## Axially and Helically Chiral Cationic Radical Bicarbazoles: SOMO-HOMO Level Inversion and Chirality Impact on the Stability of Mono- and Diradical Cations

Sitthichok Kasemthaveechok, ${ }^{\dagger}$ Laura Abella, ${ }^{\ddagger}$ Marion Jean, ${ }^{\S}$ Marie Cordier, ${ }^{\dagger}$ Thierry Roisnel, ${ }^{\dagger}$ Nicolas Vanthuyne, ${ }^{\S}$ Thierry Guizouarn, ${ }^{\dagger}$ Olivier Cador, ${ }^{\dagger}$ Jochen Autschbach, ${ }^{*, \neq}$ Jeanne Crassous, ${ }^{\dagger}$ and Ludovic Favereau, ${ }^{*, \dagger}$<br>† Univ Rennes, CNRS, ISCR - UMR 6226, F-35000 Rennes, France.<br>₹ Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York 14260, USA.<br>§ Aix Marseille University, CNRS Centrale Marseille, iSm2, 13284 Marseille, France.

## Table of Contents

A. General methods S2
B. Synthetic procedures S4
C. Crystal structures S8
D. Preparative Separation of $1 \quad \mathrm{~S} 12$
E. Steady-state photophysical characterizations S15
F. Kinetic dissociation analysis of $1^{\bullet+}, 3^{\bullet+}, 3^{\bullet+}$ and $3^{2 \bullet 2+} \quad$ S24
G. NMR spectra S28
H. Computational part S40

## A. General method

${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra were recorded at room temperature on an AVANCE III 400 BRUKER at Centre Régional de Measures Physiques de l'Ouest (CRMPO), Université de Rennes 1. Chemical shifts $\delta$ are given in ppm and coupling constants $J$ in Hz . Chemical shifts for ${ }^{1} \mathrm{H}$ NMR spectra are referenced relative to residual protium in the deuterated solvent $\left({ }^{1} \mathrm{H} \delta=7.26 \mathrm{ppm}, \mathrm{CDCl}_{3}, \delta=\right.$ $5.32 \mathrm{ppm}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ). ${ }^{13} \mathrm{C}$ shifts are referenced to deuterated solvent $\left(\delta=77.2 \mathrm{ppm}\right.$ for $\mathrm{CDCl}_{3}, \delta=$ 53.8 ppm for $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ ).

Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with Merck 5735 Kieselgel 60F254. Column chromatography was carried out with Merck 5735 Kieselgel 60F (0.040-0.063 mm mesh). All commercial chemicals were purchased and used as received.

High-resolution mass spectrometry (HR-MS) determinations were performed at CRMPO on a Bruker MaXis 4G by ASAP ( + or - ) or ESI with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ as solvent techniques. Experimental and calculated masses are given with consideration of the mass of the electron.

Low-resolution mass spectrometry (LR-MS) determinations were performed on a Bruker Daltonics flexControl Experimental and calculated masses are given with consideration of the mass of the electron.

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 were the saturated potassium chloride calomel electrode (SCE). The supporting electrolyte was $0.1 \mathrm{NBu}_{4} \mathrm{NPF}_{6}$ (tetrabutylammonium hexafluorophosphate) in dichloromethane and solutions were purged with argon before the measurements. All potentials are quoted relative to SCE.

UV-Visible/NIR (UV-vis-NIR, in $\mathrm{M}^{-1} \mathrm{~cm}^{-1}$ ) absorption spectra were recorded on a Jasco V-770 spectrophotometer. Fluorescence spectra were measured on an FL 920 Edinburgh fluorimeter, while absolute fluorescence quantum yields $\Phi$ were recorded with a Hamamatsu C9920-03 integrating sphere.

Spectroelectrochemical measurement were performed with potentiostat-galvanostat Princeton by using optically transparent thin-layer electrochemical (OTTLE) cell as OMNI-cell body. The optical pathlength is ca. 0.2 cm .

Optical rotations were measured on a Jasco P-2000 polarimeter with a sodium lamp (589 nm) in a 1 or 10 cm cell, thermostated at $25^{\circ} \mathrm{C}$ with a Peltier controlled cell holder. Specific rotations are given in $10^{-1} \mathrm{deg} \cdot \mathrm{cm}^{2} \cdot \mathrm{~g}-1$, and molar rotations are given in $10^{-3} \mathrm{deg} \cdot \mathrm{cm}^{2} \cdot \mathrm{~mol}^{-1}$. Electronic circular dichroism (ECD, in $\mathrm{M}^{-1} \mathrm{~cm}^{-1}$ ) was measured on a Jasco J-815 Circular Dichroism Spectrometer IFR140 facility. Part of this work has been performed using the PRISM core facility (Biogenouest©, UMS Biosit, Université de Rennes 1 - Campus de Villejean-35043 Rennes Cedex, France).

The circularly polarized luminescence (CPL) measurements were performed using a home-built CPL spectrofluoropolarimeter (constructed with the help of the JASCO Company). The samples were excited using a $90^{\circ}$ geometry with a Xenon ozone-free lamp 150 W LS. The following parameters were used: emission slit width $\approx 2 \mathrm{~mm}$, integration time $=4 \mathrm{sec}$, scan speed $=50$ $\mathrm{nm} / \mathrm{min}$, accumulations $=5$. The concentration of all the samples was ca. $10^{-6} \mathrm{M}$. Excitation of the samples was performed at 350 nm .

Electron paramagnetic resonance (EPR) measurements were carried out with a Bruker 300 spectrometer (X-band, 100 kHz field modulation). Frozen solution spectra were obtained by very rapidly cooling down the solution to avoid the formation of small crystallites.

The DC and AC magnetic susceptibility measurements were performed on solid polycrystalline samples with a Quantum Design MPMS-XL SQUID magnetometer between 2 and 300 K in applied magnetic field of 0.2 T for temperatures of $2-20 \mathrm{~K}$ and 1 T for temperatures of $20-300 \mathrm{~K}$. These measurements were all corrected for the diamagnetic contribution as calculated with Pascal's constants.

## B. Synthetic procedures

BICOL was synthesized by using a synthetic method from Botman and co-workers with an improvement from Hoen. ${ }^{[1]}$ All analytical data for BICOL, 1' and 3' were in accordance with references. ${ }^{[2]}$


3-OMeCBz

1) i.
2) $\mathrm{VO}(\mathrm{acac})_{2}, \mathrm{O}_{2}$ MeCN, rt, 24 h

iii.
$\square \begin{array}{ll}1^{\prime}(\mathrm{R}=\mathrm{H}) & (99 \%) \\ 3^{\prime}(\mathrm{R}=t \mathrm{Bu}-) & (26 \%)\end{array}$



Scheme 1. Carbazole and BICOL derivatives synthesis.
( $\pm$ )-3,3'-dimethoxy-4,4'-bis-(9-methyl-9 H -carbazole) (1) ${ }^{[3]}$


In a pre-dried schlenk flask, $300 \mathrm{mg}(0.82 \mathrm{mmol})$ of $( \pm)$-BICOL was dissolved in 25 mL of acetone under inert atmosphere. Sodium hydroxide ( $22 \mathrm{M} \mathrm{aq}, 0.88 \mathrm{~mL}, 20 \mathrm{eq}$ ) was added and the reaction mixture was stirred for 5 minutes at room temperature before heated to reflux. Then 2.75 mL of dimethylsulfate ( $24.6 \mathrm{mmoL}, 30 \mathrm{eq}$ ) was added and the reaction mixture was further refluxed for 2 h . After cooling down to room temperature, the reaction solution was poured in 20 mL dichloromethane and washed with water ( $2 \times 30 \mathrm{~mL}$ ) and brine ( $1 \times 30 \mathrm{~mL}$ ). The organic phase was dried over $\mathrm{MgSO}_{4}$, and the solvents evaporated under reduce pressure. The crude product was passed through a short silica plug (1:1 n-heptane $/ \mathrm{CH}_{2} \mathrm{Cl}_{2}$ eluent system) to yield 1 ( 270 mg , $77 \%$ ) as off white solid.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta 7.58\left(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}^{2}\right), 7.44\left(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}^{1}\right), 7.34(\mathrm{~d}, J=8.2 \mathrm{~Hz}$, $1 \mathrm{H}^{8}$ ), $7.28\left(\mathrm{ddd}, J=8.2,6.9,1.3 \mathrm{~Hz}, 1 \mathrm{H}^{7}\right), 6.66\left(\mathrm{ddd}, J=8.0,7.0,1.1 \mathrm{~Hz}, 1 \mathrm{H}^{6}\right), 6.53(\mathrm{dt}, J=7.9,0.9$ $\left.\mathrm{Hz}, 1 \mathrm{H}^{5}\right), 3.93\left(\mathrm{~s}, 3 \mathrm{H}^{3}\right), 3.75\left(\mathrm{~d}, J=4.2 \mathrm{~Hz}, 3 \mathrm{H}^{9}\right)$
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta 150.9,141.9,136.9,125.4\left(\mathrm{C}-\mathrm{H}^{7}\right), 122.5,122.0,121.4\left(\mathrm{C}-\mathrm{H}^{5}\right), 120.0$, $118.0\left(\mathrm{C}-\mathrm{H}^{6}\right), 112.1\left(\mathrm{C}-\mathrm{H}^{1}\right), 108.1\left(\mathrm{C}-\mathrm{H}^{8}\right), 108.0\left(\mathrm{C}-\mathrm{H}^{2}\right), 57.6\left(\mathrm{C}^{3}-\mathrm{OCH}_{3}\right), 29.1\left(\mathrm{~N}^{9}-\mathrm{CH}_{3}\right)$.

HR-MS Thermo-Fisher Q-Exactive, ESI (+), $\mathrm{CH}_{3} \mathrm{OH} / \mathrm{CH}_{2} \mathrm{Cl}_{2}(90 / 10)$; ion [M+Na] ${ }^{+}, \mathrm{C}_{28} \mathrm{H}_{24} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Na}$, $\mathrm{m} / \mathrm{z}$ calculated $443.173, \mathrm{~m} / \mathrm{z}$ experimental $443.1728(\Delta=0 \mathrm{ppm})$.

## Experimental optical rotation values

$(+)-1:[\alpha]_{D}^{25}=+107 \pm 2 \%,[\phi]_{D}^{25}=+450\left(\mathrm{c}=1.3 \times 10^{-3}, \mathrm{DCM}\right)$.
$(-)-1:[\alpha]_{D}^{25}=-115 \pm 2 \%,[\phi]_{D}^{25}=-485\left(c=1.2 \times 10^{-3}, \mathrm{DCM}\right)$.
( $\pm$ )-3,3'-methylenedioxy-4,4'-bis-(9-methyl-9 H -carbazole) $(2)^{[3-4]}$


Boron tribromide ( 1 M in dichloromethane, $0.6 \mathrm{mmol}, 6 \mathrm{eq}$ ) was slowly added to a solution of $(+)-/(-)-1(35 \mathrm{mg}, 0.100 \mathrm{mmol})$ in dry dichloromethane ( 5 mL ) at room temperature and stirred for 3 h . The crude mixture was diluted and washed with water, then dried over $\mathrm{MgSO}_{4}$, filtered and evaporated under pressure. The obtained solid was dissolved in 30 mL of acetone and transfered to a pre-dried schlenk flask under argon. Potassium carbonate 150 mg ( 10 eq.) was added. The reaction mixture was stirred for 5 minutes at room temperature before heated to reflux. Then, $20 \mu \mathrm{~L}$ of diiodomethane ( $0.300 \mathrm{mmoL}, 3 \mathrm{eq}$ ) was added and further refluxed for 16 h. The reaction mixture was allowed to cool down to room temperature and the medium was diluted with EtOAc. The mixture was then extracted with water ( $2 \times 30 \mathrm{~mL}$ ) and brine ( $1 \times 30 \mathrm{~mL}$ ). The organic phase was dried over $\mathrm{MgSO}_{4}$, and the solvents evaporated under reduce pressure. The crude mixture was passed through short silica plugs ( $1: 1 n$-heptane $/ \mathrm{CH}_{2} \mathrm{Cl}_{2}$ eluent system) to yield (+)-2 (34 mg, $90 \%$ ) and (-)-2 ( $35 \mathrm{mg}, 93 \%$ ) as off-white solids.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.56\left(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 1 \mathrm{H}^{2}\right), 7.49\left(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 1 \mathrm{H}^{1}\right), 7.35(\mathrm{~d}, J=8.2 \mathrm{~Hz}$, $\left.1 \mathrm{H}^{8}\right), 7.28-7.22\left(\mathrm{~m}, 1 \mathrm{H}^{7}\right), 6.95\left(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}^{5}\right), 6.52\left(\mathrm{ddd}, J=8.1,7.1,1.0 \mathrm{~Hz}^{2} 1 \mathrm{H}^{6}\right), 5.65(\mathrm{~s}$, $1 \mathrm{H}^{3}$ ), $3.98\left(\mathrm{~s}, 3 \mathrm{H}^{9}\right)$.
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta 146.1,141.9,139.0,125.6$ (C-H7$), 125.2,122.7\left(\mathrm{C}-\mathrm{H}^{5}\right), 122.1,121.2$, $118.6\left(\mathrm{C}-\mathrm{H}^{1}\right), 117.8\left(\mathrm{C}-\mathrm{H}^{6}\right), 108.9\left(\mathrm{C}-\mathrm{H}^{2}\right), 108.1\left(\mathrm{C}-\mathrm{H}^{8}\right), 103.8\left(\mathrm{C}^{3}-\mathrm{OCH}_{3}\right), 29.3 .\left(\mathrm{N}^{9}-\mathrm{CH}_{3}\right)$.

HR-MS Thermo-Fisher Q-Exactive, ESI (+), $\mathrm{CH}_{3} \mathrm{OH} / \mathrm{CH}_{2} \mathrm{Cl}_{2}(90 / 10)$; ion [M+Na] ${ }^{+}, \mathrm{C}_{27} \mathrm{H}_{20} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Na}$, $\mathrm{m} / \mathrm{z}$ calculated $427.1417 \mathrm{~m} / \mathrm{z}$ experimental $427.1420(\Delta=1 \mathrm{ppm})$.

