

Supplementary Materials

New Crambescidin-type Alkaloids from the Indonesian Marine Sponge *Clathria bulbotoxa*

Kasmiati Kasmiati^{1,2}, Yukio Yoshioka³, Tetsuji Okamoto³, and Makoto Ojika^{1,*}

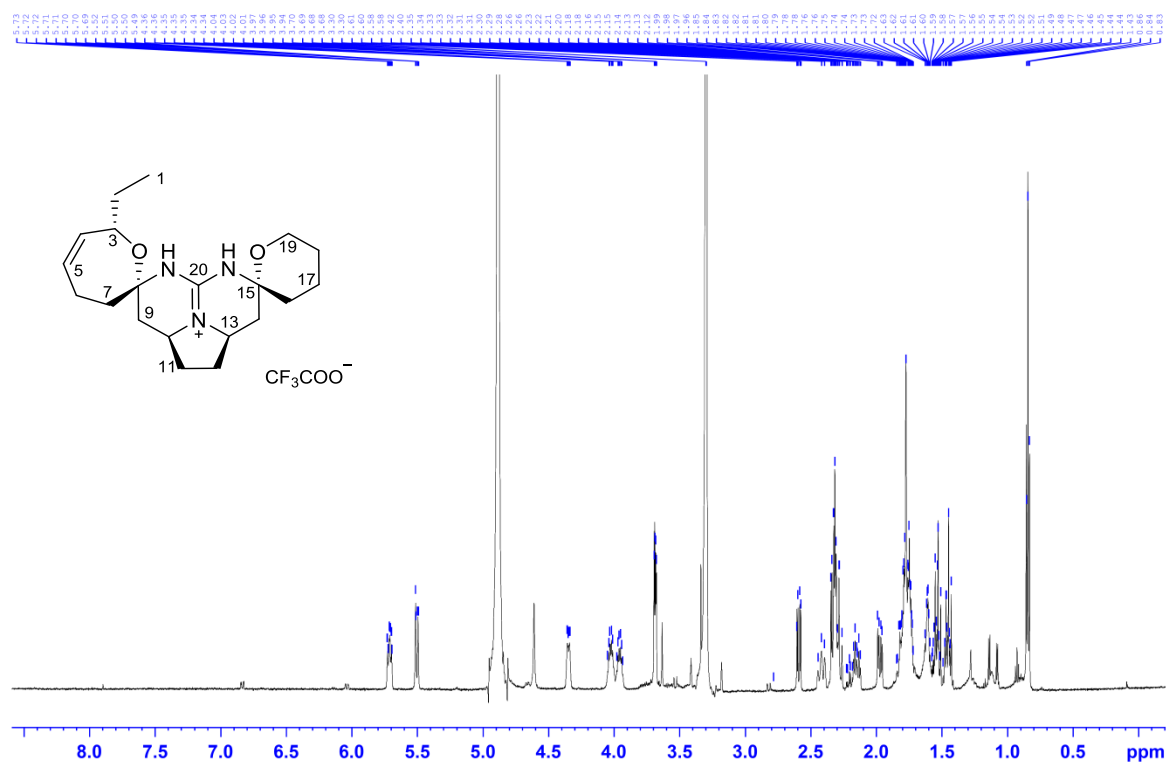
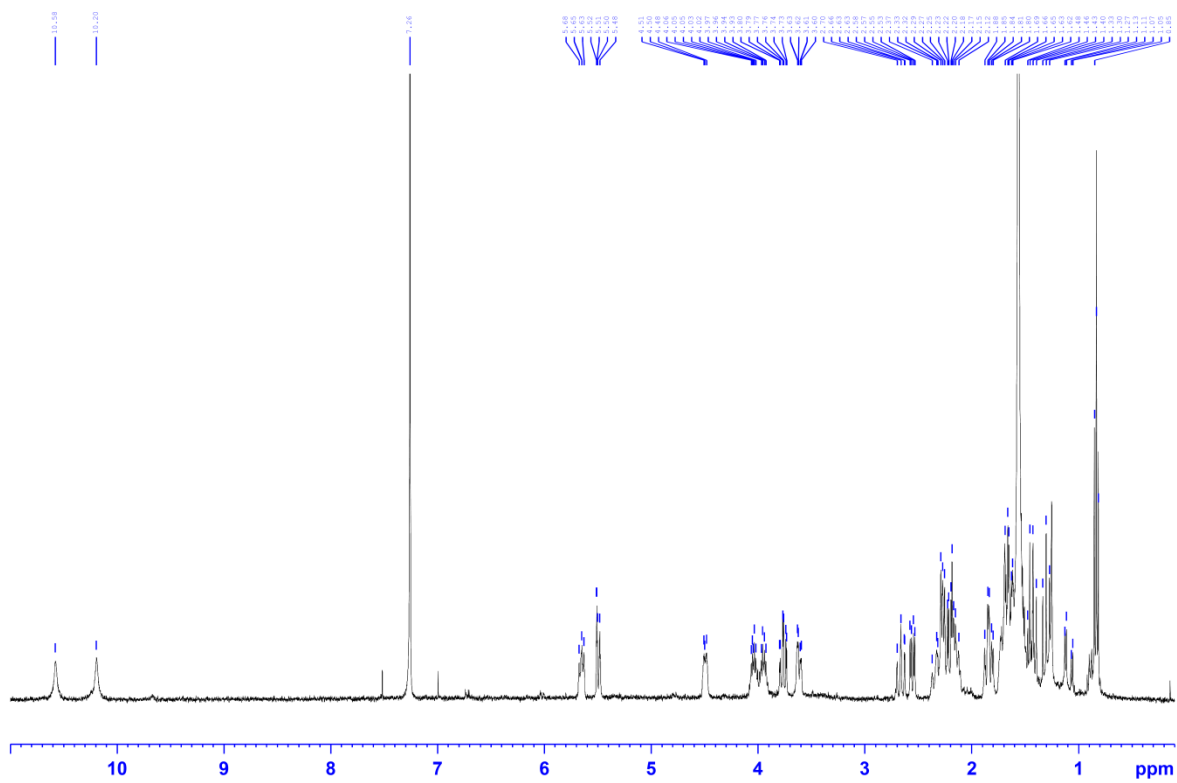
Contents

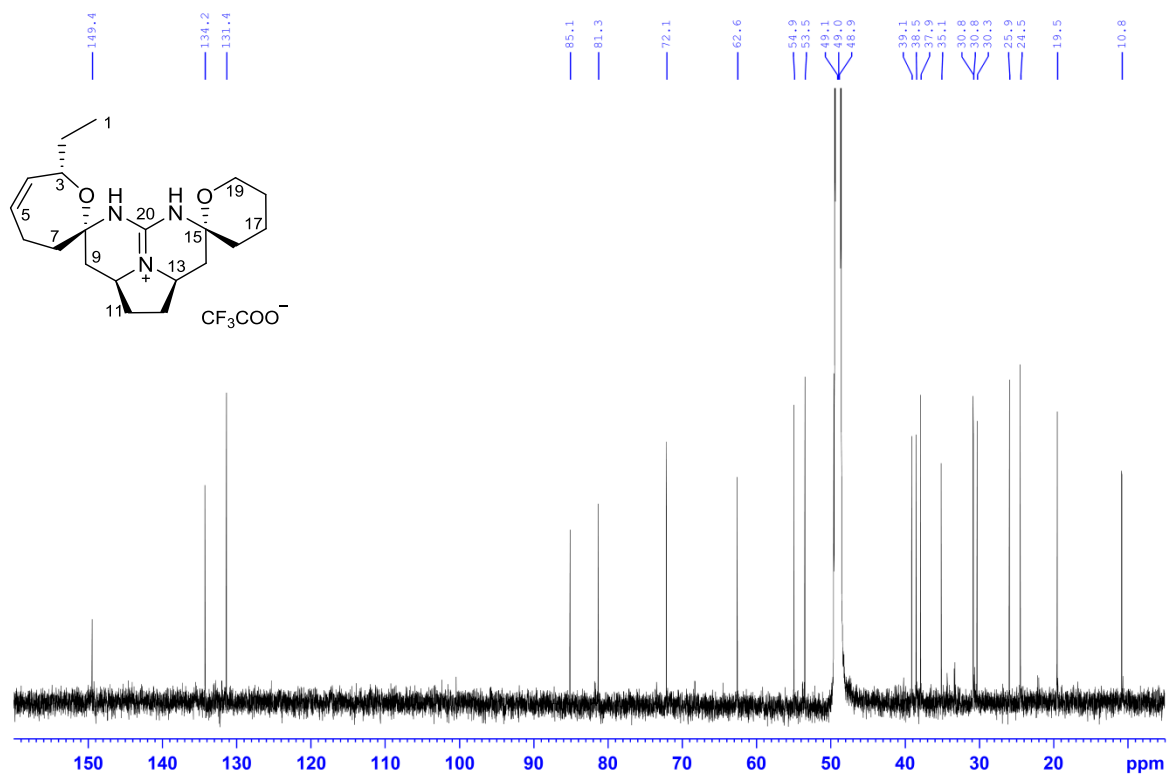
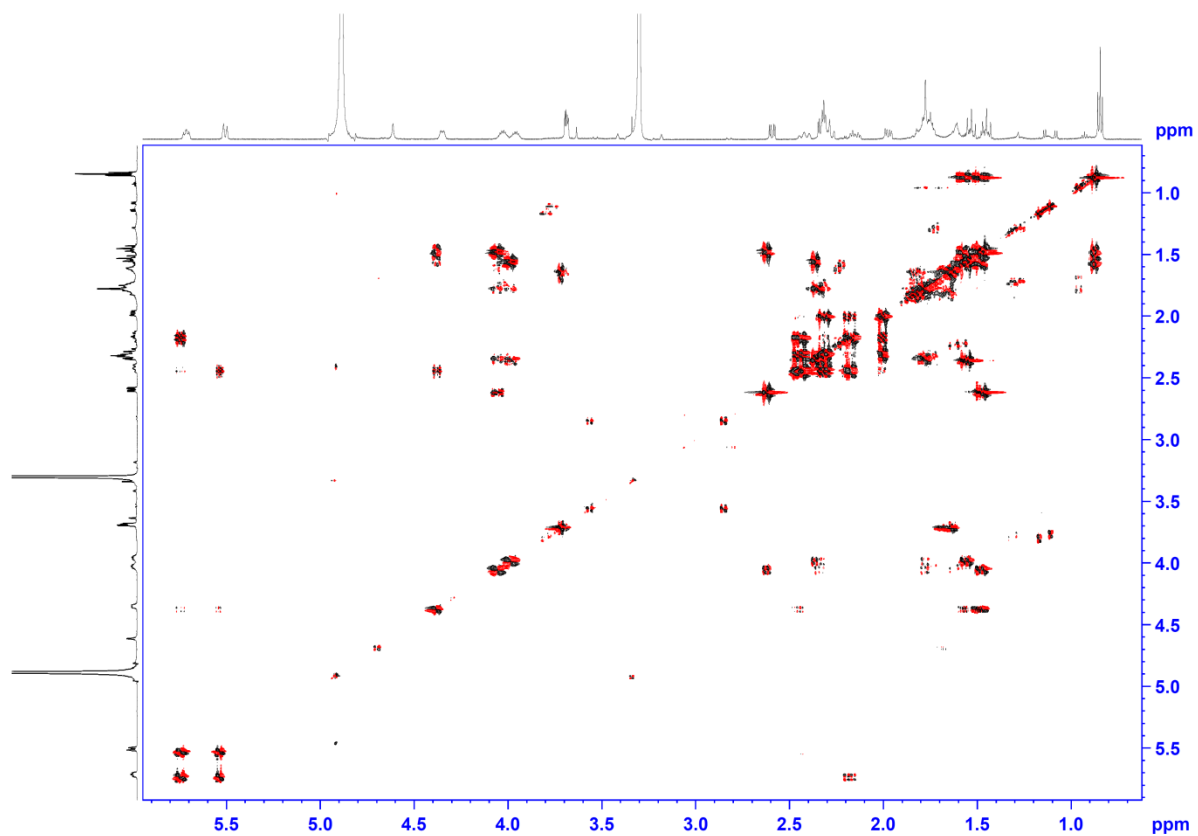
Table S1: NMR data of **2** (600 MHz, acetone-*d*₆)
Figure S1: ¹H NMR spectrum of **1** (600 MHz, CD₃OD)
Figure S2: ¹H NMR spectrum of **1** (400 MHz, CDCl₃)
Figure S3: ¹³C NMR spectrum of **1** (150 MHz, CD₃OD)
Figure S4: DQF-COSY spectrum of **1** (600 MHz, CD₃OD)
Figure S5: HSQC spectrum of **1** (600 MHz, CD₃OD)
Figure S6: HMBC spectrum of **1** (600 MHz, CD₃OD)
Figure S7: NOESY spectrum of **1** (600 MHz, CD₃OD)
Figure S8: IR spectrum of **1**
Figure S9: ESI-TOF-MS(+) spectra of **1–3**
Figure S10: ¹H NMR spectrum of **2** (400 MHz, CD₃OD)
Figure S11: ¹³C NMR spectrum of **2** (100 MHz, CD₃OD)
Figure S12: DQF-COSY spectrum of **2** (400 MHz, CD₃OD)
Figure S13: HSQC spectrum of **2** (400 MHz, CD₃OD)
Figure S14: HMBC spectrum of **2** (400 MHz, CD₃OD)
Figure S15: NOESY spectrum of **2** (400 MHz, CD₃OD)
Figure S16: IR spectrum of **2**
Figure S17: ¹H NMR spectrum of **2** (600 MHz, acetone-*d*₆)
Figure S18: ¹³C NMR spectrum of **2** (150 MHz, acetone-*d*₆)
Figure S19: DQF-COSY spectrum of **2** (600 MHz, acetone-*d*₆)
Figure S20: HSQC spectrum of **2** (600 MHz, acetone-*d*₆)
Figure S21: HMBC spectrum of **2** (600 MHz, acetone-*d*₆)
Figure S22: NOESY spectrum of **2** (600 MHz, acetone-*d*₆)
Figure S23: ¹H NMR spectrum of **3** (600 MHz, CD₃OD)
Figure S24: ¹H NMR spectrum of **3** (400 MHz, CDCl₃)
Figure S25: ¹³C NMR spectrum of **3** (150 MHz, CD₃OD)
Figure S26: DQF-COSY spectrum of **3** (600 MHz, CD₃OD)
Figure S27: HSQC spectrum of **3** (600 MHz, CD₃OD)
Figure S28: HMBC spectrum of **3** (600 MHz, CD₃OD)
Figure S29: IR spectrum of **3**
Figure S30: ¹H NMR spectrum of **4** (400 MHz, CD₃OD)
Figure S31: ¹H NMR spectrum of **5** (400 MHz, CD₃OD)
Figure S32: ¹H NMR spectrum of **6** (400 MHz, CD₃OD)
Figure S33: Anti-oomycete activity of compounds **1–6**

