An expedient one-pot synthesis of *para-tert*-butylcalix[8]- and [9]arene.

Sean P. Bew* and Sunil V. Sharma.
School of Chemical Sciences & Pharmacy, University of East Anglia, Norwich, NR4 7TJ, UK.
s.bew@uea.ac.uk

General protocols

All reactions requiring anhydrous conditions were conducted in flame-dried glass apparatus under an atmosphere of argon. Dichloromethane was freshly distilled from calcium hydride. Water refers to distilled water. All commercially available reagents were used as supplied. Melting points were recorded using open capillary tubes on a Gallenkamp melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000FT infrared spectrometer either as a neat sample or KBr discs where stated. ^{1}H- and ^{13}C-NMR spectra were recorded in Fourier transform mode at the field strength specified either on a Bruker AC-400 or a Varian Gemini 300 spectrometer and unless otherwise stated deuterated chloroform was used as solvent. The ^{1}H-spectra were recorded in ppm and referenced to the residual $CHCl_3$ signal located at δ 7.26. ^{13}C-NMR spectra were recorded in ppm and referenced to the residual $CHCl_3$ signal found at δ 77.00. Multiplicities in the NMR spectra are described as: s = singlet, d = doublet, t = triplet, q= quartet, m = multiplet, br = broad; coupling constants are reported in Hz. Low resolution mass spectra were run on a Voyager-DE-STR spectrometer. Ion mass/charge (m/z) ratios are reported as values in atomic mass units. Microwave syntheses were performed on a Personal Chemistry Emrys Creator. Thin layer chromatography was performed on Merck aluminium plates coated with 0.2 mm silica gel-60 F_{254}. Flash column chromatography was performed on silica gel (Kieselgel 60).

General Procedure For Calixarene Synthesis

To a solution of *para-tert*-butylphenol (3 g, 20 mmol) in CH_2Cl_2 (80 mL) was added tin(IV) chloride (5.47 g, 2.5 mL, 21 mmol) in CH_2Cl_2 (50 mL) at 15 °C under argon. The reaction was stirred for 30 min at 15 °C. Whilst maintaining this temperature using a cold-water circulator a solution of s-trioxane (1.98 g, 22 mmol) in CH_2Cl_2 (20 mL) was added over 4 h using a syringe pump. The reaction mixture was stirred at this temperature for a further 16 h. The removal of small aliquots for HPLC analysis indicated completion of the reaction. The reaction was quenched by addition of aqueous HCl (50 mL, 1M). The organic layer was separated and washed again with aqueous HCl (25 mL, 1M). The combined aqueous fractions were further extracted with CH_2Cl_2 (25 mL). The combined organic extracts were dried over $MgSO_4$, filtered through a column of silica (50 g) and the solvent evaporated under reduced pressure affording a mixture of products as a pale yellow solid.

Representative procedure for the purification and isolation of calix[6], calix[7], calix[8] and calix[9]arene:*

Partial separation of calix[8]arene from the mixture of calixarene reaction products was achieved as follows. The product* was refluxed with n-hexane (200 mL) for 2 h and then allowed to stand at room temperature overnight. The insoluble white precipitate was collected by filtration. HPLC analysis indicated that this solid consisted of calix[8]arene (0.72g, ~95% purity, Fig 27). The clear filtrate comprising all of the other calixarenes (Fig 26) was collected and the solvent evaporated under reduced pressure. Purification and isolation of the component calixarenes was achieved by flash column chromatography.

A 40 mm i.d. column was dry packed with 20 cm of silica gel and eluted with 600 mL of toluene/n-hexane (40/60) until the eluent was no longer warm (the warm eluent was discarded). Using toluene/n-hexane/dichloromethane (40/40/20) the n-hexane soluble fraction was applied to the column. Eluting the column using toluene/n-hexane (40/60, 5 mL/min) fractions of 100 mL were collected until 600 mL had passed through the column.

The column was eluted with, in the following order: i) 45/55, ii) 50/50, iii) 55/45, iv) 60/40, v) 75/25 (toluene/n-hexane mixtures) collecting 5 x 50 mL fractions for each solvent mixture. HPLC analysis of all the fractions indicated that the first 400 – 600 mL of solvent contained pure calix[8]arene (160 mg, >99% HPLC purity, Fig 28). Analysis of the emerging eluent afforded:

Calix[6]arene (80 mg, 91.2% HPLC purity, Fig 29) followed by
Calix[7]arene (78 mg, 98.4% HPLC purity, Fig 30).

Further fractions consisted of impure calix[9]arene contaminated with calix[6-8]arenes (180 mg, containing 79% calix[9]arene by HPLC). The final fractions afforded calix[9]arene (99% HPLC purity, Fig 31) as a white solid. The recovered yields of calix[8]arene (890 mg) was 53% and for calix[9]arene (445 mg) 70%.

Procedure for the purification and isolation of calix[8] and calix[9]arene:

Partial separation of calix[8]arene from the mixture of calixarene reaction products was achieved as follows. 2.1g of pale yellow solid (comprising 58.4% calix[8] and

* 3.1 g; Note: This mixture consisted of calix[4]arene (1.8%), calix[6]arene (9.5%), calix[7]arene (9.4%), calix[8]arene (49.5%), calix[9]arene (18.9%) the HPLC trace of this mixture is shown in Fig 25

33.9% calix[9]) was refluxed in n-hexane (200 mL) for 2 h and then allowed to stand at room temperature overnight. The insoluble calix[8]arene (1.07g) was collected by filtration. The clear filtrate comprising the impure calix[9]arene was collected and the solvent evaporated under reduced pressure. Purification and isolation of the component calixarenes was achieved by flash column chromatography as detailed above.

The column was eluted with, in the following order: i) 45/55, ii) 50/50, iii) 55/45, iv) 60/40, v) 75/25 (toluene/n-hexane mixtures) collecting 5 x 50 mL fractions for each solvent mixture. HPLC analysis of all the fractions indicated that the first 150 – 350 mL of solvent contained pure calix[8]arene (83 mg. Total combined yield 1.07 + 0.083 = 1.15g, 55% yield >99% HPLC purity). Analysis of the emerging eluent afforded calix[9]arene (484 mg, 23%, >99% HPLC purity).

HPLC Procedure:

HPLC analysis was performed on a Perkin-Elmer LC 200 instrument equipped with a diode-array detector and Varian Pursuit RP C18 column (4.6 mm i.d., 25 cm) packed with 5 μm silica. The analysis procedure followed was similar to that reported by Gutsche et al.[1] The HPLC separation of calix[4-9]arenes was achieved using a mixture of two eluents (at 280 nm), A and B at a flow rate of 2 mL/min. Eluent A was MeCN with 1% AcOH and eluent B was a mixture of CH_2Cl_2 and *tert*-butyl methyl ether (12:9 ratio) with 1% AcOH. An isocratic run using a 80/20 mixture of A and B for 12 min was found suitable for separation of calix[4-9]arenes. (Note: A significant shift in retention times was observed as a function of room temperature. Higher retention times were noticed in cold conditions.)

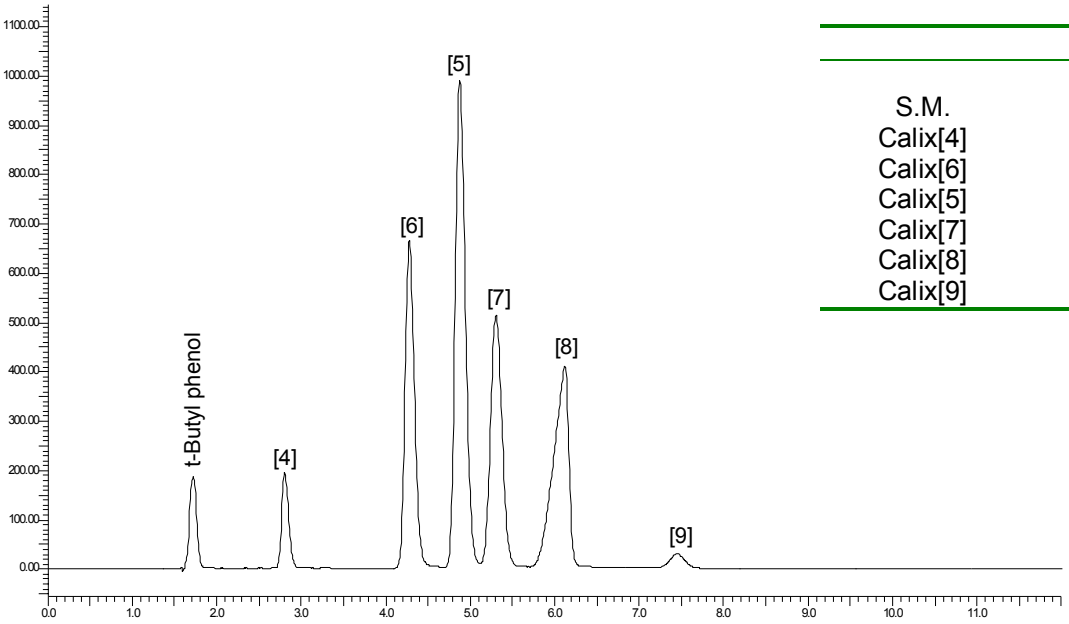
5,11,17,23,29,35,41,47-Octakis(1,1-dimethylethyl)-49,50,51,52,53,54,55,56-octahydroxycalix[8]arene

mp >360 °C; FT-IR (thin film) 3191, 2953, 2348, 1485, 1201; ^{1}H NMR ($CDCl_3$) δ9.62 (s, 1H, ArO*H*), 7.17 (s, 2H, Ar*H*), 4.35 (d, 1H, *J* = 12.8, ArC*H*HAr), 3.48 (d, 1H, *J* = 12.8, ArCH*H*Ar), 1.24 (s, 9H, C(C*H*$_3$)$_3$); ^{13}C NMR ($CDCl_3$) δ 146.8, 144.9, and 128.9 (Ar), 125.7 (ArH), 34.2 (*C*(CH$_3$)$_3$), 32.5 (Ar*C*H$_2$Ar), 31.7 (C(*C*H$_3$)$_3$); LSMS (MALDI) *m/z* calc'd for ($C_{88}H_{112}O_8Na$) required 1320.8, found 1320.8.

5,11,17,23,29,35,41,47,53-Nonakis(1,1-dimethylethyl)-55,56,57,58,59,60,61,62,63-nonahydroxycalix[9]arene[1]

mp 302–304 °C; FT-IR (thin film) 3194, 2955, 2360, 1484, 1202; ^{1}H NMR ($CDCl_3$ - Pyridine d_5, 10%) δ 7.09 (d, 2H, J = 3.3, Ar*H*), 3.84 (br s, 2H, ArC*H*$_2$Ar), 1.17 (s, 9H, C(C*H*$_3$)$_3$); ^{13}C NMR ($CDCl_3$) δ 147.2, 144.5, and 128.0 (Ar), 125.9 (ArH), 34.2 (*C*(CH$_3$)$_3$), 32.6 (Ar*C*H$_2$Ar), 31.5 (C(*C*H$_3$)$_3$); LSMS (MALDI) *m/z* calc'd for ($C_{99}H_{126}O_9Na$) required 1482.9, found 1483.0.

[1] D. R. Stewart, C. D. Gutsche, *J. Am. Chem. Soc.*, **1999**, *121*, 4136.

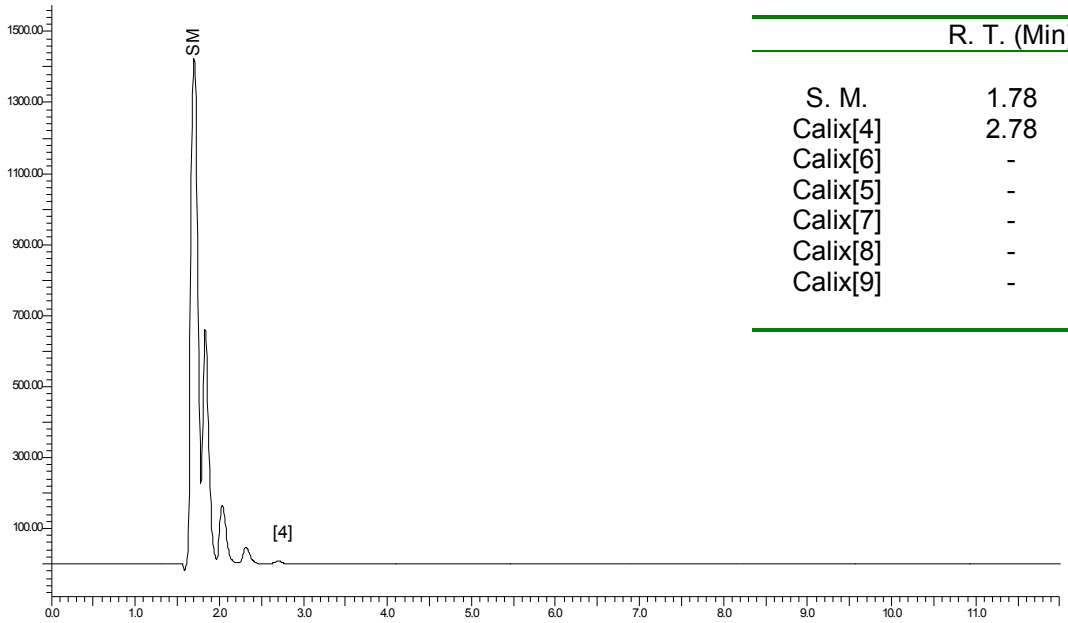


	R. T. (Min)
S.M.	1.73
Calix[4]	2.81
Calix[6]	4.31
Calix[5]	4.79
Calix[7]	5.35
Calix[8]	6.10
Calix[9]	7.48

Fig 1: HPLC chromatogram of the standard mixture of calix[4-9]arenes and *para-tert*-butyl phenol.

