Supplementary material for:

A one-pot synthesis of 2,2'-disubstituted diindolylmethanes (DIMs) *via* a sequential Sonogashira coupling and cycloisomerization/C3-functionalization of 2-iodolanilines

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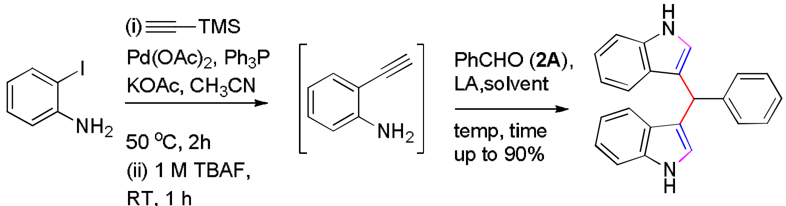
Table 1. Optimization studies[a]



1a

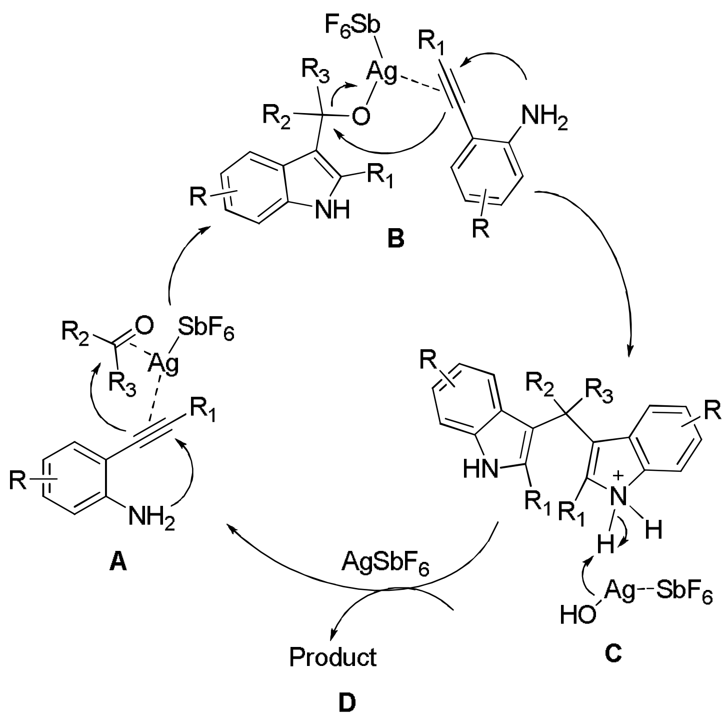
3aA

entry	LA	mol%	solvent	temperature (° C)	time	yield (%)[b]
1	$Zn(OTf)_2$	10	CH_3CN	25	12 h	NR[c]
2	$Cu(OTf)_2$	10	CH_3CN	25	12 h	NR[c]
3	AgOTf	10	CH_3CN	25	12 h	NR[c]
4	AgOAc	10	CH_3CN	25	12 h	NR[c]
5	AgOTf	10	CH_3CN	50	12 h	NR[c]
6	AgOTf	10	CH_2Cl_2	25	8 h	35[d]
7	AgOAc	10	CH_2Cl_2	25	12 h	NR[c]
8	$AgClO_4$	10	CH_2Cl_2	25	12 h	20[d]
9	$AgSbF_6$	10	CH_2Cl_2	25	8 h	40[e]
10	$AgBF_4$	10	CH_2Cl_2	25	8 h	25[d]
11	$AgPF_6$	10	CH_2Cl_2	25	8 h	20[d]
12	$AgNO_3$	10	CH_2Cl_2	25	8 h	NR[c]
13	$AgSbF_6$	10	DCE	25	8 h	65[e]
14	$AgSbF_6$	10	THF	25	8 h	20[d]
15	$AgSbF_6$	10	Et_2O	25	8 h	NR[c]
16	$AgSbF_6$	10	EtOH	25	8 h	NR[c]
17	$AgSbF_6$	10	dioxane	25	8 h	NR[c]
18	$AgSbF_6$	10	benzene	25	8 h	NR[c]
19	$AgSbF_6$	10	toluene	25	8 h	40[d]
20	$AgSbF_6$	10	DME	25	8 h	NR[c]
21	$AgSbF_6$	10	DMF	25	8 h	NR[c]
22	AgOTf	10	DCE	25	8 h	60[e]
23	$AgSbF_6$	10	DCE	40	3 h	90
24	$AgSbF_6$	10	DCE	50	2 h	90
25	$AgSbF_6$	10	DCE	60	2 h	90
26	AgOTf	10	DCE	40	3 h	87
27	AgOTf	10	DCE	50	2 h	85
28	AgOTf	10	DCE	60	2 h	85
29	**$AgSbF_6$**	**5**	DCE	**50**	**2.5 h**	**90**
30	**AgOTf**	**5**	DCE	**50**	**2.5 h**	**88**
31	$AgSbF_6$	2.5	DCE	50	6 h	50[f]
32	AgOTf	2.5	DCE	50	6 h	51[f]

[a]reactions were carried out using 0.4 mmol of each 2-iodo aniline and trimethyl silyl acetylene, 0.2 mmol of benzaldehyde in the presence of 10 mol% of LA. [b]Yield of isolated product after column purification. [c]No reaction. Both **1a** and **2A** were recovered. [d]Unreacted **1a** and **2A** were recovered. [e]Unreacted **2A** and indole of **1a** were recovered. [f]Unreacted **1a**, indole of **1a** and unreacted **2A** were recovered.

Plausible mechanism for the formation of DIMs

On the basis of the above mentioned results of the domino process, we could propose a plausible mechanism where Ag(I) could initiate the coordination with both the alkyne unit[1] as well as carbonyl moiety (Scheme 2), and this could help sequential cycloisomerzation of unprotected *o*-alkynyl anilines followed by Friedel–Craft reaction of C3 of the first indole moiety to the carbonyl carbon of aryl and heteroaryl aldehyde or aliphatic ketones to produce an intermediate **B**. The Ag(I) of this intermediate may then activate the second *o*- alkynylaniline which would lead to second indole annulations, forming the intermediate **C**. This bond forming-bond breaking cascade would allow the formation of our desired products DIMs. Water is removed and the Ag(I) catalyst is regenerated as shown below.



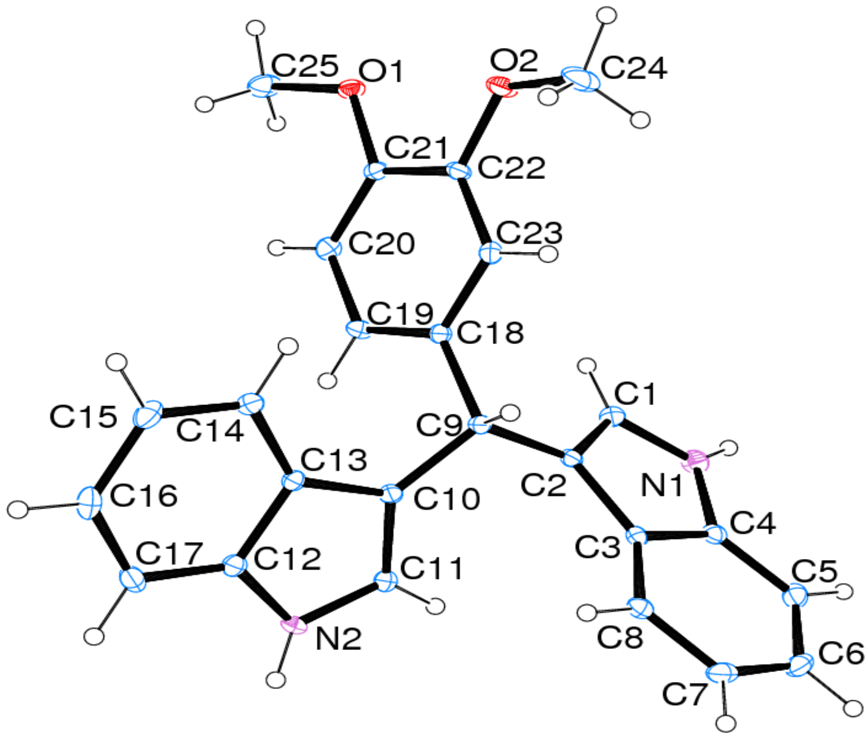
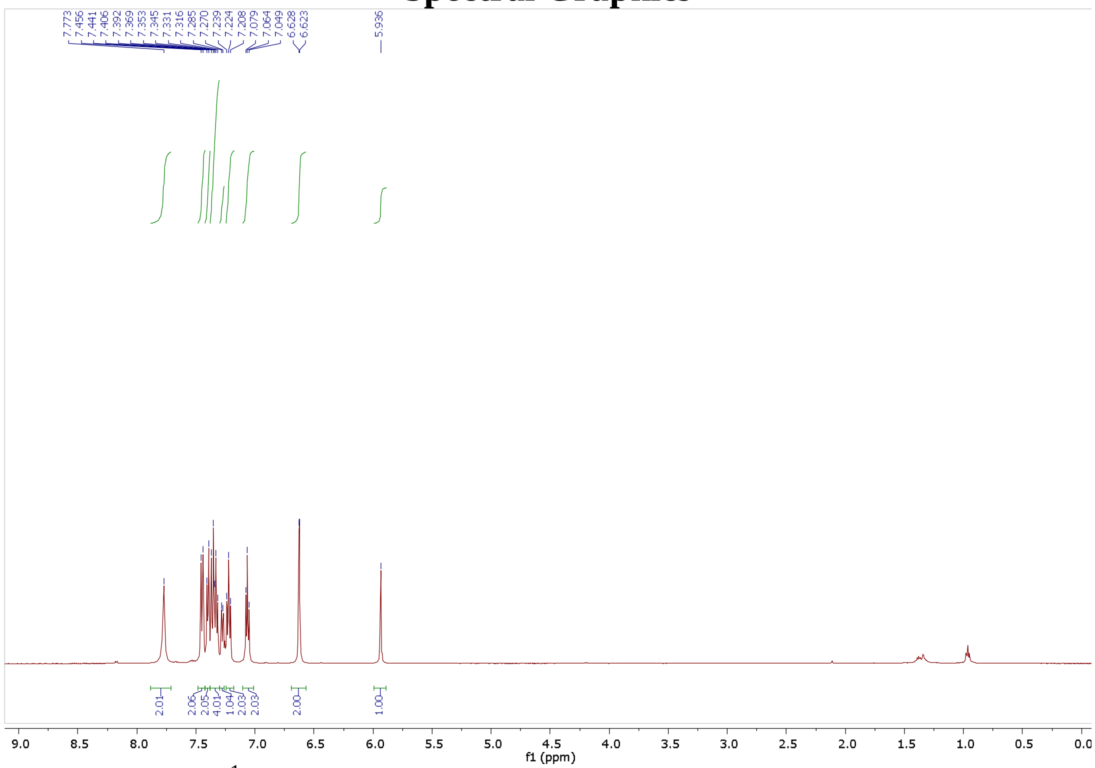


Figure 1: X-ray crystal structure of compound **3aM** (CCDC-1528295)

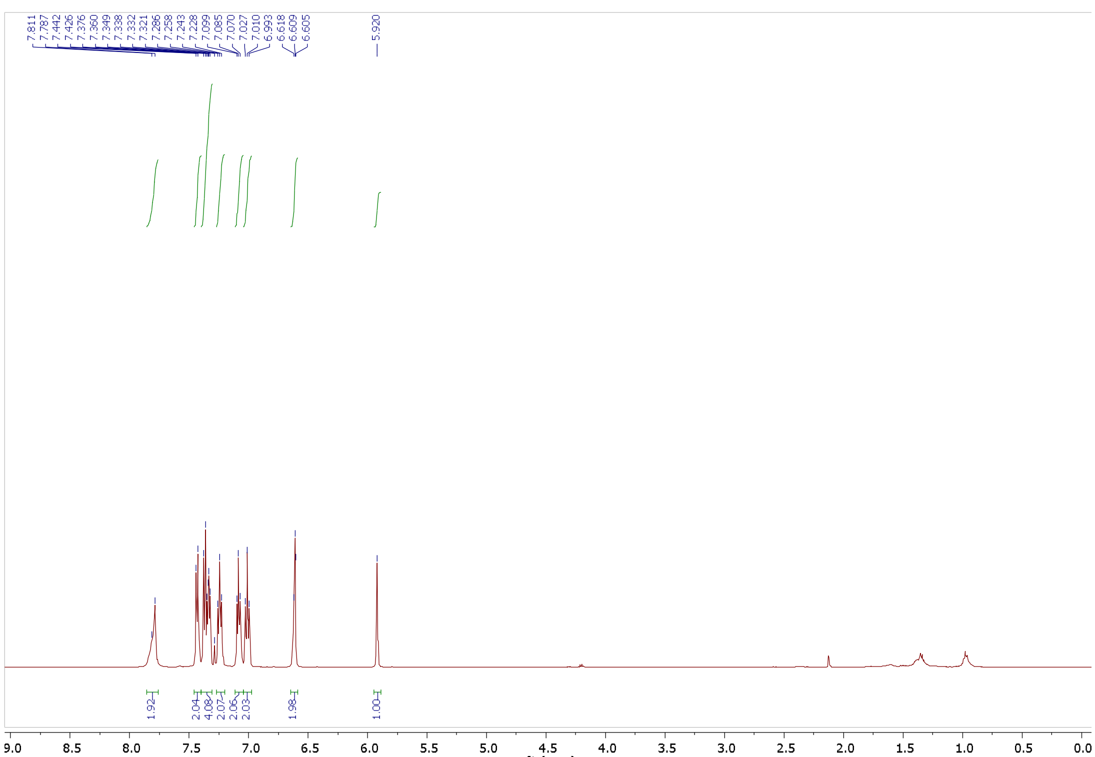
References:

(1) (a) C. H. Oh, S. Karmakar, H. S. Park, Y. C. Ahn and J. W. Kim, *J. Am. Chem. Soc*. 2010, **132**, 1792; (b) M. Bera and S. Roy, *J. Org. Chem*. 2009, **74**, 8814; (c) J. Zhao, C. O. Hughes and F. D. Toste, *J. Am. Chem. Soc*. 2006, **128**, 7436; (d) J. T. Binder, and S. F. Kirsch, *Org. Lett*. 2006, **8**, 2151; (e) K. K. Klausmeyer, R. P. Feazell and J. H. Reibenspies, *Inorg. Chem*. 2004, **43**, 1130.

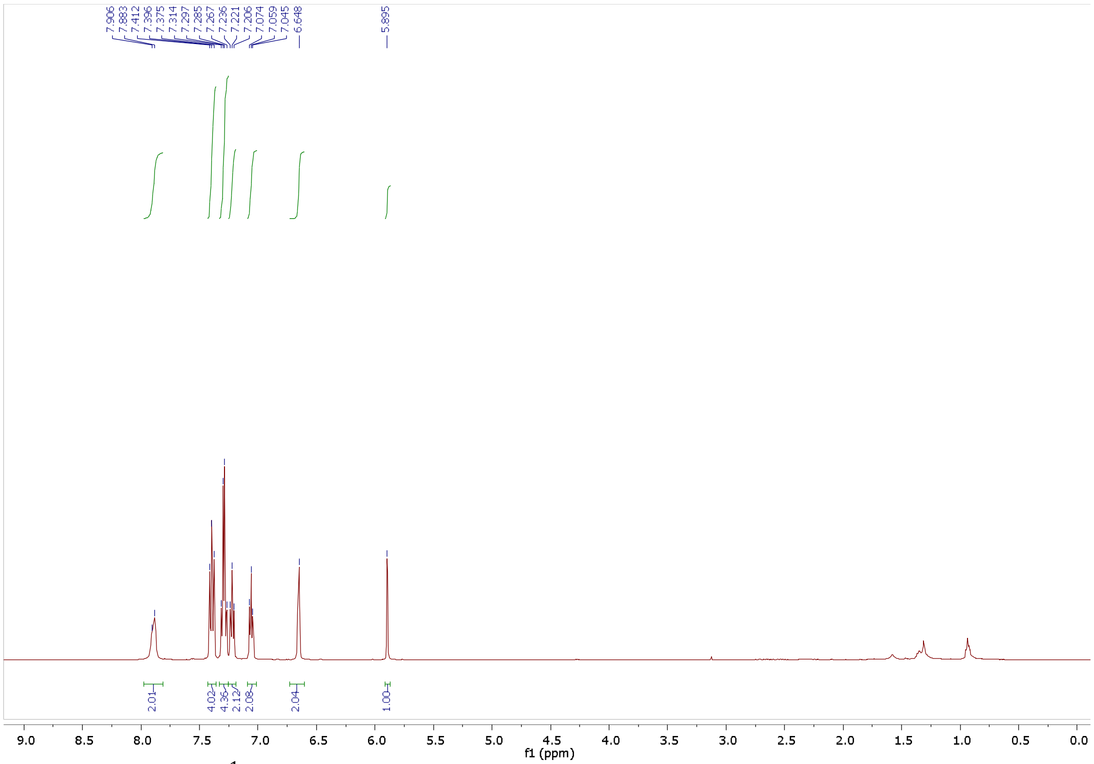
Spectral Graphics



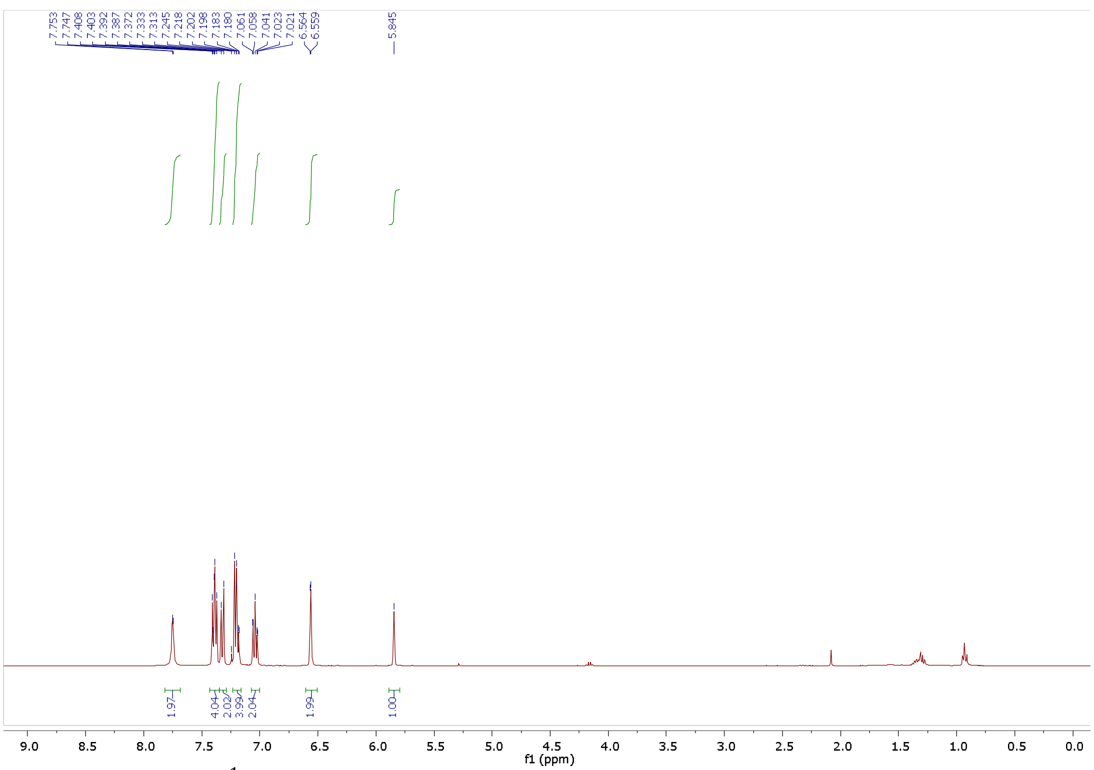
^{1}H NMR (500 MHz, $CDCl_3$) of Compound (**3aA**)



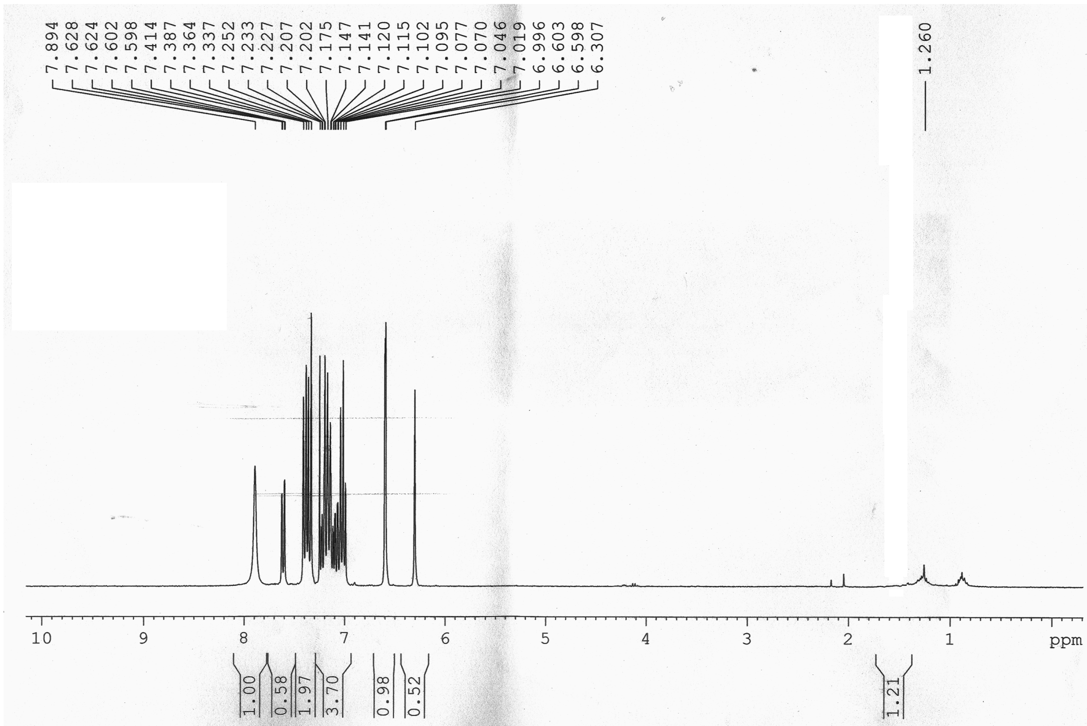
^{1}H NMR (500 MHz, $CDCl_3$) of Compound (**3aB**)



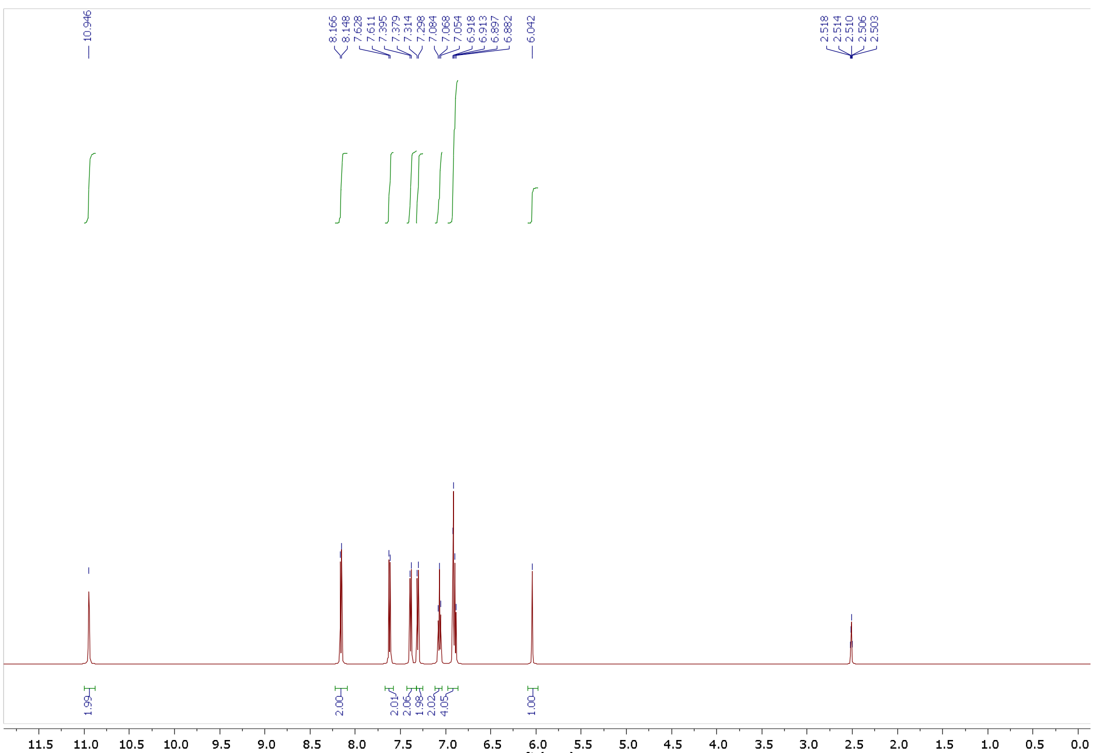
^{1}H NMR (500 MHz, $CDCl_3$) of Compound (**3aC**)



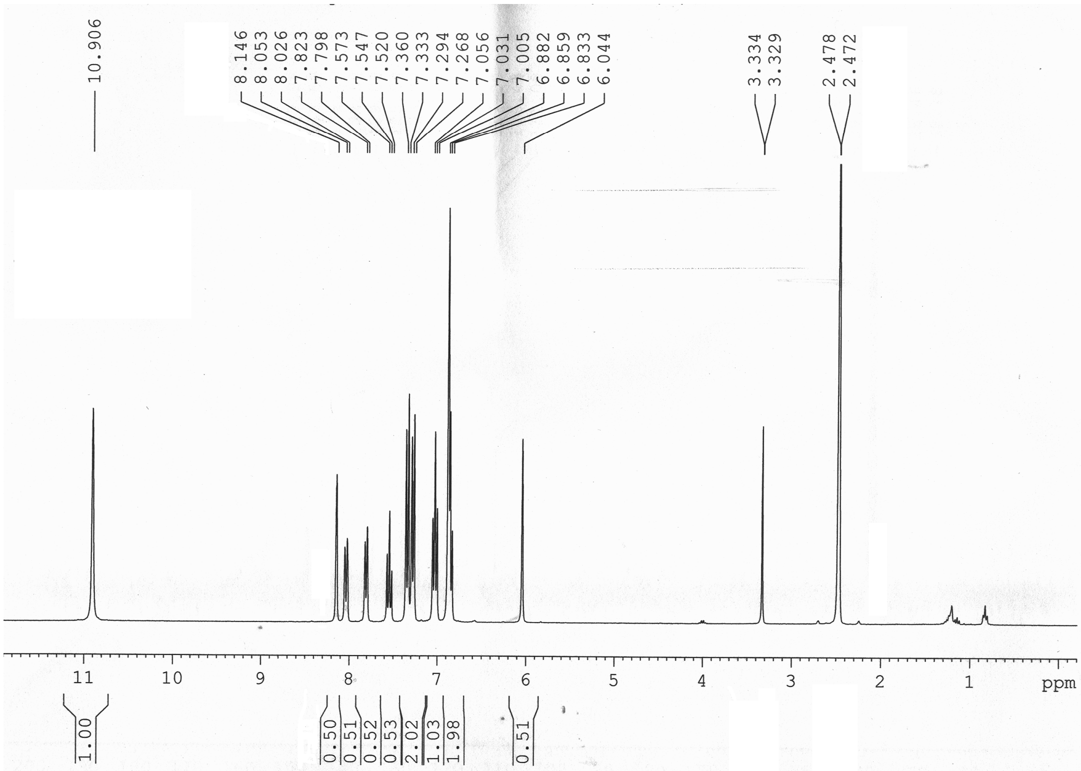
^{1}H NMR (400 MHz, $CDCl_3$) of Compound (**3aD**)



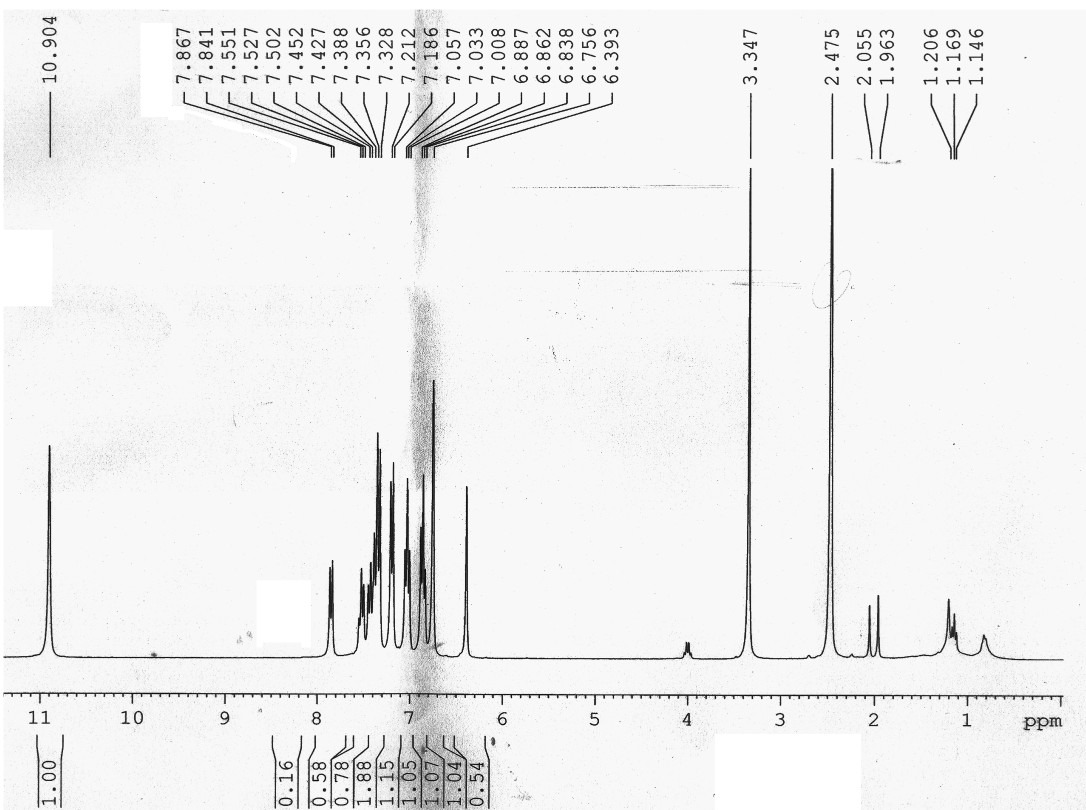
^{1}H NMR (300 MHz, $CDCl_3$) of Compound (**3aE**)



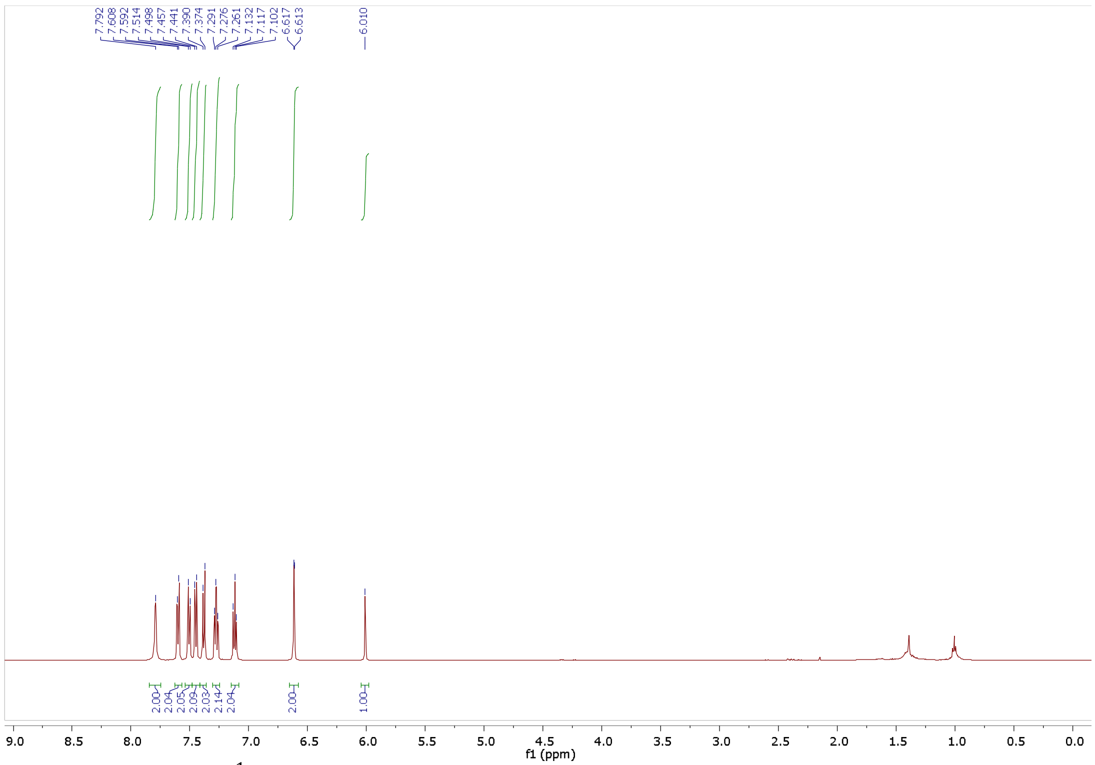
^{1}H NMR (500 MHz, DMSO-d_6) of Compound (**3aF**)



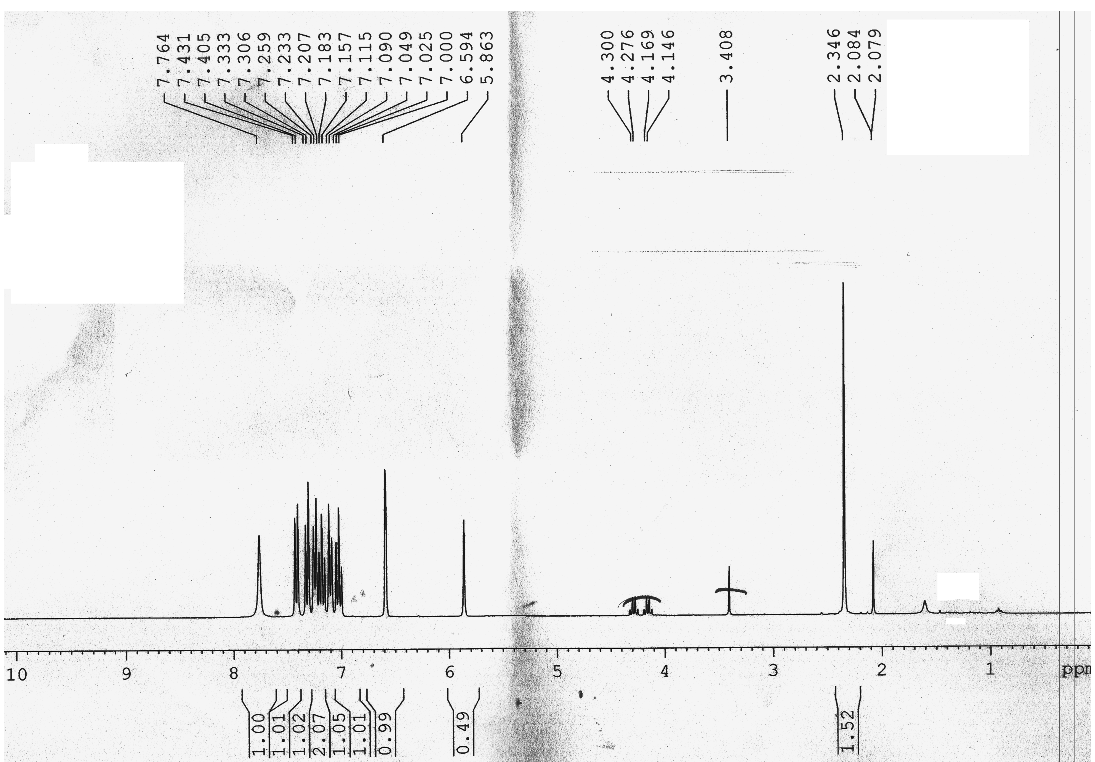
^{1}H NMR (300 MHz, DMSO-d_6) of Compound (**3aG**)



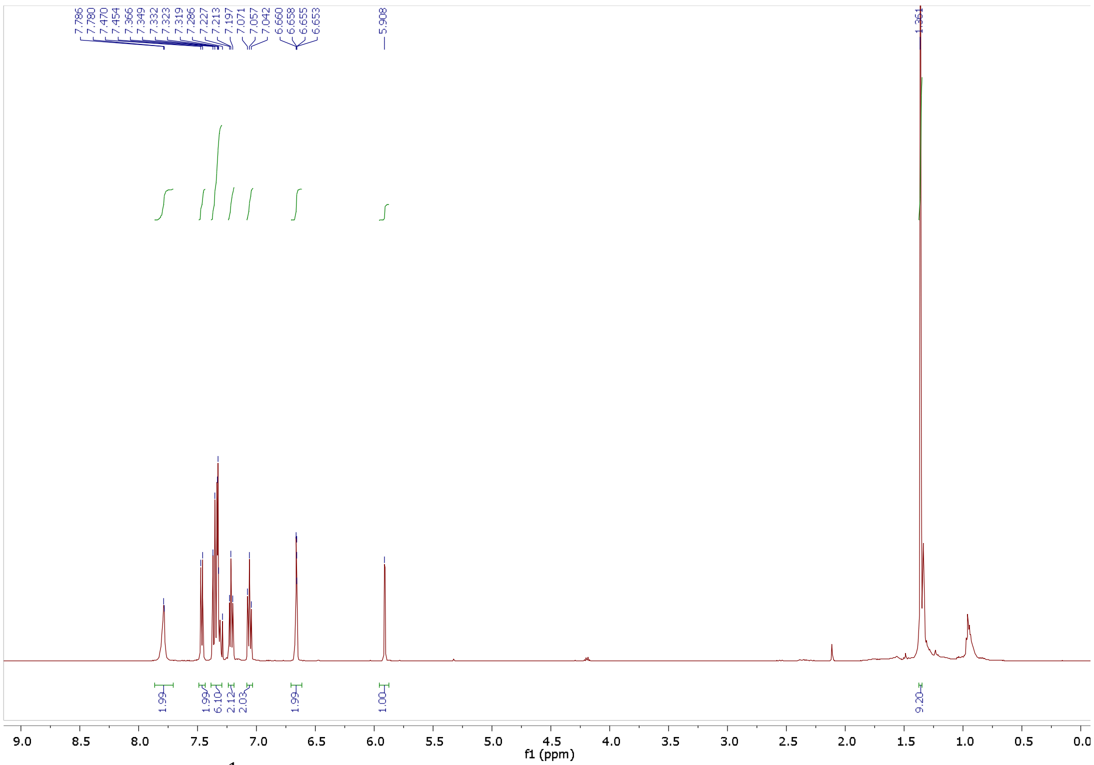
^{1}H NMR (300 MHz, DMSO-d_6) of Compound (**3aH**)



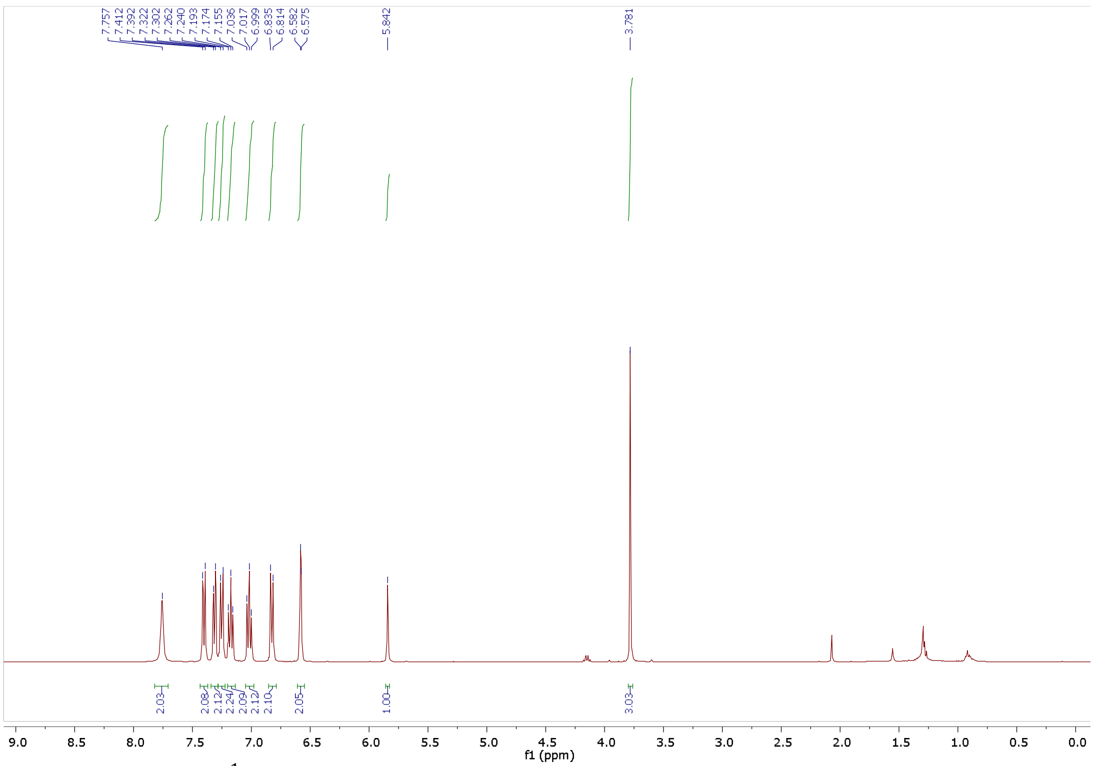
^{1}H NMR (500 MHz, $CDCl_3$) of Compound (**3aI**)



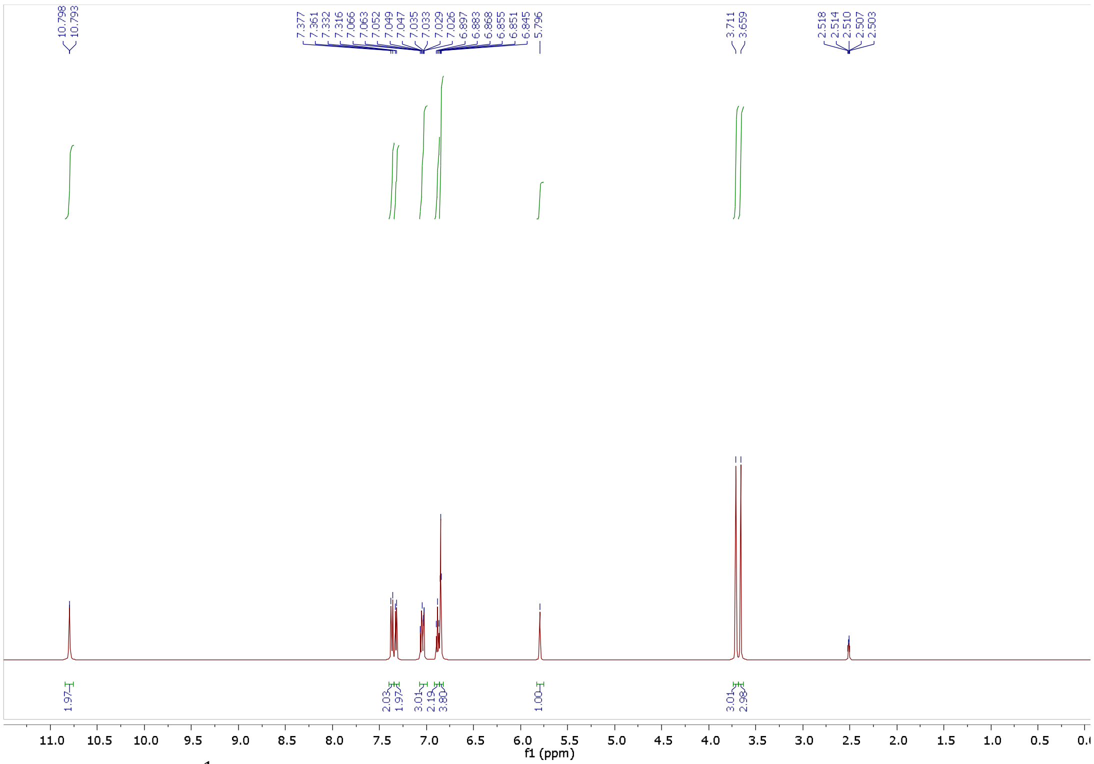
^{1}H NMR (500 MHz, $CDCl_3$) of Compound (**3aJ**)



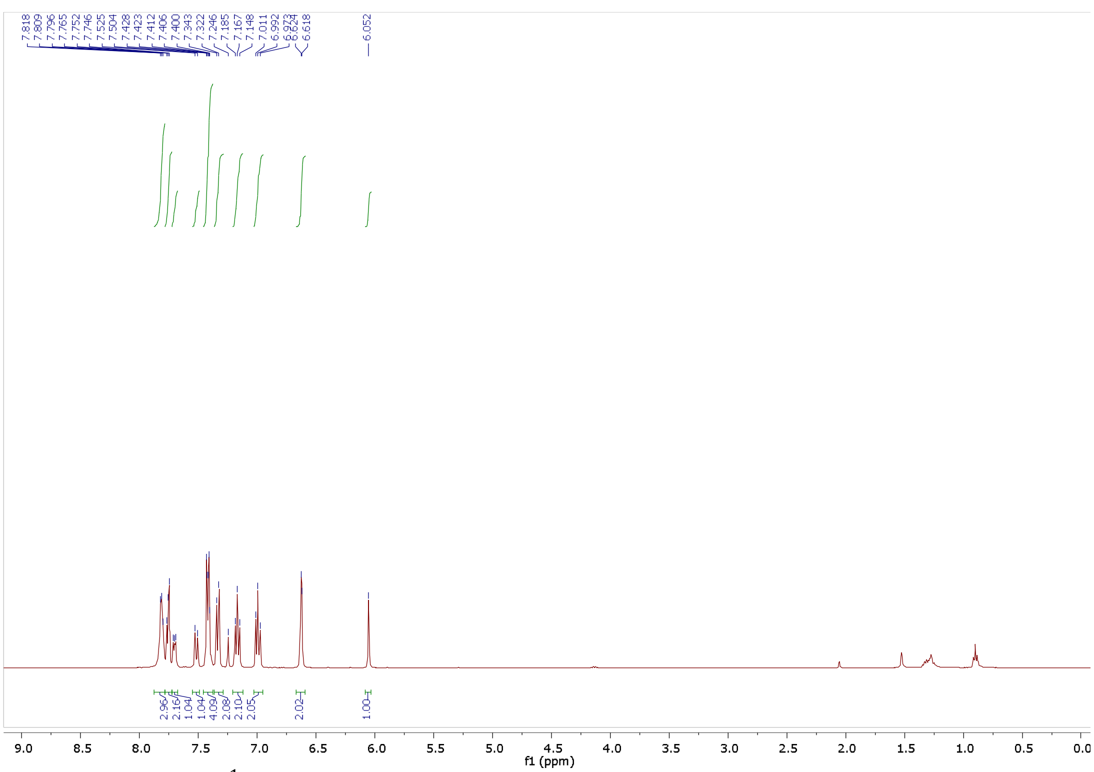
^{1}H NMR (500 MHz, $CDCl_3$) of Compound (**3aK**)



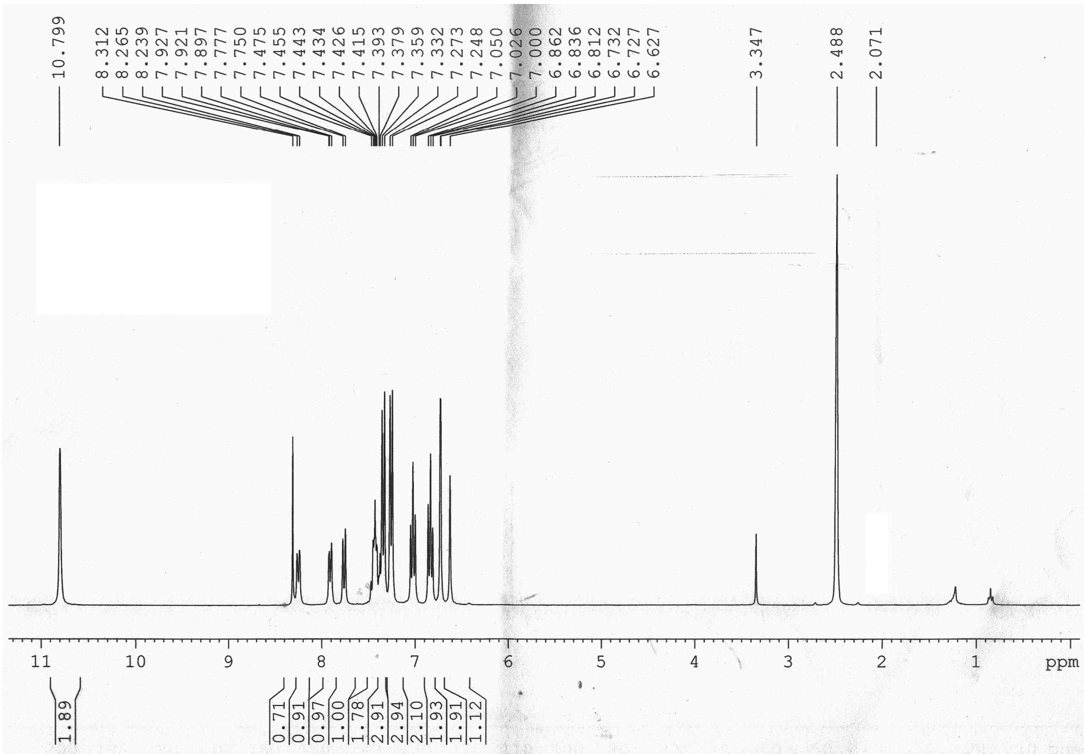
^{1}H NMR (400 MHz, $CDCl_3$) of Compound (**3aL**)