## Experimental optical rotation values

$(+)-2:[\alpha]_{D}^{25}=+640 \pm 1 \%,[\phi]_{D}^{25}=+2,570\left(c=1.3 \times 10^{-3}, \mathrm{DCM}\right)$.
$(-)-2:[\alpha]_{D}^{25}=-650 \pm 2 \%,[\phi]_{D}^{25}=-2,640\left(c=1.1 \times 10^{-3}, \mathrm{DCM}\right)$.
( $\pm$ )-3,3'-dimethoxy-6,6'-di(1,1-dimethylethyl)-4,4'-bis-(9-methyl-9H-carbazole) (3)


A stirred solution of $1(150 \mathrm{mg}, 0.48 \mathrm{mmol})$ and zinc chloride anhydrous ( $150 \mathrm{mg}, 3 \mathrm{eq}$. ) in the nitromethane $(9 \mathrm{~mL})$. Then, $t-\mathrm{BuCl}(120 \mu \mathrm{~L})$ was added with and stirred for 16 h under argon atmosphere. After that, water was poured to the mixture and extracted with dichloromethane ( $3 \times 10 \mathrm{~mL}$ ). The organic phase was washed with water, saturated $\mathrm{NaHCO}_{3}$, and brine $(1 \times 10 \mathrm{~mL})$. The organic phase was dried over $\mathrm{MgSO}_{4}$, and the solvents evaporated under reduce pressure. The crude mixture was passed through short silica plugs (1:1 $n$-heptane $/ \mathrm{CH}_{2} \mathrm{Cl}_{2}$ eluent system) to yield 3 ( $190 \mathrm{mg},>99 \%$ ) as off-white solid.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta 7.50\left(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}^{2}\right), 7.39\left(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}^{1}\right), 7.30(\mathrm{dd}, J=8.6$, $\left.2.0 \mathrm{~Hz}, 1 \mathrm{H}^{7}\right), 7.20\left(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 1 \mathrm{H}^{8}\right), 6.52\left(\mathrm{~d}, J=2.0 \mathrm{~Hz}, 1 \mathrm{H}^{5}\right), 3.83\left(\mathrm{~s}, 3 \mathrm{H}^{9}\right), 3.74\left(\mathrm{~s}, 3 \mathrm{H}^{3}\right), 0.97$ (s, 9H6).
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta 150.9,140.7,140.2,137.4,123.2\left(\mathrm{C}^{7}-\mathrm{H}^{7}\right), 122.3,122.3,119.9,118.0$, $111.3\left(\mathrm{C}^{1}-\mathrm{H}^{1}\right), 107.8\left(\mathrm{C}^{2}-\mathrm{H}^{2}\right), 107.4\left(\mathrm{C}^{8}-\mathrm{H}^{8}\right), 57.4\left(\mathrm{C}^{3}-\mathrm{OCH}_{3}\right), 34.0,31.3\left(\mathrm{C}^{6}-\mathrm{CH}_{3}\right), 29.1\left(\mathrm{~N}^{9}-\mathrm{CH}_{3}\right)$.

HR-MS Thermo-Fisher Q-Exactive, ESI (+), $\mathrm{CH}_{3} \mathrm{OH} / \mathrm{CH}_{2} \mathrm{Cl}_{2}(90 / 10)$; ion [M+Na]+, $\mathrm{C}_{36} \mathrm{H}_{40} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Na}$, $\mathrm{m} / \mathrm{z}$ calculated $555.2982, \mathrm{~m} / \mathrm{z}$ experimental 555.2983 ( $\Delta=0 \mathrm{ppm}$ ).

## Experimental optical rotation values

$(+)-3:[\alpha]_{D}^{25}=+150 \pm 4 \%,[\phi]_{D}^{25}=+780\left(\mathrm{c}=2.0 \times 10^{-3}, \mathrm{DCM}\right)$.
$(-)-3:[\alpha]_{D}^{25}=-160 \pm 3 \%,[\phi]_{D}^{25}=-850\left(c=1.5 \times 10^{-3}, \mathrm{DCM}\right)$.
$( \pm)-3,3^{\prime}$-methylenedioxy-6,6'-di(1,1-dimethylethyl)-4,4'-bis-(9-methyl-9 H -carbazole) (4)


Boron tribromide ( 1 M in dichloromethane, $0.45 \mathrm{mmol}, 6 \mathrm{eq}$ ) was slowly added to a solution of 3 ( $40 \mathrm{mg}, 0.075 \mathrm{mmol}$ ) in dry dichloromethane ( 5 mL ) at room temperature and stirred for 3 h . The crude mixture was diluted and washed with water, then dried over $\mathrm{MgSO}_{4}$, filtered and evaporated under pressure. The obtained solid was dissolved in 30 mL of acetone and transfered to a pre-dried schlenk flask under argon. Potassium carbonate 105 mg ( 10 eq .) was added. The reaction mixture was stirred for 5 minutes at room temperature before heated to reflux. Then, $20 \mu \mathrm{~L}$ of diiodomethane ( $0.300 \mathrm{mmoL}, 3 \mathrm{eq}$ ) was added and further refluxed for 16 $h$. The reaction mixture was allowed to cool down to room temperature and the medium was diluted with EtOAc. The mixture was then extracted with water ( $2 \times 30 \mathrm{~mL}$ ) and brine ( $1 \times 30 \mathrm{~mL}$ ). The organic phase was dried over $\mathrm{MgSO}_{4}$, and the solvents evaporated under reduce pressure. The crude mixture was purified over silica gel column chromatography (n-heptane/ethyl acetate $=19: 1$ ) to give 4 as a white solid ( $10 \mathrm{mg}, 25 \%$ ).
${ }^{1} \mathrm{H}^{2}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta 7.59\left(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 1 \mathrm{H}^{2}\right), 7.50\left(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 1 \mathrm{H}^{1}\right), 7.31-7.29\left(\mathrm{~m}, 2 \mathrm{H}^{7-}\right.$ $\left.{ }^{8}\right), 6.89-6.72\left(\mathrm{~m}, 1 \mathrm{H}^{5}\right), 5.70\left(\mathrm{~s}, 1 \mathrm{H}^{3}\right), 3.96\left(\mathrm{~s}, 3 \mathrm{H}^{9}\right), 0.66\left(\mathrm{~s}, 9 \mathrm{H}^{6}\right)$.
${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta$ 146.5, 141.1, 140.7, 139.7, 125.7, 124.1 ( $\left.\mathrm{C}^{7}-\mathrm{H}^{7}\right), 122.2,121.9,120.6$ $\left(\mathrm{C}^{5}-\mathrm{H}^{5}\right), 118.7\left(\mathrm{C}^{1}-\mathrm{H}^{1}\right), 109.2\left(\mathrm{C}^{2}-\mathrm{H}^{2}\right), 107.7\left(\mathrm{C}^{8}-\mathrm{H}^{8}\right), 104.4\left(\mathrm{C}^{3}-\mathrm{OCH}_{3}\right), 34.3,31.3\left(\mathrm{C}^{6}-\mathrm{CH}_{3}\right), 29.8\left(\mathrm{~N}^{9}-\right.$ $\mathrm{CH}_{3}$ ).

HR-MS Thermo-Fisher Q-Exactive, ESI (+), $\mathrm{CH}_{3} \mathrm{OH} / \mathrm{CH}_{2} \mathrm{Cl}_{2}(90 / 10)$; ion [M+Na]+, $\mathrm{C}_{35} \mathrm{H}_{36} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Na}$, $\mathrm{m} / \mathrm{z}$ calculated $539.2669, \mathrm{~m} / \mathrm{z}$ experimental 539.2671 ( $\Delta=0 \mathrm{ppm}$ ).

## Experimental optical rotation values

$(+)-4:[\alpha]_{D}^{25}=+300 \pm 2 \%,[\phi]_{D}^{25}=+1,530\left(\mathrm{c}=2.1 \times 10^{-3}, \mathrm{DCM}\right)$.
$(-)-4:[\alpha]_{D}^{25}=-290 \pm 4 \%,[\phi]_{D}^{25}=-1,500\left(\mathrm{c}=1.8 \times 10^{-3}, \mathrm{DCM}\right)$.
3-methoxy-9-methyl-9 H -carbazole ( $\mathbf{1}^{\prime}$ )


1 1
A stirred solution of 3-methoxy-9 H -carbazole ( $200 \mathrm{mg}, 1.01 \mathrm{mmol}$ ) was dissolved by 5 mL of acetone under inert atmosphere. Sodium hydroxide ( $22 \mathrm{M} \mathrm{aq}, 0.05 \mathrm{~mL}$ ) was added and stirred for 5 minutes at room temperature. The reaction mixture was heated to reflux temperature, then 1.5 mL of dimethylsulfate ( $15 \mathrm{mmoL}, 15 \mathrm{eq}$ ) was added. The reaction mixture was refluxed for 2 h. After cooling down to room temperature, the reaction solution was poured in 20 mL dichloromethane and washed with water ( $2 \times 30 \mathrm{~mL}$ ) and brine ( $1 \times 30 \mathrm{~mL}$ ). The organic phase was dried over $\mathrm{MgSO}_{4}$, and the solvents evaporated under reduce pressure. The crude product was passed through a short silica plug (1:1 $n$-heptane $/ \mathrm{CH}_{2} \mathrm{Cl}_{2}$ eluent system) to yield 1 ' as a white solid ( $200 \mathrm{mg}, 93 \%$ yield).
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.08(\mathrm{dt}, J=7.8,1.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.62(\mathrm{~d}, J=2.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.49$ (ddd, $J=$ $8.3,7.1,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.42-7.35(\mathrm{~m}, 1 \mathrm{H}), 7.31(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.23(\mathrm{ddd}, J=8.0,7.1,1.0 \mathrm{~Hz}$, $1 \mathrm{H}), 7.15(\mathrm{dd}, J=8.8,2.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.96(\mathrm{~s}, 3 \mathrm{H}), 3.82(\mathrm{~s}, 3 \mathrm{H})$. NMR spectrum of 3 ' was in accordance to a reference. ${ }^{[2]}$

3-methoxy-6-(1,1-dimethylethyl)-9-methyl-9 H -carbazole (3')

$1^{\prime}$

$3^{\prime}$

1' was mixed with zinc chloride anhydrous ( $50 \mathrm{mg}, 0.35 \mathrm{mmol}, 3 \mathrm{eq}$.) in 3 mL nitromethane. Then, $t-\mathrm{BuCl}(40 \mu \mathrm{~L}, 0.35 \mathrm{mmol}, 3 \mathrm{eq})$ was added with and stirred for 16 h under argon atmosphere. After that, water was poured to the mixture and extracted with dichloromethane ( $3 \times 10 \mathrm{~mL}$ ). The organic phase was washed with water, saturated $\mathrm{NaHCO}_{3}$, and brine ( $1 \times 10 \mathrm{~mL}$ ). The organic phase was dried over $\mathrm{MgSO}_{4}$, and the solvents evaporated under reduce pressure. The crude mixture was passed through short silica plugs ( $1: 1 n$-heptane $/ \mathrm{CH}_{2} \mathrm{Cl}_{2}$ eluent system) to yield $3^{\prime}$ as off-white solid ( $8.5 \mathrm{mg}, 26 \%$ yield).
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta 7.53\left(\mathrm{~s}, 1 \mathrm{H}_{2}\right), 7.43\left(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}_{1}\right), 7.34\left(\mathrm{dd}, J=8.5,2.0 \mathrm{~Hz}, 1 \mathrm{H}_{7}\right)$, $7.23\left(\mathrm{dm}, J=8.6 \mathrm{~Hz}, 1 \mathrm{H}_{8}\right), 6.56\left(\mathrm{~d}, J=1.9 \mathrm{~Hz}, 1 \mathrm{H}_{5}\right), 3.87\left(\mathrm{~s}, 3 \mathrm{H}_{3}\right), 3.78\left(\mathrm{~s}, 3 \mathrm{H}_{9}\right), 1.01\left(\mathrm{~s}, 9 \mathrm{H}_{6}\right)$. NMR spectrum of 3' was in accordance to a reference. ${ }^{[2]}$

## C. X-ray crystallographic data



Figure S1. ORTEP diagrams of compound 1 with ellipsoids at $50 \%$ probability (at 150 K ).


Figure S2. ORTEP diagrams of compound 2 with ellipsoids at $50 \%$ probability (at 150 K ).

Table S1. X-ray crystallographic data for compound 1 and 2.

| Compound | 1 | 2 |
| :---: | :---: | :---: |
| Empirical formula | $\mathrm{C}_{28} \mathrm{H}_{24} \mathrm{~N}_{2} \mathrm{O}_{2}$ | $\mathrm{C}_{27} \mathrm{H}_{20} \mathrm{~N}_{2} \mathrm{O}_{2}$ |
| CCDC number | 2016849 | 2017143 |
| Formula weight (g/mol) | 420.49 | 404.45 |
| Temperature | 150 K | 150 K |
| Wavelength | 0.71073 | 0.71073 |
| Crystal system, | triclinic | monoclinic |
| space group | P-1 | C 2/c |
| a (A) | 9.5316(10) | 13.408(2) |
| b (A) | 9.9882(11) | 18.225(2) |
| c ( $\AA$ ) | 12.1305(13) | 7.9041(11) |
| a (A) | 74.757(4) | 90 |
| $\mathrm{b}(\AA)$ | 77.144(4) | 94.302(6) |
| g (Å) | 74.314(4) | 90 |
| Volume ( $\AA^{3}$ ) | 1058.4(2) | 1926.0(4) |
| Z | 2 | 4 |
| Colour | colourless | colourless |
| $\mathrm{r}_{\text {calculated }}\left(\mathrm{g} . \mathrm{cm}^{-3}\right)$ | 1.319 | 1.395 |
| Absorption coefficient ( $\mathrm{mm}^{-1}$ ) | 0.083 | 0.089 |
| F(000) | 444 | 848 |
| Crystal size (mm) | 0.460 * 0.270 * 0.230 | 0.590 * 0.180 * 0.075 |
| $q$ range for data collection (0) | 2.169 to 27.604 | 3.047 to 27.484 |
| $\mathrm{T}_{\text {min }}, \mathrm{T}_{\text {max }}$ | 0.858, 0.981 | 0.578, 0.993 |
| Limited indices | $\begin{aligned} & -12 \leq \mathrm{h} \leq 12 \\ & -12 \leq \mathrm{k} \leq 13 \\ & -15 \leq \mathrm{l} \leq 15 \\ & \hline \end{aligned}$ | $\begin{aligned} & -17 \leq \mathrm{h} \leq 17 \\ & -23 \leq \mathrm{k} \leq 21 \\ & -10 \leq 1 \leq 10 \\ & \hline \end{aligned}$ |
| Reflections collected | 19999 | 5867 |
| Reflections unique | 4856 [R(int) $=0.0527]$ | 2216 [R(int) $=0.0834$ ] |
| Reflections [I>2sigma(I)] | 3871 | 1807 |
| Data completeness | 0.987 | 0.996 |
| Absorption correction type | multi-scan | multi-scan |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 4856 / 0 / 296 | 2216 / 0/141 |
| Goodness-of-fit | 1.045 | 1.063 |
| Final R indices [I>2sigma(I)] | $\begin{aligned} & \mathrm{R} 1=0.0466, \mathrm{wR} 2= \\ & 0.1179 \end{aligned}$ | $\begin{aligned} & \mathrm{R} 1=0.0572, \mathrm{wR} 2= \\ & 0.1507 \end{aligned}$ |
| R indices (all data) | $\begin{aligned} & \mathrm{R} 1=0.0619, \mathrm{wR} 2= \\ & 0.1269 \end{aligned}$ | $\begin{aligned} & \mathrm{R} 1=0.0697, \mathrm{wR} 2= \\ & 0.1631 \end{aligned}$ |
| Largest diff. peak and hole | 0.308 and -0.279 e. $\approx-3$ | 0.385 and -0.343 e. $\approx-3$ |



Figure S3. ORTEP diagrams of compound $\mathbf{3}$ with ellipsoids at $50 \%$ probability (at 150 K ).


Figure S4. ORTEP diagrams of compound 4 with ellipsoids at $50 \%$ probability (at 150 K ).

