Supporting information

Chiral thiouronium salts: synthesis, characterisation and application in NMR *enantio*-discrimination of chiral oxoanions

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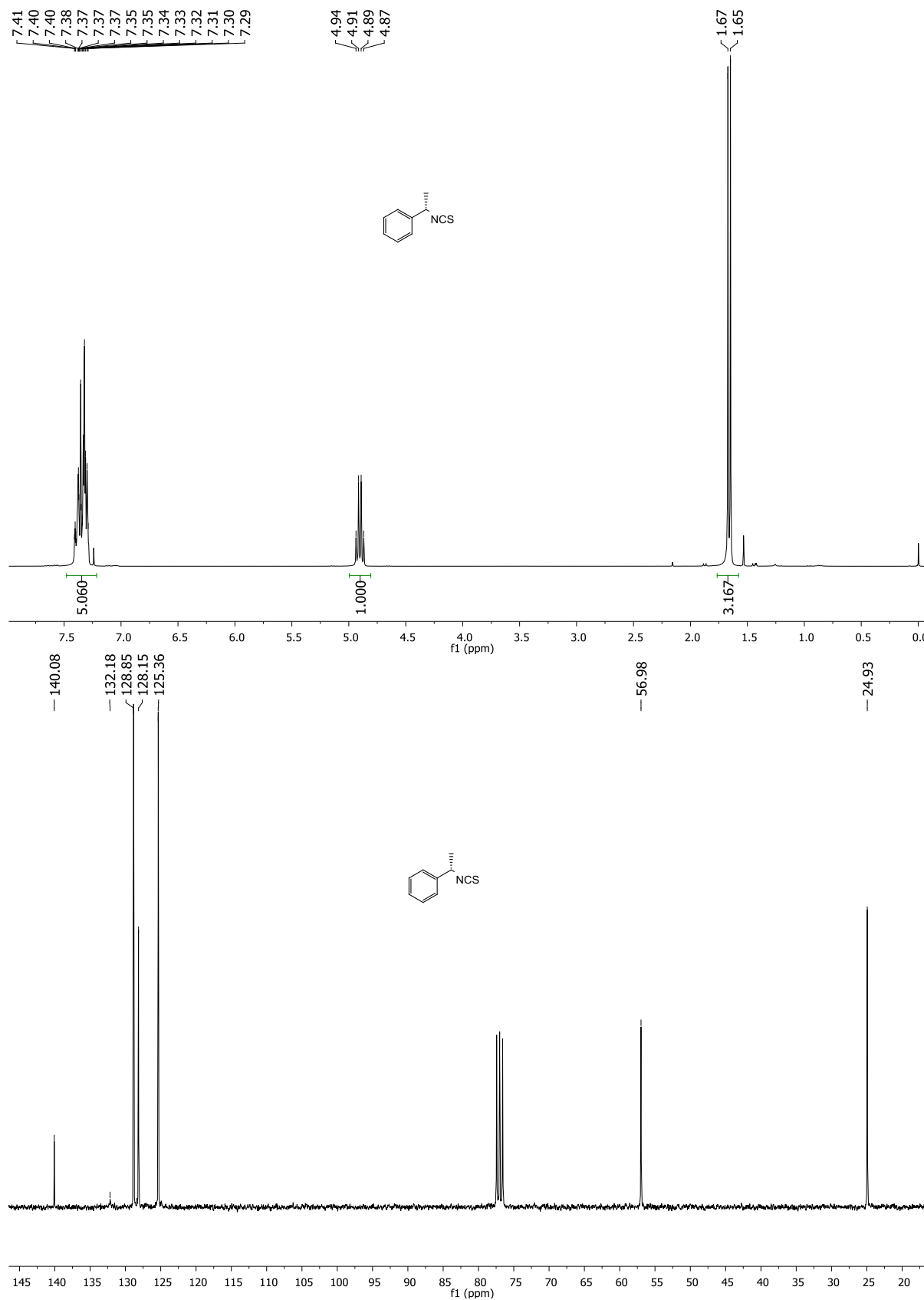
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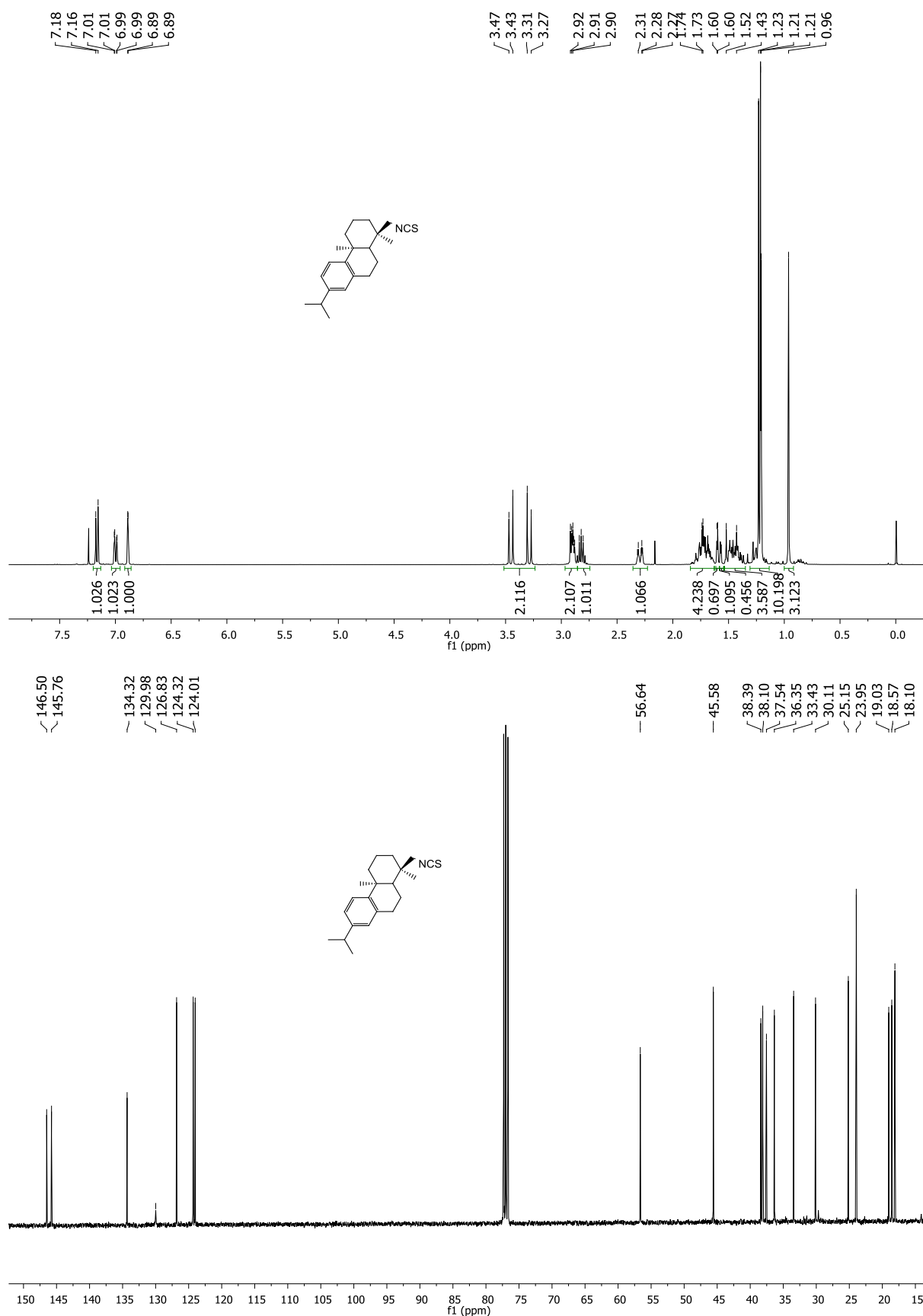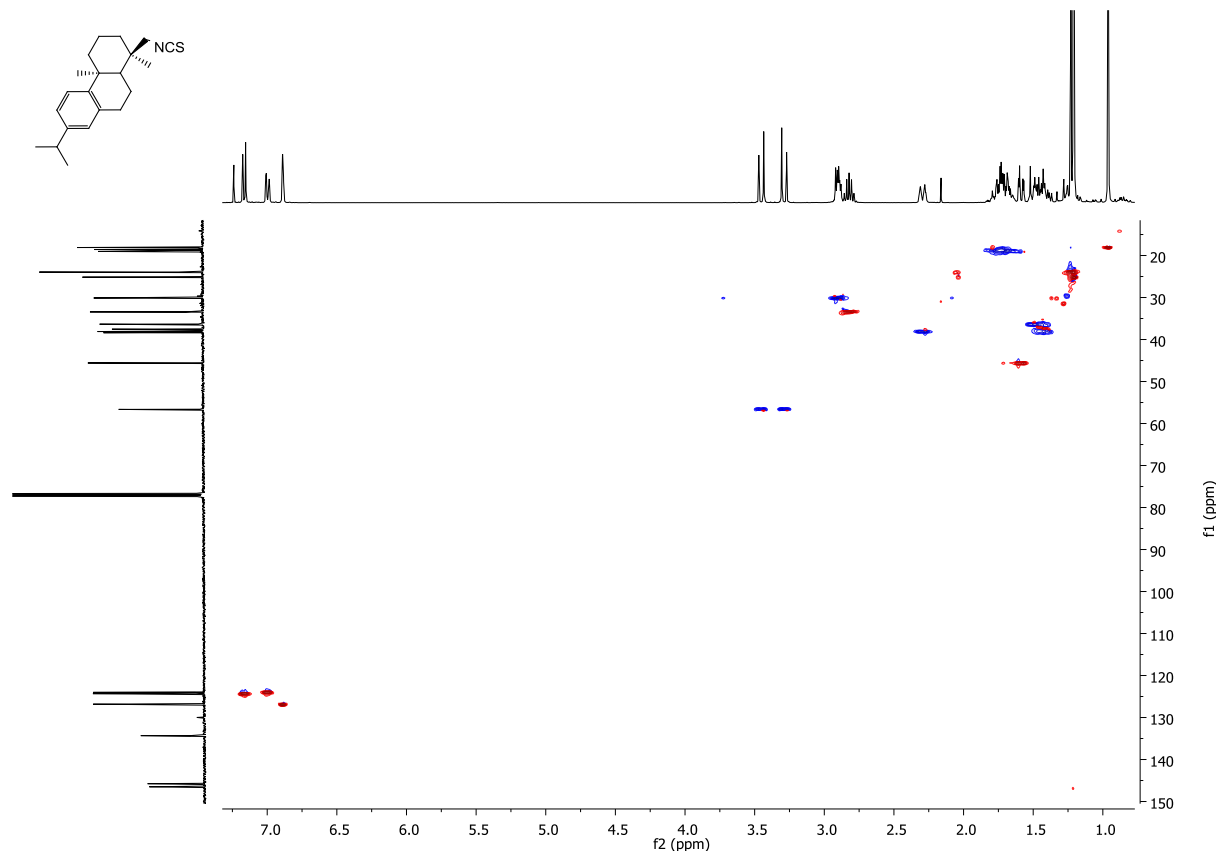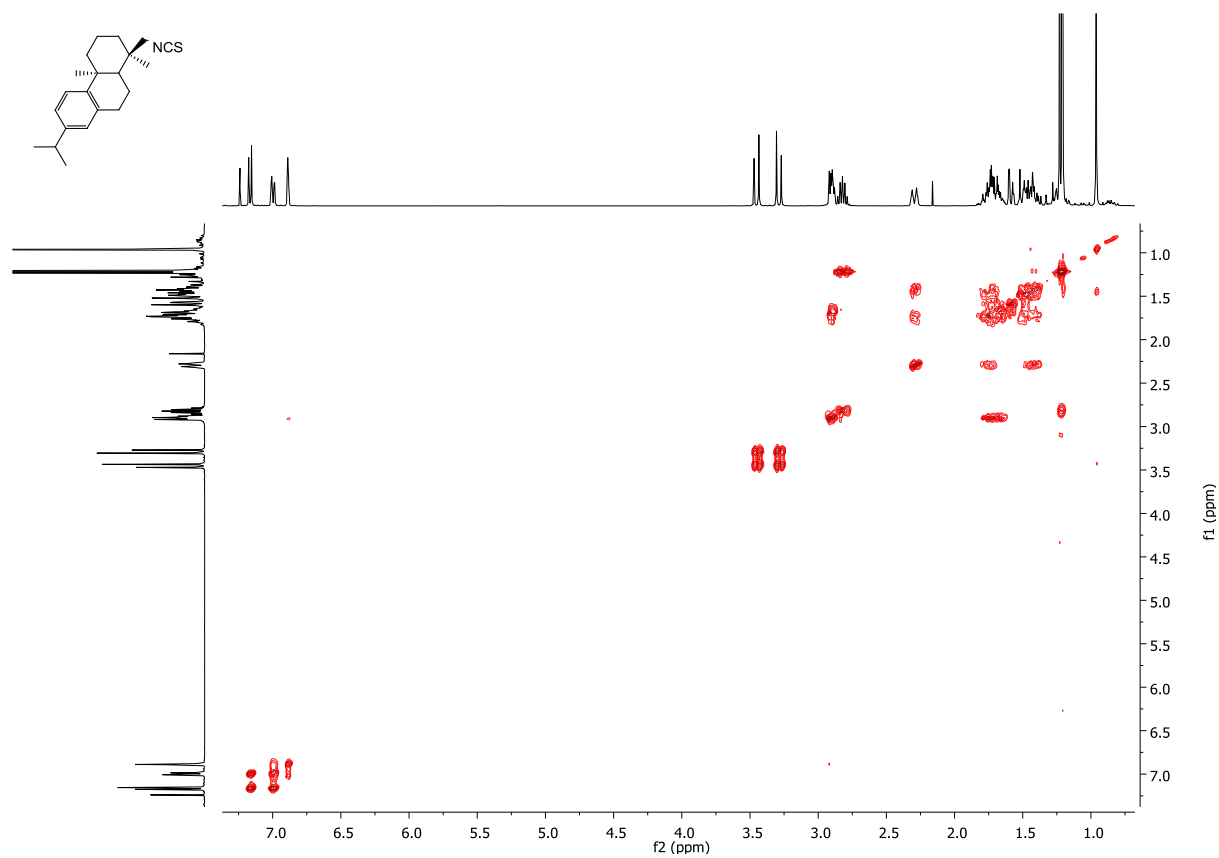
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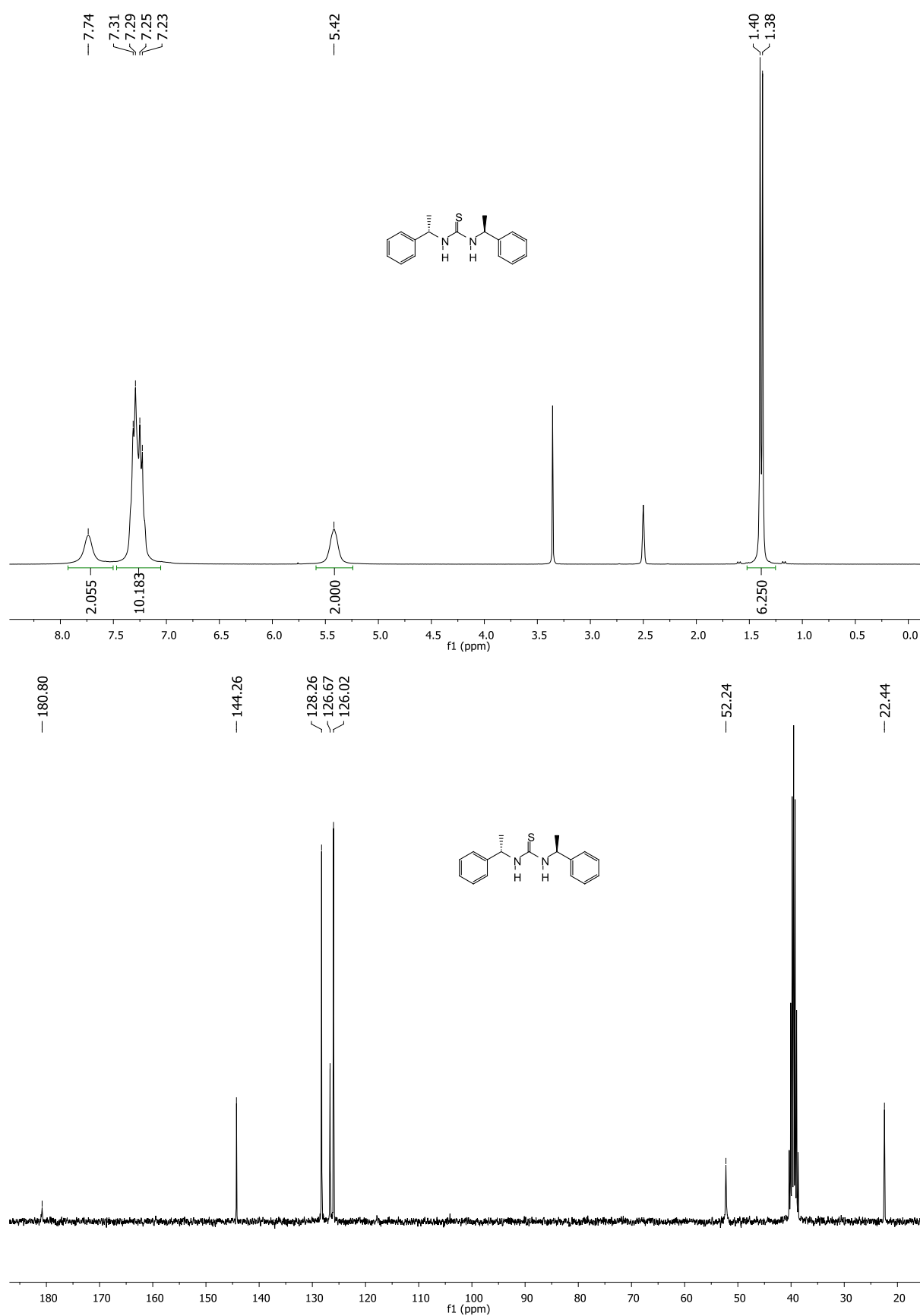
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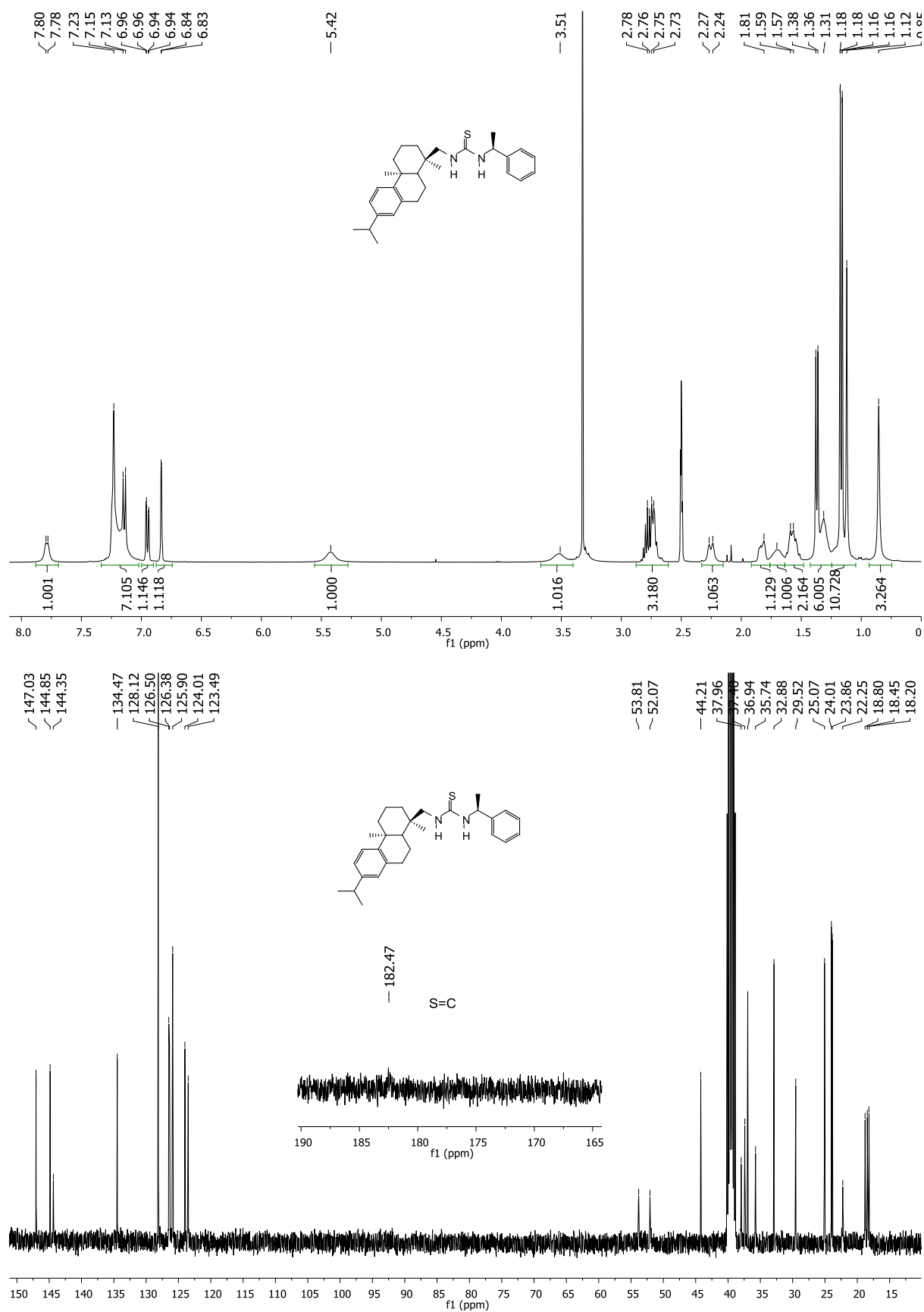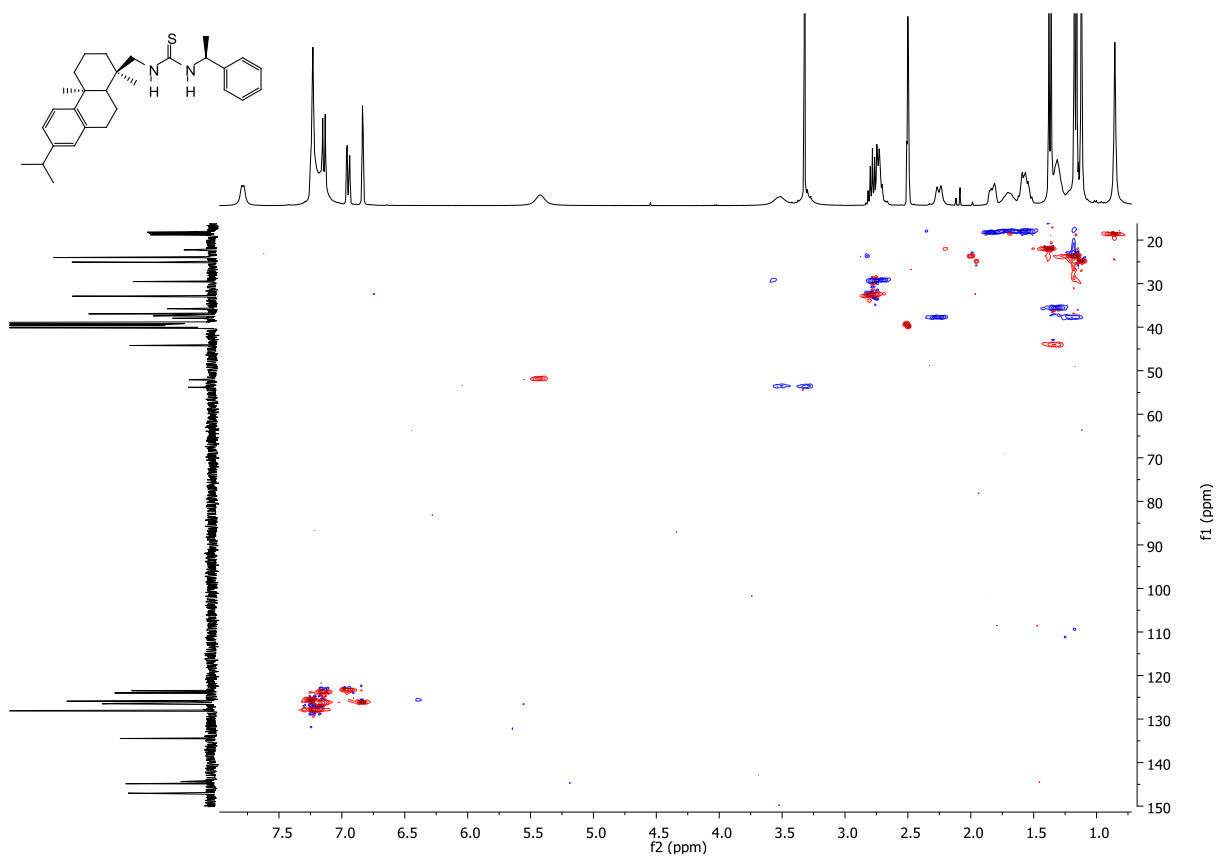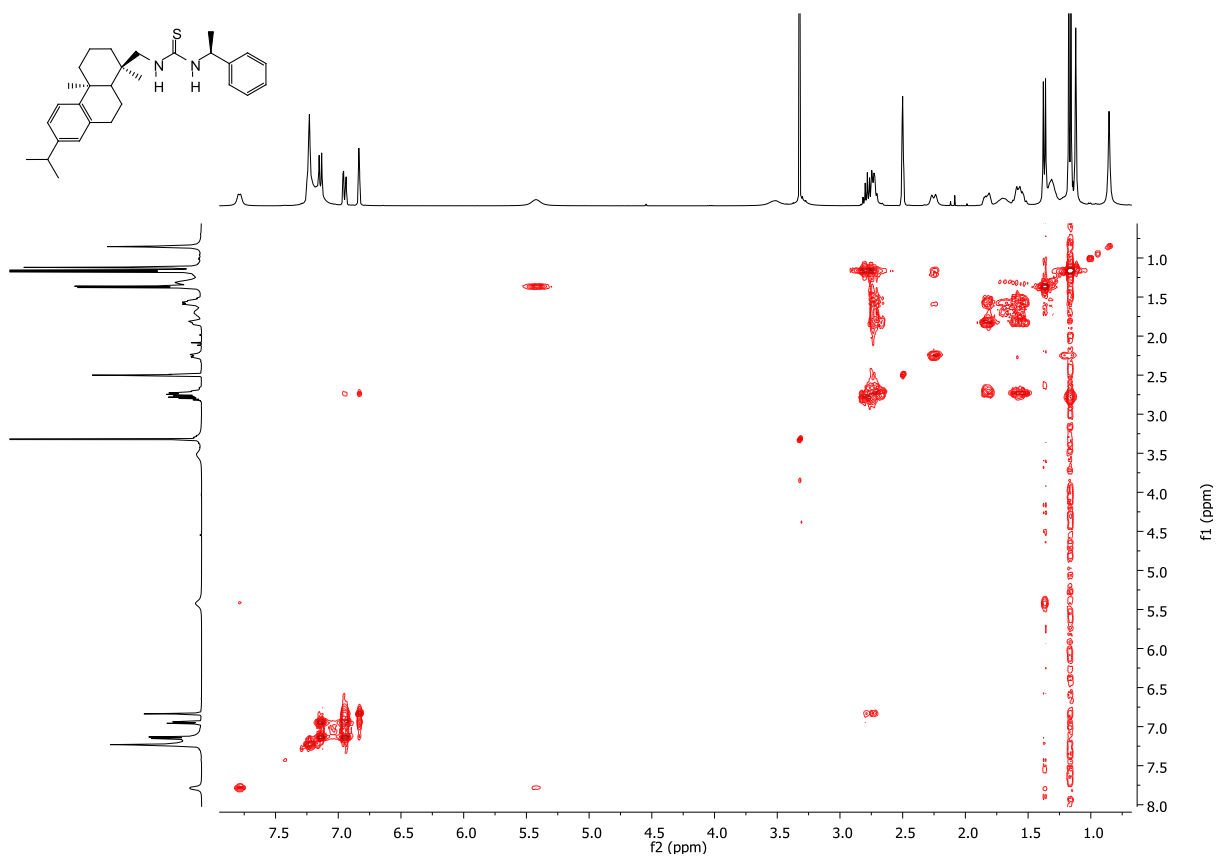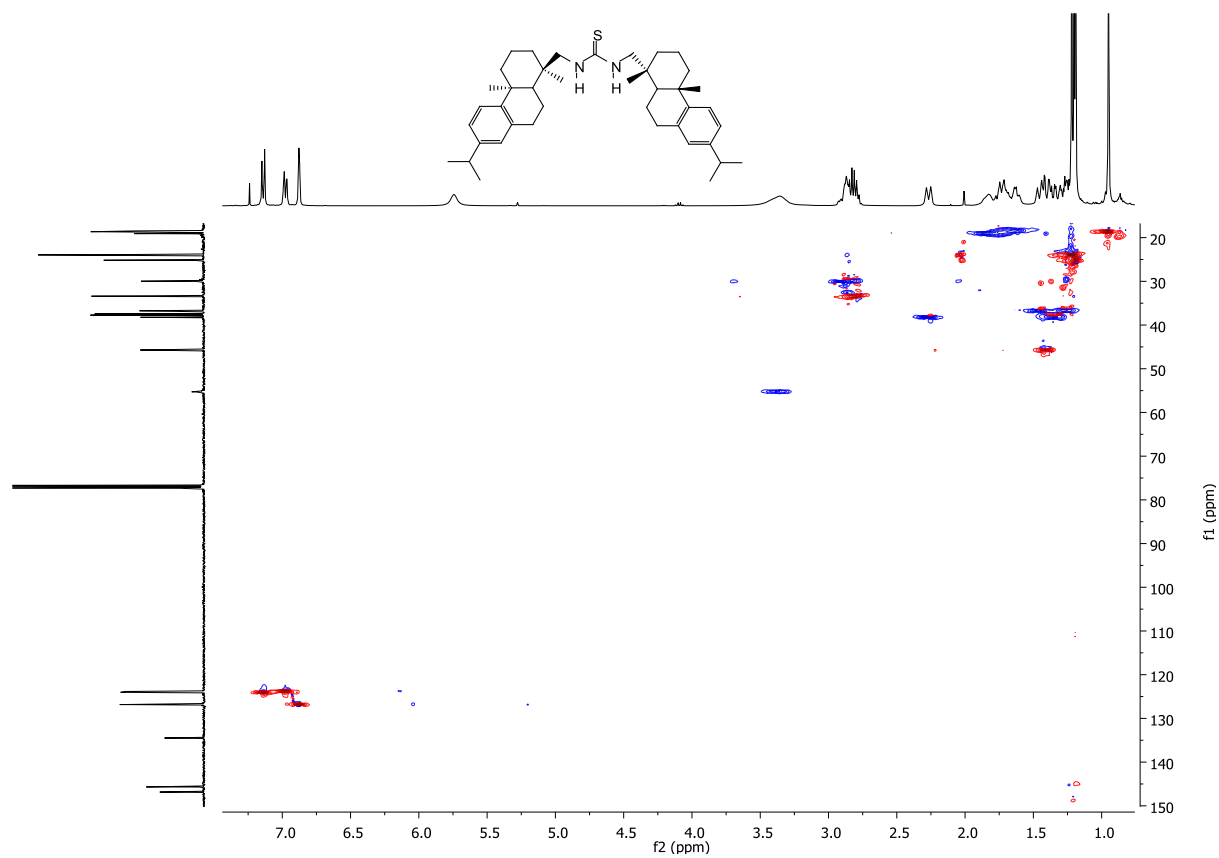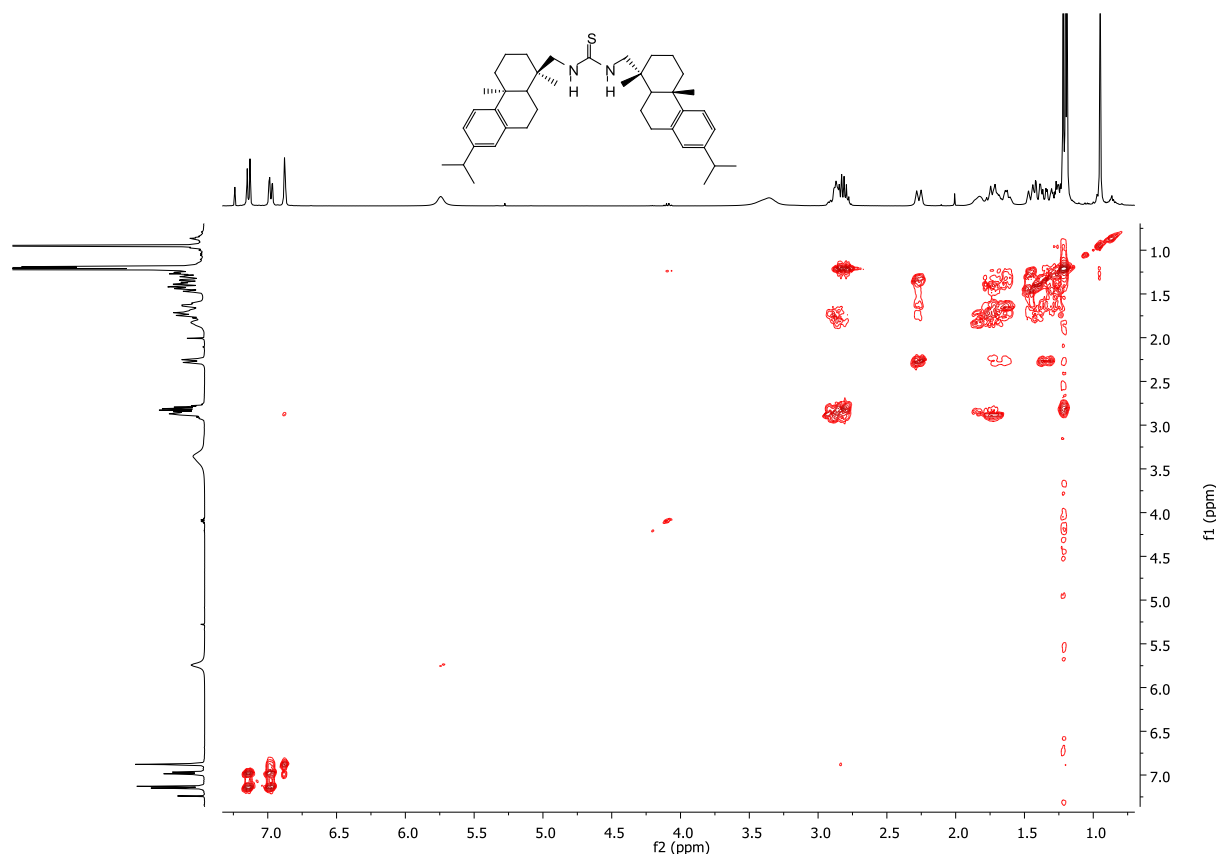
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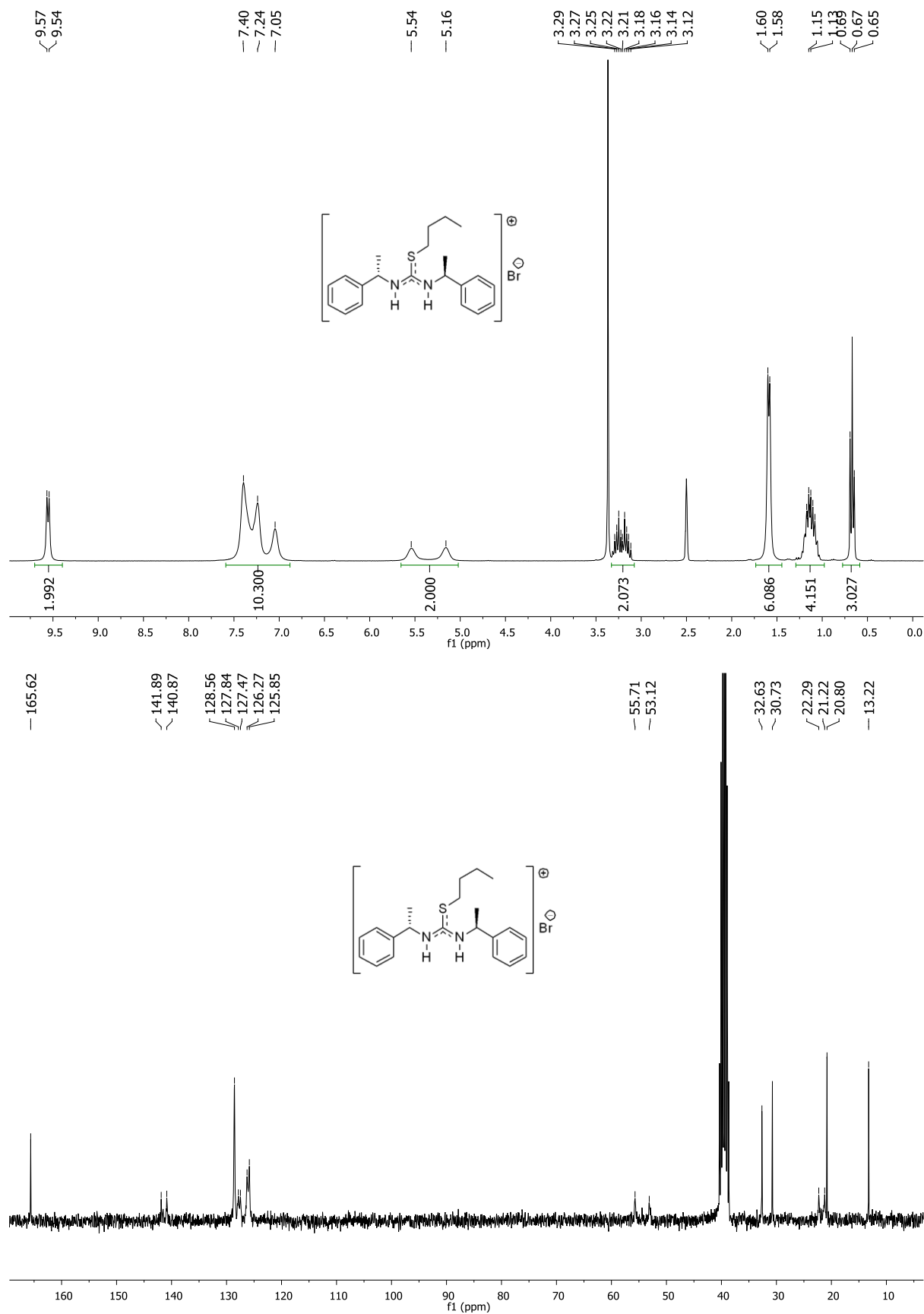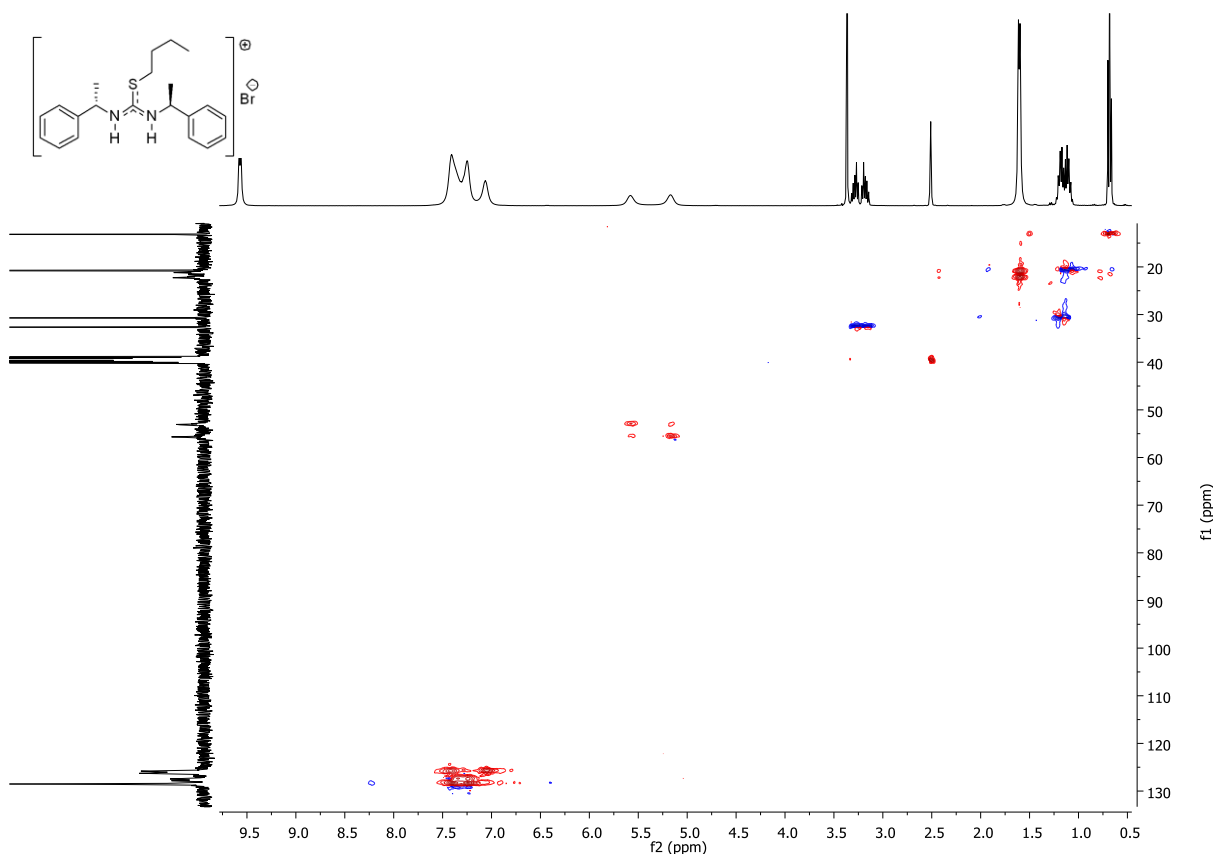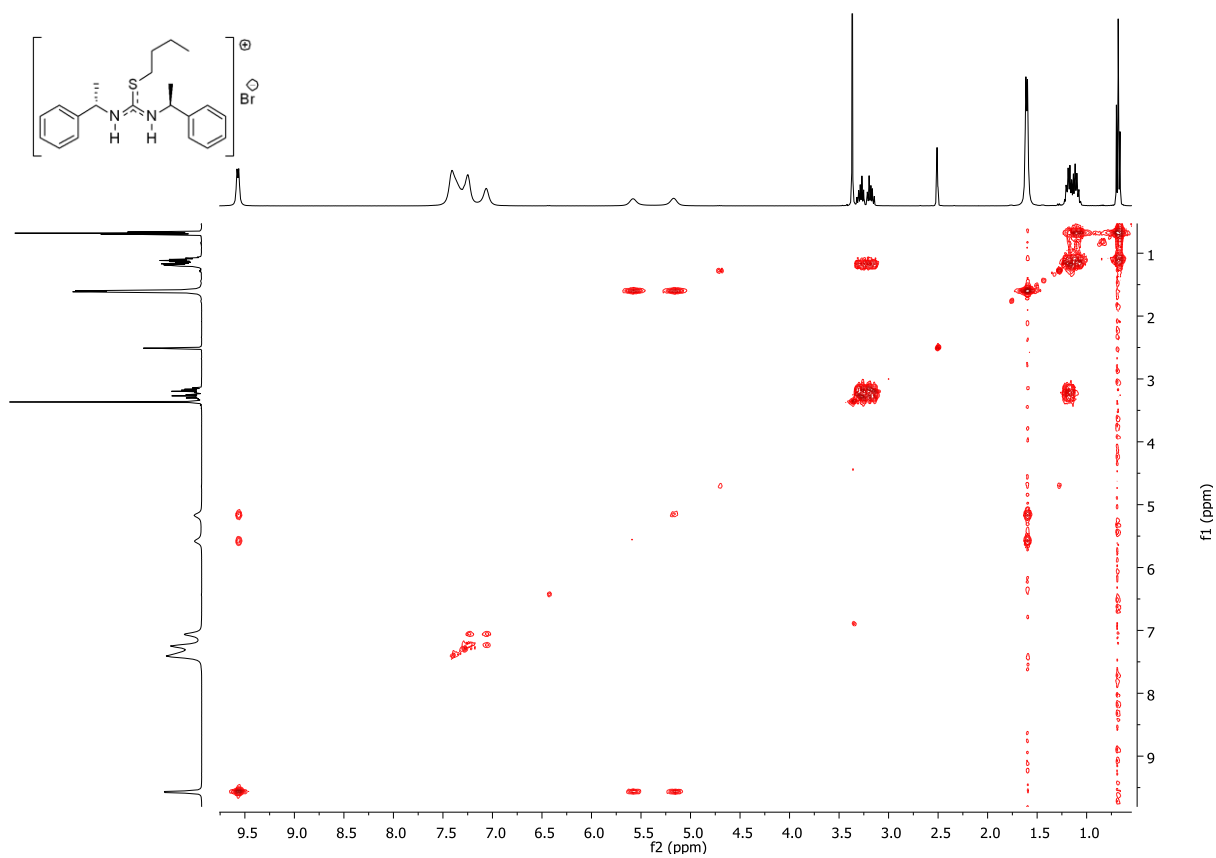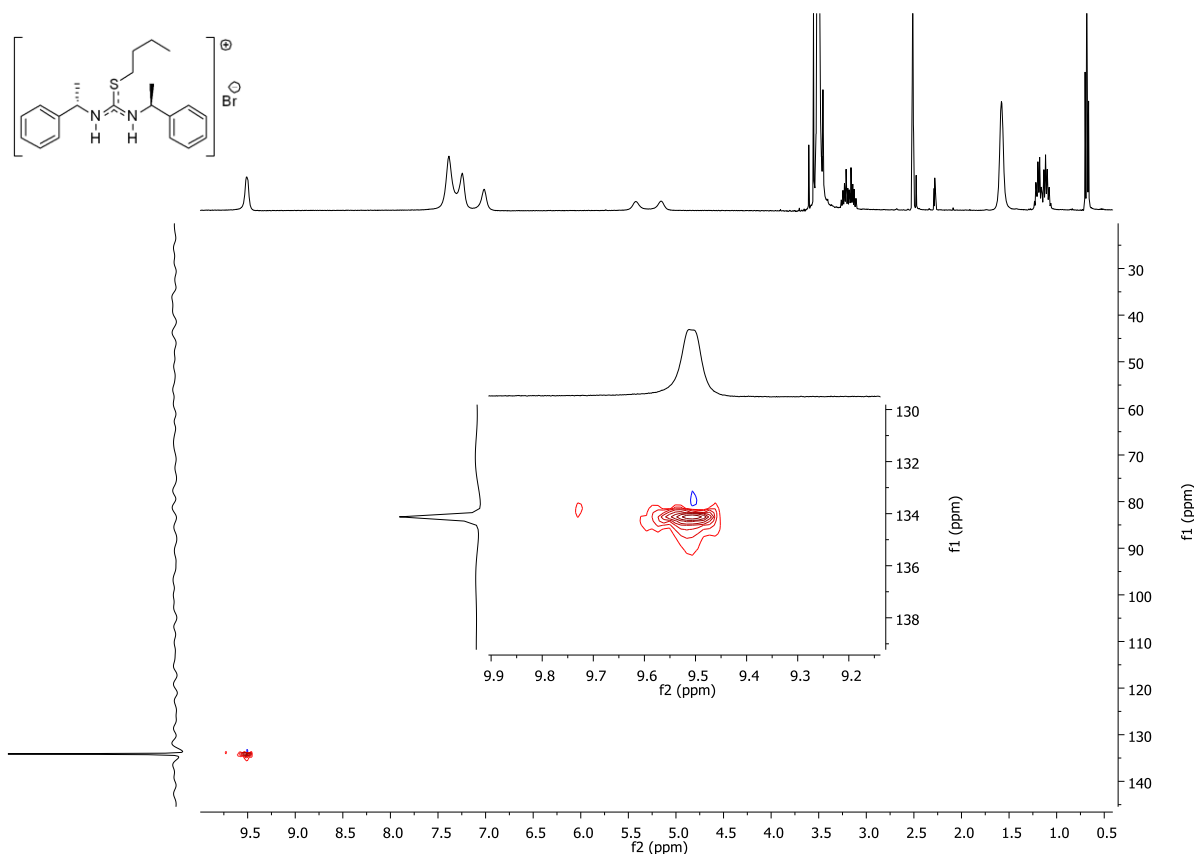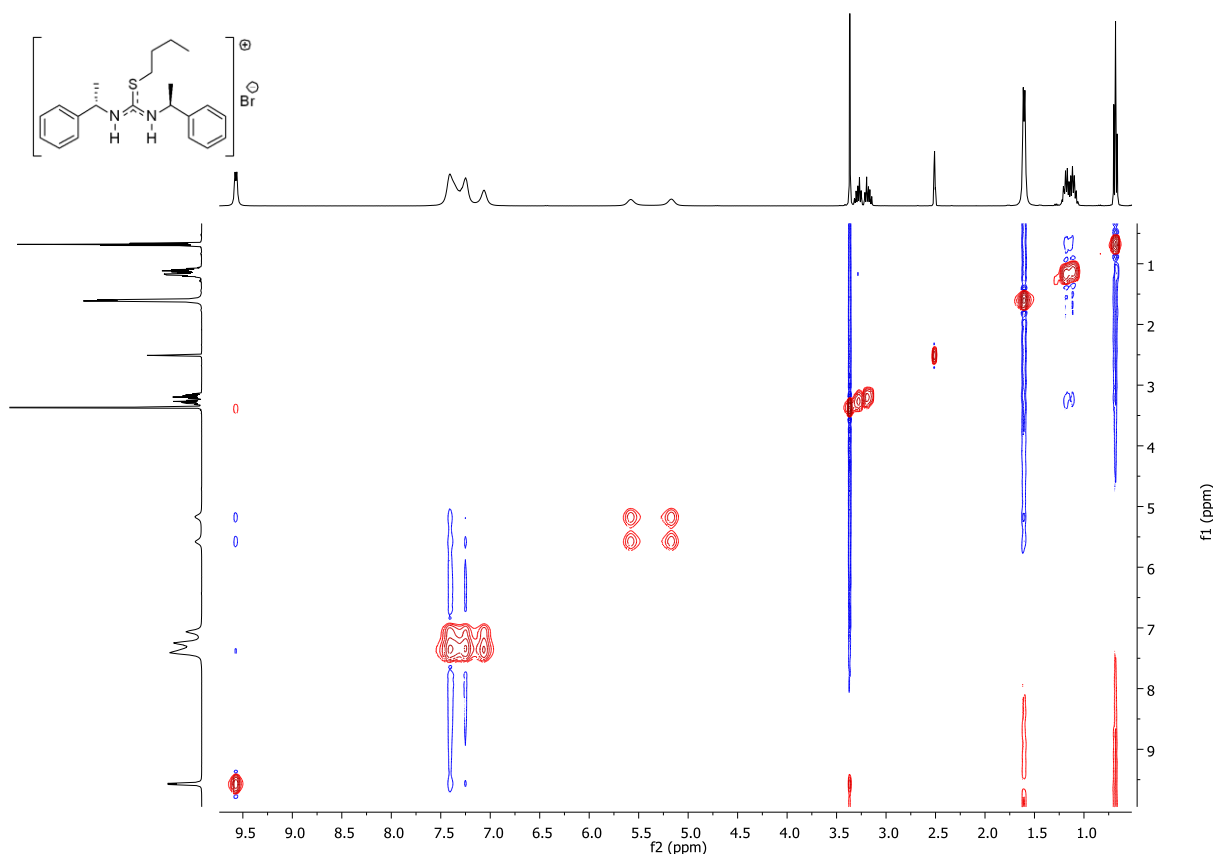
