Supporting Information

TDDFT-ECD and DFT-NMR studies of thaigranatins A-E and granatumin L isolated from *Xylocarpus granatum*

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ECD data of **1**-**6**:

Thaigranatin A (**1**): ECD (MeCN, λ [nm] (Δε), c 0.34 mM): 260sh (–0.25), 234sh (–0.82), ≤ 190 (≤ –17.40) nm.

Thaigranatin B (**2**): ECD (MeCN, λ [nm] (Δε), c 0.37 mM): 237sh (0.63), 217 (2.22), ≤ 190 (≤ –14.05) nm.

Thaigranatin C (**3**): ECD (MeCN, λ [nm] (Δε), c 0.34 mM): 286sh (0.69), 244sh (0.88), 220 (3.70), 199 (–9.26) nm.

Thaigranatin D (**4**): ECD (MeCN, λ [nm] (Δε), c 0.34 mM): 282sh (0.30), 248sh (1.58), 220 (8.31), 196 (–12.22) nm.

Thaigranatin E (**5**): ECD (MeCN, λ [nm] (Δε), c 0.34 mM): 285sh (0.20), 254 (0.70), 219 (–2.60), 195 (8.65) nm.

Granatumin L (**6**): ECD (MeCN, λ [nm] (Δε), c 0.35 mM): 220sh (–3.02), ≤ 190 (≤ –12.52) nm.

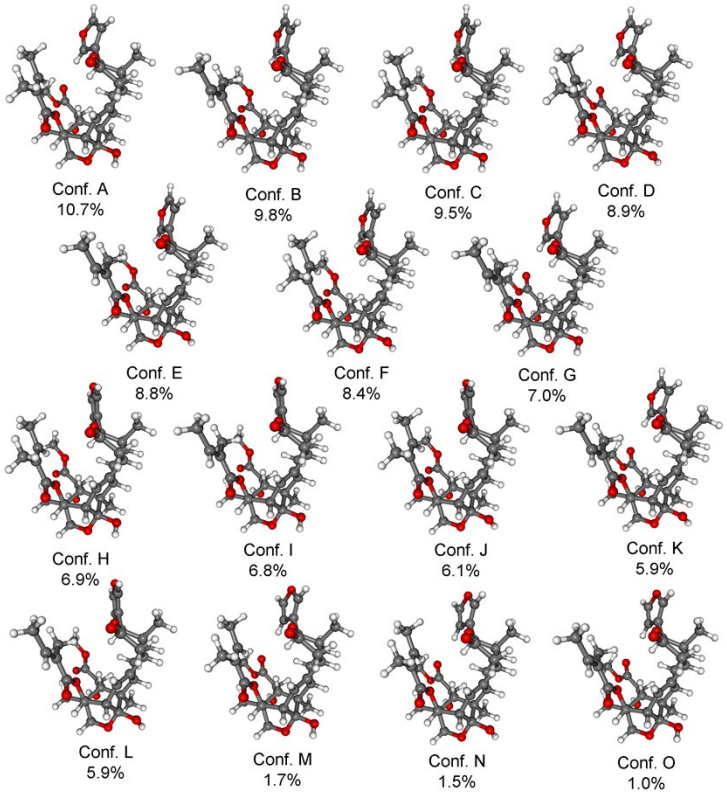

Fig. S1 Structure and population of the low-energy CAM-B3LYP/TZVP PCM/MeCN conformers (≥ 1%) of (1*R*,2*S*,3*R*,4*S*,5*S*,6*R*,9*S*,10*R*,13*R*,14*S*,17*R*)-**1**.

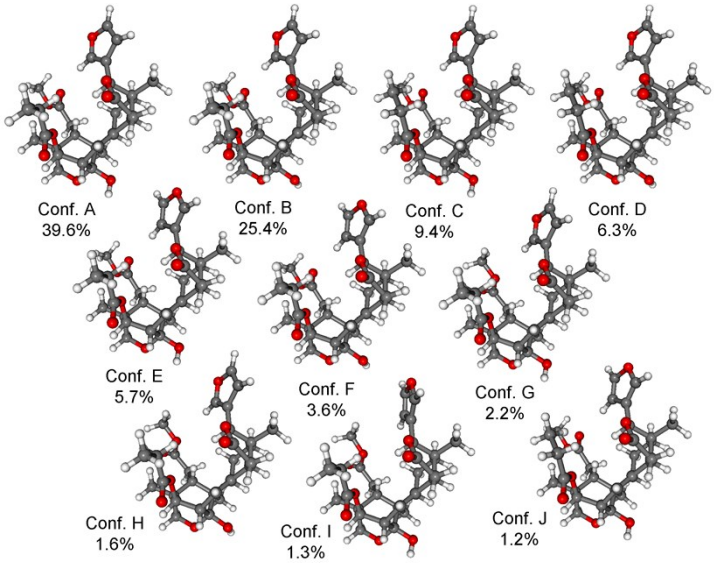

Fig. S2 Structure and population of the low-energy CAM-B3LYP/TZVP PCM/MeCN conformers (≥ 1%) of (1*R*,2*S*,3*R*,4*S*,5*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-**2**.

