Supplementary Information for

Dynamic Chirality Beyond Configuration: Reversible Exchange of Chirality Type

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1) General Methods

For manipulations that were carried out in an argon-filled glovebox or using standard Schlenk techniques, glassware was dried in overnight at 150 °C in an oven or by flame under vacuum. Dry solvents were received using an MBraun Solvent Purification System or distilled from sodium wire and benzophenone or calcium hydride, as appropriate, degassed by freeze-pump-thaw, and stored over activated 3Å molecular sieves prior to use. Thin-layer chromatography was carried out on aluminum-backed silica gel 60 (F254) plates from MERCK (grain-size distribution 60/20 μm) and visualized using UV light. Column chromatography was performed with silica gel (spherical, particle size 60 μm, neutral) purchased from Silicycle or Sigma Aldrich.

NMR spectra were recorded on Bruker (300 MHz, 400 MHz), Varian (500 MHz), or Joel (400 MHz, 500 MHz) spectrometers at 25 °C. ^{1}H NMR chemical shifts are reported relative to TMS (δ in ppm) and were referenced via residual proton resonances of the corresponding deuterated solvent ($CHCl_3$: 7.26 ppm; C_6D_5H : 7.16 ppm; DCM-d_1: 5.32 ppm; THF-d_7: 3.58 ppm; ACN-d_2: 1.94 ppm; DMSO-d_5: 2.50 ppm) whereas ^{13}C{^{1}H} NMR spectra are reported relative to TMS using the natural-abundance carbon resonances ($CDCl_3$: 77.16 ppm; C_6D_6: 128.06 ppm; DCM-d_2: 53.84 ppm; THF-d_8: 67.21 ppm; ACN-d_3: 1.32 ppm; DMSO-d_6: 39.52 ppm).

Electron paramagnetic resonance (EPR) measurements were carried out with a Bruker 300 spectrometer (X-band, 100 kHz field modulation).

Preparative chiral HPLC were performed on an Agilent 1260 Infinity unit (pump G1311C, autosampler G1329B, DAD G1365D and fraction collector G1364C), monitored by Agilent OpenLAB CDS Chemstation LC at Aix Marseille University.

Trade name	Chiral stationary phase	Seller*
Chiralcel OD-3	Cellulose tris(3,5-dimethylphenylcarbamate) coated on 3 μm silica	Daicel
Lux-Amylose-1	Amylose tris(3,5-dimethylphenylcarbamate) immobilized on 5 μm silica	Phenomenex

*Phenomenex: Danaher Corporation (Torrance, USA); Daicel: Daicel Corporation (Osaka, Japan)

High Resolution Mass Spectrometry (HRMS) were recorded on a Waters QTof-I spectrometer using ESI at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO), Université de Rennes 1 as well as the UC San Diego Mass Spectrometry Laboratory on an Agilent 6230 Accurate-Mass TOF-MS spectrometer.

Single crystal X-ray diffraction data were collected on Bruker Apex or D8-Venture diffractometers using Mo-Kα radiation (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.54178 Å).

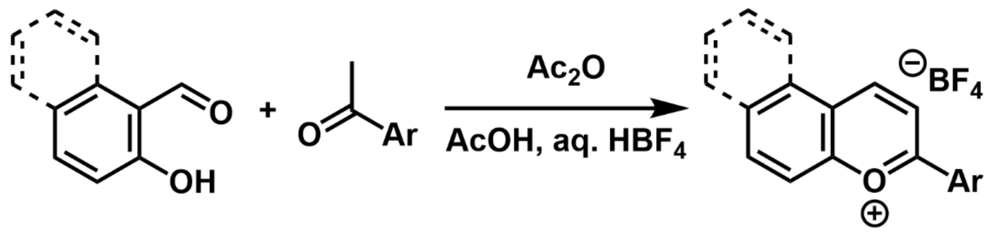
UV-Visible absorption spectra were recorded on a Jasco V-770 spectrophotometer.

Electronic Circular Dichroism (ECD) were measured on a JASCO J-815 spectrometer equipped with a JASCO Peltier cell holder PTC-423 to maintain the temperature at 25.0 ± 0.2°C. A quartz cell with a 1 cm optical path length was used. The CD spectrometer was purged with nitrogen before recording each spectrum, which was baseline subtracted. The baseline was always measured for the same solvent and in the same cell as the samples. Acquisition parameters: 0.5 nm interval, scanning speed 50 nm/min, band width 2 nm, and 3 accumulations per sample. Spectra are presented without smoothing or further data processing.

Mesityl acetophenone[1] and chiral CAAC ***rac*-2**[2] were prepared according to known literature procedures. All other starting materials were purchased from commercial sources and used without further purification.

2) Synthetic Procedures

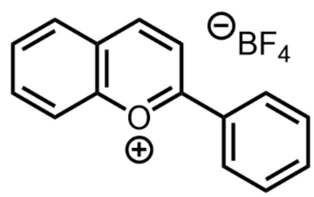
Preparation of chromenylium tetrafluoroborate salts 1a-b



General Procedure

A round-bottom flask was charged with ketone (1 eq.), 2-hydroxy aryl aldehyde (1 eq.), and a magnetic stir bar. AcOH (1.5 mL per mmol) was added, followed by 50% aq. HBF_4 (0.3 mL per mmol). Acetic anhydride (1.5 mL per mmol) was slowly added via dropping funnel over 30 minutes. After the addition was complete, the dropping funnel was replaced with an air condenser. The reaction mixture was stirred at the indicated temperature for the indicated time, then poured into 500 mL of Et_2O. After stirring for 30 minutes, the suspension was filtered and the solid washed with 500 mL of Et_2O. Drying the solid under vacuum at 80 °C for 2 days afforded dry product, which was used without further purification.

2-phenylchromenylium tetrafluoroborate [1a]:



Prepared according to the general procedure from acetophenone (2.41 g, 20.1 mmol) and salicylaldehyde (2.45 g, 20.1 mmol). Room temperature, 16 h. Deep blue-green powder, 2.07 g (7.04 mmol, 35% yield).

^{1}H NMR (500 MHz, 25°C, ACN-d_3) δ = 9.50 (d, J = 8.9 Hz, 1H), 8.72 (d, J = 8.9 Hz, 1H), 8.59 – 8.55 (m, 2H), 8.40 – 8.36 (m, 3H), 8.04 (ddd, J = 8.2, 5.7, 2.6 Hz, 1H), 7.97 (t, J = 7.5 Hz, 1H), 7.84 – 7.80 (m, 2H).

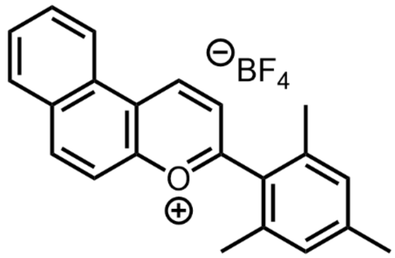
^{13}C{^{1}H} NMR (126 MHz, 25°C, ACN-d_3) δ = 176.82, 158.90, 157.66, 141.28, 138.78, 131.71, 131.63, 131.45, 131.32, 129.67, 125.75, 120.33, 118.95.

^{19}F NMR (282 MHz, 25°C, ACN-d_3) δ = -151.10 (small), -151.15.

HRMS: calc. for M+ $C_{15}H_{11}O^+$ m/z: 207.08044; found 207.0805 (0 ppm).

Spectral data matched those reported previously.[3]

3-mesitylbenzo[*f*]chromenylium tetrafluoroborate [1b]:



Prepared according to the general procedure from mesityl acetophenone (2.52 g, 14.6 mmol) and 2-hydroxynaphthaldehyde (2.48 g, 15.3 mmol). Reflux, 5 h. Brown-orange powder, 2.77 g (7.17 mmol, 49% yield).

^{1}H NMR (300 MHz, 25°C, ACN-d$_3$) δ = 10.21 (d, J = 8.7 Hz, 1H), 8.97 (d, J = 8.3 Hz, 1H), 8.87 (d, J = 9.3 Hz, 1H), 8.45 (d, J = 8.7 Hz, 1H), 8.35 (dd, J = 8.0, 1.2 Hz, 1H), 8.24 (dd, J = 9.2, 0.8 Hz, 1H), 8.13 (ddd, J = 8.3, 7.2, 1.4 Hz, 1H), 8.05 (ddd, J = 8.0, 7.3, 1.2 Hz, 1H), 7.04 (s, 2H), 2.42 (s, 3H), 2.38 (s, 6H).

^{13}C{^{1}H} NMR (101 MHz, 25°C, ACN-d$_3$) δ = 176.39, 162.11, 152.74, 145.40, 145.33, 139.93, 132.59, 132.33, 131.67, 131.33, 130.97, 128.63, 127.81, 125.07, 124.98, 124.27, 118.16, 21.41, 20.65.

^{19}F NMR (282 MHz, 25°C, ACN-d$_3$) δ = -151.10 (small), -151.15.

HRMS: calc. for M+ $C_{22}H_{19}O^{+}$ m/z: 299.14304; found 299.1430 (0 ppm).

Assignment of Absolute Configuration – Planar Chirality

The absolute configurations of planar chiral overcrowded alkenes were assigned according to the Cahn-Ingold-Prelog priority system.[4,5] Below, we derive both chirality and helicity descriptors, although helicity descriptors are preferred and used throughout the main text. Readers are referred to the "Blue Book," P-92.1.1-3, as well as section 2.5.2 of Prelog and Helmchen, *ACIE*, **1982**, 21, 567-583 for further details.

Chirality rule: Using **3a** as an example, we derive the enantiomorphic five-point figures, C_s-tetrahedra, and the corresponding preferred torsion angles (Figure S1). Note, because the relative priorities of **(a)**, **C***, **(y)**, and **(z)** are the same in both **3a** and **3b**, the relationship between chirality descriptor and preferred torsion angle does not change.

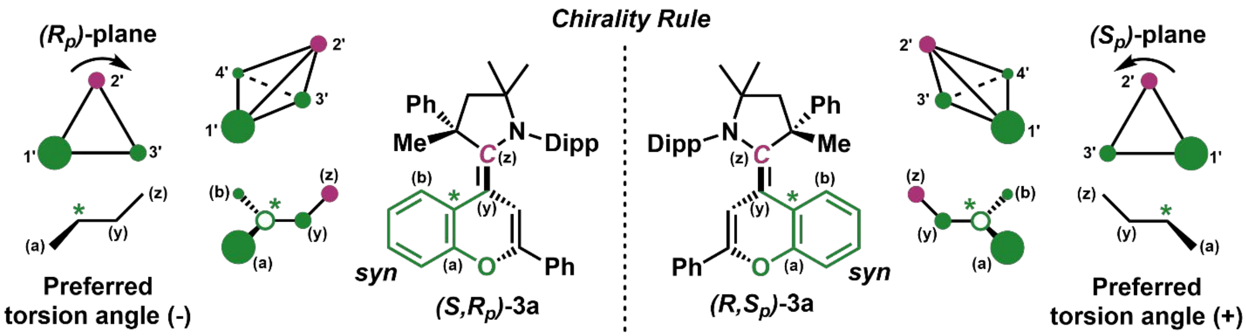


Figure S1. Determining chirality descriptors for planar chiral overcrowded alkenes.

Helicity rule: Viewing the five-point figures along the '**(y)-***' axis (Figure S2), the sense of helicity is determined by rotating **(z)** towards the highest priority substituent, **(a)**. Counterclockwise rotation indicates a left-handed helix, $\boldsymbol{M_p}$, with a negative preferred torsion angle. Conversely, clockwise rotation indicates a right-handed helix, $\boldsymbol{P_p}$, with a positive preferred torsion angle. As for the chirality rule, the relationship between helicity descriptor and preferred torsion angle does not change for **3b**.

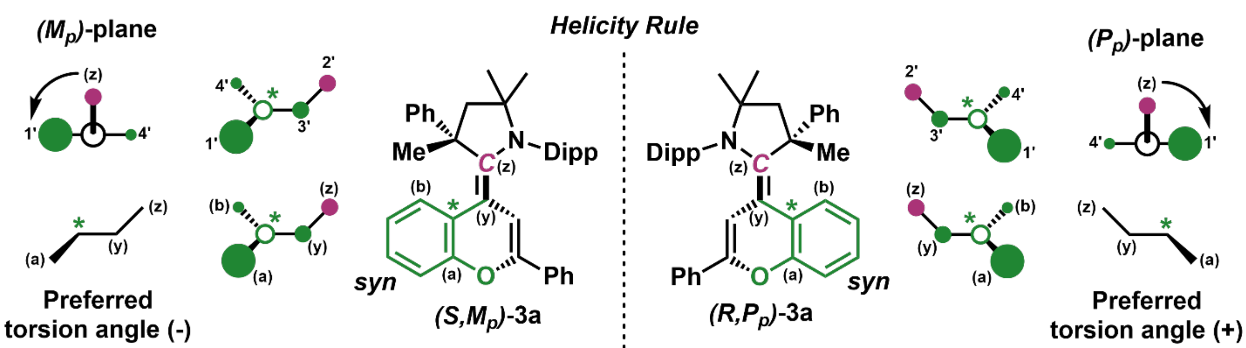


Figure S2. Determining helicity descriptors for planar chiral overcrowded alkenes.

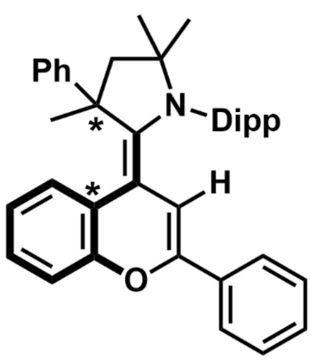
From these derivations, the equivalence between $\boldsymbol{R_p}$ and $\boldsymbol{M_p}$, $\boldsymbol{S_p}$ and $\boldsymbol{P_p}$, is clear. Note, in the context of the overcrowded alkenes from this work, a correlation between the sense of helicity and the orientation (*syn* or *anti*) of the chromene ring relative to the phenyl substituent of the stereogenic α-carbon center is observed: When the stereogenic α-carbon is ***S**, syn* = $\boldsymbol{R_p}$ = $\boldsymbol{M_p}$, while *anti* = $\boldsymbol{S_p}$ = $\boldsymbol{P_p}$. A change in orientation is equivalent to configurational inversion of the stereogenic plane.

Preparation of planar chiral overcrowded alkenes *rac*-3a-b

General Procedure

In a glovebox, a THF solution of chiral CAAC ***rac*-2** (2 eq.) was prepared at room temperature according to a previously described procedure [2]. In one portion, the appropriate chromenylium tetrafluoroborate (1 eq.) was added, resulting in a deeply colored suspension. The reaction vessel was sealed and stirred at room temperature overnight. After 16 h, the flask was removed from the glovebox and unsealed, and the reaction was vigorously stirred while diluting five-fold with hexanes. The resulting suspension was filtered through a pad of dry silica (ht. = 4 cm, Ø = 5 cm), eluting with Et_2O. Removal of volatiles under vacuum yielded the alkene, which was further purified by flash column chromatography if necessary.

Alkene *rac*-3a:



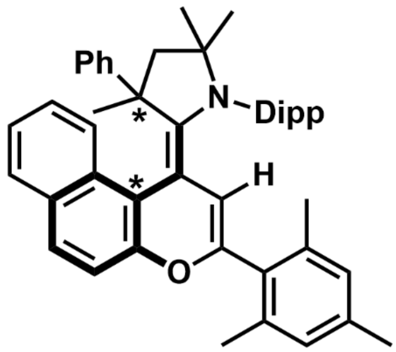
Prepared according to the general procedure from **1a** (738 mg, 2.51 mmol). Gradient of 0% to 20% Et_2O in hexanes. Yellow-orange foam, 1.25 g (2.26 mmol, 90% yield). Single crystals for XRD analysis were obtained by slow evaporation of a solution in hexanes.

^{1}H NMR (400 MHz, 25°C, C_6D_6) δ = 7.74 (d, J = 8.3 Hz, 2H), 7.24 (t, J = 7.9 Hz, 2H), 7.22 – 7.18 (m, 5H), 7.10 – 7.05 (m, 2H), 7.04 (dd, J = 8.0, 1.5 Hz, 1H) 6.99 (dd, J = 6.3, 3.1 Hz, 1H), 6.79 (ddd, J = 8.0, 7.2, 1.5 Hz, 1H), 6.55 (ddd, J = 8.6, 7.2, 1.5 Hz, 1H), 6.24 (s, 1H), 3.86 (sept, J = 6.8 Hz, 1H), 3.12 (sept, J = 6.8 Hz, 1H), 2.23 (s, 2H), 1.91 (s, 3H), 1.36 (d, J = 6.8 Hz, 3H), 1.31 (d, J = 6.8 Hz, 3H), 1.24 (d, J = 6.8 Hz, 3H), 1.13 (d, J = 6.8 Hz, 3H), 1.12 (s, 3H), 0.73 (s, 3H). *One aryl peak overlaps with solvent.*

^{13}C{^{1}H} NMR (101 MHz, 25°C, C_6D_6) δ = 155.20, 150.20, 148.47, 147.92, 146.86, 146.61, 141.25, 135.13, 129.41, 128.66, 128.57, 127.54, 126.50, 126.36, 126.00, 125.80, 125.13, 124.82, 122.13, 116.59, 107.47, 99.10, 64.10, 62.39, 51.16, 29.97, 29.32, 28.88, 28.65, 28.45, 25.59, 24.88, 24.40, 23.43.

HRMS: calc. for M+ $C_{40}H_{43}NO^+$ m/z: 553.33392; found 553.3336 (1 ppm)

Alkene *rac*-3b:



Prepared according to the general procedure from **1c** (1.158 g, 3.00 mmol). Gradient of 0% to 10% Et_2O in petroleum ether. Yellow-orange foam, 1.328 g (2.06 mmol, 69% yield). NMR analysis indicates a 9:1 mixture of E:Z isomers (Figure S3). Heating a slurry in hexanes at 60°C overnight, followed by removal of volatiles under vacuum, gave the E isomer in quantitative yield. Single crystals for XRD analysis were obtained by slow evaporation of a solution in petroleum ether.

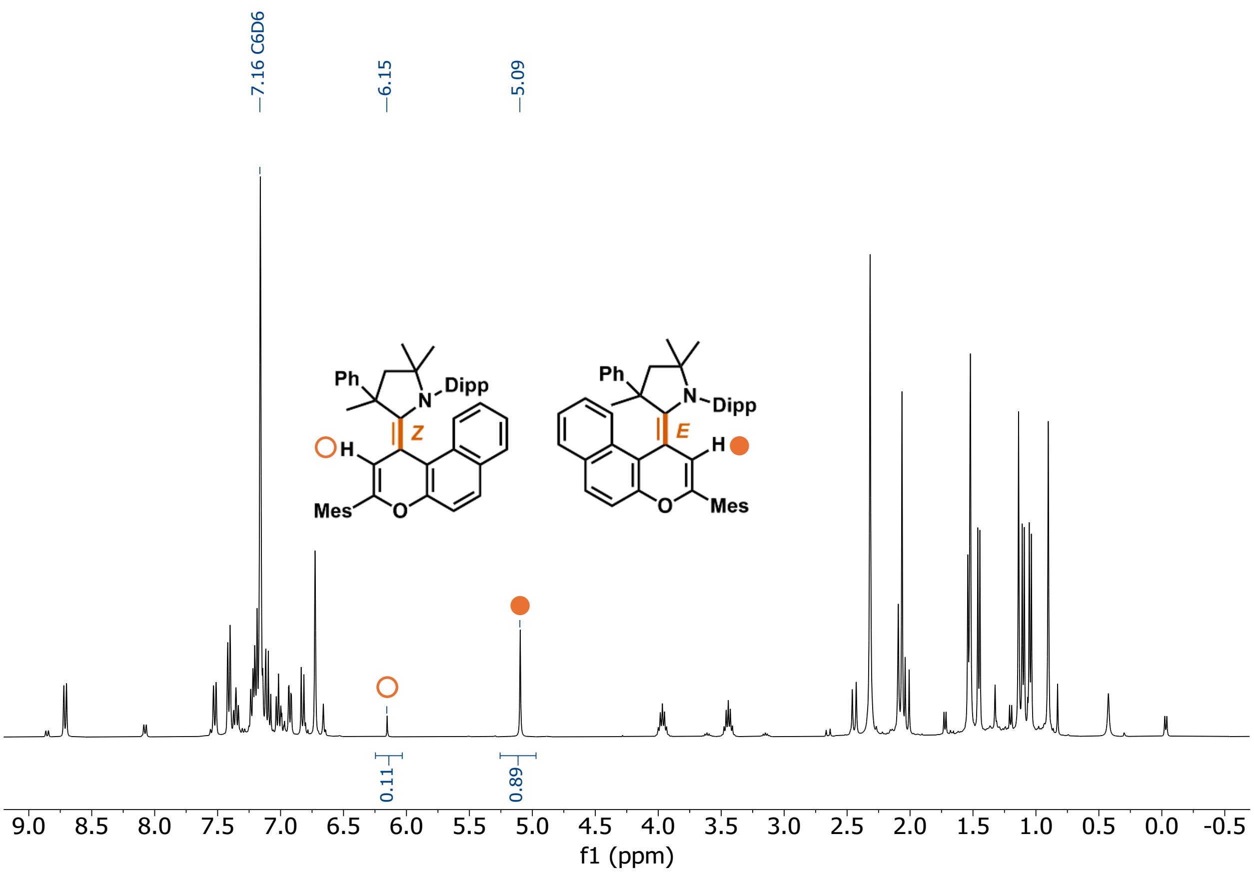


Figure S3. ^{1}H NMR (400 MHz, 25°C, C_6D_6) spectrum of initially obtained 9:1 E:Z mixture of ***rac*-3b**.

^{1}H NMR (400 MHz, 25°C, THF-d_8) δ = 8.50 (d, J = 8.4 Hz, 1H), 7.60 (d, J = 7.2 Hz, 1H), 7.36 – 7.29 (m, 5H), 7.27 – 7.22 (m, 2H), 7.10 – 7.06 (m, 3H), 7.00 (t, J = 7.3 Hz, 1H), 6.72 (s, 2H), 6.68 (d, J = 8.7 Hz, 1H), 4.85 (s, 1H), 3.87 (sept, J = 6.6 Hz, 1H), 3.32 (sept, J = 6.7 Hz, 1H), 2.64 (d, J = 12.5 Hz, 1H), 2.29 (d, J = 12.5 Hz, 1H), 2.18 (s, 3H), 2.11 (s, 6H), 1.46 (d, J = 6.6 Hz, 3H), 1.38 (d, J = 6.5 Hz, 3H), 1.34 (s, 3H), 1.27 (s, 3H), 1.12 (d, J = 6.5 Hz, 3H), 0.97 (s, 3H), 0.83 (d, J = 6.6 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, 25°C, THF-d_8) δ = 155.36, 153.52, 151.85, 149.88, 149.62, 148.30, 138.48, 137.31, 136.89, 134.77, 132.50, 132.29, 129.45, 128.86, 128.38, 128.33, 127.83, 127.24, 126.58, 126.34, 126.29, 126.12, 124.35, 122.78, 117.77, 115.03, 96.12, 66.06, 58.84, 53.18, 31.72, 30.23, 30.18, 29.88, 29.43, 26.92, 25.49, 21.93, 21.25.

HRMS: calc. for M+ $C_{47}H_{51}NO^+$ m/z: 645.39652; found 645.3970 (1 ppm).

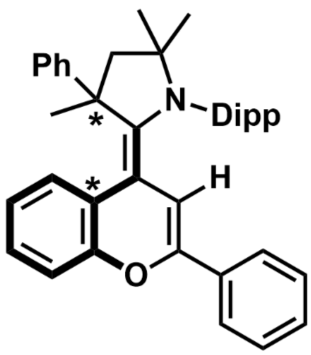
Enantiomeric Resolution of Alkenes by Chiral HPLC

Absolute configuration was assigned based on the ECD spectra of received products, which was analyzed in conjunction with computationally simulated ECD spectra. Specifically, the signs of the experimentally observed and computationally simulated exciton couplets were compared (See Figures S33 – S34).

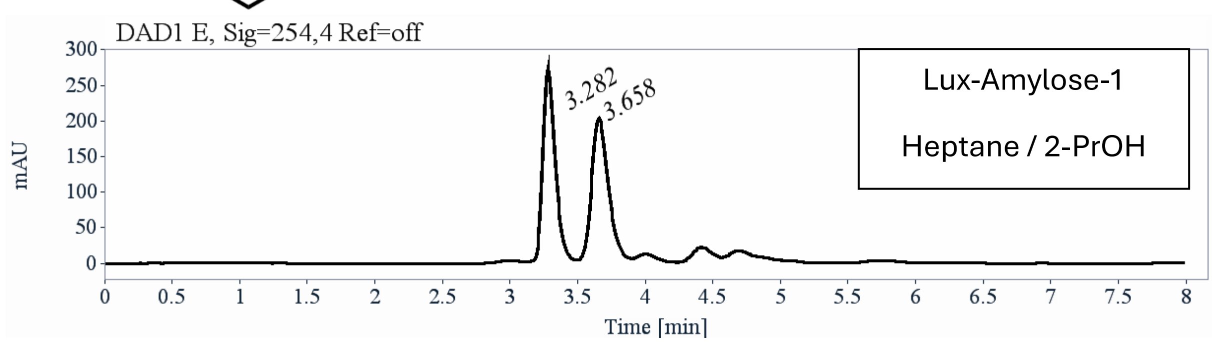
Order	AbsConfig	Mass (mg)	Yield (%)	ee (%)
1st	*(S,M$_p$)*-3a	70	35	>99.5
2nd	*(R,P$_p$)*-3a	67	34	>98.5
1st	*(R,M$_p$)*-3b	62	32	>99.5
2nd	*(S,P$_p$)*-3b	53	27	>99.5

Table S1. Obtained masses, yields, and enantiopurities for **3a-b** following preparative chiral HPLC.

Analytical chiral HPLC separation for compound *rac*-3a



The sample is dissolved in heptane, injected on the chiral column, and detected with a UV detector at 254 nm. The flow-rate is 1 mL/min.



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
3.28	1724	50.26	0.11		
3.66	1707	49.74	0.24	2.13	1.93
Sum	3431	100.00			

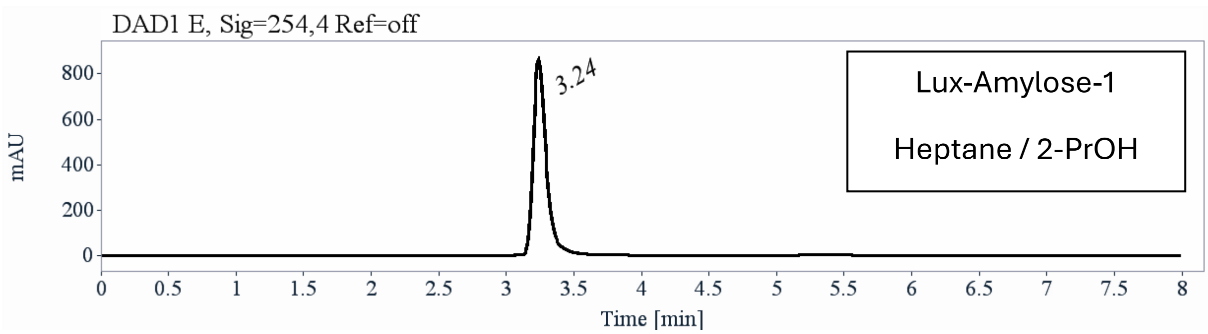
Preparative chiral HPLC separation for *rac*-3a

Sample preparation: About 200 mg of compound ***rac*-3a** are dissolved in 55 mL of hexane.

Chromatographic conditions: Lux-Amylose-1 (250 x 10 mm), hexane / 2-PrOH (99/1) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

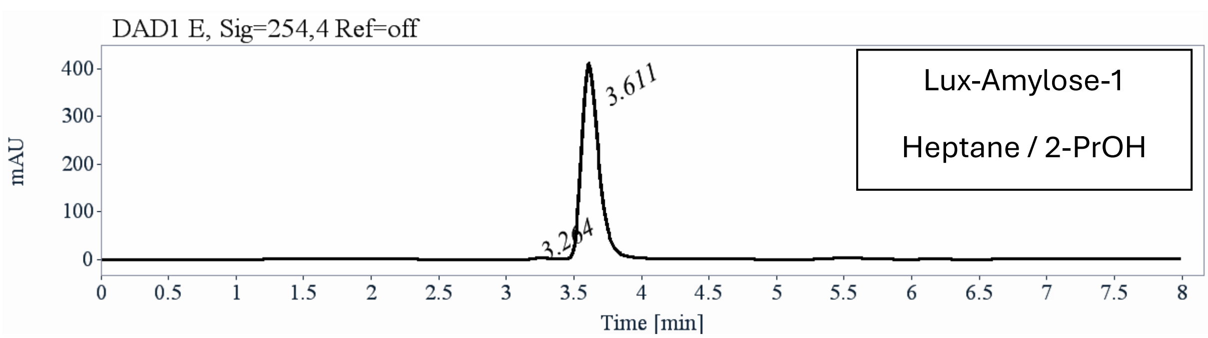
Injections (stacked): 275 times 200 µL, every 2.4 minutes.

First fraction: 70 mg of the first eluted enantiomer with ee > 99.5 % (***(S,M$_p$)*-3a:** 35% yield).



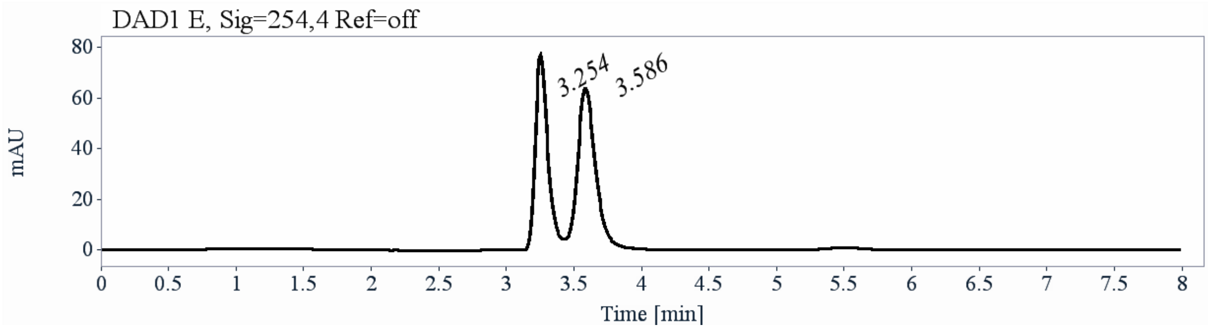
RT [min]	Area	Area%
3.24	5824	100.00
Sum	5824	100.00

Second fraction: 67 mg of the second eluted enantiomer with ee > 98.5 % (***(R,P$_p$)*-3a:** 34% yield).

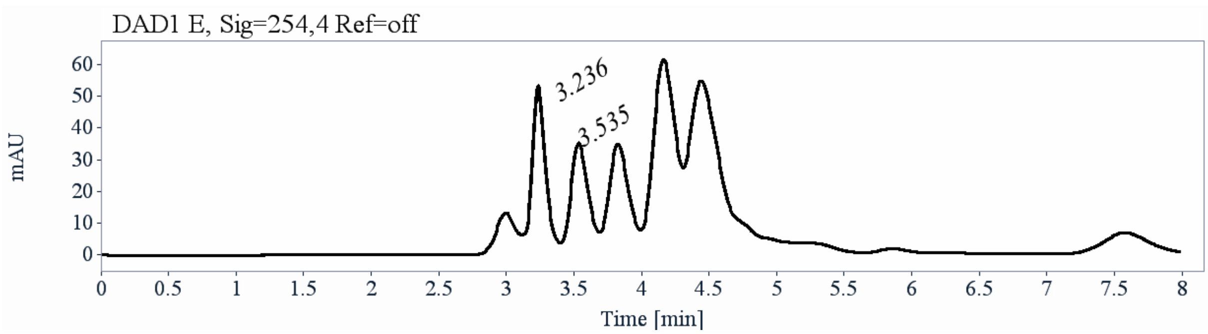


RT [min]	Area	Area%
3.26	22	0.60
3.61	3647	99.40
Sum	3669	100.00

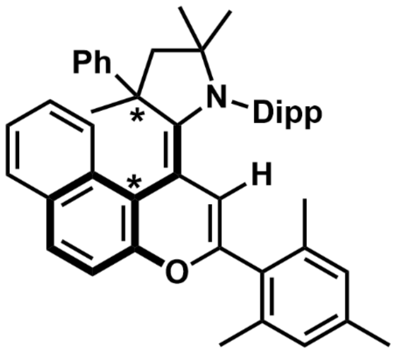
Mixture of the first and the second enantiomers: 14 mg



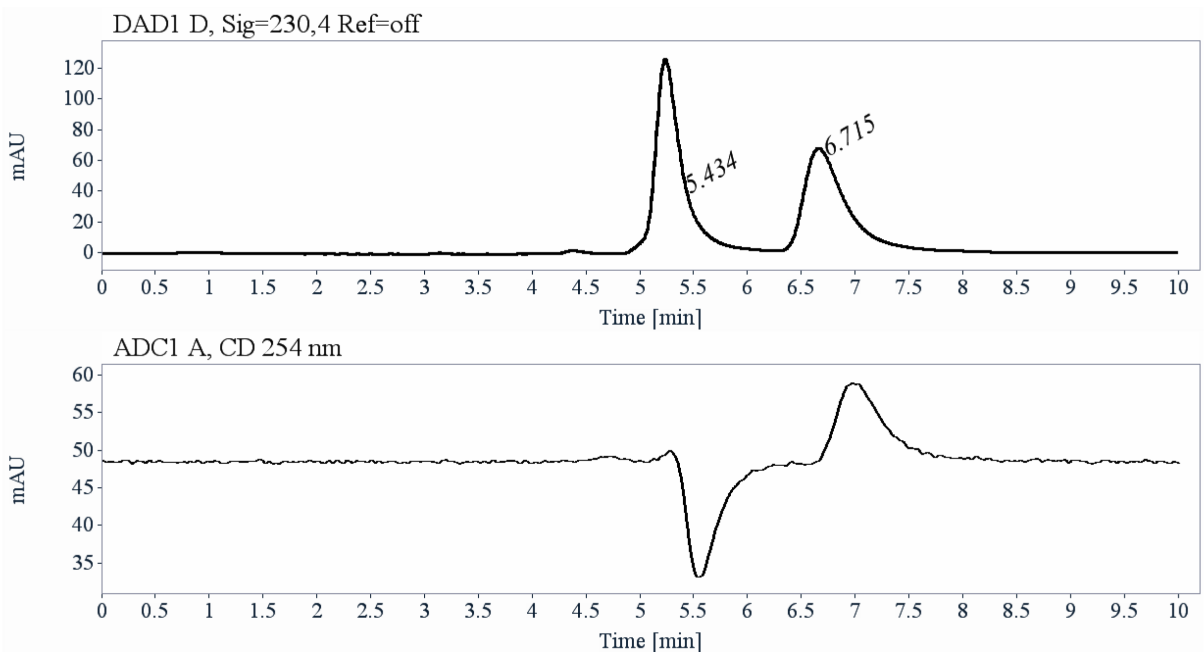
Intermediate: 49 mg



Analytical chiral HPLC separation for compound *rac*-3b



The sample is dissolved in heptane, injected on the chiral column, and detected with a UV detector at 230 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.43	2142	52.13	0.84		
6.72	1967	47.87	1.28	1.52	0.81
Sum	4109	100.00			

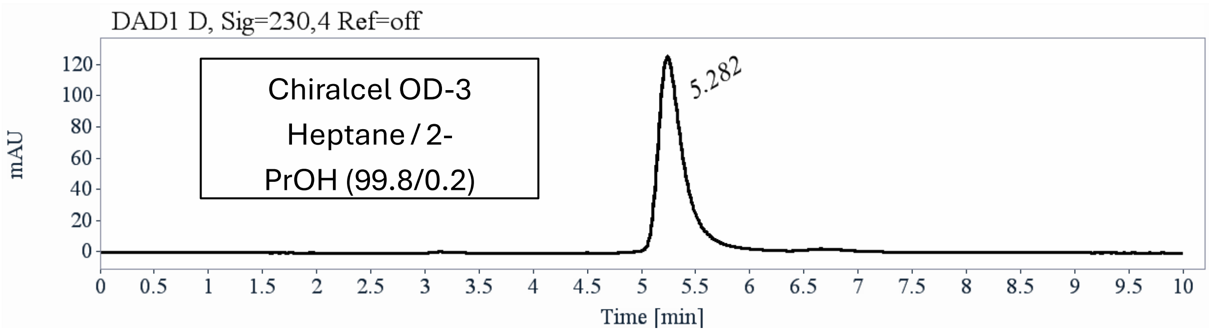
Preparative chiral HPLC separation for compound *rac*-3b

Sample preparation: About 195 mg of compound ***rac*-3b** are dissolved in 160 mL of hexane.

Chromatographic conditions: Chiralcel OD-3 (250 x 10 mm), hexane / 2-PrOH (99.8/0.2) as mobile phase, flow-rate = 5 mL/min, UV detection at 290 nm.

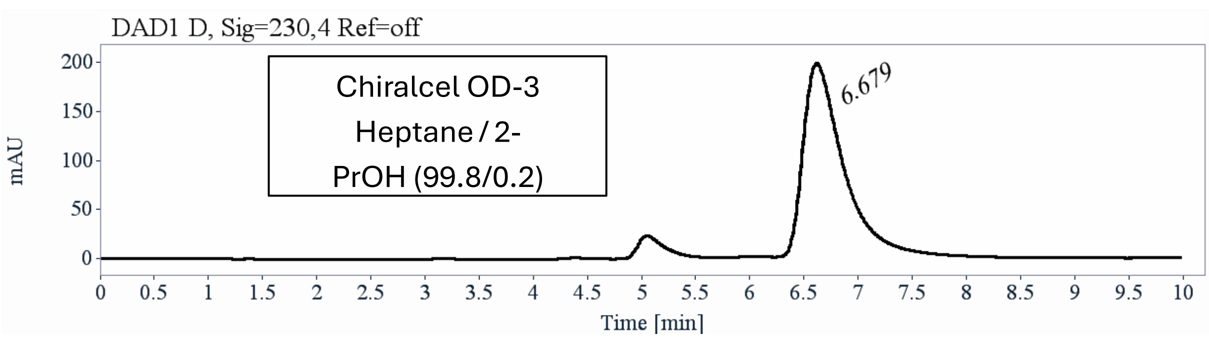
Injections (stacked): 230 times 700 μL, every 3.5 minutes.

The first eluted fraction (78 mg of the first eluted enantiomer with ee = 90 %) is purified again in the same chromatographic conditions (67 stacked injections of 600 μL every 3.5 minutes) to obtain 62 mg of the first eluted enantiomer with ee > 99.5 % (***(R,M$_p$)*-3b:** 32% yield).



RT [min]	Area	Area%
5.28	2248	100.00
Sum	2248	100.00

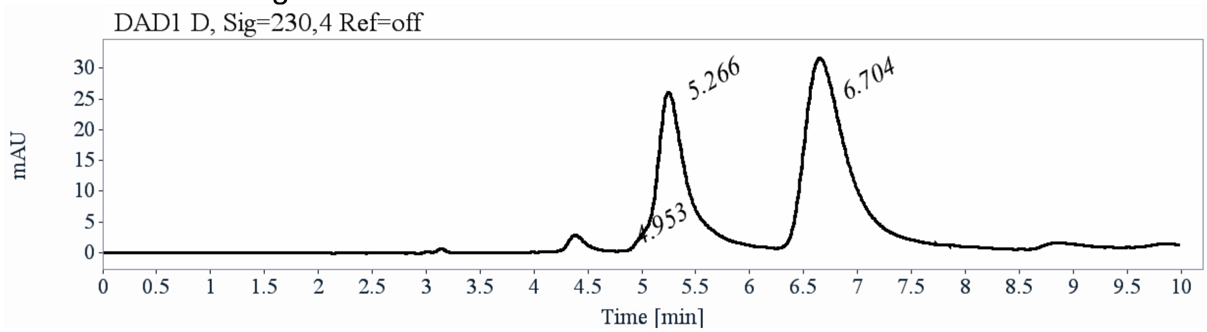
The second eluted fraction (73 mg of the second eluted enantiomer with ee =82%) is purified again in the same chromatographic conditions (63 stacked injections of 400 μL every 3.7 minutes) to obtain 53 mg of the second eluted enantiomer with ee > 99.5 % (***(S,P$_p$)*-3b:** 27% yield).



The peak at 5 minutes is not the first enantiomer but an impurity.