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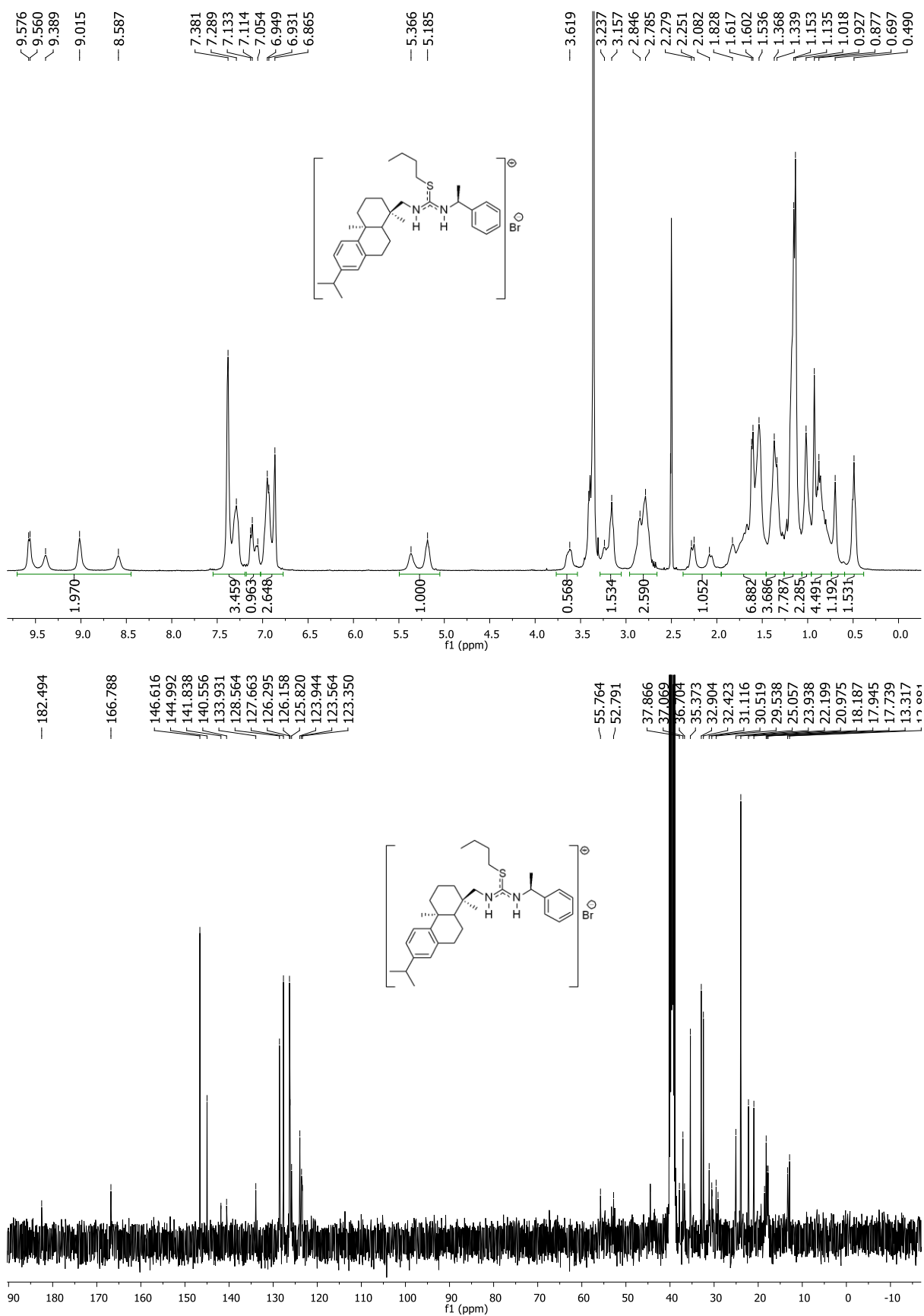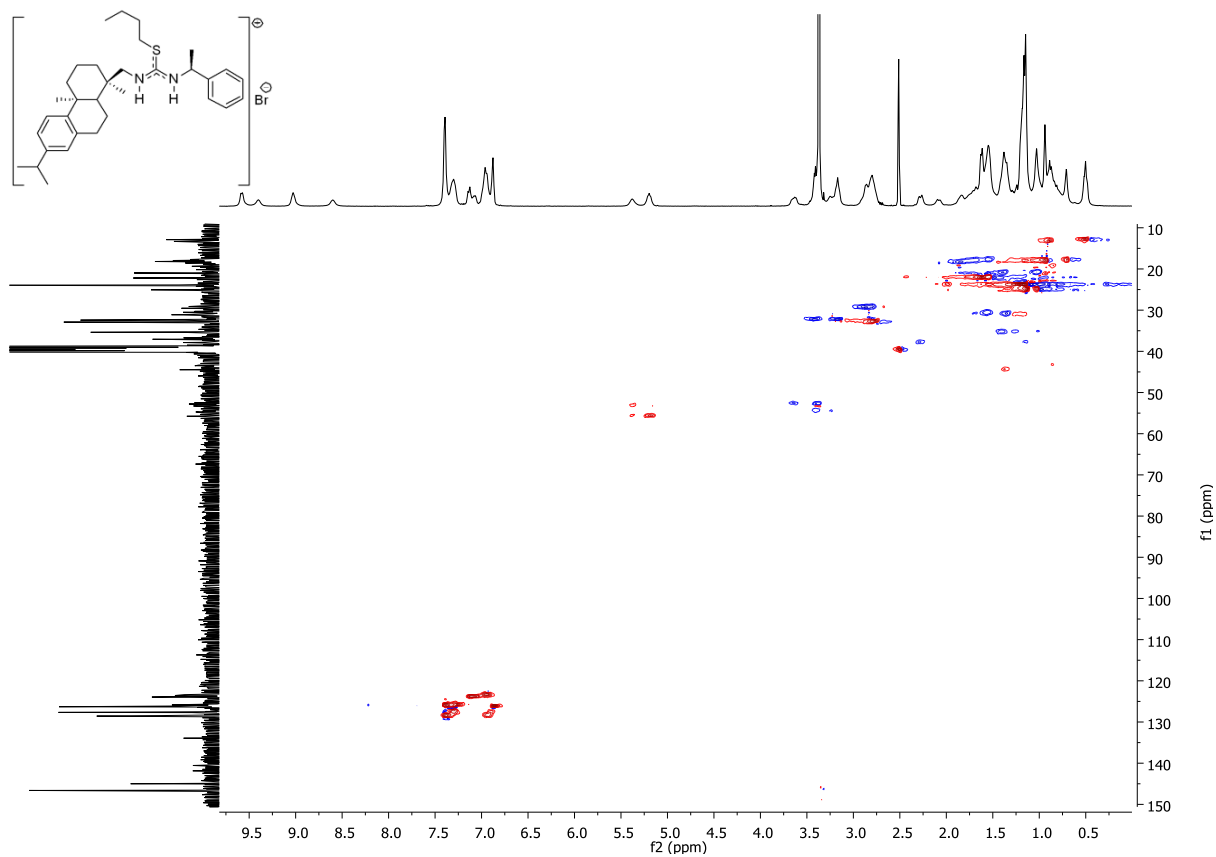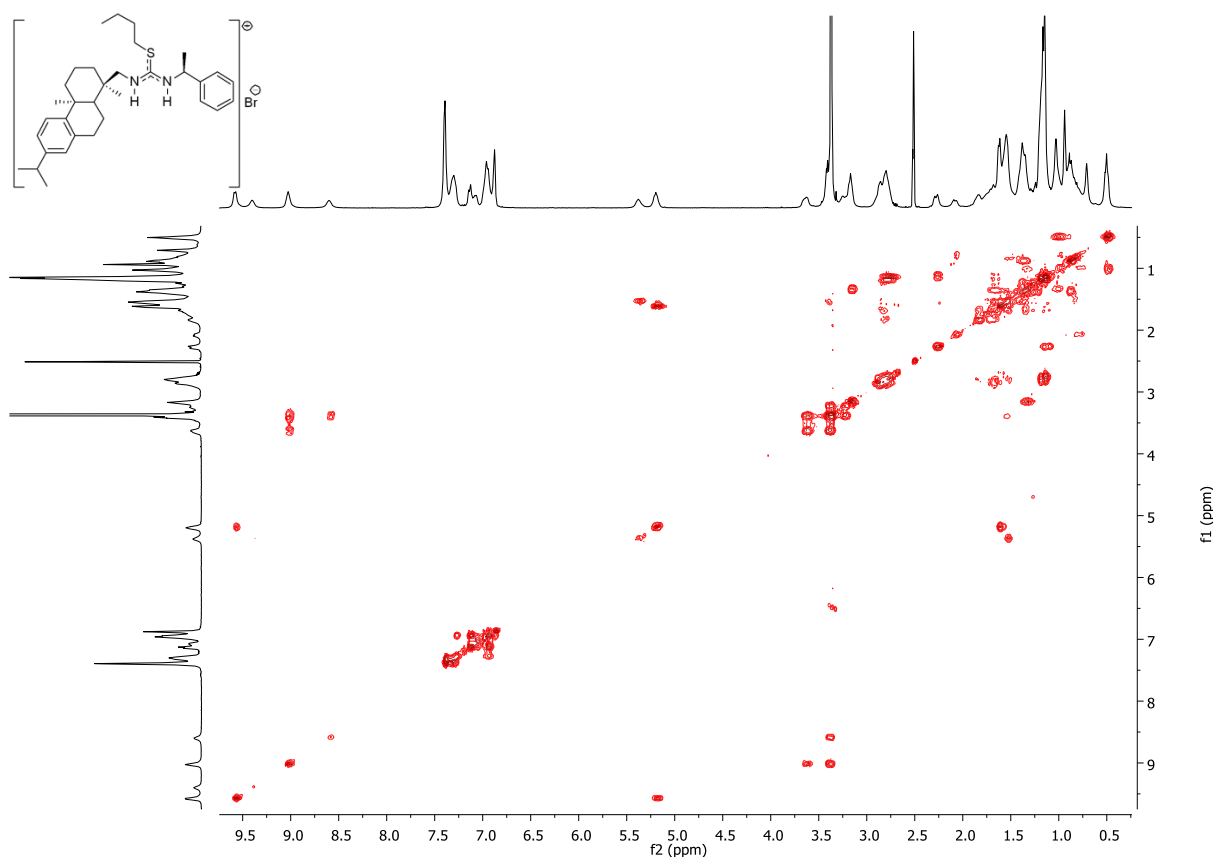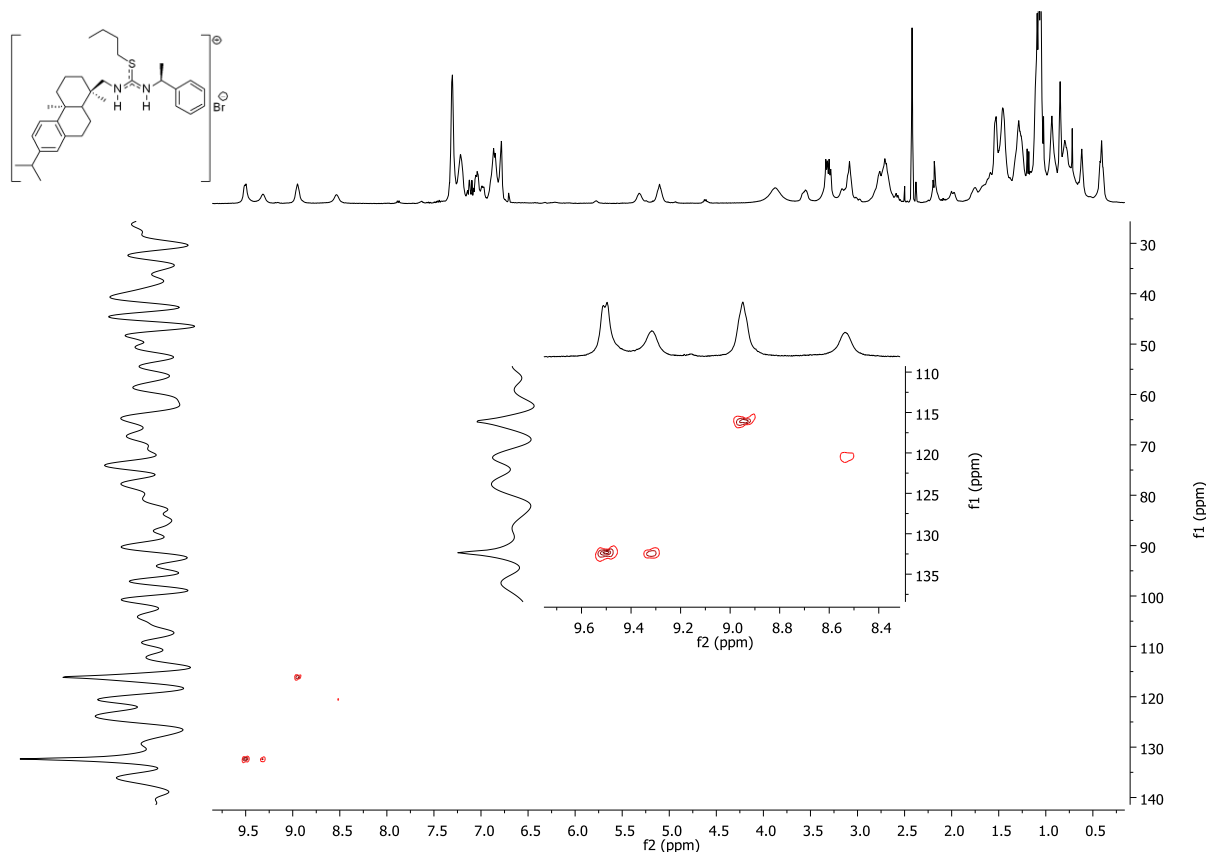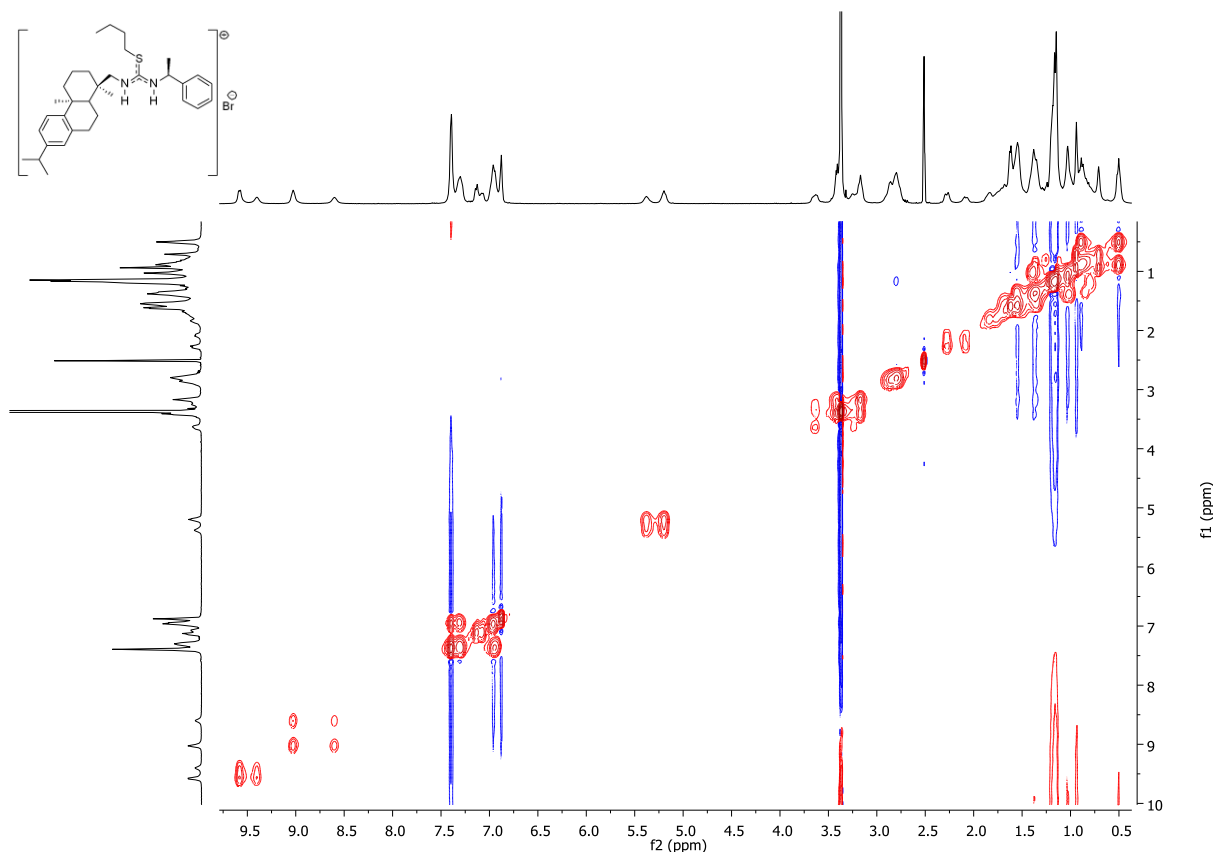
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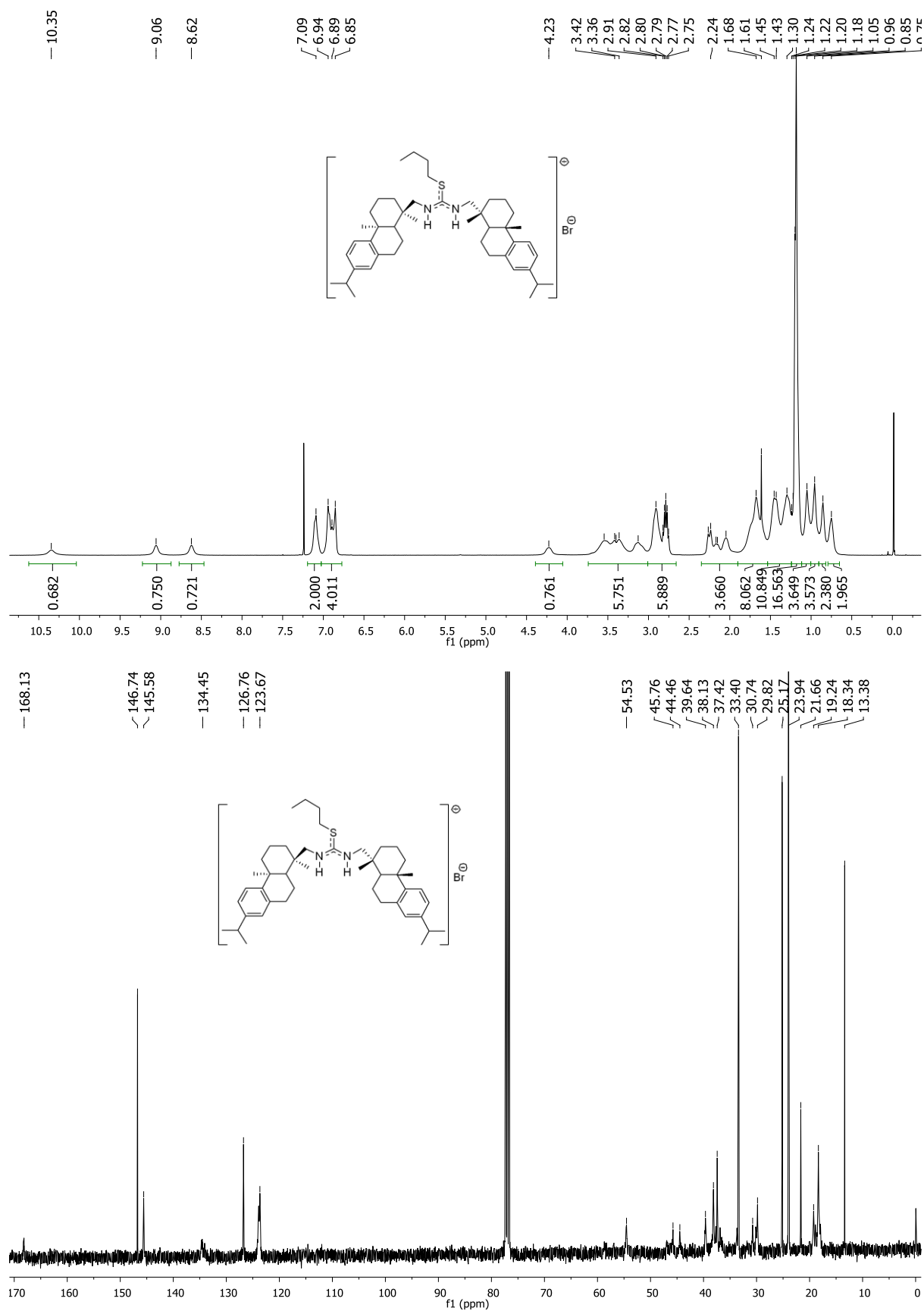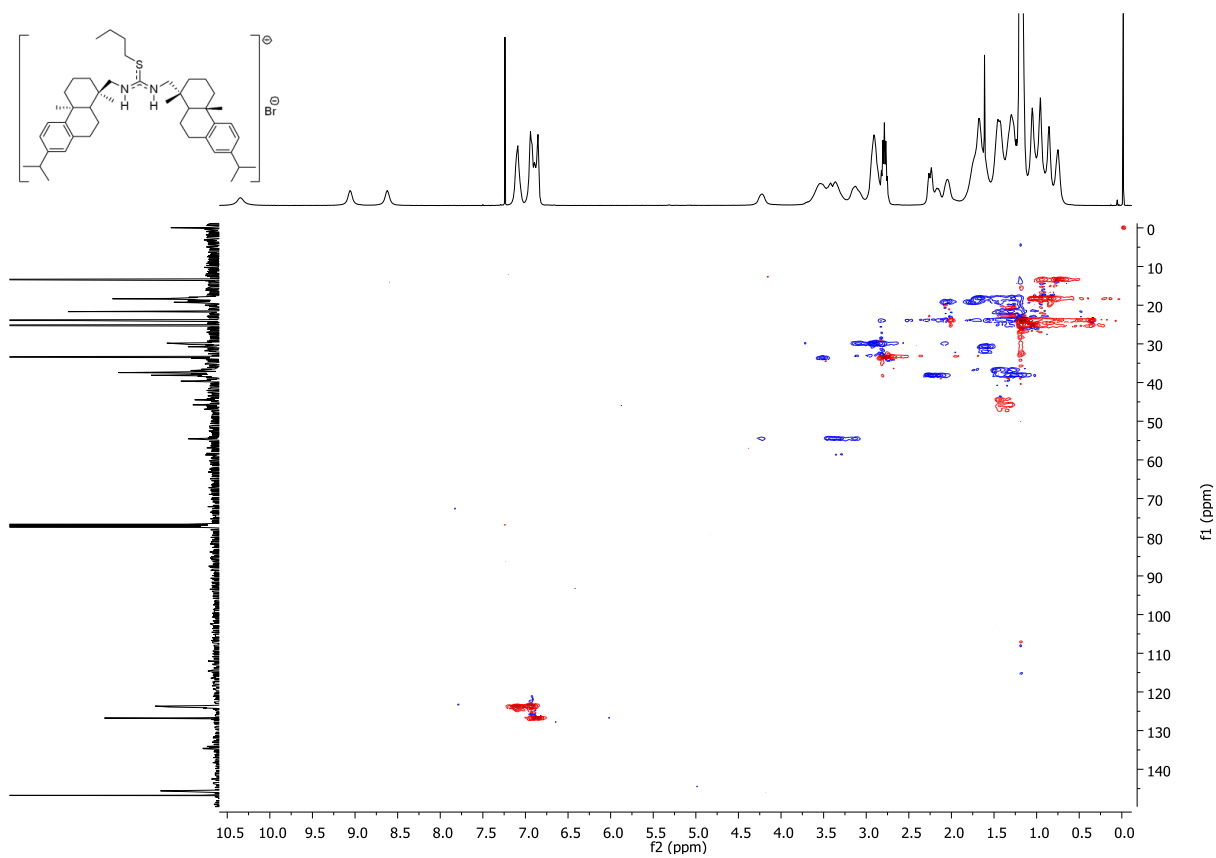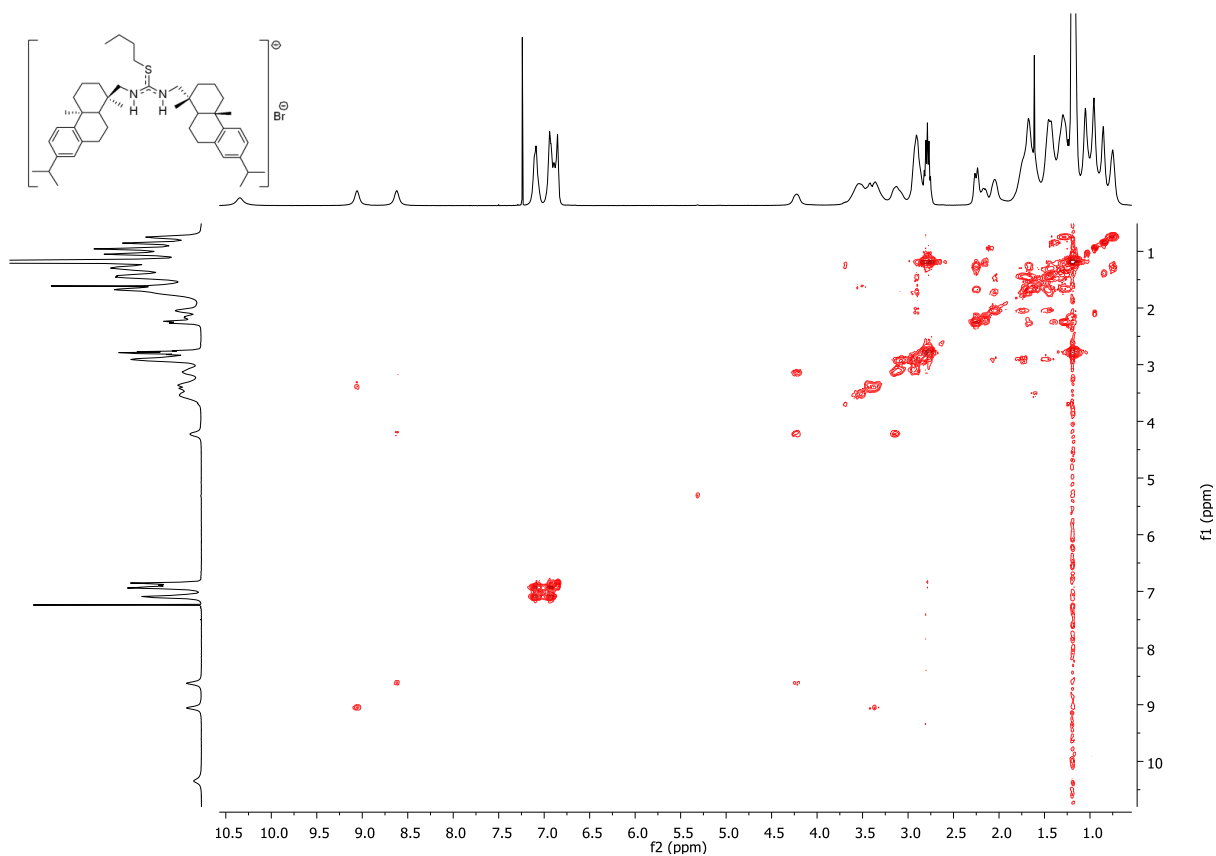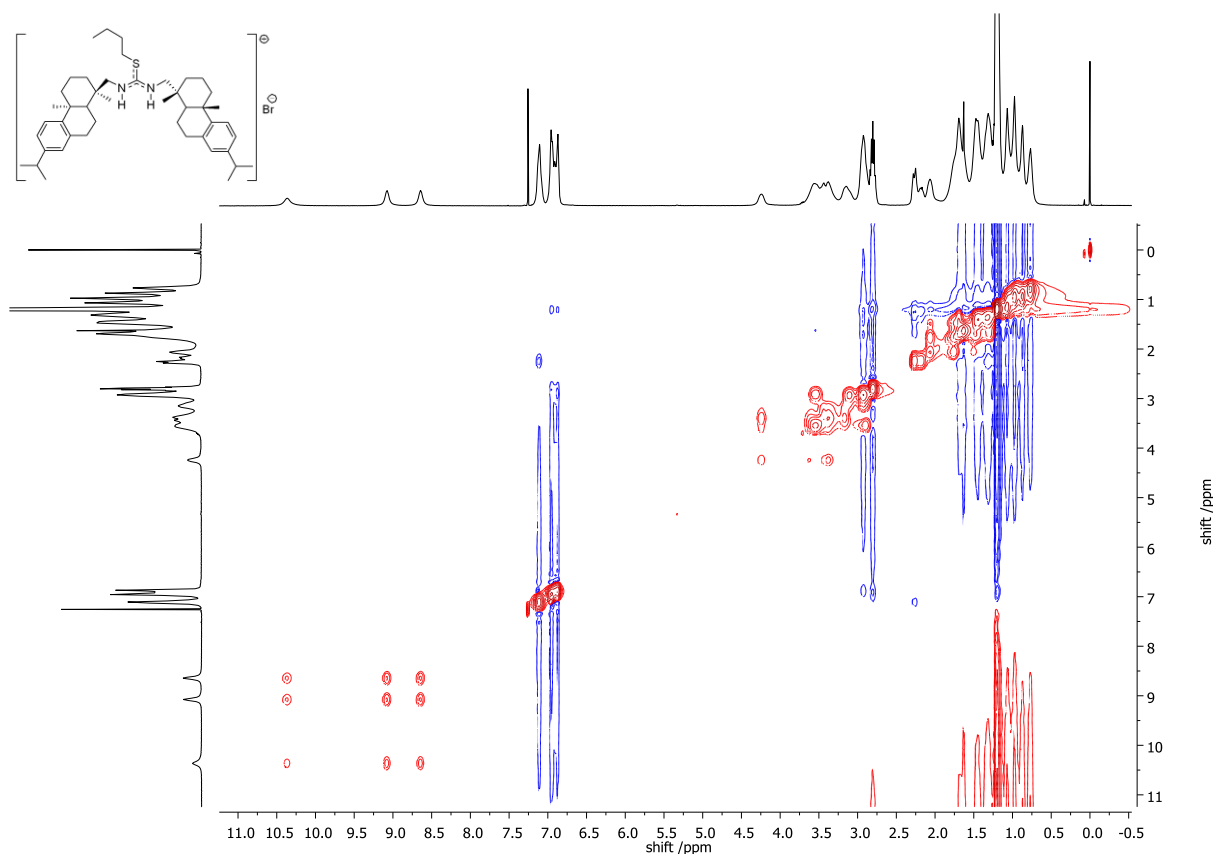
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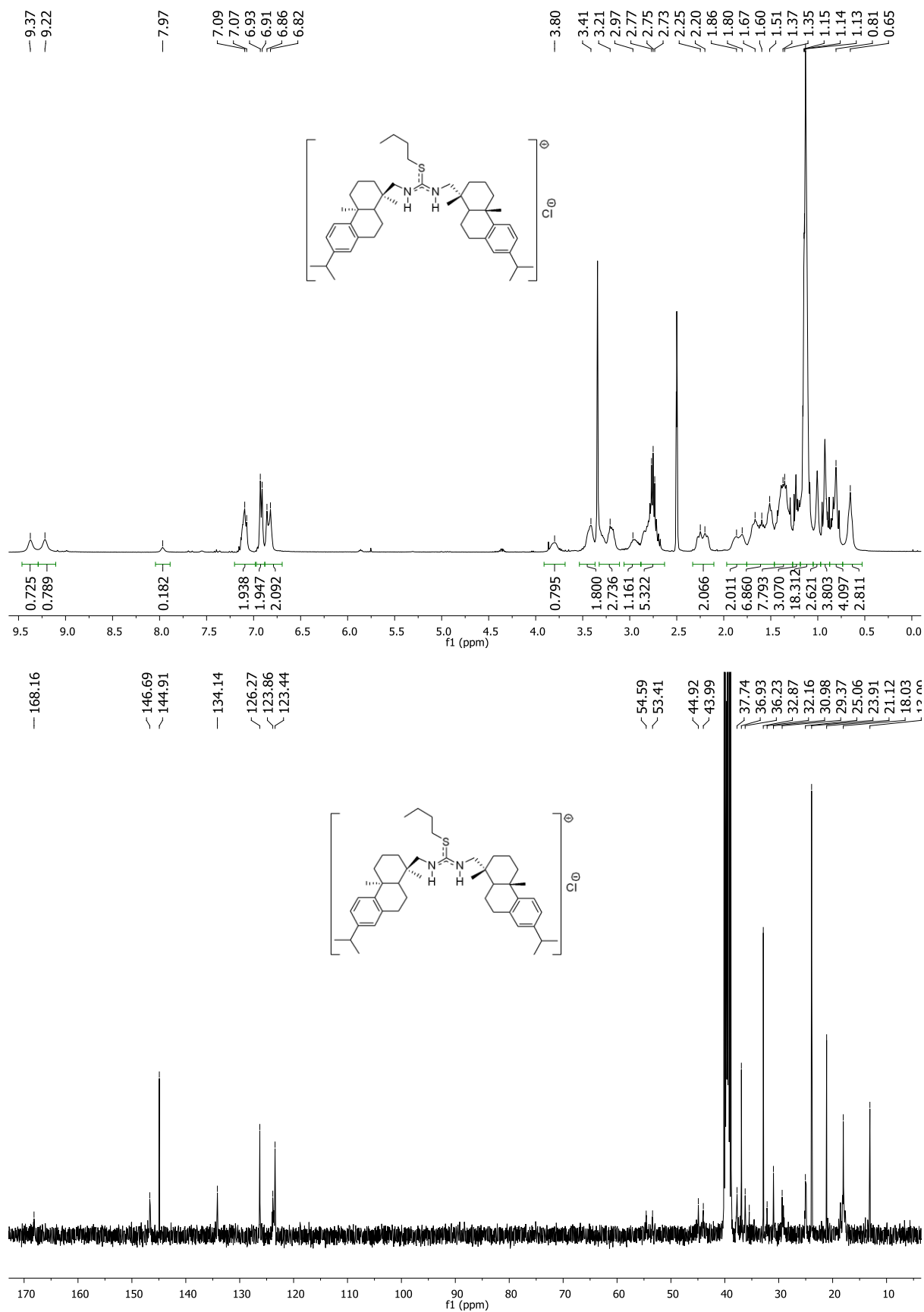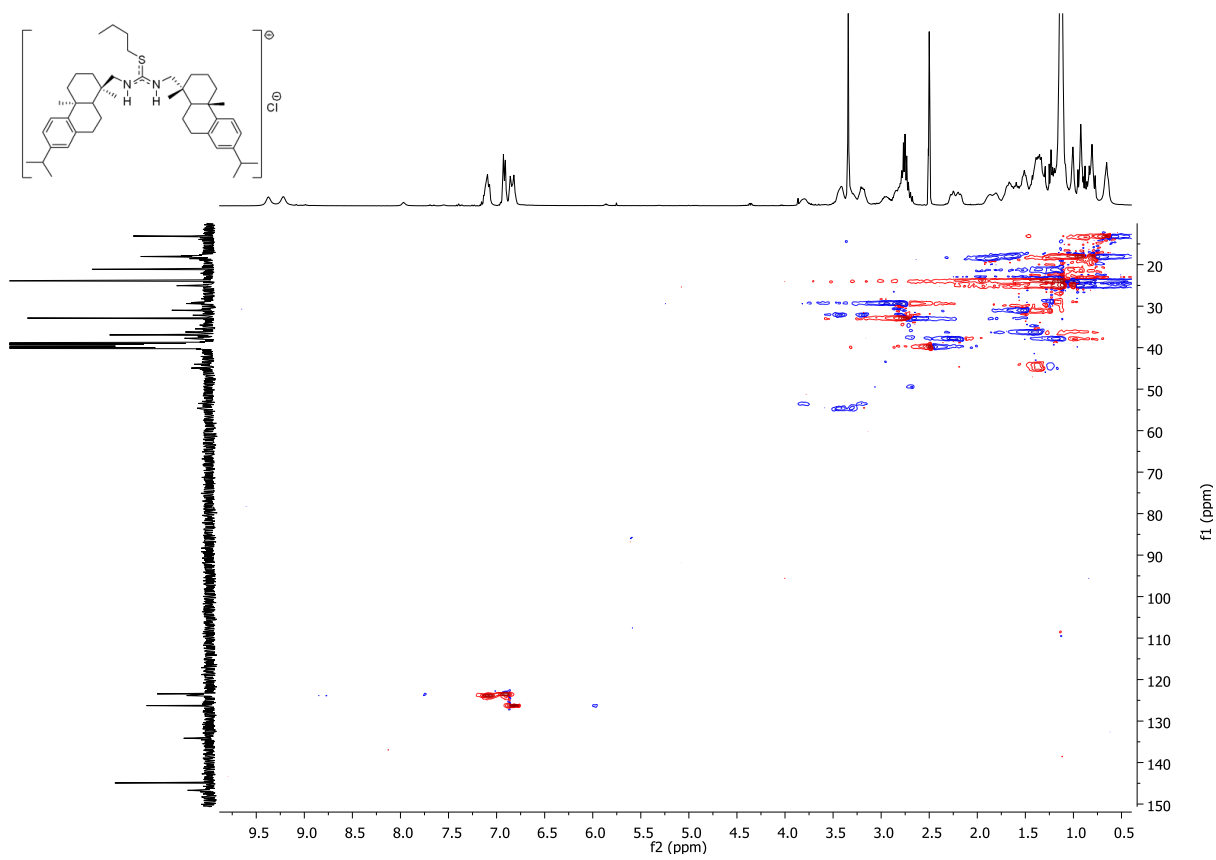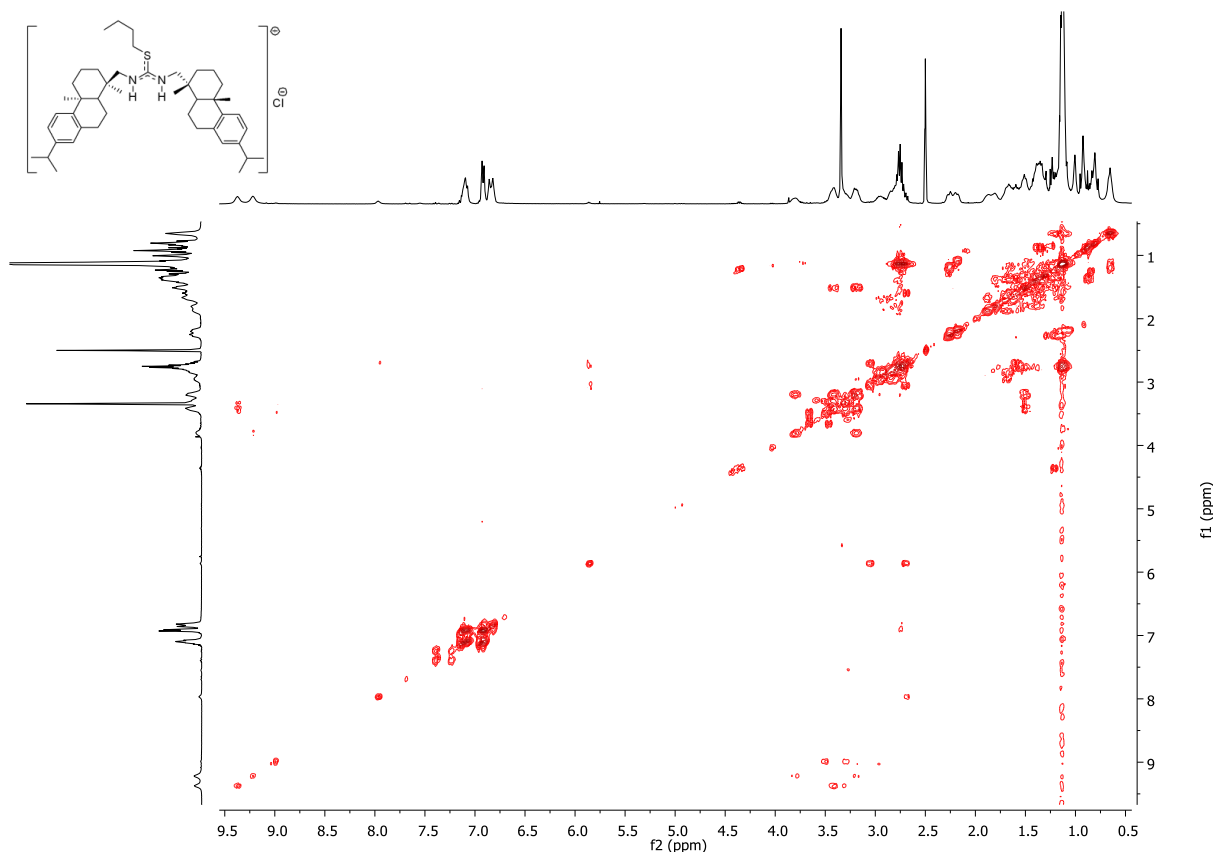
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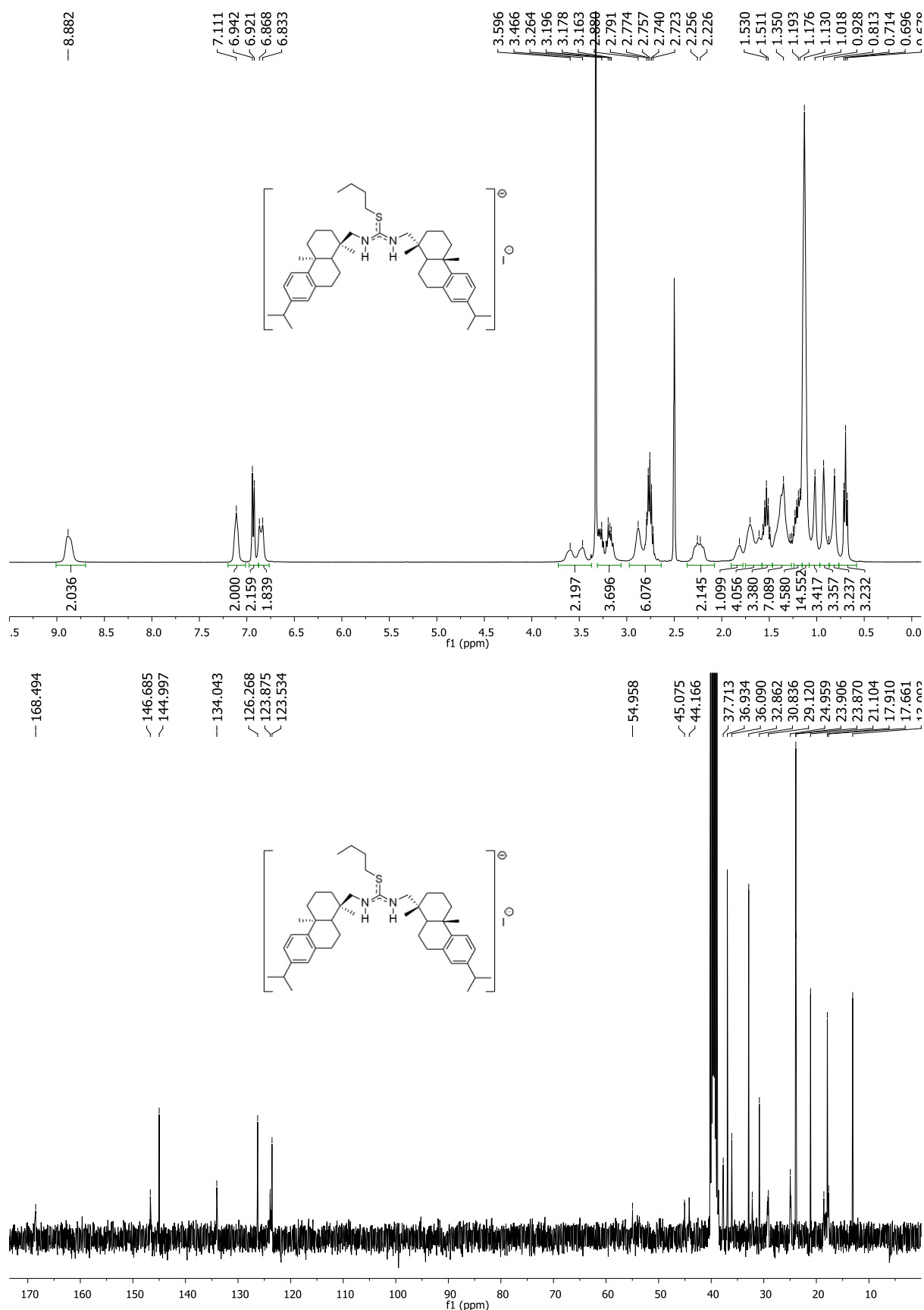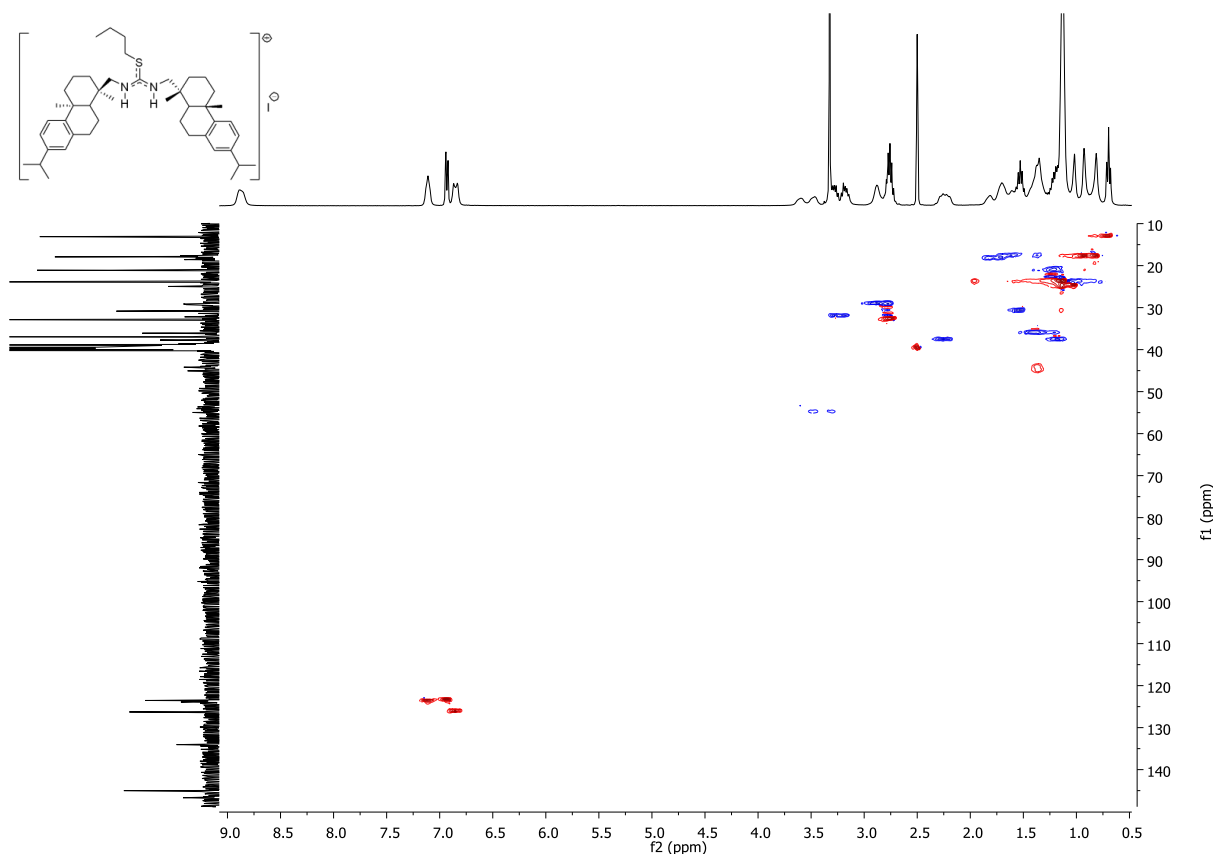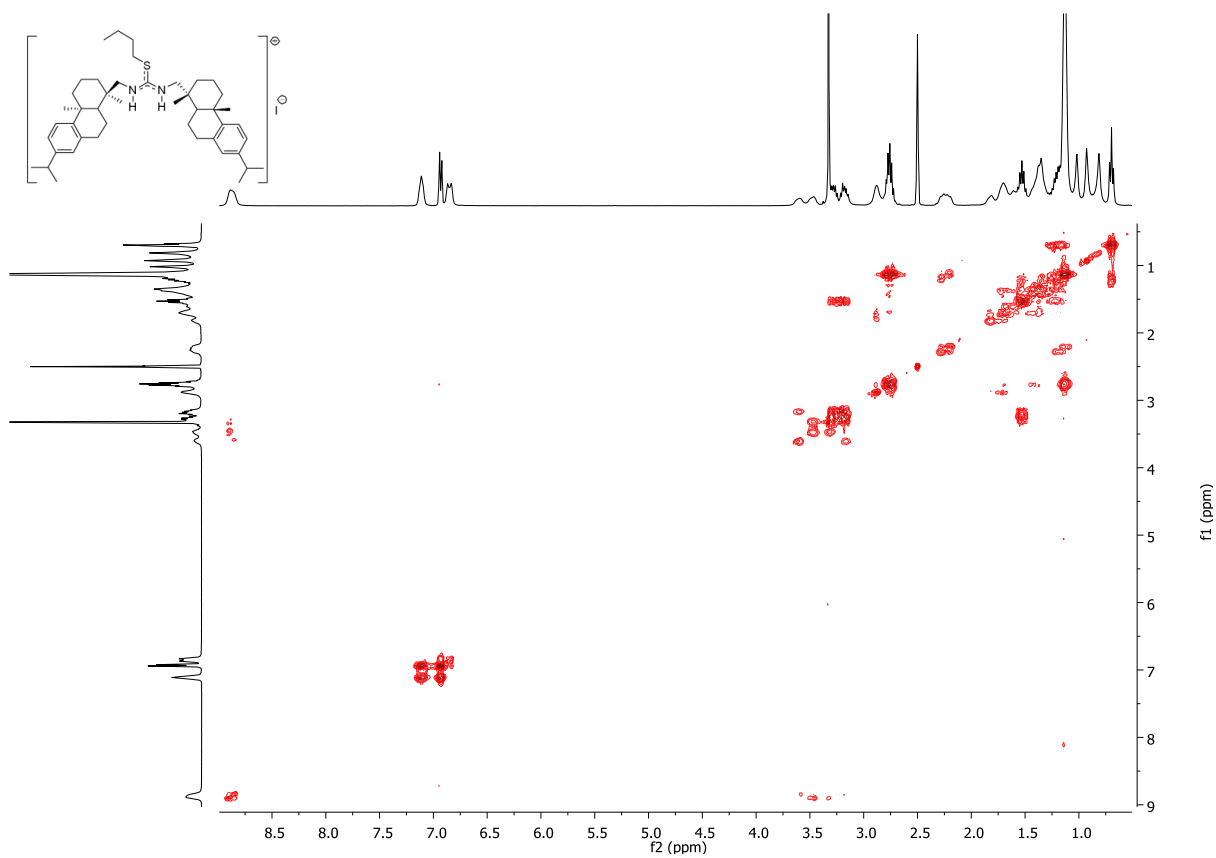
