Supporting Information

For

Cyclic Peptoids as Mycotoxins Mimics: an Exploration of their Structural and Biological Properties

Assunta D'Amato,[†] Raffaele Volpe,[†] Maria Carmela Vaccaro,[‡] Stefania Terracciano,[‡] Ines Bruno,[‡] Massimo Tosolini,[§] Consiglia Tedesco,[†] Giovanni Pierri,[†] Paolo Tecilla,[§] Chiara Costabile,[†] Giorgio Della Sala,[†] Irene Izzo,*[†] Francesco De Riccardis*[†]

[†] *Department of Chemistry and Biology "A. Zambelli", University of Salerno, Via Giovanni Paolo II, 132, Fisciano (SA), 84084, Italy*

[‡] *Department of Pharmacy, University of Salerno, Via Giovanni Paolo II, 132, Fisciano (SA), 84084, Italy*

[§] *Department of Chemical and Pharmaceutical Sciences, University of Trieste, Via Giorgieri, 1, Trieste, 34127, Italy*

Corresponding authors: Francesco De Riccardis, dericca@unisa.it; Irene Izzo, iizzo@unisa.it

Table of contents

List of abbreviations

ACN: acetonitrile

Ar: aryl

Bn: benzyl

CCCP: carbonyl cyanide 3-chlorophenylhydrazone

COSY: correlation spectroscopy

DCM: dichloromethane

DMSO: dimethyl sulfoxide

DIC*: N,N'*-diisopropylcarbodiimide

DIPEA: *N,N*-diisopropylethylamine

DMF: dimethylformamide

EYPG: egg yolk phosphatidylglycerol

EYPC: egg yolk phosphatidylcholine

ESI: electrospray ionisation

FTICR-MS: Fourier transform ion cyclotron resonance mass spectrometry

HATU: *O*-(7-azabenzotriazol-1-yl)-*N,N,N',N'*-tetramethyluronium hexafluorophosphate

HEPES: 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid

HFIP: hexafluoroisopropanol

HMBC: heteronuclear multiple bond correlation

HMQC: heteronuclear multiple quantum coherence

HPTS: 8-hydroxypyrene-1,3,6-trisulfonic acid

HRMS: high resolution mass spectrometry

IC_{50}: inhibitory concentration

i-Bu: iso-butyl

i-Pr: iso-propyl

MTT: [3-4,5-dimethyldiazol-2-yl]-2,5-diphenyl tetrazolium bromide

PC: phosphatidylcholine

PG: phosphatidylglycerol

Ph: phenyl

PI: propidium iodide

ROESY: rotating-frame nuclear Overhauser effect correlation spectroscopy

RP HPLC: reversed-phase high-performance liquid chromatography

SEC: size exclusion chromatography

TCDE: tetrachlorodideuteroethane

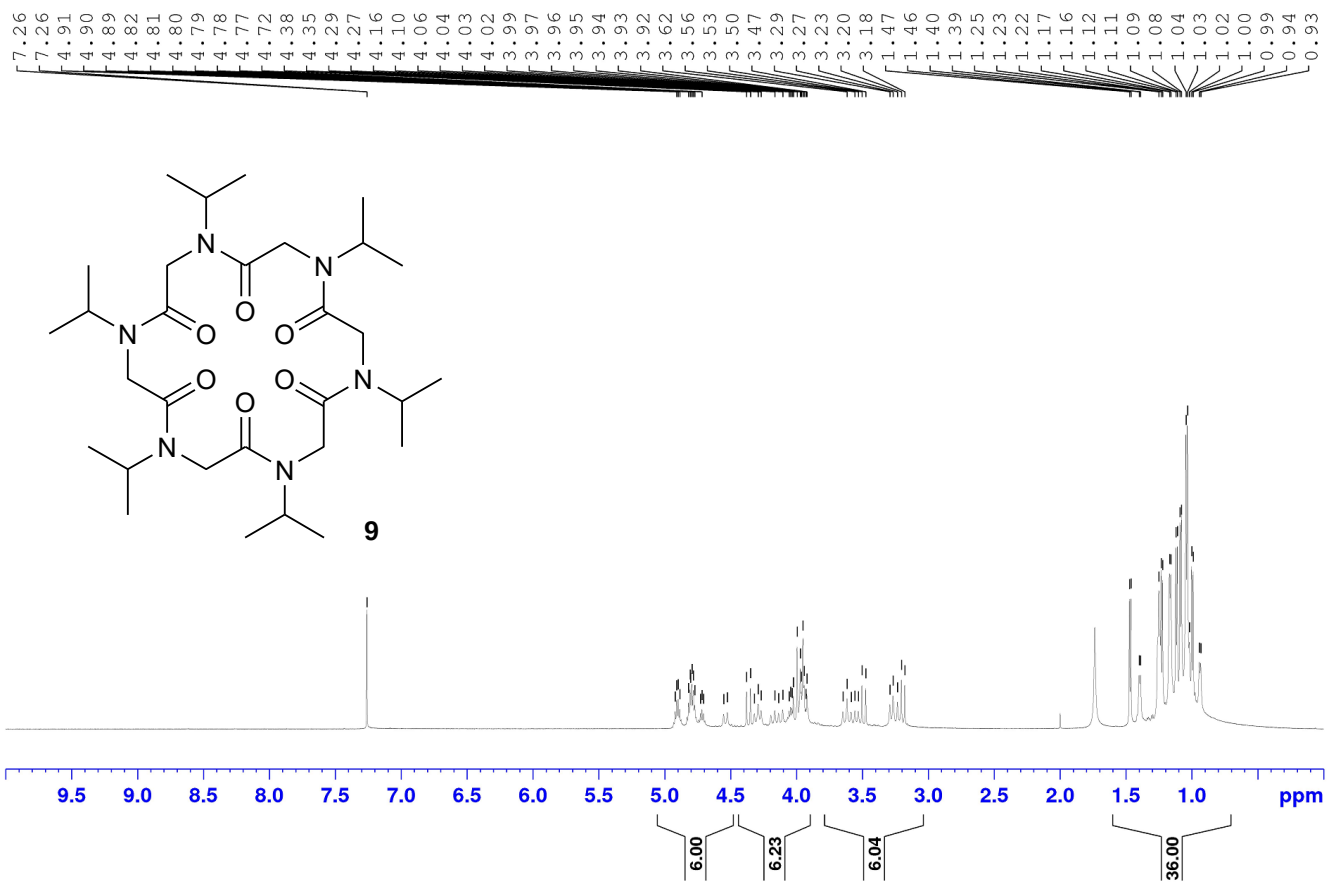
TFA: trifluoroacetic acid

TFPB: tetrakis[3,5-bis(trifluoromethyl)phenyl]borate

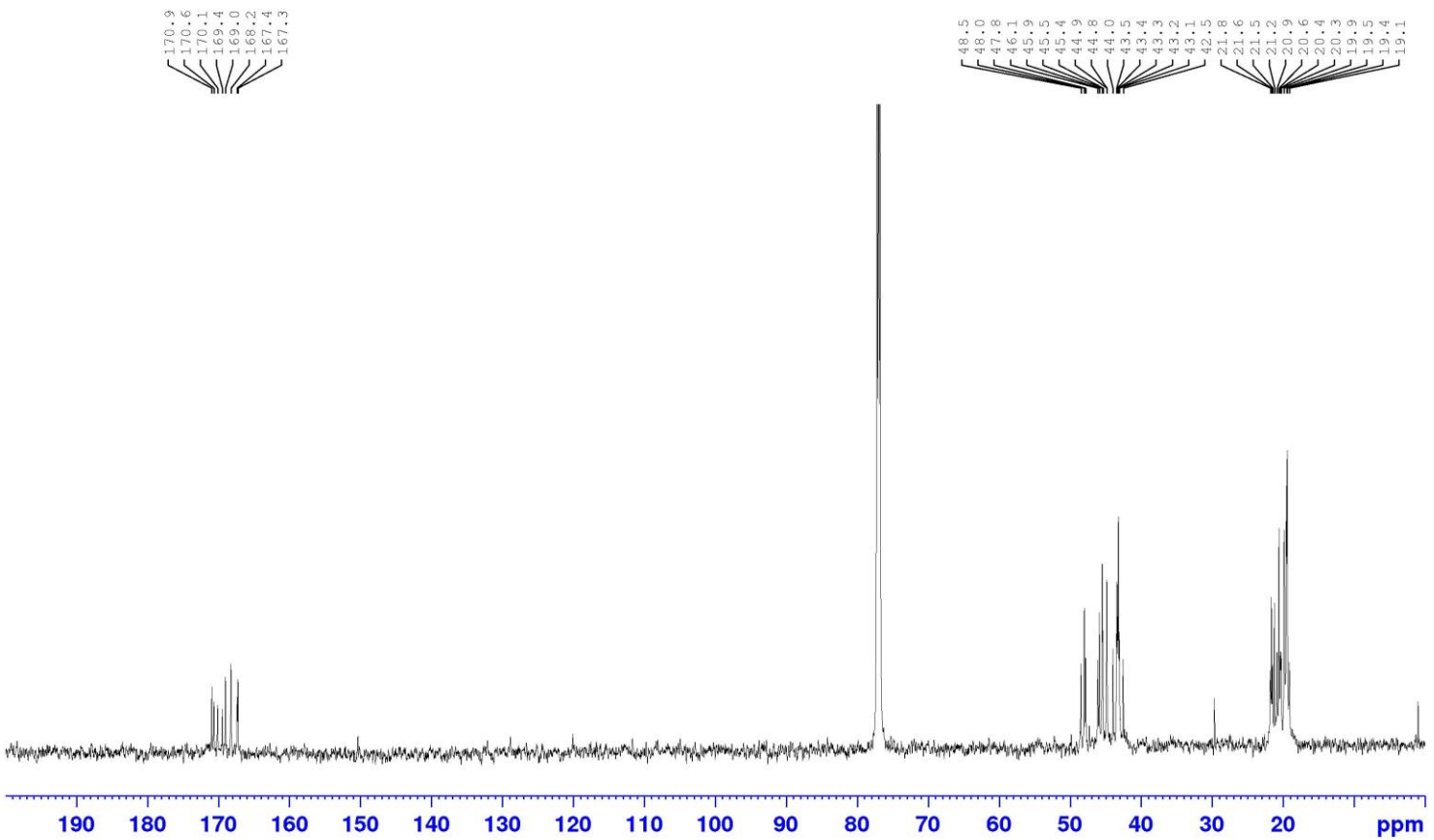
TLC: thin layer chromatography

^{1}H-, ^{13}C NMR and mass spectra

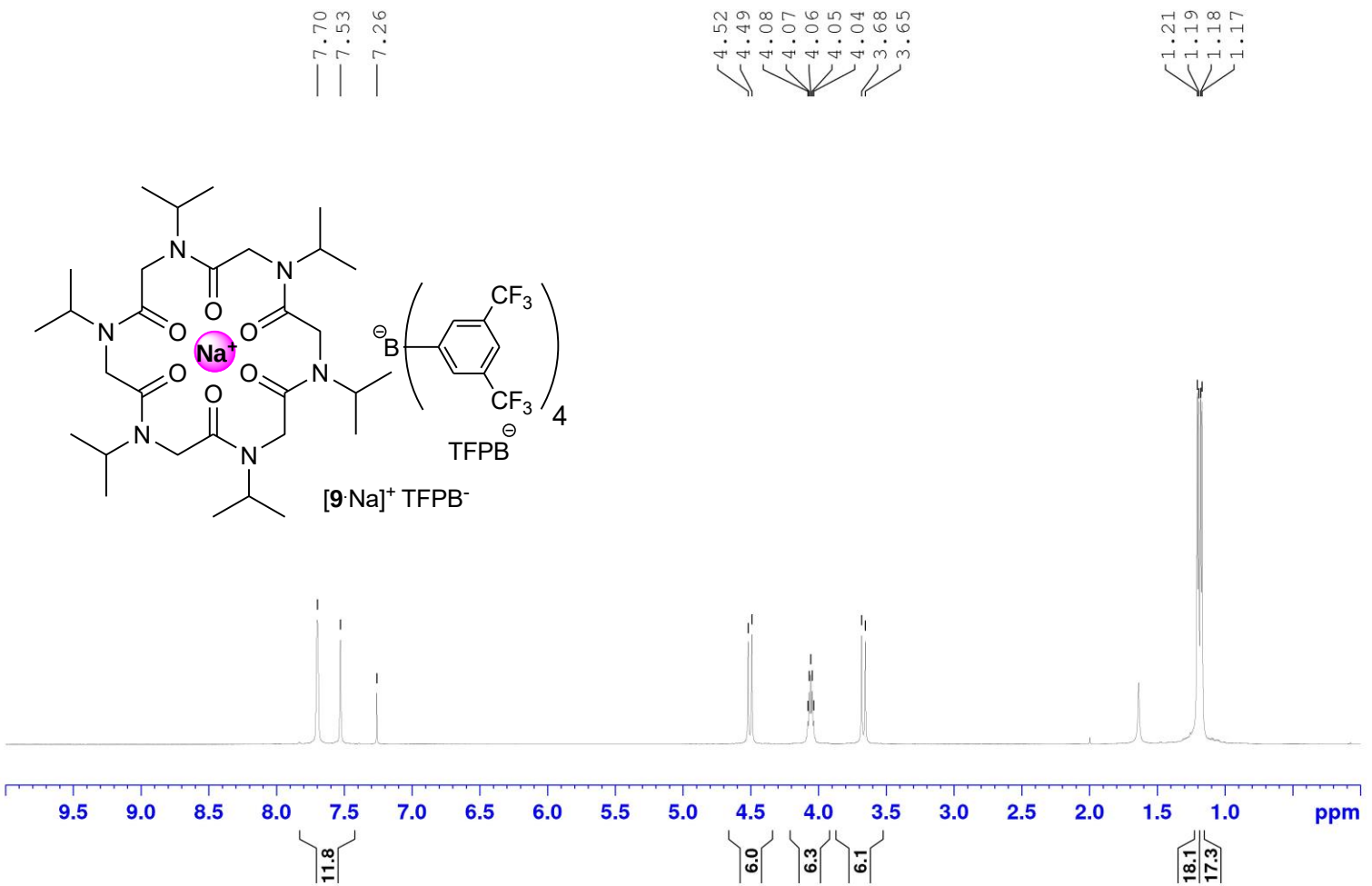
1.1 1D and 2D spectra of cyclic peptoids **9-14** and their complexes



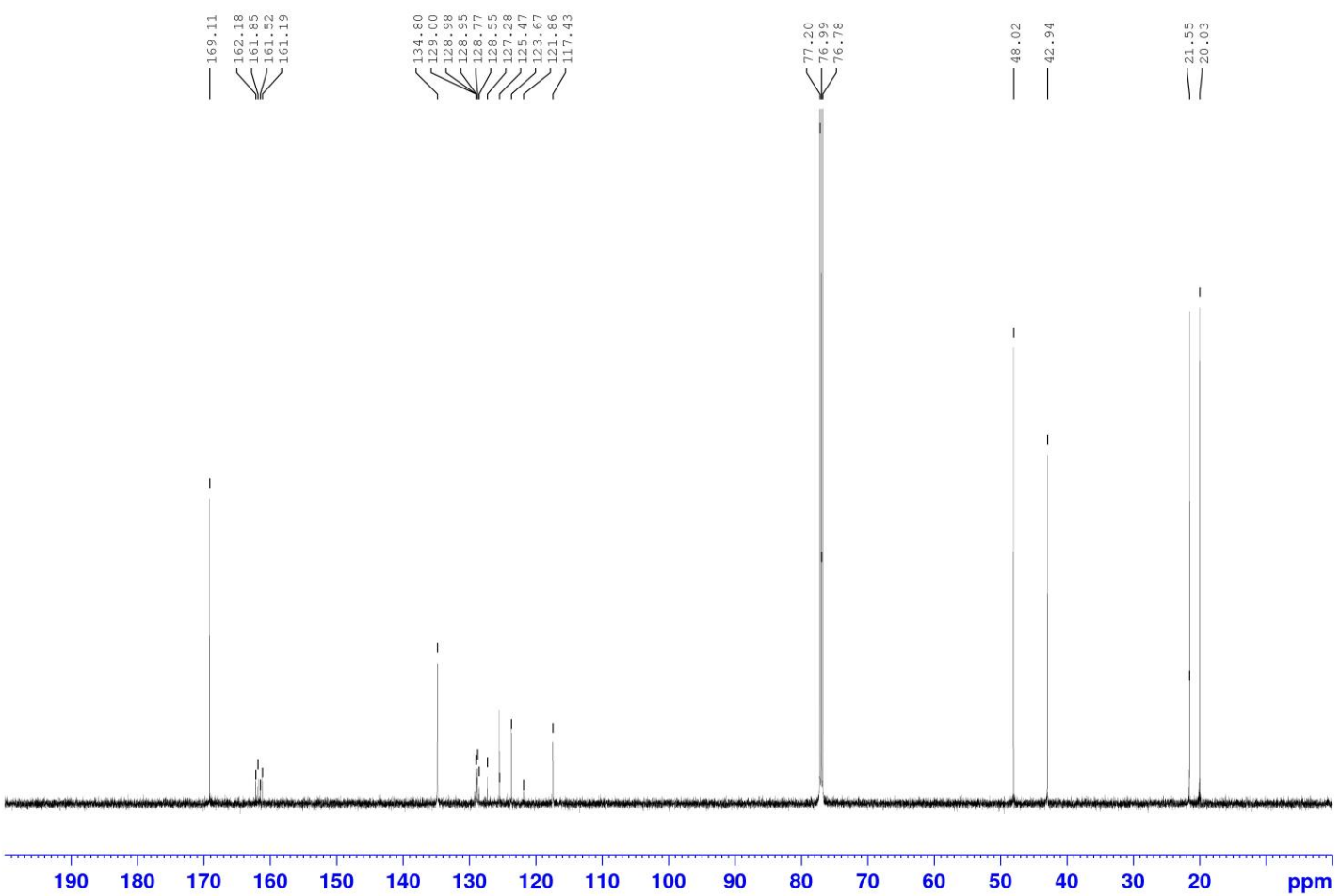
9: ^{1}H NMR (600 MHz, $CDCl_3$)



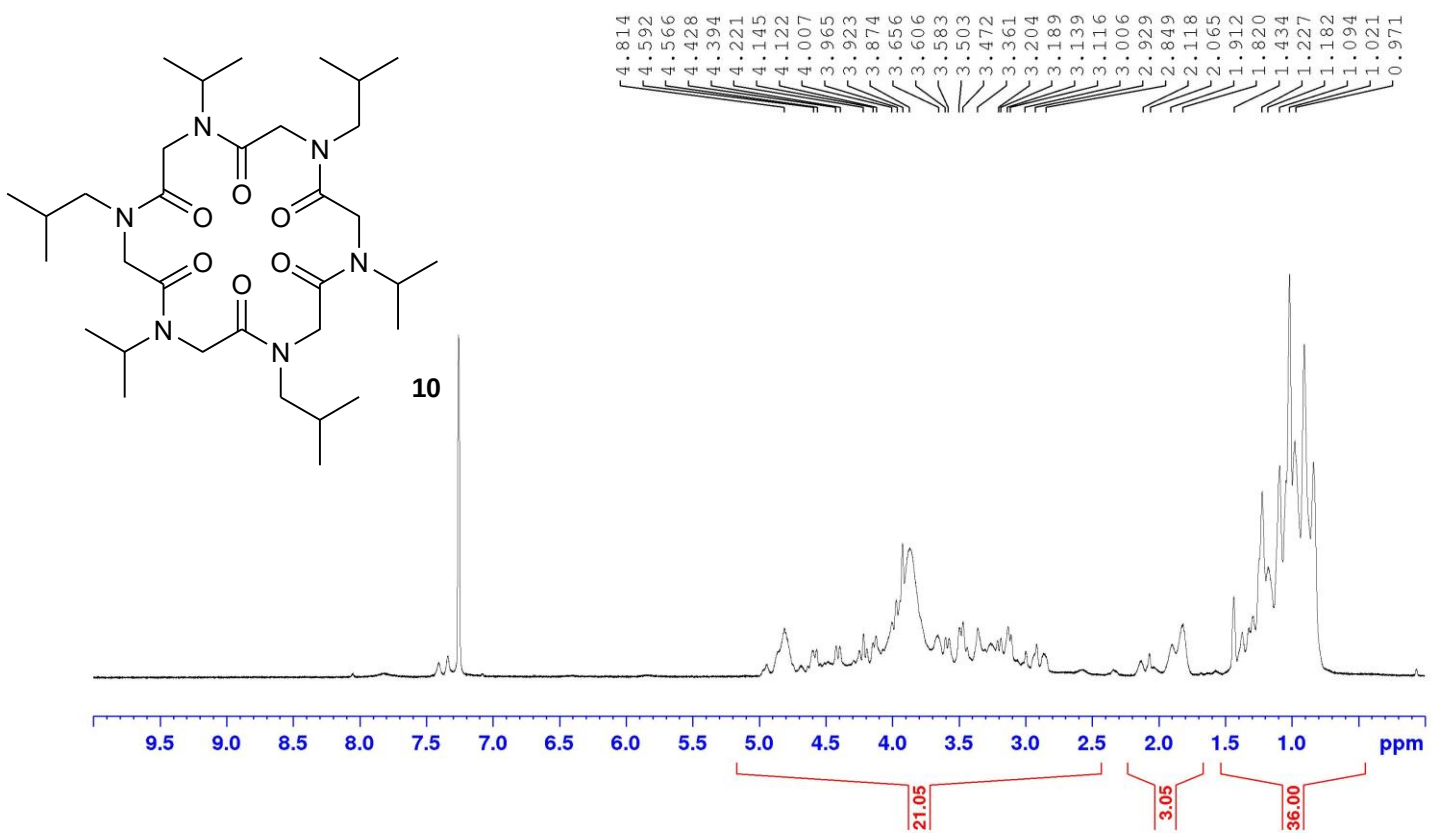
9: ^{13}C NMR (150 MHz, $CDCl_3$)



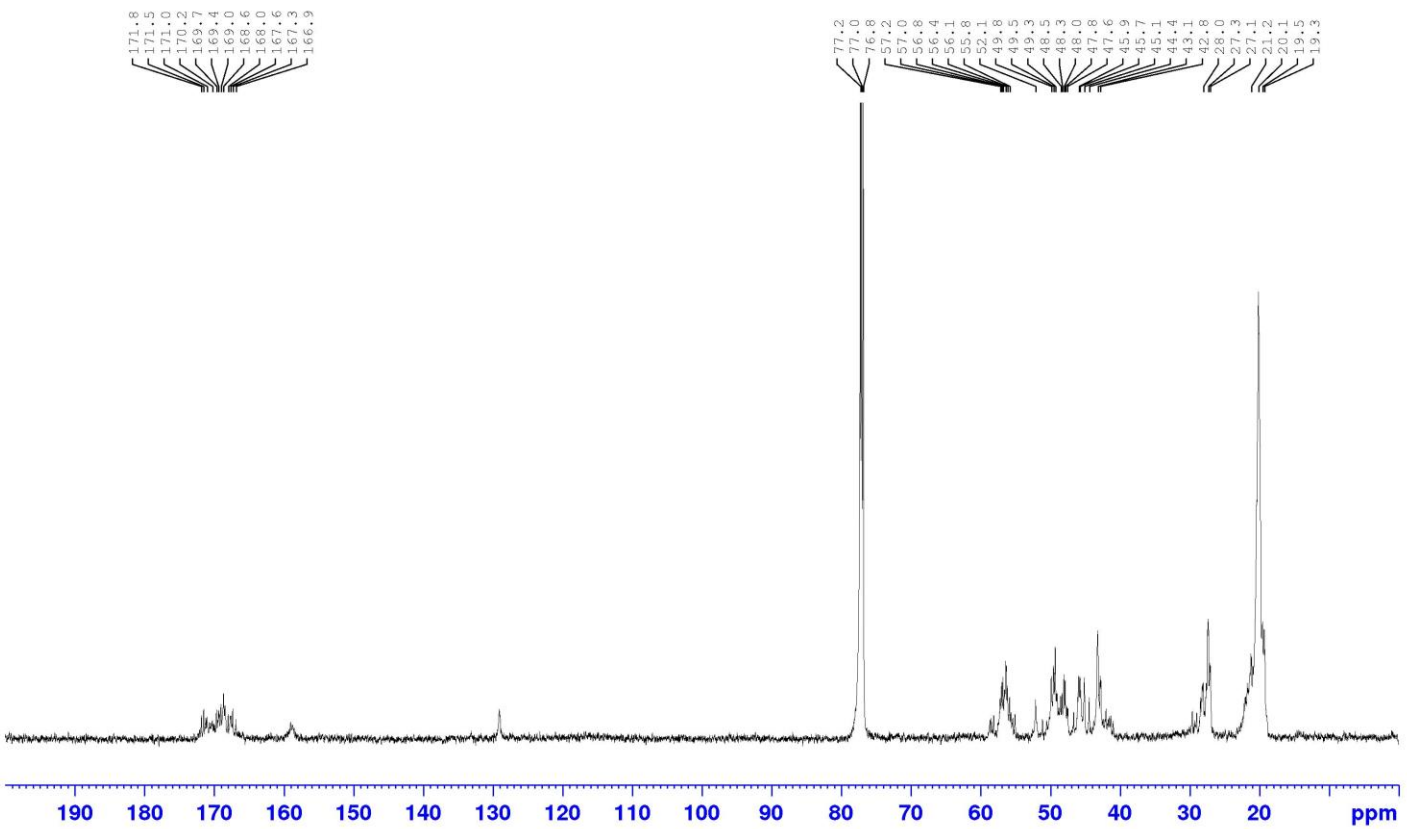
[**9**·Na]$^+$ TFPB$^-$: ^{1}H NMR (600 MHz, $CDCl_3$)



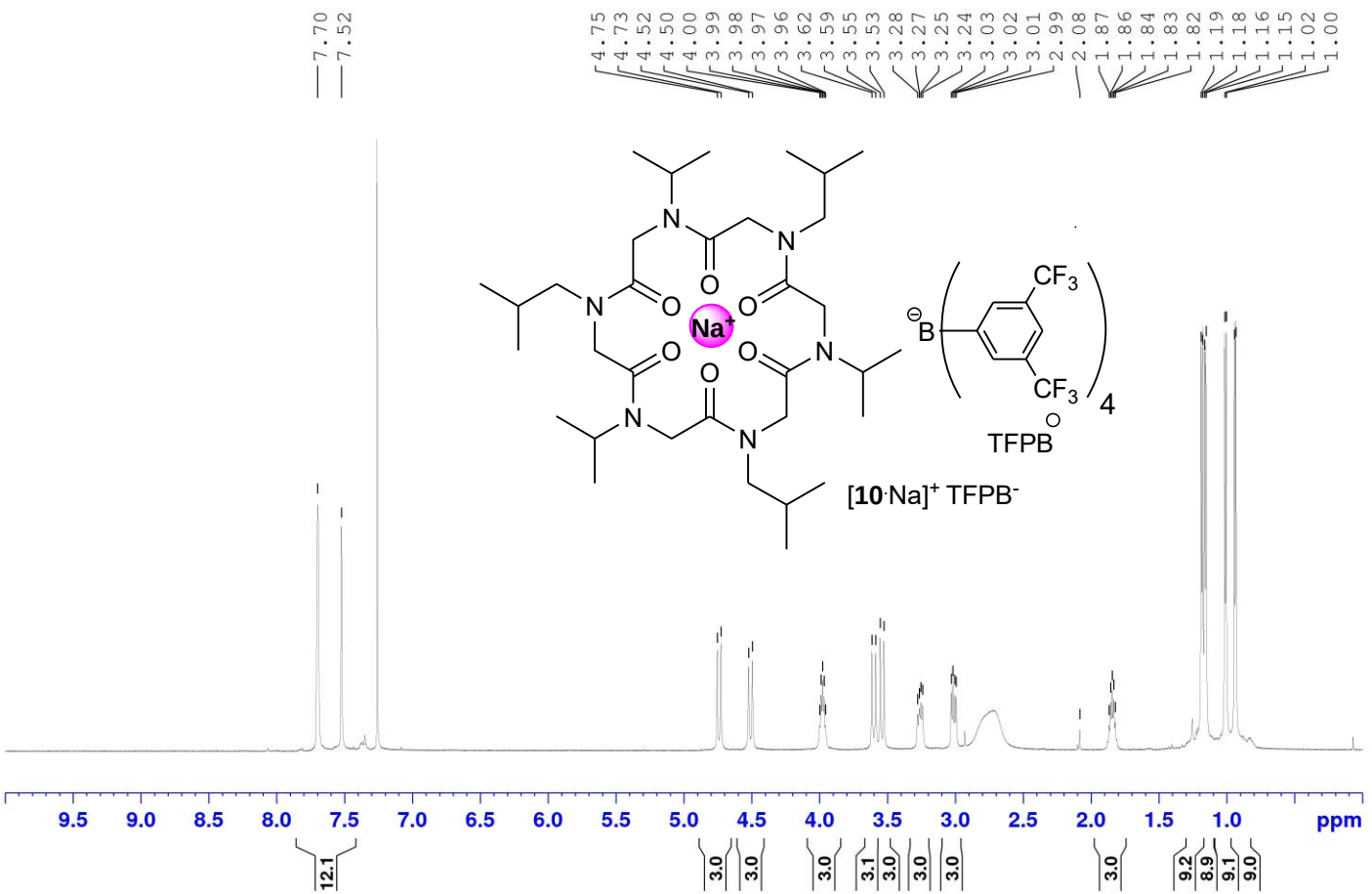
[**9**·Na]$^{+}$ TFPB^{-}: ^{13}C NMR (150 MHz, $CDCl_3$)



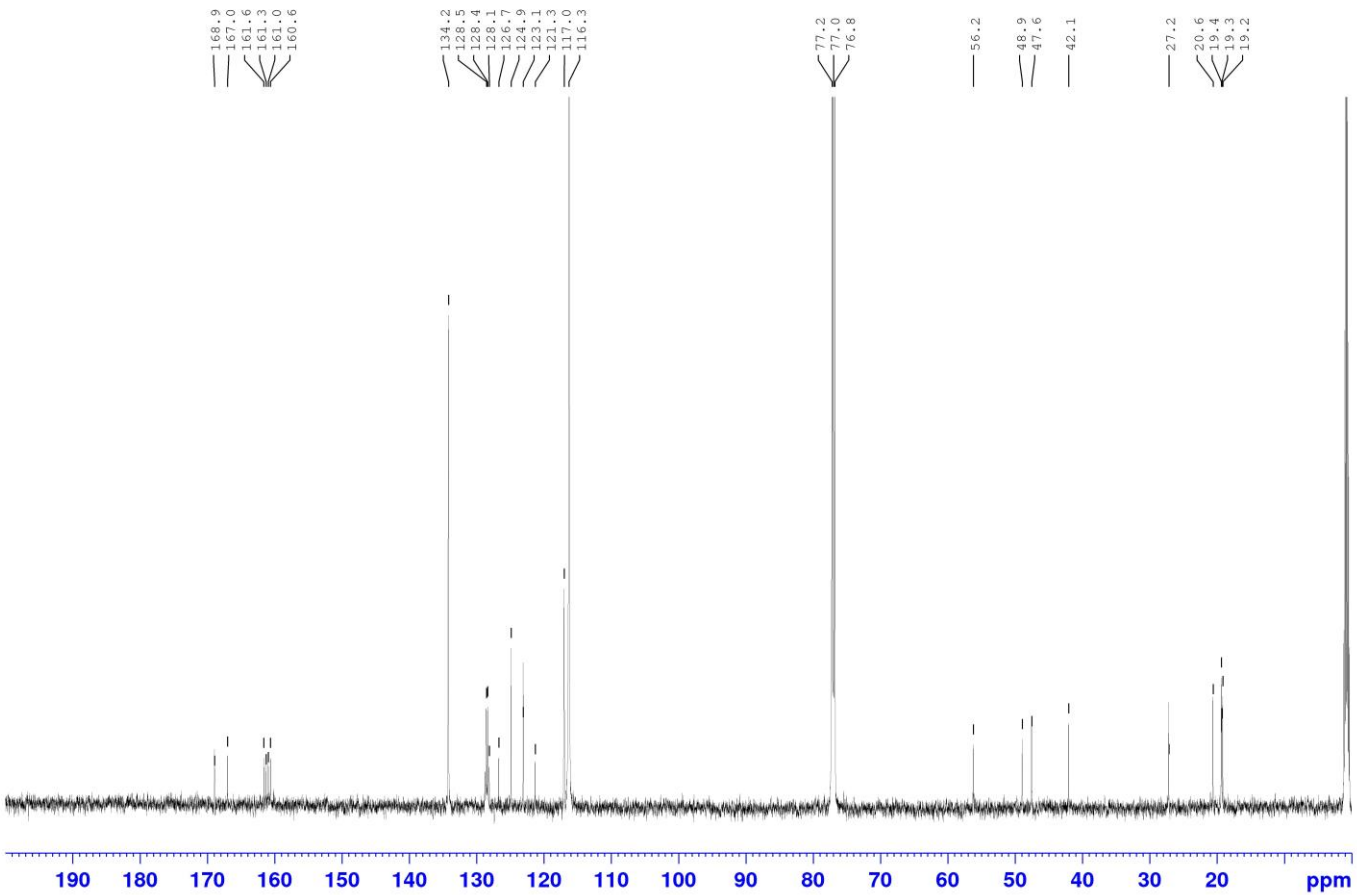
10: ^{1}H NMR (600 MHz, $CDCl_3$)



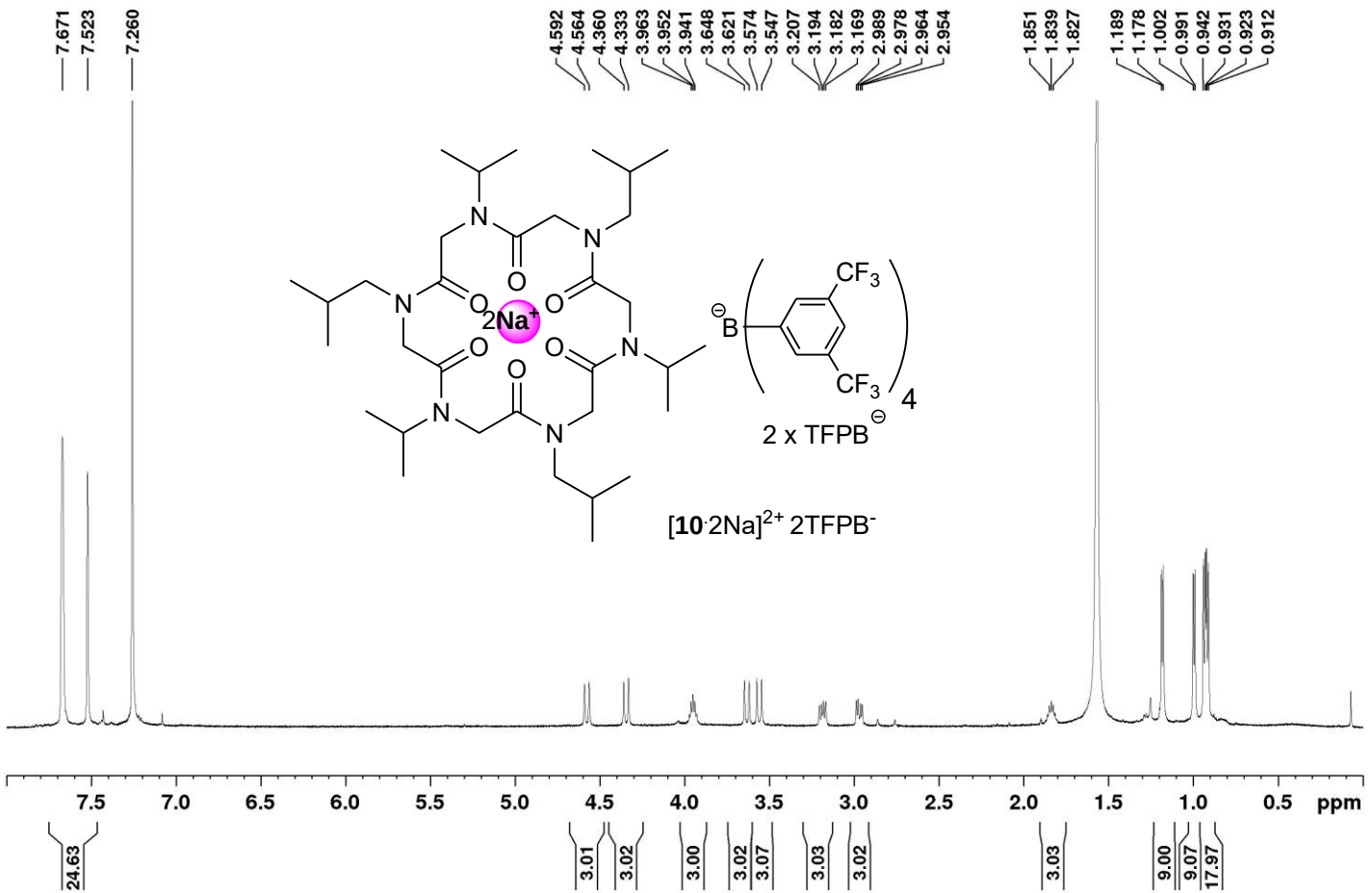
10: ^{13}C NMR (150 MHz, $CDCl_3$)



