Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary information (ESI) for

Deciphering the degree of proton-transfer in pyrido-cyclophanes by chiroptical outcomes in non-aqueous solvents

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Table of Contents

1. General Methods

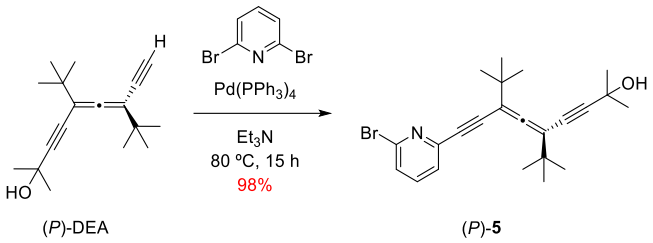
All reactions were carried out under nitrogen atmosphere unless otherwise stated. Reactions that required anhydrous conditions were carried out in oven-dried glassware at 120 °C for at least 24 hours. The reaction flasks were further dried by heating and subsequent cooling under a stream of nitrogen. The transfer of solvents or anhydrous solutions was carried out using syringes or cannulas, dried as described and stored in a desiccator with potassium hydroxide. Solvents were dried according to published methods and distilled before use.[1] Triethylamine was freshly distilled from CaH_2 under argon atmosphere. All other reagents were commercial compounds of the highest purity available. Silica gel 60F-254 Merck was used for thin layer chromatography and were visualized by exposure to UV light (254 nm) and revealed by treatment with a solution of phosphomolybdic acid or potassium permanganate. Merck silica gel 60 (230-240 mesh) was used under pressure for flash column chromatography.

^{1}H-NMR spectra were recorded at 25 ^{o}C (unless otherwise stated) on Bruker AMX-400 at 400 MHz with residual protic solvent as internal reference [$CDCl_3$, δ_H = 7.26 ppm]. Chemical shifts (δ) are given in parts per million (ppm) and coupling constants (J) are given in Hertz (Hz). The proton spectra are reported as follows: chemical shift δ (multiplicity, coupling constant *J*, number of protons). The following symbols were used for the description of coupling patterns: multiplet (m), singlet (s), doublet (d), triplet (t). ^{13}C-NMR spectra were recorded on the same spectrometer at 100 MHz at 25 ^{o}C (unless otherwise stated) with residual protic solvent as internal reference [$CDCl_3$, δ = 77.16 ppm]. ECD and UV-Vis spectra were recorded on a Jasco J-815 spectropolarimeter using a one-centimetre thick quartz cuvette at 25 °C. The background was always obtained against the solvent. ESI mass spectra were recorded with an APEX3 instrument. Ions were generated using a Combi MALDI-- electrospray ionization (ESI) source. High-resolution mass spectra were taken on a VG Autospec instrument.

Crystallographic data were collected at 100 K using a Bruker D8 Venture diffractometer with a Photon II CMOS detector and Mo-Kα radiation (λ = 0.71073 Å) generated by an Incoatec high brillance microfocus source equipped with Incoatec Helios multilayer optics. The software APEX4[2] was used for collecting frames of data, indexing reflections, and determination of lattice parameters, SAINT[3] for integration of intensity of reflections, and SADABS[4] for scaling and empirical absorption correction. The structure was solved by dualspace algorithm using the program SHELXT.[5] All non-hydrogen atoms were refined with anisotropic displacement parameters by full-matrix least-squares calculations on F^2 using the program SHELXL[6] with OLEX2[7]. Hydrogen atoms were inserted at calculated positions and constrained with isotropic displacement; except for the hydrogen atoms of water molecule and the pyridinium proton, which were located from a Fourier-difference map and refined restraining the O-H and N-H distances. Drawings were produced with PLATON.[8]

2. Synthetic procedures

Synthesis of (*P*)-9-(6-bromopyridin-2-yl)-5,7-di-tert-butyl-2-methylnona-5,6-dien-3,8-diyn-2-ol ((*P*)-**5**)



2,6-dibromopyridine (200 mg, 0.85 mmol, 5 eq) and $Pd(PPh_3)_4$ (20 mg, 0.017 mmol, 0.1 eq) were placed into a Schlenk tube flamed and purged with N_2. Then, (*P*)-DEA (45 mg, 0.17 mmol, 1 eq) dissolved in 10 mL of freshly distilled Et_3N was added. The reaction mixture was stirred at 80 °C for 15 h. The solvent was removed under reduce pressure and the remaining solid dissolved in AcOEt (10 mL). It was washed with distilled water (20 mL x 3) and sat. aq. NaCl solution (20 mL x 1). The organic phase was dried with $Na_2SO_{4\ (anh)}$ and the solvent removed under reduced pressure. Purification was carried out by flash chromatography (SiO_2, Hex:AcOEt 85:15) to recover unreacted 2,6-dibromopyrdine and to give (*P*)-**5** as a yellowish oil in 98% yield (71 mg).

(*P*)-**5:** **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.47 (m, 1H, Ar-H), 7.38 (m, 2H, Ar-H), 1.55 (s, 6H; CH_3), 1.18 (s, 9H; tBu), 1.12 (s, 9H; tBu). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 212.2, 144.3, 141.8, 138.3, 127.3, 126.2, 103.6, 102.5, 98.1, 90.6, 85.4, 75.5, 65.8, 35.8, 35.6, 31.6, 29.2, 29.0. **UV/Vis** ($CHCl_3$): λmax (ε)= 250.0 nm (21056 mol^{-1} dm^3 cm^{-1}), 276.0 nm (15988 mol^{-1} dm^3 cm^{-1}), 308.0 nm (25674 mol^{-1} dm^3 cm^{-1}). **HRMS-ESI**: *m/z* calcd. for $C_{23}H_{28}BrNO$ 414.1354; found $C_{23}H_{27}BrN$ 396.1370 (M^+-H_2O, reorganization of McLafferty).

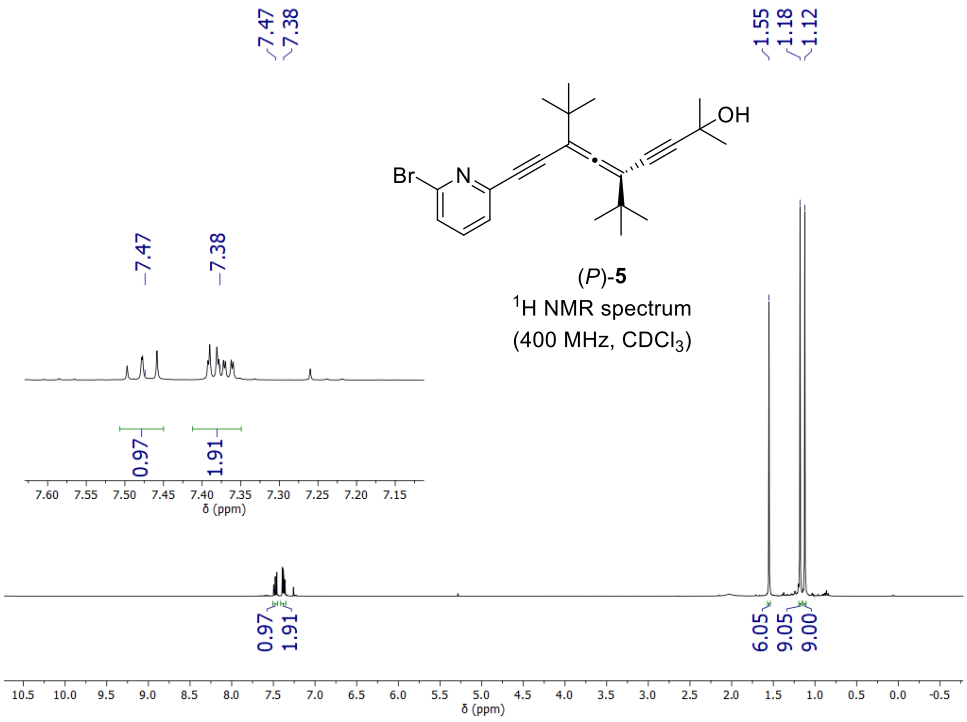


*Figure S1. (P)-**5** ^{1}H-NMR ($CDCl_3$) spectrum.*

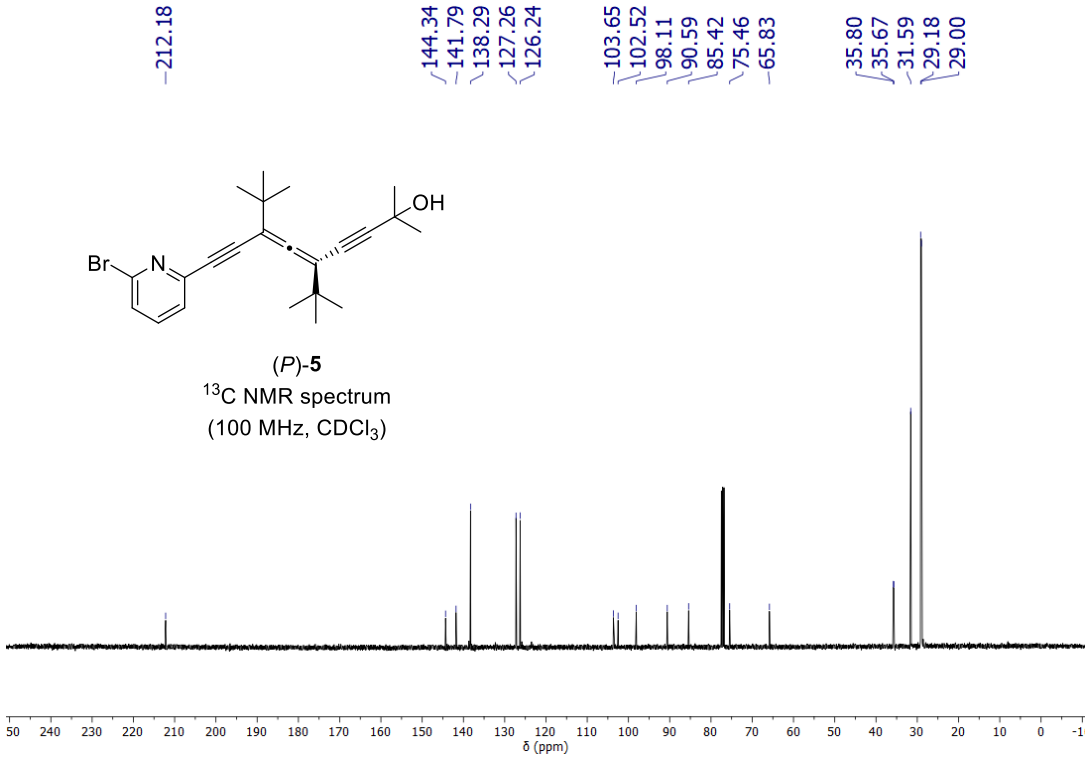


*Figure S2. (P)-**5** ^{13}C-NMR ($CDCl_3$) spectrum.*

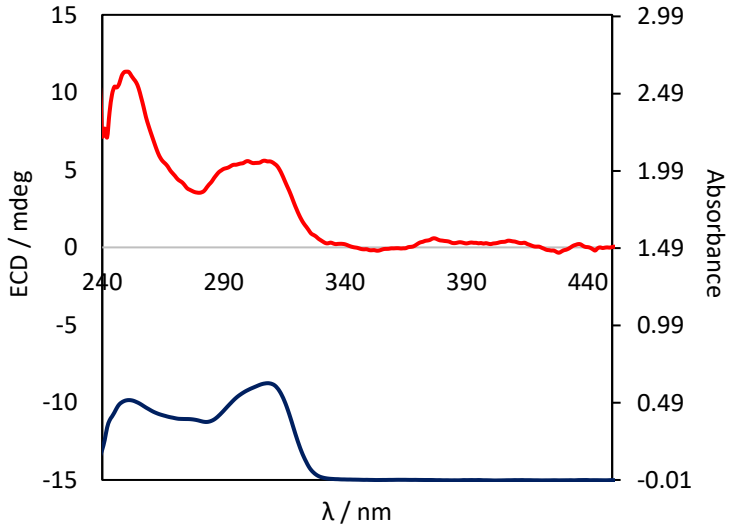
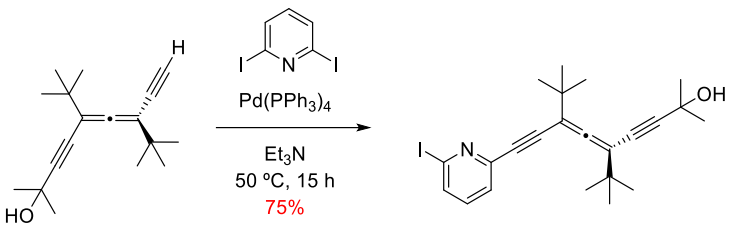


*Figure S3. Red line (P)-**5** CD spectrum [Chloroform, $2.4 \cdot 10^{-5}$ M]. Blue line (P)-**5** UV/Vis spectrum [Chloroform, $2.4 \cdot 10^{-5}$ M].*

Synthesis of (*P*)-9-(6-iodopyridin-2-yl)-5,7-di-tert-butyl-2-methylnona-5,6-dien-3,8-diyn-2-ol ((*P*)-**7**)



(*P*)-DEA (*P*)-**7**

2,6-diiodomopyridine (160 mg, 0.48 mmol, 2.8 eq) and $Pd(PPh_3)_4$ (20 mg, 0.017 mmol, 0.1 eq) were placed into a Schlenk tube flamed and purged with N_2. Then, (*P*)-DEA (45 mg, 0.17 mmol, 1 eq) dissolved in 10 mL of freshly distilled Et_3N was added. The reaction mixture was stirred at 50 °C for 15 h.* The solvent was removed under reduce pressure and the remaining solid dissolved in AcOEt (10mL). It was washed with distilled water (20 mL x 3) and sat. aq. NaCl solution (20 mL x 1). The organic phase was dried with $Na_2SO_{4\ (anh)}$ and the solvent removed under reduced pressure. Purification was carried out by flash chromatography (SiO_2, Hex:AcOEt 85:15) to recover unreacted 2,6-diiodopyrdine and to give (*P*)-**7** as a yellowish oil in 75% yield (59 mg).

*The same reaction can be carried out at 40 °C but it takes more time (48 h) for the starting material ((*P*)-DEA) to be completely consumed.

^{1}H-NMR (400 MHz, CDCl3): δ= 7.63 (d, *J* = 7.8 Hz, 1H; Ar-H), 7.39 (d, *J* = 7.8 Hz, 1H; Ar-H), 7.25 (t, *J* = 7.8 Hz, 1H; Ar-H), 1.56 (s, 6H; CH_3), 1.18 (s, 9H; tBu), 1.12 (s, 9H; tBu). **^{13}C-NMR** (100 MHz, CDCl3) δ= 212.1 (C), 144.70 (C), 137.3 (CH), 134.0 (CH), 126.7 (CH), 117.4 (C), 117.4 (C), 103.6 (C), 102.5 (C), 98.0 (C), 90.7 (C), 85.4 (C), 75.5 (C), 65.8 (C), 35.8(C), 35.7 (C), 31.6 (CH_3), 29.2 (tBu), 29.0 (tBu). **UV/Vis** ($CHCl_3$): λmax (ε)= 250.0 nm (23600 mol^{-1} dm^3 cm^{-1}), 310.0 nm (23066 mol^{-1} dm^3 cm^{-1}). **ESI-HR-MS**: m/z calc. for $C_{23}H_{29}INO^+$ 462.1289; found 462.1288.

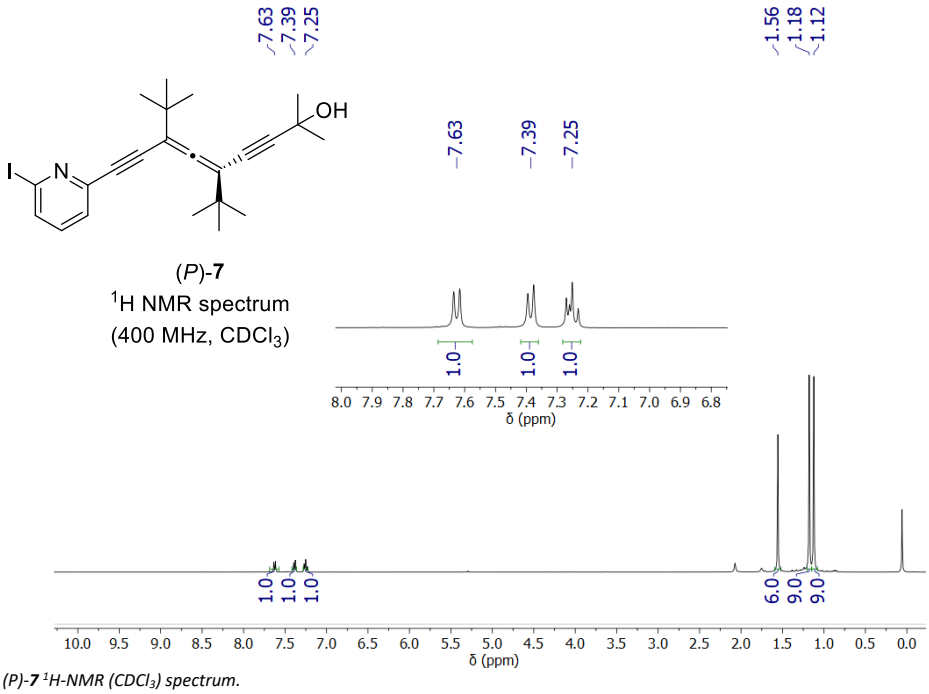


*Figure S4. (P)-**7** ^{1}H-NMR ($CDCl_3$) spectrum.*

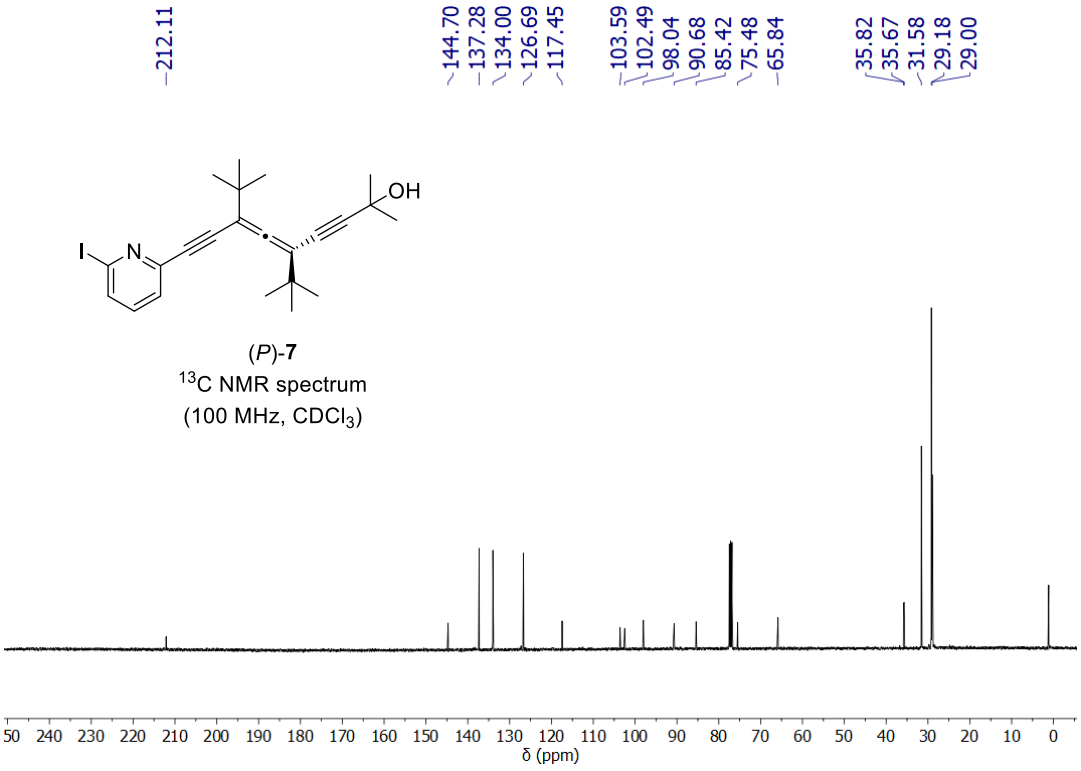


*Figure S5. (P)-**7** ^{13}C-NMR ($CDCl_3$) spectrum.*

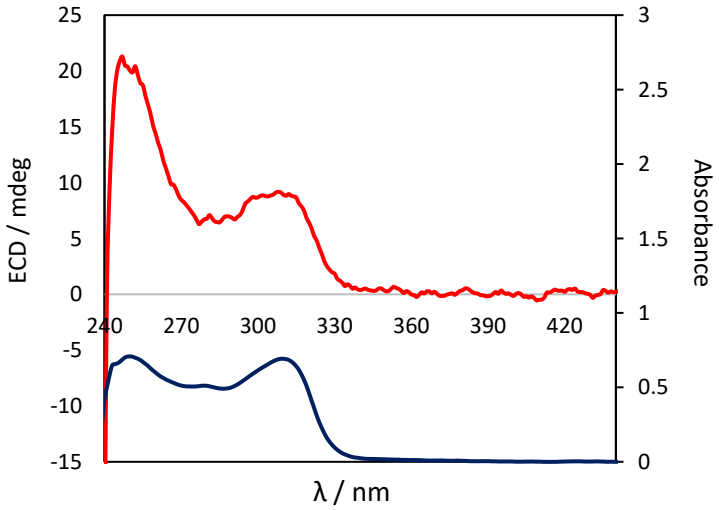
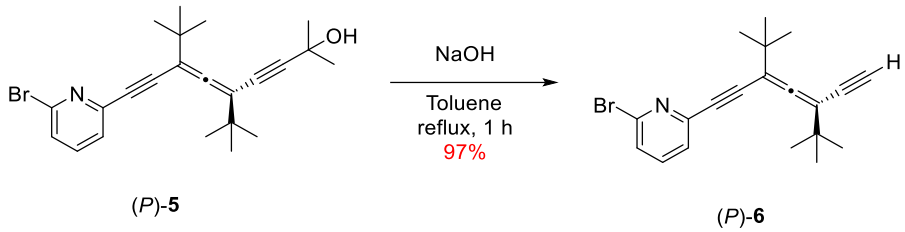


*Figure S6. Red line (P)-**7** CD spectrum [Chloroform, 3.0 ·10^{-5} M]. Blue line (P)-**7** UV/Vis spectrum [Chloroform, 3.0·10^{-5} M].*

Synthesis of (*P*)-2-bromo-6-(3,5-di-tert-butylhepta-3,4-dien-1,6-diyn-1-yl)pyridine ((*P*)-**6**)



(*P*)-**5** (*P*)-**6**

Pulverized NaOH (2 g, 50 mmol, 300 eq) was placed into a 100 mL round-bottom flask and flamed while purging with N_2. (*P*)-**5** (72 mg, 0.17 mmol, 1 eq) was also purged with N_2, dissolved in dry toluene (20 mL) and transferred *via* cannula to the previous flask. The reaction mixture was stirred and refluxed for 1 h. Then, the solvent was removed under reduce pressure and distilled water was added (20 mL). The aqueous phase was extracted with AcOEt (20 mL x 3). The organic phase was dried with $Na_2SO_{4\,(anh)}$ and the solvent removed under reduced pressure. (*P*)-**6** was obtained as a white solid in 98% yield (59 mg) and no further purification was needed.

Note: The reproducibility of the reaction and its yield depend on the purity of the starting reagent ((*P*)-**5**), which must be completely free from any traces of Pd.

^{1}H-NMR (400 MHz, $CDCl_3$) δ= 7.48 (m, 1H; Ar-H), 7.38 (m, 1H; Ar-H), 3.02 (s, 1H; $C_{sp}H$), 1.18 (s, 9H; tBu), 1.14 (s, 9H; tBu). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ= 212.8 (C), 144.2 (C), 141.7 (C), 138.3 (CH), 127.3(CH), 126.3 (CH), 103.2 (C), 102.9 (C), 90.8 (C), 84.9 (C), 81.3 (CH), 77.1 (C), 35.8 (C), 35.4 (C), 29.1 (tBu), 28.9 (tBu). **UV/Vis** ($CHCl_3$): λmax (ε)= 250.0 nm (29097 mol^{-1} dm^3 cm^{-1}), 305.0 nm (25750 mol^{-1} dm^3 cm^{-1}). **ESI-HR-MS**: m/z calc. for $C_{20}H_{23}BrN^+$ 356.1012; found 356.1008.

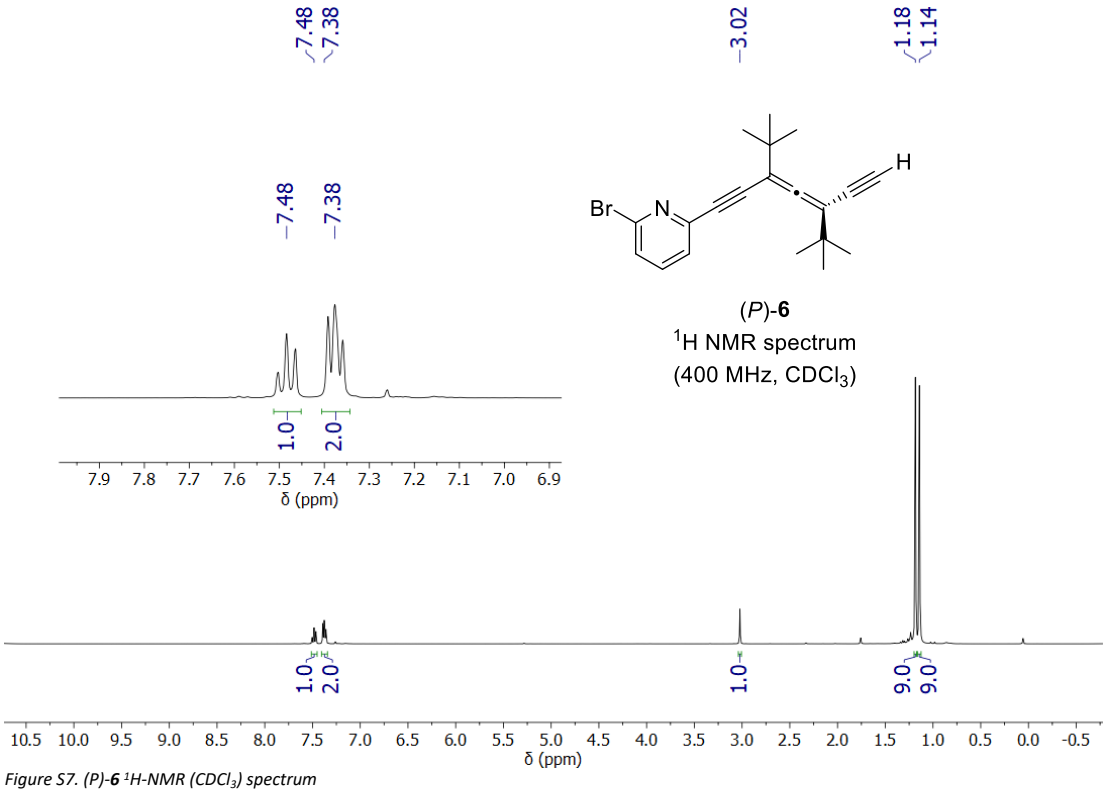


*Figure S7. (P)-**6** ^{1}H-NMR ($CDCl_3$) spectrum*

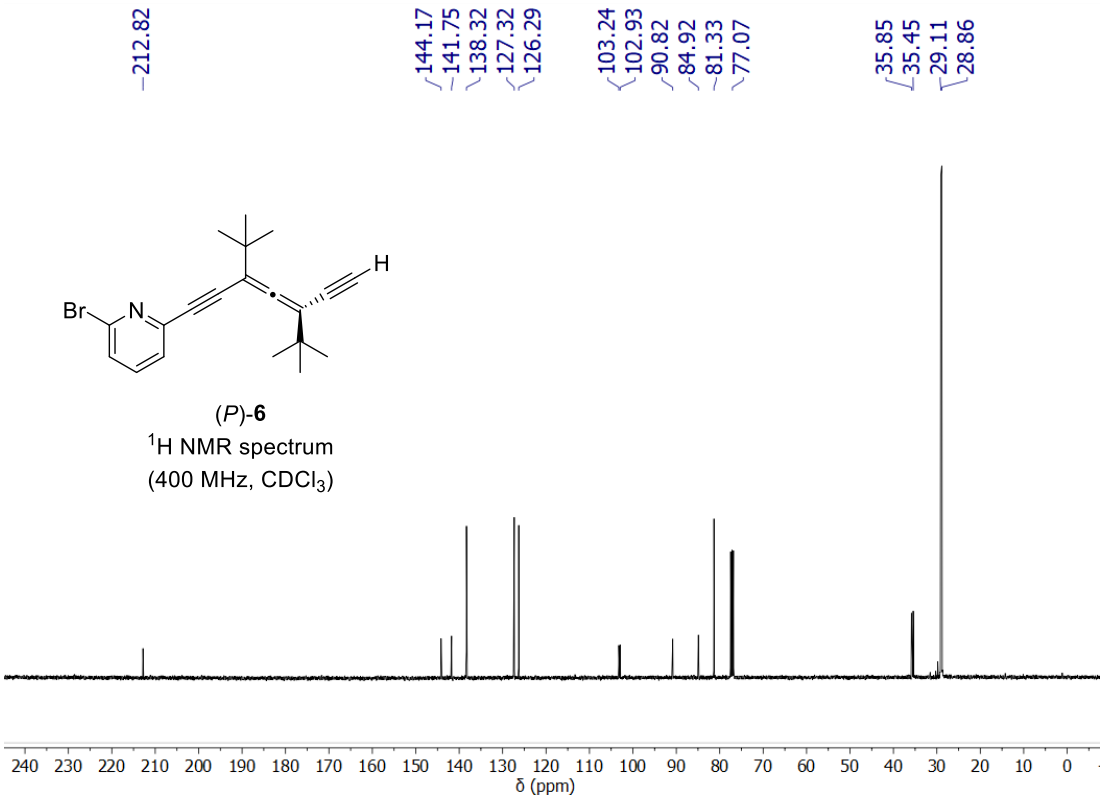


*Figure S8. (P)-**6** ^{13}C-NMR ($CDCl_3$) spectrum.*

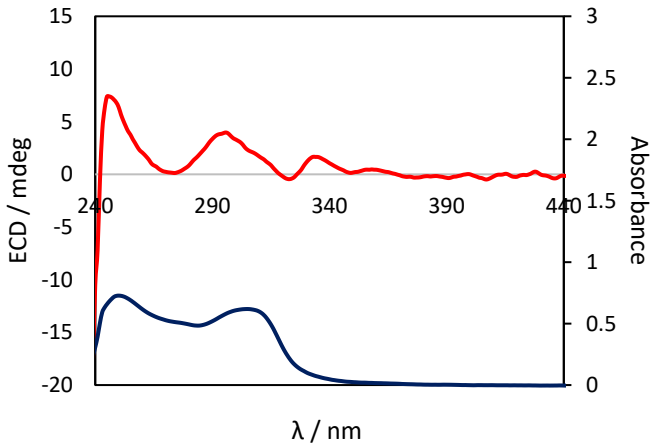
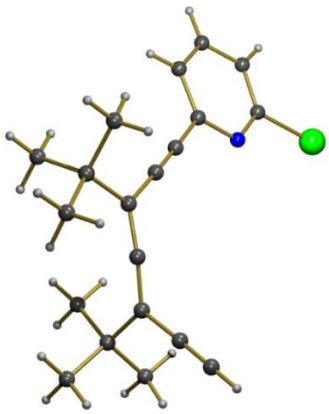


*Figure S9. Red line (P)-**6** CD spectrum [Chloroform, 2.4·10^{-5} M]. Blue line (P)-**6** UV/Vis spectrum [Chloroform, 2.4·10^{-5} M].*

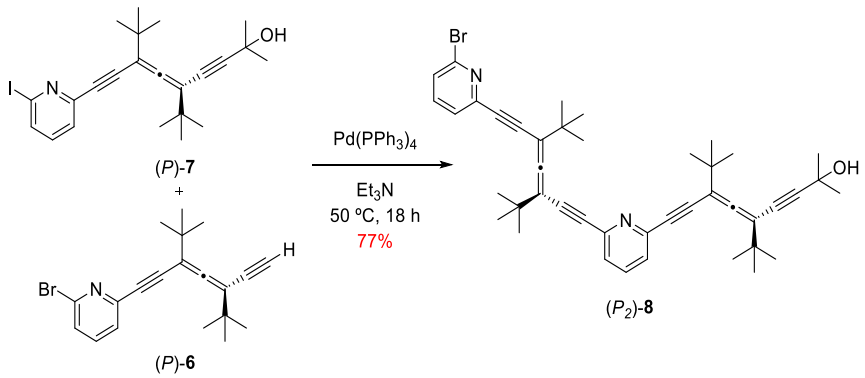
Crystallographic data of (*P*)-**6**

Crystals suitable for x-ray diffraction could be grown from the slow evaporation of a solution of compound (*P*)-**6** in Et_3N.



Empirical formula $C_{20}H_{22}BrN$
Formula weight 356.29
Temperature 100.0 K
Wavelength 0.71073 Å
Crystal system Orthorhombic
Space group $P2_12_12_1$
Unit cell dimensions
a = 6.9366(3) Å α = 90°
b = 11.9824(4) Å β = 90°
c = 21.9980(7) Å γ = 90°
Volume 1828.41(12) $Å^3$
Z 4
Density (calculated) 1.294 mg/m^3
Absorption coefficient 2.245 mm^{-1}
F(000) 736
Crystal size 0.297 x 0.112 x 0.093 mm^3
Theta range for data collection 1.935 to 28.295°.
Index ranges $-9\leq h\leq 9$, $-15\leq k\leq 15$, $-29\leq l\leq 29$
Reflections collected 32635
Independent reflections 4556 [R(int) = 0.0350]
Completeness to theta = 25.242° 99.9 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.7457 and 0.5742
Refinement method Full-matrix least-squares on F^2
Data / restraints / parameters 4556 / 0 / 205
Goodness-of-fit on F^2 1.061
Final R indices [I>2sigma(I)] R_1 = 0.0240, wR_2 = 0.0580
R indices (all data) R_1 = 0.0263, wR_2 = 0.0593
Absolute structure parameter -0.002(3)
Extinction coefficient n/a
Largest diff. peak and hole 0.493 and -0.605 $e.Å^{-3}$

Synthesis of (*P*)-9-(6-((*P*)-7-(6-bromopyridin-2-yl)-3,5-di-tert-butylhepta-3,4-dien-1,6-diyn-1-yl)pyridin-2-yl)-5,7-di-tert-butyl-2-methylnona-5,6-dien-3,8-diyn-2-ol ((*P*$_2$)-**8**)



$Pd(PPh_3)_4$ (14 mg, 0.012 mmol, 0.1 eq) was placed into a Schlenk tube flamed and purged with N_2. Then, (*P*)-**6** (40 mg, 0.11 mmol, 1 eq) and (*P*)-**7** (53 mg, 0.11 mmol, 1 eq) were added dissolved in 5 mL of freshly distilled Et_3N. The reaction mixture was stirred at 50 °C for 18 h. The solvent was removed under reduce pressure and the remaining solid dissolved in AcOEt (20 mL). It was washed with distilled water (20 mL x3) and sat. aq. NaCl solution (20 mL x1). The organic phase was dried with $Na_2SO_{4\ (anh)}$ and the solvent removed under reduced pressure. Purification was carried out by flash chromatography (SiO_2, Hex:AcOEt 75:25) to give (*P*$_2$)-**8** as a white solid in 77% yield (59 mg).

^{1}H-NMR (400 MHz, CDCl3) δ= 7.62 (t, *J* = 7.3 Hz, 1H; Ar-H), 7.51 (t, *J* = 7.2 Hz, 1H; Ar-H), 7.39 (m, 4H; Ar-H), 1.57 (s, 6H; CH_3), 1.23 (s, 9H; tBu), 1.22 (s, 9H; tBu), 1.20 (s, 9H; tBu), 1.14 (s, 9H; tBu). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ= 213.0 (C), 211.9 (C), 144.1 (C), 144.0 (C), 143.8 (C), 141.7 (C), 138.2 (CH), 136.2 (CH), 127.2 (CH), 126.4 (CH), 126.3 (CH), 103.5 (C), 103.3 (C), 103.2 (C), 102.5 (C), 97.8 (C), 92.1 (C), 91.3 (C), 91.0 (C), 84.8 (C), 84.0 (C), 83.3 (C), 75.5 (C), 65.7 (C), 35.89 (C), 35.86 (C), 35.7 (C), 35.5 (C) , 31.49 (CH_3), 31.47 (CH_3), 29.09 (tBu), 29.08 (tBu), 29.06 (tBu), 28.9 (tBu). **UV/Vis** ($CHCl_3$): λmax (ε)= 250.0 nm (29017 mol^{-1} dm^3 cm^{-1}), 319.0 nm (38713 mol^{-1} dm^3 cm^{-1}). **ESI-HR-MS**: m/z calc. for $C_{43}H_{50}BrN_2O^+$ 689.31266; found 689.31010.
*

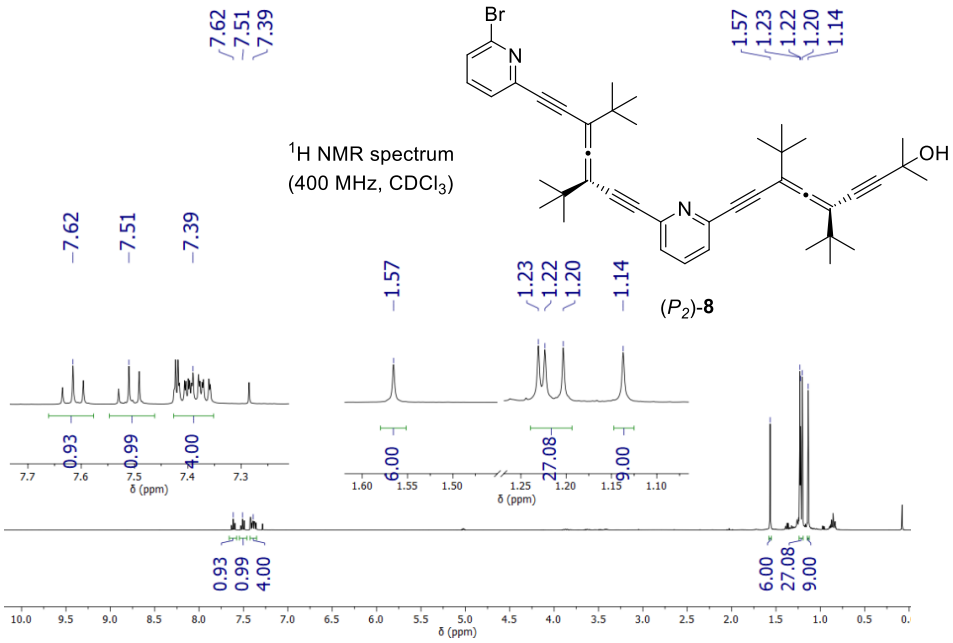


*Figure S10. (P$_2$)-**8** ^{1}H-NMR ($CDCl_3$) spectrum.*Show solvents signal.*

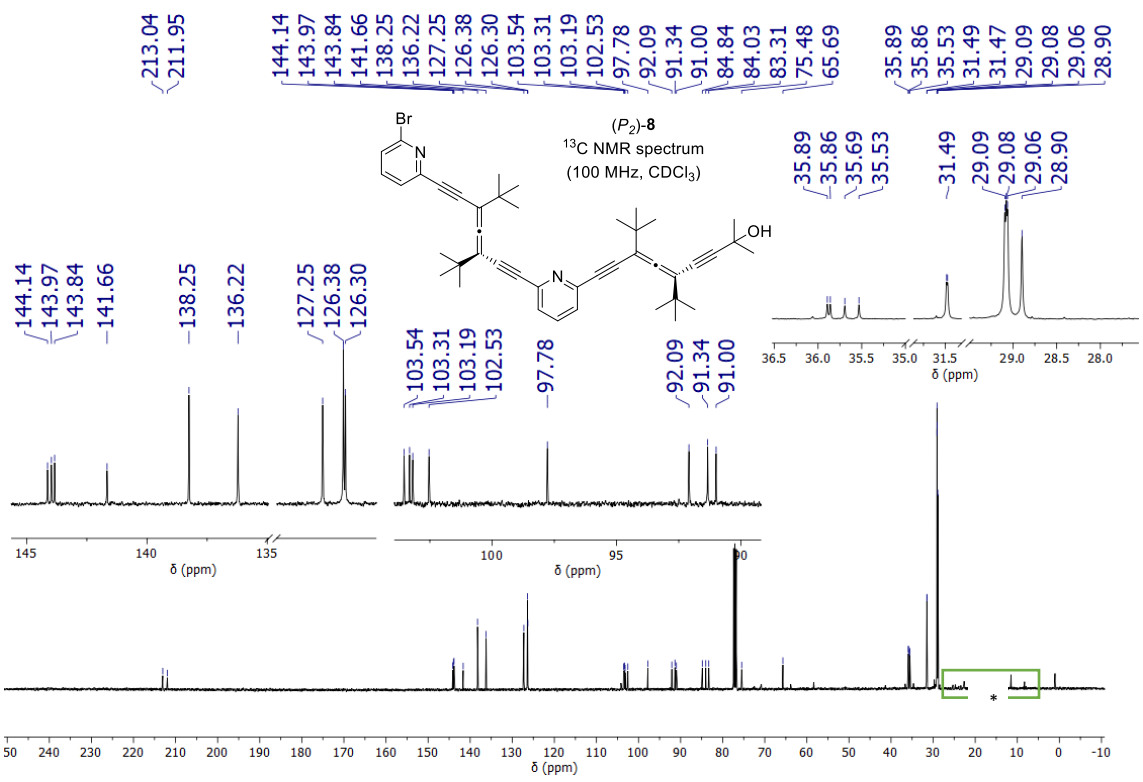


*Figure S11. (P_2)-**8** ^{13}C-NMR ($CDCl_3$) spectrum. *Show solvents signals.*

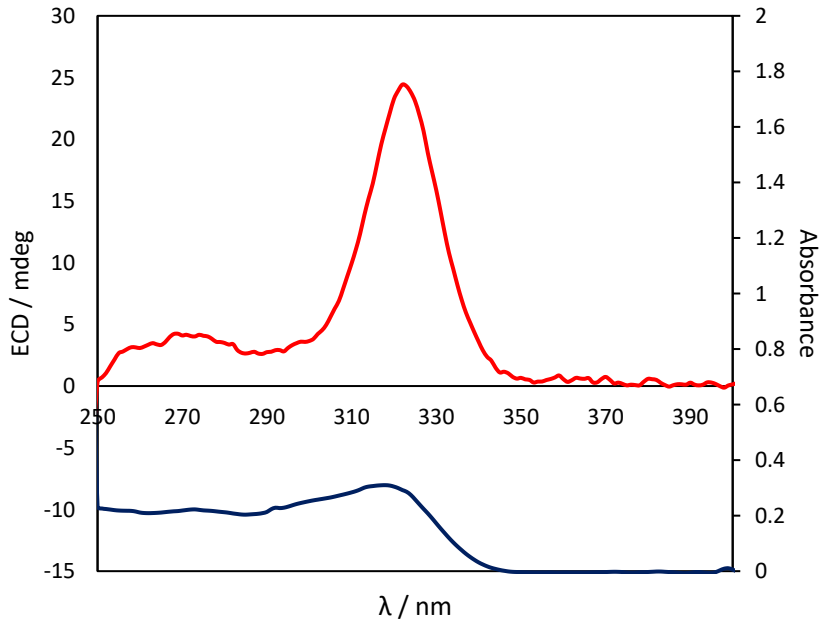
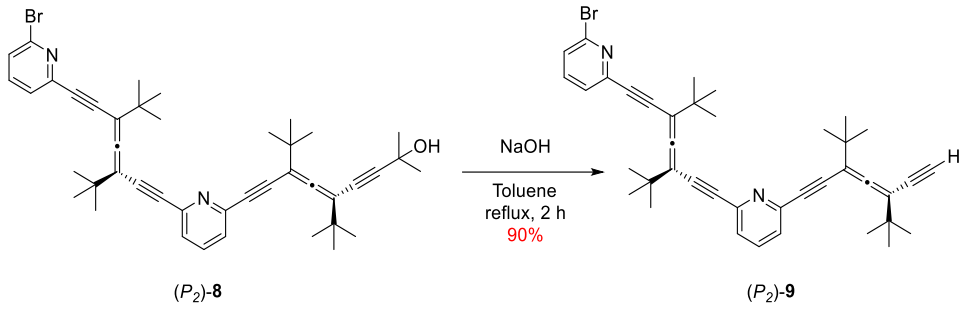


*Figure S12. Red line (P_2)-**8** CD spectrum [Chloroform, $8.0 \cdot 10^{-6}$ M]. Blue line (P_2)-**8** UV/Vis spectrum [Chloroform, $8.0 \cdot 10^{-6}$ M].*

Synthesis of 2-bromo-6-((*P*)-3,5-di-*tert*-butyl-7-(6-((*P*)-3,5-di-*tert*-butylhepta-3,4-dien-1,6-diyn-1-yl)pyridin-2-yl)hepta-3,4-dien-1,6-diyn-1-yl)pyridine ((*P*$_2$)-**9**)



(*P*$_2$)-**8** (*P*$_2$)-**9**

Pulverized NaOH (0.94 g, 23.4 mmol, 300 eq) was placed into a 100 mL round-bottom flask and flamed while purging with N_2. (*P*$_2$)-**8** (54 mg, 0.078 mmol, 1 eq) was also purged with N_2, dissolved in dry toluene (20 mL) and transferred *via* cannula to the previous flask. The reaction mixture was stirred and refluxed for 2 h. Then, the solvent was removed under reduce pressure and distilled water was added (20 mL). The aqueous phase was extracted with AcOEt (20 mL x3). The organic phase was dried with $Na_2SO_{4\,(anh)}$ and the solvent removed under reduced pressure. Purification was carried out by flash chromatography (SiO_2, Hex:AcOEt 90:10) to give (*P*$_2$)-**9** as a white solid in 90% yield (44 mg).

