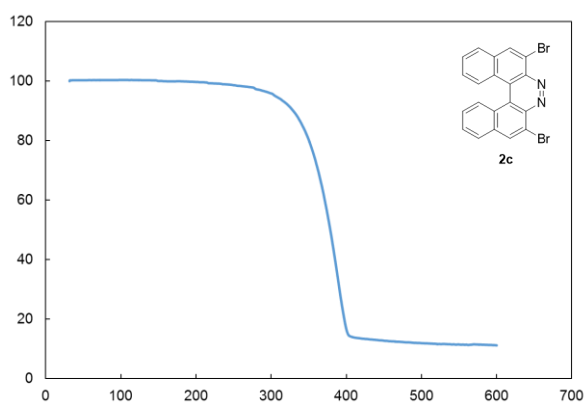
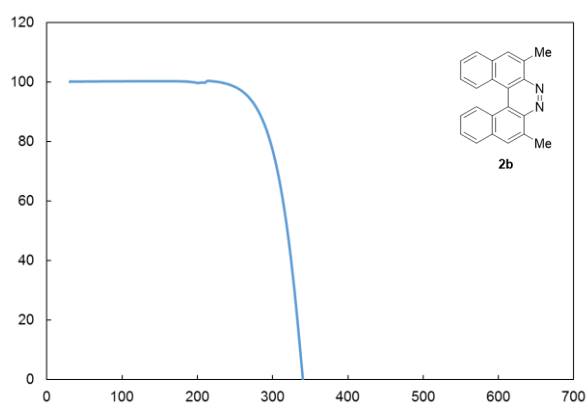
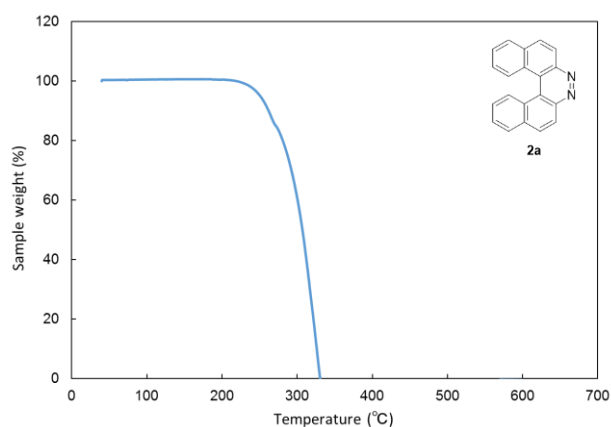
$$\text{LUMO} = -(4.8 + {}^{\text{red}}E_{1/2} \text{ vs. Fc/Fc}^+) \quad (\text{S1})$$

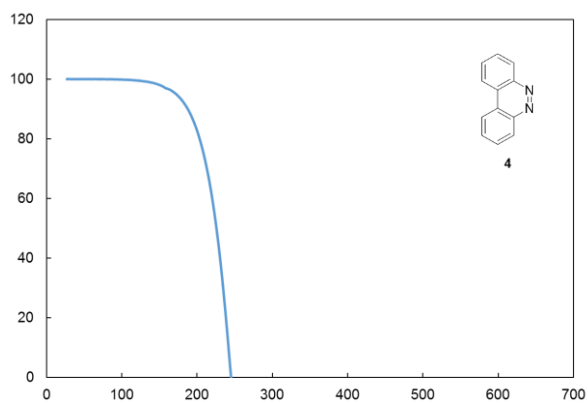
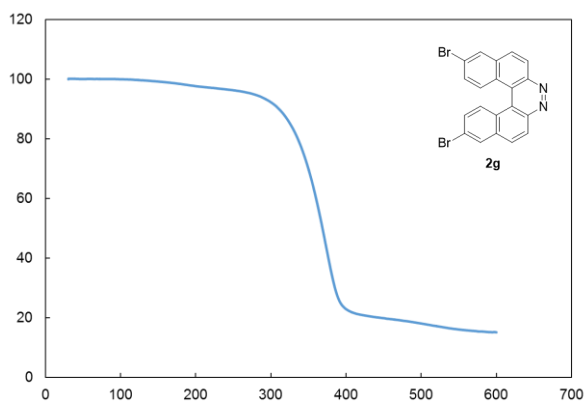
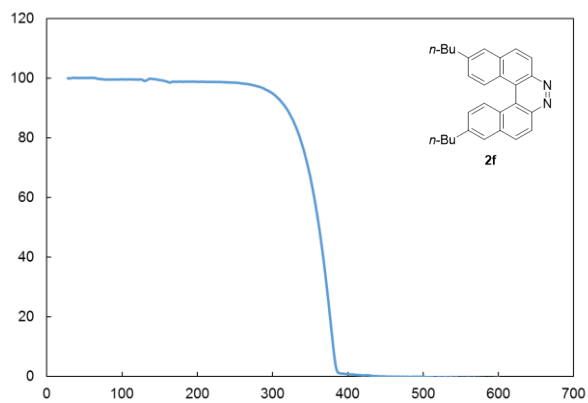
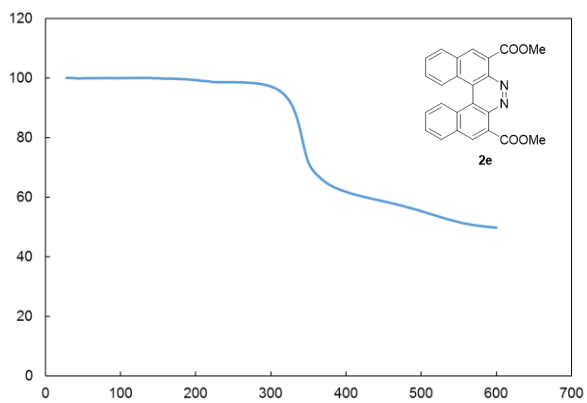




Thermogravimetric analysis (TGA)