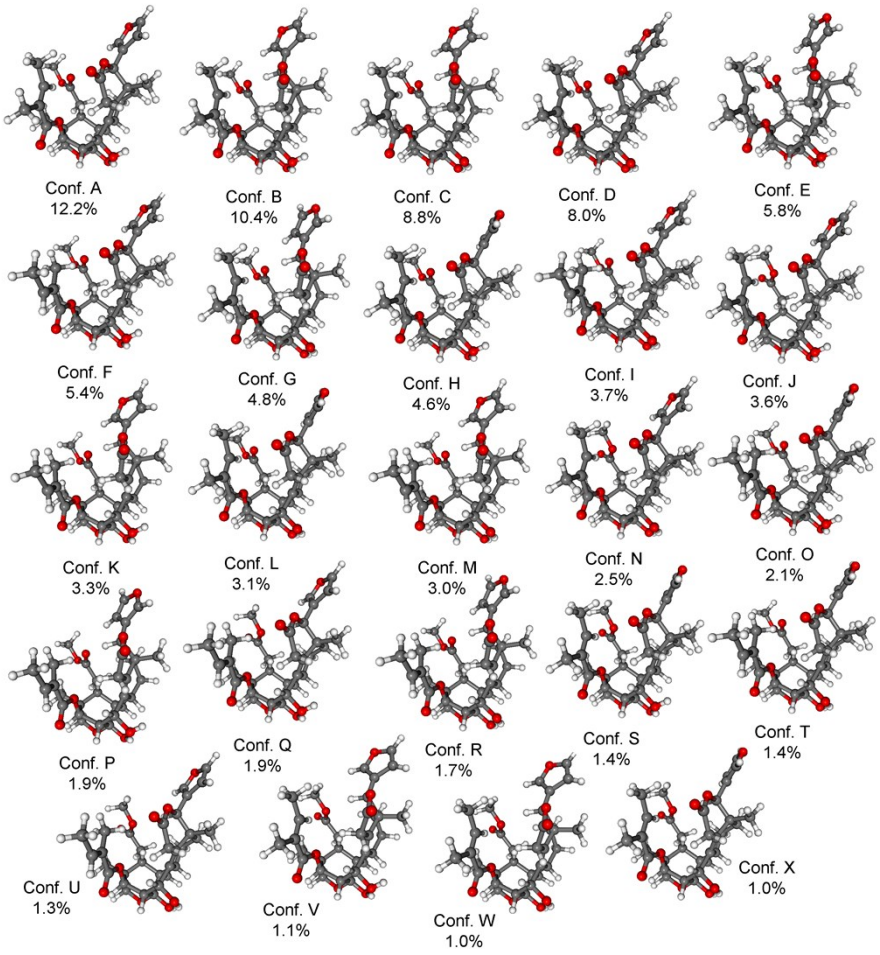

Fig. S3 Structure and population of the low-energy CAM-B3LYP/TZVP PCM/MeCN conformers (≥ 1%) of (1*R*,2*S*,3*R*,4*S*,5*S*,9*S*,10*R*,13*R*,17*R*,30*R*)-**3**.

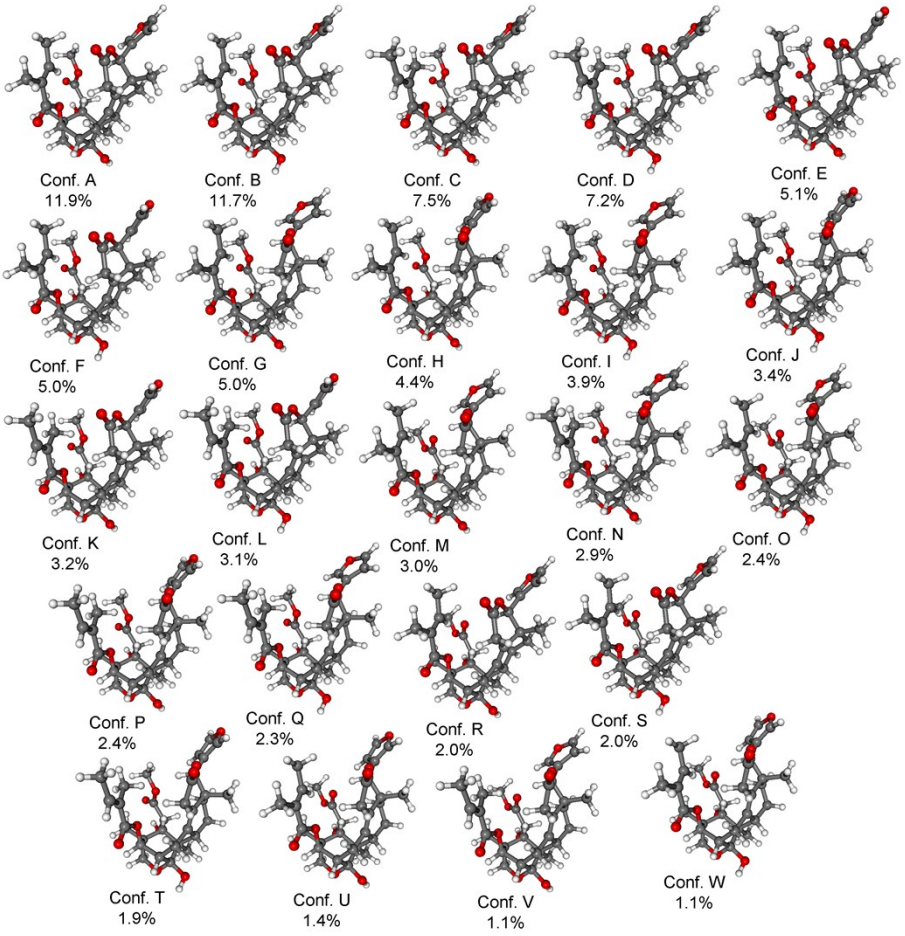

Fig. S4 Structure and population of the low-energy CAM-B3LYP/TZVP PCM/MeCN conformers (≥ 1%) of (1*R*,2*S*,3*R*,4*S*,5*S*,6*R*,9*S*,10*R*,13*R*,17*R*)-**4**.

