

First Synthesis of Naphthalene Annulated Oxepins

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1. Experimental Section

General considerations: All Reagents and solvents were purchased from commercial suppliers and used without further purification. 1,1'-bi-8-naphthol (**2**)^[1] and 2,2'-Dihydroxy-*o*-terphenyl (**8**)^[2] were synthesized according to literature procedures. Reactions were carried out under argon atmosphere in dry solvents and monitored in situ by thin-layer chromatography (TLC) carried out on silica gel plates (Merck KGaA; 60 F₁₅₄), using UV light at 254 nm as the visualizing agent to assure consumption of starting materials prior to work up. Melting points were determined with melting point system Mettler Toledo MP90 and are uncorrected. NMR spectra were recorded on Bruker Avance II spectrometer (¹H: 500 MHz, ¹³C: 126 MHz) at room temperature. Chemical shifts are reported in parts per million (ppm) calibrated using residual non deuterated solvent as internal reference (CDCl₃ at δ 7.26 ppm (¹H NMR) & δ 77.16 ppm (¹³C NMR), TCE-d₂ at δ 6.0 ppm (¹H NMR) & δ 73.78 ppm (¹³C NMR), DMSO-d₆ δ 2.50 ppm (¹H NMR) & δ 39.52 ppm (¹³C NMR)). Integration is determined as the relative number of atoms. APCI mass spectra were recorded on Agilent 6130 and Bruker Esquire 3000 mass spectrometers. High resolution mass spectrometry was performed on Thermo Fisher Scientific LTQ-XL-Orbitrap. The absorption and emission spectra were recorded using Perkin Elmer Lambda 9, Lambda 850 and Hitachi F-4500 spectrometer respectively. Absolute quantum yields were determined by Hamamatsu Photonic Multi-Channel Analyzer C10027 calibrated integrating sphere system. All spectra were measured at 22 °C in toluene without degassing (concentration: 10⁻⁴-10⁻⁵ M).

Dinaphth[1,8-bc:1',8'-ef]oxepin (3): 1,1'-Bi-8-naphthol (**2**) (24.4 g; 85 mmol) and *p*-TsOH (17.8 g; 93.7 mmol; 110 mol%) in toluene (500 mL) were refluxed for 3 h. After cooling to room temperature the solution was quenched with saturated K₂CO₃-solution. The organic phase was separated, washed with water and dried over MgSO₄, filtered and concentrated under reduced pressure. The resulting dark yellow solid was recrystallized from heptane to yield 19.8 g (87%, 73.8 mmol) of **3** as dark yellow crystals. M.p.: 151 °C. ¹H NMR (500 MHz, CDCl₃): δ = 8.19 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.66 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.43 (dd, *J* = 7.4, 1.8 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃): δ = 154.2, 136.1, 134.2, 128.7, 127.8, 126.2 (2C), 126.2, 124.7, 117.3. HRMS (APCI): *m/z* calcd. for C₂₀H₁₂O: [M]⁺ 268.0888, found: 268.0882.

4,4'-Dibromo-dinaphth[1,8-bc:1',8'-ef]oxepin (4): To a solution of **3** (19.6 g, 73.1 mmol) in DMF (200 mL) at 40 °C was added NBS (27.3 g; 153.4 mmol; 210 mol%) in darkness. The reaction mixture was stirred 30 min forming a yellow precipitate. After cooling to room temperature the precipitate was filtered off and washed with EtOH to yield **4** as yellow powder in 87% (27 g, 63.4 mmol) yield. ¹H NMR (500 MHz, TCE-d₂): δ = 8.27 (d, *J* = 8.2 Hz, 1H), 8.19 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H). ¹³C NMR (126 MHz, TCE-d₂): δ = 153.2, 134.1, 133.4, 130.1, 129.3, 128.1, 127.6, 127.2, 117.9, 117.5.

4,4'-Diphenyl-dinaphth[1,8-bc:1',8'-ef]oxepin (5a): A mixture of **4** (35 g; 82.1 mmol), phenylboronic acid (22.0 g; 180.7 mmol; 220 mol%) and K₃PO₄ (38.3 g; 180.7 mmol; 220 mol%) in toluene (500 mL), dioxane (250 mL) and water (125 mL) was degassed by passing argon through the mixture for 30 min. Pd(OAc)₂ (461 mg; 2.05 mmol; 2.5 mol%) and P(*o*-Tol)₃ (1.25 g; 4.11 mmol; 5 mol%) were added to the reaction and the mixture was stirred at 70 °C for 2 d. After completion of the reaction, the organic phase was separated and dried over MgSO₄. The solvent was removed in vacuo to afford a dark yellow solid. The product was purified by column chromatography (SiO₂; *n*-heptane/CH₂Cl₂, 5/1) to yield greenish foam, which was dissolved in CH₂Cl₂ and precipitated on the addition of ethanol. The resulting fine yellow powder was filtered off to yield **5a** in 53% (18.2 g, 43.3 mmol) yield. M.p.: 162 °C. *T*_g: 58 °C. ¹H NMR (500 MHz, DMSO-d₆): δ = 8.37 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.58-7.55 (m, 2H), 7.54-7.50 (m, 2H), 7.47-7.43 (m, 4H). ¹³C NMR (126 MHz, DMSO-d₆): δ = 153.0, 140.0, 136.5, 133.5, 133.3, 130.0 (2C), 128.5 (2C), 128.4, 127.5, 127.2, 126.8, 126.3, 126.1, 116.7. HRMS (APCI): *m/z* calcd. for C₃₂H₂₁O: [M+H]⁺ 421.1593, found: 421.1579.

Bis-5,5'-*m*-terphenyl-dinaphth[1,8-bc:1',8'-ef]oxepin (5b): Upon reacting **4** (1.5 g; 3.52 mmol) and 2.41 g (8.80 mmol, 250 mol%) of 5'-*m*-terphenylboronic acid according to the procedure of compound **3**, the title compound was obtained in 59% (1.5 g, 207 mmol) yield. M.p.: 162 °C. *T*_g: 144 °C. ¹H NMR (500 MHz, CDCl₃): δ = 8.19 (d, *J* = 7.4 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.90 (t, *J* = 1.7 Hz, 1H), 7.74-7.71 (m, 6H), 7.55 (d, *J* = 2.2 Hz, 2H), 7.51-7.47 (m, 5H), 7.39 (t, *J* = 7.4 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃): δ = 154.0, 142.0, 142.0, 141.1, 136.7, 134.9, 134.2, 129.0, 128.5, 128.3, 127.7, 127.5 (2C), 127.1, 126.8, 126.5, 125.2, 116.8. MS (APCI): *m/z* calcd. for C₅₆H₃₇O: [M+H]⁺ 725.3, found: 725.2.

2,2'-Dibromo-4,4'-diphenyl-dinaphth[1,8-bc:1',8'-ef]oxepin (6): To a solution of **5a** (2 g, 4.76 mmol) in DMF (20 mL) at 80 °C was added NBS (1.78 g; 9.99 mmol; 210 mol%). The reaction mixture was stirred at this temperature for 1 h forming a yellow precipitate. After cooling to room temperature the precipitate was filtered off and washed with EtOH to yield **6** as yellow powder in 44% (1.20 g, 2.08 mmol) yield. ¹H NMR (500 MHz, TCE-d₂): δ = 7.87 (d, *J* = 8.7 Hz, 2H), 7.73 (s, 1H), 7.55-7.49 (m, 6H). ¹³C NMR (126 MHz, TCE-d₂): δ = 148.7, 138.9, 137.2, 134.4, 132.3, 131.5, 130.1, 130.0, 128.4, 127.8, 127.2, 126.6, 125.3, 110.9. MS (APCI): *m/z* calcd. for C₃₂H₁₉Br₂O: [M+H]⁺ 579.0, found: 578.9.

2,2',4,4'-Tetraphenyl-dinaphth[1,8-bc:1',8'-ef]oxepin (7): Upon reacting **6** (5 g; 8.65 mmol) and 2.32 g (19.02 mmol, 220 mol%) of phenylboronic acid according to the procedure as for compound **5a**, the title compound **7** was obtained in 65% (3.2 g, 5.59 mmol) yield. M.p.: 283 °C. ¹H NMR (500 MHz, TCE-d₂): δ = 7.93 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 1H), 7.57-7.49 (m, 5H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.43 (s, 1H), 7.31-7.28 (m, 2H), 7.02-7.00 (m, 3H). ¹³C NMR (126 MHz, TCE-d₂): δ = 149.3, 140.3, 138.0, 136.1, 135.4, 132.4, 130.4, 130.2, 129.7, 129.3, 129.1, 128.3, 127.7, 127.2, 126.8, 126.6, 126.2, 125.8. HRMS (APCI): *m/z* calcd. for C₄₄H₂₉O: [M+H]⁺ 573.2219, found: 573.2205.

Tribenz[b,d,f]oxepin (9): In a flask equipped with Dean Stark trap, **8** (10.5 g, 40.03 mmol) was heated to 150 °C in the presence of *p*-TsOH (8.0 g, 42.03 mmol) for 12 h. After cooling to 100 °C, the reaction mixture was diluted with toluene and water and thereafter was allowed to cool to room temperature. The organic phase was separated, dried and evaporated to dryness. The residue was subject to column chromatography (SiO₂; *n*-heptane/CH₂Cl₂, 10/1) to yield **9** as colorless powder in 56% (5.5 g, 22.5 mmol) yield. ¹H NMR (500 MHz, CDCl₃): δ = 7.67 (dd, *J* = 5.8, 3.4 Hz, 1H), 7.61 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.52 (dd, *J* = 5.8, 3.4 Hz, 1H), 7.40-7.34 (m, 2H), 7.28 (td, *J* = 7.2, 1.9 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃): δ = 160.3, 136.8, 133.0, 129.8, 129.5, 129.5, 128.2, 125.7, 121.0. The analytical data was in accordance with the literature^[2].

