SUPPORTING INFORMATION

Using carbon dioxide and calix[4]arenes to separate sodium

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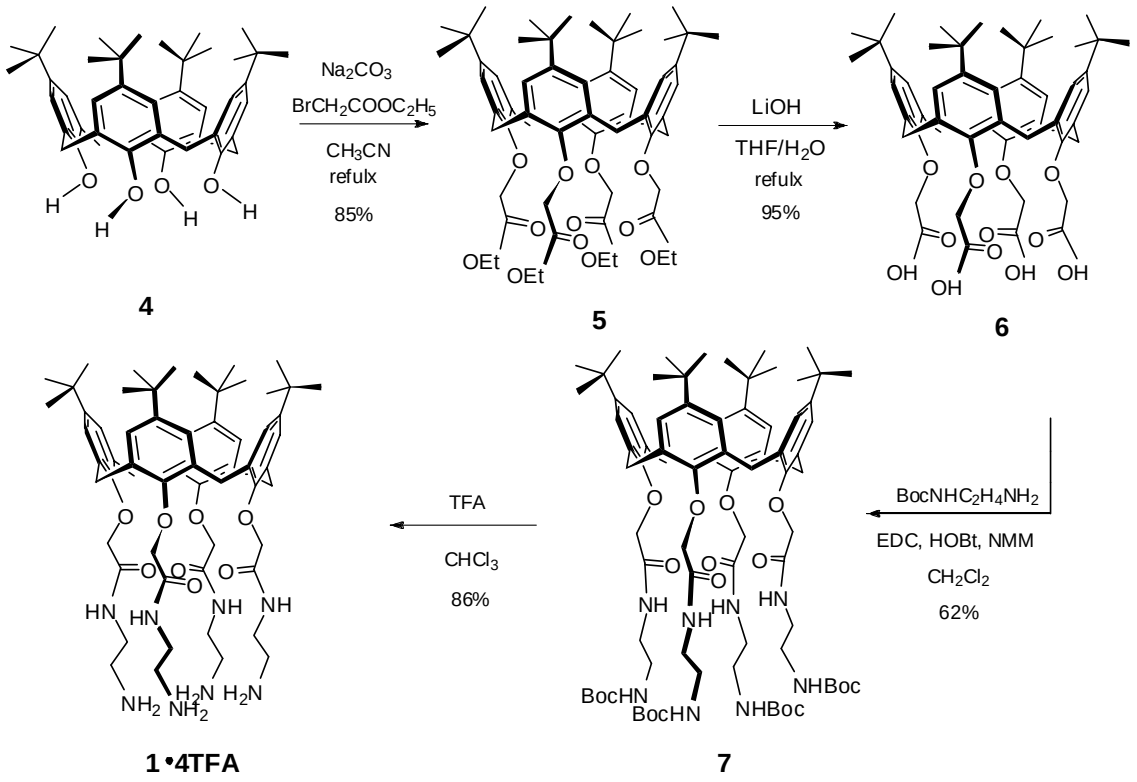
General. Melting points were determined on a Mel-Temp apparatus (Laboratory Devices, Inc.) and are uncorrected. ^{1}H, ^{13}C NMR, COSY NMR spectra were recorded at 295 ± 1 K on JEOL 300 and 500 MHz spectrometers. Chemical shifts were measured relative to residual non-deuterated solvent resonances. FTIR spectra were recorded on a Bruker Vector 22 FTIR spectrometer. ESI-TOF high-resolution mass spectra were recorded on an Agilent ESI-TOF mass spectrometer at the Scripps Center for Mass Spectrometry (La Jolla, CA). Elemental analysis was performed on a Perkin-Elmer 2400 CHN analyzer. All experiments with moisture- and/or air-sensitive compounds were performed under a dried nitrogen atmosphere. All reagents were purchased from Sigma-Aldrich (St. Louis, MO) and AK Scientific (Mountain View, CA) used as received. Calixarenes **5**[1] and **6**[2] were prepared by known protocols.

