Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

Synthesis of Nano-Scale Carceplexes from Deep-Cavity Cavitands

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General experimental methods. All reagents were purchased from various commercial sources and used without further purification. All reactions were run under a nitrogen atmosphere. The synthesis of **1** has been reported previously.[31] Flash chromatography (silica gel 60 Å, 230-400 mesh; Natland International) was used for product purification. Melting points were determined on a Mel-Temp II apparatus and are uncorrected. The NMR spectra were recorded on a Varian 400 MHz or 500 MHz spectrometer. The mass spectra were recorded on an Applied Biosystems 4700 Reflector MALDI-TOF mass spectrometer and high-resolution mass spectra were obtained with internal calibration using Opti-TOF^{TM} Cal Mix 5 (Applied Biosystems). Elemental analyses were performed by Atlantic Microlab Inc.

General procedure for the synthesis of carceplexes: To a mixture of the tetraphenol **1** (87 mg; 0.05 mmol) and the corresponding template (0.5 mmol) in anhydrous DMA (25 mL) under nitrogen atmosphere was added DBU (37 μL; 0.25 mmol). After stirring at rt for 10 min, $BrCH_2Cl$ (34 μL; 0.5 mmol) was added and the reaction mixture was heated to 60 °C for 24 h. After this time, an additional portion of $BrCH_2Cl$ (34 μL; 0.5 mmol) was added and the reaction was continued for another 24 h. The reaction mixture was then cooled to rt. DMA was removed under reduced pressure, water was added and extracted with $CHCl_3$ (three times). The organic layers were combined, dried with anhydrous Na_2SO_4, filtered and the solvent was removed. The crude product was loaded on a column (SiO_2) and eluted with CH_2Cl_2/hexane (9:1) to 100% CH_2Cl_2 to give the carceplex as a white solid. An analytical sample was prepared by washing the solid with ether (three times) and drying at 120 °C under vacuum for 3 h.

Carceplex 3@2: The crude product was washed with methanol to remove excess template before purifying by column chromatography. Yield = 5%; Mp > 250 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ –3.01 (d, *J* = 2.4 Hz, 1H), –1.23 (s, 3H), –0.91-1.28 (m, 3H), –0.71-0.74 (m, 1H), –0.35-0.37 (m, 3H), –0.16 (s, 3H), 0.06-0.07 (m, 3H), 0.18-0.20 (m, 1H), 0.37-0.40 (m, 2H), 0.65-0.68 (m, 1H), 0.77 (m, 1H), 0.94 (m, 2H), 1.04-1.12 (m, 2H), 1.21-1.25 (m, 1H), 2.51-2.63 (m, 32H), 4.04 (m, 1H), 4.30 (s, 4H), 4.56 (s, 4H), 4.80 (t, *J* = 7.4 Hz, 8H), 5.95 (s, 8H), 6.32 (s, 8H), 6.58-6.60 (m, 24H), 7.10-7.12 (m, 16H), 7.20-7.22 (m, 48H), 7.48-7.52 (m, 8H). MS (MALDI-TOF) *m/z*: $(M + Ag)^+$ calcd, 3935.98; found, 3936.58. Anal. Calcd for $C_{247}H_{188}O_{42}\cdot 0.5CH_2Cl_2$: C, 76.80; H, 4.92. Found C, 76.69; H, 4.84.

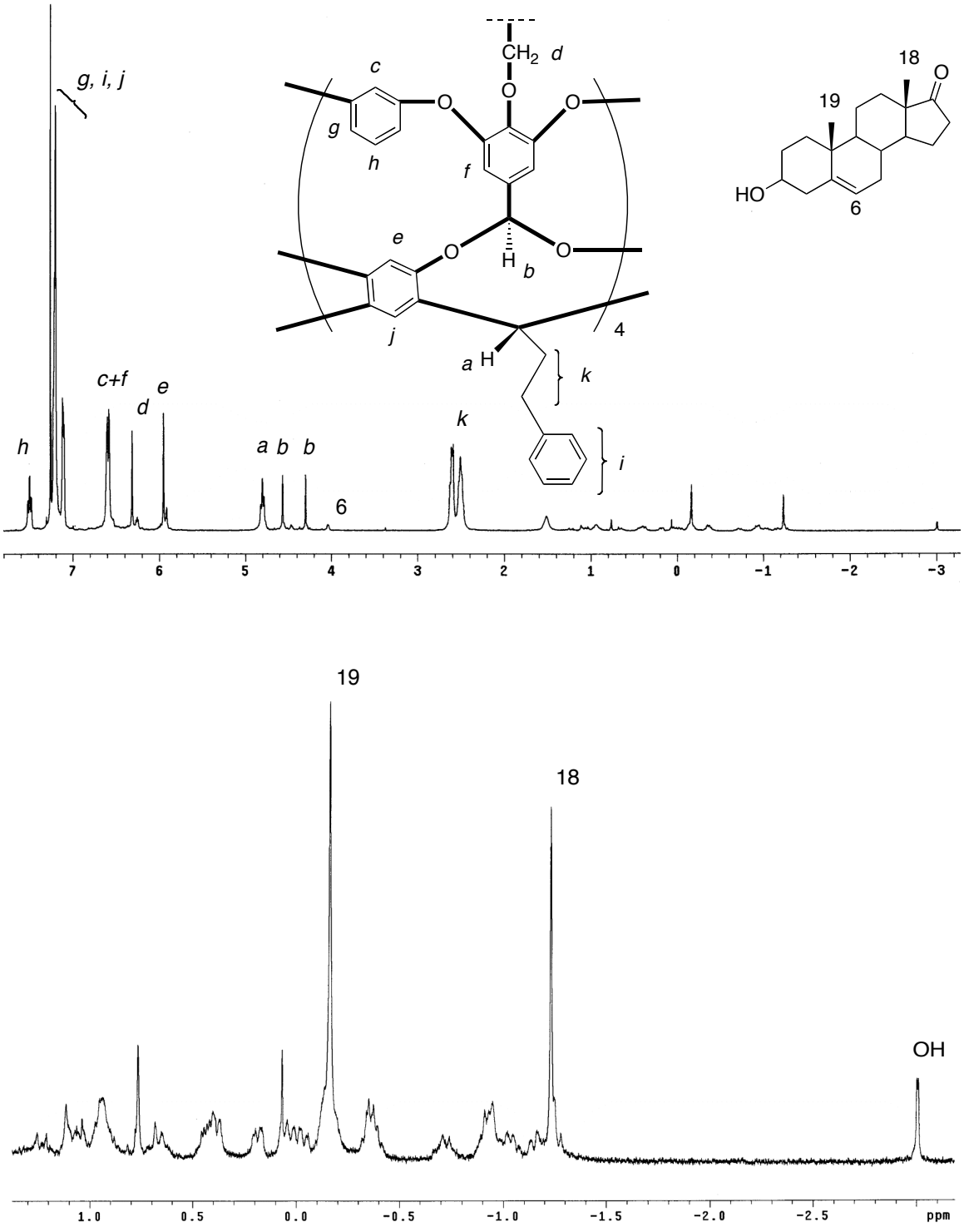
Carceplex 4@2: Yield = 9%; Mp > 250 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ –1.69 (m, 1H), –1.45-1.50 (m, 2H), –1.34 (s, 3H), –1.21-1.26 (m, 2H), –0.79-1.02 (m, 6H), –0.46-0.59 (m, 4H), –0.36 (s, 3H), –0.03-0.04 (m, 2H), 0.24-0.53 (m, 6H), 0.69 (m, 2H), 0.88-0.90 (m, 1H), 2.51-2.63 (m, 32H), 4.22 (s, 4H), 4.31 (s, 4H), 4.80 (t, *J* = 7.6 Hz, 8H), 5.90 (s, 4H), 5.94 (s, 4H), 6.35 (s, 8H), 6.52 (s, 4H), 6.56 (s, 4H), 6.59 (s, 4H), 6.62 (s, 4H), 6.73-6.75 (m, 8H), 7.10-7.12 (m, 16H), 7.20 (m, 48 H), 7.47-7.52 (m, 8H); MS (MALDI-TOF) *m/z*: $(M + Ag)^+$ calcd, 3908.01; found, 3908.94. Anal. Calcd for $C_{247}H_{192}O_{40}\cdot H_2O$: C, 77.70; H, 5.12. Found C, 77.41; H, 5.09.