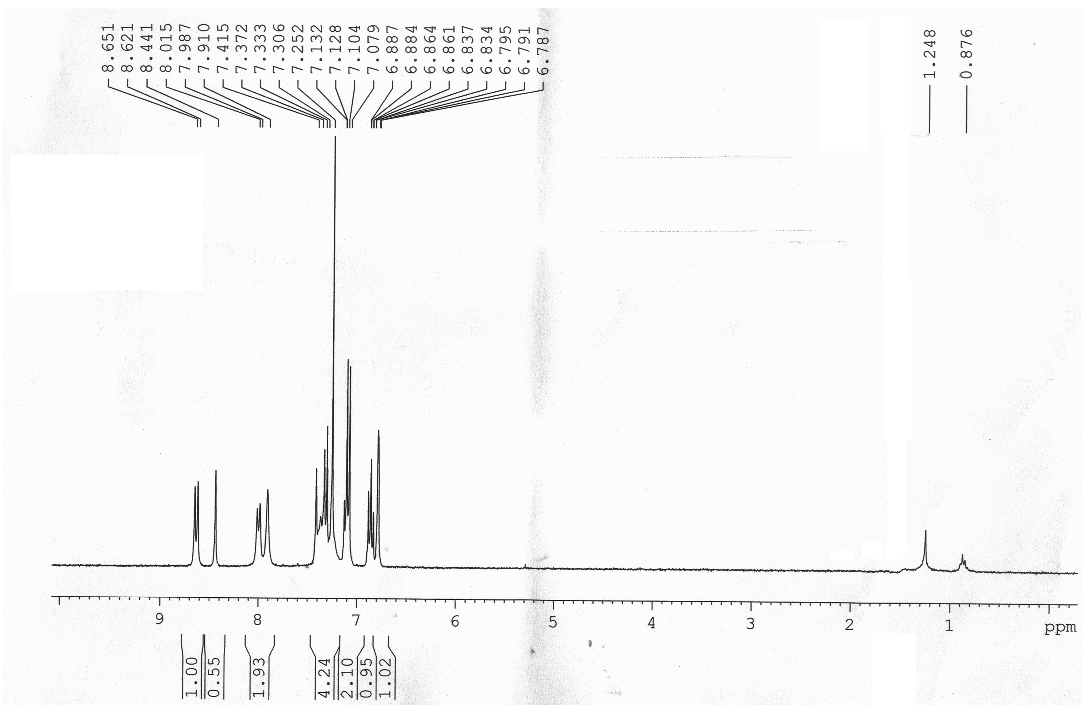
^{1}H NMR (500 MHz, DMSO-d_6) of Compound (**3aM**)



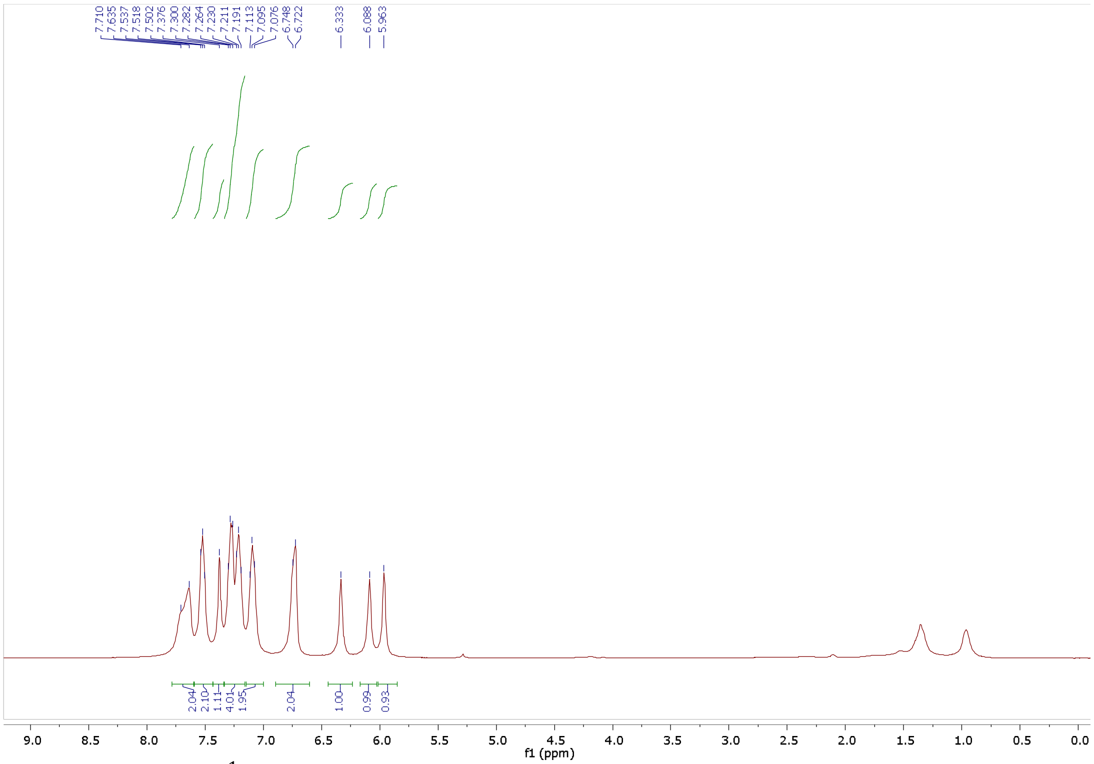
^{1}H NMR (400 MHz, $CDCl_3$) of Compound (**3aN**)



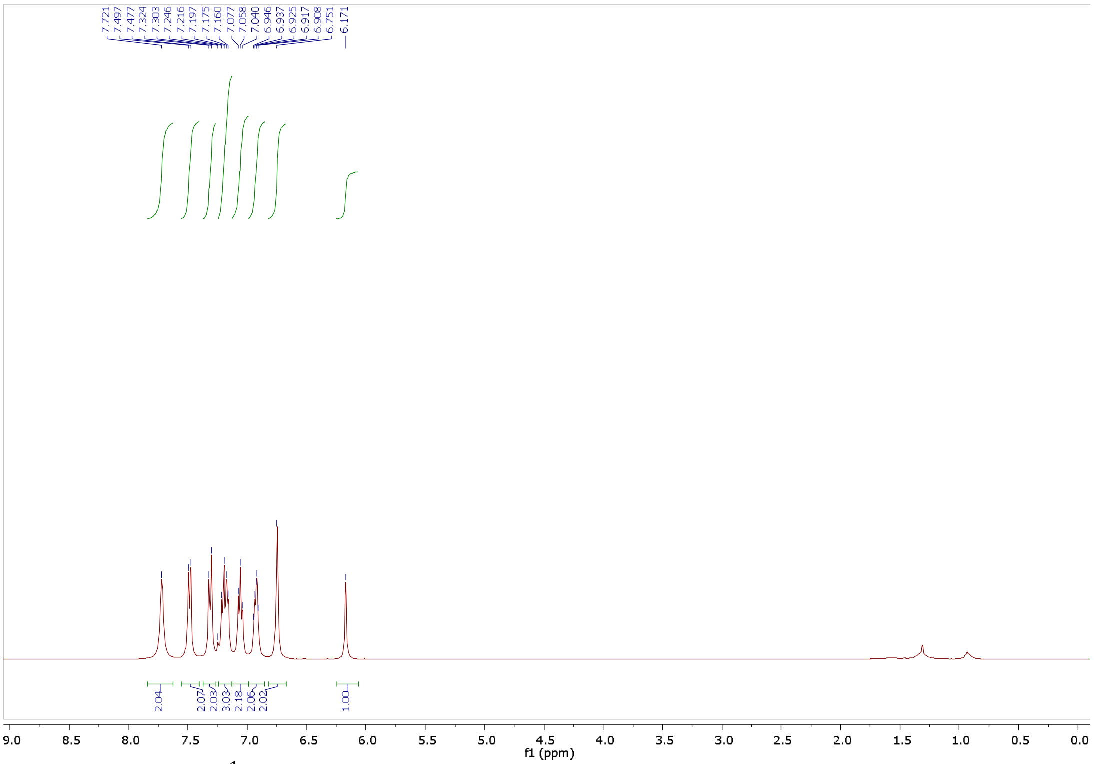
^{1}H NMR (300 MHz, DMSO-d_6) of Compound (**3aO**)



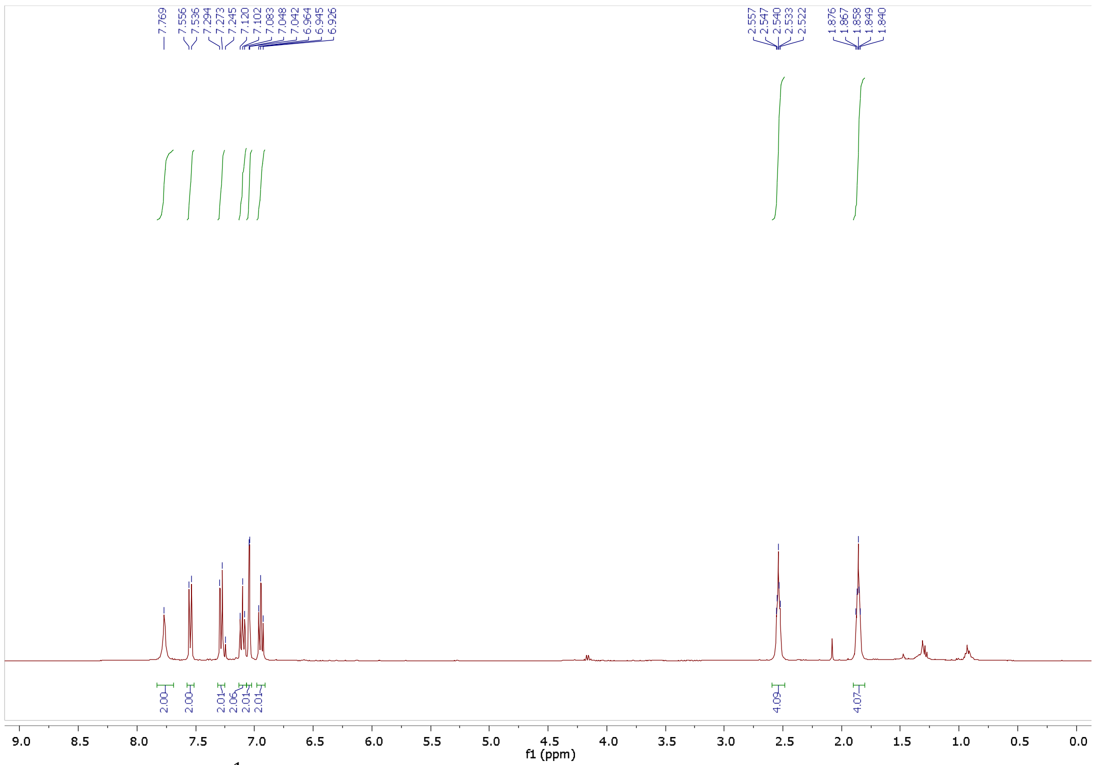
^{1}H NMR (300 MHz, $CDCl_3$) of Compound (**3aP)**



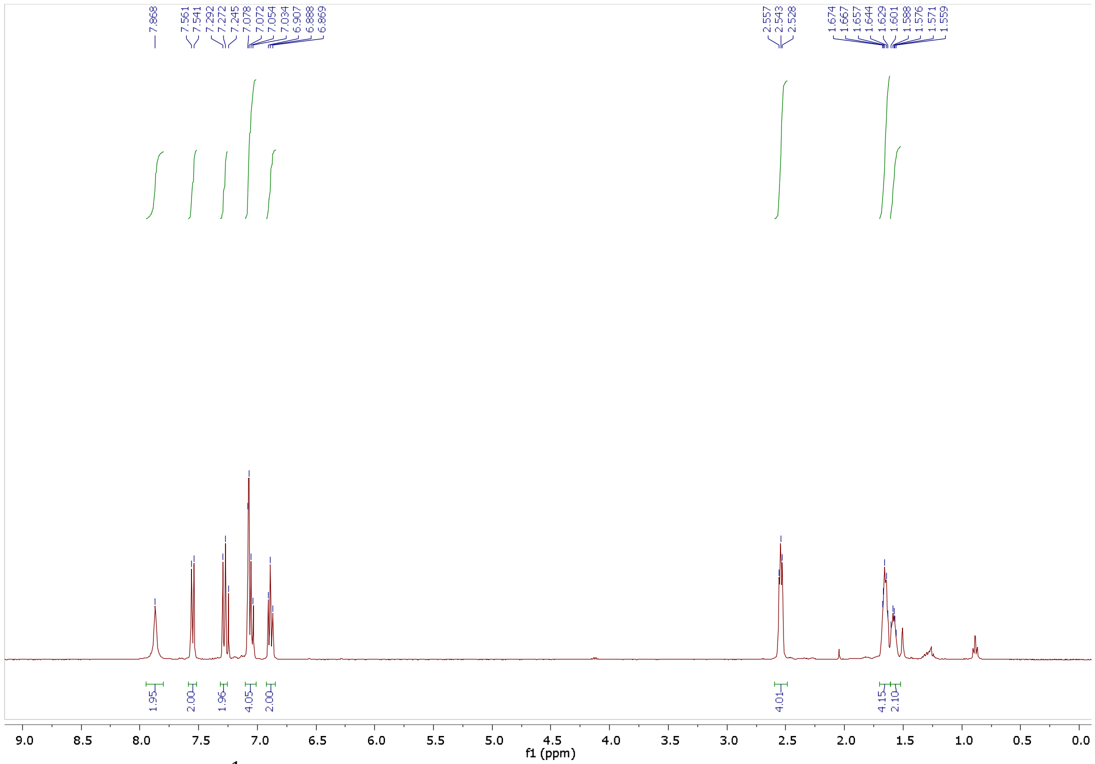
^{1}H NMR (400 MHz, $CDCl_3$) of Compound (**3aQ**)



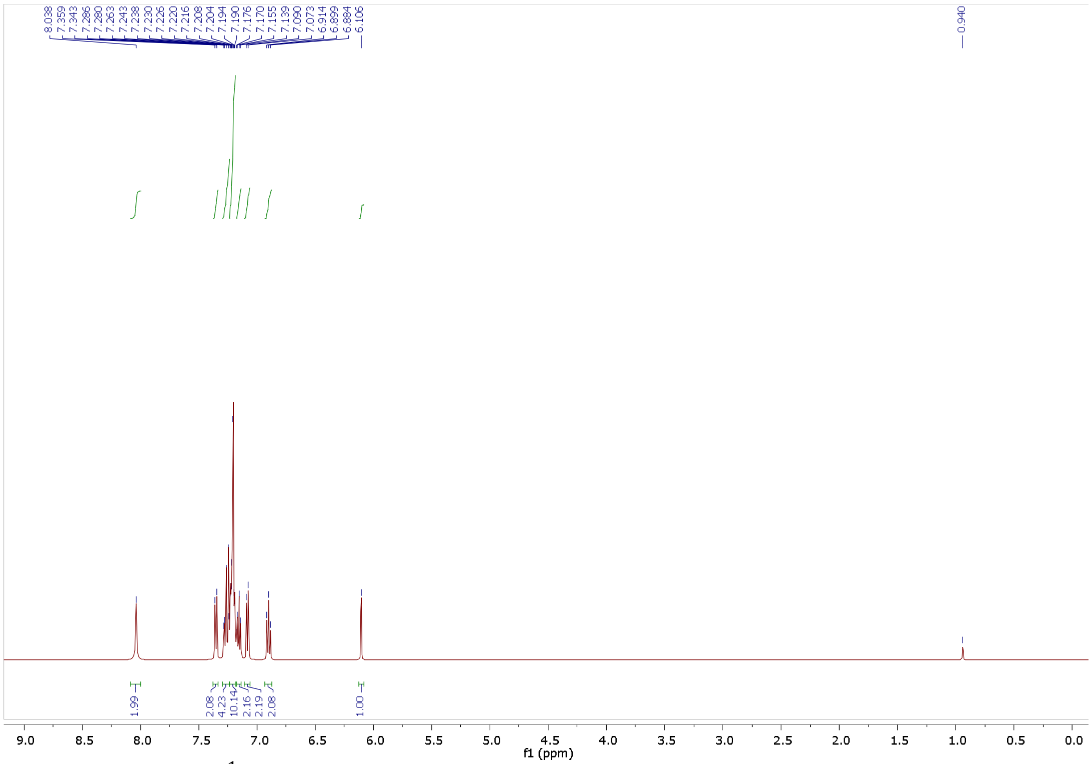
^{1}H NMR (400 MHz, $CDCl_3$) of Compound (**3aR**)



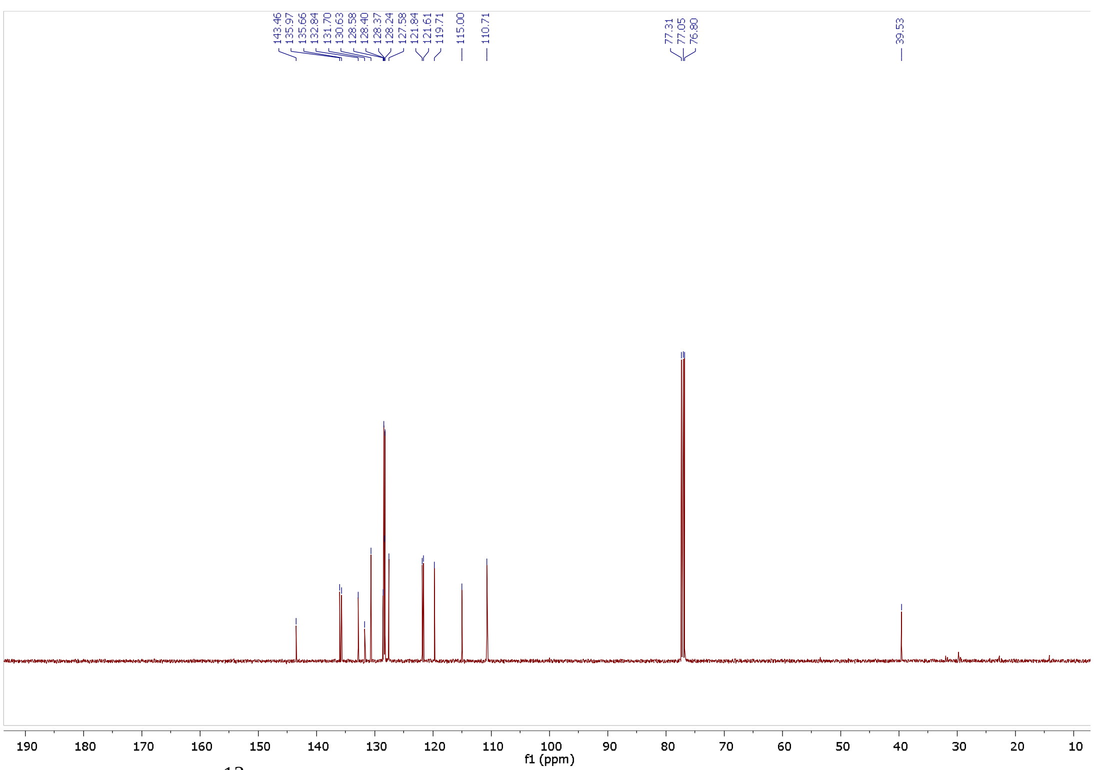
^{1}H NMR (400 MHz, $CDCl_3$) of Compound (**3aS**)



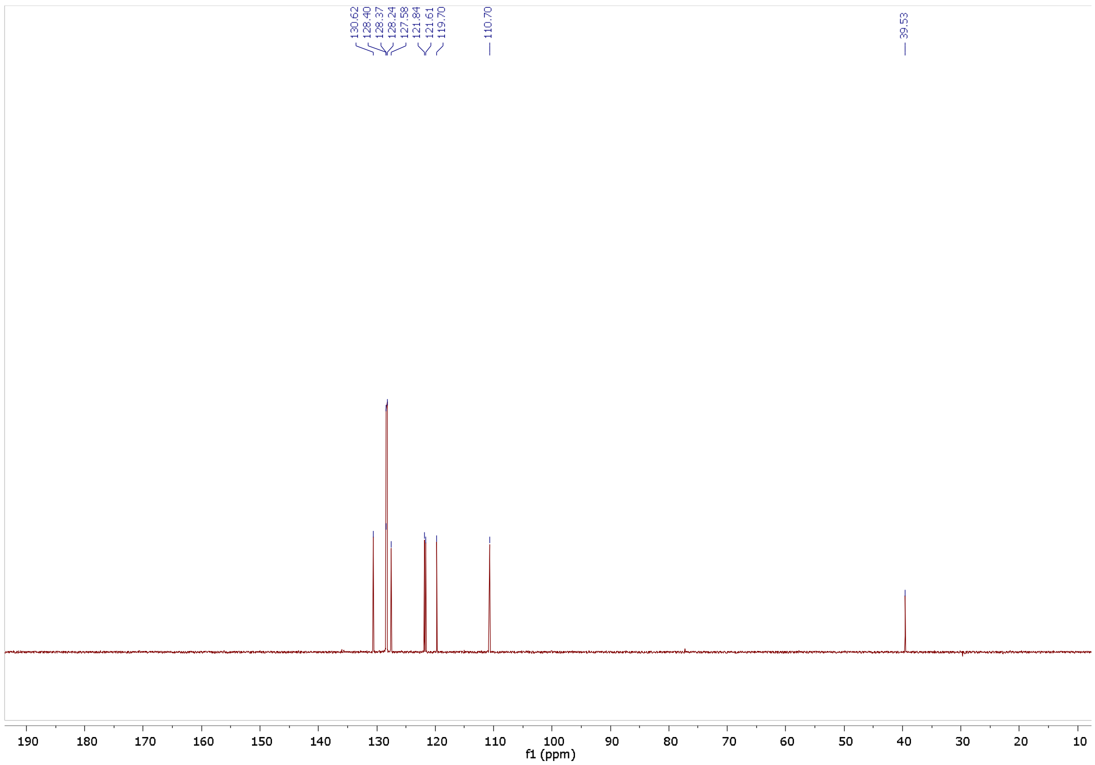
^{1}H NMR (400 MHz, $CDCl_3$) of Compound (**3aT**)



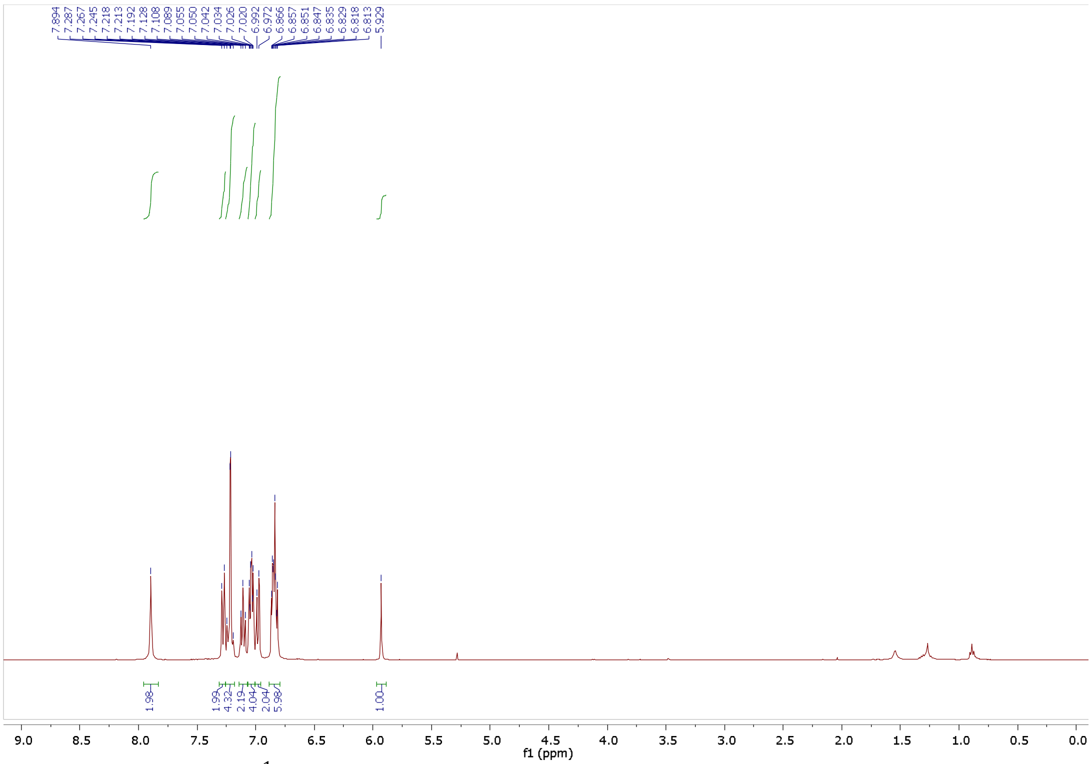
^{1}H NMR (500 MHz, $CDCl_3$) of Compound (**3bC**)



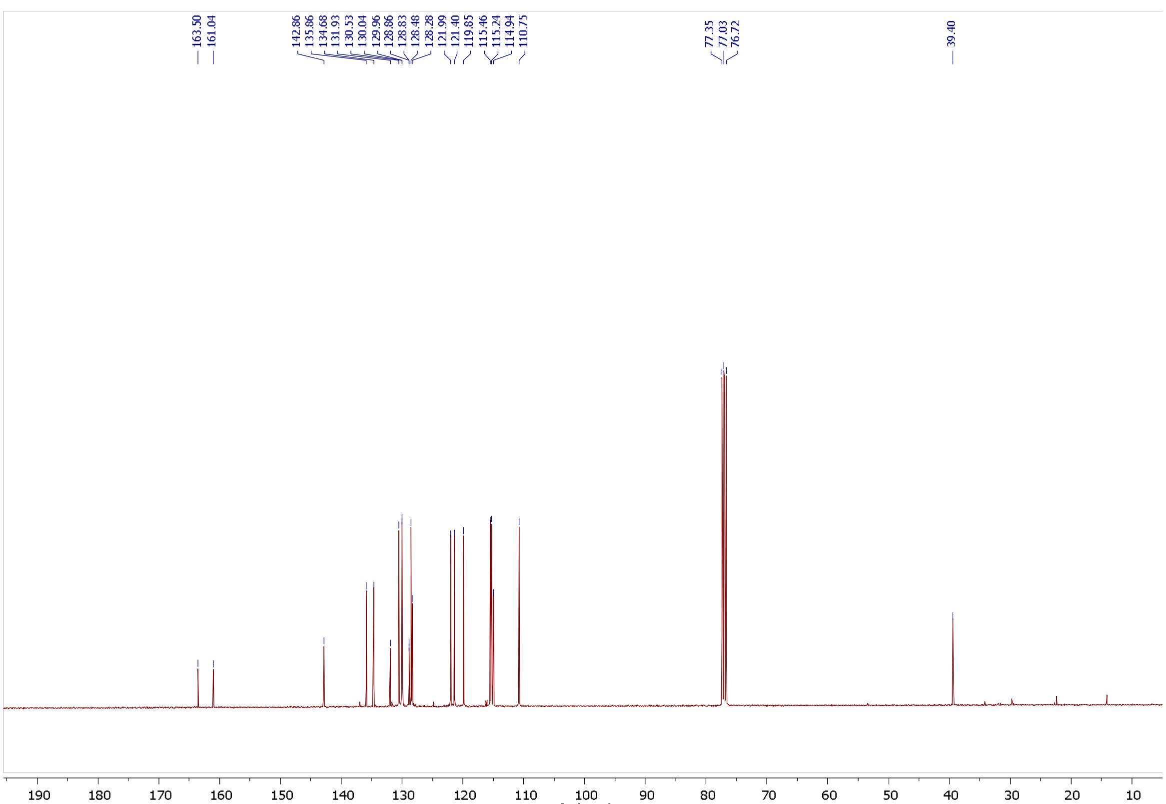
^{13}C NMR (125 MHz, $CDCl_3$) of Compound (**3bC**)



DEPT NMR (125 MHz, $CDCl_3$) of Compound (**3bC**)



^{1}H NMR (400 MHz, $CDCl_3$) of Compound (**3cC**)



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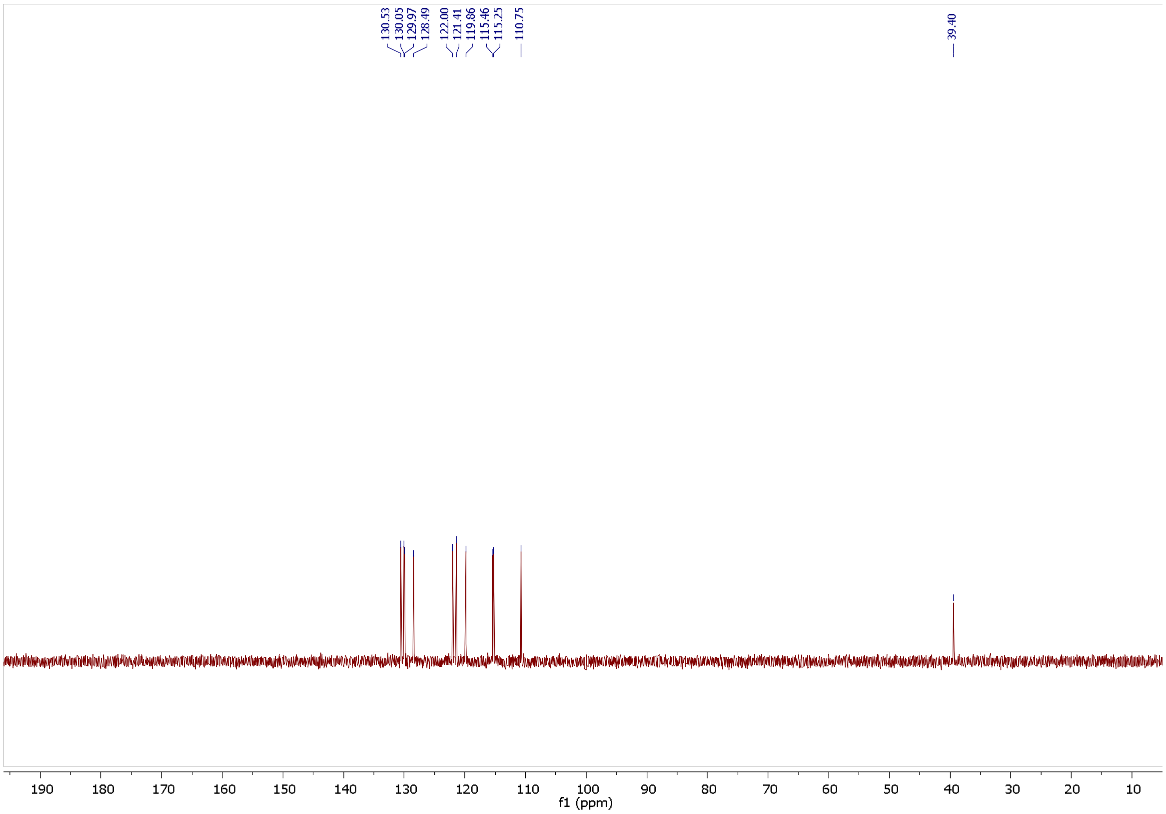
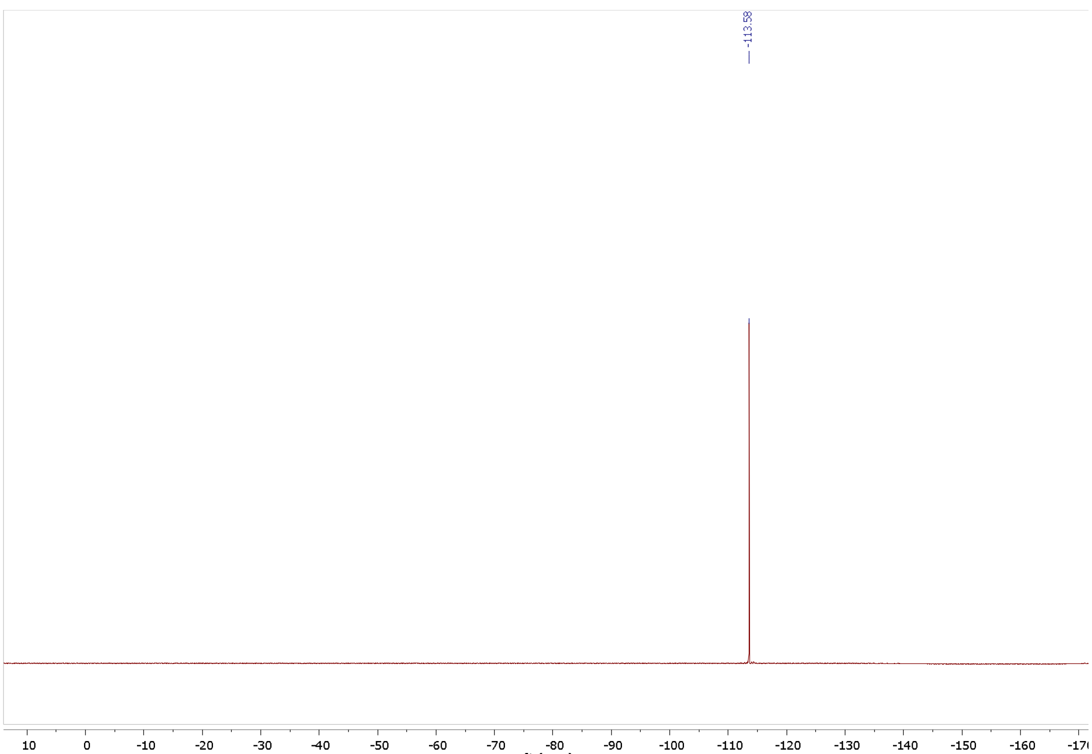
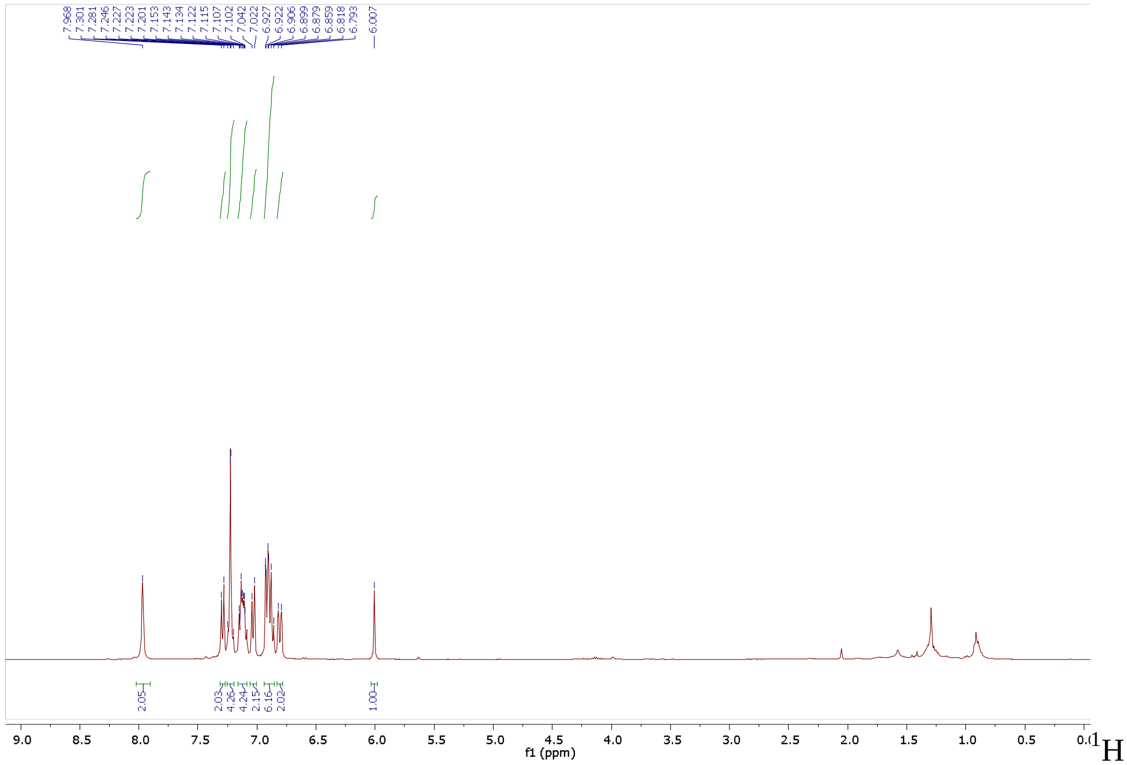


DEPT NMR (125 MHz, $CDCl_3$) of Compound (**3cC**)



^{19}F NMR (376 MHz, $CDCl_3$) of Compound (**3cC**)



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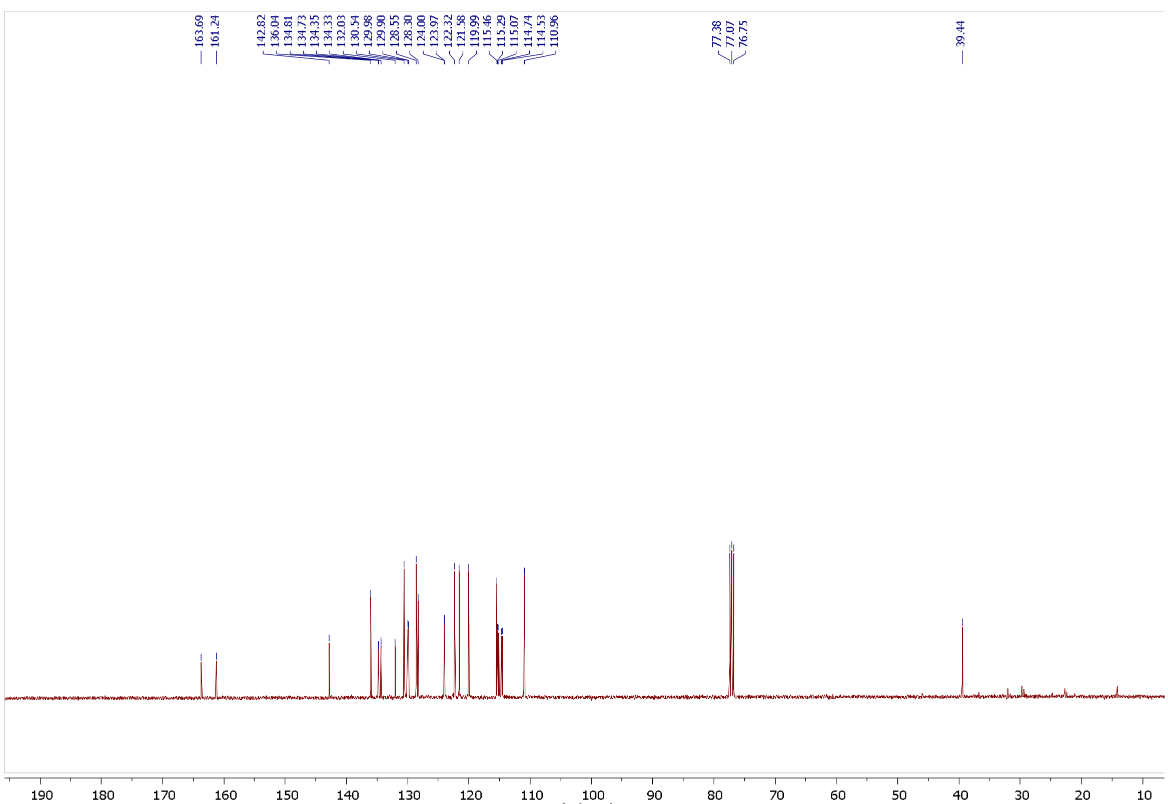

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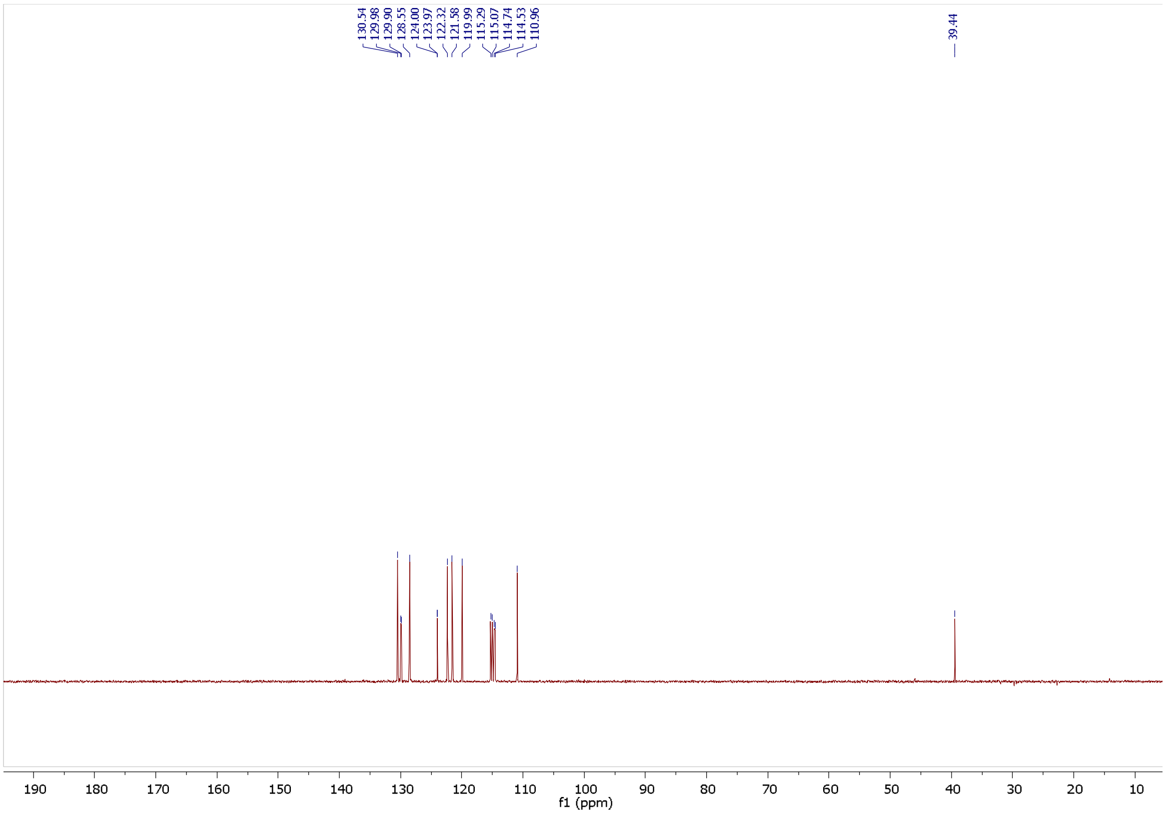
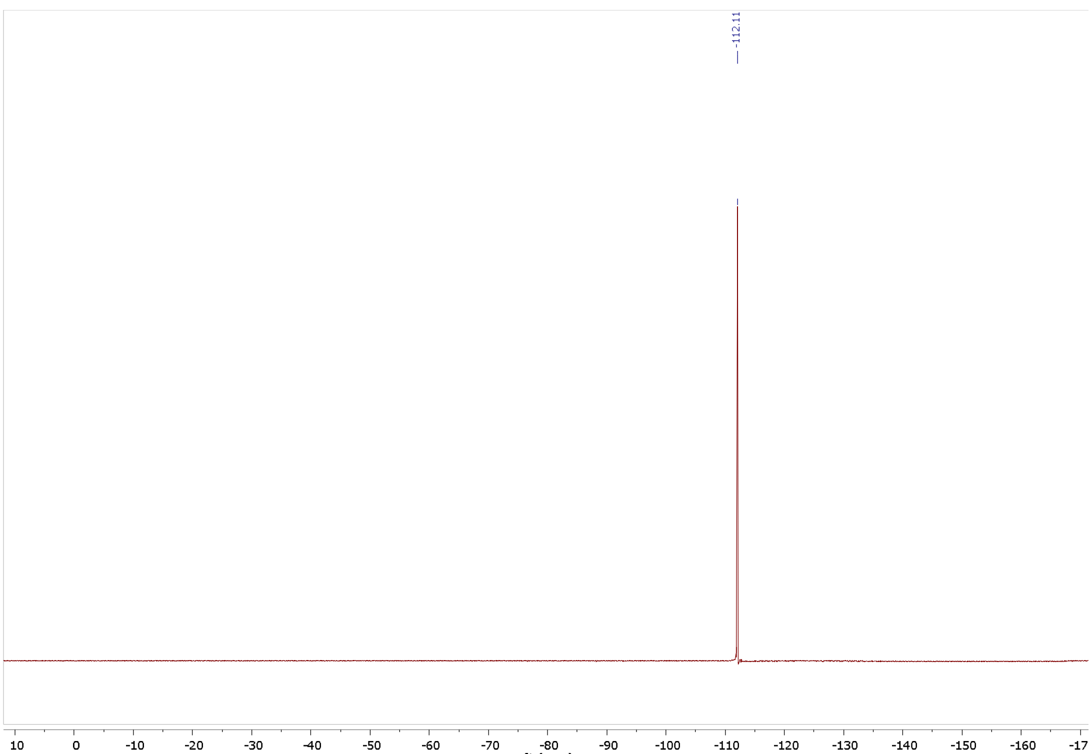
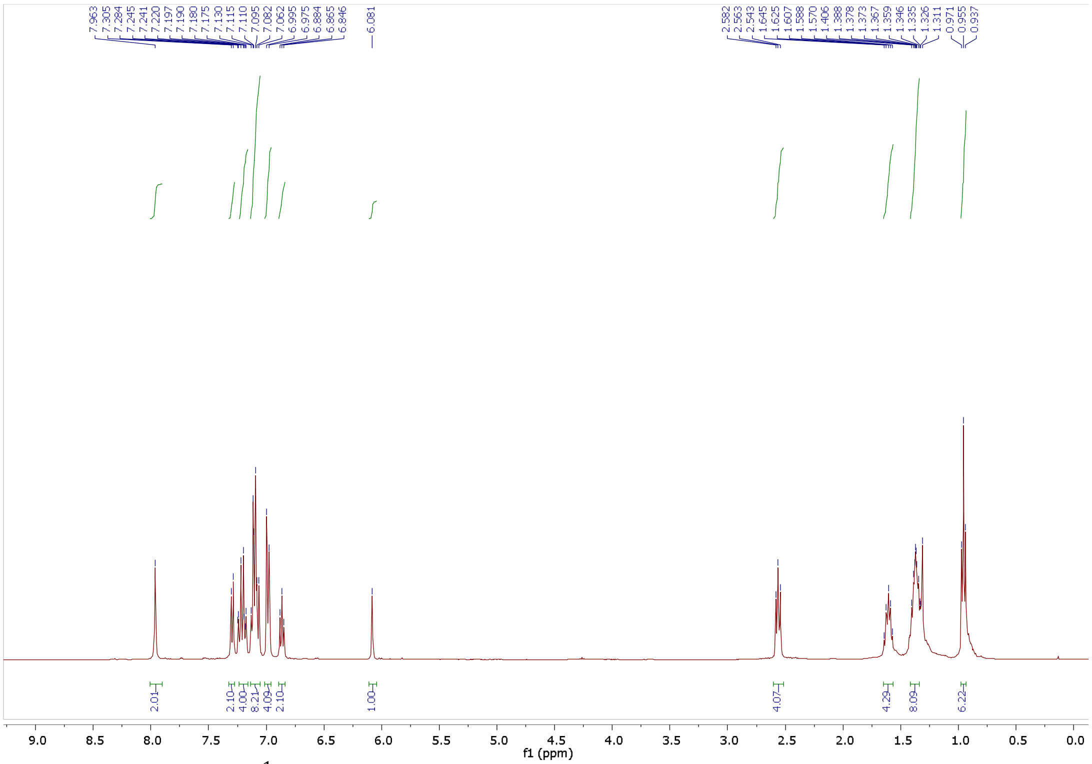


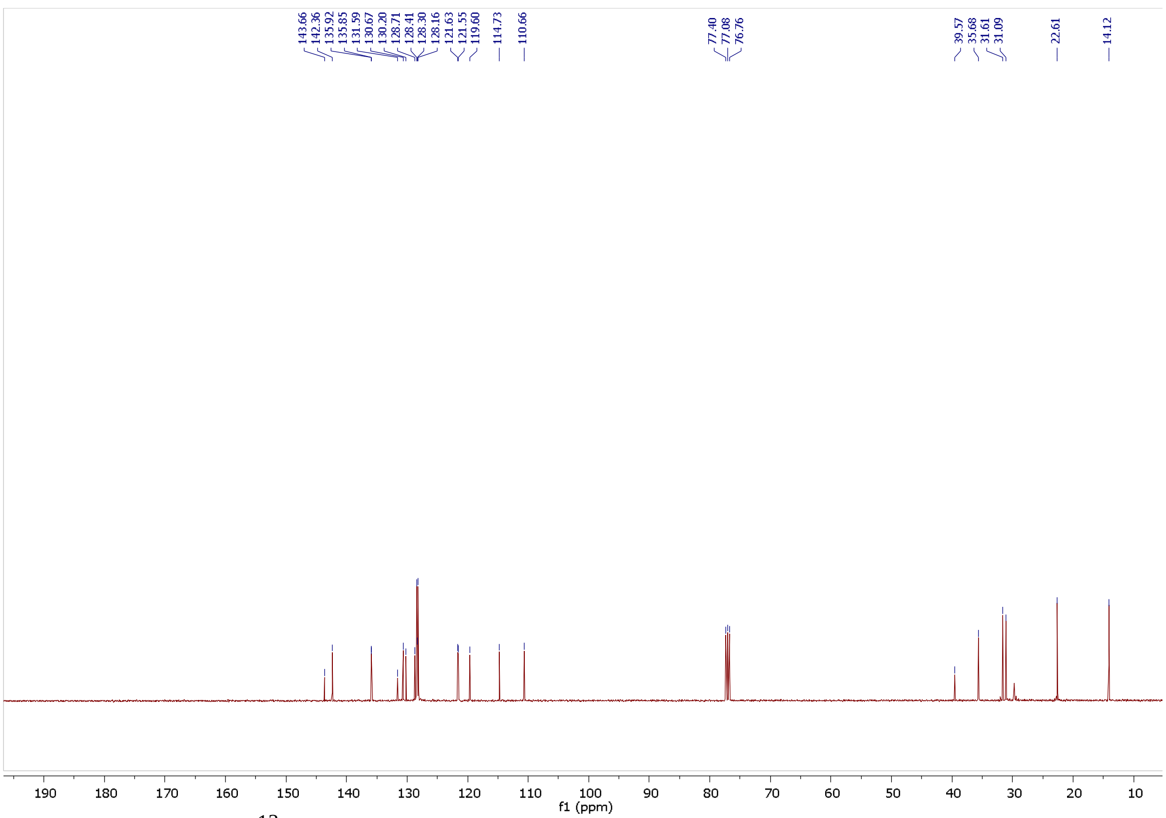
DEPT NMR (100 MHz, $CDCl_3$) of Compound (**3dC**)



