Supplementary Material (ESI) for Organic & Biomolecular Chemistry

SUPPORTING INFORMATION

A combined experimental and theoretical study of the thermal cycloaddition of aryl azides with activated alkenes

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Table S1. B3LYP/6-31G* Total energies in gas phase and in solution, of the stationary points involved in the thermal domino reactions of the β-dicarbonyl compounds **2** with the phenyl azides **1**.

	E	Esolv
1	-600.339478	-600.351888
1e	-395.838293	-395.845107
2a	-345.783930	-345.798120
2'a-*Z*	-345.799880	-345.806354
2'a-*E*	-345.781300	-345.796587
2b	-421.025418	-421.034564
2'b-*Z*	-421.028507	-421.034809
2'b-*E*	-421.012961	-421.027779
TS11ea	-741.600612	-741.612040
TS12ea	-741.587347	-741.600954
6ea	-741.643397	-741.656283
6ea	-741.638813	-741.658358
TS11a	-946.106113	-946.122814
TS12a	-946.087754	-946.106151
61a	-946.146725	-946.164719
62a	-946.142062	-946.166785
TS11b	-1021.334266	-1021.351315
TS12b	-1021.320116	-1021.337592
61b	-1021.377031	-1021.395400
62b	-1021.376075	-1021.397792
IN11a	-1120.965805	-1121.050323
IN12a	-1120.956200	-1121.038231
TS21a	-1120.959295	-1121.041749
TS22a	-1120.948580	-1121.032334
31a	-869.748115	-869.766034
32b	-869.736532	-869.755960
IN11b	-1196.196328	-1196.281071
IN12b	-1196.190484	-1196.272085
TS21b	-1196.190990	-1196.272255
TS22b	-1196.185951	-1196.265085
31b	-944.974472	-944.994347
32b	-944.970063	-944.988637

Table S2. B3LYP/6-311+G** Total (E, in au.) and relative energies (ΔE, in kcal/mol) in gas phase and in solution, of the stationary points involved in the thermal domino reactions of the β-dicarbonyl compounds **2** with the phenyl azides **1**.

	E	ΔE	Esolv	ΔEsolv
1	-600.506010		-600.520865	
1e	-395.943084		-395.951121	
2a	-345.890473		-345.890473	
2'a-*Z*	-345.911074	-12.9	-345.911074	-7.2
2'a-*E*	-345.893729	-2.0	-345.893729	-2.1
2b	-421.156795		-421.156795	
2'b-*Z*	-421.163543	-4.2	-421.163543	-2.2
2'b-*E*	-421.149430	4.6	-421.149430	1.2
TS11ea	-741.811345	26.9	-741.825137	28.2
TS12ea	-741.798498	34.9	-741.814887	34.7
6ea	-741.846959	4.5	-741.865055	3.2
6ea	-741.848999	3.2	-741.871886	-1.1
TS11a	-946.378068	24.5	-946.397931	26.3
TS12a	-946.360917	35.3	-946.383078	35.6
61a	-946.416262	0.5	-946.437569	1.4
62a	-946.413912	2.0	-946.443010	-2.0
TS11b	-1021.630101	20.5	-1021.650338	23.9
TS12b	-1021.616738	28.9	-1021.637672	31.9
61b	-1021.670566	-4.9	-1021.692365	-2.5
62b	-1021.670825	-5.0	-1021.697461	-5.7
IN11a	-1121.283449		-1121.371536	
IN12a	-1121.273672		-1121.359182	
TS21a	-1121.277386	3.8	-1121.362875	5.4
TS22a	-1121.266585	4.5	-1121.354225	3.1
31a	-869.984287	-16.1	-870.005820	-23.7
32b	-869.973009	-9.0	-869.995799	-17.4
IN11b	-1196.537390		-1196.625392	
IN12b	-1196.531042		-1196.625392	
TS21b	-1196.532351	3.2	-1196.616796	5.4
TS22b	-1196.526985	2.6	-1196.612751	7.9
31b	-945.234333	-18.8	-945.257916	-25.9
32b	-945.229914	-16.1	-945.251972	-22.2

Table S3. B3LYP/6-311+G** Lengths (in angstroms), asynchronicity (Δl), charge transfer (CT, in e), and bond orders (BO) of the C-N forming bonds involved in the 32CA reactions between the enols **2'** and the phenyl azides **1**.

	N1-C5(4)	N3-C4(5)	Δl	CT	BO N1-C5(4)	BO N3-C4(5)
TS11ea	1.998	2.157	0.16	-0.18	0.47	0.31
TS12ea	1.885	2.155	0.27	-0.09	0.50	0.35
TS11a	1.952	2.228	0.28	-0.27	0.50	0.27
TS12a	1.892	2.135	0.24	-0.14	0.50	0.36
TS11b	1.957	2.240	0.28	-0.27	0.50	0.26
TS12b	1.935	2.128	0.19	-0.16	0.47	0.36

Table S4. B3LYP/6-311+G** Lengths of the breaking and forming bonds (in angstroms) at the TSs involved in the water elimination.

	C4-O6	O8-H7	H7-O6	H9-N10
TS21a	1.629	1.286	1.129	2.037
TS22a	1.700	1.550	1.019	2.244
TS21b	1.621	1.268	1.142	1.983
TS22b	1.747	1.542	1.021	2.140

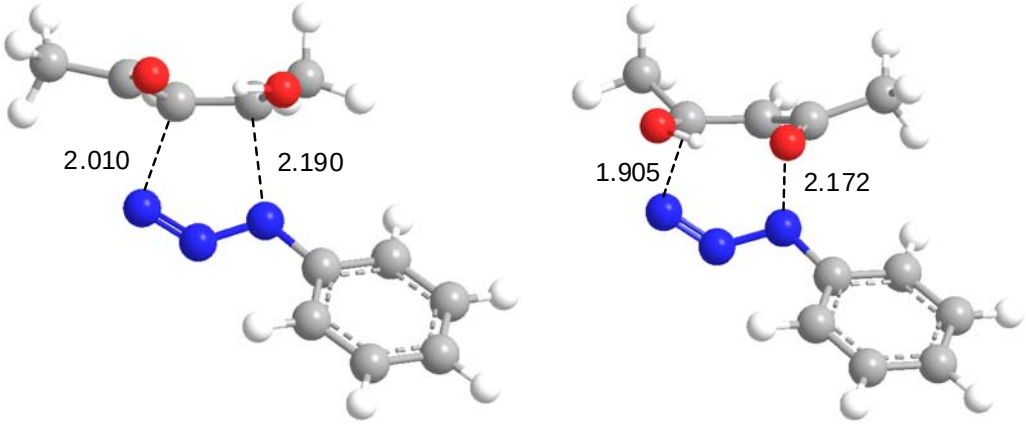
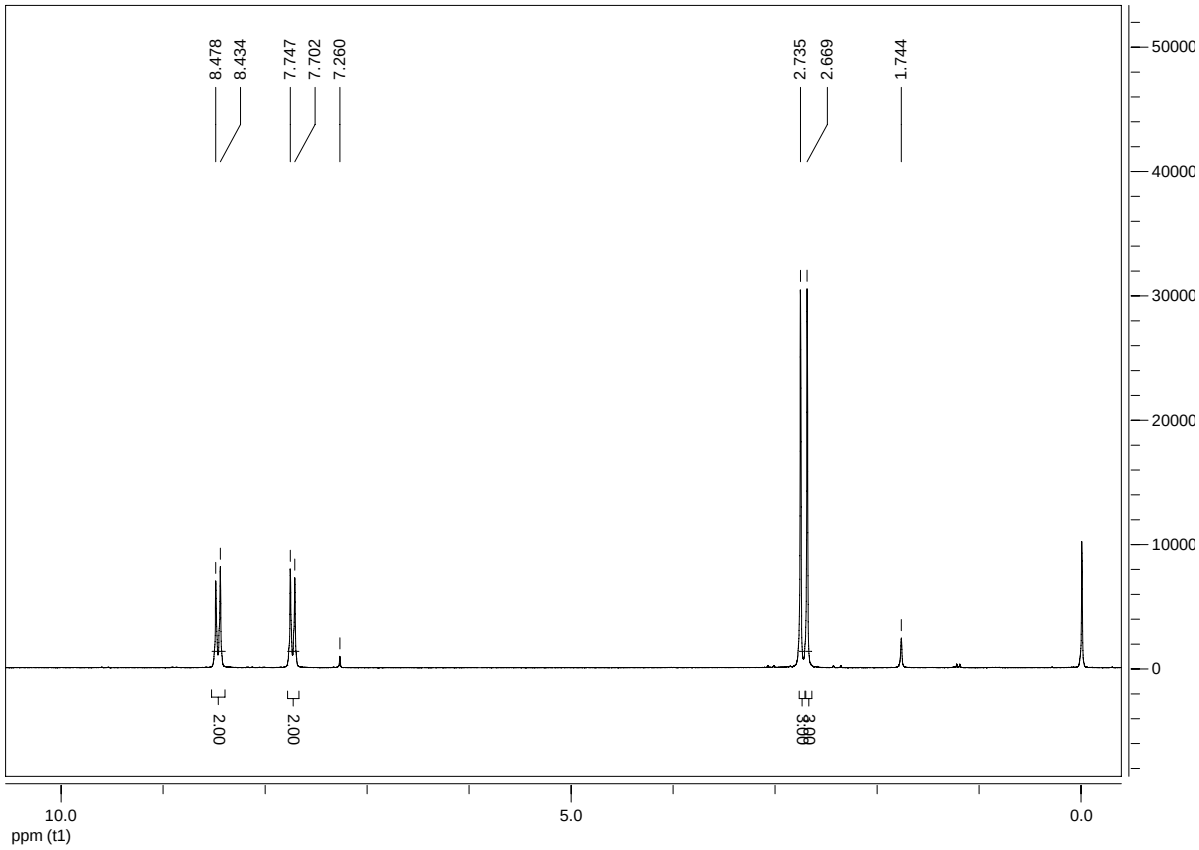


