

# Supplementary Information for

## Circularly Polarized Luminescence from Cyclic(Alkyl)(Amino) Carbene Derived Propellers

Jan Lorkowski <sup>[a],[b]\*</sup>, Dylan Bouetard<sup>[b]</sup>, Patrick Yorkgitis<sup>[a]</sup>, Milan Gembicky<sup>[a]</sup>, Thierry Roisnel<sup>[b]</sup>, Nicolas Vanthuyne<sup>[e]</sup>, Dominik Munz<sup>[d]\*</sup>, Ludovic Favereau <sup>[c]\*</sup>, Guy Bertrand<sup>[a]</sup>, Marc Mauduit<sup>[b]\*</sup>, Rodolphe Jazzar<sup>[a]\*</sup>

[a] Dr. J. Lorkowski, P. Yorkgitis, Dr. Milan Gembicky, Prof. Dr. G. Bertrand, Dr. R. Jazzar  
UCSD–CNRS Joint Research Laboratory (UMI 3555), Department of Chemistry and Biochemistry,  
University of California, San Diego, La Jolla, CA 92093–0343, United States.

[b] Dr. J. Lorkowski, D. Bouetard Dr. T. Roisnel, Dr. M. Mauduit  
Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR UMR 6226, F-35000 Rennes, France.

[c] Dr. L. Favereau  
Univ Rennes, CNRS, ISCR – UMR 6226 , F-35000 Rennes, France

[d] Prof. Dr. Dominik Munz  
Coordination Chemistry, Saarland University, Campus C4.1, 66123 Saarbrücken, Germany.

[e] Dr. N. Vanthuyne  
Centrale Marseille, ISM2, Aix Marseille Univ., CNRS, F-13013 Marseille, France, Marseille, France

e-mail: [jalorkowski@ucsd.edu](mailto:jalorkowski@ucsd.edu); [dominik.munz@uni-saarland.de](mailto:dominik.munz@uni-saarland.de); [ludovic.favereau@univ-rennes1.fr](mailto:ludovic.favereau@univ-rennes1.fr); [marc.mauduit@ensc-rennes.fr](mailto:marc.mauduit@ensc-rennes.fr); [rjazzar@ucsd.edu](mailto:rjazzar@ucsd.edu)

### Table of Content

1) General methods .....	2
2) Synthetic procedures.....	4
3) Crystal data, data collection and structure refinement .....	7
4) Additional photophysical data .....	11
5) Computational Details .....	14
6) NMR spectra.....	27
7) Chiral HPLC data .....	34

## 1) General methods

For manipulations that were carried out in an argon filled glovebox or using standard Schlenk techniques, glassware was dried in an oven overnight at 150 °C. Dry toluene and tetrahydrofuran were received using MBraun Solvent Purification Systems and freeze-pump-thaw degassed prior to use. Thin layer chromatography was carried out on aluminium backed silica gel 60 (F254) plates from MERCK (grain-size distribution 60/20 µm) and visualized using UV light. Columns chromatography were performed with silica gel (spherical, particle size 40 µm, neutral) purchased from Sigma-Aldrich. NMR spectra were recorded on a Bruker ARX400 400 MHz spectrometer at 25°C. <sup>1</sup>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<sub>3</sub>: 7.26 ppm; C<sub>6</sub>D<sub>5</sub>H: 7.16 ppm) whereas <sup>13</sup>C{<sup>1</sup>H} NMR spectra are reported relative to TMS using the natural-abundance carbon resonances (CDCl<sub>3</sub>: 77.16 ppm; C<sub>6</sub>D<sub>6</sub>: 128.0 ppm). Coupling constants are given in Hertz. 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. X-Ray crystallography data were collected on a a D8 Venture (Bruker-AXS) diffractometer equipped with a CMOS-PHOTON70 detector, using Cu-Kα radiation (1.54184 Å, multilayer) at T = 150 K. Data reduction was performed using the SHELXT program. The structures were resolved using the software SHELXS-97 by the direct methods and refined using SHELXL-2013-4. 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. Optical rotations were measured at Aix Marseille University on a Jasco P-2000 polarimeter with a sodium lamp (589 nm), a halogen lamp (578, 546, 436, 405, 365 and 325 nm), in a 10 cm cell, thermostatic at 25°C with a Peltier controlled cell holder. Electronic Circular Dichroism (ECD) and UV spectra 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 CD quartz cell of 1 mm of 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: 0.1 nm as intervals, scanning speed 50 nm/min, band width 2 nm, and 3 accumulations per sample. The spectra are presented without smoothing and further data processing. Steady-state fluorescence measurements were performed on dilute solutions (ca. 10<sup>-6</sup> M, optical density < 0.1) contained in standard 1 cm quartz cuvettes, using a JASCO (FP-8350) or an Edinburgh Instrument (FLS920)

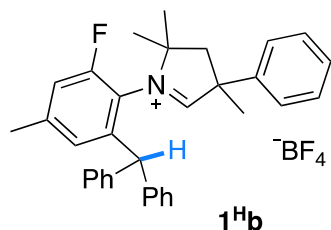
spectrometers in photon-counting mode, or using a gated mode for phosphorescence spectra. The circularly polarized luminescence (CPL) measurements were performed using a home-built CPL spectrofluoropolarimeter (built with the help of the JASCO Company). The samples were excited using a 90° geometry with a Xenon ozone-free lamp 150 W LS. The following parameters were used: emission slit width  $\approx$  10 nm, integration time = 8 sec, scan speed = 50 nm/min, accumulations = 5. The concentration of all the samples was  $10^{-6}$  M. Excitation of the samples was performed at 330 nm.

## 2) Synthetic procedures

### a) Carbene precursors **1<sup>H</sup>a-b**

Anilines for the preparation of **1<sup>H</sup>b** and compounds **1<sup>H</sup>a** were prepared according to the previously reported procedures.<sup>1</sup> Compound **1<sup>H</sup>b** was prepared according to the same synthetic method as **1<sup>H</sup>a** using fluorinated aniline as starting material.

Starting from 600 mg of fluorinated aniline, **1<sup>H</sup>b** was isolated as a 748 mg of white powder in 64% yield over 2 steps as a racemic mixture of two atropisomers.



**<sup>1</sup>H NMR (400 MHz, 25°C, CDCl<sub>3</sub>):**  $\delta$  = 8.87 (s, 0.5H, NCH), 8.12 (s, 0.5H, NCH), 7.80 – 7.07 (m, 10H), 7.02 (t, J = 8.6 Hz, 2H), 6.94 – 6.83 (m, 2H), 6.75 – 6.62 (m, 2H), 5.65 (s, 0.5H), 5.34 (s, 0.5H), 3.01 (d, J = 13.9 Hz, 0.5H, CHH), 2.94 (d, J = 14.1 Hz, 0.5H, CHH), 2.79 (d, J = 9.3 Hz, 0.5H, CHH), 2.76 (d, J = 9.3 Hz, 0.5H, CHH), 2.33 (s, 1.5H), 2.30 (s, 1.5H), 1.97 (s, 1.5H), 1.82 (s, 1.5H), 1.77 (s, 1.5H), 1.74 (d, <sup>ts</sup>J(C,F) = 5.3 Hz, 1.5H), 1.45 (s, 1.5H), , 1.43 (s, 1.5H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, 25°C, CDCl<sub>3</sub>):**  $\delta$  = 192.9 (NCH), 192.5 (NCH), 156.6 (d, <sup>1</sup>J(C,F) = 255.1 Hz), 156.4 (d, <sup>1</sup>J(C,F) = 253.9 Hz), 144.8 (d, <sup>2</sup>J(C,F) = 38.9 Hz), 144.7 (d, <sup>2</sup>J(C,F) = 38.5 Hz), 141.1 (d, <sup>3</sup>J(C,F) = 10.0 Hz), 140.8, 140.6 (d, <sup>3</sup>J(C,F) = 8.1 Hz), 140.5, 140.3, 139.6, 129.96, 129.8, 129.6, 129.5, 129.4, 129.2, 129.0, 128.9, 128.7, 128.7, 128.3 (d, <sup>4</sup>J(C,F) = 2.7 Hz), 128.2 (d, <sup>4</sup>J(C,F) = 2.3 Hz), 127.7, 127.6, 119.0 (d, <sup>3</sup>J(C,F) = 13.1 Hz), 118.8 (d, <sup>3</sup>J(C,F) = 13.1 Hz), 116.9 (d, <sup>2</sup>J(C,F) = 20.4 Hz), 116.8 (d, <sup>2</sup>J(C,F) = 20.0 Hz), 85.5, 84.0, 56.0, 55.2, 52.0 (d, <sup>4</sup>J(C,F) = 1.9 Hz), 51.2 (d, <sup>4</sup>J(C,F) = 1.9 Hz), 49.4, 47.6, 29.2, 28.8, 28.0, 27.9 (d, <sup>ts</sup>J(C,F) = 7.9 Hz),, 27.5 (d, <sup>ts</sup>J(C,F) = 7.3 Hz), 27.0, 21.9 (d, <sup>4</sup>J(C,F) = 1.9 Hz), 21.9 (d, <sup>4</sup>J(C,F) = 1.9 Hz).

**<sup>19</sup>F{<sup>1</sup>H} NMR (376 MHz, CDCl<sub>3</sub>)**  $\delta$  = -114.36, -115.44, -151.88 (small), -151.93.

**<sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, CDCl<sub>3</sub>)**  $\delta$  = -1.00

**HRMS:** calc. for [M-BF<sub>4</sub>]<sup>+</sup> m/z: 462.25915 found 462.2600

<sup>1</sup> F. Vermersch, L. Oliveira, J. Hunter, M. Soleilhavoup, R. Jazzar, G. Bertrand, *J. Org. Chem.* **2022**, 87, 3511–3518 (for CAAC iminium) and M. Mauduit and H. Clavier et al. . *J. Am. Chem. Soc.* **2020**, 142, 1, 93–98 (for fluorinated aniline)

## b) Carbene insertion products 2a–b

In a glovebox, the iminium salt (**1<sup>H</sup>a** or **1<sup>H</sup>b**, 1 equiv.) and KHMDS (1.2 equiv.) were placed in a Schlenk tube and THF was added (ca. 5 ml for 100 mg of iminium salts). The Schlenk tube was then sealed, taken outside the glovebox and the reaction mixture was stirred at RT for 2h. All the volatiles were then removed under vacuum and the racemic mixture of products was isolated by column chromatography on silica (pentane/Et<sub>2</sub>O) at ambient conditions. Single crystals suitable for X-ray diffraction studies were received by slow evaporation of Et<sub>2</sub>O/EtOH solutions.

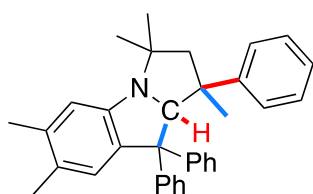
### 2a

Starting from 1g of **1<sup>H</sup>a** and 0.56 g of KHMDS in 50 ml of THF 759 mg of rac-**2a** was isolated in 87% yield as a white sticky solid in 75% dr.

**HRMS:** calc. for [M]<sup>+</sup> m/z: 457.2764 found 457.2762

Analytically pure samples for NMR studies were obtained after chiral HPLC separation.

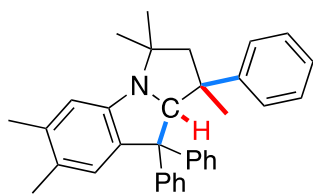
#### Major - **2a**



**<sup>1</sup>H NMR (400 MHz, 25°C, C<sub>6</sub>D<sub>6</sub>):** δ = 7.88 – 7.51 (m, 2H), 7.18 (d, J = 7.0 Hz, 2H), 7.10 – 7.02 (m, 2H), 7.00 (s, 1H), 6.99 – 6.93 (m, 6H), 6.92 – 6.86 (m, 1H), 6.85 – 6.81 (m, 2H), 6.63 (s, 1H), 5.59 (s, 1H, NCH), 2.32 (d, J = 13.1 Hz, 1H, CHH), 2.09 (s, 3H), 1.93 (s, 3H), 1.69 (d, J = 13.0 Hz, 1H, CHH), 1.57 (s, 3H), 1.53 (s, 3H), 0.93 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, 25°C, C<sub>6</sub>D<sub>6</sub>):** δ = 153.9, 147.1, 146.2, 141.2, 135.3, 133.7, 131.7, 128.5, 128.4, 128.2, 126.9, 126.9, 126.6, 126.2, 126.0, 125.5, 124.7, 111.6, 84.8, 64.5, 58.8, 58.4, 49.2, 32.5, 26.5, 20.6, 20.5, 19.4.

#### Minor - **2a'**

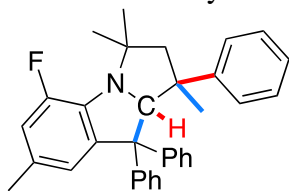


**<sup>1</sup>H NMR (400 MHz, 25°C, C<sub>6</sub>D<sub>6</sub>):** δ = 7.59 – 7.55 (m, 2H), 7.15 – 7.08 (m, 2H), 7.03 – 6.97 (m, 1H), 6.96 – 6.91 (m, 2H), 6.88 – 6.65 (m, 10H), 5.24 (s, 1H, NCH), 2.14 (d, J = 13.2 Hz, 1H, CHH), 2.11 (s, 3H), 1.93 (d, J = 13.2 Hz, 1H, CHH), 1.89 (s, 3H), 1.53 (s, 3H), 1.51 (s, 3H), 1.45 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, 25°C, C<sub>6</sub>D<sub>6</sub>):** δ = 150.3, 147.9, 146.0, 141.5, 137.7, 135.5, 131.6, 128.4, 128.2, 127.8, 127.5, 126.8, 126.3, 126.1, 125.9, 125.1, 112.2, 85.5, 62.3, 60.1, 58.3, 47.3, 31.0, 28.9, 27.8, 20.5, 19.5.

## 2b

Starting from 150 mg of **1<sup>H</sup>b** and 82 mg of KHMDS in 15ml of dry THF 99 mg of rac-**2b** was isolated in 78% yield as a colorless solid in 99% de.



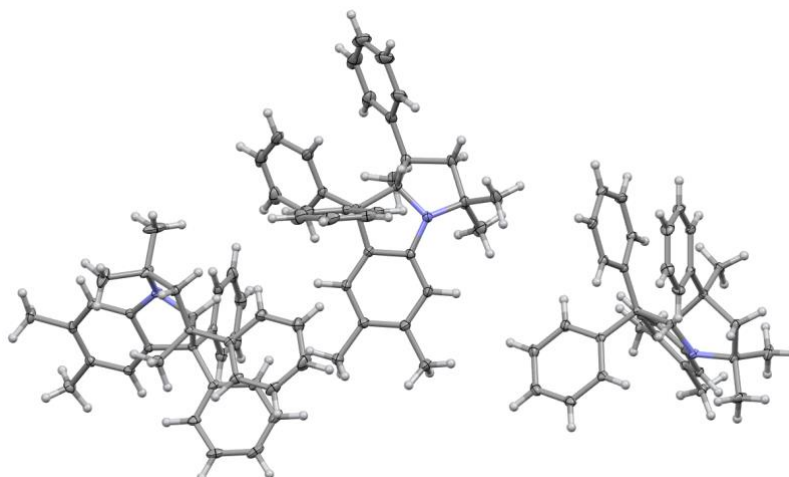
**<sup>1</sup>H NMR (400 MHz, 25°C, CDCl<sub>3</sub>):** δ 7.28-7.25 (m, 2H, overlapping with chloroform), 7.19 – 7.02 (m, 9H), 6.92 (broad m,  $J = 4.9$  Hz, 4H), 6.65 – 6.61 (m, 1H, 6-CH), 6.61 – 6.59 (m, 1H, 8-CH), 5.57 (s, 1H, NCH), 2.50 (d,  $J = 13.0$  Hz, 1H, CHH), 2.16 (s, 3H), 1.93 (d,  $J = 13.0$  Hz, 1H, CHH), 1.65 (s, 3H), 1.63 (d,  $J = 2.7$  Hz, 3H, 3-CH<sub>3</sub> proximate to F), 0.85 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, 25°C, CDCl<sub>3</sub>):** δ = 153.0, 148.1 (d,  $^1J(\text{C,F}) = 239.7$  Hz, C-F), 145.9, 140.3, 139.8 (d,  $^3J(\text{C,F}) = 5.4$  Hz, C<sub>Ar</sub>-CH<sub>3</sub>), 133.1 (d,  $^2J(\text{C,F}) = 11.6$  Hz, C<sub>Ar</sub>-N), 131.4, 128.2, 128.1, 127.7, 127.6, 126.8 (d,  $^3J(\text{C,F}) = 2.7$  Hz), 126.4, 126.2, 125.8, 125.6, 123.4 (d,  $^4J(\text{C,F}) = 2.3$  Hz), 115.7 (d,  $^2J(\text{C,F}) = 20.8$  Hz, C<sub>Ar</sub>-H), 85.7 (N-C-H), 64.7 (d,  $^4J(\text{C,F}) = 1.9$  Hz), 59.5, 59.2 (d,  $^4J(\text{C,F}) = 1.9$  Hz), 48.14 (CH<sub>2</sub>), 32.71 (d,  $^{\text{ts}}J(\text{C,F}) = 3.1$  Hz, CH<sub>3</sub>), 27.0 (d,  $^{\text{ts}}J = 11.9$  Hz, CH<sub>3</sub>), 20.8 (d,  $^4J(\text{C,F}) = 1.3$  Hz, p-CH<sub>3</sub>). 20.79 (α-CH<sub>3</sub>)

**<sup>19</sup>F{<sup>1</sup>H} NMR (376 MHz, CDCl<sub>3</sub>)** δ = -126.73.

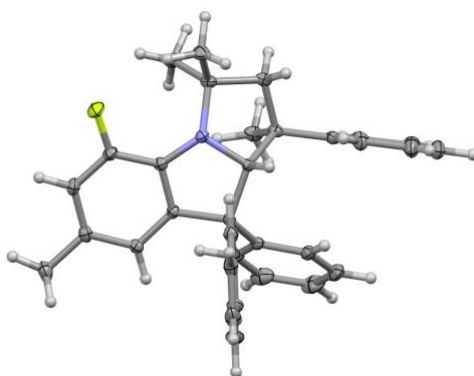
**HRMS:** calc. for [M+H]<sup>+</sup> C<sub>33</sub>H<sub>33</sub>N m/z: 462.25915, found 462.2589

### 3) Crystal data, data collection and structure refinement



#### Crystal data and structure refinement for (R,S)-2a .

CCDC/FIZ Karlsruhe	2252188
Empirical formula	C <sub>34</sub> H <sub>35</sub> N
Formula weight	457.63
Temperature/K	150.15
Crystal system	triclinic
Space group	P1
a/Å	9.3921(14)
b/Å	9.3835(14)
c/Å	23.426(3)
$\alpha$ /°	89.553(5)
$\beta$ /°	78.639(5)
$\gamma$ /°	72.282(5)
Volume/Å <sup>3</sup>	1925.1(5)
Z	3
$\rho_{\text{calc}}/\text{cm}^3$	1.184
$\mu/\text{mm}^{-1}$	0.507
F(000)	738.0
Crystal size/mm <sup>3</sup>	0.58 × 0.33 × 0.26
Radiation	CuK $\alpha$ ( $\lambda$ = 1.54184)
2 $\theta$ range for data collection/°	3.854 to 145.142
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -28 ≤ l ≤ 28
Reflections collected	28418
Independent reflections	12516 [R <sub>int</sub> = 0.0328, R <sub>sigma</sub> = 0.0411]
Data/restraints/parameters	12516/3/962
Goodness-of-fit on F <sup>2</sup>	1.038
Final R indexes [I ≥ 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0377, wR <sub>2</sub> = 0.0961
Final R indexes [all data]	R <sub>1</sub> = 0.0379, wR <sub>2</sub> = 0.0962
Largest diff. peak/hole / e Å <sup>-3</sup>	0.37/-0.27
Flack parameter	0.00(16)



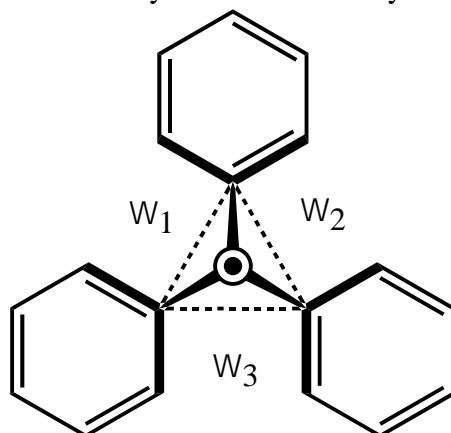
**Crystal data and structure refinement for (S,R)-2b.**

CCDC/FIZ Karlsruhe	2252189
Empirical formula	C <sub>33</sub> H <sub>32</sub> FN
Formula weight	461.59
Temperature/K	150(2)
Crystal system	monoclinic
Space group	P2 <sub>1</sub>
a/Å	9.1435(11)
b/Å	11.5310(15)
c/Å	12.3271(15)
α/°	90
β/°	102.293(4)
γ/°	90
Volume/Å <sup>3</sup>	1269.9(3)
Z	2
ρ <sub>calc</sub> /cm <sup>3</sup>	1.207
μ/mm <sup>-1</sup>	0.576
F(000)	492.0
Crystal size/mm <sup>3</sup>	0.34 × 0.27 × 0.19
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	11.002 to 161.48
Index ranges	-11 ≤ h ≤ 11, -14 ≤ k ≤ 13, -15 ≤ l ≤ 15
Reflections collected	18309
Independent reflections	5135 [R <sub>int</sub> = 0.0344, R <sub>sigma</sub> = 0.0344]
Data/restraints/parameters	5135/1/320
Goodness-of-fit on F <sup>2</sup>	1.058
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.0357, wR <sub>2</sub> = 0.0938
Final R indexes [all data]	R <sub>1</sub> = 0.0359, wR <sub>2</sub> = 0.0941
Largest diff. peak/hole / e Å <sup>-3</sup>	0.21/-0.19
Flack parameter	-0.06(6)



