Supporting Information

A Facile Approach toward 1,2-Diazabenzo[*ghi*]perylene Derivatives: Structures and Electronic Properties

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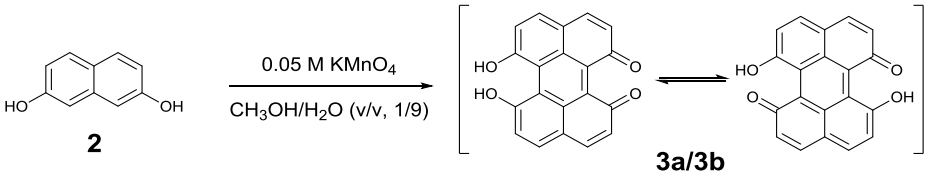
1. General information

Solvents were purified and dried by standard methods prior to use. All commercially available reagents were used without further purification unless otherwise noted. Column chromatography was generally performed on silica gel (200 – 300 mesh) and reactions were monitored by thin layer chromatography (TLC) using silica gel GF254 plates with UV light to visualize the course of reaction. ^{1}H and ^{13}C NMR data were recorded on a 400 MHz spectrometer using $CDCl_3$ or CD_3OD as solvent at room temperature. The chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. High-resolution mass spectra (HRMS) were recorded on a Finnigan MAT TSQ 7000. Absorption spectra were recorded on a SHIMADZU UV-3600plus. Photoluminescence spectra were recorded on a Thermo Scientific Lumina. High resolution APCI mass spectra were recorded on a Bruker amazonX instrument. IR spectra were measured on a Nicolet 380 spectrometer. Cyclic voltammetry (CV) was performed on a Chenhua 650D electrochemical analyzer in anhydrous solvents containing recrystallized tetra-*n*-butyl-ammonium hexafluorophosphate ($TBAPF_6$, 0.1M) as supporting electrolyte at 298 K.

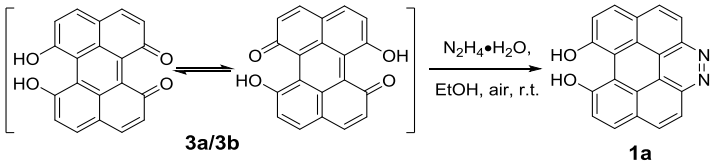
2. Synthetic section

Perylenequinonoid (3a/3b)



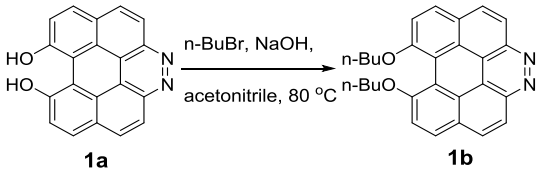
To a solution of 2,7-dihydroxynaphthalene **2** (600 mg, 3.75 mmol, 1.0 equiv) in methanol (60 mL) and water (540 mL) was added 0.05 M potassium permanganate solution (1.5 mL, 0.075 mmol, 0.02 equiv) at room temperature. After magnetically stirring for 12 h, the dark blue solution was acidified with 2 M HCl. A dark green precipitate was allowed to settle over 2 h, after which the majority of the solution was decanted, the solid was isolated by filtration and washed with dichloromethane and ethyl acetate. Compound **3a/3b** was obtained as a dark green solid (512 mg, yield: 87%). Our characterization data were in full agreement with those of the literature reported.[S1]

7,8-Dihydroxybenzo[4,10]anthra[1,9,8-*cdef*]cinnoline (1a)



To a solution of perylenequinonoid **3a**/**3b** (2 g, 6.37 mmol, 1.0 equiv) in 20 mL of EtOH was slowly added N_2H_4•H_2O (64.00 mmol, 10.0 equiv) at room temperature. The mixture was vigorously stirred for 20 min, and then diluted with 30 mL EtOH. The reaction was allowed to proceed overnight. The reaction mixture was concentrated to 10 mL via rotary evaporation, ethyl acetate (60 mL) was added, and the solid precipitated from the mixture. The raw product was isolated by filtration and washed with dichloromethane, and then further purified by recrystallization (ethyl acetate/methanol=3:1) to give **1a** as a reddish brown solid (1.68 g, 85% yield). ^{1}H NMR (400 MHz, CD_3OD): δ 8.33 (d, *J* = 9.0 Hz, 2H), 8.27 - 8.18 (m, 4H), 7.69 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, CD_3OD): δ 162.90, 146.62, 133.13, 129.20, 126.30, 125.02, 124.30, 121.53, 120.59, 120.25. HRMS (APCI) *m/z*: Calcd for $C_{20}H_{11}N_2O_2^+$ $[M+1]^+$: 311.0815; Found: 311.0811 (error = -1.3 ppm).

7,8-Dibutoxybenzo[4,10]anthra[1,9,8-*cdef*]cinnoline (1b)



A round bottom flask was charged with **1a** (500 mg, 1.61 mmol, 1.0 equiv) and *n*-butyl bromide (1.53 mL, 7.08 mmol, 4.4 equiv), and *N*,*N*-dimethylformamide (5 mL). Then NaOH (567.8 mg, 7.08 mmol, 4.4 equiv) was added with stirring. The reaction mixture was heated to 60 ℃, and kept stirring overnight. The reaction was cooled to room temperature after completion as indicated by TLC analysis. The reaction was quenched by water (50 mL). The residue was extracted with CH_2Cl_2 (100 mL). The extract was washed with aqueous NaOH (3 × 50 mL, 10% w) and dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation. The residue was chromatographed (CH_2Cl_2/ ethyl acetate v/v= 5/1) to give **1b** as a yellow solid (272 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, *J* = 9.0 Hz, 2H), 8.29 - 8.35 (m, 4H), 7.85 (d, *J* = 8.6 Hz, 2H), 4.27 (t, *J* = 6.7 Hz, 4H), 1.92 – 1.84 (m, 4H), 1.43 -

1.47 (m, 4H), 0.94 (t, J = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.81, 145.59, 130.37, 127.86, 125.13, 125.04, 123.71, 117.15, 117.01, 115.41, 31.70, 19.19, 13.93. HRMS (MALDI-TOF) *m/z*: Calcd for $C_{28}H_{26}N_2O_2$ $[M]^+$: 422.1994; Found: 422.1992 (error = -0.5 ppm).

3. DFT calculations

Geometric optimization of was performed at B3LYP/6-31+G* level of theory using the Gaussian 09 package.[S2] Nucleus independent chemical shifts (NICS) were calculated using the gauge invariant atomic orbital (GIAO) approach at the GIAO-B3LYP/6-311+G(d,p) level $NICS(1)_{zz}$ values were averaged by two positions (above and below the plane) of all the equivalent rings. TD DFT calculations were conducted at PBE/6-31+G* level.

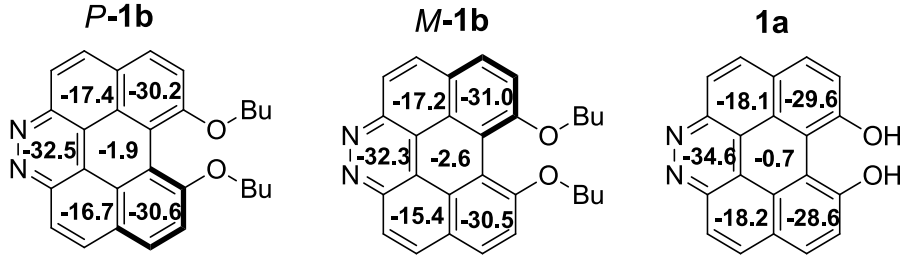


Figure S1 $NICS(1)_{zz}$ values (in ppm) of **1a** and **1b** (*P*-enantiomer and *M*-enantiomer) calculated at the GIAO-B3LYP/6-311+G(d, p) level.

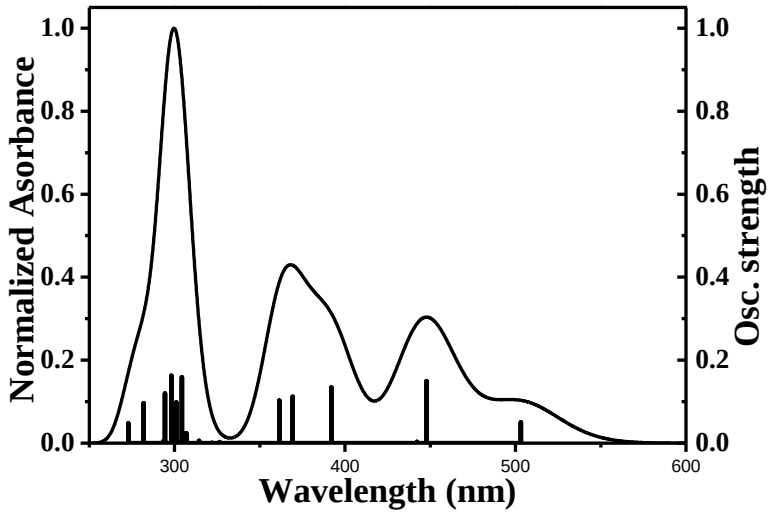


Figure S2 Calculated (PBE/6-31+G*) absorption spectrum of **1a**.

