Supporting information

Novel chiral ionic liquids: physicochemical properties and investigation of the internal rotameric behaviour in the neat system†

Magdalena B. Foreiter,* H.Q. Nimal Gunaratne,* Peter Nockemann, Kenneth R. Seddon and Geetha Srinivasan

QUILL Research Centre, The Queen`s University of Belfast,

Belfast BT9 5AG, Northern Ireland, UK

†*School of Chemistry and Chemical Engineering, The Queen's University of Belfast,*

Belfast BT9 5AG, Northern Ireland, UK

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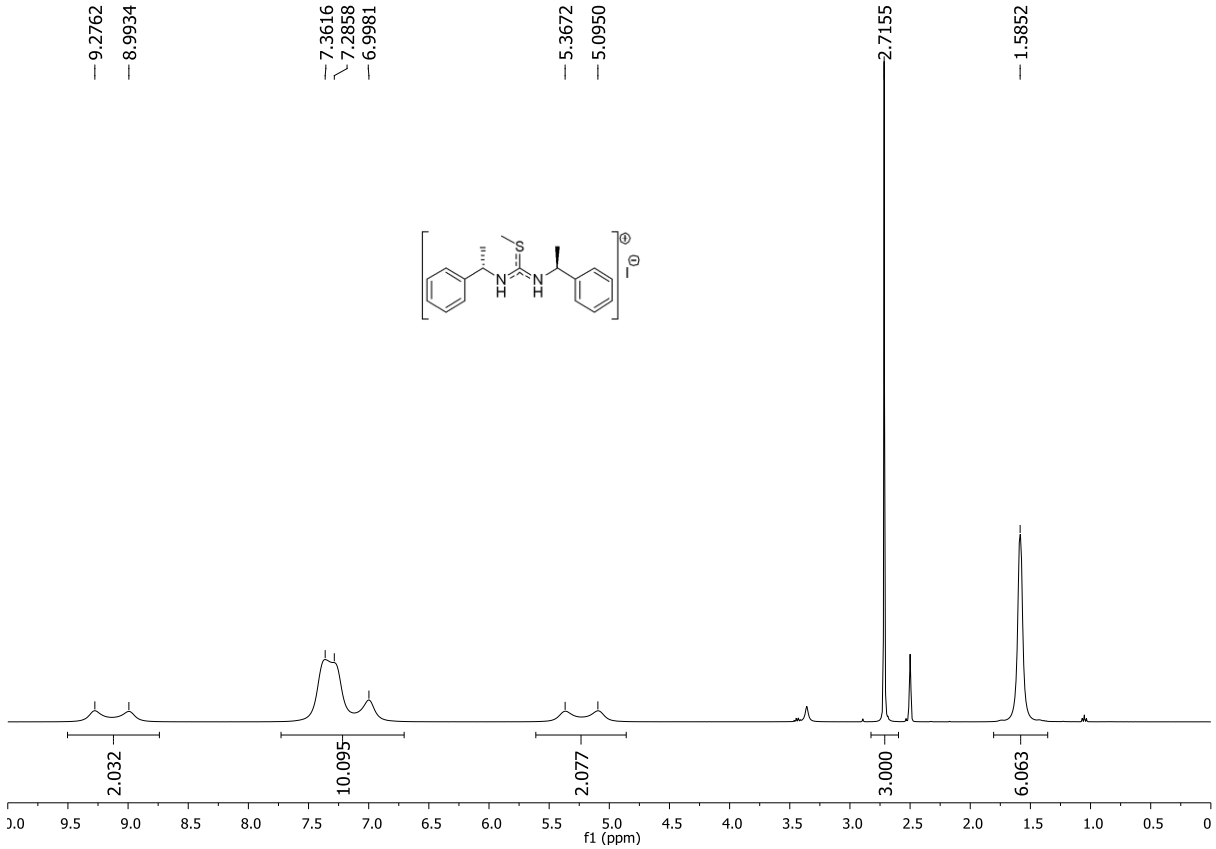
1. Spectral characterisation data

Figure S1. ^{1}H and ^{13}C NMR spectra for (*S*)-[C_1petu]I in DMSO-d_6 solution (400 and 101 MHz respectively).



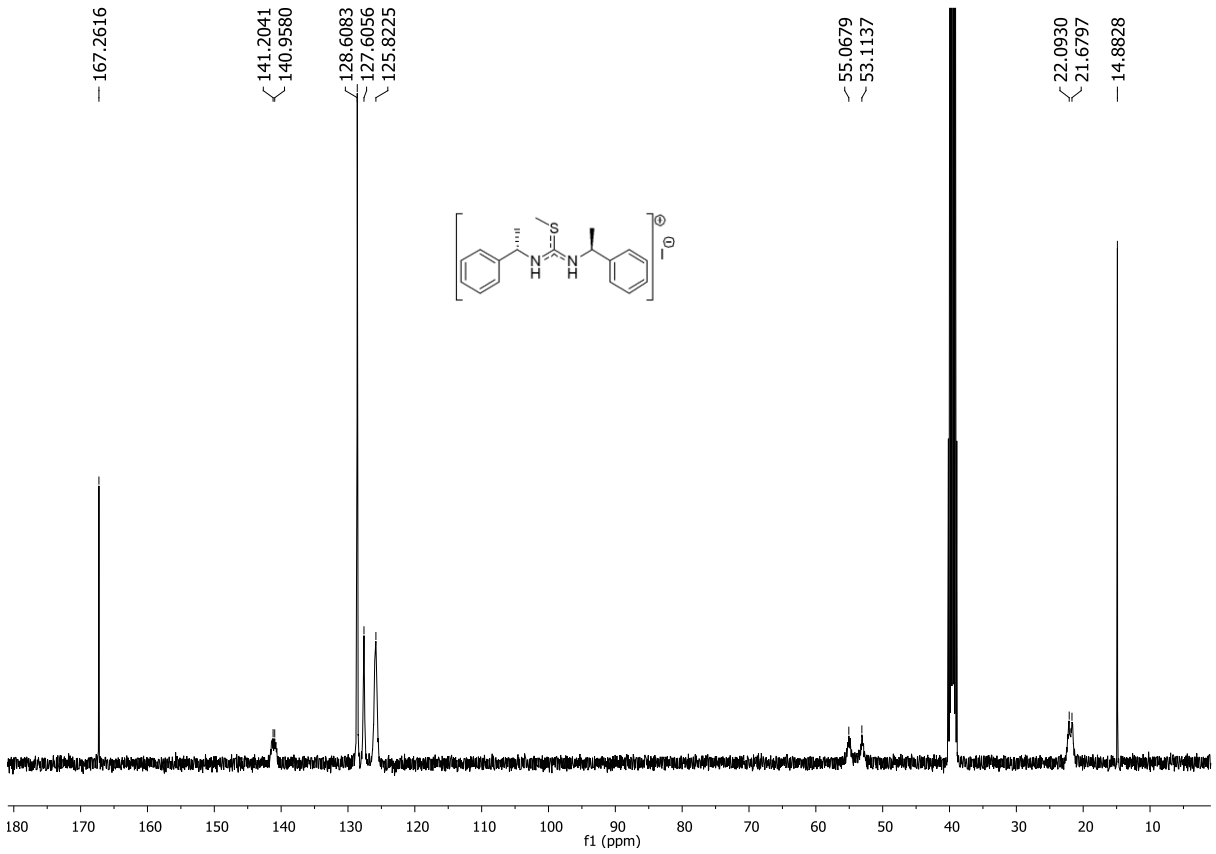


Figure S2. ^{1}H and ^{13}C NMR spectra for (*S*)-[C_2petu]Br in DMSO-d_6 solution (300 and 75 MHz respectively).

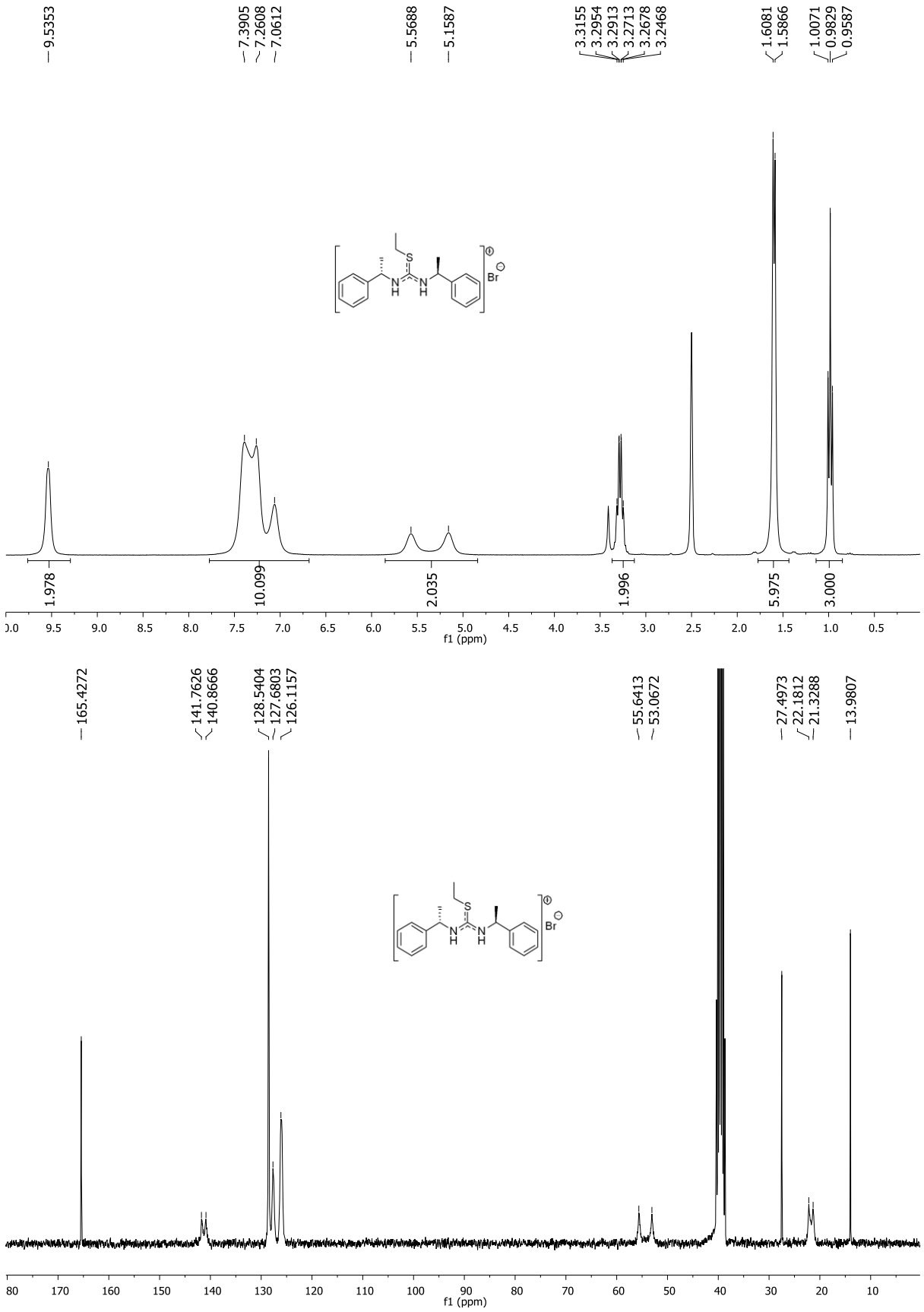


Figure S3. ^{1}H and ^{13}C NMR spectra for (*S*)-[C_2petu]I in DMSO-d_6 solution (300 and 75 MHz respectively).

