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Compact CPL emitters based on a [2.2]paracyclophane scaffold: Recent developments and future perspectives

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Supporting information

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General remarks

All reactions were carried out under inert atmosphere, (in oven-dried glassware, using dry solvents unless otherwise specified. All commercially available compounds were purchased from Aldrich Chemical Co., Acros Organics or Alfa Aesar and used as received. Analytical thin layer chromatography (TLC) was performed on silica gel plates (Merck 60F254) visualized with a UV lamp (254 nm). Flash chromatography was performed on silica gel (60-230 mesh) unless otherwise specified. Organic extracts were dried over anhydrous $MgSO_4$. NMR spectra (^1H and $^{13}C\{^1H\}$) were recorded on Bruker Avancell 500 spectrometer, at 500 MHz (H value) in $CDCl_3$. Spectra were referenced to residual chloroform (7.26 ppm, ^1H; 77.0 ppm, $^{13}C\{^1H\}$). Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), and m (multiplet or overlap of nonequivalent resonances), dd (doublet of doublet), td (triplet of doublet), and br (broad signal). Coupling constants, *J*, are reported in hertz (Hz). DEPT-135 experiments were used to assign ^{13}C NMR spectra. All NMR spectra were obtained at 300K unless otherwise specified. All microwave-mediated reactions were carried out using a Biotage Initiator™ Exp or an Anton Paar Monowave microwave synthesizer. The microwave reactions were carried out in 2 - 5 mL vials. Optical rotations (αD) were measured on a Perkin Elmer polarimeter (model 341) at 20 °C. IR spectra were obtained using a spectrum one FT-IR spectrometer (Perkin Elmer). High Resolution mass spectra were recorded on a ThermoFischer Exactive Orbitrap spectrometer. HPLC analyses were performed on a Shimadzu chromatograph equipped with a diode array UV/VIS detector. Absorption and fluorescence spectra were recorded on UV-2700 spectrophotometer (Shimadzu) and F-7000 fluorescence spectrometer (Hitachi), respectively. The photophysical measurements were performed on air-equilibrated solutions, using quarts cuvettes with 1 cm optical path length. Electronic circular dichroism (ECD, in $M^{-1}\,cm^{-1}$) was measured on a Jasco J-815 Circular Dichroism Spectrometer (IFR140 facility - Biosit - Université de Rennes 1). The circularly polarized luminescence (CPL) measurements were performed using a home-built CPL spectrofluoropolarimeter (set-up by JASCO company). The samples were excited using a 90° geometry with a Xenon ozone-free lamp 150 W LS. The following parameters were used: emission slit width ≈ 2 mm, integration time = 4 sec, scan speed = 50 nm/min, accumulations = 5. The concentration of all the samples was ~ 10^{-4} M in CH_2Cl_2. Excitation of the samples were performed at 360 nm.

Enantiopure aldehydes (R_p)-**1a** and (S_p)-**1a** were prepared according to a method developed in our laboratory and described previously.[1] Optically active naphthalene derivatives (R_p)-**5a** and (S_p)-**5a** were prepared according to a previously reported procedure.[2]

[1] M.-L. Delcourt, S. Turcaud, E. Benedetti, L. Micouin, *Adv. Synth. Catal.* 2016, **358**, 1213.

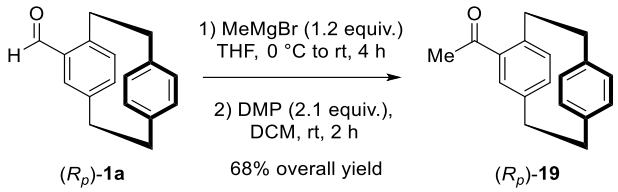
[2] E. Benedetti, M.-L. Delcourt, B. Gatin-Fraudet, S. Turcaud, L. Micouin, *RSC Adv.* 2017, **7**, 5047.

List of abbreviations

ATH	Asymmetric transfer hydrogenation
CPL	Circularly polarized luminescence
CVD	Chemical vapour deposition
DBU	1,8-Diazabicyclo(5.4.0)undec-7-ene
DCC	Dicyclohexylcarbodiimide
DCE	1,2-Dichloroethane
DCM	Dichloromethane
DIBAL-H	Diisobutylaluminium hydride
DMAP	4-(Dimethylamino)pyridine
DMP	Dess-Martin periodinane
DMSO	Dimethyl sulfoxide
DNA	Deoxyribonucleic acid
ECD	Electronic circular dichroism
equiv.	equivalents
ESI	Electrospray ionization
Et_2O	Diethyl ether
EtOH	Ethanol
g_{asb}	Absorption dissymmetry factor
g_{lum}	Luminescence dissymmetry factor
HPLC	High pressure liquid chromatography
IR	Infrared
MeOH	Methanol
min	minutes
µw	Microwave irradiation
NMR	Nuclear magnetic resonance
OFET	Organic field-effect transistors
OLED	Organic light-emitting diodes
pCp	[2.2]paracyclophane
$PhNO_2$	Nitrobenzene
θ	Quantum yield
quant.	quantitative
rt	Room temperature
THF	tetrahydrofuran
TLC	Thin layer chromatography
UV-Vis	Ultra-violet and visible
VCD	Vibrational circular dichroism

Experimental procedures ad characterization data

(R_p)-4-acetyl [2.2]paracyclophane **19**



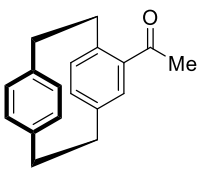
(R_p)-**1a** (R_p)-**19**

In a flame and vacuum-dried 100 mL round bottom flask, under argon, (R_p)-**1a** (500 mg, 2.12 mmol, 1.0 equiv.) was dissolved in dry THF (30 mL) and cooled to 0 °C using an ice bath, MeMgBr (3 M in Et_2O, 0.85 mL, 2.54 mmol, 1.2 equiv.) was subsequently added dropwise using a syringe. The brown mixture was allowed to warm back to rt and was stirred for 4 h. After cooling back to 0 °C, the reaction was quenched by addition of NH_4Cl (15 mL), then diluted with water (30 mL) and EtOAc (30 mL). The resulting immiscible phases were separated, and the aqueous layer was extracted with EtOAc (2 x 15 mL). The combined organic layers were washed with water (20 mL) and brine (20 mL), dried over $MgSO_4$, gravity filtered and evaporated under reduced pressure. The crude oily residue was dissolved in dry DCM (40 mL) and Dess-Martin periodinane (DMP, 1.75 g, 4.12 mmol, 2.1 equiv.) was added. The cloudy reaction mixture was stirred for 2 h at rt before addition of sat'd aq. $NaHCO_3$ (20 mL) and water (20 mL). The resulting immiscible phases were separated, and the aqueous layer was extracted with DCM (2 x 15 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, gravity filtered and concentrated under reduced pressure. The obtained solid residue was purified by column chromatography (SiO_2) using pentane:EtOAc (10:1) as the eluent to yield (R_p)-**19** (365 mg, 1.46 mmol, 68%) as an amorphous white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (d, *J* = 1.8 Hz, 1H), 6.66 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.59 – 6.48 (m, 3H), 6.46 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.38 (dd, *J* = 7.8, 1.8 Hz, 1H), 4.00-3.92 (m, 1H), 3.23 – 3.12 (m, 4H), 3.07 – 2.98 (m, 2H), 2.87 – 2.79 (m, 1H), 2.47 (s, 3H) ppm.
^{13}C NMR (125 MHz, $CDCl_3$) δ 200.3 (C), 141.6 (C), 140.3 (C), 139.7 (C), 139.1 (C), 137.8 (C), 136.4 (CH), 136.3 (CH), 134.2 (CH), 133.0 (CH), 132.8 (CH), 132.0 (CH), 131.1 (CH), 36.0 (CH_2), 35.1 (CH_2), 35.1(CH_2), 34.8 (CH_2), 28.7 (CH_3) ppm.
IR ν 2930, 1737, 1672, 1552, 1434, 1353, 1265, 1237, 950, 899, 855, 794, 732 cm^{-1}.
$[\alpha]_{589}$ −17 (c 1.15, $CHCl_3$).
Known compound. Spectroscopic data are in agreement with the literature.[3]

(S_p)-4-acetyl [2.2]paracyclophane **19**

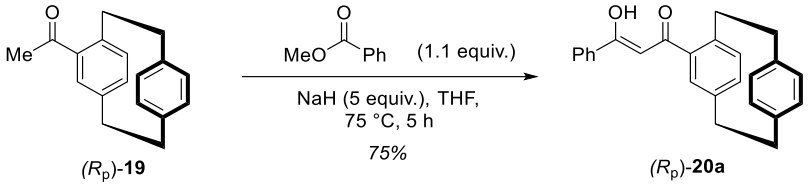
Compound (S_p)-**19** was prepared following the procedure employed to synthesize product (R_p)-**19**: (S_p)-**1a** (700 mg, 2.96 mmol, 1.0 equiv.) and MeMgBr (3 M in Et_2O, 3.55 mmol, 1.2 equiv.) in dry THF (45 mL) for 4 h; this residue and DMP (1.75 g, 4.12 mmol, 1.5 equiv.) in dry DCM (45 mL). (S_p)-**19** (279 mg, 1.11 mmol, 38% over the two steps) was obtained as an amorphous white solid. **$[\alpha]_{589}$** = + 32 (c 2, $CHCl_3$).



(S_p)-**19**

[3] S. Irii, T. Ogaki, H. Miyashita, K. Nobori, Y. Ozawa, M. Abe, H. Sato, E. Ohta, Y. Matsui, H. Ikeda, *Tetrahedron Lett.* 2022, **101**, 153913.

(R_p)-(Z)-1-(1,4(1,4)-dibenzenacyclohexaphane-12-yl)-3-hydroxy-3-phenylprop-2-en-1-one **20a**



In a flame and vacuum-dried vial, under an argon atmoshpere, NaH (60% in mineral oil, 80 mg, 2.0 mmol, 5 equiv) was suspended in dry THF (1 mL). (R_p)-**19** (100 mg, 0.4 mmol, 1.0 equiv.) was dissolved in dry THF (1.5 mL) and slowly added dropwise at rt. The suspension was stirred for 1 h before addition of methyl benzoate (55 µL, 0.44 mmol, 1 mL). The vial was then sealed and heated to 75 °C in an oil bath. After 5 h, the orange solution was cooled to 0 °C, and a diluted HCl aq. solution (2 N, 5mL) was slowly added. Water (5 mL) and EtOAc (10 mL) were then added, and the resulting immiscible phases were separated. The aqueous layer was extracted with EtOAc (2 x 5 mL). The combined organic layers were washed with water (10 mL) and brine (10 mL), dried over $MgSO_4$, gravity filtered and evaporated under reduced pressure. The crude residue was purified by column chromatography (SiO_2) using Cy:EtOAc (20:1) as the eluent to yield (R_p)-**20a** (107 mg, 0.3 mmol, 75 %) as an orange sticky solid.