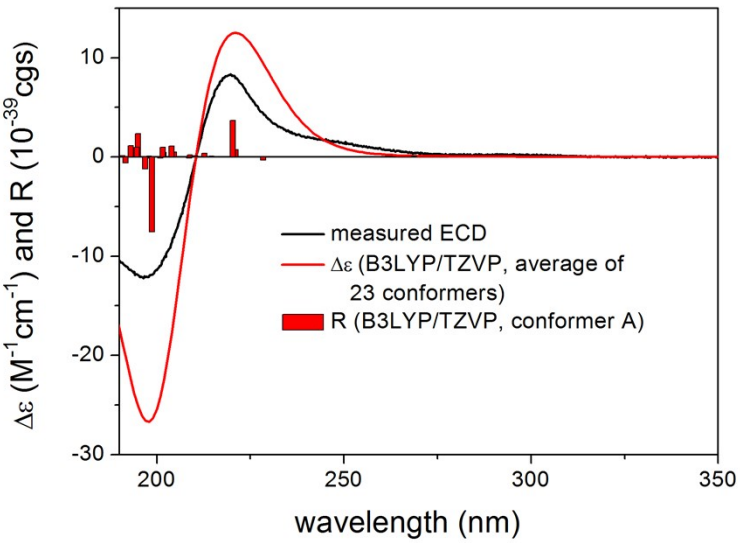

Fig. S5 Experimental ECD spectrum of **4** in MeCN compared with the Boltzmann-weighted B3LYP/TZVP PCM/MeCN ECD spectrum of (1*R*,2*S*,3*R*,4*S*,5*S*,6*R*,9*S*,10*R*,13*R*,17*R*)-**4**. Level of optimization: CAM-B3LYP/TZVP PCM/MeCN. Bars represent the rotatory strength values of the lowest-energy conformer.

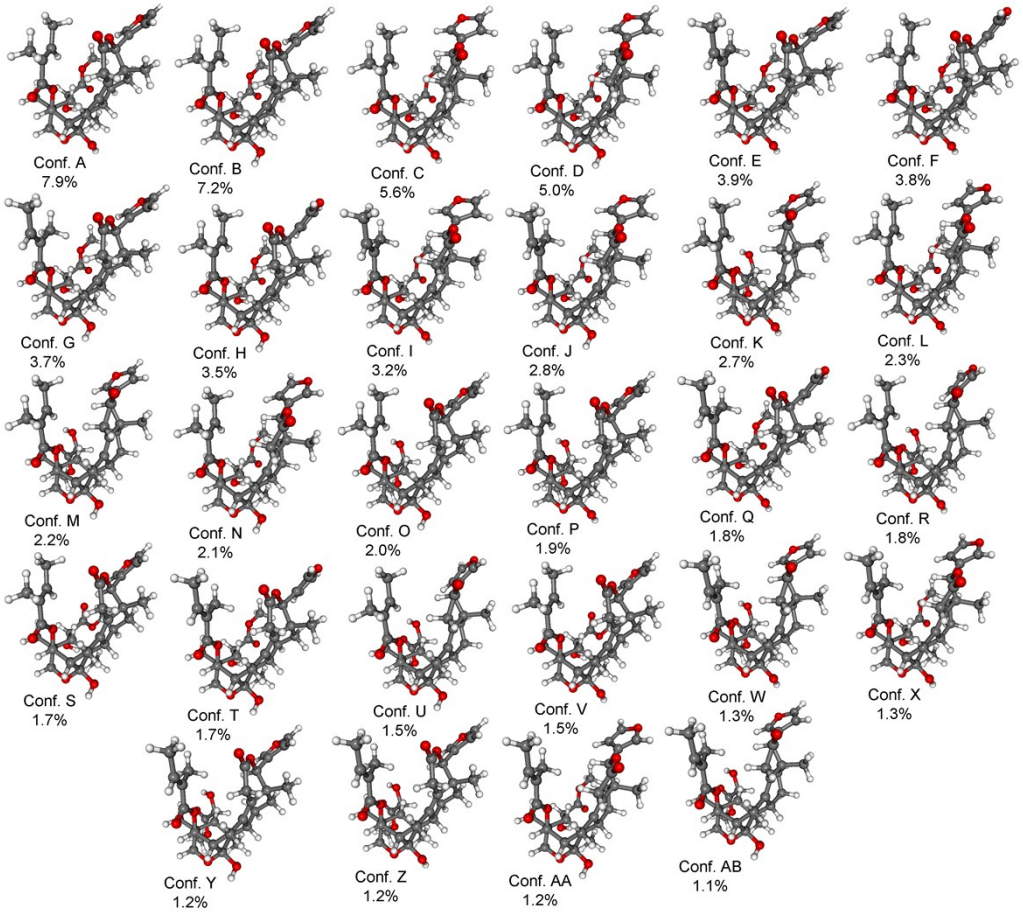

Fig. S6 Structure and population of the low-energy CAM-B3LYP/TZVP PCM/MeCN conformers (≥ 1%) of (1*R*,2*S*,3*R*,4*S*,5*S*,6*S*,9*S*,10*R*,13*R*,17*R*)-**4**.