Carceplex 5@2: Yield = 2%; Mp > 250 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ –2.15 (s, 3H), –1.49 (s, 3H), –0.53-0.71 (m, 4H), –0.19-0.25 (m, 6H), 0.30 (s, 3H), 0.42-0.64 (m,

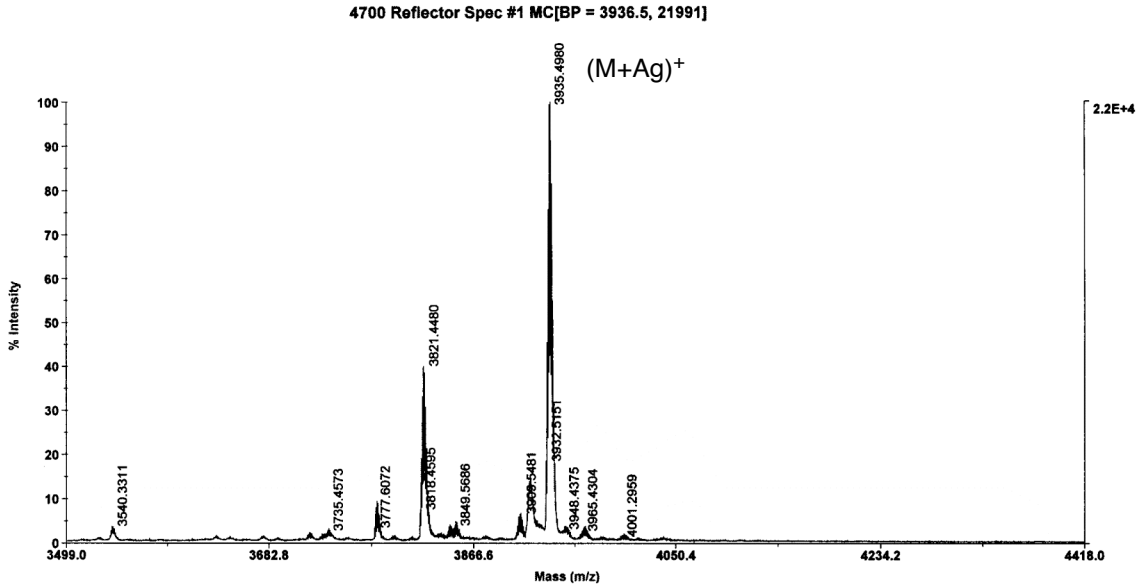
4H), 0.82-0.95 (m, 3H), 1.21-1.25 (m, 1H), 1.36 (m, 2H), 2.51-2.61 (m, 32H), 3.03 (s, 1H), 4.38 (s, 4H), 4.41 (s, 4H), 4.76-4.85 (m, 8H), 5.83 (s, 4H), 5.99 (s, 4H), 6.32 (d, *J* = 5.2 Hz, 4H), 6.42 (d, *J* = 5.2 Hz, 4H), 6.52 (s, 4H), 6.54 (s, 4H), 6.57 (s, 4H), 6.63-6.64 (m, 8H), 6.69 (t, *J* = 2.0 Hz, 4H), 7.10-7.13 (m, 16H), 7.18-7.24 (m, 48H), 7.47-7.53 (m, 8H). HRMS (MALDI-TOF) *m/z*: $(C_{249}H_{190}O_{42} + Ag)^+$ calcd, 3958.1783; found, 3958.1809.

Carceplex 9@2: Yield = 5%; Mp > 250 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ –0.76 (s, 4H), –0.52 (s, 4H), –0.04 (d, *J* = 11.6 Hz, 8H), 0.37 (d, *J* = 11.2 Hz, 8H), 1.73 (s, 4H), 2.51-2.61 (m, 32H), 4.23 (s, 8H), 4.81 (t, *J* = 7.8 Hz, 8H), 5.92 (s, 8H), 6.35 (s, 8H), 6.55 (s, 16H), 6.72 (m, 8H), 7.10-7.11 (m, 16H), 7.20-7.26 (m, 48H), 7.50 (m, 8H). HRMS (MALDI-TOF) *m/z*: $(C_{248}H_{188}O_{40}+ Ag)^+$ calcd, 3915.1828; found, 3915.1809.