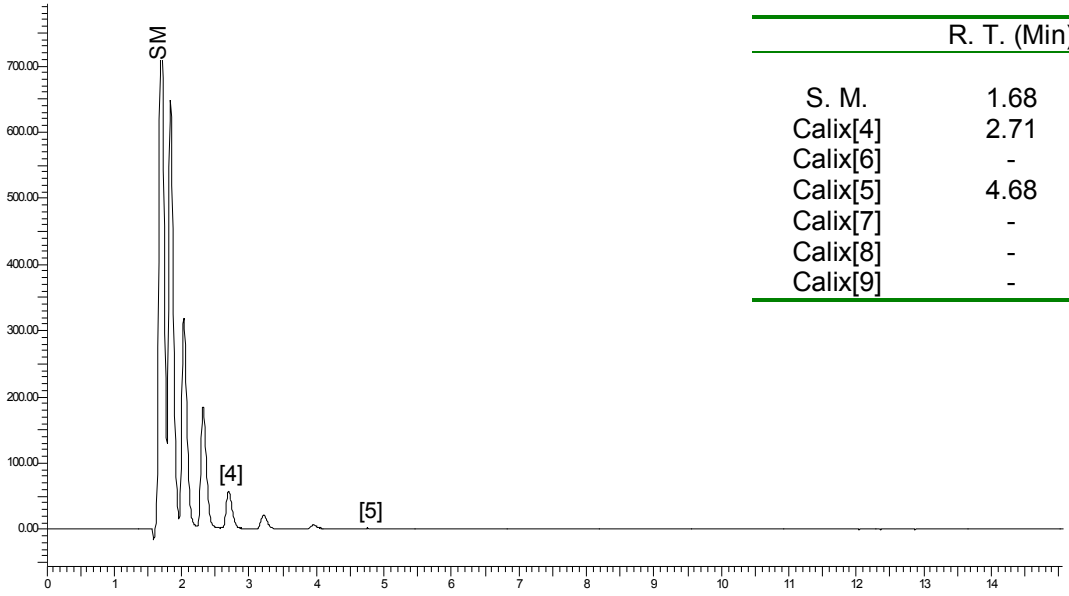
Reaction 1 (Table 1)

A solution of *para-tert*-butyl phenol (150 mg, 1 mmol), tin(IV) chloride (5.2 mg, 2 mol%) and s-trioxane (100 mg, 1.1 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature. A small aliquot was removed for HPLC analysis after 30 and 180 min.



	R. T. (Min)	Comp. (%)
S. M.	1.78	88
Calix[4]	2.78	0.5
Calix[6]	-	-
Calix[5]	-	-
Calix[7]	-	-
Calix[8]	-	-
Calix[9]	-	-

Fig 2: HPLC chromatogram of the reaction mixture after 30 min using 2 mol% tin(IV) chloride.

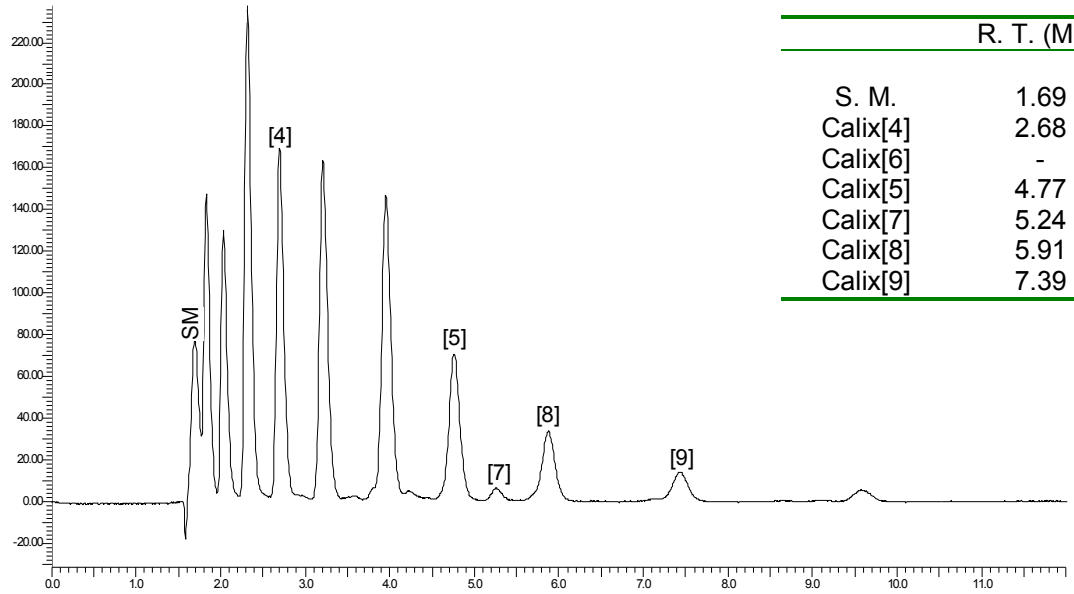


	R. T. (Min)	Comp. (%)
S. M.	1.68	36
Calix[4]	2.71	5
Calix[6]	-	-
Calix[5]	4.68	0.4
Calix[7]	-	-
Calix[8]	-	-
Calix[9]	-	-

Fig 3: HPLC chromatogram of the reaction mixture after 180 min using 2 mol% tin(IV) chloride.

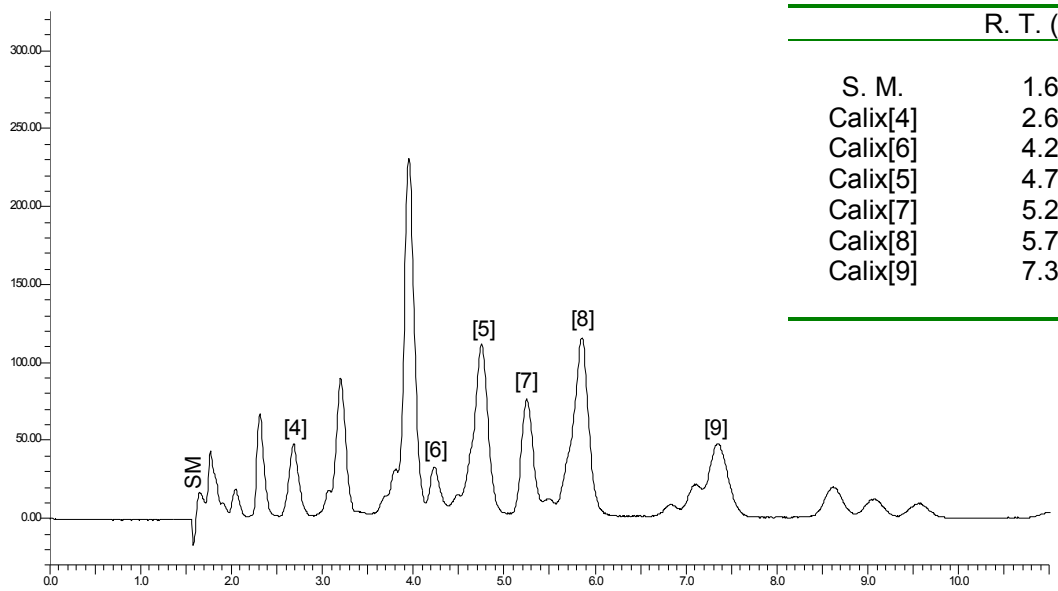
Reaction 2 (Table 1)

A solution of *para*-*tert*-butyl phenol (150 mg, 1 mmol), tin(IV) chloride (26 mg, 10 mol%) and s-trioxane (100 mg, 1.1 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature. A small aliquot was removed for HPLC analysis after 30 and 180 min.



	R. T. (Min)	Comp. (%)
S. M.	1.69	8
Calix[4]	2.68	14
Calix[6]	-	-
Calix[5]	4.77	6.4
Calix[7]	5.24	0.5
Calix[8]	5.91	5
Calix[9]	7.39	2.4

Fig 4: HPLC chromatogram of the reaction mixture after 30 min using 10 mol% tin(IV) chloride.

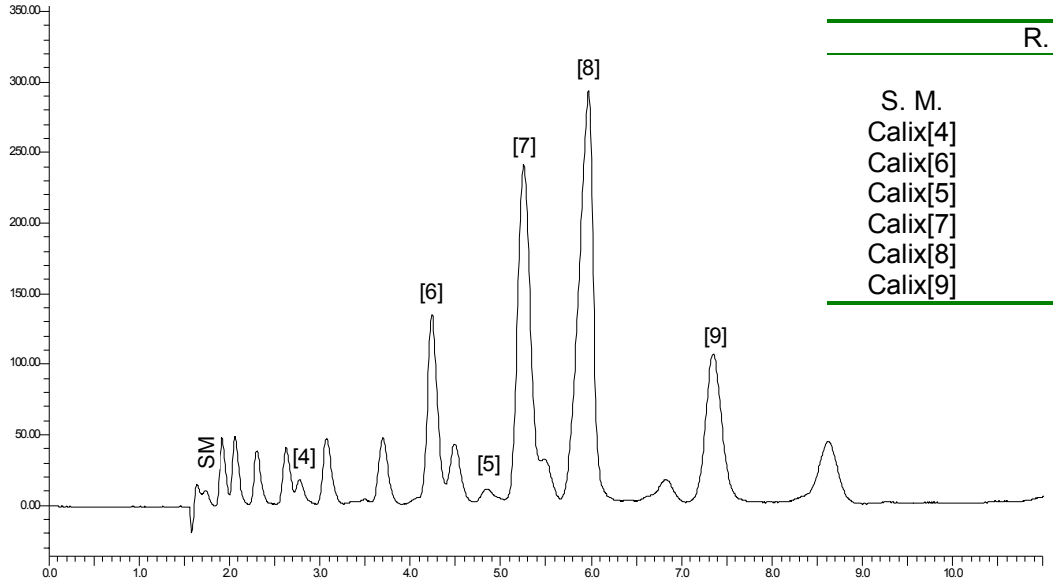


	R. T. (Min)	Comp. (%)
S. M.	1.68	2.1
Calix[4]	2.68	5.3
Calix[6]	4.25	1.9
Calix[5]	4.74	12.8
Calix[7]	5.22	6.3
Calix[8]	5.78	13.4
Calix[9]	7.35	6.2

Fig 5: HPLC chromatogram of the reaction mixture after 180 min using 10 mol% tin(IV) chloride.

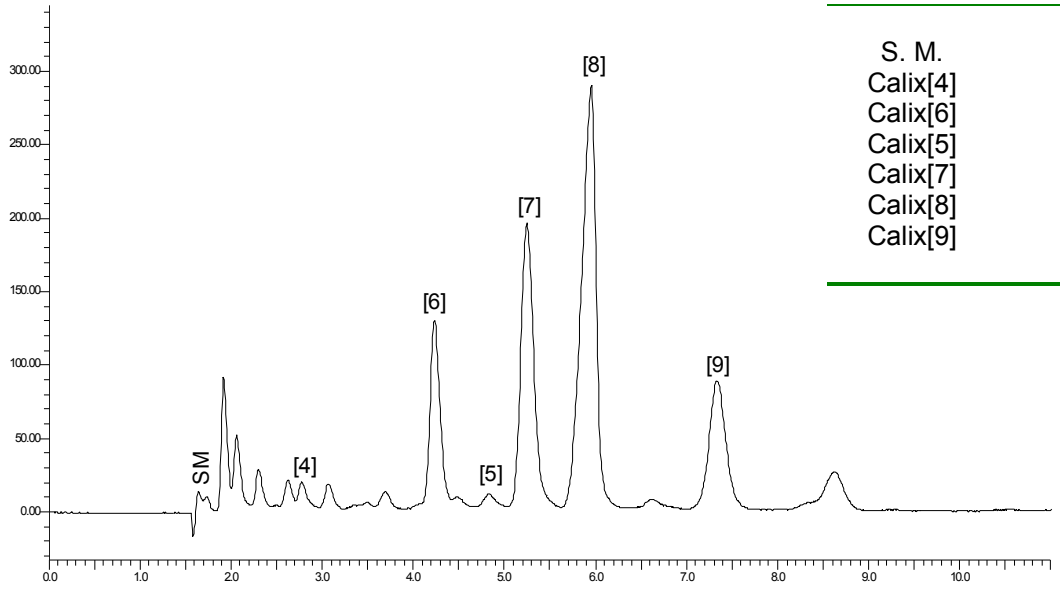
Reaction 3 (Table 1)

A solution of *para*-*tert*-butyl phenol (150 mg, 1 mmol), tin(IV) chloride (65 mg, 25 mol%) and s-trioxane (100 mg, 1.1 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature. A small aliquot was removed for HPLC analysis after 30 and 180 min.



	R. T. (Min)	Comp. (%)
S. M.	1.66	1.8
Calix[4]	2.76	1.7
Calix[6]	4.24	8.4
Calix[5]	4.81	0.9
Calix[7]	5.20	23.9
Calix[8]	5.93	26.3
Calix[9]	7.32	11.8

Fig 6: HPLC chromatogram of the reaction mixture after 30 min using 25 mol% tin(IV) chloride.