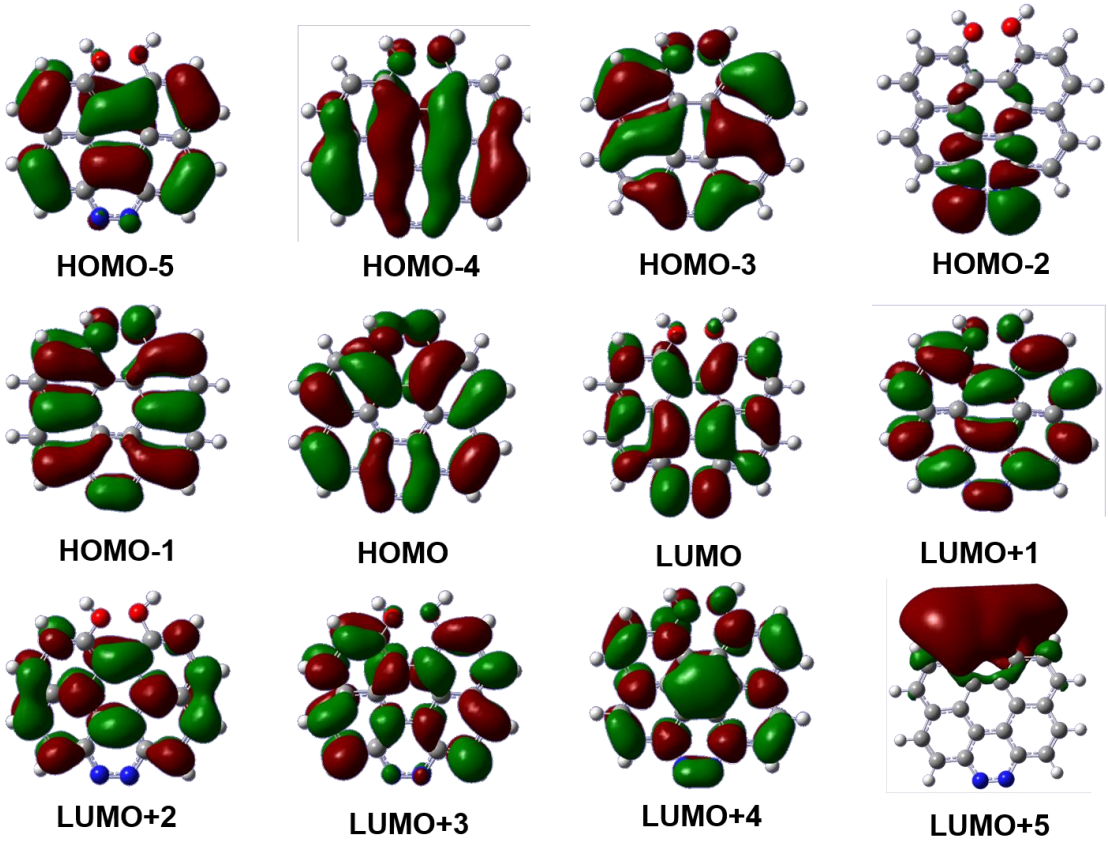


Figure S3 Calculated MOs profiles of **1a** at the PBE/6-31+G* level.

Table S1. Major transitions of **1a** calculated by TDDFT

excited state	Energy (eV)	Wavelength (nm)	oscillator strength (f)	description
1	2.4658	503.16372	0.0500	H-2→L+1 (-0.14642) H→L (0.68424)
2	2.7683	448.18159	0.0011	H-1→L+1 (0.70544)
3	2.7709	447.76105	0.1493	H–2→L (0.21214) H→L+1 (0.65822)
4	2.8052	442.28615	0.0031	H-1→L (0.70324)
5	3.1654	391.95713	0.1338	H–2→L (0.61857) H→L+1 (-0.17135) H→L+2 (0.25879)
6	3.3603	369.22331	0.1119	H–3→L (-0.17140) H–2→L+1 (0.62431) H→L (0.10554) H→L+3 (-0.22617)
7	3.4332	361.38329	0.1028	H–2→L (-0.21779) H→L+1 (0.11823) H→L+2 (0.64531)
8	3.6803	337.11956	0.0001	H–1→L+2 (0.70649)
9	3.8007	326.44016	0.0022	H-5→L+1 (0.18588) H-3→L (-0.45449) H→L+3 (0.48761)
10	3.8537	321.95062	0.0004	H–5→L (0.13699)

				H-4→L+1 (-0.11628) H-3→L+1 (0.39810) H→L+4 (0.54727)
11	3.9471	314.33232	0.0053	H–4→L (0.65702) H–2→L+2 (-0.21749)
12	4.0437	306.82323	0.0243	H–4→L+1 (0.55419) H–3→L+1 (0.35874) H-1→L+3 (0.12701) H→L+4 (-0.12205)
13	4.0533	306.09654	1E-4	H-4→L+1 (-0.10949) H-1→L+3 (0.68618)
14	4.078	304.24255	0.1587	H-5→L (0.63713) H-4→L+1 (0.14218) H-3→L+1 (-0.14275) H-1→L+3 (0.10510)
15	4.1228	300.93652	0.0981	H-5→L+1 (0.22656) H-3→L (0.25752) H-2→L+1 (0.11609) H-1→L+4 (0.56924) H→L+3 (0.14965)
16	4.1609	298.18095	0.1625	H-5→L++1 (-0.39697) H-3→L (-0.29733) H-2→L+1 (-0.13969) H-2→L+2 (-0.13596) H-1→L+4 (0.40072) H→L+3 (-0.12232)
17	4.2154	294.32583	0.1198	H-6→L+1 (-0.11016) H-5→L+1 (0.14337) H-4→L (0.17927) H-3→L (-0.15643) H-2→L+1 (-0.10960) H-2→L+2 (0.56682) H→L+3 (-0.20718)
18	4.2307	293.26142	0.0045	H-4→L+1 (-0.33061) H-3→L+1 (0.31741) H-2→L+3 (0.41927) H→L+4 (-0.29886)
19	4.4021	281.84301	0.0964	H-5→L+1 (0.44428) H-3→L (-0.13897) H-2→L+1 (-0.10535) H-2→L+2 (-0.27665) H-2→L+4 (-0.23063) H→L+3 (-0.31444)
20	4.5473	272.84347	0.0474	H-5→L+2 (-0.12344) H-2→L+4 (-0.35624) H→L+5 (0.54722) H→L+6 (0.17633)

4. Photophysical and electrochemical properties

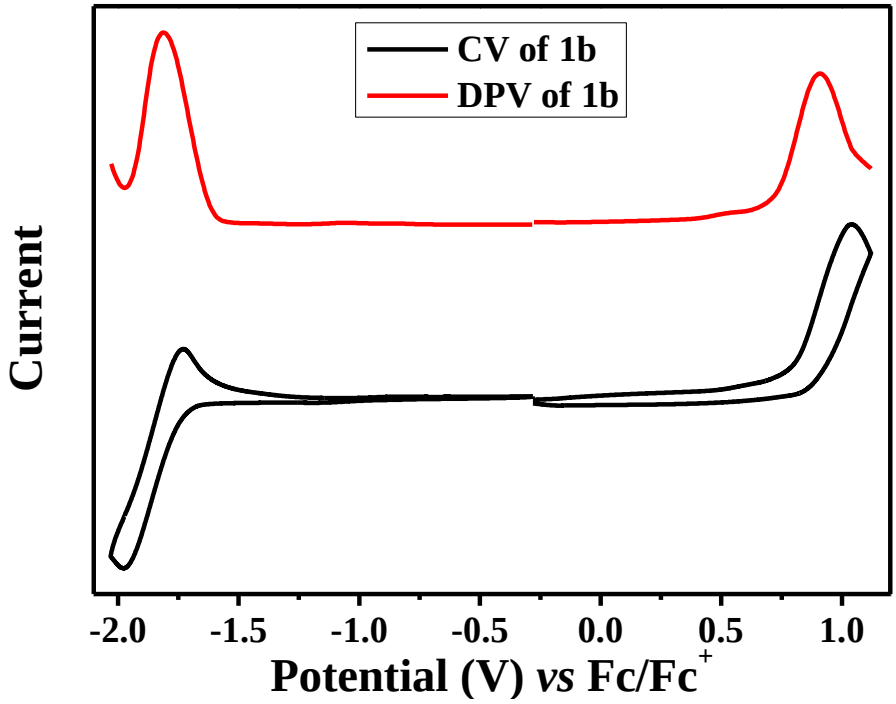


Figure S4 Cyclic voltammograms (black) and differential pulse voltammograms (red) of **1b** in dry dichloromethane with 0.1 M Bu_4NPF_6 as supporting electrolyte, Ag/AgCl as reference electrode, Au disk as working electrode, Pt wire as counter electrode, and scan rates at 50 mV/s.

Table S2. Summary of the photophysical and electrochemical properties of **1a** and **1b**.

Compd	λ_{abs}^{max} (nm)	λ_{em}^{max} (nm)	Φ_F	E_g^{opt} [a] (eV)	E_{HOMO}^{EC}[b] (eV)	E_{LUMO}^{EC}[c] (eV)	E_g^{EC} (eV)	E_{HOMO}^{cal}[d] (eV)	E_{LUMO}^{cal}[d] (eV)
1a	276, 343, 430, 510	628	0.17[e]	2.44	-	-	-	-5.63	-2.27
1b	267, 336, 402, 472	521	0.12[f]	2.17	-5.60	-3.07	2.53	-5.36	-1.96

[a] Estimated from absorption onsets. [b] Estimated from onsets of oxidative waves in CV measurements. [c] Estimated from onsets of reduction waves in CV measurements. [d] Obtained from DFT calculations at the BLYP/6-31+G(d) level on Gaussian 09 program. [e] Measured with cresyl violet acetate[S3] (in methanol, Φ_F: 0.54) as a reference. [f] Measured with fluorescein[S4] (in 0.1 M NaOH, Φ_F: 0.79) as a reference.

5. X-ray crystallographic data of 1b

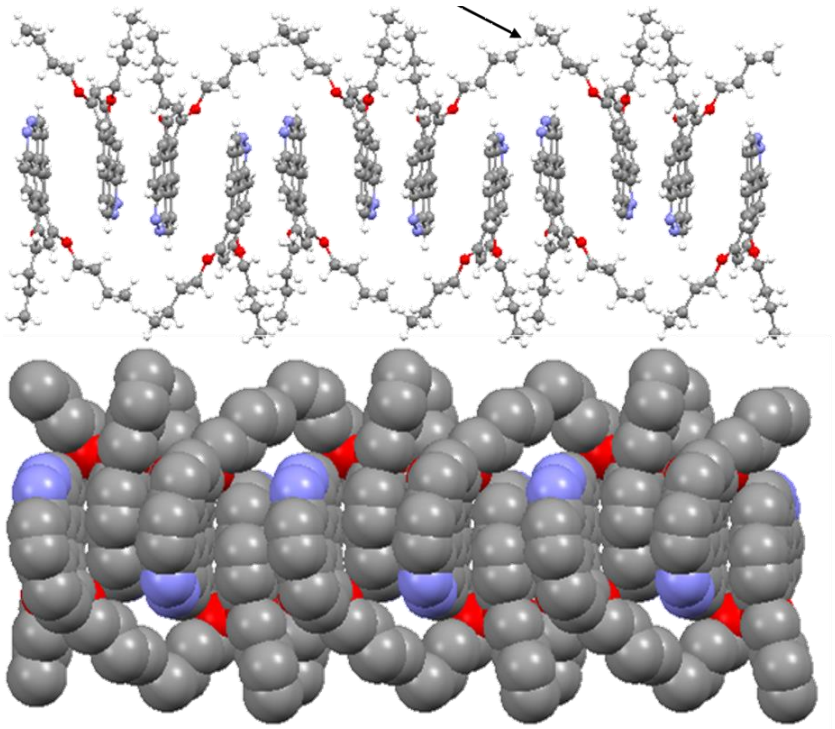
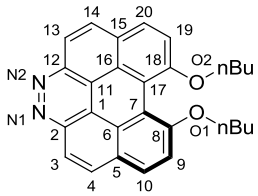
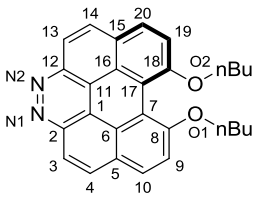


Figure S5 Molecular packing structure of **1b**.