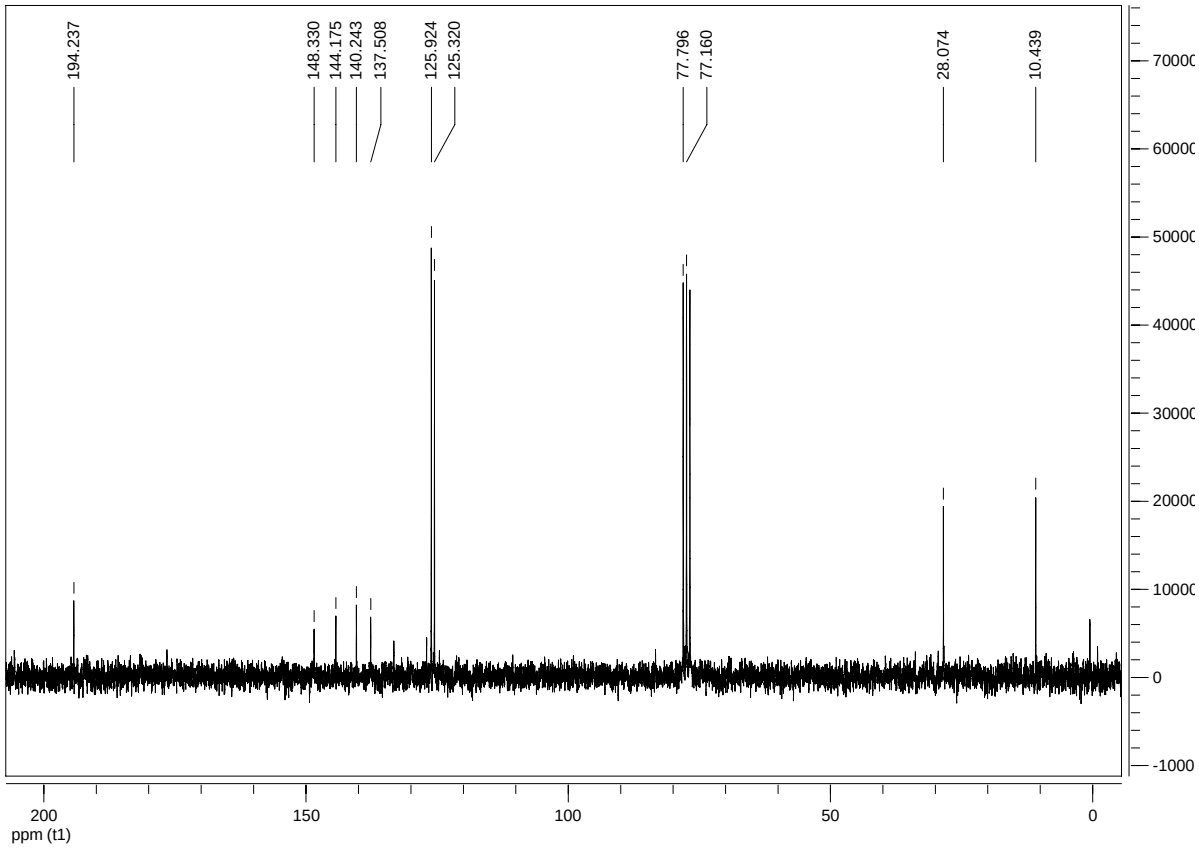
Figure S1. B3LYP/6-31G* Transition states involved in the regioisomeric channels 1 and 2 associated with the 13DC reaction between the enol **2'a**-*Z* and phenyl azide (**1e**).

Compound **3a**

^{1}H NMR (300 MHz, $CDCl_3$):

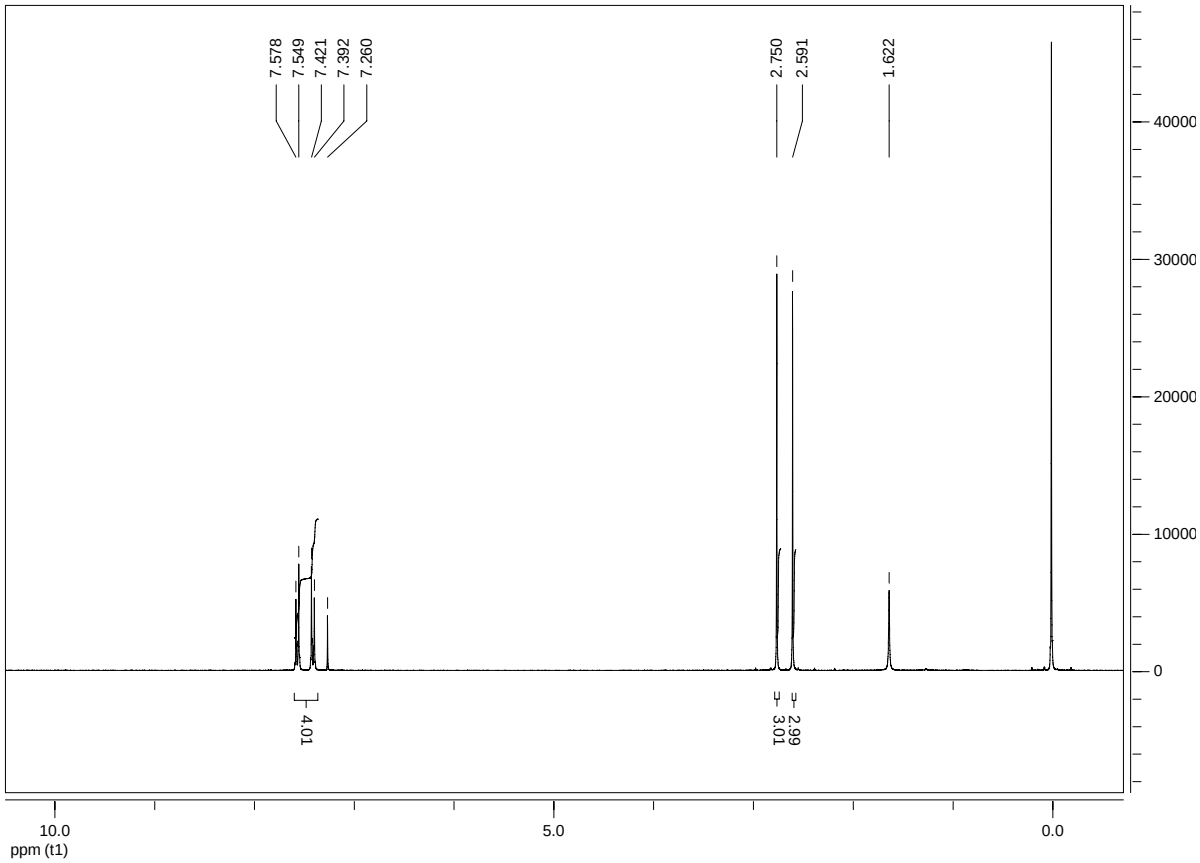


^{13}C NMR (75 MHz, $CDCl_3$):

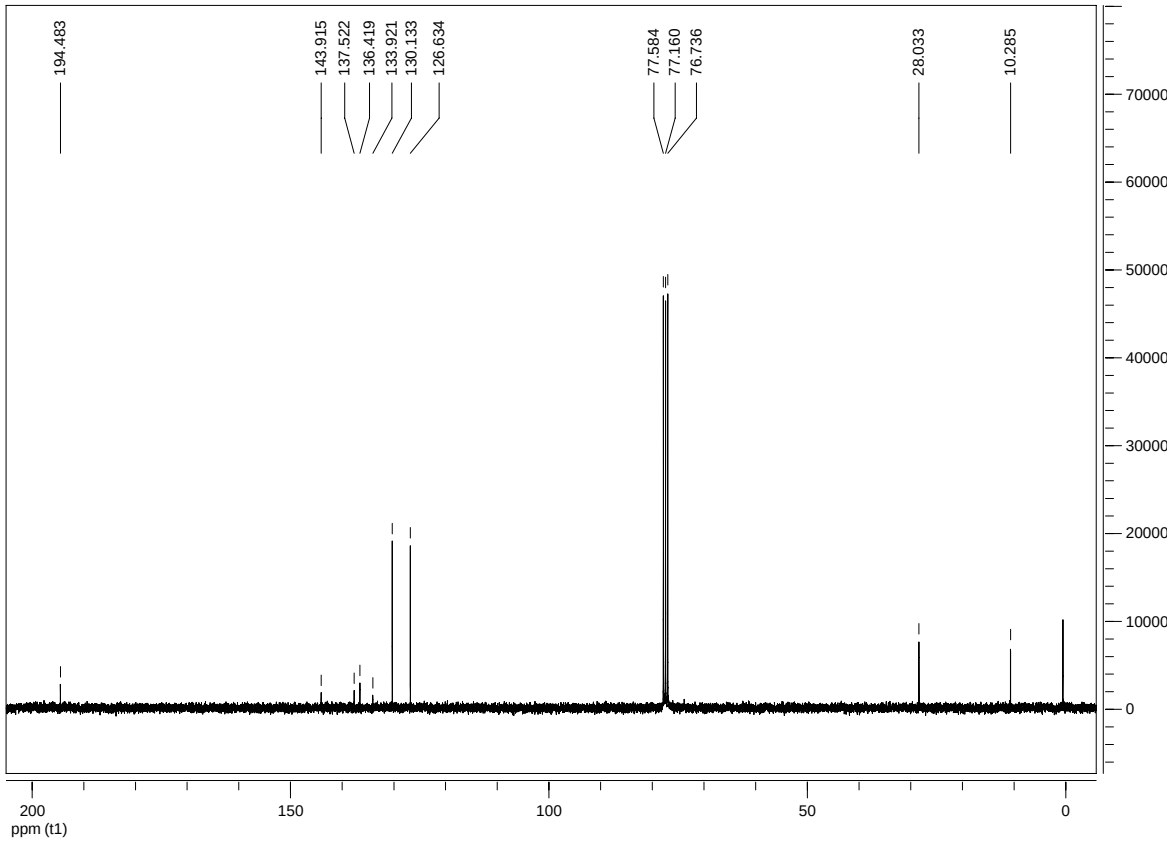


Compound **3b**

^{1}H NMR (300 MHz, $CDCl_3$):

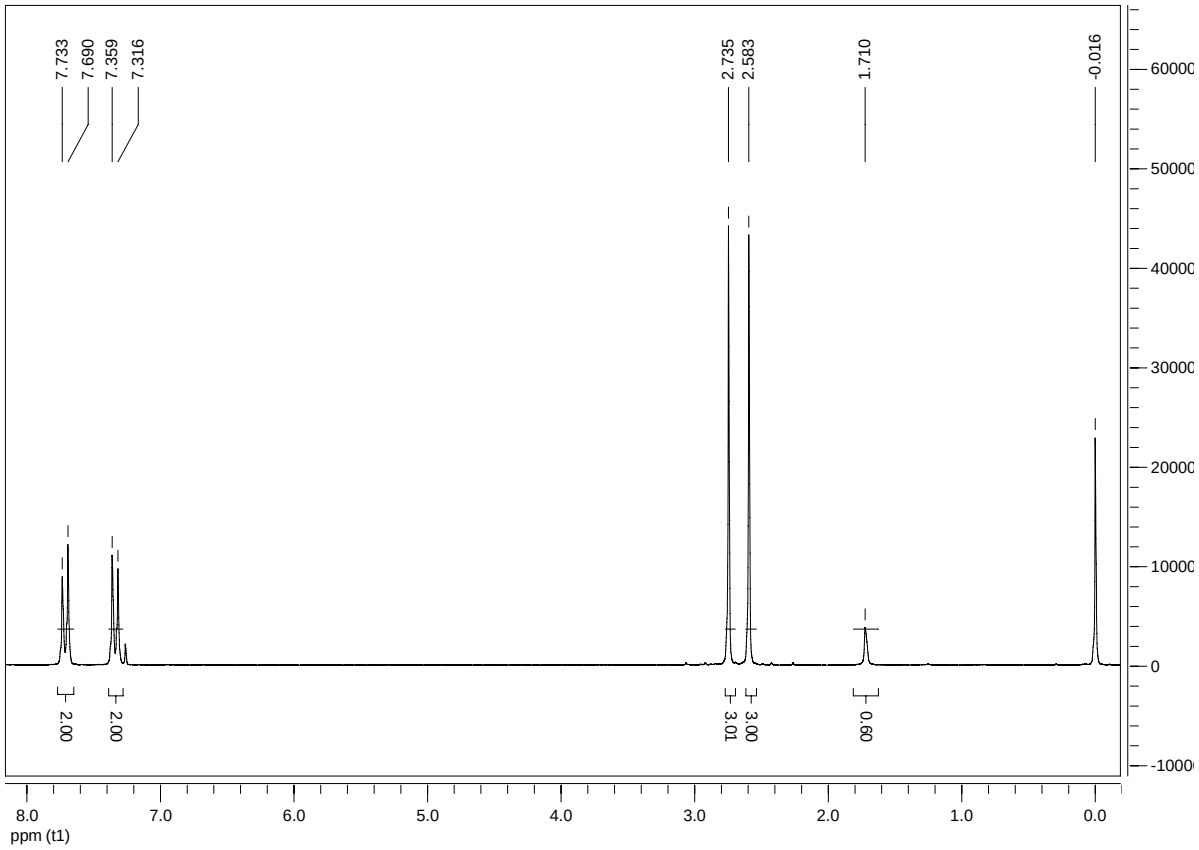


^{13}C NMR (75 MHz, $CDCl_3$):