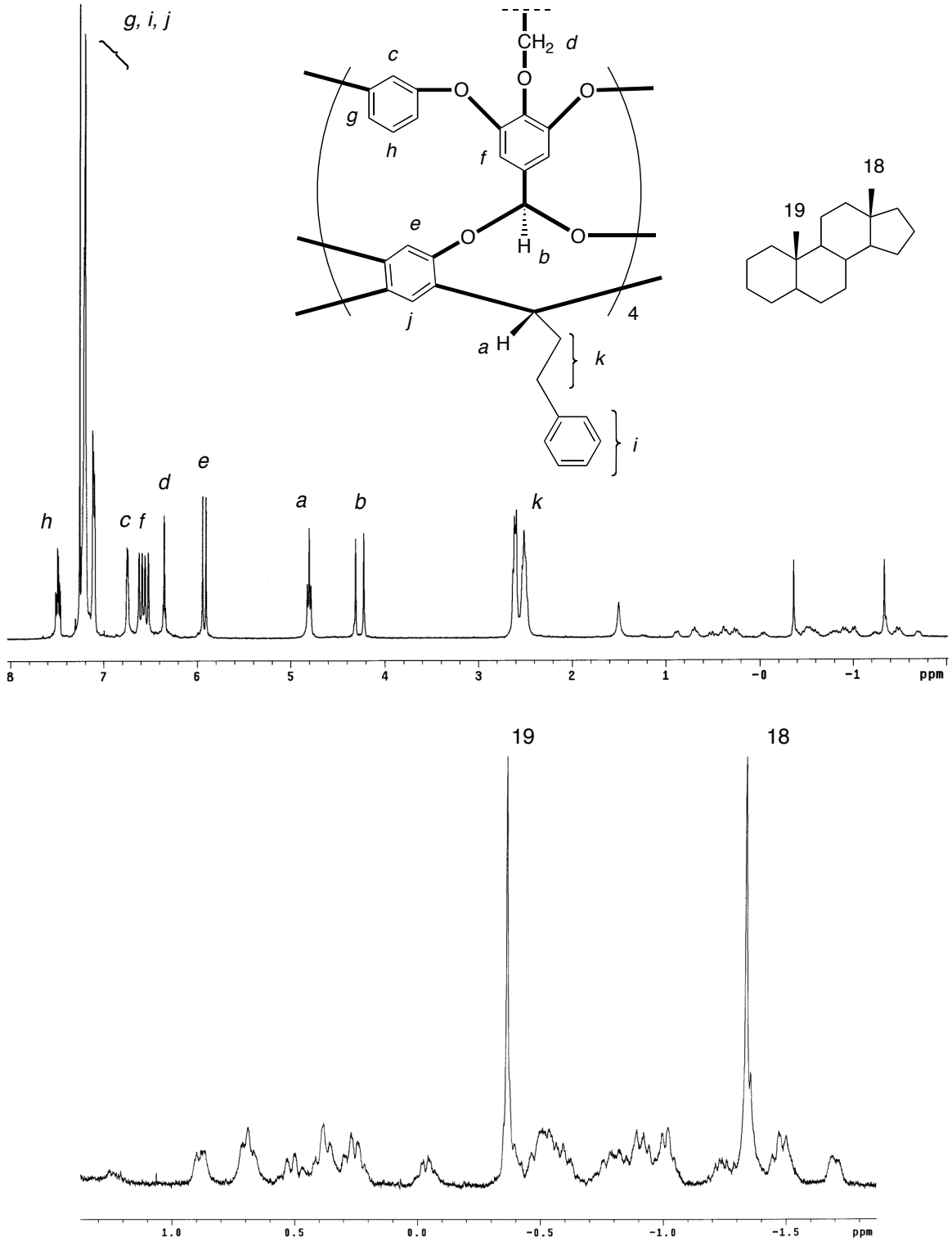
Carceplex 10@2: Yield = 38%; Mp > 250 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ – 0.88 (d, *J* = 11.6 Hz, 6H), – 0.33 (s, 6H), – 0.04 (d, *J* = 11.2 Hz, 6H), 0.45 (s, 12H), 2.49-2.63 (m, 32H), 4.18 (s, 8H), 4.80 (t, *J* = 7.8 Hz, 8H), 5.91 (s, 8H), 6.36 (s, 8H), 6.55 (s, 16H), 6.77 (t, *J* = 2.2 Hz, 8H), 7.10-7.12 (m, 16H), 7.20-7.23 (m, 48H), 7.50 (t, *J* = 8.2 Hz, 8H). MS (MALDI-TOF) *m/z*: $(M + Ag)^+$ calcd, 3918.01; found, 3917.64. Anal. Calcd for $C_{248}H_{190}O_{40}\cdot H_2O$: C, 77.81; H, 5.06. Found C, 77.64; H, 5.06.