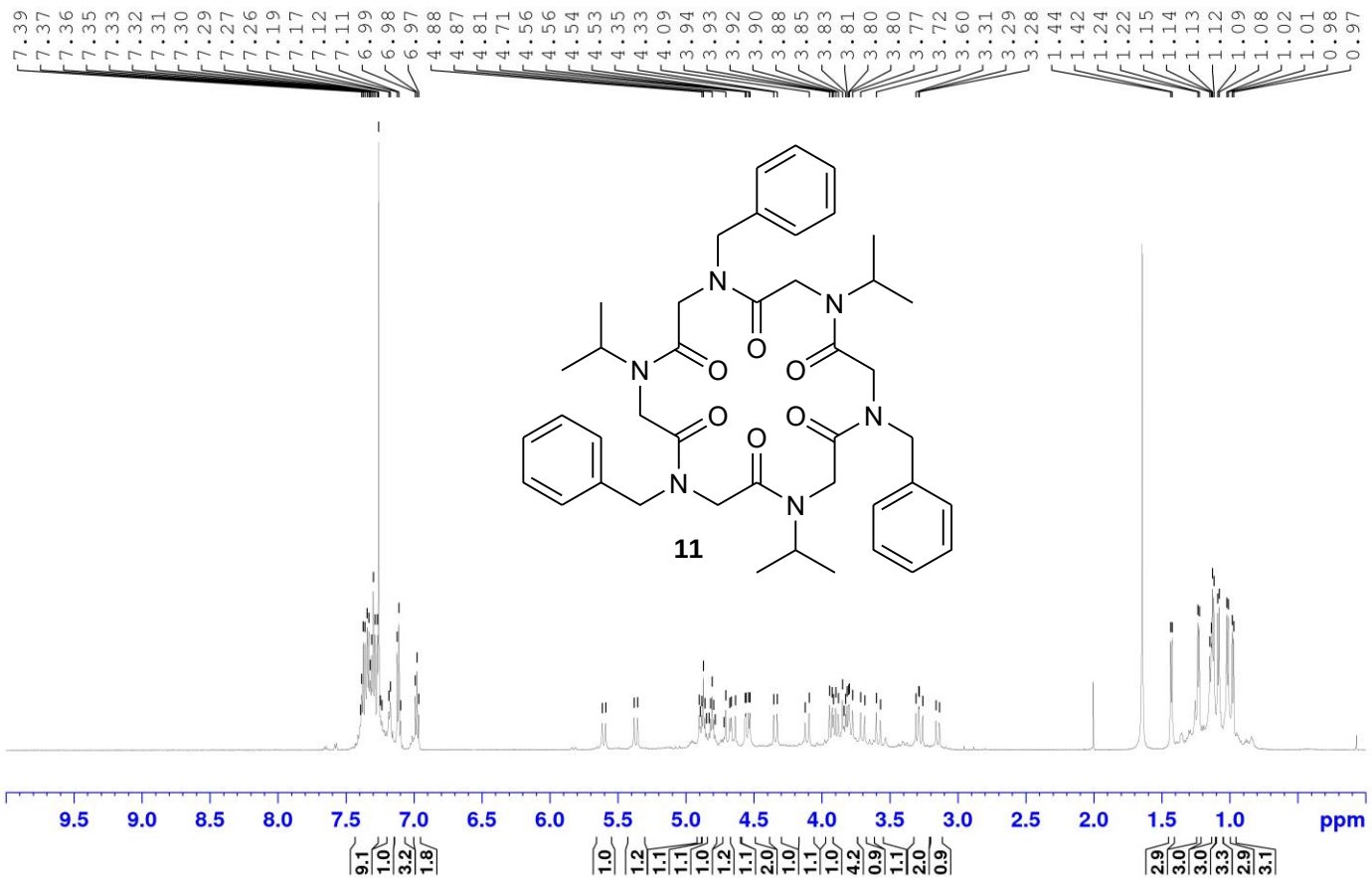
[**10**·Na]$^+$ TFPB$^-$: ^{1}H NMR (600 MHz, $CDCl_3$)



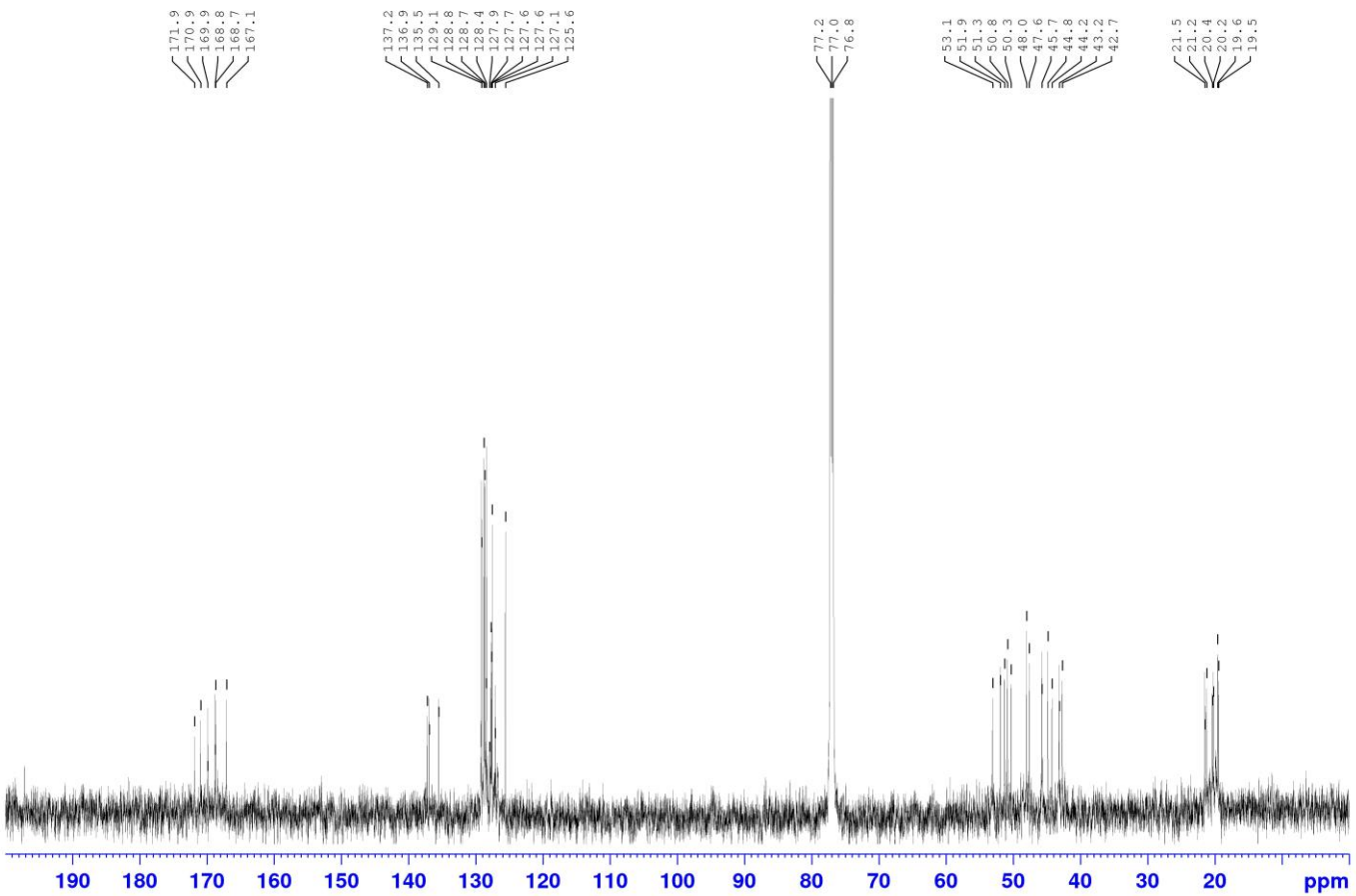
[**10**·Na]$^{+}$ TFPB^{-}: ^{13}C NMR (150 MHz, $CDCl_3$)



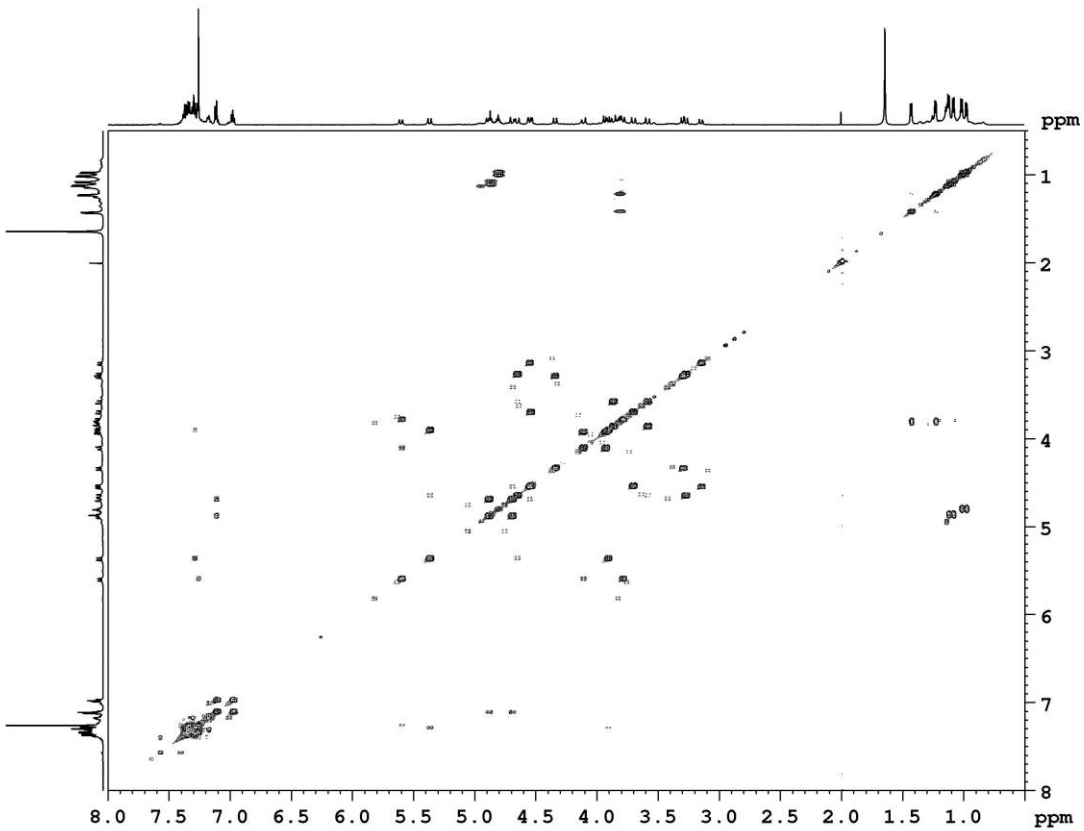
[**10**·2Na]$^{2+}$ 2TFPB^{-}: ^{1}H NMR (600 MHz, $CDCl_3$)



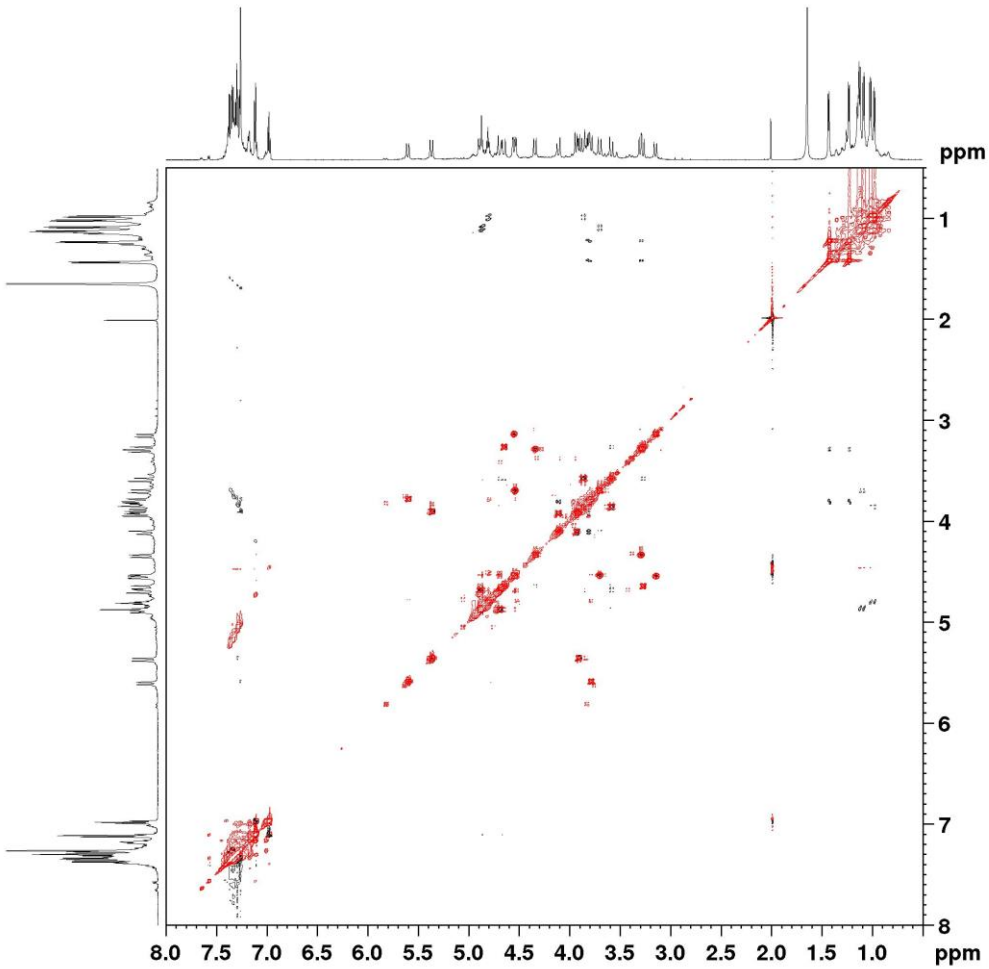
11: ^{1}H NMR (600 MHz, $CDCl_3$)



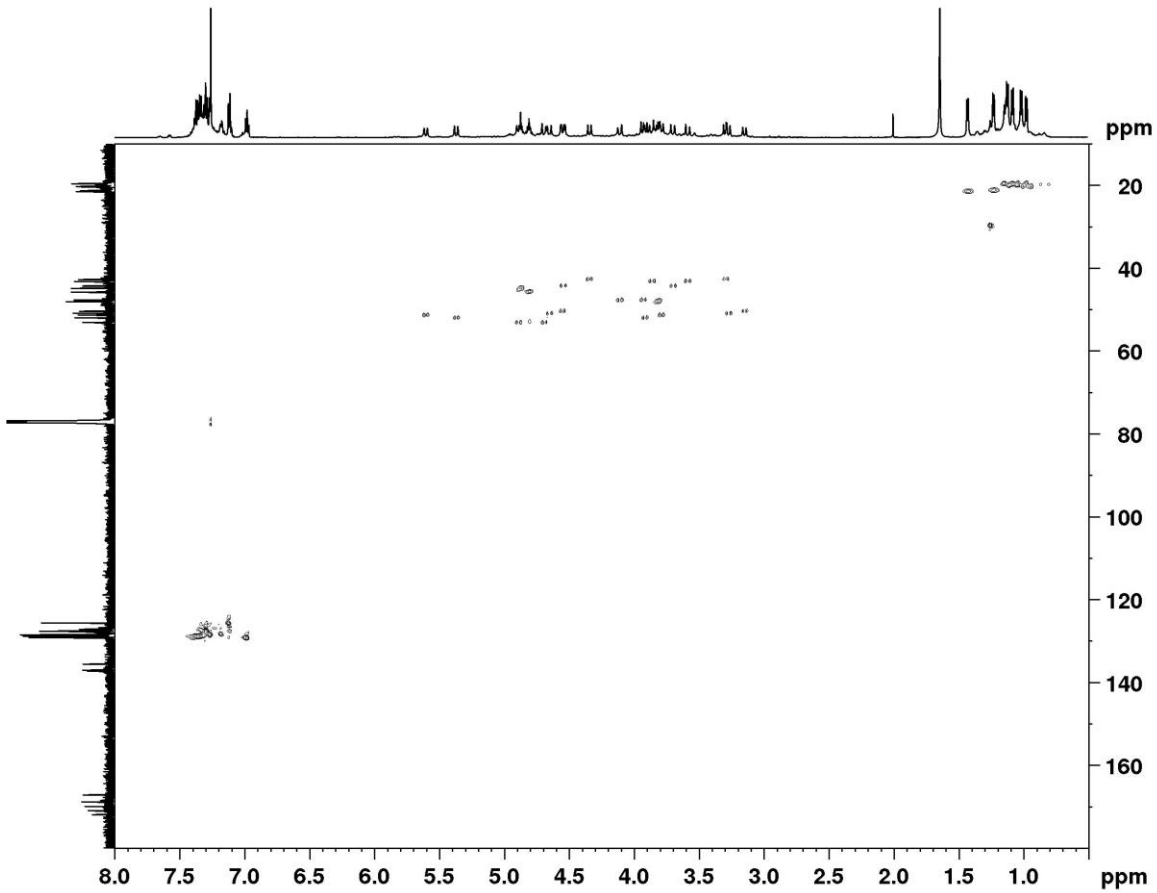
11: ^{13}C NMR (150 MHz, $CDCl_3$)



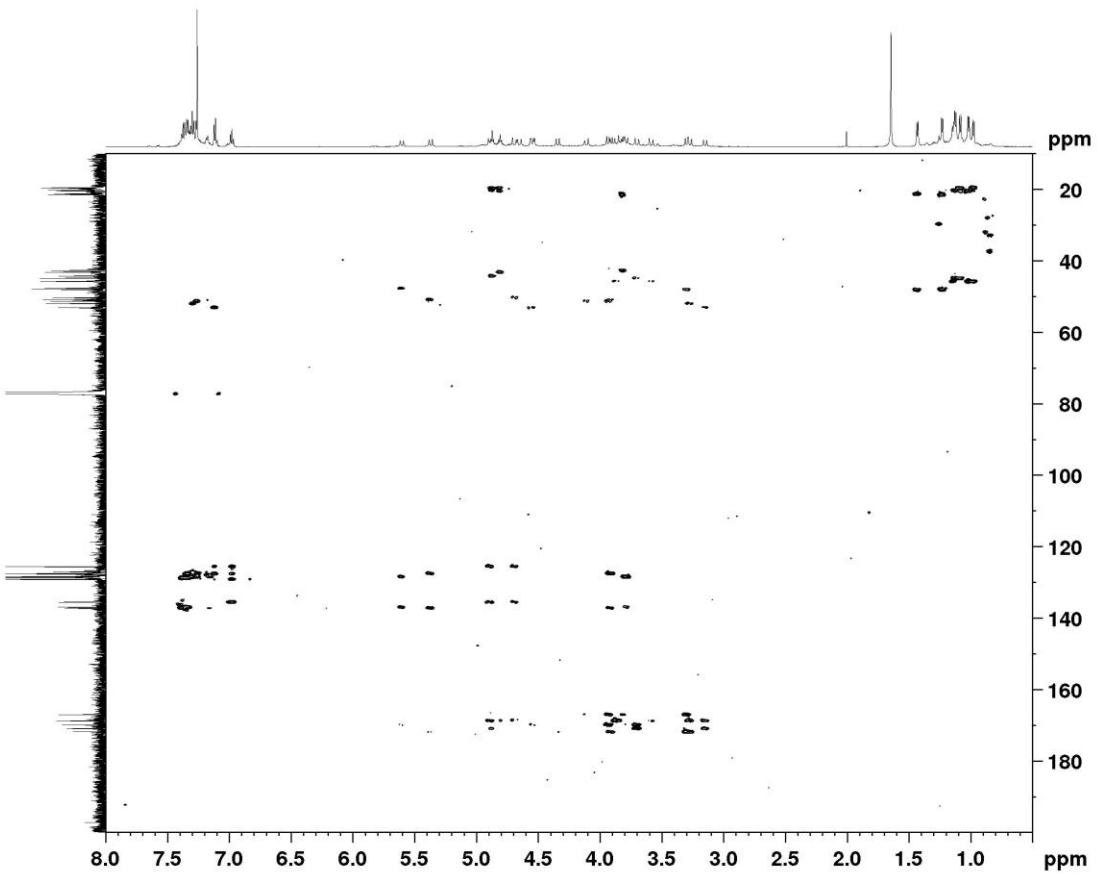
11: COSY SPECTRUM (600 MHz, $CDCl_3$)



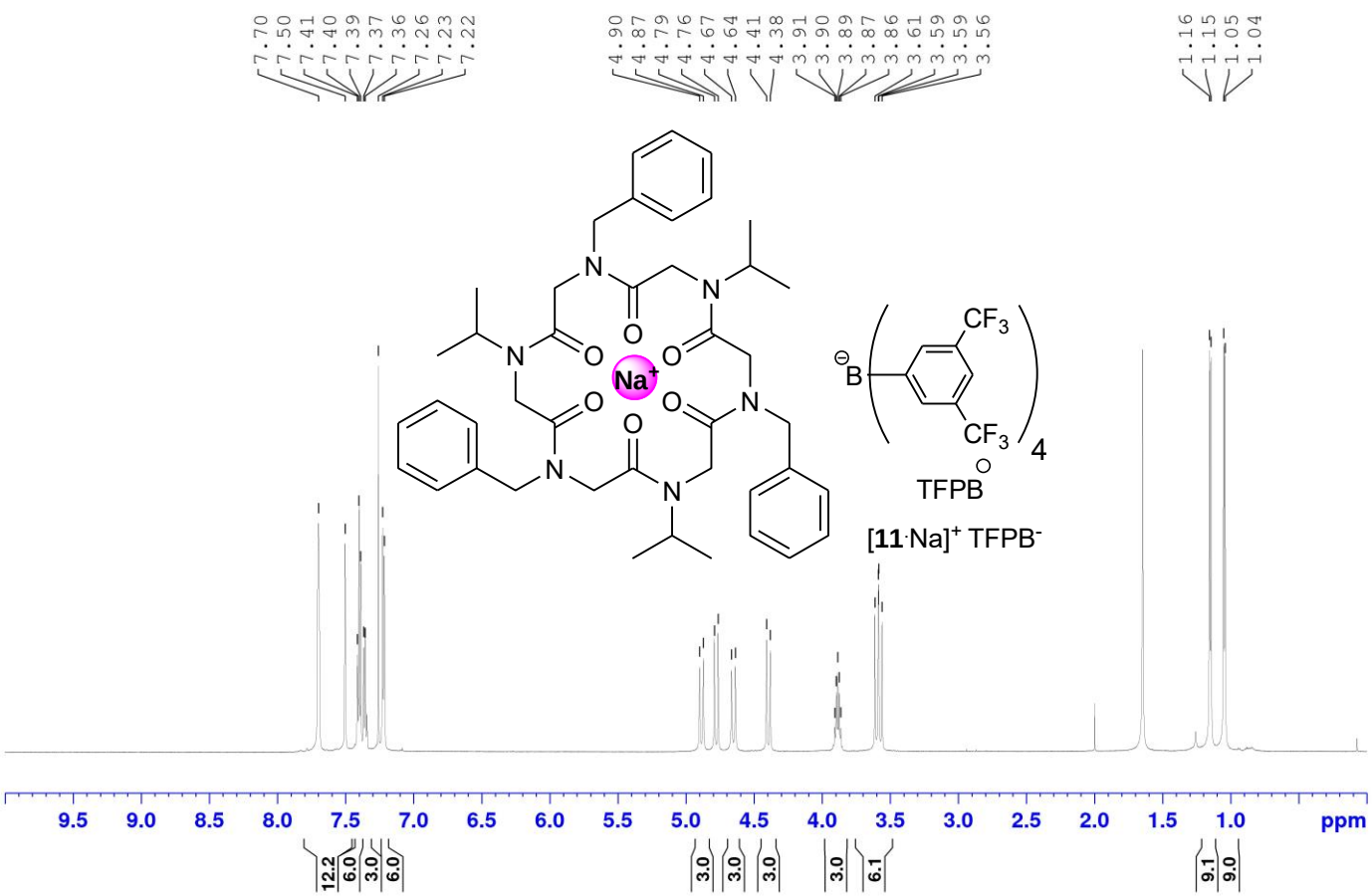
11: ROESY SPECTRUM (600 MHz, $CDCl_3$)



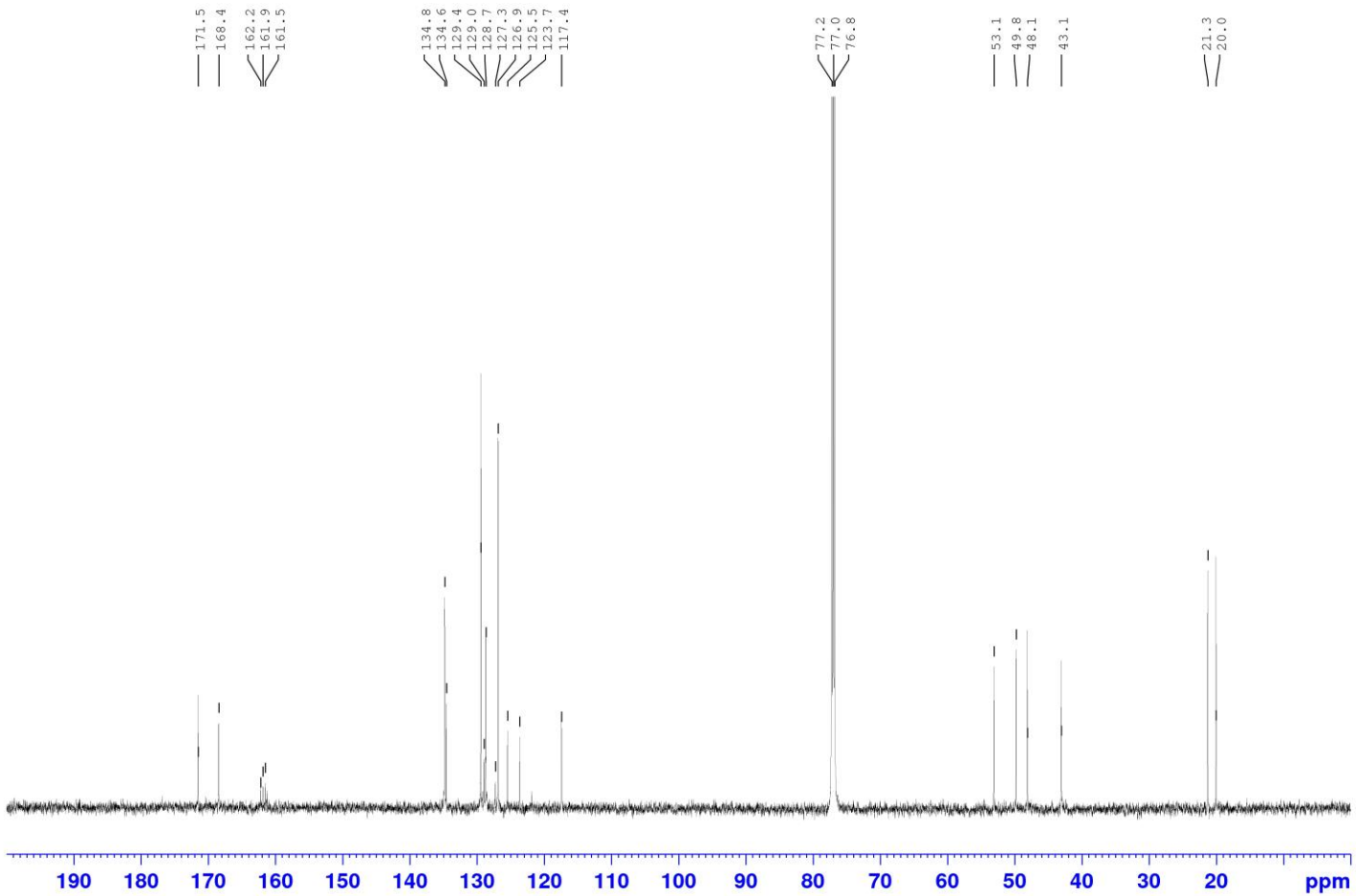
11: HSQC SPECTRUM (600 MHz, $CDCl_3$)



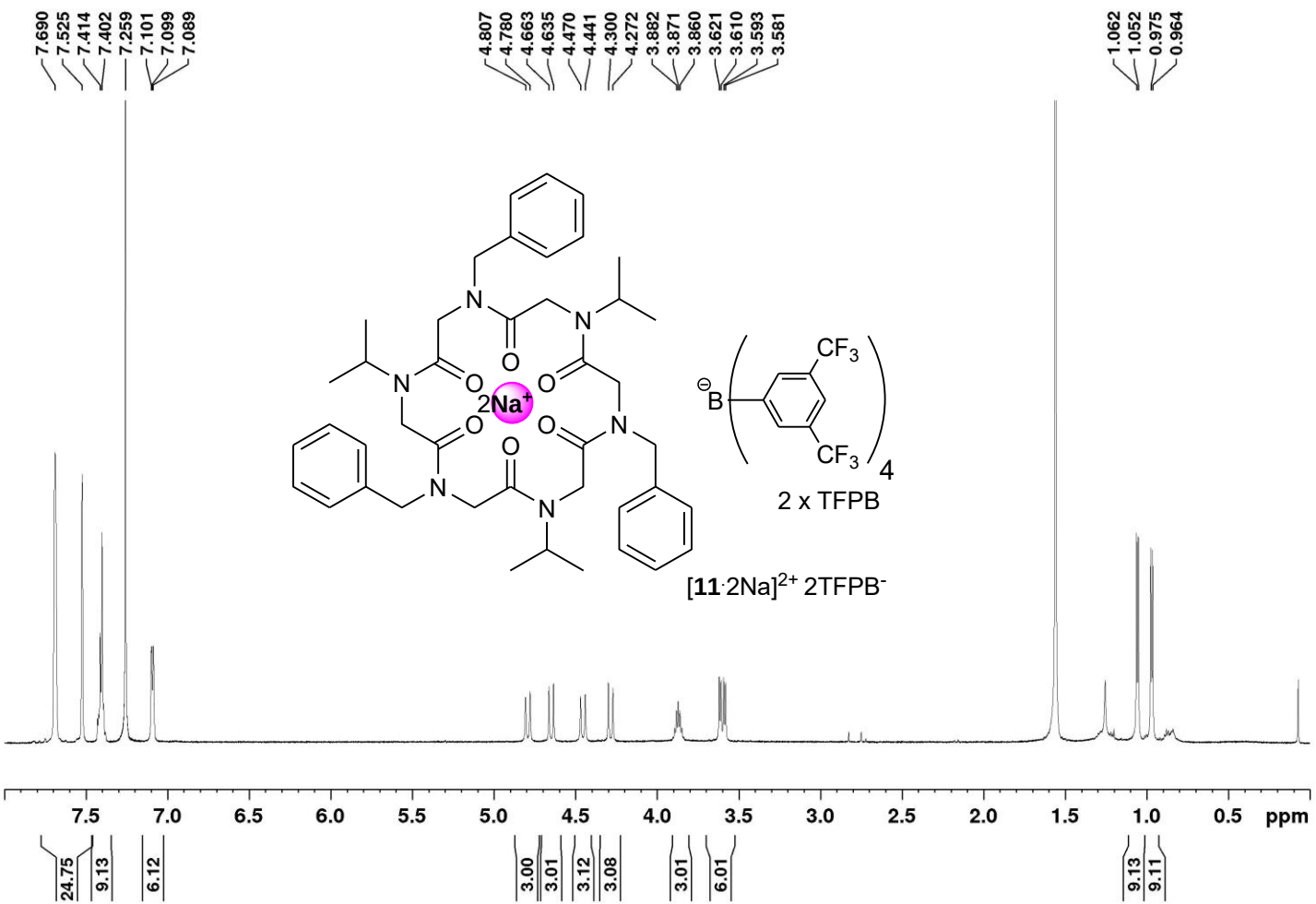
11: HMBC SPECTRUM (600 MHz, $CDCl_3$)



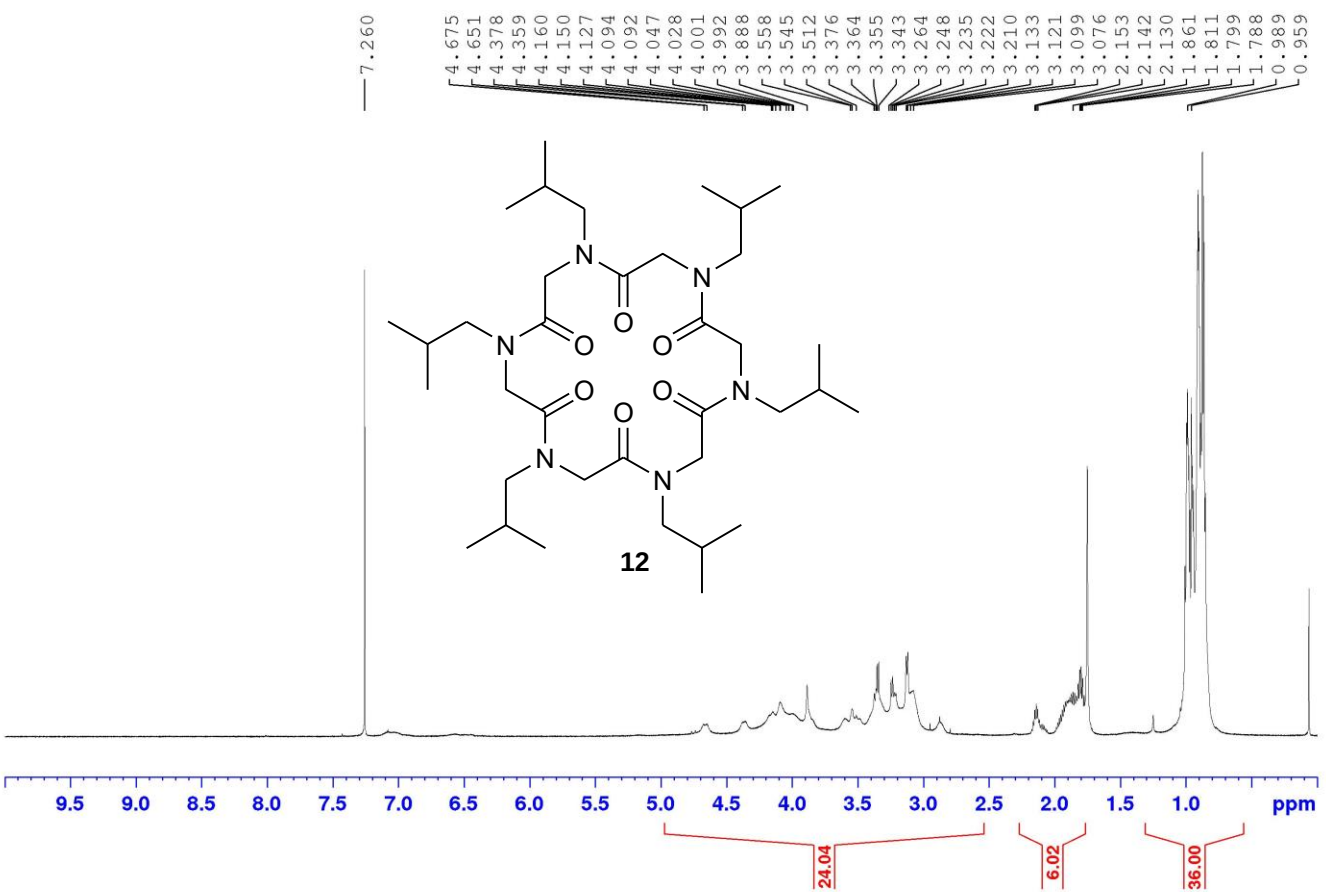
[**11**·Na]$^+$ TFPB$^-$: ^{1}H NMR (600 MHz, $CDCl_3$)



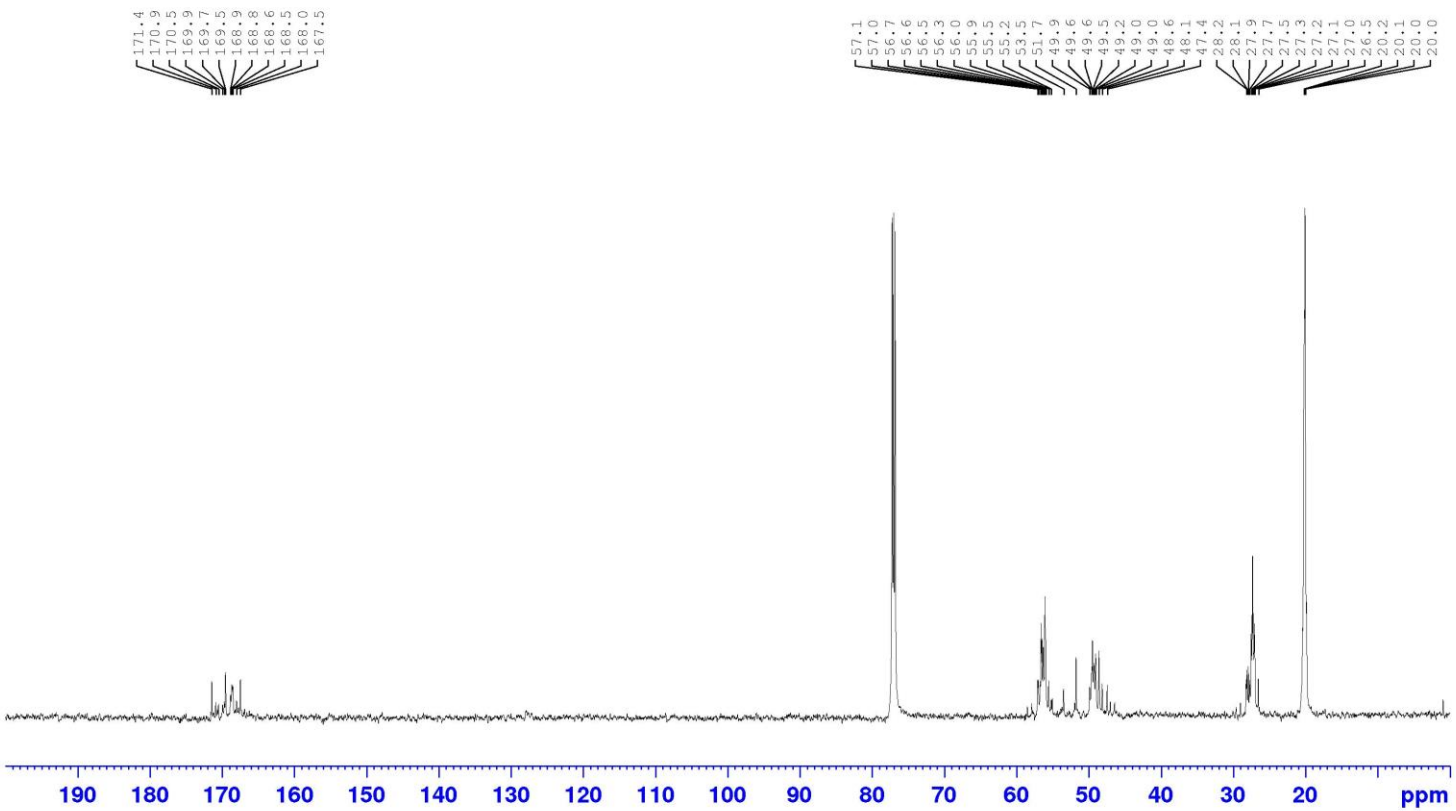
[**11**·Na]$^{+}$ TFPB^{-}: ^{13}C NMR (150 MHz, $CDCl_3$)



