Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

For

Synthesis and Characterization of new Na^+ Complexes of N-benzyl Cyclic Peptoids and their role in the Ring Opening Polymerization of L-Lactide.

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List of abbreviations

ACN: acetonitrile

Bn: benzyl

COSY: correlation spectroscopy

DCM: dichloromethane

DIC*: N,N'*-diisopropylcarbodiimide

DIPEA: *N,N*-diisopropylethylamine

DMF: dimethylformamide

ESI: electrospray ionisation

FTICR-MS: Fourier transform ion cyclotron resonance mass spectrometry

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

HFIP: hexafluoroisopropanol

HMBC: heteronuclear multiple bond correlation

HSQC: heteronuclear multiple quantum coherence

HRMS: high resolution mass spectrometry

Ph: phenyl

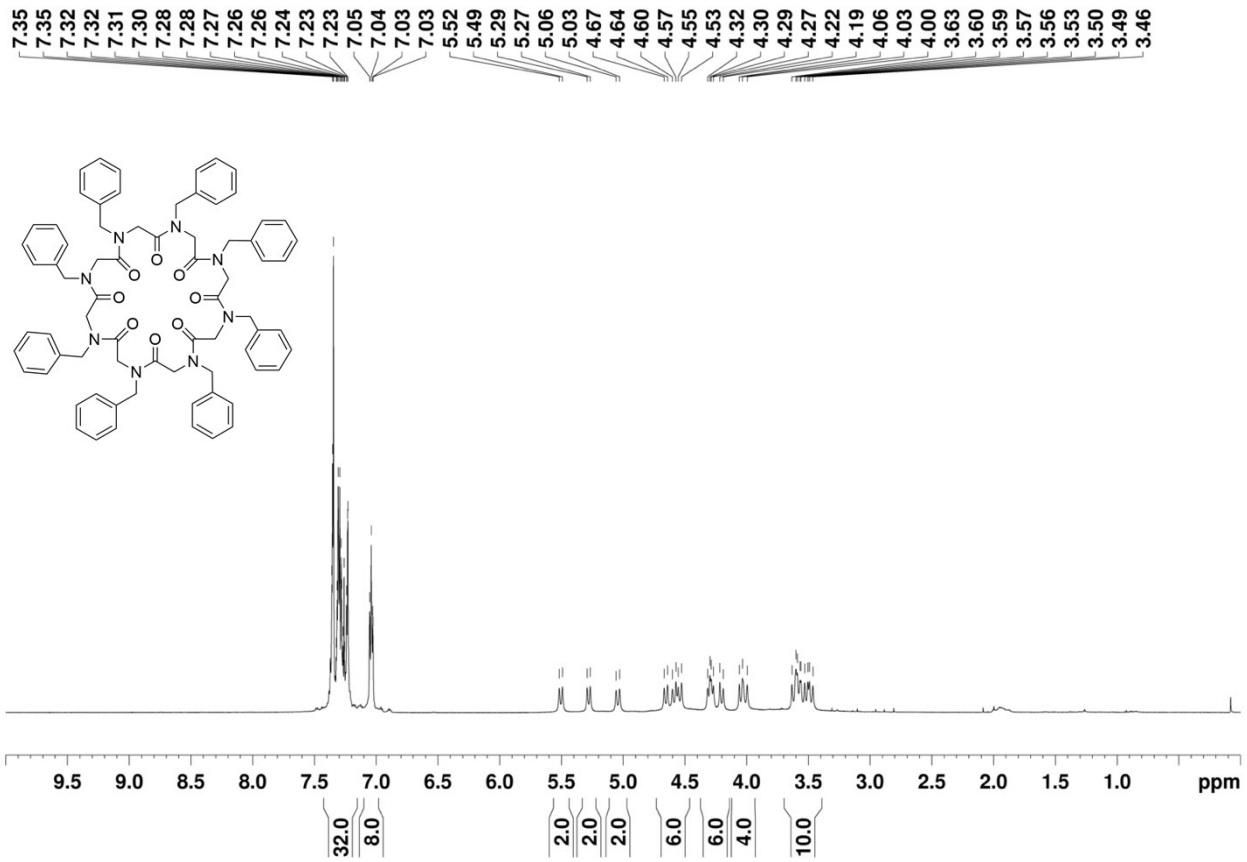
RP HPLC: reversed-phase high-performance liquid chromatography

TFA: trifluoroacetic acid

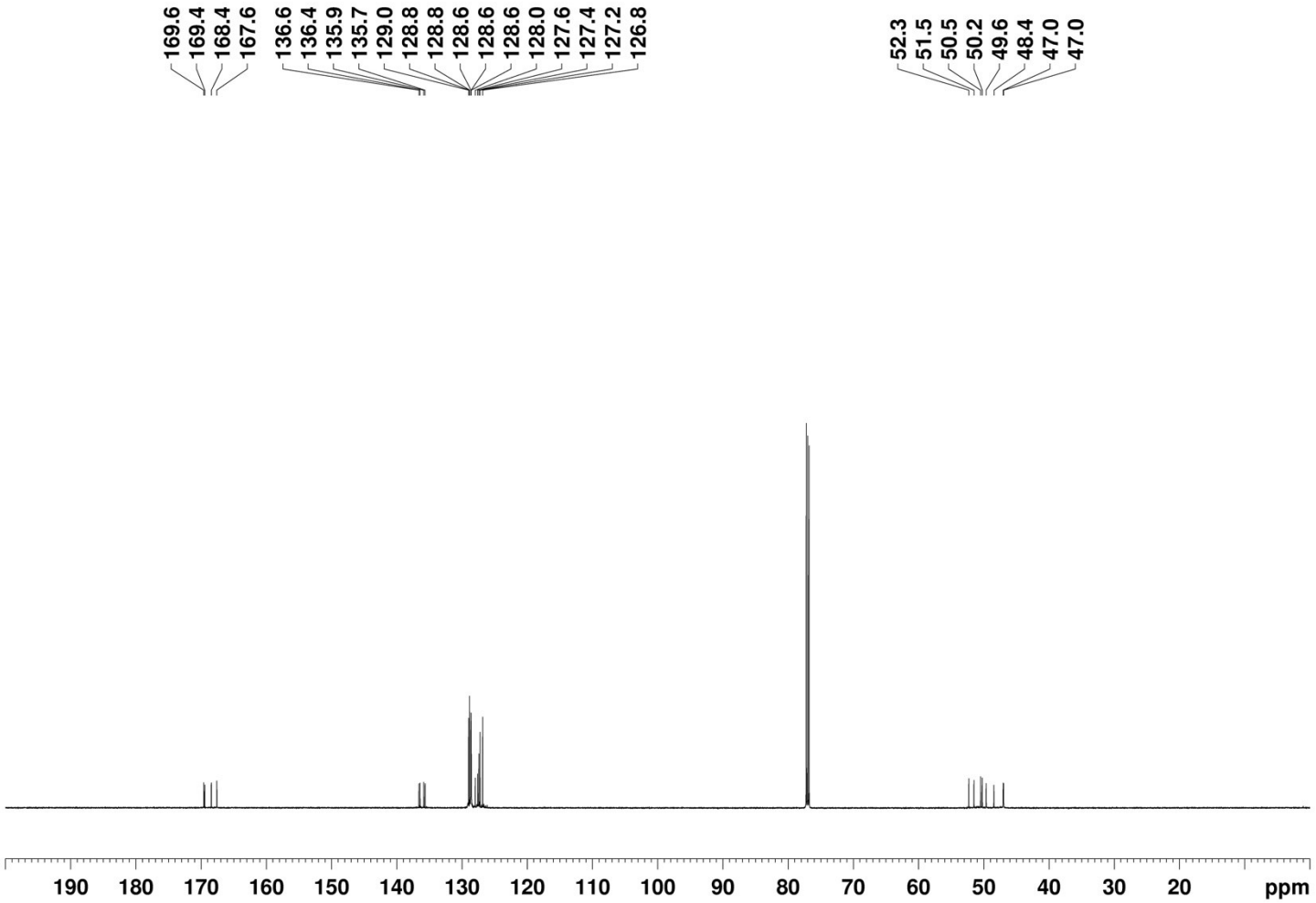
TFPB: tetrakis[3,5-bis(trifluoromethyl)phenyl]borate

1.0 ^{1}H-, ^{13}C NMR and two-dimensional spectra

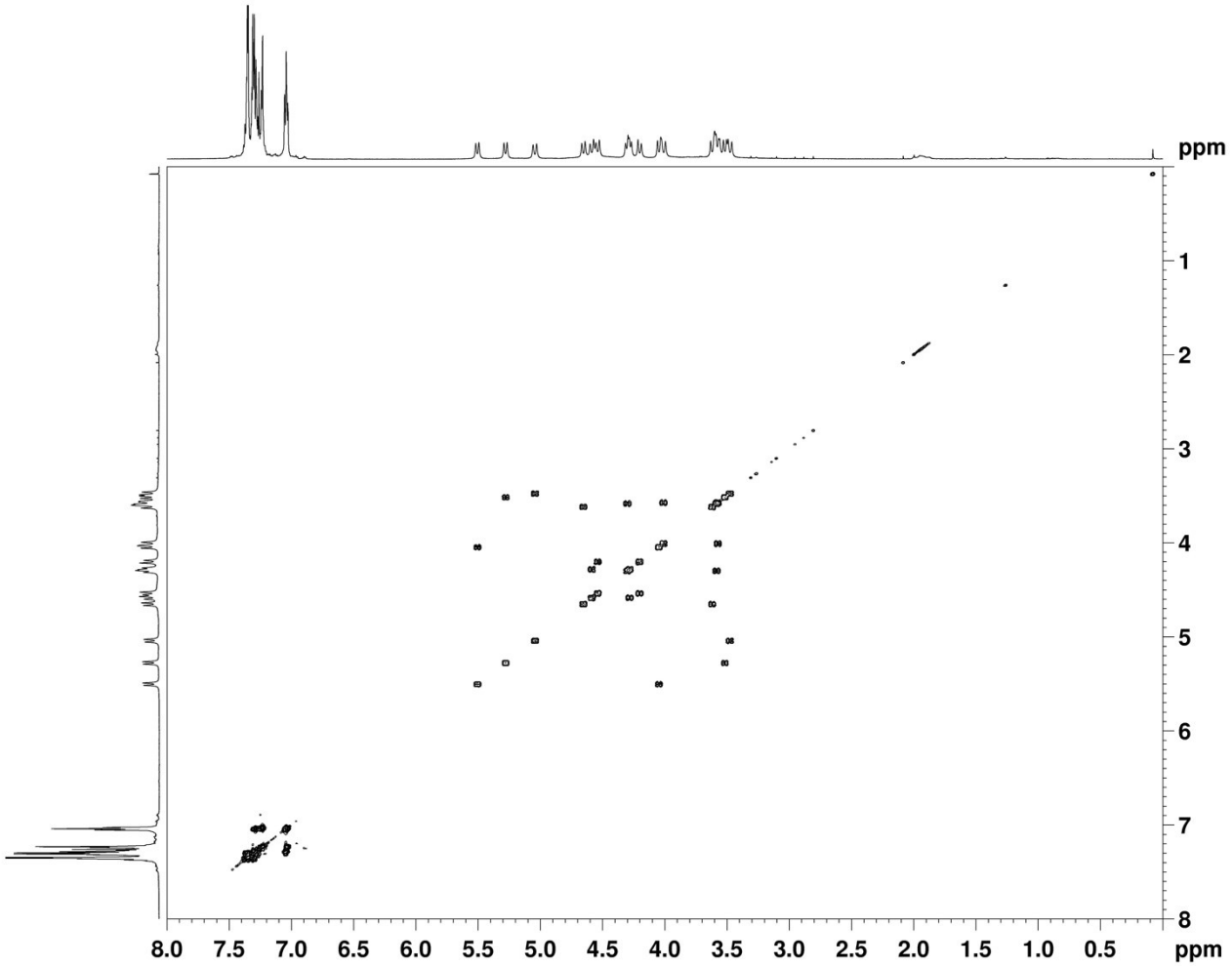
1.1 1D and 2D spectra of cyclic derivative 3 and 1D and 2D spectra of $[1{\cdot}2Na]^{2+}2[TFPB]^{-}$ and $[3{\cdot}Na]^{+}[TFPB]^{-}$, $[3{\cdot}2Na]^{2+}2[TFPB]^{-}$



