

ELECTRONIC SUPPLEMENTARY INFORMATION

Synthesis of Hyperpolarizable Biomaterials at Molecular Level based on Pyridinium-Chitosan Complexes

Antonio Franconetti,^a Lidia Contreras-Bernal,^a Rafael Prado-Gotor^b and Francisca Cabrera-Escribano^{,a}*

^aDepartamento de Química Orgánica, Facultad de Química, Universidad de Sevilla, C/ Profesor García González 1, 41012 Sevilla, Spain

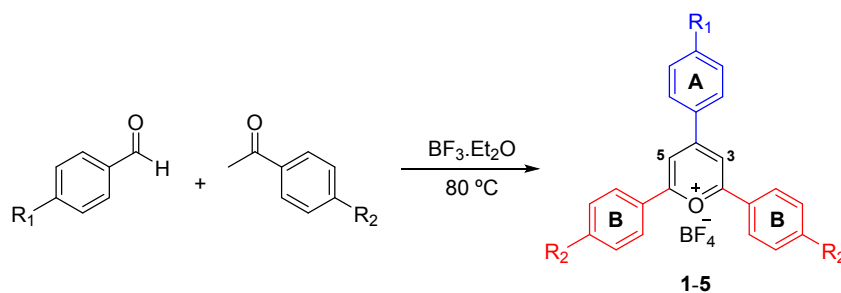
^bDepartamento de Química Física, Facultad de Química, Universidad de Sevilla, C/ Profesor García González 1, 41012 Sevilla, Spain

* fcabrera@us.es

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1. Synthesis of spectral data of pyrylium compounds (1-6)



Compound	R ₁	R ₂	Yield (%)
1	H	H	34
2	H	F	38
3	Ph	F	74
4	Ph	H	70
5	Ph	Me	25
6	OMe	F	11

General Procedure

BF₃·Et₂O (3.1 equiv.) was added dropwise under a N₂ atmosphere to a solution of *p*-substituted benzaldehyde (1 equiv.) and *p*-substituted acetophenone (3 equiv.). The mixture was heated to 80 °C until the reaction was complete, monitored by TLC (1:4 EtOAc–hexane). The residue was eventually treated with EtOH or Et₂O. Crystallization from acetone gave the corresponding pure pyrylium tetrafluoroborate.⁴⁹

2,4,6-Triphenylpyrylium tetrafluoroborate (1)

¹H NMR (500 MHz, DMSO-*d*₆): δ = 9.17 (s, 2H, H-3 and H-5), 8.60 (d, 6H, *J* = 7.5 Hz, H-2a, 6a, 2b,6b, 2c and 6c), 7.88 (t, 3H, *J* = 7.5 Hz, H-4a, 4b and 4c), 7.81 (t, 6H, *J* = 8.0 Hz, H-3a, 5a, 3b, 5b, 3c and 5c).

2,6-Di-(4-fluorophenyl)-4-phenylpyrylium tetrafluoroborate (2)

¹H NMR (500 MHz, DMSO-*d*₆): δ = 9.14 (s, 2H, H-3 and H-5), 8.69 (dd, 4H, *J* = 5.2, *J* = 9.0 Hz, H-2b, 6b, 2c and 6c), 8.59 (d, 2H, *J* = 7.4, H-2a and 6a), 7.88 (t, 1H, *J* = 7.5, H-4a), 7.79 (t, 2H, *J* = 8.1, H-3a and 5a), 7.66 (t, 4H, *J* = 8.8, H-3b, 5b, 3c and 5c)

4-Biphenyl-2,6-di-(4-fluorophenyl)pyrylium tetrafluoroborate (3)

^1H NMR (500 MHz, DMSO- d_6): δ = 9.19 (s, 2H, H-3 and H-5), 8.73 (d, 2H, J = 8.7 Hz, H-2a and 6a), 8.70 (dd, 4H, J = 5.3, J = 9.0 Hz, H-2b, 6b, 2c and 6c), 8.12 (d, 2H, J = 8.6 Hz, H-3a and 5a), 7.94 (d, 2H, J = 7.2 Hz, H-2d and 6d), 7.67 (t, 4H, J = 8.8, H-3b, 5b, 3c and 5c), 7.58 (t, 2H, J = 7.2 Hz, H-3d and 5d), 7.51 (t, 1H, J = 7.4 Hz, H-4d).

4-Biphenyl-2,6-diphenylpyrylium tetrafluoroborate (4)

^1H NMR (500 MHz, DMSO- d_6): δ = 9.21 (s, 2H, H-3 and H-5), 8.75 (d, 2H, J = 8.6 Hz, H-2a and 6a), 8.61 (d, 4H, J = 8.2, H-2b, 6b, 2c and 6c), 8.12 (d, 2H, J = 8.6 Hz, H-3a and 5a), 7.94 (d, 2H, J = 8.1 Hz, H-2d and 6d), 7.88 (t, 2H, J = 7.4 Hz, H-3d and 5d), 7.81 (t, 4H, J = 7.9 Hz, H-3b, 5b, 3c and 5c), 7.58 (t, 2H, J = 7.2 Hz, H-4b and 4c), 7.52 (t, 1H, J = 7.3 Hz, H-4d).

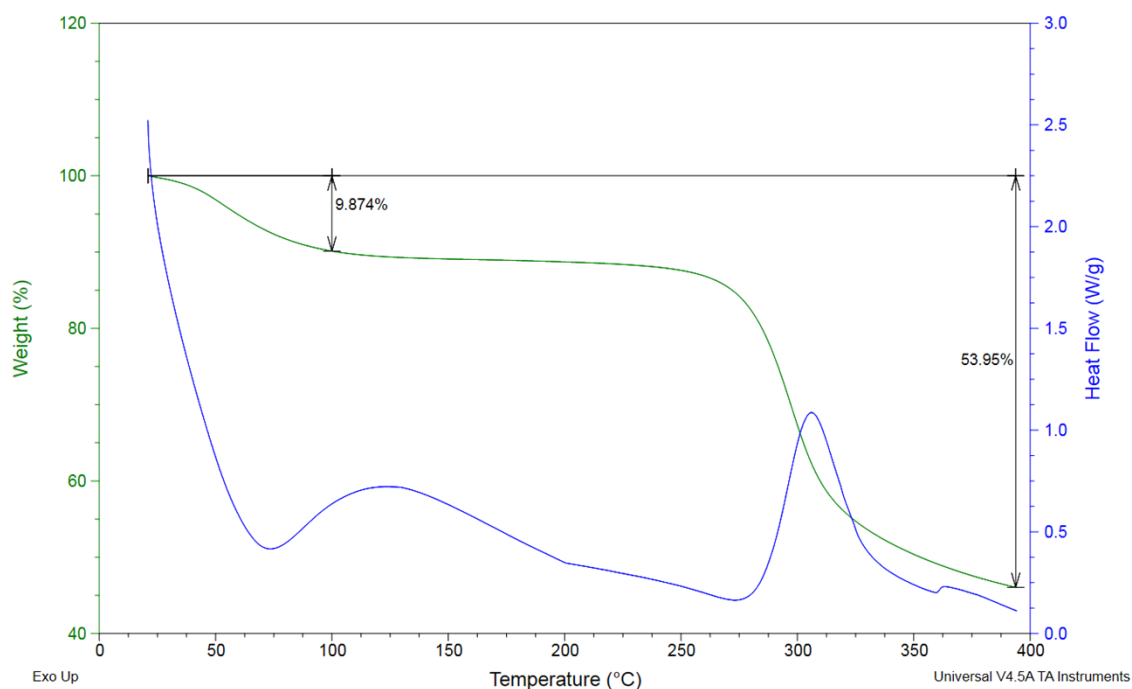
4-Biphenyl-2,6-di-(4-methylphenyl)pyrylium tetrafluoroborate (5)

$\text{BF}_3 \cdot \text{Et}_2\text{O}$ (812 μL , 6.58 mmol) was added dropwise under N_2 atmosphere to a solution of biphenyl-4-carboxaldehyde (500 mg, 2.74 mmol) and 4-methylacetophenone (732 μL , 5.49 mmol) in toluene (2 mL). The mixture was heated to 80°C until the reaction was complete (4 h) monitoring by TLC (1:4 EtOAc-hexane). The residue was washed with EtOH (5 mL). Crystallization from acetone gave compound **5** (282 mg, 25 %) as an orange solid; m.p. (decomp): 291–292 °C; IR ν_{max} 1597, 1481, 1458, 1002, 840, 817, 765, 727 and 687 cm^{-1} ; UV-vis (AcOH/H₂O/MeOH): λ_{max} 421 and 288 nm; Fluorescence (AcOH/H₂O/MeOH): λ_{em} 535 nm; ^1H NMR (500 MHz, DMSO- d_6): δ 9.09 (2H, s), 8.70 (2H, d, J 8.6 Hz), 8.49 (4H, d, J 8.3 Hz), 8.09 (2H, d, J 8.5 Hz), 7.92 (2H, d, J 8.6 Hz), 7.61 (4H, d, J 8.3 Hz), 7.58 (2H, t, J 7.8 Hz), 7.51 (1H, t, J 7.3 Hz) and 2.52 (6H, s); ^{13}C NMR (125 MHz, DMSO- d_6): δ 169.1, 166.6, 146.3, 146.1, 138.1, 131.4, 130.7, 130.5, 129.2, 129.1, 128.7, 127.8, 127.3, 126.6, 113.9 and 21.5; ^{19}F NMR (470 MHz, DMSO- d_6): δ -148.32 ($^{10}\text{BF}_4^-$) and -148.37 ($J_{\text{F,B11}}$ 1.1 Hz, $^{11}\text{BF}_4^-$); CIHRMS: m/z 414.1983, calcd for $\text{C}_{31}\text{H}_{26}\text{O}^+ + \text{H}$: 414.1984.

2,6-Di-(4-fluorophenyl)-4-(4-methoxyphenyl)pyrylium tetrafluoroborate (6)

^1H NMR (500 MHz, DMSO- d_6): δ 9.02 (s, 2H, H-3 and H-5), 8.70 (d, 2H, J = 9.1 Hz, H-2a and 6a), 8.64 (dd, 4H, J = 5.3, J = 8.9 Hz, H-2b, 6b, 2c and 6c), 7.64 (t, 2H, J = 8.9 Hz, H-3b, 5b, 3c and 5c), 7.33 (d, 2H, J = 9.1 Hz, H-3a and 5a), 4.00 (s, 3H, OCH₃);

2. Figure S1. DSC-TGA thermogram for starting material CS 1



3. Calculation of DS value from DS₁ and DS₂ parameters (Table S1).

The second form to calculate the DS value is as followed:

$$\text{DS (\%)} = (\text{DS}_1 + \text{DS}_2)/2$$

$$\text{and DS}_1 \text{ (\%)} = I_{\text{Ar}} / (n \times I_{\text{H1}}) \times 100; \text{DS}_2 \text{ (\%)} = I_{\text{Ar}} / (n \times I_{\text{H2}}) \times 100$$

where I_{Ar} is the integral value relative to aromatic protons of pyrylium moieties, n is the number of aromatic protons and $I_{\text{H1}}/ I_{\text{H2}}$ are the peaks areas of H-1 and H-2 protons respectively of chitosan polymer

Table S1

Compound	R ₁	R ₂	DS (%)	Yield (%)
7	H	H	1.4 (0.9 ^a , 2.2 ^b , 4.3 ^c)	97 (90 ^a , 65 ^b , 94 ^c)
8	H	F	1.4 (3.0 ^c)	87 (77 ^c)
9	Ph	F	1.2	76
10	Ph	H	0.5	70
11	Ph	Me	1.1	99
12a	OMe	F	0.4	73

^a Corresponding to compound **13** from **CS 2**; ^b Corresponding to compound **14** from **CS 3**; ^c synthesized at pH 5.1

4. Table S2. Theoretical calculations by B3LYP/6-31G (d,p) method of distances and dihedral angles for some pyridinium tetrafluoroborates.

Compound	$R_{B\cdots N}$ (Å)	$R_{F\cdots C(5)}$ (Å)	$R_{F\cdots H(5)}$ (Å)	$R_{F\cdots H(1)}$ (Å)	$R_{F\cdots H(6)}$ (Å)	R_c (Å)	ϕ_2 (°)	ϕ_4 (°)	ϕ_6 (°)
7	3.777	3.540	4.218	2.343	2.146	4.346	-61.9	32.6	70.5
8	3.791	3.542	4.220	2.340	2.125	4.354	-61.1	32.4	69.9
9	3.710	2.816	2.958	2.268	2.223	3.618	-84.6	45.4	97.4
10	3.811	3.562	4.246	2.356	2.154	4.378	-61.8	31.3	70.1
11	3.847	3.641	4.332	2.350	2.158	4.442	-59.7	31.1	68.1
12	3.825	3.601	4.258	2.339	2.131	4.407	-60.5	28.1	69.0

5. Cartesian coordinates and energies for pyridinium complexes

Compound 7:

Center Number	Z	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.082396	-0.521117	-2.654221
2	6	0	1.558065	0.749154	-1.956469
3	6	0	1.311892	0.569418	-0.434963
4	6	0	2.418557	-0.260122	0.254586
5	8	0	2.798650	-1.412784	-0.470875
6	6	0	3.168390	-1.261727	-1.846619
7	6	0	4.568267	-0.665339	-2.040563
8	8	0	2.479060	1.822820	-2.069363
9	7	0	-0.141363	0.197411	-0.202291
10	6	0	-1.026138	1.253721	-0.327153
11	6	0	-2.393758	1.034673	-0.312417
12	6	0	-2.936149	-0.243494	-0.148015
13	6	0	-2.012614	-1.269457	0.042485
14	6	0	-0.634497	-1.060104	0.042840
15	6	0	0.162003	-2.283866	0.370629
16	6	0	-0.583956	2.672162	-0.489856
17	6	0	-4.394013	-0.483179	-0.142767
18	6	0	-4.954751	-1.486449	0.665899
19	6	0	-6.329792	-1.707864	0.667612
20	6	0	-7.165963	-0.937403	-0.142299
21	6	0	-6.620492	0.061577	-0.951082
22	6	0	-5.246982	0.290667	-0.948465
23	6	0	0.211881	-3.337325	-0.551971
24	6	0	0.793472	-4.551592	-0.194902
25	6	0	1.306763	-4.729983	1.091230
26	6	0	1.221813	-3.693808	2.020381
27	6	0	0.639762	-2.473853	1.674362
28	6	0	0.046448	3.364467	0.556180
29	6	0	0.332494	4.720585	0.404358

30	6	0	-0.004382	5.394332	-0.770707
31	6	0	-0.640104	4.709291	-1.806762
32	6	0	-0.937951	3.354728	-1.663857
33	8	0	3.474696	0.646866	0.427185
34	6	0	4.316429	0.338307	1.543496
35	8	0	0.929614	-1.324642	-2.908967
36	6	0	1.082264	-2.247610	-3.971562
37	1	0	2.519080	-0.211565	-3.619562
38	1	0	0.605014	0.997380	-2.441731
39	1	0	1.421086	1.545907	0.018751
40	1	0	2.081440	-0.622608	1.223489
41	1	0	3.189973	-2.296733	-2.205554
42	1	0	4.592998	0.394223	-1.788839
43	1	0	5.277499	-1.194820	-1.399370
44	1	0	4.886950	-0.797716	-3.081663
45	1	0	2.575531	2.034630	-3.007217
46	1	0	-3.034847	1.903852	-0.379808
47	1	0	-2.345364	-2.285713	0.207435
48	1	0	-4.317266	-2.069061	1.323060
49	1	0	-6.748828	-2.477010	1.308870
50	1	0	-7.265042	0.660484	-1.587064
51	1	0	-4.829441	1.055059	-1.596490
52	1	0	-0.190325	-3.193207	-1.547463
53	1	0	0.840711	-5.359565	-0.919433
54	1	0	1.603302	-3.826756	3.028007
55	1	0	0.571792	-1.676505	2.405349
56	1	0	0.324154	2.848475	1.470188
57	1	0	0.822092	5.247717	1.217068
58	1	0	-0.909159	5.226709	-2.722869
59	1	0	-1.441374	2.821990	-2.466240
60	1	0	5.053672	1.141496	1.597685
61	1	0	3.729307	0.308629	2.465198
62	1	0	4.835428	-0.617314	1.394553
63	1	0	0.113923	-2.732595	-4.116488
64	1	0	1.365715	-1.738626	-4.905390
65	1	0	1.830753	-3.022317	-3.756668
66	9	0	1.722860	-0.219979	3.501217
67	5	0	0.888877	0.922855	3.382374
68	9	0	0.372489	1.292375	4.604621
69	9	0	1.639452	1.964140	2.793376
70	9	0	-0.162988	0.588729	2.471470
71	1	0	1.759897	-5.676965	1.369537
72	1	0	0.225342	6.450201	-0.878347
73	1	0	-8.237443	-1.112015	-0.141278

E(B3LYP) = -1980.64080303 a.u.