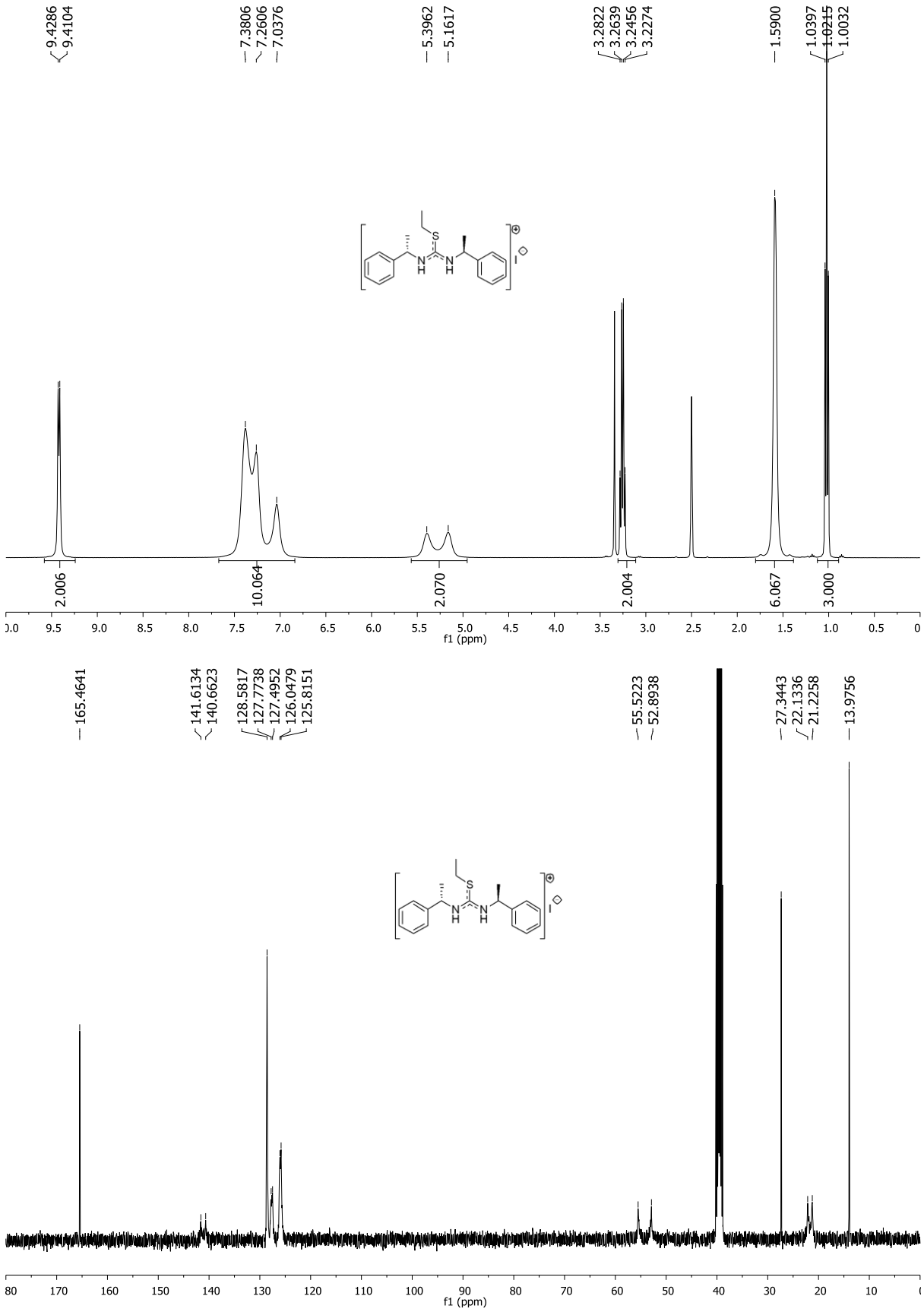


Figure S4. ^{1}H and ^{13}C NMR spectra for (*S*)-[C_3petu]I in DMSO-d_6 solution (300 and 75 MHz respectively).

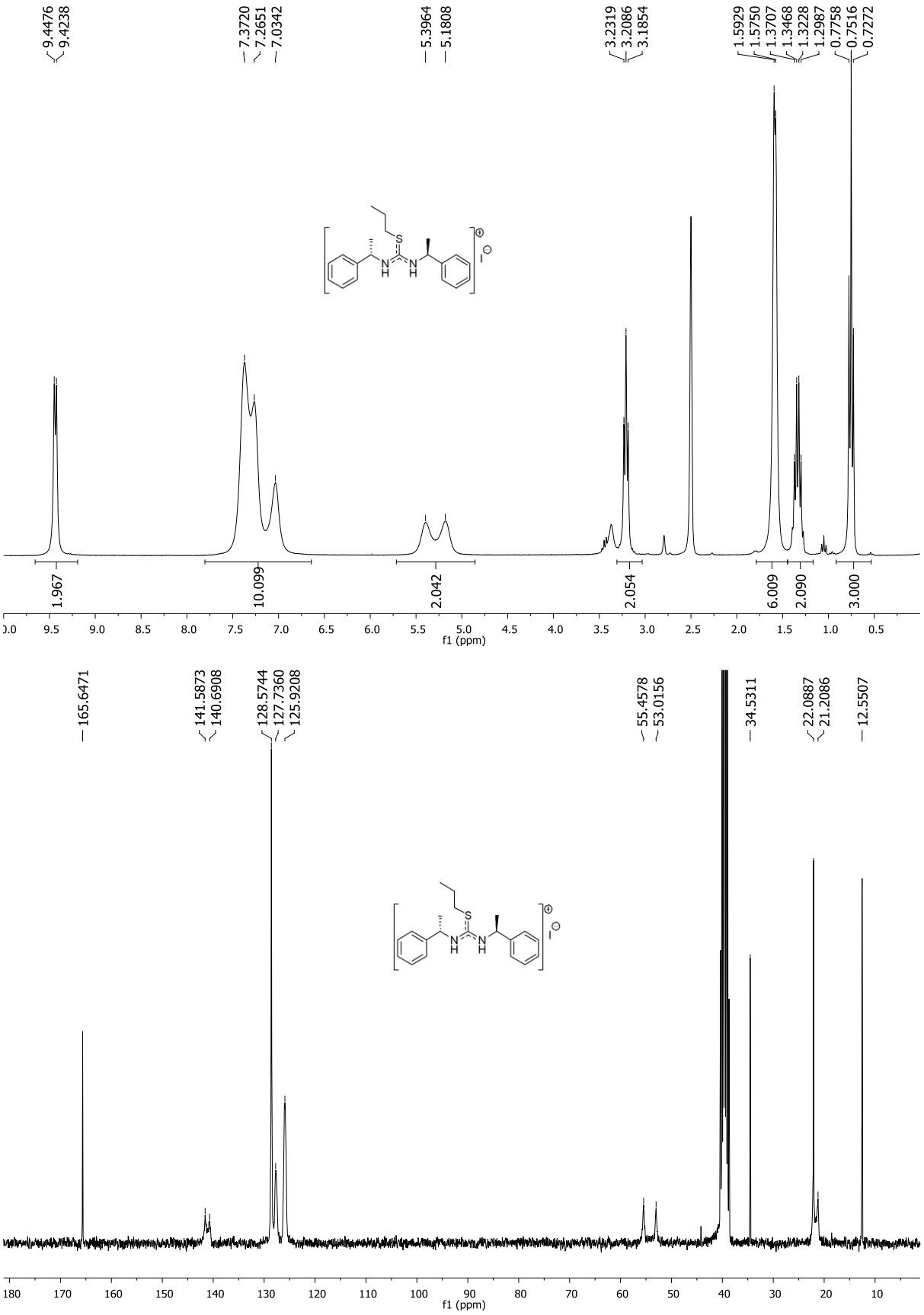


Figure S5. ^{1}H and ^{13}C NMR spectra for (*S*)-[C_4petu]I in DMSO-d_6 solution (400 and 101 MHz respectively).

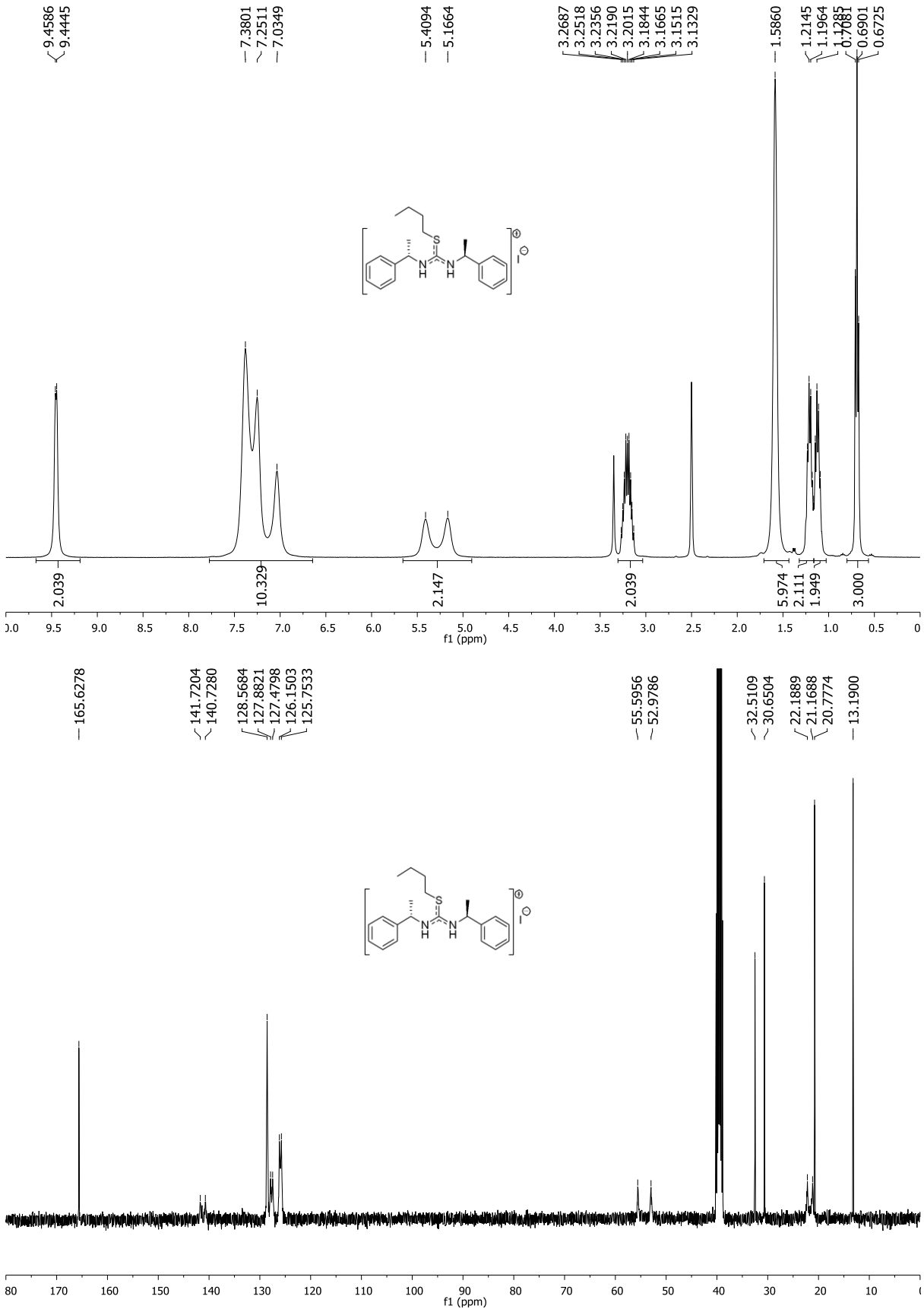


Figure S6. ^{1}H and ^{13}C NMR spectra for (*S*)-[C_6petu]I in DMSO-d_6 solution (400 and 101 MHz respectively).