Table S1: NMR data of **2** (600 MHz, acetone-*d*₆)

Position	δ_C (ppm)	δ_H (ppm), m, J (Hz)
1	13.7, CH ₃	0.85, t (7.2)
2	19.1, CH ₂	1.34, m
3	38.4, CH ₂	1.37, m
4	69.9, CH	3.70, t (9.9)
5a	31.6, CH ₂	1.19, m
5b		1.59, m
6a	18.9, CH ₂ ^a	1.62, m
6b		2.29, m
7a	34.4, CH ₂ ^b	1.62, m
7b		1.74, m
8	81.0, C ^c	
9a	40.3, CH ₂ ^d	1.62, m
9b		2.16, t (12.9) ^g
10	53.2, CH ^e	4.00, m
11a	30.5, CH ₂ ^f	1.78, m
11b		2.31, m
12a	30.4, CH ₂ ^f	1.78, m
12b		2.31, m
13	52.7, CH ^e	4.00, m
14a	40.4, CH ₂ ^d	1.62, m
14b		2.15, t (12.9) ^g
15	81.1, C ^c	
16a	34.3, CH ₂ ^b	1.62, m
16b		1.74, m
17a	18.7, CH ₂ ^a	1.62, m
17b		2.29, m
18a	33.1, CH ₂	1.16, m
18b		1.64, m
19	67.1, CH	3.80, m
20	22.1, CH ₃	1.06, d (6.0)
21	149.4, C	
NHa		10.13, s
NHb		10.16, s

The number of hydrogen on carbon was determined by HSQC. ^{a-g} Interchangeable signals within the same marks.

Figure S1: ^1H NMR spectrum of **1** (600 MHz, CD_3OD).Figure S2: ^1H NMR spectrum of **1** (400 MHz, CDCl_3).

Figure S3: ^{13}C NMR spectrum of 1 (150 MHz, CD_3OD).Figure S4: DQF-COSY spectrum of 1 (600 MHz, CD_3OD).

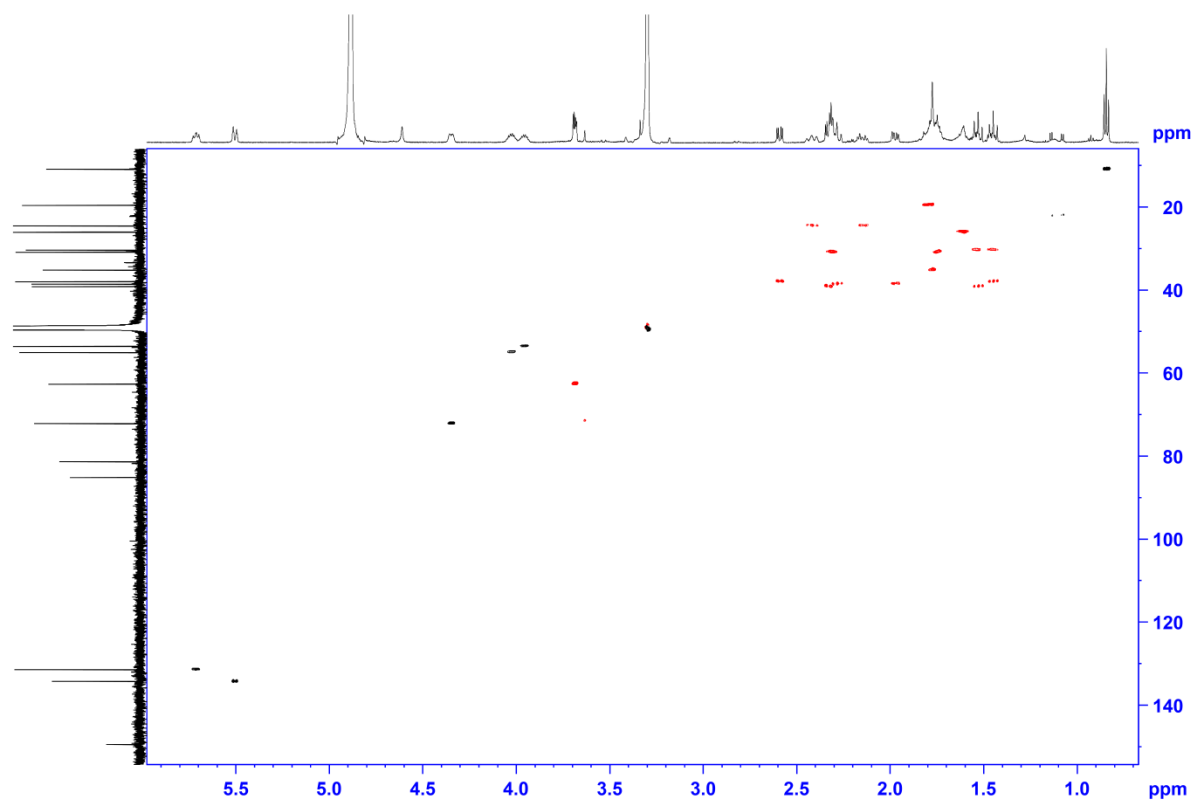


Figure S5: HSQC spectrum of **1** (600 MHz, CD₃OD).

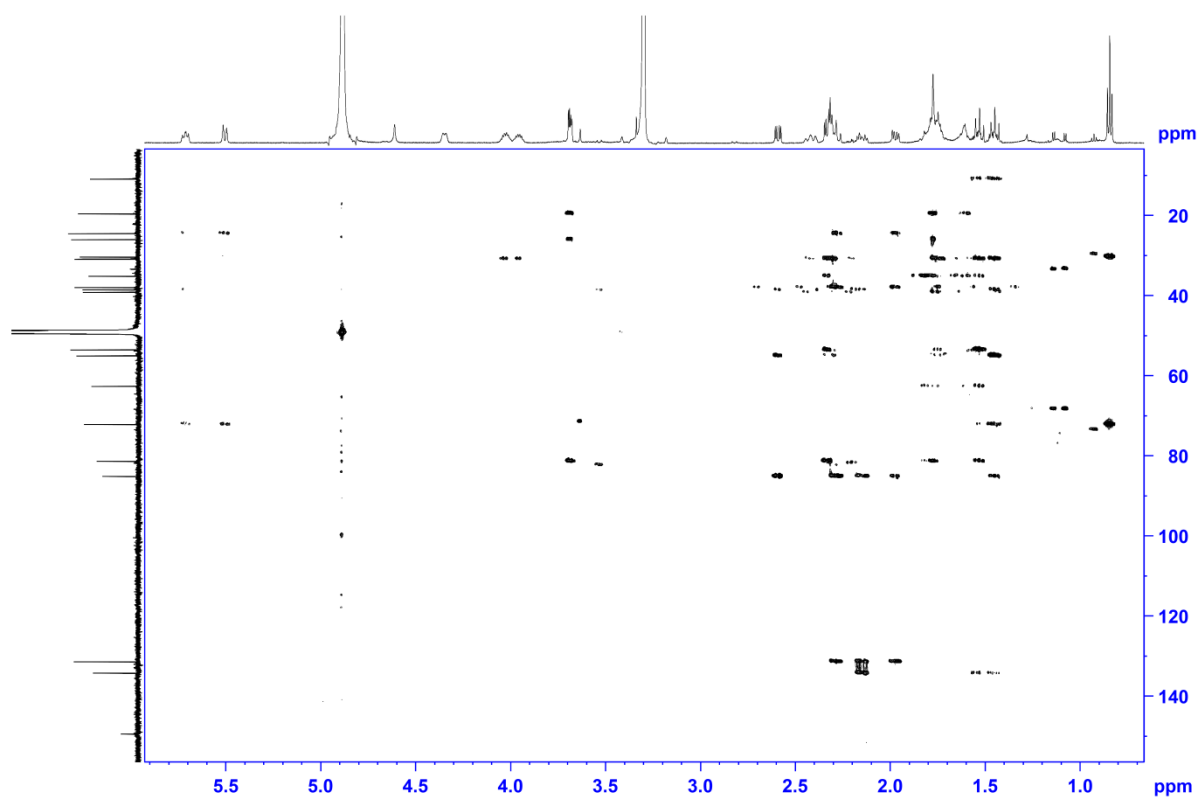


Figure S6: HMBC spectrum of **1** (600 MHz, CD₃OD).

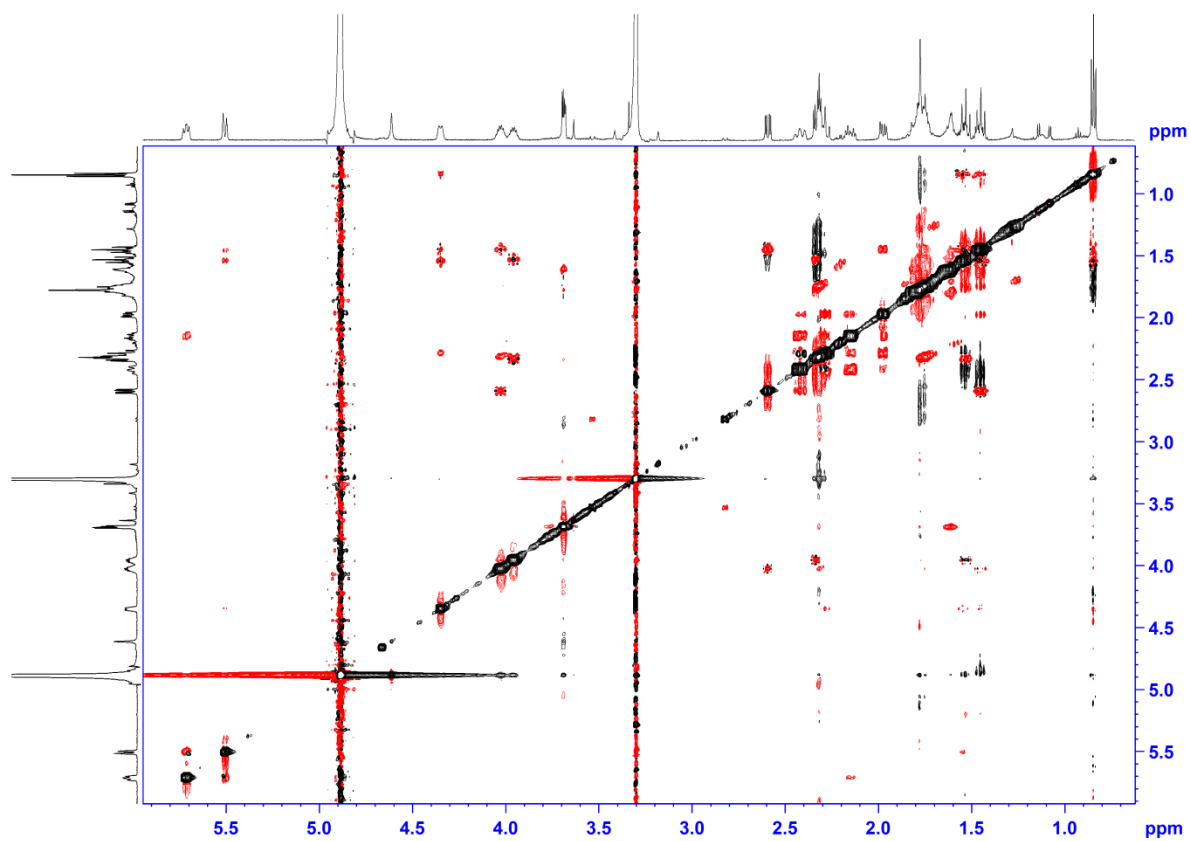


Figure S7: NOESY spectrum 1 (600 MHz, CD₃OD).

