Electronic Supplementary Information (ESI) for

Oxidative Skeletal Rearrangement of 1,1'-Binaphthalene-2,2'-Diamines (BINAMs) via C–C Bond Cleavage and Nitrogen Migration : A Versatile Synthesis of U-Shaped Azaacenes

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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. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JMTC-400/54/SS spectrometer (^{1}H 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. Single crystal X-ray diffraction data were collected on a Rigaku R-AXIS RAPID diffractometer with a graphite monochromated Cu-Kα radiation. 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 F_{254} and Fuji Silysia Chromatorex NH, 0.25 mm thickness). Compounds were visualized with UV lamp.

Materials

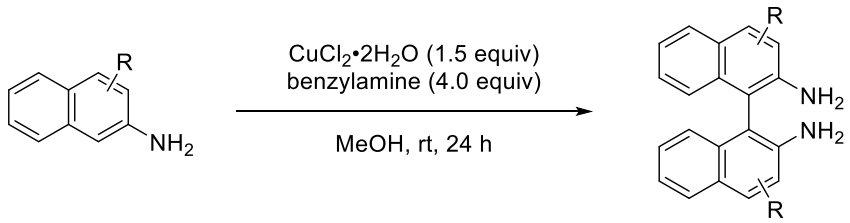
1,1'-binaphthalene-2,2'-diamine (BINAM) was purchased from Sigma-Aldrich and used as received. *N*-iodophthalimide (NIPh)[S1] [20919-42-0], *N*-iodosaccharin (NISac)[S2] [86340-94-5], *N*-iodopyrrolidone (NIPy)[S3] [1267636-41-8], 2,4,6,8-tetraiodoglycouril (TIG)[S4] [176799-09-0], 2-aminonaphthalene[S5] [91-59-8] and [SIPr-Pd(cinnamyl)Cl][S6] [884879-24-7] were prepared according to the procedures in literature. Piperidine, morpholine and triethylamine were purified by Kugelrohr distillation, 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, CH_3CN and Et_2O were purchased as dehydrated grade and dried by passing through a glass contour solvent dispensing system (Nikko Hansen & Co., Ltd.). Dehydrated CH_2Cl_2, toluene, benzene and dimethoxyethane (DME) were purchased from Kanto Chemical Co., Inc and used as received. Cyclohexane and *n*-octane were distilled using CaH_2 as a dehydrating agent. DMF was distilled using $CaSO_4$ as a dehydrating agent. Spectroscopic grade CH_2Cl_2 was purchased from Nacalai Tesque Inc. for the measurement of UV-vis spectra. CH_2Cl_2 (fluorescence spectroscopic grade) was purchased from Kanto Chemical Co., Inc. for the measurement of emission spectra. Biaryldiamines **1b**[S7] [360779-01-7], **1d**[S8] [1051425-55-8], **1e**[S9] [1229013-43-7], **1g**[S10] [861890-12-2], **1h**[S11] [103278-14-4], **5**[S12] [93013-27-5], **8**[S13] [1454-80-4] and dimethyl 2,2'-diamino-1,1'-binaphthalene-3,3'-

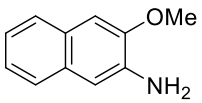
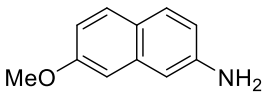
dicarboxylate (**S1**)[S14] [155855-47-3] were prepared according to the procedures in literature. Biaryldiamines **1c** and **1f** were prepared by modified oxidative coupling method[S11] of corresponding aminonaphthalene as follows.

A Typical Procedure for the Preparation of Dimethoxy-substituted BINAMs

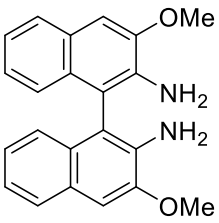
Methanol was degassed through freeze-pump-thaw cycling for three times before use. To a three-necked round-bottomed flask (500 mL) equipped with a magnetic stir bar, was added $CuCl_2$•$2H_2O$ (3.27 g, 19.2 mmol) under the air. The flask was capped with a rubber septum and evacuated and refilled with N_2 gas for three times. Degassed methanol (105 mL) and a methanol solution of benzylamine (5.49 g, 51.2 mmol, 64 mL) were added to the flask through the septum, and the mixture was purged by bubbling N_2 gas for 5 min. A methanol solution of 3-methoxynaphthalen-2-amine (2.22 g, 12.8 mmol, 64 mL) was added to the solution through the septum, and the mixture was stirred under N_2 atmosphere at room temperature for 24 h. With cooling the flask in an ice bath, the reaction mixture was acidified with 12 M HCl aq. (64 mL), stirred for 5 min, treated with 28% NH_3 aq. (128 mL), and stirred for another 5 min. The resulting mixture was diluted with water (1.28 L) and extracted with CH_2Cl_2 (100 mL × 3). The organic extract was dried over Na_2SO_4 and concentrated under vacuum to give the crude product, which was purified by flash column chromatography on silica gel to give biaryldiamine **1c** (31%).

Table S1. Preparation of Dimethoxy-substituted BINAMs



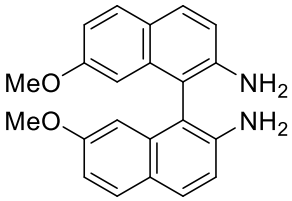
entry	starting material	product	yield (%)
1	 (12.8 mmol)	**1c**	31
2	 (7 mmol)	**1f**	31

3,3'-dimethoxy-1,1'-binaphthalene-2,2'-diamine (1c) [1434075-68-9]



Spectroscopic data were in agreement with those previously reported;[S15] Purified by flash column chromatography on silica gel (hexane/EtOAc 95:5 to 8:2); Pale yellow solid; R_f 0.13 (hexane/EtOAc 8:2).

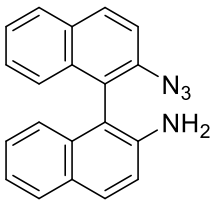
7,7'-dimethoxy-1,1'-binaphthalene-2,2'-diamine (1f) [1434075-66-7]



Spectroscopic data were in agreement with those previously reported;[S15] Purified by flash column chromatography on silica gel (hexane/EtOAc 8:2); Pale yellow solid; R_f 0.18 (hexane/EtOAc 7:3).

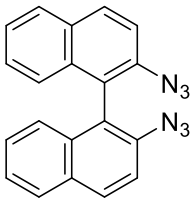
Preparation of Binaphthalene Azides

2'-azido-[1,1'-binaphthalen]-2-amine (10)



Prepared from 1,1'-binaphthalene-2,2'-diamine (**1a**) according to the modified procedure described in literature:[S16] To a two-necked round-bottomed flask (100 mL) equipped with a magnetic stir bar, was added diamine **1a** (1.42 g, 5.0 mmol) under the air. The flask was capped with a rubber septum and evacuated and refilled with N_2 gas for three times. CH_3CN (50 mL) was added through the septum, and the mixture was cooled to 0 °C in an ice bath. To the mixture, was added *t*-BuONO (386.7 mg, 3.75 mmol), followed by adding $TMSN_3$ (345.6 mg, 3.0 mmol) dropwise. The resulting solution was stirred at room temperature for 1 h and concentrated under vacuum to give a residue. The crude product was purified by column chromatography on NH silica gel (hexane/EtOAc 10:0 to 9:1) to give product **10**. Pale yellow solid (636.2 mg, 41%); mp 62 °C (dec.); R_f 0.25 (hexane/EtOAc 8:2, NH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.57 (br, 2H), 6.89 (d, J = 7.2 Hz, 1H), 7.13 (d, J = 8.8 Hz, 1H), 7.18–7.28 (m, 3H), 7.32 (dd, J = 7.6, 8.0 Hz, 1H), 7.45 (dd, J = 7.6, 8.8 Hz, 1H), 7.50 (d, J = 8.8 Hz, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.8, 117.9, 118.0, 122.5, 123.4, 123.8, 125.5, 125.6, 126.8, 127.6, 128.0, 128.2, 128.3, 129.8, 130.2, 131.4, 133.4, 133.8, 136.6, 142.0; IR (ATR) ν 2104, 1618, 1506, 1287, 808, 746 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 310 (M^+, 48), 281 ($[C_{20}H_{13}N_2]^+$, 100) , 140 ($[C_{10}H_6N]^+$, 41); HRMS (EI): *m/z* calcd for $C_{20}H_{14}N_4$ (M) 310.1218, found 310.1216.

2,2'-diazido-1,1'-binaphthyl (11)



Prepared from 1,1'-binaphthalene-2,2'-diamine (**1a**) according to the modified procedure described in literature:[S17] To a two-necked round-bottomed flask (30 mL) equipped with a magnetic stir bar, was added diamine **1a** (284.3 mg, 1.0 mmol) under the air. The flask was capped with a rubber septum and evacuated and refilled with N_2 gas for three times. With keeping temperature of the mixture at 0 °C using an ice bath, 2 N HCl aq. (7 mL) was added through the septum. To the mixture, was added an aqueous solution of sodium nitrite (207.0 mg, 3.0 mmol, 1.5 mL) dropwise. The resultant solution was stirred at 0 °C for 1 h. An aqueous solution of sodium azide (266.5 mg, 4.1 mmol, 1.5 mL) was added dropwise, and the mixture was allowed to warm to room temperature, and stirred for 12 h. Pale yellow precipitate was collected by filtration, washed with water (1 mL × 3), and dried under vacuum to give product **11**. Pale yellow solid (292.6 mg, 87%); mp 167–169 °C (dec.); R_f 0.30 (hexane/EtOAc 95:5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, J = 8.8 Hz, 2H), 7.30 (dd, J = 6.8, 7.6 Hz, 2H), 7.44 (dd, J = 6.8, 7.2 Hz, 2H), 7.51 (d, J = 7.6 Hz, 2H), 7.92 (d, J = 8.4 Hz, 2H), 8.05 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 117.2, 122.9, 125.4, 125.5, 127.4, 128.3, 130.4, 130.9, 133.4, 136.0; IR (ATR) ν 2107, 1298, 813, 749 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 336 (M^+, 5), 279 ($[C_{20}H_{11}N_2]^+$, 100), 266 ($[C_{20}H_{12}N]^+$, 21), 252 ($[C_{20}H_{12}]^+$, 14); HRMS (EI): *m/z* calcd for $C_{20}H_{12}N_6$ (M) 336.1123, found 336.1121.

Optimization Studies of Reaction Conditions

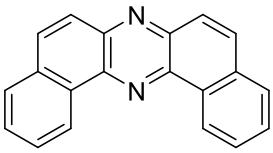
A Typical procedure for the optimization studies

To a two-necked reaction tube (20 mL, Table S2) or a two-necked round-bottomed flask (50 mL, Table S3–S5) 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 N_2 gas for three times, and an appropriate solvent was added through the septum. To the mixture, was added an appropriate oxidant under a stream of N_2 gas at the indicated temperature. The resulting solution was stirred for 3 h before quenched with aqueous $Na_2S_2O_3$ (1.0 M, 20 mL), and the resulting mixture was extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the crude product. The yields of products were calculated by the integration of ^{1}H NMR signals of the crude product. Separation by flash column chromatography on silica gel gave the compounds **2a**, **3a** and **4a**.

Note: t-BuOI was prepared in situ from NaI and t-BuOCl as follows:* To a two-necked reaction tube (20 mL) equipped with a magnetic stir bar, was added 1,1'-binaphthalene-2,2'-diamine (1a**) (0.2 mmol) and NaI (0.8 mmol) under the air. The tube was capped with a rubber septum and evacuated and refilled with N_2 gas for three times,

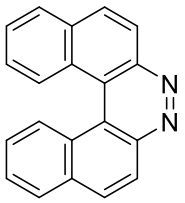
and THF (5 mL) was added through the septum. To the mixture, was added *t*-BuOCl (0.8 mmol) through the septum.

Dibenzo[*a,j*]phenazine (2a) [224-56-6]



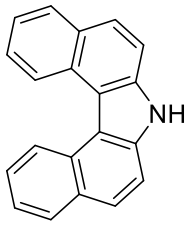
Spectroscopic data were in agreement with those previously reported;[S18] Purified by flash column chromatography on silica gel (hexane/EtOAc 99:1 to 8:2) and recrystallization from $CHCl_3$; Yellow solid; mp 243 °C; R_f 0.38 (hexane/EtOAc 8:2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.88 (m, 4H), 7.98 (d, J = 8.0 Hz, 2H), 8.07 (d, J = 9.2 Hz, 2H), 8.10 (d, J = 9.2 Hz, 2H), 9.62 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.1, 126.9, 127.6, 128.1, 129.2, 131.3, 132.4, 133.2, 140.5, 142.7; IR (ATR) ν 3035, 1350, 840, 800, 746 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 280 (M^+, 100), 140 ($[C_{10}H_6N]^+$, 15), 126 ($[C_{10}H_6]^+$, 11); HRMS (EI): *m/z* calcd for $C_{20}H_{12}N_2$ (M) 280.1000, found 280.1001

7,8-Diaza[5]helicene (3a) [188-55-6]



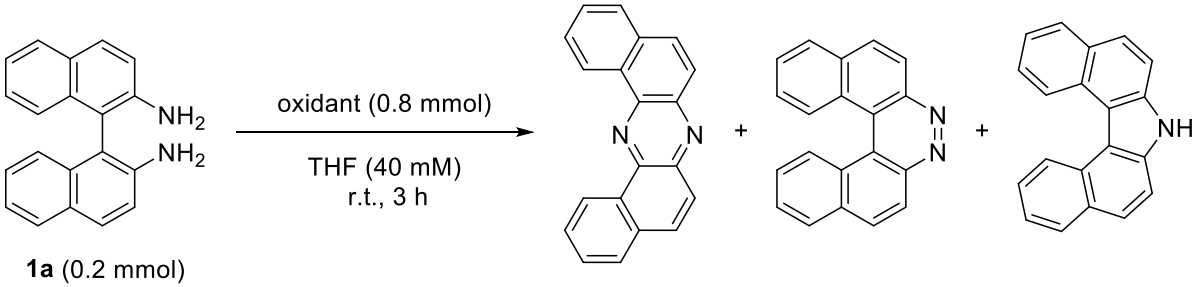
Spectroscopic data were in agreement with those previously reported;[S19] Purified by flash column chromatography on silica gel (hexane/EtOAc, 99:1 to 5:5); Brown solid; R_f 0.15 (hexane/EtOAc 8:2); MS (EI): *m/z* (relative intensity, %) 280 (M^+, 70), 252 ($[M–N_2]^+$, 100); HRMS (EI): *m/z* calcd for $C_{20}H_{12}N_2$ (M) 280.1000, found 280.1002.

***7H*-Dibenzo[*c,g*]carbazole (4a)** [194-59-2]

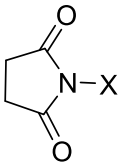
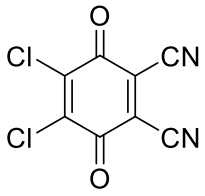


Spectroscopic data were in agreement with those previously reported;[S15, S20] Purified by flash column chromatography on silica gel (hexane/EtOAc, 99:1 to 7:3); Colorless solid; R_f 0.25 (hexane/EtOAc 8:2). MS (EI): *m/z* (relative intensity, %) 267 (M^+, 100); HRMS (EI): *m/z* calcd for $C_{20}H_{13}N$ (M) 267.1048, found 267.1051.

Table S2. Effect of Oxidants

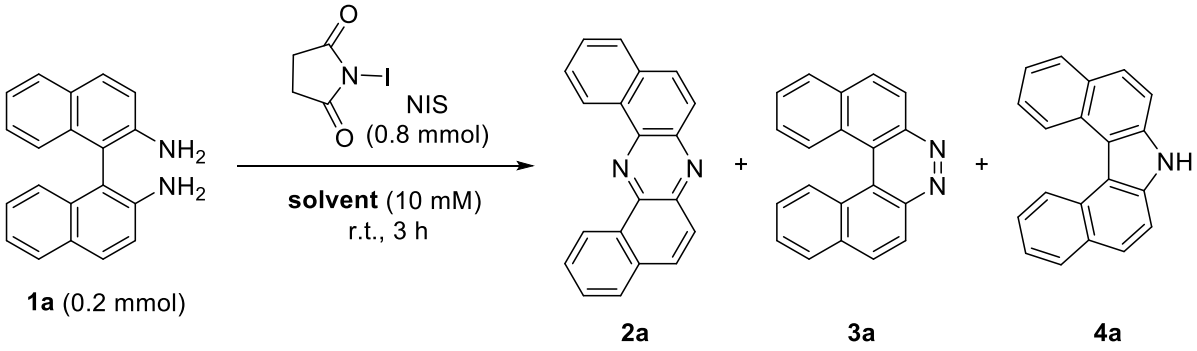


1a (0.2 mmol) **2a** **3a** **4a**

entry	**oxidant**	yield (%)[a]			recovery of **1a** (%)[a]
		2a	**3a**	**4a**	
1	*t*-BuOI	28[b]	15[b]	7[b]	0
2	 X = I	39	0	10	0
3	Br	0	0	0	0
4	Cl	0	0	0	60
5	I_2	0	0	0	100
6	$PhI(OAc)_2$	0	0	0	0
7	$PhI(OTFA)_2$	8	0	0	0
8	PhIO	0	0	0	100
9	*t*-BuOCl	0	58	0	0
10		0	0	0	0
11[c]	MnO_2	0	0	0	0

[a] ^{1}H NMR yields. [b] isolated yield. [c] 1.2 mmol of MnO_2 was applied under reflux conditions (70 °C) for 3 h.

Table S3. Effect of Solvents

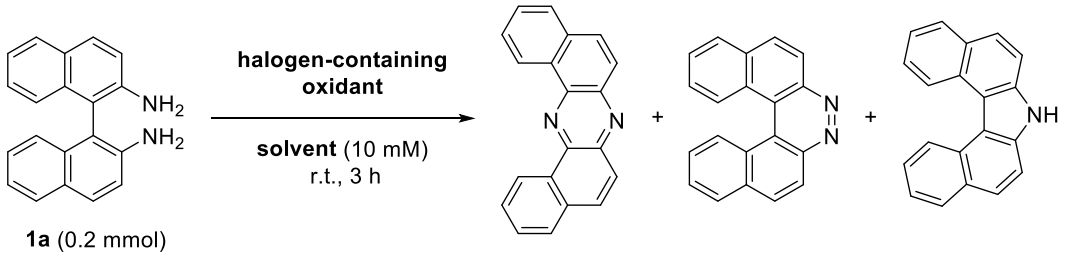


entry	solvent	yield (%)[a]			recovery of **1a** (%)[a]
		2a	**3a**	**4a**	
1	THF[b]	39	0	10	0
2	THF	46	0	20	0
3	CH_3CN	39	0	13	0
4	CH_2Cl_2	22	0	0	0
5	toluene	22	0	3	0
6	DMF	27	0	5	0
7	Et_2O	34	0	5	0
8	2-propanol	35	0	5	0
9	EtOH	42	0	10	0
10	MeOH	44	0	6	0
11	*t*-BuOH	47	0	4	0

[a] ^{1}H NMR yields. [b] 40 mM

Note:* Alcohol solvents (entries 9–11) were good in terms of solubility of BINAM, probably thereby giving good yields of the rearranged product **2a. Therefore, as a whole, MeOH and EtOH are the options for the rearrangement reactions using other BINAMs. In fact, in the case of the reaction leading to **2h**, MeOH gave better result than *t*-BuOH because of the solubility of the starting diamine. Despite the melting point of *t*-BuOH is very close to room temperature (lit. 25.3 ˚C), the experiment is implementable under the suitably temperature-controlled environment, and the reaction mixture is not solidified during the duration of the reaction.