^{1}H-NMR (400 MHz, $CDCl_3$) δ= 7.59 (t, *J* = 7.8 , 1H, Ar), 7.49 (t, *J* = 7.7 , 1H, Ar), 7.37 (m, 4H, Ar), 3.01 (s, 1H, alk), 1.21 (s, 9H, ^{t}Bu), 1.20 (s, 9H, ^{t}Bu), 1.19 (s, 9H, ^{t}Bu), 1.14 (s, 9H, ^{t}Bu) **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 213.1 (C), 212.7 (C), 144.2 (C), 144.0 (C) , 143.9 (C), 141.7 (C), 138.3 (CH), 136.3 (CH), 127.2 (CH), 126.5 (CH), 126.4 (CH), 103.6 (C), 103.3 (C), 103.1 (C), 103.0 (C), 92.2 (C), 91.7 (C), 91.1 (C), 84.9 (C), 83.7 (C), 83.4 (C), 81.0 (alk, CH), 77.2 (C), 35.98 (C), 35.94 (C), 35.86 (C), 29.17 (^{t}Bu), 29.15 (^{t}Bu), 28.88 (^{t}Bu). **UV/Vis** ($CHCl_3$): λmax (ε)= 251.0 nm (36560 mol^{-1} dm^3 cm^{-1}), 269.0 nm (34572 mol^{-1} dm^3 cm^{-1}), 316.0 nm (41923 mol^{-1} dm^3 cm^{-1}). **HRMS-ESI**: *m/z* calcd. for $C_{40}H_{43}BrN_2$ 630.2589; found 630.2610 $[M+H]^+$.

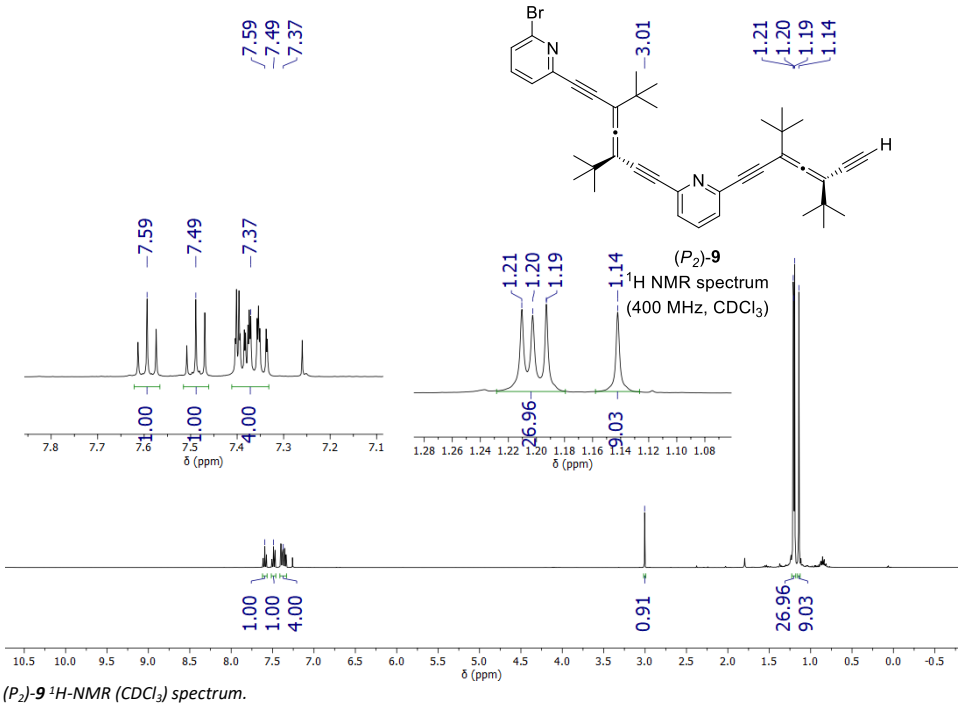


*Figure S13. (P$_2$)-**9** ^{1}H-NMR ($CDCl_3$) spectrum.*

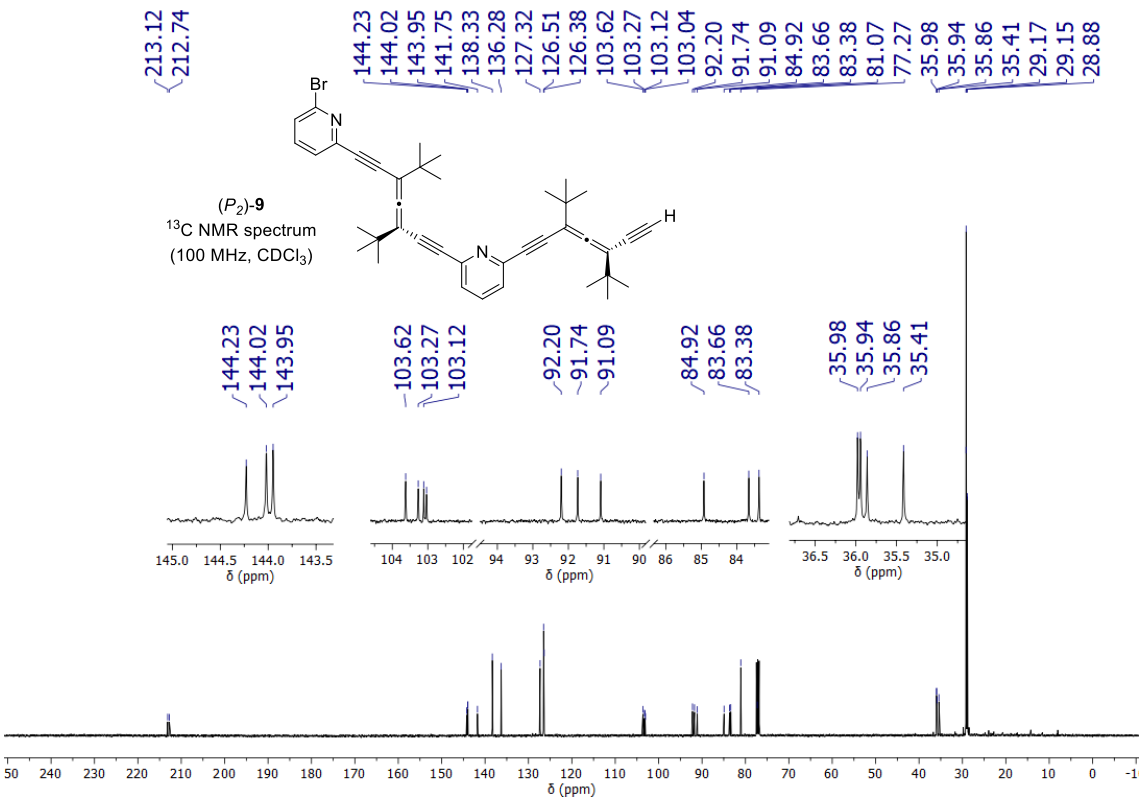


*Figure S14. (P_2)-**9** ^{13}C-NMR ($CDCl_3$) spectrum.*

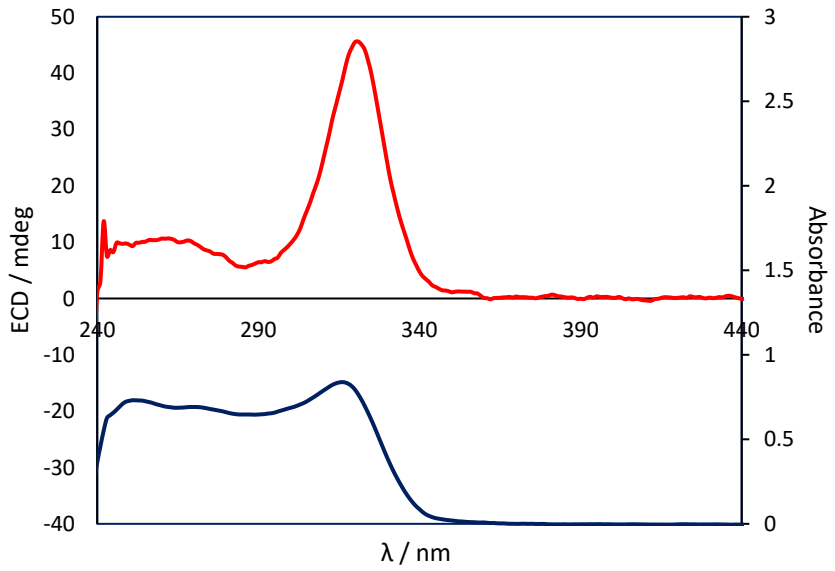
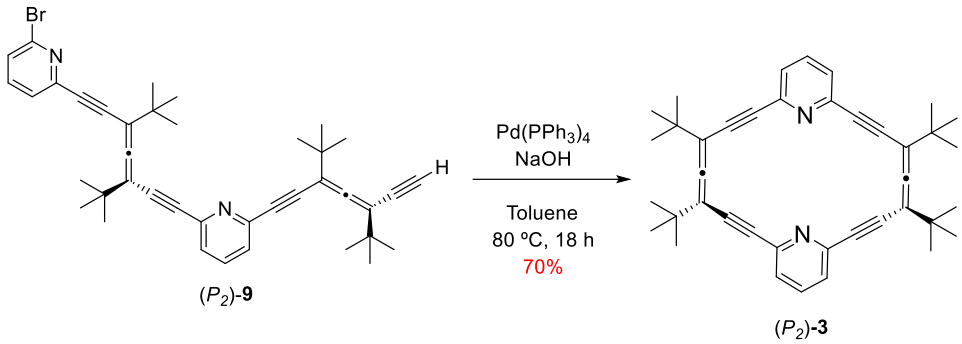


*Figure S15. Red line (P_2)-**9** CD spectrum [Chloroform, $2.0 \cdot 10^{-5}$ M]. Blue line (P_2)-**9** UV/Vis spectrum [Chloroform, $2.0 \cdot 10^{-5}$ M].*

Synthesis of [7_2]-pyridoallenophane ((*P*$_2$)-**3**)



Pulverized NaOH (1600 mg, 40 mmol, 1000 eq) was placed into a Schlenk tube and flamed while purging with N_2. (*P*$_2$)-**9** (25 mg, 0.04 mmol, 1 eq), $Pd(PPh_3)_4$ (10 mg, 0.01 mmol, 0.25 eq) and dry toluene (80 mL) were added. The reaction mixture was stirred and at 80 °C for 18 h. Then, the solvent was removed under reduce pressure and distilled water was added (50 mL). The aqueous phase was extracted with AcOEt (50 mL x 3). The organic phase was dried with Na_2SO_4 (anh) and the solvent removed under reduced pressure. Purification was carried out by flash chromatography (SiO_2, Hex:AcOEt 90:10) to give (*P*$_2$)-**3** as a white solid in 70% yield (16 mg).

The exact same procedure was followed but starting from the (*M*)-**DEA** enantiomer, to arrive at (*M*$_2$)-**3** with similar results.

^{1}H-NMR (400 MHz, $CDCl_3$) *δ*= 7.59 (t, *J* = 7.8 , 2H, Ar), 7.27 (d, *J* = 7.8 , 4H, Ar), 1.21 (s, 36H, ^{t}Bu). **^{13}C-NMR** (100 MHz, $CDCl_3$) *δ* 214.5 (C), 144.8 (C), 136.5 (CH), 124.7 (CH), 103.8 (C), 92.8 (C), 83.9 (C), 35.3 (C), 29.3 (^{t}Bu). **UV/Vis** ($CHCl_3$): λmax (ε)= 264.0 nm (22925 mol^{-1} dm^3 cm^{-1}), 288.0 nm (18428 mol^{-1} dm^3 cm^{-1}), 313.0 nm (7138 mol^{-1} dm^3 cm^{-1}). **HRMS-ESI**: *m/z* calcd. for $C_{40}H_{43}N_2^+$ 551.3431; found 551.3421 $[M+H]^+$.

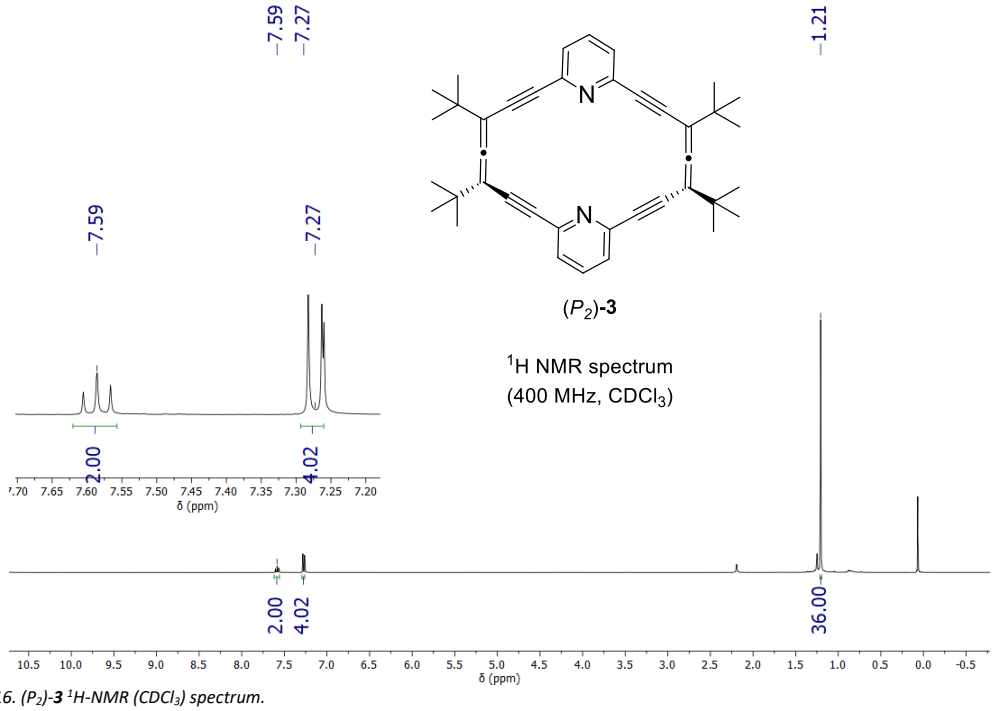


*Figure S16. (P$_2$)-**3** ^{1}H-NMR ($CDCl_3$) spectrum.*

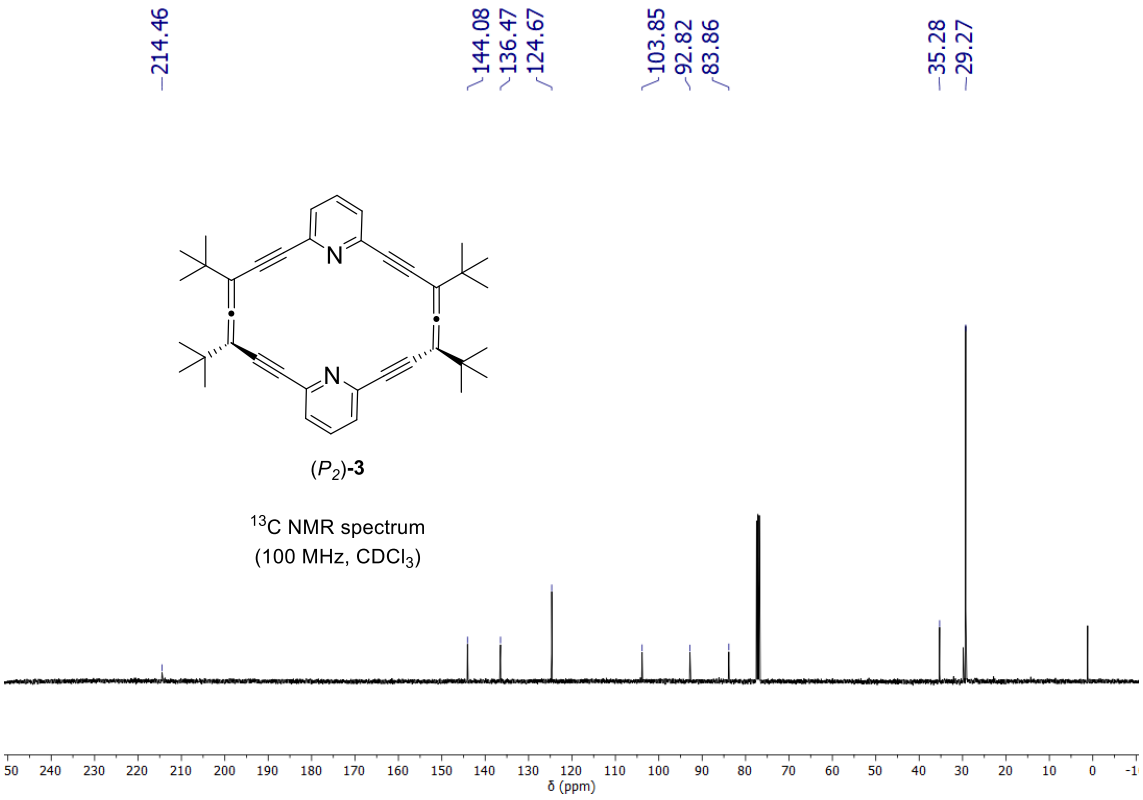


*Figure S17. (P_2)-**3** ^{13}C-NMR ($CDCl_3$) spectrum.*

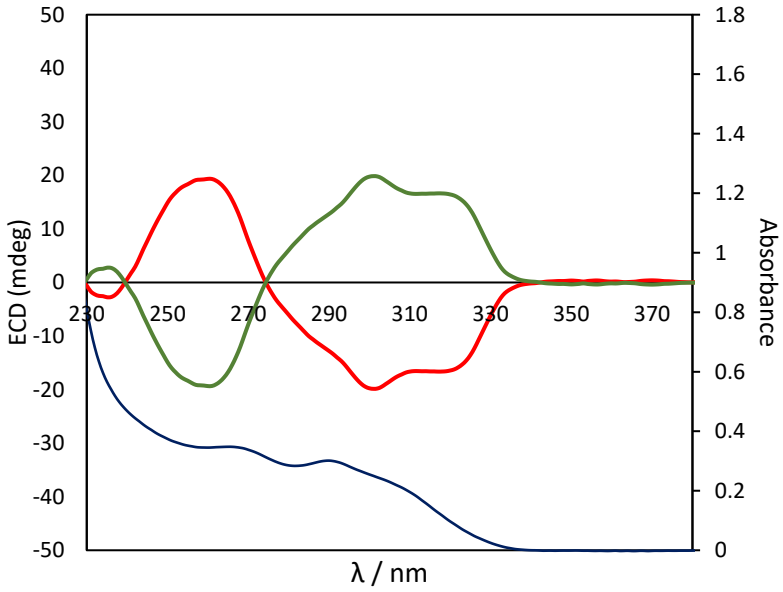
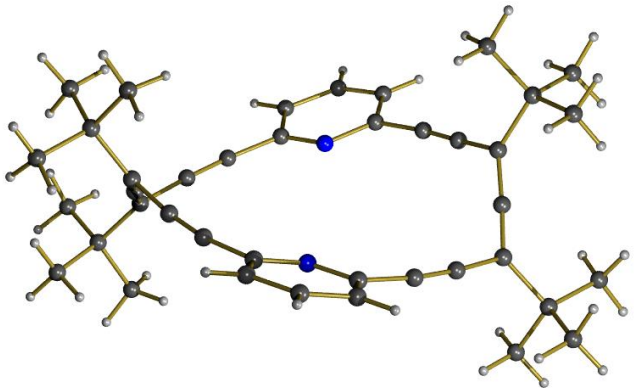


*Figure S18. Red line (P_2)-**3** and Green line (M_2)-**3** CD spectra. Blue line (P_2)/(M_2)-**3** UV/Vis spectrum [Chloroform, $1.5 \cdot 10^{-5}$ M].*

Crystallographic data of (P_2)-**3**

Crystals suitable for x-ray diffraction could be grown from the slow evaporation at room temperature of a solution of compound (P_2)-**3** in Et_3N.



Empirical formula	$C_{40}H_{42}N_2$	
Formula weight	550.75	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	$P3_2$	
Unit cell dimensions	α = 15.9045(6) Å	α= 90°.
	b = 15.9045(6) Å	β= 90°.
	c = 14.9589(10) Å	γ = 120°.
Volume	3277.0(3) $Å^3$	
Z	3	
Density (calculated)	0.837 Mg/m^3	
Absorption coefficient	0.048 mm^{-1}	
F(000)	888	
Crystal size	0.273 x 0.122 x 0.119 mm^3	
Theta range for data collection	2.010 to 28.296°.	
Index ranges	-21<=h<=21, -21<=k<=21, -19<=l<=19	
Reflections collected	57905	
Independent reflections	10819 [R(int) = 0.0528]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6195	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10819 / 1 / 391	

Goodness-of-fit on F^2	1.022
Final R indices [I>2sigma(I)]	R1 = 0.0386, wR2 = 0.0903
R indices (all data)	R1 = 0.0508, wR2 = 0.0959
Absolute structure parameter	-1.1(8)
Extinction coefficient	n/a
Largest diff. peak and hole	0.128 and -0.153 e.$Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 32071301_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	5589(1)	3357(1)	3127(1)	31(1)
N(2)	5082(1)	5134(1)	6506(1)	42(1)
C(1)	6442(1)	3842(1)	2684(1)	31(1)
C(2)	6730(1)	3410(1)	2039(1)	33(1)
C(3)	6121(1)	2443(1)	1836(1)	36(1)
C(4)	5245(1)	1931(1)	2282(1)	32(1)
C(5)	5014(1)	2412(1)	2926(1)	29(1)
C(6)	4151(1)	1935(1)	3477(1)	33(1)
C(7)	3498(1)	1616(1)	4002(1)	35(1)
C(8)	2766(1)	1294(1)	4689(1)	38(1)
C(9)	3075(1)	1509(1)	5525(1)	40(1)
C(10)	3446(1)	1732(1)	6326(1)	40(1)
C(11)	3752(1)	2694(1)	6663(1)	41(1)
C(12)	4077(1)	3509(2)	6930(1)	46(1)
C(13)	4531(1)	4531(2)	7155(1)	48(1)
C(14)	4405(2)	4864(2)	7988(1)	62(1)
C(15)	4862(2)	5841(2)	8137(2)	70(1)
C(16)	5442(2)	6474(2)	7479(2)	64(1)
C(17)	5542(1)	6091(2)	6677(1)	47(1)
C(18)	6152(2)	6677(1)	5954(1)	46(1)
C(19)	6644(2)	7027(1)	5294(1)	45(1)
C(20)	7193(2)	7382(1)	4485(1)	45(1)
C(21)	7628(2)	6931(1)	4173(1)	43(1)
C(22)	8062(1)	6462(1)	3869(1)	40(1)
C(23)	7504(1)	5597(1)	3348(1)	37(1)
C(24)	7047(1)	4825(1)	2983(1)	36(1)

C(25)	1687(1)	774(2)	4424(1)	46(1)
C(26)	1504(2)	10(2)	3720(2)	67(1)
C(27)	1051(1)	304(2)	5239(1)	56(1)
C(28)	1462(2)	1529(2)	4024(1)	60(1)
C(29)	3624(2)	1050(2)	6926(1)	51(1)
C(30)	3255(4)	84(3)	6459(2)	115(1)
C(31)	3076(2)	884(2)	7806(2)	65(1)
C(32)	4706(2)	1542(3)	7135(2)	91(1)
C(33)	7208(2)	8248(1)	4012(1)	58(1)
C(34)	6161(3)	8044(2)	3904(3)	108(1)
C(35)	7765(3)	9126(2)	4605(2)	100(1)
C(36)	7655(4)	8413(2)	3104(2)	111(1)
C(37)	9123(1)	6779(1)	4064(1)	44(1)
C(38)	9527(2)	7544(2)	4798(2)	62(1)
C(39)	9689(2)	7202(2)	3196(1)	58(1)
C(40)	9208(2)	5905(2)	4342(2)	57(1)

3. Acid Titration Experiments and Mathematical fitting

The complexation processes were monitored by CD titration. A solution of the macrocycle in CH_3CN was prepared, placed in a one-centimeter thick quartz cuvette and different volumes of acid solutions in CH_3CN were added, the mixture was stirred and ECD and UV-Vis signals were recorded after each addition. Every acid solution was freshly prepared immediately before use. Each experiment was replicated at least 3 times to verify reproducibility.

In order to corroborate that the end point of the titration was reached, high acid concentrations have to be used (*vide infra*). However, only values ranging from 0 to up to 1 M were used for the mathematical fittings to ensure that the values obtained are reliable, due to the fact that large amounts of acid in acetonitrile could change the pK_a values for the acids.

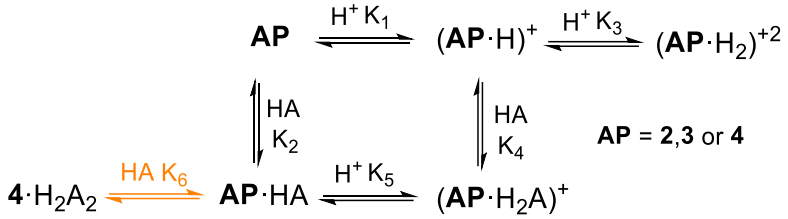


*Table S3. AP = allenophane. Values of the constants obtained from the mathematical fitting of each one of the titrations for each one of the macrocycles with the corresponding acids. * Constants obtained from the other constants of the equilibrium system. **Estimated constant from the Brønsted correlation.*

Allenophane	Acid	pK_a[a]	$logK_1$	$logK_2$	$logK_3$	$logK_4$	$logK_5$	$logK_6$
2	TfOH	2.5	4.15	7.81	3.40	8.30	4.64	-
	H_2SO_4	7.2	4.15	5.89	3.40	5.71	3.97*	-
	MsOH	10.0	4.15	4.20	3.40	4.17	4.12*	-
	TFA	12.6	4.15	3.66	3.40	3.12	3.61*	-
	TsOH	8.5	4.15	7.37	3.40	2.00	-1.22*	-
	HCl	8.9	4.15	5.17	3.40	-	-	-
3	TfOH	2.5	8.06	10.40	5.42	8.22	5.88*	-
	H_2SO_4	7.2	8.06	5.27	5.42	4.60	7.39*	-
	TFA	12.6	8.06	-1.0**	5.42	0.55	9.61*	-
	HCl	8.9	8.06	4.22	5.42	5.50	-	-
4	TfOH	2.5	8.06	12.80	6.50	9.70	5.00	10.00
	H_2SO_4	7.2	8.06	6.90	6.50	3.80	5.00	5.20
	TFA	12.6	8.06	1.20	6.50	-1.90	5.00	2.20
	HCl	8.9	8.06	3.30	6.50	-0.60	5.00	3.51

Equilibria system for the titration with 1,2-ethanedisulfonic acid as bidentate acid:

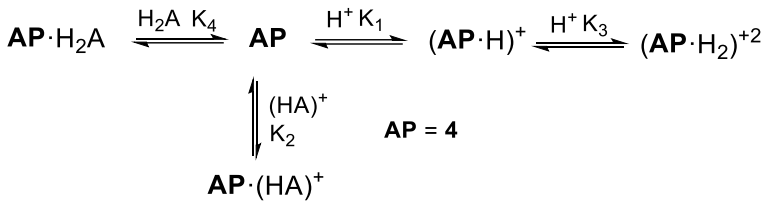


*Table S4. AP = allenophane. Values of the constants obtained from the mathematical fitting of the titration of **4** with 1,2-ethanedisulfonic acid.*

Allenophane	Acid	pK_{a1}	pK_{a2}	$logK_1$	$logK_2$	$logK_3$	$logK_4$
4	1,2-EDA	7.1	11.1	8.06	4.00	6.50	11.37

3.1. Titration experiment of (P_2)-2 with H_2SO_4

A 4.00 x 10^{-5} M solution of (P_2)-**2** in CH_3CN was titrated with different volumes of H_2SO_4 solutions in the same solvent (0.002 M to 4 M). To ensure completion of the titration the last additions were made with undiluted acid.

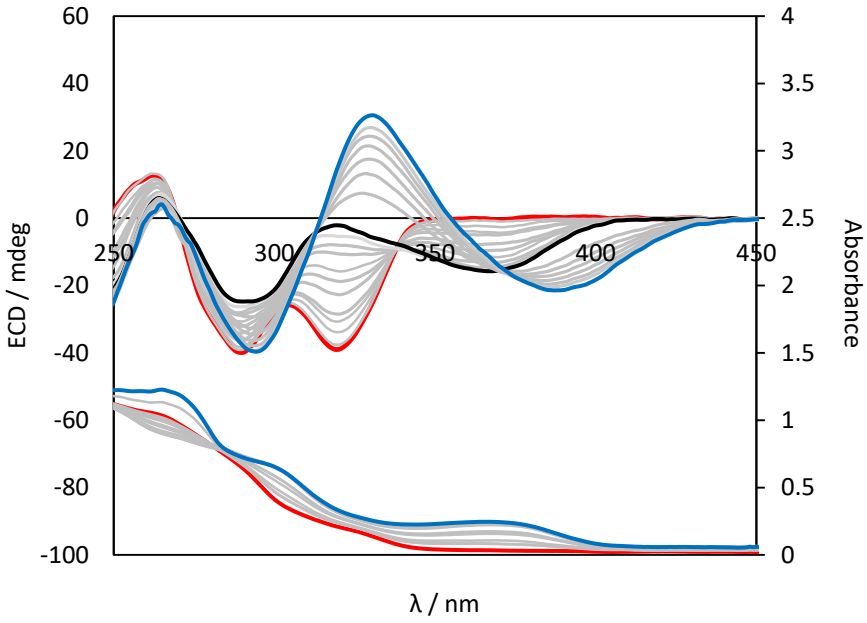


*Figure S19. Change of the ECD and UV/Vis spectra of (P_2)-**2** upon addition of H_2SO_4 (acid concentration in the cuvette ranging from 0 to 3.3 M). Red line: ECD and UV/Vis signal before adding H_2SO_4. Black line: ECD at the first saturation point. Blue line: ECD and UV/Vis signal at the final saturation value of H_2SO_4. Grey lines: Changes with increasing amounts of acid.*

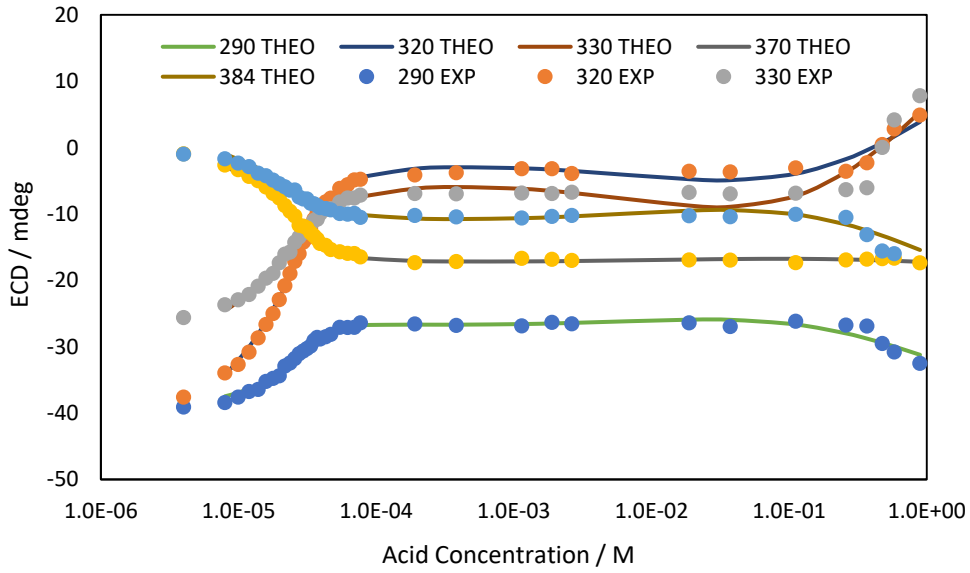


Figure S20. Experimental ECD signals variation with H_2SO_4 additions at 290, 320, 330, 370 and 384 nm (scatters) and mathematical adjustment (lines) to the processes presented in S19.

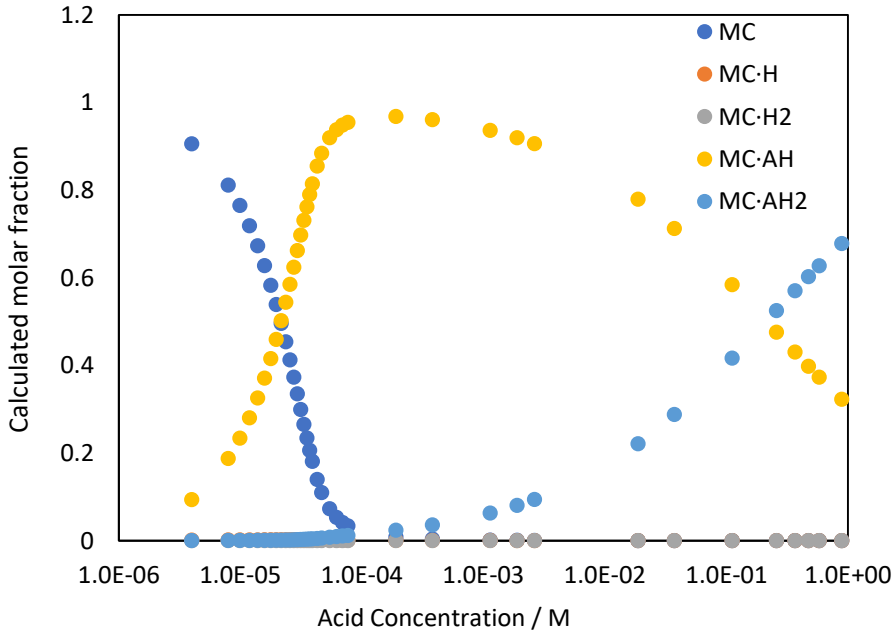


*Figure S21. Representation of the variation in concentration of all formed species during the titration of (P_2)-**2** with H_2SO_4.*

3.2. Titration experiment of (P_2)-2 with MsOH

A 1.00 x 10^{-05} M solution of (P_2)-**2** in CH_3CN was titrated with different volumes of MsOH solutions in the same solvent (5 x 10^{-04} M and 1 M). To ensure completion of the titration the last additions were made with undiluted acid.

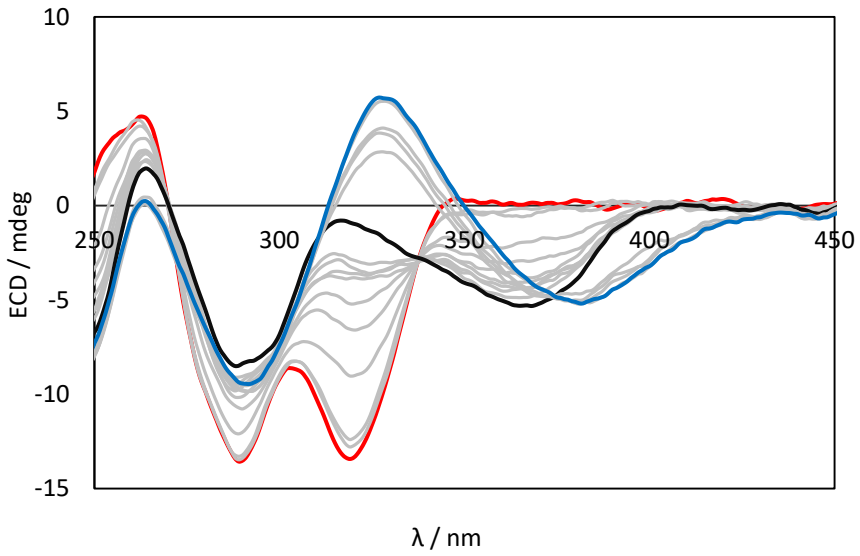


*Figure S22. Change of the ECD and UV/Vis spectra of (P_2)-**2** upon addition of MsOH (acid concentration in the cuvette ranging from 0 to 7 M). Red line: ECD signal before adding MsOH. Black line: ECD at the first saturation point. Blue line: ECD signal at the final saturation value of MsOH. Grey lines: Changes with increasing amounts of acid.*

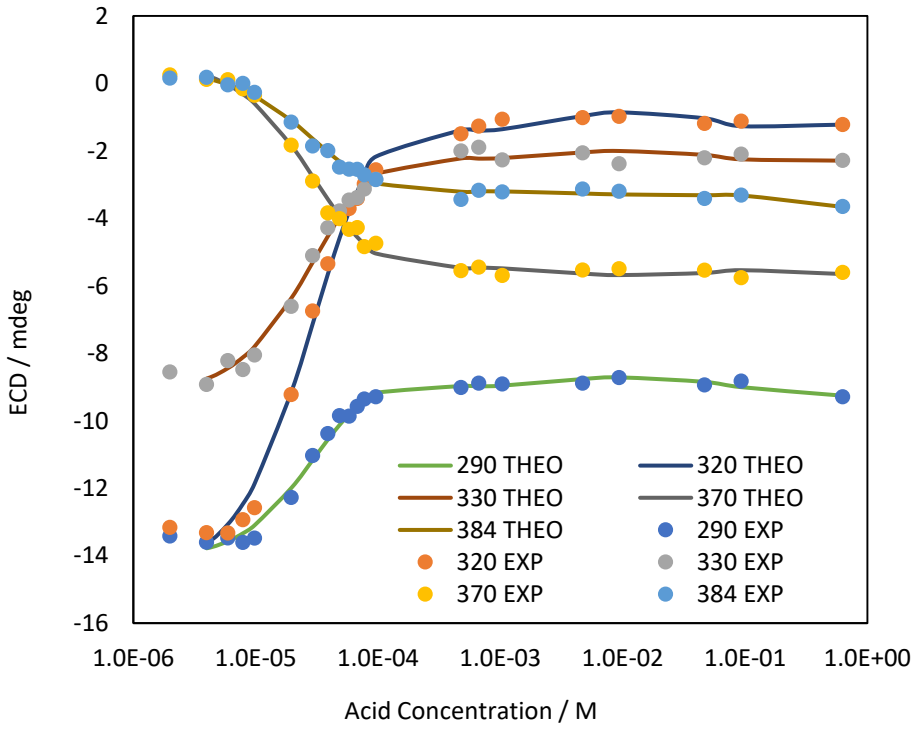


Figure S23. Experimental ECD signals variation with MsOH additions at 290, 320, 330, 370 and 384 nm (scatters) and mathematical adjustment (lines) to the processes presented in S22.

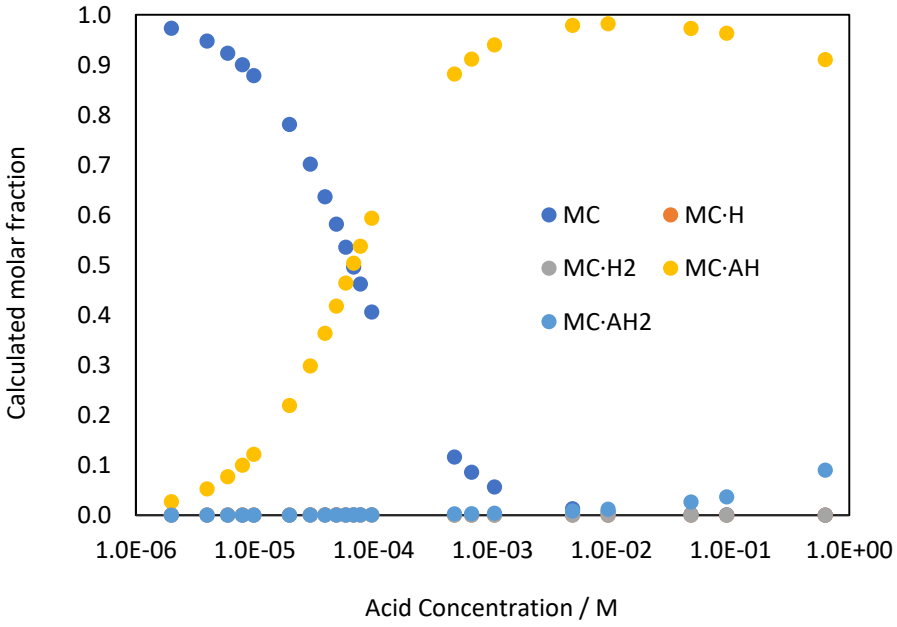


Figure S24. Representation of the variation in concentration of all formed species during the titration of (P_2)-2 with MsOH.

3.3. Titration experiment of (P_2)-2 with TFA

A 1.00 x 10^{-05} M solution of (P_2)-**2** in CH_3CN was titrated with different volumes of TFA solutions in the same solvent (1.00 x 10^{-03} M to 1 M). To ensure completion of the titration the last additions were made with undiluted acid.

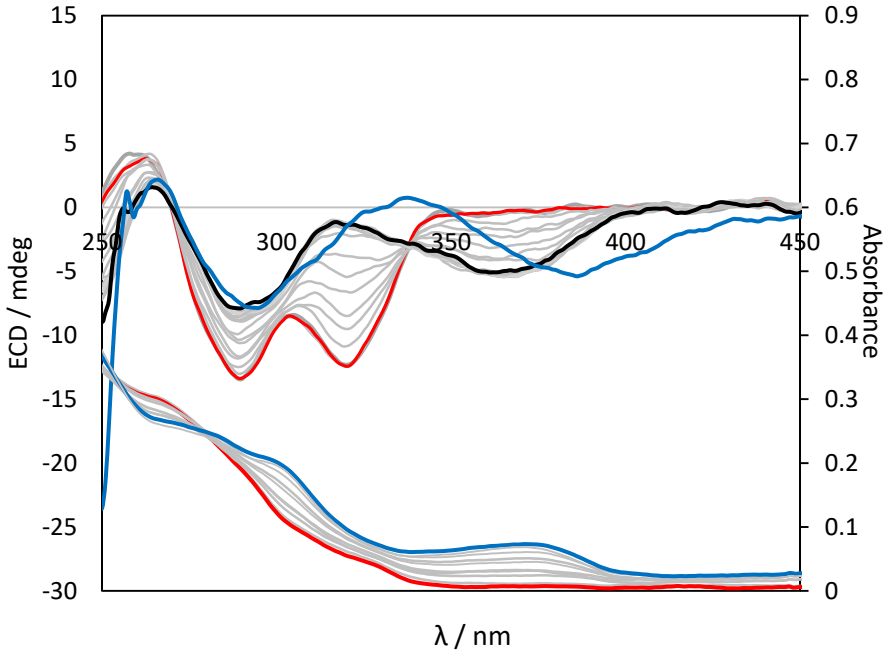


*Figure S25. Change of the ECD and UV/Vis spectra of (P_2)-**2** upon addition of TFA (acid concentration in the cuvette ranging from 0 to 10 M). Red line: ECD signal before adding TFA. Black line: ECD at the first saturation point. Blue line: ECD signal at the final saturation value of TFA. Grey lines: Changes with increasing amounts of acid.*

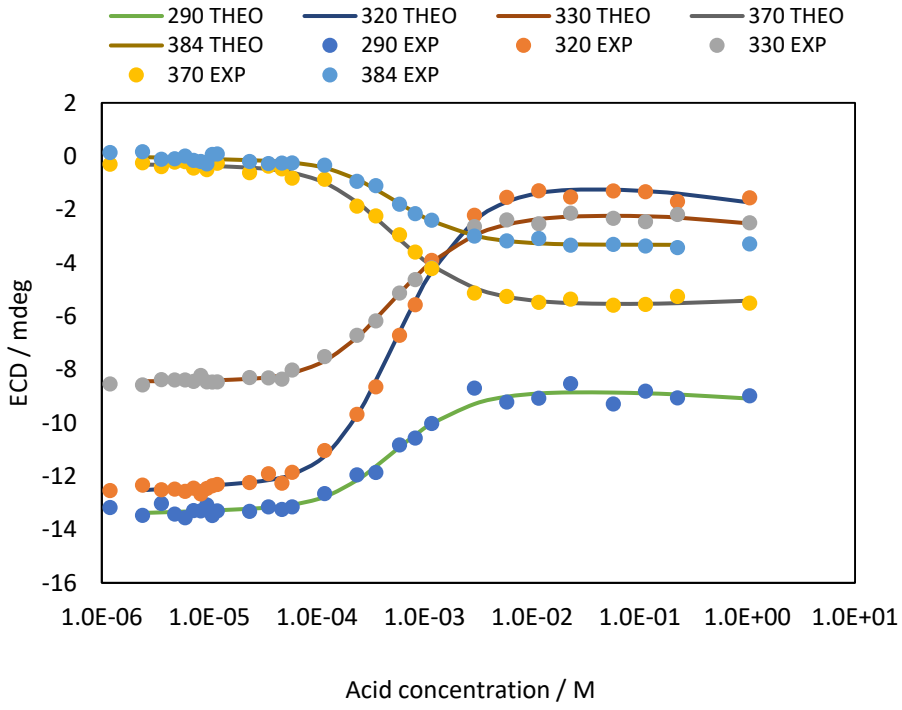


Figure S26. Experimental ECD signals variation with TFA additions at 290, 320, 330, 370 and 384 nm (scatters) and mathematical adjustment (lines) to the processes presented in S25.