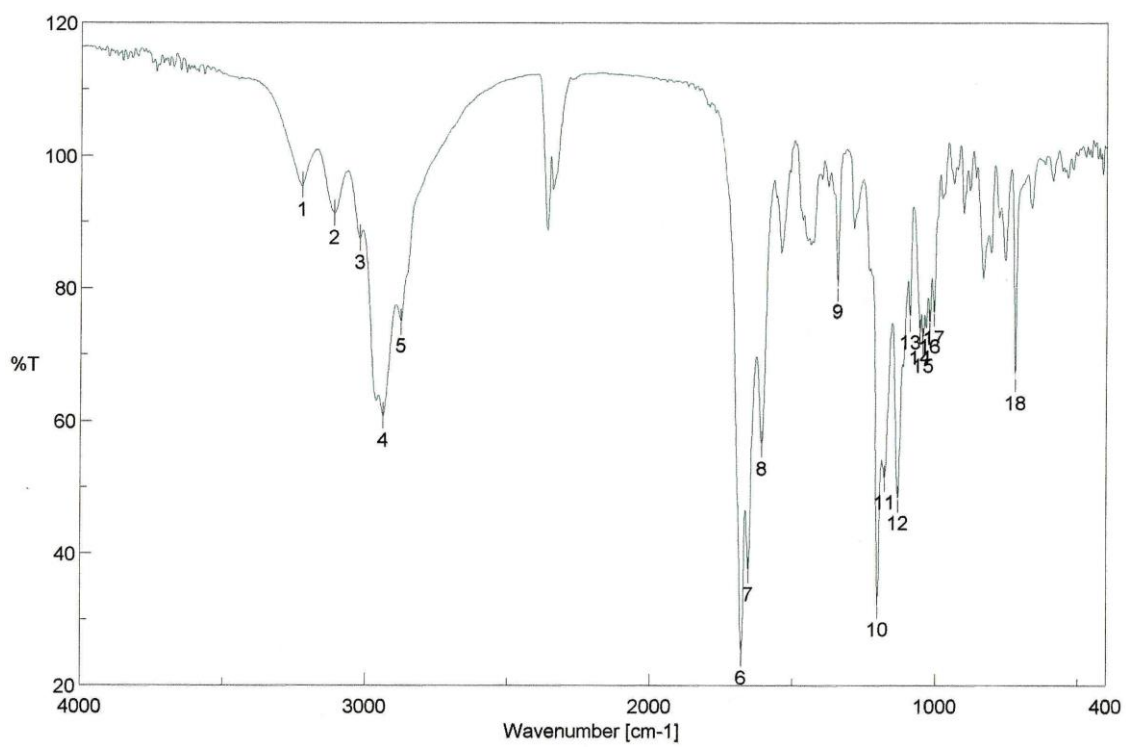


Figure S8: IR spectrum of 1.

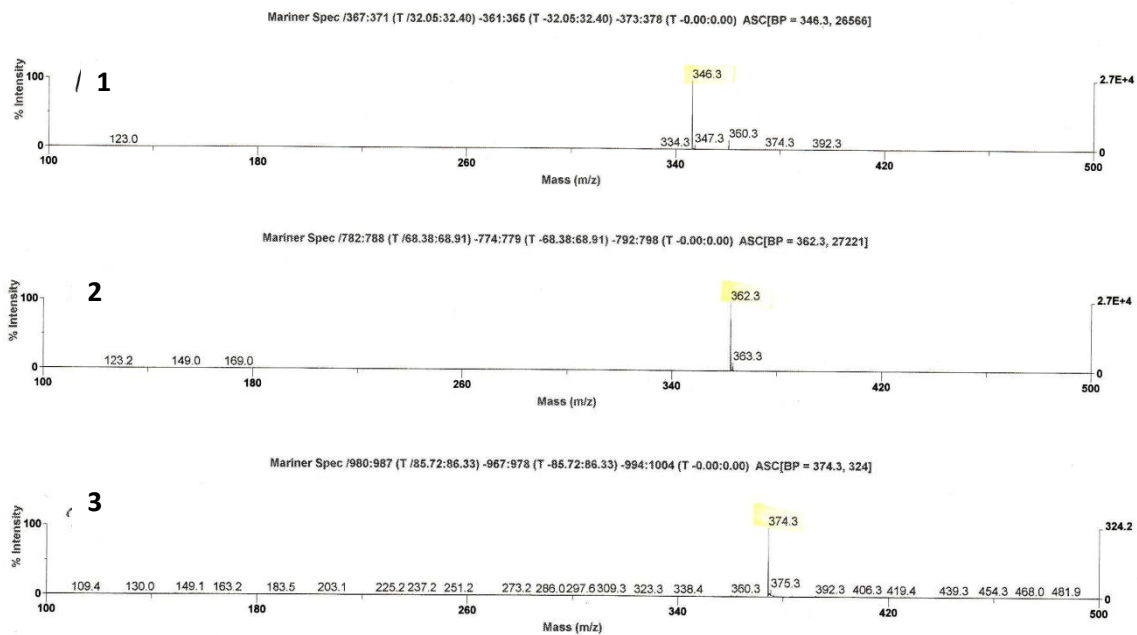
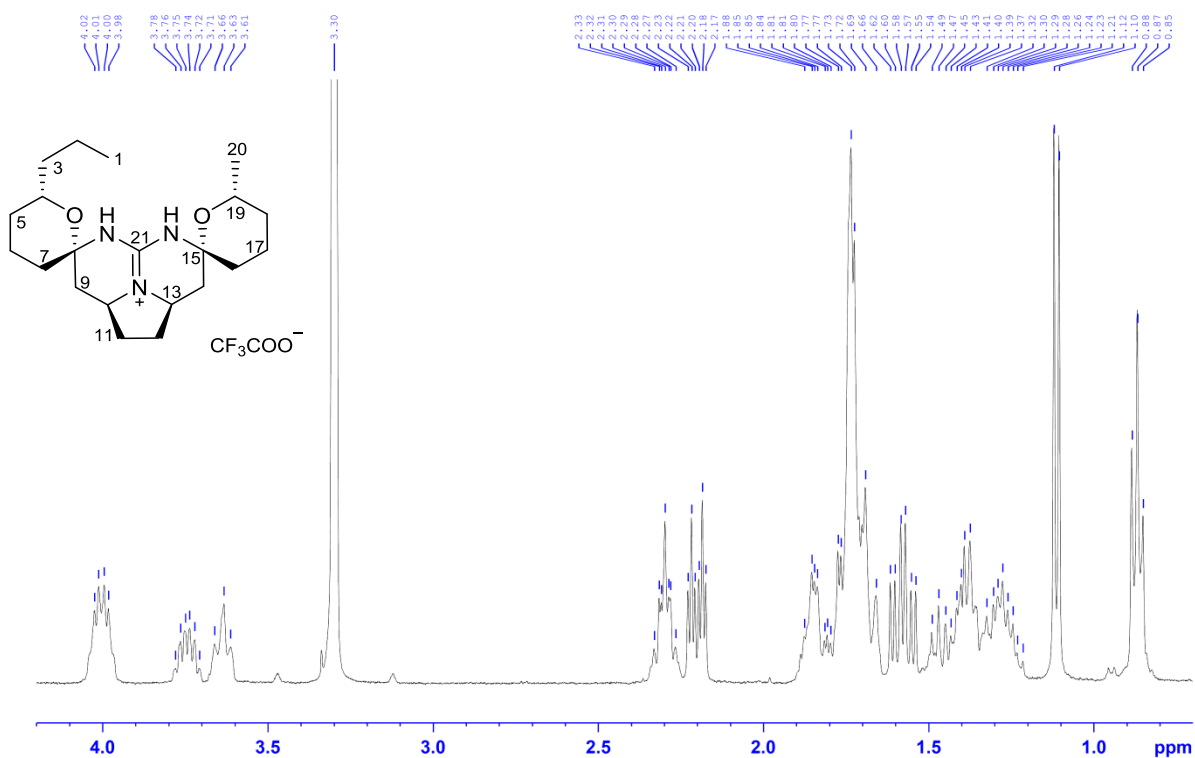
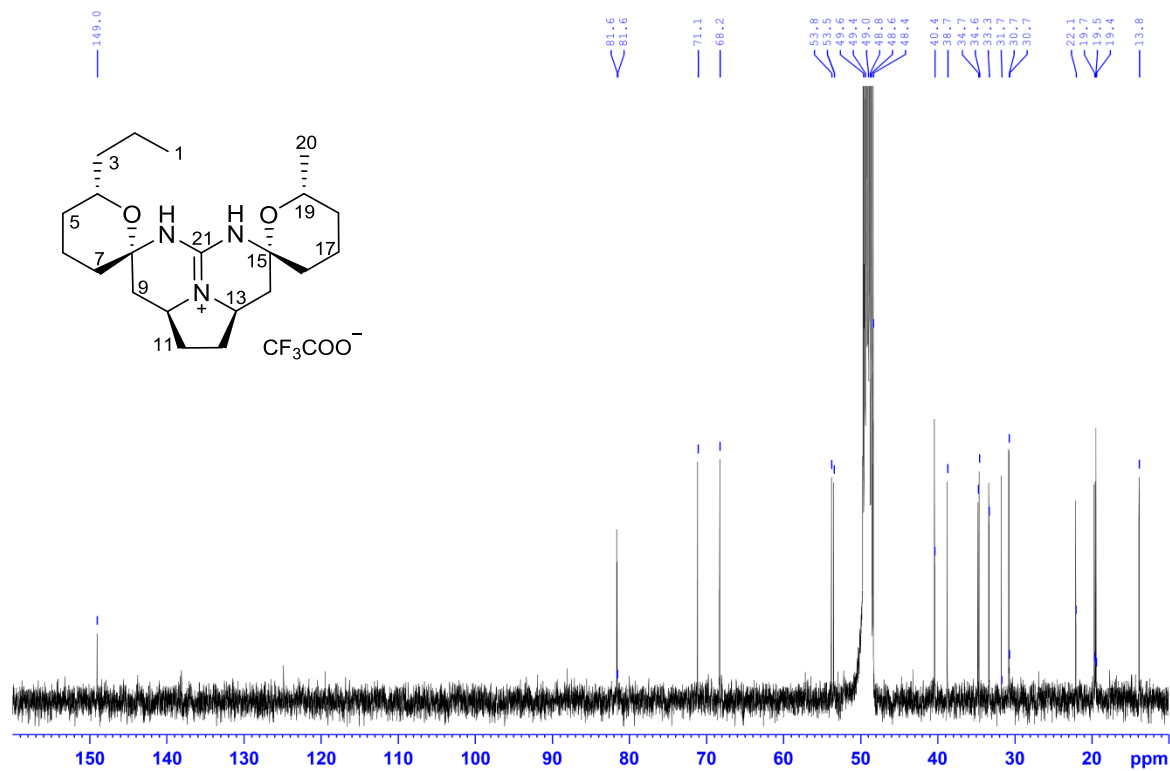
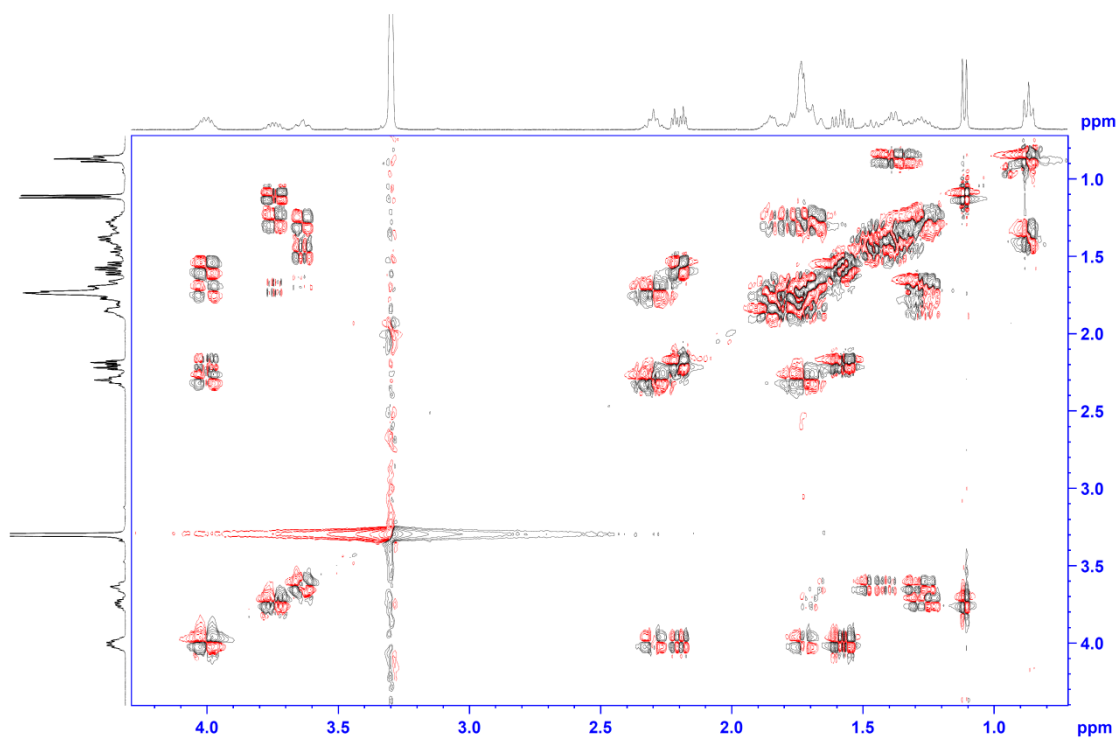


Figure S9: ESI-TOF-MS(+) spectra of 1–3.