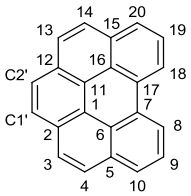
Table S3. Selected experimental bond lengths (Å) and angles (deg) for *P*-enantiomeric-like **1b**, *M*-enantiomeric-like **1b**, benzo[*ghi*]perylene[S5] and Benzo[*c*]cinnoline[S6]. We relabeled all atom numbers manually for ease of comparison.



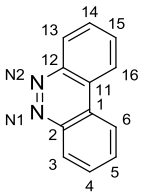
1b (P)



1b (M)



Benzo[ghi]perylene



Benzo[c]cinnoline

bond lengths and angles	***P*-1b**	***M*-1b**	**benzo[*ghi*]perylene**	**Benzo[*c*]cinnoline**
N1-N2 (C1′-C2′)	1.320	1.327	1.399	1.292
N1-C2	1.364	1.349	1.390	1.401
N2-C12	1.359	1.344	1.403	1.392
C1-C2	1.391	1.408	1.410	1.410
C1-C11	1.387	1.380	1.439	1.436
C11-C12	1.395	1.412	1.402	1.412
C3-C4	1.354	1.344	1.331	1.369
C13-C14	1.336	1.337	1.351	1.376
C7-C17	1.465	1.465	1.484	-
N1-N2-C12	120.09	120.93	121.0	119.9
N2-N1-C2	119.55	120.15	120.1	120.7
C2-N1-N2-C12	2.46	-2.1	-	0.3
C8-C7-C17-C18	30.05	-29.56	-	-

C6-C1-C11-C16	7.79	-6.5	-	2.5

Table S4. Crystallographic data and structure refinement for **1b**.

Identification code	**1b**	
Empirical formula	C_{28} H_{26} N_2 O_2	
Formula weight	422.51	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 15.600(6) Å	α= 90 °.
	b = 19.578(8) Å	β= 103.371(9) °.
	c = 15.071(6) Å	γ= 90 °.
Volume	4478(3) $Å^3$	
Z	8	
Density (calculated)	1.253 Mg/m^3	
Absorption coefficient	0.079 mm^{-1}	
F(000)	1792	
Crystal size	0.200 x 0.160 x 0.120 mm^3	
Theta range for data collection	1.698 to 25.000 °.	
Index ranges	-16<=h<=18, -20<=k<=23, -17<=l<=17	
Reflections collected	24566	
Independent reflections	7887 [R(int) = 0.0635]	
Completeness to theta = 25.242 °	97.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6604	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7887 / 32 / 600	
Goodness-of-fit on F^2	0.966	
Final R indices [I>2sigma(I)]	R1 = 0.0714, wR2 = 0.1911	
R indices (all data)	R1 = 0.1929, wR2 = 0.2556	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.314 and -0.185 e.$Å^{-3}$	

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)

N(1)	187(5)	3746(4)	1797(4)	161(2)
N(2)	853(5)	4061(3)	2344(5)	158(2)
N(3)	4183(5)	1414(3)	7438(5)	146(2)
N(4)	4883(4)	1709(3)	7968(4)	144(2)
O(1)	1430(2)	607(1)	4051(2)	101(1)
O(2)	2901(2)	855(2)	3664(2)	89(1)
O(3)	2206(2)	4662(2)	6213(2)	117(1)
O(4)	3670(2)	4882(1)	5785(2)	110(1)
C(1)	751(4)	2648(3)	2393(3)	94(1)
C(2)	126(5)	3054(4)	1816(4)	124(2)
C(3)	-615(5)	2744(5)	1240(5)	148(2)
C(4)	-745(3)	2071(4)	1276(4)	129(2)
C(5)	-140(3)	1632(3)	1885(3)	97(1)
C(6)	630(3)	1933(3)	2431(3)	85(1)
C(7)	1263(3)	1548(2)	3060(3)	75(1)
C(8)	987(3)	901(2)	3258(3)	82(1)
C(9)	251(3)	588(2)	2692(3)	96(1)
C(10)	-278(3)	954(3)	2009(4)	108(2)
C(11)	1465(4)	2977(3)	2948(3)	92(1)
C(12)	1495(5)	3686(3)	2902(4)	118(2)
C(13)	2216(6)	4038(3)	3433(5)	139(2)
C(14)	2898(4)	3684(3)	3948(4)	120(2)
C(15)	2904(4)	2945(2)	3974(3)	90(1)
C(16)	2157(3)	2593(2)	3496(3)	81(1)
C(17)	2097(3)	1875(2)	3503(3)	75(1)
C(18)	2890(3)	1523(2)	3871(3)	78(1)
C(19)	3620(3)	1870(2)	4373(3)	87(1)
C(20)	3627(3)	2566(3)	4445(3)	98(1)
C(21)	1144(3)	-22(2)	4329(3)	112(2)
C(22)	1637(3)	-166(3)	5276(4)	126(2)
C(23)	1390(5)	-831(4)	5624(4)	208(4)
C(24)	1840(5)	-890(4)	6549(6)	234(4)
C(25)	3617(3)	440(2)	4099(3)	91(1)
C(26)	3436(2)	-274(2)	3734(3)	92(1)
C(27)	4160(3)	-771(2)	4139(3)	114(2)
C(28)	3933(3)	-1495(2)	3820(4)	143(2)
C(29)	3598(4)	2509(2)	6878(4)	91(1)

C(30)	3541(6)	1790(3)	6912(5)	120(2)
C(31)	2800(6)	1465(3)	6395(5)	146(3)
C(32)	2131(5)	1826(4)	5899(4)	133(2)
C(33)	2148(5)	2564(3)	5883(4)	110(2)
C(34)	2910(4)	2897(2)	6349(3)	89(1)
C(35)	2990(3)	3626(2)	6355(3)	83(1)
C(36)	2217(4)	3990(3)	6021(3)	97(1)
C(37)	1466(4)	3653(3)	5529(3)	117(2)
C(38)	1441(4)	2955(4)	5448(3)	121(2)
C(39)	4336(4)	2816(3)	7411(3)	92(1)
C(40)	4973(5)	2394(3)	7964(4)	110(2)
C(41)	5739(5)	2689(4)	8531(4)	135(2)
C(42)	5869(3)	3366(4)	8498(4)	121(2)
C(43)	5263(3)	3797(3)	7907(3)	95(1)
C(44)	4469(4)	3538(2)	7378(3)	83(1)
C(45)	3845(3)	3934(2)	6767(3)	78(1)
C(46)	4139(3)	4580(2)	6560(3)	87(1)
C(47)	4895(3)	4865(2)	7111(3)	98(1)
C(48)	5427(3)	4477(3)	7788(3)	103(1)
C(49)	1442(3)	5058(3)	5933(4)	129(2)
C(50)	1669(4)	5788(3)	6366(4)	153(2)
C(51)	946(4)	6253(5)	6128(5)	189(3)
C(52)	1251(6)	6975(4)	6477(6)	234(4)
C(53)	3960(3)	5519(2)	5532(3)	125(2)
C(54)	3407(4)	5710(2)	4626(4)	135(2)
C(55)	3729(8)	6379(6)	4287(9)	134(2)
C(56)	3151(6)	6647(5)	3455(6)	143(3)
C(55')	3212(10)	6453(8)	4249(15)	170(6)
C(56')	4154(9)	6555(10)	4236(14)	168(5)

Table S6. Bond lengths [Å] and angles [°] for **1b**.

N(1)-N(2)	1.320(7)	N(4)-C(40)	1.349(7)
N(1)-C(2)	1.358(7)	O(1)-C(8)	1.361(4)
N(2)-C(12)	1.363(7)	O(1)-C(21)	1.406(4)
N(3)-N(4)	1.326(7)	O(2)-C(18)	1.346(4)
N(3)-C(30)	1.343(7)	O(2)-C(25)	1.413(4)
		O(3)-C(36)	1.347(5)
		O(3)-C(49)	1.403(5)
		O(4)-C(46)	1.362(4)