Imaginary frequencies: 0

Compound 8:

Center Number	Z	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.065909	0.282165	-2.702111
2	6	0	1.196562	1.276661	-1.908359
3	6	0	1.038522	0.916004	-0.407414
4	6	0	2.343163	0.382817	0.226310
5	8	0	3.033952	-0.542518	-0.589755
6	6	0	3.330176	-0.170743	-1.941764
7	6	0	4.488684	0.827484	-2.060228
8	8	0	1.751579	2.582577	-1.924149
9	7	0	-0.248470	0.137768	-0.206474
10	6	0	-1.394070	0.914181	-0.224752
11	6	0	-2.646915	0.322789	-0.232081
12	6	0	-2.810055	-1.065381	-0.194473
13	6	0	-1.633471	-1.807837	-0.107461
14	6	0	-0.367906	-1.225161	-0.086814
15	6	0	0.749386	-2.198225	0.114820
16	6	0	-1.363067	2.406933	-0.245123
17	6	0	-4.144021	-1.699675	-0.205703
18	6	0	-4.380138	-2.888972	0.505252
19	6	0	-5.640486	-3.481201	0.494201
20	6	0	-6.682441	-2.901622	-0.232140
21	6	0	-6.459558	-1.721397	-0.943949
22	6	0	-5.202772	-1.122006	-0.927381
23	6	0	1.069698	-3.099377	-0.909155
24	6	0	1.981813	-4.127021	-0.686330
25	6	0	2.546201	-4.252733	0.578481
26	6	0	2.213537	-3.399694	1.622406
27	6	0	1.299074	-2.373409	1.393430
28	6	0	-0.909045	3.145564	0.861488
29	6	0	-1.003459	4.534437	0.853704
30	6	0	-1.553175	5.171962	-0.252874
31	6	0	-2.021058	4.466471	-1.355471
32	6	0	-1.930775	3.076305	-1.339985
33	9	0	3.429264	-5.247706	0.797699
34	9	0	-1.640739	6.515439	-0.259571
35	8	0	3.094125	1.536172	0.497914
36	6	0	4.007787	1.378053	1.589079
37	8	0	1.200160	-0.799639	-3.046368
38	6	0	1.614055	-1.542983	-4.178730
39	1	0	2.383747	0.788542	-3.630153
40	1	0	0.205035	1.265492	-2.381447
41	1	0	0.878389	1.847951	0.117696
42	1	0	2.133453	-0.145460	1.154262
43	1	0	3.654384	-1.118039	-2.386237
44	1	0	4.202061	1.821036	-1.717425
45	1	0	5.328506	0.477608	-1.454743

46	1	0	4.823194	0.886079	-3.103018
47	1	0	1.822382	2.867037	-2.845054
48	1	0	-3.505422	0.981199	-0.209343
49	1	0	-1.669239	-2.887200	-0.041034
50	1	0	-3.586024	-3.329940	1.099142
51	1	0	-5.811034	-4.391292	1.060754
52	1	0	-7.264205	-1.268818	-1.515164
53	1	0	-5.033757	-0.215760	-1.500778
54	1	0	0.615692	-2.982424	-1.885189
55	1	0	2.253828	-4.827614	-1.468115
56	1	0	2.659008	-3.540110	2.600798
57	1	0	1.029890	-1.705864	2.204041
58	1	0	-0.468803	2.643882	1.718644
59	1	0	-0.655884	5.119751	1.697480
60	1	0	-2.446905	5.001380	-2.196937
61	1	0	-2.298595	2.508086	-2.189627
62	1	0	4.475323	2.353306	1.736141
63	1	0	3.470702	1.082820	2.494241
64	1	0	4.783117	0.638703	1.351186
65	1	0	0.825671	-2.269040	-4.391288
66	1	0	1.741830	-0.893370	-5.057783
67	1	0	2.552586	-2.087612	-4.008740
68	9	0	1.715262	-0.132625	3.457054
69	5	0	0.595878	0.740689	3.439584
70	9	0	0.030663	0.855344	4.688958
71	9	0	1.019257	1.993919	2.938606
72	9	0	-0.345542	0.206552	2.505431
73	1	0	-7.663965	-3.365532	-0.240878

E(B3LYP) = -2179.10495306 a.u.

Imaginary frequencies: 0

Compound 9:

Center Number	Z	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	4.462653	-0.150798	-1.669179
2	6	0	3.486430	0.947436	-1.195113
3	6	0	2.567154	0.575129	-0.001956
4	6	0	3.168809	-0.448925	0.987763
5	8	0	3.957505	-1.444122	0.368691
6	6	0	5.001281	-1.033099	-0.523165
7	6	0	6.206325	-0.399753	0.184194
8	8	0	4.208279	2.085123	-0.732256
9	7	0	1.123727	0.339895	-0.400215
10	6	0	0.363346	1.486347	-0.533780
11	6	0	-1.007877	1.417911	-0.698407

12	6	0	-1.686058	0.198904	-0.625961
13	6	0	-0.887230	-0.939506	-0.537428
14	6	0	0.497418	-0.884694	-0.448305
15	6	0	1.179091	-2.215973	-0.428049
16	6	0	0.962284	2.852348	-0.424197
17	6	0	-3.156350	0.111891	-0.594622
18	6	0	-3.773912	-0.708624	0.364878
19	6	0	-5.160606	-0.793020	0.419900
20	6	0	-5.973502	-0.075965	-0.475585
21	6	0	-5.343443	0.749149	-1.424001
22	6	0	-3.957969	0.850874	-1.477787
23	6	0	1.712600	-2.744870	-1.608412
24	6	0	2.192028	-4.052779	-1.640782
25	6	0	2.118044	-4.818597	-0.484000
26	6	0	1.563567	-4.328875	0.692448
27	6	0	1.074363	-3.025330	0.715414
28	6	0	1.075971	3.456017	0.839244
29	6	0	1.541045	4.764130	0.946941
30	6	0	1.873624	5.457509	-0.211702
31	6	0	1.750221	4.891391	-1.474896
32	6	0	1.285781	3.580638	-1.575218
33	9	0	2.585087	-6.083704	-0.511648
34	9	0	2.321444	6.723932	-0.110072
35	8	0	3.891985	0.330516	1.908851
36	6	0	4.131073	-0.344158	3.148938
37	8	0	3.780494	-0.880100	-2.683931
38	6	0	4.623239	-1.604622	-3.561513
39	6	0	-7.452849	-0.178462	-0.416776
40	6	0	-8.120145	-0.273216	0.816370
41	6	0	-9.509308	-0.369159	0.871271
42	6	0	-10.261199	-0.373793	-0.304770
43	6	0	-9.612002	-0.281043	-1.536922
44	6	0	-8.222925	-0.183526	-1.592241
45	1	0	5.323158	0.363526	-2.131937
46	1	0	2.861401	1.198154	-2.062705
47	1	0	2.513140	1.479023	0.592614
48	1	0	2.381868	-0.987589	1.514393
49	1	0	5.326950	-1.981596	-0.962483
50	1	0	5.978449	0.598067	0.558542
51	1	0	6.508541	-1.028413	1.025388
52	1	0	7.050919	-0.337160	-0.512267
53	1	0	4.771743	2.398341	-1.452173
54	1	0	-1.553029	2.351369	-0.762516
55	1	0	-1.340911	-1.921140	-0.527655
56	1	0	-3.157315	-1.223167	1.095670
57	1	0	-5.622093	-1.436436	1.162238
58	1	0	-5.948616	1.334834	-2.108702
59	1	0	-3.494566	1.492585	-2.222120
60	1	0	1.762370	-2.134069	-2.500077
61	1	0	2.606930	-4.484618	-2.544887

62	1	0	1.511963	-4.964216	1.569522
63	1	0	0.636794	-2.622542	1.622921
64	1	0	0.804854	2.884672	1.721900
65	1	0	1.642217	5.249027	1.911399
66	1	0	2.005868	5.474742	-2.352449
67	1	0	1.168683	3.128112	-2.555610
68	1	0	4.645187	0.372421	3.792199
69	1	0	3.182760	-0.645126	3.605142
70	1	0	4.770681	-1.223514	3.005210
71	1	0	3.984229	-2.026256	-4.340756
72	1	0	5.369192	-0.946227	-4.032555
73	1	0	5.151189	-2.427387	-3.061657
74	1	0	-7.547286	-0.243470	1.738154
75	1	0	-10.005426	-0.432238	1.835328
76	1	0	-11.343608	-0.449220	-0.261355
77	1	0	-10.187283	-0.293029	-2.458141
78	1	0	-7.726191	-0.139218	-2.556883
79	5	0	-0.140504	-0.281304	3.032430
80	9	0	-0.676080	0.180028	4.210262
81	9	0	0.952418	-1.159118	3.266232
82	9	0	-1.103659	-0.991296	2.269965
83	9	0	0.346540	0.802641	2.238513

-----:
E(B3LYP) = -2410.17145082 a.u.

Imaginary frequencies: 0

Compound 10:

Center Number	Z	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	3.234822	-0.688463	-2.674719
2	6	0	2.838132	0.621788	-1.967919
3	6	0	2.577935	0.459172	-0.446818
4	6	0	3.589763	-0.485214	0.239020
5	8	0	3.858553	-1.661613	-0.497800
6	6	0	4.243477	-1.535577	-1.871490
7	6	0	5.693848	-1.071647	-2.055951
8	8	0	3.861373	1.599634	-2.073997
9	7	0	1.095644	0.245701	-0.207022
10	6	0	0.331367	1.394916	-0.307767
11	6	0	-1.051461	1.327616	-0.287552
12	6	0	-1.731327	0.114176	-0.138838
13	6	0	-0.924013	-1.010427	0.028488
14	6	0	0.468250	-0.954139	0.021693
15	6	0	1.127559	-2.262623	0.329577
16	6	0	0.927460	2.758471	-0.445444
17	6	0	-3.204190	0.039128	-0.120452
18	6	0	-3.872354	-0.919664	0.660161

19	6	0	-5.260330	-0.981438	0.678806
20	6	0	-6.040373	-0.095603	-0.084756
21	6	0	-5.368116	0.859702	-0.867059
22	6	0	-3.980546	0.929747	-0.881639
23	6	0	1.061462	-3.302298	-0.607451
24	6	0	1.502686	-4.578836	-0.266836
25	6	0	1.990350	-4.831203	1.016966
26	6	0	2.022058	-3.804157	1.959645
27	6	0	1.581359	-2.522058	1.630112
28	6	0	1.635076	3.354523	0.610701
29	6	0	2.072632	4.672102	0.482781
30	6	0	1.811672	5.402127	-0.677969
31	6	0	1.100179	4.813268	-1.723878
32	6	0	0.651024	3.498684	-1.605131
33	8	0	4.730727	0.308851	0.433277
34	6	0	5.535584	-0.113251	1.539410
35	8	0	2.009740	-1.373754	-2.935175
36	6	0	2.073635	-2.302029	-4.002374
37	6	0	-7.521895	-0.163692	-0.063013
38	6	0	-8.212065	-0.464620	1.123679
39	6	0	-9.603952	-0.526763	1.144056
40	6	0	-10.335375	-0.291065	-0.021220
41	6	0	-9.663307	0.008529	-1.207367
42	6	0	-8.271507	0.072570	-1.227998
43	1	0	3.700495	-0.417824	-3.638333
44	1	0	1.913716	0.967574	-2.449620
45	1	0	2.793255	1.417599	0.007137
46	1	0	3.209890	-0.824276	1.200804
47	1	0	4.167792	-2.565081	-2.238668
48	1	0	5.817396	-0.023726	-1.785037
49	1	0	6.348613	-1.676413	-1.423440
50	1	0	6.001041	-1.215689	-3.098947
51	1	0	3.995576	1.790140	-3.011852
52	1	0	-1.592446	2.263592	-0.334415
53	1	0	-1.365577	-1.986075	0.182597
54	1	0	-3.303110	-1.604055	1.280834
55	1	0	-5.748878	-1.739423	1.282494
56	1	0	-5.942220	1.570768	-1.452502
57	1	0	-3.493887	1.673006	-1.505721
58	1	0	0.678639	-3.100215	-1.600424
59	1	0	1.460072	-5.377379	-1.002060
60	1	0	2.385376	-3.992404	2.965179
61	1	0	1.603526	-1.731272	2.370995
62	1	0	1.855714	2.793692	1.514061
63	1	0	2.620903	5.124649	1.302965
64	1	0	0.889971	5.375243	-2.629087
65	1	0	0.088952	3.041640	-2.415189
66	1	0	6.347463	0.612219	1.617657
67	1	0	4.946047	-0.112825	2.460162
68	1	0	5.958827	-1.110167	1.361573

69	1	0	1.064033	-2.693724	-4.147576
70	1	0	2.401978	-1.817128	-4.934362
71	1	0	2.747078	-3.144107	-3.792625
72	1	0	-7.655062	-0.621603	2.042347
73	1	0	-10.117976	-0.750900	2.074046
74	1	0	-11.419965	-0.339936	-0.004948
75	1	0	-10.223178	0.185135	-2.121064
76	1	0	-7.757904	0.279937	-2.161970
77	5	0	2.183187	0.792745	3.404122
78	9	0	1.687686	1.180829	4.629549
79	9	0	2.895398	-0.431446	3.502258
80	9	0	1.116383	0.588542	2.472079
81	9	0	3.043344	1.767605	2.853749
82	1	0	2.333488	-5.826977	1.282563
83	1	0	2.159390	6.427156	-0.766920

E(B3LYP) = -2211.70505404 a.u.

Imaginary frequencies: 0

Compound 11:

Center Number	Z	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.038706	0.506789	-2.795369
2	6	0	-2.658474	-0.747696	-1.986782
3	6	0	-2.444884	-0.479131	-0.473373
4	6	0	-3.478078	0.505887	0.115894
5	8	0	-3.732889	1.625786	-0.709363
6	6	0	-4.074072	1.402438	-2.082160
7	6	0	-5.516647	0.918921	-2.278838
8	8	0	-3.675421	-1.736224	-2.055471
9	7	0	-0.970280	-0.251460	-0.204732
10	6	0	-0.208865	-1.407850	-0.188892
11	6	0	1.174612	-1.339009	-0.165269
12	6	0	1.854988	-0.117271	-0.129030
13	6	0	1.049150	1.019202	-0.067399
14	6	0	-0.343252	0.964098	-0.075707
15	6	0	-1.009189	2.287266	0.122926
16	6	0	-0.808238	-2.774346	-0.196209
17	6	0	3.328189	-0.041544	-0.110070
18	6	0	3.993252	0.985303	0.581671
19	6	0	5.381163	1.048841	0.600963
20	6	0	6.164408	0.096249	-0.073647
21	6	0	5.495508	-0.927856	-0.766482
22	6	0	4.107888	-0.998893	-0.781253
23	6	0	-0.912628	3.268294	-0.871430
24	6	0	-1.366429	4.561544	-0.627459
25	6	0	-1.905437	4.916259	0.616150

26	6	0	-1.954493	3.935665	1.614313
27	6	0	-1.505539	2.636937	1.386372
28	6	0	-1.558818	-3.251792	0.891809
29	6	0	-1.996140	-4.572092	0.896140
30	6	0	-1.708097	-5.449829	-0.159347
31	6	0	-0.949330	-4.964668	-1.230264
32	6	0	-0.495711	-3.646475	-1.247786
33	8	0	-4.620810	-0.280139	0.334439
34	6	0	-5.463742	0.219096	1.378375
35	8	0	-1.809120	1.177072	-3.071141
36	6	0	-1.850473	2.041266	-4.191620
37	6	0	7.645876	0.166881	-0.051426
38	6	0	8.330178	0.573886	1.106721
39	6	0	9.721916	0.638913	1.128250
40	6	0	10.459219	0.300127	-0.007541
41	6	0	9.793062	-0.105193	-1.165265
42	6	0	8.401381	-0.172002	-1.186902
43	6	0	-2.428620	6.309213	0.869820
44	6	0	-2.215992	-6.870916	-0.139614
45	1	0	-3.476994	0.166514	-3.749937
46	1	0	-1.718637	-1.122230	-2.414428
47	1	0	-2.675466	-1.406154	0.033976
48	1	0	-3.127150	0.914662	1.061393
49	1	0	-3.991803	2.404560	-2.517366
50	1	0	-5.645868	-0.109071	-1.942039
51	1	0	-6.192792	1.561566	-1.709274
52	1	0	-5.792198	0.990304	-3.338078
53	1	0	-3.778436	-1.992712	-2.981459
54	1	0	1.714557	-2.275437	-0.116311
55	1	0	1.491249	2.004148	0.003721
56	1	0	3.421318	1.724221	1.133534
57	1	0	5.867541	1.859310	1.134135
58	1	0	6.072028	-1.690591	-1.280066
59	1	0	3.623860	-1.796863	-1.335817
60	1	0	-0.493100	3.010469	-1.836524
61	1	0	-1.295189	5.309477	-1.413454
62	1	0	-2.345444	4.185358	2.597050
63	1	0	-1.549379	1.902419	2.181968
64	1	0	-1.806333	-2.597922	1.722437
65	1	0	-2.574392	-4.924174	1.746061
66	1	0	-0.705941	-5.624447	-2.058983
67	1	0	0.098948	-3.291611	-2.085442
68	1	0	-6.269607	-0.508622	1.490780
69	1	0	-4.902974	0.300655	2.313231
70	1	0	-5.892511	1.192650	1.108032
71	1	0	-0.834051	2.409647	-4.349807
72	1	0	-2.177483	1.506739	-5.096622
73	1	0	-2.513176	2.903408	-4.037805
74	1	0	7.768420	0.812423	2.004726
75	1	0	10.231244	0.946268	2.036810

76	1	0	11.543704	0.351204	0.009534
77	1	0	10.357481	-0.362438	-2.056767
78	1	0	7.892773	-0.462321	-2.101293
79	1	0	-1.971647	7.039934	0.195905
80	1	0	-3.513791	6.354494	0.715289
81	1	0	-2.236695	6.627351	1.898978
82	1	0	-2.016311	-7.350908	0.823955
83	1	0	-3.301120	-6.902068	-0.294191
84	1	0	-1.751347	-7.475645	-0.923206
85	5	0	-2.196884	-0.492727	3.433786
86	9	0	-1.711695	-0.748034	4.698143
87	9	0	-2.902532	0.738789	3.394414
88	9	0	-1.119898	-0.392385	2.494251
89	9	0	-3.055275	-1.517451	2.984548

E(B3LYP) = -2290.34747440 a.u.