Table S2. X-ray crystallographic data for compound 3 and 4.

| Compound | 3 | 4 |
| :---: | :---: | :---: |
| Empirical formula | $\mathrm{C}_{36} \mathrm{H}_{40} \mathrm{~N}_{2} \mathrm{O}_{2}$ | $\mathrm{C}_{35} \mathrm{H}_{36} \mathrm{~N}_{2} \mathrm{O}_{2}$ |
| CCDC number | 2016850 | 2017144 |
| Formula weight (g/mol) | 532.70 | 516.66 |
| Temperature | 150 K | 150 K |
| Wavelength | 0.71073 | 0.71073 |
| Crystal system, | monoclinic | monoclinic |
| space group | P $21 / \mathrm{n}$ | P $21 / \mathrm{n}$ |
| a ( $\AA$ ) | 13.1390(17) | 16.902(3) |
| b (A) | 34.437(5) | 9.9528(18) |
| c ( $\AA$ ) | 13.4698(19) | 17.758(2) |
| a (A) | 90 | 90 |
| b (A) | 92.046(5) | 99.900(6) |
| $\mathrm{g}(\AA)$ | 90 | 90 |
| Volume ( $\AA^{3}$ ) | 6090.8(15) | 2942.8(8) |
| Z | 8 | 4 |
| Colour | colourless | yellow |
| $\mathrm{r}_{\text {calculated }}$ (g.cm ${ }^{-3}$ ) | 1.162 | 1.166 |
| Absorption coefficient ( $\mathrm{mm}^{-1}$ ) | 0.071 | 0.072 |
| F(000) | 2288 | 1104 |
| Crystal size (mm) | 0.540 * 0.420 * 0.300 | 0.660 * 0.650 * 0.200 |
| $q$ range for data collection ( ${ }^{\circ}$ ) | 2.208 to 27.550 | 2.354 to 27.519 |
| $\mathrm{T}_{\text {min }}, \mathrm{T}_{\text {max }}$ | 0.835, 0.979 | 0.593, 0.986 |
| Limited indices | $\begin{aligned} & -15 \leq \mathrm{h} \leq 17 \\ & -44 \leq \mathrm{k} \leq 41 \\ & -17 \leq \mathrm{l} \leq 17 \\ & \hline \end{aligned}$ | $\begin{aligned} & -21 \leq \mathrm{h} \leq 21 \\ & -11 \leq \mathrm{k} \leq 12 \\ & -23 \leq 1 \leq 22 \\ & \hline \end{aligned}$ |
| Reflections collected | 55868 | 23327 |
| Reflections unique | 13753 [R(int) $=0.0647]$ | 6630 [R(int) $=0.0735$ ] |
| Reflections [I>2sigma(I)] | 9784 | 4505 |
| Data completeness | 0.979 | 0.981 |
| Absorption correction type | multi-scan | multi-scan |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 13757 / 0 / 741 | 6630 / 52 / 383 |
| Goodness-of-fit | 0.992 | 1.078 |
| Final R indices [I>2sigma(I)] | $\begin{aligned} & \mathrm{R} 1=0.0601 \\ & \mathrm{wR} 2=0.1397 \end{aligned}$ | $\begin{aligned} & \mathrm{R} 1=0.0917 \\ & \mathrm{wR} 2=0.2346 \\ & \hline \end{aligned}$ |
| R indices (all data) | $\mathrm{R} 1=0.0920, \mathrm{wR} 2=0.1577$ | $\begin{aligned} & \mathrm{R} 1=0.1255, \mathrm{wR} 2= \\ & 0.2641 \end{aligned}$ |
| Largest diff. peak and hole | 0.648 and -0.403 e. $\approx-3$ | 0.507 and -0.425 e. $\approx-3$ |

## D. Preparative separation of enantiomer 1.

## Analytical chiral HPLC separation for compound 1

- The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 230 nm and a circular dichroism detector at 254 nm . The flow-rate is $1 \mathrm{~mL} / \mathrm{min}$.

| Column | Mobile Phase | $\mathbf{t}_{1}$ | $\mathbf{k}_{1}$ | $\mathbf{t}_{2}$ | $\mathbf{k}_{\mathbf{2}}$ | $\boldsymbol{\alpha}$ | $\mathbf{R}_{\mathbf{s}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Chiralpak IB | Heptane / isopropanol / <br> dichloromethane (90/5/5) | $7.90(-)$ | 1.68 | $9.65(+)$ | 2.27 | 1.35 | 3.32 |

DADI C, Sig $=230,4$ Ref-off



| RT [min] | Area | Area\% | Capacity Factor | Enantioselectivity | Resolution <br> (USP) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 7.90 | 8004 | 49.19 | 1.68 |  |  |
| 9.65 | 8267 | 50.81 | 2.27 | 1.35 | 3.32 |
| Sum | 16271 | 100.00 |  |  |  |

Preparative separation for compound 1:

- Sample preparation: About 440 mg of compound 1 are dissolved in 32 mL of dichloromethane.
- Chromatographic conditions: $(R, R)$-Whelk-01 (250 x 4.6 mm ), hexane / dichloromethane $(75 / 25)$ as mobile phase, flow-rate $=5 \mathrm{~mL} / \mathrm{min}$, UV detection at 254 nm .
- Injections (stacked): 400 times $80 \mu \mathrm{~L}$, every 4.5 minutes.
- First fraction: 155 mg of the first eluted with ee $>95.5 \%$

DAD1 C, Sig=230,4 Ref=off


| RT [min] | Area | Area\% |
| :---: | :---: | :---: |
| 7.81 | 40602 | 97.84 |
| 9.70 | 894 | 2.16 |
| Sum | 41497 | 100.00 |

- Second fraction: 144 mg of the second eluted enantiomer on Chiralpak IB with ee $>99.5 \%$

- Intermediate fraction: 130 mg


| RT [min] | Area | Area\% |
| :---: | :---: | :---: |
| 7.90 | 4900 | 46.99 |
| 9.64 | 5527 | 53.01 |
| Sum | 10426 | 100.00 |

## Kinetic of enantiomerization of 1 in 1,2-dichlorobenzene

About 0.9 mg of the second eluted enantiomer of 1 is heated in about 15 mL of 1,2 dichlorobenzene at $180^{\circ} \mathrm{C} .20 \mu \mathrm{~L}$ are taken and then injected on Chiralpak IC ( $90: 10$ heptane / 2$\operatorname{PrOH}, 1 \mathrm{~mL} / \mathrm{min}, \mathrm{UV} 290 \mathrm{~nm}$ ). The percentage decrease of the second eluted enantiomer of 1 is monitored.

| Time (min) | \% second eluted enantiomer | $\ln ((\% \mathrm{t}-50 \%) /(\%(\mathrm{t}=0)-50 \%))$ |
| :---: | :---: | :---: |
| 0 | 99.02 | 0.00000 |
| 1422 | 98.18 | -0.01728 |
| 2940 | 97.22 | -0.03741 |
| 7583 | 95.31 | -0.07870 |
| 9015 | 93.97 | -0.10872 |
| 11561 | 92.99 | -0.13126 |

$\mathrm{k}_{\text {enantiomerisation }}=9.40 \times 10^{-8} \mathrm{~s}^{-1}\left(180^{\circ} \mathrm{C}, 1,2\right.$-dichlorobenzene $)$
$\Delta \mathrm{G}^{\neq}=173.5 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}\left(180^{\circ} \mathrm{C}, 1,2\right.$-dichlorobenzene)
$\mathrm{t}_{1 / 2}=43$ days $\left(180^{\circ} \mathrm{C}, 1,2\right.$-dichlorobenzene)
Time (minutes)


## E. Steady-state physical characterizations

i) neutral state characterization


Figure S5. ECD spectra (solid line) and CPL spectra (dot line) of compounds 1 (black), 2 (red), 3 (green), 4 (blue) in dichloromethane (ca. $10^{-5} \mathrm{M}$ ) at 298 K

Electronic circular dichroism (ECD) spectra of enantiopure (+)-/(-)-1 and (+)-/(-)2 clearly highlight the impact of the carbazoles dihedral angle on the chiroptical properties (Figure S5). Indeed, although a qualitatively similar ECD signature was obtained for (+)-1 and (+)-2, with a positive exciton couplet around 250 nm , a positive band at ca. 310 nm and a low-energy negative broad band between 340 and $400 \mathrm{~nm},(+)-2$ showed a much higher overall ECD intensity in the long-wavelength region than ( + )-1. This is notably illustrated by the signals at 250 and 320 nm , respectively associated to $\Delta e=+190$ and + $150 \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ for ( + )-2, and $\Delta e=+110$ and $+40 \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ for ( + )-1. Further computational details have been performed and are detail below (Figure S54 and table S7-8).

Corresponding mirror-image CPL spectra were also obtained for both pairs of enantiomers, enabling us to determine promising $g_{\text {lum }}$ factors of $0.6 \times 10^{-3}$ and $1.5 \times 10^{-3}$ for 1 and 2, respectively (Figure S5).


Figure S6. UV-vis spectra (solid line) and fluorescence spectra (dash line) of compound 1 (black), 2 (red), $\mathbf{3}$ (green), 4 (blue), $\mathbf{1}^{\prime}$ (violet) and $\mathbf{3}^{\prime}$ (orange) in dichloromethane (ca. $10^{-5} \mathrm{M}$ ) at 298 K .

Table S3: Fluorescence quantum yield ( $\Phi$ ) of 1-4.

| Compound | $\boldsymbol{\Phi}$ |
| :---: | :---: |
| $\mathbf{1}$ | 22 |
| 2 | 15 |
| 3 | 24 |
| 4 | 17 |

Table S4. Oxidation potential ( $E_{0 \mathrm{x}}$ in V ) of 1-4, $1^{\prime}$ and $3^{\prime}$ versus saturated calomel electrode (SCE).

| Compound | $\boldsymbol{E}_{\boldsymbol{0} \boldsymbol{x}}$ | $\boldsymbol{E}_{\boldsymbol{0} \boldsymbol{x}}^{\mathbf{1}}$ | $\boldsymbol{E}_{\boldsymbol{0} \boldsymbol{x}}^{\mathbf{3}}$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | +0.92 | +1.11 | +1.63 |
| $\mathbf{2}$ | +1.14 | +1.40 | - |
| $\mathbf{3}(\mathrm{DCM})$ | +0.87 | +1.10 | - |
| $\mathbf{3}(\mathrm{MeCN})$ | +0.79 | +0.98 | - |
| $\mathbf{4}$ | +1.06 | +1.37 | - |
| $\mathbf{1}^{\prime}$ | +0.95 | +1.60 | - |
| $\mathbf{3}^{\prime}$ | +0.87 | +1.63 | - |



Figure S7. Cyclic voltammograms of 4 versus saturated calomel electrode (SCE) as the reference and $0.2 \mathrm{M} \mathrm{Bu}_{4} \mathrm{NPF}_{6}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ with ferrocene as internal standard.


Figure S8. UV-vis-NIR absorption spectra during the electrochemical oxidation of 1. The spectra were measured in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ with $0.2 \mathrm{M} n$ - $\mathrm{Bu}_{4} \mathrm{NPF}_{6}$ at 298 K .


Figure S9. UV-vis-NIR absorption spectra during the electrochemical oxidation of 2 . The spectra were measured in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ with $0.2 \mathrm{M} n-\mathrm{Bu}_{4} \mathrm{NPF}_{6}$ at 298 K .


Figure S10. UV-vis-NIR absorption spectra during the electrochemical oxidation of 3. The spectra were measured in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ with $0.2 \mathrm{M} n-\mathrm{Bu}_{4} \mathrm{NPF}_{6}$ at 298 K .


Figure S11. UV-vis-NIR absorption spectra during the electrochemical oxidation of 4. The spectra were measured in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ with $0.2 \mathrm{M} n-\mathrm{Bu}_{4} \mathrm{NPF}_{6}$ at 298 K .

## iii) radical state characterizations.

- Radical cations.

BICOL derivatives 1, 3 and carbazole 3' were dissolved in dichloromethane at room temperature under air saturated atmosphere. Then, an excess amount of silver(I)tetrafluoroborate ( $E_{0 \mathrm{x}}=1.11 \mathrm{~V} v s \mathrm{SCE}$ ) ${ }^{[5]}$ was added and the reaction mixture was further stirred for 10 min while its color turned to green (Scheme 2). Those solutions were filtrated through syringe filter to separated cuvettes and recorded UV-vis-NIR spectrum.


Scheme 2. BICOL radical's generation.


Figure S12. UV-vis-NIR absorption spectra of 1 (black) and $1^{\bullet+} \mathrm{BF}_{4^{-}}$(red) in dichloromethane at 298 K.


Figure S13. UV-vis-NIR absorption spectra of $\mathbf{3}$ (black) and $3^{\bullet+} \mathrm{BF}_{4}$ - (red) in dichloromethane at 298 K.


Figure S14. UV-vis-NIR absorption spectra of $\mathbf{3}^{\prime}$ (black) and $\mathbf{3}^{\prime \bullet+} \mathbf{B F}_{4^{-}}$(red) in dichloromethane at 298 K.


Figure S15. ECD spectra of compound $3^{\bullet+}$ in dichloromethane (ca. $10^{-5} \mathrm{M}$ ) at 298 K . Inset: Vis-NIR ECD spectra of compound $3^{\bullet+}$ in dichloromethane (ca. $10^{-3} \mathrm{M}$ ) at 298 K .


Simulated EPR spectra of monoradicals $1^{*}$. (left) and $3^{+ \text {. }}$ (right) suggesting te presence of an organic radical with a $1 / 2$ spin.
Figure S16. Top: EPR spectra of monoradical ( $1^{\bullet+}$ (black), $3^{\bullet+}$ (green) and $3^{\mathbf{\bullet}+}$ (dark yellow)) with $\mathrm{AgBF}_{4}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and $4^{\bullet+}$ (blue) with 1.0 equivalent of magic blue in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at 298 K . Bottom: Simulated EPR spectra of $\mathbf{1}^{\bullet+}$ (left) and $\mathbf{3}^{\bullet+}$ (right).

## UV-vis titration studies

Oxidation process in dichloromethane were studied by UV-vis-NIR spectroscopy at 298 K . Solution of each molecule ( $10^{-5} \mathrm{M}$ ) was prepared using dry-dichloromethane as a solvent. Increasing number of $\left(4-\mathrm{BrPh}_{3} \mathrm{NSbCl}_{6}\right.$ (so-called magic blue, $E_{0 \mathrm{x}}=1.16 \mathrm{~V}$ vs SCE ) ${ }^{[5]}$ equivalents were added to the separate vials under argon ( 3.0 mL in a 1 cm -pathlength quartz cell). The BICOL's derivatives concentration was kept constant.


Figure S17. UV-vis titration studies of $\mathbf{1}$ by magic blue in dichloromethane $\left(c=7 \times 10^{-5} \mathrm{M}\right)$ at 298 K.


Figure S18. UV-vis titration studies of $\mathbf{2}$ by magic blue dichloromethane $\left(c=7 \times 10^{-5} \mathrm{M}\right)$ at 298 K.


Figure S19. UV-vis titration studies of $\mathbf{3}$ by magic blue in dichloromethane ( $\mathrm{c}=7 \times 10^{-5} \mathrm{M}$ ) at 298 K. * denotes an excess of magic blue oxidant.

- Diradical dications.


Figure S20. Schematic illustration of the electronic configurations that can be obtained upon oxidation of a radical exhibiting a SOMO/HOMO inversion.

To a dry and degassed acetonitrile solution of 3, 2 equivalents of magic blue oxidant ( $E_{0 \mathrm{x}}$ $=1.05 \mathrm{~V} v s \mathrm{SCE}$ in acetonitrile) were added and the resulting solution was further stirred at room temperature for 5 min while its color turned to dark green (Scheme 3). This solution was then
transferred to a dedicated cuvette for UV-vis-NIR and ECD analysis. The same procedure was performed for both enantiomers of 3 .