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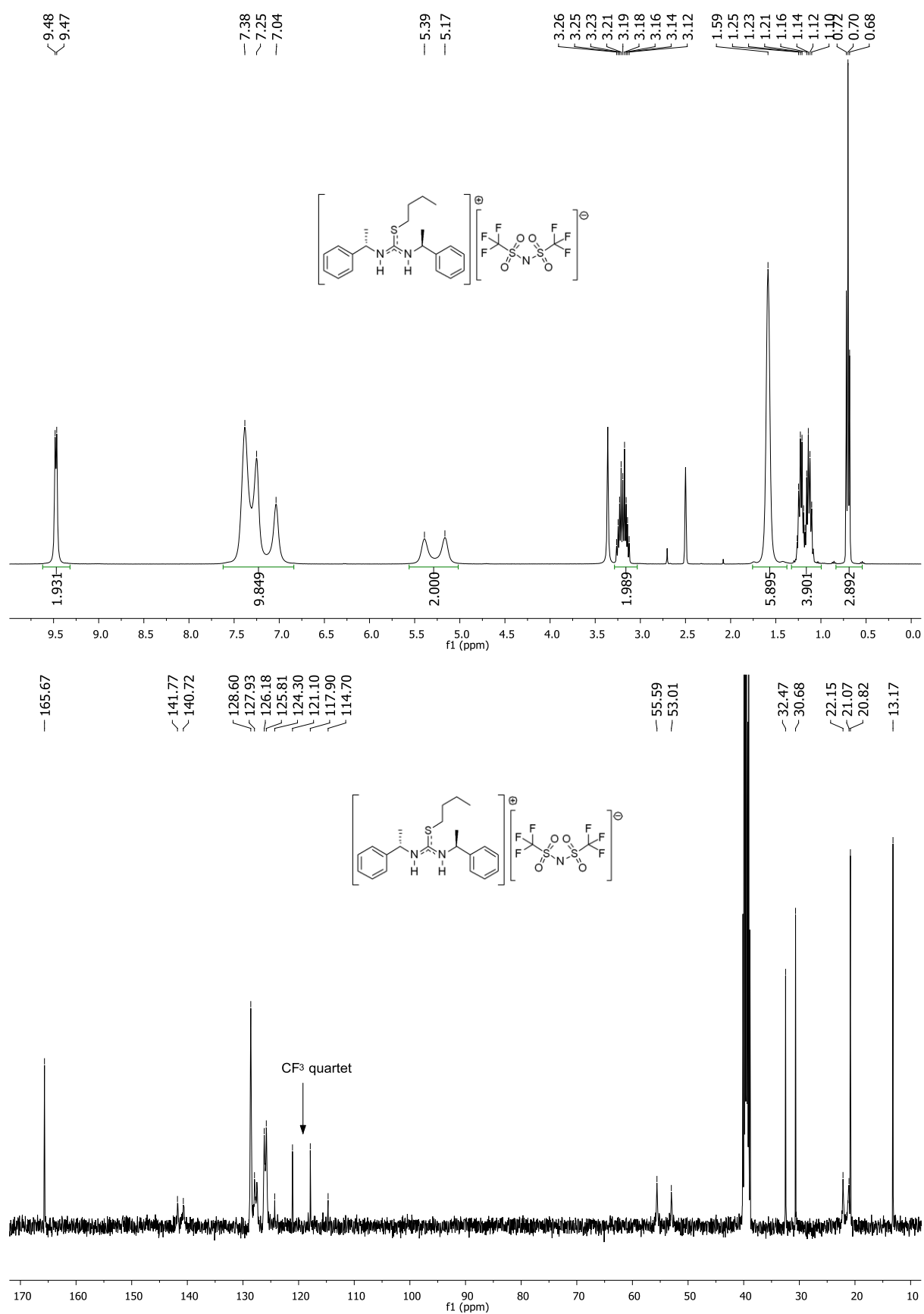
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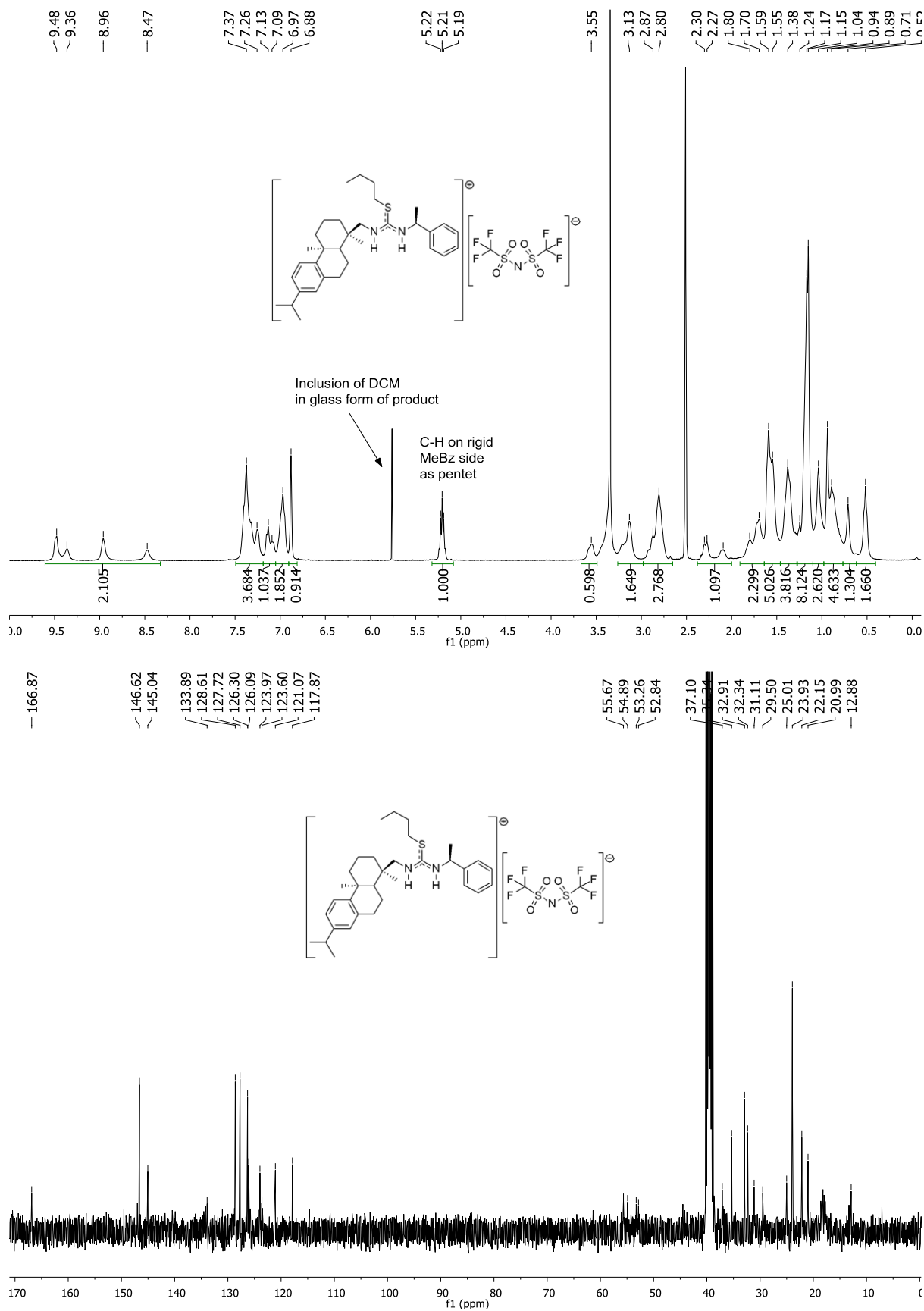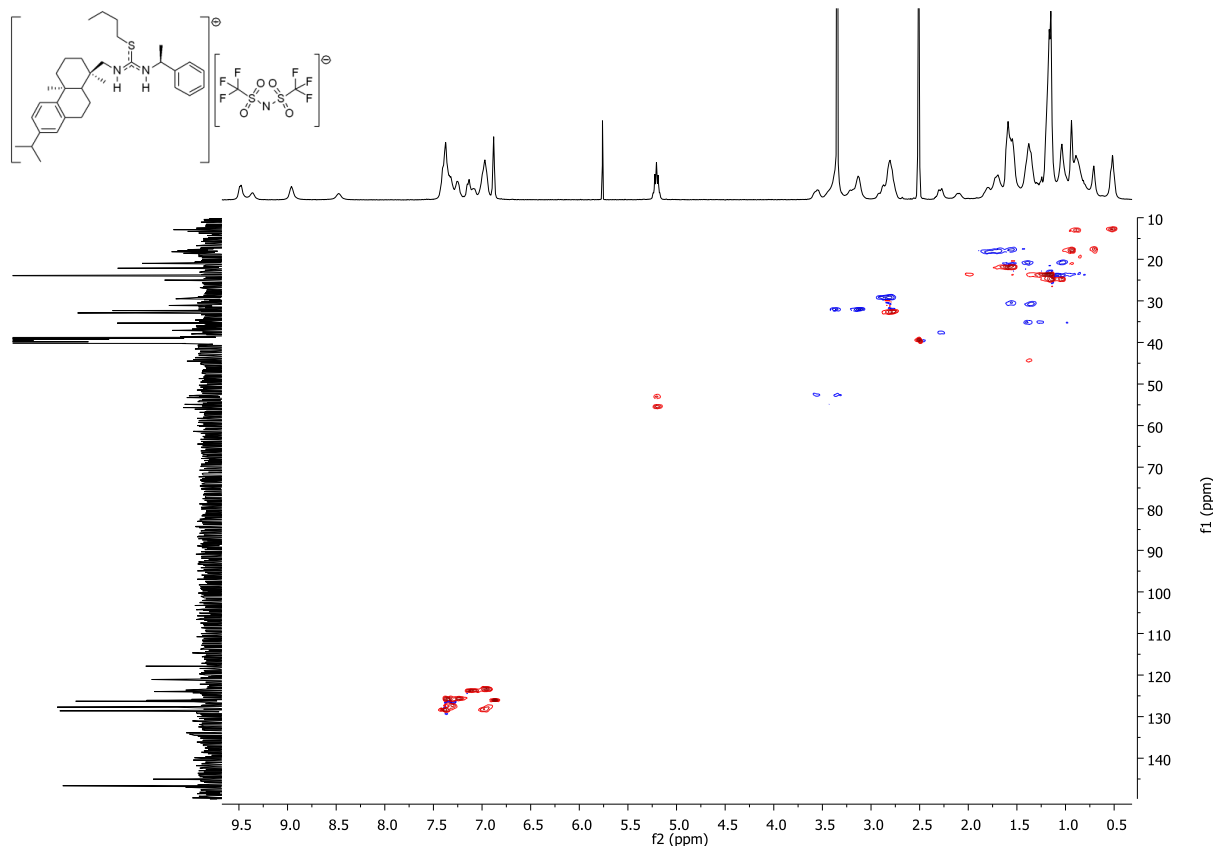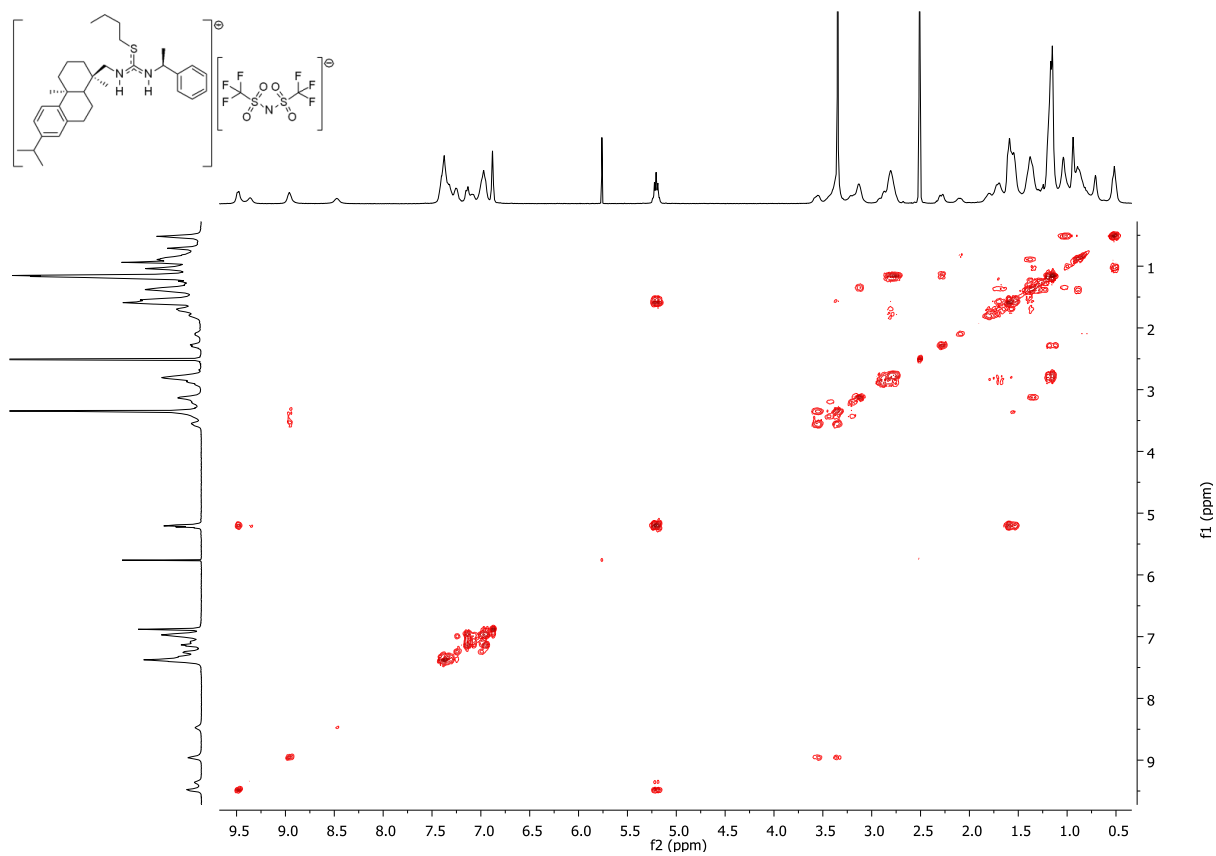
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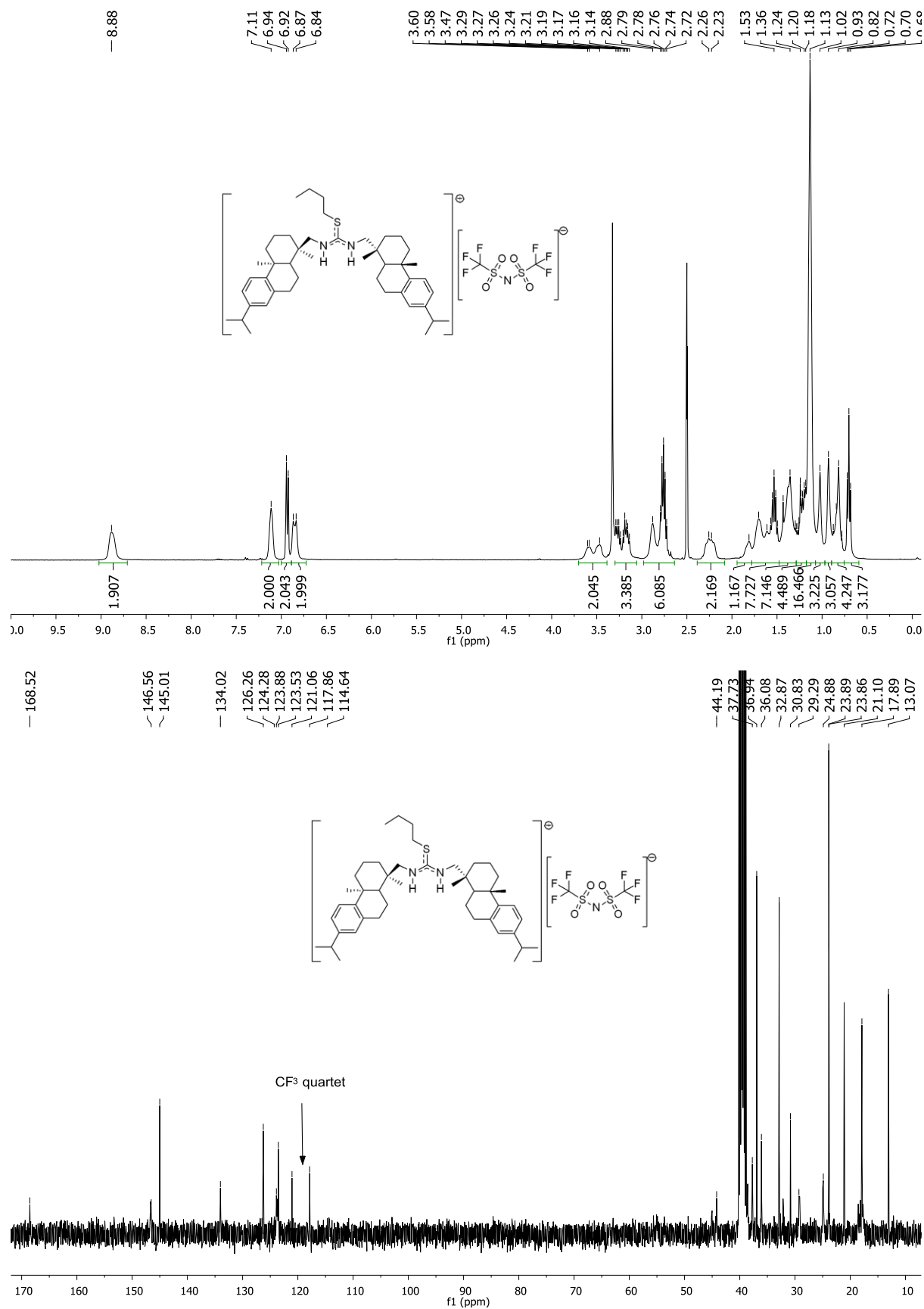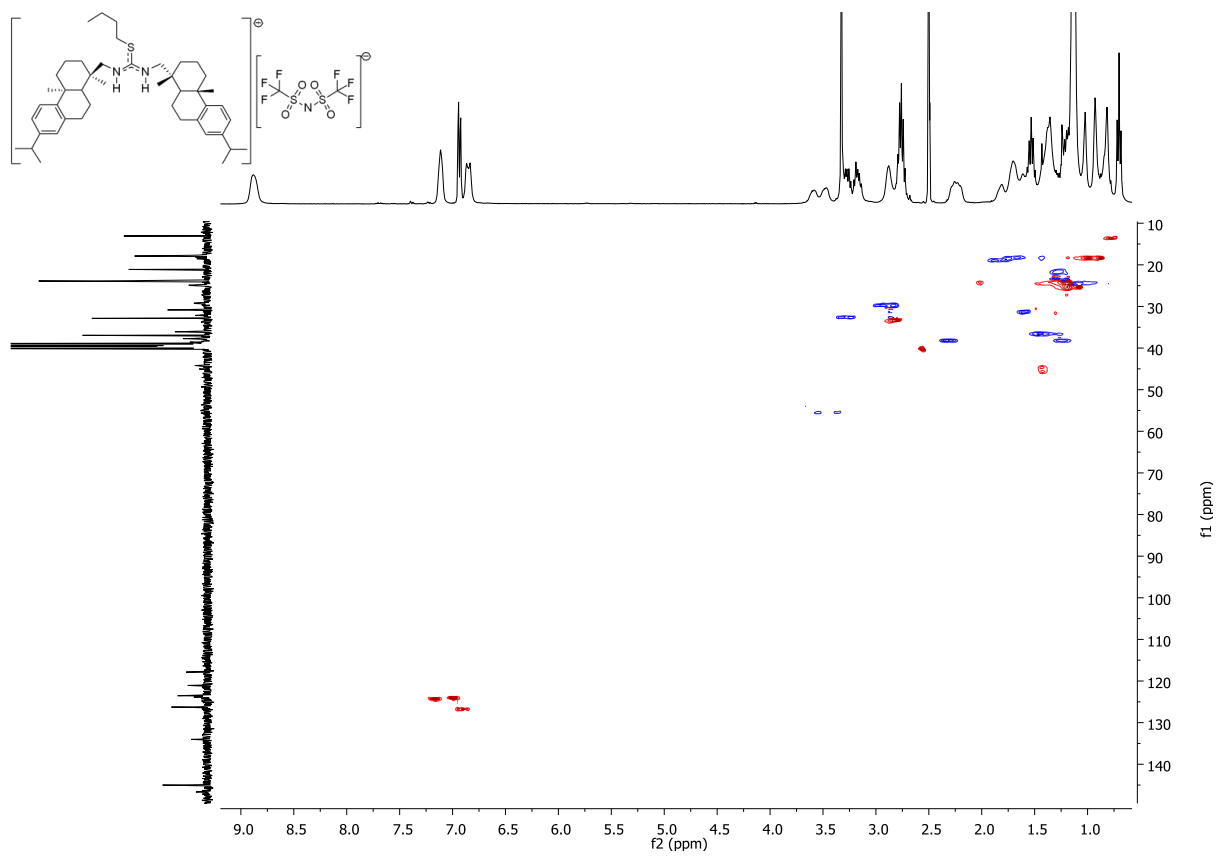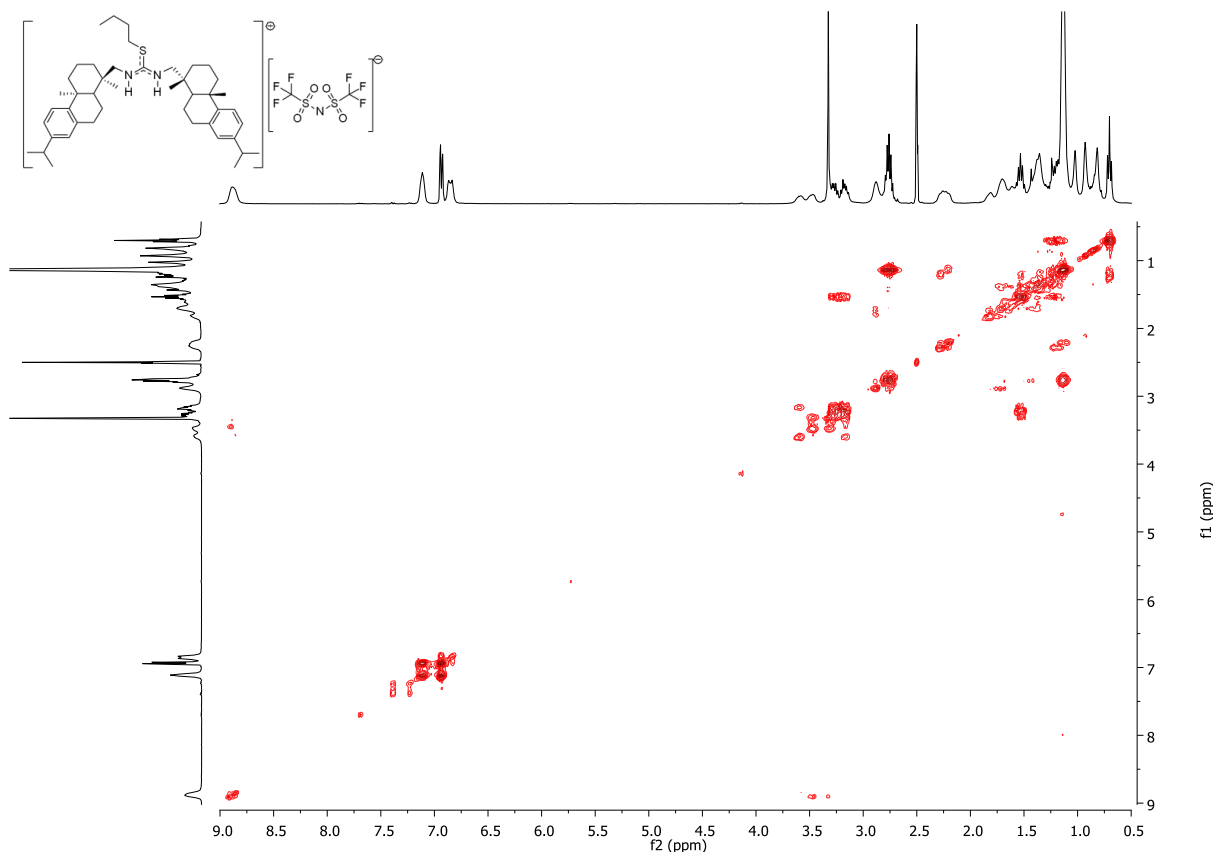
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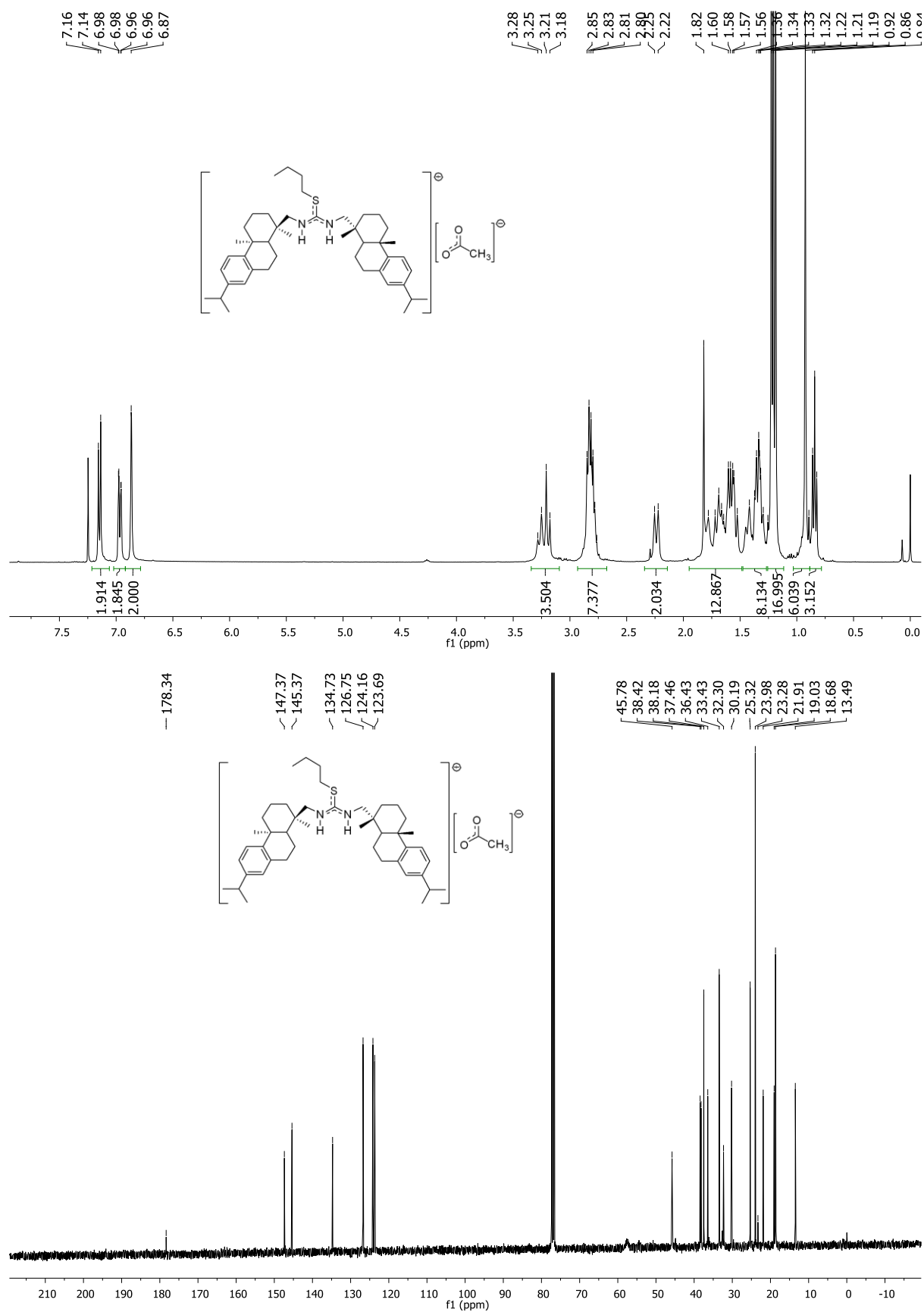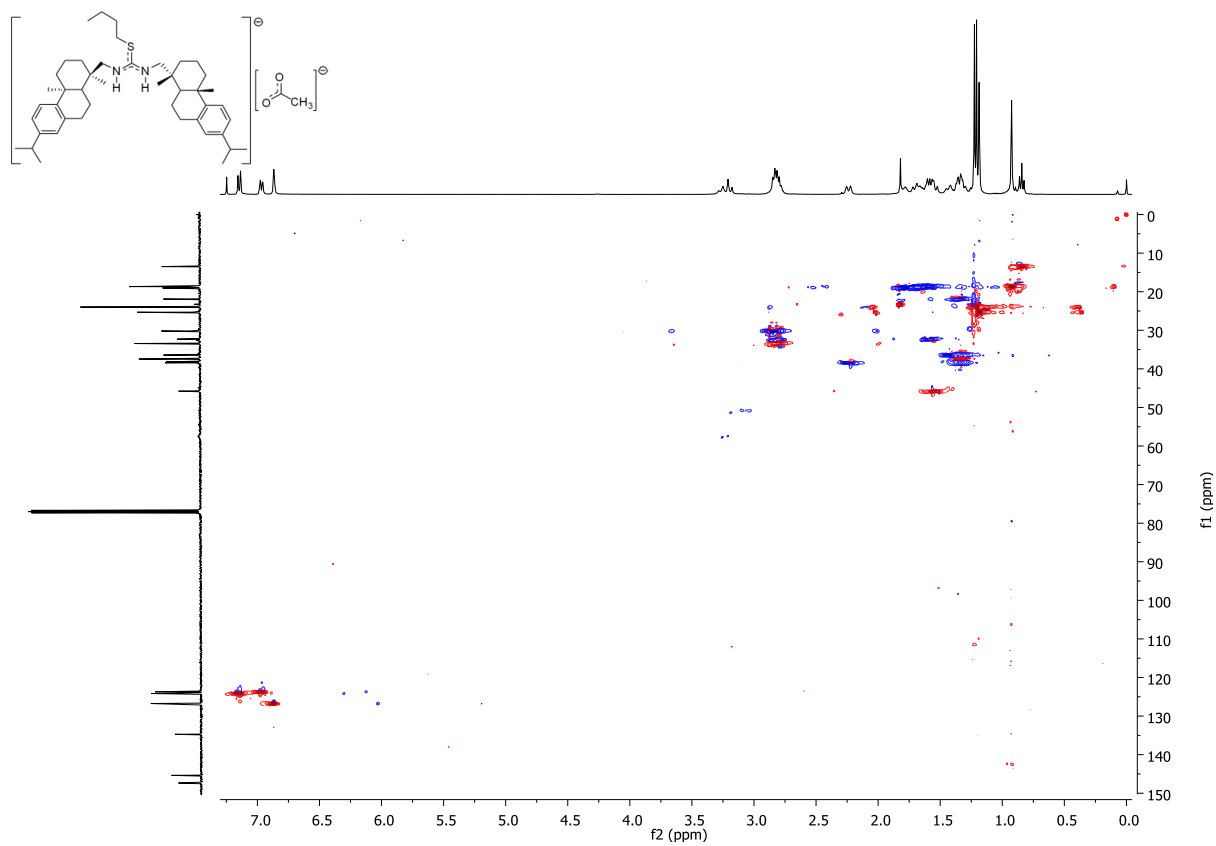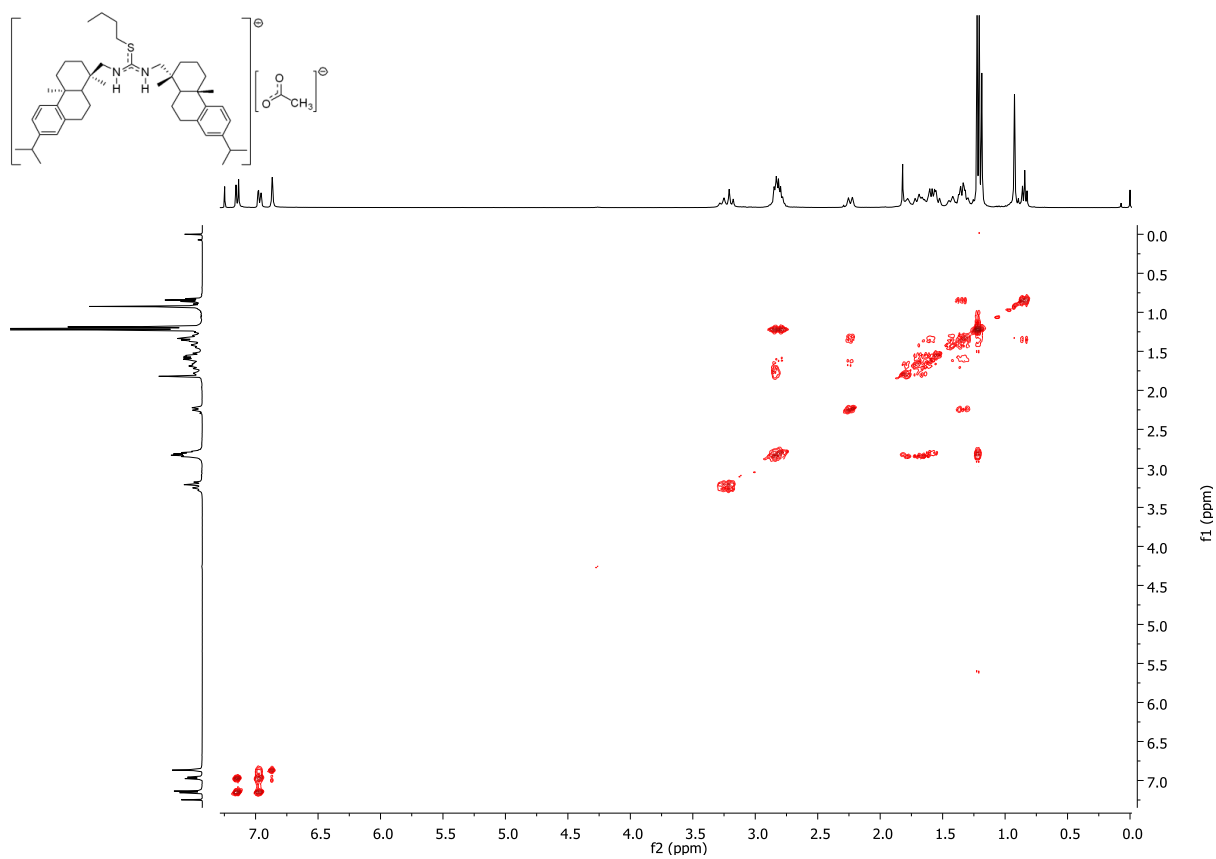
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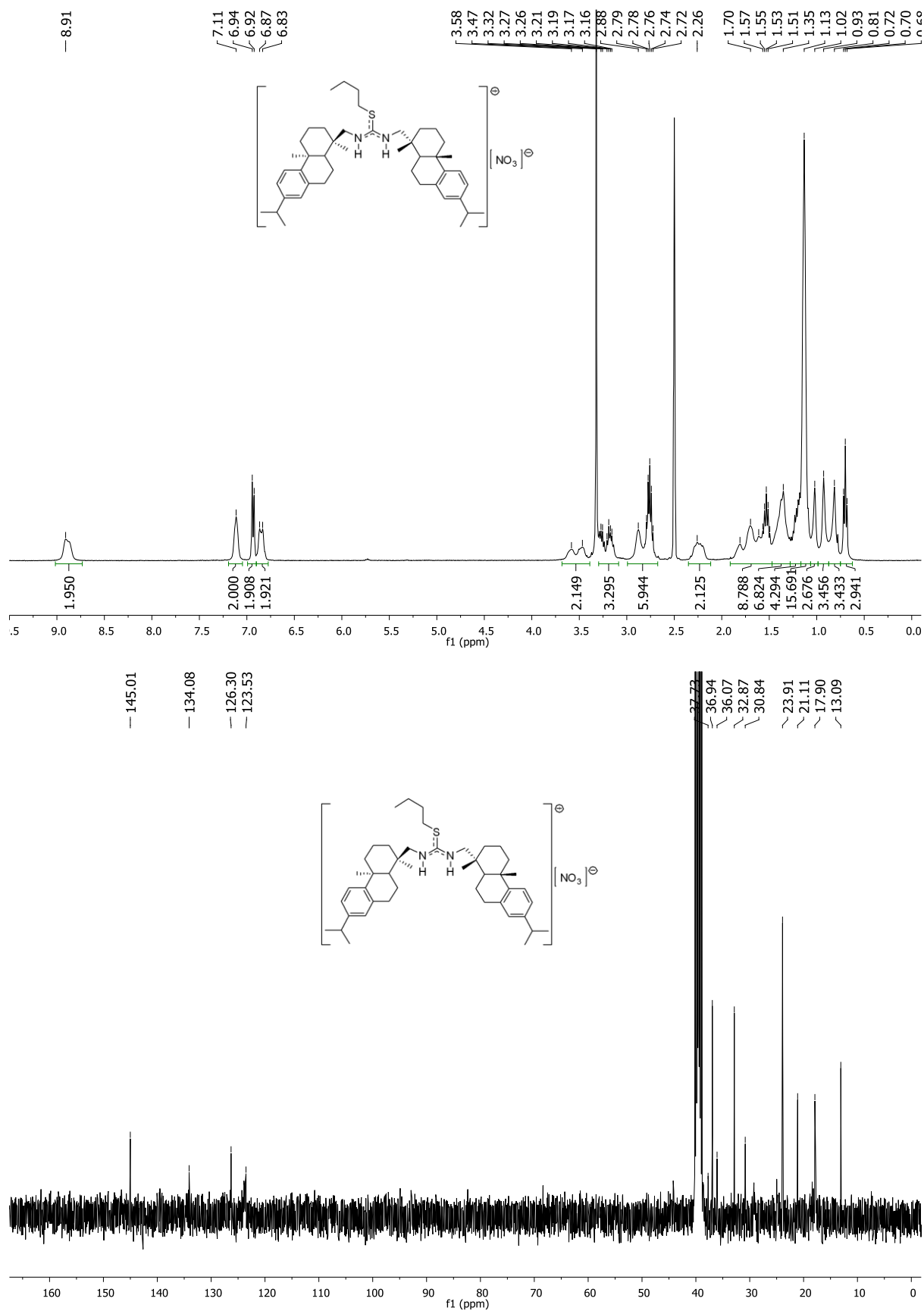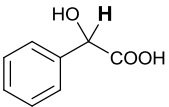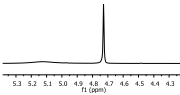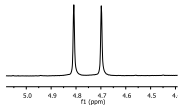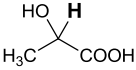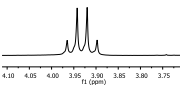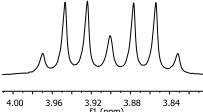