Imaginary frequencies: 0

Compound 12:

Center Number	Z	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.366136	-0.387185	-2.788342
2	6	0	1.839641	0.834857	-2.009866
3	6	0	1.670182	0.592121	-0.485804
4	6	0	2.801893	-0.267466	0.122186
5	8	0	3.165077	-1.376282	-0.677531
6	6	0	3.490585	-1.146019	-2.053659
7	6	0	4.871439	-0.510596	-2.259336
8	8	0	2.726164	1.938675	-2.114855
9	7	0	0.228993	0.229760	-0.187743
10	6	0	-0.644126	1.304348	-0.184336
11	6	0	-2.012385	1.101145	-0.134780
12	6	0	-2.573241	-0.180280	-0.061719
13	6	0	-1.654396	-1.229033	0.014081
14	6	0	-0.276120	-1.037169	-0.020657
15	6	0	0.523601	-2.283613	0.182630
16	6	0	-0.180657	2.722695	-0.232408
17	6	0	-4.027287	-0.401088	-0.025213
18	6	0	-4.582606	-1.511698	0.644148
19	6	0	-5.950431	-1.717861	0.676911
20	6	0	-6.817437	-0.820717	0.030027
21	6	0	-6.286423	0.288364	-0.643532
22	6	0	-4.908701	0.488393	-0.659159
23	6	0	0.520504	-3.274228	-0.808310
24	6	0	1.114661	-4.510998	-0.573464
25	6	0	1.687004	-4.748059	0.671651
26	6	0	1.665857	-3.799476	1.685512

27	6	0	1.068457	-2.563935	1.444493
28	6	0	0.525935	3.296862	0.838838
29	6	0	0.841466	4.652446	0.814199
30	6	0	0.445784	5.422508	-0.273775
31	6	0	-0.262262	4.883830	-1.341807
32	6	0	-0.580839	3.527830	-1.309614
33	9	0	2.263182	-5.945227	0.902433
34	9	0	0.753479	6.733389	-0.296717
35	8	0	3.858715	0.635245	0.314810
36	6	0	4.755807	0.247161	1.361395
37	8	0	1.224147	-1.200736	-3.055284
38	6	0	1.367203	-2.061828	-4.170225
39	8	0	-8.138355	-1.113378	0.115589
40	6	0	-9.074125	-0.232456	-0.496127
41	1	0	2.768144	-0.017965	-3.748004
42	1	0	0.857756	1.075826	-2.440389
43	1	0	1.815374	1.552753	-0.010605
44	1	0	2.498101	-0.685512	1.079879
45	1	0	3.520708	-2.160123	-2.466870
46	1	0	4.883848	0.534256	-1.951409
47	1	0	5.612529	-1.057878	-1.671494
48	1	0	5.157673	-0.580419	-3.315782
49	1	0	2.828618	2.153281	-3.051571
50	1	0	-2.639509	1.981825	-0.093154
51	1	0	-1.993904	-2.251412	0.113557
52	1	0	-3.936477	-2.200547	1.178385
53	1	0	-6.379617	-2.561029	1.206992
54	1	0	-6.931016	0.990718	-1.157406
55	1	0	-4.515363	1.340572	-1.204659
56	1	0	0.067198	-3.066338	-1.769469
57	1	0	1.135396	-5.286868	-1.330854
58	1	0	2.105141	-4.026007	2.650463
59	1	0	1.041949	-1.820083	2.232339
60	1	0	0.842700	2.689868	1.681978
61	1	0	1.387908	5.109997	1.631140
62	1	0	-0.553973	5.519111	-2.170607
63	1	0	-1.138591	3.090952	-2.133084
64	1	0	5.484877	1.054596	1.450017
65	1	0	4.212750	0.131124	2.303071
66	1	0	5.278055	-0.684269	1.108401
67	1	0	0.405913	-2.560454	-4.315675
68	1	0	1.613383	-1.497094	-5.082260
69	1	0	2.137897	-2.829532	-4.017839
70	1	0	-10.058054	-0.655452	-0.292788
71	1	0	-9.016155	0.774705	-0.066563
72	1	0	-8.921435	-0.174982	-1.580594
73	9	0	2.248464	-0.506419	3.398387
74	5	0	1.427954	0.652517	3.419920
75	9	0	0.957541	0.907557	4.688416
76	9	0	2.173985	1.737075	2.908696

77 9 0 0.342100 0.418532 2.517005

E(B3LYP) = -2293.63216049 a.u.

Imaginary frequencies: 0

Compound 12a:

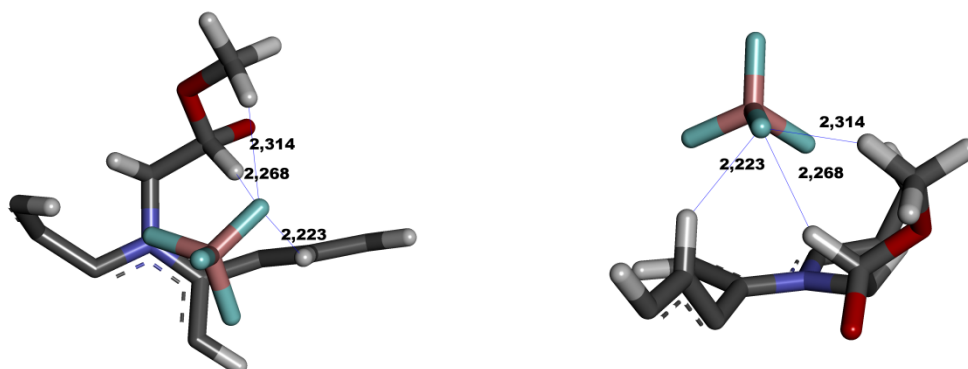
Center Number	Z	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.740788	-0.180586	-2.408610
2	6	0	2.307796	1.016299	-1.542223
3	6	0	1.855323	0.594687	-0.119511
4	6	0	2.917707	-0.342005	0.495685
5	8	0	3.312668	-1.402620	-0.321431
6	6	0	3.700337	-1.149651	-1.686061
7	6	0	5.176969	-0.754916	-1.803211
8	8	0	3.355169	1.965400	-1.444197
9	7	0	0.393218	0.210957	-0.076969
10	6	0	-0.479954	1.282656	-0.151446
11	6	0	-1.845612	1.072746	-0.222021
12	6	0	-2.406019	-0.210376	-0.211180
13	6	0	-1.496289	-1.257559	-0.079654
14	6	0	-0.122802	-1.056301	0.025014
15	6	0	0.660297	-2.306556	0.280600
16	6	0	-0.029792	2.710190	-0.211608
17	6	0	-3.858263	-0.434206	-0.304315
18	6	0	-4.376749	-1.597752	-0.907824
19	6	0	-5.741442	-1.810861	-1.000391
20	6	0	-6.640842	-0.866569	-0.477743
21	6	0	-6.146182	0.293938	0.132719
22	6	0	-4.770798	0.499765	0.208696
23	6	0	0.898925	-3.211705	-0.761055
24	6	0	1.480326	-4.449793	-0.500224
25	6	0	1.797264	-4.772290	0.814698
26	6	0	1.528923	-3.911422	1.871053
27	6	0	0.942651	-2.674590	1.604187
28	6	0	0.551941	3.356822	0.893233
29	6	0	0.833560	4.719860	0.831487
30	6	0	0.530981	5.426470	-0.326667
31	6	0	-0.053879	4.817172	-1.429871
32	6	0	-0.341236	3.455727	-1.360200
33	9	0	2.362135	-5.971166	1.071299
34	9	0	0.806780	6.744432	-0.382029
35	8	0	4.031406	0.518530	0.764136
36	6	0	4.403092	0.609771	2.149842
37	8	0	1.535035	-0.830041	-2.827923
38	6	0	1.638823	-1.481313	-4.080789
39	8	0	-7.957351	-1.169076	-0.612779

40	6	0	-8.920996	-0.257468	-0.098471
41	1	0	3.255600	0.236484	-3.285518
42	1	0	1.480324	1.498030	-2.069028
43	1	0	1.899928	1.460872	0.525396
44	1	0	2.556957	-0.773503	1.425948
45	1	0	3.578799	-2.133433	-2.152611
46	1	0	5.358751	0.272063	-1.488490
47	1	0	5.780350	-1.422695	-1.183517
48	1	0	5.504622	-0.857470	-2.843936
49	1	0	3.859273	1.754075	-0.637528
50	1	0	-2.474674	1.949791	-0.299858
51	1	0	-1.843808	-2.276561	0.025919
52	1	0	-3.699715	-2.330655	-1.335150
53	1	0	-6.142221	-2.699168	-1.476449
54	1	0	-6.816602	1.030405	0.558039
55	1	0	-4.405967	1.388161	0.714174
56	1	0	0.651037	-2.932732	-1.777569
57	1	0	1.686062	-5.161812	-1.292022
58	1	0	1.760497	-4.218392	2.885232
59	1	0	0.657689	-1.988656	2.400119
60	1	0	0.789822	2.781572	1.789900
61	1	0	1.280493	5.237806	1.673028
62	1	0	-0.275425	5.401643	-2.315691
63	1	0	-0.804169	2.965618	-2.211720
64	1	0	5.216014	1.337224	2.199906
65	1	0	3.550845	0.937443	2.753634
66	1	0	4.771157	-0.360684	2.506015
67	1	0	0.655598	-1.900165	-4.309628
68	1	0	1.917891	-0.775909	-4.877408
69	1	0	2.373169	-2.299855	-4.071186
70	1	0	-9.894187	-0.699911	-0.312696
71	1	0	-8.812565	-0.127425	0.984986
72	1	0	-8.851522	0.720541	-0.589986
73	6	0	0.061136	1.091690	4.807525
74	6	0	0.336747	0.574209	3.384707
75	8	0	1.332890	1.095856	2.783865
76	8	0	-0.439005	-0.295398	2.915982
77	1	0	0.985590	1.095493	5.393672
78	1	0	-0.287873	2.130228	4.759716
79	1	0	-0.697381	0.487773	5.310187

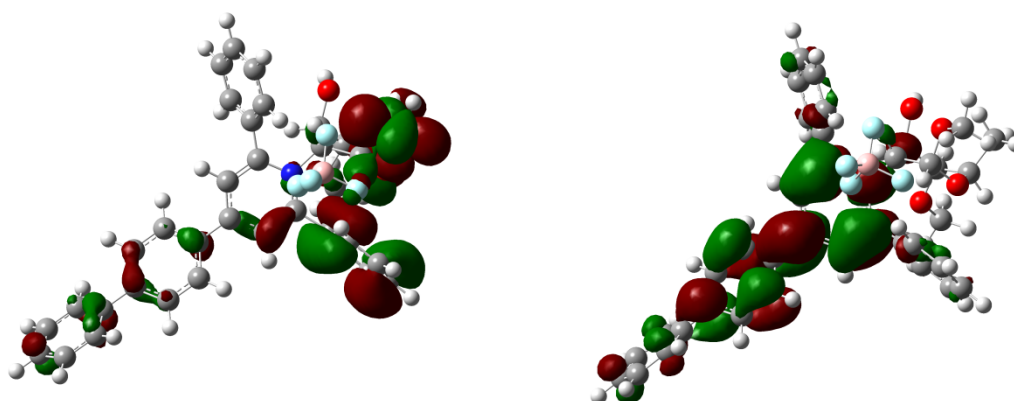
E(B3LYP) = -2097.65983455 a.u.

Imaginary frequencies: 0

6. **Figure S2.** Scheme of calculated tripod-type interaction CH–anion for compound **9** (distance in Å) at two points of view.



7. **Figure S3.** Molecular orbital and energies for HOMO-LUMO of NLO-phore **10**.



HOMO (**10**): -6.46 eV

LUMO (**10**): -2.69 eV

8. ^1H , ^{19}F , diffusion experiment and ^{13}C CPMAS NMR spectra of new compounds

Figure S4. Compound 7 (pH 4.3): ^1H NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 700 MHz)

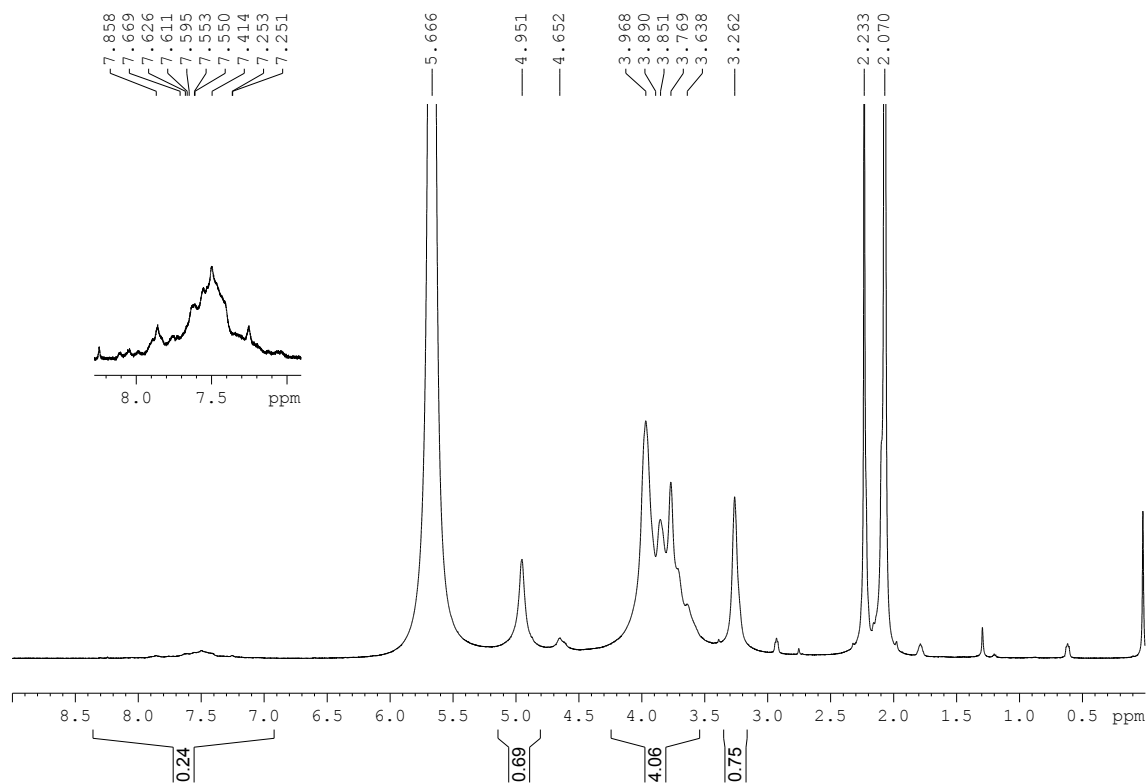


Figure S5. Compound 7 (pH 5.1): ^1H NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 700 MHz)