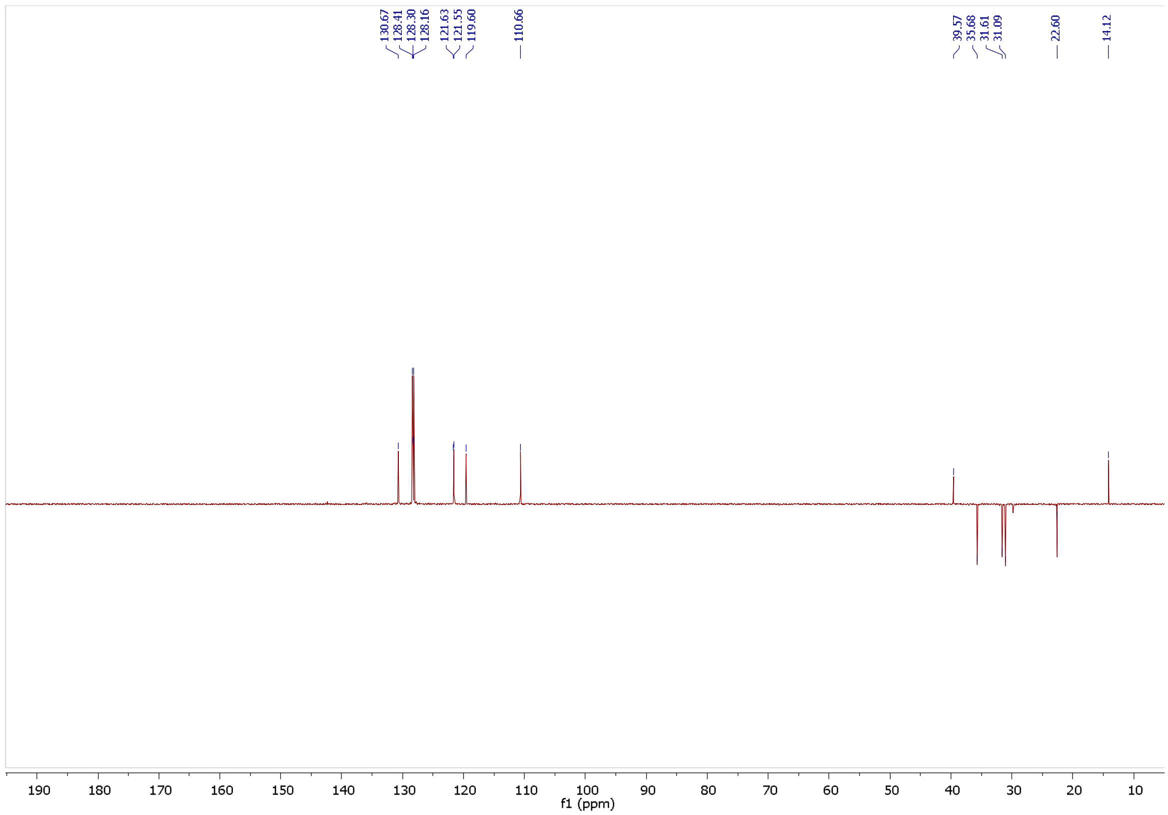
^{19}F NMR (376 MHz, $CDCl_3$) of Compound (**3dC**)



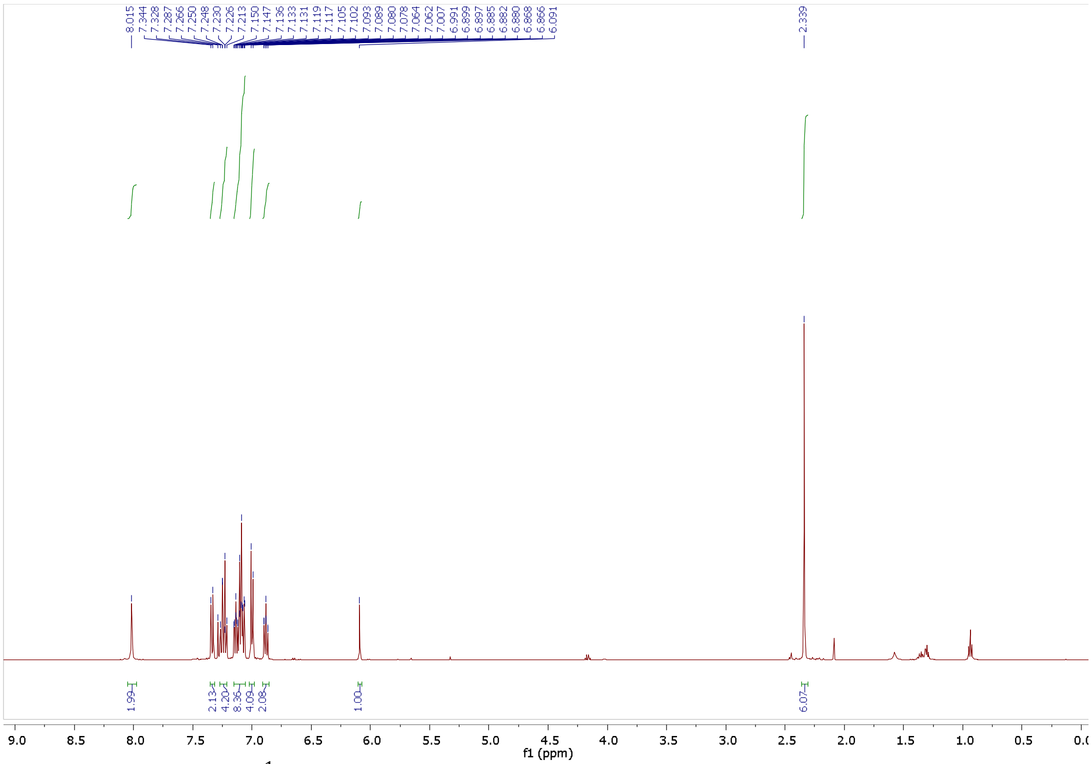
^{1}H NMR (400 MHz, $CDCl_3$) of Compound (**3eC**)



^{13}C NMR (100 MHz, $CDCl_3$) of Compound (**3eC)**



DEPT NMR (125 MHz, $CDCl_3$) of Compound (**3eC**)



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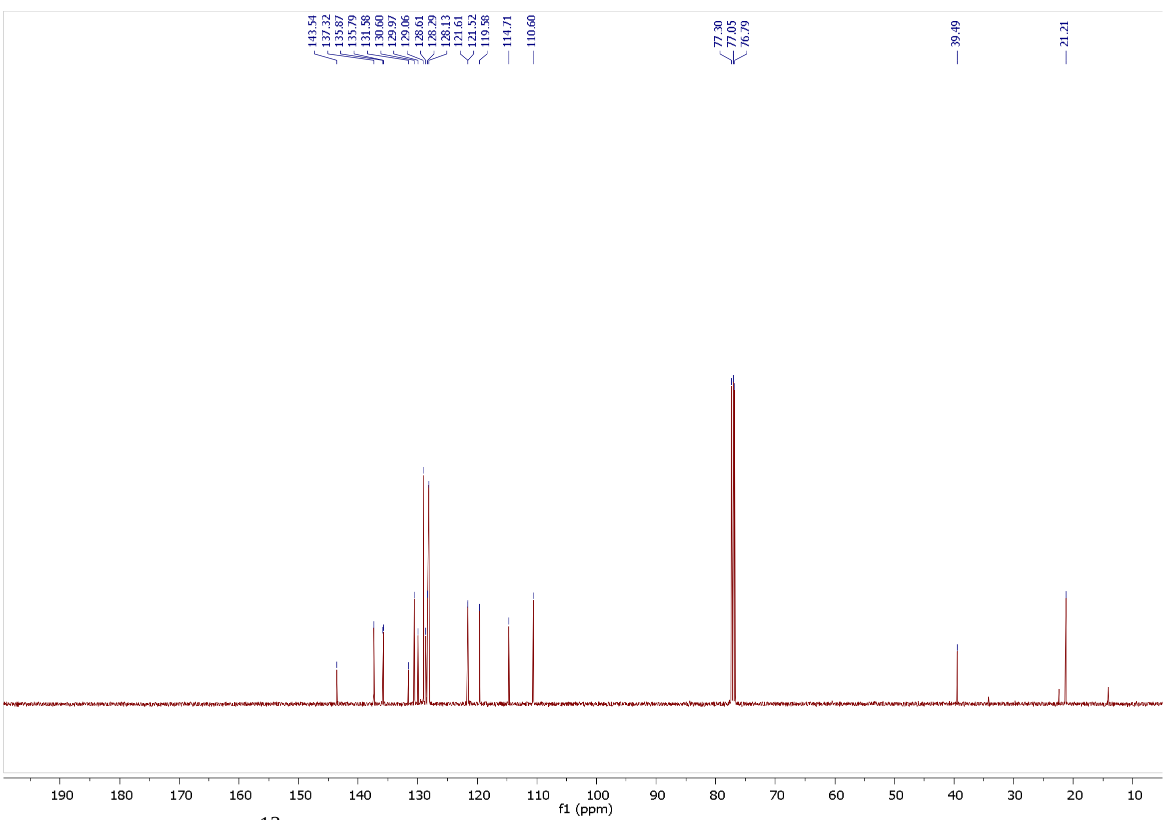

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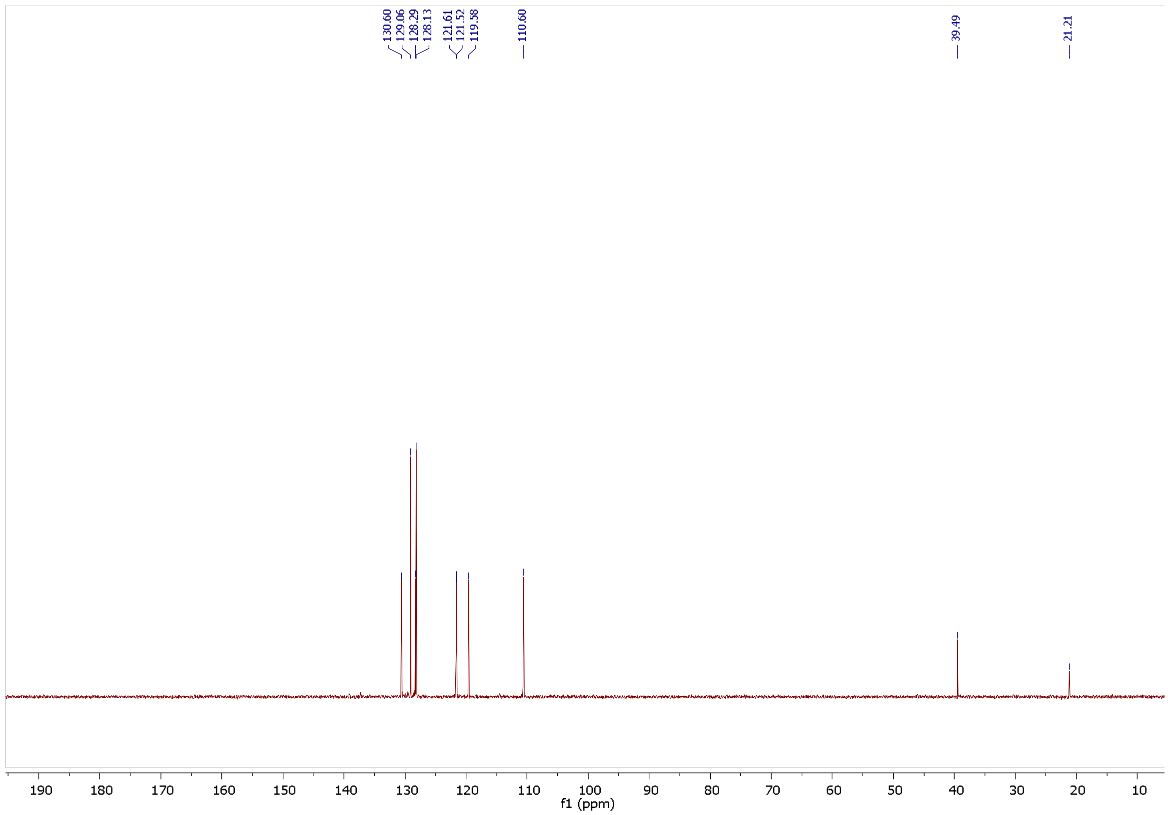

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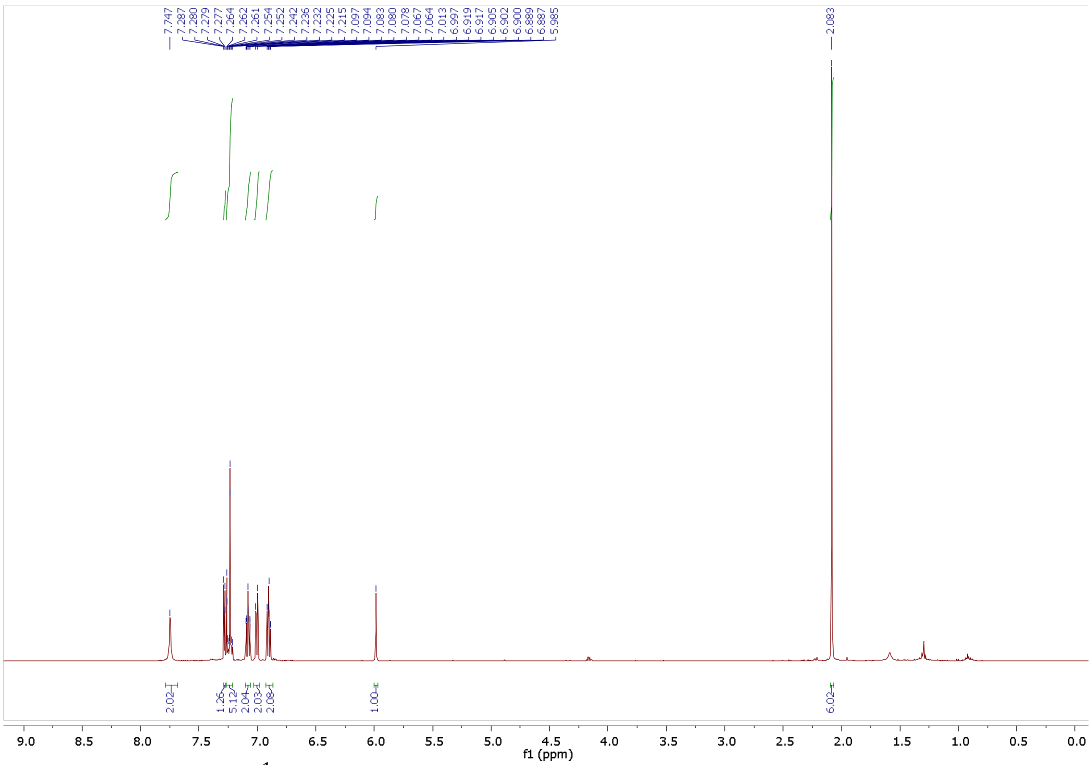

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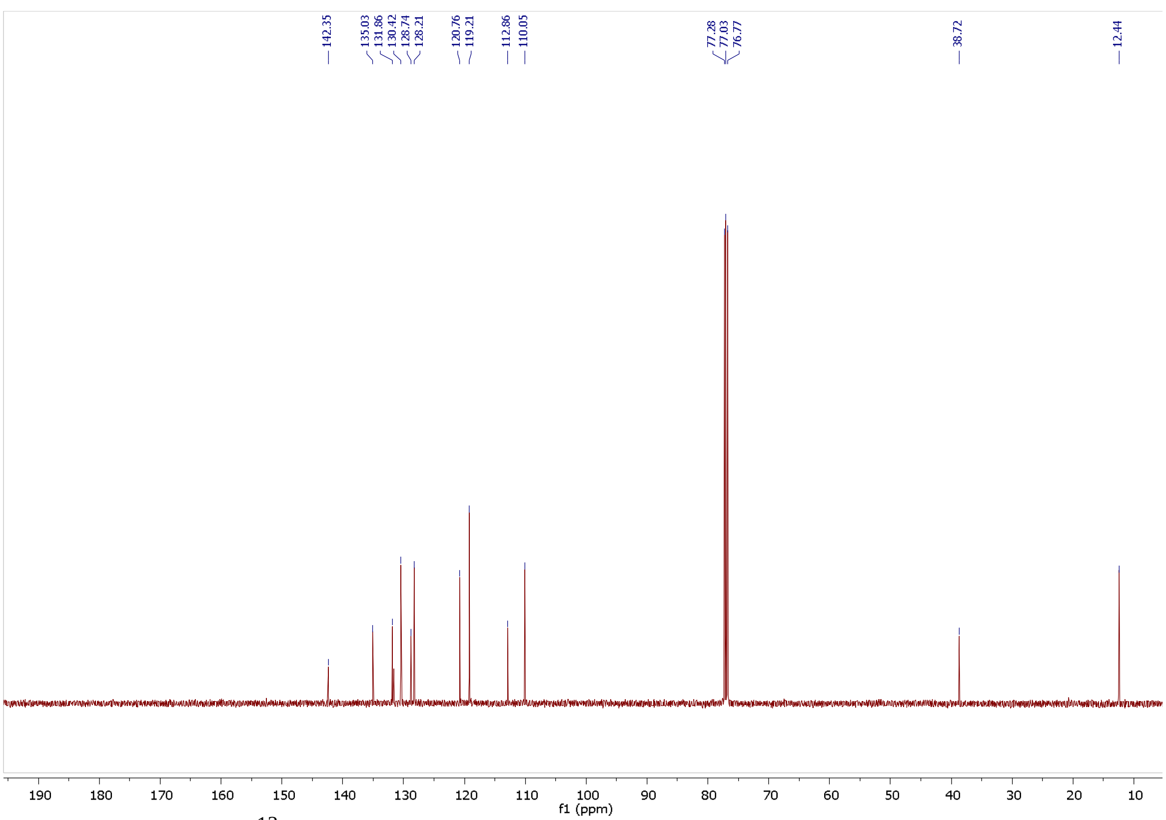
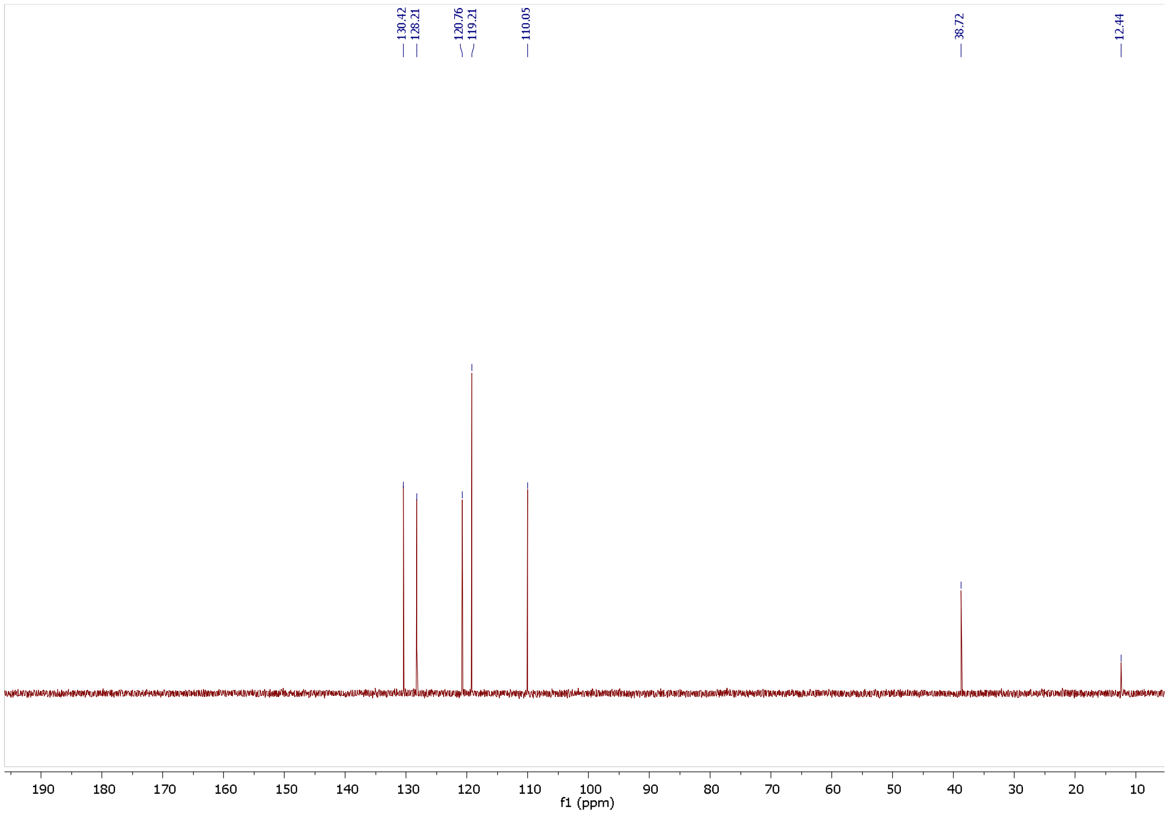


^{13}C NMR (125 MHz, $CDCl_3$) of Compound (**3gC)**



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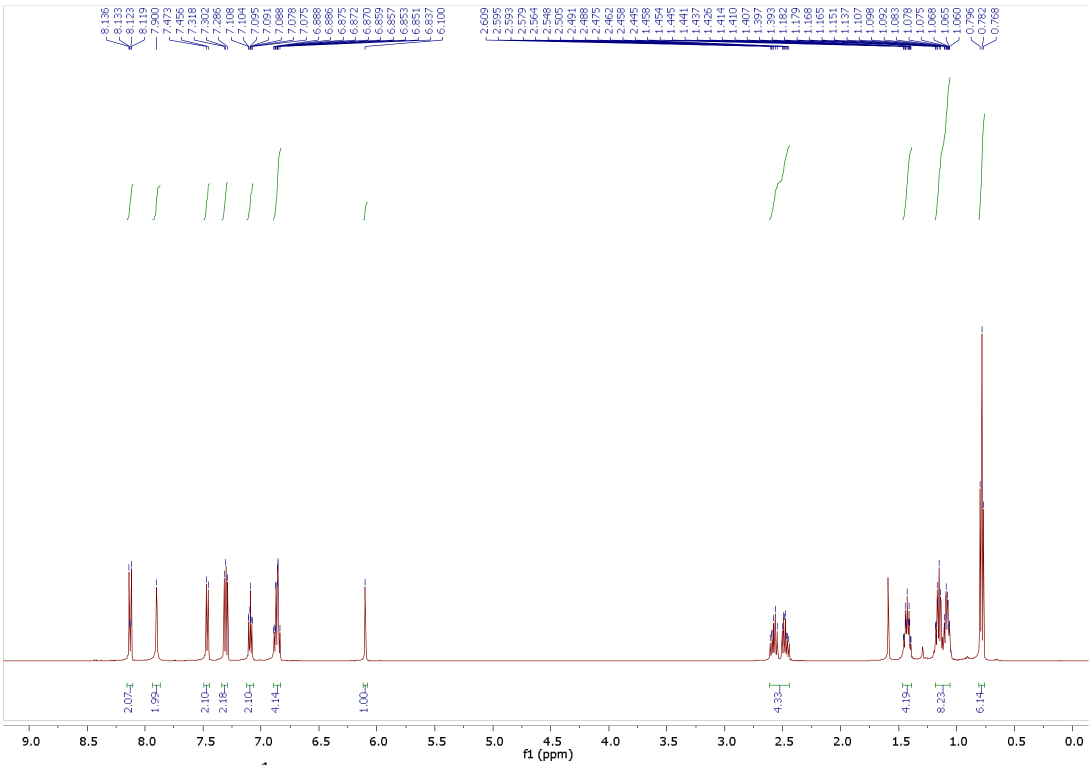
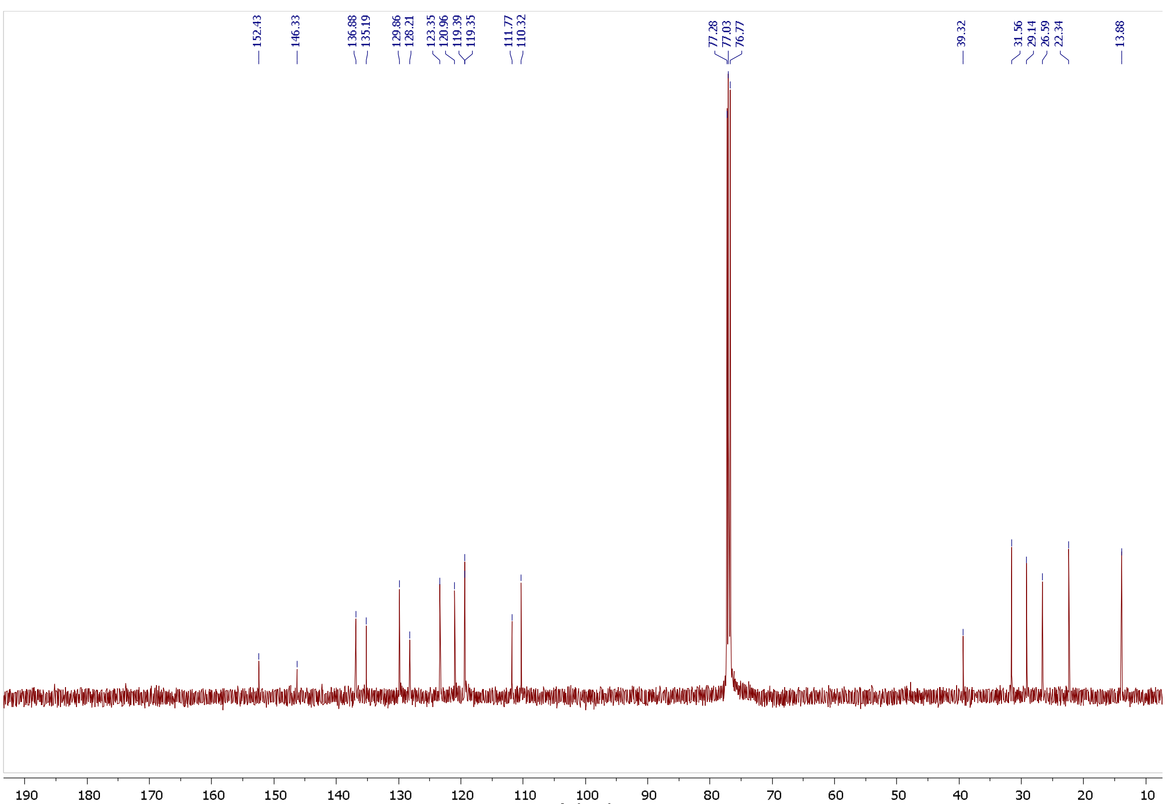


^{1}H NMR (500 MHz, $CDCl_3$) of Compound (**3hC**)



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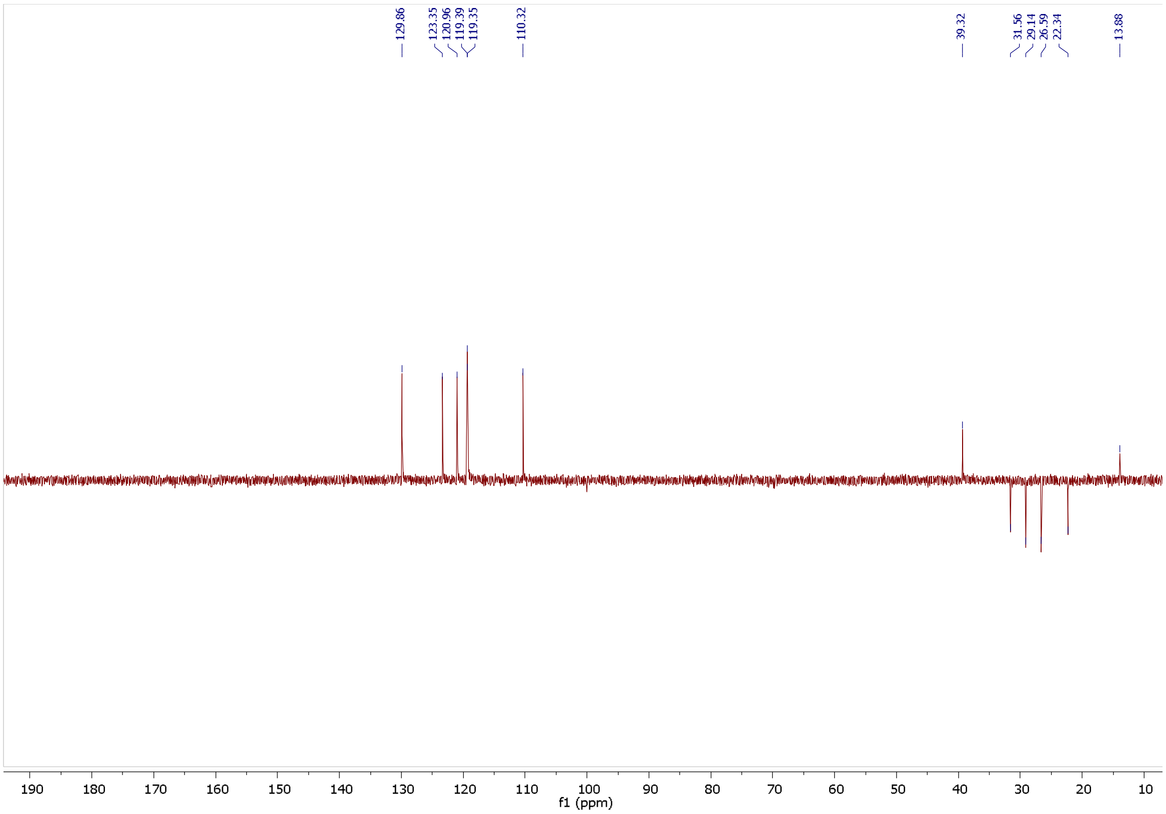
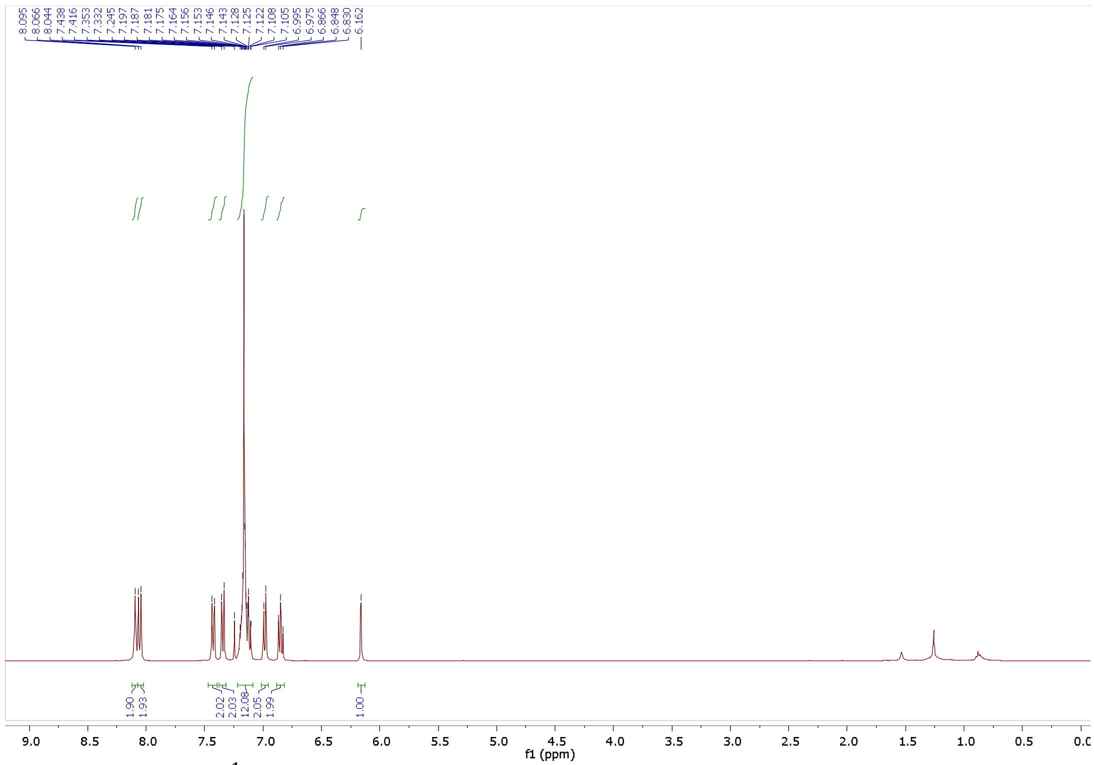


DEPT NMR (125 MHz, $CDCl_3$) of Compound (**3hC**)



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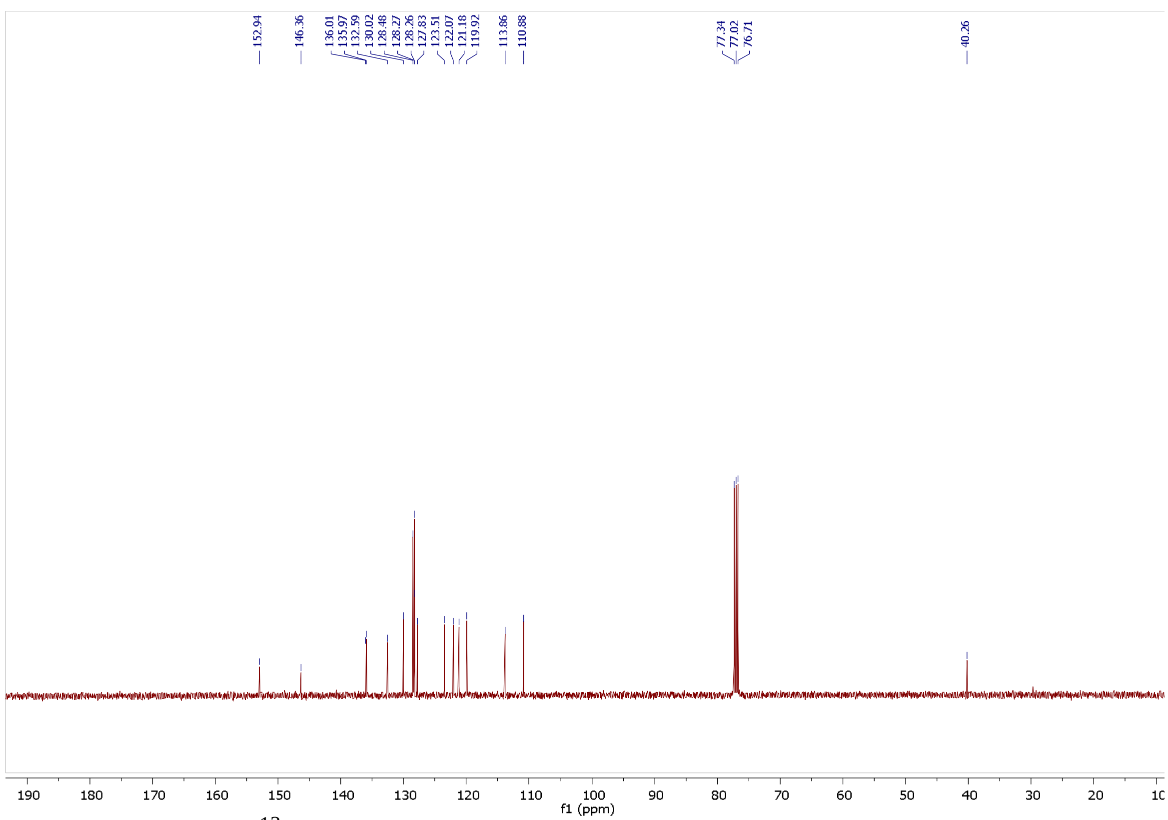

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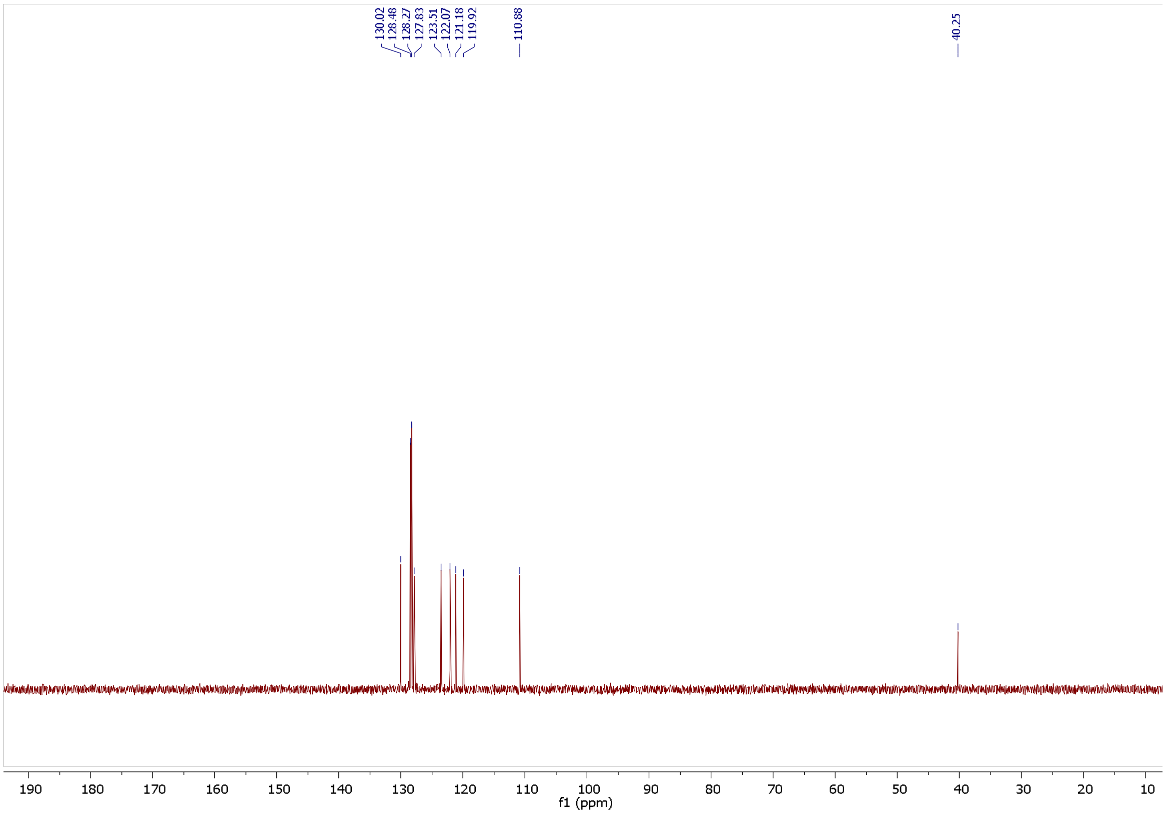
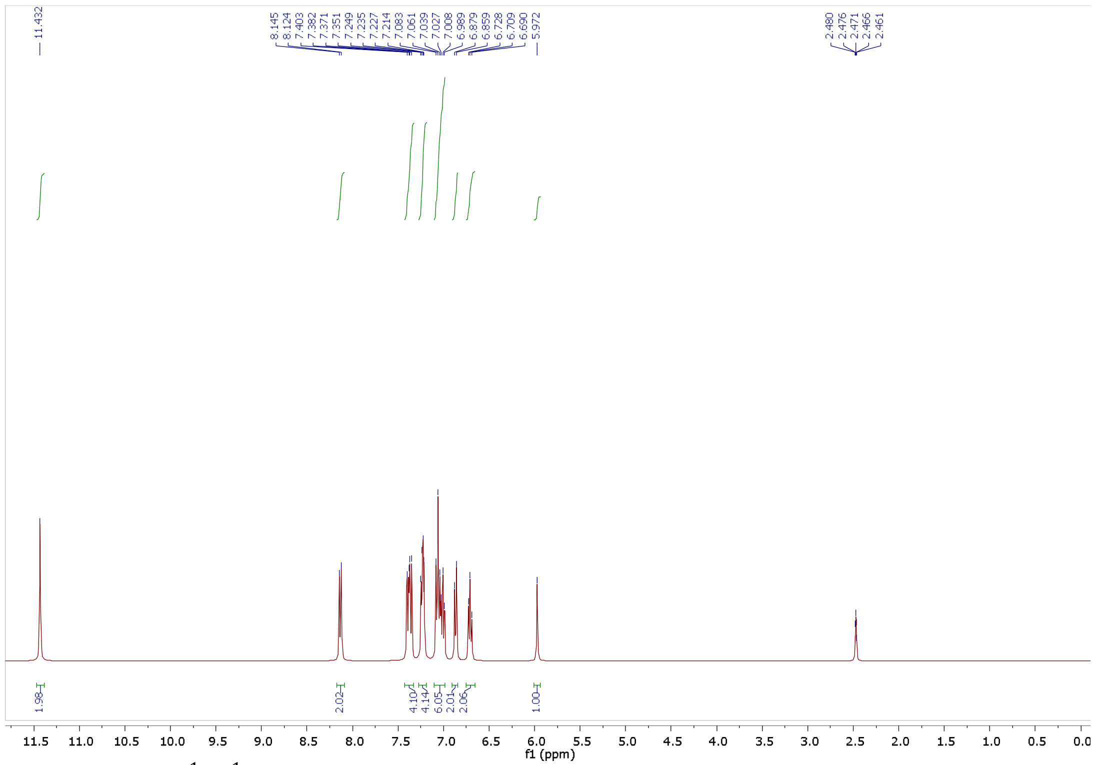
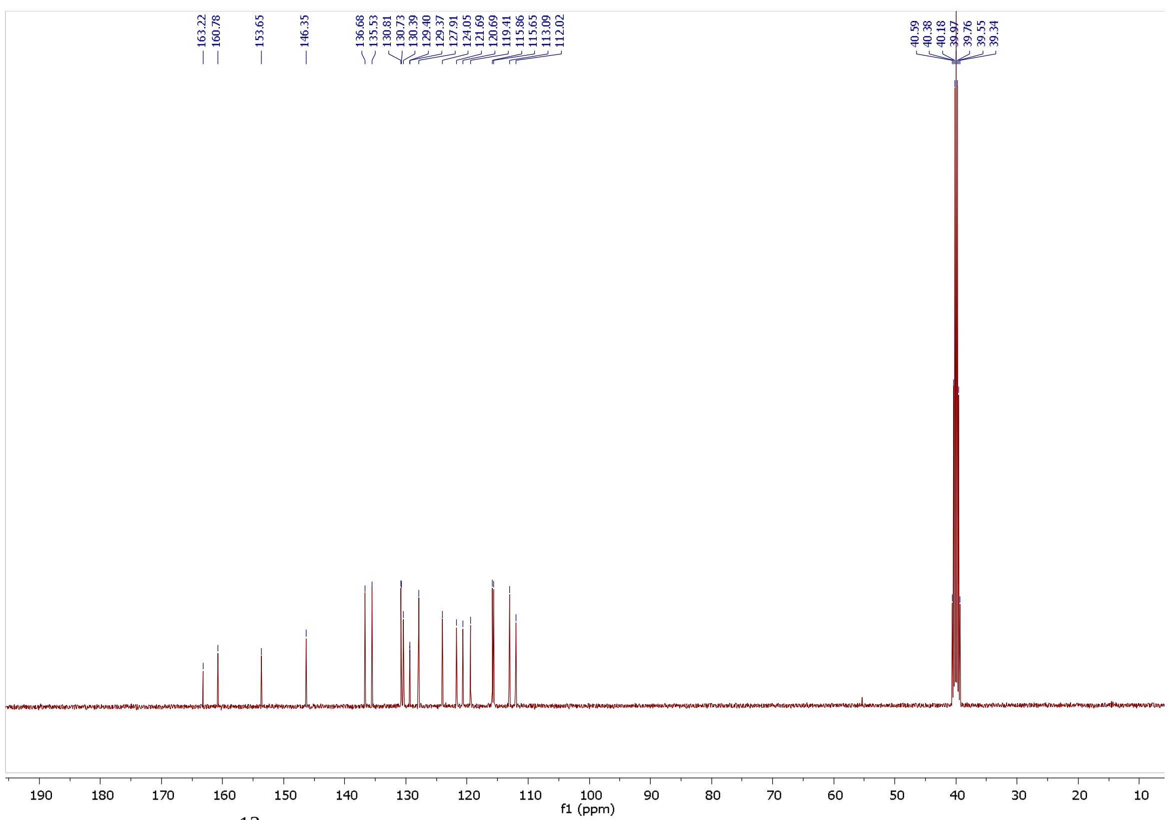


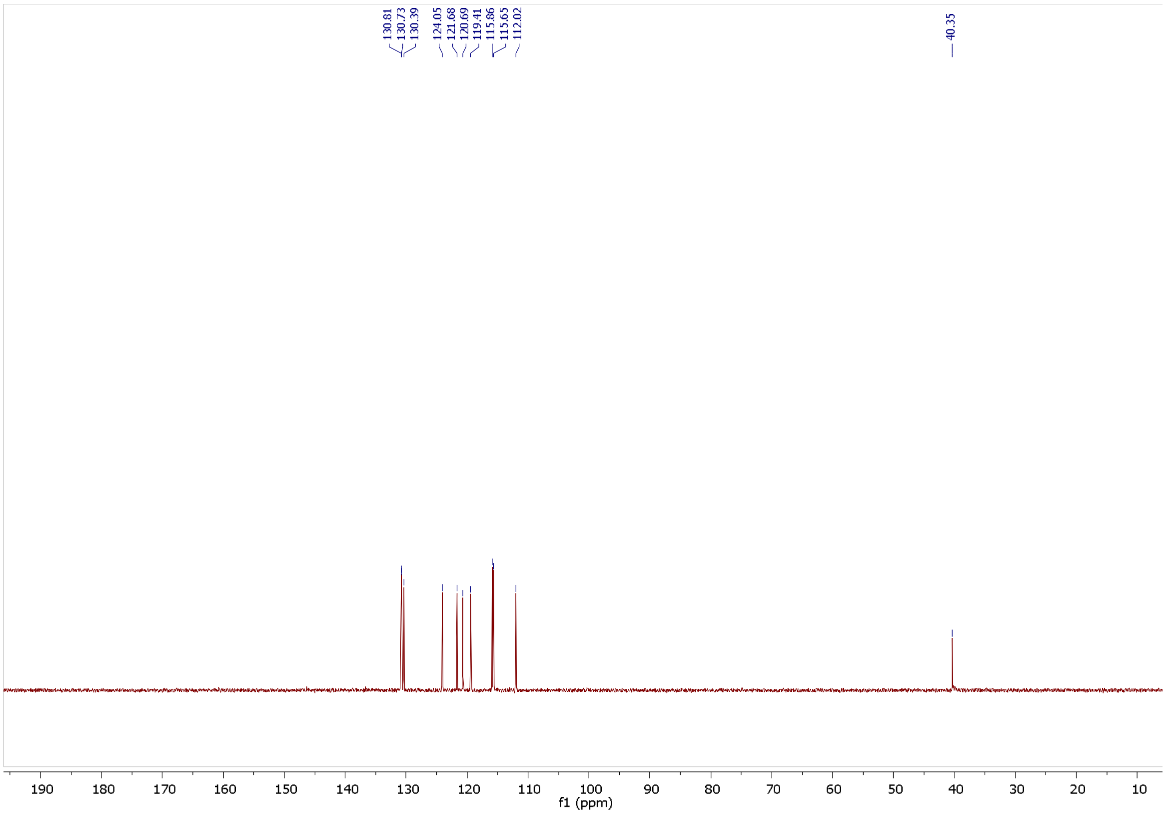
DEPT NMR (125 MHz, $CDCl_3$) of Compound (**3bF**)



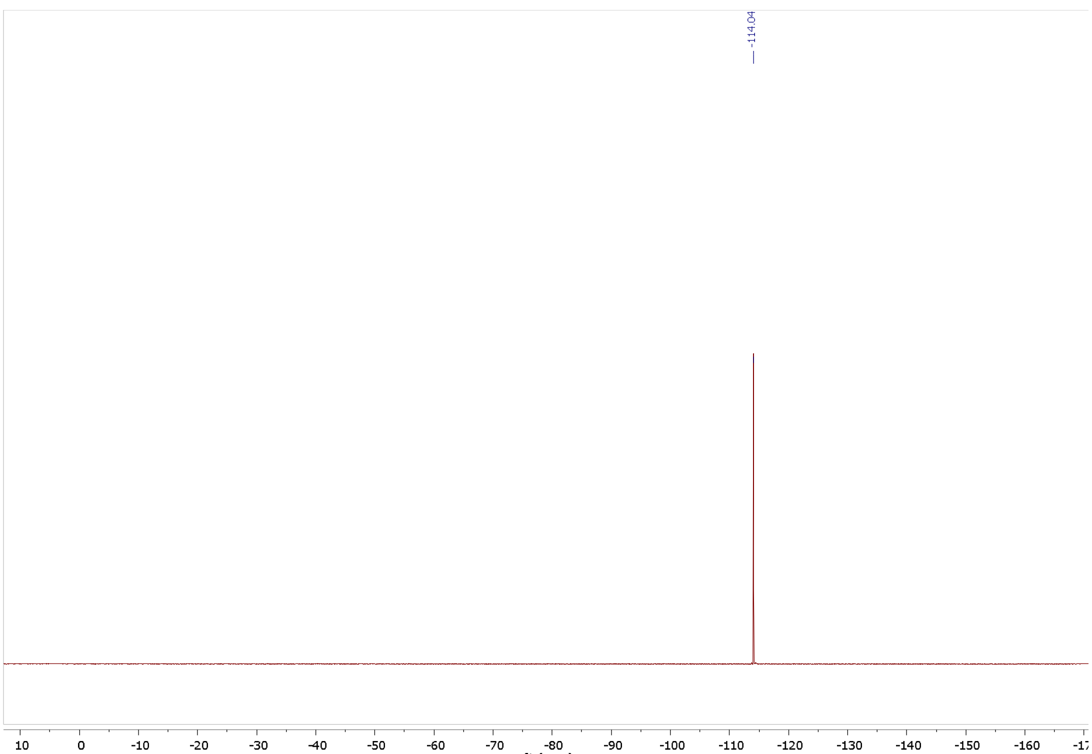
^{1}H ^{1}H NMR (400 MHz, DMSO-d_6) of Compound (**3cF**)



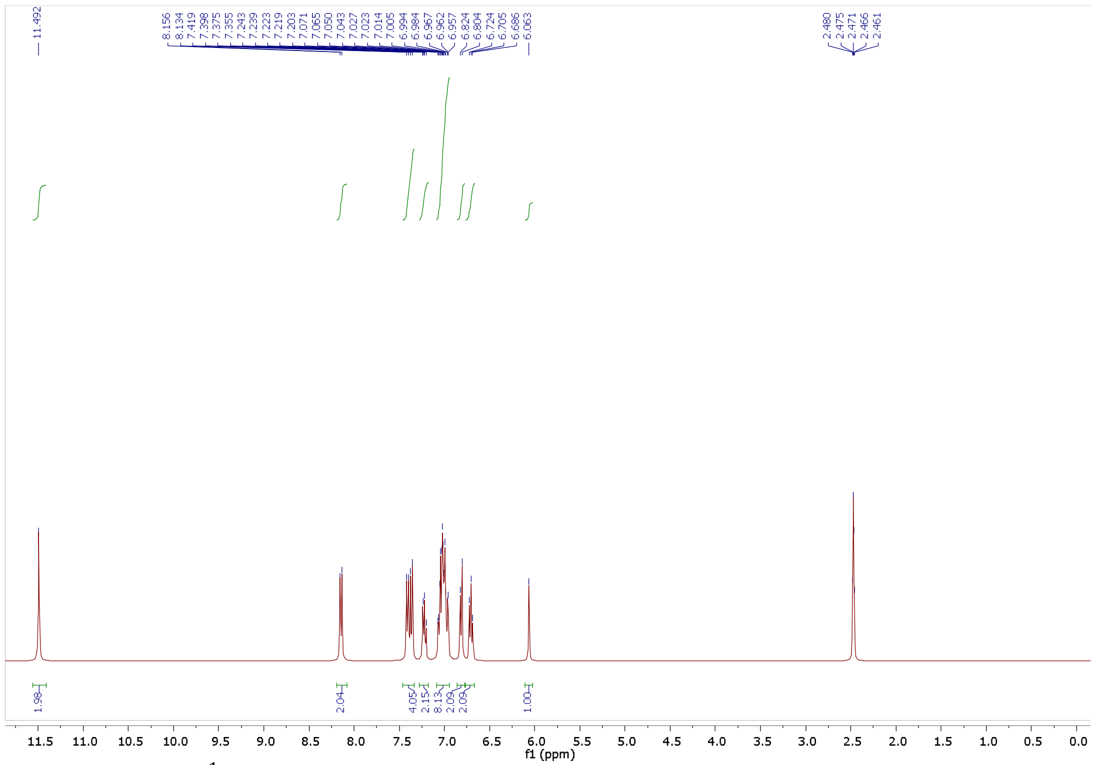
^{13}C NMR (100 MHz, DMSO-d_6) of Compound (**3cF**)