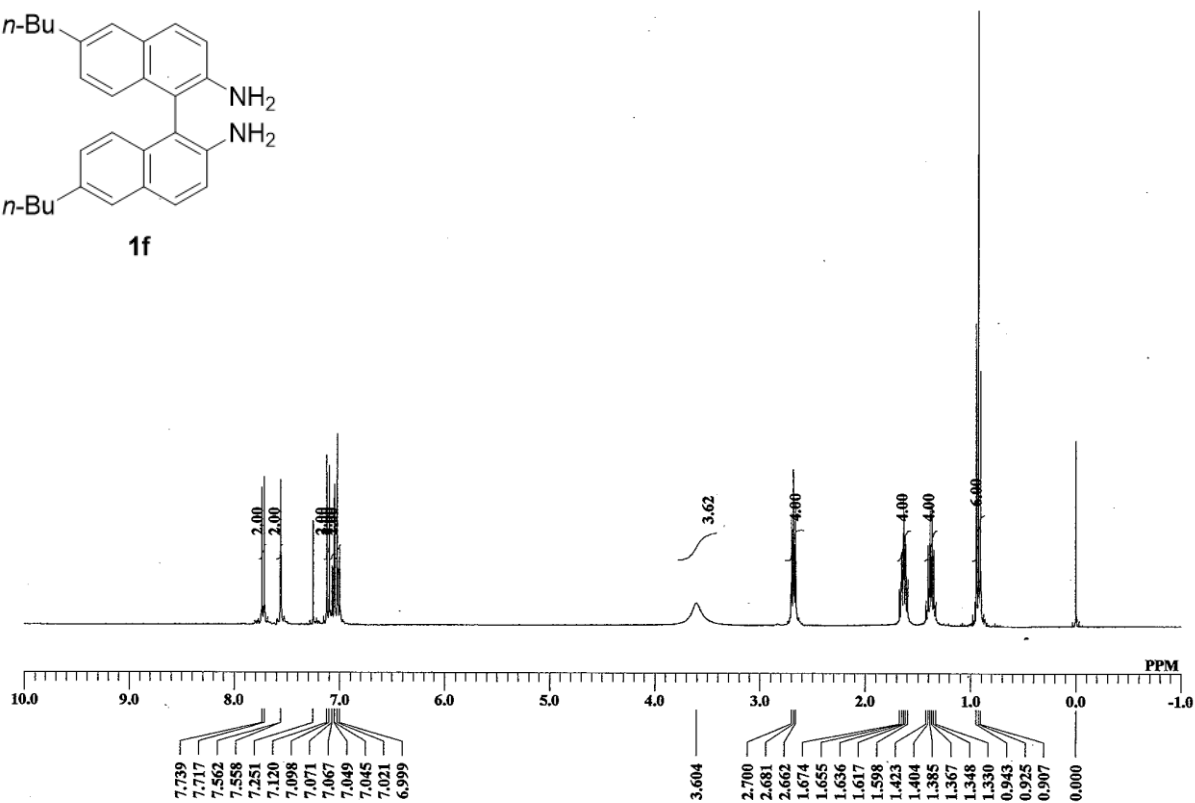
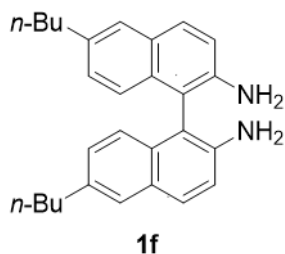
All the TGA profiles of diazahelicenes **2** and cinnoline **4** were measured under the nitrogen flow (200 mL/min), starting from 40 °C to 600 °C at the ramp rate of 10 °C/min.



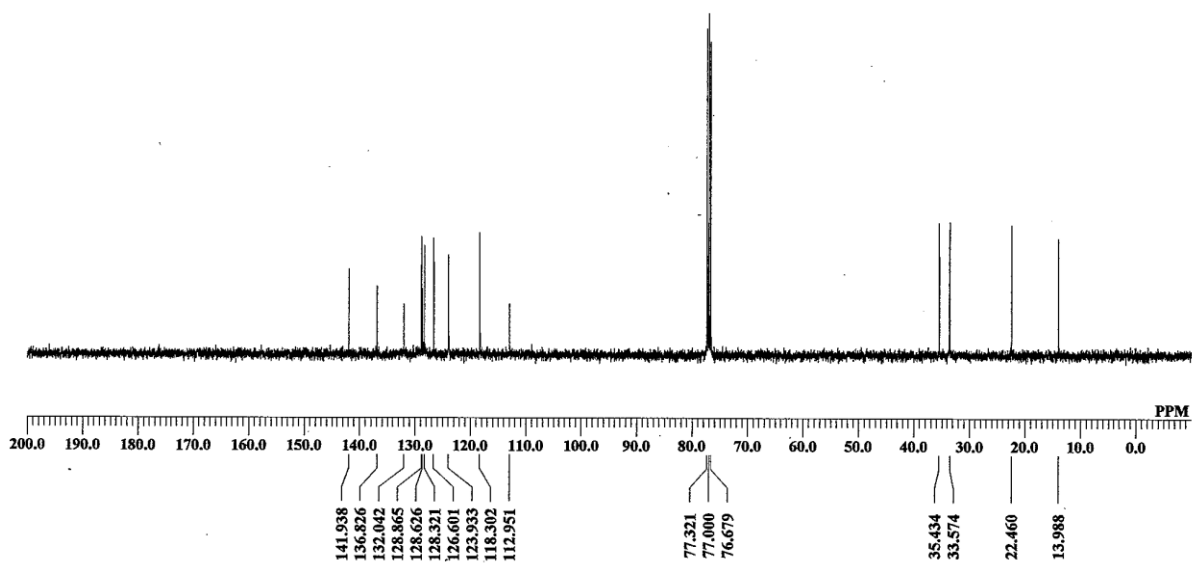


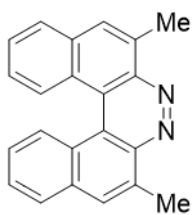
^1H and ^{13}C NMR spectra

^1H NMR: (400 MHz, CDCl_3)