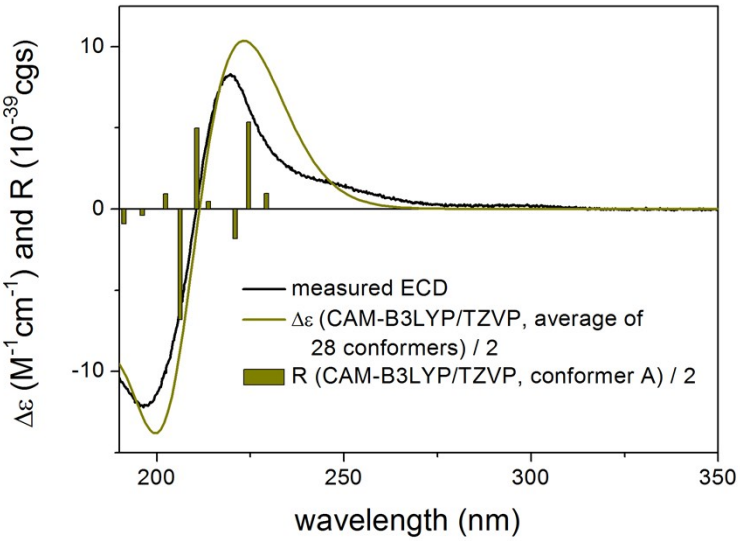

Fig. S7 Experimental ECD spectrum of **4** in MeCN compared with the Boltzmann-weighted CAM-B3LYP/TZVP PCM/MeCN ECD spectrum of (1*R*,2*S*,3*R*,4*S*,5*S*,6*S*,9*S*,10*R*,13*R*,17*R*)-**4**. Level of optimization: CAM-B3LYP/TZVP PCM/MeCN. Bars represent the rotatory strength values of the lowest-energy conformer.

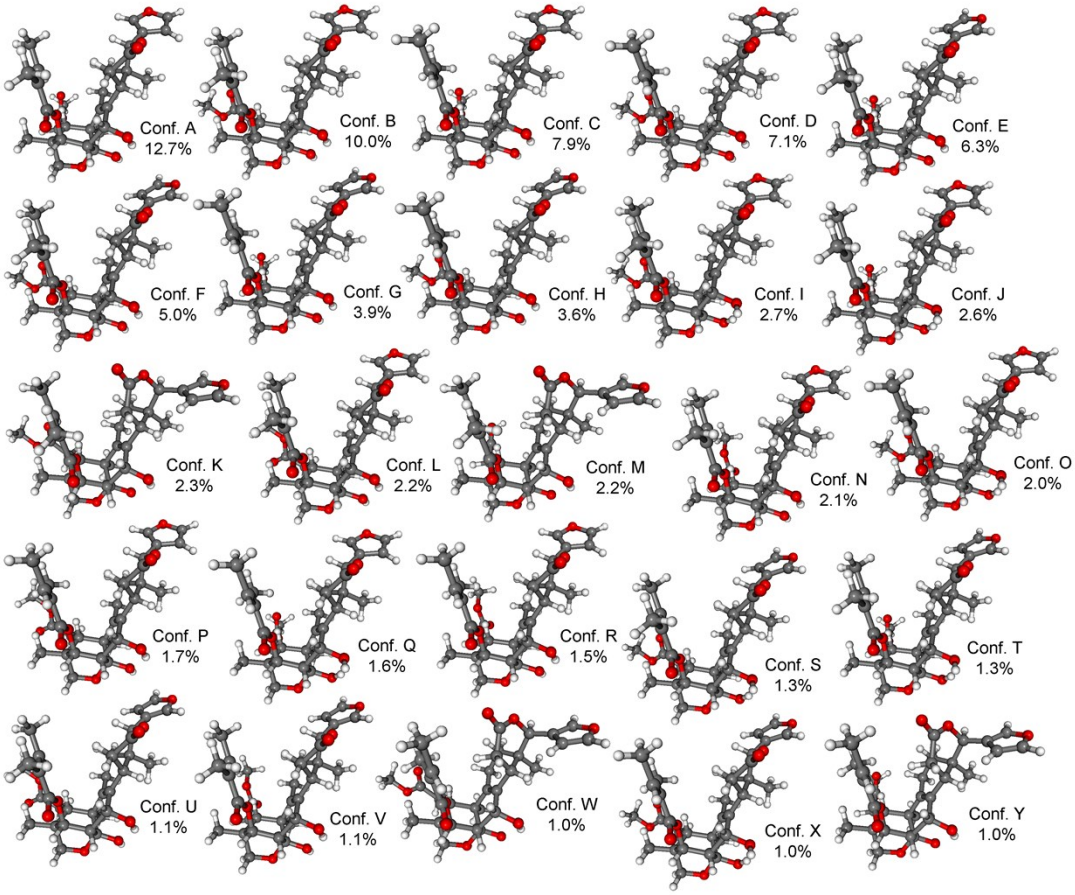

Fig. S8 Structure and population of the low-energy CAM-B3LYP/TZVP PCM/MeCN conformers (≥ 1%) of (1*R*,2*S*,3*R*,4*S*,5*S*,10*S*,13*R*,14*R*,17*R*,30*R*)-**5**.