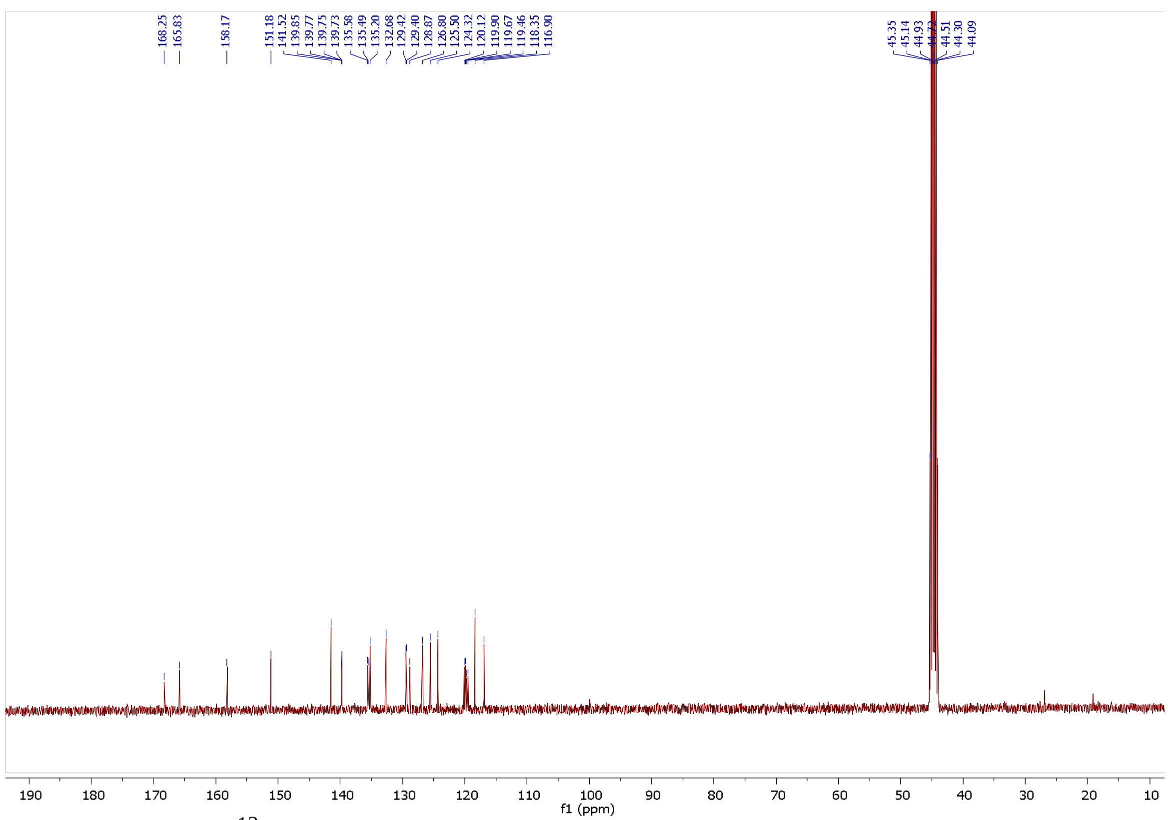
DEPT NMR (100 MHz, DMSO-d_6) of Compound (**3cF**)



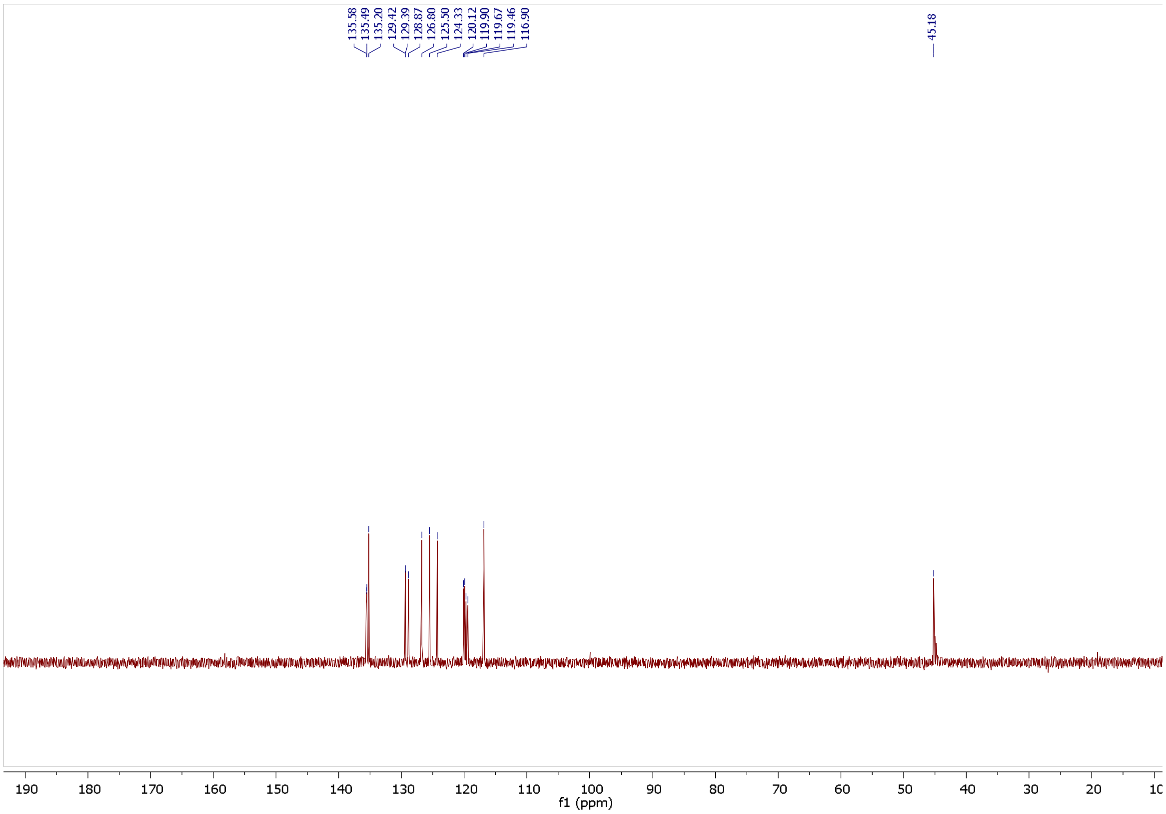
^{19}F NMR (376 MHz, DMSO-d_6) of Compound (**3cF**)



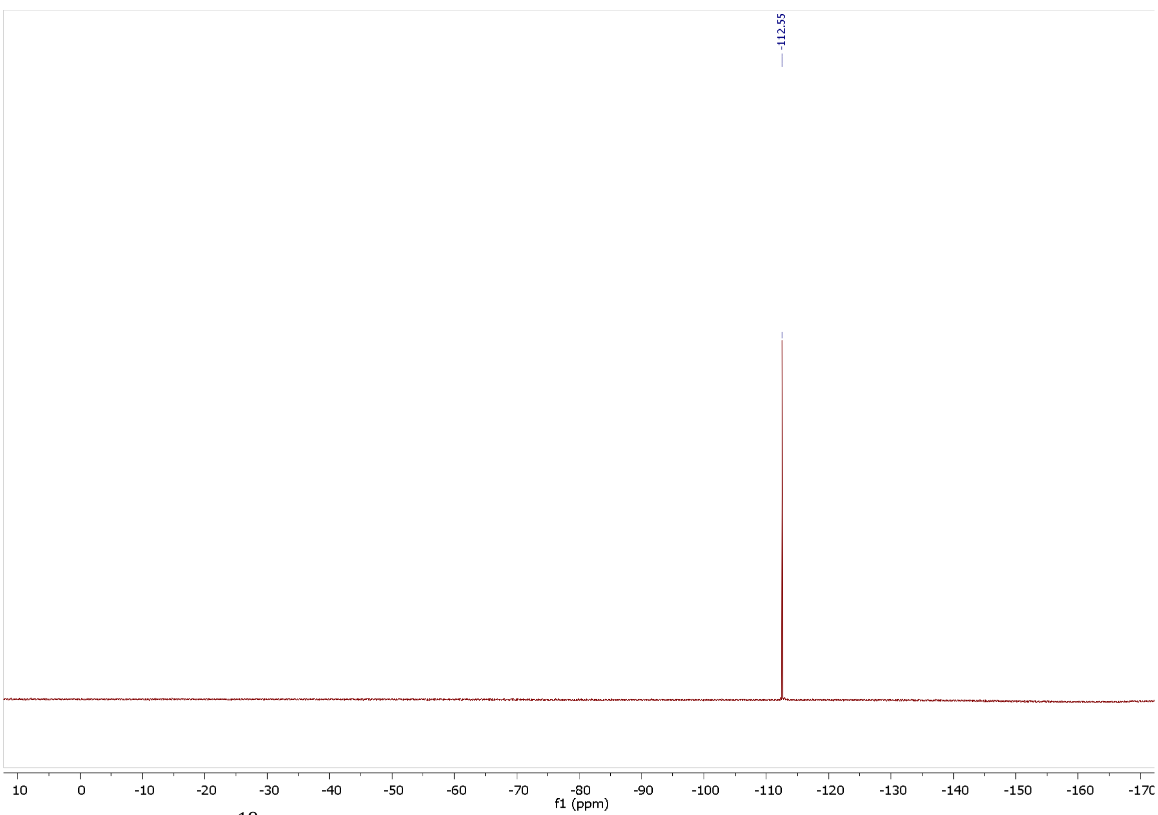
^{1}H NMR (400 MHz, DMSO-d_6) of Compound (**3dF**)



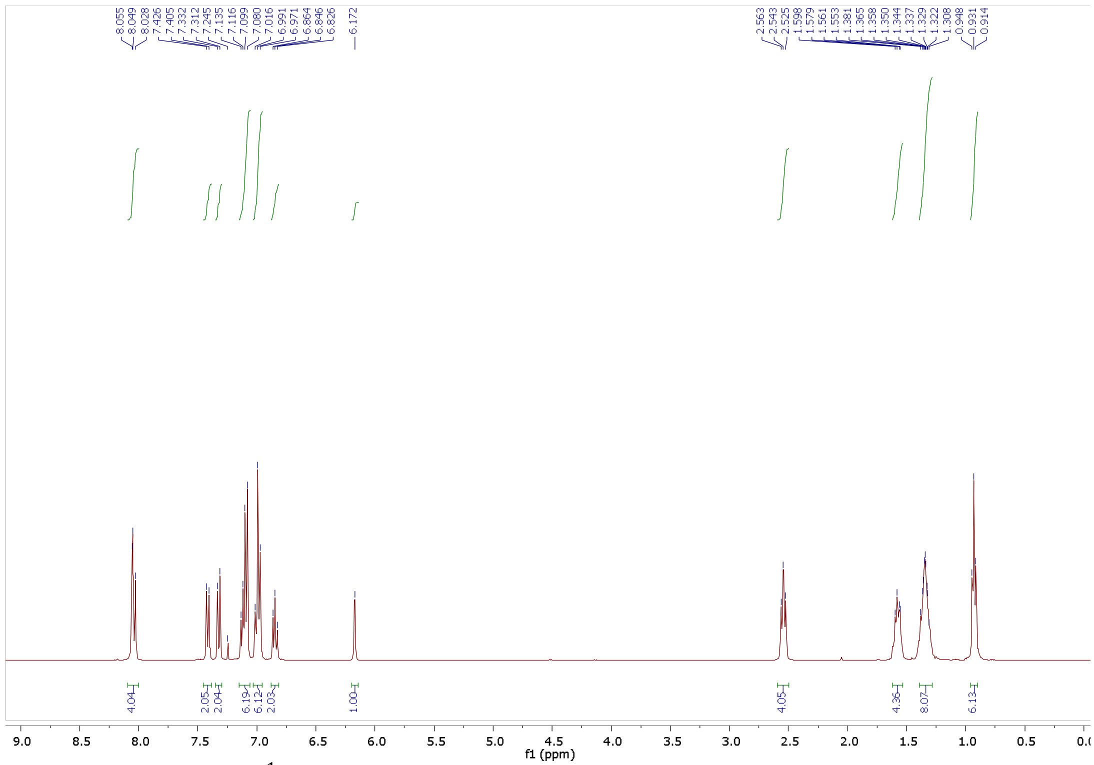
^{13}C NMR (100 MHz, DMSO-d_6) of Compound (**3dF)**



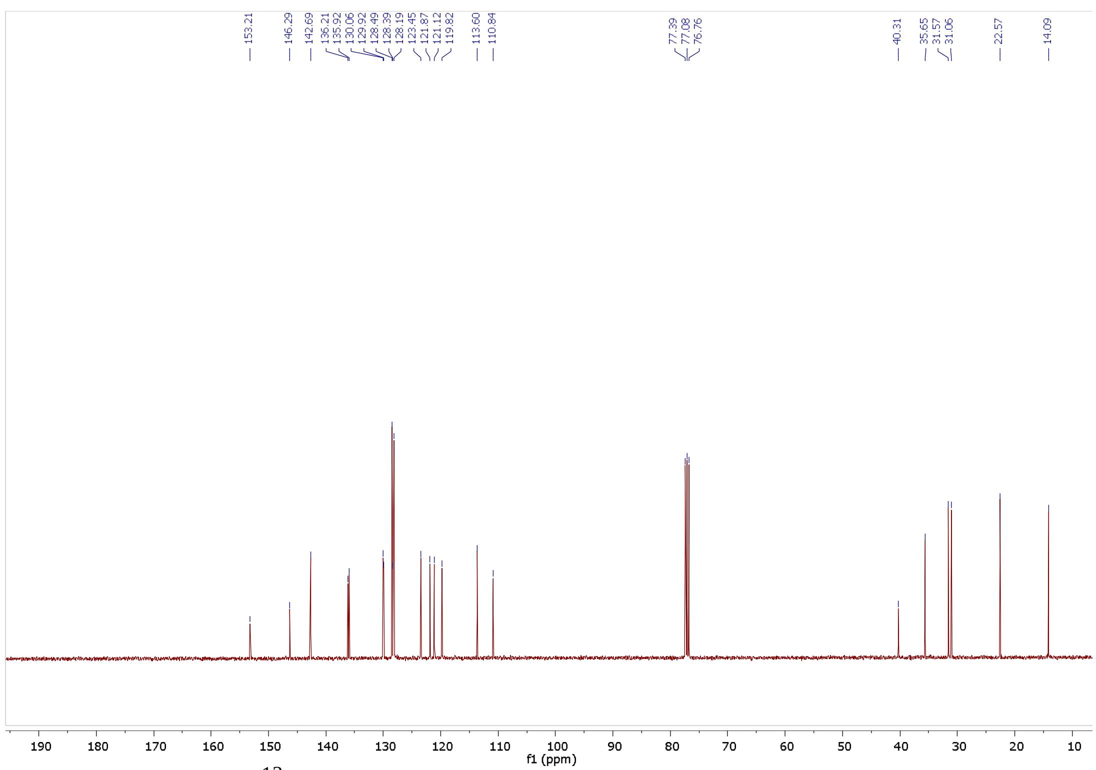
DEPT NMR (100 MHz, DMSO-d_6) of Compound (**3dF**)



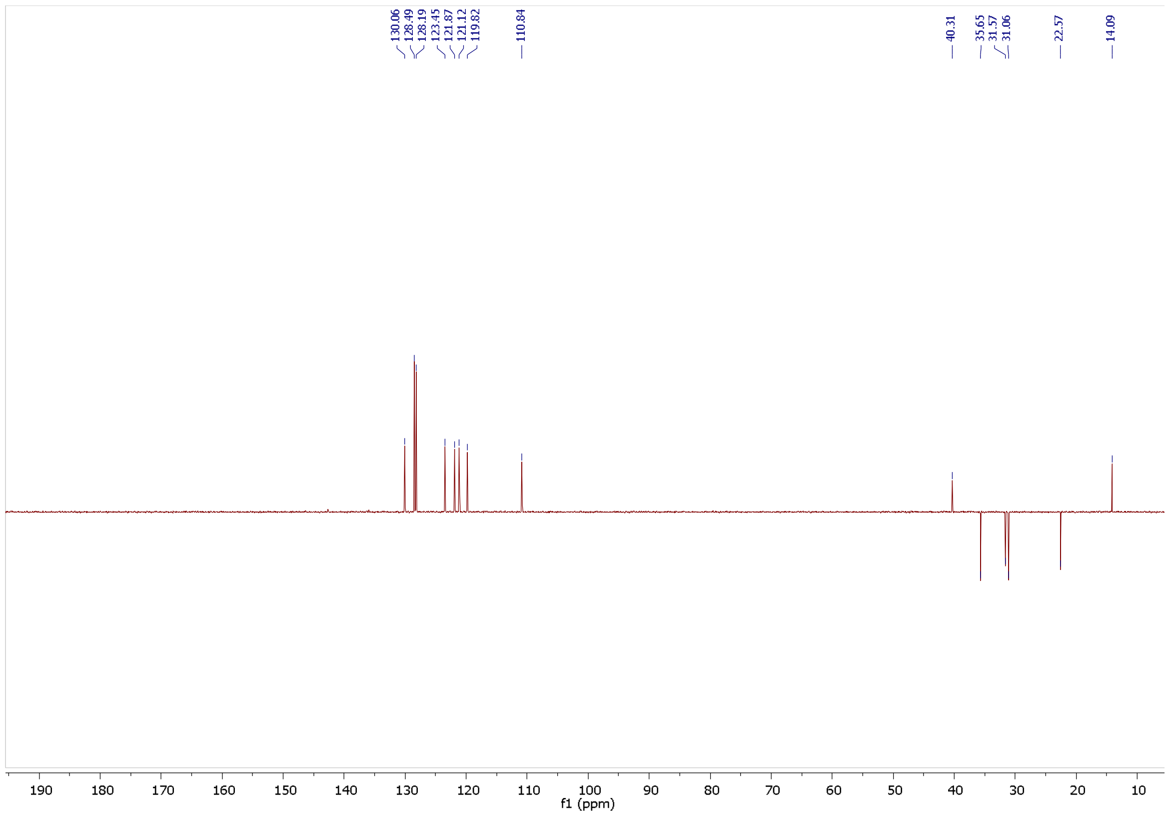
^{19}F NMR (376 MHz, DMSO-d_6) of Compound (**3dF**)



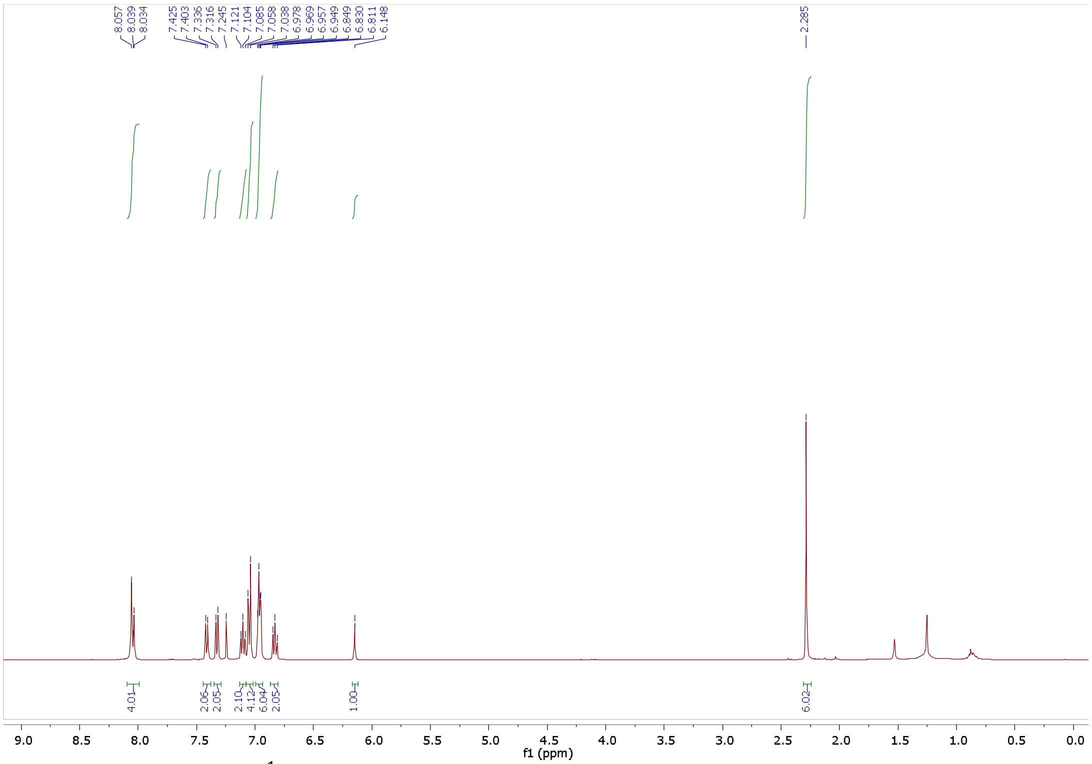
^{1}H NMR (400 MHz, $CDCl_3$) of Compound (**3eF**)



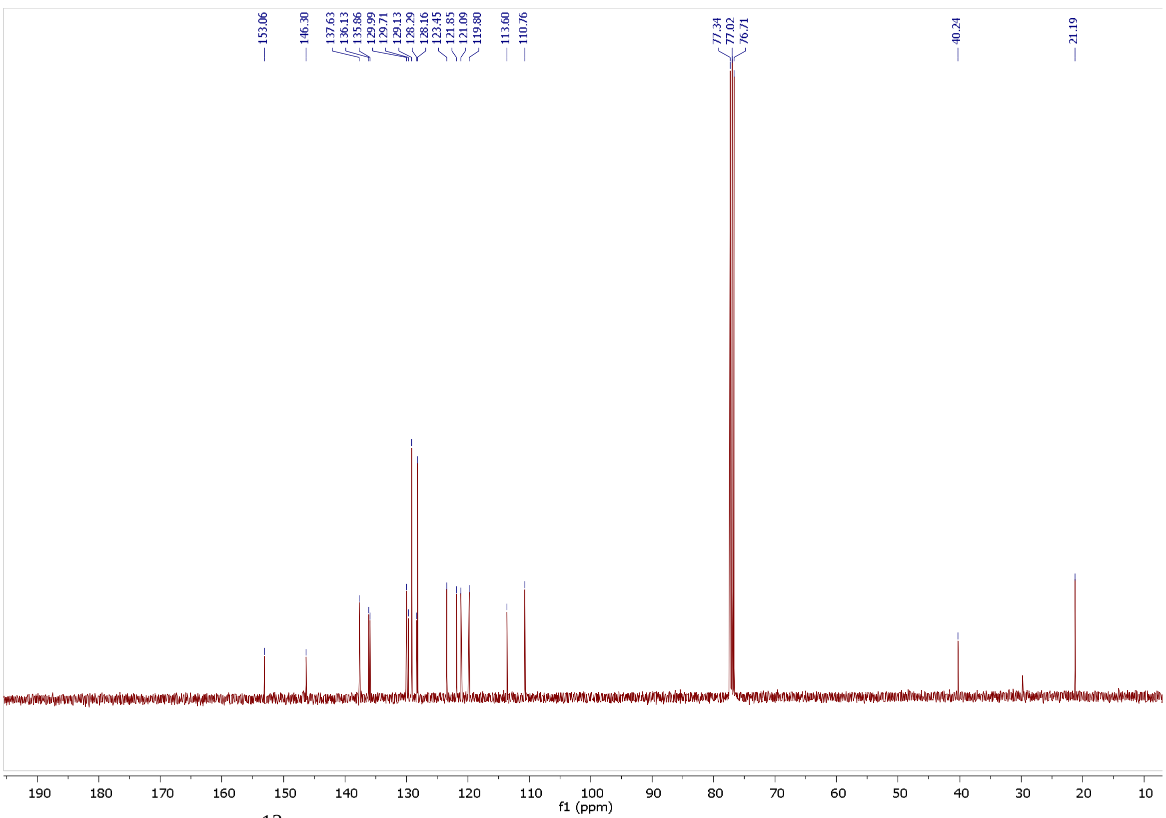
^{13}C NMR (100 MHz, $CDCl_3$) of Compound (**3eF)**



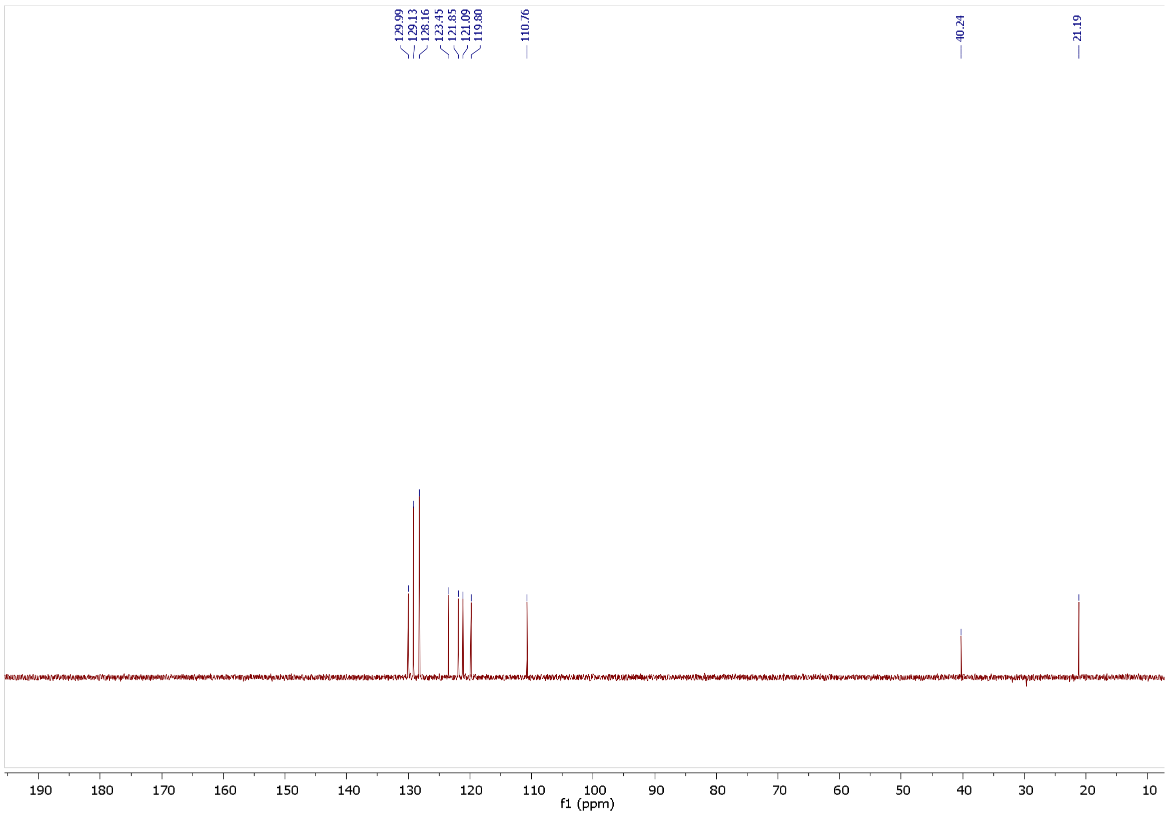
DEPT NMR (100 MHz, $CDCl_3$) of Compound (**3eF**)



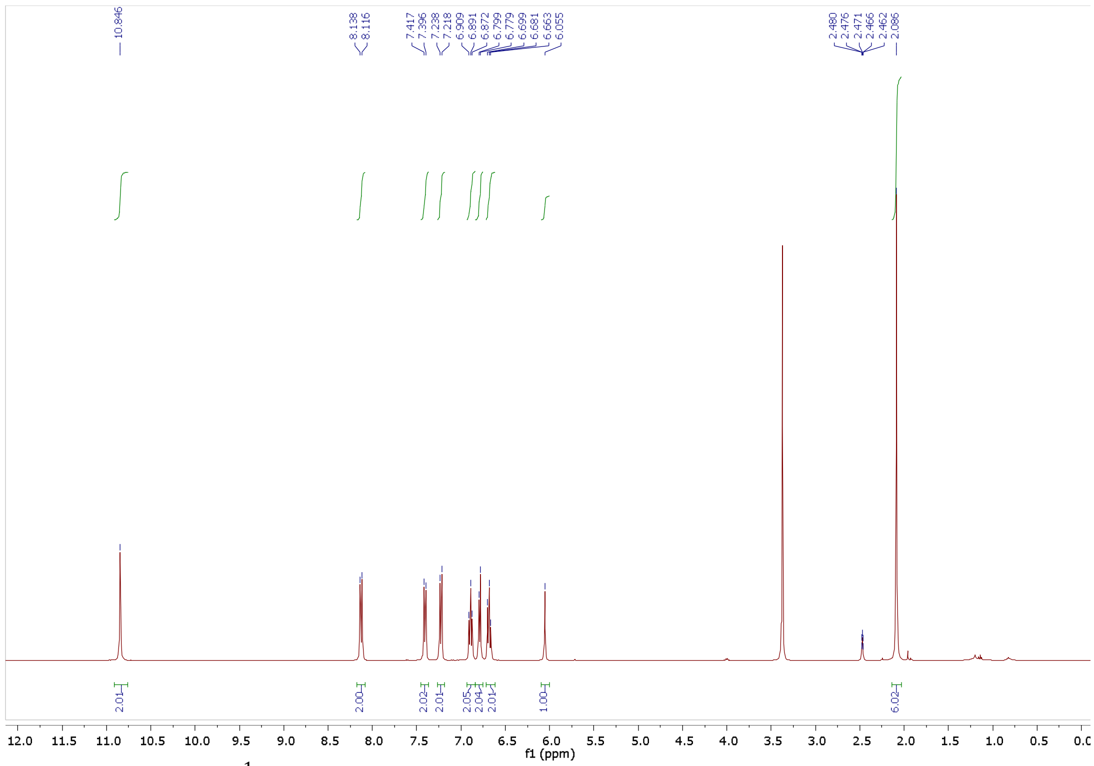
^{1}H NMR (400 MHz, $CDCl_3$) of Compound (**3fF**)



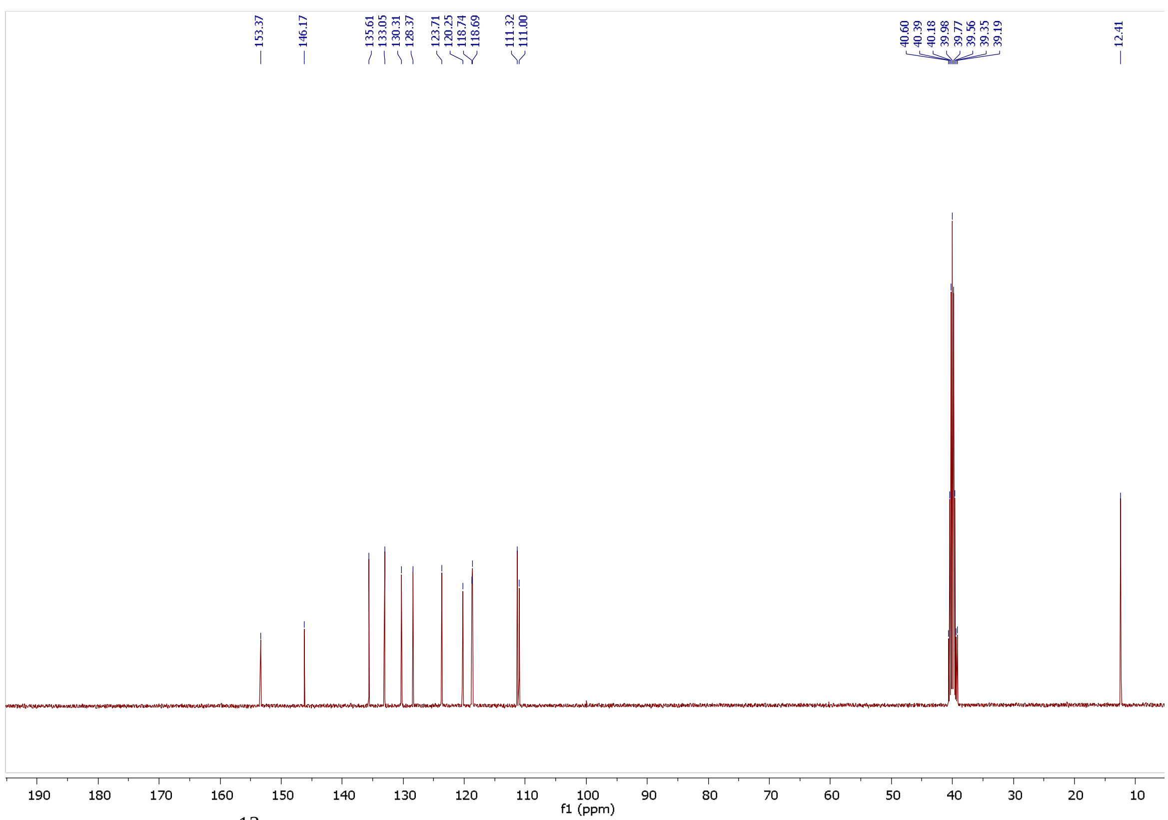
^{13}C NMR (100 MHz, $CDCl_3$) of Compound (**3fF)**



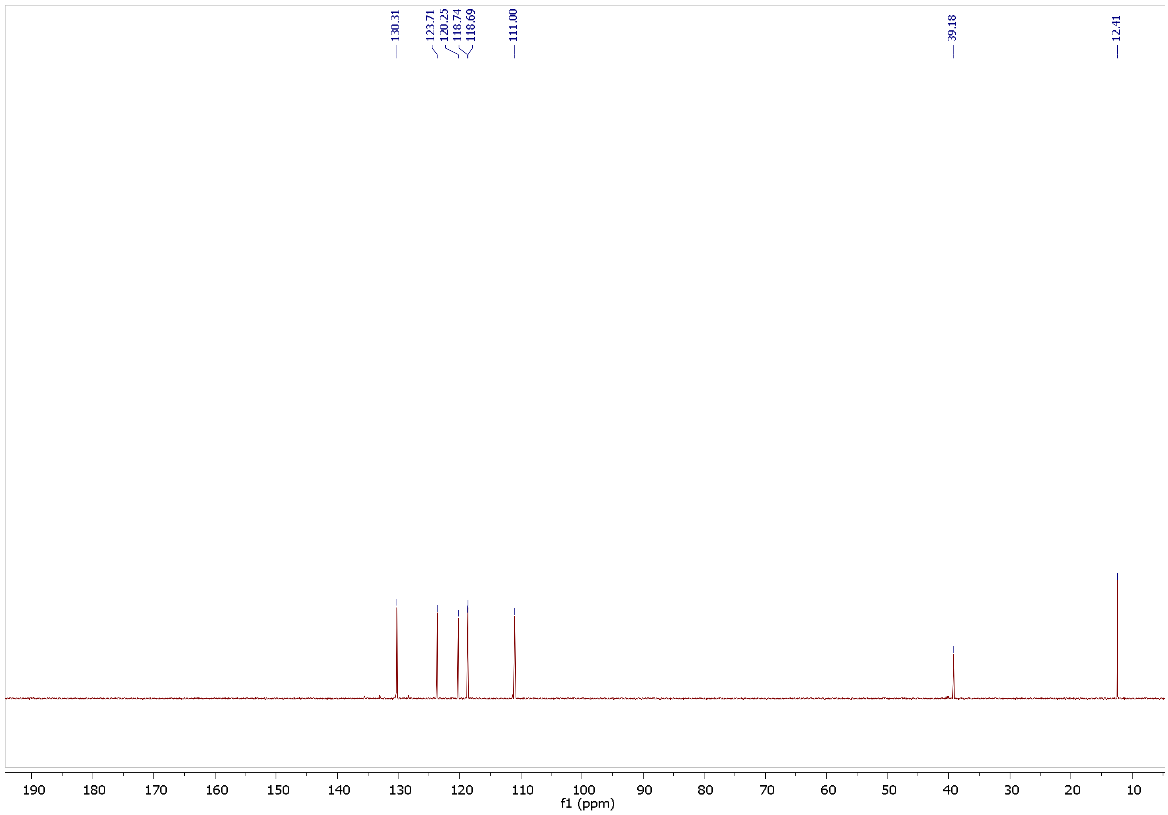
DEPT NMR (100 MHz, $CDCl_3$) of Compound (**3fF**)



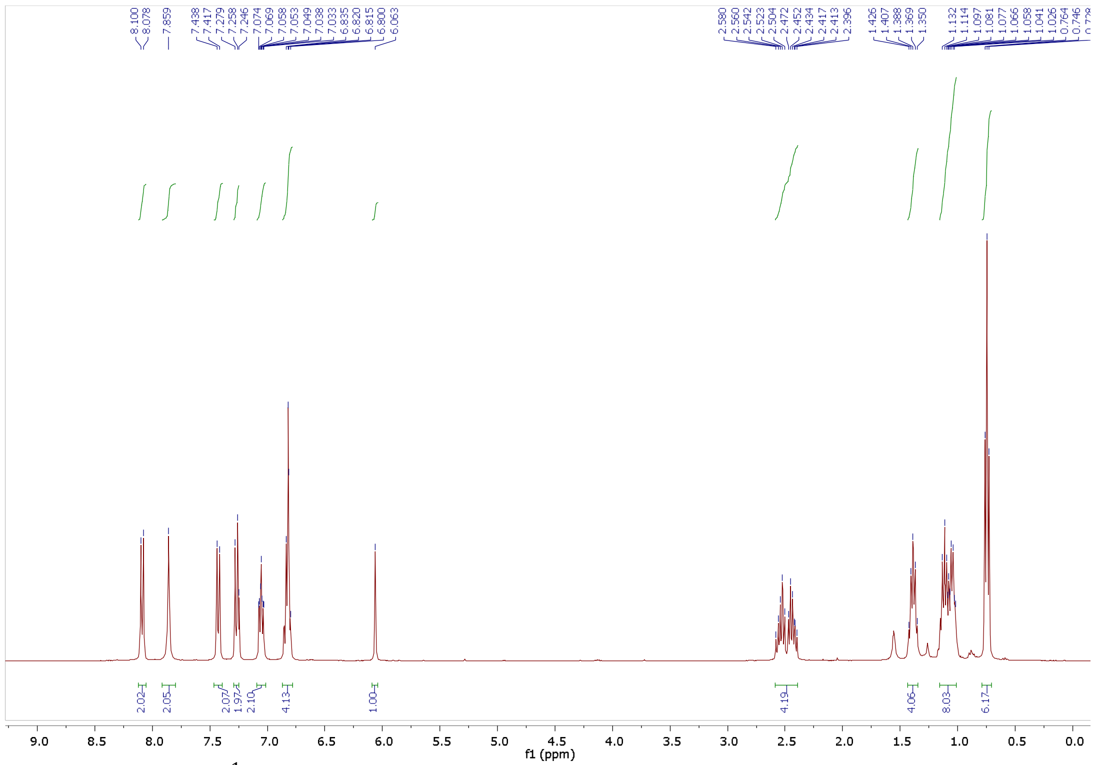
^{1}H NMR (400 MHz, DMSO-d_6) of Compound (**3gF**)



^{13}C NMR (100 MHz, DMSO-d_6) of Compound (**3gF**)



DEPT NMR (100 MHz, DMSO-d_6) of Compound (**3gF**)



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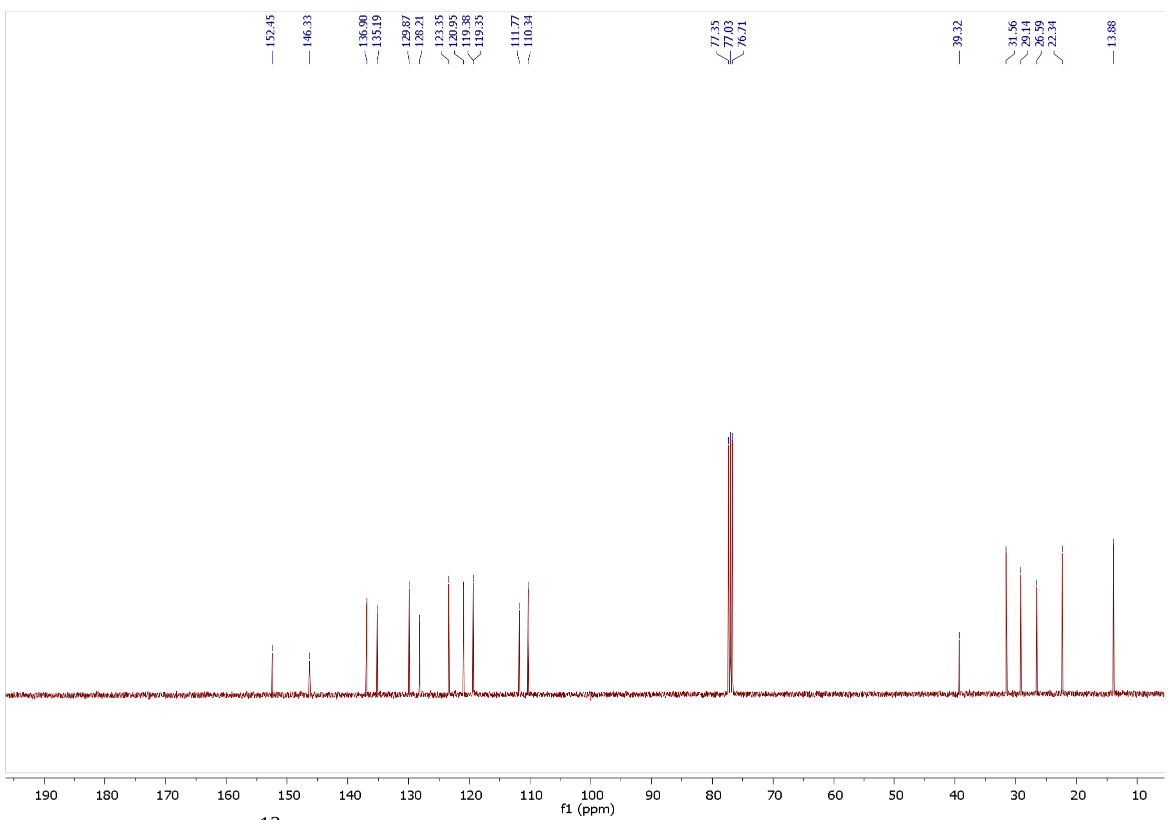
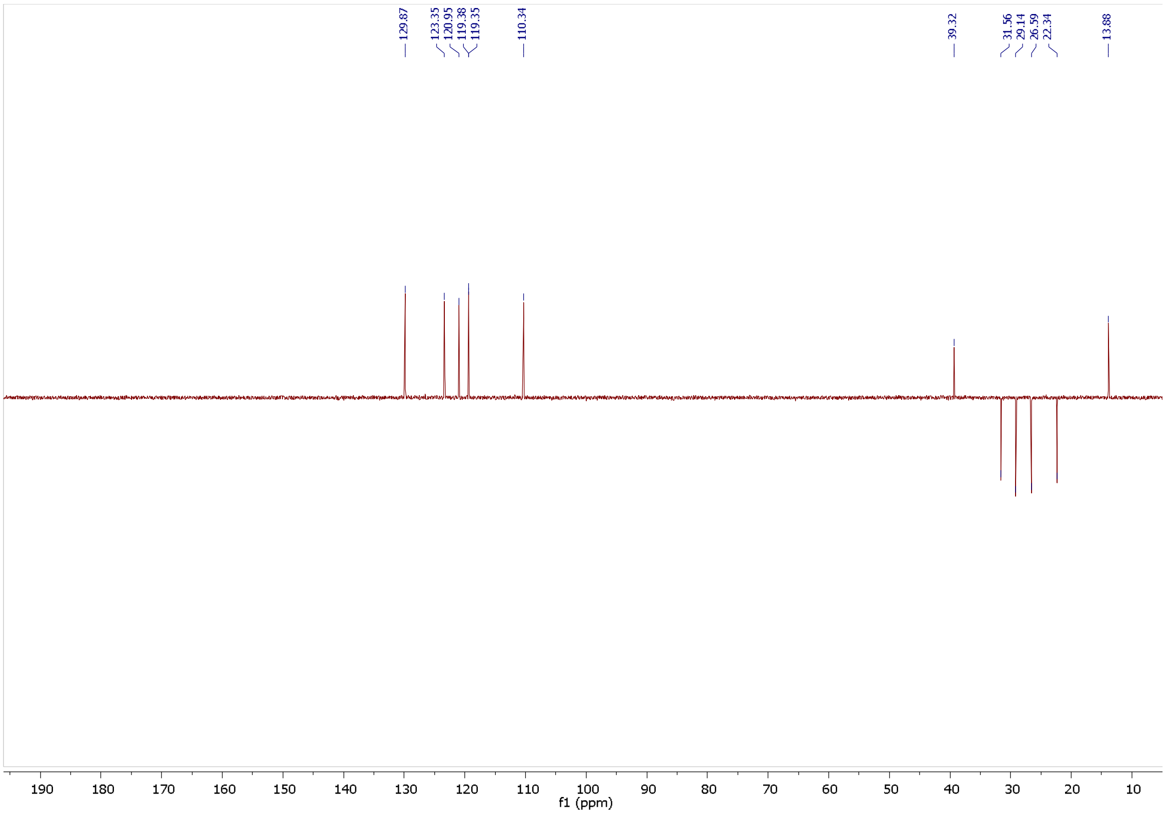
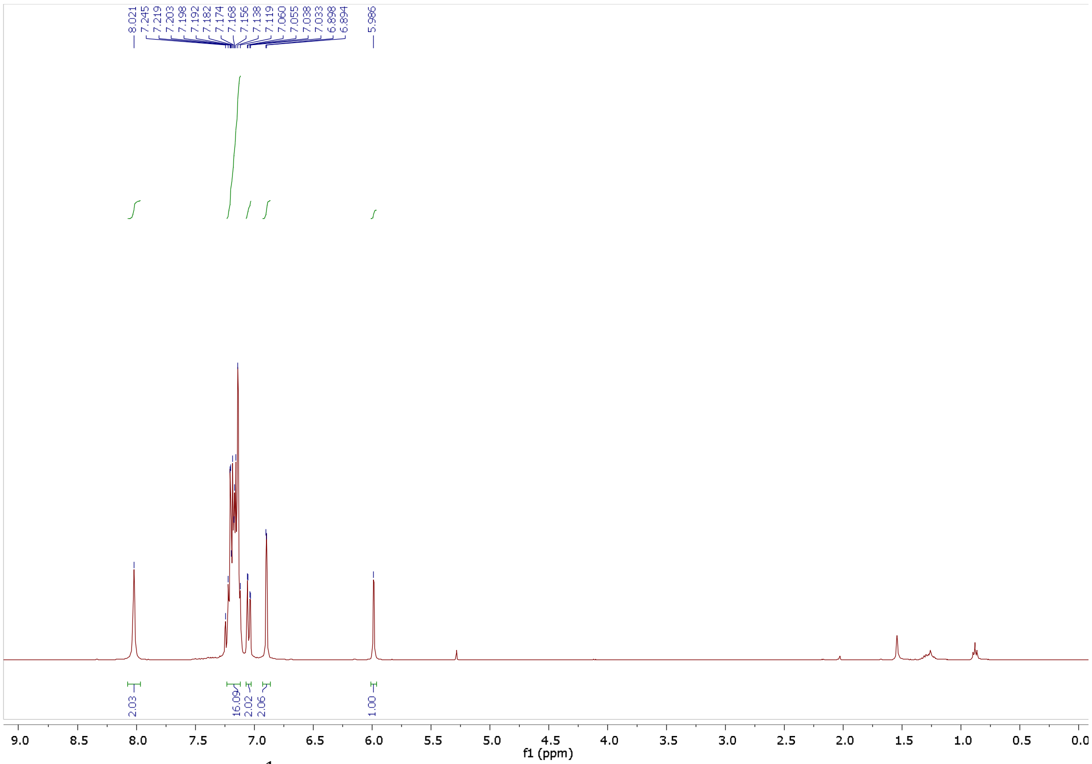


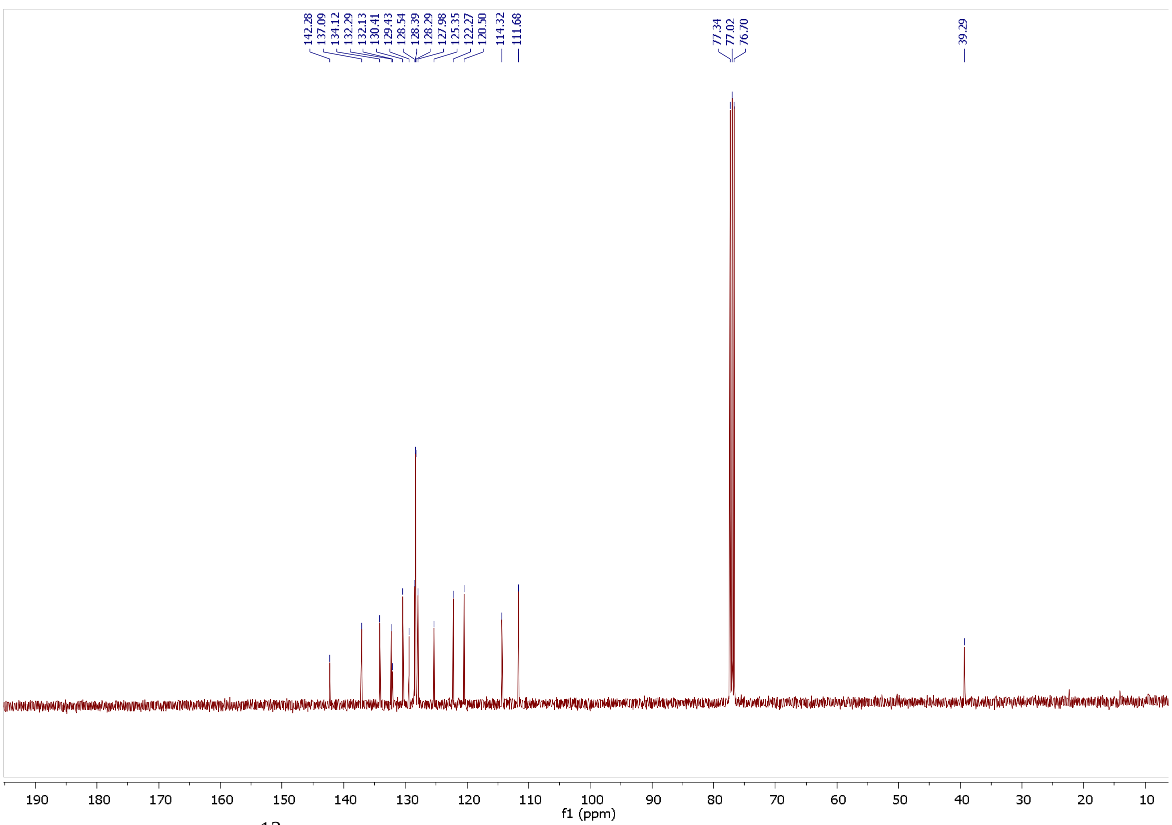
^{13}C NMR (100 MHz, $CDCl_3$) of Compound (**3hF)**