Figure S10: ¹H NMR spectrum of 2 (400 MHz, CD₃OD).

Figure S11: ^{13}C NMR spectrum of 2 (100 MHz, CD_3OD).Figure S12: DQF-COSY spectrum of 2 (400 MHz, CD_3OD).

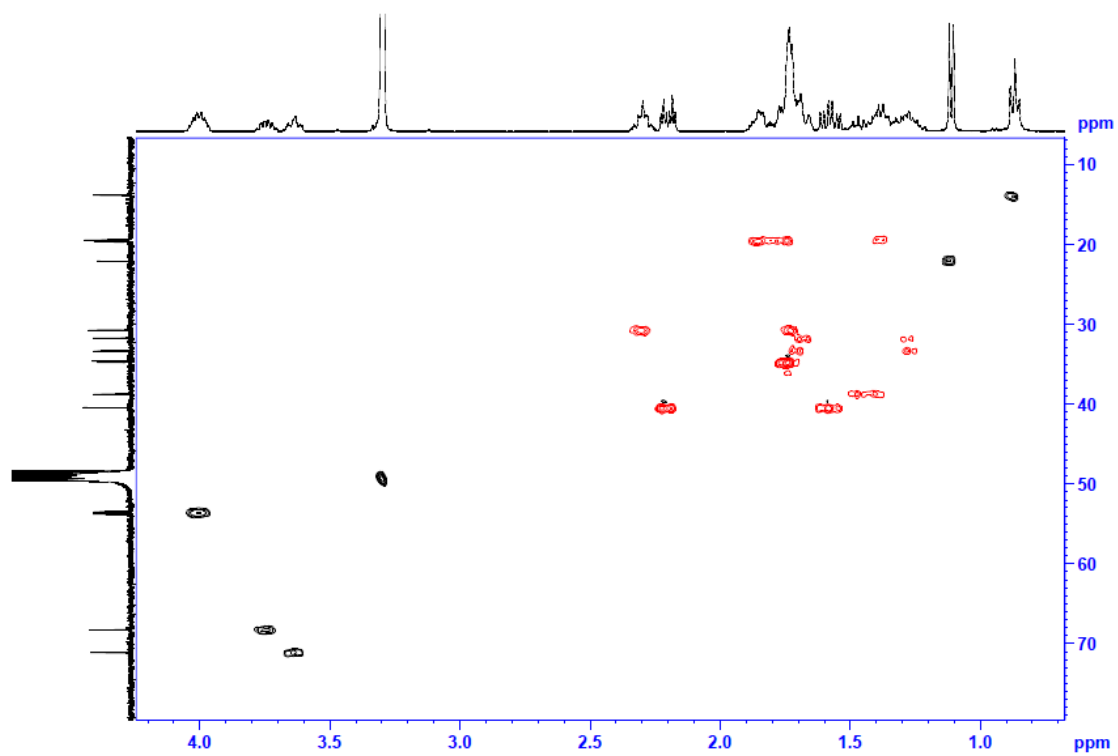


Figure S13: HSQC spectrum of **2** (400 MHz, CD₃OD).

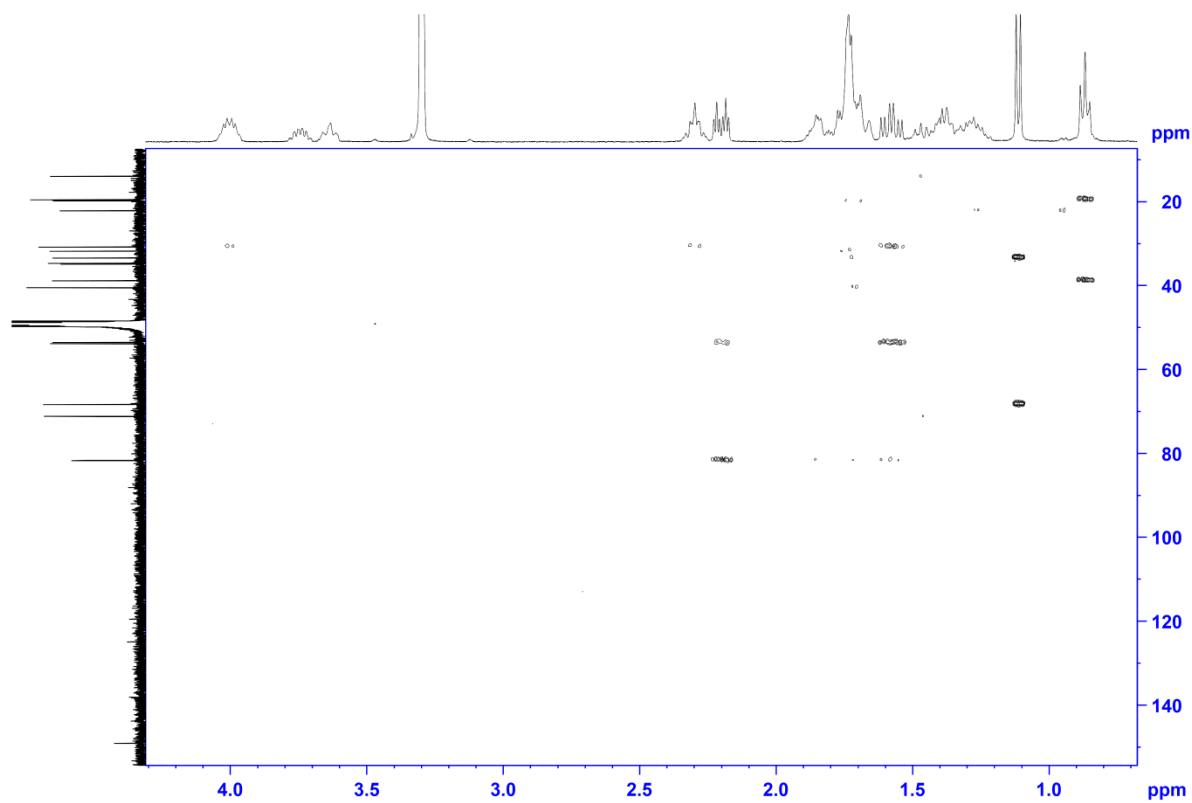


Figure S14: HMBC spectrum of **2** (400 MHz, CD₃OD).

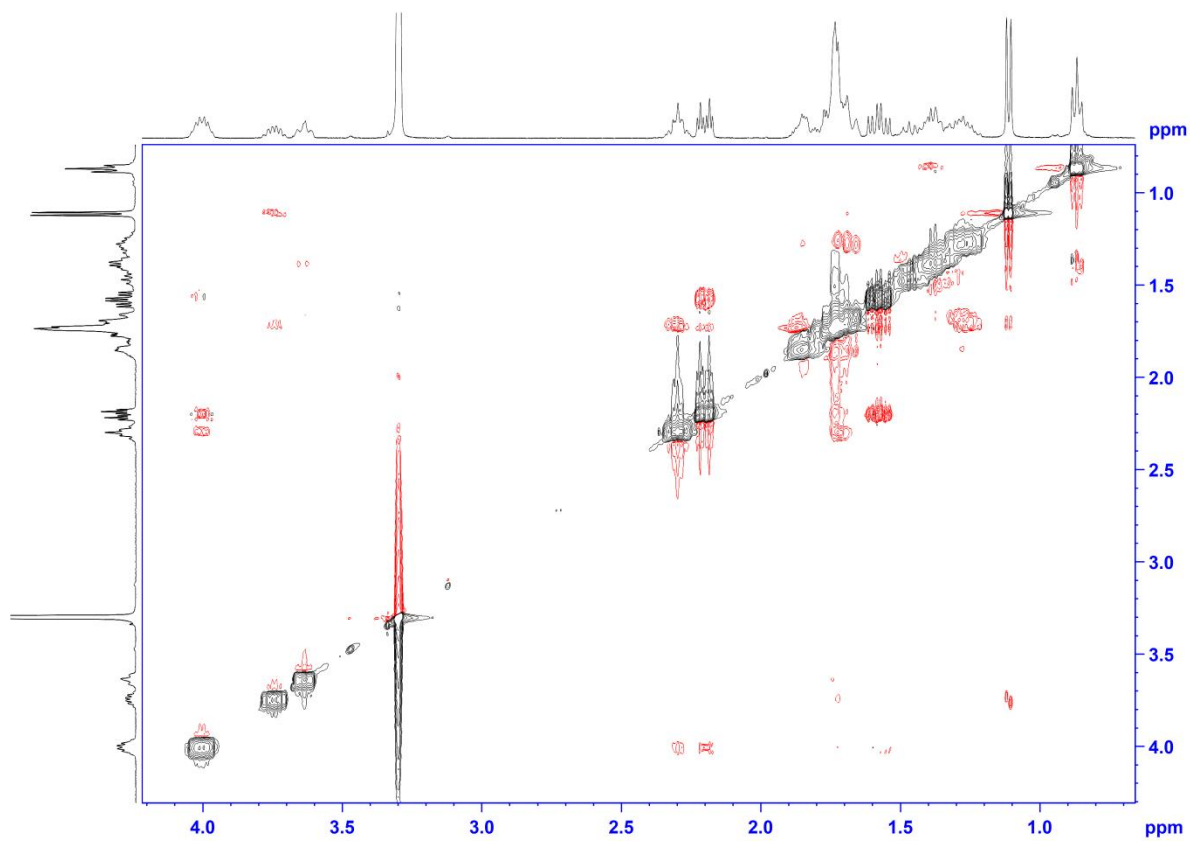
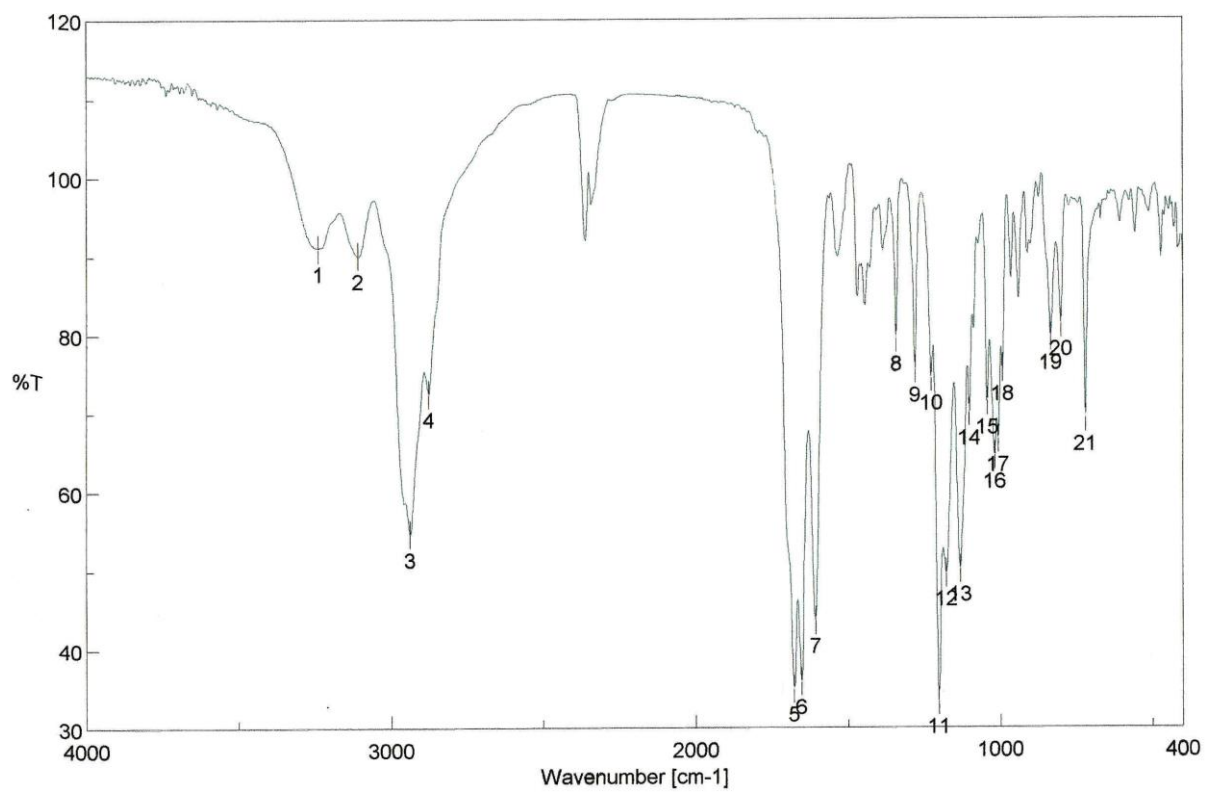
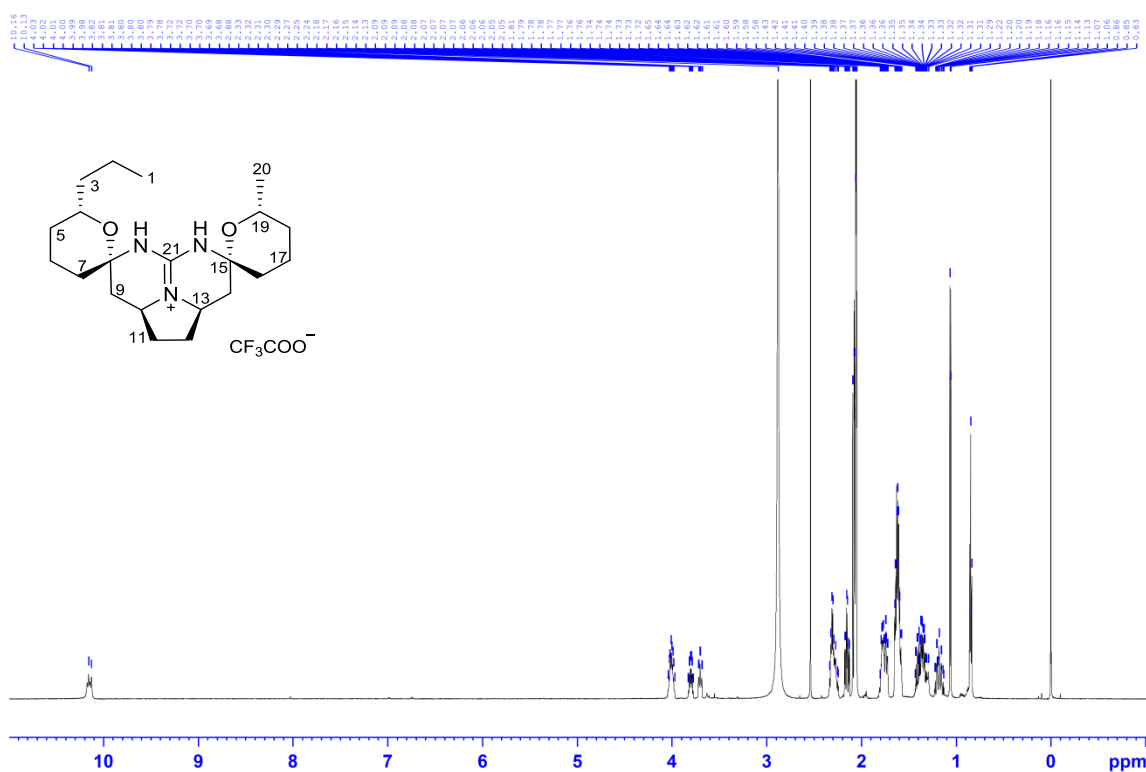
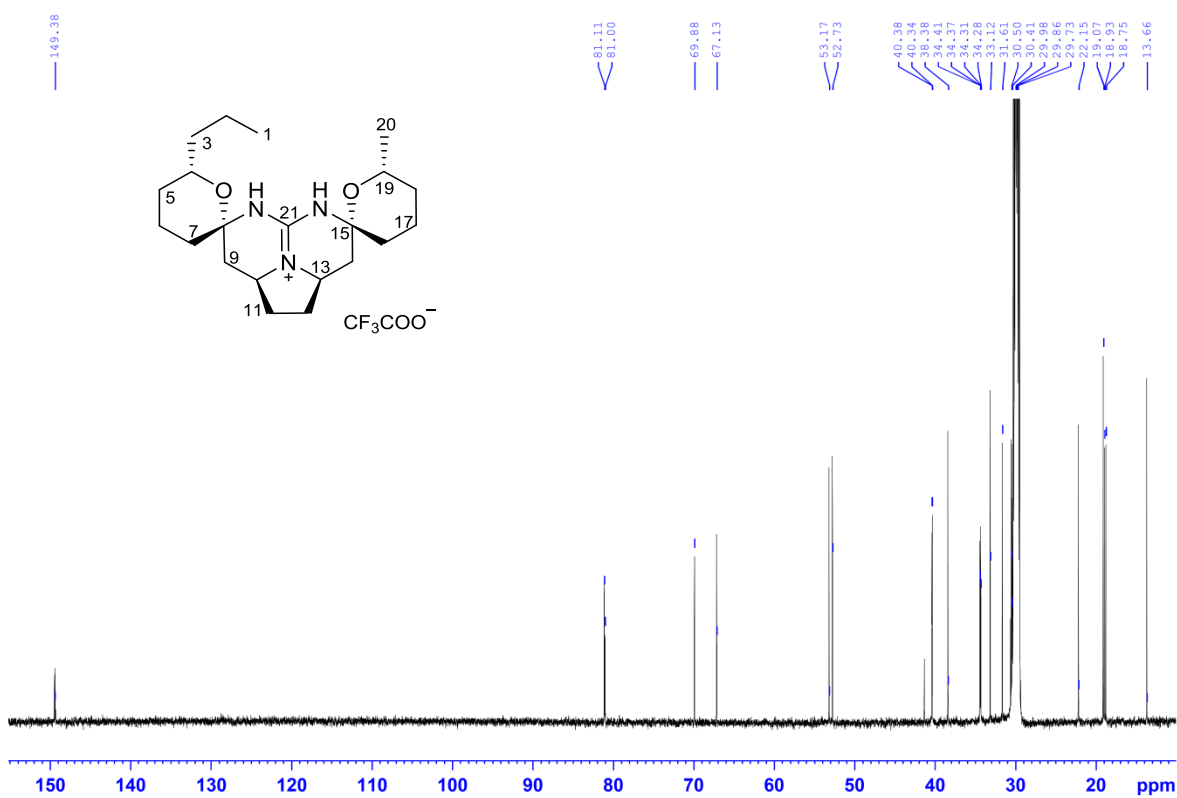
Figure S15: NOESY spectrum of 2 (400 MHz, CD₃OD).