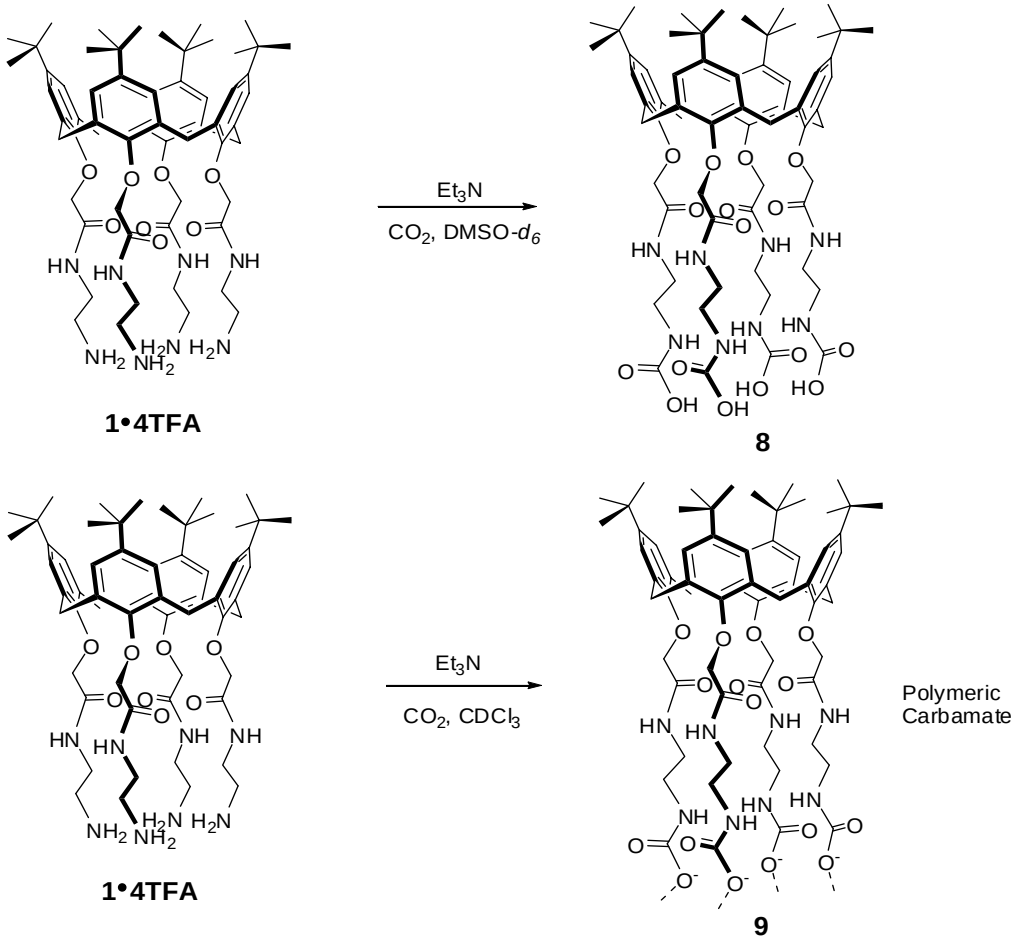


Scheme 1. Preparation of t-Bu calix[4]arene derivatives.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetra-[BocHNC_2H_4NHC(O)CH_2O]-calix[4]-arene (7): *N*-Boc-ethylenediamine (0.24 mL, 1.5 mmol) and *t*-Bu-calix[4]arene tetraacid **6** (220 mg, 0.25 mmol) were mixed with EDC•HCl (191 mg, 1.0 mmol), HOBt (135 mg, 1.0 mmol) and NMM (0.1 mL) in dry CH_2Cl_2 (25 mL) and stirred at 0 ºC overnight. The solution was evaporated to dryness. The solid was dissolved in CH_2Cl_2 (50 mL) and washed with 5% aq HCl (50 mL) and water (3 x 50 mL) and evaporated. The residue was recrystallized form MeOH to give tetraamide **7** as a white solid (259 mg, 62 %); m.p. > 240 ^{o}C (decomp); IR (KBr, cm^{-1}): ν 2964, 2880, 1692, 1534, 1480, 1392, 1365, 1251, 1174, 1126, 1043, 871; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.98 (br t, 4 H), 6.78 (s, 8 H), 5.49 (br, 4 H), 4.53 (d, J = 13.1 Hz, 4 H), 4.50 (s, 8 H), 3.50 (d, J = 5.1 Hz, 8 H), 3.29 (d, J = 5.1 Hz, 8 H), 3.24 (d, J = 13.1 Hz, 4 H), 1.43 (s, 36 H), 1.07 (s, 36 H); ^{13}C NMR ($CDCl_3$, 500 MHz): δ 170.4, 156.6, 152.8, 146.0, 132.7, 126.0, 79.2, 74.3, 45.0, 40.8, 39.5, 34.0,

