Supporting Information

Original electroactive and fluorescent bichromophores based on tetrazine and triphenylamine derivatives: Towards an efficient fluorescent switch

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Content:

List of figures and tables:

Electrochemistry

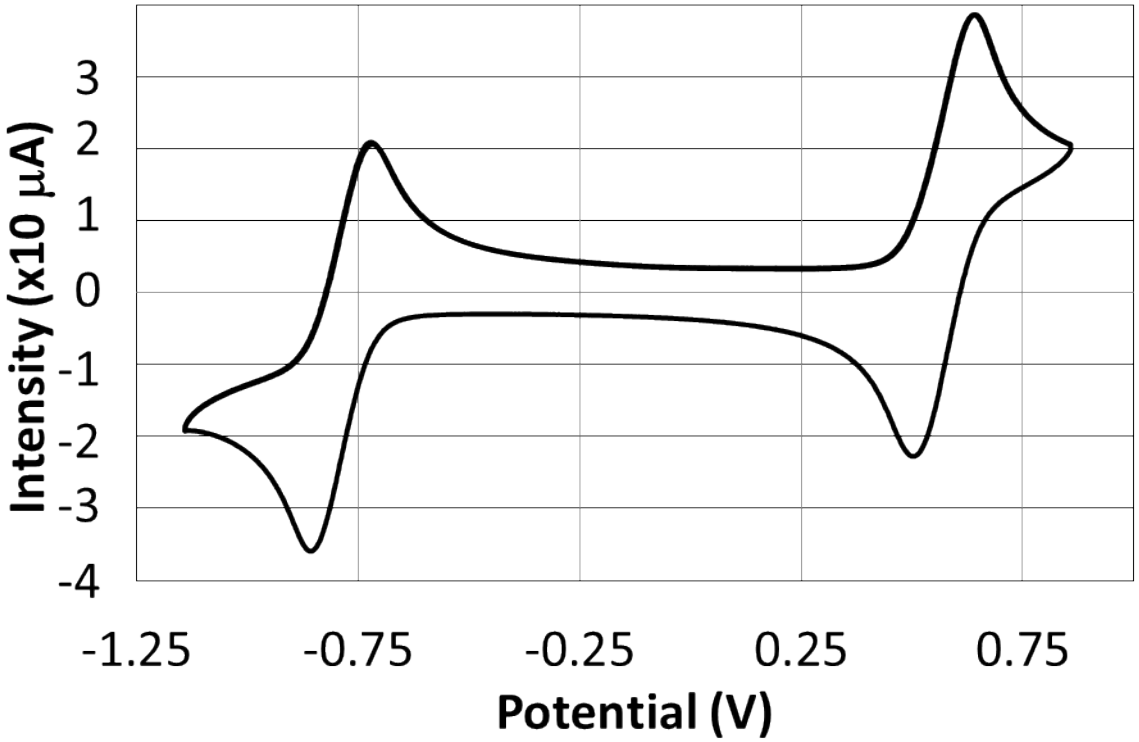


Figure S 1 Cyclic voltammetry of **2** (10^{-5} M) in dichloromethane + 0.1 M Bu_4NPF_6 on C. Potentials are referenced to Fc^+/Fc. Scan rate: 100 mV/s.

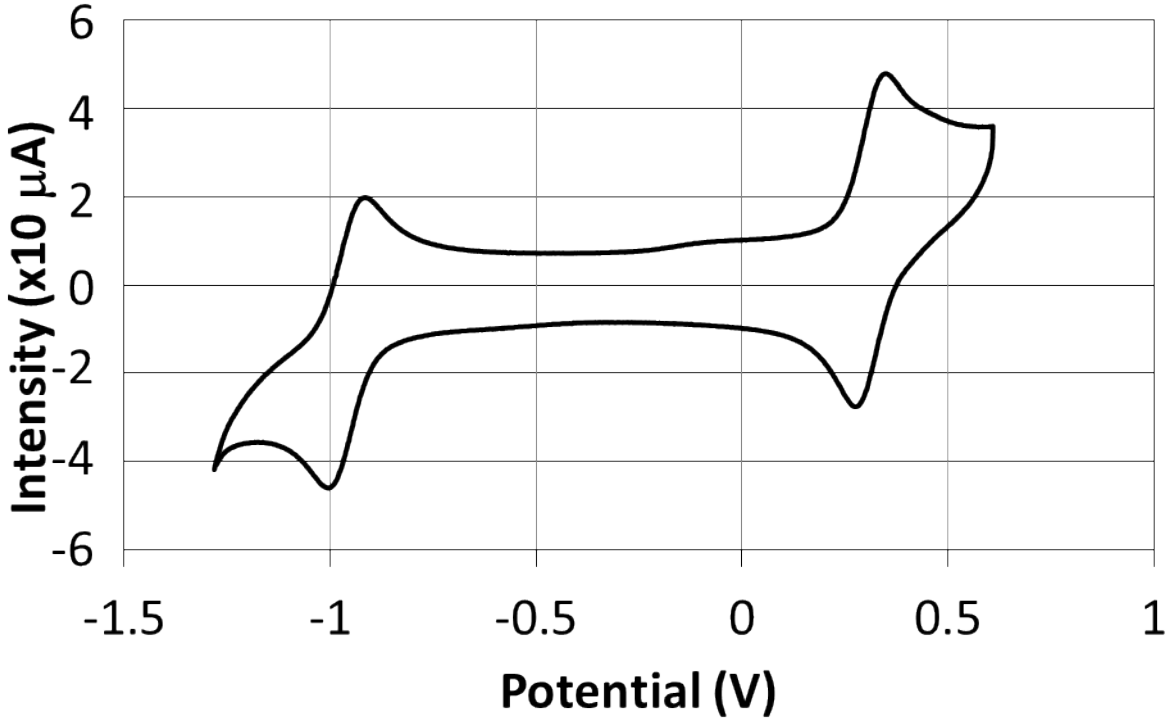


Figure S 2. Cyclic voltammetry of **3** (10^{-5} M) in dichloromethane + 0.1 M Bu_4NPF_6 on C. Potentials are referenced to Fc^+/Fc. Scan rate: 100 mV/s.

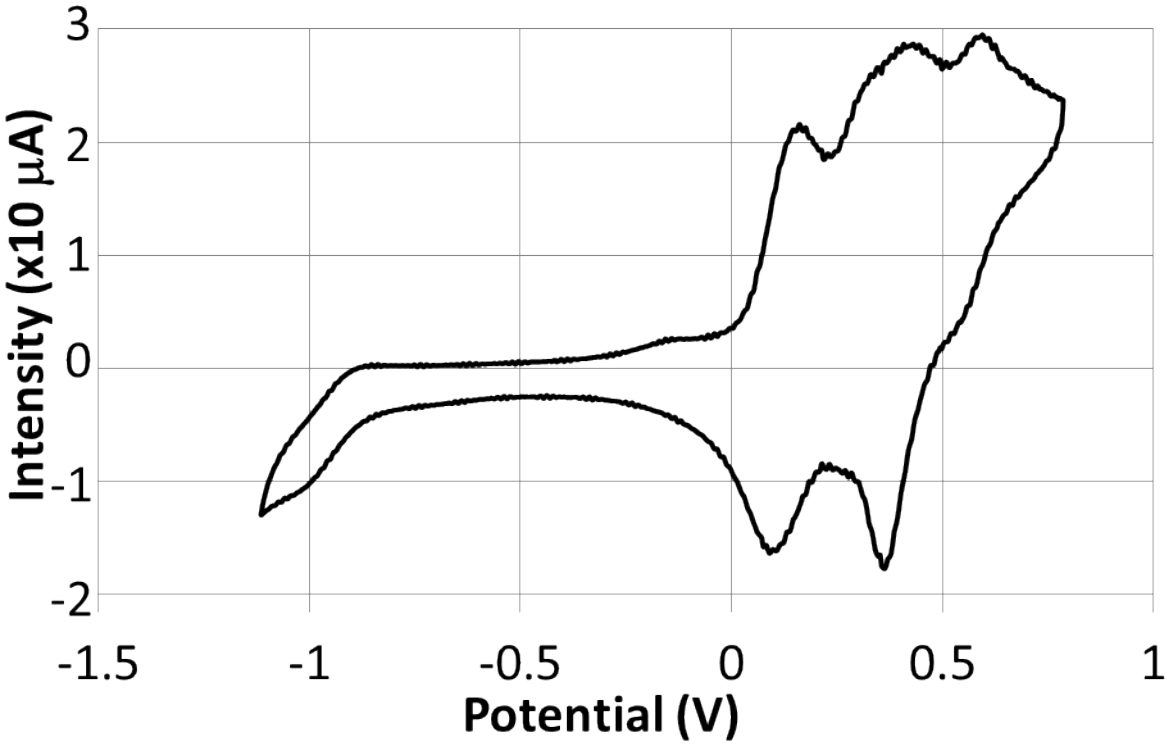


Figure S 3. Cyclic voltammetry of **4** (10^{-5} M) in dichloromethane + 0.1 M Bu_4NPF_6 on C. Potentials are referenced to Fc^+/Fc. Scan rate: 100 mV/s.

Spectroscopy and redox-dependant spectroscopy

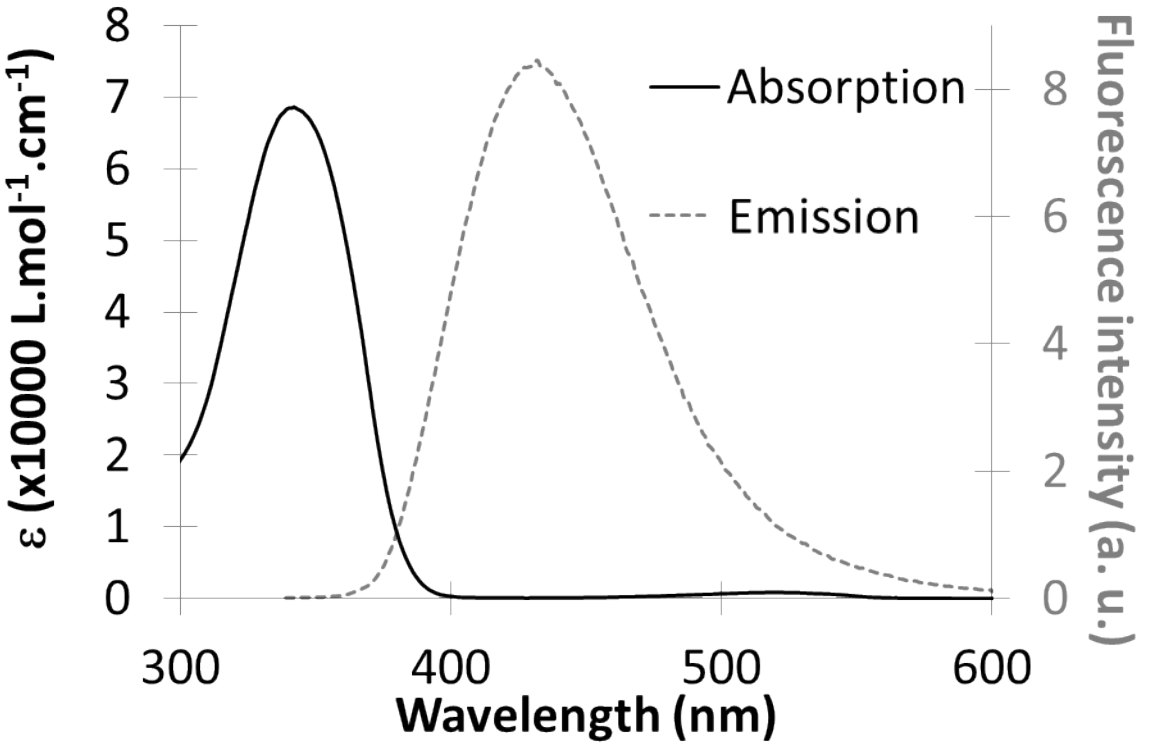


Figure S 4. Molar absorption coefficient and emission spectra (λ_{em}=326 nm) of compound **1** in dichloromethane.

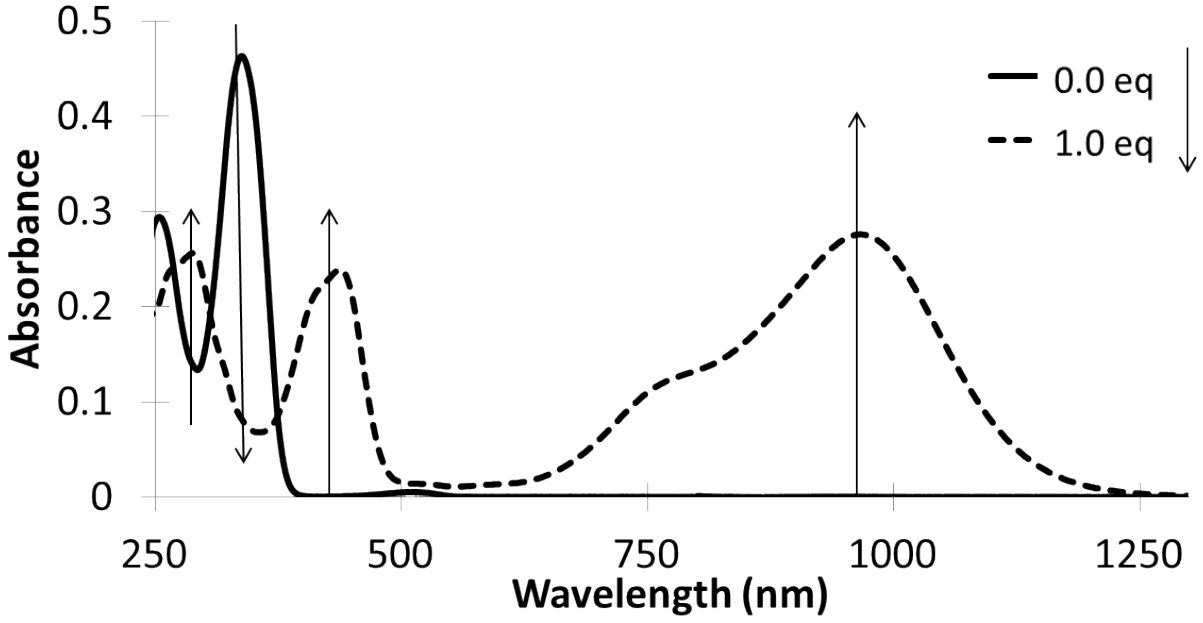


Figure S 5. Absorption spectra recorded upon oxidation of **1** by $Cu(ClO_4)_2$ in CH_3CN as a function of R=[Cu^{II}]/[**1**], [**1**]=1 10^{-5} mol.L^{-1}.

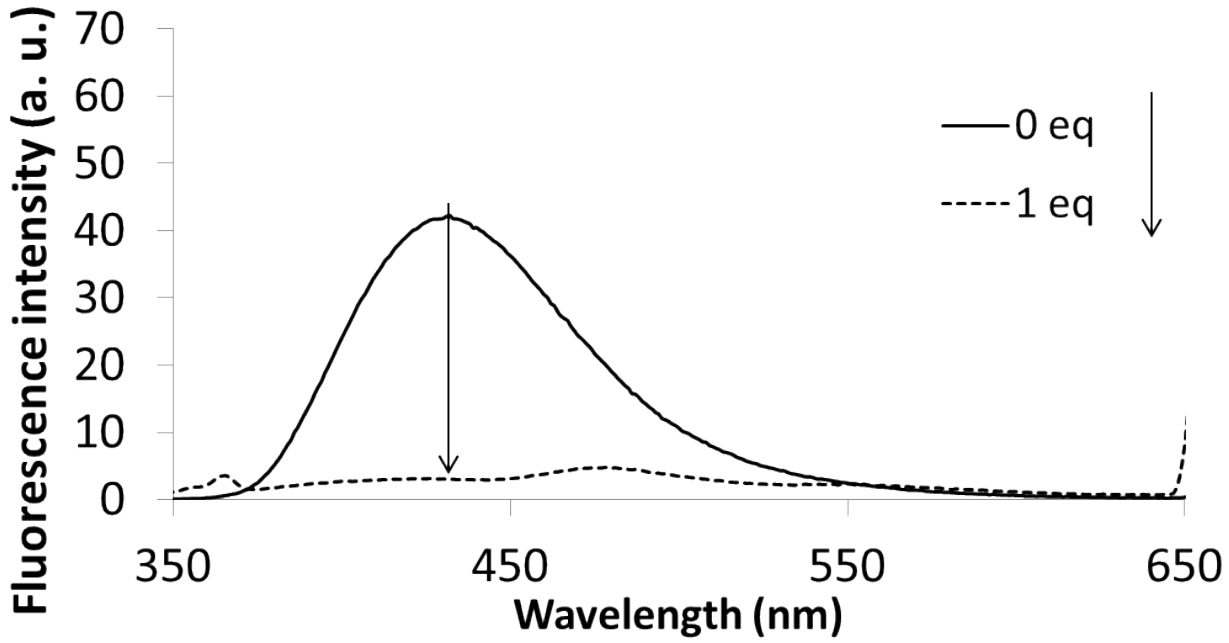


Figure S 6. Emission spectra recorded upon oxidation of **1** by $Cu(ClO_4)_2$ in CH_3CN as a function of R=[Cu^{II}]/[**1**], [**1**]=1 10^{-5} mol.L^{-1}, λ_{exc}=329 nm.