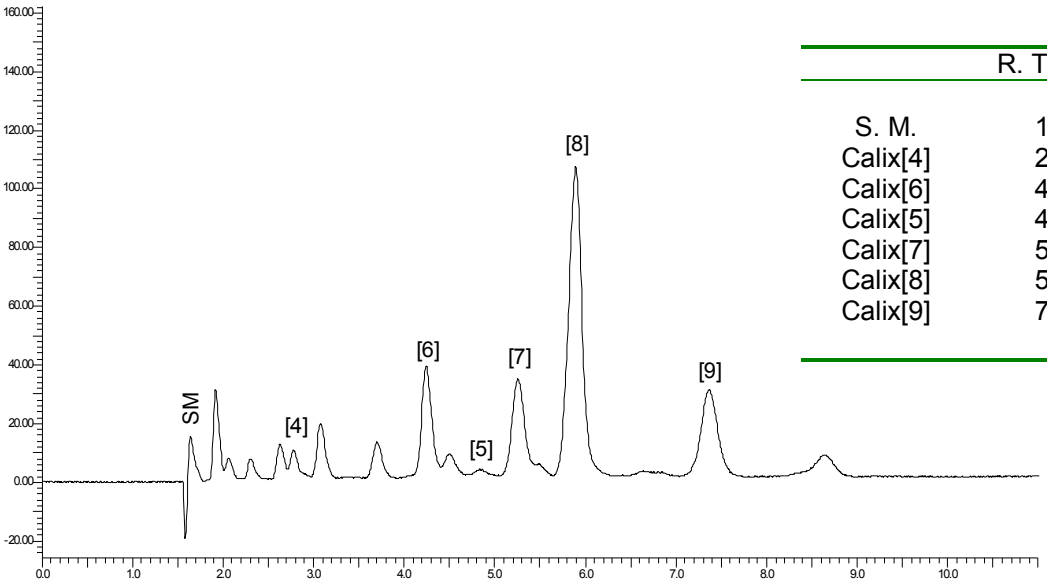


	R. T. (Min)	Comp. (%)
S. M.	1.68	1.4
Calix[4]	2.77	2.7
Calix[6]	4.23	10.5
Calix[5]	4.83	2.4
Calix[7]	5.25	16.3
Calix[8]	5.96	25.2
Calix[9]	7.33	9.9

Fig 7: HPLC chromatogram of the reaction mixture after 180 min using 25 mol% tin(IV) chloride.

Reaction 4 (Table 1)

A solution of *para-tert*-butyl phenol (150 mg, 1 mmol), tin(IV) chloride (130 mg, 50 mol%) and s-trioxane (100 mg, 1.1 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature. A small aliquot was removed for HPLC analysis after 30 min.

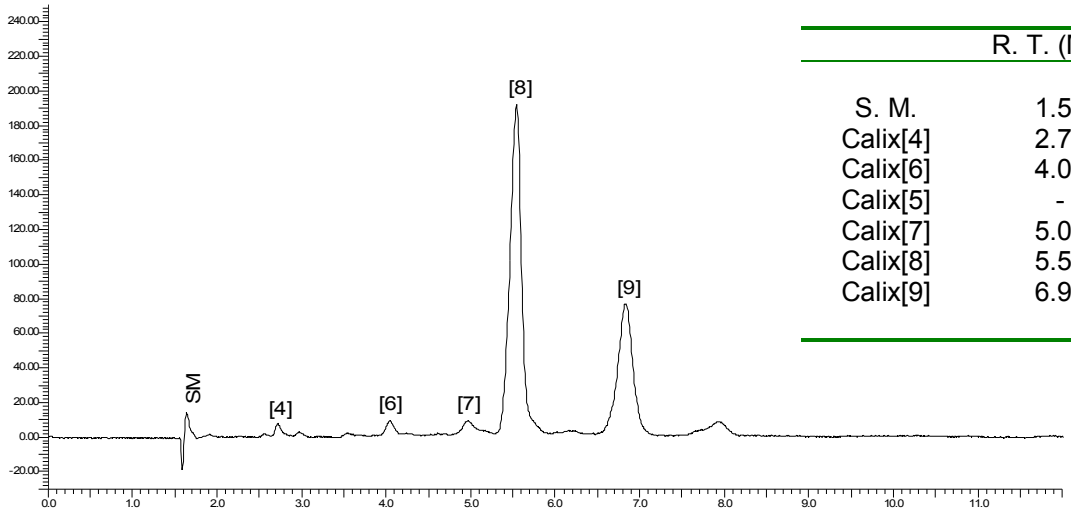


	R. T. (Min)	Comp. (%)
S. M.	1.64	1.4
Calix[4]	2.78	0.9
Calix[6]	4.24	9.2
Calix[5]	4.83	0.4
Calix[7]	5.25	10.3
Calix[8]	5.89	35.3
Calix[9]	7.36	12.4

Fig 8: HPLC chromatogram of the reaction mixture after 30 min using 50 mol% tin(IV) chloride.

Reaction 5 (Table 1)

A solution of *para-tert*-butyl phenol (150 mg, 1 mmol), tin(IV) chloride (260 mg, 100 mol%) and s-trioxane (100 mg, 1.1 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature. A small aliquot was removed for HPLC analysis after 60 min.



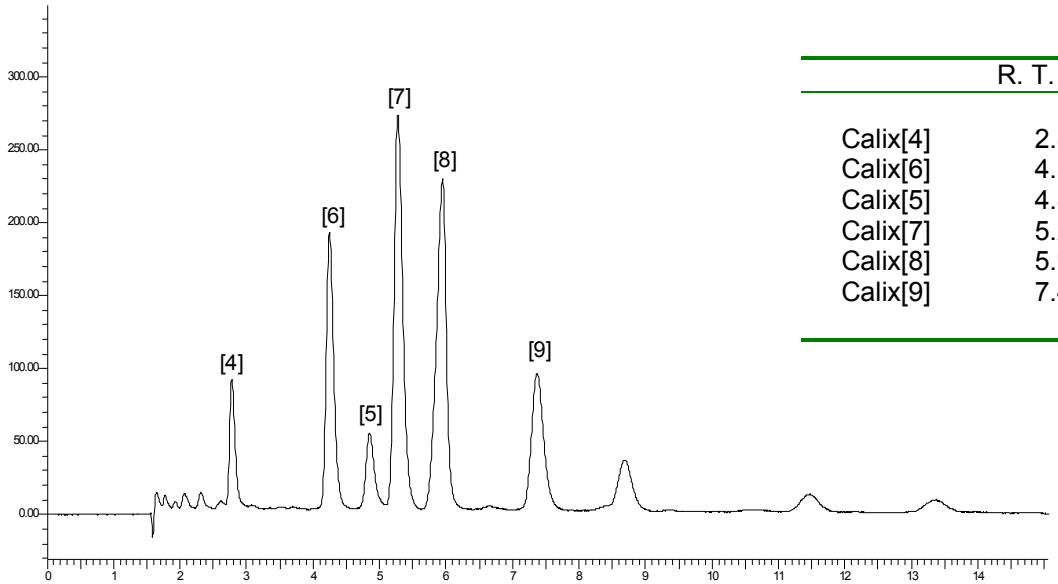
	R. T. (Min*)	Comp. (%)
S. M.	1.58	<1.0
Calix[4]	2.72	1.6
Calix[6]	4.05	1.8
Calix[5]	-	-
Calix[7]	5.06	3.1
Calix[8]	5.54	55.3
Calix[9]	6.91	29.8

Fig 9: HPLC chromatogram of the reaction mixture after 60 min using 100 mol% tin(IV) chloride.

A shift in retention time was observed due to temperature increase (confirmed by analyzing standard mixture).

Reaction 6 (Table 2)

A solution of *para-tert*-butyl phenol (150 mg, 1 mmol), tin(IV) chloride (5.2 mg, 2 mol%) and s-trioxane (100 mg, 1.1 mmol) in CH_2Cl_2 (5 mL) was placed in a Smith reaction tube, which was equipped with a PTFE coated rubber septa and subsequently sealed with an aluminum crimp cap. The solution was heated in a Personal Chemistry microwave synthesizer at 120 °C for 30 min.

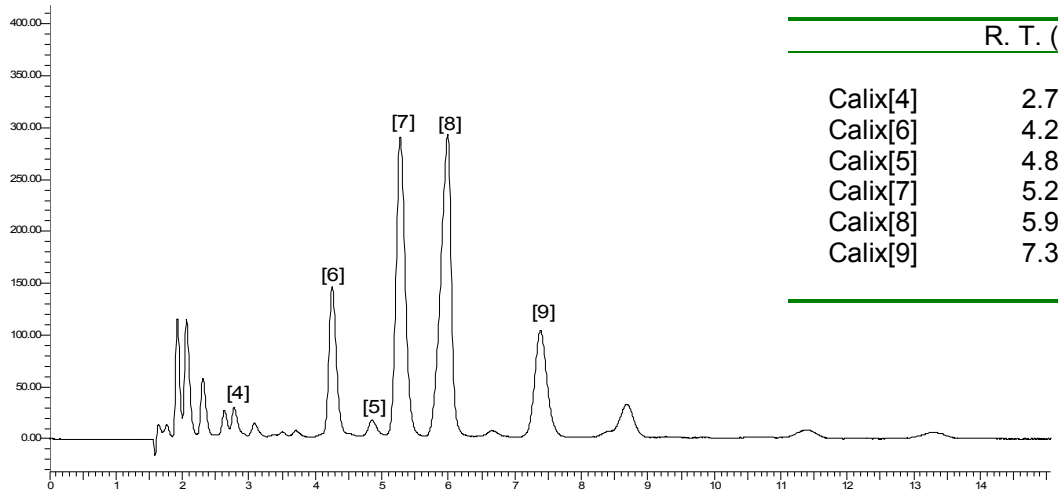


	R. T. (Min)	Comp. (%)
Calix[4]	2.84	5.3
Calix[6]	4.31	14.8
Calix[5]	4.85	4.7
Calix[7]	5.23	25.1
Calix[8]	5.98	24.2
Calix[9]	7.44	12.3

Fig 10: HPLC chromatogram of the reaction mixture after microwave heating at 120 °C for 30 min.

Reaction 7 (Table 2)

A solution of *para-tert*-butyl phenol (150 mg, 1 mmol), tin(IV) chloride (26 mg, 10 mol%) and s-trioxane (100 mg, 1.1 mmol) in CH_2Cl_2 (5 mL) was placed in a sealed reaction tube (detailed above) and irradiated with microwaves at 75 °C for 15 min.

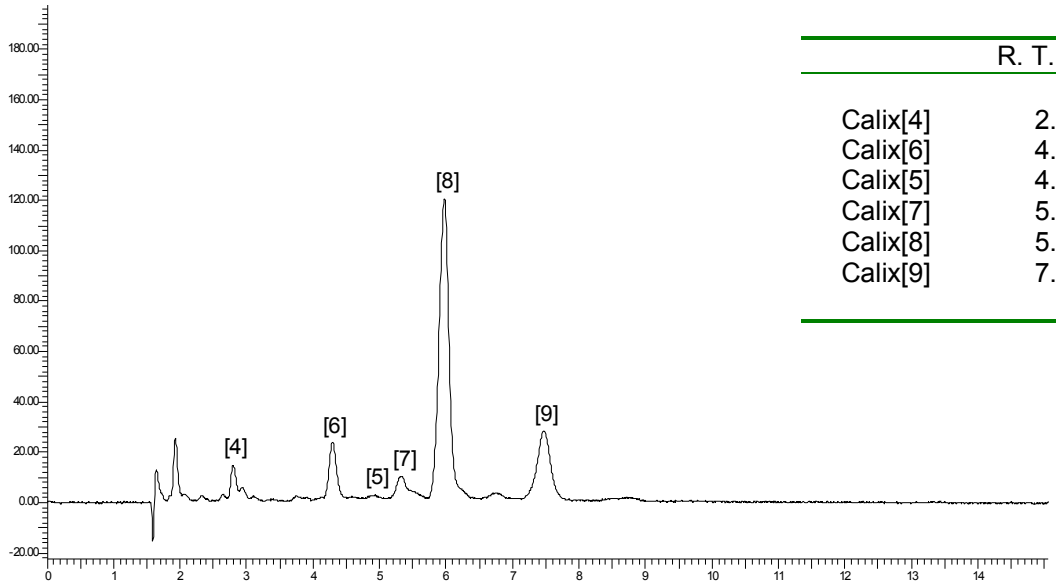


	R. T. (Min)	Comp. (%)
Calix[4]	2.78	2.7
Calix[6]	4.25	2.9
Calix[5]	4.85	10.8
Calix[7]	5.28	20.1
Calix[8]	5.96	22.8
Calix[9]	7.39	9.9

Fig 11: HPLC chromatogram of the reaction mixture after microwave heating at 75 °C for 15 min.

Reaction 8 (Table 2)

A solution of *para-tert*-butyl phenol (150 mg, 1 mmol), tin(IV) chloride (260 mg, 100 mol%) and s-trioxane (100 mg, 1.1 mmol) in CH_2Cl_2 (5 mL) was placed in a sealed reaction tube (detailed above) and irradiated with microwaves at 60 °C for 1 min.