Differential scanning calorimetry

The phase transition temperatures were determined with TA Instruments Q2000 differential scanning calorimeter during heating in the second heating run with 20 °C/min from 0 °C to 300-400 °C under argon atmosphere.

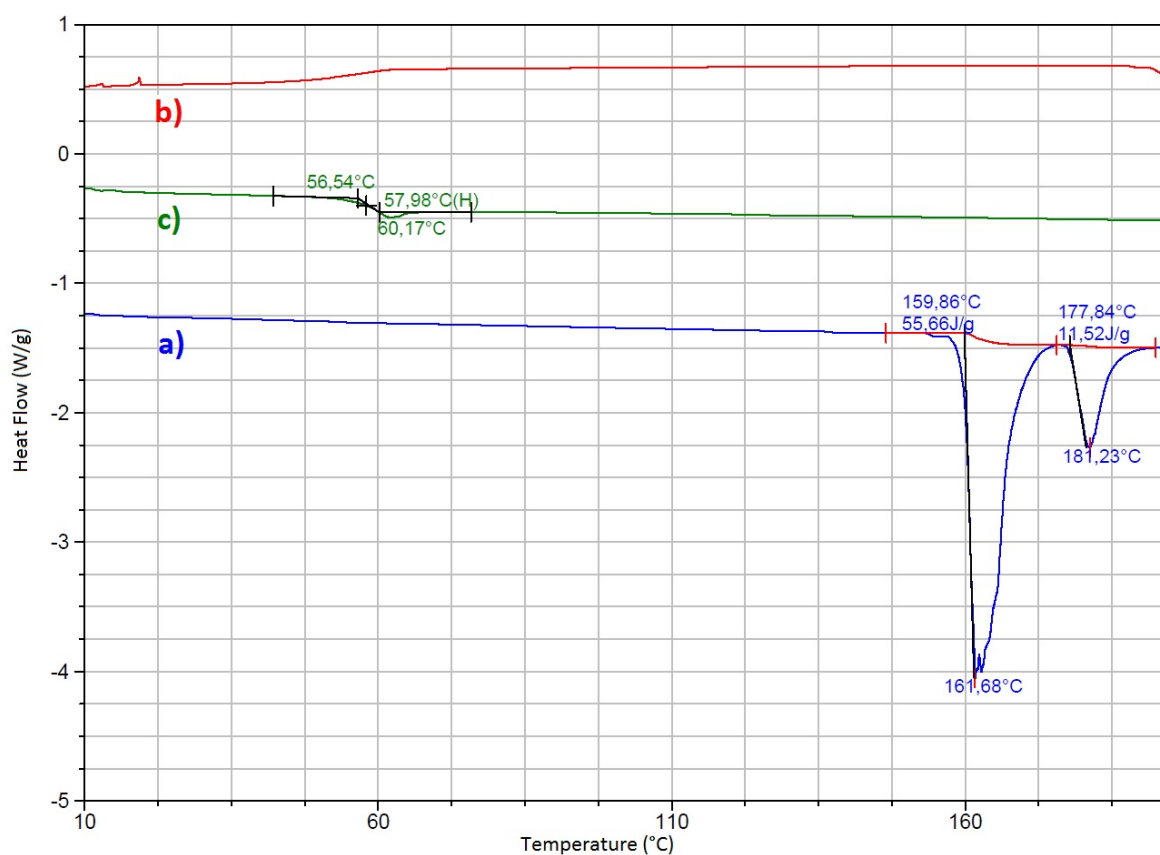


Figure S1. DSC curves of **5a**: (a) first heating; (b) cooling; and (c) second heating (Heating rate 20 °C/min).

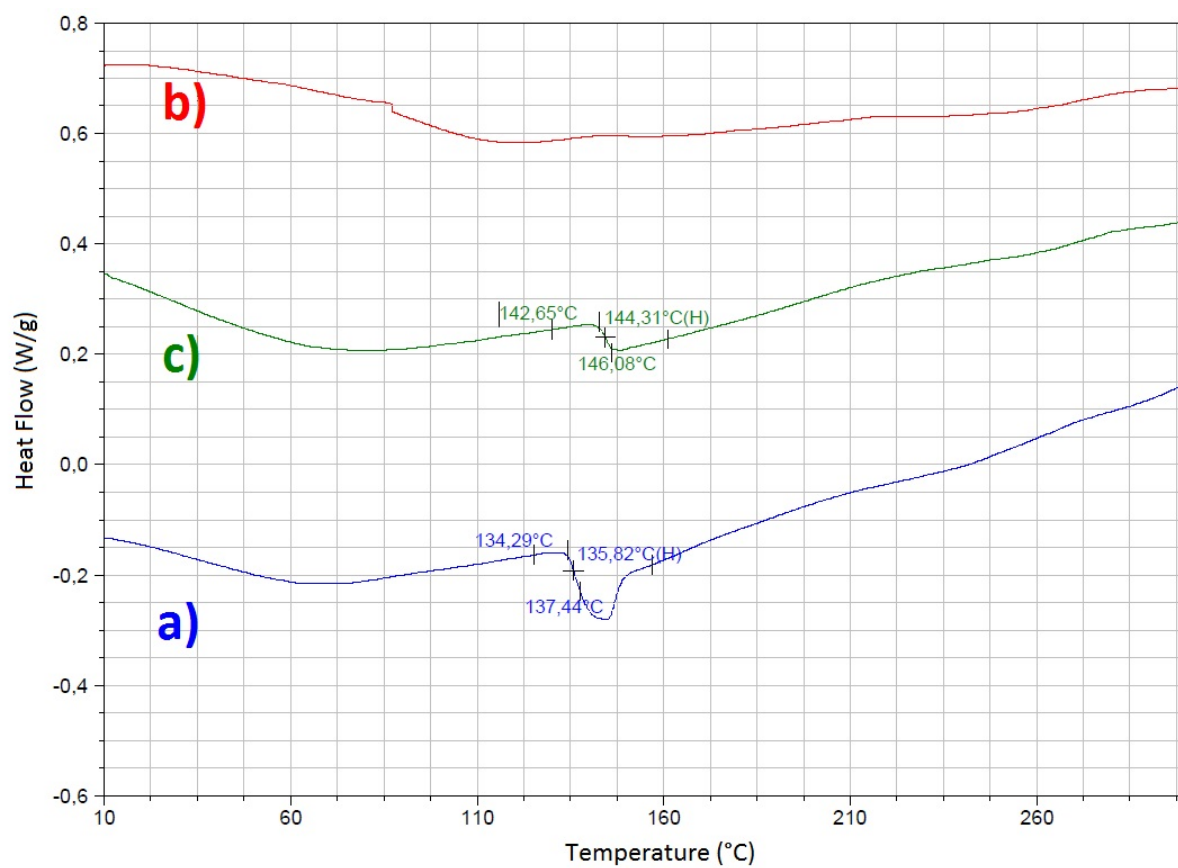


Figure S1. DSC curves of **5b**: (a) first heating; (b) cooling; and (c) second heating (Heating rate 20 °C/min).

X-ray Crystallography

X-ray structure-data of **3**, **7** and **9** was collected with a Bruker APEX-II using graphite-monochromated Mo-K α radiation for **3** and **9** and Agilent SuperNova using Cu-K α radiation for **7**. The structures were solved by direct methods (SHELXS-97).

Table S1. Crystal data and structure refinement details.