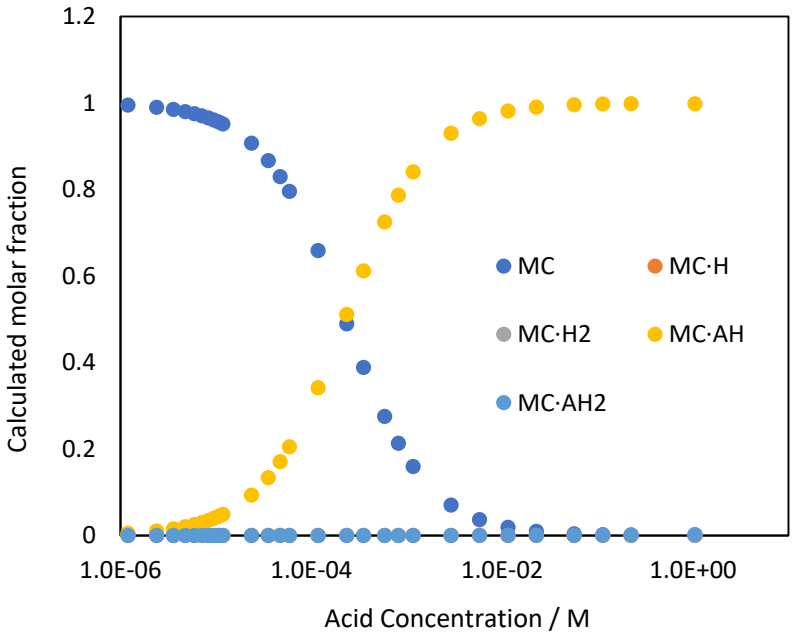


*Figure S26. Representation of the variation in concentration of all formed species during the titration of (P_2)-**2** with TFA.*

3.4. Titration experiment of (P_2)-2 with TsOH

A 1.5 x 10^{-05} M solution of (P_2)-**2** in CH_3CN was titrated with different volumes of TsOH solutions in the same solvent (1.0 x 10^{-03} M and 1 M). In the particular case of TsOH, saturation point was not reached due to the high absorption of the acid in this range of wavelengths. However, the obtained points could be mathematically adjusted to the previously proposed equilibria system, showing the same pattern of behavior as the rest of the oxoacids tested.

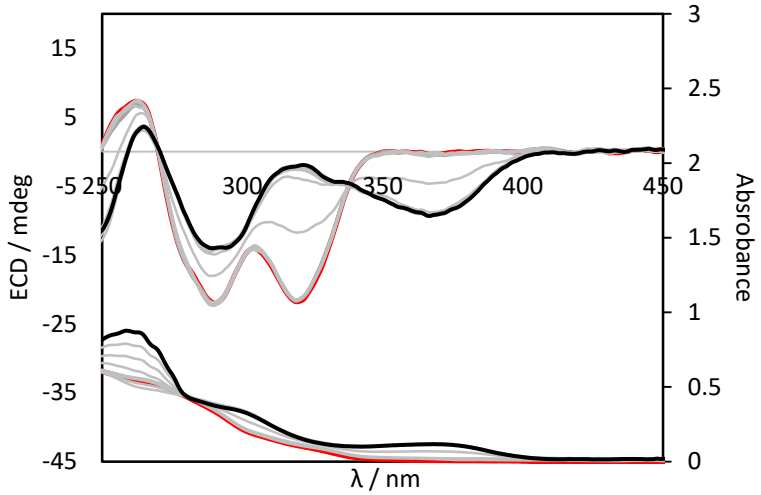


*Figure S27. Change of the ECD and UV/Vis spectra of (P_2)-**2** upon addition of TsOH (acid concentration in the cuvette ranging from 0 to 8 x 10^{-03} M). Red line: ECD and UV/Vis signal before adding TsOH. Black line: ECD and UV/Vis signal at the saturation value of TsOH. Grey lines: Changes with increasing amounts of acid.*

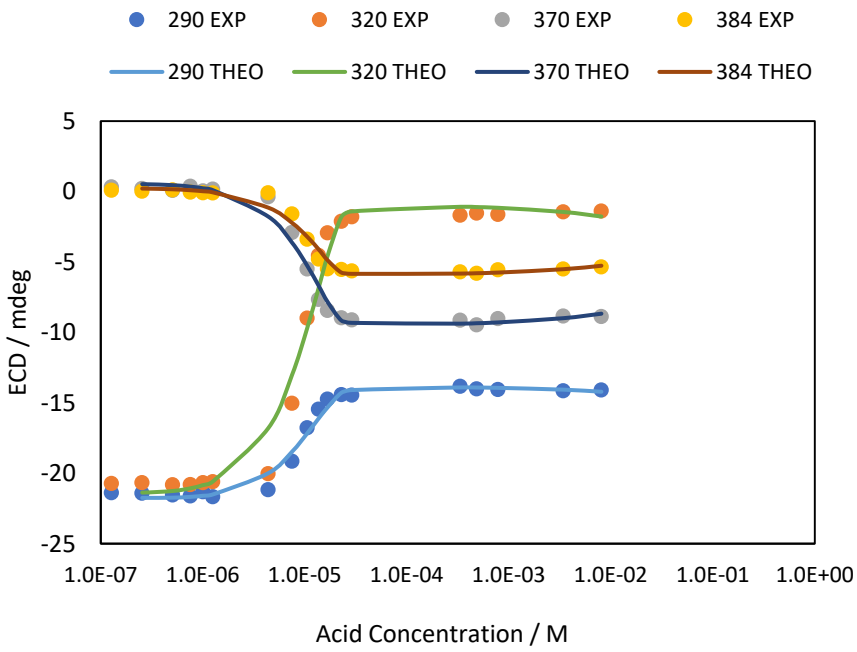


Figure S28. Experimental ECD signals variation with TsOH additions at 290, 320, 330, 370 and 384 nm (scatters) and mathematical adjustment (lines) to the processes presented in S27.

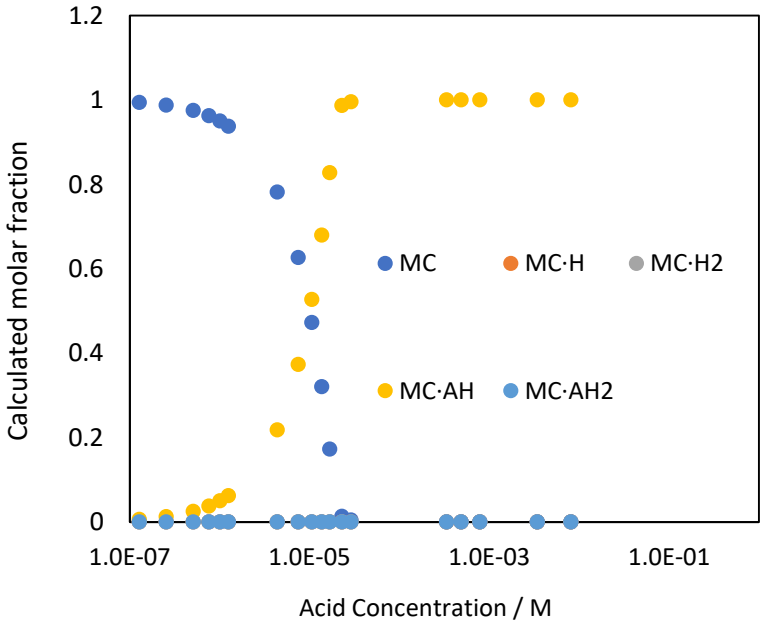


*Figure S29. Representation of the variation in concentration of all formed species during the titration of (P_2)-**2** with TsOH.*

3.5. Titration experiment of (P_2)-2 with HCl

A 2.00 x 10^{-05} M solution of (P_2)-**2** in CH_3CN was titrated with different volumes of HCl in dioxane diluted in acetonitrile (5 x 10^{-04} M to 0.5 M). To ensure completion of the titration the last additions were made with the commercial solution of HCl in dioxane 4 M.

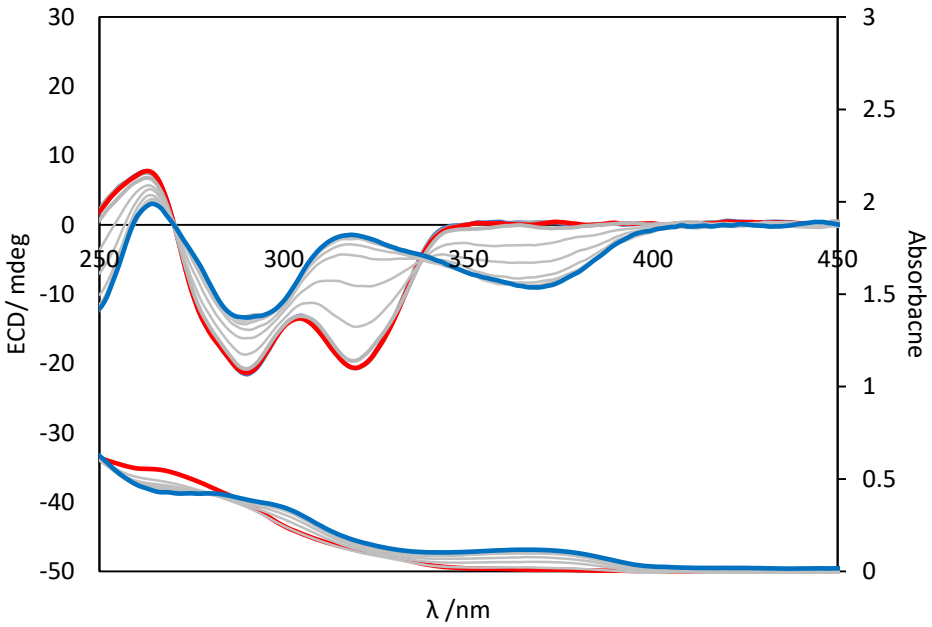


*Figure S30. Change of the ECD and UV/Vis spectra of (P_2)-**2** upon addition of HCl (acid concentration in the cuvette ranging from 0 to 1.7 M). Red line: ECD and UV/Vis signal before adding HCl. Blue line: ECD and UV/Vis signal at the saturation value of HCl. Grey lines: Changes with increasing amounts of acid.*

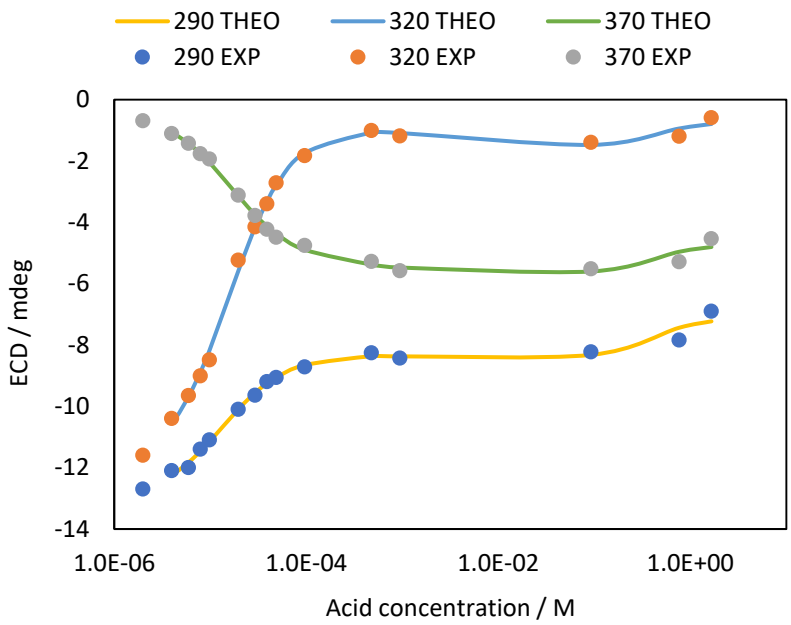


Figure S31. Experimental ECD signals variation with HCl additions at 290, 320, 330, 370 and 384 nm (scatters) and mathematical adjustment (lines) to the processes presented in S30.

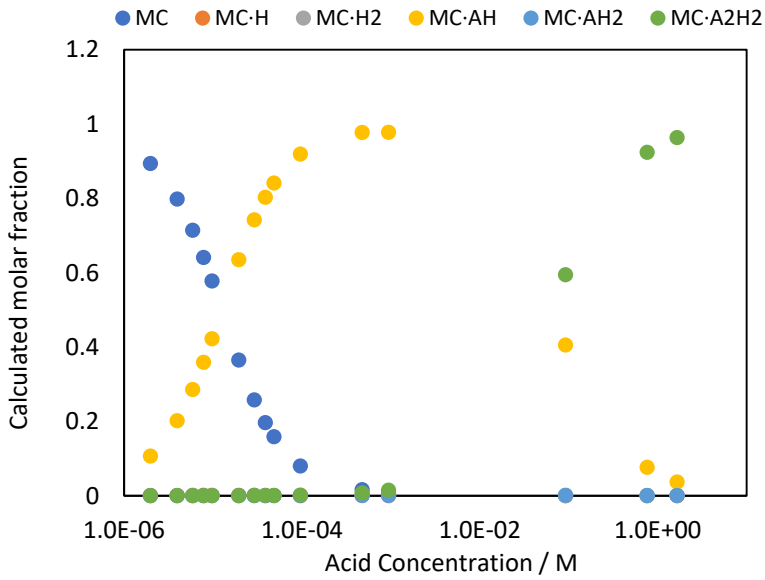


*Figure S32. Representation of the variation in concentration of all formed species during the titration of (P_2)-**2** with HCl.*

3.6. Titration experiment of (P_2)-3 with TfOH

A 1.5x 10^{-05} M solution of (P_2)-**3** in CH_3CN was titrated with different volumes of TfOH solutions in the same solvent (5x 10^{-04} M to 0.5 M). To ensure completion of the titration the last additions were made with undiluted acid.

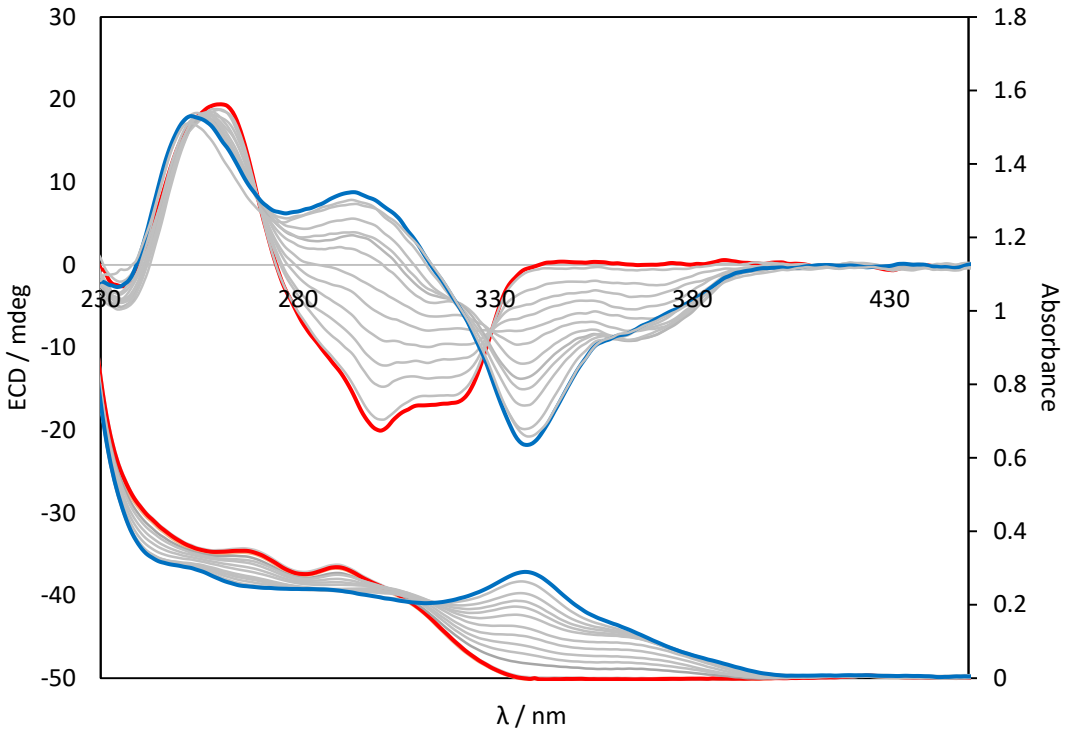


*Figure S33. Change of the ECD and UV/Vis spectra of (P_2)-**3** upon addition of TfOH (acid concentration in the cuvette ranging from 0 to 0.14 M). Red line: ECD and UV/Vis signal before adding TfOH. Blue line: ECD and UV/Vis signal at the saturation value of TfOH. Grey lines: Changes with increasing amounts of acid.*

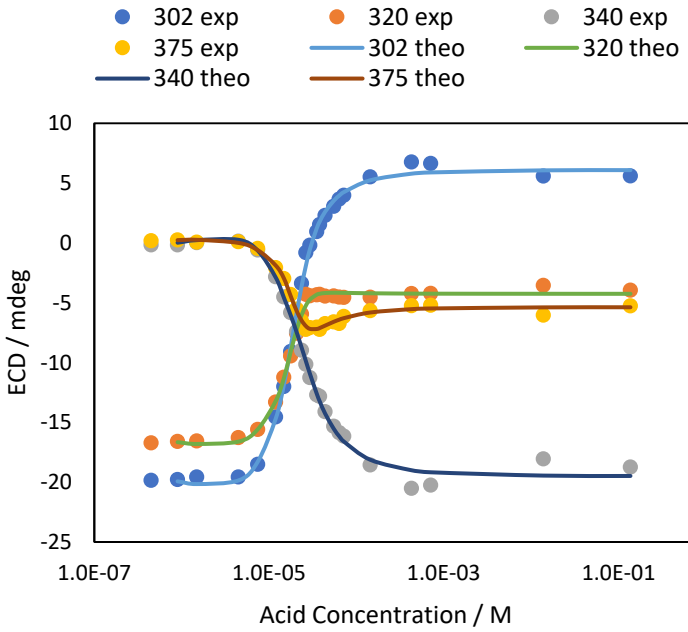


Figure S34. Experimental ECD signals variation with TfOH additions at 302, 320, 340 and 375 nm (scatters) and mathematical adjustment (lines) to the processes presented in S33.

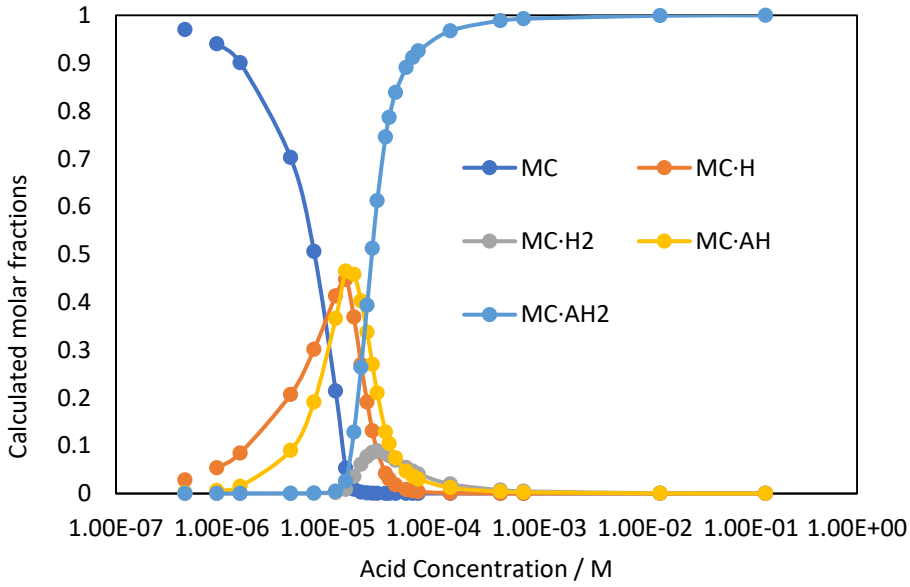


*Figure S35. Representation of the variation in concentration of all formed species during the titration of (P_2)-**3** with TfOH.*

3.7. Titration experiment of (P_2)-3 with H_2SO_4

A 1.50 x 10^{-05} M solution of (P_2)-**3** in CH_3CN was titrated with different volumes of H_2SO_4 solutions in the same solvent (1 x 10^{-03} M to 1 M). To ensure completion of the titration the last additions were made with undiluted acid.

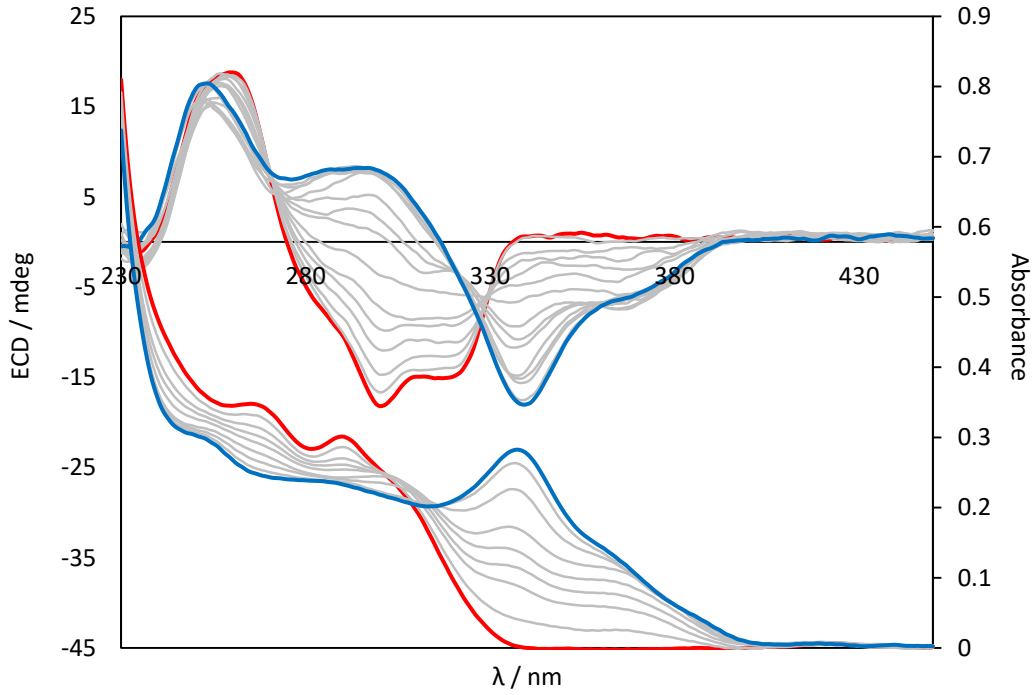


*Figure S36. Change of the ECD and UV/Vis spectra of (P_2)-**3** upon addition of H_2SO_4 (acid concentration in the cuvette ranging from 0 to 5.1 M). Red line: ECD and UV/Vis signal before adding H_2SO_4. Blue line: ECD and UV/Vis signal at the saturation value of H_2SO_4. Grey lines: Changes with increasing amounts of acid.*

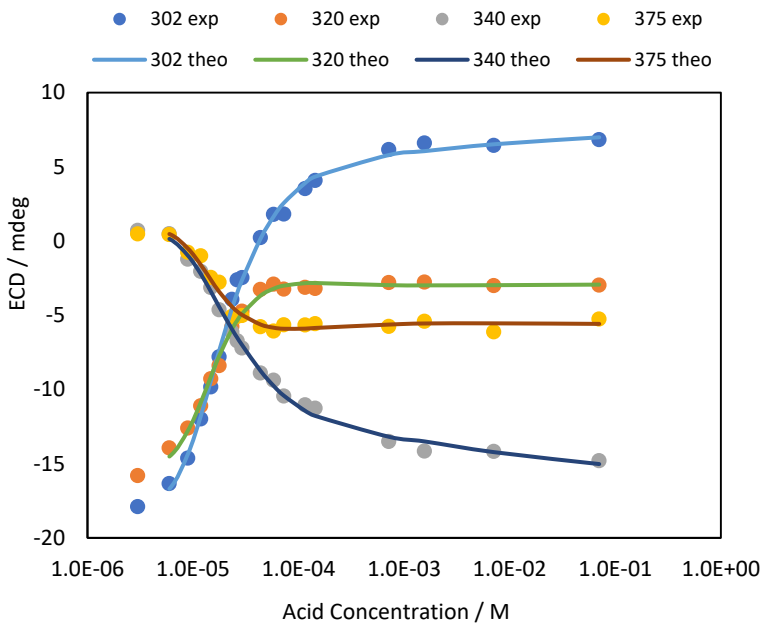


Figure S37. Experimental ECD signals variation with H_2SO_4 additions at 302, 320, 340 and 375 nm (scatters) and mathematical adjustment (lines) to the processes presented in S36.

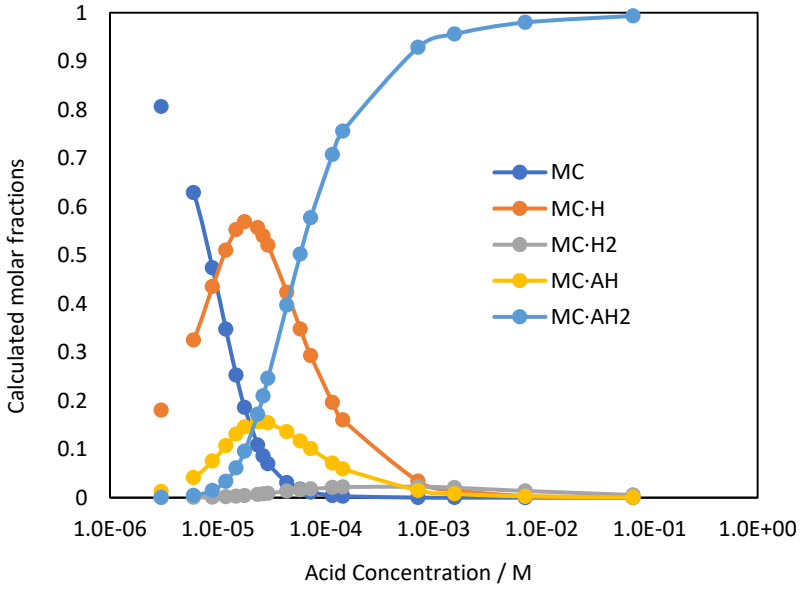


*Figure S38. Representation of the variation in concentration of all formed species during the titration of (P_2)-**3** with H_2SO_4.*

3.8. Titration experiment of (P_2)-3 with HCl

A 1.50 x 10^{-05} M solution of (P_2)-**3** in CH_3CN was titrated with different volumes of HCl in dioxane diluted in acetonitrile (1 x 10^{-03} M to 1 M). To ensure completion of the titration the last additions were made with the commercial solution of HCl in dioxane 4 M.

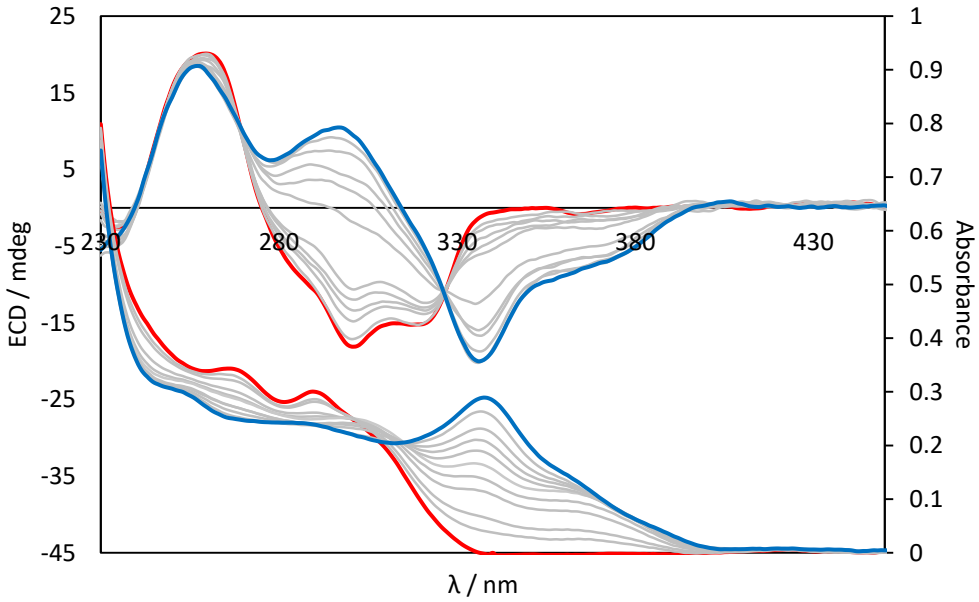


*Figure S39. Change of the ECD and UV/Vis spectra of (P_2)-**3** upon addition of HCl (acid concentration in the cuvette ranging from 0 to 0.2 M). Red line: ECD and UV/Vis signal before adding HCl. Blue line: ECD and UV/Vis signal at the saturation value of HCl. Grey lines: Changes with increasing amounts of acid.*

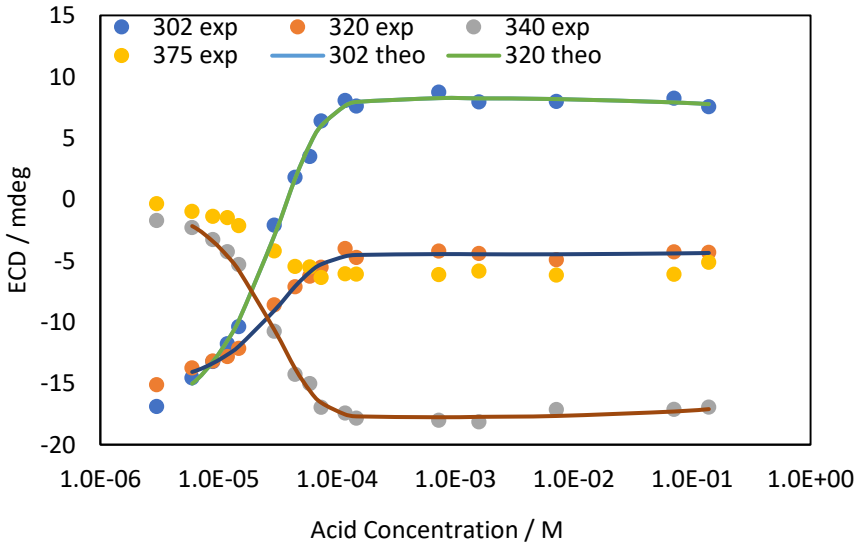


Figure S40. Experimental ECD signals variation with HCl additions at 302, 320 and 340 nm (scatters) and mathematical adjustment (lines) to the processes presented in S39.

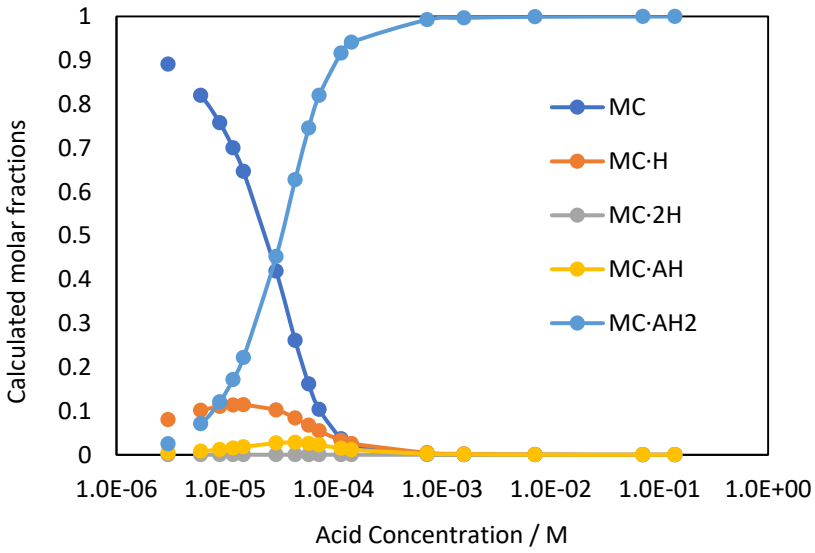


*Figure S41. Representation of the variation in concentration of all formed species during the titration of (P_2)-**3** with HCl.*

3.9 Titration experiment of (P_2)-3 with TFA

A 1.50 x 10^{-05} M solution of (P_2)-**3** in CH_3CN was titrated with different volumes of TFA solutions in acetonitrile (1 x 10^{-03} M to 1 M). To ensure completion of the titration the last additions were made with undiluted acid. In this particular case, the constants were inferred from Brønsted correlation.

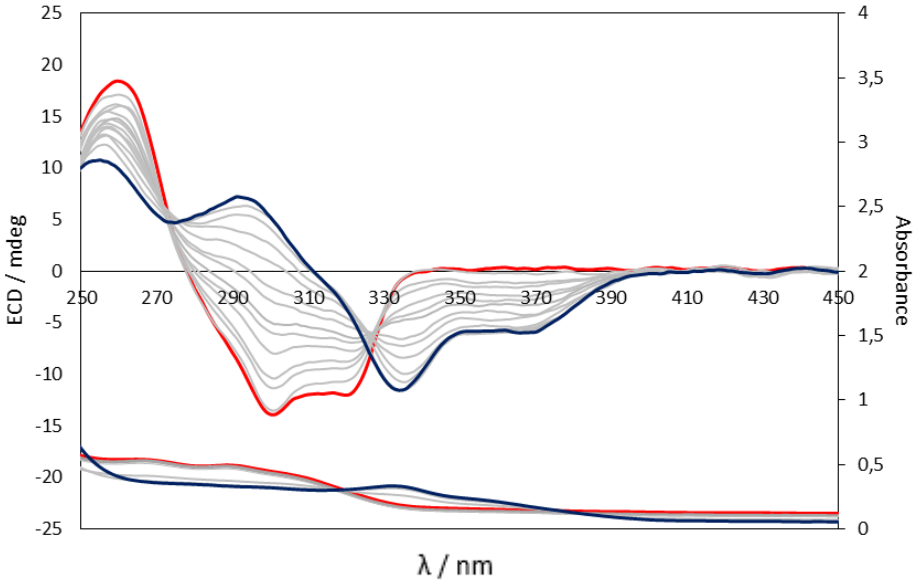


*Figure S42. Change of the ECD and UV/Vis spectra of (P_2)-**3** upon addition of TFA (acid concentration in the cuvette ranging from 0 to 0.5 M). Red line: ECD and UV/Vis signal before adding TFA. Blue line: ECD and UV/Vis signal at the saturation value of TFA. Grey lines: Changes with increasing amounts of acid.*

3.10 Crystallographic data of 3·TfOH

Crystallographic data of (*rac*)-**3·H ·TfO·H_2O**

Crystals suitable for x-ray diffraction could be grown from the slow evaporation of a solution of compound (*rac*)-**3** in acetonitrile with 1 eq. of TfOH at room temperature.

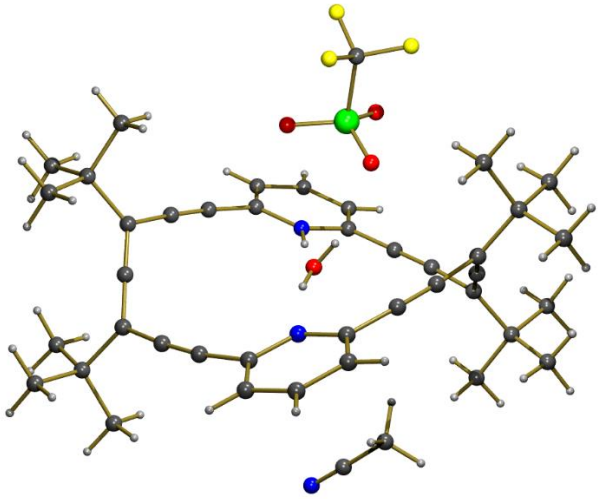


Table S5. Crystal data and structure refinement for (*rac*)-**3H ·TfO·H_2O**

Empirical formula	$C_{43}H_{48}F_3N_3O_4S$	
Formula weight	759.90	
Temperature	100.00 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C1c1	
Unit cell dimensions	a = 20.397(2) Å	α= 90°.
	b = 15.4975(19) Å	β= 117.517(4)°.
	c = 15.0856(17) Å	γ = 90°.
Volume	4229.2(9) $Å^3$	
Z	4	
Density (calculated)	1.193 Mg/m^3	
Absorption coefficient	0.132 mm^{-1}	
F(000)	1608	
Crystal size	0.271 x 0.266 x 0.197 mm^3	
Theta range for data collection	1.931 to 28.297°.	
Index ranges	-27<=h<=27, -19<=k<=20, -20<=l<=20	
Reflections collected	51900	
Independent reflections	10454 [R(int) = 0.0255]	
Completeness to theta = 25.242°	99.9 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6966
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10454 / 5 / 509
Goodness-of-fit on F^2	1.082
Final R indices [I>2sigma(I)]	R1 = 0.0333, wR2 = 0.0919
R indices (all data)	R1 = 0.0348, wR2 = 0.0940
Absolute structure parameter	0.094(17)
Extinction coefficient	n/a
Largest diff. peak and hole	0.296 and -0.273 e.$Å^{-3}$

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	6288(1)	5982(1)	6746(1)	24(1)
F(1)	7229(1)	6978(1)	6480(1)	46(1)
F(2)	7718(1)	5835(1)	7340(1)	41(1)
F(3)	7029(1)	5741(1)	5750(1)	44(1)
O(1)	5717(1)	6363(1)	5842(1)	27(1)
O(2)	6444(1)	6432(2)	7653(1)	41(1)
O(3)	6244(1)	5056(1)	6786(2)	36(1)
C(41)	7111(1)	6143(2)	6581(2)	28(1)
O(1W)	4349(1)	5478(1)	5159(1)	30(1)
N(1)	4878(1)	5236(1)	7177(1)	16(1)
N(2)	3513(1)	5292(1)	2874(1)	19(1)
C(1)	5176(1)	4489(1)	7671(1)	17(1)
C(2)	5483(1)	4472(1)	8708(2)	20(1)
C(3)	5474(1)	5220(1)	9217(2)	22(1)
C(4)	5168(1)	5972(1)	8691(2)	20(1)
C(5)	4875(1)	5978(1)	7650(2)	18(1)
C(6)	4576(1)	6724(1)	7049(2)	20(1)
C(7)	4340(1)	7311(1)	6469(2)	19(1)
C(8)	4024(1)	7960(1)	5706(2)	18(1)
C(9)	4263(1)	7982(1)	5030(2)	20(1)
C(10)	4488(1)	7969(1)	4343(2)	18(1)
C(11)	4136(1)	7340(1)	3562(2)	20(1)

C(12)	3853(1)	6755(1)	2985(2)	20(1)
C(13)	3511(1)	6016(1)	2373(2)	20(1)
C(013)	5555(1)	1994(1)	5784(2)	19(1)
C(14)	3202(1)	6052(2)	1333(2)	30(1)
C(15)	2864(2)	5322(2)	783(2)	38(1)
C(16)	2853(1)	4576(2)	1280(2)	31(1)
C(17)	3193(1)	4580(1)	2323(2)	20(1)
C(18)	3251(1)	3817(1)	2902(2)	20(1)
C(19)	3374(1)	3221(1)	3462(2)	19(1)
C(20)	3570(1)	2571(1)	4226(1)	17(1)
C(21)	4254(1)	2577(1)	4948(2)	18(1)
C(23)	5054(1)	3203(1)	6478(1)	18(1)
C(24)	5132(1)	3761(1)	7067(2)	19(1)
C(25)	3432(1)	8564(1)	5707(2)	19(1)
C(26)	3804(1)	9164(2)	6619(2)	27(1)
C(27)	3087(1)	9088(2)	4741(2)	27(1)
C(28)	2828(1)	8030(2)	5787(2)	28(1)
C(29)	5084(1)	8569(1)	4339(2)	20(1)
C(30)	5453(2)	9067(2)	5327(2)	31(1)
C(31)	4714(1)	9191(2)	3451(2)	28(1)
C(32)	5670(1)	8032(1)	4220(2)	26(1)
C(33)	4926(1)	2588(1)	5698(1)	16(1)
C(34)	5716(1)	1355(1)	6639(2)	25(1)
C(35)	6245(1)	2540(2)	6022(2)	26(1)
C(36)	5324(1)	1502(2)	4804(2)	26(1)
C(37)	2997(1)	1906(1)	4187(2)	18(1)
C(38)	3308(1)	1415(1)	5181(2)	24(1)
C(39)	2281(1)	2369(2)	3995(2)	25(1)
C(40)	2852(1)	1277(1)	3329(2)	24(1)
N(3)	1447(2)	5426(3)	3653(3)	77(1)
C(42)	1722(2)	5932(2)	3390(3)	51(1)
C(43)	2087(2)	6570(2)	3072(3)	62(1)

Crystallographic data of (*rac*)-**$3H_2 \cdot (TfO)_2 \cdot H_2O$**

Crystals suitable for x-ray diffraction could be grown from the slow evaporation of a solution of compound (*rac*)-**3** in acetonitrile:ethanol (1:1) with 10 eq. of TfOH at 4 °C.

