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Supporting Information

Correlations between ECD spectra and absolute configuration of bridged-ring lactones: Revisiting Beecham's rule

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Fig. S1 Sector distribution of structures and calculated ECD spectra for 1-4. a) Sector distribution of substituents at β -C and β '-C for 1a-1i, 1j-1l, 2a-2l, 3a-3e, 4a-4d; b) general structures of 1-4; c)

calculated ECD spectra of **1a-1e**; d) calculated ECD spectra of **2a-2e**; e) calculated ECD spectra of **1f-1h**, **2f-2h**; f) calculated ECD spectra of **1j-1k**, **2j-2k**; g) calculated ECD spectra of **3a-3e**; h) calculated ECD spectra of **4a-4c**.



Fig. S1 Sector distribution of structures and calculated ECD spectra for **5a-6c**. a) Sector distribution of substituents at β -C and β '-C for **5a-5c**, and **6a-6c**; b) structures of **5a-6c**; c) calculated ECD spectra of **5a-6c**. Note: *indicates that the ECD data were converted from molar ellipticity values.



Fig. S2 Sector distribution of structures and calculated ECD spectra for 7-9. a) Sector distribution of substituents at β -C and β '-C for 7-9 and core structures; b) structures and simplified structures of 7-9; c) calculated ECD spectra of 7 and simplified structures; d) calculated ECD spectra of 8-9 and simplified structures.



Fig. S3 Sector distribution of structures and calculated ECD spectra for 10-11b. a) Sector distribution of substituents at β -C and β '-C for 10-11b and core structures; b) structures and simplified structures of 10-11b; c) calculated ECD spectra of 10 and simplified structures; d) calculated ECD spectra of 11a-11b and simplified structures.



Fig. S4 Sector distribution of structures and calculated ECD spectra for 12a-12b. a) Sector distribution of substituents at β -C and β '-C for 12a-12b and core structures; b) structures and simplified structures of 12a-12b; c) calculated ECD spectra of 12a-12b and simplified structures.



Fig. S5 Sector distribution of structures and calculated ECD spectra for 13-16. a) Sector distribution of substituents at β -C and β '-C for 13-16 and core structures; b) structures and simplified structures of 13-16; c) calculated ECD spectra of 13, 16a-16b and simplified structures.



Fig. S7 Comparison between experimental and calculated UV and ECD spectra for compound **13**. a) Experimental UV spectra; b) calculated UV spectra with calibration of a 7-nm redshift; c) experimental ECD spectra; d) calculated ECD spectra with calibration of a 7-nm redshift. * Figures a and c are cited from Fen Zhao, Yun-Bao Liu, Shuang-Gang Ma, Jing Qu, Shi-Shan Yu, Zhen-Feng Fang, Li Li, Yi-Kang Si, Jian-Jun Zhang, New sesquiterpenes from the roots of Coriaria nepalensis, *Tetrahedron* 2012, 68(31), 6204-6210. Copyright Elsevier Ltd. Reuse with permission.



Fig. S8 Sector distribution of structures and calculated ECD spectra for 17-18. a) Sector distribution of substituents at β -C and β '-C for 17-18 and core structures; b) structures and simplified structures of 17-18; c) calculated ECD spectra of 17-18 and simplified structures.



Fig. S9 Sector distribution of structures and calculated ECD for 19-23b. a) Sector distribution of substituents at β -C and β '-C for 19-23b; b) structures of 19-23b; c) calculated ECD spectra of (20-23)a; d) calculated ECD spectra of 19, (20-23)b.



Fig. S10 Sector distribution of structures and calculated ECD spectra for 24-27.a) Sector distribution of substituents at β -C and β '-C for 24-27 and core structures; b) structures and simplified structures of 24-27; c) calculated ECD spectra of 24 and simplified structures; d) calculated ECD spectra of 25 and simplified structures; e) calculated ECD spectra of 26 and simplified structures; f) calculated ECD spectra of 27 and simplified structures.



 Exp. : +1.56 (221 nm)
 Calc. : +1.50 (210.8 nm)
 Calc. : -0.46 (211.4 nm)
 Exp. : -1.16 (217 nm)

 Calc. : +1.32 (213.0 nm)
 Calc. : -2.02 (213.2 nm)
 Calc. : -2.02 (213.2 nm)



Fig. S11 Sector distribution of structures and calculated ECD spectra for 28-29. a) Sector distribution of substituents at β -C and β '-C for 28-29 and core structures; b) structures and simplified structures of 28-29; c) calculated ECD spectra of 28-29 and simplified structures.



Fig. S12 Sector distribution of structures and calculated ECD for 30. a) Sector distribution of substituents at β -C and β '-C for 30 and core structures; b) structures and simplified structures of 30; c) calculated ECD spectra of 30 and simplified structures.