	3	7	9
Molecular formula	C ₂₀ H ₁₂ O	C ₄₄ H ₂₈ O	C ₃₆ H ₂₄ O ₂
Molecular weight	268.30 g/mol	572.66 g/mol	488.55 g/mol
Diffractometer	Bruker APEX-II CCD	Agilent SuperNova, Atlas CCD	Bruker APEX-II CCD
Radiation	Mo K α (0.71073 Å), graphite	Cu K α (1.5418 Å), X-ray mirrors	Mo K α (0.71073 Å), graphite
Crystal size	(0.1 x 0.1 x 0.1) mm ³	(0.4212 x 0.2811 x 0.1181) mm ³	(0.416 x 0.195 x 0.114) mm ³
Crystal system, space group	monoclinic, P-2 ₁ /C	triclinic, P-1	monoclinic, P-2 ₁ /C
Lattice parameters	a = 8.4538(3) Å b = 13.4041(4) Å c = 11.2408(4) Å $\alpha, \beta, \gamma = 90^\circ, 93.812(2)^\circ, 90^\circ$	a = 10.9104(5) Å b = 11.7223(10) Å c = 12.8808(9) Å $\alpha, \beta, \gamma = 112.582(7)^\circ, 103.862(5)^\circ, 95.539(5)^\circ$	a = 14.442(2) Å b = 10.2549(16) Å c = 17.944(13) Å $\alpha, \beta, \gamma = 90^\circ, 112.500(2)^\circ, 90^\circ$
Unit cell volume	1270.94(7) Å ³	1443.76(17) Å ³	2455.2(7) Å ³
Formula units per unit cell	4	2	4
F(000)	560	600	1024
Calculated density	1.402 g/cm ³	1.317 g/cm ³	1.322 g/cm ³
Linear absorption coeff.	0.085 mm ⁻¹	0.593 mm ⁻¹	0.080 mm ⁻¹
Scan	Φ and ω -scans	ω -scans	Φ and ω -scans
Index limits	-11 \leq h \leq 11; -17 \leq k \leq 17; -14 \leq l \leq 14	-13 \leq h \leq 11; -14 \leq k \leq 14; -16 \leq l \leq 15	-18 \leq h \leq 18; -12 \leq k \leq 13; -22 \leq l \leq 23
R _{int} (internal consistency of the dataset)	0.0185	0.0222	0.0294
Reflections collected /unique	19500 / 3013	27946 / 5788	21556 / 5789
Refined parameters / restraints	190 / 0	407 / 0	343 / 0
R1 (all data)	0.0532	0.0461	0.0633
R1 (I > 2 σ)	0.0461	0.0438	0.0382
wR ² (all data)	0.1240	0.1605	0.0814
wR ² (I > 2 σ)	0.1305	0.1644	0.0941
Goof S	1.025	1.436	1.013
Max./min. differential electron density	max: 0.645 / min: -0.241 eÅ ⁻³	max: 0.262 / min: -0.272 eÅ ⁻³	max: 0.316 / min: -0.256 eÅ ⁻³

Cyclic Voltammetry

Cyclic voltammetry was performed on a Metrohm μ AUTOLABIII in anhydrous CH_2Cl_2 (oxidation) and THF solutions (reduction) of tetra-*n*-butylammonium hexafluorophosphate (0.11 M) under argon atmosphere at a scan speed of 0.5 V/s. A gold electrode was used as a working electrode and a platinum-wire as the counter-electrode. An Ag/AgCl 3 M KCl//0.025 M TMAcI (in ethylene glycol) electrode was used as the reference electrode for reduction scans and an Ag/AgCl 3 M KCl//0.4 M TEABr (in ethylene glycol) electrode for oxidation scans. The CV curves were calibrated using the ferrocene/ferrocenium (Fc/Fc^+) redox couple as an internal standard. HOMO and LUMO energy levels were estimated from the equations

$$E_{\text{HOMO}} = -(4.8 + {}^{\text{Ox}}E_{1/2} - {}^{\text{Fc/Fc}^+}E_{1/2})$$

$$E_{\text{LUMO}} = -(4.8 + {}^{\text{Red}}E_{1/2} - {}^{\text{Fc/Fc}^+}E_{1/2}),$$

assuming the absolute energy of Fc/Fc^+ to 4.8 eV^[3] below the vacuum level. The half-wave potentials for the Fc/Fc^+ -couple (${}^{\text{Fc/Fc}^+}E_{1/2}$), the oxidation (${}^{\text{Ox}}E_{1/2}$) and the reduction (${}^{\text{Red}}E_{1/2}$) were estimated from the average of anodic and cathodic peak potentials.

Quantum chemical calculations

Geometry optimization for all molecules was performed at the DFT/B3LYP/6-31G(d) level of theory using Gaussian 09 software.^[4] The HOMO energy of **3** was calculated from the LUMO energy level and the absorption edge.

Table S2. Measured and corrected HOMO and LUMO values.

Compound	HOMO (eV)		LUMO (eV)	
	Measured	Calculated	Measured	Calculated
3	-	-5.27	-2.38	-1.59
5a	-5.68	-5.33	-2.36	-1.56
5b	-5.68	-5.35	-2.43	-1.58
7	-5.54	-5.06	-2.31	-1.40

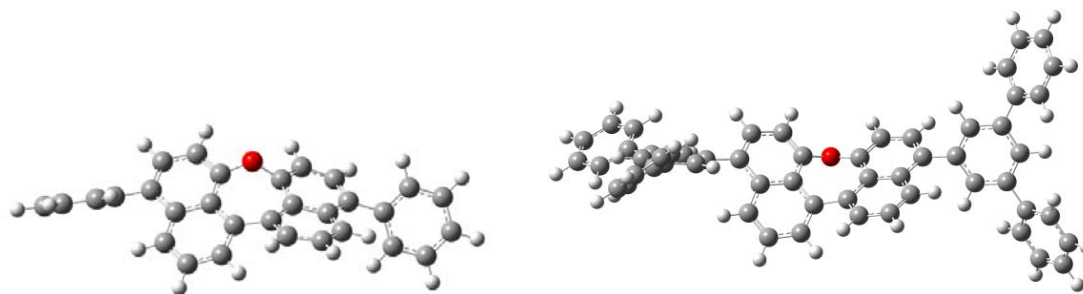


Figure S3. Optimized geometry of **5a** and **5b**. Structures exhibit 32° dihedral-angle between naphthalene planes.

2. Absorption and emission spectra in solid state

The measurements from solid state were performed on Perkin Elmer Lambda 850 for absorption and Hitachi F-4500 for emission respectively. 50 nm thick films were prepared from toluene solution (15 mg/ml) by spin-coating on quartz glass-substrates (3x3 cm) with 2900 rpm.

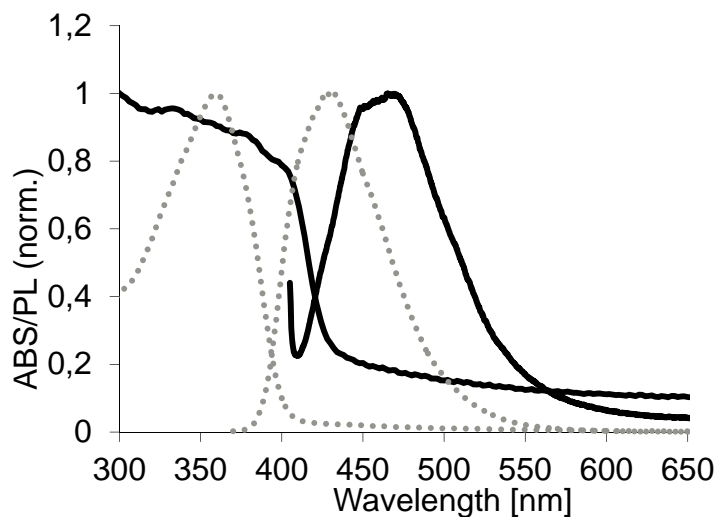


Figure S4. Normalized absorption (left) and emission (right) spectra of 50 nm film (solid line) and of toluene-solution (dotted line) of compound **3** (recorded at T=298 K).

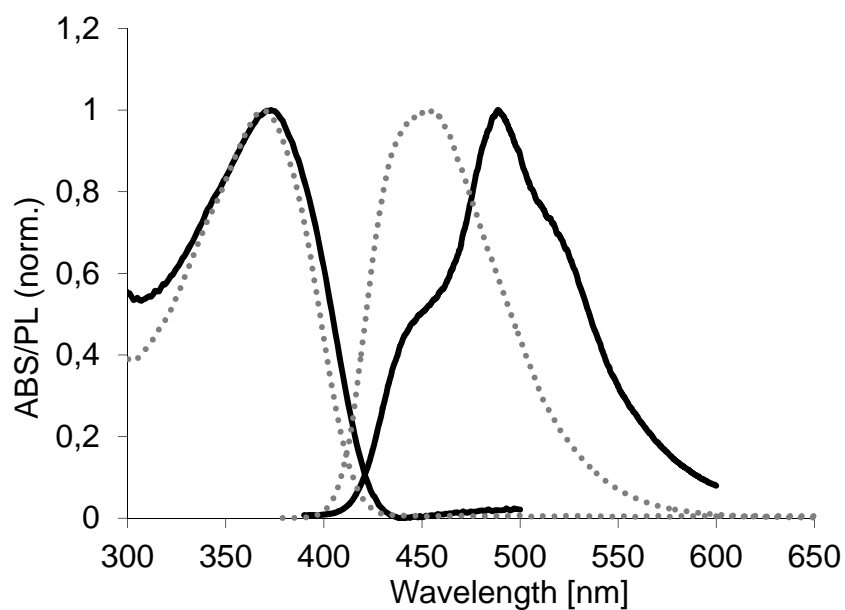


Figure S5. Normalized absorption (left) and emission (right) spectra of 50 nm film (solid line) and of toluene-solution (dotted line) of compound **5a** (recorded at T=298 K).