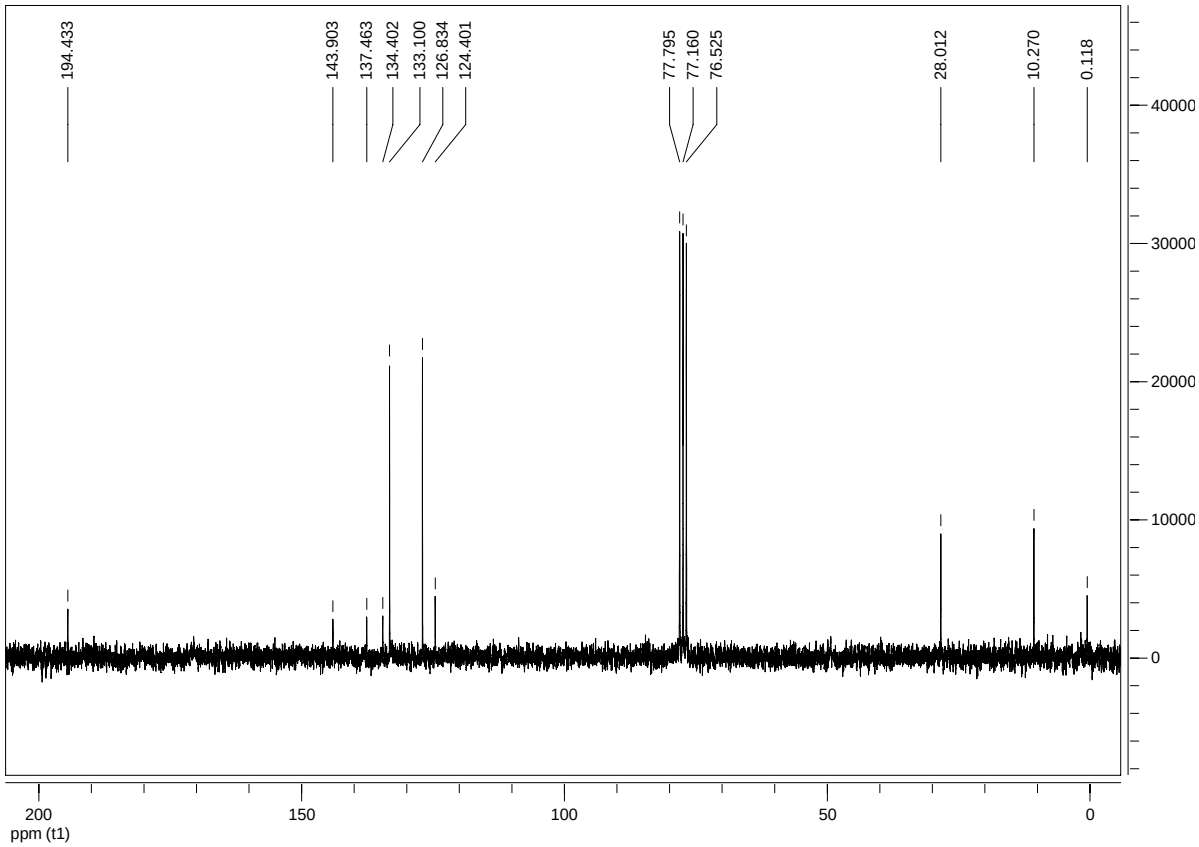


Compound **3c**

^{1}H NMR (300 MHz, $CDCl_3$):

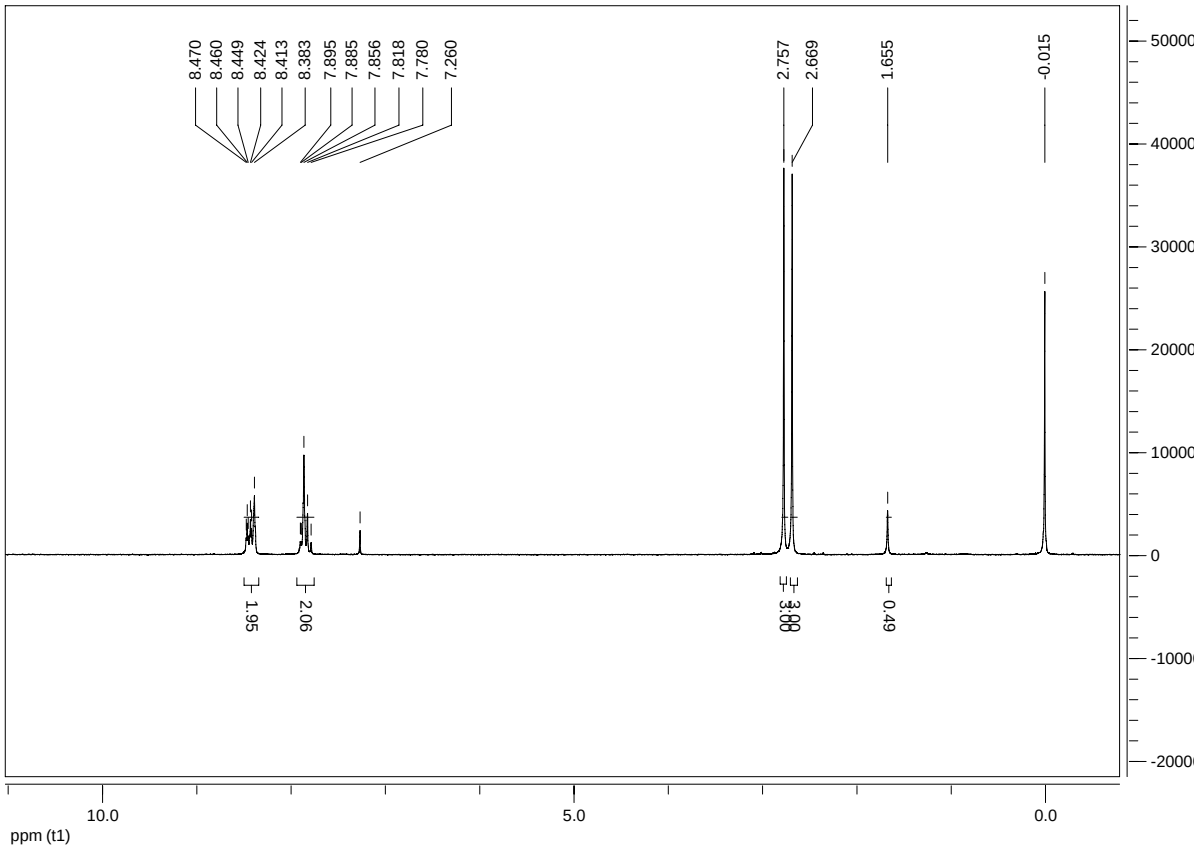


^{13}C NMR (75 MHz, $CDCl_3$):

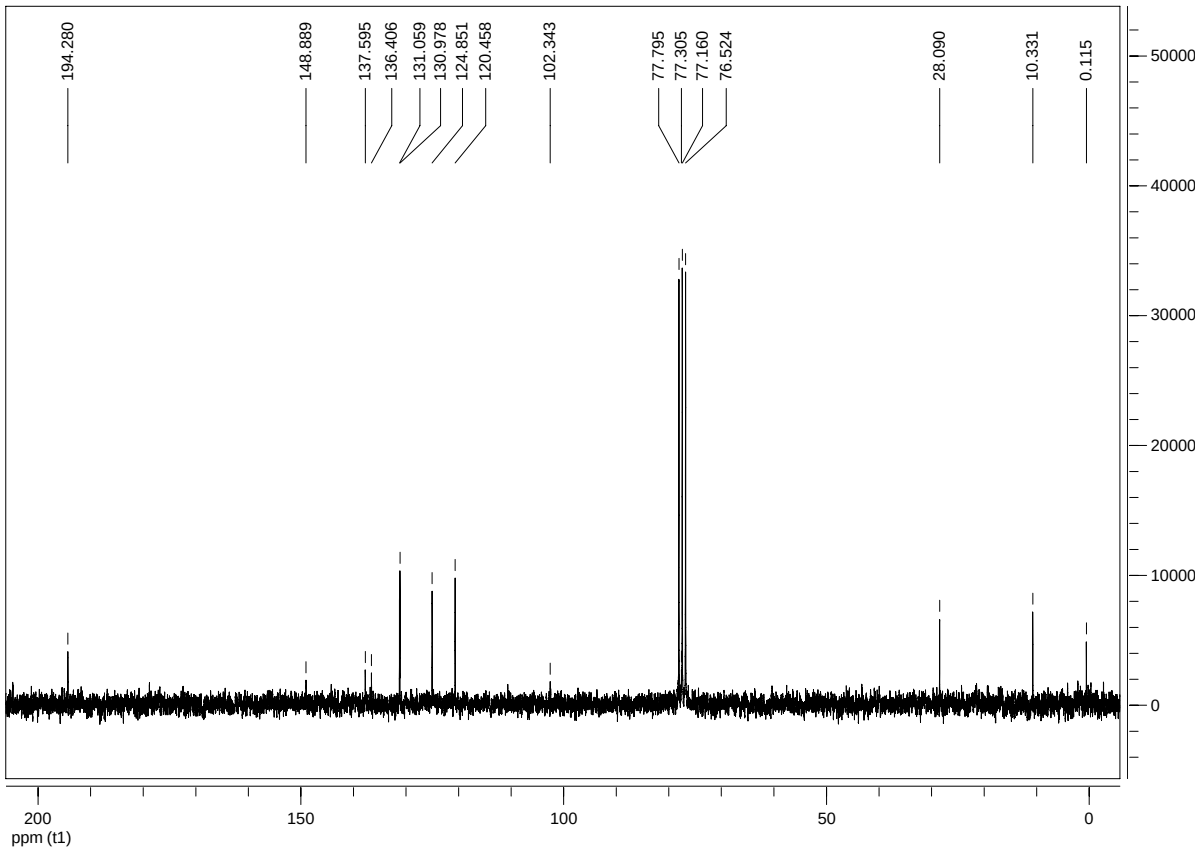


Compound **3d**

^{1}H NMR (300 MHz, $CDCl_3$):