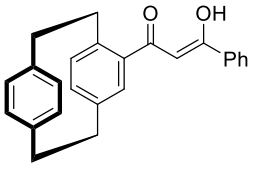
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.91 (m, 2H), 7.54 (dd, *J* = 5.0, 3.7 Hz, 1H), 7.53 – 7.42 (m, 2H), 6.92 (d, *J* = 1.8 Hz, 1H), 6.72 – 6.62 (m, 2H), 6.63 – 6.51 (m, 3H), 6.49 (s, 1H), 6.46 (dd, *J* = 7.8, 1.6 Hz, 1H), 3.94 – 3.86 (m, 1H), 3.24 – 3.11 (m, 3H), 3.05 (ddd, *J* = 15.1, 6.9, 3.4 Hz, 2H), 2.96 (ddd, *J* = 13.1, 9.4, 6.9 Hz, 2H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.7 (C), 183.9 (C), 140.4 (C), 140.1 (C), 139.9 (C), 139.3 (C), 136.7 (C), 136.4 (CH), 136.0 (CH), 135.5 (C), 132.8 (CH), 132.7 (CH), 132.6 (CH), 132.4 (CH), 132.3 (CH), 131.7 (CH), 128.7 (2CH), 127.0 (2CH), 96.8 (CH), 35.7 (CH_2), 35.5 (CH_2), 35.3 (CH_2), 35.2 (CH_2) ppm. **IR** ν 2927, 1738, 1599, 1566, 1456, 1365, 1228, 1217, 913, 775, 744 cm^{-1}.

$[\alpha]_{589}$ = −124 (c 0.4, $CHCl_3$).

Known compound. Spectroscopic data are in agreement with the literature. [4]

(S_p)-(Z)-1-(1,4(1,4)-dibenzenacyclohexaphane-12-yl)-3-hydroxy-3-phenylprop-2-en-1-one **20a**



(S_p)-**20a**

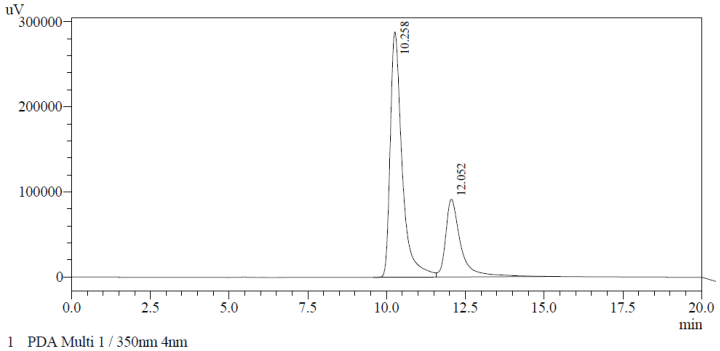
Compound (S_p)-**20a** was prepared following the procedure employed to synthesize product (R_p)-**20a:** NaH (60% in mineral oil, 144 mg, 3.6 mmol, 5 equiv.), (S_p)-**19** (180 mg, 0.72 mmol, 1.0 equiv.), methyl benzoate (100 µL, 0.79 mmol, 1.1 equiv.) in dry THF (4.5 mL). (S_p)-20a (189 mg, 0.53 mmol, 74 % yield) was isolated as an orange sticky solid. Spectroscopic data correspond to that of previously described for compound (R_p)-**20a**.

$[\alpha]_{589}$ = +119 (c 0.36, $CHCl_3$).

[4] M. Tanaka, S. Muraoka, Y. Matsui, E. Ohta, A. Sakai, T. Ogaki, Y. Yoshimoto, K. Mizuno, H. Ikeda, *ChemPhotoChem* 2017, **1**, 188.

HPLC analysis : t_{R1}= 10.3 min; t_{R2} = 12.1 min. [Column = Chiralcel OD (250 x 4.6 mm); eluent = *n*-heptane/*i*-PrOH (9:1); T = 20 °C; flow = 1 mL/min; λ = 350 nm).]

Co-injection of (R_p)-**20a** and (S_p)-**20a**.



1 PDA Multi 1 / 350nm 4nm

PeakTable

PDA Ch1 350nm 4nm

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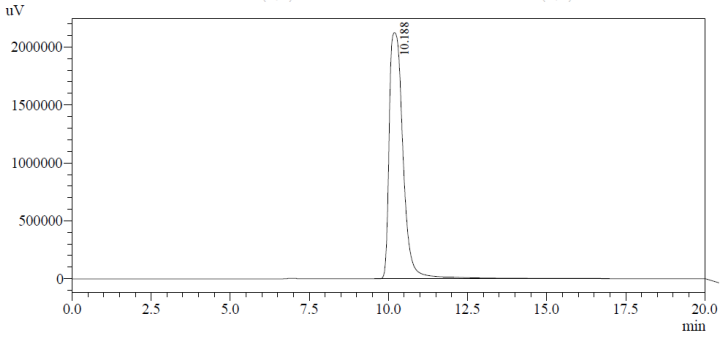
2	12.052	3067774	91368	28.840	24.052
Total		10637354	379870	100.000	100.000

Injection of pure (R_p)-**20a**: t_R = 10.2 min.



1 PDA Multi 1 / 350nm 4nm

PeakTable

PDA Ch1 350nm 4nm

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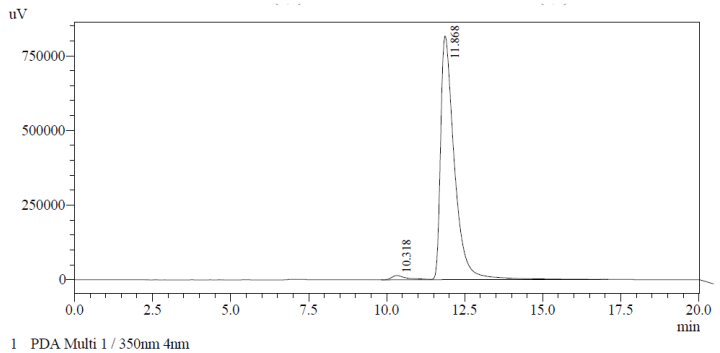
Injection of pure (S_p)-**20a**: t_R = 11.9 min.



1 PDA Multi 1 / 350nm 4nm

PeakTable

PDA Ch1 350nm 4nm

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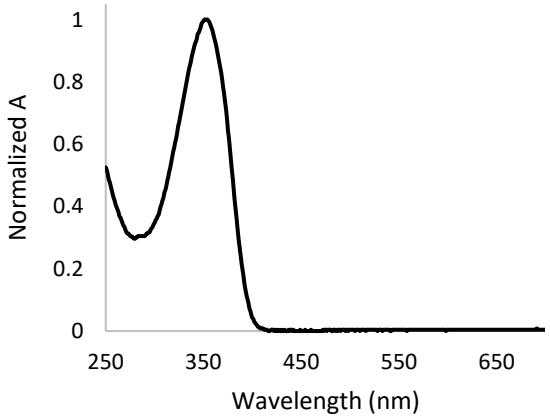
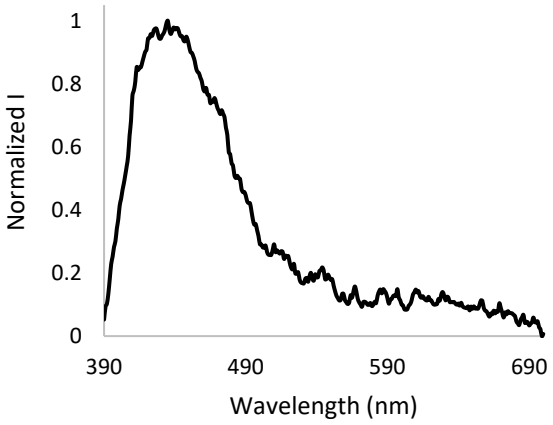
2	11.868	25214739	816198	98.073	98.265
Total		25710237	830606	100.000	100.000

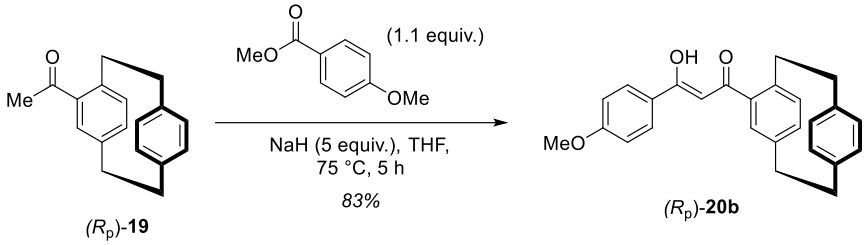
UV-Vis absorption and fluorescence emission :

Absorbance max: 354 nm (10^{-5} M solution in DCM); Emission max: 435 nm (10^{-5} M solution in $CHCl_3$, λ_{ex} = 350 nm).





(R_p)-(Z)-1-(1,4(1,4)-dibenzenacyclohexaphane-12-yl)-3-hydroxy-3-(4-methoxyphenyl)prop-2-en-1-one
20b



Compound (R_p)-**20b** was prepared following the procedure employed to synthesize product (R_p)-**20a**: NaH (60% in mineral oil, 32 mg, 0.8 mmol, 5 equiv.), (*Rp*)-**19** (40 mg, 0.16 mmol, 1.0 equiv.), methyl *p*-anisate (29 mg, 0.18 mmol, 1.1 equiv.) in dry THF (1 mL). Column eluent = Cy:EtOAc 10:1. (R_p)-3.46 (51 mg, 0.13 mmol, 83 %) was obtained as a yellow amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96-7.91 (m, 2H), 7.00-6.96 (m, 2H), 6.91-6.88 (m, 1H), 6.67 (dd, *J* = 1.4, 9 Hz, 1H), 6.62 (dd, *J* = 1.7, 8.5 Hz, 1H), 6.59-6.52 (m, 3H), 6.46 (dd, *J* = 1.3, 8 Hz, 1H), 6.4 (s, 1H), 3.95-3.82 (m, 5H), 3.22-3.09 (m, 4H), 3.09-3.00 (m, 2H), 3.00-2.88 (m, 1H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$) δ 187.8 (C), 184.7 (C), 163.1 (C), 140.1 (C), 139.9 (C), 139.9 (C), 139.3 (C), 136.8 (C), 136.3 (CH), 135.7 (CH), 132.8 (CH), 132.6 (CH), 132.4 (CH), 131.8 (CH), 129.2 (CH), 128.2 (CH), 114.0 (CH), 113.9 (CH), 113.6 (CH), 96.0 (CH), 55.5 (CH_3), 35.6 (CH_2), 35.5 (CH_2), 35.3 (CH_2), 35.2 (CH_2) ppm.