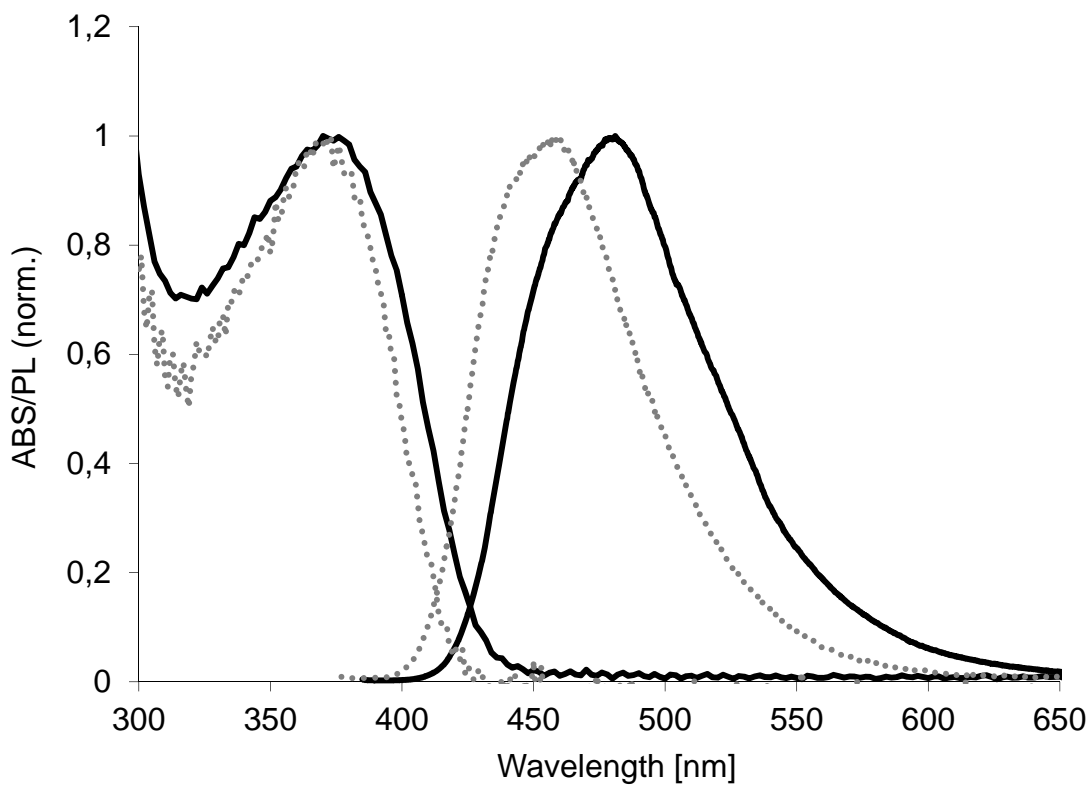


Figure S6. Normalized absorption (left) and emission (right) spectra of 50 nm film (solid line) and of toluene-solution (dotted line) of compound **5b** (recorded at T=298 K).

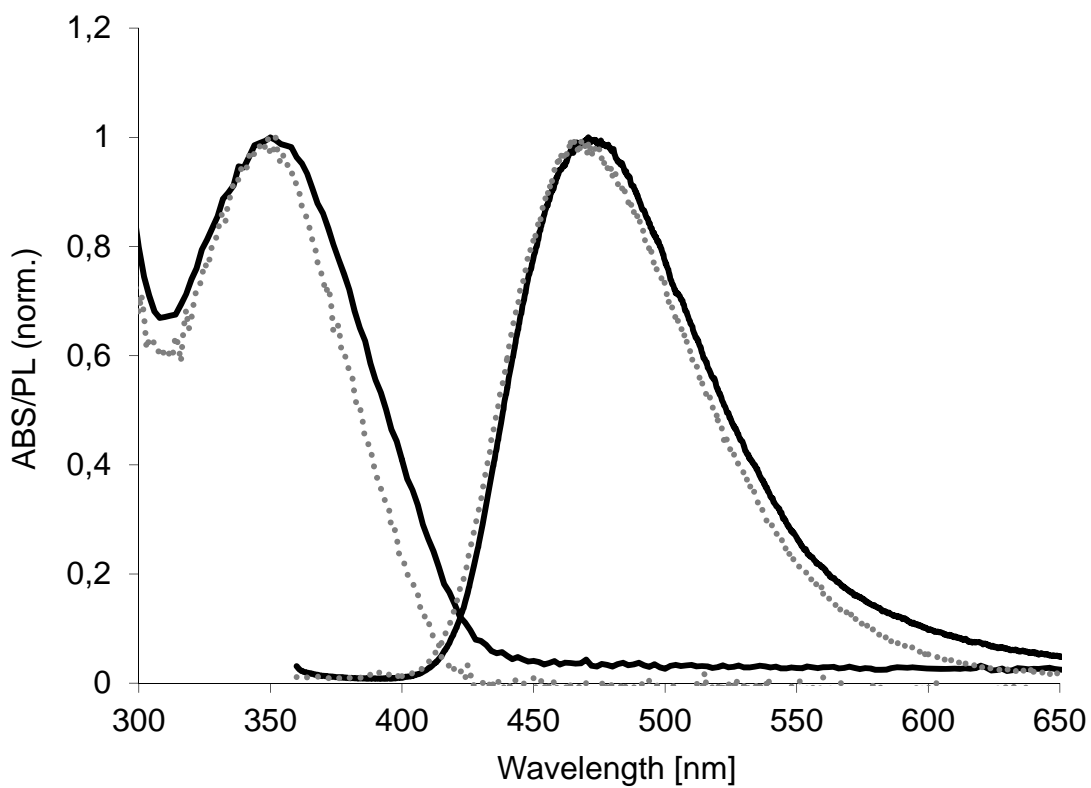


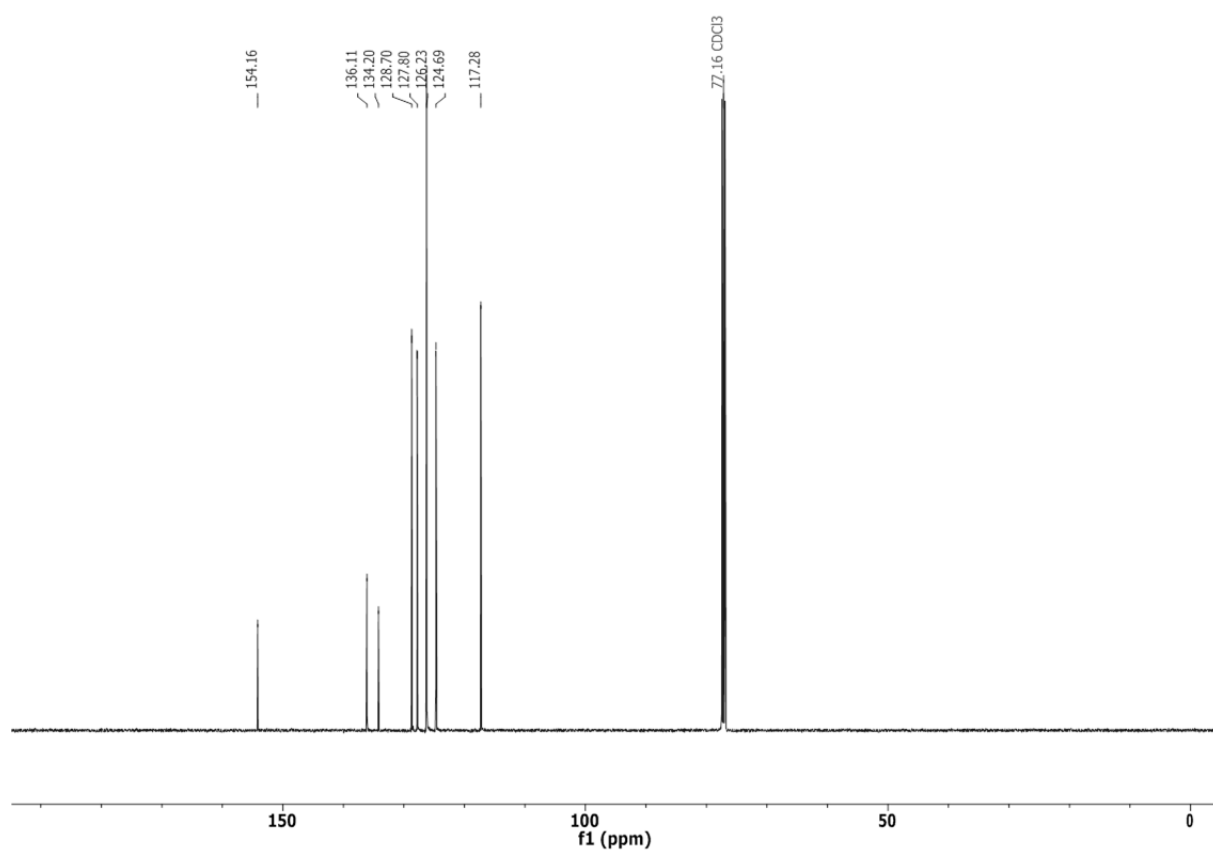
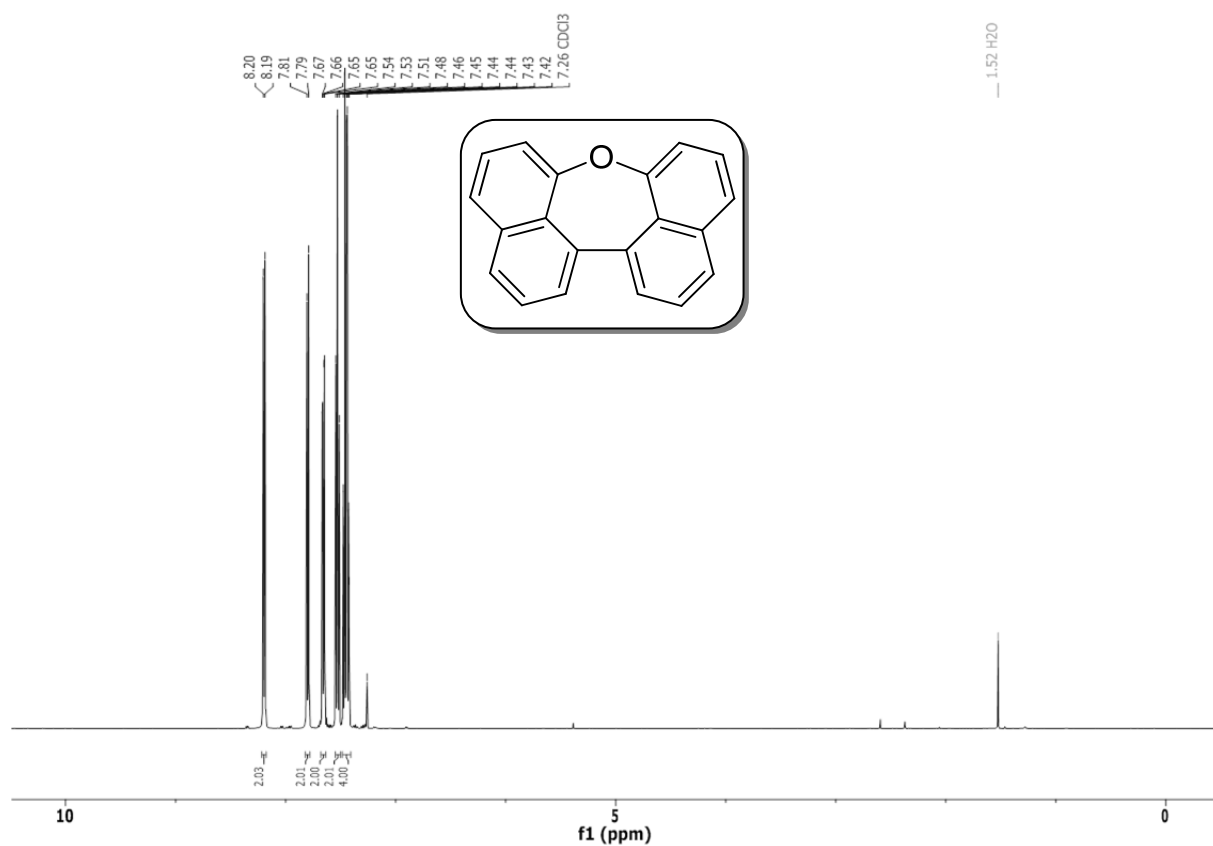
Figure S7. Normalized absorption (left) and emission (right) spectra of 50 nm film (solid line) and of toluene-solution (dotted line) of compound **7** (recorded at T=298 K).

