

Electronic Supplementary Information

NMR Method for Relative Stereochemical Assignments of the Tricyclic Core of Cephalosporolides, Penisporolides and Related Synthetic Analogues

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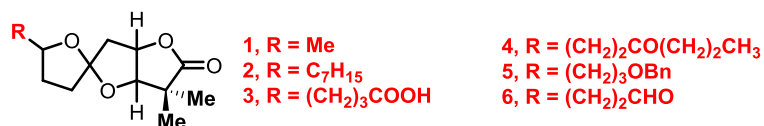
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General Information:

^1H and ^{13}C NMR spectra and data used in this study were reported in the literature with deuterated chloroform as the solvent.

Table S-1: Analysis results of ^1H NMR data of compounds **A1** to **D6**¹



	SAFL-A	SAFL-B	SAFL-C	SAFL-D
H4 (SSC)	A1: 5.10, t A2: 5.10, t A3: 5.13, t A4: 5.10, t A5: 5.10, t A6: 5.11, t	B1: 5.02, ddd B2: 5.02, ddd B3: 5.02, ddd B4: 5.01, ddd B5: 5.01, ddd B6: 5.01, ddd	C1: 5.02, ddd C2: 5.02, ddd C3: 5.02, ddd C4: 5.02, ddd C5: 5.02, ddd C6: 5.01, ddd	D1: 5.08, t D2: 5.08, t D3: 5.09, t D4: 5.08, t D5: 5.07, t D6: 5.09, t
	average: 5.11	average: 5.02	average: 5.02	average: 5.08
	SD: 0.012	SD: 0.005	SD: 0.004	SD: 0.008
H5 ($\Delta\delta$)	A1: 0.33 A2: 0.34 A3: 0.34 A4: 0.33 A5: 0.32 A6: 0.32	B1: 0.14 B2: 0.15 B3: 0.15 B4: 0.14 B5: 0.15 B6: 0.13	C1: 0.15 C2: 0.16 C3: 0.15 C4: 0.15 C5: 0.15 C6: 0.13	D1: 0.32 D2: 0.32 D3: 0.33 D4: 0.32 D5: 0.32 D6: 0.31
	average: 0.33	average: 0.14	average: 0.15	average: 0.32
	SD: 0.009	SD: 0.008	SD: 0.010	SD: 0.006
H8 ($\Delta\delta$)	A1: 0.65 A2: 0.63 A3: 0.60 A4: 0.63 A5: 0.61 A6: 0.62	B1: 0.24 B2: 0.22 B3: 0.21 B4: 0.21 B5: 0.22 B6: 0.18	C1: 0.63 C2: 0.62 C3: 0.59 C4: 0.58 C5: 0.57 C6: 0.58	D1: 0.33 D2: 0.34 D3: 0.32 D4: 0.31 D5: 0.31 D6: 0.30
	average: 0.62	average: 0.22	average: 0.60	average: 0.32
	SD: 0.018	SD: 0.020	SD: 0.024	SD: 0.015

¹ Wang, J.; Tong, R. *J. Org. Chem.* **2016**, *81*, 4325.

Table S-2: ¹³C-NMR data of compounds **A1–D1**¹

position	A1	B1	C1	D1	Mean	SD
1	180.91	181.00	180.89	180.73	180.88	0.11
2	44.28	44.46	44.44	44.49	44.42	0.09
3	86.69	85.06	85.22	87.02	86.00	1.00
4	80.00	80.38	80.52	79.87	80.19	0.31
5	41.76	41.95	42.52	41.75	42.00	0.36
6	115.13	115.48	115.62	115.26	115.37	0.22
7	34.67	37.47	35.85	36.64	36.16	1.19
8	31.40	32.38	31.91	32.37	32.02	0.46
9	75.46	67.97	74.89	77.70	74.01	4.20