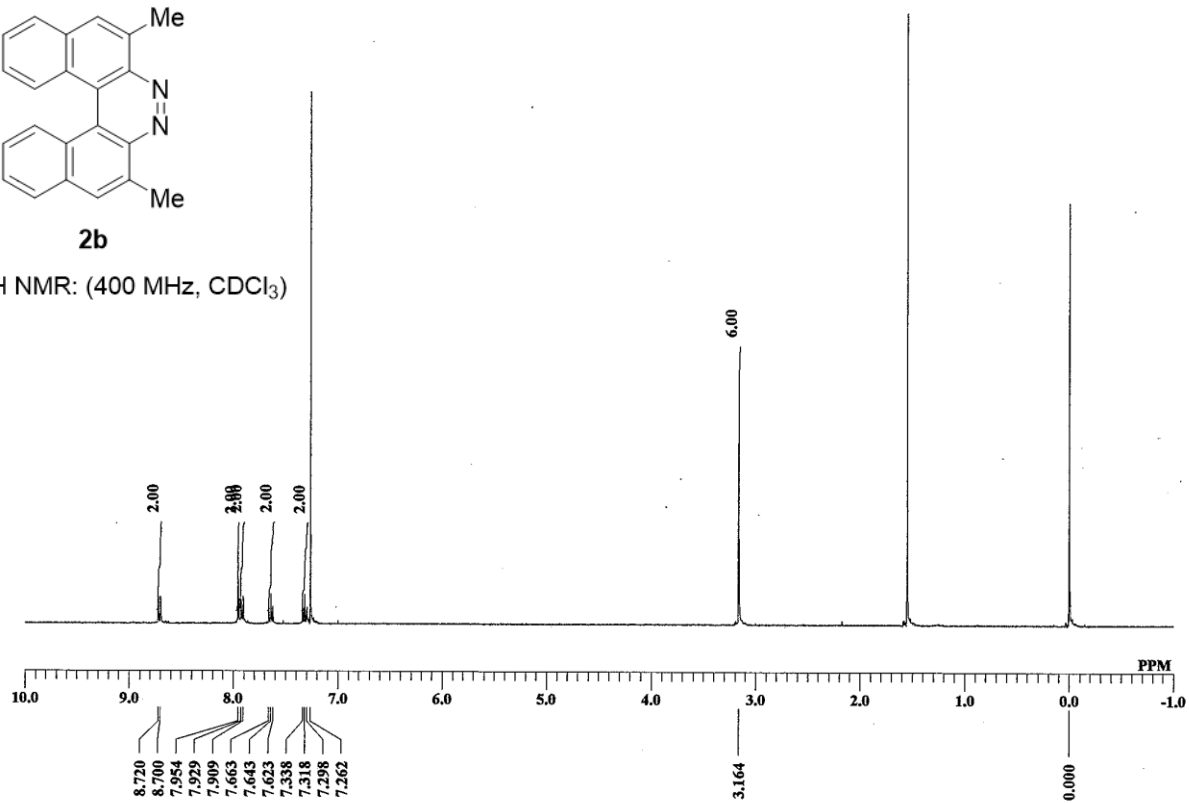
^{13}C NMR: (100 MHz, CDCl_3)