Fig. S13 Sector distribution of structures and calculated ECD spectra for 31-32. a) Sector distribution of substituents at β -C and β '-C for 31-32 and core structures; b) structures and simplified structures of 31-32; c) calculated ECD spectra of 31 and simplified structures; d) calculated ECD spectra of 32 and derivative structures.



Fig. S14 Sector distribution of structures and calculated ECD spectra for 33a-33c. a) Sector distribution of substituents at β -C and β '-C for 33a-33c; b) structures of 33a-33c; c) calculated ECD spectra of 33a-33c.



Fig. S15 Sector distribution of structures and calculated ECD spectra for 34a-34b. a) Sector distribution of substituents at β -C and β '-C for 34a-34b and core structures; b) structures and simplified structures of 34a-34b; c) calculated ECD spectra of 34a-34b and simplified structures (the solid line corresponds to the left Y-axis, and the dashed line corresponds to the right Y-axis).



Fig. S16 Sector distribution of structures and calculated ECD spectra for 1a-2a. a) Sector distribution of substituents at β -C and β '-C for 1a, 1a-A, 2a, 2a-A; b) structures and derivative structures of 1a-2a; c) calculated ECD spectra of 1a-2a and derivative structures.



Fig. S17 Sector distribution of structures and calculated ECD spectra for 35a-35c. a) Sector distribution of substituents at β -C and β '-C for 35a-35c and core structures; b) structures of 35a-35c and derivative structures; c) calculated ECD spectra of 35a-35c and derivative structures.



Fig. S18 Sector distribution of structures and calculated ECD spectra for 36a-36d. a) Sector distribution of substituents at β -C and β '-C for 36a-36d; b) structures of 36a-36d; c) calculated ECD spectra of 36a-36d (the solid line corresponds to the left Y-axis and the dashed line corresponds to the right Y-axis).



Fig. S19 Sector distribution of structures and calculated ECD spectra for 37. a) Sector distribution of substituents at β -C and β '-C for 37 and core structures; b) structures and simplified structures of 37; c) calculated ECD spectra of 37 and simplified structures.



Fig. S20 Sector distribution of structures and calculated ECD spectra for 38. a) Sector distribution of substituents at β -C and β '-C for 38 and core structures; b) structures and simplified structures of 38; c) calculated ECD spectra of 38 and simplified structures.



Fig. S21 Sector distribution of structures and calculated ECD spectra for 39-44. a) Sector distribution of substituents at β -C and β '-C for 39-44 and core structures; b) structures and simplified structures of 39-44; c) calculated ECD spectra of 39, 41 and simplified structures (the solid line corresponds to the left Y-axis and the dashed line corresponds to the right Y-axis); d) calculated ECD spectra of 40, 42-44.



Fig. S22 Sector distribution of structures and calculated ECD spectra for 45. a) Sector distribution of substituents at β -C and β '-C for 45 and core structures; b) structures and simplified structures of 45; c) calculated ECD spectra of 45 and simplified structures.



Fig. S23 Sector distribution of structures and calculated ECD spectra for 46. a) Sector distribution of substituents at β -C and β '-C for 46 and core structures; b) structures and simplified structures of 46; c) calculated ECD spectra of 46 and simplified structures.



Fig. S24 Sector distribution of structures and calculated ECD spectra for 47-50. a) Sector distribution of substituents at β -C and β '-C for 47-50; b) structures of 47-50; c) calculated ECD spectra of 47-50.



Fig. S25 Sector distribution of structures and calculated ECD spectra for 51. a) Sector distribution of substituents at β -C and β '-C for 51; b) structure of 51; c) calculated ECD spectra of 51.



Fig. S26 Transition MOs involved in the main excitations of 2j-2l. Note: 2j-2k at the B3LYP /6-311G(d,p) level and 2l at the B3LYP/(C, H, O: 6-311G(d,p); I: def2TZVP) level with an isovalue of 0.05.



Fig. S27 Transition MOs involved in the main excitations of **33a-33c** at the B3LYP/6-311G(d,p) level with an isovalue of 0.05.



Fig. S28 Transition MOs involved in the main excitations of **36a-36b**. Note: **36a** at the B3LYP /6-311G(d,p) level and **36b** at the B3LYP/(C, H, O: 6-311G(d,p); I: def2TZVP) level with an isovalue of 0.05.



Fig. S29 Transition MOs involved in the main excitations of 38, 39 and 41 at the B3LYP/6-311G(d,p) level with an isovalue of 0.05.



Fig. S30 Transition MOs involved in the main excitations of **48** and **50** at the B3LYP/6-311G(d,p) level with an isovalue of 0.05.