Figure S16: IR spectrum of 2.

Figure S17: ^1H NMR spectrum of **2** (600 MHz, acetone- d_6).Figure S18: ^{13}C NMR spectrum of **2** (150 MHz, acetone- d_6).

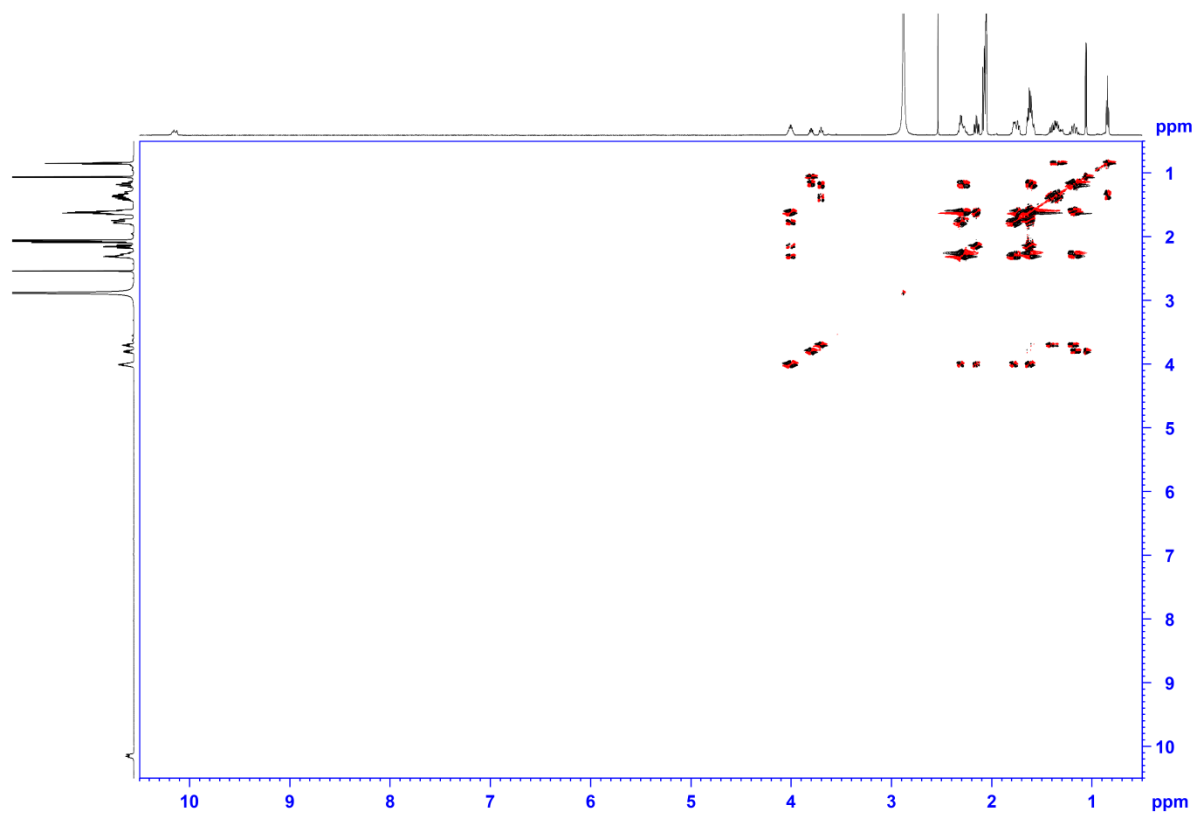


Figure S19: DQF-COSY spectrum of **2** (600 MHz, acetone-*d*₆).

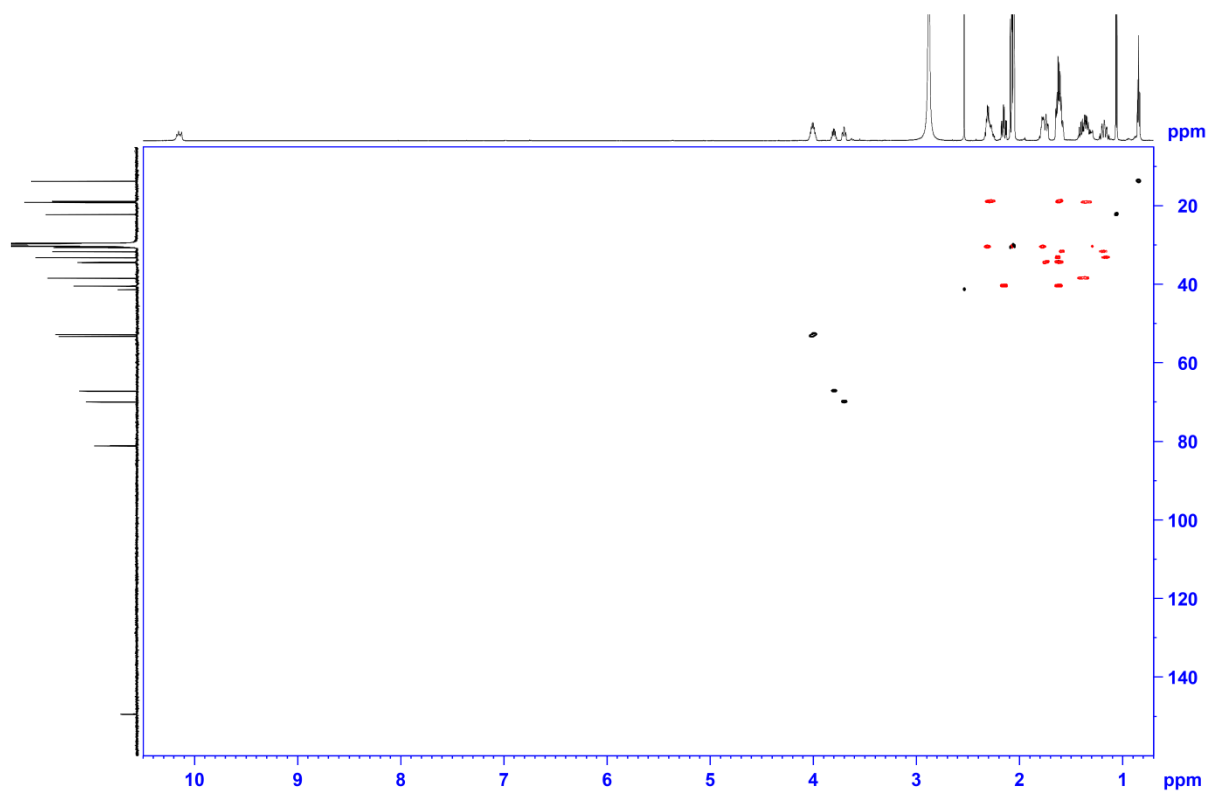


Figure S20: HSQC spectrum of **2** (600 MHz, acetone-*d*₆).

