

Supplementary Information

Divergent Chiron Approach for the First Total Synthesis of (+)-Pseudonocardide A, (+)-Pseudonocardide C and an epimer of *ent*-Pseudonocardide D

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Table 1: Comparison of ^1H NMR and ^{13}C NMR data of natural (–)-Pseudonocardide A **1** and synthetic (+)-Pseudonocardide A *ent*-**1** in CDCl_3

Pseudonocardide A				
<i>pos.</i>	Reported ⁶ NMR data for (–)- 1 in CDCl_3		Synthetic NMR data for (+)- 1 in CDCl_3	
	δ_{H} , mult. (<i>J</i> in Hz)	δ_{C}	δ_{H} , mult. (<i>J</i> in Hz)	δ_{C}
1	–	176.9	–	176.6
2	2.62–2.56 (m, 1H), 2.53 (dd, <i>J</i> = 17.8, 8.8 Hz, 1H)	27.8	2.62–2.56 (m, 1H), 2.52 (dd, <i>J</i> = 18.0, 9.0 Hz, 1H)	27.7
3	2.38–2.33 (m, 1H), 2.31–2.26 (m, 1H)	22.1	2.38–2.33 (m, 1H), 2.31–2.26 (m, 1H)	22.2
4	4.61 (q, <i>J</i> = 6.9 Hz, 1H)	79.4	4.60 (q, 6.5 Hz, 1H)	79.3
5	3.87 (t, <i>J</i> = 5.2, 5 Hz, 1H)	73.6	3.88–3.85 (m, 1H),	73.6
6	4.58 (dd, <i>J</i> = 9.0, 5.3)	67.5	4.60–4.56 (m, 1H),	67.5
7	5.50 (t, <i>J</i> = 10.1 Hz, 1H)	126.0	5.49 (t, <i>J</i> = 10.5 Hz, 1H)	126.0
8	5.74 (dt, <i>J</i> = 10.8, 7.5 Hz, 1H)	135.9	5.73 (dt, <i>J</i> = 10.5, 7.5 Hz, 1H)	136.0
9	2.19 (q, <i>J</i> = 7.2 Hz, 1H), 2.12 (dd, <i>J</i> = 14.4, 6.9 Hz, 1H)	27.3	2.17 (q, <i>J</i> = 7.5 Hz, 1H), 2.11 (dd, <i>J</i> = 14.5, 7.5 Hz, 1H)	27.3
10	1.38–1.35 (m, 2H)	28.3	1.38–1.35 (m, 2H)	28.3
11	1.32–1.25 (m, 2H)	28.8	1.32–1.24 (m, 2H)	28.8
12	1.32–1.25 (m, 2H)	31.0	1.32–1.24 (m, 2H)	31.0
13	1.32–1.25 (m, 2H)	21.9	1.32–1.24 (m, 2H)	21.9
14	0.89 (t, <i>J</i> = 6.8 Hz, 3H)	13.4	0.88 (t, <i>J</i> = 7.0 Hz, 3H)	13.4

Table 2: Comparison of ^1H NMR and ^{13}C NMR data of natural (–)-Pseudonocardide C **3** and synthetic (+)-Pseudonocardide C *ent*-**3** in CDCl_3 .

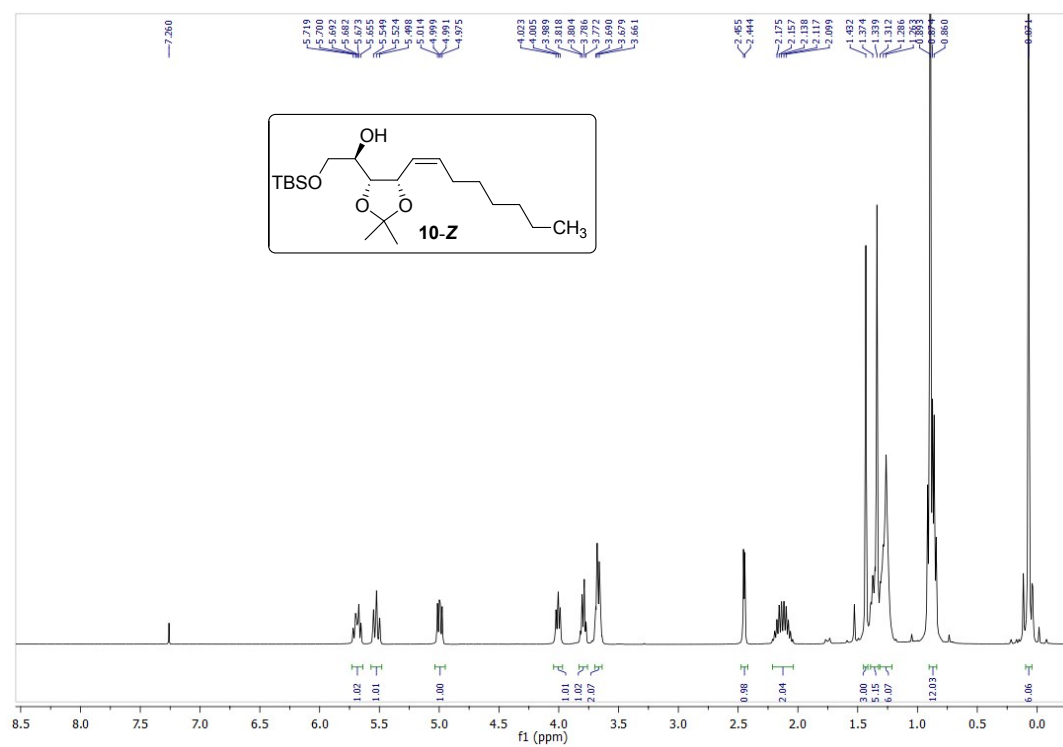
Pseudonocardide C				
<i>pos.</i>	Reported ⁶ NMR data for (–)- 3 in CDCl_3		Synthetic NMR data for (+)- 3 in CDCl_3	
	δ_{H} , mult. (<i>J</i> in Hz)	δ_{C}	δ_{H} , mult. (<i>J</i> in Hz)	δ_{C}
1	–	174.6	–	174.5
2	2.91 (dd, <i>J</i> = 17.6, 7.8 Hz, 1H), 2.67 (dd, <i>J</i> = 17.6, 8.1 Hz, 1H)	37.1	2.90 (dd, <i>J</i> = 17.6, 8.0 Hz, 1H), 2.63 (dd, <i>J</i> = 17.6, 8.0 Hz, 1H)	37.1
3	4.75 (q, <i>J</i> = 6.7 Hz, 2H)	67.0	4.74 (q, <i>J</i> = 6.8 Hz, 1H)	67.1
4	4.35 (brs, 1H)	85.7	4.35 (dd, <i>J</i> = 5.6, 3.6 Hz, 1H)	85.7
5	3.94 (d, <i>J</i> = 2.2 Hz, 1H)	72.8	3.93 (brs, 1H)	72.9
6	4.79–4.78 (m, 1H)	69.5	4.77 (dd, <i>J</i> = 8.8, 3.6 Hz, 1H)	69.5
7	5.46 (t, <i>J</i> = 10.0 Hz, 1H)	126.0	5.46 (t, <i>J</i> = 10.4 Hz, 1H)	126.1
8	5.71 (q, <i>J</i> = 8.4 Hz, 1H)	136.3	5.71 (dt, <i>J</i> = 10.4, 7.2 Hz, 1H)	136.4
9	2.16–2.12 (m, 1H), 2.10–2.06 (m, 1H)	28.2	2.17–2.13 (m, 1H), 2.10–2.05 (m, 1H)	28.2
10	1.39–1.36 (m, 2H)	29.6	1.39–1.36 (m, 2H)	29.6
11	1.30–1.24 (m, 2H)	29.1	1.30–1.24 (m, 2H)	29.1
12	1.30–1.24 (m, 2H)	31.8	1.30–1.24 (m, 2H)	31.8
13	1.30–1.24 (m, 2H)	22.7	1.30–1.24 (m, 2H)	22.7
14	0.89 (t, <i>J</i> = 6.8 Hz, 3H)	14.2	0.89 (t, <i>J</i> = 6.8 Hz, 3H)	14.2

Table 3: ¹H NMR data of natural Pseudonocardide D **4** and ¹H NMR and ¹³C NMR synthetic epimer of Pseudonocardide D [*3-epi-ent-4*] in CDCl₃

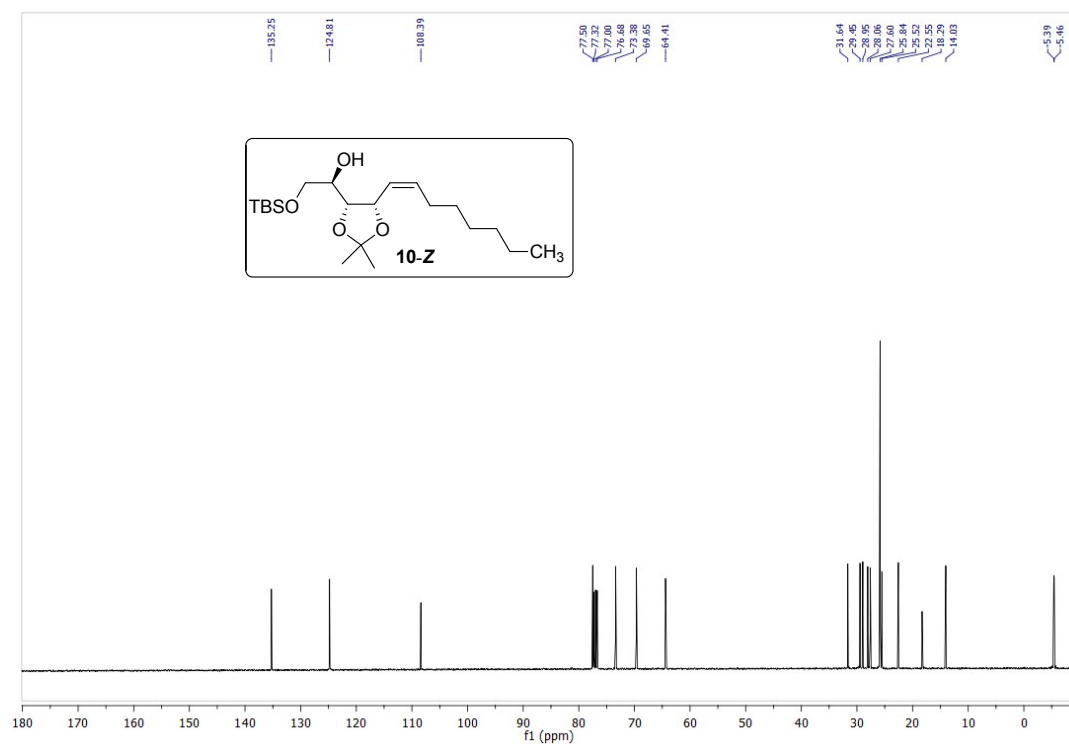
Pseudonocardide D				
<i>pos.</i>	Reported ⁶ NMR data for 4 in CDCl ₃		Synthetic NMR data for <i>3-epi-ent-4</i>	
	δ _H , mult. (<i>J</i> in Hz)	δ _C *	δ _H , mult. (<i>J</i> in Hz)	δ _C
1	–	–	–	175.2
2	2.66 (dd, <i>J</i> = 17.5, 7.9 Hz, 1H), 2.91 (dd, <i>J</i> = 17.6, 7.8 Hz, 1H)	–	2.86 (dd, <i>J</i> = 18.8, 6.8 Hz, 1H), 2.73 (dd, <i>J</i> = 18.8, 0.8 Hz, 1H)	37.0
3	4.75 (q, <i>J</i> = 7.5 Hz, 1H)	–	4.91–4.85 (m, 1H)	75.2
4	4.78 (dd, <i>J</i> = 8.3, 3.4 Hz, 1H)	–	4.99 (t, <i>J</i> = 4.8 Hz, 1H)	82.8
5	3.93 (t, <i>J</i> = 6.0 Hz, 1H)	–	3.94 (ddd, <i>J</i> = 10.0, 9.2, 4.8 Hz, 1H)	77.2
6	4.35 (t, <i>J</i> = 4.9 Hz, 1H)	–	4.44 (t, <i>J</i> = 8.4 Hz, 1H)	76.2
7	5.47 (t, <i>J</i> = 9.8 Hz, 1H)	–	5.37–5.27 (m, 1H)	125.3
8	5.72 (dt, <i>J</i> = 10.8, 7.7 Hz, 1H)	–	5.79 (dt, <i>J</i> = 10.8, 7.6 Hz, 1H)	137.9
9	2.16 (q, <i>J</i> = 7.2 Hz, 1H), 2.10 (q, <i>J</i> = 7.1 Hz, 1H)	–	2.15–2.07 (m, 2H)	28.1
10	1.39–1.36 (m, 2H)	–	1.40–1.33 (m, 2H)	29.7
11	1.32–1.25 (m, 2H)	–	1.30–1.24 (m, 2H)	28.9
12	1.32–1.25 (m, 2H)	–	1.30–1.24 (m, 2H)	31.7
13	1.32–1.25 (m, 2H)	–	1.30–1.24 (m, 2H)	22.6
14	0.89 (t, <i>J</i> = 5.6 Hz, 3H)	–	0.88 (t, <i>J</i> = 7.2 Hz, 3H)	14.0

*¹³C-NMR of natural Pseudonocardide D **4** is not reported.