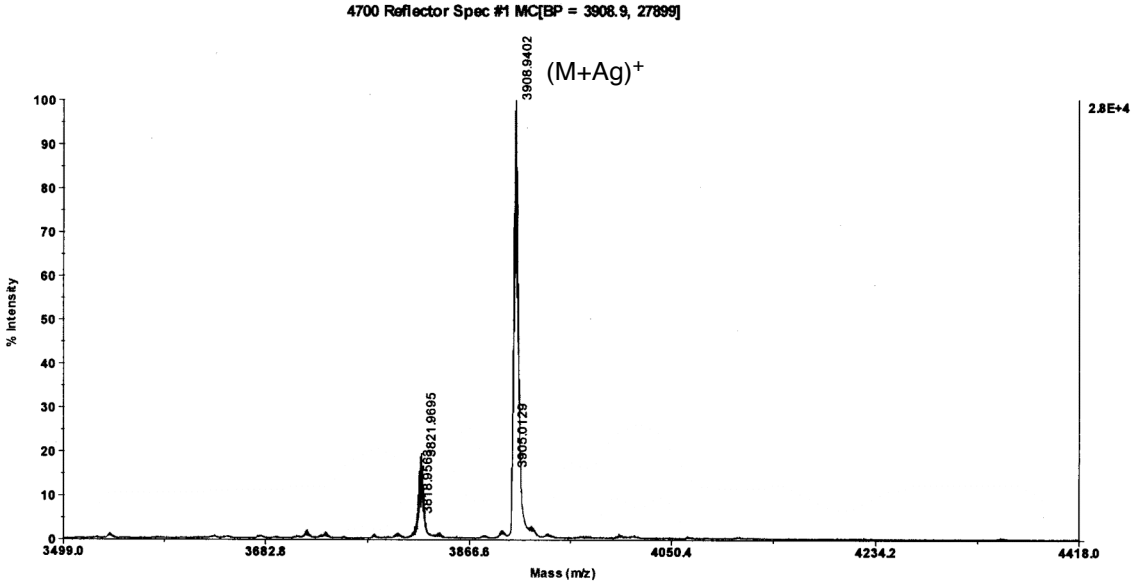
^{1}H NMR spectrum of carceplex **3@2**



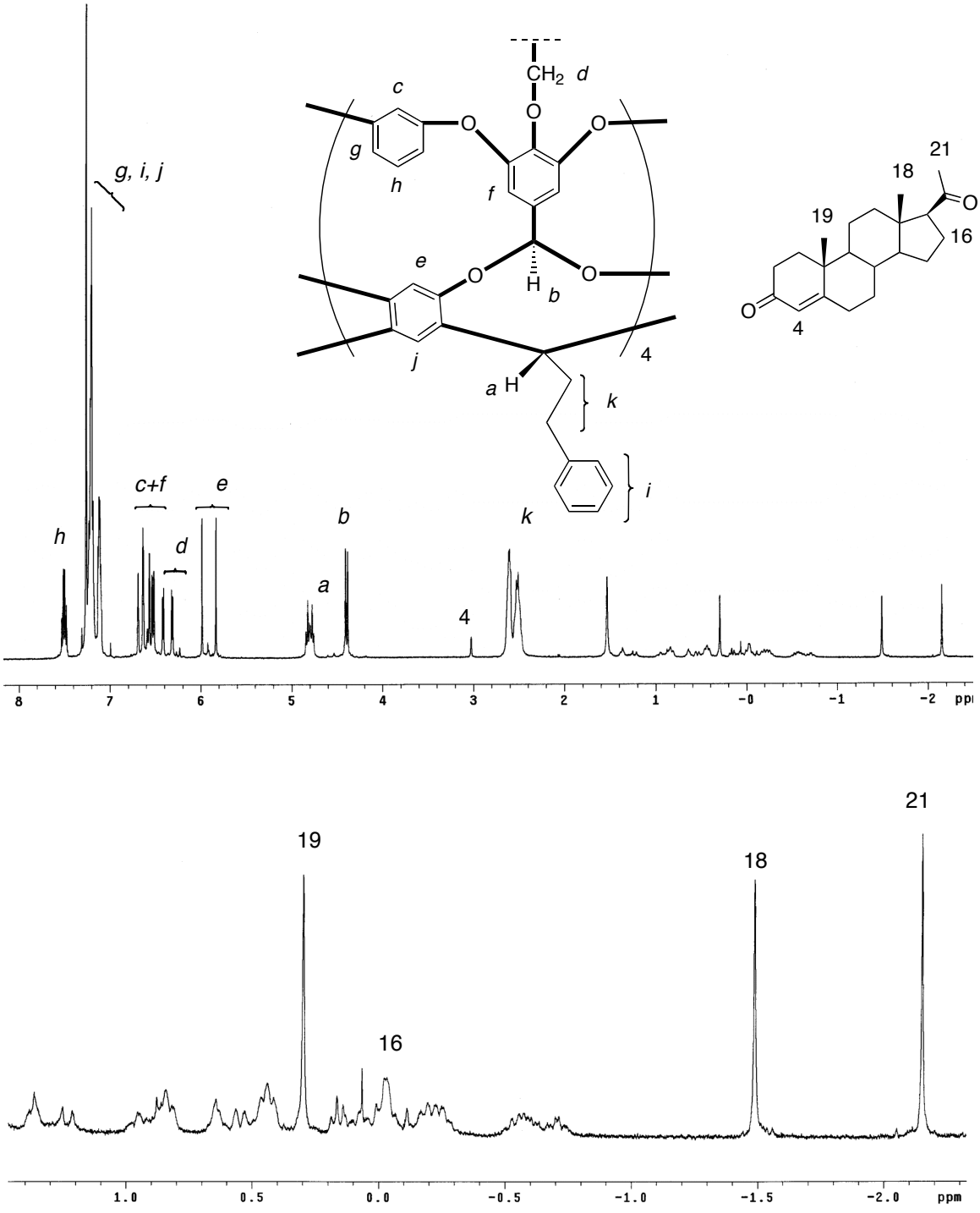
MALDI-MS spectrum of carceplex **3@2**



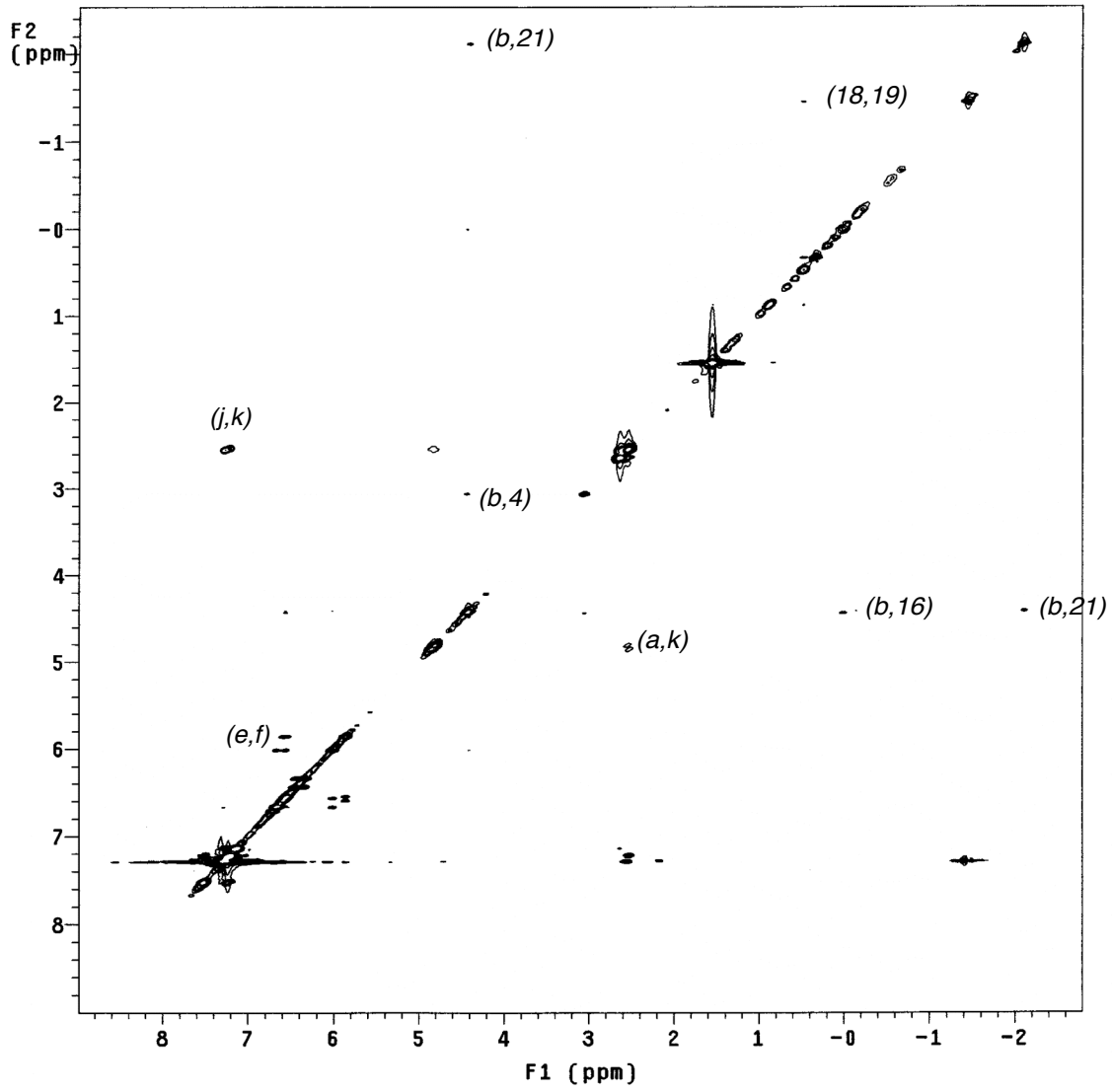