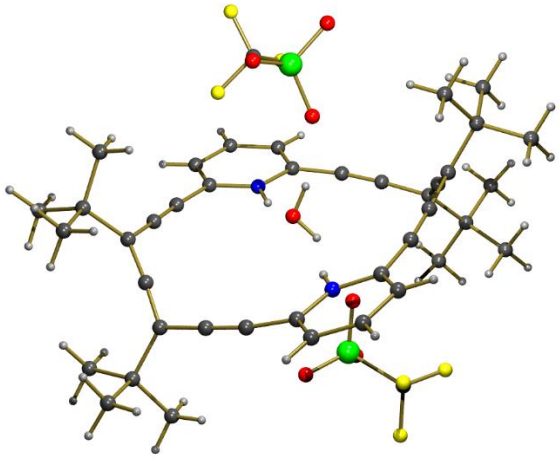


Table S7. Crystal data and structure refinement for (*rac*)-**$3H_2 \cdot (TfO)_2 \cdot H_2O$**

Empirical formula	$C_{42}H_{46}F_6N_2O_7S_2$	
Formula weight	868.93	
Temperature	100.00 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P_{-1}	
Unit cell dimensions	a = 12.3450(13) Å	α= 71.543(3)°.
	b = 12.3737(13) Å	β= 68.335(3)°.
	c = 16.5570(17) Å	γ = 76.357(4)°.
Volume	2209.2(4) $Å^3$	
Z	2	
Density (calculated)	1.306 Mg/m^3	
Absorption coefficient	0.195 mm^{-1}	
F(000)	908	
Crystal size	0.185 x 0.164 x 0.111 mm^3	
Theta range for data collection	2.330 to 26.459°.	
Index ranges	-14<=h<=15, -14<=k<=15, 0<=l<=20	
Reflections collected	83964	
Independent reflections	13252 [R(int) = 0.0886]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.745372 and 0.475353	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	13252 / 2 / 551
Goodness-of-fit on F^2	1.028
Final R indices [I>2sigma(I)]	R1 = 0.0946, wR2 = 0.2517
R indices (all data)	R1 = 0.1118, wR2 = 0.2714
Extinction coefficient	n/a
Largest diff. peak and hole	1.427 and -0.809 e.$Å^{-3}$

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5663(5)	6251(4)	38(3)	39(1)
C(2)	6026(5)	6555(5)	-877(3)	49(1)
C(3)	6946(5)	5858(6)	-1352(4)	51(1)
C(4)	7458(5)	4853(5)	-897(3)	47(1)
C(5)	7063(4)	4559(4)	27(3)	34(1)
C(6)	7503(4)	3543(4)	580(3)	34(1)
C(7)	7746(4)	2722(4)	1130(3)	31(1)
C(8)	7953(4)	1750(4)	1830(3)	29(1)
C(9)	8121(4)	1947(4)	2505(3)	31(1)
C(10)	8297(4)	2133(4)	3183(3)	28(1)
C(11)	7252(4)	2407(4)	3889(3)	30(1)
C(12)	6367(4)	2680(4)	4453(3)	35(1)
C(13)	5309(4)	3146(4)	5029(3)	32(1)
C(14)	5066(5)	2988(5)	5946(3)	44(1)
C(15)	4039(5)	3545(6)	6427(3)	53(2)
C(16)	3260(5)	4284(5)	6005(3)	44(1)
C(17)	3525(4)	4440(4)	5085(3)	30(1)
C(18)	2855(4)	5224(4)	4555(3)	31(1)
C(19)	2431(4)	5893(4)	4012(3)	28(1)
C(20)	1968(4)	6660(4)	3325(3)	27(1)
C(21)	2700(4)	7248(4)	2617(3)	32(1)
C(22)	3376(4)	7900(4)	1887(3)	32(1)
C(23)	4107(4)	7365(4)	1180(3)	36(1)
C(24)	4781(5)	6907(4)	605(3)	38(1)
C(25)	7942(4)	530(4)	1776(3)	31(1)
C(26)	9124(5)	143(5)	1140(3)	46(1)

C(27)	7735(6)	-306(5)	2717(3)	50(1)
C(28)	6923(6)	548(6)	1461(5)	57(2)
C(29)	9500(4)	2106(4)	3253(3)	30(1)
C(30)	10463(5)	2029(5)	2356(3)	41(1)
C(31)	9702(5)	1064(4)	4011(3)	41(1)
C(32)	9535(5)	3213(4)	3466(3)	40(1)
C(33)	3441(5)	9150(4)	1791(3)	40(1)
C(34)	2946(6)	9898(5)	1042(4)	50(1)
C(35)	4711(6)	9314(6)	1556(5)	58(2)
C(36)	2710(5)	9493(5)	2679(4)	44(1)
C(37)	664(4)	6726(4)	3434(3)	30(1)
C(38)	396(5)	7533(5)	2592(3)	43(1)
C(39)	396(5)	5527(4)	3581(3)	37(1)
C(40)	-85(5)	7209(5)	4255(3)	40(1)
N(1)	6187(4)	5256(3)	465(3)	34(1)
N(2)	4524(4)	3859(4)	4645(3)	35(1)
C(41)	8571(6)	6791(5)	407(3)	49(1)
F(1)	7448(5)	7182(4)	437(3)	82(1)
F(2)	9200(4)	7660(4)	-18(2)	71(1)
F(3)	8969(5)	6017(4)	-54(2)	74(1)
O(1)	7889(4)	5283(4)	1918(2)	52(1)
O(2)	8124(4)	7150(4)	1948(2)	51(1)
O(3)	9853(4)	5829(5)	1426(3)	61(1)
S(1)	8624(1)	6209(1)	1554(1)	38(1)
C(42)	3637(5)	1093(5)	4372(3)	46(1)
F(4)	4457(5)	277(5)	4231(3)	103(2)
F(5)	2630(5)	676(5)	4642(3)	93(2)
F(6)	3610(6)	1443(5)	5073(2)	91(2)
O(4)	4756(6)	2775(7)	3290(3)	101(3)
O(5)	3831(7)	1819(4)	2713(3)	88(2)
O(6)	2751(7)	3092(5)	3648(4)	110(3)
S(2)	3722(1)	2313(1)	3401(1)	38(1)
O(1W)	5755(4)	4703(5)	2279(4)	67(1)

3.11 Titration experiment of (P_4)-4 with TfOH

A 6.24 x 10^{-06} M solution of (P_4)-**4** in CH_3CN was titrated with different volumes of TfOH solutions in the same solvent (10^{-4} M to 10^{-2} M).

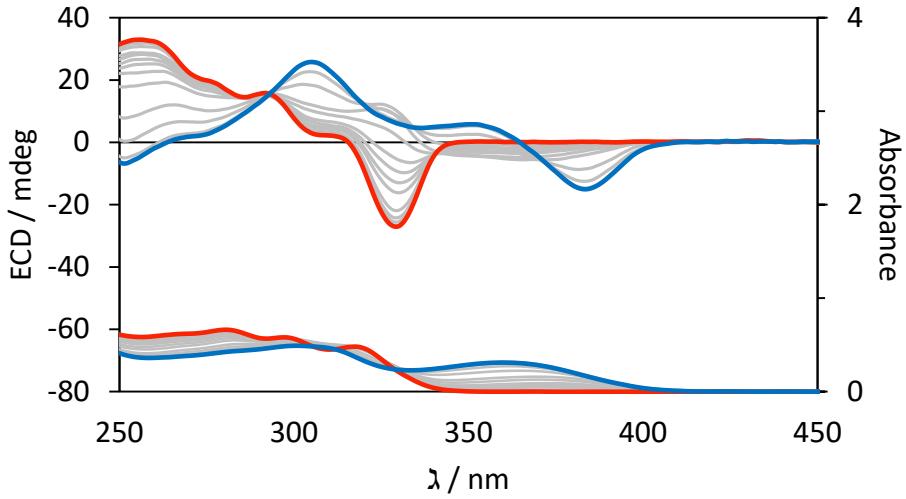


*Figure S43. Change of the ECD and UV/Vis spectra of (P_4)-**4** upon addition of TfOH (acid concentration in the cuvette ranging from 0 to 1.06 x 10^{-03} M). Red line: ECD and UV/Vis signal before adding TfOH. Blue line: ECD and UV/Vis signal at the saturation value of TfOH. Grey lines: Changes with increasing amounts of acid.*

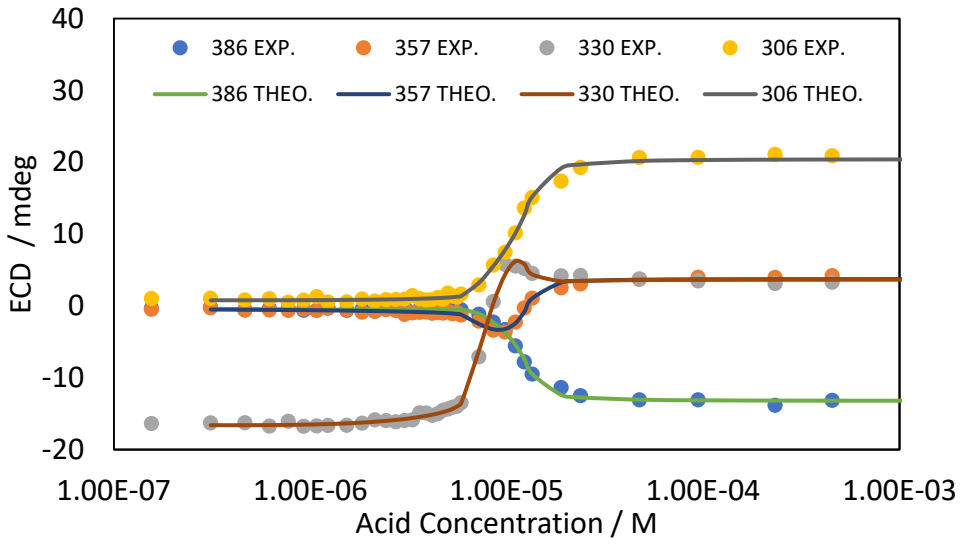


Figure S44. Experimental ECD signals variation with TfOH additions at 306, 330, 357 and 386 nm (scatters) and mathematical adjustment (lines) to the processes presented in S43.

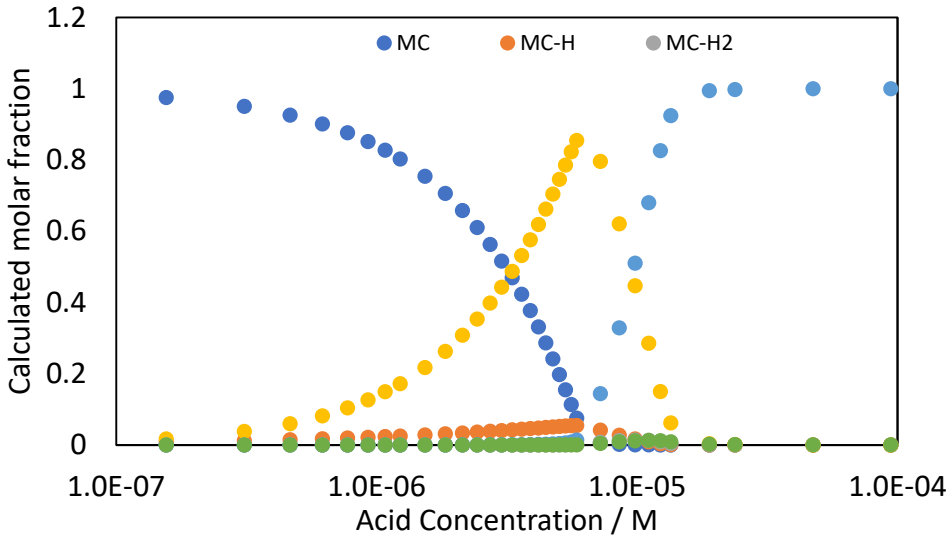


*Figure S45. Representation of the variation in concentration of all formed species during the titration of (P_4)-**4** with TfOH.*

Crystallographic data of TfOH@(P_4)-**4**

Crystals suitable for x-ray diffraction could be grown from the slow evaporation of a mixture of 10 mg of (P_4)-**4** and 12 µL of TfOH in a mixture of EtOH/DCM.

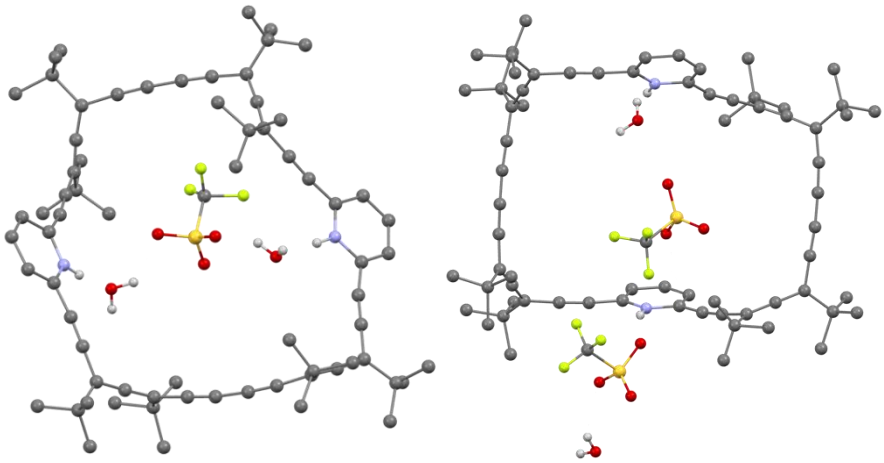


Table S9. Crystal data and structure refinement for TfOH@(P_4)-**4**

Empirical formula	C144 H169.40 F12 N4 O16.70 S4	
Formula weight	2579.67	
Temperature	100.00 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 14.4379(19) Å	a= 109.952(4)°.
	b = 16.1575(19) Å	b= 99.875(4)°.

	c = 18.516(2) Å	g = 104.352(4)°.
Volume	3774.7(8) $Å^3$	
Z	1	
Density (calculated)	1.135 Mg/m^3	
Absorption coefficient	0.136 mm^{-1}	
F(000)	1367	
Crystal size	0.256 x 0.224 x 0.039 mm^3	
Theta range for data collection	2.007 to 25.350°.	
Index ranges	-17<=h<=17, -19<=k<=19, -22<=l<=22	
Reflections collected	168008	
Independent reflections	27587 [R(int) = 0.0824]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7289 and 0.6738	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	27587 / 598 / 1892	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0898, wR2 = 0.2317	
R indices (all data)	R1 = 0.1380, wR2 = 0.2702	
Absolute structure parameter	-0.01(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.498 and -0.349 $e.Å^{-3}$	

Table S10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(2)	11673(6)	9186(6)	6149(5)	59(2)
C(3)	12428(9)	9987(7)	6673(6)	85(3)
C(4)	12877(10)	10638(8)	6399(7)	102(4)
C(5)	12566(8)	10471(7)	5595(6)	86(3)
C(6)	11811(7)	9653(6)	5087(5)	63(2)
C(7)	11482(6)	9435(6)	4260(5)	58(2)
C(8)	11294(6)	9328(6)	3564(6)	58(2)
C(9)	11061(6)	9216(6)	2755(5)	58(2)
C(10)	10351(6)	8451(6)	2231(5)	56(2)

C(11)	9649(6)	7642(6)	1756(5)	59(2)
C(12)	8633(6)	7574(6)	1709(5)	60(2)
C(13)	7782(6)	7497(6)	1726(5)	57(2)
C(14)	6865(6)	7466(6)	1830(5)	55(2)
C(15)	6098(6)	7464(6)	1996(5)	60(2)
C(16)	5175(6)	7443(6)	2192(5)	62(2)
C(17)	4527(6)	6612(6)	2015(5)	58(2)
C(18)	3902(5)	5793(6)	1839(4)	53(2)
C(19)	3867(5)	5453(6)	2456(5)	54(2)
C(20)	3820(6)	5245(7)	3013(5)	64(2)
C(22)	3708(7)	4964(8)	3662(5)	70(2)
C(23)	3182(9)	4075(8)	3542(6)	86(3)
C(24)	3040(9)	3854(9)	4187(7)	93(3)
C(25)	3407(10)	4563(9)	4956(6)	95(3)
C(26)	3907(8)	5449(9)	5059(5)	81(3)
C(27)	4288(7)	6215(9)	5830(6)	82(3)
C(28)	4574(7)	6732(9)	6522(7)	86(3)
C(29)	4890(8)	7397(10)	7355(7)	97(4)
C(30)	5319(9)	7111(10)	7875(7)	101(4)
C(31)	5779(8)	6861(10)	8400(6)	106(4)
C(32)	6849(9)	7067(9)	8527(6)	101(4)
C(33)	7701(9)	7207(9)	8573(5)	91(3)
C(34)	8676(9)	7377(10)	8579(6)	95(3)
C(35)	9538(10)	7506(11)	8541(7)	102(4)
C(36)	10500(9)	7544(10)	8382(7)	101(4)
C(37)	10546(8)	7420(9)	7666(7)	85(3)
C(38)	10548(7)	7177(8)	6910(6)	76(3)
C(39)	10902(7)	7903(7)	6634(5)	68(2)
C(40)	11204(6)	8474(6)	6394(5)	62(2)
C(41)	11683(5)	9981(6)	2538(5)	58(2)
C(42)	11785(6)	10940(6)	3123(6)	67(2)
C(43)	12715(7)	9875(8)	2594(8)	85(3)
C(44)	11183(7)	9841(7)	1684(6)	70(2)
C(45)	9846(6)	6768(6)	1250(6)	69(2)
C(46)	10948(7)	6973(7)	1336(7)	80(3)
C(47)	9234(8)	6418(8)	385(6)	86(3)
C(48)	9505(8)	6027(7)	1593(8)	88(3)
C(49)	4977(7)	8357(7)	2561(6)	77(3)

C(50)	4910(11)	8805(10)	1976(10)	115(4)
C(51)	5818(11)	8961(9)	3350(9)	118(5)
C(52)	3995(9)	8170(9)	2796(10)	109(4)
C(53)	3195(5)	5177(6)	983(4)	55(2)
C(54)	3618(7)	4444(8)	593(6)	77(3)
C(55)	3128(7)	5797(8)	519(6)	76(3)
C(56)	2153(6)	4727(7)	1042(6)	70(2)
C(57)	4735(10)	8297(11)	7551(9)	125(5)
C(58)	5051(13)	8878(14)	8499(10)	172(8)
C(59)	3655(9)	8221(11)	7229(8)	113(4)
C(60)	5384(17)	8863(14)	7177(18)	211(13)
C(61)	5253(11)	6335(16)	8864(8)	150(6)
C(62)	5672(13)	6949(18)	9742(8)	217(11)
C(63)	4144(10)	6139(14)	8587(7)	156(7)
C(64)	5502(19)	5400(20)	8622(16)	211(8)
C(65)	11402(11)	7679(14)	9053(8)	125(5)
C(66)	11226(17)	6788(16)	9206(10)	160(7)
C(67)	11464(12)	8476(17)	9796(10)	170(8)
C(68)	12323(11)	7877(18)	8826(9)	160(8)
C(69)	10234(8)	6156(8)	6325(7)	84(3)
C(70)	11187(9)	5955(9)	6200(8)	99(3)
C(71)	9567(8)	6020(7)	5539(7)	83(3)
C(72)	9677(12)	5513(10)	6675(10)	122(5)
N(1)	11377(5)	9051(5)	5377(4)	57(2)
N(21)	4045(5)	5644(6)	4406(4)	69(2)
C(2')	-255(6)	640(6)	5013(5)	60(2)
C(3')	-786(6)	-202(6)	4961(6)	63(2)
C(4')	-1400(7)	-878(6)	4240(6)	71(2)
C(5')	-1421(7)	-683(6)	3559(6)	69(2)
C(6')	-864(5)	159(5)	3613(5)	51(2)
C(7')	-900(5)	379(6)	2933(5)	56(2)
C(8')	-979(5)	493(5)	2331(5)	51(2)
C(9')	-1056(5)	660(5)	1605(5)	52(2)
C(10')	-441(5)	1443(6)	1646(5)	55(2)
C(11')	174(6)	2226(6)	1696(6)	64(2)
C(12')	1153(6)	2289(6)	1631(5)	55(2)
C(13')	1981(5)	2371(5)	1594(5)	50(2)
C(14')	2965(5)	2488(6)	1607(4)	50(2)

C(15')	3833(5)	2628(6)	1666(4)	51(2)
C(16')	4863(5)	2732(6)	1764(5)	53(2)
C(17')	5541(5)	3508(7)	2306(5)	55(2)
C(18')	6196(5)	4278(6)	2867(5)	53(2)
C(19')	6404(5)	4363(6)	3682(5)	52(2)
C(20')	6557(5)	4476(5)	4375(5)	53(2)
C(22')	6681(5)	4728(6)	5205(5)	54(2)
C(23')	6591(7)	5567(6)	5700(6)	71(2)
C(24')	6673(8)	5760(7)	6491(6)	75(2)
C(25')	6835(7)	5120(6)	6806(5)	69(2)
C(26')	6922(6)	4302(6)	6311(5)	54(2)
C(27')	7016(7)	3596(6)	6580(5)	65(2)
C(28')	6977(8)	2976(7)	6789(6)	73(2)
C(29')	6872(10)	2216(8)	7047(8)	96(4)
C(30')	6712(10)	2376(8)	7742(8)	93(3)
C(31')	6508(9)	2514(9)	8428(8)	95(3)
C(32')	5503(9)	2322(8)	8450(6)	82(3)
C(33')	4659(9)	2191(7)	8487(5)	75(3)
C(34')	3679(8)	2063(7)	8475(5)	71(2)
C(35')	2810(8)	1945(7)	8423(5)	73(2)
C(36')	1776(8)	1847(8)	8277(5)	81(3)
C(37')	1427(9)	2198(8)	7768(6)	92(3)
C(38')	1106(11)	2542(9)	7268(7)	116(4)
C(39')	708(9)	1908(8)	6446(7)	90(3)
C(40')	328(8)	1368(8)	5758(7)	80(3)
C(41')	-1806(6)	-75(6)	833(5)	63(2)
C(42')	-2857(7)	-311(8)	991(7)	90(3)
C(43')	-1546(8)	-958(7)	596(6)	83(3)
C(44')	-1869(10)	276(11)	172(8)	125(6)
C(45')	-144(8)	3085(8)	1785(10)	104(4)
C(46')	-191(9)	3238(10)	1006(11)	124(5)
C(47')	624(13)	3879(9)	2517(14)	168(9)
C(48')	-1154(10)	2933(9)	1963(14)	157(8)
C(49')	5116(6)	1898(7)	1227(5)	64(2)
C(50')	4620(8)	1679(8)	343(6)	82(3)
C(51')	4700(8)	1052(7)	1431(7)	79(3)
C(52')	6234(6)	2153(8)	1364(7)	79(3)
C(53')	6776(6)	5120(6)	2722(5)	57(2)

C(54')	7889(6)	5215(7)	2945(6)	71(2)
C(55')	6617(7)	6008(6)	3264(5)	66(2)
C(56')	6398(7)	4957(8)	1850(6)	77(3)
C(57')	6954(19)	1286(11)	6497(15)	157(6)
C(58')	6820(30)	631(15)	6880(19)	250(11)
C(59')	7914(18)	1423(13)	6307(14)	173(7)
C(60')	6070(20)	874(15)	5794(19)	218(9)
C(61')	7308(10)	2852(15)	9198(11)	136(7)
C(62')	7203(15)	2017(16)	9462(13)	167(8)
C(63')	7190(12)	3692(18)	9810(11)	180(10)
C(64')	8368(11)	3178(19)	9094(13)	193(11)
C(65')	1125(8)	1353(8)	8676(6)	81(3)
C(66')	1183(10)	370(8)	8430(8)	96(3)
C(67')	44(8)	1313(10)	8429(7)	98(3)
C(68')	1561(9)	1906(9)	9591(6)	94(3)
C(69')	1114(17)	3556(11)	7494(9)	161(6)
C(70')	1670(20)	3945(14)	7009(12)	217(9)
C(71')	1711(18)	4119(12)	8355(10)	181(8)
C(72')	-1(17)	3507(11)	7285(11)	174(7)
N(1')	-275(4)	801(4)	4332(4)	51(2)
N(21')	6853(5)	4138(4)	5524(4)	54(2)
C(73)	8219(11)	8460(14)	6664(10)	138(6)
F(1)	7831(12)	8887(14)	7191(7)	253(9)
F(2)	9199(9)	9052(9)	6847(11)	261(9)
F(3)	8405(6)	7726(9)	6838(5)	144(3)
O(1)	7536(8)	8908(6)	5590(8)	134(4)
O(2)	6666(5)	7478(6)	5612(6)	112(3)
O(3)	8210(7)	7653(7)	5271(6)	116(3)
S(1)	7617(2)	8091(2)	5682(2)	80(1)
C(74)	2031(10)	6695(10)	3535(9)	66(3)
F(4)	1751(8)	6040(6)	2804(5)	82(2)
F(5)	1886(9)	7470(7)	3458(8)	79(3)
F(6)	3038(6)	6933(6)	3760(6)	83(2)
O(4)	1788(6)	5628(6)	4283(6)	60(2)
O(5)	1894(7)	7242(7)	4968(6)	66(2)
O(6)	415(5)	6169(5)	3850(5)	62(2)
S(2)	1480(2)	6412(2)	4238(2)	57(1)
C(74B)	1790(20)	6740(20)	3469(16)	157(11)

F(4B)	2530(30)	6570(30)	3160(30)	185(13)
F(5B)	940(20)	6030(20)	3078(19)	166(10)
F(6B)	1690(40)	7510(30)	3400(30)	171(15)
O(4B)	2360(30)	6070(20)	4460(20)	139(11)
O(5B)	3056(19)	7710(20)	4830(20)	160(11)
O(6B)	1300(20)	7090(30)	4780(20)	145(12)
S(2B)	2142(10)	6908(12)	4521(10)	127(4)
C(75)	7193(11)	1862(10)	3514(11)	77(4)
F(7)	6767(13)	1064(9)	3515(11)	174(6)
F(8)	7558(9)	1639(8)	2898(6)	104(3)
F(9)	6531(8)	2221(8)	3343(6)	113(3)
O(7)	7563(15)	2789(13)	4983(9)	118(6)
O(8)	8537(9)	3449(7)	4271(10)	110(4)
O(9)	8816(10)	2133(10)	4517(9)	118(4)
S(3)	8158(3)	2632(3)	4430(3)	74(1)
C(75B)	7870(20)	2230(20)	3535(19)	163(11)
F(7B)	7250(40)	1360(30)	3130(30)	210(16)
F(8B)	8770(30)	2330(30)	3420(20)	177(11)
F(9B)	7510(30)	2860(30)	3402(19)	177(12)
O(7B)	6970(30)	2430(30)	4640(30)	154(15)
O(8B)	8730(30)	3330(20)	4980(20)	157(12)
O(9B)	8190(30)	1590(30)	4610(20)	153(12)
S(3B)	7970(20)	2400(20)	4572(17)	174(11)
C(76)	4487(10)	2178(10)	4730(10)	87(4)
F(10)	5456(8)	2312(9)	4889(9)	105(4)
F(11)	4283(10)	2424(10)	4133(8)	108(4)
F(12)	4044(9)	1270(8)	4454(8)	103(4)
O(10)	4380(10)	2355(10)	6129(10)	86(3)
O(11)	4699(11)	3769(10)	5855(12)	86(3)
O(12)	3050(11)	2545(14)	5273(15)	86(3)
S(4)	4100(5)	2813(5)	5612(5)	61(2)
C(76B)	4177(13)	3429(15)	6743(13)	141(7)
F(10B)	5096(12)	3621(15)	7174(11)	149(6)
F(11B)	3499(14)	2965(15)	6979(13)	156(6)
F(12B)	4051(15)	4238(14)	6846(13)	162(6)
O(10B)	4120(20)	1951(17)	5640(20)	200(11)
O(11B)	4646(16)	3439(17)	5510(13)	141(9)
O(12B)	2885(14)	2710(20)	5397(18)	162(10)

S(4B)	3898(12)	2780(14)	5661(12)	176(7)
O(1W)	9717(4)	7628(4)	4448(4)	66(1)
O(2W)	4917(6)	7390(6)	4690(5)	101(2)
O(3W)	1036(5)	2386(5)	4523(4)	81(2)
O(4W)	673(7)	3950(7)	4489(8)	138(4)
O(5W)	3852(10)	8573(10)	5308(10)	135(5)

3.12 Titration experiment of (P_4)-4 with H_2SO_4

A 6.24 x 10^{-06} M solution of (P_4)-**4** in CH_3CN was titrated with different volumes of H_2SO_4 solutions in the same solvent (4 x 10^{-04} M and 0.1 M). To ensure completion of the titration the last additions were made with undiluted acid.

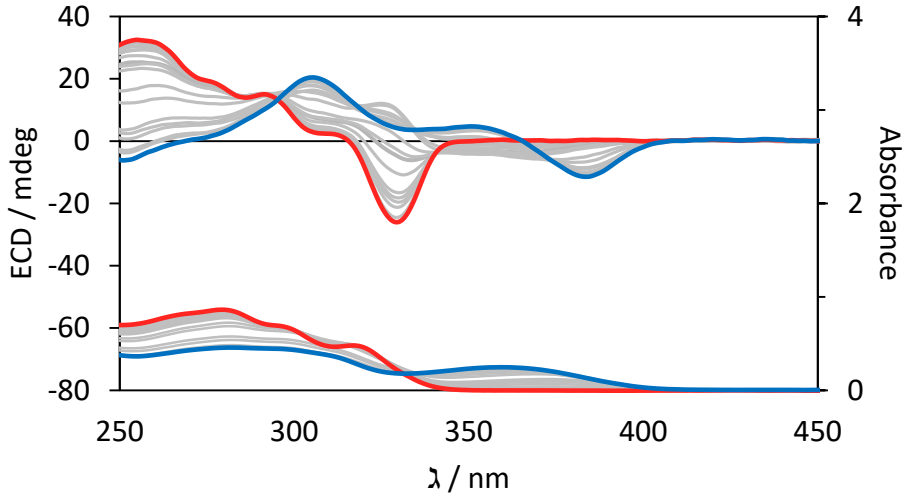


*Figure S46. Change of the ECD and UV/Vis spectra of (P_4)-**4** upon addition of H_2SO_4 (acid concentration in the cuvette ranging from 0 to 0.19 M). Red line: ECD and UV/Vis signal before adding H_2SO_4. Blue line: ECD and UV/Vis signal at the saturation value of H_2SO_4. Grey lines: Changes with increasing amounts of acid.*

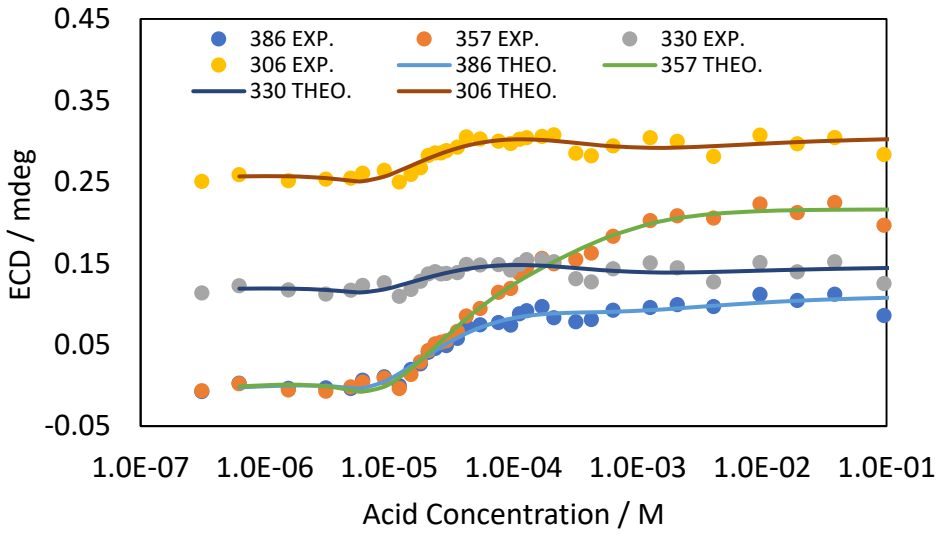


Figure S47. Experimental ECD signals variation with H_2SO_4 additions at 306, 330, 357 and 386 nm (scatters) and mathematical adjustment (lines) to the processes presented in S46.

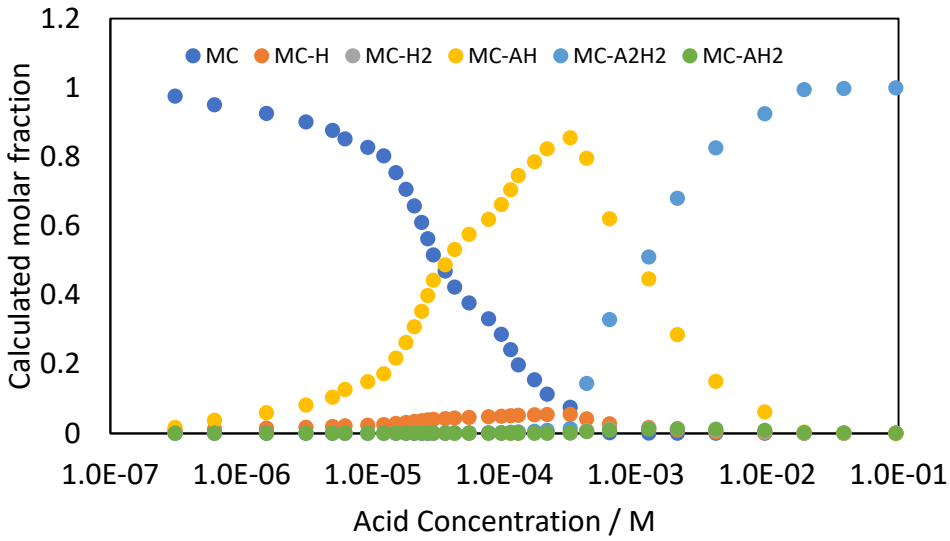


*Figure S48. Representation of the variation in concentration of all formed species during the titration of (P_4)-**4** with H_2SO_4.*

3.13 Titration experiment of (P_4)-4 with TFA

A 6.24 x 10^{-06} M solution of (P_4)-**4** in CH_3CN was titrated with different volumes of TFA solutions in the same solvent (10^{-03} M and 0.3 M). To ensure completion of the titration the last additions were made with undiluted acid.

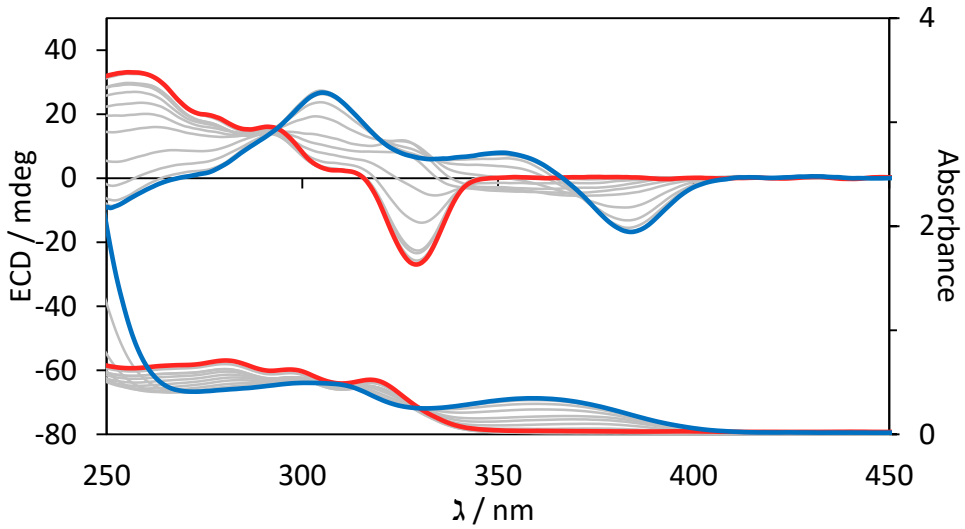


*Figure S49. Change of the ECD and UV/Vis spectra of (P_4)-**4** upon addition of TFA (acid concentration in the cuvette ranging from 0 to 3.8 M). Red line: ECD and UV/Vis signal before adding TFA. Blue line: ECD and UV/Vi signal at the saturation value of TFA. Grey lines: Changes with increasing amounts of acid.*

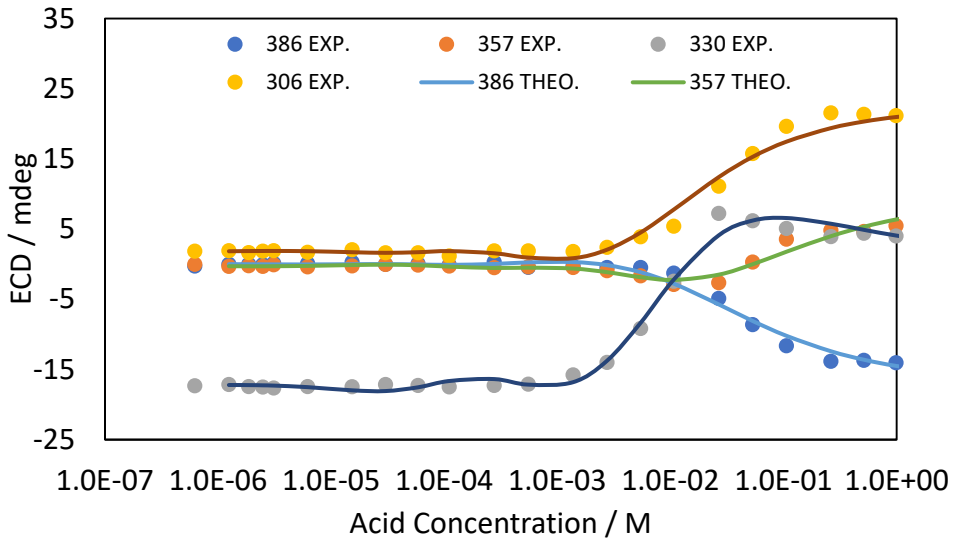


Figure S50. Experimental ECD signals variation with TFA additions at 306, 330, 357 and 386 nm (scatters) and mathematical adjustment (lines) to the processes presented in S49.

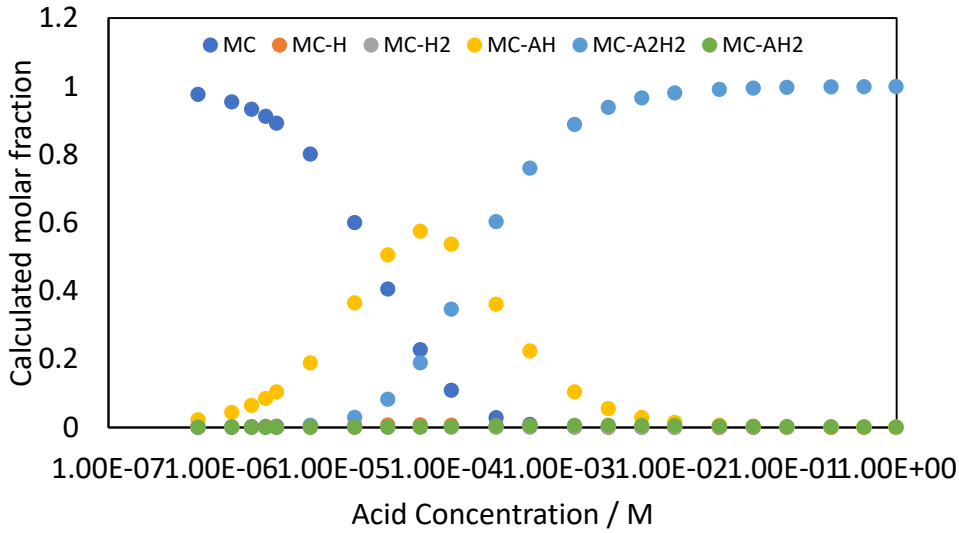


*Figure S51. Representation of the variation in concentration of all formed species during the titration of (P_4)-**4** with TFA.*

3.14 Titration experiment of (P_4)-4 with HCl

A 6.24 x 10^{-06} M solution of (P_4)-**4** in CH_3CN was titrated with different volumes of HCl in dioxane diluted in acetonitrile (4 x 10^{-04} M and 0.1 M). To ensure completion of the titration the last additions were made with the commercial solution of HCl in dioxane (4 M).

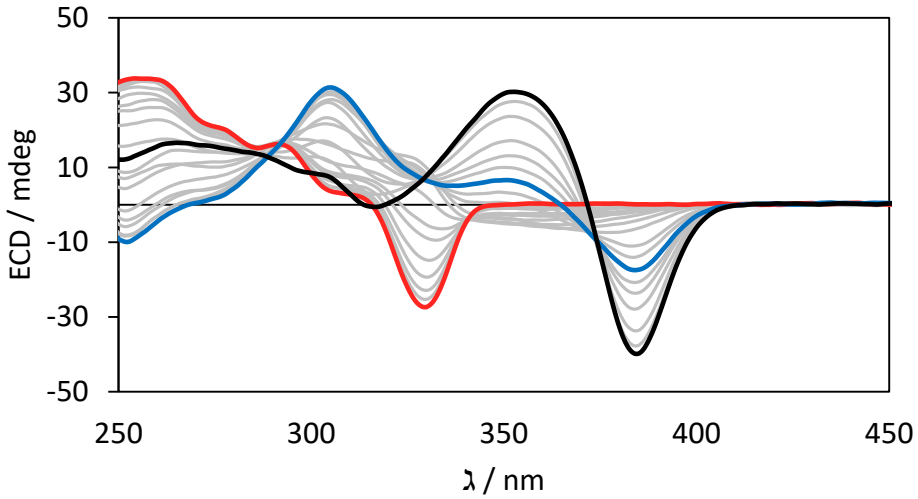


*Figure S52. Change of the ECD and UV/Vis spectra of (P_4)-**4** upon addition of HCl (acid concentration in the cuvette ranging from 0 to 2.4 M). Red line: ECD and UV/Vis signal before adding HCl. Blue line: ECD signal at the first saturation point, being **4**.H_2A_2 the main species, with an HCl concentration of 5.94 x 10^{-03} M. Black line: ECD signal at the saturation value of HCl. Grey lines: Changes with increasing amounts of acid.*

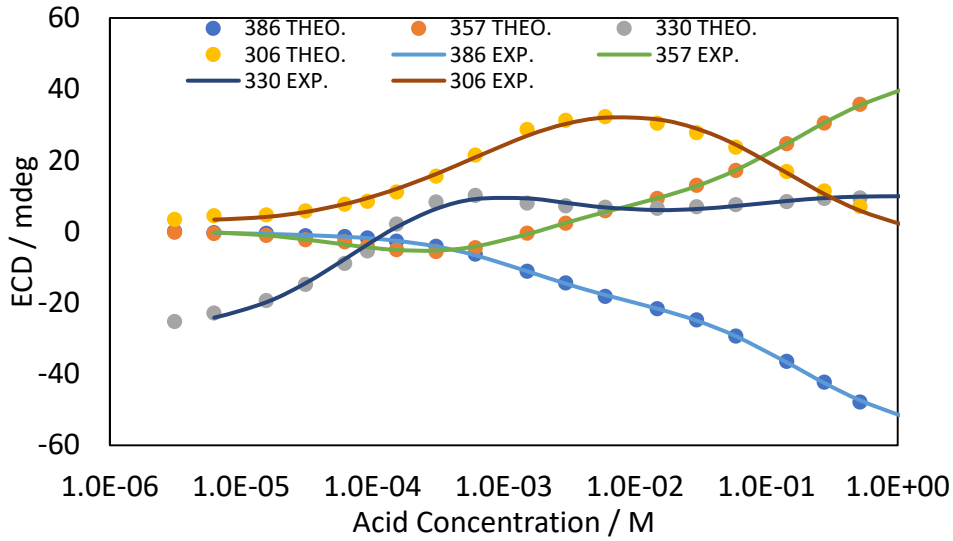


Figure S53. Experimental ECD signals variation with HCl additions at 306, 330, 357 and 386 nm (scatters) and mathematical adjustment (lines) to the processes presented in S52.

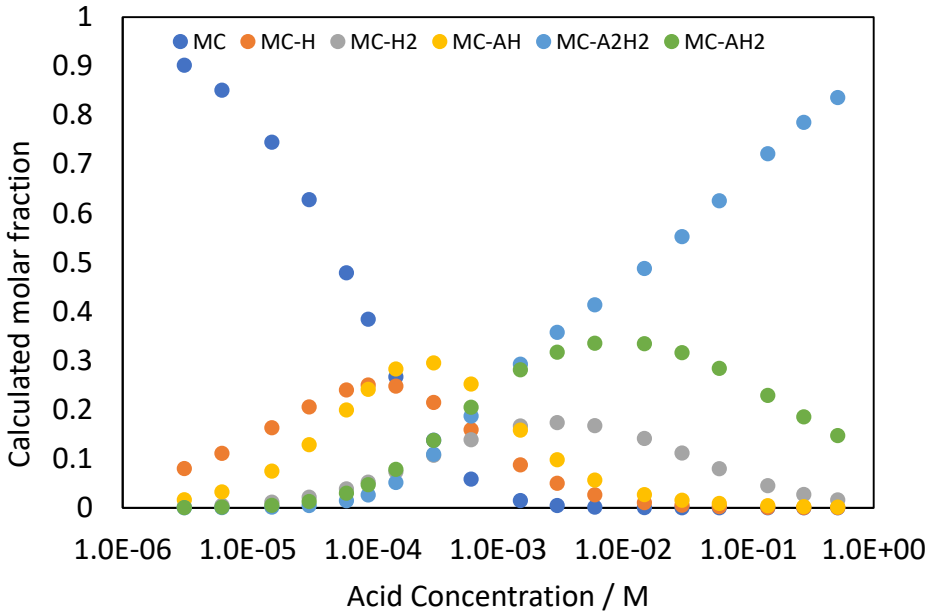


*Figure S54. Representation of the variation in concentration of all formed species during the titration of (P_4)-**4** with HCl.*

3.15 Titration experiment of (P_4)-4 with 1,2-ethanedisulfonic acid

A 6.24 x 10^{-06} M solution of (P_4)-**4** in CH_3CN was titrated with different volumes of 1,2-ethanedisulfonic acid solution in the same solvent (6.24 x 10^{-03} M).