Table S-3: ¹³C-NMR data of compounds **A2–D2**¹

position	A2	B2	C2	D2	Mean	SD
1	180.75	181.01	180.93	180.59	180.82	0.19
2	44.22	44.42	44.46	44.50	44.40	0.12
3	86.70	85.02	85.20	87.07	86.00	1.04
4	79.93	80.82	80.57	81.91	80.81	0.83
5	41.80	41.86	42.37	41.64	41.92	0.32
6	114.94	115.21	115.46	115.07	115.17	0.22
7	34.47	37.00	35.67	36.31	36.08	0.74
8	29.86	30.62	30.03	30.83	30.34	0.46
9	79.62	80.42	79.00	79.79	79.71	0.58

Table S-4: ¹³C-NMR data of compounds **A3–D3**¹

position	A3	B3	C3	D3	Mean	SD
1	181.43	180.94	180.88	181.12	181.09	0.25
2	44.47	44.43	44.46	44.72	44.52	0.13
3	86.71	85.10	85.27	87.11	86.05	1.01
4	80.24	80.36	80.50	81.46	80.64	0.56
5	41.87	41.81	42.31	41.67	41.92	0.28
6	115.23	115.33	115.55	115.26	115.34	0.14
7	34.34	36.83	35.52	36.21	35.73	1.07
8	30.11	30.59	30.04	30.92	30.42	0.42
9	79.38	80.14	78.31	80.04	79.47	0.84

Table S-5: ¹³C-NMR data of compounds **A4–D4**¹

position	A4	B4	C4	D4	Mean	SD
1	180.86	180.87	180.81	180.78	180.83	0.04
2	44.76	44.83	44.79	44.82	44.80	0.03
3	86.59	85.11	85.30	87.05	86.01	0.95
4	79.89	80.32	80.45	80.57	80.31	0.30
5	41.74	41.76	42.23	41.55	41.82	0.29
6	114.92	115.34	115.60	115.13	115.25	0.29
7	34.24	36.96	35.58	36.13	35.73	1.14
8	30.14	30.82	30.00	30.93	30.47	0.47
9	78.45	79.74	78.01	79.77	78.99	0.90

Table S-6: ¹³C-NMR data of compounds **A5–D5**¹

position	A5	B5	C5	D5	Mean	SD
1	180.77	180.99	180.92	180.64	180.83	0.16
2	44.23	44.40	44.45	44.53	44.40	0.13
3	86.69	85.01	85.21	87.08	86.00	1.04
4	79.91	80.43	80.53	81.52	80.60	0.67
5	41.78	41.81	42.31	41.63	41.88	0.30
6	115.01	115.24	115.51	115.15	115.23	0.21
7	34.41	36.93	35.60	36.27	35.80	1.08
8	29.87	30.59	29.99	30.85	30.33	0.47
9	79.33	80.39	78.62	79.79	79.53	0.75

Table S-7: ¹³C-NMR data of compounds **A6–D6**¹

position	A6	B6	C6	D6	Mean	SD
1	180.87	180.80	180.78	180.75	180.80	0.05
2	44.29	44.48	44.39	44.57	44.43	0.12
3	86.65	85.25	85.23	87.00	86.03	0.93
4	79.86	80.28	80.37	80.17	80.17	0.22
5	41.68	41.77	41.99	41.46	41.73	0.22
6	114.95	115.47	115.55	115.15	115.28	0.28
7	34.26	37.02	35.47	36.08	35.71	1.16
8	29.94	30.41	29.76	30.81	30.23	0.47
9	78.12	79.49	77.56	79.74	78.73	1.05

Table S-8: Mean of chemical shifts of different carbons in compounds **A1–D6** with the same configurations