RT [min]	Area	Area%
6.68	5354	100.00
Sum	5354	100.00

Intermediate1: 30 mg



22 mg of the second eluted enantiomer with ee = 30 %

Intermediate2: 16 mg

Assignment of Absolute Configuration – Axial Chirality

The absolute configuration of axially chiral dications was assigned according to the Cahn-Ingold-Prelog priority system.[4,5] Both chirality and helicity descriptors are derived, although helicity descriptors are preferred. Readers are referred to the "Blue Book," P-92.1.1-3, as well as section 2.5.2 of Prelog and Helmchen, *ACIE*, **1982**, 21, 567-583 for further details.

Chirality rule: Using **3a^{++}** as an example, we derive the enantiomorphic six-point figures, C_s-tetrahedra, and the corresponding preferred torsion angles (Figure S4). Note, because the relative priorities of **(a)**, **(b)**, **(C$_\alpha$)**, and **(N)** are the same in **3b^{++}**, the relationship between chirality descriptor and preferred torsion angle does not change.

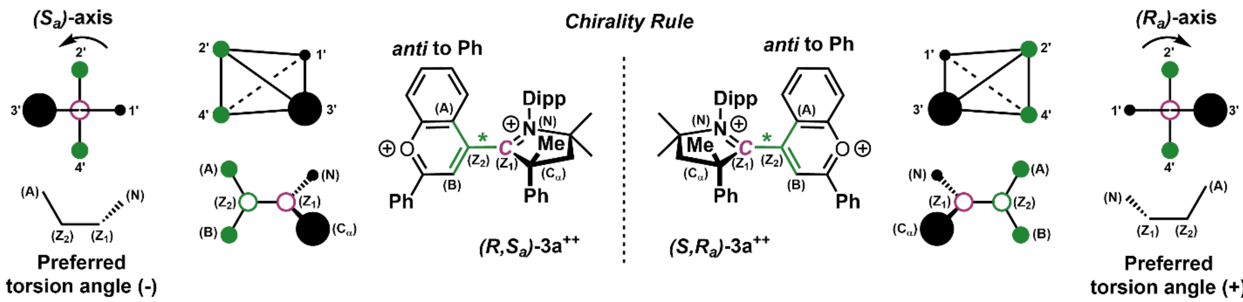


Figure S4. Determining chirality descriptors for axially chiral dications.

Helicity rule: Viewing the six-point figures along the '**(Z$_2$)-(Z$_1$)**' axis (Figure S5), the sense of helicity is determined by rotating the highest-priority substituent on the near side towards the highest priority substituent of the far side, **(A)** or **(B)**. Counterclockwise rotation indicates a left-handed helix, ***M$_a$***, with a negative preferred torsion angle. Conversely, clockwise rotation indicates a right-handed helix, ***P$_a$***, with a positive preferred torsion angle. As for the chirality rule, the helicity assignment based on the preferred torsion angle does not change for **3b^{++}**.

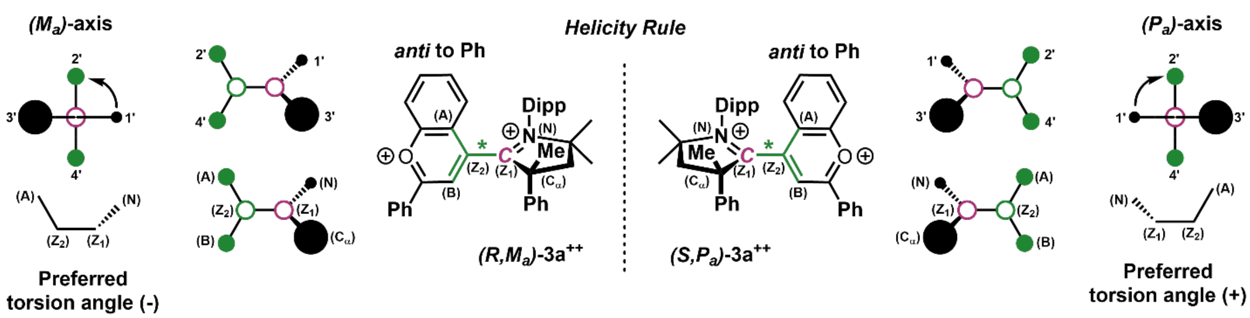


Figure S5. Determining helicity descriptors for axially chiral dications.

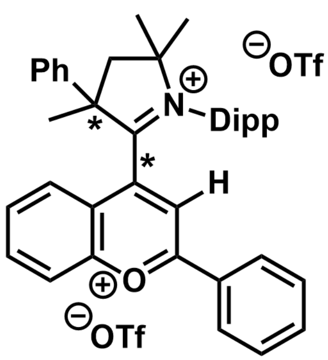
From these derivations, the equivalence between ***R$_a$*** and ***P$_a$***, ***S$_a$*** and ***M$_a$***, is clear. Note, in the context of the specific dications from this work, a correlation between the sense of helicity and the orientation (*syn* or *anti*) of the chromene ring relative to the phenyl substituent of the α-carbon is observed: When the stereogenic α-carbon center is ***S***, *anti* = $\boldsymbol{R_a}$ = $\boldsymbol{P_a}$, while *syn* = $\boldsymbol{S_a}$ = $\boldsymbol{M_a}$. A change in orientation is equivalent to a configurational inversion of the stereogenic axis.

Preparation of axially chiral dications

General Procedure

In a glovebox, a Schlenk flask was charged with the appropriate alkene (1 eq.), AgOTf (2 eq.), and a magnetic stir bar. The flask was sealed, transferred to a Schlenk line, then equipped with a septum. DCM (5 mL per mmol) was added via syringe at room temperature. A tenebrous solution formed immediately. After stirring for 1 h, the solution was cannula-filtered into another Schlenk flask, washing the remaining solids with DCM as needed to affect quantitative transfer. Volatiles were removed under vacuum at room-temperature, yielding the products as deeply colored residues.

Dication [*rac*-3a^{++}][OTf]$_2$



Prepared according to the general procedure from ***rac*-3a** (100 mg, 0.18 mmol). Dark yellow, 128 mg (0.15 mmol, 83% yield).

In DCM-d$_2$, a 3:2 ratio of atropisomers is observed. Due to peak overlap and complex splitting, not all peaks in the aryl regions of the ^{1}H and ^{13}C spectra could be unambiguously assigned between major and minor atropisomers.

In THF-d$_8$, a 4:1 ratio of atropisomers is observed, enabling the unambiguous assignment of all peaks for the major atropisomer.

^{1}H NMR (500 MHz, 25°C, DCM-d$_2$) δ = 8.93 (d, J = 7.4 Hz, 2H, *MAJOR*), 8.87 (d, J = 7.0 Hz, 1H, *minor*), 8.87 (s, 1H, *MAJOR*), 8.44 – 8.38 (m, 3H, *minor*), 8.22 (d, J = 8.6 Hz, 1H, *MAJOR*), 8.10 (t, J = 8.7 Hz, 1H, *MAJOR*), 8.01 (t, J = 7.5 Hz, 1H, *MAJOR*), 7.94 (t, J = 7.4 Hz, 1H, *minor*), 7.89 (d, J = 7.3 Hz, 2H, *minor*), 7.83 (t, J = 8.0 Hz, 1H, *MAJOR*), 7.76 – 7.67 (m), 7.55 – 7.53 (m, 2H, *MAJOR*), 7.48 (t, J = 7.2 Hz, 2H, *minor*), 7.46 – 7.41 (m), 7.33 – 7.29 (m), 7.23 – 7.17 (m), 6.95 (d, J = 8.3 Hz, 1H, *MAJOR*), 6.66 (s, 1H, *minor*), 3.92 (d, J = 14.2 Hz, 1H, *MAJOR*), 3.67 (d, J = 14.7 Hz, 1H, *minor*), 3.28 (d, J = 14.7 Hz, 1H, *minor*), 3.21 (sept, J = 6.3 Hz, 1H, *MAJOR*), 3.05 (sept, J = 6.4 Hz, 1H, *minor*), 3.01 (d, J = 14.3 Hz, 1H, *MAJOR*), 2.74 (sept, J = 6.4 Hz, 1H, *MAJOR*), 2.55 (sept, J = 6.4 Hz, 1H, *minor*), 2.53 (s, 3H, *MAJOR*), 2.30 (s, 3H, *minor*), 2.21 (s, 3H, *minor*), 1.99 (s, 3H, *MAJOR*), 1.93 (s, 3H, *MAJOR*), 1.82 (s, 3H, *minor*), 1.53 (d, J = 6.3 Hz, 3H, *MAJOR*), 1.47 (d, J = 6.3 Hz, 3H, *minor*), 1.42 (d, J = 6.3 Hz, 3H, *MAJOR*), 1.40 (d, J = 6.3 Hz, 3H, *minor*), 1.13 (d, J = 6.4 Hz, 3H, *MAJOR*), 0.85 (d, J = 6.4 Hz, 3H, *minor*), 0.32 (d, J = 6.4 Hz, 3H, *MAJOR*), 0.19 (d, J = 6.6 Hz, 3H, *minor*).

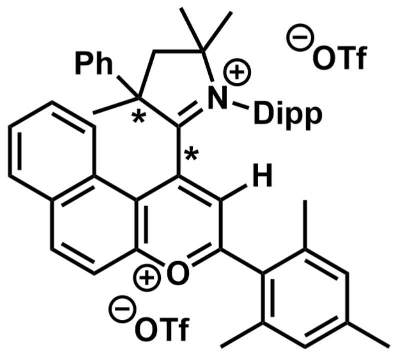
$^{13}C\{^{1}H\}$ NMR (126 MHz, 25°C, DCM-d_2) δ = 192.63 (*MAJOR*), 191.59 (*minor*), 176.67 (*MAJOR*), 174.16 (*minor*), 157.11 (*minor*), 155.50 (*MAJOR*), 149.88 (*MAJOR*), 149.55 (*minor*), 145.47 (*MAJOR*), 145.37 (*minor*), 144.93 (*MAJOR*), 144.63 (*minor*), 141.41 (*MAJOR*), 141.02 (*MAJOR*), 140.53 (*minor*), 137.24 (*minor*), 136.12 (*MAJOR*), 133.95, 133.71, 133.22, 133.01, 131.64, 131.60, 131.34, 131.29, 131.25, 130.79, 130.46, 130.35, 129.85, 129.56, 128.85, 128.72, 128.45, 128.23, 128.11, 128.08, 127.77, 127.75, 127.57, 127.06, 121.42 (*minor*), 121.21 (*minor*), 120.98 (q, *J* = 320.3 Hz), 120.46 (*MAJOR*), 120.30 (*MAJOR*), 118.28 (*MAJOR*), 117.94 (*minor*), 89.80 (*minor*), 89.30 (*MAJOR*), 62.81 (*minor*), 61.91 (*MAJOR*), 47.88 (*minor*), 46.59 (*MAJOR*), 32.40 (*minor*), 30.56 (*MAJOR*), 30.28 (*MAJOR*), 30.17 (*MAJOR*), 30.14 (*MAJOR*), 30.03 (*minor*), 29.87 (*MAJOR)*, 29.15 (*minor*), 28.83 (*minor*), 28.68 (*MAJOR)*, 28.23 (*minor*), 28.15 (*MAJOR)*, 27.45 (*minor*), 27.20 (*minor*), 25.23 (*minor*), 25.10 (*MAJOR)*, 24.93 (*MAJOR)*, 24.89 (*minor*).

^{19}F NMR (471 MHz, 25°C, DCM-d_2) δ = -76.40

^{1}H NMR (500 MHz, 25°C, THF-d_8) δ = 9.16 (d, J = 7.7 Hz, 2H), 9.02 (s, 1H), 8.49 (d, J = 8.6 Hz, 1H), 8.15 (t, J = 7.9 Hz, 1H), 8.00 (t, J = 7.5 Hz, 1H), 7.83 (t, J = 7.9 Hz, 2H), 7.69 (t, J = 8.4 Hz, 2H), 7.65 (d, J = 7.9 Hz, 1H), 7.53 – 7.41 (m, 4H), 7.18 (t, J = 7.8 Hz, 2H), 7.08 (t, J = 7.4 Hz, 1H), 4.18 (d, J = 14.0 Hz, 1H), 3.39 (sept, J = 6.5 Hz, 1H), 3.12 – 2.95 (m, 3H), 2.60 (s, 3H), 2.04 (s, 3H), 1.96 (s, 3H), 1.60 (d, J = 6.1 Hz, 3H), 1.45 (d, J = 6.1 Hz, 3H), 1.29 (d, J = 6.4 Hz, 3H), 0.32 (d, J = 6.4 Hz, 3H). *Only peaks for the major atropisomer are reported.*

$^{13}C\{^{1}H\}$ NMR (126 MHz, 25°C, THF-d_8) δ = 194.53, 177.97, 156.08, 150.38, 147.38, 146.21, 141.52, 140.85, 137.46, 134.42, 133.34, 132.60, 131.66, 130.55, 130.44, 129.93, 129.76, 129.41, 128.42, 128.23, 121.46, 121.11, 120.85 (q, *J* = 353.45 Hz), 120.68, 90.16, 67.92, 62.71, 45.93, 31.64, 30.92, 30.49, 30.40, 30.00, 28.98, 28.57. *Only peaks for the major atropisomer are reported. Two peaks overlap with the solvent signal at 25.46 ppm.*

Dication [*rac*-3b^{++}][OTf]$_2$



Prepared according to the general procedure from ***rac*-3b** (100 mg, 0.16 mmol). Dark red, 132 mg (0.14 mmol, 87% yield).

For SbF_6^- salt, the procedure was reproduced using $AgSbF_6$ in place of AgOTf. Vapor diffusion of Et_2O into a DCM solution yielded diffraction quality crystals.

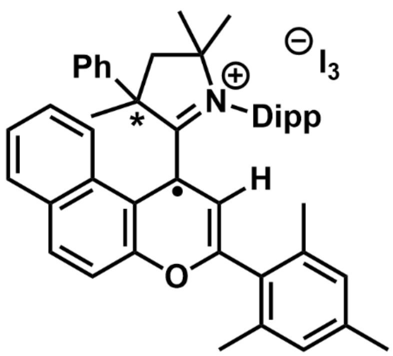
In DCM-d$_2$, a 5:2 ratio of atropisomers is observed. Due to peak overlap and complex splitting, unambiguous assignment of all aryl peaks between major and minor atropisomers was not possible.

^{1}H NMR (400 MHz, 25°C, DCM-d$_2$) δ = 9.01 (d, *J* = 9.2 Hz, 1H, *minor*), 8.74 (d, *J* = 9.2 Hz, 1H, *MAJOR*), 8.56 (d, *J* = 3.5 Hz, 2H, *minor*), 8.44 (d, *J* = 7.9 Hz, 1H, *minor*), 8.28 (d, *J* = 9.2 Hz, 1H, *minor*), 8.18 (t, *J* = 8.1 Hz, 1H, *minor*), 8.18 (d, *J* = 9.2 Hz, 1H, *MAJOR*), 8.08 (d, *J* = 6.6 Hz, 1H, *MAJOR*), 8.00 (s, 1H), 7.83 (dd, *J* = 8.4, 2.2 Hz, 1H, *MAJOR*), 7.79 (t, *J* = 7.6 Hz, 1H, *MAJOR*), 7.65 (td, *J* = 7.9, 1.5 Hz, 1H, *MAJOR*), 7.58 (d, *J* = 7.6 Hz, 1H, *MAJOR*), 7.53 (d, *J* = 8.4 Hz, 1H, *MAJOR*), 7.42 (d, *J* = 4.3 Hz, 1H, *minor*), 7.40 (d, *J* = 7.8 Hz, 1H, *minor*), , 7.39 (d, *J* = 7.9 Hz, 1H, *MAJOR*), 7.24 (dd, *J* = 7.9, 1.6 Hz, 1H, *MAJOR*), 7.17 (s, 2H, *MAJOR*), 7.11 (dd, *J* = 7.8, 1.5 Hz, 1H, *minor*), 7.06 (dd, *J* = 7.8, 1.5 Hz, 1H, *minor*), 7.01 (dd, *J* = 7.9, 1.6 Hz, 2H, *MAJOR*), 6.97 (s, 1H, *minor*), 6.97 (s, 2H, *minor*), 6.93 (t, *J* = 7.3 Hz, 1H, *MAJOR*)., 4.25 (d, *J* = 14.5 Hz, 1H, *MAJOR*), 4.07 (d, *J* = 15.3 Hz, 1H, *minor*), 3.53 (d, *J* = 15.4 Hz, 1H, *minor*), 3.34 (d, *J* = 14.4 Hz, 1H, *MAJOR*), 2.89 (sept, *J* = 6.3 Hz, 1H, *MAJOR*), 2.53 (s, 3H, *MAJOR*), 2.49 (sept, *J* = 6.5 Hz, 1H, *minor*), 2.43 (s, 3H, *MAJOR*), 2.40 (broad, 6H, *MAJOR*), 2.33 (s, 3H, *minor*), 2.29 (sept, *J* = 6.4 Hz, 1H, *MAJOR*), 2.15 (s, 3H, *minor*), 2.10 (s, 3H, *minor*), 2.02 (s, 3H, *MAJOR*), 2.01 (s, 3H, *minor*), 1.98 (s, 3H, *MAJOR*), 1.78 (broad, 6H, *MAJOR*), 1.45 (d, *J* = 6.1 Hz, 3H, *MAJOR*), 1.22 (d, *J* = 6.3 Hz, 3H, *minor*), 0.99 (d, *J* = 6.4 Hz, 3H, *minor*), 0.95 (d, *J* = 6.4 Hz, 3H, *MAJOR*), 0.92 (d, *J* = 6.6 Hz, 3H, *MAJOR*), 0.43 (d, *J* = 6.3 Hz, 3H, *minor*), -0.67 (d, *J* = 6.4 Hz, 3H, *minor*), -0.78 (d, *J* = 6.4 Hz, 3H, *MAJOR*).

^{13}C{^{1}H} NMR (101 MHz, 25°C, DCM-d$_2$) δ = 197.28 (*MAJOR)*, 194.65 (*minor*), 175.55 (*MAJOR)*, 174.46 (*minor*), 164.49 (*minor*), 161.91 (*MAJOR)*, 148.82 (*minor*), 148.03 (*MAJOR)*, 147.36 (*MAJOR)*, 147.23 (*minor*), 147.02 (*MAJOR)*, 146.83 (*minor*), 146.09 (*MAJOR)*, 145.88 (*minor*), 145.84 (*minor*), 145.30 (*MAJOR)*, 140.76 (*MAJOR)*, 138.59 (*minor*), 138.57 (*minor*), 136.98 (*MAJOR)*, 133.61 (*minor*), 133.52 (*minor*), 133.37 (*minor*), 133.32 (*minor*), 133.12 (*minor*), 132.53 (*MAJOR)*, 132.04 (*MAJOR)*, 131.85 (*MAJOR)*, 131.76 (*MAJOR)*, 131.63 (*minor*), 131.08, 131.00 (*MAJOR)*, 130.66 (*MAJOR)*, 130.24 (*minor*), 130.22 (*minor*), 129.84 (*minor*), 128.78, 128.59 (*MAJOR)*, 128.52 (*minor*), 128.36, 128.07, 127.95, 127.90, 127.81, 127.07 (*MAJOR)*, 125.38, 125.20, 124.99, 124.57, 123.62, 123.35 (*minor*), 121.16, 120.85 (*MAJOR)*, 120.71 (q, *J* = 320.5 Hz), 119.78 (*minor*), 119.18 (*MAJOR)*, 88.89 (*MAJOR)*, 88.86 (*minor*), 66.53 (*minor*), 65.10 (*MAJOR)*, 45.26 (*minor*), 45.01 (*MAJOR)*, 36.14 (*MAJOR)*, 32.56 (*minor*), 31.12 (*MAJOR)*, 30.33 (*MAJOR)*, 30.05 (*MAJOR)*, 29.61 (*minor*), 29.61 (*minor*), 28.45 (*minor*), 28.31 (*MAJOR)*, 27.78 (*minor*), 26.88 (*MAJOR)*, 26.70 (*minor*), 25.84 (*MAJOR)*, 24.94 (*minor*), 24.92 (*minor*), 24.75 (*MAJOR)*, 24.70 (*MAJOR)*, 24.10 (*minor*), 21.97 (*MAJOR)*, 21.62 (*minor*), 21.35 (*MAJOR)*, 20.22 (*minor*).

^{19}F NMR (471 MHz, 25°C, DCM-d_2) δ = -78.39

Radical cation [*rac*-3b$^{•+}$][I_3]:



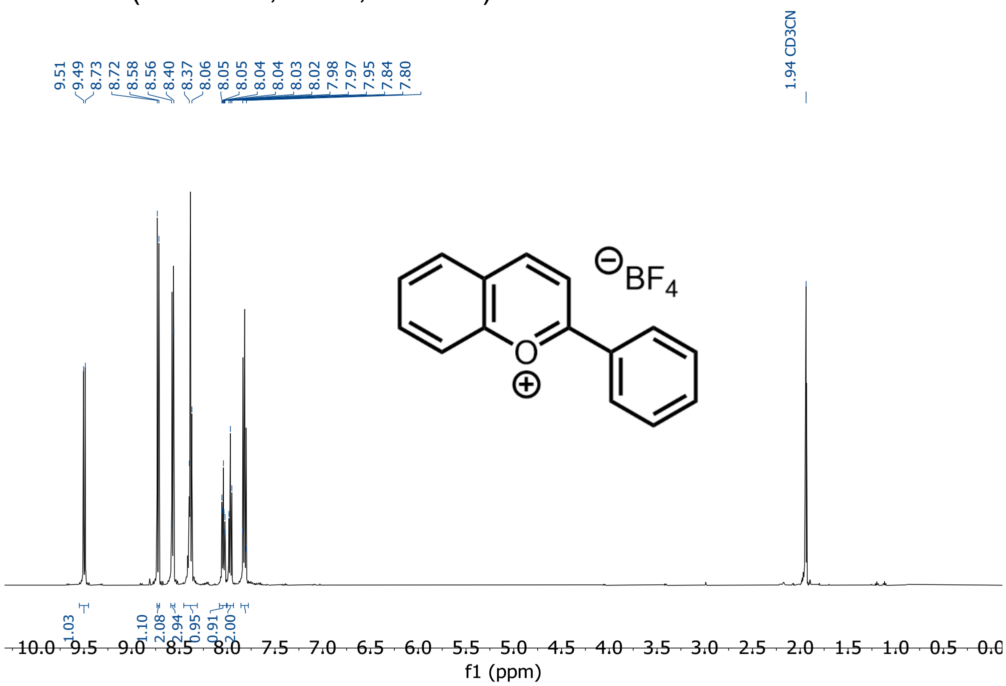
Under an argon atmosphere, a Schlenk flask was charged with ***rac*-3b** (100 mg, 0.15 mmol, 1 eq.), I_2 (80 mg, 0.32 mmol, 2.1 eq.) and a magnetic stir bar. DCM (2 mL) was slowly added via syringe at room temperature, producing a deep black-purple solution. After stirring for 1 h, the solution was concentrated under vacuum at room-temperature, leaving a black residue, which was washed with toluene till the washings were colorless. Crystalline material was obtained by vapor diffusion of Et_2O into a DCM solution. Black rods, 78 mg, (0.076 mmol, 51% yield).

X-Band EPR: g = 2.002 (1xN: 12.2 MHz; 1xH: 6.4 MHz; 1xH: 4.3 MHz; 1xH: 2.4 MHz; 3xH: 0.6 MHz; 1xH: 0.5 MHz).

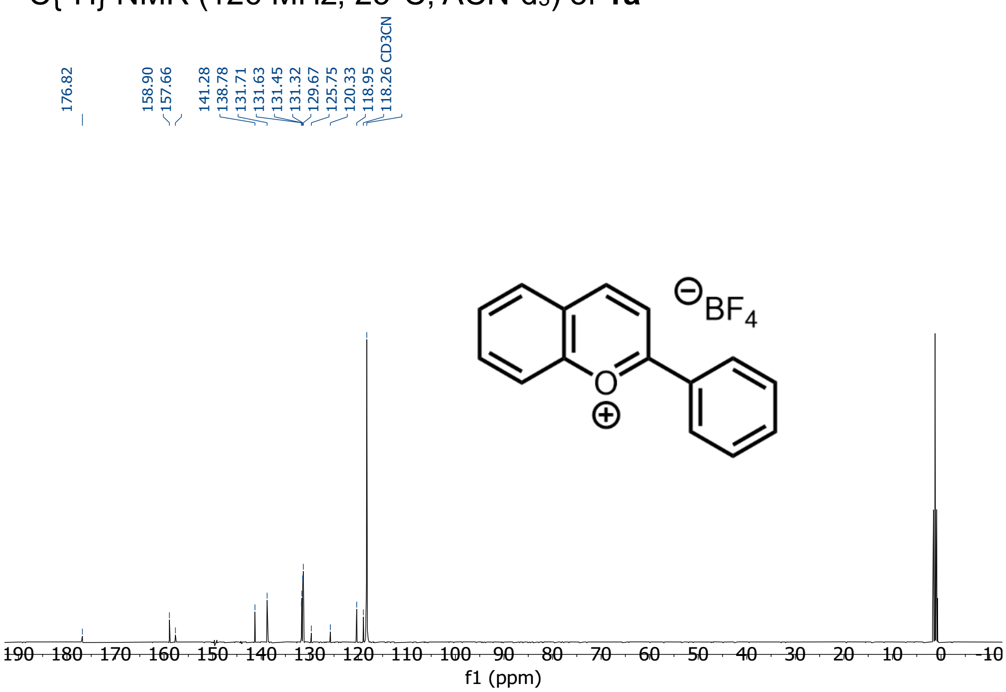
3) NMR Characterization

1D NMR Spectra

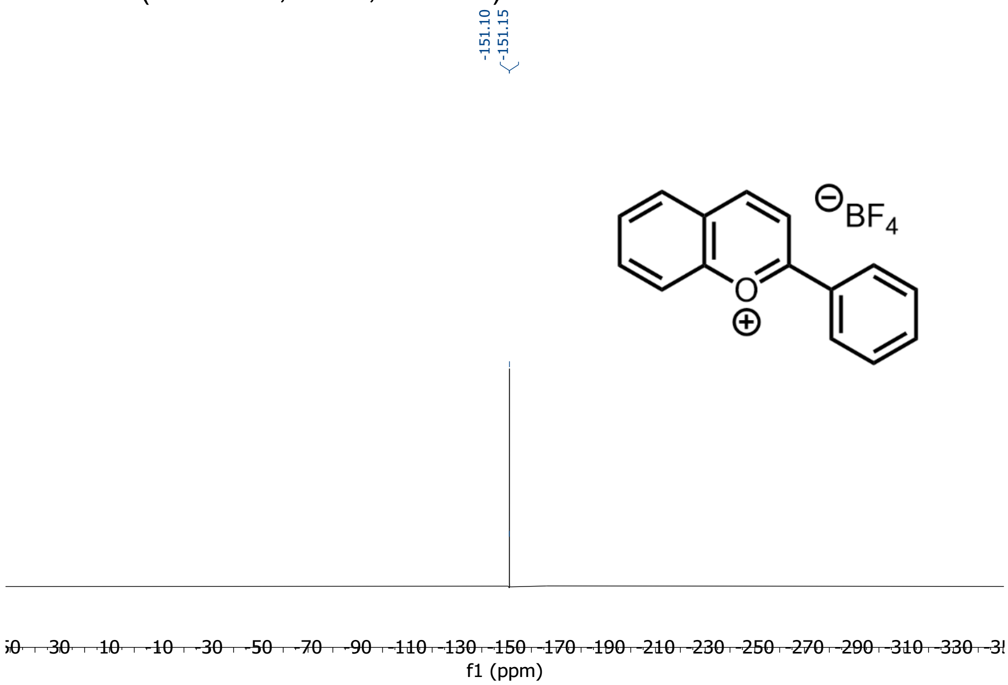
^{1}H NMR (500 MHz, 25°C, ACN-d_3) of **1a**



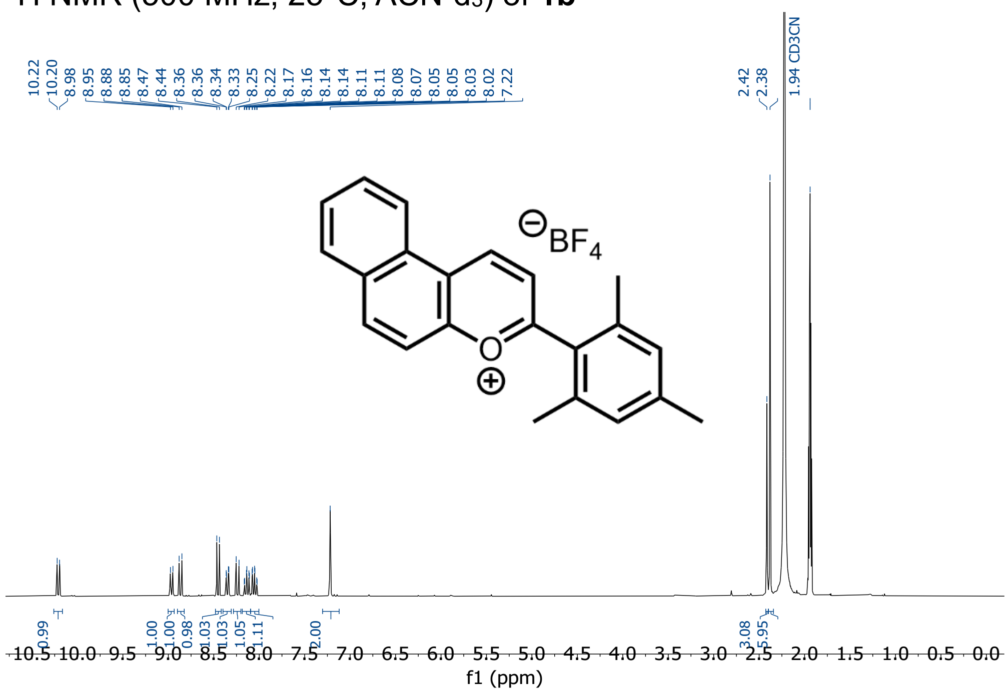
^{13}C{^{1}H} NMR (126 MHz, 25°C, ACN-d_3) of **1a**



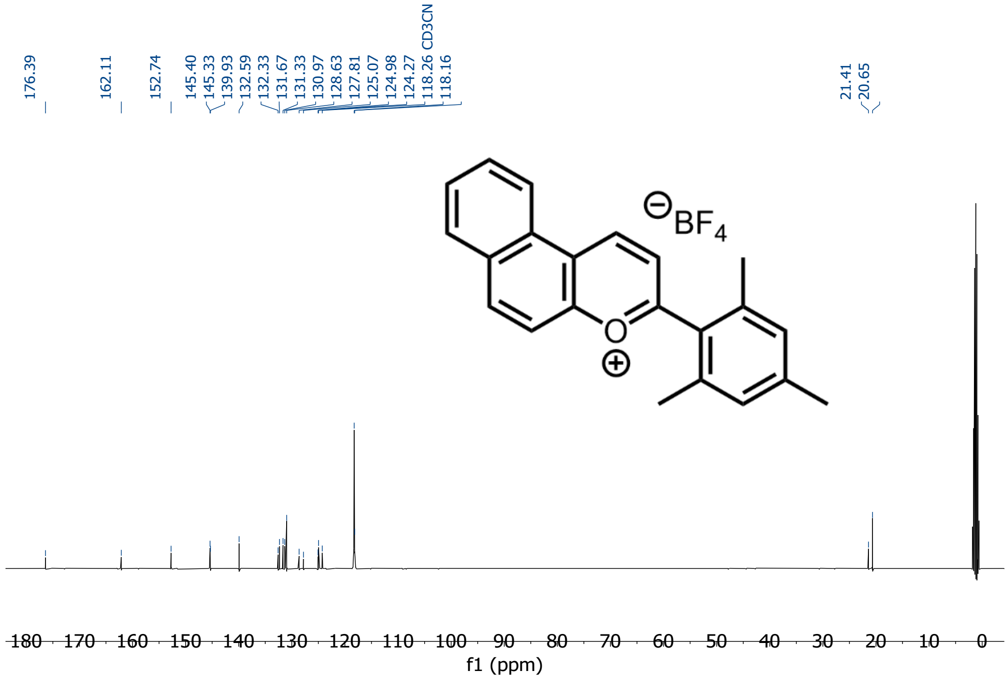
^{19}F NMR (282 MHz, 25°C, ACN-d_3) of **1a**



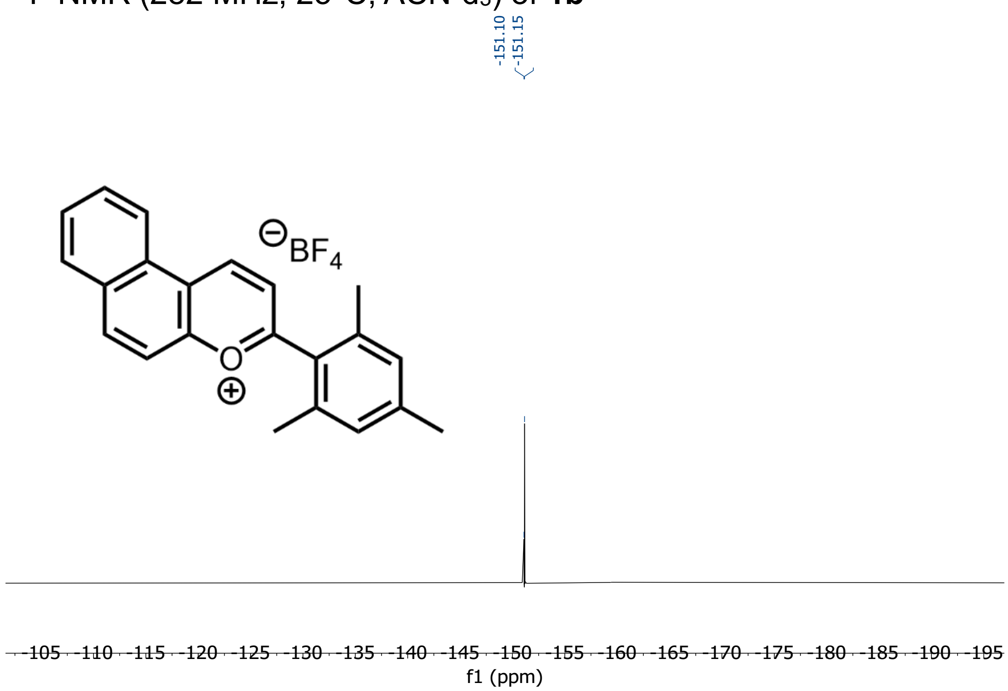
^{1}H NMR (500 MHz, 25°C, ACN-d_3) of **1b**



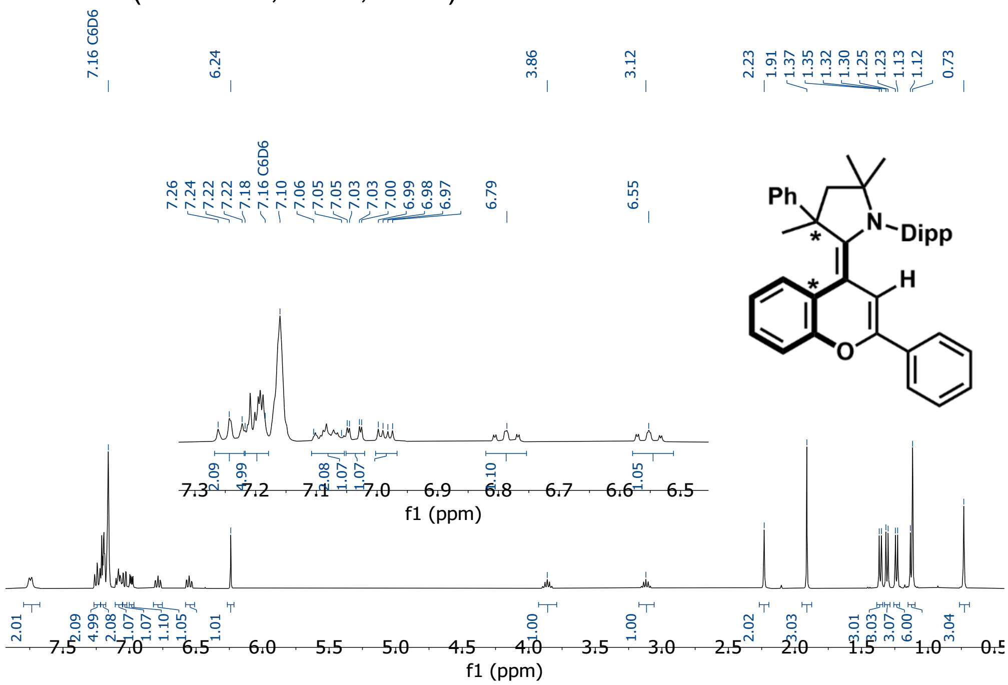
$^{13}C\{^{1}H\}$ NMR (101 MHz, 25°C, ACN-d3) of **1b**



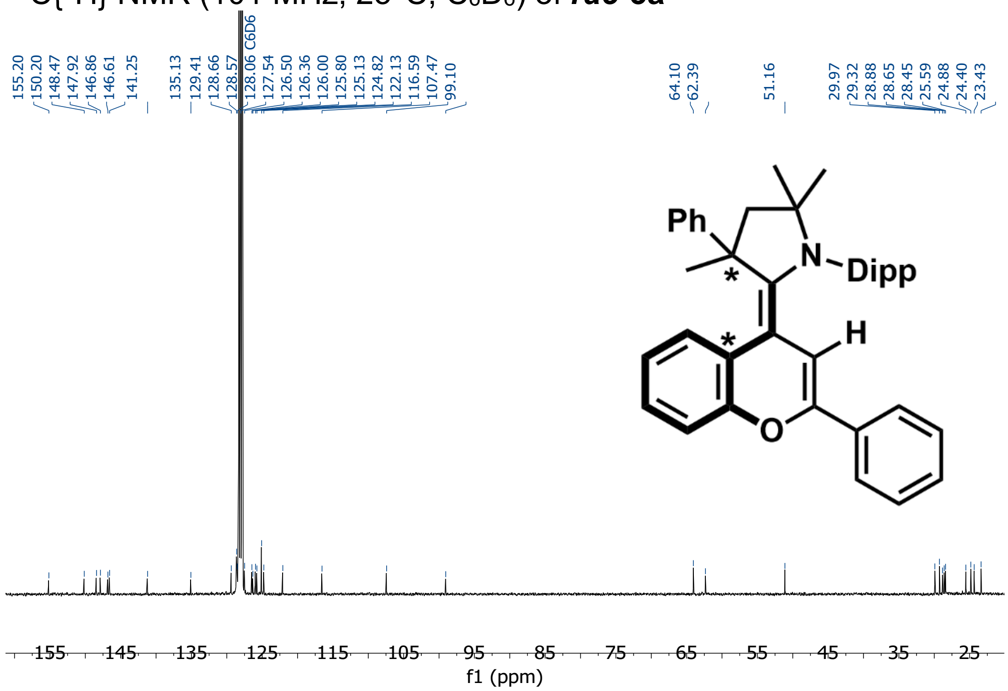
^{19}F NMR (282 MHz, 25°C, ACN-d3) of **1b**



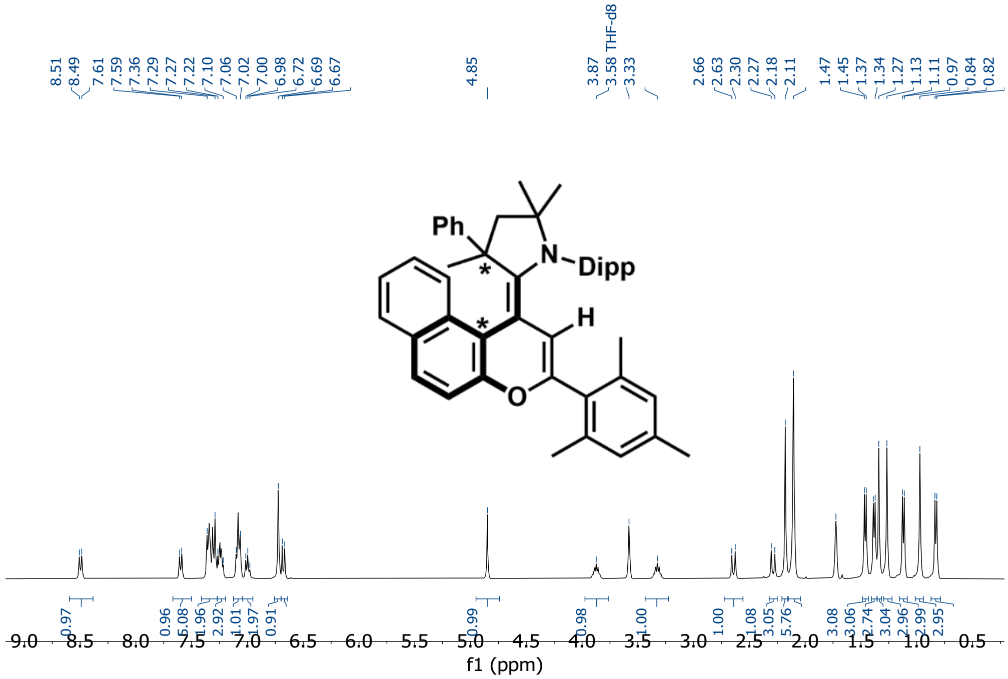
^{1}H NMR (400 MHz, 25°C, C_6D_6) of ***rac*-3a**