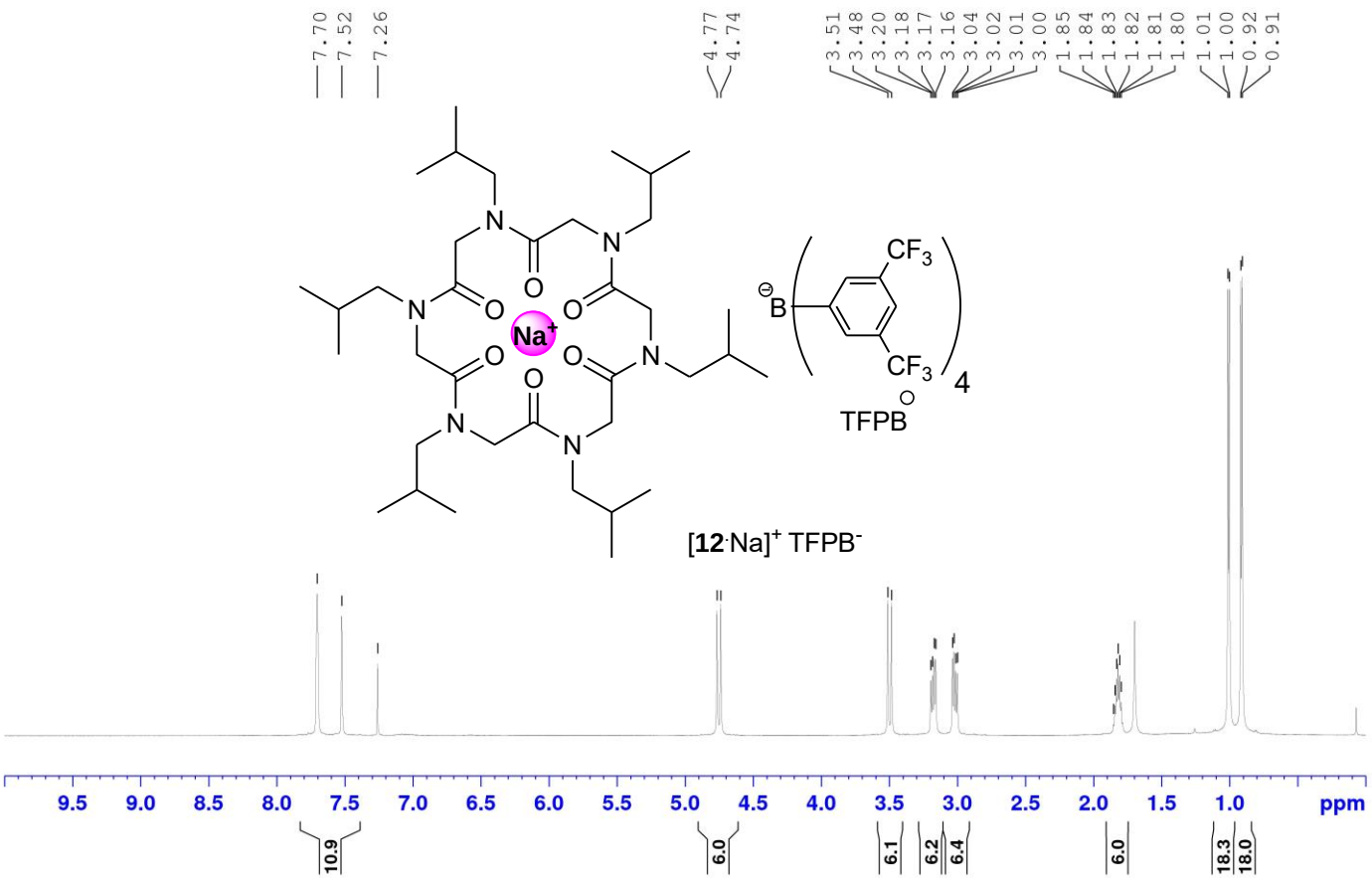
[**11**·2Na]$^{2+}$ 2TFPB^{-}: ^{1}H NMR (600 MHz, $CDCl_3$)



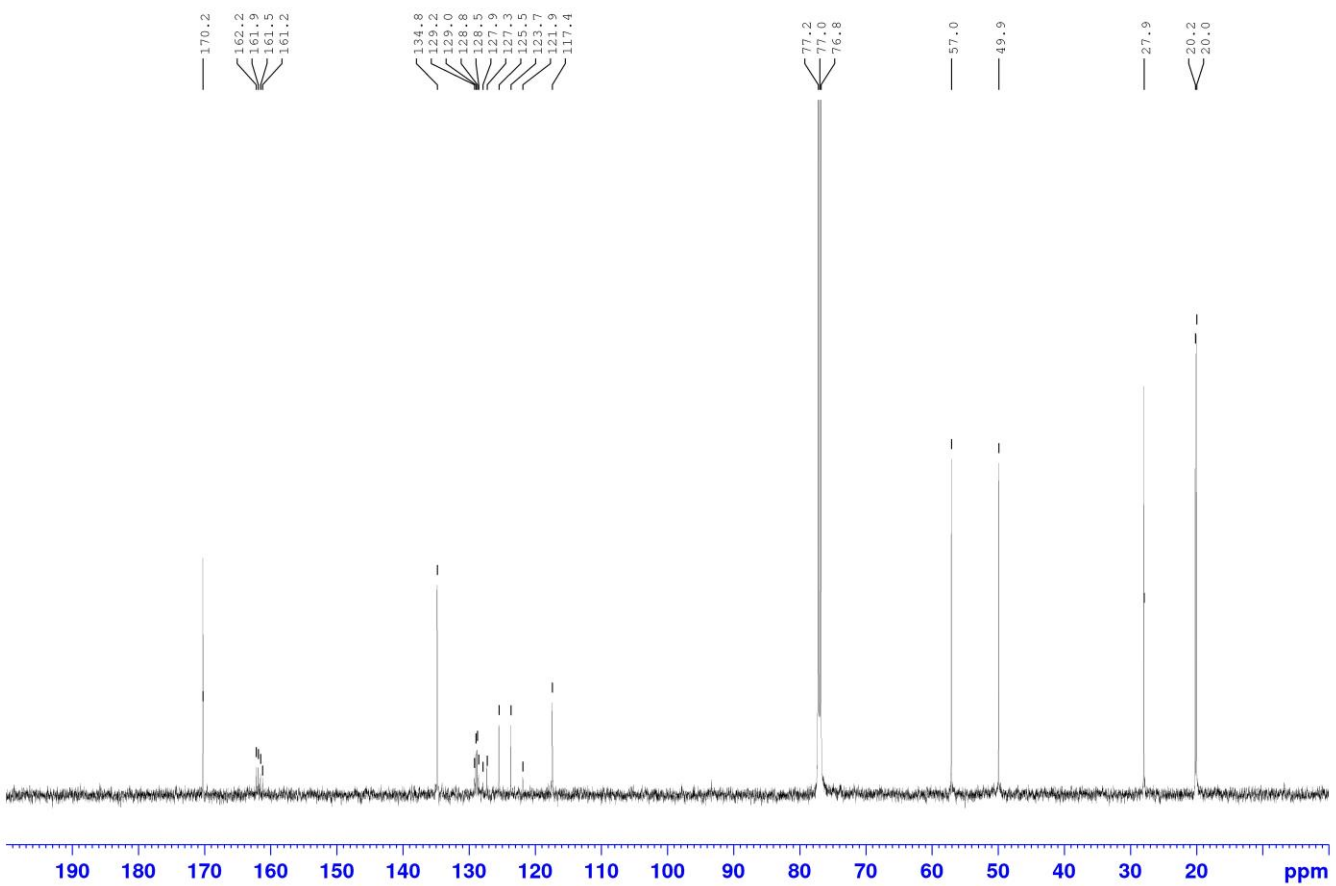
12: ^{1}H NMR (600 MHz, $CDCl_3$)



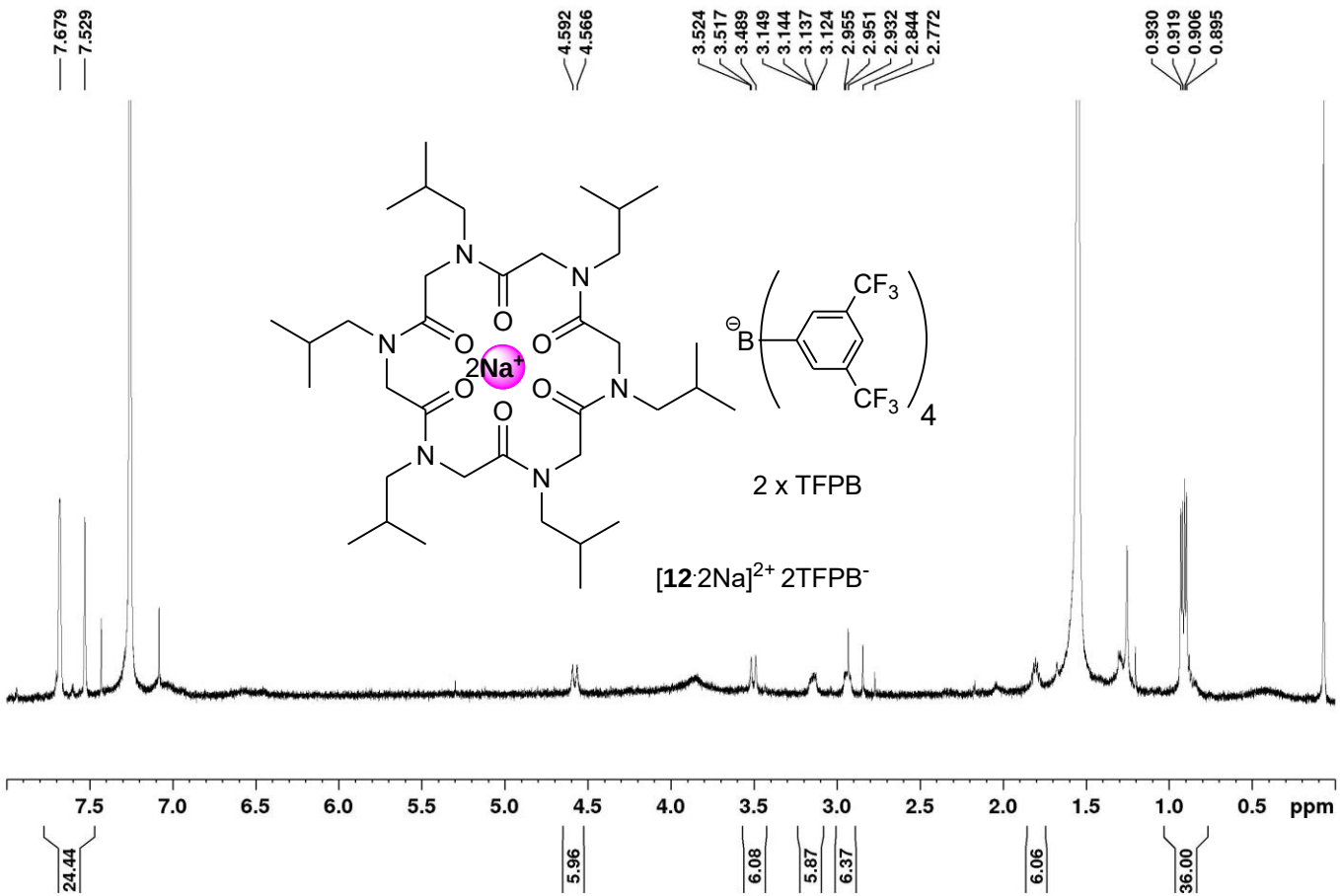
12: ^{13}C NMR (150 MHz, $CDCl_3$)



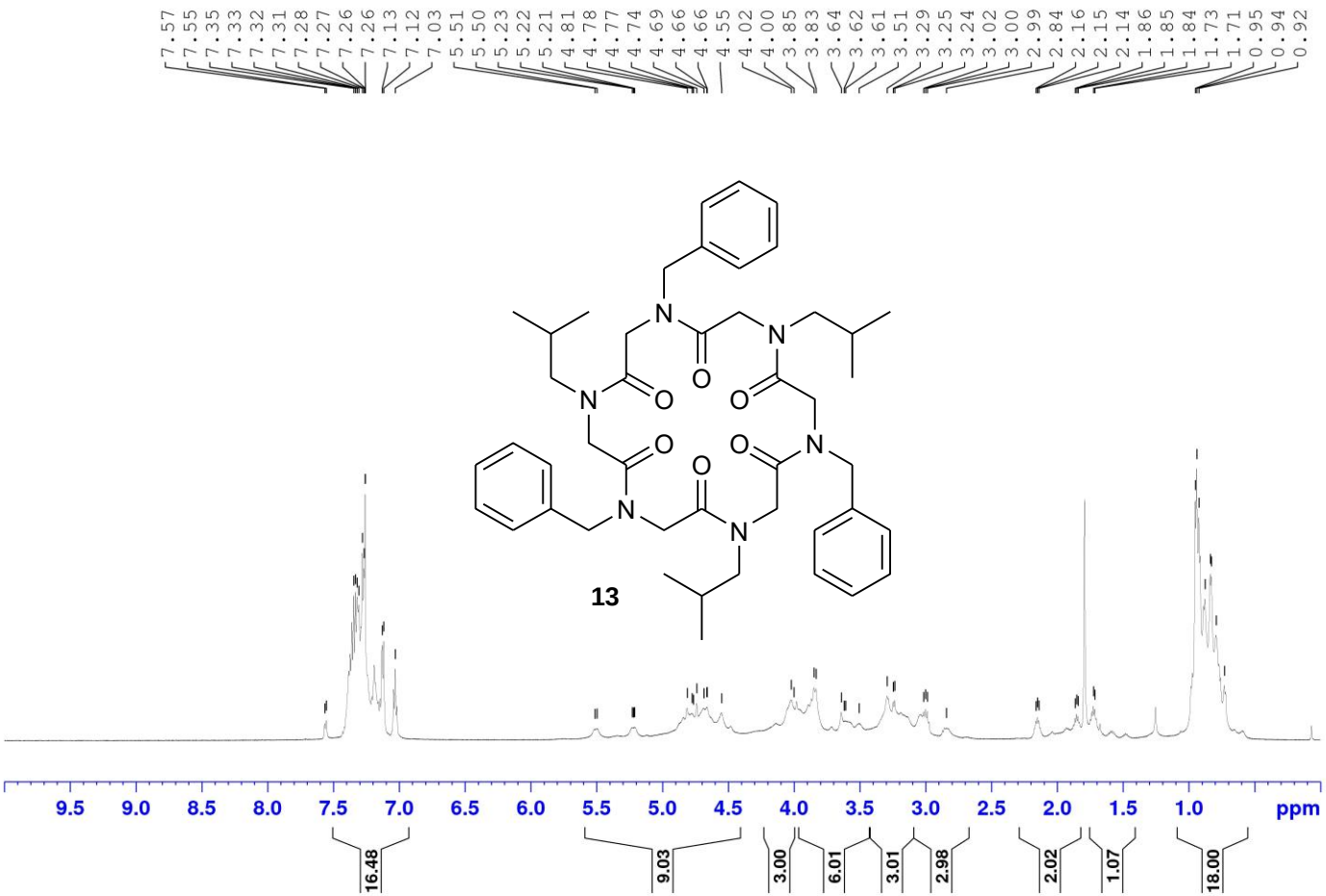
[**12**·Na]$^+$ TFPB$^-$: ^{1}H NMR (600 MHz, $CDCl_3$)



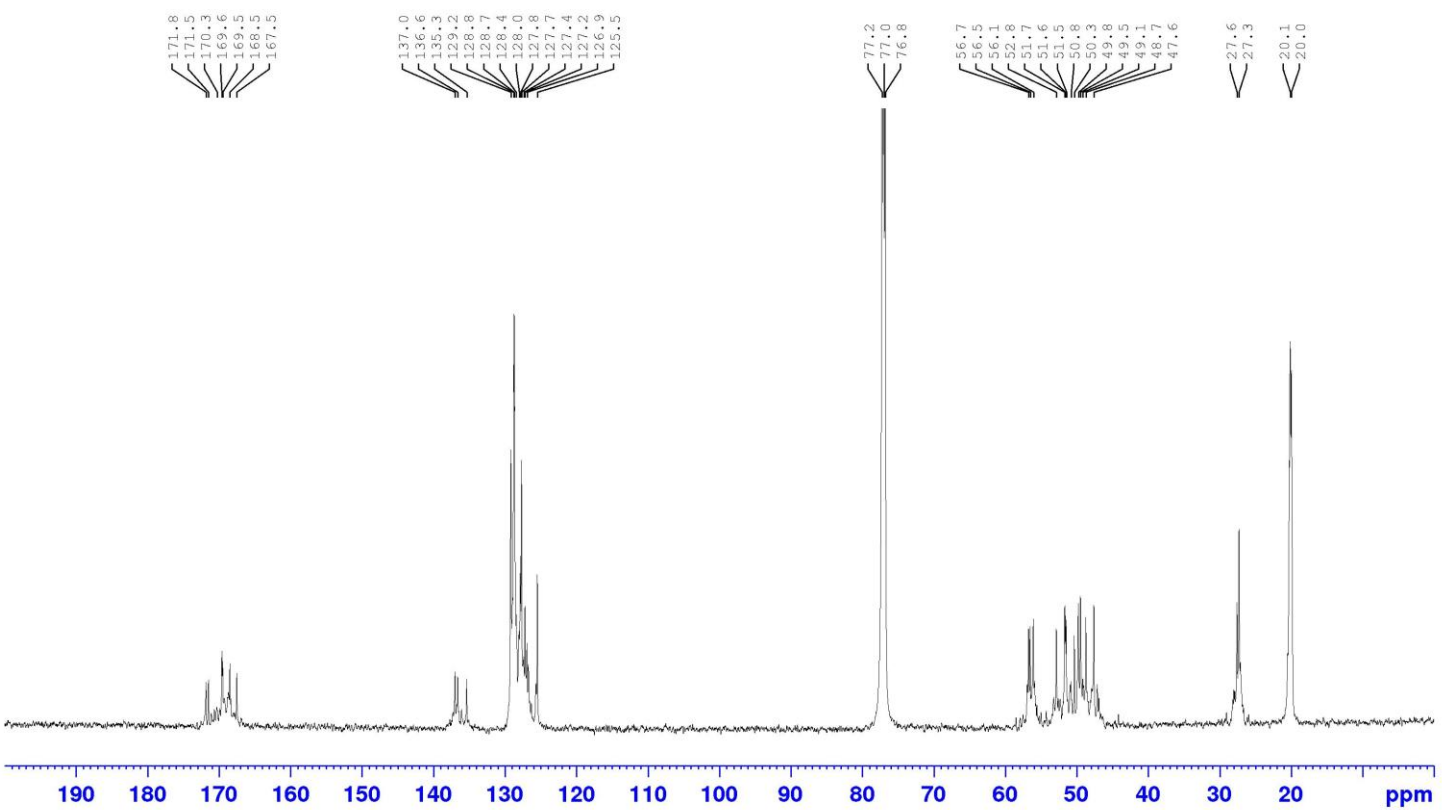
[**12**·Na]$^{+}$ TFPB^{-}: ^{13}C NMR (150 MHz, $CDCl_3$)



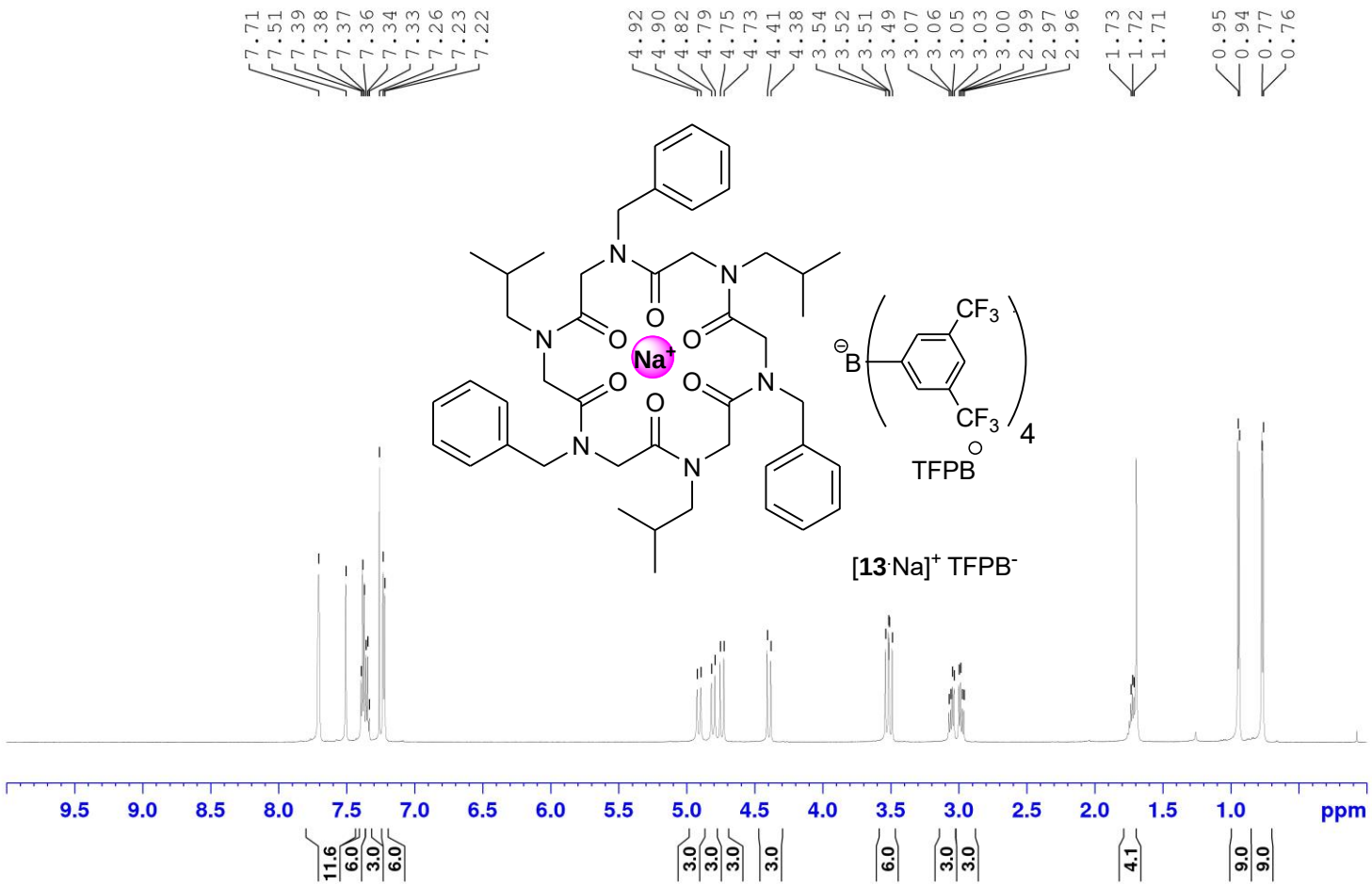
[**12**·2Na]$^{2+}$ 2TFPB^{-}: ^{1}H NMR (600 MHz, $CDCl_3$)



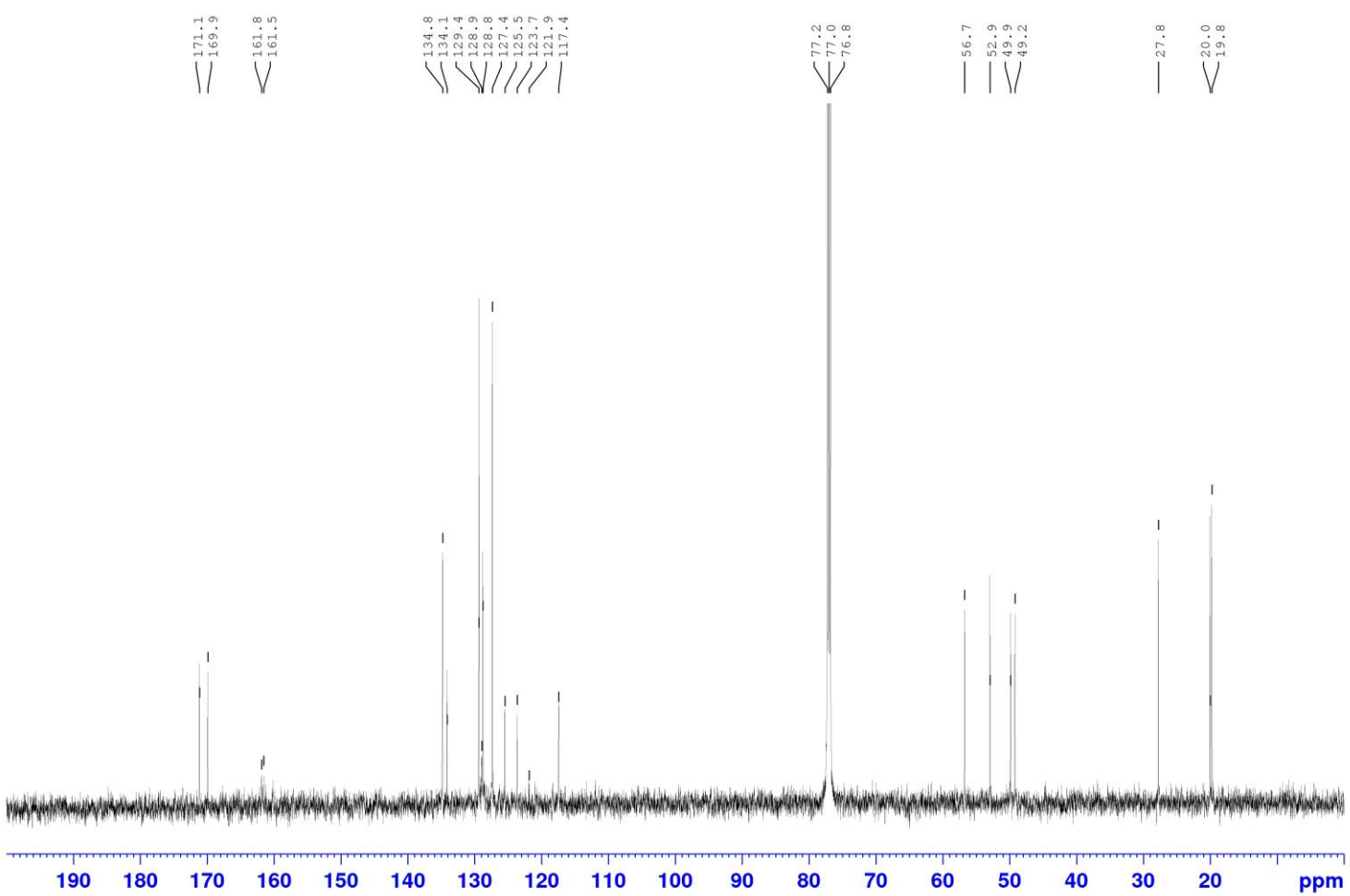
13: ^{1}H NMR (600 MHz, $CDCl_3$)



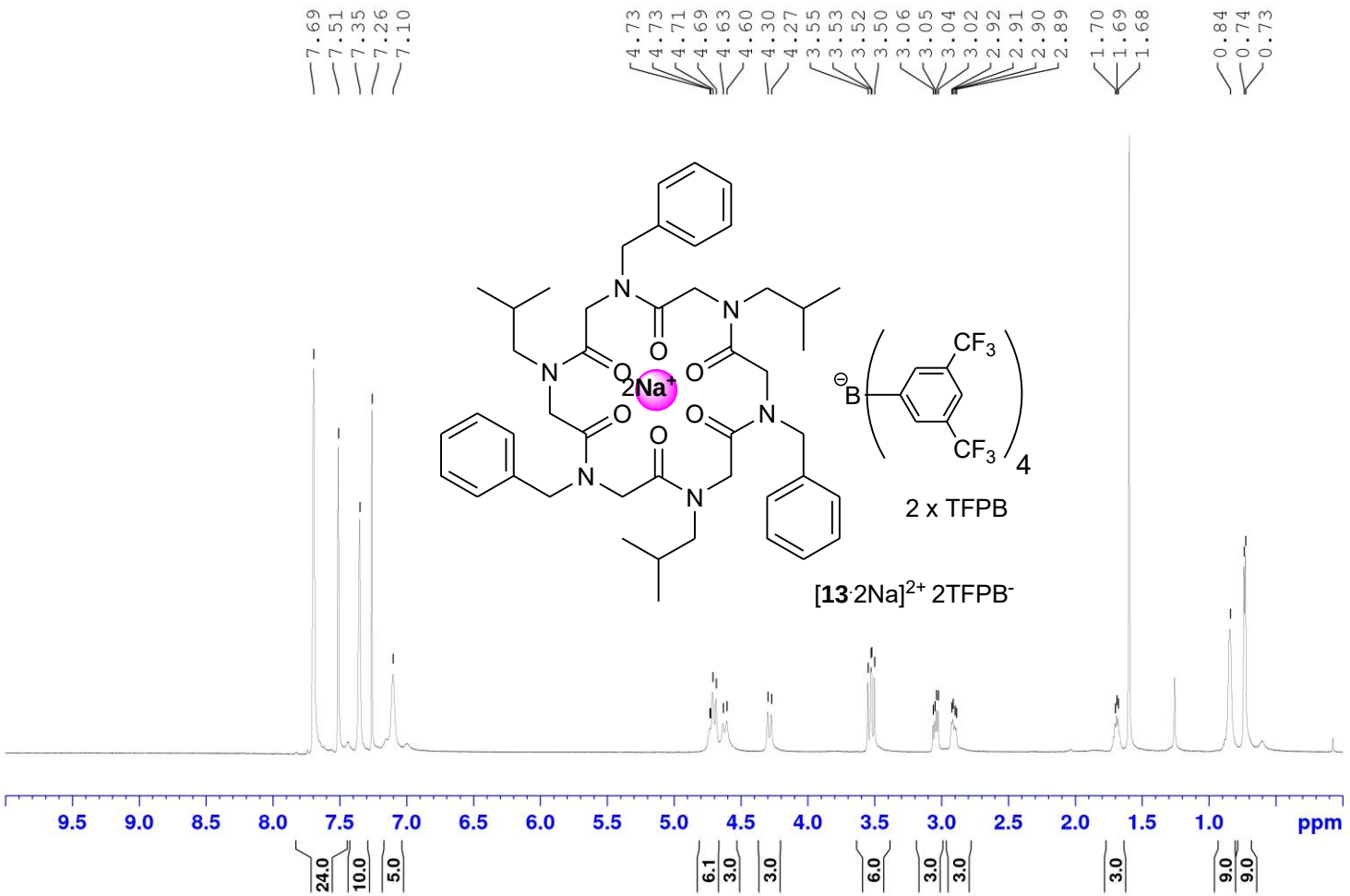
13: ^{13}C NMR (150 MHz, $CDCl_3$)



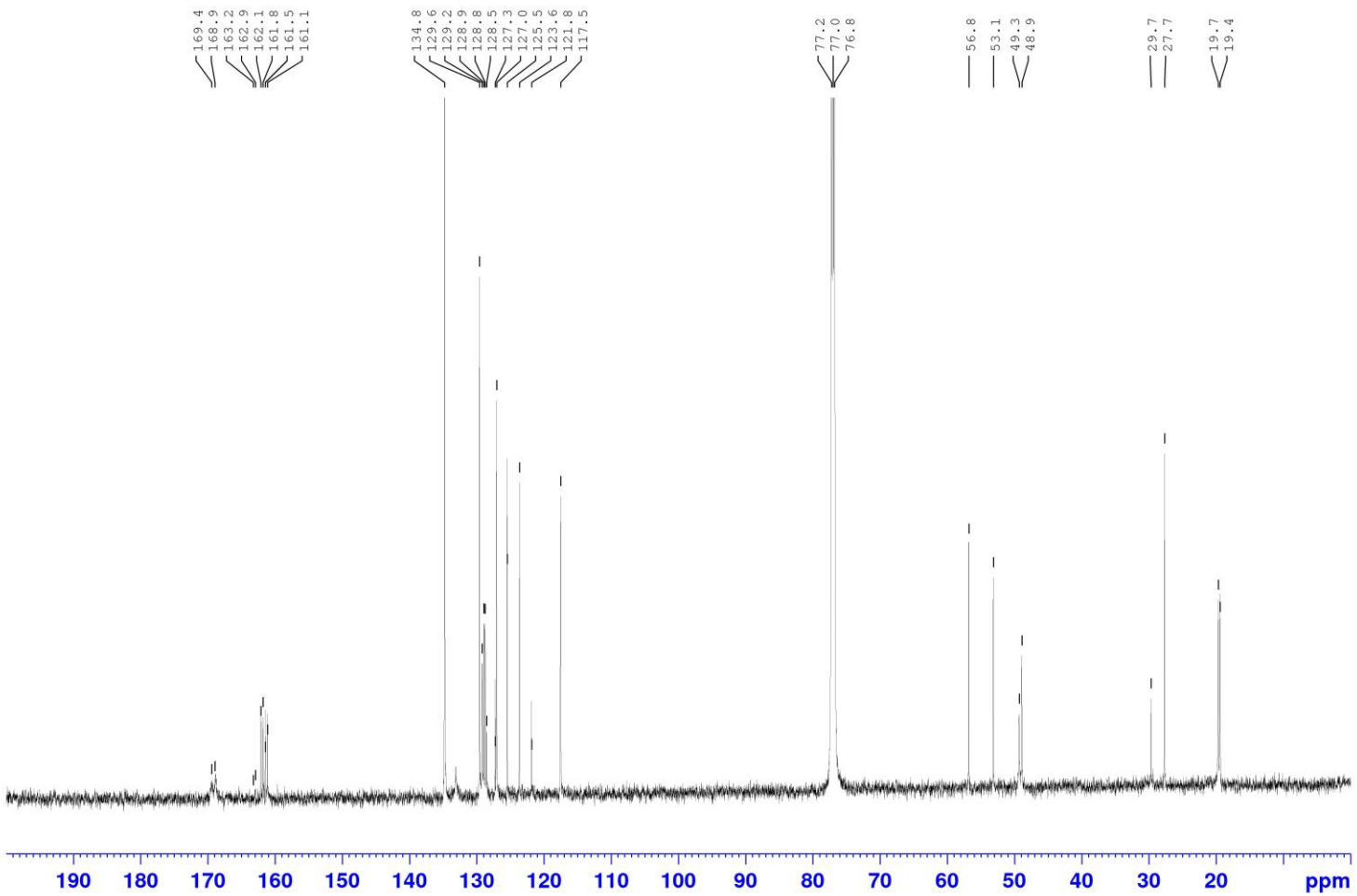
[**13**·Na]$^+$ TFPB$^-$: ^{1}H NMR (600 MHz, $CDCl_3$)