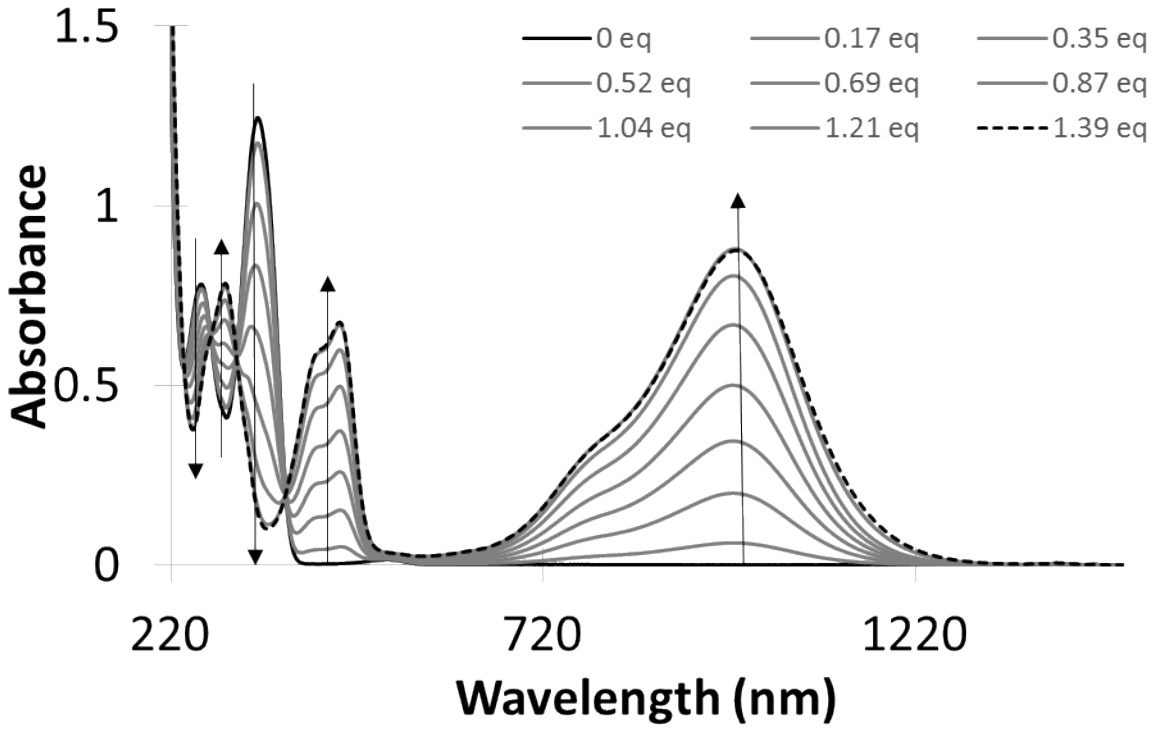


Figure S 7. Absorption spectra recorded upon oxidation of **3** by $Cu(ClO_4)_2$ in CH_3CN as a function of R=[Cu^{II}]/[**3**], [**3**]=1 10^{-5} mol.L^{-1}.

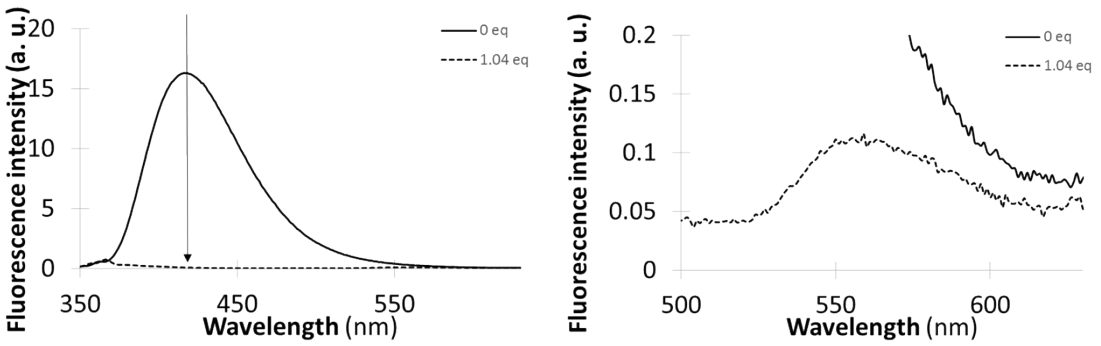


Figure S 8. Emission spectra recorded upon oxidation of **3** by $Cu(ClO_4)_2$ in CH_3CN as a function of $R=[Cu^{II}]/[\mathbf{3}]$, $[\mathbf{3}]=1.10^{-5}$ $mol.L^{-1}$, $\lambda_{exc}=326$ nm.

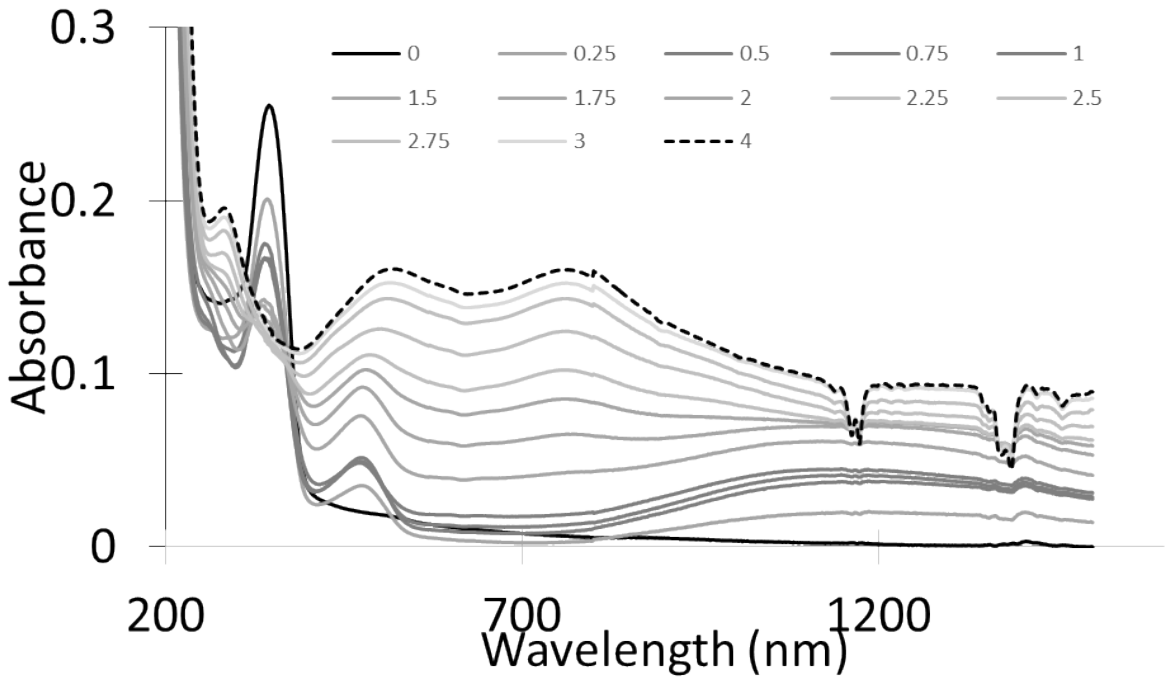


Figure S 9. Absorption spectra recorded upon oxidation of **4** by $Cu(ClO_4)_2$ in CH_3CN as a function of $R=[Cu^{II}]/[\mathbf{4}]$, $[\mathbf{4}]=1\ 10^{-5}$ $mol.L^{-1}$.

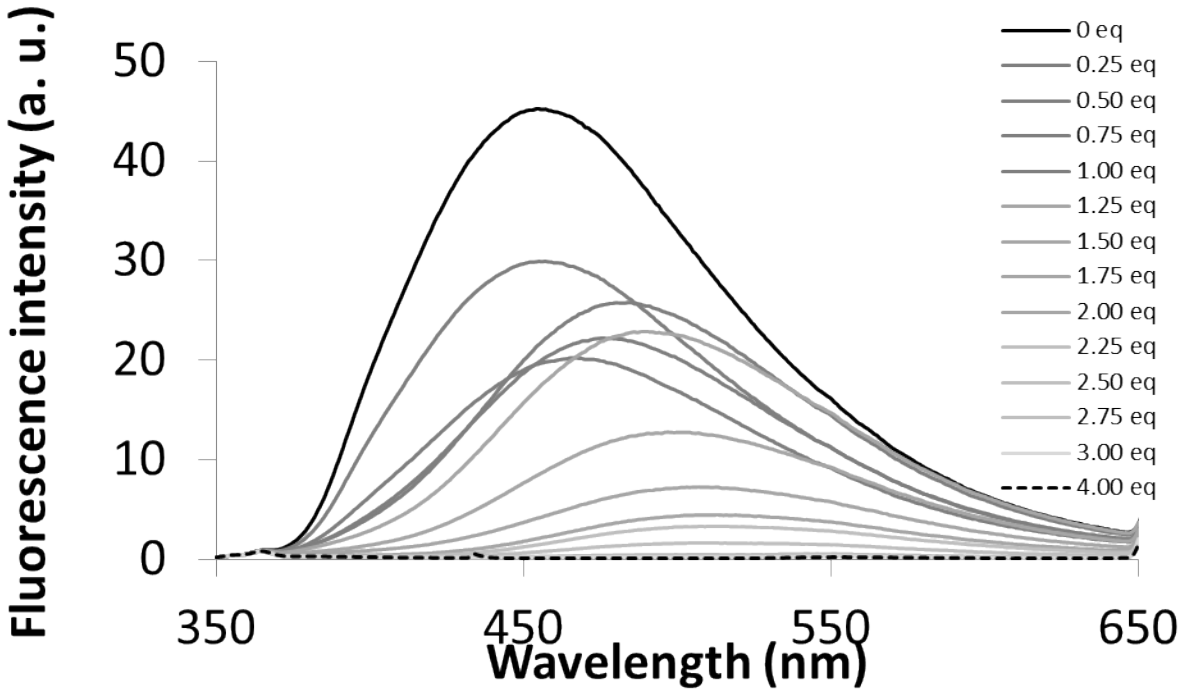


Figure S 10. Emission spectra recorded upon oxidation of **4** by $Cu(ClO_4)_2$ in CH_3CN as a function of R=[Cu^{II}]/[**4**], [**4**]=1.10^{-5} mol.L^{-1}, λ_{exc}=326 nm.

The evolution of the emission spectra of **4** upon oxidation shown in Figure S 7 is due triphenylamine part and is discussed in another paper.[6]

Theoretical calculations

Table S 1. Results of TD-DFT calculations for **1**

Wavelength (nm)	Oscillator strength	Major contributions
533	0.0044	H-11->LUMO (85%)
361	0.74	HOMO->L+2 (91%)
347	0.66	HOMO->L+3 (90%)
340	0.04	HOMO->L+4 (92%)
321	0.03	H-13->LUMO (84%)

Table S 2. Atomic coordinates of compound **1** after geometry optimization

Number	Atomic number	X	Y	Z
1	7	-2.52496	-0.00714	0.032383
2	6	-3.58276	-0.96616	-0.03457
3	6	-3.56011	-2.11997	0.765545
4	6	-4.67074	-0.77128	-0.90045
5	6	-4.58767	-3.05434	0.688356
6	1	-2.72492	-2.28422	1.434236
7	6	-5.70561	-1.69901	-0.95712
8	1	-4.70403	0.118398	-1.51599
9	6	-5.68513	-2.86319	-0.16937
10	1	-4.53608	-3.95294	1.29221
11	1	-6.54951	-1.51503	-1.61187
12	6	-1.17073	-0.43691	0.109259
13	6	-0.73939	-1.58878	-0.57206
14	6	-0.22896	0.281817	0.866746
15	6	0.584322	-2.00605	-0.49229
16	1	-1.45271	-2.15736	-1.15403
17	6	1.096351	-0.13302	0.92935
18	1	-0.54313	1.173828	1.392447
19	6	1.5326	-1.28608	0.254506
20	1	0.887021	-2.91059	-1.00721
21	1	1.809227	0.452973	1.497942
22	6	-2.83643	1.387864	0.00343
23	6	-3.92773	1.892792	0.728316
24	6	-2.06396	2.281668	-0.75576
25	6	-4.23874	3.248031	0.686899
26	1	-4.53662	1.212717	1.310002
27	6	-2.36788	3.63877	-0.77641
28	1	-1.21766	1.906085	-1.31637
29	6	-3.46361	4.151878	-0.06041
30	1	-5.10267	3.6126	1.230554
31	1	-1.74233	4.315521	-1.34686
32	6	-6.78519	-3.85795	-0.23947
33	6	-7.37251	-4.20667	-1.47205
34	6	-7.27315	-4.48205	0.916892
35	6	-8.39799	-5.13751	-1.53881
36	1	-6.9981	-3.75848	-2.38508
37	6	-8.30431	-5.42049	0.856991
38	1	-6.85879	-4.21244	1.881613
39	6	-8.87567	-5.75619	-0.37364
40	1	-8.84641	-5.41816	-2.48273
41	1	-8.65916	-5.87255	1.773308
42	6	2.949646	-1.72527	0.324427
43	6	3.605648	-2.2327	-0.8105
44	6	3.673203	-1.64573	1.527029
45	6	4.935483	-2.64296	-0.74384
46	1	3.073731	-2.28276	-1.75344
47	6	5.004272	-2.05276	1.588544

48	1	3.177998	-1.28789	2.422194
49	6	5.654606	-2.55816	0.455244
50	1	5.422305	-3.03058	-1.63313
51	1	5.539847	-1.99522	2.530885
52	6	-3.79051	5.599817	-0.09526
53	6	-3.69517	6.335818	-1.29316
54	6	-4.20134	6.280188	1.059316
55	6	-3.99686	7.688517	-1.32851
56	1	-3.40524	5.82937	-2.20642
57	6	-4.50742	7.641621	1.030856
58	1	-4.25781	5.744691	2.000161
59	6	-4.40653	8.357531	-0.16527
60	1	-3.93566	8.258043	-2.24649
61	1	-4.81109	8.133044	1.945355
62	8	-9.90016	-6.67128	-0.55151
63	8	-4.68247	9.707123	-0.31019
64	6	-10.4243	-7.35051	0.628874
65	1	-10.8642	-6.64196	1.341284
66	1	-11.1986	-8.01756	0.249469
67	1	-9.64794	-7.93636	1.136036
68	6	-5.11068	10.44986	0.870637
69	1	-4.34381	10.43935	1.654776
70	1	-5.26372	11.47099	0.520851
71	1	-6.04907	10.05488	1.278788
72	6	7.11988	-2.95382	0.512202
73	6	7.988412	-1.73347	0.195926
74	1	7.340334	-3.74091	-0.21569
75	1	7.385265	-3.32593	1.506802
76	1	7.801772	-1.34158	-0.80638
77	1	7.851944	-0.92888	0.921706
78	8	9.399476	-2.22673	0.271475
79	6	10.38427	-1.3482	0.054947
80	6	12.33441	0.267949	-0.34558
81	7	11.6452	-1.87514	0.139174
82	7	12.66955	-1.00869	-0.07545
83	7	11.11902	0.802771	-0.43255
84	7	10.06735	-0.06133	-0.21872
85	17	13.71997	1.389022	-0.6241