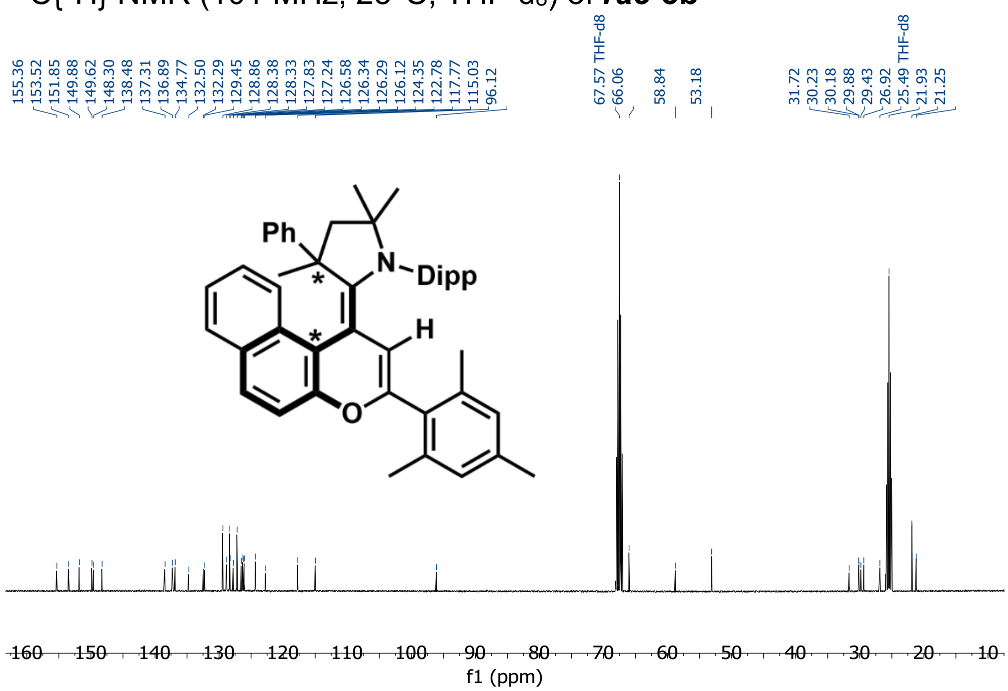
$^{13}C\{^{1}H\}$ NMR (101 MHz, 25°C, C_6D_6) of ***rac*-3a**



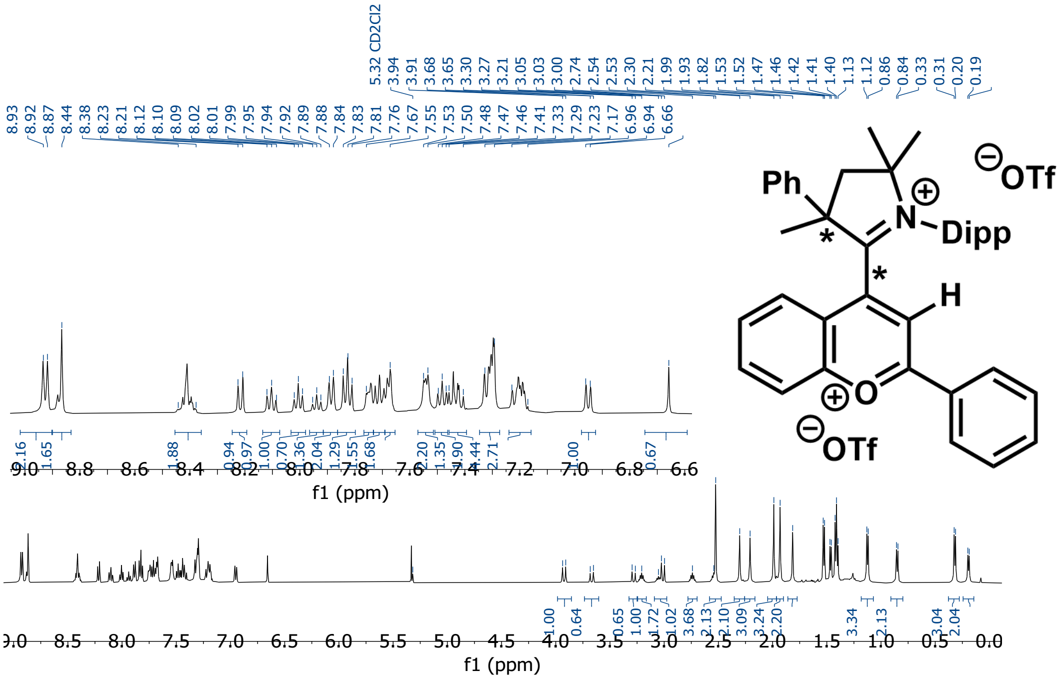
^{1}H NMR (400 MHz, 25°C, THF-d_8) of ***rac*-3b**



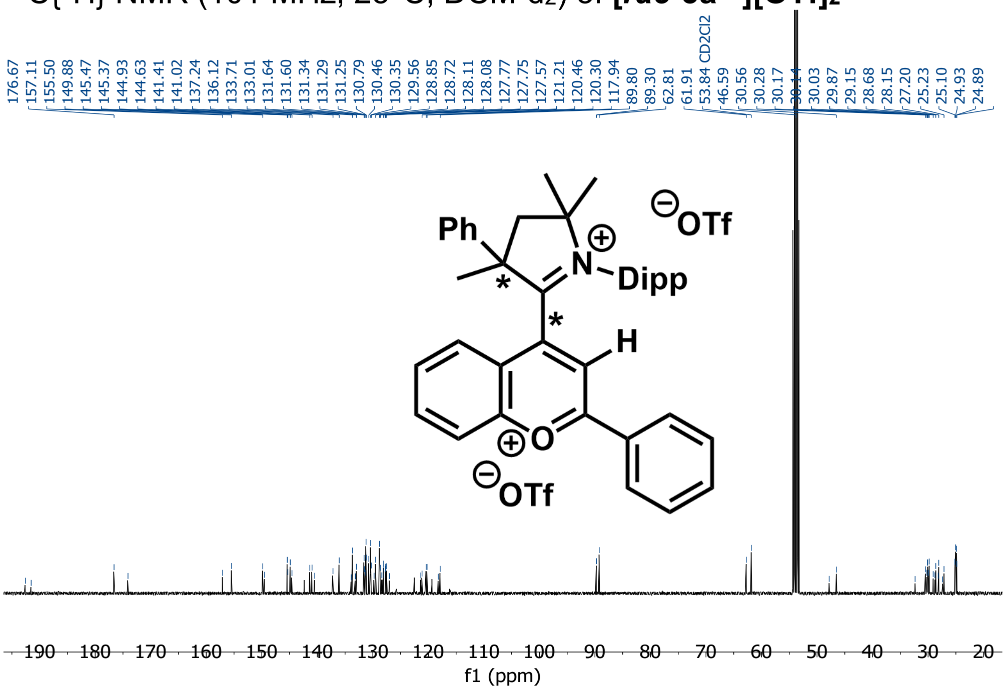
$^{13}C\{^{1}H\}$ NMR (101 MHz, 25°C, THF-d_8) of ***rac*-3b**



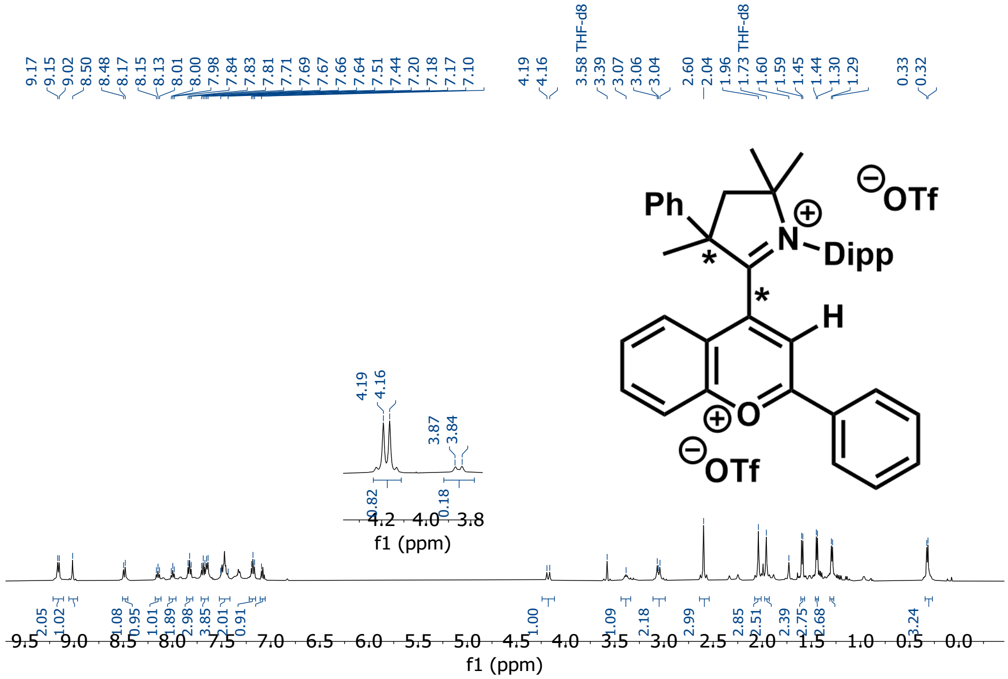
^{1}H NMR (500 MHz, 25°C, DCM-d$_2$) of **[*rac*-3a^{++}][OTf]$_2$**



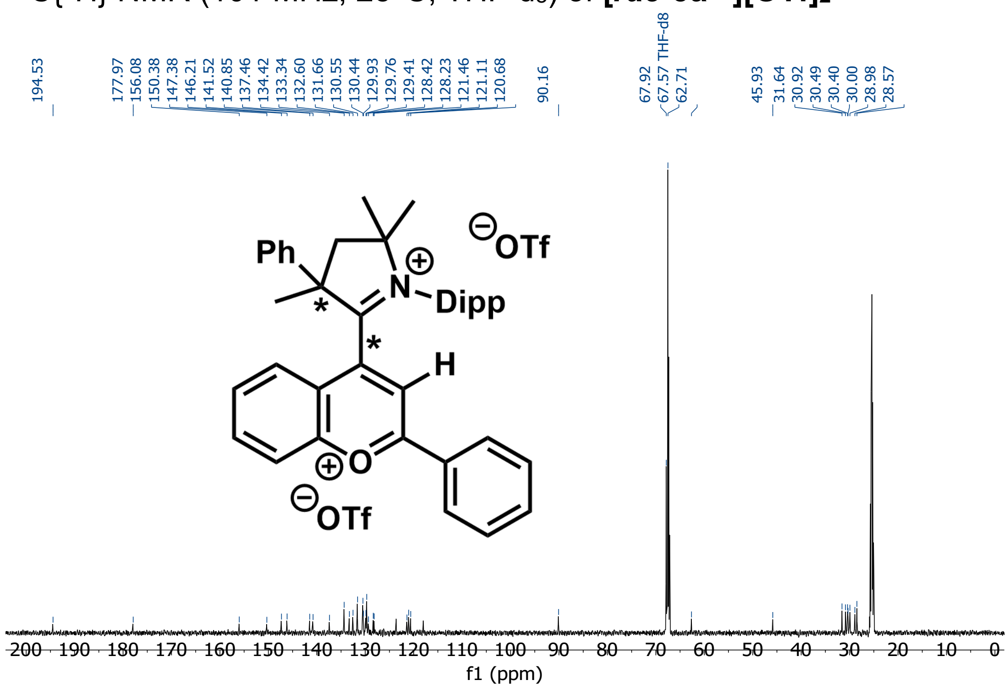
$^{13}C\{^{1}H\}$ NMR (101 MHz, 25°C, DCM-d$_2$) of **[*rac*-3a^{++}][OTf]$_2$**



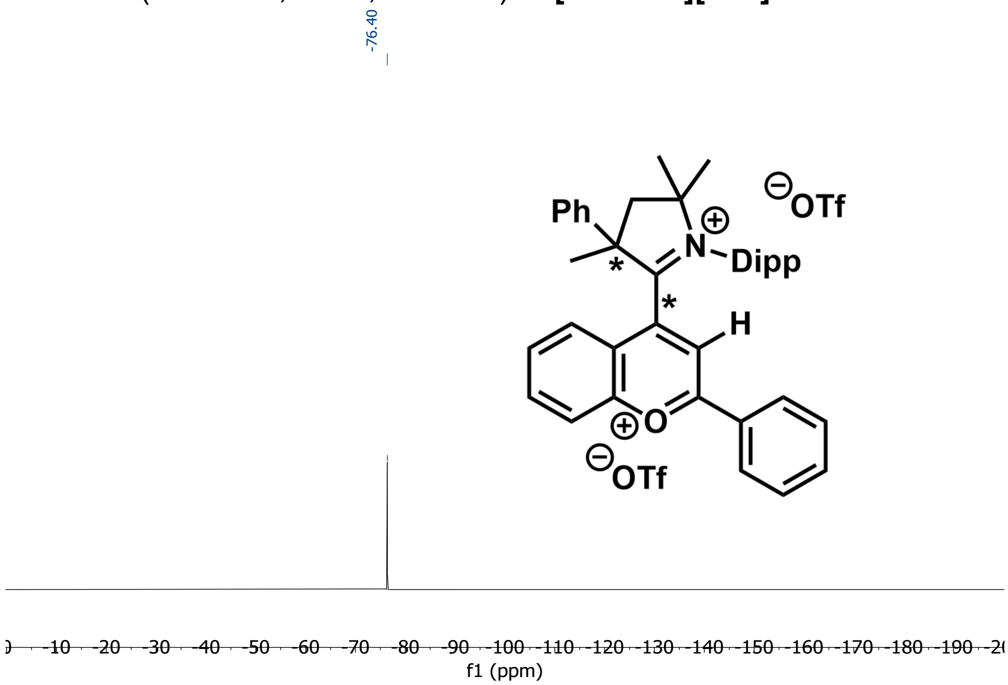
^{1}H NMR (500 MHz, 25°C, THF-d$_8$) of **[*rac*-3a^{++}][OTf]$_2$**



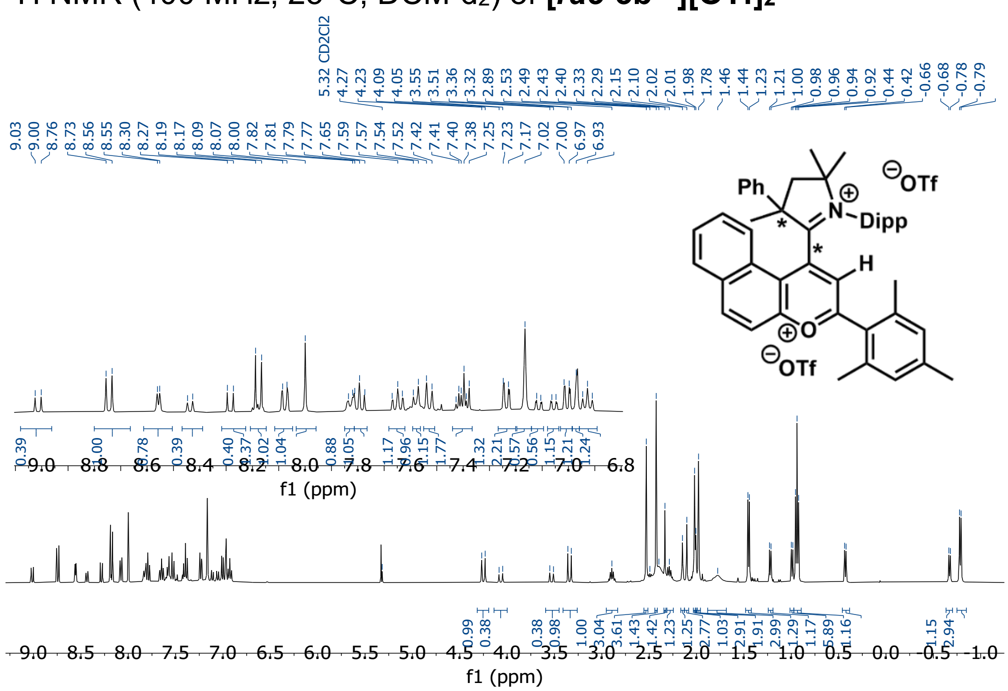
$^{13}C\{^{1}H\}$ NMR (101 MHz, 25°C, THF-d$_8$) of **[*rac*-3a^{++}][OTf]$_2$**



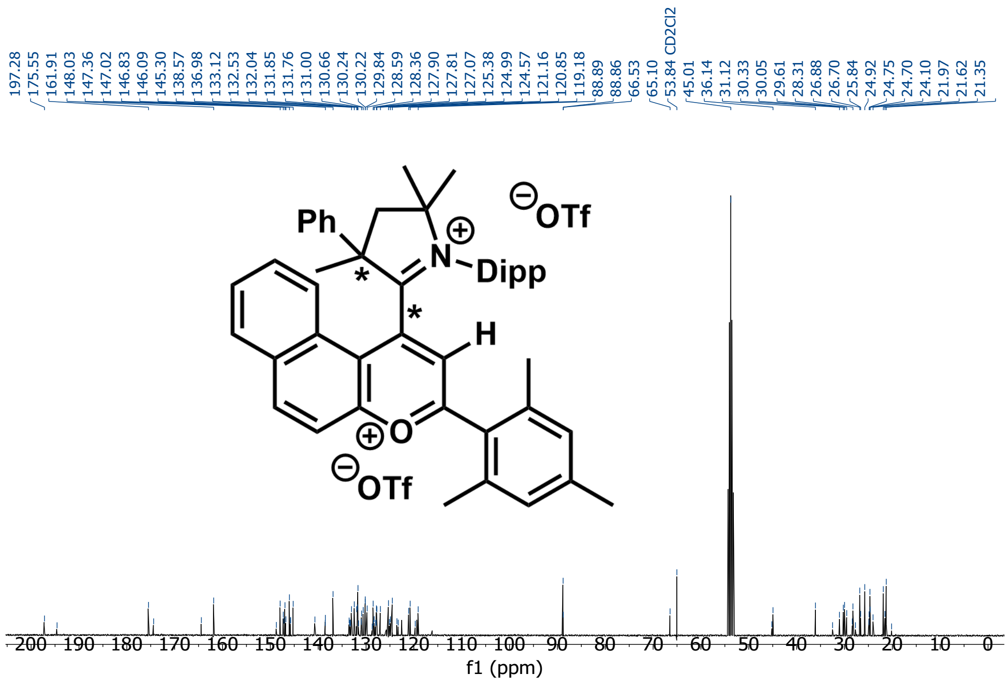
^{19}F NMR (500 MHz, 25°C, DCM-d$_2$) of **[*rac*-3a^{++}][OTf]$_2$**



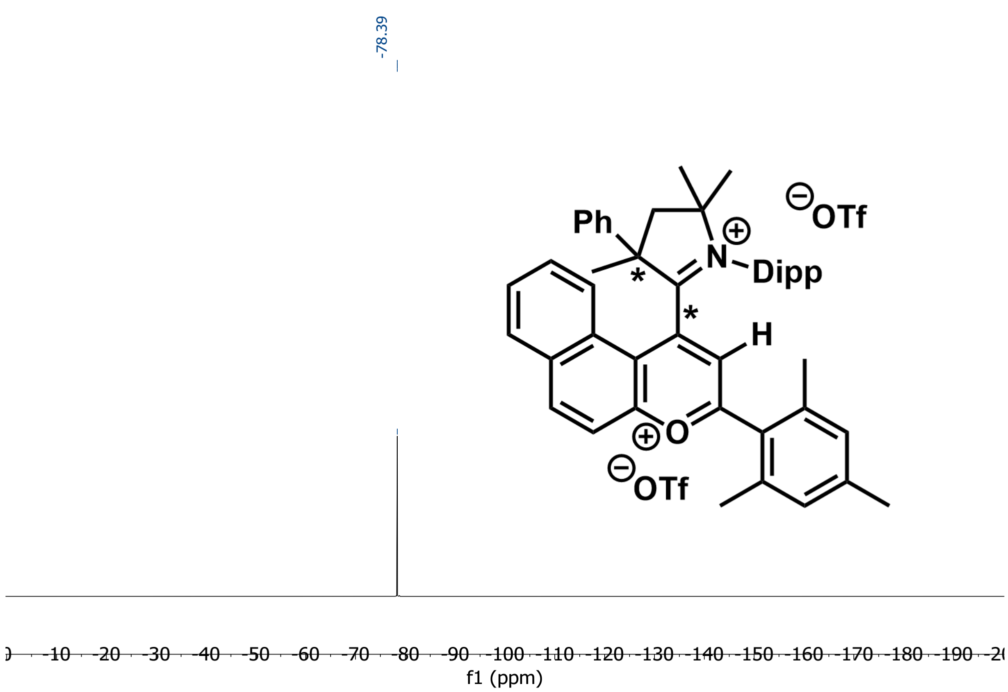
^{1}H NMR (400 MHz, 25°C, DCM-d$_2$) of **[*rac*-3b^{++}][OTf]$_2$**



$^{13}C\{^{1}H\}$ NMR (101 MHz, 25°C, DCM-d_2) of **[*rac*-3b^{++}][OTf]$_2$**



^{19}F NMR (471 MHz, 25°C, DCM-d_2) of **[*rac*-3b^{++}][OTf]$_2$**



Chemical Switching Experiments

A solution of the appropriate alkene was prepared in THF-d_8. An initial ^1H NMR spectrum was taken. 2.2 eq. of AgOTf were added the sample was sonicated until the color change was complete (*ca.* 10 minutes). Solids were allowed to settle, and a second ^1H NMR spectrum was taken. Then, 2 eq. of Zn^0 powder were added. The sample was sonicated until the color had fully reverted (*ca.* 1 h for **3a**, overnight for **3b**), after which solids were allowed to settle and the final ^1H NMR spectrum was taken.

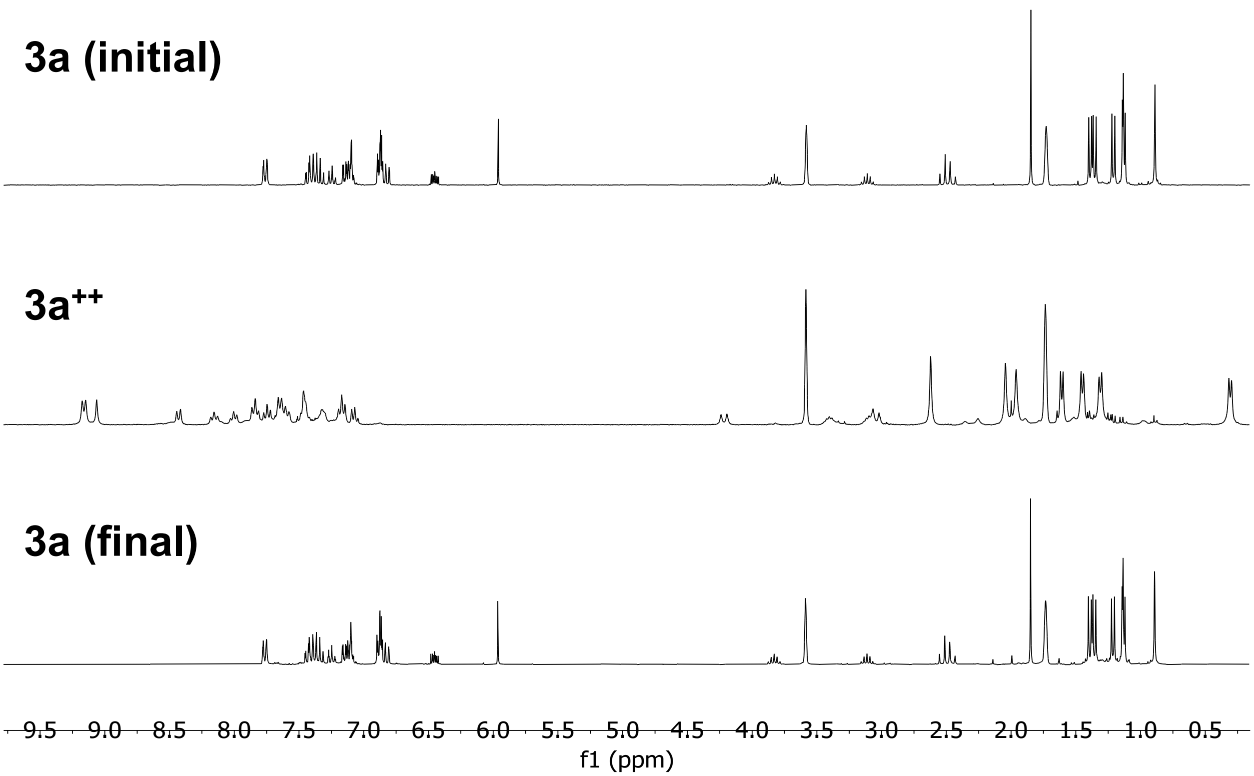


Figure S5. ^1H NMR (300 MHz, 25°C, THF-d_8) of **3a** → **3a^{++}** → **3a**

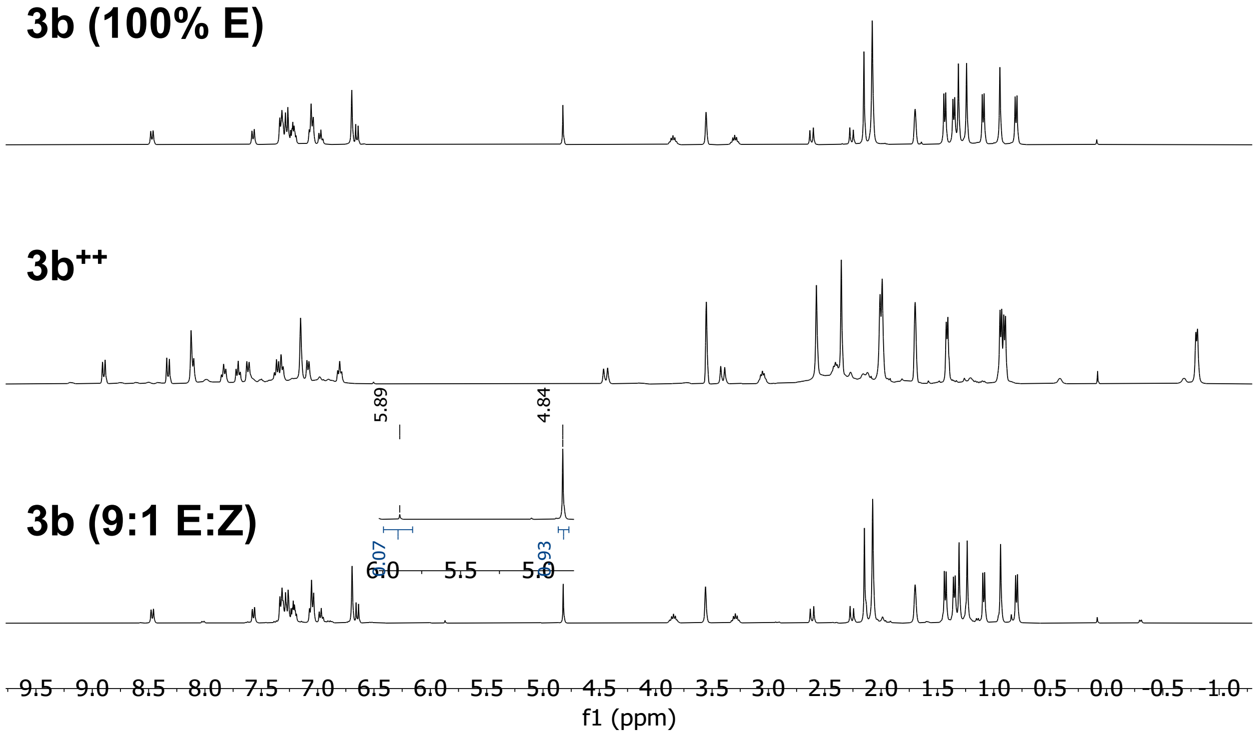


Figure S6. [1]H NMR (400 MHz, 25°C, THF-d_8) of **3b (100% E)** → **$3b^{++}$** → **3b (9:1 E:Z)**

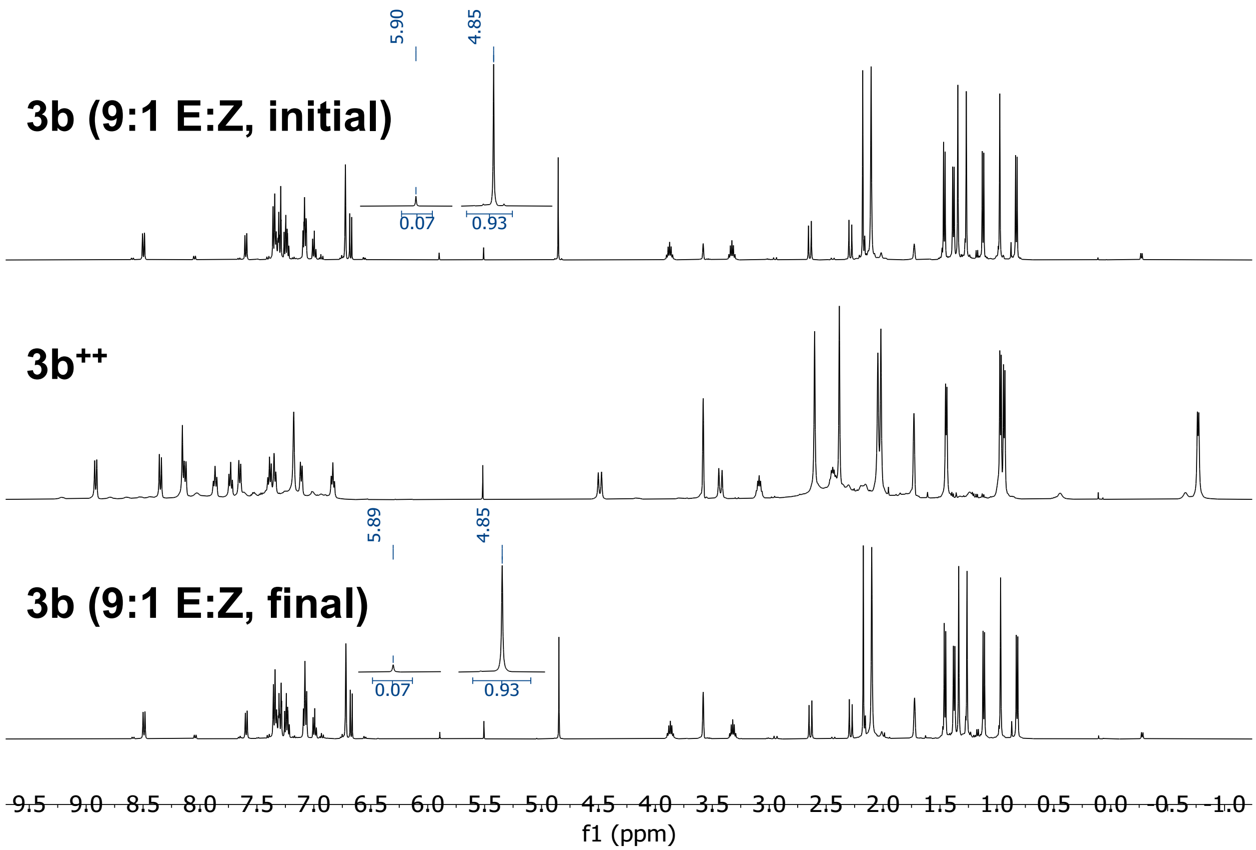


Figure S7. ^{1}H NMR (500 MHz, 25°C, THF-d_8) of **3b (9:1 E:Z)** → **$3b^{•+}$** → **3b (9:1 E:Z)**

2D NMR Analysis and Spectra

Determining the olefinic and planar stereochemistry of 3a by ^{1}H-^{1}H NOESY analysis

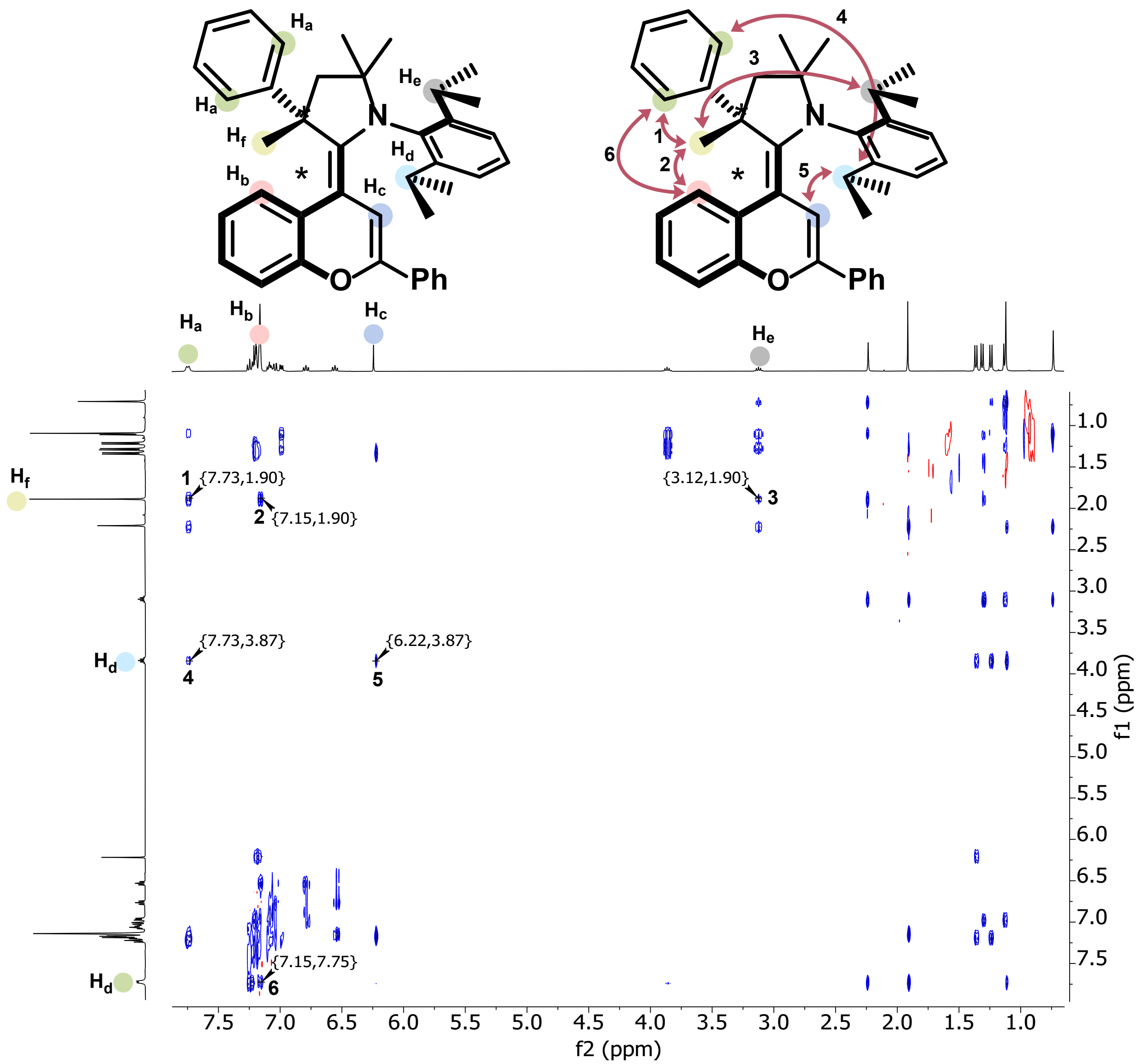


Figure S8. ^{1}H-^{1}H NOESY NMR (400 MHz, 25°C, C_6D_6) of **3a**

The E-configuration of the central olefinic bond is unambiguously determined by the correlation (**5**) between the olefinic proton, $\mathbf{H_c}$ (6.22 ppm), and $\mathbf{H_d}$ (3.87 ppm), one of the two tertiary protons of the N-Dipp isopropyl groups. This configuration is corroborated by the absence of any correlations between $\mathbf{H_c}$ and $\mathbf{H_f}$ (1.90 ppm), the methyl substituent of the stereogenic carbon. $\mathbf{H_f}$ is unambiguously identified as such by the correlation (**3**) with $\mathbf{H_a}$ (7.73 ppm), the *o*-protons of the phenyl substituent on the stereogenic carbon.

Correlations between the substituents on the stereogenic carbon and the two isopropyl septets allows clear differentiation of the corresponding isopropyl groups as being either *syn* or *anti* to the methyl substituent on the stereogenic carbon. Specifically, the correlation (**4**) between $\mathbf{H_a}$ and $\mathbf{H_d}$ reveals $\mathbf{H_d}$ as *anti*, while the correlation (**3**) between $\mathbf{H_f}$ and $\mathbf{H_e}$ (3.12 ppm) reveals $\mathbf{H_f}$ as *syn*.

The relative configuration of the stereogenic plane is determined by the absolute configuration of the stereogenic carbon center. The interior aryl C-H proton, $\mathbf{H_b}$ (7.15 ppm), is poorly resolved in the 1D spectrum. However, the well-resolved correlation (**2**) between $\mathbf{H_f}$ and another aryl signal besides $\mathbf{H_a}$ enables $\mathbf{H_b}$ to be located in the 2D spectrum; besides $\mathbf{H_a}$, $\mathbf{H_b}$ (7.15 ppm) is the only aryl proton which could be expected to correlate with $\mathbf{H_f}$. Based on the correlations of $\mathbf{H_b}$ to both $\mathbf{H_a}$ (**6**) and $\mathbf{H_f}$ (**2**), we propose that the solution state conformation of **4a** resembles that which is observed in the crystal state. Furthermore, the olefinic proton, $\mathbf{H_c}$, only correlates (**5**) to one of the two isopropyl septets. In the crystal structure of **3a**, $\mathbf{H_c}$ is tilted towards $\mathbf{H_d}$ and away from $\mathbf{H_e}$. This is corroborated by computational modeling of **3a** in the solution state, which predicts the conformation observed in the crystal structure to be thermodynamically preferred in the solution state. Notably, in the higher energy planar configuration, $\mathbf{H_c}$ is directed *away* from $\mathbf{H_e}$. Thus, the absolute configurations of the enantiomers present in racemic **3a** are ***(S,M$_p$)*** and ***(R,P$_p$)***.