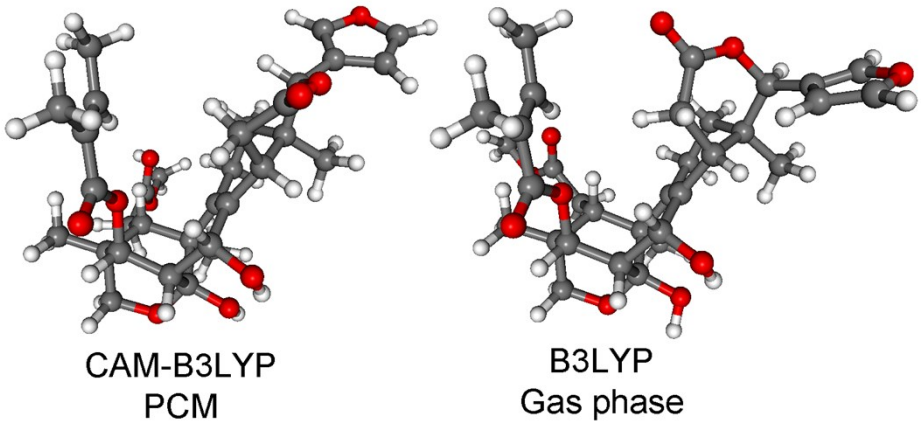

Fig. S9 Comparison of the lowest-energy CAM-B3LYP/TZVP PCM/MeCN (12.7%) and B3LYP/6-31+G(d,p) gas-phase (10.8%) conformers of (1*R*,2*S*,3*R*,4*S*,5*S*,10*S*,13*R*,14*R*,17*R*,30*R*)-**5**. (Different view.)

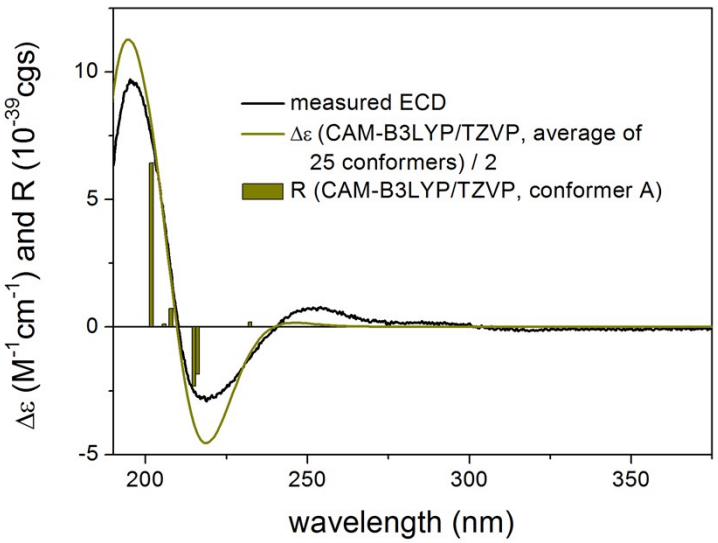

Fig. S10 Experimental ECD spectrum of **5** in MeCN compared with the Boltzmann-weighted CAM-B3LYP/TZVP PCM/MeCN ECD spectrum of (1*R*,2*S*,3*R*,4*S*,5*S*,10*S*,13*R*,14*R*,17*R*,30*R*)-**5**. Level of optimization: CAM-B3LYP/TZVP PCM/MeCN. Bars represent the rotatory strength values of the lowest-energy conformer.

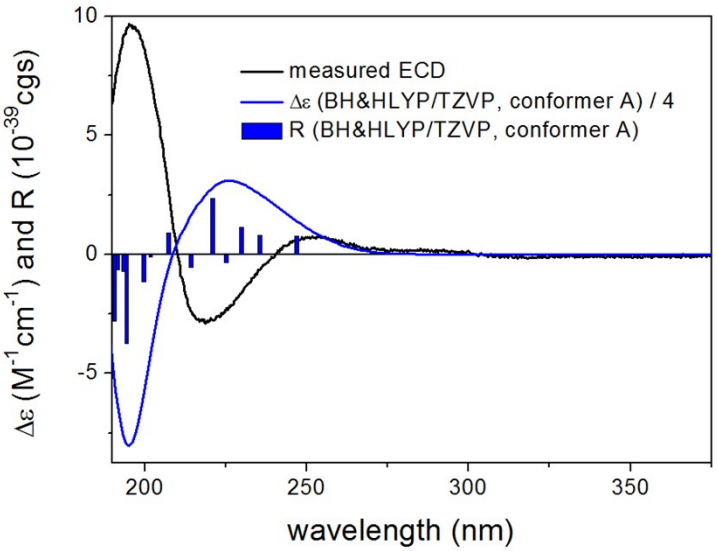

Fig. S11 Experimental ECD spectrum of **5** in MeCN compared with the lowest-energy BH&HLYP/TZVP ECD spectrum of (1*R*,2*S*,3*R*,4*S*,5*S*,10*S*,13*R*,14*R*,17*R*,30*R*)-**5**. Level of optimization: B3LYP/6-31+G(d,p). Bars represent the rotatory strength values of the lowest-energy conformer.