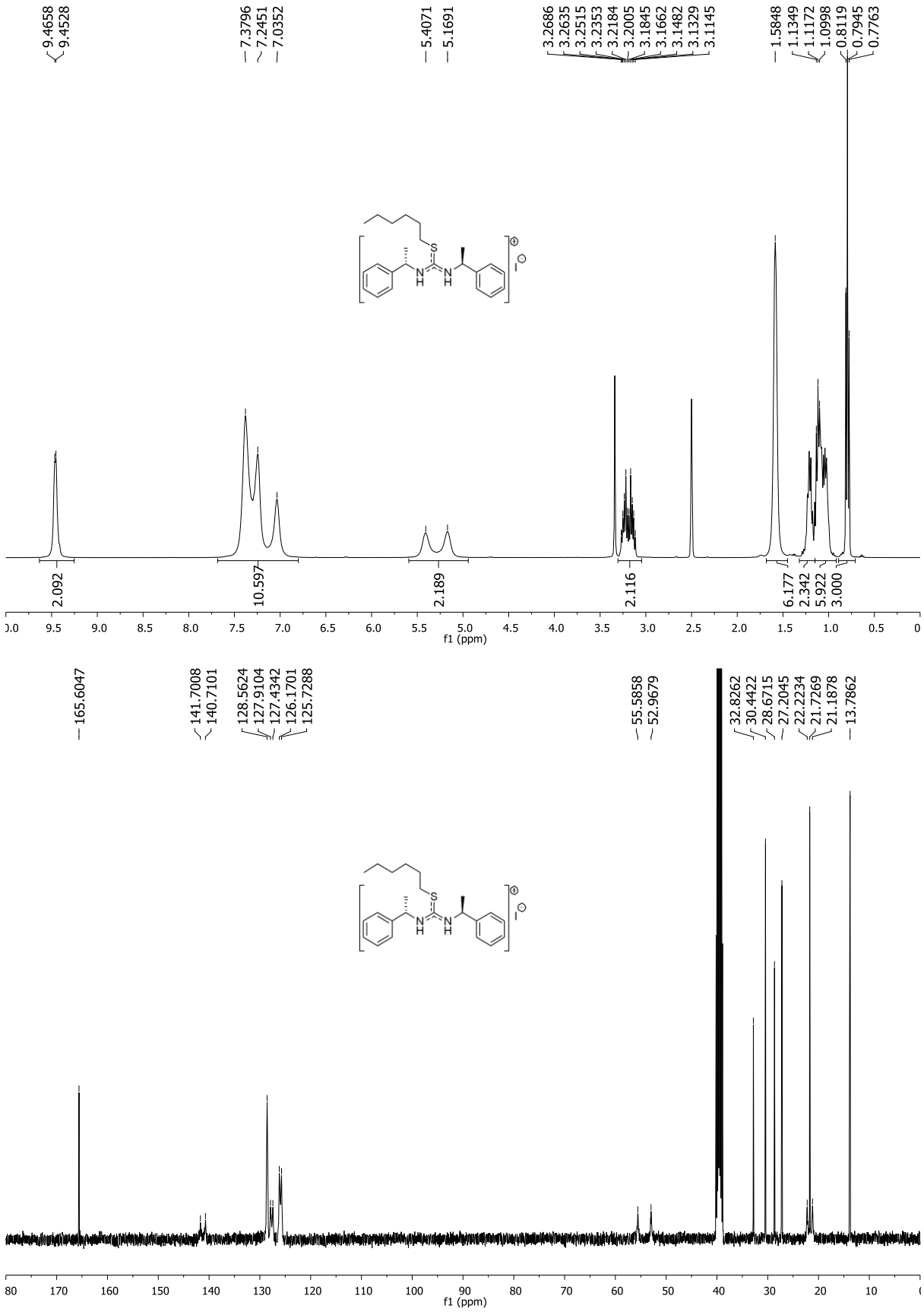


Figure S7. ^{1}H and ^{13}C NMR spectra for (*S*)-[C_8petu]I in DMSO-d_6 solution (400 and 101 MHz respectively).

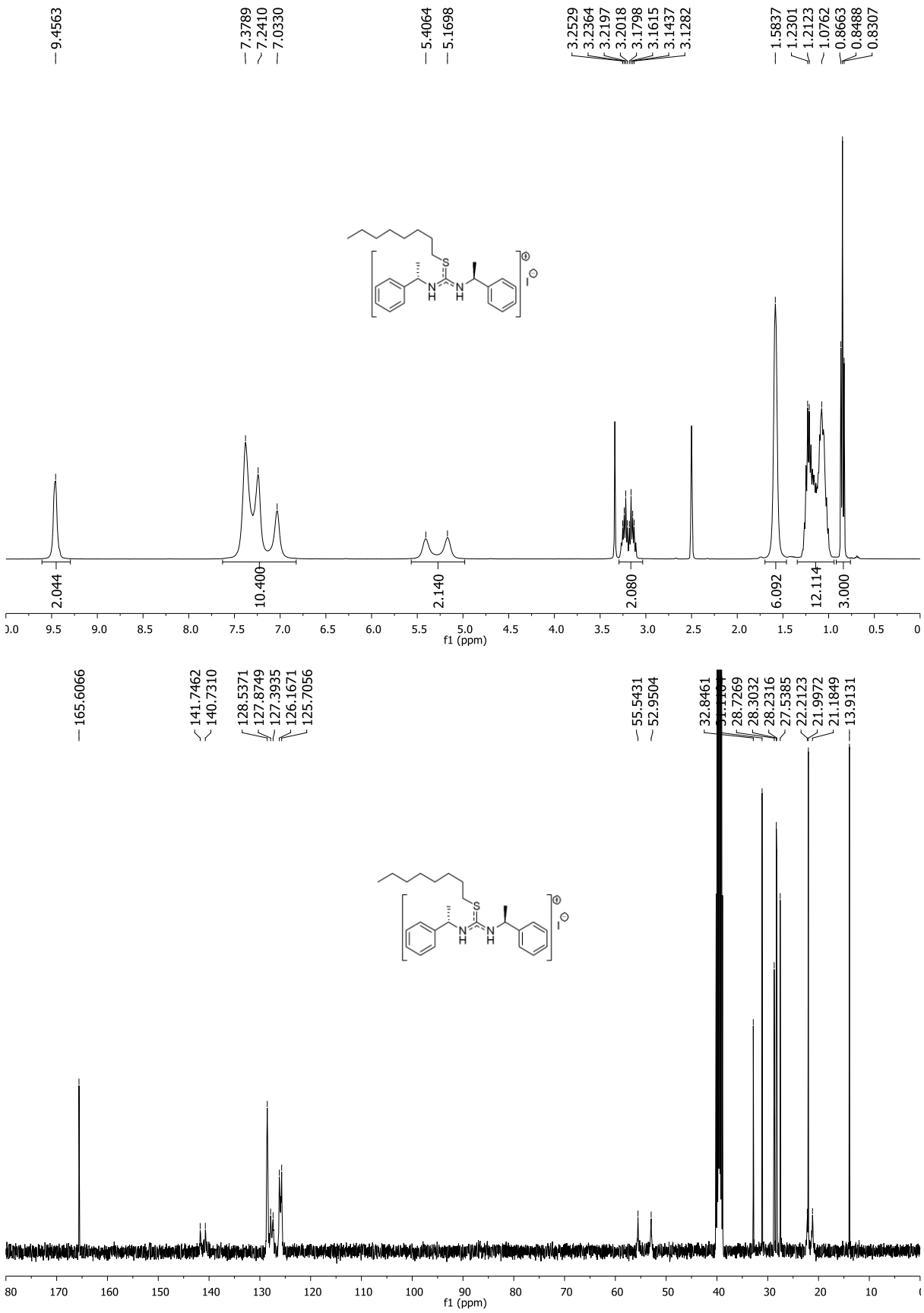


Figure S8. ^{1}H and ^{13}C NMR spectra for (*S*)-[C_{10}petu]I in DMSO-d_6 solution (400 and 101 MHz respectively).

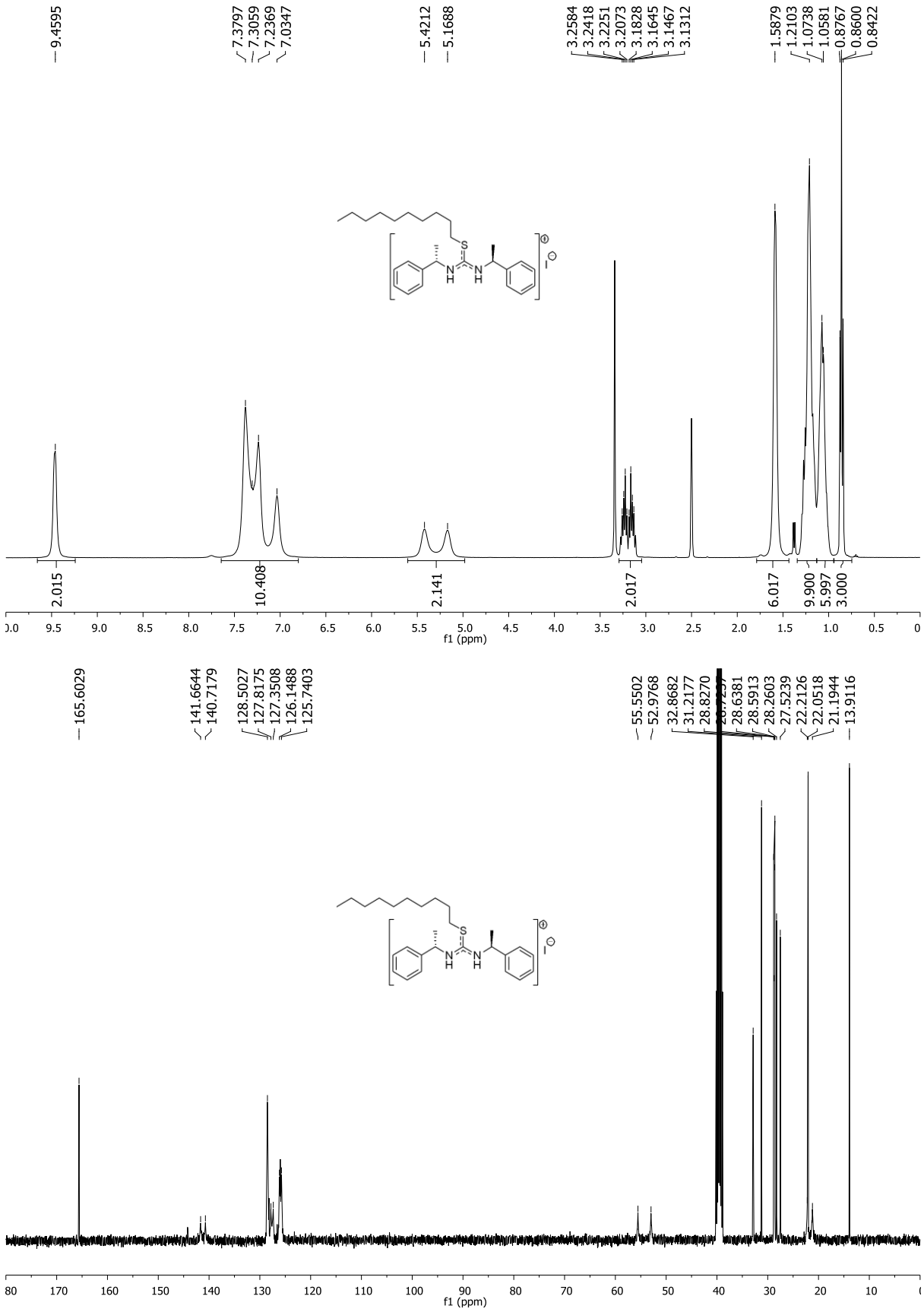


Figure S9. ^{1}H and ^{13}C NMR spectra for (*S*)-[C_{12}petu]I in DMSO-d_6 solution (400 and 101 MHz respectively).

