Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Epoxy-Amine Oligomers from Terpenes with Applications in Synergistic Antifungal Treatments

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Supplementary Information

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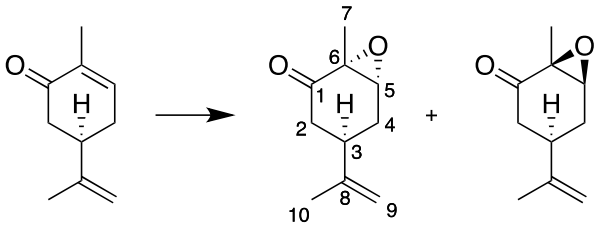
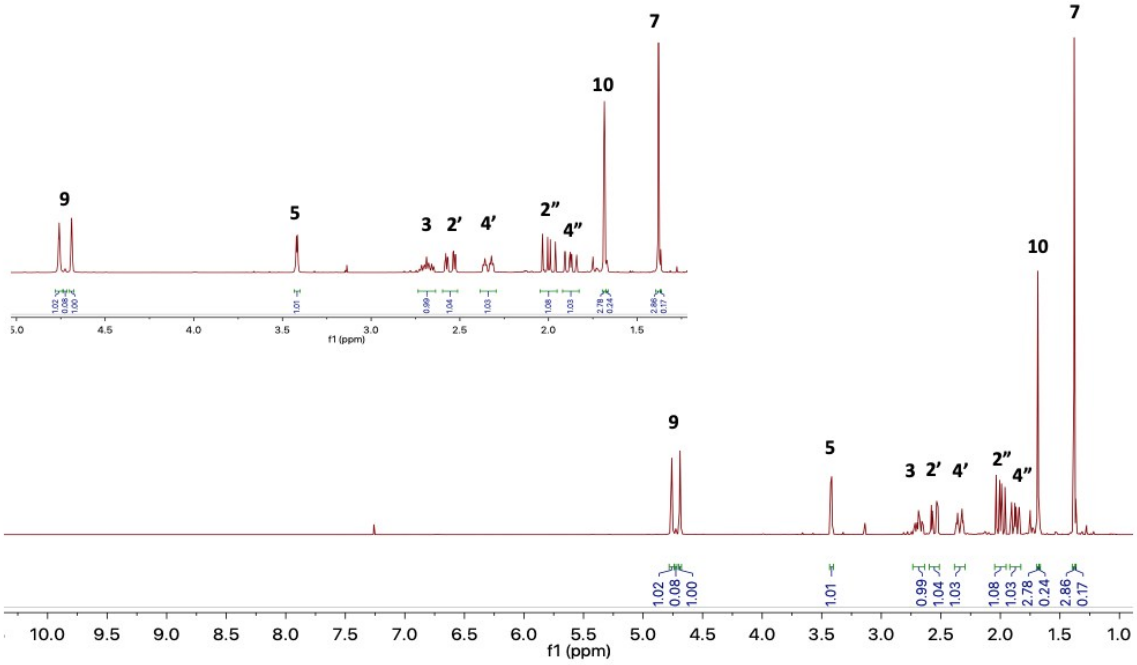
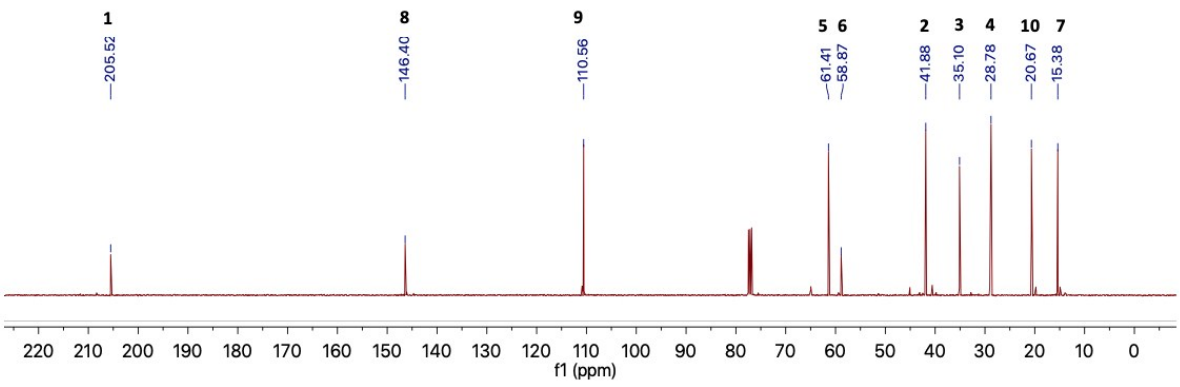
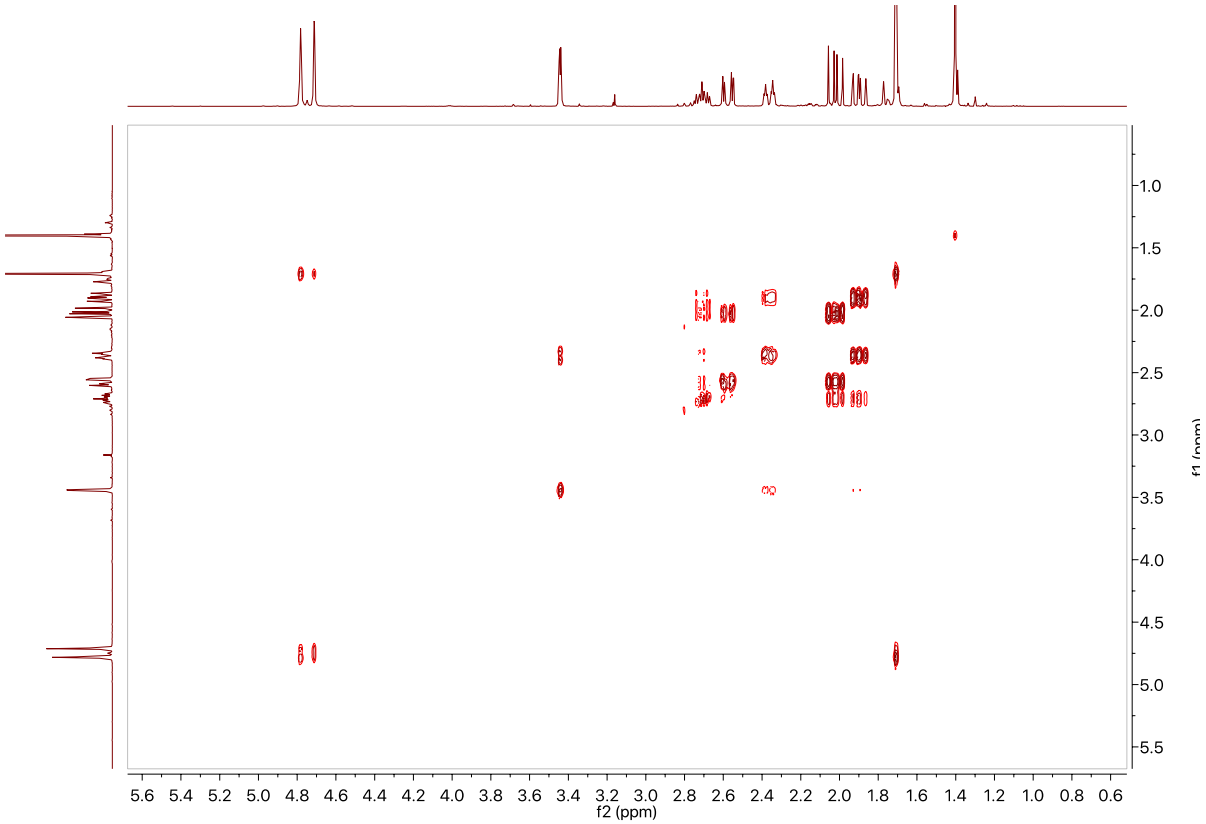
1. Synthesis of **1a** and **1b**: **(1*R*,4*R*,6*R*)-1-methyl-4-(prop-1-en-2-yl)-7-oxabicyclo[4.1.0]heptan-2-one** only peaks for the major diastereomer **1a** are reported.