31.4, 28.5; ESI-TOF m/z 1449.8880, ([M + H^+], calcd for $C_{80}H_{120}N_8O_{16}$ 1449.8895); Calcd for $C_{80}H_{120}N_8O_{16}$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.36; H, 8.17; N, 7.96.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetra-[$H_2NC_2H_4NHC(O)CH_2O$]-calix[4]arene TFA salt (1 • 4TFA): Tetraamide **7** (145 mg, 0.1 mmol) and TFA (0.5 mL, 6.5 mmol) were dissolved in dry CH_2Cl_2 (10 mL) and stirred overnight. The solvent was removed, and Et_2O (20 mL) was added to precipitate tetraamine **1** as a TFA salt (129 mg, 86 %); m.p. 182-185 ^oC (decomp); IR (KBr, cm^{-1}): ν 2964, 2083, 1659, 1535, 1461, 1392, 1363, 1300, 1178, 1135, 1052, 872; ^1H NMR (DMSO-d_6, 300 MHz): δ 8.43 (br t, 4 H), 7.90 (br, 12 H), 6.81 (s, 8 H), 4.50 (d, J = 12.9 Hz, 4 H), 4.47 (s, 8 H), 3.40-3.38 (br q, 8 H), 3.20 (d, J = 12.9 Hz, 4 H), 2.90 (br, 8 H), 1.02 (s, 36 H); ^{13}C NMR (DMSO-d_6, 300 MHz): δ 169.6, 159.0 (q, J = 29.8 Hz, CF_3C=O), 151.3, 146.8, 133.4, 126.1, 117.0 (q, J = 295.2 Hz, CF_3C=O), 74.4, 42.8, 41.8, 34.1, 31.6; ESI-TOF m/z 1049.6782, ([Free amine + H^+], calcd for $C_{60}H_{89}N_8O_8$ 1449.6803); Calcd for $C_{68}H_{92}F_{12}N_8O_{16}$: C, 54.25; H, 6.16; N, 7.44. Found: C, 54.36; H, 6.17; N, 7.36.



Scheme 2. Reactions of t-Bu calix[4]arene tetraamine with CO_2.

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetra-[$H_2NC_2H4NHC(O)CH_2O$]-calix[4]-arene carbamic acid (8): Compound **1**•4TFA (15 mg, 0.01 mmol) and TEA (0.02 mL) were dissolved in DMSO-d_6 (0.5 mL), after which CO_2 was then introduced to form carbamic acid **8**: ^{1}H NMR (DMSO-d_6, 300 MHz): δ 8.33 (br, 4 H), 6.81 (s, 8 H), 6.68 (br, 4 H), 4.52 (d, J = 12.0 Hz, 4 H), 4.46 (s, 8 H), 3.10 (d, J = 12.0 Hz, 4 H), 3.06 (br, 8 H), 1.04 (s, 36 H).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetra-[$H_2NC_2H_4NHC(O)CH_2O$]-calix[4]arene carbamate (9): ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.50 (br t, 4 H), 6.85 (s + br s, 12 H), 6.80-6.00 (br), 4.55 (s, 8 H), 4.40 (d, J = 12.4 Hz, 4 H), 3.42 (m, 8 H), 3.21 (d, J = 12.4 Hz, 4 H), 2.90-2.85 (m, 24 H), 1.02 (m, 60 H). ^{13}C NMR (DMSO-d_6, 300 MHz): δ 170.5, 159.7 (q, J = 30.5 Hz, CF_3C=O), 153.3, 145.1, 133.5, 125.9, 117.5 (q, J = 297.5 Hz,

CF_3C=O), 74.4, 46.2, 37.6, 34.1, 31.6, 10.1. Due to the low concentration, the carbamate *C*=O singlet cannot be detected.[3]

Extraction of alkali-metal perchlorates ($MClO_4$) by calixarene (1); a general procedure: Compound **1** (15.0 mg, 0.01 mmol) was dissolved in 1 mL $CHCl_3$ in the presence of TEA (0.02 mL). Alkali-metal perchlorate (0.01 mmol) was added and the suspension was stirred overnight. The solution was separated. CO_2 (or $^{13}CO_2$) was then introduced and the precipitate was collected and dried. The ^{13}C NMR spectrum of calixarene-Na^+ carbamate polymer **3** was measured with $^{13}CO_2$ gas.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetra-[$H_2NC_2H_4NHC(O)CH_2O$]-calix[4]arene $NaClO_4$ complex (2): ^{1}H NMR (DMSO-d_6, 300 MHz): δ 8.43 (br, 4 H), 7.12 (s, 8 H), 4.40 (s, 8 H), 4.34 (d, *J* = 12.0 Hz, 4 H),3.40-3.37 (m, 8 H), 3.33 (d, *J* = 12.0 Hz, 4 H), 3.03-2.88 (br, 8 H), 1.12 (m, 36 H); ^{13}C NMR (DMSO-d_6, 300 MHz): δ 170.6, 160.0 (q, *J* = 31.2 Hz, CF_3*C*=O), 151.8, 147.0, 134.3, 126.3, 117.6 (q, *J* = 295.2 Hz, *C*F_3C=O), 74.8, 46.2, 37.4, 34.4, 31.5, 30.6, 9.4.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetra-[$H_2NC_2H_4NHC(O)CH_2O$]-calix[4]arene $NaClO_4$ complex carbamate (3): Obtained from **2** using ^{13}C-labeled CO_2. ^{13}C NMR (DMSO-d_6, 300 MHz): δ 170.5, 160.4 (^{13}*C*=O), 159.7 (q, *J* = 31.6 Hz, CF_3*C*=O), 151.6, 147.0, 134.5, 126.3, 117.7 (q, *J* = 296.8 Hz, *C*F_3C=O), 74.9, 46.2, 37.8, 34.5, 31.5, 30.6, 10.1.