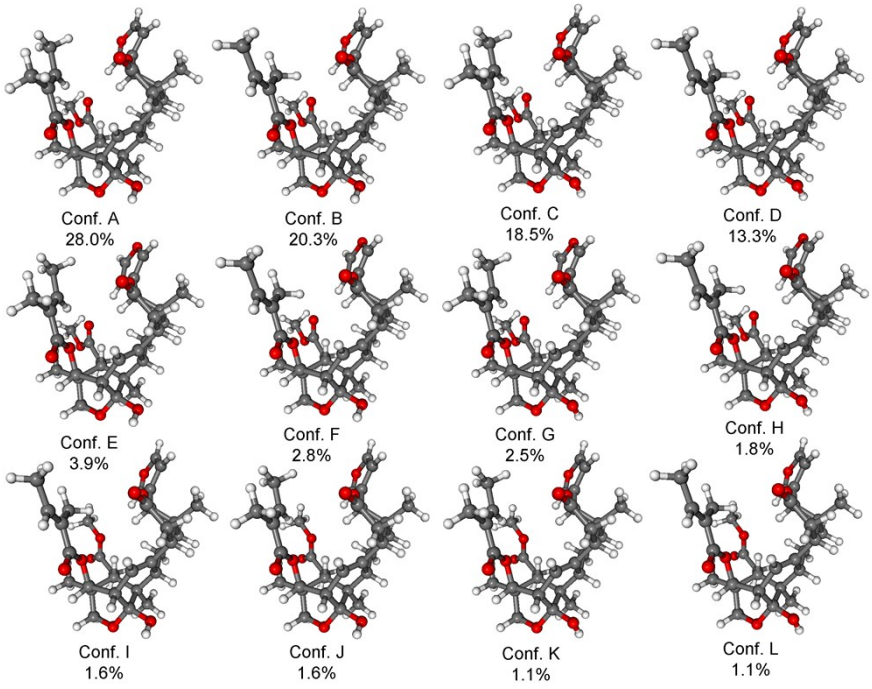

Fig. S12 Structure and population of the low-energy CAM-B3LYP/TZVP PCM/MeCN conformers (≥ 1%) of (1*R*,2*S*,3*R*,4*S*,5*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-**6**.

Table S1 Test comparison of the experimental[1] and the mPW1PW91/6-311+G(2d,p) // B3LYP/6-31+G(d,p) ^{13}C NMR data of (1*R*,2*S*,3*R*,4*S*,5*S*,6*R*,9*S*,10*R*,13*R*,14*S*,17*R*)-**1**. For a better comparison Δδ values over 2.5 were marked with yellow and those over 5.0 with red.

Carbon	Exp.	Calcd.	Δδ
C-1	96.9	98.54	1.64
C-2	45.3	47.63	2.33
C-3	76.2	78.12	1.92
C-4	36.6	40.10	3.50
C-5	39.6	41.03	1.43
C-6	72.5	74.90	2.40
C-7	176.1	178.81	2.71
C-8	138.3	141.49	3.19
C-9	48.9	49.57	0.67
C-10	42.1	45.69	3.59
C-11	20.4	21.93	1.53
C-12	34.6	35.30	0.70
C-13	36.7	40.64	3.94
C-14	44.8	47.90	3.10
C-15	29.6	30.10	0.50
C-16	169.3	167.75	1.55
C-17	76.6	75.80	0.80
C-18	21.2	20.85	0.35
C-19	14.9	13.73	1.17
C-20	121.6	125.18	3.58
C-21	140.3	141.94	1.64
C-22	109.3	110.56	1.26
C-23	143.1	142.69	0.41
C-28	15.8	15.01	0.79
C-29	70.1	71.07	0.97
C-30	120.2	124.94	4.74
C-31	53.2	52.56	0.64
C-32	167.2	167.98	0.78
C-33	127.8	129.55	1.75
C-34	138.7	144.62	5.92
C-35	14.6	15.14	0.54
C-36	11.7	12.11	0.41
CMAE	N/A	N/A	1.89

Table S2 Test comparison of the experimental[1] and the mPW1PW91/6-311+G(2d,p) // B3LYP/6-31+G(d,p) ^{13}C NMR data of (1*R*,2*S*,3*R*,4*S*,5*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-**2**. For a better comparison Δδ values over 2.5 were marked with yellow and those over 5.0 with red.

Carbon	Exp.	Calcd.	Δδ
C-1	96.9	98.19	1.29
C-2	45.1	47.87	2.77
C-3	75.2	76.67	1.47
C-4	36.2	39.71	3.51
C-5	35.0	38.79	3.79
C-6	31.9	32.45	0.55
C-7	173.9	177.09	3.19
C-8	138.4	142.96	4.56
C-9	47.8	48.49	0.69
C-10	41.6	44.90	3.30
C-11	19.4	20.66	1.26
C-12	34.5	35.43	0.93
C-13	36.9	40.39	3.49
C-14	45.0	47.77	2.77
C-15	30.1	30.49	0.39
C-16	170.1	169.08	1.02
C-17	77.0	75.96	1.04
C-18	21.9	21.31	0.59
C-19	14.4	14.42	0.02
C-20	120.8	123.93	3.13
C-21	141.8	145.00	3.20
C-22	109.7	110.78	1.08
C-23	143.0	142.70	0.30
C-28	14.8	14.28	0.52
C-29	68.0	69.26	1.26
C-30	119.9	124.39	4.49
C-31	52.1	51.45	0.65
C-32	174.5	176.02	1.52
C-33	27.2	28.23	1.03
C-34	8.8	8.33	0.47
CMAE	N/A	N/A	1.81

Table S3 Test comparison of the experimental[1] and the mPW1PW91/6-311+G(2d,p) // B3LYP/6-31+G(d,p) ^{13}C NMR data of (1*R*,2*S*,3*R*,4*S*,5*S*,9*S*,10*R*,13*R*,17*R*,30*R*)-**3**. For a better comparison Δδ values over 2.5 were marked with yellow and those over 5.0 with red.