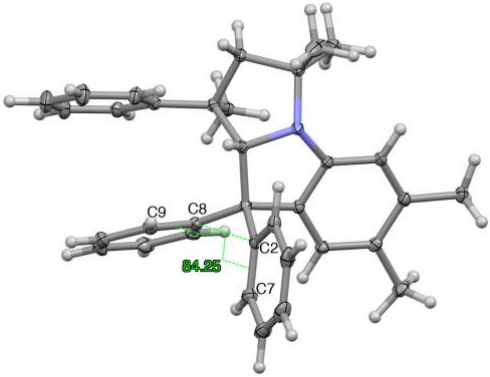
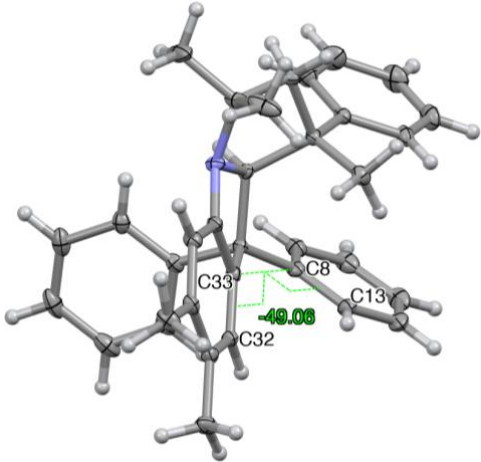
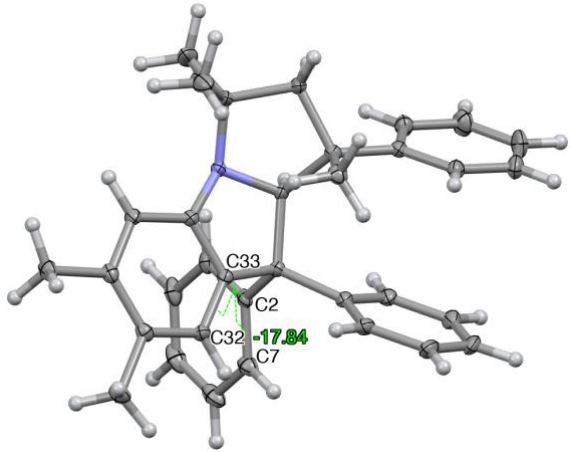
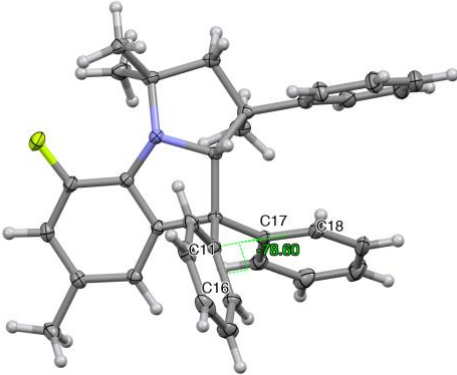
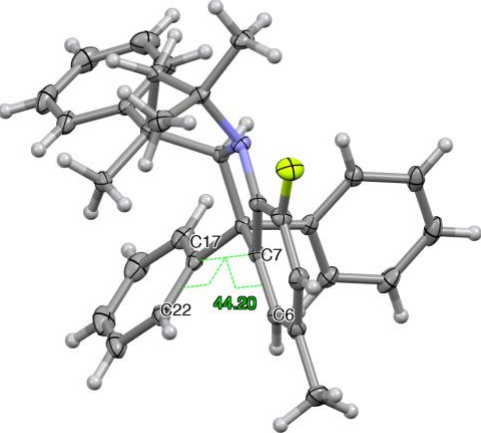
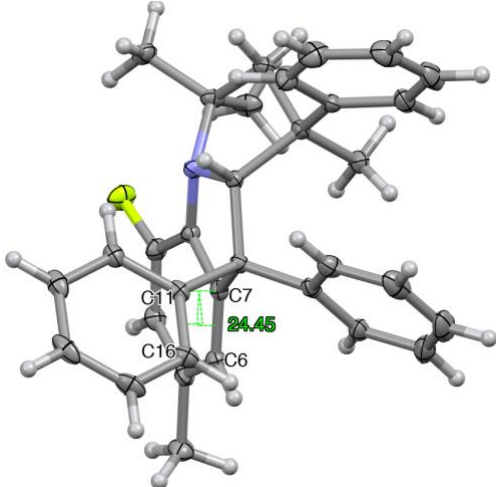
Assignment of propeller chirality:

Following Gawroński's work<sup>2</sup>, dihedral angles  $\omega_1$ ,  $\omega_2$ ,  $\omega_3$ , defined by the nearest C<sub>ipso</sub>-C<sub>ortho</sub> bonds in the two phenyl rings, connected by an imaginary bond between the two C<sub>ipso</sub> atoms were considered as most informative of trityl molecule helicity.

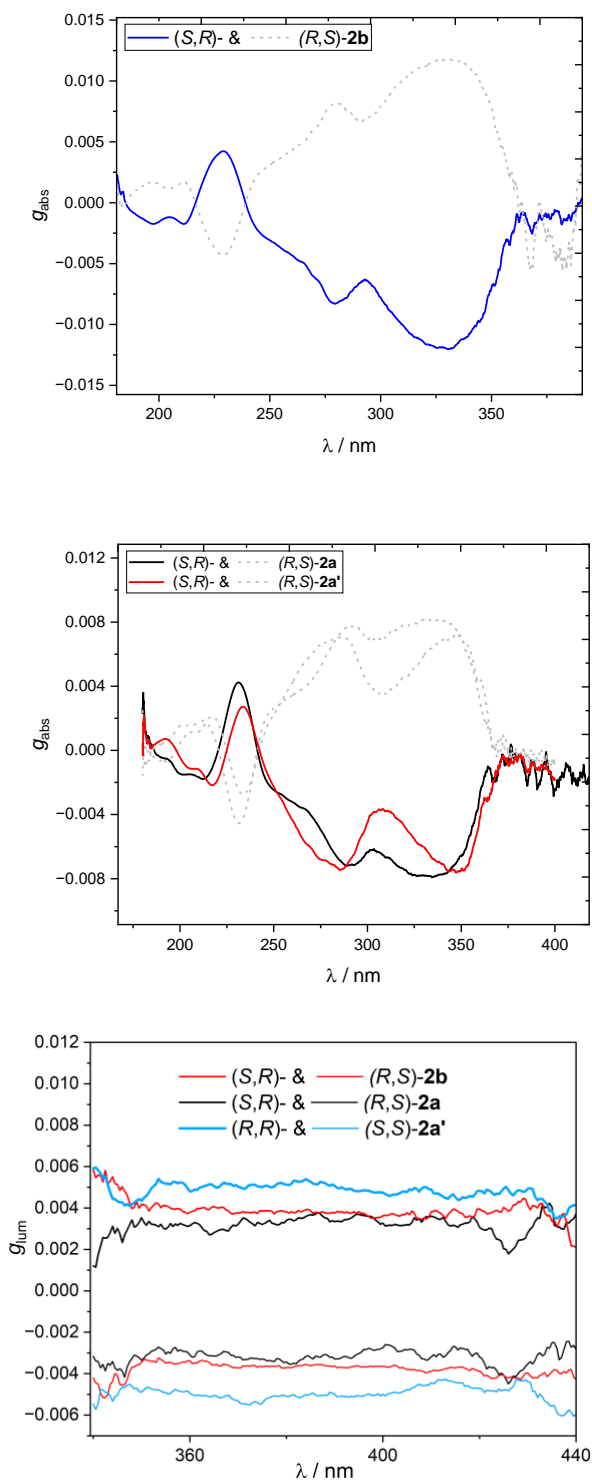


<sup>2</sup> J. Ściebura, P. Skowronek, J. Gawronski, *Angew. Chemie - Int. Ed.* **2009**, *48*, 7069–7072; *Angew. Chemie* **2009**, *121*, 7203–7206.

Table S1

	$\omega_1$ ( $^\circ$ )	$\omega_2$ ( $^\circ$ )	$\omega_3$ ( $^\circ$ )	Heli.
<b>(R,S)2a</b>	84	-49	-17	<b>P</b>
				
<b>(S,R)2b</b>	-78	44	24	<b>M</b>
				

#### 4) Additional photophysical data



**Figure S1.** *Top:* Absorption dissymmetry factor  $g_{\text{abs}}$  spectra of (S,R)-2b (solid blue line). *Middle:* (S,R)-2a and (S,R)-2a' (black and red solid lines, respectively), with their corresponding enantiomers in grey, recorded in dichloromethane solutions ( $\sim 10^{-6}$  M) at 298 K. *Bottom:*  $g_{\text{lum}}$  spectra of spectra of (S,R)- and (R,S)-2b (solid and dotted blue lines, respectively), (S,R)- and (R,S)-2a (solid and dotted black lines, respectively) and (R,R)- and (S,S)-2a' (solid and dotted red lines, respectively) measured in toluene ( $\sim 10^{-5}$  M) at 298 K.

**Table S2.** Experimental photophysical and chiroptical properties of compounds **2a**, **2a'** and **2b**, in toluene at room temperature, and in 2-Methyltetrahydrofuran at 77 K.

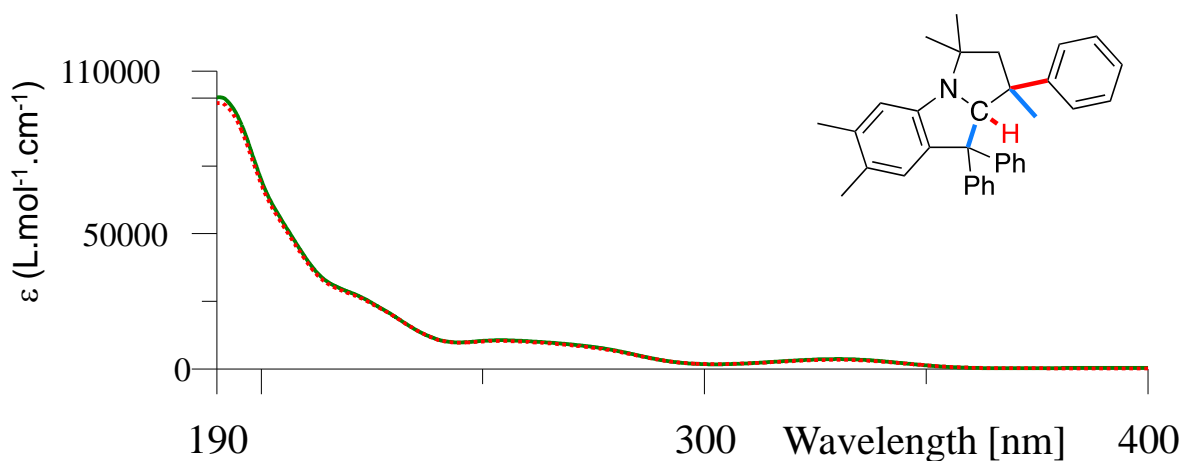
Compounds	$\epsilon / M^{-1} (\lambda_{exc})$	$\lambda_{em}$ Tol (nm) /	$\tau_{Fluo}^b$ [ns] / $\tau_{Phos}^c$	$ g_{lum}  (\times 10^{-3})$	$B_{CPL} (M^{-1} cm^{-1})^d$
		$\phi_{fluo}^a$ (%)	[s]	Tol	
<b>2b</b>	3610 (330 nm)	381 / 12	3.9 / 1.6	5.3	0.69
<b>2a</b>	2500 (330 nm)	384 / 10	5.1 / 2.4	3.8	0.80
<b>2a'</b>	2590 (330 nm)	381 / 6	4.6 / 3.4	3.5	0.27

<sup>a</sup> absolute fluorescence quantum yields were determined using an integrating sphere at room temperature in toluene solutions.

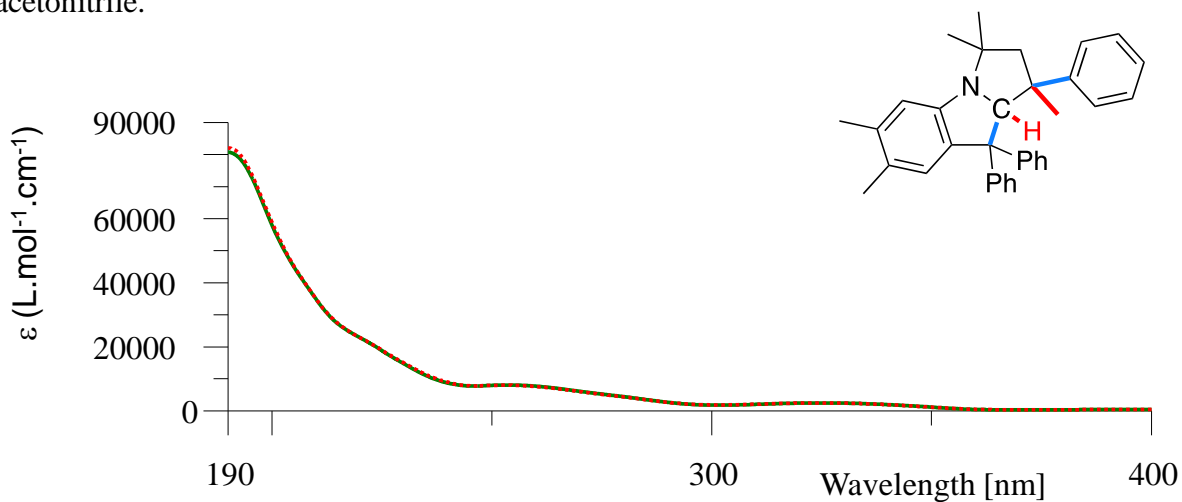
<sup>b</sup> measured at room temperature in toluene solutions.

<sup>c</sup> measured at 77 K in 2-MeTHF matrix.

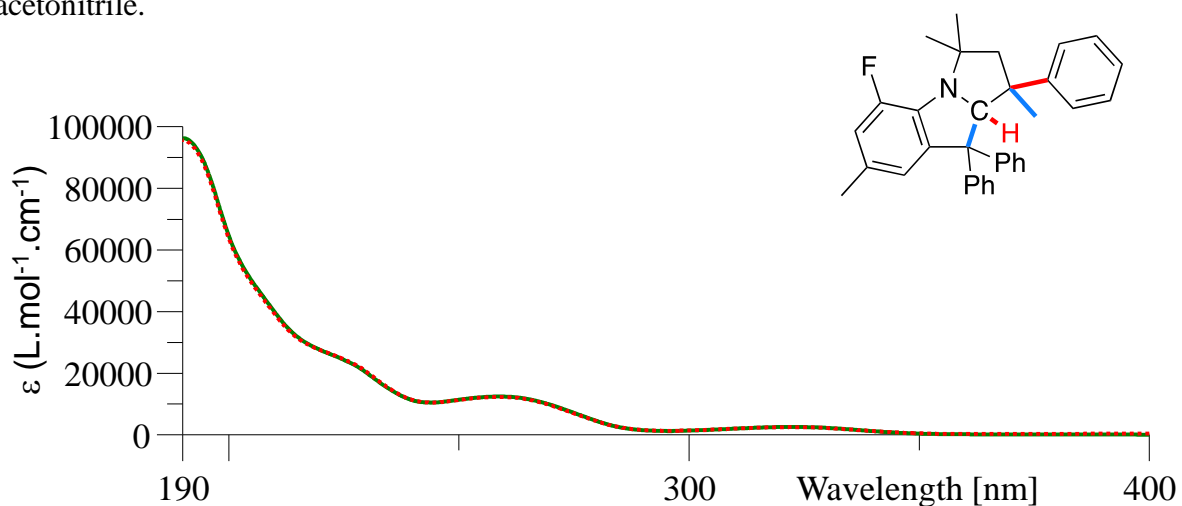
<sup>d</sup> calculated using the formula:  $B_{CPL} = \epsilon \times \phi \times g_{lum}/2$



**Fig. S2** UV-vis spectra of **(S,R)-2a** (green solid line) and **(R,S)-2a** (red dotted line) in acetonitrile.



**Fig. S3** UV-vis spectra of **(R,R)-2a'** (green solid line) and **(S,S)-2a'** (red dotted line) in acetonitrile.



**Fig. S4** UV-vis spectra of **(S,R)-2b** (green solid line) and **(R,S)-2b** (red dotted line) in acetonitrile.

## 5) Computational Details

The computations were performed with ORCA v5.03.<sup>3</sup>

All geometry optimizations were performed with the composite method r<sup>2</sup>SCAN-3c<sup>4</sup>, which includes D4-dispersion- and geometrical counter-poise (gCP) correction for the basis set superposition error (BSSE) at the triple- $\zeta$  level of theory. It allows for excellent accuracy at moderate computational demand for all-organic molecules as are the subject of the study herein. Solvation effects in dichloromethane were accounted for by the SMD model, yet the solvation evolved to not change the global minimum of the molecular conformational space.<sup>5</sup> The conformational scans (Fig. S5–S9), followed by localization of the respective ground- and transition states, were performed by twisting each of the three phenyl substituents. These structures were verified as true minima (1<sup>st</sup> order maxima, respectively) by the absence of (presence of only one, respectively) imaginary eigenvalues in the harmonic vibrational frequency analysis. Refinement of the electronic energies by computing DLPNO-CCSD(T)/def2-TZVPP single points (*normalpno* settings; SMD=DCM) afforded only minor deviations from the r<sup>2</sup>SCAN-3c results (Figs. S16, S17).<sup>6</sup>

For the calculation of the CD spectra of the global-minimum conformer, the cam-B3LYP<sup>7</sup> as well as the  $\omega$ B97X<sup>8</sup> functional were screened in combination with *tightscf* settings and the def2-TZVPP basis set (RIJCOSX: def2/J auxiliary basis set) within the framework of either conventional TD-DFT (without the Tamm-Dancoff approximation; *TDA False*, 35 roots), or simplified TD-DFT (sTD-DFT)<sup>9</sup>. For the latter, the default settings were chosen (*Ethresh 8.0; axstda 0.56*). Here, solvation effects in acetonitrile were included by the SMD model. Errors introduced by the RIJCOSX approximation were assessed to be negligible ( $\Delta E < 5 \text{ cm}^{-1}$ ). The sTD-DFT method with the cam-B3LYP functional evolved to be in best agreement with the experimental data (Fig. S13–S15), yet all approaches are in qualitative agreement with the experiment and reproduced the shapes of the experimental spectra. Plotted canonical orbitals relate as well to the cam-B3LYP functional. Orbitals and vectors were plotted with IBOView<sup>10</sup> and Chemcraft<sup>11</sup>. In Figure 6, the vectors are scaled by 1.89 for clarity.

The dissymmetry factors ( $g_{\text{abs}}$ ), transition electric- ( $\vec{\mu}_e$ ) and transition magnetic ( $\vec{\mu}_m$ ) dipole moment vectors as well as rotatory strengths ( $R$ ) were calculated as described in much detail elsewhere.<sup>12</sup> Specifically,  $g_{\text{abs}}$  was calculated from the vector norms  $|\mu_e|$  and  $|\mu_m|$  of the transition electric- and transition magnetic dipole moment vectors  $\vec{\mu}_e$  and  $\vec{\mu}_m$ , respectively, as well as the angle  $\theta$  between the two:

$$g_{\text{abs}} = \frac{4 \cos\theta_{e,m} |\mu_e| |\mu_m|}{|\mu_e|^2 + |\mu_m|^2} \quad (\text{equation S1})$$

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

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

<sup>3</sup> Neese, F. *WIREs Comput. Mol. Sci.* **2012**, 2, 73; b) Neese, F. *WIREs Comput. Mol. Sci.* **2018**, 8, e1327; c) Neese, F.; Wennmohs, F.; Becker, U.; Riplinger, C. *J. Chem. Phys.* **2020**, 152, 224108; d) Neese, F. *WIREs Comput. Mol. Sci.* **2022**;12:e1606.

<sup>4</sup> Grimme, S.; Hansen, A.; Ehlert, S.; Mewes, J.-M. *J. Chem. Phys.* **2021**, 154, 064103.

<sup>5</sup> Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *Phys. Chem. B* **2009**, 113, 6378.

<sup>6</sup> a) Riplinger, C.; Neese, F. *J. Chem. Phys.* **2013**, 138, 034106; b) Riplinger, C.; Sandhoefer, B.; Hansen, A.; Neese, F. *J. Chem. Phys.* **2013**, 139, 134101; c) Neese, F.; Hansen, A.; Wennmohs, F.; Grimme, S. *Acc. Chem. Res.* **2009**, 42, 641; d) Hansen, A.; Liakos, D. G.; Neese, F. *J. Chem. Phys.* **2011**, 135, 214102; e) Liakos, D. G.; Hansen, A.; Neese, F. *J. Chem. Theory Comput.* **2011**, 7, 76–87; f) Neese, F.; Hansen, A.; Liakos, D. G. *J. Chem. Phys.* **2009**, 131, 064103.

<sup>7</sup> Yanai, T.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett.* **2004**, 393, 51.