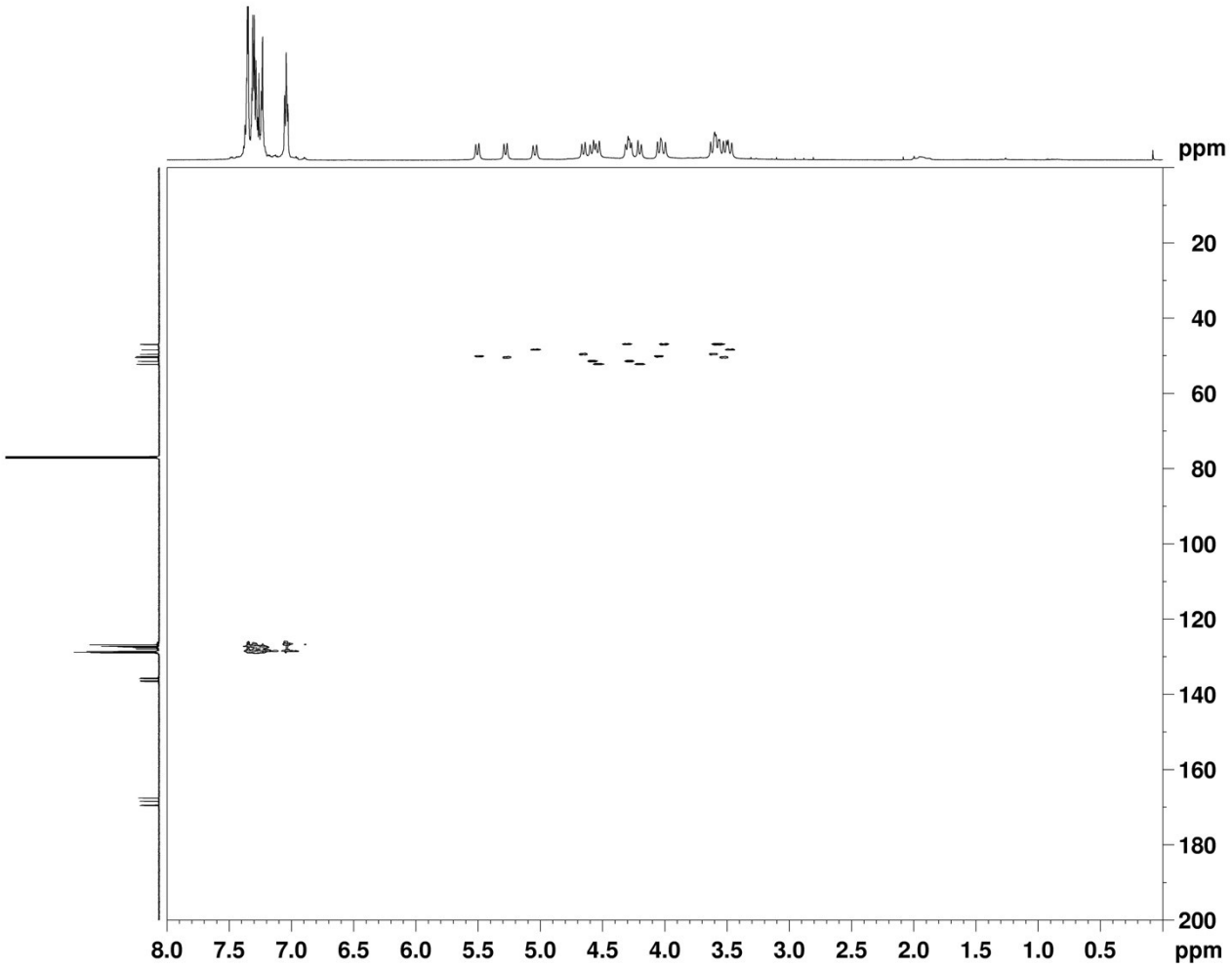
3: ^{1}H NMR (600 MHz, $CDCl_3$)



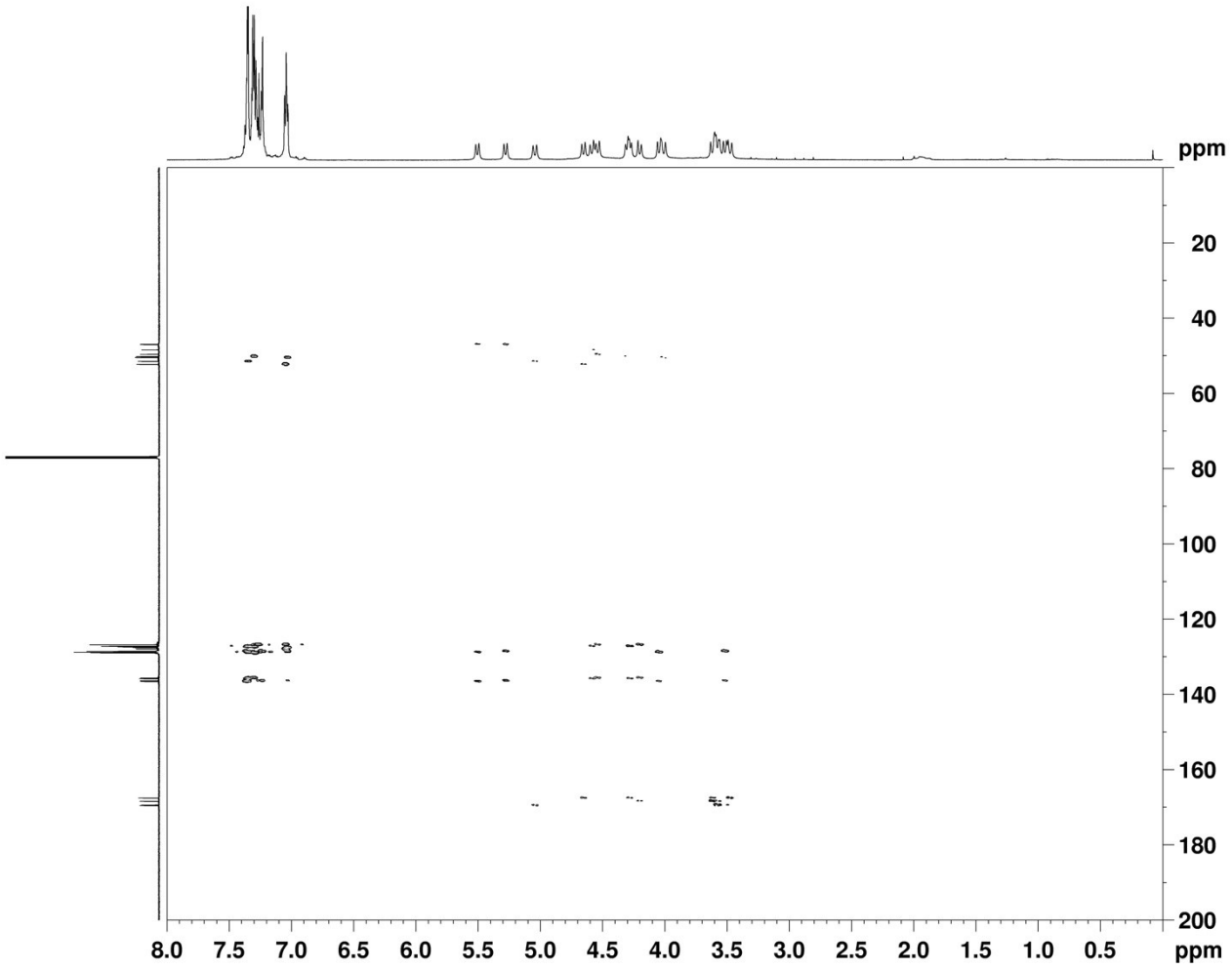
3: ^{1}H NMR (150 MHz, $CDCl_3$)



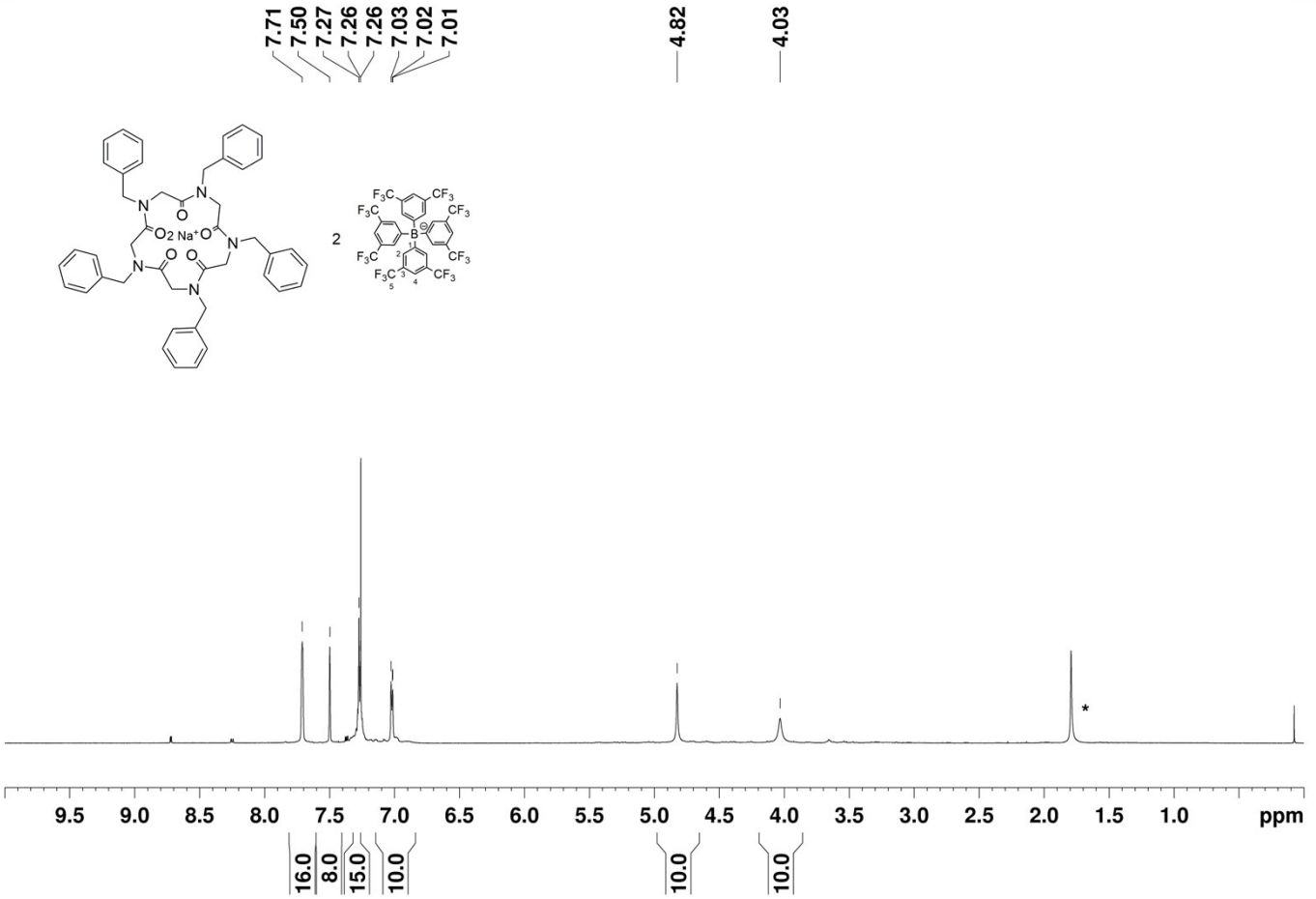
3: COSY SPECTRUM (600 MHz, $CDCl_3$)