For SQUID experiment, 16 mg (2 eq.) of magic blue were added into an acetonitrile solution contained $5 \mathrm{mg}\left(1 \times 10^{-4} \mathrm{mmol}\right)$ of 3 under argon atmosphere. Then, the solution was allowed to stir and controlled by UV-vis-NIR. After full conversion to $3^{2+2}$, the solution was dried under vacuum. 6.0 mg of this solid was loaded to capsules and mounted in the colorless plastic straws. After background SQUID run, magnetization for the background, $\mathrm{M}_{\mathrm{bck}}$, was point-by-point subtracted from magnetization for the sample, $\mathrm{M}_{\text {sample }}$, to provide corrected magnetization, $\mathrm{M}_{\text {radical }}$, accounting for diamagnetism of sample holder. Thus, $\mathrm{M}_{\text {radical }}$ corresponded to mass of 3.3 mg .

$$
3 \xrightarrow[\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3} \text { (sat'd) }]{\stackrel{(4-\mathrm{BrPh})_{3} \mathrm{NSbCl}_{6}}{\mathrm{MeCN}}} 3^{2 \bullet 2+} \mathbf{2 S b C l}_{6}^{-}
$$

Scheme $3.3^{302+}$ radical's generation and deactivation process.

## Recovery analysis of $\mathbf{3}^{\mathbf{2 0}} \mathbf{2 0}^{+}$

To a solution of BICOL derivatives $\mathbf{3}(5 \mathrm{mg}, 9.39 \mu \mathrm{M})$ in 10 mL acetonitrile ( MeCN ) under argon atmosphere, 16.2 mg of magic blue (2.1 equivalent) were added and the solution stirred for 10 minutes under argon atmosphere to ensure full conversion. Then, the solution was quenched by addition of $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ (sat'd, aq). The color changed from dark green to yellow. The solution was evaporated under reduced pressure and purified by column chromatography $\left(\mathrm{SiO}_{2}\right.$, pentane/DCM, 1:1) to obtain a white powder of $3\left(4.0 \mathrm{mg}, 80 \%\right.$ recovery), which was confirmed by ${ }^{1} \mathrm{H}$ NMR spectrum $\left(400 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right)$ as depicted in Figure $\mathbf{S 2 1}$. Since the nmr of the crude reaction shows only starting material 3 and reduced magic blue oxidant, and no presence of other side products, it is reasonable to say that the loss of 1 mg occurred during the purification step (and not from a possible degradation of $\mathbf{3}^{\mathbf{2 0 2 +}}$ ).


Figure $\operatorname{S21}$. ECD spectra of compound $3^{\bullet+}$ and $\mathbf{3}^{\mathbf{2 \bullet}+\text { in }}$ acetonitrile form NIR-ECD recorded in range from 400 to $1100 \mathrm{~nm}\left(c a .10^{-3} \mathrm{M}\right)$ at 298 K .


Figure S22. Variable temperature EPR spectra of diradical $\mathbf{3}^{\mathbf{2 0 2 +}}$ (left) and half-field region showing no forbidden transition after 100 scans (right).


MrNへNN気


Figure S23. ${ }^{1} \mathrm{H}$ NMR spectrum ( $400 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 298 \mathrm{~K}$ ) of sample obtained after quench of diradical dication $\mathbf{3}^{202+} 2 \mathrm{SbCl}_{6}$ in acetonitrile, before (top, * denotes the presence of $(p-\mathrm{BrPh})_{3} \mathrm{~N}$ spectator) and after (bottom) purification by column chromatography.

## Kinetic analysis of $1^{\bullet+}, 3^{\bullet+}, 3^{\bullet \bullet+}$ and $3^{2 \bullet 2+}$ dissociation

All radical species in this analysis was prepared according to the described procedure (vide supra) and added directly to the separated cuvettes under argon or air atmosphere. After measurement of monoradical, sample was reduced by $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ (sat'd, aq) and analyzed by lowresolution mass spectrometry (LR-MS) using dithranol as matrix carrier. For $3^{2 \mathbf{2}+2}$, specific procedure will be described in its corresponding section.

## Compound $1^{\bullet}+$



Figure S24. UV-vis-NIR absorption spectra of $\mathbf{1}^{\bullet+}$ in dichloromethane at 298 K under argon atmosphere (left) and air atmosphere (right).


Figure S25. First-order fitting plot of $\ln \left(A / A_{0}\right)$ of $\mathbf{1}^{\cdot+}$ as a function of time at 782 nm under argon atmosphere (black) and air atmosphere (red).

Table S5. Linear fitting from first-order fitting equation with half-life calculation

| Environment | A | B | $\mathrm{r}^{2}$ | half-life (min) |
| :---: | :---: | :---: | :---: | :---: |
| Air | -0.00306 | -0.00439 | 0.9944 | $158 \pm 29$ |
| Ar | 0.00795 | $-8.34031 \times 10^{-4}$ | 0.9927 | $831 \pm 48$ |



Wraknt Daltorica tlexContral
Dinplay Doreennhot - Genemared on 2020-0月-22 4 4ha3n50n
Figure S26. LRMS spectrum (dithranol, $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ) of the sample obtained after quench of monoradical cation $1^{++}$under argon atmosphere. The spectrum suggests that an oligomerization process occurred as one of degradation pathway of $\mathbf{1}^{++}$.


Araker Daltonlea EloxControl
Display ficreenuhot - Generated on 2020-09-21 14h27m26:
Figure S27. LRMS spectrum (dithranol, $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ) of the sample obtained after quench of monoradical cation $1^{\bullet+}$ under air atmosphere. The spectrum suggests that an oligomerization process occurred as one of degradation pathway of $1^{++}$.

## Compound $3^{\boldsymbol{\bullet}+}$ and $3^{\mathbf{\prime \bullet}+}$



Figure S28. UV-vis-NIR absorption spectra of $\mathbf{3}^{\cdot+}$ in dichloromethane ( $5 \times 10^{-5} \mathrm{M}$ ) under argon atmosphere at 298 K .



Figure S29. UV-vis-NIR absorption spectra of 3•+ (left) and $\mathbf{3}^{\prime}+{ }^{(r i g h t)}$ ) in dichloromethane ( $5 \times$ $10^{-5} \mathrm{M}$ ) under air atmosphere at 298 K .


Figure S30. Left: Zeroth-order fitting plot of absorption of $\mathbf{3 \cdot +}$ as a function of time under argon atmosphere. Right: Zeroth-order fitting plot of absorption of 3•+ (black) and $3^{\prime \cdot+}$ (red) as a function of time under air atmosphere (black).

Table S6. Linear fitting from optical density as a function of time in several kinetic order with half-life calculation

| Compound | Environment | A | B | $\mathrm{r}^{2}$ | half-life <br> (hours) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $3^{\bullet+}$ | Air | 0.243 | -0.00125 | 0.9565 | $97 \pm 0.2$ |
|  | Ar | 0.634 | -0.00342 | 0.9932 | $93 \pm 0.2$ |
| $3^{\cdot} \cdot+$ | Air | 0.133 | -0.000798 | 0.9438 | $84 \pm 0.2$ |



Briker Daltenite flextontrol
tiaplay sercenahot - Menerated on 2020-05-25 23h53m39n
Figure S31. LRMS spectrum (dithranol, $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ) of the sample obtained after quench of monoradical cation $3^{\bullet+}$ after 96 h . The spectrum suggested that $3^{\bullet+}$ is stable.

## Compound $3^{2 \boldsymbol{\bullet}}{ }^{2+}$ (solid state)

To a solution of BICOL derivatives $\mathbf{3}(5 \mathrm{mg}, 9.39 \mu \mathrm{M}$ ) in 10 mL acetonitrile (MeCN) under argon atmosphere, 16.2 mg of magic blue ( 2.1 equivalent) were added and stirred for 10 minutes under argon atmosphere. Then, 0.5 mL was taken in to 6 separated vials, evaporated under reduced pressure and store at $-20^{\circ} \mathrm{C}$. Every 24 hours, each vial was refilled with degassed MeCN and recorded UV-vis-NIR spectrum (Figure S32).


Figure S32. UV-vis-NIR absorption spectra of $\mathbf{3}^{\mathbf{2 0 2 +}}$ in acetonitrile under argon atmosphere at 298 K.
G. NMR Spectra


Figure S33. ${ }^{1} \mathrm{H}$ NMR spectrum of 1 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(400 \mathrm{MHz})$. * denote traces of water.


Figure S34. ${ }^{1} \mathrm{H}-{ }^{1} \mathrm{H}$ COSY spectrum of 1 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(400 \mathrm{MHz})$.


$-57.60$
요


Figure S35. ${ }^{13} \mathrm{C}$ NMR spectrum of 1 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(100 \mathrm{MHz})$.


Figure S36. ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ HSQC spectrum of $1 \mathrm{in} \mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(400 \mathrm{MHz})$.



Figure S37. ${ }^{1} \mathrm{H}$ NMR spectrum of 2 in $\mathrm{CDCl}_{3}$ at $298 \mathrm{~K}(400 \mathrm{MHz})$. * denote traces of water.


Figure S38. ${ }^{1} \mathrm{H}-1 \mathrm{H}$ COSY spectrum of 2 in $\mathrm{CDCl}_{3}$ at $298 \mathrm{~K}(400 \mathrm{MHz})$.



Figure S39. ${ }^{13} \mathrm{C}$ NMR spectrum of 2 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(100 \mathrm{MHz})$.


Figure S40. ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ HSQC spectrum of 2 at $298 \mathrm{~K}(400 \mathrm{MHz})$.



Figure S41. ${ }^{1} \mathrm{H}$ NMR spectrum of 3 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(400 \mathrm{MHz})$.

* denote traces of water. \$ denotes traces of heptane.


Figure S42. ${ }^{1} \mathrm{H}-{ }^{1} \mathrm{H}$ COSY spectrum of 3 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(400 \mathrm{MHz})$.


Figure $\mathrm{S} 43 .{ }^{13} \mathrm{C}$ NMR spectrum of 3 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(100 \mathrm{MHz})$.


Figure S44. ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ HSQC spectrum of 3 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(400 \mathrm{MHz})$.


Figure S45. ${ }^{1} \mathrm{H}$ NMR spectrum of 4 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(400 \mathrm{MHz})$.

* denote traces of water. $\$$ denotes traces of heptane.


Figure S46．${ }^{1} \mathrm{H}-{ }^{-1} \mathrm{H}$ COSY spectrum of 4 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(400 \mathrm{MHz})$ ．


Figure S47．${ }^{13} \mathrm{C}$ NMR spectrum of 4 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(100 \mathrm{MHz})$ ．


Figure S48. ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ HSQC spectrum of 4 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(400 \mathrm{MHz})$.

## H Computational Part

Kohn-Sham Density functional theory (DFT) as implemented in the Gaussian (G16) package [6] was used for all computations, employing the PBE0 functional [7] and the def2-SV(P) basis [8,9]. For neutral and oxidized species, solvent effects were considered by means of the polarizable continuum model (PCM) [10] for dichloromethane and acetonitrile, respectively, to match the experimental conditions. 'D3' dispersion corrections were included in the calculations [11]. Excited state energies, transition moments, excited state structures and their vibrational normal modes were obtained from time-dependent DFT (TD-DFT) response theory.
For the absorption and electronic circular dichroism (ECD) spectra we calculated the 200 lowestenergy vertical spin-allowed electronic excitations. The transitions were subsequently Gaussianbroadened with $\sigma=0.20 \mathrm{eV}$ to simulate the spectral envelopes. For overviews of the theoretical approach to model natural optical activity by quantum chemical calculations, in particular via TDDFT, see, for example, References [12,13]. Different functionals and solvent effects were tested for these compounds; see Figures S73-S76.

For neutral compounds, we calculated the electronic emission and circularly polarized luminescence (CPL) spectra using the first electronic transition in the excited state optimization in gas phase, and followed by Gaussian broadening with $\sigma=0.2 \mathrm{eV}$ for the transition. Test calculations including the state-specific solvation correction were performed. The Franck-Condon-Herzberg-Teller (FCHT) approximation [14] was employed for the vibronic intensities, with the optimized structures and harmonic force fields of the ground state and first excited state used as input.

## RESULTS

The optimized structures of the carbazole derivatives are shown in Figure S49. The dihedral angle between the carbazole units are $76.9^{\circ}$ (Expt. $87.1^{\circ}$ ) for 1, $52.2^{\circ}$ (Expt. $52.4^{\circ}$ ) for 2 and, $65.5^{\circ}$ and $106.6^{\circ}$ (Expt. 98-102${ }^{\circ}$ ) for 3 . Two conformers were found for bicarbazole $\mathbf{3}$ (see Figure S50). The most stable conformer is the one with the smaller dihedral angle ( $65^{\circ}$ ). The conformer with a dihedral angle of $106.6^{\circ}$ is predicted to be $1.84 \mathrm{kcal} \cdot \mathrm{mol}^{-1}$ higher in energy (Boltzmann population of $4 \%$ at 298 K ). Therefore, carbazole 3 does not crystallize in its lowest-energy conformer, which is very likely due to a more effective crystal packing favoring the slightly less stable conformer in the solid. When the calculated spectra for the two conformers are compared (vide infra), there is a much better match for the $65^{\circ}$ conformer, thereby lending strong support for the higher abundance of this conformer in solution.


Figure S49. Optimized structures of carbazole compounds 1,2 and 3. The dihedral angle between the carbazole units are 76.9으 (Expt. 87.1 ${ }^{\circ}$ ) for 1, $52.2^{\circ}$ (Expt. 52.4ㅇ) for 2 and, $65.5^{\circ}$ (Expt. 98$102^{\circ}$ ) for 3.


Figure S50. Conformers of $\mathbf{3}$ with a different dihedral angle; $65.5^{\circ}$ (blue) and $106.6^{\circ}$ (red).


Figure S51. Experimental (Expt.) and calculated (Calc.) absorption spectra for ( + )-1 (black) and $(+)-2$ (red). Selected transitions and oscillator strengths indicated as 'stick spectra'. Predominant excitations are numbered according to Tables S7-S8.

Table S7. Selected excitations and occupied (occ)-unoccupied (unocc) MO pair contributions (greater than $10 \%$ ) for (+)-1. H and L indicate the HOMO and LUMO, respectively.

| Excitation | $\mathrm{E}[\mathrm{eV}]$ | $\lambda[\mathrm{nm}]$ | $f$ | $\mathrm{R}[10-40 \mathrm{cgs}]$ | occ. no. | unocc no. | $\%$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\# 1$ | 3.788 | 327 | 0.144 | -23.02 | $111(\mathrm{H})$ | $112(\mathrm{~L})$ | 93 |
| $\# 5$ | 4.355 | 285 | 0.117 | 271.87 | 109 | 112 | 91 |
| $\# 6$ | 4.426 | 280 | 0.110 | -142.64 | 108 | 112 | 88 |
| $\# 9$ | 5.024 | 247 | 0.410 | 694.34 | 111 | 114 | 78 |
| $\# 10$ | 5.062 | 245 | 0.243 | -374.12 | 110 | 114 | 82 |
| $\# 11$ | 5.146 | 241 | 0.300 | 363.52 | 110 | 115 | 39 |
|  |  |  |  |  | 107 | 112 | 30 |
| $\# 12$ | 5.148 | 241 | 0.498 | -538.15 | 111 | 115 | 63 |
| $\# 14$ | 5.371 | 231 | 0.073 | -234.47 | 106 | 112 | 81 |
| $\# 15$ | 5.379 | 230 | 0.129 | 30.08 | 109 | 114 | 58 |
| $\# 17$ | 5.489 | 226 | 0.079 | -187.98 | 107 | 113 | 79 |

Table S8. Selected excitations and occupied (occ)-unoccupied (unocc) MO pair contributions (greater than $10 \%$ ) for (+)-2. H and L indicate the HOMO and LUMO, respectively.

| Excitation | $\mathrm{E}[\mathrm{eV}]$ | $\lambda[\mathrm{nm}]$ | $f$ | $\mathrm{R}[10-40 \mathrm{cgs}]$ | occ. no. | unocc no. | $\%$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| \#1 | 3.492 | 355 | 0.199 | -49.15 | $106(\mathrm{H})$ | $107(\mathrm{~L})$ | 97 |
| \#2 | 3.645 | 340 | 0.020 | -54.73 | 105 | 107 | 95 |
| \#3 | 4.058 | 306 | 0.096 | 372.62 | 104 | 107 | 94 |
| $\# 5$ | 4.281 | 290 | 0.141 | -66.46 | 106 | 108 | 75 |
| $\# 7$ | 4.749 | 261 | 0.053 | 104.60 | 102 | 107 | 61 |
|  |  |  |  |  | 106 | 109 | 19 |
| \#10 | 4.978 | 249 | 0.104 | 180.38 | 103 | 108 | 38 |
|  |  |  |  |  | 106 | 109 | 34 |
| \#11 | 4.998 | 248 | 0.111 | 4.45 | 105 | 110 | 19 |
|  |  |  |  |  | 105 | 107 | 44 |
| \#13 | 5.156 | 240 | 0.179 | 615.07 | 105 | 110 | 52 |
|  |  |  |  |  | 103 | 108 | 19 |
| \#14 | 5.202 | 238 | 0.742 | -805.41 | 106 | 110 | 56 |
|  |  |  |  |  | 104 | 108 | 28 |
| \#16 | 5.440 | 228 | 0.169 | 130.09 | 104 | 109 | 64 |
| \#17 | 5.546 | 224 | 0.178 | -279.34 | 102 | 108 | 73 |



Figure S52. Isosurfaces ( $\pm 0.030 \mathrm{au}$ ) of Molecular Orbitals (MOs) involved in the selected transitions for (+)-1. Values listed in parentheses are the corresponding orbitals energies in eV.