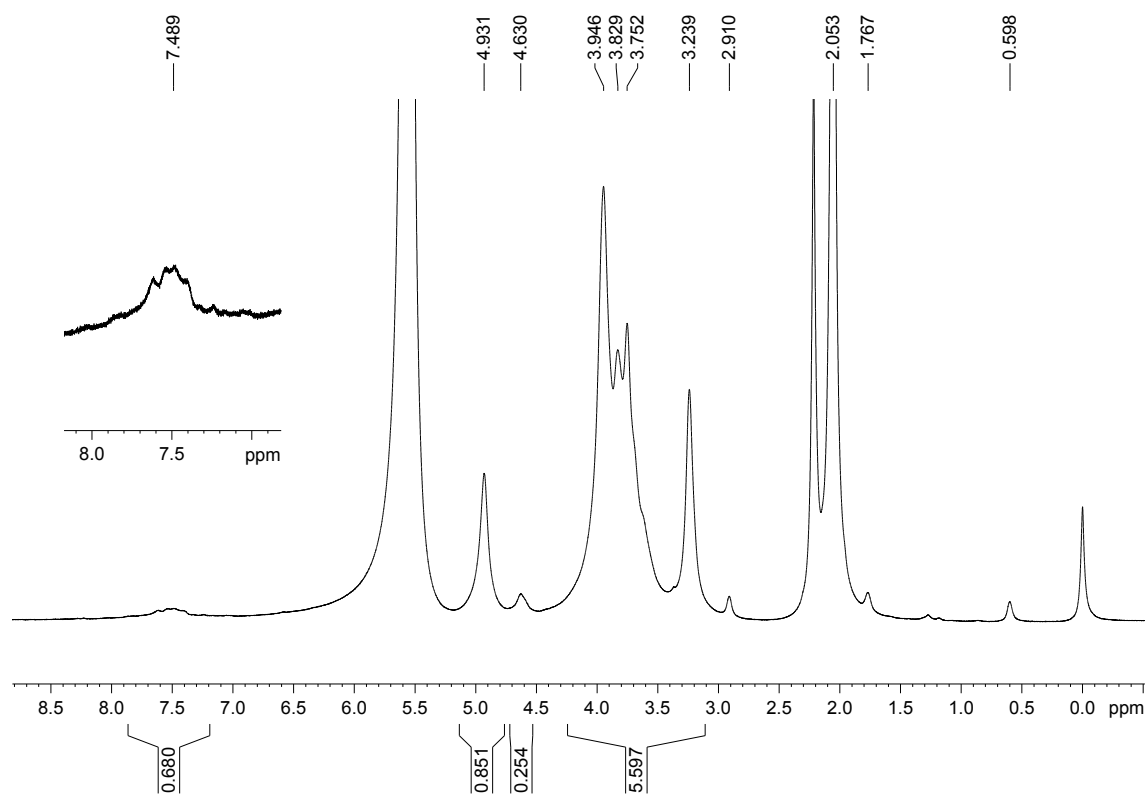


Figure S6. Compound 7: ^{13}C CPMAS NMR spectrum

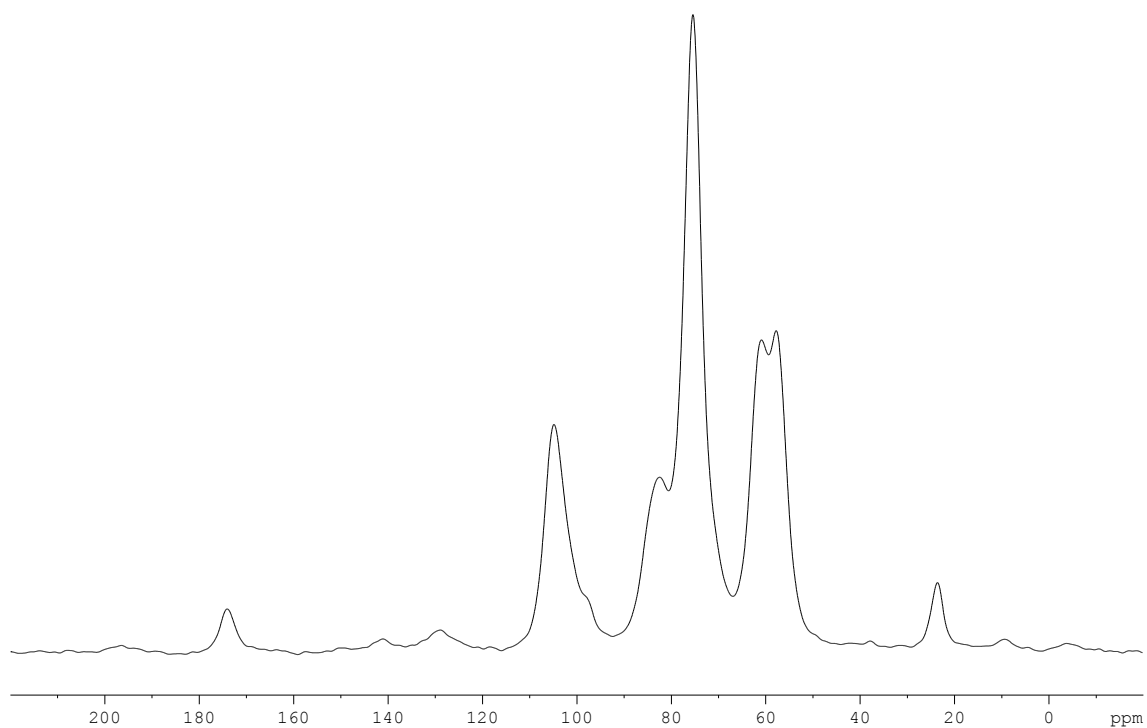


Figure S7. Compound 7: Diffusion-filtered ^1H NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 500 MHz)

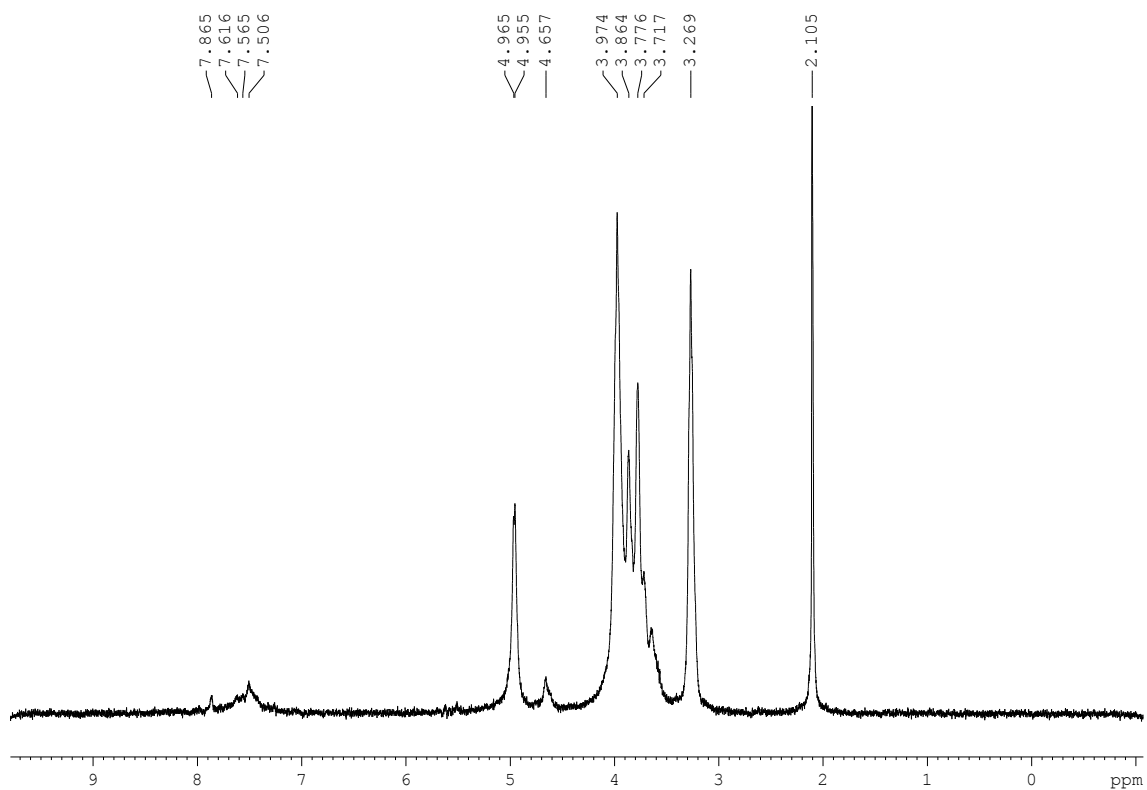


Figure S8. Compound 7: ^{19}F NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 500 MHz)

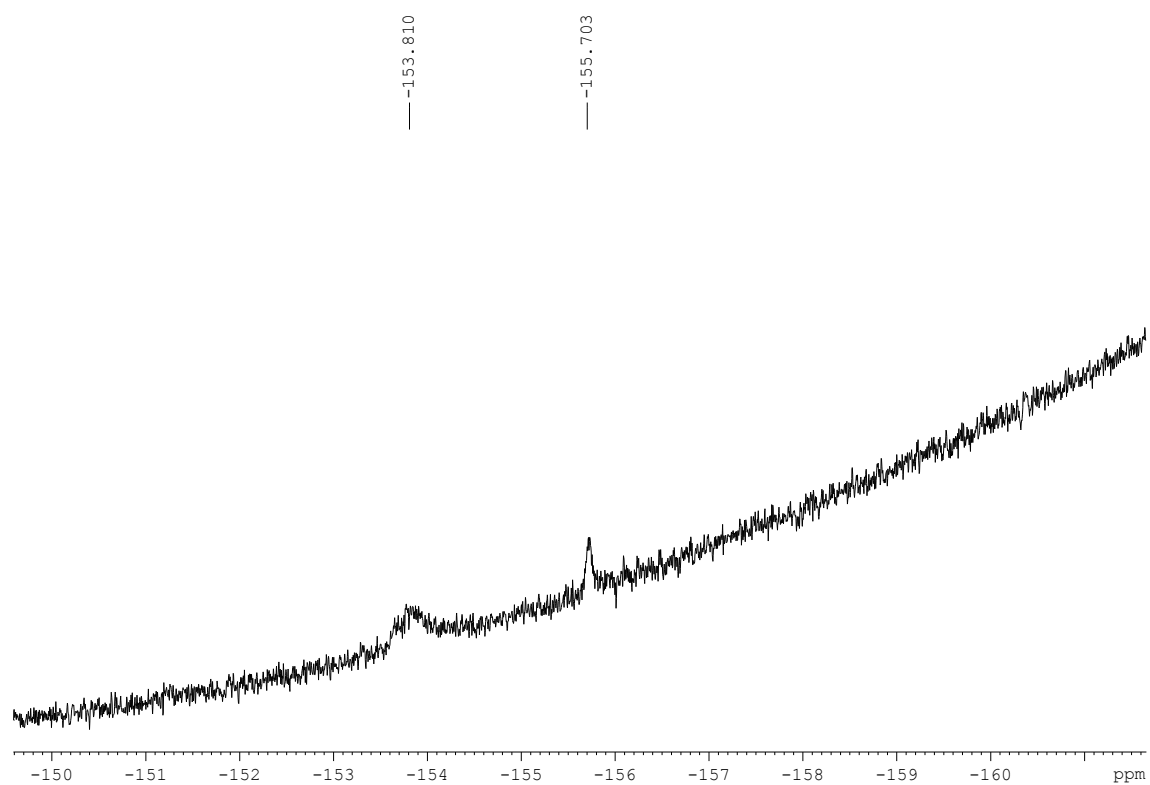


Figure S9. Compound 8 (pH 4.2): ^1H NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 700 MHz)

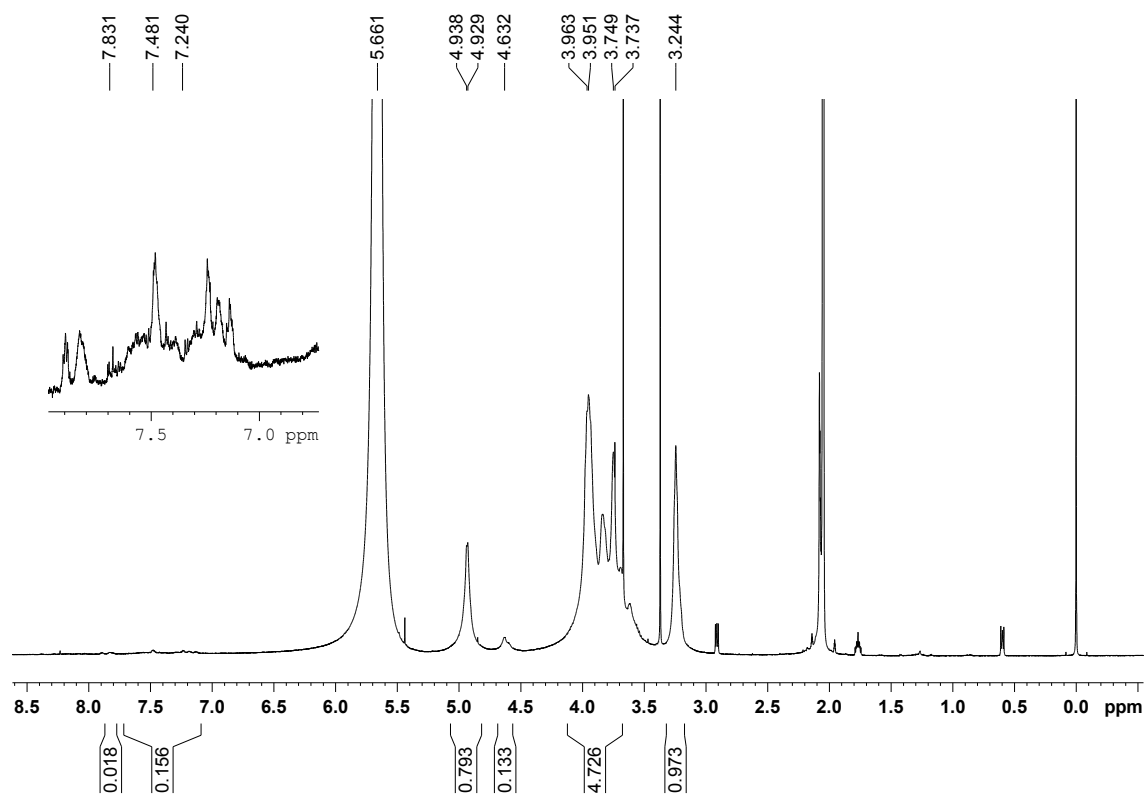


Figure S10. Compound **8** (pH 5.1): ^1H NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 700 MHz)

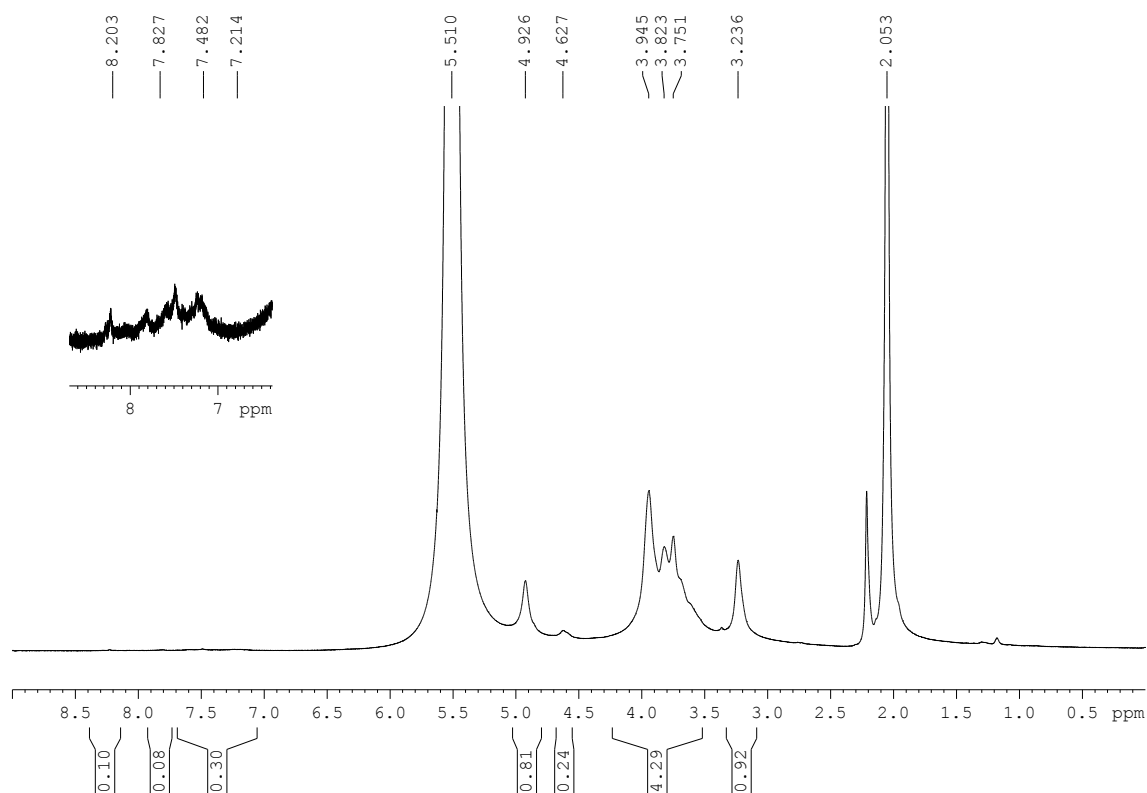


Figure S11. Compound **8**: Diffusion-filtered ^1H NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 500 MHz)