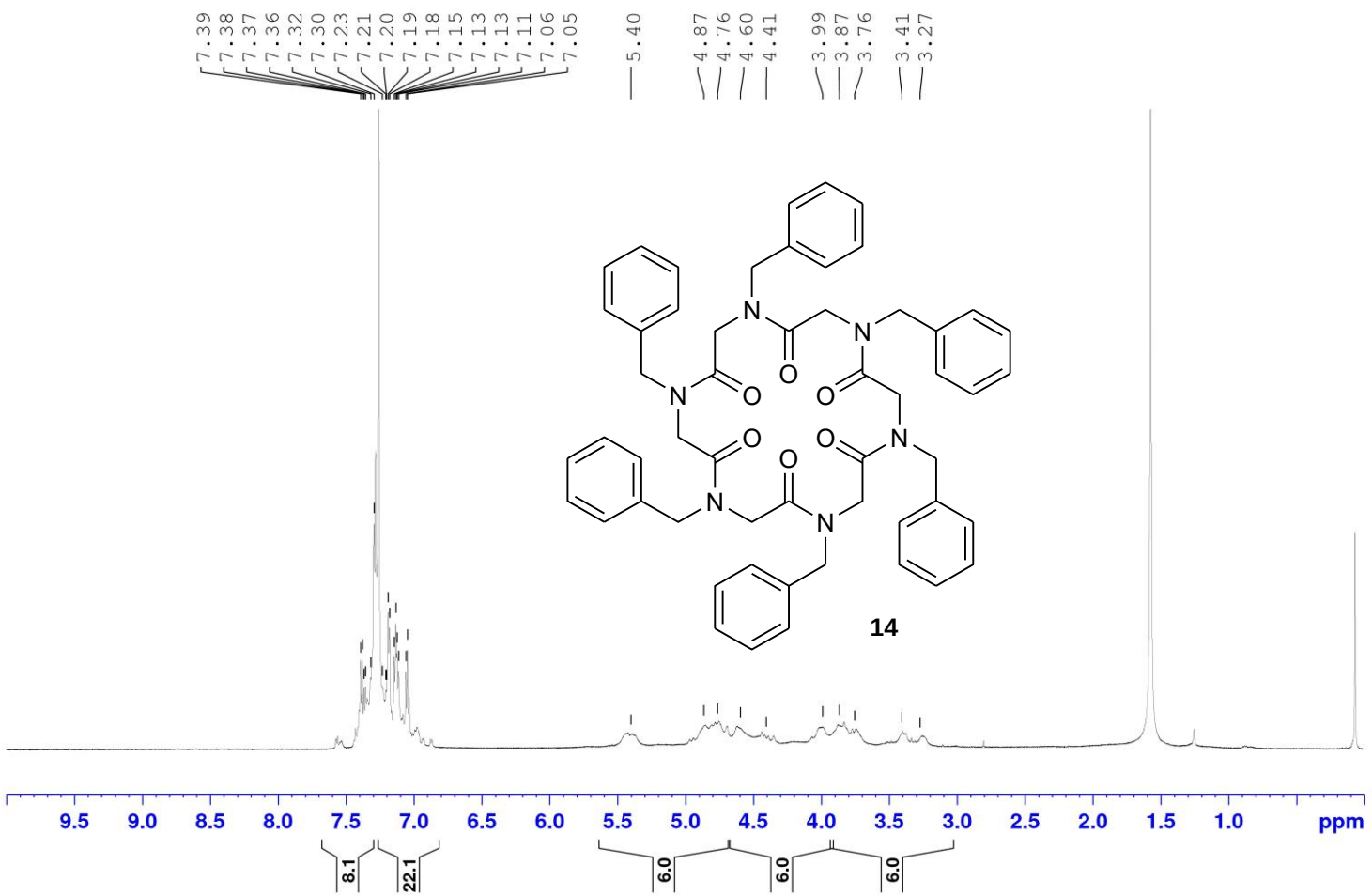
[**13**·Na]$^{+}$ TFPB^{-}: ^{13}C NMR (150 MHz, $CDCl_3$)



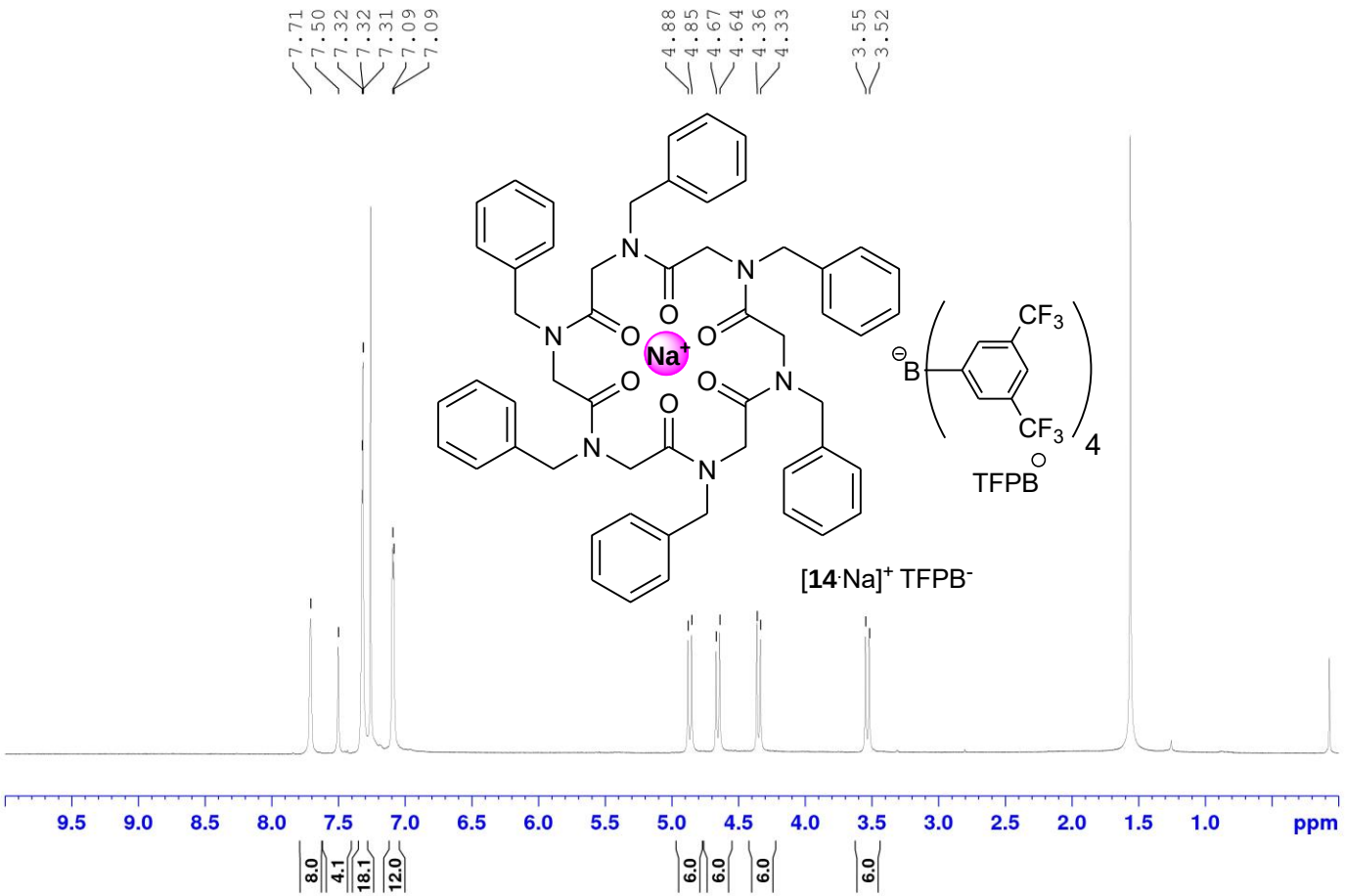
[**13**·2Na]$^{2+}$ 2TFPB^{-}: ^{1}H NMR (600 MHz, $CDCl_3$)



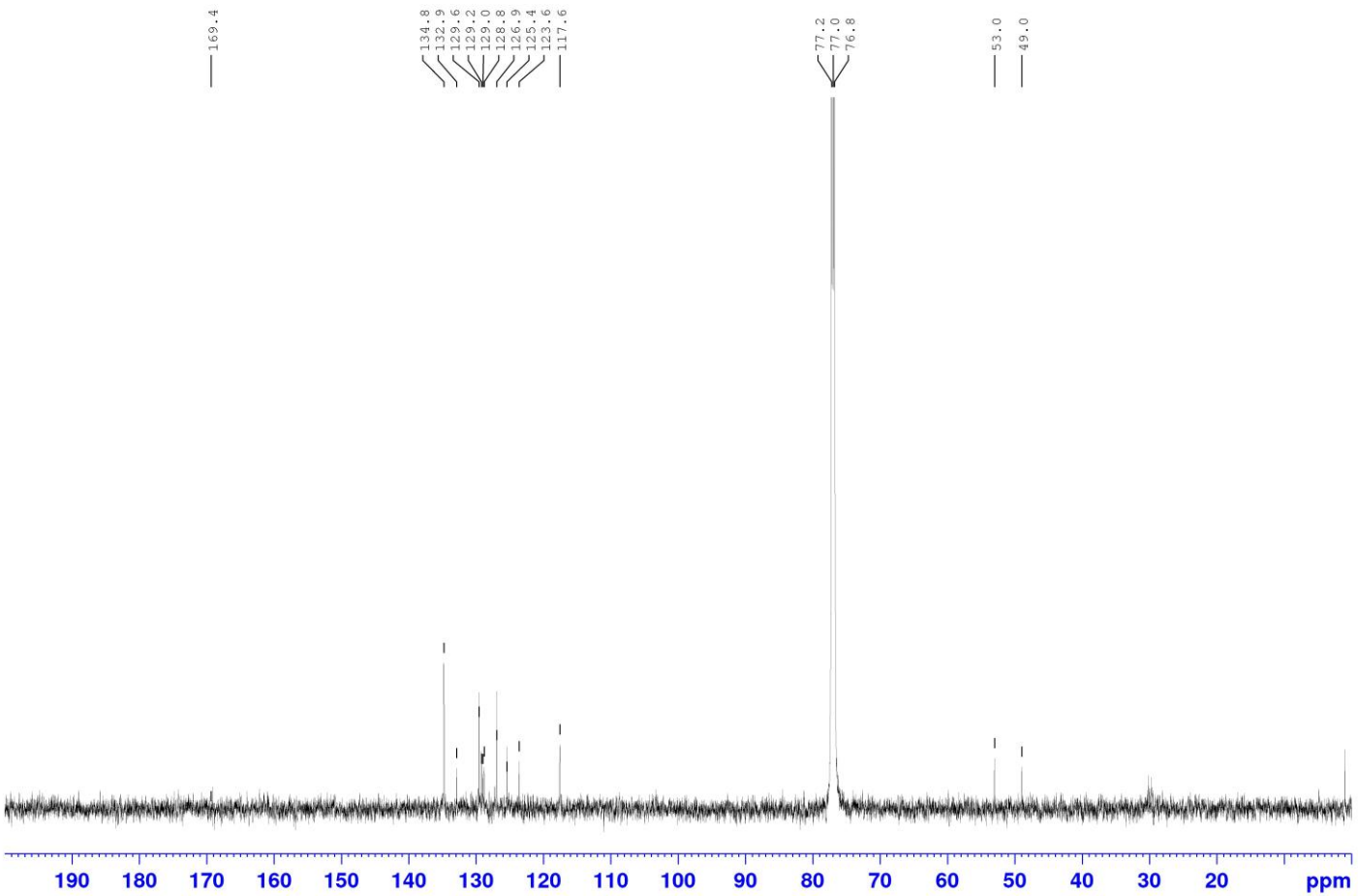
[**13**·2Na]$^{2+}$ 2TFPB^{-}: ^{13}C NMR (150 MHz, $CDCl_3$)



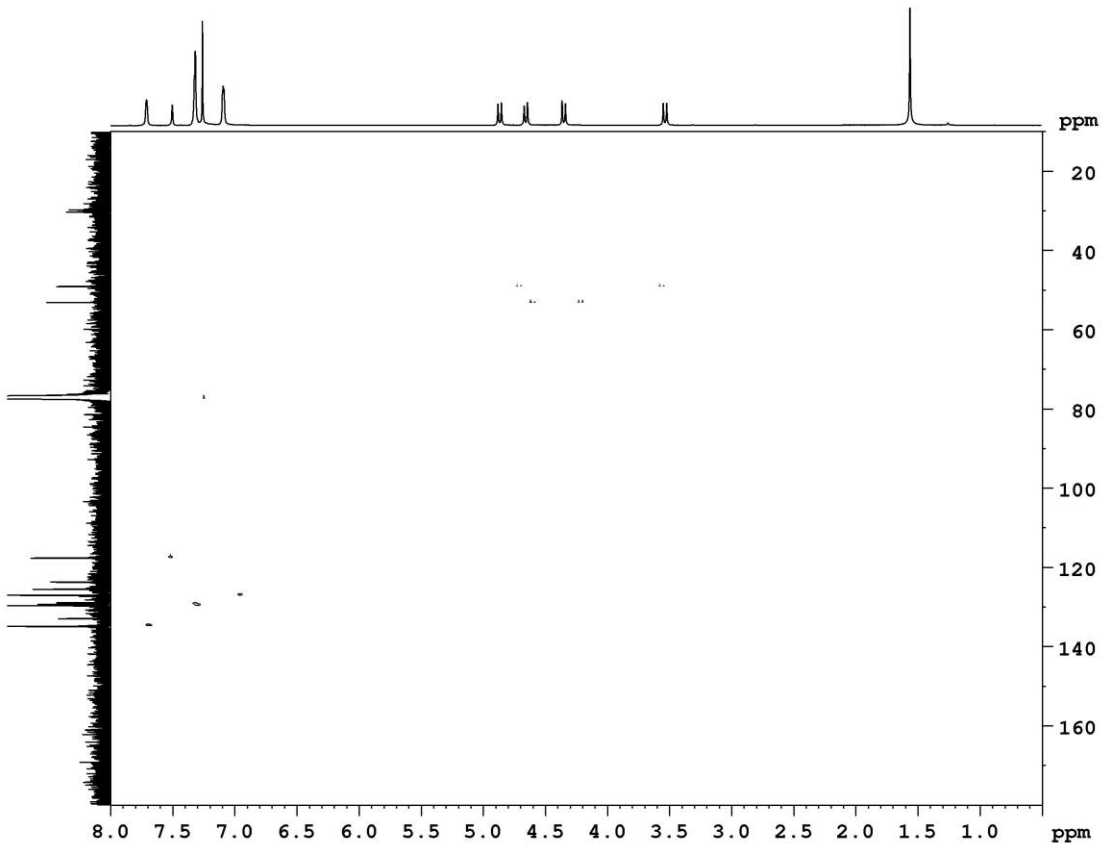
14: ^{1}H NMR (600 MHz, $CDCl_3$)



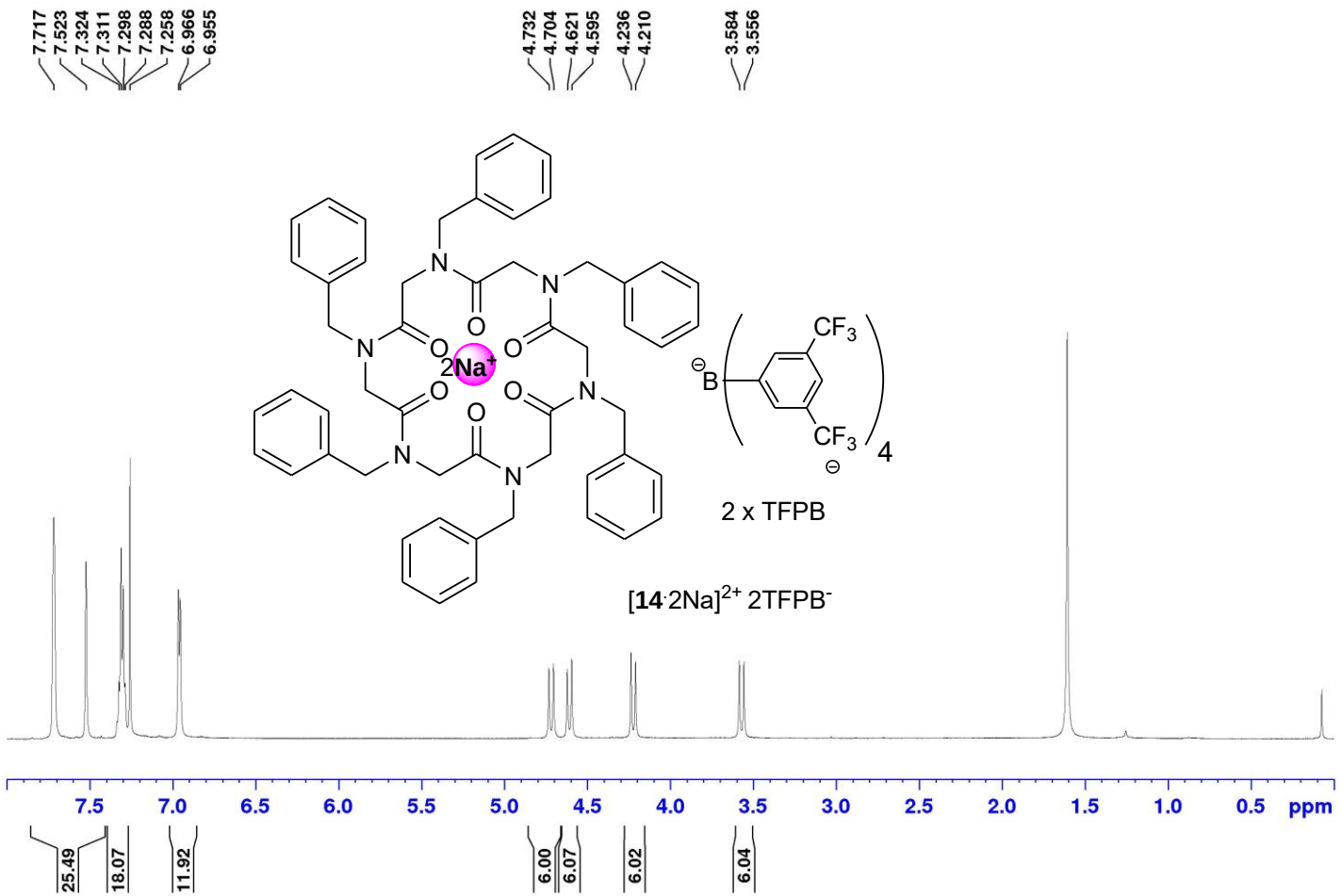
[**14**·Na]$^{+}$ TFPB^{-}: ^{1}H NMR (600 MHz, $CDCl_3$)



[**14**·Na]$^{+}$ TFPB^{-}: ^{13}C NMR (150 MHz, $CDCl_3$)



[**14**·Na]$^{+}$ TFPB^{-}: HSQC SPECTRUM (600 MHz, $CDCl_3$)



[**14**·2Na]$^{2+}$ 2TFPB^{-}:^{1}H NMR (600 MHz, $CDCl_3$)

1.2 ^{1}H NMR variable temperature experiments on **11**

11 was dissolved in $C_2D_2Cl_4$ (TCDE, 5.0 mM solution), then ^{1}H NMR spectra were acquired at different temperatures, increasing 5 Kelvin each time. The coalescence was observed at 323 K for the two doublets respectively at 4.54 and 3.14 ppm (AX system, O=C-CH_2-*N*-Bn). Subsequently, the $\Delta G_c^{\neq}$ was evaluated according to the following relation:

$$\Delta G_c^{\neq} = aT_c\left[9.972 + \log\left(\frac{T_c}{\sqrt{\Delta\nu^2 + 6J^2}}\right)\right]$$

Where T_c is the coalescence temperature, $\Delta\nu$ is the difference in Hertz between the two doublets and *J* is the coupling constant between the two signals.[1]

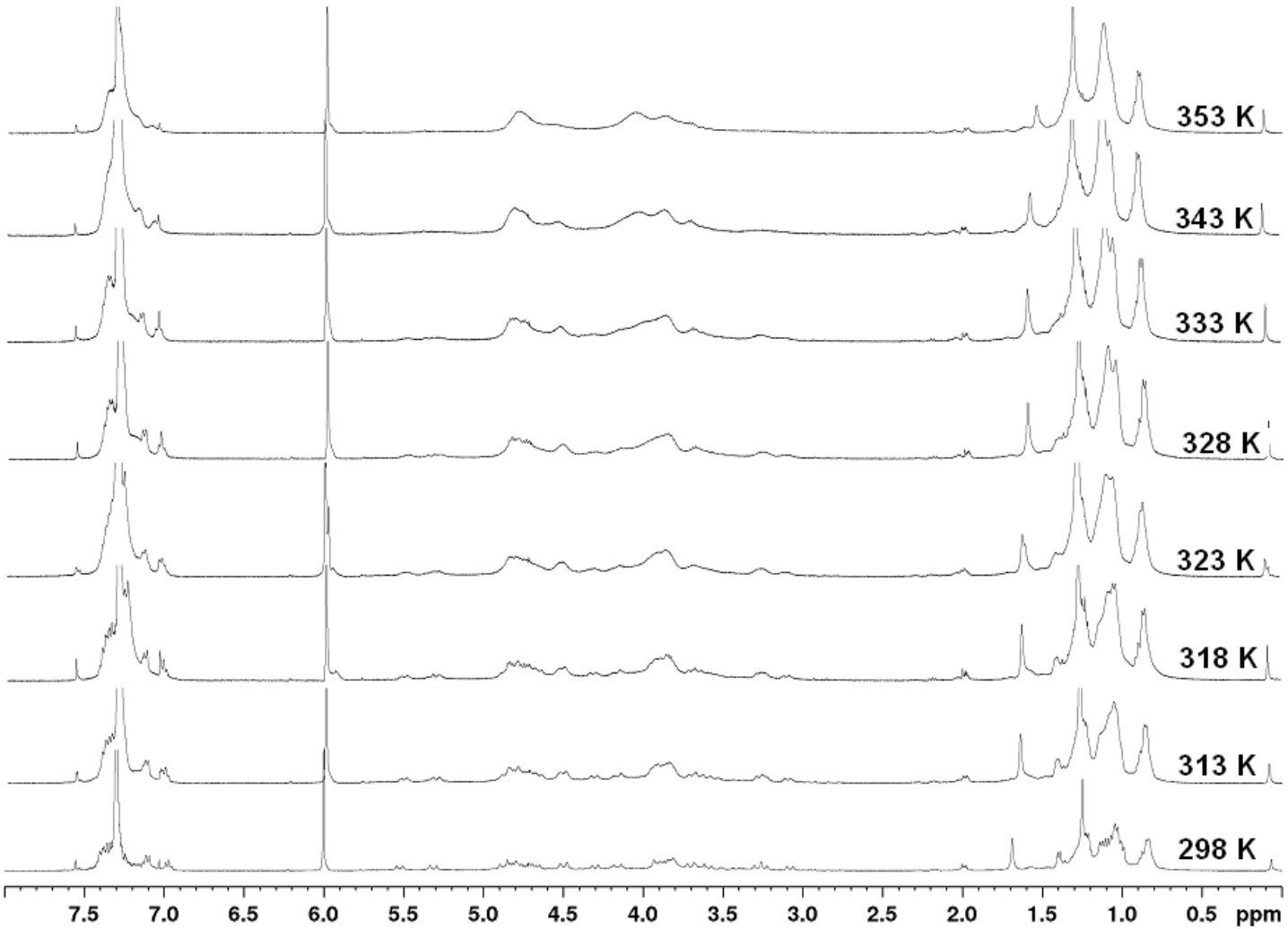


Figure S1. Variable temperature ^{1}H NMR spectra of compound **11** (400 MHz, $C_2D_2Cl_4$, 5.0 mM solution).

1.3 ^{1}H NMR titration of cyclic peptoids **9-14** with NaTFPB

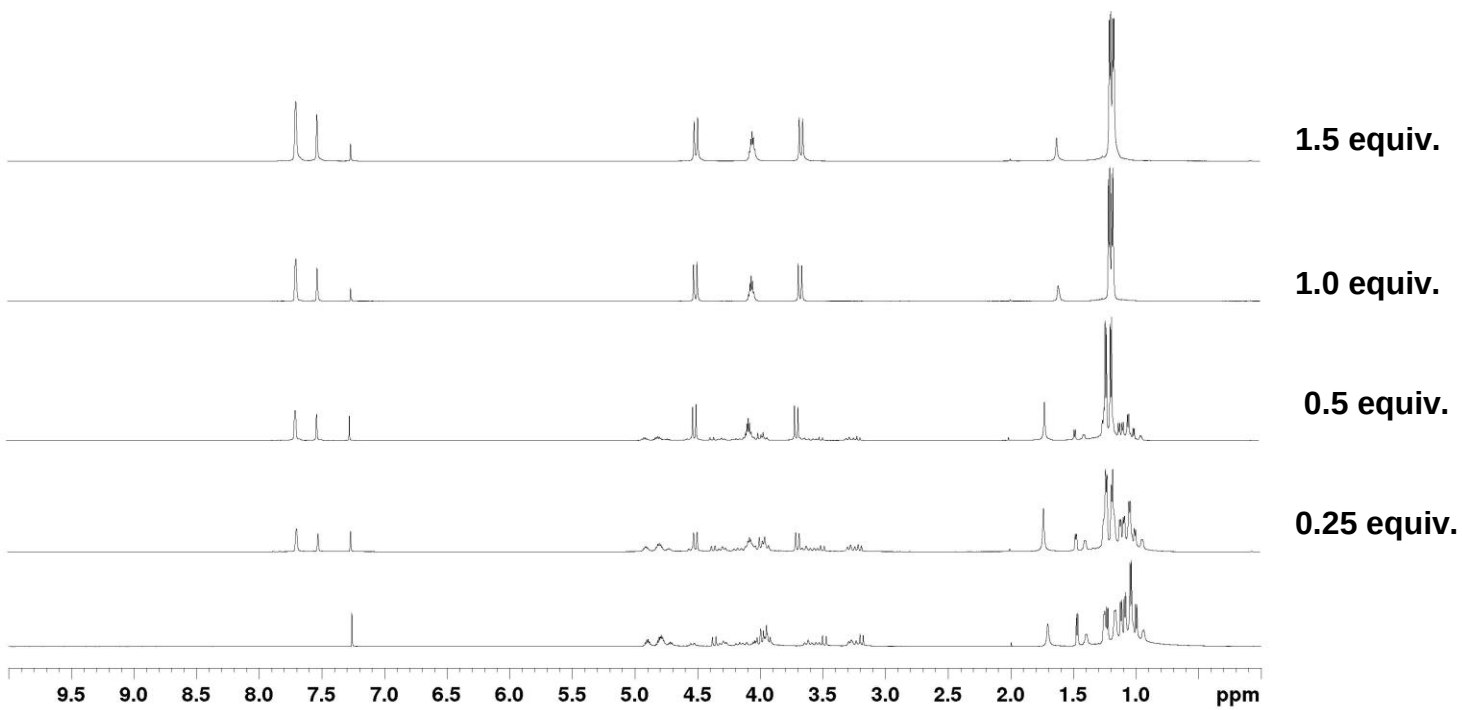


Figure S2. Quantitative step-wise addition of NaTFPB to **9**. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K, 5.0 mM solution)

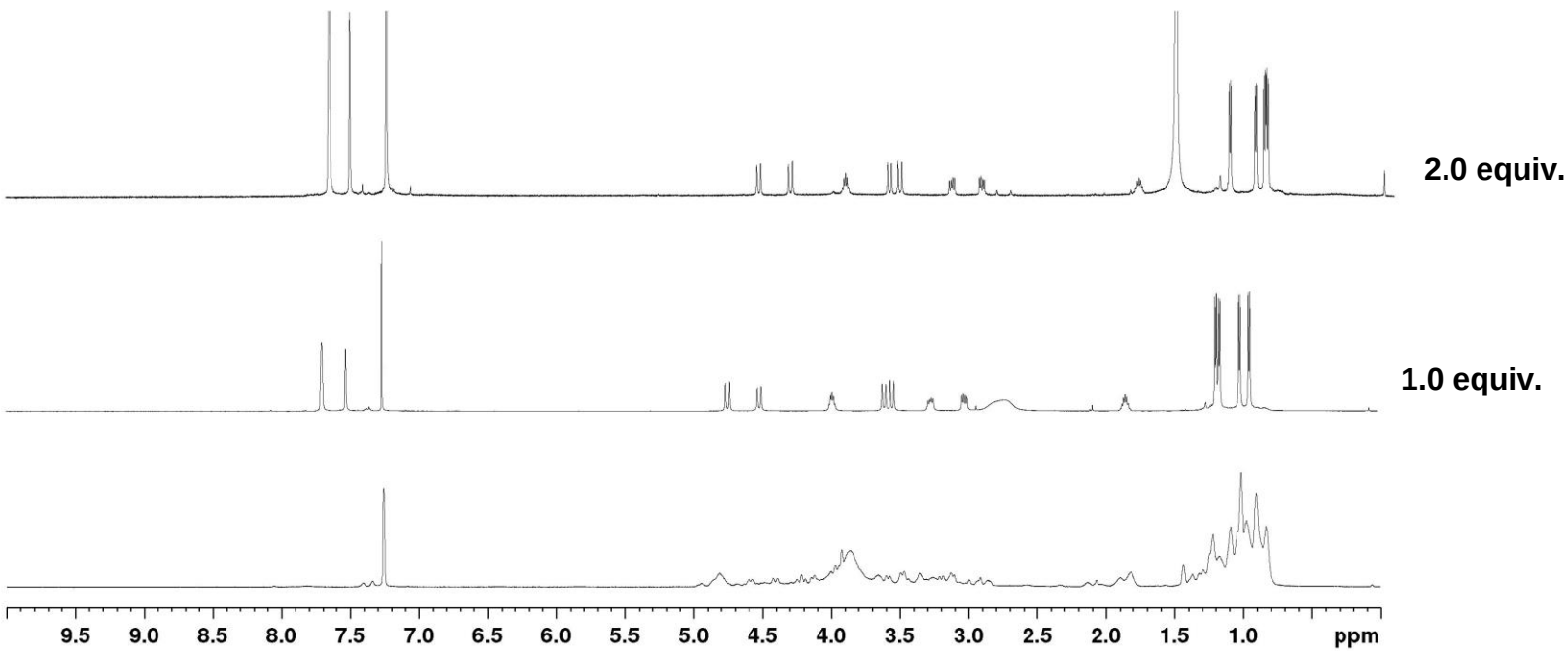


Figure S3. Quantitative step-wise addition of NaTFPB to **10**. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K, 5.0 mM solution)

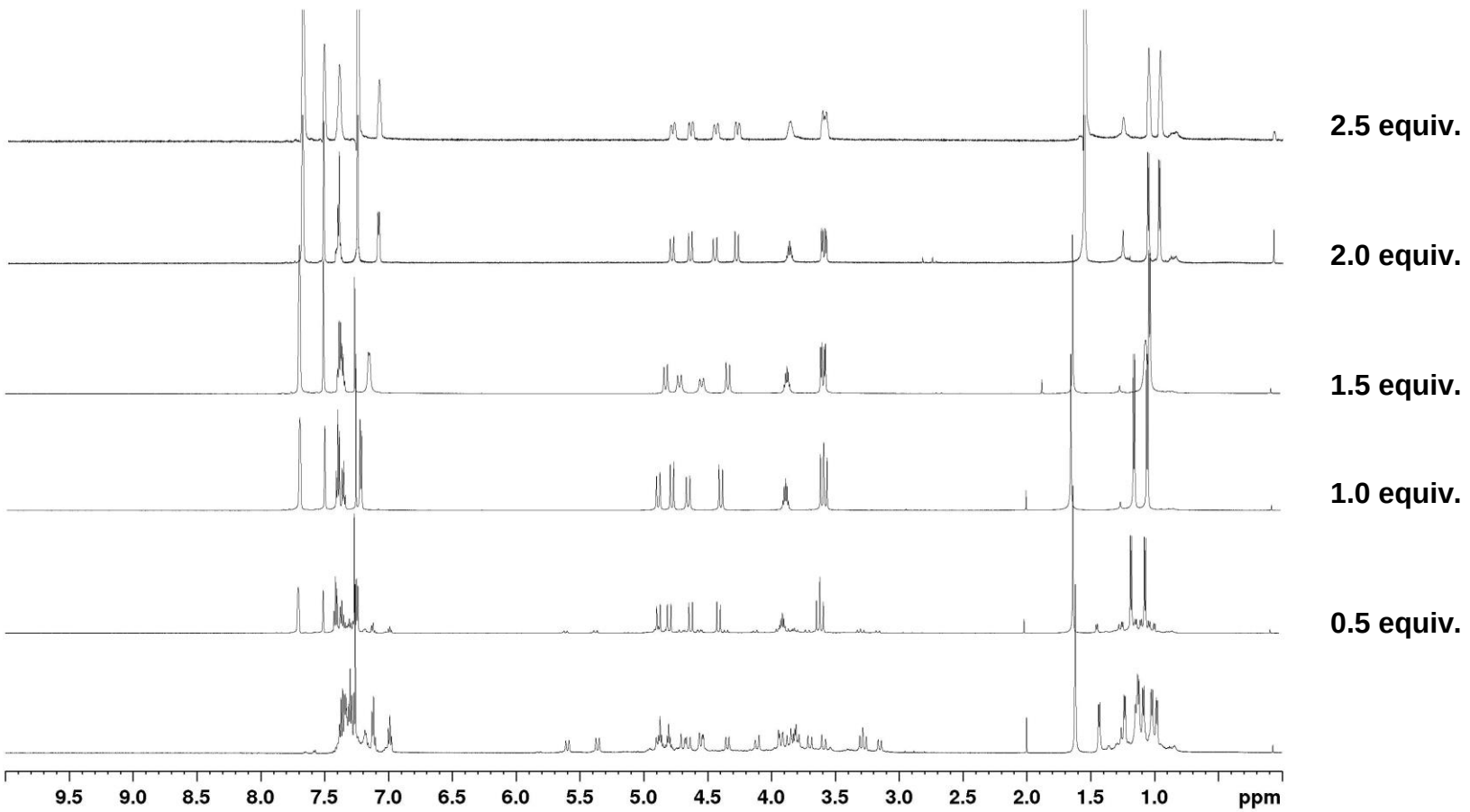


Figure S4. Quantitative step-wise addition of NaTFPB to **11**. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K, 5.0 mM solution)

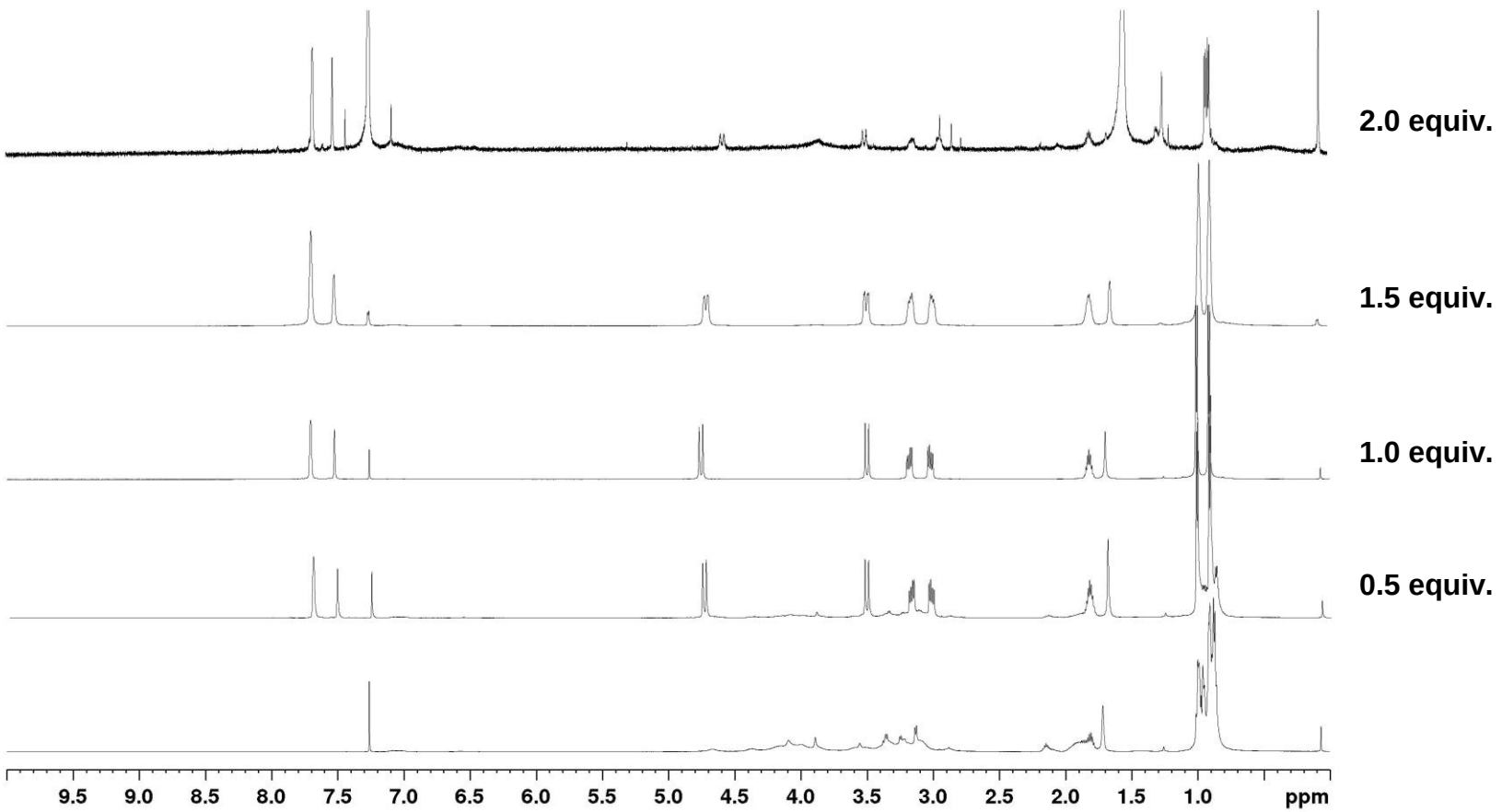


Figure S5. Quantitative step-wise addition of NaTFPB to **12**. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K, 5.0 mM solution)