O(4)-C(53)	1.409(5)	C(22)-H(22B)	0.9700
C(1)-C(11)	1.387(6)	C(23)-C(24)	1.412(8)
C(1)-C(2)	1.395(6)	C(23)-H(23A)	0.9700
C(1)-C(6)	1.414(6)	C(23)-H(23B)	0.9700
C(2)-C(3)	1.412(7)	C(24)-H(24A)	0.9600
C(3)-C(4)	1.335(7)	C(24)-H(24B)	0.9600
C(3)-H(3)	0.9300	C(24)-H(24C)	0.9600
C(4)-C(5)	1.440(6)	C(25)-C(26)	1.505(5)
C(4)-H(4)	0.9300	C(25)-H(25A)	0.9700
C(5)-C(10)	1.365(6)	C(25)-H(25B)	0.9700
C(5)-C(6)	1.418(6)	C(26)-C(27)	1.507(5)
C(6)-C(7)	1.417(5)	C(26)-H(26A)	0.9700
C(7)-C(8)	1.394(5)	C(26)-H(26B)	0.9700
C(7)-C(17)	1.465(5)	C(27)-C(28)	1.513(6)
C(8)-C(9)	1.403(5)	C(27)-H(27A)	0.9700
C(9)-C(10)	1.364(6)	C(27)-H(27B)	0.9700
C(9)-H(9)	0.9300	C(28)-H(28A)	0.9600
C(10)-H(10)	0.9300	C(28)-H(28B)	0.9600
C(11)-C(12)	1.391(6)	C(28)-H(28C)	0.9600
C(11)-C(16)	1.416(6)	C(29)-C(39)	1.379(6)
C(12)-C(13)	1.401(7)	C(29)-C(34)	1.404(6)
C(13)-C(14)	1.354(7)	C(29)-C(30)	1.413(7)
C(13)-H(13)	0.9300	C(30)-C(31)	1.391(8)
C(14)-C(15)	1.447(6)	C(31)-C(32)	1.336(8)
C(14)-H(14)	0.9300	C(31)-H(31)	0.9300
C(15)-C(20)	1.399(6)	C(32)-C(33)	1.445(7)
C(15)-C(16)	1.402(5)	C(32)-H(32)	0.9300
C(16)-C(17)	1.408(5)	C(33)-C(38)	1.379(7)
C(17)-C(18)	1.412(5)	C(33)-C(34)	1.394(6)
C(18)-C(19)	1.390(5)	C(34)-C(35)	1.432(5)
C(19)-C(20)	1.366(5)	C(35)-C(36)	1.392(6)
C(19)-H(19)	0.9300	C(35)-C(45)	1.465(5)
C(20)-H(20)	0.9300	C(36)-C(37)	1.398(6)
C(21)-C(22)	1.484(5)	C(37)-C(38)	1.372(6)
C(21)-H(21A)	0.9700	C(37)-H(37)	0.9300
C(21)-H(21B)	0.9700	C(38)-H(38)	0.9300
C(22)-C(23)	1.487(7)	C(39)-C(40)	1.408(6)
C(22)-H(22A)	0.9700	C(39)-C(44)	1.431(6)

C(40)-C(41)	1.421(7)	C(56)-H(56B)	0.9600
C(41)-C(42)	1.342(7)	C(56)-H(56C)	0.9600
C(41)-H(41)	0.9300	C(55')-C(56')	1.487(14)
C(42)-C(43)	1.419(6)	C(55')-H(55C)	0.9700
C(42)-H(42)	0.9300	C(55')-H(55D)	0.9700
C(43)-C(48)	1.375(6)	C(56')-H(56D)	0.9600
C(43)-C(44)	1.403(5)	C(56')-H(56E)	0.9600
C(44)-C(45)	1.407(5)	C(56')-H(56F)	0.9600
C(45)-C(46)	1.404(5)		
C(46)-C(47)	1.393(5)	N(2)-N(1)-C(2)	120.2(7)
C(47)-C(48)	1.384(6)	N(1)-N(2)-C(12)	119.5(7)
C(47)-H(47)	0.9300	N(4)-N(3)-C(30)	121.0(7)
C(48)-H(48)	0.9300	N(3)-N(4)-C(40)	120.2(6)
C(49)-C(50)	1.576(7)	C(8)-O(1)-C(21)	120.0(3)
C(49)-H(49A)	0.9700	C(18)-O(2)-C(25)	120.1(3)
C(49)-H(49B)	0.9700	C(36)-O(3)-C(49)	121.9(4)
C(50)-C(51)	1.429(7)	C(46)-O(4)-C(53)	118.3(4)
C(50)-H(50A)	0.9700	C(11)-C(1)-C(2)	117.3(6)
C(50)-H(50B)	0.9700	C(11)-C(1)-C(6)	122.1(5)
C(51)-C(52)	1.543(8)	C(2)-C(1)-C(6)	120.5(6)
C(51)-H(51A)	0.9700	N(1)-C(2)-C(1)	122.6(7)
C(51)-H(51B)	0.9700	N(1)-C(2)-C(3)	117.8(7)
C(52)-H(52A)	0.9600	C(1)-C(2)-C(3)	119.6(7)
C(52)-H(52B)	0.9600	C(4)-C(3)-C(2)	120.6(7)
C(52)-H(52C)	0.9600	C(4)-C(3)-H(3)	119.7
C(53)-C(54)	1.485(6)	C(2)-C(3)-H(3)	119.7
C(53)-H(53A)	0.9700	C(3)-C(4)-C(5)	122.1(6)
C(53)-H(53B)	0.9700	C(3)-C(4)-H(4)	119.0
C(54)-C(55)	1.531(10)	C(5)-C(4)-H(4)	119.0
C(54)-C(55')	1.565(15)	C(10)-C(5)-C(6)	117.7(5)
C(54)-H(54A)	0.9571	C(10)-C(5)-C(4)	124.5(6)
C(54)-H(54B)	0.9584	C(6)-C(5)-C(4)	117.7(5)
C(54)-H(54C)	0.9664	C(1)-C(6)-C(7)	118.3(5)
C(54)-H(54D)	0.9658	C(1)-C(6)-C(5)	119.4(5)
C(55)-C(56)	1.462(12)	C(7)-C(6)-C(5)	122.2(5)
C(55)-H(55A)	0.9700	C(8)-C(7)-C(6)	115.2(4)
C(55)-H(55B)	0.9700	C(8)-C(7)-C(17)	125.8(4)
C(56)-H(56A)	0.9600	C(6)-C(7)-C(17)	118.7(4)

O(1)-C(8)-C(7)	117.0(4)	C(15)-C(20)-H(20)	120.1
O(1)-C(8)-C(9)	121.8(4)	O(1)-C(21)-C(22)	108.9(4)
C(7)-C(8)-C(9)	121.1(4)	O(1)-C(21)-H(21A)	109.9
C(10)-C(9)-C(8)	119.9(4)	C(22)-C(21)-H(21A)	109.9
C(10)-C(9)-H(9)	120.1	O(1)-C(21)-H(21B)	109.9
C(8)-C(9)-H(9)	120.1	C(22)-C(21)-H(21B)	109.9
C(9)-C(10)-C(5)	121.8(5)	H(21A)-C(21)-H(21B)	108.3
C(9)-C(10)-H(10)	119.1	C(21)-C(22)-C(23)	112.8(4)
C(5)-C(10)-H(10)	119.1	C(21)-C(22)-H(22A)	109.0
C(1)-C(11)-C(12)	117.8(6)	C(23)-C(22)-H(22A)	109.0
C(1)-C(11)-C(16)	120.1(5)	C(21)-C(22)-H(22B)	109.0
C(12)-C(11)-C(16)	122.0(6)	C(23)-C(22)-H(22B)	109.0
N(2)-C(12)-C(11)	122.6(7)	H(22A)-C(22)-H(22B)	107.8
N(2)-C(12)-C(13)	117.8(7)	C(24)-C(23)-C(22)	108.0(7)
C(11)-C(12)-C(13)	119.6(7)	C(24)-C(23)-H(23A)	110.1
C(14)-C(13)-C(12)	119.7(6)	C(22)-C(23)-H(23A)	110.1
C(14)-C(13)-H(13)	120.1	C(24)-C(23)-H(23B)	110.1
C(12)-C(13)-H(13)	120.1	C(22)-C(23)-H(23B)	110.1
C(13)-C(14)-C(15)	121.8(6)	H(23A)-C(23)-H(23B)	108.4
C(13)-C(14)-H(14)	119.1	C(23)-C(24)-H(24A)	109.5
C(15)-C(14)-H(14)	119.1	C(23)-C(24)-H(24B)	109.5
C(20)-C(15)-C(16)	118.4(4)	H(24A)-C(24)-H(24B)	109.5
C(20)-C(15)-C(14)	122.9(5)	C(23)-C(24)-H(24C)	109.5
C(16)-C(15)-C(14)	118.6(5)	H(24A)-C(24)-H(24C)	109.5
C(15)-C(16)-C(17)	122.4(5)	H(24B)-C(24)-H(24C)	109.5
C(15)-C(16)-C(11)	118.0(5)	O(2)-C(25)-C(26)	107.6(3)
C(17)-C(16)-C(11)	119.5(4)	O(2)-C(25)-H(25A)	110.2
C(16)-C(17)-C(18)	115.9(4)	C(26)-C(25)-H(25A)	110.2
C(16)-C(17)-C(7)	119.0(4)	O(2)-C(25)-H(25B)	110.2
C(18)-C(17)-C(7)	124.8(4)	C(26)-C(25)-H(25B)	110.2
O(2)-C(18)-C(19)	123.3(4)	H(25A)-C(25)-H(25B)	108.5
O(2)-C(18)-C(17)	116.1(4)	C(25)-C(26)-C(27)	113.1(4)
C(19)-C(18)-C(17)	120.5(4)	C(25)-C(26)-H(26A)	109.0
C(20)-C(19)-C(18)	121.4(4)	C(27)-C(26)-H(26A)	109.0
C(20)-C(19)-H(19)	119.3	C(25)-C(26)-H(26B)	109.0
C(18)-C(19)-H(19)	119.3	C(27)-C(26)-H(26B)	109.0
C(19)-C(20)-C(15)	119.9(4)	H(26A)-C(26)-H(26B)	107.8
C(19)-C(20)-H(20)	120.1	C(26)-C(27)-C(28)	112.2(4)