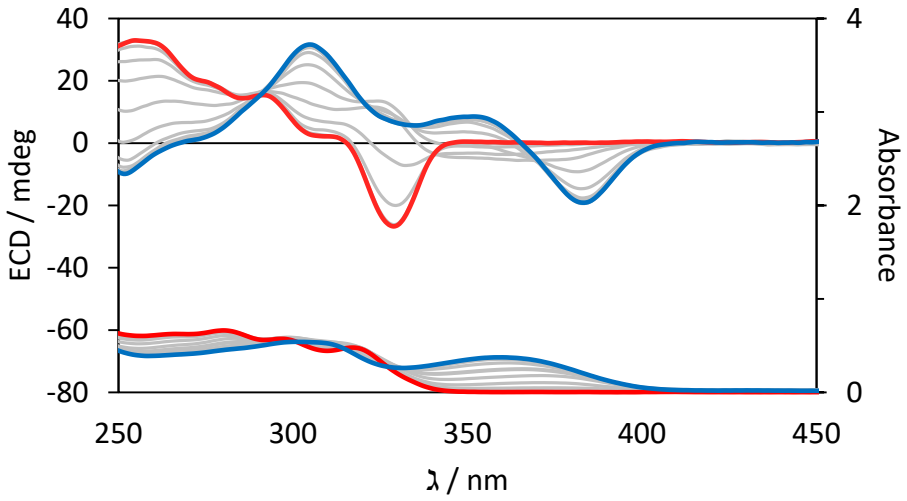


*Figure S55. Change of the ECD and UV/Vis spectra of (P_4)-**4** upon addition of 1,2-ethanedisulfonic acid (acid concentration in the cuvette ranging from 0 to 9.18 x 10^{-05} M). Red line: ECD and UV/Vis signal before adding 1,2-ethanedisulfonic acid. Blue line: ECD and UV/Vis signal at the saturation value of 1,2-ethanedisulfonic acid. Grey lines: Changes with increasing amounts of acid.*

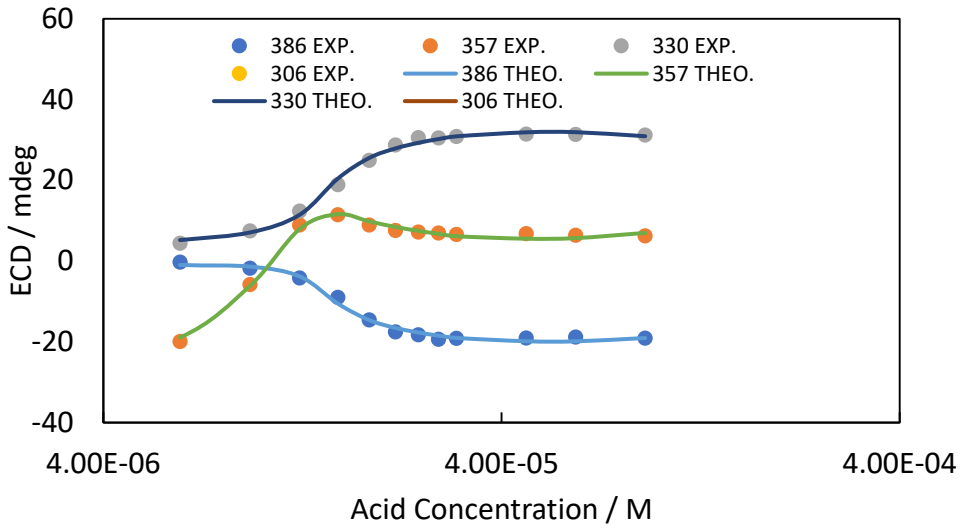


Figure S56. Experimental ECD signals variation with 1,2-ethanedisulfonic acid additions at 306, 330, 357 and 386 nm (scatters) and mathematical adjustment (lines) to the processes presented in S55.

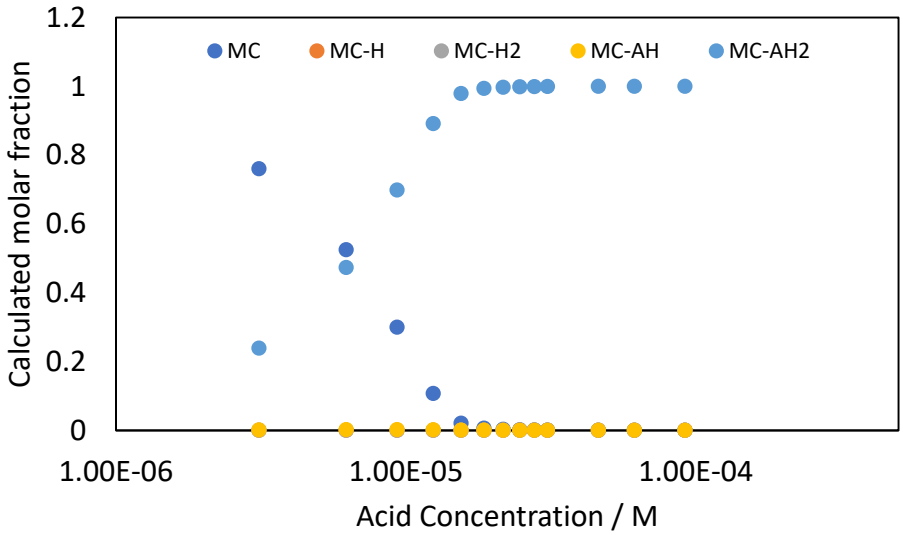


*Figure S57. Representation of the variation in concentration of all formed species during the titration of (P_4)-**4** with 1,2-ethanedisulfonic acid.*

4 Computational Details

The geometry and frequencies of the macrocycles and complexes, as well as their circular dichroism spectra, were computationally calculated using *Gaussian09*[9] and the CAM-B3LYP[10] method with the 6-31g+(d,p) basis set, including solvation effects using the SMD model[11] with acetonitrile parameters. The CAM-B3LYP calculations were performed without symmetry constrains so as not to leave out new conformations that may arise. The tertbutyl groups were replaced by methyl groups to save calculation time, after having verified the overlap of the geometries obtained in both cases. The structures were characterized as minima in the potential surface by analytical computation of vibrational frequencies. Excited state energies and properties have been computed at TD-DFT level. It offers a good compromise between accuracy and feasibility of the computations for systems as large as those investigated here even in cases in which different electronic excited states lie close in energy.[12] For circular dichroism spectra, the first 50 excited states were computed.

4.1 CAM-B3LYP/6-31g+(d,p) XYZ geometries (Å)

(P_2)-2

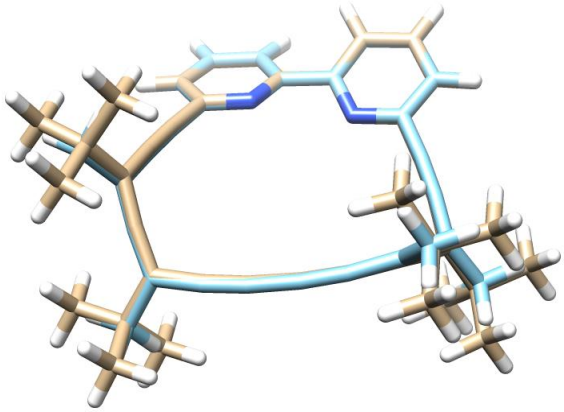
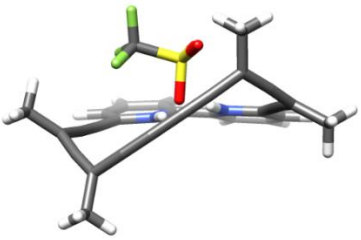


*Figure S58a. Overlay of optimized conformations with tertbutyl (gold) and methyl groups (cyan) for (P_2)-**2** (P-bpy).*

(P_2)-2 (*M*-bpy) – TfOH



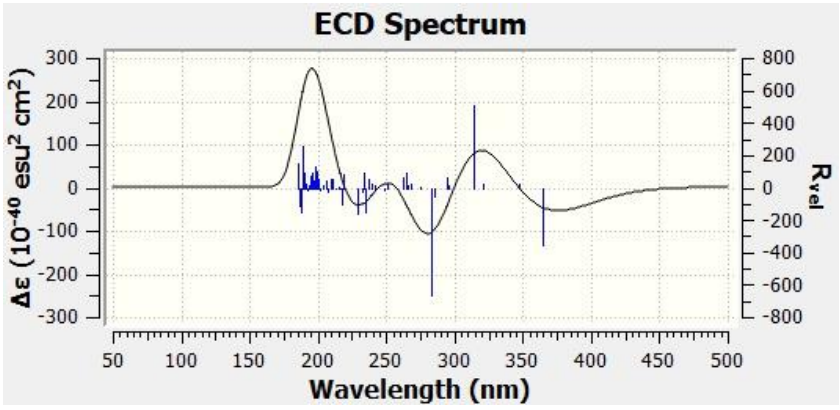


*Figure S58. (P_2)-**2** (M-bpy) – TfOH complex and ECD calculated spectrum.*

N	-1.96026900	-1.92860200	-0.67290600
C	-1.48036300	-3.19186000	-0.70303300
C	-2.34834300	-4.22154200	-1.02493400
C	-3.69686200	-3.93290700	-1.27345200
C	-4.15979000	-2.63390700	-1.20550500
C	-3.25732700	-1.60510600	-0.89056100
C	-0.03650000	-3.44340300	-0.44427800
N	0.85710500	-2.43027400	-0.55421000
C	2.19889900	-2.59510800	-0.43896800
C	2.69893600	-3.87426200	-0.16022600
C	1.80959000	-4.91865900	0.00994200
C	0.43412300	-4.71037100	-0.14185600
C	3.01693100	-1.45460300	-0.58477100
C	3.67192600	-0.43303500	-0.64828100

C	4.39329000	0.80075800	-0.62092000
C	3.95263700	1.76038100	-1.41238500
C	3.39807500	2.69628100	-2.15156300
C	2.23551300	3.30975500	-1.58054900
C	1.18309000	3.63706700	-1.07028200
C	-0.03464400	3.84709300	-0.47541700
C	-1.12569600	3.87770500	0.05620200
C	-2.38841800	3.69098100	0.70487200
C	-2.55157700	4.08866100	2.15307400
C	-3.62097500	-0.24821700	-0.79252600
C	-3.88565500	0.93696000	-0.72334200
C	-4.14311100	2.34110800	-0.71652200
C	-3.30817100	3.07026100	0.00256200
C	-5.27873300	2.88405400	-1.55805100
C	5.52425800	0.94944300	0.37587800
C	3.85738500	3.07877300	-3.53936900
H	-1.99032500	-5.23914300	-1.10914400
H	-4.37792500	-4.74033000	-1.52339500
H	-5.19780900	-2.38073200	-1.38518200
H	-0.25568800	-5.53152900	0.00190300
H	2.17602900	-5.90978300	0.25836200
H	3.77031000	-4.00646600	-0.06697600
H	-5.14357800	2.60757900	-2.60781900
H	-6.23482200	2.47811900	-1.21476300
H	-5.30861900	3.97168100	-1.47906100
H	-1.78739800	3.57916900	2.74540200
H	-2.42062400	5.16960500	2.25693200
H	-3.54047500	3.80707200	2.51823500
H	3.04232100	2.93249200	-4.25369300
H	4.13624800	4.13624100	-3.55496300
H	4.71702800	2.47801100	-3.84063300
H	5.14961100	0.79770200	1.39255900
H	6.30559200	0.20924400	0.18078100
H	5.95469800	1.94891500	0.30082900
H	-1.33434300	-1.12756300	-0.40876900
H	0.53306700	-1.42801800	-0.55491100
O	-0.15214500	-0.00794700	0.01565900
S	-0.45057700	0.07284700	1.50285900
C	1.24170700	0.08471100	2.24622500
O	-1.06007200	1.31914400	1.91380700
O	-1.03950200	-1.19346000	1.94784100
F	1.16934500	0.32701900	3.54513800
F	1.81403400	-1.11709800	2.06675000
F	2.01114100	1.00189600	1.66790300

(P_2)-2 (M-bpy) – H_2SO_4

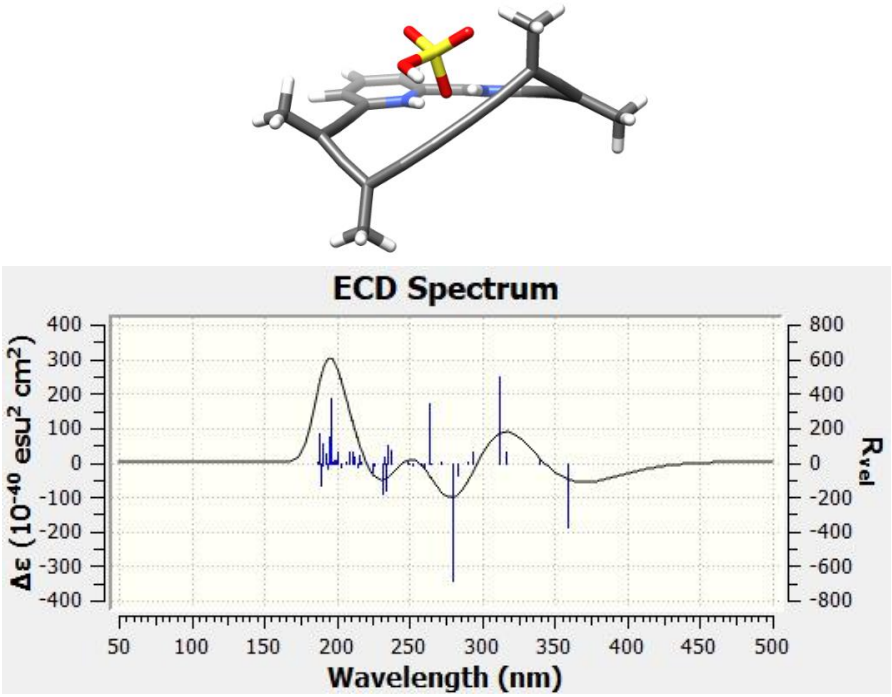
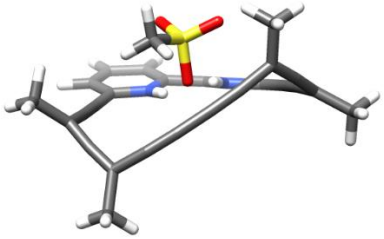


*Figure S59. (P_2)-**2** (M-bpy) – H_2SO_4 complex and ECD calculated spectrum.*

N	-1.88215200	-1.95802400	-0.45108300
C	-1.41369200	-3.22613400	-0.44940500
C	-2.27735200	-4.25056100	-0.79853500
C	-3.61137500	-3.95162200	-1.10609400
C	-4.06408600	-2.64778000	-1.06909700
C	-3.16567200	-1.62461300	-0.72552400
C	0.01553200	-3.48877800	-0.12805200
N	0.92319300	-2.48496000	-0.20865000
C	2.25688400	-2.66141000	-0.03606300
C	2.73231000	-3.94257000	0.27467500
C	1.82648400	-4.97699700	0.41644300
C	0.46069500	-4.75725800	0.20508700
C	3.09137800	-1.52999300	-0.15735500
C	3.75837100	-0.51522100	-0.20222300
C	4.48992000	0.71197100	-0.15537600
C	4.09224500	1.66836200	-0.97307900
C	3.57834000	2.60257800	-1.74312700
C	2.39885200	3.23211700	-1.22694200
C	1.32916700	3.57393000	-0.76430000
C	0.08963200	3.80079100	-0.22306200
C	-1.02242900	3.84648700	0.26189400
C	-2.31303000	3.67754700	0.85847900
C	-2.53297300	4.09002100	2.29498500
C	-3.51989900	-0.26354100	-0.65478800
C	-3.77570600	0.92464500	-0.60721500
C	-4.01954700	2.33114300	-0.62356800
C	-3.20848100	3.05903000	0.12357400
C	-5.11349800	2.87693300	-1.51686700
C	5.57943200	0.85922200	0.88677700
C	4.09921400	2.96799400	-3.11368700
H	-1.92603200	-5.27219600	-0.85866500
H	-4.28916700	-4.75490200	-1.37736700
H	-5.09113400	-2.38657000	-1.29450400
H	-0.24250100	-5.57057400	0.32690400
H	2.17250900	-5.96918100	0.68875700

H	3.79748700	-4.08392600	0.41407500
H	-4.93708300	2.58957500	-2.55755000
H	-6.08706200	2.48312700	-1.21055500
H	-5.13609100	3.96547100	-1.44876200
H	-1.79933200	3.57886700	2.92339200
H	-2.39598500	5.17060200	2.39476000
H	-3.53902400	3.82105900	2.62067600
H	3.31347600	2.82278600	-3.86035700
H	4.38876100	4.02262000	-3.12682300
H	4.96486200	2.35647600	-3.37322800
H	5.16096900	0.72033700	1.88808900
H	6.36102900	0.10998800	0.73123500
H	6.02234800	1.85389400	0.82112700
H	-1.25978300	-1.16075400	-0.16681200
H	0.60820200	-1.48014500	-0.23293500
S	0.07785500	0.21628500	1.62821900
O	-0.13728500	-0.14229200	0.14533600
O	0.53373200	-0.96563100	2.34821000
O	-1.05002000	0.97731400	2.13874800
O	1.36738900	1.18776700	1.58803000
H	1.10579500	2.04875000	1.21724400

(P_2)-2 (*M*-bpy) – MsOH



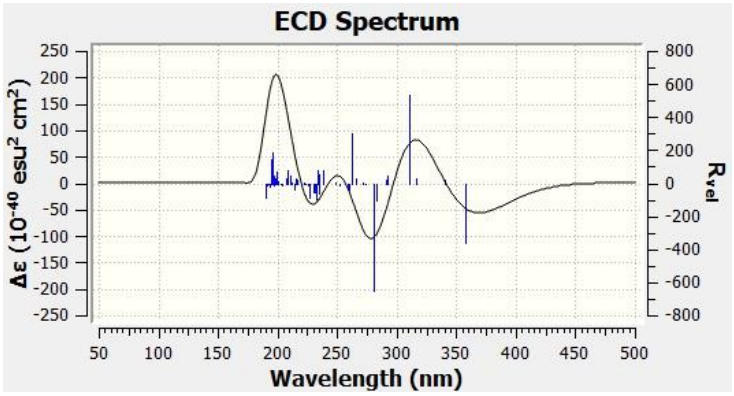
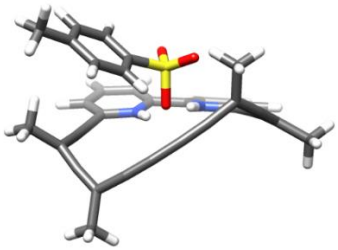


*Figure S60. (P_2)-**2** (M-bpy) – MsOH complex and ECD calculated spectrum.*

N	-1.84429700	-1.90298600	-0.52394000
C	-1.37920700	-3.17284900	-0.53082600
C	-2.24315200	-4.19118700	-0.89667000
C	-3.57355300	-3.88506400	-1.21273500
C	-4.02241000	-2.58015100	-1.16746700
C	-3.12374100	-1.56317000	-0.80664700
C	0.04635600	-3.44313100	-0.19978500
N	0.95775300	-2.44161500	-0.26374500
C	2.28945800	-2.62396600	-0.08097900

C	2.75815500	-3.90949000	0.22177700
C	1.84786800	-4.94222600	0.34624800
C	0.48463300	-4.71608500	0.12537300
C	3.12856100	-1.49419900	-0.18476500
C	3.79913800	-0.48123600	-0.21455000
C	4.53416500	0.74307700	-0.15010700
C	4.14650500	1.70829200	-0.96223200
C	3.64214400	2.65127100	-1.72789700
C	2.46031800	3.27984600	-1.21590200
C	1.38783000	3.62084700	-0.75918700
C	0.14446400	3.84672600	-0.22639200
C	-0.97153000	3.89155600	0.24952400
C	-2.26769000	3.72130800	0.83355400
C	-2.49853000	4.12117500	2.27191400
C	-3.47418100	-0.20163800	-0.72643100
C	-3.72660100	0.98688400	-0.66999300
C	-3.96581600	2.39426100	-0.67534600
C	-3.15882100	3.11254800	0.08537300
C	-5.05038700	2.95186500	-1.57277700
C	5.61523600	0.87711600	0.90256700
C	4.17581700	3.02766400	-3.09053900
H	-1.89458700	-5.21336200	-0.96330700
H	-4.25156600	-4.68358200	-1.49719300
H	-5.04666700	-2.31351600	-1.39913500
H	-0.22215900	-5.52819700	0.23366600
H	2.18840400	-5.93801200	0.61225700
H	3.82165200	-4.05560400	0.36888200
H	-4.86604100	2.67358400	-2.61455200
H	-6.02776900	2.55841700	-1.27840000
H	-5.07009300	4.03979400	-1.49475800
H	-1.77189100	3.60183300	2.90174100
H	-2.35895700	5.20033300	2.38288000
H	-3.50816600	3.85249100	2.58655400
H	3.39600100	2.89194100	-3.84515900
H	4.46882100	4.08141600	-3.09142400
H	5.04169100	2.41575700	-3.34840200
H	5.18783200	0.73032900	1.89896300
H	6.39573900	0.12680900	0.74670200
H	6.06185700	1.87090300	0.84991500
H	-1.21970600	-1.11151000	-0.22887800
H	0.64563400	-1.43496700	-0.28002700
C	1.15604900	1.16595700	2.15047400
H	2.10689700	0.78311200	1.78365900
H	1.17241500	1.25603600	3.23702100
H	0.91395900	2.12006700	1.68612400
S	-0.12764300	-0.00018000	1.75060000
O	-0.08347900	-0.12137300	0.20313200
O	0.25477100	-1.30739500	2.31746900
O	-1.40649900	0.56814400	2.17484800

(P_2)-2 (*M*-bpy) – TsOH



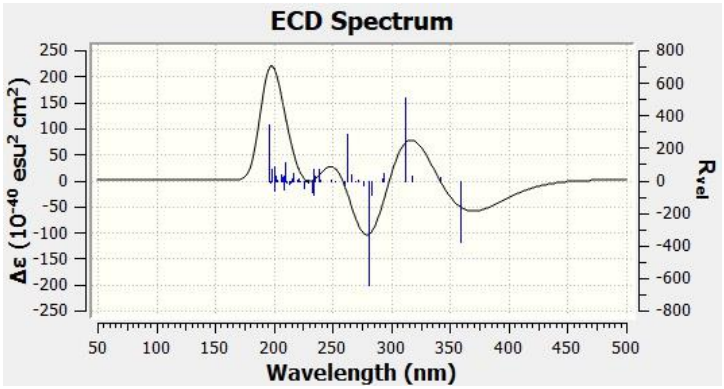
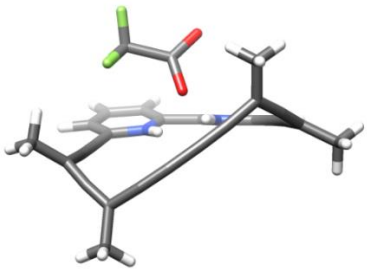


*Figure S61. (P_2)-**2** (M-bpy) – TsOH complex and ECD calculated spectrum.*

N	-2.91314500	-1.27107300	-0.32770200
C	-2.85488000	-2.62151400	-0.34459600
C	-4.04086400	-3.33390600	-0.40110400
C	-5.25977800	-2.64266200	-0.40300000
C	-5.28333400	-1.26298300	-0.35554000
C	-4.06705900	-0.56235300	-0.31252400
C	-1.53399700	-3.30717200	-0.35462300
N	-0.42124900	-2.62684600	-0.72359900
C	0.80030400	-3.20099500	-0.86098300
C	0.93827900	-4.56675300	-0.57880800
C	-0.16704000	-5.27694200	-0.14920400
C	-1.41461600	-4.65169600	-0.04452100
C	1.87356300	-2.37675900	-1.26092300
C	2.77698500	-1.61286200	-1.53830800
C	3.82552000	-0.66645300	-1.75795500
C	3.53690600	0.36741000	-2.52561300
C	3.14644100	1.41539600	-3.21778000
C	2.37317600	2.37272600	-2.48324700
C	1.60291700	3.02268500	-1.80549100
C	0.66169500	3.61462800	-1.00264800
C	-0.22946100	3.99534300	-0.27131500
C	-1.32076500	4.22565100	0.62652500
C	-1.04342600	4.68227000	2.03955100
C	-3.97447400	0.84181400	-0.26013100
C	-3.84791300	2.05139900	-0.24082600
C	-3.66184700	3.46545300	-0.30239900
C	-2.51255600	3.91046600	0.17400800
C	-4.73266900	4.32013400	-0.94696000
C	5.13390200	-0.85991700	-1.01937000
C	3.39265600	1.60811800	-4.69612600
H	-4.03331800	-4.41385800	-0.46763600
H	-6.18964500	-3.20109800	-0.44479700
H	-6.20975500	-0.70123900	-0.34827400
H	-2.27277900	-5.21284400	0.30113200
H	-0.07272700	-6.32797000	0.10527700
H	1.91377200	-5.02572800	-0.68729900

H	-4.91445700	3.99505800	-1.97555000
H	-5.67036100	4.24044600	-0.38917900
H	-4.41529500	5.36380900	-0.95600900
H	-0.36080200	3.97077500	2.51093500
H	-0.57331400	5.66975200	2.02371700
H	-1.96940500	4.73134700	2.61462400
H	2.43878600	1.71046700	-5.22114300
H	3.96763900	2.52472200	-4.85575000
H	3.94582800	0.76284700	-5.10865100
H	4.95684400	-0.86717100	0.06027100
H	5.59486800	-1.81104600	-1.30098100
H	5.81954000	-0.04696200	-1.26197900
H	-2.03311600	-0.70153800	-0.26079200
H	-0.42021200	-1.57360500	-0.74528000
S	-0.42228500	-0.06647600	1.46375900
O	-0.55278000	-0.10947300	-0.07926300
O	-0.89991100	-1.36688300	1.98149500
O	-1.05900900	1.14066000	1.98458300
C	1.31823000	0.03336100	1.82677700
C	2.04258200	1.15196000	1.42532400
C	1.91351000	-0.96435900	2.58781900
C	3.37673900	1.26158000	1.78978100
H	1.56546600	1.93005900	0.84163800
C	3.25209900	-0.83736200	2.94813800
H	1.32396700	-1.81478300	2.91083400
C	4.00077700	0.27595500	2.56358000
H	3.94178200	2.13555700	1.47855000
H	3.71582600	-1.61045600	3.55383700
C	5.43238200	0.43679900	3.00180000
H	6.04083300	0.90372800	2.22279700
H	5.49348400	1.07746000	3.88780800
H	5.88356700	-0.52387000	3.26048400

(*P*$_2$)-2 (*M*-bpy) – TFA



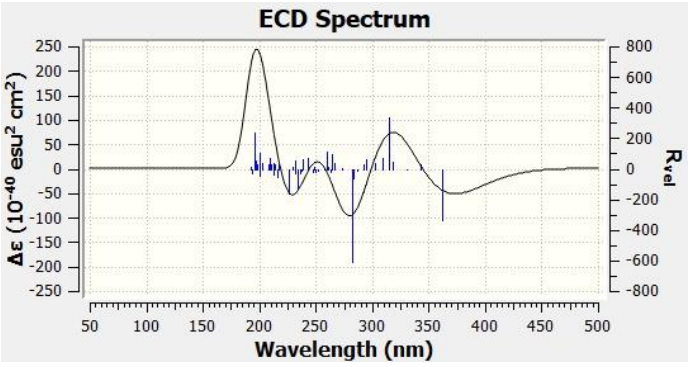
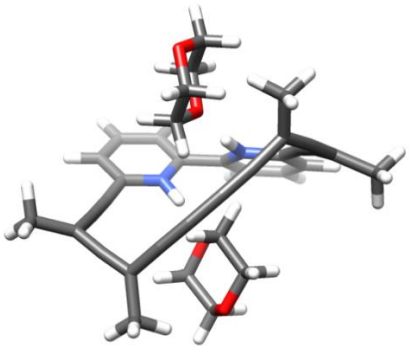


*Figure S62. (P$_2$)-**2** (M-bpy) – TFA complex and ECD calculated spectrum.*

N	-1.96026900	-1.92860200	-0.67290600
C	-1.48036300	-3.19186000	-0.70303300
C	-2.34834300	-4.22154200	-1.02493400
C	-3.69686200	-3.93290700	-1.27345200
C	-4.15979000	-2.63390700	-1.20550500
C	-3.25732700	-1.60510600	-0.89056100
C	-0.03650000	-3.44340300	-0.44427800
N	0.85710500	-2.43027400	-0.55421000
C	2.19889900	-2.59510800	-0.43896800
C	2.69893600	-3.87426200	-0.16022600
C	1.80959000	-4.91865900	0.00994200
C	0.43412300	-4.71037100	-0.14185600
C	3.01693100	-1.45460300	-0.58477100
C	3.67192600	-0.43303500	-0.64828100
C	4.39329000	0.80075800	-0.62092000
C	3.95263700	1.76038100	-1.41238500
C	3.39807500	2.69628100	-2.15156300
C	2.23551300	3.30975500	-1.58054900
C	1.18309000	3.63706700	-1.07028200
C	-0.03464400	3.84709300	-0.47541700
C	-1.12569600	3.87770500	0.05620200
C	-2.38841800	3.69098100	0.70487200
C	-2.55157700	4.08866100	2.15307400
C	-3.62097500	-0.24821700	-0.79252600
C	-3.88565500	0.93696000	-0.72334200
C	-4.14311100	2.34110800	-0.71652200
C	-3.30817100	3.07026100	0.00256200
C	-5.27873300	2.88405400	-1.55805100
C	5.52425800	0.94944300	0.37587800
C	3.85738500	3.07877300	-3.53936900
H	-1.99032500	-5.23914300	-1.10914400
H	-4.37792500	-4.74033000	-1.52339500
H	-5.19780900	-2.38073200	-1.38518200
H	-0.25568800	-5.53152900	0.00190300
H	2.17602900	-5.90978300	0.25836200
H	3.77031000	-4.00646600	-0.06697600
H	-5.14357800	2.60757900	-2.60781900
H	-6.23482200	2.47811900	-1.21476300
H	-5.30861900	3.97168100	-1.47906100
H	-1.78739800	3.57916900	2.74540200
H	-2.42062400	5.16960500	2.25693200
H	-3.54047500	3.80707200	2.51823500
H	3.04232100	2.93249200	-4.25369300
H	4.13624800	4.13624100	-3.55496300
H	4.71702800	2.47801100	-3.84063300
H	5.14961100	0.79770200	1.39255900
H	6.30559200	0.20924400	0.18078100
H	5.95469800	1.94891500	0.30082900
H	-1.33434300	-1.12756300	-0.40876900
H	0.53306700	-1.42801800	-0.55491100
C	1.11051407	-1.79154842	2.83009158
F	1.01786216	-1.82789675	4.17641785
F	1.48807671	-3.00406676	2.37211152
F	2.02595180	-0.86824715	2.46678932
C	-0.47216743	-1.36228507	2.13781112
O	-1.67463386	-1.77013576	2.79555902
O	-0.54118108	-0.60957674	0.92390532

(P_2)-2 (*M*-bpy) – Dioxane



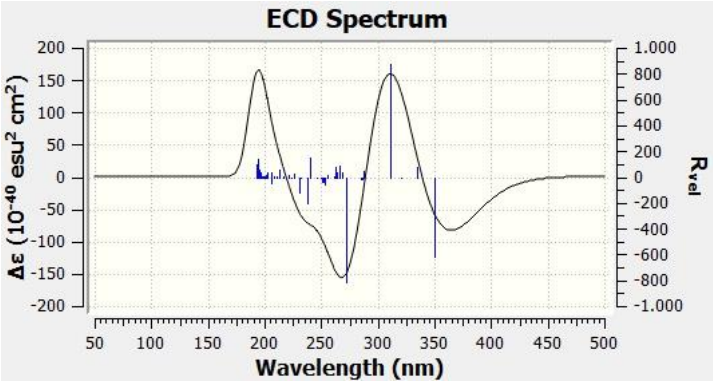
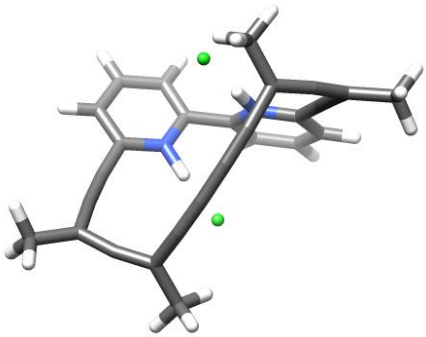


*Figure S63. (P_2)-**2** (M-bpy) – (Dioxane)$_2$ complex and ECD calculated spectrum.*

N	1.28045600	2.33715900	-0.56660800
C	0.42935000	3.37044500	-0.78911800
C	0.72872500	4.31045500	-1.74825600
C	1.91159700	4.16545100	-2.48832300
C	2.73804000	3.08001900	-2.27899600
C	2.40580600	2.13460000	-1.29633800
C	-0.81254600	3.40058600	0.02408600
N	-1.54800800	2.26235300	0.05294700
C	-2.65618000	2.11589300	0.82050600
C	-3.09667500	3.21874300	1.56870300
C	-2.38971300	4.40332700	1.51550400
C	-1.21988900	4.49890400	0.74700300
C	-3.27951000	0.85240400	0.85355200
C	-3.72063500	-0.27297400	0.97557900
C	-4.15057600	-1.61524000	1.20236100
C	-3.62369600	-2.54289100	0.42438900
C	-3.02401100	-3.43065400	-0.33578700
C	-1.67316500	-3.75832400	0.01531600
C	-0.48497200	-3.84851300	0.24179000
C	0.86423300	-3.76976600	0.46948000
C	2.04535300	-3.55222300	0.63967700
C	3.38263500	-3.08303900	0.85830700
C	4.12551900	-3.48204200	2.11328300
C	3.15368400	0.96316800	-1.06547900
C	3.70460500	-0.11647800	-0.98461400
C	4.25043300	-1.43515500	-1.00129300
C	3.85670700	-2.26388200	-0.05257300
C	5.15469800	-1.82690100	-2.15307200

C	-5.09872400	-1.89352000	2.35068900
C	-3.62754800	-4.02131100	-1.59043100
H	0.04623600	5.12977100	-1.93921200
H	2.16619400	4.90058000	-3.24469500
H	3.64224200	2.93491200	-2.85689200
H	-0.63032500	5.40773300	0.73626800
H	-2.72880500	5.26092300	2.08731800
H	-3.98836900	3.11604000	2.17460100
H	4.66126000	-1.65020400	-3.11222700
H	6.07499300	-1.23753000	-2.12839600
H	5.41684600	-2.88235000	-2.08133400
H	3.53498800	-3.24667000	3.00215900
H	4.29887900	-4.56131700	2.10431100
H	5.08784000	-2.97339200	2.17407000
H	-3.02720400	-3.74044000	-2.46034300
H	-3.63520400	-5.11145700	-1.51528800
H	-4.65077800	-3.67157500	-1.72969300
H	-4.68481000	-1.52561000	3.29303000
H	-6.05698300	-1.39590800	2.18057900
H	-5.27465100	-2.96542300	2.43910200
H	1.11111000	1.72089100	0.26991900
H	-1.30522700	1.48280300	-0.62423800
C	0.30589000	-0.08183200	2.26879900
C	1.26932600	-0.83046700	3.16851000
O	1.66101900	-0.01572200	4.25420500
C	2.30088800	1.16136700	3.80365600
C	1.36085900	1.95696800	2.91831400
O	0.90436600	1.14819800	1.81506500
H	0.06181100	-0.66445900	1.37852100
H	-0.61536700	0.15894300	2.81333300
H	2.15086300	-1.14185800	2.59059000
H	0.78754700	-1.71733800	3.58518200
H	2.57204700	1.74126600	4.68809900
H	3.21802500	0.90852700	3.25145900
H	0.48733300	2.28772800	3.49353900
H	1.86327800	2.82639200	2.48662900
C	-2.01030000	-0.39074800	-3.97180400
C	-2.27876100	0.38411700	-2.69706400
O	-1.06497000	0.51392900	-1.91995600
C	-0.45418800	-0.76977700	-1.67026300
C	-0.23847900	-1.51859700	-2.97069900
O	-1.46437300	-1.65898500	-3.66026500
H	-2.94298300	-0.56154000	-4.51294200
H	-1.32223200	0.16668300	-4.62335100
H	-3.03030800	-0.13393700	-2.09003300
H	-2.61815200	1.39953400	-2.91410300
H	0.49835200	-0.57231400	-1.17264100
H	-1.10419600	-1.34633900	-1.00503600
H	0.49011600	-0.98877200	-3.60196300
H	0.13747000	-2.52292000	-2.76543200

(P_2)-2 (*M*-bpy) – HCl



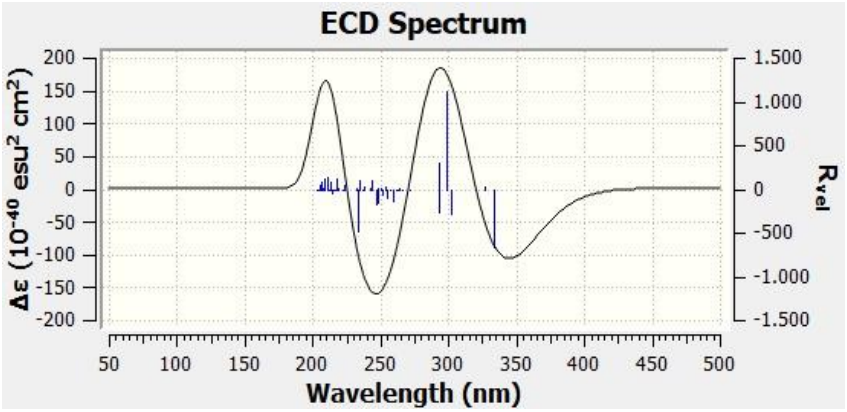


*Figure S64. (P_2)-**2** (M-bpy) – $(HCl)_2$ complex and ECD calculated spectrum.*

N	1.49801400	1.92354800	-0.22237200
C	0.59708500	2.89016100	-0.44795900
C	0.77514700	3.79883200	-1.47156800
C	1.90073400	3.66762900	-2.28420600
C	2.80151100	2.64278700	-2.06218100
C	2.58095300	1.75406200	-1.00462600
C	-0.59732200	2.89007800	0.44776000
N	-1.49839100	1.92374100	0.22164000
C	-2.58143400	1.75413300	1.00370500
C	-2.80194300	2.64247400	2.06158600
C	-1.90098700	3.66707500	2.28415600
C	-0.77528300	3.79839300	1.47172100
C	-3.42175800	0.65086300	0.71739300
C	-3.99755500	-0.38043100	0.45344200
C	-4.52378400	-1.67121600	0.13080400
C	-3.78048200	-2.35640500	-0.71447800
C	-2.85956700	-2.86817500	-1.49896600
C	-1.66979900	-3.35031100	-0.86841400
C	-0.60553900	-3.53692400	-0.31797200
C	0.60585300	-3.53684600	0.31976000
C	1.67017000	-3.35004700	0.87002400
C	2.86016300	-2.86760800	1.50006000
C	2.91545600	-2.80378100	3.00786900
C	3.42107600	0.65056500	-0.71864400
C	3.99679600	-0.38074600	-0.45460000
C	4.52301800	-1.67139900	-0.13164200
C	3.78042400	-2.35620600	0.71457000
C	5.77337800	-2.17375200	-0.81184000
C	-5.77468400	-2.17300600	0.81032200

C	-2.91431800	-2.80513600	-3.00692900
H	0.02886000	4.56144400	-1.65473800
H	2.05702300	4.35670300	-3.10701400
H	3.66952500	2.50158900	-2.69326700
H	-0.02881500	4.56073600	1.65525500
H	-2.05724700	4.35580200	3.10725800
H	-3.67004500	2.50116100	2.69252400
H	5.64635900	-2.17022900	-1.89835300
H	6.62667400	-1.53303400	-0.57083800
H	5.99677700	-3.19081100	-0.48758400
H	2.15068000	-2.10085100	3.35131500
H	2.71617900	-3.78755200	3.44065600
H	3.89190200	-2.45269200	3.34369400
H	-2.14947100	-2.10231800	-3.35042500
H	-2.71483200	-3.78913200	-3.43910300
H	-3.89070100	-2.45432300	-3.34321400
H	-5.64851200	-2.16891300	1.89693500
H	-6.62770800	-1.53229000	0.56834200
H	-5.99803300	-3.19020500	0.48646600
H	1.36615200	1.30494600	0.72329700
H	-1.36621200	1.30527500	-0.72434800
Cl	-1.09055900	0.67400600	-2.32405100
Cl	1.09174900	0.67559900	2.32483800

(P_2)-3-tertbuthyl

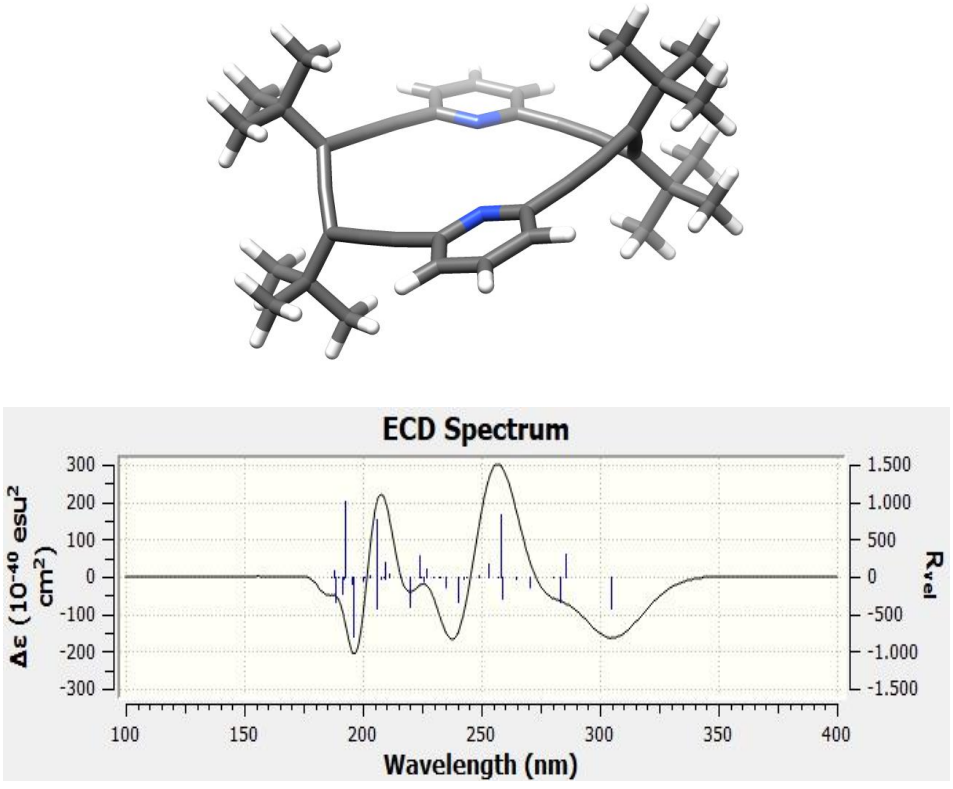


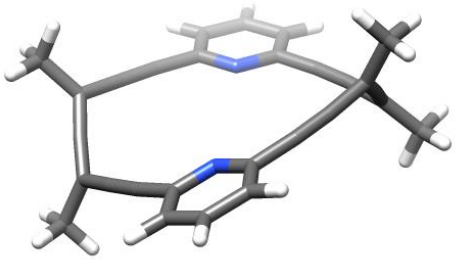
*Figure S65a. (P_2)-**3**-tertbuthyl and ECD calculated spectrum.*

N	-0.00272800	-0.03004600	2.95179800
C	-0.20693600	1.11598500	3.65099500
C	-0.41469500	2.29117000	2.86209600
C	-0.58708700	3.21286700	2.08183400
C	-0.82711900	4.20716000	1.07547800