1a : **1b**
9:1



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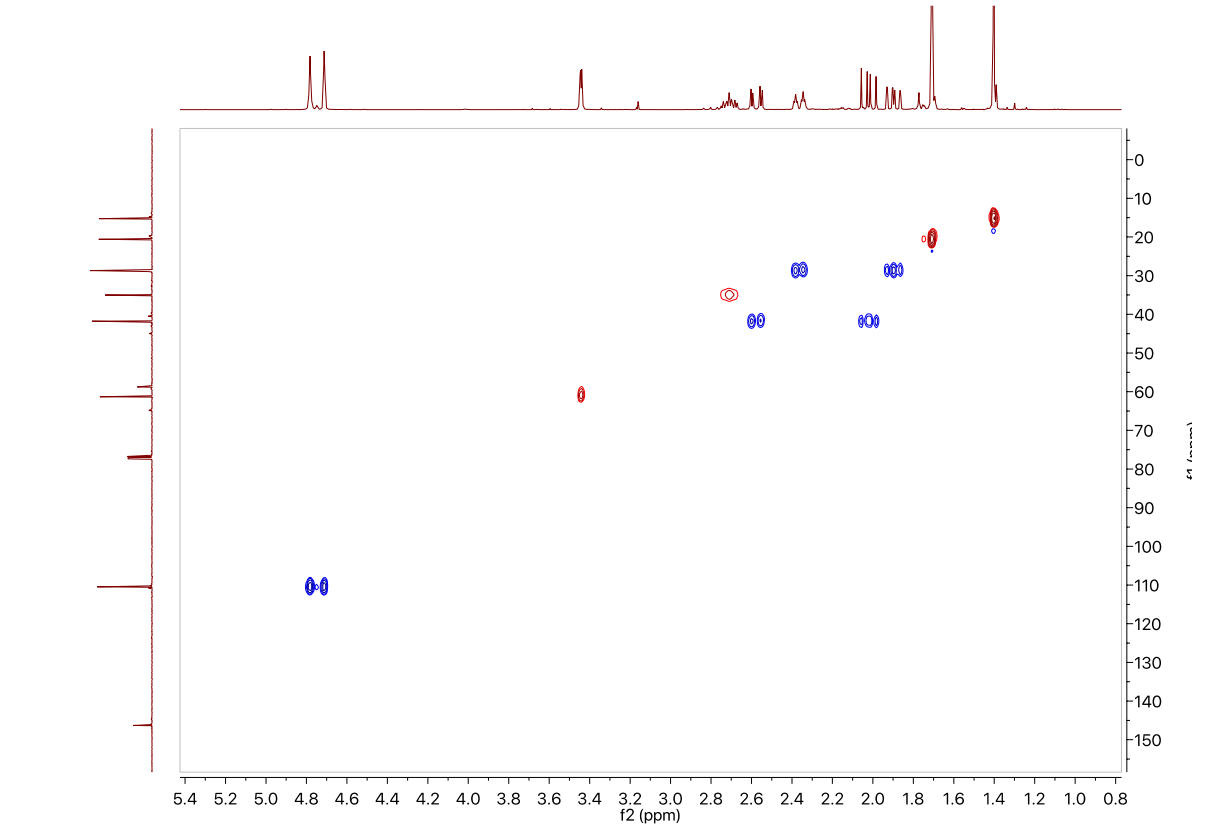
f2 (ppm)
1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5
f1 (ppm)