C(26)-C(27)-H(27A)	109.2	C(37)-C(38)-C(33)	120.6(5)
C(28)-C(27)-H(27A)	109.2	C(37)-C(38)-H(38)	119.7
C(26)-C(27)-H(27B)	109.2	C(33)-C(38)-H(38)	119.7
C(28)-C(27)-H(27B)	109.2	C(29)-C(39)-C(40)	118.0(6)
H(27A)-C(27)-H(27B)	107.9	C(29)-C(39)-C(44)	121.2(5)
C(27)-C(28)-H(28A)	109.5	C(40)-C(39)-C(44)	120.8(6)
C(27)-C(28)-H(28B)	109.5	N(4)-C(40)-C(39)	121.7(7)
H(28A)-C(28)-H(28B)	109.5	N(4)-C(40)-C(41)	118.4(7)
C(27)-C(28)-H(28C)	109.5	C(39)-C(40)-C(41)	119.9(6)
H(28A)-C(28)-H(28C)	109.5	C(42)-C(41)-C(40)	119.5(6)
H(28B)-C(28)-H(28C)	109.5	C(42)-C(41)-H(41)	120.3
C(39)-C(29)-C(34)	121.4(5)	C(40)-C(41)-H(41)	120.3
C(39)-C(29)-C(30)	117.7(6)	C(41)-C(42)-C(43)	121.7(6)
C(34)-C(29)-C(30)	120.9(6)	C(41)-C(42)-H(42)	119.1
N(3)-C(30)-C(31)	119.4(7)	C(43)-C(42)-H(42)	119.1
N(3)-C(30)-C(29)	121.5(7)	C(48)-C(43)-C(44)	116.2(5)
C(31)-C(30)-C(29)	119.1(7)	C(48)-C(43)-C(42)	122.7(6)
C(32)-C(31)-C(30)	120.8(7)	C(44)-C(43)-C(42)	121.0(5)
C(32)-C(31)-H(31)	119.6	C(43)-C(44)-C(45)	124.0(4)
C(30)-C(31)-H(31)	119.6	C(43)-C(44)-C(39)	116.9(5)
C(31)-C(32)-C(33)	121.5(7)	C(45)-C(44)-C(39)	118.9(5)
C(31)-C(32)-H(32)	119.2	C(46)-C(45)-C(44)	115.4(4)
C(33)-C(32)-H(32)	119.2	C(46)-C(45)-C(35)	126.0(4)
C(38)-C(33)-C(34)	118.3(6)	C(44)-C(45)-C(35)	118.4(4)
C(38)-C(33)-C(32)	123.2(7)	O(4)-C(46)-C(47)	123.3(4)
C(34)-C(33)-C(32)	118.5(6)	O(4)-C(46)-C(45)	116.4(4)
C(33)-C(34)-C(29)	119.0(5)	C(47)-C(46)-C(45)	120.2(4)
C(33)-C(34)-C(35)	122.2(5)	C(48)-C(47)-C(46)	120.0(4)
C(29)-C(34)-C(35)	118.7(5)	C(48)-C(47)-H(47)	120.0
C(36)-C(35)-C(34)	116.2(5)	C(46)-C(47)-H(47)	120.0
C(36)-C(35)-C(45)	124.8(4)	C(43)-C(48)-C(47)	122.0(5)
C(34)-C(35)-C(45)	118.9(5)	C(43)-C(48)-H(48)	119.0
O(3)-C(36)-C(35)	118.4(4)	C(47)-C(48)-H(48)	119.0
O(3)-C(36)-C(37)	121.5(6)	O(3)-C(49)-C(50)	106.5(4)
C(35)-C(36)-C(37)	120.0(5)	O(3)-C(49)-H(49A)	110.4
C(38)-C(37)-C(36)	121.3(5)	C(50)-C(49)-H(49A)	110.4
C(38)-C(37)-H(37)	119.3	O(3)-C(49)-H(49B)	110.4
C(36)-C(37)-H(37)	119.3	C(50)-C(49)-H(49B)	110.4

H(49A)-C(49)-H(49B)	108.6	H(54A)-C(54)-H(54B)	108.1
C(51)-C(50)-C(49)	112.7(6)	C(53)-C(54)-H(54C)	104.1
C(51)-C(50)-H(50A)	109.1	C(55')-C(54)-H(54C)	105.6
C(49)-C(50)-H(50A)	109.1	C(53)-C(54)-H(54D)	106.5
C(51)-C(50)-H(50B)	109.1	C(55')-C(54)-H(54D)	107.7
C(49)-C(50)-H(50B)	109.1	H(54C)-C(54)-H(54D)	105.0
H(50A)-C(50)-H(50B)	107.8	C(56)-C(55)-C(54)	114.1(8)
C(50)-C(51)-C(52)	109.6(7)	C(56)-C(55)-H(55A)	108.7
C(50)-C(51)-H(51A)	109.7	C(54)-C(55)-H(55A)	108.7
C(52)-C(51)-H(51A)	109.7	C(56)-C(55)-H(55B)	108.7
C(50)-C(51)-H(51B)	109.7	C(54)-C(55)-H(55B)	108.7
C(52)-C(51)-H(51B)	109.7	H(55A)-C(55)-H(55B)	107.6
H(51A)-C(51)-H(51B)	108.2	C(55)-C(56)-H(56A)	109.5
C(51)-C(52)-H(52A)	109.5	C(55)-C(56)-H(56B)	109.5
C(51)-C(52)-H(52B)	109.5	H(56A)-C(56)-H(56B)	109.5
H(52A)-C(52)-H(52B)	109.5	C(55)-C(56)-H(56C)	109.5
C(51)-C(52)-H(52C)	109.5	H(56A)-C(56)-H(56C)	109.5
H(52A)-C(52)-H(52C)	109.5	H(56B)-C(56)-H(56C)	109.5
H(52B)-C(52)-H(52C)	109.5	C(56')-C(55')-C(54)	91.1(12)
O(4)-C(53)-C(54)	108.5(4)	C(56')-C(55')-H(55C)	113.4
O(4)-C(53)-H(53A)	110.0	C(54)-C(55')-H(55C)	113.4
C(54)-C(53)-H(53A)	110.0	C(56')-C(55')-H(55D)	113.4
O(4)-C(53)-H(53B)	110.0	C(54)-C(55')-H(55D)	113.4
C(54)-C(53)-H(53B)	110.0	H(55C)-C(55')-H(55D)	110.7
H(53A)-C(53)-H(53B)	108.4	C(55')-C(56')-H(56D)	109.5
C(53)-C(54)-C(55)	110.9(6)	C(55')-C(56')-H(56E)	109.5
C(53)-C(54)-C(55')	126.2(9)	H(56D)-C(56')-H(56E)	109.5
C(53)-C(54)-H(54A)	109.3	C(55')-C(56')-H(56F)	109.5
C(55)-C(54)-H(54A)	109.5	H(56D)-C(56')-H(56F)	109.5
C(53)-C(54)-H(54B)	109.3	H(56E)-C(56')-H(56F)	109.5
C(55)-C(54)-H(54B)	109.8		

Table S7. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	213(7)	128(6)	155(6)	36(4)	67(4)	75(5)

N(2)	243(8)	91(4)	164(6)	31(4)	99(5)	64(5)
N(3)	219(7)	77(4)	181(6)	17(4)	123(5)	37(4)
N(4)	200(6)	97(5)	166(5)	52(4)	105(4)	58(4)
O(1)	106(2)	92(2)	97(2)	17(2)	9(2)	-35(2)
O(2)	77(2)	73(2)	105(2)	3(2)	-1(2)	-1(2)
O(3)	110(3)	88(2)	141(3)	16(2)	4(2)	8(2)
O(4)	142(3)	71(2)	109(2)	18(2)	12(2)	-22(2)
C(1)	114(4)	90(4)	90(3)	14(3)	50(3)	30(3)
C(2)	146(6)	120(5)	113(4)	19(4)	45(4)	48(5)
C(3)	140(6)	176(7)	126(5)	33(5)	29(4)	63(6)
C(4)	99(4)	179(6)	105(4)	10(5)	18(3)	35(5)
C(5)	79(3)	127(4)	87(3)	2(3)	23(3)	13(4)
C(6)	91(3)	96(4)	74(3)	5(3)	29(3)	17(3)
C(7)	87(3)	71(3)	72(3)	0(2)	29(2)	-12(2)
C(8)	74(3)	94(3)	78(3)	1(3)	19(2)	-7(3)
C(9)	85(3)	100(4)	101(3)	-5(3)	21(3)	-20(3)
C(10)	82(3)	139(5)	99(4)	-8(4)	13(3)	-16(3)
C(11)	126(4)	80(4)	82(3)	3(3)	51(3)	12(3)
C(12)	193(6)	67(4)	119(5)	4(4)	88(4)	20(4)
C(13)	227(8)	69(4)	147(6)	-14(4)	98(6)	0(5)
C(14)	185(6)	86(4)	110(4)	-29(3)	75(4)	-49(4)
C(15)	124(4)	80(4)	82(3)	-12(3)	53(3)	-29(3)
C(16)	107(4)	76(3)	69(3)	-6(2)	41(3)	-11(3)
C(17)	91(3)	68(3)	71(3)	2(2)	29(2)	-9(3)
C(18)	88(3)	75(3)	74(3)	1(2)	23(2)	-15(3)
C(19)	86(3)	97(4)	79(3)	-5(3)	20(2)	-22(3)
C(20)	109(4)	110(4)	80(3)	-23(3)	34(3)	-37(3)
C(21)	107(3)	101(4)	126(4)	21(3)	22(3)	-27(3)
C(22)	141(4)	99(4)	124(4)	36(3)	0(3)	-33(3)
C(23)	282(9)	214(8)	92(4)	28(5)	-26(5)	33(7)
C(24)	193(7)	232(9)	307(11)	45(8)	123(8)	18(6)
C(25)	84(3)	93(3)	95(3)	12(3)	16(2)	-5(3)
C(26)	78(3)	88(3)	104(3)	21(3)	10(2)	-1(2)
C(27)	101(3)	110(4)	121(4)	31(3)	8(3)	11(3)
C(28)	170(5)	89(4)	170(5)	2(3)	42(4)	22(3)
C(29)	141(5)	66(3)	83(3)	1(3)	60(3)	5(3)
C(30)	197(7)	67(4)	129(5)	9(4)	107(5)	12(4)
C(31)	240(9)	75(5)	161(7)	-25(4)	122(6)	-39(5)