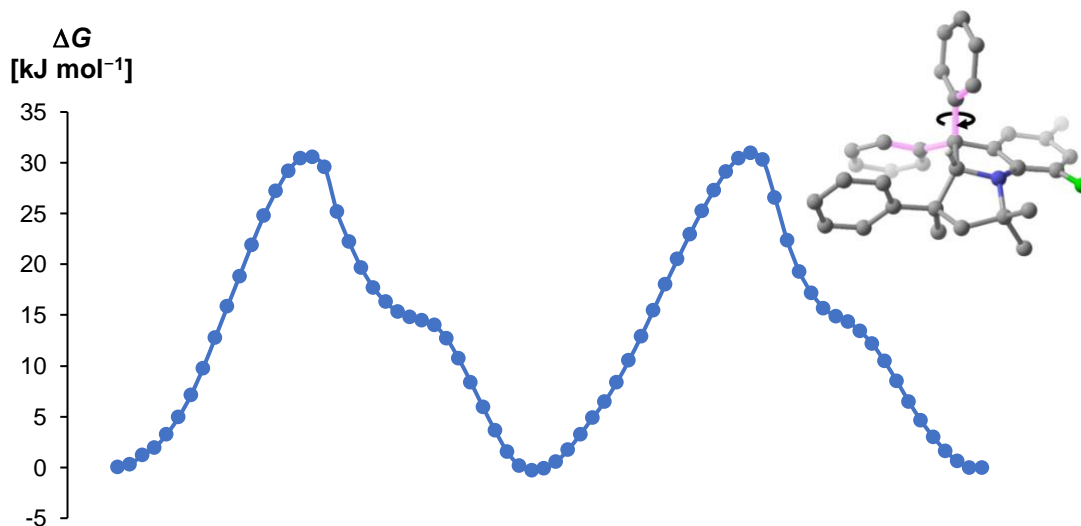
<sup>8</sup> Chai, J.-D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, 10, 6615.

<sup>9</sup> a) Grimme, S. *J. Chem. Phys.* **2013**, 138, 244104; b) Bannwarth, C.; Grimme, S. *Comp. Theor. Chem.* **2014**, 45-53, 1040-1041; c) Wergifosse, M.d.; Seibert, J.; Grimme, S. *J. Chem. Phys.* **2020**, 153, 084116.

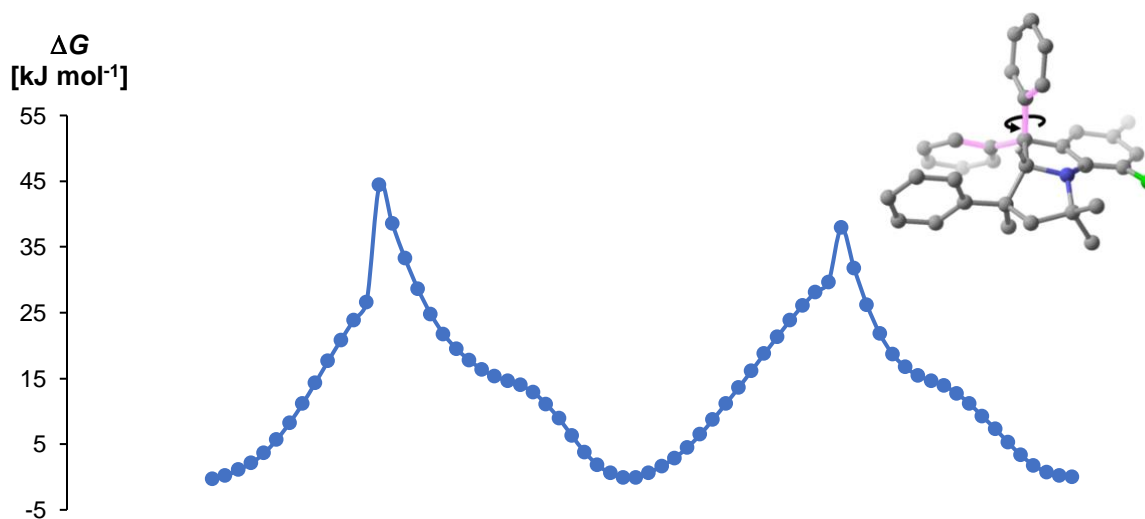
<sup>10</sup> Knizia, G. *J. Chem. Theory Comput.* **2013**, 9, 4834.

<sup>11</sup> <https://www.chemcraftprog.com>

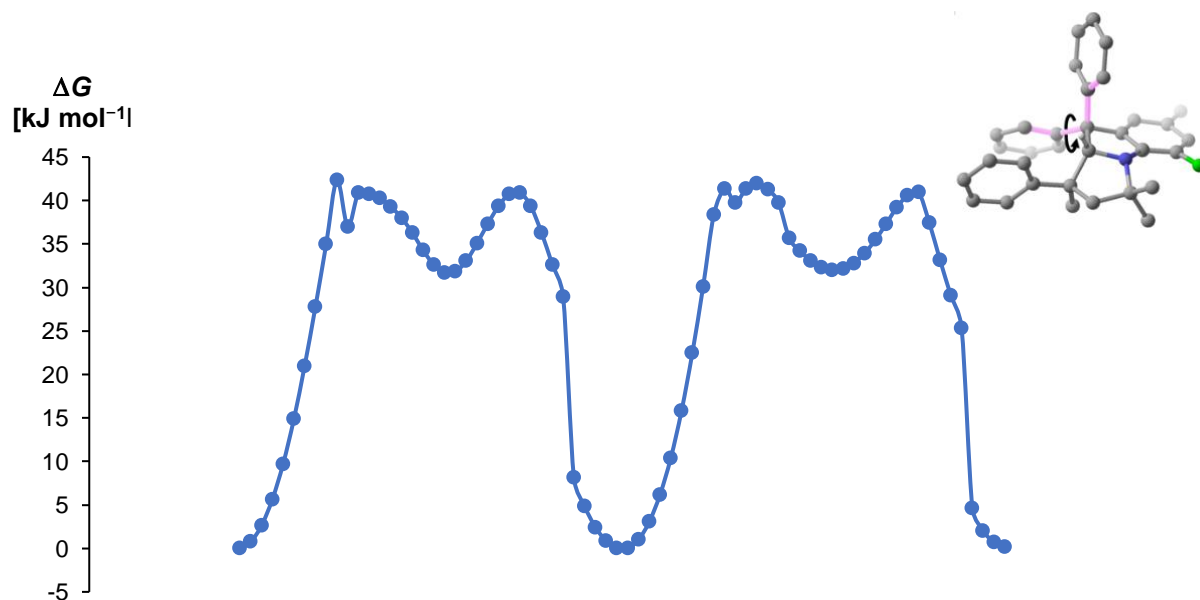
<sup>12</sup> Kubo, H.; Hirose, T.; Nakashima, T.; Kawai, T.; Hasegawa, J.; Matsuda, K. *J. Phys. Chem. Lett.* **2021**, 12, 1, 686.



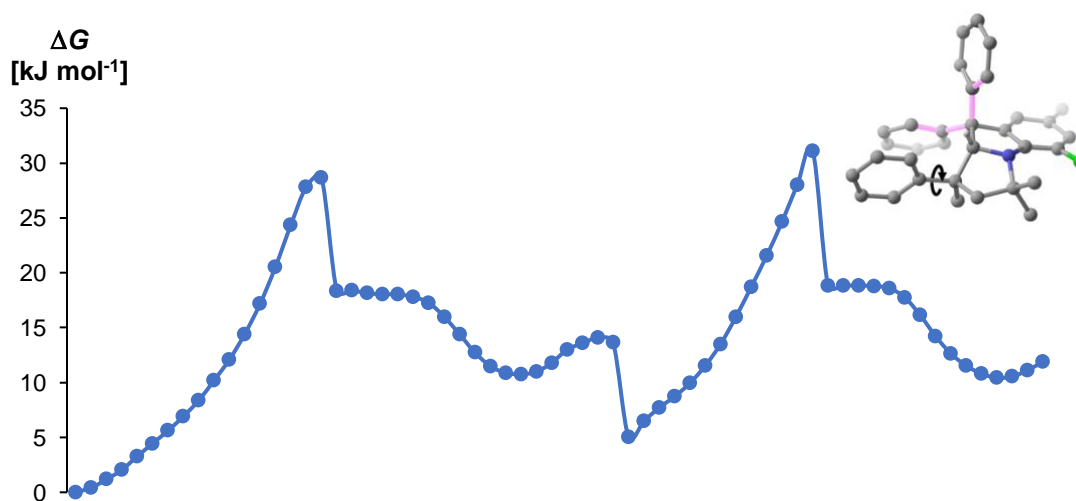
**Fig. S5.** The clockwise rotation of the axial phenyl ring in (S,R)-2b does not lead to a gear. The barrier for gear-slippage is +30  $\text{kJ mol}^{-1}$ .



**Fig. S6.** The anticlockwise rotation of the axial phenyl ring in (S,R)-2b does not lead to a gear. The barrier for gear-slippage is +44  $\text{kJ mol}^{-1}$ .

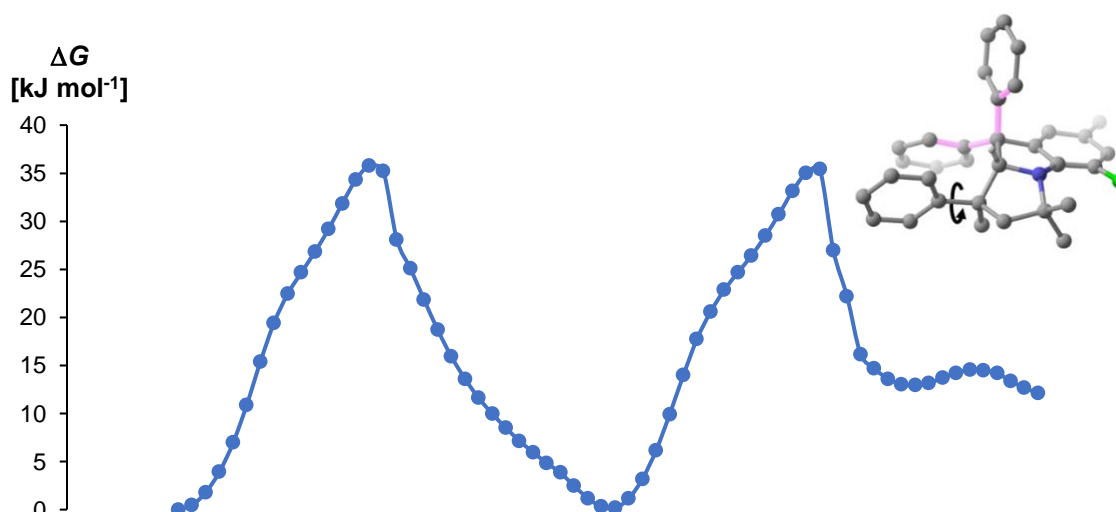


**Fig. S7.** The anti-clockwise rotation of the equatorial phenyl ring 2 in  $(S, R)$ -**2b** does not lead to a gear. The barrier for gear-slippage is  $+42 \text{ kJ mol}^{-1}$ .

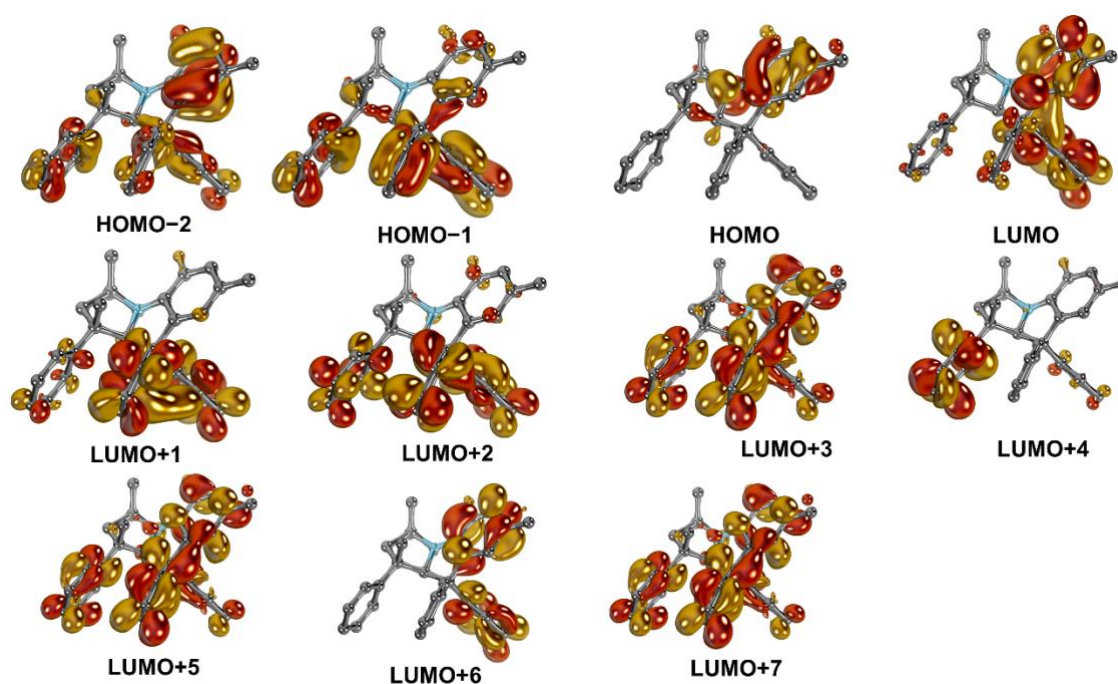


**Fig. S8.** The clockwise rotation of the phenyl ring attached to the CAAC-scaffold in  $(S, R)$ -**2b** does not lead to a gear, yet flips the axial/equatorial positions of the adjacent two phenyl groups.





**Fig. S9.** The anti-clockwise rotation of the phenyl ring attached to the CAAC-scaffold in (*S*, *R*)-**2b** does not lead to a gear, yet flips the axial/equatorial positions of the adjacent two phenyl groups.



**Fig. S10.** Canonical orbitals in (*S*, *R*)-**2b**.

S1 Transition	0.78 ( 77-> 78)	0.08 ( 77-> 84)	0.03 ( 77-> 85)
S2 Transition	0.20 ( 77-> 83)	0.15 ( 77-> 79)	0.13 ( 77-> 80)
S10 Transition ...	0.47 ( 76-> 78)	0.15 ( 77-> 83)	0.15 ( 75-> 78)
S17 Transition ...	0.11 ( 75-> 83)	0.11 ( 75-> 85)	0.09 ( 69-> 78)

**Fig. S11.** Nature of selected electronic transitions in (*S*, *R*)-**2b** according to sTD-DFT calculations.

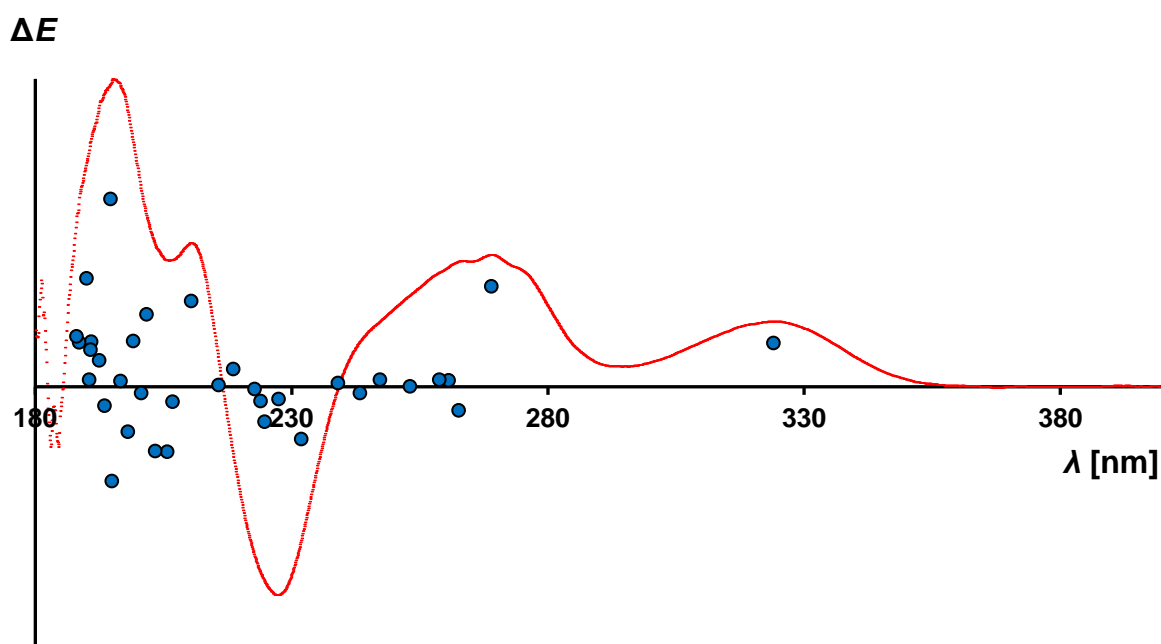
**S1**

122a -> 123a : 0.799937  
122a -> 126a : 0.029272  
122a -> 129a : 0.086607  
122a -> 130a : 0.016265

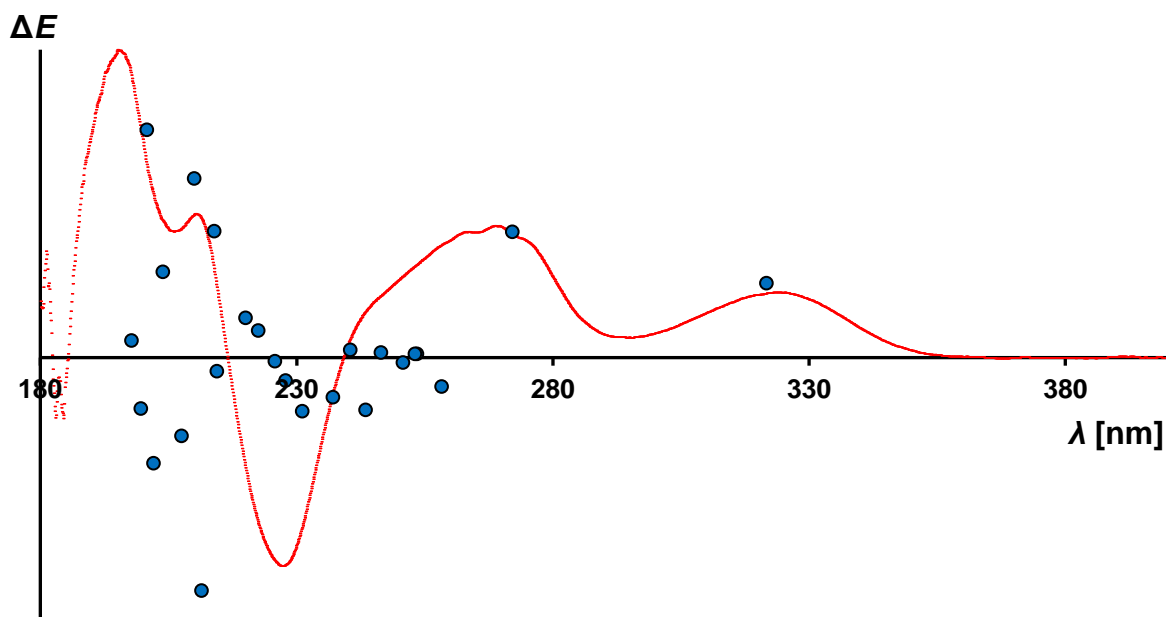
**S2**

120a -> 123a : 0.044257  
121a -> 123a : 0.016343  
122a -> 123a : 0.024976  
122a -> 124a : 0.124144  
122a -> 125a : 0.118353  
122a -> 127a : 0.059829  
122a -> 128a : 0.285643  
122a -> 130a : 0.229762

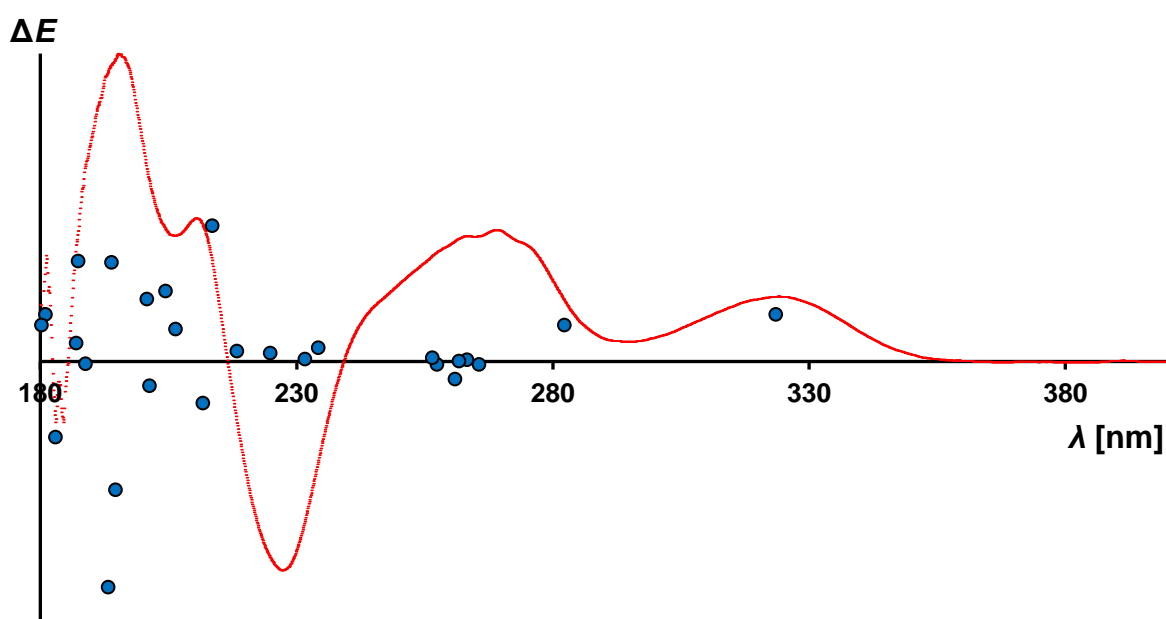
**Fig. S12.** Nature of selected electronic transitions in (*S,R*)-**2b** according to TD-DFT calculations.