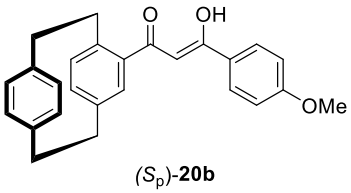
IR ν 2929, 1715, 1603, 1508, 1456, 1438, 1306 1259, 1231, 1173, 1029, 844, 803 cm^{-1}.

HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}O_3$ 385.1798; Found 385.1787

$[\alpha]_{589}$ = – 166 (c 0.6, $CHCl_3$).

Novel compound. Copies of the NMR spectra are provided at the end of the document.

(S_p)-(Z)-1-(1,4(1,4)-dibenzenacyclohexaphane-12-yl)-3-hydroxy-3-(4-methoxyphenyl)prop-2-en-1-one
20b

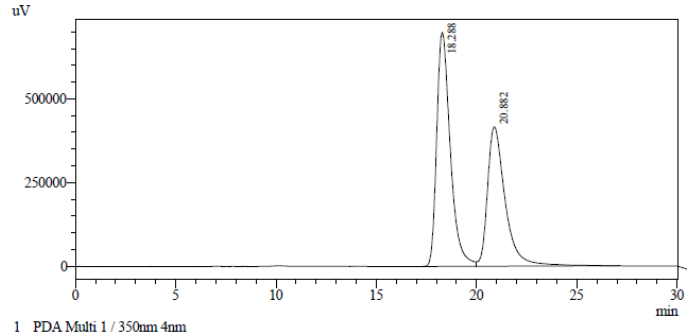


Compound (S_p)-**20b** was prepared following the procedure employed to synthesize product (R_p)-**20a**: NaH (60% in mineral oil, 40 mg, 1 mmol, 5 equiv.), (S_p)-**19** (50 mg, 0.2 mmol, 1.0 equiv.), methyl *p*-anisate (36.5 mg, 0.22 mmol, 1.1 equiv.) in dry THF (1.25 mL). Column eluent = Cy:EtOAc 10:1. (R_p)-3.46 (51 mg, 0.13 mmol, 76 %) was obtained as a yellow amorphous solid. Spectroscopic data correspond to that previously described for compound *(R_p)*-**20b**

$[\alpha]_{589}$ =+159 (c 0.8, $CHCl_3$).

HPLC analysis : t_{R1}= 18.3 min; t_{R2} = 20.9 min. [Column = Chiralcel OD (250 x 4.6 mm); eluent = *n*-heptane/*i*-PrOH (9:1); T = 20 °C; flow = 1 mL/min; λ = 350 nm).]

Co-injection of (R_p)-**20b** and (S_p)-**20b**.



1 PDA Multi 1 / 350nm 4nm

PeakTable

PDA Ch1 350nm 4nm

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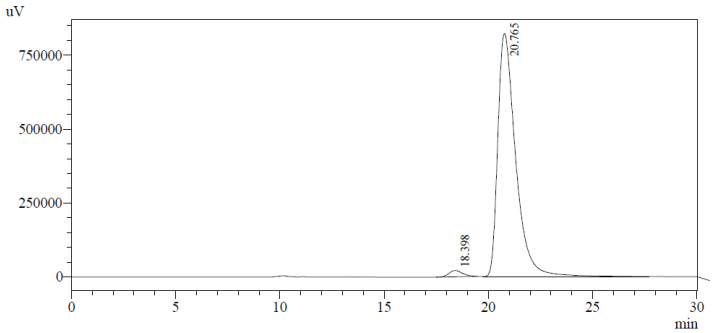
2	20.882	25630714	415847	43.828	37.327
Total		58480189	1114067	100.000	100.000

Injection of pure (R_p)-**3.46**: t_{R1}= 18.4 min; t_{R2} = 20.8 min



1 PDA Multi 1 / 350nm 4nm

PeakTable

PDA Ch1 350nm 4nm

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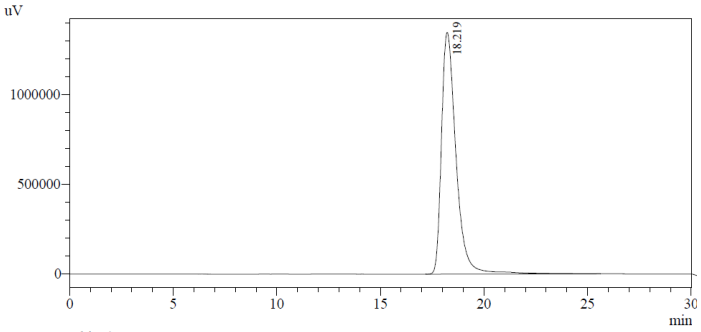
1	18.398	962236	21405	1.926	2.535
2	20.765	48998629	822865	98.074	97.465
Total		49960865	844270	100.000	100.000

Injection of pure (S_p)-**3.46**: t_{R1}= 18.2 min



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PeakTable

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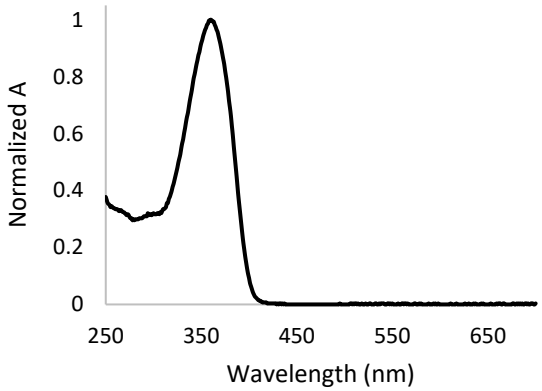
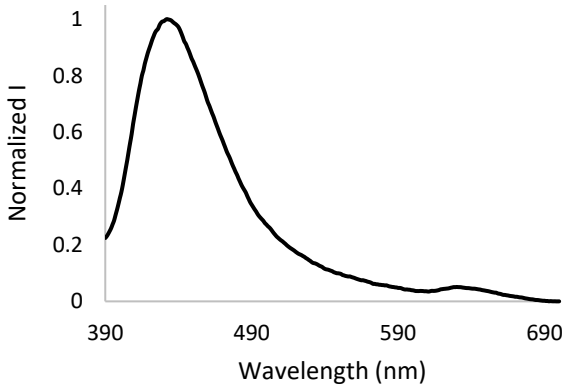
Total		65888016	1347037	100.000	100.000

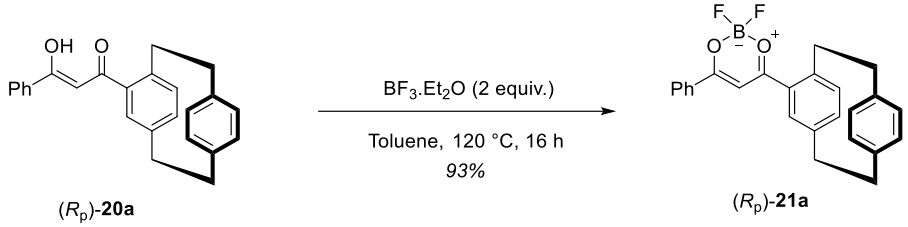
UV-vis absorption and fluorescence emission spectroscopy:

Absorbance max: 360 nm (10^{-5} M solution in $CHCl_3$); Emission max: 435 nm (10^{-6} M solution in $CHCl_3$, λ_{ex} = 360 nm).





(R_p)-4-(1,4(1,4)-dibenzenacyclohexaphane-12-yl)-2,2-difluoro-6-phenyl-2H-1,3l3,2l4-dioxaborinine
21a

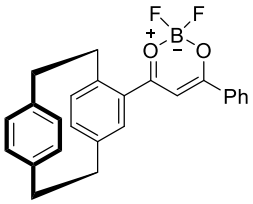


(R_p)-**20a** (R_p)-**21a**

In a flame and vacuum-dried vial, under argon atmosphere, (R_p)-**20a** (44 mg, 0.12 mmol, 1.0 equiv.) was dissolved in dry toluene (1 mL). $BF_3{\cdot}ET_2O$ (30 µL, 0.24 mmol, 2.0 equiv.) was slowly added dropwise at rt, turning the orange solution brown. The vial was and sealed and the reaction mixture was heated at 120 °C for 16 h. The solution was then cooled back to rt and evaporated under reduced pressure. The resulting crude residue was purified by column chromatography (SiO_2) using pentane:EtOAc (8:2) as the eluent to yield (R_p)-**21a** (45 mg, 0.11 mmol, 93 %) as a bright yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 – 8.06 (m, 2H), 7.73 – 7.62 (m, 1H), 7.56 (dd, *J* = 10.7, 5.0 Hz, 2H), 7.10 (d, *J* = 1.8 Hz, 1H), 6.84 (s, 1H), 6.78 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 664 – 6.58 (m, 2H), 6.58 – 6.54 (m, 1H), 6.49 – 6.45 (m, 1H), 4.00 (ddd, *J* = 13.1, 9.0, 2.9 Hz, 1H), 3.30 – 3.12 (m, 4H), 3.12 – 2.97 (m, 3H) ppm.
^{13}C NMR (125 MHz, $CDCl_3$) 185.8 (C), 181.9 (C), 143.4 (C), 140.8 (C), 139.7 (C), 139.2 (C), 138.6 (CH), 137.3 (CH), 134.9 (CH), 134.2 (CH), 133.1 (C), 132.8 (CH), 132.7 (CH), 132.3 (CH), 132.2 (C), 132.1 (CH), 129.2 (2CH), 128.8 (2CH), 96.6 (CH), 36.7 (CH_2), 35.6 (CH_2), 35.2 (CH_2), 35.0 (CH_2) ppm.
^{19}F NMR (470 MHz, $CDCl_3$) δ 139.96 (qd, *J* = 74.8, 29.1 Hz, 2F) ppm.
IR ν 2927, 2855, 1733, 1593, 1533, 1491, 1364, 1235, 1173, 1071, 1041, 908, 780, 719 cm^{-1}.
$[\alpha]_{589}$ = −82 (c 1, $CHCl_3$).
Known compound. Spectroscopic data are in agreement with the literature.[3]