Number of imaginary frequencies: 0

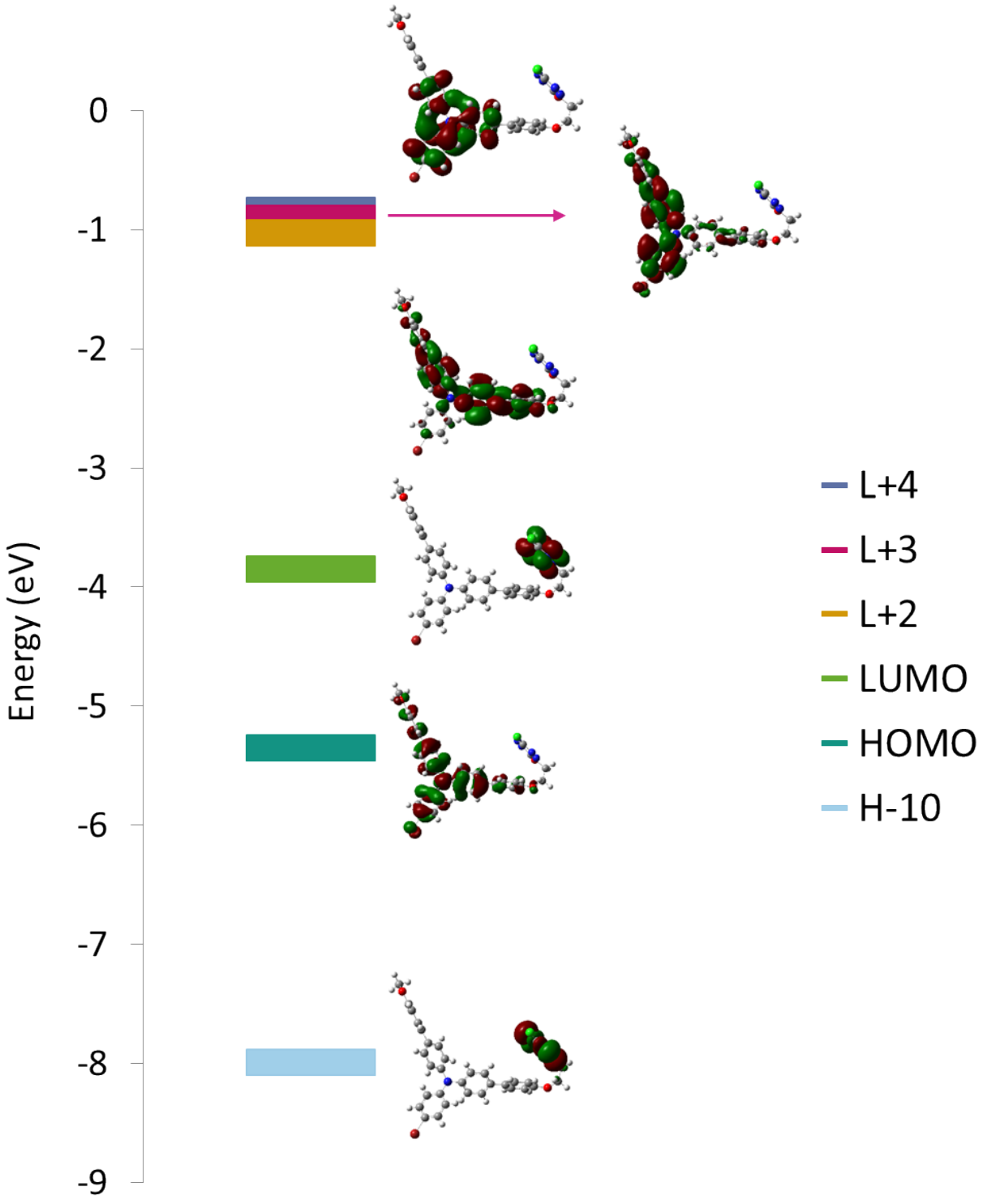


Figure S 11 Representation of the energy levels and the main molecular orbitals involved in the electronic transitions of **2**

Table S 3 Results of TD-DFT calculations for **2**

Wavelength (nm)	**Osc. Strength**	**Major contribs**
532	0.0064	H-10->LUMO (85%)
345	0.64	HOMO->L+2 (87%)
340	0.06	HOMO->L+4 (90%)

334	0.49	HOMO->L+3 (90%)

Table S 4 Atomic coordinates of compound **2** after geometry optimization

Number	Atomic number	X	Y	Z
1	7	-2.31007	-1.33917	-0.13445
2	6	-0.89628	-1.41259	-0.32632
3	6	-0.32919	-2.43479	-1.10497
4	6	-0.04312	-0.46172	0.25684
5	6	1.048453	-2.50871	-1.28125
6	1	-0.97472	-3.17612	-1.55815
7	6	1.332177	-0.52991	0.060374
8	1	-0.46782	0.337333	0.850598
9	6	1.908693	-1.5572	-0.70644
10	1	1.467175	-3.32179	-1.86309
11	1	1.96945	0.231397	0.495191
12	6	-3.06143	-2.52699	0.091519
13	6	-2.53248	-3.57465	0.864712
14	6	-4.34845	-2.68034	-0.45189
15	6	-3.26479	-4.73881	1.077643
16	1	-1.54508	-3.47278	1.294818
17	6	-5.08177	-3.8411	-0.22132
18	1	-4.77107	-1.88587	-1.05244
19	6	-4.53906	-4.87035	0.538678
20	1	-2.84999	-5.53977	1.674765
21	1	-6.07154	-3.95093	-0.64399
22	6	-2.96405	-0.06807	-0.15694
23	6	-2.59215	0.910432	-1.09264
24	6	-3.98477	0.232308	0.759318
25	6	-3.21564	2.153737	-1.1015
26	1	-1.80053	0.693811	-1.79818
27	6	-4.61914	1.469964	0.730732
28	1	-4.28358	-0.51452	1.483551
29	6	-4.24564	2.459882	-0.19503
30	1	-2.89183	2.906314	-1.81095
31	1	-5.42292	1.671925	1.429246
32	35	-5.55351	-6.48371	0.848553
33	6	-4.91381	3.785774	-0.2114
34	6	-5.22892	4.425632	-1.41804
35	6	-5.24887	4.443918	0.988718
36	6	-5.85179	5.674373	-1.4378
37	1	-5.00687	3.930477	-2.35645
38	6	-5.86897	5.683908	0.976493
39	1	-4.99269	3.984424	1.936238
40	6	-6.17703	6.314298	-0.23852
41	1	-6.08628	6.131208	-2.38977
42	1	-6.11901	6.200385	1.893842
43	8	-6.79309	7.550849	-0.13854
44	6	-7.11571	8.257196	-1.374
45	1	-7.57216	9.193454	-1.05214
46	1	-6.21622	8.468505	-1.96503
47	1	-7.82693	7.692521	-1.98918
48	6	3.378206	-1.63679	-0.90239
49	6	3.927846	-1.97919	-2.15182
50	6	4.265325	-1.37845	0.15278
51	6	5.301894	-2.05215	-2.33363
52	1	3.2677	-2.15919	-2.9921
53	6	5.647534	-1.45309	-0.02288

54	1	3.868808	-1.14672	1.134728
55	6	6.176377	-1.7872	-1.27271
56	1	5.731137	-2.30146	-3.29487
57	1	6.290305	-1.26923	0.827594
58	8	7.532311	-1.94483	-1.56505
59	6	8.538036	-1.29488	-0.73371
60	1	8.235602	-1.19914	0.30875
61	1	9.426869	-1.9297	-0.79063
62	6	8.890504	0.074276	-1.30806
63	1	9.161768	-0.01205	-2.35861
64	1	9.692994	0.530069	-0.72256
65	8	7.722964	0.996945	-1.35072
66	6	7.302528	1.55707	-0.20902
67	6	6.428582	2.692234	1.919499
68	7	7.873463	1.192697	0.959366
69	7	7.403984	1.807271	2.10197
70	7	5.847511	3.069991	0.761959
71	7	6.303602	2.479327	-0.37102
72	17	5.793805	3.497325	3.401695