Figure S53. Isosurfaces ( $\pm 0.030 \mathrm{au}$ ) of Molecular Orbitals (MOs) involved in the selected transitions for (+)-2. Values listed in parentheses are the corresponding orbitals energies in eV.


Figure S54. Experimental (Expt.) and calculated (Calc.) electronic circular dichroism (ECD) spectra for ( + )-1 (solid black line) and (+)-2 (solid red line). Corresponding ( - )-enantiomers are represented in dashed lines. Selected transitions and rotatory strengths indicated as 'stick spectra'. Predominant excitations are numbered according to Tables S7-S8.

Emission and CPL Spectroscopy. The computed normalized emission and circularly polarized luminescence (CPL) spectra of $\mathbf{1}$ and $\mathbf{2}$ are displayed in Figure S55. The excited state geometries of 1 and 2 show significant differences in the helical carbazoles respect to the ground state geometries (Figure S56). For this reason, reasonable Franck-Condon factors could not be obtained. Therefore, the first electronic transition in the excited state optimization in gas phase has been used to plot both simulated spectra, which appears in the following order in the simulated emission and CPL spectra; (+)-1 at $24019 \mathrm{~cm}^{-1}$ and (+)-2 at $23479 \mathrm{~cm}^{-1}$, indicating that the emission of 2 is red shifted from 1. Experiments also reproduce this order. The calculated spacing between the band maxima of 1 and 2 is 0.067 eV , while for experiments it is 0.106 eV for the emission and 0.136 eV for the CPL, respectively. Thus, calculations in gas phase reasonably agree with experiments (Figure S56 and Table S9). In this case, calculations including the statespecific solvation correction do not match very well with the experimental data.


Figure S55. Calculated emission (left) and circularly polarized luminescence (right) spectra using the first electronic transition in the excited state optimization in gas phase. The intensities are plotted based on Gaussian broadening with $\sigma=0.2 \mathrm{eV}$. Corresponding experimental data is indicated in dashed lines.


1


2

Figure S56. Overlay of the optimized equilibrium ground state, $\mathrm{S}_{0}$, (red) and excited state, $\mathrm{S}_{1}$, (blue) structures of carbazoles 1 and 2.

Table S9. Experimental (Expt.) and calculated emission spectroscopy data for 1 and 2 (in eV). First electronic transition in the excited state optimization in gas phase and vertical emission energy from the first excited state to ground state emission including the state-specific (SS-PCM) solvation correction.

| Carbazole | Expt. $\tilde{v}$ | $\mathrm{~S}_{0}-\mathrm{S}_{1}$ | $\mathrm{~S}_{0}-\mathrm{S}_{1}(\mathrm{SS}$-PCM $)$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | 3.073 | 2.978 | 2.794 |
| $\mathbf{2}$ | 2.967 | 2.911 | 2.860 |

## Electrochemistry and radical $1^{\bullet+}$



Figure S57. Orbital energies (in eV) and isosurfaces of frontier molecular orbitals computed for the neutral $(+)-1$ (left) and the monoradical ( + )- $1^{\bullet+}$ (right). Isosurfaces of $\pm 0.030$ au for the neutral and the monoradical.

The total spin $\mathrm{S}^{2}$ expectation value before annihilation is 0.761 for $1^{\cdot+}$ and 0.764 for $2^{\cdot+}$, with 0.750 being the correct number for a doublet. Although some spin contamination exists, it is not large for either compound.


Figure S58. Orbital energies (in eV) and isosurfaces of frontier molecular orbitals computed for neutral ( + )-2 (left) and the monoradical ( + )-2•+ (right). Isosurfaces of $\pm 0.030$ au for the neutral and the monoradical.


Figure S59. Experimental (Expt.) and calculated (Calc.) absorption spectra for ( + ) - 1 in neutral (black) and monoradical (red) forms. Selected transitions and oscillator strengths indicated as 'stick spectra'. Predominant transitions for the monoradical are numbered according to Table S10.

Table S10. Selected excitations and occupied (occ)-unoccupied (unocc) MO pair contributions (greater than 10\%) for ( + )- $1^{\bullet+}$. S and L indicate the SOMO and LUMO, respectively.

| Excitation | $\mathrm{E}[\mathrm{eV}]$ | $\lambda[\mathrm{nm}]$ | $f$ | $\mathrm{R}[10-40 \mathrm{cgs}]$ | occ. no. | unocc no. | $\%$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\# 4$ | 1.694 | 732 | 0.047 | -24.68 | $107 \beta$ | $111 \beta(\mathrm{~L})$ | 93 |
| $\# 5$ | 1.889 | 657 | 0.090 | 17.76 | $106 \beta$ | $111 \beta$ | 90 |
| $\# 10$ | 3.138 | 395 | 0.048 | 7.33 | $102 \beta$ | $111 \beta$ | 73 |
| $\# 15$ | 3.692 | 336 | 0.021 | -21.62 | $109 \alpha(\mathrm{~S})$ | $112 \alpha$ | 55 |
| $\# 18$ | 3.770 | 329 | 0.070 | -10.91 | $110 \beta$ | $113 \beta$ | 48 |
|  |  |  |  |  | $111 \alpha$ | $113 \alpha$ | 33 |
| $\# 22$ | 4.050 | 306 | 0.024 | 13.73 | $108 \beta$ | $112 \beta$ | 13 |
| $\# 24$ | 4.225 | 293 | 0.031 | 34.67 | $109 \beta$ | $112 \beta$ | 66 |
| $\# 30$ | 4.456 | 278 | 0.066 | 32.75 | $109 \beta$ | $113 \beta$ | 41 |
|  |  |  |  |  | $110 \alpha$ | $113 \alpha$ | 24 |
| $\# 39$ | 4.764 | 260 | 0.503 | 168.87 | $108 \beta$ | $112 \beta$ | 26 |
|  |  |  |  |  | $108 \alpha$ | $112 \alpha$ | 21 |
| $\# 45$ | 4.962 | 250 | 0.586 | -68.42 | $110 \beta$ | $115 \beta$ | 32 |
|  |  |  |  |  | $111 \alpha$ | $115 \alpha$ | 22 |




Figure S60. Experimental (Expt.) and calculated (Calc.) ECD spectra for (+)-1 in neutral (black) and monoradical (red) forms. Selected transitions and rotatory strengths for the monoradical are indicated as 'stick spectra'. Predominant transitions for the monoradical are numbered according to Table S10. $M$-enantiomers are represented in dashed lines.


Figure S61. Isosurfaces ( $\pm 0.030 \mathrm{au}$ ) of Molecular Orbitals (MOs) involved in the selected transitions for ( + )- $1^{\bullet+}$. Values listed in parentheses are the corresponding orbitals energies in eV .


Figure S62. Isosurfaces ( $\pm 0.030 \mathrm{au}$ ) of Molecular Orbitals (MOs) involved in the selected transitions for ( + )-2•+. Values listed in parentheses are the corresponding orbitals energies in eV .

## Diradical $3^{2+}$ and related characterization

Two conformers with different dihedral angle between the carbazole fragments were found in the calculations for bicarbazole 3 and its corresponding radicals $3 \cdot+$ and $3^{2 \cdot 2+}$ (see Scheme S50 and Table S11). All these species of Table S11 were characterized as minima. For 3, $\mathbf{3}^{\bullet+}$ and $\mathbf{3 2 0}^{2 \cdot+}$, the most stable conformer is the one with the smaller dihedral angle of about 60-65 (Table S11).

For $3^{\cdot+}$, the loss of one electron reduces the torsion angle from $65^{\circ}$ to $60^{\circ}$. This conformer is 3.0 $\mathrm{kcal} \cdot \mathrm{mol}^{-1}$ lower in energy than the other conformer with a dihedral of $118^{\circ}$. The calculated Boltzmann population at 298 K for the latter conformer is therefore low, around $0.6 \%$. In the case of $\mathbf{3}^{2 \cdot 2+}$, the spin-triplet conformer with a dihedral angle of $64^{\circ}$ is predicted to be the lowest in energy, followed by the spin-triplet conformer with a dihedral of $112^{\circ}$ at $2.63 \mathrm{kcal} \cdot \mathrm{mol}^{-1}$ (Boltzmann population at 298 K of $1.2 \%$ ). Both conformers with a spin-singlet electronic configuration are higher in energy with a negligible Boltzmann population at 298 K (see Table S11).

Table S11. Dihedral angle (in degrees) between the carbazole segments, relative energies (in $\mathrm{kcal} \cdot \mathrm{mol}^{-1}$ ) and Boltzmann population ratio at $298 \mathrm{~K}(\mathrm{in} \%)$ for the different systems of (+)-3 in neutral, monoradical and diradical forms. For ( + )- $\mathbf{3}^{2 \cdot 2+}$, the spin multiplicity state is also indicated.

| Carbazole | Dihedral angle $\left({ }^{\circ}\right)$ | Erel $\left(\mathrm{kcal} \cdot \mathrm{mol}^{-1}\right)$ | Boltzmann population at $298 \mathrm{~K} \mathrm{( } \mathrm{\%)}$ |
| :---: | :---: | :---: | :---: |
| $(+)-3$ |  |  |  |
|  | 65 | 0.00 | 95.7 |
| $(+)-3^{+}$ | 106 | 1.84 | 4.3 |
|  |  |  |  |
|  | 60 | 0.00 | 99.4 |
| $(+)-\mathbf{3 2}^{2+}$ | 118 | 3.00 | 0.6 |
| Singlet | 55 | 8.87 | $3.1 \cdot 10^{-5}$ |
| Triplet | 64 | 0.00 | 98.8 |
| Singlet | 131 | 12.74 | $4.5 \cdot 10^{-8}$ |
| Triplet | 112 | 2.63 | 1.2 |

Figures S63-S64 show the isosurfaces of the frontier molecular orbitals and their energies for 3, $3 \cdot+$ and $32 \cdot 2+$. Like 1 and 2 , neutral carbazole $\mathbf{3}$ is a closed-shell system with a small energetic splitting ( 0.191 eV ) between HOMO and HOMO-1 from in-phase and out-of-phase FFO linear combinations. The HOMO and HOMO-1 present $\pi$-orbitals of the conjugated carbazole system, including some contributions on the nitrogen and oxygen atoms. As seen in Figure S64, molecular orbitals of $\mathbf{3}$ are expanded over the two carbazolyl moieties.

As for $1^{\bullet+}$ and $2^{\bullet+}$, the calculated spin densities of $3^{\bullet+}$ are also represented by spin-polarized KS systems where the $\alpha$-spin HOMO has a matching occupied $\beta$-spin HOMO, with both having very similar orbital energies. The 'non-Aufbau' SOMO-HOMO inversion is also observed in $3^{\bullet+}$, along with a degree of localization of the MOs on the fragments upon ionization (Figure S63). The LUMO density corresponds closely to the calculated spin density (Figure S65). Therefore, the LUMO represents the $\beta$-spin 'electron hole' in the system. The spin contamination of $3^{++}$is somewhat more pronounced, with an $\mathrm{S}^{2}$ expectation value of 0.766 , but still acceptable.


Figure S63. Orbital energies (in eV) and isosurfaces of frontier molecular orbitals computed for the neutral ( + )-3 (left) and monoradical ( + )-3•+ (right). Isosurfaces of $\pm 0.030$ au for the neutral and the radical.


Figure S64. Orbital energies (in eV) and isosurfaces ( $\pm 0.030 \mathrm{au}$ ) of frontier molecular orbitals computed for the diradical ( + )-32•2+.

$3^{+}$

$3^{2+}$

Figure S65. (Left) DFT-optimized structure of (+)-3•+. (Right) Calculated spin density for (+)-3•+ and ( + )-32•2+. Isosurfaces of $\pm 0.002$ au.

Absorption Spectroscopy. The experimental and simulated absorption spectra for 3, 3•+ and $\mathbf{3}^{2 \cdot 2+}$ are shown in Figure S66. The calculations were performed using the lowest-energy conformer in each case. Calculations agree reasonably well with the experiments, after accounting for blue shifts of 0.1-0.4 eV.

As in 1 and 2 , three spectral bands are observed for $\mathbf{3}$. The assigned transitions for the two lowestenergy bands are qualitatively the same for 1 and 3 , thus only the main differences are for the strong absorption band at $240-250 \mathrm{~nm}$. Figure S 67 shows the corresponding molecular orbitals of 3 associated to the most intense excitations (Table S12). With the exception of the HOMO-2 and HOMO-3, the isosurfaces of the molecular orbitals are delocalized over the two carbazole moieties. The lowest-energy excitation at 367 nm corresponds to the HOMO-LUMO transition, where the HOMO is localized on the $\pi$-conjugated system including the nitrogen and oxygen atoms and the LUMO only on the $\pi$-conjugated system excluding the nitrogen and oxygen atoms. The second lowest-energy band at 295 nm is due to transitions \#5 and \#6 corresponding to HOMO-2 to LUMO and HOMO-3 to LUMO transitions, respectively. HOMO-2 and HOMO-3 are near-degenerate in energy, with a very small energetic splitting of 0.060 eV , resulting as in-phase and out-of-phase FFO combinations. A combination of several excitations, in particular \#13 and \#14 showing the highest oscillator strengths, creates the strong absorption band at 250 nm , involving different $\pi$ $\rightarrow \pi^{*}$ electronic transitions between the carbazolyl units. Note that similar simulated absorption spectra are observed for the two conformers of $\mathbf{3}$ with different dihedral angle (Figure S68).


Figure S66. Experimental (Expt.) and calculated (Calc.) absorption spectra for ( + )-3 in neutral (black), monoradical (red) and diradical (blue) forms. Selected transitions and oscillator strengths indicated as 'stick spectra'. Predominant transitions are numbered according to Tables S12-S14.