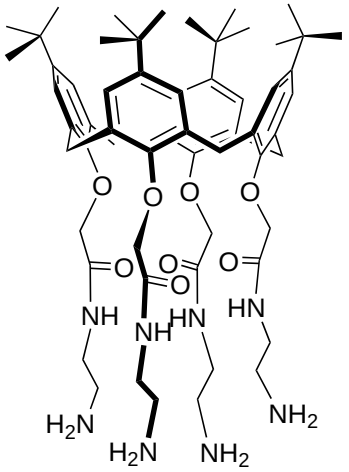
REFERENCES

1 M. A. McKervey, E. M. Seward, G. Ferguson, B. Ruhl, S. J. Harris, *J. Chem. Soc*., *Chem. Commun.* 1985, **7**, 388.

2 A. Arduini, A. Pochini, S. Reverberi, R. Ungaro, *J. Chem. Soc., Chem. Commun.* 1984, 981.

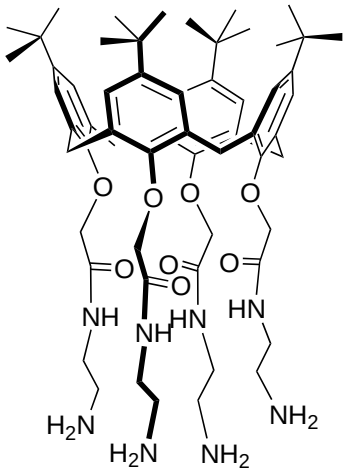
3 *(a)* M. George, R. G. Weiss, *Langmuir* 2002, **18**, 7124. *(b)* M. George, R. G. Weiss, *Langmuir* 2003, **19**, 8168.

^{1}H NMR in DMSO-d_6 for compound **1**



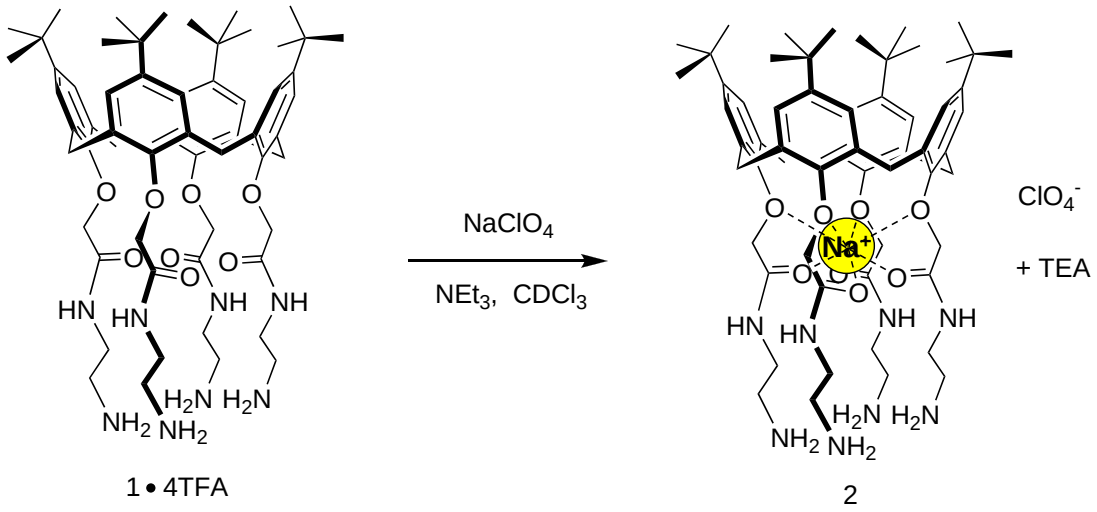
1•4TFA

^{13}C NMR in DMSO-d_6 for compound **1**



1•4TFA

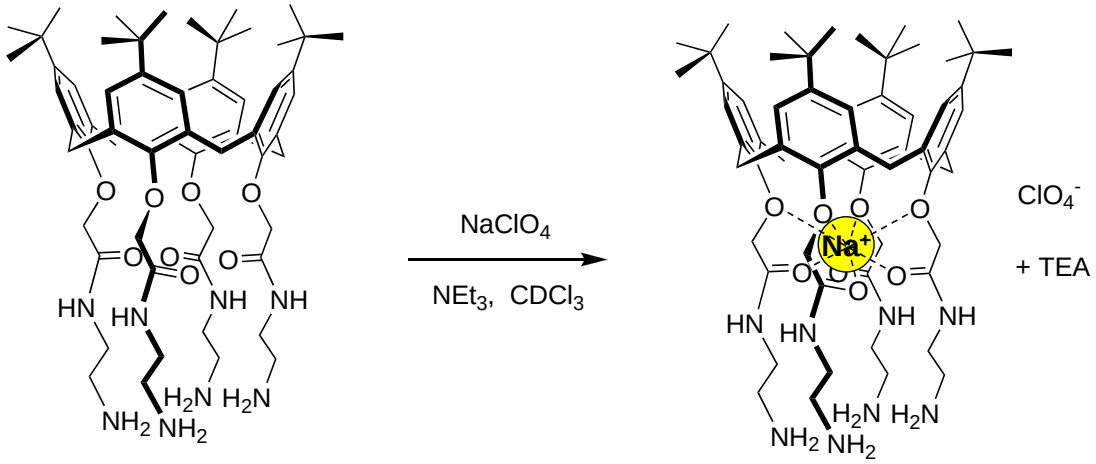
^{1}H NMR in DMSO-d_6 for compound **2**