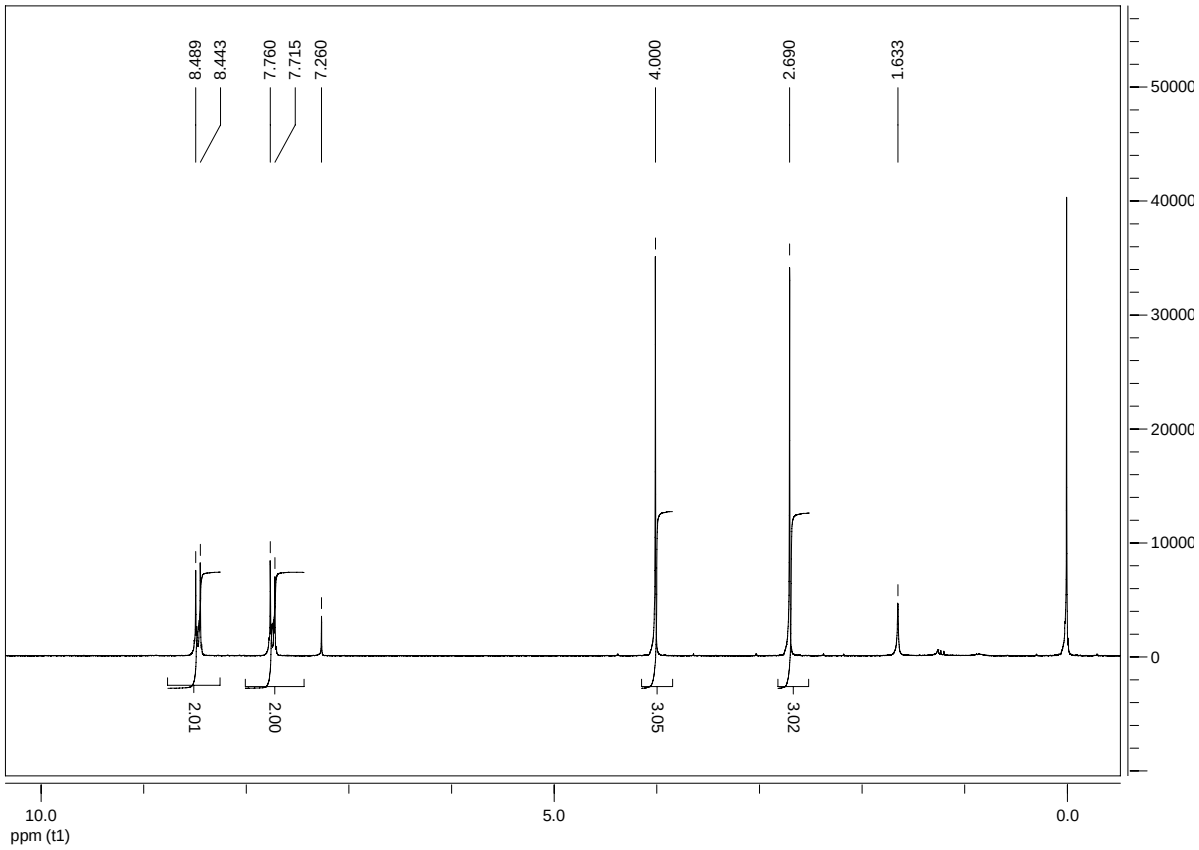


^{13}C NMR (75 MHz, $CDCl_3$):

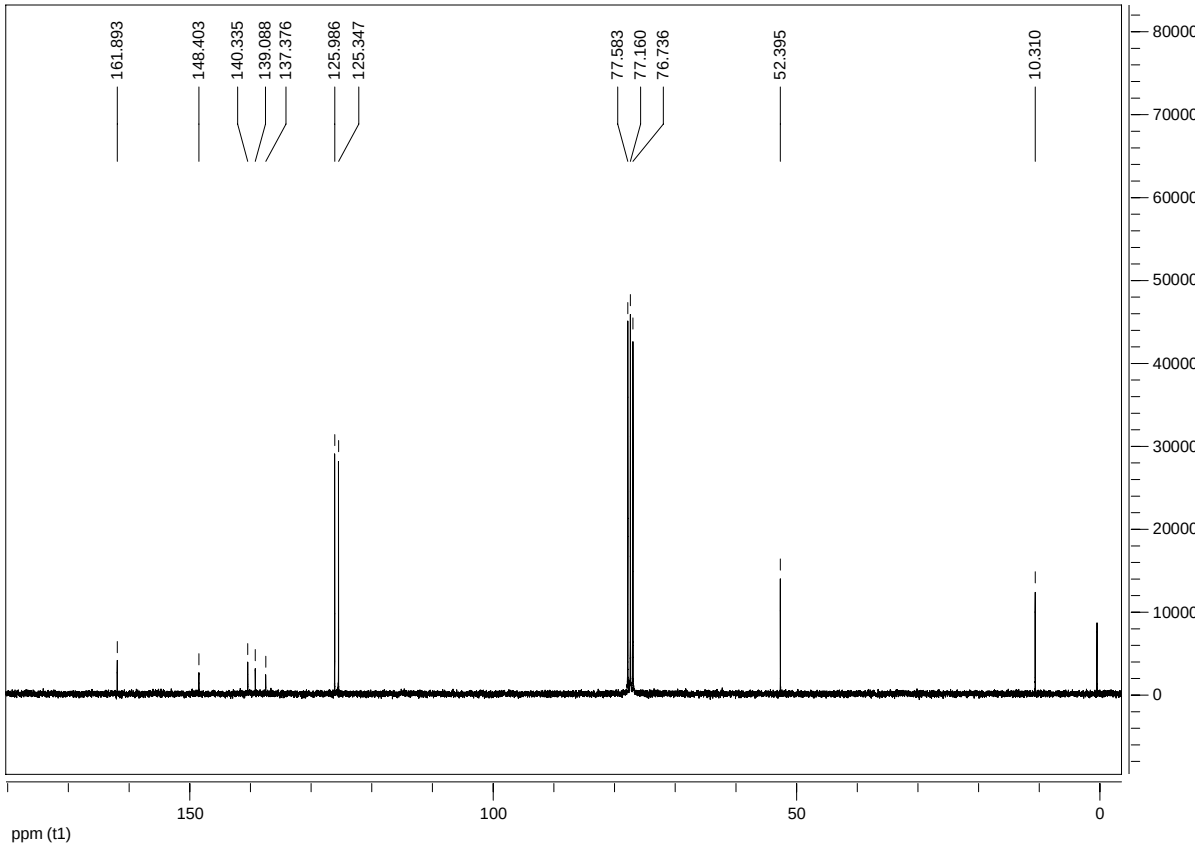


Compound **3e**

^{1}H NMR (300 MHz, $CDCl_3$):

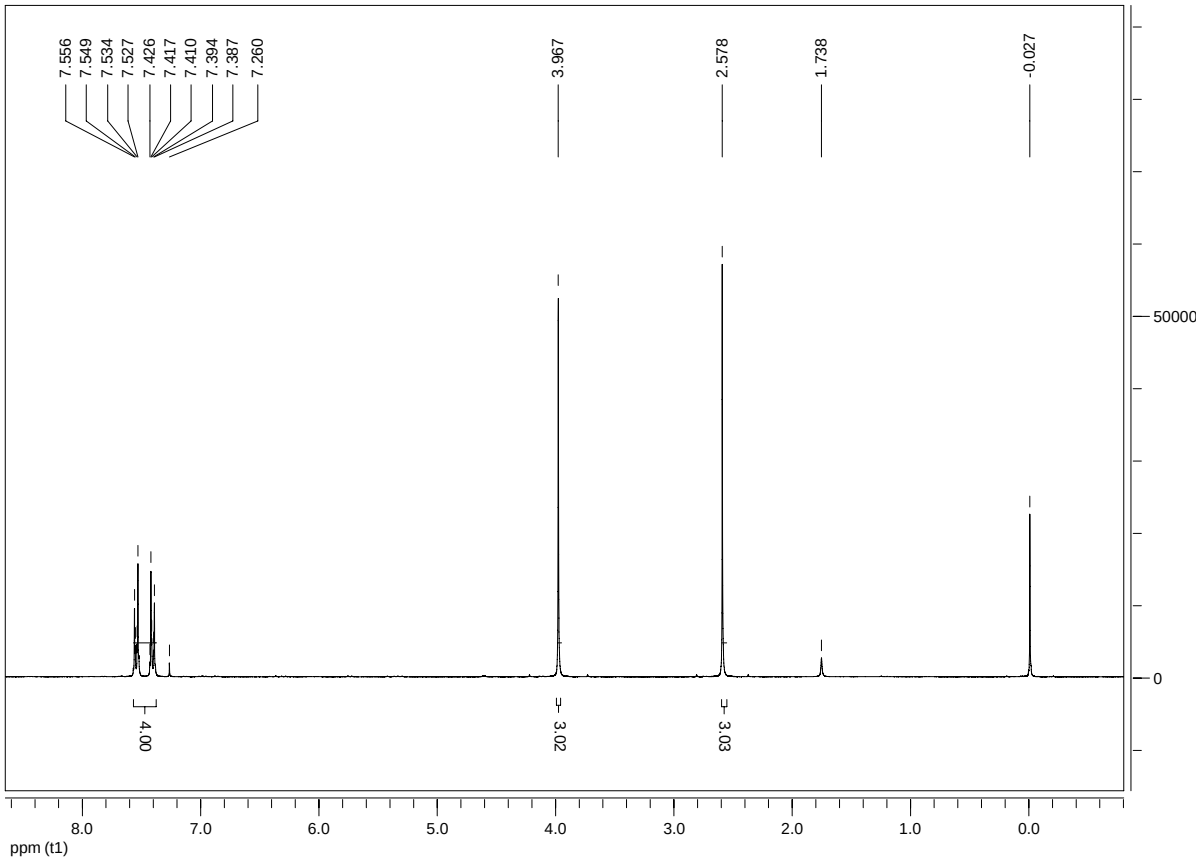


^{13}C NMR (75 MHz, $CDCl_3$):