For $3^{+}$, the calculated absorption spectra appear significantly modified. Excitations \#1 and \#4 cause two low-energy bands at 3179 (not observed) and 812 nm , respectively, in the simulated UV/Vis spectra of $3^{\bullet+}$ due to $\pi \rightarrow \pi^{*}$ electronic transitions to the $\beta$ 'electron hole' LUMO (Figure

S67 and Table S13). The third band of $3^{\bullet+}$ at 397 nm corresponds to the first lowest-energy band of 3 at 367 nm , which remains unchanged but notably red shifted by 0.260 eV . In $3^{\cdot+}$, we also observe a wide absorption band at 250 nm caused by several transitions, but predominantly for excitation \#53 which again is attributed to a transition to the $\beta$ 'electron hole' LUMO. Furthermore, this band presents a slight decrease in intensity and the broadness includes the corresponding peak at 290 nm of the neutral.

For $\mathbf{3}^{2 \bullet 2+}$, the absorption spectra seem to be also slightly changed, but showing similar features as $3^{+}$. Two low-energy bands at 1200 nm and 700 nm appear, caused by excitations to the LUMO and LUMO+1 (Figure S68 and Table S14). These two first excitations are blue shifted by 0.641 and 0.252 eV , respectively, for $\mathbf{3}^{2 \cdot 2+}$ compared to $3^{\cdot+}$. The band at 375 nm also remains unchanged in $3^{2 \cdot 2+}$, whereas the band at 260 nm is slightly weaker and wider due to excitations \#41 and \#55, which overlaps the absorption band at 250 and 290 nm of the neutral compound 3.


Figure S67. Isosurfaces ( $\pm 0.030 \mathrm{au}$ ) of Molecular Orbitals (MOs) involved in the selected transitions for (+)-3. Values listed in parentheses are the corresponding orbitals energies in eV .


Figure S68. Calculated absorption spectra for the two conformers with different dihedral angles of (+)-3.


Figure S69. Isosurfaces ( $\pm 0.030 \mathrm{au}$ ) of Molecular Orbitals (MOs) involved in the selected transitions for $(+)-3 \cdot+$. Values listed in parentheses are the corresponding orbitals energies in eV .


Figure S70. Isosurfaces ( $\pm 0.030 \mathrm{au}$ ) of Molecular Orbitals (MOs) involved in the selected transitions for ( + )- $\mathbf{3 2 0}^{22+}$. Values listed in parentheses are the corresponding orbitals energies in eV.

Table S12. Selected excitations and occupied (occ)-unoccupied (unocc) MO pair contributions (greater than $15 \%$ ) for (+)-3. H and L indicate the HOMO and LUMO, respectively.

| Excitation | $\mathrm{E}[\mathrm{eV}]$ | $\lambda[\mathrm{nm}]$ | $f$ | $\mathrm{R}[10-40 \mathrm{cgs}]$ | occ. no. | unocc no. | $\%$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\# 1$ | 3.381 | 367 | 0.144 | -36.23 | $143(\mathrm{H})$ | $144(\mathrm{~L})$ | 98 |
| $\# 4$ | 4.166 | 298 | 0.100 | 271.50 | 141 | 144 | 88 |
| $\# 6$ | 4.231 | 293 | 0.145 | -120.64 | 140 | 144 | 86 |
| $\# 10$ | 4.846 | 256 | 0.167 | 475.04 | 143 | 146 | 35 |
|  |  |  |  |  | 140 | 145 | 32 |
| $\# 11$ | 4.871 | 255 | 0.183 | -25.64 | 138 | 144 | 42 |
|  |  |  |  |  | 142 | 146 | 40 |
| $\# 12$ | 4.911 | 252 | 0.153 | -95.38 | 143 | 147 | 62 |
| $\# 13$ | 4.992 | 248 | 0.436 | -307.56 | 138 | 144 | 25 |
|  |  |  |  |  | 142 | 147 | 18 |
| $\# 14$ | 5.013 | 247 | 0.368 | 86.73 | 142 | 147 | 65 |
| $\# 15$ | 5.262 | 236 | 0.146 | -273.85 | 139 | 145 | 79 |

Table S13. Selected excitations and occupied (occ)-unoccupied (unocc) MO pair contributions (greater than $15 \%$ ) for ( + )- $3^{+}$. $S$ and L indicate the SOMO and LUMO, respectively.

| Excitation | $\mathrm{E}[\mathrm{eV}]$ | $\lambda[\mathrm{nm}]$ | $f$ | $\mathrm{R}\left[10^{-40} \mathrm{cgs}\right]$ | occ. no. | unocc no. | $\%$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| \#1 | 0.390 | 3179 | 0.038 | -41.47 | $142 \beta$ | $143 \beta(\mathrm{~L})$ | 100 |
| $\# 4$ | 1.528 | 812 | 0.102 | -72.90 | $139 \beta$ | $143 \beta$ | 88 |
| $\# 5$ | 1.746 | 710 | 0.032 | 47.34 | $138 \beta$ | $143 \beta$ | 96 |
| $\# 11$ | 3.121 | 397 | 0.067 | -10.56 | $143 \alpha$ | $144 \alpha$ | 27 |
| $\# 14$ | 3.512 | 353 | 0.030 | -69.46 | $142 \alpha(\mathrm{~S})$ | $144 \alpha$ | 59 |
| \#24 | 3.999 | 310 | 0.067 | 74.24 | $141 \alpha$ | $144 \alpha$ | 37 |
|  |  |  |  |  | $141 \beta$ | $144 \beta$ | 23 |
| \#32 | 4.280 | 290 | 0.114 | 98.39 | $140 \alpha$ | $144 \alpha$ | 36 |
|  |  |  |  |  | $140 \beta$ | $144 \beta$ | 33 |
| \#39 | 4.570 | 271 | 0.039 | 122.69 | $139 \alpha$ | $144 \alpha$ | 32 |
|  |  |  |  |  | $139 \beta$ | $144 \beta$ | 18 |
| \#46 | 4.828 | 257 | 0.046 | 179.80 | $138 \beta$ | $144 \beta$ | 24 |
|  |  |  |  |  | $138 \alpha$ | $144 \alpha$ | 23 |
| \#53 | 4.997 | 248 | 0.182 | -191.36 | $119 \beta$ | $143 \beta$ | 17 |
| \#54 | 5.028 | 247 | 0.048 | 150.91 | $142 \beta$ | $148 \beta$ | 19 |
|  |  |  |  |  | $140 \beta$ | $145 \beta$ | 18 |

Table S14. Selected excitations and occupied (occ)-unoccupied (unocc) MO pair contributions (greater than 10\%) for (+)-3202+. S and L indicate the SOMO and LUMO, respectively.

| Excitation | $\mathrm{E}[\mathrm{eV}]$ | $\lambda[\mathrm{nm}]$ | $f$ | $\mathrm{R}[10-40 \mathrm{cgs}]$ | occ. no. | unocc no. | $\%$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| \#1 | 1.031 | 1203 | 0.014 | 47.15 | $141 \beta$ | $142 \beta(\mathrm{~L})$ | 64 |
|  |  |  |  |  | $141 \beta$ | $143 \beta$ | 27 |
| \#2 | 1.102 | 1125 | 0.019 | -42.52 | $140 \beta$ | $142 \beta$ | 58 |
|  |  |  |  |  | $140 \beta$ | $143 \beta$ | 29 |
| \#3 | 1.563 | 793 | 0.060 | 145.32 | $139 \beta$ | $142 \beta$ | 77 |
| \#6 | 1.780 | 697 | 0.158 | -174.43 | $138 \beta$ | $142 \beta$ | 68 |
| \#13 | 3.273 | 379 | 0.061 | -9.46 | $143 \alpha(\mathrm{~S})$ | $144 \alpha$ | 15 |
| \#15 | 3.332 | 372 | 0.056 | 7.83 | $143 \alpha$ | $144 \alpha$ | 57 |
| \#41 | 4.254 | 291 | 0.104 | 148.25 | $141 \alpha$ | $144 \alpha$ | 37 |
|  |  |  |  |  | $141 \beta$ | $144 \beta$ | 27 |
| \#48 | 4.546 | 273 | 0.099 | 156.59 | $143 \alpha$ | $146 \alpha$ | 18 |
| \#49 | 4.567 | 272 | 0.091 | 19.81 | $143 \alpha$ | $147 \alpha$ | 11 |
| \#55 | 4.711 | 263 | 0.206 | -95.33 | $141 \alpha$ | $145 \alpha$ | 19 |

ECD Spectroscopy. The experimental and calculated ECD spectra of 3 and $3^{*+}$ are displayed in Figure S71. Calculations reproduce very well the experiments, having some calculated bands blue shifted by 0.1 eV , which is usual in the TD-DFT calculations. Here we discuss the ECD for the ( + ) or $P$ enantiomers. Test calculations on the ECD spectra were performed by the two conformers with different dihedral angle for each system (Figure S72). We note that the ECD spectra of the conformer with a large torsion angle show some similar peaks as experiments but some with a different sign. Thus, we proceed to analyze the calculations for the lowest-energy conformers of $(+)-3$ and (+)-3*+, which are the ones that better agree with experiments.

The UV/vis and ECD spectra of $(+)-3$ share the same electronic transitions. Additionally, excitations \#10 at 256 nm and \#15 at 236 nm become actives in the ECD spectra.

The one-electron oxidation of 3 leads to few modifications of the ECD spectrum, mostly due to a wide and weaker band between 250 and 320 nm , involving several $\pi \rightarrow \pi^{*}$ transitions to the $\alpha$ LUMO and $\beta$-LUMO +1 (Table S13). Once again, the new long-wavelength bands in the absorption spectra of the monoradical are negligible in the ECD spectrum.


Figure S71. Experimental (Expt.) and calculated (Calc.) ECD spectra for ( + )-3 in neutral (black) and monoradical (red) forms. Selected transitions and rotatory strengths for the radicals are indicated as 'stick spectra'. Predominant transitions are numbered according to Tables S12 and S13. $M$-enantiomers are represented in dashed lines.


Figure S72. Calculated ECD spectra for the two different conformers of (+)-3 (left) and (+)-3•+ (right). Conformer with a dihedral angle of 1100 is plotted in purple for both systems, while the other conformer $\left(65^{\circ}\right)$ appears in black and red for $(+)-3$ and $(+)-3 \cdot+$, respectively.


Figure S73. Experimental (Expt.) and calculated absorption spectra for 1 (red), 2 (orange) and 3 (green). Test calculations varying the functional: B3LYP, CAMB3LYP, M06-HF, PBE0 and TPSSh.


Figure S74. Calculated absorption spectra for 1, 2 and 3 derivatives. Test on functionals and solvent effects.


Figure S75. Experimental (Expt.) and calculated ECD spectra for 1 (red), 2 (orange) and $\mathbf{3}$ (green). Test calculations varying the functional: B3LYP, CAMB3LYP, M06-HF, PBE0 and TPSSh.




Figure S76. Calculated ECD spectra for 1, 2 and 3 derivatives. Test on functionals and solvent effects.


Figure S77. Orbital energies (in eV ) and isosurfaces ( $\pm 0.030 \mathrm{au}$ ) of some molecular orbitals for $1{ }^{1+}$.


Figure S78. Orbital energies (in eV) and isosurfaces ( $\pm 0.030 \mathrm{au}$ ) of some molecular orbitals for $2 \cdot+$.


Figure S79. Orbital energies (in eV) and isosurfaces ( $\pm 0.030 \mathrm{au}$ ) of some molecular orbitals for $3 \cdot+$.

Table S15. Relative energies (in eV) for a model of (+)-1•+ varying the dihedral angle from $40^{\circ}$ to $140^{\circ}$. The model of $(+)-1^{\bullet+}$ replaces the methyl groups of both methoxy groups by hydrogens. Data from single points calculations of model of $(+)-1^{\bullet+}$.

| Dihedral angle $\left({ }^{\circ}\right)$ | Relative energy $(\mathrm{eV})$ |
| :---: | :---: |
| 40 | 1.18 |
| 60 | 0.01 |
| 73.5 | 0.00 |
| 80 | 0.02 |
| 100 | 0.07 |
| 120 | 0.43 |
| 140 | 6.48 |

Table S16. Orbital energies (in eV ) for a model of $(+)-1^{\bullet+}$ varying the dihedral angle. The model of $(+)-1^{+}$replaces the methyl groups of both methoxy groups by hydrogens. Data from single points calculations of model (+)-1•+. Energies for the SOMO, HOMO, and $\beta$-LUMO, and energy differences between the SOMO/HOMO and SOMO/ $\beta$-LUMO. The corresponding MOs are displayed in Figures S80-S86.

| Dihedral angle $\left({ }^{\circ}\right)$ | SOMO | HOMO | $\beta$-LUMO | SOMO/HOMO | SOMO/ $\beta$-LUMO |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 40 | -6.92 | -6.16 | -4.78 | 0.77 | 2.14 |
| 60 | -6.86 | -6.11 | -4.88 | 0.75 | 1.98 |
| 73.5 | -6.92 | -6.04 | -4.92 | 0.88 | 2.00 |
| 80 | -6.95 | -6.02 | -4.94 | 0.94 | 2.02 |
| 100 | -6.96 | -6.03 | -4.95 | 0.93 | 2.02 |
| 120 | -6.85 | -6.19 | -4.90 | 0.66 | 1.95 |
| 140 | -6.20 | -6.67 | -4.68 | -0.47 | 1.52 |



$\beta$


Figure S80. Orbital energies (in eV ) and isosurfaces ( $\pm 0.030 \mathrm{au}$ ) of model $1^{\bullet+}$, where the methyl groups of both methoxy groups are replaced by hydrogens. Data from a single point calculation of model $(+)-1^{\bullet+}$ with a dihedral angle of $73.5^{\circ}$, that it is the optimal in $1^{\bullet+}$ system.


Figure S81. Orbital energies (in eV ) and isosurfaces ( $\pm 0.030$ au) of model $1^{\bullet+}$, where the methyl groups of both methoxy groups are replaced by hydrogens. Data from a single point calculation of model $(+)-1^{+}+$with a dihedral angle of $40^{\circ}$.


Figure S82. Orbital energies (in eV) and isosurfaces ( $\pm 0.030 \mathrm{au}$ ) of model $1^{\bullet+}$, where the methyl groups of both methoxy groups are replaced by hydrogens. Data from a single point calculation of model $(+)-1^{+}+$with a dihedral angle of $60^{\circ}$.


Figure S83. Orbital energies (in eV) and isosurfaces ( $\pm 0.030 \mathrm{au}$ ) of model $1^{\bullet+}$, where the methyl groups of both methoxy groups are replaced by hydrogens. Data from a single point calculation of model ( + )-1++ with a dihedral angle of $80^{\circ}$.


Figure S84. Orbital energies (in eV ) and isosurfaces ( $\pm 0.030 \mathrm{au}$ ) of model $1^{\bullet+}$, where the methyl groups of both methoxy groups are replaced by hydrogens. Data from a single point calculation of model ( + )-1•+ with a dihedral angle of $100^{\circ}$.


Figure S85. Orbital energies (in eV ) and isosurfaces ( $\pm 0.030 \mathrm{au}$ ) of model $1^{\bullet+}$, where the methyl groups of both methoxy groups are replaced by hydrogens. Data from a single point calculation of model (+)-1•+ with a dihedral angle of $120^{\circ}$.


Figure S86. Orbital energies (in eV ) and isosurfaces ( $\pm 0.030 \mathrm{au}$ ) of model $1^{\bullet+}$, where the methyl groups of both methoxy groups are replaced by hydrogens. Data from a single point calculation of model (+)-1•+ with a dihedral angle of $140^{\circ}$.