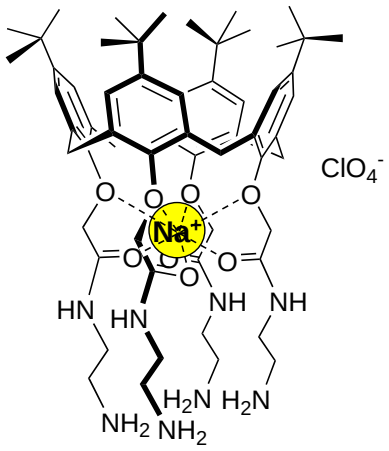
1 • 4TFA

2

^{13}C NMR in DMSO-d_6 for compound **2**



^{1}H NMR in DMSO-d_6 for compound **3**



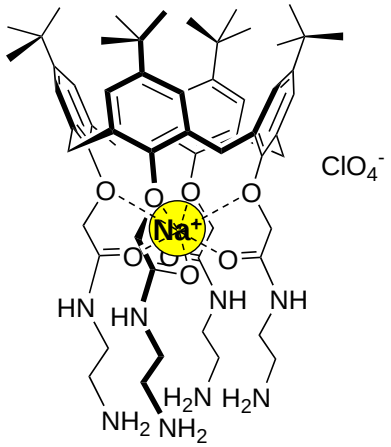
2

$^{13}CO_2$

NEt_3, $CDCl_3$

Precipitate **3**

^{13}C NMR in DMSO-d_6 for compound **3**