(S_p)-4-(1,4(1,4)-dibenzenacyclohexaphane-12-yl)-2,2-difluoro-6-phenyl-2H-1,3l3,2l4-dioxaborinine
21a



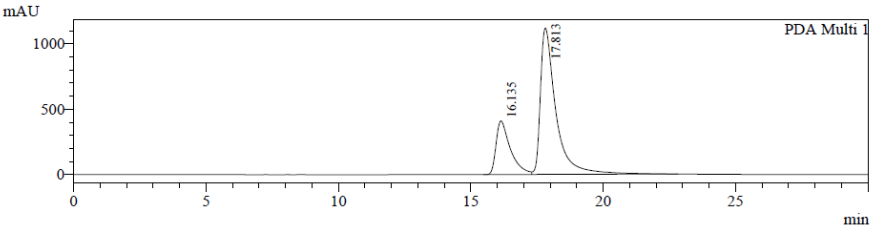
(S_p)-**21a**

Compound (S_p)-**21a** was prepared following the procedure employed to synthesize product (R_p)-**21a :** (S_p)-**20a** (49 mg, 0.14 mmol, 1.0 equiv.), $BF_3{\cdot}Et_2O$ (33 µL, 0.26 mmol, 2.0 equiv.) in dry toluene (1 mL). (S_p)-**21a** was obtained (54 mg, 0.14 mmol, 99 %) as a yellow amorphous solid. Spectroscopic data correspond to that previously described for compound (R_p)-**21a**.

$[\alpha]_{589}$ = +71 (c 1.1, $CHCl_3$).

HPLC analysis : t_{R1}= 16.1 min; t_{R2} = 17.8 min. [Column = Chiralcel OD (250 x 4.6 mm); eluent = *n*-heptane/*i*-PrOH (9:1); T = 20 °C; flow = 1 mL/min; λ = 350 nm).]

Co-injection of (R_p)-**21a** and (S_p)-**21a**.



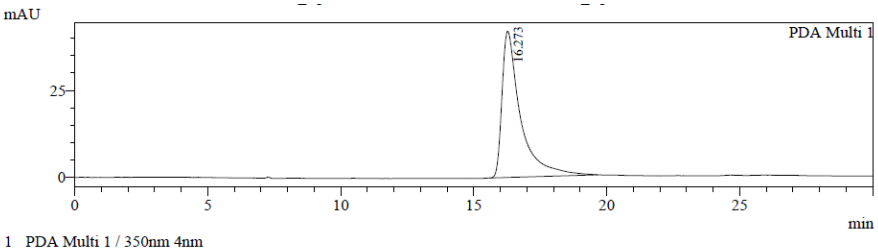
1 PDA Multi 1 / 350nm 4nm

PeakTable

PDA Ch1 350nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.135	15440860	410692	25.236	26.824
2	17.813	45743845	1120344	74.764	73.176
Total		61184705	1531037	100.000	100.000

Injection of (R_p)-**21a:** t_{R1}= 16.3 min



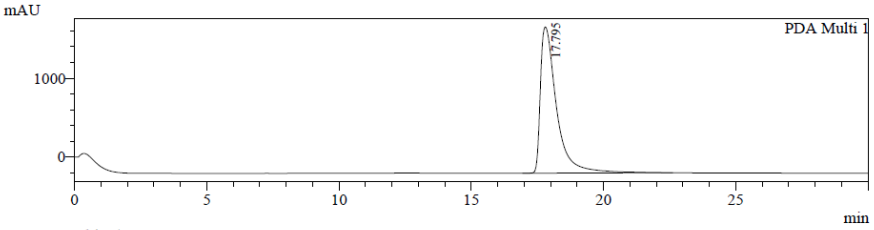
1 PDA Multi 1 / 350nm 4nm

PeakTable

PDA Ch1 350nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.273	2036788	42046	100.000	100.000
Total		2036788	42046	100.000	100.000

Injection of (S_p)-**21a**: t_{R2} = 17.8 min.



1 PDA Multi 1 / 350nm 4nm

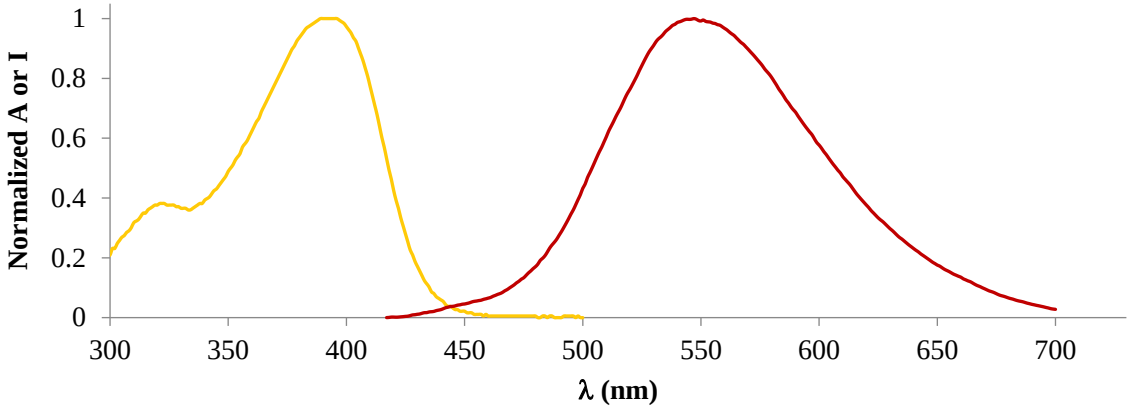
PeakTable

PDA Ch1 350nm 4nm

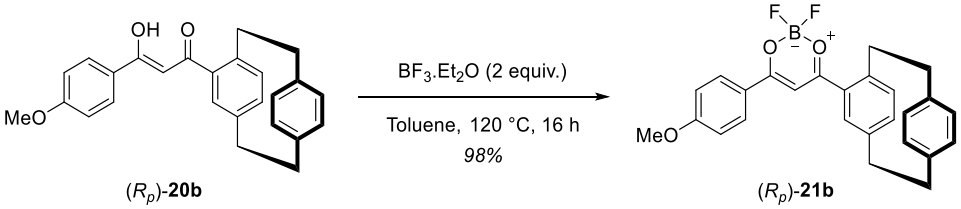
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.795	78878294	1853850	100.000	100.000
Total		78878294	1853850	100.000	100.000

UV-vis absorption and fluorescence emission spectroscopy:

Absorbance max: 390 nm (10^{-5} M solution in $CHCl_3$; yellow line); Emission max: 505 nm (10^{-6} M solution in $CHCl_3$, λ_{ex} = 360 nm, red line).



(R_p)-4-(1,4(1,4)-dibenzenacyclohexaphane-12-yl)-2,2-difluoro-6-(4-methoxyphenyl)-2H-1,3l3,2l4-dioxaborinine **21b**

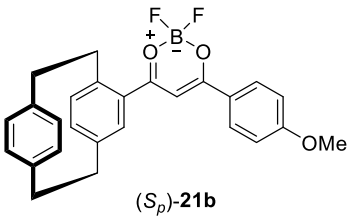


(R_p)-**20b** (R_p)-**21b**

Compound (R_p)-**21b** was prepared following the procedure employed to synthesize product (R_p)-**20a**: (R_p)-**20b** (15 mg, 0.04 mmol, 1.0 equiv.), $BF_3{\cdot}Et_2O$ (10 µL, 0.08 mmol, 2.0 equiv.) in dry toluene (0.5 mL). Cy:DCM (2:1). (R_p)-**20b** was obtained (16.5 mg, 0.04 mmol, 98 %) as a yellow amorphous solid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10-8.02 (m, 2H), 7.00 (d, *J* = 1.8 Hz, 1H), 7.00-6.93 (m, 2H), 6.71-6.65 (m, 2H), 6.60-6.54 (m, 2H), 6.51 (qd, *J* = 1.8, 8 Hz, 2H), 6.48 (dd, *J* = 1.7, 8 Hz, 2H), 3.91 (td, *J* = 3, 11.1 Hz, 1H), 3.86 (s, 3H), 3.19-3.06 (m, 4H), 3.04-2.88 (m, 3H) ppm.
^{13}C NMR (125 MHz, $CDCl_3$) δ 184.2 (C), 181.1 (C), 165.5 (C), 142.8 (C), 140.7 (C), 139.8 (C), 138.1 (CH), 138.1 (CH), 137.1 (CH), 134.0 (CH), 133.4 (C), 132.8 (CH), 132.7 (CH), 132.3 (CH), 132.1 (CH), 131.4 (CH), 114.7 (CH), 95.8 (CH), 55.8 (CH_3), 36.6 (CH_2), 35.6 (CH_2), 35.2 (CH_2), 35.1 (CH_2) ppm.
IR ν 2930, 1738, 1541, 1506, 1364, 1239, 1178, 1040, 911, 813, 734 cm^{-1}.
HRMS (ESI-Orbitrap) m/z: [M+Na] Calcd for $C_{26}H_{23}BF_2O_3Na$ 455.1601; Found 455.1584.
$[\alpha]_{589}$ = -438 (c 0.34, $CHCl_3$).

Novel compound. Copies of the NMR spectra are provided at the end of the document.