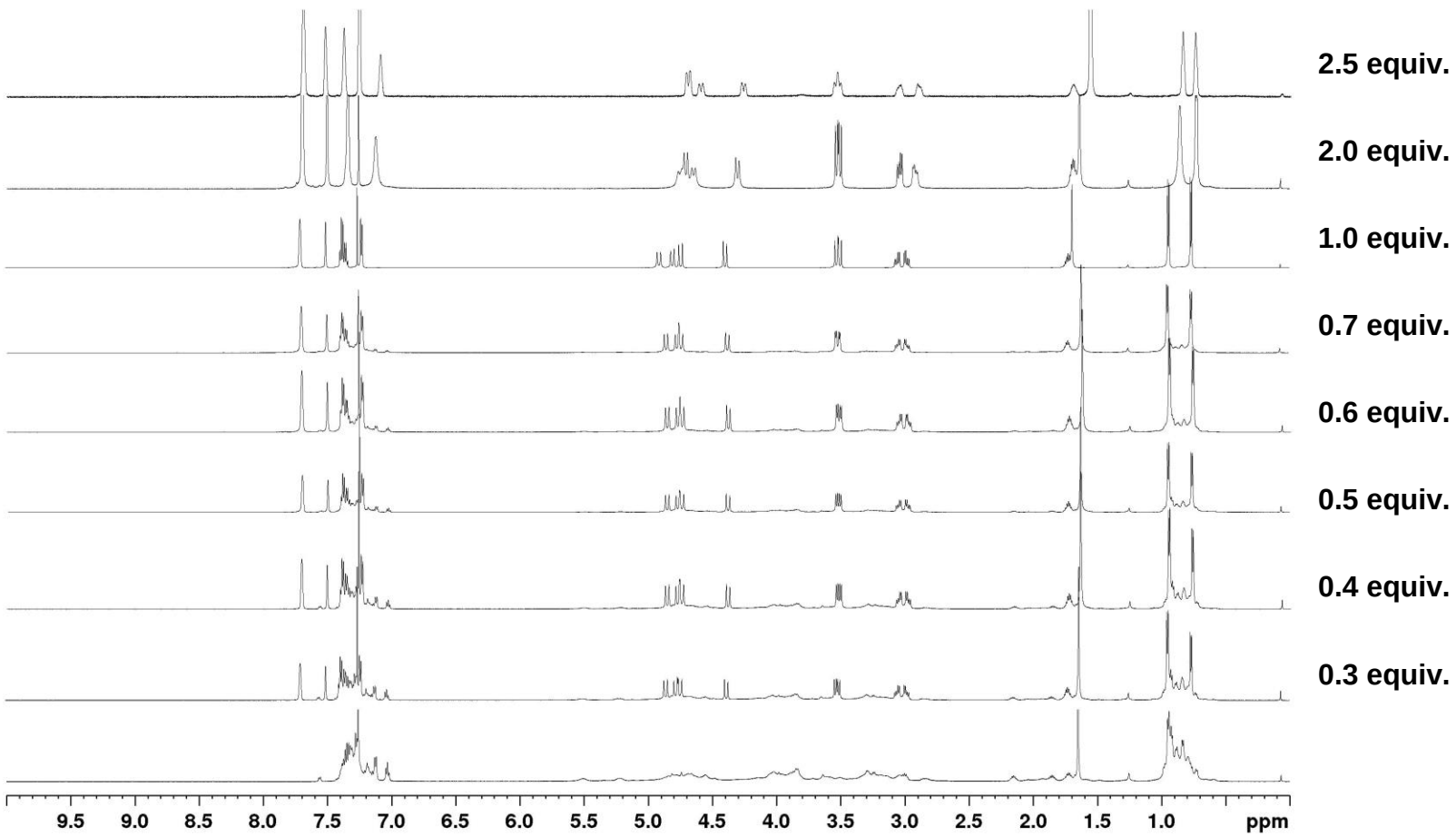


Figure S6. Quantitative step-wise addition of NaTFPB to **13**. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K, 5.0 mM solution)

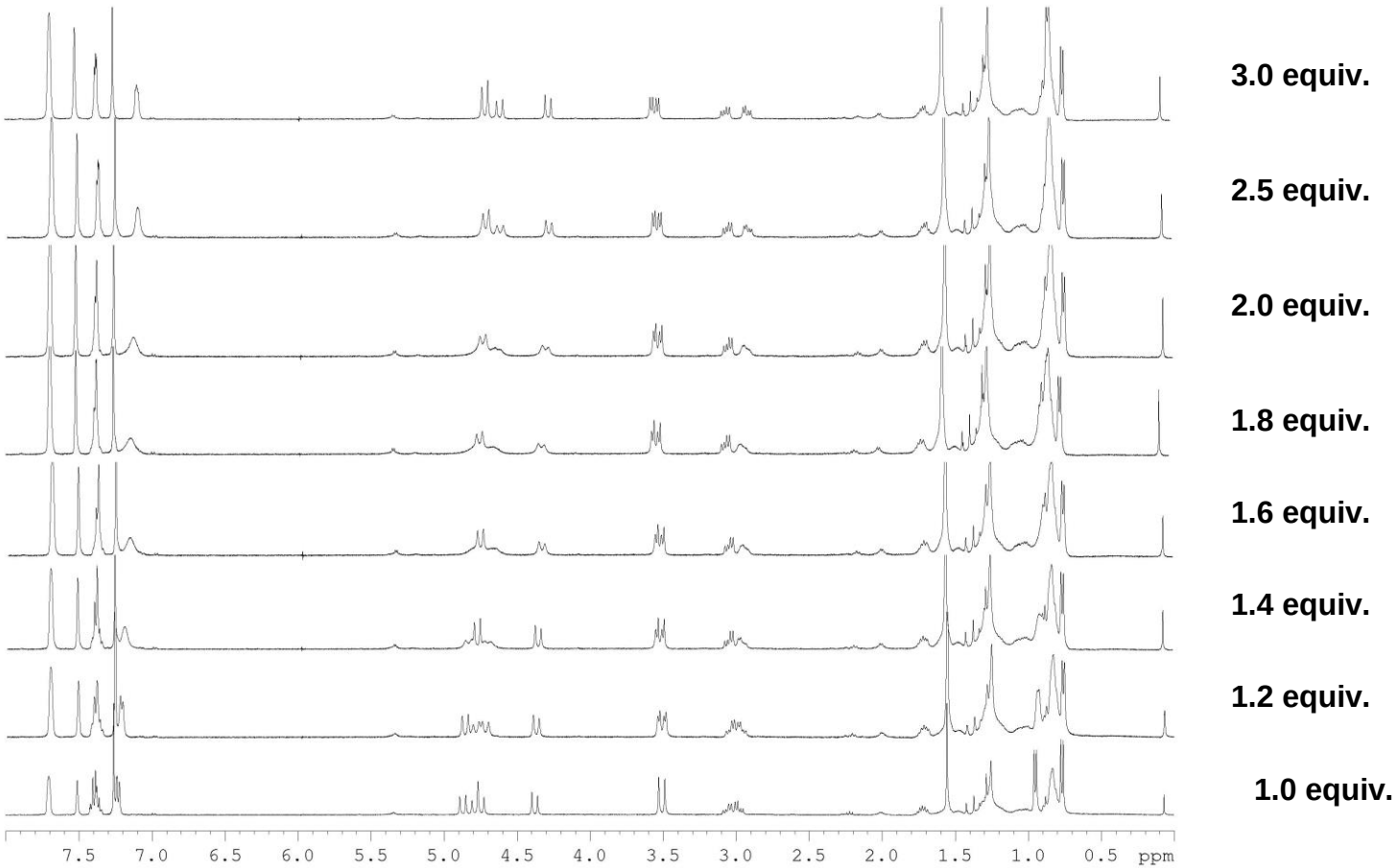


Figure S7. Quantitative step-wise addition of NaTFPB to [**13**·Na]$^+$ TFPB$^-$ in order to calculate the apparent K_{a2}. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K, 1.0 mM solution). The K_{a2} was calculated using the program winEQNMR.[2]

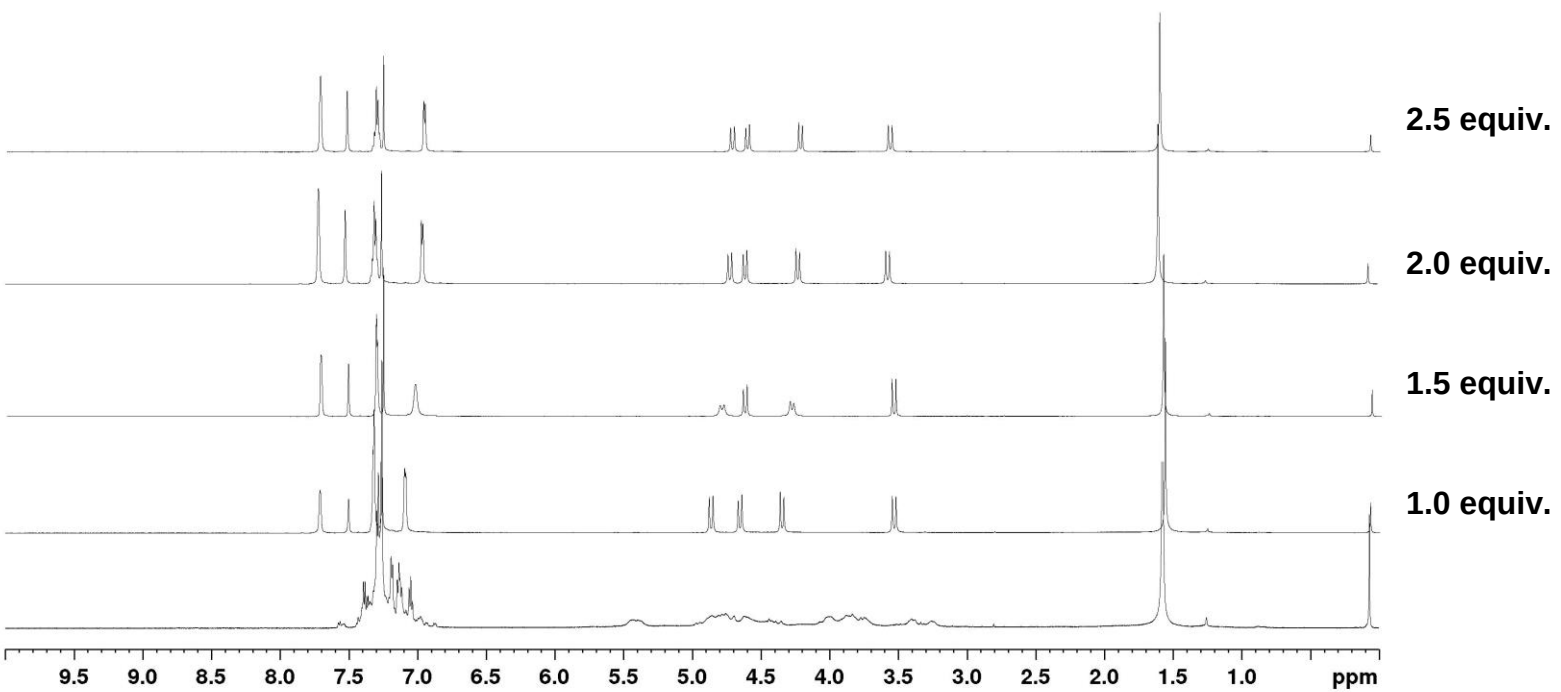


Figure S8. Quantitative step-wise addition of NaTFPB to **14**. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K, 5.0 mM solution)

1.4 ESI MS spectra of **9-14** treated with 2 equivalents on NaTFPB

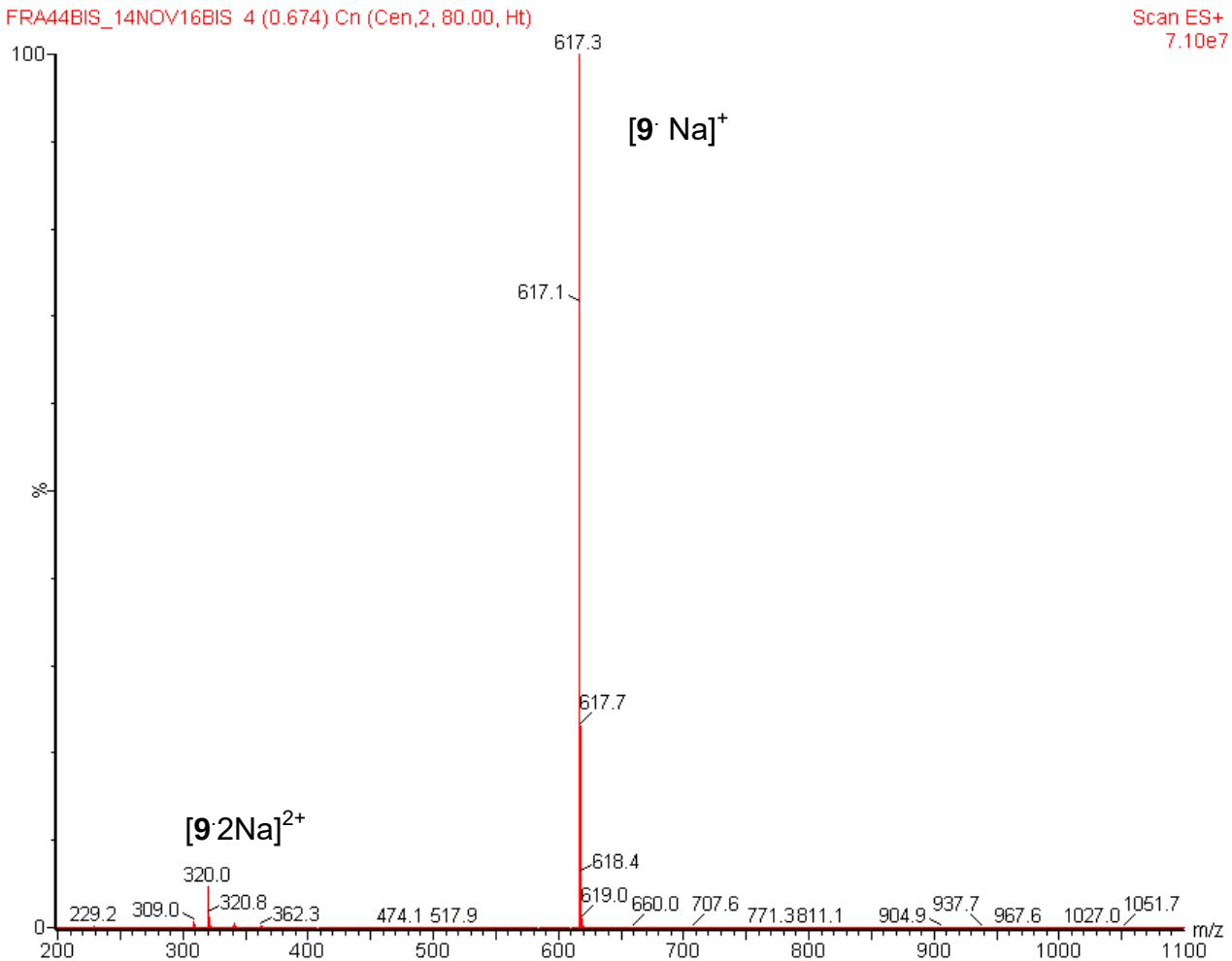


Figure S9. ESI MS spectrum of **9** treated with two equivalents of NaTFPB (presence of the $[\mathbf{9}\cdot Na]^+$ peak (100%) and 4% of $[\mathbf{9}\cdot 2Na]^{2+}$)

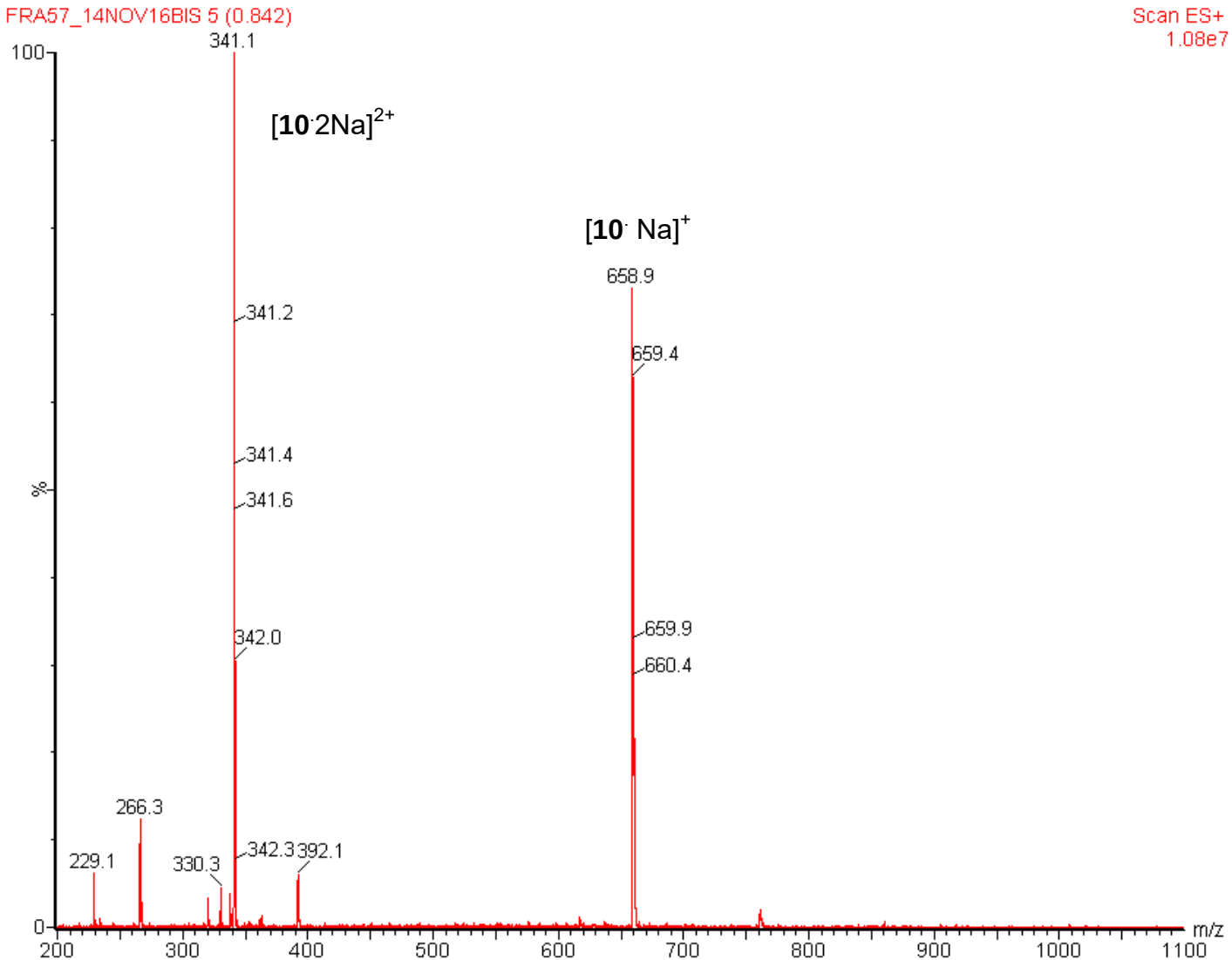


Figure S10. ESI MS spectrum of **10** treated with two equivalents of NaTFPB ([**10**·2Na]$^{2+}$ plus [**10**·Na]$^{+}$)

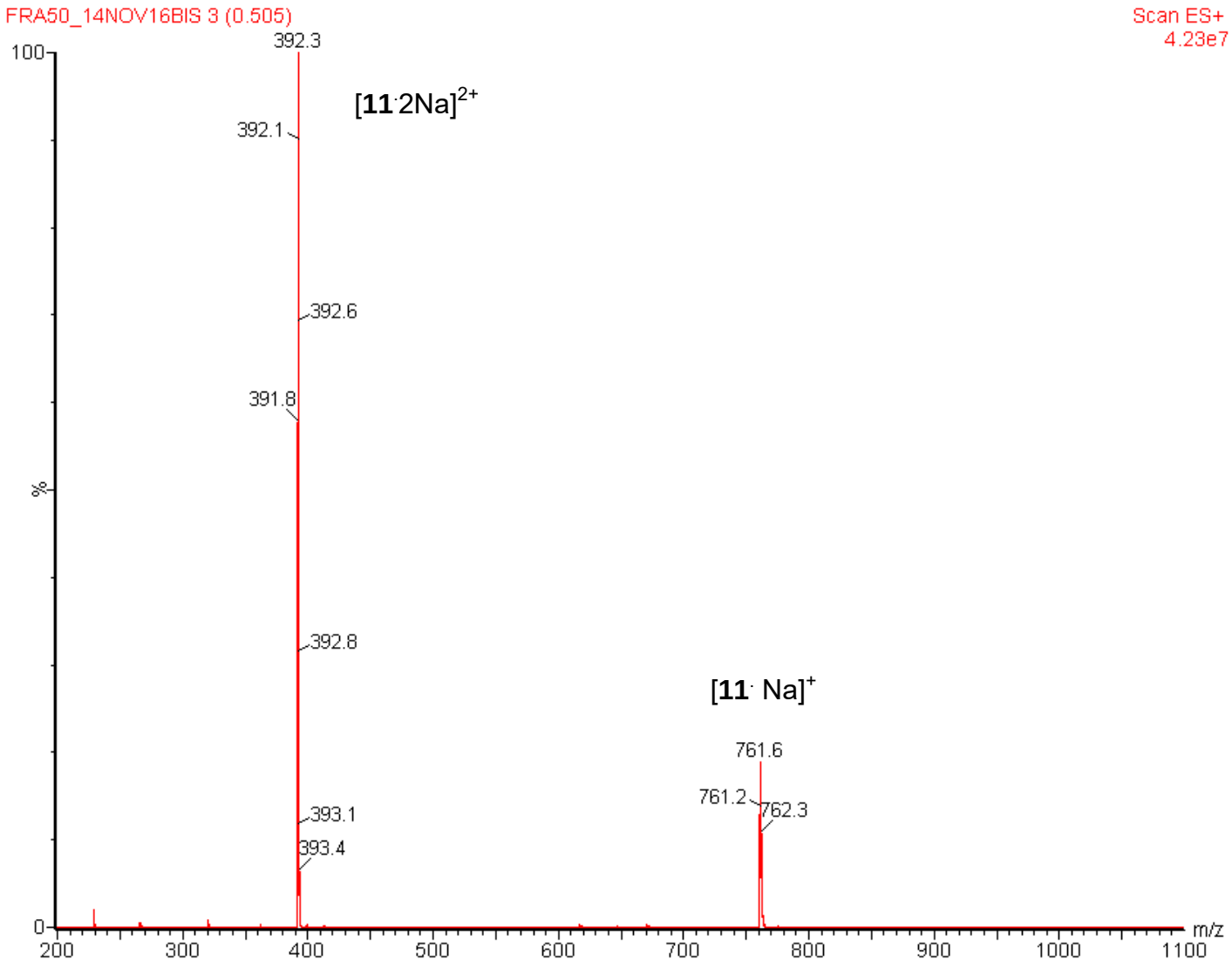


Figure S11. ESI MS spectrum of **11** treated with two equivalents of NaTFPB ([**11**·2Na]$^{2+}$ plus [**11**·Na]$^{+}$)

Figure S12. ESI MS spectrum of **12** treated with two equivalents of NaTFPB ([**12**·2Na]$^{2+}$ plus [**12**·Na]$^{+}$)

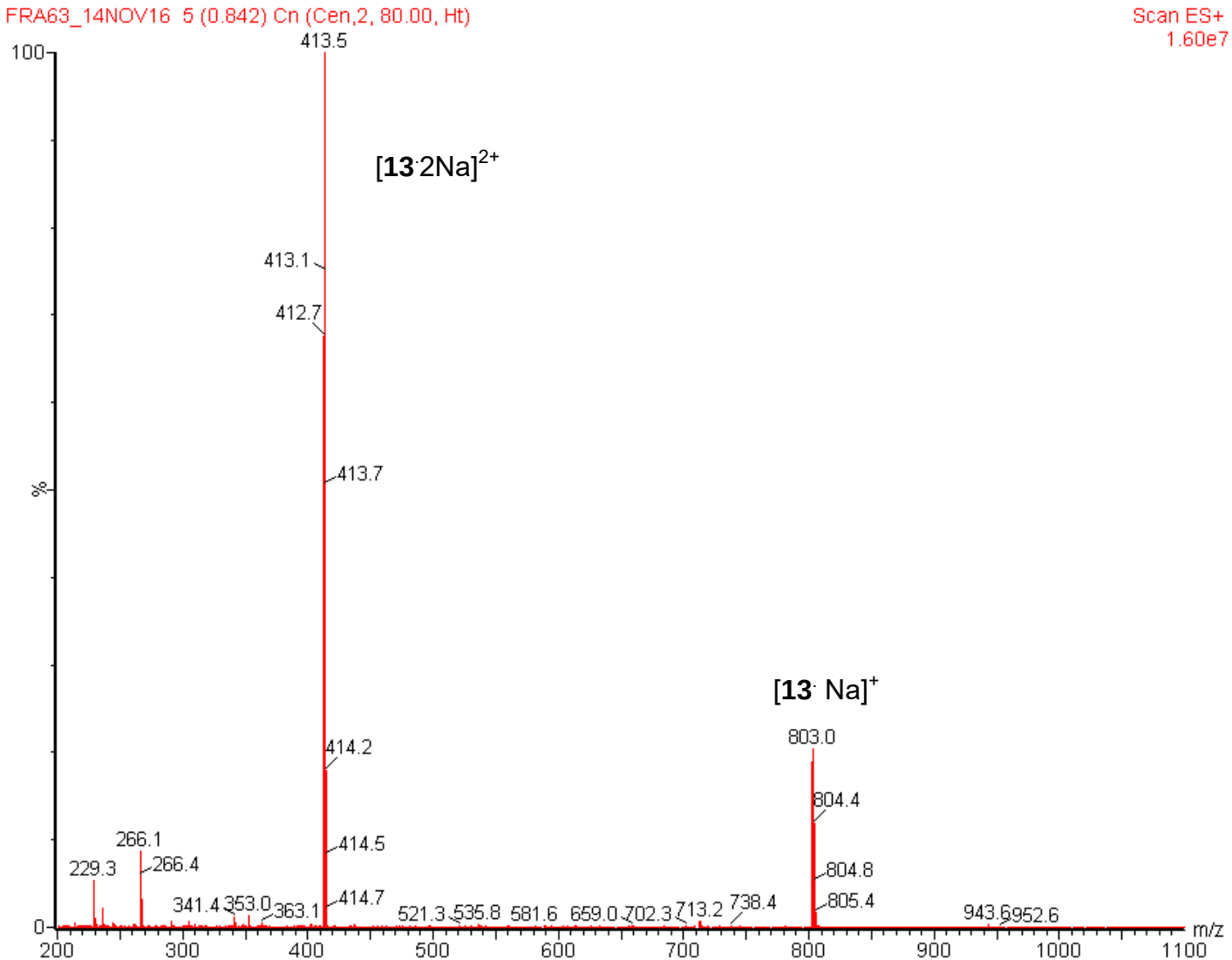


Figure S13. ESI MS spectrum of **13** treated with two equivalents of NaTFPB ([**13**·2Na]$^{2+}$ plus [**13**·Na]$^{+}$)

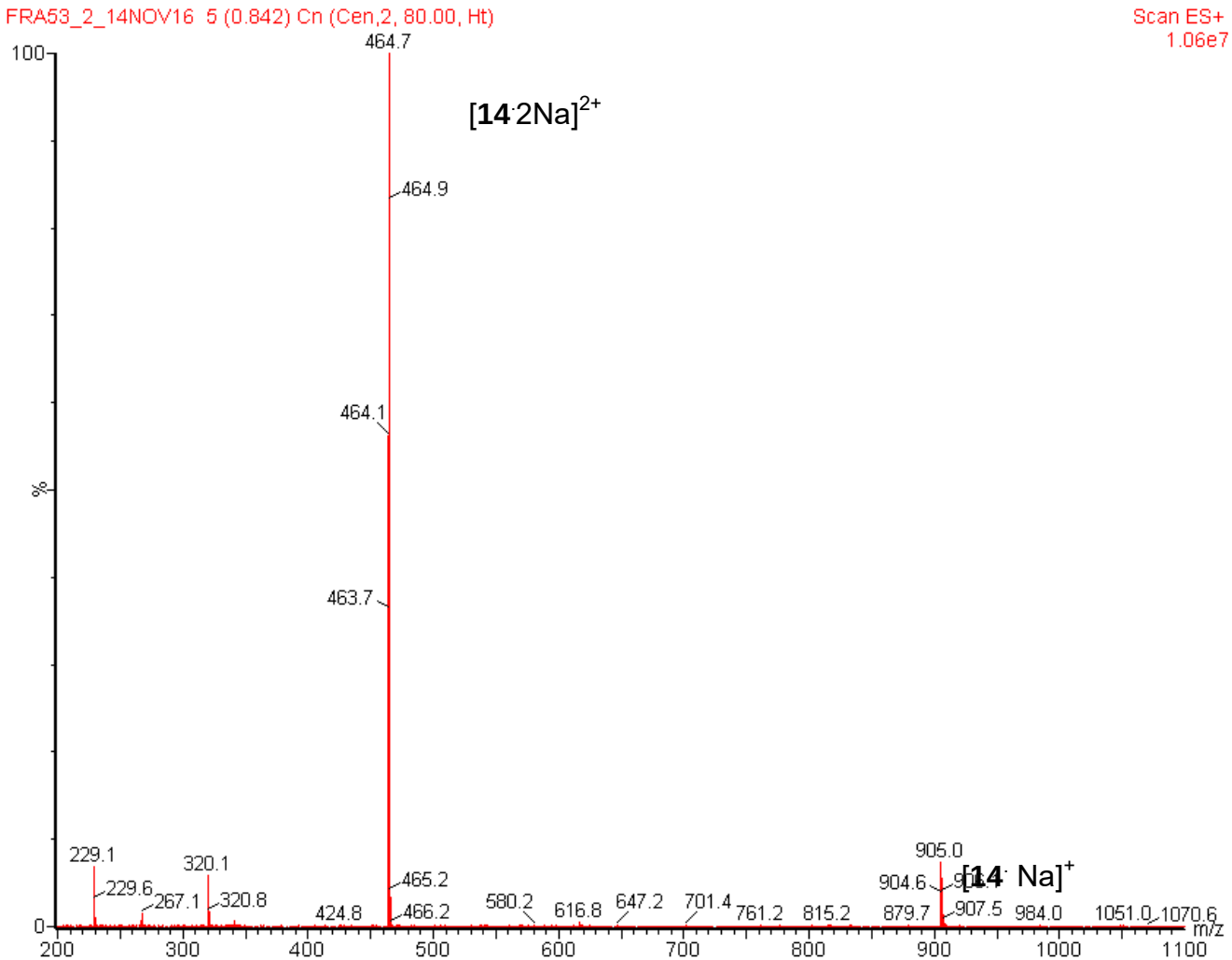


Figure S14. ESI MS spectrum of **14** treated with two equivalents of NaTFPB ([**14**·2Na]$^{2+}$ plus [**14**·Na]$^{+}$)

2.0 HPLC chromatograms

2.1 HPLC chromatograms of linear peptoids 15-19 as crude mixtures.

Conditions: 5 → 100% A in 30 min (A, 0.1% TFA in acetonitrile, B, 0.1% TFA in water); flow: 1 mL min^{-1}, 220 nm.

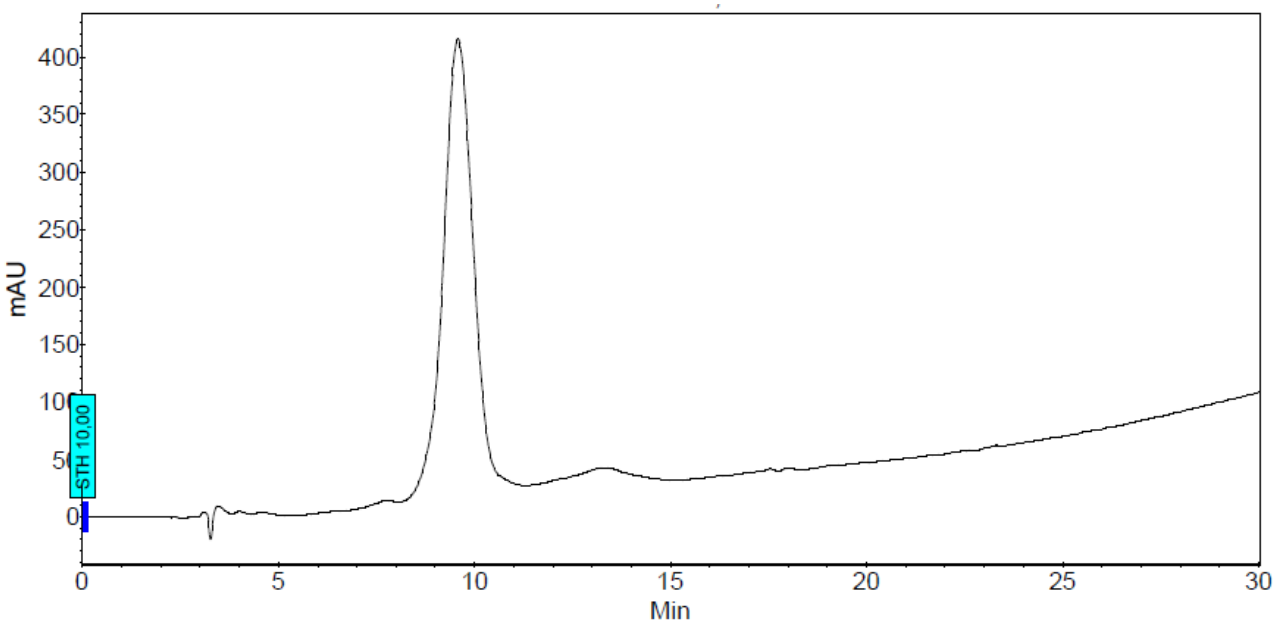


Figure S15. HPLC analysis of **15**

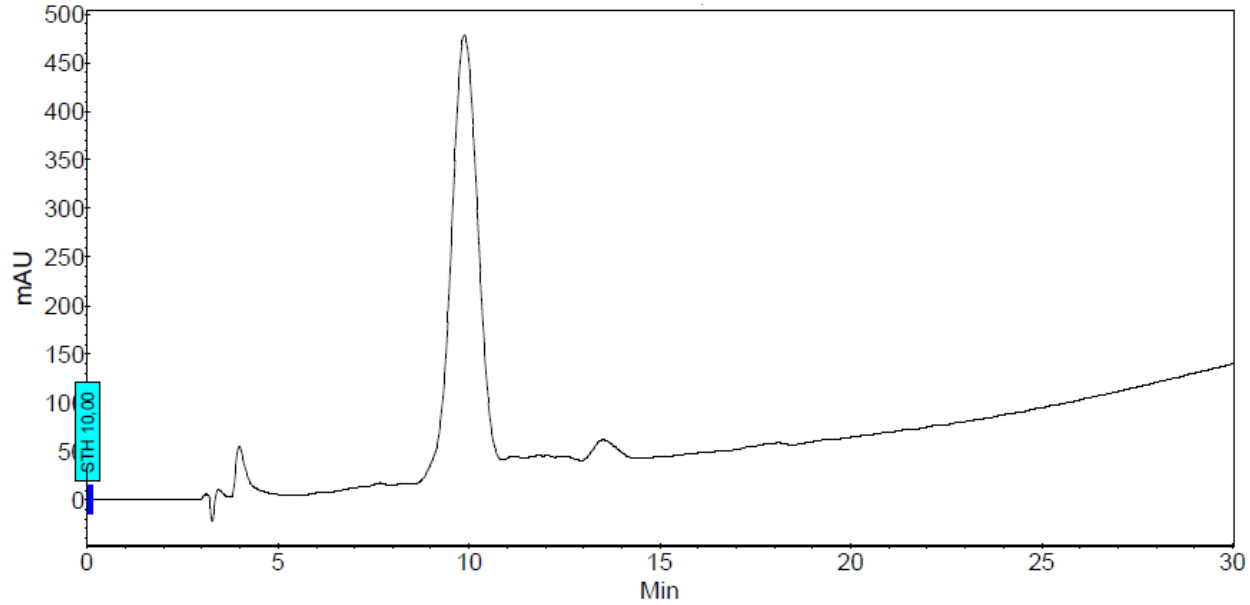


Figure S16. HPLC analysis of **16**

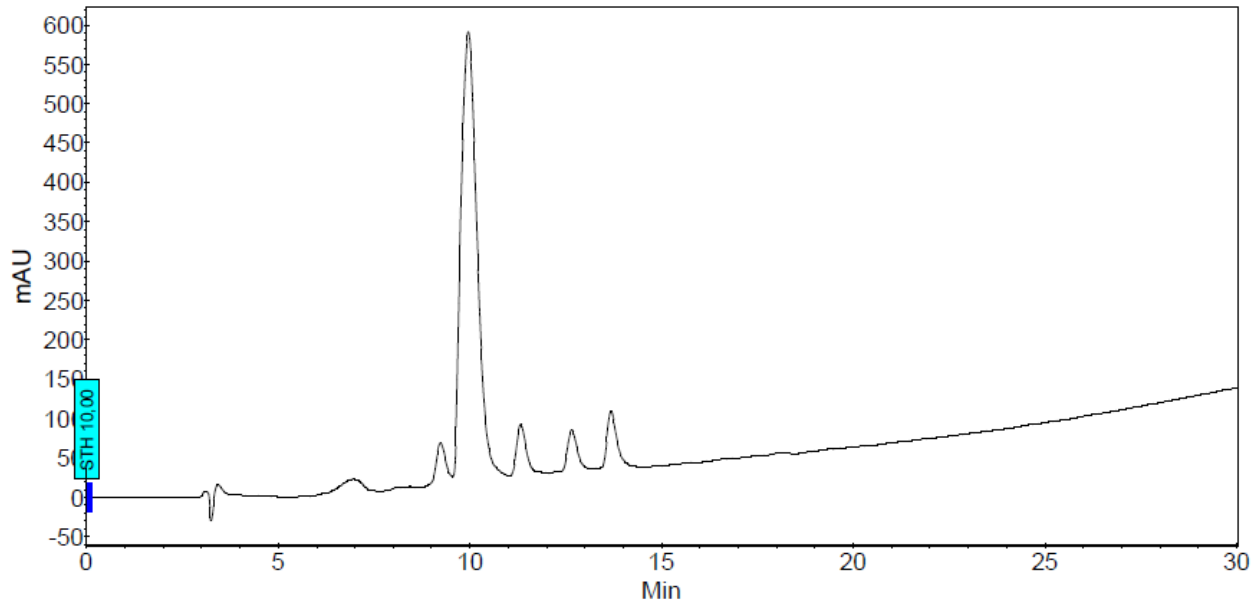


Figure S17. HPLC analysis of **17**

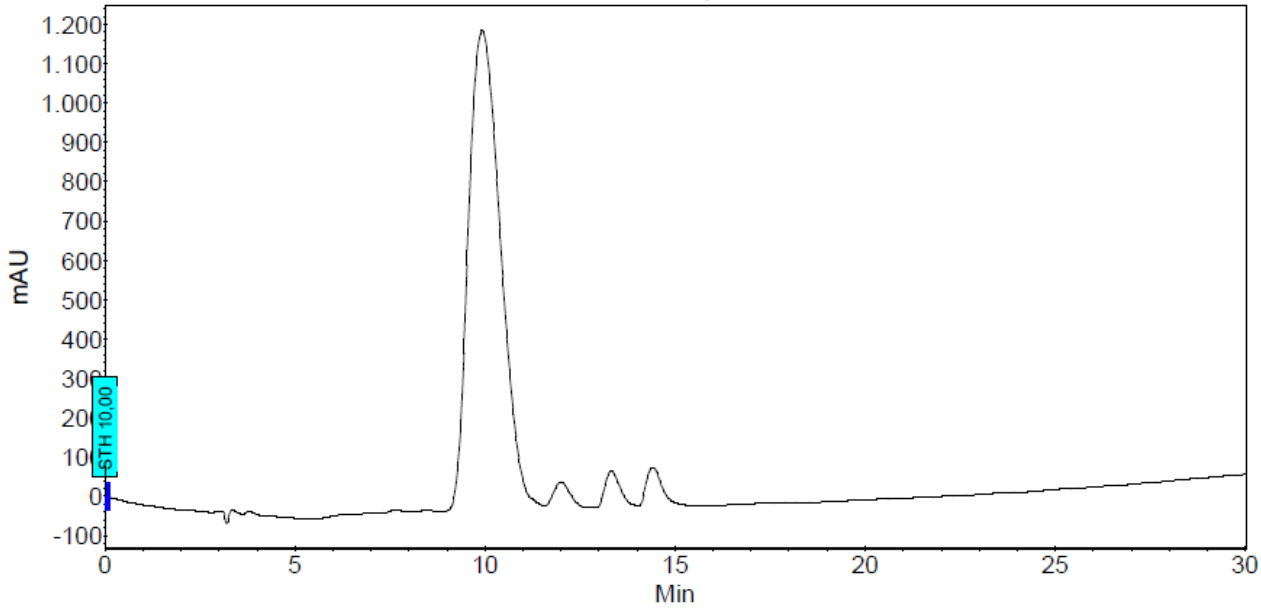


Figure S18. HPLC analysis of **18**

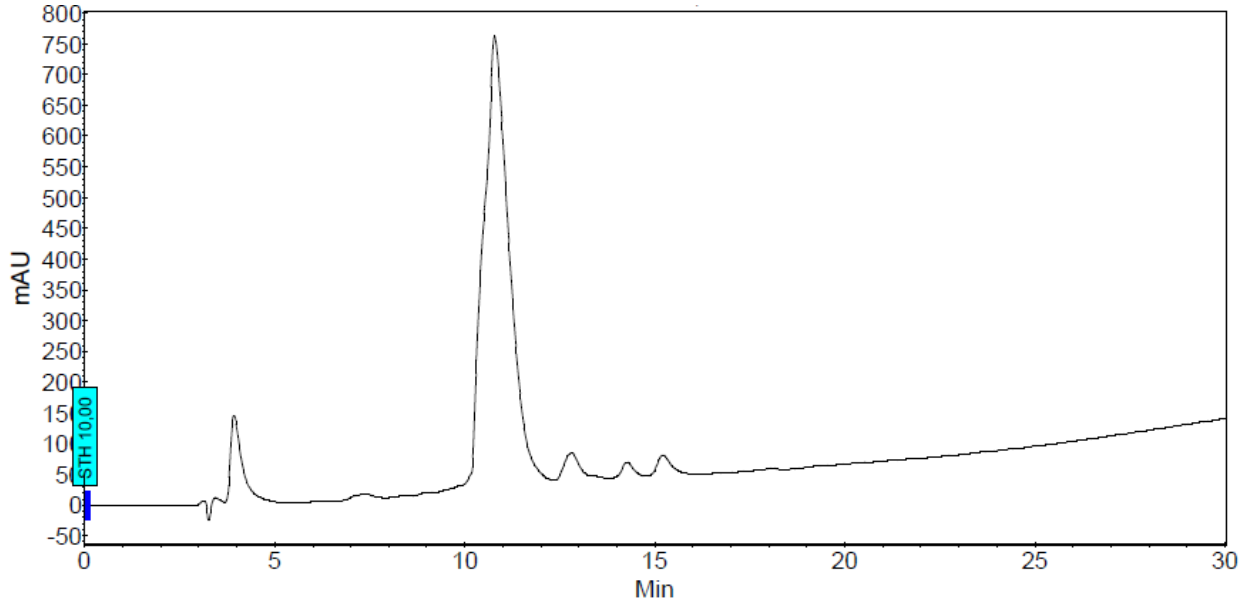


Figure S19. HPLC analysis of **19**

2.2 HPLC chromatograms of cyclic peptoids 9-13.
Conditions: 5 → 100% A in 30 min (A, 0.1% TFA in acetonitrile, B, 0.1% TFA in water); flow: 1 mL min^{-1}, 220 nm.