^{1}H NMR spectra of carceplex **4@2**



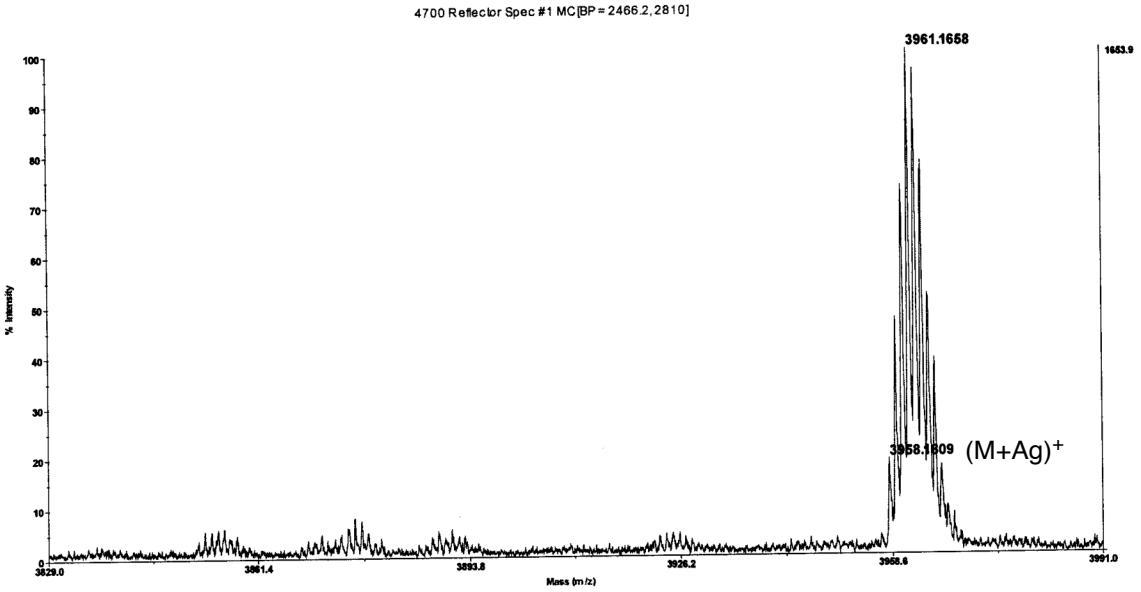
MALDI-MS spectrum of carceplex **4@2**



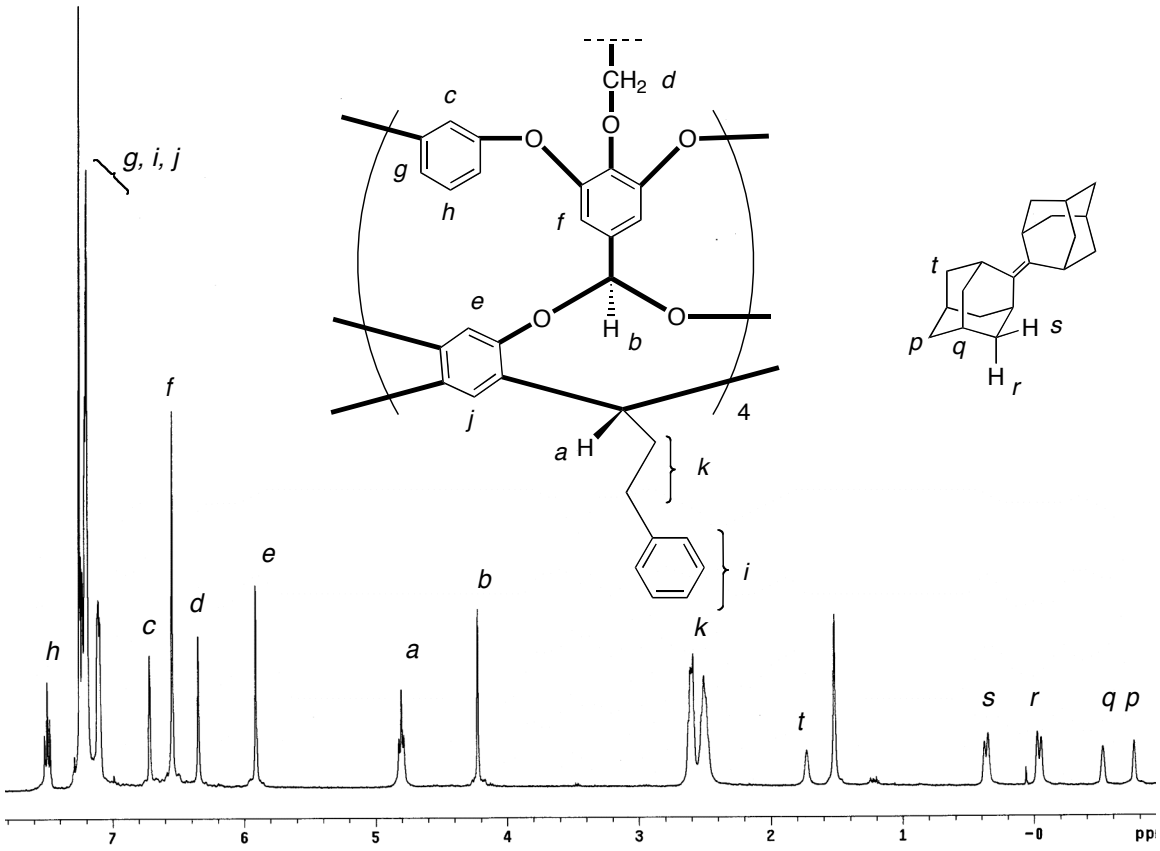