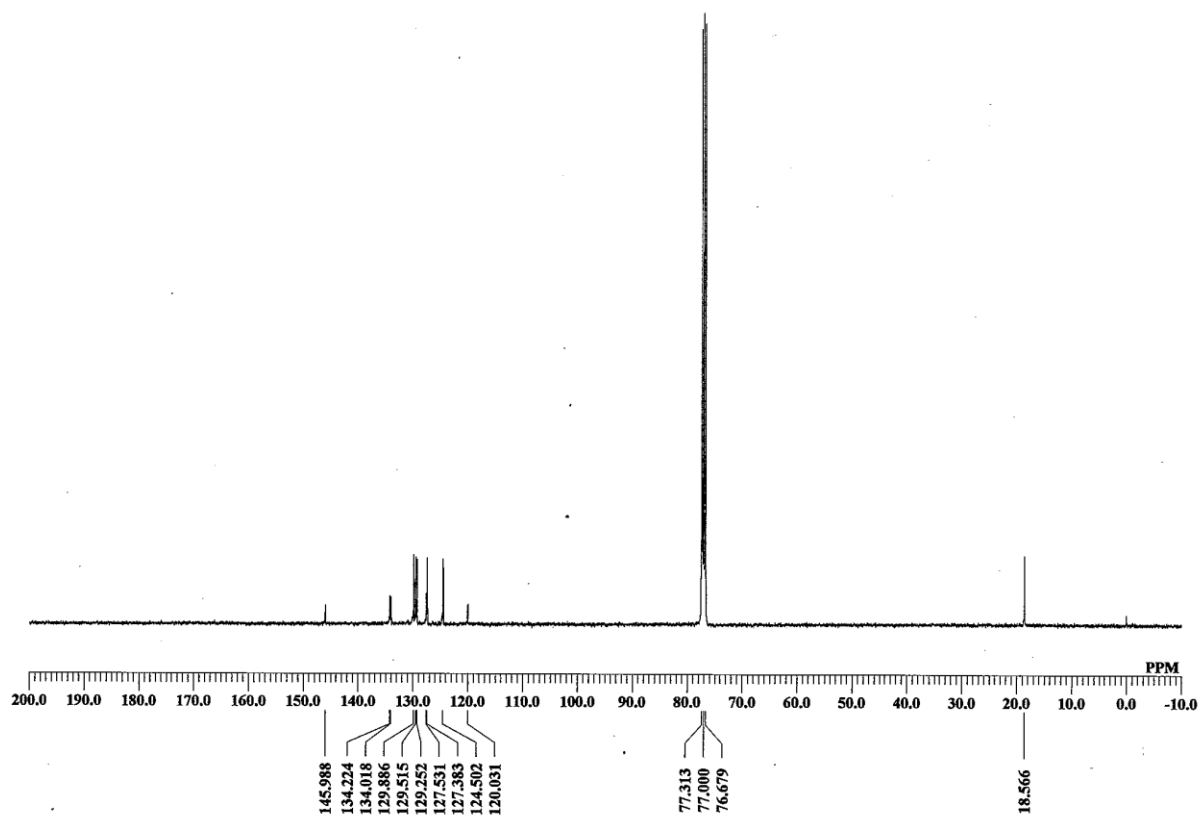


2b

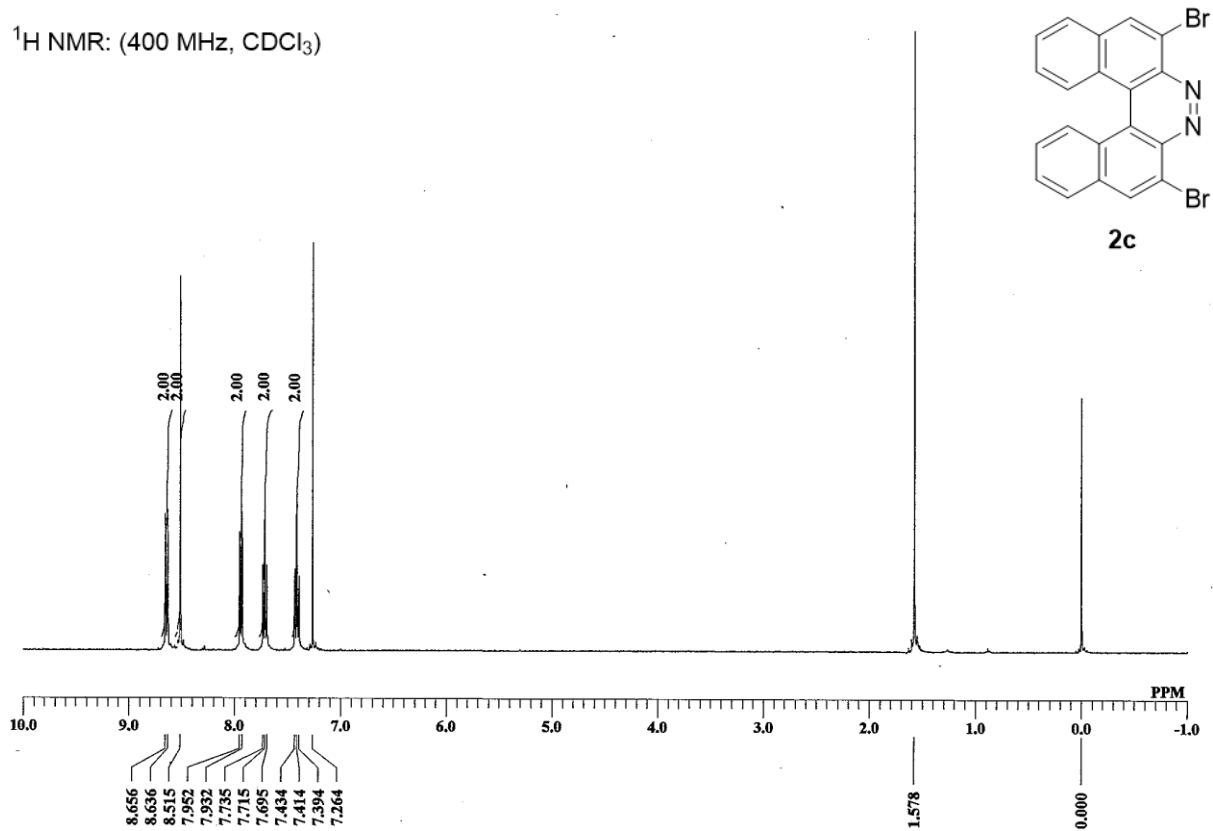
$^1\text{H NMR}$: (400 MHz, CDCl_3)



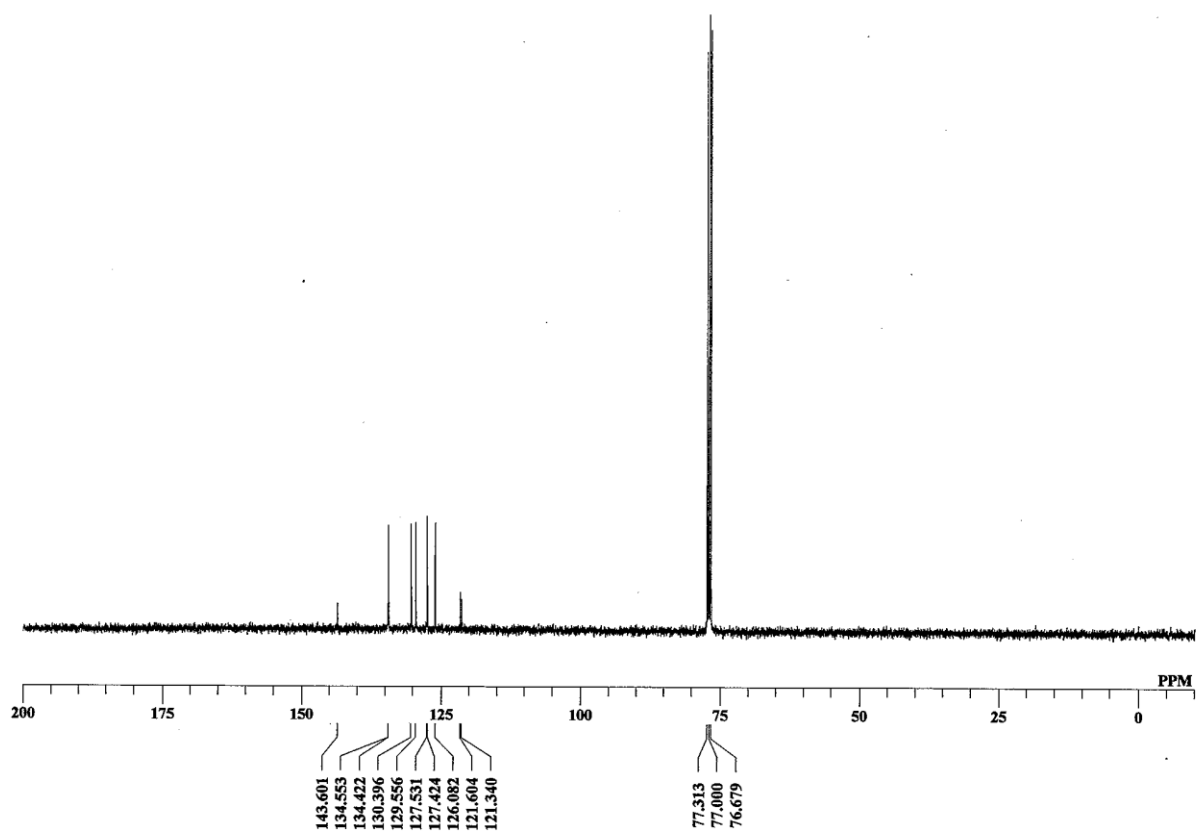
$^{13}\text{C NMR}$: (100 MHz, CDCl_3)