Table S17. Relative energies (in eV ) for a model of $(+)-1^{\bullet+}$ varying the dihedral angle. The model of $(+)-1^{+}$replaces the methyl groups of both methoxy groups by hydrogens. Data from partial optimizations of the geometry (i.e. constraining the dihedral angle).

| Dihedral angle $\left({ }^{\circ}\right)$ | Relative energy $(\mathrm{eV})$ |
| :---: | :---: |
| 40 | 0.02 |
| 60 | 0.00 |
| 73.5 | 0.01 |
| 80 | 0.03 |
| 100 | 0.04 |
| 120 | 0.01 |
| 140 | 0.06 |

Table S18. Orbital energies (in eV ) for a model of $(+)-1^{\bullet+}$ varying the dihedral angle. The model of $(+)-1^{+}$replaces the methyl groups of both methoxy groups by hydrogens. Data from partial optimizations of the geometry (i.e. constraining the dihedral angle). Energies for the SOMO, HOMO, and $\beta$-LUMO, and energy differences between the SOMO/HOMO and SOMO/ $\beta$-LUMO. The corresponding MOs are displayed in Figures S87.

| Dihedral angle $\left(^{\circ}\right)$ | SOMO | HOMO | $\beta$-LUMO | SOMO/HOMO | SOMO/ $\beta$-LUMO |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 40 | -6.86 | -6.20 | -4.82 | 0.66 | 2.04 |
| 60 | -6.86 | -6.10 | -4.85 | 0.75 | 2.00 |
| 73.5 | -6.88 | -6.06 | -4.87 | 0.82 | 2.01 |
| 80 | -6.90 | -6.04 | -4.88 | 0.86 | 2.02 |
| 100 | -6.92 | -6.01 | -4.89 | 0.91 | 2.03 |
| 120 | -6.92 | -6.10 | -4.86 | 0.82 | 2.06 |
| 140 | -6.73 | -6.19 | -4.81 | 0.54 | 1.91 |



Figure S87. Orbital energies (in eV) and isosurfaces ( $\pm 0.030 \mathrm{au}$ ) of model $1^{\bullet+}$, which the methyl groups of both methoxy groups are replaced by hydrogens. Data from partial optimizations of the geometry (i.e. constraining the dihedral angle). Dihedral angles of a) $40^{\circ}$, b) $60^{\circ}$, c) $73.6^{\circ}$, d) $80^{\circ}$, e) $100^{\circ}$, f) $120^{\circ}$, and g) $140^{\circ}$.


Figure S88. Orbital energies (in eV ) and isosurfaces ( $\pm 0.030 \mathrm{au}$ ) of $1^{1 \cdot+}$. Test on different functionals and solvent effects; a) PBE0/PCM, b) PBE0/gas phase, c) PBE/PCM, d) HF/PCM, e) B3LYP/PCM, and f) CAMB3LYP/PCM.


Figure S89. Orbital energies (in eV ) and isosurfaces ( $\pm 0.030 \mathrm{au}$ ) of $2 \cdot+$. Test on different functionals; a) PBE0, b) B3LYP, and c) CAMB3LYP.

## REFERENCES

[1] a) Peter N. M. Botman, M. Postma, J. Fraanje, K. Goubitz, H. Schenk, Jan H. v. Maarseveen, H. Hiemstra, Eur. J. Org. Chem. 2002, 2002, 1952-1955.; b) R. Hoen, University of Groningen (Wöhrmann Print Service, Zutphen, the Netherlands), 2006.
[2] S. Lin, X. He, J. Meng, H. Gu, P. Zhang, J. Wu, Eur. J. Org. Chem. 2017, 2017, 443-447.
[3] S. K. Ku, J. H. Lee, Y. O, W. Lee, G. Y. Song, J. S. Bae, Bioorg. Med. Chem. Lett. 2015, 25, 43044307.
[4] Y. Li, A. Urbas, Q. Li, J. Am. Chem. Soc. 2012, 134, 9573-9576.
[5] N. G. Connelly, W. E. Geiger, Chem. Rev. 1996, 96, 877-910.
[6] M. J. Frisch, G. W. Trucks, H. B. Schlegel et al. "Gaussian 16, Revision B.01", Gaussian, Inc., Wallingford CT, 2016. URL: www.gaussian.com.
[7] C. Adamo, V. Barone, J. Chem. Phys., 1999, 110, 6158-69.
[8] F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys., 2005, 7, 3297-305.
[9] F. Weigend, Phys. Chem. Chem. Phys., 2006, 8, 1057-65.
[10] G. Scalmani, M. J. Frisch, J. Chem. Phys., 2010, 132, 114110.
[11] S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys., 2010, 132, 154104.
[12] M. Srebro-Hooper, J. Autschbach, Annu. Rev. Phys. Chem., 2017, 68, 399-420.
[13] J. Autschbach, L. Nitsch-Velasquez, M. Rudolph, Top. Curr. Chem., 2011, 298, 1-98.
[14] F. Santoro, A. Lami, R. Improta, J. Bloino, V. Barone, J. Chem. Phys., 2008, 128, 224311.

| xyz coordinates |  |  |  | C | 2.844752 | -1.527218 | -0.675480 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  | C | -3.147612 | -2.740328 | 1.304826 |
| (+)-1 |  |  |  | C | 3.147613 | -2.740328 | -1.304826 |
| C | -3.045292 | 1.191358 | -1.919390 | H | -4.131295 | -3.205394 | 1.204585 |
| H | -3.967738 | 1.212771 | -2.504146 | H | 4.131295 | -3.205394 | -1.204585 |
| C | 4.965117 | -1.059851 | 1.019187 | C | -2.157747 | -3.335247 | 2.080307 |
| H | 5.474879 | -0.137294 | 1.339214 | H | -2.372242 | -4.283714 | 2.582564 |
| H | 5.597007 | -1.544892 | 0.260001 | C | -0.895530 | -2.736875 | 2.239228 |
| H | 4.873614 | -1.735655 | 1.889651 | H | -0.141134 | -3.224212 | 2.863661 |
| N | 3.684059 | -0.738149 | 0.451240 | C | -0.596530 | -1.532401 | 1.612356 |
| C | 3.061010 | -1.412226 | -0.578203 | C | 0.596530 | -1.532401 | -1.612356 |
| C | 3.515703 | -2.504270 | -1.326127 | H | 0.383958 | -1.070609 | 1.743226 |
| H | 4.484655 | -2.968937 | -1.128105 | H | -0.383958 | -1.070609 | -1.743227 |
| C | 2.689194 | -2.990568 | -2.335176 | C | -1.569212 | -0.914524 | 0.813472 |
| H | 3.024953 | -3.843921 | -2.932648 | C | 1.569212 | -0.914524 | -0.813472 |
| C | 1.434954 | -2.412587 | -2.598650 | C | -5.029757 | -0.981139 | -0.433018 |
| H | 0.809782 | -2.820247 | -3.398417 | C | 5.029757 | -0.981139 | 0.433018 |
| C | 0.979105 | -1.333297 | -1.848137 | H | -5.709767 | -0.473645 | 0.276127 |
| H | 0.001581 | -0.888254 | -2.049353 | H | 5.709767 | -0.473646 | -0.276127 |
| C | 1.790216 | -0.824039 | -0.824787 | H | -5.231212 | -2.062217 | -0.404636 |
| C | 1.649548 | 0.250758 | 0.131475 | H | 5.231212 | -2.062218 | 0.404637 |
| C | 0.631128 | 1.184282 | 0.388631 | H | -5.250883 | -0.626531 | -1.452264 |
| C | 0.838093 | 2.110918 | 1.416074 | H | 5.250883 | -0.626530 | 1.452264 |
| C | 2.020309 | 2.100923 | 2.176056 | C | 2.157747 | -3.335247 | -2.080307 |
| H | 2.124383 | 2.845606 | 2.970006 | H | 2.372242 | -4.283714 | -2.582564 |
| C | 3.034543 | 1.180659 | 1.934517 | C | 0.895530 | -2.736875 | -2.239228 |
| H | 3.945085 | 1.185622 | 2.538054 | H | 0.141134 | -3.224212 | -2.863661 |
| C | 2.840994 | 0.258317 | 0.902078 |  |  |  |  |
| 0 | -0.115963 | 3.049801 | 1.692066 | (+) |  |  |  |
| C | -0.966062 | -1.351427 | 1.830506 | C | -3.106516 | -2.832434 | -0.188599 |
| H | 0.010646 | -0.904767 | 2.032235 | H | -3.901657 | -3.437234 | -0.628046 |
| C | -1.777587 | -0.843458 | 0.806850 | C | -3.069791 | -1.443313 | -0.411133 |
| C | -1.643122 | 0.238720 | -0.141898 | 0 | -3.975415 | -0.789574 | -1.175342 |
| C | -0.632718 | 1.183837 | $-0.388043$ | C | -5.065485 | -1.492487 | -1.702344 |
| C | -2.833791 | 0.243820 | -0.913664 | H | -4.746744 | -2.281943 | -2.410385 |
| C | -4.971503 | -1.055298 | -1.005977 | H | -5.676863 | -0.756222 | -2.245750 |
| H | -5.214462 | -2.118482 | -0.858698 | H | -5.681953 | -1.952028 | -0.905721 |
| H | -4.999266 | -0.852468 | -2.088199 | C | -2.045567 | -0.652469 | 0.139967 |
| H | -5.745958 | -0.441596 | -0.509497 | C | -1.995469 | 0.804518 | -0.132565 |
| C | -1.098990 | 2.632805 | 2.614139 | C | -0.966508 | 1.380739 | -0.894059 |
| H | -1.647951 | 1.745181 | 2.245785 | C | 0.200005 | 0.838062 | -1.559302 |
| H | -1.805079 | 3.469115 | 2.735659 | C | 0.709984 | -0.451725 | -1.720264 |
| H | -0.650193 | 2.391725 | 3.597716 | H | 0.144494 | -1.294181 | -1.319219 |
| N | -3.656978 | -0.781656 | -0.491801 | C | 1.937110 | -0.665738 | -2.354291 |
| C | -3.044853 | -1.437268 | 0.555922 | C | 2.631596 | 0.457801 | -2.847562 |
| C | -3.507120 | -2.516910 | 1.317065 | H | 3.594722 | 0.326579 | -3.345266 |
| H | -4.486492 | -2.966260 | 1.135551 | C | 2.144297 | 1.758463 | -2.721709 |
| C | -2.680481 | -3.001627 | 2.326801 | H | 2.721616 | 2.600640 | -3.111337 |
| H | -3.021853 | -3.845504 | 2.934465 | C | 0.921903 | 1.946769 | -2.073764 |
| C | -1.422829 | -2.428235 | 2.584064 | N | 0.234259 | 3.110282 | -1.797780 |
| H | -0.798726 | -2.833036 | 3.386120 | C | -0.894957 | 2.788646 | -1.064141 |
| C | -2.038929 | 2.122942 | -2.150303 | C | -1.855335 | 3.629565 | -0.507877 |
| H | -2.156804 | 2.886935 | -2.923691 | H | -1.804921 | 4.714919 | -0.622327 |
| C | -0.850974 | 2.125518 | -1.399277 | C | -2.890881 | 3.052809 | 0.227046 |
| 0 | 0.094066 | 3.077222 | -1.662304 | H | -3.641769 | 3.708752 | 0.670860 |
| C | 1.079104 | 2.682113 | -2.591803 | C | -2.963179 | 1.661537 | 0.423582 |
| H | 1.635146 | 1.792937 | -2.237944 | C | 2.488772 | -2.093646 | -2.441531 |
| H | 1.778856 | 3.525420 | -2.700978 | C | 2.710777 | -2.627650 | -1.016085 |
| H | 0.630938 | 2.453005 | -3.578531 | H | 3.115749 | -3.656207 | -1.045124 |
|  |  |  |  | H | 1.771517 | -2.648630 | -0.436885 |
| (+)-2 |  |  |  | H | 3.423835 | -1.989808 | -0.464135 |
| 0 | -0.330682 | 3.527570 | -1.120543 | C | 1.480751 | -2.996711 | -3.170347 |
| 0 | 0.330682 | 3.527570 | 1.120543 | H | 1.865475 | -4.031097 | -3.233202 |
| N | -3.647669 | -0.737802 | -0.119551 | H | 1.298703 | -2.634544 | -4.197840 |
| N | 3.647669 | -0.737802 | 0.119551 | H | 0.510001 | -3.032978 | -2.646404 |
| C | 0.000000 | 4.298611 | 0.000000 | C | 3.820936 | -2.157195 | -3.193127 |
| H | -0.849238 | 4.926261 | 0.323438 | H | 4.604344 | -1.564449 | -2.689325 |
| H | 0.849238 | 4.926261 | -0.323438 | H | 3.723446 | -1.791219 | -4.230440 |
| C | -1.190973 | 2.482764 | -0.888224 | H | 4.173719 | -3.202618 | -3.238847 |
| C | 1.190973 | 2.482764 | 0.888224 | C | 0.681835 | 4.445645 | -2.078027 |
| C | -2.499542 | 2.556962 | -1.380403 | H | -0.179245 | 5.087438 | -2.325406 |
| C | 2.499542 | 2.556962 | 1.380403 | H | 1.353825 | 4.436646 | -2.949399 |
| H | -2.801613 | 3.459406 | -1.917947 | H | 1.220297 | 4.890264 | -1.219277 |
| H | 2.801613 | 3.459406 | 1.917947 | 0 | -3.923248 | 1.066031 | 1.168698 |
| C | -3.389061 | 1.504348 | -1.196007 | C | -4.951028 | 1.844037 | 1.715046 |
| C | 3.389061 | 1.504348 | 1.196007 | H | -4.567006 | 2.588962 | 2.438781 |
| H | -4.408475 | 1.563387 | -1.583661 | H | -5.619501 | 1.148402 | 2.244550 |
| H | 4.408475 | 1.563387 | 1.583660 | H | -5.529708 | 2.370062 | 0.931281 |
| C | -2.943593 | 0.395044 | -0.471609 | C | -2.127664 | -3.471556 | 0.571708 |
| C | 2.943593 | 0.395044 | 0.471609 | H | -2.165369 | -4.554468 | 0.711567 |
| C | -1.624090 | 0.315174 | 0.052554 | C | -1.109885 | -2.696352 | 1.122354 |
| C | 1.624090 | 0.315174 | -0.052554 | C | -1.066726 | -1.291069 | 0.919209 |
| C | -0.708755 | 1.354355 | -0.208529 | C | 0.133869 | -0.828938 | 1.582622 |
| C | 0.708755 | 1.354355 | 0.208529 | C | 0.757505 | 0.420175 | 1.693395 |
| C | -2.844752 | -1.527218 | 0.675480 | H | 0.262984 | 1.288403 | 1.262932 |