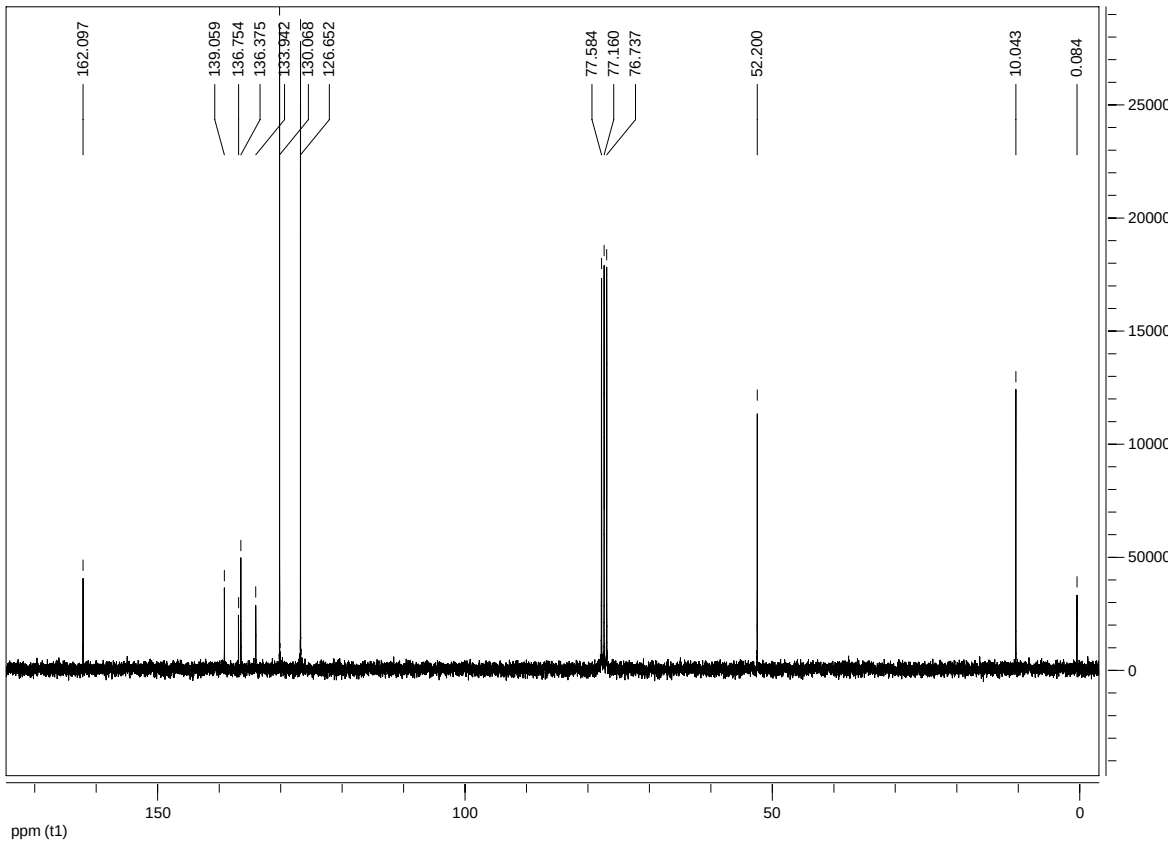


Compound **3f**

^{1}H NMR (300 MHz, $CDCl_3$):

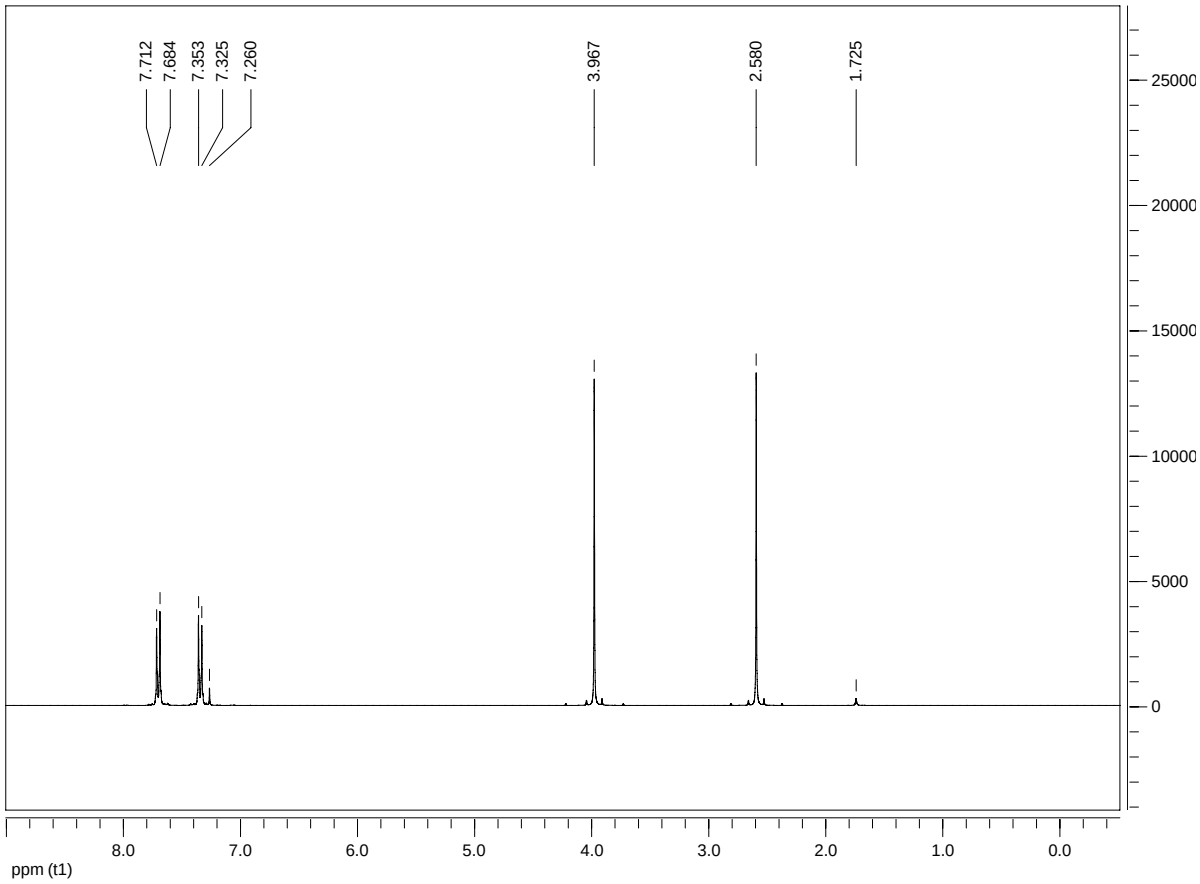


^{13}C NMR (75 MHz, $CDCl_3$):

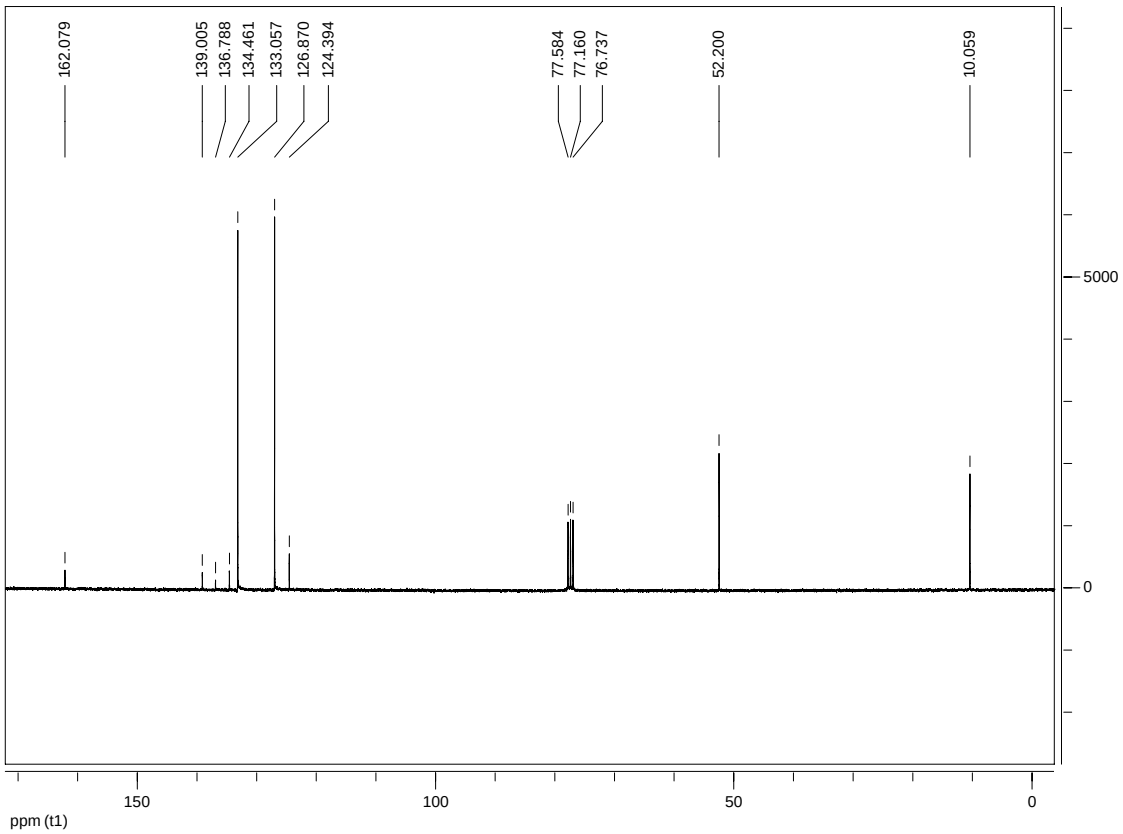


Compound **3g**

^{1}H NMR (300 MHz, $CDCl_3$):

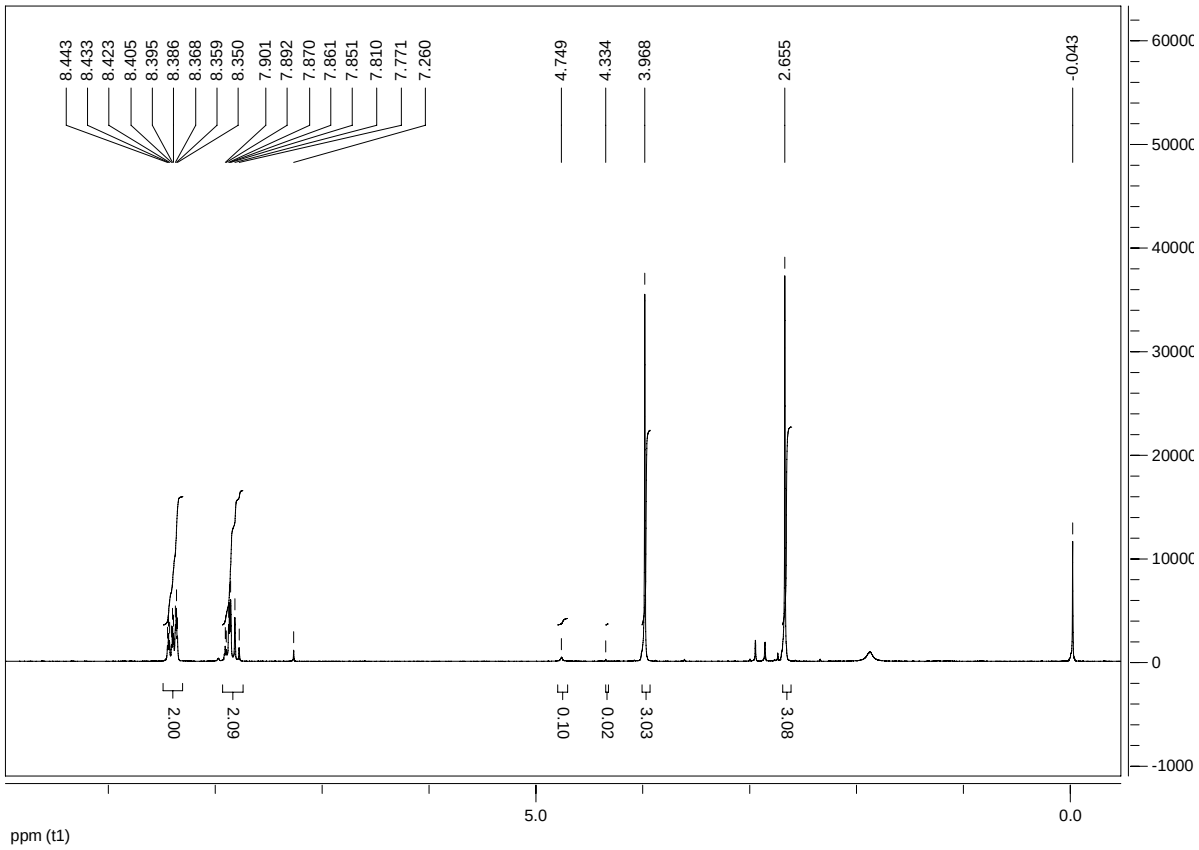


^{13}C NMR (75 MHz, $CDCl_3$):

