Electronic Supplementary Information for:

The fundamental relation between electrohelicity and molecular optical activity

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Note on units

In the Gaussian program,[1] the electric and magnetic transition dipoles are reported in atomic units while the rotatory strengths are reported in cgs units. The following unit conversions were applied.[2,3]

Electric transition dipole moments calculated in velocity-gauge are given in bohr-electron$\times$hartree. This is converted to dipole length units by dividing with the electronic transition energy, and then to cgs units by multiplying with 2.541746×10^{-18} esu cm.[3,4]

Magnetic transition dipole moments are given in bohr-magnetons. This is converted to cgs units by multiplying with 9.274×10^{-21} erg/Gauss.[3,4]
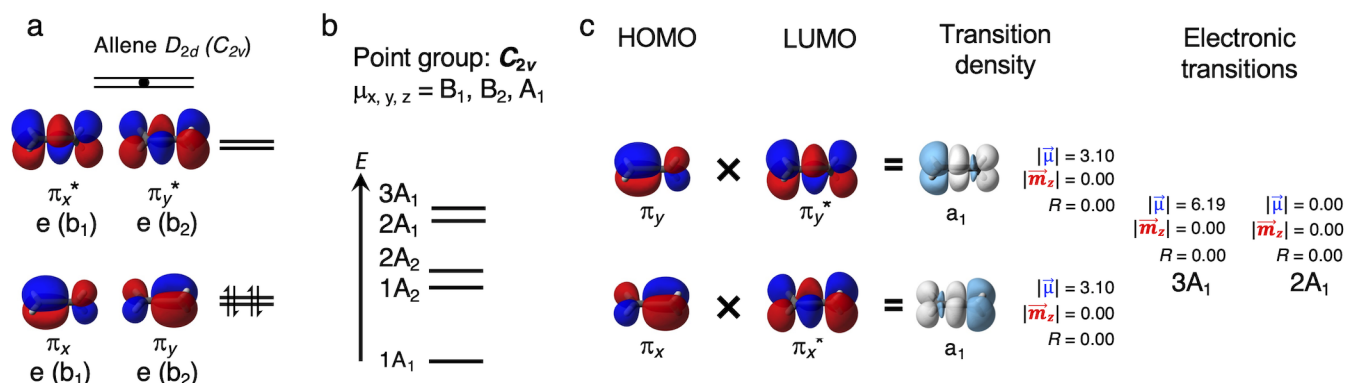
Additional figures

Figure S1: Allene described in C_{2v} symmetry. a) Frontier MOs. b) Diagram of electronic transitions. c) Direct products of frontier π-MOs. μ is in 10^{-18} esu·cm.

Figure S2: Overview of the $\pi - \pi^*$ transitions of allene and cycloallenes with their MO contributions, oscillator strengths, and rotatory strengths listed. Only MO contributions over 40% are shown. Note that the transitions are not sorted by energy.