3. References

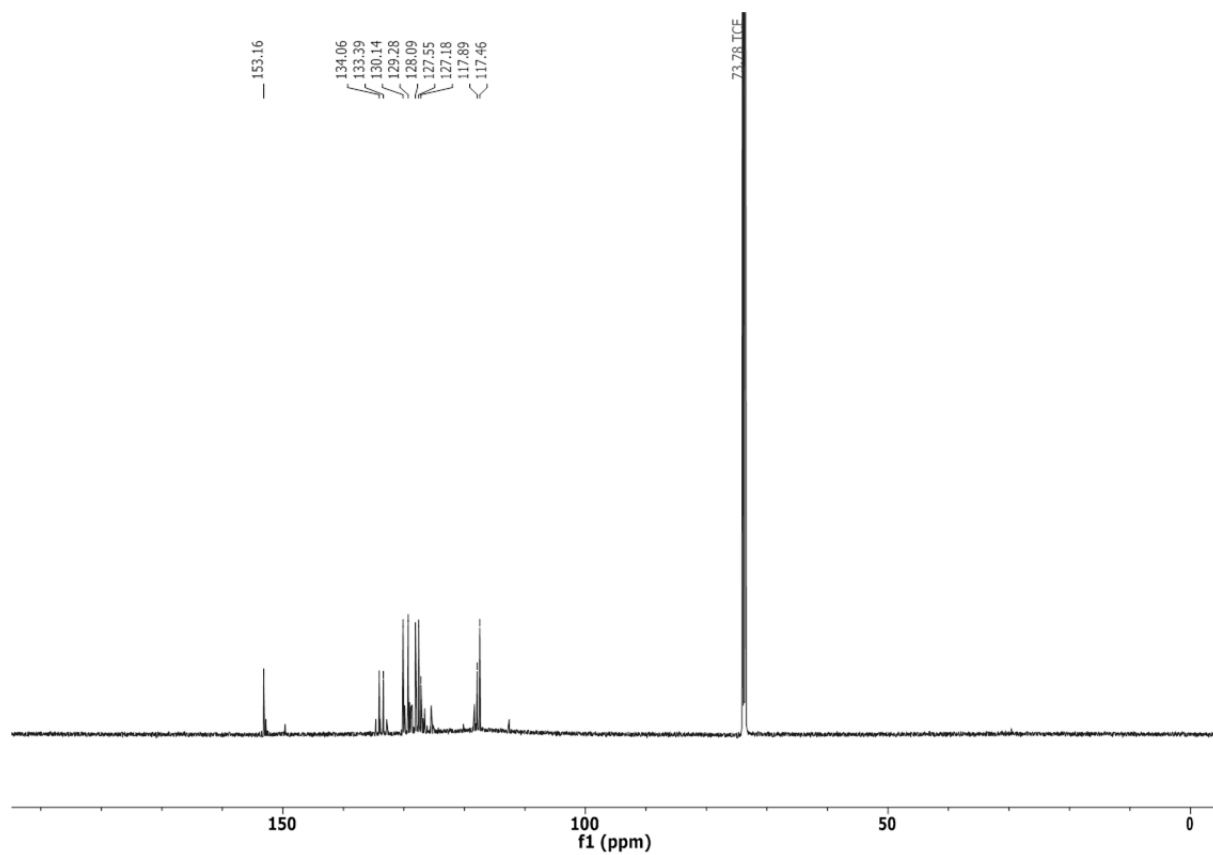
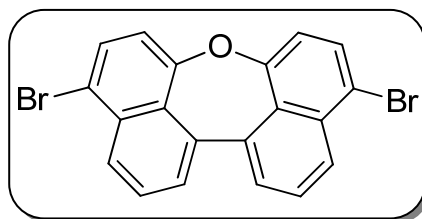
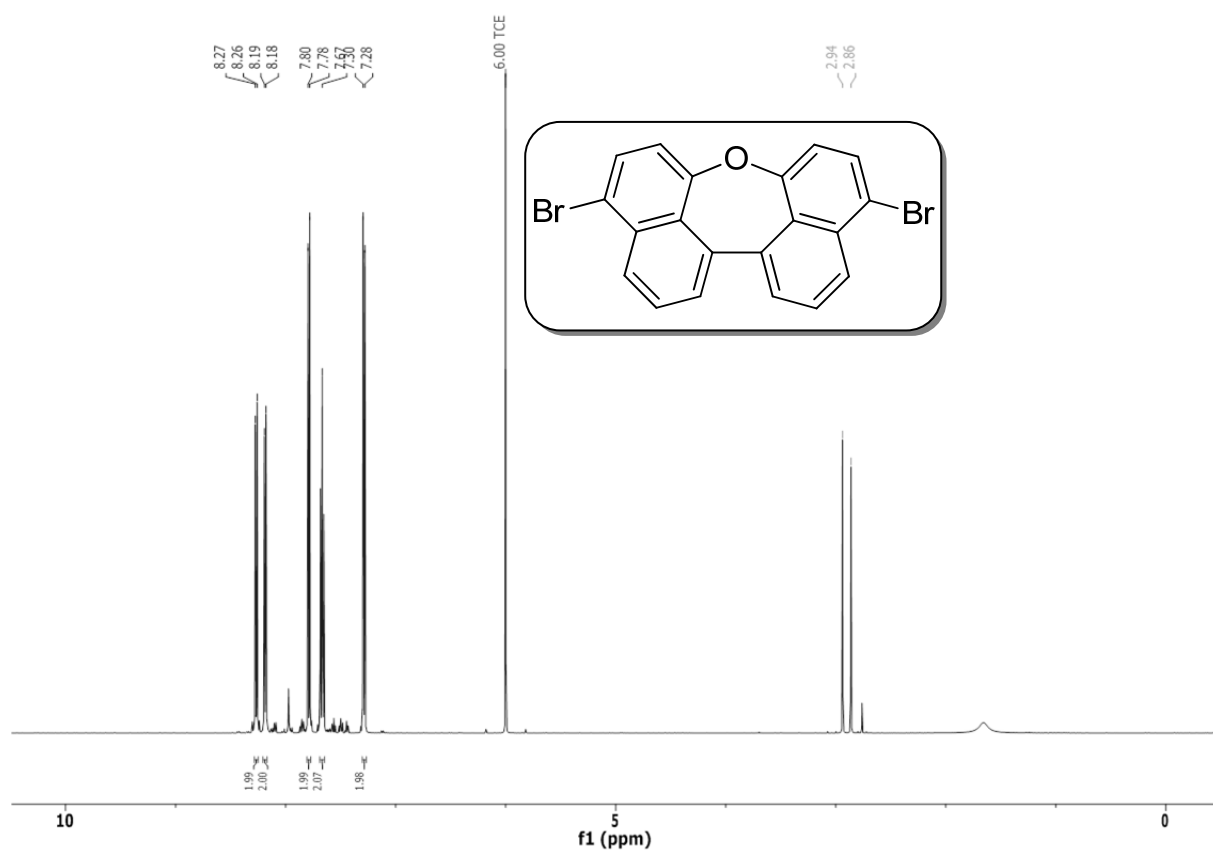
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- [3] J. Pommerehne, H. Vestweber, W. Guss, R. F. Mahrt, H. Bässler, M. Porsch, J. Daub, *Adv. Mater.* **1995**, *7*, 551-554.
- [4] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox,