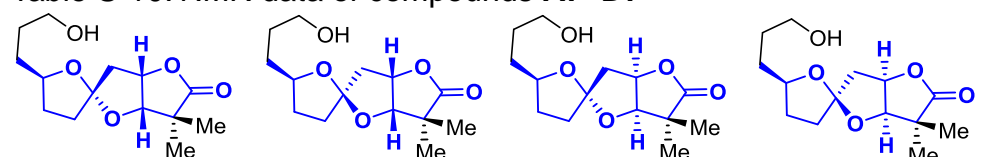
Position	A	B	C	D	SD*
1	180.93	180.94	180.87	180.77	0.078
2	44.38	44.50	44.50	44.61	0.094
3	86.67	85.09	85.24	87.06	0.996
4	79.97	80.43	80.49	80.92	0.389
5	41.77	41.83	42.29	41.62	0.289
6	115.03	115.35	115.55	115.17	0.225
7	34.40	37.04	35.62	36.27	1.118
8	30.22	30.90	30.29	31.12	0.446
9	78.39	78.03	77.73	79.47	0.760

Table S-9: SD of chemical shifts of different carbons in compounds **A1–D6** with the same configurations

Position	SD				σ
	A	B	C	D	
1	0.25	0.08	0.06	0.19	0.54
2	0.21	0.16	0.15	0.13	0.58
3	0.04	0.09	0.04	0.04	19.0
4	0.14	0.20	0.07	0.83	1.25
5	0.06	0.07	0.18	0.10	2.82
6	0.12	0.11	0.06	0.08	2.43
7	0.16	0.22	0.13	0.20	6.30
8	0.59	0.74	0.80	0.62	0.65
9	1.55	4.94	1.48	0.87	0.34

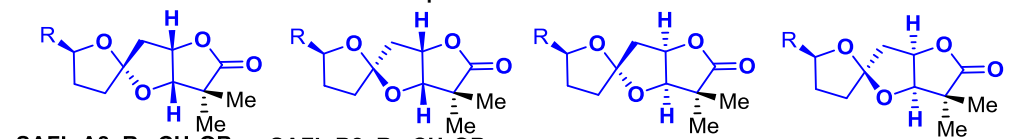
$$\sigma = SD^* / [(SD(A) + SD(B) + SD(C) + SD(D)) / 4]$$

Table S-10: NMR data of compounds **A7–D7**¹



entry	A7	B7	C7	D7
δ_5	5.10, t	5.02, ddd	5.02, ddd	5.09, t
$\Delta\delta_5$	0.32	0.13	0.14	0.32
$\Delta\delta_8$	0.60	0.19	0.52	0.28
δ_{C3}	86.66	85.24	85.33	87.03
δ_{C7}	34.32	37.03	35.58	36.23
results	✓	✓	✓	✓

Table S-11: NMR data of compounds **A8–D9**²

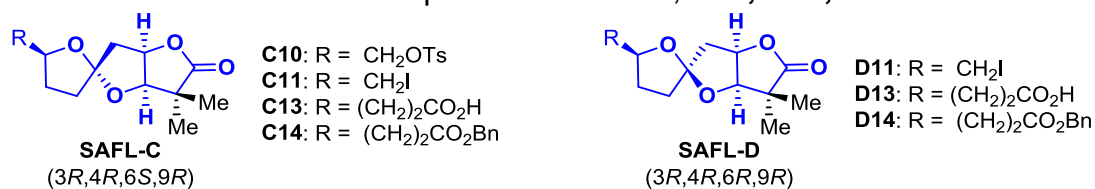


entry	A8	B8	C8	D8	A9	B9
δ_4	5.10, t	5.00, ddd	5.02, ddd	5.06, t	5.14, t	5.05, ddd
$\Delta\delta_5$	0.33	0.23	0.22	0.33	0.31	0.08
$\Delta\delta_8$	0.2~0.4	0.20	0.30	0.2*	0.1~0.2	0.1~0.2
δ_{C3}	86.9	85.1 [#] (79.0)	85.3 [#] (77.7)	87.3 [#] (79.7)	86.8	85.4 [#] (80.9)
δ_{C7}	34.2	36.1	35.2	36.0	34.5	37.2
results	✓	✓	✓	✓	CNMR rule ✓	CNMR rule ✓