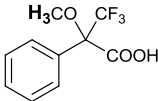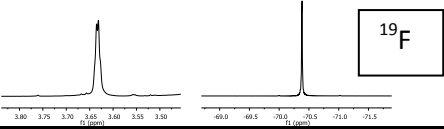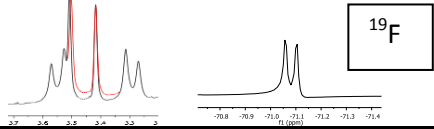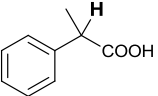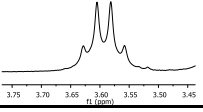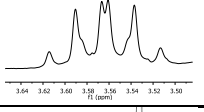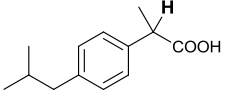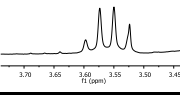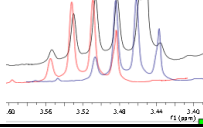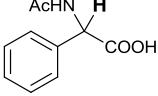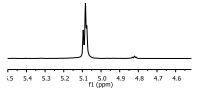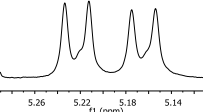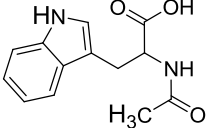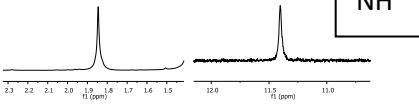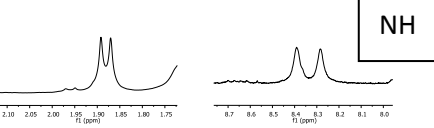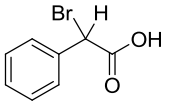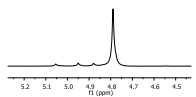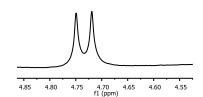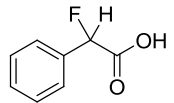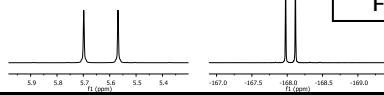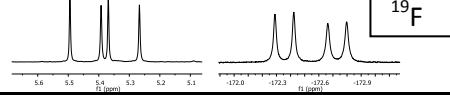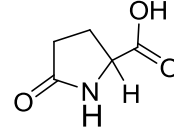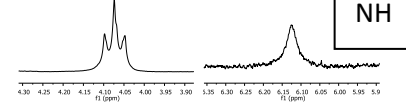