C(32)	204(7)	100(6)	123(5)	-39(4)	95(5)	-62(4)
C(33)	161(5)	103(5)	80(3)	-20(3)	60(4)	-47(4)
C(34)	140(4)	70(3)	69(3)	-8(3)	47(3)	-18(3)
C(35)	116(4)	69(3)	72(3)	6(2)	33(3)	1(3)
C(36)	124(4)	78(4)	91(3)	2(3)	27(3)	-23(3)
C(37)	130(5)	128(5)	94(4)	15(3)	25(3)	-30(4)
C(38)	134(5)	156(6)	81(4)	-16(4)	41(3)	-58(5)
C(39)	128(4)	86(4)	76(3)	5(3)	52(3)	22(3)
C(40)	136(5)	97(5)	115(4)	30(4)	68(4)	36(4)
C(41)	140(6)	150(6)	129(5)	48(5)	59(4)	52(5)
C(42)	97(4)	168(6)	103(4)	21(4)	31(3)	35(4)
C(43)	94(4)	105(4)	89(3)	0(3)	29(3)	10(3)
C(44)	117(4)	67(3)	75(3)	2(2)	41(3)	12(3)
C(45)	100(3)	62(3)	74(3)	-6(2)	24(2)	-2(3)
C(46)	111(4)	62(3)	88(3)	0(3)	21(3)	-2(3)
C(47)	115(4)	78(3)	104(4)	-16(3)	29(3)	-19(3)
C(48)	97(4)	114(4)	97(4)	-13(3)	22(3)	-5(3)
C(49)	112(4)	131(5)	139(5)	38(4)	21(3)	21(4)
C(50)	128(5)	141(5)	174(6)	39(5)	2(4)	67(4)
C(51)	168(6)	248(9)	158(6)	49(6)	51(5)	35(7)
C(52)	324(11)	150(7)	254(9)	-30(7)	120(8)	7(7)
C(53)	182(4)	78(3)	120(3)	16(3)	42(3)	-20(3)
C(54)	192(4)	89(3)	130(3)	26(3)	48(3)	-13(3)
C(55)	191(5)	94(4)	127(4)	27(4)	56(4)	-6(4)
C(56)	191(7)	123(6)	133(6)	42(5)	73(5)	15(5)
C(55')	171(12)	169(13)	180(12)	-30(11)	64(12)	-21(11)
C(56')	181(12)	164(13)	178(12)	-39(11)	78(11)	-20(10)

Table S8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **1b**.

	x	y	z	U(eq)
H(3)	-1017	3011	833	177
H(4)	-1242	1880	895	154
H(9)	124	133	2782	115
H(10)	-746	735	1617	130
H(13)	2226	4513	3431	166
H(14)	3375	3922	4295	144
H(19)	4114	1624	4666	104
H(20)	4111	2787	4807	117
H(21A)	1246	-383	3925	135
H(21B)	517	-2	4303	135
H(22A)	1526	197	5673	151
H(22B)	2263	-168	5297	151
H(23A)	759	-849	5570	249
H(23B)	1554	-1204	5273	249
H(24A)	2452	-978	6586	350
H(24B)	1592	-1259	6826	350
H(24C)	1780	-472	6862	350
H(25A)	3674	445	4754	109
H(25B)	4161	610	3973	109
H(26A)	3363	-265	3078	110
H(26B)	2888	-433	3861	110
H(27A)	4266	-755	4799	136
H(27B)	4698	-634	3970	136
H(28A)	3436	-1650	4039	214
H(28B)	4429	-1787	4052	214
H(28C)	3791	-1508	3165	214
H(31)	2769	991	6394	175
H(32)	1643	1597	5557	160
H(37)	973	3908	5253	141
H(38)	943	2744	5095	145
H(41)	6146	2416	8923	162
H(42)	6370	3556	8873	146
H(47)	5043	5316	7023	118

H(48)	5909	4682	8174	124
H(49A)	957	4857	6144	154
H(49B)	1277	5090	5273	154
H(50A)	1839	5744	7025	184
H(50B)	2167	5973	6163	184
H(51A)	471	6104	6398	227
H(51B)	729	6262	5471	227
H(52A)	1573	6948	7101	351
H(52B)	745	7264	6435	351
H(52C)	1623	7162	6111	351
H(53A)	4573	5491	5503	151
H(53B)	3907	5863	5981	151
H(54A)	2809	5762	4670	162
H(54B)	3429	5351	4199	162
H(54C)	2839	5512	4620	162
H(54D)	3629	5452	4180	162
H(55A)	3786	6719	4764	161
H(55B)	4310	6304	4176	161
H(56A)	3092	6314	2977	215
H(56B)	3400	7058	3276	215
H(56C)	2582	6744	3566	215
H(55C)	2818	6469	3648	204
H(55D)	3009	6756	4666	204
H(56D)	4520	6411	4809	252
H(56E)	4257	7030	4140	252
H(56F)	4292	6290	3752	252

Table S9. Torsion angles [°] for **1b**.

C(2)-N(1)-N(2)-C(12)	2.5(10)
C(30)-N(3)-N(4)-C(40)	-2.1(9)
N(2)-N(1)-C(2)-C(1)	-0.6(9)
N(2)-N(1)-C(2)-C(3)	177.8(6)
C(11)-C(1)-C(2)-N(1)	-1.3(7)
C(6)-C(1)-C(2)-N(1)	175.9(5)
C(11)-C(1)-C(2)-C(3)	-179.7(5)
C(6)-C(1)-C(2)-C(3)	-2.5(7)
N(1)-C(2)-C(3)-C(4)	-175.1(6)

C(1)-C(2)-C(3)-C(4)	3.4(9)
C(2)-C(3)-C(4)-C(5)	-0.8(9)
C(3)-C(4)-C(5)-C(10)	173.9(5)
C(3)-C(4)-C(5)-C(6)	-2.6(8)
C(11)-C(1)-C(6)-C(7)	0.0(6)
C(2)-C(1)-C(6)-C(7)	-177.0(4)
C(11)-C(1)-C(6)-C(5)	176.2(4)
C(2)-C(1)-C(6)-C(5)	-0.8(6)
C(10)-C(5)-C(6)-C(1)	-173.4(4)
C(4)-C(5)-C(6)-C(1)	3.3(6)
C(10)-C(5)-C(6)-C(7)	2.7(6)
C(4)-C(5)-C(6)-C(7)	179.3(4)
C(1)-C(6)-C(7)-C(8)	161.9(3)
C(5)-C(6)-C(7)-C(8)	-14.1(5)
C(1)-C(6)-C(7)-C(17)	-12.4(5)
C(5)-C(6)-C(7)-C(17)	171.5(3)
C(21)-O(1)-C(8)-C(7)	175.0(4)
C(21)-O(1)-C(8)-C(9)	-1.1(6)
C(6)-C(7)-C(8)-O(1)	-158.9(3)
C(17)-C(7)-C(8)-O(1)	15.0(6)
C(6)-C(7)-C(8)-C(9)	17.2(5)
C(17)-C(7)-C(8)-C(9)	-168.9(4)
O(1)-C(8)-C(9)-C(10)	166.7(4)
C(7)-C(8)-C(9)-C(10)	-9.2(6)
C(8)-C(9)-C(10)-C(5)	-3.5(7)
C(6)-C(5)-C(10)-C(9)	6.5(7)
C(4)-C(5)-C(10)-C(9)	-169.9(4)
C(2)-C(1)-C(11)-C(12)	1.2(6)
C(6)-C(1)-C(11)-C(12)	-175.9(4)
C(2)-C(1)-C(11)-C(16)	-175.0(4)
C(6)-C(1)-C(11)-C(16)	7.9(6)
N(1)-N(2)-C(12)-C(11)	-2.5(9)
N(1)-N(2)-C(12)-C(13)	176.3(6)
C(1)-C(11)-C(12)-N(2)	0.6(7)
C(16)-C(11)-C(12)-N(2)	176.8(4)
C(1)-C(11)-C(12)-C(13)	-178.3(4)
C(16)-C(11)-C(12)-C(13)	-2.1(7)
N(2)-C(12)-C(13)-C(14)	-175.4(5)

C(11)-C(12)-C(13)-C(14)	3.5(8)
C(12)-C(13)-C(14)-C(15)	-0.4(8)
C(13)-C(14)-C(15)-C(20)	175.0(5)
C(13)-C(14)-C(15)-C(16)	-4.0(7)
C(20)-C(15)-C(16)-C(17)	2.6(5)
C(14)-C(15)-C(16)-C(17)	-178.3(4)
C(20)-C(15)-C(16)-C(11)	-173.8(4)
C(14)-C(15)-C(16)-C(11)	5.3(5)
C(1)-C(11)-C(16)-C(15)	173.7(4)
C(12)-C(11)-C(16)-C(15)	-2.4(6)
C(1)-C(11)-C(16)-C(17)	-2.8(5)
C(12)-C(11)-C(16)-C(17)	-178.9(4)
C(15)-C(16)-C(17)-C(18)	-11.7(5)
C(11)-C(16)-C(17)-C(18)	164.6(3)
C(15)-C(16)-C(17)-C(7)	174.0(3)
C(11)-C(16)-C(17)-C(7)	-9.6(5)
C(8)-C(7)-C(17)-C(16)	-156.4(4)
C(6)-C(7)-C(17)-C(16)	17.3(5)
C(8)-C(7)-C(17)-C(18)	30.0(6)
C(6)-C(7)-C(17)-C(18)	-156.4(4)
C(25)-O(2)-C(18)-C(19)	12.3(5)
C(25)-O(2)-C(18)-C(17)	-171.3(3)
C(16)-C(17)-C(18)-O(2)	-162.7(3)
C(7)-C(17)-C(18)-O(2)	11.2(5)
C(16)-C(17)-C(18)-C(19)	13.8(5)
C(7)-C(17)-C(18)-C(19)	-172.4(3)
O(2)-C(18)-C(19)-C(20)	169.3(4)
C(17)-C(18)-C(19)-C(20)	-6.9(6)
C(18)-C(19)-C(20)-C(15)	-2.9(6)
C(16)-C(15)-C(20)-C(19)	5.1(6)
C(14)-C(15)-C(20)-C(19)	-174.0(4)
C(8)-O(1)-C(21)-C(22)	-170.3(4)
O(1)-C(21)-C(22)-C(23)	-178.8(5)
C(21)-C(22)-C(23)-C(24)	-175.1(6)
C(18)-O(2)-C(25)-C(26)	179.5(3)
O(2)-C(25)-C(26)-C(27)	179.4(3)
C(25)-C(26)-C(27)-C(28)	175.5(4)
N(4)-N(3)-C(30)-C(31)	-177.3(5)