5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
f2 (ppm)
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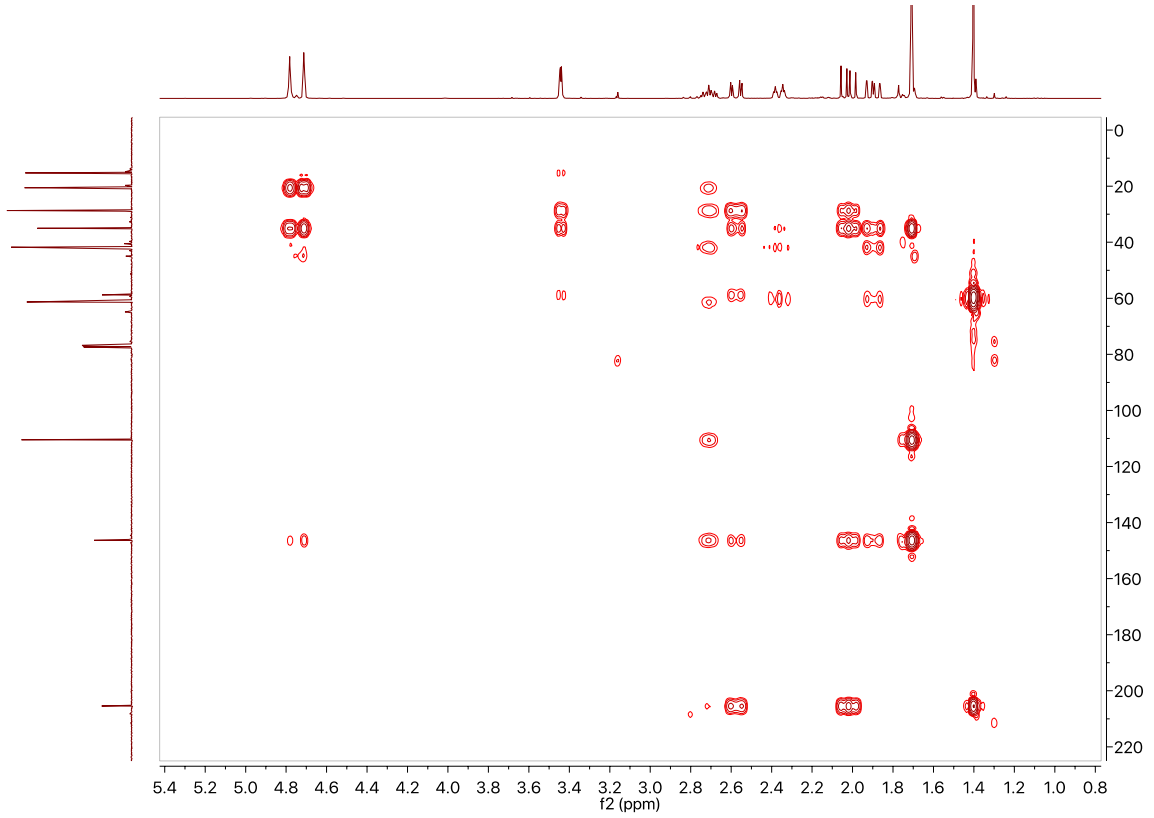
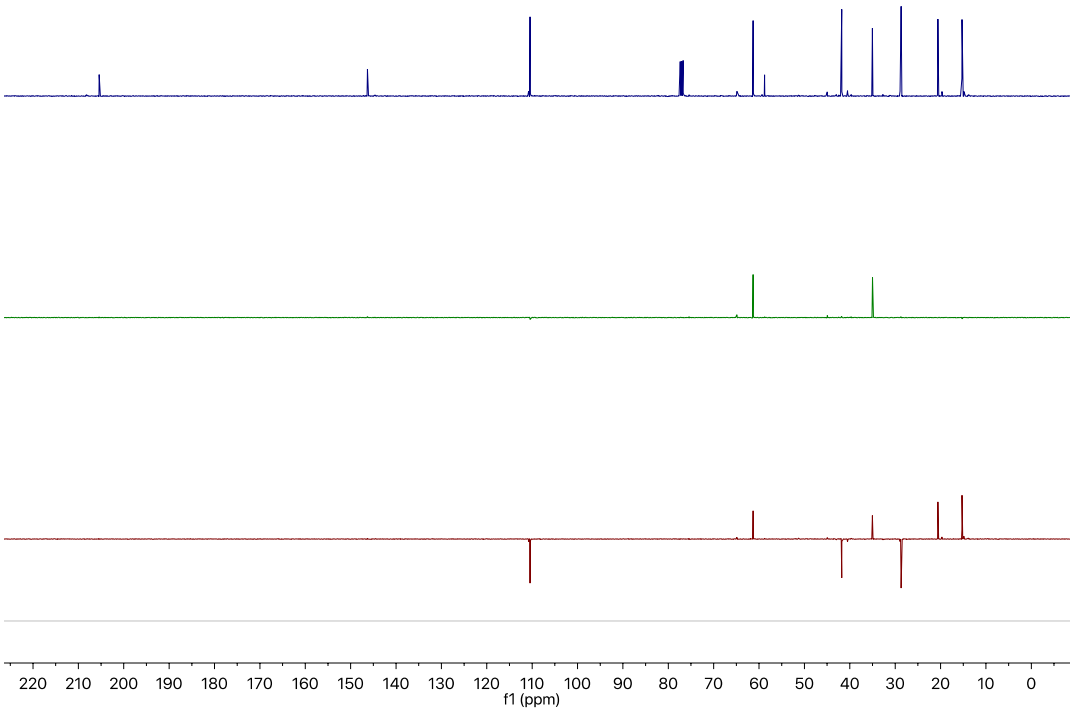
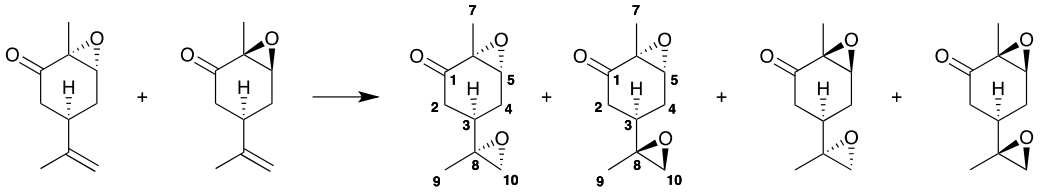
f1 (ppm)


0
20
40
60
80
100
120
140
160
180
200
220
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
f2 (ppm)


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

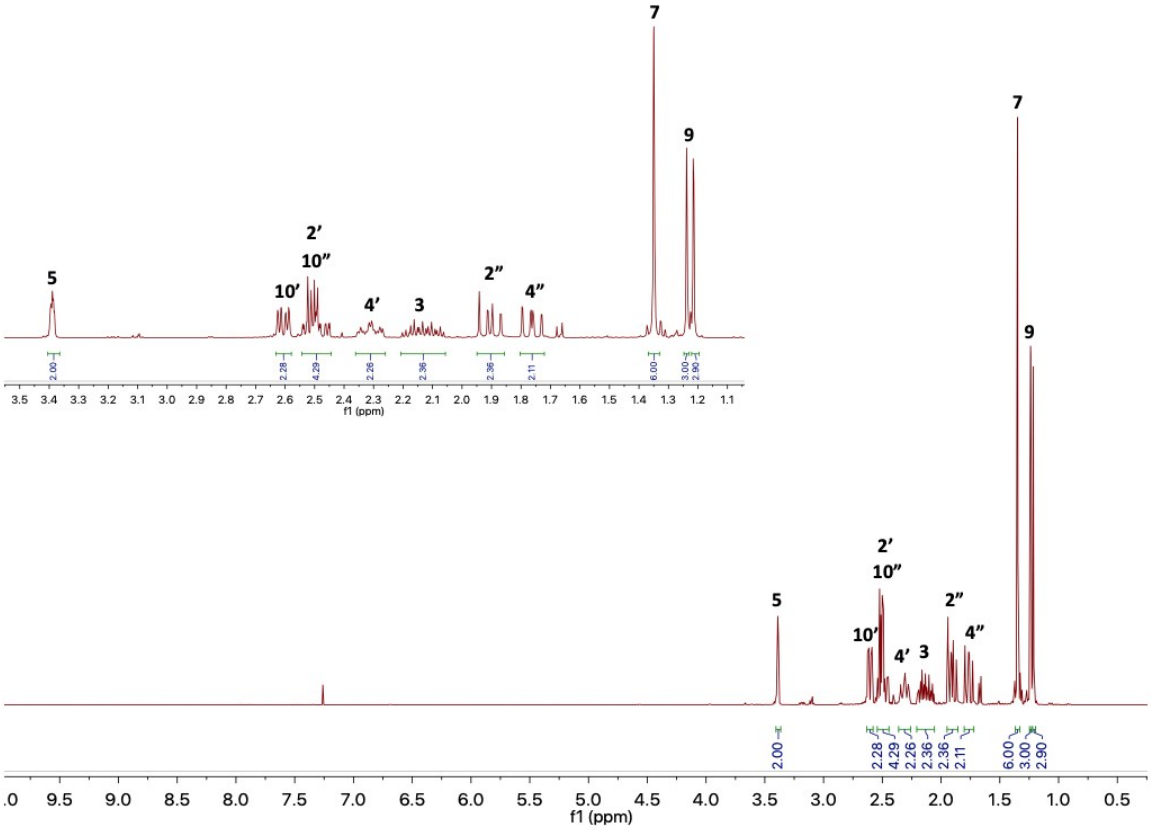
FTIR (ATR) ν_{max}/ cm^{-1} = 3083, 2978, 2936, 1705 (C=O), 1646 (C=C), 1439, 1377, 1323, 1270 (C-O), 1117, 1047, 989, 953, 890, 854, 814, 736, 702, 652, 616, 522, 504, 474, 447, 428; **^{1}H NMR**: (400 MHz, $CDCl_3$) δ_H = 4.83 – 4.75 (m, 1H), 4.75 – 4.63 (m, 1H), 3.44 (dd, *J* = 3.1, 1.2, 1H), 2.78 – 2.65 (m, 1H), 2.65 – 2.49 (m, 1H), 2.42 – 2.31 (m, 1H), 2.17 – 1.96 (m, 1H), 1.96 – 1.84 (m, 1H), 1.71 (s, 3H), 1.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C = 205.3, 146.2, 110.4, 61.24, 58.7, 41.7, 34.9, 28.6, 20.5, 15.22; **HRMS** (ESI^+) *m/z* [$M+Na^+$] calculated for $[C_{10}H_{14}NaO_2]^+$ 189.0891 found 189.0886 ($M + Na^+$).