| C | 2.002033 | 0.543739 | 2.306396 |
| :---: | :---: | :---: | :---: |
| C | 2.591310 | -0.620805 | 2.852445 |
| H | 3.569480 | -0.551388 | 3.338318 |
| C | 1.989259 | -1.872049 | 2.786333 |
| H | 2.488770 | -2.747493 | 3.208746 |
| C | 0.754120 | -1.975228 | 2.136713 |
| N | -0.020931 | -3.087014 | 1.882830 |
| C | 2.760318 | 1.874316 | 2.340060 |
| C | 4.056681 | 1.723019 | 1.525751 |
| H | 3.827856 | 1.453140 | 0.478921 |
| H | 4.711647 | 0.938387 | 1.942712 |
| H | 4.625640 | 2.671027 | 1.522744 |
| C | 1.945139 | 3.016224 | 1.724137 |
| H | 1.708943 | 2.825413 | 0.662464 |
| H | 2.524028 | 3.955434 | 1.774203 |
| H | 0.995142 | 3.179049 | 2.262472 |
| C | 3.101654 | 2.251435 | 3.789698 |
| H | 3.660662 | 3.204523 | 3.819662 |
| H | 3.725450 | 1.483618 | 4.278994 |
| H | 2.182059 | 2.373621 | 4.389262 |
| C | 0.319947 | -4.445330 | 2.201567 |
| H | 0.956409 | -4.467772 | 3.099145 |
| H | 0.858581 | -4.942528 | 1.372370 |
| H | -0.593503 | -5.019826 | 2.424356 |
| (+)-1+ |  |  |  |
| C | -3.255041 | 0.804931 | -1.901485 |
| H | -4.214957 | 0.684645 | -2.405882 |
| C | 4.793080 | -1.276754 | 0.930469 |
| H | 5.358824 | -0.366398 | 1.183034 |
| H | 5.394811 | -1.858172 | 0.216305 |
| H | 4.651575 | -1.875529 | 1.848700 |
| N | 3.536317 | -0.918420 | 0.327632 |
| C | 2.872005 | -1.628146 | -0.648227 |
| C | 3.257016 | -2.803503 | -1.304927 |
| H | 4.194908 | -3.310014 | -1.065669 |
| C | 2.401881 | -3.316122 | -2.274921 |
| H | 2.682959 | -4.234108 | -2.800077 |
| C | 1.186667 | -2.682756 | -2.592637 |
| H | 0.538630 | -3.111780 | -3.362112 |
| C | 0.800562 | -1.519766 | -1.935204 |
| H | -0.145600 | -1.035342 | -2.187269 |
| C | 1.640463 | -0.982403 | -0.949315 |
| C | 1.569042 | 0.169325 | -0.080611 |
| C | 0.613638 | 1.177512 | 0.115828 |
| C | 0.858025 | 2.159961 | 1.088501 |
| C | 2.037349 | 2.131170 | 1.854413 |
| H | 2.218029 | 2.893949 | 2.613173 |
| C | 2.988914 | 1.131278 | 1.669607 |
| H | 3.890048 | 1.118872 | 2.286578 |
| C | 2.756611 | 0.158940 | 0.695828 |
| 0 | -0.101429 | 3.103249 | 1.211180 |
| C | -0.718987 | -1.052664 | 2.004629 |
| H | 0.243594 | -0.544442 | 2.081677 |
| C | -1.621881 | -0.738844 | 0.989577 |
| C | -1.632644 | 0.203822 | -0.121239 |
| C | -0.698302 | 1.126603 | -0.572450 |
| C | -2.897706 | 0.030009 | -0.774185 |
| C | -4.924354 | -1.408613 | -0.475272 |
| H | -4.892336 | -2.497772 | -0.639412 |
| H | -5.281605 | -0.919524 | -1.389753 |
| H | -5.620626 | -1.186879 | 0.350284 |
| C | 0.030908 | 4.103526 | 2.193179 |
| H | 0.078051 | 3.666739 | 3.207612 |
| H | -0.866845 | 4.733126 | 2.112663 |
| H | 0.926870 | 4.727252 | 2.019555 |
| N | -3.603202 | -0.931678 | -0.142242 |
| C | -2.859321 | -1.419360 | 0.935041 |
| C | -3.220158 | -2.402337 | 1.848664 |
| H | -4.181432 | -2.917093 | 1.791147 |
| C | -2.297775 | -2.705689 | 2.855157 |
| H | -2.545457 | -3.474301 | 3.592322 |
| C | -1.071063 | -2.039859 | 2.933335 |
| H | -0.370370 | -2.293924 | 3.733191 |
| C | -2.345921 | 1.726191 | -2.342493 |
| H | -2.558518 | 2.358786 | -3.206717 |
| C | -1.074006 | 1.910295 | -1.711258 |
| 0 | -0.342854 | 2.816615 | -2.321543 |
| C | 0.937557 | 3.277780 | -1.913752 |
| H | 0.860851 | 3.787630 | -0.941902 |
| H | 1.243889 | 3.991597 | -2.690214 |
| H | 1.657816 | 2.447304 | -1.859571 |

+) $-1^{+}$
$-4.2149570 .684645-2.405882$ $4.793080-1.276754 \quad 0.930469$ $\begin{array}{llll}5.358824 & -0.366398 & 1.183034\end{array}$ $\begin{array}{llll}5.394811 & -1.858172 & 0.216305\end{array}$ $\begin{array}{lll}1.851575 & -1.875529 & 1.848700\end{array}$ $3.536317-0.918420 \quad 0.327632$ $2.872005-1.628146-0.648227$ 4.194908 -3.310014 -1.065669 $2.401881-3.316122-2.274921$ $2.682959-4.234108-2.800077$ $0.538630-3.111780-3.362112$ $0.800562-1.519766-1.935204$ $-0.145600-1.035342-2.187269$ $\begin{array}{lll}1.640463 & -0.982403 & -0.949315\end{array}$ $1.5690420 .169325-0.080611$ $\begin{array}{llll}0.613638 & 1.177512 & 0.115828\end{array}$ $0.858025 \quad 2.159961 \quad 1.088501$ $2.218029 \quad 2.893949 \quad 2.613173$ $\begin{array}{llll}2.988914 & 1.131278 & 1.669607\end{array}$ $3.890048 \quad 1.118872 \quad 2.286578$ $\begin{array}{lll}2.756611 & 0.158940 & 0.695828\end{array}$ 0.1014293 .1032491 .211180 $0.243594-0.544442 \quad 2.081677$ $-1.621881-0.738844 \quad 0.989577$ $-1.6326440 .203822-0.121239$ $\begin{array}{llll} & 0.126603 & -0.572450\end{array}$ $-2.897706 \quad 0.030009-0.774185$ $-4.892336-2.497772-0.639412$ $-5.281605-0.919524-1.389753$ $-5.620626-1.186879 \quad 0.350284$ $\begin{array}{lll}0.030908 & 4.103526 & 2.193179\end{array}$ 0.86681 $\begin{array}{lll}0.926870 & 4.727252 & 2.019555\end{array}$ -3.603202 -0.931678 -0.142242 .859321-1.419360 0.935041 $-4.181432-2.9170931 .791147$ $-2.297775-2.705689 \quad 2.855157$ $071063-3.474301-3.592322$ $-0.370370-2.293924 \quad 3.733191$ $-2.345921 \quad 1.726191-2.342493$ 074006 -3.306878 $-0.342854 \quad 2.816615-2.321543$ $\begin{array}{llll}0.937557 & 3.277780 & -1.913752\end{array}$ $1.2438893 .991597-2.690214$ $1.657816 \quad 2.447304-1.859571$

0
(+)-3+
C $\quad-3.169407-2.813474 \quad-0.591792$
H $\quad-3.989792-3.335417-1.085909$
C $\quad-3.113941-1.406916-0.604972$
$0 \quad-3.997631-0.639059-1.253460$
$-5.160659-1.211340-1.804930$ $-4.915575-1.907850-2.627126$ $-5.751282-0.375370-2.205679$ -5.750878 -1.740140 -1.034793 $-2.050798-0.712300 \quad 0.030810$ $-2.035003 \quad 0.757444-0.020371$ $-1.016630 \quad 1.494095-0.620914$ $0.1965871 .132200-1.333239$ $0.794127-0.070921-1.693490$ $0.294096-1.009144-1.452132$ $\begin{array}{llll}2.042373 & -0.081500 & -2.338320\end{array}$ $2.6572451 .152272-2.631503$ $3.6266891 .171531-3.131635$ $2.074749 \quad 2.375151-2.303746$ $\begin{array}{llll}2.577220 & 3.314039 & -2.546215\end{array}$ 0.842909 2.351237 -1.651610 $\begin{array}{llll}0.074286 & 3.409471 & -1.206070\end{array}$ $-1.039192 \quad 2.919033-0.581956$ $-2.095393 \quad 3.6208450 .020716$ $\begin{array}{lll}-2.119564 & 4.711930 & 0.043300\end{array}$ -3.119602 2.8973820 .605537 -3.938389 3.4343571 .085302 $-3.0939951 .48577810 .613699$ $2.703398-1.426562-2.646419$ $3.008457-2.132252-1.312900$ $3.495870-3.106488-1.498337$ $\begin{array}{llll}2.091615 & -2.316926 & -0.727799\end{array}$ $\begin{array}{llll}2.683553 & -1.520417 & -0.688607\end{array}$

| C | 1.748910 | -2.296882 | -3.480187 |
| :---: | :---: | :---: | :---: |
| H | 2.222104 | -3.269940 | -3.702179 |
| H | 1.503949 | -1.806940 | -4.439066 |
| H | 0.803488 | -2.502060 | -2.949427 |
| C | 4.013536 | -1.267985 | -3.422180 |
| H | 4.766960 | -0.702953 | -2.846547 |
| H | 3.858072 | -0.757221 | -4.388641 |
| H | 4.439202 | -2.263961 | -3.634395 |
| C | 0.443972 | 4.794458 | -1.365325 |
| H | -0.381396 | 5.442544 | -1.044321 |
| H | 0.666242 | 5.002645 | -2.424256 |
| H | 1.336443 | 5.022416 | -0.757826 |
| 0 | -3.991157 | 0.745185 | 1.247736 |
| C | -5.124735 | 1.335733 | 1.850566 |
| H | -4.829359 | 2.010494 | 2.672928 |
| H | -5.717266 | 0.504216 | 2.255676 |
| H | -5.724635 | 1.888028 | 1.106464 |
| C | -2.170984 | -3.561076 | 0.019973 |
| H | -2.221585 | -4.651807 | 0.000755 |
| C | -1.111845 | -2.887859 | 0.636221 |
| C | -1.046669 | -1.467947 | 0.654547 |
| C | 0.167461 | -1.132796 | 1.367358 |
| C | 0.808666 | 0.068830 | 1.689552 |
| H | 0.327122 | 1.009708 | 1.433413 |
| C | 2.061285 | 0.062675 | 2.301980 |
| C | 2.637226 | -1.187590 | 2.636007 |
| H | 3.619183 | -1.215478 | 3.116692 |
| C | 2.015070 | -2.397743 | 2.364728 |
| H | 2.497110 | -3.341542 | 2.629013 |
| C | 0.774469 | -2.363931 | 1.716833 |
| N | -0.019314 | -3.406220 | 1.294658 |
| C | 2.845646 | 1.352510 | 2.552118 |
| C | 4.119764 | 1.319403 | 1.689502 |
| H | 3.862009 | 1.242159 | 0.617640 |
| H | 4.765899 | 0.462304 | 1.946423 |
| H | 4.708405 | 2.242890 | 1.838092 |
| C | 2.043410 | 2.599439 | 2.167643 |
| H | 1.793394 | 2.608591 | 1.092122 |
| H | 2.641504 | 3.503605 | 2.375344 |
| H | 1.104942 | 2.678933 | 2.743583 |
| C | 3.226189 | 1.459963 | 4.036886 |
| H | 3.802895 | 2.384911 | 4.217129 |
| H | 3.848163 | 0.610602 | 4.367332 |
| H | 2.323241 | 1.488935 | 4.672193 |
| C | 0.300620 | -4.803177 | 1.439215 |
| H | 0.794228 | -4.972537 | 2.408289 |
| H | 0.970187 | -5.146537 | 0.630086 |
| H | -0.621885 | -5.401041 | 1.418583 |

(+)-3 ${ }^{2+}$

| C | 3.289048 | -2.768311 | 0.630122 |
| :---: | :---: | :---: | :---: |
| H | 4.146701 | -3.254332 | 1.095211 |
| C | 3.182782 | -1.359730 | 0.628314 |
| 0 | 4.007174 | -0.567457 | 1.269635 |
| C | 5.187677 | -1.061479 | 1.887215 |
| H | 4.931023 | -1.754829 | 2.705319 |
| H | 5.699099 | -0.179663 | 2.293705 |
| H | 5.831796 | -1.561454 | 1.144991 |
| C | 2.070633 | -0.689881 | -0.009656 |
| C | 2.045290 | 0.767335 | 0.003288 |
| C | 1.006279 | 1.528697 | 0.527639 |
| C | -0.222624 | 1.210153 | 1.233861 |
| C | -0.823073 | 0.038105 | 1.673604 |
| H | -0.319332 | -0.916272 | 1.522652 |
| C | -2.085032 | 0.077306 | 2.297743 |
| C | -2.704242 | 1.330650 | 2.492428 |
| H | -3.681159 | 1.384169 | 2.974033 |
| C | -2.113712 | 2.524283 | 2.093895 |
| H | -2.612101 | 3.479938 | 2.268334 |
| C | -0.868611 | 2.450898 | 1.464578 |
| N | -0.082779 | 3.473820 | 0.983641 |
| C | 1.041488 | 2.949352 | 0.421475 |
| C | 2.134751 | 3.625361 | -0.157680 |
| H | 2.165045 | 4.714672 | -0.218392 |
| C | 3.181297 | 2.885064 | -0.664551 |
| H | 4.024519 | 3.397630 | -1.127468 |
| C | 3.136848 | 1.471959 | -0.633075 |
| C | -2.756201 | -1.236800 | 2.689141 |
| C | -3.054863 | -2.023838 | 1.398137 |
| H | -3.560964 | -2.974380 | 1.644123 |
| H | -2.132181 | -2.264098 | 0.844100 |
| H | -3.711137 | -1.445581 | 0.724200 |
| C | -1.813016 | -2.057521 | 3.584713 |
| H | -2.298371 | -3.009276 | 3.863491 |

$-1.572734-1.5088924 .512118$ $-0.865419-2.306538 \quad 3.077511$ $-4.072069-1.0196823 .440596$ $-4.819346-0.495073 \quad 2.820773$ -3.922092 -0.4445754 .370895 $-4.501765-1.9975263 .717233$ $-0.440134 \quad 4.8708151 .079778$ $\begin{array}{lll}0.363556 & 5.494886 & 0.671130\end{array}$ $\begin{array}{llll}-0.604650 & 5.140374 & 2.135174\end{array}$ $-1.364855 \quad 5.0553370 .508654$ $4.003912 \quad 0.706900-1.248292$ $\begin{array}{llll}5.170513 & 1.239797 & -1.861289\end{array}$ $4.8944821 .897265-2.702358$ $\begin{array}{llll}5.728993 & 0.372226 & -2.235049\end{array}$ $5.777947 \quad 1.789350-1.123245$ $\begin{array}{llll}2.284147 & -3.542460 & 0.086723\end{array}$ $2.362709-4.630643 \quad 0.121666$ $1.170162-2.903308-0.491769$ $1.068991-1.483682-0.560343$ $-0.167384-1.204259-1.267378$ $-0.829095-0.043369-1.658301$ $-0.366521 \quad 0.924045-1.480904$ $-2.094371-0.121477-2.257963$ $-2.646384-1.400851-2.512493$ -3.629717 -1.478169 -2.982563 $-1.992747-2.576403-2.179072$ $-2.443148-3.548112-2.390783$ $-0.749637-2.464567-1.544048$ 0.078806 -3.462998 -1.087060 $-2.907502 \quad 1.129703-2.577680$ $-4.1735051 .111048-1.700147$ $-3.9060541 .103593-0.628176$ -4.802403 $0.227369-1.902366$ $-4.781445 \quad 2.011656-1.898809$ $-2.135607 \quad 2.417403-2.277050$ $-1.885405 \quad 2.501811-1.205068$ $-2.759341 \quad 3.289301-2.537474$ $-1.2029242 .487000-2.863125$ $-3.301230 \quad 1.131827-4.064061$ -3.898918 $2.032042-4.291346$ $-3.9085160 .251988-4.335427$ $-2.4044521 .142262-4.707982$ $-0.212413-4.871527-1.224635$ $-0.410693-5.107182-2.282064$ $-1.100105-5.126613-0.622239$ $0.640291-5.468660-0.879646$