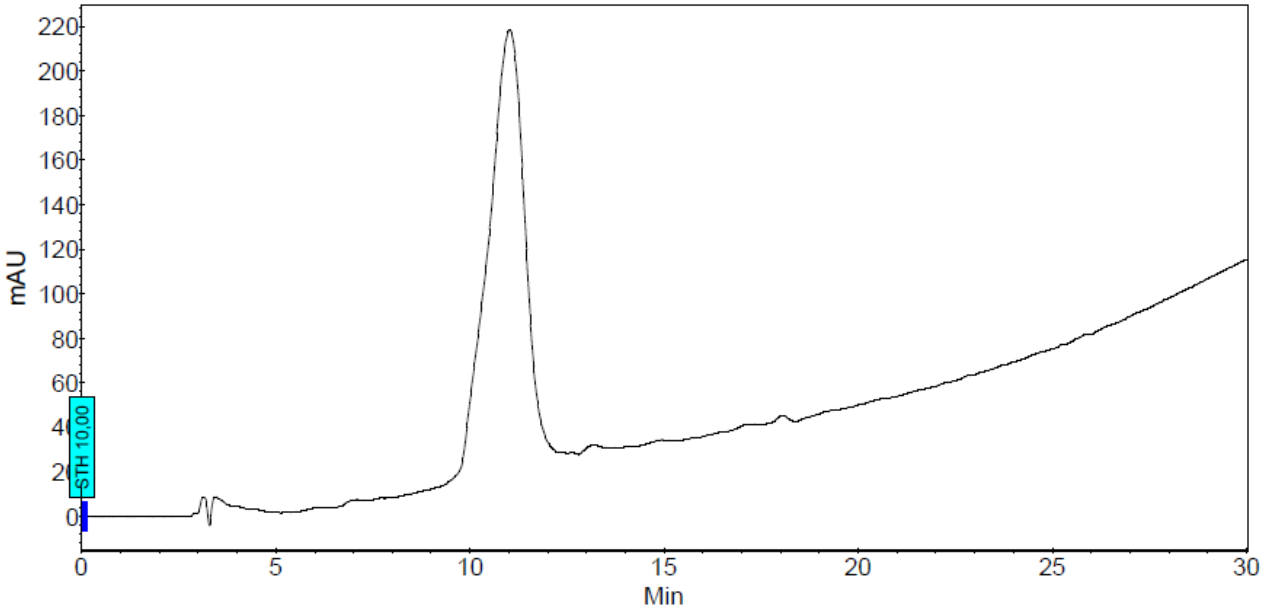


Figure S20. HPLC analysis of **9**

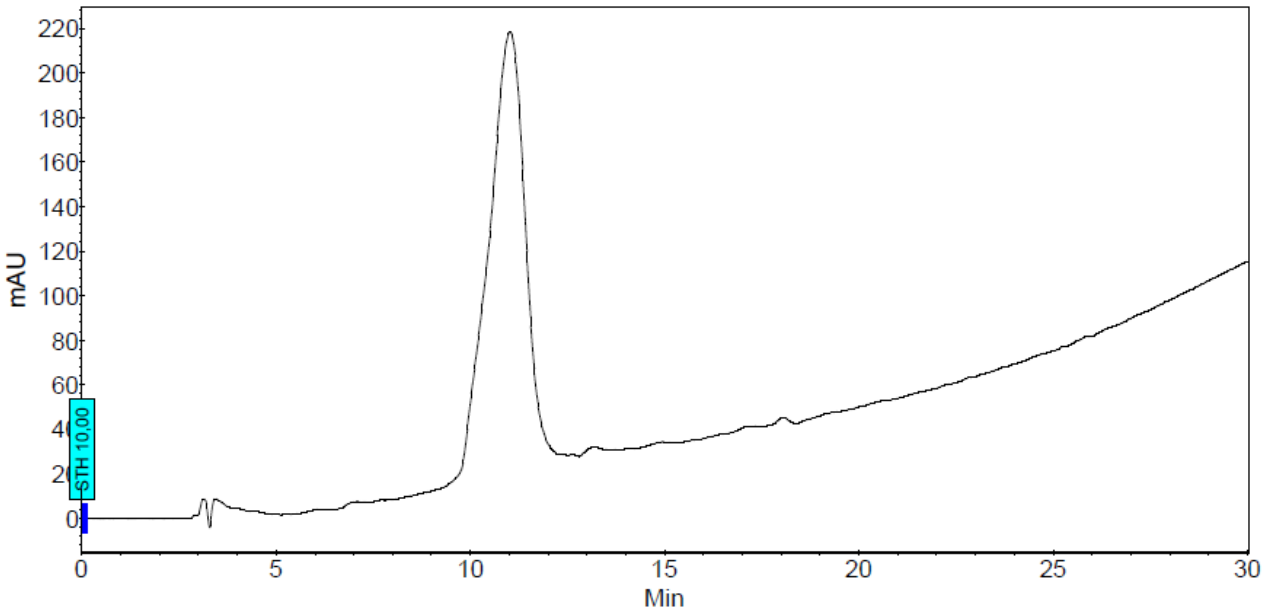


Figure S21. HPLC analysis of **10**

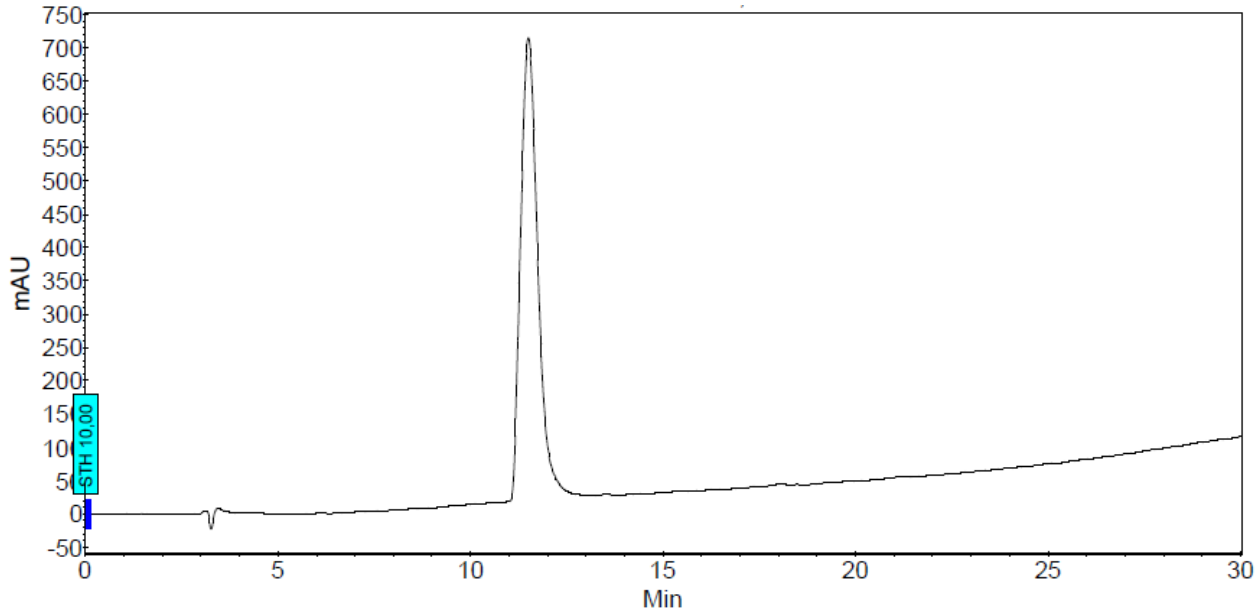


Figure S22. HPLC analysis of **11**

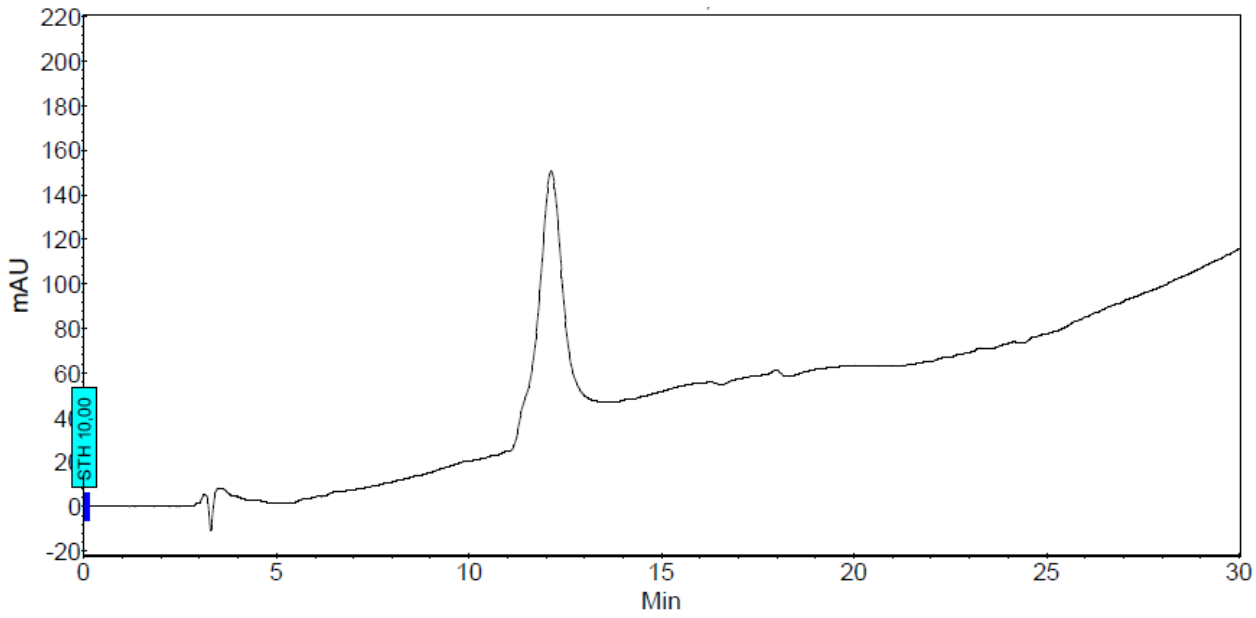


Figure S23. HPLC analysis of **12**

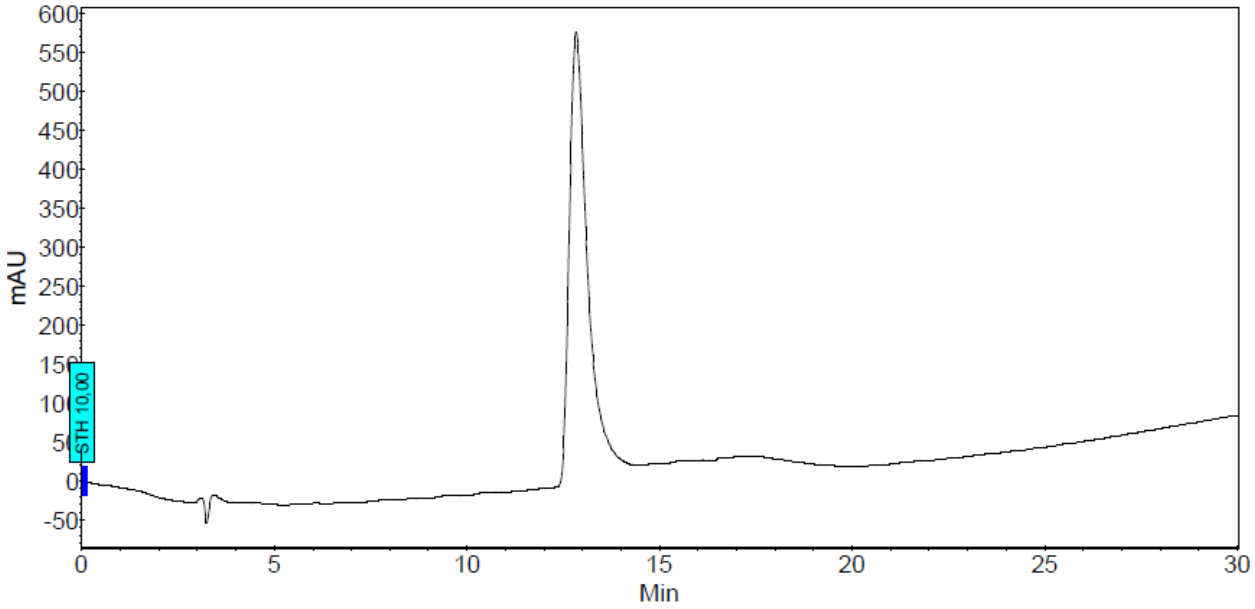


Figure S24. HPLC analysis of **13**

3.0 Computational details

3.1 Minimum energy structures of 11, 11a, 11b, $[11{\cdot}Na]^+$, beauvericin (8), $[13{\cdot}Na]^+$, $[13{\cdot}2Na]^{2+}$, $TFPB^-$ and NaTFPB

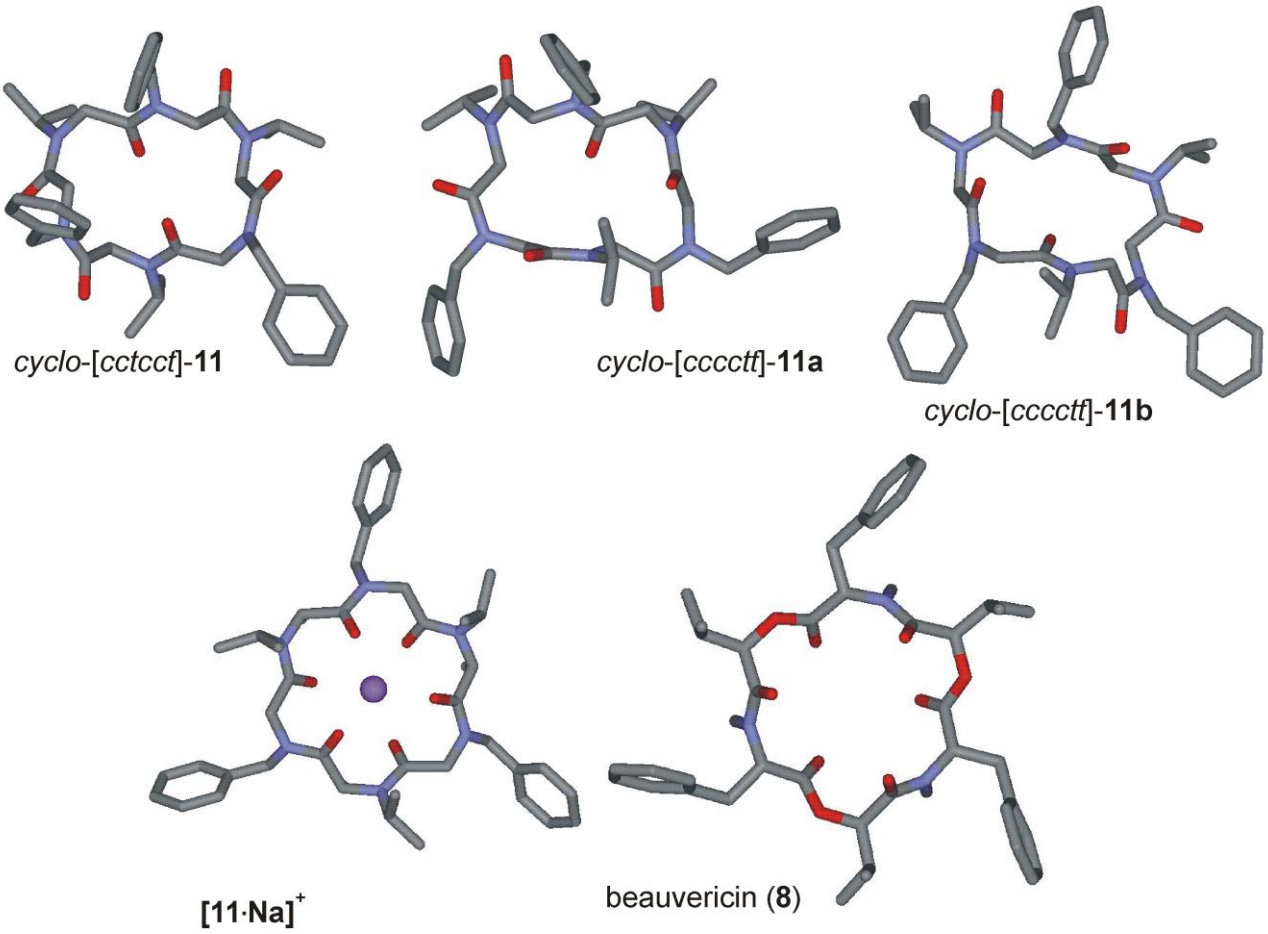


Figure S25. Minimum energy structures for *cyclo*-[*cis-N*Val-*cis-N*Phe-*trans-N*Val-*cis-N*Phe-*cis-N*Val-*trans-N*Phe], *cyclo*-[*cis-N*Val-*cis-N*Phe-*trans-N*Val-*trans-N*Phe-*cis-N*Val-*cis-N*Phe]-**11a**, *cyclo*-[*cis-N*Phe-*cis-N*Val-*trans-N*Phe-*trans-N*Val-*cis-N*Phe-*cis-N*Val]-**11b**, all-*trans*-[**11**·$Na]^+$ and beauvericin (**8**). Hydrogen atoms have been omitted for clarity. Atom type: C grey, N light blue, O red, Na^+ blue.

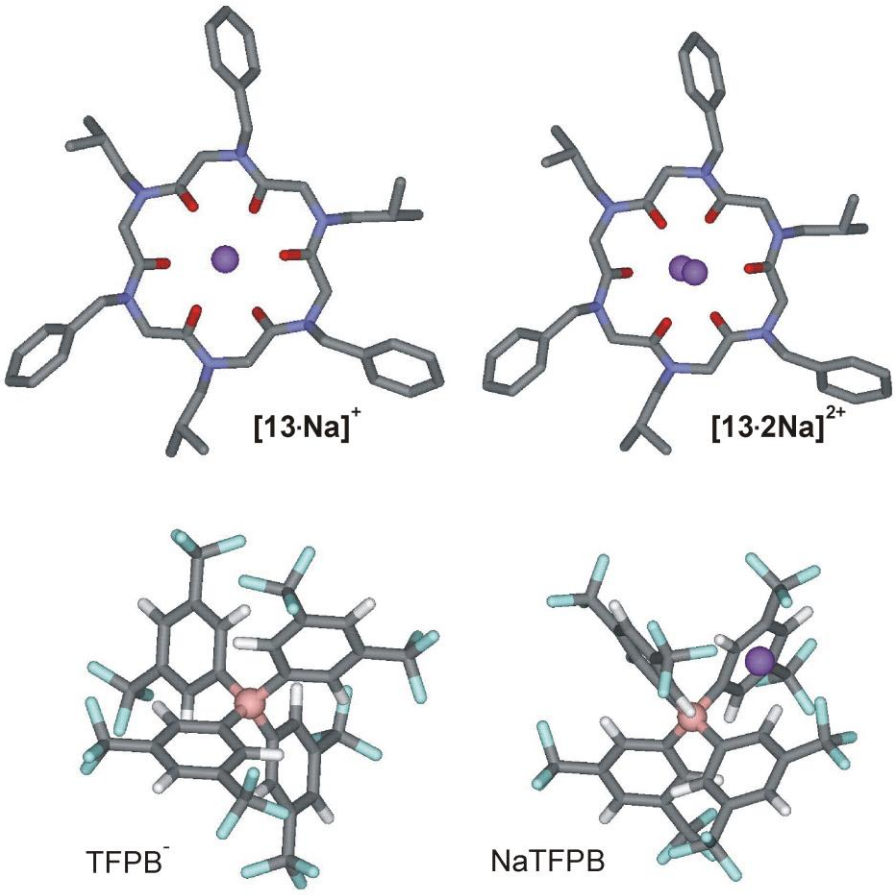


Figure S26. Minimum energy structures for [**13**·Na]$^{+}$ and [**13**·2Na]$^{2+}$ and TFPB^{-} and NaTFPB. Hydrogen atoms have been omitted for clarity. Atom type: C grey, N light blue, O red, B pink, Na^{+} blue.

3.2 Cartesian coordinates and gas phase internal energies of calculated structures 11, 11a, 11b, [11·Na]$^+$, beauvericin (8), 13, [13·Na]$^+$, [13·2Na]$^{2+}$, TFPB$^-$ and NaTFPB.

108

11 E(gas)=-2413.70864427 A.U. G(gas)=-2412.919962 E($CHCl_3$)=-2413.72989577

O	0.809614	-0.825881	-0.106285
N	3.337792	0.005429	0.567729
C	3.139611	-0.598145	-0.741058
H	3.774713	-1.496929	-0.788902
H	3.503142	0.075906	-1.531177
O	-0.322119	-3.785165	-1.952529
N	1.309610	-1.382453	-2.256535
C	1.653226	-0.966914	-1.003846
O	-3.315535	-0.999875	-3.336387
N	-2.062967	-2.436349	-1.319034
C	3.649170	-0.912781	1.677877
H	2.844945	-1.664011	1.752270
H	3.621894	-0.298004	2.588946
O	-0.888367	1.683818	-1.405906
N	-3.485156	0.939661	-2.117874
C	4.995201	-1.591345	1.520555
O	0.176249	4.716781	0.808575
N	-1.461570	2.346067	0.697816
C	5.095256	-2.990493	1.497246
H	4.187521	-3.595189	1.579813
O	3.015929	1.767411	2.000235
N	1.936186	3.449666	0.052234
C	6.341803	-3.617673	1.374555
H	6.402050	-4.708267	1.358934
C	7.504111	-2.848601	1.268337
H	8.477328	-3.334830	1.171516
C	7.414853	-1.450120	1.287095
H	8.320670	-0.844134	1.210214
C	6.170760	-0.827535	1.412573
H	6.103054	0.263263	1.432405
C	-0.131852	-1.448663	-2.525545
H	-0.279489	-1.569334	-3.607990
H	-0.574698	-0.487183	-2.238834
C	-0.825910	-2.660416	-1.879432
C	2.272811	-1.616423	-3.362064
H	3.269368	-1.621517	-2.899150
C	2.069898	-2.993528	-4.008315
H	2.056605	-3.787389	-3.251012
H	2.883468	-3.183526	-4.725068
H	1.118724	-3.048909	-4.557852
C	2.229474	-0.478962	-4.396060
H	1.249889	-0.430784	-4.895652
H	2.990789	-0.644461	-5.173366
H	2.418095	0.499144	-3.928770

C	-2.581820	-1.107687	-1.029397
H	-1.787749	-0.510909	-0.559443
H	-3.379521	-1.220358	-0.276077
C	-3.158648	-0.390478	-2.275380
C	-2.913627	-3.587676	-0.996643
H	-2.406896	-4.465172	-1.425600
H	-3.879854	-3.464041	-1.513610
C	-3.137078	-3.797463	0.490268
C	-4.422526	-4.065292	0.985123
H	-5.271248	-4.082044	0.294885
C	-4.628378	-4.317650	2.346929
H	-5.635421	-4.526653	2.715287
C	-3.546440	-4.298847	3.232514
H	-3.703134	-4.498137	4.295087
C	-2.260493	-4.022500	2.749132
H	-1.410268	-4.008219	3.435330
C	-2.056747	-3.772703	1.389005
H	-1.053461	-3.558602	1.013085
C	-3.266160	1.659652	-0.872616
H	-3.717232	1.120479	-0.023473
H	-3.803136	2.617095	-0.942753
C	-1.765245	1.927296	-0.566778
C	-4.011152	1.687085	-3.291017
H	-3.944660	0.958738	-4.111317
C	-5.486697	2.060634	-3.090579
H	-6.095626	1.166077	-2.895692
H	-5.876897	2.551203	-3.995259
H	-5.625168	2.764209	-2.252852
C	-3.138095	2.900707	-3.632264
H	-3.196944	3.686230	-2.861323
H	-3.483638	3.346458	-4.577236
H	-2.085048	2.609692	-3.741099
C	-0.044473	2.341655	1.078645
H	0.392405	1.403473	0.720022
H	0.008013	2.331265	2.177592
C	0.693122	3.608774	0.615172
C	-2.414535	2.942519	1.639852
H	-3.358561	3.137028	1.109500
H	-2.013607	3.930197	1.920302
C	-2.692395	2.114426	2.886726
C	-3.114155	2.766429	4.057074
H	-3.183616	3.858047	4.070963
C	-3.438626	2.034806	5.203099
H	-3.762081	2.556806	6.106565
C	-3.338873	0.638458	5.196166
H	-3.588663	0.065888	6.092070
C	-2.906979	-0.018080	4.039303
H	-2.819861	-1.106608	4.021799
C	-2.585027	0.716753	2.892584
H	-2.227146	0.196544	2.000912
C	2.452971	2.144997	-0.333901

H	3.290266	2.304393	-1.031427
H	1.677677	1.599069	-0.893887
C	2.956760	1.298108	0.863334
C	2.743794	4.661683	-0.233731
H	2.184770	5.468120	0.261839
C	2.784566	4.964789	-1.738951
H	3.321132	4.183478	-2.302740
H	3.309973	5.915349	-1.918248
H	1.767598	5.050261	-2.147162
C	4.141927	4.566739	0.387917
H	4.080218	4.321554	1.456609
H	4.661599	5.530125	0.272721
H	4.764009	3.801045	-0.104686

108

11a E(gas)=-2413.69025655 A.U. G(gas)=-2412.899340 E($CHCl_3$)=-2413.71138569

N	2.745041	0.926087	-1.699188
C	2.216743	2.141293	-1.092326
C	0.713125	1.951575	-0.738321
N	0.047857	2.970740	-0.128211
C	-1.377014	2.756034	0.193895
C	-2.278216	3.089706	-1.012103
N	-3.104108	2.117983	-1.519327
C	-2.932192	0.702581	-1.199244
C	-3.867112	0.159599	-0.092039
N	-3.580146	-1.111736	0.369474
C	-2.285831	-1.770507	0.211870
C	-1.379977	-1.568742	1.468033
N	-0.045058	-1.851493	1.352562
C	0.558590	-2.176653	0.047780
C	1.826495	-3.037087	0.180018
N	2.938075	-2.663347	-0.559310
C	0.573764	4.337480	0.048388
C	-3.972227	2.506850	-2.667777
C	-4.549815	-1.767282	1.272844
C	2.974798	-1.554499	-1.508564
C	2.875188	-0.152532	-0.852872
C	2.920478	0.879376	-3.171519
O	0.155788	0.872436	-0.996891
O	-2.242200	4.244857	-1.463438
O	-4.857495	0.792674	0.276856
O	2.850621	-0.018393	0.371717
C	0.858132	-1.594563	2.524856
O	-1.889609	-1.178700	2.524511
C	-3.244969	2.270846	-4.000945
C	-5.342417	1.826447	-2.626156
H	-4.107809	3.590276	-2.543852
H	-3.868285	2.621624	-4.837734
H	-2.293467	2.820155	-4.027631
H	-3.041655	1.200019	-4.166980
H	-5.977413	2.258762	-3.414494
H	-5.275140	0.743466	-2.819703

H	-5.826297	1.966906	-1.652044
H	-3.143748	0.117808	-2.110945
H	-1.871886	0.530729	-0.978187
C	-5.020717	-3.103921	0.732287
H	-4.084442	-1.884600	2.261213
H	-5.387516	-1.062452	1.371077
C	-4.808729	-4.284771	1.460384
C	-5.258089	-5.518917	0.973726
C	-5.923786	-5.587091	-0.253720
C	-6.140274	-4.414863	-0.990298
C	-5.692964	-3.185353	-0.500247
H	-4.287569	-4.233671	2.420439
H	-5.083989	-6.427756	1.554411
H	-6.275350	-6.548156	-0.635727
H	-6.668025	-4.460307	-1.946040
H	-5.872412	-2.271606	-1.072927
H	-2.461410	-2.852675	0.075522
H	-1.792378	-1.417160	-0.699333
C	0.818869	-0.135802	3.000889
C	0.603678	-2.601684	3.653685
H	1.867578	-1.767919	2.130498
H	1.613034	0.011337	3.749806
H	1.022503	0.542400	2.160957
H	-0.146786	0.115485	3.454844
H	1.350504	-2.454523	4.449886
H	-0.395073	-2.459651	4.087098
H	0.698880	-3.628590	3.275414
H	-0.137009	-2.815697	-0.519741
H	0.718830	-1.253111	-0.525535
H	3.227624	-0.148004	-3.407016
C	1.620874	1.167958	-3.937597
C	4.067348	1.804556	-3.613108
H	1.785626	1.021666	-5.015763
H	0.809124	0.507030	-3.607360
H	1.288388	2.207855	-3.795849
H	4.254210	1.683591	-4.690800
H	3.824709	2.864845	-3.441338
H	4.994348	1.570786	-3.070479
H	2.783045	2.377705	-0.179348
H	2.346439	2.973158	-1.797677
C	0.528458	4.827720	1.485499
H	1.610021	4.357028	-0.315311
H	-0.019684	5.009074	-0.592477
C	1.112185	4.086889	2.526044
C	1.093733	4.570730	3.836895
C	0.493816	5.803421	4.123704
C	-0.093710	6.545057	3.094388
C	-0.078926	6.056613	1.782769
H	1.572268	3.118524	2.312341
H	1.547368	3.983240	4.638020
H	0.477941	6.179353	5.148972

H	-0.573514	7.501786	3.312082
H	-0.551842	6.629344	0.980463
H	-1.499248	1.744868	0.594146
H	-1.644313	3.468189	0.987175
O	1.819982	-4.052698	0.879125
C	4.099954	-3.571669	-0.551506
H	3.929910	-1.634962	-2.048932
H	2.173543	-1.652052	-2.260584
C	5.427327	-2.883684	-0.304606
H	3.887906	-4.312038	0.234128
H	4.143705	-4.120362	-1.510282
C	5.591338	-1.969387	0.750090
C	6.838679	-1.388683	0.995136
C	7.941879	-1.715128	0.196228
C	7.787577	-2.620891	-0.857765
C	6.536174	-3.195948	-1.107441
H	4.729676	-1.696403	1.362590
H	6.950897	-0.679122	1.818103
H	8.916155	-1.262453	0.393399
H	8.640534	-2.879037	-1.489655
H	6.419753	-3.904183	-1.933405

108

11b E(gas)=-2413.68171261 A.U. G(gas)=-2412.891079 E($CHCl_3$)=-2413.70253829

N	1.416667	3.080563	0.012969
C	0.538258	2.877150	1.159819
C	-0.386332	1.658364	0.902180
N	-1.390430	1.359200	1.774754
C	-2.126916	0.116382	1.471231
C	-3.233044	0.309571	0.408776
N	-3.328555	-0.609689	-0.613483
C	-2.138380	-1.225317	-1.199732
C	-2.152373	-2.769468	-1.215278
N	-0.952174	-3.380140	-1.482027
C	0.291538	-2.629875	-1.607093
C	1.029518	-2.471219	-0.246857
N	2.206541	-1.757714	-0.242072
C	2.463499	-0.755121	-1.293046
C	3.942529	-0.323801	-1.361917
N	4.215088	1.024021	-1.443870
C	-1.879008	2.199070	2.916773
C	-4.537921	-0.522978	-1.467971
C	-0.855466	-4.873990	-1.534875
C	3.171930	2.044017	-1.447070
C	2.517337	2.250474	-0.055215
C	0.817201	3.757136	-1.148200
O	-0.159184	0.939376	-0.089259
O	-4.066979	1.207030	0.563187
O	-3.205173	-3.396262	-1.059804
O	2.950437	1.660396	0.934328
C	2.849862	-1.606154	1.086042
O	0.576608	-2.996796	0.771223

H	-2.056695	-0.884277	-2.251284
H	-1.258772	-0.812320	-0.695931
H	0.223906	-5.063538	-1.649064
C	-1.301074	-5.560159	-0.236598
H	0.953746	-3.163810	-2.309110
H	0.100830	-1.648493	-2.060978
H	2.263595	-1.211553	-2.275590
H	1.770637	0.088276	-1.157634
H	1.166945	2.663878	2.033533
H	-0.030711	3.796095	1.348900
C	-0.819443	2.450691	4.001420
C	-2.595521	3.477572	2.458535
H	-1.411166	-0.676989	1.227779
H	-2.656481	-0.189770	2.384967
O	4.830092	-1.180849	-1.395836
C	5.639513	1.491136	-1.442901
H	3.625094	2.984669	-1.795053
H	2.388024	1.796382	-2.178691
H	5.557229	2.589862	-1.432613
C	6.394346	1.079296	-0.171368
H	1.566493	3.801606	-1.949916
H	-0.033339	3.163669	-1.527741
C	0.361166	5.171784	-0.829074
C	1.251944	6.102918	-0.268936
C	0.839082	7.411637	-0.006608
C	-0.471424	7.808249	-0.303611
C	-1.365145	6.887958	-0.858722
C	-0.950202	5.575796	-1.117603
H	2.272126	5.793075	-0.027072
H	1.541161	8.126062	0.429067
H	-0.794302	8.831060	-0.098160
H	-2.390400	7.187587	-1.086363
H	-1.654356	4.856227	-1.544384
C	6.373804	1.089535	-2.730682
H	7.367788	1.593216	-0.146930
H	5.826637	1.364906	0.725355
H	6.570760	-0.003068	-0.150443
H	6.491874	0.000213	-2.785864
H	5.828040	1.433127	-3.622849
H	7.372653	1.552099	-2.743995
H	2.088056	-1.286564	1.813704
C	3.520337	-2.872267	1.590113
H	3.579608	-0.790754	1.001423
C	4.451807	-3.566633	0.801152
C	5.091889	-4.705184	1.301289
C	4.815402	-5.162671	2.595313
C	3.889309	-4.474771	3.386676
C	3.244461	-3.340359	2.882923
H	4.676200	-3.196274	-0.201693
H	5.816066	-5.235698	0.677871
H	5.316654	-6.052554	2.983407

H	3.658615	-4.828786	4.394338
H	2.502297	-2.819491	3.493757
C	-1.572176	-5.426136	-2.776393
H	-1.033106	-6.627234	-0.287110
H	-0.789960	-5.109578	0.624161
H	-2.385966	-5.475582	-0.098836
H	-2.653389	-5.247395	-2.708352
H	-1.192780	-4.958259	-3.698135
H	-1.402794	-6.511233	-2.851313
H	-4.389327	-1.258235	-2.271046
C	-5.843288	-0.823622	-0.753363
H	-4.591809	0.484081	-1.917548
C	-6.868073	0.132724	-0.722266
C	-8.096205	-0.156570	-0.118465
C	-8.308750	-1.407725	0.470401
C	-7.287113	-2.365042	0.449033
C	-6.062132	-2.078915	-0.161970
H	-6.692517	1.119229	-1.158919
H	-8.884709	0.599619	-0.100184
H	-9.266057	-1.635455	0.945363
H	-7.447889	-3.345655	0.903834
H	-5.262831	-2.822642	-0.196378
H	-2.649586	1.560892	3.372222
H	-1.322635	2.808642	4.912283
H	-0.276754	1.528146	4.253986
H	-0.089740	3.220157	3.714646
H	-3.069391	3.959044	3.327948
H	-1.908457	4.212442	2.013593
H	-3.373938	3.223206	1.727275

109

[**11**·Na]$^+$ E(gas)=-2575.92111650 A.U.