	Allene	1,3-Dimethylallene	R-1,3-diethylallene (+119°)	R-1,3-diethylallene (−119°)	Ethylallene	1,1-Diethylallene
π_M^*	2.157 eV	2.446 eV	2.462 eV	2.296 eV	2.401 eV	2.559 eV
π_P^*	2.157 eV	2.489 eV	2.344 eV	2.505 eV	2.198 eV	2.464 eV
π_M	− 9.600 eV	− 8.929 eV	− 8.887 eV	− 8.911 eV	− 9.059 eV	− 8.678 eV
π_P	− 9.600 eV	− 8.930 eV	− 8.914 eV	− 8.883 eV	− 9.395 eV	− 9.219 eV
$2B_1$	47% $\pi_M \rightarrow \pi_M^*$ 47% $\pi_P \rightarrow \pi_P^*$ $f = 1.199$ R = 0.00	49% $\pi_M \rightarrow \pi_M^*$ 41% $\pi_P \rightarrow \pi_P^*$ $f = 1.253$ R = 55.4	47% $\pi_M \rightarrow \pi_M^*$ 47% $\pi_P \rightarrow \pi_P^*$ $f = 1.472$ R = 141	49% $\pi_M \rightarrow \pi_M^*$ 43% $\pi_P \rightarrow \pi_P^*$ $f = 1.442$ R = -81.39	50% $\pi_P \rightarrow \pi_P^*$ $f = 1.295$ R = 35.4	62% $\pi_P \rightarrow \pi_P^*$ $f = 1.273$ R = 82.2
$3A$	49% $\pi_P \rightarrow \pi_M^*$ 49% $\pi_M \rightarrow \pi_P^*$ $f = 0.000$ R = 0.00	49% $\pi_P \rightarrow \pi_M^*$ 49% $\pi_M \rightarrow \pi_P^*$ $f = 0.000$ R = 1.94	51% $\pi_P \rightarrow \pi_M^*$ 46% $\pi_M \rightarrow \pi_P^*$ $f = 0.001$ R = 6.38	46% $\pi_P \rightarrow \pi_M^*$ 51% $\pi_M \rightarrow \pi_P^*$ $f = 0.000$ R = 2.43	87% $\pi_P \rightarrow \pi_M^*$ $f = 0.000$ R = 2.50	78% $\pi_P \rightarrow \pi_M^*$ $f = 0.000$ R = 2.00
$2A$	50% $\pi_M \rightarrow \pi_P^*$ 50% $\pi_P \rightarrow \pi_M^*$ $f = 0.000$ R = 0.00	47% $\pi_M \rightarrow \pi_P^*$ 48% $\pi_P \rightarrow \pi_M^*$ $f = 0.000$ R = -0.15	47% $\pi_M \rightarrow \pi_P^*$ 47% $\pi_P \rightarrow \pi_M^*$ $f = 0.000$ R = 0.27	45% $\pi_M \rightarrow \pi_P^*$ 48% $\pi_P \rightarrow \pi_M^*$ $f = 0.000$ R = 0.03	87% $\pi_M \rightarrow \pi_P^*$ $f = 0.000$ R = -3.49	81% $\pi_M \rightarrow \pi_P^*$ $f = 0.000$ R = -1.16
$1B_1$	50% $\pi_P \rightarrow \pi_P^*$ 50% $\pi_M \rightarrow \pi_M^*$ $f = 0.000$ R = 0.00	47% $\pi_P \rightarrow \pi_P^*$ 47% $\pi_M \rightarrow \pi_M^*$ $f = 0.000$ R = 2.27	47% $\pi_P \rightarrow \pi_P^*$ 47% $\pi_M \rightarrow \pi_M^*$ $f = 0.000$ R = -4.49	47% $\pi_P \rightarrow \pi_P^*$ 46% $\pi_M \rightarrow \pi_M^*$ $f = 0.000$ R = 9.04	53% $\pi_M \rightarrow \pi_M^*$ $f = 0.000$ R = 1.55	65% $\pi_M \rightarrow \pi_M^*$ $f = 0.148$ R = 3.17

Figure S3: Overview of the $\pi - \pi^*$ transitions of substituted allenes with their MO contributions, oscillator strengths, and rotatory strengths listed. Only MO contributions over 40% are shown. R-1,3-diethyallene is shown in its two optimized C_2 symmetry conformers with both C=C-C-C ethyl dihedral angles at $\pm 119°$. Note that the transitions are not sorted by energy.