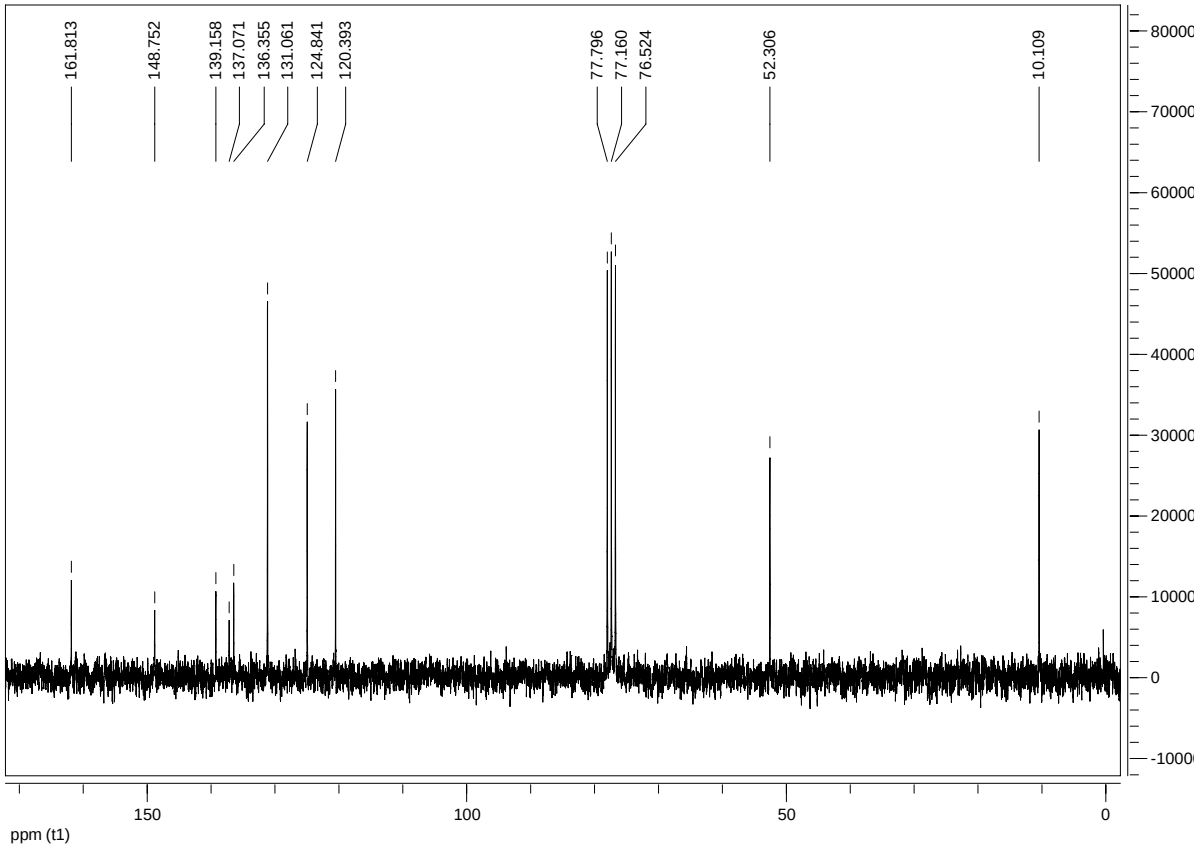


Compound **3h**

^{1}H NMR (300 MHz, $CDCl_3$):

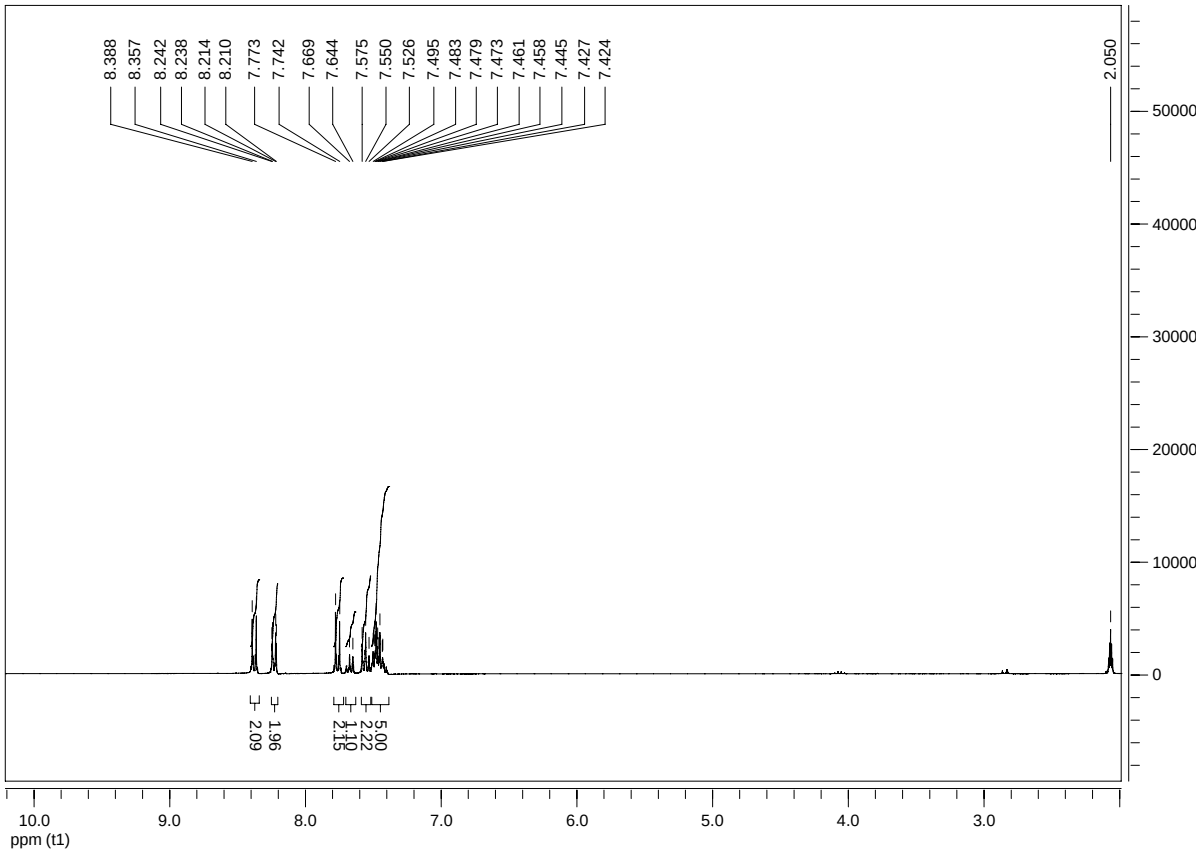


^{13}C NMR (75 MHz, $CDCl_3$):

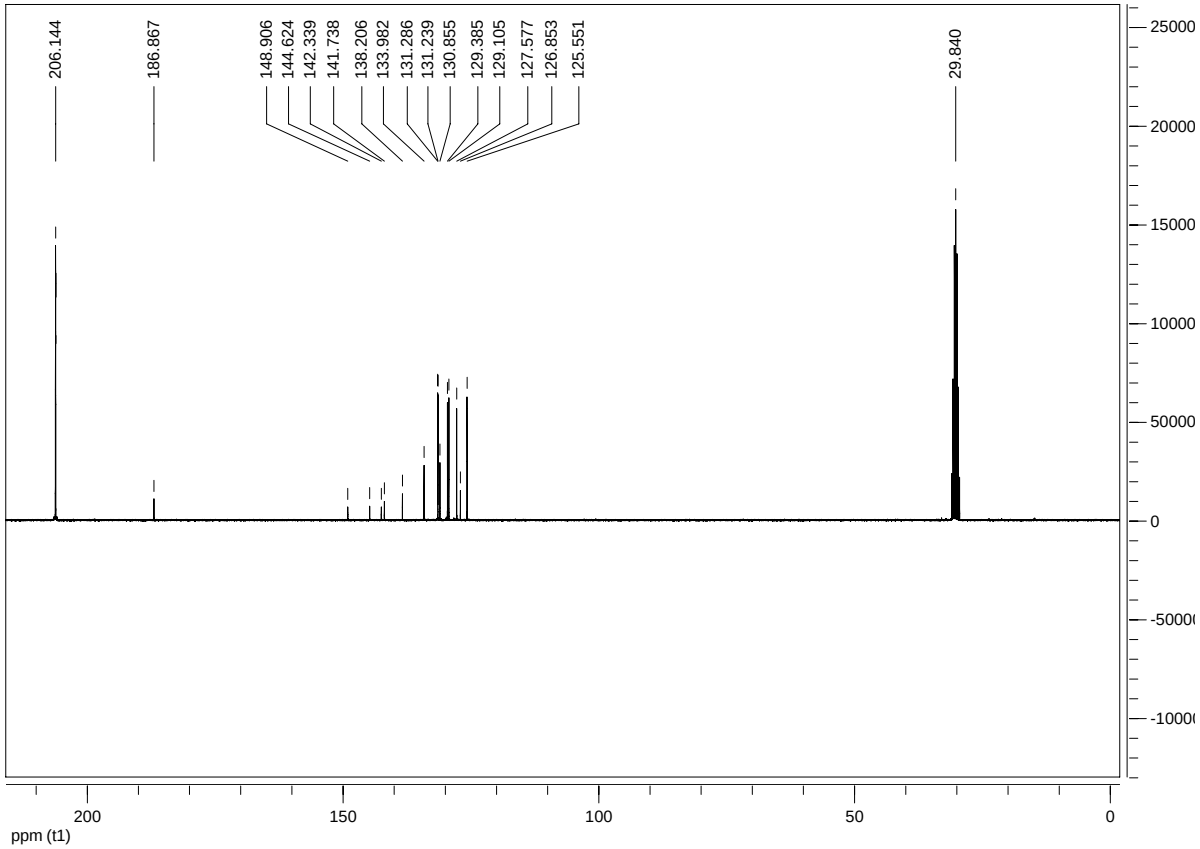


Compound **5a**

^{1}H NMR (300 MHz, $(CD_3)_2CO$):