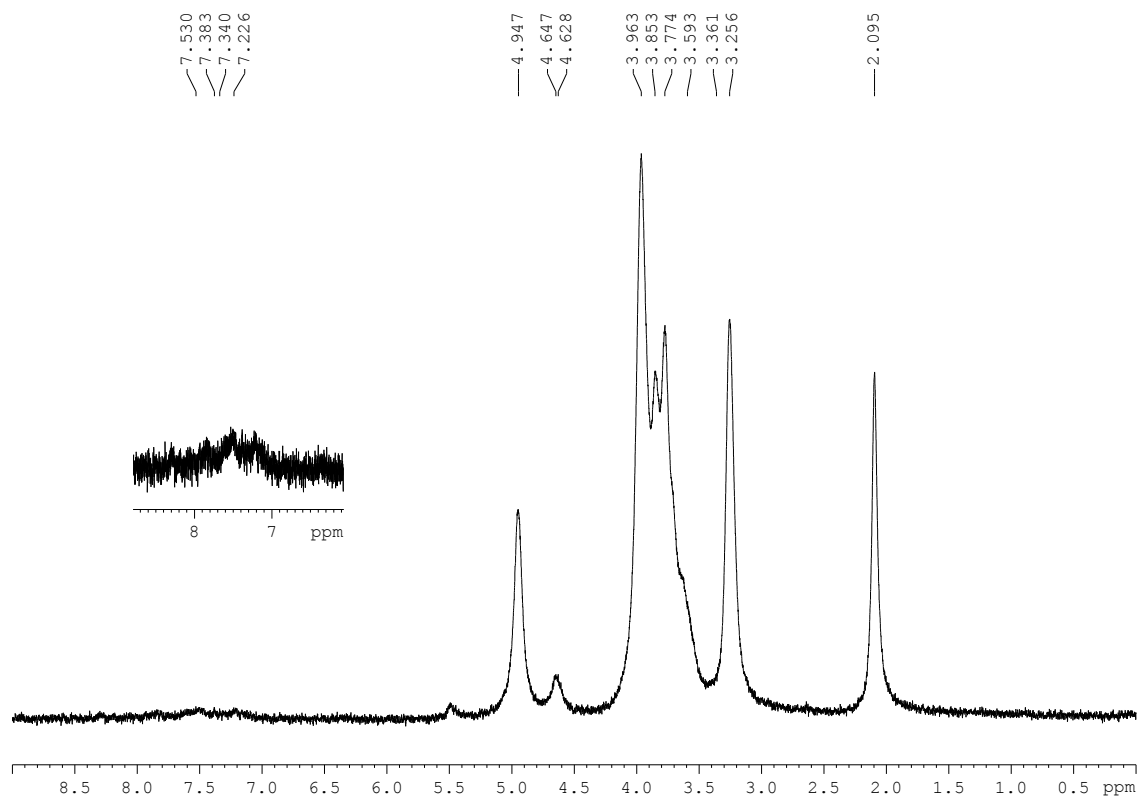


Figure S12. Compound **8**: ^{13}C CPMAS NMR spectrum

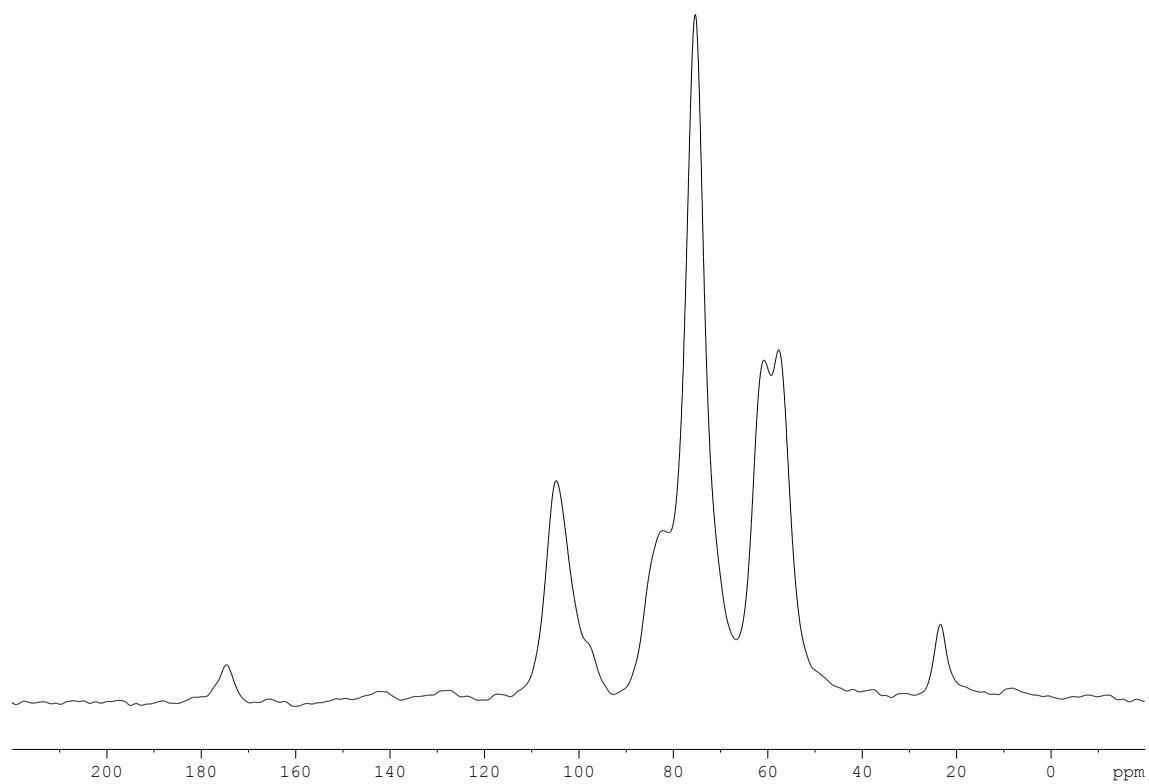


Figure S13. Compound **8**: ^{19}F NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 500 MHz)

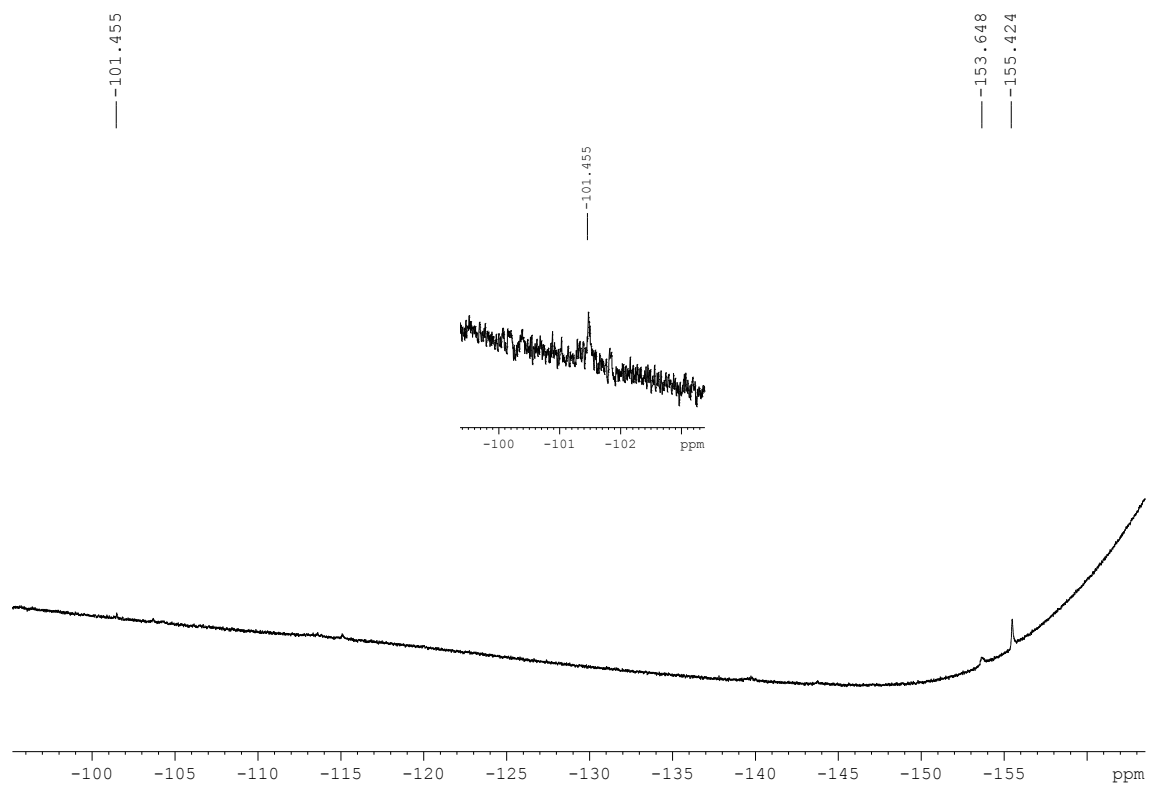


Figure S14. Compound **9**: ^1H NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 700 MHz)

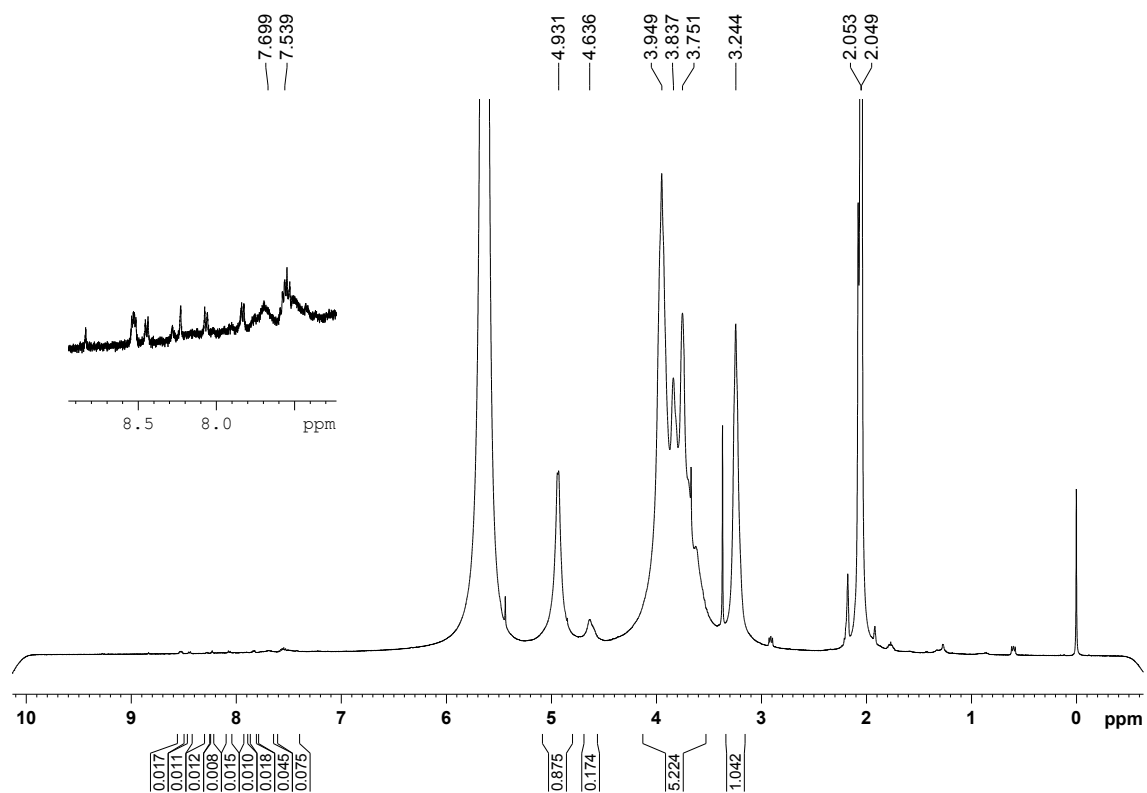


Figure S15. Compound **9**: Diffusion-filtered ^1H NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 500 MHz)

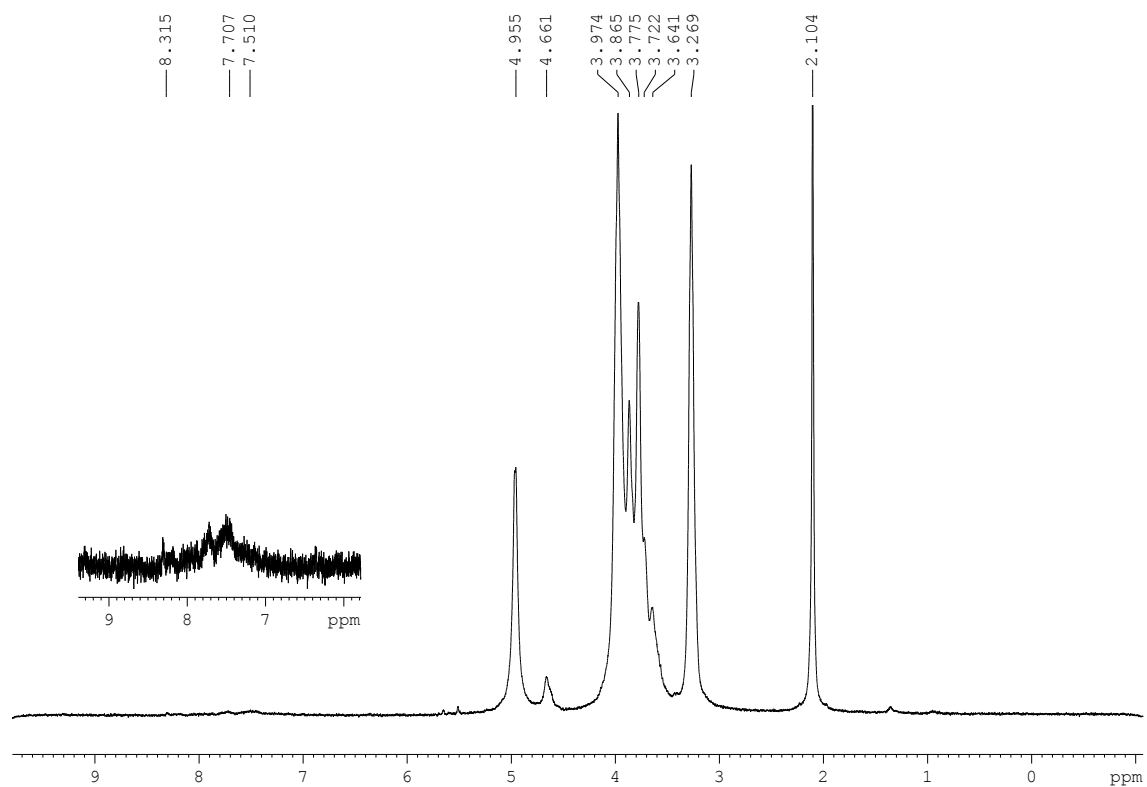


Figure S16. Compound **9**: ^{13}C CPMAS NMR spectrum

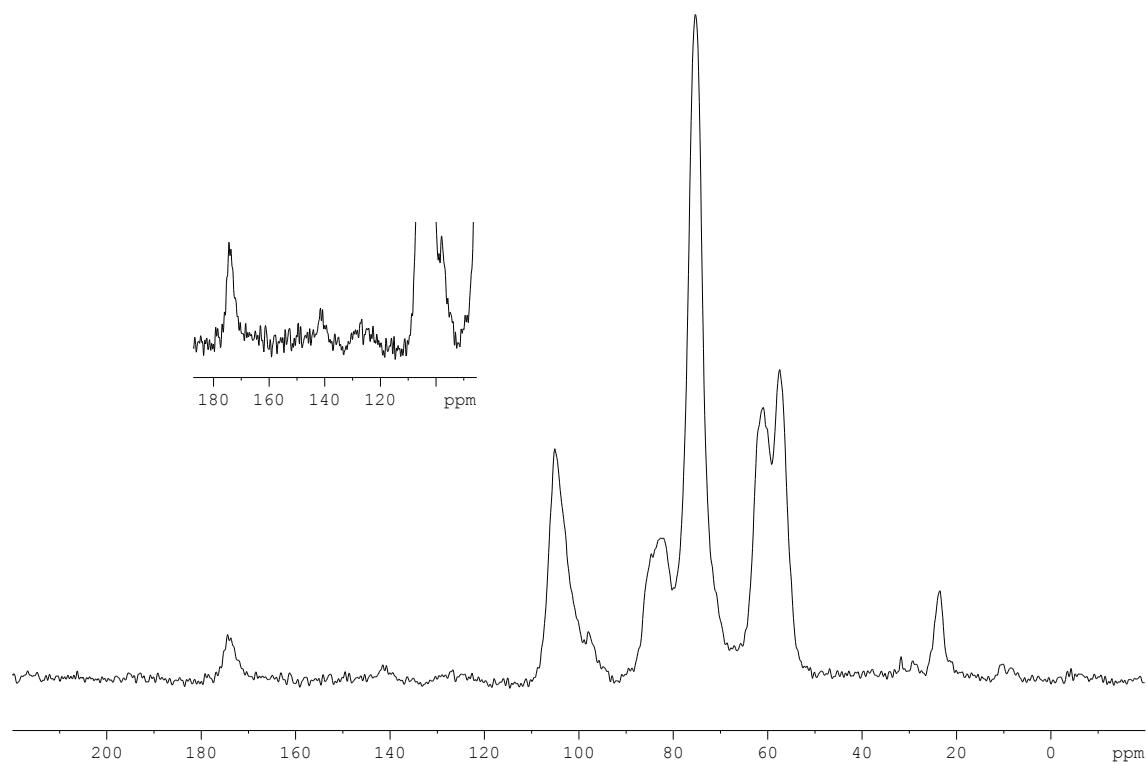


Figure S17. Compound **9**: ^{19}F NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 500 MHz)