Allene
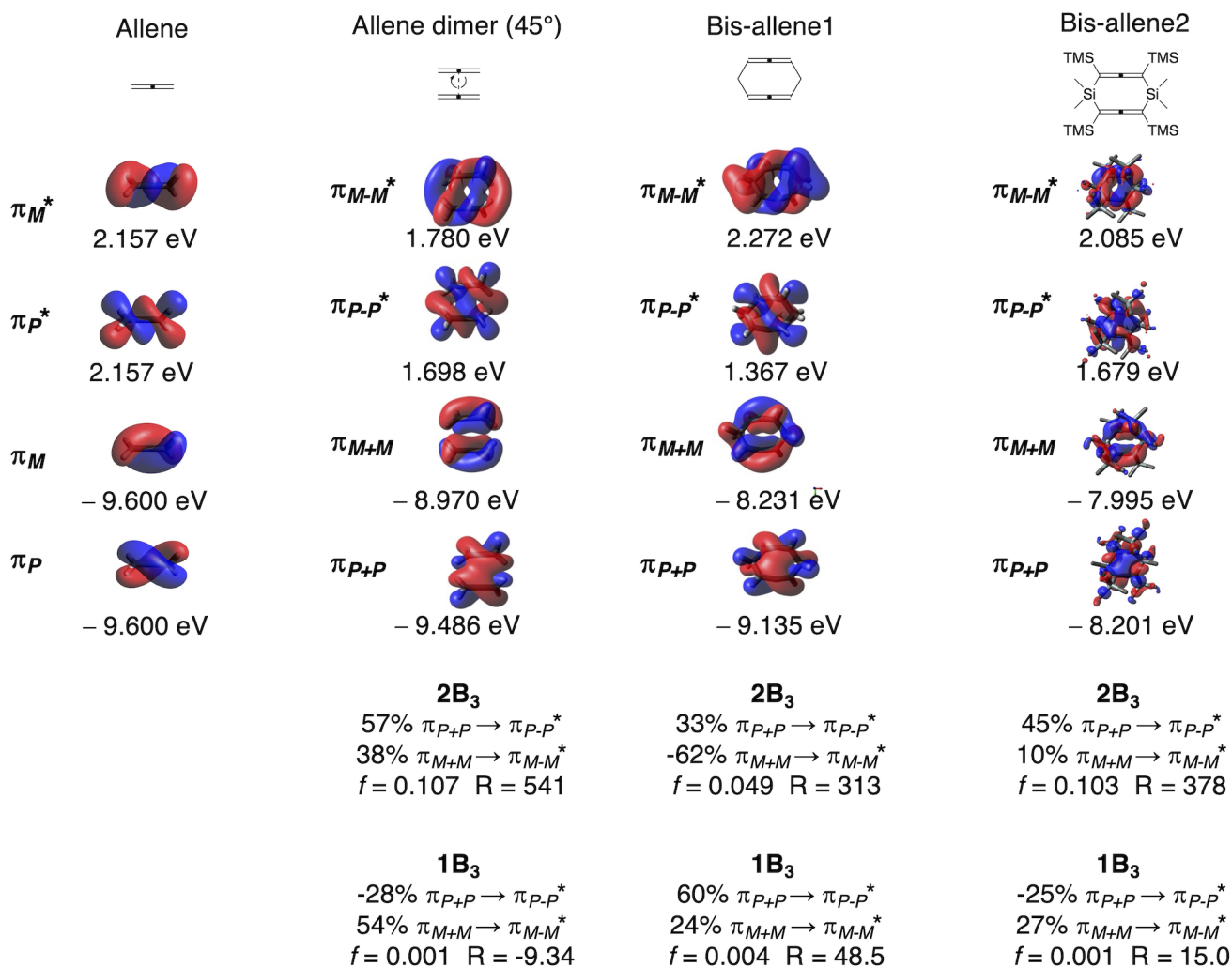
π_M^*
2.157 eV

π_P^*
2.157 eV

π_M
-9.600 eV

π_P
-9.600 eV

Allene dimer (45°)

$\pi_{M\text{-}M}^*$
1.780 eV

$\pi_{P\text{-}P}^*$
1.698 eV

π_{M+M}
-8.970 eV

π_{P+P}
-9.486 eV

2B$_3$
57% $\pi_{P+P} \rightarrow \pi_{P\text{-}P}^*$
38% $\pi_{M+M} \rightarrow \pi_{M\text{-}M}^*$
$f = 0.107$ R = 541

1B$_3$
-28% $\pi_{P+P} \rightarrow \pi_{P\text{-}P}^*$
54% $\pi_{M+M} \rightarrow \pi_{M\text{-}M}^*$
$f = 0.001$ R = -9.34

Bis-allene1

$\pi_{M\text{-}M}^*$
2.272 eV

$\pi_{P\text{-}P}^*$
1.367 eV

π_{M+M}
-8.231 eV

π_{P+P}
-9.135 eV

2B$_3$
33% $\pi_{P+P} \rightarrow \pi_{P\text{-}P}^*$
-62% $\pi_{M+M} \rightarrow \pi_{M\text{-}M}^*$
$f = 0.049$ R = 313