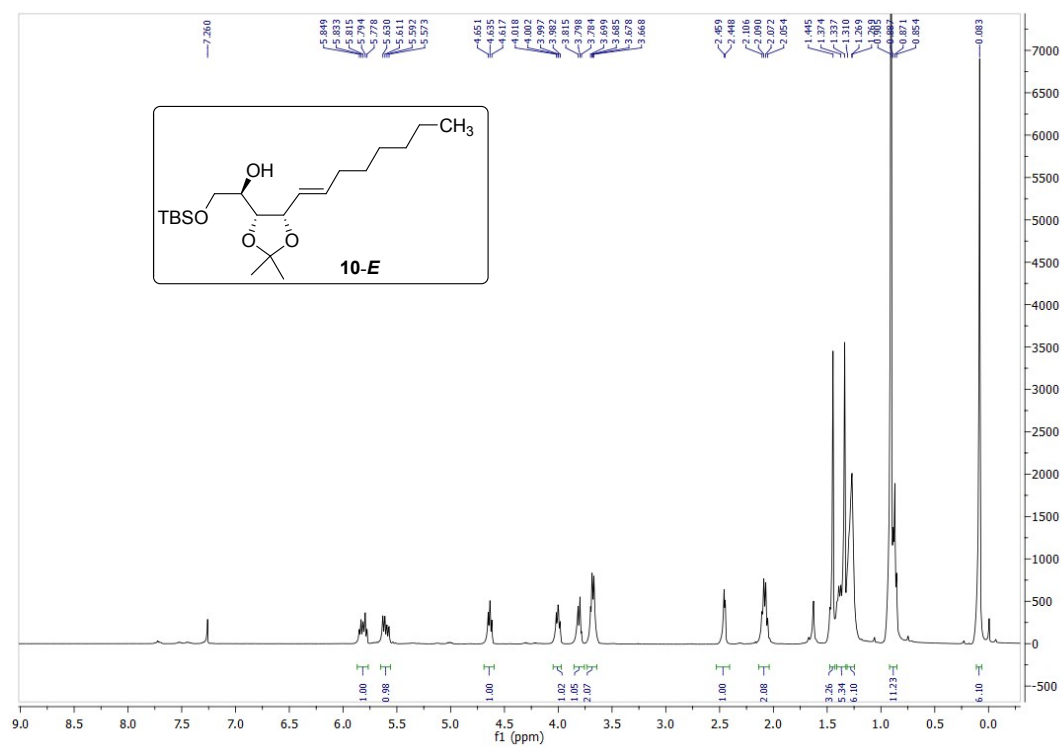
^1H NMR of compound **10-Z** (400 MHz) in CDCl_3



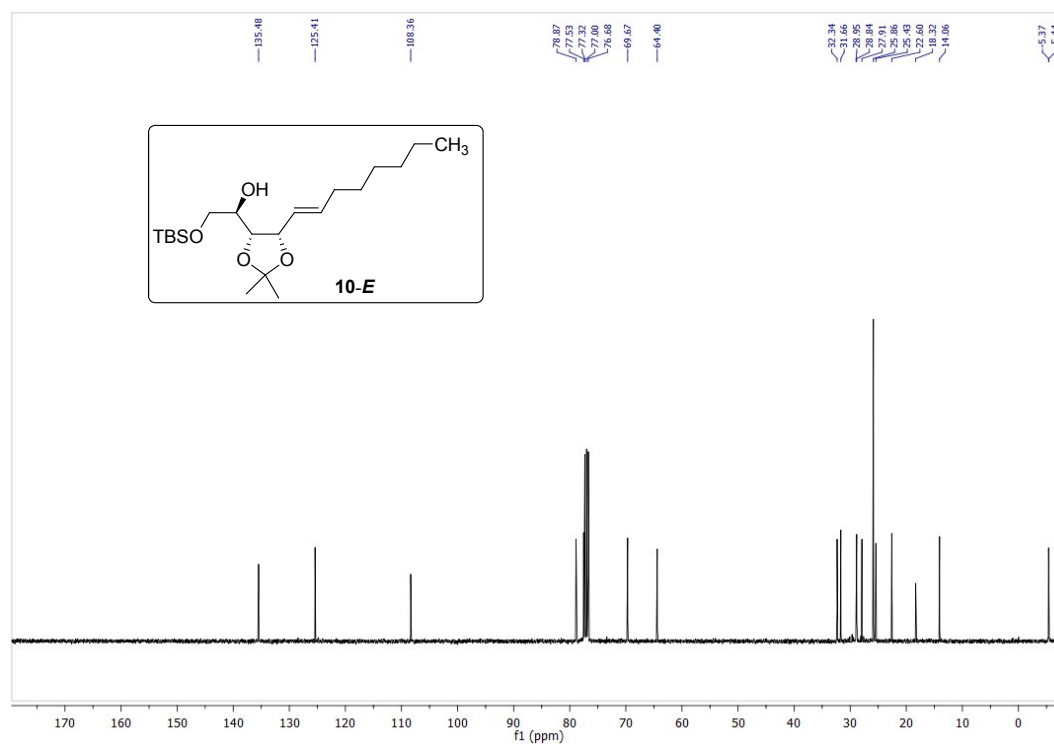
^{13}C NMR of compound **10-Z** (100 MHz) in CDCl_3



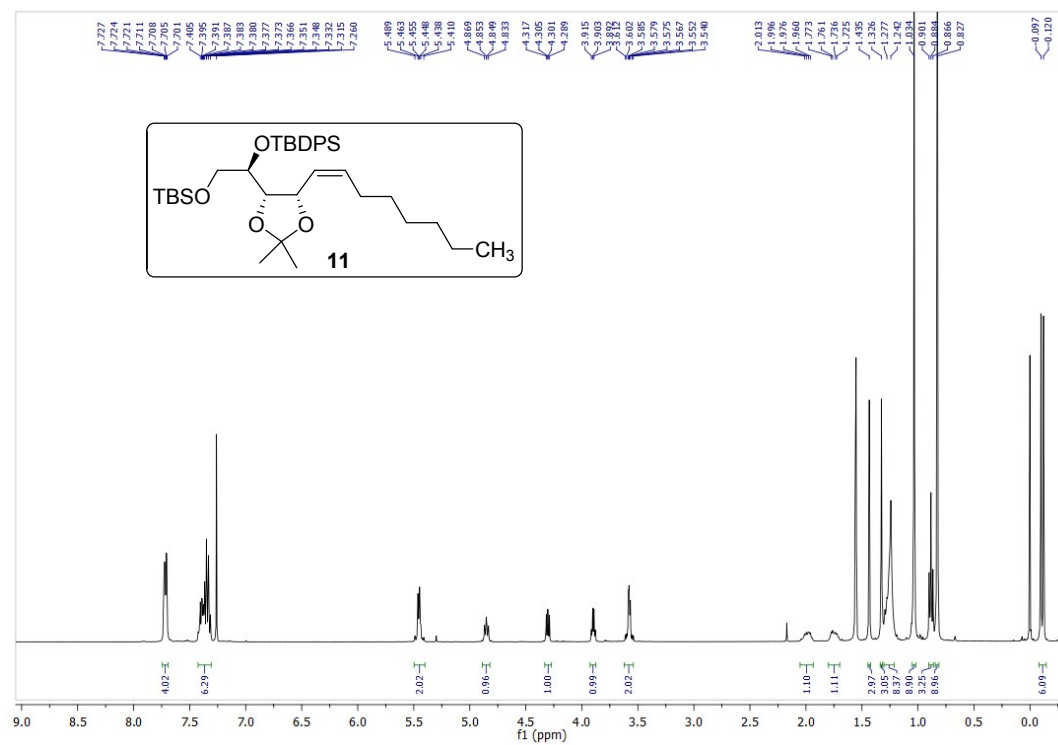
^1H NMR of compound **10-E** (400 MHz) in CDCl_3