C	1.654424	2.527689	-0.173114
N	2.901705	2.271218	0.328189
C	3.556261	1.093003	-0.248716
C	3.002324	-0.231882	0.334600
C	0.854717	3.745046	0.334434
C	-3.028592	0.176557	-0.154042
N	-3.435505	1.378288	0.356887
C	-2.748485	2.541626	-0.211646
C	-1.319598	2.715527	0.361645
N	-0.530819	3.711987	-0.135809
O	-2.155687	0.125803	-1.039776
O	-0.899418	1.949167	1.244023
O	1.161766	1.800014	-1.054847
O	2.141083	-0.214264	1.229493
C	-4.347563	1.613145	1.526024
C	-0.855823	4.519985	-1.326584
C	3.577300	2.932673	1.495356
C	1.349249	-2.718521	-0.178192
N	0.514500	-3.673036	0.334628
C	-0.840855	-3.655993	-0.223280

C	-1.698046	-2.500672	0.353735
C	2.809469	-2.629598	0.313043
N	-2.955599	-2.307916	-0.140772
C	-3.675820	-1.131273	0.346576
N	3.461649	-1.411705	-0.170198
O	0.951310	-1.930163	-1.054902
O	-1.244173	-1.766188	1.246285
C	-3.495516	-2.976663	-1.340729
C	4.326620	-1.540152	-1.356211
C	0.776450	-4.589121	1.494185
H	4.638086	1.172278	-0.071322
H	3.380055	1.094301	-1.333382
H	1.306107	4.674187	-0.037525
H	0.865700	3.774316	1.430120
H	-2.675203	2.401589	-1.299303
H	-3.355355	3.437334	-0.018379
H	-1.315776	-4.625890	-0.018674
H	-0.763885	-3.528303	-1.312005
H	3.385336	-3.485649	-0.063369
H	2.842737	-2.654413	1.409168
H	-3.700713	-1.144673	1.442571
H	-4.709540	-1.202391	-0.018264
Na	-0.004858	-0.004992	0.082991
C	5.479755	-2.508678	-1.159996
H	3.707482	-1.858080	-2.212187
H	4.718343	-0.545217	-1.604518
H	-0.127289	-5.215770	1.514167
C	1.955244	-5.546909	1.270055
C	0.837998	-3.859215	2.844755
C	-4.924055	-3.461310	-1.170181
H	-3.430227	-2.280698	-2.194077
H	-2.847595	-3.830841	-1.575150
H	-4.437893	2.709463	1.545745
C	-5.764451	1.066361	1.312475
C	-3.736350	1.197327	2.872565
H	-1.921252	4.383753	-1.551103
C	-0.557398	5.998154	-1.152198
H	-0.295429	4.119891	-2.188440
H	4.564976	2.448344	1.506221
C	3.835468	4.430851	1.281924
C	2.921400	2.616165	2.848072
C	-5.891270	-3.149719	-2.136243
C	-7.200329	-3.629691	-2.015793
C	-7.557005	-4.421898	-0.921231
C	-6.599108	-4.734318	0.051345
C	-5.291023	-4.259966	-0.074387
H	-5.616807	-2.529581	-2.993723
H	-7.941513	-3.380293	-2.777011
H	-8.577166	-4.797018	-0.825624
H	-6.871572	-5.355382	0.906528
H	-4.549905	-4.507036	0.689919

H	-6.433519	1.505024	2.066586
H	-6.152407	1.333560	0.319619
H	-5.821549	-0.023811	1.432739
H	-4.354094	1.600828	3.688695
H	-3.700928	0.106492	3.000439
H	-2.714219	1.581077	2.973072
C	0.165132	6.686469	-2.137258
C	0.408558	8.058819	-2.014095
C	-0.061117	8.755108	-0.896868
C	-0.777053	8.074441	0.095586
C	-1.025925	6.705784	-0.032636
H	0.535432	6.145459	-3.011926
H	0.968276	8.582561	-2.790882
H	0.130519	9.824701	-0.797474
H	-1.145945	8.613772	0.969871
H	-1.582280	6.180241	0.747798
H	4.545632	4.785212	2.042664
H	4.273600	4.625043	0.292568
H	2.927661	5.038710	1.388415
H	3.599149	2.927316	3.656419
H	1.974183	3.153126	2.995906
H	2.719942	1.542134	2.942742
C	5.753339	-3.478028	-2.135833
C	6.844602	-4.342727	-1.994064
C	7.668616	-4.252254	-0.868619
C	7.397677	-3.293101	0.114721
C	6.312208	-2.426014	-0.032006
H	5.112154	-3.552552	-3.018244
H	7.048615	-5.089297	-2.763593
H	8.517975	-4.927754	-0.755355
H	8.037284	-3.218038	0.995931
H	6.103154	-1.681669	0.740318
H	1.898355	-6.358398	2.009437
H	1.921012	-5.999469	0.268982
H	2.931411	-5.064142	1.406104
H	0.804127	-4.600089	3.657167
H	1.764930	-3.281400	2.969200
H	-0.005881	-3.166923	2.953778

114

Beauvericin **8** E(gas)=-2591.30604082

C	1.354184	-2.851697	0.006164
N	2.414741	-2.456525	-0.784295
C	3.280718	-1.407819	-0.240757
C	2.955804	-0.049503	-0.883984
C	0.401374	-3.922625	-0.577844
C	-3.156353	0.261013	0.007367
N	-3.327324	-0.862254	-0.776091
C	-2.856024	-2.130318	-0.214869
C	-1.511837	-2.533499	-0.843368
O	-0.957640	-3.579001	-0.167367
O	-2.703120	0.214826	1.152412

O	-0.995657	-1.995380	-1.803799
O	1.169822	-2.416045	1.143974
O	2.229752	0.118305	-1.844650
C	-3.712122	-0.798829	-2.191475
C	2.546860	-2.841867	-2.194794
C	1.795462	2.590504	-0.021742
N	0.911437	3.315113	-0.795486
C	-0.421618	3.537945	-0.231016
C	-1.445349	2.583443	-0.867569
C	3.190586	2.304932	-0.628614
O	-2.627308	2.623111	-0.189780
C	-3.602426	1.614697	-0.596493
O	3.584787	0.960567	-0.218464
O	1.527596	2.207889	1.118471
O	-1.238149	1.872936	-1.832291
C	1.158420	3.628408	-2.208241
C	4.793782	-1.736222	-0.317629
H	2.986697	-1.316184	0.816946
C	0.719590	-5.345489	-0.073861
H	0.425219	-3.907672	-1.675272
H	-2.639314	-1.910651	0.842669
C	-3.895178	-3.277806	-0.291008
C	-0.890368	5.014039	-0.286975
H	-0.338569	3.227577	0.822837
C	4.266637	3.299959	-0.146681
H	3.146838	2.313039	-1.725492
H	-3.592519	1.573675	-1.693309
C	-4.997889	2.057420	-0.109853
H	0.300559	4.187049	-2.599240
H	2.048777	4.264480	-2.326921
H	1.257808	2.711519	-2.806899
H	-3.743234	-1.817942	-2.592890
H	-4.715818	-0.363912	-2.313956
H	-2.973483	-0.234414	-2.778597
H	3.449634	-2.374057	-2.603399
H	2.661263	-3.931317	-2.302741
H	1.691551	-2.484065	-2.785849
C	0.050156	5.976318	0.409699
H	-1.031536	5.330981	-1.333273
H	-1.885610	5.048995	0.183606
C	5.565797	3.118293	-0.949909
H	3.855378	4.299434	-0.382545
C	4.530158	3.236953	1.365735
C	5.173829	-3.027247	0.378615
H	5.122574	-1.775968	-1.368993
H	5.325526	-0.887475	0.140652
C	-0.104491	-6.387160	-0.849904
H	1.786762	-5.501461	-0.319628
C	0.548793	-5.515093	1.443593
C	-5.214998	-2.951866	0.378326
H	-4.077290	-3.559066	-1.341136

H	-3.433225	-4.155732	0.187845
C	-5.481947	3.279450	-0.908994
H	-5.664454	1.207177	-0.347434
C	-5.071195	2.313950	1.403318
H	5.230340	4.035445	1.655245
H	3.605887	3.352264	1.946547
H	4.980270	2.272161	1.641935
H	6.308425	3.875519	-0.656008
H	6.006563	2.127224	-0.762295
H	5.393492	3.216100	-2.033586
H	0.881185	-6.520147	1.745436
H	1.126374	-4.769865	2.005493
H	-0.507262	-5.404622	1.730497
H	0.174430	-7.405785	-0.540354
H	-1.179903	-6.260220	-0.652745
H	0.055635	-6.307845	-1.936959
H	-6.110118	2.533813	1.693271
H	-4.719502	1.449963	1.981763
H	-4.449503	3.177522	1.681747
H	-6.505827	3.552055	-0.611459
H	-4.835797	4.150463	-0.720801
H	-5.484991	3.083822	-1.993113
C	5.745713	-4.087463	-0.341830
C	6.116851	-5.276489	0.297128
C	5.917799	-5.422571	1.673207
C	5.347179	-4.372694	2.403249
C	4.979673	-3.186852	1.761798
H	5.909953	-3.977357	-1.417720
H	6.564161	-6.087901	-0.281887
H	6.206584	-6.348185	2.175978
H	5.188873	-4.476968	3.479016
H	4.532811	-2.376657	2.344041
C	0.681650	7.005507	-0.305945
C	1.538149	7.908849	0.334534
C	1.777352	7.792837	1.707115
C	1.154276	6.769697	2.432210
C	0.298837	5.871101	1.789229
H	0.493929	7.105621	-1.378944
H	2.016501	8.705246	-0.240495
H	2.444314	8.495875	2.210941
H	1.334081	6.671630	3.505181
H	-0.178687	5.075649	2.367404
C	-6.410546	-2.962844	-0.357257
C	-7.637685	-2.684575	0.256252
C	-7.685460	-2.386806	1.621404
C	-6.499598	-2.370303	2.365922
C	-5.276894	-2.650673	1.750016
H	-6.380934	-3.201012	-1.424525
H	-8.556847	-2.702606	-0.334100
H	-8.640695	-2.169522	2.104392
H	-6.526747	-2.139094	3.433178

H -4.359087 -2.630654 2.343389
117
13 E(gas)=-2531.68175455 A.U. G(gas)= -2530.812992 E($CHCl_3$)= -2531.69768748

C	-1.577827	2.805561	0.106813
N	-2.371363	2.426736	-0.942480
C	-3.508534	1.544720	-0.634945
C	-3.195817	0.058220	-0.899789
C	-0.413302	3.778418	-0.153829
C	3.233952	-0.032364	0.088962
N	3.281512	0.840277	-0.964701
C	3.095579	2.268121	-0.660082
C	1.652360	2.746472	-0.917384
N	0.894262	3.172206	0.143278
O	3.028259	0.344869	1.255954
O	1.234351	2.784676	-2.085958
O	-1.785913	2.419316	1.270507
O	-3.011819	-0.315701	-2.069317
C	3.405193	0.443089	-2.386277
C	1.277571	3.081118	1.559477
C	-2.107067	2.751976	-2.363238
C	-1.631942	-2.771349	0.110627
N	-0.911280	-3.278235	-0.937233
C	0.421685	-3.820764	-0.630173
C	1.552572	-2.809561	-0.906745
C	-3.057263	-2.249924	-0.148852
N	2.308018	-2.354105	0.143411
C	3.485032	-1.528897	-0.171868
N	-3.188414	-0.816577	0.156117
O	-1.189113	-2.748830	1.272363
O	1.784011	-2.477250	-2.080546
C	2.048652	-2.625824	1.564581
C	-3.307661	-0.445463	1.573510
C	-1.330703	-3.224394	-2.356780
H	-4.327490	1.795628	-1.322717
H	-3.833327	1.747578	0.390531
H	-0.557757	4.623631	0.536936
H	-0.381602	4.154073	-1.180859
H	3.440602	2.448456	0.362992
H	3.720967	2.847120	-1.353253
H	0.611135	-4.661156	-1.311849
H	0.411221	-4.195399	0.398307
H	-3.717577	-2.801998	0.537825
H	-3.396396	-2.404561	-1.177354
H	3.778388	-1.748231	-1.202647
H	4.297733	-1.827463	0.508351
C	-4.712219	-0.567316	2.147253
H	-2.620757	-1.105308	2.125749
H	-2.912886	0.575186	1.701722
H	-0.402872	-3.202670	-2.948124
C	-2.232559	-4.388653	-2.821161
H	-1.835089	-2.262684	-2.534096

C	2.863122	-3.769096	2.152805
H	2.272844	-1.692933	2.104770
H	0.968637	-2.798571	1.696118
H	2.905615	1.232848	-2.967345
C	4.850932	0.242419	-2.889993
H	2.820734	-0.475978	-2.542421
H	1.970178	2.233120	1.681478
C	1.866784	4.358111	2.141540
H	0.364910	2.806587	2.110951
H	-2.542331	1.928977	-2.950193
C	-2.669330	4.107210	-2.844201
H	-1.020356	2.713537	-2.531631
C	2.956349	-3.880462	3.551437
C	3.659263	-4.933771	4.140609
C	4.292871	-5.892677	3.339954
C	4.214177	-5.786483	1.948704
C	3.502909	-4.732719	1.360388
H	2.470483	-3.131049	4.182863
H	3.719113	-5.003817	5.229283
H	4.847242	-6.713896	3.799464
H	4.709122	-6.525634	1.314187
H	3.453145	-4.656993	0.271339
C	4.802296	-0.221434	-4.354877
C	5.729667	1.491651	-2.731499
H	5.308891	-0.568187	-2.292638
C	1.933399	4.493712	3.539445
C	2.499577	5.629735	4.122346
C	3.002403	6.658919	3.316080
C	2.933721	6.538038	1.925564
C	2.371189	5.394625	1.343481
H	1.536285	3.697203	4.175264
H	2.543464	5.716068	5.210614
H	3.440854	7.549917	3.770796
H	3.318338	7.336677	1.286684
H	2.318328	5.313306	0.254999
C	-2.248856	4.322421	-4.307161
C	-4.191329	4.227507	-2.680072
H	-2.201878	4.903831	-2.235501
C	-4.871717	-0.573283	3.544288
C	-6.142499	-0.644413	4.119510
C	-7.280510	-0.721365	3.306363
C	-7.132739	-0.725418	1.916744
C	-5.857353	-0.647455	1.342370
H	-3.987203	-0.520165	4.185562
H	-6.245980	-0.645768	5.207167
H	-8.274441	-0.781642	3.755078
H	-8.012912	-0.790363	1.272543
H	-5.753676	-0.656755	0.254569
C	-2.637405	-4.143976	-4.283785
C	-1.581304	-5.768447	-2.648151
H	-3.151909	-4.371505	-2.206316

H	-2.583933	5.305456	-4.671749
H	-1.155656	4.269423	-4.424639
H	-2.695208	3.554091	-4.960075
H	-4.545418	5.205599	-3.041467
H	-4.713859	3.449952	-3.262405
H	-4.499264	4.136607	-1.627283
H	5.814272	-0.429358	-4.734796
H	4.200781	-1.136235	-4.468547
H	4.357425	0.556116	-4.997804
H	6.747310	1.301107	-3.106579
H	5.318508	2.339367	-3.305104
H	5.821389	1.798720	-1.678454
H	-3.324317	-4.927729	-4.637956
H	-3.137586	-3.171163	-4.406748
H	-1.752740	-4.152817	-4.941942
H	-2.259569	-6.564578	-2.992803
H	-0.653528	-5.844520	-3.240011
H	-1.337675	-5.979027	-1.595564

118

[**13**·Na]$^+$ E(gas)=-2693.90697362 A.U. G(gas)= -2693.037636 E($CHCl_3$)= -2693.95502394

C	-2.971703	-0.511596	-0.198148
N	-3.690318	0.570995	0.221555
C	-3.260088	1.865636	-0.305713
C	-1.926486	2.313342	0.351064
C	-3.254381	-1.885157	0.454624
C	1.929083	-2.320304	-0.199540
N	1.348037	-3.479190	0.230241
C	0.012067	-3.756916	-0.295492
C	-1.044367	-2.824963	0.357032
N	-2.343784	-2.906931	-0.059812
O	1.392144	-1.612433	-1.068421
O	-0.701158	-2.017834	1.233972
O	-2.089889	-0.403276	-1.067035
O	-1.403157	1.612388	1.230293
C	1.862822	-4.300922	1.342184
C	-2.800128	-3.683644	-1.227897
C	-4.674444	0.537063	1.320635
C	1.045761	2.824215	-0.196140
N	2.339935	2.902199	0.231387
C	3.249520	1.886340	-0.297666
C	2.971429	0.504164	0.351719
C	-0.005625	3.755167	0.453916
N	3.690557	-0.578709	-0.071236
C	3.264923	-1.879531	0.443724
N	-1.344289	3.478323	-0.064797
O	0.703048	2.006622	-1.067309
O	2.104121	0.395286	1.231600
C	4.588260	-0.581386	-1.240759
C	-1.784755	4.264111	-1.232263
C	2.796941	3.764889	1.337335
H	-4.055559	2.601277	-0.124554

H	-3.111038	1.774159	-1.391251
H	-4.285443	-2.217420	0.267843
H	-3.111567	-1.800455	1.541430
H	0.015639	-3.587193	-1.381961
H	-0.225466	-4.813203	-0.109222
H	4.282920	2.208843	-0.110187
H	3.100847	1.808894	-1.384356
H	0.223290	4.814558	0.268430
H	-0.007610	3.589267	1.540636
H	3.130339	-1.800658	1.531912
H	4.064659	-2.607929	0.247988
Na	0.000928	-0.002555	0.086860
C	-1.826675	5.758593	-0.964676
H	-1.114663	4.047941	-2.081913
H	-2.786102	3.916414	-1.519585
H	3.610779	3.228688	1.851356
C	3.282001	5.168822	0.917963
H	1.986481	3.856552	2.075280
C	5.903835	-1.295890	-0.984326
H	4.064334	-1.043694	-2.094883
H	4.789500	0.462187	-1.517330
H	0.990308	-4.749010	1.844258
C	2.854928	-5.411275	0.935672
H	2.328160	-3.639841	2.088202
H	-2.001450	-4.384045	-1.506450
C	-4.081019	-4.457376	-0.968538
H	-2.937575	-2.997998	-2.081786
H	-4.631481	1.516177	1.824571
C	-6.127202	0.238077	0.892820
H	-4.346628	-0.198558	2.070050
C	6.390107	-2.226151	-1.915149
C	7.625614	-2.853785	-1.715866
C	8.382948	-2.562471	-0.577263
C	7.901050	-1.640943	0.360913
C	6.671320	-1.009506	0.156679
H	5.799811	-2.457761	-2.806386
H	7.994242	-3.572623	-2.450526
H	9.346038	-3.051761	-0.419207
H	8.488833	-1.410474	1.251971
H	6.298450	-0.294190	0.894635
C	3.374952	-6.107178	2.203313
C	2.241155	-6.420075	-0.045092
H	3.712655	-4.927389	0.433881
C	-5.152810	-4.361988	-1.868199
C	-6.321302	-5.106249	-1.665943
C	-6.430863	-5.948810	-0.555920
C	-5.367619	-6.045616	0.350748
C	-4.199917	-5.306472	0.144407
H	-5.071292	-3.703301	-2.737534
H	-7.146737	-5.025037	-2.376128
H	-7.341572	-6.529265	-0.395701

H	-5.448387	-6.703315	1.218787
H	-3.374739	-5.383279	0.857715
C	-7.011388	0.150737	2.146298
C	-6.669515	1.271810	-0.104106
H	-6.135170	-0.749902	0.397342
C	-1.222002	6.649913	-1.863453
C	-1.294448	8.032252	-1.653080
C	-1.966610	8.535717	-0.535353
C	-2.567196	7.652543	0.370759
C	-2.499915	6.273549	0.155571
H	-0.695579	6.259805	-2.739252
H	-0.823117	8.715174	-2.362879
H	-2.022911	9.613184	-0.368451
H	-3.093940	8.041224	1.244855
H	-2.968530	5.589099	0.867898
C	3.632977	5.975695	2.177867
C	4.463377	5.116492	-0.060821
H	2.441281	5.674632	0.409048
H	4.122027	-6.872999	1.949314
H	3.847949	-5.394579	2.896826
H	2.555450	-6.609711	2.742982
H	2.977773	-7.188884	-0.321540
H	1.380062	-6.939904	0.408225
H	1.905976	-5.938894	-0.976422
H	3.946017	6.995908	1.912593
H	2.776367	6.056194	2.865010
H	4.464468	5.506061	2.728766
H	4.779079	6.132140	-0.341332
H	5.335019	4.616939	0.395251
H	4.205620	4.585666	-0.989701
H	-8.047104	-0.101515	1.876326
H	-6.650734	-0.617101	2.848264
H	-7.033357	1.114103	2.681733
H	-7.701061	1.025644	-0.396374
H	-6.686924	2.280770	0.341908
H	-6.068360	1.310123	-1.025059

119

[**13**·2Na]$^{2+}$ E(gas)=-2856.02950154 A.U. G(gas)= -2855.162833 E($CHCl_3$)= -2856.18365522

C	0.375787	-2.991925	-0.286326
N	-0.704034	-3.631291	0.231123
C	-2.010536	-3.199448	-0.257795
C	-2.402804	-1.817935	0.318946
C	1.764213	-3.352279	0.275712
C	2.388826	1.825006	-0.266321
N	3.482523	1.208804	0.249997
C	3.766434	-0.133683	-0.249048
C	2.763553	-1.169756	0.311854
N	2.791761	-2.427699	-0.192368
O	1.704940	1.290483	-1.164988
O	1.949997	-0.845888	1.201076
O	0.253852	-2.130504	-1.183020

O	-1.708195	-1.281242	1.205877
C	4.330956	1.762847	1.331260
C	3.692549	-2.904854	-1.270412
C	-0.642704	-4.662533	1.293764
C	-2.787175	1.161838	-0.260875
N	-2.800199	2.417226	0.254343
C	-1.776944	3.332981	-0.242547
C	-0.380707	2.983796	0.325265
C	-3.791401	0.140280	0.305569
N	0.695908	3.639082	-0.174028
C	2.009036	3.208263	0.294952
N	-3.511755	-1.210521	-0.170356
O	-1.982655	0.836116	-1.159837
O	-0.256985	2.117032	1.214427
C	0.659698	4.652438	-1.258027
C	-4.376713	-1.740556	-1.253510
C	-3.716416	2.883253	1.322143
H	-2.754687	-3.956480	0.024428
H	-1.984428	-3.144185	-1.355269
H	2.056707	-4.367119	-0.031013
H	1.736557	-3.336467	1.374153
H	3.714036	-0.128403	-1.346892
H	4.792400	-0.401270	0.037753
H	-2.058605	4.356082	0.040913
H	-1.749951	3.282138	-1.340180
H	-4.818210	0.398988	0.008754
H	-3.755179	0.151726	1.403857
H	2.009081	3.179328	1.393484
H	2.743727	3.966160	-0.013964
Na	-0.004471	-0.004079	1.937356
C	-5.853682	-1.702583	-0.908060
H	-4.189990	-1.153273	-2.168221
H	-4.068853	-2.772802	-1.462086
H	-3.184591	3.675523	1.871902
C	-5.084000	3.413832	0.840025
H	-3.868760	2.065018	2.041445
C	1.452886	5.903323	-0.929597
H	1.050088	4.192056	-2.181232
H	-0.389214	4.915675	-1.443984
H	4.746352	0.902785	1.879776
C	5.476374	2.688744	0.869911
H	3.688226	2.295790	2.046939
H	4.422907	-2.113566	-1.481659
C	4.414079	-4.192065	-0.916333
H	3.095064	-3.049283	-2.186162
H	-1.592365	-4.603664	1.848233
C	-0.415998	-6.107910	0.801011
H	0.144499	-4.385768	2.010201
C	2.459990	6.342880	-1.801939
C	3.168562	7.520156	-1.532926
C	2.879551	8.262681	-0.384499

C	1.878042	7.828450	0.493651
C	1.166398	6.657668	0.221117
H	2.683656	5.770464	-2.706860
H	3.943587	7.857593	-2.223683
H	3.429098	9.182059	-0.174304
H	1.645601	8.411042	1.387247
H	0.382525	6.330666	0.910369
C	4.329397	-5.300815	-1.771612
C	5.029394	-6.477795	-1.479373
C	5.813975	-6.556451	-0.325246
C	5.900667	-5.454978	0.535924
C	5.207370	-4.278753	0.240627
H	3.723467	-5.241925	-2.680444
H	4.962935	-7.331450	-2.156508
H	6.362387	-7.472321	-0.097542
H	6.518978	-5.511636	1.433950
H	5.286374	-3.422527	0.916800
C	-0.254808	-7.028072	2.021957
C	-1.536645	-6.599148	-0.125849
H	0.531963	-6.125457	0.232506
C	-6.752756	-1.033119	-1.751719
C	-8.123955	-1.029591	-1.468501
C	-8.604812	-1.690609	-0.334766
C	-7.712954	-2.357681	0.515312
C	-6.345647	-2.365903	0.229037
H	-6.382308	-0.522817	-2.645547
H	-8.815639	-0.513512	-2.137006
H	-9.673780	-1.691882	-0.114004
H	-8.087566	-2.880580	1.397453
H	-5.657838	-2.894198	0.895633
C	-5.933497	3.773863	2.069811
C	-4.950986	4.606390	-0.117459
H	-5.593584	2.594974	0.299856
Na	-0.009363	0.001415	-1.861416
C	6.195601	3.241799	2.110930
C	6.458188	1.987951	-0.079751
H	5.025605	3.541043	0.329075
H	6.993094	3.937995	1.815446
H	5.509010	3.785862	2.777834
H	6.663741	2.431620	2.693085
H	7.256855	2.679368	-0.384217
H	6.943592	1.128754	0.413120
H	5.969756	1.633512	-1.000630
H	-6.932279	4.114764	1.763013
H	-6.066997	2.913793	2.744070
H	-5.469055	4.589457	2.647344
H	-5.943421	4.953086	-0.439426
H	-4.454012	5.458542	0.375973
H	-4.386975	4.351629	-1.027936
H	-0.050330	-8.059765	1.703009
H	0.574879	-6.709340	2.671839

H -1.173873 -7.047274 2.630054
H -1.340687 -7.630695 -0.451837
H -2.509272 -6.602159 0.394211
H -1.627486 -5.985557 -1.035435
69
TFPB E(gas)=-3649.30702872 G(gas)= -3649.025082 E($CHCl_3$)= -3649.34095198
B 0.001168 -0.001781 0.001495
C -0.957290 -0.214194 1.330966
C 0.992358 -1.304083 -0.233711
C 0.994214 1.305879 0.186911
C -1.026208 0.207211 -1.276763
C -0.873013 0.553400 2.505211
C -1.733914 0.345997 3.597449
C -2.710650 -0.648773 3.557537
C -2.818264 -1.427493 2.397435
C -1.967220 -1.204068 1.309905
H -0.123997 1.345455 2.575991
C -1.562467 1.190565 4.835318
H -3.373564 -0.814667 4.406272
C -3.911427 -2.463685 2.313996
H -2.093160 -1.815429 0.413057
C 1.976429 -1.255158 -1.248191
C 2.853156 -2.318277 -1.491555
C 2.797962 -3.479385 -0.709980
C 1.847818 -3.546631 0.308927
C 0.961087 -2.479659 0.536777
H 2.060639 -0.355756 -1.863222
C 3.919295 -2.200272 -2.552215
H 3.482300 -4.307715 -0.891393
C 1.736352 -4.790988 1.154259
H 0.234933 -2.571305 1.347375
C 0.913195 2.481049 -0.579254
C 1.801996 3.555544 -0.397498
C 2.806461 3.494360 0.567433
C 2.913051 2.331751 1.343233
C 2.031974 1.263231 1.147346
H 0.145136 2.567327 -1.351206
C 1.631042 4.796854 -1.237087
H 3.492694 4.328350 0.713669
C 4.033863 2.234035 2.348031
H 2.157518 0.363246 1.754184
C -2.038629 1.192911 -1.202875
C -2.947340 1.408281 -2.243658
C -2.896484 0.628457 -3.407498
C -1.919040 -0.361110 -3.498503
C -1.000348 -0.561963 -2.452485
H -2.121267 1.803209 -0.300497
C -4.036909 2.444344 -2.121796
H -3.606827 0.788952 -4.218346
C -1.811017 -1.209712 -4.740903
H -0.253255 -1.351523 -2.560874

F 3.823698 1.267816 3.284231
F 5.236738 1.945950 1.751163
F 4.222259 3.410939 3.026043
F 2.698603 5.647104 -1.146440
F 1.469989 4.506619 -2.563368
F 0.527000 5.521150 -0.866330
F 4.200510 -3.405204 -3.140897
F 3.573989 -1.341761 -3.552868
F 5.107779 -1.742361 -2.039045
F 1.593658 -4.505356 2.483160
F 0.650859 -5.554582 0.807517
F 2.830733 -5.604250 1.041623
F -2.611358 1.072293 5.705480
F -0.435722 0.850239 5.539341
F -1.442678 2.520389 4.541605
F -3.636270 -3.449589 1.414736
F -4.137068 -3.076382 3.519027
F -5.113057 -1.916509 1.936658
F -4.181553 3.175612 -3.273325
F -5.263929 1.876500 -1.880585
F -3.814562 3.332690 -1.114600
F -1.684896 -2.539441 -4.448738
F -2.898895 -1.088662 -5.560971
F -0.716629 -0.878953 -5.498203
70
NaTFPB E(gas)-3811.52239772 A.U. G(gas)= -3811.23723 E($CHCl_3$)= -3811.54853395
B 0.410027 0.160580 0.030594
C -0.498064 1.432672 -0.508734
C 2.028508 0.414842 -0.012140
C 0.046235 -1.144225 -0.924046
C -0.164453 -0.162022 1.554899
C -1.492686 1.287247 -1.489106
C -2.455605 2.283255 -1.742256
C -2.403844 3.507868 -1.081304
C -1.373731 3.708882 -0.148354
C -0.467745 2.687541 0.150245
H -1.530391 0.367284 -2.081826
C -3.590692 1.932859 -2.659941
H -3.146557 4.283148 -1.272083
C -1.312992 5.046707 0.561632
H 0.262535 2.857926 0.943735
C 2.914211 -0.659935 0.216967
C 4.306038 -0.500778 0.191962
C 4.873636 0.747409 -0.078025
C 4.018916 1.823031 -0.330938
C 2.626830 1.654894 -0.302963
H 2.511464 -1.661032 0.393625
C 5.182262 -1.698900 0.477660
H 5.955022 0.875918 -0.099931
C 4.586629 3.175854 -0.695602
H 2.001341 2.521102 -0.526835

C	-0.921067	-2.105089	-0.589063
C	-1.357786	-3.086352	-1.501895
C	-0.791819	-3.179070	-2.771261
C	0.223296	-2.269445	-3.108122
C	0.620151	-1.272792	-2.212639
H	-1.336077	-2.112937	0.425317
C	-2.498405	-3.972182	-1.088269
H	-1.121980	-3.938095	-3.481090
C	0.840416	-2.375521	-4.488874
H	1.395193	-0.567581	-2.519650
C	-1.522422	0.064808	1.848258
C	-2.143740	-0.401483	3.014044
C	-1.398597	-1.057235	3.996691
C	-0.026938	-1.221514	3.772497
C	0.570960	-0.798334	2.575082
H	-2.116072	0.664043	1.150033
C	-3.623141	-0.183633	3.154409
H	-1.864311	-1.422316	4.911308
C	0.832805	-1.915836	4.810212
H	1.641076	-0.970497	2.438749
F	1.862898	-1.504789	-4.673088
F	1.321975	-3.630469	-4.723848
F	-0.088296	-2.124089	-5.463175
F	-2.893466	-4.847976	-2.027459
F	-2.278158	-4.646067	0.061348
F	-3.640113	-3.156816	-0.818448
F	6.500212	-1.453943	0.243314
F	5.076813	-2.101233	1.782158
F	4.830909	-2.776736	-0.287372
F	3.918906	4.192754	-0.073747
F	5.901787	3.297199	-0.364110
F	4.492621	3.416852	-2.040936
F	-4.507114	2.903692	-2.811501
F	-3.199914	1.516715	-3.884008
F	-4.299591	0.818337	-2.108856
F	-0.296263	5.118734	1.456082
F	-1.151120	6.071280	-0.325812
F	-2.472767	5.299045	1.242983
F	-4.195987	-0.901982	4.136289
F	-3.969923	1.115092	3.322161
F	-4.279963	-0.577170	1.953362
F	1.250460	-3.140680	4.371540
F	1.951842	-1.195693	5.097794
F	0.167493	-2.117633	5.982138
Na	-3.499411	-0.768256	-0.400163

4.0 Ionophoric Activity

4.1 Ion selectivity with the HPTS assay

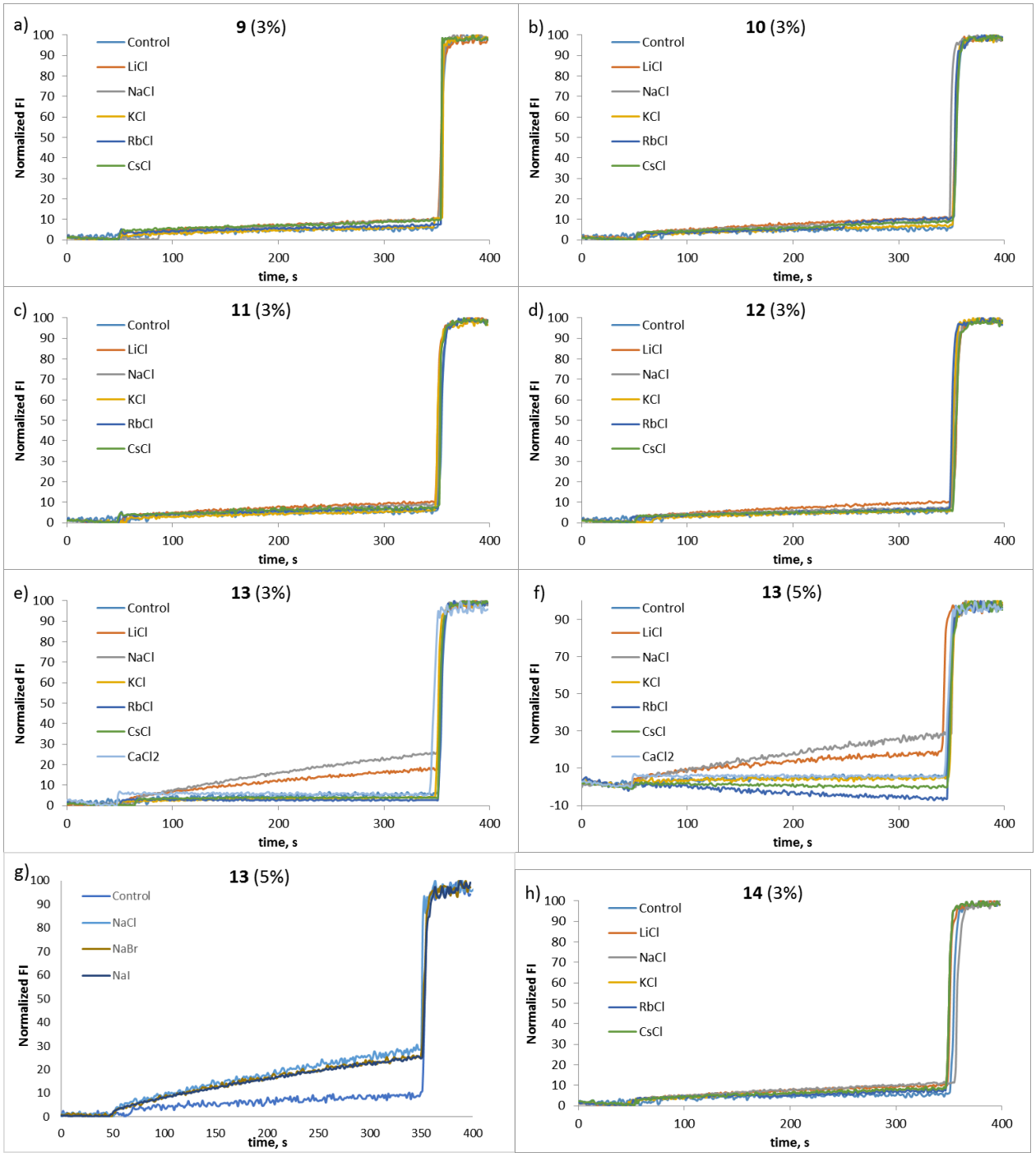


Figure S27. Normalized fluorescence time courses for cyclopeptoids **9-14** in the HPTS assay in the presence of the different alkaline or calcium cations (100 mM MCl or 50mM $CaCl_2$, pH 7.0, base pulse by addition of 50 µL of 0.5M MOH (CsOH in the case of $CaCl_2$)) or different halide anions (100 mM NaX, pH 7.0, base pulse by addition of 50 µL of 0.5M NaOH). The liposome were made of 95:5 EYPC/EYPG (100 nm diameter) and loaded with HPTS (0.1 mM HPTS, 25 mM HEPES, 100 mM NaCl, pH 7.0) and diluted to 0.17 mM total lipid concentration with the appropriate buffer solution. The concentration of the ionophores is showed in each figure and it is expressed in mol%

with respect to the total concentration of lipids. The control trace is recorded in the absence of ionophore. The kinetic experiments were performed at 25 °C. Base pulse at 50 s and addition of TRITON X-100 (40 µL of 5% aqueous solution) to lyse the liposomes at 350 s.