4. Copies of ^1H -, and ^{13}C -NMR spectra

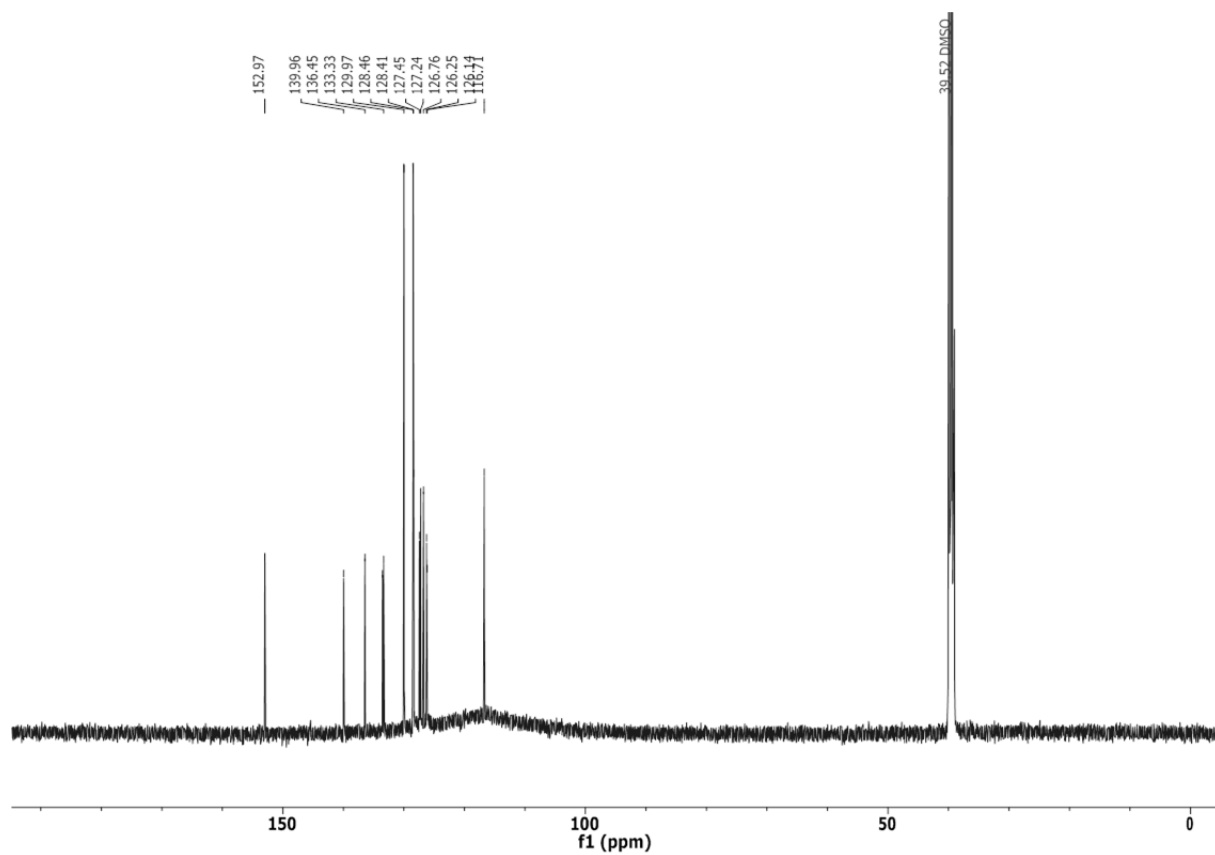
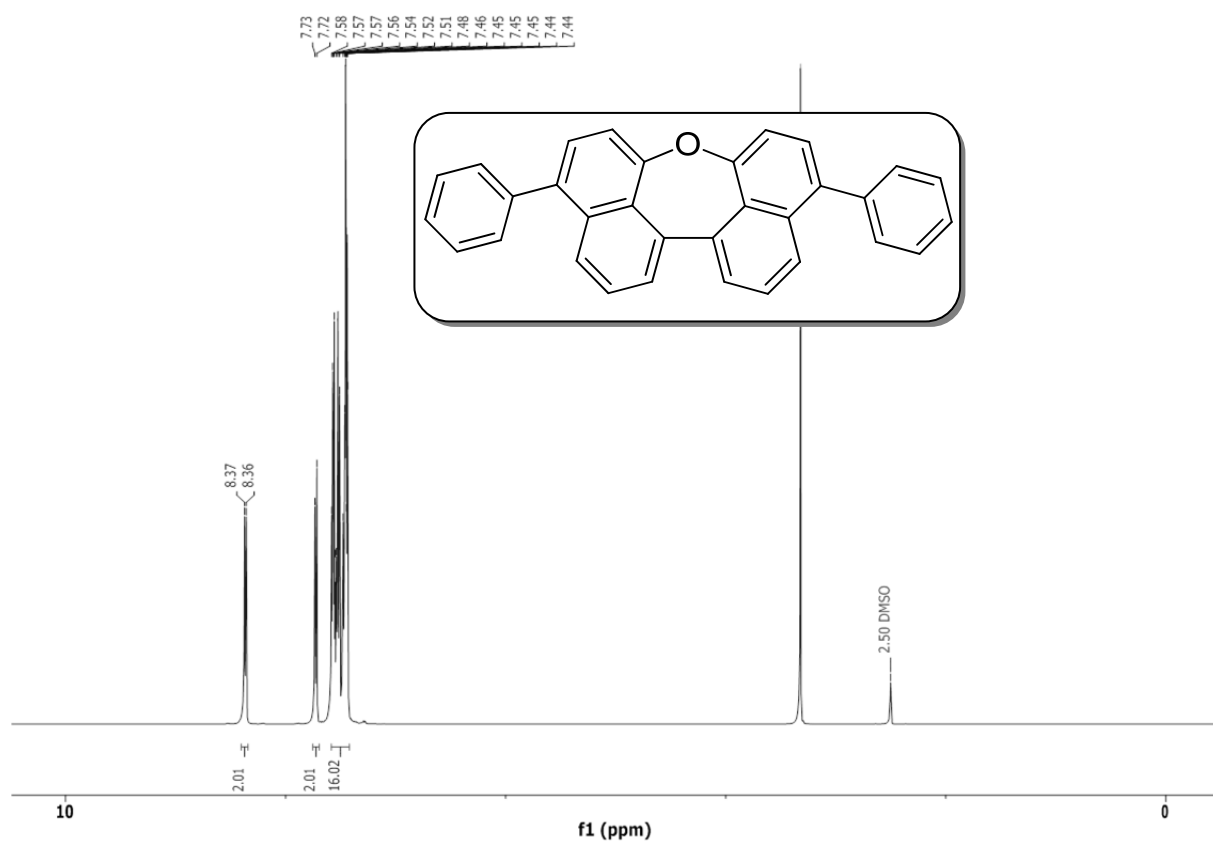
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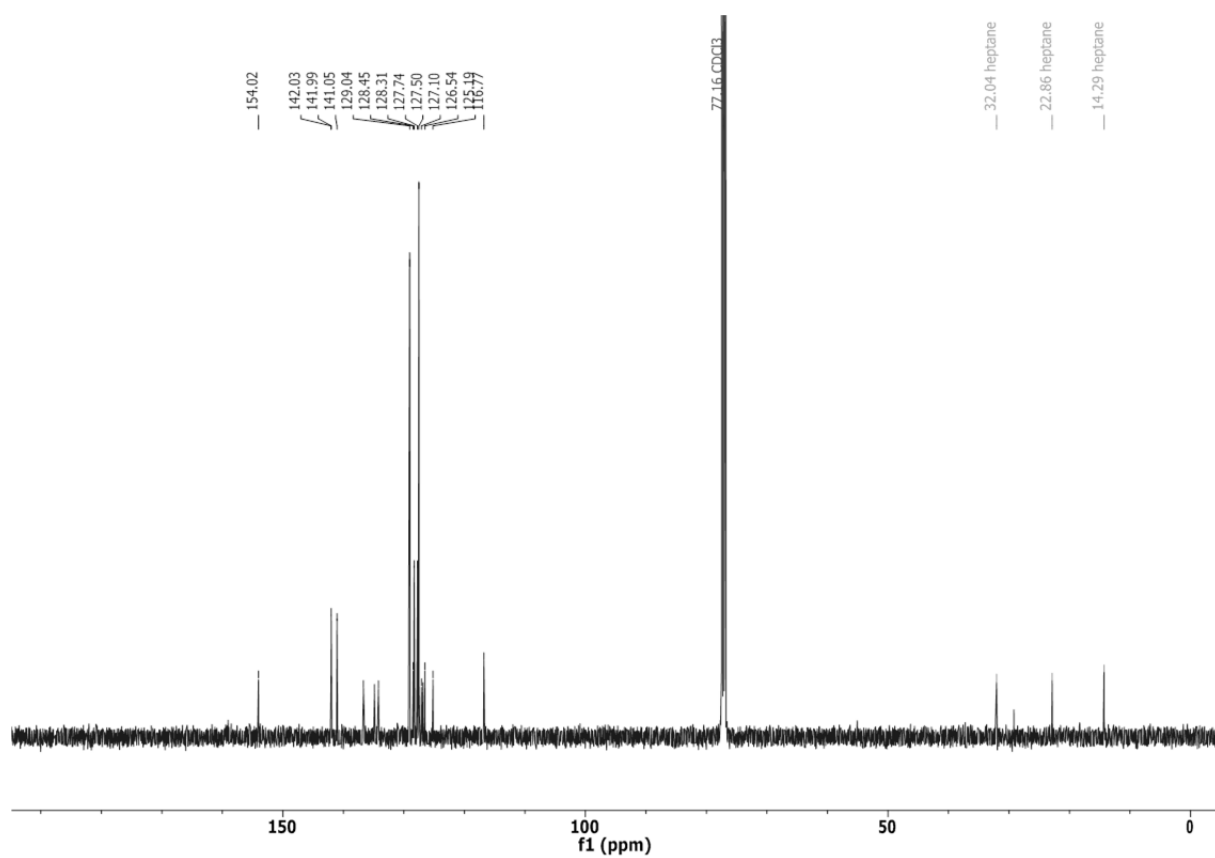
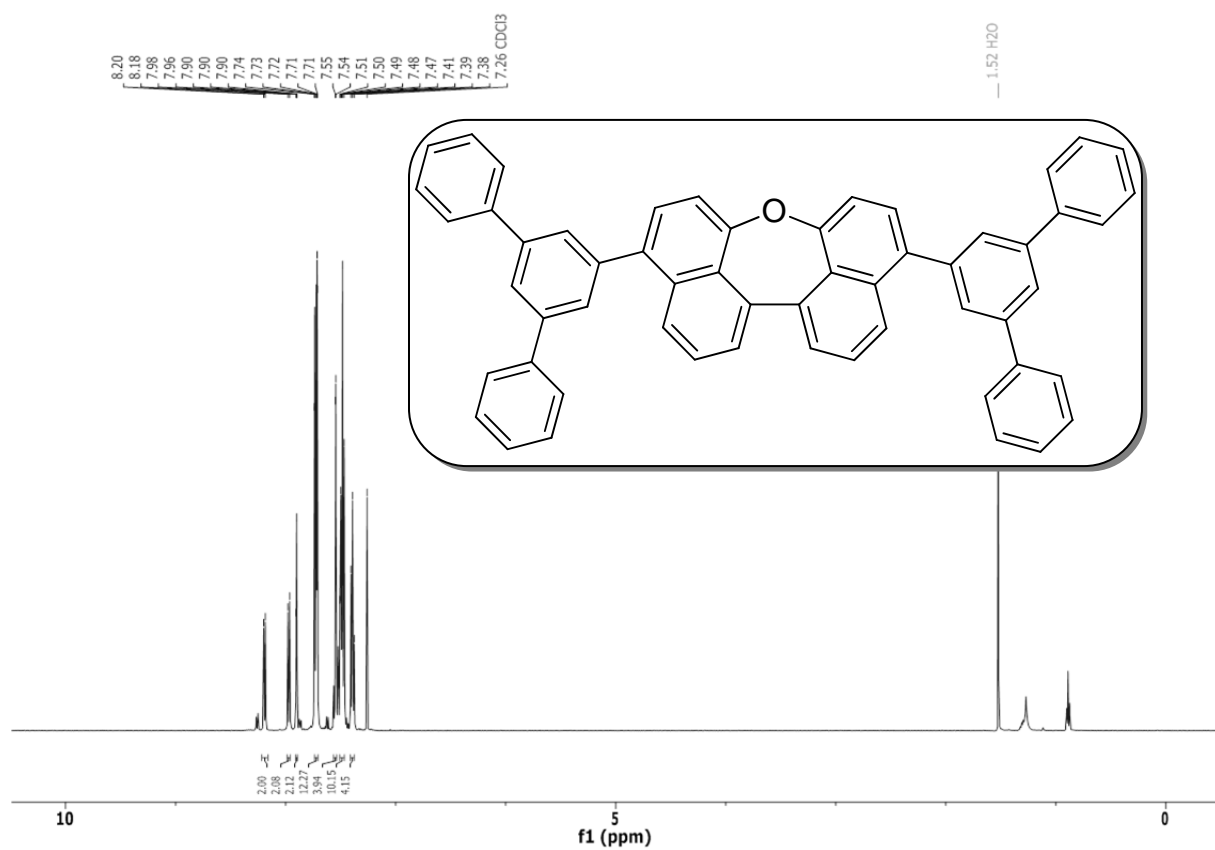
4,4'-Dibromo-dinaphth[1,8-bc:1',8'-ef]oxepin (4)