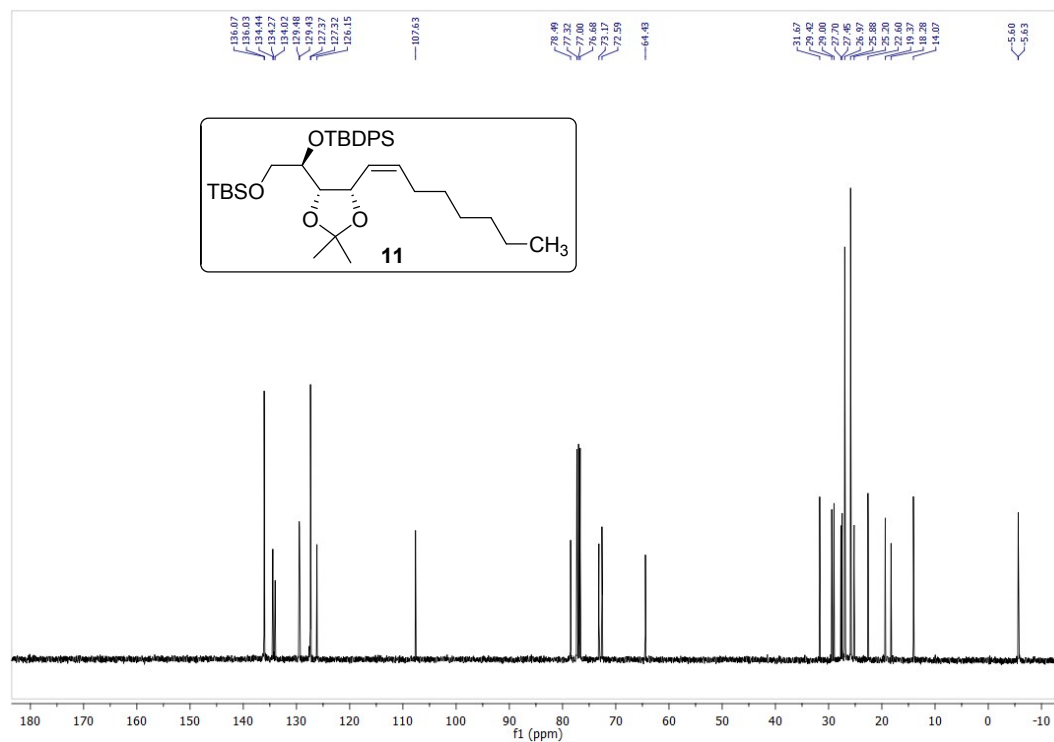
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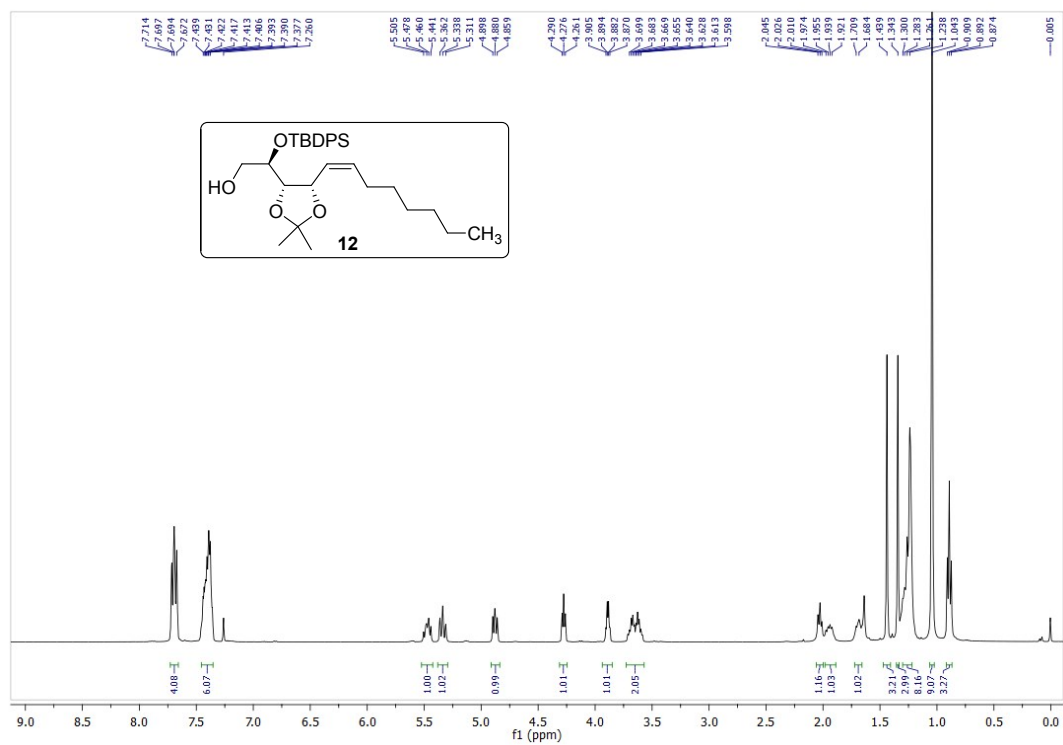
^1H NMR of compound **11** (400 MHz) in CDCl_3



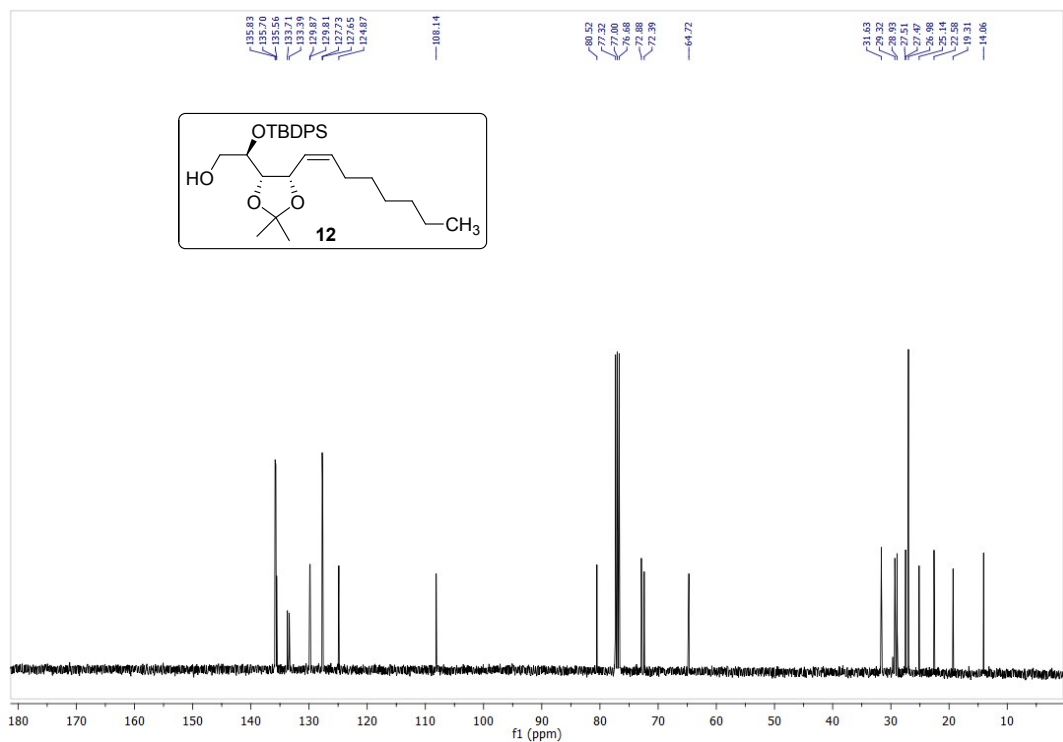
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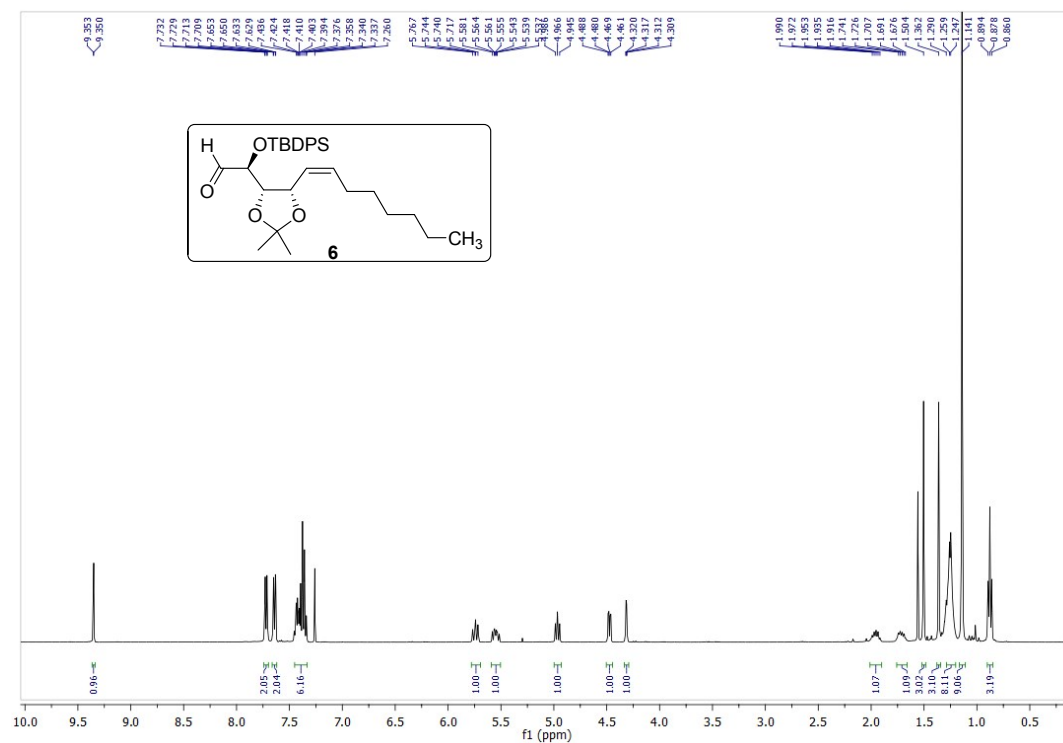
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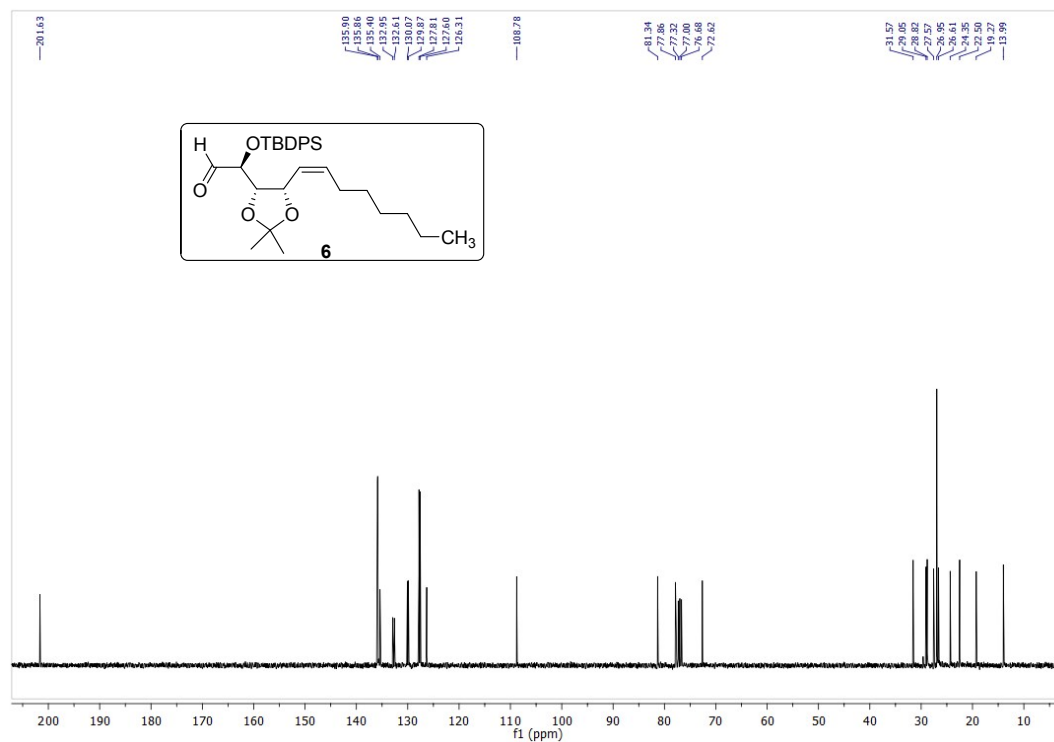
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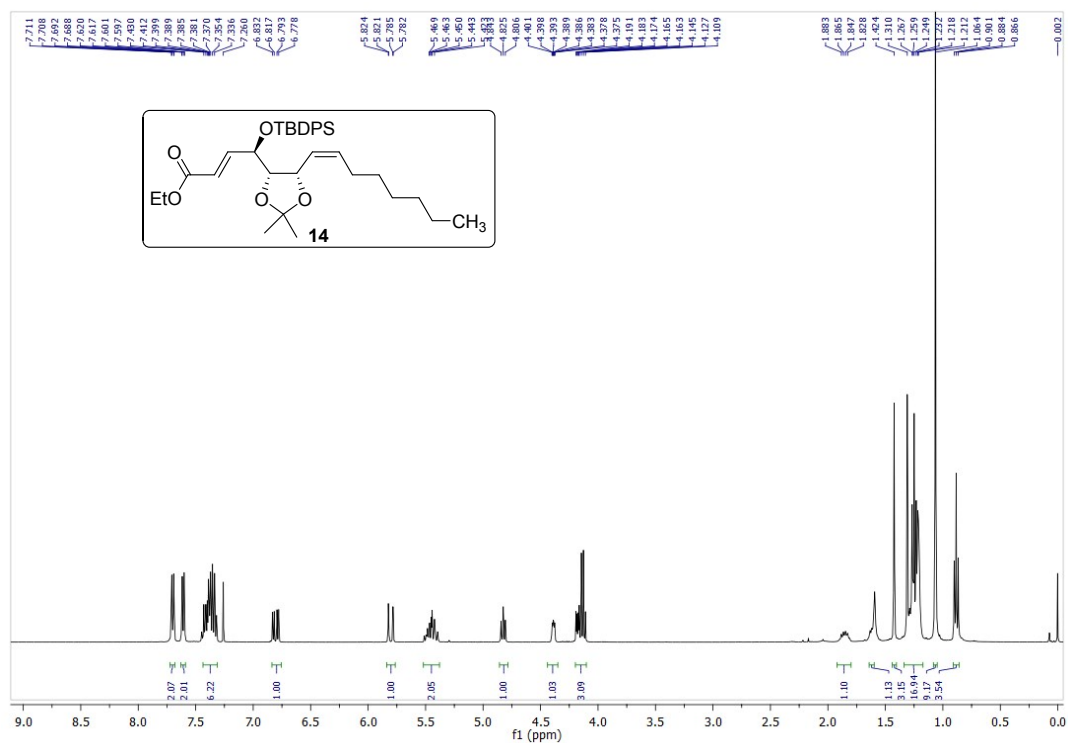
^1H NMR of compound **6** (400 MHz) in CDCl_3