DEPT NMR (100 MHz, $CDCl_3$) of Compound (**3hF**)



^{1}H NMR (400 MHz, $CDCl_3$) of Compound (**3iC**)



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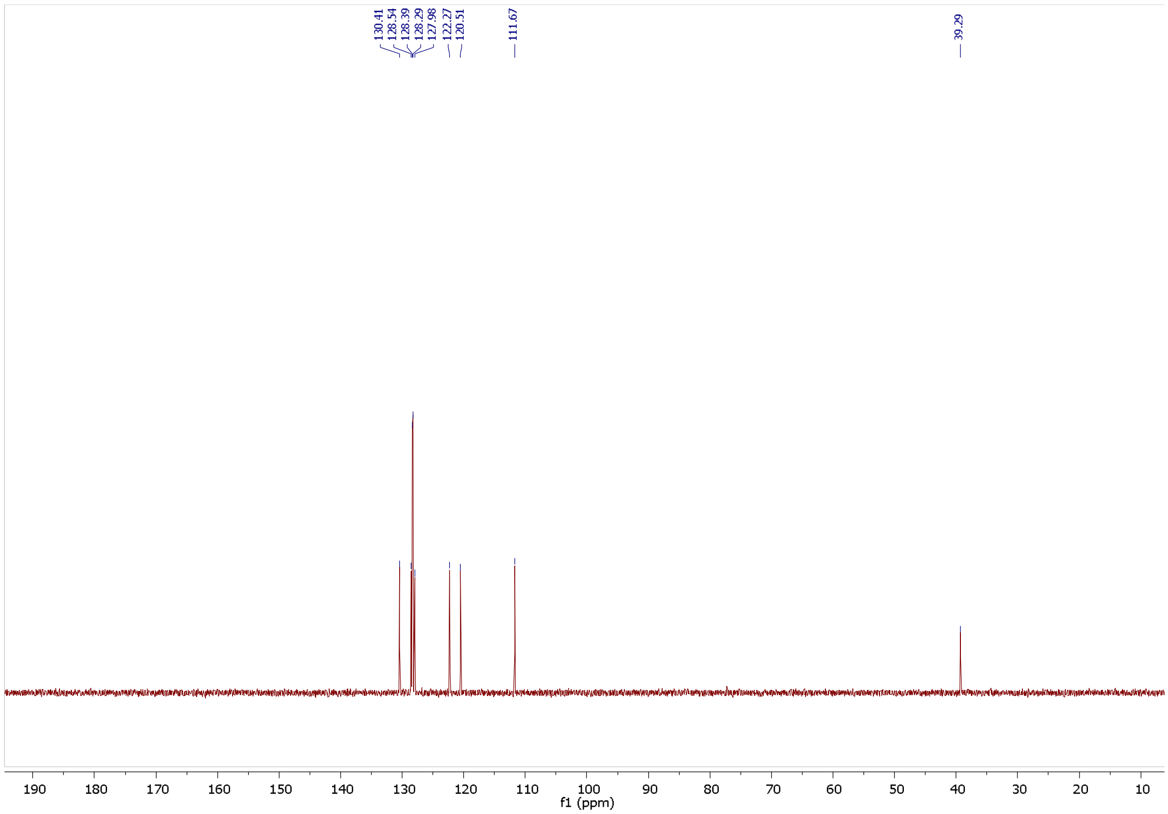
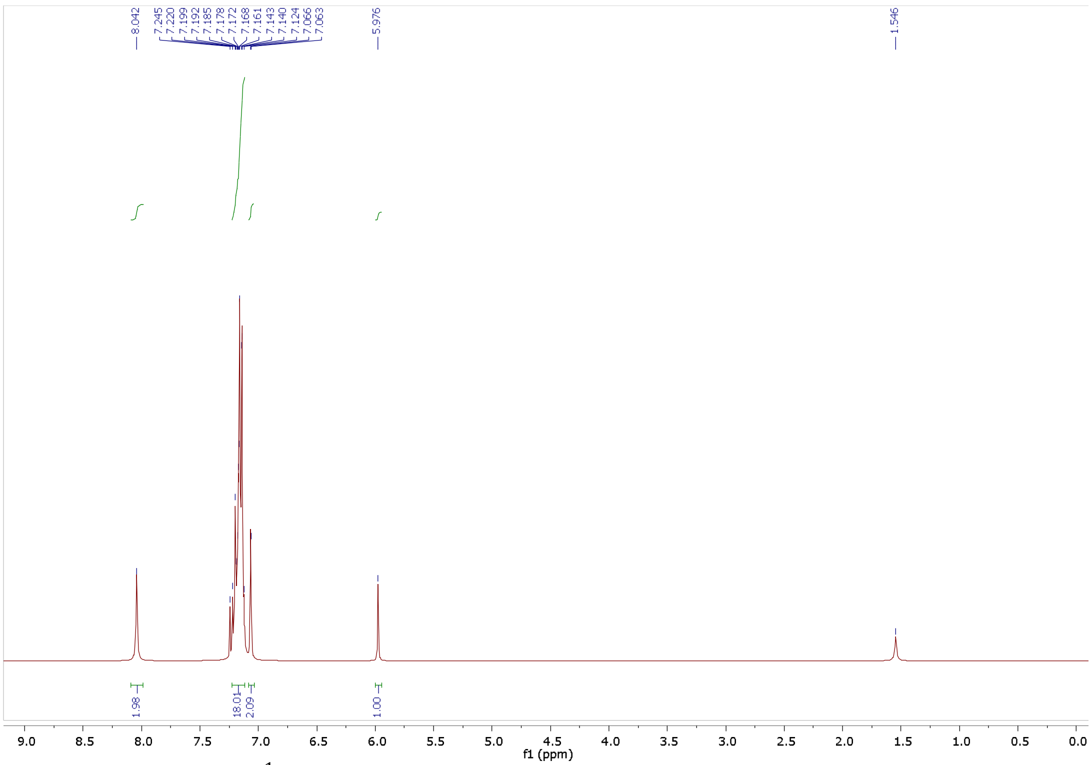


DEPT NMR (100 MHz, $CDCl_3$) of Compound (**3iC**)



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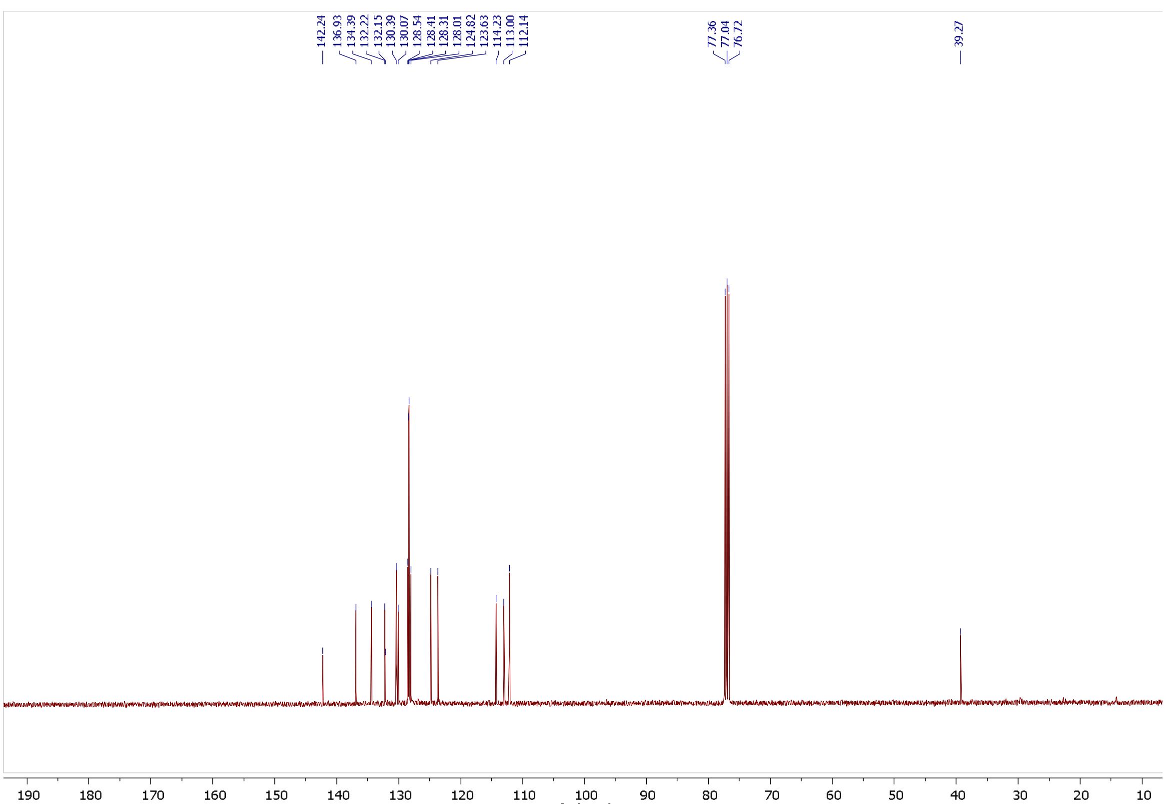
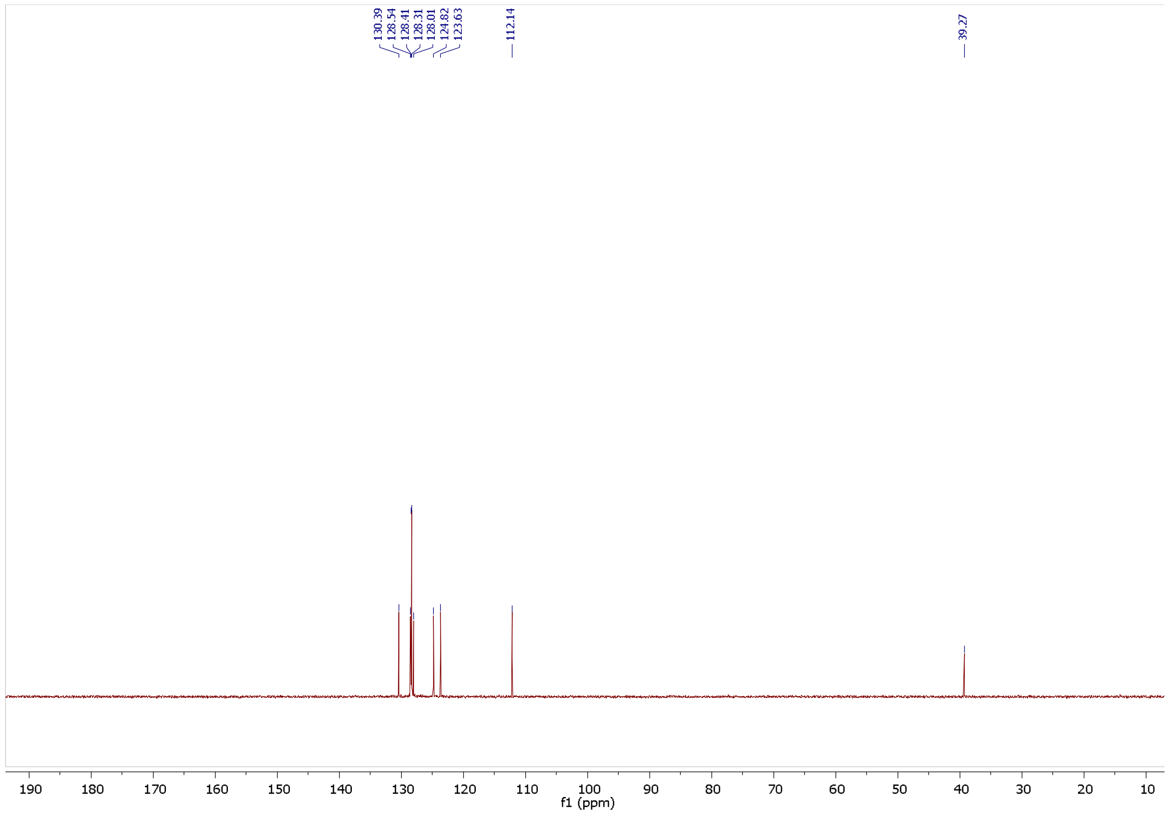
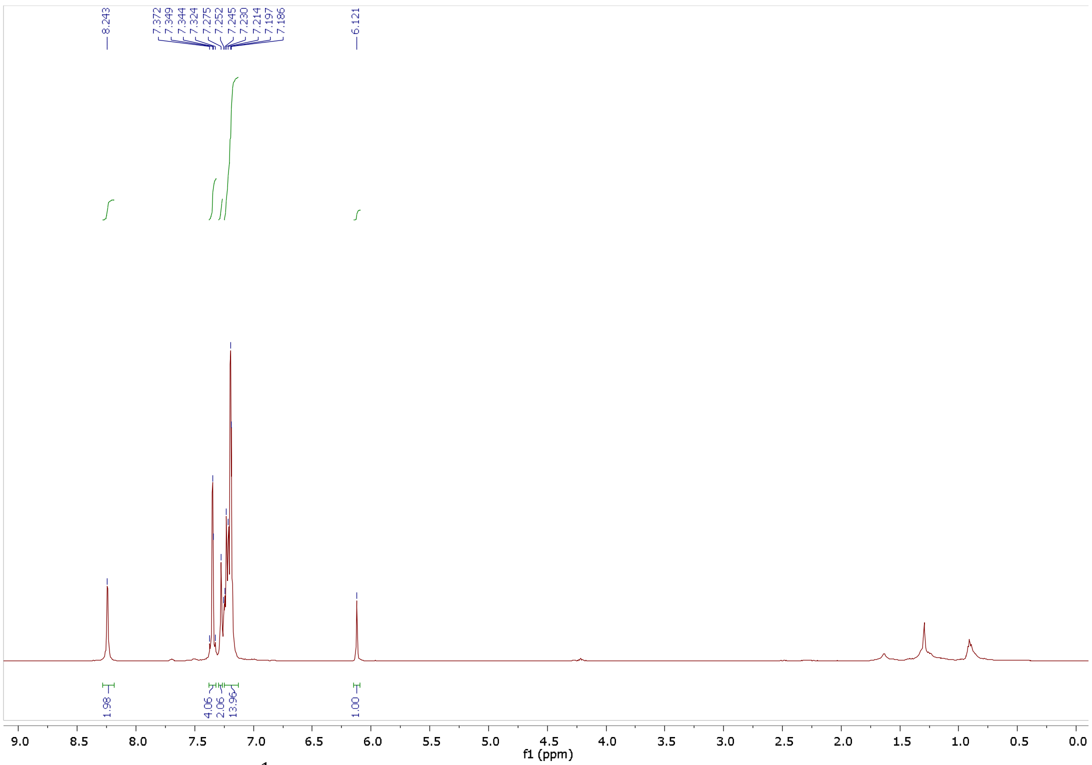


^{13}C NMR (100 MHz, $CDCl_3$) of Compound (**3jC)**



DEPT NMR (100 MHz, $CDCl_3$) of Compound (**3jC**)



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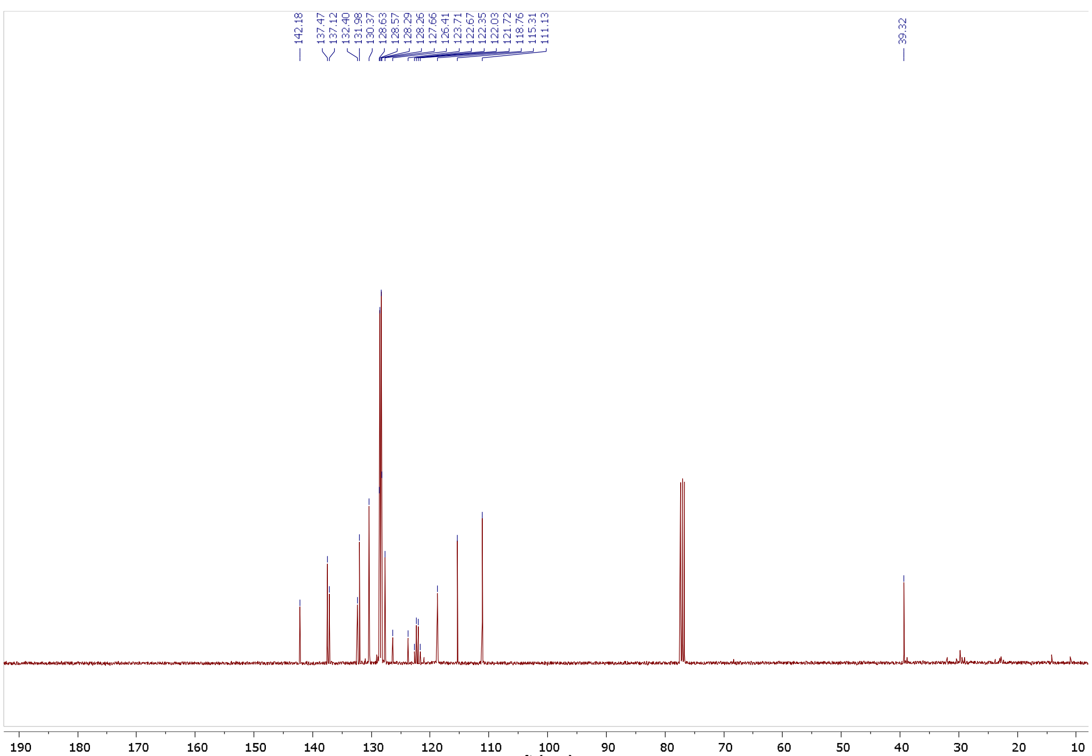
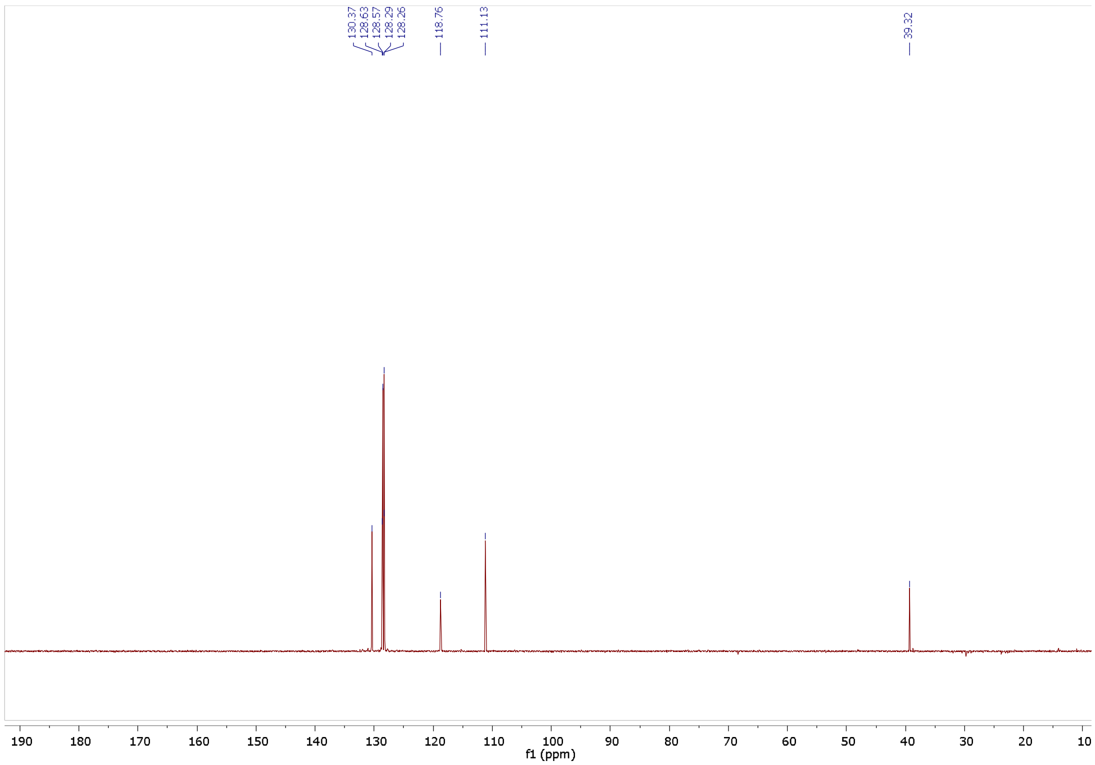
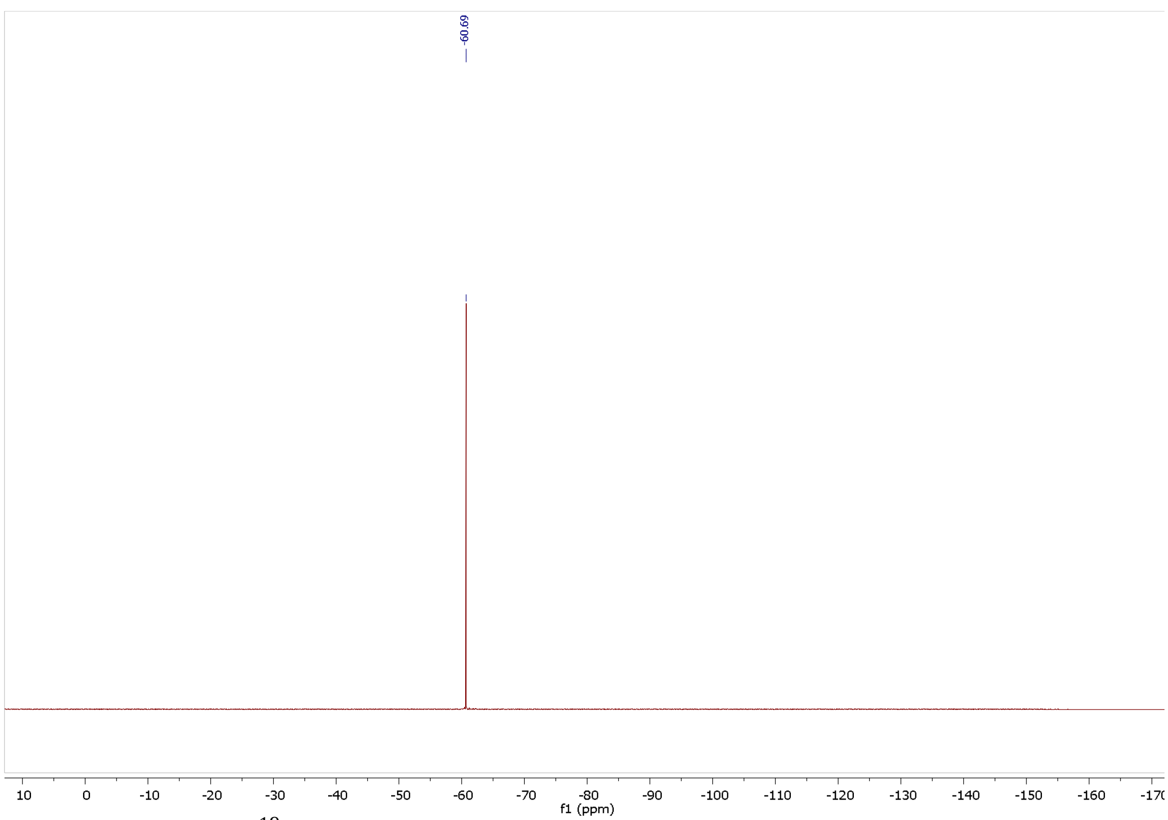


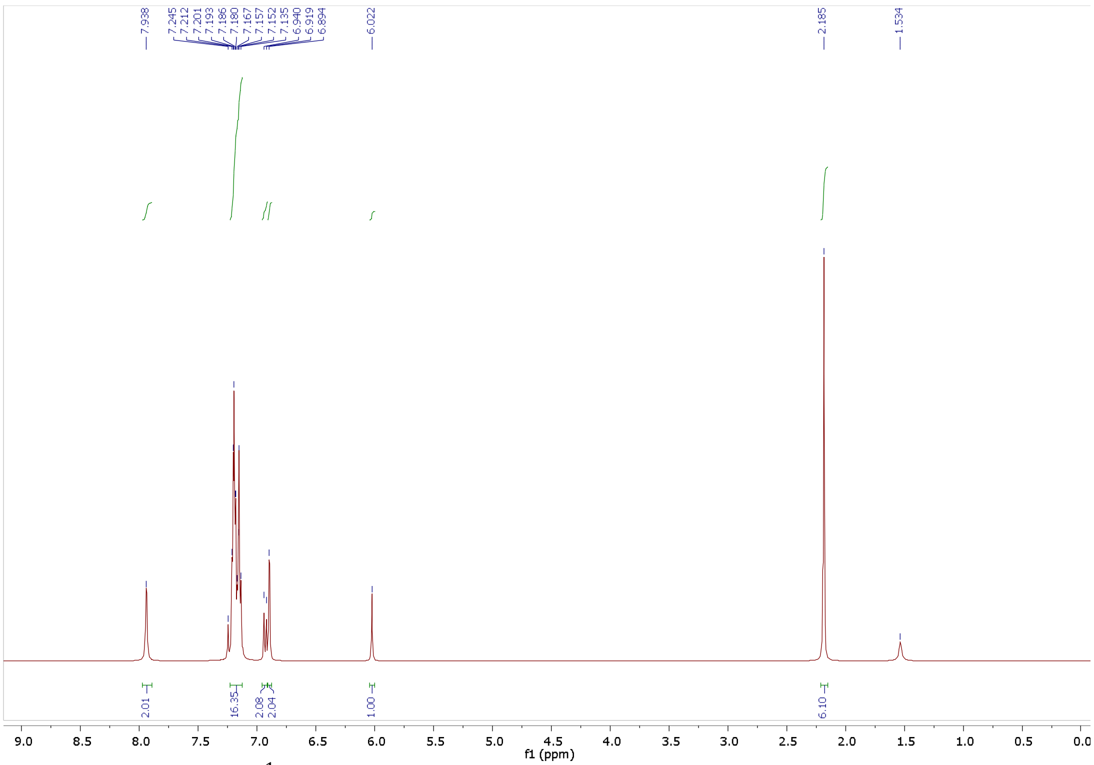
^{13}C NMR (100 MHz, $CDCl_3$) of Compound (**3kC)**



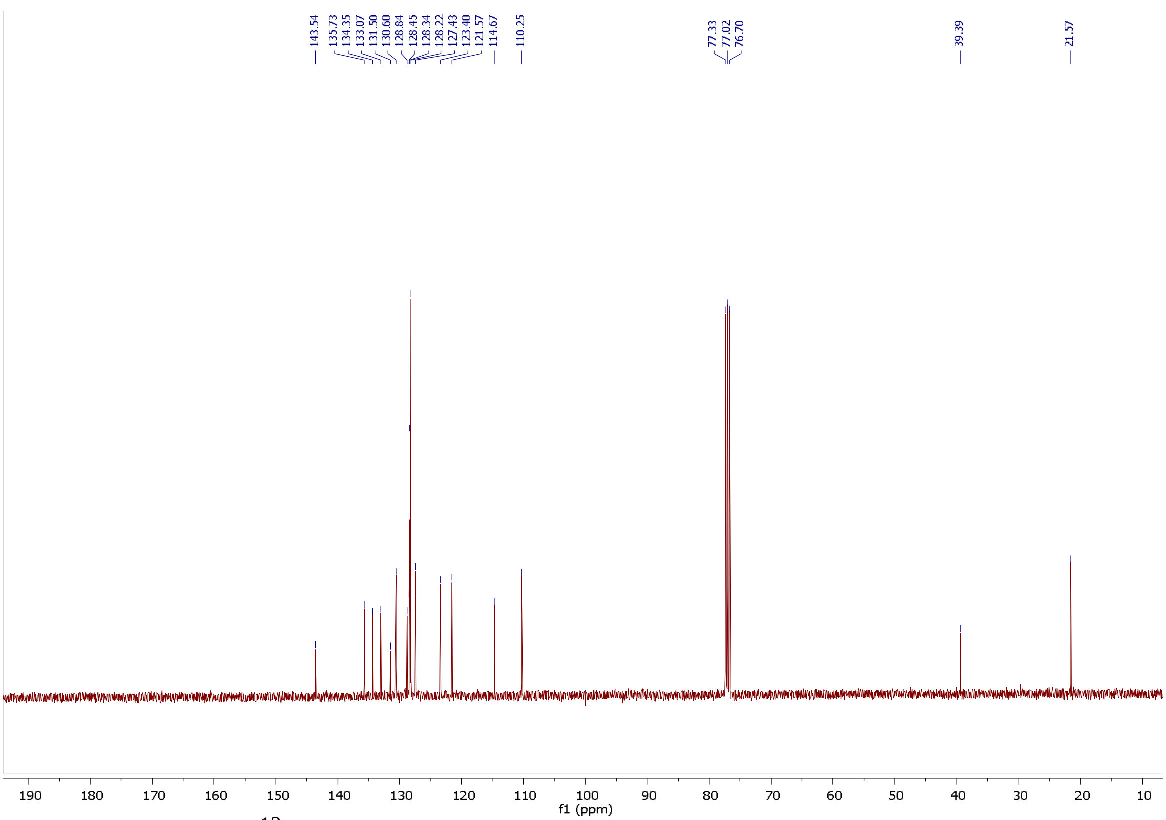
DEPT NMR (100 MHz, $CDCl_3$) of Compound (**3kC**)



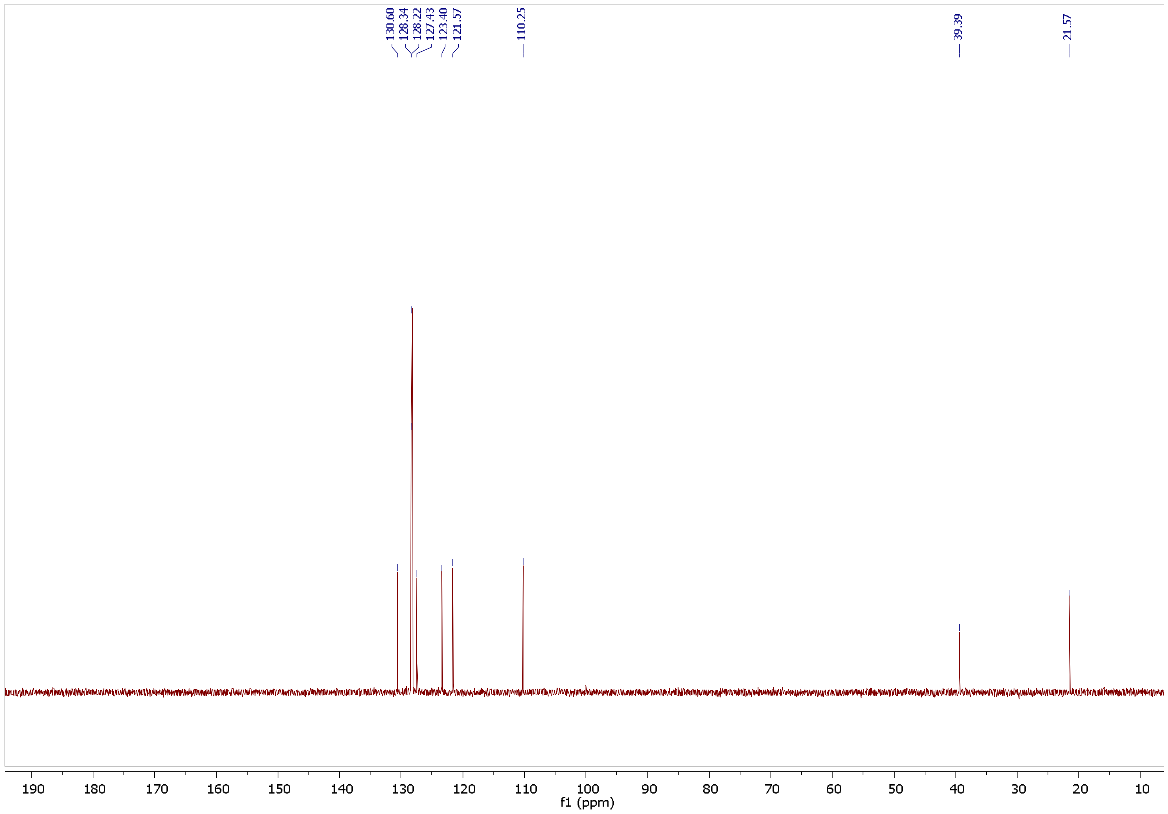
^{19}F NMR (376 MHz, $CDCl_3$) of Compound (**3kC**)



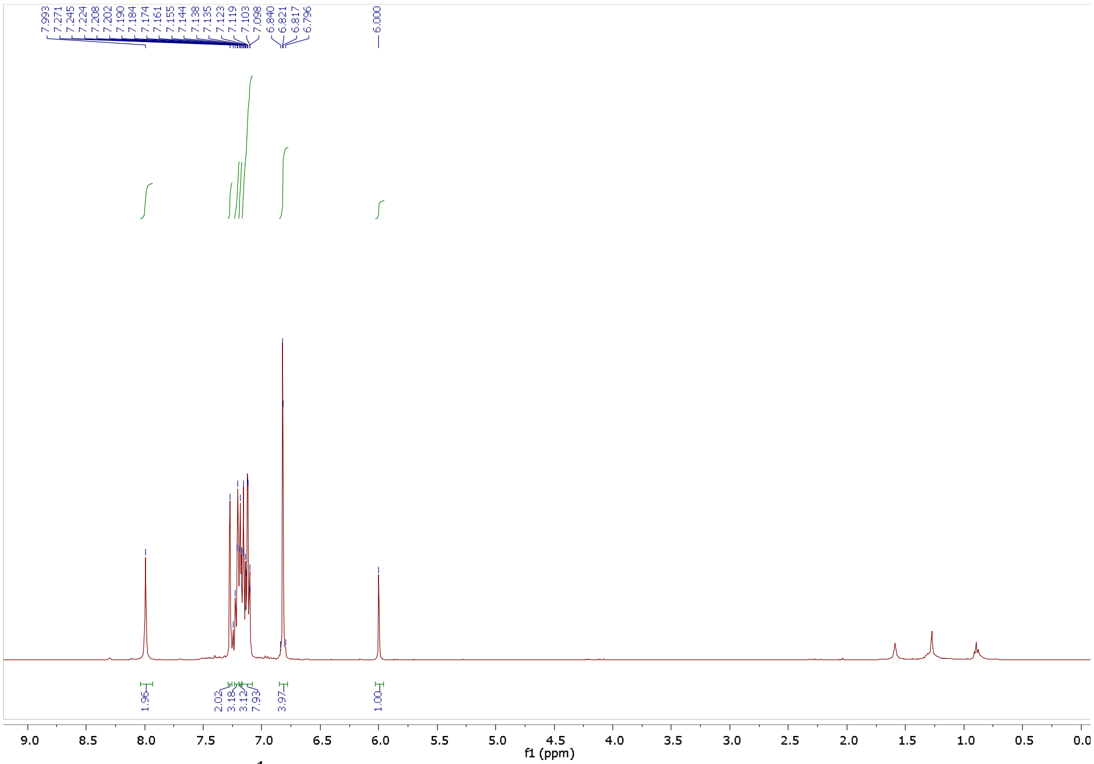
^{1}H NMR (400 MHz, $CDCl_3$) of Compound (**3lC**)



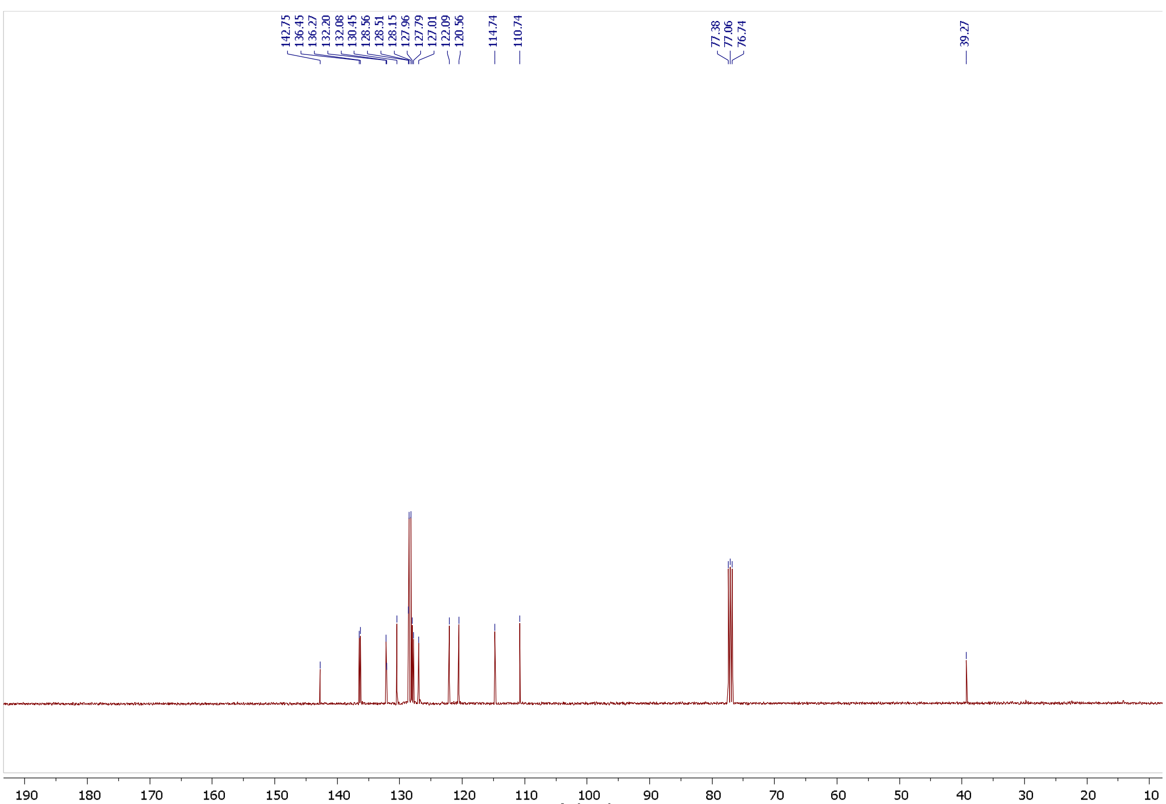
^{13}C NMR (100 MHz, $CDCl_3$) of Compound (**3lC**)



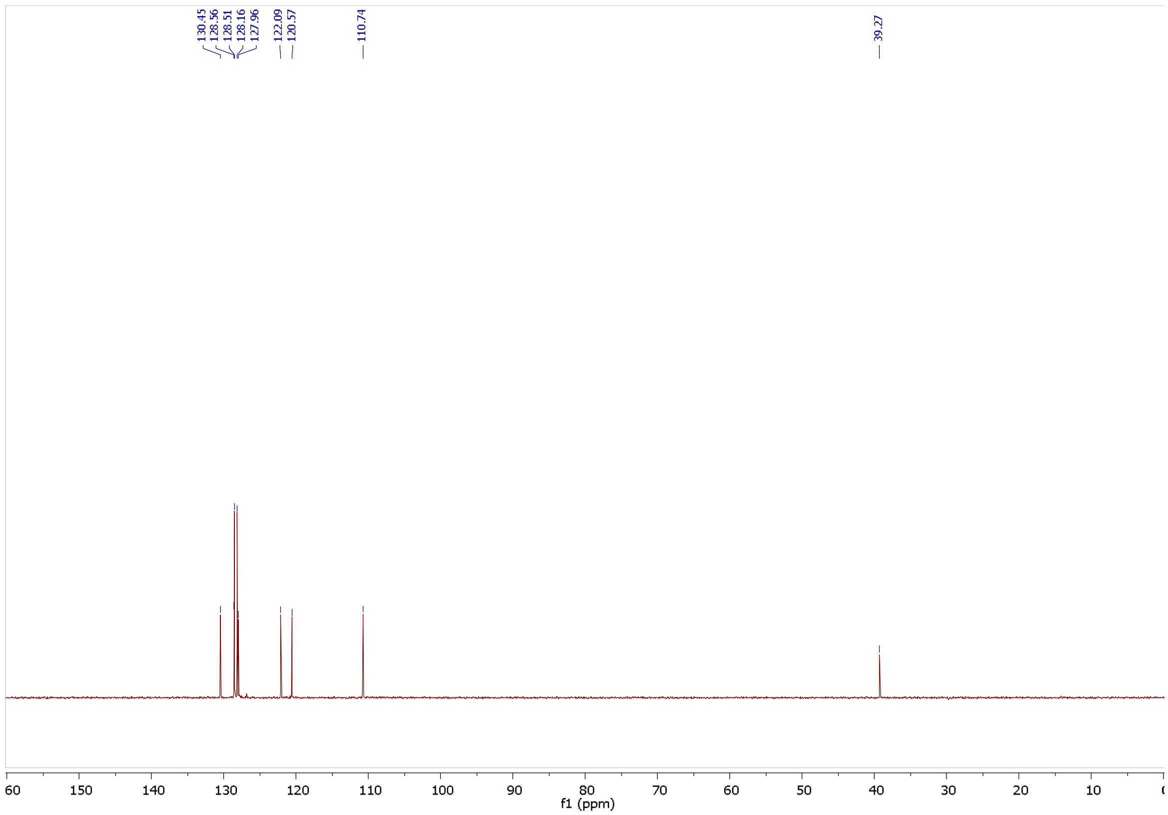
DEPT NMR (100 MHz, $CDCl_3$) of Compound (**3lC**)



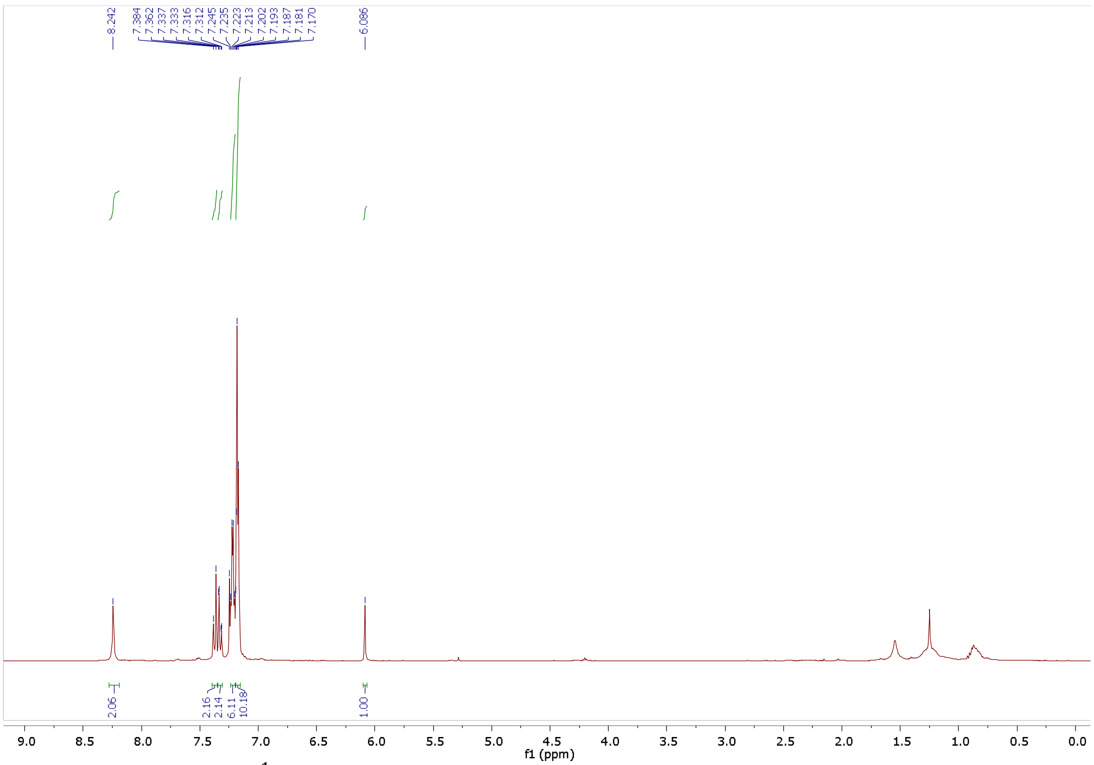
^{1}H NMR (400 MHz, $CDCl_3$) of Compound (**3mC**)



^{13}C NMR (100 MHz, $CDCl_3$) of Compound (**3mC)**



DEPT NMR (100 MHz, $CDCl_3$) of Compound (**3mC**)



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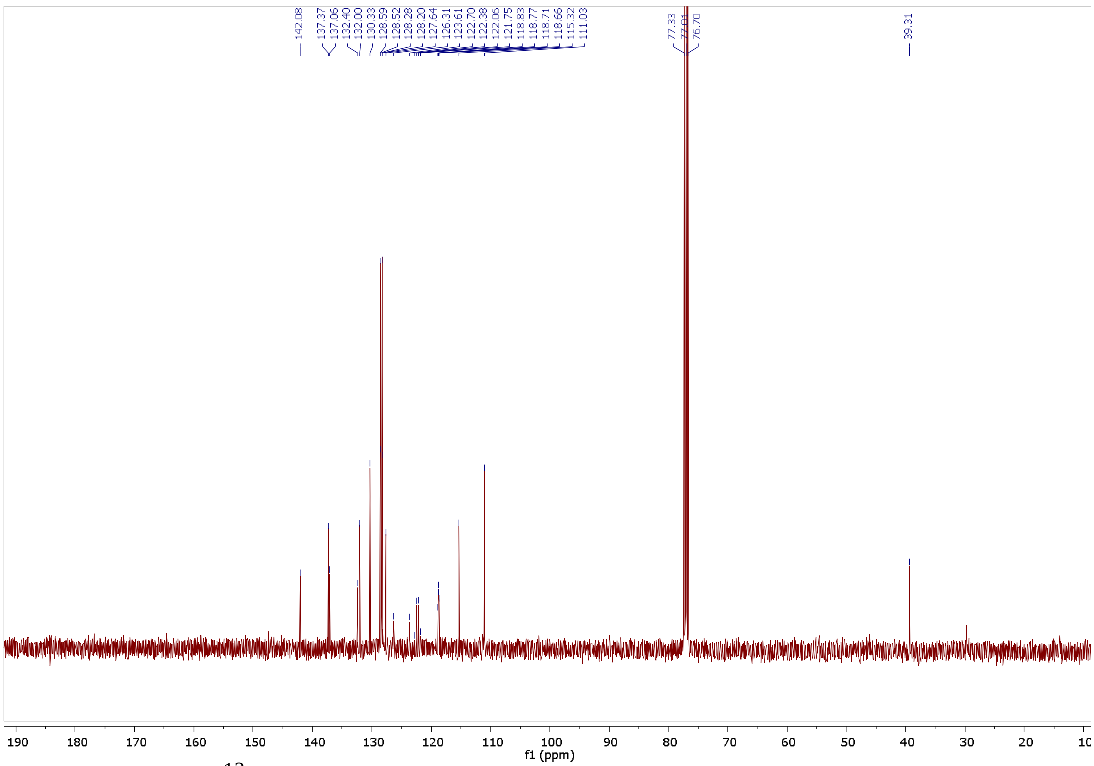
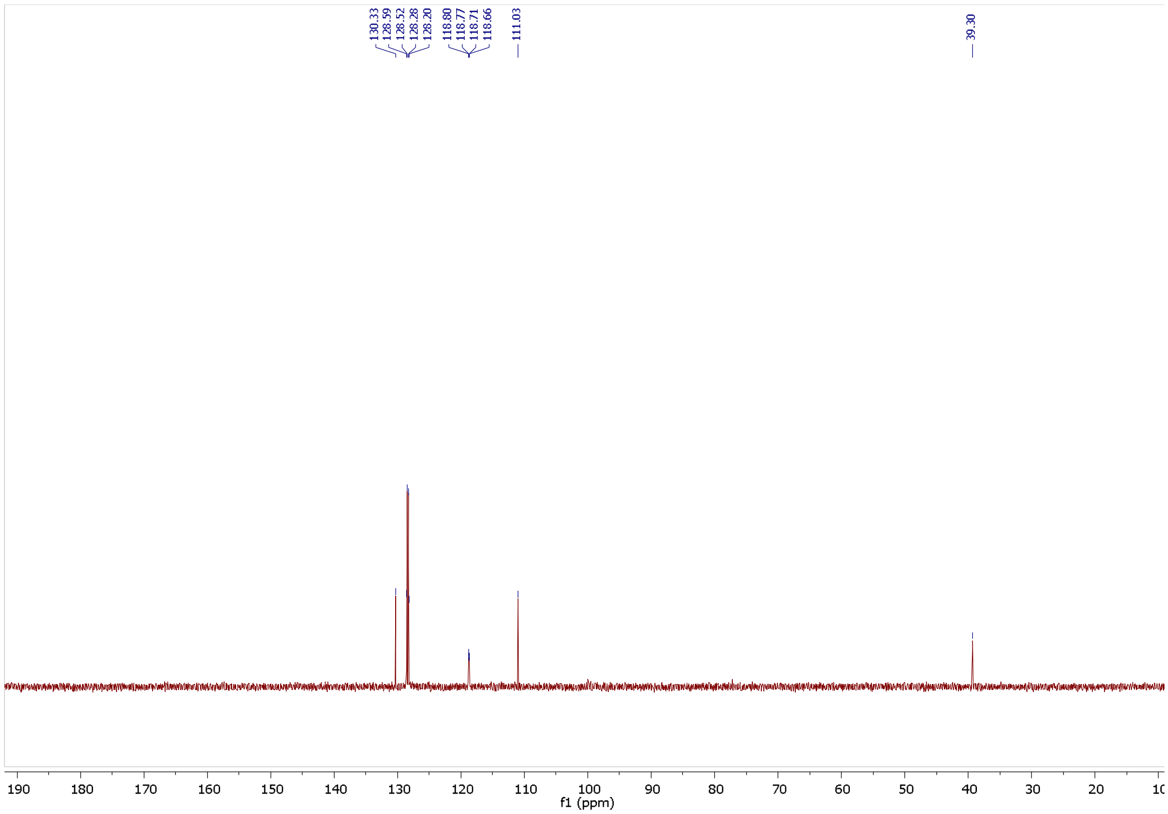
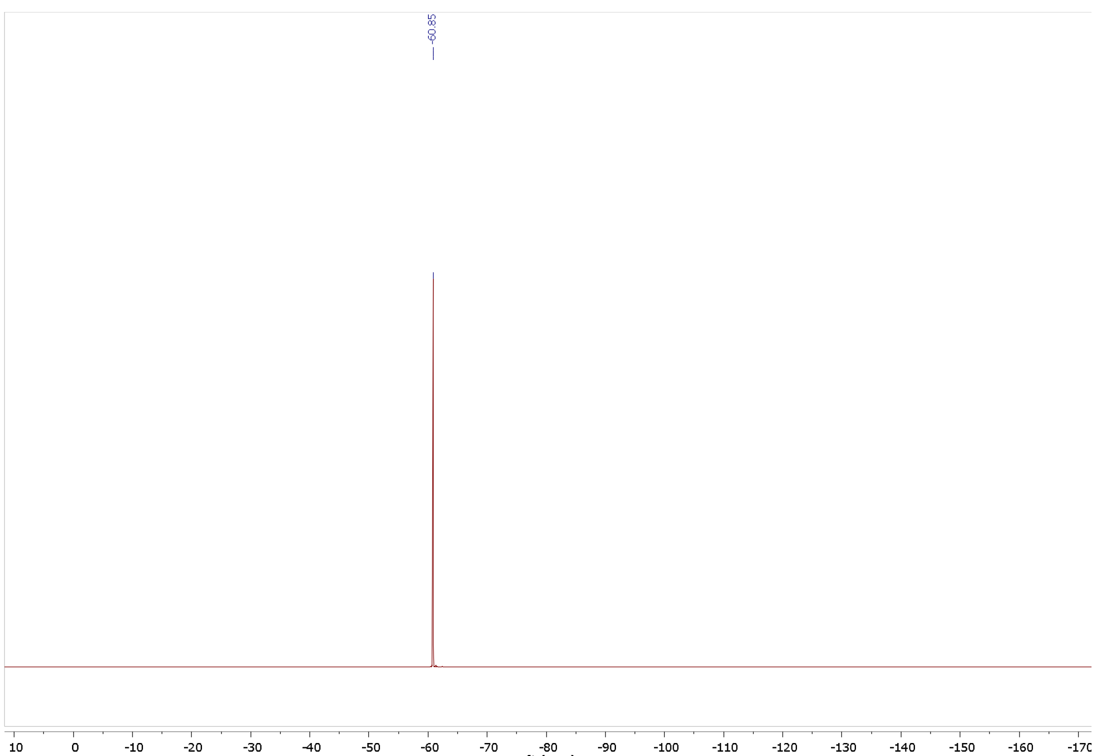