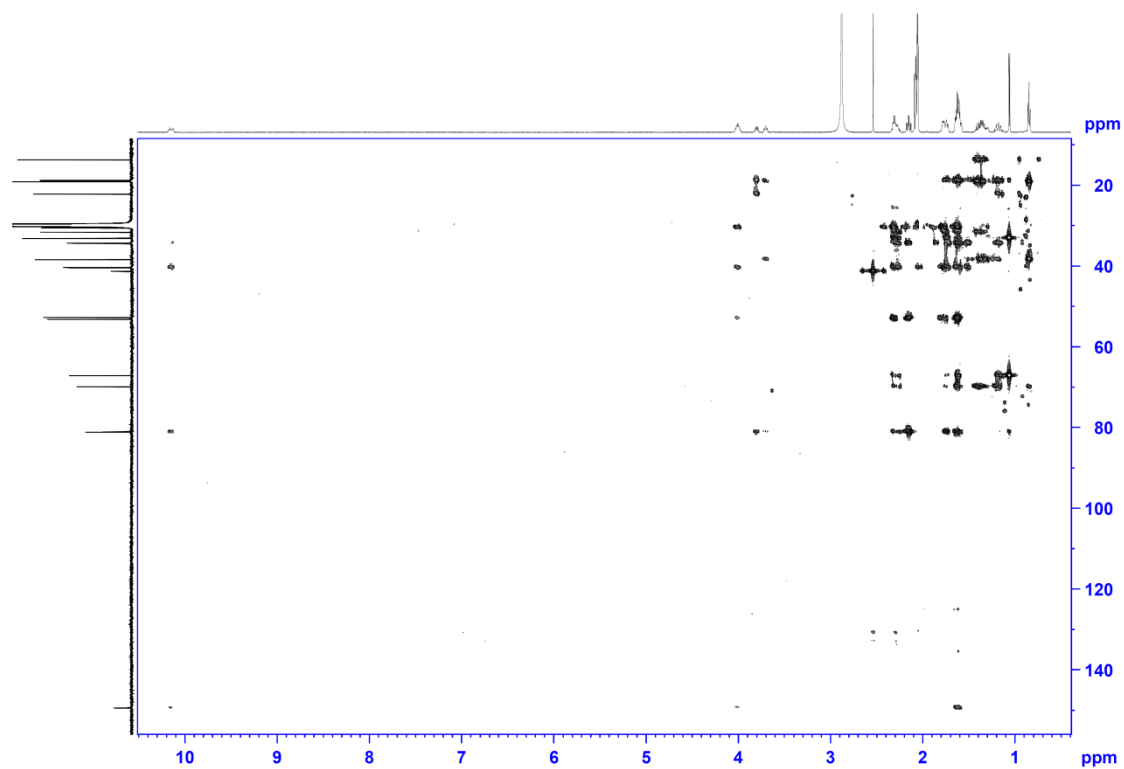


Figure S21: HMBC spectrum of **2** (600 MHz, acetone-*d*₆).

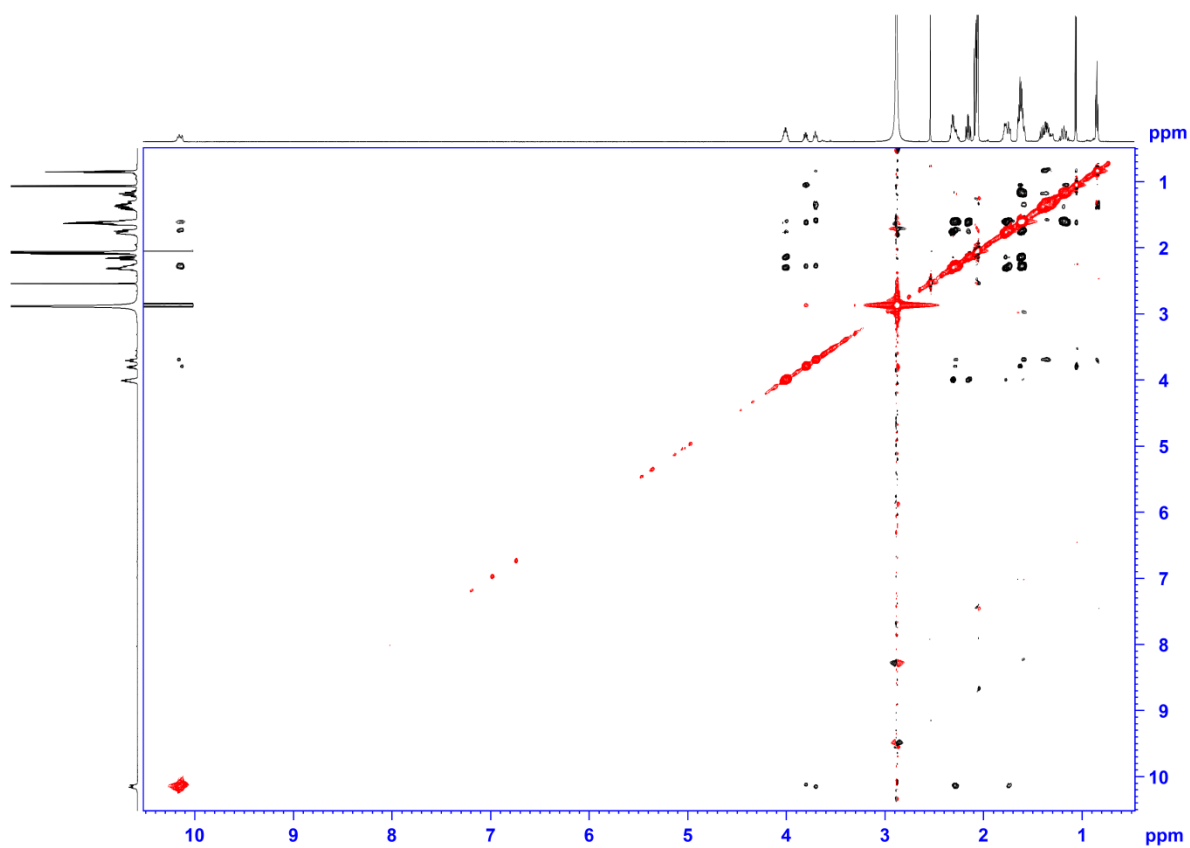
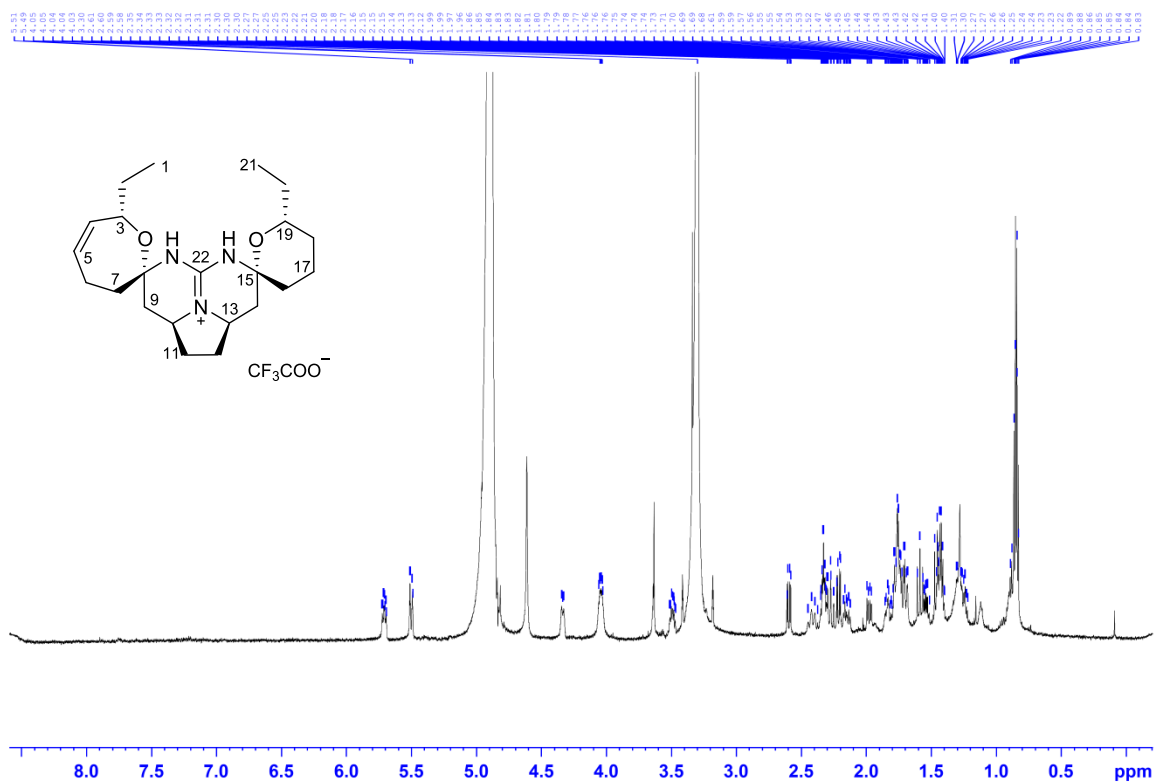