Determining the olefinic and planar stereochemistry of 3b by ^{1}H-^{1}H NOESY analysis

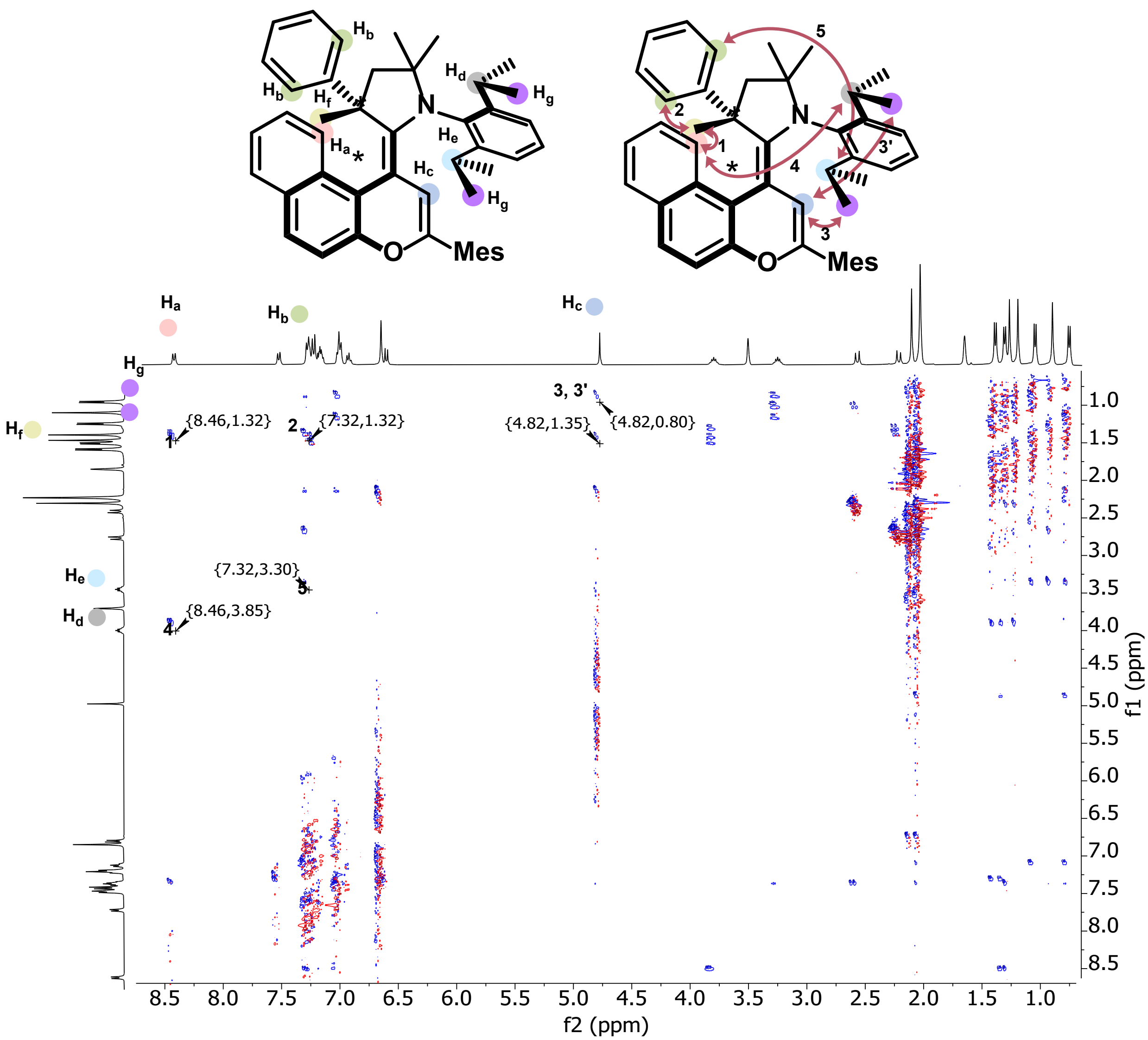


Figure S9. ^{1}H-^{1}H NOESY NMR (400 MHz, 25°C, THF-d_8) of **3b**

The E-configuration of the central olefinic bond is unambiguously determined by correlations (**3**, **3'**) between the olefinic proton, **H$_c$** (4.82 ppm), and one of the isopropyl methyls H$_g$ (1.35 ppm, 0.80 ppm). This configuration is corroborated by the absence of any correlations between **H$_c$** and **H$_f$** (1.32 ppm), the methyl substituent of the stereogenic carbon. **H$_f$** is unambiguously identified as such by the correlation (**2**) with **H$_b$** (7.32 ppm), the *o*-protons of the phenyl substituent on the stereogenic carbon. Furthermore, the "bay position" aryl C-H proton, **H$_a$** (8.46 ppm), correlates (**1**) with **H$_f$**, supporting this assignment.

The relative configuration of the stereogenic plane is determined by the absolute configuration of the stereogenic carbon center. **H_a** correlates (**1**) with **H_f** as well as (**4**) **H_d** (3.85 ppm), one of the two isopropyl septets. The other isopropyl septet, **H_e** (3.30 ppm), correlates (**5**) with **H_b**. Given that **H_a** and **H_b** correlate with distinct isopropyl septets, **H_a** and **H_b** must lie on opposing sides of the stereogenic carbon center. Thus, we propose that the solution state conformation of **3b** resembles that which is observed in the crystal state; the absolute configurations of the enantiomers present in racemic **3b** are ***(S,P_p)*** and ***(R,M_p)***.

Identifying the minor Z-olefin stereoisomer of 3b by ^{1}H-^{1}H NOESY analysis

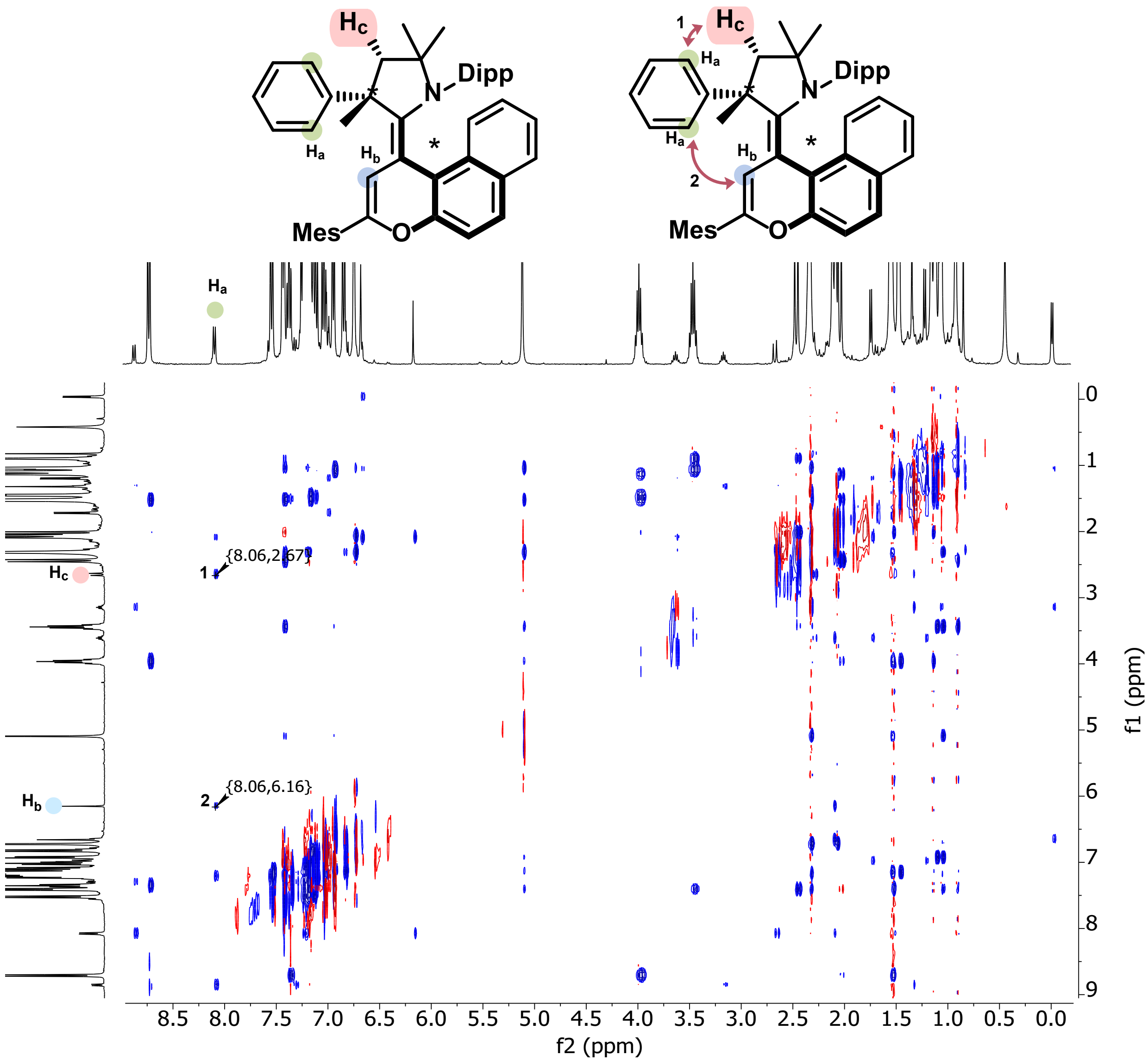


Figure S10. ^{1}H-^{1}H NOESY NMR (400 MHz, 25°C, C_6D_6) of 9:1 E:Z mixture of **3b**

The Z-configuration of the central olefinic bond in the minor stereoisomer of **3b** is unambiguously determined by the correlation (**2**) between the olefinic proton, $\mathbf{H_b}$ (6.16 ppm), and the *o*-phenyl protons $\mathbf{H_a}$ (8.06 ppm). The assignment of $\mathbf{H_a}$ is supported by the correlation (**1**) between this doublet and one of the two diastereotopic methylene protons, $\mathbf{H_c}$ (2.67) ppm. Correlation **2** requires that $\mathbf{H_b}$ and $\mathbf{H_a}$ be *cis* in reference to the central olefinic bond.

Determining the axial stereochemistry of atropisomeric 3a^{++} by ^{1}H-^{1}H NOESY analysis

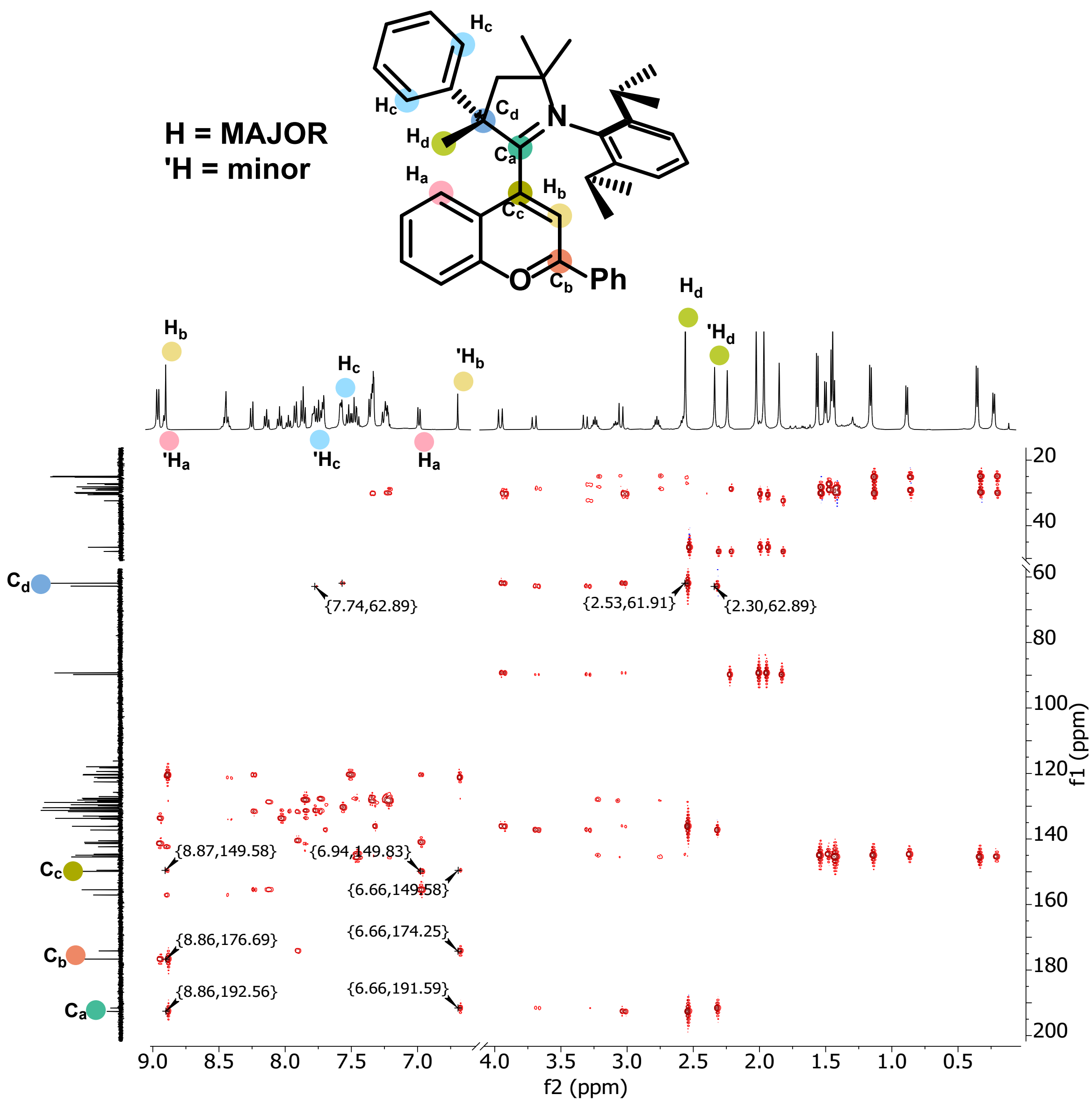


Figure S11. ^{1}H-^{13}C HMBC NMR (500 MHz, 25°C, DCM-d$_2$) of **[3a^{++}][OTf]$_2$**; formal charges and anions omitted for clarity.

HMBC was used to assign key proton resonances for both the major and minor atropisomers:

- The *ortho* protons, H$_c$ (7.74 ppm, minor; 7.53 ppm, MAJOR) of the phenyl substituent of the stereogenic carbon C$_d$ (61.91 ppm, MAJOR; 62.89 ppm, minor),
- The protons for the methyl substituent of the same carbon, H$_d$ (2.53 ppm, MAJOR; 2.30 ppm, minor).

- The “interior” aryl protons of the chromenylium ring: H_a (8.87 ppm, MAJOR; 6.94 ppm, minor), which presents as a doublet, and H_b (8.86 ppm, MAJOR; 6.66 ppm, minor), which presents as a singlet.

With these resonances located, it is possible to assign the configuration of the central stereogenic axis using NOESY.

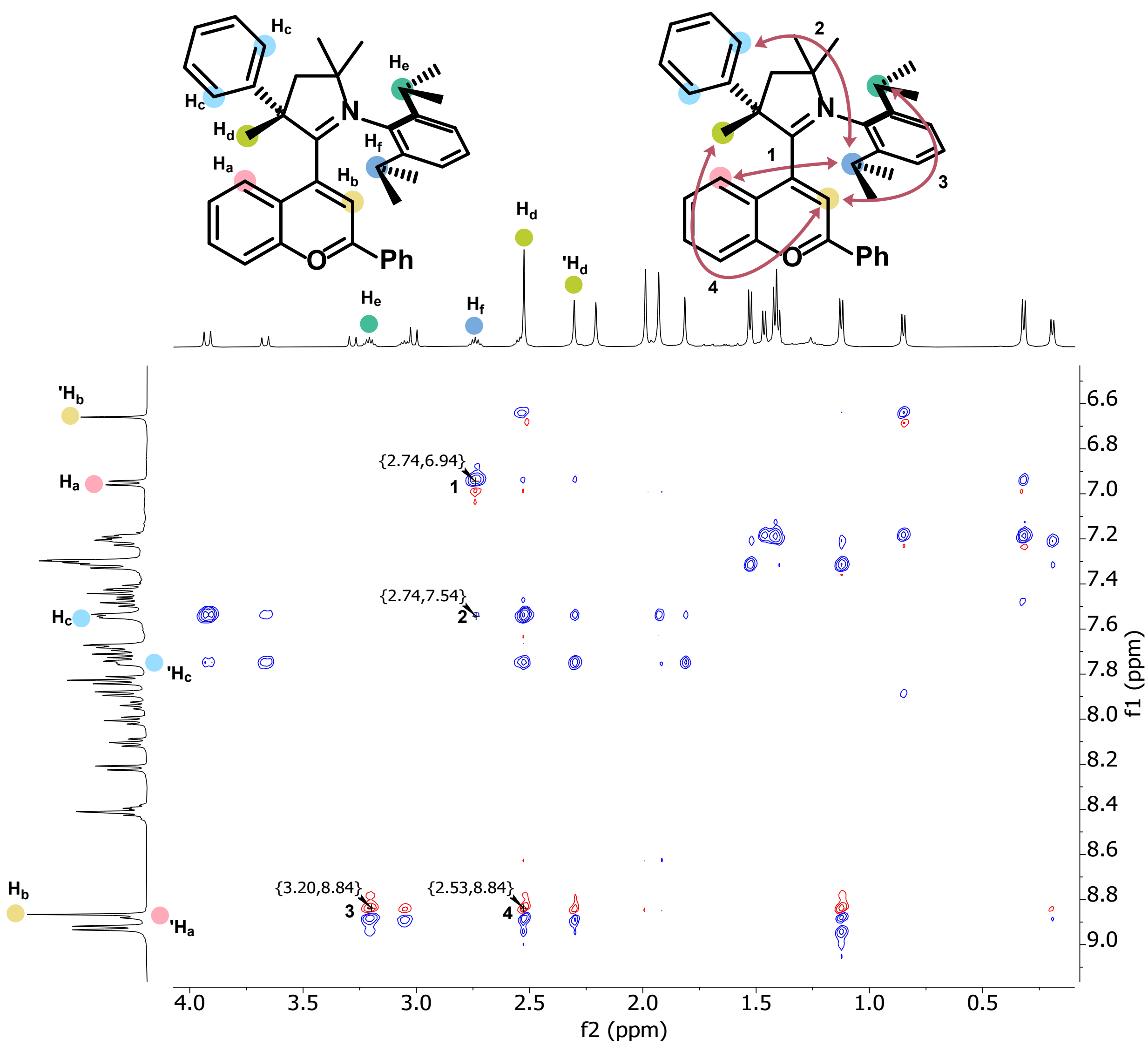


Figure S12. ^{1}H-^{1}H NOESY NMR (400 MHz, 25°C, DMC-d2) of **[3a^{++}][OTf]$_2$**; formal charges and anions omitted for clarity.

The *syn* and *anti* isopropyl protons were assigned based on the correlation (**2**) between **H$_f$** (2.74 ppm) and **H$_d$**. Thus, **H$_f$** is *syn* to the phenyl substituent of the stereogenic carbon center and *anti* to the corresponding methyl. Consequently, the fact that **H$_a$** correlates (**1**) to **H$_f$** necessitates that these, too, are *syn*, and therefore that the chromenylium ring is directed towards the phenyl substituent. This is corroborated by correlations (**3**, **4**) of the methyl substituent protons, **H$_d$**, and the other isopropyl proton, **H$_e$** (3.20 ppm) with **H$_b$**, which lay on the opposite side of the chromenylium ring as **H$_a$**. Based upon this analysis, the absolute configurations of the major atropisomer are ***(S,M$_a$)*** and ***(R,P$_a$)***, while the minor are ***(S,P$_a$)*** and ***(R,M$_a$)***.

Determining the axial stereochemistry of atropisomeric 3b^{++} by ^{1}H-^{1}H NOESY analysis

HMBC was used to assign key proton resonances for the major atropisomer. Namely, the interior aryl proton singlet, H$_a$ (7.99 ppm), and the methyl substitutent of the stereogenic carbon center, H$_b$ (2.53 ppm).

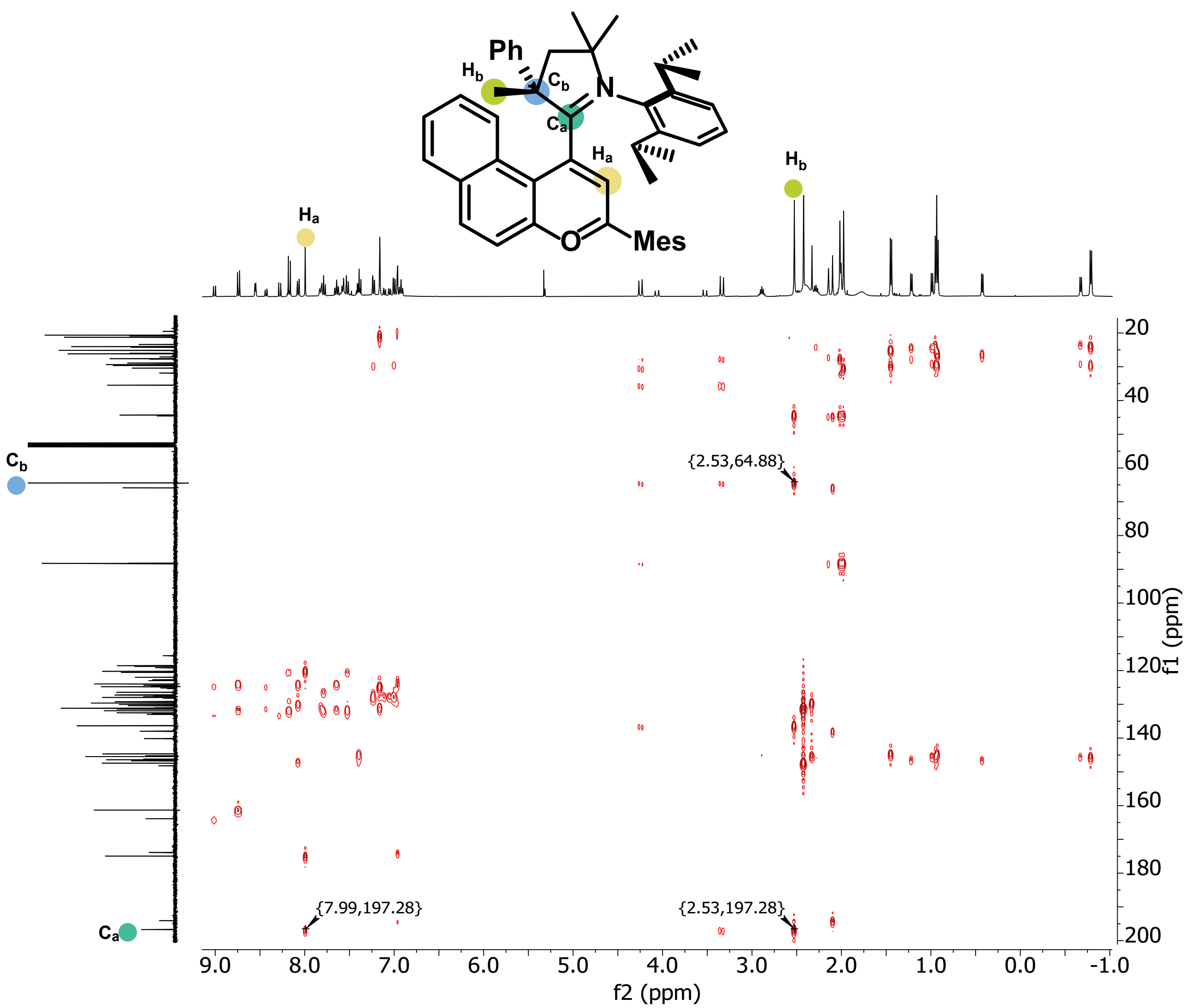


Figure S13. ^{1}H-^{13}C HMBC NMR (500 MHz, 25°C, DCM-d$_2$) of **[3b^{++}][OTf]$_2$**; formal charges and anions omitted for clarity.

With these resonances located, it is possible to assign the configuration of the central stereogenic axis using NOESY.

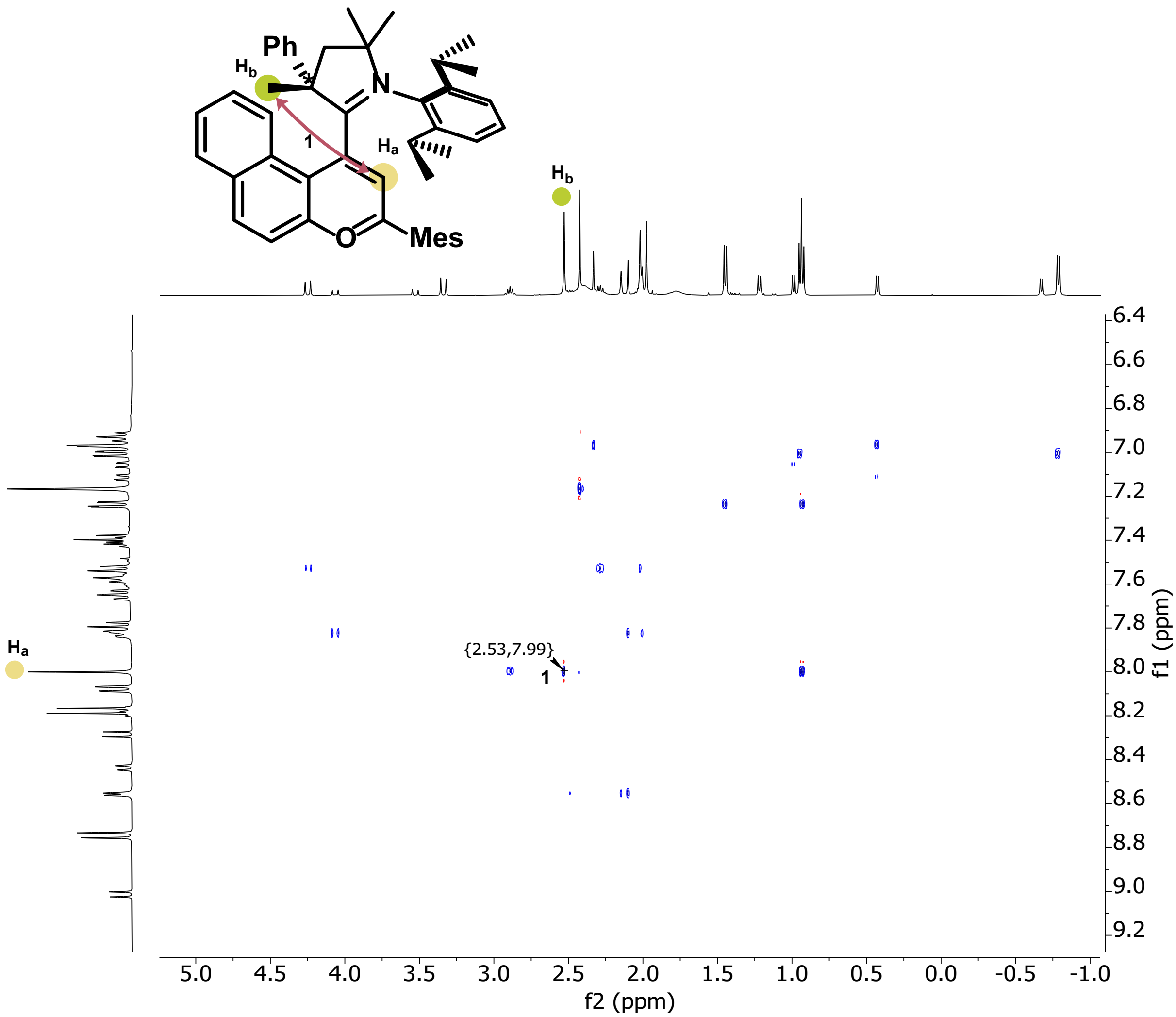
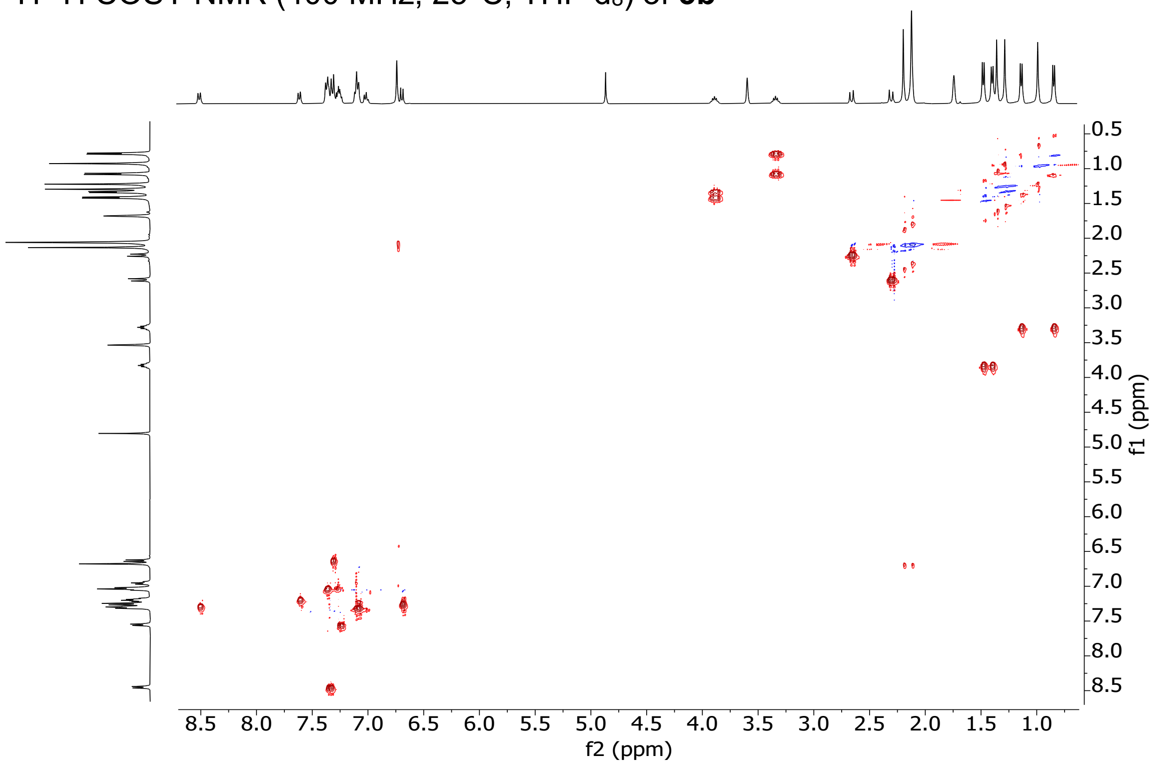


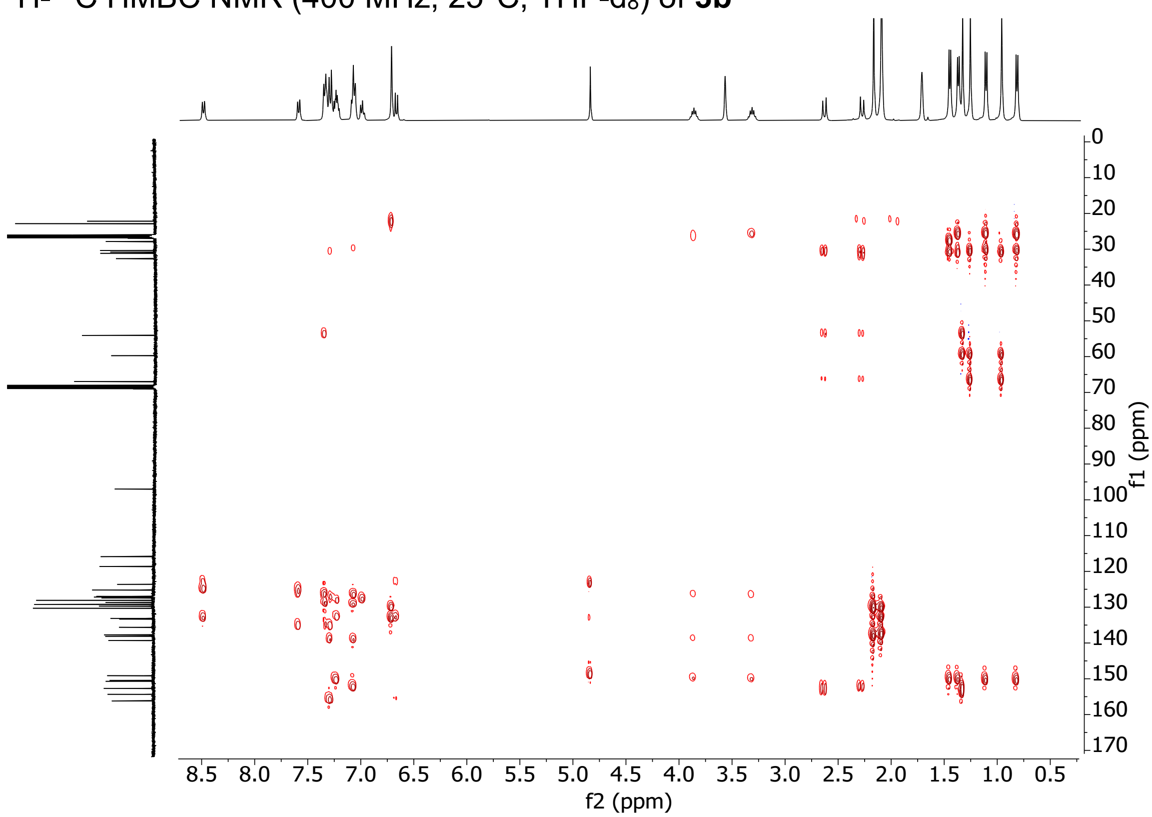
Figure S14. [1]H-[1]H NOESY NMR (400 MHz, 25°C, DCM-d2) of **[3b^{++}][OTf]$_2$**; formal charges and anions omitted for clarity.

The correlation (**1**) between H_a and H_b necessitates that these are *syn*. Therefore, the benzochromenylium ring is directed towards the phenyl substituent. This configuration of the stereogenic axis is like that which is observed in the solid state. Based upon this analysis, the absolute configurations of the major atropisomer are ***(S,M$_a$)*** and ***(R,P$_a$)***, while the minor are ***(S,P$_a$)*** and ***(R,M$_a$)***.

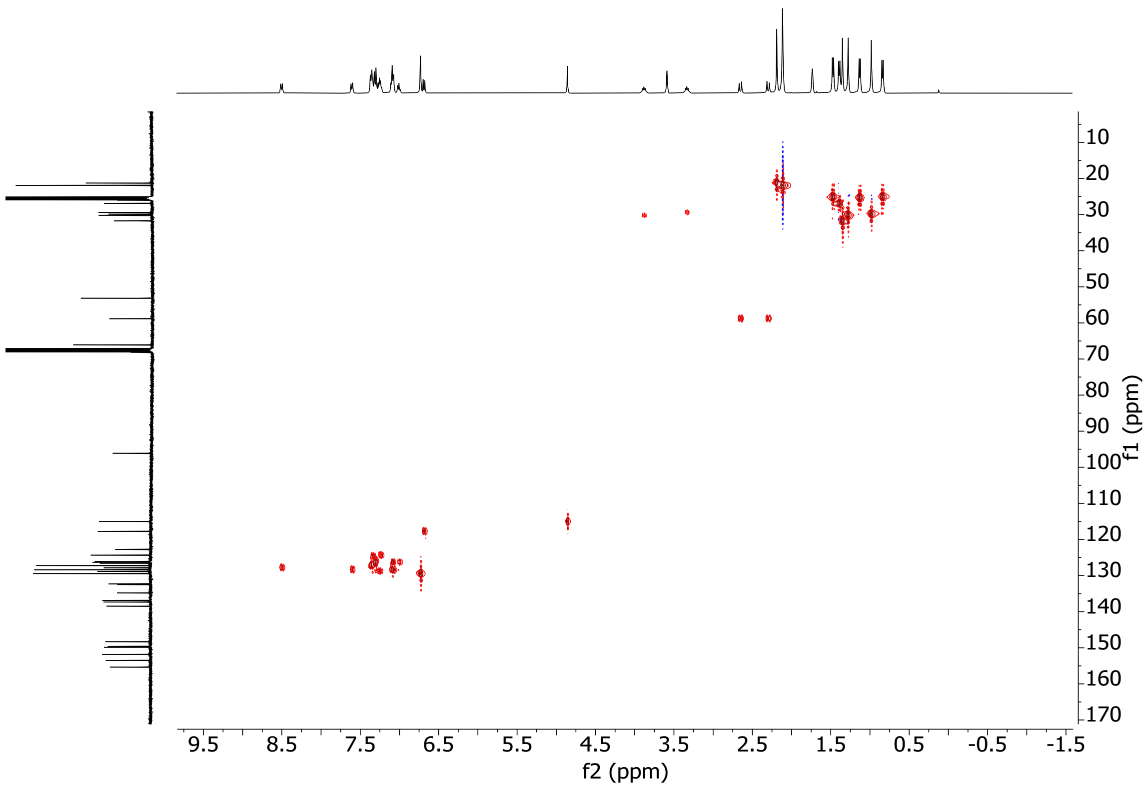
^{1}H-^{1}H COSY NMR (400 MHz, 25°C, THF-d_8) of **3b**



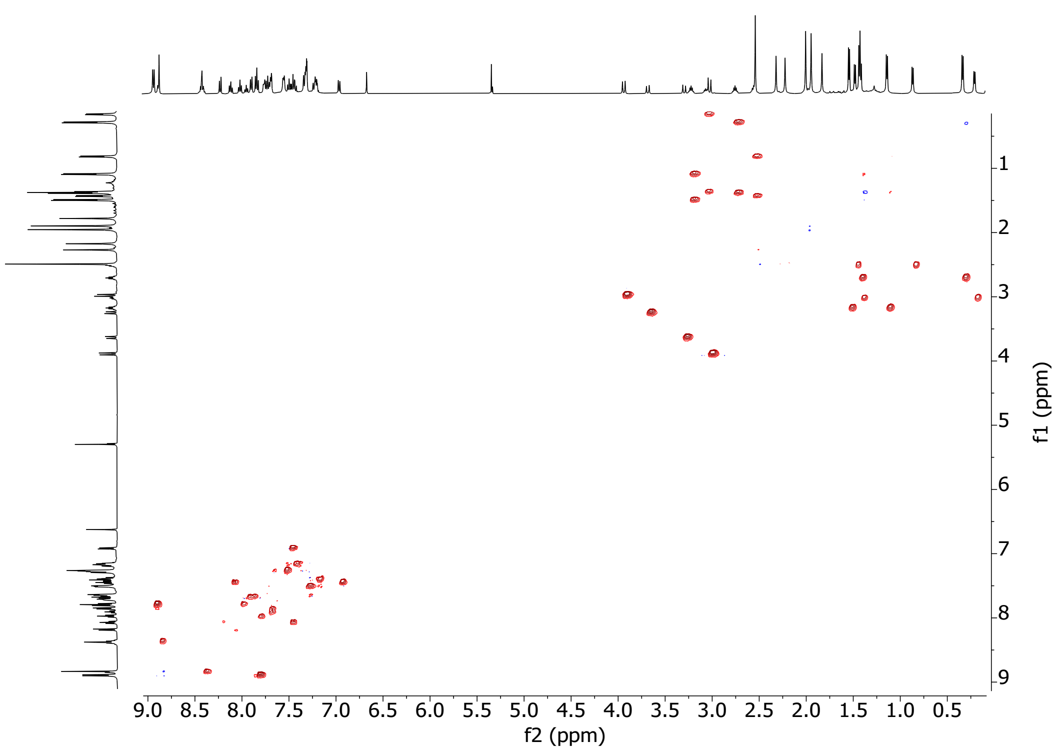
^{1}H-^{13}C HMBC NMR (400 MHz, 25°C, THF-d_8) of **3b**



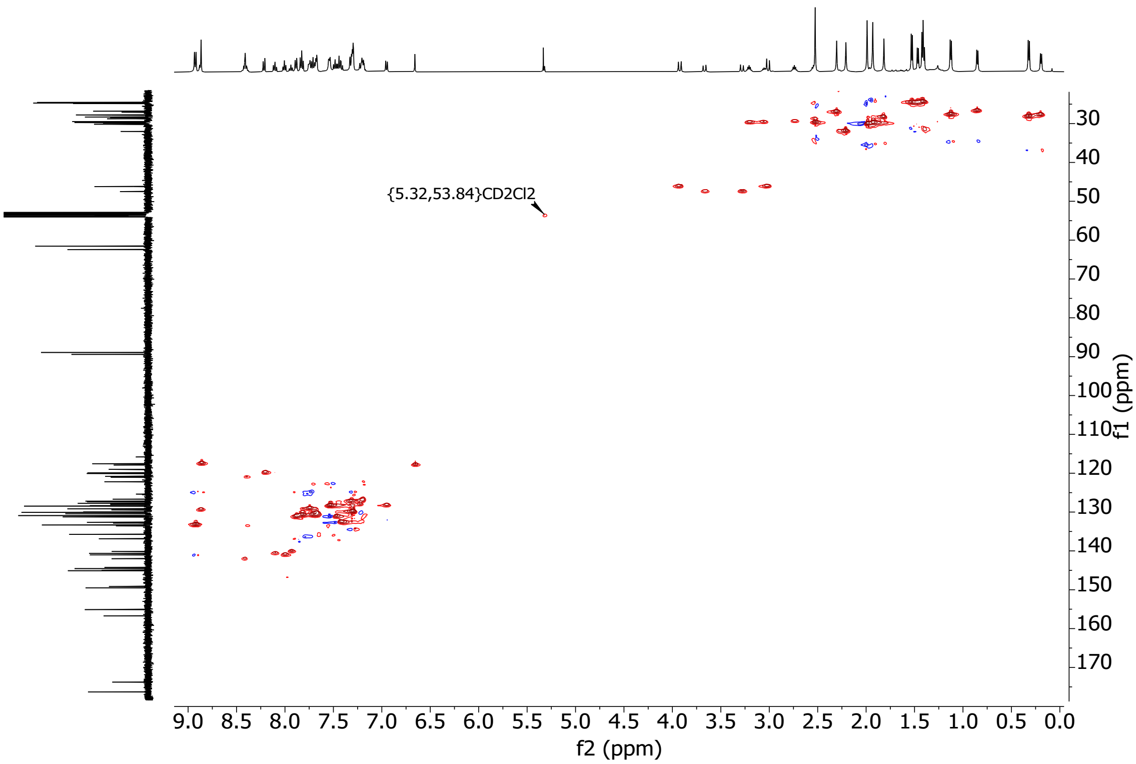
^{1}H-^{13}C HMQC NMR (400 MHz, 25°C, THF-d_8) of **3b**