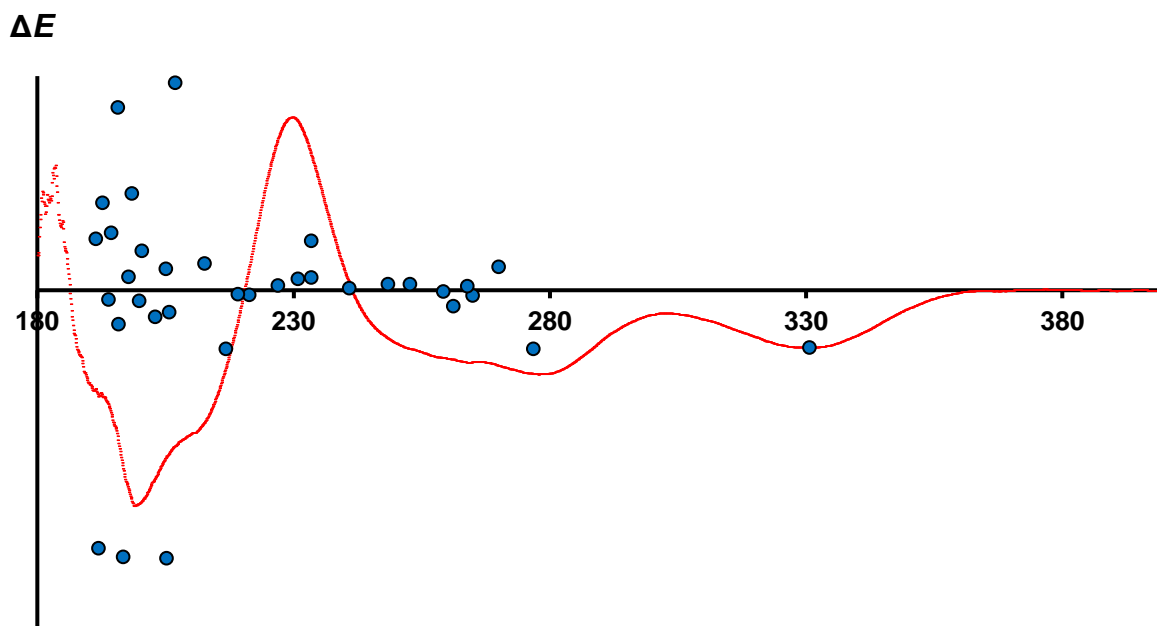
**Fig. S13.** Fit of experimental CD spectrum (red line) with computed transitions (blue dots; sTD-DFT, cam-B3LYP) of (*S,R*)-**2b**. Computed values are scaled by  $+2500 \text{ cm}^{-1}$ , relative intensities  $\Delta E$  are adjusted for clarity.



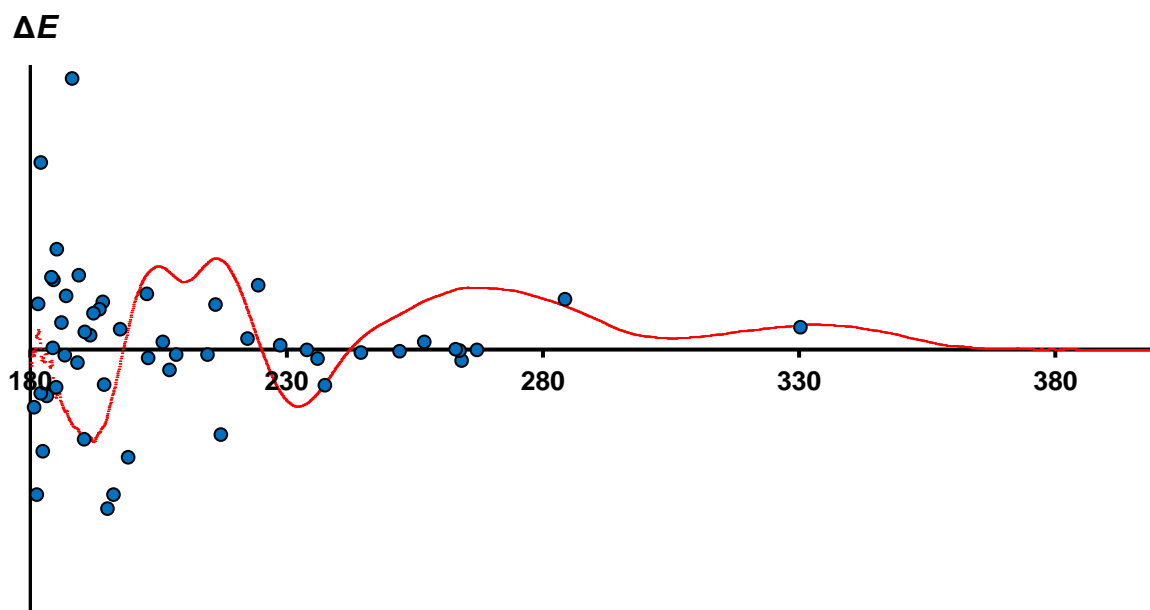
**Fig. S14.** Fit of experimental CD spectrum (red line) with computed transitions (blue dots; TD-DFT, cam-B3LYP) of (*S,R*)-**2b**. Computed values are scaled by  $-3500 \text{ cm}^{-1}$ , relative intensities  $\Delta E$  are adjusted for clarity.



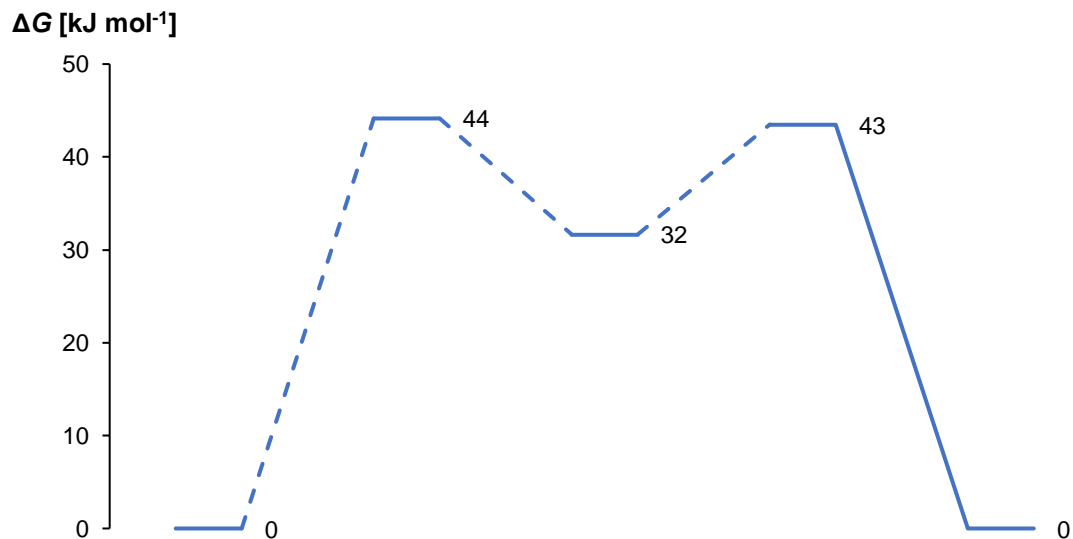
**Fig. S15.** Fit of experimental CD spectrum (red line) with computed transitions (blue dots; sTD-DFT,  $\omega$ B97X) of (*S,R*)-**2b**. Computed values are scaled by  $-5000 \text{ cm}^{-1}$ , relative intensities  $\Delta E$  are adjusted for clarity.



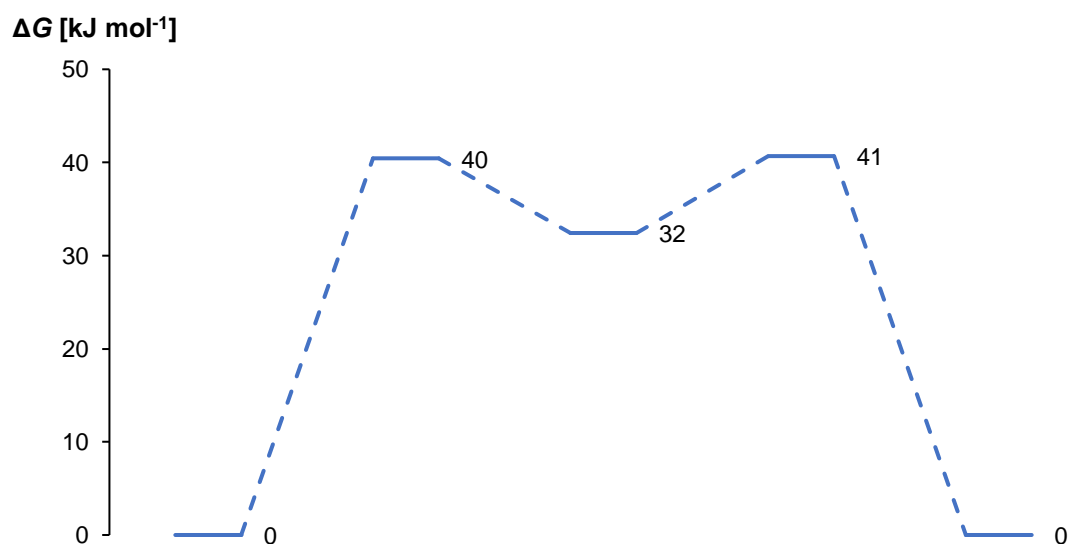
**Fig. S16.** Fit of experimental CD spectrum (red line) with computed transitions (blue dots; sTD-DFT, cam-B3LYP) of **(*R,S*)-2a**. Computed values are scaled by  $+2000 \text{ cm}^{-1}$ , relative intensities  $\Delta E$  are adjusted for clarity.



**Fig. S17.** Fit of experimental CD spectrum (red line) with computed transitions (blue dots; sTD-DFT, cam-B3LYP) of **(*R,R*)-2a'**. Computed values are scaled by  $+2000 \text{ cm}^{-1}$ , relative intensities  $\Delta E$  are adjusted for clarity.



**Fig. S18.** Reaction energy profile at the DLPNO-CCSD(T)/def2-TZVPP(SMD=DCM)//r<sup>2</sup>SCAN-3c(SMD=DCM) level of theory for rotational mode of (*S,R*)-**2b** depicted in Fig. 4.



**Fig. S19.** Reaction energy profile at the r<sup>2</sup>SCAN-3c(SMD=DCM) level of theory for rotational mode of (*S,R*)-**2b** depicted in Fig. 4.

**Table S3.** Energies.

	<i>Imag</i>	<i>E</i> [Eh]	<i>G</i> [Eh]	$\Delta G$ [kJ mol <sup>-1</sup> ]	<i>E</i> <sub>CCSD(T)</sub> [Eh]	<i>G</i> <sub>CCSD(T)</sub> [Eh]	$\Delta G$ [kJ mol <sup>-1</sup> ]
<b>gs1</b>	n.a.	-1431.10037	-1430.59598	0.0	-1428.85907	-1428.35467	0.0
<b>ts1</b>	i47	-1431.08454	-1430.57916	44.1	-1428.84464	-1428.33926	40.5
<b>gs2</b>	n.a.	-1431.08817	-1430.58392	31.7	-1428.84657	-1428.34233	32.4
<b>ts2</b>	i53	-1431.08464	-1430.57935	43.7	-1428.84441	-1428.33912	40.8

## XYZ Coordinates

67

GS1

7	-6.123654000	-5.965350000	-0.196453000
6	-5.480851000	-4.790960000	0.174363000
6	-5.553283000	-4.055001000	1.355203000
6	-4.874567000	-2.859159000	1.517577000
1	-4.952756000	-2.344766000	2.472278000
6	-4.138563000	-2.308684000	0.463431000
6	-4.144271000	-2.977487000	-0.766980000
1	-3.654041000	-2.524025000	-1.624641000
6	-4.797841000	-4.192283000	-0.900596000
9	-6.363287000	-4.470349000	2.371514000
6	-3.375066000	-1.026345000	0.650051000
1	-3.889823000	-0.352183000	1.342231000
1	-2.376277000	-1.216717000	1.064050000
1	-3.239669000	-0.505106000	-0.302638000
6	-5.169314000	-4.949919000	-2.172197000
6	-4.089298000	-5.172567000	-3.223184000
6	-2.741481000	-4.889246000	-3.008009000
1	-2.416701000	-4.494540000	-2.050480000
6	-1.795495000	-5.127590000	-4.004995000
1	-0.749516000	-4.901356000	-3.815142000
6	-2.185232000	-5.650881000	-5.233496000
1	-1.447766000	-5.835490000	-6.010022000
6	-3.531767000	-5.932826000	-5.460980000
1	-3.850897000	-6.343328000	-6.415386000
6	-4.471279000	-5.691783000	-4.466429000
1	-5.519829000	-5.907421000	-4.655538000
6	-6.307952000	-4.095841000	-2.783742000
6	-7.654194000	-4.285373000	-2.458989000
1	-7.955591000	-5.079269000	-1.783589000
6	-8.637861000	-3.442303000	-2.977034000
1	-9.678018000	-3.613331000	-2.712109000
6	-8.296277000	-2.392380000	-3.821950000
1	-9.064643000	-1.739779000	-4.227504000
6	-6.954807000	-2.184815000	-4.139109000
1	-6.668344000	-1.365912000	-4.793850000
6	-5.975172000	-3.024985000	-3.623307000
1	-4.934405000	-2.849700000	-3.881464000
6	-5.733976000	-6.288422000	-1.589444000
6	-4.870359000	-7.583865000	-1.452267000
6	-4.814812000	-8.413026000	-2.732865000
6	-3.613637000	-8.930602000	-3.229366000
1	-2.679884000	-8.746689000	-2.709884000
6	-3.578138000	-9.679897000	-4.404831000
1	-2.626190000	-10.061589000	-4.765087000
6	-4.745967000	-9.934148000	-5.114614000
1	-4.718528000	-10.512024000	-6.034466000
6	-5.955054000	-9.445932000	-4.622496000
1	-6.881028000	-9.643962000	-5.156340000
6	-5.987765000	-8.705373000	-3.446497000
1	-6.950275000	-8.348847000	-3.089979000
6	-5.739307000	-8.301546000	-0.388893000
1	-5.178504000	-9.094865000	0.114297000
1	-6.605986000	-8.762674000	-0.874625000
6	-6.230015000	-7.221561000	0.616584000
6	-7.697800000	-7.460127000	0.979876000
1	-8.325286000	-7.448872000	0.081813000
1	-7.815068000	-8.434729000	1.468710000

1	-8.058424000	-6.686257000	1.666408000
6	-5.386388000	-7.239186000	1.896159000
1	-5.806410000	-6.598824000	2.672374000
1	-5.383915000	-8.262810000	2.284317000
1	-4.347640000	-6.946644000	1.726431000
1	-6.623922000	-6.564273000	-2.166141000
6	-3.476736000	-7.305270000	-0.875451000
1	-3.519301000	-6.542292000	-0.096622000
1	-2.784265000	-6.944976000	-1.636183000
1	-3.055971000	-8.214370000	-0.432003000

**67**  
**TS1**

7	-6.259323000	-5.946943000	-0.378263000
6	-5.587567000	-4.843511000	0.127986000
6	-5.788368000	-4.179590000	1.334451000
6	-4.986149000	-3.126541000	1.733730000
1	-5.163563000	-2.669045000	2.703842000
6	-3.984224000	-2.657733000	0.883083000
6	-3.882918000	-3.209986000	-0.402352000
1	-3.165023000	-2.757589000	-1.072107000
6	-4.693958000	-4.268113000	-0.795285000
9	-6.836253000	-4.528712000	2.134875000
6	-3.057952000	-1.557287000	1.322928000
1	-3.561673000	-0.859317000	1.999371000
1	-2.190380000	-1.961845000	1.860441000
1	-2.677441000	-0.993069000	0.465858000
6	-5.053296000	-4.867320000	-2.158669000
6	-3.999158000	-4.918795000	-3.268363000
6	-3.070538000	-3.887610000	-3.460309000
1	-3.054982000	-3.026588000	-2.809121000
6	-2.172685000	-3.907838000	-4.524358000
1	-1.461936000	-3.092834000	-4.632636000
6	-2.195003000	-4.946084000	-5.450373000
1	-1.494026000	-4.961818000	-6.280469000
6	-3.151445000	-5.945381000	-5.310565000
1	-3.215513000	-6.749640000	-6.039039000
6	-4.042343000	-5.922547000	-4.241071000
1	-4.788431000	-6.701402000	-4.180459000
6	-6.225491000	-4.013687000	-2.750261000
6	-6.589041000	-2.772171000	-2.225340000
1	-6.069219000	-2.372249000	-1.361138000
6	-7.622662000	-2.028029000	-2.795328000
1	-7.885496000	-1.066008000	-2.363150000
6	-8.313940000	-2.510232000	-3.900038000
1	-9.120204000	-1.931336000	-4.342240000
6	-7.957526000	-3.746958000	-4.435060000
1	-8.483839000	-4.140399000	-5.300758000
6	-6.925219000	-4.485675000	-3.868778000
1	-6.662444000	-5.440201000	-4.315941000
6	-5.695264000	-6.251084000	-1.723499000
6	-4.871557000	-7.570868000	-1.505286000
6	-4.750802000	-8.482520000	-2.726612000
6	-3.531407000	-9.042925000	-3.118193000
1	-2.622522000	-8.814307000	-2.572997000
6	-3.445719000	-9.886249000	-4.225623000
1	-2.481325000	-10.303022000	-4.504761000
6	-4.578216000	-10.186814000	-4.973376000
1	-4.510606000	-10.837796000	-5.840717000
6	-5.804749000	-9.646377000	-4.589406000

1	-6.703348000	-9.874725000	-5.156725000
6	-5.889195000	-8.817742000	-3.476901000
1	-6.861459000	-8.416180000	-3.202624000
6	-5.816332000	-8.281606000	-0.502040000
1	-5.272780000	-9.037582000	0.072986000
1	-6.608785000	-8.796763000	-1.052532000
6	-6.448329000	-7.210409000	0.417813000
6	-7.946097000	-7.464428000	0.596458000
1	-8.455752000	-7.445215000	-0.373091000
1	-8.116198000	-8.445354000	1.056185000
1	-8.394916000	-6.699959000	1.240037000
6	-5.758089000	-7.234160000	1.787963000
1	-6.248782000	-6.593924000	2.520739000
1	-5.815308000	-8.259934000	2.165888000
1	-4.700371000	-6.963068000	1.731693000
1	-6.516290000	-6.483663000	-2.408303000
6	-3.513933000	-7.270553000	-0.864673000
1	-3.627899000	-6.594084000	-0.016606000
1	-2.833425000	-6.790163000	-1.575422000
1	-3.041656000	-8.187145000	-0.495665000

**67**  
**GS2**

7	-6.195575000	-5.934349000	-0.348258000
6	-5.462444000	-4.863902000	0.141596000
6	-5.524258000	-4.195900000	1.362257000
6	-4.669980000	-3.148333000	1.666941000
1	-4.741488000	-2.692566000	2.651517000
6	-3.752901000	-2.681139000	0.722613000
6	-3.778126000	-3.247681000	-0.560049000
1	-3.128092000	-2.844378000	-1.330732000
6	-4.637389000	-4.294204000	-0.844655000
9	-6.478891000	-4.524123000	2.280019000
6	-2.778185000	-1.589655000	1.069977000
1	-3.198124000	-0.899043000	1.808301000
1	-1.856352000	-2.004158000	1.498611000
1	-2.495253000	-1.015560000	0.182191000
6	-5.051897000	-4.894693000	-2.180310000
6	-3.962791000	-4.817390000	-3.249897000
6	-3.624948000	-3.540370000	-3.729863000
1	-4.158120000	-2.669310000	-3.359713000
6	-2.638360000	-3.366890000	-4.692132000
1	-2.398343000	-2.364829000	-5.037687000
6	-1.973642000	-4.470808000	-5.224248000
1	-1.207500000	-4.339240000	-5.983514000
6	-2.320211000	-5.741598000	-4.783318000
1	-1.831831000	-6.619086000	-5.199647000
6	-3.303590000	-5.909693000	-3.807471000
1	-3.560864000	-6.914483000	-3.509641000
6	-6.267816000	-4.096192000	-2.737790000
6	-6.840304000	-3.007356000	-2.083792000
1	-6.437191000	-2.666460000	-1.134927000
6	-7.931581000	-2.338186000	-2.641494000
1	-8.362873000	-1.490772000	-2.115007000
6	-8.463678000	-2.748290000	-3.858189000
1	-9.311571000	-2.224786000	-4.291572000
6	-7.896082000	-3.837856000	-4.519398000
1	-8.298584000	-4.167887000	-5.473526000
6	-6.810550000	-4.502429000	-3.963250000
1	-6.368691000	-5.344788000	-4.492230000



6	-5.691385000	-6.267281000	-1.715439000
6	-4.968160000	-7.640995000	-1.512201000
6	-4.885342000	-8.527146000	-2.755950000
6	-3.772474000	-9.343504000	-2.993526000
1	-2.928638000	-9.327170000	-2.312045000
6	-3.709917000	-10.176206000	-4.109505000
1	-2.829160000	-10.793809000	-4.265387000
6	-4.761068000	-10.216040000	-5.018778000
1	-4.710813000	-10.859336000	-5.892970000
6	-5.883948000	-9.424492000	-4.787689000
1	-6.720085000	-9.448793000	-5.481760000
6	-5.947969000	-8.600565000	-3.669048000
1	-6.848804000	-8.013591000	-3.516943000
6	-6.012054000	-8.286172000	-0.562855000
1	-5.587605000	-9.144183000	-0.033199000
1	-6.855807000	-8.647683000	-1.160901000
6	-6.506813000	-7.189201000	0.413514000
6	-8.020147000	-7.289735000	0.614825000
1	-8.542653000	-7.191925000	-0.342899000
1	-8.282400000	-8.259295000	1.055162000
1	-8.374115000	-6.500177000	1.286783000
6	-5.804189000	-7.326508000	1.770493000
1	-6.255596000	-6.694964000	2.535367000
1	-5.914021000	-8.364653000	2.099390000
1	-4.735058000	-7.106705000	1.719319000
1	-6.551068000	-6.455473000	-2.362445000
6	-3.617987000	-7.479233000	-0.802757000
1	-3.682872000	-6.725478000	-0.017200000
1	-2.829254000	-7.156116000	-1.488089000
1	-3.302866000	-8.417892000	-0.335177000