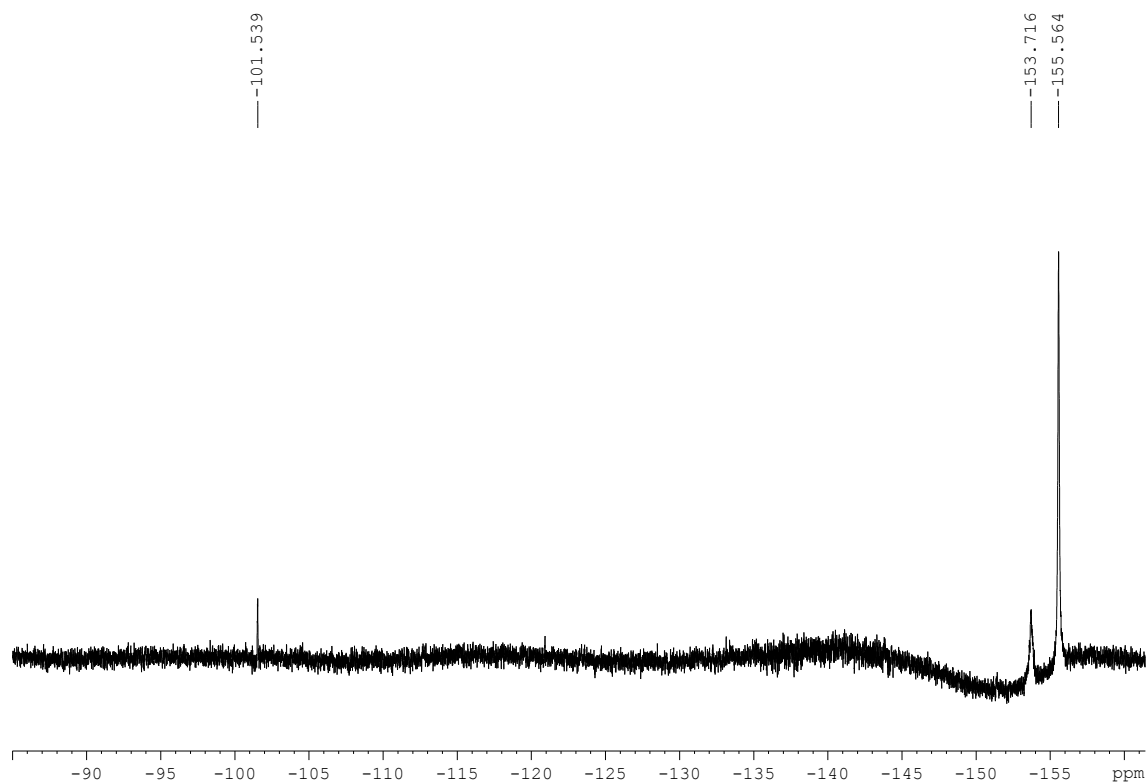


Figure S18. Compound **10**: ^1H NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 700 MHz)

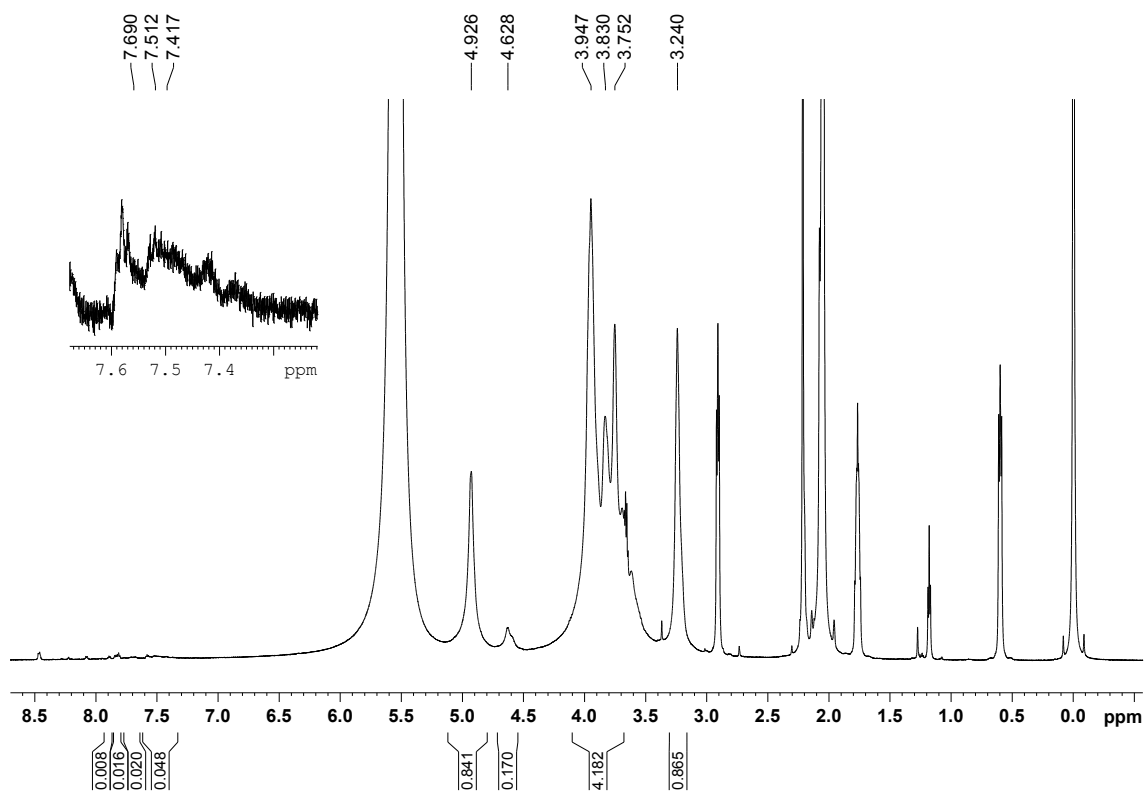


Figure S19. Compound **10**: Diffusion-filtered ^1H NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 500 MHz)

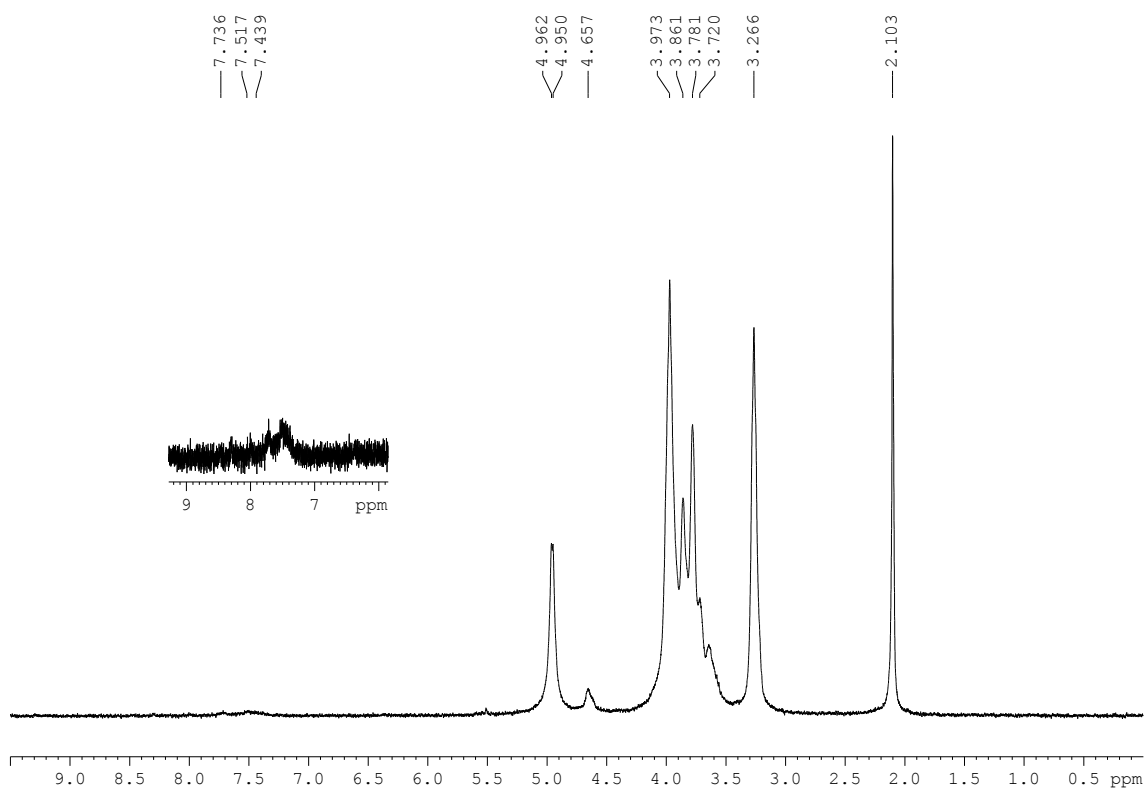


Figure S20. Compound **10**: ^{13}C CPMAS NMR spectrum

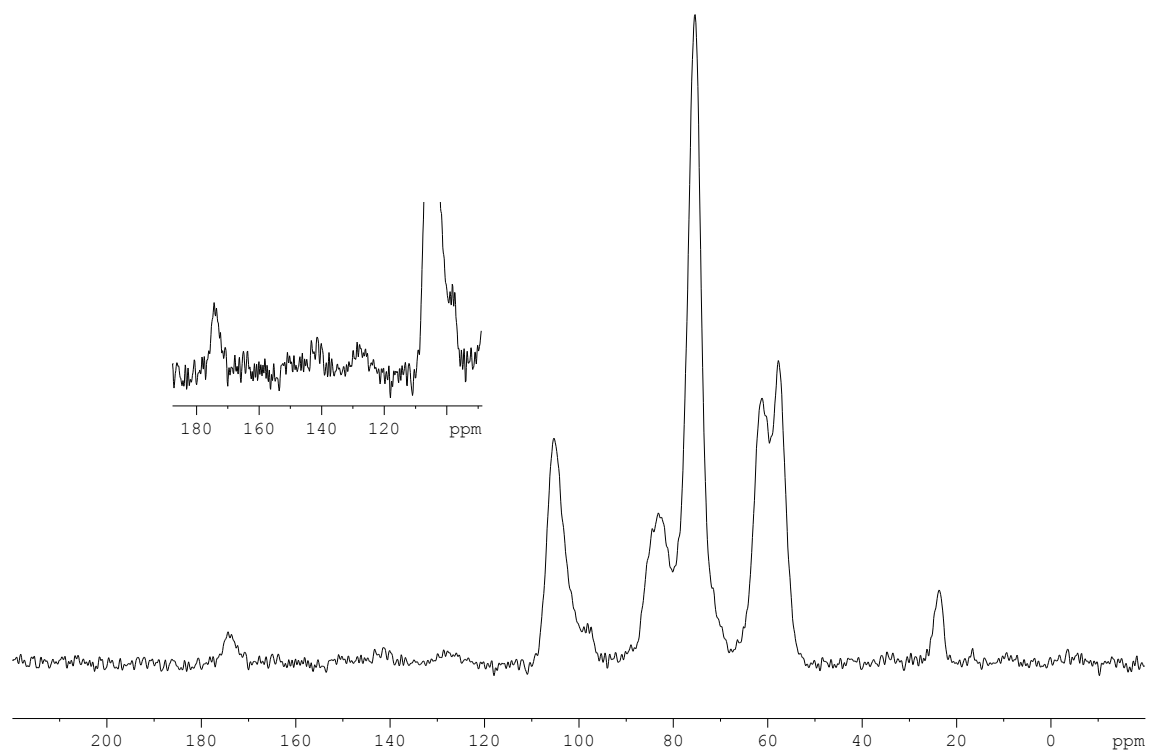


Figure S21. Compound **10**: ^{19}F NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 500 MHz)

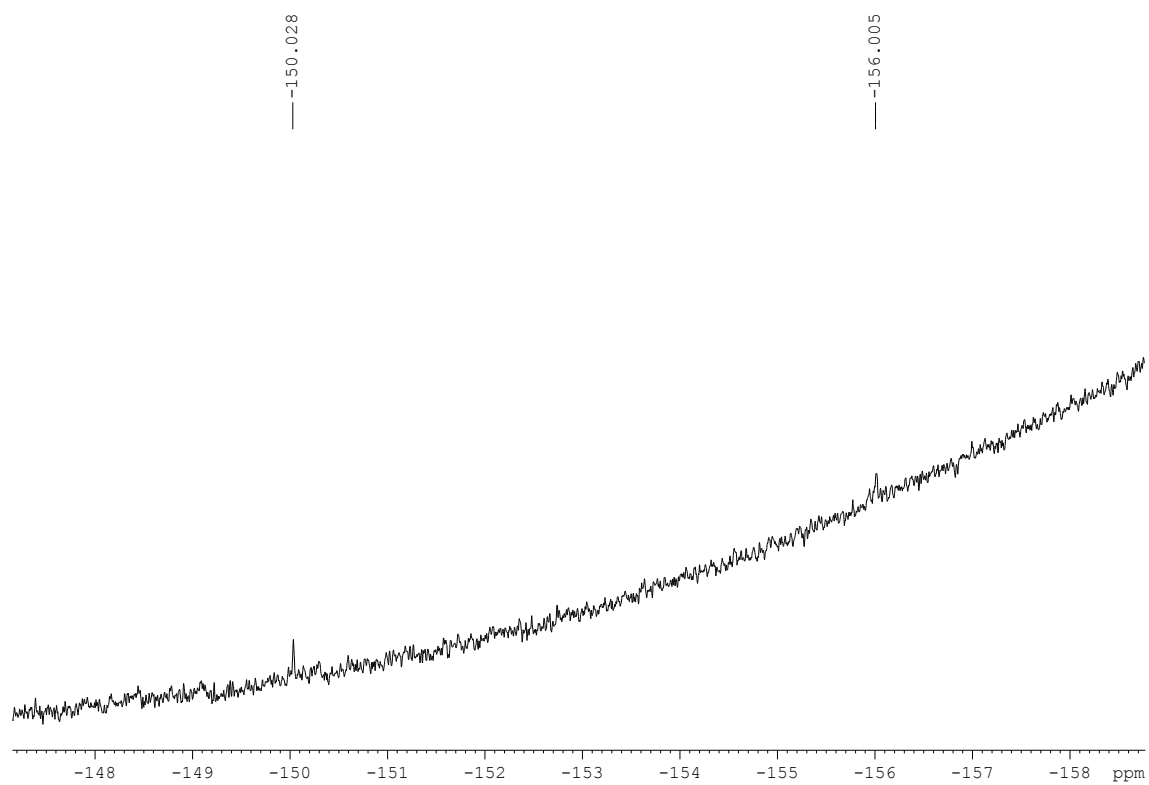


Figure S22. Compound **11**: ^1H NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 700 MHz)