C	0.00018900	4.27322400	0.04333000
C	0.82730200	4.22850100	-0.99010800
C	0.58733200	3.25485500	-2.01646100
C	0.41473700	2.34910200	-2.81513000
C	0.20648500	1.19019500	-3.62761600
N	0.00335800	0.03003100	-2.95181000
C	-0.19901600	-1.11606400	-3.65143700
C	-0.40842500	-2.29125000	-2.86297400
C	-0.58239200	-3.21295900	-2.08307600
C	-0.82436600	-4.20725900	-1.07719000
C	0.00082900	-4.27317900	-0.04334200
C	0.82579300	-4.22840900	0.99181300
C	0.58356900	-3.25480000	2.01767900
C	0.40912900	-2.34908700	2.81598900
C	0.19890600	-1.19022200	3.62803100
C	0.20391700	-1.24060900	5.03669800
C	-0.21705100	1.13742800	5.06038300
C	-0.00783400	-0.05880100	5.75039400
C	0.21485800	1.24051400	-5.03627000
C	-0.20575500	-1.13757700	-5.06084300
C	0.00495400	0.05864700	-5.75041200
H	0.36748200	-2.18392600	5.54447000
H	-0.38252300	2.07012200	5.58681500
H	-0.00979600	-0.06995500	6.83533200
H	0.37953800	2.18382500	-5.54369400
H	-0.36983500	-2.07031800	-5.58762600
H	0.00558100	0.06974500	-6.83535200
C	-2.08430700	5.10550200	1.22753200
C	-3.34034100	4.19904000	1.28595100
H	-3.27688300	3.48819400	2.11618200
H	-4.23900800	4.81241800	1.42479400
H	-3.45206500	3.62830900	0.35749000
C	-1.95964300	5.90988900	2.54641000
H	-1.09050600	6.57706300	2.51670500
H	-2.85688900	6.52130400	2.70154200
H	-1.84783800	5.24029900	3.40600100
C	-2.20737500	6.07675600	0.03640600
H	-1.33869300	6.74171500	-0.02762700
H	-2.29039100	5.53392300	-0.91135800
H	-3.10309700	6.69717800	0.15494400
C	2.08410900	5.13020600	-1.12396100
C	1.95812200	5.96268700	-2.42520400
H	2.85534800	6.57707400	-2.56827000
H	1.84534300	5.31152300	-3.29873700
H	1.08917500	6.62927000	-2.38046000
C	2.20790900	6.07558400	0.08769900
H	1.33810000	6.73730600	0.16801600
H	2.29383700	5.51250100	1.02332300
H	3.10228600	6.70006700	-0.01908100
C	3.34029800	4.22555700	-1.20303400
H	3.45232200	3.63418000	-0.28762600
H	3.27677100	3.53353000	-2.04900200
H	4.23882800	4.84204600	-1.32828000
C	-2.08114300	-5.10574100	-1.23180000
C	-2.20648000	-6.07710300	-0.04100200
H	-1.33788400	-6.74201400	0.02467100
H	-2.29139200	-5.53436200	0.90664400
H	-3.10193000	-6.69756500	-0.16136300
C	-3.33715800	-4.19940800	-1.29263000
H	-3.45073300	-3.62870700	-0.36437500
H	-3.27218500	-3.48853600	-2.12272200
H	-4.23549100	-4.81288200	-1.43321000
C	-1.95379200	-5.91000800	-2.55049300

H	-1.84044200	-5.24032900	-3.40981200
H	-1.08460100	-6.57703700	-2.51916800
H	-2.85063600	-6.52155800	-2.70740400
C	2.08244400	-5.12993400	1.12824100
C	1.95403900	-5.96227100	2.42933900
H	2.85102500	-6.57659300	2.57417200
H	1.83958200	-5.31100400	3.30257700
H	1.08520900	-6.62890000	2.38304100
C	2.20877900	-6.07543800	-0.08305700
H	1.33927100	-6.73735900	-0.16496400
H	2.29639000	-5.51245600	-1.01858500
H	3.10308700	-6.69970600	0.02553500
C	3.33834900	-4.22509300	1.20966200
H	3.45203300	-3.63375800	0.29443200
H	3.27311400	-3.53302400	2.05546700
H	4.23672900	-4.84144700	1.33665400

(P_2)-3-methyl



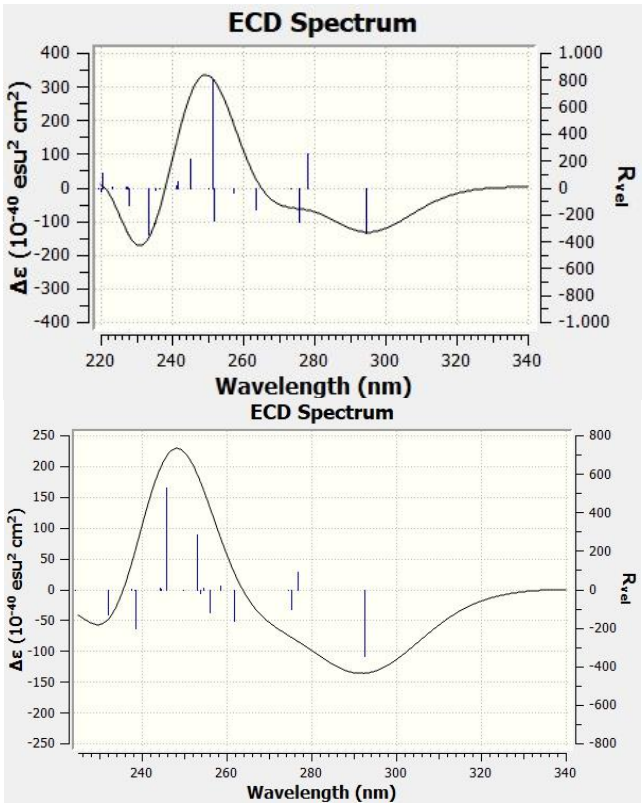


*Figure S65b. (P_2)-**3**-methyl. TOP: ECD calculated spectrum (CAM-B3LYP 6-31g+(d,p) scrf=(smd,solvent=acetonitrile)). Bottom: ECD calculated spectrum ((CAM-B3LYP 6-31g+(d,p) gas phase).*

N	-0.00616800	2.93595700	-0.00016900
C	-1.13949600	3.62301800	0.20232700
C	-2.31268300	2.81254900	0.41490500
C	-3.21946400	2.02517000	0.58366800
C	-4.21514000	1.01473000	0.82844300
C	-4.25696300	-0.00851000	0.00027400
C	-4.21068100	-1.03150300	-0.82796000
C	-3.21102300	-2.03793600	-0.58289300
C	-2.30101000	-2.82162800	-0.41441700
C	-1.12453600	-3.62746800	-0.20241300
N	0.00612500	-2.93598900	-0.00001300
C	1.13950400	-3.62304800	0.20220100
C	2.31273100	-2.81258000	0.41456100
C	3.21952700	-2.02519200	0.58319400
C	4.21497900	-1.01461400	0.82831400
C	4.25691900	0.00866100	0.00019400
C	4.21081600	1.03162600	-0.82808400
C	3.21098000	2.03796900	-0.58337600
C	2.30087200	2.82159300	-0.41509600
C	1.12446100	3.62743500	-0.20275100
C	1.17177100	5.02673900	-0.21287000
C	-1.19229300	5.02213200	0.21224700
C	-0.01164200	5.72619600	-0.00036900
C	-1.17183100	-5.02677100	-0.21261900
C	1.19232200	-5.02216200	0.21200800
C	0.01163600	-5.72622800	-0.00041200
H	2.11311000	5.53789700	-0.38192400
H	-2.13563700	5.52962000	0.38118500
H	-0.01377900	6.81151500	-0.00046100
H	-2.11319900	-5.53793000	-0.38150700
H	2.13570800	-5.52965000	0.38070600
H	0.01378700	-6.81154600	-0.00058000
C	-5.09488900	1.14970800	2.05119000
H	-4.47582300	1.19266700	2.95211700
H	-5.67446100	2.07563000	1.99169100
H	-5.77861600	0.30246700	2.12324200
C	-5.08997700	-1.17033900	-2.05059400
H	-4.47081700	-1.21084800	-2.95156800
H	-5.66564300	-2.09868200	-1.99089500
H	-5.77727100	-0.32599300	-2.12273400
C	5.09029700	1.17036100	-2.05059700
H	4.47127800	1.21074700	-2.95167300
H	5.66591900	2.09873200	-1.99090800
H	5.77763500	0.32603300	-2.12253600
C	5.09475000	-1.14978900	2.05102200
H	4.47569400	-1.19292300	2.95194800
H	5.67434800	-2.07568400	1.99135600
H	5.77845500	-0.30254100	2.12321800

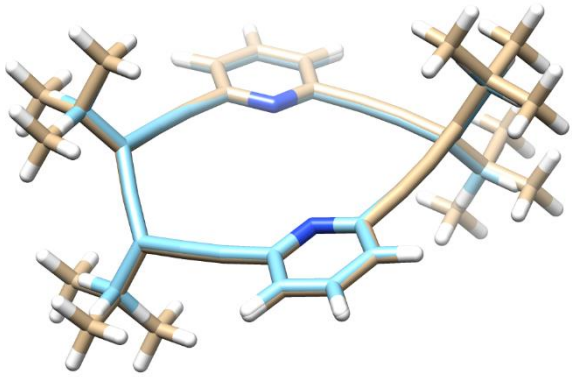
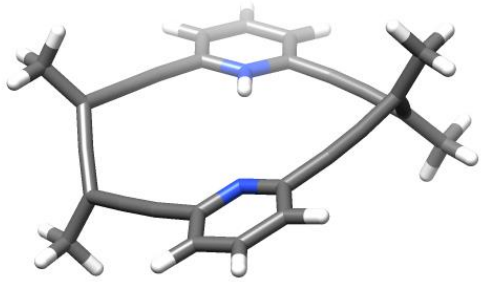


*Figure S65c. Overlay of optimized conformations with tertbutyl (gold) and methyl groups (cyan) for (P_2)-**3**.*

(P_2)-3·H



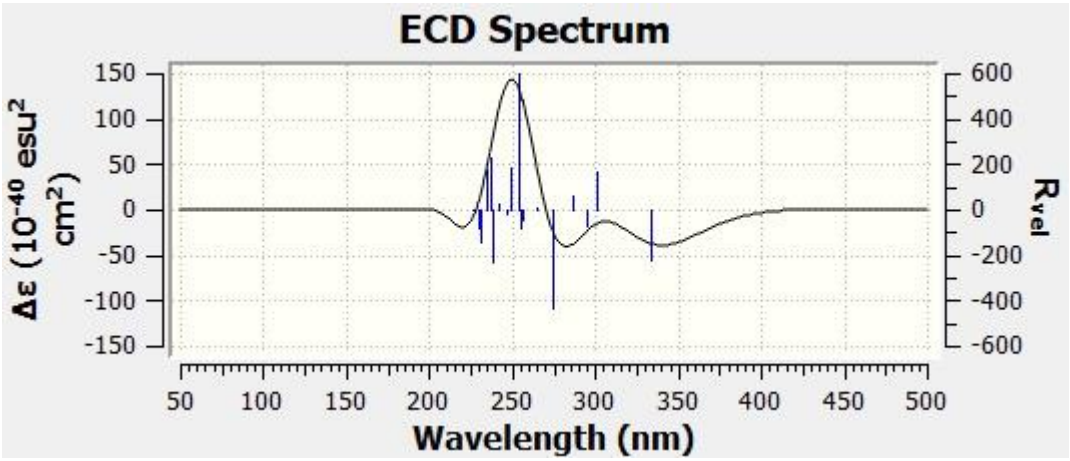


*Figure S66. (P_2)-**3·H** and ECD calculated spectrum.*

N	1.30961100	-2.66541700	0.00256200
C	2.62753400	-2.79141000	0.21425600
C	3.32658400	-1.54780900	0.42134100
C	3.78770400	-0.43869700	0.58587900
C	4.22748900	0.91046300	0.82374100
C	3.80985200	1.83735900	-0.01202800
C	3.32394100	2.73360800	-0.84656600
C	1.98923700	3.20051000	-0.59385000

C	0.83781900	3.53774300	-0.42087600
C	-0.54689800	3.78771800	-0.20723700
N	-1.32734400	2.70295200	0.00992800
C	-2.66169200	2.75976900	0.23180200
C	-3.32184500	1.51480100	0.43124100
C	-3.76648600	0.39820800	0.58989900
C	-4.22027000	-0.94470100	0.82214500
C	-3.79332600	-1.86929800	-0.01377700
C	-3.30081800	-2.75665200	-0.85162600
C	-1.97019600	-3.24054500	-0.59524400
C	-0.81493100	-3.56217800	-0.41760200
C	0.59277300	-3.78071500	-0.19643600
C	1.15697500	-5.06176300	-0.19448300
C	3.28243300	-4.02828200	0.23797800
C	2.52543500	-5.17641400	0.02806400
C	-1.14095300	5.04559200	-0.20629700
C	-3.28165600	4.00505000	0.24575300
C	-2.51110300	5.14373300	0.02355900
H	0.53228100	-5.93212100	-0.36237800
H	4.35113800	-4.07511900	0.41560200
H	2.99836200	-6.15314500	0.03800600
H	-0.52569300	5.91969900	-0.38043700
H	-4.34825000	4.06132200	0.42471800
H	-2.98439700	6.11994200	0.02923200
C	5.07621800	1.19385300	2.04253700
H	4.54738100	0.87262100	2.94449900
H	6.01286400	0.63262700	1.97741400
H	5.29899000	2.25945100	2.11243400
C	4.04662800	3.24956500	-2.07100200
H	3.46357100	3.02786000	-2.96935800
H	4.16935100	4.33407400	-1.99988100
H	5.02826500	2.78086800	-2.15166800
C	-4.02228500	-3.23903100	-2.08983700
H	-3.42724500	-3.00812300	-2.97808700
H	-4.15513200	-4.32360600	-2.03951300
H	-4.99888200	-2.76006600	-2.17265600
C	-5.09512800	-1.21172500	2.02657500
H	-4.58060900	-0.89654900	2.93875400
H	-6.02532900	-0.64252400	1.94299000
H	-5.32856100	-2.27524300	2.09154400
H	-0.88218200	1.78276400	0.00390700

(P_2)-3·2H

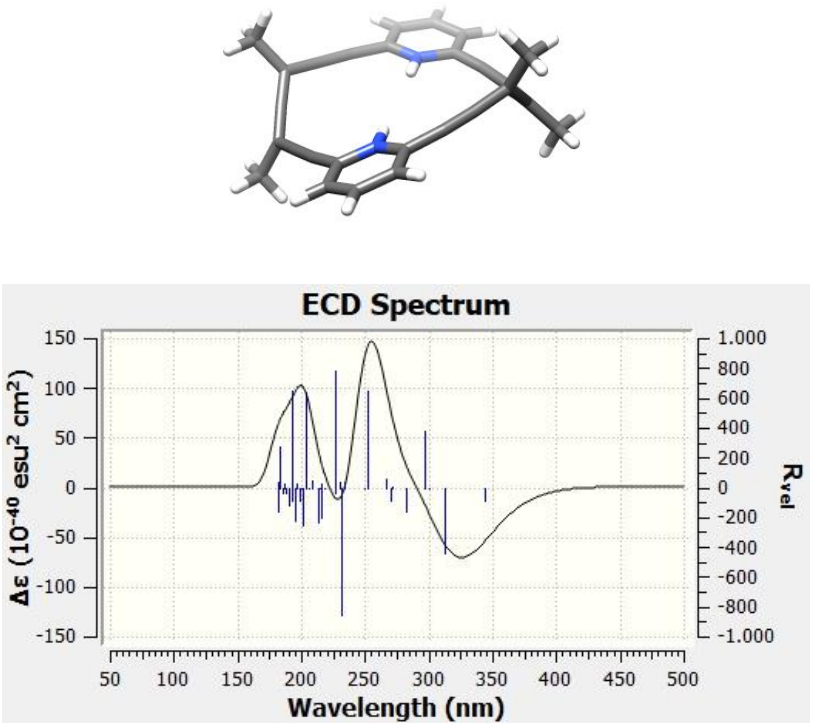


*Figure S67. (P_2)-**3·2H** and ECD calculated spectrum.*

N	2.96966300	0.74851500	-0.01281600
C	3.27986600	2.05462600	0.15997600
C	2.18482200	2.93078100	0.40669300
C	1.17076700	3.56219700	0.61041900
C	-0.05900000	4.24386500	0.90422100
C	-1.06234300	4.05709800	0.07313200
C	-2.05449600	3.81392800	-0.75749700
C	-2.79203300	2.59923100	-0.55113400
C	-3.36435600	1.53888500	-0.42121200
C	-3.88064100	0.22226300	-0.26054600
N	-2.96986500	-0.74771900	-0.01179900
C	-3.27941300	-2.05392600	0.16119800
C	-2.18408400	-2.92916800	0.40992800
C	-1.17012500	-3.56037500	0.61475100
C	0.05900000	-4.24491500	0.90459900
C	1.06149200	-4.05730300	0.07267600
C	2.05329700	-3.81330600	-0.75814100
C	2.79087200	-2.59876000	-0.55079600
C	3.36351200	-1.53865800	-0.42015500
C	3.88019500	-0.22217300	-0.25973200
C	5.22312900	0.13069400	-0.34369300
C	4.61458600	2.43704000	0.08495200
C	5.58051700	1.46532200	-0.16835100
C	-5.22323000	-0.13149400	-0.34606600
C	-4.61377500	-2.43726600	0.08455000
C	-5.57999300	-1.46627300	-0.17050800
H	5.95985300	-0.63799500	-0.54154100
H	4.87452500	3.47961800	0.22083300
H	6.62479400	1.75302800	-0.22997300
H	-5.96018100	0.63661300	-0.54532800
H	-4.87321300	-3.47994100	0.22063500
H	-6.62400900	-1.75466400	-0.23336400
C	-0.13787700	5.07595200	2.16481700

H	0.09453500	4.45548100	3.03483300
H	0.59293500	5.88817000	2.11653100
H	-1.13814500	5.49649700	2.27485200
C	-2.42378200	4.69262300	-1.93143000
H	-2.36029400	4.11862300	-2.85993900
H	-3.45185800	5.04729800	-1.81579400
H	-1.75112100	5.54943500	-1.98691500
C	2.42337300	-4.69179200	-1.93195900
H	2.36021300	-4.11770100	-2.86043500
H	3.45147200	-5.04625600	-1.81587800
H	1.75094300	-5.54876100	-1.98786000
C	0.13909200	-5.07862600	2.16404600
H	-0.09147100	-4.45902400	3.03517600
H	-0.59249900	-5.89014500	2.11586600
H	1.13916600	-5.50017300	2.27205000
H	-1.98646900	-0.47623900	0.04624800
H	1.98599600	0.47773600	0.04387100

(P_2)-3-TfOH

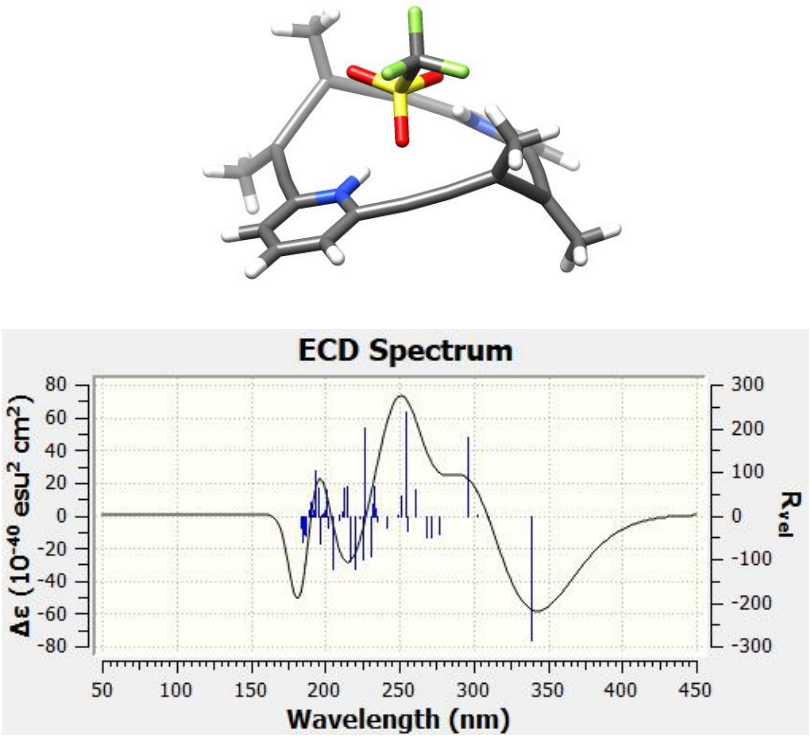


*Figure S68. (P_2)-**3**-TfOH complex and ECD calculated spectrum.*

N	-2.18475300	1.96360500	-0.91768300
C	-3.45553500	1.50611000	-1.02647000
C	-3.65552500	0.14066400	-0.68219600
C	-3.60619400	-1.02622100	-0.37015400
C	-3.45449800	-2.38481800	0.06333400
C	-2.58711000	-3.13012400	-0.58210300
C	-1.72752400	-3.85924200	-1.25980700
C	-0.32770400	-3.73259800	-0.98672200
C	0.86915600	-3.59272300	-0.87293200
C	2.24474200	-3.24228300	-0.89008600
N	2.58053100	-2.03572700	-0.38133800
C	3.81702200	-1.49225000	-0.48602500
C	3.93824000	-0.14554000	-0.04605900
C	3.78332400	1.01119900	0.27130100

C	3.49606200	2.35357500	0.68564300
C	2.86989500	3.12802400	-0.16806700
C	2.18710600	3.87303400	-1.01032000
C	0.76510000	3.70348700	-1.05164300
C	-0.42953300	3.53346400	-1.13989300
C	-1.80759600	3.21816100	-1.25285600
C	-2.77960800	4.10692800	-1.71017200
C	-4.44514000	2.37136500	-1.47594400
C	-4.09583400	3.67658000	-1.81017000
C	3.24259200	-4.01948500	-1.47466600
C	4.83164300	-2.24416600	-1.06612400
C	4.53686500	-3.51881500	-1.54013900
H	-2.48888600	5.11463900	-1.97708800
H	-5.46299700	2.01398900	-1.56235100
H	-4.85927100	4.36311600	-2.16030300
H	2.98816800	-4.99193400	-1.87570000
H	5.82440600	-1.82103600	-1.14737900
H	5.32133900	-4.11896000	-1.98868500
C	-4.24221900	-2.85364800	1.26720200
H	-4.03143900	-2.21573000	2.12823700
H	-5.31357000	-2.80217500	1.05526300
H	-3.98081900	-3.88231200	1.51607100
C	-2.13854400	-4.78462500	-2.38803300
H	-1.64900700	-4.49024600	-3.32013800
H	-1.84281000	-5.81185400	-2.15862400
H	-3.21890500	-4.75486600	-2.53100000
C	2.81712600	4.87195400	-1.95760300
H	2.57441700	4.62193900	-2.99389100
H	2.43765400	5.87693000	-1.75402900
H	3.90092100	4.87627600	-1.83969400
C	3.80526200	2.74751300	2.11243700
H	3.20776400	2.13312000	2.79047200
H	4.86450000	2.59068000	2.33104500
H	3.55741300	3.79595100	2.27785600
H	-1.46464600	1.29791500	-0.51269600
C	-1.08182300	-0.25987000	2.69154700
F	-0.56083500	-0.20327200	3.91134400
F	-1.52122000	-1.50285800	2.46702900
F	-2.12931500	0.57245000	2.62694800
S	0.17727400	0.23053300	1.42238800
O	1.17631800	-0.85882400	1.50357800
H	1.87643900	-1.50989300	0.20260000
O	-0.56854200	0.17837600	0.13418100
O	0.62176900	1.55545100	1.83066600

(P_2)-3-H_2SO_4

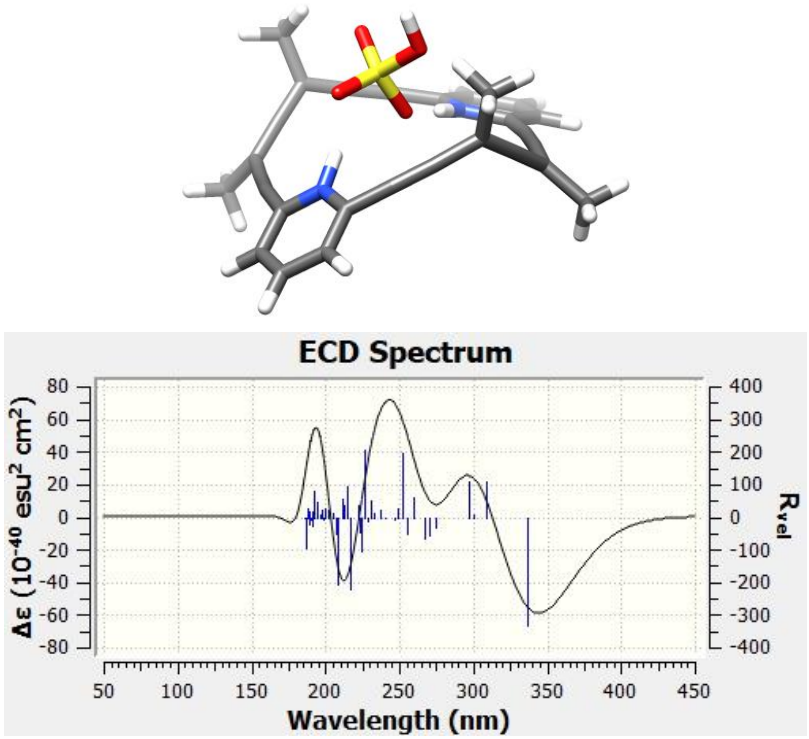


*Figure S69. (P_2)-**3**-H_2SO_4 complex and ECD calculated spectrum.*

N	-1.12708600	-2.91852500	-0.29594400
C	-2.36683200	-3.02347700	-0.82446700
C	-3.20940100	-1.88472400	-0.70686200
C	-3.78969600	-0.82289000	-0.69669400
C	-4.41466300	0.46419200	-0.77471900
C	-3.91427200	1.43569000	-0.04219000
C	-3.37120900	2.38505700	0.68441300
C	-2.19196500	3.02947300	0.17984700
C	-1.14535700	3.50894600	-0.18913400
C	0.17744400	3.84486200	-0.59875100
N	1.08371700	2.84281900	-0.53037100
C	2.37133500	2.97191100	-0.91977500
C	3.17797400	1.80272700	-0.84540700
C	3.75046200	0.73788900	-0.80670500
C	4.36752200	-0.55612100	-0.83341900
C	3.90650000	-1.47368900	-0.01131500
C	3.38752900	-2.36793700	0.79833200
C	2.18726700	-3.02784100	0.36691700
C	1.13201200	-3.50659100	0.02172100
C	-0.16243300	-3.85267500	-0.46289600
C	-0.47047700	-5.02266700	-1.14187000
C	-2.70735600	-4.18522700	-1.50913500
C	-1.75654300	-5.18804800	-1.64736900
C	0.58286700	5.08772900	-1.06459100
C	2.80908000	4.20430500	-1.39214900
C	1.90730800	5.25941200	-1.45466300
H	0.29435000	-5.77678500	-1.27636300
H	-3.69994200	-4.28135400	-1.93019900
H	-2.01167700	-6.09988500	-2.17635700
H	-0.13535100	5.89584000	-1.12061600
H	3.83929600	4.31822900	-1.70446200
H	2.23773400	6.22576300	-1.81954600

C	-5.56249100	0.64297300	-1.74268000
H	-5.24592800	0.38185900	-2.75659000
H	-6.39099000	-0.01548700	-1.46592400
H	-5.91229700	1.67610600	-1.73259300
C	-3.85757100	2.77663300	2.06100600
H	-3.06617300	2.59457600	2.79298300
H	-4.10951300	3.84089000	2.08066700
H	-4.74057700	2.19655300	2.33309700
C	3.92825700	-2.68441600	2.17294300
H	3.16239300	-2.49206300	2.92925400
H	4.20674000	-3.74072900	2.23152000
H	4.80584300	-2.07312100	2.38763400
C	5.46521400	-0.80313500	-1.84348100
H	5.09437500	-0.62001300	-2.85612700
H	6.30200100	-0.12269700	-1.66090400
H	5.82277900	-1.83139000	-1.77462000
H	0.77116400	1.92347400	-0.13363500
H	-0.92266000	-2.10898500	0.32955100
O	0.30022800	0.48050000	0.47242500
S	-0.13175200	0.07570500	1.82890700
O	-0.84860800	-1.22204200	1.79986100
O	1.29816400	-0.21127000	2.56424200
H	1.14587000	-0.33121600	3.52017700
O	-0.80214000	1.10842800	2.62138400

(P_2)-3-TFA

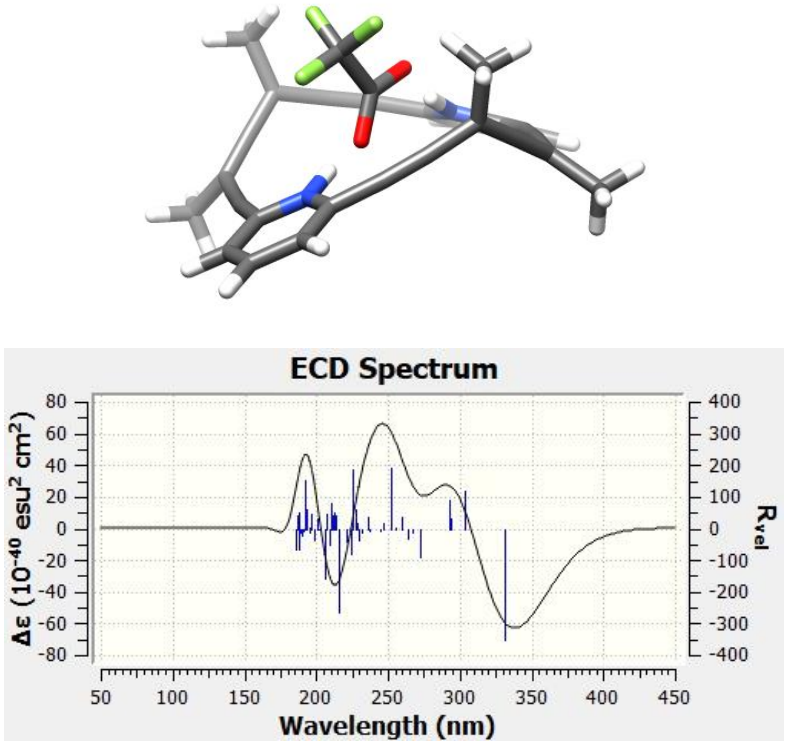
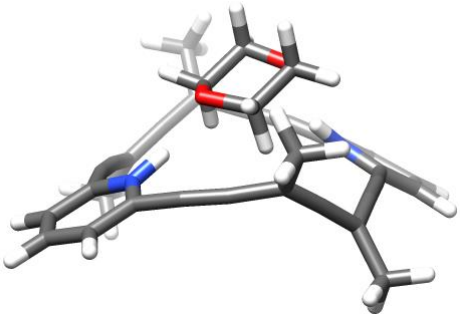


*Figure S70. (P_2)-**3**-TFA complex and ECD calculated spectrum.*

N	-2.59998100	-1.23177800	-0.82588900
C	-2.62242600	-2.58249700	-0.85063300
C	-1.43961100	-3.23333700	-0.39724700
C	-0.36836500	-3.60952000	0.01792100
C	0.90808500	-3.95797700	0.57428000

C	1.98269700	-3.63589700	-0.10837300
C	3.04374100	-3.27688600	-0.79775600
C	3.47776600	-1.91626600	-0.69333000
C	3.78980400	-0.74778400	-0.67691800
C	3.94990500	0.66282300	-0.74081600
N	2.93059300	1.40558600	-0.26102100
C	2.88178100	2.75093000	-0.37226300
C	1.67356100	3.36347800	0.06978700
C	0.55439700	3.68124900	0.39669100
C	-0.79061900	3.95524200	0.81602000
C	-1.75457400	3.73872900	-0.04906600
C	-2.70406200	3.46719300	-0.91835400
C	-3.13692200	2.10493100	-1.01337300
C	-3.44919300	0.94180100	-1.12421300
C	-3.63920400	-0.46293000	-1.21542500
C	-4.80015900	-1.08032500	-1.67603400
C	-3.76604100	-3.23182700	-1.30204000
C	-4.85326200	-2.46782400	-1.71469800
C	5.04354900	1.30461100	-1.31971400
C	3.95331100	3.42674900	-0.94503700
C	5.04145800	2.69079300	-1.40390600
H	-5.63703900	-0.46983600	-1.98971000
H	-3.78927200	-4.31365800	-1.32383200
H	-5.75232800	-2.96094600	-2.06852700
H	5.86695900	0.71290700	-1.69842400
H	3.91829300	4.50515700	-1.03022500
H	5.88796800	3.20336100	-1.84819200
C	0.94064500	-4.60185100	1.94414700
H	0.45077800	-3.95407400	2.67509800
H	0.41067700	-5.55782300	1.92244400
H	1.97014600	-4.77579200	2.25757300
C	3.78370600	-4.19979800	-1.74216000
H	3.77598200	-3.79212300	-2.75647500
H	4.82530600	-4.30415000	-1.42683700
H	3.32016000	-5.18644700	-1.75351700
C	-3.32590200	4.49303700	-1.84058200
H	-3.18035100	4.20344500	-2.88467100
H	-4.40115000	4.56435100	-1.65603900
H	-2.87638300	5.47300000	-1.67918800
C	-1.02110700	4.39352800	2.24635300
H	-0.63526500	3.63765800	2.93553500
H	-0.49729500	5.33286700	2.44188700
H	-2.08537500	4.53607200	2.43466200
H	-1.71114300	-0.74399000	-0.45068800
C	-0.74497500	-0.39306900	2.32157500
F	-0.84088400	0.62993100	3.18168500
F	-0.19655400	-1.43389500	2.96962600
F	-1.99883600	-0.75073500	1.97833500
C	0.10599900	-0.00135500	1.08486000
O	1.25877600	0.37760400	1.36920500
O	-0.41780500	-0.09028800	-0.04381600
H	2.13982000	0.91143000	0.31939400

(P_2)-3-Dioxane



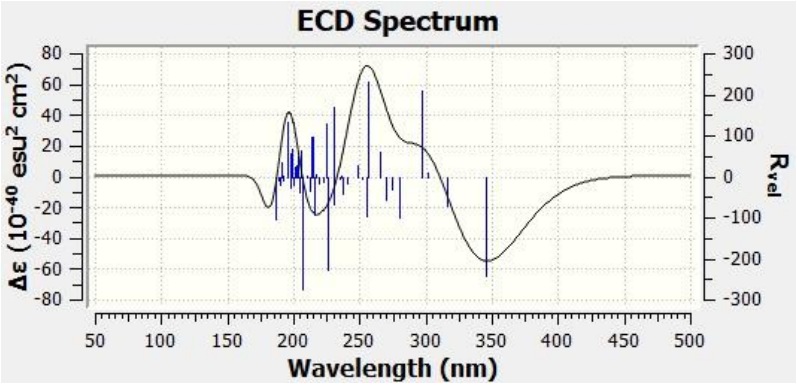
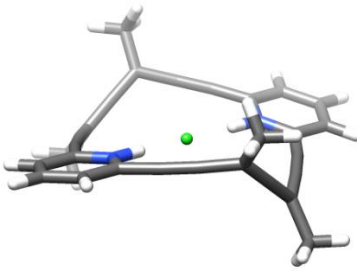


*Figure S71. (P_2)-**3**-Dioxane complex and ECD calculated spectrum.*

N	2.26083600	-2.20648700	-0.21919200
C	3.52163300	-1.77448500	-0.48485000
C	3.81086500	-0.43351700	-0.10511900
C	3.87170800	0.75403700	0.12136800
C	3.83346300	2.15145900	0.45873300
C	2.99385300	2.90715400	-0.21655700
C	2.18372400	3.65446500	-0.93598100
C	0.77814100	3.67219100	-0.64664100
C	-0.42660600	3.63850000	-0.52505300
C	-1.83518600	3.45049500	-0.56472800
N	-2.31676000	2.25583800	-0.13633100
C	-3.60404900	1.85571900	-0.31322100
C	-3.88882100	0.49692700	-0.00181500
C	-3.97478000	-0.69720000	0.17514000
C	-3.94211100	-2.10255900	0.47617800
C	-3.09631000	-2.84175100	-0.20926900
C	-2.28165000	-3.57041900	-0.94286900
C	-0.87310500	-3.58384300	-0.66743200
C	0.33568000	-3.55230400	-0.58040500
C	1.73908600	-3.35913500	-0.70843200
C	2.58149900	-4.21934400	-1.40709500
C	4.37911800	-2.61439300	-1.18151300
C	3.90685000	-3.85213300	-1.61272100
C	-2.72839500	4.36891500	-1.10817000
C	-4.51271500	2.75556400	-0.85367500
C	-4.06994800	4.02266700	-1.22496200
H	2.18554100	-5.15060800	-1.79179200
H	5.38922600	-2.28665300	-1.39217400
H	4.57086400	-4.52174500	-2.14928300
H	-2.35973700	5.33024500	-1.44275200
H	-5.54242100	2.45084700	-0.99132200

H	-4.77363700	4.73611800	-1.64088100
C	4.71566300	2.65498300	1.58239900
H	4.53971500	2.09140100	2.50247700
H	5.76714700	2.53033600	1.31051200
H	4.52690900	3.71170000	1.77120000
C	2.65443600	4.46142900	-2.13134000
H	2.11884000	4.15598800	-3.03363000
H	2.46063600	5.52378100	-1.96208200
H	3.72393700	4.32226400	-2.28828900
C	-2.75102300	-4.35848600	-2.15208100
H	-2.22274500	-4.03133800	-3.05108300
H	-2.54855000	-5.42239400	-2.00412800
H	-3.82231800	-4.22471900	-2.30125800
C	-4.81850800	-2.62648100	1.59454000
H	-4.62753300	-2.08452200	2.52463600
H	-5.87121400	-2.48633000	1.33540700
H	-4.63718800	-3.68892800	1.75655300
H	1.70750100	-1.65763100	0.46081100
H	-1.68828600	1.64031900	0.41441900
C	1.45390300	0.22133600	2.56965800
C	0.61524400	1.11286300	1.68193600
O	-0.77664600	0.78479900	1.76932600
C	-1.05453300	-0.61574400	1.65481000
C	-0.14109000	-1.46110500	2.51423700
O	1.21674100	-1.14136200	2.20685500
H	2.51606900	0.41634100	2.42841000
H	1.20597100	0.36079700	3.62811800
H	0.94683700	1.00665300	0.64032100
H	0.70219400	2.15963700	1.97598900
H	-2.09055400	-0.74155200	1.96265100
H	-0.95604500	-0.91787900	0.60293900
H	-0.31814800	-1.28856600	3.58195600
H	-0.28851200	-2.52137000	2.30106300

(P_2)-3-HCl



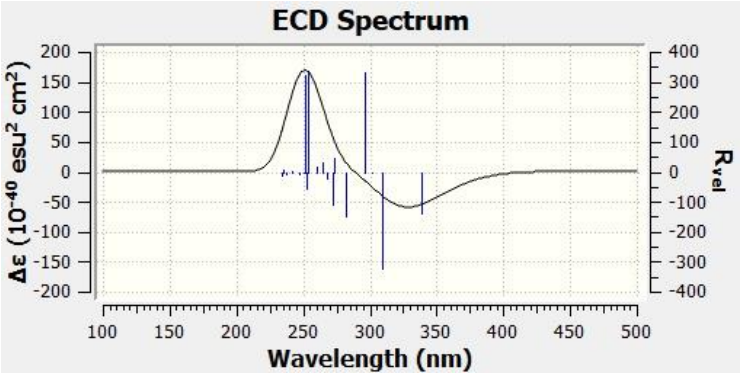


*Figure S72. (P_2)-**3**-HCl complex and ECD calculated spectrum.*

N	1.14778700	-2.77808100	-0.04100800
C	0.29737100	-3.78456100	-0.34581000
C	-1.08194300	-3.45384200	-0.44672200
C	-2.22411700	-3.07045100	-0.54792100
C	-3.54044400	-2.53164300	-0.72980000
C	-3.92940400	-1.58230400	0.09218600
C	-4.25887100	-0.60320300	0.90410200
C	-3.76077300	0.70387400	0.58513100
C	-3.24659100	1.77199200	0.34908200
C	-2.48802400	2.93891200	0.05335200
N	-1.14774100	2.77807600	-0.04093400
C	-0.29734100	3.78456400	-0.34575000
C	1.08197100	3.45386000	-0.44672000
C	2.22412100	3.07040100	-0.54806700
C	3.54046900	2.53161900	-0.72985600
C	3.92941100	1.58230800	0.09217100
C	4.25874900	0.60322900	0.90416400
C	3.76074600	-0.70387300	0.58514800
C	3.24663800	-1.77203100	0.34911700
C	2.48806600	-2.93893700	0.05334500
C	3.03159700	-4.19998200	-0.15296300
C	0.81201300	-5.05769300	-0.56060000
C	2.18297600	-5.25805300	-0.45777000
C	-3.03158100	4.19993500	-0.15300200
C	-0.81200800	5.05767700	-0.56060600
C	-2.18297200	5.25802100	-0.45780300
H	4.10305000	-4.33422600	-0.07703200
H	0.13649600	-5.86773900	-0.80390300
H	2.59493100	-6.24796800	-0.62085400
H	-4.10304200	4.33415100	-0.07712300
H	-0.13650100	5.86772500	-0.80393600
H	-2.59494200	6.24792000	-0.62094000
C	-4.36984800	-3.03969300	-1.88734100
H	-3.83632800	-2.88496800	-2.82958400
H	-4.55400900	-4.11196200	-1.77372800
H	-5.32671900	-2.51766800	-1.92844700
C	-5.05748000	-0.78318300	2.17429500
H	-4.47031400	-0.45541800	3.03700000
H	-5.96770400	-0.17786300	2.13360000
H	-5.33262900	-1.83047100	2.30610100
C	5.05718300	0.78324900	2.17446500
H	4.46990300	0.45549800	3.03709700
H	5.96741900	0.17793700	2.13390600
H	5.33230600	1.83054200	2.30628400
C	4.36993800	3.03966900	-1.88735200
H	3.83647400	2.88493300	-2.82962500
H	4.55408500	4.11193900	-1.77373200
H	5.32681700	2.51765200	-1.92840000
H	-0.75036000	1.82858200	0.15090200
H	0.75042600	-1.82859600	0.15079800
Cl	0.00007100	0.00005200	0.76672800

(P_2)-3-TfOH-H_2O

This geometry was obtained directly from crystallographic data (Table S5/S6) and its ECD spectrum calculated in the same way as in the previous cases.