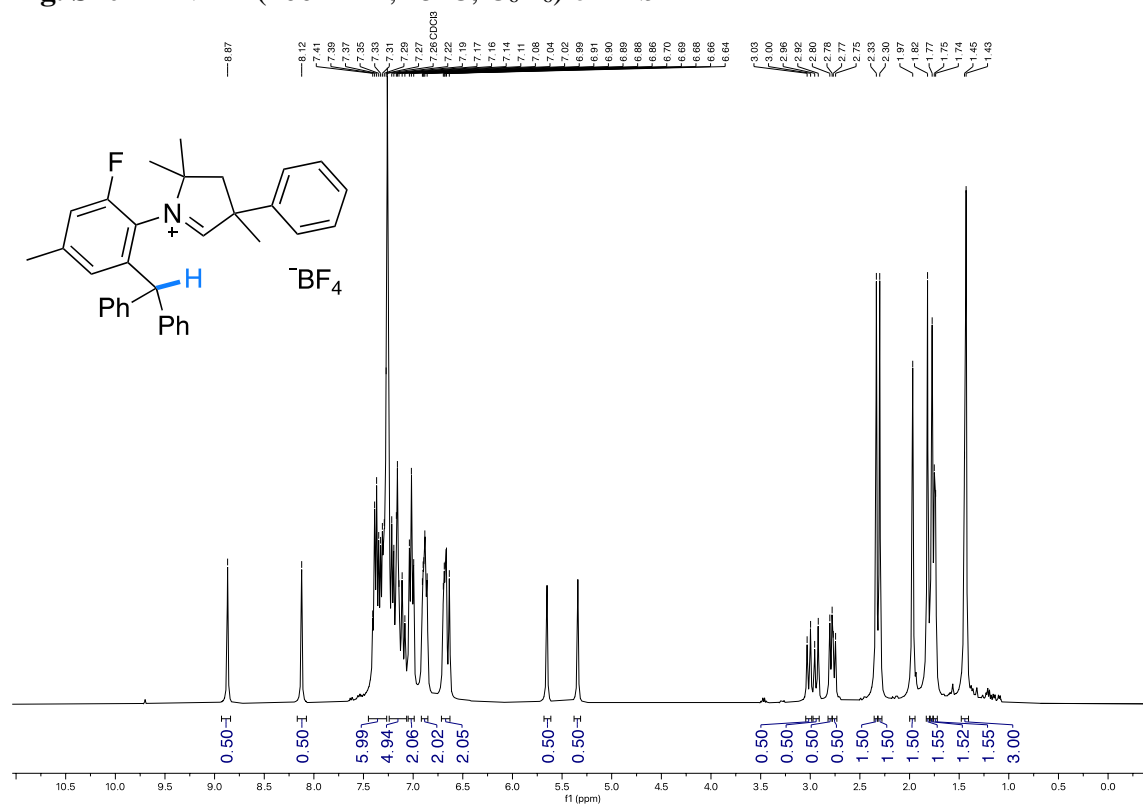
**67  
TS2**

7	-6.225641000	-5.897022000	-0.344588000
6	-5.363513000	-4.923967000	0.160692000
6	-5.234997000	-4.308069000	1.402611000
6	-4.280782000	-3.325978000	1.641003000
1	-4.211815000	-2.918666000	2.646813000
6	-3.444478000	-2.864680000	0.624615000
6	-3.633929000	-3.388193000	-0.663604000
1	-3.058190000	-3.002188000	-1.502513000
6	-4.576520000	-4.371875000	-0.877065000
9	-6.063512000	-4.625811000	2.437055000
6	-2.384114000	-1.833646000	0.896671000
1	-2.605245000	-1.263928000	1.804284000
1	-1.401061000	-2.302903000	1.032984000
1	-2.293335000	-1.130755000	0.061962000
6	-5.110651000	-4.907334000	-2.191999000
6	-4.093930000	-4.889470000	-3.338210000
6	-4.246280000	-4.029729000	-4.434523000
1	-5.115616000	-3.386805000	-4.508370000
6	-3.291363000	-3.969749000	-5.448222000
1	-3.445050000	-3.290942000	-6.282933000
6	-2.152775000	-4.764998000	-5.393737000
1	-1.410429000	-4.723848000	-6.186192000
6	-1.972927000	-5.605767000	-4.299071000
1	-1.084415000	-6.227442000	-4.224561000
6	-2.925117000	-5.654781000	-3.286763000
1	-2.742479000	-6.298884000	-2.441175000
6	-6.360699000	-4.075896000	-2.591853000

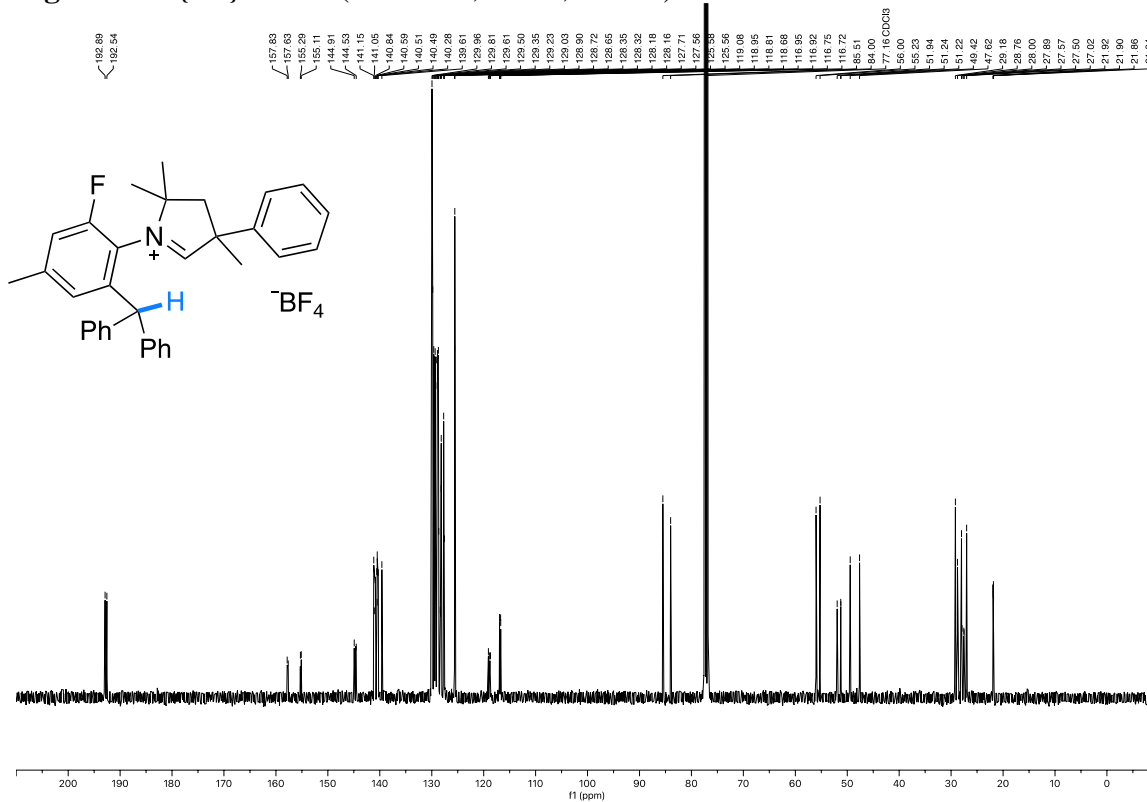
6	-6.668188000	-2.849852000	-2.003904000
1	-6.030434000	-2.445236000	-1.224127000
6	-7.793653000	-2.127616000	-2.402657000
1	-8.014742000	-1.177048000	-1.924204000
6	-8.628130000	-2.617315000	-3.400606000
1	-9.505668000	-2.055836000	-3.709725000
6	-8.323396000	-3.836442000	-4.004563000
1	-8.958220000	-4.229214000	-4.794539000
6	-7.203070000	-4.554577000	-3.603693000
1	-6.967572000	-5.489821000	-4.107156000
6	-5.714291000	-6.265192000	-1.687207000
6	-4.983361000	-7.629452000	-1.423320000
6	-4.706050000	-8.400264000	-2.708414000
6	-3.461602000	-8.985033000	-2.969121000
1	-2.655993000	-8.901347000	-2.247565000
6	-3.218646000	-9.672731000	-4.157082000
1	-2.239211000	-10.112067000	-4.328459000
6	-4.215757000	-9.793520000	-5.118572000
1	-4.025612000	-10.324511000	-6.047309000
6	-5.465335000	-9.229142000	-4.870739000
1	-6.260694000	-9.319549000	-5.606031000
6	-5.706674000	-8.549543000	-3.681599000
1	-6.697794000	-8.136800000	-3.516282000
6	-6.135044000	-8.278691000	-0.606082000
1	-5.762163000	-9.109300000	0.000477000
1	-6.898498000	-8.675235000	-1.283374000
6	-6.760266000	-7.149501000	0.283176000
6	-8.283305000	-7.136954000	0.113830000
1	-8.557810000	-6.976610000	-0.934900000
1	-8.708661000	-8.094837000	0.436489000
1	-8.730323000	-6.338551000	0.716346000
6	-6.431230000	-7.356954000	1.760153000
1	-7.016453000	-6.694901000	2.399388000
1	-6.697123000	-8.386587000	2.020481000
1	-5.370582000	-7.219217000	1.987781000
1	-6.565311000	-6.514389000	-2.324157000
6	-3.770739000	-7.566468000	-0.482440000
1	-4.011531000	-7.015362000	0.426582000
1	-2.879360000	-7.100638000	-0.902423000
1	-3.498993000	-8.583073000	-0.177969000

## 6) NMR spectra

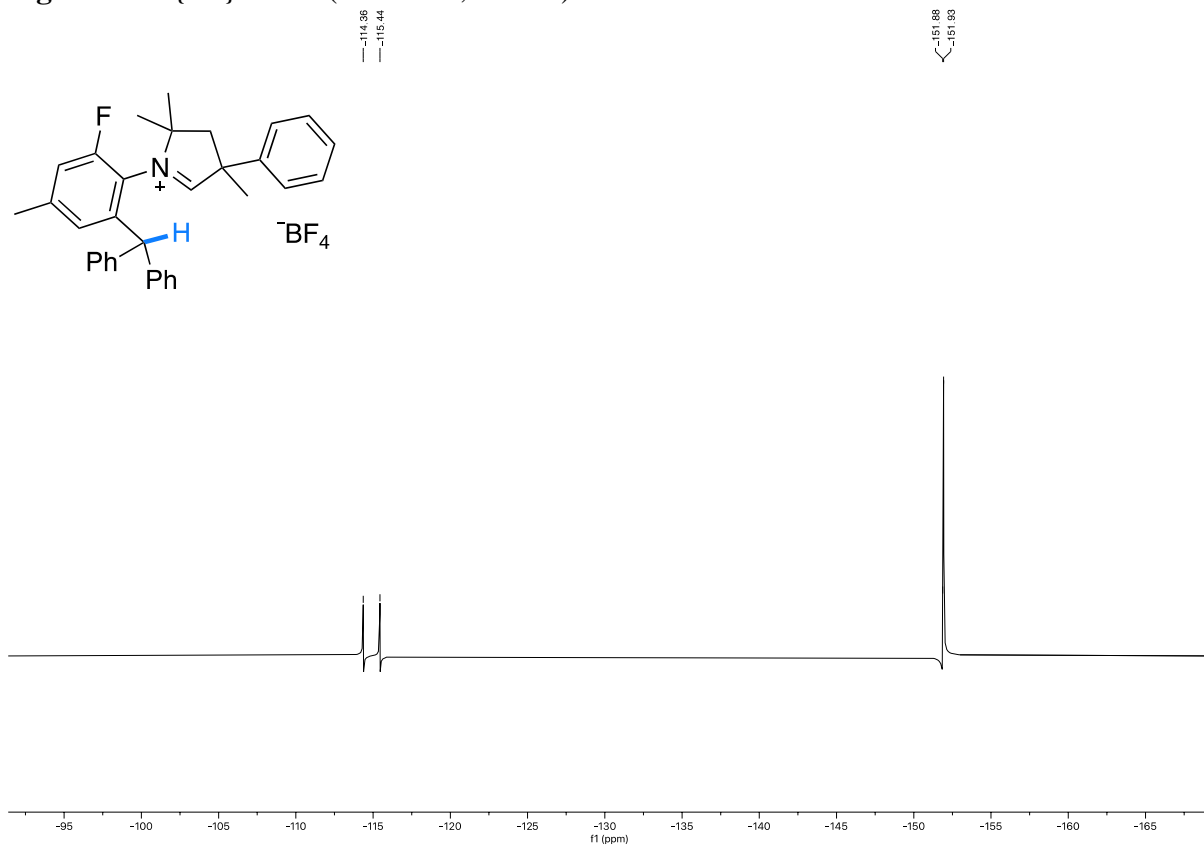
**Fig. S20.**  $^1\text{H}$  NMR (400 MHz, 25°C,  $\text{C}_6\text{D}_6$ ) of **1<sup>Hb</sup>**



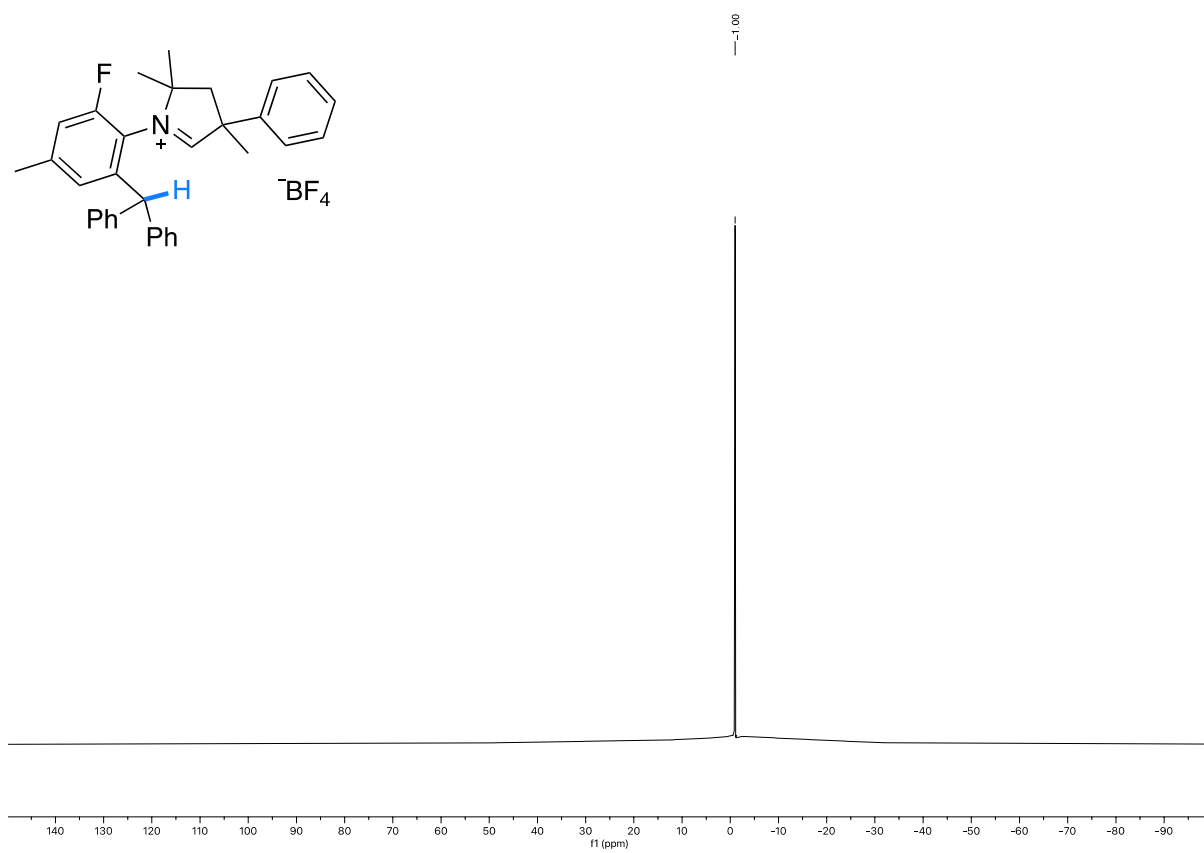
**Fig. S21.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, 25 °C,  $\text{CDCl}_3$ ) of **1<sup>Hb</sup>**



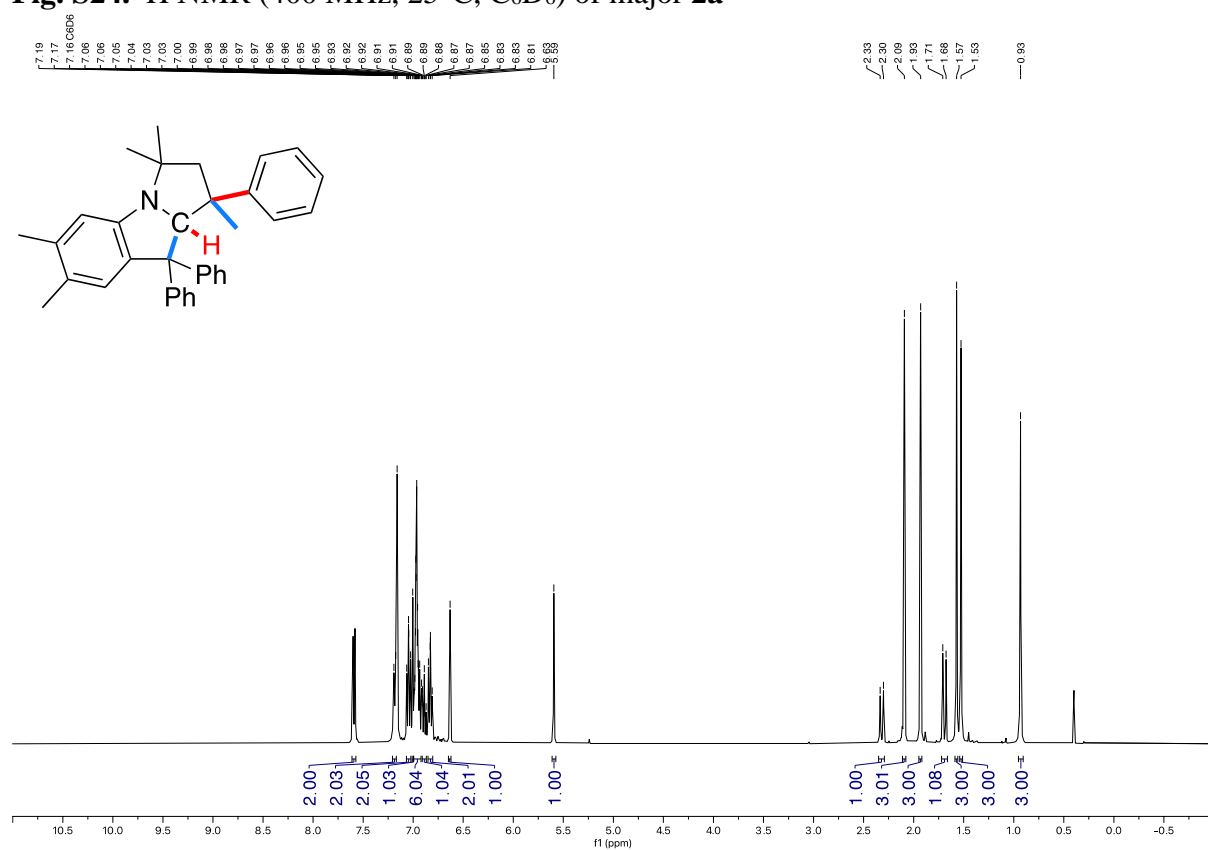
**Fig. S22.**  $^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of  $1^{\text{Hb}}$