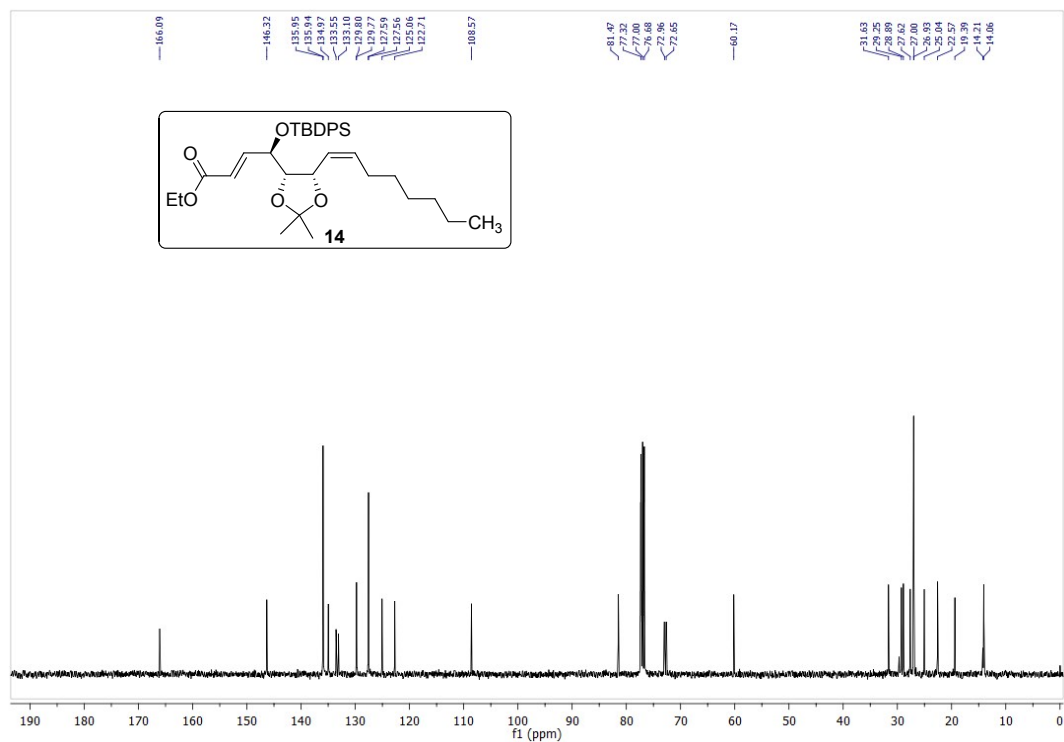
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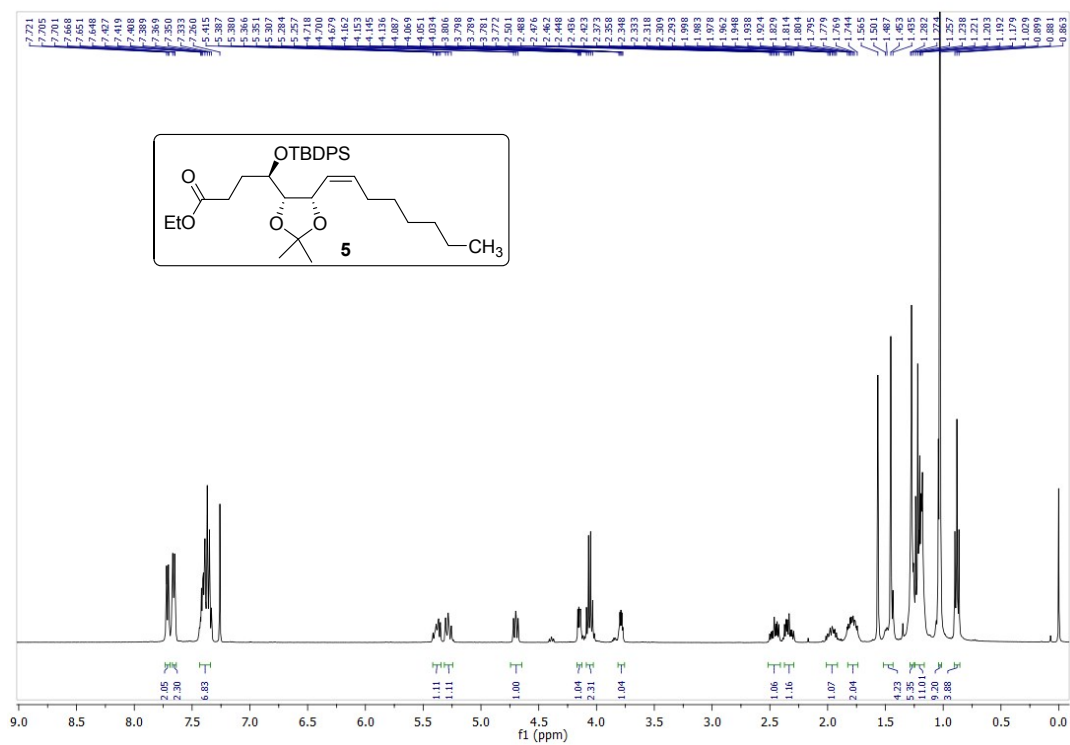
^1H NMR of compound **14** (400 MHz) in CDCl_3



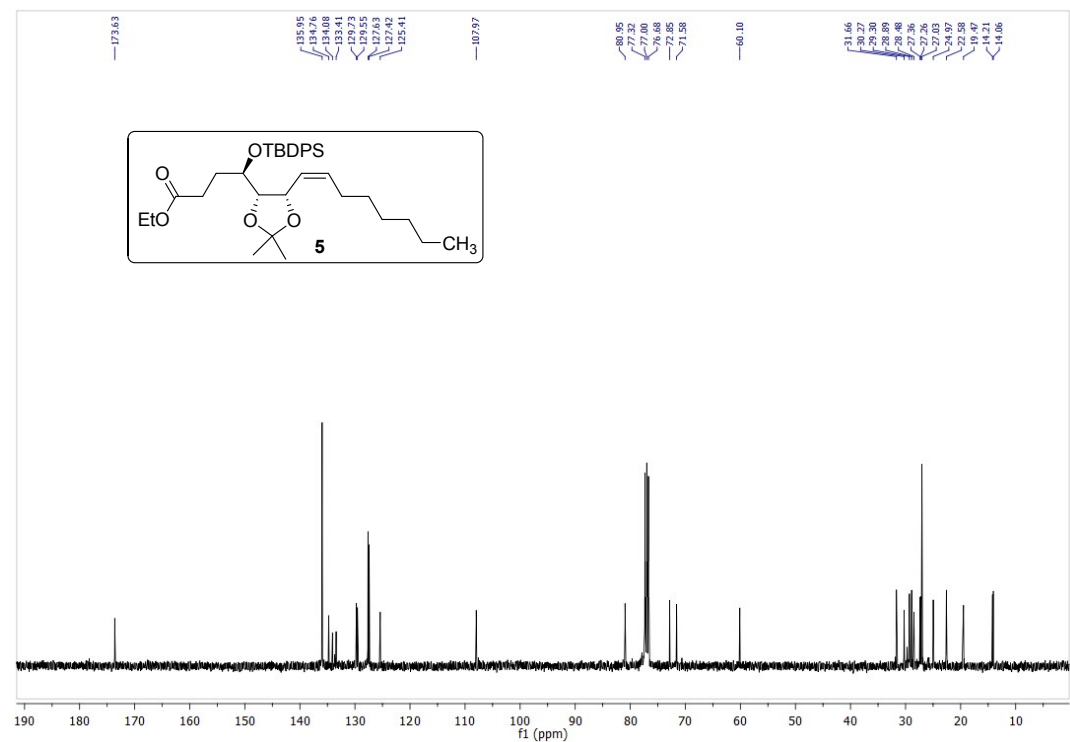
^{13}C NMR of compound **14** (100 MHz) in CDCl_3



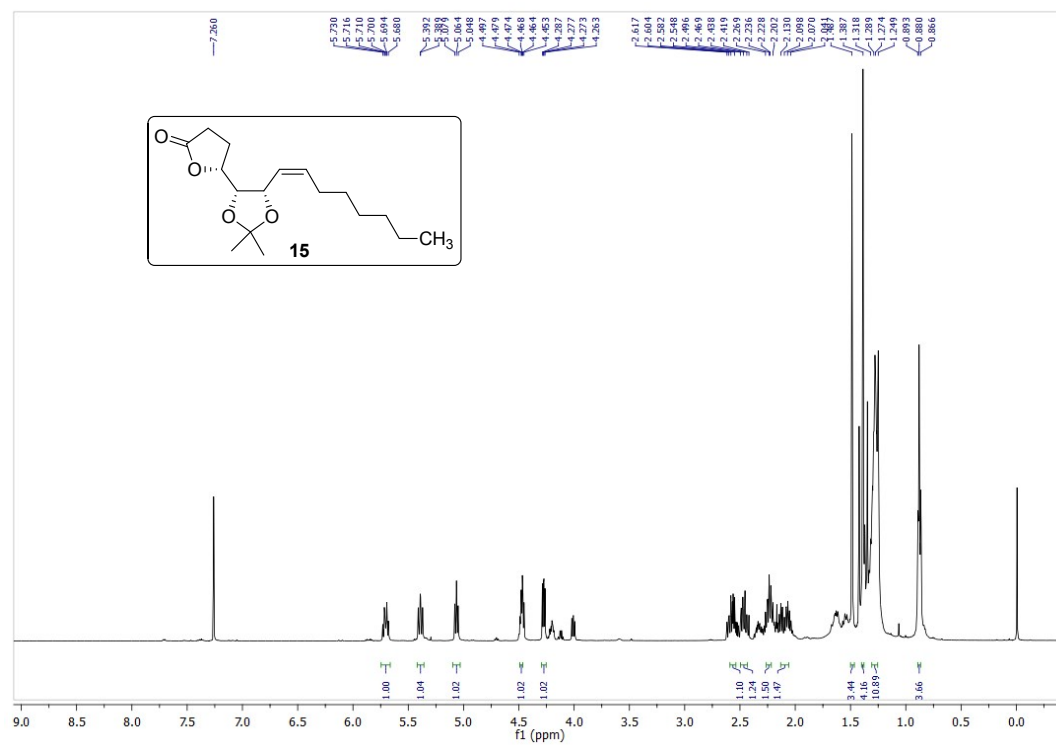
^1H NMR of compound **5** (400 MHz) in CDCl_3