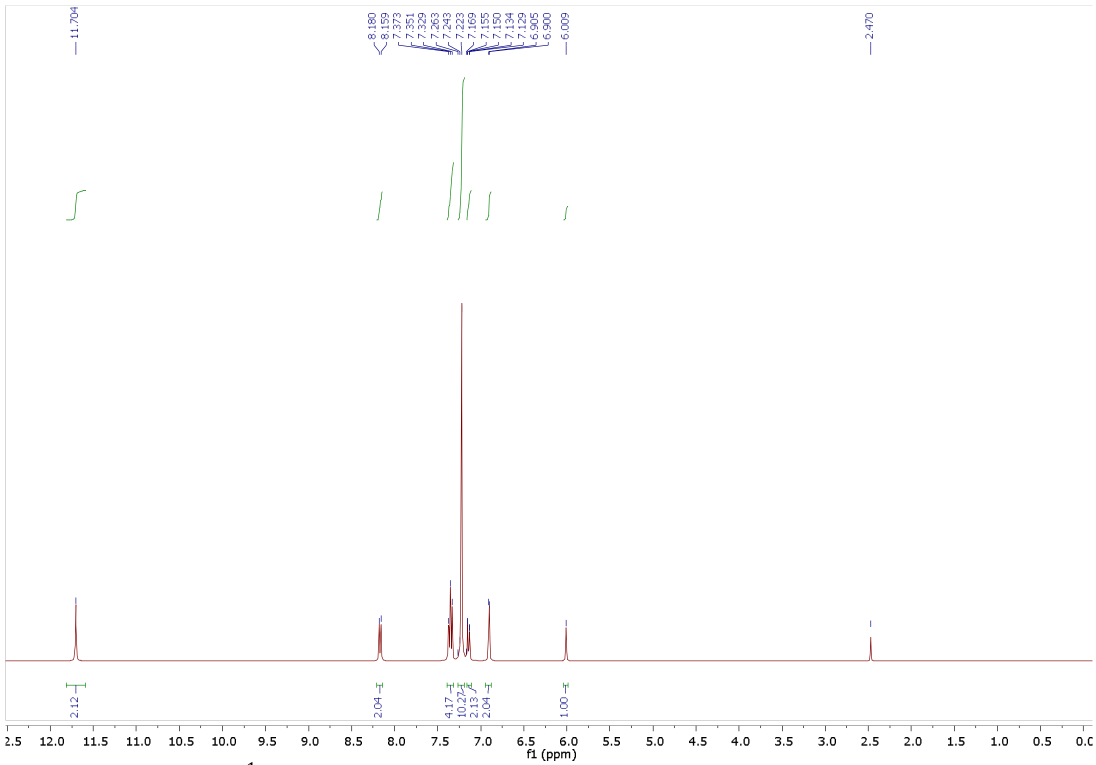
^{13}C NMR (100 MHz, $CDCl_3$) of Compound (**3nC)**



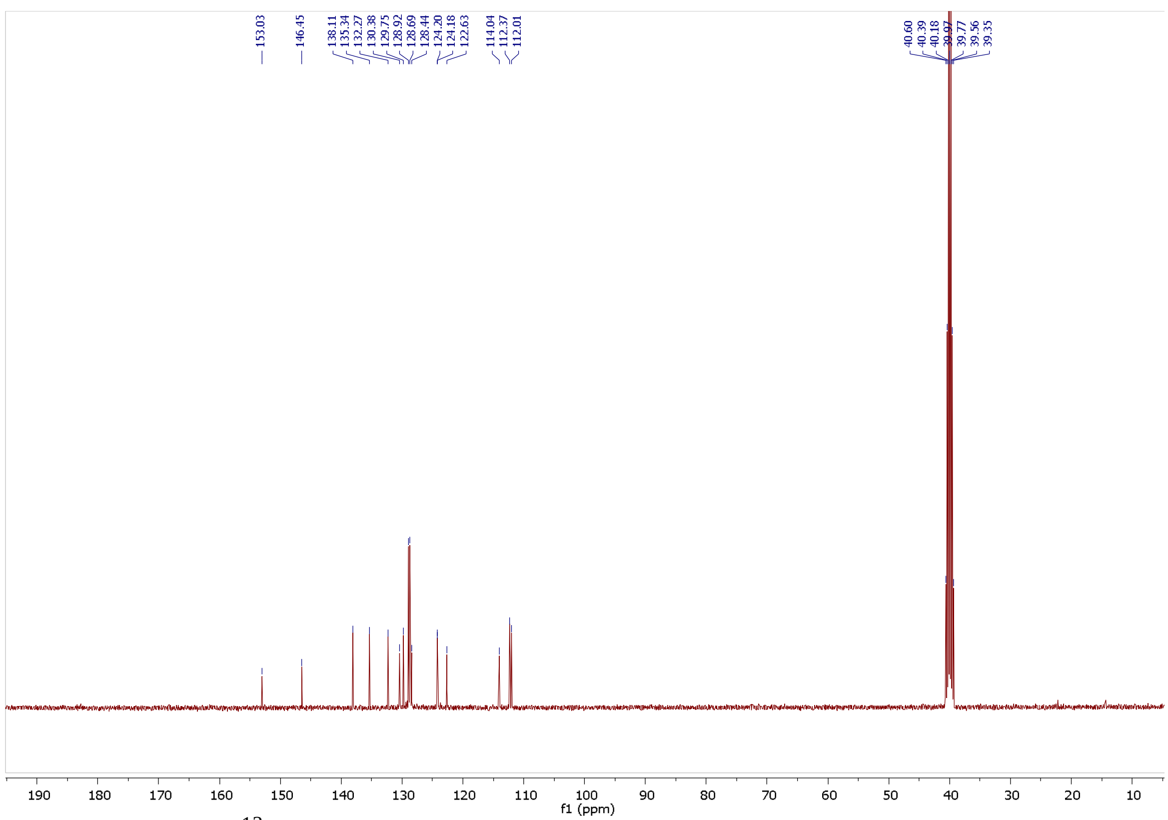
DEPT NMR (100 MHz, $CDCl_3$) of Compound (**3nC**)



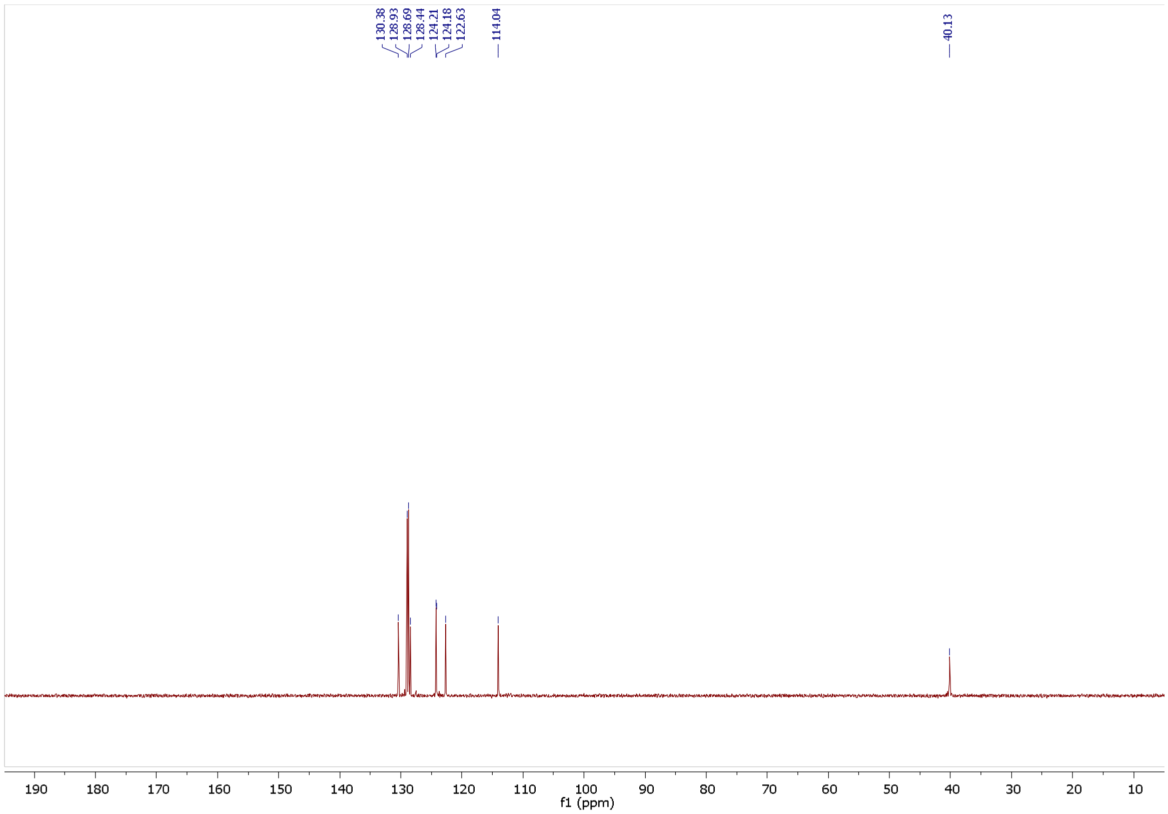
^{19}F NMR (376 MHz, $CDCl_3$) of Compound (**3nC**)



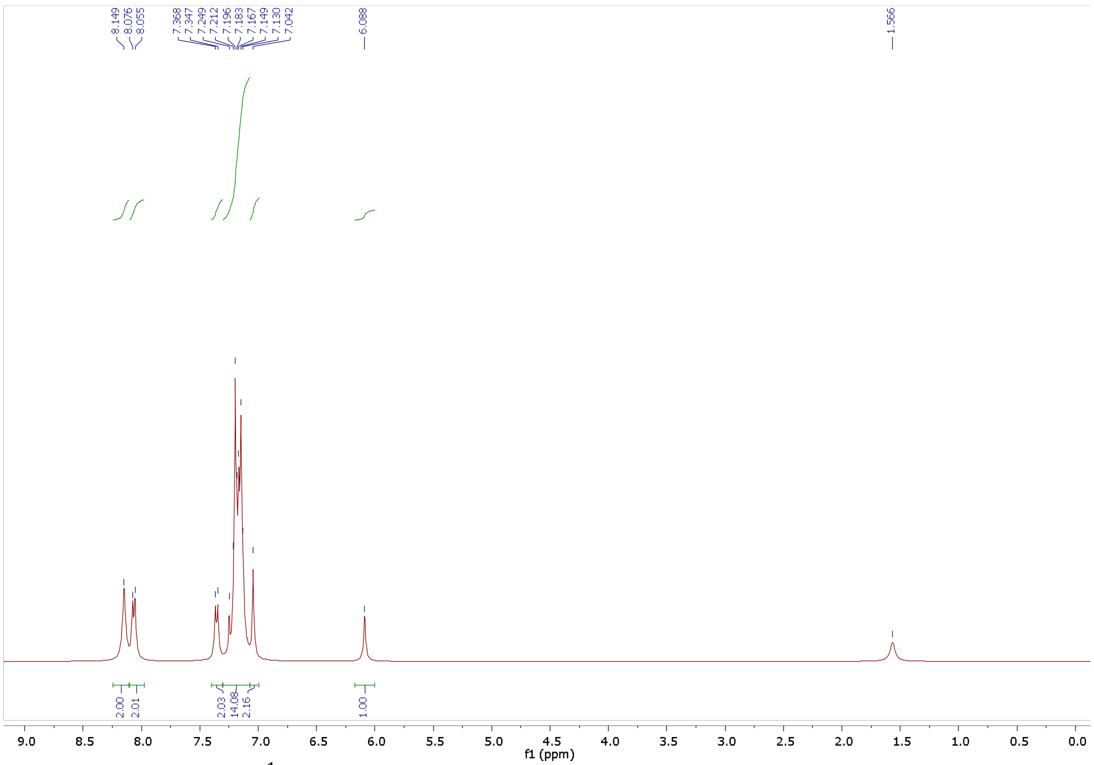
^{1}H NMR (400 MHz, DMSO-d_6) of Compound (**3iF**)



^{13}C NMR (100 MHz, DMSO-d_6) of Compound (**3iF**)



DEPT NMR (100 MHz, DMSO-d_6) of Compound (**3iF**)



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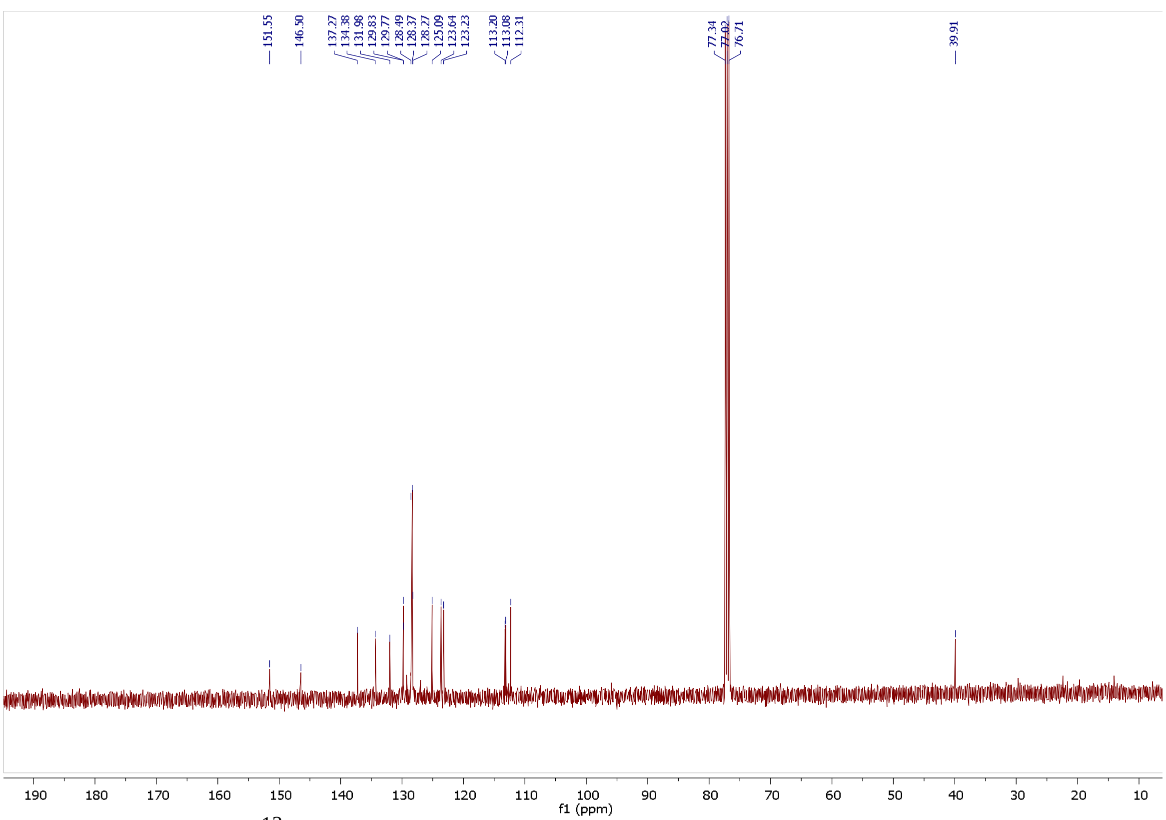

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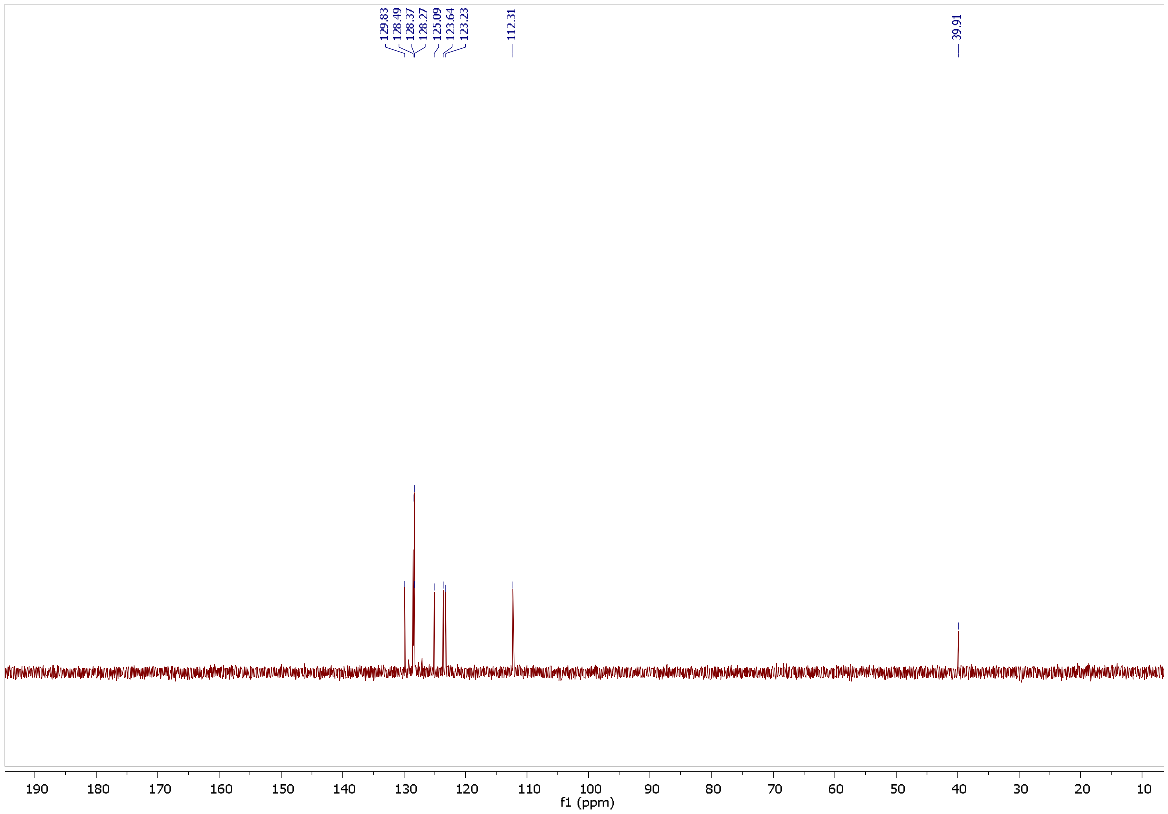

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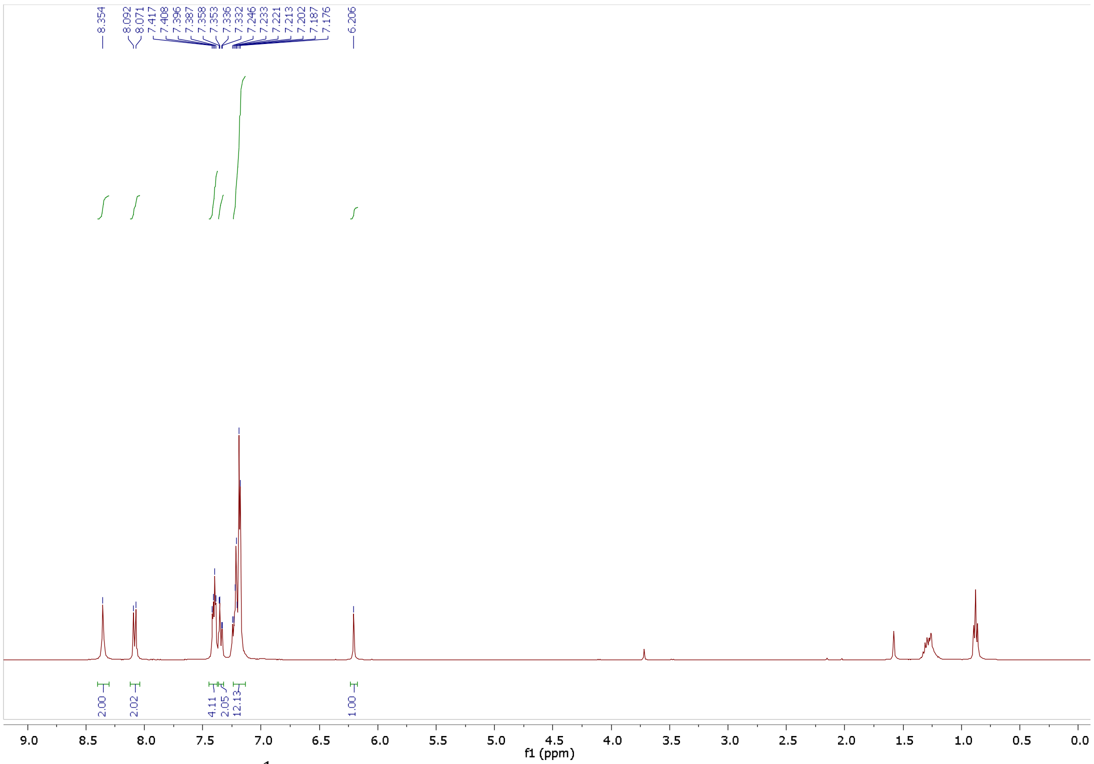
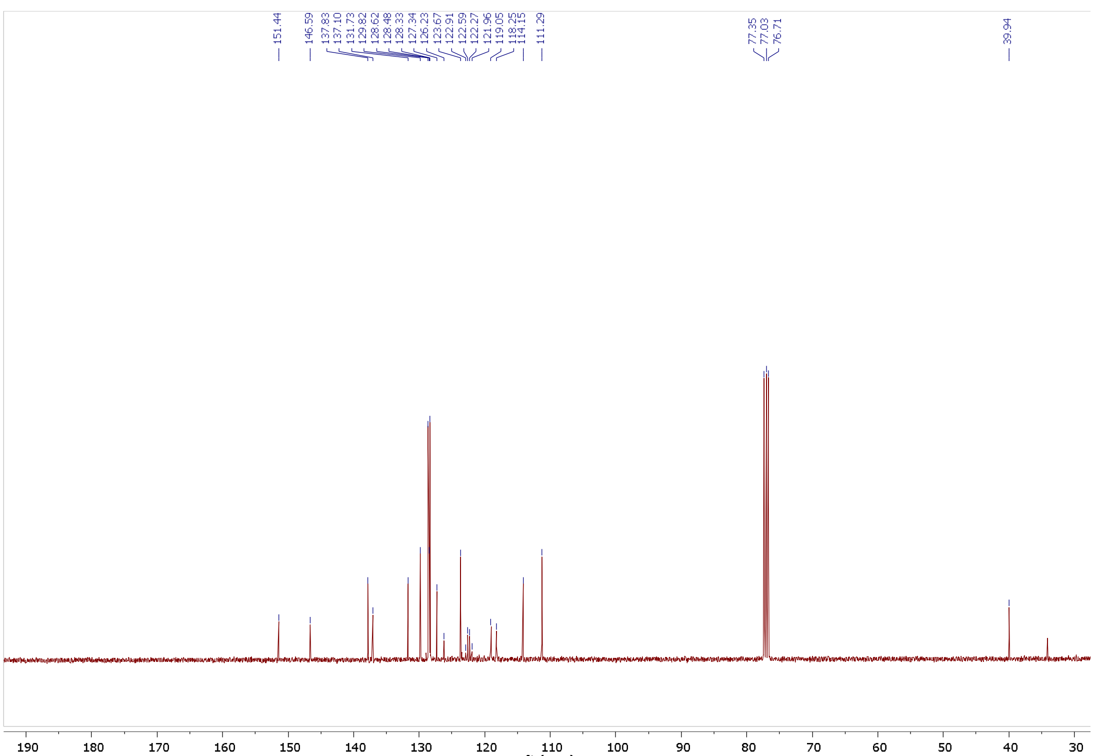


^{1}H NMR (400 MHz, $CDCl_3$) of Compound (**3kF**)



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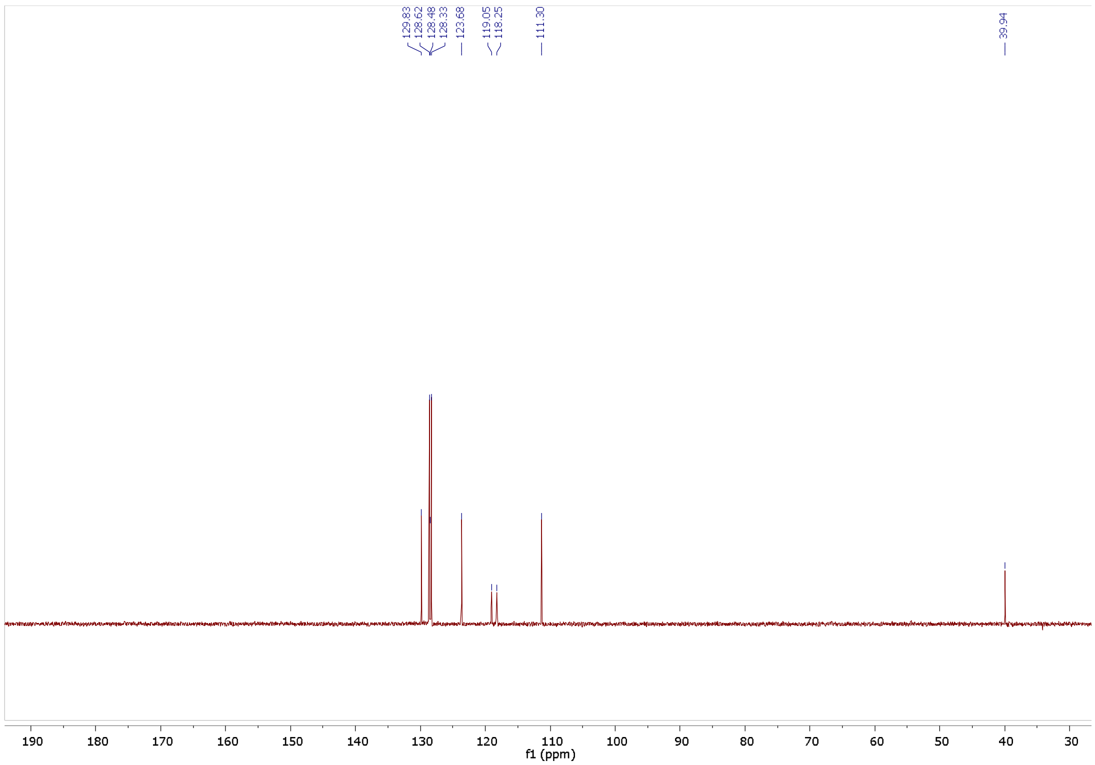
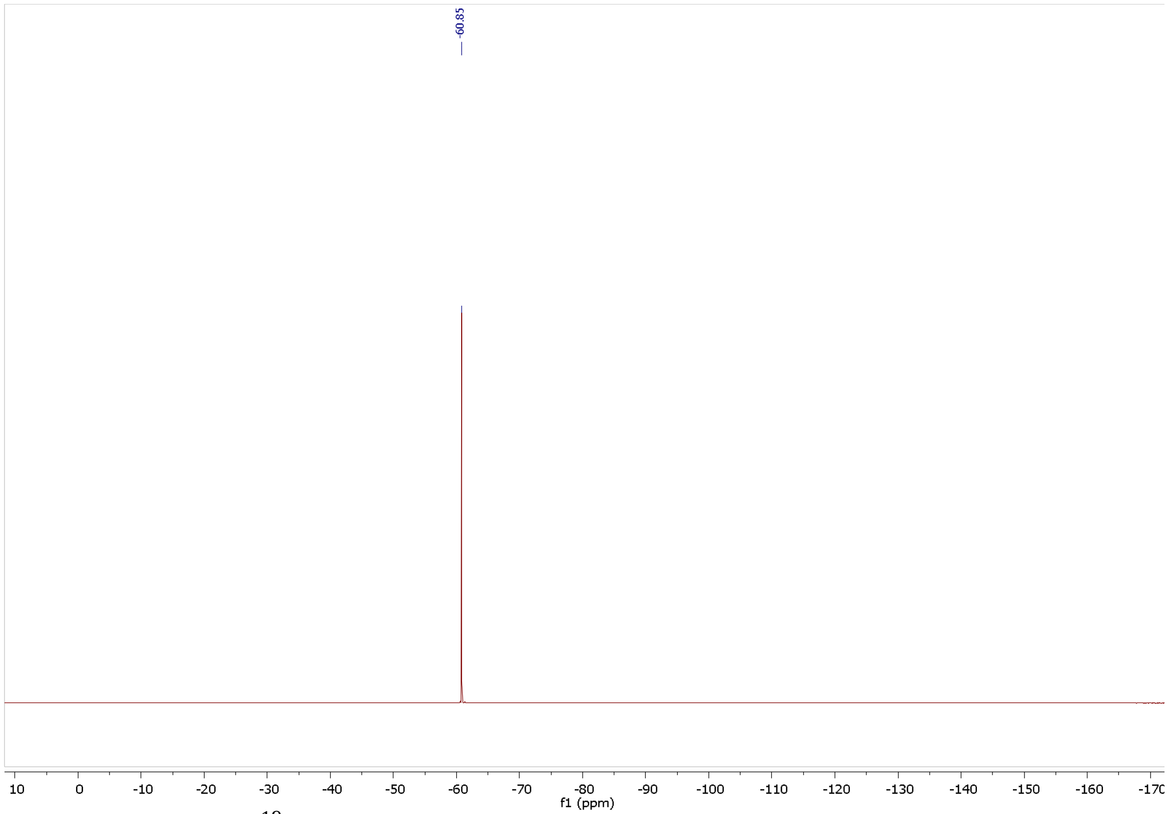
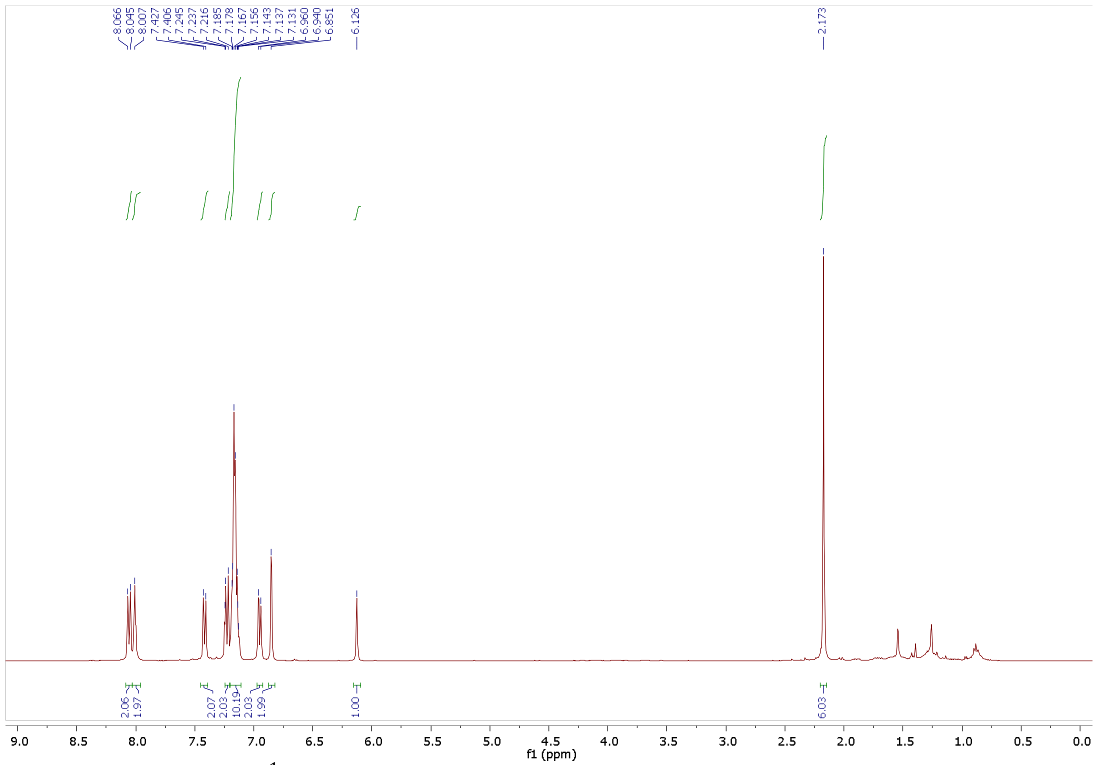


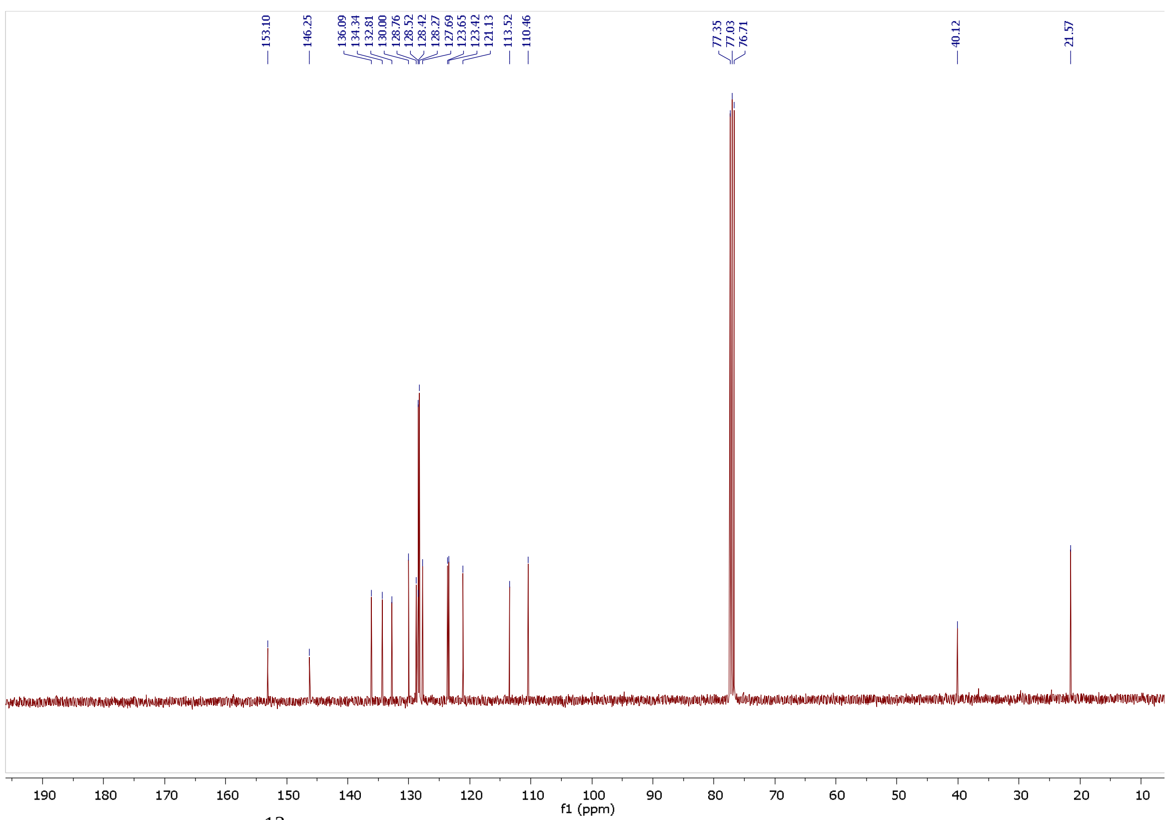
DEPT NMR (100 MHz, $CDCl_3$) of Compound (**3kF**)



^{19}F NMR (376 MHz, $CDCl_3$) of Compound (**3kF**)



^{1}H NMR (400 MHz, $CDCl_3$) of Compound (**3lF**)



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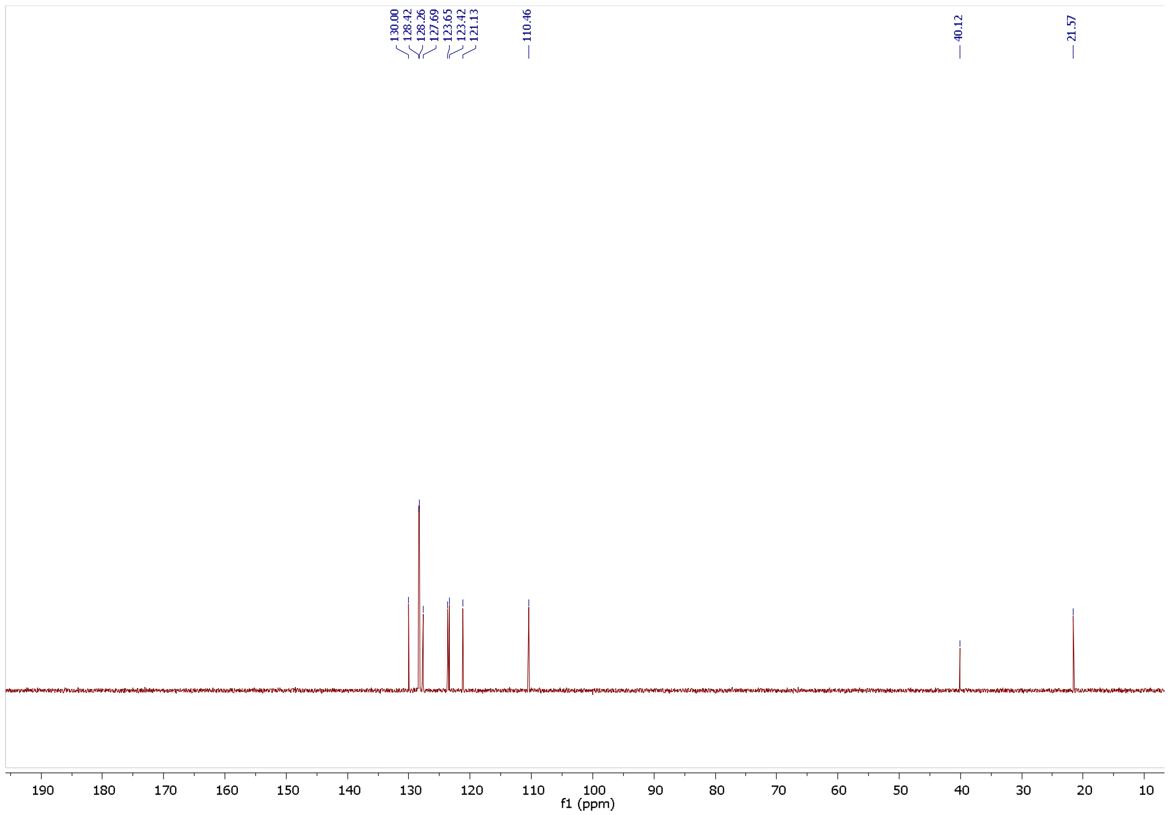
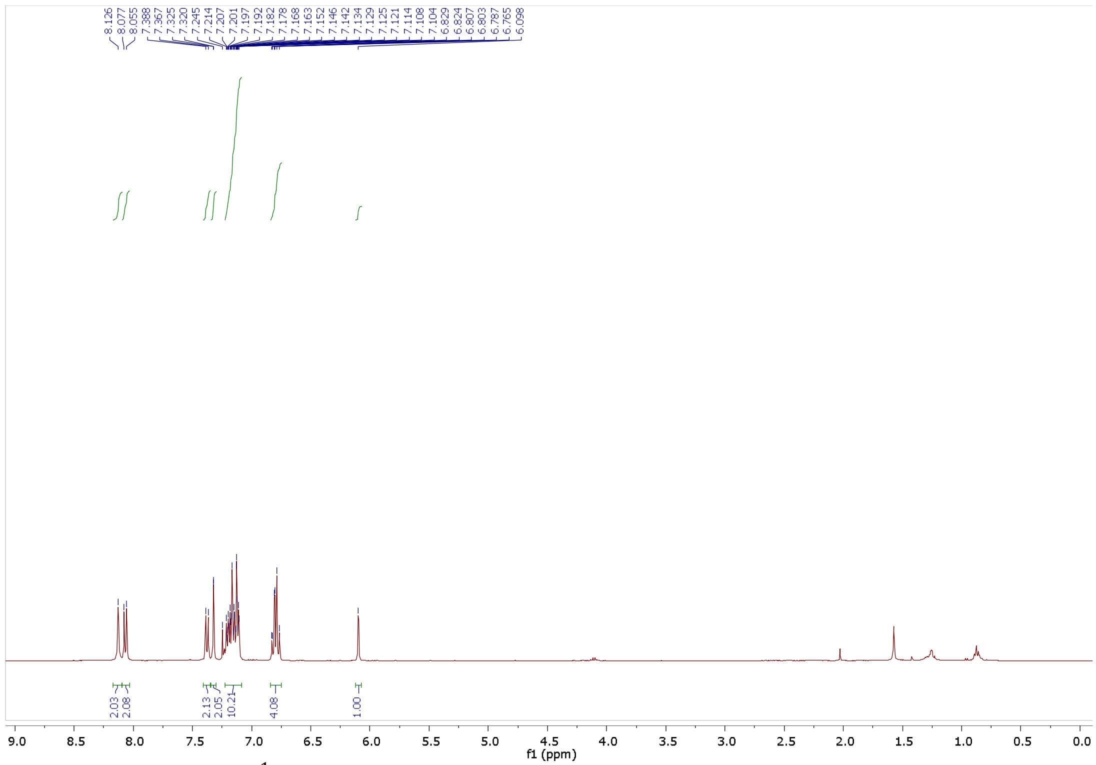
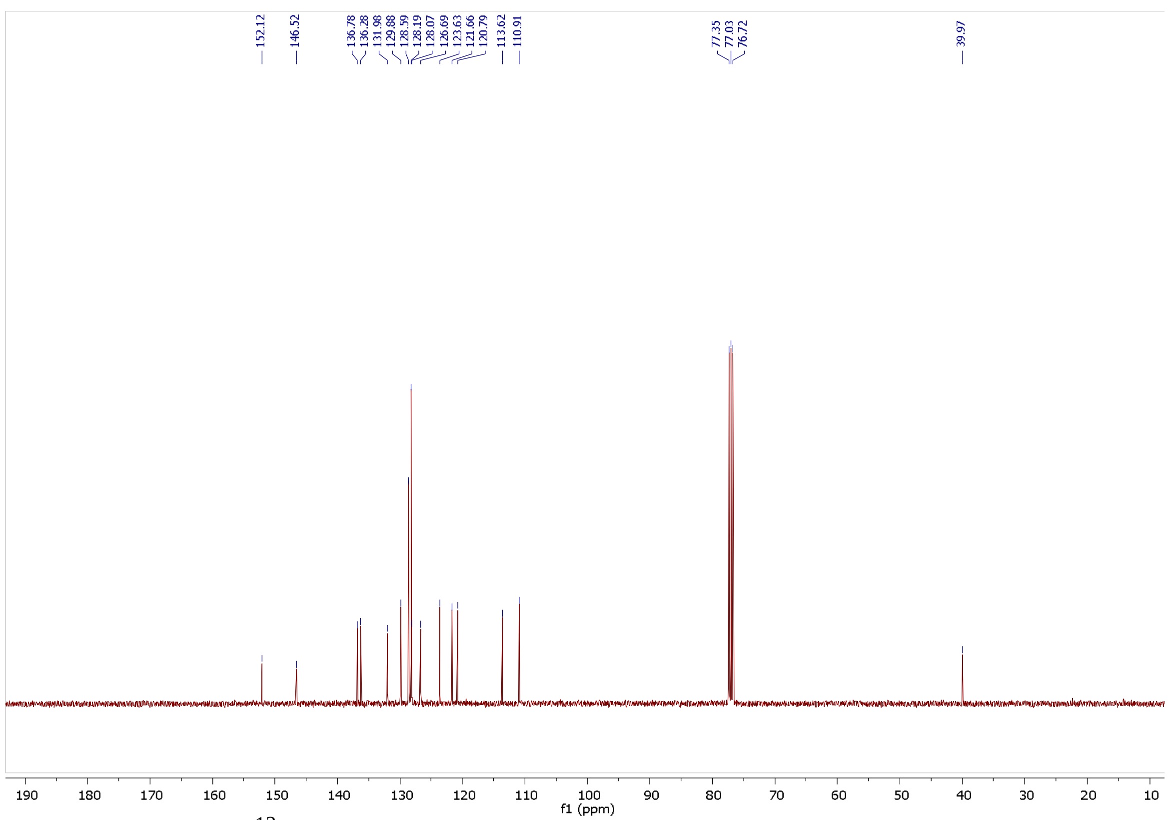


DEPT NMR (100 MHz, $CDCl_3$) of Compound (**3lF**)



^{1}H NMR (400 MHz, $CDCl_3$) of Compound (**3mF**)



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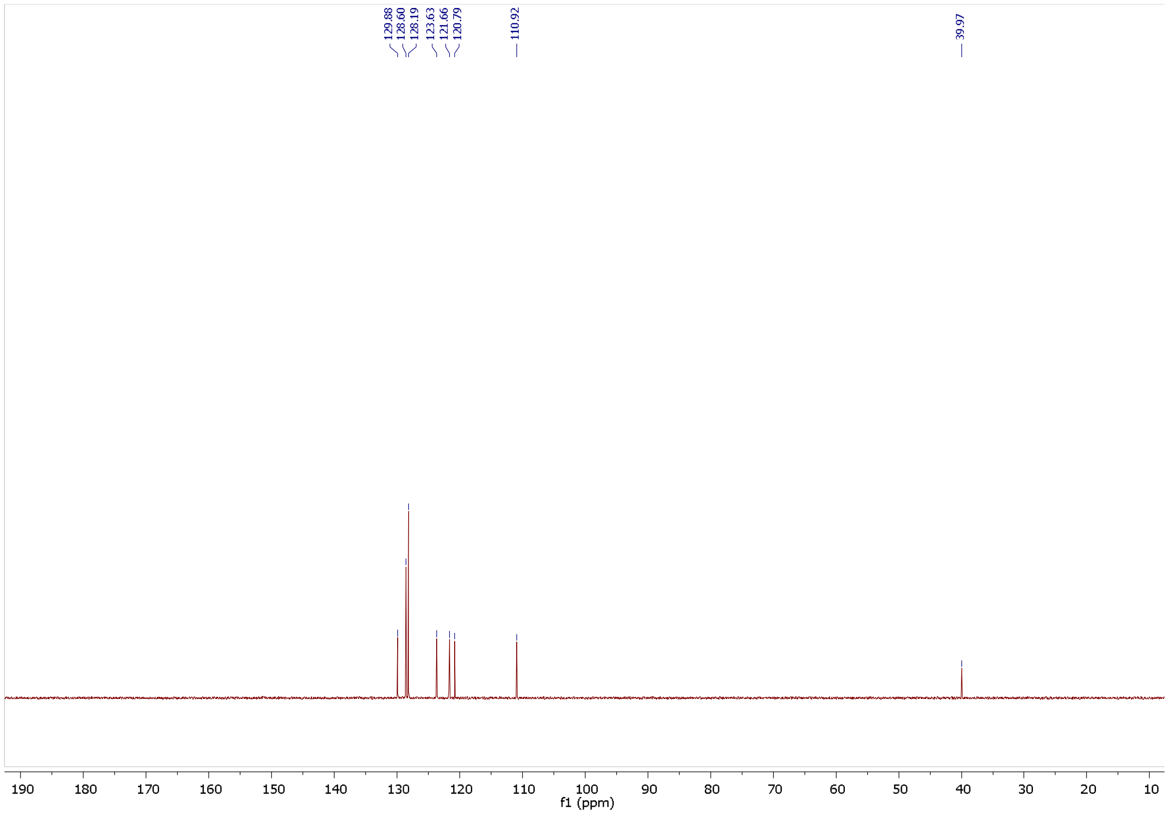
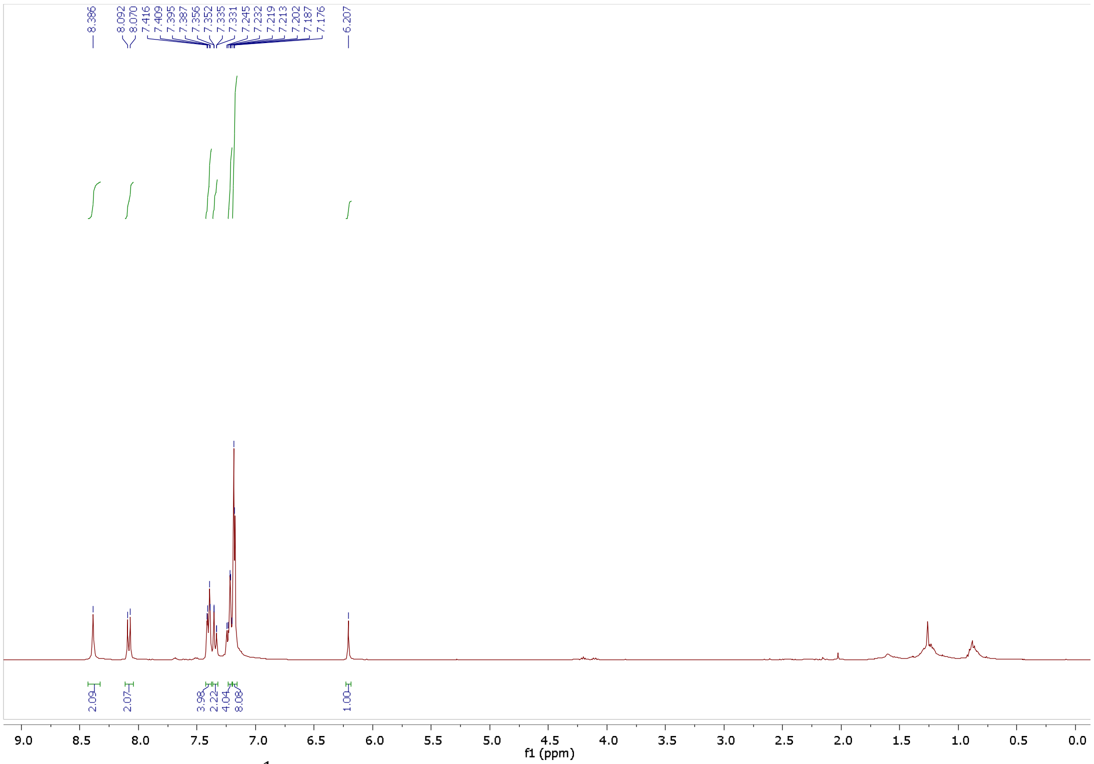