Table S4. Effect of Halogen-containing Oxidants



1a (0.2 mmol) **2a** **3a** **4a**

entry	halogen-containing oxidant (equiv)	solvent	yield (%) [a]			recovery of **1a** (%) [a]
			2a	**3a**	**4**	
1	BPIT (4)	MeOH	0	0	0	0
2	BPIT (4)	*t*-BuOH	0	0	0	71
3	NIPh (4)	*t*-BuOH	0	0	0	100
4	NISac (4)	*t*-BuOH	0	0	0	47
5	NIPy (4)	MeOH	53 [b]	0	10 [b]	0
6	NIPy (4)	*t*-BuOH	36	0	trace	0
7	TIG (1)	MeOH	31	0	8	0
8	TIG (1)	*t*-BuOH	6	0	0	61
9	DIH (1)	MeOH	3	0	12	59
10	DIH (2)	MeOH	55	0	6	0
11	DIH (2)	*t*-BuOH	49	0	3	0
12	DIH (4)	MeOH	68 [b]	0	0	0
13	DIH (8)	MeOH	72 [b]	0	0	0
14	**DIH (8)**	***t*-BuOH**	**77** [b]	0	0	0
15	NIS (8)	MeOH	76 [b]	0	0	0
16	NIS (8)	*t*-BuOH	61	0	0	0
17	NIS (16)	MeOH	67	0	0	0
18	I_2 (4)	*t*-BuOH	0	0	0	100
19	NBS (4)	*t*-BuOH	0	0	0	0 [b]
20	*t*-BuOCl (4)	*t*-BuOH	0	89 [c]	0	0

[a] ^{1}H NMR yields. [b] 6,6'-Dibromo BINAM was produced in 31% yield. [c] Isolated yield.

structures of halogen-containing oxidants

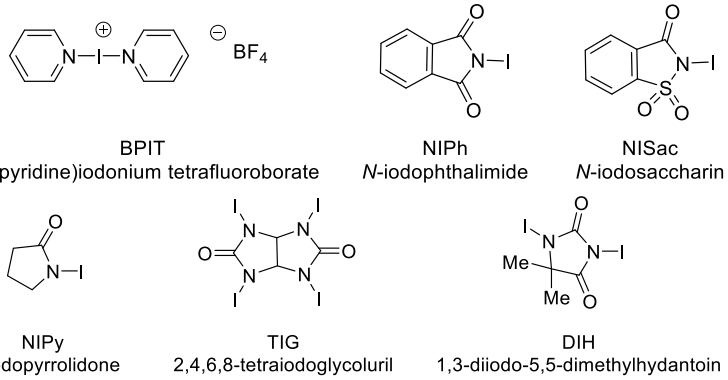
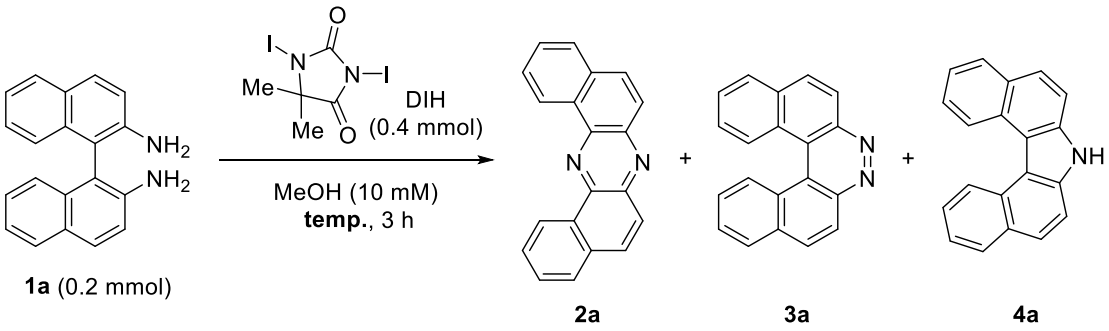


Table S5. Effect of Reaction Temperatures



entry	**temp.** (°C)	yield (%)[a]			recovery of **1a** (%)[a]
		2a	**3a**	**4a**	
1	0	42	0	5	0
2	–20	trace	0	trace	0
3	–40	0	0	0	34

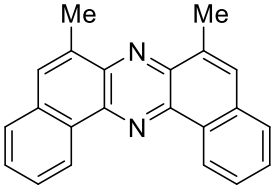
[a] ^{1}H NMR yields.

Oxidative Skeletal Rearrangement of Biaryldiamines 1

A Typical Procedure for the Skeletal Rearrangement of Biaryldiamines 1

To a two-necked round-bottomed flask (50 mL) equipped with a magnetic stir bar, was added biaryldiamine **1** (0.2 mmol) under the air. The flask was capped with a rubber septum and evacuated and refilled with N_2 gas for three times, and ROH (R = *t*-Bu or Me) (20 mL) was added through the septum. To the mixture, was added 1,3-diiodo-5,5-dimethylhydantoin (DIH) (607.8 mg, 1.6 mmol) under a stream of N_2 gas at room temperature. The resulting solution was stirred for the indicated time (Table 2 in the text) before quenched with aqueous $Na_2S_2O_3$ (1.0 M, 20 mL), and the resulting mixture was extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the crude product. Purification by flash column chromatography on silica gel gave the corresponding dibenzo[*a*,*j*]phenazine (for example, compound **2a**: 43.1 mg, 77%).

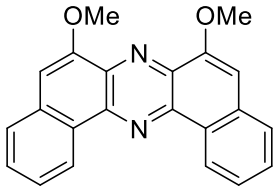
6,8-Dimethyldibenzo[*a*,*j*]phenazine (2b)



Purified by flash column chromatography on silica gel (hexane/EtOAc 95:5) and recrystallization from $CHCl_3$; Yellow solid (40.7 mg, 66%); mp 234 °C; R_f 0.60 (hexane/EtOAc 8:2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.95 (d, J = 1.2 Hz, 6H), 7.72–7.79 (m, 4H), 7.87–7.89 (m, 4H), 9.54 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9, 125.0, 126.5, 127.3, 129.0, 130.2, 130.6, 133.4, 135.1, 139.8, 142.0; IR (ATR) ν 2916, 1479, 1331,

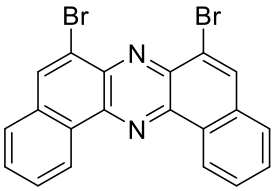
1119, 881, 756 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 308 (M^+, 100), 154 ($[C_{11}H_8N]^+$, 12) , 140 ($[C_{11}H_8]^+$, 7); HRMS (EI): *m/z* calcd for $C_{22}H_{16}N_2$ (M) 308.1313, found 308.1313.

6,8-Dimethoxydibenzo[*a,j*]phenazine (2c)



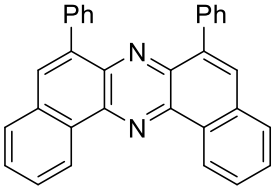
Purified by flash column chromatography on NH silica gel (hexane/EtOAc 9:1 to 5:5) and recrystallization from $CHCl_3$; Yellow solid (65.4 mg, 96%); mp 305 °C (dec.); R_f 0.18 (hexane/EtOAc 5:5, NH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (s, 6H), 7.29 (s, 2H), 7.69–7.77 (m, 4H), 7.87 (d, *J* = 8.0 Hz, 2H), 9.50 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.1, 106.5, 125.2, 125.3, 126.9, 127.1, 129.9, 133.9, 136.3, 141.3, 152.6; IR (ATR) *ν* 2924, 1624, 1572, 1472, 1344, 1288, 1165, 1136, 839, 744 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 340 (M^+, 100), 311 ($[C_{20}H_{11}N_2O_2]^+$, 44) , 294 ($[C_{20}H_{10}N_2O]^+$, 82), 170 ($[C_{11}H_8NO]$); HRMS (EI): *m/z* calcd for $C_{22}H_{16}N_2O_2$ (M) 340.1212, found 340.1211.

6,8-Dibromodibenzo[*a,j*]phenazine (2d)



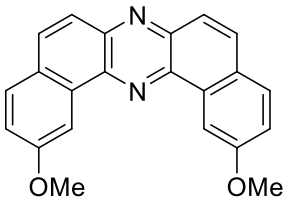
Purified by flash column chromatography on silica gel (hexane/EtOAc, 95:5 to 8:2) and recrystallization from $CHCl_3$; Yellow solid (32.4 mg, 37%); mp 286–287 °C (dec.); R_f 0.48 (hexane/EtOAc 8:2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.92 (m, 6H), 8.49 (s, 2H), 9.52 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.0, 125.8, 127.6, 128.2, 130.3, 130.4, 133.6, 135.5, 140.0, 140.9; IR (ATR) *ν* 3064, 1506, 1378, 1324, 1216, 1012, 913, 890, 746 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 438 (M^+, 100), 278 ($[C_{20}H_{10}N_2]^+$, 35), 218 ($[C_{10}H_5BrN]^+$, 8), 139 ($[C_{10}H_5N]^+$, 21); HRMS (EI): *m/z* calcd for $C_{20}H_{10}Br_2N_2$ (M) 435.9211, found 435.9207.

6,8-Diphenyldibenzo[*a,j*]phenazine (2e)



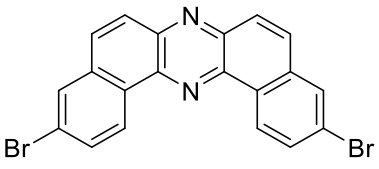
Purified by flash column chromatography on silica gel (hexane/CH_2Cl_2, 10:0 to 9:1) and recrystallization from $CHCl_3$; Yellow solid (67.5 mg, 78%); mp 267–268 °C; R_f 0.30 (hexane/CH_2Cl_2 8:2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.40 (m, 6H), 7.78–7.89 (m, 8H), 8.00 (d, *J* = 7.6 Hz, 2H), 8.14 (s, 2H), 9.66 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.2, 127.3, 127.4, 127.7, 128.2, 129.5, 130.9, 131.0, 131.7, 133.2, 138.2, 138.3, 140.1, 140.9; IR (ATR) *ν* 3061, 1960, 1495, 1379, 1335, 897, 768 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 432 (M^+, 100), 216 ($[C_{16}H_{10}N]^+$, 9); HRMS (EI): *m/z* calcd for $C_{32}H_{20}N_2$ (M) 432.1626, found 432.1624.

2,12-Dimethoxydibenzo[*a*,*j*]phenazine (2f)



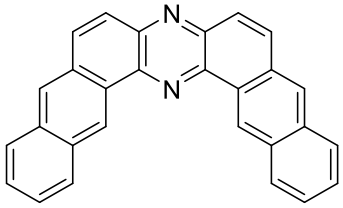
Purified by flash column chromatography on NH silica gel (hexane/EtOAc 9:1 to 5:5) and recrystallization from $CHCl_3$; Yellow solid (42.2 mg, 62%); mp 260–261 °C; R_f 0.23 (hexane/ EtOAc 8:2, NH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.15 (s, 6H), 7.41 (dd, J = 2.4, 8.8 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H), 7.93 (d, J = 9.2 Hz, 2H), 8.03 (d, J = 9.2 Hz, 2H), 8.99 (d, J = 2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 106.3, 118.8, 124.4, 127.7, 129.7, 132.1, 132.9, 139.6, 143.2, 159.3; IR (ATR) ν 3004, 2960, 1611, 1519, 1465, 1336, 1223, 1029, 873, 828 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 340 (M^+, 100), 310 ($[C_{20}H_{10}N_2O_2]^+$, 8), 170 ($[C_{11}H_8NO]^+$, 11); HRMS (EI): *m/z* calcd for $C_{22}H_{16}N_2O_2$ (M) 340.1212, found 340.1211.

3,11-Dibromodibenzo[*a*,*j*]phenazine (2g)



Purified by flash column chromatography on silica gel (hexane/EtOAc, 95:5 to 8:2) and recrystallization from $CHCl_3$; Yellow solid (43.8 mg, 50%); mp 317–318 °C (dec.); R_f 0.35 (hexane/EtOAc 8:2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, J = 2.0, 8.8 Hz, 2H), 8.01 (d, J = 9.2 Hz, 2H), 8.10 (d, J = 9.2 Hz, 2H), 8.15 (d, J = 2.0 Hz, 2H), 9.44 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.0, 127.0, 128.3, 129.8, 130.5, 130.9, 131.4, 134.6, 140.4, 142.8; IR (ATR) ν 3053, 1589, 1462, 1352, 1180, 1072, 991, 877, 848, 804, 788, 713 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 438 (M^+, 100), 278 ($[C_{20}H_{10}N_2]^+$, 17), 218 ($[C_{10}H_5BrN]^+$, 7), 139 ($[C_{10}H_5N]^+$, 17); HRMS (EI): *m/z* calcd for $C_{20}H_{10}Br_2N_2$ (M) 435.9211, found 435.9209.

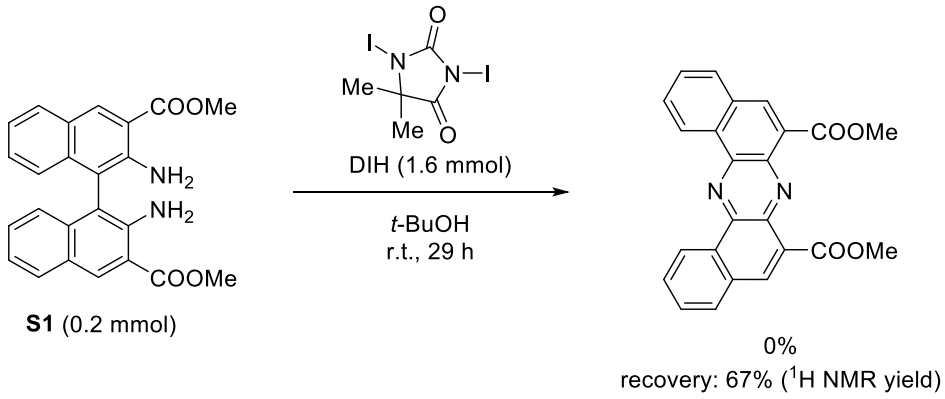
Dinaphtho[2,3-*a*:2',3'-*j*]phenazine (2h)



Purified by flash column chromatography on silica gel (hexane/EtOAc 8:2) and recrystallization from $CHCl_3$; Yellow solid (17.5 mg, 23%); mp 331 °C (dec.); R_f 0.15 (hexane/EtOAc 8:2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.73 (m, 4H), 7.95 (d, J = 9.2 Hz, 2H), 8.13–8.16 (m, 4H), 8.44 (d, J = 7.2 Hz, 2H), 8.47 (s, 2H), 10.17 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.1, 126.5, 127.0, 127.2, 128.2, 129.2, 131.0, 132.3, 133.0, 133.4, 141.4, 143.4 (Two carbons were not identified, probably due to the overlap of signals.); IR (ATR) ν 3048, 1491, 1320, 896, 885, 749 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 380 (M^+, 100), 190 ($[C_{14}H_8N]^+$, 31) , 176 ($[C_{14}H_8]^+$, 8); HRMS (EI): *m/z* calcd for $C_{28}H_{16}N_2$ (M) 380.1313, found 380.1309.

Under the optimized conditions, diamine **S1** did not undergo rearrangement, and 67% of **S1** was recovered (Scheme S1).

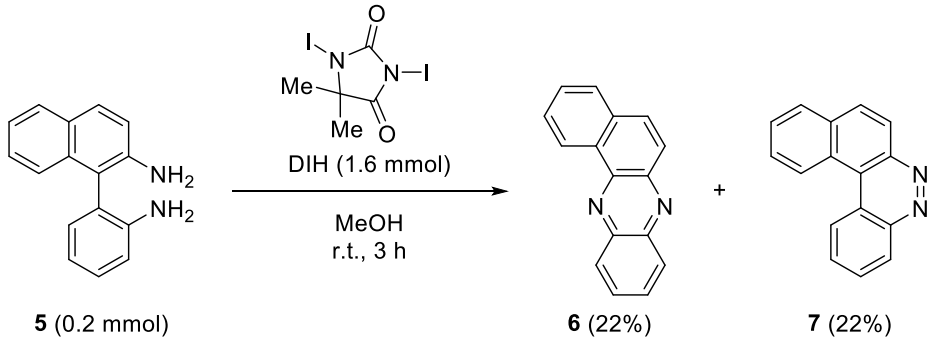
Scheme S1. Reaction of Biaryldiamine S1 with DIH



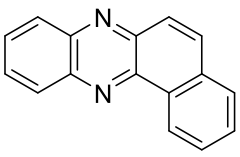
Experiments for the Survey of the Influence of Naphthalene Unit

The experiments were conducted in the same way as those for the oxidative skeletal rearrangement of biaryldiamines **1**, using biaryldiamine **5** and **8** as a starting material instead of **1** (Scheme S2 and S3).

Scheme S2. Reaction of Biaryldiamine 5 with DIH

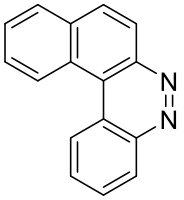


Benzo[*a*]phenazine (6) [225-61-6]



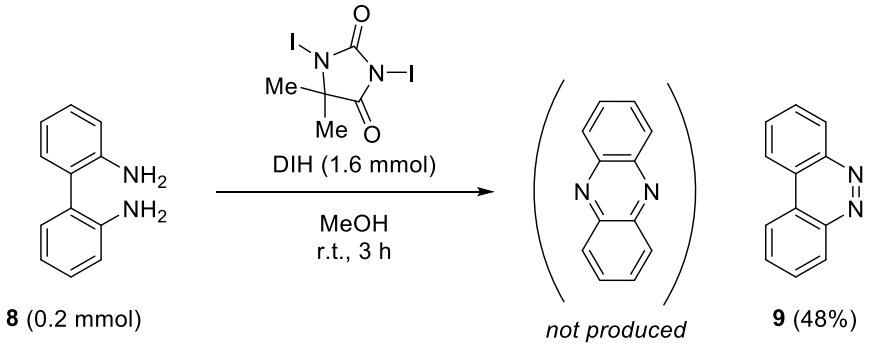
Spectroscopic data were in agreement with those previously reported;[S21] Purified by flash column chromatography on silica gel (hexane/EtOAc 10:0 to 9:1); Brown solid (10.1 mg, 22%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–8.05 (m, 7H), 8.29–8.31 (m, 1H), 8.38–8.40 (m, 1H), 9.44 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.4, 127.2, 128.0, 128.2, 129.2, 129.7, 129.8, 129.9, 130.1, 131.1, 133.2, 133.4, 142.0, 142.7 (2C), 143.6; MS (EI): *m/z* (relative intensity, %) 230 (M^+, 100).

Dibenzo[*c,f*]cinnoline (7) [195-31-3]

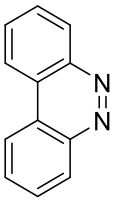


Purified by flash column chromatography on silica gel (hexane/EtOAc 95:5 to 8:2); Yellow solid (12.3 mg, 22%); mp 122–124 °C; R_f 0.38 (hexane/EtOAc 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.84 (m, 2H), 7.94–8.02 (m, 2H), 8.10–8.14 (m, 1H), 8.18 (d, J = 8.8 Hz, 1H), 8.61 (d, J = 7.6 Hz, 1H), 8.85 (d, J = 7.6 Hz, 1H), 9.13 (d, J = 8.8 Hz, 1H), 9.20–9.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 119.1, 121.7, 125.5, 127.5, 128.2, 128.7, 128.8 (2C), 129.1, 130.6, 131.3, 131.4, 131.6, 134.8, 144.8, 147.4: IR (ATR) *v* 2926, 1715, 1516, 1379, 1287, 1092, 829, 781, 752 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 230 (M^+, 97), 202 ($[C_{16}H_{10}]^+$, 100); HRMS (EI): *m/z* calcd for $C_{16}H_{10}N_2$ (M) 230.0844, found 230.0842.

Scheme S3. Reaction of Biaryldiamine 8 with DIH



Benzo[*c*]cinnnoline (9) [230-17-1]

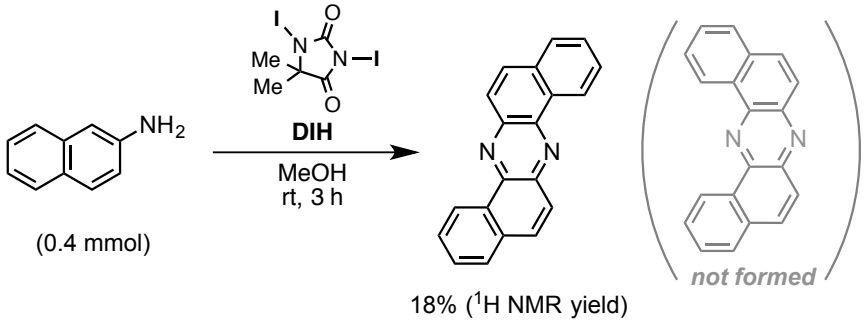


Spectroscopic data were in agreement with those previously reported;[S22] Purified by flash column chromatography on silica gel (hexane/EtOAc 95:5 to 8:2); Yellow solid; R_f 0.18 (hexane/EtOAc 8:2).

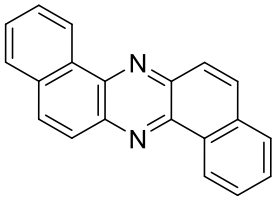
Control Experiment: Reaction of 2-aminonaphthalene with DIH

The experiments were conducted in the same way as those for the oxidative skeletal rearrangement of biaryldiamines **1**, using 2-aminonaphthalene (0.4 mmol) as a starting material instead of **1** (Scheme S4). The reaction gave only [*a,h*]-isomer in a low yield, excluding the possibility of the reaction pathway from BINAM to [*a,j*]-isomer **2a** via 2-aminonaphthalene.

Scheme S4. Reaction of 2-aminonaphthalene with DIH



Dibenzo[*a,h*]phenazine [226-47-1]



Spectroscopic data were in agreement with those previously reported;[S18] Purified by flash column chromatography on silica gel (hexane/EtOAc 95:5 to 8:2); Yellow solid.

Cross-over Experiment

The experiment was conducted in the same way as those for the oxidative skeletal rearrangement of biaryldiamines **1** except for using a mixture of biaryldiamines **1a** (0.1 mmol) and **1c** (0.1 mmol) as a starting material.