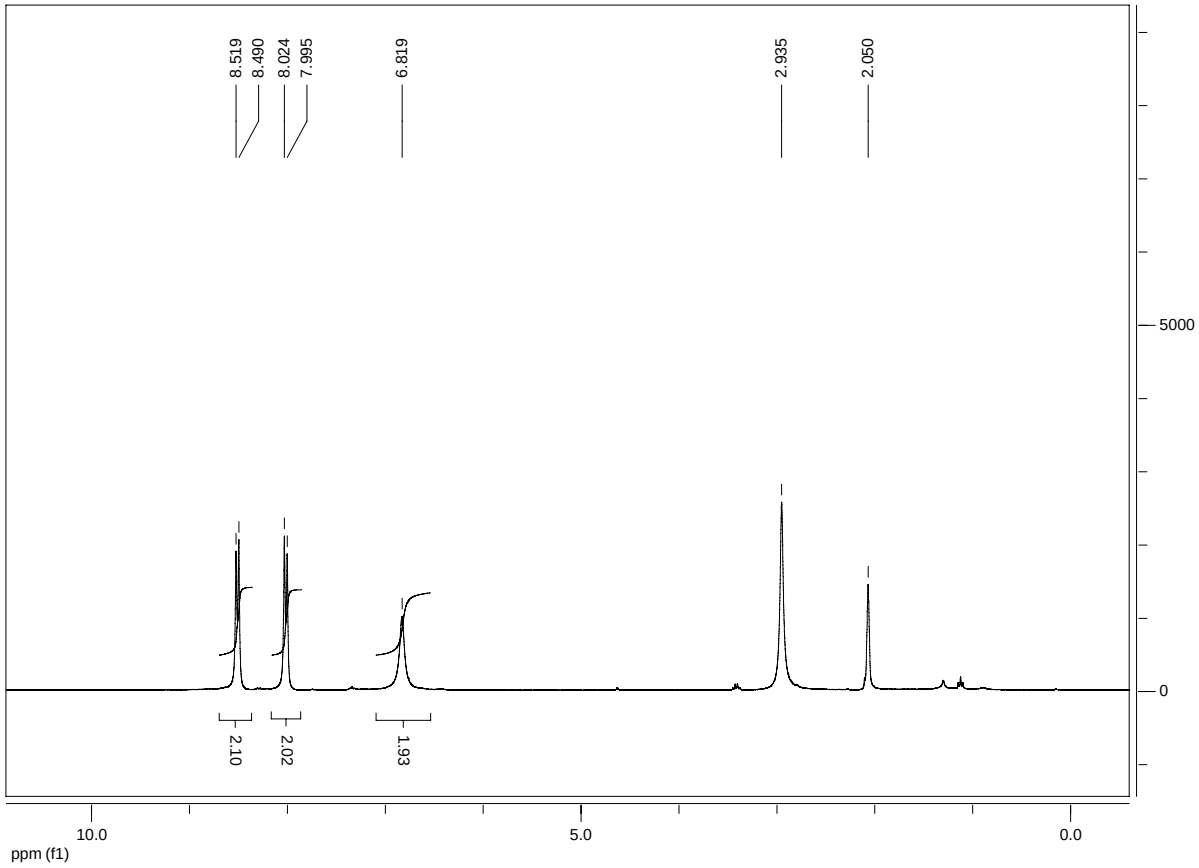


^{13}C NMR (75 MHz, $(CD_3)_2CO$):

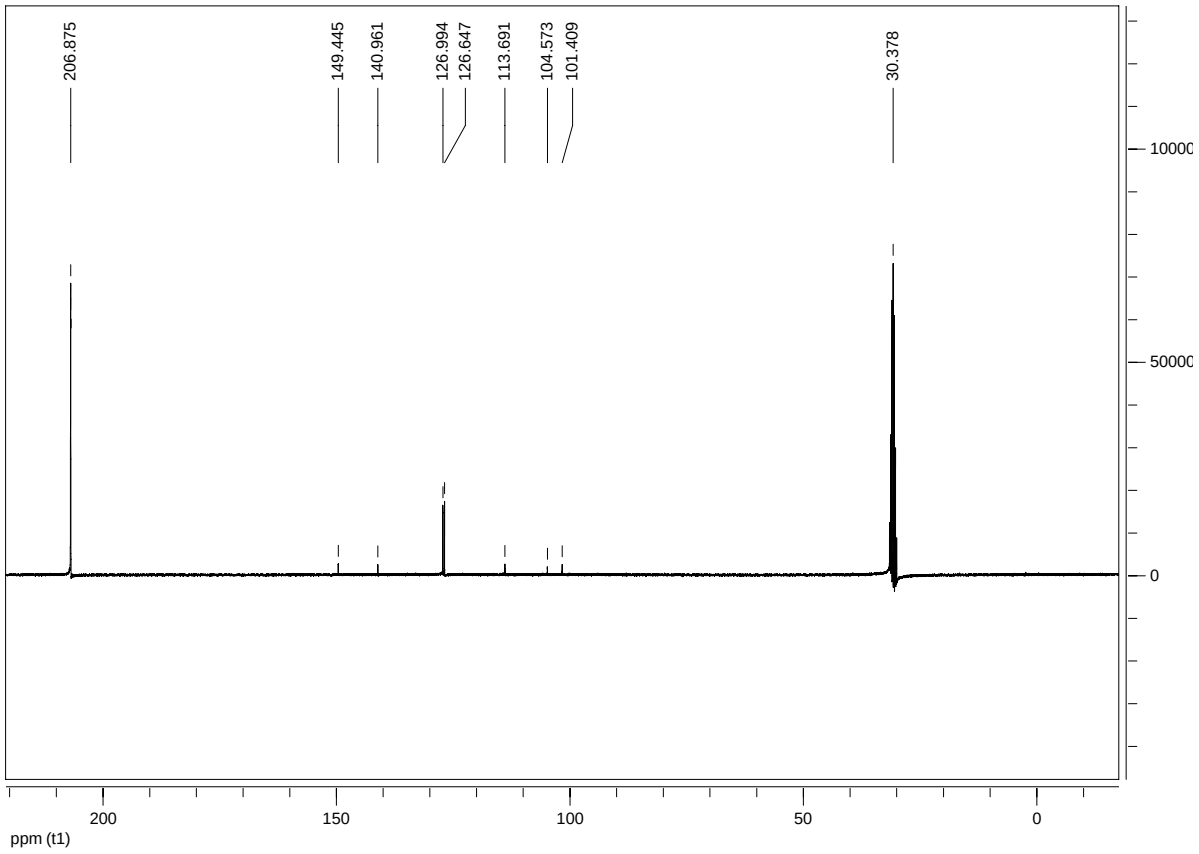


Compound **5b**

^{1}H NMR (300 MHz, $(CD_3)_2CO$):

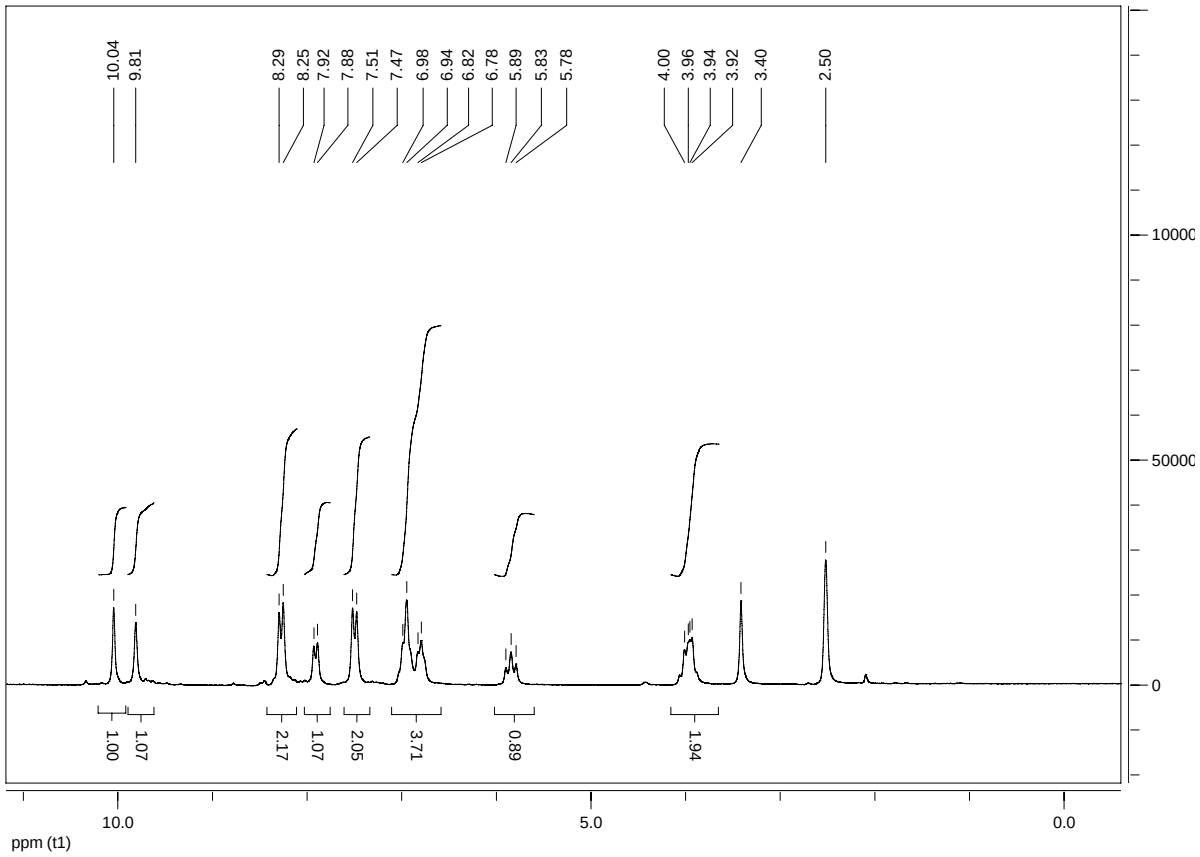


^{13}C NMR (75 MHz, $(CD_3)_2CO$):