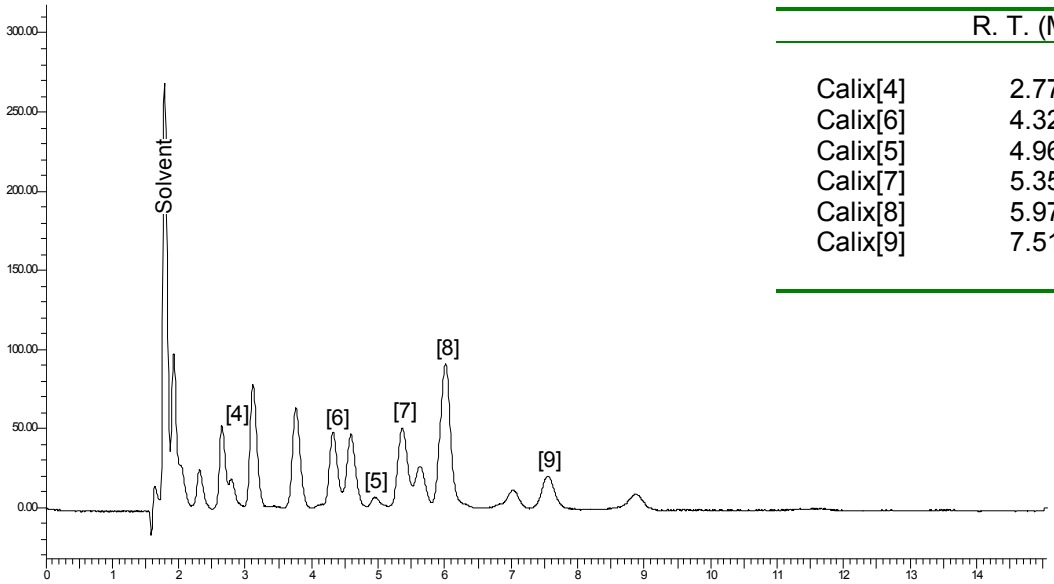


	R. T. (Min)	Comp. (%)
Calix[4]	2.79	4.2
Calix[6]	4.29	7.9
Calix[5]	4.90	0.5
Calix[7]	5.32	5.2
Calix[8]	5.98	54.7
Calix[9]	7.47	17.0

Fig 12: HPLC chromatogram of the reaction mixture after microwave heating at 60 °C for 1 min.

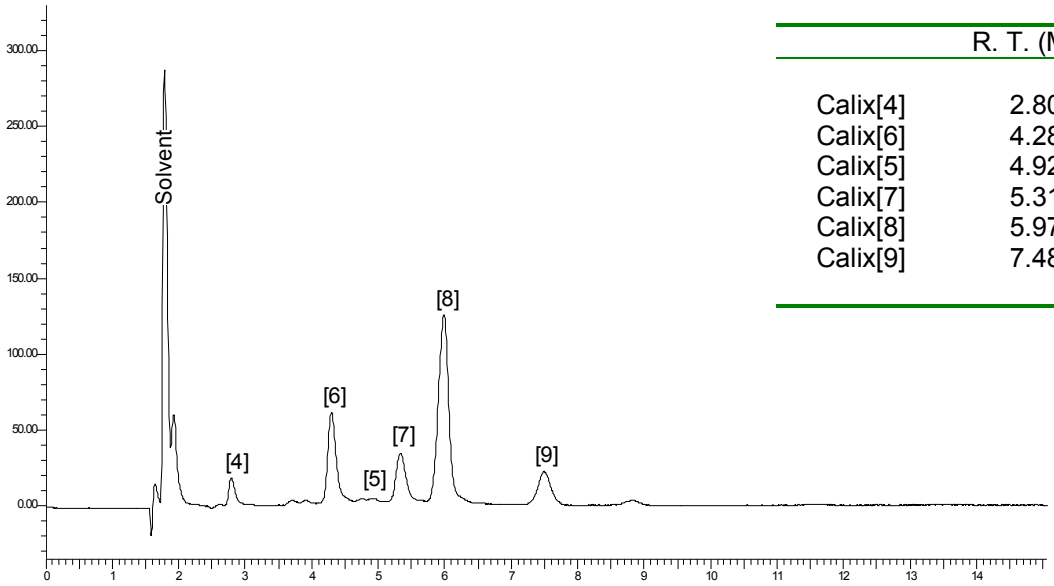
Reaction 9 (Table 3)

A solution of *para-tert*-butyl phenol (150 mg, 1 mmol), tin(IV) chloride (260 mg, 100 mol%) and s-trioxane (100 mg, 1.1 mmol) in chlorobenzene (5 mL) was stirred at room temperature. A small aliquot was removed for HPLC analysis after 1 and 15 h.



	R. T. (Min)	Comp. (%)
Calix[4]	2.77	0.9
Calix[6]	4.32	8.3
Calix[5]	4.96	0.7
Calix[7]	5.35	10.2
Calix[8]	5.97	19.7
Calix[9]	7.51	5.8

Fig 13: HPLC chromatogram of the reaction mixture using chlorobenzene solvent after 1 h.

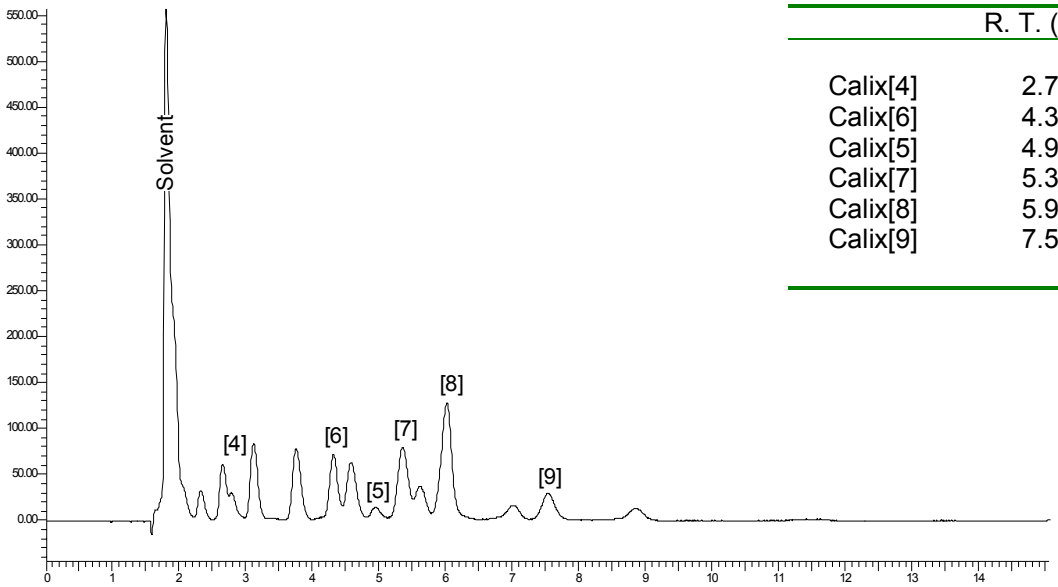


	R. T. (Min)	Comp. (%)
Calix[4]	2.80	5.6
Calix[6]	4.28	18.2
Calix[5]	4.92	0.5
Calix[7]	5.31	12.2
Calix[8]	5.97	43.4
Calix[9]	7.48	9.2

Fig 14: HPLC chromatogram of the reaction mixture using chlorobenzene solvent after 15 h.

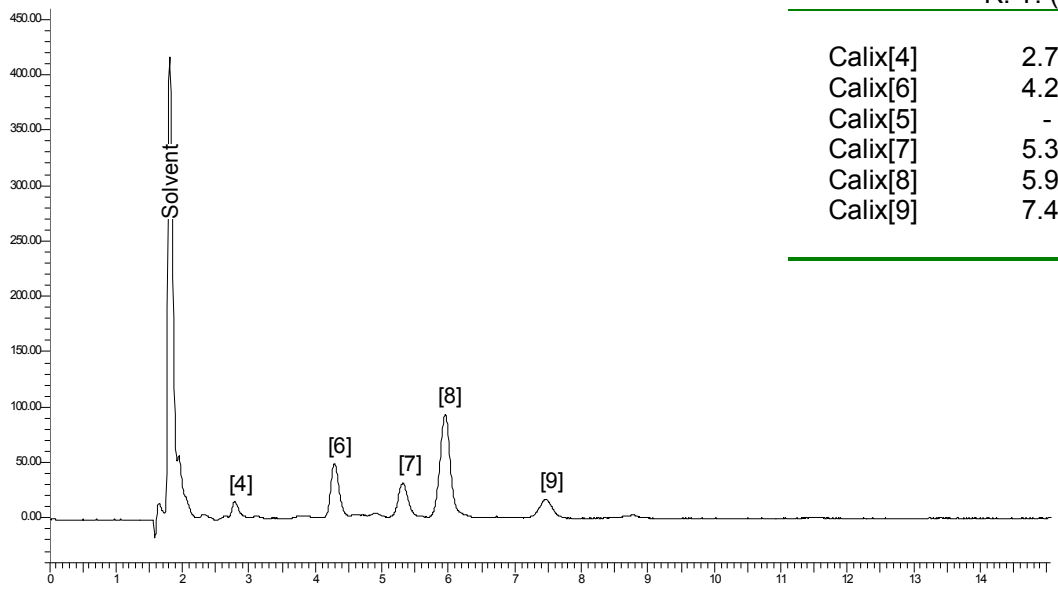
Reaction 10 (Table 3)

A solution of *para-tert*-butyl phenol (150 mg, 1 mmol), tin(IV) chloride (260 mg, 100 mol%) and s-trioxane (100 mg, 1.1 mmol) in bromobenzene (5 mL) was stirred at room temperature. A small aliquot was removed for HPLC analysis after 1 and 15 h.



	R. T. (Min)	Comp. (%)
Calix[4]	2.76	2.8
Calix[6]	4.31	7.8
Calix[5]	4.92	2.1
Calix[7]	5.35	12.3
Calix[8]	5.98	20.9
Calix[9]	7.50	6.2

Fig 15: HPLC chromatogram of the reaction mixture using bromobenzene solvent after 1 h.

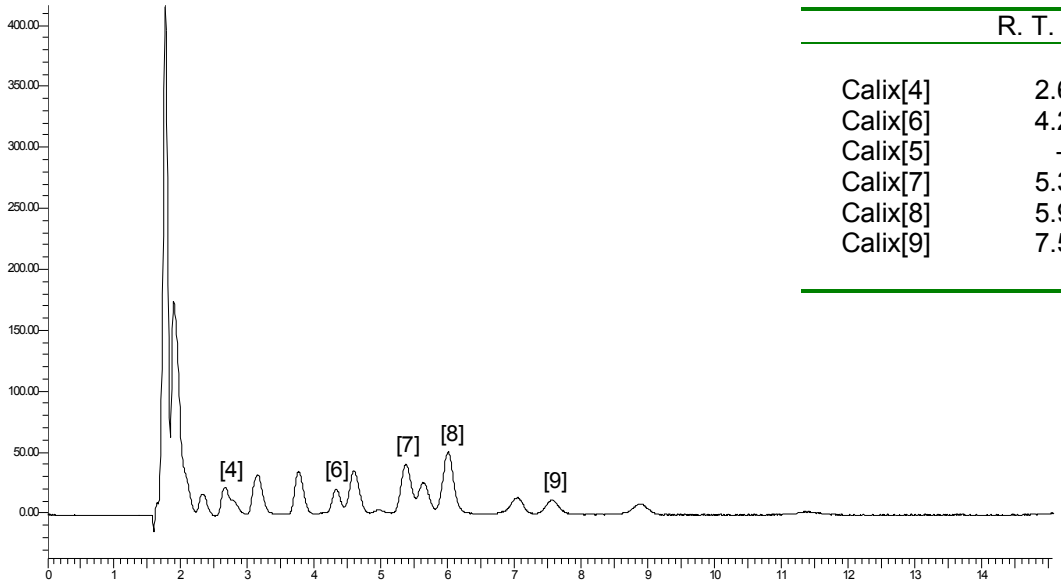


	R. T. (Min)	Comp. (%)
Calix[4]	2.77	5.7
Calix[6]	4.26	18.1
Calix[5]	-	-
Calix[7]	5.31	14.9
Calix[8]	5.95	46.2
Calix[9]	7.46	10.8

Fig 16: HPLC chromatogram of the reaction mixture using bromobenzene solvent after 15 h.

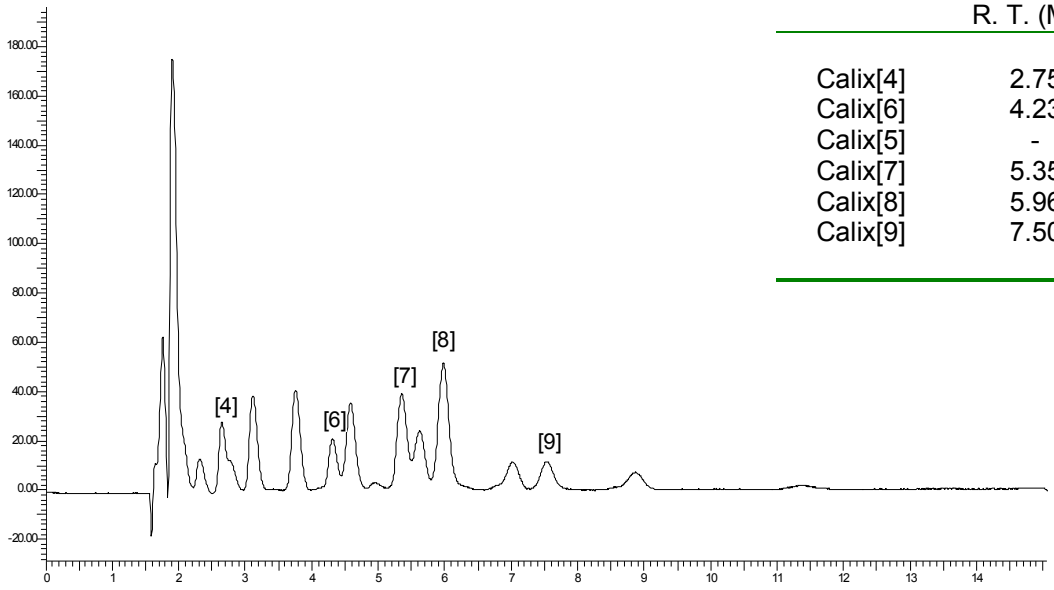
Reaction 11 (Table 3)

A solution of *para*-*tert*-butyl phenol (150 mg, 1 mmol), tin(IV) chloride (260 mg, 100 mol%) and s-trioxane (100 mg, 1.1 mmol) in carbon tetrachloride (5 mL) was stirred at room temperature. A small aliquot was removed for HPLC analysis after 1 and 15 h.