Scheme S5. Cross-over Experiment

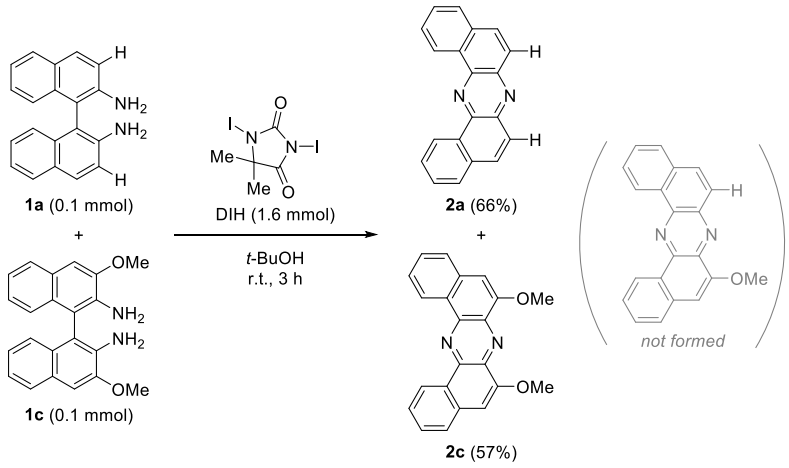


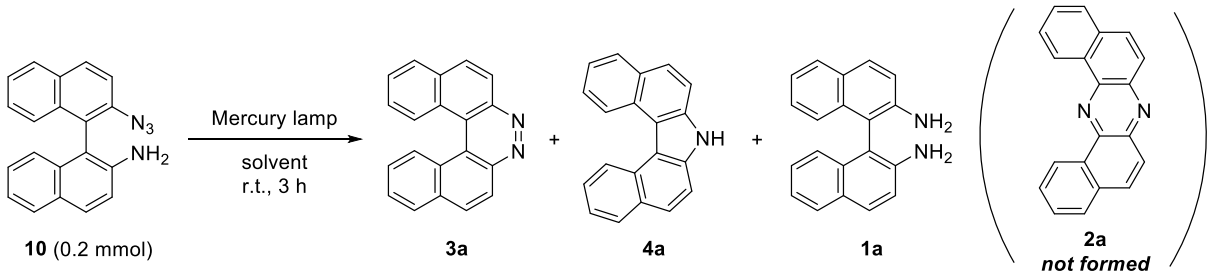
Photo- and Thermal-induced Decomposition of Binaphthalene Azides

A Typical Procedure for the Photo-induced Decomposition of Binaphthalene Azides

A solvent was degassed through freeze-pump-thaw cycling for three times before use. To a quartz tube (150 mL) equipped with a magnetic stir bar, was added binaphthalene azide (**10** or **11**) (0.2 mmol) under the air. The tube was capped with a rubber septum and evacuated and refilled with N_2 gas for three times, and an appropriate solvent (20 mL) was added through the septum. The resulting mixture was irradiated with UV light (Riko 400 W high pressure Hg lamp UVL-400HA) under N_2 atmosphere at room temperature. After irradiation for 3 h, the solvent was concentrated under vacuum to give the crude product. Separation by flash column chromatography on silica gel gave the compounds **3a**, **4a** and **1a**.

**Note: To maintain a constant reaction temperature, the apparatus was submerged in a water bath during the reaction.*

Table S6. Photo-induced Decomposition of Binaphthalene Azide 10

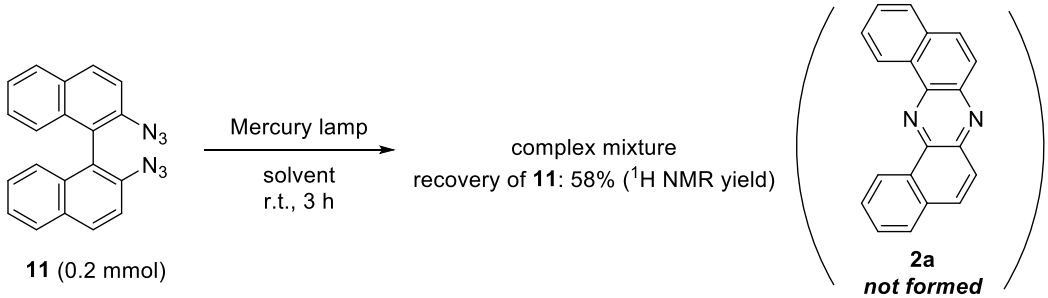


10 (0.2 mmol) **3a** **4a** **1a** **2a** ***not formed***

entry	solvent	yield (%)			recovery of **10** (%)
		3a	**4a**	**1a**	
1	*t*-BuOH	16 [a]	7 [a]	48 [a]	0
2	cyclohexane	25	5	37	0
3	benzene	17	23	8	0

[a] ^{1}H NMR yield.

Scheme S6. Photo-induced Decomposition of Binaphthalene Azide 11

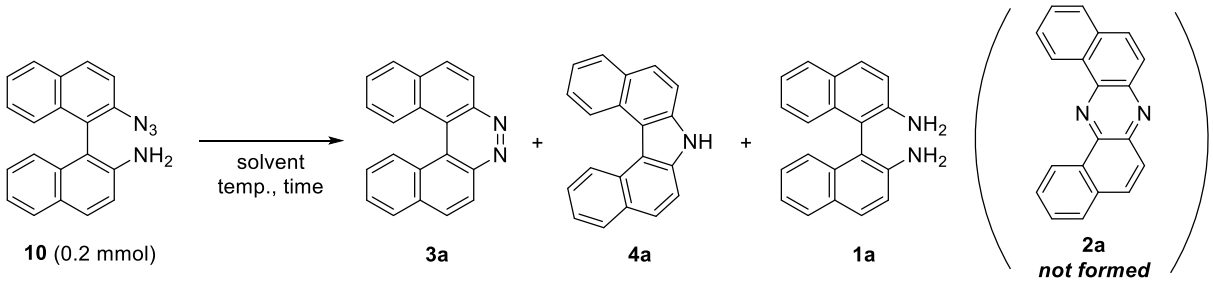


11 (0.2 mmol) **2a** ***not formed***

A Typical Procedure for the Thermal-induced Decomposition of Binaphthalene Azides

A solvent was degassed through freeze-pump-thaw cycling for three times before use. To a two-necked round-bottomed flask (50 mL) equipped with a magnetic stir bar, was added binaphthalene azide (**10** or **11**) (0.2 mmol) under the air. The flask was capped with a rubber septum and evacuated and refilled with N_2 gas for three times, and an appropriate solvent (20 mL) was added through the septum. The resulting mixture was stirred under N_2 atmosphere at the indicated temperature in an oil bath for 3 h. The solvent was concentrated under vacuum to give the crude product. Separation by flash column chromatography on silica gel gave the compounds **3a**, **4a** and **1a**.

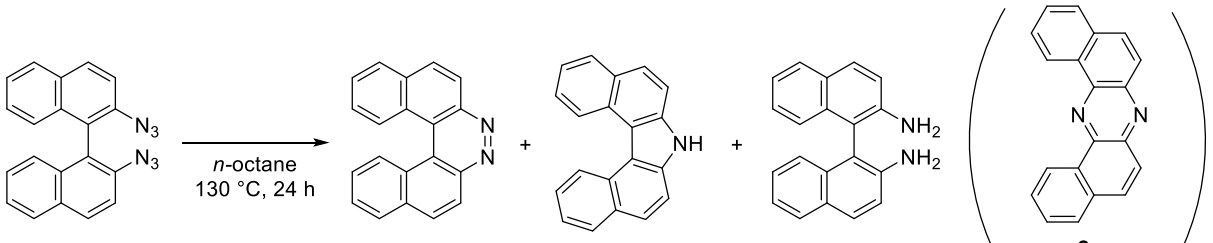
Table S7. Thermal-induced Decomposition of Binaphthalene Azide 10



10 (0.2 mmol) **3a** **4a** **1a** **2a** ***not formed***

entry	solvent	temp. (°C)	time (h)	yield (%)			recovery of **10** (%)
				3a	**4a**	**1a**	
1	*t*-BuOH	80	1.5	0	0	0	100
2	*n*-octane	130	24	26	3	38	0

Scheme S7. Thermal-induced Decomposition of Binaphthalene Azide 11

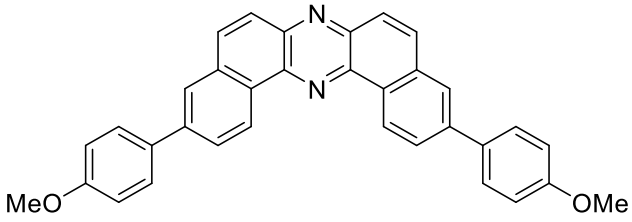


11 (0.2 mmol) **3a** (27%)[a] **4a** (0%) **1a** (33%)[a] recovery of **11**: 15%[a] **2a** ***not formed***

[a] ^{1}H NMR yield.

Pd-Catalyzed Functionalization of Phenazine 2g

3,11-bis(4-methoxyphenyl)dibenzo[*a,j*]phenazine (2i)



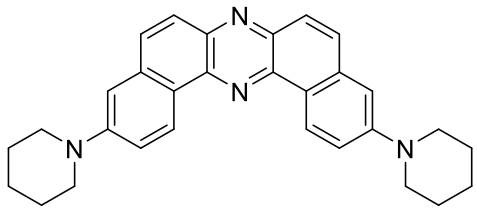
Synthesized from dibromophenazine **2g** by a slightly modified Nolan's method:[S6] 2-Propanol was degassed through freeze-pump-thaw cycling for three times before use. In a glovebox, to a two-necked reaction tube (5 mL) equipped with a magnetic stir bar, was added potassium *tert*-butoxide (24.6 mg, 0.22 mmol), and the tube was capped with a rubber septum. Outside the glovebox, phenazine **2g** (43.8 mg, 0.10 mmol), *p*-methoxyphenyl boronic acid (33.4 mg, 0.22 mmol), [SIPr-Pd(cinnamyl)Cl] (1.3 mg, 2 mol%) and 2-propanol (1 mL) were added to the test tube under a stream of N_2 gas at room temperature, and the mixture was stirred at 60 °C for 24 h. Water was added to the reaction mixture, and the organic layer was extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated in vacuo. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 5:5 to 0:10) and recrystallization from $CHCl_3$ to give product **2i**. Yellow solid (36.9 mg, 77%); mp 265–266 °C; R_f 0.10 (hexane/EtOAc 5:5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (s, 6H), 7.08 (d, J = 8.4 Hz, 4H), 7.76 (d, J = 8.4 Hz, 4H), 8.05–8.11 (m, 8H), 9.62 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 114.5, 125.6, 125.8, 126.5, 127.3, 128.6, 129.8, 132.5, 133.0, 133.7, 140.7, 141.7, 142.6, 159.6; IR (ATR) ν 3036, 2835, 1607, 1512, 1474, 1354, 1248, 1179, 1032, 837, 812, 797, 718 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 492 (M^+, 100), 477 ($[C_{33}H_{21}N_2O_2]^+$, 10) , 246 ($[C_{17}H_{12}NO]^+$, 19); HRMS (EI): *m/z* calcd for $C_{34}H_{24}N_2O_2$ (M) 492.1838, found 492.1840.

A Typical Procedure for the Synthesis of Diaminodibenzo[a,j]phenazines 2j and 2k

Diaminophenazines **2j** and **2k** were synthesized from dibromophenazine **2g** by a slightly modified Nolan's method:[S6] Dimethoxyethane (DME) was degassed through freeze-pump-thaw cycling for three times before use. In a glovebox, to a two-necked reaction tube (5 mL) equipped with a magnetic stir bar, was added potassium *tert*-butoxide (24.6 mg, 0.22 mmol), and the tube was capped with a rubber septum. Outside the glovebox, phenazine **2g** (43.8 mg, 0.10 mmol), [SIPr-Pd(cinnamyl)Cl] (1.3 mg, 2 mol%), DME (1 mL) and amine (piperidine or morpholine) (0.22 mmol) were added under a stream of N_2 gas at room temperature, and the mixture was stirred at 60 °C for 24 h. Water was added to the reaction mixture, and the organic layer was extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated in vacuo to give the crude product. The crude product was purified by flash column chromatography

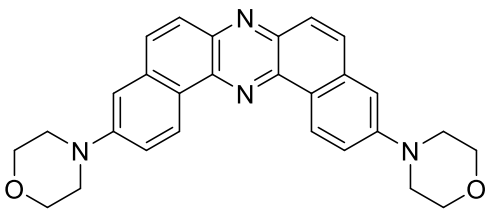
on NH silica gel and recrystallization from benzene to give the corresponding diaminodibenzo[*a,j*]phenazine.

3,11-dipiperidinodibenzo[*a,j*]phenazine (2j)



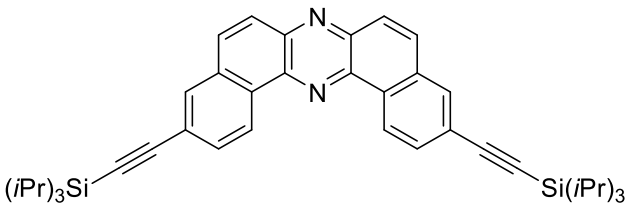
Purified by flash column chromatography on NH silica gel (hexane/EtOAc 97:3) and recrystallization from benzene; Orange solid (33.5 mg, 75%); mp 262 °C (dec.); R_f 0.20 (hexane/EtOAc 8:2, NH silica); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65–1.71 (m, 4H), 1.77–1.83 (m, 8H), 3.43 (t, J = 5.4 Hz, 8H), 7.28 (d, J = 2.8 Hz, 2H), 7.49 (dd, J = 2.8, 8.8 Hz, 2H), 7.88 (d, J = 9.2 Hz, 2H), 7.94 (d, J = 9.2 Hz, 2H), 9.38 (d, J = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.4, 25.7, 50.0, 111.6, 117.8, 123.3, 126.2, 127.2, 131.5, 134.9, 141.0, 141.0, 152.5; IR (ATR) *v* 3063, 2934, 1611, 1479, 1350, 1242, 1209, 1159, 1128, 957, 864, 847, 783, 716 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 446 (M^+, 100), 223 ($[C_{15}H_{15}N_2]^+$, 9); HRMS (EI): *m/z* calcd for $C_{30}H_{30}N_4$ (M) 446.2470, found 446.2474.

3,11-dimorpholinodibenzo[*a,j*]phenazine (2k)



Purified by flash column chromatography on NH silica gel (hexane/EtOAc 9:1) and recrystallization from benzene; Yellow solid (34.7 mg, 77%); mp 284 °C (dec.); R_f 0.33 (hexane/EtOAc 5:5, NH silica);^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 (t, J = 4.8 Hz, 8H), 3.96 (t, J = 4.8 Hz, 8H), 7.25 (d, J = 2.4 Hz, 2H), 7.46 (dd, J = 2.4, 9.2 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H), 7.97 (d, J = 9.2 Hz, 2H), 9.41 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.8, 66.8, 111.3, 117.0, 124.1, 126.3, 127.5, 131.5, 134.7, 140.9, 141.2, 151.8; IR (ATR) *v* 2857, 1611, 1477, 1445, 1356, 1240, 1227, 1117, 961, 891, 852, 818, 789, 721 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 450 (M^+, 100), 392 ($[C_{25}H_{20}N_4O]^+$, 15), 334 ($[C_{22}H_{14}N_4]^+$, 20), 225 ($[C_{14}H_{13}N_2O]^+$, 6), 167 ($[C_{10}H_5N_3]^+$, 19), 153 ($[C_{10}H_5N_2]^+$, 9), 139 ($[C_{10}H_5N]^+$, 4); HRMS (EI): *m/z* calcd for $C_{28}H_{26}N_4O_2$ (M) 450.2056, found 450.2053.

3,11-bis((triisopropylsilyl)ethynyl)dibenzo[*a,j*]phenazine (2l)

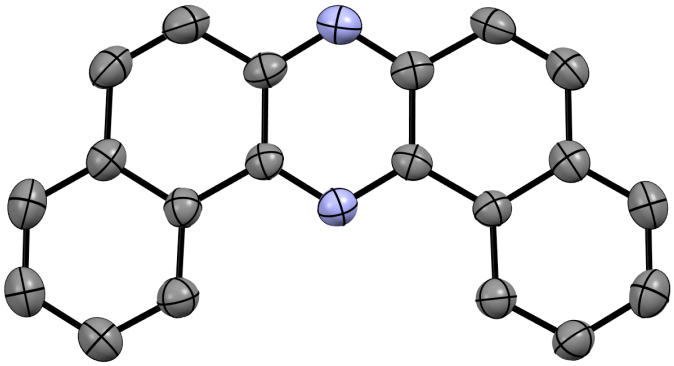


Synthesized from dibromophenazine **2g** through a typical Sonogashira coupling reaction:[S23] THF (1.5 mL) and NEt_3 (0.15 mL) were degassed through freeze-pump-thaw cycling for three times before use. A two-necked reaction tube (5 mL) equipped with a magnetic stir bar was capped with a rubber septum, flame-dried, and refilled with N_2 gas. To the tube, were added

phenazine **2g** (43.8 mg, 0.10 mmol), (triisopropylsilyl)acetylene (43.7 mg, 0.24 mmol), $[PdCl_2(PPh_3)_2]$ (10.5 mg, 15 mol%), CuI (6.5 mg, 34 mol%), THF (1.5 mL) and NEt_3 (0.15 mL) under a stream of N_2 gas at room temperature, and the resulting mixture was stirred at 60 °C for 3 h. After the completion of the reaction, the mixture was cooled to room temperature and filtered. The filtrate was evaporated in vacuo, and the crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 95:5) and recrystallization from $CHCl_3$ to give product **2l**. Yellow solid (40.7 mg, 76%); mp 302–303 °C; R_f 0.53 (hexane/EtOAc 8:2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20–1.22 (m, 42H), 7.91 (dd, J = 1.2, 8.4 Hz, 2H), 8.03 (d, J = 9.2 Hz, 2H), 8.07 (d, J = 9.2 Hz, 2H), 8.10 (d, J = 1.2 Hz, 2H), 9.50 (J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.3, 18.7, 93.3, 106.8, 124.5, 125.1, 127.6, 130.7, 130.9, 131.8, 132.1, 133.0, 140.4, 143.0; IR (ATR) ν 2941, 2862, 2156, 1470, 1354, 1147, 993, 881, 851, 799, 741 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 640 (M^+, 29), 597 ($[C_{39}H_{45}N_2Si_2]^+$, 100), 555 ($[C_{36}H_{39}N_2Si_2]^+$, 39), 541 ($[C_{35}H_{37}N_2Si_2]^+$, 37), 527 ($[C_{34}H_{35}N_2Si_2]^+$, 51), 221 ($[C_{15}H_{13}Si]^+$, 45), 207 ($[C_{14}H_{11}Si]^+$, 45); HRMS (EI): *m/z* calcd for $C_{42}H_{52}N_2Si_2$ (M) 640.3669, found 640.3671.