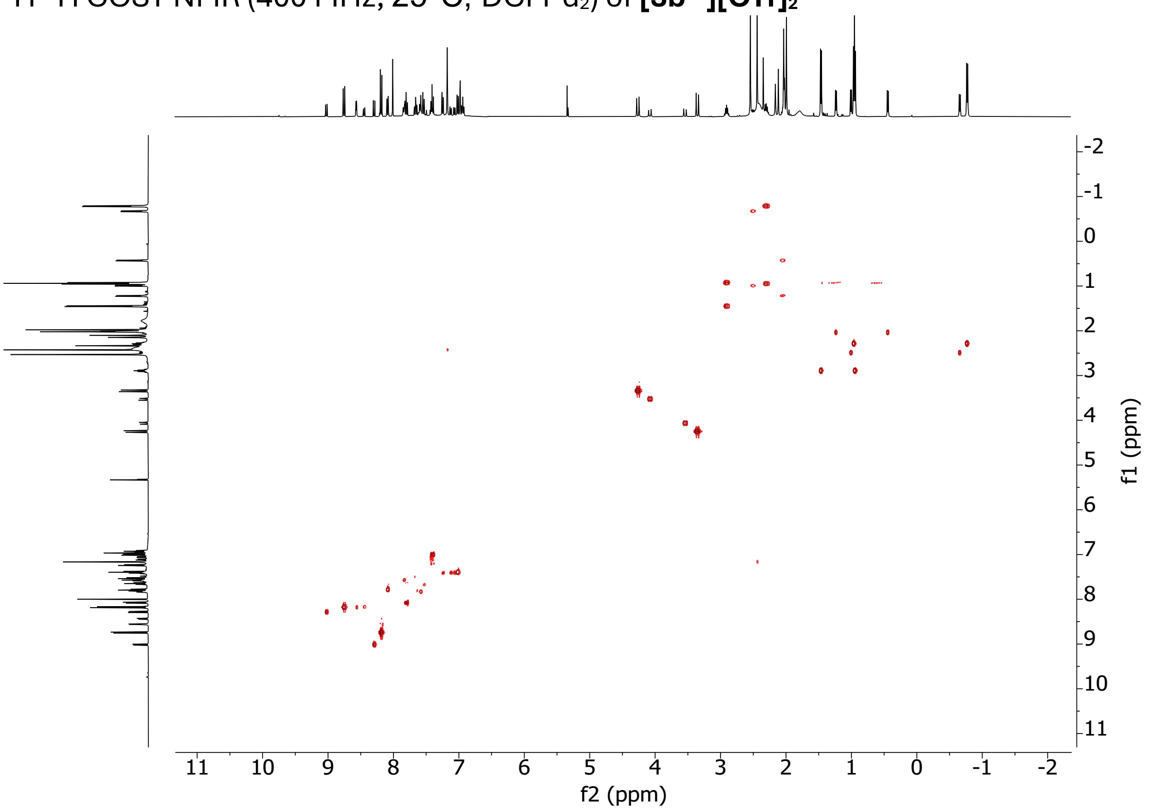
^{1}H-^{1}H COSY NMR (400 MHz, 25°C, DCM-d_2) of **[3a^{++}][OTf]$_2$**



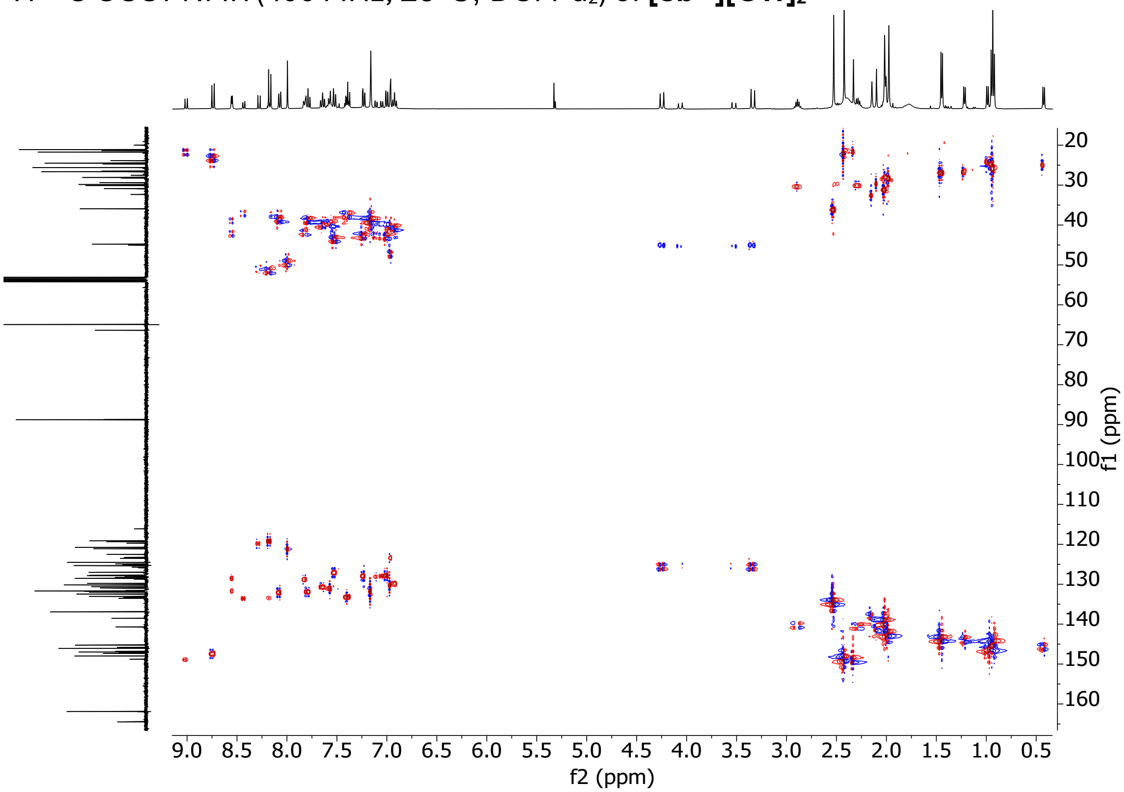
^{1}H-^{13}C HSQC NMR (400 MHz, 25°C, DCM-d$_2$) of **[3a^{++}][OTf]$_2$**



^{1}H-^{1}H COSY NMR (400 MHz, 25°C, DCM-d$_2$) of **[3b^{++}][OTf]$_2$**



[1]H-[13]C COSY NMR (400 MHz, 25°C, DCM-d_2) of **[3b^{++}][OTf]$_2$**



4) Cyclic Voltammetry

Electrochemical measurements were performed with a potentiostat-galvanostat AutoLab PGSTAT 302N controlled by resident GPES (General Purpose Electrochemical System 4.9) software using a conventional single-compartment three-electrode cell. The working and auxiliary electrodes were platinum electrodes and the reference electrode was the saturated potassium chloride calomel electrode (SCE). The supporting electrolyte was 0.1 M Bu_4NPF_6 (tetrabutylammonium hexafluorophosphate) in dichloromethane and solutions were purged with argon before the measurements. All potentials are quoted relative to $Fc^{0/+}$.

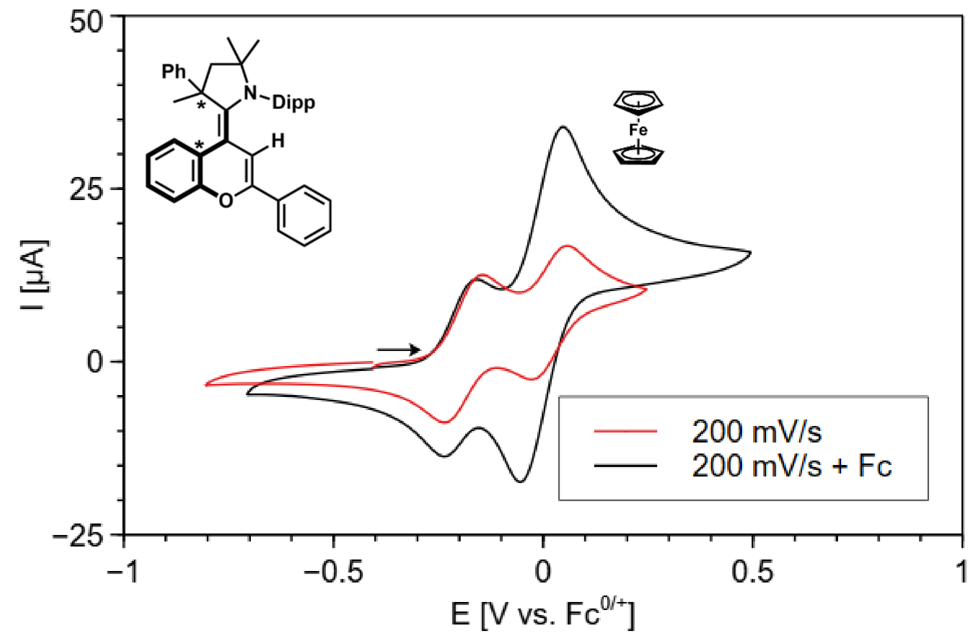


Figure S15. Cyclic voltammograms of **3a** (~0.5 mg/mL) in DCM (0.1 M $[NBu_4][PF_6]$) at room temperature with and without ferrocene as an internal standard. Scan rate of 200 mV/s (arrow indicates scanning direction).

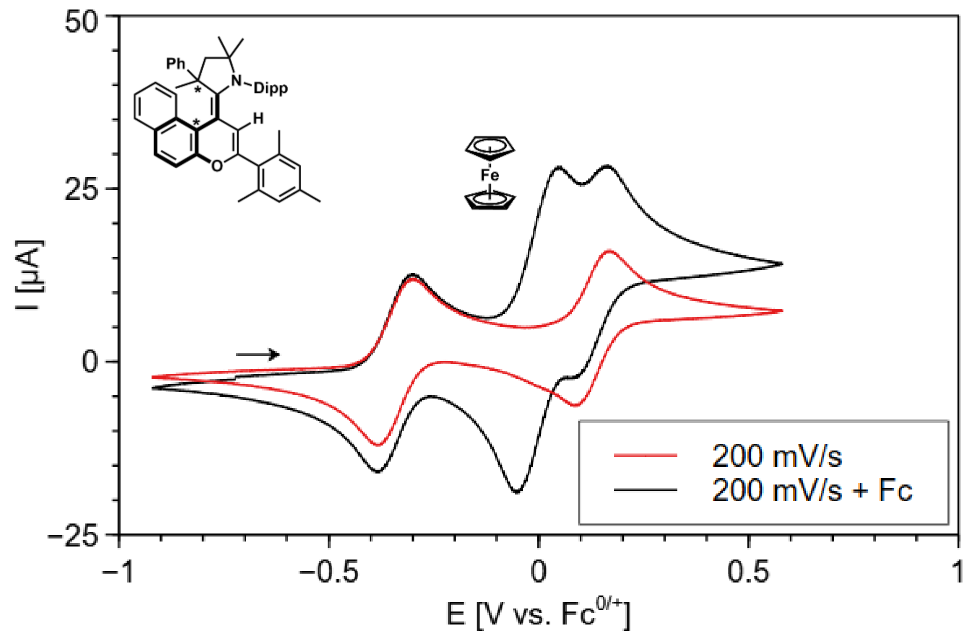


Figure S16. Cyclic voltammograms of **3b** (~0.5 mg/mL) in DCM (0.1 M [NBu_4][PF_6]) at room temperature with and without ferrocene as an internal standard. Scan rate of 200 mV/s (arrow indicates scanning direction).

5) EPR Measurements

Samples for EPR analysis were prepared by *in situ* oxidation of the corresponding neutral hybrids using iodine in DCM (~ 1 μM). To interpret the experimental spectra, simulated spectra were obtained by parameter fitting using WinSim2002. Input values for hyperfine coupling constants were obtained from density functional theory calculations (See "Hyperfine Coupling Constants and Spin Densities").

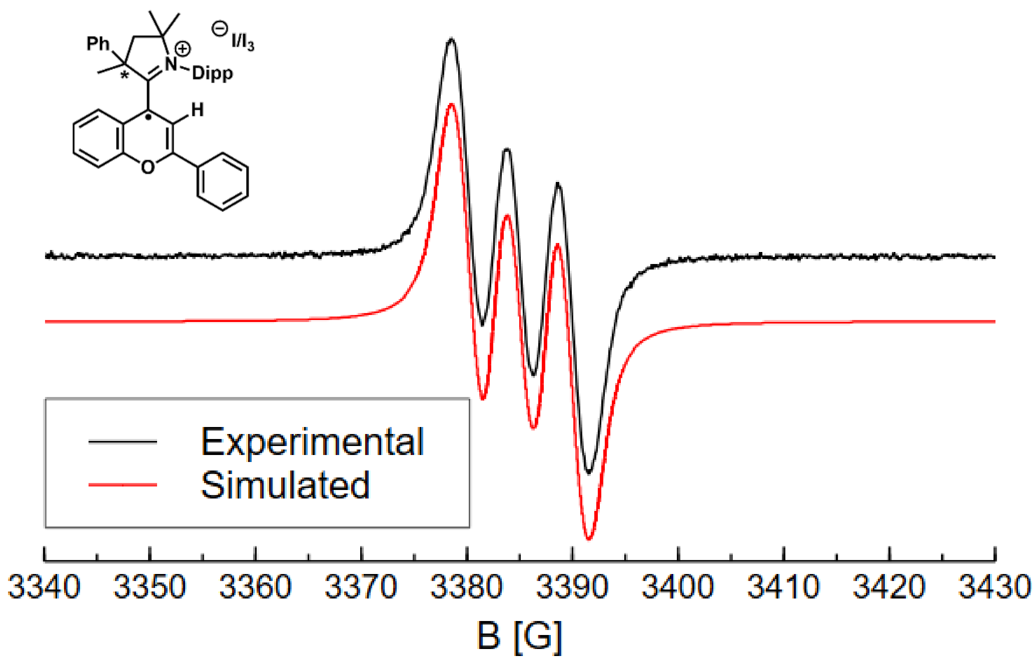


Figure S17. X-Band EPR spectrum of **3a**$^{\bullet+}$ in DCM (1μM). g = 2.0037; LW = 1.603; Hyperfine coupling constants: 1xN: 13.5 MHz; 1xH: 4.0 MHz; 1xH: 3.0 MHz; 1xH: 2.2 MHz; 1xH: 2.1 MHz; 1xH: 1.5 MHz.

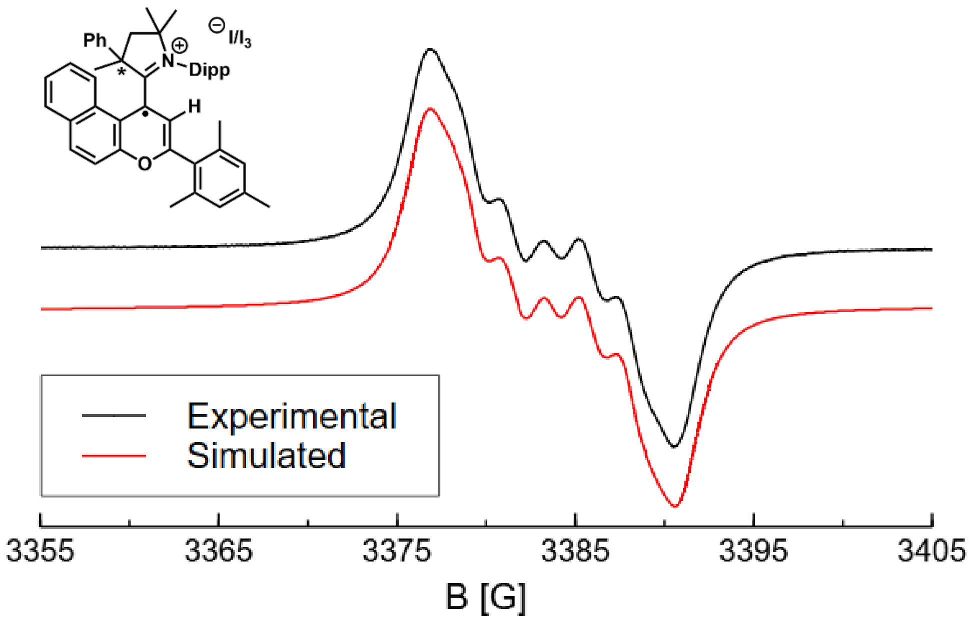


Figure S18. X-Band EPR spectrum of **3b$^{•+}$** in DCM (1μM). g = 2.0019; LW = 1.442; Hyperfine coupling constants: 1xN: 12.2 MHz; 1xH: 6.4 MHz; 1xH: 4.3 MHz; 1xH: 2.4 MHz; 3xH: 0.6 MHz; 1xH: 0.5 MHz.

6) UV-Visible Spectroscopy

Radical cations were prepared by *in situ* oxidation with 1 equivalent of iodine, delivered as a solution in DCM. Dications were prepared as solutions with the same concentration in DCM by oxidation with a slight excess of $AgSbF_6$, then filtration through a 0.45 μm PTFE syringe filter to remove precipitated solids before analysis. Filters should be dried in a desiccator prior to use, to limit decomposition due to hydrolysis from ambient water.

Compound	λ_{abs} (nm)	ε ($M^{-1}\cdot cm^{-1}$)
3a	370	13055
3a$^{\bullet+}$	501	9273
	366	30649
	292	51109
3a^{++}	440	8099
	266	10629
3b	370	8341
	328	7977
3b$^{\bullet+}$	546	7489
	494	7673
	363	26350
	292	51257
3b^{++}	518	12885
	304	12935

Table S2. Tabulated spectroscopic data for all compounds in DCM.

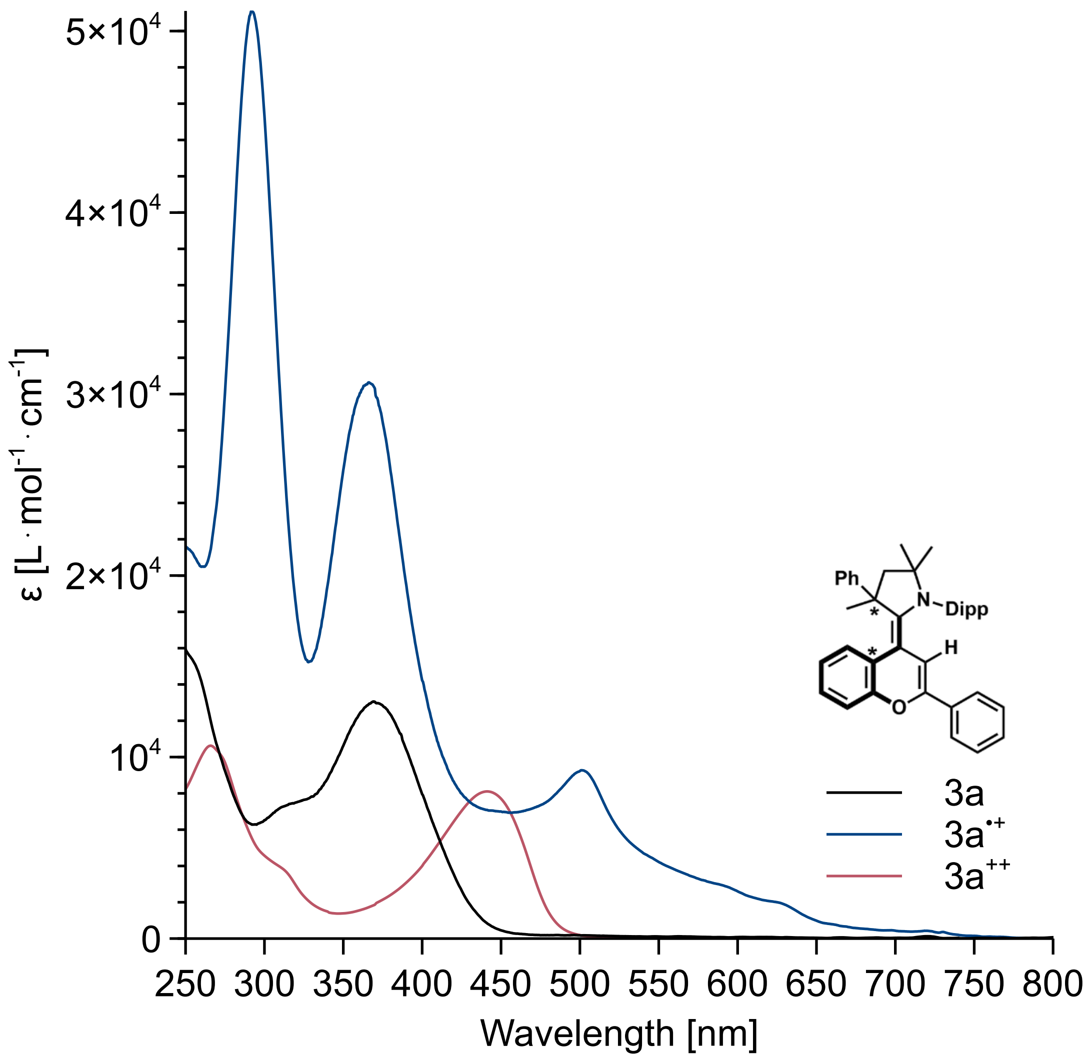


Figure S19. UV-vis spectra of **3a** (black line), **3a$^{\bullet+}$** (blue line), and **3a^{++}** (red line) in DCM.

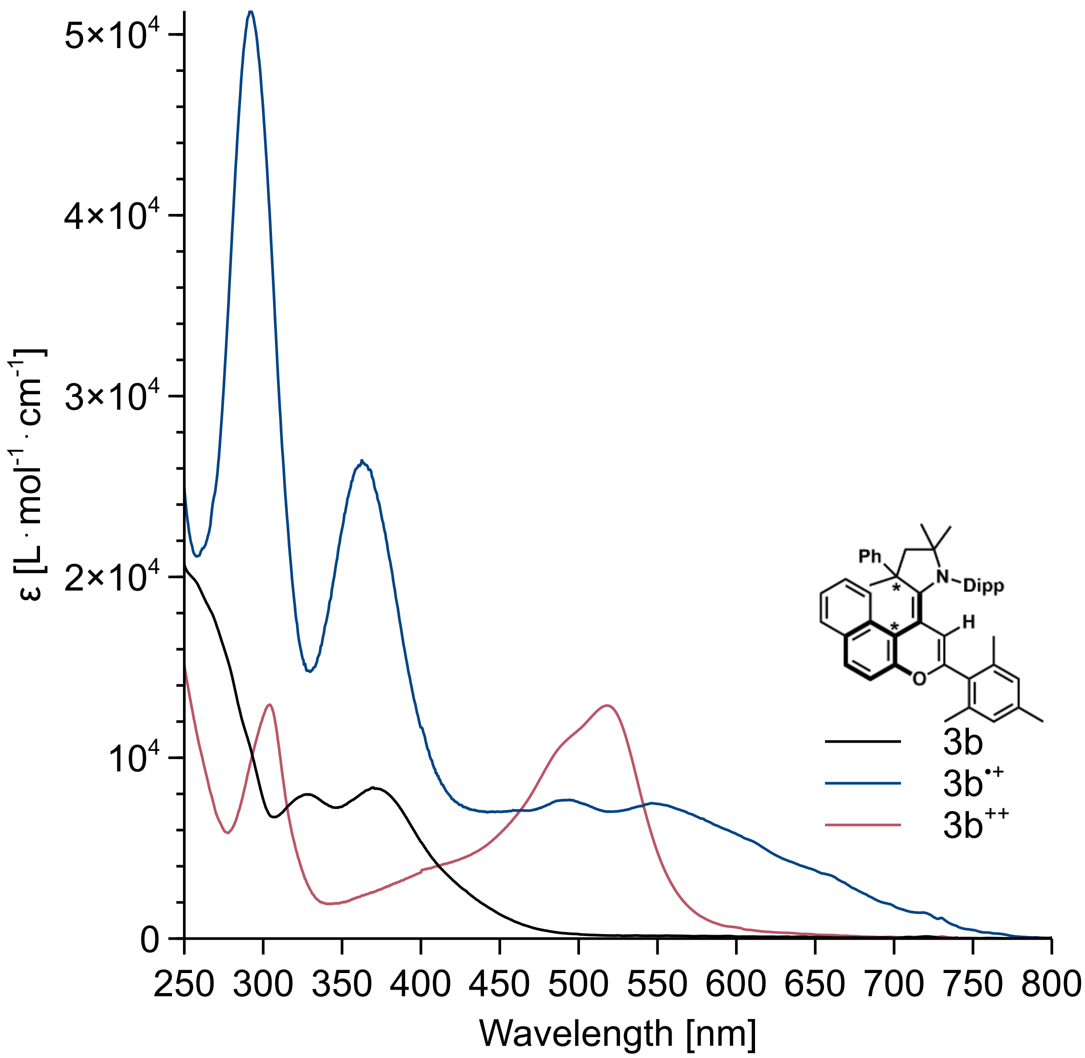


Figure S20. UV-vis spectra of **3b** (black line), **3b•+** (blue line), and **3b++** (red line) in DCM.

7) Electronic Circular Dichroism Spectroscopy

Radical cations were prepared by *in situ* oxidation with 1 equivalent of iodine, delivered as a solution in DCM. Dications were prepared as solutions in DCM by oxidation with a slight excess of $AgSbF_6$, then filtration through a 0.45 µm PTFE syringe filter to remove precipitated solids before analysis. Filters should be dried in a desiccator prior to use to avoid decomposition due to hydrolysis by ambient water.

Compound	$\|g_{abs}\|$ (λ_{abs})
3a	9.7 x 10^{-4} (390 nm)
3a$^{•+}$	1.0 x 10^{-4} (500 nm)
3a^{++}	8.8 x 10^{-5} (450 nm)
3b	2.3 x 10^{-3} (420 nm)
3b$^{•+}$	7.0 x 10^{-4} (665 nm)
3b^{++}	2.1 x 10^{-4} (510 nm)

Table S3. Experimental absolute absorption dissymmetry factors (**$|g_{abs}|$**) for all compounds in DCM.

Note, the g_{abs} spectra for both enantiomers of **3a$^{•+}$** (Figure S25) shows a weak peak around 500 nm, which is difficult to discern on account of noise. The ECD spectra of the enantiomers of **3a$^{•+}$** alone are included for clarity (Figure S22).

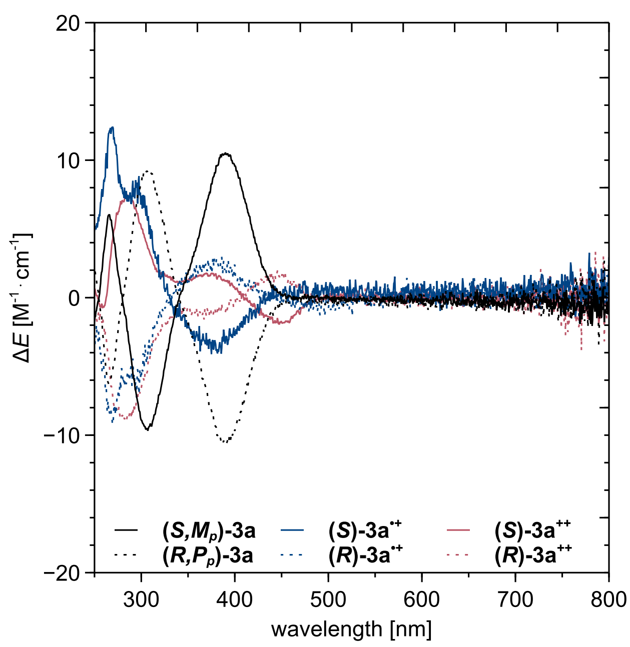


Figure S21. Electronic circular dichroism spectra of ***(S,M$_p$)*-3a** (black solid lines), ***(R,P$_p$)*-3a** (black dotted lines), and the corresponding redox series (radical cations and dications, blue and red lines, respectively) recorded in DCM (~10^{-6} M) at 298 K.

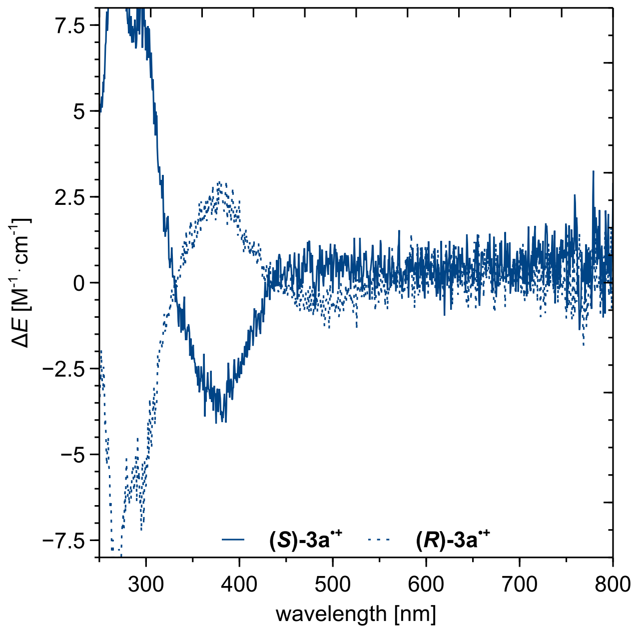


Figure S22. Electronic circular dichroism spectra of ***(S,M$_p$)*-3a$^{•+}$** (blue solid lines) and ***(R,P$_p$)*-3a$^{•+}$** (blue dotted lines), emphasizing the weak transition at ~ 500 nm. Recorded in DCM (~10^{-6} M) at 298 K.

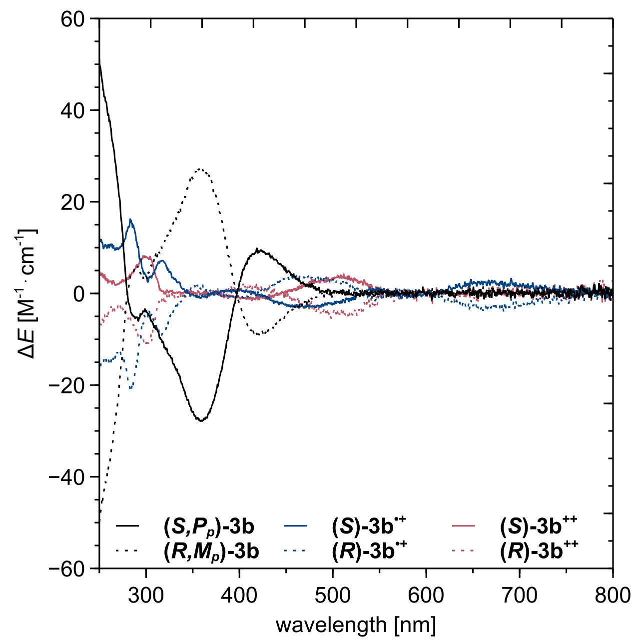


Figure S23. Electronic circular dichroism spectra of ***(S,P$_p$)*-3b** (black solid lines), ***(R,M$_p$)*-3b** (black dotted lines), and the corresponding redox series (radical cations and dications, blue and red lines, respectively) recorded in DCM (~10^{-6} M) at 298 K.

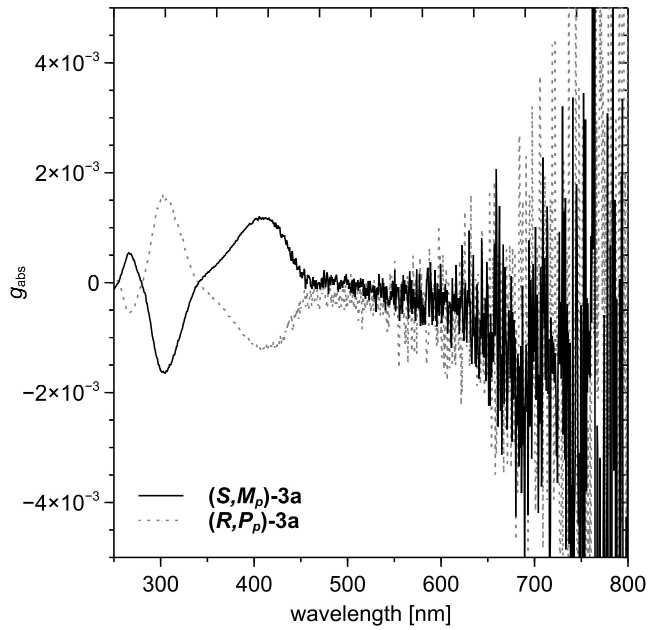


Figure S24. Absorption dissymmetry factor (**g$_{abs}$**) spectra of ***(S,M$_p$)*-3a** (black solid lines) and ***(R,P$_p$)*-3a** (black dotted lines) recorded in DCM (~10^{-6} M) at 298 K.

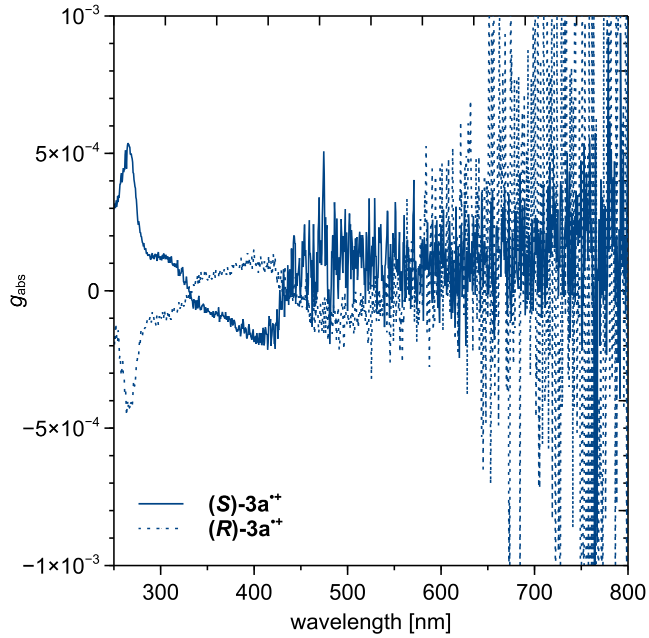


Figure S25. Absorption dissymmetry factor (**g$_{abs}$**) spectra of ***(S)*-3a$^{•+}$** (blue solid lines) and ***(R)*-3a$^{•+}$** (blue dotted lines) recorded in DCM (~10^{-6} M) at 298 K.

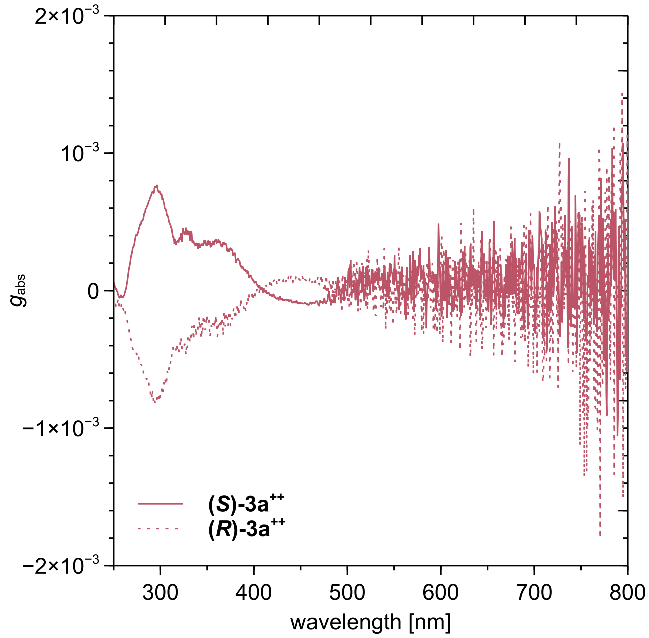


Figure S26. Absorption dissymmetry factor ($\mathbf{g_{abs}}$) spectra of ***(S)*-3a^{++}** (red solid lines) and ***(R)*-3a^{++}** (red dotted lines) recorded in DCM (~10^{-6} M) at 298 K.

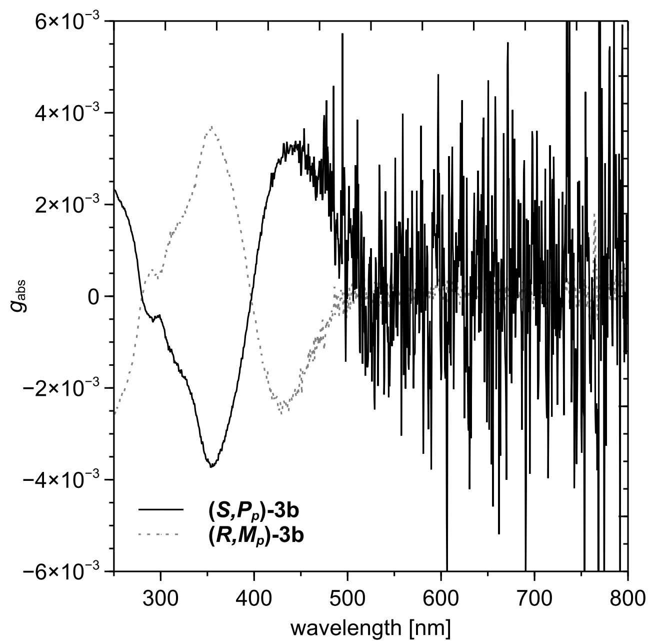


Figure S27. Absorption dissymmetry factor ($\mathbf{g_{abs}}$) spectra of ***(S,P$_p$)*-3b** (black solid lines) and ***(R,M$_p$)*-3b** (black dotted lines) recorded in DCM (~10^{-6} M) at 298 K.

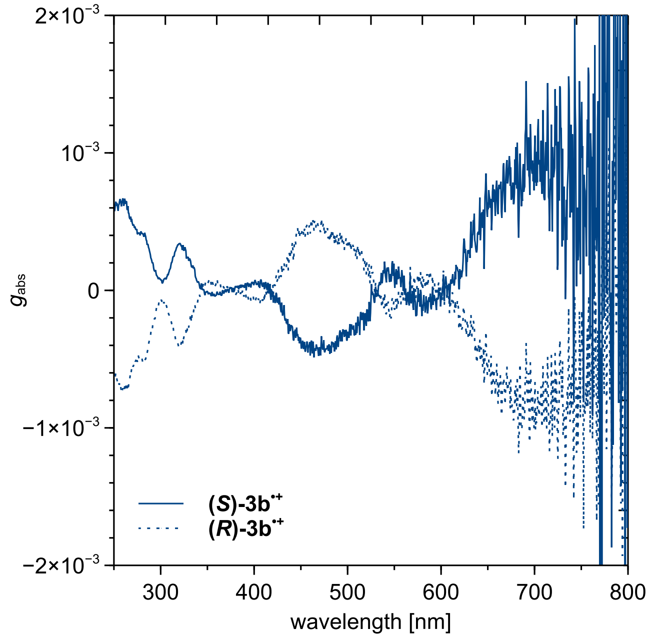


Figure S28. Absorption dissymmetry factor (**g_{abs}**) spectra of ***(S)*-3b$^{\bullet+}$** (blue solid lines) and ***(R)*-3b$^{\bullet+}$** (blue dotted lines) recorded in DCM (~10^{-6} M) at 298 K.

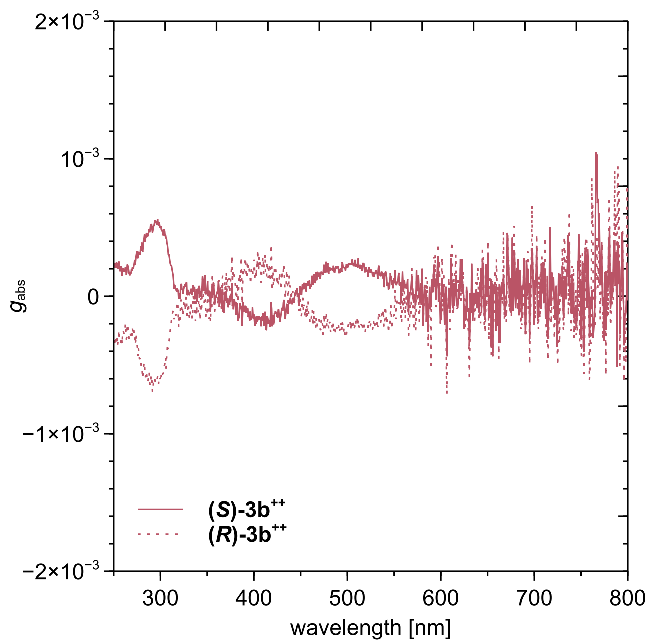
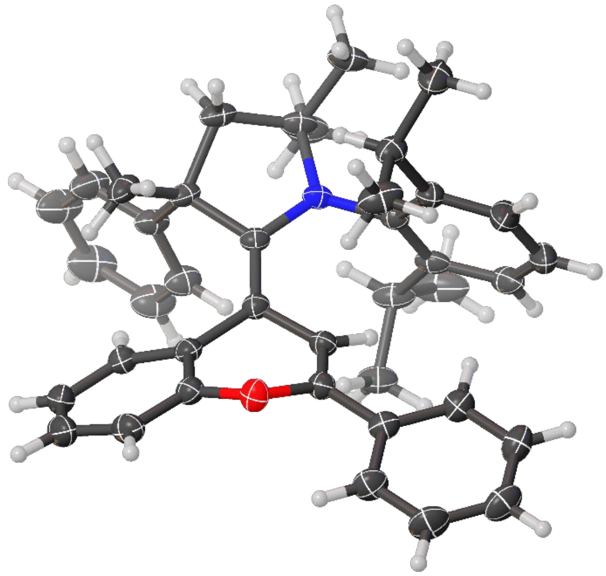


Figure S29. Absorption dissymmetry factor (**g_{abs}**) spectra of ***(S)*-3b^{++}** (red solid lines) and ***(R)*-3b^{++}** (red dotted lines) recorded in DCM (~10^{-6} M) at 298 K.