	R. T. (Min)	Comp. (%)
Calix[4]	2.69	5.0
Calix[6]	4.25	4.1
Calix[5]	-	-
Calix[7]	5.38	5.7
Calix[8]	5.99	7.9
Calix[9]	7.52	1.9

Fig 17: HPLC chromatogram of the reaction mixture using carbon tetrachloride solvent after 1 h.

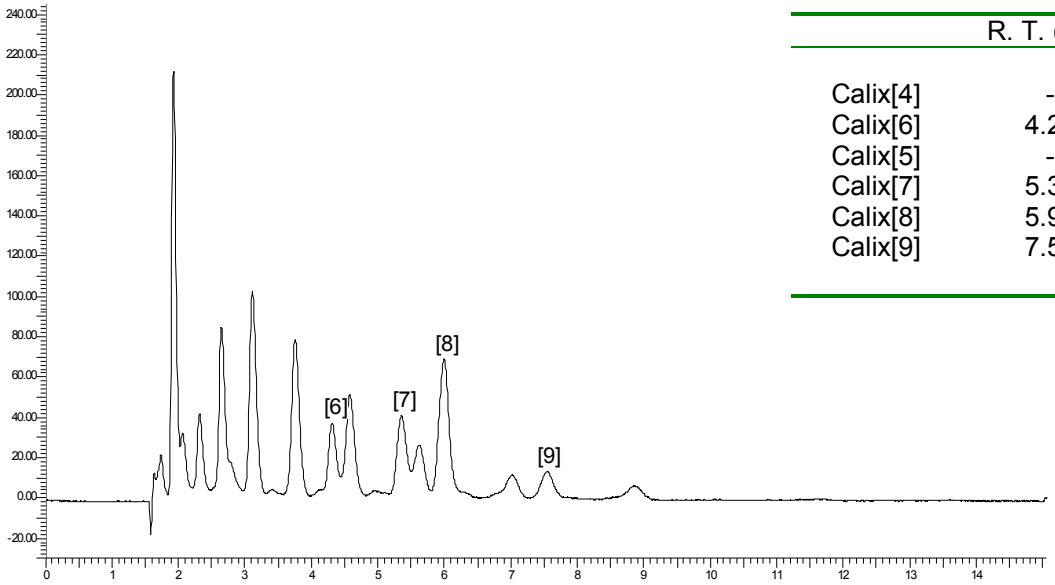


	R. T. (Min)	Comp. (%)
Calix[4]	2.75	7.0
Calix[6]	4.23	4.2
Calix[5]	-	-
Calix[7]	5.35	8.1
Calix[8]	5.96	11.4
Calix[9]	7.50	2.8

Fig 18: HPLC chromatogram of the reaction mixture using carbon tetrachloride solvent after 15 h.

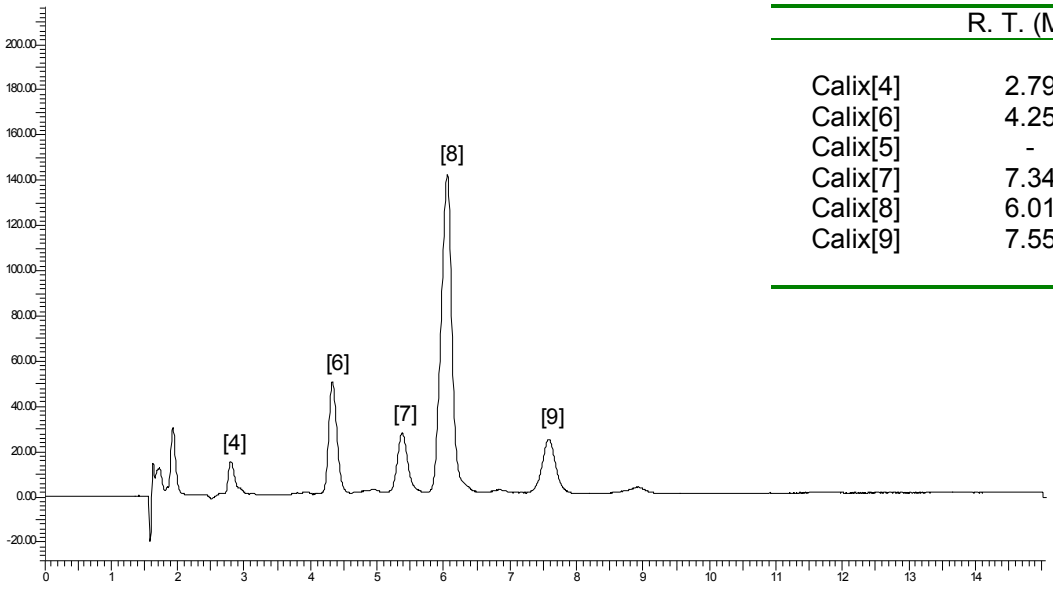
Reaction 12 (Table 3)

A solution of *para*-*tert*-butyl phenol (150 mg, 1 mmol), tin(IV) chloride (260 mg, 100 mol%) and s-trioxane (100 mg, 1.1 mmol) in chloroform (5 mL) was stirred at room temperature. A small aliquot was removed for HPLC analysis after 1 and 15 h.



	R. T. (Min)	Comp. (%)
Calix[4]	-	-
Calix[6]	4.28	6.2
Calix[5]	-	-
Calix[7]	5.34	6.4
Calix[8]	5.97	12.1
Calix[9]	7.52	3.2

Fig 19: HPLC chromatogram of the reaction mixture using chloroform solvent after 1 h.

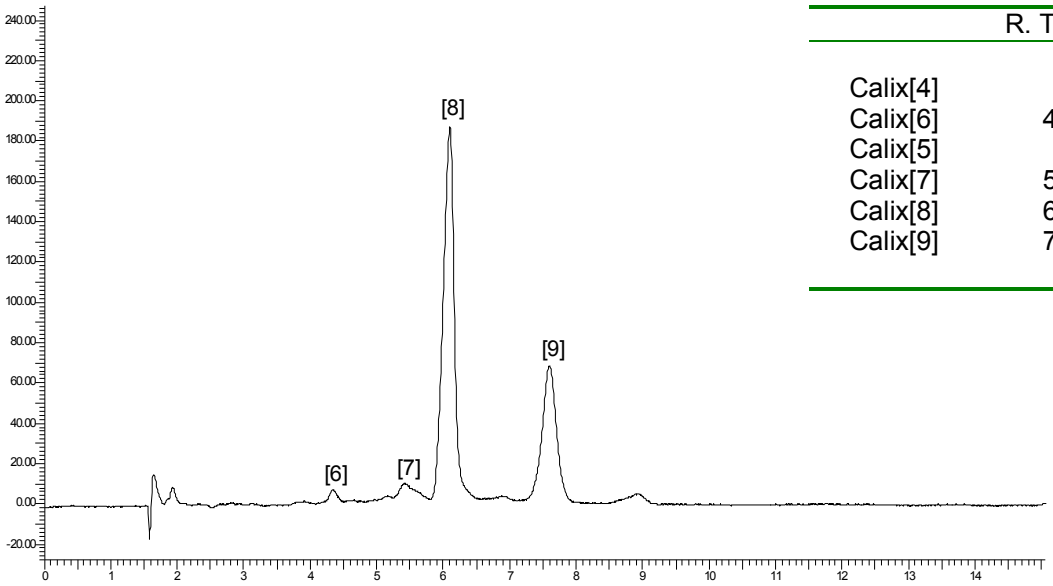


	R. T. (Min)	Comp. (%)
Calix[4]	2.79	5.2
Calix[6]	4.25	14.1
Calix[5]	-	-
Calix[7]	7.34	8.9
Calix[8]	6.01	52.8
Calix[9]	7.55	11.2

Fig 20: HPLC chromatogram of the reaction mixture using chloroform solvent after 15 h.

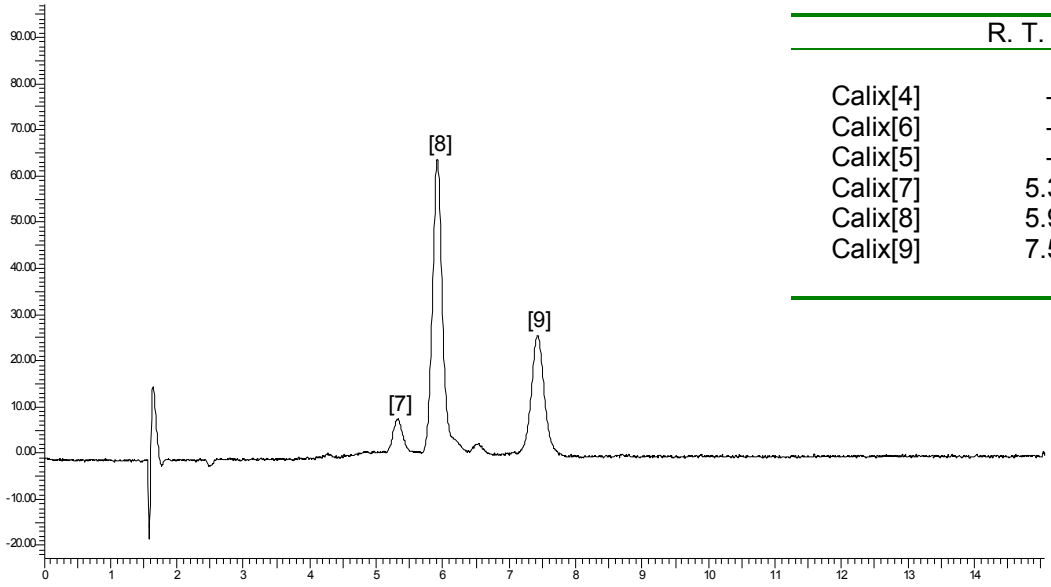
Reaction 13 (Table 3)

A solution of *para*-*tert*-butyl phenol (150 mg, 1 mmol), tin(IV) chloride (260 mg, 100 mol%) and s-trioxane (100 mg, 1.1 mmol) in 1,2-dichloroethane (5 mL) was stirred at room temperature. A small aliquot was removed for HPLC analysis after 1 and 15 h.



	R. T. (Min)	Comp. (%)
Calix[4]	-	-
Calix[6]	4.31	1.8
Calix[5]	-	-
Calix[7]	5.35	3.7
Calix[8]	6.08	57.8
Calix[9]	7.58	28.1

Fig 21: HPLC chromatogram of the reaction mixture using 1,2-dichloroethane solvent after 1 h.

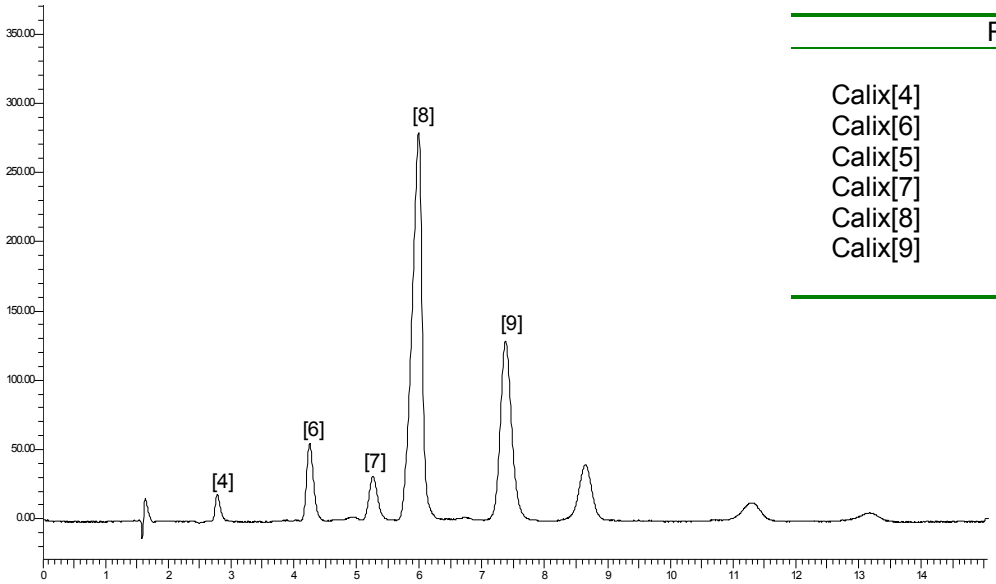


	R. T. (Min)	Comp. (%)
Calix[4]	-	-
Calix[6]	-	-
Calix[5]	-	-
Calix[7]	5.32	6.8
Calix[8]	5.98	58.1
Calix[9]	7.51	32.7

Fig 22: HPLC chromatogram of the reaction mixture using 1,2-dichloroethane solvent after 15 h.

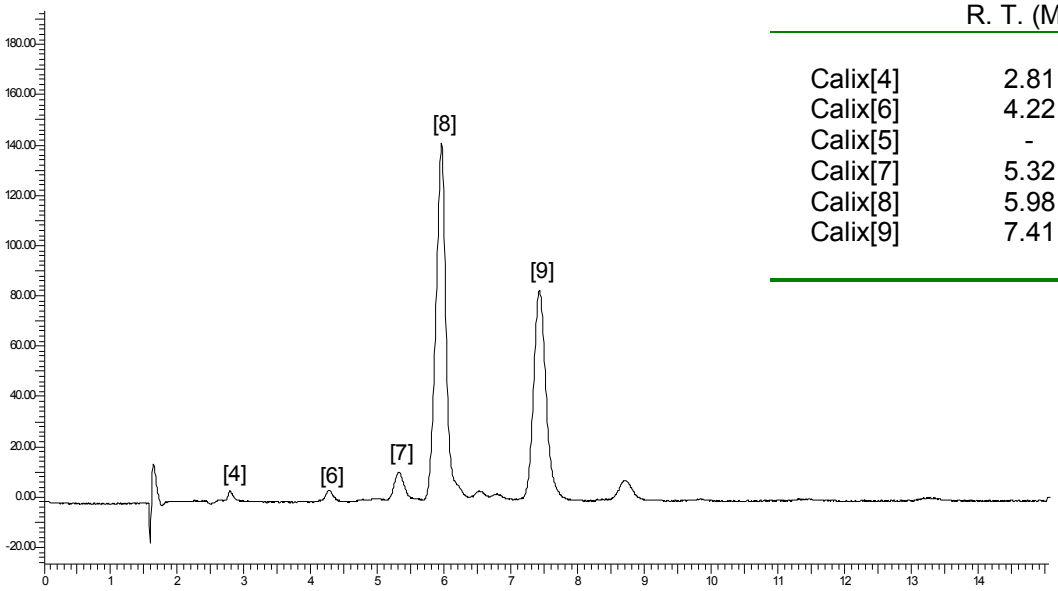
Reaction 14 (Table 3)

A solution of *para*-*tert*-butyl phenol (150 mg, 1 mmol), tin(IV) chloride (260 mg, 100 mol%) and s-trioxane (100 mg, 1.1 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature. A small aliquot was removed for HPLC analysis after 1 and 15 h.