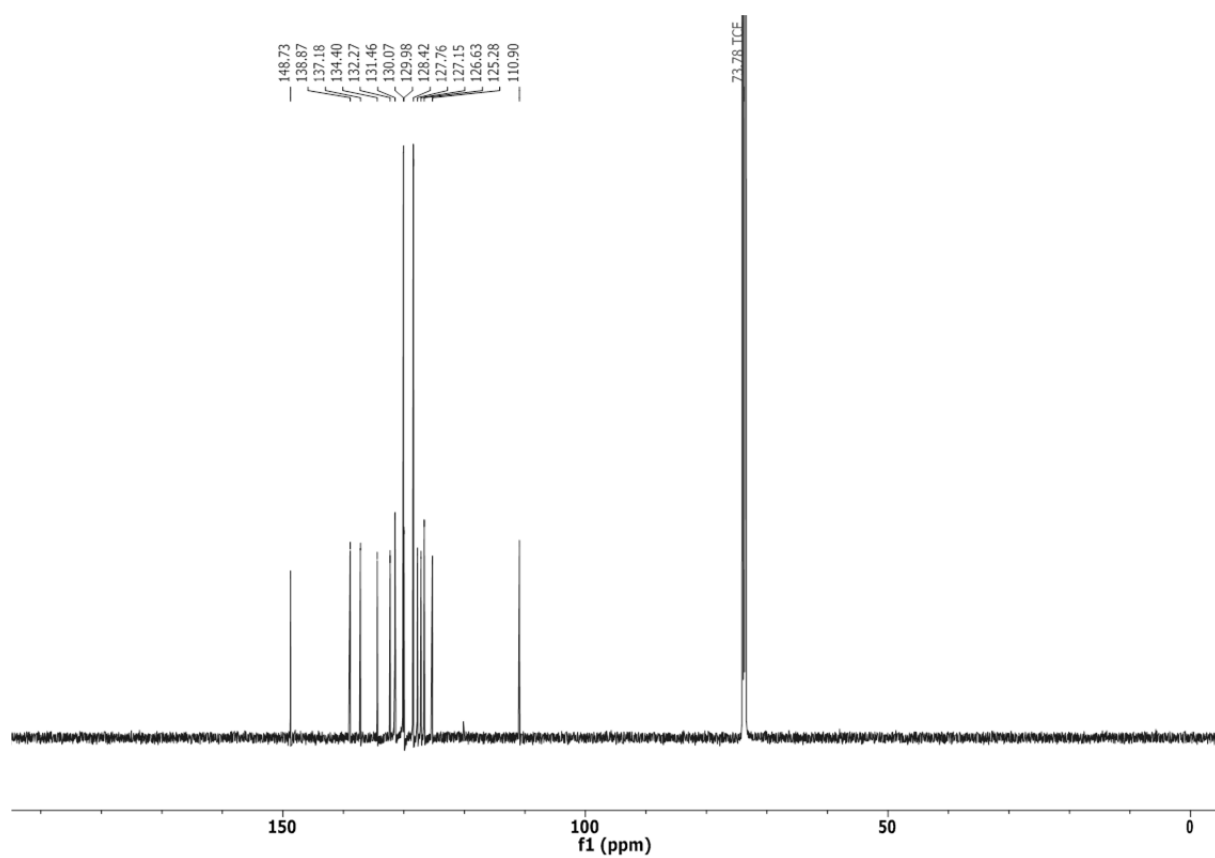
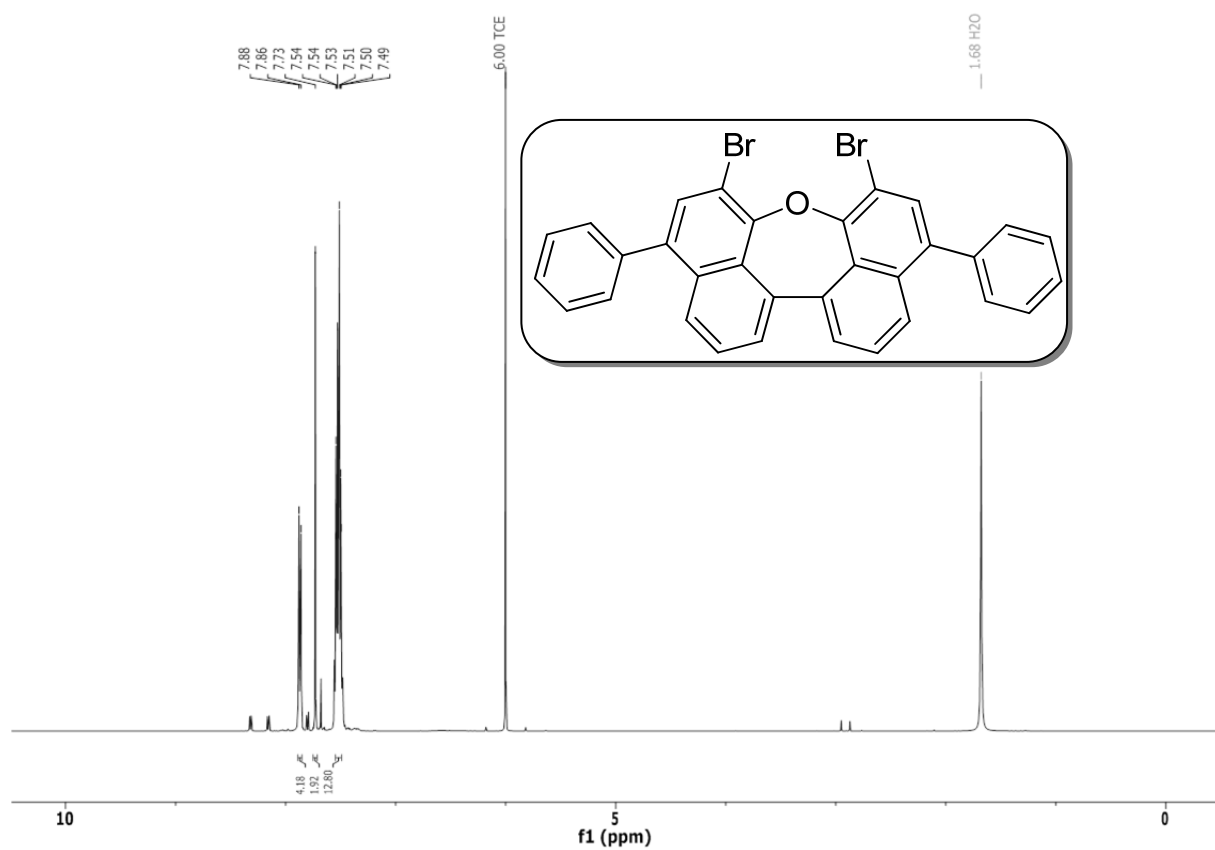
4,4'-Diphenyl-dinaphth[1,8-bc:1',8'-ef]oxepin (5a)