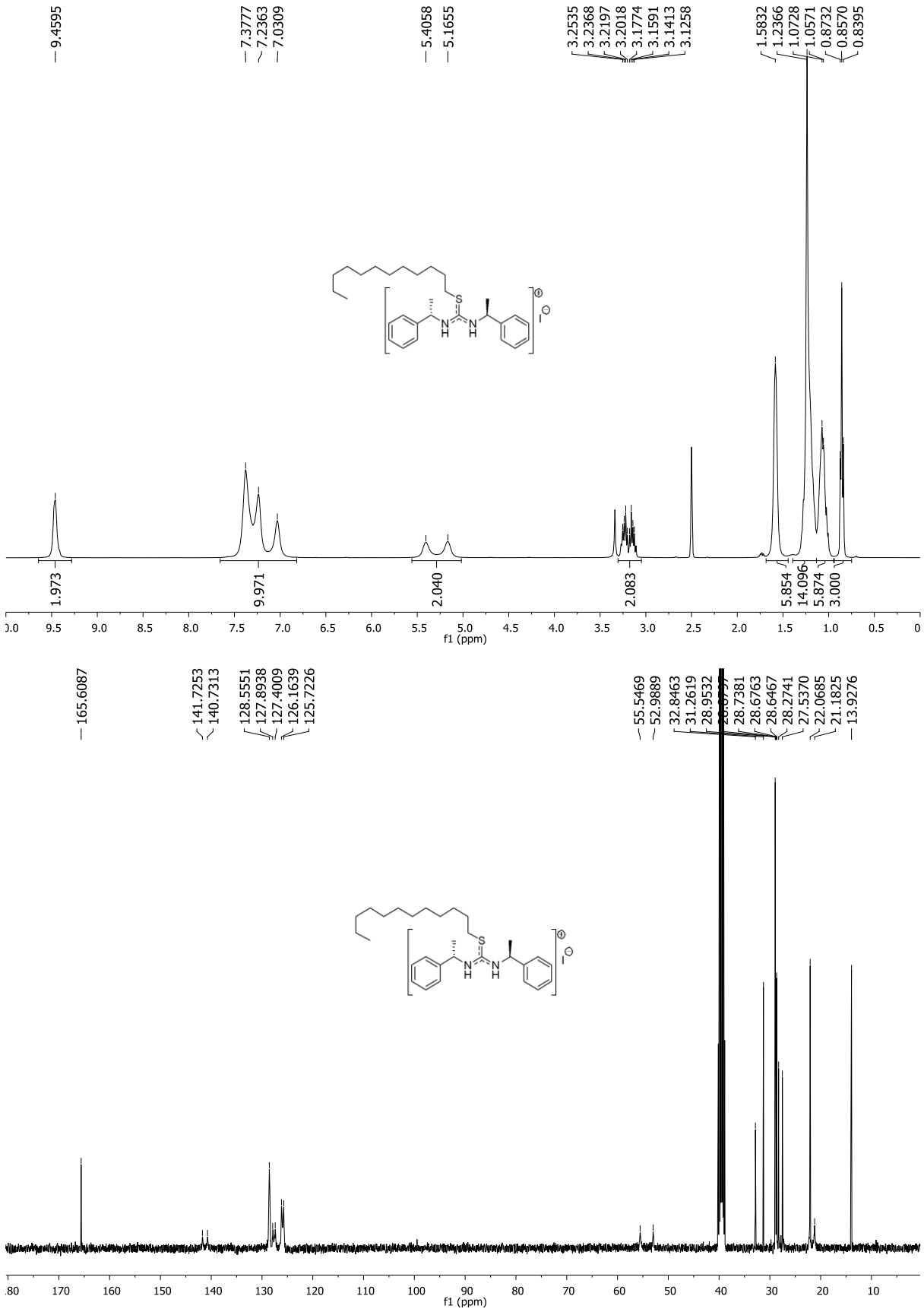


Figure S10. ^{1}H and ^{13}C NMR spectra for (*S*)-[C_{16}petu]I in DMSO-d_6 solution (400 and 101 MHz respectively).

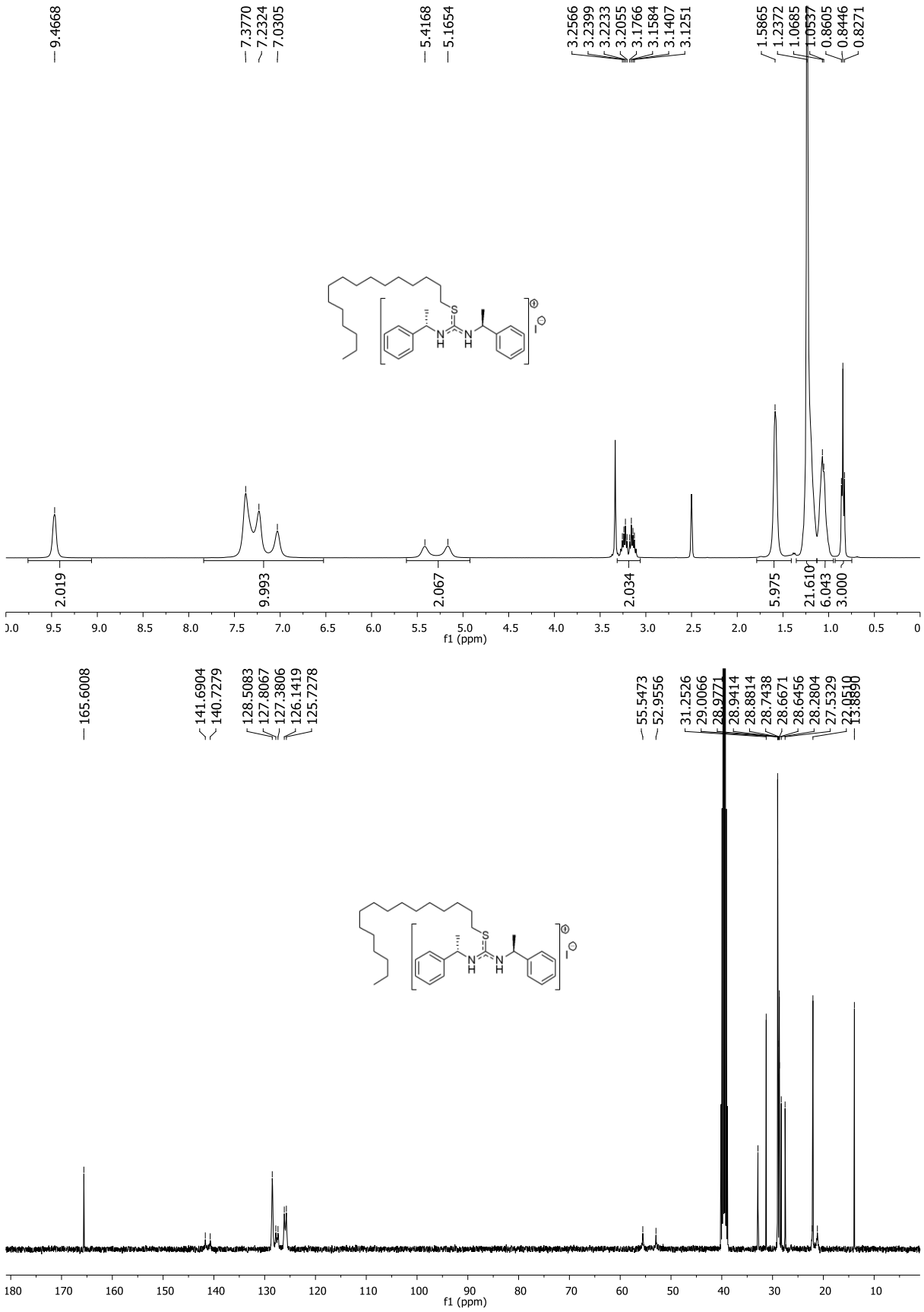
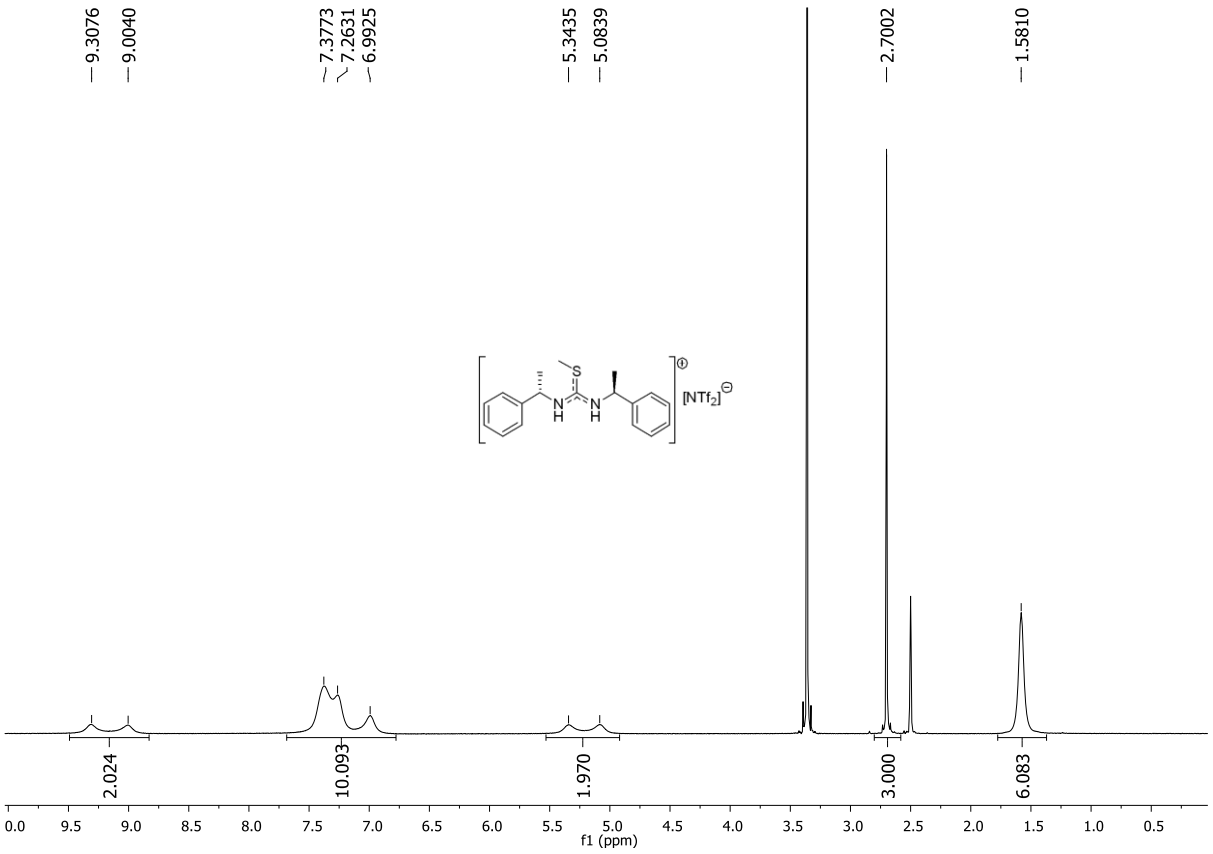


Figure S11. ^{1}H and ^{13}C NMR spectra for (*S*)-[C_1petu][NTf_2] in DMSO-d_6 solution (500 and 125 MHz respectively).