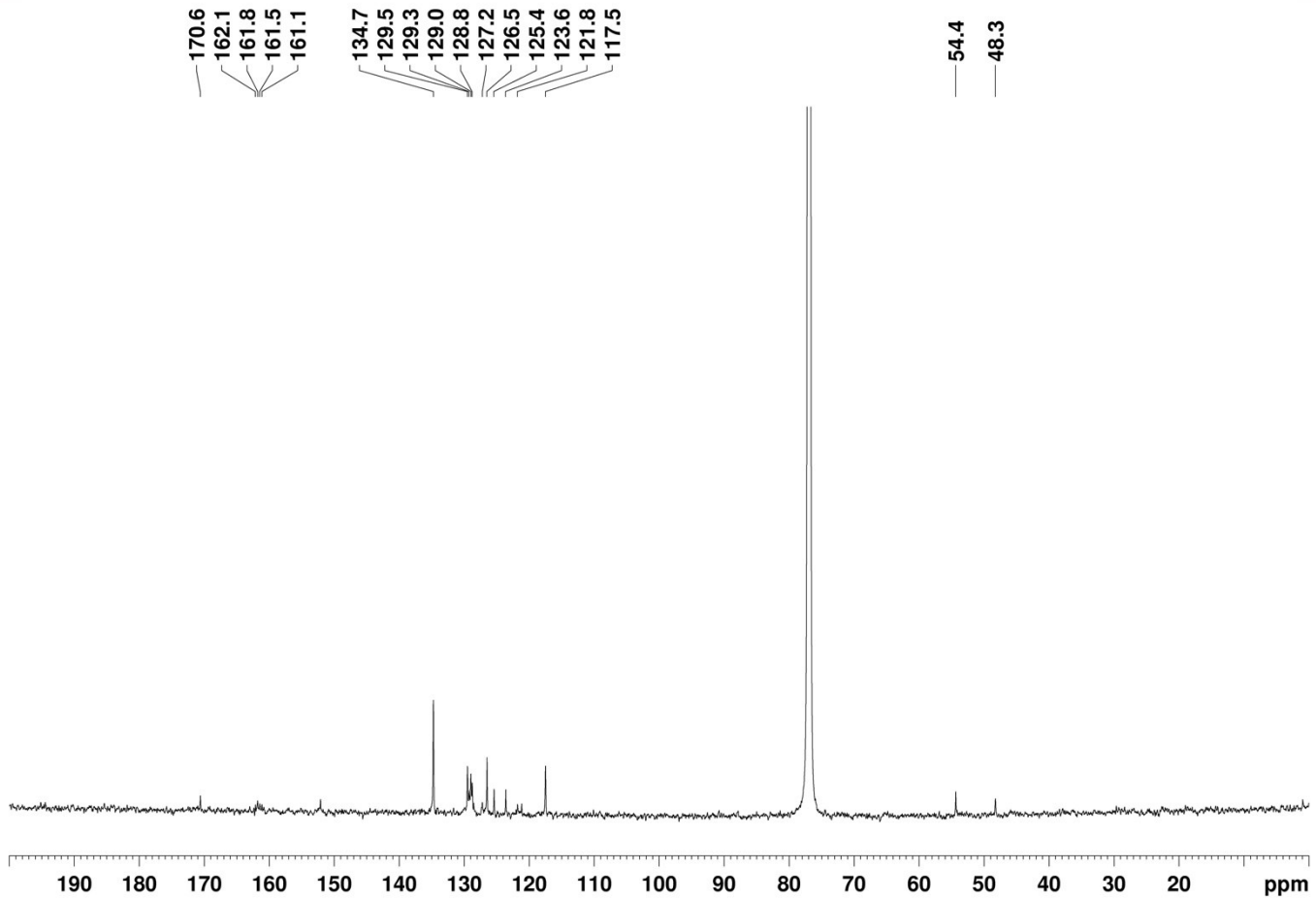
3: HSQC SPECTRUM (600 MHz, $CDCl_3$)



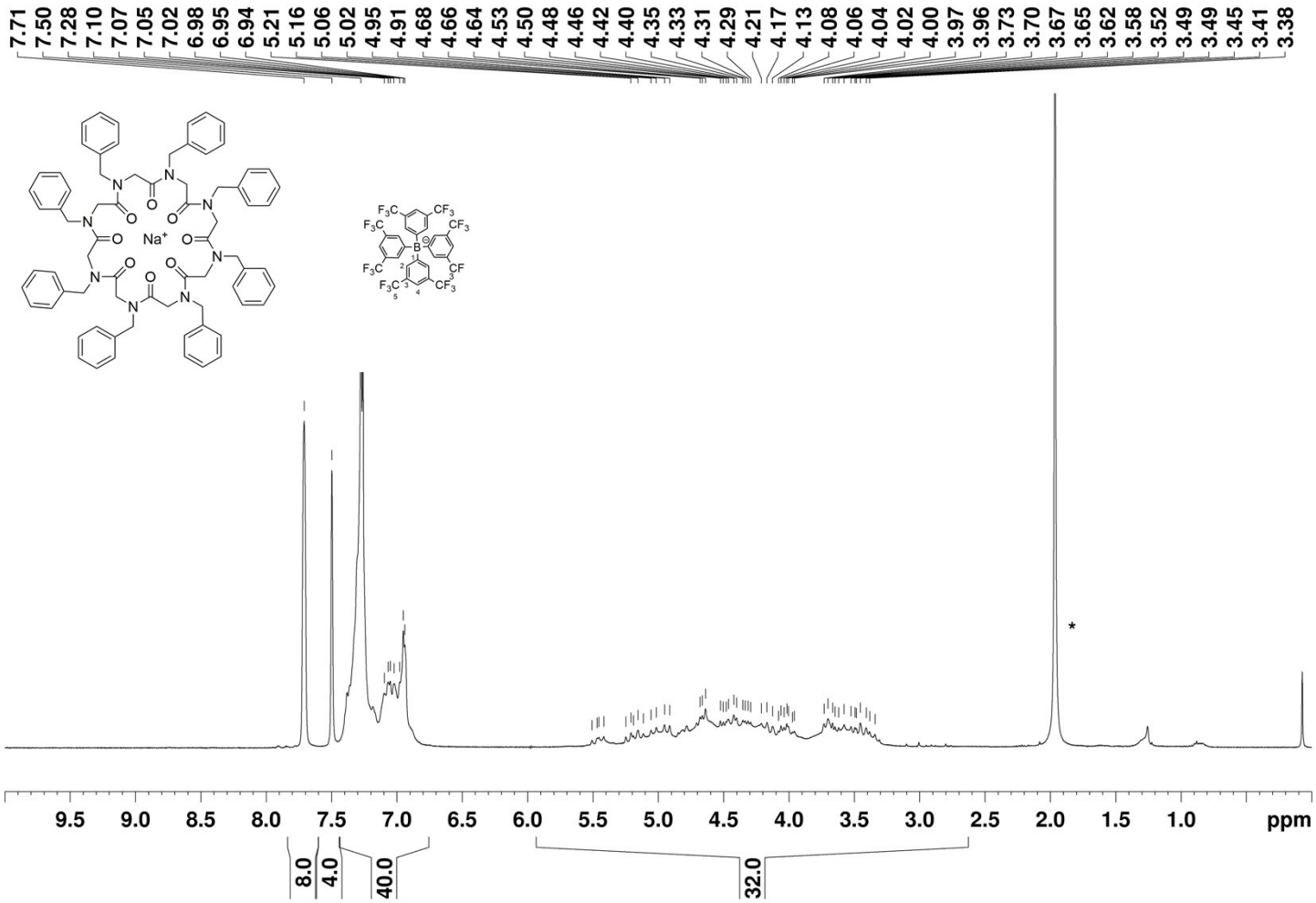
3: HMBC SPECTRUM (600 MHz, $CDCl_3$)



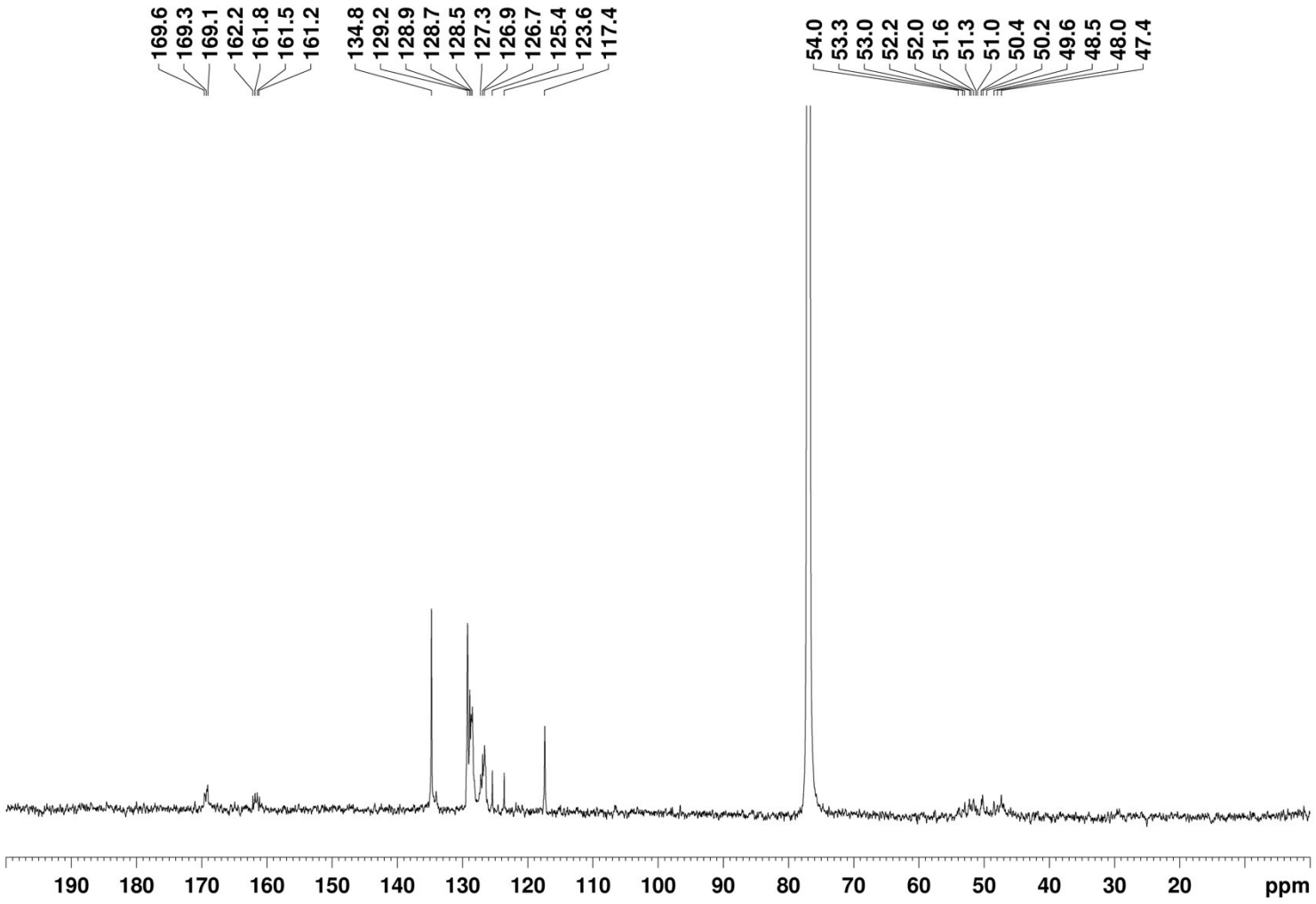
[1·2Na]$^{2+}$2[TFPB]$^{-}$: ^{1}H NMR (600 MHz, $CDCl_3$). Water impurities are labelled with a black asterisk.