X-ray crystallographic experiment of 2a. The X-ray Diffraction data of the single crystal of **2a**, which has grown from a $CHCl_3$ solution, were collected on a Rigaku R-AXIS RAPID diffractometer with graphite monochromated CuKa radiation (λ = 1.54187 Å) to a $2\theta_{max}$ value of 136.4° at 277 K. The crystal structure was solved by direct methods (SHELX97) and refined by full-matrix least-squares method on F^2 (SHELX97). The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using the riding model. The crystal data are summarized in Table S8. CCDC-1004407 contains the supplementary crystallographic data for **2a**, which are available free of charge from the Cambridge Crystallographic Data Center (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

Table S8. Summary of Crystallographic Data of **2a**



Empirical Formula	$C_{20}H_{12}N_2$	
Formula Weight	280.33	
Crystal System	Orthorhombic	
Space Group	$P2_12_12_1$ (#19)	
Unit cell dimensions	a = 3.8813(1) Å	$\alpha = 90°$
	b = 11.6430(3) Å	$\beta = 90°$
	c = 29.5312(8) Å	$\gamma = 90°$
V	1334.50(6) Å^3	
Z	4	
T	277 K	
D_{calcd}	1.395 g/cm^3	
R_1 [I>2σ(I)]	0.0503	
$wR(F^2)$ (all data)	0.1344	
Crystal size	0.500 × 0.040 × 0.030 mm^3	
GOF	1.003	
Reflections collected/unique (R_{int})	15392/2436 [R_{int} = 0.0455]	

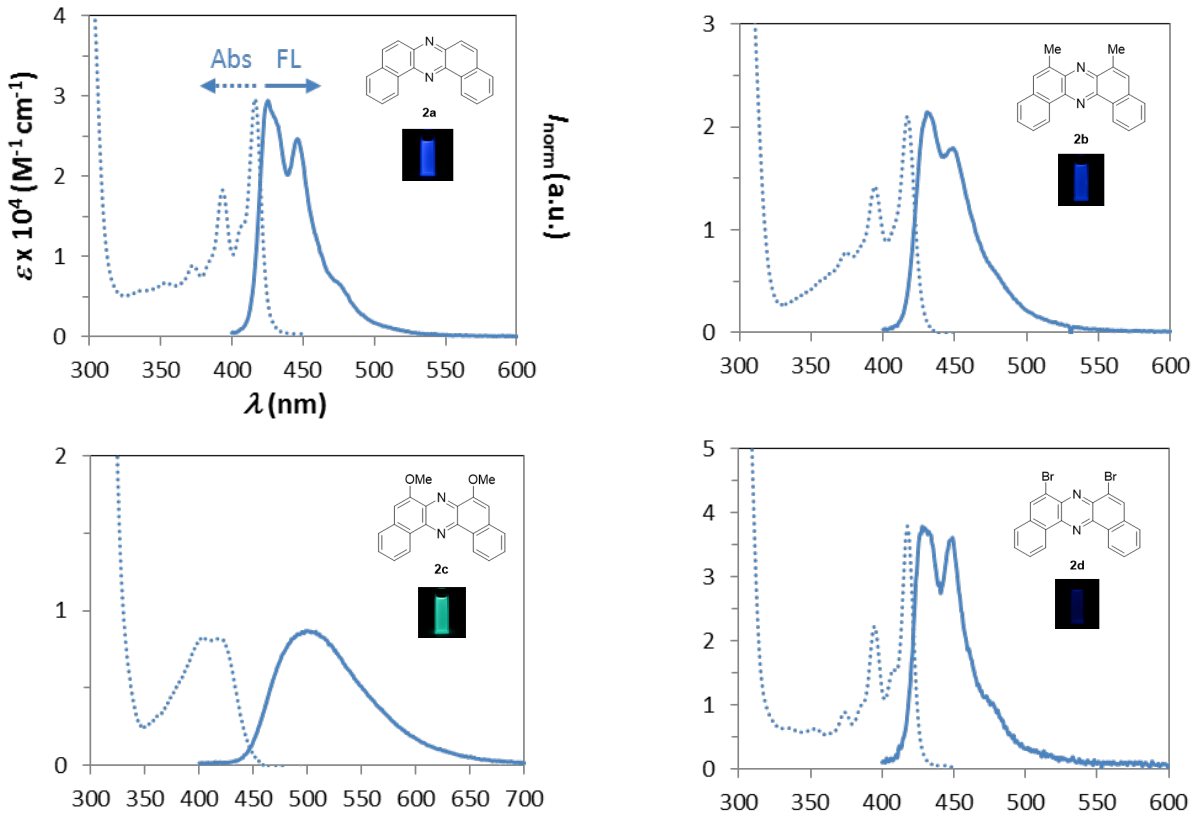
Physicochemical Properties of Phenazines 2

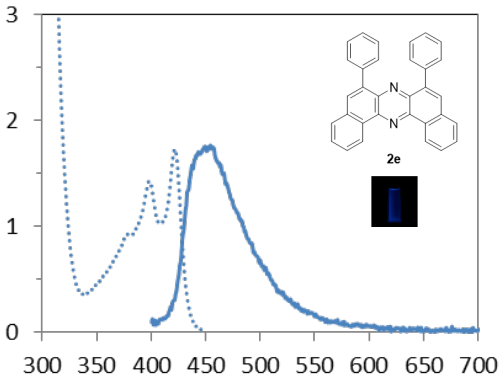
Table S9. Summary of Physicochemical Properties of **2**

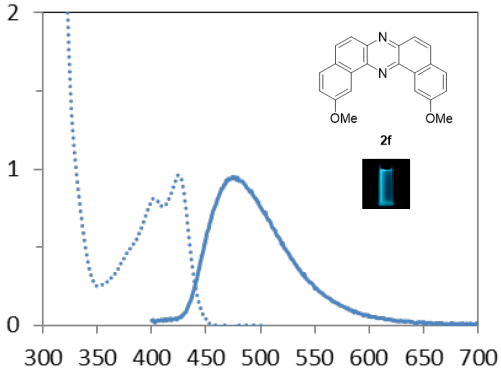
	Absorption		Emission (solution)			Emission (solid)			CV (vs. Fc/Fc^+)				TGA
	λ_{max} (nm)	ε ($M^{-1}cm^{-1}$)	λ_{ex} (nm)	λ_{max} (nm)	Φ_{FL}	λ_{ex} (nm)	λ_{max} (nm)	Φ_{FL}	$^{red}E_{pc}$ (V)	$^{red}E_{pa}$ (V)	$^{red}E_{1/2}$ (V)	LUMO level (eV)	T_d (5wt% loss) (°C)
2a	416	2970	300	425	0.14	350	524	0.18	–1.93	–1.83	–1.88	–2.92	221
2b	417	2100	300	431	0.10	300	481	0.02	–2.03	–1.93	–1.98	–2.82	230
2c	418	820	300	499	0.24	300	508	0.11	–1.96	–1.85	–1.90	–2.90	192
2d	418	3790	300	428	0.02	300	-	0.01	–1.80	–1.72	–1.76	–3.04	116
2e	422	1729	300	454	0.03	300	469	<0.01	–1.94	–1.85	–1.90	–2.90	313
2f	425	960	300	475	0.11	300	-	0.02	–1.94	–1.86	–1.90	–2.90	283
2g	418	3510	300	427	0.02	300	-	0.01	–1.81	–1.73	–1.77	–3.03	280
2h	467	2251	300	485	0.55	300	537	0.11	–1.98	–1.88	–1.93	–2.87	310
2i	435	3896	300	461	0.50	350	483	0.07	-	-	-	-	403
2j	463	2789	300	561	0.47	280	543	0.05	-	-	-	-	360
2k	452	2798	300	543	0.42	370	543	<0.01	-	-	-	-	354
2l	432	5569	300	464	0.32	400	471	0.07	–1.80	–1.72	–1.76	–3.04	365

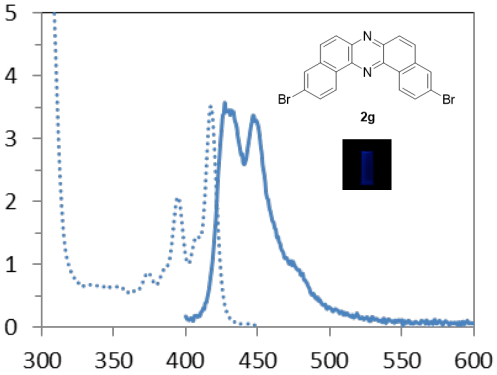
UV-vis and Emission Spectra

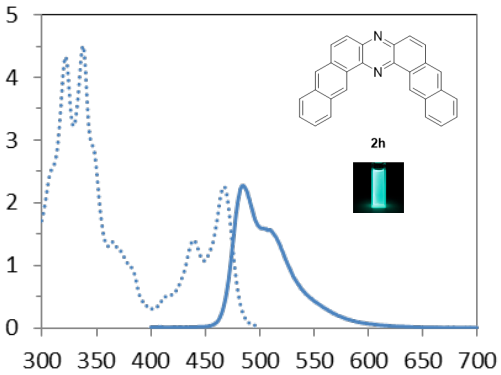
Dichloromethane (spectroscopic grade) was purged with N_2 for 30 min before the measurements. UV-vis and emission spectra of phenazines **2** were measured at room temperature using CH_2Cl_2 solutions (1.0×10^{-5} M).

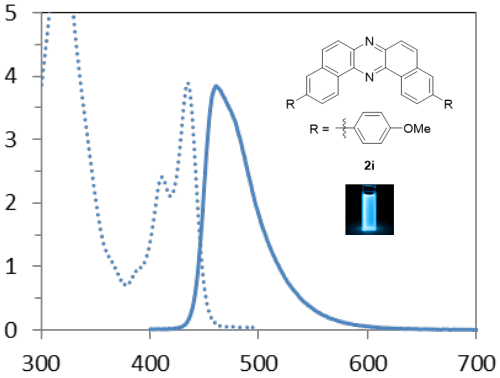


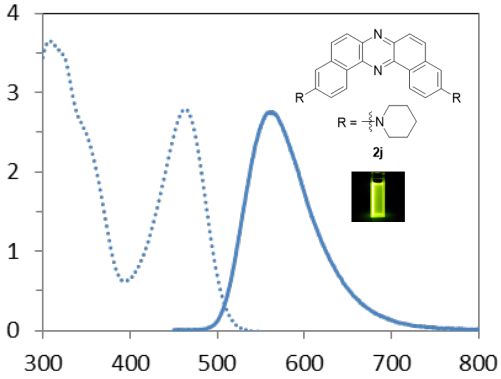

2e

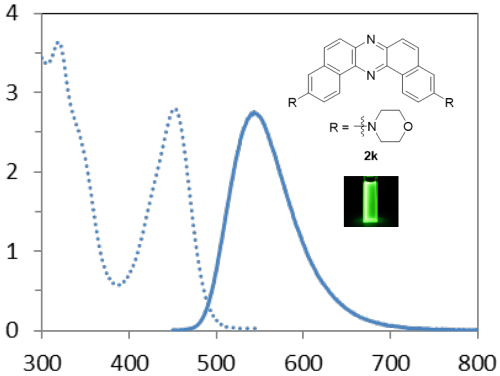

OMe
OMe
2f

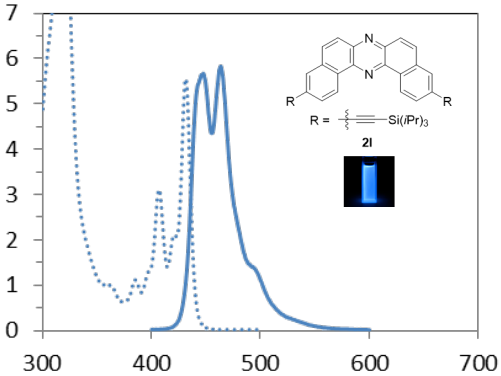

Br
Br
2g


2h


R
R
R = OMe
2i


R
R
R =
2j

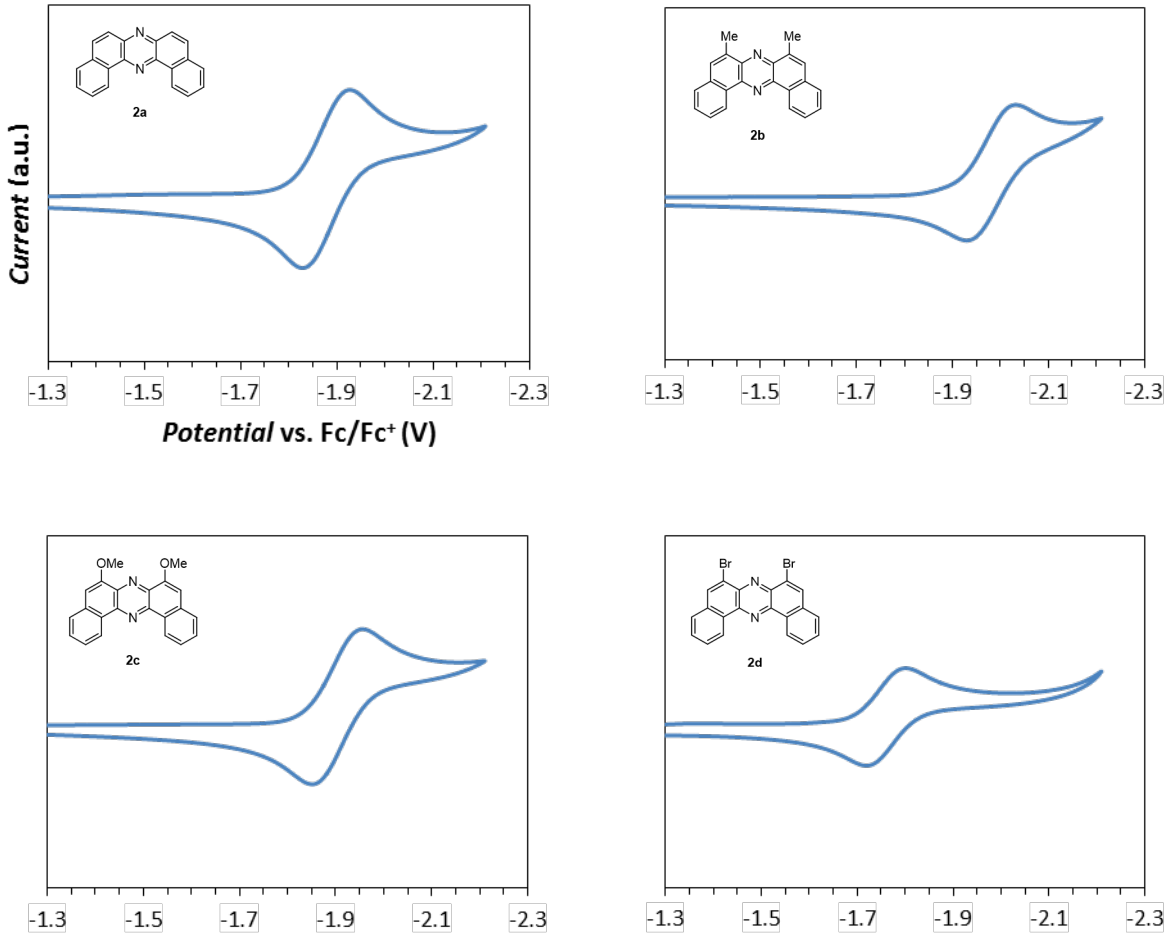

R
R
R =
O
2k

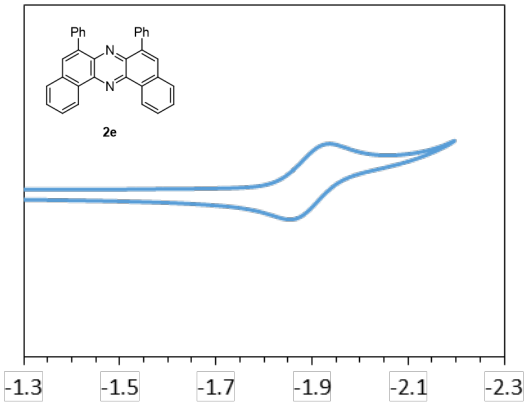

R
R
R = Si(iPr)3
2l

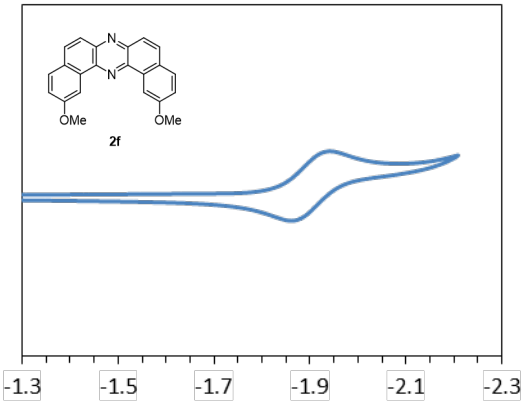
Cyclic Voltammograms of 2

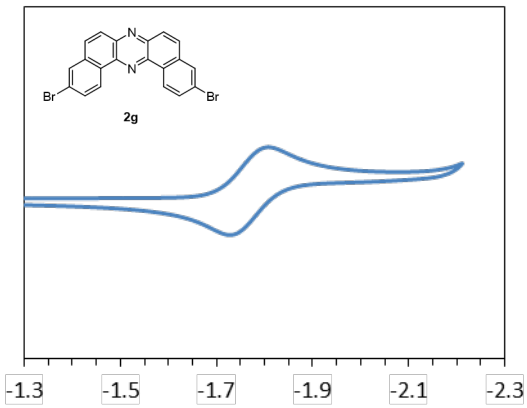
Cyclic voltammetry experiments were conducted at room temperature with CH_2Cl_2 solutions of **2** (5.0×10^{-4} M) containing 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte in a cell equipped with a Pt as the working electrode (scanning rate: 100 m/V). A Pt wire and an Ag wire 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.

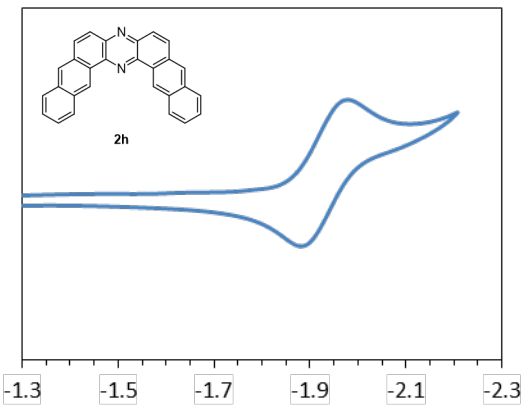
$$\text{LUMO} = -(4.8 + {}^{red}E_{1/2} \text{ vs. } Fc/Fc^+) \qquad \text{(S1)}$$

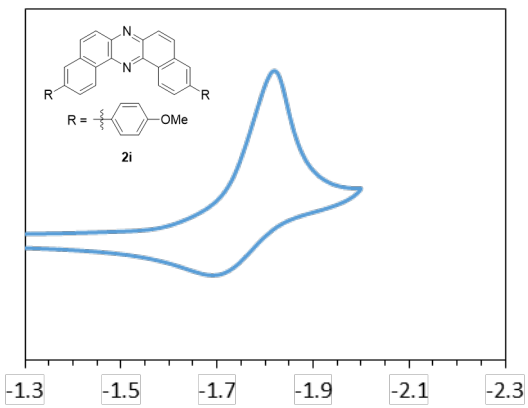


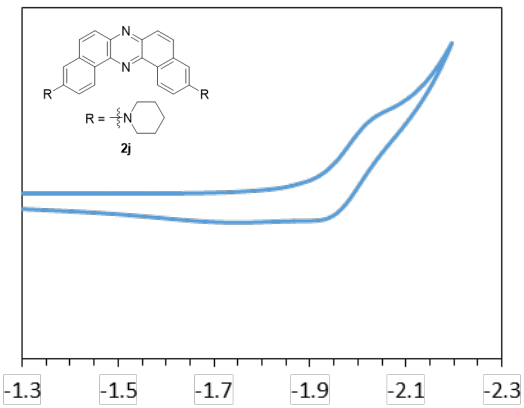

Ph
Ph
N
N
2e
-1.3
-1.5
-1.7
-1.9
-2.1
-2.3

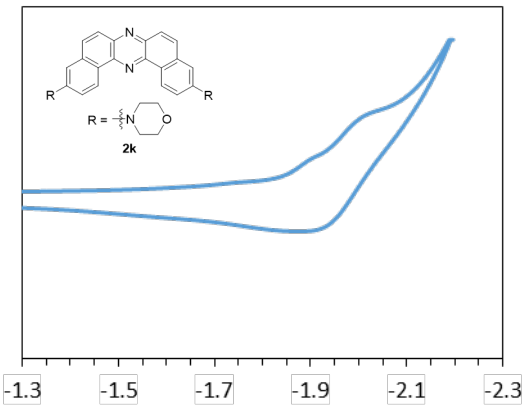

N
N
OMe
OMe
2f
-1.3
-1.5
-1.7
-1.9
-2.1
-2.3

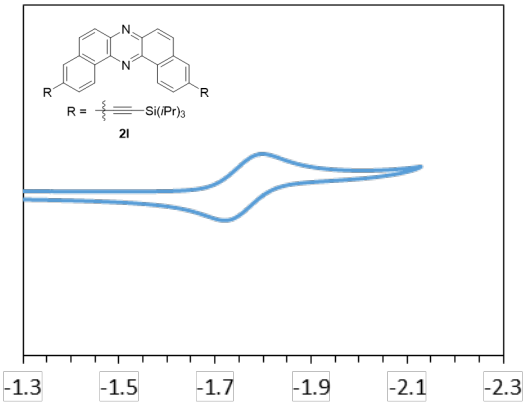

N
N
Br
Br
2g
-1.3
-1.5
-1.7
-1.9
-2.1
-2.3


N
N
2h
-1.3
-1.5
-1.7
-1.9
-2.1
-2.3


N
N
R
R
R =
OMe
2i
-1.3
-1.5
-1.7
-1.9
-2.1
-2.3

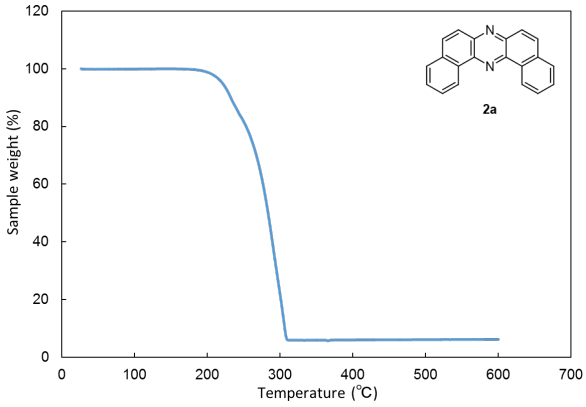

N
N
R
R
R =
N
2j
-1.3
-1.5
-1.7
-1.9
-2.1
-2.3

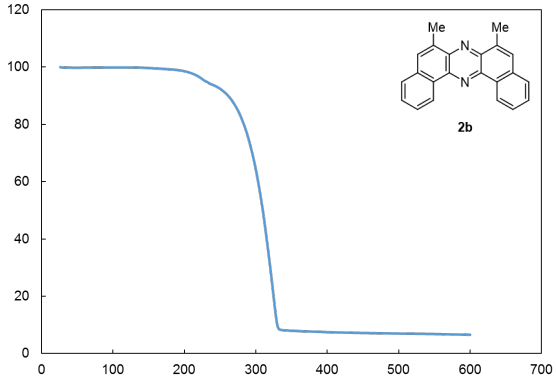


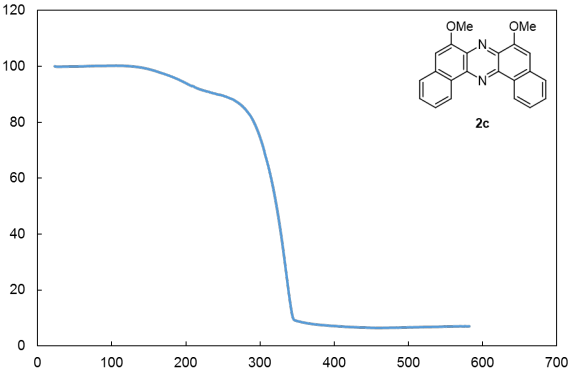


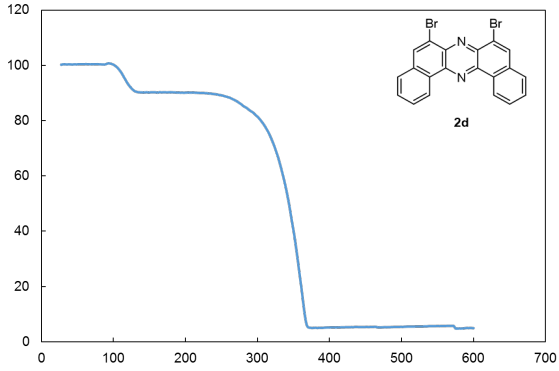
Profiles of Thermogravimetric Analysis (TGA)

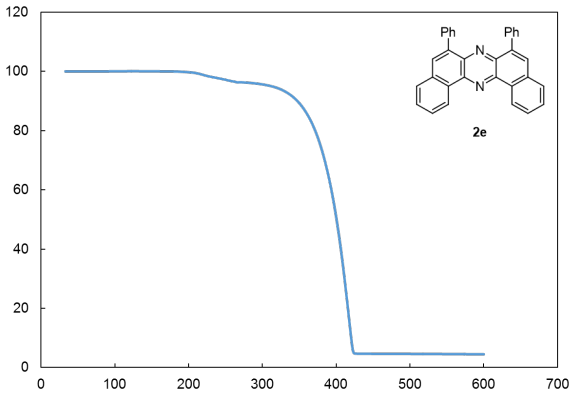
All the TGA profiles of **2** were measured under the nitrogen flow (200 mL/min), starting from 40 °C to 600 °C at the ramp rate of 10 °C/min.