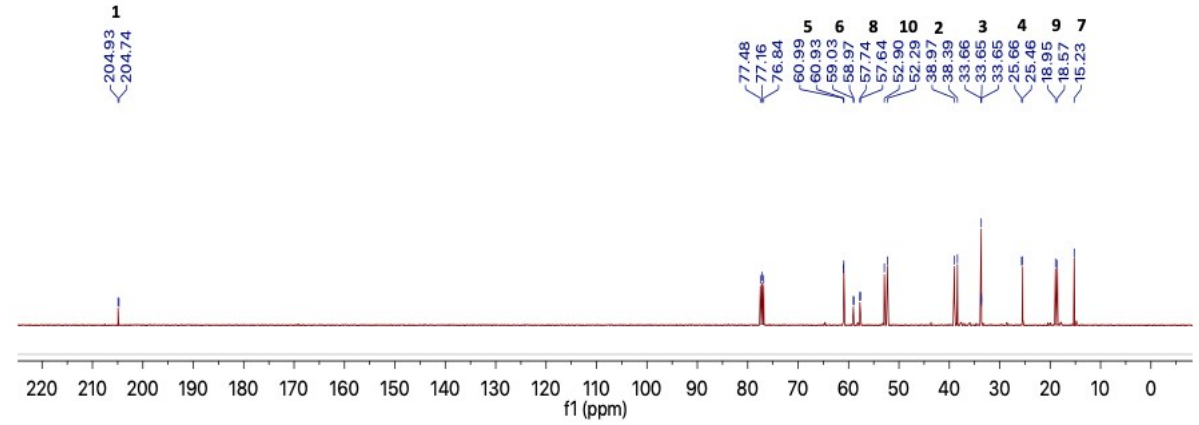
2. Synthesis of **2a** and **2b: (1*R*,4*R*,6*R*)-1-methyl-4-((*R*)-2-methyloxiran-2-yl)-7-oxabicyclo[4.1.0]heptan-2-one (2a) and (1*R*,4*R*,6*R*)-1-methyl-4-((*S*)-2-methyloxiran-2-yl)-7-oxabicyclo[4.1.0]heptan-2-one (2b)** only peaks for the major diastereomers **2a** and **2b** are reported.