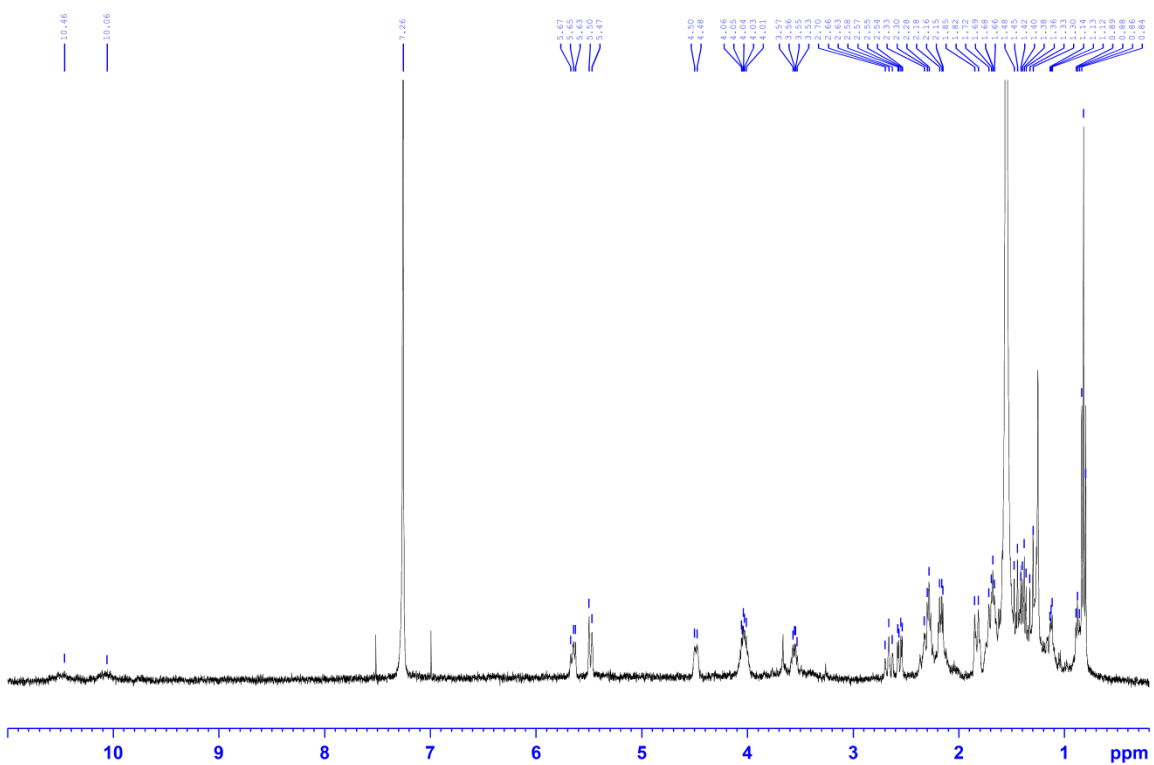
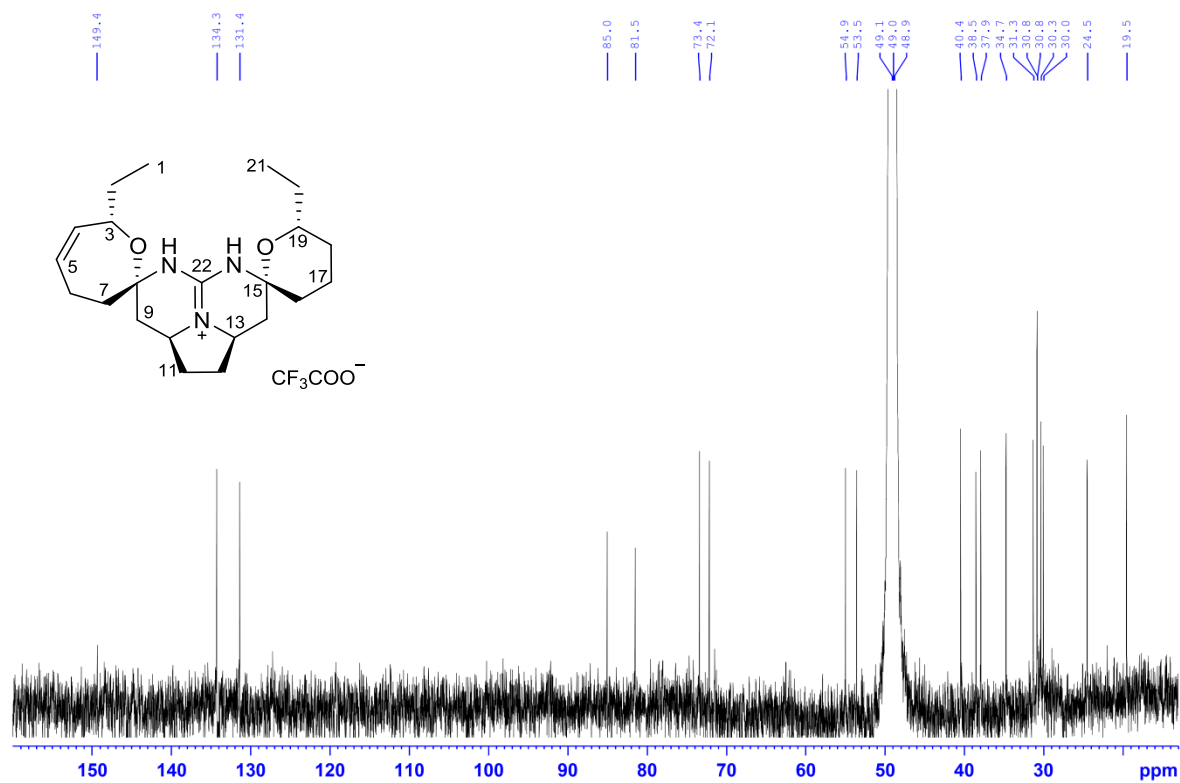
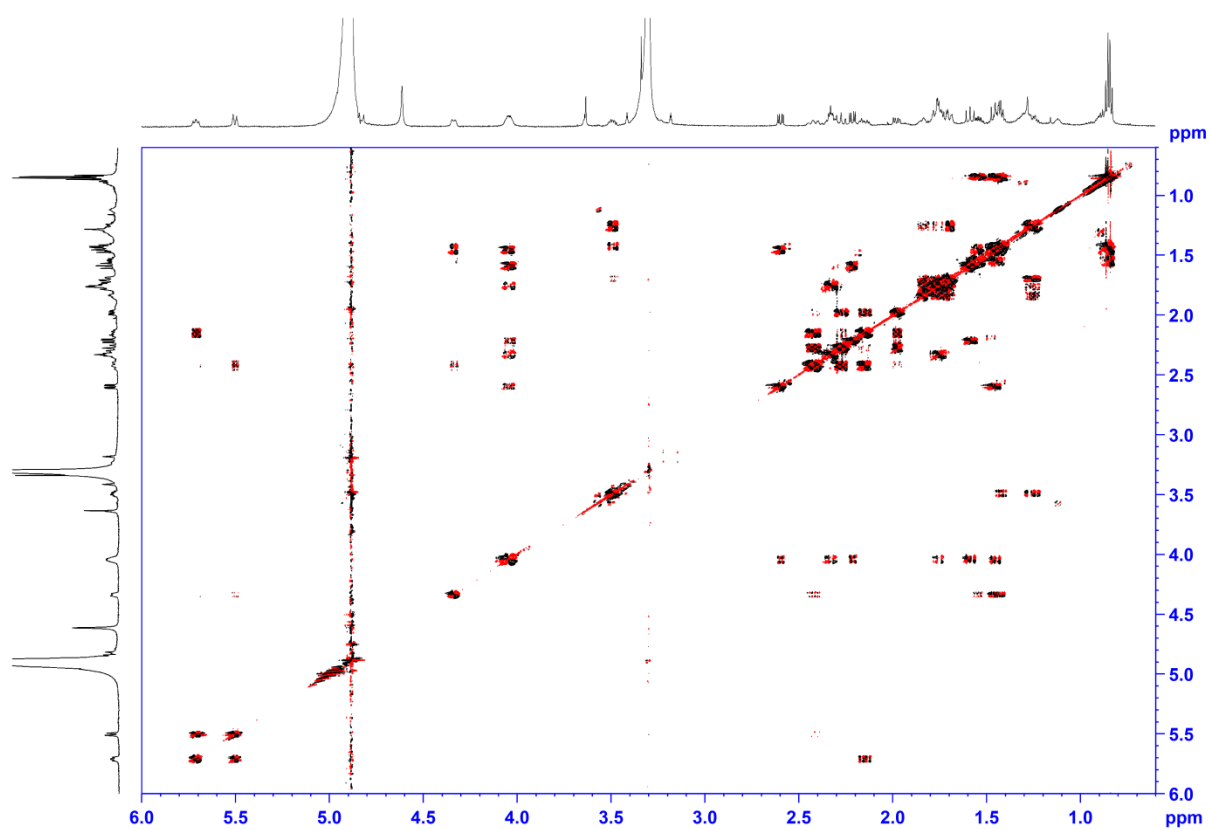
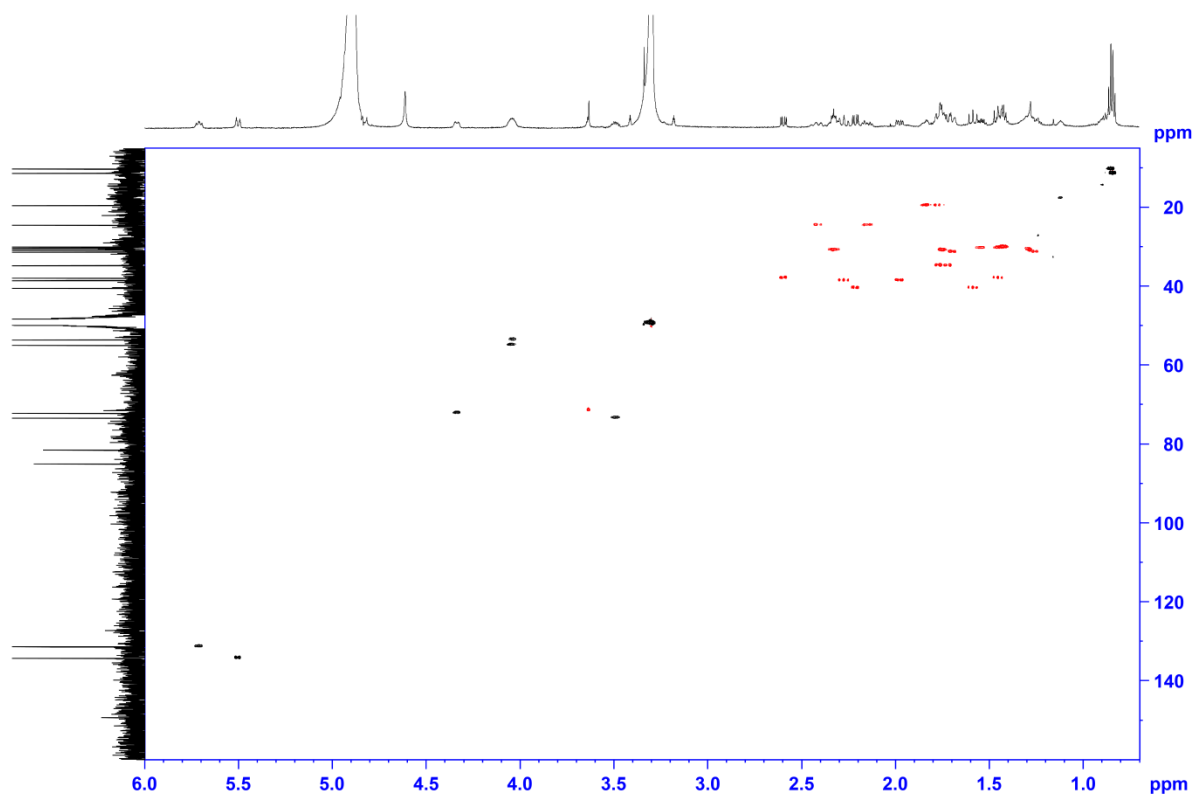
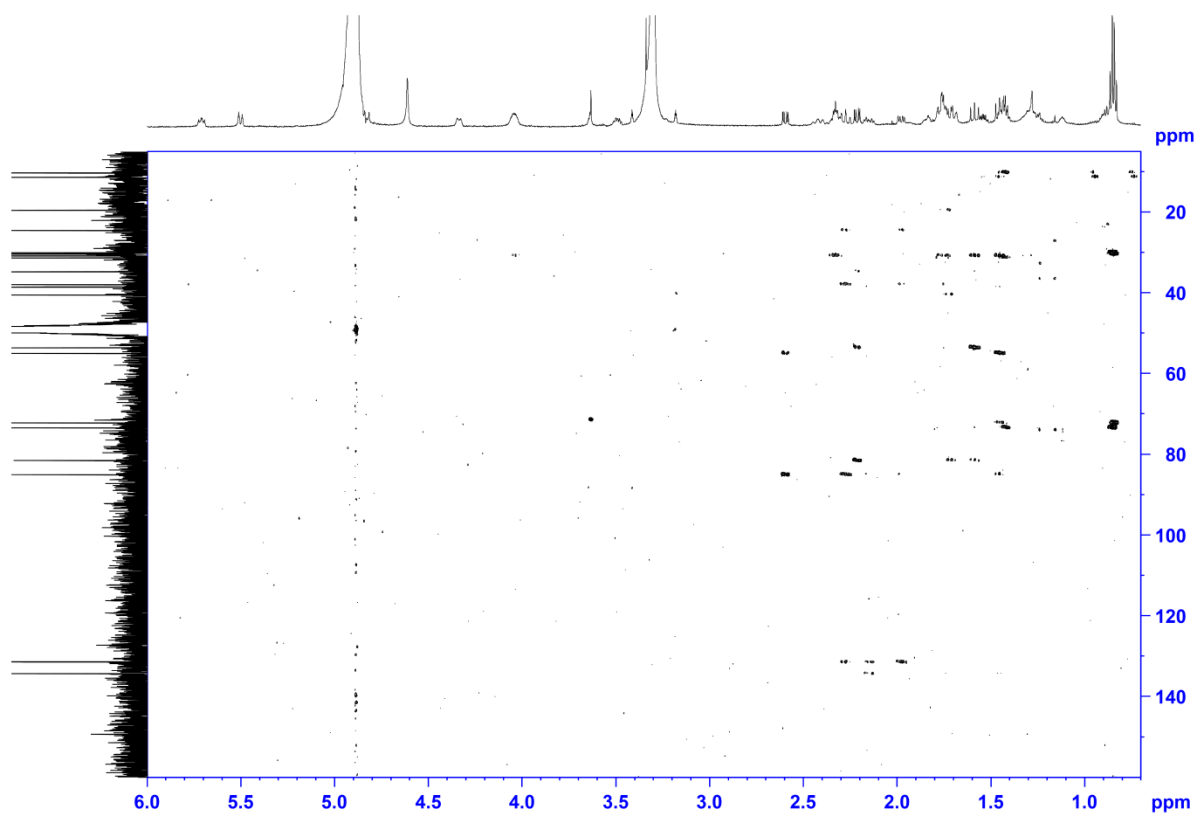