^{1}H NMR spectrum of carceplex **5@2**



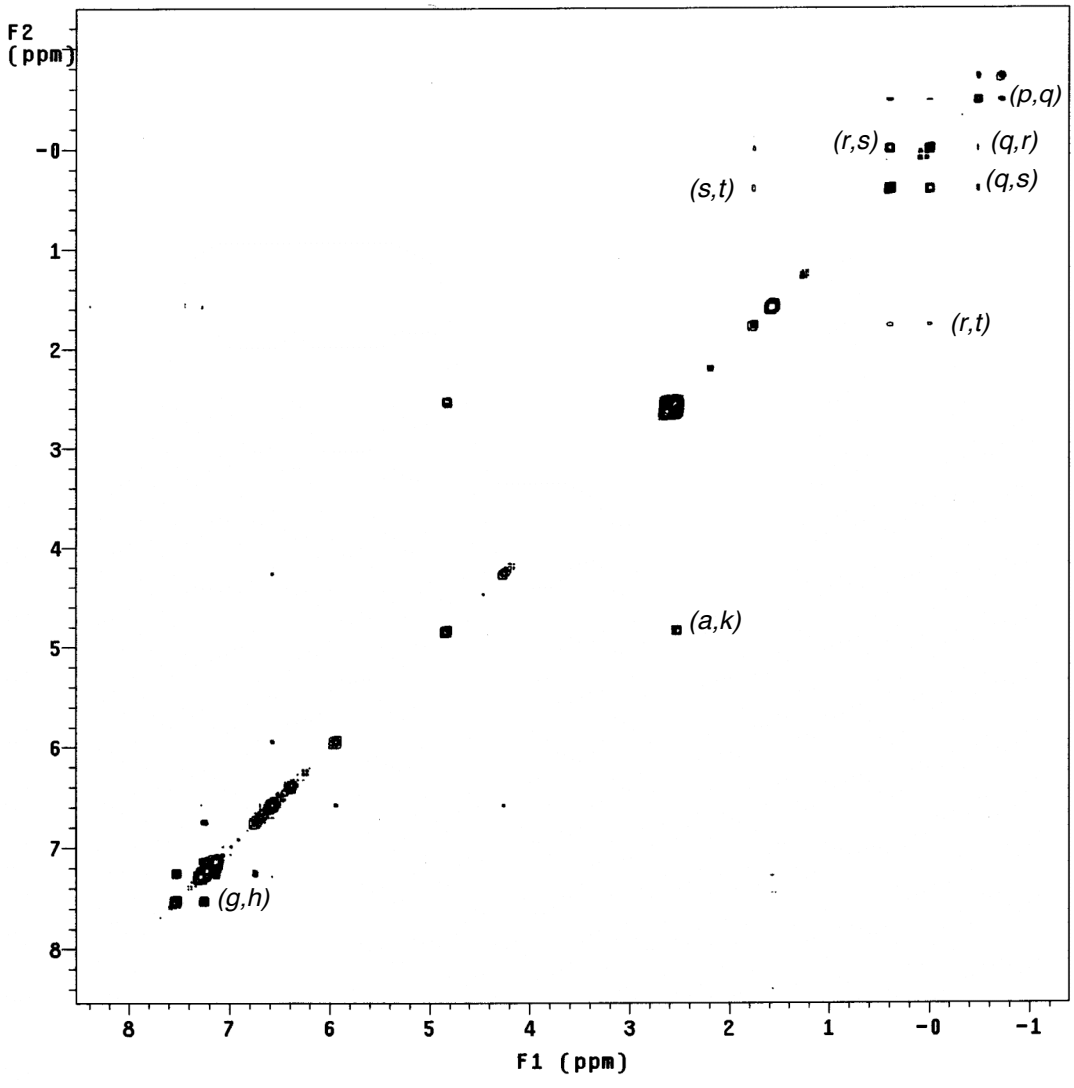
NOESY spectrum of carceplex **5@2**



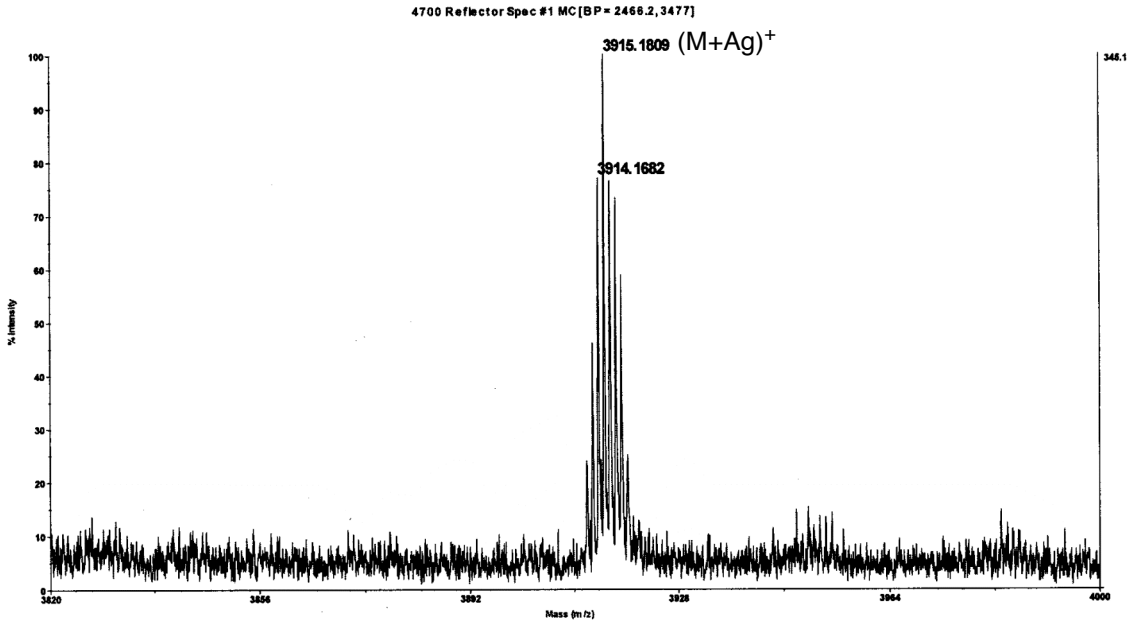
MALDI-TOF (HRMS) spectrum of carceplex **5@2**