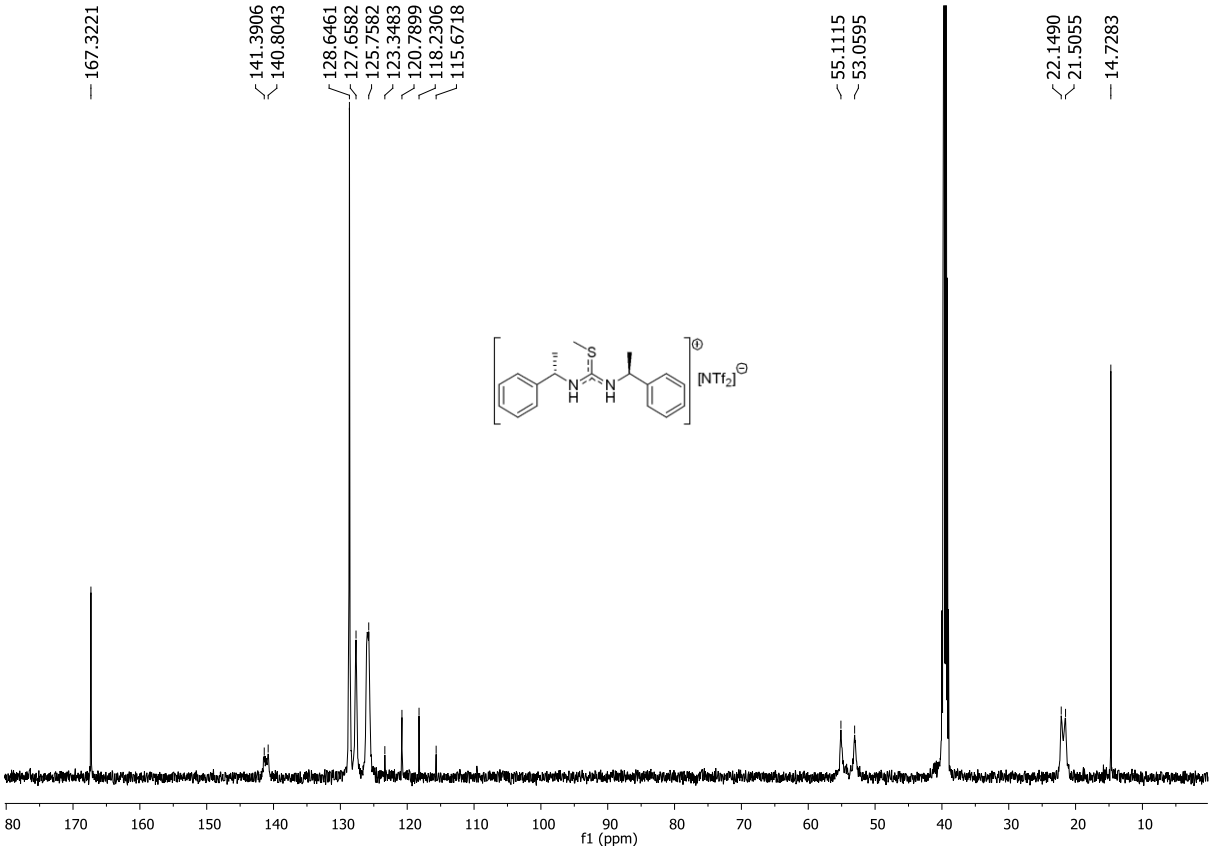


Figure S12. ^{1}H and ^{13}C NMR spectra for (*S*)-[C_2petu][NTf_2] in DMSO-d_6 solution (500 and 125 MHz respectively).

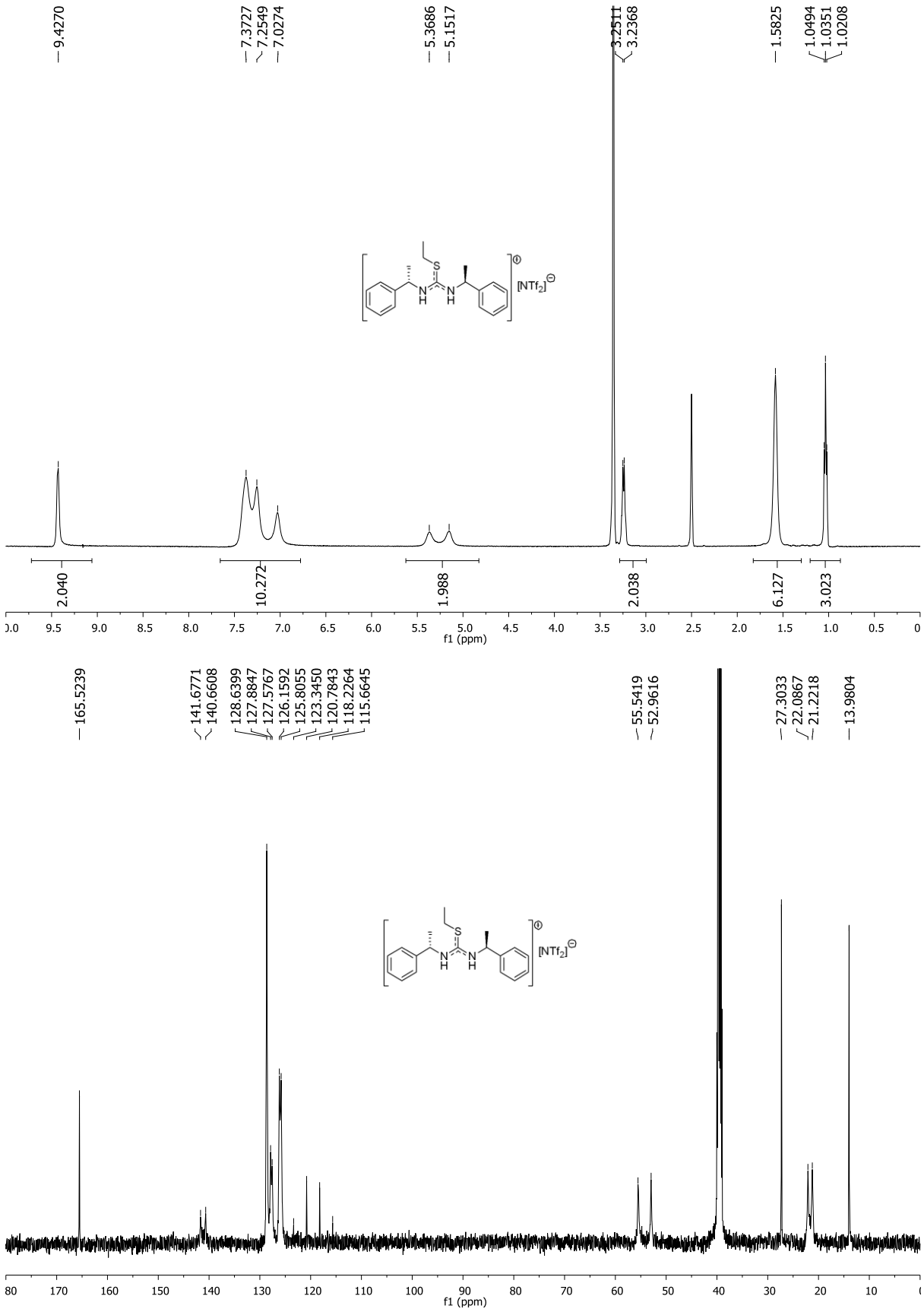


Figure S13. ^{1}H and ^{13}C NMR spectra for (*S*)-[C_3petu][NTf_2] in DMSO-d_6 solution (400 and 101 MHz respectively).

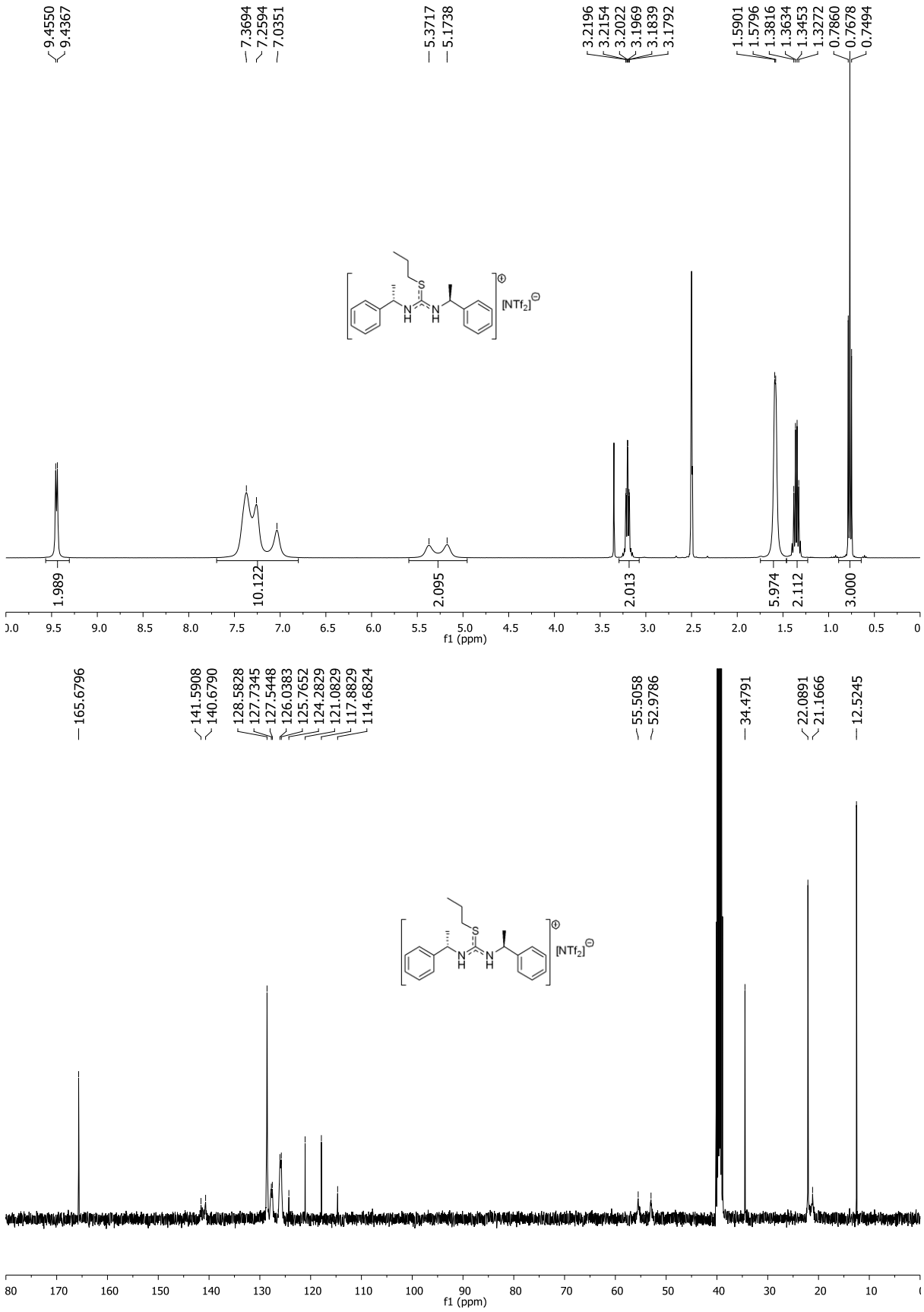


Figure S14. ^{1}H and ^{13}C NMR spectra for (*S*)-[C_4petu][PF_6] in DMSO-d_6 solution (400 and 101 MHz respectively).

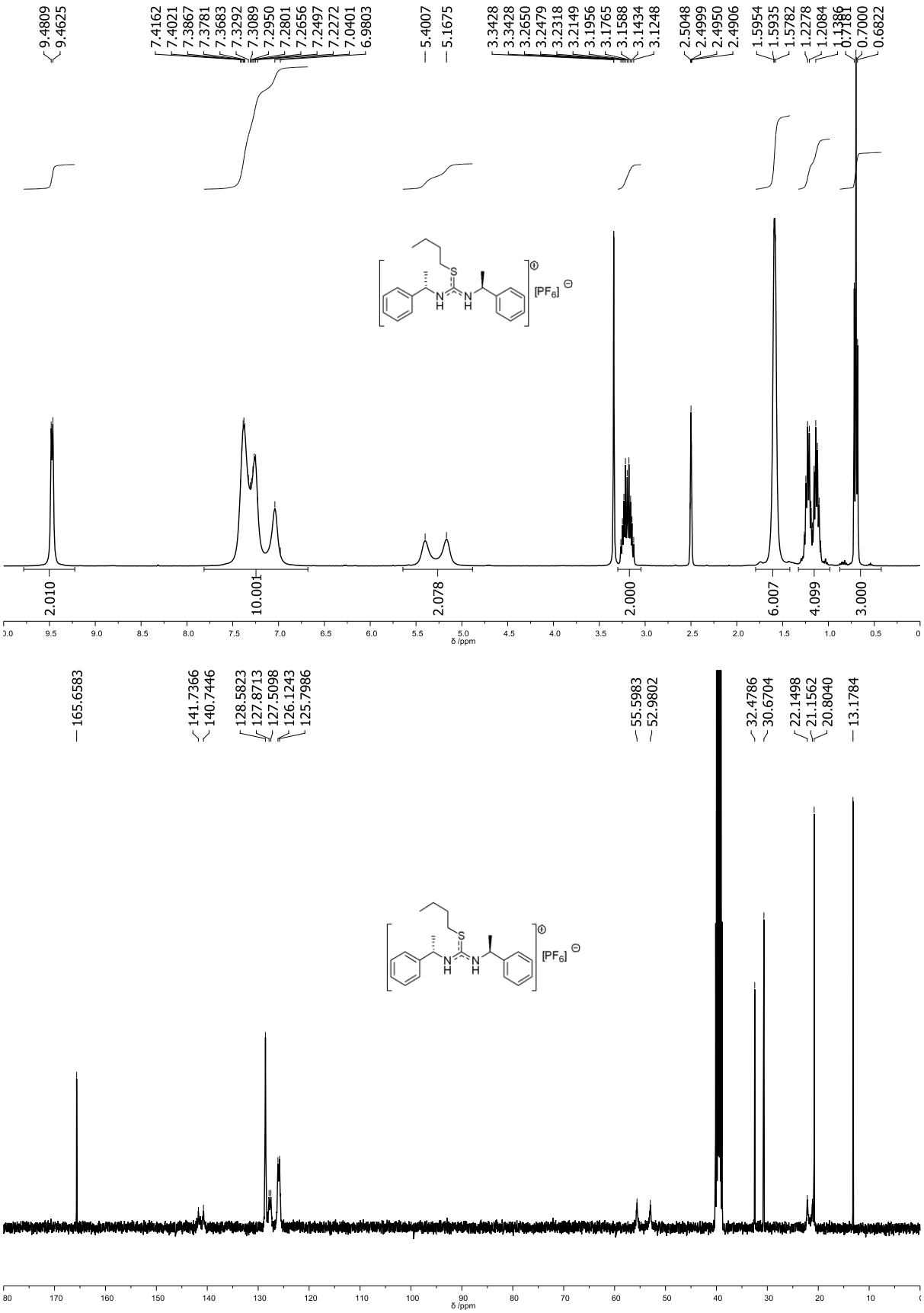


Figure S15. ^{1}H and ^{13}C NMR spectra for (*S*)-[C_6petu][NTf_2] in DMSO-d_6 solution (400 and 101 MHz respectively).