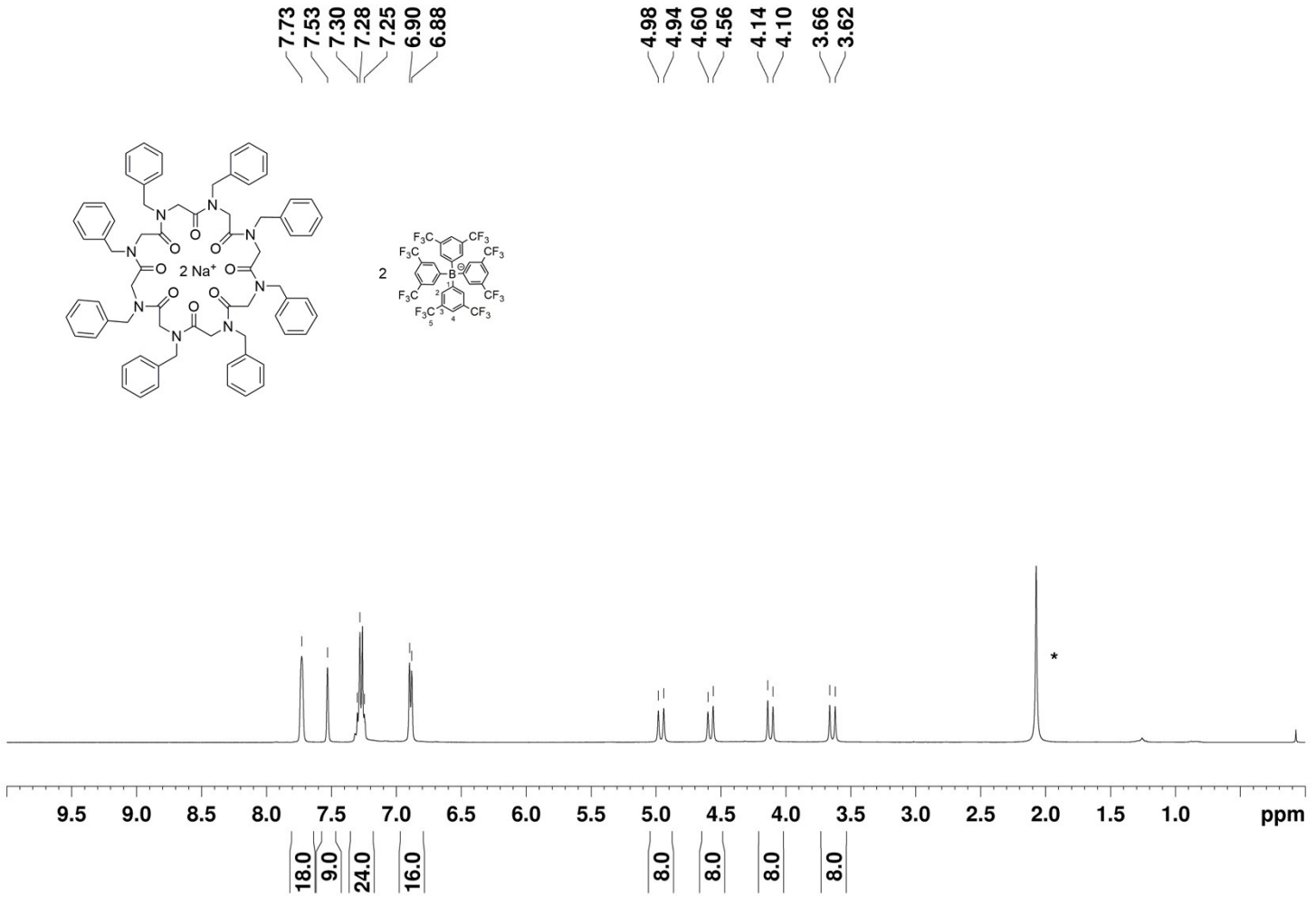
[1·2Na]$^{2+}$2[TFPB]$^{-}$: ^{13}C NMR (150 MHz, $CDCl_3$)



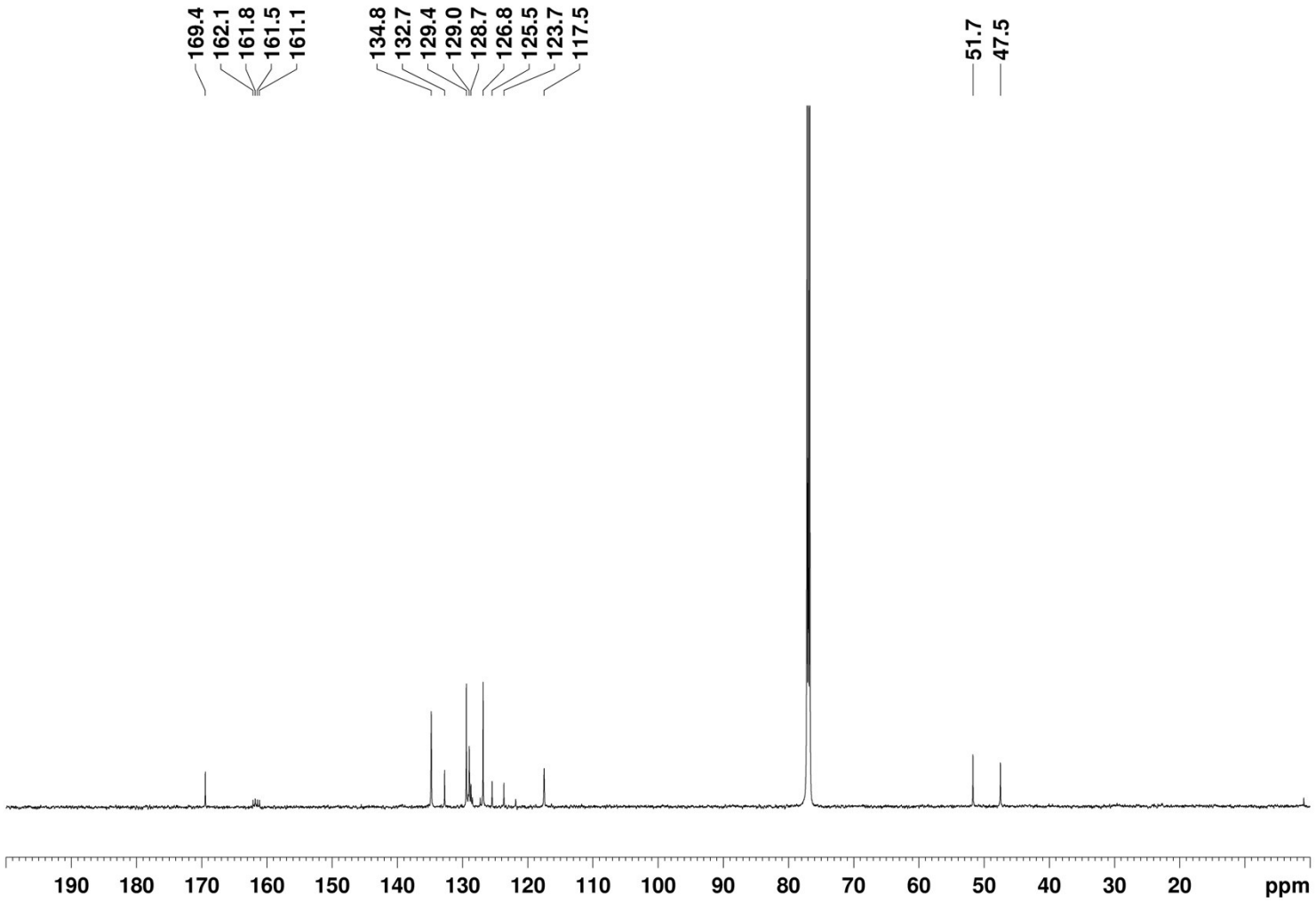
[3·Na]$^{+}$TFPB^{-}: ^{1}H NMR (400 MHz, $CDCl_3$). Water impurities are labelled with a black asterisk.



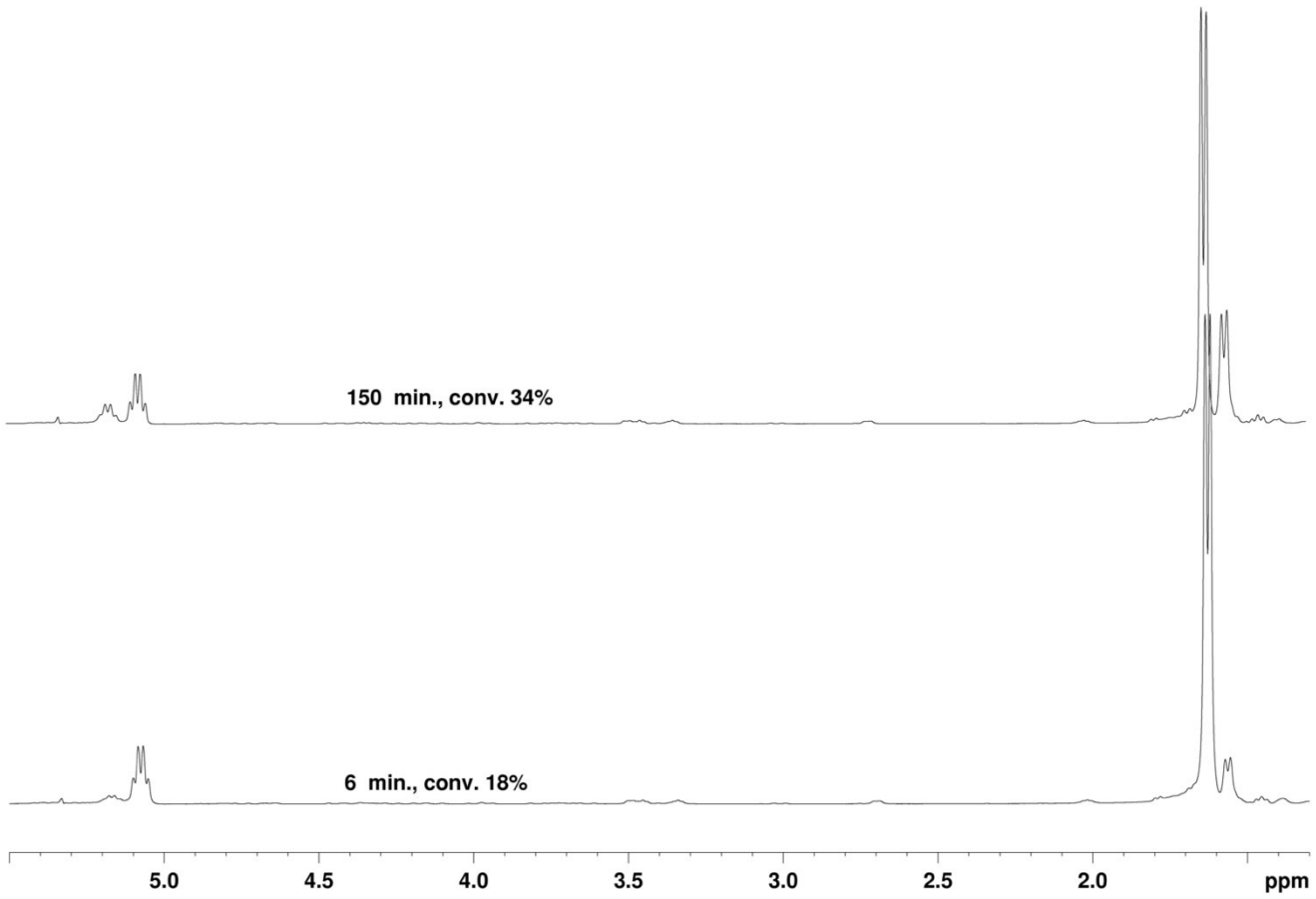
[3·Na]$^{+}$TFPB^{-}: ^{13}C NMR (150 MHz, $CDCl_3$)