N(4)-N(3)-C(30)-C(29)	2.2(8)
C(39)-C(29)-C(30)-N(3)	-0.5(6)
C(34)-C(29)-C(30)-N(3)	-177.9(4)
C(39)-C(29)-C(30)-C(31)	179.0(4)
C(34)-C(29)-C(30)-C(31)	1.5(6)
N(3)-C(30)-C(31)-C(32)	176.8(6)
C(29)-C(30)-C(31)-C(32)	-2.7(8)
C(30)-C(31)-C(32)-C(33)	-0.2(9)
C(31)-C(32)-C(33)-C(38)	-174.0(6)
C(31)-C(32)-C(33)-C(34)	4.4(8)
C(38)-C(33)-C(34)-C(29)	173.0(4)
C(32)-C(33)-C(34)-C(29)	-5.4(6)
C(38)-C(33)-C(34)-C(35)	-2.7(6)
C(32)-C(33)-C(34)-C(35)	178.9(4)
C(39)-C(29)-C(34)-C(33)	-174.7(4)
C(30)-C(29)-C(34)-C(33)	2.6(6)
C(39)-C(29)-C(34)-C(35)	1.2(6)
C(30)-C(29)-C(34)-C(35)	178.5(3)
C(33)-C(34)-C(35)-C(36)	11.8(5)
C(29)-C(34)-C(35)-C(36)	-163.9(4)
C(33)-C(34)-C(35)-C(45)	-172.8(3)
C(29)-C(34)-C(35)-C(45)	11.5(5)
C(49)-O(3)-C(36)-C(35)	-177.4(4)
C(49)-O(3)-C(36)-C(37)	0.1(6)
C(34)-C(35)-C(36)-O(3)	163.9(3)
C(45)-C(35)-C(36)-O(3)	-11.2(6)
C(34)-C(35)-C(36)-C(37)	-13.7(6)
C(45)-C(35)-C(36)-C(37)	171.3(4)
O(3)-C(36)-C(37)-C(38)	-170.5(4)
C(35)-C(36)-C(37)-C(38)	7.0(7)
C(36)-C(37)-C(38)-C(33)	2.8(7)
C(34)-C(33)-C(38)-C(37)	-4.8(7)
C(32)-C(33)-C(38)-C(37)	173.6(4)
C(34)-C(29)-C(39)-C(40)	176.3(4)
C(30)-C(29)-C(39)-C(40)	-1.1(6)
C(34)-C(29)-C(39)-C(44)	-6.2(6)
C(30)-C(29)-C(39)-C(44)	176.4(3)
N(3)-N(4)-C(40)-C(39)	0.4(8)

N(3)-N(4)-C(40)-C(41)	-179.1(5)
C(29)-C(39)-C(40)-N(4)	1.2(6)
C(44)-C(39)-C(40)-N(4)	-176.4(4)
C(29)-C(39)-C(40)-C(41)	-179.3(4)
C(44)-C(39)-C(40)-C(41)	3.1(6)
N(4)-C(40)-C(41)-C(42)	176.0(5)
C(39)-C(40)-C(41)-C(42)	-3.5(8)
C(40)-C(41)-C(42)-C(43)	-0.3(8)
C(41)-C(42)-C(43)-C(48)	-172.8(5)
C(41)-C(42)-C(43)-C(44)	4.5(7)
C(48)-C(43)-C(44)-C(45)	-1.5(6)
C(42)-C(43)-C(44)-C(45)	-179.0(4)
C(48)-C(43)-C(44)-C(39)	172.8(4)
C(42)-C(43)-C(44)-C(39)	-4.7(6)
C(29)-C(39)-C(44)-C(43)	-176.5(4)
C(40)-C(39)-C(44)-C(43)	0.9(5)
C(29)-C(39)-C(44)-C(45)	-2.0(6)
C(40)-C(39)-C(44)-C(45)	175.5(4)
C(43)-C(44)-C(45)-C(46)	13.3(6)
C(39)-C(44)-C(45)-C(46)	-160.9(3)
C(43)-C(44)-C(45)-C(35)	-171.4(4)
C(39)-C(44)-C(45)-C(35)	14.5(5)
C(36)-C(35)-C(45)-C(46)	-29.6(6)
C(34)-C(35)-C(45)-C(46)	155.5(4)
C(36)-C(35)-C(45)-C(44)	155.6(4)
C(34)-C(35)-C(45)-C(44)	-19.3(5)
C(53)-O(4)-C(46)-C(47)	-0.7(6)
C(53)-O(4)-C(46)-C(45)	-177.7(4)
C(44)-C(45)-C(46)-O(4)	160.4(3)
C(35)-C(45)-C(46)-O(4)	-14.5(6)
C(44)-C(45)-C(46)-C(47)	-16.6(5)
C(35)-C(45)-C(46)-C(47)	168.4(4)
O(4)-C(46)-C(47)-C(48)	-168.0(4)
C(45)-C(46)-C(47)-C(48)	8.9(6)
C(44)-C(43)-C(48)-C(47)	-7.4(6)
C(42)-C(43)-C(48)-C(47)	170.0(4)
C(46)-C(47)-C(48)-C(43)	3.9(7)
C(36)-O(3)-C(49)-C(50)	174.6(4)

O(3)-C(49)-C(50)-C(51)	179.4(5)
C(49)-C(50)-C(51)-C(52)	-173.1(6)
C(46)-O(4)-C(53)-C(54)	174.2(4)
O(4)-C(53)-C(54)-C(55)	-176.4(7)
O(4)-C(53)-C(54)-C(55')	153.6(8)
C(53)-C(54)-C(55)-C(56)	-172.4(8)
C(55')-C(54)-C(55)-C(56)	-45.6(18)
C(53)-C(54)-C(55')-C(56')	65.8(14)
C(55)-C(54)-C(55')-C(56')	-2.0(18)

Table S10. Hydrogen bonds for **1b** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(9)-H(9)...N(2)#1	0.93	2.57	3.445(7)	155.9
C(47)-H(47)...N(3)#2	0.93	2.51	3.358(8)	152.3

Symmetry transformations used to generate equivalent atoms:

#1 -x, y-1/2,-z+1/2 #2 -x+1,y+1/2,-z+3/2

6. ^{1}H and ^{13}C NMR spectra of all new compounds

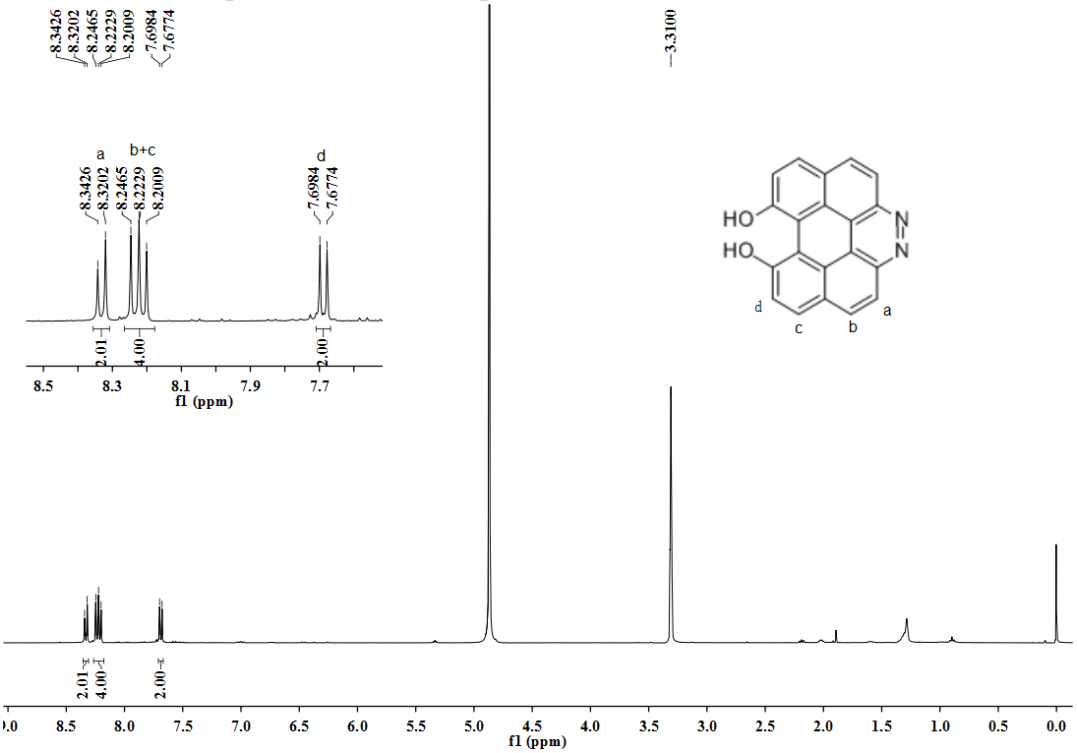


Figure S6. ^{1}H NMR (400 M) spectra of **1a** in CD_3OD at 298K.

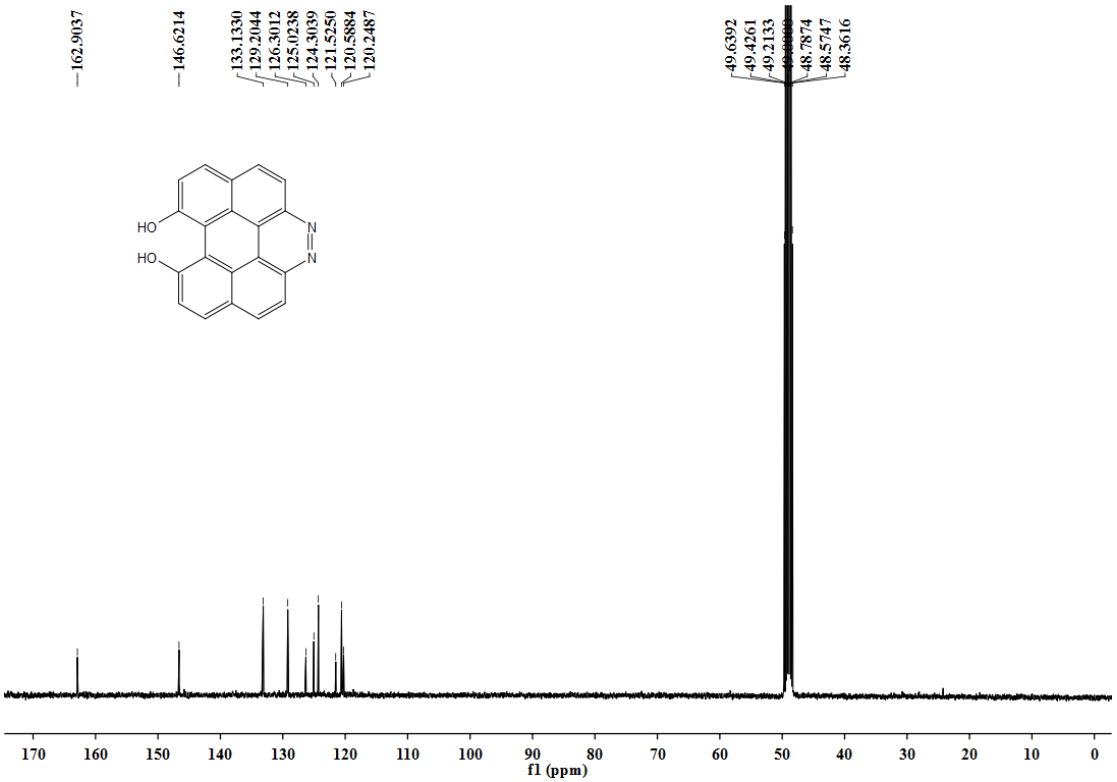


Figure S7. ^{13}C NMR (100 M) spectra of **1a** in CD_3OD at 298K.