(S_p)-4-(1,4(1,4)-dibenzenacyclohexaphane-12-yl)-2,2-difluoro-6-(4-methoxyphenyl)-2H-1,3l3,2l4-dioxaborinine **21b**



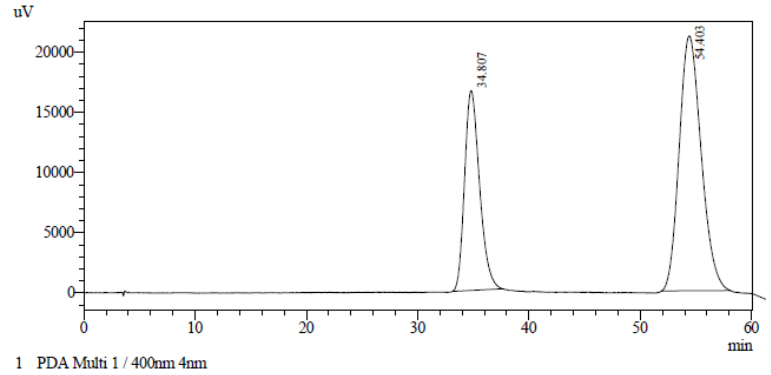
(S_p)-**21b**

Compound (S_p)-**21b** was prepared following the procedure employed to synthesize product (R_p)-**21a**: (S_p)-**20b** (20 mg, 0.05 mmol, 1.0 equiv.), $BF_3{\cdot}Et_2O$ (13 µL, 0.10 mmol, 2.0 equiv.) in dry toluene (0.5 mL). Cy:DCM (2:1). (S_p)-**21b** was obtained (20.2 mg, 0.05 mmol, 90 %) as a yellow amorphous solid. Spectroscopic data correspond to that previously described for compound (R_p)-**21b**.

$[\alpha]_{589}$ = +444 (c 0.43, $CHCl_3$).

HPLC analysis : t_{R1}= 34.8 min; t_{R2} = 54.4 min. [Column = Chiralcel OD (250 x 4.6 mm); eluent = *n*-heptane/*i*-PrOH (8:2); T = 20 °C; flow = 1 mL/min; λ = 400 nm).]

Co-injection of (R_p)-**21b** and (S_p)-**21b**.



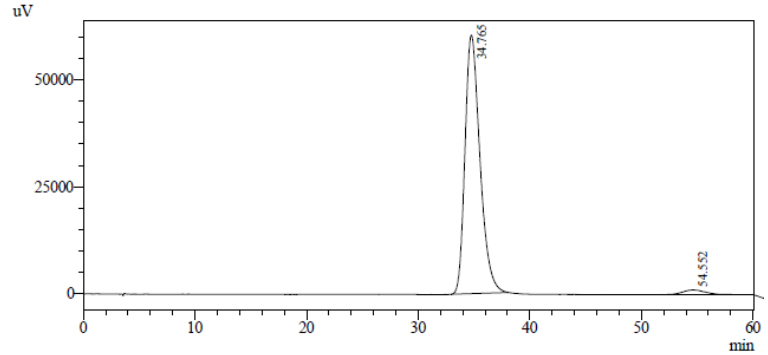
1 PDA Multi 1 / 400nm 4nm

PeakTable

PDA Ch1 400nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.807	1554374	16597	34.806	43.935
2	54.403	2911448	21179	65.194	56.065
Total		4465822	37776	100.000	100.000

Injection of (R_p)-**21b:** t_{R1}= 34.8 min; t_{R2} = 54.6 min



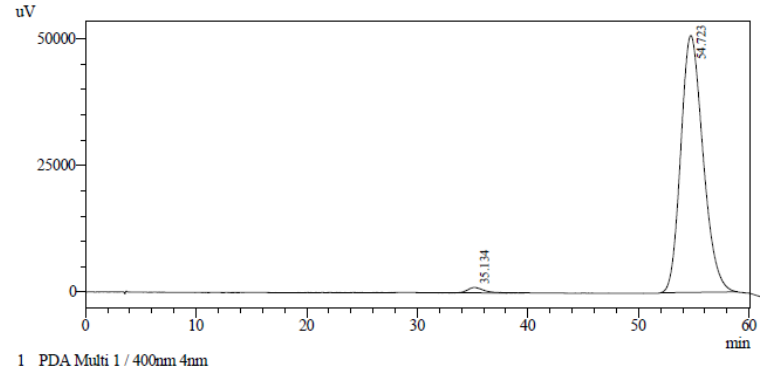
1 PDA Multi 1 / 400nm 4nm

PeakTable

PDA Ch1 400nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.765	5630465	60387	97.338	98.202
2	54.552	153977	1105	2.662	1.798
Total		5784442	61493	100.000	100.000

Injection of (S_p)-**3.47**: t_{R1}= 35.1 min; t_{R2} = 54.7 min



1 PDA Multi 1 / 400nm 4nm

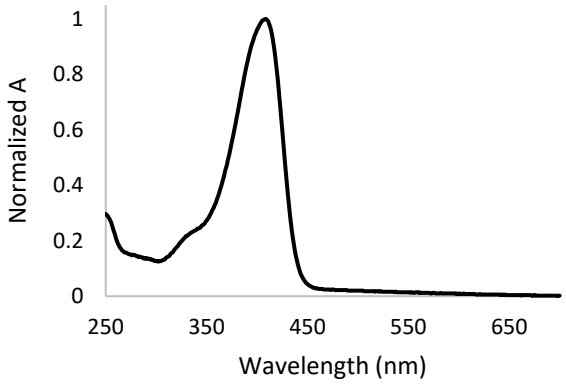
PeakTable

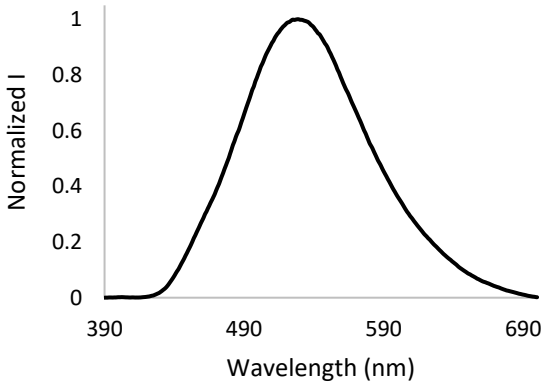
PDA Ch1 400nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.134	105727	1053	1.468	2.035
2	54.723	7098795	50706	98.532	97.965
Total		7204522	51759	100.000	100.000

UV-vis absorption and fluorescence emission spectroscopy:

Absorbance max: 408 nm (10^{-5} M solution in $CHCl_3$); Emission max: 535 nm (10^{-6} M solution in $CHCl_3$, λ_{ex} = 360 nm). QY = 2,6 %[5]



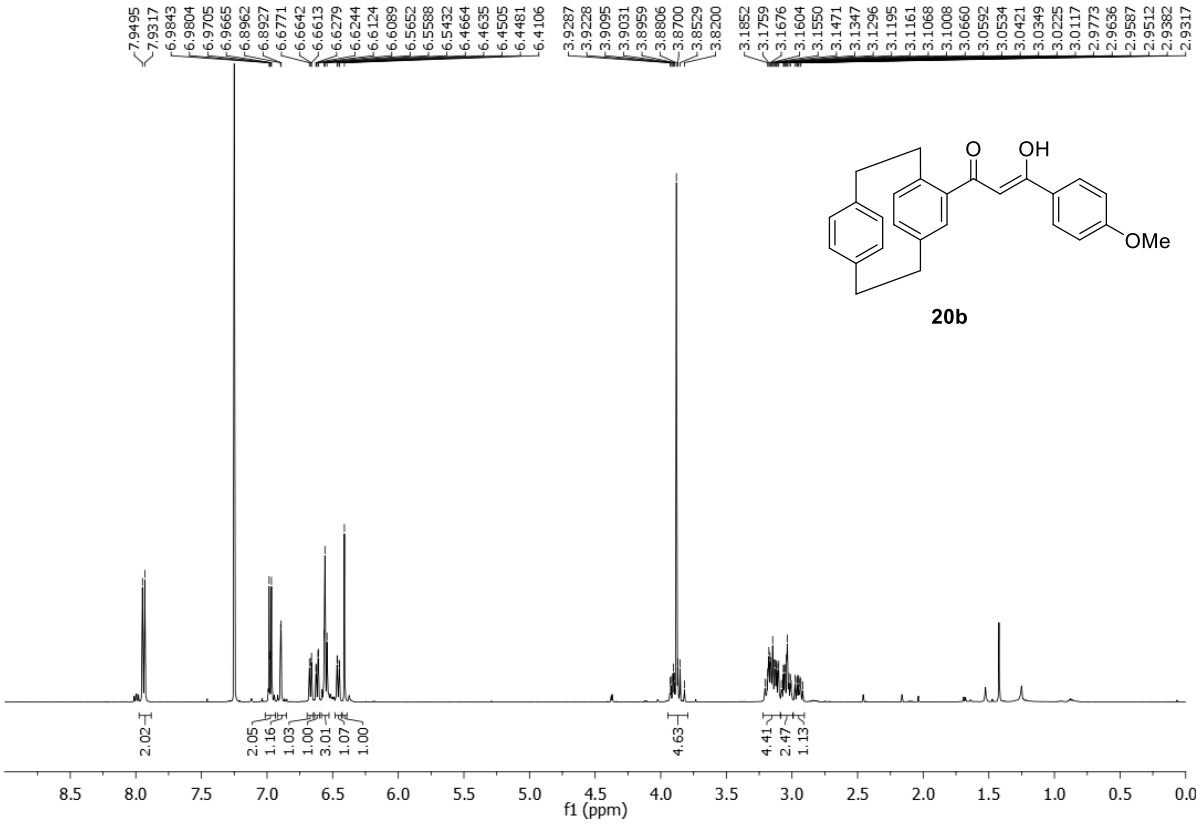


[5] Relative quantum yield (QY) was calculated using anthracene in cyclohexane as fluorescence standard (QY = 36%). The excitation wavelength was fixed at 340 nm for both the sample and the standard.