* wrong assignment of H8; [#] wrong assignment of C3 or C7

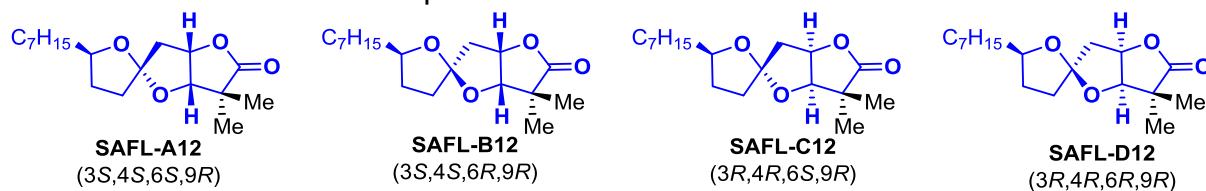
² Finch, O. C.; Furkert, D. P.; Brimble, M. A. *Tetrahedron* **2014**, *70*, 590.

Table S-12: NMR data of compounds **C10–C14**, **D11**, **D13**, **D14**³



entry	C10	C11	C13	C14	D11	D13	D14
δ ₄	4.99 (ddd)	5.05 (ddd)	5.03 (ddd)	5.01 (ddd)	5.07 (t)	5.08 (t)	5.09 (t)
Δδ ₅	0.15	0.21	0.13	0.15	0.34	0.32	0.31
Δδ ₈	0.54	0.55	0.53	0.57	0.32	0.32	0.31
δ _{C3}	85.57	85.61	85.37	85.30	87.63	86.90	87.16
δ _{C7}	35.04	35.47	35.62	35.59	36.55	36.12	36.31
results	✓	✓	✓	✓	✓	✓	✓

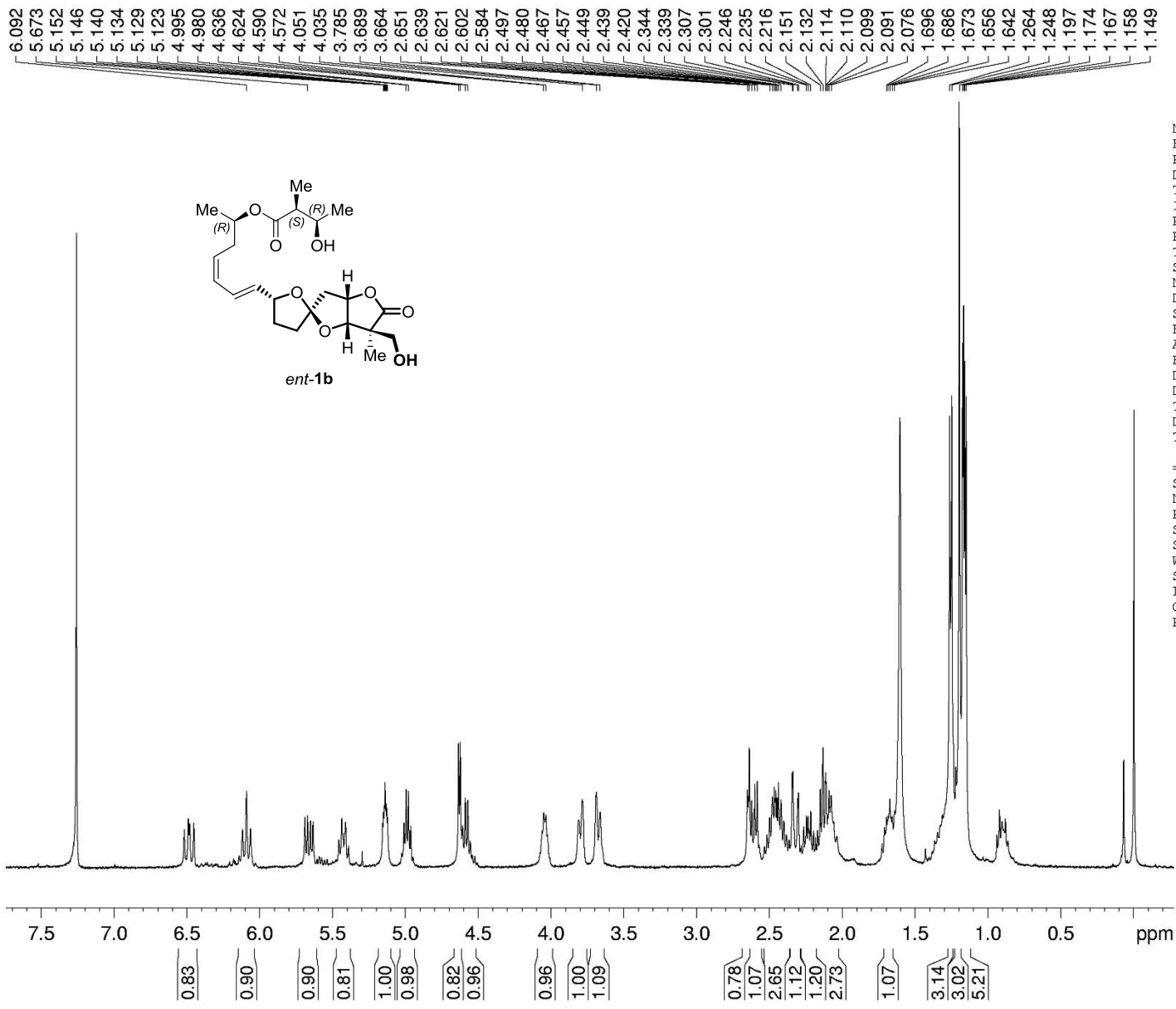
Table S-13: NMR data of compounds **A12–D12**⁴