Number of imaginary frequencies: 0

NMR characterizations

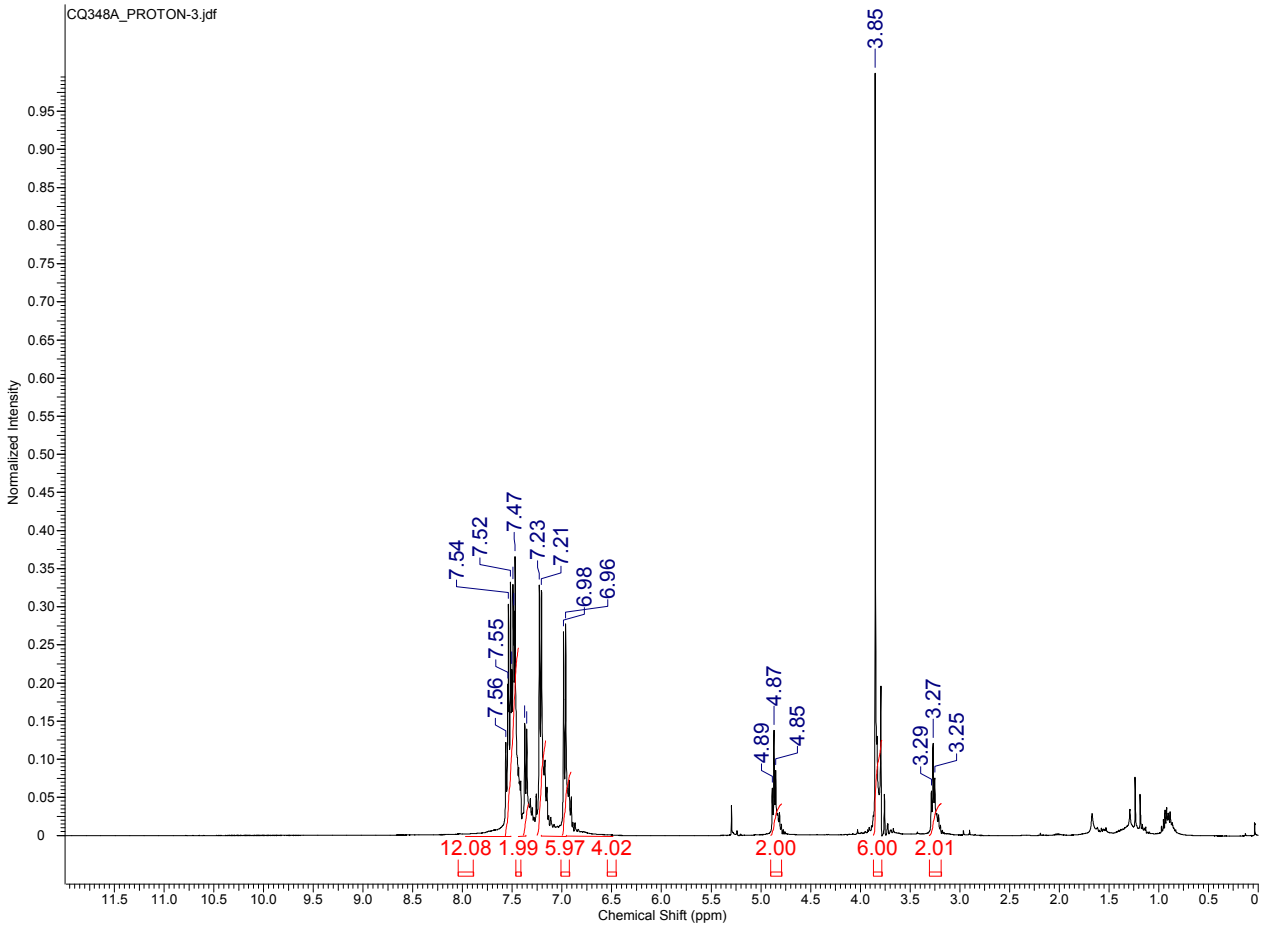


Figure S 12 ^{1}H NMR of **1** in $CDCl_3$

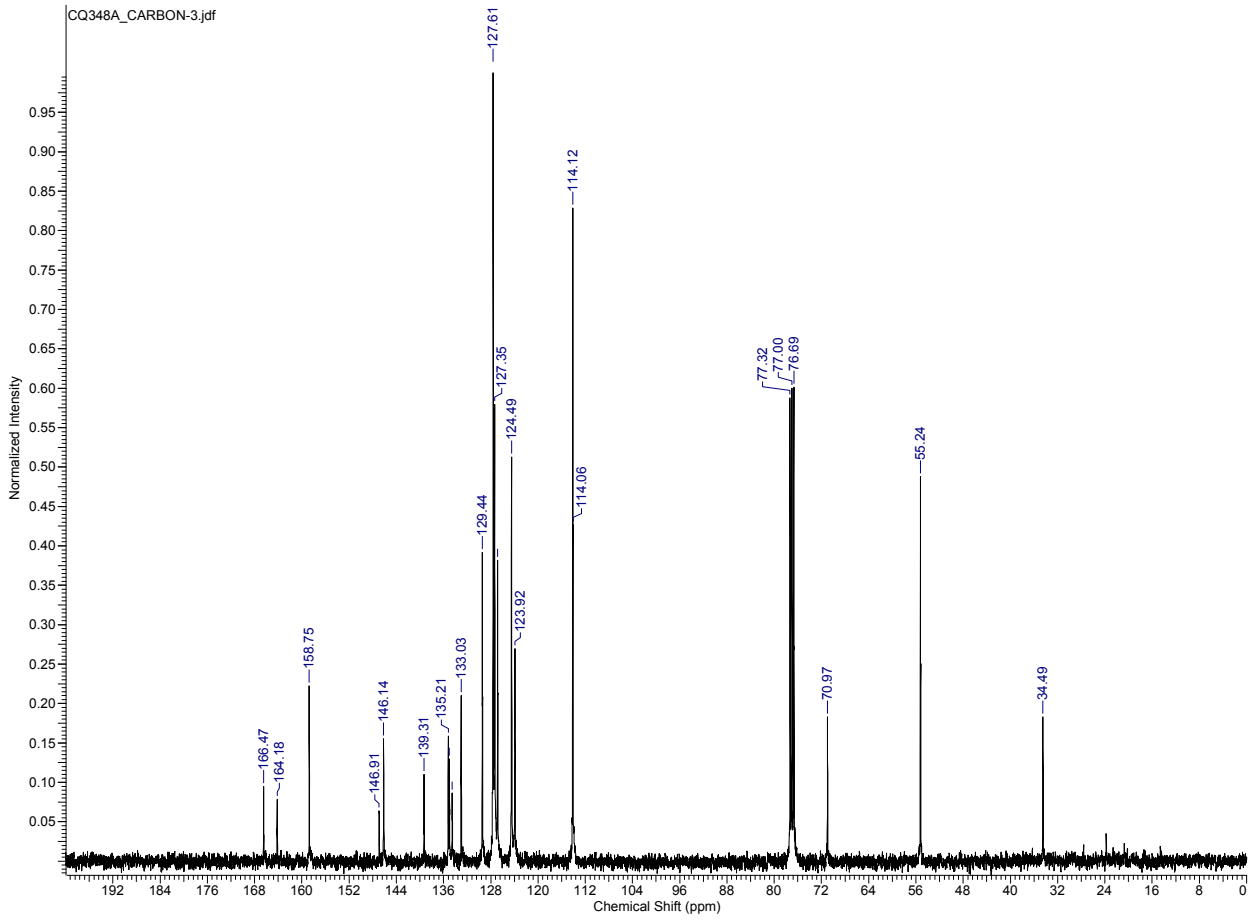


Figure S 13 ^{13}C NMR of **1** in $CDCl_3$

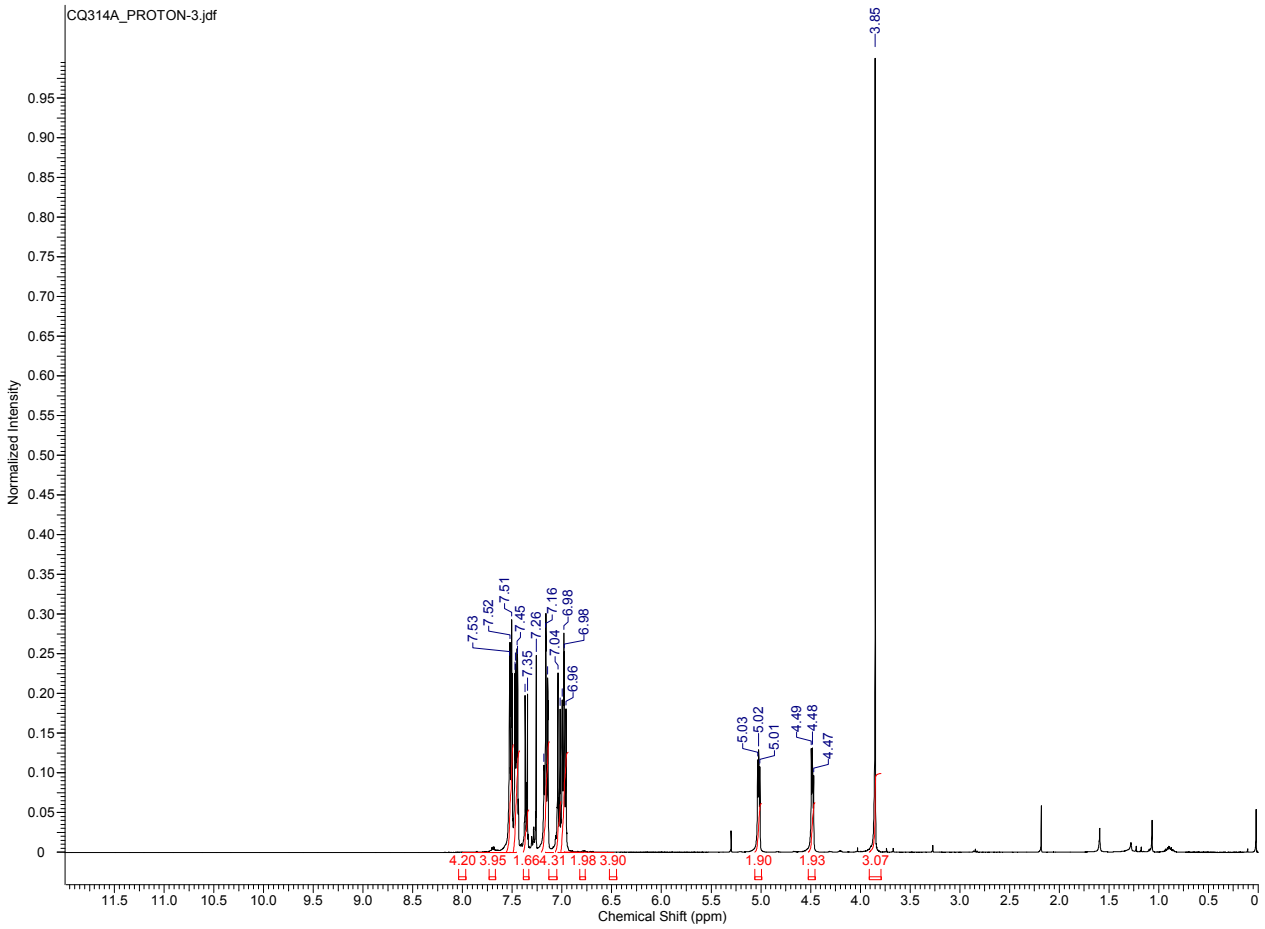


Figure S 14 ^{1}H NMR of **2** in $CDCl_3$

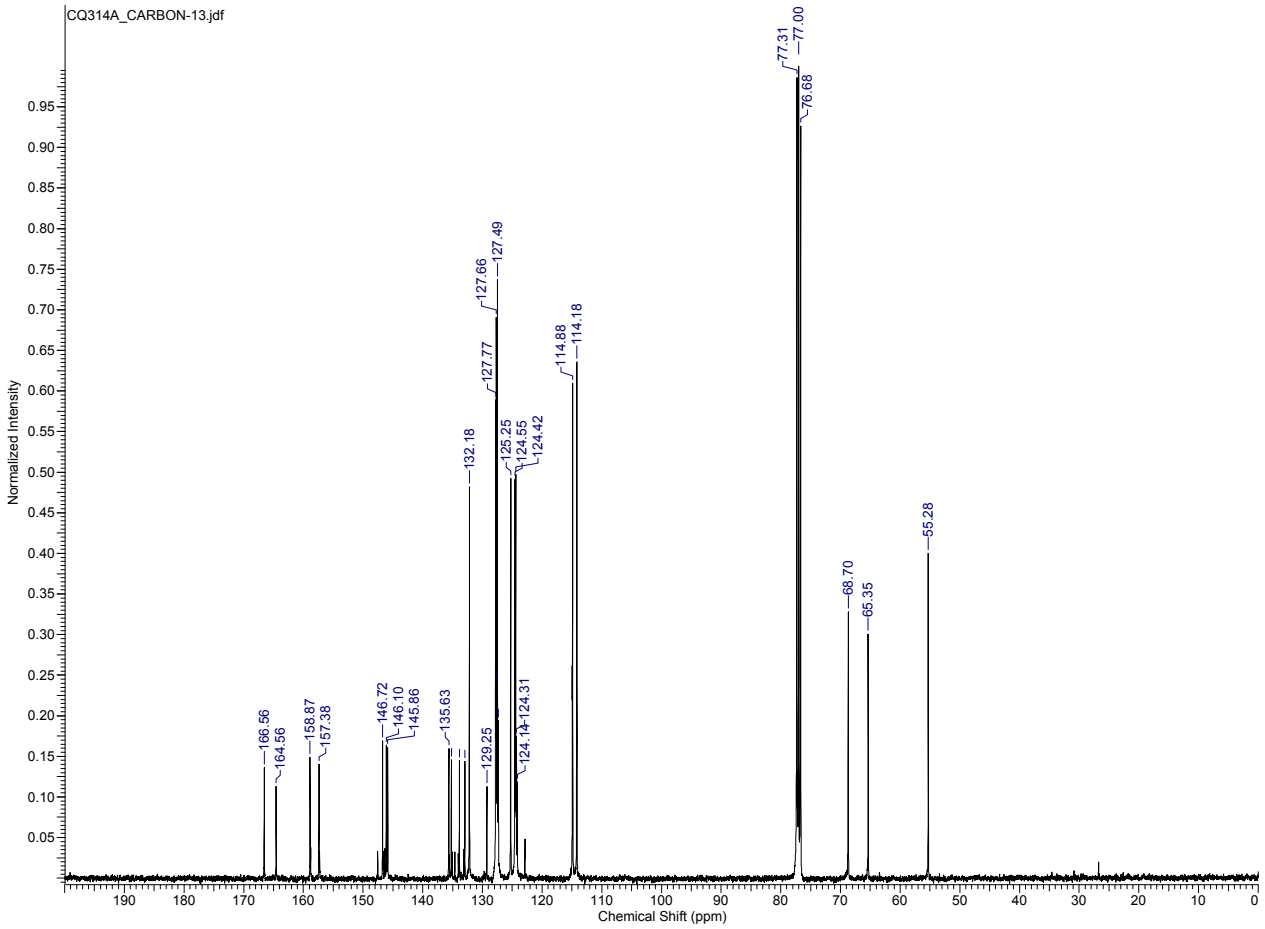


Figure S 15 ^{13}C NMR of **2** in $CDCl_3$

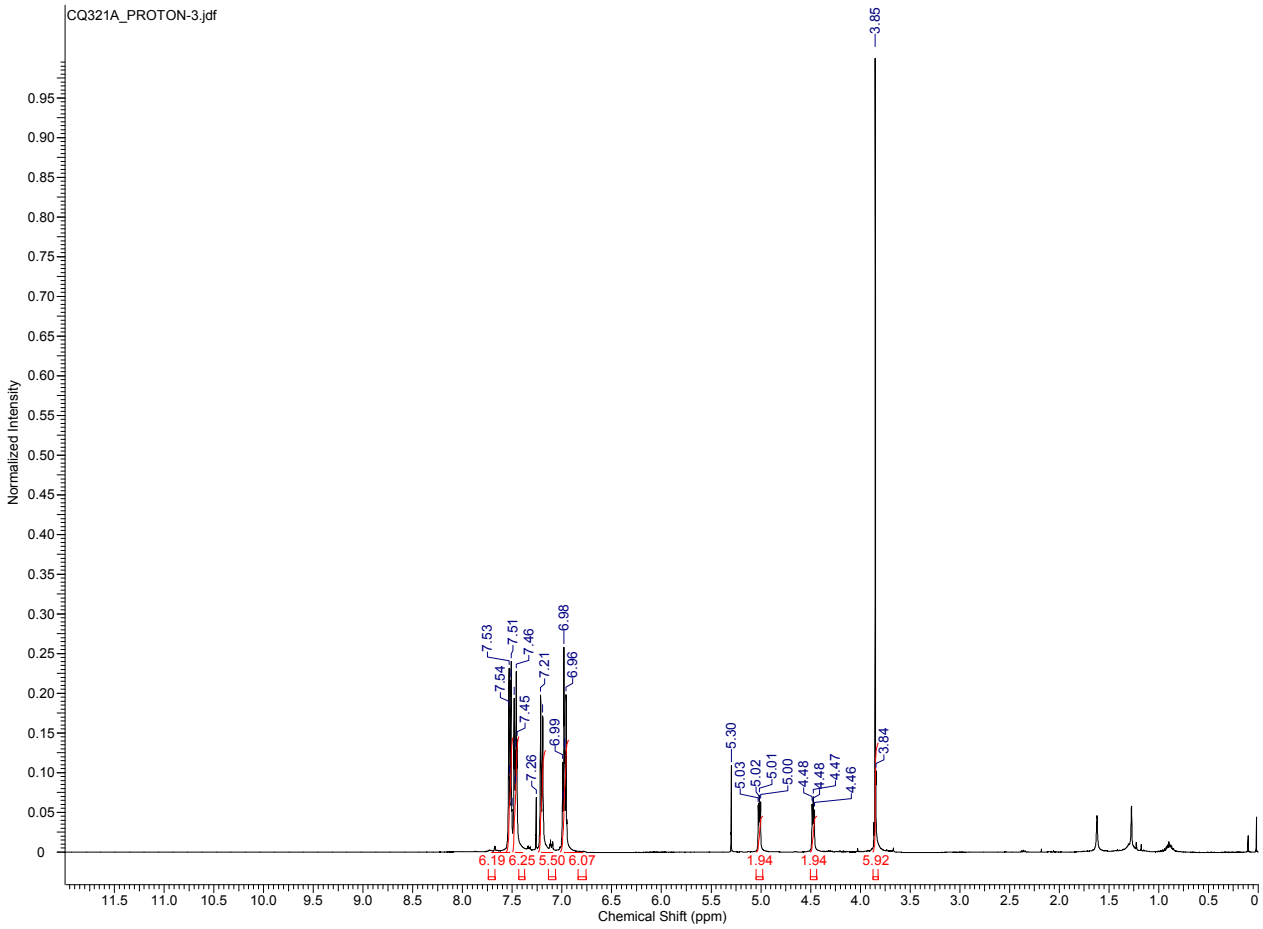