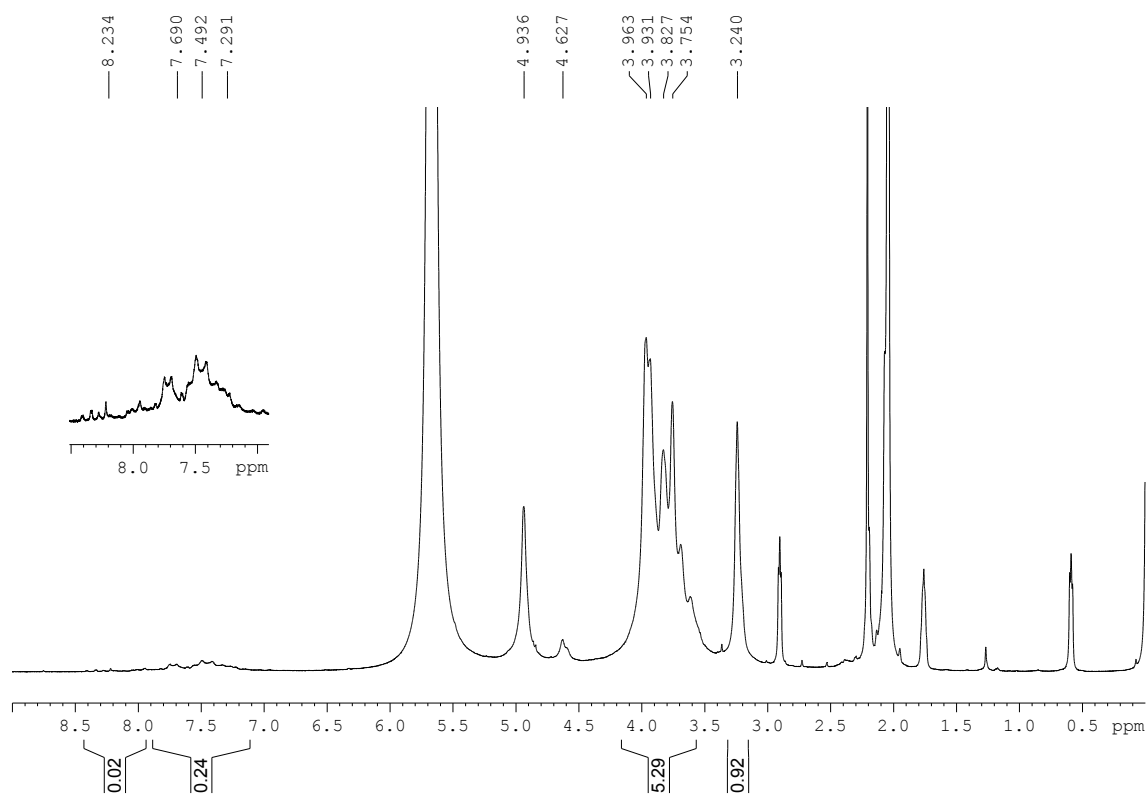


Figure S23. Compound **11**: Diffusion-filtered ^1H NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 500 MHz)

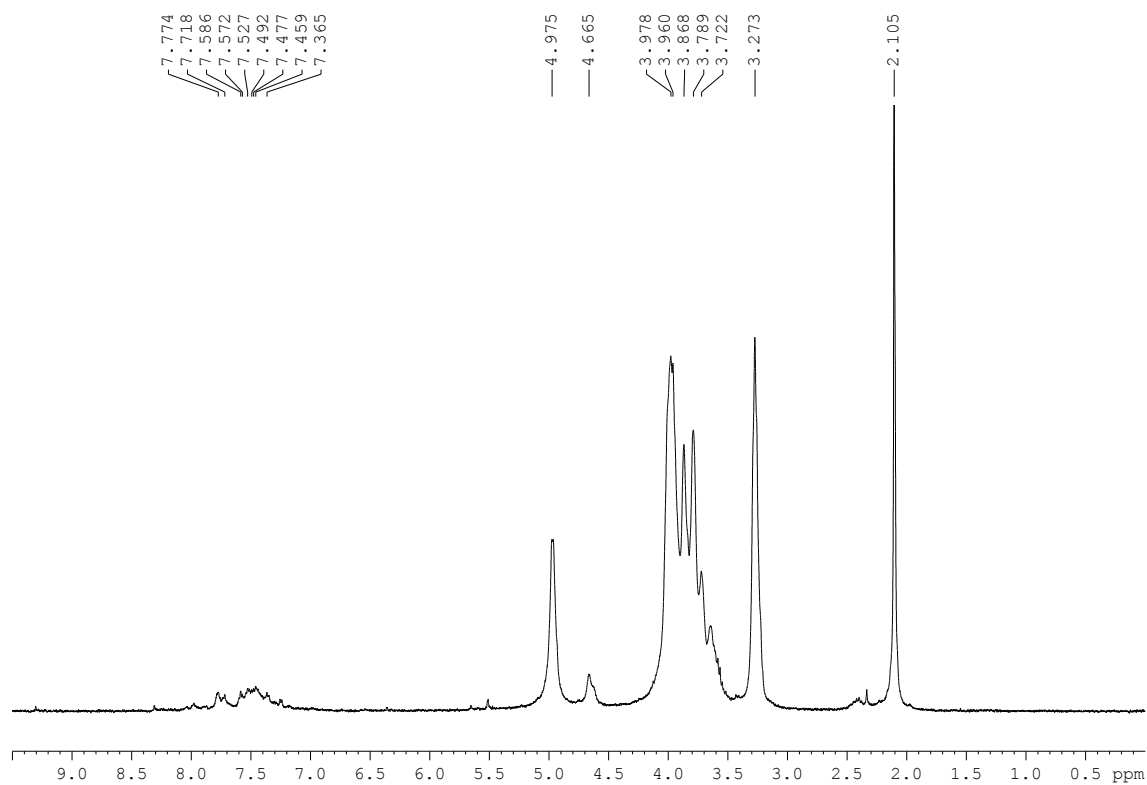


Figure S24. Compound 11: ^{13}C CPMAS NMR spectrum

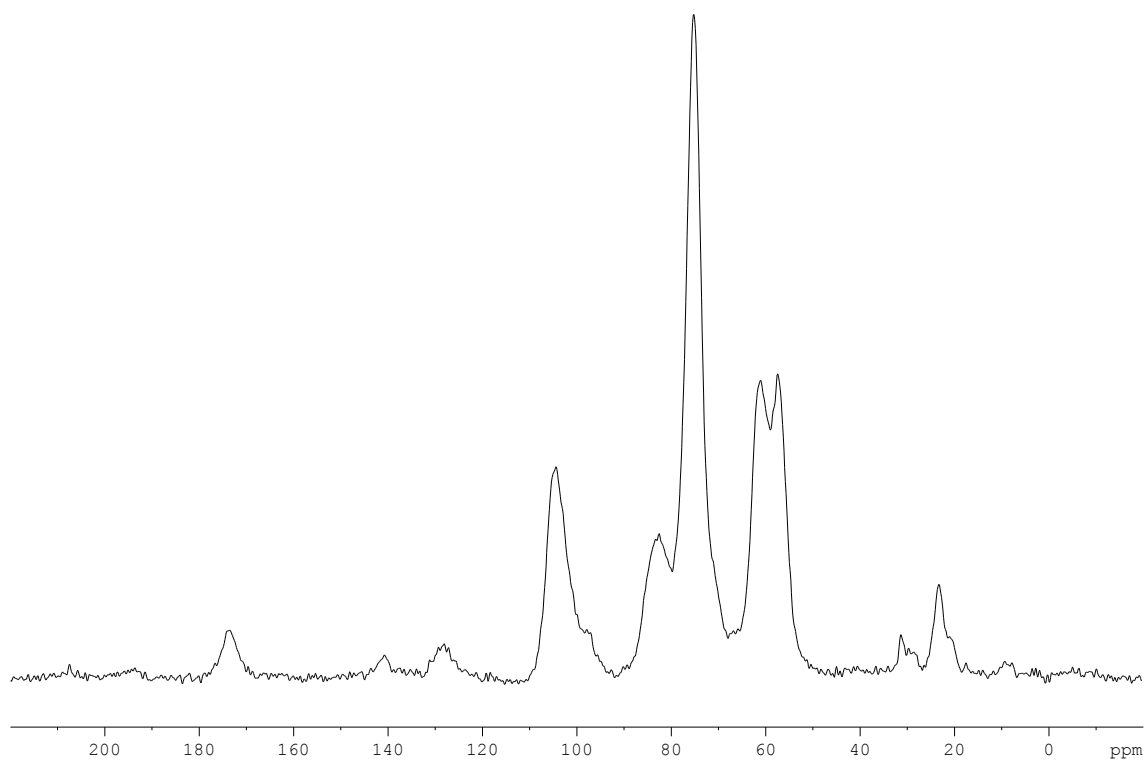


Figure S25. Compound 11: ^{19}F NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 500 MHz)

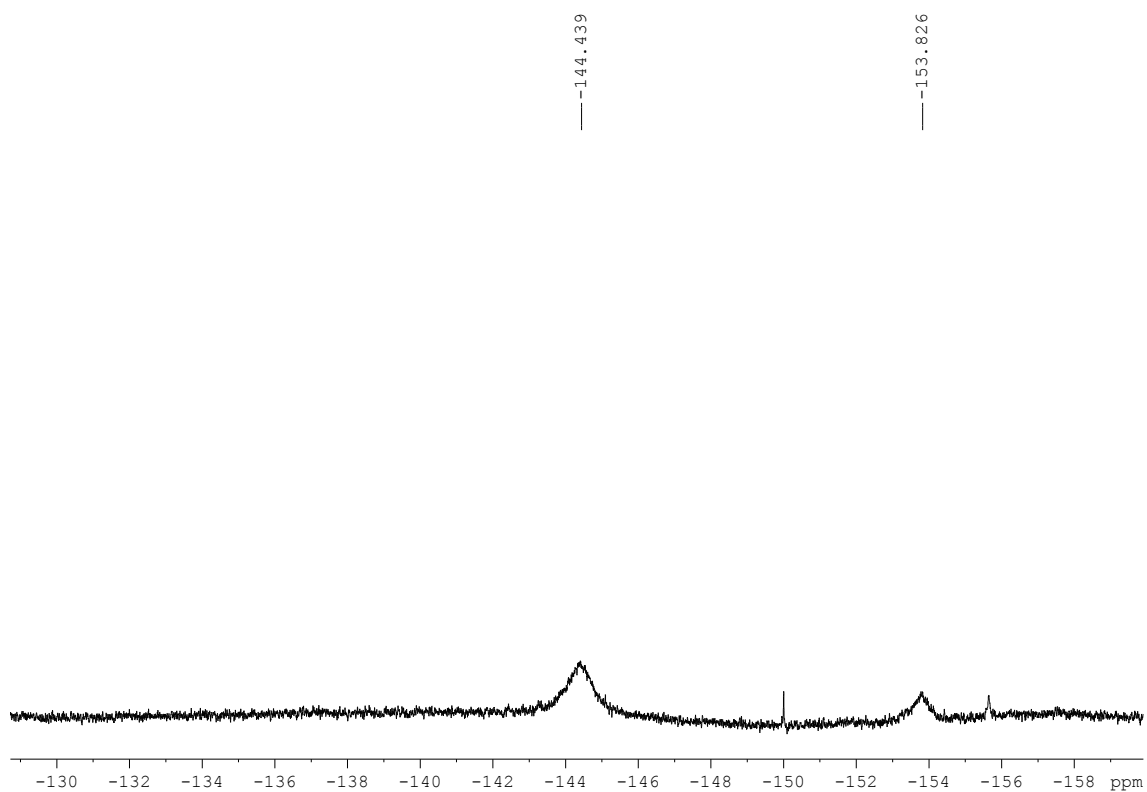


Figure S26. Compound **12**: ^1H NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 700 MHz)

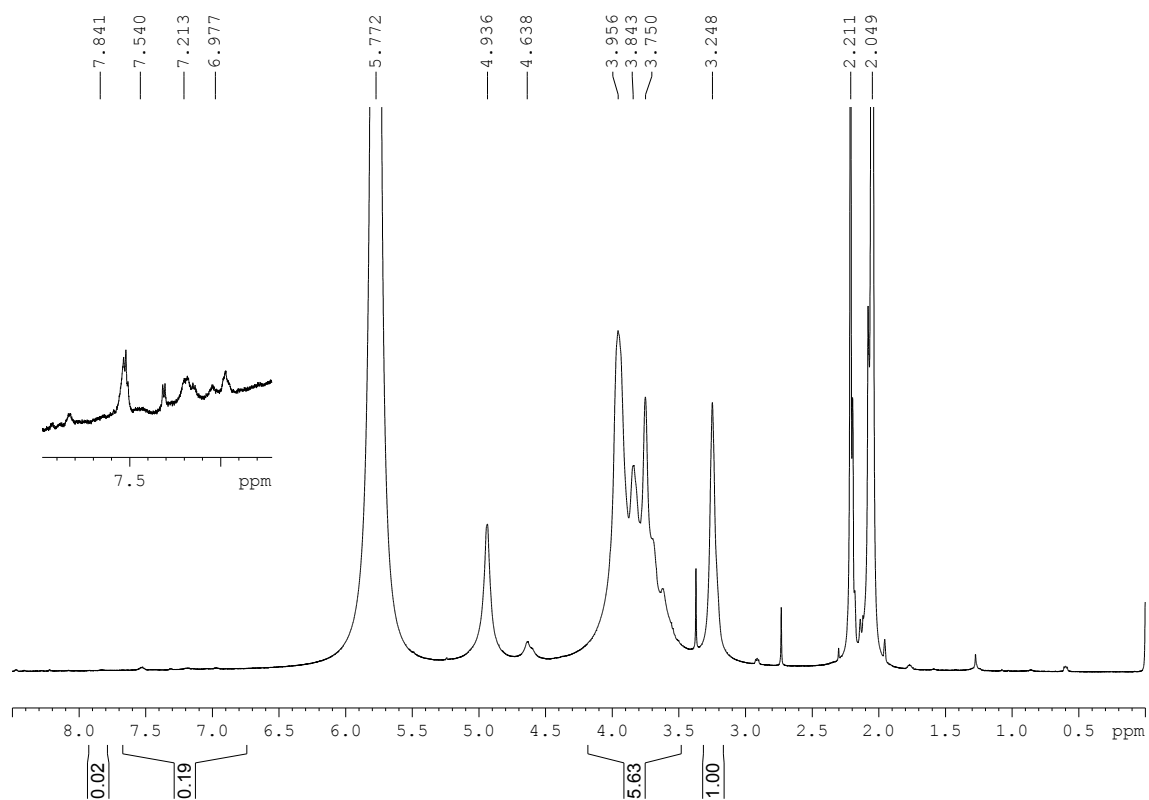


Figure S27. Compound **12**: Diffusion-filtered ^1H NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 500 MHz)