	R. T. (Min)	Comp. (%)
Calix[4]	2.81	1.8
Calix[6]	4.28	7.1
Calix[5]	-	-
Calix[7]	5.32	4.9
Calix[8]	5.98	46.1
Calix[9]	7.41	24.2

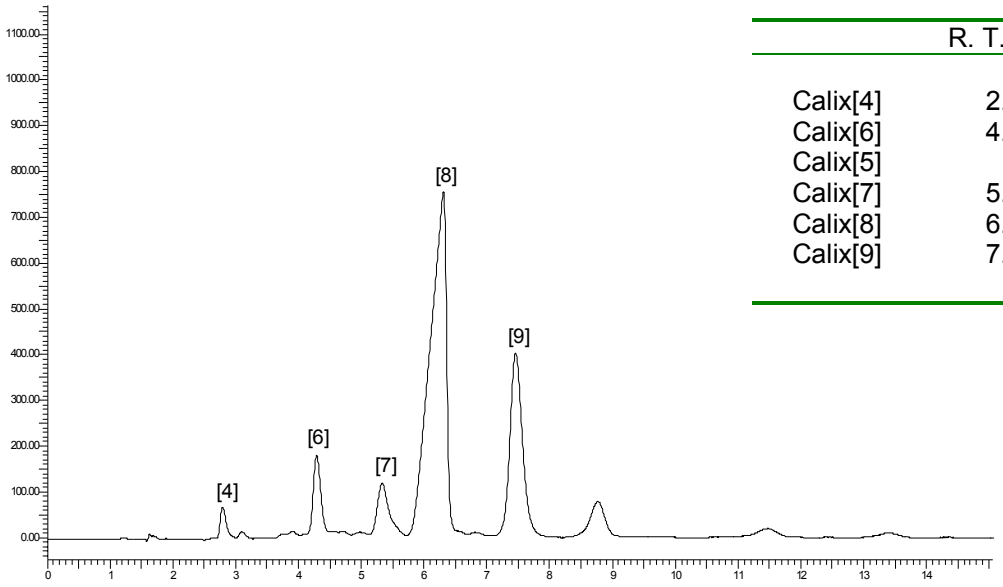
Fig 23: HPLC chromatogram of the reaction mixture using CH_2Cl_2 solvent after 1 h.



	R. T. (Min)	Comp. (%)
Calix[4]	2.81	0.8
Calix[6]	4.22	1.6
Calix[5]	-	-
Calix[7]	5.32	3.7
Calix[8]	5.98	51.1
Calix[9]	7.41	36.3

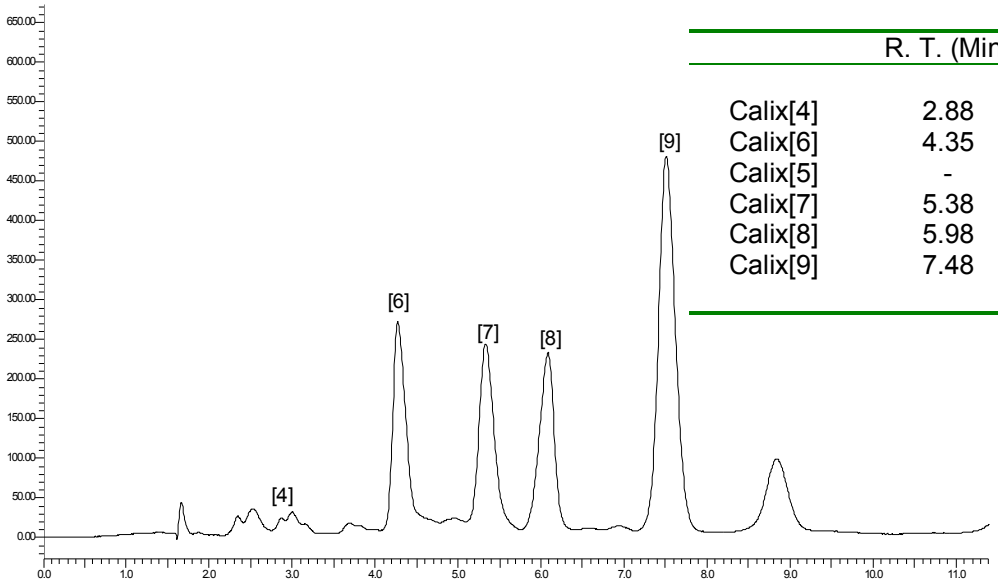
Fig 24: HPLC chromatogram of the reaction mixture using CH_2Cl_2 solvent after 15 h.

Isolation and Purification Studies:



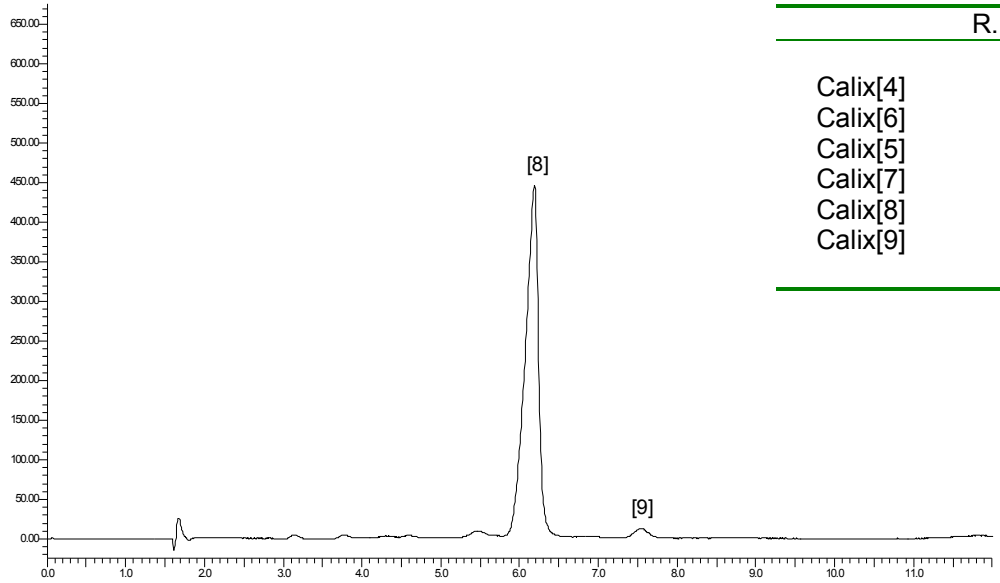
	R. T. (Min)	Comp. (%)
Calix[4]	2.68	1.8
Calix[6]	4.48	9.5
Calix[5]	-	-
Calix[7]	5.61	9.4
Calix[8]	6.24	49.5
Calix[9]	7.59	18.9

Fig 25: HPLC chromatogram of the crude product used for isolation studies



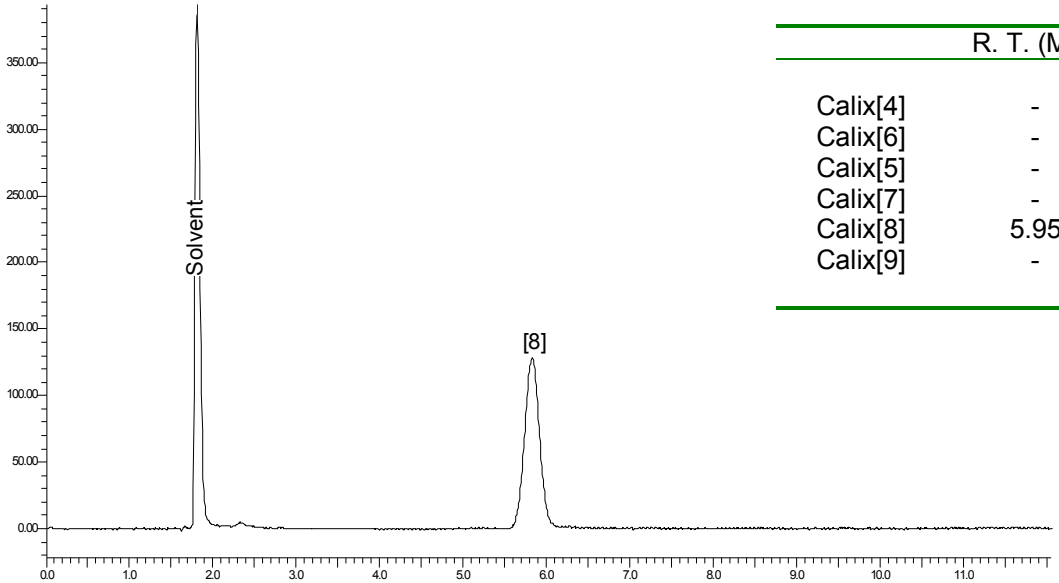
	R. T. (Min)	Comp. (%)
Calix[4]	2.88	3.5
Calix[6]	4.35	14.8
Calix[5]	-	-
Calix[7]	5.38	15.7
Calix[8]	5.98	15.9
Calix[9]	7.48	36.8

Fig 26: HPLC chromatogram of the n-hexane soluble fraction



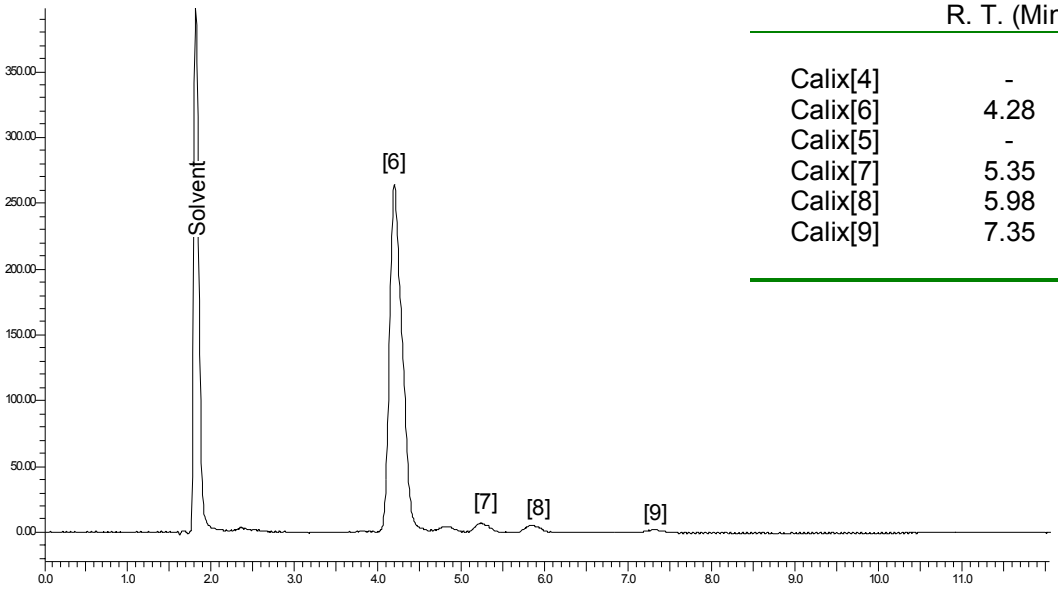
	R. T. (Min)	Comp. (%)
Calix[4]	-	-
Calix[6]	-	-
Calix[5]	-	-
Calix[7]	5.44	0.2
Calix[8]	6.12	94.8
Calix[9]	7.54	2.6

Fig 27: HPLC chromatogram of the n-hexane insoluble precipitate



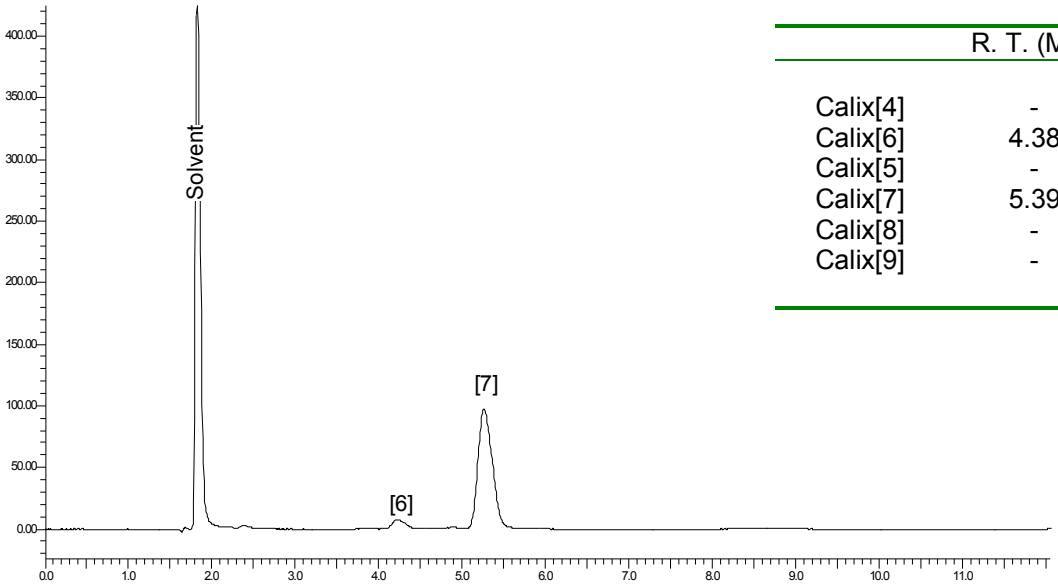
	R. T. (Min)	Comp. (%)
Calix[4]	-	-
Calix[6]	-	-
Calix[5]	-	-
Calix[7]	-	-
Calix[8]	5.95	99.3
Calix[9]	-	-