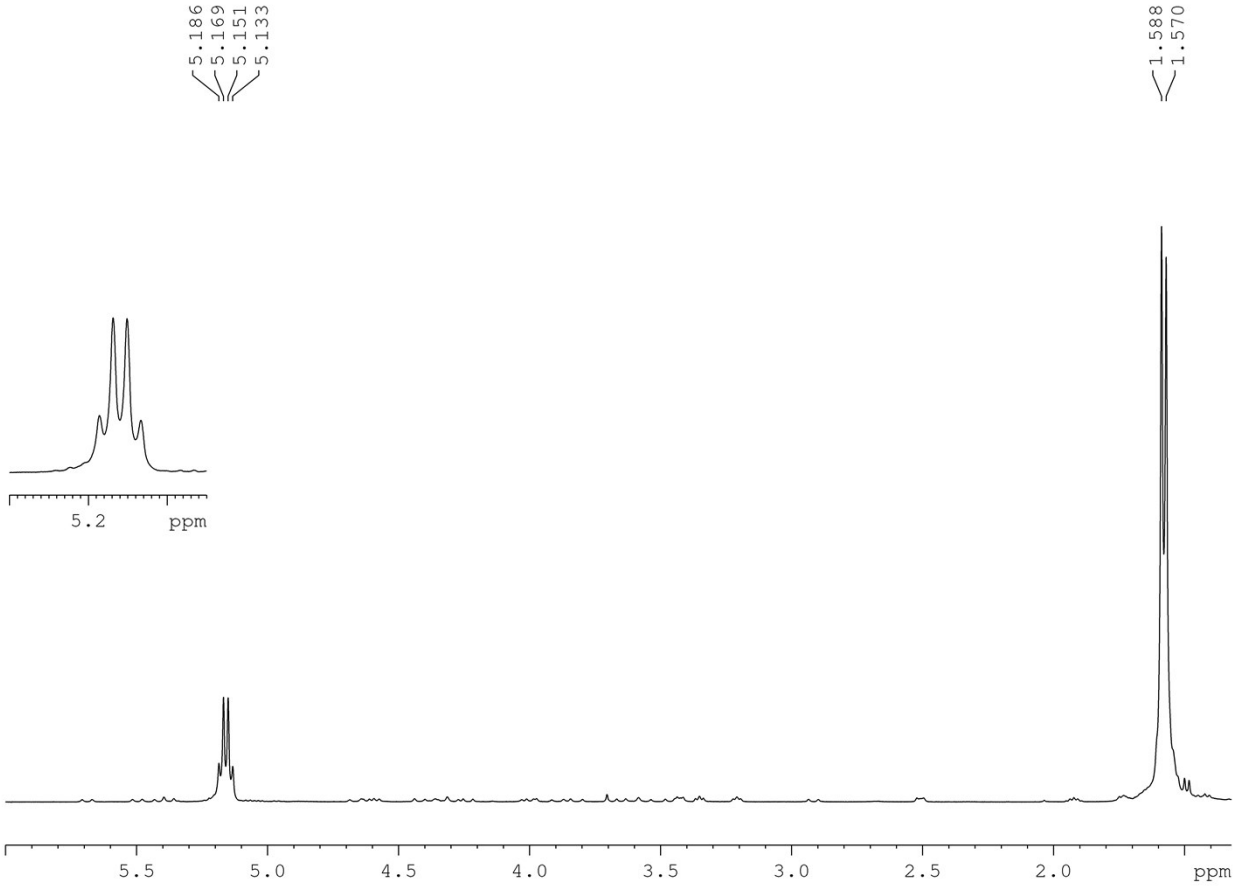
[3·2Na]$^{2+}$2[TFPB]$^{-}$: ^{1}H NMR (400 MHz, $CDCl_3$). Water impurities are labelled with a black asterisk.



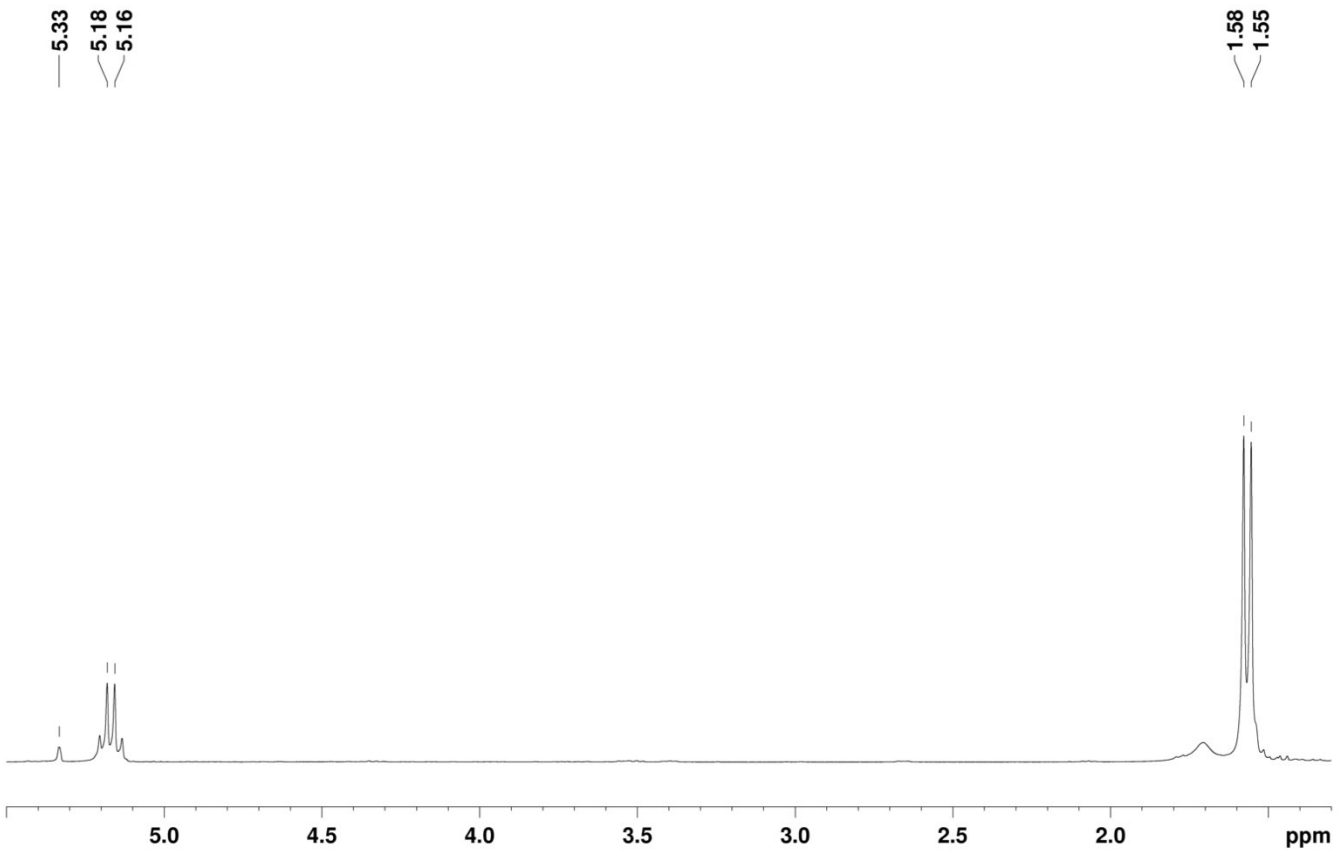
[3·2Na]$^{2+}$2[TFPB]$^{-}$: ^{13}C NMR (150 MHz, $CDCl_3$)



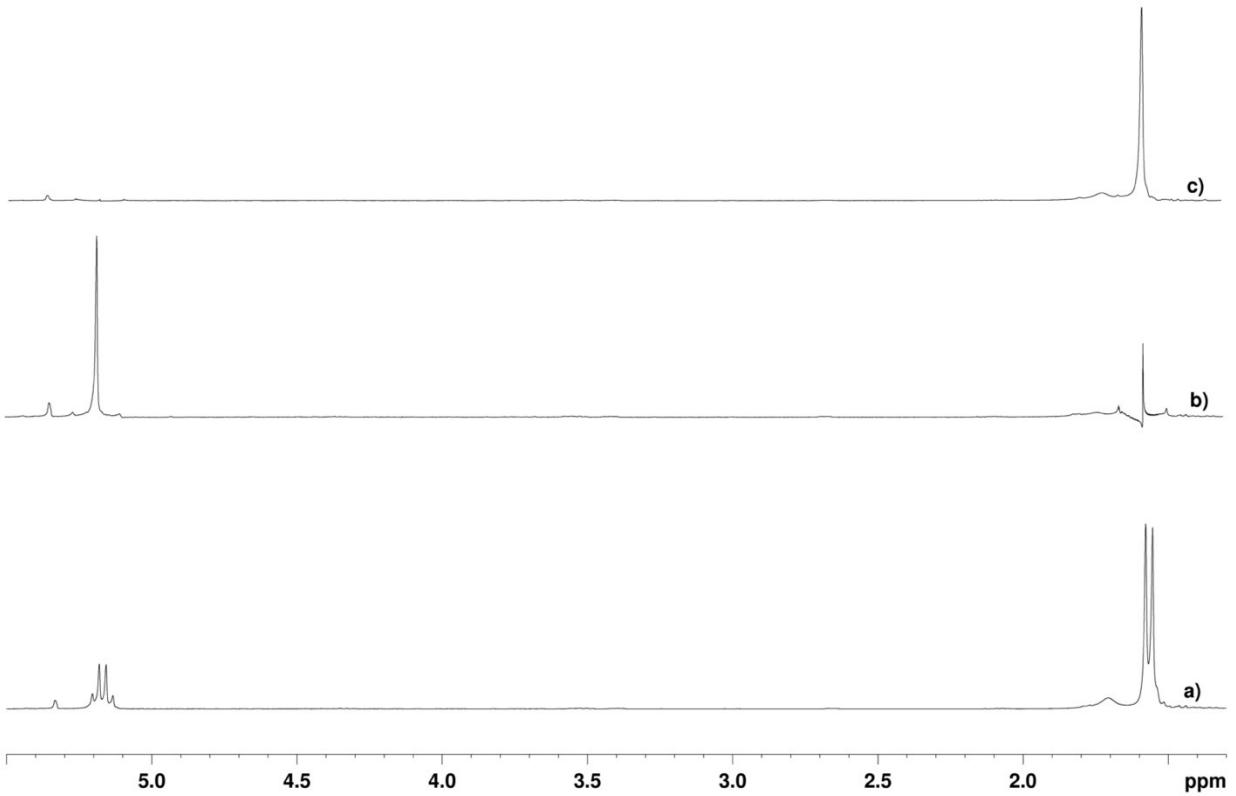
^{1}H NMR of $_L$-LA polymerization in the presence of *[1·2Na]*$^{2+}$
(L-LA:Na^+:DBU:iPrOH ratio 100:1:1:1, CD_2Cl_2, T = 20°C and L-LA 0.5 M.)



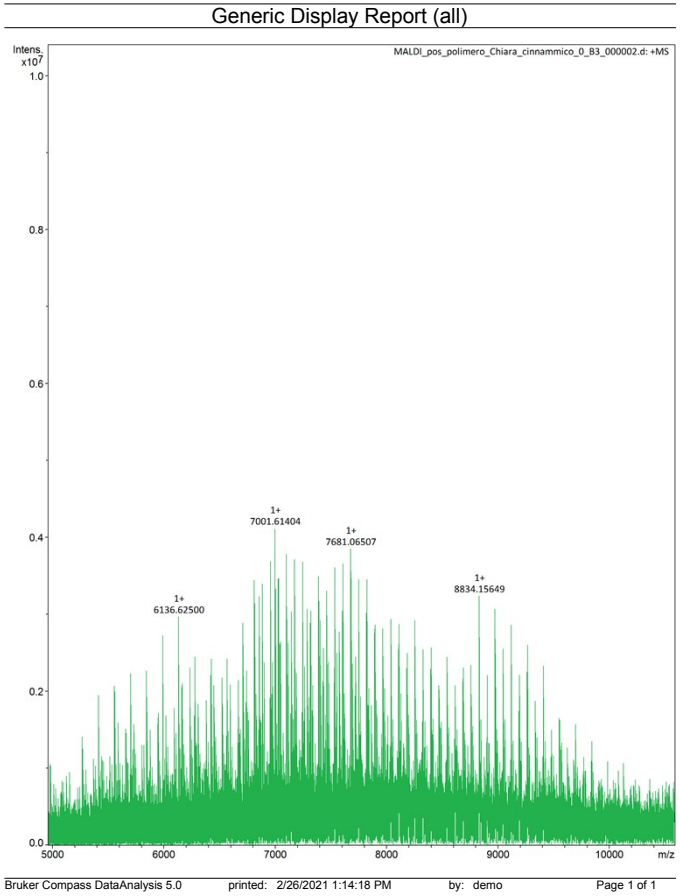
^{1}H NMR of PLA obtained in the presence of $[1{\cdot}2Na]^{2+}$
(L-LA:Na^+:DBU:iPrOH ratio 20:1:1:1, CD_2Cl_2, T = 20°C and L-LA 0.4 M.)