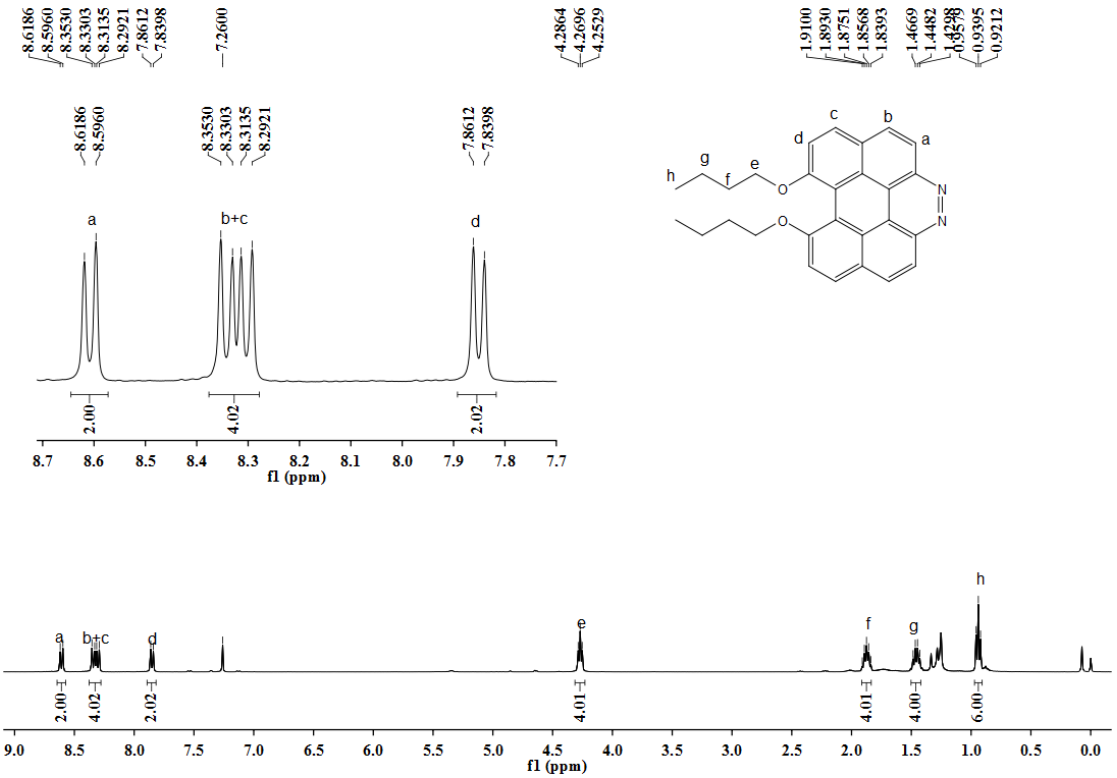


Figure S8. ^{1}H NMR spectra (400 M) of **1b** in $CDCl_3$ at 298K.

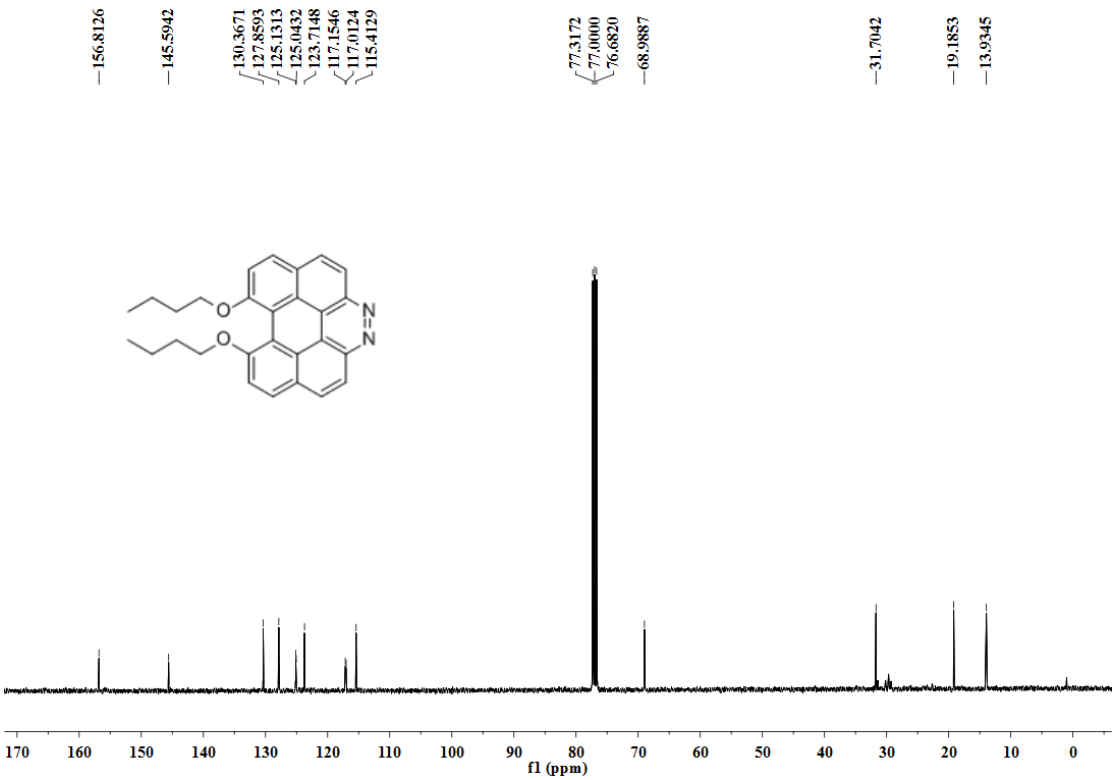


Figure S9. ^{13}C NMR (100 M) spectra of **1b** in $CDCl_3$ at 298K.

7. Mass spectra of all new compounds

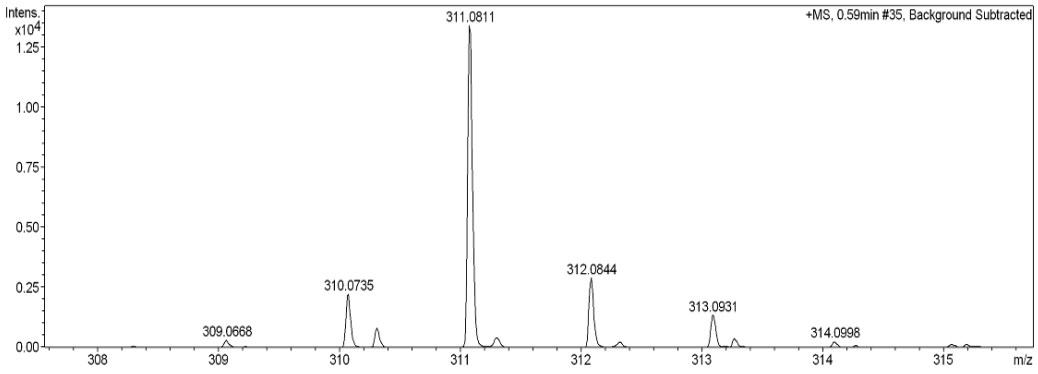


Figure S10. HR mass spectrum (APCI) $[M]^+$ spectrum of compound **1a**.

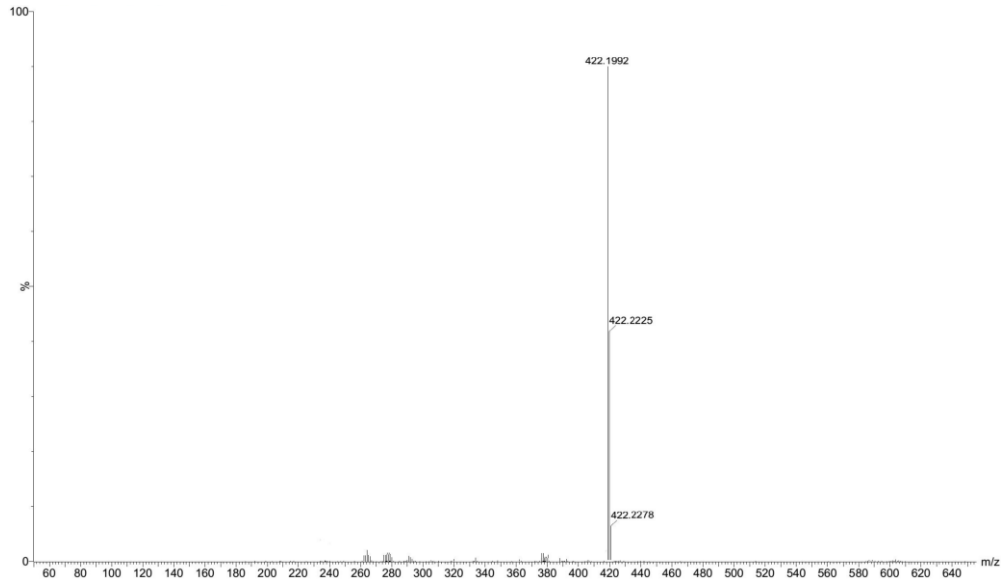


Figure S11. HR mass spectrum (MALDI-TOF) $[M]^+$ spectrum of compound **1b**.

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