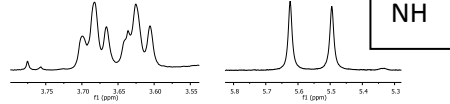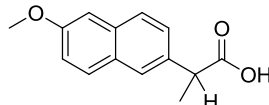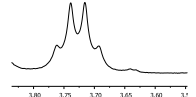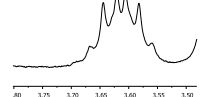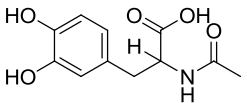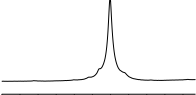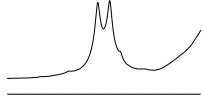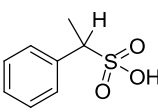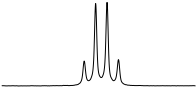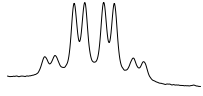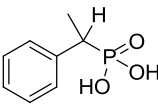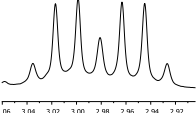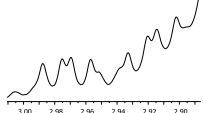
Figure S16. ^{1}H NMR, ^{13}C NMR, COSY and HSQC spectra for salt [**2c**][OTf] (400 MHz, DMSO-d_6).
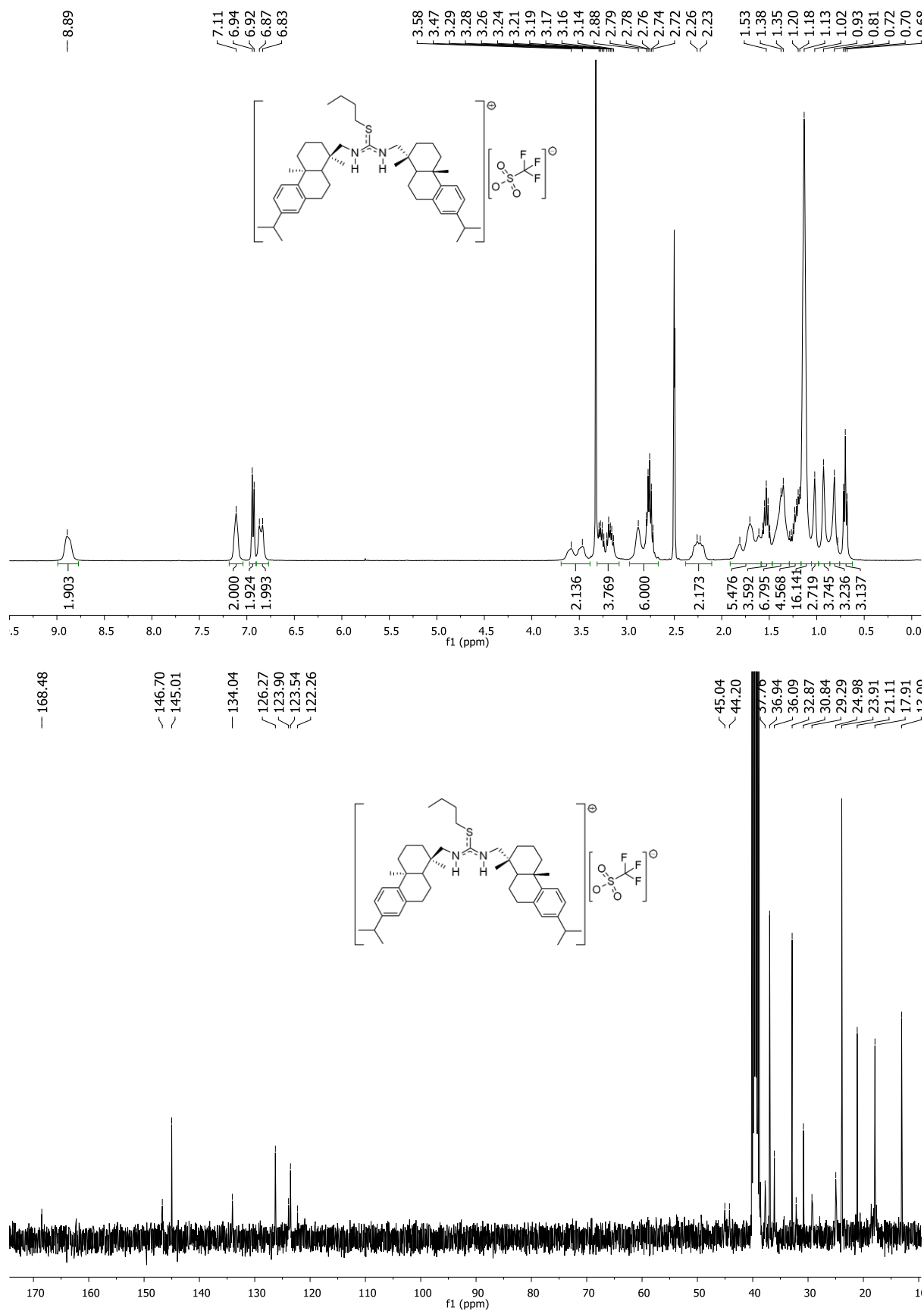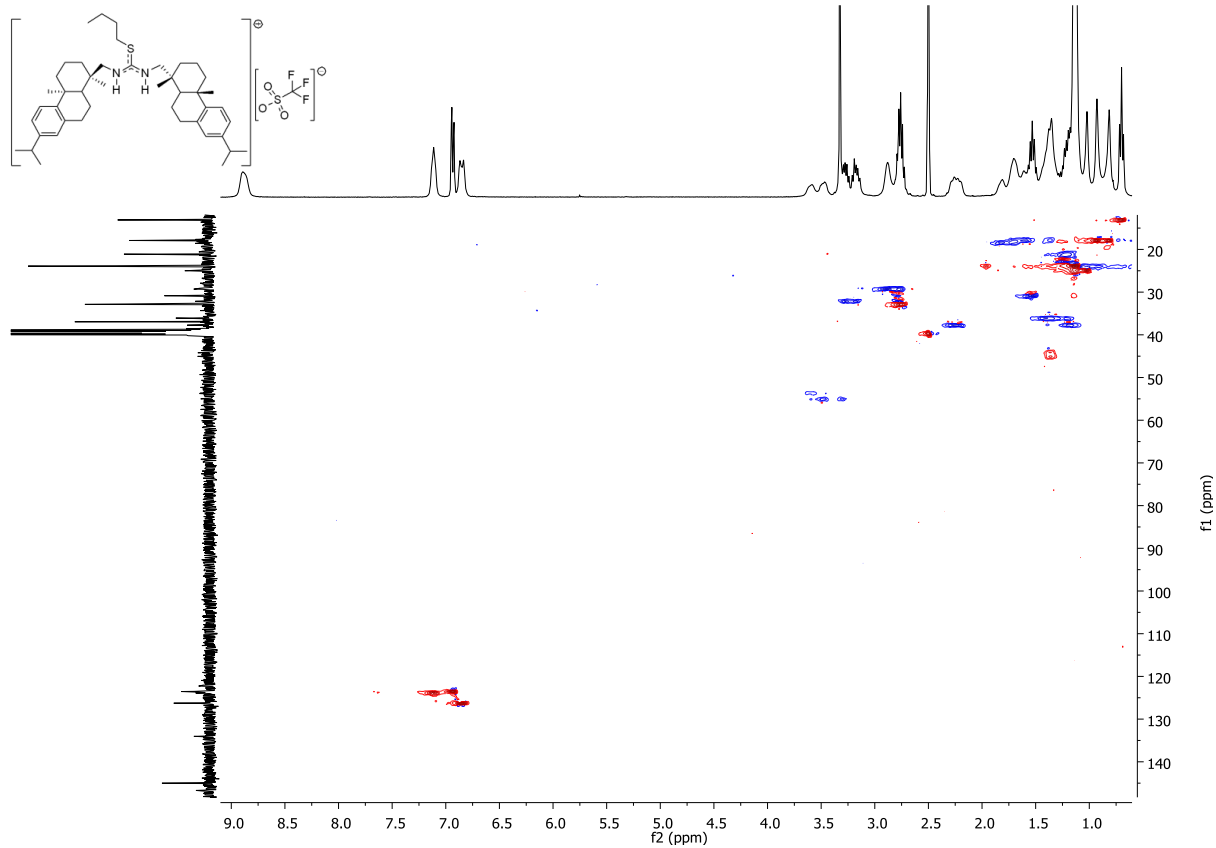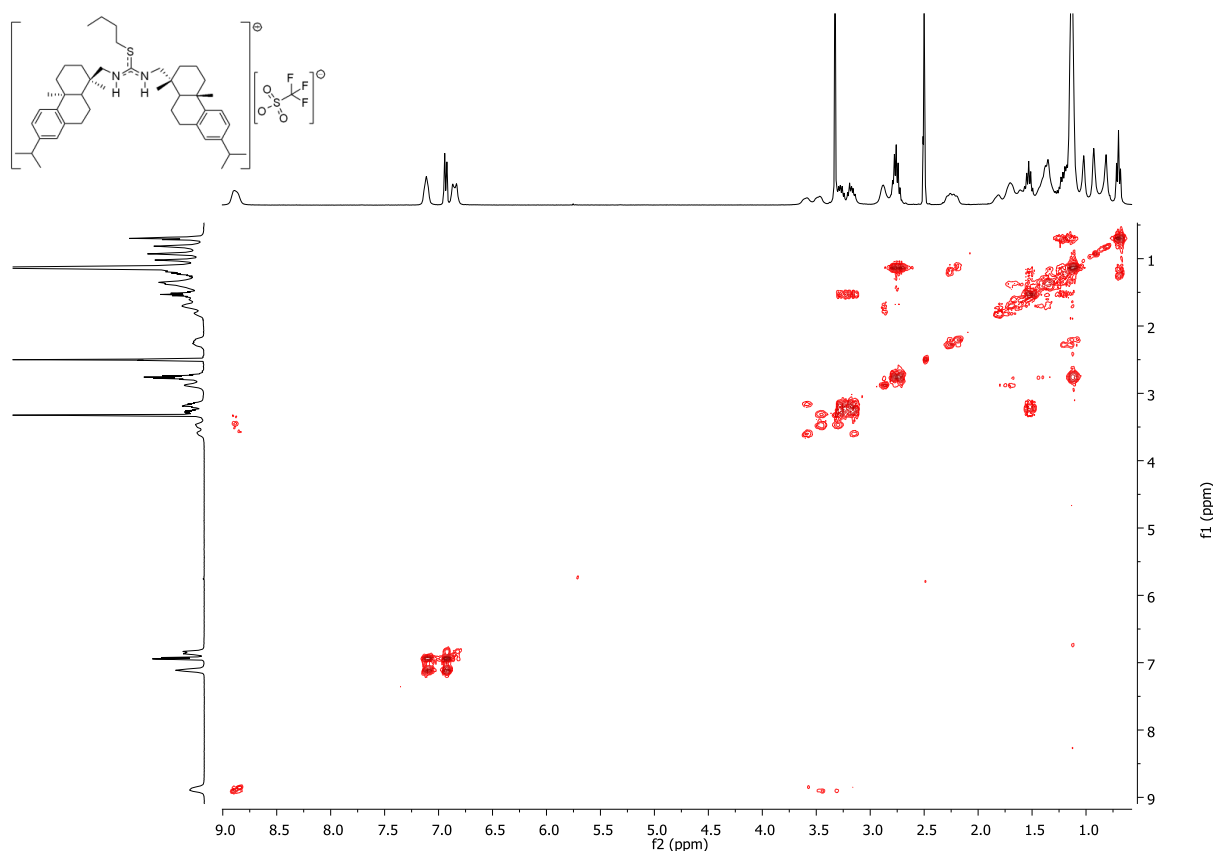
2. **NMR traces used for determination of peak non-equivalences in tetrabutylammonium salts of chosen racemic acids in presence of [2c][NTf$_2$] using ^{1}H NMR (300 MHz) in CDCl$_3$ at 20 °C.**