1B$_3$
60% $\pi_{P+P} \rightarrow \pi_{P\text{-}P}^*$
24% $\pi_{M+M} \rightarrow \pi_{M\text{-}M}^*$
$f = 0.004$ R = 48.5

Bis-allene2

TMS   TMS
Si   Si
TMS   TMS

$\pi_{M\text{-}M}^*$
2.085 eV

$\pi_{P\text{-}P}^*$
1.679 eV

π_{M+M}
-7.995 eV

π_{P+P}
-8.201 eV

2B$_3$
45% $\pi_{P+P} \rightarrow \pi_{P\text{-}P}^*$
10% $\pi_{M+M} \rightarrow \pi_{M\text{-}M}^*$
$f = 0.103$ R = 378

1B$_3$
-25% $\pi_{P+P} \rightarrow \pi_{P\text{-}P}^*$
27% $\pi_{M+M} \rightarrow \pi_{M\text{-}M}^*$
$f = 0.001$ R = 15.0

Figure S4: Overview of the B$_3$ transitions of the allene dimer and bis-allenes with their MO contributions, oscillator strengths, and rotatory strengths listed. Hydrogens are omitted on Bis-allene2 for clarity.
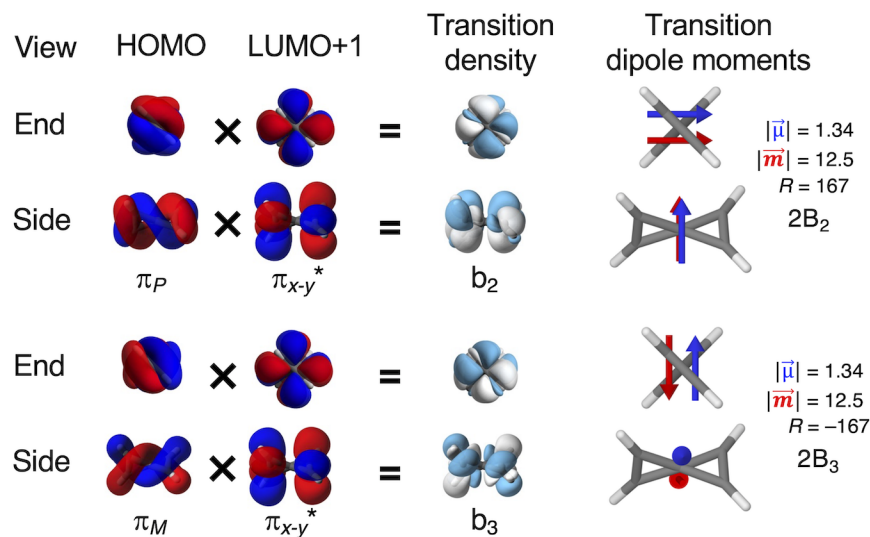
Figure S5: Direct products of the two HOMO→ LUMO+1 transitions of spiropentadiene in D_2 symmetry viewed from end and side of the molecule. The electric (blue) and magnetic (red) transition dipole moments, and the rotatory strengths is provided for the electronic transitions (right column). $\vec{\mu}$ is given in 10^{-18}esu·cm. $\vec{m}$ is given in 10^{-21}erg/G. R is given in 10^{-40} erg·esu·cm/G.
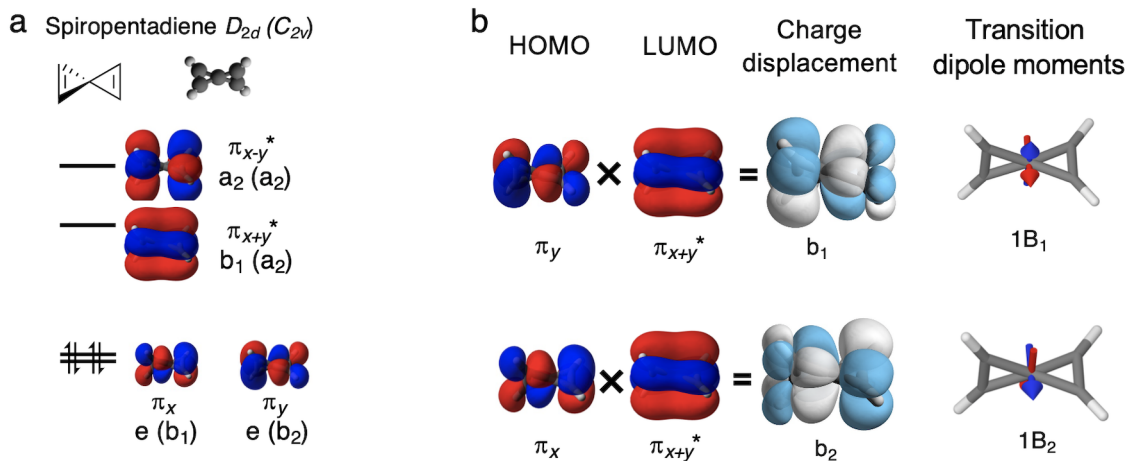