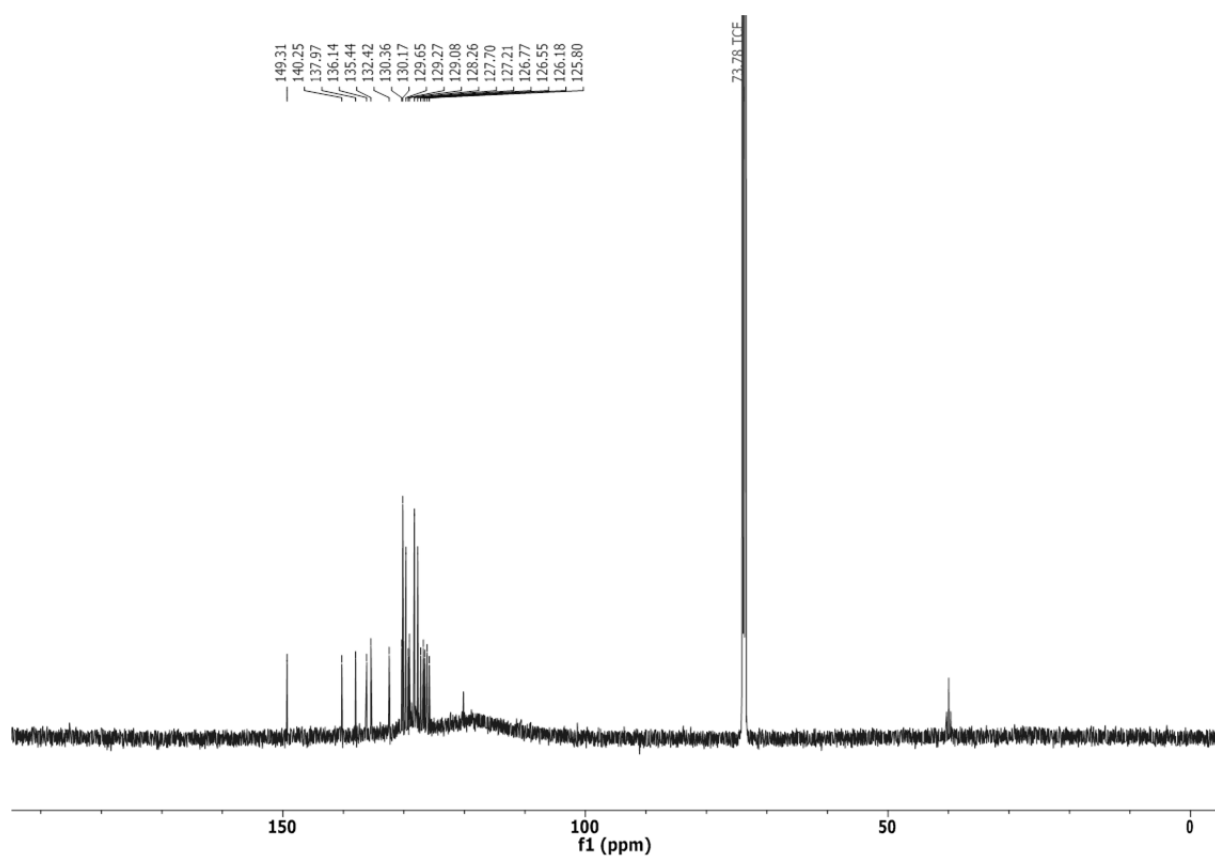
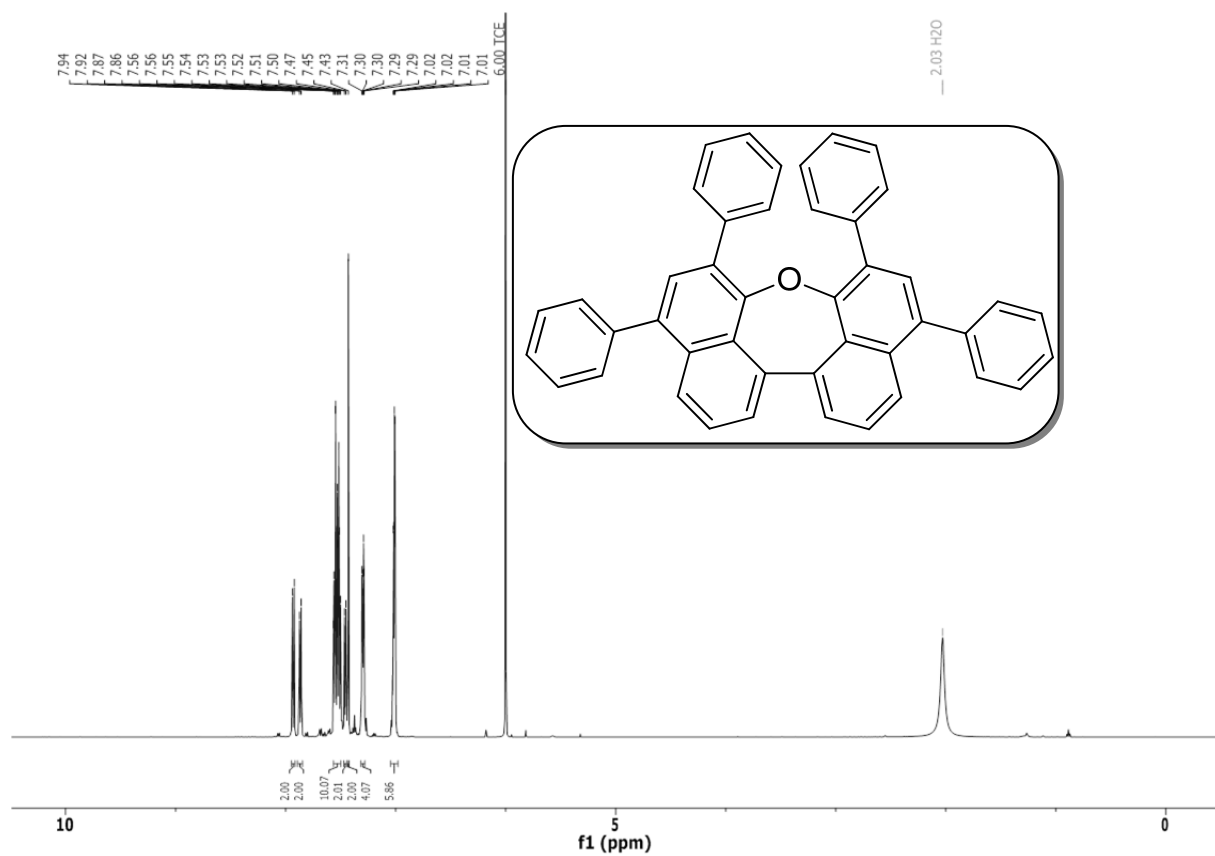
Bis-5,5'-*m*-terphenyl-dinaphth[1,8-bc:1',8'-ef]oxepin (5b)



2,2'-Dibromo-4,4'-diphenyl-dinaphth[1,8-bc:1',8'-ef]oxepin (6)



2,2',4,4'-Tetraphenyl-dinaphth[1,8-bc:1',8'-ef]oxepin (7)



Tribenz[b,d,f]oxepin (9)