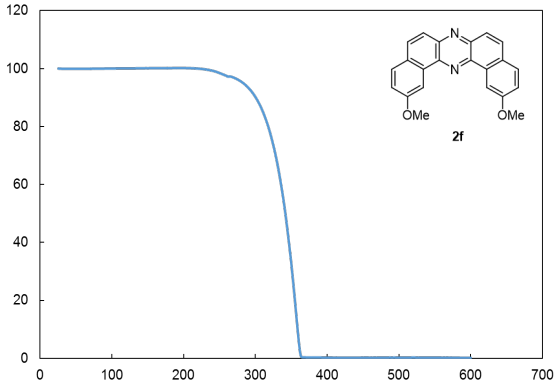


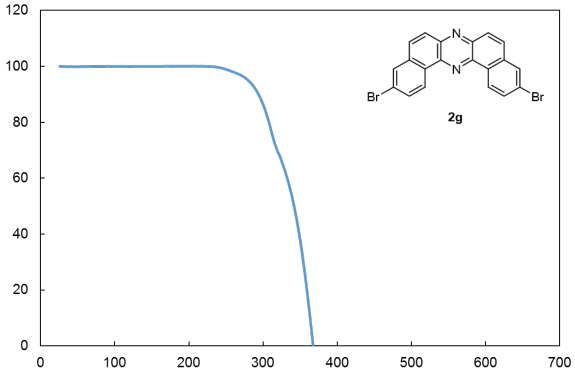


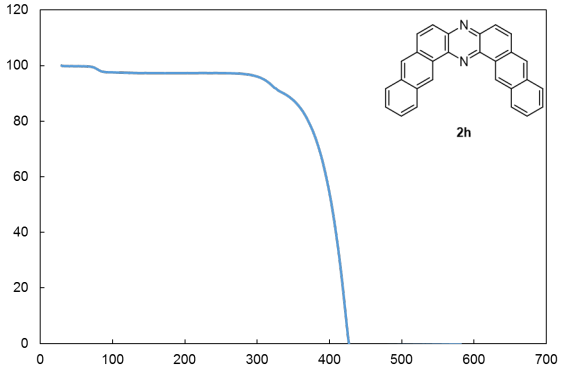


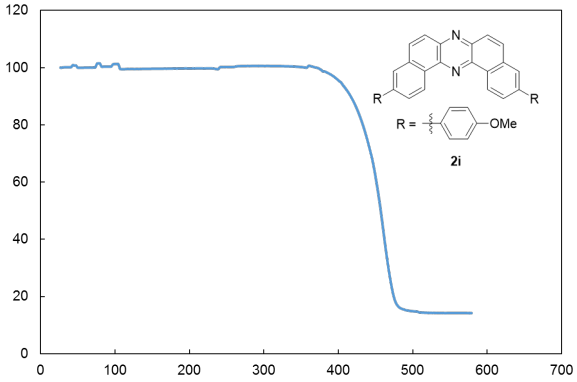


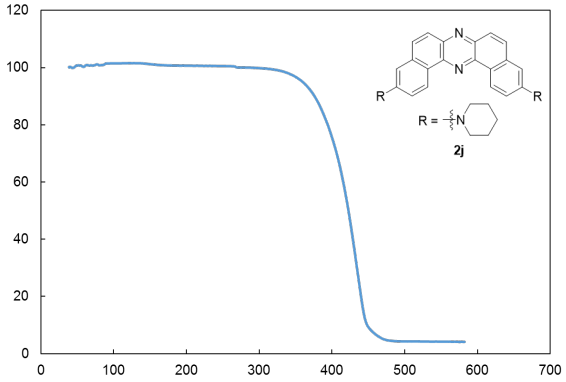

Ph
Ph
N
N
2e

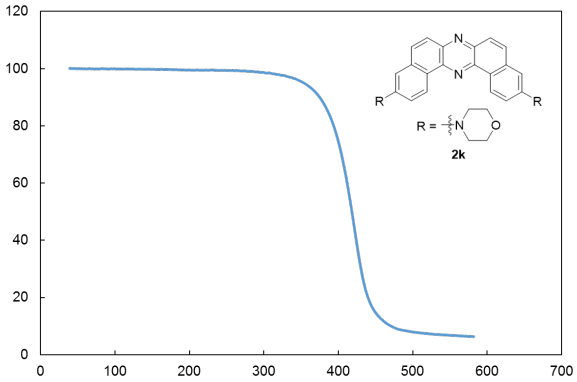

N
N
OMe
OMe
2f

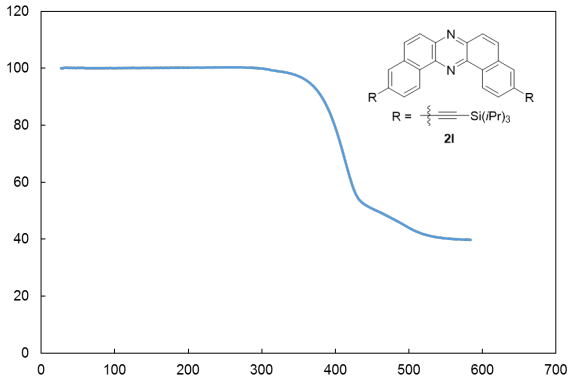

N
N
Br
Br
2g


N
N
2h


N
N
R
R
R =
OMe
2i

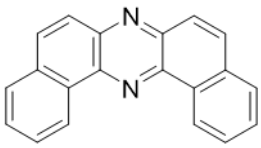

N
N
R
R
R =
N
2j


N
N
R
R
R =
N
O
2k

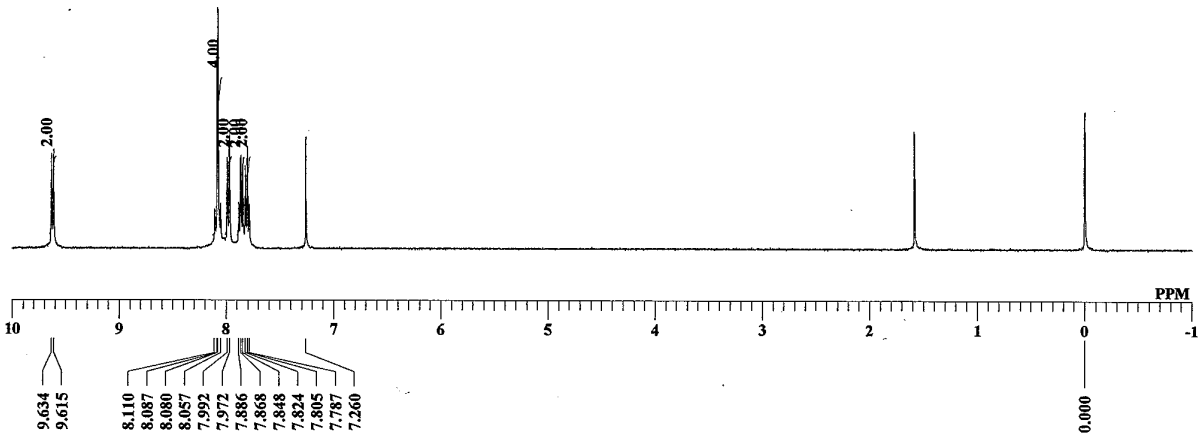

N
N
R
R
R =
Si(iPr)3
2l

^{1}H and ^{13}C NMR Spectra

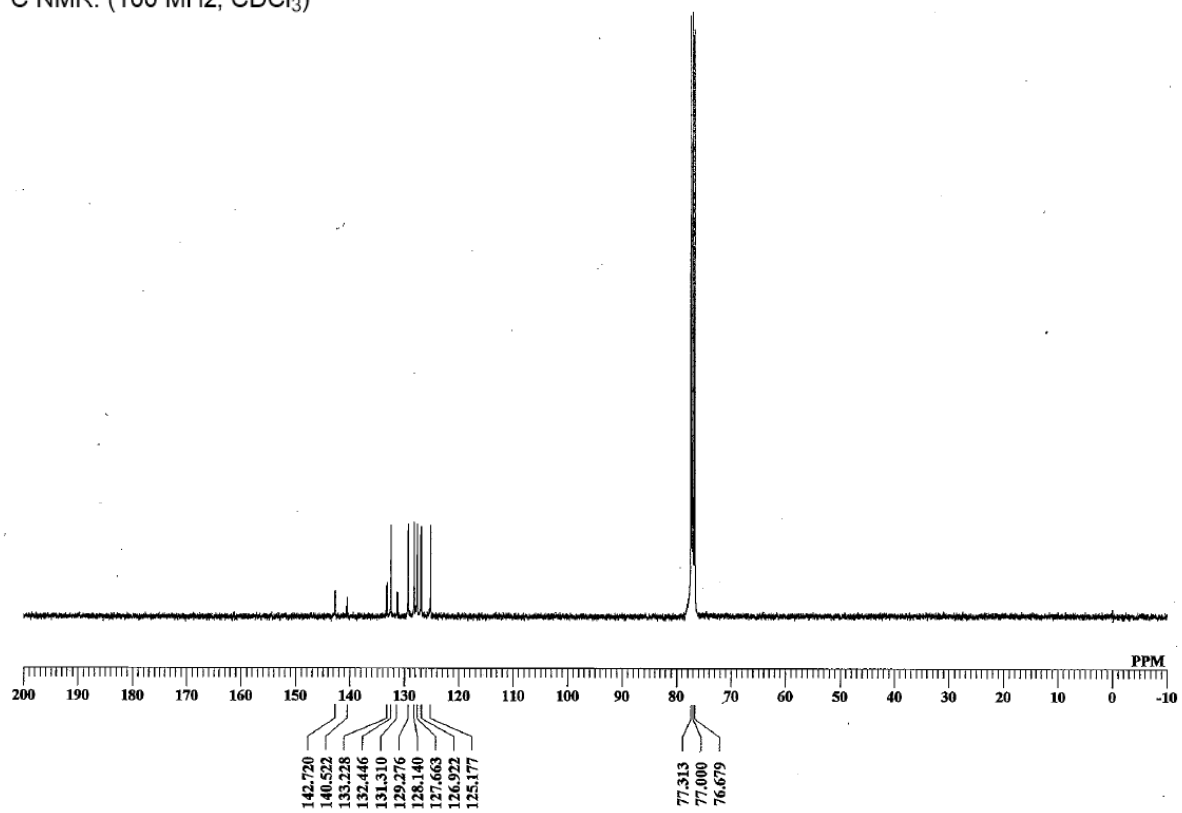
^{1}H NMR: (400 MHz, $CDCl_3$)



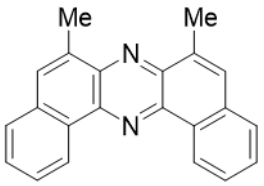
2a



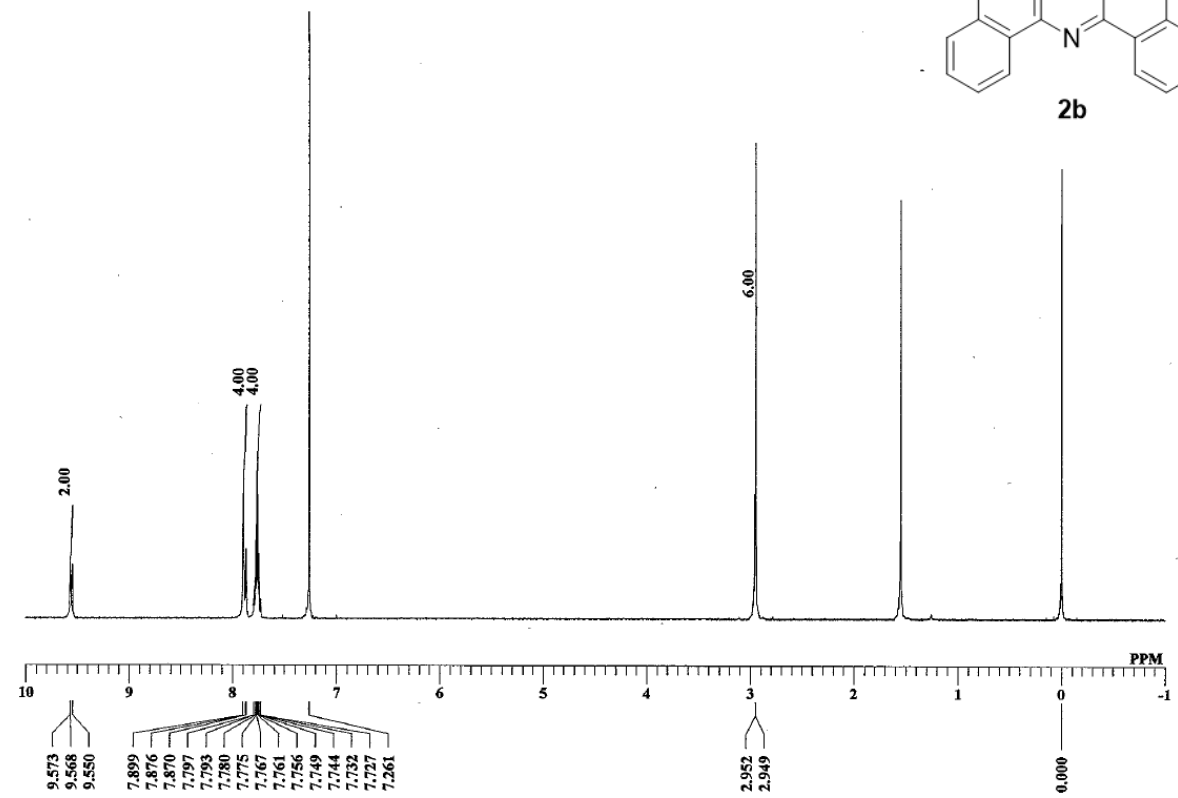
^{13}C NMR: (100 MHz, $CDCl_3$)



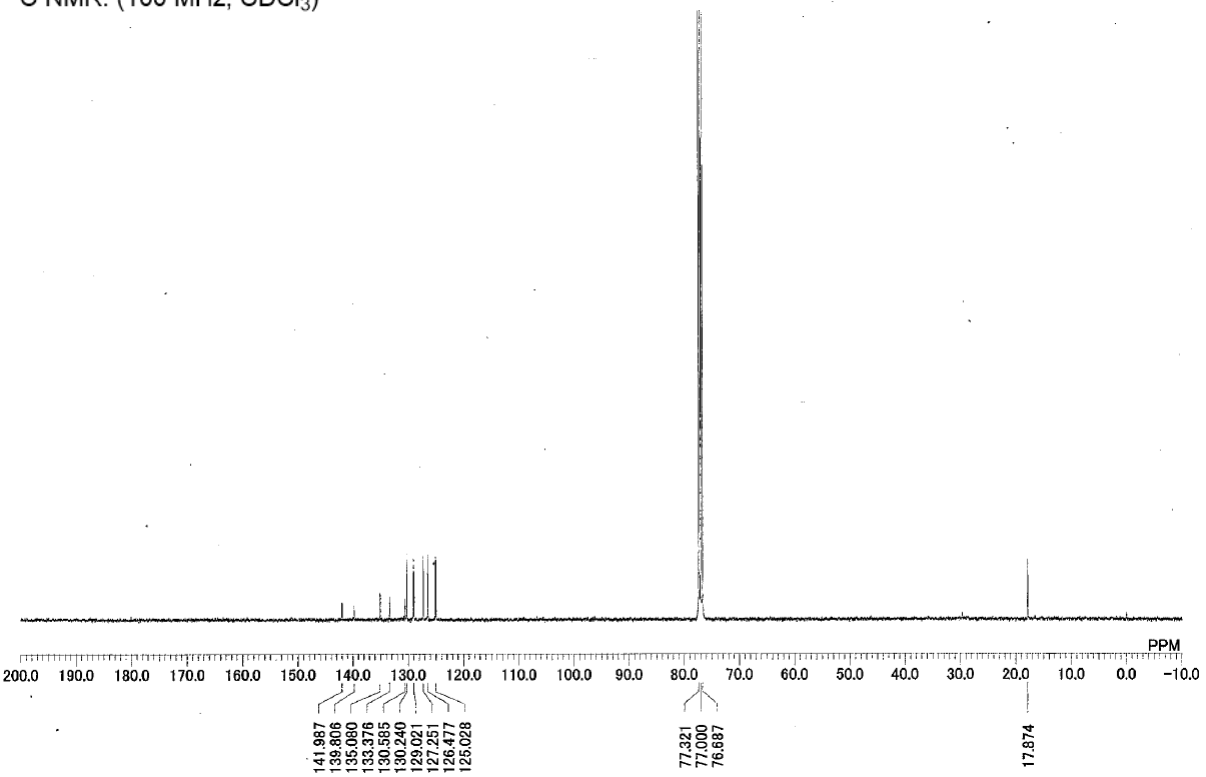
^{1}H NMR: (400 MHz, $CDCl_3$)