DEPT NMR (100 MHz, $CDCl_3$) of Compound (**3mF**)



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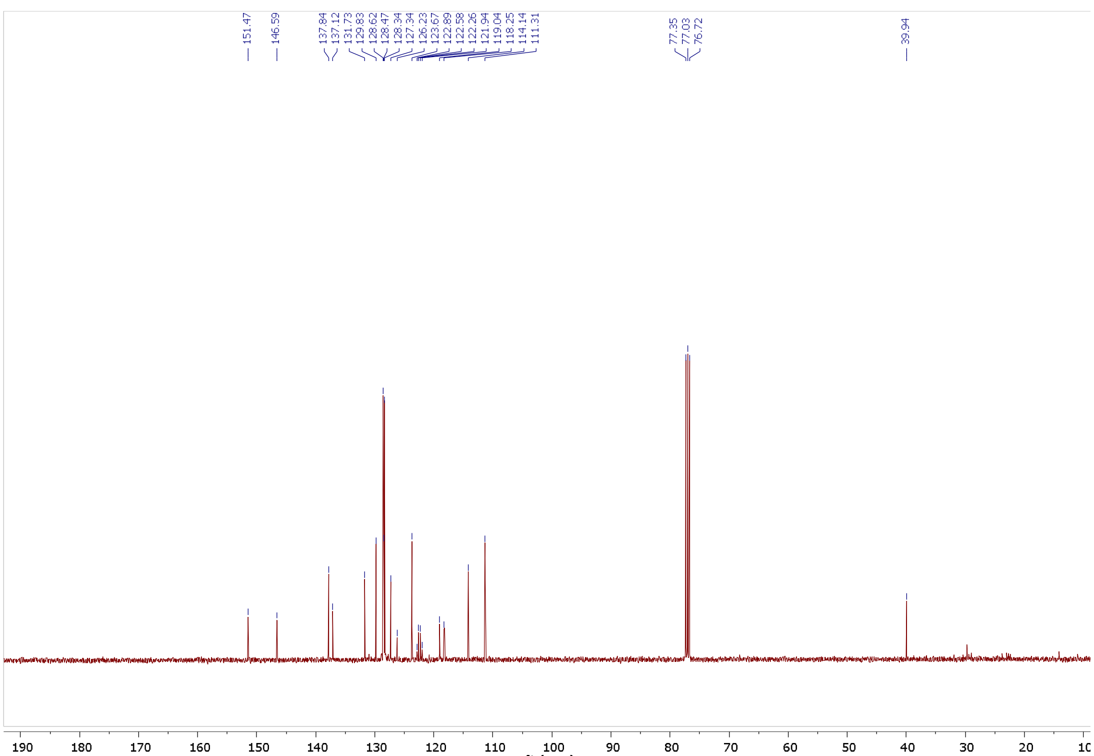

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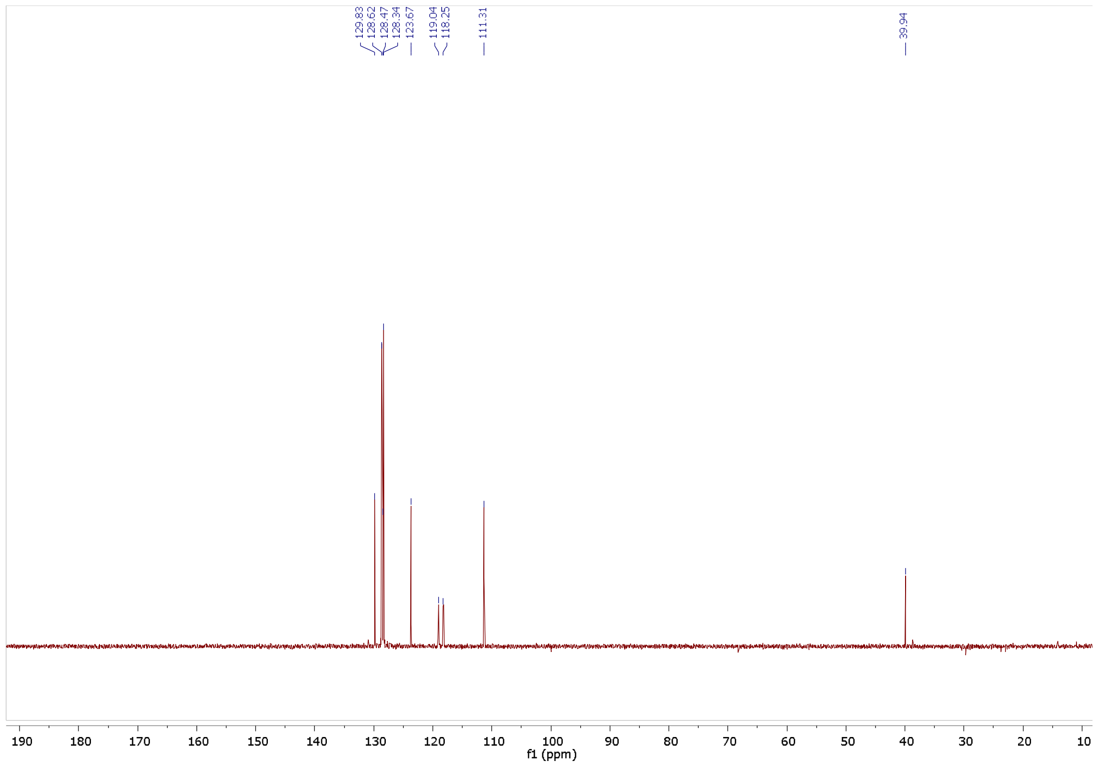
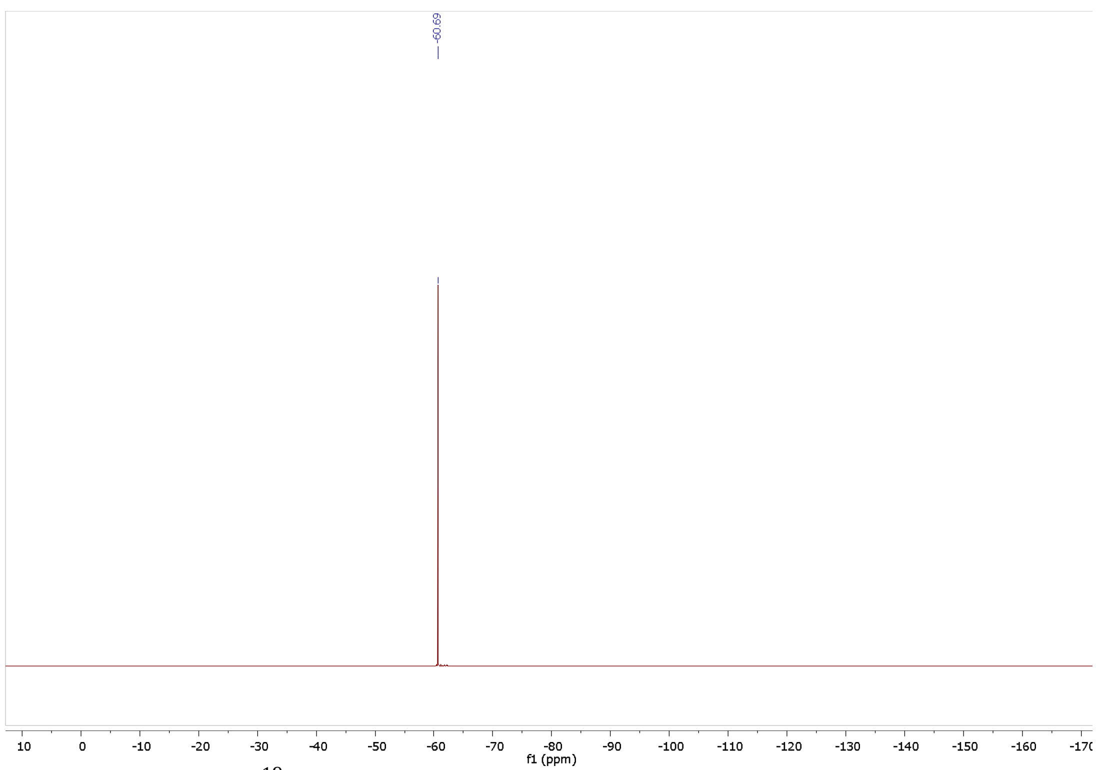
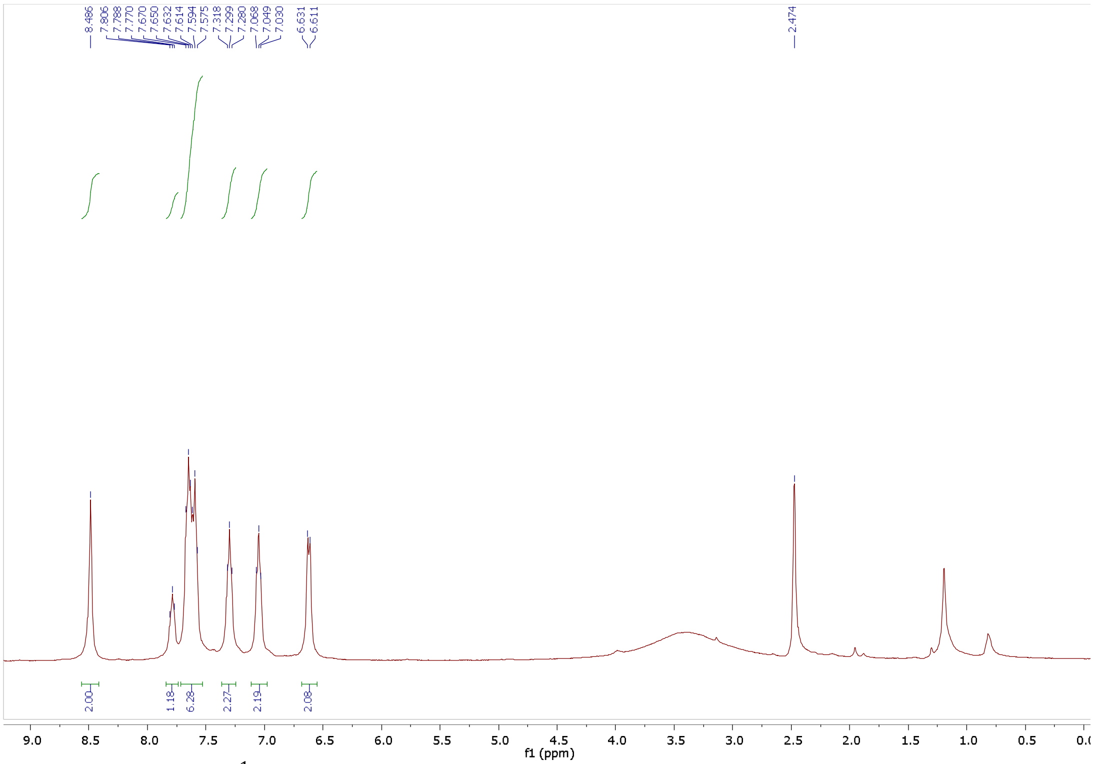


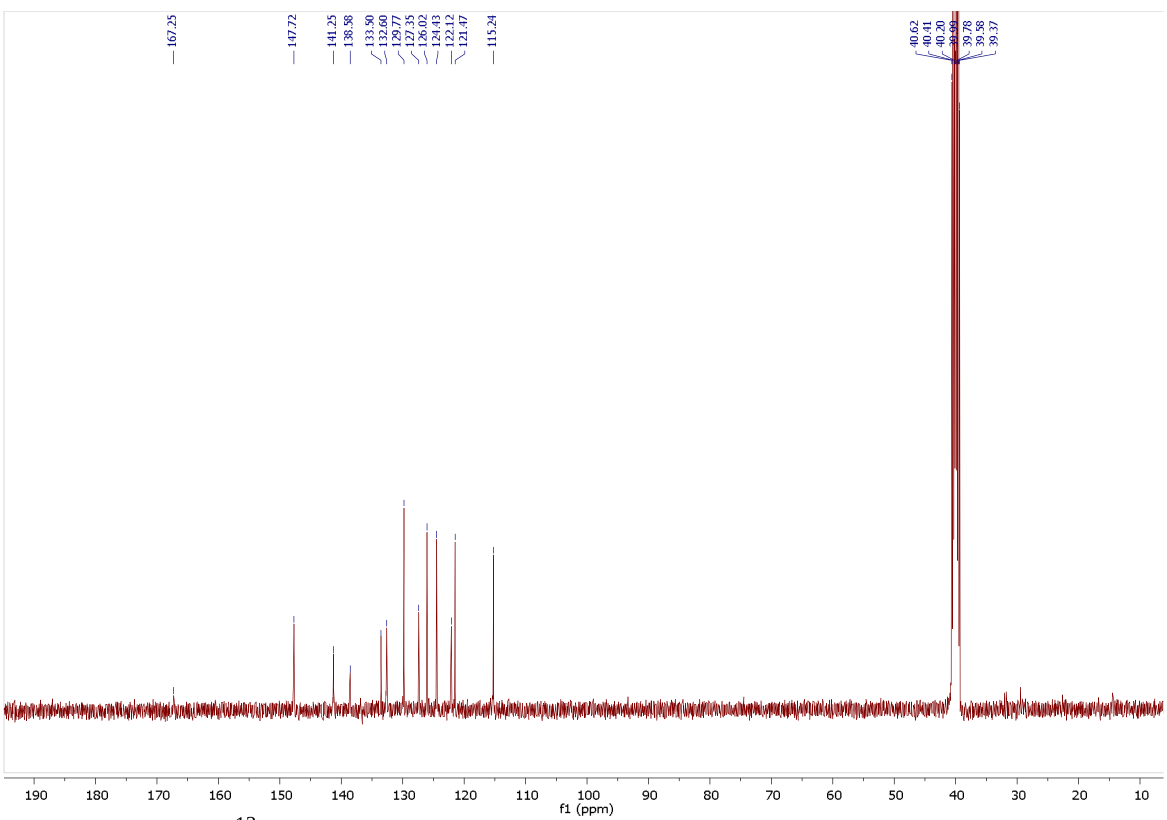
DEPT NMR (100 MHz, $CDCl_3$) of Compound (**3nF**)



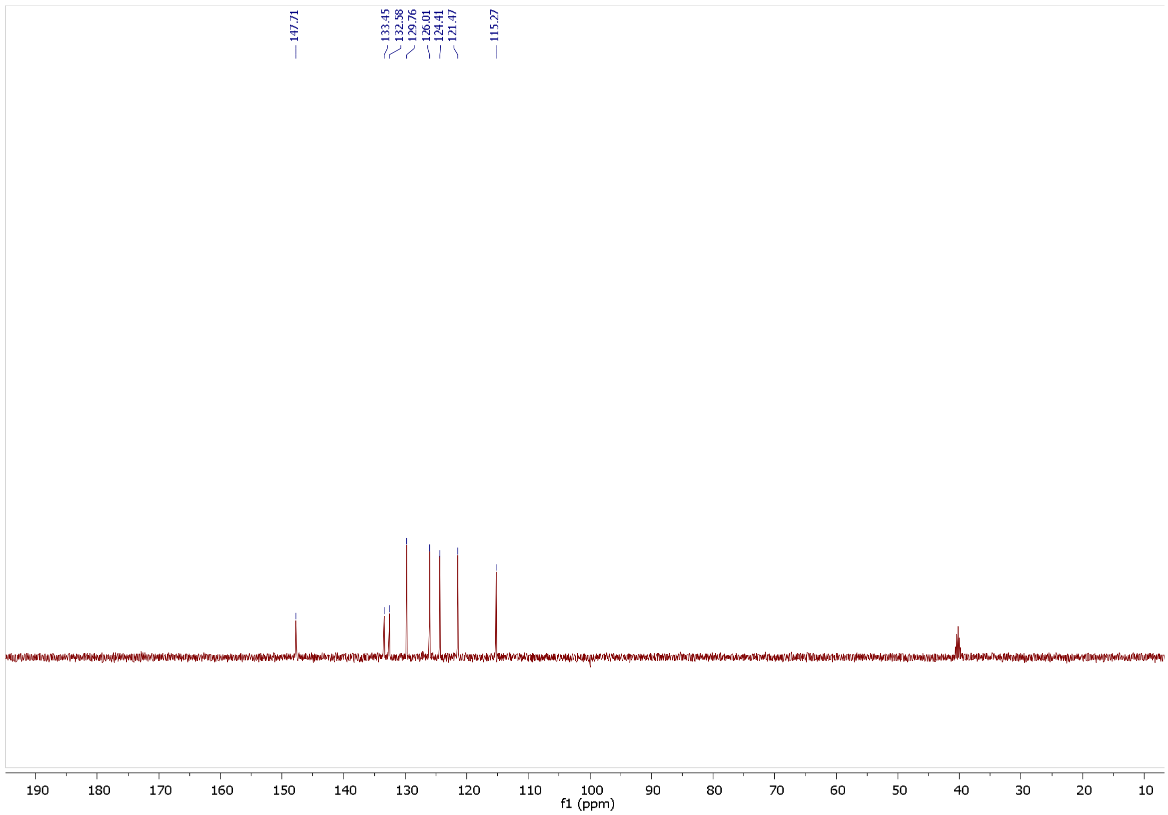
^{19}F NMR (376 MHz, $CDCl_3$) of Compound (**3nF**)



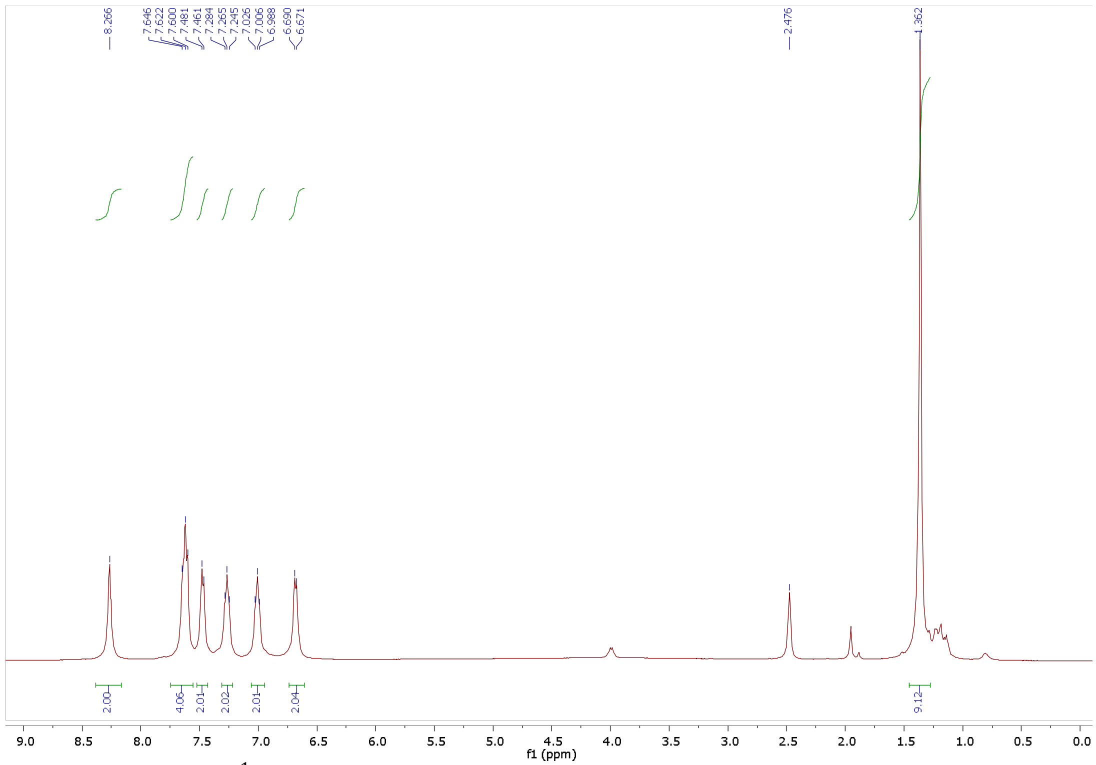
^{1}H NMR (400 MHz, DMSO-d$_6$) of Compound (**5aA**)



^{13}C NMR (100 MHz, DMSO-d$_6$) of Compound (**5aA)**



DEPT NMR (100 MHz, DMSO-d_6) of Compound (**5aA**)



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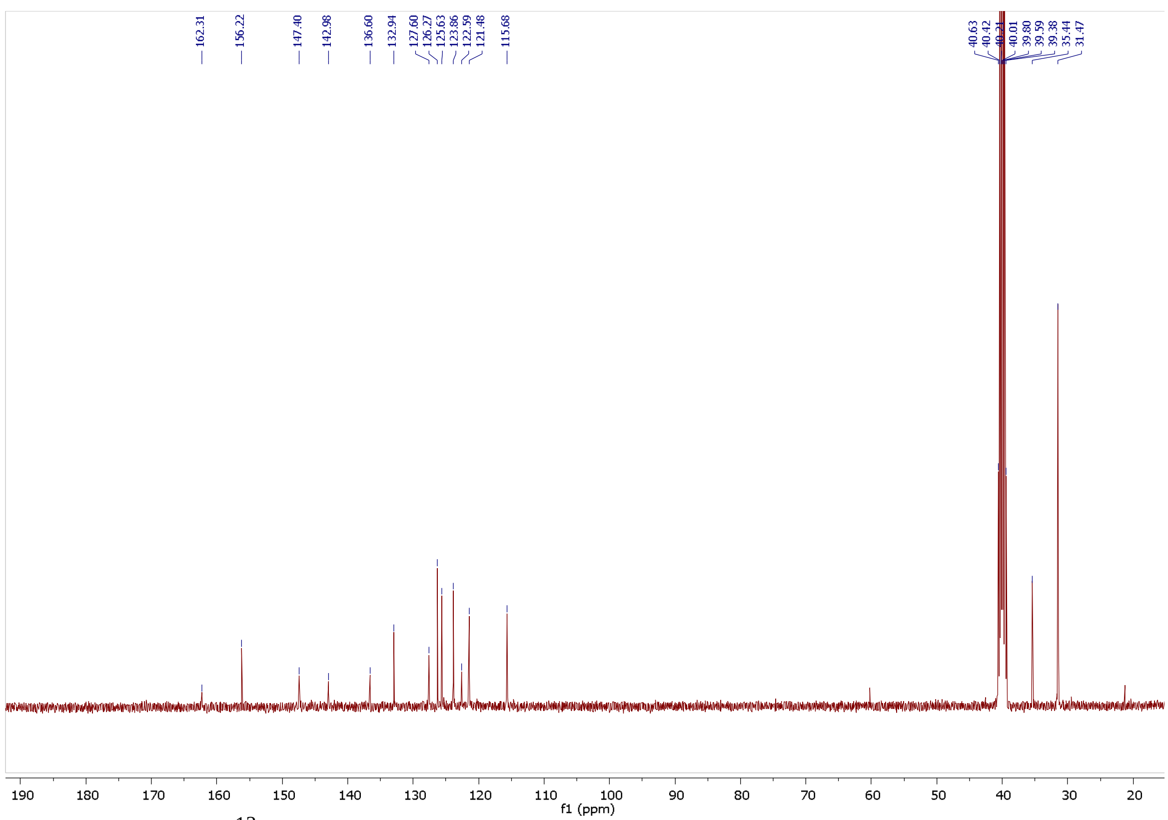
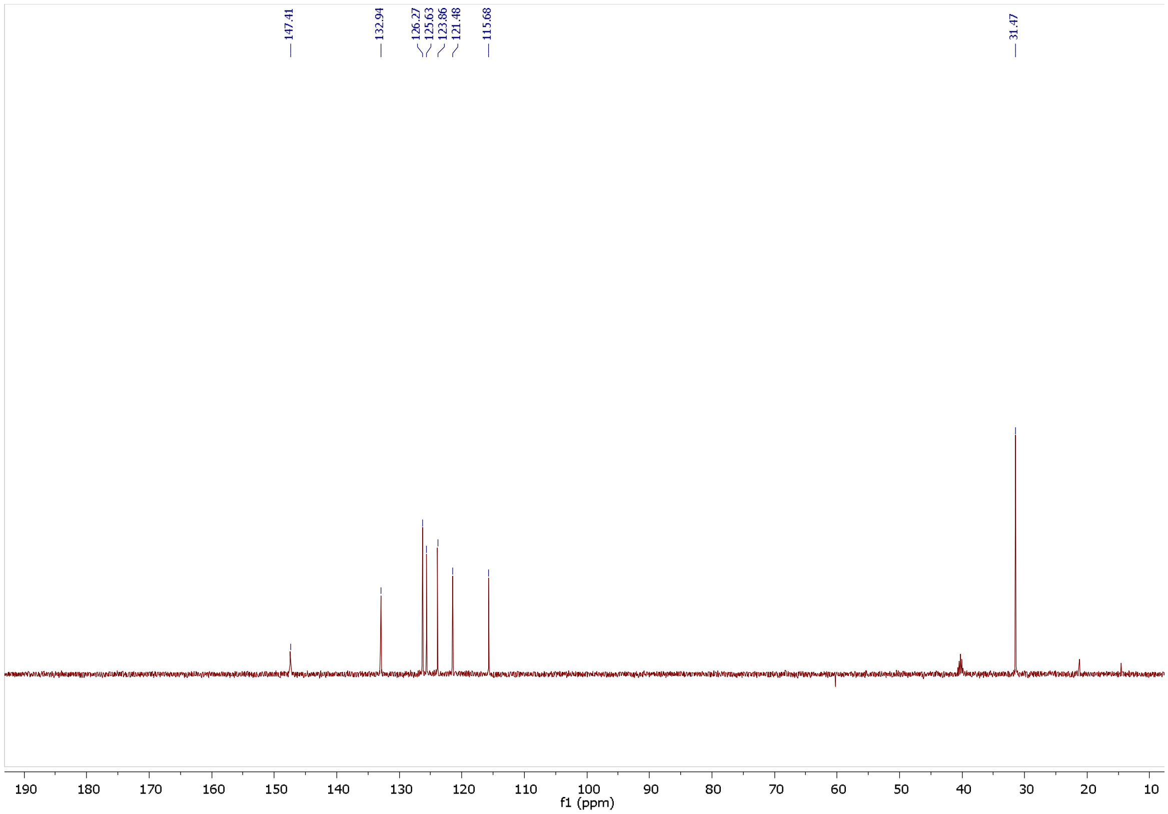
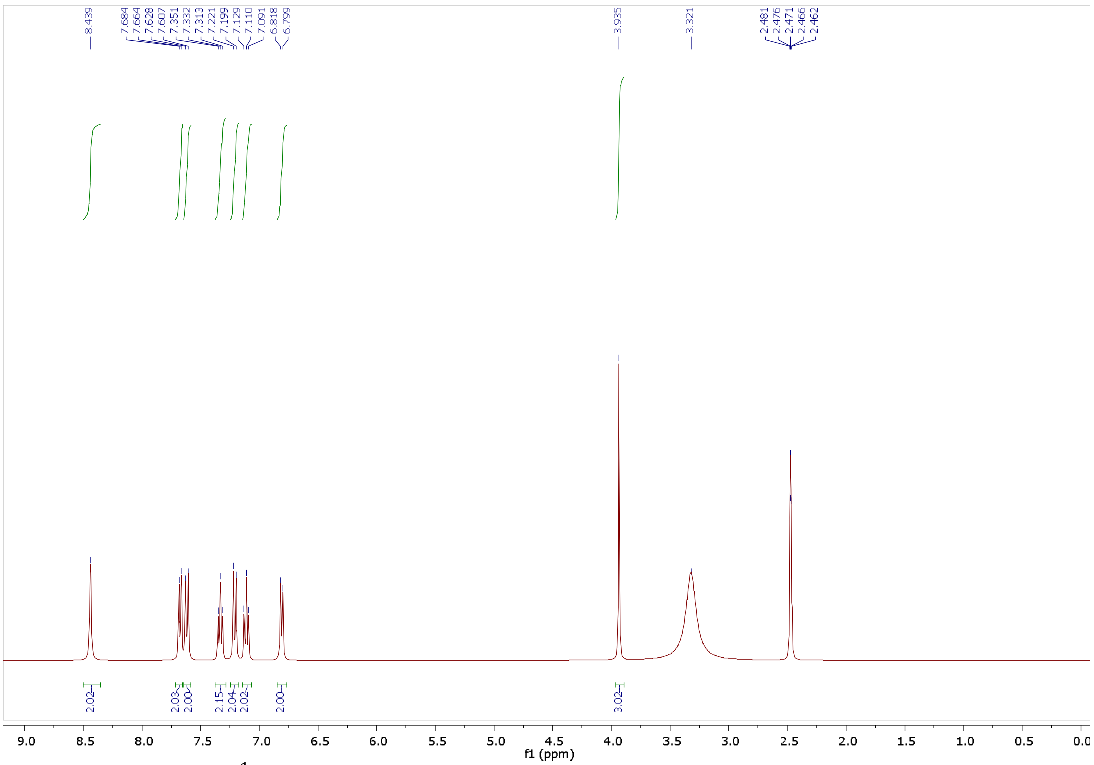


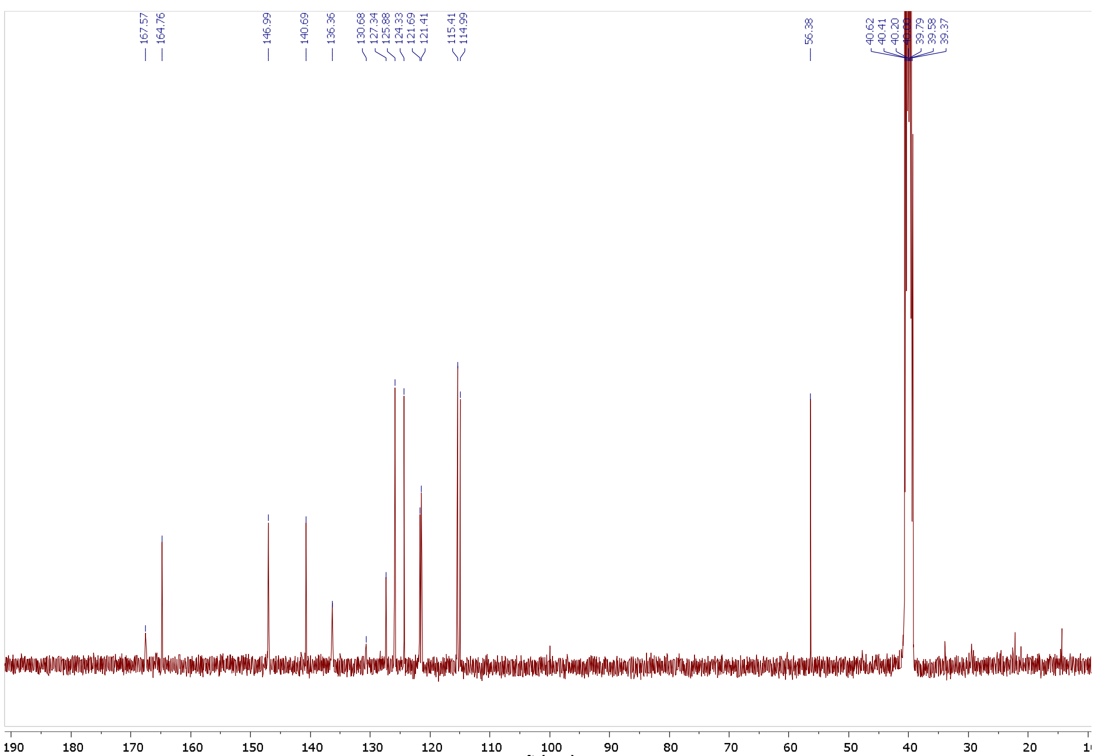
^{13}C NMR (100 MHz, DMSO-d_6) of Compound (**5aK**)



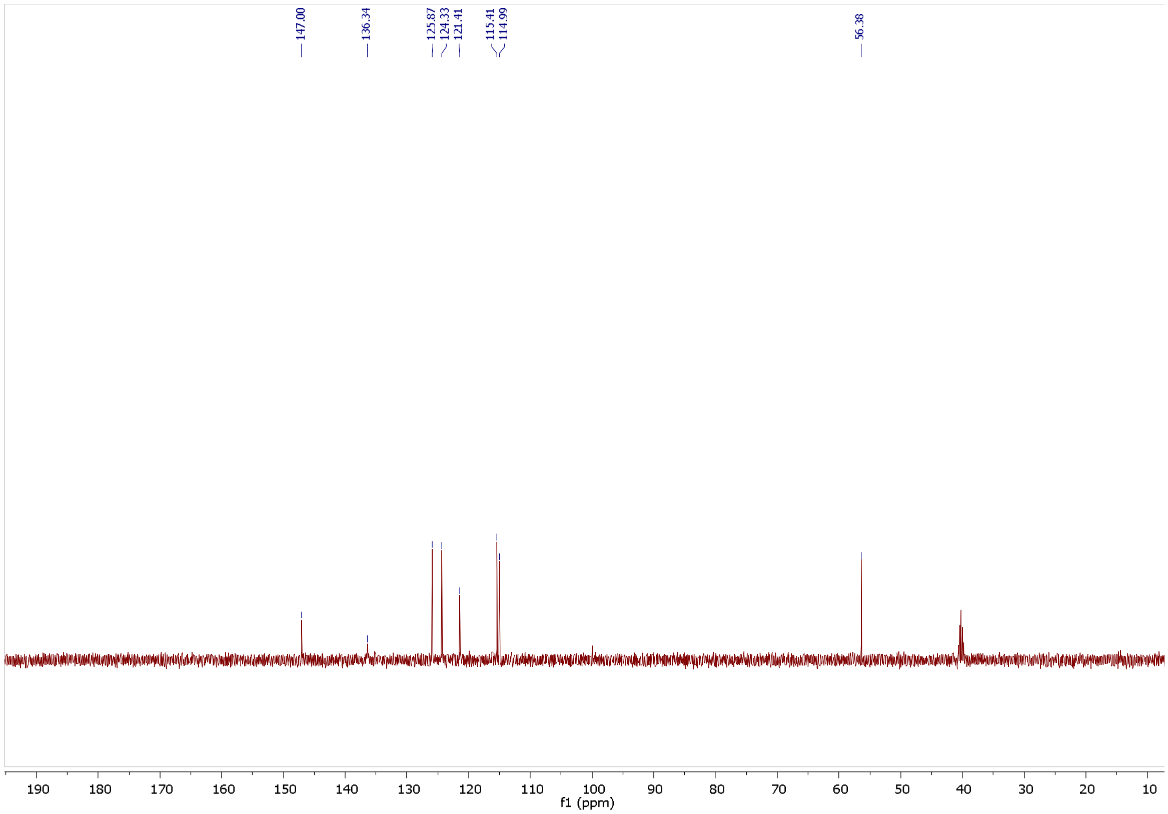
DEPT NMR (100 MHz, DMSO-d_6) of Compound (**5aK**)



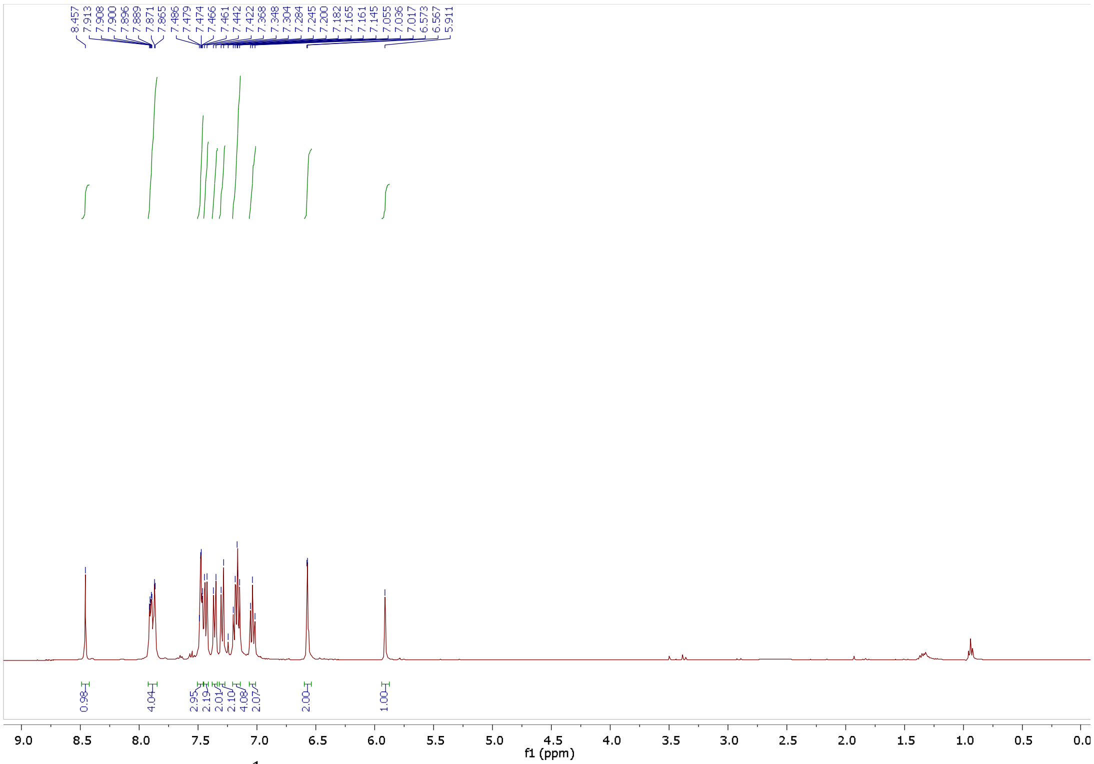
^{1}H NMR (400 MHz, DMSO-d_6) of Compound (**5aL**)



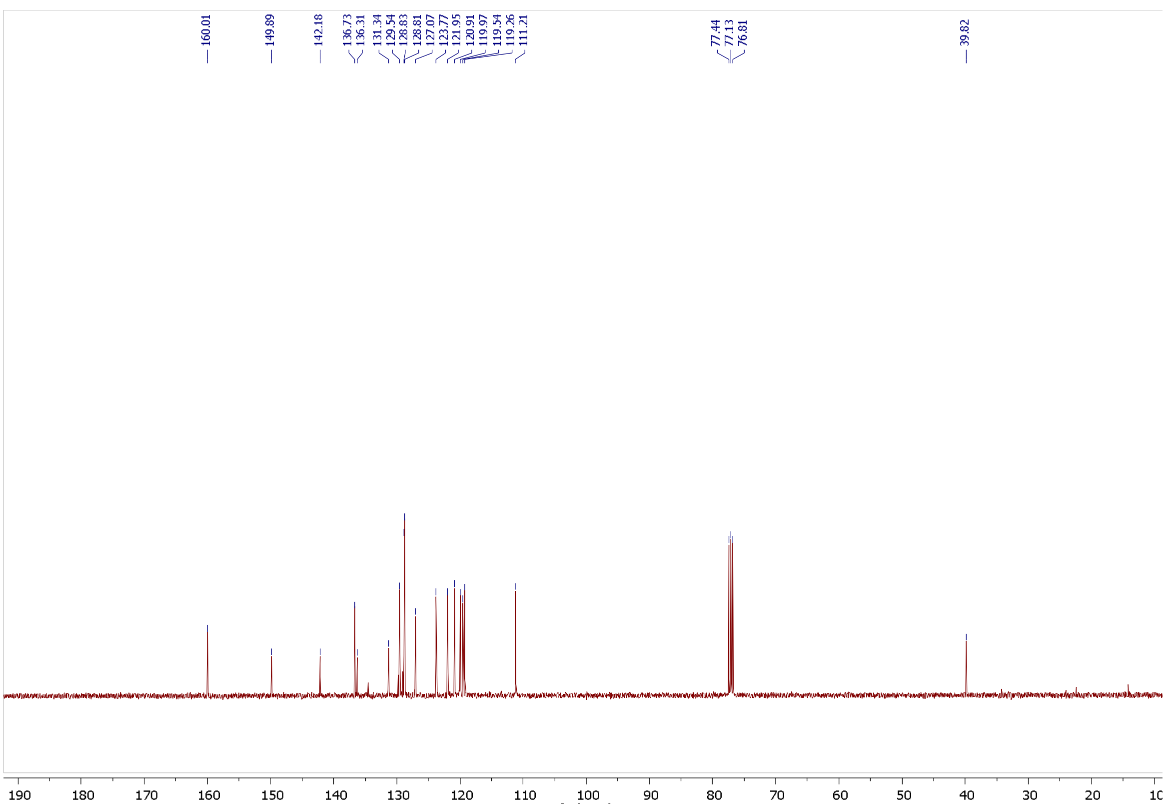
^{13}C NMR (100 MHz, DMSO-d_6) of Compound (**5aL**)



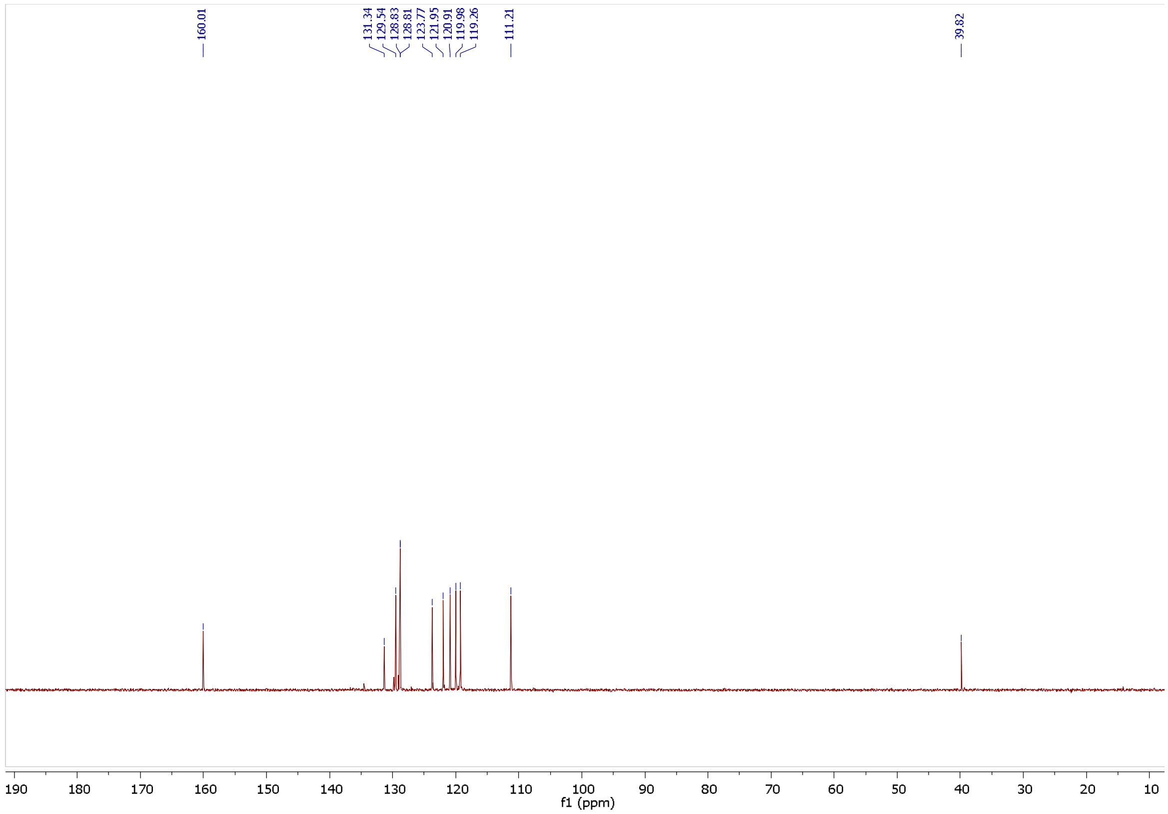
DEPT NMR (100 MHz, DMSO-d_6) of Compound (**5aL**)



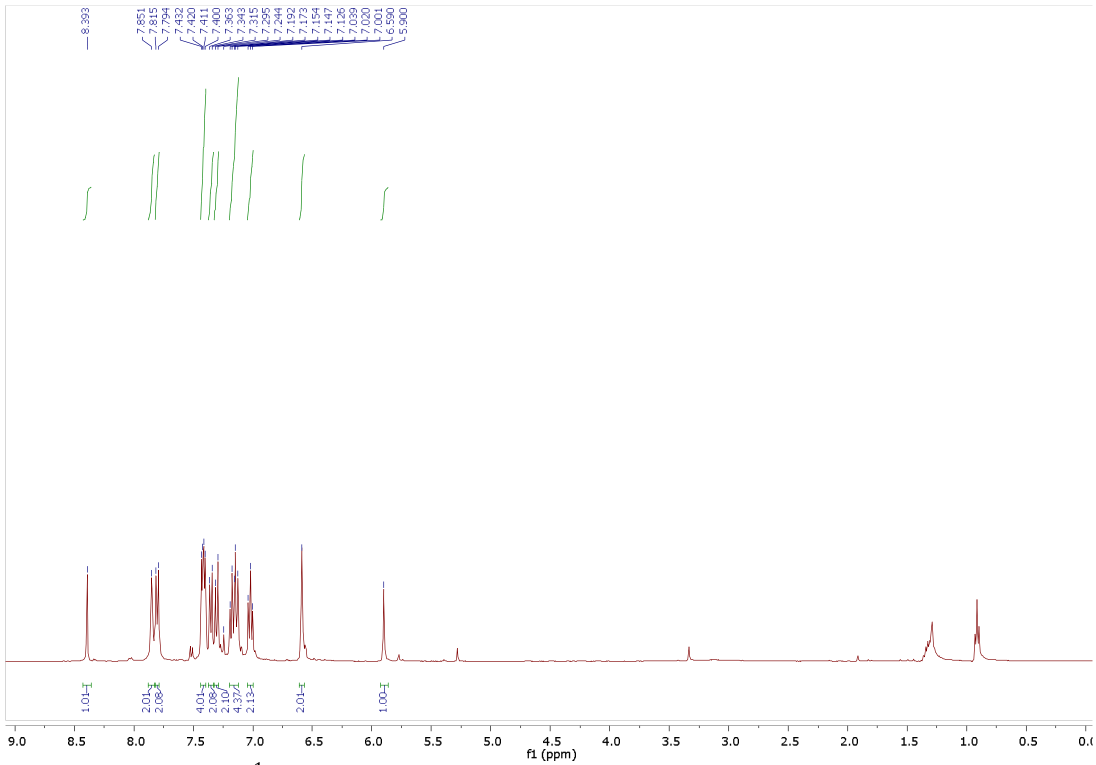
^{1}H NMR (400 MHz, $CDCl_3$) of Compound (**7aFA**)



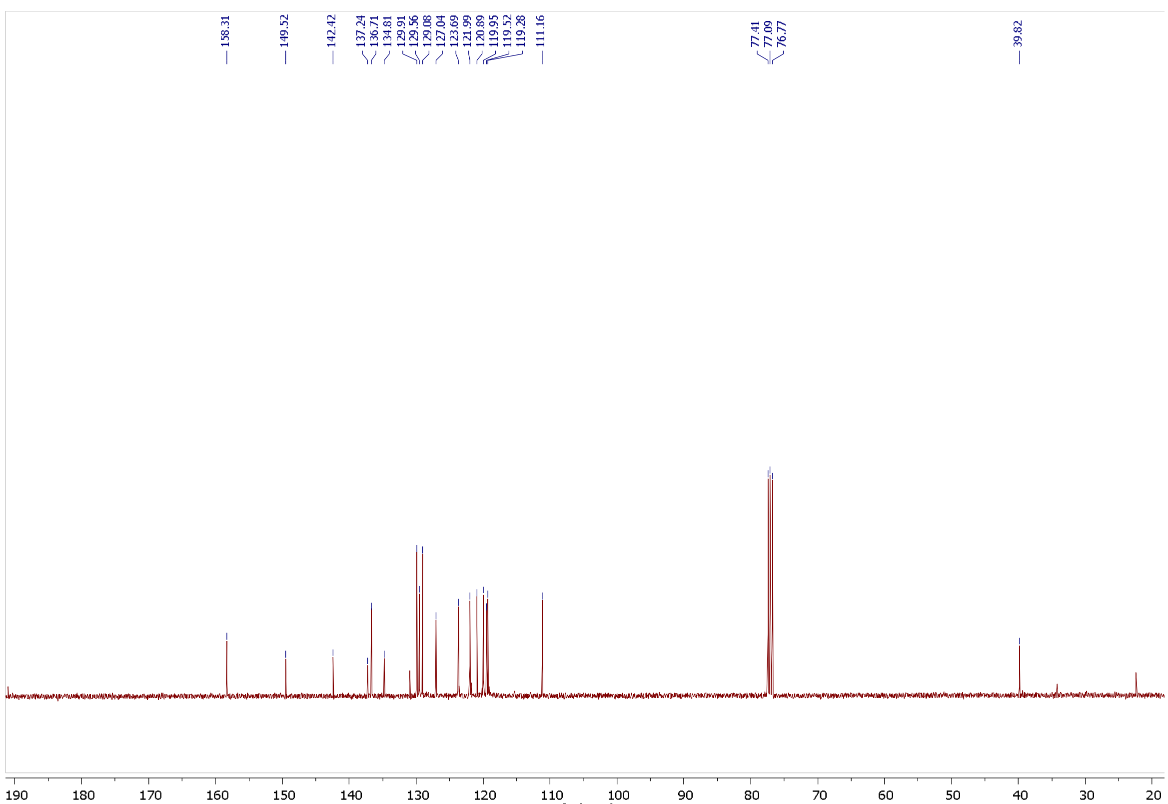
^{13}C NMR (100 MHz, $CDCl_3$) of Compound (**7aFA)**