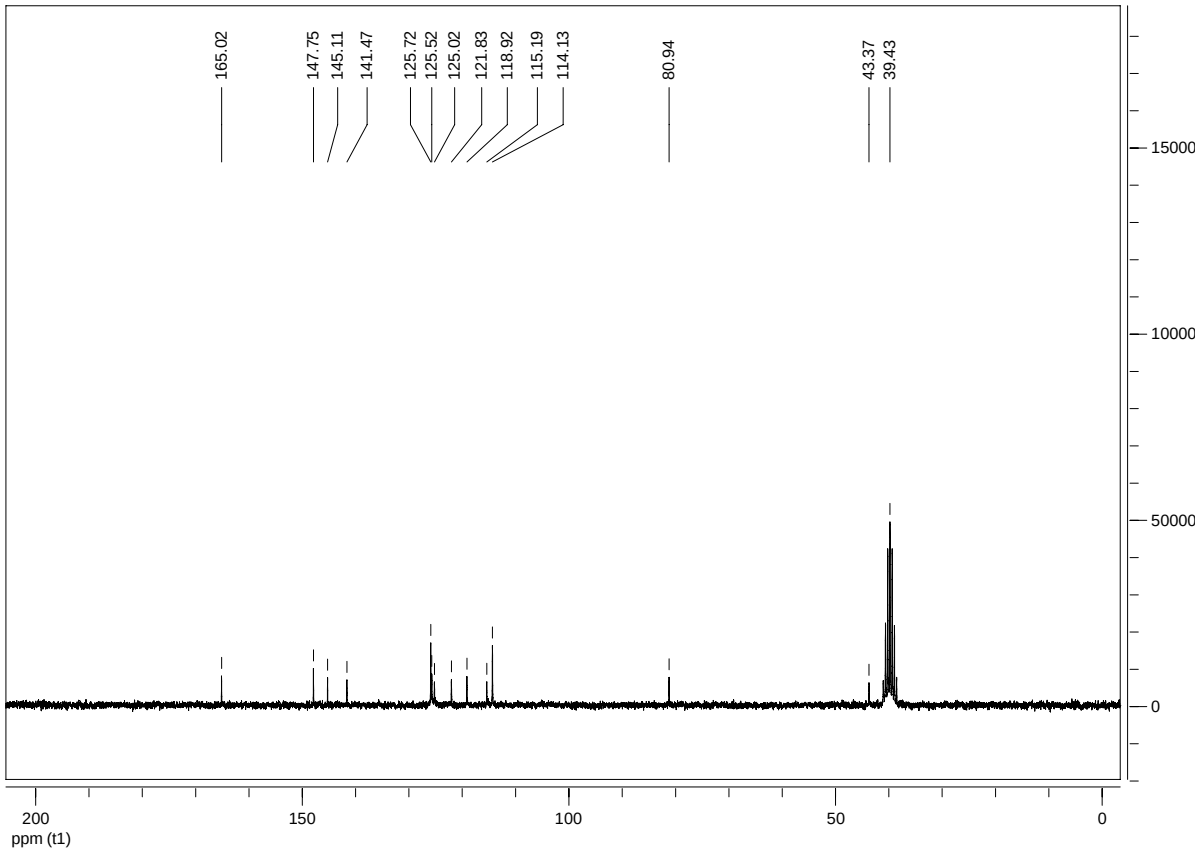


Compound **8**

^{1}H NMR (200 MHz, $(CD_3)_2SO$):

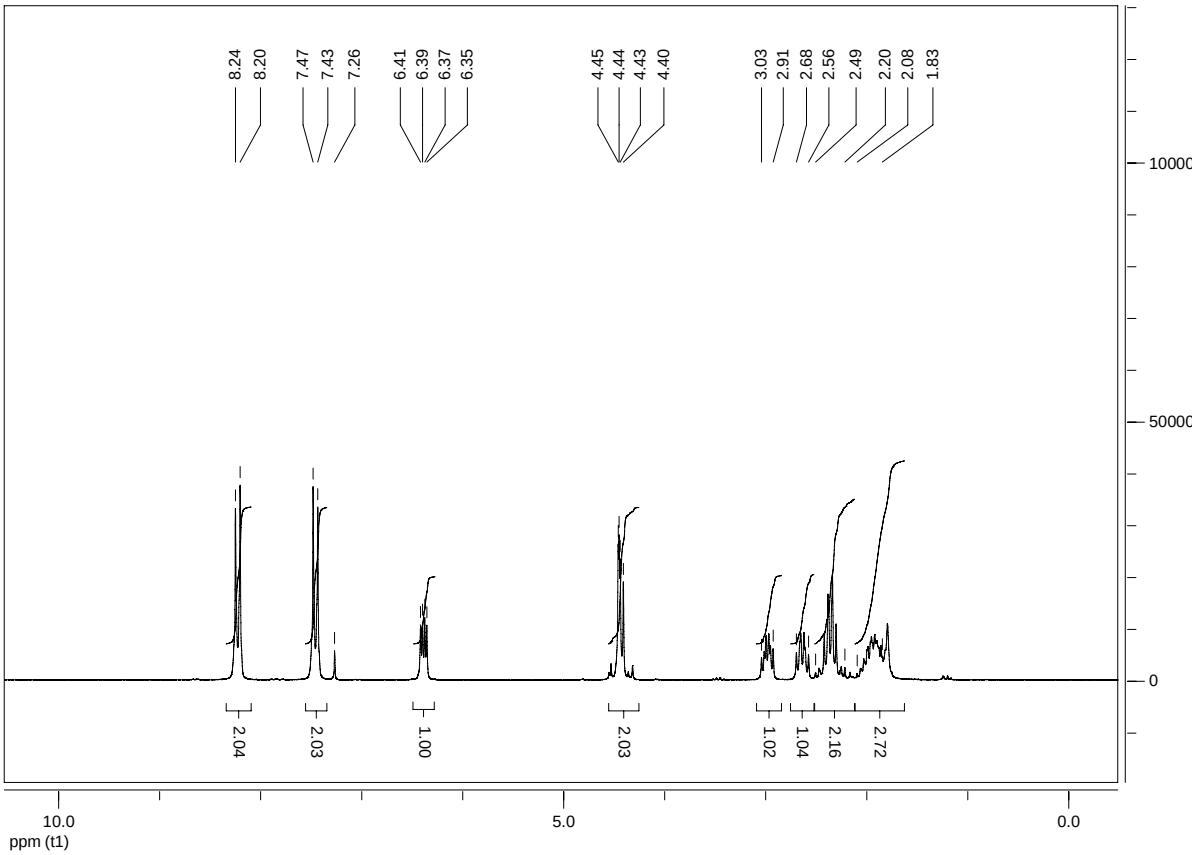


^{13}C NMR (50 MHz, $(CD_3)_2SO$):

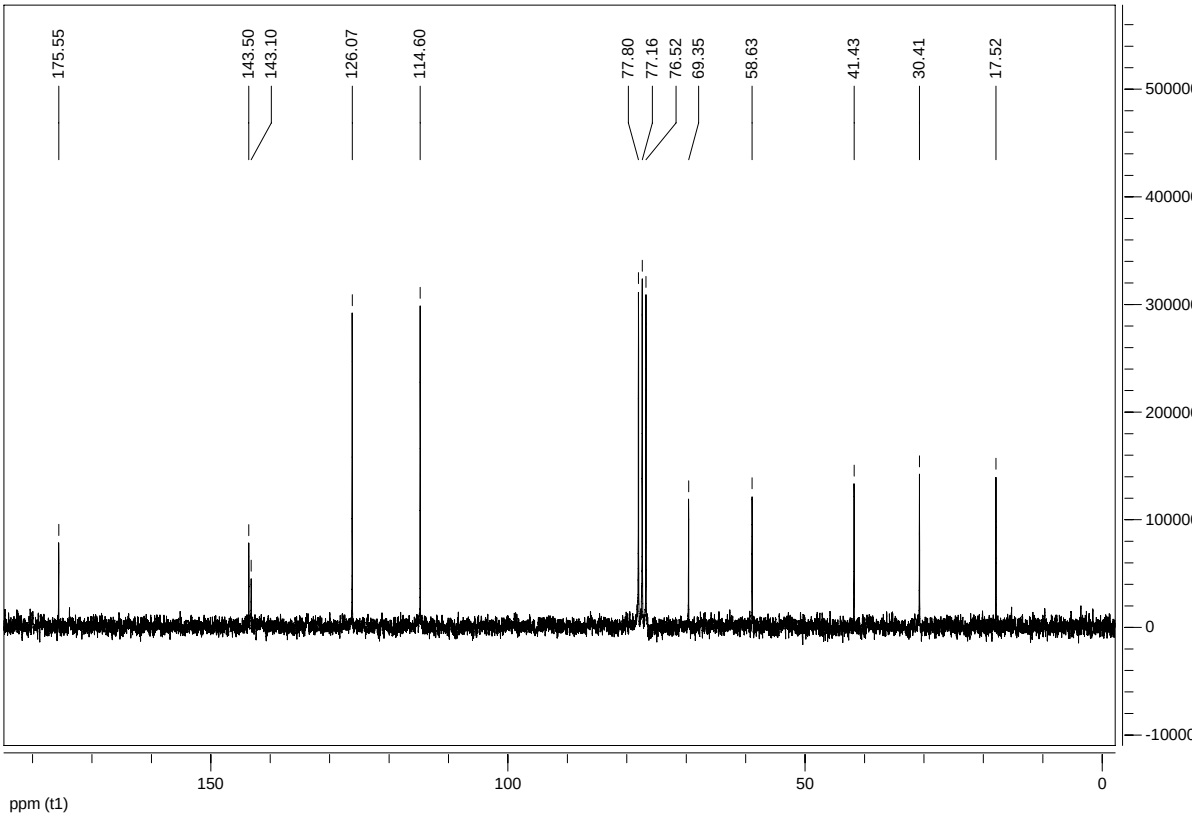


Compound **10**

^{1}H NMR (200 MHz, $CDCl_3$):



^{13}C NMR (50 MHz, $CDCl_3$):



X-Ray diagrams

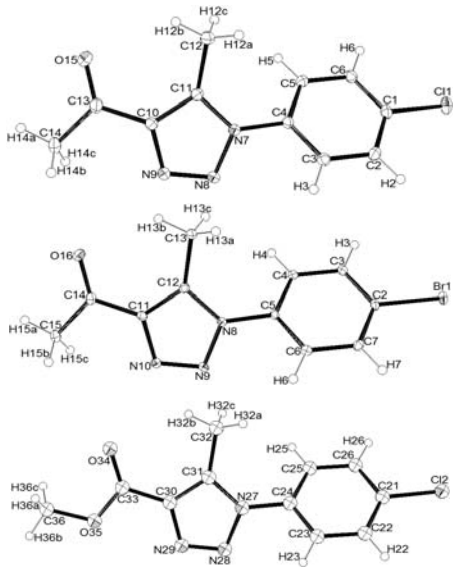


Fig. 1 ORTEP diagrams (30% probability) of cycloadducts **3b**,**c**, and **3f**.

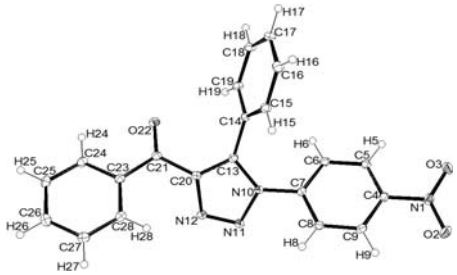


Fig. 2 ORTEP diagram (30% probability) of cycloadduct **5a**.