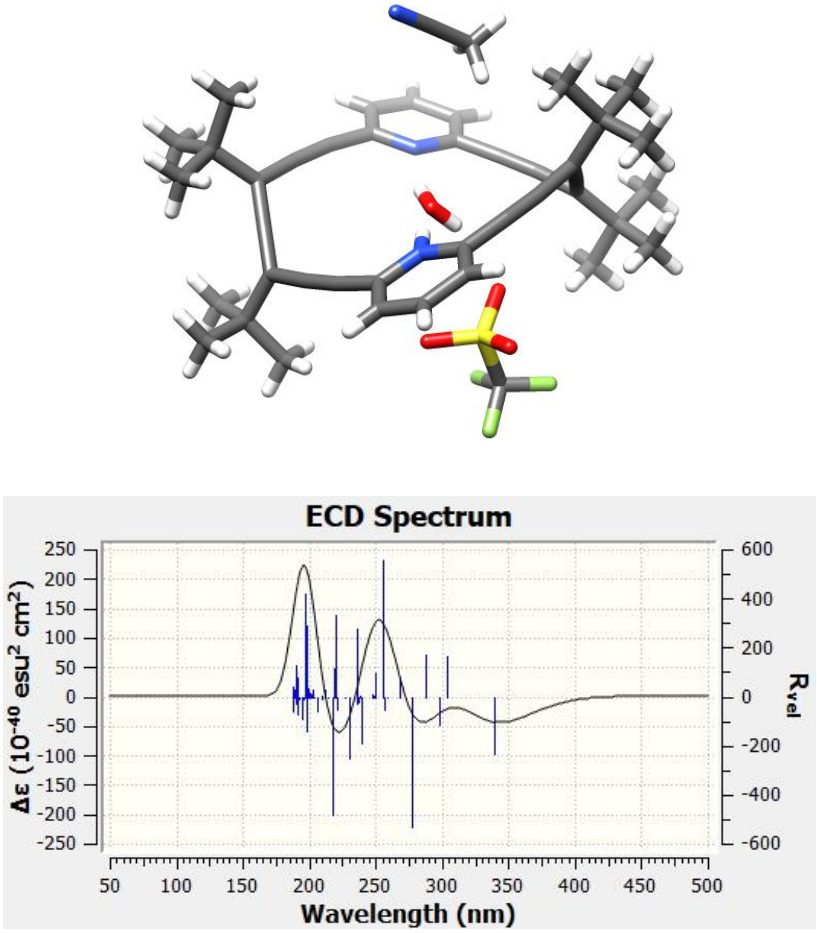


*Figure S73a. (P_2)-**3**-TfOH-H_2O complex obtained from crystallographic data and ECD calculated spectrum.*

S	1.14149500	-3.03845700	-0.66222200
F	2.82691700	-3.89563300	-2.49632000
F	1.17037700	-5.21781500	-2.14400200
F	0.86786600	-3.38280500	-3.22840800
O	1.60976100	-1.70343600	-0.97331200
O	1.88620900	-3.72710900	0.35250100
O	-0.29274600	-3.15061900	-0.57356100
C	1.52280800	-3.94013900	-2.20229200
O	-0.00201200	0.29460300	0.24364600
H	-0.30183100	0.94140400	-0.15837200
H	0.56160200	-0.02474400	-0.28048100
N	-0.23259700	-1.65754400	2.16095300
N	-0.48812200	2.73131100	-1.56374800
C	-1.32115500	-2.45391600	2.33119900
C	-1.26839700	-3.48449500	3.26398900
H	-2.01797900	-4.05347700	3.39349200
C	-0.10280900	-3.67409700	4.00750500
H	-0.05906900	-4.37060600	4.65205500
C	0.99142500	-2.84716500	3.80650600
H	1.78229000	-2.96753800	4.31889900
C	0.92309100	-1.83403600	2.84409300

C	2.00719100	-0.97137100	2.52776300
C	2.85697800	-0.22487100	2.13229900
C	3.78434300	0.74480500	1.61588900
C	3.84137800	0.86879700	0.30529500
C	3.84020100	1.01333600	-0.99939900
C	2.79054600	1.84058300	-1.53506400
C	1.82712500	2.46373500	-1.89732800
C	0.61476100	3.15681800	-2.21932500
C	-5.15384000	-2.13961200	-0.96941700
C	0.58934700	4.19546800	-3.15225100
H	1.38029600	4.45072900	-3.61236600
C	-0.60669400	4.84667100	-3.39534300
H	-0.64566100	5.56617200	-4.01444600
C	-1.74560000	4.43672600	-2.72511800
H	-2.57517500	4.87712200	-2.86712900
C	-1.65342200	3.36318300	-1.83576600
C	-2.80603300	2.81368200	-1.16347900
C	-3.68862800	2.21954500	-0.61592700
C	-4.63754300	1.39944600	0.09434700
C	-4.49490400	0.09531500	-0.00952200
C	-3.35501100	-1.75817000	0.83592500
C	-2.46660300	-2.13507600	1.54420300
C	4.61784900	1.57795500	2.59098200
C	5.62781400	0.63864100	3.27189500
H	5.14542400	-0.06109100	3.75990200
H	6.18049600	1.15161900	3.89775200
H	6.20083600	0.22683400	2.59181700
C	5.34225900	2.69076800	1.83857100
H	5.96850100	2.29690900	1.19610500
H	5.83556600	3.24849200	2.47589300
H	4.68754600	3.24195200	1.36089100
C	3.69536800	2.19987600	3.64757300
H	3.07247100	2.81948400	3.21349500
H	4.23427400	2.68639300	4.30599600
H	3.19041400	1.49119200	4.09834700
C	4.86454900	0.36228200	-1.93688100
C	5.72008200	-0.63544100	-1.15015600
H	6.21513200	-0.16044800	-0.45028500
H	6.35208200	-1.07383400	-1.75728500
H	5.14007800	-1.31022100	-0.73925000
C	5.73851800	1.47365900	-2.53922600
H	5.17112600	2.10846300	-3.02454600
H	6.38922500	1.07895400	-3.15659500
H	6.21242800	1.94206700	-1.82064300
C	4.13078100	-0.37809700	-3.06123500
H	3.56880900	-1.08263200	-2.67614000
H	4.78572200	-0.77910300	-3.67019300
H	3.56884700	0.25393100	-3.55629200
C	-4.34485900	-1.20866300	-0.05471300
C	-6.08972200	-2.97190300	-0.07928600
H	-5.55800000	-3.48215700	0.56666700
H	-6.60701100	-3.58976700	-0.63720300
H	-6.70124400	-2.37476700	0.40004900
C	-4.18982900	-3.06579300	-1.72671000
H	-3.64622400	-2.53536500	-2.34617800
H	-4.70379300	-3.73085700	-2.23041300
H	-3.60420100	-3.52159000	-1.08656600
C	-5.97702700	-1.31805500	-1.96491800
H	-6.59087300	-0.73136000	-1.47577300
H	-6.49143000	-1.92206000	-2.54034400
H	-5.37573300	-0.77502900	-2.51630300
C	-5.75905800	2.03677800	0.93200500
C	-6.43718800	0.95473400	1.78091100

H	-7.17105300	1.35374300	2.29336200
H	-5.78236700	0.56501800	2.39721000
H	-6.79129100	0.25385500	1.19455500
C	-5.17039100	3.12281300	1.83397400
H	-4.65375700	3.75404600	1.29072900
H	-4.58358900	2.71026800	2.50183800
H	-5.89639000	3.60004200	2.28737700
C	-6.77574000	2.65419900	-0.03921700
H	-7.18903200	1.94473700	-0.57414700
H	-6.31852400	3.28636700	-0.63239400
H	-7.46841600	3.12577400	0.46902600
H	-0.18692800	-0.98167400	1.64107600
N	-0.60637700	4.85074900	2.82432100
C	0.21259800	4.74862000	2.04234500
C	1.24866400	4.58850800	1.04572700
H	0.91508200	4.89503700	0.17696600
H	1.50009200	3.64394200	0.98526100
H	2.03150400	5.11998900	1.30129800

(*P*$_2$)-3-TfOH-H$_2$O- re-optimized

This geometry was obtained by re-optimization [(CAM-B3LYP 6-31g(d)] of crystallographic geometries (Table S5/S6) and its ECD spectrum calculated in the same way as in the previous cases.

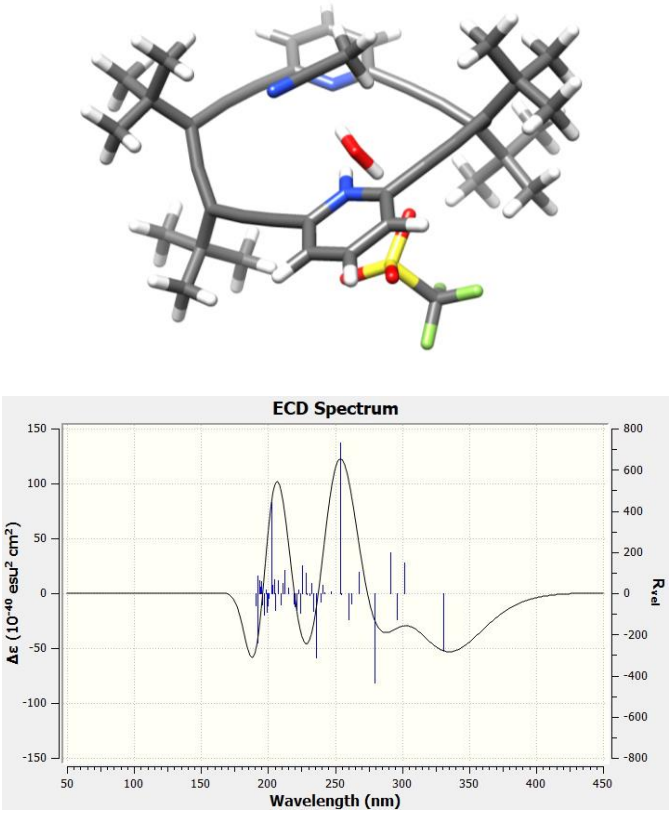


*Figure S73b. (P$_2$)-**3**-TfOH-H$_2$O complex re-optimized from crystallographic data and ECD calculated spectrum.*

S	1.19240600	-2.84774300	-0.90005400
F	3.78736900	-3.51738200	-1.21153200
F	2.35479900	-5.07094700	-1.90632200
F	2.67919800	-3.23324700	-3.11969600
O	1.69901200	-1.28517600	-1.04438500
O	1.30755200	-3.43816700	0.61246600
O	-0.16418500	-3.20947600	-1.71383600
C	2.59950300	-3.73167300	-1.85240300
O	0.05633700	0.37413100	0.12445100
H	-0.42282900	1.07940600	-0.36548400
H	0.69828000	-0.14310300	-0.44883900
N	-0.05815400	-1.28442400	2.10501200
N	-0.82608700	2.80567900	-1.47446000
C	-1.07637800	-2.16758100	2.25083100
C	-0.95953800	-3.19815000	3.18122800
H	-1.77432700	-3.89906400	3.28962900
C	0.20475300	-3.30988600	3.92979300
H	0.30958500	-4.11230700	4.64955500
C	1.24331600	-2.40658000	3.74263100
H	2.17155100	-2.48847300	4.28924300
C	1.10469800	-1.39478000	2.79586500
C	2.13898700	-0.47738200	2.48720900
C	2.99014400	0.29805600	2.11149500
C	3.89916700	1.26156500	1.56318900
C	3.87513300	1.40663400	0.25314100
C	3.68816700	1.50967200	-1.04505300
C	2.56277200	2.29291800	-1.46860200
C	1.52283700	2.84564100	-1.75123200
C	0.24582100	3.41843200	-2.03181500
C	-4.60736400	-2.47606800	-1.29832800
C	0.11211600	4.55313300	-2.84081600
H	0.99455400	5.01020500	-3.26845300
C	-1.15791800	5.06604800	-3.07580500
H	-1.28699300	5.94352400	-3.69808800
C	-2.26094000	4.43926000	-2.50955700
H	-3.26565900	4.80447200	-2.67585300
C	-2.06244700	3.30362000	-1.71419500
C	-3.15814200	2.60336300	-1.12780300
C	-4.03762100	1.94214600	-0.62084300
C	-4.95374300	1.04589600	0.02656300
C	-4.68934700	-0.23722300	-0.10744800
C	-3.15645800	-1.79970900	0.69339100
C	-2.21499900	-1.99469800	1.42829900
C	4.77510300	2.08246900	2.52303300
C	5.65193400	1.11452900	3.34100500
H	5.03690300	0.40631400	3.90452400
H	6.26855500	1.67391200	4.05228300
H	6.31578200	0.54282300	2.68549100
C	5.66795500	3.04904800	1.73459800
H	6.33571500	2.50688300	1.05800500
H	6.28319900	3.63394000	2.42511600
H	5.07047700	3.74345600	1.13635700
C	3.86050100	2.88141900	3.47298400
H	3.24312600	3.58975800	2.91089000
H	4.46334700	3.44720400	4.19078800
H	3.19769400	2.21554700	4.03438400
C	4.56484800	0.81517900	-2.10405200
C	5.36998100	-0.31833500	-1.45431000
H	5.99721400	0.05104300	-0.63608400
H	6.02520200	-0.77853400	-2.20046100
H	4.70138900	-1.08896900	-1.06234800

C	5.51819300	1.87397900	-2.69675700
H	4.95798600	2.70729600	-3.13353900
H	6.12887600	1.42416100	-3.48651600
H	6.18794000	2.27465300	-1.92885100
C	3.67374700	0.23427200	-3.21693900
H	2.95578600	-0.47880900	-2.80477100
H	4.30074800	-0.28059000	-3.95242300
H	3.12207300	1.02396500	-3.73590400
C	-4.20975800	-1.45853800	-0.21729100
C	-4.93087400	-3.82343400	-0.62604000
H	-4.06657800	-4.20690800	-0.07639600
H	-5.20067100	-4.56175900	-1.38769600
H	-5.77062800	-3.72572000	0.07006300
C	-3.41657600	-2.64457700	-2.26562300
H	-3.20824500	-1.70424800	-2.78546900
H	-3.65709800	-3.40403500	-3.01751800
H	-2.49826700	-2.95047900	-1.75533000
C	-5.83658300	-1.97338300	-2.06688400
H	-6.69874600	-1.85017000	-1.40286700
H	-6.10443000	-2.69433100	-2.84513000
H	-5.63594800	-1.01224700	-2.54968700
C	-6.09492000	1.62428800	0.87450000
C	-6.88330500	0.49206200	1.54520600
H	-7.70203800	0.91163200	2.13770800
H	-6.24275500	-0.09155000	2.21286500
H	-7.31291600	-0.18733900	0.80220200
C	-5.48668900	2.54191600	1.95414900
H	-4.95159900	3.38098700	1.49873600
H	-4.77926400	1.99448900	2.58377500
H	-6.28206300	2.94865100	2.58767100
C	-7.02846600	2.43953700	-0.04136000
H	-7.49011600	1.79880300	-0.79929600
H	-6.47896000	3.23538500	-0.55368700
H	-7.82553700	2.90127000	0.55069100
H	-0.13063100	-0.52640600	1.33190300
N	-2.18502700	1.44017200	3.15583900
C	-1.29300200	2.06127500	2.73415200
C	-0.17210400	2.81658400	2.19432300
H	-0.53078700	3.69535200	1.65295400
H	0.38748200	2.18582600	1.49722200
H	0.49294600	3.14601300	2.99653400

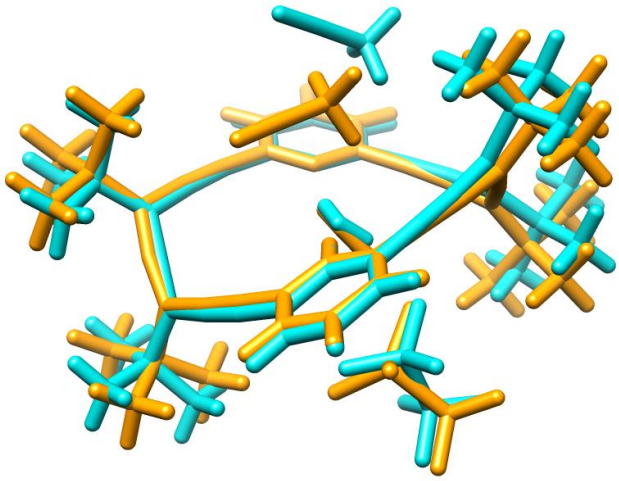


*Figure S73c. Superposition of (P_2)-**3**-TfOH-H_2O complexes from crystallographic data (green) and re-optimized (orange) of geometry.*

(P_2)-3-$(TfOH)_2$-H_2O

This geometry was obtained directly from crystallographic data (Table S7/S8) and its ECD spectrum calculated in the same way as in the previous cases.

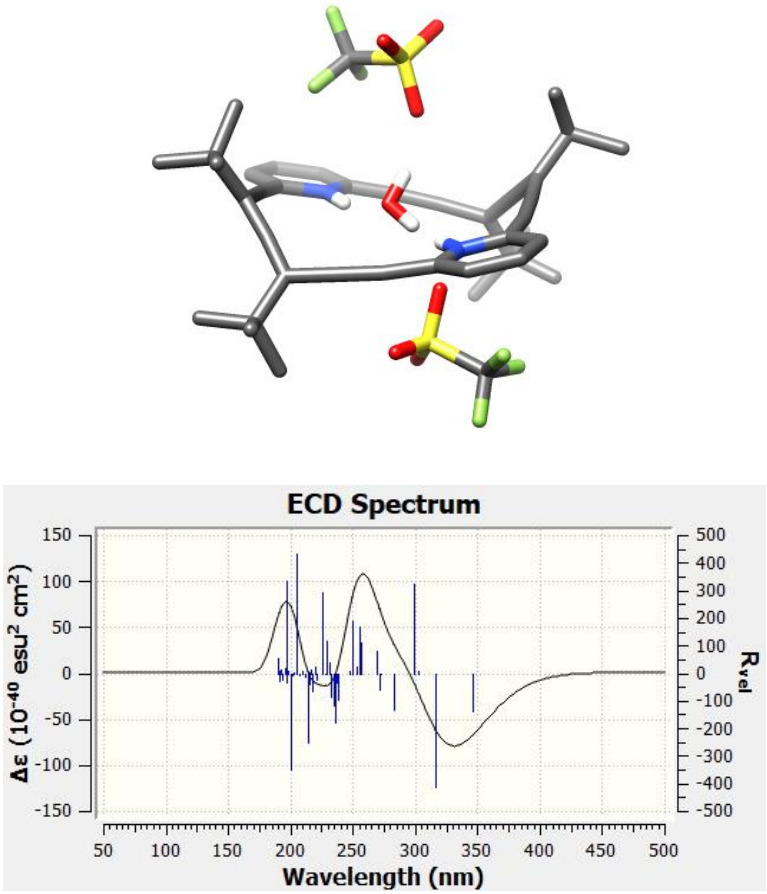


*Figure S74. (P_2)-**3**-$(TfOH)_2$ -H_2O complex obtained from crystallographic data and ECD calculated spectrum.*

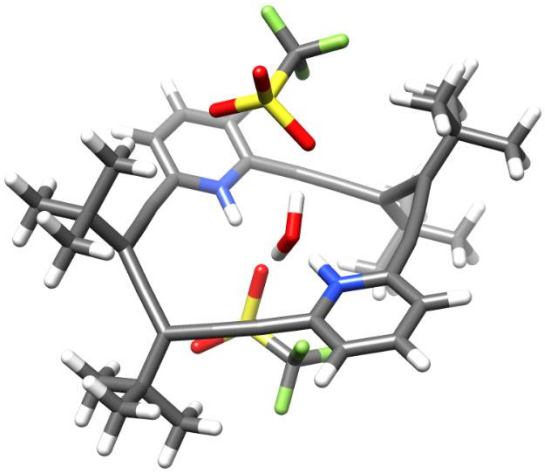
C	8.83860000	7.53140000	0.05660000
C	8.81620000	7.53920000	-1.30520000
H	8.36940000	8.23450000	-1.77160000
C	9.45810000	6.51530000	-2.01210000
H	9.46850000	6.53090000	-2.96120000
C	10.07500000	5.48480000	-1.33490000
H	10.49700000	4.77940000	-1.81130000
C	10.06640000	5.49260000	0.04020000
C	10.65100000	4.48710000	0.86320000
C	11.04760000	3.71500000	1.68170000
C	11.44730000	2.81990000	2.72340000
C	12.12480000	3.32070000	3.72800000
C	12.81080000	3.80950000	4.73700000
C	12.03230000	4.41510000	5.78770000
C	11.36410000	4.96390000	6.62710000
C	10.54610000	5.74950000	7.48430000
C	10.76050000	5.91810000	8.84900000
H	11.46110000	5.44600000	9.28460000
C	9.94930000	6.77590000	9.56480000
H	10.08070000	6.87260000	10.50110000
C	8.94540000	7.49950000	8.93680000
H	8.39900000	8.09890000	9.43120000

C	8.75570000	7.32730000	7.56760000
C	7.83340000	8.06280000	6.77880000
C	7.17330000	8.65490000	5.97070000
C	6.40570000	9.30860000	4.94830000
C	7.04820000	9.73880000	3.89470000
C	7.62680000	10.23730000	2.80830000
C	7.94090000	9.31750000	1.75610000
C	8.28780000	8.54190000	0.90040000
C	11.04470000	1.33180000	2.64310000
C	12.00210000	0.61770000	1.69660000
H	12.90300000	0.61830000	2.08300000
H	12.01600000	1.08240000	0.83450000
H	11.70350000	-0.30620000	1.56600000
C	11.12030000	0.69450000	4.04350000
H	10.83950000	-0.24360000	3.99050000
H	10.52760000	1.17850000	4.65470000
H	12.04120000	0.74120000	4.37420000
C	9.59940000	1.23030000	2.17430000
H	9.28610000	0.30770000	2.27680000
H	9.54290000	1.49130000	1.23080000
H	9.03890000	1.82780000	2.71190000
C	14.33080000	3.80440000	4.84120000
C	14.94890000	3.36110000	3.50630000
H	14.61210000	2.47190000	3.27050000
H	15.92430000	3.32940000	3.59290000
H	14.70340000	4.00040000	2.80520000
C	14.73940000	2.84790000	5.96930000
H	14.34990000	3.15550000	6.81510000
H	15.71610000	2.83190000	6.04710000
H	14.41250000	1.94660000	5.76830000
C	14.82730000	5.21880000	5.15820000
H	14.56490000	5.82610000	4.43480000
H	15.80300000	5.21170000	5.24140000
H	14.42880000	5.52290000	6.00030000
C	8.01320000	11.70280000	2.66540000
C	7.16260000	12.30940000	1.55070000
H	7.31930000	11.81840000	0.71690000
H	7.40890000	13.24960000	1.42730000
H	6.21510000	12.24840000	1.79250000
C	9.48520000	11.80810000	2.31570000
H	10.02140000	11.41100000	3.03470000
H	9.72970000	12.75130000	2.21030000
H	9.65810000	11.33000000	1.47830000
C	7.75370000	12.46250000	3.98690000
H	6.79590000	12.44130000	4.19270000
H	8.04730000	13.39220000	3.89120000
H	8.25370000	12.03450000	4.71270000
C	4.88180000	9.43060000	5.11060000
C	4.27180000	10.07170000	3.85750000
H	4.63710000	10.97350000	3.74210000
H	3.29880000	10.12300000	3.95800000
H	4.49160000	9.52700000	3.07310000
C	4.29090000	8.04630000	5.32930000
H	4.40530000	7.50990000	4.51670000
H	3.33530000	8.12730000	5.53400000
H	4.74890000	7.60920000	6.07650000
C	4.60000000	10.33240000	6.33240000
H	4.96030000	9.90980000	7.13950000
H	3.63210000	10.45380000	6.43170000
H	5.02670000	11.20390000	6.20040000
N	9.45610000	6.50190000	0.69200000
N	9.55040000	6.45670000	6.91280000
H	9.39830000	6.46210000	1.57450000

H	9.53650000	6.39670000	6.03920000
C	12.81170000	8.32500000	0.60570000
F	11.55780000	8.80690000	0.65040000
F	13.58200000	9.20380000	-0.02680000
F	12.79530000	7.21410000	-0.08040000
O	12.45320000	7.10260000	2.85440000
O	13.30660000	9.35930000	2.89910000
O	14.73640000	7.56670000	2.12220000
S	13.40860000	8.07370000	2.31240000
C	7.48130000	3.02390000	6.50650000
F	8.16920000	1.98760000	6.29670000
F	6.28150000	2.62810000	6.90830000
F	7.97860000	3.71890000	7.54970000
O	8.69220000	4.62330000	4.89620000
O	6.91860000	3.24820000	4.03750000
O	6.52840000	5.14450000	5.42900000
S	7.34840000	4.11130000	5.06080000
O	9.87020000	6.54630000	3.39170000
H	10.73610000	6.58010000	3.31290000
H	9.73080000	5.97000000	4.02700000

(P_2)-3-(TfOH)$_2$-H$_2$O- re-optimized

This geometry was obtained by re-optimization [(CAM-B3LYP 6-31g(d)] of crystallographic data (Table S7/S8) and its ECD spectrum calculated in the same way as in the previous cases.



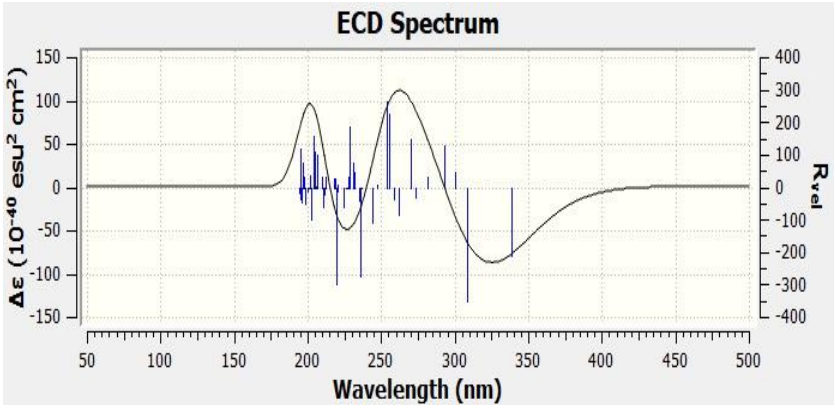


*Figure S74b. (P_2)-**3**-(TfOH)$_2$-H$_2$O complex re-optimized from crystallographic data and ECD calculated spectrum.*

C	-1.87247049	-2.69475365	2.51883798
C	-2.10608249	-3.77919765	3.37065998
H	-3.12063849	-4.03652365	3.64203498
C	-1.01901249	-4.50586965	3.84639998
H	-1.18110949	-5.34718465	4.50941998
C	0.27517051	-4.16378865	3.46405198
H	1.13366751	-4.72456265	3.80706898
C	0.45714251	-3.07256065	2.61064498
C	1.72361051	-2.64246565	2.11577898
C	2.69787451	-2.15162665	1.58691598
C	3.80859551	-1.49967965	0.95442998
C	3.73693851	-1.24621765	-0.33563402
C	3.63615451	-0.97226065	-1.61978702
C	2.99492051	0.25228635	-2.00433402
C	2.41093451	1.27063235	-2.30342702
C	1.57472151	2.40873735	-2.43966702
C	2.00534151	3.69008535	-2.76481802
H	3.04760051	3.85417435	-2.99577502
C	1.08572251	4.73704035	-2.74667102
H	1.41111151	5.73921735	-2.99721002
C	-0.23134949	4.51855735	-2.36324602
H	-0.93951849	5.32982235	-2.28040902
C	-0.63282749	3.22769335	-2.02159102
C	-1.88179849	2.89391635	-1.44546702
C	-2.79485749	2.52363635	-0.73858802
C	-3.78383849	2.14600135	0.22390598
C	-4.15435749	0.88672935	0.32964998
C	-4.50083349	-0.37412065	0.48202698
C	-3.66613349	-1.20516765	1.30117698
C	-2.90565549	-1.91011565	1.92991598
C	5.00889851	-1.10117165	1.83755998
C	5.76546651	-2.38315965	2.23842698
H	6.17782351	-2.88731965	1.35843498
H	5.10415451	-3.08436265	2.75740698
H	6.59255851	-2.13496765	2.91169498
C	5.94379051	-0.15839965	1.06807998
H	6.80247551	0.09837135	1.69580698
H	5.42848251	0.76827135	0.80004298
H	6.32026451	-0.62375365	0.15170698
C	4.48412851	-0.38400565	3.09598798
H	5.32761051	-0.04769365	3.70760698
H	3.86750851	-1.05109265	3.70497298
H	3.88059651	0.48411135	2.82400098
C	4.11522151	-1.91112065	-2.74529202
C	4.79077051	-3.15399165	-2.15251702
H	5.66737651	-2.88505565	-1.55443902
H	5.11897051	-3.81455365	-2.96066402
H	4.10087751	-3.71417365	-1.51449102
C	5.11876251	-1.14963665	-3.63245202
H	4.66534651	-0.25125365	-4.06139602
H	5.44836351	-1.79000865	-4.45690302
H	6.00073151	-0.84896865	-3.05777302
C	2.89072651	-2.33554265	-3.58103902
H	2.17365951	-2.88997465	-2.97052802
H	3.20922251	-2.97899265	-4.40774102
H	2.36730451	-1.47315065	-4.00378502
C	-5.74220849	-1.00674765	-0.18180402
C	-6.80806949	-1.22318365	0.91182998
H	-6.42698249	-1.86594065	1.71222198
H	-7.69288949	-1.70402665	0.48187198
H	-7.11505649	-0.27019165	1.35417298
C	-5.36082149	-2.35881565	-0.81256902
H	-4.60646949	-2.22044765	-1.59008102

H	-6.24840049	-2.81194365	-1.26639602
H	-4.97296749	-3.05417365	-0.06184302
C	-6.28235949	-0.07567665	-1.27547202
H	-6.57717149	0.89637235	-0.86713502
H	-7.16362549	-0.52789465	-1.74085202
H	-5.52475049	0.08455235	-2.04783602
C	-4.26781349	3.25916835	1.18264598
C	-5.35453049	2.72316235	2.12337998
H	-6.22995549	2.37542135	1.56523798
H	-5.67634949	3.51962635	2.80091398
H	-4.98203249	1.89234835	2.72946798
C	-3.05854949	3.74231835	2.01056698
H	-2.67528749	2.93810935	2.64558398
H	-3.35812849	4.57373935	2.65719698
H	-2.23459449	4.08079235	1.37601098
C	-4.83809849	4.42304635	0.35006198
H	-4.08549249	4.82980835	-0.33114802
H	-5.16492949	5.22932935	1.01443698
H	-5.69864649	4.09714035	-0.24305302
N	-0.60765249	-2.35920965	2.17741398
N	0.26423851	2.21988235	-2.14333302
H	-0.41597551	-1.46283835	1.56121702
H	-0.06875149	1.23389735	-1.96006002
C	-1.43107879	-2.72263835	-2.11001822
F	-1.47909679	-2.67344635	-0.74450522
F	-2.45788579	-3.48798335	-2.56975222
F	-0.24471679	-3.26182035	-2.50180022
O	-0.58982821	-0.56275365	-1.55914978
O	-3.13688221	-1.00631665	-2.47240778
O	-0.92611021	-1.38210565	-4.12714878
S	-1.56489221	-1.35490765	-2.64328878
C	3.03536074	3.28821959	1.37920329
F	3.90327674	2.65665559	2.22226629
F	3.11819474	4.63441159	1.57200929
F	3.38340274	3.00044059	0.08684229
O	1.86723126	1.22831241	1.29948671
O	1.33890526	3.18809941	3.17149771
O	0.80654626	3.62363341	0.48496271
S	1.65544726	2.83266241	1.62674571
O	-0.18454300	-0.46691500	0.86025300
H	-0.44944700	-0.49550600	-0.10754700
H	0.52699800	0.23019000	1.11676900

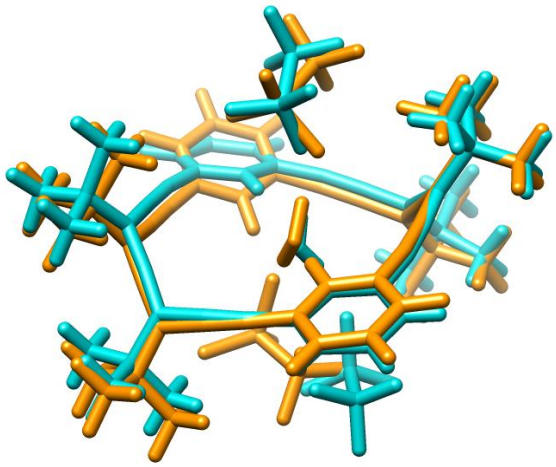


*Figure S74c. Superposition of (P_2)-**3**-$(TfOH)_2$-H_2O complexes from crystallographic data (green) and re-optimized geometry (orange).*

(P_4)-4

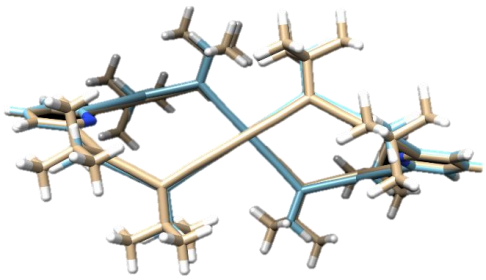
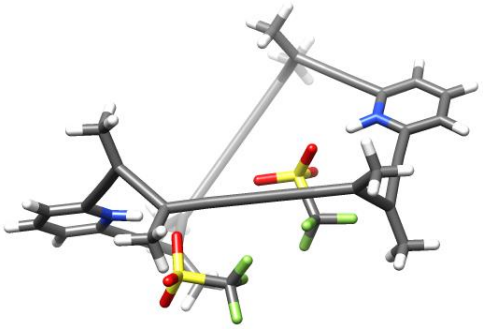


*Figure S75a. Overlay of optimized conformations with tertbutyl (gold) and methyl groups (cyan) for (P_4)-**4**.*

(P_4)-4 – $(TfOH)_2$



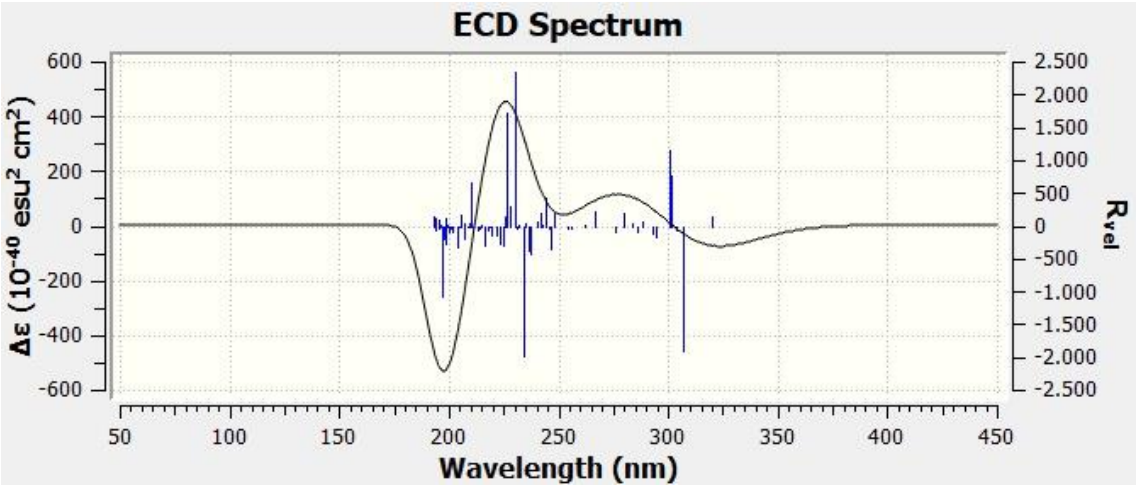


*Figure S75. (P_4)-**4** – TfOH complex and ECD calculated spectrum.*

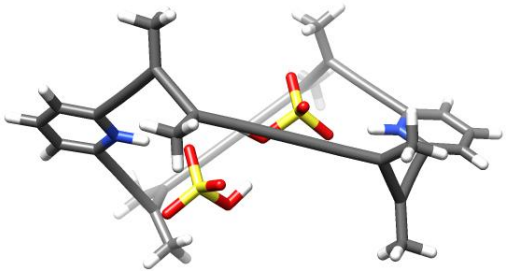
C	1.2890850	5.4747810	0.8359430
C	2.5057250	4.9812620	1.2248340
C	0.2162530	5.9145530	0.4827010
C	3.5825110	4.5467730	1.5720920
C	-3.6377750	4.3181140	-0.9622860

C	-4.4925880	3.5850930	-0.5260300
C	5.2447410	0.6668720	2.8645520
C	5.3477260	-0.4355540	2.3821970
C	-6.1630960	0.8327950	1.1136130
C	-5.5475110	2.7630350	-0.0133900
C	-6.8814400	3.1392580	-0.1749320
C	-7.8730220	2.3145960	0.3336950
C	-7.5167610	1.1453190	0.9882120
C	-5.4011560	-1.3652360	2.3601210
C	-4.0414260	-5.3364750	1.1992090
C	-3.0863520	-5.6881870	0.5408820
C	-1.9847270	-6.0396030	-0.1919190
C	-0.9916230	-6.3091650	-0.8325230
C	2.8075570	-4.2208800	-1.2131750
C	4.7050720	-3.4061690	0.4297120
N	4.5688630	-2.1901440	0.9854700
C	5.8077940	-4.2195720	0.6934830
C	5.5243900	-1.7389530	1.8154730
H	-8.9181260	2.5823590	0.2214620
H	-7.1196270	4.0617540	-0.6901580
H	7.6560880	-4.3664820	1.7793750
C	6.7889720	-3.7544280	1.5554980
C	0.1918070	-6.6075950	-1.5798130
C	1.7796190	-4.5933430	-2.1419330
C	5.1251300	1.9596590	3.4741080
C	4.8823570	4.0834850	1.9498810
C	-1.0323820	6.4937250	0.0922080
C	-2.6366220	5.1817490	-1.5193090
C	-4.9568370	-2.5227440	3.0819380
C	-5.1549520	-4.8995890	1.9849020
C	1.0025960	-5.6157820	-1.8730420
C	4.9958120	3.0197390	2.7117180
C	-1.8303590	5.8321220	-0.7142650
C	-5.0838130	-3.7114510	2.5420050
N	-5.2011010	1.6294530	0.6183300
C	6.6534280	-2.4980960	2.1256890
H	7.4003430	-2.0977760	2.8003290
H	-8.2617990	0.4762690	1.4011310
H	5.8793580	-5.1935900	0.2248760
C	-5.7425040	-0.3584550	1.7874470
C	3.6694260	-3.8424830	-0.4570520
C	5.1699320	2.0295270	4.9853670
C	6.0783520	4.8617990	1.4429320

C	1.6401950	-3.7506230	-3.3916360
C	-1.3672900	7.8676400	0.6335270
C	-2.5787370	5.3073610	-3.0264860
C	-6.3404400	-5.8262930	2.1342430
C	-4.3298660	-2.2934000	4.4400610
C	0.4432840	-8.0421580	-1.9874750
H	6.0311220	5.8978220	1.7925360
H	7.0079600	4.4106460	1.7947610
H	6.0820430	4.8767260	0.3486680
H	4.3578600	1.4348920	5.4151480
H	6.1160560	1.6214620	5.3545480
H	5.0718650	3.0619250	5.3257780
H	0.7957710	-4.0907780	-3.9940440
H	1.4917310	-2.7035120	-3.1127520
H	2.5529390	-3.8128950	-3.9929760
H	1.3787520	-8.1247740	-2.5438680
H	-0.3763470	-8.4068830	-2.6144050
H	0.4985130	-8.6832420	-1.1021210
H	-6.7663360	-6.0575260	1.1529350
H	-7.1113250	-5.3666900	2.7555320
H	-6.0286260	-6.7690680	2.5944550
H	-2.3393700	8.1998100	0.2645280
H	-0.6045300	8.5904610	0.3277720
H	-1.3902610	7.8466910	1.7274770
H	-2.3948310	4.3286320	-3.4804230
H	-3.5325180	5.6816200	-3.4114110
H	-1.7824750	5.9917330	-3.3247550
H	-4.0403890	-3.2422510	4.8957490
H	-3.4437540	-1.6621350	4.3265210
H	-5.0334740	-1.7799490	5.1027980
H	3.8331580	-1.5391890	0.6487510
H	-4.1954060	1.3211340	0.6372720
S	-2.1959950	-0.2642110	-0.4645840
O	-3.2553510	-1.1855480	-0.8908330
O	-0.9087410	-0.8621160	-0.1032250
O	-2.6498280	0.7989370	0.4762480
C	-1.8257300	0.6987130	-2.0074920
F	-0.9295490	1.6631840	-1.7744270
F	-2.9387600	1.2721180	-2.4870940
F	-1.3367970	-0.1082860	-2.9585420
S	3.9422650	0.3816350	-1.5218020
O	4.4761240	-0.6042070	-2.4713570
O	4.8317720	1.5018530	-1.1913170

O	3.2267670	-0.2067970	-0.3608710
C	2.5607250	1.1893760	-2.4580890
F	1.9605870	2.1273720	-1.7156430
F	1.6388040	0.2919890	-2.8273080
F	3.0292890	1.7797570	-3.5684800

(P_4)-4 – (H_2SO_4)$_2$



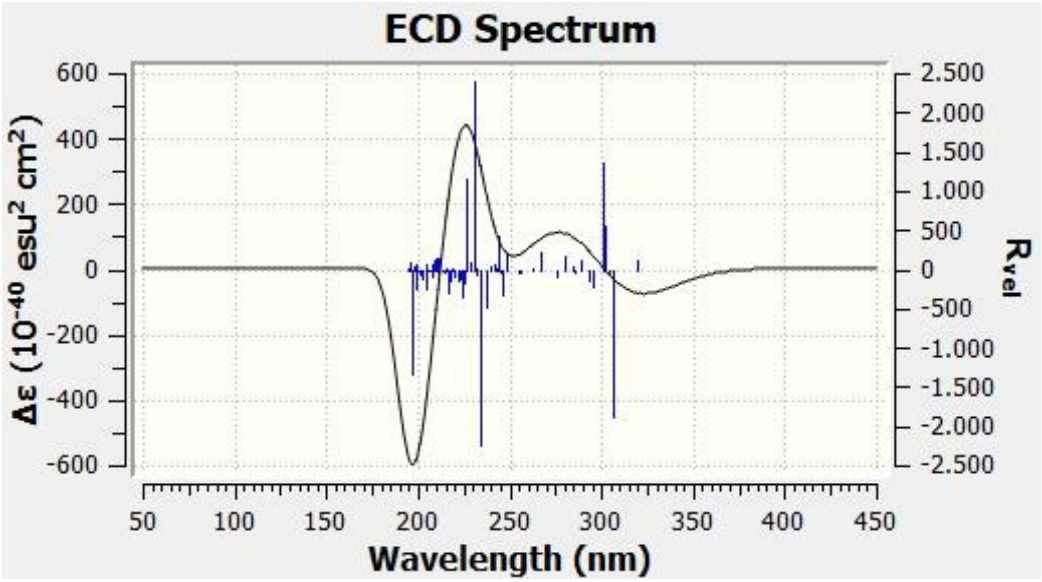


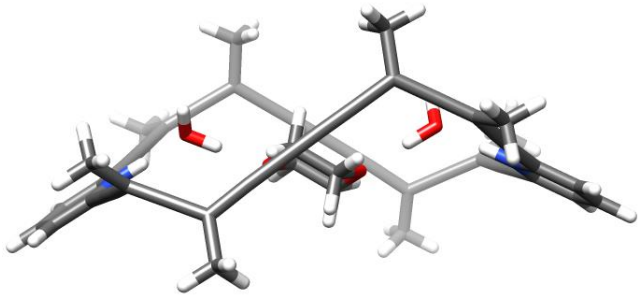
*Figure S76. (P_4)-**4** – H_2SO_4 complex and ECD calculated spectrum.*

C	-0.2807210	-5.7334490	-0.0679800
C	-1.5728680	-5.5049220	0.3233560
C	0.8596590	-5.9389360	-0.4235860
C	-2.7160570	-5.3050740	0.6726630
C	4.3412280	-3.5561060	-1.7239440
C	5.0342580	-2.6945630	-1.2383550
C	-5.1092390	-1.8904190	2.1217720
C	-5.4206200	-0.8057990	1.6913580
C	6.1266150	0.2424860	0.5601600

C	5.9057640	-1.7108970	-0.6687990
C	7.2884870	-1.8133230	-0.8254100
C	8.0973580	-0.8391840	-0.2608010
C	7.5160850	0.2044780	0.4430560
C	4.9433240	2.1857170	1.8978410
C	2.8474120	5.8723710	0.9063480
C	1.8471630	6.0654790	0.2494800
C	0.7037680	6.2337090	-0.4842850
C	-0.3179740	6.3380730	-1.1280580
C	-3.6367010	3.5762010	-1.6736920
C	-5.3522550	2.3277810	-0.1046620
N	-4.9866190	1.1346780	0.3943040
C	-6.5937400	2.8981370	0.1791210
C	-5.8426960	0.4657020	1.1850180
H	9.1753630	-0.8936790	-0.3679070
H	7.7050040	-2.6450700	-1.3802980
H	-8.4434360	2.6296250	1.2390580
C	-7.4723810	2.2089990	1.0008380
C	-1.5312270	6.4392930	-1.8802430
C	-2.6937110	4.1869450	-2.5657320
C	-4.7455450	-3.1647640	2.6703490
C	-4.0838750	-5.1217040	1.0500340
C	2.1998260	-6.2451150	-0.8200970
C	3.5308920	-4.5678350	-2.3389290
C	4.2774530	3.1974130	2.6668340
C	4.0186760	5.6200270	1.6890260
C	-2.1319120	5.3254720	-2.2346930
C	-4.4072830	-4.1398900	1.8601390
C	2.8602100	-5.4017390	-1.5800280
C	4.1753320	4.4139660	2.1869950
N	5.3411740	-0.6992080	0.0107830
C	-7.0998370	0.9754500	1.5121370
H	-7.7598620	0.4046170	2.1538490
H	8.1140200	0.9832890	0.9003760
H	-6.8494890	3.8623180	-0.2432200
C	5.4778230	1.2942450	1.2832920
C	-4.4143420	3.0005020	-0.9514930
C	-4.7871790	-3.3182620	4.1755060
C	-5.1022750	-6.0900610	0.4858330
C	-2.3840930	3.4513720	-3.8519850
C	2.7909690	-7.5538480	-0.3398900
C	3.5097010	-4.6259410	-3.8511750
C	5.0006310	6.7498150	1.9030480

C	3.6968240	2.7827710	4.0014240
C	-2.0532930	7.8168370	-2.2226210
H	-4.8574820	-7.1136920	0.7859200
H	-6.1043570	-5.8456420	0.8430240
H	-5.0948560	-6.0501000	-0.6077840
H	-4.1091720	-2.6002500	4.6472330
H	-5.7972300	-3.1201330	4.5476700
H	-4.4931530	-4.3280410	4.4674550
H	-1.6172800	3.9784650	-4.4227940
H	-2.0373140	2.4400350	-3.6213280
H	-3.2870670	3.3661950	-4.4651480
H	-2.9828420	7.7449250	-2.7903050
H	-1.3153870	8.3644460	-2.8171620
H	-2.2384750	8.3895470	-1.3085090
H	5.3808430	7.1083650	0.9414330
H	5.8414120	6.4172320	2.5145840
H	4.5083630	7.5899690	2.4027070
H	3.8117510	-7.6726020	-0.7077760
H	2.1852890	-8.3941850	-0.6930810
H	2.8012980	-7.5841630	0.7540320
H	3.1427290	-3.6796160	-4.2605530
H	4.5208190	-4.7886690	-4.2373030
H	2.8636390	-5.4354660	-4.1956110
H	3.2253220	3.6334290	4.4972410
H	2.9509410	1.9985630	3.8424960
H	4.4817500	2.3823190	4.6506120
S	-2.5241970	-0.6366500	-1.5968010
O	-3.6484070	-0.2768000	-2.4646210
O	-2.2346510	-2.0695870	-1.4836600
O	-2.5849860	0.0409700	-0.2519910
S	1.4964810	-0.5294900	0.8977310
O	1.1295240	-1.9387900	1.0805700
O	2.6497130	-0.3168730	-0.0136110
O	1.5518270	0.2598420	2.1351080
O	-1.2371520	0.0487570	-2.3255620
H	-0.4758140	0.0123210	-1.7053600
O	0.2802140	0.1489230	0.0000050
H	-0.5810340	0.0777380	0.4635130
H	-4.0467260	0.7196880	0.1503150
H	4.2975310	-0.6218320	0.0872130