1a 1b 2a 2b 2c 2d

9:9:1:1




1
204.93
204.74
5 6 8 10 2 3 4 9 7
77.48
77.16
76.84
60.99
60.93
59.03
58.97
57.74
57.64
52.90
52.29
38.97
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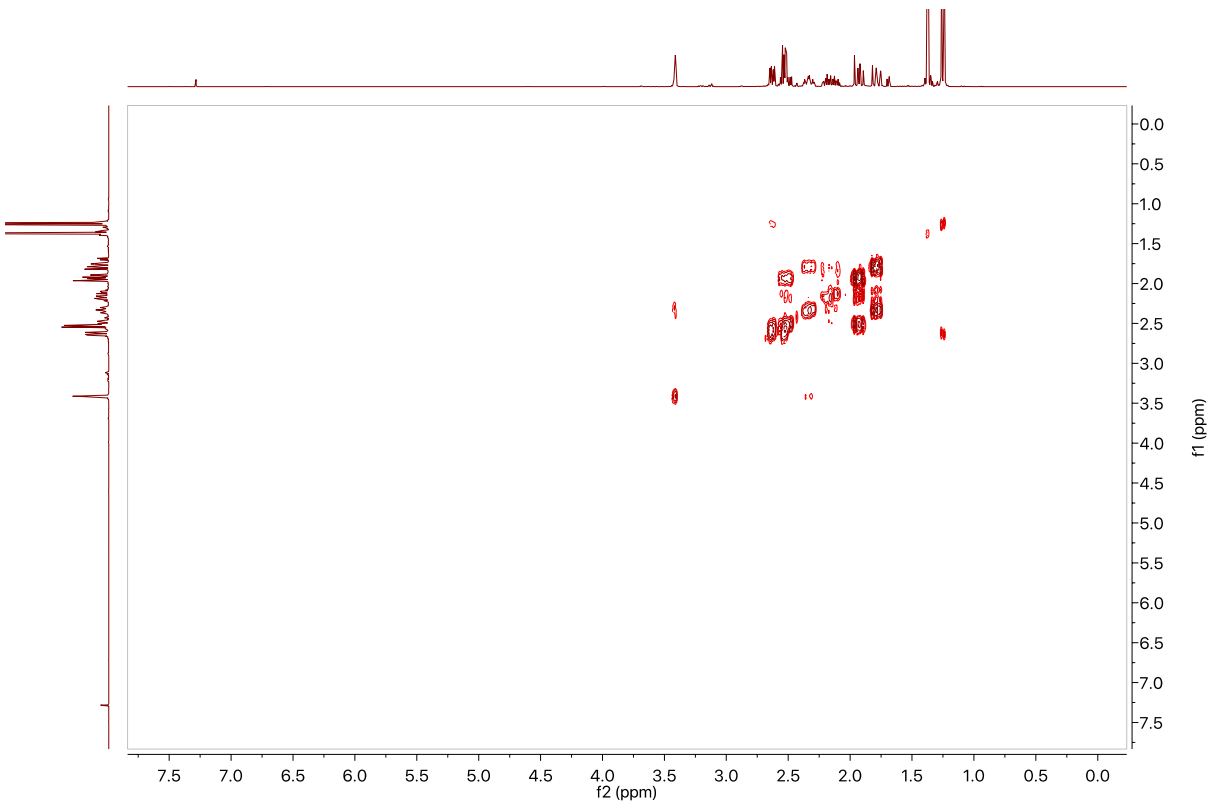
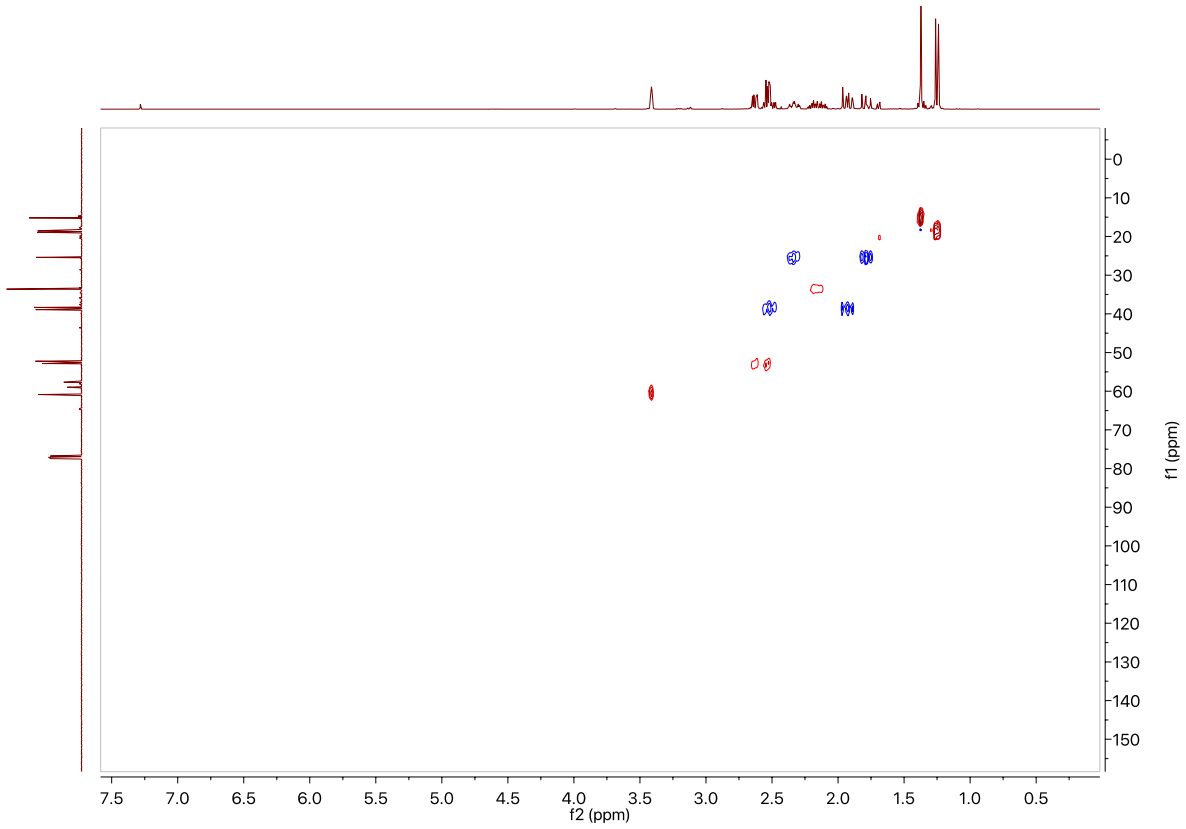
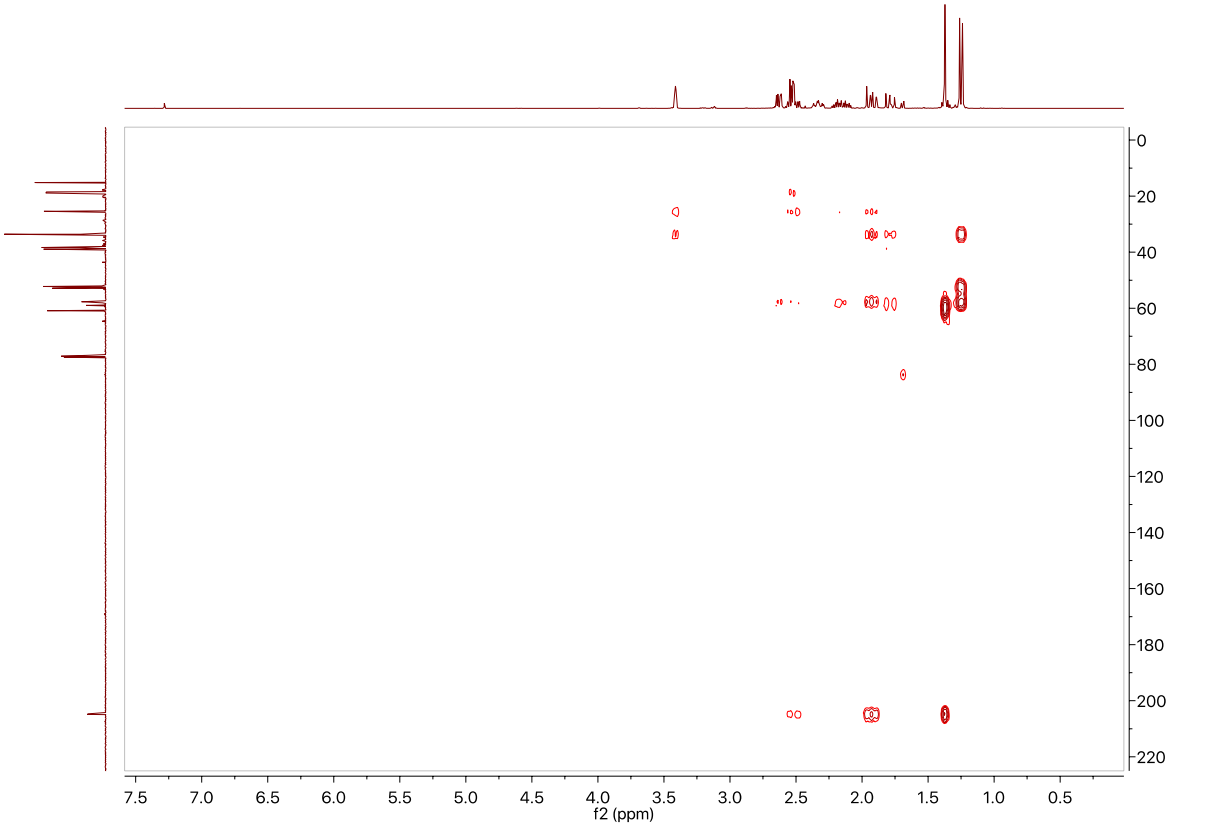
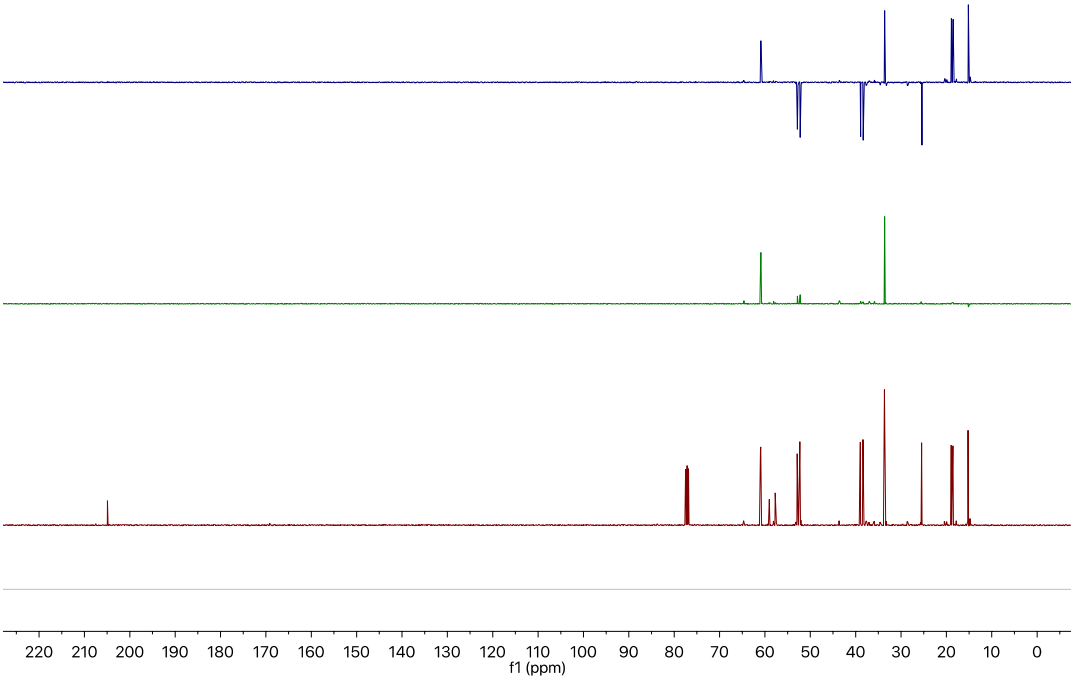
33.65
25.66
25.46
18.95
18.57
15.23
f1 (ppm)


f2 (ppm)
f1 (ppm)