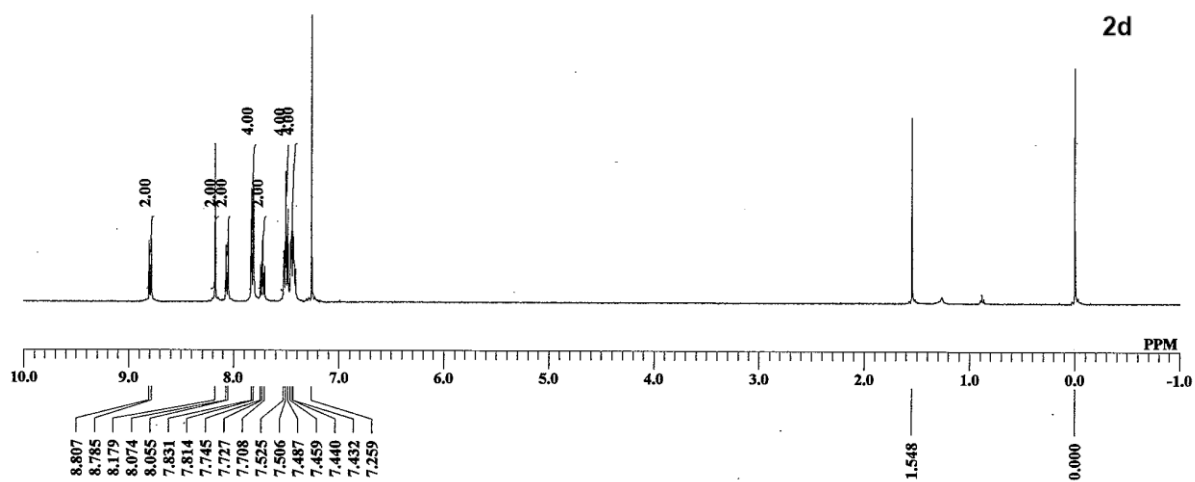
^1H NMR: (400 MHz, CDCl_3)



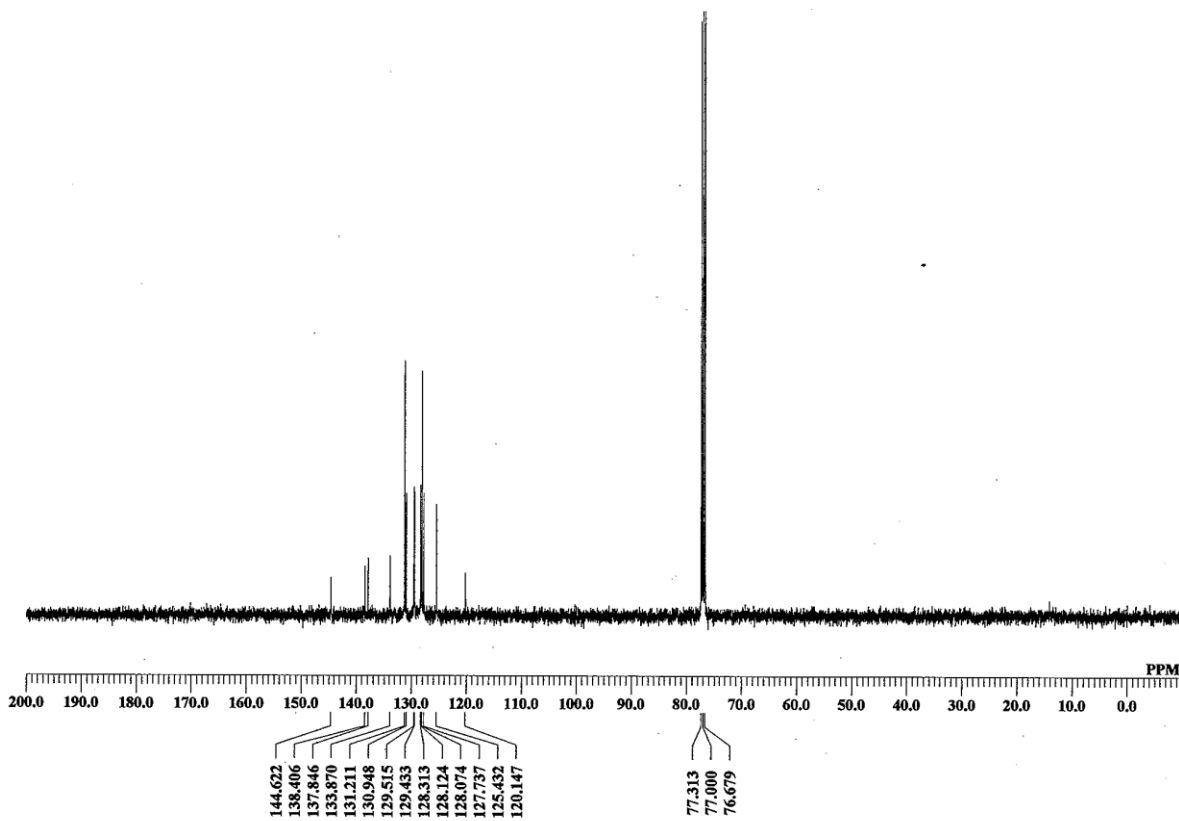
^{13}C NMR: (100 MHz, CDCl_3)