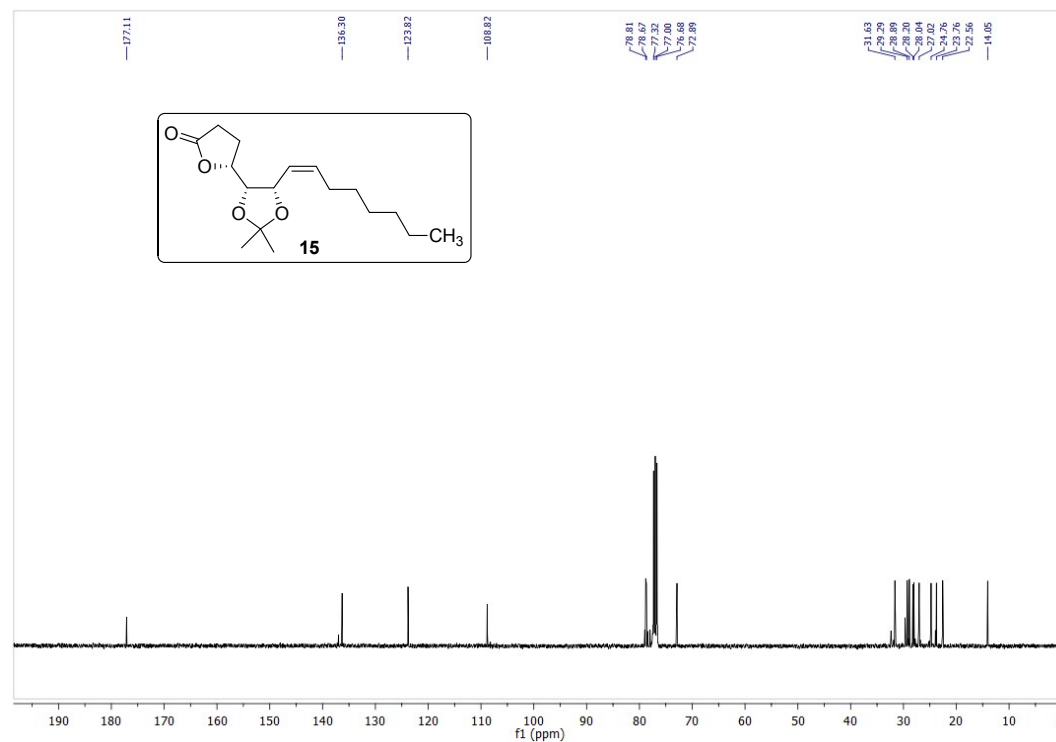
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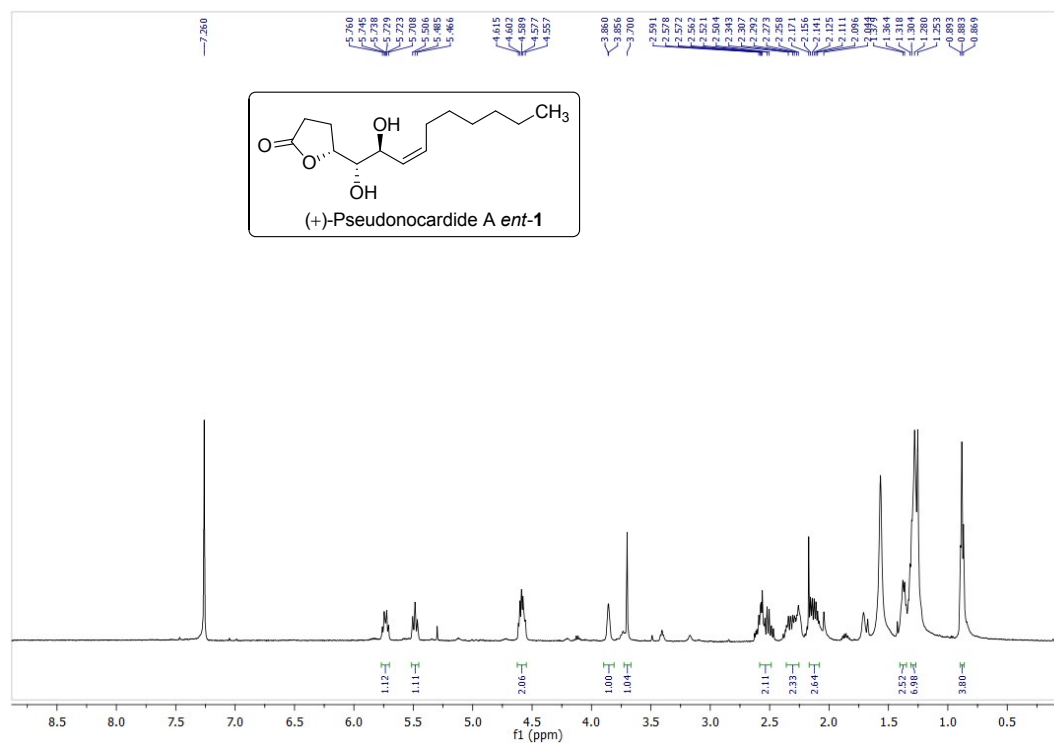
^1H NMR of compound **15** (500 MHz) in CDCl_3



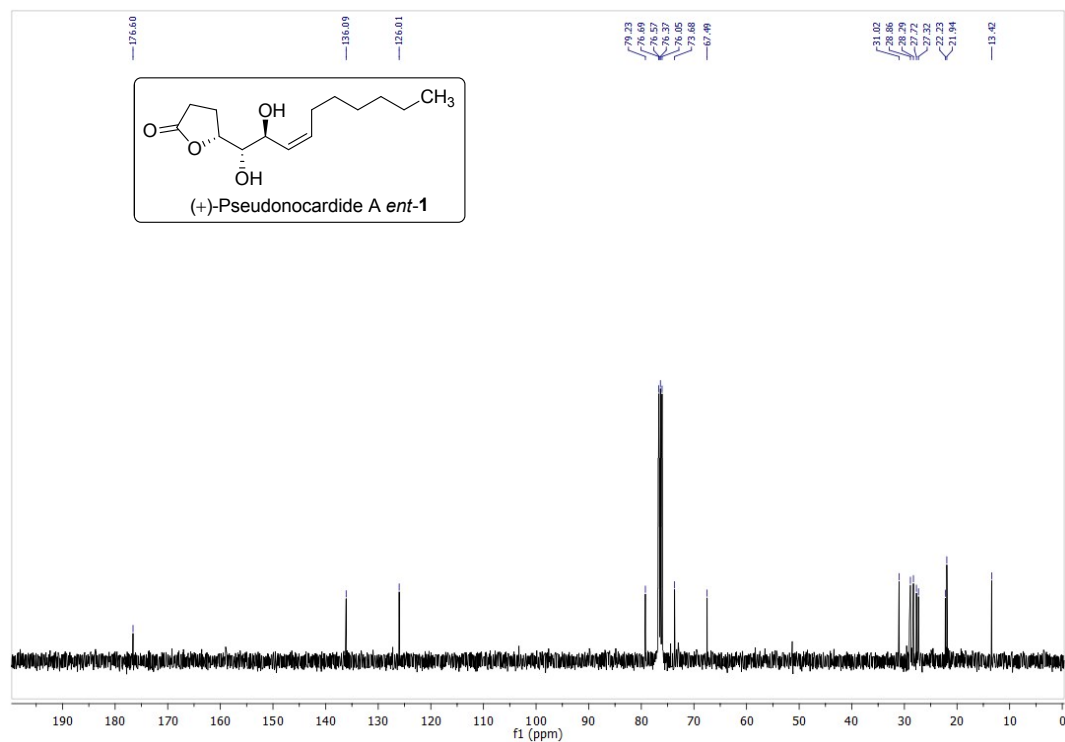
^{13}C NMR of compound **15** (100 MHz) in CDCl_3



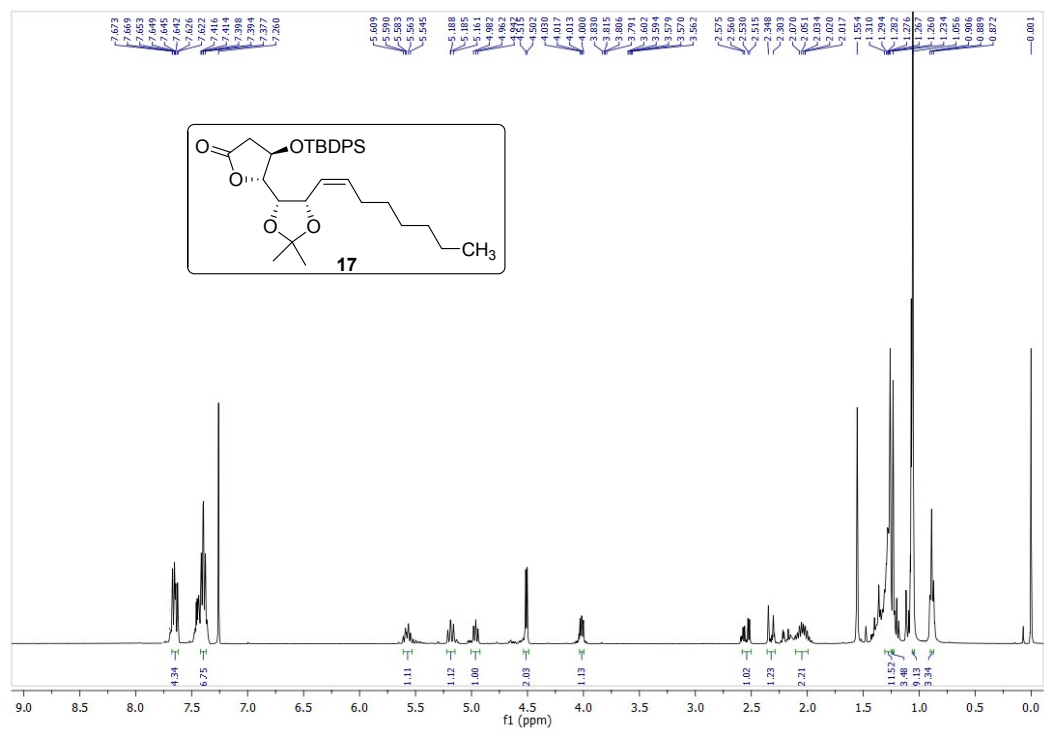
^1H NMR of (+)-Pseudonocardide A *ent*-1 (500 MHz) in CDCl_3



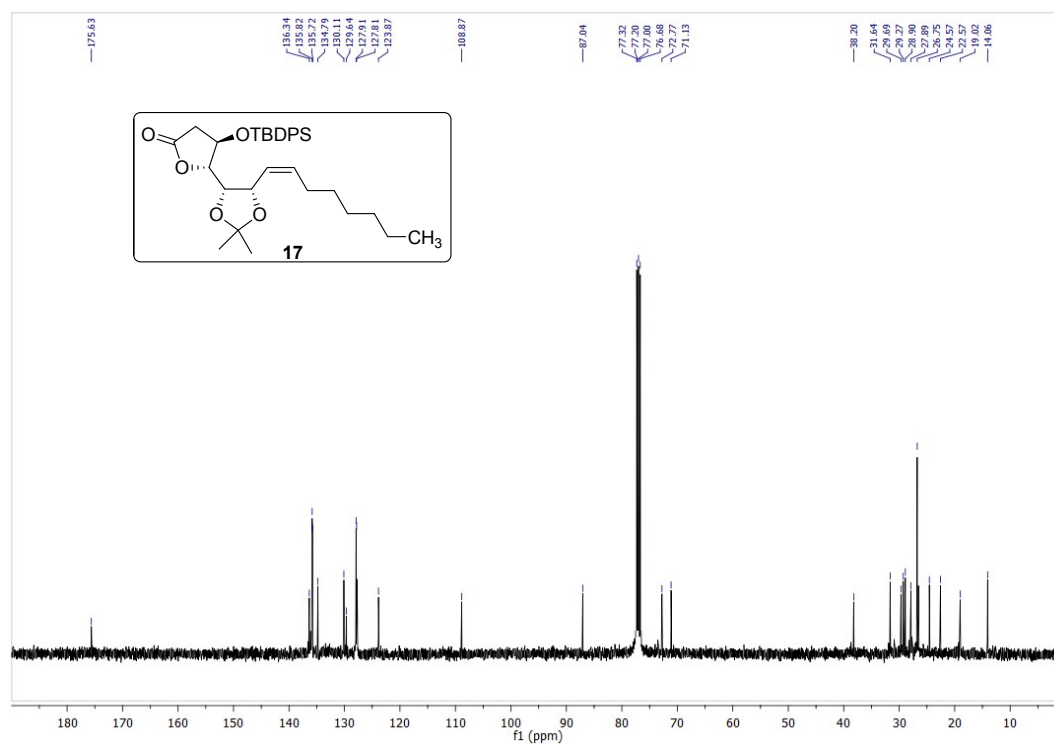
^{13}C NMR of (+)-Pseudonocardide A *ent*-1 (100 MHz) in CDCl_3