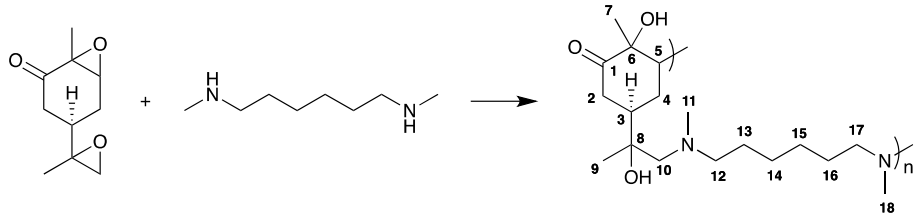

0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)

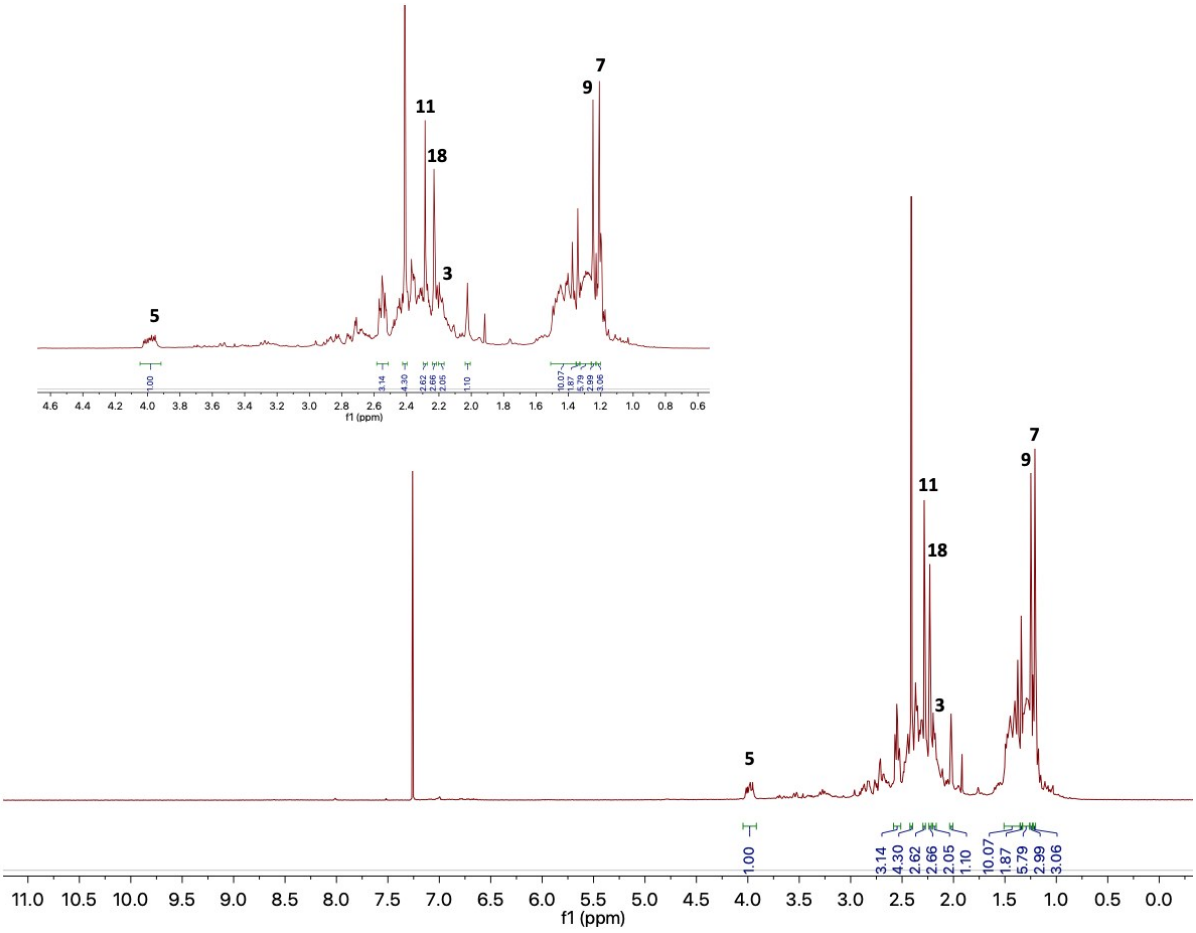

0
20
40
60
80
100
120
140
160
180
200
220
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)