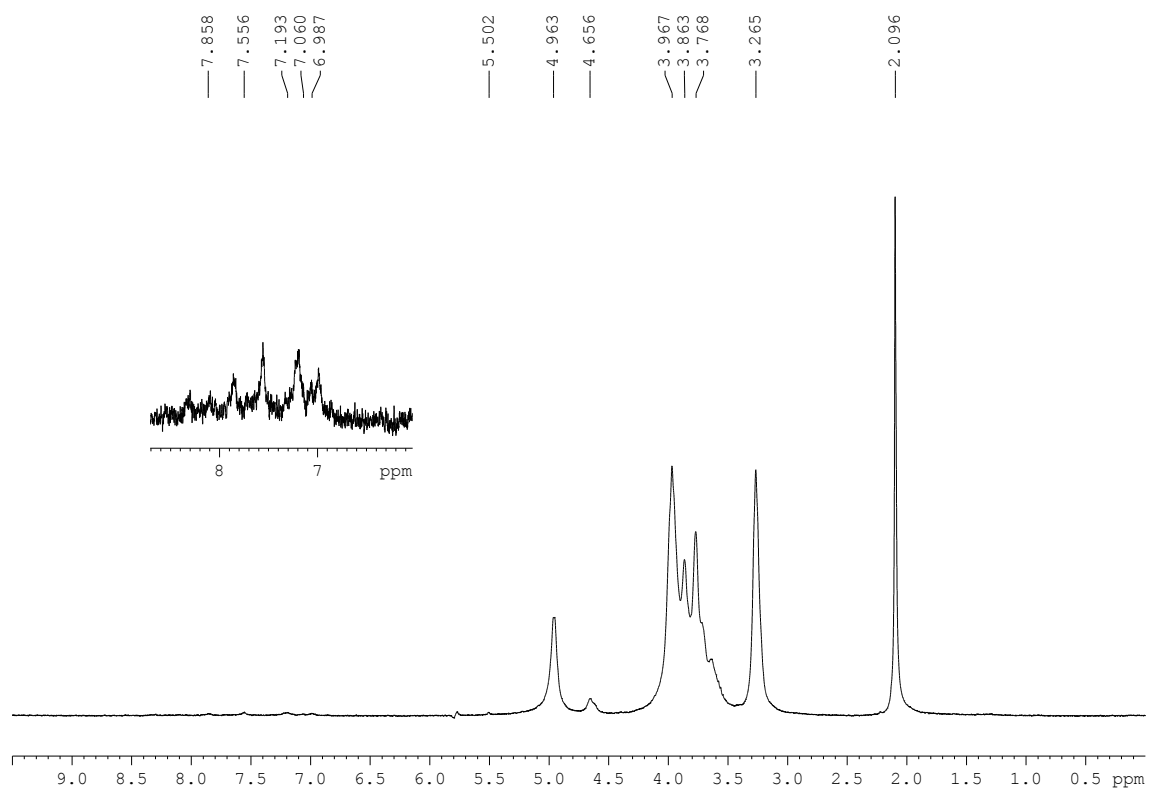


Figure S28. Compound **12a**: ^1H NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 700 MHz)

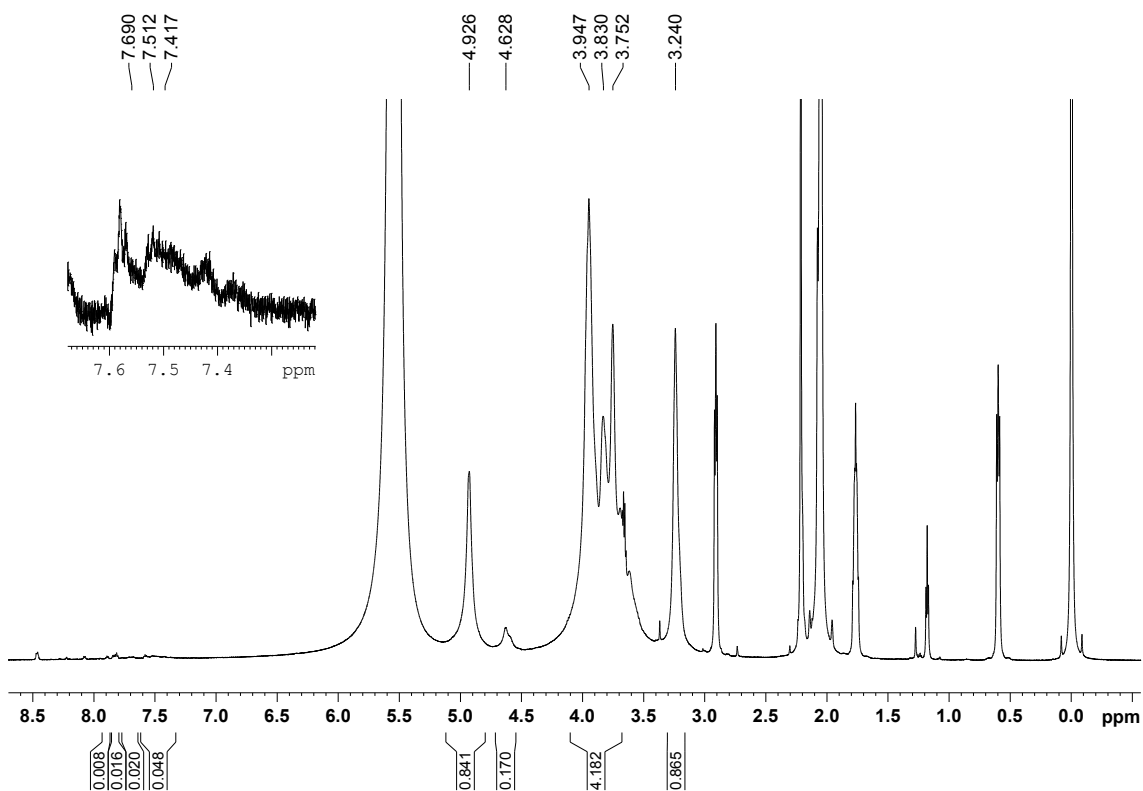


Figure S29. Compound **12a**: Diffusion-filtered ^1H NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 500 MHz)

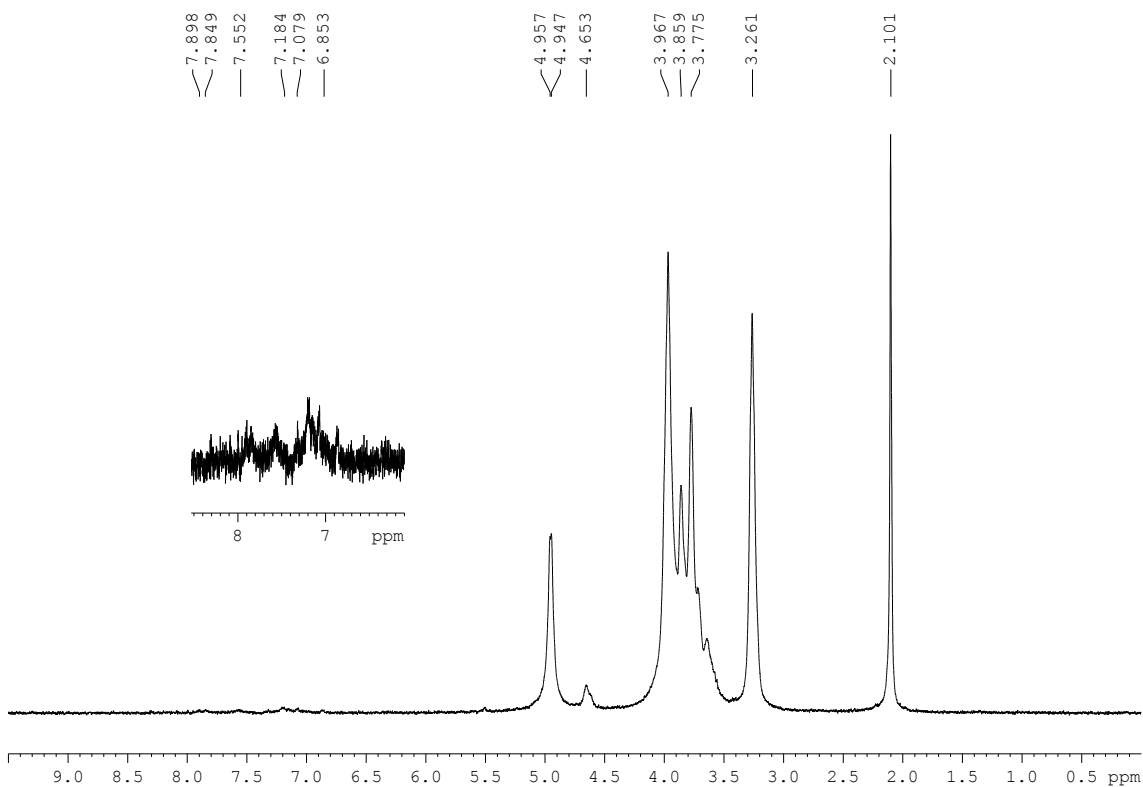


Figure S30. Compound **12a**: ^{13}C CPMAS NMR spectrum

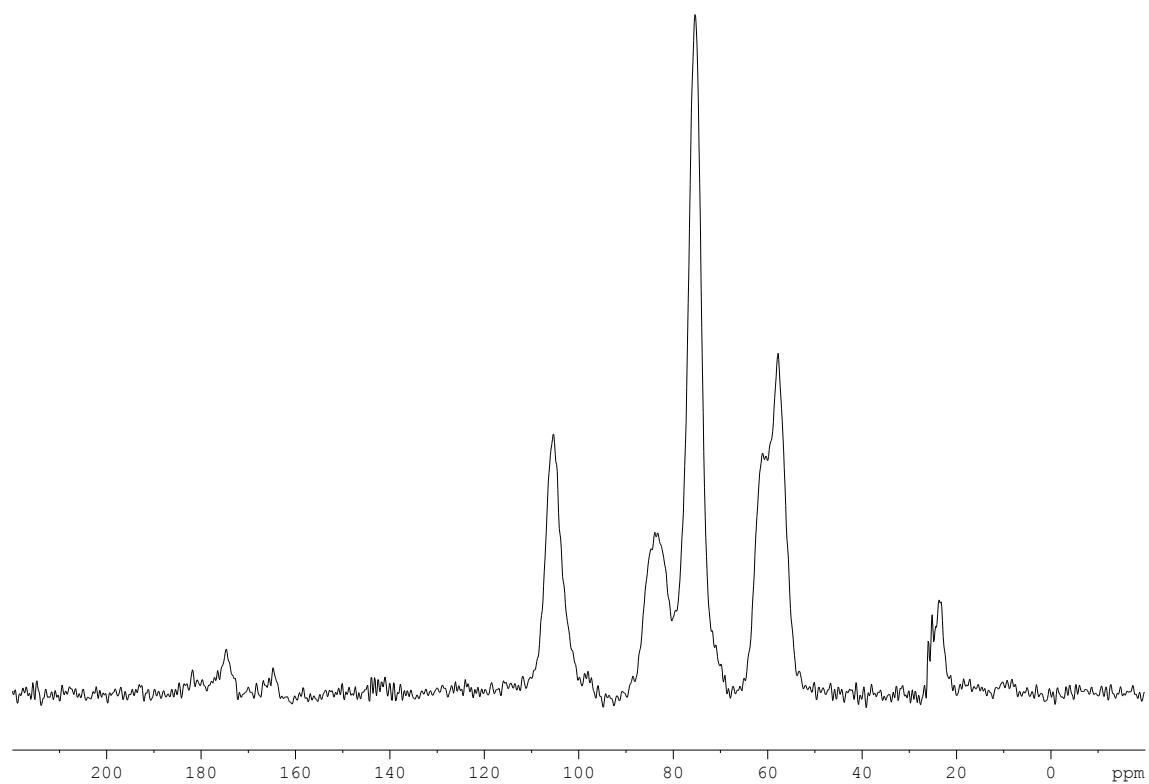


Figure S31. Compound **12a**: ^{19}F NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 500 MHz)

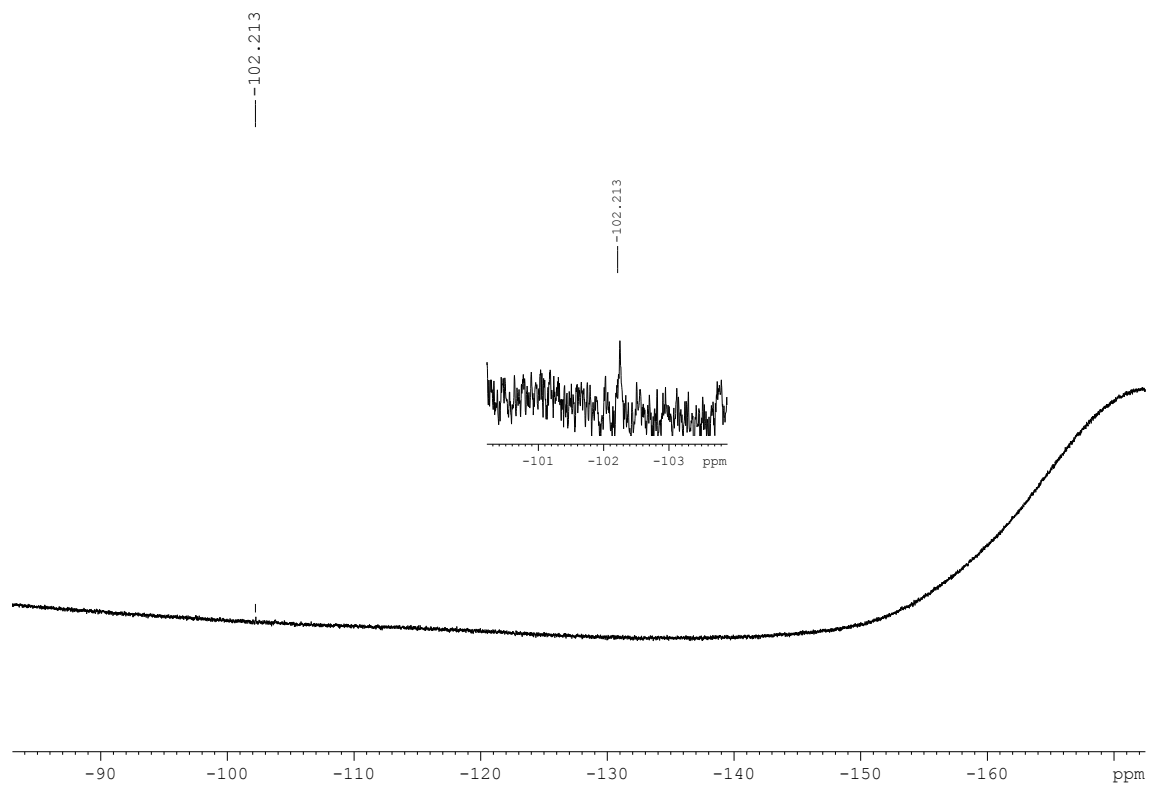


Figure S32. Compound 13: ^1H NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 700 MHz)

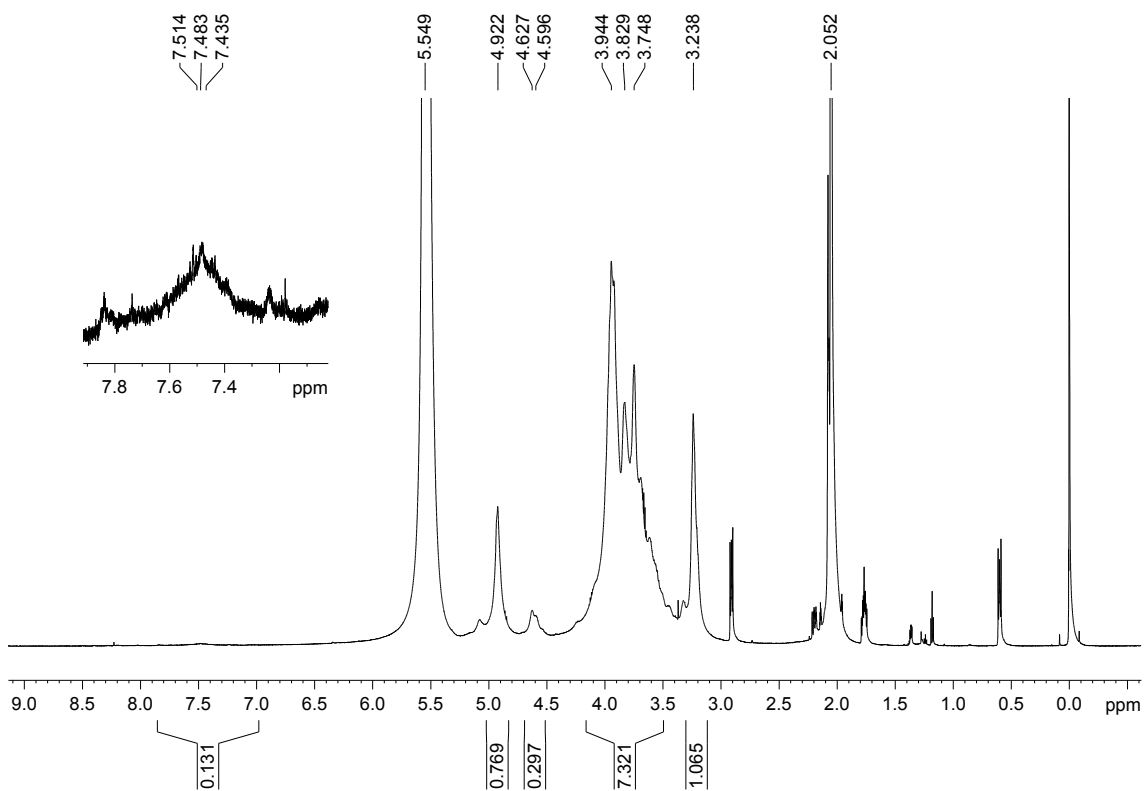


Figure S33. Compound 14: ^1H NMR spectrum ($\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ 700 MHz)