8) XRD Analysis

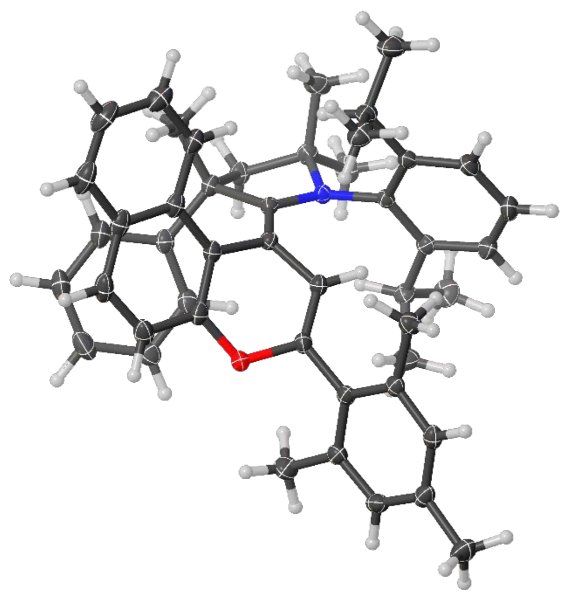


Crystal data and structure refinement features for *rac*-3a

CCDC Deposition Number	2488689
Empirical formula	$C_{40}H_{43}NO$
Formula weight	553.75
Temperature	100
Radiation type	Mo-Kα (λ = 0.71073 Å)
Crystal system	monoclinic
Space group	P-21/c
a (Å)	9.8476(4)
b (Å)	16.5956(6)
c (Å)	19.5216(7)
α (°)	90
β (°)	97.4790(10)
γ (°)	90
Volume ($Å^3$)	3163.2(2)
Z	4
ρ_{calc} (g/cm^3)	1.163
μ (mm^{-1})	0.068
F(000)	1192.0
Crystal size (mm)	0.1 x 0.1 x 0.1
Crystal color	yellow
Crystal description	prism
2Θ range for data collection (°)	4.84 to 59.22
Index ranges	$-13 \le h \le 13$, $-21 \le k \le 21$, $-27 \le l \le 26$
Reflections collected	42468
Unique reflections	8603 [R_{int} = 0.0976]
Data / restraints / parameters	8603 / 0 / 386

Goodness-of-fit	1.003
Final R indices [I ≥ 2σ (I)]	R_1 = 0.0542, wR_2 = 0.1102
Final R indices [all data]	R_1 = 0.1324, wR_2 = 0.1413
Largest diff. hole and peak e•Å^{-3}	-0.22 and 0.20

-

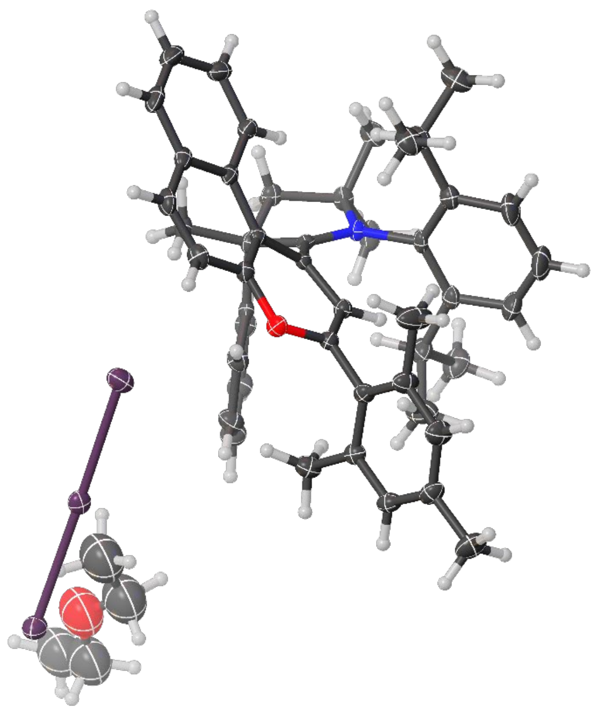


Crystal data and structure refinement features for *rac*-3b

CCDC Deposition Number	2488690
Empirical formula	$C_{47}H_{51}NO$
Formula weight	645.89
Temperature	150(2) K
Radiation type	Mo-Kα (λ = 0.71073 Å)
Crystal system	monoclinic
Space group	P-21/c
a (Å)	16.8363(18)
b (Å)	10.7483(12)
c (Å)	20.356(2)
α (°)	90
β (°)	98.788(4)
γ (°)	90
Volume (Å^3)	3640.4(7)
Z	4
ρ_{calc} (g/cm^3)	1.178
μ (mm^{-1})	0.069

F(000)	1392
Crystal size (mm)	0.27 x 0.21 x 0.14
Crystal color	yellow
Crystal description	prism
2Θ range for data collection (°)	4.4 to 54.958
Index ranges	$-21 \le h \le 20$, $-13 \le k \le 13$, $-26 \le l \le 24$
Reflections collected	28155
Unique reflections	8307 [R_{int} = 0.0508]
Data / restraints / parameters	8307 / 0 / 452
Goodness-of-fit	1.040
Final R indices [I ≥ 2σ (I)]	R_1 = 0.0496, wR_2 = 0.1091
Final R indices [all data]	R_1 = 0.0654, wR_2 = 0.1170
Largest diff. hole and peak e•Å^{-3}	-0.21 and 0.26

-

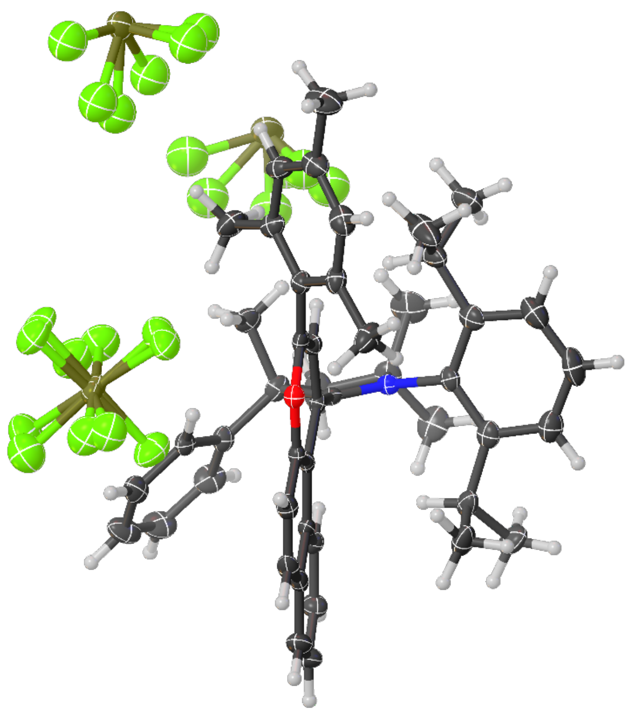


Crystal data and structure refinement features for *rac*-3b$^{\bullet+}$

CCDC Deposition Number	2488692
Empirical formula	$C_{98}H_{112}I_6N_2O_3$
Formula weight	2127.29
Temperature	150(2) K
Radiation type	Mo-Kα (λ = 0.71073 Å)
Crystal system	triclinic
Space group	P-1
a (Å)	10.7490(12)
b (Å)	13.7879(14)

c (Å)	16.0621(16)
α (°)	78.407(3)
β (°)	75.739(3)
γ (°)	89.266(4)
Volume (Å^3)	2258.4(4)
Z	1
ρ_{calc} (g/cm^3)	1.564
μ (mm^{-1})	2.113
F(000)	1056
Crystal size (mm)	0.13 x 0.2 x 0.28
Crystal color	black
Crystal description	prism
2Θ range for data collection (°)	3.912 to 51.362
Index ranges	-13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -17 ≤ l ≤ 19
Reflections collected	30649
Unique reflections	8547 [R(int) = 0.0286]
Data / restraints / parameters	8547 / 38 / 500
Goodness-of-fit	1.041
Final R indices [I ≥ 2σ (I)]	R_1 = 0.0304, wR_2 = 0.0746
Final R indices [all data]	R_1 = 0.0358, wR_2 = 0.0803
Largest diff. hole and peak e•Å^{-3}	-1.37 and 2.43

-



Crystal data and structure refinement features for [*rac*-3b^{++}][SbF$_6$]$_2$

CCDC Deposition Number	2488693
Empirical formula	$C_{47}H_{51}F_{12}NOSb_2$
Formula weight	1117.39

Temperature	150(2) K
Radiation type	Mo-Kα (λ = 0.71073 Å)
Crystal system	triclinic
Space group	P-1
a (Å)	9.6256(10)
b (Å)	11.6000(13)
c (Å)	22.777(3)
α (°)	86.362(4)
β (°)	78.497(4)
γ (°)	75.573(4)
Volume ($Å^3$)	2413.3(5)
Z	2
ρ_{calc} (g/cm^3)	1.538
μ (mm^{-1})	1.200
F(000)	1116
Crystal size (mm)	0.23 x 0.2 x 0.05
Crystal color	orange
Crystal description	prism
2Θ range for data collection (°)	4.036 to 51.362
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 14, -27 ≤ l ≤ 27
Reflections collected	33009
Unique reflections	9156 [R_{int} = 0.0455; R_{sigma} = 0.0430]
Data / restraints / parameters	9156 / 293 / 641
Goodness-of-fit	1.051
Final R indices [I ≥ 2σ (I)]	R_1 = 0.0726, wR_2 = 0.1934
Final R indices [all data]	R_1 = 0.0849, wR_2 = 0.2038
Largest diff. hole and peak $e•Å^{-3}$	-2.71 and 3.71

-

9) Computational Section

Computational Methods

All calculations were performed using Orca 6.0.1.[6] Unless stated otherwise, all default parameters were used. For all calculations, options DefGrid2 and TightSCF were employed. All calculations using the Global Optimizer Algorithm (GOAT), as implemented in ORCA, used Grimme's semi-empirical GFN2-XTB[7] method for downhill steps and the GFN-FF[8] method for uphill steps, with the ALPB solvation model.[9] Minima and transition states were verified by the presence of zero or one imaginary vibrational mode, respectively. Final reported Gibbs free energies were obtained by adding the Gibbs free energy minus the electronic energy from frequency calculations to the relevant single point electronic energies. Cartesian coordinates (Å), canonical orbitals, spin surfaces, and transition densities were visualized using ChemCraft. For consistency, all molecules are presented with the stereogenic carbon center of the ^{Chi}CAAC fragment in the ***(S)*** configuration.

Hyperfine coupling constants were assessed at the PBE0/N07D/CPCM(DCM)[10,11] level of theory using geometries for the lowest energy conformer of a given absolute configuration. N07D is a modified 6-31G basis set specifically designed for modeling radicals.[12,13] Spin-orbit coupling (SOC) was treated using the spin-orbit mean-field (SOMF(1X)) approach,[14] with the resolution of identity (RI) used to approximate the Coulombic portion;[15] the necessary auxiliary basis set was automatically generated.[16] Cubes for the total spin density were generated in ChemCraft.

Simplified TD-DFT (sTD-DFT)[17,18] calculations were performed using the ωB97x-D3[19] and CAM-B3LYP[20] functionals, as well as the def2-TZVPP[21] basis set and CPCM solvation with parameters for DCM. Further, the RIJCOSX approximation was employed,[22,23] using the def2/J auxiliary basis set.[24] Ultimately, the CAM-B3LYP functional was determined to be in best agreement with the experimental data (Figures S34 – S35), yet both approaches are in qualitative agreement with the experiment and reproduced the shapes of the experimental spectra. Spectral convolution was performed in ChemCraft.

Full TD-DFT calculations, *without* the Tamm-Dancoff approximation, were performed using the CAM-B3LYP functional, maintaining other parameters for the level of theory as in the sTD-DFT calculations. Transition density cube files were generated with orca_plot using a grid interval of 120. From these calculations, the transition electric- ($|\mu|$) and transition magnetic ($|m|$) dipole moment vector norms, the angle between the corresponding vectors (θ), and ultimately the dissymmetry factors (g_{abs}), were calculated as described in much detail by Kubo *et al*.[25] Specifically, g_{abs} was calculated according to equation S1.

$g_{\mathrm{abs}} = \frac{4\cos\theta_{\mu,m}\,|\mu||m|}{|\mu|^2+|m|^2}$ (equation S1)

With: 1 a.u. = 2.54×10^{-18} cgs (electric dipole) (equation S2)

And: 1 a.u. = 1.857×10^{-20} cgs (magnetic dipole) (equation S3)

All output files are available for download, free of charge, from the UCSD Library Digital Collections.[26]

To generate conformational ensembles for **3a-b** and the respective radical cations and dications, a multistep computational workflow was applied, an adaptation of the *CREST/CENSO* workflow developed by Grimme and coworkers.[27]

Step 1: For each stereoisomer, an initial conformational ensemble was generated using GOAT.

Step 2: The electronic energies of these conformers were re-evaluated at the r^2SCAN-3c/CPCM(DCM) level of theory.[28] For each stereoisomer, all conformers with an electronic energy 3 kcal/mol or greater than the minimum were excluded.

Step 3: Geometries were reoptimized at the r^2SCAN-3c/CPCM(DCM) level of theory.

Step 4: Thermostatistical corrections to the electronic energies were obtained by a reoptimization and frequency calculation at the GFN2-XTB level of theory with the ALPB solvation model for DCM.

Step 5: Final Gibbs free energies were obtained by recalculating the electronic energies at the ωB97X-V/def2-mTZVPP/SMD(DCM) level of theory using Step 3 geometries.[29] Thermostatistical corrections obtained from Step 4 were applied to the resulting electronic energies.

Step 6: Using the Gibbs free energies obtained in Step 5, the Boltzmann populations for each conformer were obtained, assuming no kinetic barriers between states. States associated with an imaginary frequency from Step 4 were excluded.

The workflow is represented graphically in Figure S30. The resulting data are tabulated in Table S4. Select cartesian coordinates, specifically the lowest energy conformer for a given absolute configuration, for each compound, are provided in “Cartesian Coordinates.”

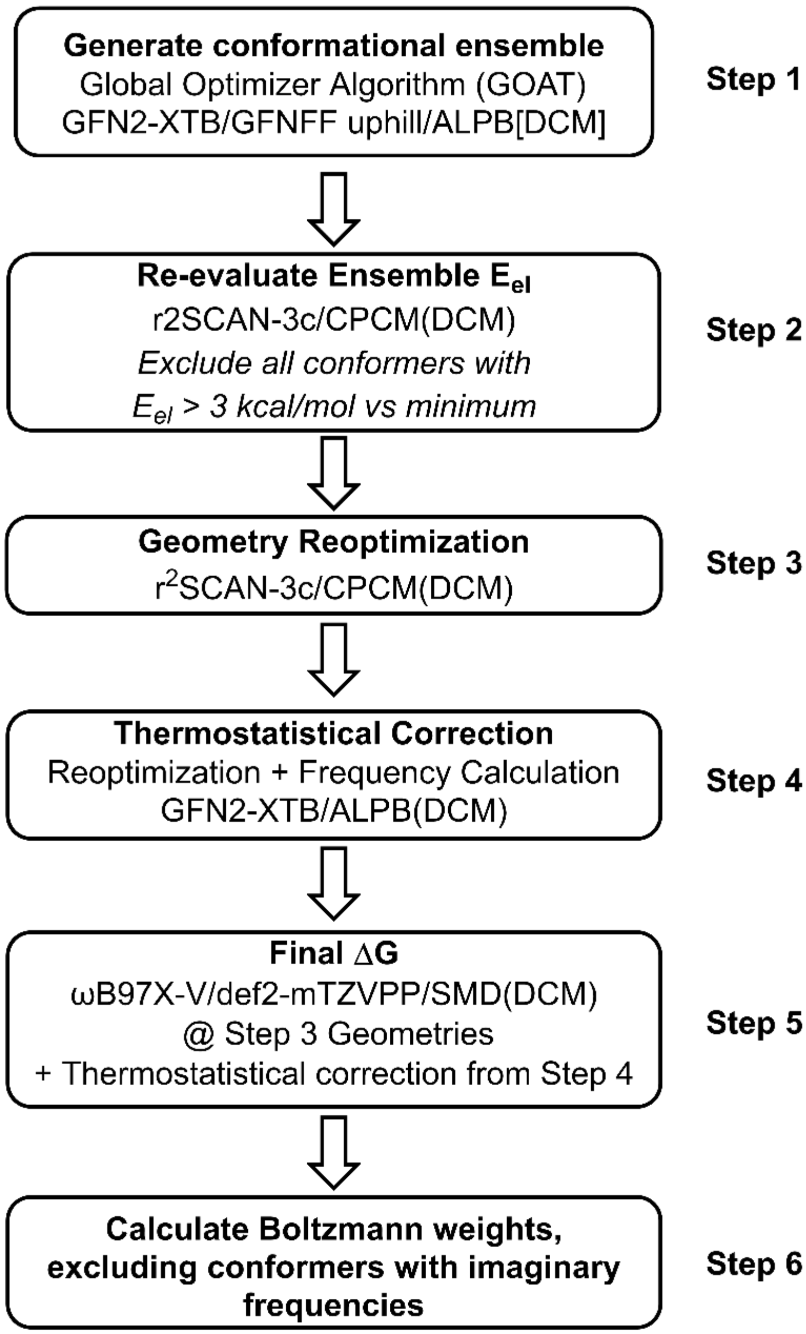


Figure S30. Graphical depiction of computational workflow for modeling the conformation ensembles of **3a-b** and the respective radical cations and dications.

To assess the barriers for atropisomerization, the following workflow was applied.

Step 1: For a given pair of stereoisomers, initial relaxed coordinate scans were performed at the GFN2-XTB/ALPB(DCM) level of theory along key torsion angles which affected epimerization in both directions.

Step 2: The electronic energies for the coordinate scans from Step 1 were reevaluated at the r^2SCAN-3c/CPCM(DCM) level of theory.

Step 3: Relaxed coordinate scans with fine intervals (step = 1°) were performed across the highest "peak" of each coordinate scan r^2SCAN-3c/CPCM(DCM).

Step 4: Frequency calculations at the r^2SCAN-3c/CPCM(DCM) level of theory were performed for the highest energy conformation from Step 3, verifying the presence of a single imaginary mode.

Step 5: In the case of a transition state (one imaginary mode), final Gibbs free energies were obtained by recalculating the electronic energy at the ωB97X-V/def2-mTZVPP/SMD(DCM) level of theory. To the resulting electronic energy, the thermostatistical corrections obtained from Step 4 were applied. The true barrier was taken as the lowest barrier obtained from all coordinate scans, regardless of direction.[30]

Step 6: Thermostatistical corrections for the lowest energy conformers of each stereoisomer were reassessed at the r^2SCAN-3c/CPCM(DCM), then used to calculate the final Gibbs free energies as in Step 5.

The workflow is represented graphically in Figure S31. The resulting data are tabulated in Table S5. Cartesian coordinates for the minima and transition states are provided in "Cartesian Coordinates"

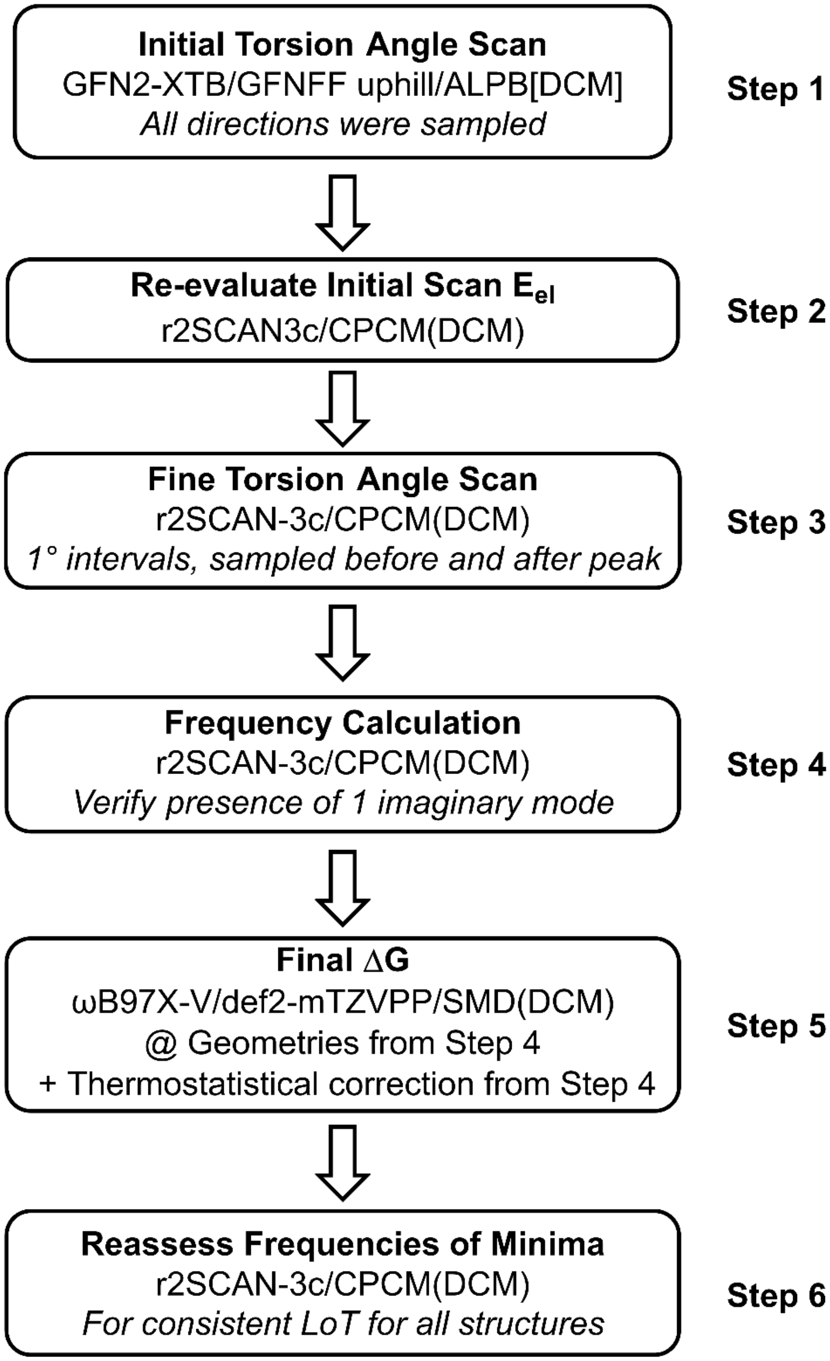


Figure S31. Graphical depiction of computational workflow for obtaining the barriers to atropisomerization of **3a, 3b**, and the respective radical cations and dications.

Conformational Ensembles

Table S4. Gibbs free energy and Boltzmann weight for conformers of all compounds.

Compound	Conf. #	AbsConfig	E(el) (H) Step 5	G-E(el) (H) Step 4	G (H) Step 5	Boltzmann Weight
3a	1	S,Mp	-1680.252043	0.647216	-1679.604827	0.87048716
	2	S,Pp	-1680.249461	0.647607	-1679.601854	0.03808033
	3	S,Pp	-1680.249202	0.647278	-1679.601924	0.04097865
	4	S,Pp	-1680.249929	0.647808	-1679.602121	0.05045387
					M-plane	0.87048716
					P-plane	0.12951284
3a+	1	S,Mp	-1680.088784	0.647730	-1679.441055	0.06867850
	2	S,Mp	-1680.088321	0.647794	-1679.440527	0.03939043
	3	S,Pp	-1680.088212	0.648057	-1679.440155	0.02663822
	4	S,Pp	-1680.090191	0.647497	-1679.442694	0.38579619
	5	S,Mp	-1680.088049	0.647480	-1679.440569	0.04120685
	6	S,Mp	-1680.089056	0.646919	-1679.442137	0.21466347
	7	S,Pp	-1680.089302	0.647701	-1679.441601	0.12205663
	8	S,Pp	-1680.088578	0.647229	-1679.441350	0.09367170
	9	S,Pp	-1680.085328	0.647546	-1679.437782	0.00219152
	10	S,Mp	-1680.084385	0.646854	-1679.437531	0.00168249
	11	S,Pp	-1680.086295	0.647936	-1679.438359	0.00402399
					M-plane	0.36562174
					P-plane	0.63437826
3a++	1	S,Ma	-1679.911895	0.647284	-1679.264610	0.23081752
	2	S,Ma	-1679.910493	0.646964	-1679.263529	0.07395955
	3	S,Pa	-1679.909160	0.647418	-1679.261742	0.01127160
	4	S,Pa	-1679.909507	0.648138	-1679.261369	0.00761509
	5	S,Ma	-1679.908827	0.646814	-1679.262013	0.01499334
	6	S,Pa	-1679.913292	0.647961	-1679.265331	0.49293156
	7	S,Pa	-1679.909253	0.646610	-1679.262643	0.02911028
	8	S,Ma	-1679.910631	0.646501	-1679.264131	0.13930105
					M-axis	0.45907146
					P-axis	0.54092854
3b	1	S,Pp	-1951.851480	-133.747486	-2085.598966	0.99651838
	2	S,Pp	-1951.848973	-133.744618	-2085.593591	0.00347793
	3	S,Mp	-1951.843412	-133.743096	-2085.586508	0.00000201
	4	S,Mp	-1951.843625	-133.742558	-2085.586183	0.00000143
	5	S,Mp	-1951.841652	-133.741139	-2085.582790	0.00000004
	6	S,Mp	-1951.844429	-133.739951	-2085.584380	0.00000021

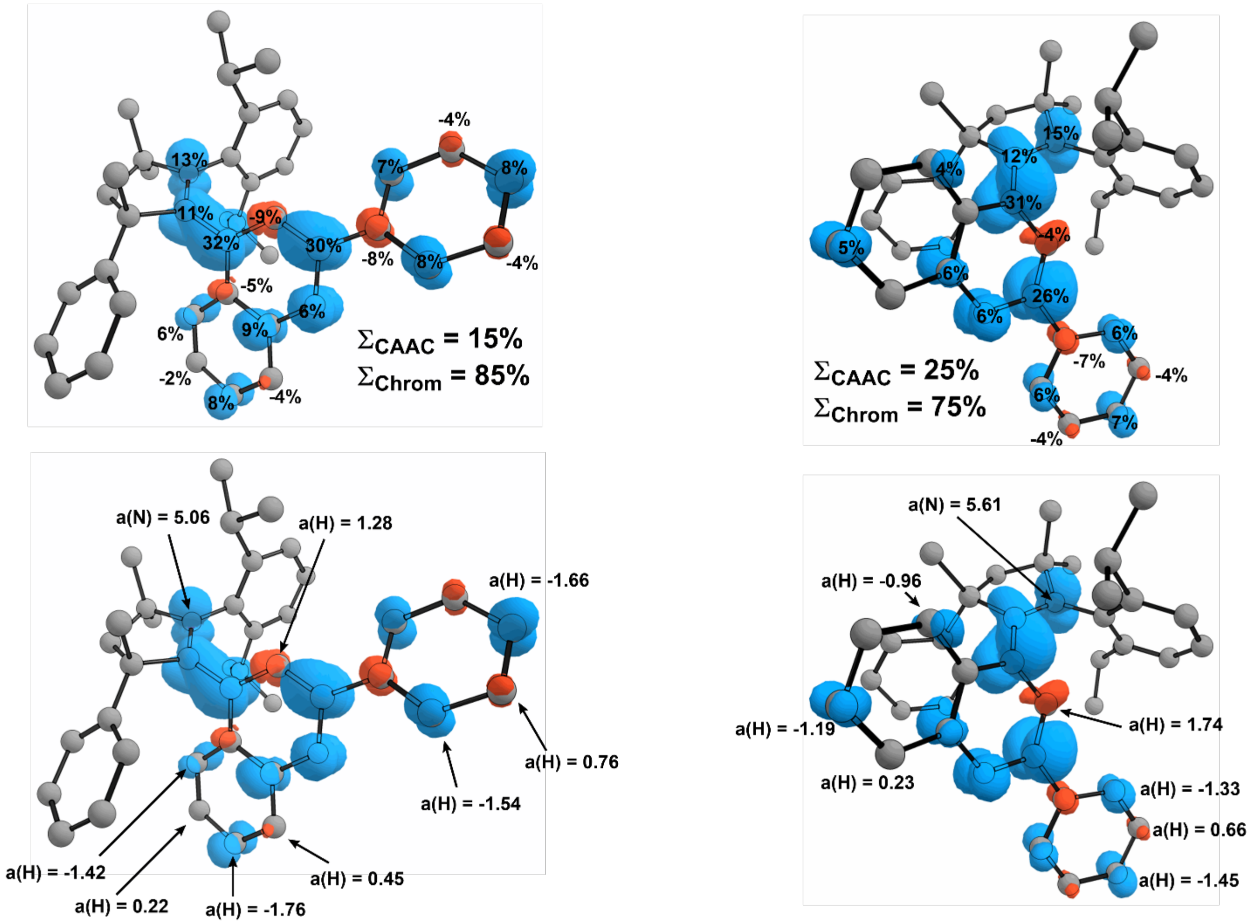
					M-plane	0.00000369
					P-plane	0.99999631
3b+	**1**	**S,Pp**	-1951.693383	-133.408642	-2085.102025	0.66832672
	2	**S,Mp**	-1951.692081	-133.407928	-2085.100009	0.08002500
	3	**S,Pp**	-1951.693420	-133.407671	-2085.101091	0.24998100
	4	**S,Mp**	-1951.689370	-133.406961	-2085.096331	0.00166729
					M-plane	0.08169228
					P-plane	0.91830772
3b++	**1**	**S,Ma**	-1951.517085	-133.034219	-2084.551304	0.99973615
	2	**S,Pa**	-1951.511360	-133.031853	-2084.543213	0.00020016
	3	**S,Pa**	-1951.511879	-133.028895	-2084.540774	0.00001536
	4	**S,Pa**	-1951.509898	-133.027801	-2084.537700	0.00000060
	5	**S,Pa**	-1951.512282	-133.028825	-2084.541107	0.00002181
	6	**S,Pa**	-1951.512372	-133.028899	-2084.541271	0.00002592
					M-axis	0.99973615
					P-axis	0.00026385

Atropisomerization Barriers

Table S5. Absolute contributions to the Gibbs free energies for assessing barriers to atropisomerization

Structure	E_{el} (H)	H (H)	-T*S (H)	G (H)	G-E_{el} (H)	v (cm^{-1})	E_{el} SPC (H)	G_{final}	G_{rel} (kcal/mol)
(S,M_p)-3a	-1679.742536	-1678.981026	-0.100318	-1679.081343	0.661193	17.46	-1680.252043	-1679.590850	0.00
TS-3a	-1679.729697	-1678.969400	-0.099009	-1679.068409	0.661288	-21.46	-1680.241259	-1679.579971	6.83
(S,P_p)- 3a	-1679.739012	-1678.977398	-0.100596	-1679.077994	0.661019	11.65	-1680.249852	-1679.588834	1.27
(S,M_p)- 3a$^{\bullet+}$	-1679.579736	-1678.816601	-0.100874	-1678.917475	0.662261	21.52	-1680.089056	-1679.426795	0.42
TS-3a$^{\bullet+}$	-1679.568758	-1678.806770	-0.099858	-1678.906628	0.662130	-27.03	-1680.081964	-1679.419834	4.79
(S,P_p)- 3a$^{\bullet+}$	-1679.580798	-1678.817148	-0.100928	-1678.918076	0.662722	13.29	-1680.090191	-1679.427470	0.00
(S,M_a)- 3a^{++}	-1679.395757	-1678.630093	-0.099534	-1678.729627	0.666131	16.96	-1679.911895	-1679.245764	0.82
TS-3a^{++}	-1679.366582	-1678.602462	-0.097365	-1678.699827	0.666754	-13.93	-1679.876979	-1679.210225	23.12
(S,P_a)- 3a^{++}	-1679.396622	-1678.630868	-0.099526	-1678.730394	0.666229	17.3	-1679.913292	-1679.247063	0.00
(S,M_p)-3b	-1951.246496	-1950.349020	-0.113592	-1950.462612	0.783883	21.84	-1951.843411	-1951.059528	5.10
TS-3b	-1951.211025	-1950.314847	-0.112226	-1950.427073	0.783953	-28.56	-1951.799073	-1951.015121	32.96
(S,P_p)- 3b	-1951.254727	-1950.357190	-0.113708	-1950.470898	0.783829	22.74	-1951.851480	-1951.067651	0.00
(S,M_p)- 3b$^{\bullet+}$	-1951.097672	-1950.198627	-0.115155	-1950.313782	0.783891	22.13	-1951.692081	-1950.908190	0.29
TS-3b$^{\bullet+}$	-1951.061217	-1950.162757	-0.113159	-1950.275916	0.785301	-28.63	-1951.658876	-1950.873575	21.72
(S,P_p)- 3b$^{\bullet+}$	-1951.099564	-1950.200185	-0.114650	-1950.314835	0.784729	18.17	-1951.693383	-1950.908654	0.00
(S,M_a)- 3b^{++}	-1950.917323	-1950.015846	-0.113068	-1950.128914	0.788409	20.29	-1951.517085	-1950.728676	0.00
TS-3b^{++}	-1950.875665	-1949.975983	-0.110781	-1950.086764	0.788901	-5.73	-1951.467311	-1950.678410	31.54
(S,P_a)- 3b^{++}	-1950.912127	-1950.011417	-0.113977	-1950.125393	0.786734	16.13	-1951.511360	-1950.724626	2.54

Hyperfine Coupling Constants and Spin Densities



***(S,M$_p$)*-3a$^{•+}$** ***(S,P$_p$)*-3a$^{•+}$**

Figure S32. Comparison of total spin density surfaces, Mulliken spin densities, and hyperfine coupling constants (Gauss) for atropisomers of **3a$^{•+}$.**

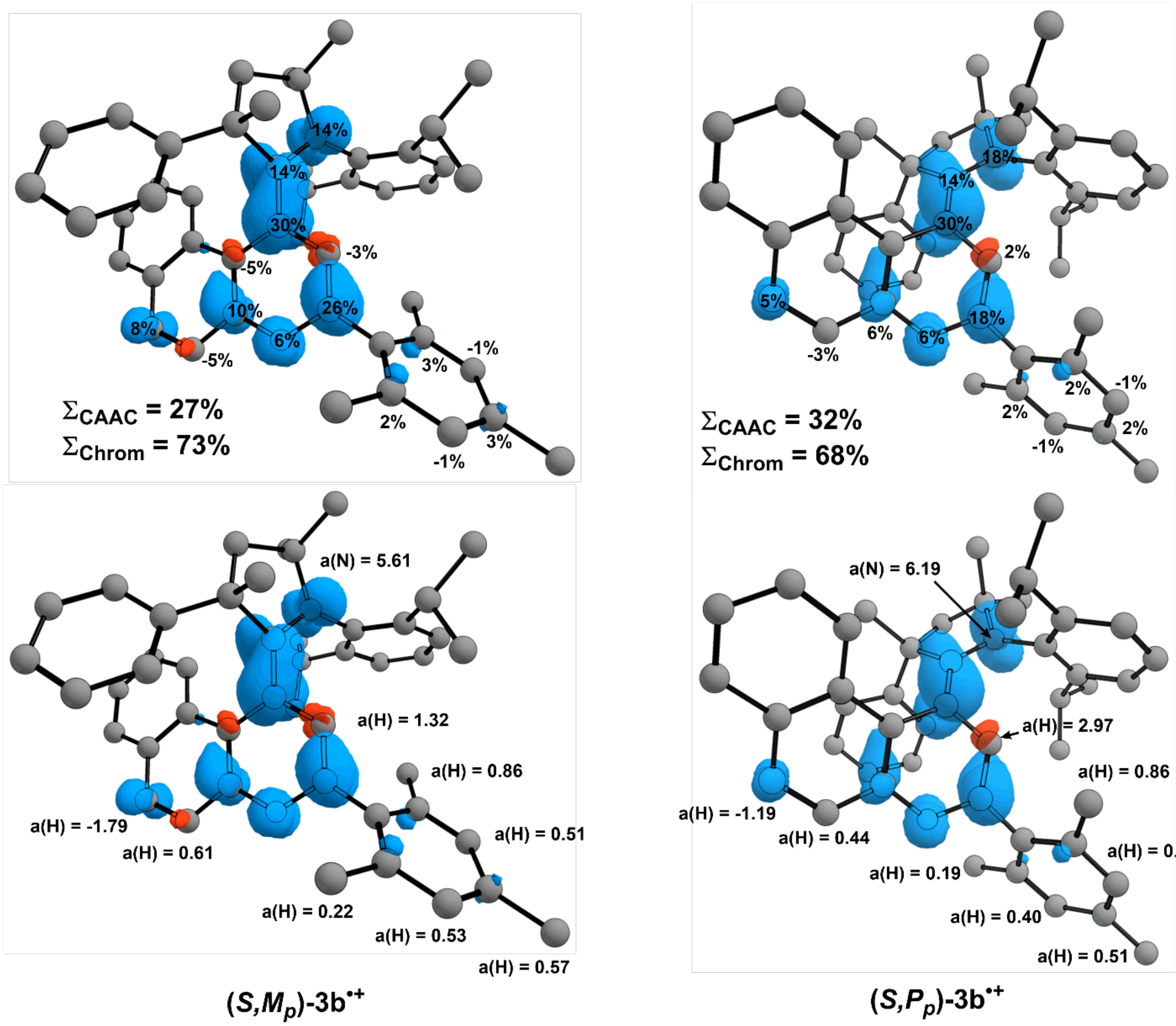


Figure S33. Comparison of total spin density surfaces, Mulliken spin densities, and hyperfine coupling constants (Gauss) for atropisomers of **3b•+**.

TD-DFT Calculations

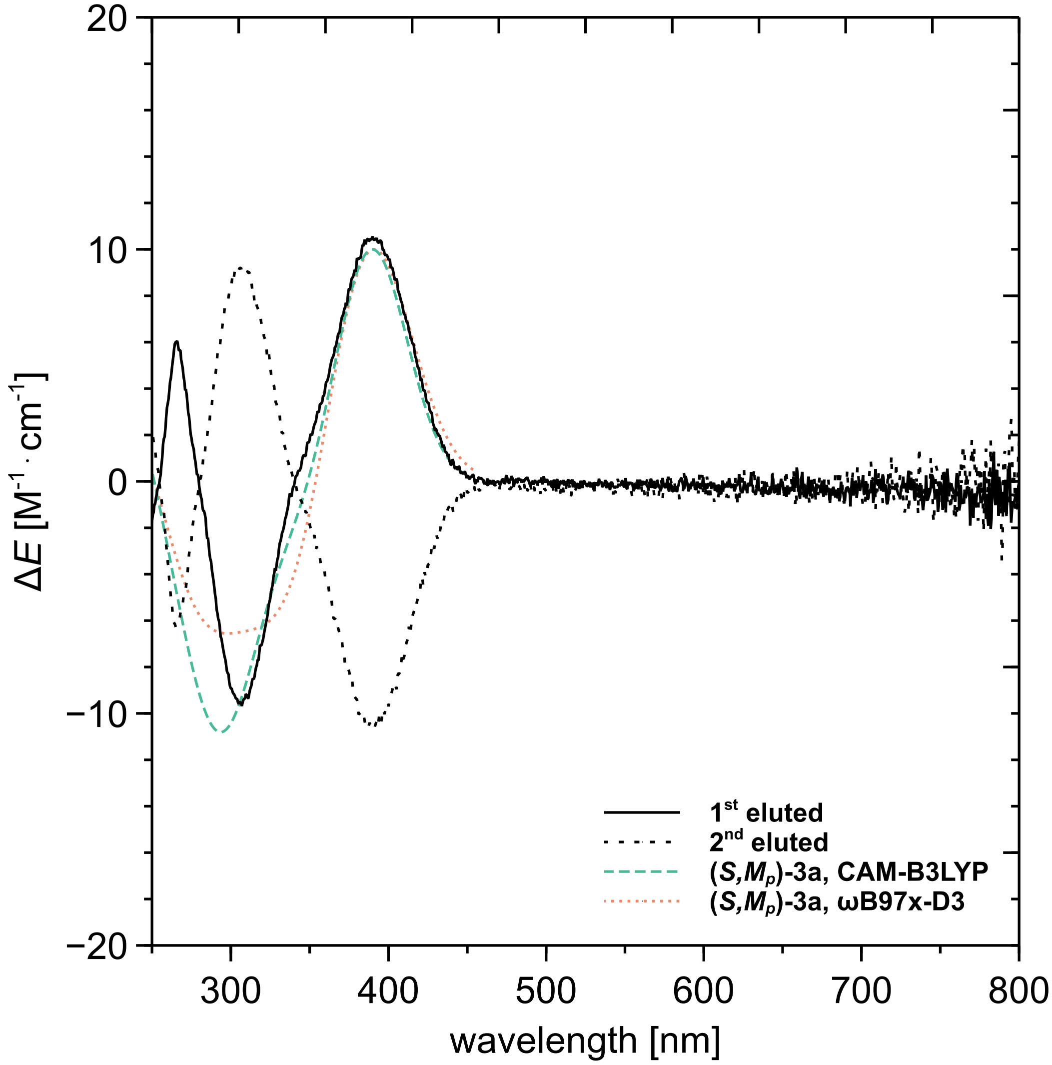


Figure S34. Comparison of experimental CD spectra (black, solid and dotted) of chiral HPLC products with computed spectra (Gaussian broadening, FWHM = 50 nm) for (***S,M$_p$***)**-3a**. Relative intensities (ΔE) are adjusted for clarity. Computed data obtained using CAM-B3LYP (green, large dash) are offset by −800 cm^{-1}, while computed data obtained using ωB97X-D3 (orange, small dash) are offset by -2900 cm^{-1}.