4.2 Ion selectivity with the HPTS assay and the protonophore CCCP

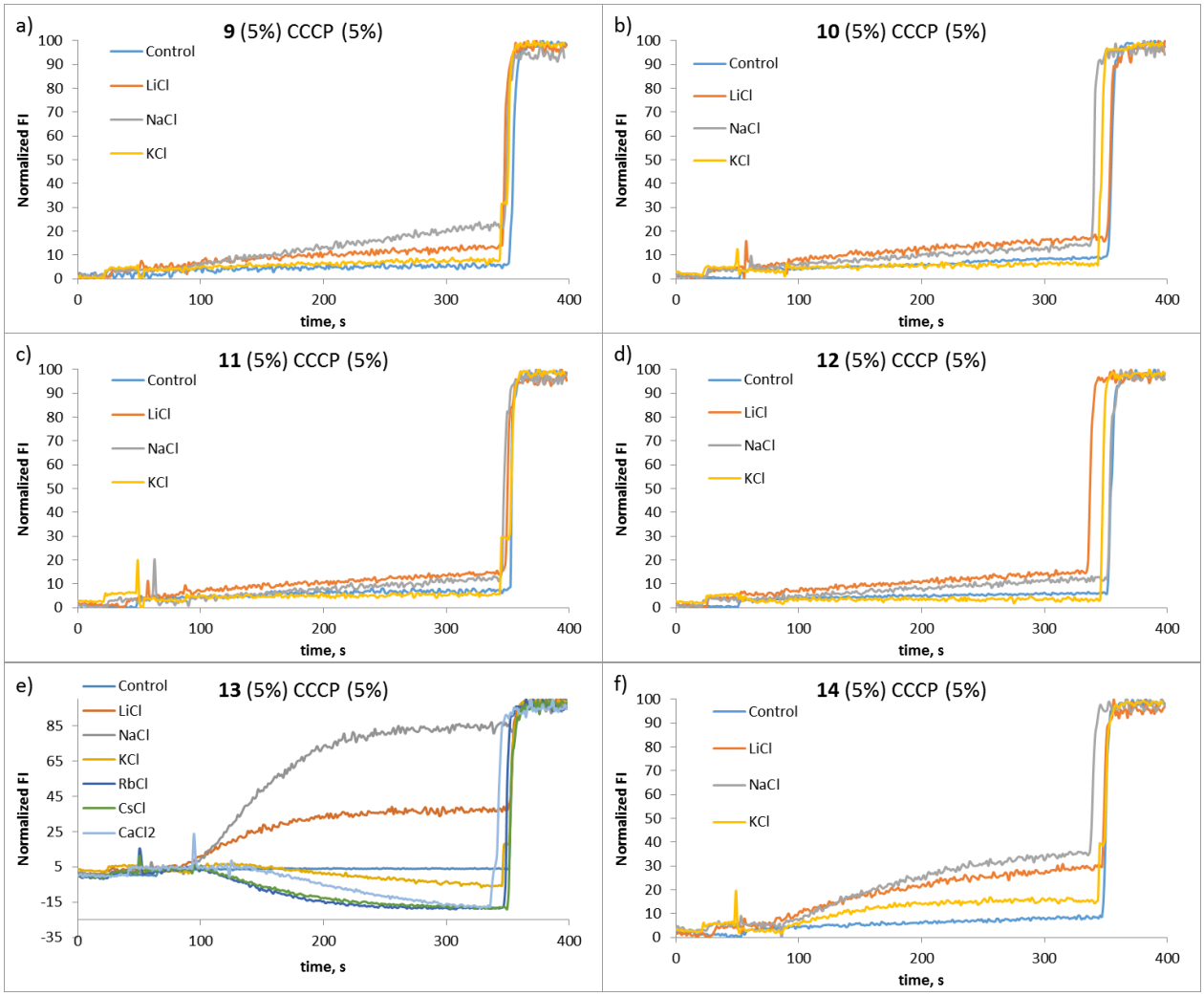


Figure S28. Normalized fluorescence time courses for cyclopeptoids **9-14** in the HPTS assay with 5 mol% of the CCCP protonophore in the presence of the different alkaline and calcium cations (100 mM MCl or 50mM $CaCl_2$, pH 7.0, base pulse by addition of 50 µL of 0.5M MOH (CsOH in the case of $CaCl_2$)). The liposome were made of 95:5 EYPC/EYPG (100 nm diameter) and loaded with HPTS (0.1 mM HPTS, 25 mM HEPES, 100 mM NaCl, pH 7.0) and diluted to 0.17 mM total lipid concentration with the appropriate buffer solution. The concentration of the ionophores is showed in each figure and it is expressed in mol% with respect to the total concentration of lipids. The control trace is recorded in the absence of ionophore. The kinetic experiments were performed at 25 °C. Base pulse at 25 s, addition of CCCP at 50s, addition of the ionophore at 90s, and addition of TRITON X-100 (40 µL of 5% aqueous solution) to lyse the liposomes at 350 s.

It is interesting to note that in the case of compounds **13** the kinetic profiles obtained with the non-transported cation (K^+, Rb^+, Cs^+ and Ca^{2+}) show a decrease of fluorescence intensity due to an

acidification of the intravesicular compartment (Figure S28e). The same effect is observed, although to a lesser extent, in the experiment without CCCP (Figure S27f). This acidification effect is due to the high Na^+/M^+ selectivity in the transport. Indeed the liposome are prepared in a buffer containing NaCl 100 mM and then diluted in the buffer containing 100 mM MCl. Therefore at the beginning of the experiment, when the base pulse is applied, the liposome contains in the inner water pool Na^+ while outside the concentration of Na^+ is much lower and the concentration of MCl is high. If the ionophore is able to transport both cations this chemical gradient is easily removed by an antiport of the two cations (Figure S29a). This process does not affect the pH of the inner water pool of the liposomes and, therefore it is not signaled by the HPTS. However, if the ionophore is able to transport only Na^+ (high Na^+/M^+ selectivity) the chemical gradient starts a transport of Na^+ from inside to outside counterbalanced by an antiport of H^+ facilitated by the CCCP which results in the acidification of the inner water pool and a lower emission intensity of HPTS. This is schematically illustrated in the Figure S29b.

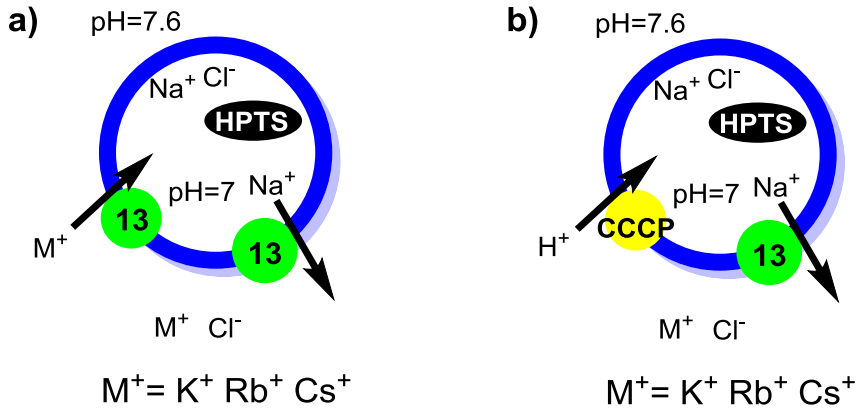


Figure S29: Schematic representation of the collapse of the chemical gradient in the ion selectivity experiment with HPTS. a) The ionophore is able to transport both cations (low Na^+/M^+ selectivity) and the chemical gradient is removed by an antiport of the two cations without affecting the internal pH and the fluorescence emission of HPTS; b) The ionophore is able to transport only Na^+ (high Na^+/M^+ selectivity) and the gradient is removed by an efflux of Na^+ promoted by **13** counterbalanced by an inverse H^+ flux facilitated by CCCP. This process results in the acidification of the liposome inner water pool.

4.3 Kinetic profiles for compound 13 in the HPTS assay and Hill analysis

Figures S30-S32 report the kinetic profiles obtained in the HPTS assay at different concentrations of **13** alone (Fig. S30), of **13** + CCCP (Fig. S31) and of **13** + CCCP + cholesterol (Fig. S32).

The kinetic data of Figures S30 and S31 were used for the Hill analysis of the transport process. The normalized fluorescent intensity (%) measured just before the addition of Triton X-100 at 1100

s in the case of **13** alone and 325 s in the case of 13+CCCP was plotted as a function of the carrier concentration. Data points were fitted to the Hill equation:

$$Y = Y_{\infty +} \frac{(Y_0 - Y_\infty)}{1 + \left(\frac{c}{EC_{50}}\right)^n}$$

where *Y* is the normalized fluorescent emission at 1100 or 325 s (%), Y_0 is Y in absence of ionophore and Y_∞ is Y after the addition of Triton X-100 (100% in our case) and *c* is the ionophore concentration (molar % ionophore to lipid). EC_{50} is defined as the carrier concentration (molar % carrier to lipid) needed to obtain 50 % of the maximum fluorescent emission possible. *n* is the Hill coefficient related to the molecularity of the species active in the transport process

The results of the fitting are reported in Figure S30 and S31.

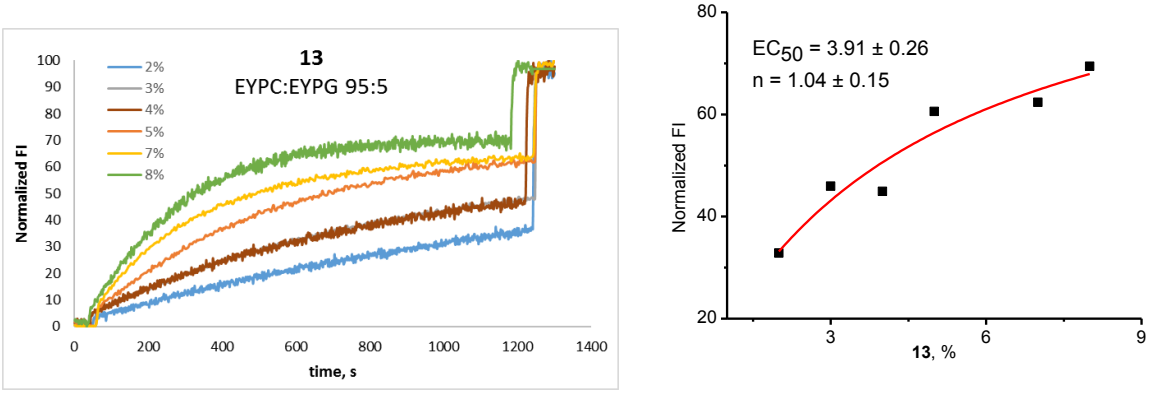


Figure S30. Left: normalized fluorescence time courses for cyclopeptoid **13** in the HPTS assay (100 mM NaCl, pH 7.0, base pulse by addition of 50 µL of 0.5M NaOH). The liposome (100 nm diameter) composition is showed in Figure, and they were diluted with HEPES buffer containing NaCl (25 mM HEPES, 100 mM NaCl, pH 7.0) to a final volume of 3mL and a concentration of 0.17 mM. The concentration of cyclopeptoid is given in the Figure. The kinetic experiments were performed at 25 °C. Base pulse at 50 s and addition of TRITON X-100 (40 µL of 5% aqueous solution) to lyse the liposomes at 1200 s. Right: Hill plot obtained by fitting the normalized fluorescence intensity measured at 1100 s.

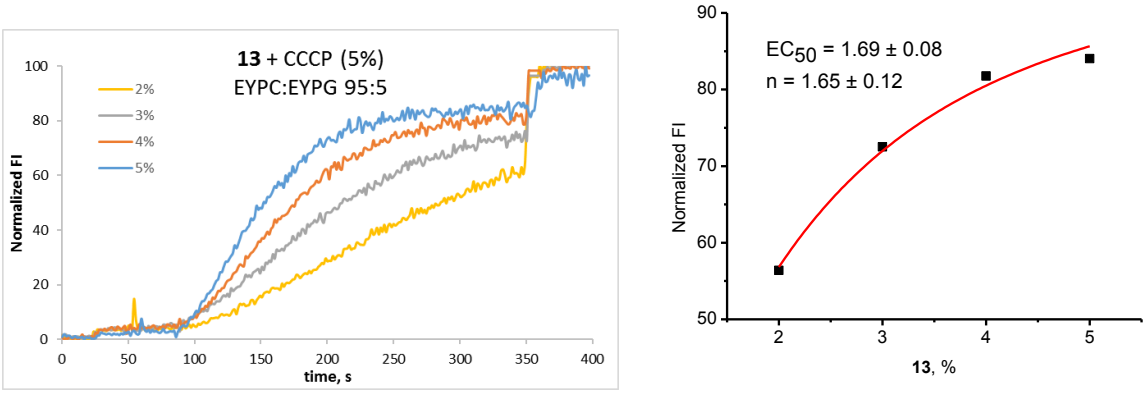


Figure S31. Normalized fluorescence time courses for cyclopeptoid **13** in the HPTS assay with 5 mol% of CCCP protonophore (100 mM MCl, pH 7.0, base pulse by addition of 50 µL of 0.5M NaOH). The liposome (100 nm diameter) composition is showed in Figure, and they were diluted with HEPES NaCl buffer (25 mM HEPES, 100 mM NaCl, pH 7.0) to a final volume of 3mL and a concentration of 0.17 mM. The concentration of cyclopeptoid is given in the Figure. The kinetic experiments were performed at 25 °C. Base pulse at 25 s, addition of CCCP at 50s, addition of the ionophore at 90s, and addition of TRITON X-100 (40 µL of 5% aqueous solution) to lyse the liposomes at 350 s. Right: Hill plot obtained by fitting the normalized fluorescence intensity measured at 325 s.

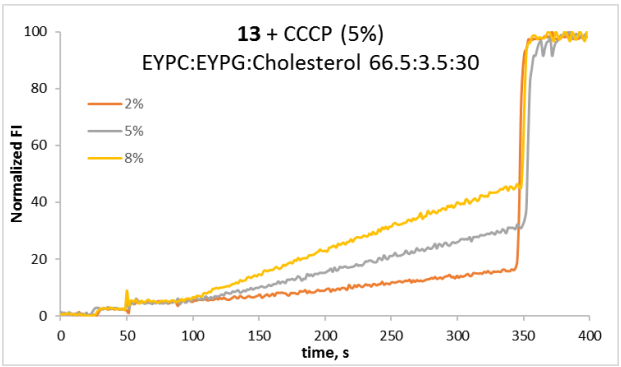


Figure S32. Normalized fluorescence time courses for cyclopeptoid **13** in the HPTS assay with 5 mol% of CCCP protonophore and with cholesterol (100 mM MCl, pH 7.0, base pulse by addition of 50 µL of 0.5M MOH). The liposome (100 nm diameter) composition is showed in Figure, and they were diluted with HEPES NaCl buffer (25 mM HEPES, 100 mM NaCl, pH 7.0) to a final volume of 3mL and a concentration of 0.17 mM. The concentration of cyclopeptoid is given in the Figure. The kinetic experiments were performed at 25 °C. Base pulse at 25 s, addition of CCCP at 50s, addition of the ionophore at 90s, and addition of TRITON X-100 (40 µL of 5% aqueous solution) to lyse the liposomes at 350 s.

4.4 Calculated logP values for compounds 9-13

The octanol/water partition coefficients for compounds **9-13** were calculated with the software ALOGPS developed by Virtual Computational Chemistry Laboratory VCCLAB (http://www.vcclab.org/lab/alogps/).

The calculated values are reported in the Table S1

Table S1. Octanol/water partition coefficients for compounds **9-13**

Compound	**9**	**10**	**11**	**12**	**13**	**14**
LogP	**2.06**	**2.64**	**3.49**	**2.91**	**4.02**	**4.87**

5.0 X-ray crystallography

ORTEP drawings for compounds **9**, **11** and **13** as Na^+ complex are reported in Figures S33, S34 and S35 respectively. The program OLEX2 was used as a drawing tool.[3]

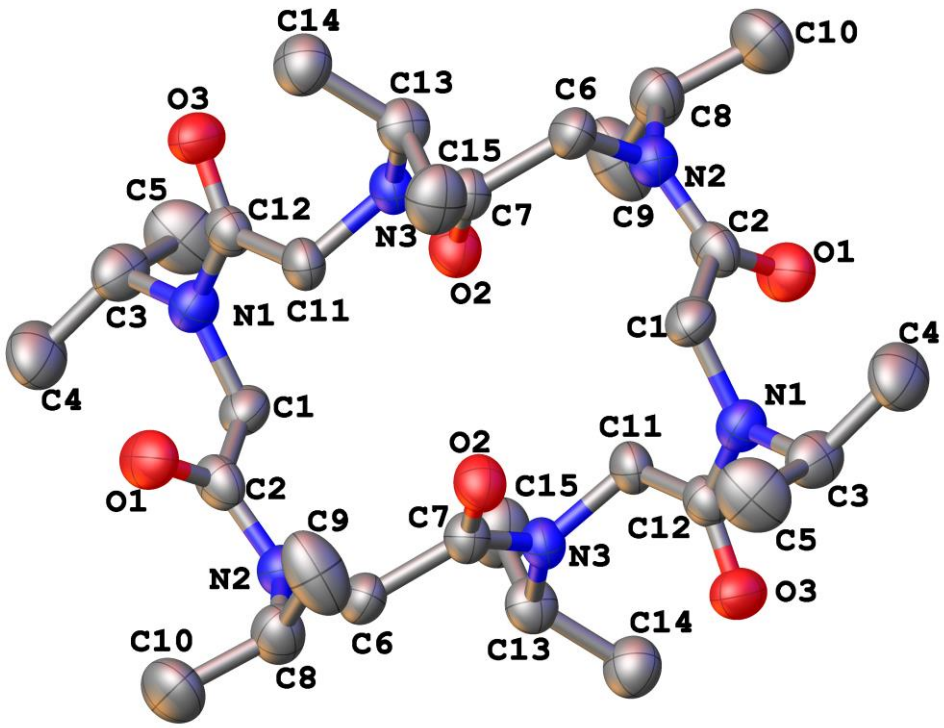


Figure S33. ORTEP drawing and atom numbering scheme for compound **9**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

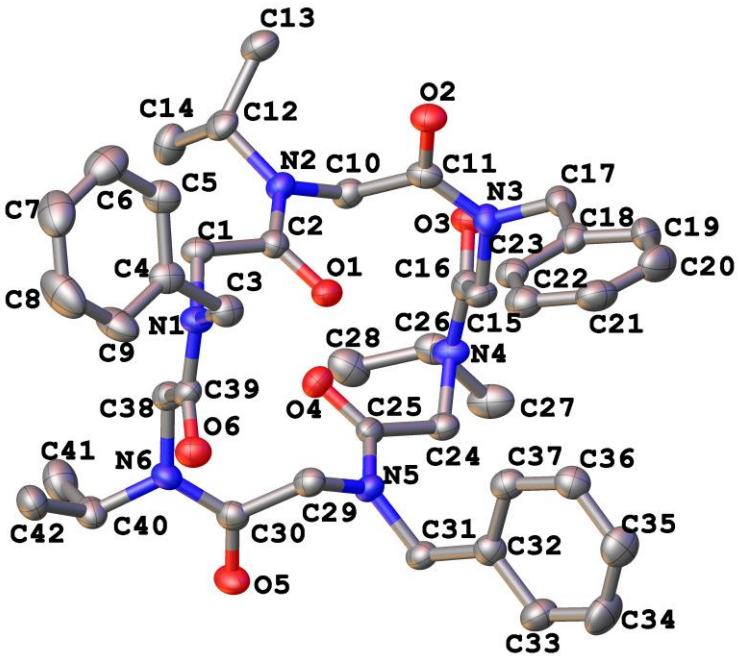


Figure S34. ORTEP drawing and atom numbering scheme for compound **11**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

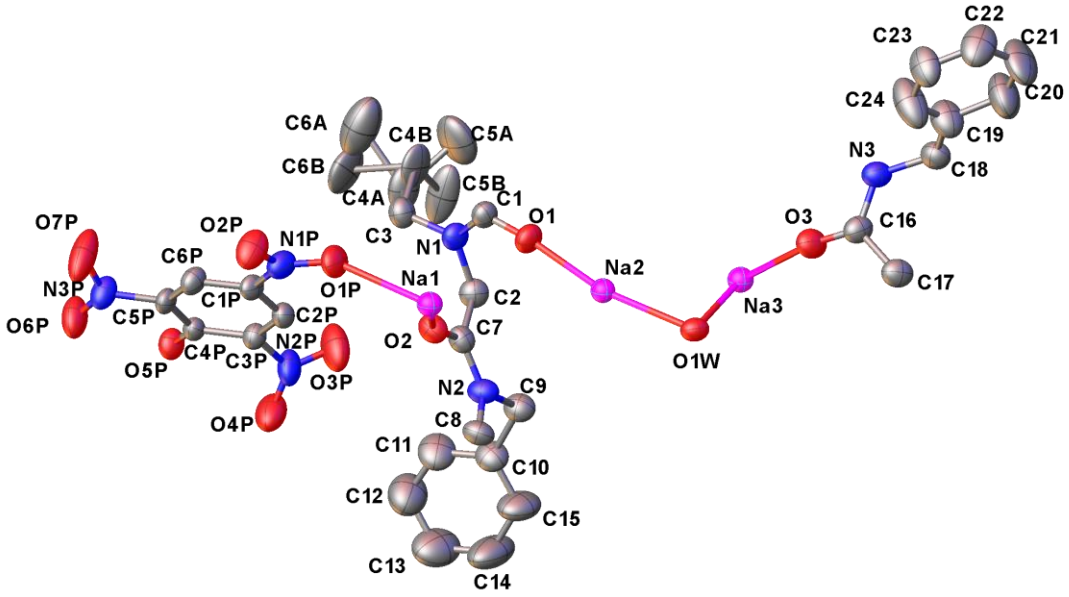


Figure S35. ORTEP drawing and atom numbering scheme for compound **13** as Na^+ complex. Thermal ellipsoids are drawn at 30% probability level. Only the asymmetric unit is shown, hydrogen atoms are omitted for clarity.

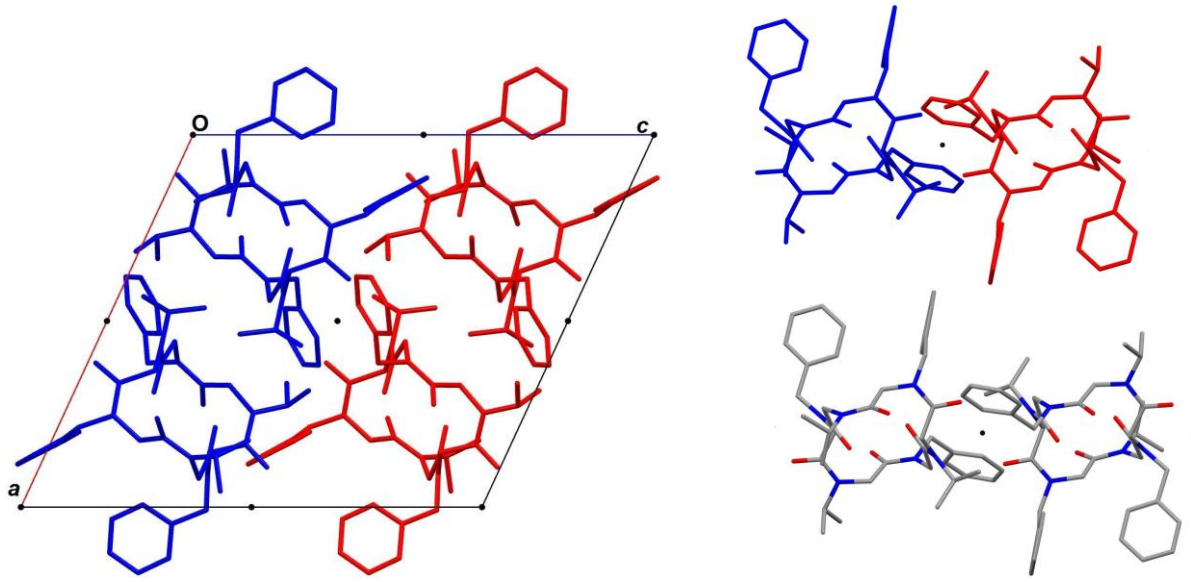


Figure S36. a) Crystal packing of **11** as viewed along the *b* axis. Red and blue molecules represent enantiomeric pairs, being related by crystallographic symmetry elements as inversion centres and *c* glide planes. Crystallographic inversion centres are indicated by black spheres. Chloroform molecules and hydrogen atoms have been omitted for clarity. b) A zoomed view of a pair of enantiomers as related by the inversion centre, c) the same pair of enantiomer with C atoms in grey, N atoms in blue and O atoms in red.

Table S2. Crystallographic data for compounds **9**, **11**, and **13** as sodium complexes

	9	**11**	**13** (Na^+ complex)
T (K)	100	100	296
Formula	$C_{30}H_{54}N_6O_6$	$C_{42}H_{54}N_6O_6$ 2 $CHCl_3$	$Na_6(H_2O)_6(C_6N_3O_7H_2)_6(C_{45}H_{60}N_6O_6)_3$ $CHCl_3$
Formula weight	594.79	977.64,	
System	monoclinic	monoclinic	cubic
Space group	$P2_1/c$	$P2_1/c$	$Pa\bar{3}$
a (Å)	9.476(5)	16.373(3)	27.360(3)
b (Å)	16.910(10)	17.935(2) Å	
c (Å)	10.655(6)	18.380(3) Å	
β (°)	103.994(14)	114.773(3)°	
V (Å^3)	1656.8(17)	4900.6(13)	20480(7)
Z	2	4	4
D_X (g cm^{-3})	1.192	1.325	1.317
λ (Å)	0.71069	0.71069	1.5418
μ (mm^{-1})	0.083	0.402	1.317
F_{000}	648	2048	8476
R1 ($I > 2\sigma_I$)	0.0991 (1237)	0.089 (5352)	0.075 (2617)
${}_wR_2$	0.306	0.303	0.247
N. of param.	196	565	484
N. of restraints	-	-	18
GooF	1.097	0.906	1.041
ρ_{min}, ρ_{max} (eÅ^{-3})	0.31,-0.32	1.08, -0.52	0.54, -0.25

6.0 Pirkle's alcohol titration of compound 11

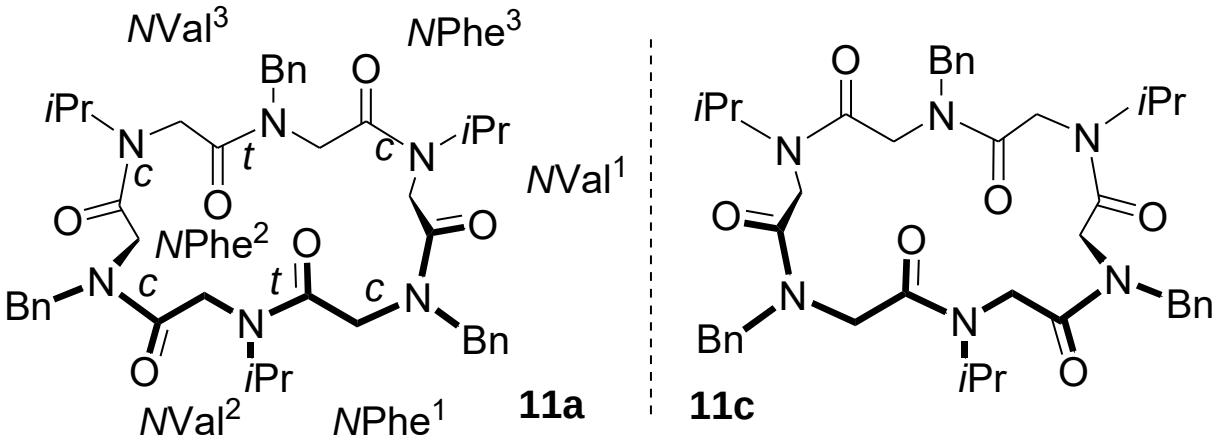


Figure S37. Schematic structure of a) **11a** and b) its mirror image (**11c**). **11a** and **11b** are not superimposable and being conformationally stable at r.t. they are chiral (coalescence temperature (T_c) at 323 K, in $C_2D_2Cl_4$ solution, 300 MHz, $\Delta G^{\ddagger}$ = 14.4 kcal mol^{-1}, see ref. 24 of the manuscript). The interaction with the chiral Pirkle's alcohol forms two diastereomeric supramolecular adducts and splits the resonances close to the interaction site (as clearly showed in Figure S38, S39).

6.1 General procedure for the Pirkle's alcohol addition to 11.

To a 12.0 mM solution of cyclic peptoid **11** in $CDCl_3$ (0.5 mL), 0.5 equivalents of Pirkle's alcohol[4] ((*R*)-1-(9-anthryl)-2,2,2-trifluoroethanol) were added. After the addition the mixture was mixed for 1 minute and the ^{1}H NMR spectrum was recorded. Further 0.5 and 1.0 equivalents of Pirkle's alcohol were added in order to increase the protons resonances' splitting (as reported in Figure S38, S39).

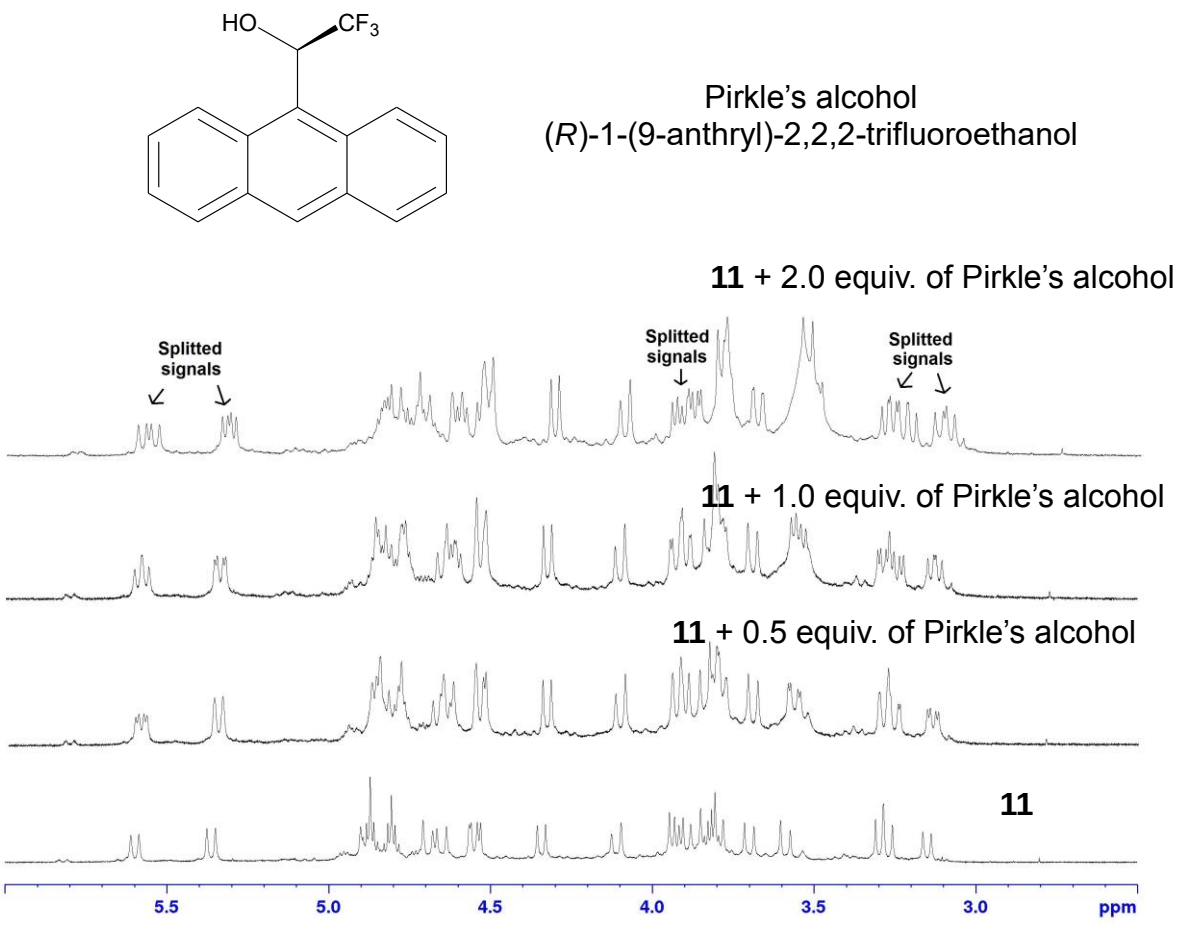


Figure S38. Quantitative step-wise addition of Pirkle's alcohol to **11**. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K, 12.0 mM solution). 6-2.5 ppm expansion.

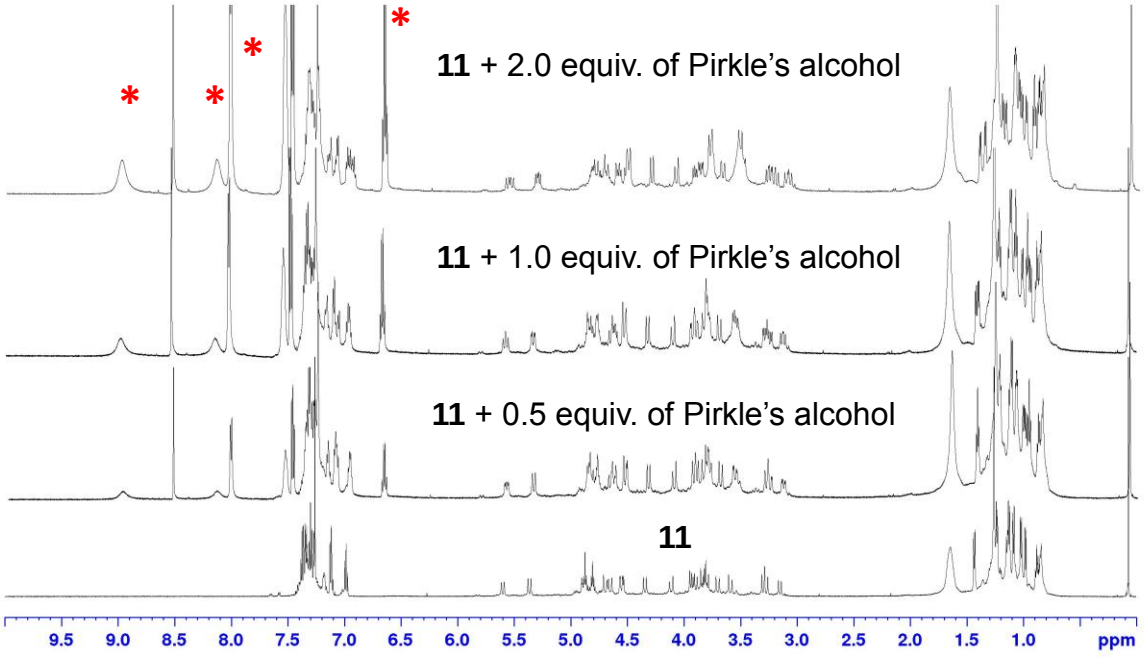


Figure S39. Quantitative step-wise addition of Pirkle's alcohol to **11**. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K, 12.0 mM solution). Full spectra. * Indicates the Pirkle's alcohol resonances.

7.0 References

1) Kurland, R. J.; Rubin, M. B.; Wise, M. B. *J. Chem. Phys.* **1964**, *40*, 2426-2427.

2) Hynes, M. J. *J. Chem. Soc., Dalton Trans.* **1993**, 311–312.

3) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.*, **2009**, *42*, 339-341.

4) W. H. Pirkle, S. D. Beare, *J. Am. Chem. Soc.* **1969**, *91*, 5150-5155.