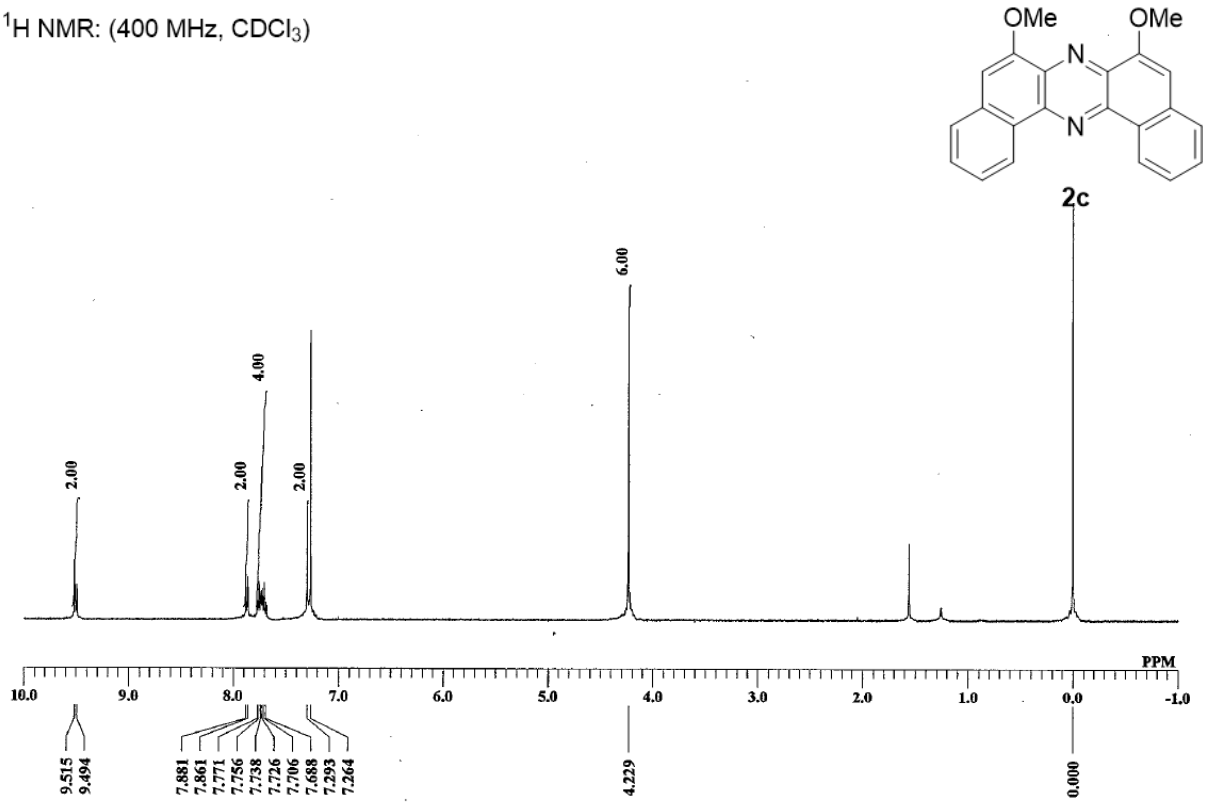
2b



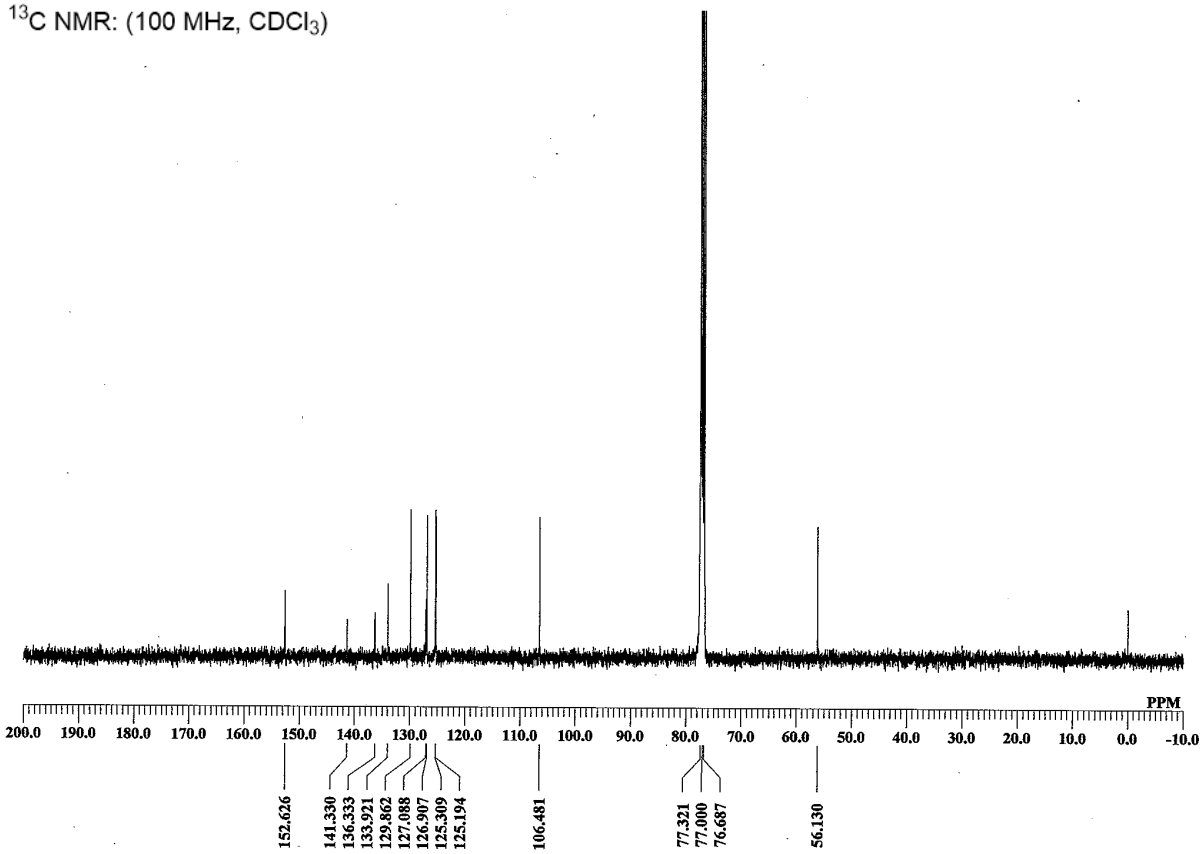
^{13}C NMR: (100 MHz, $CDCl_3$)



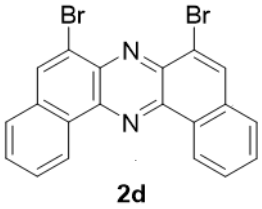
^{1}H NMR: (400 MHz, $CDCl_3$)



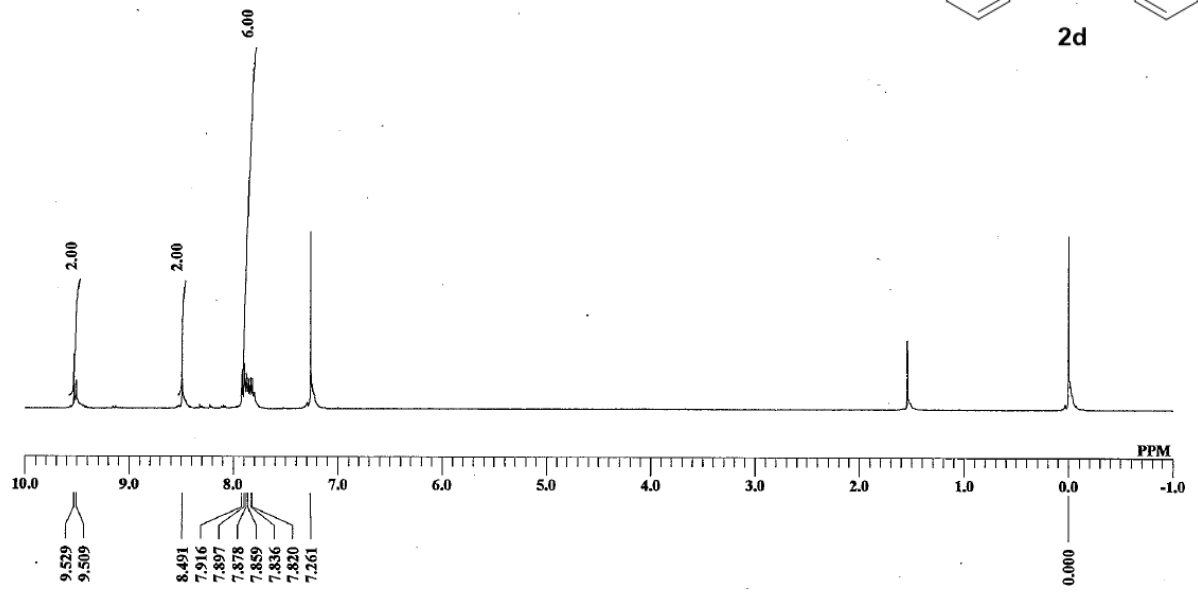
^{13}C NMR: (100 MHz, $CDCl_3$)



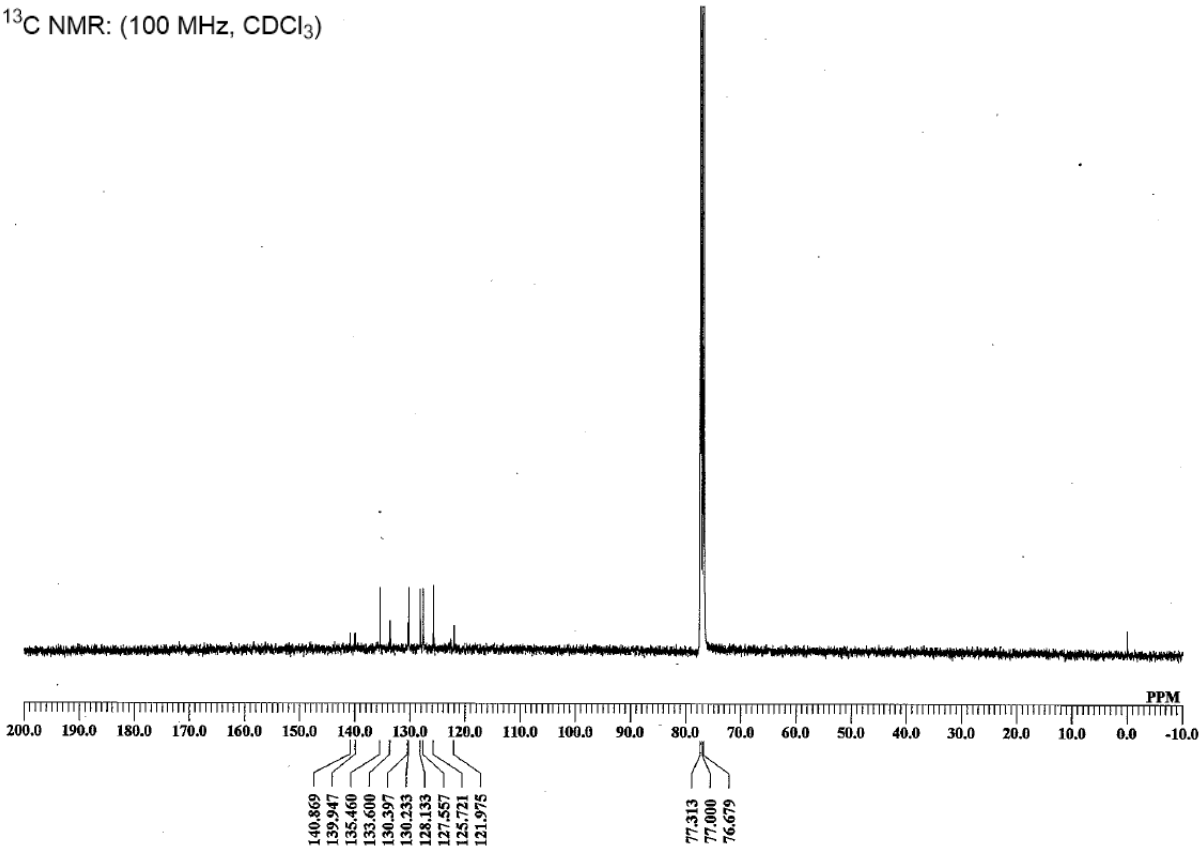
^{1}H NMR: (400 MHz, $CDCl_3$)



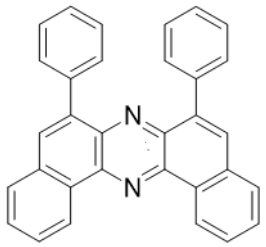
2d



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

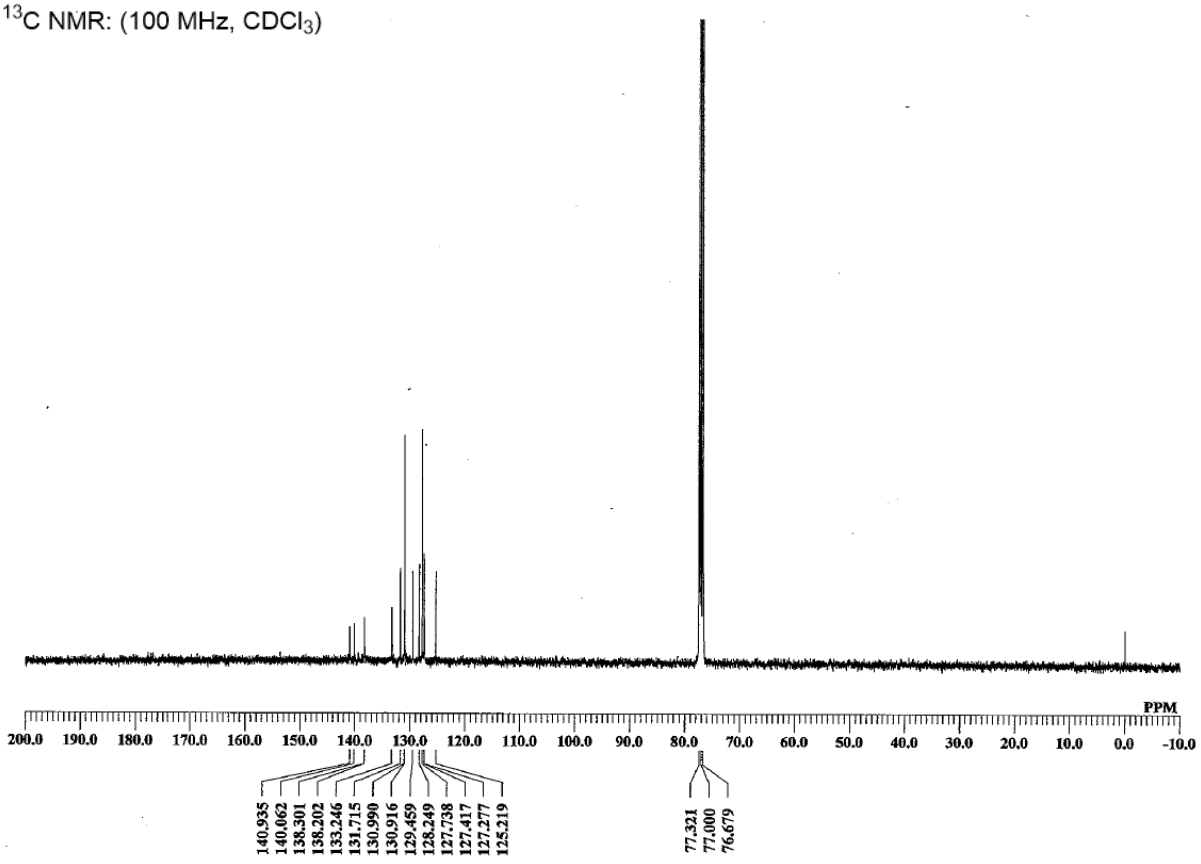


^{1}H NMR: (400 MHz, $CDCl_3$)

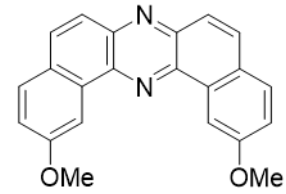


2e

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

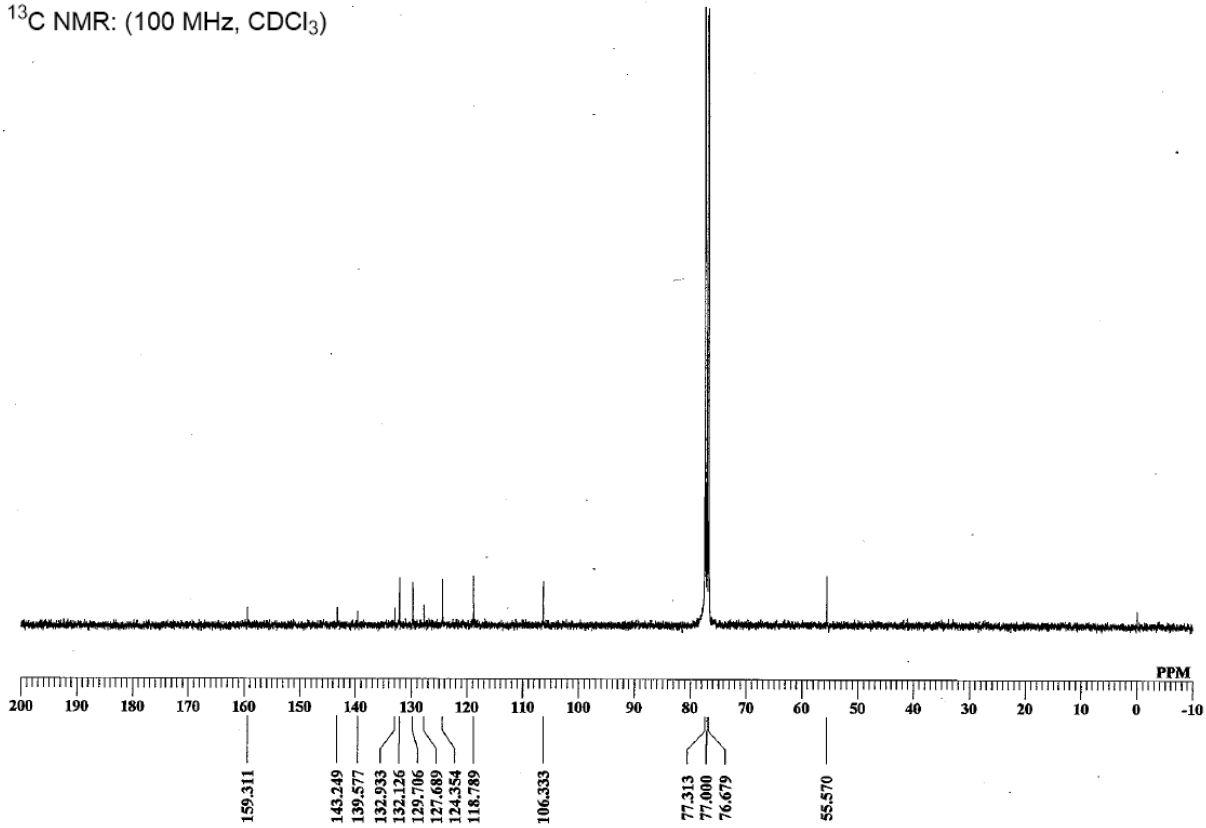


^{1}H NMR: (400 MHz, $CDCl_3$)

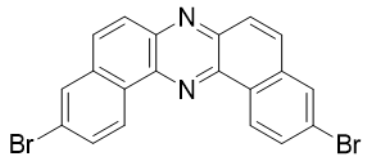


2f

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

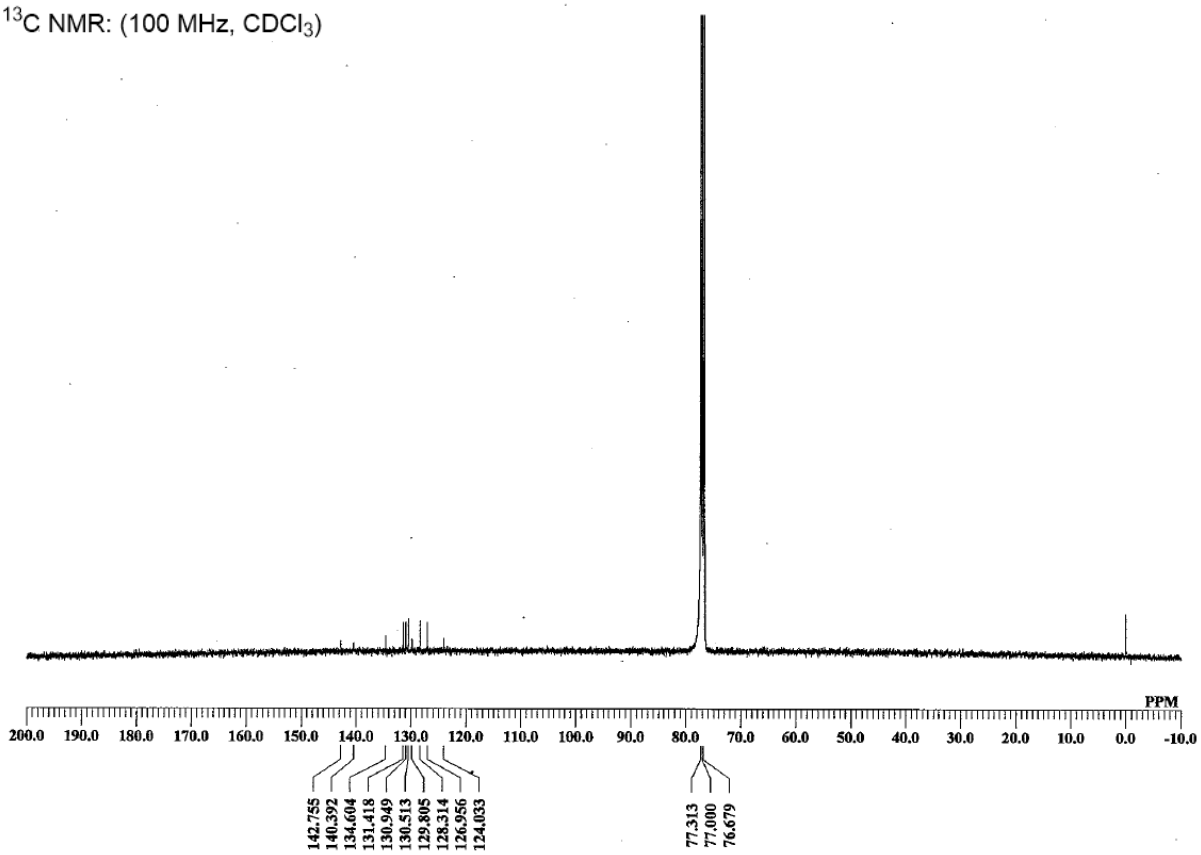


^{1}H NMR: (400 MHz, $CDCl_3$)