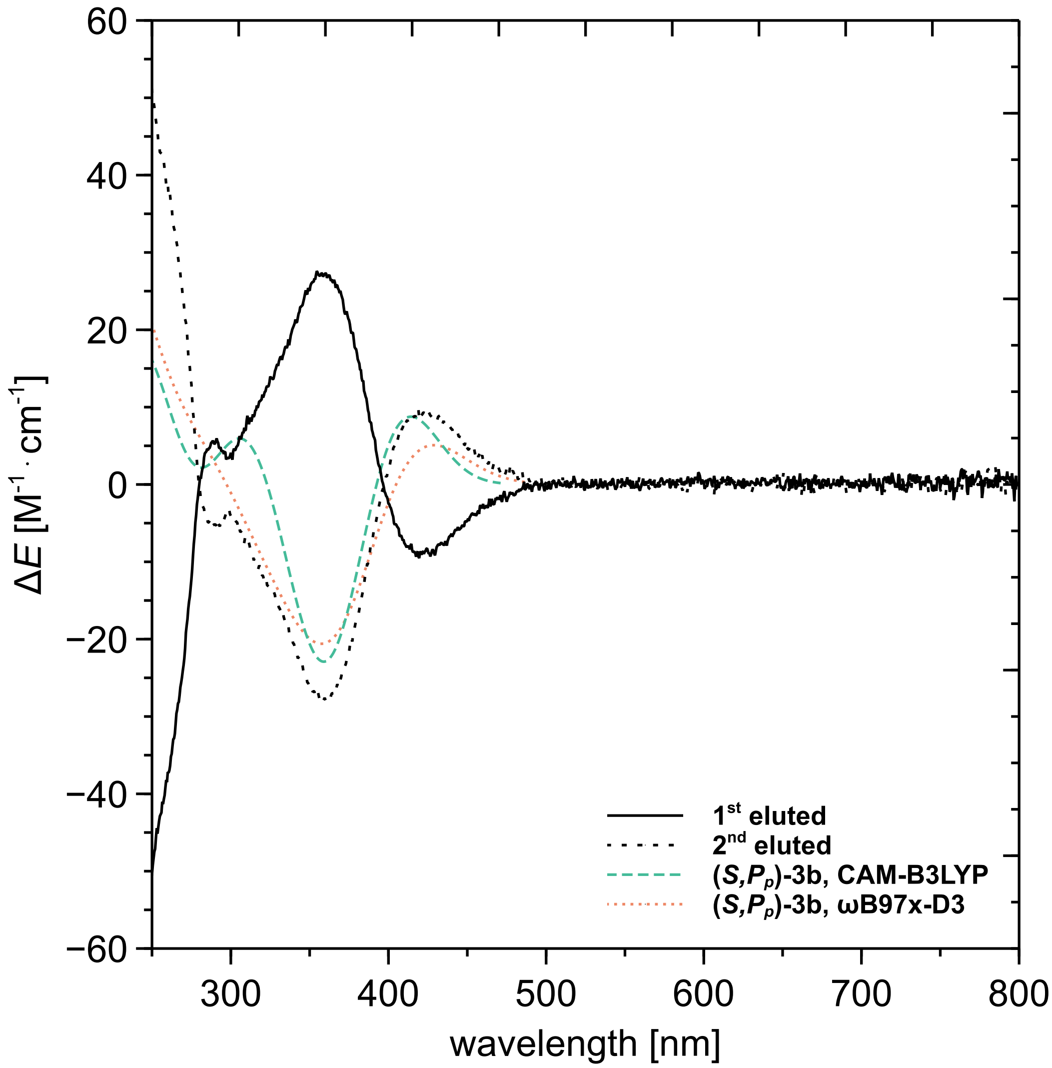


Figure S35. Comparison of experimental CD spectra (black, solid and dotted) of chiral HPLC products with computed spectra (Gaussian broadening, FWHM = 50 nm) for (***S,P$_p$***)**-3b**. Relative intensities (ΔE) are adjusted for clarity. Computed data obtained using CAM-B3LYP (green, large dash) are offset by -500 cm^{-1}, while computed data obtained using ωB97X-D3 (orange, small dash) are offset by -3500 cm^{-1}.

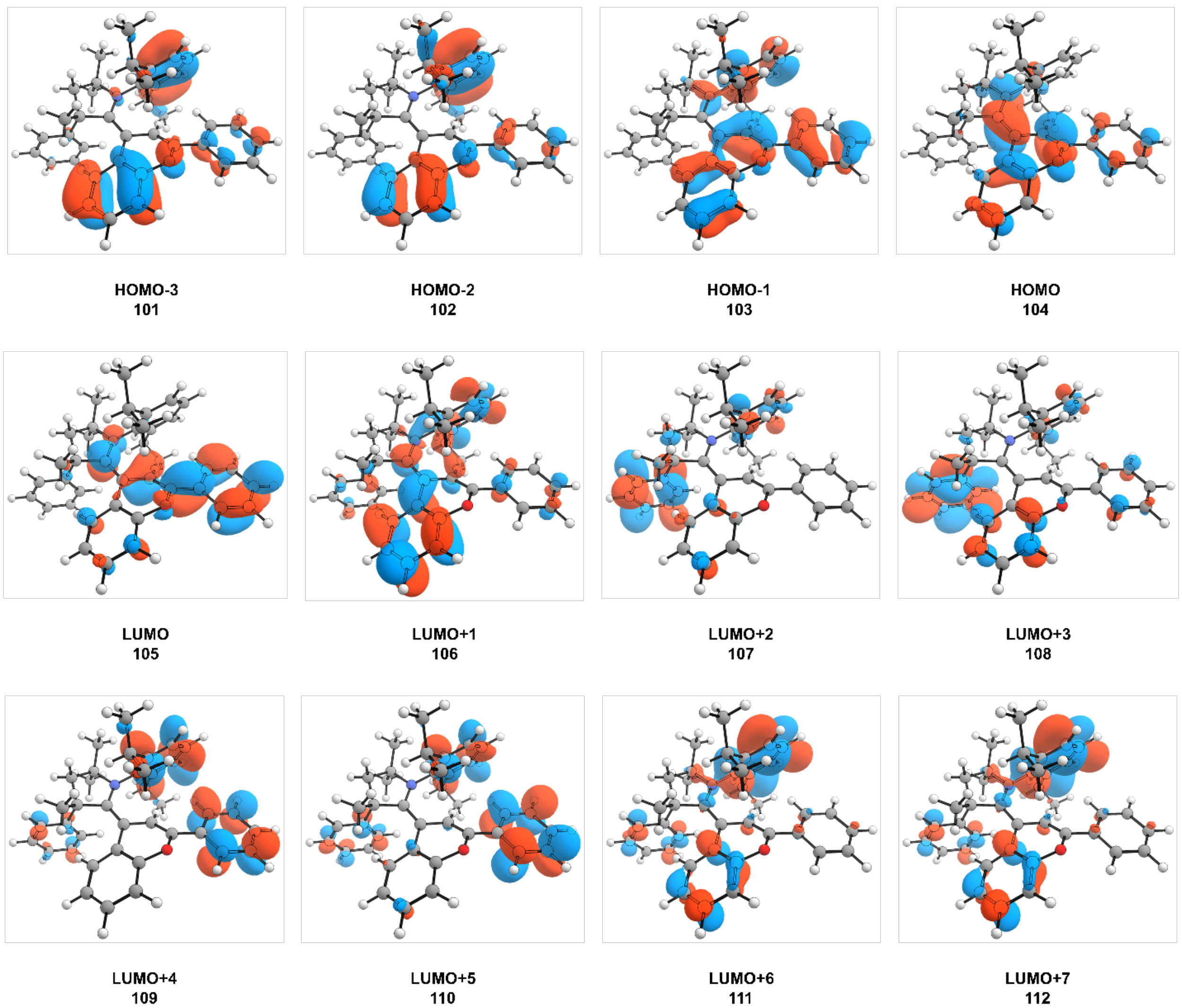


Figure S36. Canonical orbitals of **(*S*,*M*$_p$)-3a** obtained via sTD-DFT using the CAM-B3LYP functional

Transition	eV	nm	Amplitudes		
S1	3.287	377.2	0.92 (104-> 105)	0.04 (104-> 106)	0.01 (104-> 112)
S2	3.729	332.5	0.92 (104-> 106)	0.04 (104-> 105)	0.01 (104-> 114)
S3	4.086	303.4	0.44 (104-> 109)	0.34 (104-> 107)	0.15 (104-> 110)
S4	4.156	298.3	0.54 (104-> 108)	0.28 (104-> 111)	0.06 (104-> 107)
S5	4.255	291.4	0.24 (104-> 107)	0.24 (104-> 109)	0.24 (104-> 108)
S6	4.376	283.4	0.39 (104-> 111)	0.28 (104-> 107)	0.19 (104-> 110)
S7	4.389	282.5	0.52 (104-> 110)	0.25 (104-> 109)	0.07 (104-> 111)
S8	4.51	274.9	0.69 (104-> 112)	0.17 (104-> 108)	0.08 (104-> 111)
S9	4.932	251.4	0.96 (103-> 105)	0.00 (103-> 114)	0.00 (99-> 105)

Table S6. Nature of selected electronic transitions for **(*S*,*M*$_p$)-3a** obtained via sTD-DFT using the CAM-B3LYP functional

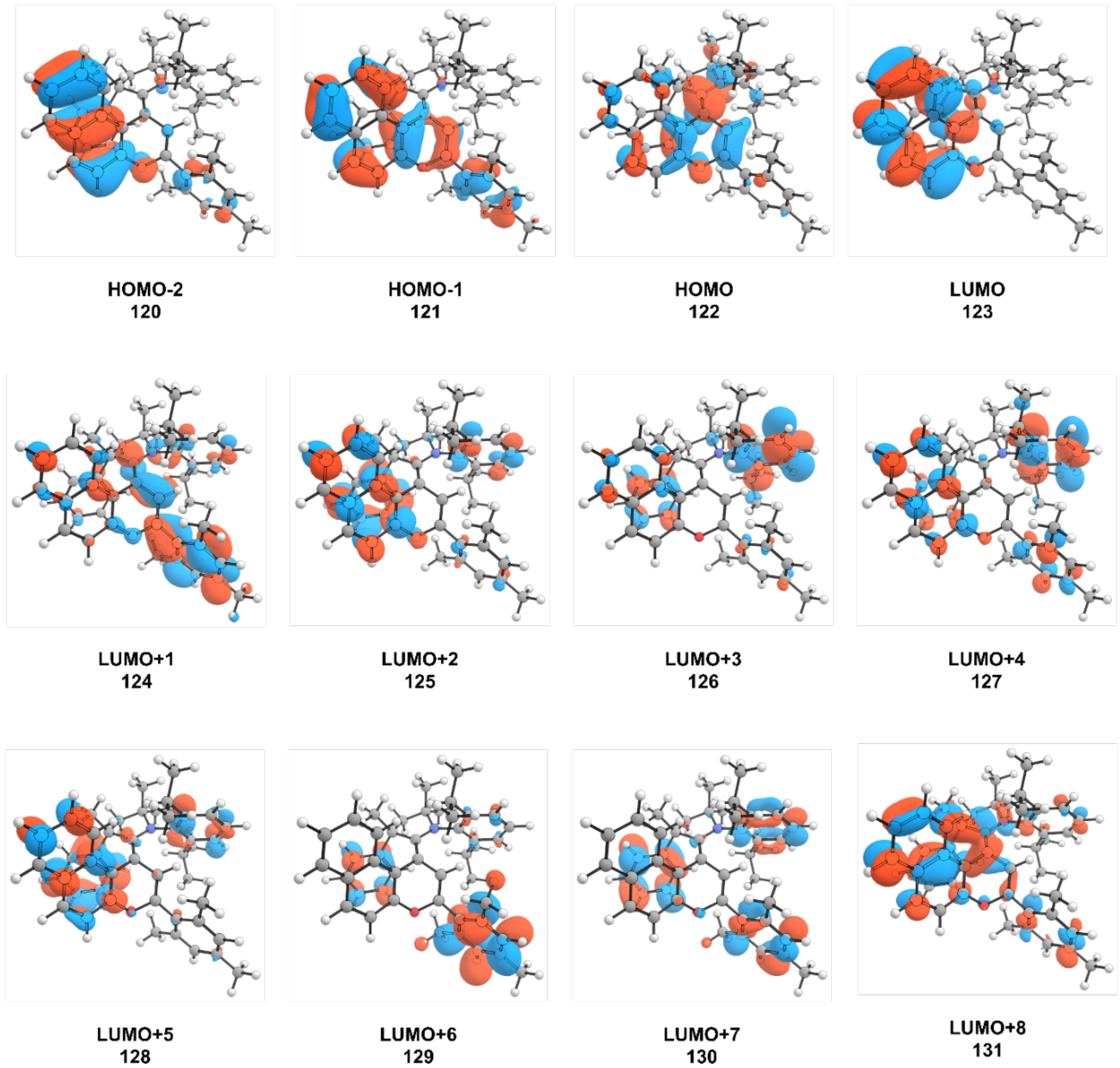


Figure S37. Canonical orbitals of **(*S*,$\boldsymbol{P_p}$)-3b** obtained via sTD-DFT using the CAM-B3LYP functional

Transition	eV	nm	Amplitudes		
S1	3.101	399.8	0.93 (122-> 123)	0.05 (122-> 124)	0.01 (122-> 134)
S2	3.507	353.6	0.91 (122-> 124)	0.04 (122-> 123)	0.01 (122-> 127)
S3	3.931	315.4	0.90 (122-> 125)	0.03 (120-> 123)	0.03 (122-> 126)
S4	4.101	302.3	0.88 (122-> 126)	0.07 (122-> 127)	0.02 (122-> 125)
S5	4.142	299.3	0.58 (122-> 127)	0.24 (122-> 128)	0.06 (120-> 123)
S6	4.164	297.8	0.69 (122-> 128)	0.24 (122-> 127)	0.02 (122-> 129)
S7	4.358	284.5	0.68 (122-> 130)	0.18 (122-> 129)	0.07 (121-> 123)
S8	4.47	277.4	0.75 (121-> 123)	0.06 (122-> 129)	0.04 (122-> 130)
S9	4.517	274.5	0.65 (122-> 129)	0.22 (122-> 130)	0.03 (122-> 127)
S10	4.589	270.2	0.84 (122-> 131)	0.04 (121-> 124)	0.02 (122-> 134)
S11	4.712	263.1	0.42 (120-> 123)	0.11 (121-> 125)	0.09 (121-> 124)

Table S7. Nature of selected electronic transitions in **(*S*,$\boldsymbol{P_p}$)-3b** obtained via sTD-DFT using the CAM-B3LYP functional

Table S8. Transition energies (E), rotatory strengths (R), transition electric dipole moments (μ), transition magnetic dipole moments (m), the angle between these two vectors (θ), and the theoretical dissymmetry factors (g_{abs}) for the first four states obtained via TD-DFT calculations using the CAM-B3LYP functional.

Compound	State	E (eV)	E (cm^{-1})	λ (nm)	R (10^{-40} cgs)	μ_x (a.u.)	μ_y (a.u.)	μ_z (a.u.)	m_x (a.u.)	m_y (a.u.)	m_y (a.u.)	$\theta_{\mu,m}$ (°)	g_{abs}
(S,M_p)-3a	S1	3.390334	27344.9	365.7	116.56492	-1.49668	1.82179	0.01709	0.21688	0.04233	0.01389	118.2694	-0.0013
	S2	3.82939	30886.1	323.8	-24.13426	-0.64794	0.66339	-1.36415	0.27677	0.33226	-0.00741	85.88475	0.00055
	S3	4.334803	34962.5	286	6.46994	-0.21534	-0.02777	0.01375	0.0552	0.01742	-0.0984	123.5418	-0.00847
	S4	4.412152	35586.4	281	14.20285	-0.40487	0.3747	0.32051	0.31613	0.24839	0.01496	96.74004	-0.00216
(S,P_p)-3a$^{\bullet+}$	D1	2.294203	18504	540.4	-6.183	-0.78476	1.41522	-0.58353	0.04225	0.02373	-0.02173	81.7512	0.000129
	D2	2.717158	21915.4	456.3	-9.28767	0.36679	-1.32092	-0.26694	-0.33104	-0.09977	0.11262	92.22275	-0.00029
	D3	3.017292	24336.1	410.9	-9.02212	0.16756	-0.79667	-0.04445	0.01728	-0.0211	0.01272	38.73156	0.000841
	D4	3.089717	24920.3	401.3	-28.11756	0.09067	0.86058	1.0658	-0.13411	0.06415	0.01557	73.10413	0.000924
(S,P_a)-3a^{++}	S1	3.185394	25691.9	389.2	18.51664	1.87814	2.2383	-0.33872	0.05003	-0.13118	-0.47349	91.54933	-0.00013
	S2	3.532097	28488.3	351	-2.50839	0.35202	-0.00869	0.00231	0.01332	-0.05062	0.08339	81.17092	0.001253
	S3	3.590279	28957.6	345.3	-3.87974	0.07115	0.12887	0.04314	0.07974	-0.03567	0.1658	73.36568	0.010212
	S4	3.68746	29741.4	336.2	-3.69457	0.19256	-0.46192	-0.21191	-0.1178	0.01767	-0.18253	86.20785	0.000775
(S,P_p)-3b	S1	3.2843	26489.7	377.5	97.54772	0.48826	-0.08789	-1.06284	-0.19914	-0.45108	0.1405	110.1254	-0.00439
	S2	3.585589	28919.7	345.8	-243.08054	1.50635	0.32318	-0.89326	0.26201	0.17669	-0.07145	26.6696	0.004748
	S3	4.136262	33361.2	299.7	-24.5065	-0.73196	0.04979	-0.2413	-0.00961	0.33469	-0.11719	79.06402	0.002545
	S4	4.32852	34911.9	286.4	61.04354	0.78139	0.32932	0.16429	-0.0605	-0.15551	-0.18868	126.5258	-0.00507
(S,P_p)-3b$^{\bullet+}$	D1	2.295058	18510.9	540.2	5.69577	-0.37035	-0.37767	-1.0412	0.04357	0.30529	-0.11463	91.80205	-0.00026
	D2	2.452194	19778.3	505.6	9.87623	-1.07258	0.16025	1.0187	0.02038	0.013	-0.00115	125.5732	-0.00028
	D3	2.684708	21653.6	461.8	-60.65573	-0.80667	-0.48892	-0.61068	-0.11471	-0.08201	0.0065	35.79502	0.002976
	D4	2.942269	23731	421.4	-36.07463	-0.94683	-0.22457	-0.21246	-0.07843	-0.03646	0.02791	32.29481	0.002253
(S,M_a)-3b^{++}	S1	2.779537	22418.5	446.1	-2.41583	2.00602	0.78408	2.25753	-0.13925	0.53213	-0.05963	89.89124	9.83E-06
	S2	3.337907	26922	371.4	-2.56416	0.073	-0.36187	0.27254	-0.27803	0.19821	0.35387	88.8773	0.000613
	S3	3.358582	27088.8	369.2	-9.51193	-0.39448	-0.17061	-0.26206	-0.23756	0.25021	0.11237	83.21608	0.002487
	S4	3.634184	29311.7	341.2	-9.04586	0.51118	0.21455	0.03947	0.04872	-0.02827	0.01158	52.86085	0.001824

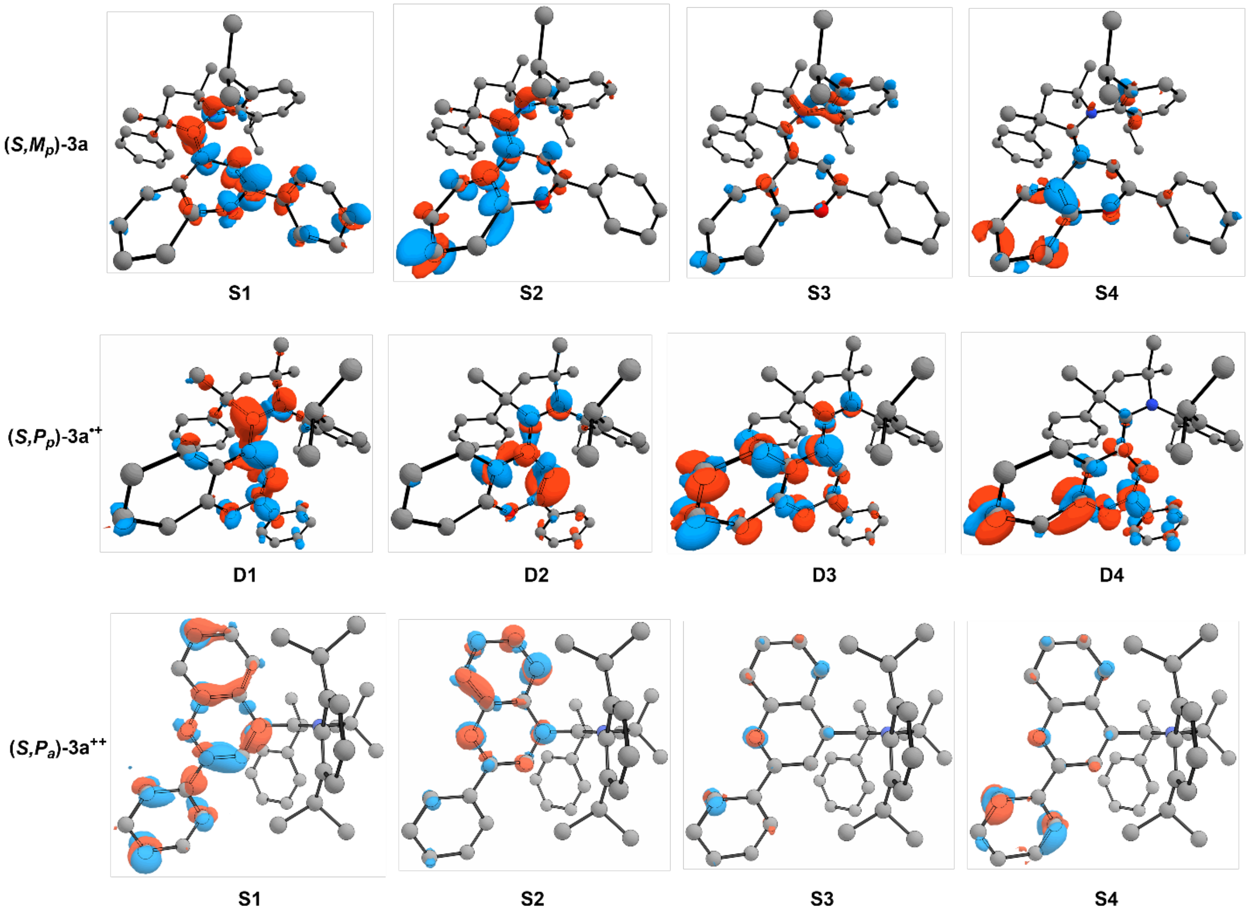


Figure S38. Transition densities for the first four transitions of **(*S,M*$_p$)-3a, (*S,P*$_p$)-3a$^{•+}$**, and **(*S,P*$_a$)-3a^{++}** obtained via TD-DFT using the CAM-B3LYP functional. Isosurface = 0.002.

S1

148a -> 149a : 0.933169
148a -> 158a : 0.017006

S2

148a -> 150a : 0.912072
148a -> 151a : 0.018115

S3

148a -> 151a : 0.288073
148a -> 152a : 0.056422
148a -> 153a : 0.145276
148a -> 154a : 0.044313
148a -> 155a : 0.394915

S4

148a -> 151a : 0.036492
148a -> 152a : 0.448664
148a -> 153a : 0.167684
148a -> 154a : 0.089354
148a -> 155a : 0.037594
148a -> 156a : 0.141415

Figure S39. Nature of selected electronic transitions in **(*S,M*$_p$)-3a** obtained via TD-DFT using the CAM-B3LYP functional

D1

148a -> 149a : 0.863092
147b -> 148b : 0.033875

D2

146a -> 149a : 0.015579
148a -> 149a : 0.044363
148a -> 150a : 0.209108
140b -> 150b : 0.014033
141b -> 148b : 0.016702
145b -> 148b : 0.034210
147b -> 148b : 0.487864
147b -> 149b : 0.016612

D3

146a -> 149a : 0.016598
148a -> 150a : 0.212183
139b -> 148b : 0.019822
141b -> 148b : 0.017982
143b -> 148b : 0.010301
144b -> 148b : 0.181562
145b -> 148b : 0.312317
146b -> 148b : 0.055598
147b -> 148b : 0.014617
147b -> 149b : 0.025375

D4

146a -> 150a : 0.011265
148a -> 150a : 0.338583
148a -> 157a : 0.010569

144b -> 148b : 0.044720
145b -> 148b : 0.052298
146b -> 148b : 0.044425
147b -> 148b : 0.289498

Figure S40. Nature of selected electronic transitions in **(*S*,*M*$_p$)-3a$^{•+}$** obtained via TD-DFT using the CAM-B3LYP functional

S1

141a -> 148a : 0.023078
144a -> 148a : 0.110470
145a -> 148a : 0.078281
146a -> 148a : 0.747922

S2

141a -> 148a : 0.388336
142a -> 148a : 0.042965
143a -> 148a : 0.038722
144a -> 148a : 0.219422
145a -> 148a : 0.026697
146a -> 148a : 0.022328
147a -> 148a : 0.237230

S3

141a -> 148a : 0.058174
142a -> 148a : 0.078587
143a -> 148a : 0.023395
144a -> 148a : 0.062689
145a -> 148a : 0.035558
146a -> 148a : 0.012720
147a -> 148a : 0.714152

S4

141a -> 148a : 0.228591
142a -> 148a : 0.169550
142a -> 150a : 0.012735
143a -> 148a : 0.010243
145a -> 148a : 0.448697
146a -> 148a : 0.070239
147a -> 148a : 0.033523

Figure S41. Nature of selected electronic transitions in **(*S,M_p*)-3a^{++}** obtained via TD-DFT using the CAM-B3LYP functional

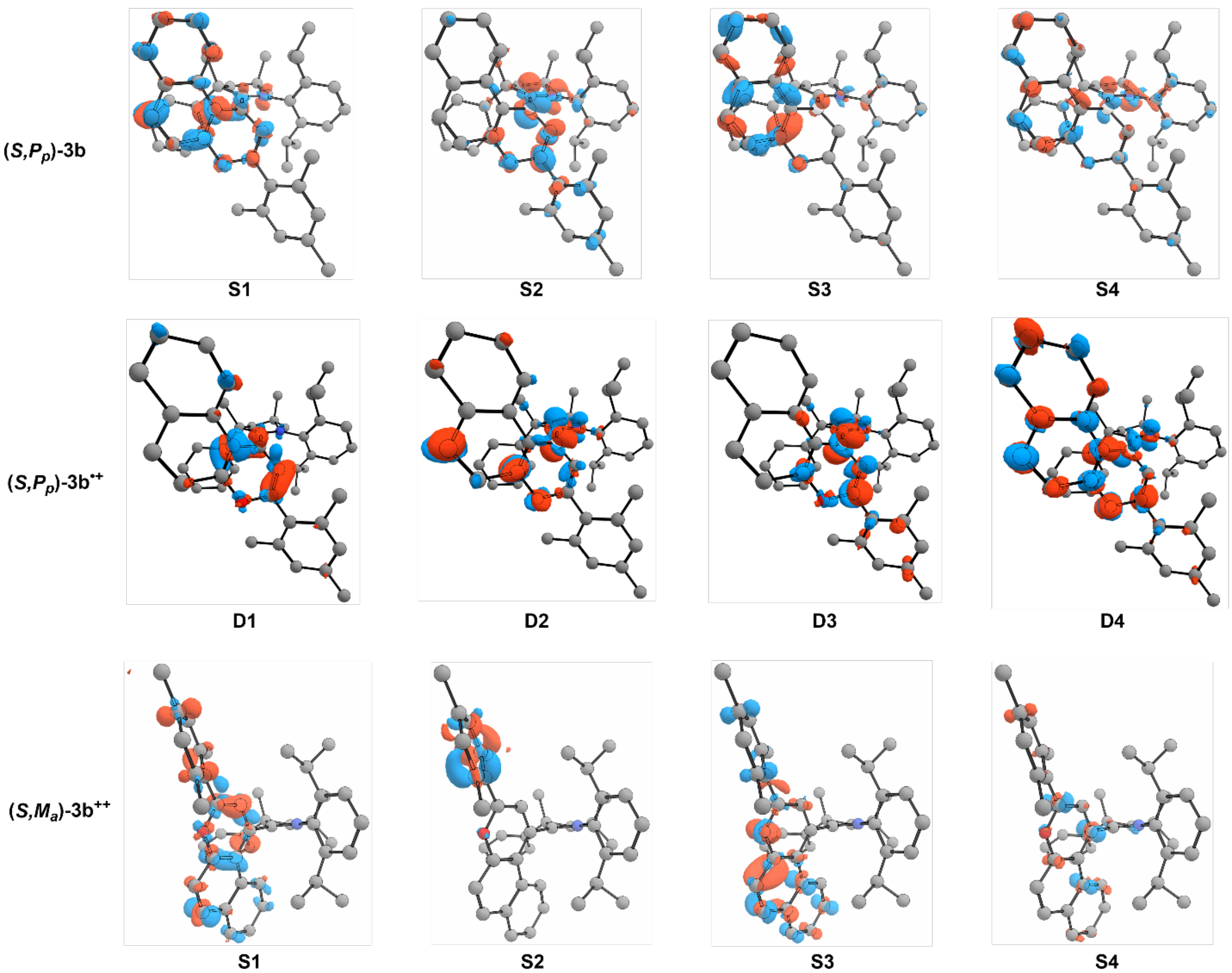


Figure S42. Transition densities for the first four transitions of **(*S,P_p*)-3b**, **(*S,P_p*)-3b$^{\bullet+}$**, and **(*S,M_a*)-3b^{++}**, obtained via TD-DFT using the CAM-B3LYP functional. Isosurface = 0.002.

S1

173a -> 174a : 0.903573
173a -> 175a : 0.027863
173a -> 182a : 0.011726
173a -> 185a : 0.011461

S2

173a -> 174a : 0.027578
173a -> 175a : 0.887889
173a -> 182a : 0.011601
173a -> 185a : 0.021491

S3

171a -> 174a : 0.090683
172a -> 175a : 0.022148
172a -> 176a : 0.011024
173a -> 176a : 0.686901
173a -> 177a : 0.028433
173a -> 178a : 0.010811
173a -> 179a : 0.073495

S4

171a -> 174a : 0.058699
172a -> 175a : 0.011837
172a -> 176a : 0.014483
172a -> 179a : 0.011099
173a -> 176a : 0.029796
173a -> 177a : 0.371919
173a -> 178a : 0.302446
173a -> 179a : 0.070524
173a -> 181a : 0.032660
173a -> 182a : 0.025123

Fig. S39. Nature of selected electronic transitions in **(*S*,*P*$_p$)-3b** according to TD-DFT calculations.

D1

172a -> 174a : 0.040264
172a -> 175a : 0.012574
173a -> 174a : 0.099131
173a -> 175a : 0.068137
164b -> 173b : 0.018037
172b -> 173b : 0.567992
172b -> 174b : 0.064031

D2

172a -> 174a : 0.010642
172a -> 175a : 0.043938
173a -> 174a : 0.519019
164b -> 173b : 0.015395

172b -> 173b : 0.225384
172b -> 174b : 0.060793

D3
172a -> 174a : 0.034067
173a -> 174a : 0.127335
173a -> 175a : 0.398991
168b -> 173b : 0.032328
169b -> 173b : 0.029673
170b -> 173b : 0.035340
170b -> 174b : 0.011972
172b -> 173b : 0.111546
172b -> 174b : 0.045327

D4
170a -> 174a : 0.011086
172a -> 175a : 0.011147
173a -> 174a : 0.011722
173a -> 175a : 0.251884
164b -> 173b : 0.032017
166b -> 173b : 0.011312
168b -> 173b : 0.179565
169b -> 173b : 0.168717
170b -> 173b : 0.136311
171b -> 173b : 0.019504
172b -> 174b : 0.011322

Figure S43. Nature of selected electronic transitions in **(*S*,*P*$_p$)-3b$^{\bullet+}$** according to TD-DFT calculations.

S1
172a -> 173a : 0.942109

S2
170a -> 173a : 0.882544
170a -> 175a : 0.030252
170a -> 177a : 0.011244
171a -> 173a : 0.056594

S3
165a -> 173a : 0.049066

167a -> 173a : 0.121281
168a -> 173a : 0.195025
169a -> 173a : 0.523738
170a -> 173a : 0.016183
171a -> 173a : 0.025370
172a -> 175a : 0.030845

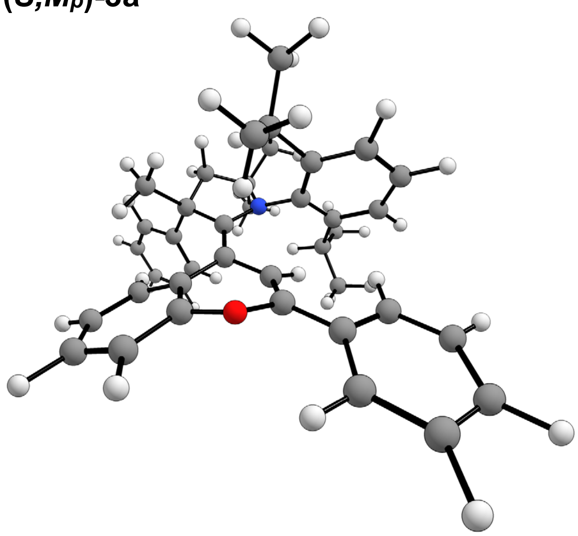
S4

165a -> 173a : 0.105317
166a -> 173a : 0.019447
168a -> 173a : 0.551096
169a -> 173a : 0.227522
171a -> 173a : 0.026804
172a -> 173a : 0.013202

Figure S44. Nature of selected electronic transitions in **(*S,P*$_p$)-3b^{++}** according to TD-DFT calculations.