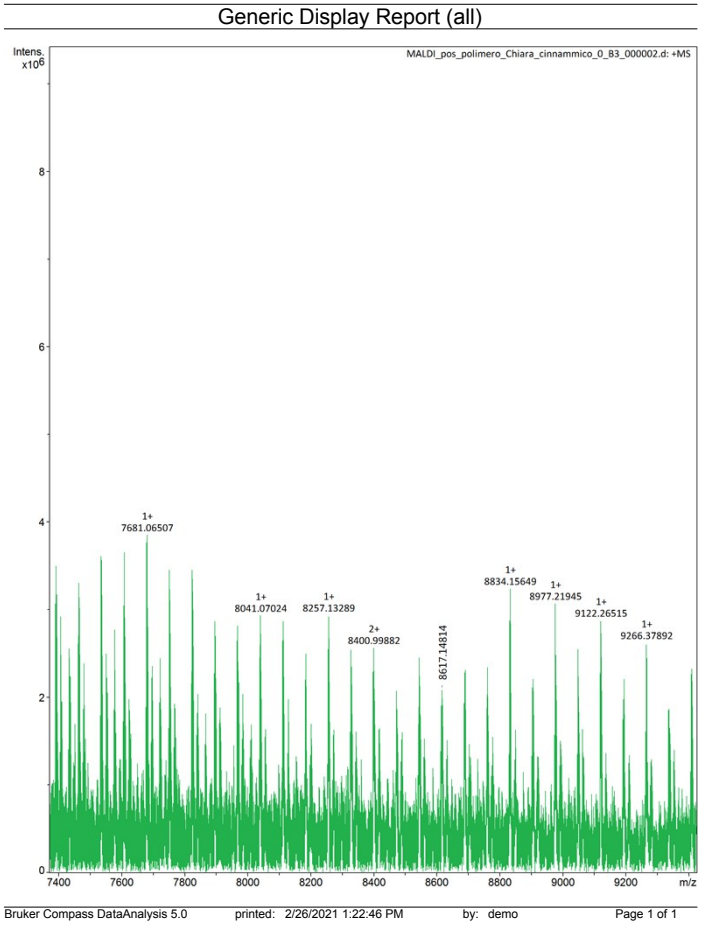
^{1}H NMR of PLA obtained in the presence of $[1{\cdot}2Na]^{2+}$
(L-LA:Na^+:DBU:iPrOH ratio 50:1:1:1, CD_2Cl_2, T = 20°C and L-LA 0.5 M.)



^{1}H decoupled NMR of PLA obtained in the presence of $[1{\cdot}2Na]^{2+}$
(L-LA:Na^{+}:DBU:iPrOH ratio 50:1:1:1, CD_2Cl_2, T = 20°C and L-LA 0.5 M.)



MALDI-MS of PLA obtained in the presence of $[1{\cdot}2Na]^{2+}$
(L-LA:Na^+:DBU:iPrOH ratio 50:1:1:1, CD_2Cl_2, T = 20°C and L-LA 0.5 M.)



MALDI-MS of PLA obtained in the presence of $[1{\cdot}2Na]^{2+}$
(L-LA:Na^+:DBU:iPrOH ratio 50:1:1:1, CD_2Cl_2, T = 20°C and L-LA 0.5 M.)

2.0 Computational details and Cartesian Coordinates

2.1 Computational details

The DFT calculations were performed with the Gaussian09 set of programs,[1] using the BP86 functional of Becke and Perdew.[2] The electronic configuration of the molecular systems was described with the standard triple zeta valence basis set with a polarization function of Ahlrichs and co-workers for H, C, N, O, Na (TZVP keyword in Gaussian).[3] The geometry optimizations were performed without symmetry constraints, and the characterization of the located stationary points was performed by analytical frequency calculations.

Topographic steric maps and %V_{Bur} calculation. %V_{Bur} was calculated with the software developed by Cavallo and coworkers[4], starting from DFT optimized structures by choosing the metal as center of the sphere, selecting atomic bondi radii scaled by 1.17 and radius sphere of 3.5.

[1] Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; N. Kudin, K.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

[2] a) Becke, A. Phys. Rev. A 1988, 38, 3098– 3100. b) Perdew, J. P. Phys. Rev. B 1986, 33, 8822– 8824. c) Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7406– 7406.

[3] Schaefer, A., Horn, H. and Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829– 5835.

[4] a) Falivene, L.; Credendino, R.; Poater, A.; Petta, A.; Serra, L.; Oliva, R.; Scarano, V.; Cavallo L. *Organometallics* **2016**, *35 (13)*, 2286–2293. b) Falivene, L.; Cao, Z.; Petta, A.; Serra, L.; Poater, A.; Oliva, R.; Scarano, V.; Cavallo, L. Nat. Chem. **2019**, 11, 872-879.

2.2 Cartesian coordinates and energies of calculated structures

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[**1**·2Na]$^{2+}$ E(gas)=-2716.88225345

C	0.819178	2.313180	-0.786397
C	-0.122952	3.234646	0.022565
N	-1.504252	2.752693	-0.140886
C	-1.852860	1.659332	0.575113
C	-3.162733	0.907137	0.250381
N	-3.015442	-0.517473	0.577708
C	-2.167410	-1.233198	-0.210028
C	-1.798405	-2.685420	0.168466
O	-1.104579	1.224710	1.481400
O	-1.656695	-0.714300	-1.222279
O	0.422551	1.918731	-1.898956
N	-0.442648	-3.003989	-0.300371
C	0.585128	-2.456569	0.391137
C	2.048934	-2.623451	-0.048382
O	0.364705	-1.786764	1.429517
N	2.714812	-1.306287	-0.051626
C	2.351451	-0.462816	-1.057583
O	1.572171	-0.871001	-1.943944
C	2.850529	0.999399	-1.102480
N	2.027069	1.922295	-0.282419
H	0.110389	3.280206	1.090355
H	-3.426264	1.011739	-0.808831
H	2.164688	-3.091962	-1.030499
H	2.787094	1.304866	-2.154696
H	3.892160	1.114186	-0.778305
C	3.760130	-1.076388	0.969480
H	2.562275	-3.251116	0.694335
C	-0.350680	-3.831195	-1.529087
H	-1.850108	-2.851361	1.250830
C	-3.827791	-1.050386	1.698452
H	-3.996710	1.306114	0.847187
C	-2.354811	3.436075	-1.150646
H	-0.072136	4.254310	-0.387668
Na	-0.274244	0.012076	-2.847800
Na	-0.189273	-0.222189	2.821022
H	-2.492040	-3.391853	-0.312949
C	2.678860	2.512185	0.913300
H	-3.360277	3.000164	-1.096271
C	-2.432909	4.934007	-0.926023
H	-1.942332	3.227390	-2.150044
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C	-2.078489	7.200835	-1.736314
C	-2.624307	7.712520	-0.555701
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H	1.961824	3.191294	1.390022
C	5.139796	2.946433	1.304190
C	6.324244	3.649814	1.054956
C	6.344704	4.662257	0.091681
C	5.178376	4.973057	-0.619272
C	3.995228	4.274655	-0.366298
H	5.128644	2.163611	2.068860
H	7.229455	3.406142	1.614097
H	7.266897	5.211865	-0.104960
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H	4.143263	-0.056014	0.837434
H	3.290491	-1.126436	1.965783
C	4.896330	-2.080234	0.895661
C	5.217469	-2.862670	2.015076
C	6.284236	-3.767863	1.966226
C	7.033950	-3.899958	0.793928
C	6.717777	-3.124347	-0.329099
C	5.655818	-2.218306	-0.278548
H	4.637627	-2.758053	2.937123
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H	7.866915	-4.604145	0.753843
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H	0.705063	-3.921321	-1.806270
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H	-0.853714	-3.282846	-2.341454
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C	-2.144692	-7.747088	-1.117273
C	-1.081317	-7.374252	-0.284803
C	-0.504410	-6.108208	-0.408998
H	-2.426494	-4.885504	-2.953267
H	-3.451536	-7.138754	-2.729797
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H	0.331649	-5.832276	0.240044
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H	-3.504169	-0.564894	2.635413
C	-5.317437	-0.825215	1.511714
C	-6.038988	-0.080828	2.456949
C	-7.418664	0.106192	2.309377
C	-8.084098	-0.446163	1.211459
C	-7.369877	-1.189217	0.262337
C	-5.994416	-1.380179	0.412630
H	-5.524781	0.344688	3.323992
H	-7.972523	0.679866	3.054721

H	-9.160042	-0.303840	1.095843
H	-7.890515	-1.628839	-0.590517
H	-5.447686	-1.969424	-0.329068

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[**2**·Na]$^+$ E(gas)=-3033.33805958

C	2.653790	-1.428561	0.273494
N	3.679958	-0.626383	-0.139377
C	3.683794	0.739707	0.382035
C	2.566828	1.585747	-0.277196
C	2.482398	-2.820245	-0.383911
C	-2.564203	-1.581999	0.271713
N	-2.382811	-2.871868	-0.141214
C	-1.201836	-3.558516	0.380595
C	0.089834	-3.014046	-0.277632
N	1.297384	-3.500561	0.136702
O	-1.840343	-1.080176	1.147151
O	0.017615	-2.138263	-1.155372
O	1.856699	-1.052454	1.148461
O	1.845511	1.085030	-1.155552
C	-3.052710	-3.473293	-1.311085
C	1.482629	-4.381955	1.306284
C	4.537238	-0.906270	-1.307788
C	-0.088647	3.014604	0.271376
N	-1.296265	3.502867	-0.141377
C	-2.481157	2.822486	0.379486
C	-2.654586	1.431857	-0.279142
C	1.202931	3.561229	-0.385487
N	-3.679246	0.629075	0.135770
C	-3.683342	-0.737077	-0.385432
N	2.383939	2.874951	0.136692
O	-0.016296	2.136645	1.146722
O	-1.860299	1.057021	-1.157453
C	-4.532582	0.908283	1.307683
C	3.050969	3.475416	1.308795
C	-1.481163	4.386116	-1.309738
H	4.678259	1.172881	0.199212
H	3.513711	0.701348	1.467041
H	3.355339	-3.463294	-0.198495
H	2.365885	-2.694398	-1.469379
H	-1.150433	-3.392346	1.465673
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H	-2.363408	2.695146	1.464628
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Na	0.000391	0.001276	-0.017922
C	3.511406	4.902065	1.068762
H	2.361556	3.438977	2.169804
H	3.917168	2.850513	1.563602

H	-1.789295	3.774981	-2.175512
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H	-0.507137	4.828273	-1.557990
C	-5.997389	0.587375	1.070993
H	-4.153221	0.334648	2.170846
H	-4.427908	1.972405	1.557367
H	-2.364486	-3.440397	-2.173210
C	-3.516560	-4.898293	-1.067530
H	-3.917652	-2.846693	-1.566161
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C	2.490832	-5.491225	1.065600
H	1.792385	-3.769347	2.170426
H	4.164836	-0.328098	-2.170983
C	6.002767	-0.593422	-1.063830
H	4.428264	-1.968949	-1.561892
C	-6.691784	-0.232509	1.972571
C	-8.053565	-0.500861	1.788264
C	-8.731827	0.043706	0.693956
C	-8.044955	0.859870	-0.213951
C	-6.687680	1.132179	-0.024937
H	-6.164586	-0.659182	2.830666
H	-8.583153	-1.137219	2.500246
H	-9.793324	-0.165355	0.547423
H	-8.571790	1.290080	-1.068295
H	-6.156992	1.769887	-0.736996
C	3.543528	-5.691501	1.970720
C	4.454767	-6.737921	1.783749
C	4.325012	-7.590003	0.683189
C	3.279485	-7.394284	-0.228214
C	2.366798	-6.353889	-0.036508
H	3.647657	-5.027204	2.833372
H	5.267232	-6.885025	2.498307
H	5.035346	-8.405611	0.534361
H	3.172442	-8.059621	-1.087526
H	1.552759	-6.206433	-0.751295
C	3.152930	5.916888	1.968198
C	3.606589	7.228144	1.780673
C	4.418512	7.537415	0.685569
C	4.777697	6.530918	-0.220017
C	4.329453	5.221610	-0.028019
H	2.518606	5.678302	2.826686
H	3.323270	8.007814	2.490723
H	4.772215	8.559492	0.536561
H	5.414474	6.767509	-1.075053
H	4.613115	4.440404	-0.738343
C	-3.164338	-5.915546	-1.966612
C	-3.621391	-7.225143	-1.775470
C	-4.430549	-7.530182	-0.677175
C	-4.783646	-6.521153	0.228042
C	-4.332047	-5.213570	0.032450
H	-2.532302	-5.680259	-2.827700