(P_4)-4 – Dioxane-$(H_2O)_2$



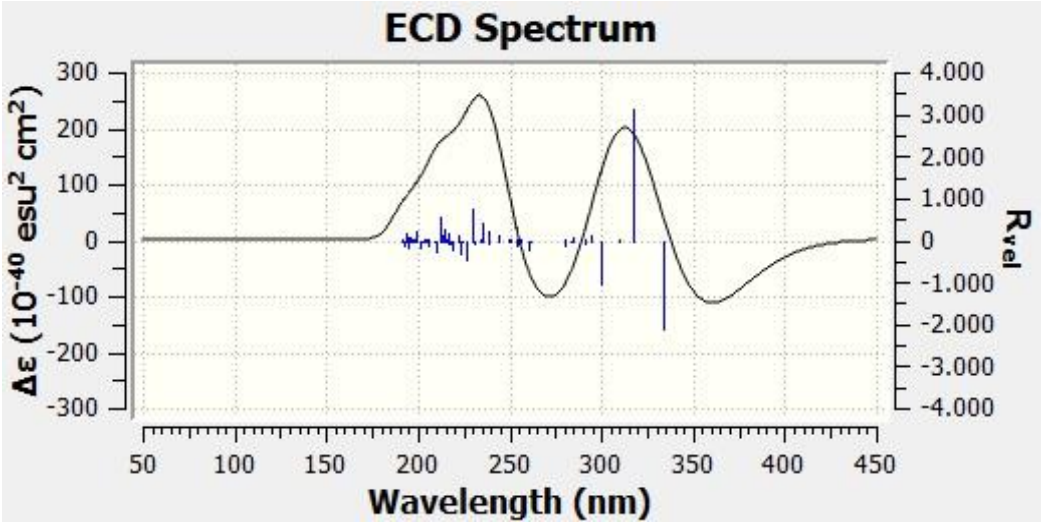


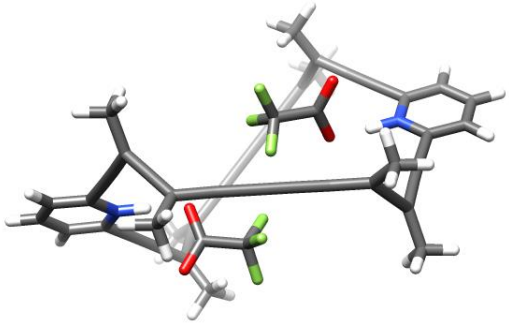
*Figure S77. (P_4)-**4** – Dioxane-$(H_2O)_2$ complex and ECD calculated spectrum.*

C	0.2862230	-4.8722100	0.8827250
C	-0.8495080	-5.0174590	0.1304080
C	1.3008240	-4.7301000	1.5321470
C	-1.8549550	-5.1287000	-0.5390440
C	5.4131980	-3.5387370	0.5293430
C	5.9683430	-2.5817550	0.0407140
C	-5.8093400	-3.1808650	-0.6334410
C	-6.2374520	-2.0589960	-0.7735940
C	6.8513800	0.8293020	-0.9202340
C	6.7002400	-1.5079680	-0.5316170
C	7.9165320	-1.7090640	-1.1773970
C	8.5964240	-0.6171280	-1.6969740
C	8.0693350	0.6617740	-1.5674470
C	5.8231020	3.2302030	-0.6065940
C	1.8351930	5.1033160	-0.5107200
C	0.8322170	4.9867570	0.1615640
C	-0.3032630	4.8414510	0.9142570
C	-1.3183720	4.7030630	1.5636320

C	-5.4280390	3.5828040	0.5328340
C	-6.6887660	1.5598980	-0.5740300
N	-6.1928740	0.3065280	-0.4614050
C	-7.8859140	1.7598800	-1.2549470
C	-6.8220100	-0.7767920	-0.9726140
H	9.5446580	-0.7620810	-2.2030110
H	8.3094890	-2.7144070	-1.2585220
H	-9.4805200	0.8110640	-2.3301020
C	-8.5469330	0.6674660	-1.7971720
C	-2.5084430	4.5224850	2.3383270
C	-4.8268330	4.7415340	1.1196640
C	-5.3576660	-4.5280910	-0.4376250
C	-3.0126130	-5.2587080	-1.3704340
C	2.4892750	-4.5459140	2.3086140
C	4.8124490	-4.7103510	1.0905150
C	5.3522410	4.5726180	-0.4249620
C	2.9861440	5.2429850	-1.3497840
C	-3.6711790	4.6234450	1.7350270
C	-4.1826020	-4.8865790	-0.9016880
C	3.6532110	-4.6142490	1.7029080
C	4.1664600	4.9025940	-0.8830460
N	6.2042460	-0.2537710	-0.4309680
C	-8.0201490	-0.6103100	-1.6559240
H	-8.5198050	-1.4793240	-2.0642620
H	8.5830700	1.5306760	-1.9582330
H	-8.2789560	2.7644460	-1.3448650
C	6.2615830	2.1112250	-0.7371340
C	-5.9753480	2.6323590	0.0232030
C	-6.2900660	-5.4725150	0.2912770
C	-2.8215640	-5.8213870	-2.7626670
C	-5.5717840	6.0537390	0.9952210
C	2.3400620	-4.2808800	3.7909700
C	5.5665870	-6.0156240	0.9460480
C	2.7761340	5.7798910	-2.7495610
C	6.2744700	5.5431620	0.2817890
C	-2.3620880	4.2220050	3.8140880
H	-2.4041050	-6.8307560	-2.7040470
H	-3.7730490	-5.8600330	-3.2948690
H	-2.1218140	-5.1974940	-3.3262350
H	-6.5034650	-5.0907250	1.2939280
H	-7.2378110	-5.5560670	-0.2485690
H	-5.8398660	-6.4625620	0.3756910
H	-5.0134300	6.8561470	1.4791820

H	-5.7161520	6.3048430	-0.0596130
H	-6.5573510	5.9725450	1.4626930
H	-3.3413310	4.1041880	4.2803220
H	-1.8257740	5.0360940	4.3100880
H	-1.7868110	3.3021950	3.9537190
H	2.0871290	5.1324760	-3.2996970
H	3.7239910	5.8305730	-3.2871740
H	2.3374510	6.7809030	-2.7043290
H	3.3178430	-4.1578710	4.2589370
H	1.8175450	-5.1145190	4.2688970
H	1.7502550	-3.3738760	3.9520280
H	5.7175240	-6.2467270	-0.1124330
H	6.5493350	-5.9365730	1.4197630
H	5.0110320	-6.8300940	1.4127710
H	5.8082620	6.5266350	0.3556590
H	6.5028640	5.1799210	1.2880130
H	7.2160380	5.6346550	-0.2674880
C	0.6918680	-1.3002610	-0.4632310
C	-0.5731580	-1.1643340	0.3555700
O	-1.3738970	-0.0870320	-0.1481200
C	-0.6437790	1.1465540	-0.1333470
C	0.6225950	1.0114570	-0.9516050
O	1.4209070	-0.0687710	-0.4586820
H	1.3466640	-2.0615370	-0.0359970
H	0.4522070	-1.5698380	-1.4998160
H	-0.3297160	-0.9723050	1.4089200
H	-1.1765660	-2.0708590	0.2831980
H	-1.2973610	1.9088590	-0.5615600
H	-0.4053800	1.4118220	0.9046030
H	0.3804150	0.8241680	-2.0055730
H	1.2258990	1.9180850	-0.8771140
O	3.8131940	0.0973460	0.7931340
H	2.9424880	0.0714330	0.3305630
H	3.7449310	0.7627060	1.4913450
O	-3.8757550	-0.0288280	0.9027680
H	-3.8801740	-0.6714000	1.6254510
H	-2.9719630	-0.0485660	0.5041990
H	-5.2848400	0.1650090	0.0502590
H	5.2763480	-0.1108000	0.0430160

(P_4)-4 – $(TFA)_2$



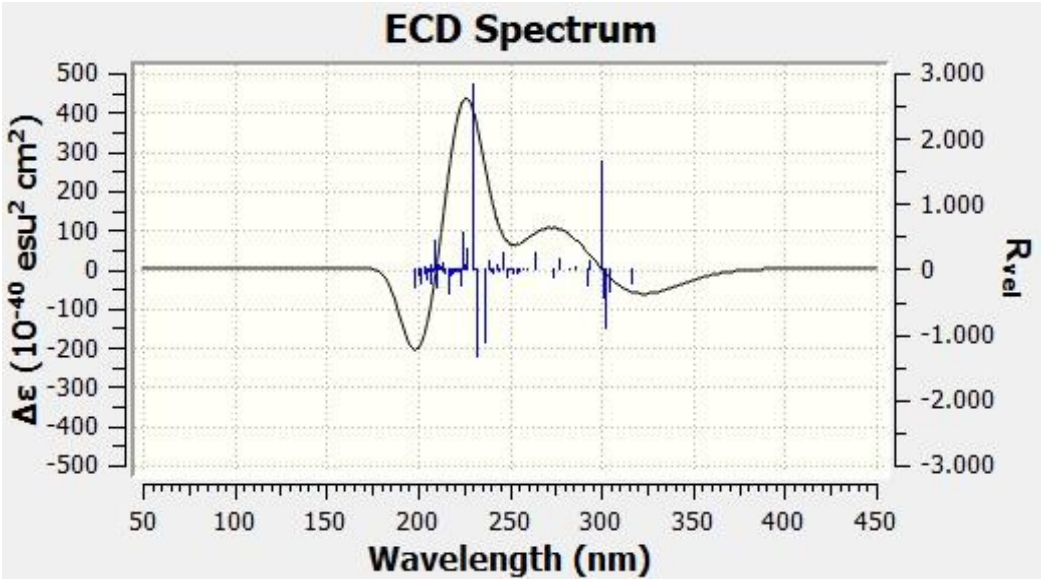


*Figure S78. (P_4)-**4** – TFA complex and ECD calculated spectrum.*

C	0.2236010	-5.6285410	-0.2149200
C	-1.0808300	-5.5398280	0.1920190
C	1.3751010	-5.7104660	-0.5843530
C	-2.2346160	-5.4637100	0.5550920
C	4.5793350	-2.9635100	-1.8794420
C	5.1855380	-2.0425350	-1.3868280
C	-4.9496680	-2.3348360	2.0801330
C	-5.3753970	-1.2817450	1.6698020
C	5.9902370	0.9644270	0.4475130
C	5.9576270	-0.9830210	-0.8099790
C	7.3417870	-0.9404290	-0.9811110
C	8.0525170	0.1032710	-0.4087910
C	7.3749120	1.0711850	0.3168240
C	4.6284180	2.7558460	1.8266240
C	2.1545110	6.2217320	0.9129850
C	1.1326190	6.3206530	0.2686100
C	-0.0299400	6.3812460	-0.4517050

C	-1.0639570	6.3895010	-1.0841830
C	-4.0874520	3.3094650	-1.6422710
C	-5.6485450	1.8684090	-0.0770970
N	-5.1571050	0.7118700	0.3994090
C	-6.9388920	2.3038480	0.2271640
C	-5.9312210	-0.0530190	1.1875790
H	9.1291910	0.1614530	-0.5268030
H	7.8353920	-1.7167010	-1.5529020
H	-8.7395930	1.8310530	1.2999530
C	-7.7331530	1.5160200	1.0460740
C	-2.2893230	6.3765390	-1.8233150
C	-3.2219100	4.0269680	-2.5333400
C	-4.4511430	-3.5729850	2.6051350
C	-3.6098320	-5.4274810	0.9480640
C	2.7352110	-5.8714000	-0.9981380
C	3.8704560	-4.0440090	-2.5027040
C	3.8706570	3.6823090	2.6176540
C	3.3539560	6.0796220	1.6806160
C	-2.7763510	5.2122120	-2.1896540
C	-4.0234440	-4.4961420	1.7765300
C	3.2972210	-4.9535170	-1.7508130
C	3.6389890	4.8888530	2.1580260
N	5.2996970	-0.0447710	-0.1093360
C	-7.2304290	0.3198920	1.5343420
H	-7.8213330	-0.3251310	2.1731330
H	7.8947090	1.9005120	0.7807650
H	-7.2968430	3.2427420	-0.1775280
C	5.2448540	1.9331820	1.1931320
C	-4.7939890	2.6462980	-0.9220350
C	-4.4603830	-3.7520900	4.1080070
C	-4.5295610	-6.4869770	0.3782030
C	-2.8524820	3.3461300	-3.8338620
C	3.4627550	-7.1193650	-0.5441630
C	3.8388470	-4.0817180	-4.0154150
C	4.2170470	7.3010870	1.9032410
C	3.3502430	3.1905810	3.9509050
C	-2.9537190	7.6980150	-2.1390460
H	-4.1777430	-7.4843310	0.6598180
H	-5.5474810	-6.3521400	0.7485430
H	-4.5382120	-6.4303710	-0.7146700
H	-3.8545420	-2.9752120	4.5846430
H	-5.4813130	-3.6643310	4.4926630
H	-4.0611040	-4.7304860	4.3812450

H	-2.1500880	3.9575970	-4.4034280
H	-2.4012420	2.3725100	-3.6224250
H	-3.7485800	3.1776250	-4.4398340
H	-3.8771140	7.5393010	-2.6990890
H	-2.2824420	8.3272630	-2.7317450
H	-3.1867200	8.2351370	-1.2143310
H	4.5479410	7.7109360	0.9438890
H	5.0941410	7.0477210	2.5015810
H	3.6466300	8.0787440	2.4206570
H	4.4862600	-7.1271370	-0.9233900
H	2.9427030	-8.0122170	-0.9048850
H	3.4880710	-7.1645560	0.5490020
H	3.3722460	-3.1722030	-4.4063800
H	4.8570550	-4.1339520	-4.4134850
H	3.2755620	-4.9482050	-4.3665220
H	2.7993620	3.9808780	4.4644510
H	2.6870960	2.3362830	3.7866080
H	4.1791580	2.8634170	4.5863430
O	3.3512040	-1.3454090	2.1780600
C	1.0318150	-1.0743390	1.6881330
O	2.7394070	-0.2688770	0.2874010
C	-1.3901300	-0.6566800	-2.1625990
O	-2.7613850	0.0365500	-0.3551380
O	-3.7465430	-0.8677680	-2.1767060
C	2.5410960	-0.8864390	1.3702520
C	-2.7880710	-0.4712710	-1.5080460
F	0.8107360	-1.6933040	2.8612060
F	0.3899600	0.1139370	1.7470590
F	0.4170460	-1.8080280	0.7359620
F	-0.9508190	-1.9251340	-1.9801780
F	-1.4209260	-0.4462150	-3.4945730
F	-0.4500190	0.1623660	-1.6615250
H	-4.1741680	0.4078180	0.1572620
H	4.2500960	-0.0997170	0.0027680

(P_4)-4 – 1,2-ethanedisulfonic acid

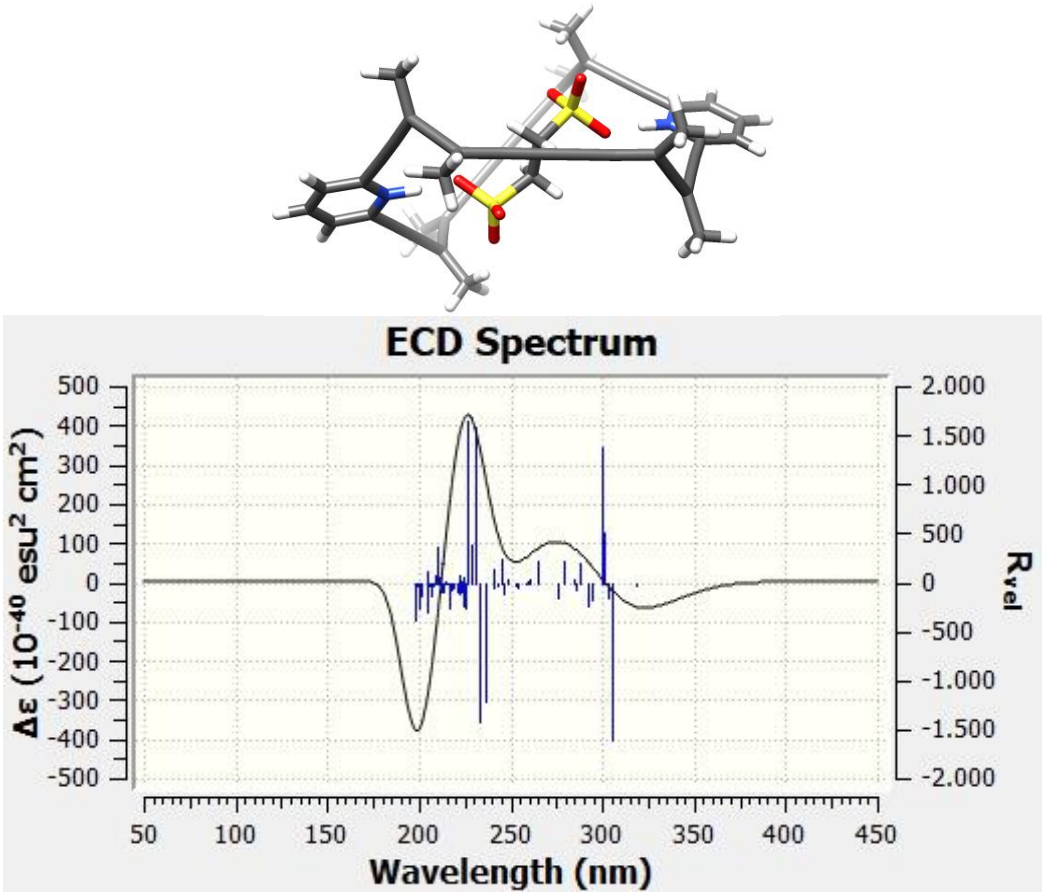


*Figure S79. (P_4)-**4** – 1,2-ethanedisulfonic acid complex and ECD calculated spectrum.*

C	-0.1812700	-5.7371270	0.2674770
C	1.1308570	-5.6472140	-0.1136390
C	-1.3397630	-5.8201210	0.6141110
C	2.2915120	-5.5700320	-0.4538740
C	-4.5704710	-3.0764400	1.8489690
C	-5.1674210	-2.1552750	1.3455310
C	5.0341590	-2.4379120	-1.9218030
C	5.4511160	-1.3850380	-1.5020180
C	-5.9376230	0.8533190	-0.5009460
C	-5.9286950	-1.0955070	0.7548100
C	-7.3159310	-1.0539480	0.8987220
C	-8.0158940	-0.0100200	0.3136850
C	-7.3247290	0.9590890	-0.3973990
C	-4.5500870	2.6469940	-1.8510640
C	-2.0966810	6.1132820	-0.8851570
C	-1.0877150	6.2120740	-0.2207090
C	0.0604220	6.2725350	0.5223880
C	1.0818010	6.2806810	1.1750830
C	4.0955710	3.2017610	1.7891240

C	5.6880160	1.7633100	0.2533980
N	5.2067070	0.6071150	-0.2340090
C	6.9838200	2.1998380	-0.0249670
C	5.9965890	-0.1565380	-1.0076350
H	-9.0947130	0.0474130	0.4105710
H	-7.8202210	-1.8311370	1.4598460
H	8.8055360	1.7292800	-1.0626890
C	7.7944860	1.4133890	-0.8289940
C	2.2924070	6.2676000	1.9381500
C	3.2122520	3.9177780	2.6637920
C	4.5467880	-3.6757620	-2.4578640
C	3.6741660	-5.5325790	-0.8196920
C	-2.7076480	-5.9822930	1.0008990
C	-3.8733390	-4.1572250	2.4848610
C	-3.7774710	3.5747700	-2.6260250
C	-3.2807190	5.9713370	-1.6763770
C	2.7728310	5.1031480	2.3127150
C	4.1034310	-4.6000840	-1.6388430
C	-3.2848920	-5.0655670	1.7433870
C	-3.5556020	4.7809350	-2.1606070
N	-5.2576500	-0.1562670	0.0682390
C	7.3021680	0.2175180	-1.3283670
H	7.9059010	-0.4264590	-1.9561210
H	-7.8357990	1.7886290	-0.8705630
H	7.3331770	3.1385010	0.3876910
C	-5.1783690	1.8232650	-1.2307330
C	4.8165140	2.5398140	1.0821630
C	4.5856790	-3.8531950	-3.9604610
C	4.5831450	-6.5921800	-0.2330220
C	2.8177310	3.2352870	3.9560510
C	-3.4253840	-7.2301700	0.5313370
C	-3.8714540	-4.1965930	3.9978580
C	-4.1399920	7.1925530	-1.9145870
C	-3.2306540	3.0848180	-3.9493270
C	2.9496800	7.5891040	2.2683330
H	4.2375240	-7.5894210	-0.5225950
H	5.6080670	-6.4563480	-0.5831310
H	4.5702750	-6.5367800	0.8598710
H	3.9888650	-3.0761360	-4.4480620
H	5.6139230	-3.7644250	-4.3248740
H	4.1924320	-4.8315160	-4.2425690
H	2.1039120	3.8457170	4.5123680
H	2.3713150	2.2616430	3.7347140

H	3.7018440	3.0666220	4.5793380
H	3.8619810	7.4303000	2.8462470
H	2.2665060	8.2173120	2.8484110
H	3.2004960	8.1273870	1.3489670
H	-4.4899260	7.6011470	-0.9614770
H	-5.0050030	6.9393490	-2.5303340
H	-3.5599760	7.9711110	-2.4198350
H	-4.4561410	-7.2389500	0.8903600
H	-2.9119930	-8.1231240	0.9012340
H	-3.4291770	-7.2741650	-0.5621630
H	-3.4131700	-3.2872450	4.3989190
H	-4.8972600	-4.2498520	4.3757750
H	-3.3146660	-5.0631460	4.3590190
H	-2.6702520	3.8760000	-4.4510740
H	-2.5703560	2.2307200	-3.7729610
H	-4.0467220	2.7578860	-4.6012970
H	4.2285470	0.3030940	-0.0124730
H	-4.2094270	-0.2314450	-0.0539940
S	-1.7389240	-0.6817580	-1.2758600
O	-1.9760460	0.1717060	-2.4622090
O	-1.7048140	-2.1335150	-1.5660510
C	-0.1174840	-0.2184240	-0.6541640
O	-2.6694870	-0.3541560	-0.1337390
C	0.3304270	-1.0935910	0.5010360
S	1.8032100	-0.4294630	1.2931530
O	2.2780450	-1.4701770	2.2336110
O	2.7583980	-0.2075980	0.1490810
O	1.4044740	0.8396310	1.9445120
H	-0.2013710	0.8307990	-0.3628430
H	0.5672870	-0.2977150	-1.5000260
H	0.5803820	-2.1018780	0.1675530
H	-0.4259910	-1.1548630	1.2867040

$((P_4)\text{-}4)_2 – (TfOH)_4\text{-}(H_2O)_5$

This geometry was obtained directly from crystallographic data (Table S9/S10) and its ECD spectrum calculated in the same way as in the previous cases.

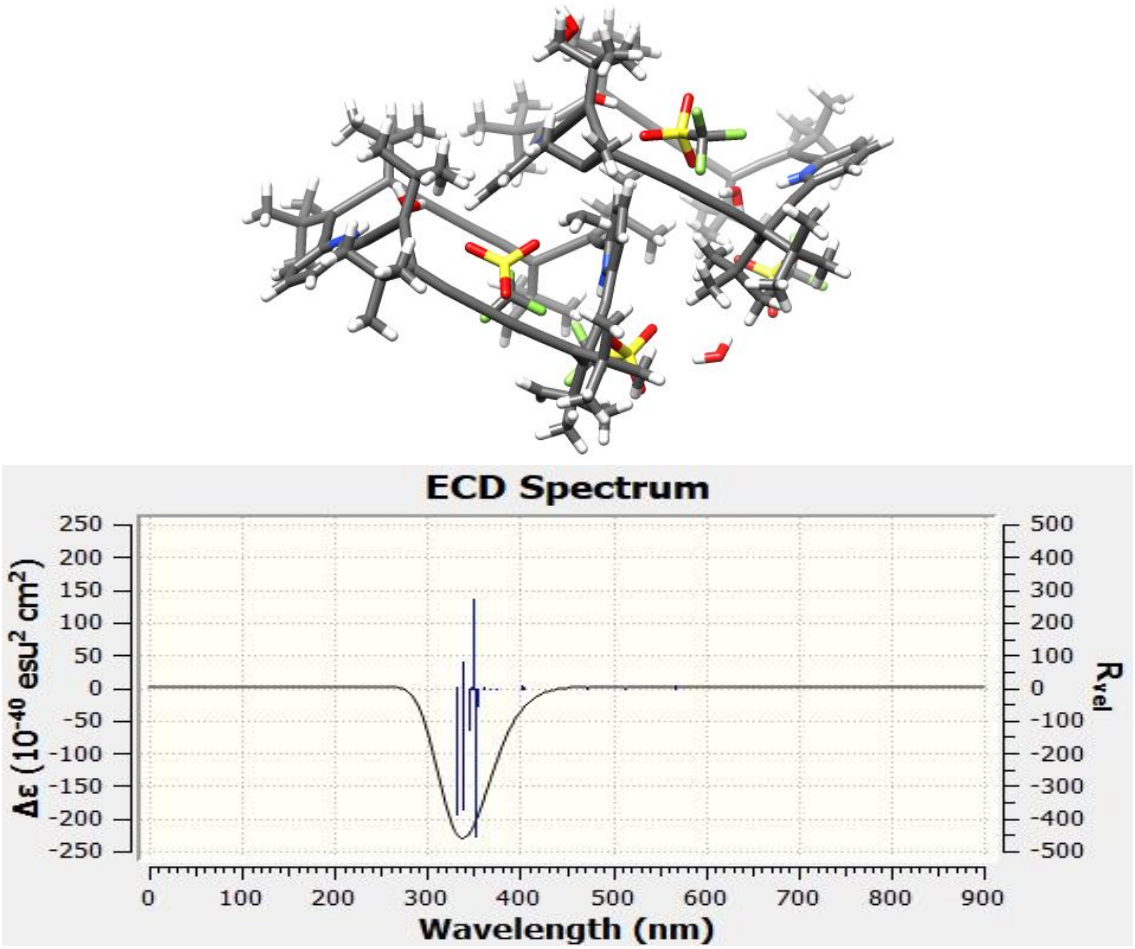


Figure S80. $((P_4)\text{-}\mathbf{4})_2 – (TfOH)_4\text{-}(H_2O)_5$ complex obtained from crystallographic data and ECD calculated spectrum.

C	-0.812104	3.409392	1.414972
C	-1.898323	3.527684	0.635947
H	-1.94734	4.222322	-0.010114
C	-2.959879	2.624696	0.777569
H	-3.735705	2.745417	0.242733
C	-2.924097	1.578457	1.652966
H	-3.634483	0.950232	1.710746
C	-1.780992	1.479258	2.464634
C	-1.685874	0.483198	3.454586
C	-1.807154	-0.461347	4.196666
C	-1.882547	-1.598891	5.150556
C	-0.060956	-1.052324	6.652867
H	0.263752	-1.169029	7.570074

H	0.103247	-0.130786	6.362981
H	0.411589	-1.671083	6.057742
C	-1.550377	-1.340695	6.60299
C	-2.315055	-0.126587	7.166332
H	-2.361706	-0.194454	8.142905
H	-3.22231	-0.111499	6.796234
H	-1.847258	0.697964	6.918182
C	-1.851264	-2.610712	7.398685
H	-1.052749	-3.178343	7.422272
H	-2.585945	-3.09793	6.970644
H	-2.10816	-2.369963	8.313314
C	-2.317741	-2.655357	4.691418
C	-2.664004	-3.834604	4.201644
C	-4.13826	-4.388502	3.997171
C	-4.245526	-5.582827	4.982831
H	-3.388562	-5.705143	5.442343
H	-4.469006	-6.397376	4.486073
H	-4.94671	-5.399875	5.642633
C	-5.096614	-3.283128	4.621983
H	-4.820626	-3.094371	5.543232
H	-6.019939	-3.611563	4.618392
H	-5.039729	-2.462475	4.089266
C	-4.294101	-4.67016	2.279157
H	-4.425747	-3.815199	1.818578
H	-5.063926	-5.253091	2.112174
H	-3.479864	-5.100099	1.943459
C	-1.616942	-4.675616	3.689979
C	-0.717757	-5.306078	3.229191
C	0.352973	-5.933753	2.619022
C	1.321353	-6.444831	2.085511
C	2.462287	-6.91653	1.3399
C	2.651933	-8.377981	1.030891
C	2.585312	-9.073867	2.363487
H	2.466521	-10.036535	2.223836
H	1.828779	-8.722652	2.877994
H	3.41725	-8.915577	2.856672
C	1.577401	-8.814817	0.052849
H	1.140679	-9.62562	0.388059
H	1.984886	-8.999807	-0.818969
H	0.91245	-8.101206	-0.042113
C	4.010989	-8.658308	0.406052
H	4.714099	-8.262822	0.962457
H	4.045077	-8.265986	-0.491244
H	4.148819	-9.626635	0.3448
C	3.255282	-5.984545	0.756938
C	3.907316	-5.046506	0.204706

C	3.446071	-4.440594	-1.168082
C	1.951266	-4.849556	-1.42035
H	1.556102	-4.248709	-2.086068
H	1.44865	-4.783731	-0.581621
H	1.916074	-5.771495	-1.750788
C	3.559769	-2.971621	-1.124968
H	4.499236	-2.720121	-1.003959
H	3.029808	-2.624782	-0.377157
H	3.225908	-2.593317	-1.965034
C	4.356708	-5.060301	-2.244018
H	5.26643	-4.710233	-2.143106
H	4.014961	-4.830408	-3.133199
H	4.36829	-6.034718	-2.140406
C	5.19851	-4.583533	0.713305
C	6.214132	-4.216064	1.1263
C	7.506859	-3.878511	1.599964
C	8.311684	-4.74986	2.286346
H	7.990874	-5.622732	2.480279
C	9.561873	-4.3938	2.697437
H	10.078888	-4.997724	3.217484
C	10.075117	-3.169173	2.363541
H	10.964059	-2.938216	2.606138
C	9.296022	-2.285612	1.679351
C	9.710892	-1.00358	1.333891
C	10.266241	0.042402	1.028899
C	10.908492	1.274257	0.724618
C	12.366312	1.48793	1.148265
C	13.21389	0.632056	0.147388
H	13.339473	-0.26856	0.512732
H	14.087721	1.055283	0.014283
H	12.74497	0.573799	-0.71116
C	12.562394	1.050912	2.551631
H	12.062621	1.643487	3.151137
H	13.515755	1.088407	2.775275
H	12.238323	0.131929	2.655935
C	12.76103	2.960294	0.999293
H	12.629322	3.241264	0.069712
H	13.703319	3.072162	1.244012
H	12.202904	3.509372	1.588673
C	10.148302	2.187365	0.053099
C	9.373972	2.96413	-0.650978
C	9.396489	3.150552	-2.164032
C	10.599516	2.349515	-2.720823
H	11.388346	2.514943	-2.163218
H	10.784008	2.634024	-3.640274
H	10.387544	1.39277	-2.711223

C	9.52396	4.634127	-2.461529
H	8.829629	5.125659	-1.974946
H	9.417213	4.784691	-3.423878
H	10.407348	4.949545	-2.177536
C	8.097749	2.56224	-2.713423
H	8.157158	1.58405	-2.714964
H	7.955624	2.8823	-3.628704
H	7.347435	2.843127	-2.148997
C	8.369206	3.735072	0.06907
C	7.489833	4.279516	0.652728
C	6.448952	4.792277	1.408896
C	5.497541	5.100462	2.067265
C	4.359016	5.456624	2.883737
C	4.482924	5.489681	4.362773
C	5.461419	6.625319	4.771313
H	6.355277	6.428035	4.421462
H	5.499588	6.6878	5.748647
H	5.146478	7.476586	4.401737
C	4.857277	4.147253	4.889694
H	4.289985	3.463901	4.475462
H	4.731588	4.131137	5.861517
H	5.796582	3.963794	4.67873
C	3.109041	5.808861	5.0112
H	2.889261	6.752355	4.863113
H	3.153031	5.630956	5.973914
H	2.417586	5.244804	4.605984
C	3.270657	5.826225	2.206682
C	2.179847	6.1442	1.563126
C	2.00113	7.550174	0.964956
C	2.965809	8.477506	1.658108
H	2.945732	9.354999	1.222213
H	3.871306	8.10657	1.604283
H	2.707685	8.573967	2.598592
C	0.556134	8.00515	1.229077
H	0.428099	8.144519	2.190571
H	-0.065913	7.317054	0.912994
H	0.385381	8.843898	0.75181
C	1.154367	5.156599	1.432608
C	0.294257	4.328331	1.41481
C	2.204221	7.486798	-0.501848
H	1.572263	6.847309	-0.891722
H	3.121004	7.19763	-0.692439
H	2.053854	8.373465	-0.891055
N	-0.76281	2.416025	2.387536
H	-0.087987	2.38267	2.951474
N	8.00986	-2.661246	1.344764

H	7.493945	-2.072003	0.943679
C	2.922882	-2.508461	3.599163
F	4.239472	-3.170397	3.710538
F	2.329854	-2.74603	4.694576
F	2.378127	-3.172573	2.569954
O	3.971074	-0.297749	4.316329
O	1.940886	-0.328613	3.112816
O	3.934997	-0.897175	1.938146
S	3.26369	-0.836541	3.195424
C	8.879349	-1.574205	-3.014705
F	9.763954	-2.504807	-3.469759
F	8.885422	-0.657369	-3.968571
F	9.408406	-1.014591	-1.916061
O	6.486832	-1.155034	-2.304728
O	7.550706	-3.197482	-1.606425
O	6.890816	-2.932893	-3.942983
S	7.282991	-2.311424	-2.688622
C	-9.120656	4.547745	-1.229608
C	-10.271265	4.62168	-1.87306
H	-10.469418	5.415432	-2.35585
C	-11.201487	3.598987	-1.877703
H	-12.034977	3.696607	-2.322968
C	-10.88848	2.459387	-1.230665
H	-11.475138	1.713664	-1.278553
C	-9.737792	2.368618	-0.508722
C	-9.413779	1.253722	0.254476
C	-9.416982	0.231734	0.951067
C	-9.414326	-0.926803	1.731374
C	-9.992297	-1.968979	1.287159
C	-10.522706	-3.133237	0.792528
C	-8.881448	-0.807398	3.227539
C	-9.787928	0.248505	4.041323
H	-10.727571	-0.026902	3.998982
H	-9.690047	1.138405	3.642673
H	-9.497344	0.275775	4.976837
C	-8.87901	-2.159736	3.871078
H	-8.67087	-2.067553	4.824313
H	-8.202622	-2.724367	3.44219
H	-9.762013	-2.572158	3.767905
C	-7.364387	-0.393372	3.054013
H	-6.801288	-1.194704	3.086589
H	-7.107363	0.216151	3.777186
H	-7.244859	0.055097	2.190861
C	-12.022803	-3.421031	0.820655
C	-12.831299	-2.347848	1.521181
H	-12.651862	-2.379989	2.484094

H	-13.785891	-2.501471	1.361439
H	-12.578912	-1.467947	1.171081
C	-12.526674	-3.532508	-0.645166
H	-12.503564	-2.64812	-1.066696
H	-13.445824	-3.872571	-0.649642
H	-11.948535	-4.147106	-1.143459
C	-12.231994	-4.744961	1.555201
H	-11.81068	-5.470015	1.048066
H	-13.191902	-4.922134	1.642212
H	-11.827537	-4.691669	2.446192
C	-9.633154	-3.974811	0.144921
C	-8.73479	-4.615582	-0.388205
C	-7.68737	-5.28008	-1.006705
C	-6.725597	-5.753182	-1.505879
C	-5.553663	-6.364295	-2.064559
C	-5.411492	-7.833487	-1.924406
C	-6.490466	-8.457494	-2.941597
H	-7.042854	-9.114797	-2.469207
H	-6.024275	-8.895723	-3.683942
H	-7.061439	-7.742025	-3.291495
C	-4.011553	-8.28597	-2.49978
H	-3.293985	-7.887873	-1.964043
H	-3.92882	-7.987811	-3.429745
H	-3.943398	-9.262949	-2.462734
C	-5.550935	-8.166875	-0.500771
H	-4.684907	-8.06215	-0.054323
H	-5.854933	-9.094173	-0.41076
H	-6.206228	-7.566703	-0.087474
C	-4.697763	-5.614839	-2.675638
C	-3.86187	-4.861276	-3.31264
C	-3.935415	-4.491212	-4.857733
C	-4.978179	-5.542433	-5.414605
H	-5.228518	-6.164281	-4.69966
H	-4.574914	-6.04164	-6.155355
H	-5.776884	-5.07282	-5.733632
C	-4.392239	-3.219168	-4.993792
H	-3.916334	-2.598647	-5.533112
H	-5.187682	-2.950047	-4.549483
C	-2.696799	-4.893784	-5.555366
H	-2.096436	-4.122545	-5.626362
H	-2.918338	-5.21908	-6.452848
H	-2.254006	-5.60694	-5.049482
C	-2.840625	-4.216781	-2.532454
C	-2.05385	-3.654577	-1.823765
C	-1.257502	-2.906493	-0.920081
C	-1.220708	-3.174765	0.412789

H	-1.68357	-3.925242	0.76629
C	-0.495737	-2.334736	1.250279
H	-0.44705	-2.518509	2.181127
C	0.151707	-1.236395	0.730525
H	0.621325	-0.648152	1.310109
C	0.124416	-0.987424	-0.602605
C	0.754191	0.140273	-1.18871
C	1.313006	1.169011	-1.534139
C	1.976112	2.390948	-1.808854
C	3.388134	2.575714	-1.214401
C	4.31333	1.492733	-1.878868
H	5.211886	1.548838	-1.491743
H	4.363014	1.653351	-2.844334
H	3.942068	0.600774	-1.714828
C	3.367348	2.326465	0.295178
H	2.978812	1.444959	0.475377
H	2.827107	3.017105	0.732848
H	4.28248	2.357574	0.644065
C	3.915393	3.981593	-1.545697
H	3.359413	4.652956	-1.0978
H	3.881649	4.123229	-2.514769
H	4.841306	4.064726	-1.235528
C	1.330032	3.301171	-2.518878
C	0.675791	4.223433	-3.230151
C	0.869123	4.428601	-4.742333
C	2.007454	3.567856	-5.261652
H	2.832742	3.795122	-4.784518
H	2.129038	3.730703	-6.220333
H	1.795222	2.622463	-5.115196
C	-0.477738	4.055983	-5.457585
H	-0.631253	3.090968	-5.382733
H	-0.425166	4.305996	-6.40374
H	-1.217539	4.538321	-5.03283
C	1.201375	5.875031	-4.986368
H	0.430435	6.431845	-4.749534
H	1.419605	6.004909	-5.932847
H	1.970629	6.130917	-4.435662
C	-0.299418	5.027968	-2.575766
C	-1.19678	5.662211	-2.067399
C	-2.206337	6.328376	-1.452603
C	-3.134602	6.824167	-0.879989
C	-4.186786	7.407859	-0.142558
C	-5.364803	7.550503	-0.700001
C	-6.541709	7.700137	-1.2713
C	-7.469156	6.555952	-1.20821
C	-8.160589	5.624679	-1.180455

C	-3.891135	7.946861	1.248961
C	-5.187235	8.37896	1.957711
H	-5.556048	7.619781	2.455749
H	-5.839427	8.680013	1.291019
H	-4.991721	9.112358	2.577666
C	-2.948799	9.083952	1.193434
H	-2.807237	9.435262	2.097332
H	-3.320807	9.789048	0.623426
H	-2.093414	8.781555	0.822966
C	-3.405316	6.685874	2.009378
H	-3.420402	6.859929	2.97367
H	-2.49123	6.468476	1.730911
H	-3.997243	5.932306	1.80418
C	-7.020553	8.983883	-1.950658
C	-6.063957	10.099008	-1.675564
H	-5.795157	10.073781	-0.733565
H	-6.4975	10.956442	-1.868855
H	-5.272149	9.997891	-2.244052
C	-7.205895	8.710686	-3.380177
H	-6.330899	8.649072	-3.817195
H	-7.723788	9.436461	-3.787007
H	-7.686831	7.864114	-3.491291
C	-8.412941	9.331147	-1.36703
H	-9.005013	8.554715	-1.450425
H	-8.794428	10.087317	-1.86004
H	-8.320106	9.571179	-0.421457
N	-8.847767	3.426689	-0.547886
H	-8.084342	3.362146	-0.114962
N	-0.590994	-1.80889	-1.418036
H	-0.628601	-1.635411	-2.279969
C	-3.633197	0.05452	-2.447501
F	-4.456942	0.389537	-3.331276
F	-2.867822	1.150732	-2.120853
F	-2.735622	-0.758781	-2.949822
O	-5.320433	0.455317	-0.432216
O	-5.127533	-1.631061	-1.592138
O	-3.297255	-0.780715	-0.236912
S	-4.496788	-0.600675	-0.852462
C	0.337247	-0.235491	-5.545847
F	1.182561	0.21322	-6.323511
F	-0.763595	-0.29115	-6.310135
F	0.127459	0.601204	-4.578111
O	-0.464467	-2.052424	-4.039179
O	1.952603	-1.67767	-4.188658
O	0.742454	-2.723479	-6.036224
S	0.68486	-1.933313	-4.896252

O	1.212154	2.119433	4.028981
H	1.865965	1.574175	3.85035
H	1.547787	2.683856	4.600578
O	0.383912	2.467158	6.734359
H	0.042107	2.880659	7.420195
H	0.18748	2.975356	6.055263
O	6.324985	-0.821121	0.412981
H	6.459383	-0.958132	-0.435715
H	5.492292	-1.039236	0.539378
O	4.166575	-3.132982	-5.188309
H	4.838979	-2.771372	-4.769083
H	3.682819	-2.458507	-5.444109
O	-6.48085	2.863535	0.527456
H	-6.7709	3.213104	1.269504
H	-5.669362	3.166589	0.446317

4.2 Aromaticity measurements

The NICS (Nucleus Independent Chemical Shift) method was employed to estimate the aromaticity in our systems. NICS values were calculated at the center of the macrocycle geometries as well as at different distances from the ring plane (GIAO CAM-B3LYP/6 31+g(d,p)). As representative examples, some of these values for macrocycles **3** and **4** are shown in Table S11.

Macrocycle	NICS (0 Å)	NICS (1 Å)	NICS (2 Å)
3	1.0086	0.7732	0.3470
4 (chair conformer)	0.0713	0.0543	0.0139

Table S11. NICS values at different distances for macrocycles **3** and **4**.

As can be observed, all of them are close to zero, indicating the non-aromatic character of the macrocyclic rings.

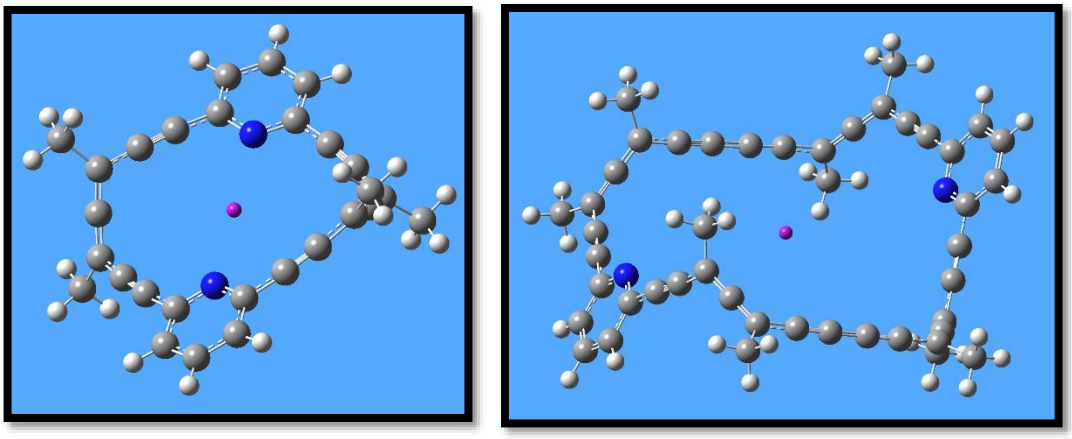


Figure S81. Calculated NICS for macrocycles 3 and 4, where the Bq atom is depicted in purple at the center of the ring.

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