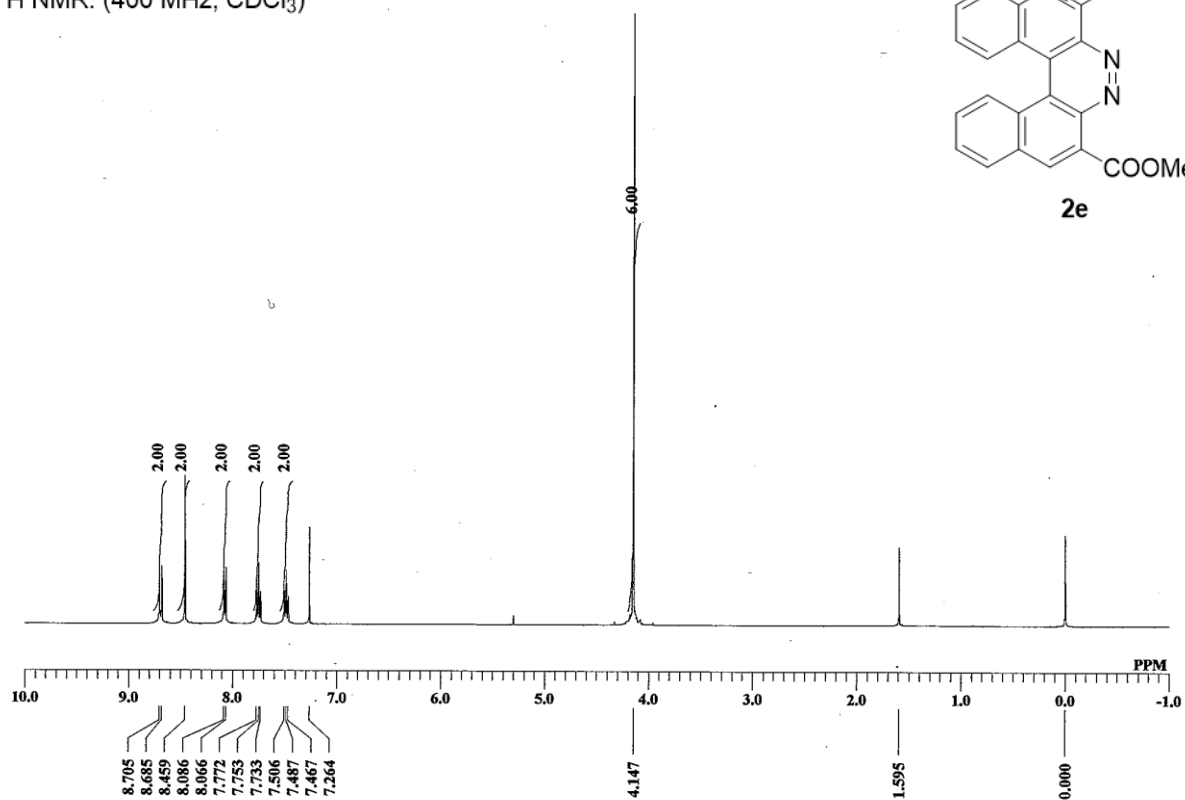
^1H NMR: (400 MHz, CDCl_3)



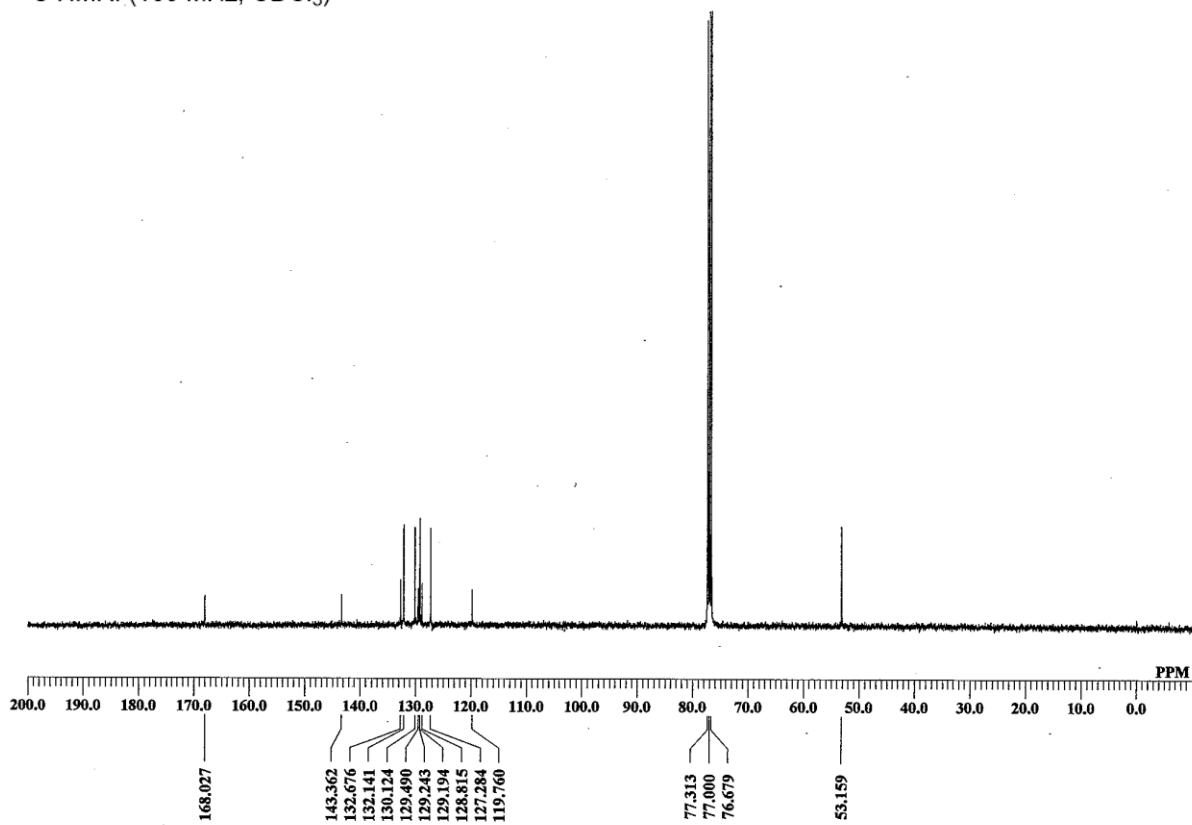
^{13}C NMR: (100 MHz, CDCl_3)