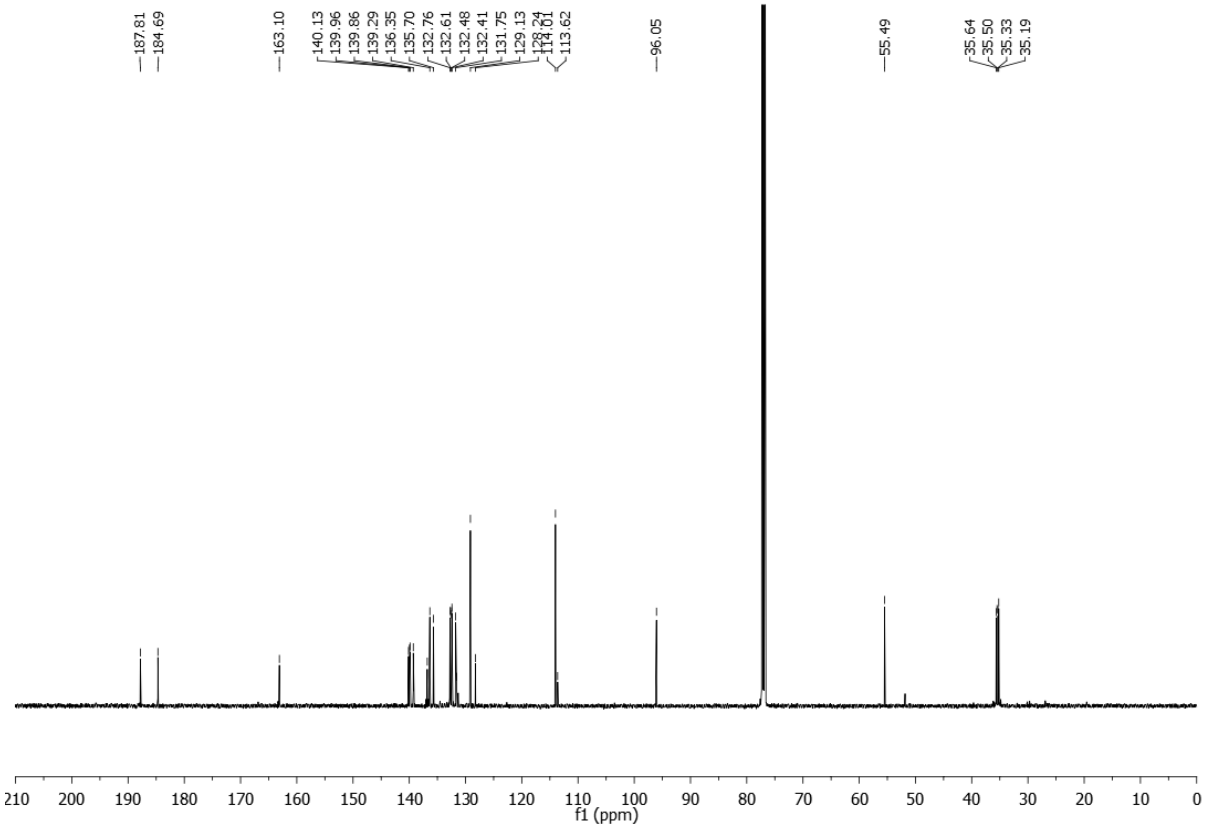
Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra

(Z)-1-(1,4(1,4)-dibenzenacyclohexaphane-12-yl)-3-hydroxy-3-(4-methoxyphenyl)prop-2-en-1-one **20b**

^{1}H NMR (500 MHz, $CDCl_3$)

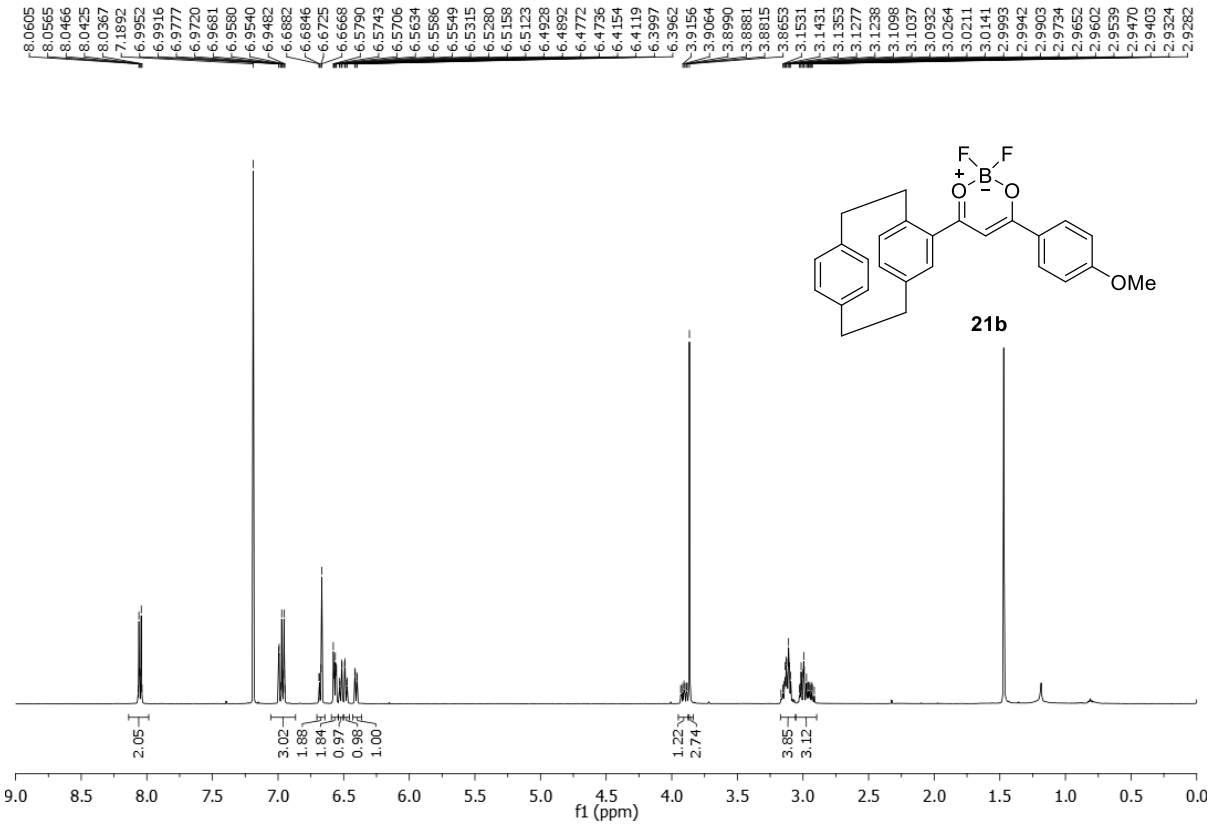


^{13}C NMR (126 MHz, $CDCl_3$)

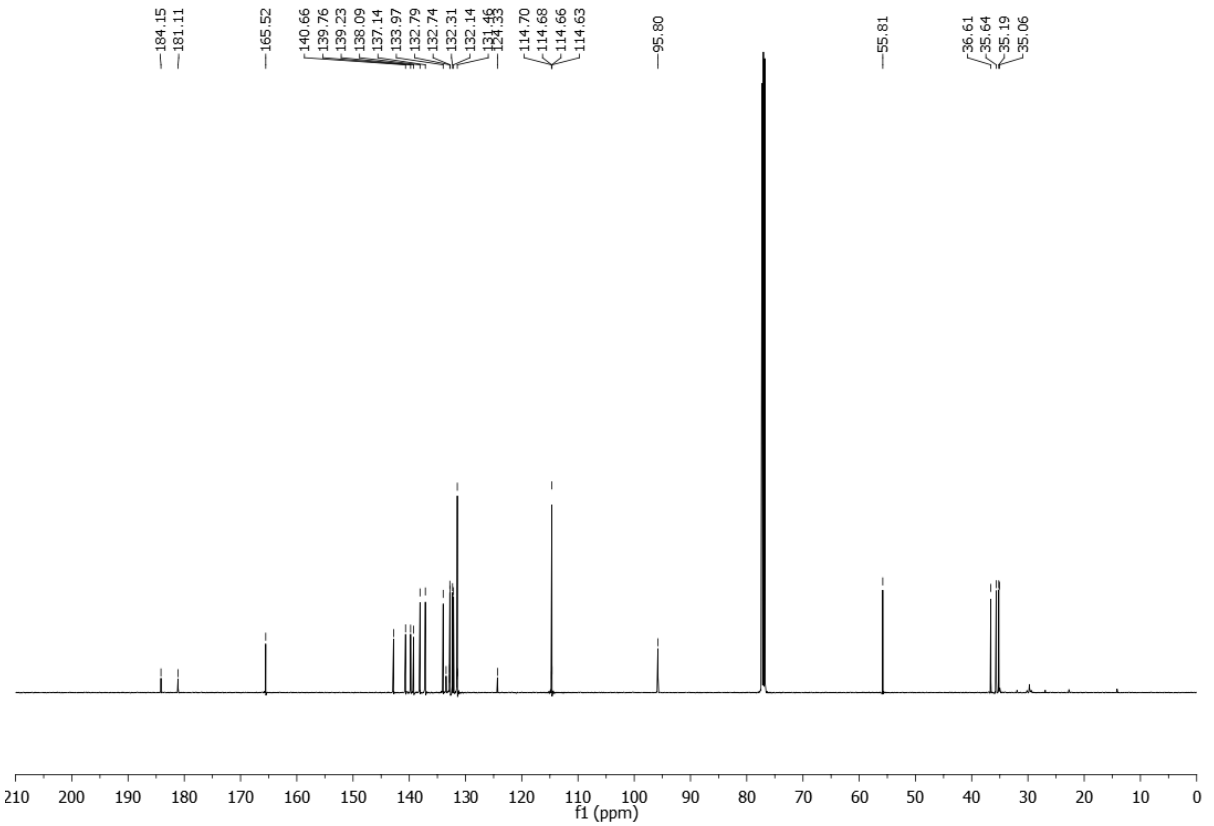


4-(1,4(1,4)-dibenzenacyclohexaphane-12-yl)-2,2-difluoro-6-(4-methoxyphenyl)-2H-1,3l3,2l4-dioxaborinine **21b**