Carbon	Exp.	Calcd.	Δδ
C-1	97.4	100.36	2.96
C-2	48.2	51.14	2.94
C-3	75.2	75.03	0.17
C-4	37.1	40.34	3.24
C-5	34.5	36.88	2.38
C-6	32.1	32.42	0.32
C-7	174.2	177.08	2.88
C-8	131.3	136.79	5.49
C-9	38.7	41.89	3.19
C-10	45.1	47.35	2.25
C-11	17.7	19.10	1.40
C-12	29.4	30.68	1.28
C-13	38.2	41.76	3.56
C-14	134.3	140.82	6.52
C-15	32.3	34.38	2.08
C-16	169.5	168.41	1.09
C-17	80.7	79.92	0.78
C-18	17.4	17.66	0.26
C-19	14.2	12.98	1.22
C-20	120.7	124.34	3.64
C-21	141.6	143.00	1.40
C-22	109.9	111.03	1.13
C-23	142.9	142.76	0.14
C-28	15.6	15.02	0.58
C-29	67.6	68.50	0.90
C-30	66.3	66.71	0.41
C-31	52.1	51.55	0.55
C-32	167.6	167.45	0.15
C-33	128.8	130.02	1.22
C-34	139.6	145.11	5.51
C-35	14.6	15.38	0.78
C-36	12.3	12.62	0.32
CMAE	N/A	N/A	1.90

Table S4 Test comparison of the experimental[1] and the mPW1PW91/6-311+G(2d,p) // B3LYP/6-31+G(d,p) ^{13}C NMR data of (1*R*,2*S*,3*R*,4*S*,5*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-**6**. For a better comparison Δδ values over 2.5 were marked with yellow and those over 5.0 with red.

Carbon	Exp.	Calcd.	Δδ
C-1	97	98.85	1.85
C-2	45.5	48.28	2.78
C-3	75.1	76.96	1.86
C-4	36.3	39.67	3.37
C-5	34.9	38.25	3.35
C-6	31.9	32.24	0.34
C-7	173.9	177.77	3.87
C-8	138.6	142.70	4.10
C-9	48.1	48.33	0.23
C-10	41.5	44.83	3.33
C-11	19.6	20.95	1.35
C-12	34.6	35.33	0.73
C-13	37	40.34	3.34
C-14	45.1	48.00	2.90
C-15	29.8	30.26	0.46
C-16	169.4	168.36	1.04
C-17	76.3	75.34	0.96
C-18	21.6	20.98	0.62
C-19	14.5	13.68	0.82
C-20	120.9	124.43	3.53
C-21	141.8	144.49	2.69
C-22	109.7	111.30	1.60
C-23	143	142.96	0.04
C-28	15	14.89	0.11
C-29	67.9	68.63	0.73
C-30	120	124.24	4.24
C-31	52.1	51.60	0.50
C-32	167.5	168.28	0.78
C-33	127.6	129.59	1.99
C-34	139.4	145.47	6.07
C-35	14.7	15.14	0.44
C-36	11.7	12.25	0.55
CMAE	N/A	N/A	1.89

Table S5 Comparison of the experimental[1] and the mPW1PW91/6-311+G(2d,p) // B3LYP/6-31+G(d,p) ^{13}C NMR data of (1*R*,2*S*,3*R*,4*S*,5*S*,6*R*,9*S*,10*R*,13*R*,17*R*)-**4** and (1*R*,2*S*,3*R*,4*S*,5*S*,6*S*,9*S*,10*R*,13*R*,17*R*)-**4**. For a better comparison Δδ values over 2.5 were marked with yellow and those over 5.0 with red.

Carbon	Exp.	calcd (6*R*)	calcd (6*S*)	Δδ (6*R*)	Δδ (6*S*)
C-1	97.1	97.97	98.03	0.87	0.93
C-2	43.6	45.61	45.68	2.01	2.08
C-3	78.5	78.96	78.86	0.46	0.36
C-4	36.6	39.67	39.68	3.07	3.08
C-5	39.3	41.41	44.97	2.11	5.67
C-6	73.1	74.27	73.21	1.17	0.11
C-7	175.8	179.32	180.09	3.52	4.29
C-8	130.6	137.07	136.44	6.47	5.84
C-9	43.9	46.91	46.89	3.01	2.99
C-10	44.7	47.76	48.89	3.06	4.19
C-11	18.2	19.87	19.25	1.67	1.05
C-12	30.3	31.45	31.33	1.15	1.03
C-13	37.8	41.04	41.04	3.24	3.24
C-14	129	133.10	133.05	4.10	4.05
C-15	33.1	34.75	34.49	1.65	1.39
C-16	169.8	168.46	168.27	1.34	1.53
C-17	81.6	81.19	81.13	0.41	0.47
C-18	18	18.61	18.21	0.61	0.21
C-19	15.1	14.65	14.91	0.45	0.19
C-20	121.1	124.26	124.27	3.16	3.17
C-21	140.9	142.04	142.24	1.14	1.34
C-22	109.8	110.82	110.96	1.02	1.16
C-23	143.1	142.92	142.90	0.18	0.20
C-28	16.4	15.38	16.74	1.02	0.34
C-29	70	70.29	69.52	0.29	0.48
C-30	26.4	27.58	27.58	1.18	1.18
C-31	53.1	52.45	52.19	0.65	0.91
C-32	167.5	167.94	168.03	0.44	0.53
C-33	128.9	130.38	130.35	1.48	1.45
C-34	138.7	144.40	144.79	5.70	6.09
C-35	14.6	15.33	15.36	0.73	0.76
C-36	12.2	12.56	12.50	0.36	0.30
CMAE	N/A	N/A	N/A	1.80	1.89