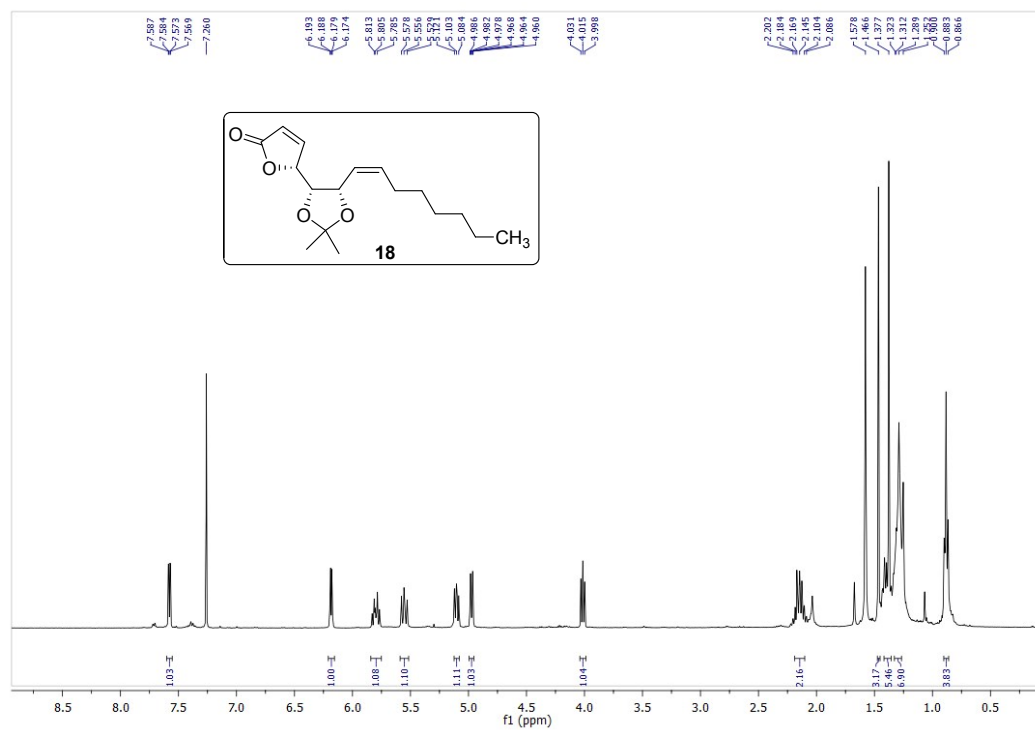
^1H NMR of compound **17** (400 MHz) in CDCl_3



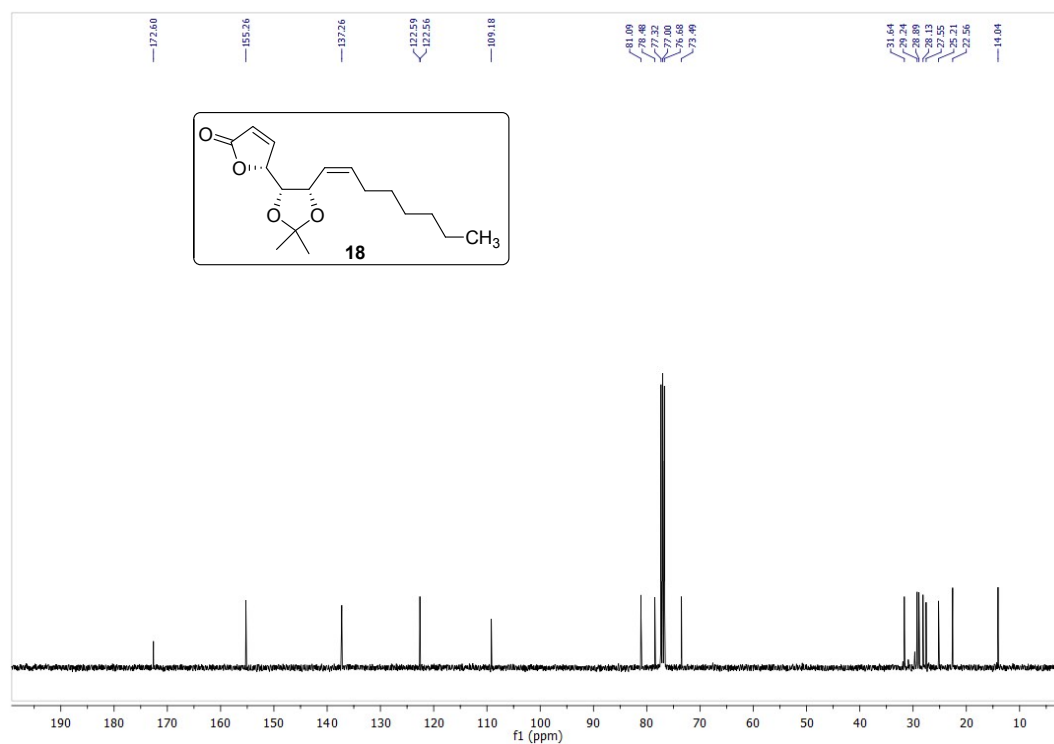
^{13}C NMR of compound **17** (100 MHz) in CDCl_3



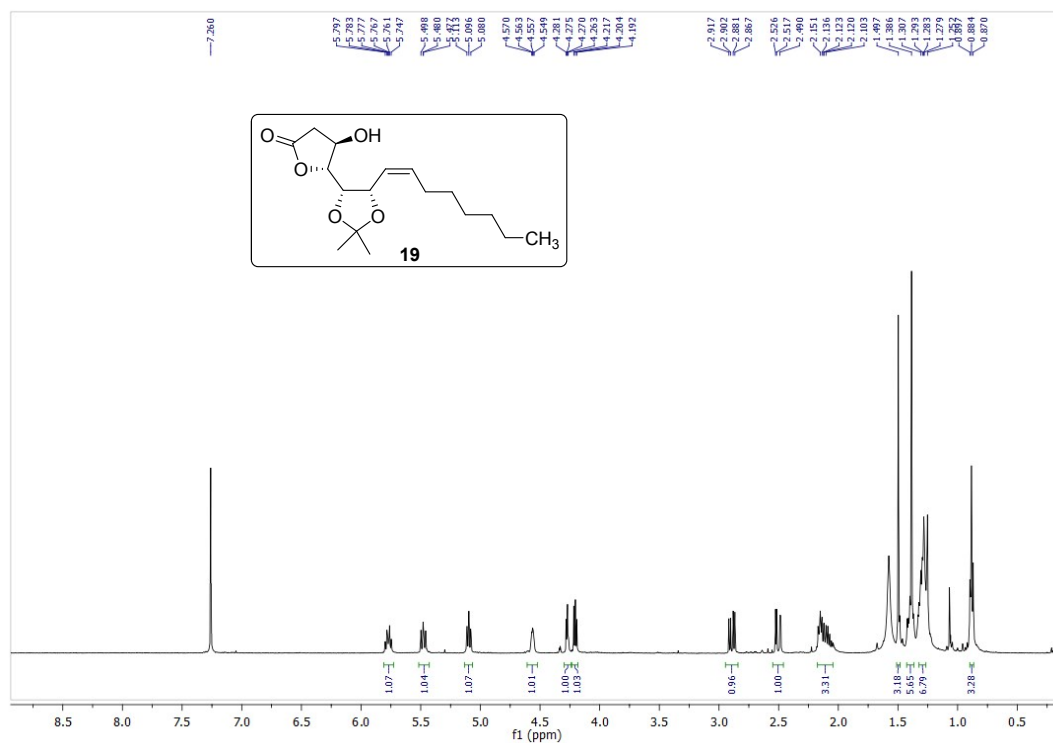
^1H NMR of compound **18** (400 MHz) in CDCl_3



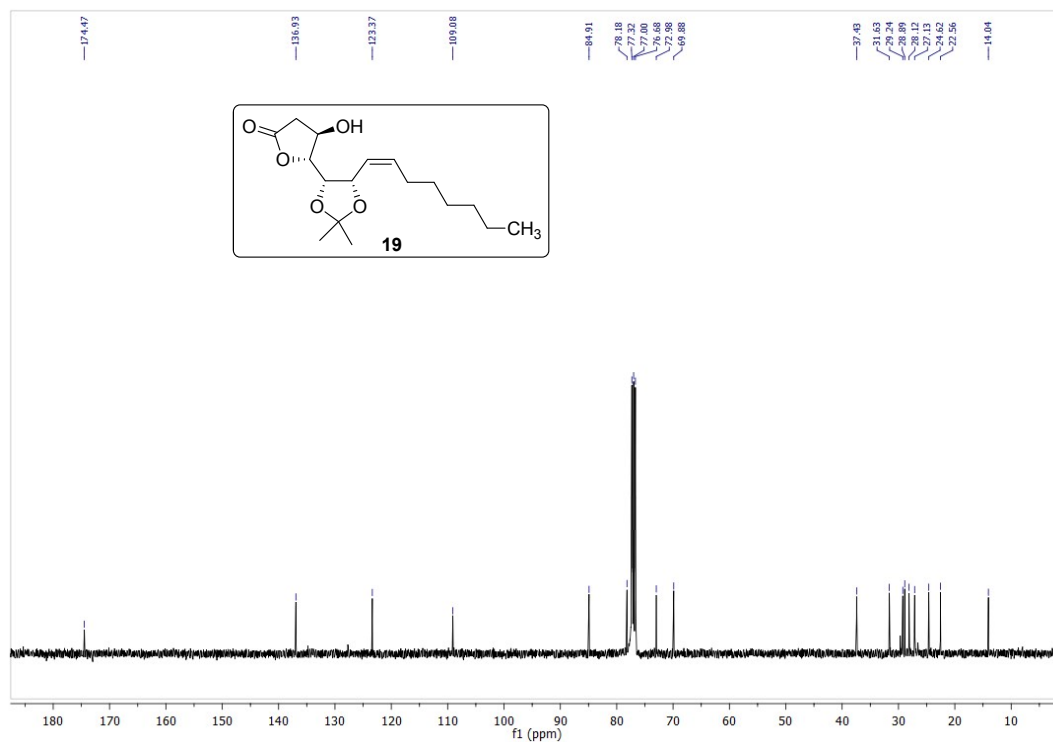
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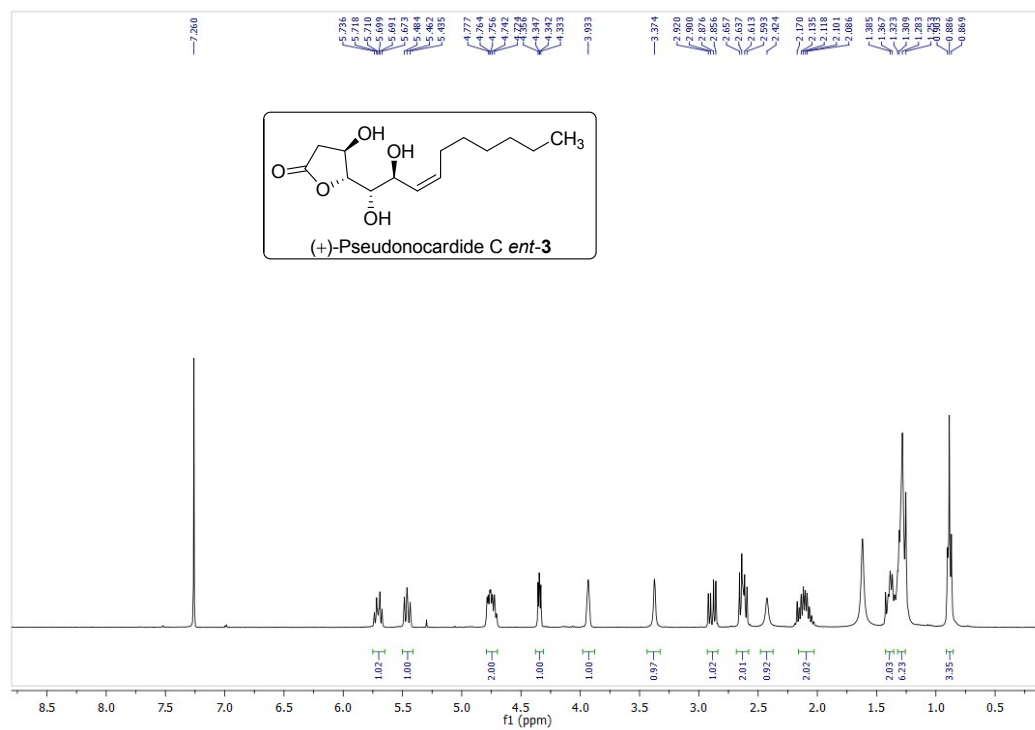
^1H NMR of compound **19** (500 MHz) in CDCl_3