Figure S 16 ^{1}H NMR of **3** in $CDCl_3$

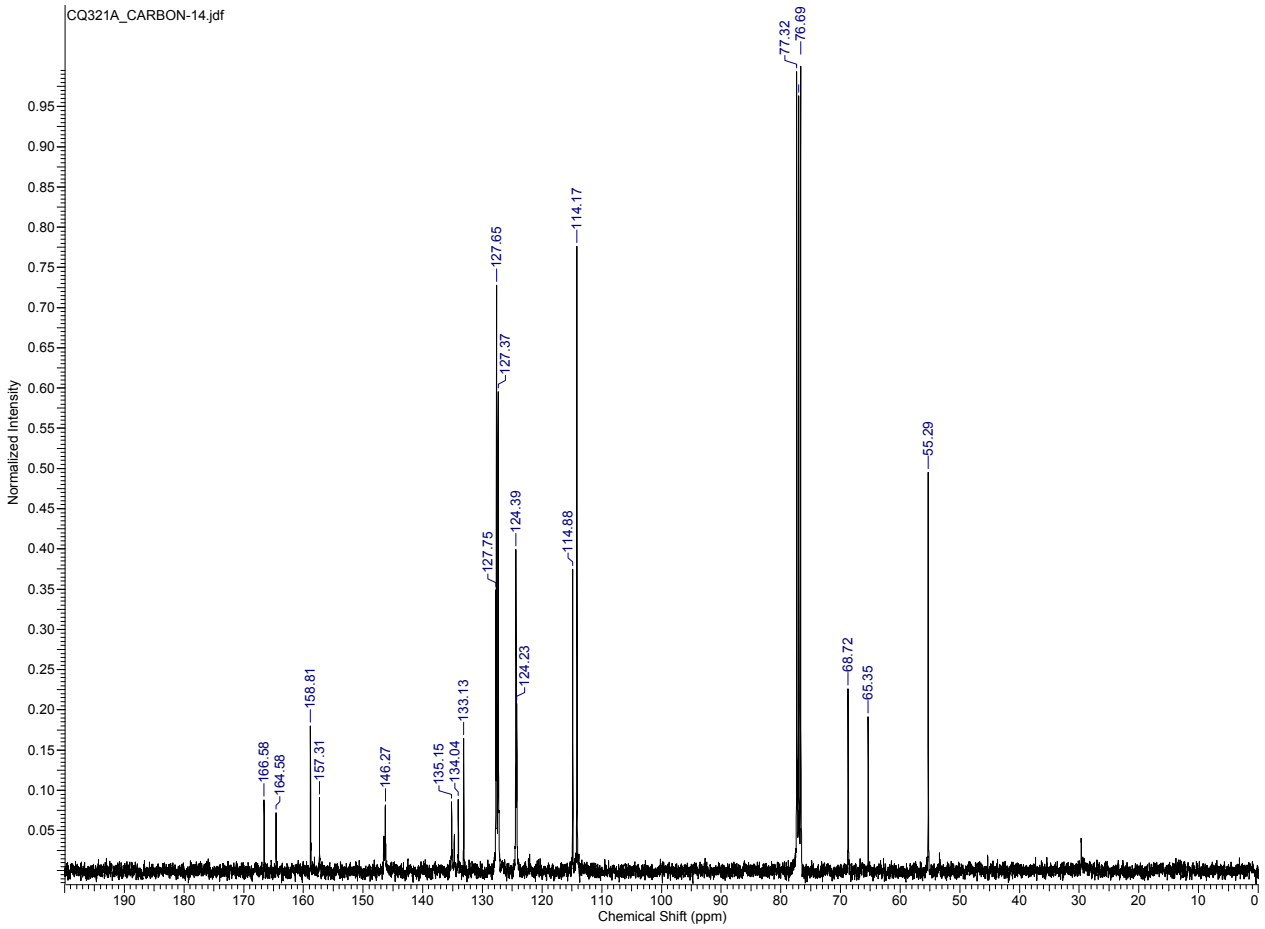


Figure S 17 ^{13}C NMR of **3** in $CDCl_3$

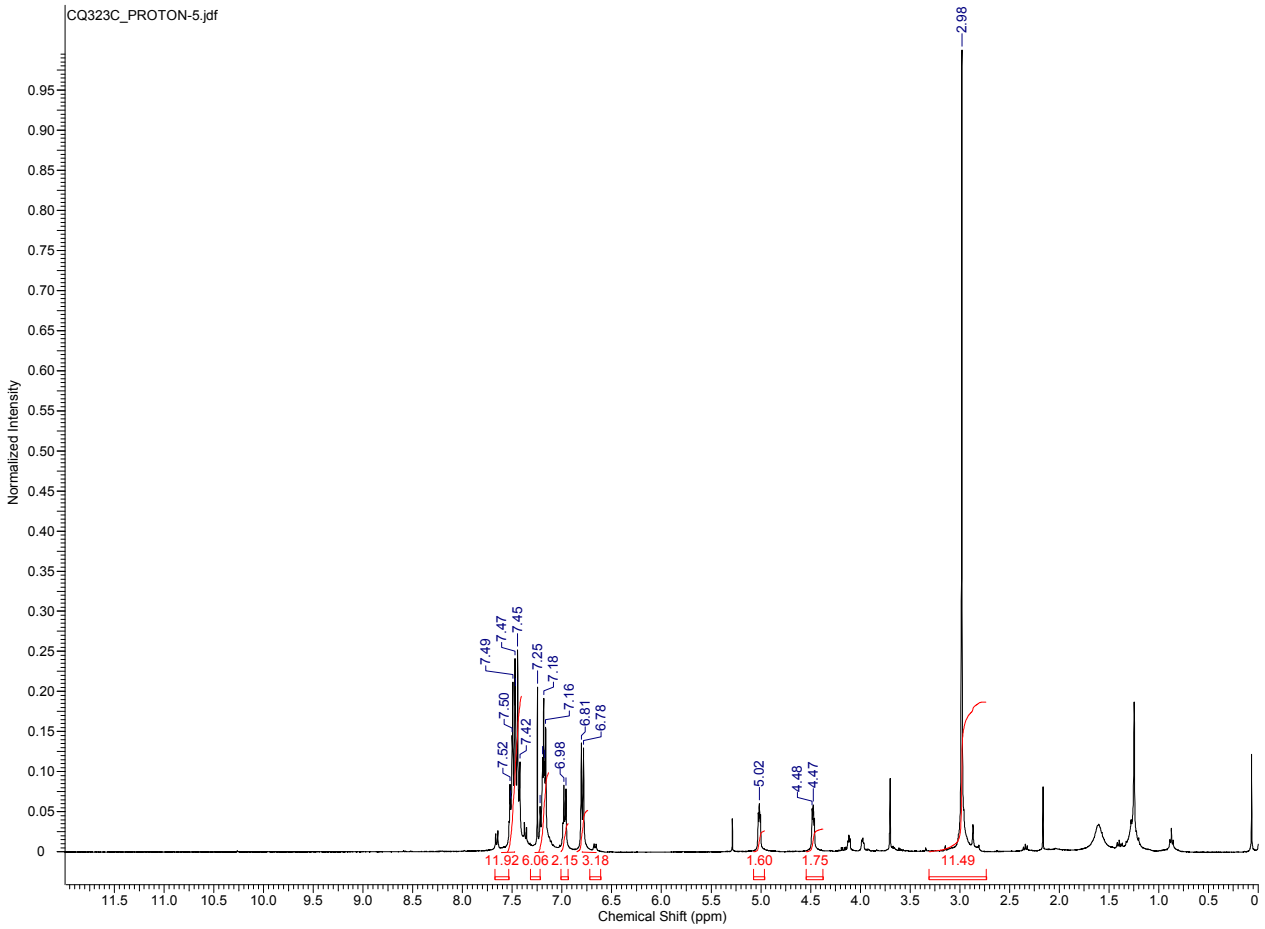


Figure S 18 ^{1}H NMR of **4** in $CDCl_3$

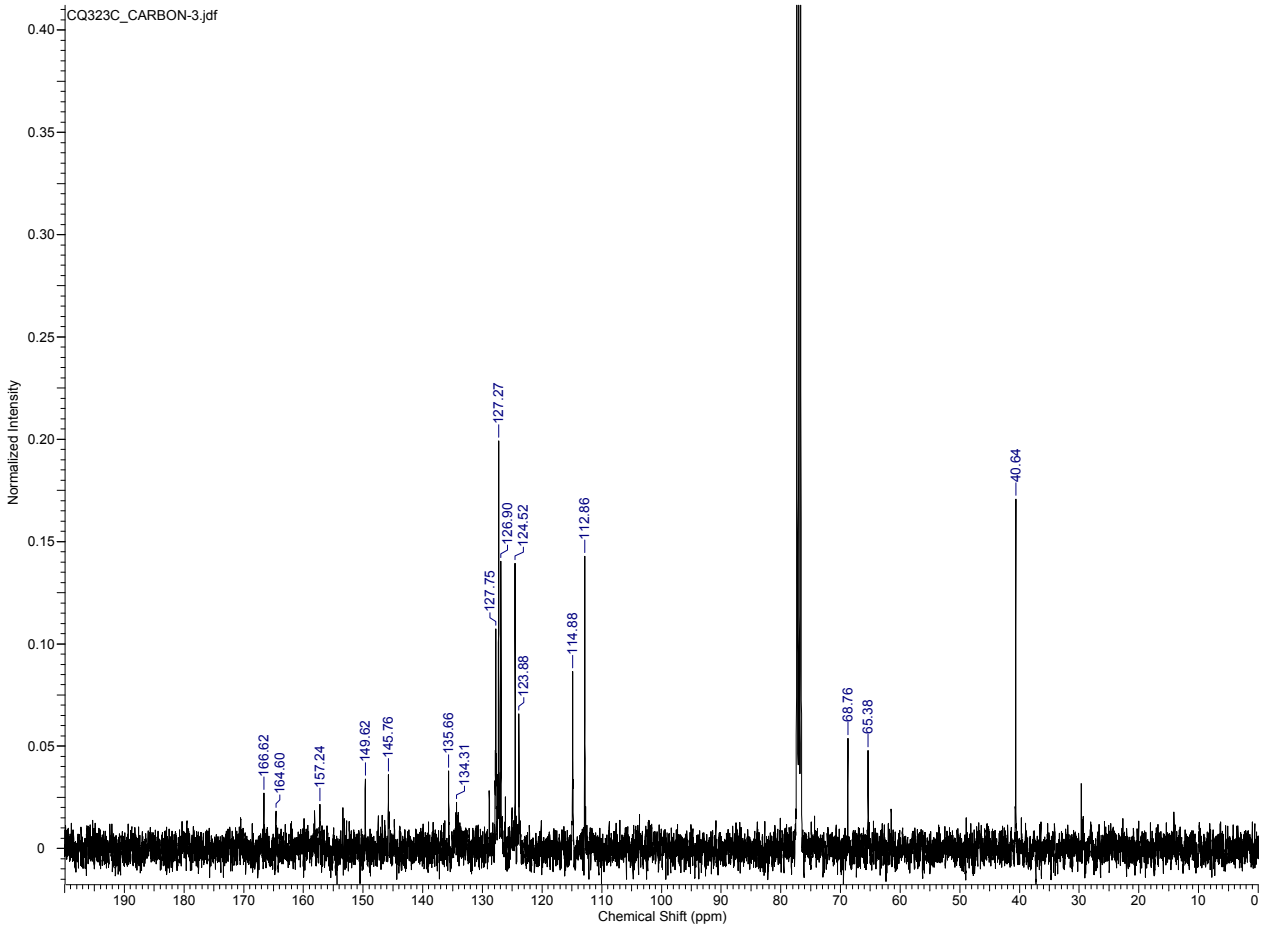


Figure S 19 ^{13}C NMR of **4** in $CDCl_3$

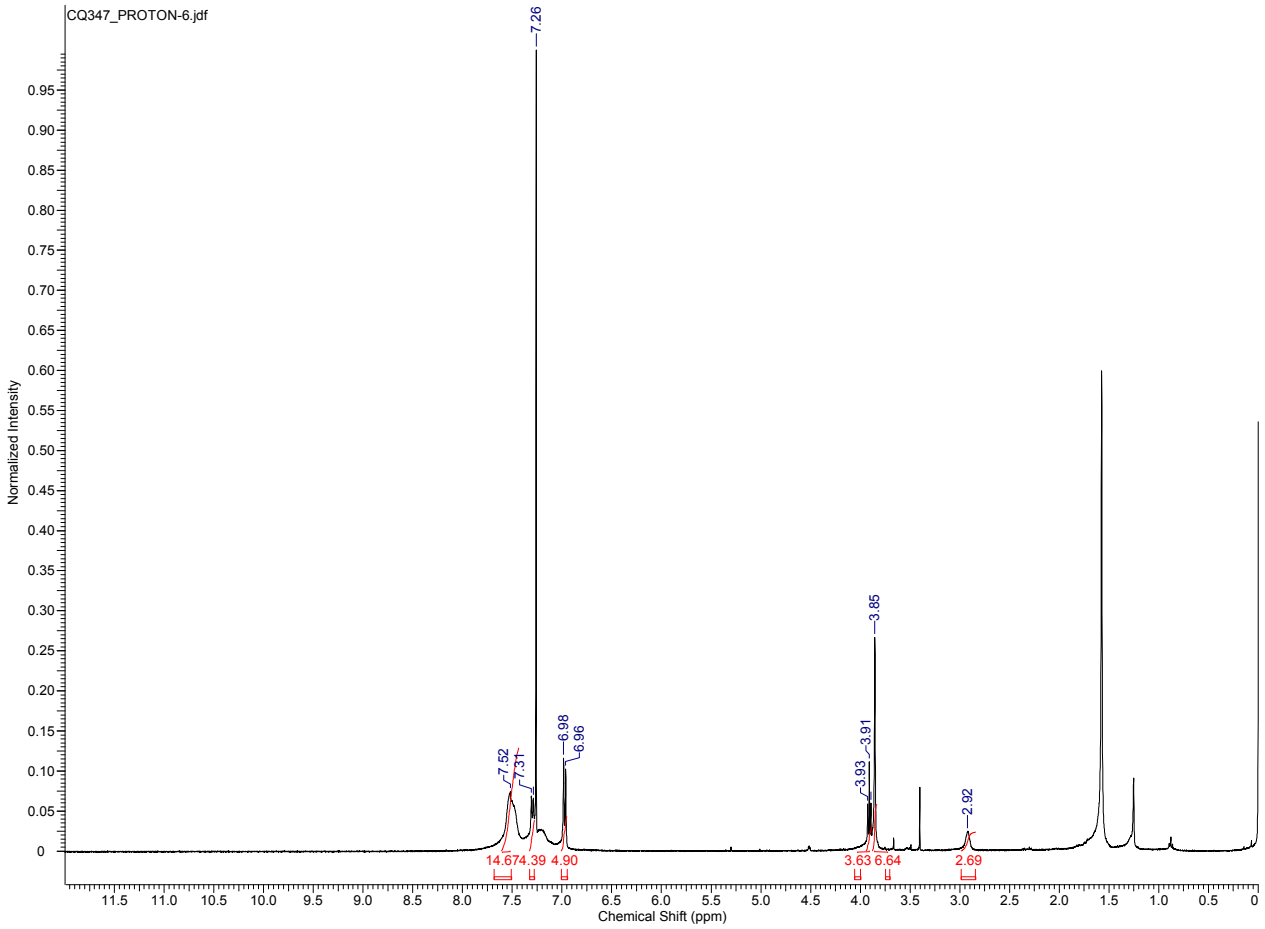


Figure S 20 ^{1}H NMR of **5** in $CDCl_3$

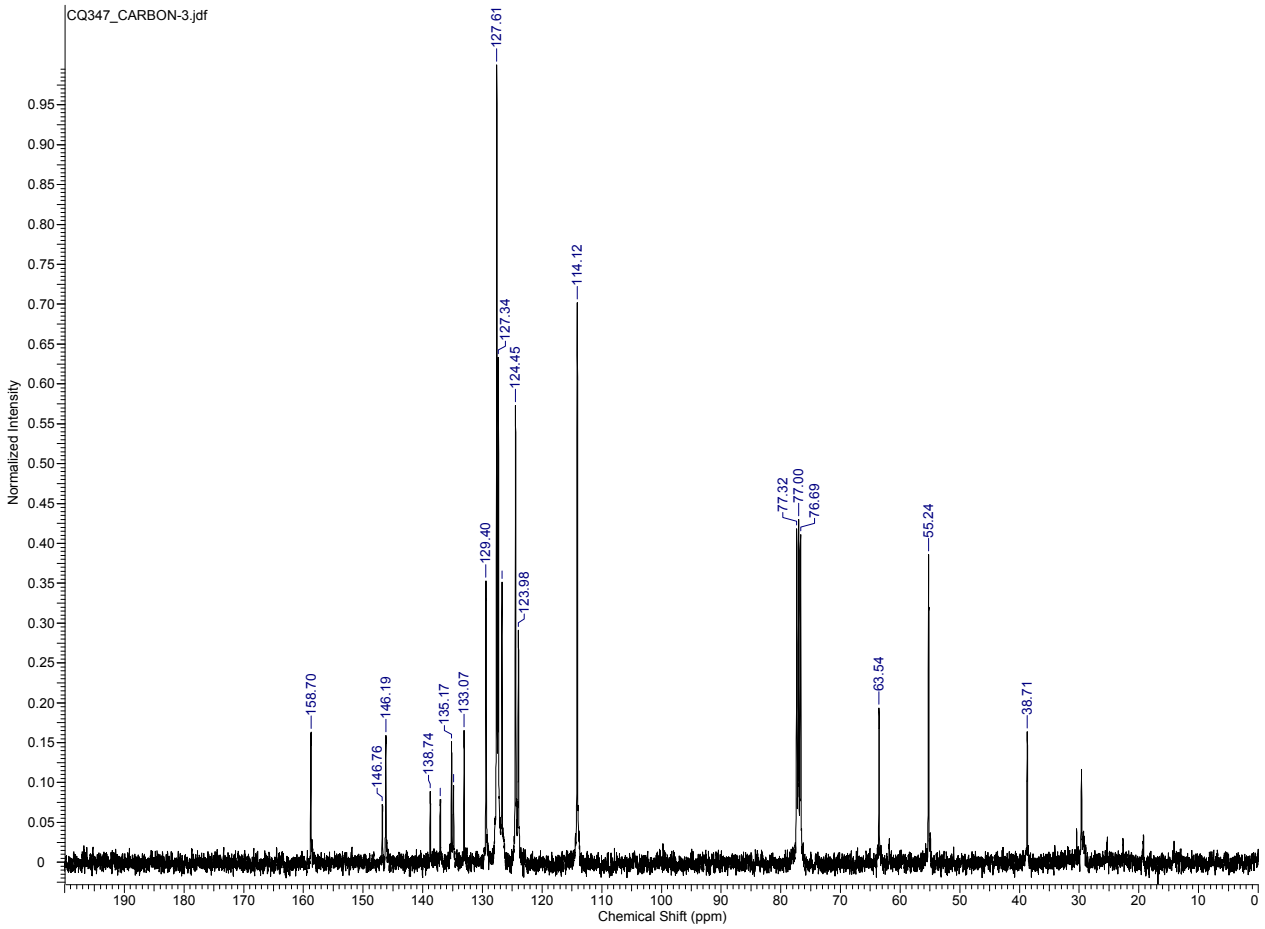