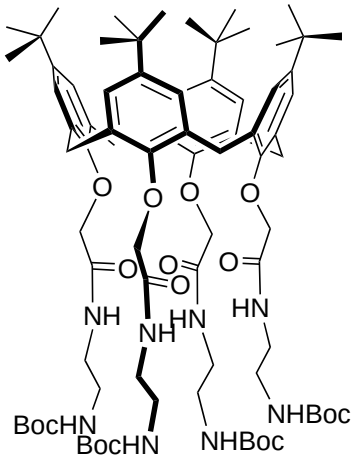
2

$^{13}CO_2$

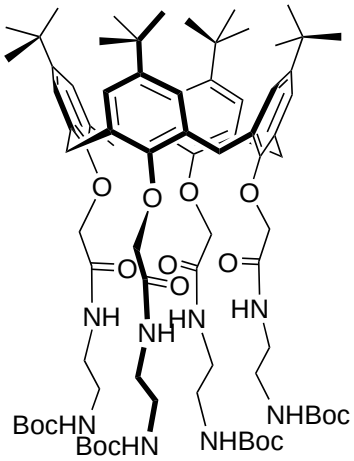
NEt_3, $CDCl_3$

Precipitate **3**

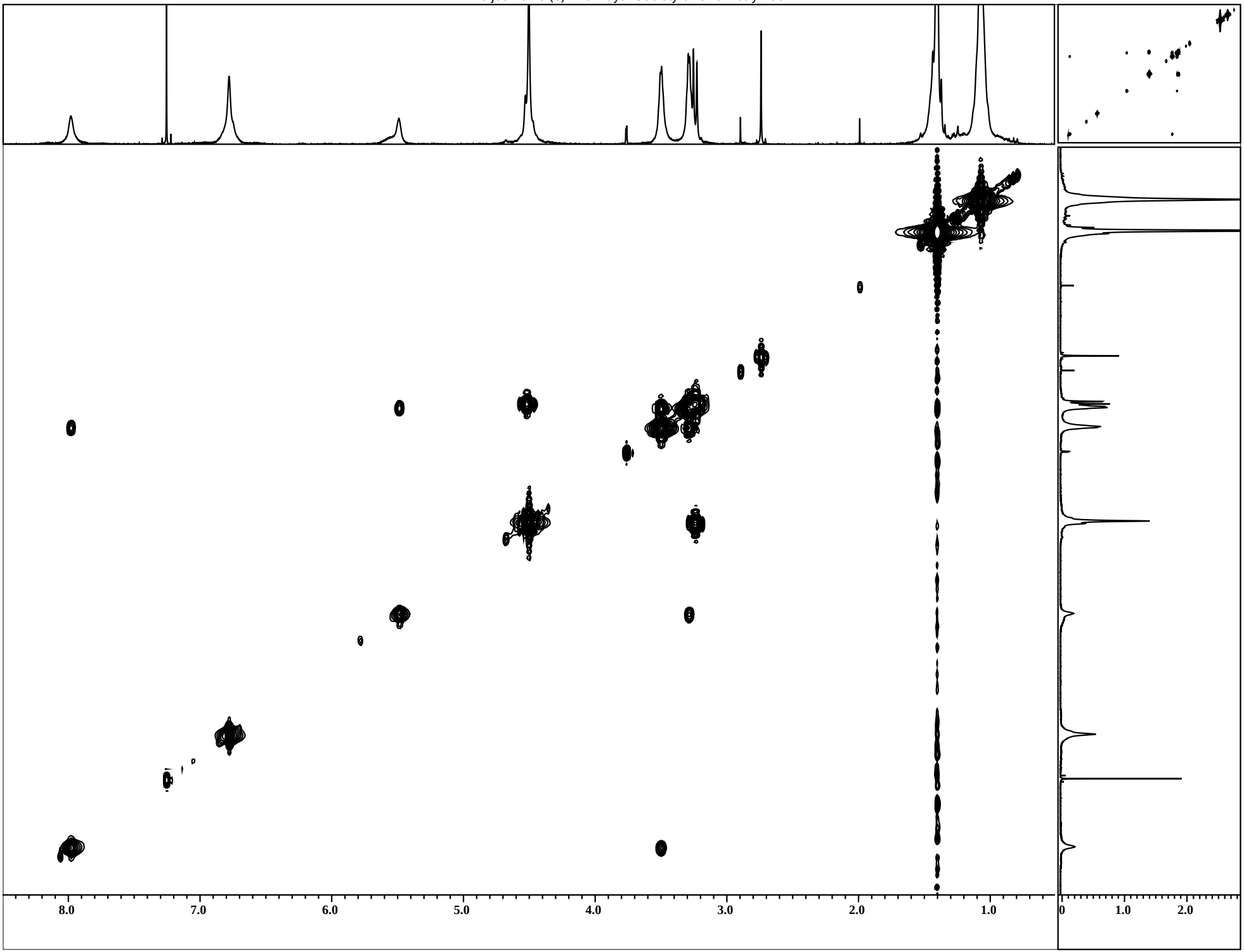
^{1}H NMR in $CDCl_3$ for compound **7**



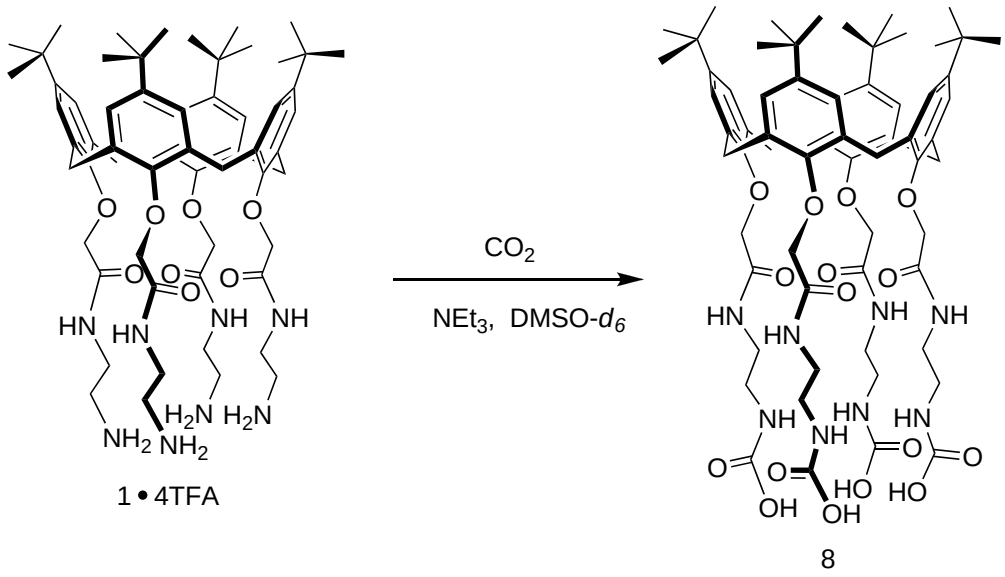
^{13}C NMR in $CDCl_3$ for compound **7**