entry	C12 ^{3a}	D12 ^{3a}	C12 ^{3b}	D12 ^{3b}	A12 ^{4a, 4b}	B12 ^{4a, 4b}	C12 ^{4a, 4b}	D12 ^{4a, 4b}
δ ₄	5.03 (ddd)	5.08 (t)	5.03 (ddd)	5.07 (t)	5.10 (t)	5.02 (ddd)	5.03 (ddd)	5.07 (t)
Δδ ₅	0.15	0.32	0.15	0.31	0.32	0.15	0.16	0.32
Δδ ₈	0.62	0.33	0.61	0.32	0.63	0.21	0.61	0.32
δ _{C3}	85.17	87.07	85.21	87.05	86.72	84.97	85.22	87.10
δ _{C7}	35.65	36.31	35.68	37.38	34.59	37.20	35.70	36.34
results	✓	✓	✓	✓	✓	✓	✓	✓

³ (a) Fernandes, R. A.; Halle, M. B. *Asian J. Org. Chem.* **2013**, 2, 593. (b) Li, J.; Zhao, C.; Liu, J.; Du, Y. *Tetrahedron* **2015**, 71, 3885.

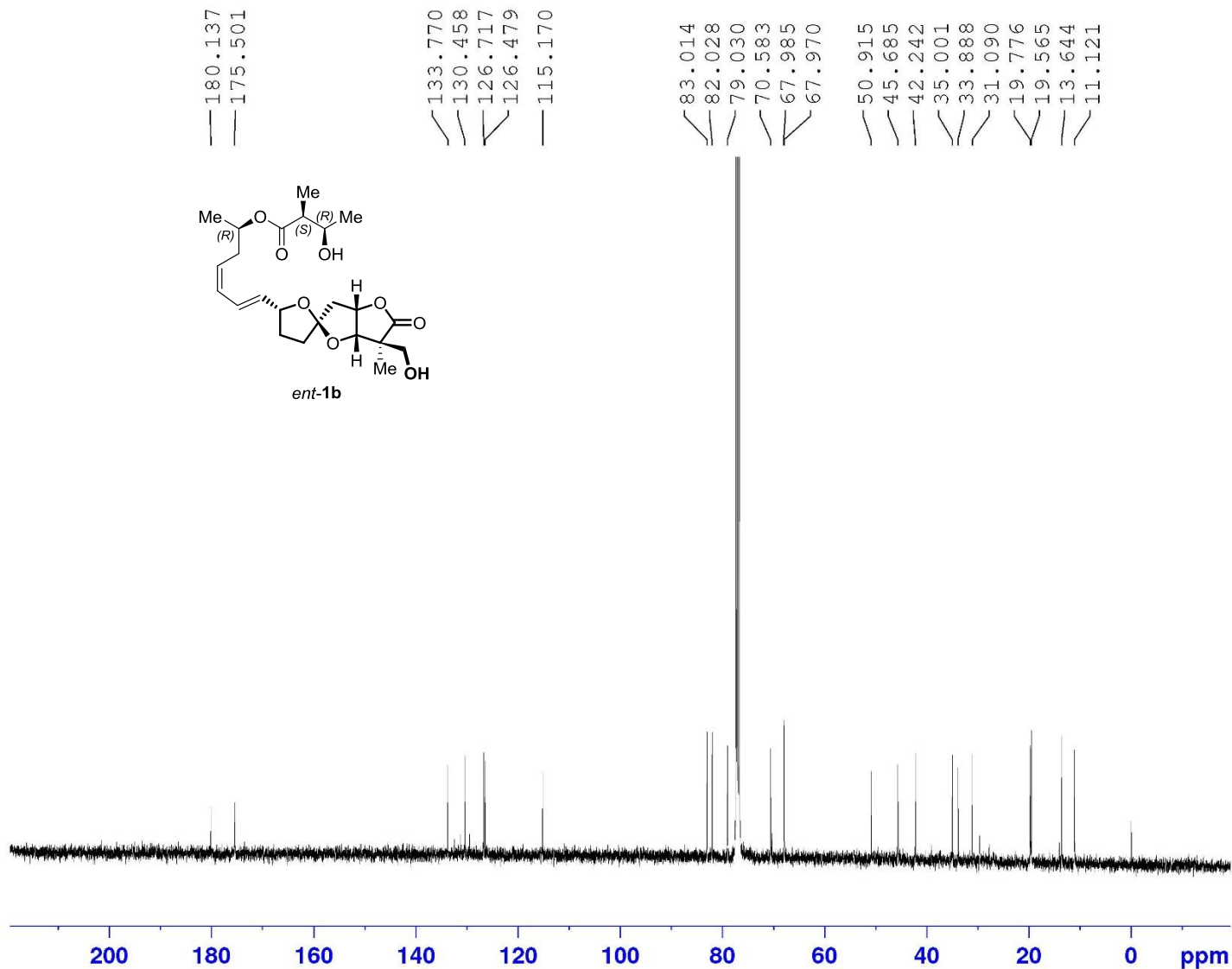
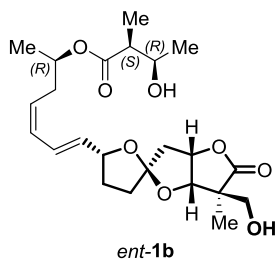
⁴ (a) Tlais, S. F.; Dudley, G. B. *Beistein J. Org. Chem.* **2012**, 8, 1287. (b) Tlais, S. F.; Dudley, G. B. *Org. Lett.* **2010**, 12, 4698. For samples of Fernandes, R. A. and Du, Y. see 3a and 3b respectively.



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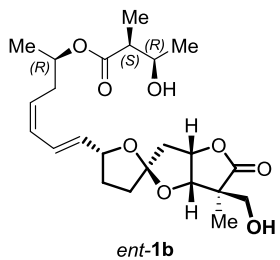
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SI        1024
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