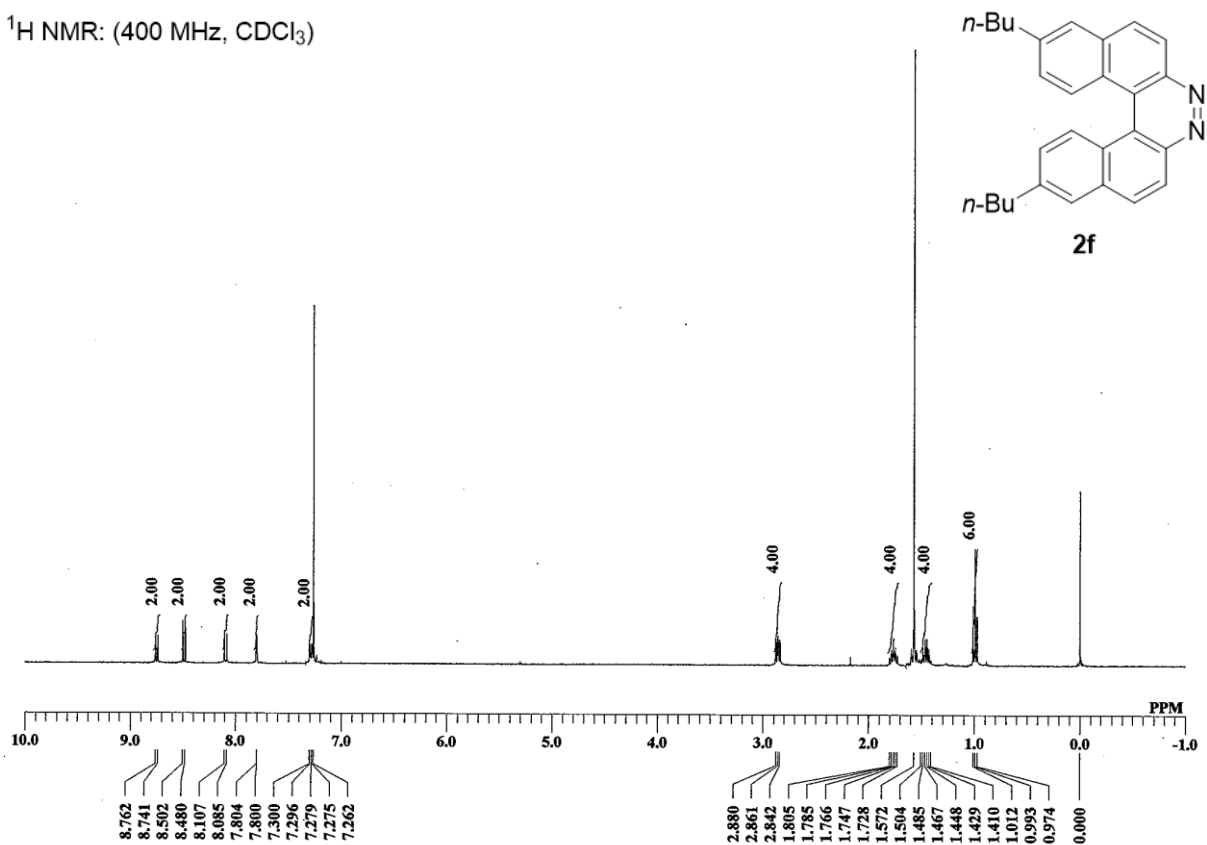
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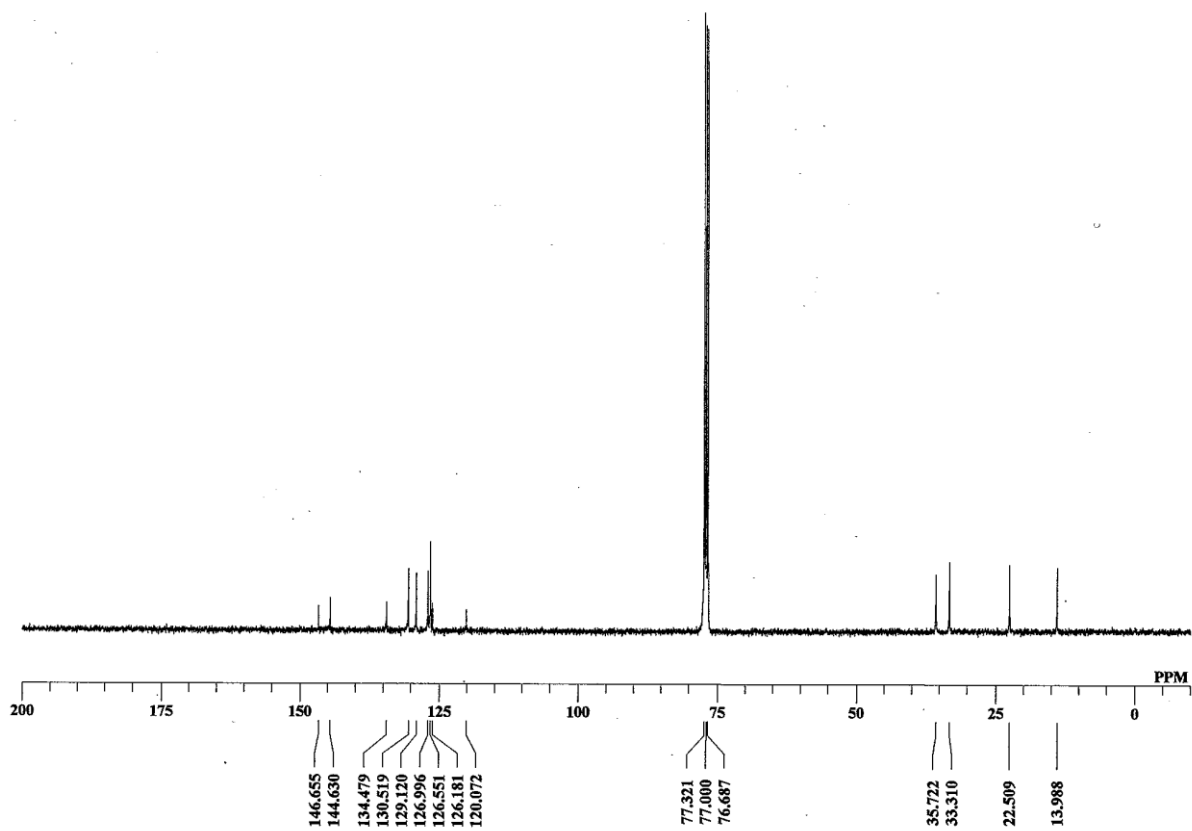
^{13}C NMR: (100 MHz, CDCl_3)