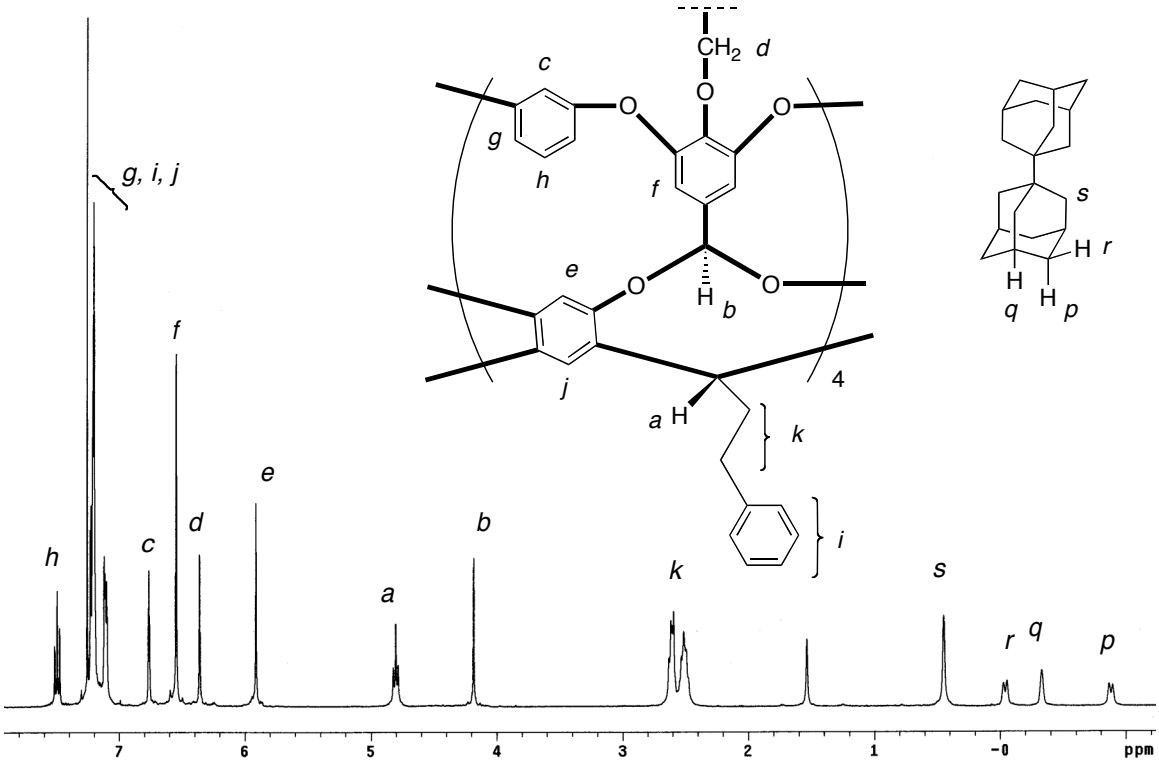
^{1}H NMR spectrum of carceplex **9@2**



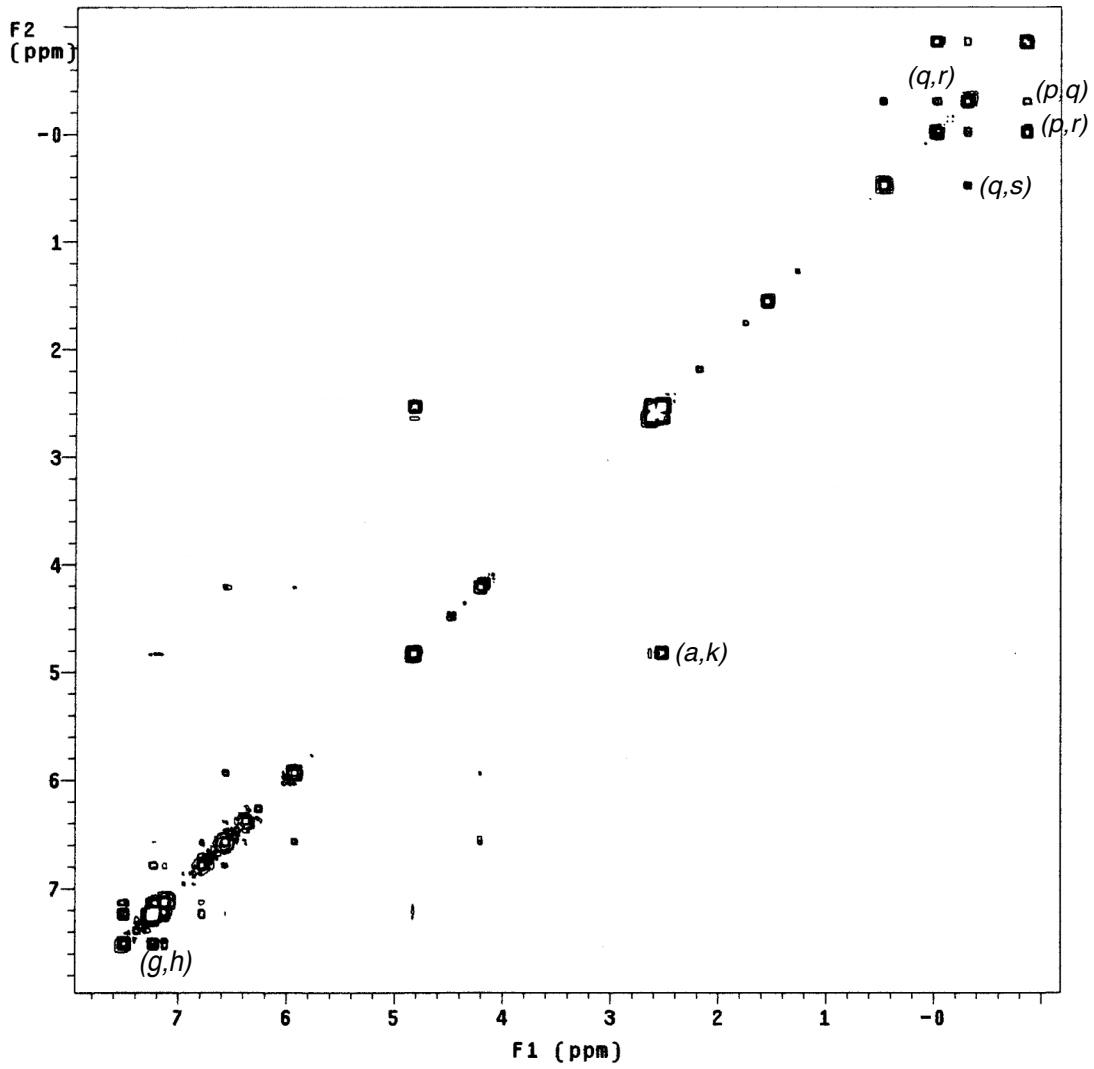
COSY spectrum of carceplex **9@2**



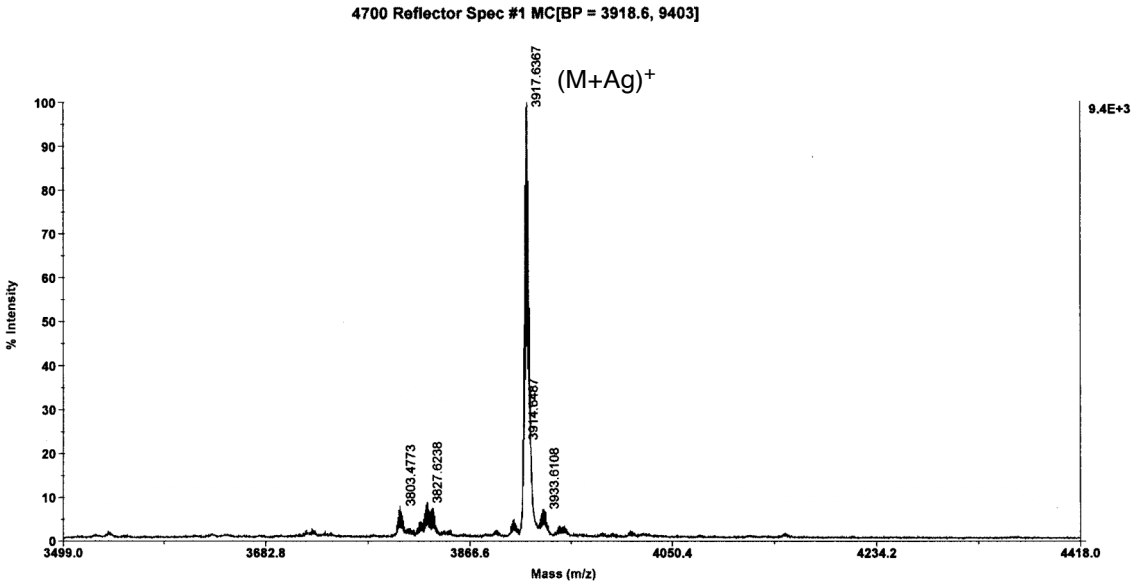
MALDI-MS (HRMS) spectra of carceplex **9@2**



^{1}H NMR spectrum of carceplex **10@2**



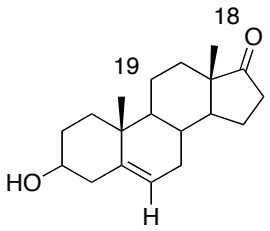
COSY spectrum of carceplex **10@2**



MALDI-MS spectrum of carceplex **10@2**

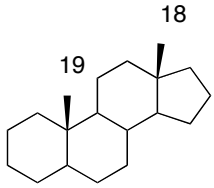
Shielding of protons of guests in carceplexes

1) **For template 3:**



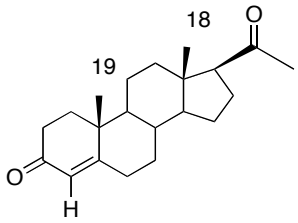
Proton	In free guest (ppm)	In carceplex (ppm)
18-Me	0.88	– 1.23 (s)
19-Me	1.03	–0.16 (s)
OH	Not observed	–3.01 (d)