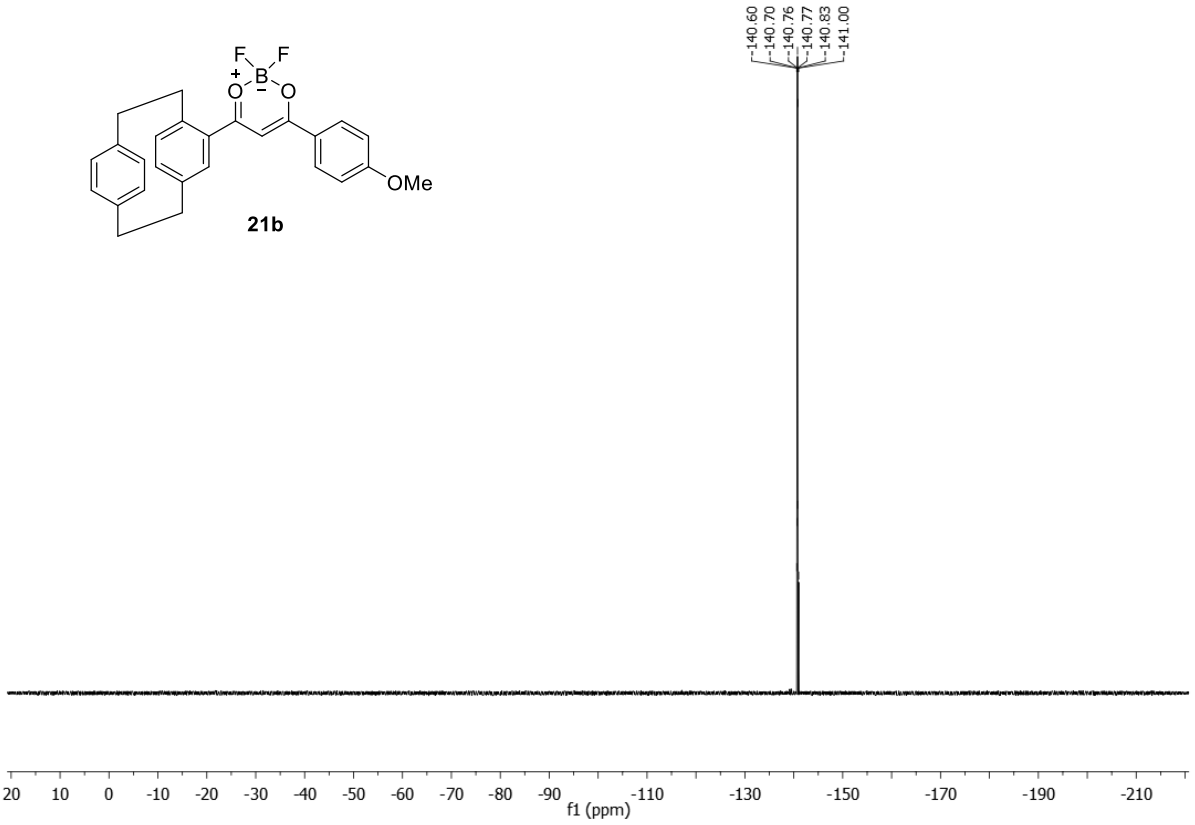
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)



Circular dichroism and circularly polarized luminescence – Dissymmetry factors

Absorption dissymmetry factors were obtained using the following formula:

$$g_{abs} = |2 [\varepsilon_L (\lambda) - \varepsilon_R (\lambda)] / [\varepsilon_L (\lambda) + \varepsilon_R (\lambda)]|$$

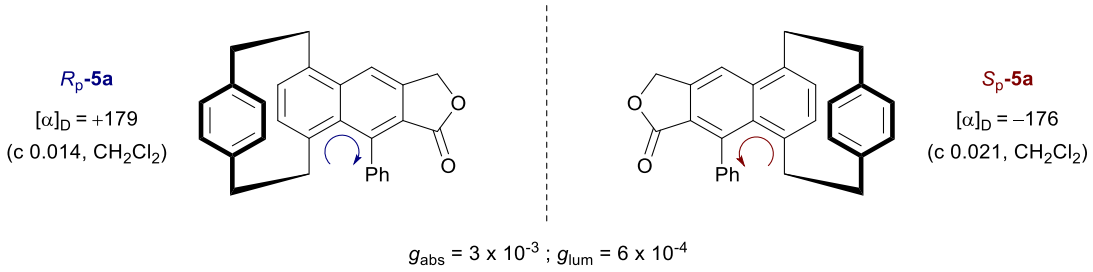
where ε_L and ε_R denote the molar extinction coefficients for left and right circularly polarized light, respectively.

Luminescence dissymmetry factors were obtained using the following formula:

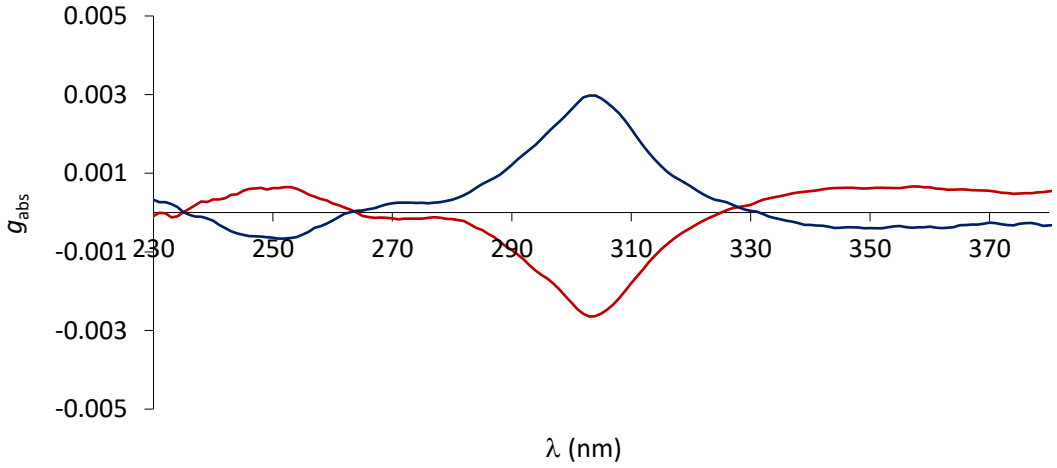
$$g_{lum} = |2 [I_L (\lambda) - I_R (\lambda)] / [I_L (\lambda) + I_R (\lambda)]|$$

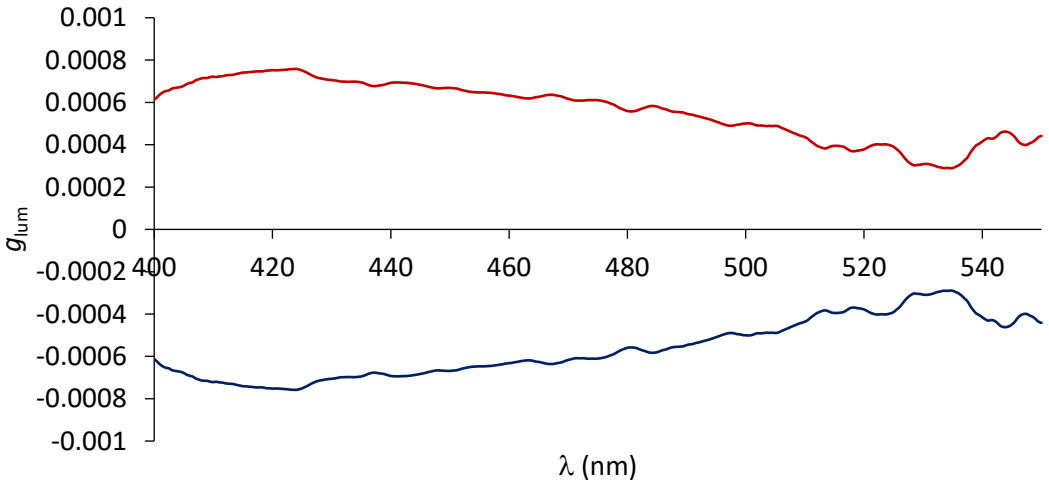
were I_L and I_R are the photoluminescence intensities of left and right circularly polarized luminescence.

*pCp-based naphthalenes S_p-**5a** and R_p-**5a***



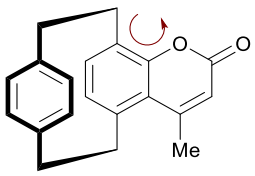
g_{abs} = 3 x 10^{-3} ; g_{lum} = 6 x 10^{-4}

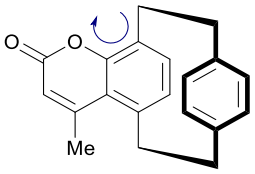




*pCp-based coumarins R_p-**10b** and S_p-**10b***

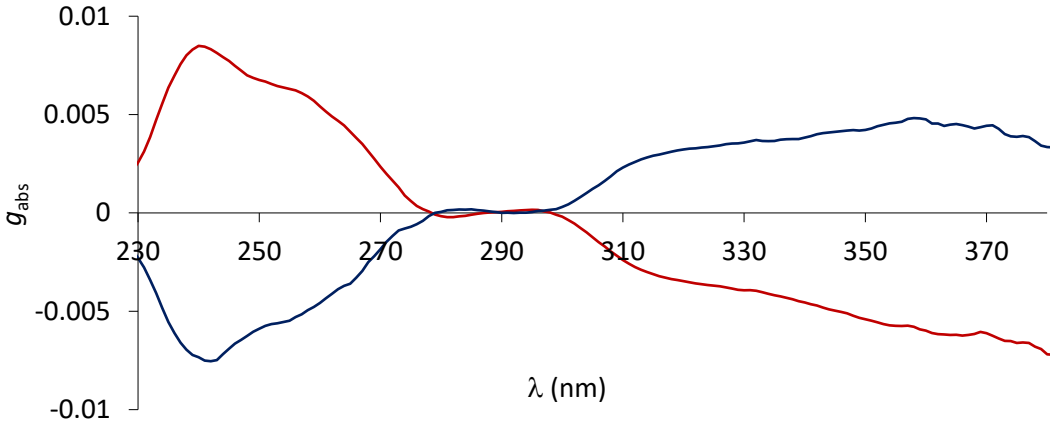
S_p-**10b**
$[\alpha]_D$ = –513
(c 1, $CHCl_3$)