Cartesian Coordinates

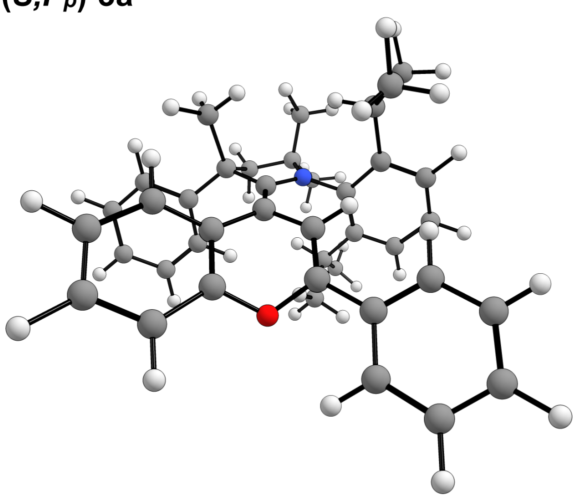
(*S,M*$_p$)-3a



O	10.517543947	13.470808079	15.403087937
N	6.998181392	16.410217849	13.555022756
C	9.035427215	16.581536614	12.175733674
C	9.712669561	13.309113853	14.284352593
C	8.667086018	14.595623116	16.515689170
C	8.149328802	14.976266322	15.180716819
C	10.253519360	12.346263961	13.327532439
C	7.734234223	16.063033616	12.368945642
C	9.870398896	13.863654413	16.557790728
C	7.387036484	16.078313024	14.856036651
C	6.835847774	17.144749822	15.817325471
C	8.577052009	14.022363119	14.168337963
H	7.965051086	13.858840520	13.295946379
C	8.042039671	14.794884446	17.758016044
H	7.067895134	15.262895359	17.792158417
C	7.140049107	15.238749091	11.388527335
C	9.809146143	12.328574798	11.994099016
H	9.077388800	13.055204824	11.654919528
C	9.722358780	17.503504318	13.168199365
H	8.987096226	17.785654919	13.925758175
C	10.317103285	11.406859133	11.090342288
H	9.959706315	11.412866677	10.063914648
C	6.057464003	17.586408767	13.515569356
C	10.480668211	13.477965043	17.744877275
H	11.420698477	12.936209359	17.695862412
C	11.244954488	11.429370245	13.713694730
H	11.607177786	11.431404650	14.736094834
C	9.870401922	13.771206204	18.958532272
H	10.343105712	13.475010396	19.890332155
C	5.625573059	16.655042146	16.625078834
C	7.924590094	17.756276437	16.730372294
H	8.181753047	17.131525853	17.584273141
H	7.579154355	18.723525771	17.108345776
H	8.833131368	17.933666687	16.146853521
C	8.633382395	14.409669569	18.956599336
H	8.116118761	14.606877087	19.891214409
C	9.720611655	16.243910261	11.006060593
H	10.726973366	16.624444913	10.852864351
C	5.023639232	15.414285210	16.397254399
H	5.444446474	14.747851926	15.648648430
C	6.388097868	18.264657049	14.844113544
H	5.546981065	18.837354380	15.244049204
H	7.226078392	18.955385267	14.690555729
C	5.852906680	13.059938125	11.542543257
H	6.230709312	12.696340099	10.580529884

H	4.852338130	12.638514880	11.690995661
H	6.501123754	12.665294791	12.331535632
C	11.755225697	10.512845952	12.799796279
H	12.518522752	9.808540085	13.119512797
C	5.776340509	14.595414373	11.569003361
H	5.399044347	14.886730549	12.553631341
C	7.851697482	14.964926544	10.218133689
H	7.400541300	14.334909434	9.455839767
C	5.070800016	17.484157500	17.606945143
H	5.506441235	18.459542007	17.804773066
C	9.135340401	15.455289557	10.025648832
H	9.681657899	15.217259785	9.116914724
C	6.343403145	18.515770020	12.339320993
H	7.377437608	18.867003250	12.344949349
H	5.684946100	19.386705624	12.422456595
H	6.142709658	18.028486610	11.379987545
C	10.226059701	18.795232301	12.503605145
H	11.077017129	18.597075545	11.843079519
H	10.562459005	19.497914777	13.273956049
H	9.447234078	19.284197854	11.909985053
C	11.293809817	10.491296853	11.486202045
H	11.695601024	9.775936054	10.774408496
C	10.889545151	16.805781452	13.882680358
H	11.657234124	16.503587189	13.160584479
H	10.552946064	15.917191603	14.420604658
H	11.352682022	17.491140103	14.601925351
C	4.579477344	17.168912622	13.457760437
H	4.316616287	16.767814454	12.477404015
H	3.959006439	18.055246840	13.630278201
H	4.331588456	16.428385640	14.220372728
C	3.908966546	15.010154417	17.127267784
H	3.463566374	14.038667170	16.930389404
C	4.787605829	15.076787762	10.495204600
H	5.068662588	14.687748201	9.509881877
H	4.760696065	16.168756382	10.424860849
H	3.776623367	14.718860380	10.720720939
C	3.958789688	17.082138830	18.341344146
H	3.549738914	17.743487547	19.100516418
C	3.371274114	15.841239195	18.105789936
H	2.504381892	15.525972552	18.679729972

(*S*,*P*$_p$)-3a



O	-10.005651156	-13.440053208	-15.618622390
N	-6.704424509	-16.353935999	-13.369227213
C	-8.846651197	-16.524474098	-12.177527677
C	-9.544359796	-13.343205633	-14.311800725
C	-7.761850644	-14.085702875	-16.293796865
C	-7.556702713	-14.644998797	-14.936526286
C	-10.477701503	-12.653974093	-13.425288084
C	-7.526096153	-16.025350581	-12.240194603
C	-9.026887480	-13.542656338	-16.586174051
C	-6.786039361	-15.751570260	-14.620319215
C	-5.844804245	-16.536405270	-15.558560921
C	-8.383861476	-13.934860799	-13.968574924
H	-8.087533927	-13.871769746	-12.935204572
C	-6.813345969	-13.985589584	-17.320229441
H	-5.797515474	-14.292726438	-17.129085536
C	-7.017709264	-15.189048586	-11.224363634
C	-10.145808301	-12.377852916	-12.085846973
H	-9.169155607	-12.647860414	-11.696635029
C	-9.461652604	-17.407294573	-13.251701920
H	-8.674750360	-17.674844030	-13.963746033
C	-11.054069074	-11.756866434	-11.242090508
H	-10.771793416	-11.553866440	-10.212400998
C	-5.830737013	-17.574701038	-13.321925414
C	-9.373618769	-13.071932657	-17.846574912
H	-10.378818153	-12.691986408	-18.004043705
C	-11.750418372	-12.272528224	-13.884161867
H	-12.031654881	-12.469621821	-14.912464474
C	-8.428916042	-13.080907590	-18.866786077
H	-8.694185951	-12.720254087	-19.856222190
C	-6.409791867	-16.865353899	-16.935793464
C	-4.462085836	-15.833777593	-15.613695229
H	-3.656434059	-16.566695762	-15.723564405
H	-4.378720530	-15.132687743	-16.444726940
H	-4.284391928	-15.265750714	-14.698524322
C	-7.135219755	-13.512280052	-18.587895064
H	-6.367836813	-13.481804069	-19.356072134
C	-9.635600854	-16.172129817	-11.080065759
H	-10.658888812	-16.533248092	-11.022580152
C	-5.568992891	-17.041415195	-18.036183228
H	-4.500137259	-16.876286921	-17.939743517
C	-5.715032124	-17.888024935	-14.810984772
H	-4.786468284	-18.405529816	-15.068085903
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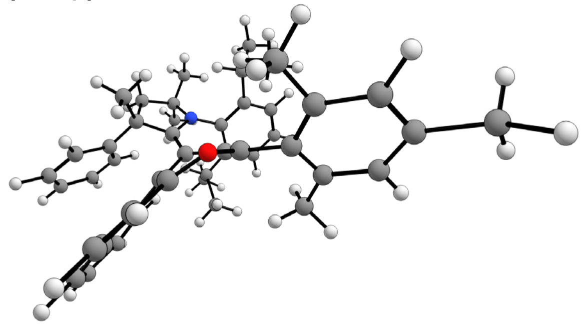

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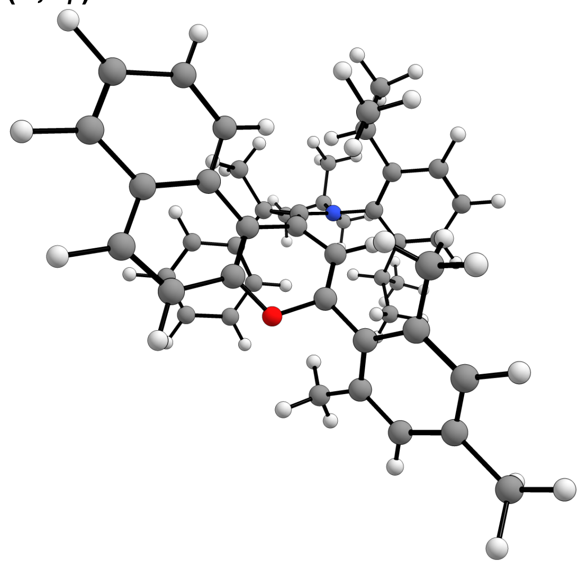

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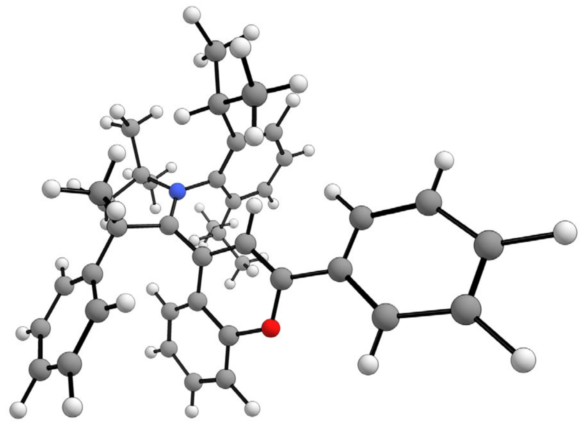

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H	4.496624545	15.892806443	10.759617078
H	3.663590107	14.504331763	11.487775357
C	6.531299406	15.440767678	19.035524840
H	7.134169413	14.791345558	19.664070703
C	5.251803714	15.817581769	19.439360968
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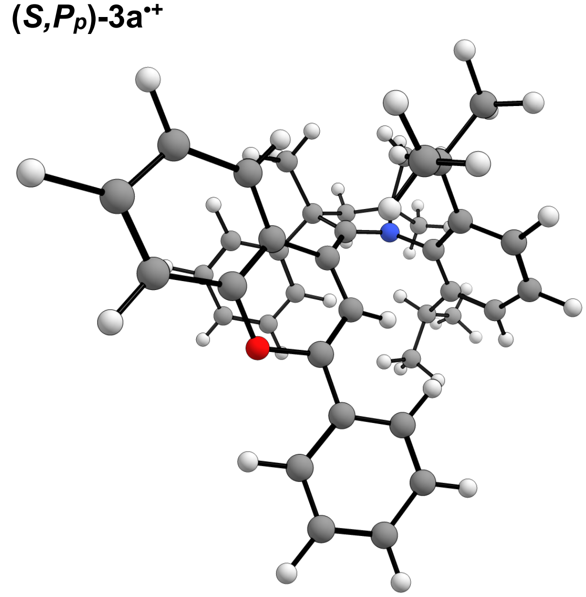
(S,P_p)-3a$^{\bullet+}$



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C	8.782455239	12.969589777	14.663548056
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C	8.237407547	15.299183786	15.069544006
C	8.921493231	11.777063158	13.842245361
C	8.194913685	16.559669038	12.380046197
C	9.063960302	13.816871428	16.838398393
C	7.406152356	16.415001736	14.705818131
C	6.284433133	16.979869198	15.610946532
C	8.438556551	14.213170533	14.196222806
H	8.210185108	14.299251998	13.146072995
C	9.168293564	16.172986642	17.250434511
H	9.124148417	17.189139228	16.877488148
C	7.678073897	15.781093131	11.318756112
C	8.793677175	10.498050827	14.409314359
H	8.584746973	10.394056735	15.468624725
C	10.191176082	17.693529272	13.586979310
H	9.430992415	17.906962777	14.343955278
C	8.916720451	9.367361356	13.613129118
H	8.809078111	8.383378960	14.059958440
C	6.369428983	18.106193925	13.407368640
C	9.531791151	13.544271598	18.117050708
H	9.704557596	12.514000840	18.411303180
C	9.193444134	11.892720424	12.467996856
H	9.337951868	12.870462640	12.016798083
C	9.810679608	14.604790479	18.966763402
H	10.188503592	14.406569339	19.965003008
C	5.522015083	15.774145756	16.183265921
C	6.694534125	17.968903443	16.717218169
H	7.181127021	17.483323563	17.560163647
H	5.786638292	18.455575220	17.086337472
H	7.359684081	18.745491928	16.338087270
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C	10.367995401	16.575318038	11.359215579
H	11.414540220	16.864869558	11.370206529
C	5.106846375	14.755023963	15.314951232
H	5.315014061	14.828445337	14.250230712
C	5.430936199	17.744106892	14.558197693
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H	5.179066217	13.360059842	11.251758463
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C	9.313262742	10.756723884	11.681490643
H	9.530197969	10.859071553	10.622250943
C	6.257261401	15.233279031	11.263694711
H	5.695046931	15.636619686	12.110065631
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C	5.234107517	15.639054316	17.542156060
H	5.529434669	16.402457794	18.252572181
C	9.876483794	15.839498105	10.292391122
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C	7.183311334	19.388668782	13.621080726
H	6.488001130	20.225845193	13.731516217
H	7.808384217	19.582976713	12.744813928
H	7.824840467	19.354275889	14.501555868
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H	11.157135903	19.588720142	14.003742657
H	10.049438601	19.655732516	12.618344587
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H	9.269515330	8.602859704	11.629988603
C	11.280891919	16.838813710	14.256561038
H	11.656893829	17.351024809	15.148761957
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H	10.899728483	15.858759628	14.557801915
C	5.630000977	18.255742382	12.086641737
H	5.083015062	19.202552129	12.129247629
H	4.903992809	17.462519660	11.911783633
H	6.326131048	18.315138116	11.244959095
C	4.436826709	13.634064110	15.786995000
H	4.133719436	12.856819171	15.091089672
C	5.546846549	15.639021189	9.960631642
H	5.648476367	16.705128972	9.743826490
H	4.480702127	15.398609176	10.031071619
H	5.955378127	15.082495494	9.110551647
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H	4.337975062	14.436893923	19.079638093
C	4.157777339	13.509061810	17.147232141
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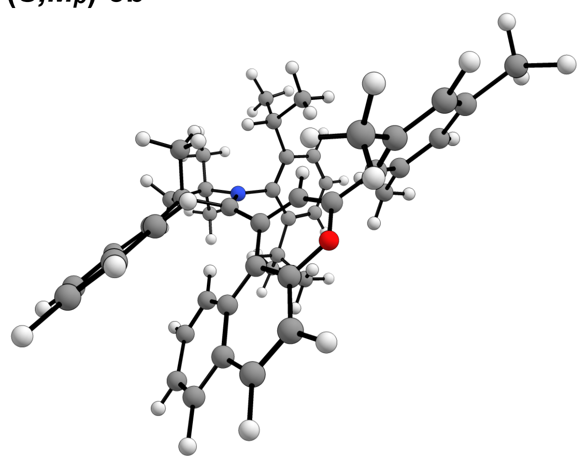
(*S*,*M*$_p$)-3b$^{\bullet+}$



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C	6.266209834	6.367187375	4.731753231
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C	6.677690561	7.727096629	4.983017437
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C	3.926450060	7.150983515	4.654528889
H	2.886108920	6.887000367	4.494013649
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H	8.813702917	7.392978677	4.944910796
C	8.386388176	9.444692724	5.230506506
H	9.438649925	9.712669263	5.257101458
C	7.403767531	10.435085656	5.399857657
H	7.694002359	11.469428497	5.558337410
C	6.074893345	10.084027450	5.356085023
H	5.298938873	10.835747697	5.474973484
C	4.627220786	2.804461696	3.062823010
C	3.590021908	2.154756816	3.771677741
C	3.009826545	1.020614699	3.213993301
H	2.223430121	0.508270363	3.765229628
C	3.417659430	0.515426746	1.976412876
C	4.439916743	1.173100402	1.296199166
H	4.760049135	0.799329779	0.325868746
C	5.060257500	2.310210407	1.815794881

C	3.133539344	2.625887585	5.127210213
H	2.595567139	1.826374129	5.642312092
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H	3.978605726	2.933677362	5.752617212
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H	1.684324766	-0.571457380	1.308573141
H	2.921268579	-1.575623733	2.060945024
H	3.172370487	-0.953651689	0.418299807
C	6.149561989	2.974492932	1.016972188
H	6.102092515	4.065470345	1.083519936
H	6.077367947	2.684523594	-0.034633723
H	7.143278744	2.673869898	1.369523907
C	8.435592212	5.093153598	5.192881017
C	8.739419897	5.282969730	6.689861807
C	10.251270656	5.545682268	6.651741815
H	10.744147748	5.193314622	7.561967988
H	10.452142079	6.615241861	6.547530895
C	10.794285624	4.824227538	5.398480162
C	8.470505792	3.880714968	7.321638193
H	9.149512976	3.126176998	6.927491825
H	7.447251251	3.543917249	7.140493831
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C	7.903578720	6.275613374	7.491410587
C	6.538623766	6.030138881	7.694040022
H	6.065980110	5.160622184	7.248618648
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C	6.328941097	8.019105504	9.042242415
H	5.720779075	8.697402399	9.634035631
C	7.689789235	8.252477147	8.882474881
H	8.155606736	9.113921961	9.352863713
C	8.469482249	7.387039323	8.116433427
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C	11.707818845	5.747001389	4.589575438
H	11.221114061	6.695673872	4.352378027
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H	12.590325004	5.963357941	5.199803669
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C	9.636799084	2.604123366	3.104660843
C	9.824534173	2.093936087	1.817634449
H	9.879862752	1.017932176	1.682303873
C	9.918662816	2.923577619	0.711942022
H	10.065677022	2.500307108	-0.277660514
C	9.788871324	4.292832448	0.872906604
H	9.821447388	4.938799514	0.000658436
C	9.615962977	4.867549751	2.134521952
C	9.444692417	1.589929632	4.225465809
H	9.357749371	2.126353085	5.172043099
C	8.149626761	0.773454229	4.042272715
H	7.242900354	1.381376765	4.099894820
H	8.086301428	0.017299723	4.832188684
H	8.149457623	0.254367827	3.077901837
C	10.618327748	0.599430045	4.325542086
H	11.591193451	1.094917885	4.318601587
H	10.597398208	-0.108839172	3.490663309
H	10.531943993	0.020979736	5.251262997
C	9.426928827	6.371080633	2.197304089
H	9.402486075	6.674049828	3.243390110
C	8.083062416	6.775116922	1.567210559
H	7.244887441	6.241667706	2.024354788
H	8.079563651	6.558328716	0.493183259
H	7.920046113	7.850638940	1.698721770
C	10.569909949	7.141362822	1.519972101
H	11.550116809	6.833799629	1.894818259
H	10.449543496	8.213935223	1.707543855
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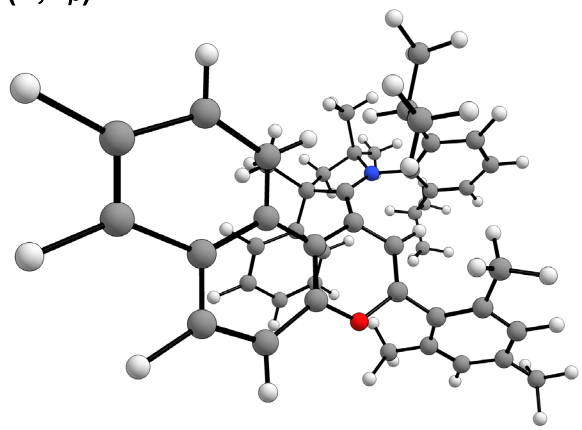
(*S*,*P*$_p$)-3b$^{•+}$



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C	6.691140999	4.147189055	4.130964546
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C	7.302274627	4.861883305	5.196089494
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C	6.654127196	5.402797238	7.626360900
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H	3.725457457	6.917943739	8.611468962
C	4.097404346	6.122586091	6.667779877
H	3.111084255	6.333996381	6.267336157
C	7.798966941	4.822373357	8.213159629
H	8.509649389	4.299861920	7.583282470
C	8.021104194	4.900985011	9.569107994
H	8.901863556	4.431272276	9.997225291
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H	7.310776180	5.661185916	11.467202475
C	5.971698576	6.132944958	9.866663650
H	5.243186898	6.625806372	10.505252065
C	4.682059819	3.660227386	2.718396461
C	4.789125853	2.269449177	2.507153962
C	4.169214029	1.715286407	1.386022504
H	4.234710334	0.640568313	1.230406181
C	3.463356342	2.494486547	0.472371921
C	3.376881264	3.870504404	0.699711534
H	2.843406831	4.495576869	-0.013962759
C	3.967435299	4.470713087	1.805998840
C	5.520581335	1.355130862	3.455157869
H	6.599765766	1.351544223	3.257715124
H	5.164538896	0.328584027	3.335213646
H	5.384870606	1.652557192	4.499028753
C	2.808782393	1.881019807	-0.732899405
H	1.729860786	2.073035956	-0.729786158
H	2.966382794	0.800149474	-0.765571453
H	3.208847802	2.316479310	-1.655656520
C	3.878798350	5.964110414	1.968004999
H	3.599883419	6.431055659	1.020150768
H	4.834108501	6.386787073	2.295666679
H	3.130006401	6.243969838	2.716920610
C	8.642528733	5.358729898	5.089164522
C	9.055187789	6.796321646	5.520617135

C	10.347658963	6.986299634	4.676882071
H	11.071217187	7.623472180	5.190188570
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C	10.908002555	5.589723062	4.409514526
C	9.418883890	7.040549197	6.995727518
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H	9.869404538	8.035695501	7.061940190
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H	7.979237622	7.021898041	3.023595170
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H	5.062416116	10.062371380	3.792548043
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H	11.234254684	4.912662594	6.484528153
H	12.624001548	5.683954774	5.699742967
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C	9.580046510	1.114286456	3.762000430
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C	9.443184447	1.057982829	2.384826901
H	9.404716474	0.097190727	1.879331697
C	9.334649479	2.232729706	1.654447959
H	9.197744233	2.179569116	0.578449100
C	9.379954911	3.482854279	2.272720274
C	9.708706763	2.302033360	5.954395767
H	9.806395455	3.327219940	6.318877673
C	8.423443246	1.705122245	6.551028534
H	8.301135378	0.661593993	6.241009388
H	7.534577289	2.259085341	6.231175305
H	8.470387072	1.729820175	7.645250218
C	10.934734356	1.522066291	6.450033459
H	11.017985156	1.617202303	7.537955321
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H	10.846953763	0.456481277	6.214046790
C	9.172989953	4.712366702	1.399395290
H	9.331139652	5.604426615	2.011157067
C	7.739055337	4.788755672	0.846099711
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H	11.193256981	4.573344131	0.540542904
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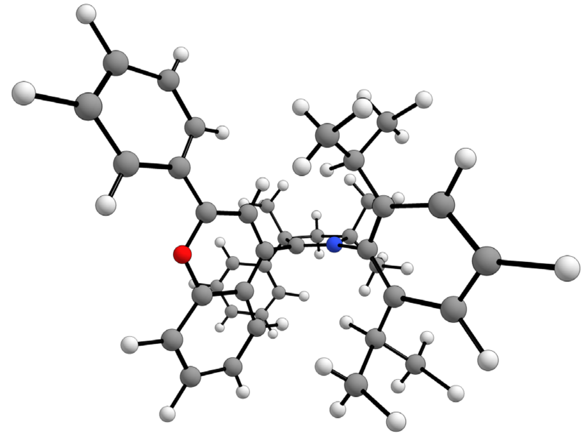
(*S*,*M*$_a$)-3a^{++}



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C	9.270351593	12.684384419	14.188896118
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C	9.112324583	14.075836543	14.196909956
H	9.939051631	14.686861148	13.867406079
C	5.653313599	14.267808146	15.629232244
H	5.445079161	15.328076842	15.675698345
C	5.786595294	16.610816177	12.093702526
C	10.375505054	10.603557405	13.451460784
H	9.429212345	10.079187915	13.525131770
C	9.645122881	16.309261247	11.619850780
H	9.866732160	16.436807529	12.685483374
C	11.508592842	9.931253151	13.030241678
H	11.447381376	8.876507199	12.781856923
C	7.782480127	18.428260574	14.162693659
C	6.163177168	11.501725248	15.512094476
H	6.384656619	10.441181708	15.458169251
C	11.681189662	12.651998411	13.645193868
H	11.770847502	13.700557683	13.908471889
C	4.981937430	11.984184522	16.043652662
H	4.241885311	11.284870112	16.419553423
C	7.566633586	16.333362163	17.181431769
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H	10.256691916	17.039277495	17.027293482
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H	9.823868481	18.548030724	13.399806616
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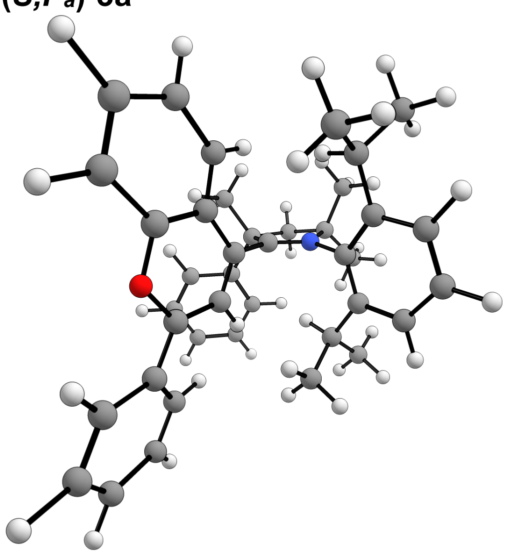

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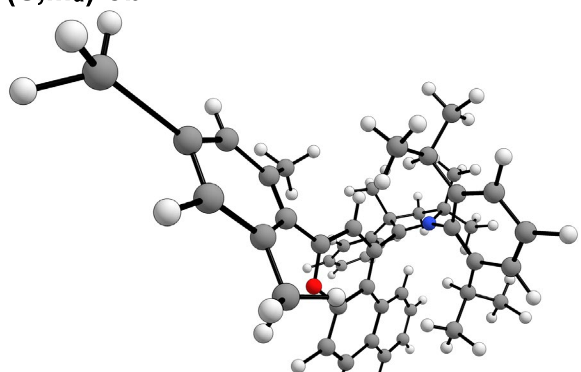

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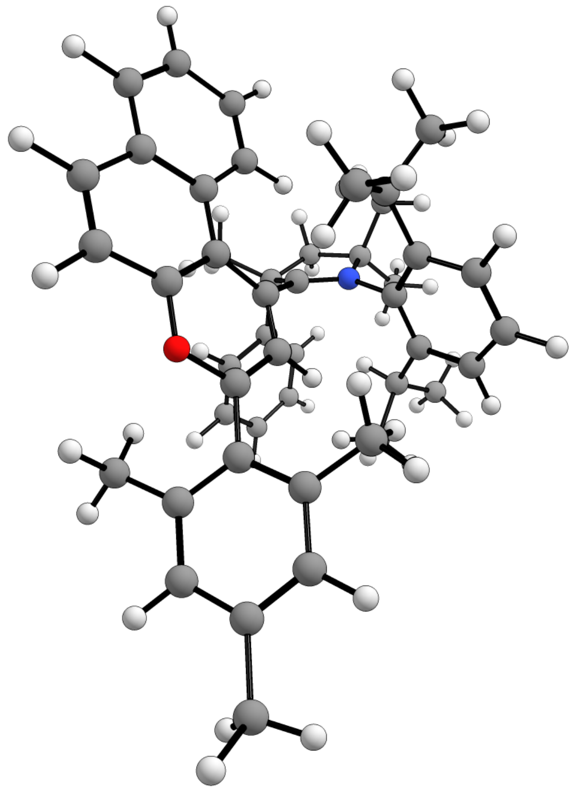

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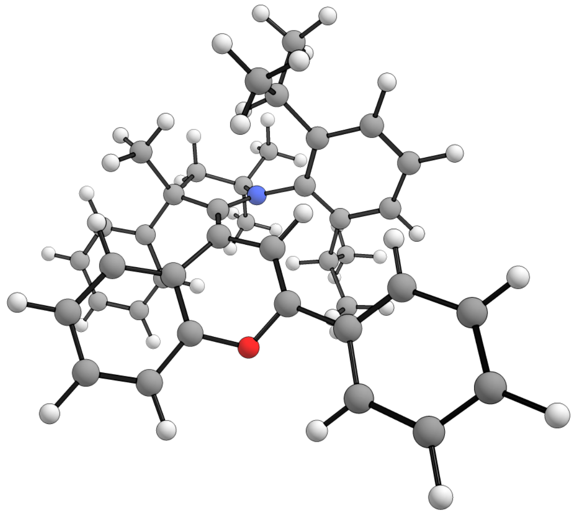
TS-3a



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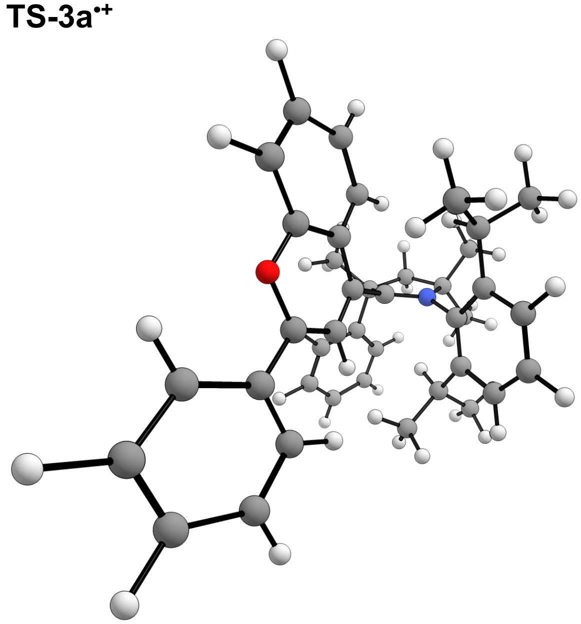

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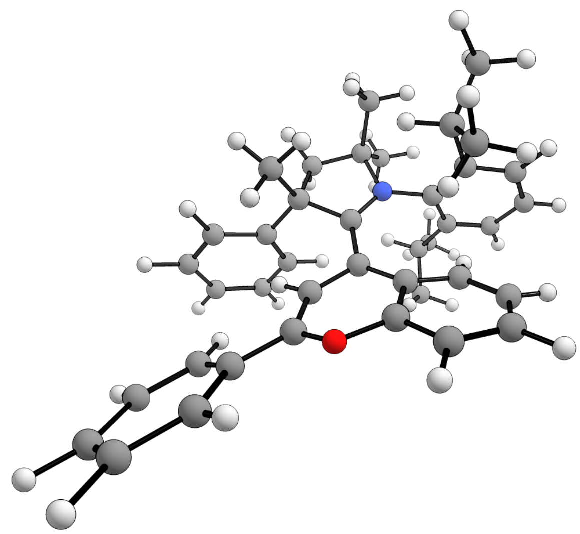

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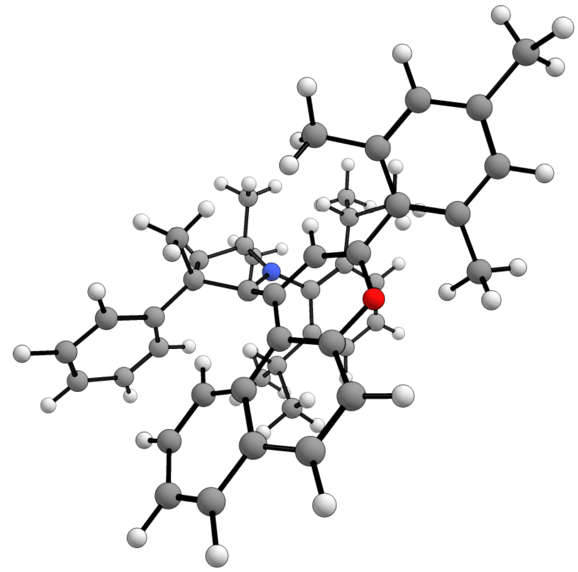
TS-3b



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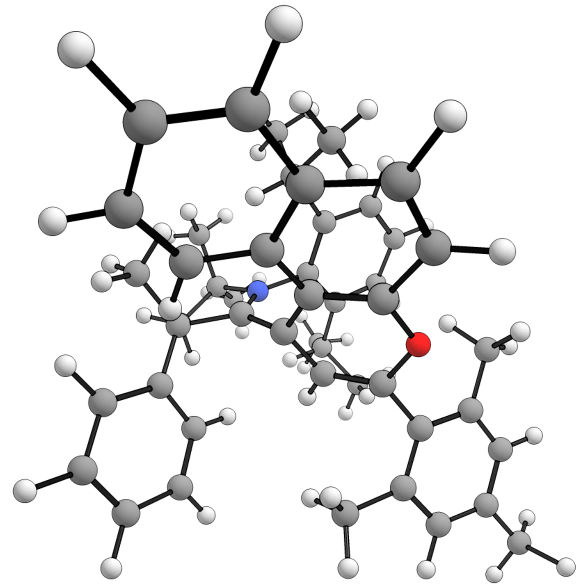
TS-3b$^{\bullet+}$



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H	9.897508363	4.598015991	2.564707028
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H	8.670529361	2.585727160	0.612377311
H	9.229024548	4.221047367	0.238735075
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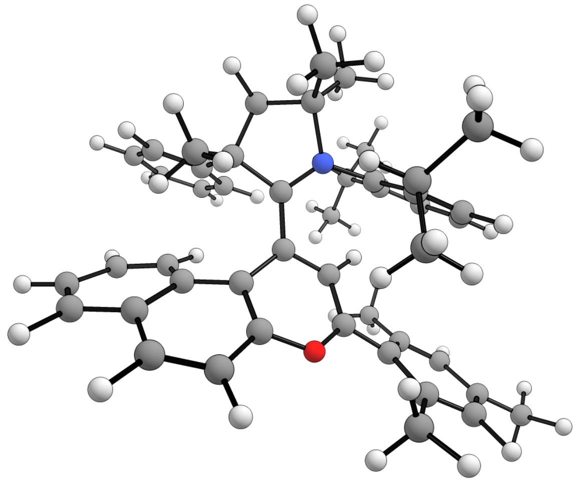
TS-3b^{++}



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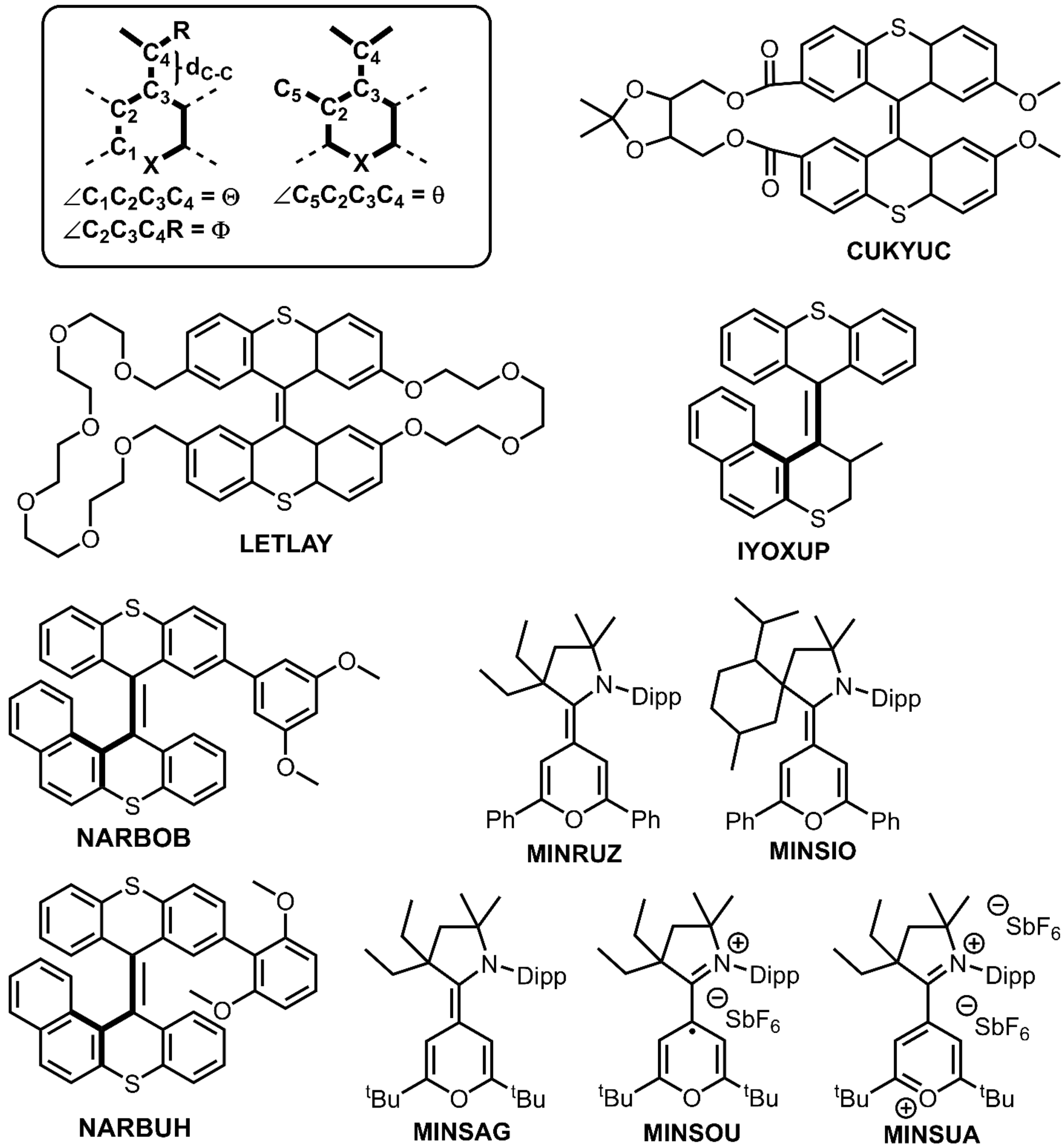

Figure S45. Select structures from the CCDC database, with CSD refcodes, for comparison with solid-state structures from this work. Values are tabulated in Table S9.

Compound	CSD Refcode	Exp/Calc	d_{C-C} (Å)	ϴ (°)	θ (°)	Φ (°)
3a	---	Exp	1.374	-146.83	37.9	179.86
	---	Calc	1.379	-150.8	34.36	176.233
3b	---	Exp	1.364	127.58	-61.2	178.85
	---	Calc	1.376	128.45	-61.15	179.08
3b+	---	Exp	1.442	157	-29.73	137.77
	---	Calc	1.433	139.5	-46.59	165.88
3b++	---	Exp	1.489	-178.51	-0.45	-103.58
	---	Calc	1.484	177.33	-2.81	-100.98
---	**IYOXUP**	---	1.349	-126.12	61.42	-175.48
---	**CUKYUK**	---	1.359	-129.53 34.80 131.25 -136.67	47.08 -46.34 50.57 -50.63	-179.38 179.08
---	**LETLAY**	---	1.347	-127.28 127.17 -135.62 135.54	54.75 -53.58 -49.61 48.85	-178.83 -173.57
---	**NARBOB**	---	1.354	-126.78	57.29	176.42
---	**NARBUH**	---	1.356	125.85	-59.85	178.59
---	**MINSAG**	---	1.373	173.76 -175.52	---	-179.95
---	**MINSOU**	---	1.433	175.46 -173.28	---	171.96
---	**MINSUA**	---	1.485	172.21 -172.08	---	91.88 -96.10
---	**MINRUZ**	---	1.378	-179.03 176.85	---	-178.16
---	**MINSIO**	---	1.373	178.87 -179.99	---	-171.5

Table S9. Key structural parameters for comparison of solid-state structures obtained in this work, computational models from this work, and experimental data for related molecules from the literature. Depending on molecular symmetry, multiple values are listed for a given parameter. See Figure S45 for more details.

10) References

1. Bains, A. K., Kundu, A., Maiti, D. & Adhikari, D. Ligand-redox assisted nickel catalysis toward stereoselective synthesis of (n+1)-membered cycloalkanes from 1,n-diols with methyl ketones. *Chem. Sci.* **12**, 14217–14223 (2021).
2. Lorkowski, J. *et al.* Singlet carbenes are stereoinductive main group ambiphiles. *J. Am. Chem. Soc.* **147**, 14777–14784 (2025).
3. Fichtner, C., Remennikov, G. & Mayr, H. Kinetics of the reactions of flavylium ions with π-nucleophiles. *Eur. J. Org. Chem.* **2001**, 4451–4456 (2001).
4. Favre, H. A. & Powell, W. H. *Nomenclature of Organic Chemistry*. (The Royal Society of Chemistry, 2013).
5. Prelog, V. & Helmchen, G. Basic principles of the CIP-system and proposals for a revision. *Angew. Chem. Int. Ed. Engl.* **21**, 567–583 (1982).
6. Neese, F. Software update: the ORCA program system—version 5.0. *WIREs Comput. Mol. Sci.* **12**, e1606 (2022).
7. Bannwarth, C., Ehlert, S. & Grimme, S. GFN2-xTB—An accurate and broadly parametrized self-consistent tight-binding quantum chemical method with multipole electrostatics and density-dependent dispersion contributions. *J. Chem. Theory Comput.* **15**, 1652–1671 (2019).
8. Spicher, S. & Grimme, S. Robust atomistic modeling of materials, organometallic, and biochemical systems. *Angew. Chem. Int. Ed.* **59**, 15665–15673 (2020).
9. Ehlert, S., Stahn, M., Spicher, S. & Grimme, S. Robust and efficient implicit solvation model for fast semiempirical methods. *J. Chem. Theory Comput.* **17**, 4250–4261 (2021).

10. York, D. M. & Karplus, M. A smooth solvation potential based on the conductor-like screening model. *J. Phys. Chem. A* **103**, 11060–11079 (1999).

11. Adamo, C. & Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **110**, 6158–6170 (1999).

12. Barone, V. & Cimino, P. Accurate and feasible computations of structural and magnetic properties of large free radicals: The PBE0/N07D model. *Chem. Phys. Lett.* **454**, 139–143 (2008).

13. Barone, V. & Cimino, P. Validation of the B3LYP/N07D and PBE0/N07D computational models for the calculation of electronic g-tensors. *J. Chem. Theory Comput.* **5**, 192–199 (2009).

14. Neese, F. Efficient and accurate approximations to the molecular spin-orbit coupling operator and their use in molecular g-tensor calculations. *J. Chem. Phys.* **122**, 034107 (2005).

15. Neese, F. An improvement of the resolution of the identity approximation for the formation of the Coulomb matrix. *J. Comput. Chem.* **24**, 1740–1747 (2003).

16. Stoychev, G. L., Auer, A. A. & Neese, F. Automatic generation of auxiliary basis sets. *J. Chem. Theory Comput.* **13**, 554–562 (2017).

17. Bannwarth, C. & Grimme, S. A simplified time-dependent density functional theory approach for electronic ultraviolet and circular dichroism spectra of very large molecules. *Comput. Theor. Chem.* **1040–1041**, 45–53 (2014).

18. de Wergifosse, M., Seibert, J. & Grimme, S. Simplified time-dependent density functional theory (sTD-DFT) for molecular optical rotation. *J. Chem. Phys.* **153**, 084116 (2020).

19. Lin, Y.-S., Li, G.-D., Mao, S.-P. & Chai, J.-D. Long-range corrected hybrid density functionals with improved dispersion corrections. *J. Chem. Theory Comput.* **9**, 263–272 (2013).
20. Yanai, T., Tew, D. P. & Handy, N. C. A new hybrid exchange–correlation functional using the coulomb-attenuating method (CAM-B3LYP). *Chem. Phys. Lett.* **393**, 51–57 (2004).
21. Weigend, F. & Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **7**, 3297–3305 (2005).
22. Neese, F. & Olbrich, G. Efficient use of the resolution of the identity approximation in time-dependent density functional calculations with hybrid density functionals. *Chem. Phys. Lett.* **362**, 170–178 (2002).
23. Neese, F., Wennmohs, F., Hansen, A. & Becker, U. Efficient, approximate and parallel hartree–fock and hybrid DFT calculations. A 'chain-of-spheres' algorithm for the hartree–fock exchange. *Chem. Phys.* **356**, 98–109 (2009).
24. Weigend, F. Accurate coulomb-fitting basis sets for H to rn. *Phys. Chem. Chem. Phys.* **8**, 1057–1065 (2006).
25. Kubo, H. *et al.* Tuning transition electric and magnetic dipole moments: [7]helicenes showing intense circularly polarized luminescence. *J. Phys. Chem. Lett.* **12**, 686–695 (2021).
26. Yorkgitis, P., Vanthuyne, N., Cordier, M., Favereau, L. & Bertrand, G. Data from: Modulating chiral function via the reversible switching of chirality type. UC San Diego Library Digital Collections https://doi.org/10.6075/J0PR7WCK (2025).

27. Bursch, M., Mewes, J.-M., Hansen, A. & Grimme, S. Best-Practice DFT Protocols for Basic Molecular Computational Chemistry. *Angew. Chem. Int. Ed.* **61**, e202205735 (2022).

28. Grimme, S., Hansen, A., Ehlert, S. & Mewes, J.-M. r2SCAN-3c: A “Swiss army knife” composite electronic-structure method. *J. Chem. Phys.* **154**, 064103 (2021).

29. Mardirossian, N. & Head-Gordon, M. ωB97X-V: A 10-parameter, range-separated hybrid, generalized gradient approximation density functional with nonlocal correlation, designed by a survival-of-the-fittest strategy. *Phys. Chem. Chem. Phys.* **16**, 9904–9924 (2014).

30. Leigh, D. A. & Pérez, E. M. Dynamic chirality: molecular shuttles and motors. in *Supramolecular Chirality* (eds Crego-Calama, M. & Reinhoudt, D. N.) 185–208 (Springer, Berlin, Heidelberg, 2006).