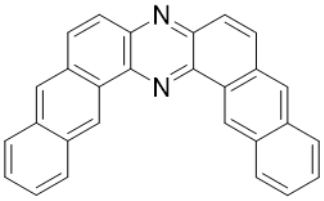


2g

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

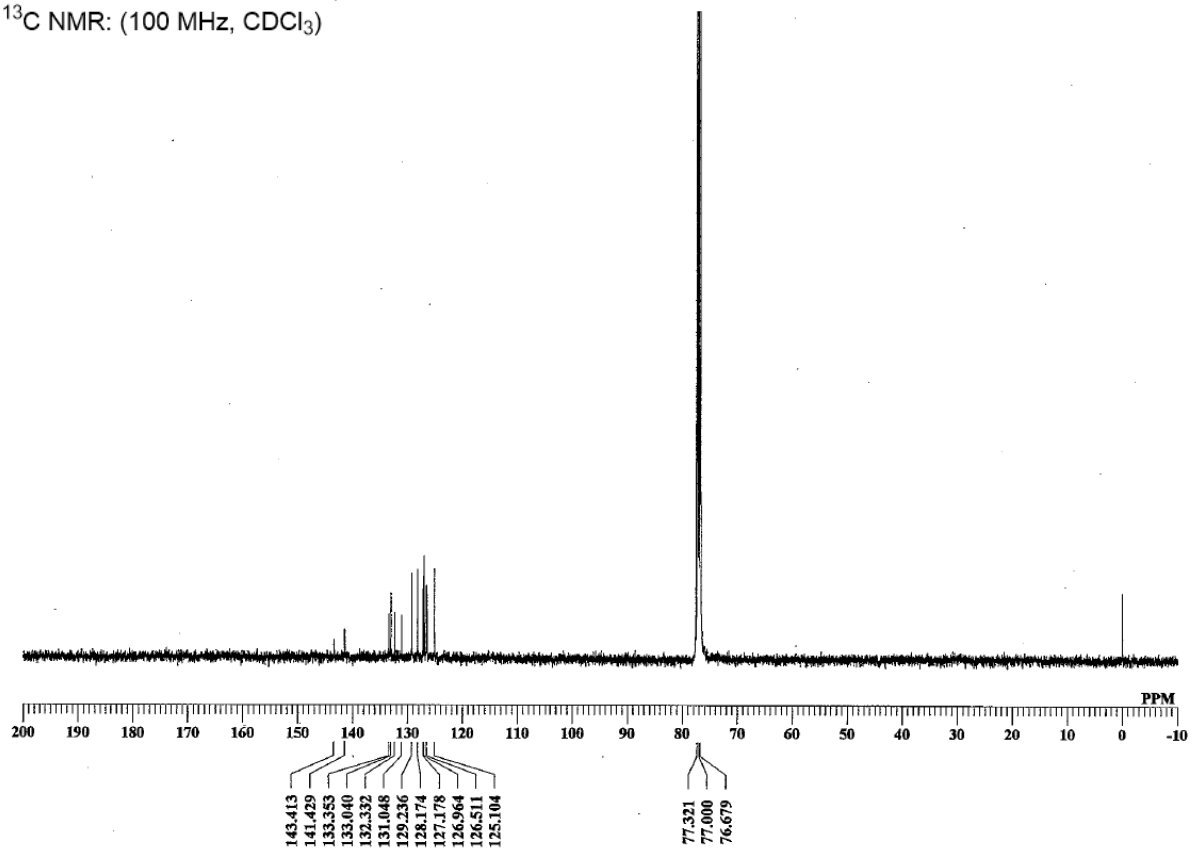


^{1}H NMR: (400 MHz, $CDCl_3$)

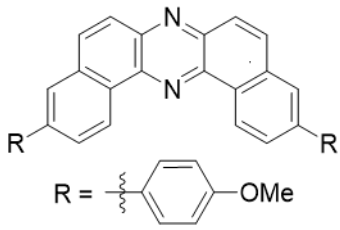


2h

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

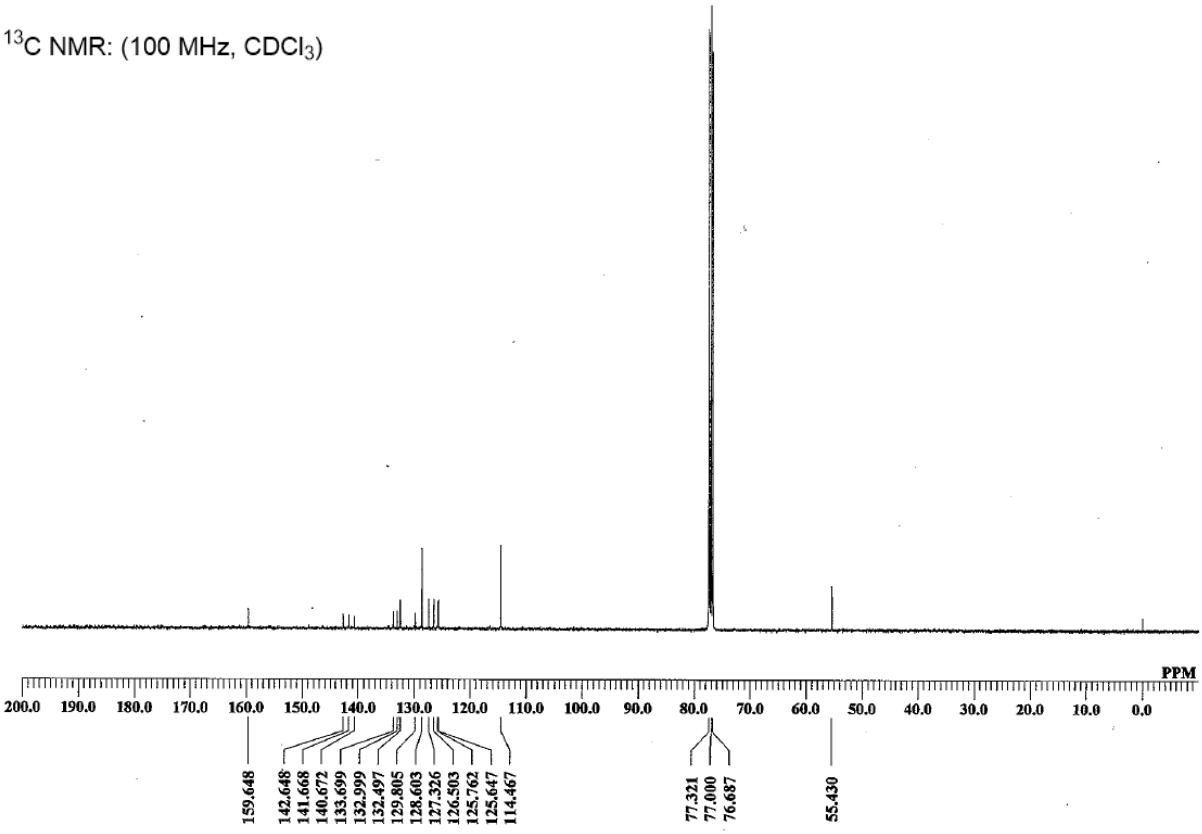


^{1}H NMR: (400 MHz, $CDCl_3$)

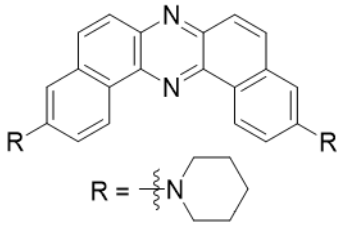


2i

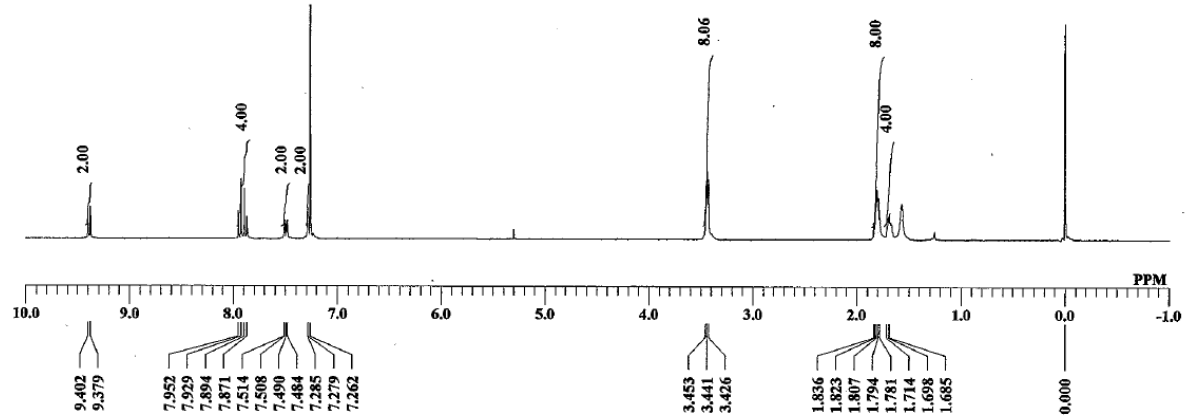
^{13}C NMR: (100 MHz, $CDCl_3$)



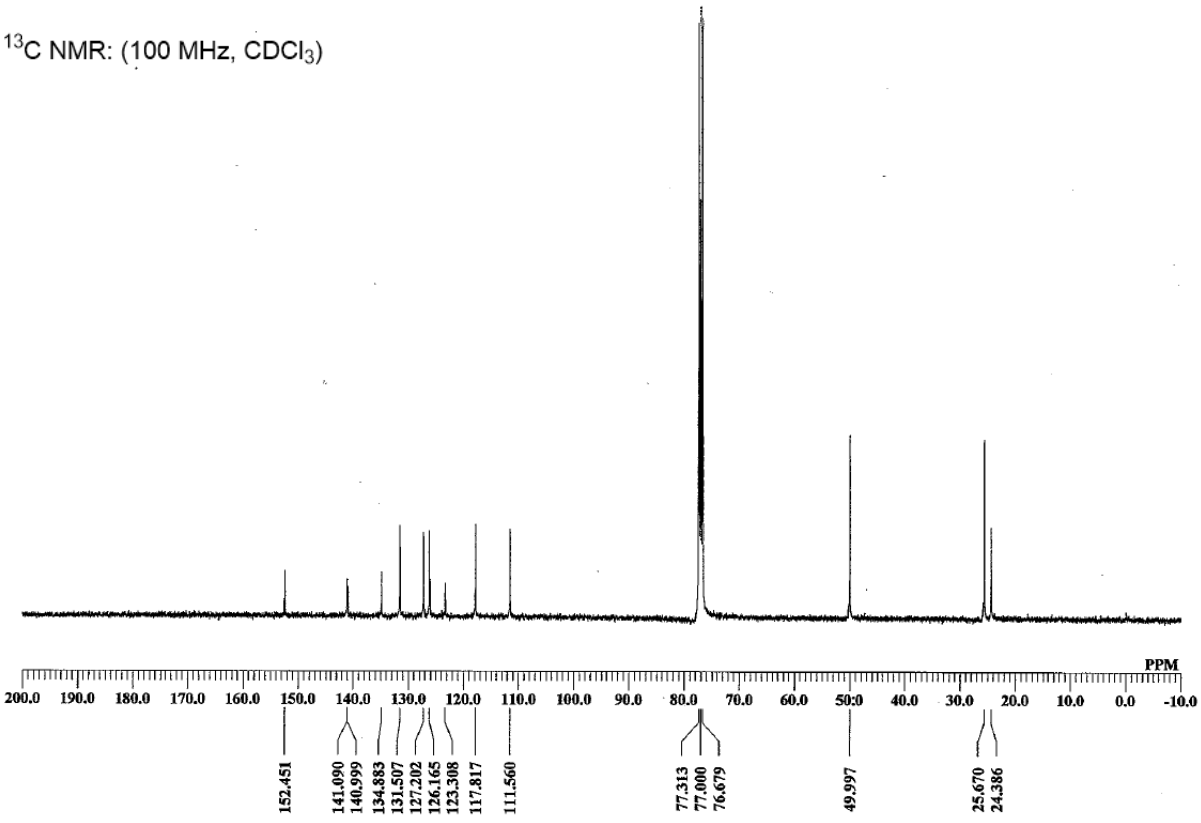
^{1}H NMR: (400 MHz, $CDCl_3$)



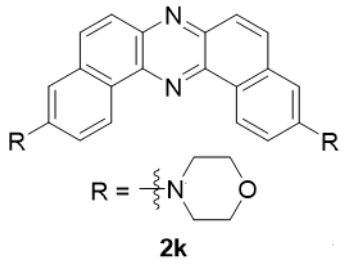
2j



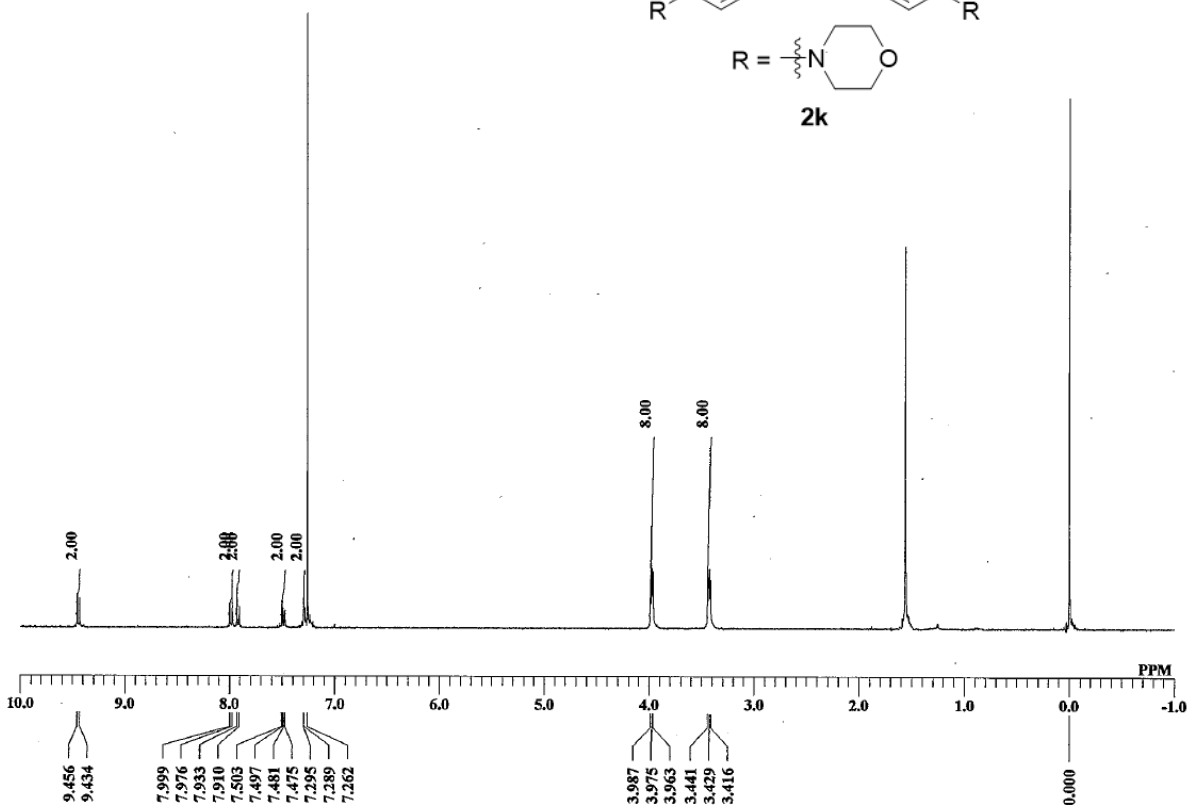
^{13}C NMR: (100 MHz, $CDCl_3$)



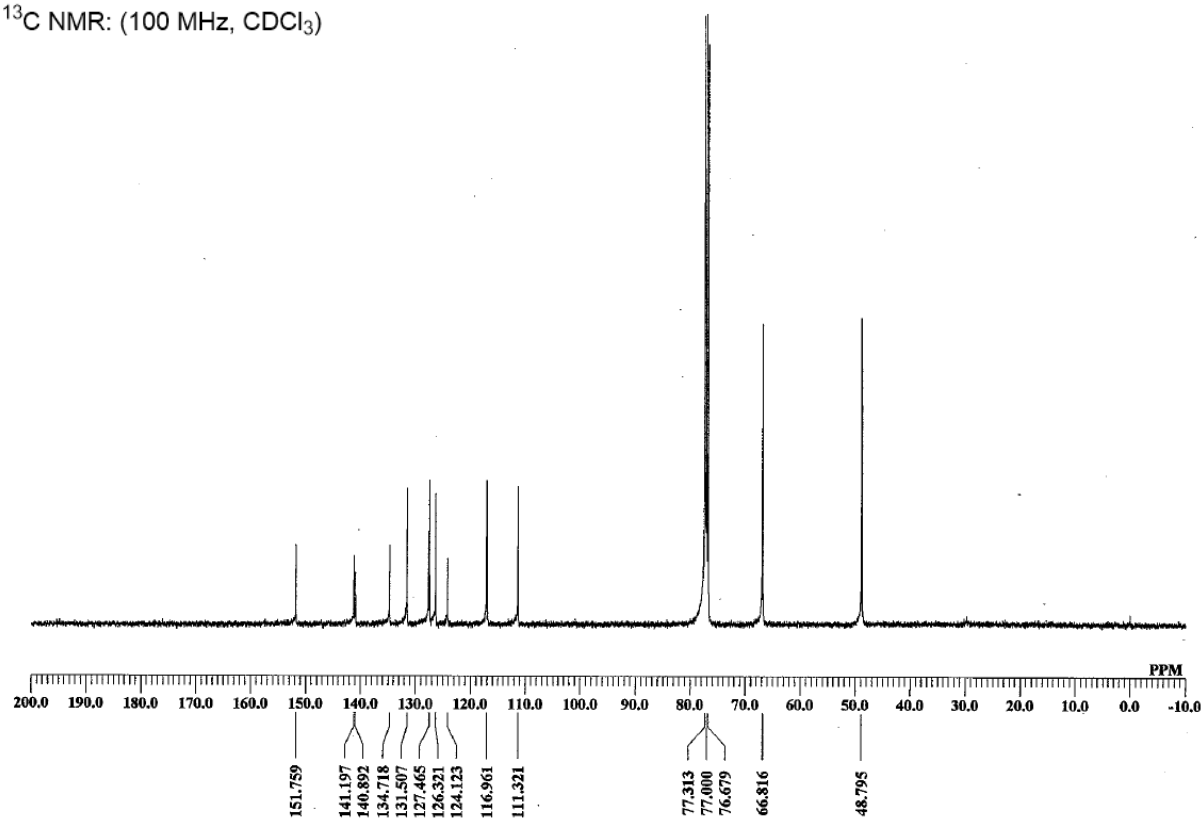
^{1}H NMR: (400 MHz, $CDCl_3$)



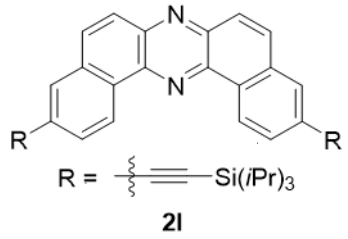
2k



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

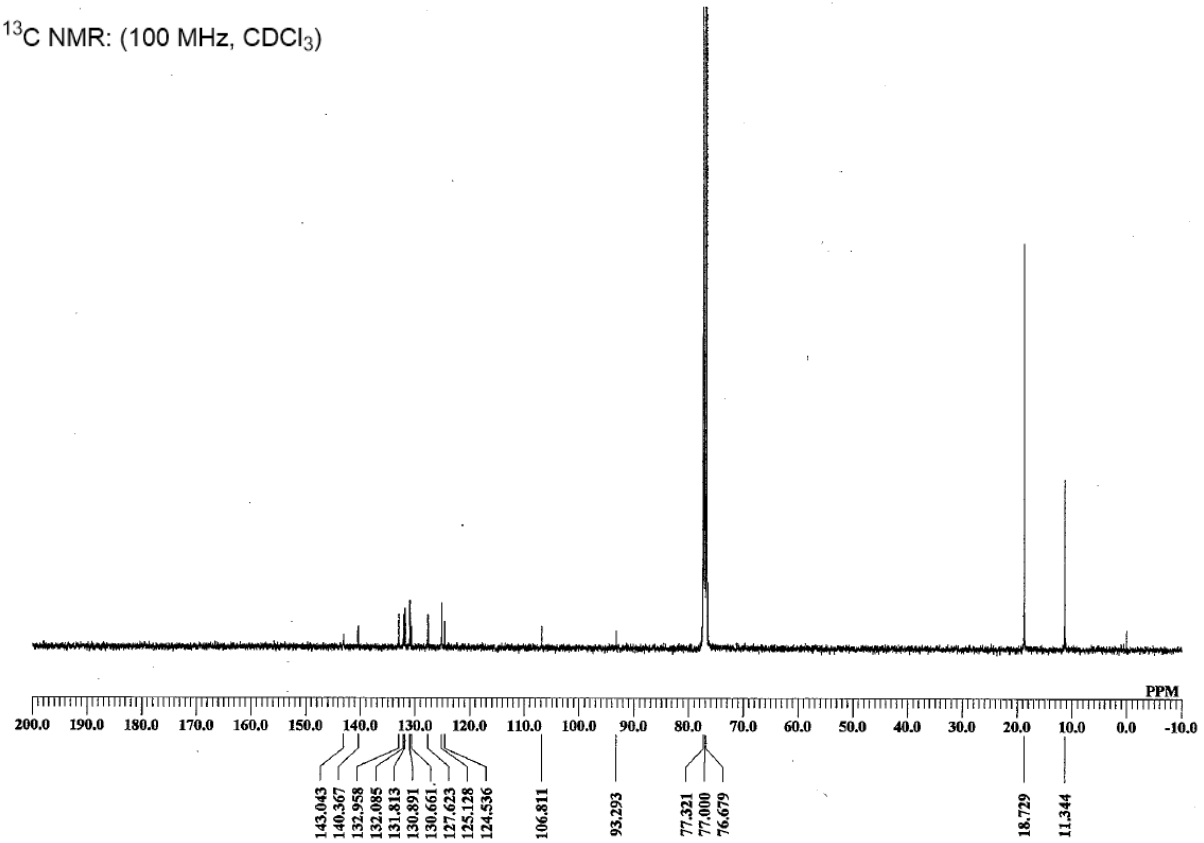


^{1}H NMR: (400 MHz, $CDCl_3$)