Figure S6: spiropentadiene described in C_{2v} symmetry. a) Frontier MOs. b) Diagram of electronic transitions. c) Direct products of frontier π-MOs.

|	Spiropentadiene (90°)	Spiropentadiene (80°)	Cyclo-spde1	Cyclo-spde2	Cyclo-spde3	Cyclo-spde4
$\pi_{x-y}{}^*$	2.601 eV	2.565 eV	2.918 eV	2.472 eV	2.653 eV	2.652 eV
$\pi_{x+y}{}^*$	1.603 eV	1.625 eV	1.948 eV	1.654 eV	1.878 eV	1.908 eV
π_M	-8.263 eV	-7.922 eV	-7.069 eV	-7.285 eV	-7.454 eV	-7.545 eV
π_P	-8.263 eV	-8.574 eV	-8.215 eV	-8.104 eV	-7.868 eV	-7.835 eV
$2B_2$	91% $\pi_P \rightarrow \pi_{x-y}{}^*$ $f = 0.039$ R = 167	93% $\pi_P \rightarrow \pi_{x-y}{}^*$ $f = 0.032$ R = 147	93% $\pi_P \rightarrow \pi_{x-y}{}^*$ $f = 0.025$ R = 128	92% $\pi_P \rightarrow \pi_{x-y}{}^*$ $f = 0.040$ R = 152	84% $\pi_P \rightarrow \pi_{x-y}{}^*$ $f = 0.051$ R = 199	86% $\pi_P \rightarrow \pi_{x-y}{}^*$ $f = 0.042$ R = 200
$1B_3$	91% $\pi_M \rightarrow \pi_{x-y}{}^*$ $f = 0.039$ R = -167	-27% $\pi_P \rightarrow \pi_{x+y}{}^*$ 70% $\pi_M \rightarrow \pi_{x-y}{}^*$ $f = 0.050$ R = -159	-13% $\pi_P \rightarrow \pi_{x+y}{}^*$ 84% $\pi_M \rightarrow \pi_{x-y}{}^*$ $f = 0.007$ R = -73.5	48% $\pi_P \rightarrow \pi_{x+y}{}^*$ 49% $\pi_M \rightarrow \pi_{x-y}{}^*$ $f = 0.084$ R = -187	-16% $\pi_P \rightarrow \pi_{x+y}{}^*$ 73% $\pi_M \rightarrow \pi_{x-y}{}^*$ $f = 0.080$ R = -230	12% $\pi_P \rightarrow \pi_{x+y}{}^*$ 77% $\pi_M \rightarrow \pi_{x-y}{}^*$ $f = 0.087$ R = -233
$1B_3$	92% $\pi_P \rightarrow \pi_{x+y}{}^*$ $f = 0.008$ R = 13.0	70% $\pi_P \rightarrow \pi_{x+y}{}^*$ 27% $\pi_M \rightarrow \pi_{x-y}{}^*$ $f = 0.002$ R = 20.5	84% $\pi_P \rightarrow \pi_{x+y}{}^*$ 14% $\pi_M \rightarrow \pi_{x-y}{}^*$ $f = 0.055$ R = -66.9	49% $\pi_P \rightarrow \pi_{x+y}{}^*$ -47% $\pi_M \rightarrow \pi_{x-y}{}^*$ $f = 0.000$ R = -5.72	80% $\pi_P \rightarrow \pi_{x+y}{}^*$ 13% $\pi_M \rightarrow \pi_{x-y}{}^*$ $f = 0.008$ R = 25.9	83% $\pi_P \rightarrow \pi_{x+y}{}^*$ -11% $\pi_M \rightarrow \pi_{x-y}{}^*$ $f = 0.011$ R = 27.1
$1B_2$	92% $\pi_M \rightarrow \pi_{x+y}{}^*$ $f = 0.008$ R = -13.0	95% $\pi_M \rightarrow \pi_{x+y}{}^*$ $f = 0.008$ R = -2.09	96% $\pi_M \rightarrow \pi_{x+y}{}^*$ $f = 0.022$ R = -15.6	95% $\pi_M \rightarrow \pi_{x+y}{}^*$ $f = 0.017$ R = -3.64	93% $\pi_M \rightarrow \pi_{x+y}{}^*$ $f = 0.015$ R = -2.69	92% $\pi_M \rightarrow \pi_{x+y}{}^*$ $f = 0.010$ R = -6.48