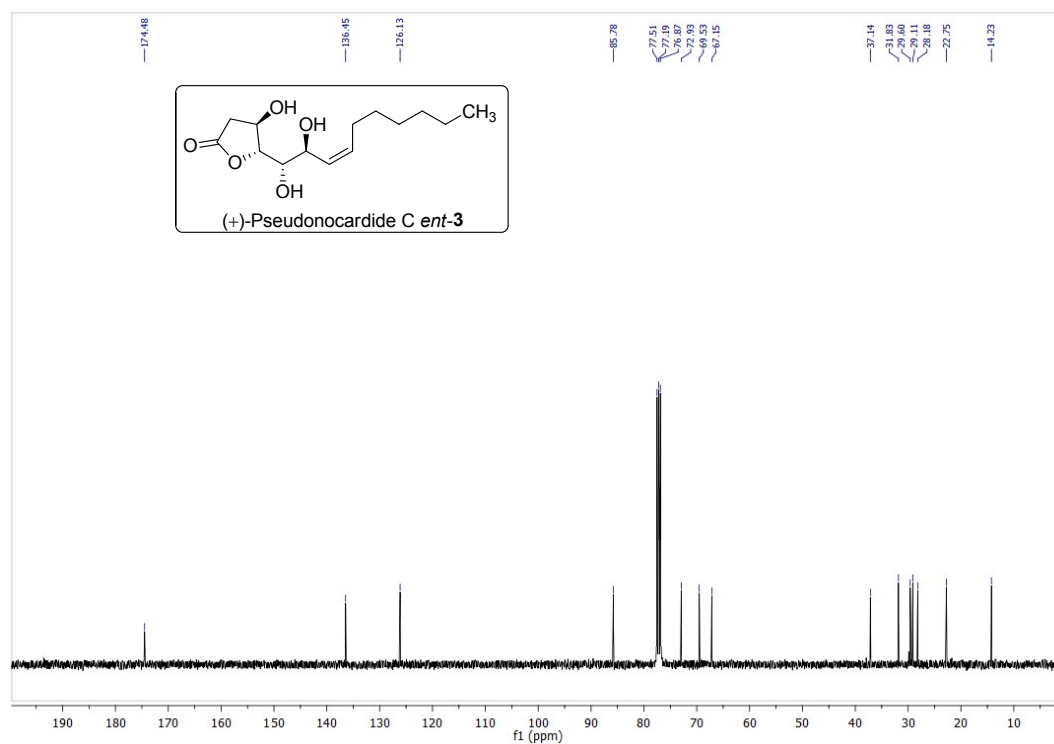
^{13}C NMR of compound **19** (100 MHz) in CDCl_3



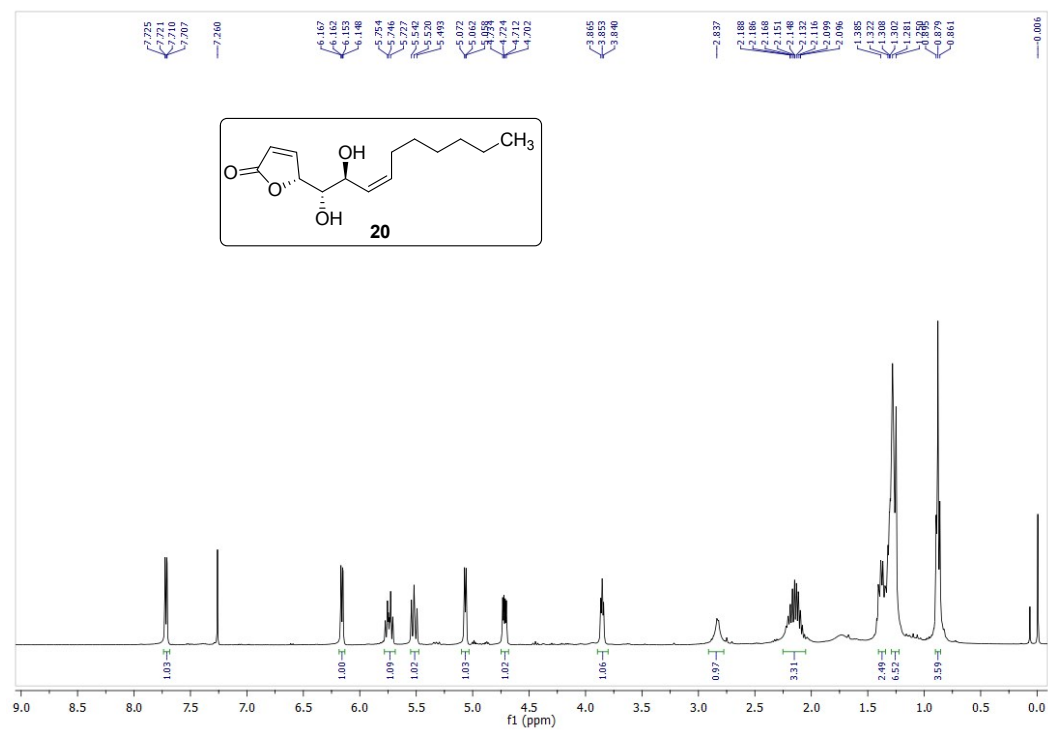
^1H NMR of (+)-Pseudonocardide C *ent*-3 (400 MHz) in CDCl_3



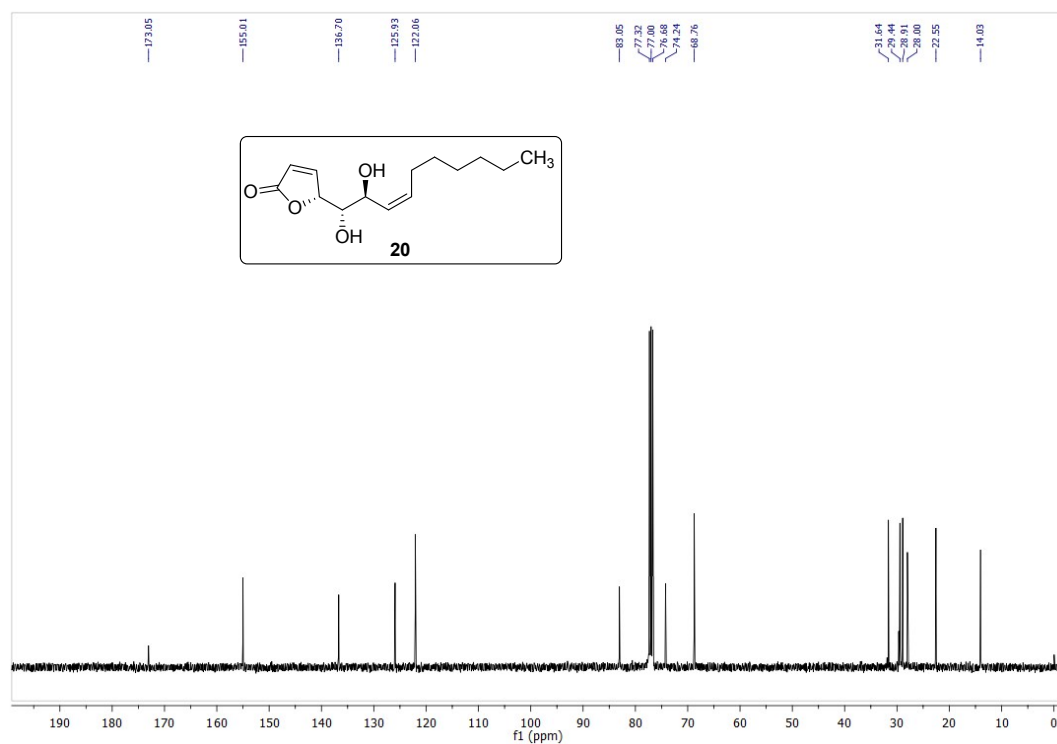
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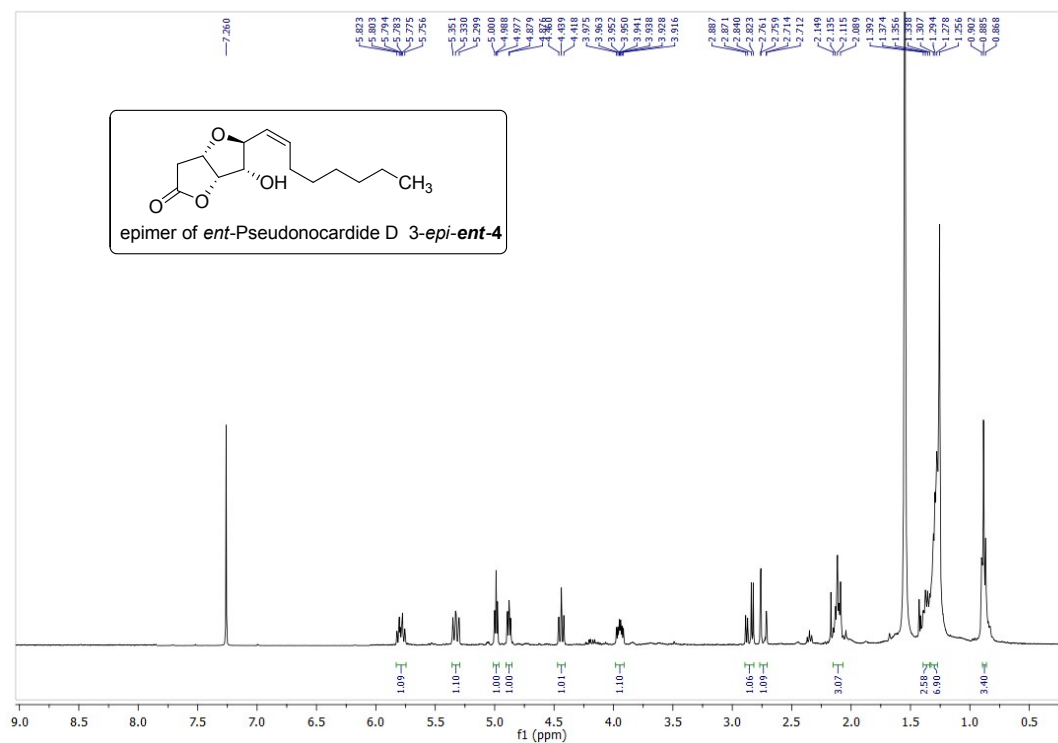
^1H NMR of compound **20** (400 MHz) in CDCl_3