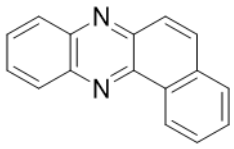


2l

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



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



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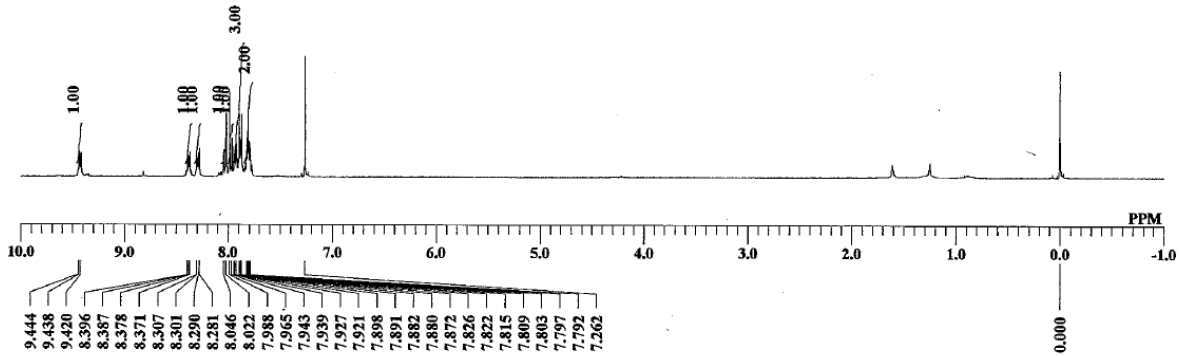
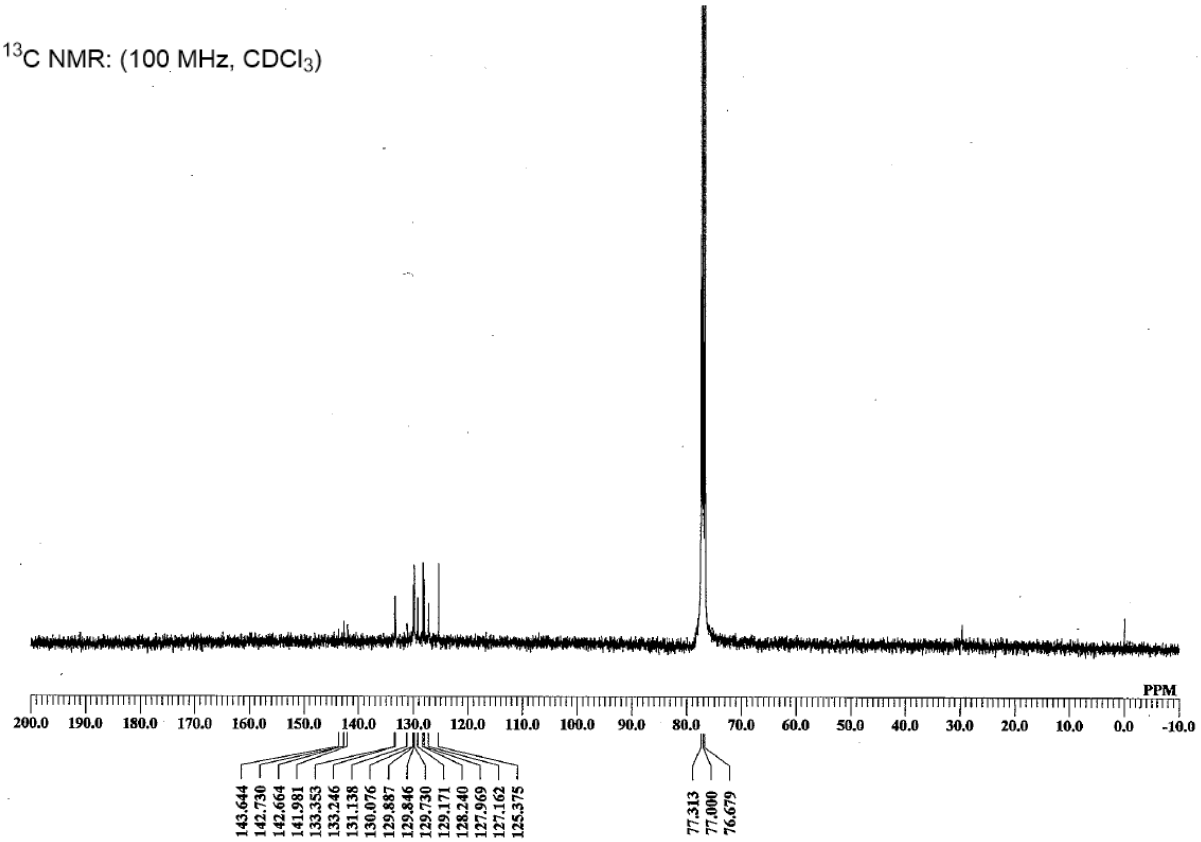
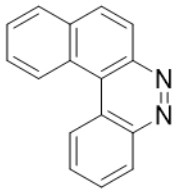


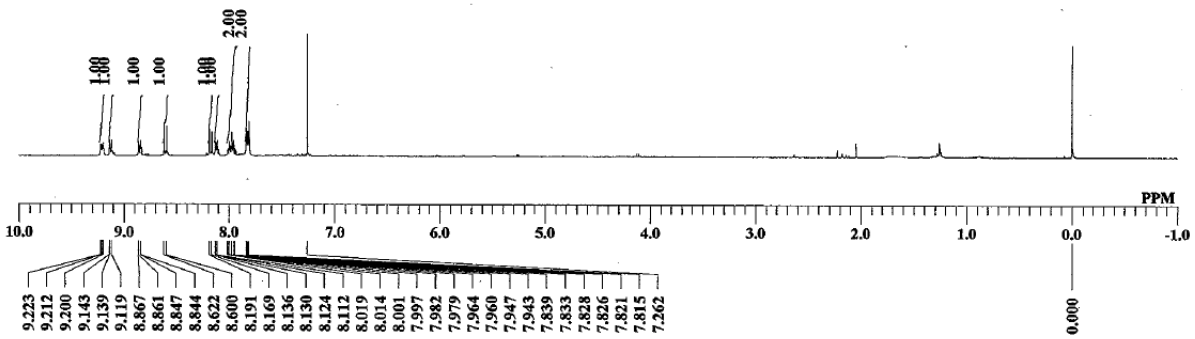
^{13}C NMR: (100 MHz, $CDCl_3$)



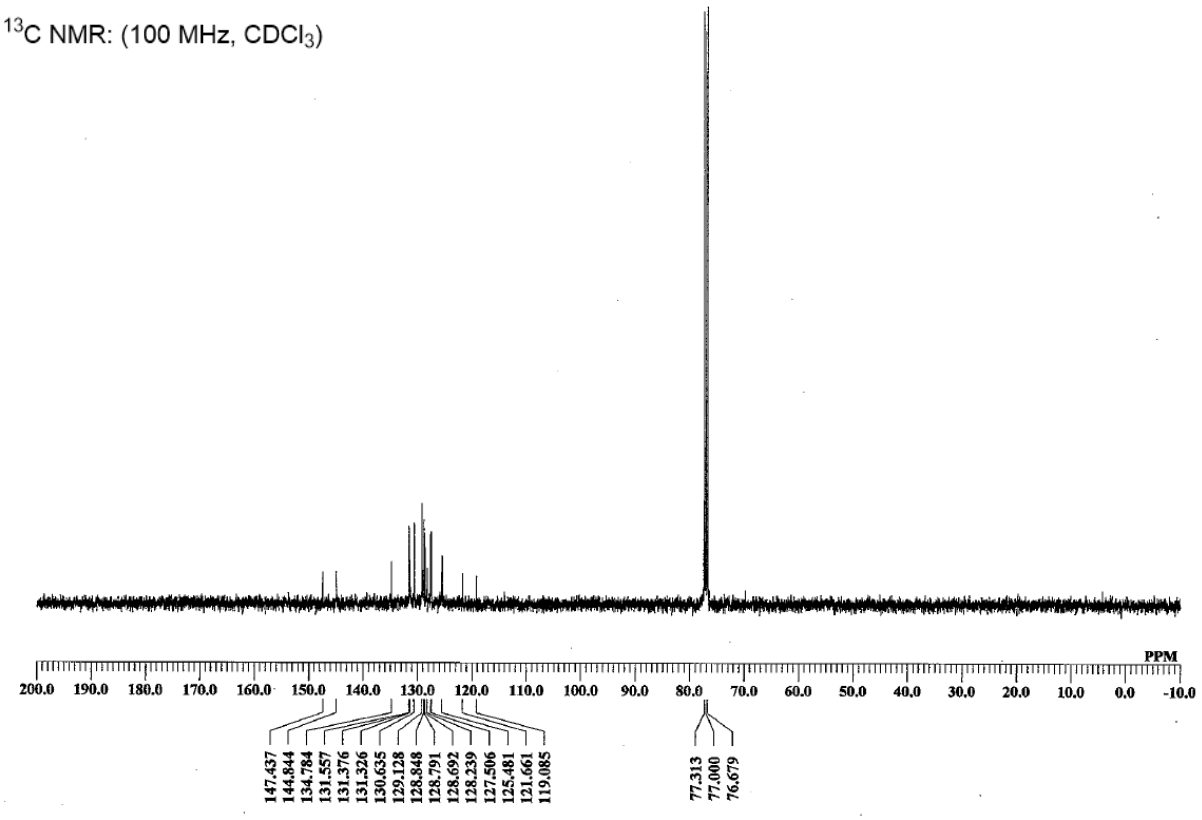
^{1}H NMR: (400 MHz, $CDCl_3$)



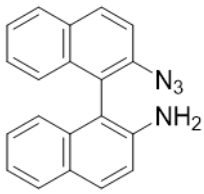
7



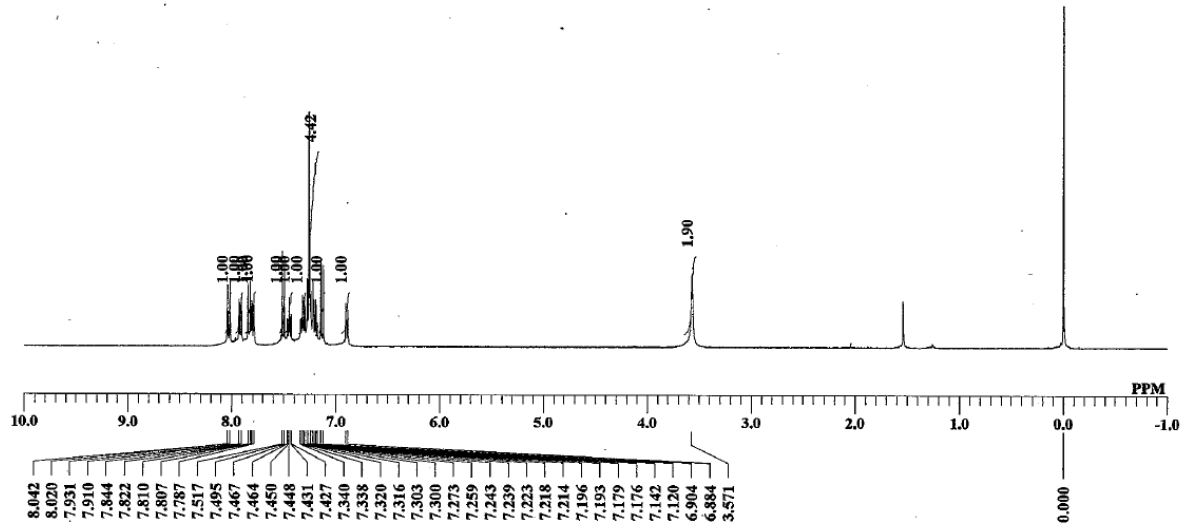
^{13}C NMR: (100 MHz, $CDCl_3$)



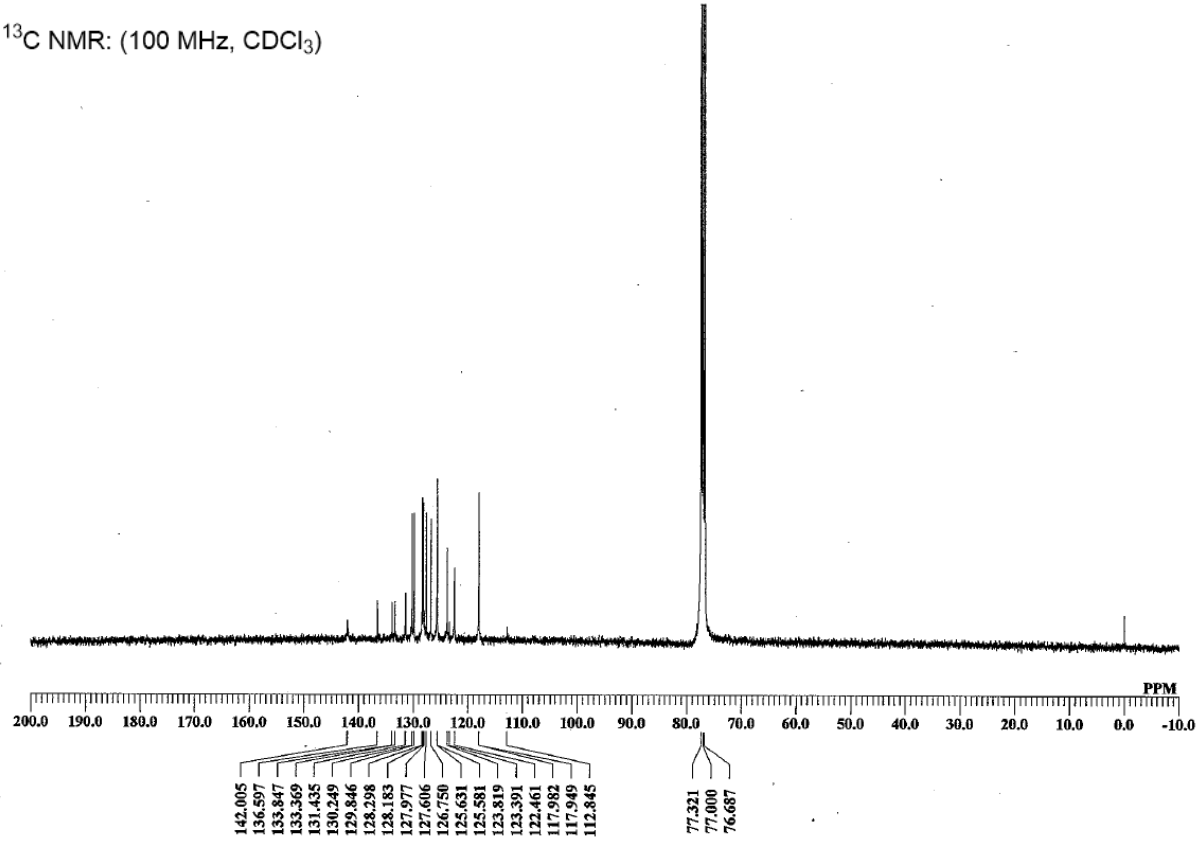
^{1}H NMR: (400 MHz, $CDCl_3$)



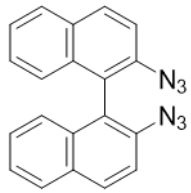
10



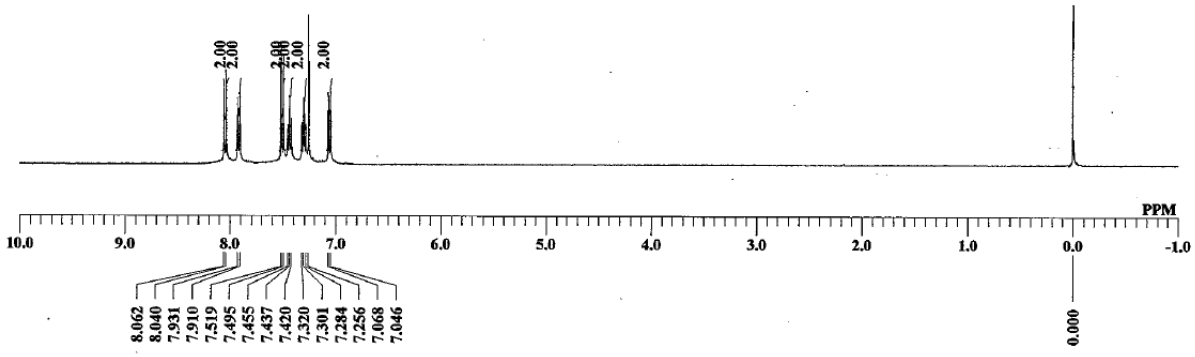
^{13}C NMR: (100 MHz, $CDCl_3$)



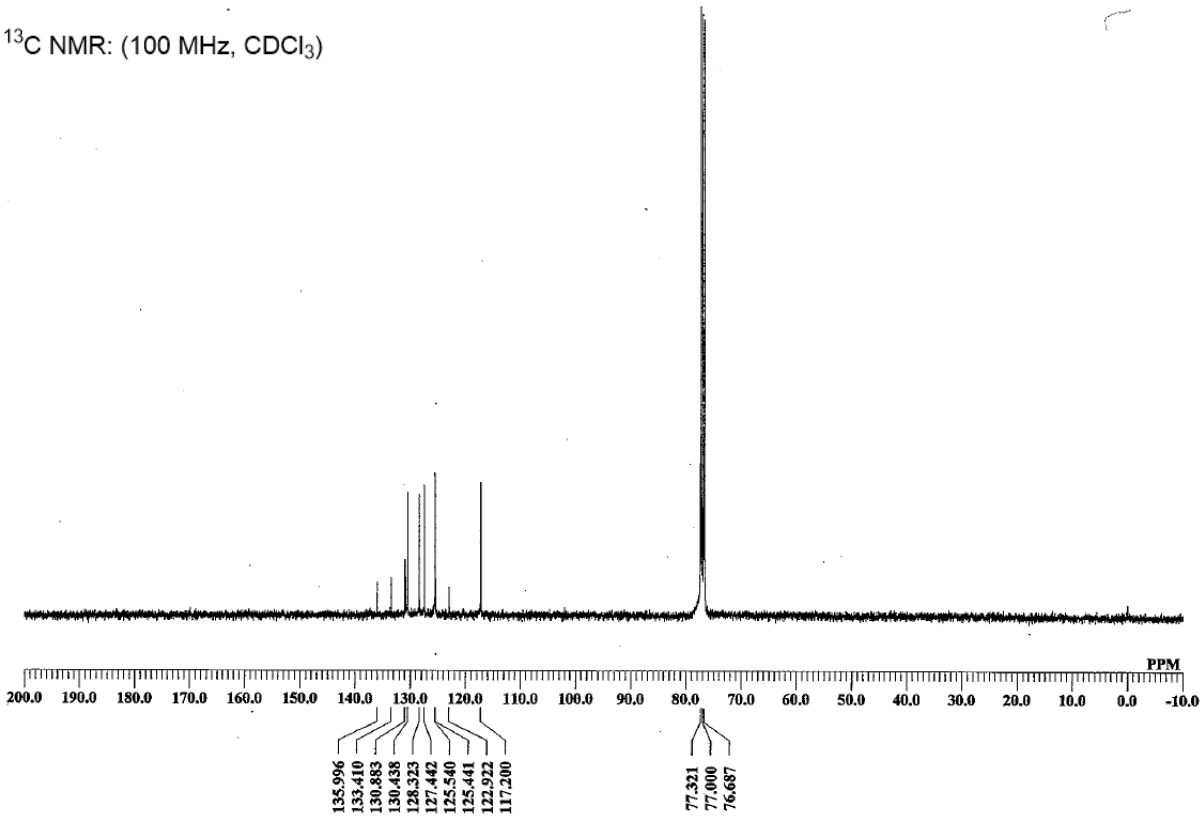
^{1}H NMR: (400 MHz, $CDCl_3$)



11



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



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