Figure S 21 ^{13}C NMR of **5** in $CDCl_3$

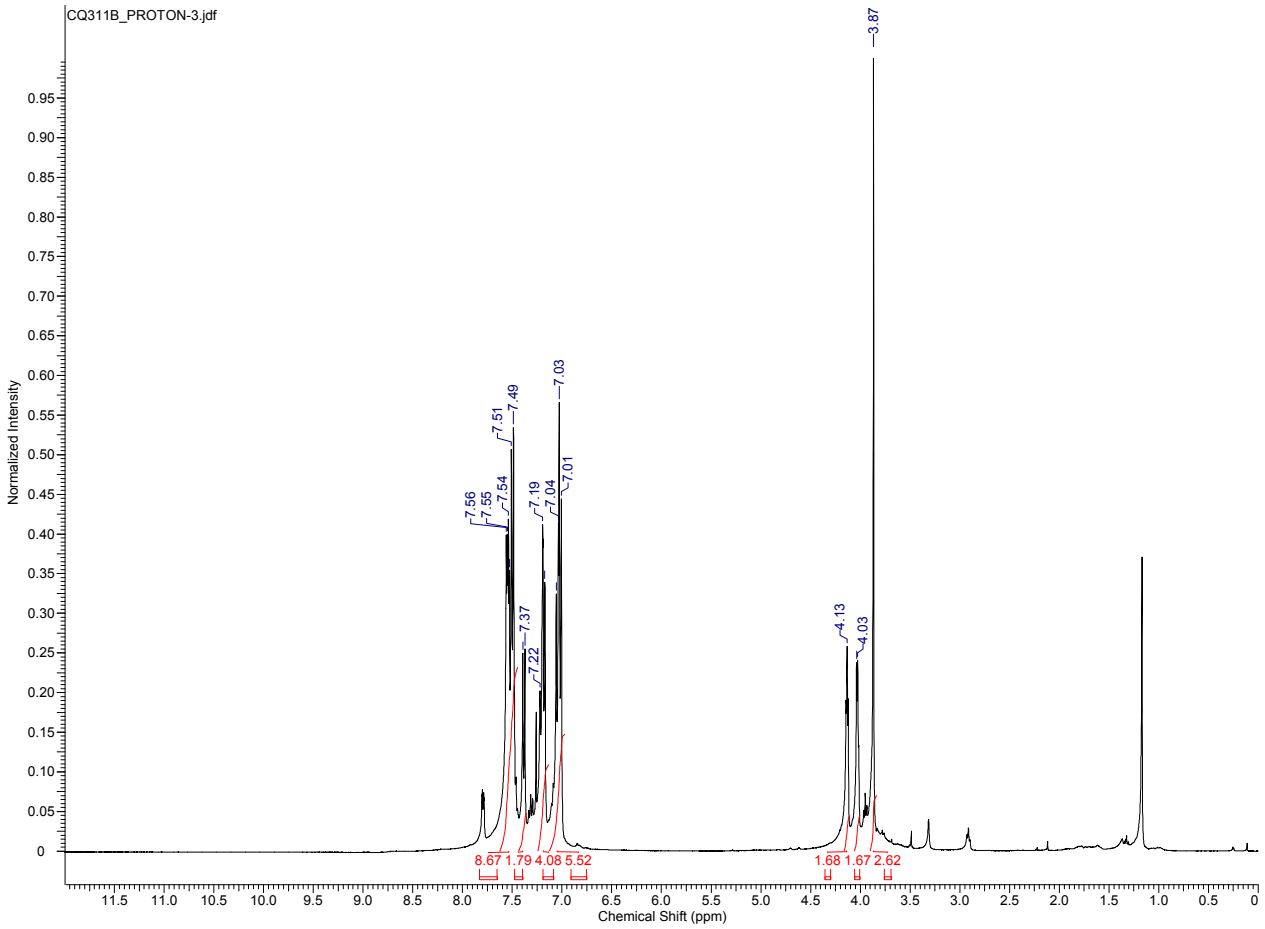


Figure S 22 ^{1}H NMR of **6** in $CDCl_3$

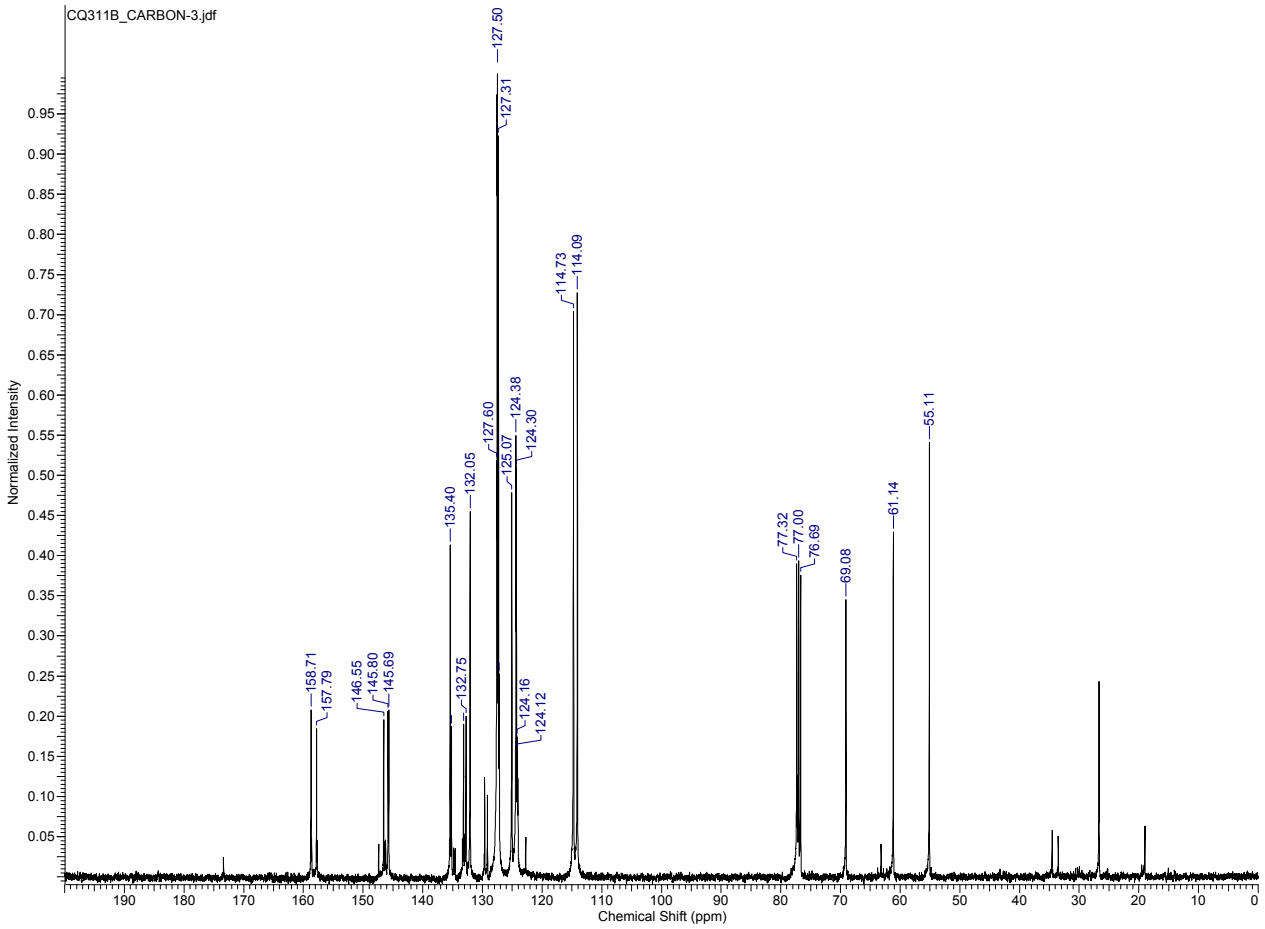


Figure S 23 ^{13}C NMR of **6** in $CDCl_3$

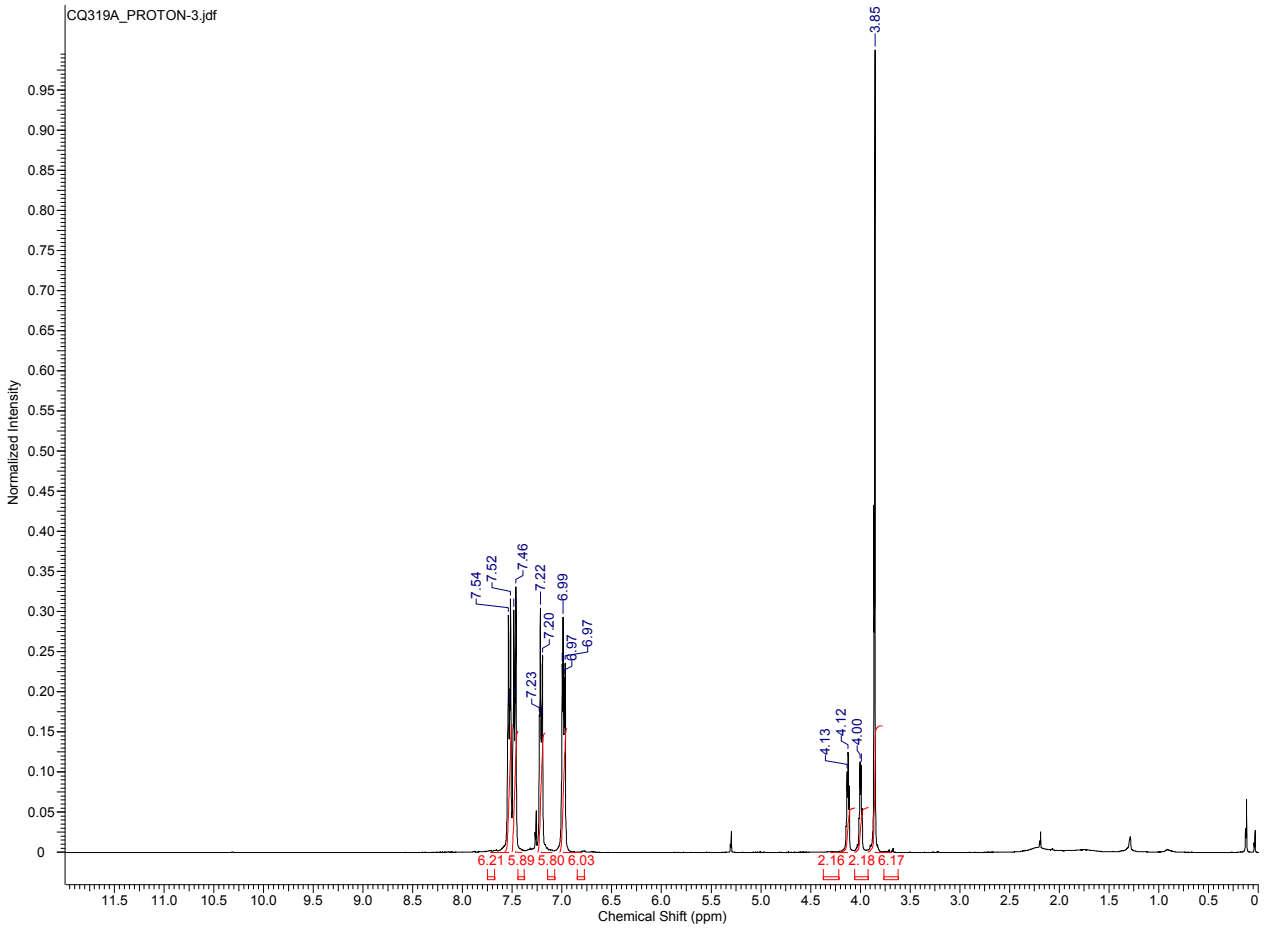


Figure S 24 ^{1}H NMR of **7** in $CDCl_3$

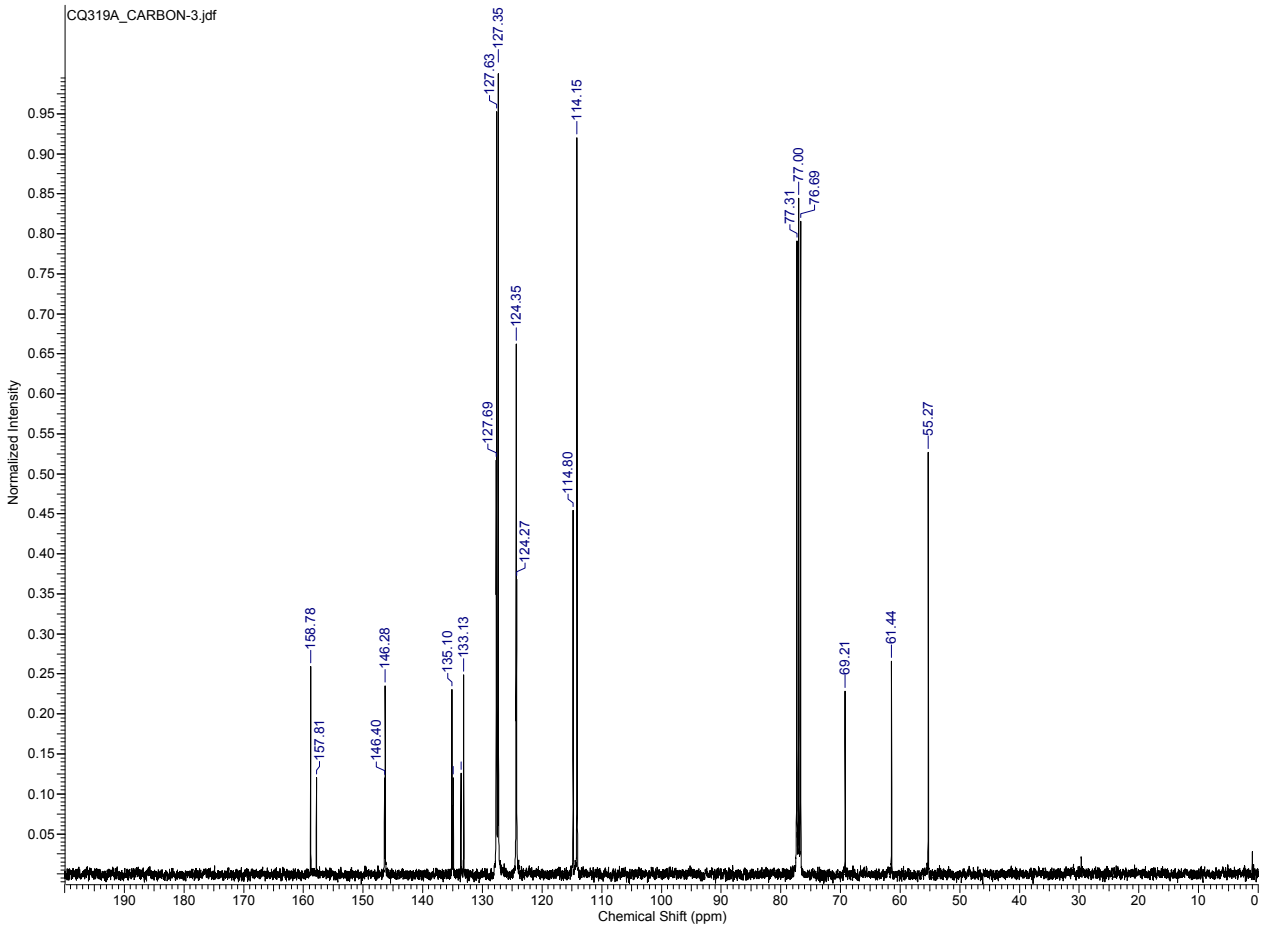


Figure S 25 ^{13}C NMR of **7** in $CDCl_3$

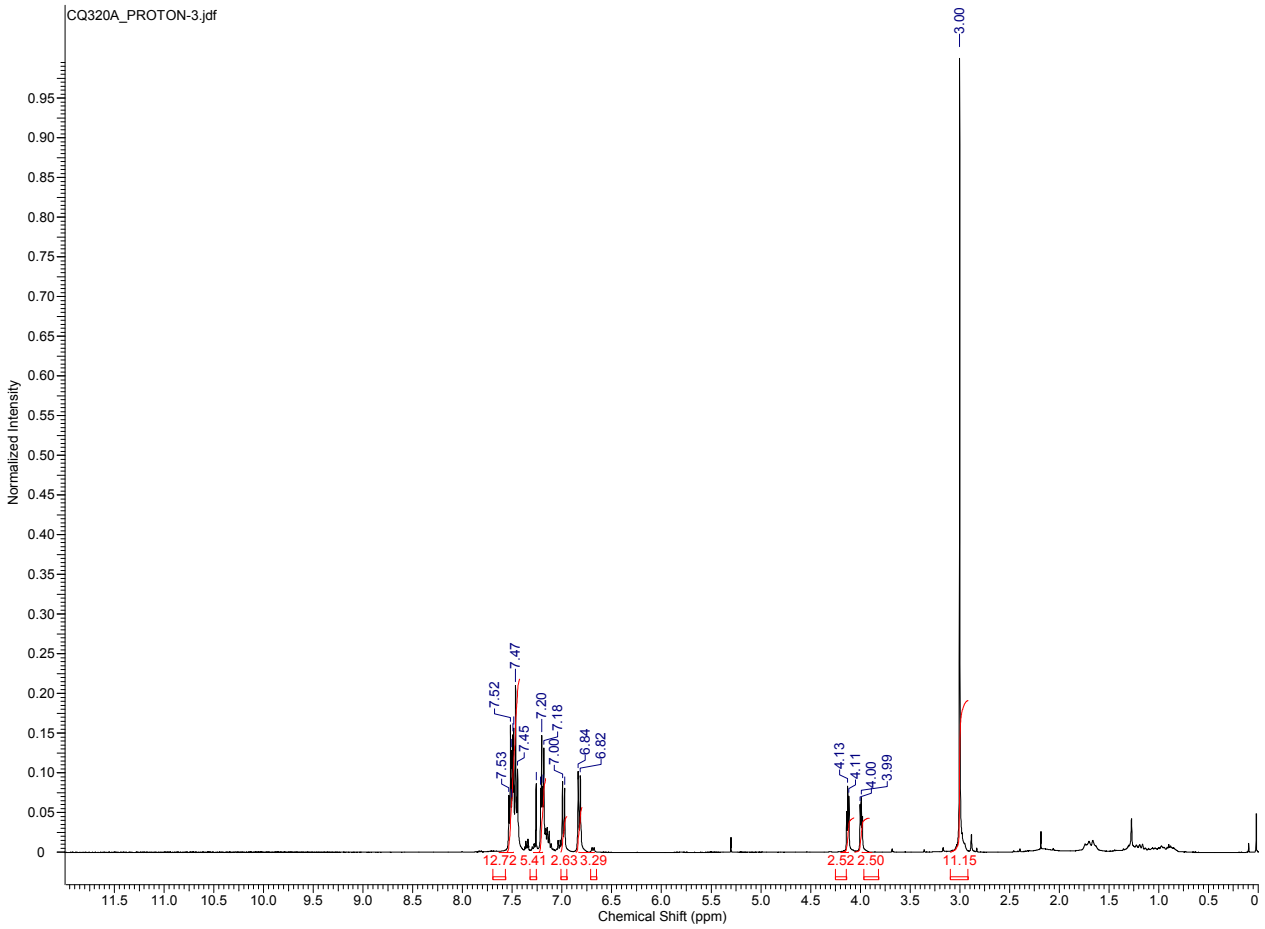


Figure S 26 ^{1}H NMR of **8** in $CDCl_3$