Table S6 Test comparison of the experimental[1] and the mPW1PW91/6-311+G(2d,p) SMD/$CHCl_3$ // mPW1PW91/6-311+G(2d,p) SMD/$CHCl_3$ ^{13}C NMR data of (1*R*,2*S*,3*R*,4*S*,5*S*,6*R*,9*S*,10*R*,13*R*,14*S*,17*R*)-**1**. For a better comparison Δδ values over 2.5 were marked with yellow and those over 5.0 with red.

Carbon	Exp.	Calcd.	Δδ
C-1	96.9	97.27	0.37
C-2	45.3	47.16	1.86
C-3	76.2	78.10	1.90
C-4	36.6	38.92	2.32
C-5	39.6	40.13	0.53
C-6	72.5	73.28	0.78
C-7	176.1	179.06	2.96
C-8	138.3	142.97	4.67
C-9	48.9	50.96	2.06
C-10	42.1	44.66	2.56
C-11	20.4	22.95	2.55
C-12	34.6	35.87	1.27
C-13	36.7	39.46	2.76
C-14	44.8	47.72	2.92
C-15	29.6	30.35	0.75
C-16	169.3	170.46	1.16
C-17	76.6	75.44	1.16
C-18	21.2	22.11	0.91
C-19	14.9	16.25	1.35
C-20	121.6	124.67	3.07
C-21	140.3	139.84	0.46
C-22	109.3	110.21	0.91
C-23	143.1	142.50	0.60
C-28	15.8	15.85	0.05
C-29	70.1	70.60	0.50
C-30	120.2	122.81	2.61
C-31	53.2	53.15	0.05
C-32	167.2	167.42	0.22
C-33	127.8	129.16	1.36
C-34	138.7	144.48	5.78
C-35	14.6	15.98	1.38
C-36	11.7	12.75	1.05
CMAE	N/A	N/A	1.65

Table S7 Comparison of the experimental[1] and the mPW1PW91/6-311+G(2d,p) SMD/$CHCl_3$ // mPW1PW91/6-311+G(2d,p) SMD/$CHCl_3$ ^{13}C NMR data of (1*R*,2*S*,3*R*,4*S*,5*S*,6*R*,9*S*,10*R*,13*R*,17*R*)-**4** and (1*R*,2*S*,3*R*,4*S*,5*S*,6*S*,9*S*,10*R*,13*R*,17*R*)-**4**. For a better comparison Δδ values over 2.5 were marked with yellow and those over 5.0 with red.

Carbon	Exp.	calcd (6*R*)	calcd (6*S*)	Δδ (6*R*)	Δδ (6*S*)
C-1	97.1	96.64	96.88	0.46	0.22
C-2	43.6	44.17	45.01	0.57	1.41
C-3	78.5	79.22	79.67	0.72	1.17
C-4	36.6	38.92	38.95	2.32	2.35
C-5	39.3	39.52	43.82	0.22	4.52
C-6	73.1	73.53	72.38	0.43	0.72
C-7	175.8	179.22	179.09	3.42	3.29
C-8	130.6	138.06	136.73	7.46	6.13
C-9	43.9	47.38	47.30	3.48	3.40
C-10	44.7	46.41	47.56	1.71	2.86
C-11	18.2	20.36	20.09	2.16	1.89
C-12	30.3	32.75	32.72	2.45	2.42
C-13	37.8	40.16	40.27	2.36	2.47
C-14	129	133.58	132.80	4.58	3.80
C-15	33.1	35.34	34.94	2.24	1.84
C-16	169.8	170.61	170.81	0.81	1.01
C-17	81.6	80.87	80.02	0.73	1.58
C-18	18	19.12	19.09	1.12	1.09
C-19	15.1	15.16	16.31	0.06	1.21
C-20	121.1	124.33	124.62	3.23	3.52
C-21	140.9	141.25	141.51	0.35	0.61
C-22	109.8	110.63	111.14	0.83	1.34
C-23	143.1	142.59	142.59	0.51	0.51
C-28	16.4	16.86	17.90	0.46	1.50
C-29	70	70.44	70.17	0.44	0.17
C-30	26.4	27.85	27.75	1.45	1.35
C-31	53.1	53.07	52.77	0.03	0.33
C-32	167.5	167.51	167.77	0.01	0.27
C-33	128.9	129.61	129.86	0.71	0.96
C-34	138.7	145.03	145.16	6.33	6.46
C-35	14.6	16.33	16.06	1.73	1.46
C-36	12.2	13.02	13.00	0.82	0.80
CMAE	N/A	N/A	N/A	1.69	1.96

[1] J. L. Ren, X. P. Zou, W. S. Li, L. Shen and J. Wu, *Mar. Drugs*, 2018, **16**, 434.