Figure S7: Overview of the $\pi - \pi^*$ transitions of spiropentadiene and cyclo-spiropentadienes (cyclo-spde) with their MO contributions, oscillator strengths, and rotatory strengths listed.
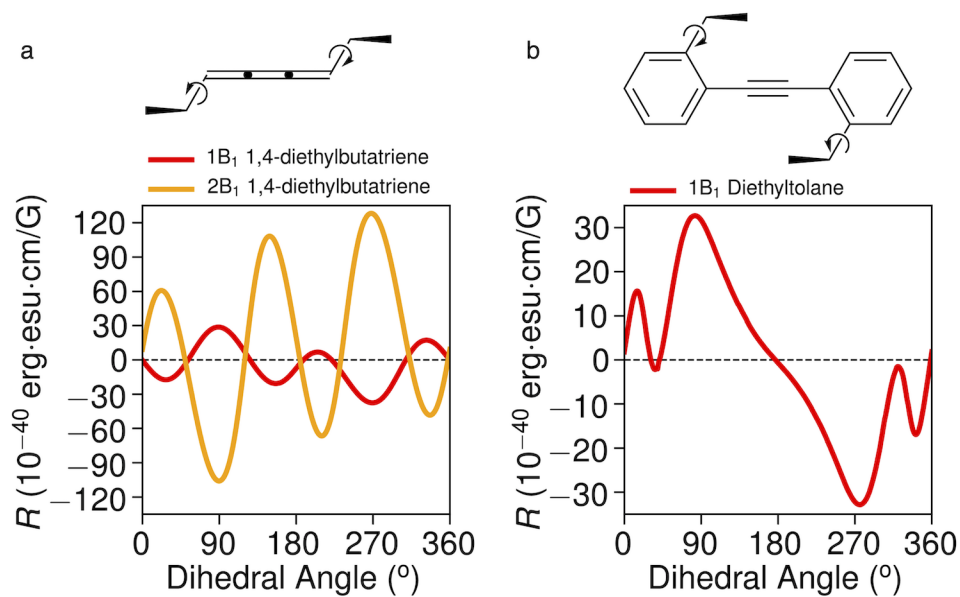
Figure S8: Rotatory strenghts computed as function of ethyl substituent torsion in 1,4-diethylbutatriene (a) and bis(2-ethyl)-tolane (b), similarly to 1,3-diethylallene as computed in the manuscript. The $\pi - \pi^*$ transitions are equivalent to those explored for butatriene and tolane in the manuscript in Figure 7 and 8, which have B_1 symmetry, but are of lower symmetry in the substituted molecules.

References

(1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H. et al. Gaussian 16 Revision A.03. 2016; Gaussian Inc. Wallingford CT.

(2) Mohr, P. J.; Taylor, B. N.; Newell, D. B. CODATA recommended values of the fundamental physical constants: 2010. *Rev. Mod. Phys.* **2012**, *84*, 1527–1605.

(3) Constants | Gaussian.com. `https://gaussian.com/constants/`.

(4) Autschbach, J. Computing chiroptical properties with first-principles theoretical methods: Background and illustrative examples. *Chirality* **2009**, *21*, E116–E152.