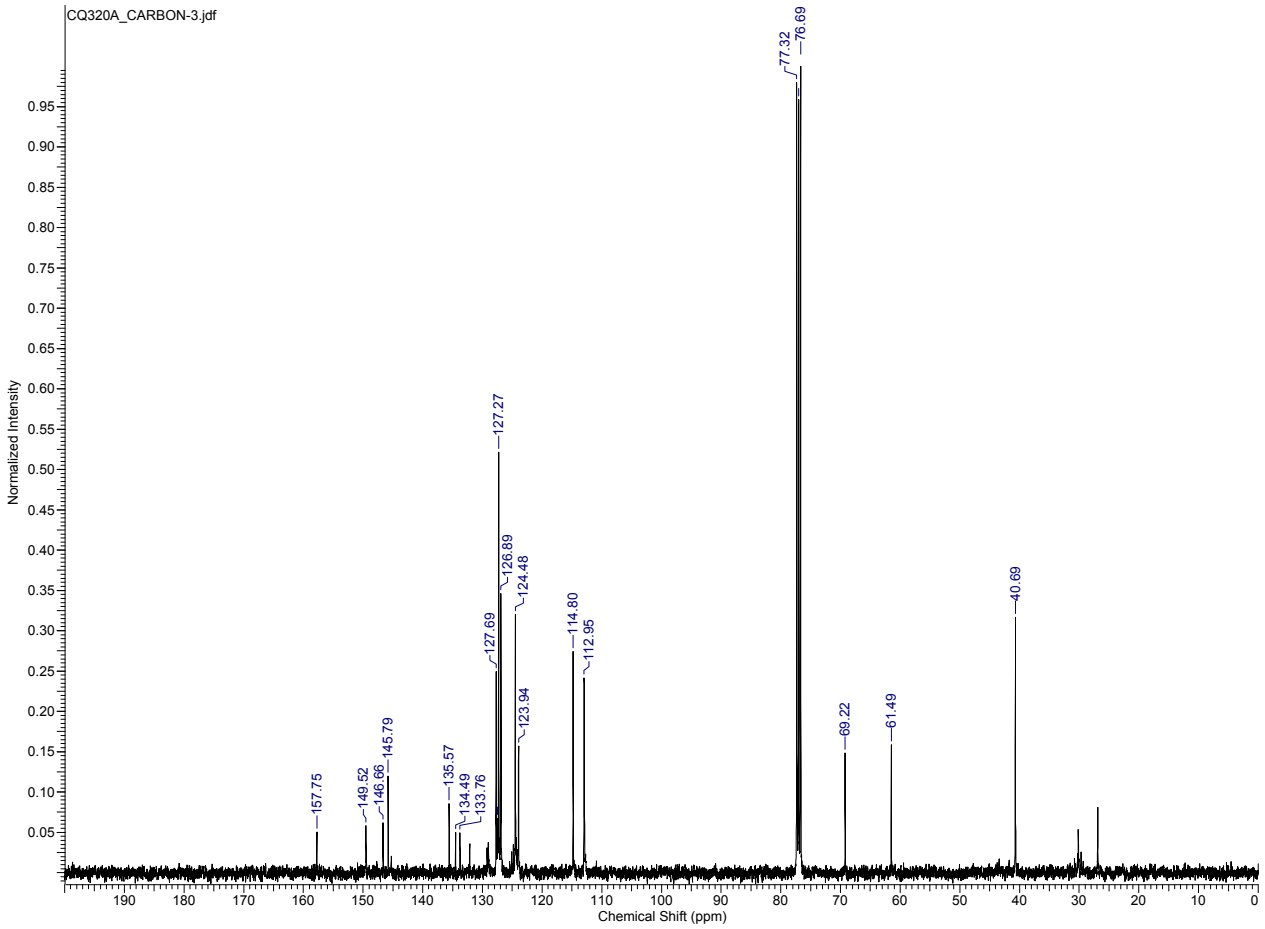


Figure S 27 ^{13}C NMR of **8** in $CDCl_3$

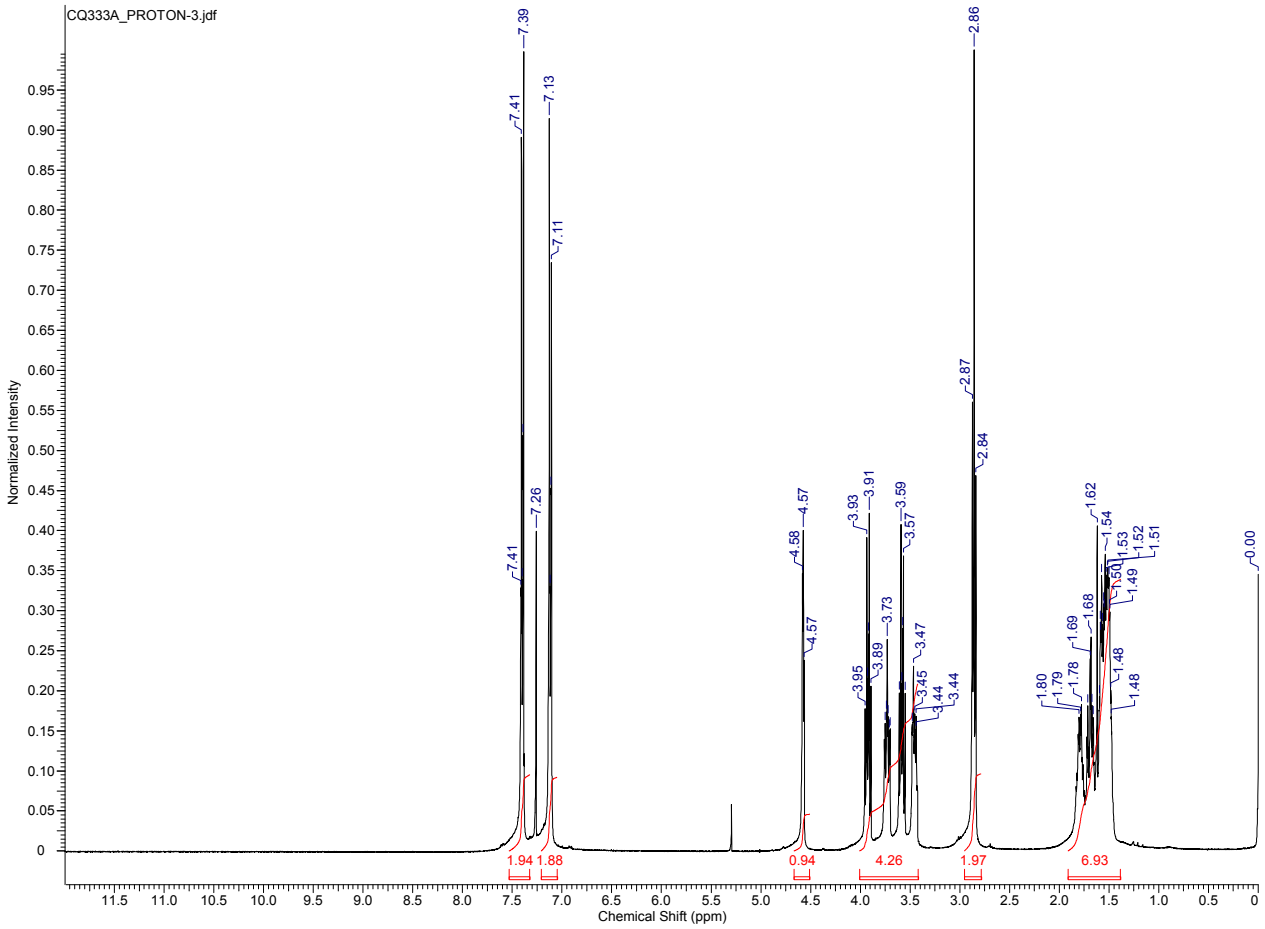


Figure S 28 ^{1}H NMR of **9** in $CDCl_3$

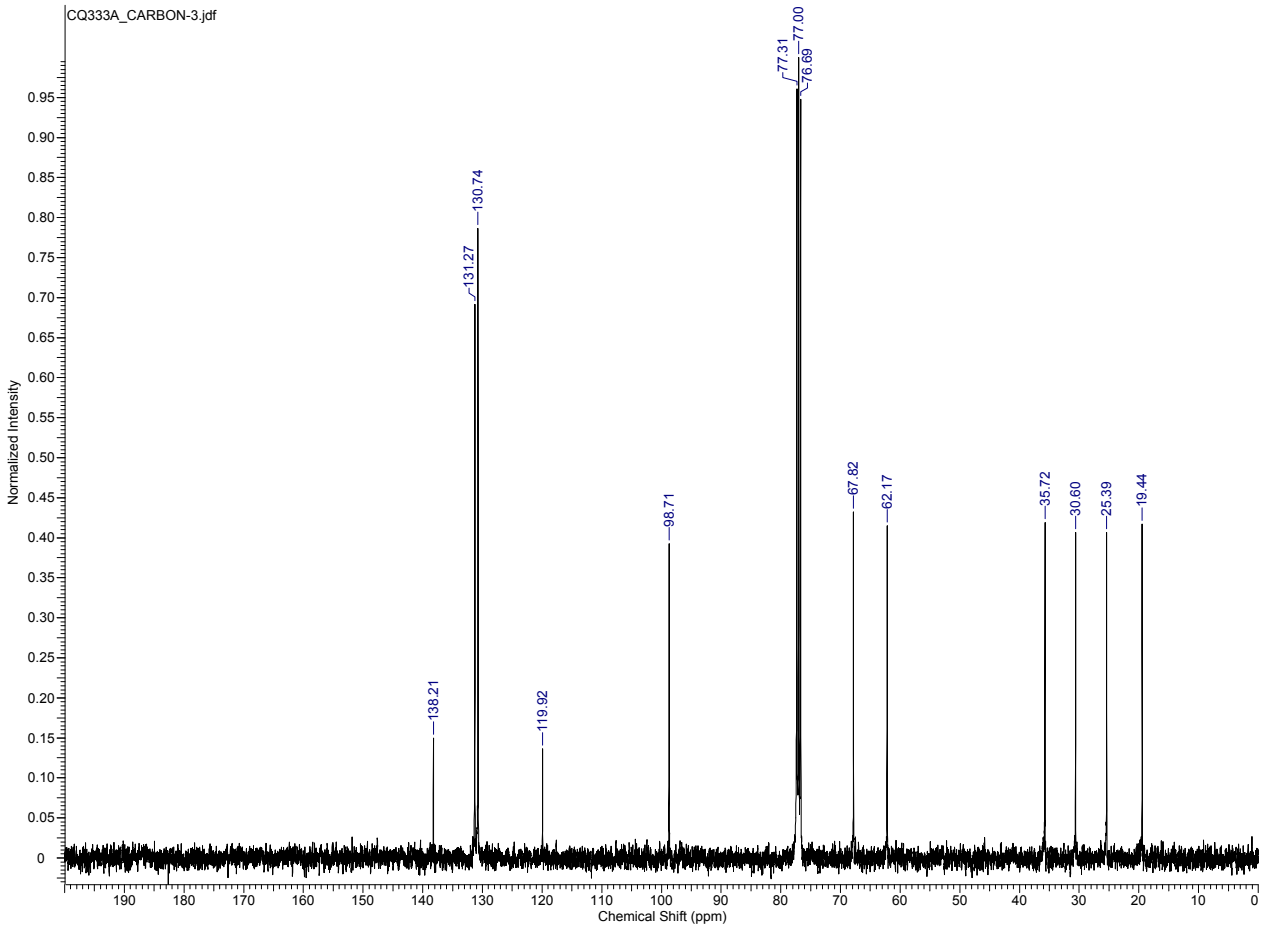


Figure S 29 ^{13}C NMR of **9** in $CDCl_3$

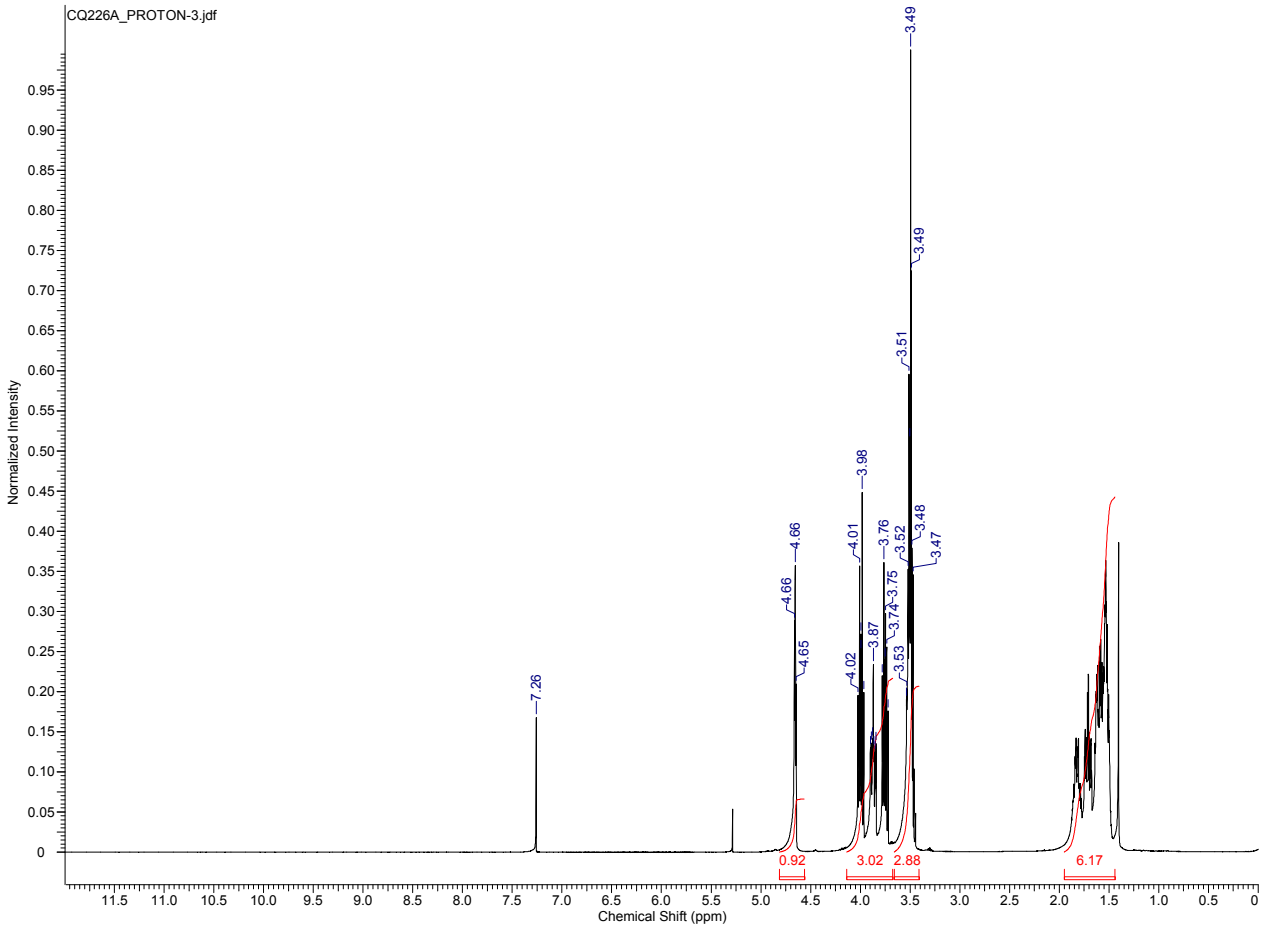


Figure S 30 ^{1}H NMR of **10** in $CDCl_3$

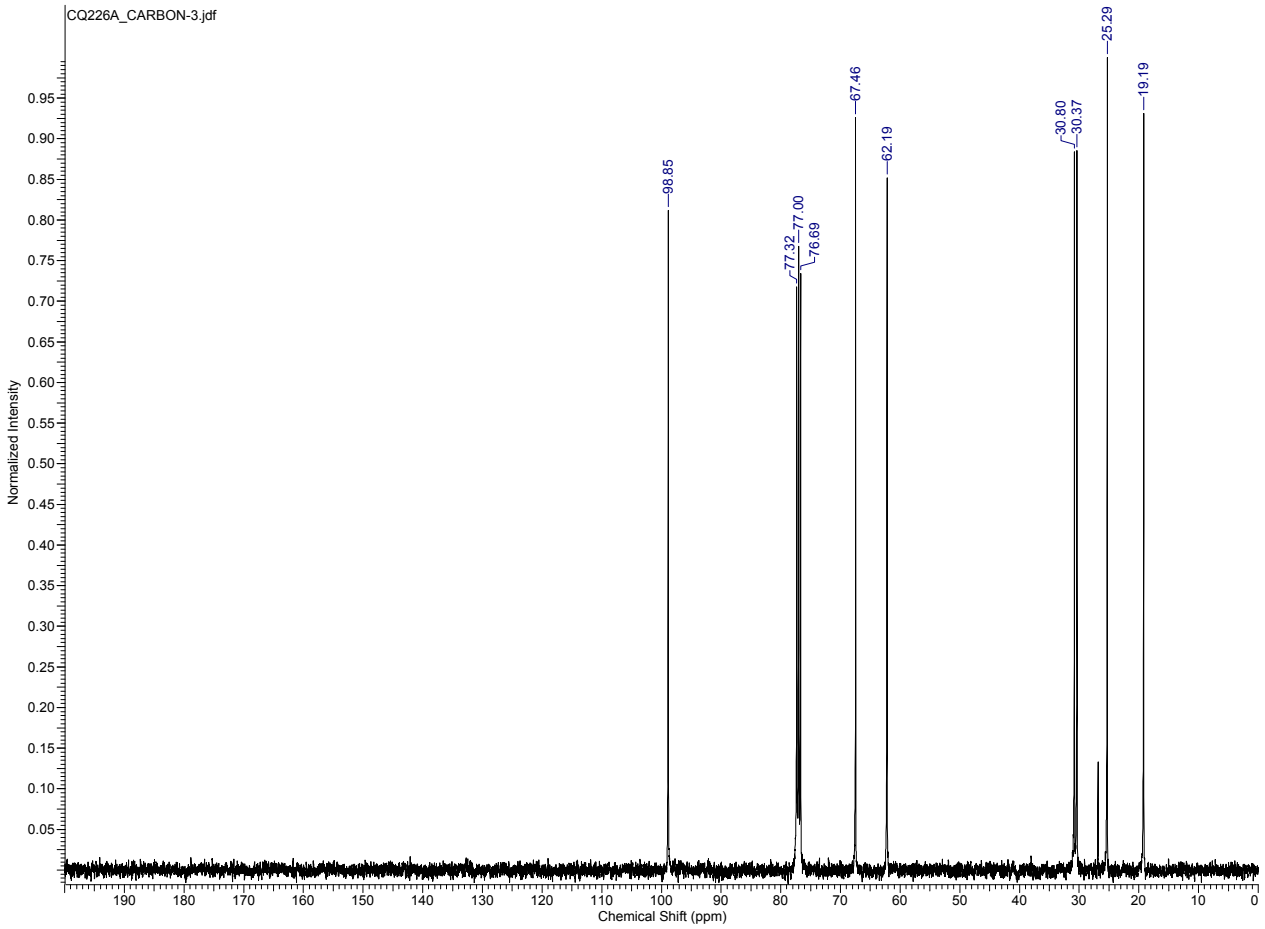


Figure S 31 ^{13}C NMR of **10** in $CDCl_3$