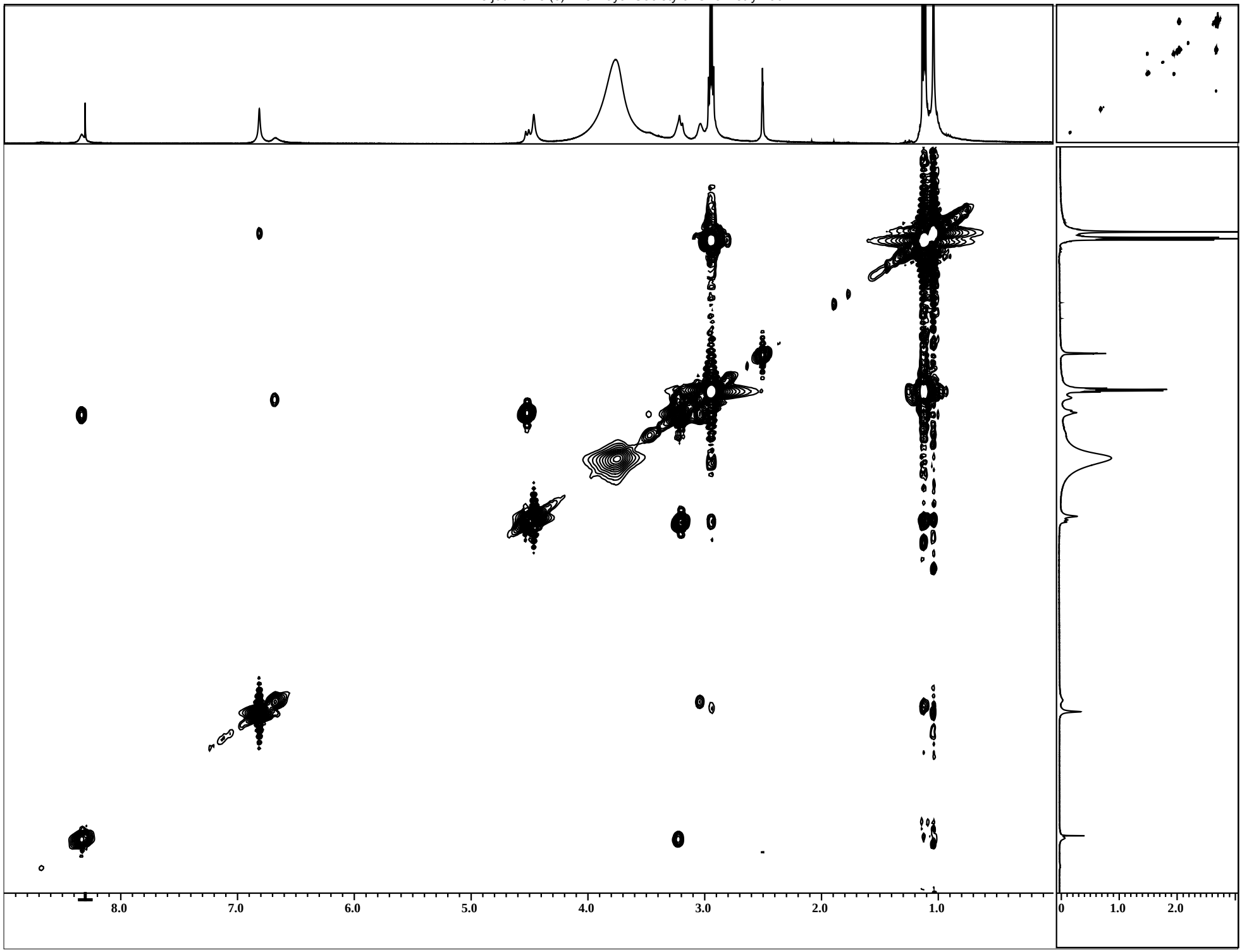
Supplementary Material (ESI) for Chemical Communications



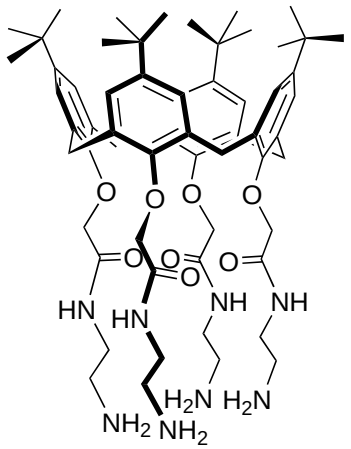
^{1}H NMR in DMSO-d_6 for compound **8**



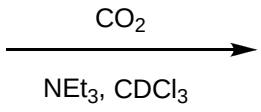
COSY in DMSO-d_6 for compound **8** with TEA



^{1}H NMR in DMSO-d_6 for compound **9**

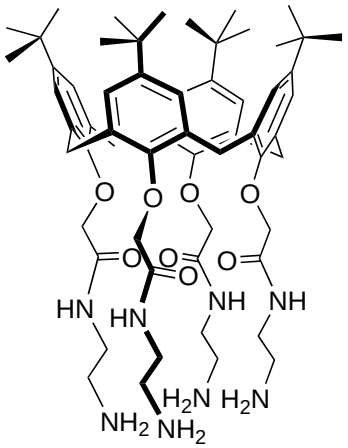


1 • 4 TFA



Precipitate **9**

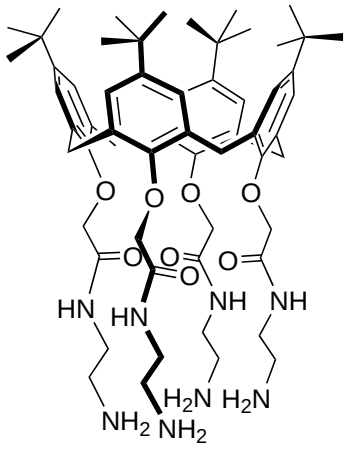
^{1}H NMR in DMSO-d_6 for compound **1** with TEA