H	-3.342839	-8.006809	-2.485211
H	-4.786910	-8.550926	-0.525384
H	-5.418329	-6.754516	1.085518
H	-4.610795	-4.430291	0.742426
C	6.707282	0.217906	-1.965256
C	8.069903	0.477785	-1.775094
C	8.738892	-0.066776	-0.675098
C	8.041810	-0.874255	0.232786
C	6.683675	-1.138107	0.038006
H	6.187388	0.644804	-2.827682
H	8.607364	1.107664	-2.486936
H	9.801036	0.135650	-0.524021
H	8.561330	-1.304226	1.091722
H	6.144901	-1.768953	0.750088
C	-3.546709	5.691512	-1.969303
C	-4.459045	6.736662	-1.780135
C	-4.326540	7.590318	-0.681158
C	-3.277156	7.397644	0.226531
C	-2.363489	6.358603	0.032623
H	-3.652798	5.026089	-2.830846
H	-5.274392	6.881608	-2.491847
H	-5.037633	8.404976	-0.530745
H	-3.167922	8.064445	1.084429
H	-1.546385	6.213351	0.744373

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[**2**·2Na]$^{2+}$ E(gas)=-3195.46130146

C	2.731151	1.278757	-0.281673
N	3.678255	0.430783	0.190813
C	3.650671	-0.939407	-0.309578
C	2.460056	-1.730789	0.271685
C	2.646512	2.690915	0.334218
C	-2.459885	1.731464	-0.272285
N	-2.213091	2.970394	0.220141
C	-1.006775	3.643204	-0.250654
C	0.266579	3.002444	0.340184
N	1.468572	3.411309	-0.137333
O	-1.742384	1.233927	-1.165725
O	0.184157	2.127492	1.227939
O	1.940359	0.931686	-1.184410
O	1.742565	-1.233148	1.165078
C	-2.978467	3.625934	1.311044
C	1.655150	4.392359	-1.238179
C	4.615948	0.732426	1.303068
C	-0.266403	-3.001975	-0.340910
N	-1.468441	-3.410866	0.136547
C	-2.646322	-2.690423	-0.335061
C	-2.730831	-1.278240	0.280829
C	1.006892	-3.642492	0.250238
N	-3.677880	-0.430201	-0.191563
C	-3.650391	0.939930	0.309015
N	2.213246	-2.969783	-0.220606

O	-0.184005	-2.127240	-1.228877
O	-1.939891	-0.931225	1.183478
C	-4.616096	-0.731729	-1.303419
C	2.978505	-3.625364	-1.311584
C	-1.655171	-4.391481	1.237723
H	4.606089	-1.414782	-0.040670
H	3.582716	-0.920005	-1.406011
H	3.533691	3.286549	0.070900
H	2.603170	2.614316	1.429208
H	-0.972485	3.593041	-1.347681
H	-1.081890	4.703445	0.035175
H	-3.533548	-3.286000	-0.071802
H	-2.602898	-2.613797	-1.430044
H	1.082081	-4.702823	-0.035235
H	0.972498	-3.591952	1.347243
H	-3.582310	0.920421	1.405441
H	-4.605893	1.415238	0.040284
Na	-0.007917	-0.017333	1.893674
C	3.334902	-5.066717	-1.000701
H	2.381324	-3.576457	-2.237755
H	3.894320	-3.045379	-1.481278
H	-1.852127	-3.839609	2.172481
C	-2.776706	-5.377520	0.975927
H	-0.711492	-4.935782	1.367845
C	-6.043569	-0.313161	-1.007391
H	-4.256668	-0.222688	-2.213611
H	-4.579979	-1.811240	-1.495202
H	-2.381323	3.577163	2.237247
C	-3.335030	5.067237	1.000073
H	-3.894207	3.045832	1.480754
H	0.711495	4.936815	-1.367798
C	2.776839	5.378184	-0.976305
H	1.851795	3.840850	-2.173212
H	4.255349	0.224764	2.213574
C	6.043213	0.312043	1.008580
H	4.580923	1.812198	1.493623
C	-6.697329	0.597683	-1.850978
C	-8.028542	0.958943	-1.610516
C	-8.713172	0.415977	-0.519580
C	-8.066689	-0.492382	0.328903
C	-6.740586	-0.857449	0.084966
H	-6.168261	1.016150	-2.712143
H	-8.530844	1.660908	-2.278784
H	-9.751834	0.694138	-0.331905
H	-8.603261	-0.924426	1.175835
H	-6.246535	-1.574573	0.746545
C	3.849220	5.474732	-1.876052
C	4.866742	6.414242	-1.670378
C	4.822632	7.259664	-0.558179
C	3.756766	7.167836	0.346439
C	2.737619	6.235740	0.136727

H	3.882386	4.822580	-2.753642
H	5.691039	6.487488	-2.382338
H	5.613790	7.994268	-0.397430
H	3.715736	7.833432	1.210812
H	1.903729	6.179918	0.842200
C	2.931845	-6.093335	-1.867892
C	3.288221	-7.422451	-1.608781
C	4.045047	-7.735086	-0.475932
C	4.449374	-6.715895	0.396099
C	4.099872	-5.389243	0.133427
H	2.346942	-5.852761	-2.760443
H	2.976880	-8.212165	-2.295125
H	4.325530	-8.770346	-0.273570
H	5.048095	-6.956719	1.276712
H	4.427573	-4.599383	0.815208
Na	0.007970	0.017966	-1.893855
C	-2.932177	6.093927	1.867272
C	-3.288710	7.422989	1.608091
C	-4.045486	7.735484	0.475172
C	-4.449601	6.716218	-0.396873
C	-4.099946	5.389622	-0.134131
H	-2.347293	5.853457	2.759863
H	-2.977524	8.212771	2.294429
H	-4.326093	8.770701	0.272762
H	-5.048266	6.956945	-1.277548
H	-4.427447	4.599691	-0.815926
C	6.695720	-0.597691	1.854328
C	8.026814	-0.960408	1.615418
C	8.712550	-0.420089	0.523862
C	8.067297	0.487104	-0.326806
C	6.741326	0.853683	-0.084393
H	6.165760	-1.014148	2.715916
H	8.528162	-1.661460	2.285361
H	9.751112	-0.699421	0.337390
H	8.604725	0.917072	-1.174250
H	6.248192	1.569892	-0.747644
C	-3.848742	-5.474596	1.876020
C	-4.866082	-6.414327	1.670442
C	-4.822135	-7.259438	0.558002
C	-3.756606	-7.167077	-0.346961
C	-2.737639	-6.234763	-0.137353
H	-3.881798	-4.822674	2.753785
H	-5.690119	-6.487972	2.382663
H	-5.613164	-7.994194	0.397318
H	-3.715703	-7.832419	-1.211537
H	-1.904015	-6.178495	-0.843103

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[**3**·Na]$^+$ E(gas)=-3990.37028491

C	3.411768	-2.514054	-0.416366
C	2.250342	-3.063397	-1.281134
C	5.591737	-1.467796	-0.257053

N	4.516087	-2.051911	-1.072773
C	5.080966	1.961832	1.410713
N	5.209226	0.508943	1.235146
C	5.335927	0.033113	-0.039964
C	-4.270232	-1.959984	0.159167
N	-4.829229	-0.661800	0.509091
C	-4.218604	0.430193	-0.027362
N	1.229749	-3.672348	-0.435829
C	0.162758	-2.907955	-0.064014
C	-0.861009	-3.523843	0.910522
C	1.732455	3.799915	1.148391
N	2.958028	3.133154	0.733066
C	3.627635	2.396694	1.687010
N	-2.231467	-3.320677	0.435649
C	-2.872703	-2.164368	0.777756
C	-4.728781	1.826290	0.390733
N	-3.936226	2.870674	-0.244804
C	-2.663249	3.015376	0.236780
C	-1.702697	3.959273	-0.508195
N	-0.534567	4.283426	0.296856
C	0.485889	3.370444	0.361630
O	0.419886	2.274887	-0.224771
O	-2.277243	2.393872	1.239023
O	-3.282117	0.316780	-0.839018
O	-2.362814	-1.315798	1.524891
O	-0.012082	-1.753445	-0.493236
O	3.318994	-2.516763	0.817474
O	5.271610	0.773640	-1.036804
O	3.117476	2.128456	2.782063
C	5.178887	-0.312134	2.456256
C	6.529093	-0.505038	3.133032
C	3.442308	3.426469	-0.621309
C	3.974123	4.839368	-0.815512
C	-0.707593	5.418548	1.224560
C	-0.929663	6.749560	0.528007
C	-4.386171	3.334477	-1.571215
C	-5.786258	3.921483	-1.557084
C	-5.828289	-0.629268	1.592570
C	-7.099898	-1.394986	1.268790
C	-2.809412	-4.340416	-0.456944
C	-3.879685	-5.223729	0.170641
C	1.555241	-4.979065	0.169515
C	0.795048	-6.168233	-0.398168
C	4.658325	-1.937166	-2.532944
C	5.748568	-2.825617	-3.113863
H	2.610244	-3.814265	-2.001274
H	1.778302	-2.240094	-1.836005
H	6.527882	-1.556211	-0.827136
H	5.690710	-2.043844	0.667604
H	5.531091	2.453758	0.542756
H	5.646615	2.242466	2.311763

H	-4.183560	-2.029551	-0.935544
H	-4.966060	-2.745591	0.488206
H	-0.745776	-2.999287	1.871872
H	-0.711275	-4.597788	1.067242
H	1.885323	4.886979	1.052777
H	1.584989	3.552660	2.213462
H	-4.640746	1.934918	1.480432
H	-5.781717	1.969008	0.106745
H	-2.185866	4.907105	-0.786758
H	-1.372837	3.457961	-1.431506
H	4.709742	-1.276772	2.211416
H	4.483769	0.188308	3.148086
H	2.605030	3.247342	-1.314942
H	4.201637	2.674610	-0.888748
H	0.170199	5.473677	1.880011
H	-1.563813	5.193155	1.883959
H	-4.337281	2.488400	-2.278631
H	-3.674237	4.089151	-1.930634
H	-6.073718	0.419331	1.804678
H	-5.366366	-1.035406	2.508477
H	-1.971072	-4.970330	-0.795123
H	-3.206560	-3.862070	-1.366484
H	1.437982	-4.926222	1.261540
H	2.634736	-5.125319	0.013124
H	4.869741	-0.880872	-2.761995
H	3.691965	-2.173219	-3.000018
Na	-1.008783	0.328940	0.245735
C	6.517032	-2.358982	-4.191615
C	7.487602	-3.175562	-4.781327
C	7.708954	-4.467470	-4.292348
C	6.956379	-4.936461	-3.209768
C	5.981987	-4.120651	-2.625957
H	6.356732	-1.345182	-4.568980
H	8.079077	-2.797634	-5.617906
H	8.470736	-5.103665	-4.747349
H	7.130602	-5.940626	-2.817072
H	5.409870	-4.489355	-1.770520
C	6.553588	-1.010264	4.444798
C	7.765809	-1.239450	5.099397
C	8.977562	-0.958293	4.455503
C	8.963385	-0.447259	3.155389
C	7.746339	-0.223745	2.497965
H	5.611316	-1.223947	4.957671
H	7.766030	-1.631765	6.118766
H	9.925730	-1.132142	4.968255
H	9.902469	-0.218185	2.646706
H	7.750885	0.182067	1.483461
C	3.869534	5.444717	-2.078979
C	4.403664	6.716125	-2.310272
C	5.039671	7.409664	-1.274293
C	5.140542	6.820537	-0.009848