Code of salt	Racemic acid	Peaks without agent	Zoom in splitted peaks	Δδ/ppm
[N$_{4444}$][3a]	HO H / C$_6$H$_5$ / COOH			0.110
[N$_{4444}$][3b]	HO H / H$_3$C COOH			0.070
[N$_{4444}$][3c]	H$_3$CO CF$_3$ / COOH (^{19}F)		(^{19}F)	0.091 (^{1}H NMR) / 0.045 (^{19}F NMR)
[N$_{4444}$][3d]	H / COOH			0.030
[N$_{4444}$][3e]	H / COOH			0.047
[N$_{4444}$][3f]	AcHN H / COOH			0.058
[N$_{4444}$][3g]	HN / O OH / NH / H$_3$C O (NH)		(NH)	0.022 (Ac) / 0.107 (Ar-NH)

$[N_{4444}][3h]$				0.030
$[N_{4444}][3i]$		^{19}F	^{19}F	0.102 (^{1}H NMR) 0.374 (^{19}F NMR)
$[N_{4444}][3j]$		NH	NH	0.058 (CH) 0.129 (NH)
$[N_{4444}][3k]$				0.038
$[N_{4444}][3l]$				0.018
$[N_{4444}][3m]$				0.006
$[N_{4444}][3n]$				0.013