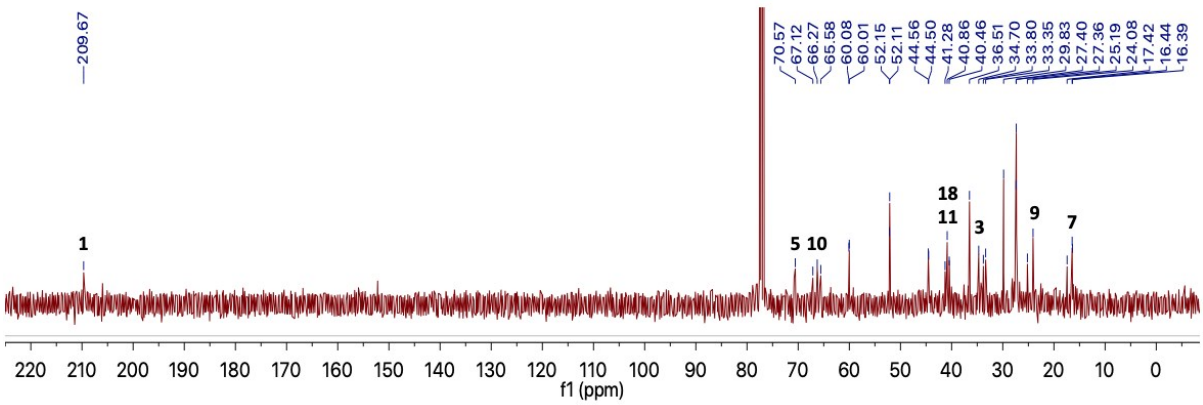


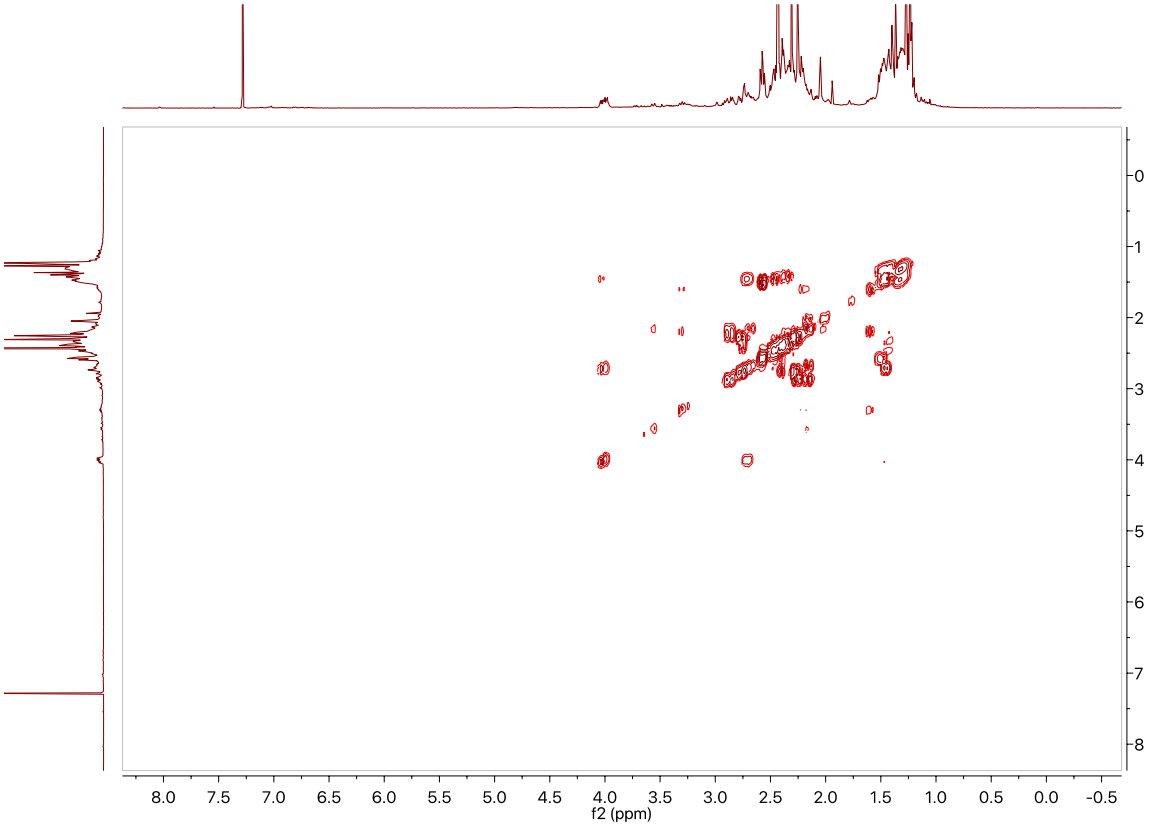
FTIR (ATR) ν_{max}/ cm^{-1} = 2979, 2943, 1704 (C=O), 1440, 1380, 1253, 1222, 1105, 1067, 958, 887, 845, 815, 654, 505, 477, 439; **^{1}H NMR**: (400 MHz, $CDCl_3$) δ_H = 3.47 – 3.38 (m, 2H), 2.71 – 2.61 (m, 2H), 2.63 – 2.48 (m, 4H), 2.43 – 2.30 (m, 2H), 2.22 – 2.10 (m, 2H), 2.02 – 1.89 (m, 2H), 1.86 – 1.75 (m, 2H), 1.41 (s, 6H), 1.29 (s, 3H), 1.27 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C =205.0, 204.8, 61.5, 61.0, 59.1, 59.0, 57.8, 57.7, 53.0, 52.3, 39.0, 38.4, 31.0, 25.7, 25.5, 19.0, 18.6, 15.27; **HRMS** (ESI^+) *m/z* [M+Na^+] calculated for $[C_{10}H_{14}NaO_3]^+$ 205.0841 found 205.0853 (M + Na^+).

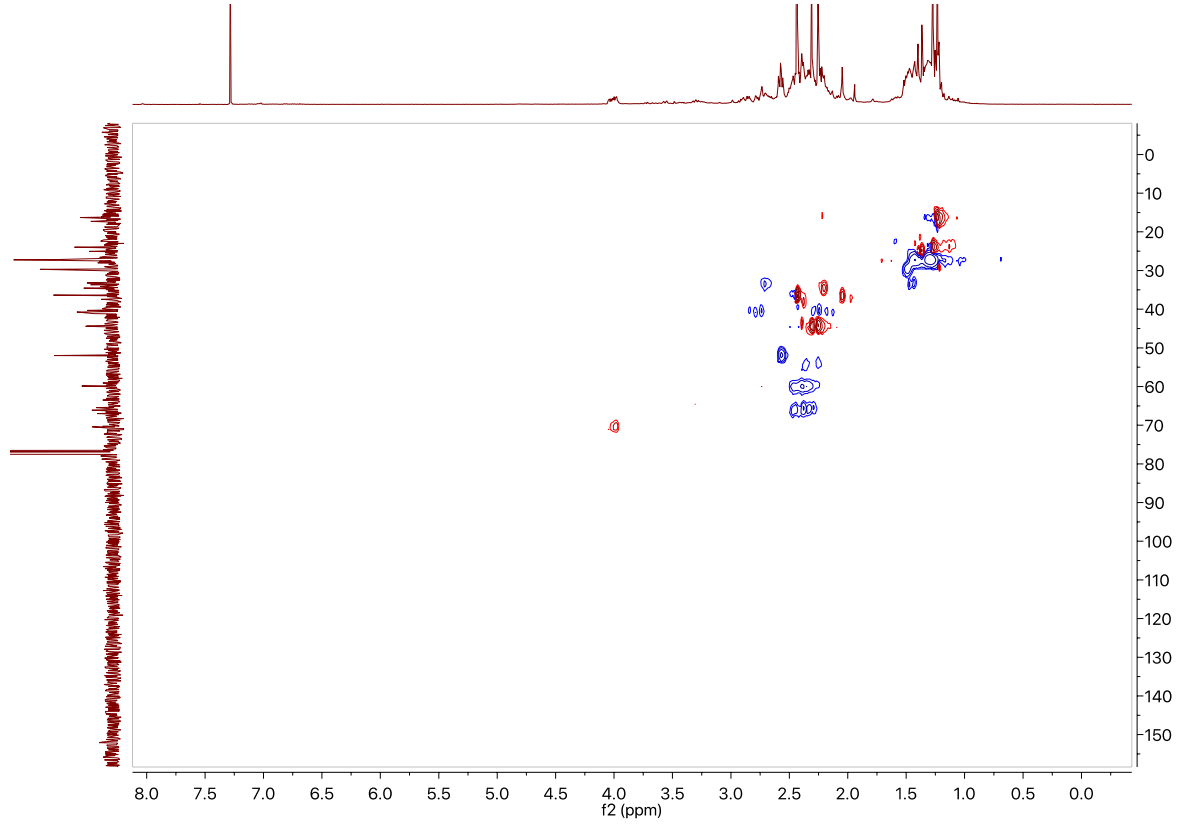
2.1. Synthesis of β-(aminoalcohol) oligomers, **4**