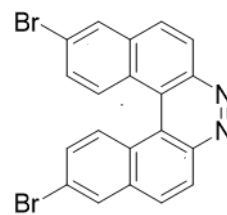
^1H NMR: (400 MHz, CDCl_3)



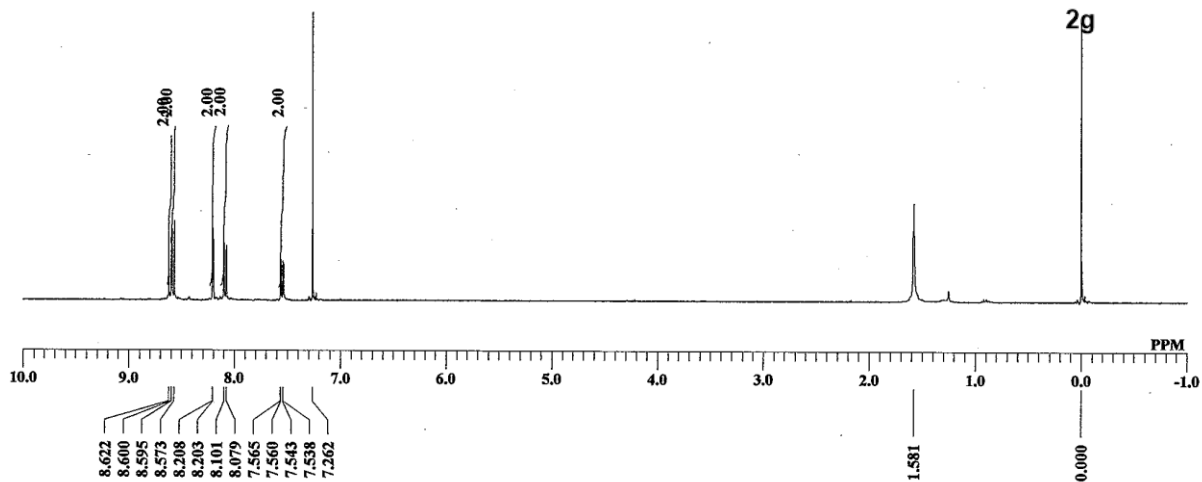
^{13}C NMR: (100 MHz, CDCl_3)



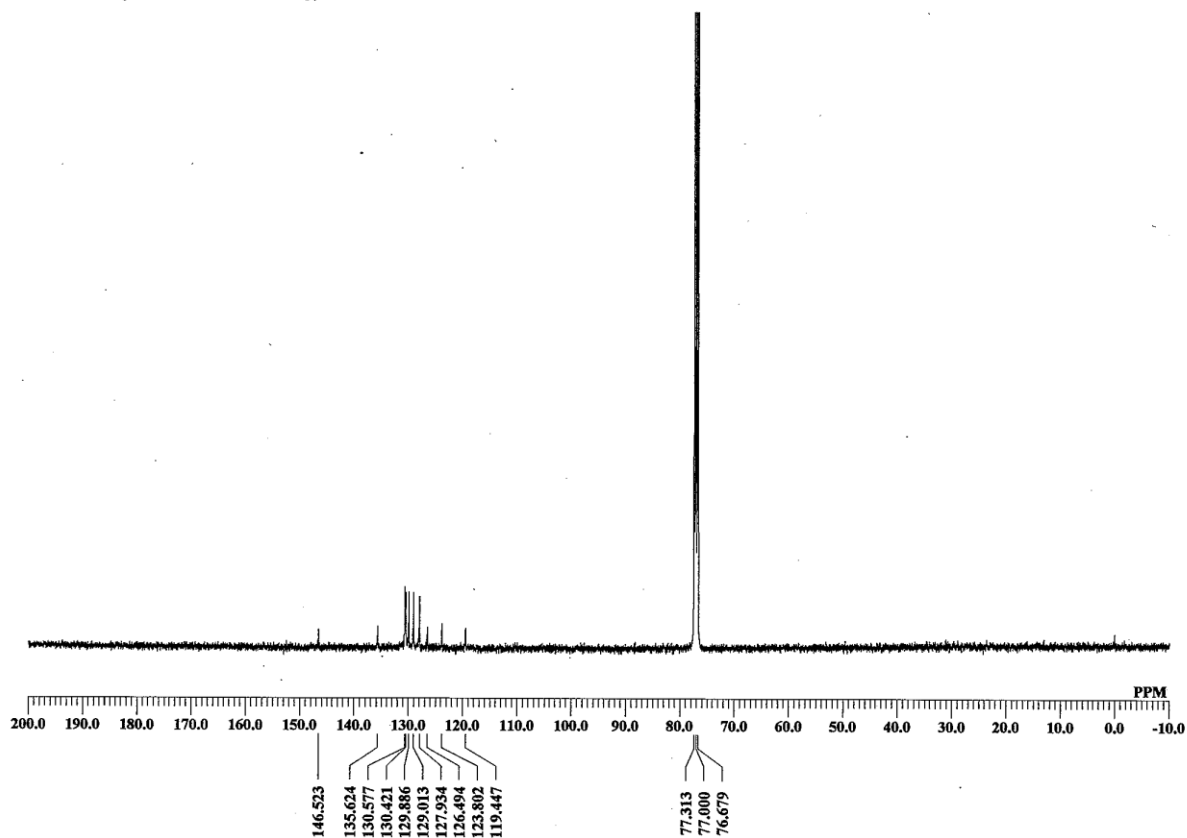
^1H NMR: (400 MHz, CDCl_3)



2g



^{13}C NMR: (100 MHz, CDCl_3)



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