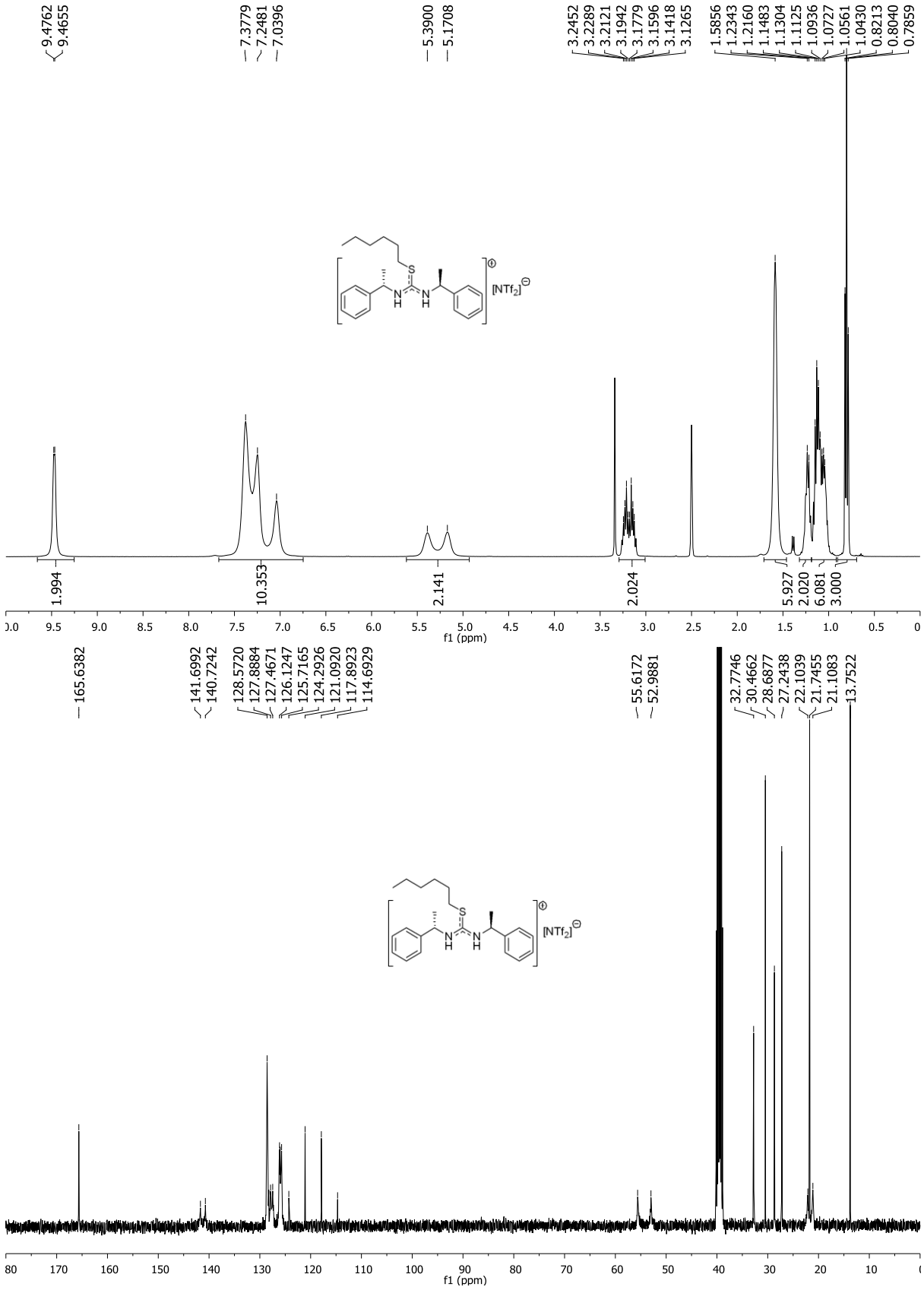
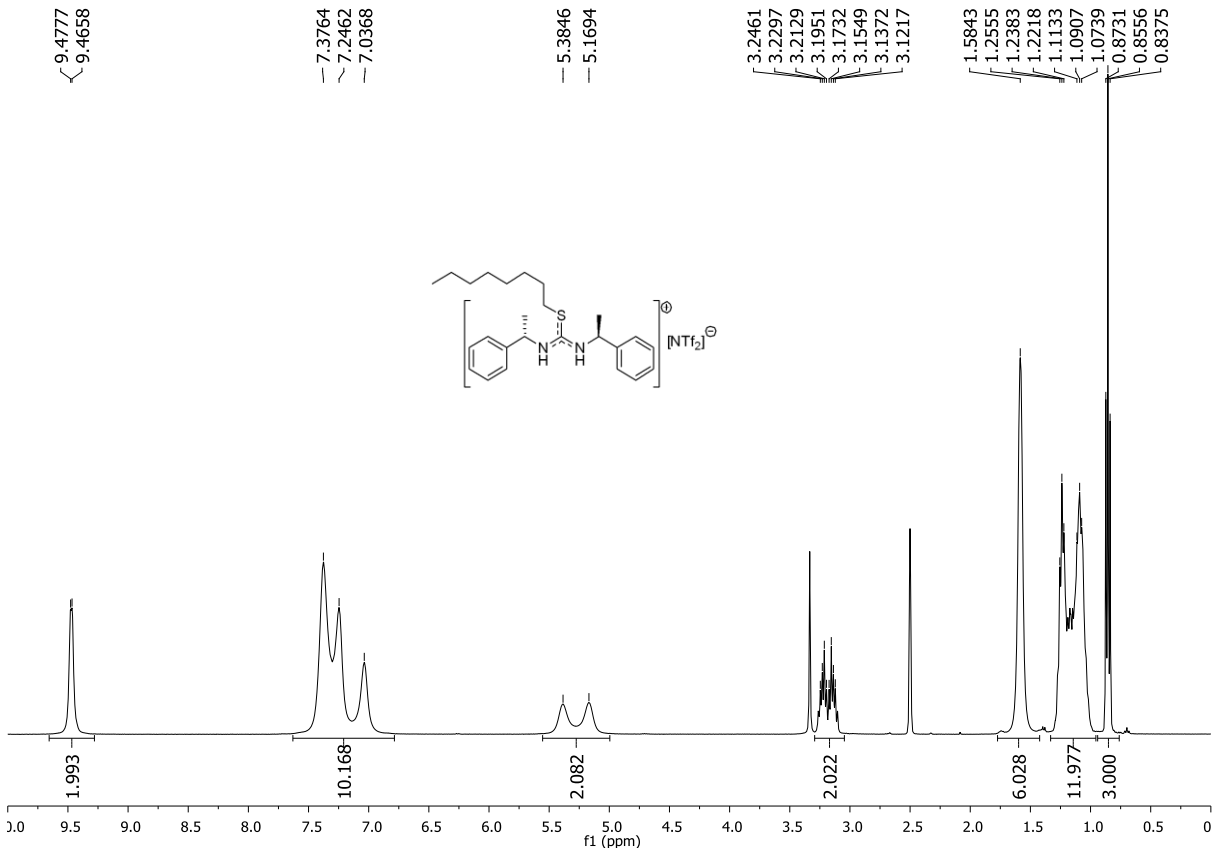


Figure S16. ^{1}H and ^{13}C NMR spectra for (*S*)-[C_8petu][NTf_2] in DMSO-d_6 solution (400 and 101 MHz respectively).



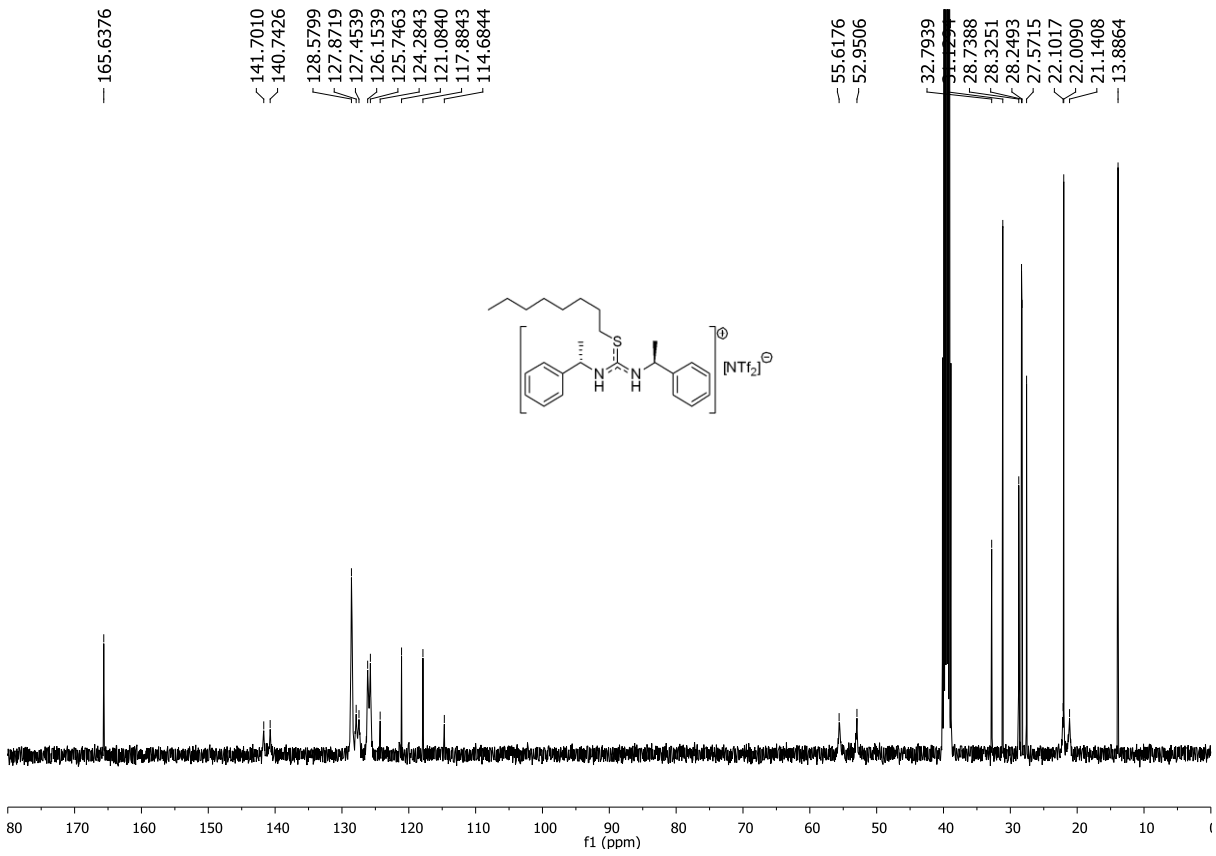


Figure S17. ^{1}H and ^{13}C NMR spectra for (*S*)-[C_{10}petu][NTf_2] in DMSO-d_6 solution (400 and 101 MHz respectively).