Fig 28: HPLC chromatogram of the fractions containing pure calix[8]arene after column chromatography



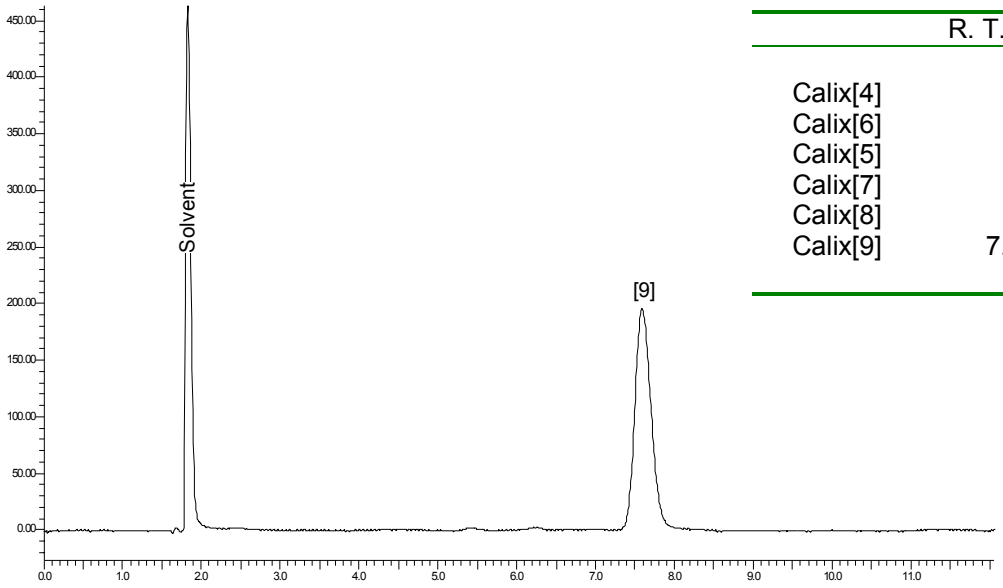
	R. T. (Min)	Comp. (%)
Calix[4]	-	-
Calix[6]	4.28	91.2
Calix[5]	-	-
Calix[7]	5.35	2.1
Calix[8]	5.98	1.9
Calix[9]	7.35	1.1

Fig 29: HPLC chromatogram of the fractions containing calix[6]arene after column chromatography



	R. T. (Min)	Comp. (%)
Calix[4]	-	-
Calix[6]	4.38	2.2
Calix[5]	-	-
Calix[7]	5.39	97.4
Calix[8]	-	-
Calix[9]	-	-

Fig 30: HPLC chromatogram of the fractions containing nearly pure calix[7]arene after column chromatography

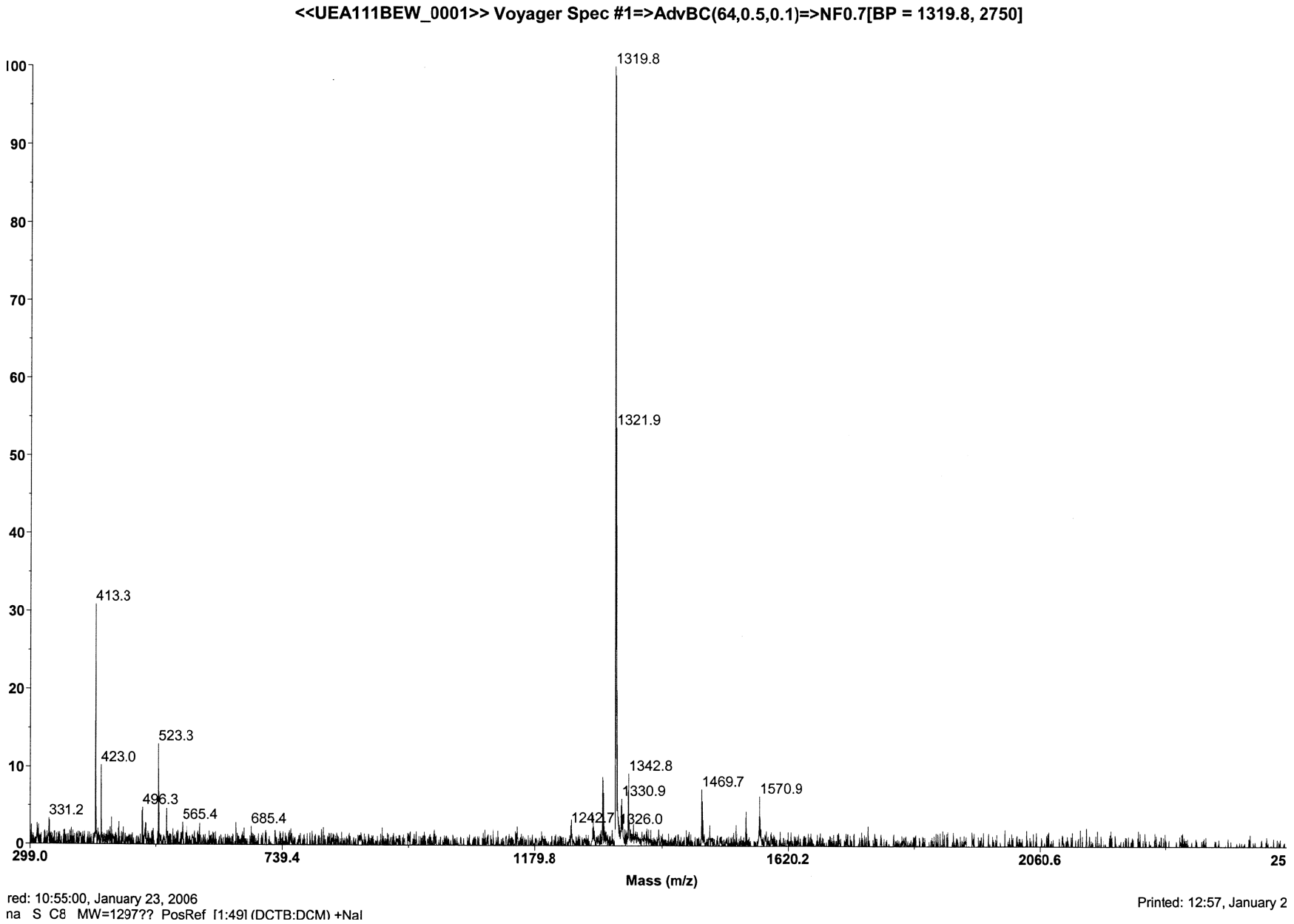


	R. T. (Min)	Comp. (%)
Calix[4]	-	-
Calix[6]	-	-
Calix[5]	-	-
Calix[7]	-	-
Calix[8]	-	-
Calix[9]	7.56	99.1

Fig 31: HPLC chromatogram of the fractions containing pure calix[9]arene after column chromatography

calix[8]arene
OH
HO
9.623
7.249
7.169
4.373
4.341
3.506
3.472
3.474
1.243
ppm

146.825
144.928
128.926
125.747
77.561
77.242
76.924
34.238
32.538
31.696
ppm
160
140
120
100
80
60
40
20
OH
OH
OH
OH
OH
OH
OH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80
70
60
50
40
30
20
10
0
1319.8
1321.9
413.3
523.3
423.0
1342.8
1330.9
1469.7
1570.9
331.2
496.3
565.4
685.4
1242.7
1326.0
299.0
739.4
1179.8
1620.2
2060.6
25
Mass (m/z)
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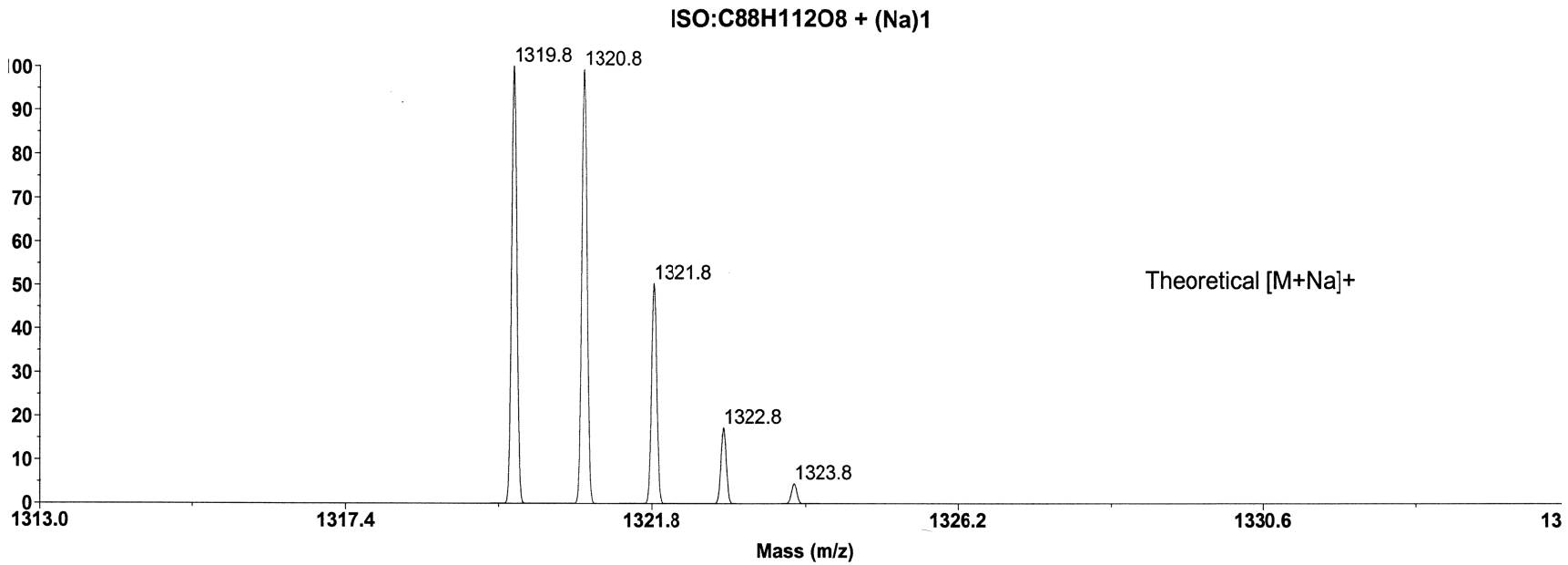
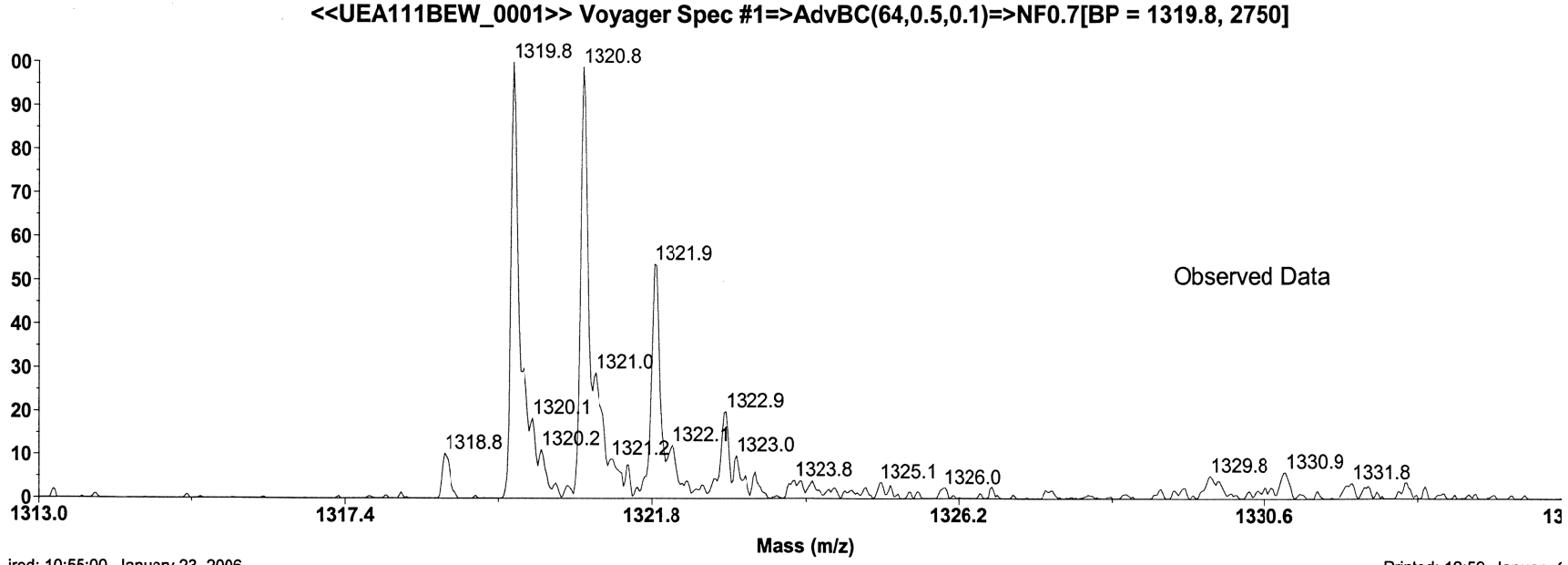
na S C8 MW=1297?? PosRef [1:491 (DCTB:DCM) +Nal
Printed: 12:57, January 2