3. Cartesian coordinates of the optimized structures at RHF/3-21G* level[28]

syn-syn-[**2a**]$^+$

OPT RHF/3-21G*

HF = -1311.4082919 A.U.

Center Number	Atomic Number	Atomic Type	X	Y	Z
1	6	0	0.495012	-0.691817	-0.025810
2	16	0	-0.194892	0.536317	-1.117531
3	7	0	-0.017106	-1.906800	-0.024204
4	7	0	1.516459	-0.410947	0.746732
5	1	0	0.432566	-2.608419	0.535375
6	1	0	1.873809	-1.142289	1.336690
7	6	0	-1.200251	1.496080	0.100545
8	6	0	-2.042175	2.526624	-0.678706
9	1	0	-0.537018	1.992190	0.792335
10	1	0	-1.842954	0.806427	0.623156
11	6	0	-2.930963	3.333993	0.290002
12	1	0	-1.391794	3.201969	-1.223658
13	1	0	-2.671004	2.008392	-1.392883
14	6	0	-3.778577	4.375850	-0.464966
15	1	0	-3.582794	2.651323	0.824634
16	1	0	-2.306629	3.836032	1.021743
17	1	0	-4.400685	4.932879	0.224998
18	1	0	-3.143629	5.080005	-0.990684
19	1	0	-4.425439	3.892756	-1.188682
20	6	0	-1.222746	-2.380827	-0.776342
21	1	0	-1.117764	-2.055663	-1.798968
22	6	0	2.367090	0.829018	0.771324
23	1	0	1.917641	1.520086	0.080296
24	6	0	-1.215452	-3.917550	-0.720854
25	1	0	-0.306479	-4.317386	-1.155419

26	1	0	-1.313443	-4.262781	0.301590
27	1	0	-2.060233	-4.294622	-1.280550
28	6	0	2.343065	1.416723	2.188204
29	1	0	2.708008	0.708233	2.920120
30	1	0	2.976146	2.293408	2.221018
31	1	0	1.335309	1.700425	2.464028
32	6	0	3.753535	0.458177	0.270874
33	6	0	4.666902	-0.201559	1.081820
34	6	0	5.909171	-0.558212	0.589078
35	6	0	6.252091	-0.255628	-0.717509
36	6	0	5.347808	0.404066	-1.529982
37	6	0	4.103086	0.755461	-1.037953
38	1	0	4.430043	-0.427451	2.103059
39	1	0	6.609216	-1.062079	1.224644
40	1	0	7.217101	-0.526221	-1.095578
41	1	0	5.609932	0.647697	-2.539729
42	1	0	3.408677	1.270096	-1.673806
43	6	0	-2.502550	-1.813357	-0.188625
44	6	0	-3.489592	-1.335736	-1.035061
45	6	0	-4.683842	-0.857270	-0.520935
46	6	0	-4.896044	-0.848097	0.845805
47	6	0	-3.912231	-1.325205	1.697110
48	6	0	-2.722395	-1.807018	1.181777
49	1	0	-3.330611	-1.335127	-2.096274
50	1	0	-5.442893	-0.496577	-1.185544
51	1	0	-5.819877	-0.481023	1.244944
52	1	0	-4.075578	-1.329570	2.756153
53	1	0	-1.972490	-2.181841	1.851011

anti-syn-[**2a**]⁺

OPT RHF/3-21G*

HF = -1311.4231507 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.354402	-0.558491	0.545913
2	16	0	-1.886470	0.234054	0.243341
3	7	0	-0.150775	-1.818299	0.195960
4	7	0	0.595579	0.131455	1.131755
5	1	0	1.512564	-0.273786	1.163139
6	6	0	-3.018526	-1.158323	-0.104891
7	6	0	-4.458941	-0.595977	-0.156036
8	1	0	-2.941268	-1.896584	0.680655
9	1	0	-2.777779	-1.598766	-1.062947
10	6	0	-5.466977	-1.716761	-0.481137
11	1	0	-4.706405	-0.150792	0.800408
12	1	0	-4.521995	0.176259	-0.914577
13	6	0	-6.908089	-1.173914	-0.531857
14	1	0	-5.214179	-2.163137	-1.437220
15	1	0	-5.398365	-2.493339	0.273539
16	1	0	-7.605918	-1.969851	-0.761023
17	1	0	-7.189722	-0.742130	0.421827
18	1	0	-7.004192	-0.410349	-1.295399
19	6	0	1.053153	-2.624440	0.550859
20	1	0	1.138399	-2.617729	1.630898
21	6	0	0.488642	1.529672	1.645266
22	1	0	-0.408880	1.585433	2.245333
23	6	0	0.803423	-4.063411	0.069451
24	1	0	-0.088212	-4.476122	0.527981
25	1	0	0.703489	-4.085722	-1.008790
26	1	0	1.647426	-4.681835	0.341312

27	6	0	1.719638	1.777538	2.533041
28	1	0	2.626472	1.705676	1.944362
29	1	0	1.665706	2.776232	2.943565
30	1	0	1.757652	1.066174	3.349861
31	6	0	0.416102	2.543533	0.515505
32	6	0	1.216844	2.423941	-0.610909
33	6	0	1.179761	3.393765	-1.595638
34	6	0	0.345619	4.491241	-1.462273
35	6	0	-0.453862	4.613908	-0.340726
36	6	0	-0.419802	3.640909	0.643395
37	1	0	1.866997	1.578785	-0.726594
38	1	0	1.801978	3.296631	-2.462614
39	1	0	0.320225	5.242482	-2.225510
40	1	0	-1.102087	5.459843	-0.231449
41	1	0	-1.045839	3.740750	1.509728
42	6	0	2.325259	-2.054716	-0.058247
43	6	0	3.484644	-2.017446	0.702094
44	6	0	4.666524	-1.542930	0.154908
45	6	0	4.693112	-1.100788	-1.154436
46	6	0	3.536364	-1.136337	-1.918102
47	6	0	2.357549	-1.611174	-1.373243
48	1	0	3.473919	-2.368821	1.717016
49	1	0	5.558055	-1.523292	0.748475
50	1	0	5.605513	-0.735069	-1.579845
51	1	0	3.555926	-0.801662	-2.935747
52	1	0	1.468315	-1.636725	-1.971754
53	1	0	-0.864093	-2.298288	-0.309715

anti-anti-[**2a**]$^+$

OPT RHF/3-21G*

HF = -1311.4123943 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.952880	-0.214665	0.693311
2	16	0	-2.606279	-0.420743	1.281372
3	7	0	-0.697090	0.644566	-0.266349
4	7	0	-0.073108	-0.962531	1.325321
5	6	0	-3.653902	0.139567	-0.110211
6	6	0	-5.109671	-0.297885	0.178220
7	1	0	-3.304517	-0.315695	-1.025605
8	1	0	-3.616440	1.217376	-0.187040
9	6	0	-6.050059	0.183103	-0.945695
10	1	0	-5.153479	-1.377811	0.252814
11	1	0	-5.436702	0.120082	1.123838
12	6	0	-7.504840	-0.248142	-0.677780
13	1	0	-6.000472	1.264379	-1.019855
14	1	0	-5.718504	-0.227871	-1.893523
15	1	0	-8.154798	0.095202	-1.473129
16	1	0	-7.581432	-1.328035	-0.621540
17	1	0	-7.863822	0.169988	0.255764
18	6	0	0.547553	0.846151	-1.073746
19	1	0	1.074215	-0.093183	-1.091931
20	6	0	1.419611	-0.874577	1.371574
21	1	0	1.689294	0.149922	1.176768
22	6	0	0.088669	1.208356	-2.499292
23	1	0	-0.528874	0.422321	-2.916922
24	1	0	-0.462015	2.142269	-2.490485
25	1	0	0.954222	1.342363	-3.132805
26	6	0	1.835874	-1.252597	2.806440

27	1	0	1.551592	-2.276331	3.021491
28	1	0	2.910626	-1.181462	2.898840
29	1	0	1.378839	-0.586776	3.528246
30	6	0	2.084518	-1.798202	0.362280
31	6	0	1.446059	-2.904841	-0.172482
32	6	0	2.117148	-3.744500	-1.047240
33	6	0	3.429259	-3.484120	-1.394982
34	6	0	4.072066	-2.377706	-0.864604
35	6	0	3.403200	-1.539576	0.007628
36	1	0	0.429540	-3.123595	0.085182
37	1	0	1.614834	-4.600522	-1.451049
38	1	0	3.947126	-4.135452	-2.069389
39	1	0	5.090057	-2.170676	-1.127107
40	1	0	3.908004	-0.684530	0.415308
41	6	0	1.436987	1.941283	-0.504115
42	6	0	2.764771	1.982077	-0.913587
43	6	0	3.605714	2.983763	-0.467266
44	6	0	3.130058	3.956512	0.396902
45	6	0	1.811877	3.918644	0.809709
46	6	0	0.967674	2.914583	0.361903
47	1	0	3.141031	1.231326	-1.582091
48	1	0	4.626258	3.006894	-0.792788
49	1	0	3.780689	4.733881	0.742663
50	1	0	1.436750	4.668002	1.477393
51	1	0	-0.049739	2.901843	0.696778
52	1	0	-1.455751	1.226441	-0.559589
53	1	0	-0.452783	-1.656073	1.943182

4. Cartesian coordinates of the optimized structures at B3LYP/STO-G* level[28]

[2c][(S)-3a]

OPT RB3LYP/STO-3G

E(RB+HF-LYP) = -2765.0956132 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.075420	-1.499955	2.539463
2	6	0	1.915945	-2.417005	1.534663
3	6	0	1.476486	-1.855876	4.015949
4	6	0	3.399779	-2.792062	2.026661
5	6	0	2.983838	-1.579367	4.325367
6	6	0	3.915613	-1.737447	3.076460
7	6	0	1.873848	-1.866233	0.074794
8	6	0	2.560268	-2.866374	-0.894080
9	6	0	4.436808	-2.905284	0.847698
10	6	0	3.369343	-4.222736	2.692332
11	6	0	1.275979	0.075592	2.376022
12	7	0	0.545089	0.735596	1.243233
13	6	0	-0.445373	-1.838907	2.361894
14	6	0	-0.607285	1.441694	1.458811
15	16	0	-1.417628	1.440156	3.095983
16	7	0	-1.160363	2.091790	0.381150
17	6	0	-2.470091	2.812502	0.510631
18	6	0	-3.516300	2.605827	-0.672455
19	6	0	-4.693707	3.591567	-0.302310
20	6	0	-4.067601	1.114181	-0.659847
21	6	0	-5.982899	3.365861	-1.139534
22	6	0	-5.420529	0.846898	-1.455548
23	6	0	-6.495283	1.902775	-0.994729
24	6	0	-2.851305	3.046557	-2.018472
25	6	0	-3.006650	0.044267	-1.067553

26	6	0	-3.458805	-1.357175	-0.562874
27	6	0	-5.893047	-0.611310	-1.110682
28	6	0	-4.970547	-1.627027	-0.744401
29	6	0	-7.259634	-0.969940	-1.235253
30	6	0	-7.708377	-2.276265	-0.988857
31	6	0	-5.437652	-2.941664	-0.498932
32	6	0	-6.797338	-3.291329	-0.612997
33	6	0	-5.291814	0.900200	-3.023997
34	6	0	-1.091104	3.196731	3.563195
35	6	0	0.404776	3.514003	3.882129
36	6	0	0.596627	5.002995	4.313185
37	6	0	2.083519	5.334377	4.628229
38	6	0	-7.266703	-4.744015	-0.336076
39	6	0	-8.253932	-4.801868	0.876708
40	6	0	-7.911913	-5.388153	-1.607770
41	1	0	1.367161	-3.376256	1.507942
42	1	0	0.843600	-1.281717	4.713890
43	1	0	1.250947	-2.921245	4.183445
44	1	0	3.100991	-0.556563	4.720946
45	1	0	3.312506	-2.268650	5.120876
46	1	0	4.917562	-2.027604	3.427865
47	1	0	4.028907	-0.766596	2.566906
48	1	0	0.822987	-1.718408	-0.223787
49	1	0	2.383022	-0.892146	-0.005198
50	1	0	2.058051	-3.850822	-0.832561
51	1	0	2.471918	-2.516007	-1.936380
52	1	0	3.072365	-4.978217	1.949030
53	1	0	4.368103	-4.487103	3.070849
54	1	0	2.659525	-4.264575	3.529796
55	1	0	0.930842	0.540320	3.319147
56	1	0	2.348216	0.302824	2.239966
57	1	0	-0.624941	-2.901749	2.581689

58	1	0	-1.054221	-1.233488	3.050454
59	1	0	-0.777664	-1.633599	1.334064
60	1	0	-2.934700	2.489539	1.462363
61	1	0	-2.272409	3.903595	0.576695
62	1	0	-4.944556	3.453774	0.763913
63	1	0	-4.344225	4.631074	-0.426647
64	1	0	-4.325315	0.920632	0.399457
65	1	0	-6.765877	4.060380	-0.788159
66	1	0	-5.793844	3.598572	-2.199952
67	1	0	-6.755118	1.714619	0.061282
68	1	0	-7.414450	1.785666	-1.591114
69	1	0	-2.400909	4.043482	-1.895852
70	1	0	-2.055792	2.350236	-2.318701
71	1	0	-3.586944	3.106767	-2.830268
72	1	0	-2.877242	0.030805	-2.160369
73	1	0	-2.033490	0.300114	-0.620472
74	1	0	-2.883401	-2.148632	-1.075889
75	1	0	-3.220851	-1.442983	0.514500
76	1	0	-7.993523	-0.211983	-1.533830
77	1	0	-8.776220	-2.508084	-1.093648
78	1	0	-4.709497	-3.713027	-0.212411
79	1	0	-5.039781	1.905718	-3.384390
80	1	0	-4.527996	0.198147	-3.386343
81	1	0	-6.255519	0.610684	-3.469880
82	1	0	-1.451630	3.879174	2.775044
83	1	0	-1.704287	3.378079	4.463086
84	1	0	0.758809	2.849849	4.689686
85	1	0	1.023434	3.311241	2.990314
86	1	0	0.236717	5.663794	3.505244
87	1	0	-0.022696	5.206341	5.204329
88	1	0	2.187420	6.388835	4.926610
89	1	0	2.457198	4.703815	5.449484

90	1	0	2.715945	5.160969	3.744082
91	1	0	-6.370699	-5.336587	-0.072997
92	1	0	-9.167516	-4.226923	0.663216
93	1	0	-8.540293	-5.844609	1.084245
94	1	0	-7.782473	-4.382831	1.778756
95	1	0	-8.818010	-4.839617	-1.905611
96	1	0	-7.203474	-5.372732	-2.449993
97	1	0	-8.190448	-6.433758	-1.403981
98	6	0	5.818876	-3.021829	1.138929
99	6	0	6.776968	-3.198949	0.126171
100	6	0	6.391009	-3.276306	-1.230189
101	6	0	7.451622	-3.466243	-2.346513
102	6	0	7.227459	-4.803650	-3.127340
103	6	0	7.471882	-2.247654	-3.327882
104	1	0	7.838900	-3.280421	0.394384
105	1	0	8.440795	-3.522642	-1.854978
106	1	0	6.257023	-4.794880	-3.645859
107	1	0	8.020664	-4.942010	-3.878400
108	1	0	7.245544	-5.661352	-2.437713
109	1	0	6.507391	-2.150450	-3.848374
110	1	0	7.666371	-1.313232	-2.779734
111	1	0	8.262016	-2.381160	-4.083049
112	6	0	5.014841	-3.172249	-1.525770
113	6	0	4.044145	-2.996730	-0.514734
114	1	0	-0.497435	2.262127	-0.595255
115	1	0	1.182618	0.930270	0.239632
116	1	0	6.164234	-2.981217	2.179030
117	1	0	4.678265	-3.224551	-2.569812
118	8	0	1.947226	1.143521	-0.744417
119	6	0	1.408358	1.912409	-1.650083
120	6	0	2.197618	2.300213	-2.989187
121	6	0	3.501500	3.088725	-2.634285

122	6	0	4.582511	2.470477	-1.964596
123	6	0	3.595145	4.449433	-2.993603
124	6	0	5.739972	3.211654	-1.659461
125	6	0	4.753843	5.190125	-2.692020
126	6	0	5.828430	4.571261	-2.022731
127	8	0	1.277993	3.082258	-3.800511
128	1	0	4.510742	1.412651	-1.676479
129	1	0	2.738433	4.893570	-3.521175
130	1	0	6.577086	2.728088	-1.137942
131	1	0	4.820991	6.248369	-2.978864
132	1	0	6.734035	5.145402	-1.785981
133	8	0	0.212889	2.483081	-1.637744
134	1	0	2.496483	1.349672	-3.497923
135	1	0	0.496500	3.123807	-3.104477

[2c][(R)-3a]

OPT RB3LYP/STO-3G

E(RB+HF-LYP) = -2765.0954461 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.362188	-2.042395	1.841987
2	6	0	2.424737	-2.602216	0.786070
3	6	0	1.570395	-2.762656	3.222138
4	6	0	3.849148	-3.014943	1.406262
5	6	0	2.985172	-2.516228	3.839910
6	6	0	4.092571	-2.256141	2.765523
7	6	0	2.547416	-1.655106	-0.448106
8	6	0	3.471490	-2.282951	-1.524923
9	6	0	5.056848	-2.739830	0.434741
10	6	0	3.859985	-4.572079	1.661095
11	6	0	1.451948	-0.465581	2.102853
12	7	0	0.582917	0.398961	1.237908