4TFA

+ TEA

^{1}H NMR in DMSO-d_6 for compound **1** with $KClO_4$

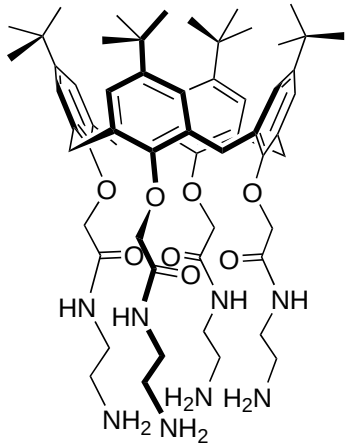


4TFA

+ TEA

+ $KClO_4$

^{1}H NMR in DMSO-d_6 for compound **1** with $CsClO_4$

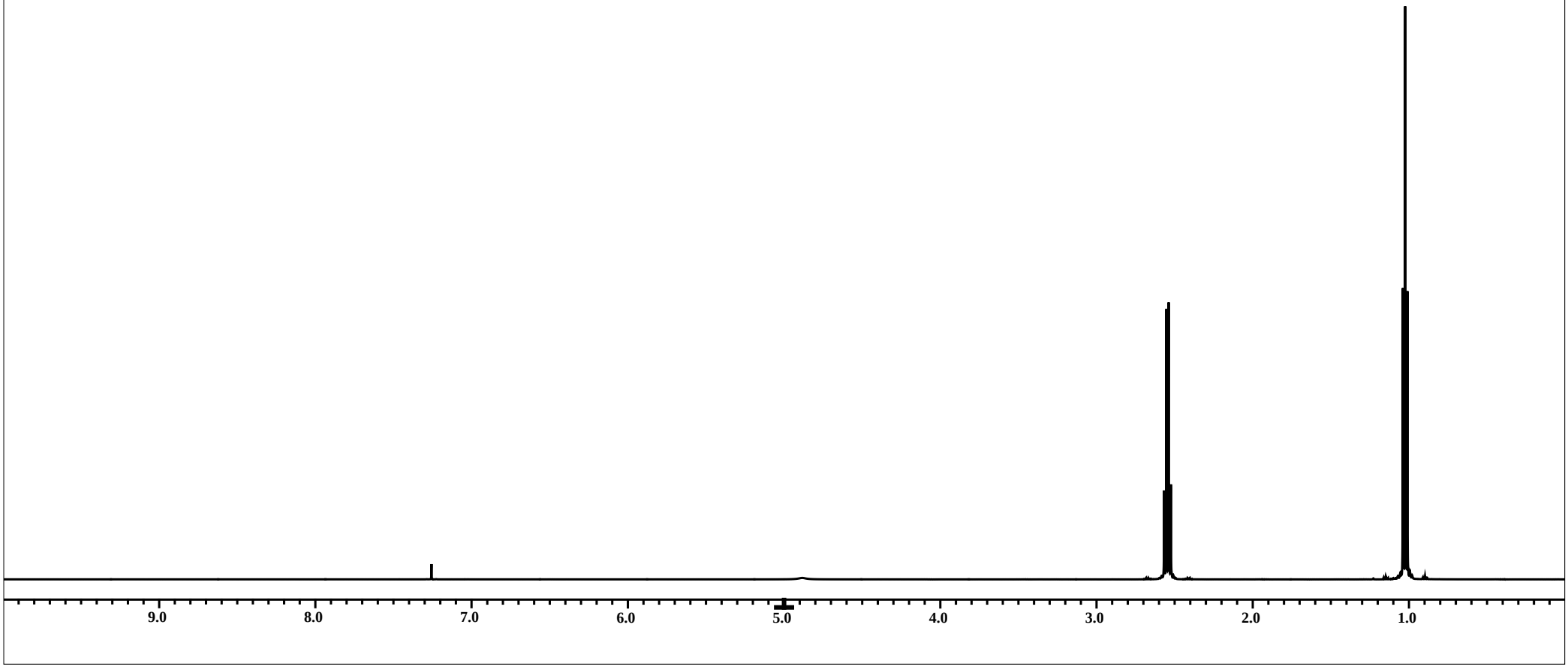


4TFA

+ TEA

+ $CsClO_4$

1H NMR in CDCl3 for solution after **2** was precipitated by CO2



1H NMR in CDCl3 for compound **2**. KClO4/NaClO4 = 1000