Alkene-H	5.38 (m)	4.04 (m)

2) **For template 4:**



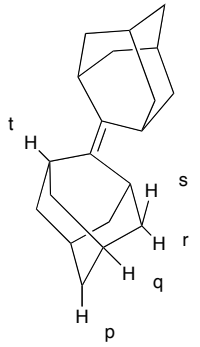
Proton	In free guest (ppm)	In carceplex (ppm)
18-Me	0.68	– 1.34 (s)
19-Me	0.78	–0.36 (s)

3) For template 5:



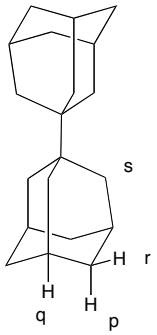
Proton	In free guest (ppm)	In carceplex (ppm)
18-Me	0.66	– 1.49 (s)
19-Me	1.18	0.30 (s)
CH_3CO	2.12	–2.15 (s)
Alkene-H	5.74 (s)	3.03 (s)

4) For template 9:



Proton	In free guest (ppm)	In carceplex (ppm)
p	1.83	– 0.76 (s)
q	1.92	–0.52 (s)
r	1.66-1.69	–0.04 (d)
s	1.83-1.86	0.37 (d)
t	2.90	1.73 (s)

5) For template 10:



Proton	In free guest (ppm)	In carceplex (ppm)
p	1.56-1.68	– 0.88 (d)
q	1.95	–0.33 (s)
r	1.56-1.68	–0.04 (d)
s	1.56	0.45 (s)