13	6	0	-0.078336	-2.401125	1.335577
14	6	0	-0.586166	0.933097	1.720032
15	16	0	-1.211397	0.430821	3.361771
16	7	0	-1.284098	1.784294	0.904969
17	6	0	-2.616086	2.324308	1.343060
18	6	0	-3.767433	2.374342	0.243664
19	6	0	-4.971389	3.056951	1.006367
20	6	0	-4.193683	0.900275	-0.174789
21	6	0	-6.325147	2.962064	0.250600
22	6	0	-5.604364	0.743897	-0.897669
23	6	0	-6.700364	1.478807	-0.036823
24	6	0	-3.297482	3.284397	-0.939719
25	6	0	-3.105003	0.134251	-0.990028
26	6	0	-3.386300	-1.396210	-0.935324
27	6	0	-5.918063	-0.792394	-0.997631
28	6	0	-4.882850	-1.762107	-1.062356
29	6	0	-7.257961	-1.244488	-1.107834
30	6	0	-7.571868	-2.603792	-1.257531
31	6	0	-5.214188	-3.130969	-1.214640
32	6	0	-6.546509	-3.577008	-1.314182
33	6	0	-5.665689	1.292337	-2.372943
34	6	0	-0.956083	2.025695	4.256351
35	6	0	0.540863	2.382525	4.525408
36	6	0	0.678546	3.722755	5.315423
37	6	0	2.164756	4.090045	5.591607
38	6	0	-6.864155	-5.086223	-1.483078
39	6	0	-7.681341	-5.636764	-0.267307
40	6	0	-7.614926	-5.365138	-2.827326
41	1	0	1.984586	-3.541829	0.405388
42	1	0	0.792819	-2.423202	3.927385
43	1	0	1.413908	-3.842806	3.070636
44	1	0	2.950348	-1.649312	4.520778

45	1	0	3.261233	-3.391158	4.451600
46	1	0	5.063412	-2.557946	3.187360
47	1	0	4.161295	-1.176784	2.554137
48	1	0	1.545195	-1.478002	-0.871786
49	1	0	2.962318	-0.678222	-0.153689
50	1	0	3.066281	-3.264713	-1.836082
51	1	0	3.508055	-1.641389	-2.421762
52	1	0	3.759832	-5.110135	0.706108
53	1	0	4.808883	-4.875062	2.128425
54	1	0	3.035651	-4.880375	2.318716
55	1	0	1.148387	-0.287298	3.150886
56	1	0	2.492883	-0.120082	1.971916
57	1	0	-0.180675	-3.491680	1.231453
58	1	0	-0.834992	-2.050952	2.054201
59	1	0	-0.283911	-1.934679	0.361486
60	1	0	-2.961139	1.709727	2.197304
61	1	0	-2.475634	3.365002	1.705171
62	1	0	-5.089222	2.565345	1.987848
63	1	0	-4.721756	4.115086	1.196117
64	1	0	-4.312125	0.360044	0.784573
65	1	0	-7.115396	3.422119	0.869321
66	1	0	-6.277137	3.531819	-0.691617
67	1	0	-6.823625	0.945452	0.921479
68	1	0	-7.668889	1.450604	-0.561719
69	1	0	-3.010999	4.271629	-0.546004
70	1	0	-2.419502	2.861200	-1.449992
71	1	0	-4.097308	3.433639	-1.675345
72	1	0	-3.092871	0.483107	-2.033788
73	1	0	-2.112615	0.337841	-0.558984
74	1	0	-2.815816	-1.914464	-1.726950
75	1	0	-3.016270	-1.792540	0.029316
76	1	0	-8.078514	-0.517841	-1.078231

77	1	0	-8.623503	-2.908849	-1.335370
78	1	0	-4.399271	-3.866672	-1.259114
79	1	0	-5.563137	2.384561	-2.413295
80	1	0	-4.882174	0.844622	-2.999857
81	1	0	-6.640574	1.026676	-2.809223
82	1	0	-1.439378	2.854868	3.712603
83	1	0	-1.484135	1.909273	5.218712
84	1	0	1.017197	1.568341	5.098883
85	1	0	1.077357	2.469696	3.564240
86	1	0	0.200815	4.534359	4.739176
87	1	0	0.136873	3.637465	6.273815
88	1	0	2.229224	5.036321	6.150282
89	1	0	2.655944	3.303633	6.184908
90	1	0	2.718336	4.207270	4.647456
91	1	0	-5.899135	-5.625470	-1.514835
92	1	0	-8.658529	-5.136123	-0.195482
93	1	0	-7.853176	-6.718095	-0.383961
94	1	0	-7.134870	-5.469166	0.673340
95	1	0	-8.589507	-4.854650	-2.842468
96	1	0	-7.021621	-5.007208	-3.682529
97	1	0	-7.787131	-6.445848	-2.948893
98	6	0	6.383486	-2.875175	0.914864
99	6	0	7.496407	-2.704406	0.074085
100	6	0	7.329322	-2.395876	-1.294133
101	6	0	8.559602	-2.194962	-2.217809
102	6	0	8.571880	-3.230259	-3.391043
103	6	0	8.623093	-0.731798	-2.769393
104	1	0	8.508335	-2.813586	0.486850
105	1	0	9.464017	-2.366192	-1.604684
106	1	0	7.692580	-3.095868	-4.038605
107	1	0	9.477307	-3.098101	-4.003419
108	1	0	8.561709	-4.258866	-2.999346

109	1	0	7.743645	-0.512466	-3.393249
110	1	0	8.650781	-0.007555	-1.941042
111	1	0	9.527252	-0.596324	-3.383004
112	6	0	6.010517	-2.272557	-1.781222
113	6	0	4.885472	-2.446618	-0.944836
114	1	0	-0.761257	2.248192	-0.092905
115	1	0	1.020204	0.802883	0.216805
116	1	0	6.560735	-3.126126	1.967716
117	1	0	5.842736	-2.029817	-2.839065
118	8	0	1.545605	1.271338	-0.869041
119	6	0	0.860777	2.221333	-1.480675
120	6	0	1.628245	2.705463	-2.800714
121	8	0	2.784245	1.835529	-2.948035
122	6	0	2.025910	4.213309	-2.670406
123	6	0	3.392134	4.555242	-2.593860
124	6	0	1.049990	5.235527	-2.629044
125	6	0	3.786121	5.902131	-2.479805
126	6	0	1.443136	6.582217	-2.511512
127	6	0	2.810625	6.918180	-2.437848
128	1	0	0.922185	2.608135	-3.663049
129	1	0	2.662720	1.307987	-2.051174
130	1	0	4.122719	3.734234	-2.636372
131	1	0	-0.015258	4.971365	-2.678974
132	1	0	4.852255	6.160967	-2.424543
133	1	0	0.681986	7.373468	-2.478405
134	1	0	3.114028	7.969792	-2.349245
135	8	0	-0.280942	2.754115	-1.131105

[2c][(R)-3d]

OPT RB3LYP/STO-3G

E(RB+HF-LYP) = -2729.7845856 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.090919	-1.325317	2.670149
2	6	0	1.932076	-2.278589	1.700818
3	6	0	1.496386	-1.624014	4.157839
4	6	0	3.421452	-2.622295	2.200108
5	6	0	3.002588	-1.328104	4.454213
6	6	0	3.933246	-1.527739	3.210248
7	6	0	1.875599	-1.791976	0.218778
8	6	0	2.571488	-2.823057	-0.710327
9	6	0	4.455680	-2.769327	1.022427
10	6	0	3.405289	-4.028287	2.917056
11	6	0	1.284513	0.243717	2.439539
12	7	0	0.538808	0.849709	1.289585
13	6	0	-0.429053	-1.676990	2.510596
14	6	0	-0.623923	1.547028	1.489600
15	16	0	-1.399160	1.628661	3.146026
16	7	0	-1.201636	2.120309	0.386531
17	6	0	-2.512993	2.839907	0.509673
18	6	0	-3.563563	2.606924	-0.664959
19	6	0	-4.769651	3.551280	-0.278668
20	6	0	-4.071679	1.099542	-0.656616
21	6	0	-6.053046	3.296925	-1.116072
22	6	0	-5.422163	0.795498	-1.444867
23	6	0	-6.524929	1.819630	-0.977882
24	6	0	-2.923640	3.081686	-2.012395
25	6	0	-2.981538	0.063627	-1.073801
26	6	0	-3.390554	-1.356633	-0.584124

27	6	0	-5.850854	-0.675871	-1.099401
28	6	0	-4.896244	-1.667052	-0.748921
29	6	0	-7.208667	-1.071522	-1.207677
30	6	0	-7.618360	-2.390467	-0.960634
31	6	0	-5.324145	-2.994995	-0.502746
32	6	0	-6.675019	-3.381438	-0.600601
33	6	0	-5.307533	0.853337	-3.014365
34	6	0	-1.081875	3.409601	3.510823
35	6	0	0.420021	3.762775	3.756397
36	6	0	0.607796	5.276249	4.093376
37	6	0	2.101117	5.644141	4.327532
38	6	0	-7.100963	-4.847276	-0.322918
39	6	0	-8.073631	-4.935931	0.899782
40	6	0	-7.741589	-5.505767	-1.589623
41	1	0	1.391002	-3.242430	1.718681
42	1	0	0.861815	-1.027303	4.834948
43	1	0	1.277233	-2.683676	4.366072
44	1	0	3.114644	-0.290261	4.810051
45	1	0	3.336852	-1.984754	5.274652
46	1	0	4.936959	-1.800544	3.570581
47	1	0	4.041168	-0.575438	2.665870
48	1	0	0.820965	-1.673511	-0.079349
49	1	0	2.366541	-0.813199	0.092785
50	1	0	2.082748	-3.810544	-0.604712
51	1	0	2.473995	-2.518473	-1.766088
52	1	0	3.112068	-4.812777	2.202844
53	1	0	4.407314	-4.270619	3.301755
54	1	0	2.698031	-4.044771	3.757603
55	1	0	0.948106	0.744581	3.367678
56	1	0	2.355375	0.466284	2.285534
57	1	0	-0.604419	-2.731803	2.769559
58	1	0	-1.037497	-1.048749	3.178799

59	1	0	-0.765444	-1.509007	1.477433
60	1	0	-2.973754	2.539042	1.471277
61	1	0	-2.322541	3.933815	0.551582
62	1	0	-5.013922	3.391980	0.786069
63	1	0	-4.452508	4.602482	-0.390023
64	1	0	-4.317313	0.894049	0.403385
65	1	0	-6.854822	3.967655	-0.760745
66	1	0	-5.870625	3.540078	-2.175288
67	1	0	-6.778037	1.619864	0.077620
68	1	0	-7.441407	1.679839	-1.573634
69	1	0	-2.600646	4.128946	-1.908682
70	1	0	-2.036716	2.484688	-2.272842
71	1	0	-3.640734	3.031511	-2.840856
72	1	0	-2.848110	0.067418	-2.166266
73	1	0	-2.019100	0.345399	-0.619108
74	1	0	-2.800400	-2.125297	-1.114850
75	1	0	-3.136630	-1.450993	0.488885
76	1	0	-7.966992	-0.333014	-1.493604
77	1	0	-8.680783	-2.651057	-1.052113
78	1	0	-4.571541	-3.746996	-0.228167
79	1	0	-5.112488	1.870850	-3.376783
80	1	0	-4.510209	0.192747	-3.382229
81	1	0	-6.258039	0.513454	-3.453223
82	1	0	-1.480170	4.047283	2.703507
83	1	0	-1.663716	3.630454	4.422633
84	1	0	0.812308	3.150924	4.587253
85	1	0	1.008358	3.515059	2.855510
86	1	0	0.205867	5.885034	3.264627
87	1	0	0.022427	5.523501	4.996340
88	1	0	2.201281	6.714616	4.563893
89	1	0	2.518010	5.064365	5.165254
90	1	0	2.699416	5.431020	3.428453

91	1	0	-6.186389	-5.415724	-0.070703
92	1	0	-9.005736	-4.387588	0.696699
93	1	0	-8.327347	-5.986917	1.108318
94	1	0	-7.605352	-4.504677	1.797711
95	1	0	-8.664353	-4.980126	-1.877427
96	1	0	-7.042078	-5.470451	-2.438691
97	1	0	-7.991083	-6.558618	-1.385434
98	6	0	5.840310	-2.858333	1.311421
99	6	0	6.796292	-3.063741	0.301980
100	6	0	6.405633	-3.198818	-1.048408
101	6	0	7.463983	-3.419269	-2.161244
102	6	0	7.247520	-4.783713	-2.895900
103	6	0	7.472267	-2.234027	-3.182913
104	1	0	7.860210	-3.122341	0.568275
105	1	0	8.455164	-3.451692	-1.671584
106	1	0	6.273916	-4.800970	-3.408174
107	1	0	8.037476	-4.940080	-3.646854
108	1	0	7.277461	-5.617726	-2.178223
109	1	0	6.506161	-2.162687	-3.704647
110	1	0	7.659097	-1.280207	-2.666370
111	1	0	8.262517	-2.385556	-3.934597
112	6	0	5.027126	-3.122719	-1.341459
113	6	0	4.058604	-2.918965	-0.333611
114	1	0	-0.558245	2.190129	-0.660850
115	1	0	1.149548	1.012706	0.250470
116	1	0	6.189649	-2.773226	2.347461
117	1	0	4.686829	-3.220858	-2.381000
118	8	0	1.864069	1.173270	-0.763055
119	6	0	1.244994	1.784605	-1.751981
120	6	0	2.051807	1.944114	-3.105641
121	6	0	2.590881	0.551968	-3.578348
122	6	0	3.208011	2.963907	-2.937460

123	6	0	4.091353	2.873919	-1.835312
124	6	0	3.413145	3.982530	-3.896255
125	6	0	5.157158	3.781520	-1.696296
126	6	0	4.481353	4.890625	-3.758360
127	6	0	5.356793	4.791174	-2.659832
128	1	0	1.343345	2.334600	-3.858784
129	1	0	3.905609	2.093488	-1.082558
130	1	0	2.732205	4.065708	-4.754179
131	1	0	5.833737	3.703758	-0.834437
132	1	0	4.629476	5.677645	-4.510090
133	1	0	6.189067	5.499365	-2.552274
134	8	0	0.030661	2.296324	-1.742336
135	1	0	1.753365	-0.134519	-3.778152
136	1	0	3.181700	0.664516	-4.500466
137	1	0	3.229916	0.110856	-2.798534

[2c][(*S*)-3d]

OPT RB3LYP/STO-3G

E(RB+HF-LYP) = -2729.78469845 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.301573	-1.859477	2.441373
2	6	0	2.173670	-2.618234	1.336559
3	6	0	1.730991	-2.363031	3.865847
4	6	0	3.683069	-2.961843	1.773281
5	6	0	3.226207	-2.054158	4.201435
6	6	0	4.151337	-2.011594	2.939188
7	6	0	2.078346	-1.919824	-0.056293
8	6	0	2.815119	-2.764367	-1.130828
9	6	0	4.711877	-2.875176	0.585143
10	6	0	3.739486	-4.460336	2.266028
11	6	0	1.431052	-0.267581	2.450027

12	7	0	0.644529	0.475040	1.412220
13	6	0	-0.205169	-2.241384	2.234320
14	6	0	-0.515485	1.129619	1.736237
15	16	0	-1.272236	0.933111	3.391421
16	7	0	-1.102193	1.876877	0.748034
17	6	0	-2.419877	2.549683	0.996529
18	6	0	-3.487831	2.480635	-0.183670
19	6	0	-4.699169	3.335647	0.361804
20	6	0	-3.971614	0.980910	-0.397020
21	6	0	-6.001532	3.181428	-0.471108
22	6	0	-5.335925	0.775164	-1.193146
23	6	0	-6.442929	1.690166	-0.545225
24	6	0	-2.876444	3.158427	-1.454842
25	6	0	-2.876078	0.043278	-0.994201
26	6	0	-3.247341	-1.441417	-0.709560
27	6	0	-5.729440	-0.741185	-1.072459
28	6	0	-4.750536	-1.754252	-0.892148
29	6	0	-7.081458	-1.144155	-1.219384
30	6	0	-7.462680	-2.493547	-1.169691
31	6	0	-5.149912	-3.112500	-0.842970
32	6	0	-6.495178	-3.507700	-0.976933
33	6	0	-5.263029	1.081794	-2.736328
34	6	0	-0.961049	2.633628	4.037165
35	6	0	0.543155	2.960685	4.303541
36	6	0	0.723243	4.391043	4.904739
37	6	0	2.218643	4.734135	5.162292
38	6	0	-6.886846	-5.007939	-0.921363
39	6	0	-7.867263	-5.301238	0.262189
40	6	0	-7.496937	-5.488276	-2.279907
41	1	0	1.677271	-3.598235	1.213242
42	1	0	1.077951	-1.902236	4.626347
43	1	0	1.556716	-3.450079	3.911935

44	1	0	3.299068	-1.083024	4.719011
45	1	0	3.595877	-2.819105	4.904396
46	1	0	5.171255	-2.285226	3.249917
47	1	0	4.205638	-0.982687	2.548274
48	1	0	1.016114	-1.812481	-0.330877
49	1	0	2.518954	-0.909626	-0.036647
50	1	0	2.378186	-3.780547	-1.172101
51	1	0	2.691260	-2.311541	-2.129097
52	1	0	3.478544	-5.139268	1.439923
53	1	0	4.754851	-4.710250	2.608684
54	1	0	3.039897	-4.639601	3.094244
55	1	0	1.090944	0.074791	3.446141
56	1	0	2.489793	0.019327	2.319504
57	1	0	-0.338864	-3.329535	2.326308
58	1	0	-0.829988	-1.748346	2.994643
59	1	0	-0.557866	-1.927276	1.241453
60	1	0	-2.862560	2.101070	1.907671
61	1	0	-2.241651	3.627447	1.199473
62	1	0	-4.912942	3.018465	1.397363
63	1	0	-4.401934	4.397920	0.398217
64	1	0	-4.186954	0.609109	0.623501
65	1	0	-6.804135	3.773439	0.002580
66	1	0	-5.855186	3.585606	-1.485967
67	1	0	-6.659532	1.326968	0.474200
68	1	0	-7.375013	1.621416	-1.129122
69	1	0	-2.572141	4.186861	-1.206878
70	1	0	-1.982790	2.620244	-1.804184
71	1	0	-3.602730	3.209090	-2.275258
72	1	0	-2.778265	0.210979	-2.077523
73	1	0	-1.904403	0.275019	-0.530720
74	1	0	-2.654892	-2.112199	-1.357509
75	1	0	-2.969345	-1.685294	0.333495

76	1	0	-7.857905	-0.386519	-1.378735
77	1	0	-8.521625	-2.758886	-1.285130
78	1	0	-4.378738	-3.881563	-0.697602
79	1	0	-5.099280	2.148409	-2.937864
80	1	0	-4.461499	0.507370	-3.221097
81	1	0	-6.216814	0.790674	-3.202071
82	1	0	-1.385242	3.390523	3.355647
83	1	0	-1.521529	2.694111	4.986345
84	1	0	0.965628	2.214996	4.999312
85	1	0	1.108559	2.889651	3.357875
86	1	0	0.290911	5.133342	4.211150
87	1	0	0.161163	4.460606	5.852477
88	1	0	2.314642	5.747144	5.582275
89	1	0	2.664659	4.021225	5.872624
90	1	0	2.793311	4.692216	4.224379
91	1	0	-5.960064	-5.584820	-0.743946
92	1	0	-8.813467	-4.755578	0.130029
93	1	0	-8.091730	-6.378075	0.311119
94	1	0	-7.419566	-4.993736	1.219540
95	1	0	-8.429097	-4.947508	-2.502149
96	1	0	-6.788813	-5.313115	-3.104162
97	1	0	-7.722432	-6.565134	-2.235590
98	6	0	6.101973	-2.934648	0.854531
99	6	0	7.057041	-2.934953	-0.176413
100	6	0	6.660133	-2.883656	-1.530734
101	6	0	7.717824	-2.879417	-2.665772
102	6	0	7.574488	-4.136205	-3.587001
103	6	0	7.646725	-1.563121	-3.508884
104	1	0	8.125198	-2.978019	0.075477
105	1	0	8.714177	-2.922006	-2.187589
106	1	0	6.599111	-4.137580	-4.096257
107	1	0	8.365793	-4.137657	-4.352642

108	1	0	7.659041	-5.060435	-2.995248
109	1	0	6.673761	-1.476926	-4.015381
110	1	0	7.781246	-0.682658	-2.862207
111	1	0	8.438299	-1.559217	-4.274251
112	6	0	5.276726	-2.836081	-1.806194
113	6	0	4.309098	-2.838505	-0.777075
114	1	0	-0.449114	2.162045	-0.261691
115	1	0	1.238393	0.810803	0.410309
116	1	0	6.456258	-2.989201	1.890885
117	1	0	4.931768	-2.792746	-2.847890
118	8	0	1.951399	1.149862	-0.564697
119	6	0	1.357559	1.973134	-1.398116
120	6	0	2.188556	2.401623	-2.676249
121	6	0	2.598144	3.895269	-2.590363
122	6	0	3.918762	4.299015	-2.893949
123	6	0	1.646572	4.879568	-2.232447
124	6	0	4.279661	5.659953	-2.843113
125	6	0	2.006965	6.238210	-2.179625
126	6	0	3.324959	6.632479	-2.488017
127	6	0	1.360592	2.118252	-3.975145
128	1	0	4.668110	3.544308	-3.168983
129	1	0	0.631280	4.544495	-1.972169
130	1	0	5.309043	5.960945	-3.080194
131	1	0	1.260763	6.992640	-1.895711
132	1	0	3.607303	7.692891	-2.447633
133	8	0	0.149436	2.497446	-1.285281
134	1	0	3.104774	1.783517	-2.687576
135	1	0	1.139305	1.042991	-4.061509
136	1	0	0.410151	2.672091	-3.944843
137	1	0	1.926912	2.433851	-4.864979

5. Visualisation of optimised [2c][3d] complexes.

[2c][(*S*)-3d]
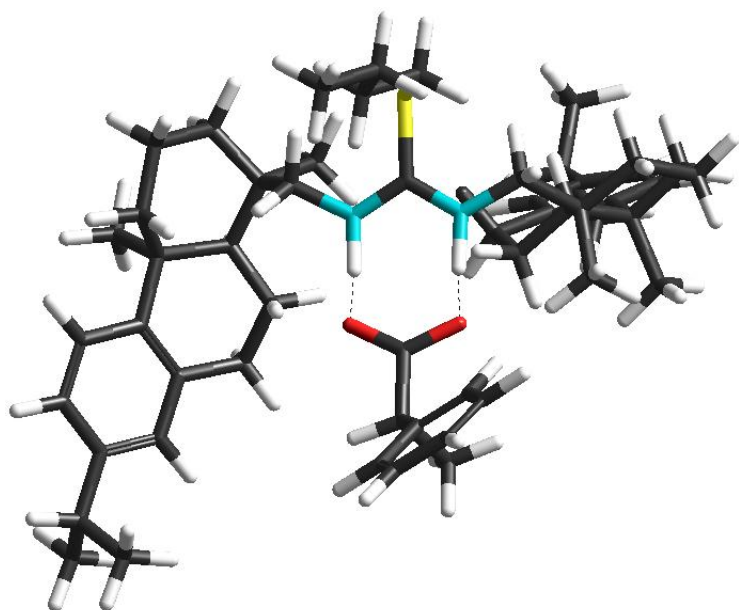
[2c][(*R*)-3d]
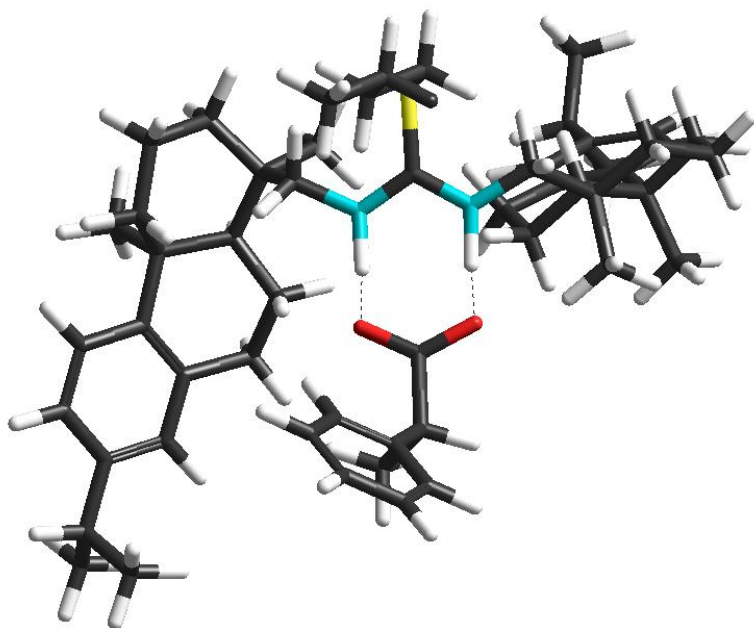
6. References

(28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J., J. A., ; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A.; Gaussian, Inc.: Pittsburgh PA, 1998.