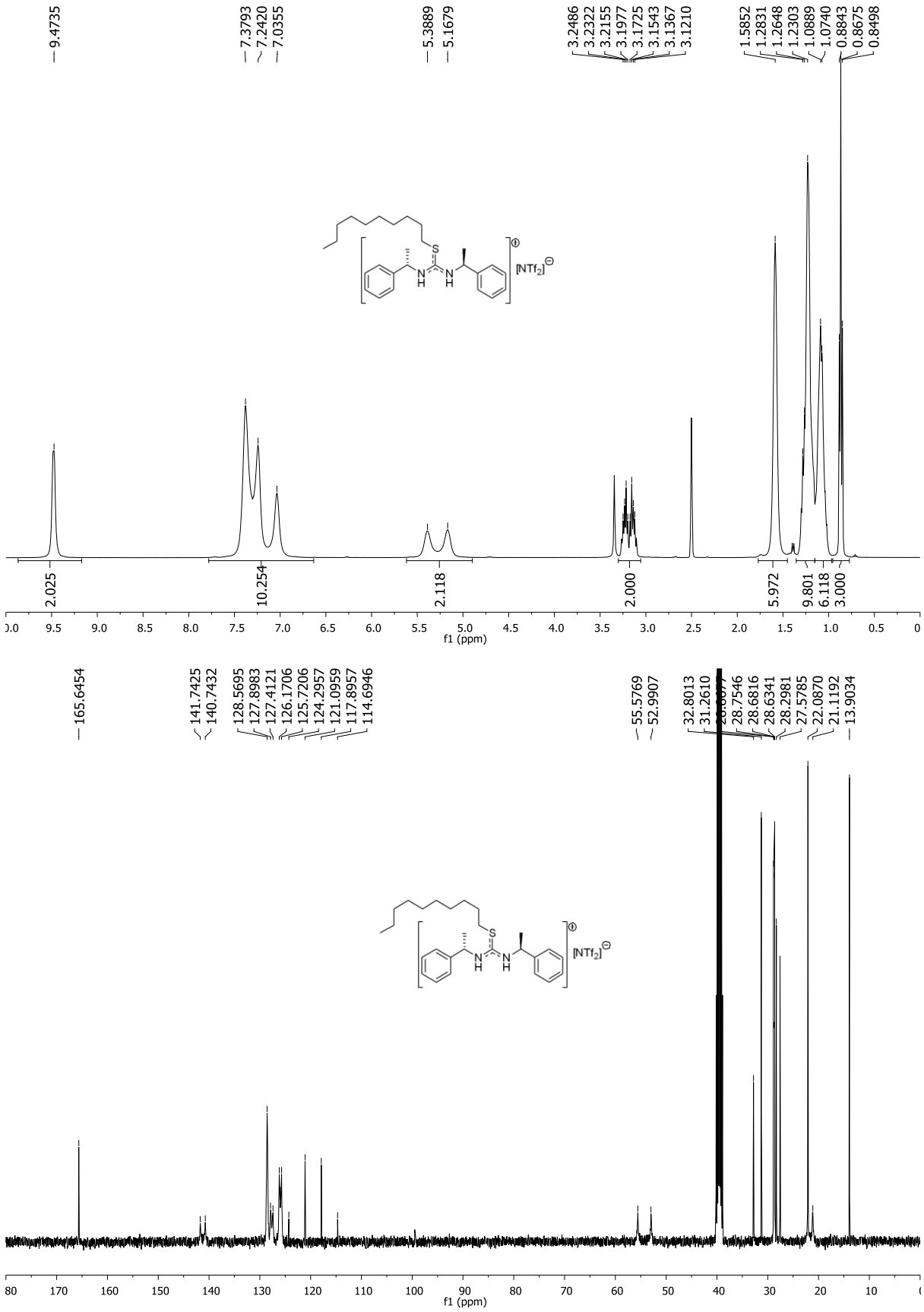


Figure S18. ^{1}H and ^{13}C NMR spectra for (*S*)-[C_{12}petu][NTf_2] in DMSO-d_6 solution (400 and 101 MHz respectively).

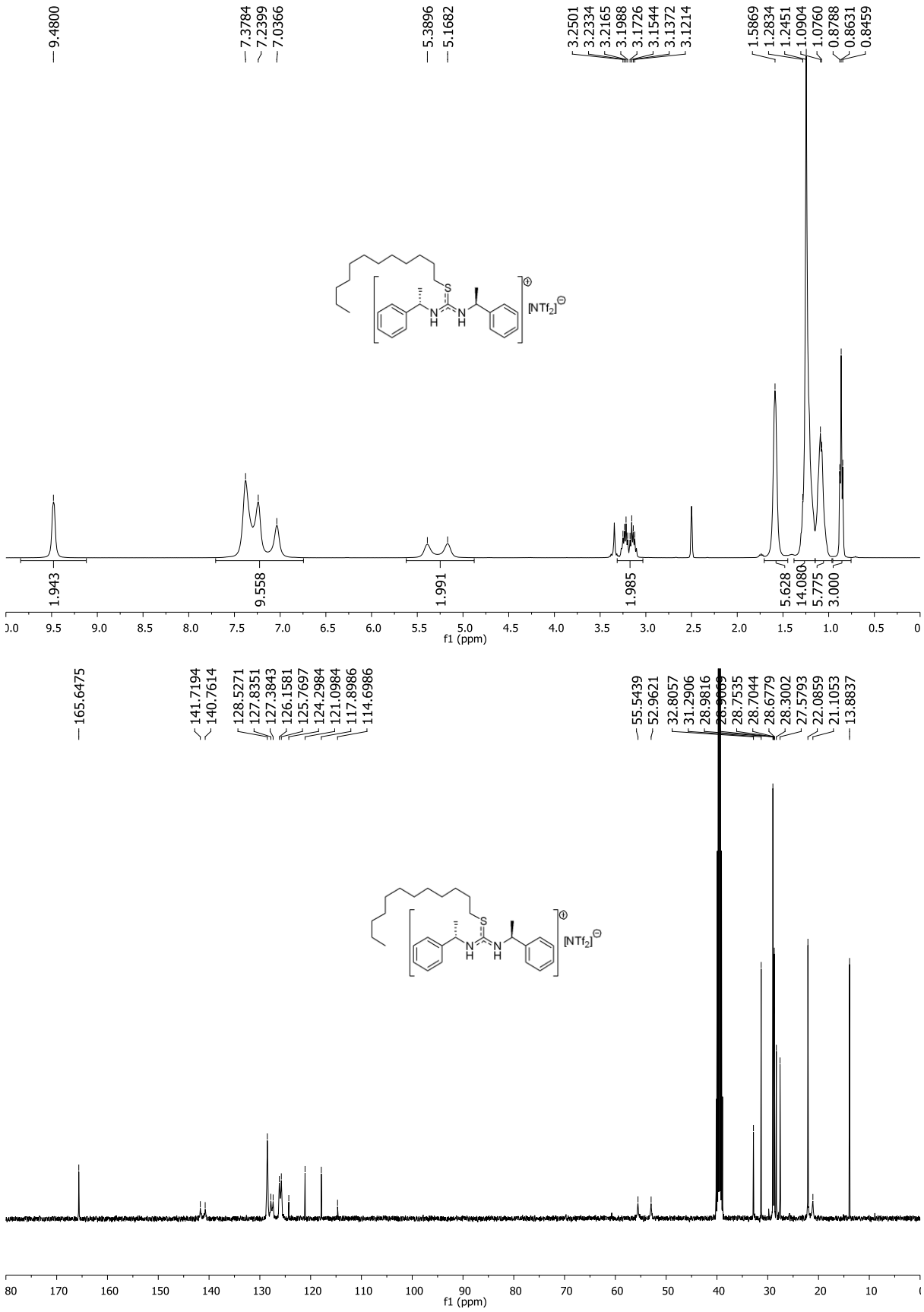


Figure S19. ^{1}H and ^{13}C NMR spectra for (*S*)-[C_{16}petu][NTf_2] in DMSO-d_6 solution (400 and 101 MHz respectively).