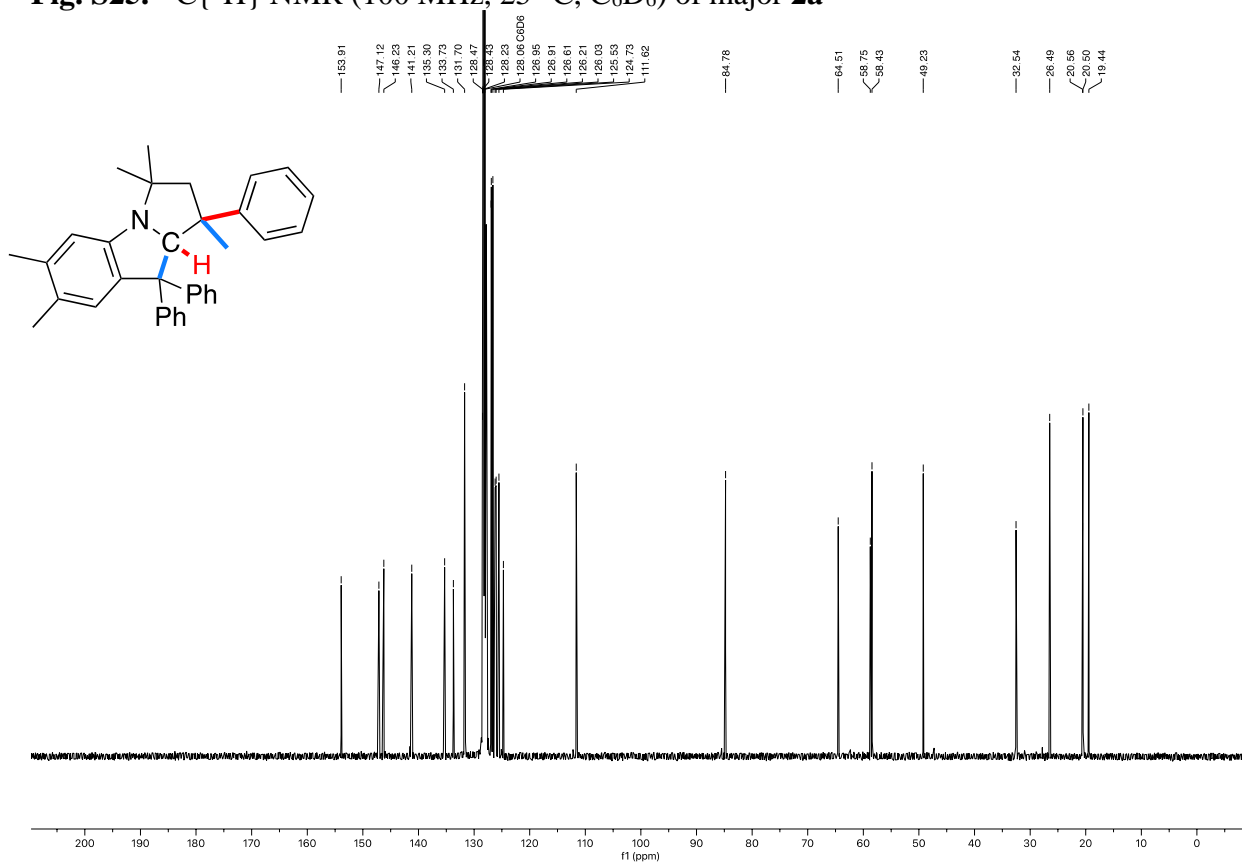
**Fig. S23.**  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CDCl}_3$ ) of  $1^{\text{Hb}}$



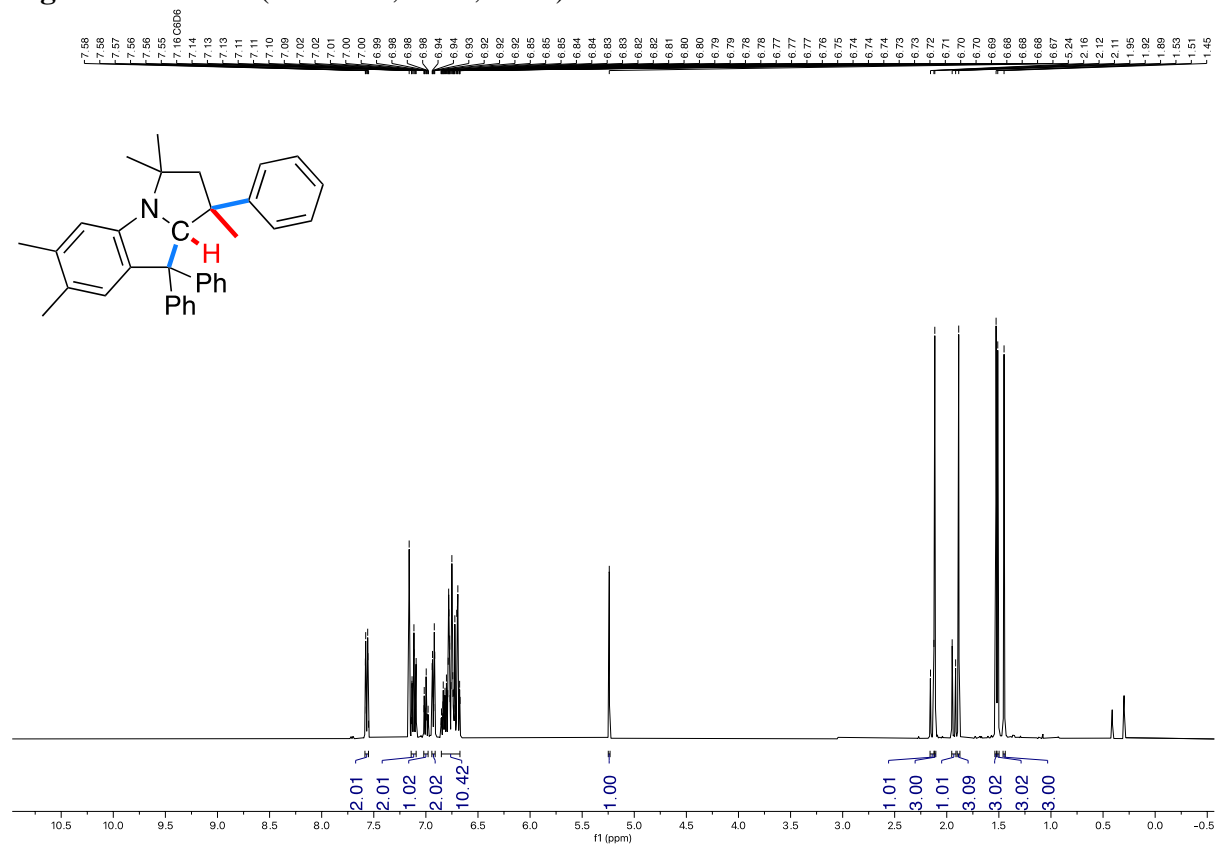
**Fig. S24.**  $^1\text{H}$  NMR (400 MHz,  $25^\circ\text{C}$ ,  $\text{C}_6\text{D}_6$ ) of major **2a**



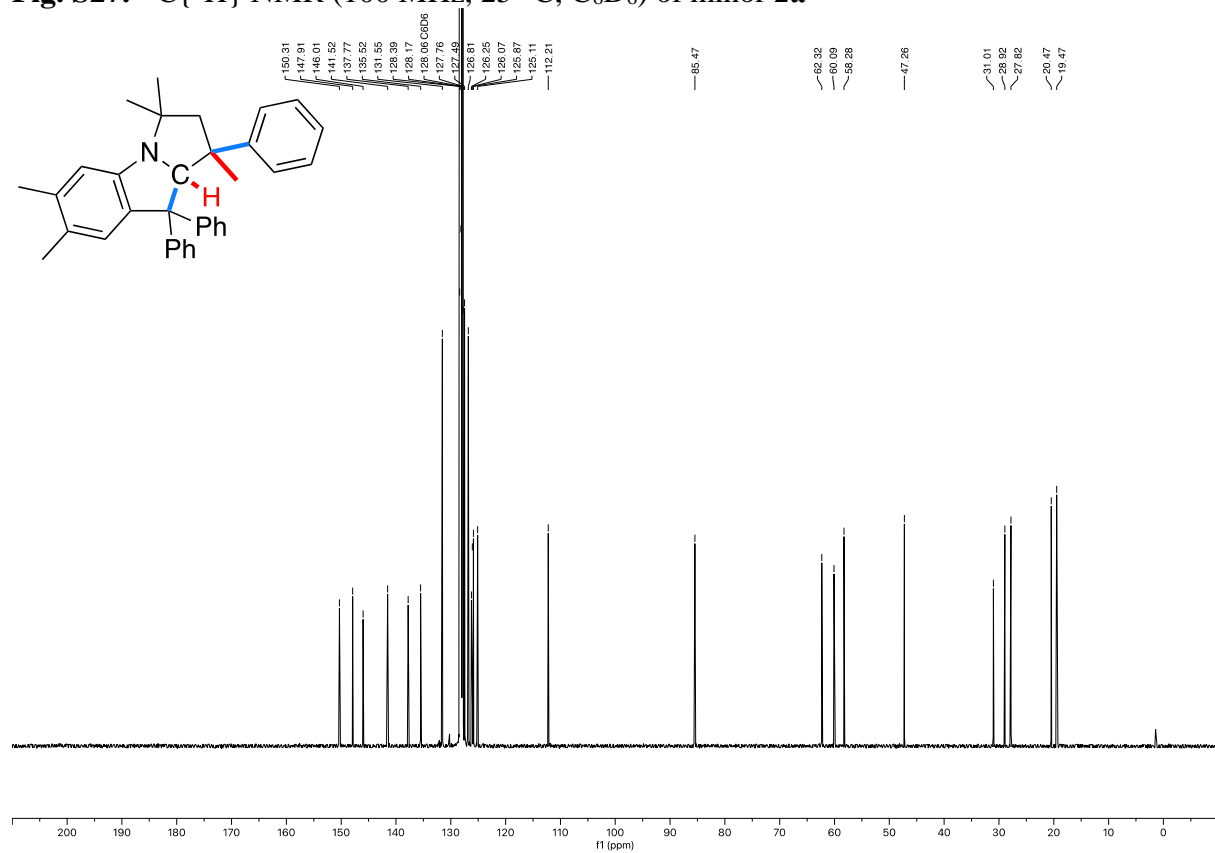
**Fig. S25.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $25^\circ\text{C}$ ,  $\text{C}_6\text{D}_6$ ) of major **2a**



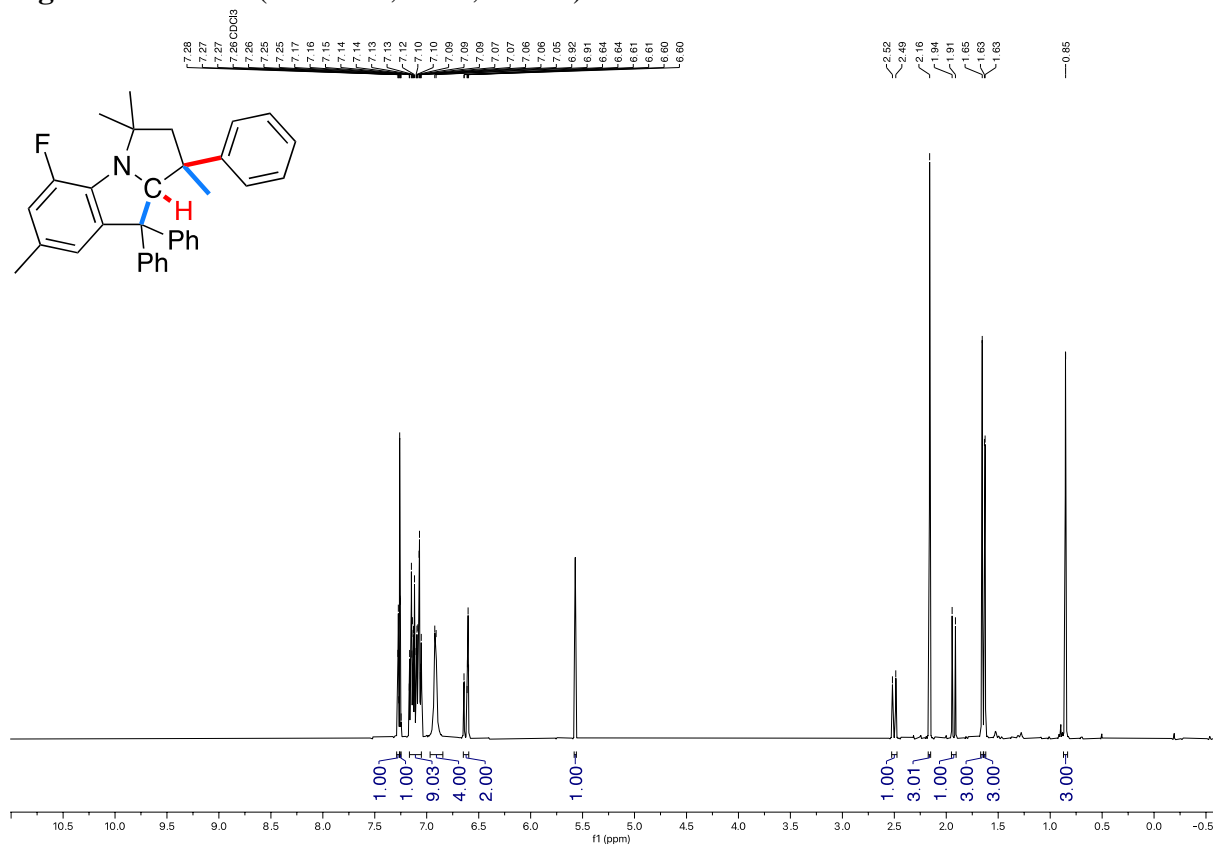
**Fig. S26.**  $^1\text{H}$  NMR (400 MHz,  $25^\circ\text{C}$ ,  $\text{C}_6\text{D}_6$ ) of minor **2a'**



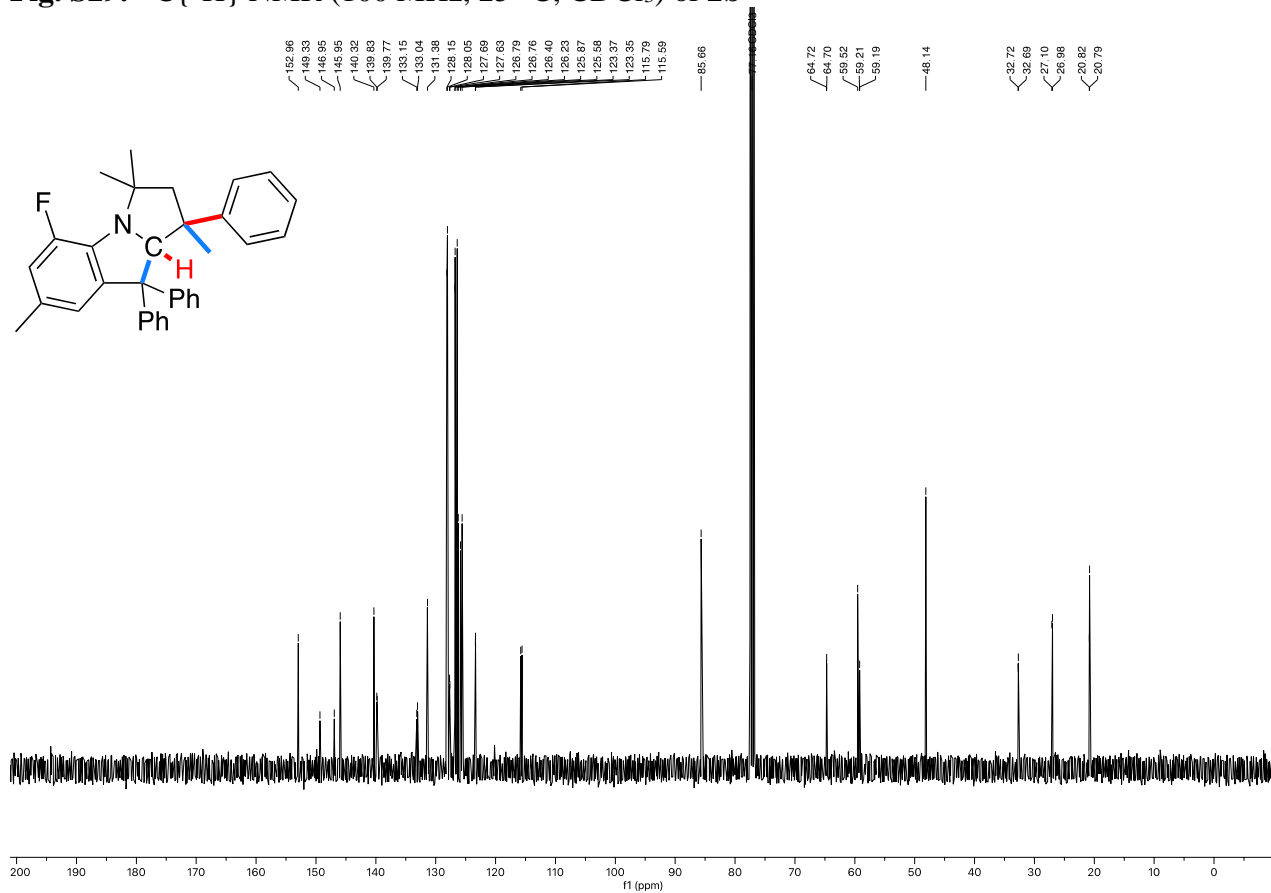
**Fig. S27.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $25^\circ\text{C}$ ,  $\text{C}_6\text{D}_6$ ) of minor **2a'**



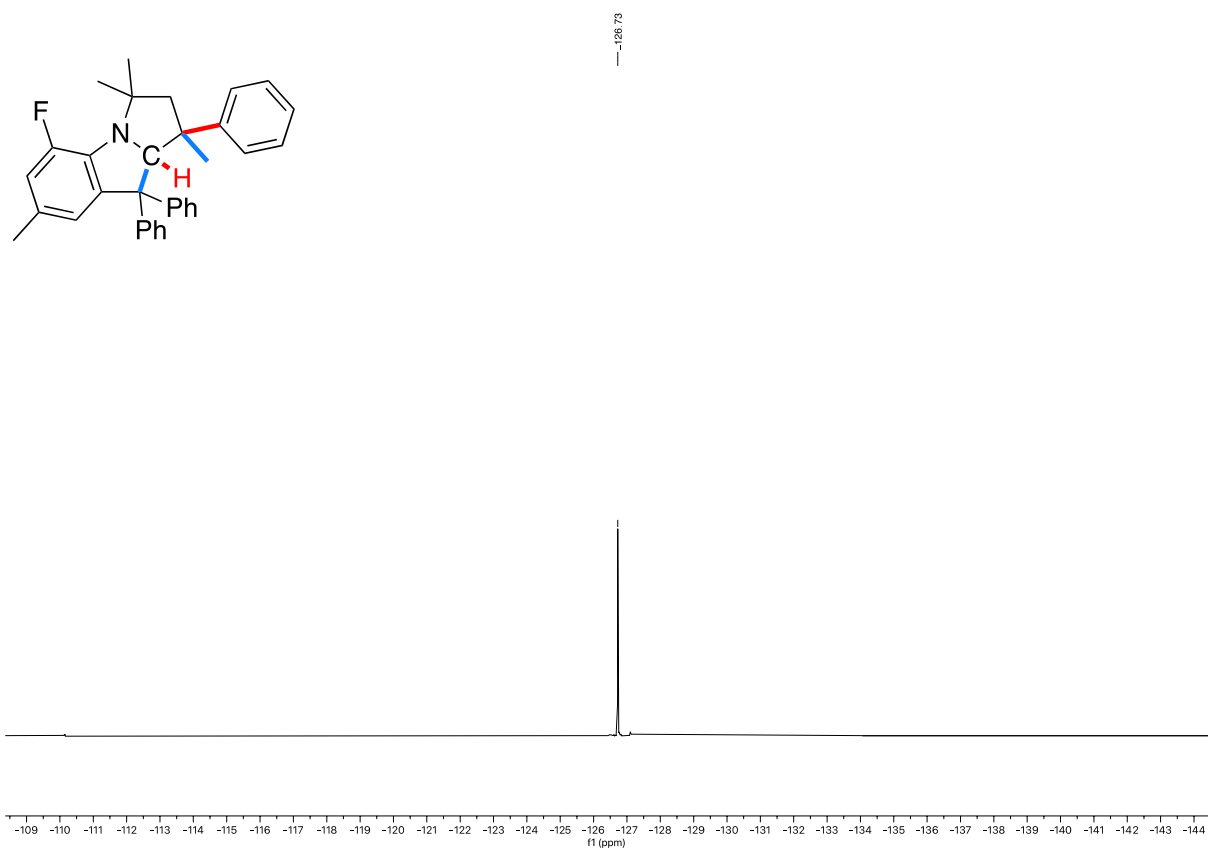
**Fig. S28.**  $^1\text{H}$  NMR (400 MHz,  $25^\circ\text{C}$ ,  $\text{CDCl}_3$ ) of **2b**