Figure S22: NOESY spectrum of **2** (600 MHz, acetone-*d*₆).

Figure S23: ^1H NMR spectrum of **3** (600 MHz, CD_3OD).Figure S24: ^1H NMR spectrum of **3** (400 MHz, CDCl_3).

Figure S25: ^{13}C NMR spectrum of 3 (150 MHz, CD_3OD).Figure S26: DQF-COSY spectrum of 3 (600 MHz, CD_3OD).

Figure S27: HSQC spectrum of **3** (600 MHz, CD₃OD).Figure S28: HMBC spectrum **3** (600 MHz, CD₃OD).

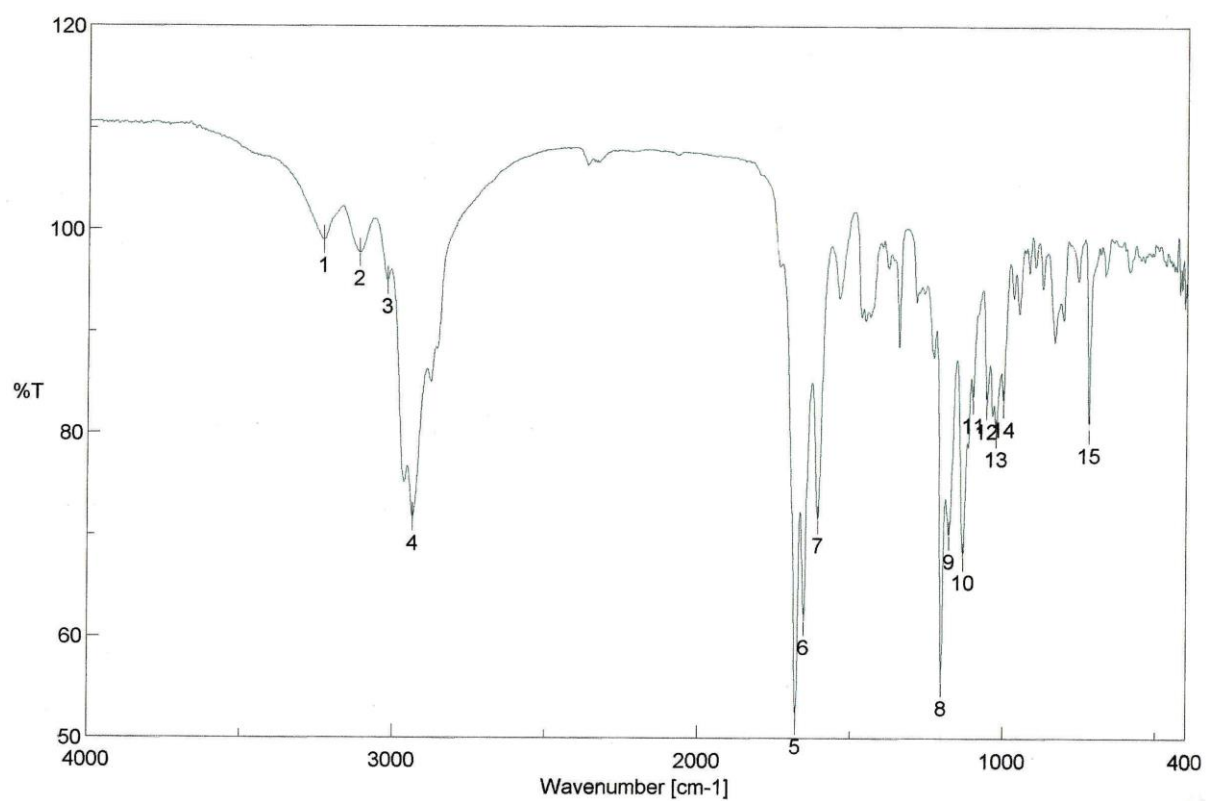
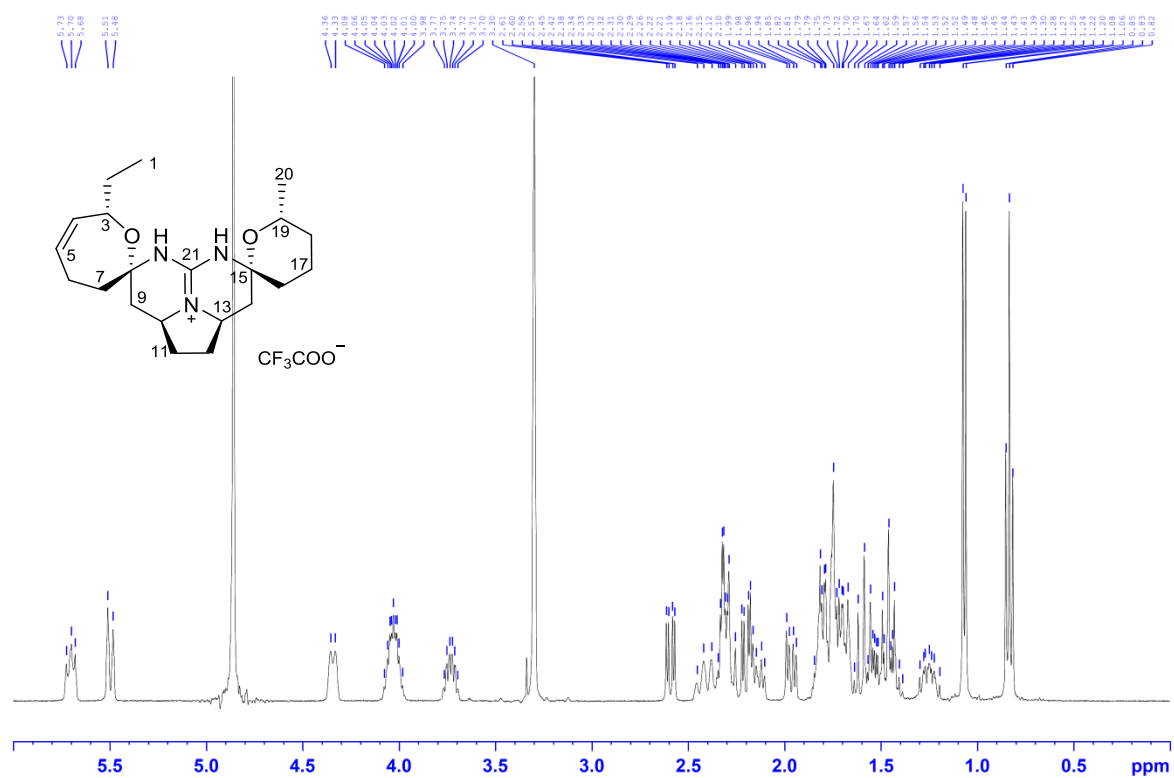
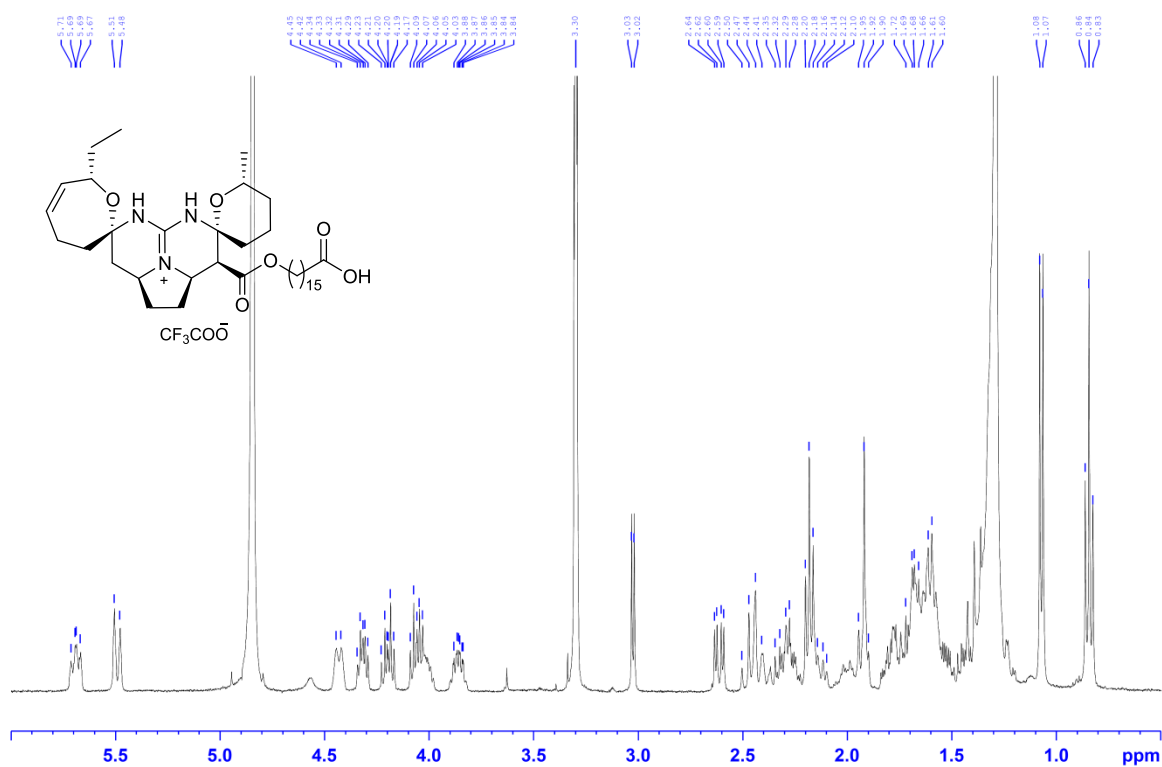
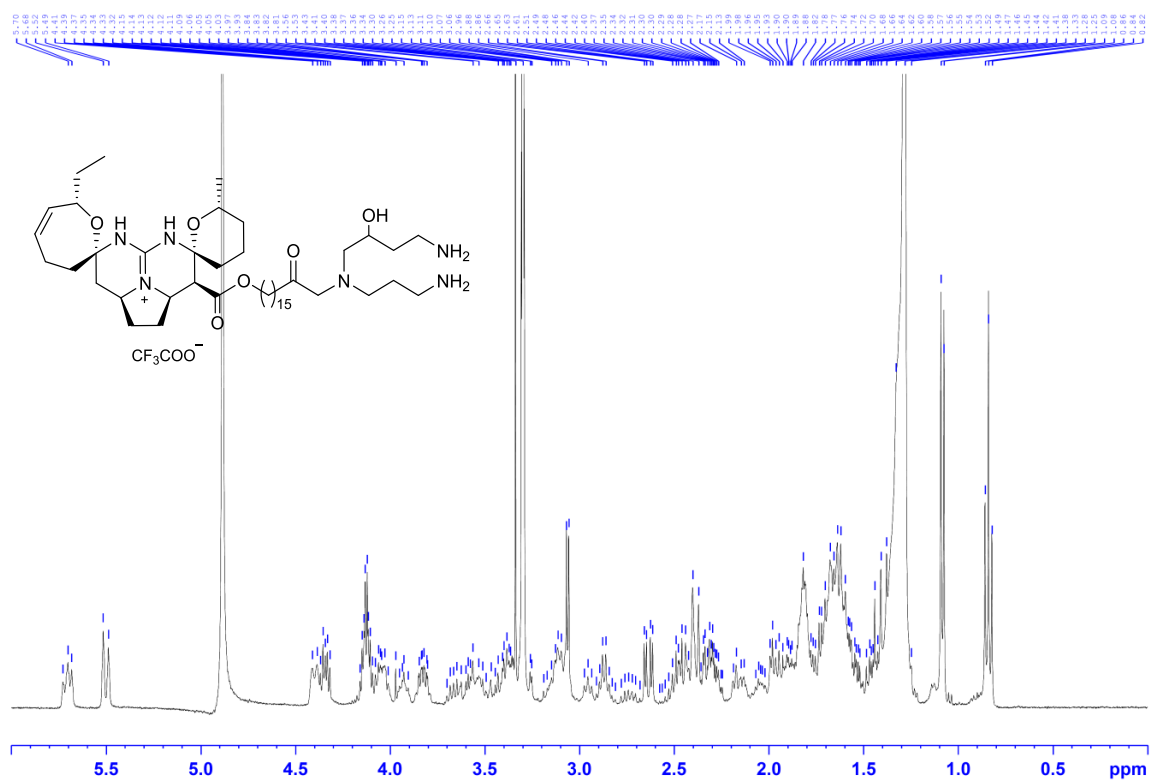


Figure S29: IR spectrum of 3.

Figure S30: ¹H NMR spectrum 4 (400 MHz, CD₃OD).

Figure S31: ¹H NMR spectrum 5 (400 MHz, CD₃OD).Figure S32: ¹H NMR spectrum 6 (400 MHz, CD₃OD).

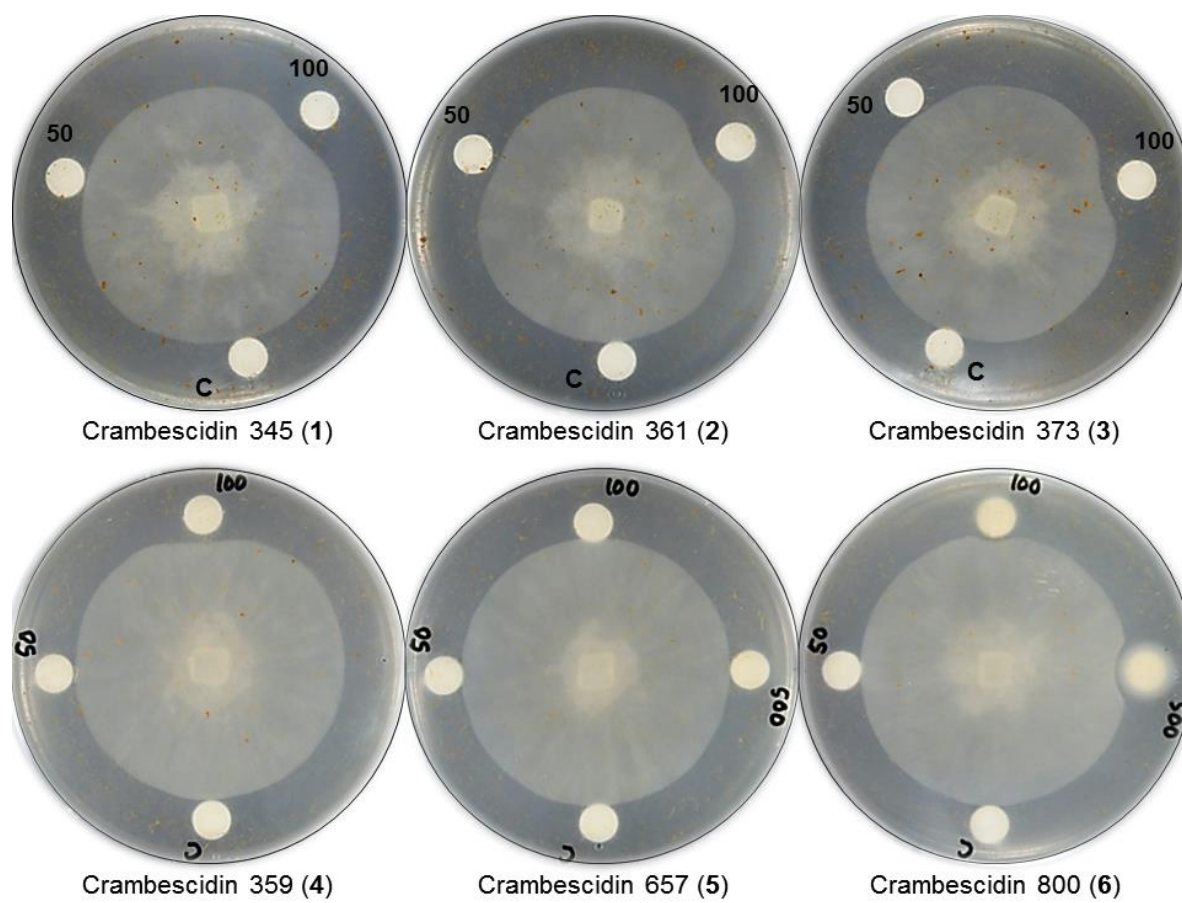


Figure S33: Anti-oomycete activity of 1–6.