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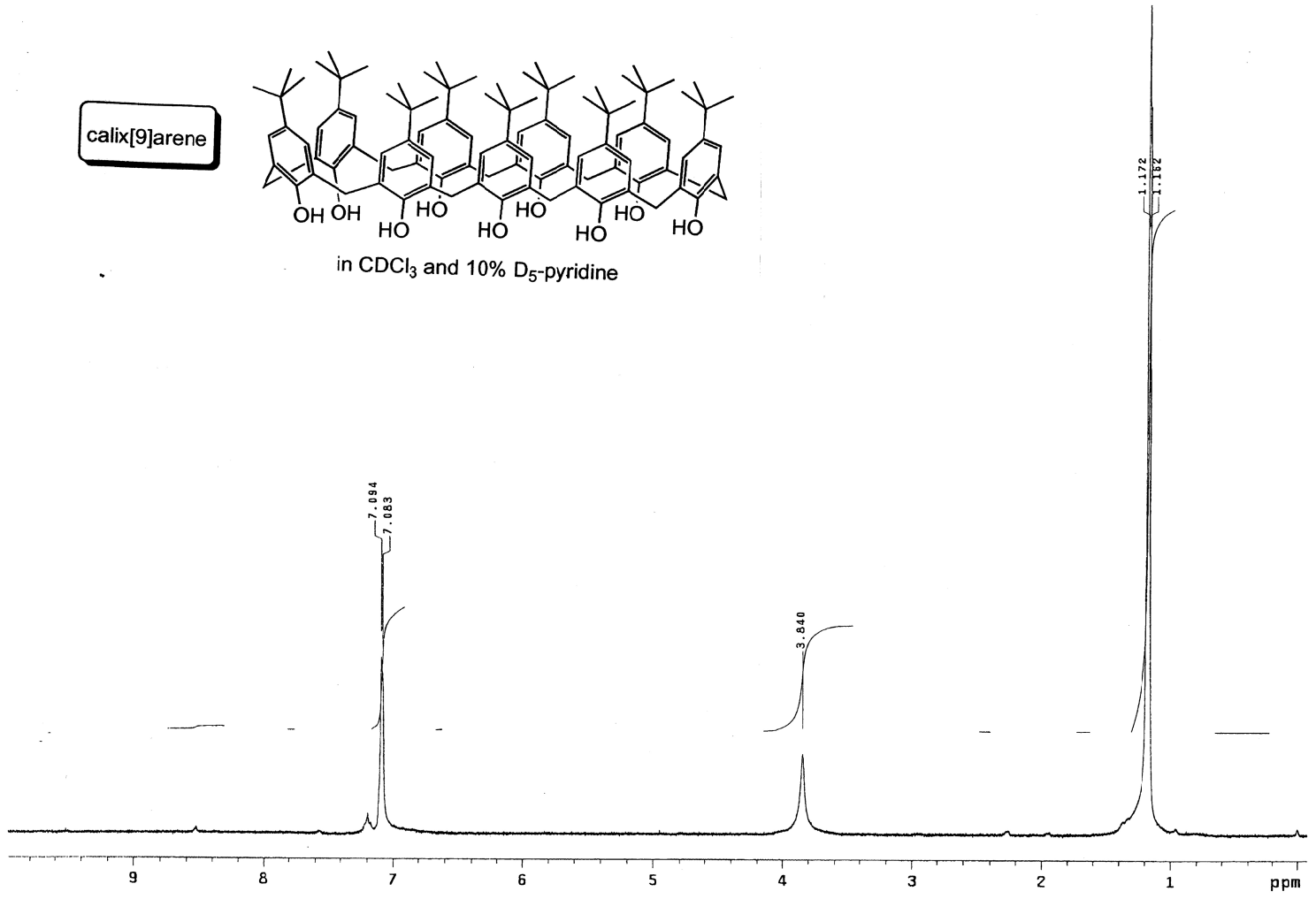
calix[9]arene
OH OH HO HO HO HO HO HO HO
in CDCl3 and 10% D5-pyridine
7.094
7.083
3.840
1.172
1.162
9
8
7
6
5
4
3
2
1
ppm

147.288
144.549
128.024
125.967
77.569
77.250
76.931
34.208
32.630
31.711
150
140
130
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70
60
50
40
30
ppm
HO
HO
HO
HO
HO
HO
HO
HO

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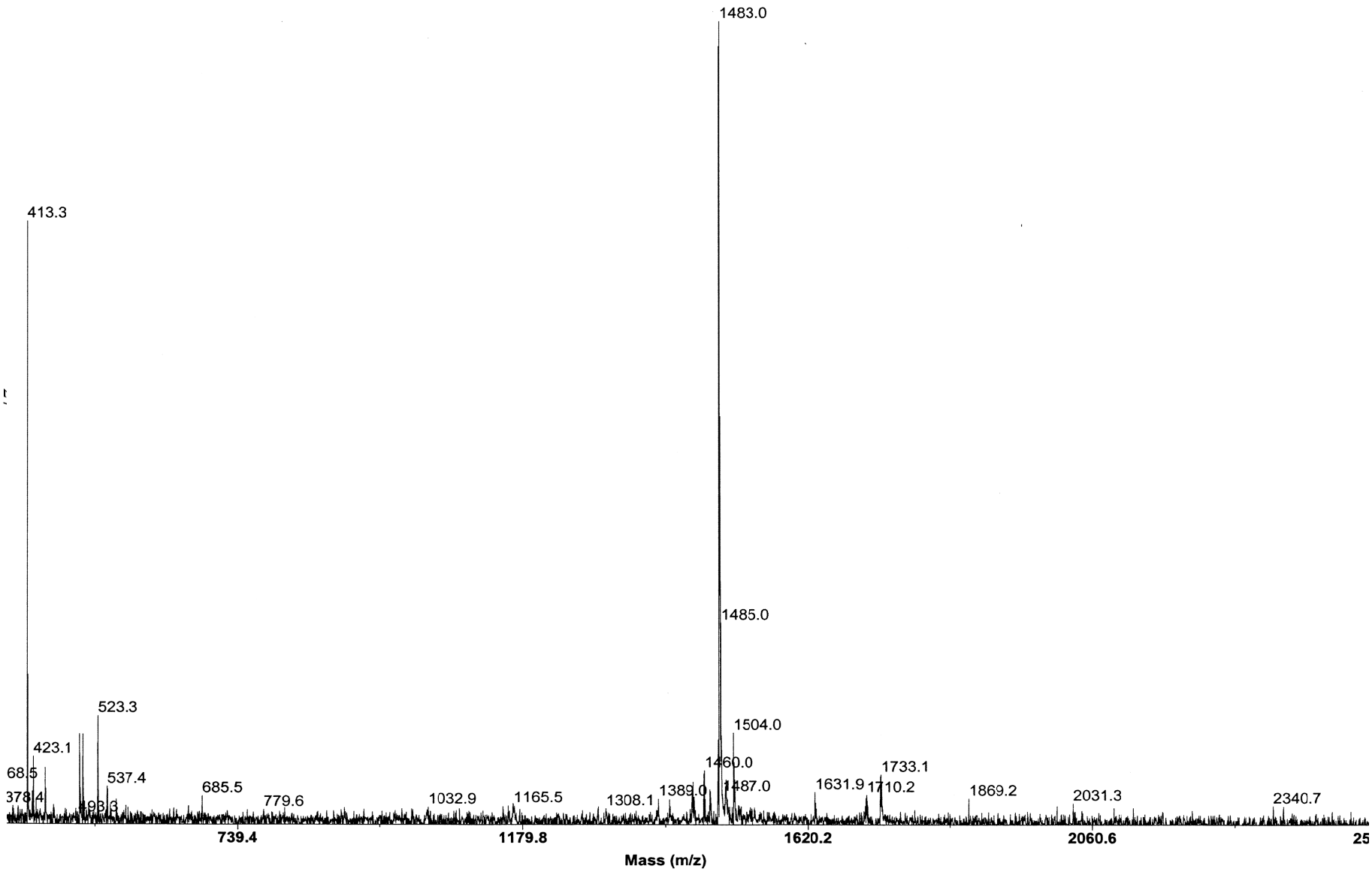

0, January 23, 2006
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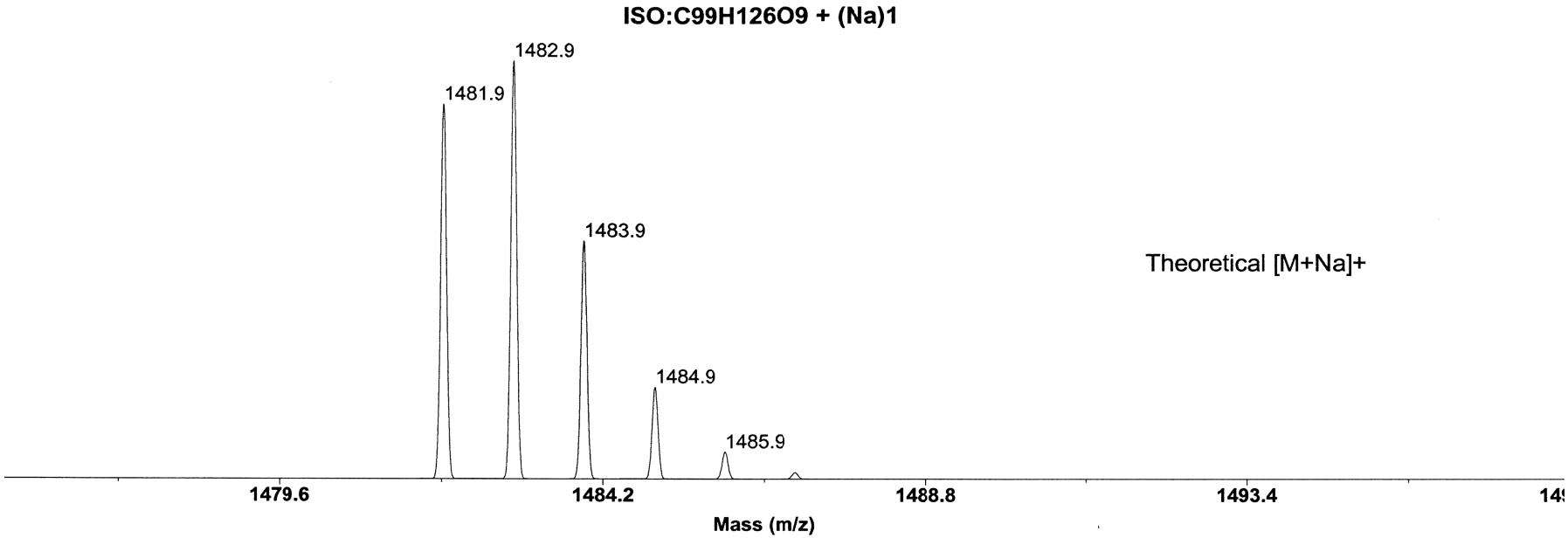

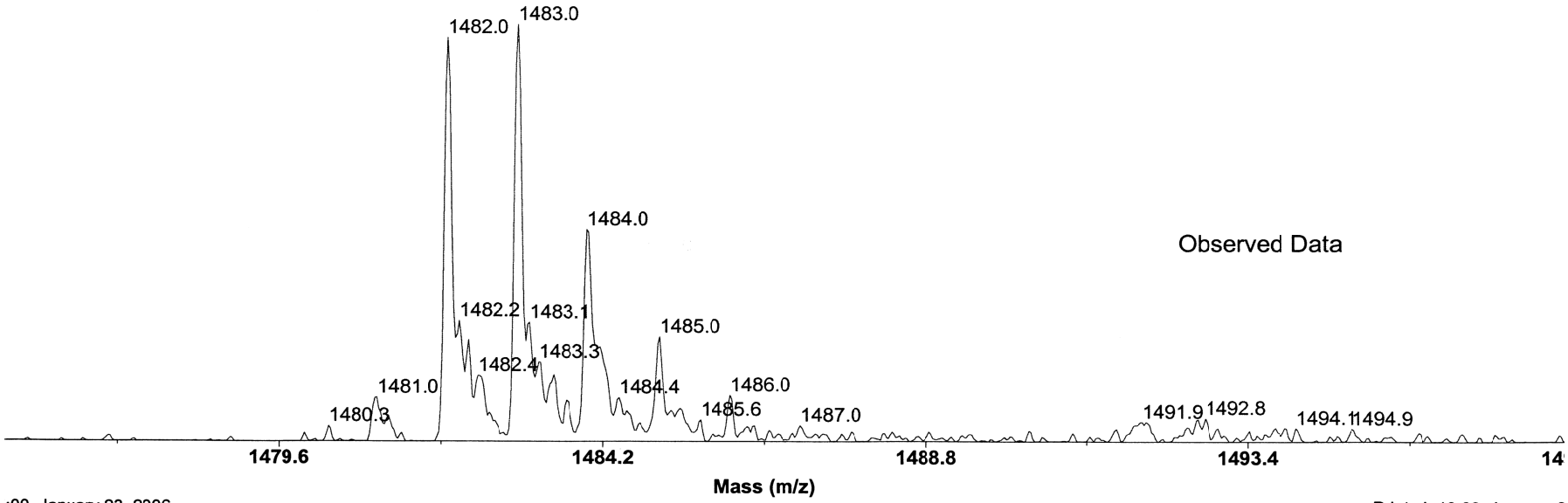

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