C	4.612989	5.544074	0.216251
H	3.373076	4.908340	-2.893132
H	4.320352	7.168285	-3.301151
H	5.454305	8.404003	-1.451825
H	5.633773	7.355052	0.804984
H	4.696917	5.095616	1.209639
C	-1.961586	7.598167	0.956600
C	-2.151149	8.849468	0.359054
C	-1.311817	9.261858	-0.680365
C	-0.281473	8.419837	-1.116442
C	-0.089775	7.172562	-0.515283
H	-2.619093	7.280096	1.771026
H	-2.956543	9.500770	0.704918
H	-1.458358	10.236777	-1.149570
H	0.380598	8.738897	-1.924004
H	0.719208	6.523827	-0.861720
C	-6.737175	3.489671	-2.493454
C	-8.017648	4.054856	-2.521248
C	-8.361177	5.053508	-1.605389
C	-7.419400	5.487003	-0.663500
C	-6.139518	4.926607	-0.641563
H	-6.471514	2.708924	-3.211978
H	-8.747209	3.712545	-3.258117
H	-9.359803	5.494394	-1.623838
H	-7.682979	6.268621	0.052130
H	-5.407514	5.267040	0.095343
C	-7.630096	-2.298469	2.200960
C	-8.831425	-2.967881	1.940691
C	-9.511117	-2.743570	0.740100
C	-8.985665	-1.847377	-0.199131
C	-7.788765	-1.176293	0.064479
H	-7.101326	-2.477071	3.141405
H	-9.233356	-3.667568	2.676256
H	-10.447781	-3.265476	0.534257
H	-9.513922	-1.668081	-1.138006
H	-7.384551	-0.478990	-0.674309
C	-4.834618	-5.831432	-0.659688
C	-5.793418	-6.698108	-0.126833
C	-5.812134	-6.964436	1.246647
C	-4.868813	-6.357185	2.081758
C	-3.907335	-5.492320	1.547050
H	-4.829145	-5.624575	-1.733919
H	-6.531428	-7.161444	-0.784921
H	-6.561586	-7.639523	1.664446
H	-4.878328	-6.558461	3.155180
H	-3.179496	-5.017751	2.209503
C	0.560658	-7.284339	0.421122
C	-0.073268	-8.422526	-0.087736
C	-0.484670	-8.458051	-1.424185
C	-0.259685	-7.348922	-2.247077
C	0.375558	-6.210779	-1.737460

H	0.881662	-7.265209	1.466787
H	-0.249388	-9.281637	0.562734
H	-0.979910	-9.345582	-1.822591
H	-0.575203	-7.370776	-3.292481
H	0.543641	-5.349041	-2.388021

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[**3**·2Na]$^{2+}$ E(gas)=-4152.51021598

C	1.837506	3.556662	0.037589
C	0.504645	3.850901	0.755352
C	4.214258	3.317732	0.029254
N	3.006984	3.830675	0.674805
C	5.215314	-0.351105	-0.414030
N	5.252030	1.106785	-0.498847
C	4.266035	1.777436	0.144862
C	-5.215353	0.351068	-0.413825
N	-5.252073	-1.106816	-0.498715
C	-4.266080	-1.777501	0.144961
N	-0.614339	3.886937	-0.186232
C	-1.213332	2.727607	-0.563778
C	-2.470537	2.820838	-1.453223
C	2.470418	-2.820795	-1.453414
N	3.648958	-2.229342	-0.805040
C	3.961528	-0.930969	-1.094925
N	-3.649053	2.229347	-0.804839
C	-3.961591	0.930971	-1.094735
C	-4.214307	-3.317794	0.029286
N	-3.007012	-3.830758	0.674780
C	-1.837556	-3.556700	0.037540
C	-0.504667	-3.850938	0.755253
N	0.614290	-3.886943	-0.186367
C	1.213250	-2.727598	-0.563915
O	0.794088	-1.604343	-0.184928
O	-1.812034	-3.035123	-1.092625
O	-3.397941	-1.169945	0.807514
O	-3.262479	0.243382	-1.859059
O	-0.794164	1.604343	-0.184829
O	1.811943	3.035133	-1.092599
O	3.397892	1.169844	0.807378
O	3.262435	-0.243356	-1.859245
C	6.273750	1.714948	-1.376451
C	7.697851	1.395104	-0.957082
C	4.487595	-3.100965	0.044879
C	5.818708	-3.514852	-0.566678
C	0.849791	-5.191814	-0.850780
C	1.935746	-6.063268	-0.240441
C	-3.129770	-4.237321	2.091956
C	-4.150965	-5.337745	2.311260
C	-6.273799	-1.714935	-1.376343
C	-7.697896	-1.395097	-0.956957
C	-4.487685	3.100927	0.045126
C	-5.818788	3.514868	-0.566416

C	-0.849841	5.191826	-0.850592
C	-1.935614	6.063368	-0.240049
C	3.129787	4.237174	2.091995
C	4.150982	5.337596	2.311316
H	0.520502	4.810233	1.289401
H	0.326834	3.053075	1.493612
H	5.084189	3.786766	0.511529
H	4.203371	3.610376	-1.029235
H	5.237676	-0.657045	0.641504
H	6.123001	-0.753112	-0.887664
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H	-6.123061	0.753101	-0.887398
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H	-2.717841	3.854406	-1.717216
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H	2.266926	-2.249741	-2.371917
H	-4.203451	-3.610396	-1.029214
H	-5.084223	-3.786848	0.511570
H	-0.520497	-4.810279	1.289286
H	-0.326841	-3.053125	1.493523
H	6.118718	2.801788	-1.379444
H	6.095549	1.366591	-2.407136
H	3.884593	-3.997694	0.258923
H	4.655653	-2.614181	1.018637
H	1.038273	-5.028121	-1.920554
H	-0.116219	-5.721446	-0.814512
H	-3.396252	-3.347729	2.687673
H	-2.142591	-4.567855	2.441851
H	-6.118776	-2.801776	-1.379380
H	-6.095599	-1.366538	-2.407014
H	-3.884678	3.997639	0.259227
H	-4.655755	2.614086	1.018853
H	-1.038523	5.028156	-1.920334
H	0.116218	5.721381	-0.814497
H	3.396296	3.347557	2.687662
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Na	1.533989	0.694211	-0.604182
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C	5.126679	5.193907	3.309030
C	6.046592	6.219535	3.556275
C	6.003035	7.395209	2.801218
C	5.035210	7.544563	1.799887
C	4.112321	6.523470	1.558901
H	5.163178	4.276784	3.904005
H	6.798391	6.098282	4.338549
H	6.720856	8.195232	2.991417
H	4.997197	8.462420	1.209855
H	3.360433	6.648643	0.774843
C	8.620578	0.940274	-1.910229
C	9.951628	0.697424	-1.551229
C	10.368471	0.900219	-0.232592

C	9.451306	1.347059	0.726852
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H	8.299540	0.782738	-2.943796
H	10.661872	0.349200	-2.303582
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H	9.774736	1.509806	1.757001
H	7.416761	1.947706	1.121704
C	6.891615	-3.820809	0.285113
C	8.109243	-4.267564	-0.237138
C	8.270374	-4.407939	-1.619844
C	7.208715	-4.097180	-2.475866
C	5.988705	-3.654707	-1.952540
H	6.775906	-3.710113	1.367242
H	8.935717	-4.500186	0.437203
H	9.221452	-4.753825	-2.028835
H	7.328624	-4.201507	-3.556186
H	5.170887	-3.410316	-2.635330
C	2.537119	-7.044581	-1.045292
C	3.483472	-7.922365	-0.508355
C	3.843500	-7.827437	0.840367
C	3.255273	-6.848324	1.647162
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C	-6.046558	-6.219713	3.556225
C	-6.003022	-7.395362	2.801128
C	-5.035215	-7.544690	1.799776
C	-4.112324	-6.523595	1.558806
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H	-6.720844	-8.195387	2.991313
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C	-9.951661	-0.697338	-1.551059
C	-10.368509	-0.900215	-0.232437
C	-9.451353	-1.347134	0.726979
C	-8.124588	-1.595511	0.366175
H	-8.299572	-0.782588	-2.943630
H	-10.661897	-0.349051	-2.303390
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H	-9.774787	-1.509946	1.757116
H	-7.416819	-1.947843	1.121793
C	-6.891671	3.820864	0.285394
C	-8.109285	4.267678	-0.236838
C	-8.270427	4.408079	-1.619540
C	-7.208792	4.097282	-2.475579

C	-5.988796	3.654747	-1.952273
H	-6.775952	3.710150	1.367520
H	-8.935741	4.500329	0.437517
H	-9.221493	4.754015	-2.028514
H	-7.328710	4.201630	-3.555896
H	-5.170996	3.410327	-2.635075
C	-2.536732	7.045034	-1.044663
C	-3.482917	7.922876	-0.507533
C	-3.843031	7.827663	0.841148
C	-3.255059	6.848204	1.647704
C	-2.305592	5.970319	1.110771
H	-2.259134	7.129780	-2.099327
H	-3.942197	8.680596	-1.145092
H	-4.580818	8.513536	1.261205
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H	-1.859009	5.207706	1.753881

3.0 X-ray crystallography

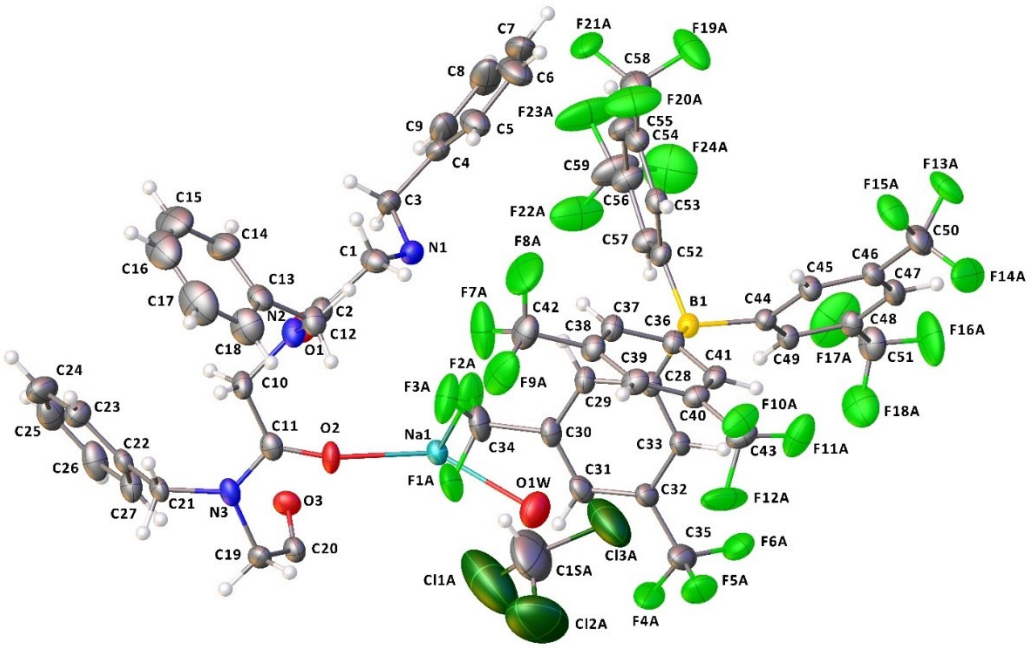

Figure S1. Full ORTEP diagram for [**2**·2Na·$(H_2O)_2$]$^{2+}$ $(TFPB)^-_2$·$CHCl_3$. Ellipsoids are drawn at 20% probability level. For clarity only one possible position is shown for the disordered CF_3 moieties and the chloroform molecule. Atom types: C grey; N blue; O red; Na cyan; F light green; B yellow.