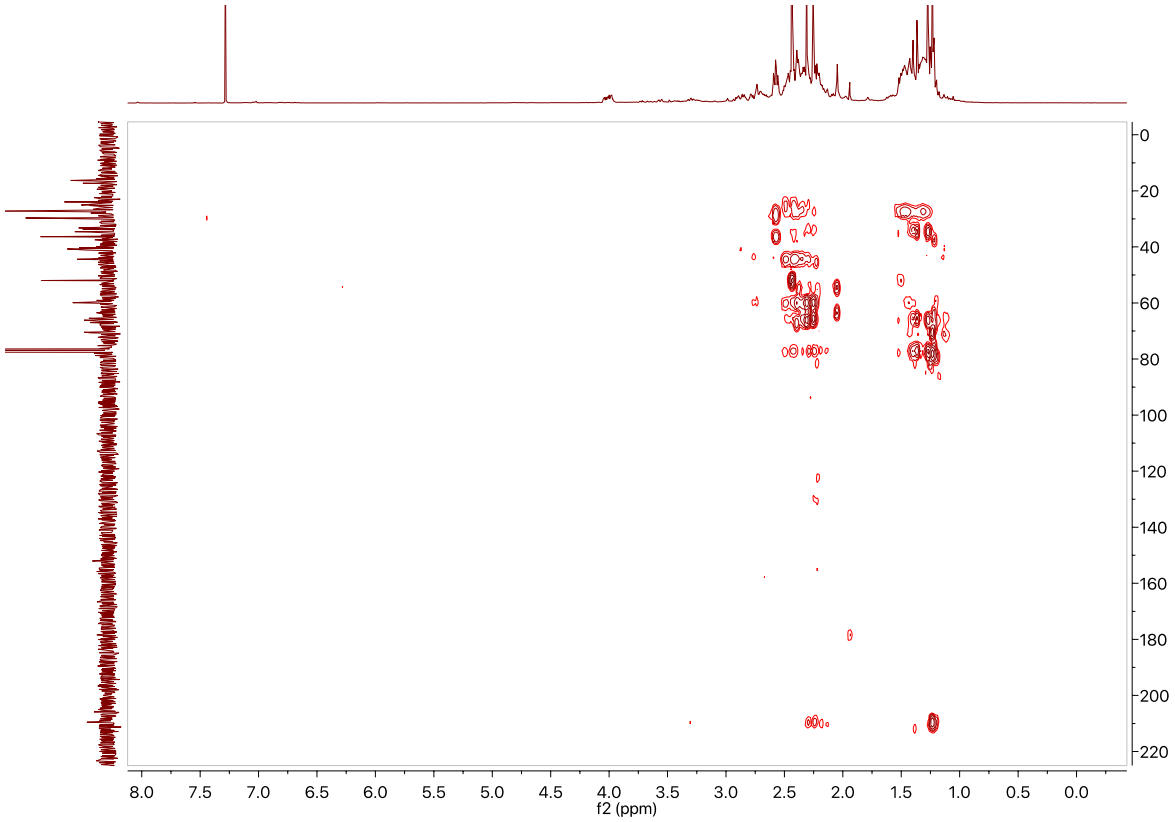


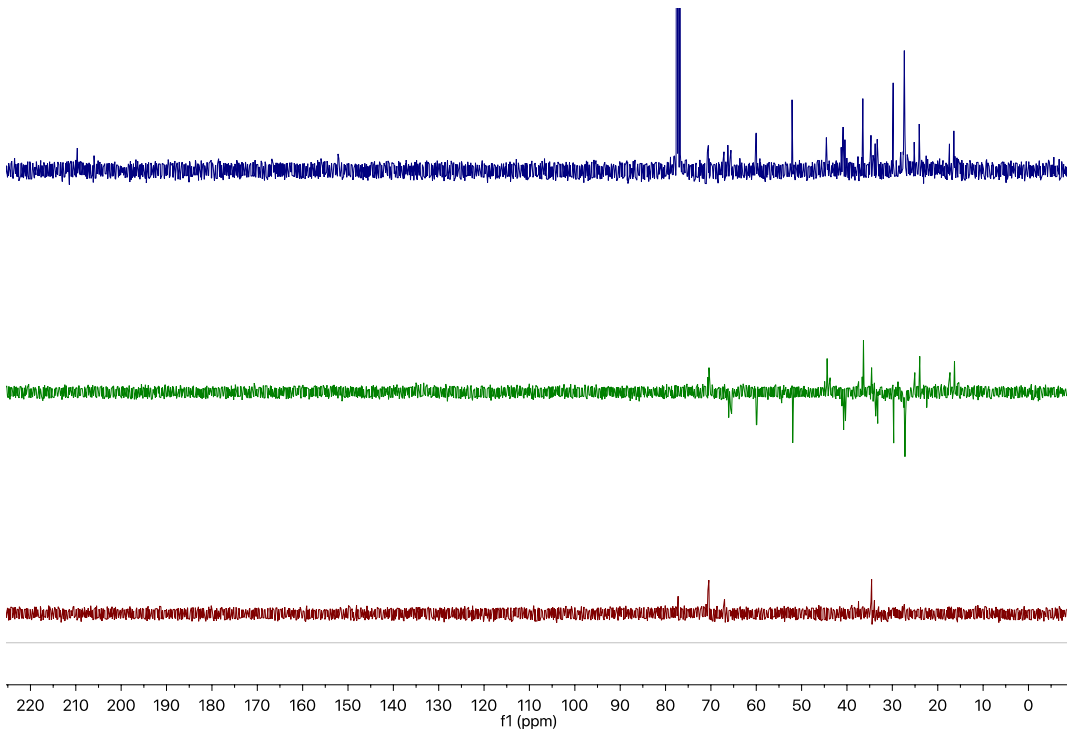





0
1
2
3
4
5
6
7
8
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f2 (ppm)


0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)


0
20
40
60
80
100
120
140
160
180
200
220
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

To a glass vial charged with **2** (3.47 mmol, 0.632 g) was added 1,6-dimethyl hexane-1,6-diamine (**3**) (3.47 mmol, 0.62 mL). The mixture was heated to the appropriate temperature as indicated in the table below, for the corresponding length of time. The product yielded a viscous, orange-brown oil when successful.

Reaction conditions		**Results**		
Time	t (°C)	M_n (Da)	M_w (Da)	Đ
5 hr	0	160	170	1.1
5 hr	22	160	170	1.1
5 hr	50	210	260	1.2
5 hr	70	400	460	1.2
5 hr	90	440	520	1.2
5 hr	110	520	670	1.3
24 hr	70	440	520	1.2
5 days	70	500	620	1.3
7 days	**70**	**520**	**700**	**1.3**

Samples tested for antifungal studies were taken from the highlighted sample conducted at 70 °C over 7 days.

FTIR (ATR) ν_{max}/ cm^{-1} = 3304, 2930, 2855, 2791, 1731, 1649, 1576, 1449, 1407, 1372, 1353, 1305, 1240, 1117, 1077, 1050, 1005, 972, 886, 838, 726, 565, 474; **^{1}H NMR**: (400 MHz, $CDCl_3$) δ_H = 4.06 – 3.87 (m), 3.02 – 1.88 (m), 1.66 – 0.92 (m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C = 209.7, 70.6, 67.1, 66.3, 65.6, 60.1, 60.0, 52.2, 52.1, 44.6, 41.3, 40.9, 40.5, 36.5, 34.7, 33.8, 33.4, 29.8, 27.4, 27.36, 25.4, 25.2, 24.1, 17.4, 16.5, 16.4; **HRMS** (ESI^+) *m/z* [M+H^+] calculated for $[C_{28}H_{49}N_2O_6]^+$ 509.3591 found 509.3587 (M + H^+).