**Fig. S29.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $25^\circ\text{C}$ ,  $\text{CDCl}_3$ ) of **2b**

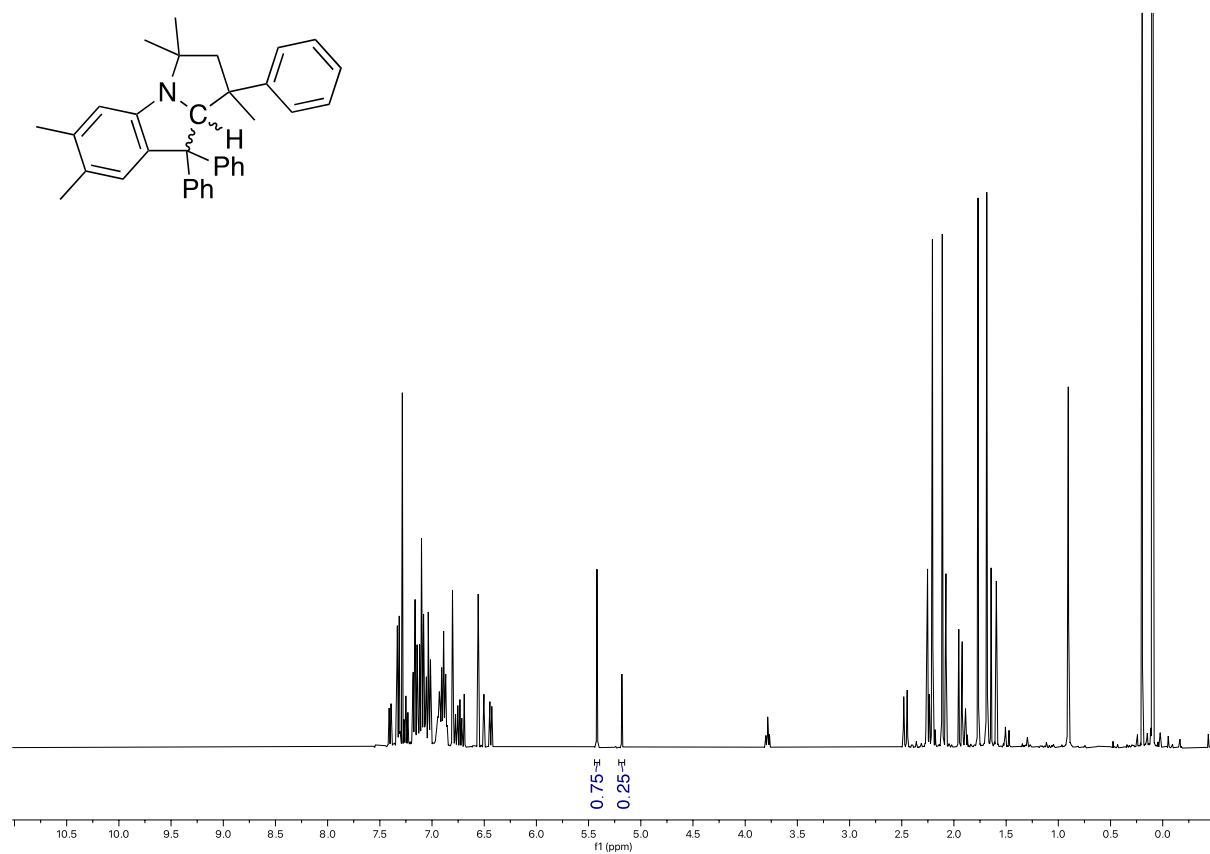


**Fig. S30.**  $^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **2b**

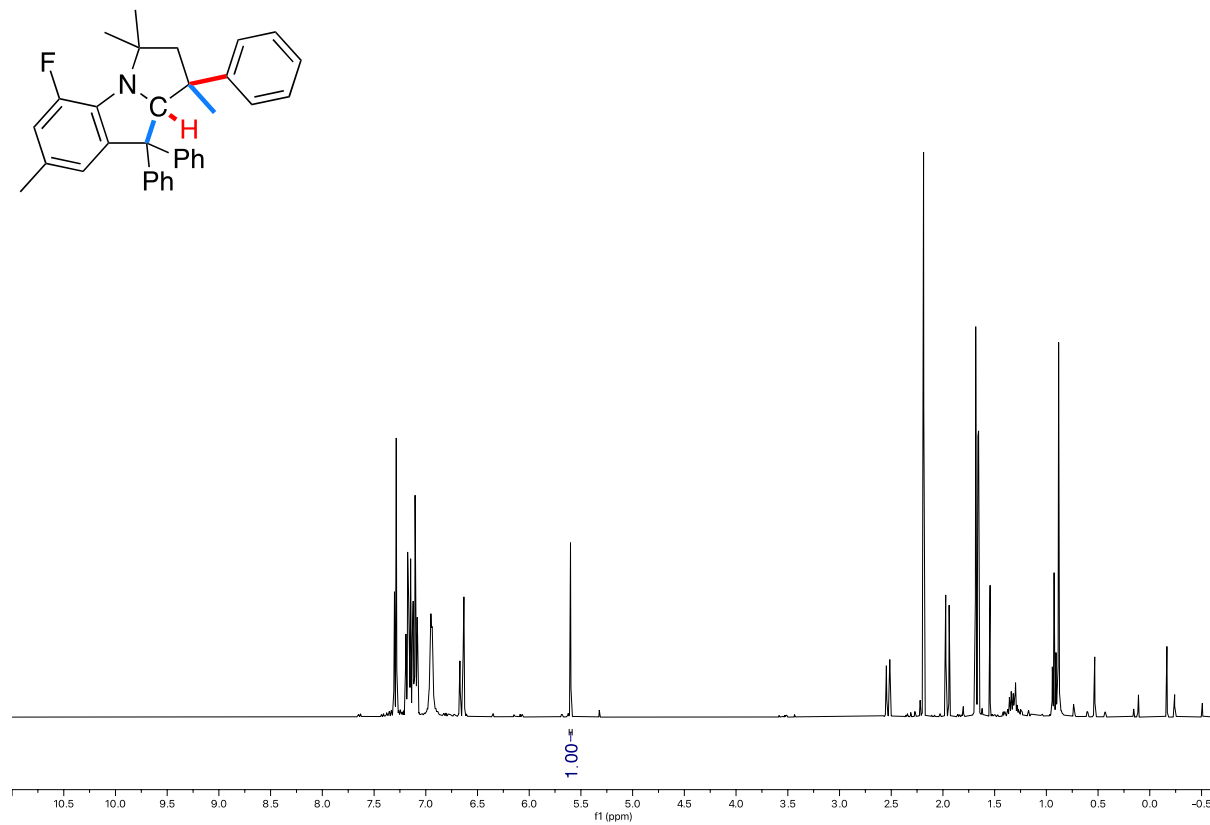




**Fig. S31.**  $^1\text{H}$  NMR (400 MHz, 25°C,  $\text{CDCl}_3$ ) of crude **2a** (75% de)

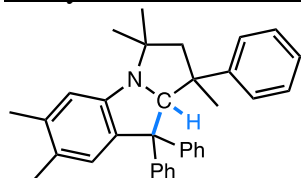


**Fig. S32.**  $^1\text{H}$  NMR (400 MHz, 25°C,  $\text{CDCl}_3$ ) of crude **2b** (99% de)

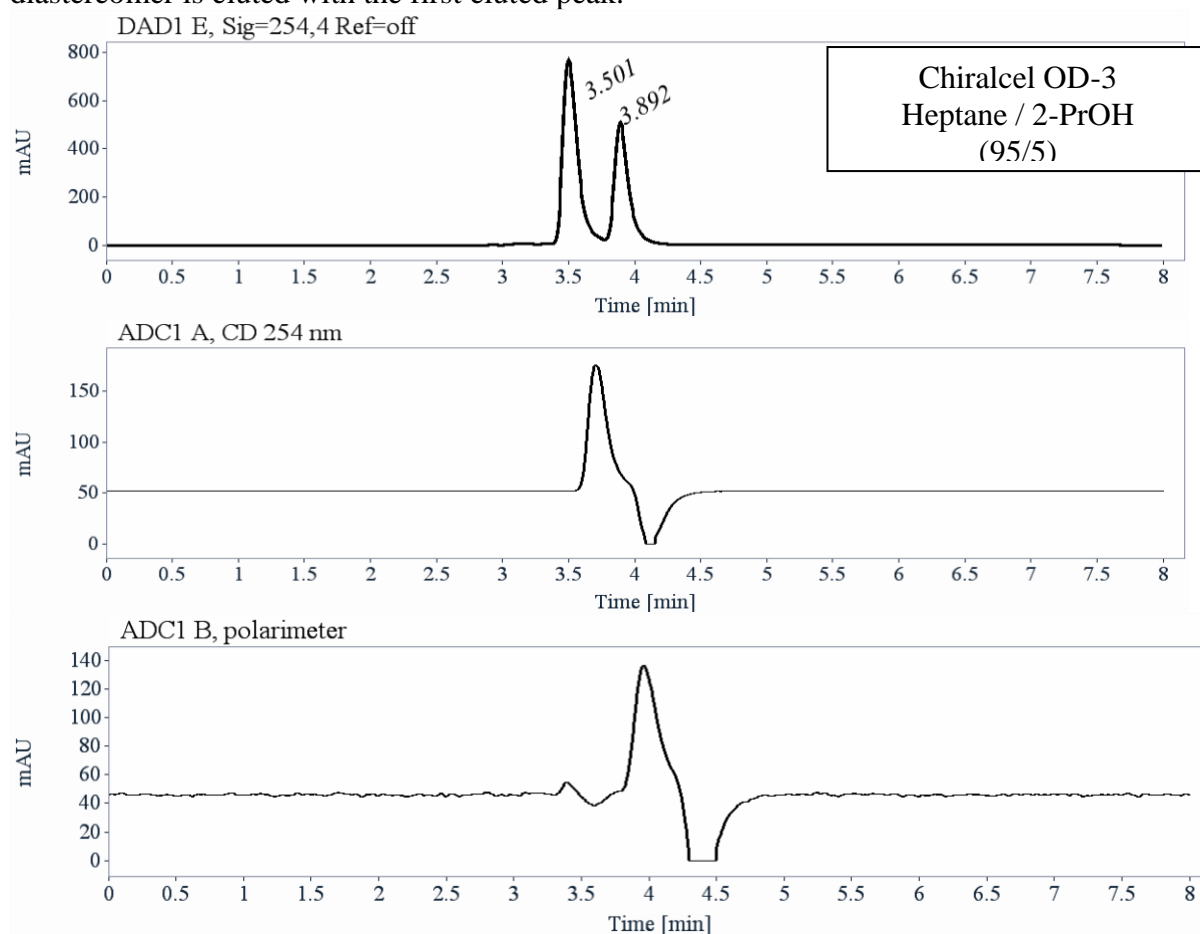


## 7) Chiral HPLC data

### Analytical chiral HPLC separation for compound **2a**

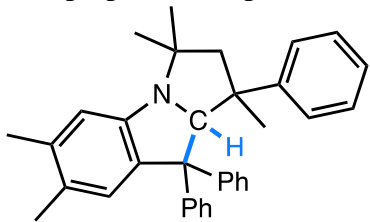


The sample is dissolved in heptane / 2-PrOH, injected on the chiral column, and detected with an UV detector at 254 nm, a circular dichroism detector at 254 nm and a polarimetric detector. The flow-rate is 1 mL/min. We did not find a chiral column that separated the four isomers. On Chiralcel OD-3, the enantiomers of the major diastereomer are separated, but the minor diastereomer is eluted with the first eluted peak.



RT [min]	Area	Area%	Capacity Factor	
3.50	6045	60.88	0.19	(+)-Majo ( <b>S,R</b> )- <b>2a</b> and mino <b>2a'</b>
3.89	3885	39.12	0.32	(-)-Majo ( <b>R,S</b> )- <b>2a</b>
Sum	9930	100.00		

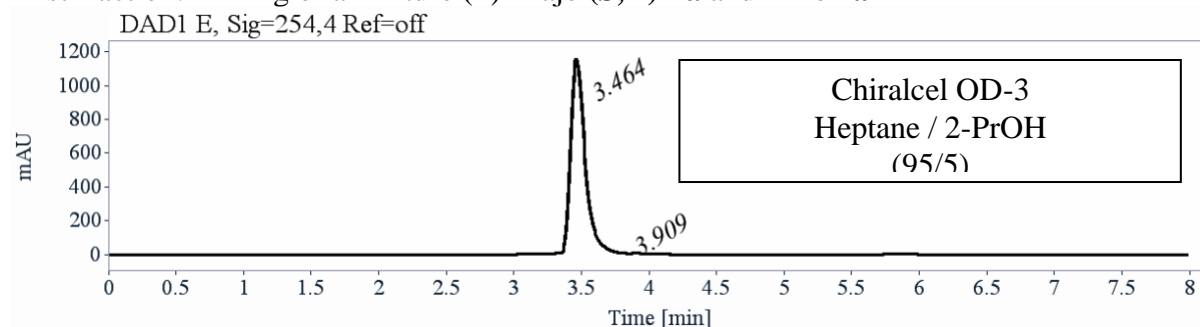
### First preparative separation for compound **2a**



Sample preparation: About 707 mg of compound **2a** are dissolved in 380 mL of hexane.  
Chromatographic conditions: Lux-Cellulose-1 (250 × 10 mm), hexane / 2-PrOH (95/5) as mobile phase, flow-rate = 5 mL/min, UV detection at 290 nm.

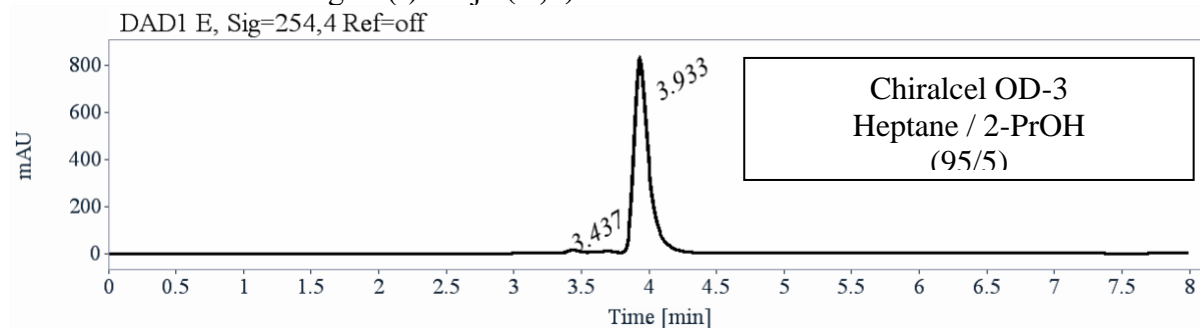
Injections (stacked): 760 times 500  $\mu$ L, every 1.3 minutes.

First fraction: 411 mg of a mixture (+)-Majo (**S,R**)-**2a** and mino **2a'**



RT [min]	Area	Area[%]
3.46	8728	99.47
3.91	46	0.53
Sum	8774	100.00

• Second fraction: 273 mg of (-)-Majo (**R,S**)-**2a** with ee > 98%

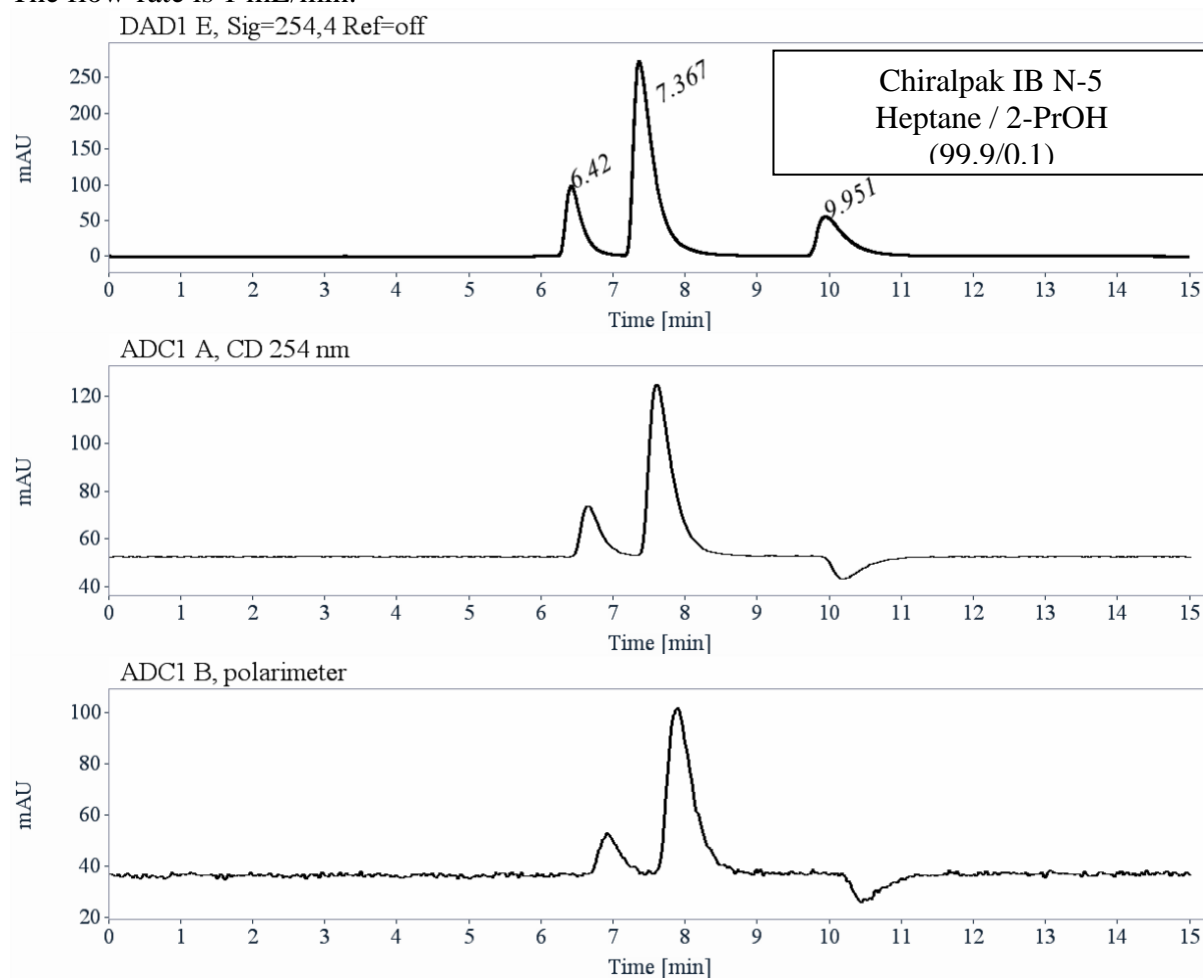


RT [min]	Area	Area%
3.44	58	0.90
3.93	6377	99.10
Sum	6436	100.00

• Intermediate: 61 mg

Analytical chiral HPLC separation for compounds (+)-Majo (**S,R**)-**2a** and mino **2a'**

The sample is dissolved in heptane / 2-PrOH, injected on the chiral column, and detected with an UV detector at 254 nm, a circular dichroism detector at 254 nm and a polarimetric detector. The flow-rate is 1 mL/min.



RT [min]	Area	Area[%]	Capacity Factor	
6.42	2624	16.50	1.18	(+)-mino ( <b>R,R</b> )- <b>2a'</b>
7.37	10990	69.11	1.50	(+)-Majo ( <b>S,R</b> )- <b>2a</b> ,
9.95	2287	14.38	2.37	(-)-mino ( <b>S,S</b> )- <b>2a'</b>
Sum	15902	100.00		

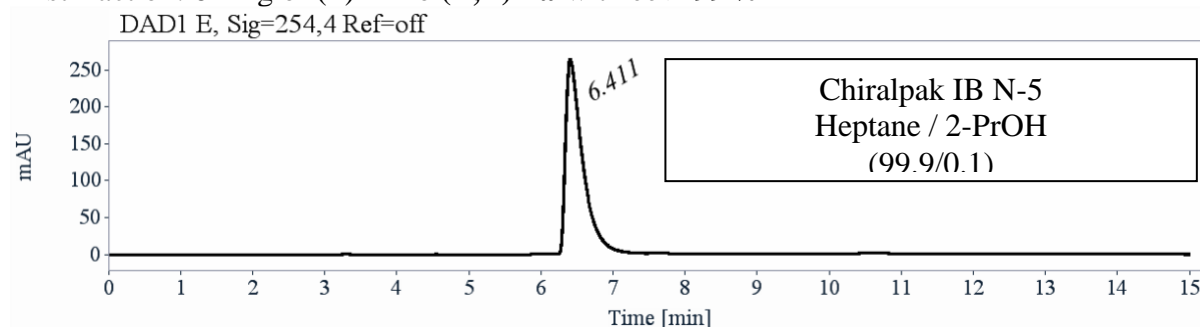
Second preparative separation for compounds (+)-Majo (S,R)-2a, and mino 2a':

Sample preparation: About 411 mg of purified compound (+)-Majo (S,R)-2a, and mino 2a' are dissolved in 40 mL of hexane.

Chromatographic conditions: Chiralpak IB N-5 (250 x 10 mm), hexane / 2-PrOH / (99.9/0.1) as mobile phase, flow-rate = 5 mL/min, UV detection at 290 nm.

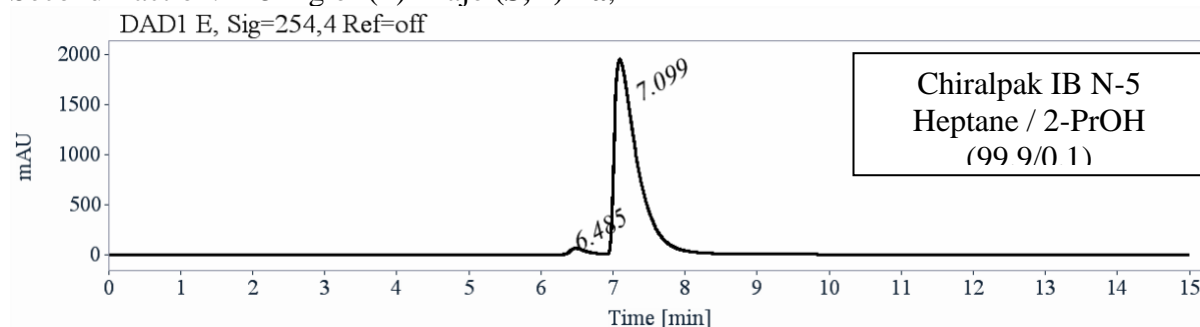
Injections (stacked): 50 times 800  $\mu$ L, every 11.8 minutes.