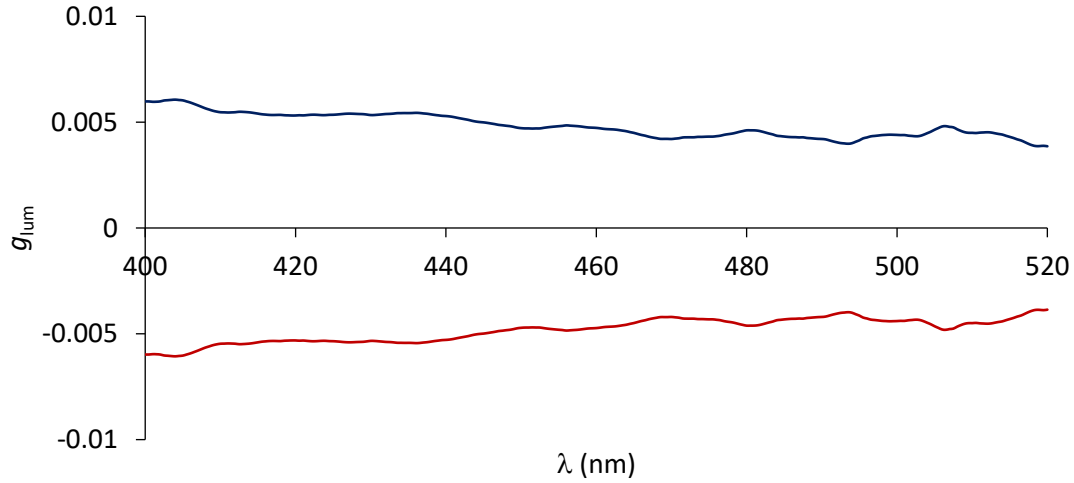




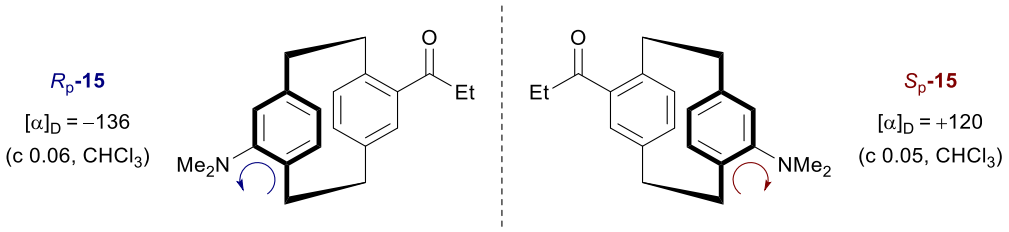
R_p-**10b**
$[\alpha]_D$ = +520
(c 0.05, $CHCl_3$)

g_{abs} = 8 x 10^{-3} ; g_{lum} = 5 x 10^{-3}

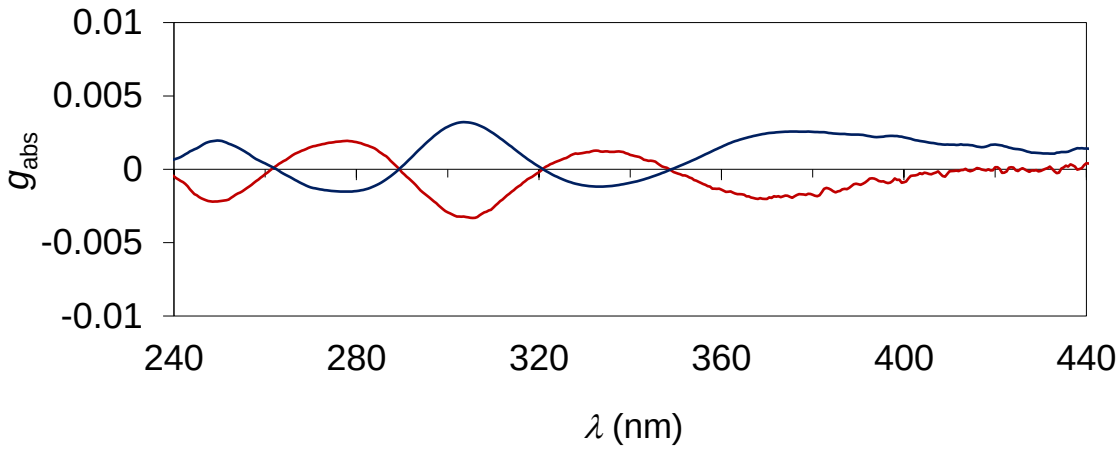


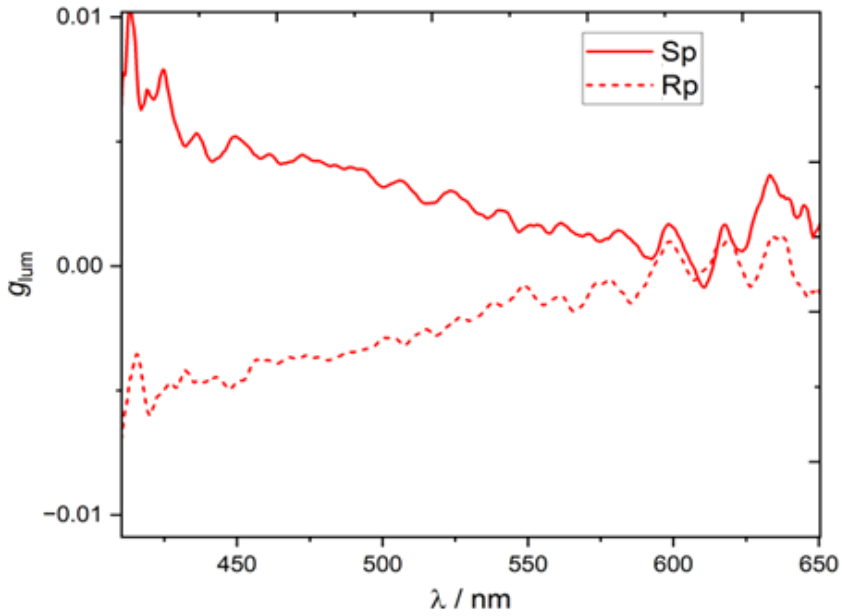


*pCp-based PRODAN derivatives R_p-**15** and S_p-**15***

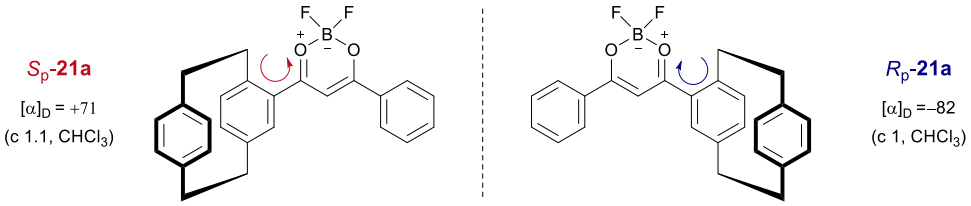


g_{abs} = 2 x 10^{-3} ; g_{lum} = 4 x 10^{-3}

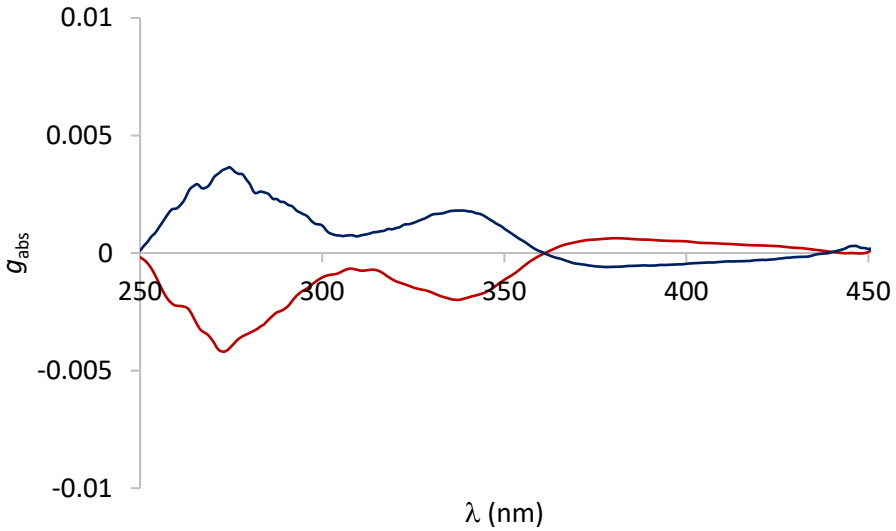


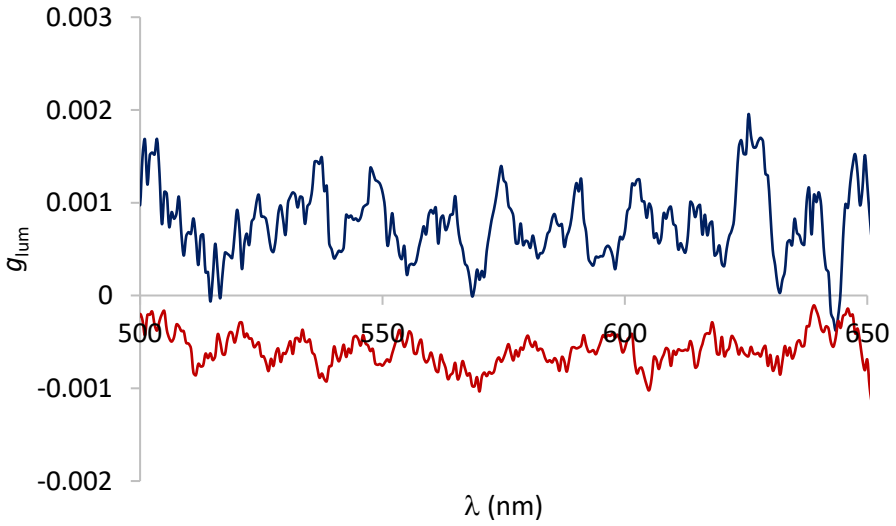


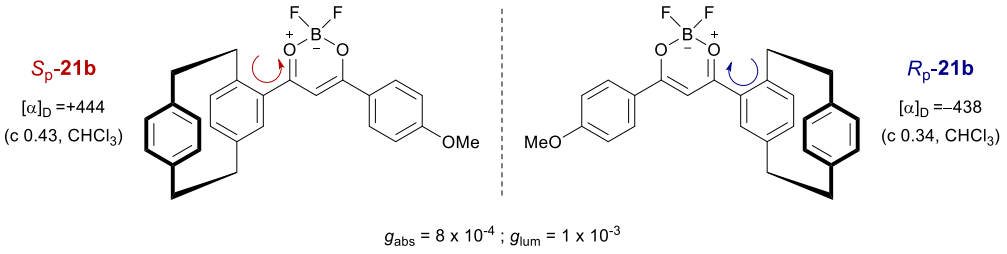
*pCp-based boron-acac R_p-**21a** and S_p-**21a***



g_{abs} = 2 x 10^{-3} ; g_{lum} = 2 x 10^{-3}







g_{abs} = 8 x 10^{-4} ; g_{lum} = 1 x 10^{-3}