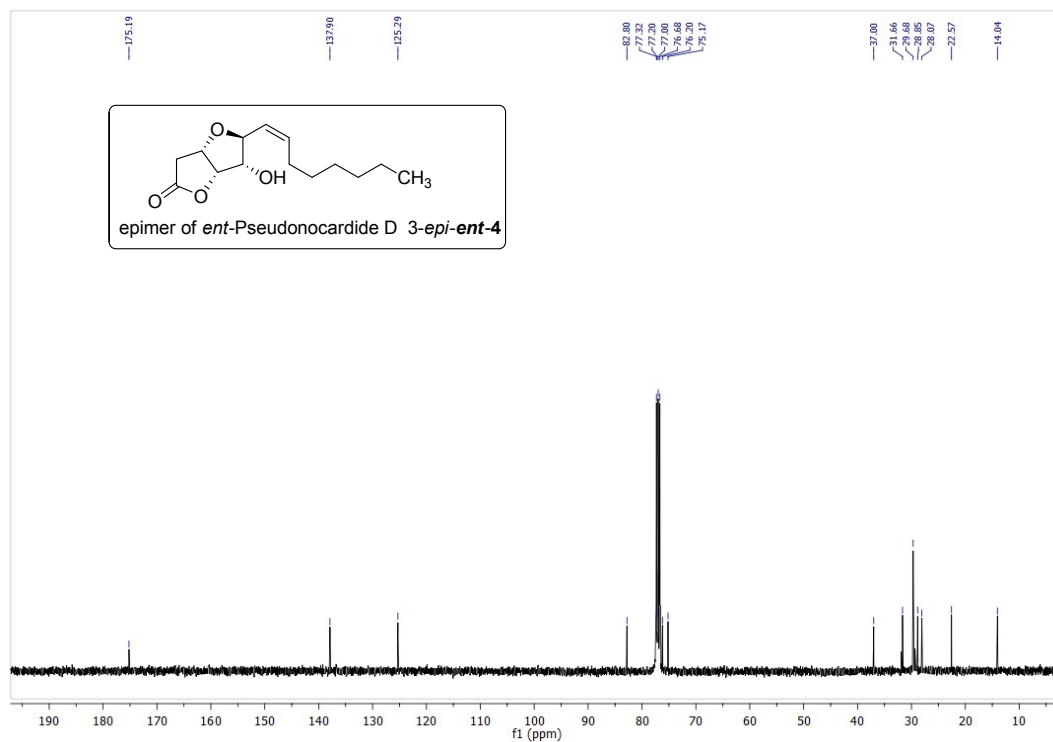
^{13}C NMR of compound **20** (100 MHz) in CDCl_3



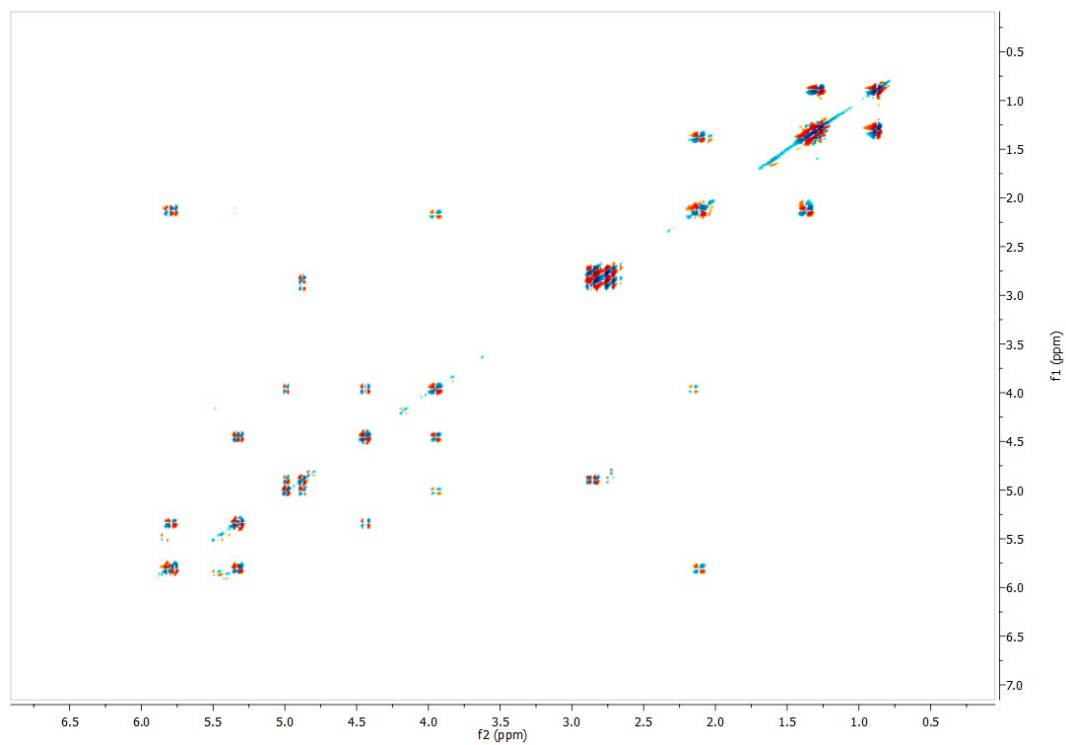
^1H NMR of epimer of *ent*-Pseudonocardide D [3-*epi-ent*-4] (400 MHz) in CDCl_3



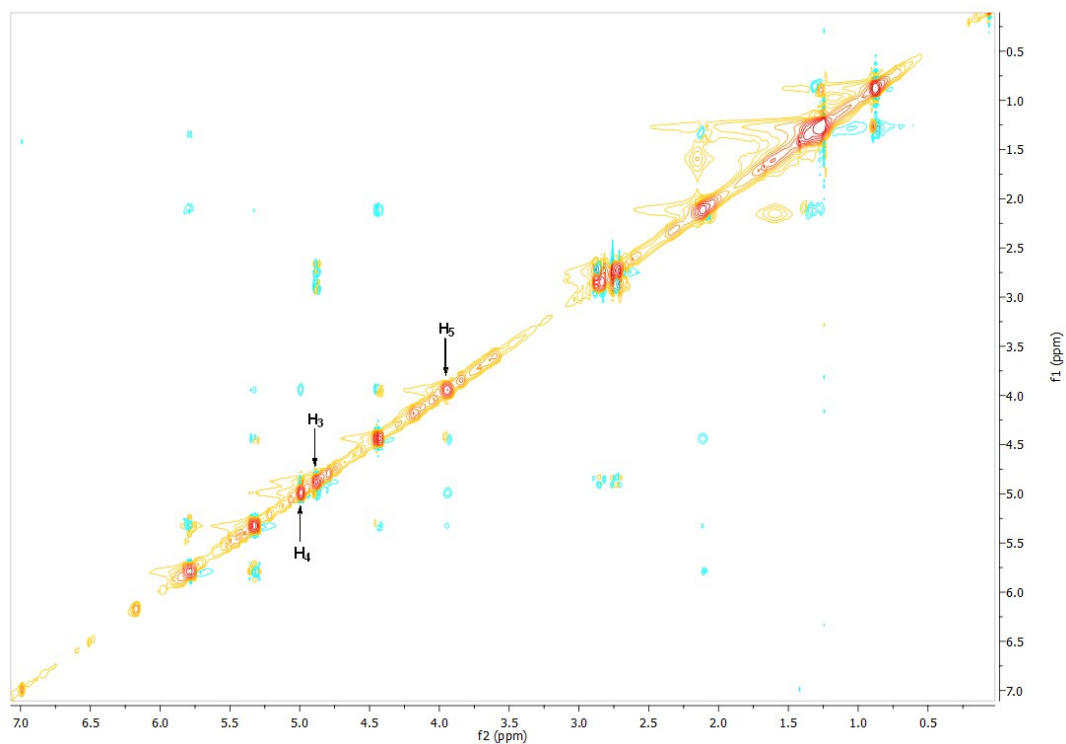
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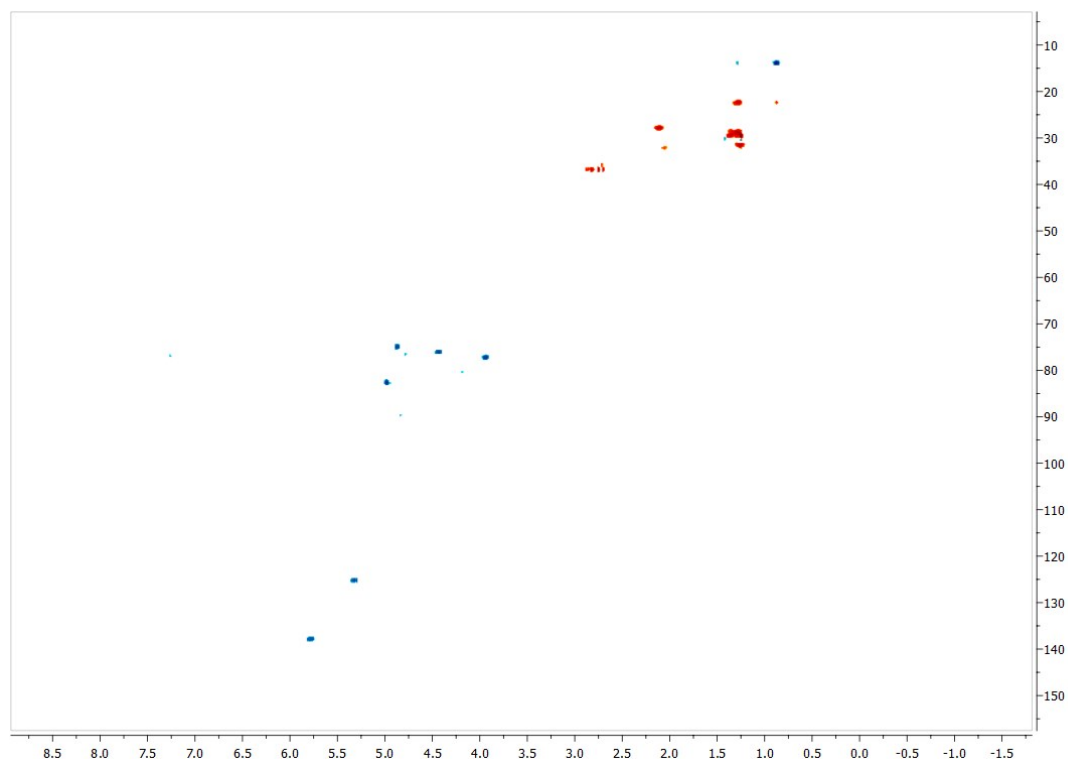
^1H - ^1H COSY of epimer of *ent*-Pseudonocardide D [3-*epi-ent-4*] in CDCl_3



^1H - ^1H NOESY of epimer of *ent*-Pseudonocardide D [3-*epi-ent-4*] in CDCl_3



^1H - ^{13}C HSQC of epimer of *ent*-Pseudonocardide D [3-*epi-ent*-4] in CDCl_3



HRMS-ESI analysis of epimer of *ent*-Pseudonocardide D [3-*epi-ent*-4]