First fraction: 64 mg of (+)-mino (R,R)-2a' with ee > 99 %



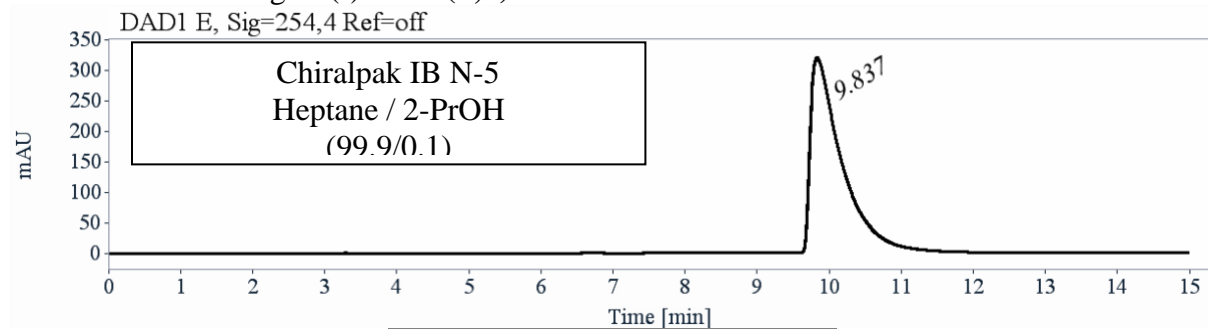
RT [min]	Area	Area%
6.41	4376	100.00
Sum	4376	100.00

Second fraction: 225 mg of (+)-Majo (S,R)-2a,



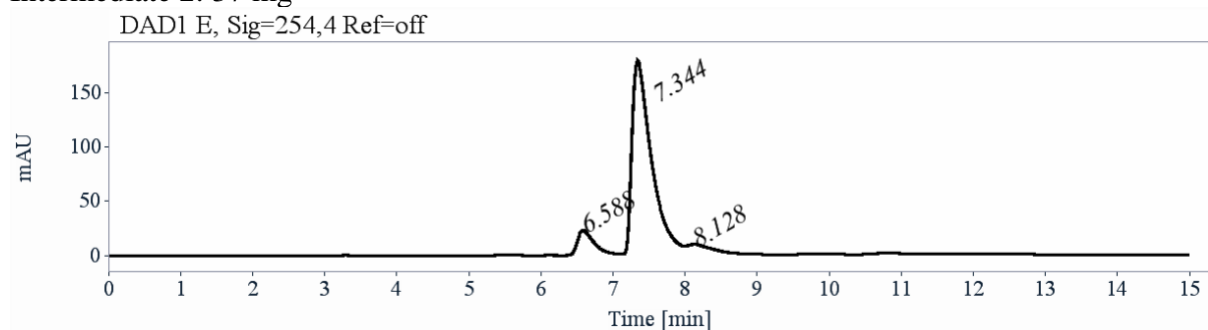
RT [min]	Area	Area%
6.48	1478	1.93
7.10	75052	98.07
Sum	76530	100.00

Third fraction: 79 mg of (-)-mino (*S,S*)-**2a'** with ee > 99 %



RT [min]	Area	Area%
9.84	9735	100.00
Sum	9735	100.00

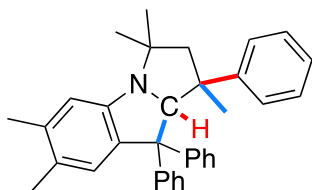
Intermediate 2: 37 mg



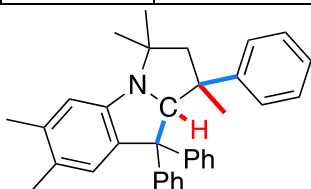
RT [min]	Area	Area%
6.59	379	9.37
7.34	3406	84.18
8.13	261	6.45
Sum	4046	100.00

### Optical rotations

Optical rotations were measured on a Jasco P-2000 polarimeter with a halogen lamp (589, 578, 546, 436 and 405 nm), in a 10 cm cell, thermostated at 25 °C with a Peltier controlled cell holder.



$\lambda$ (nm)	(+)-Majo ( <b>S,R</b> )- <b>2a</b> , <i>First</i> eluted enantiomer on Chiralcel OD-3 $[\alpha]_{\lambda}^{25}$ (CH <sub>2</sub> Cl <sub>2</sub> , c = 0.21)	(-)-Majo ( <b>R,S</b> )- <b>2a</b> <i>Second</i> eluted enantiomer on Chiralcel OD-3 $[\alpha]_{\lambda}^{25}$ (CH <sub>2</sub> Cl <sub>2</sub> , c = 0.24)
589	+ 620	- 620
578	+ 650	- 650
546	+ 770	- 780
436	+ 1600	- 1600
405	+ 2400	- 2400



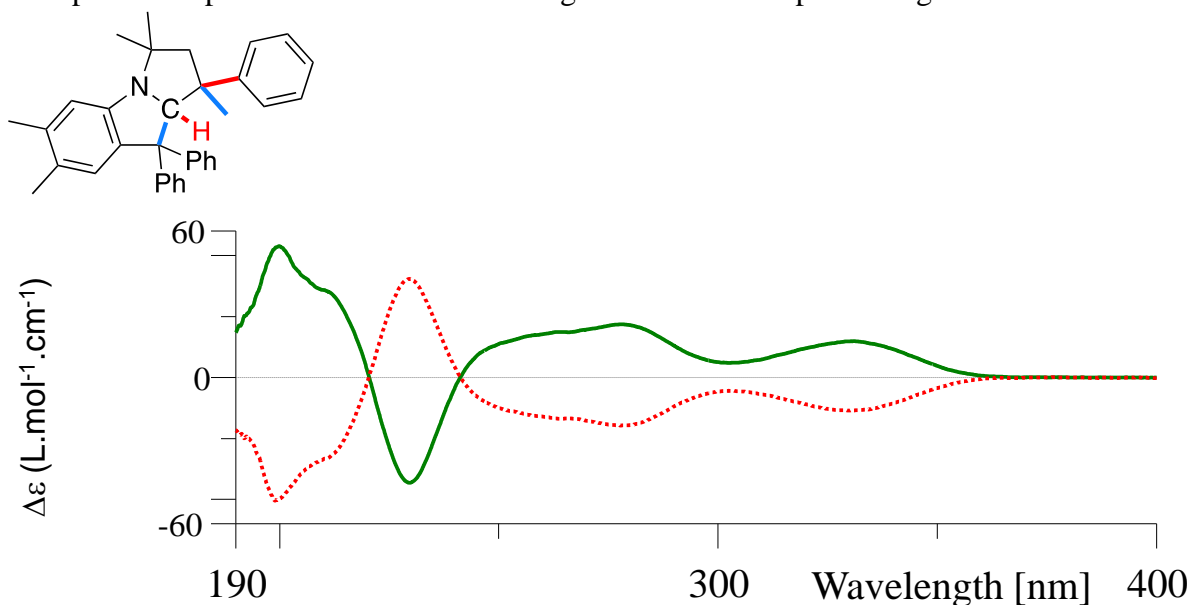
$\lambda$ (nm)	(+)-mino ( <b>R,R</b> )- <b>2a'</b> , <i>First</i> eluted enantiomer on Chiralpak IB N-5 $[\alpha]_{\lambda}^{25}$ (CH <sub>2</sub> Cl <sub>2</sub> , c = 0.21)	(-)-mino ( <b>S,S</b> )- <b>2a'</b> <i>Second</i> eluted enantiomer on Chiralpak IB N-5 $[\alpha]_{\lambda}^{25}$ (CH <sub>2</sub> Cl <sub>2</sub> , c = 0.28)
589	+ 470	- 470
578	+ 490	- 490
546	+ 590	- 590
436	+ 1200	- 1200
405	+ 1800	- 1800

### Electronic Circular Dichroism

ECD and UV spectra were measured on a JASCO J-815 spectrometer equipped with a JASCO Peltier cell holder PTC-423 to maintain the temperature at  $25.0 \pm 0.2$  °C. A CD quartz cell of 1 mm of optical pathlength was used. The CD spectrometer was purged with nitrogen before recording each spectrum, which was baseline subtracted.

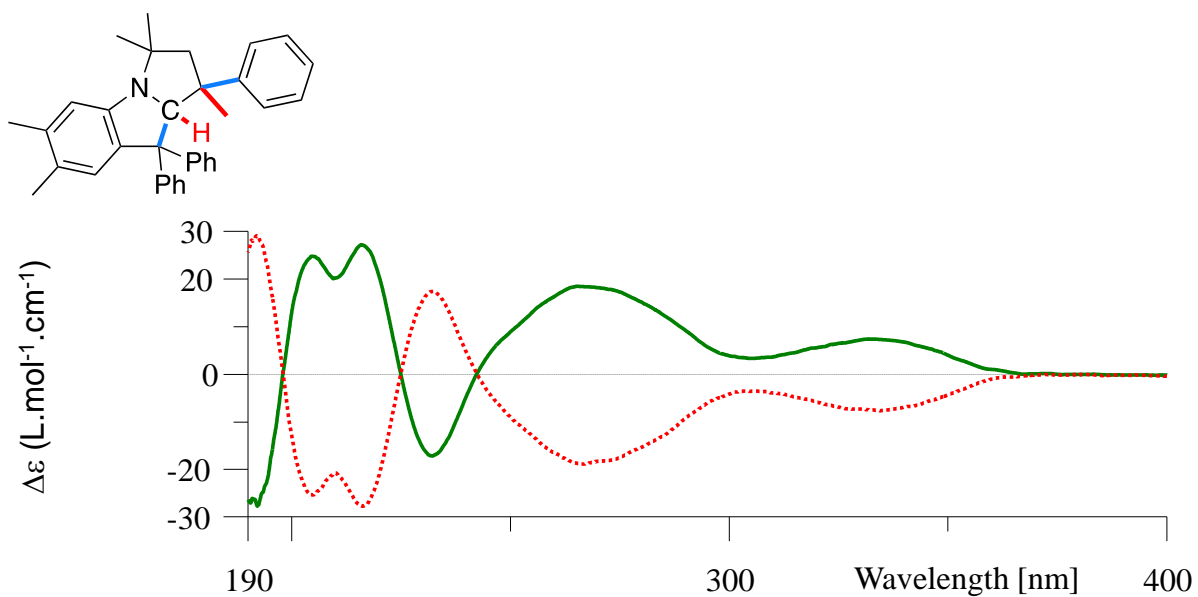
The baseline was always measured for the same solvent and in the same cell as the samples.

The spectra are presented without smoothing and further data processing.



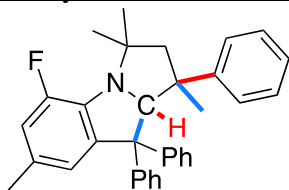
**Fig. S33.** ECP spectra of (+)-Majo (**S,R**)-**2a**, *first* eluted isomer on Chiralcel OD-3 : green solid line, concentration =  $0.199$  mmol.L<sup>-1</sup> in acetonitrile. and (-)-Majo (**R,S**)-**2a**, *second* eluted isomer on Chiralcel OD-3: red dotted line, concentration =  $0.201$  mmol.L<sup>-1</sup> in acetonitrile. Acquisition parameters: 0.1 nm as intervals, scanning speed 50 nm/min, band width 2 nm, and 3 accumulations per sample.



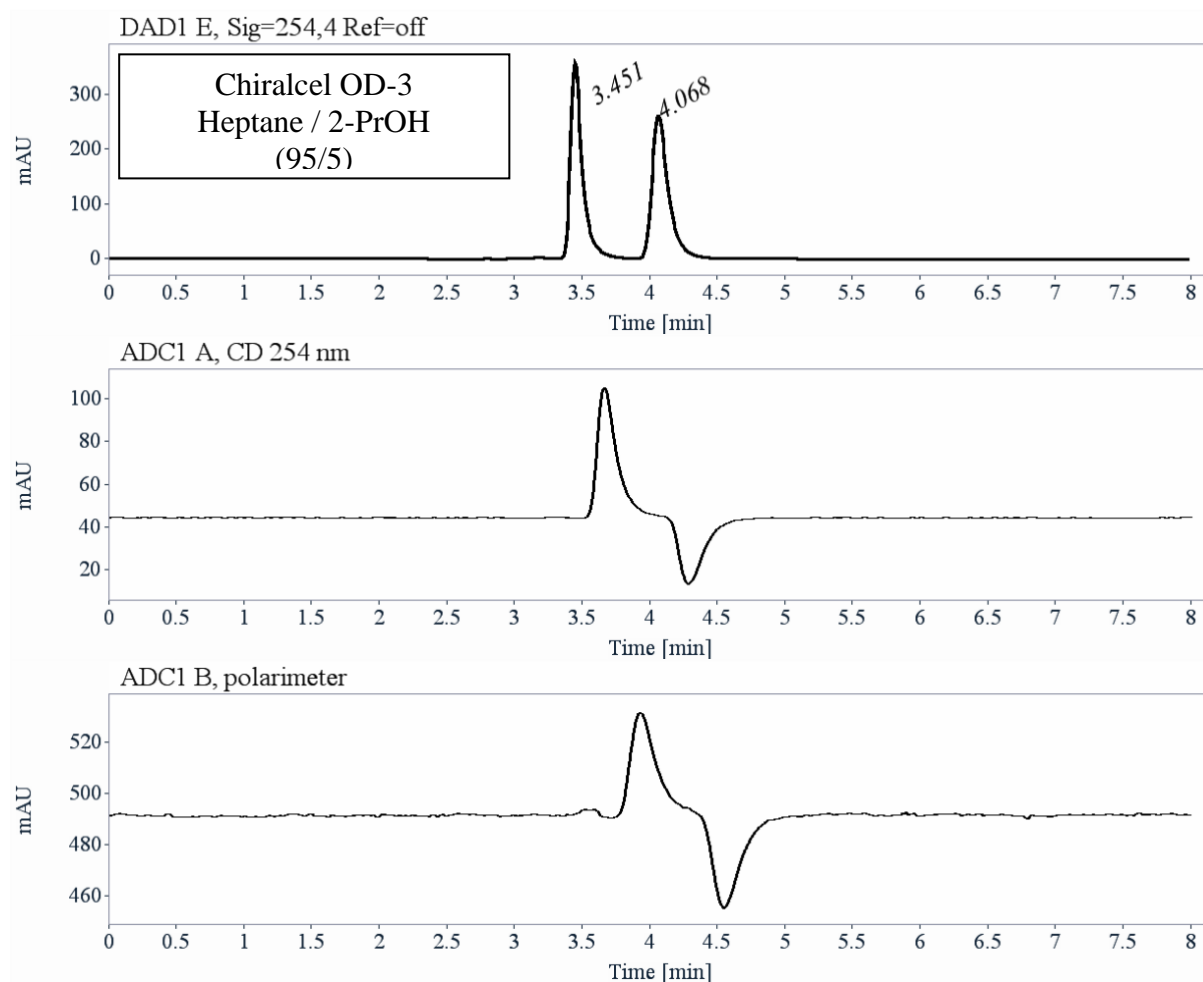


**Fig. S34** ECD spectra of (+)-mino (*R,R*)-**2a'**, *first* eluted isomer on Chiralpak IB N-5 : green solid line, concentration = 0.233 mmol.L<sup>-1</sup> in acetonitrile and (-)-mino (*S,S*)-**2a'**, *second* eluted isomer on Chiralpak IB N-5: red dotted line, concentration = 0.200 mmol.L<sup>-1</sup> in acetonitrile. Acquisition parameters: 0.1 nm as intervals, scanning speed 50 nm/min, band width 2 nm, and 3 accumulations per sample.

## Analytical chiral HPLC separation for compound **2b**

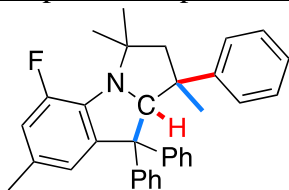


The sample is dissolved in heptane / 2-PrOH, injected on the chiral column, and detected with an UV detector at 254 nm, a circular dichroism detector at 254 nm and a polarimetric detector. The flow-rate is 1 mL/min.

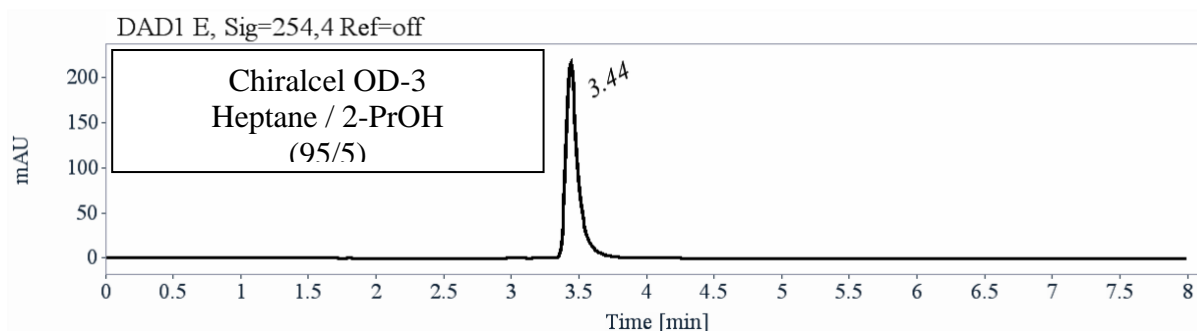


RT [min]	Area	Area[%]	Capacity Factor	Enantioselectivity	Resolution (USP)
3.45	2223	49.98	0.17		
4.07	2224	50.02	0.38	2.23	3.44
Sum	4447	100.00			

## Preparative separation for compound **2b**

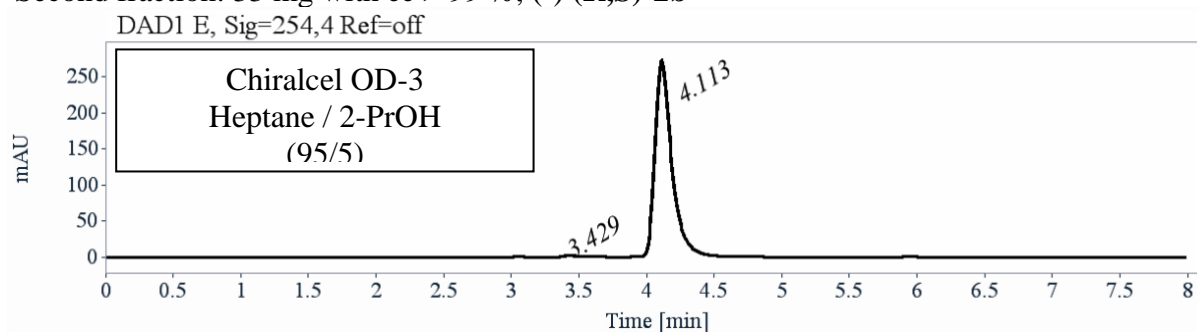


Sample preparation: About 70 mg of compound **2b** are dissolved in 5.2 mL of the mobile phase. Chromatographic conditions: Lux-Cellulose-1 (250 x 10 mm), hexane / 2-PrOH (95/5) as mobile phase, flow-rate = 5 mL/min, UV detection at 280 nm. Injections (stacked): 35 times 150  $\mu$ L, every 2 minutes. First fraction: 33 mg with ee > 99.5 % (+) (**S,R**)-**2b**



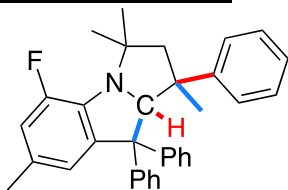
RT [min]	Area	Area [%]
3.44	1353	100.00
Sum	1353	100.00

Second fraction: 33 mg with ee > 99 %, (-) (**R,S**)-**2b**



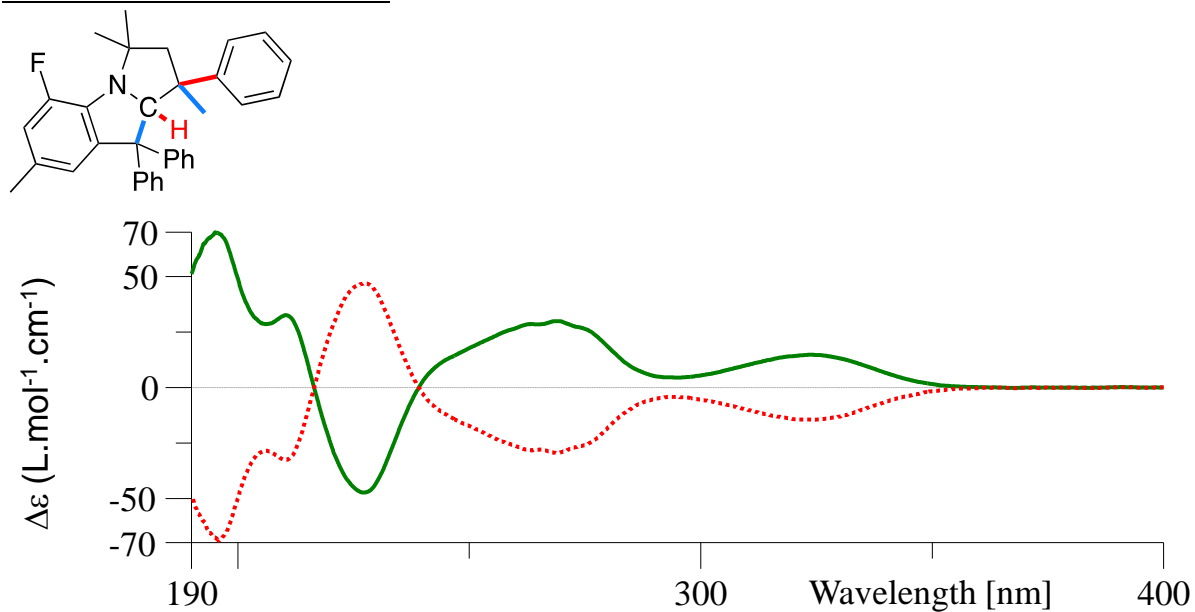
RT [min]	Area	Area [%]
3.43	11	0.46
4.11	2380	99.54
Sum	2391	100.00

## Optical rotations



$\lambda$ (nm)	(+) ( <b>S,R</b> )- <b>2b</b> First eluted enantiomer on Chiralcel OD-3 $[\alpha]_{\lambda}^{25}$ (CH <sub>2</sub> Cl <sub>2</sub> , c = 0.17)	(-) ( <b>R,S</b> )- <b>2b</b> Second eluted enantiomer on Chiralcel OD-3 $[\alpha]_{\lambda}^{25}$ (CH <sub>2</sub> Cl <sub>2</sub> , c = 0.18)
589	+ 625	- 625
578	+ 660	- 660
546	+ 790	- 790
436	+ 1600	- 1600
405	+ 2300	- 2300

## Electronic Circular Dichroism



**Fig. S35** ECD spectra of (+) (**S,R**)-**2b** first eluted isomer on Chiralcel OD3: green solid line, concentration =  $0.198 \text{ mmol}\cdot\text{L}^{-1}$  in acetonitrile and (-) (**R,S**)-**2b**, second eluted isomer on Chiralcel OD3: red dotted line, concentration =  $0.195 \text{ mmol}\cdot\text{L}^{-1}$  in acetonitrile. Acquisition parameters: 0.1 nm as intervals, scanning speed 50 nm/min, band width 2 nm, and 3 accumulations per sample.