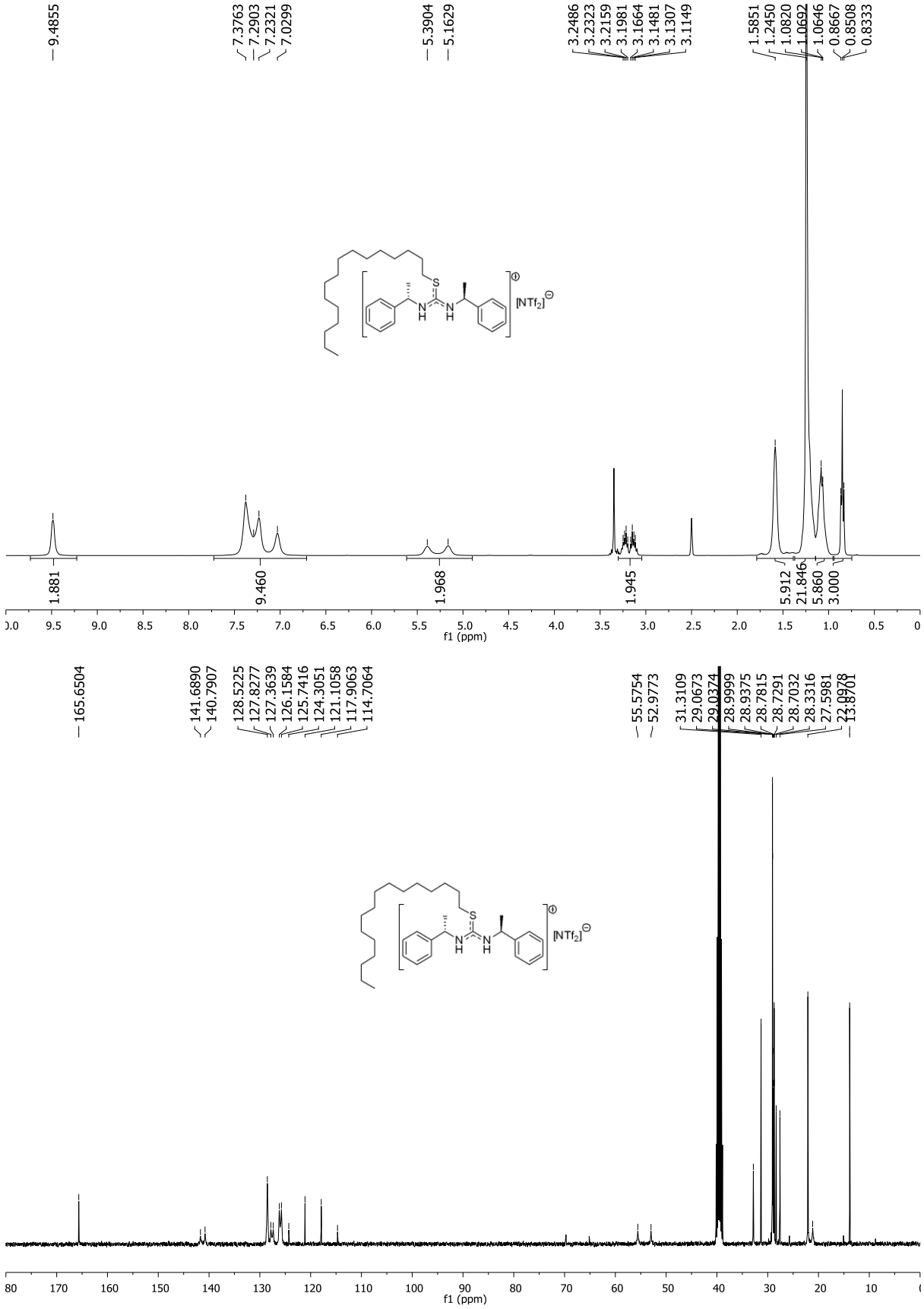
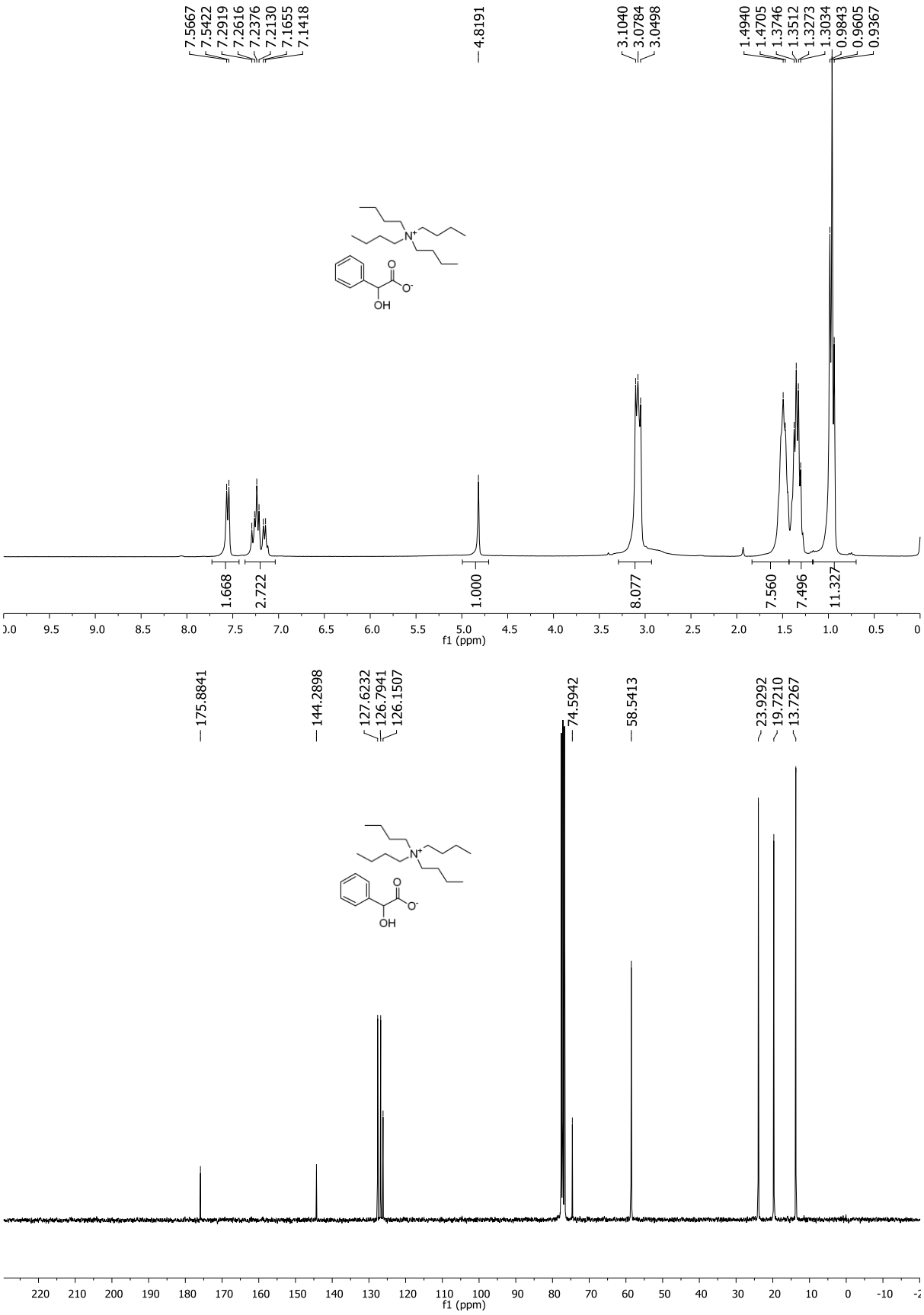


Figure S20. ^{1}H and ^{13}C NMR spectra for [N_{4444}][mand] in $CDCl_3$ solution (300 and 75 MHz respectively).



2. Comparison of ^{1}H NMR spectra of (*S*)-[C_4petu]Br in various deuteriated solvents.

Given that the solvent-solute interactions may play a crucial role during the rotameric process (as indicated by the peak shape in the NMR spectrum), here is a comparison of a few different deuteriated solvents used for analysis of (*S*)-[C_4petu]Br as an example (Figure S21). It is clear that non-hydrogen bonding chloroform gives the most broadened and imprecise spectrum. Better results are obtained with propanone, which can be an acceptor of the hydrogen bond to the thiouronium receptor centre, therefore the peak shape is slightly improved, because the rotamer is here better stabilised. Strong hydrogen-bonding solvents, such as dimethylformamide and dimethylsulfoxide, stabilise the cationic rotamer the most, what is indicated by the great spectral sharpness of peaks.

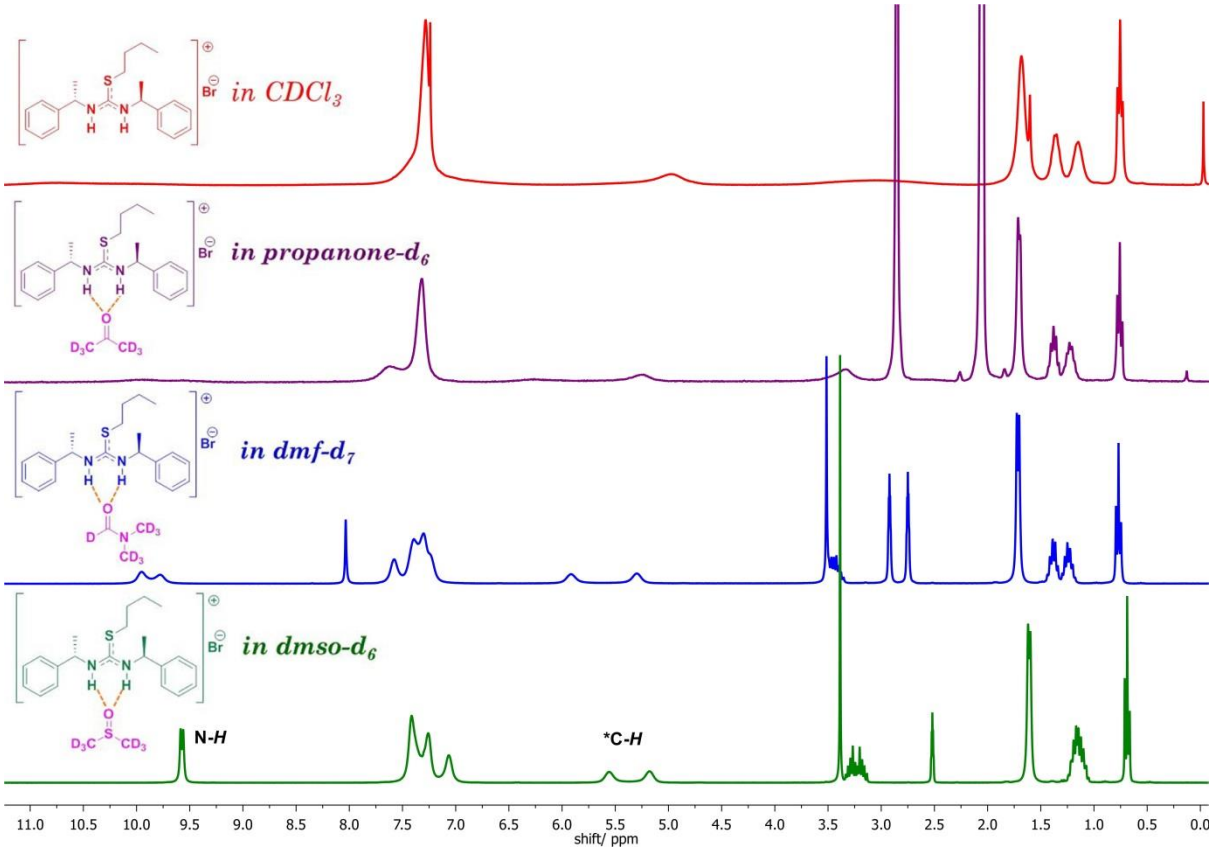


Figure S21. ^{1}H NMR spectra of (*S*)-[C_4petu]Br in various solvents (300 MHz).

3. Data from density and viscosity measurements (Table S1 and S2).

Table S1 Densities in g cm^{-3} of chiral ionic liquid series in a range of temperatures.

T /°C \ Chain	C_1	C_2	C_3	C_4	C_6	C_8	C_{10}	C_{12}	C_{16}
W /ppm	24.20	31.75	38.95	183.00	52.00	27.75	51.85	16.75	56.17
20	1.38859	1.35996	1.33948	1.32323	1.28659	1.25954	1.23348	1.20747	1.16711
30	1.37948	1.35095	1.33069	1.31444	1.27804	1.25115	1.22525	1.19951	1.15920
40	1.37044	1.34202	1.32193	1.30572	1.26947	1.24276	1.21701	1.19147	1.15126
50	1.36150	1.33317	1.31326	1.29708	1.26113	1.23454	1.20895	1.18358	1.14348
60	1.35268	1.32447	1.30469	1.28856	1.25280	1.22636	1.20090	1.17564	1.13572
70	1.34400	1.31578	1.29609	1.28006	1.24450	1.21820	1.19288	1.16771	1.12798
80	1.33531	1.30719	1.28759	1.27168	1.23627	1.21012	1.18494	1.15986	1.12031
90	1.32667	1.29867	1.27918	1.26335	1.22811	1.20248	1.17706	1.15209	1.11270

Table S2 Viscosities in Pa s of chiral ionic liquid series in a range of temperatures.

T /°C \ Chain	C_1	C_2	C_3	C_4	C_6	C_8	C_{10}	C_{12}	C_{16}
W /ppm	24.20	31.75	38.95	183.00	52.00	27.75	14.70	16.75	11.30
20	25.320000	8.552000	6.949000	4.704000	4.194000	3.659000	3.2280000	2.251000	1.8940000
25	15.990000	5.855000	4.834000	3.284000	3.099000	2.755000	2.3940000	1.746000	1.4690000
30	7.691000	3.405000	2.928000	1.991000	1.977000	1.817000	1.5900000	1.208000	1.0210000
35	3.794000	2.003000	1.783000	1.213000	1.264000	1.197000	1.0550000	0.831500	0.7090000
40	1.990000	1.222000	1.119000	0.763500	0.827800	0.805900	0.7128000	0.582400	0.4999000
45	1.115000	0.781100	0.730000	0.497500	0.559600	0.555600	0.4959000	0.417700	0.3616000
50	0.666300	0.517200	0.493800	0.336800	0.388100	0.395300	0.3538000	0.305000	0.2676000
55	0.421100	0.356100	0.344000	0.236400	0.277100	0.288200	0.2576000	0.226900	0.2018000
60	0.281400	0.253500	0.248100	0.170600	0.203100	0.214400	0.1926000	0.173000	0.1547000
65	0.194600	0.185500	0.183100	0.127400	0.152100	0.162800	0.1476000	0.134000	0.1203000
70	0.139000	0.139100	0.141700	0.097170	0.116500	0.125500	0.1152000	0.105400	0.0949000
75	0.102700	0.107300	0.107400	0.075780	0.091210	0.098750	0.0915600	0.083790	0.0754900
80	0.076750	0.082730	0.084280	0.059970	0.072770	0.078900	0.0734000	0.068030	0.0611900
85	0.058750	0.066750	0.067110	0.047950	0.058400	0.063700	0.0591800	0.055920	0.0505700
90	0.046180	0.053900	0.054330	0.038450	0.047050	0.052310	0.0483500	0.046780	0.0423000
95	0.037190	0.043860	0.044510	0.031080	0.038370	0.043460	0.0395400	0.039450	0.0360400
100	-	-		-	0.031860	-	3.2280000	-	0.0310900