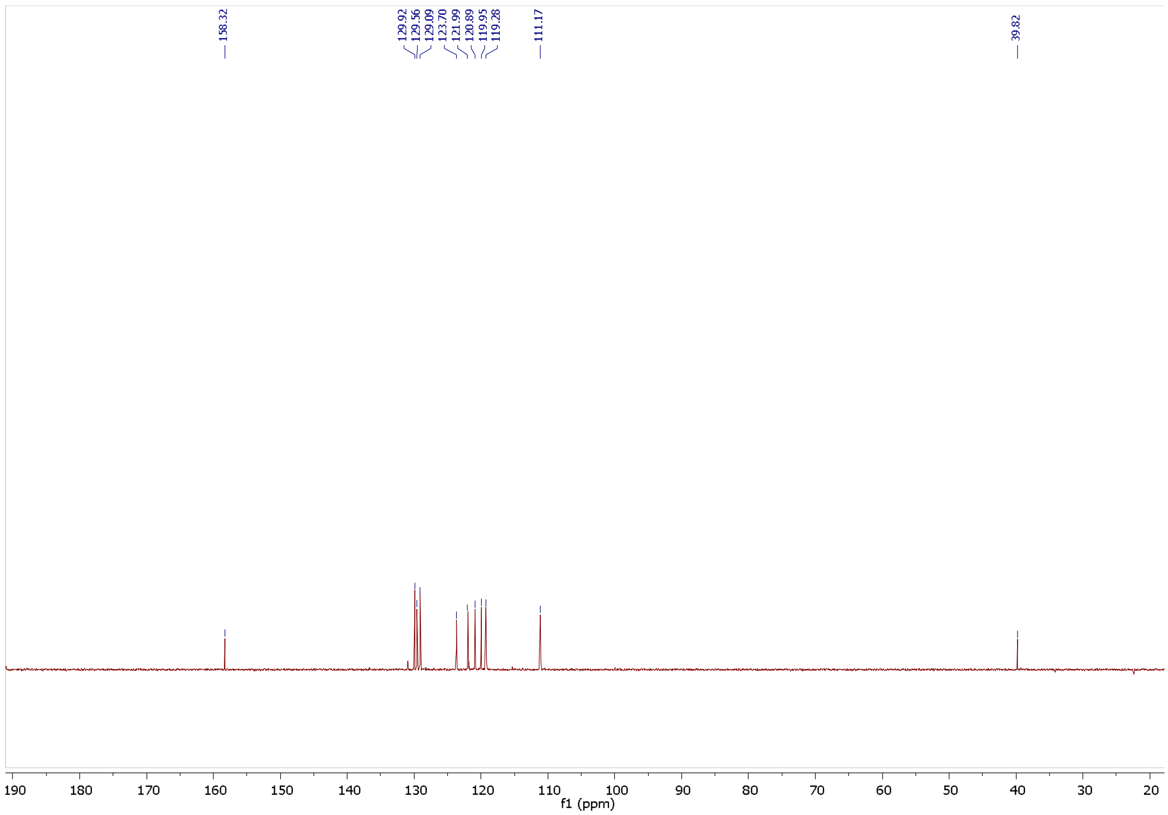
DEPT NMR (100 MHz, $CDCl_3$) of Compound (**7aFA**)



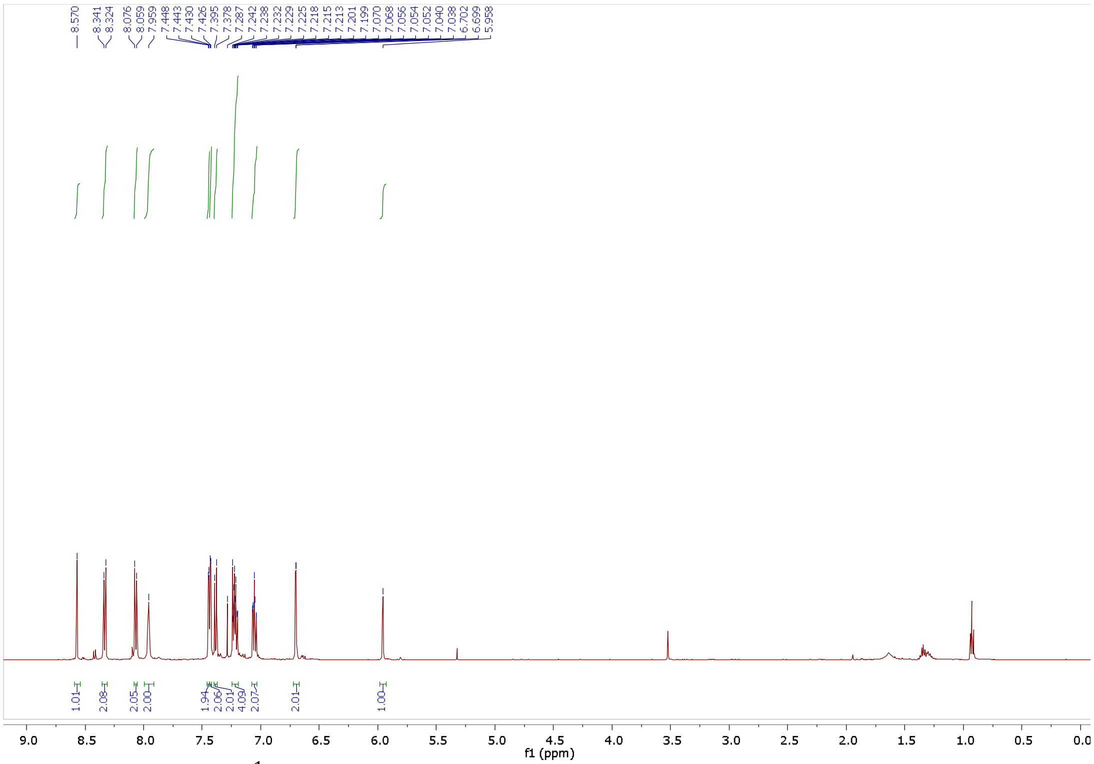
^{1}H NMR (400 MHz, $CDCl_3$) of Compound (**7aFC**)



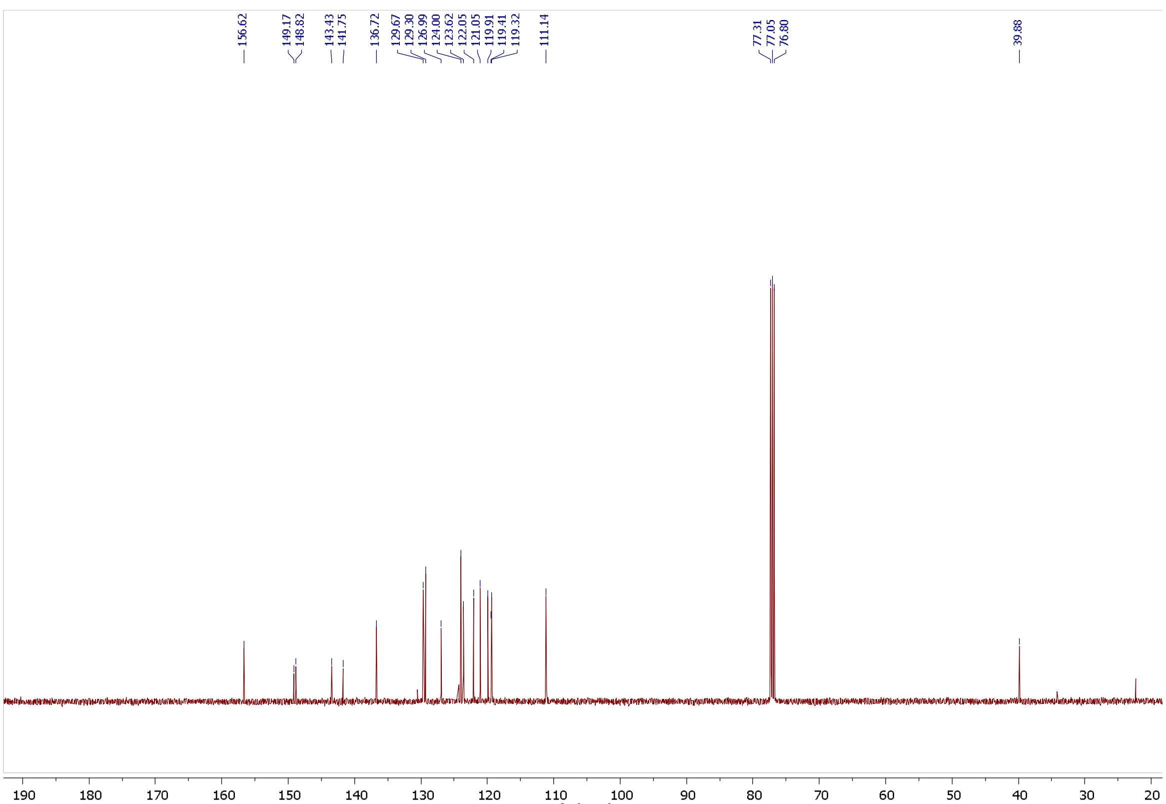
^{13}C NMR (100 MHz, $CDCl_3$) of Compound (**7aFC)**



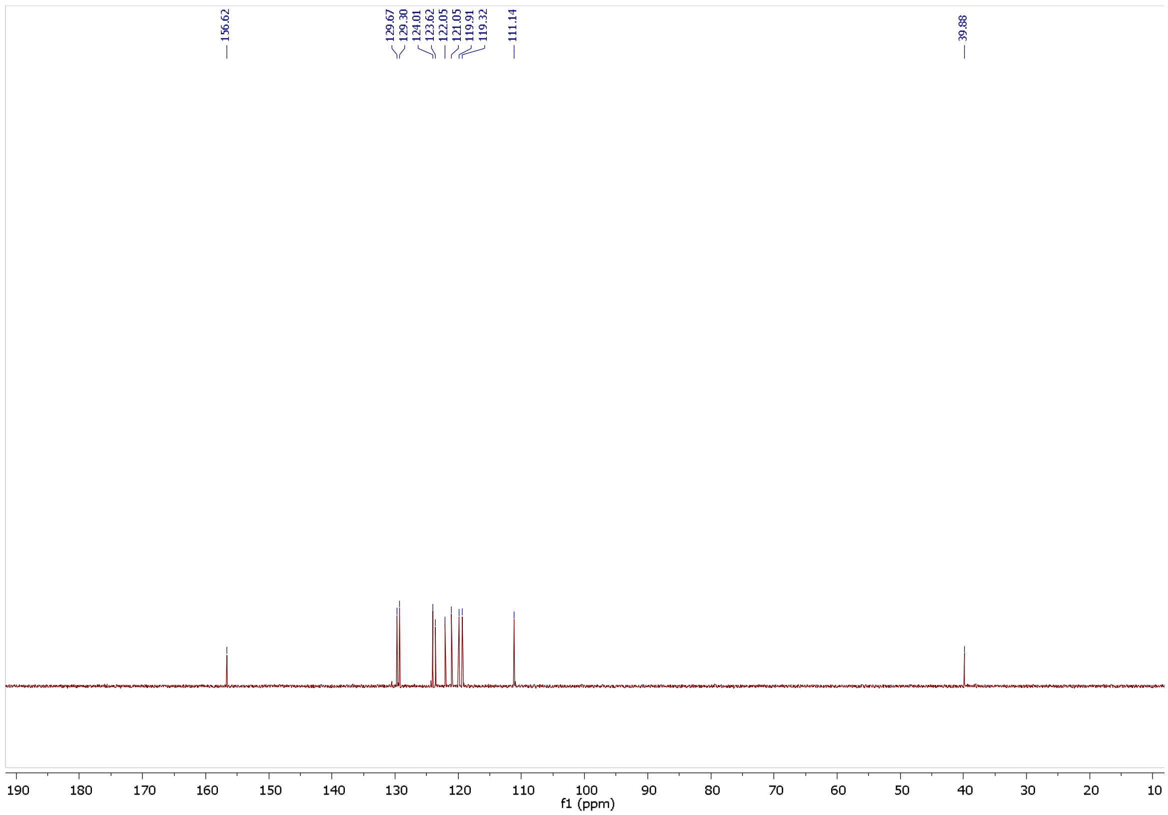
DEPT NMR (100 MHz, $CDCl_3$) of Compound (**7aFC**)



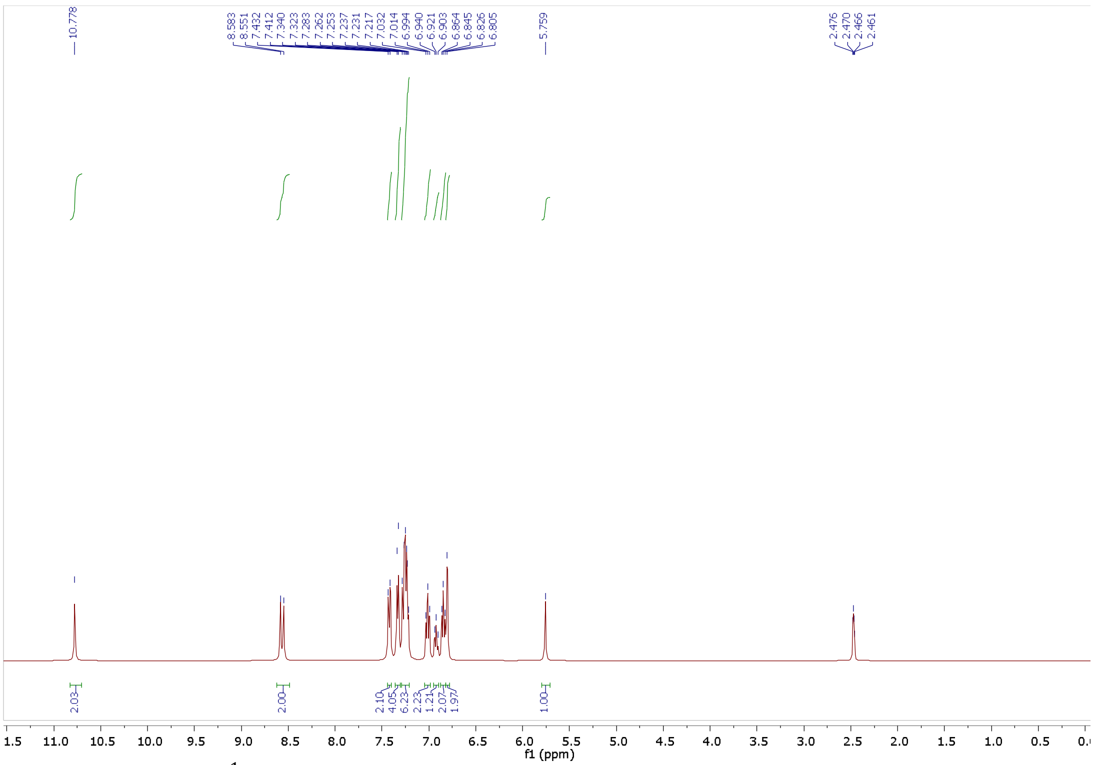
^{1}H NMR (500 MHz, $CDCl_3$) of Compound (**7aFF**)



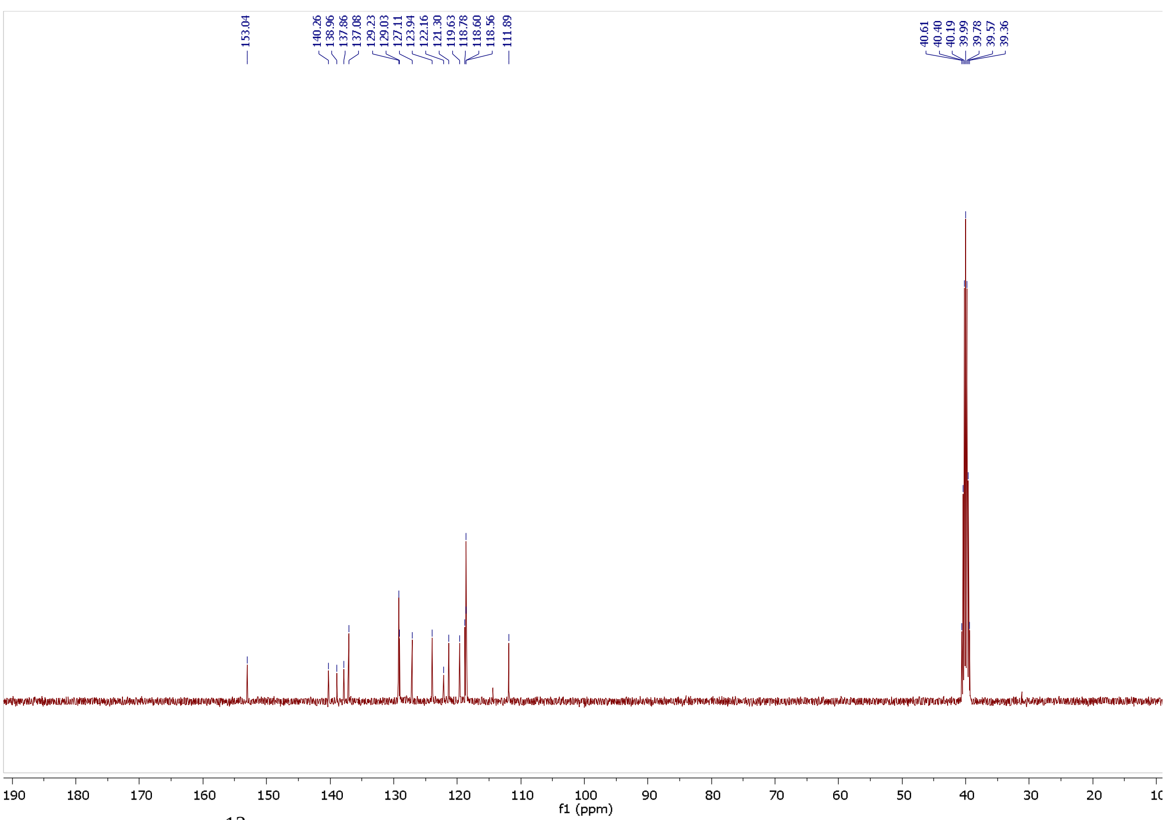
^{13}C NMR (125 MHz, $CDCl_3$) of Compound (**7aFF**)



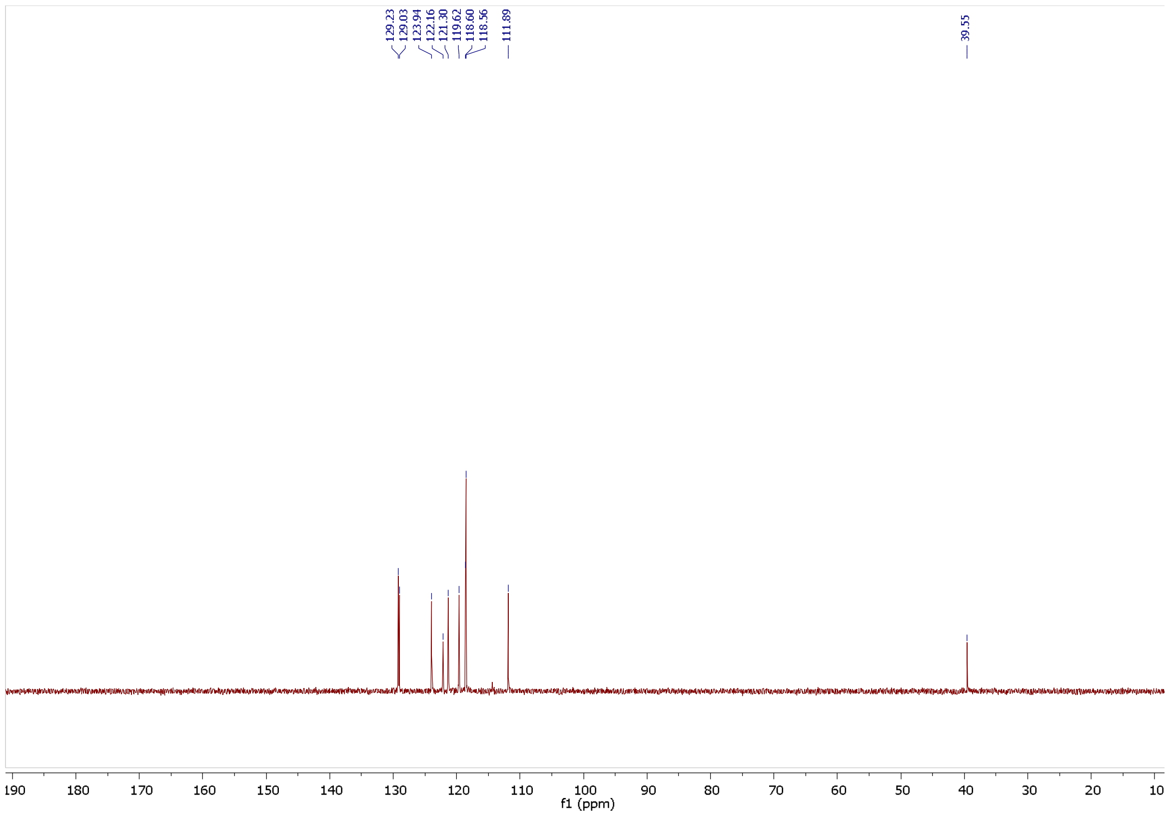
DEPT NMR (125 MHz, $CDCl_3$) of Compound (**7aFF**)



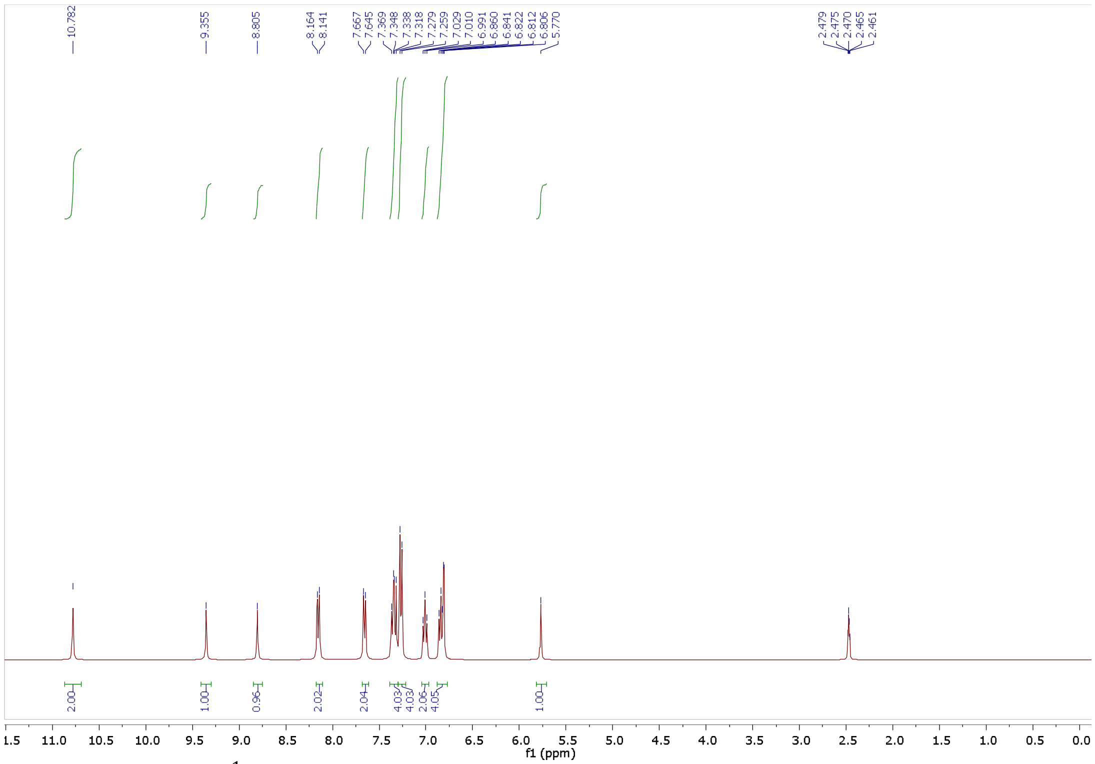
^{1}H NMR (400 MHz, DMSO-d_6) of Compound (**9aFA**)



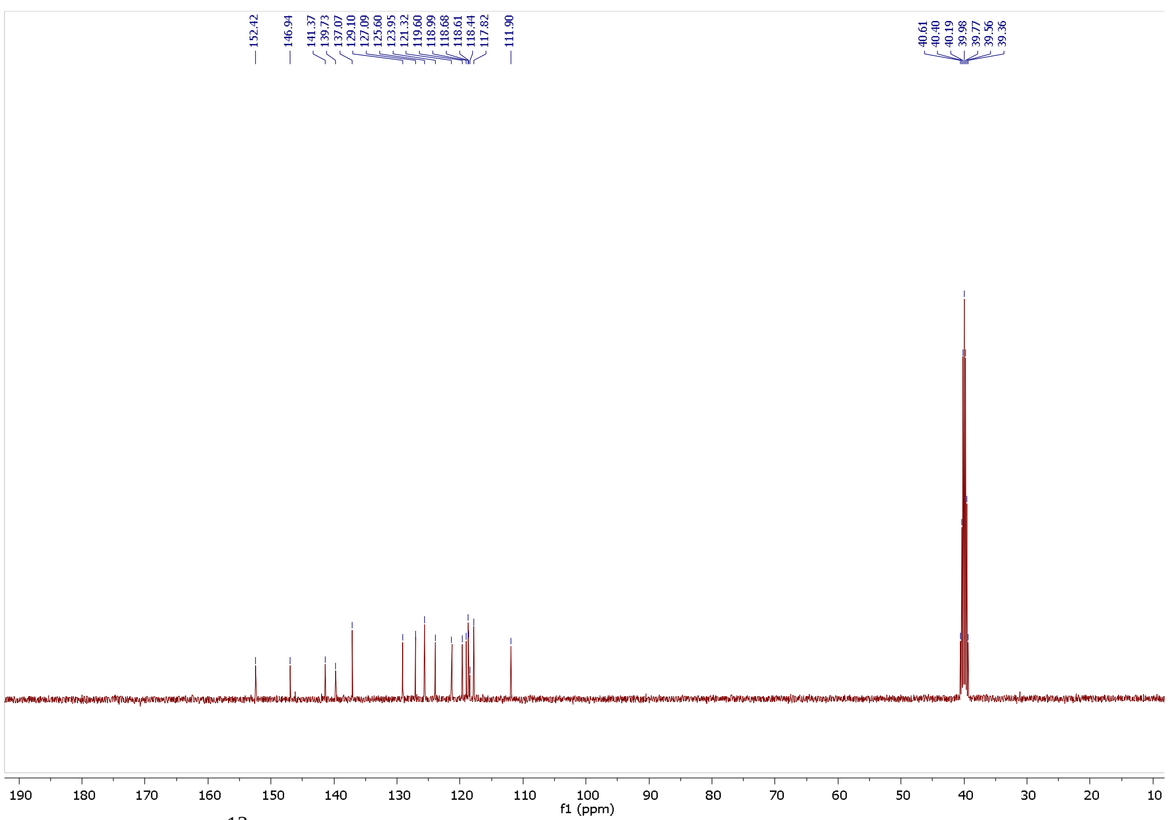
^{13}C NMR (100 MHz, DMSO-d_6) of Compound (**9aFA**)



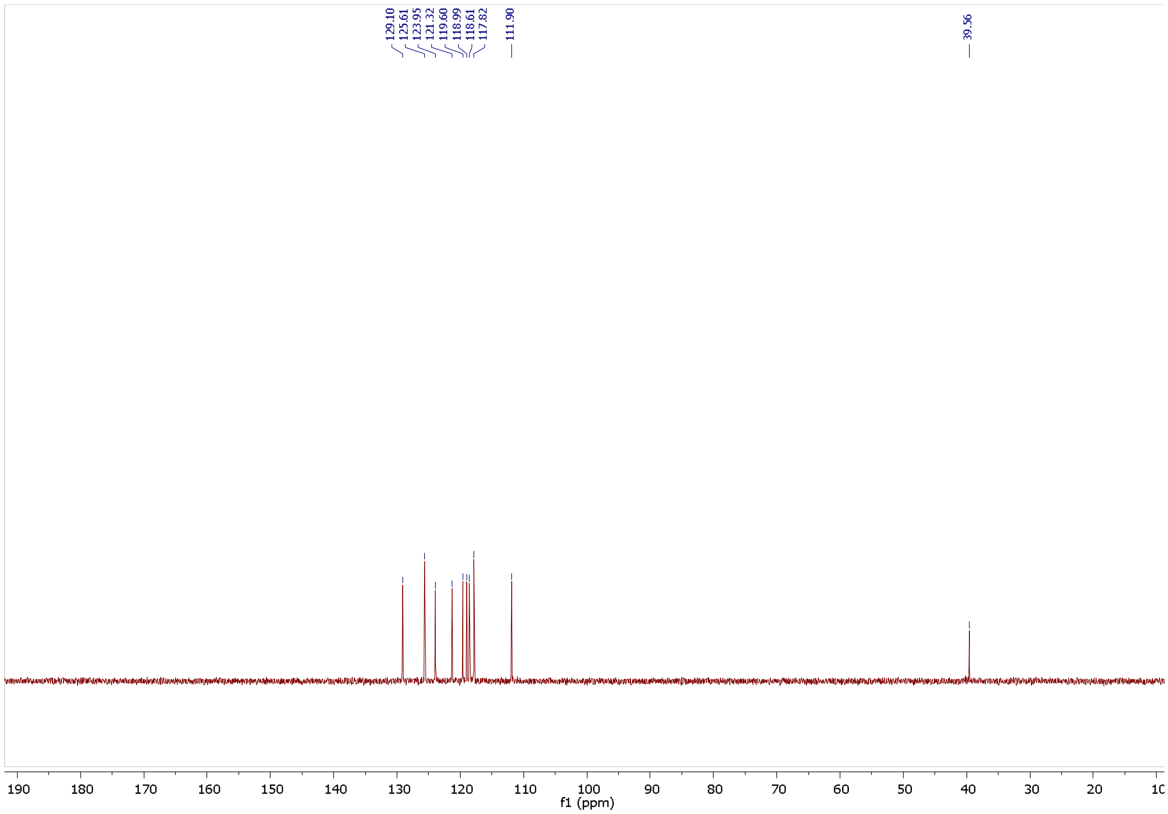
DEPT NMR (100 MHz, DMSO-d_6) of Compound (**9aFA)**



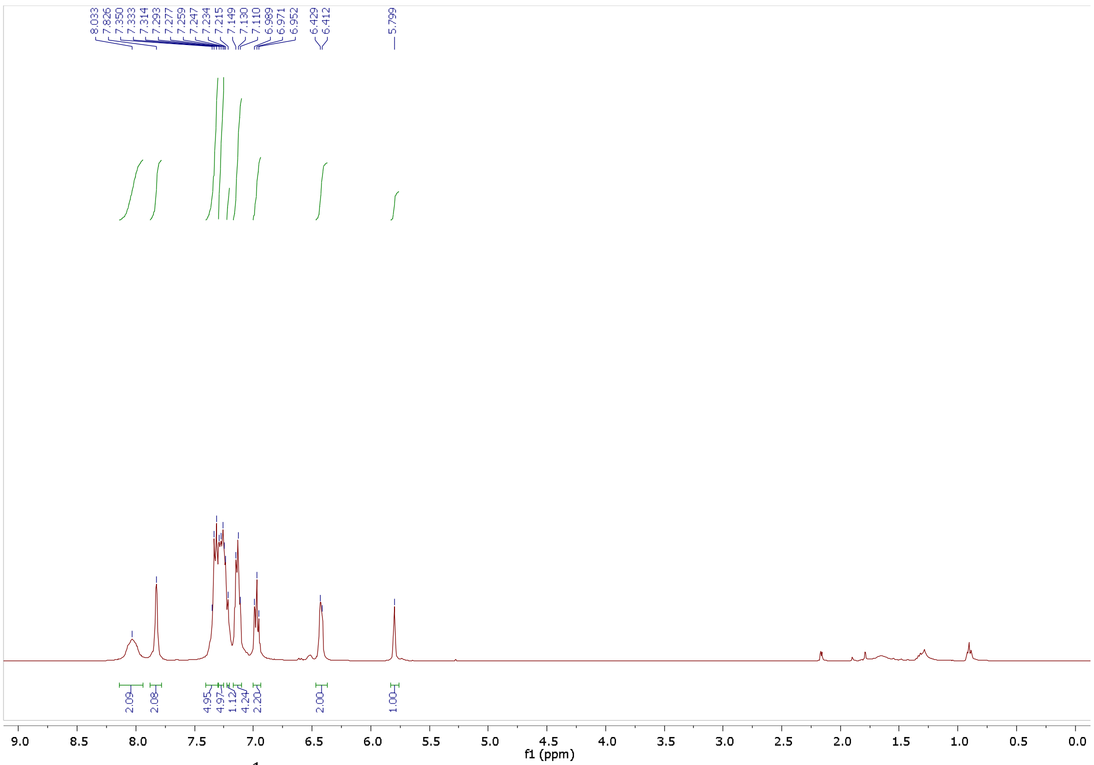
^{1}H NMR (400 MHz, DMSO-d_6) of Compound (**9aFB**)



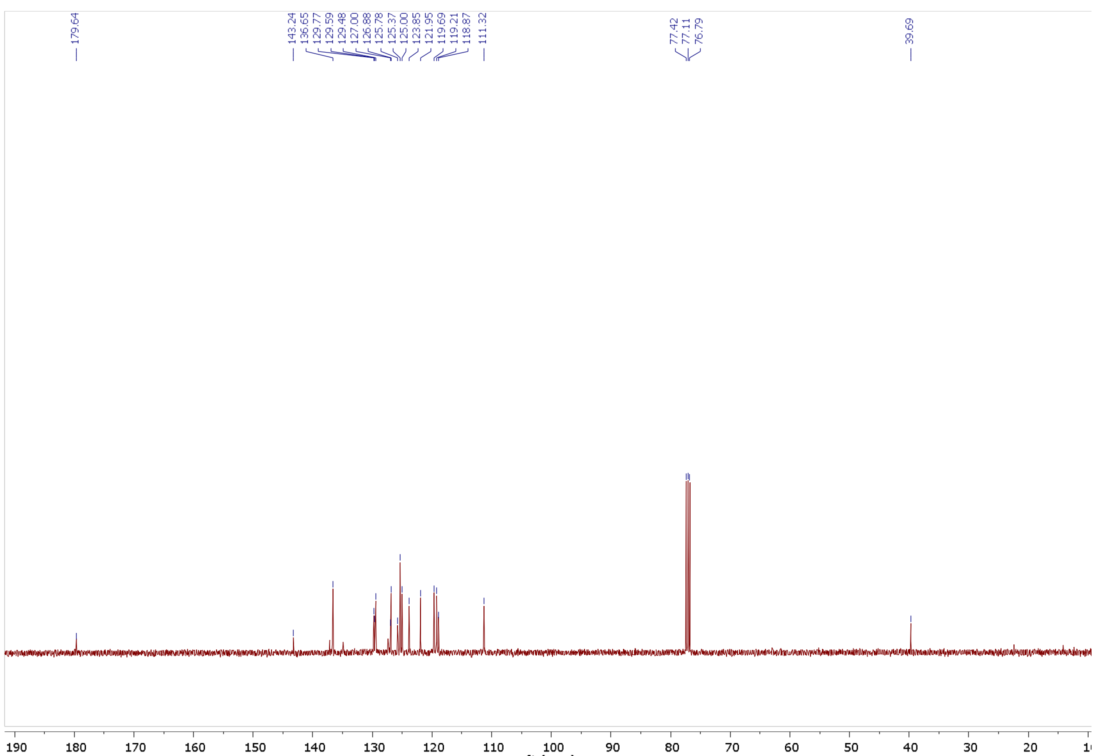
^{13}C NMR (100 MHz, DMSO-d_6) of Compound (**9aFB)**



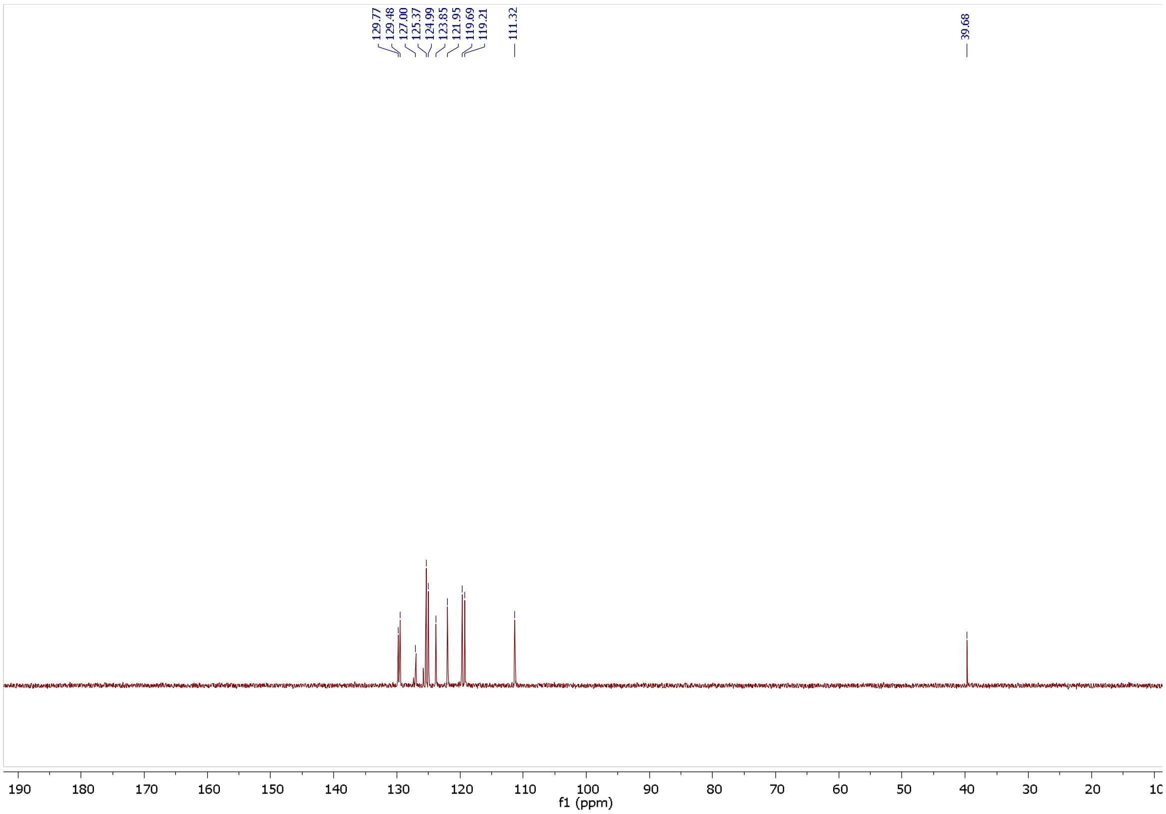
DEPT NMR (100 MHz, DMSO-d_6) of Compound (**9aFB**)



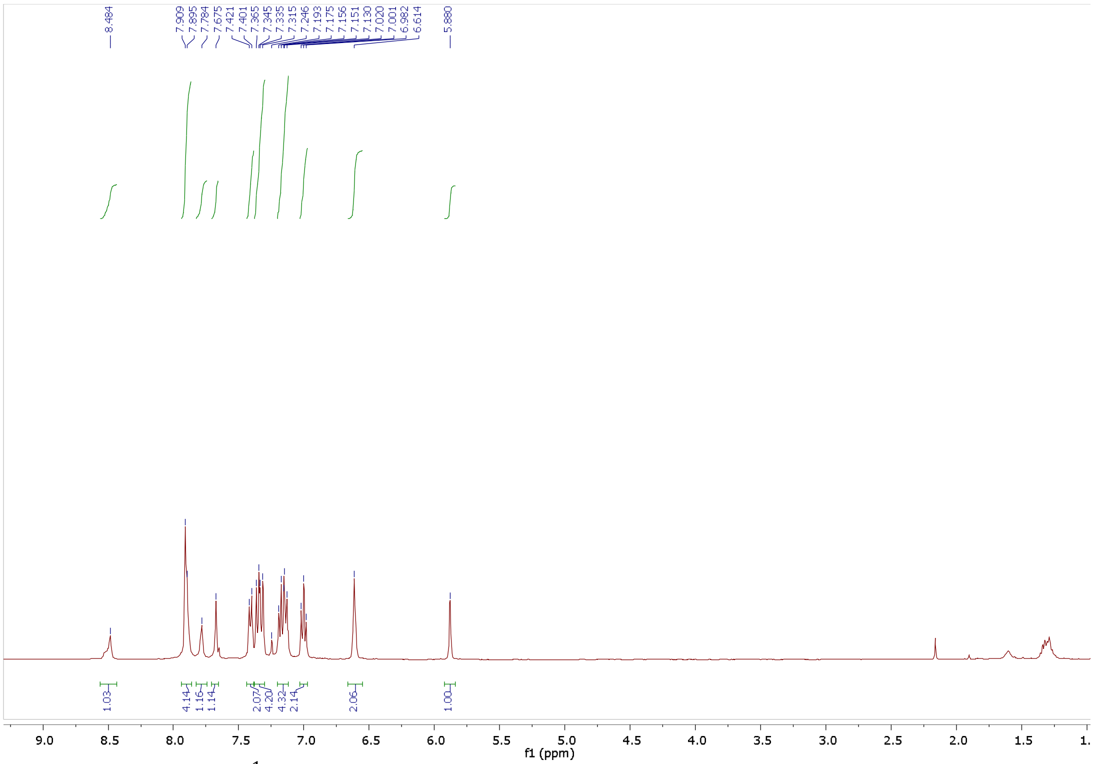
^{1}H NMR (400 MHz, $CDCl_3$) of Compound (**9aFC**)



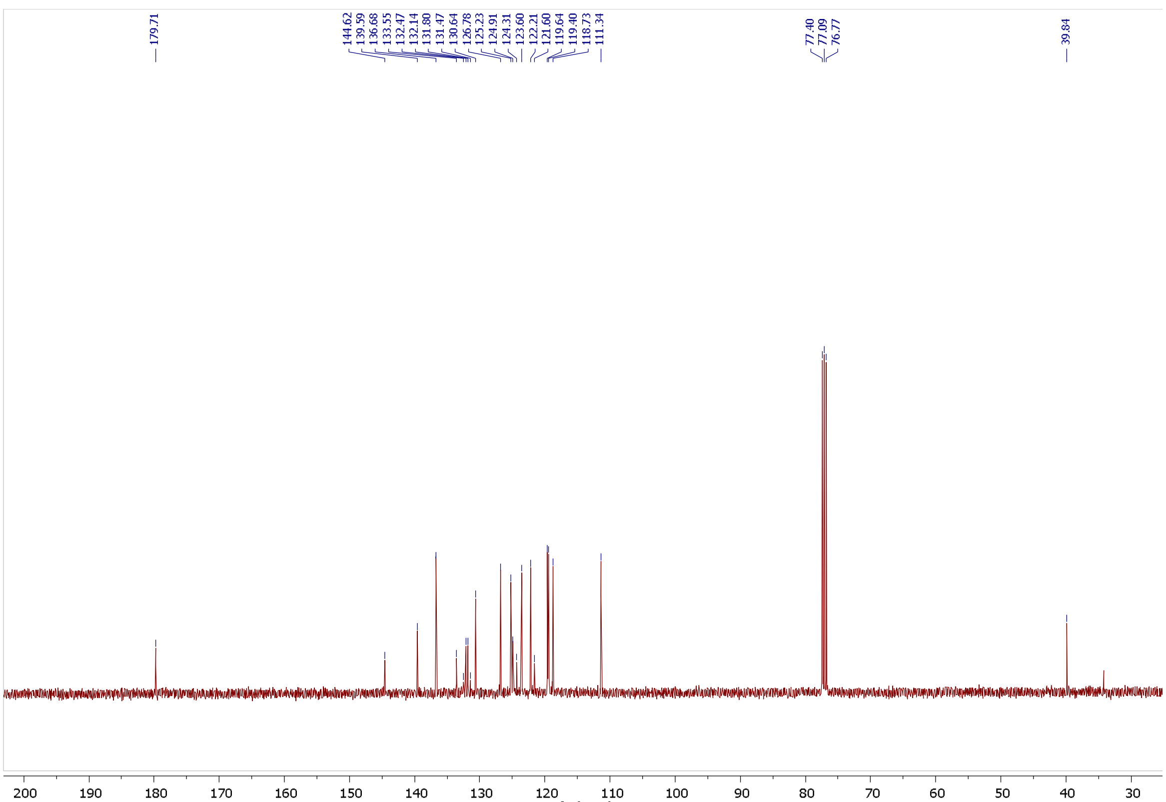
^{13}C NMR (100 MHz, $CDCl_3$) of Compound (**9aFC)**



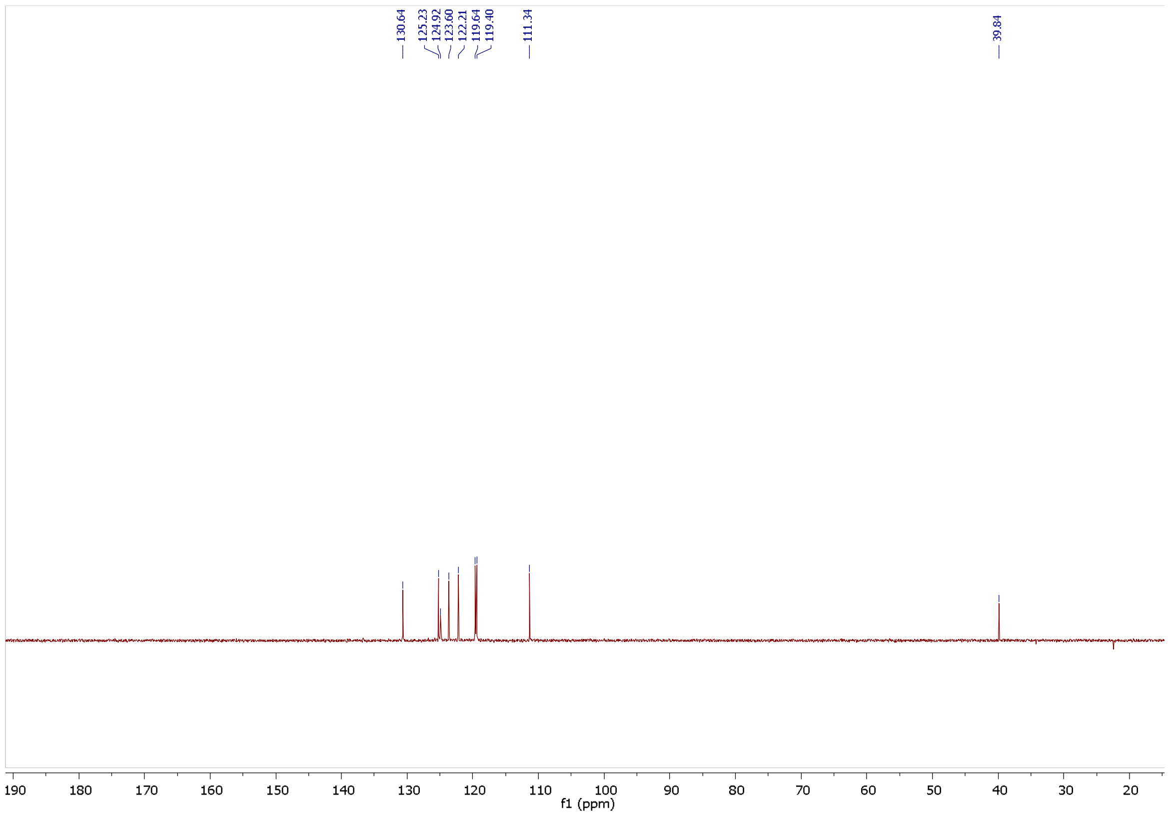
DEPT NMR (100 MHz, $CDCl_3$) of Compound (**9aFC**)



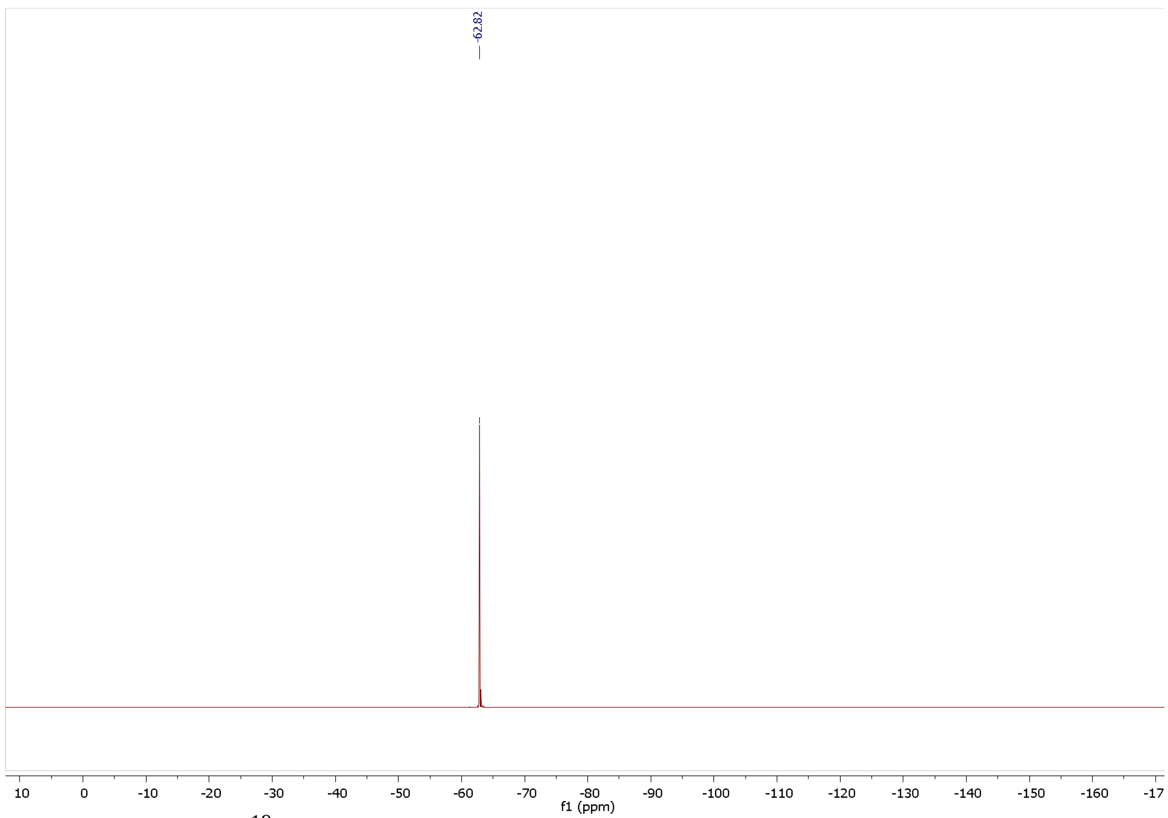
^1H NMR (400 MHz, $CDCl_3$) of Compound (**9aFD**)



^{13}C NMR (100 MHz, $CDCl_3$) of Compound (**9aFD**)



DEPT NMR (100 MHz, $CDCl_3$) of Compound (**9aFD**)



^{19}F NMR (376 MHz, $CDCl_3$) of Compound (**9aFD**)