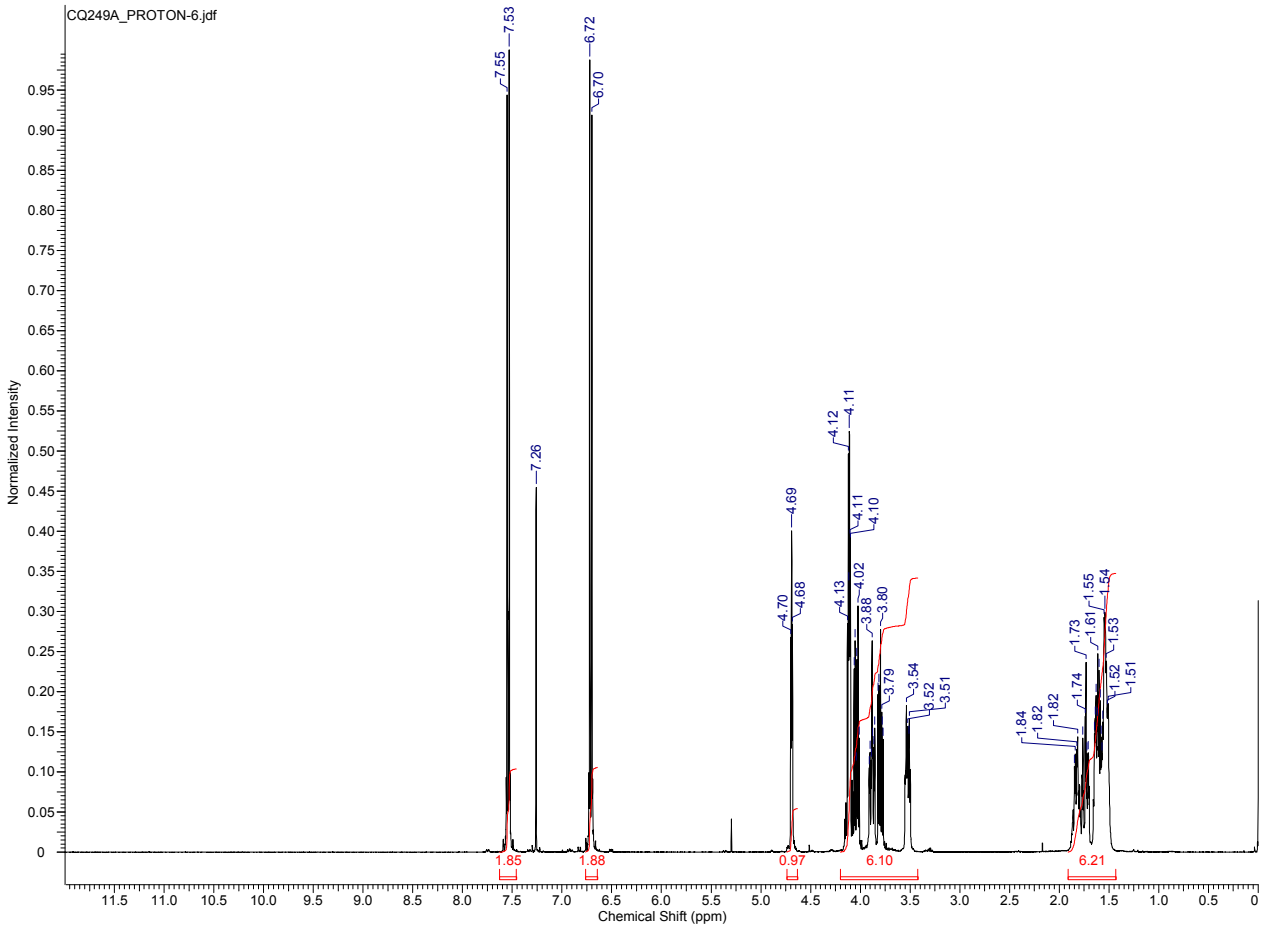


Figure S 32 ^{1}H NMR of **11** in $CDCl_3$

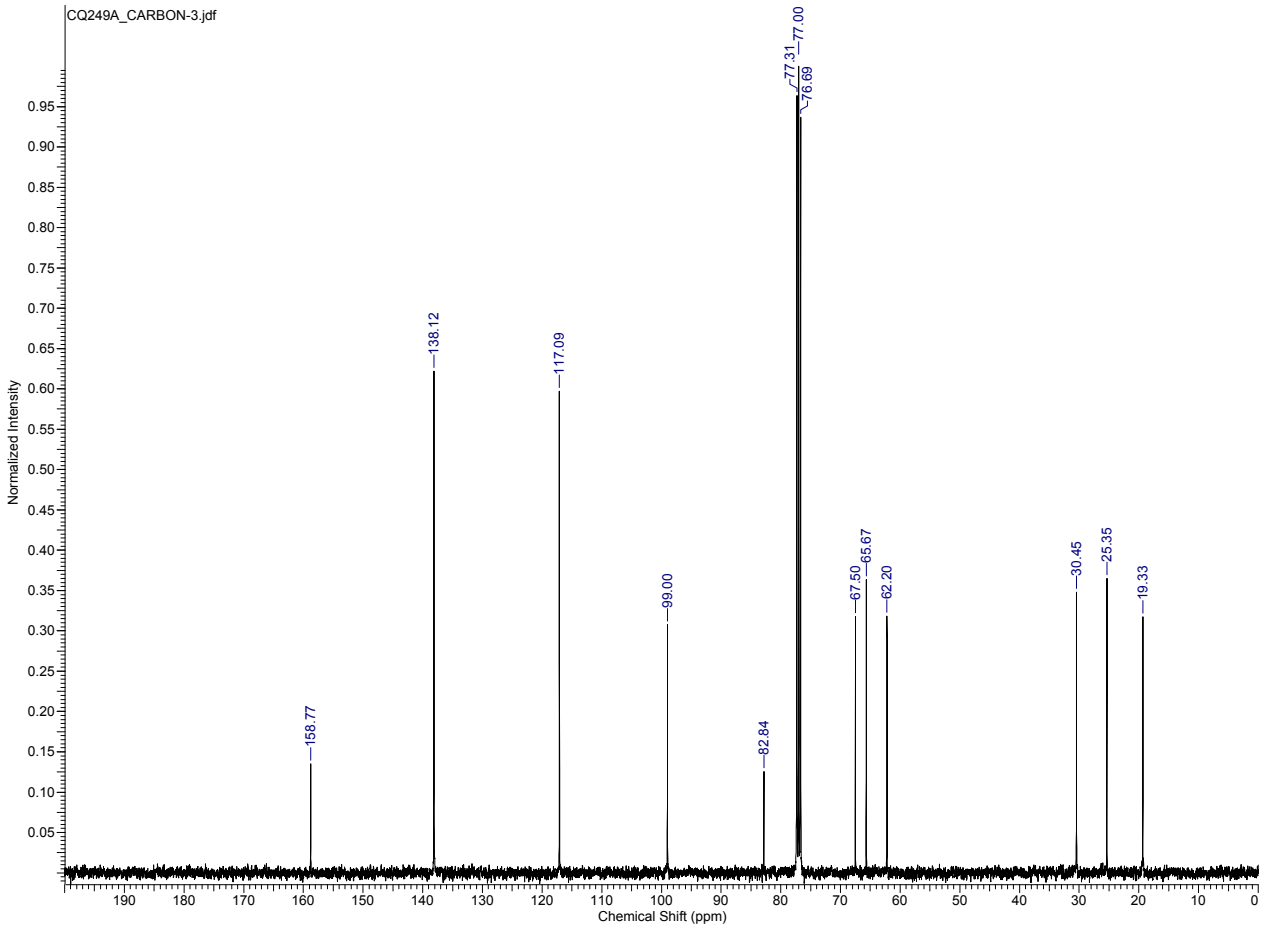


Figure S 33 ^{13}C NMR of **11** in $CDCl_3$

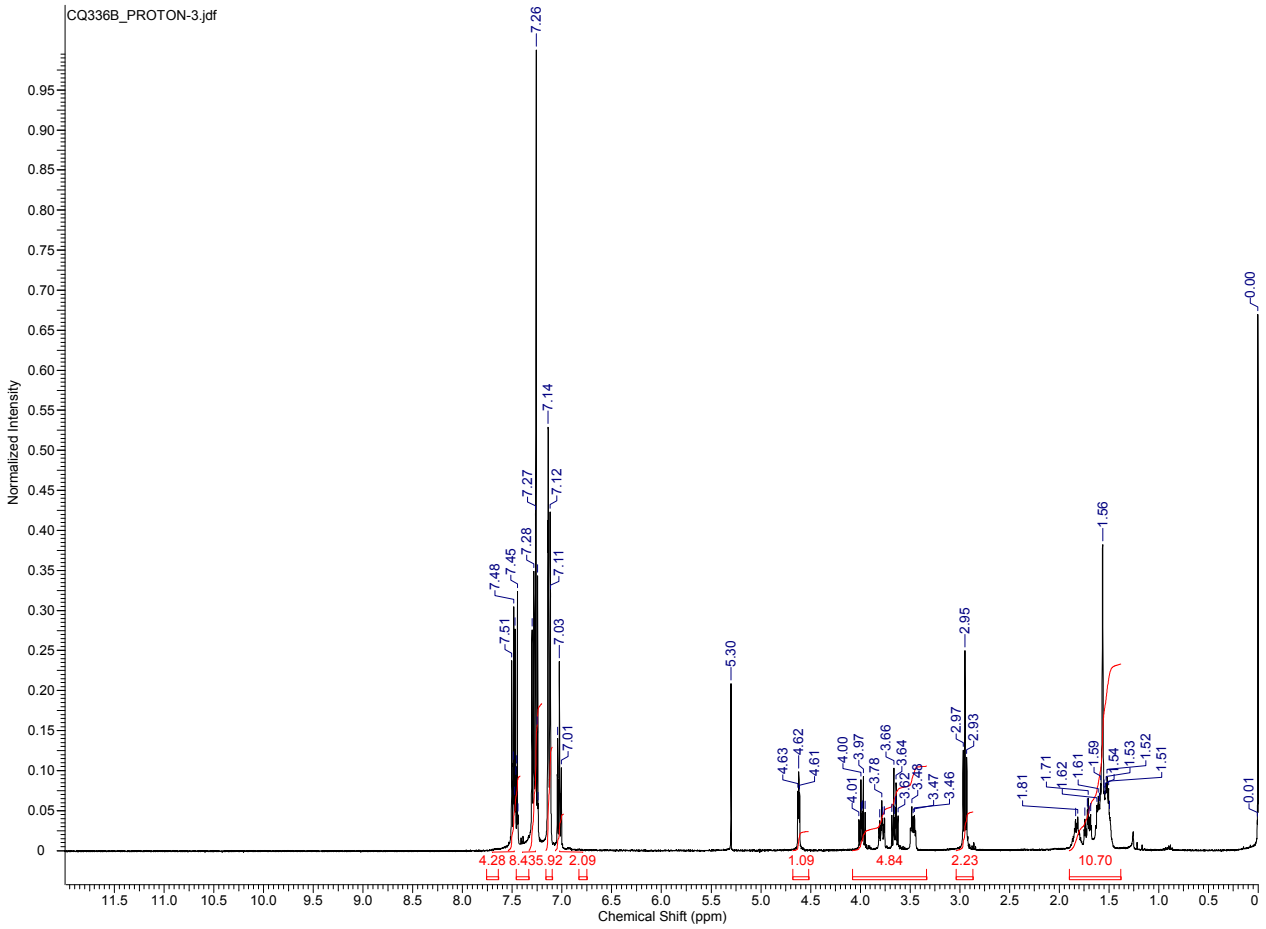


Figure S 34 ^{1}H NMR of **12** in $CDCl_3$

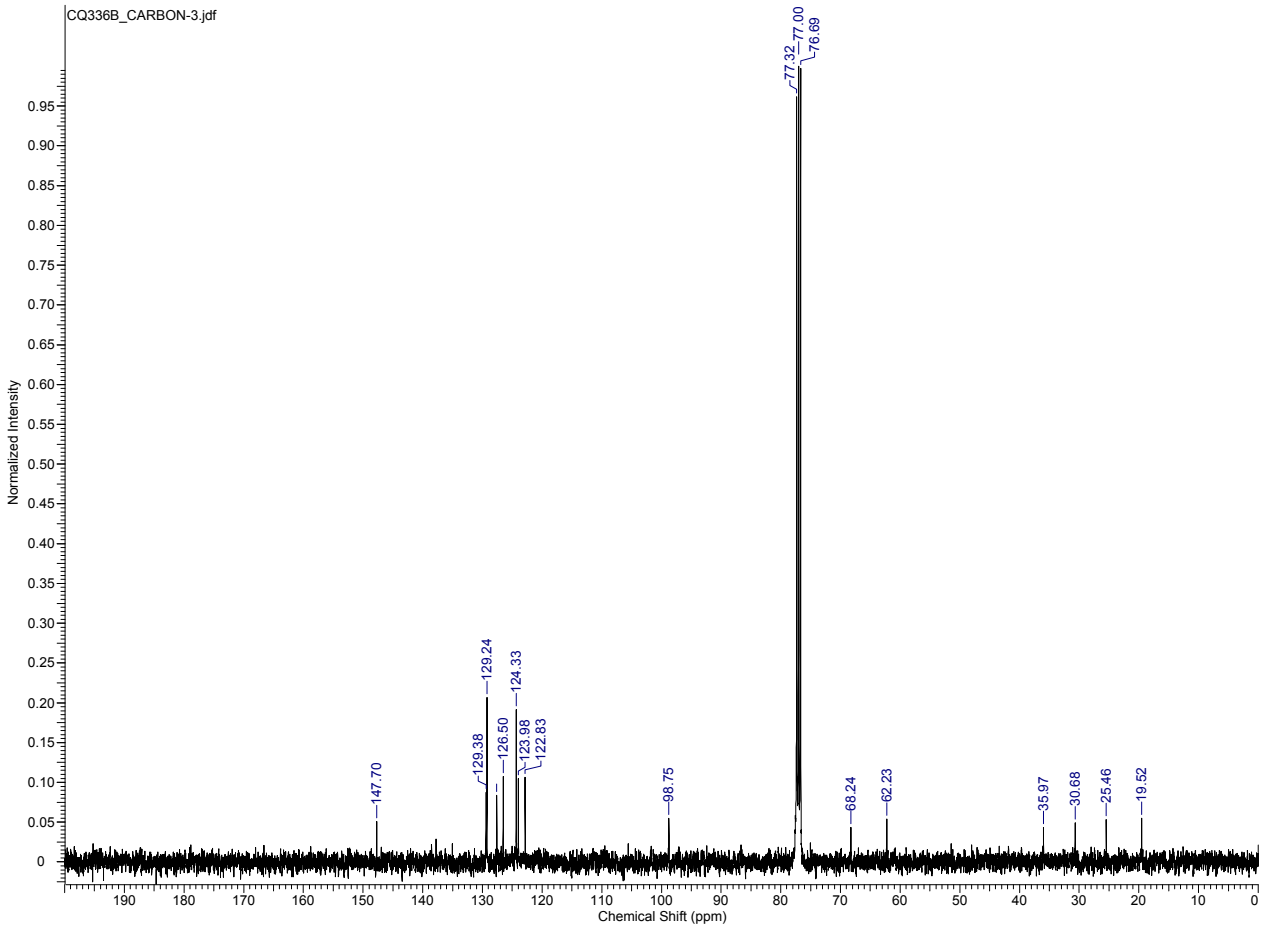


Figure S 35 ^{13}C NMR of **12** in $CDCl_3$

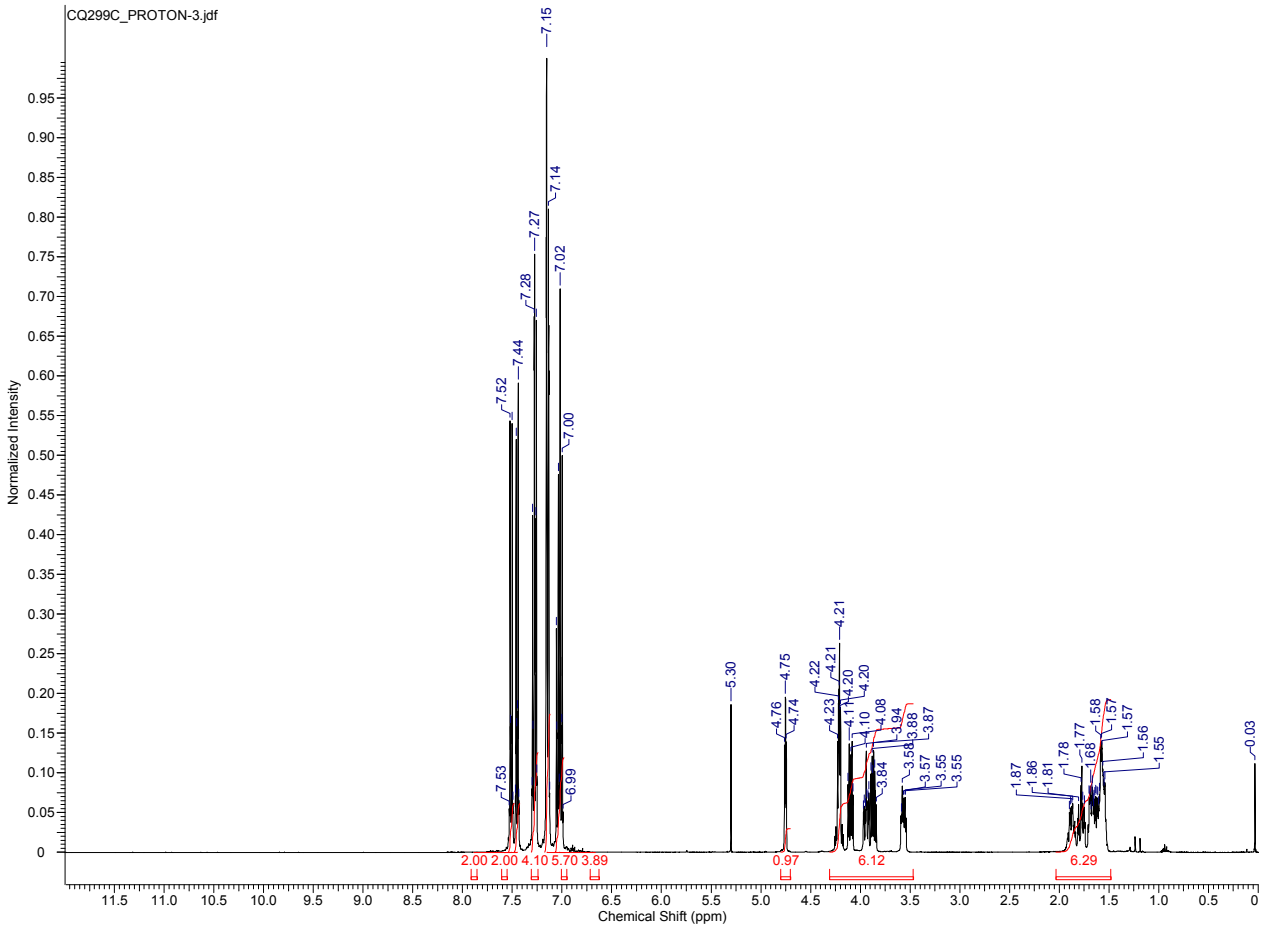


Figure S 36 ^{1}H NMR of **13** in $CDCl_3$

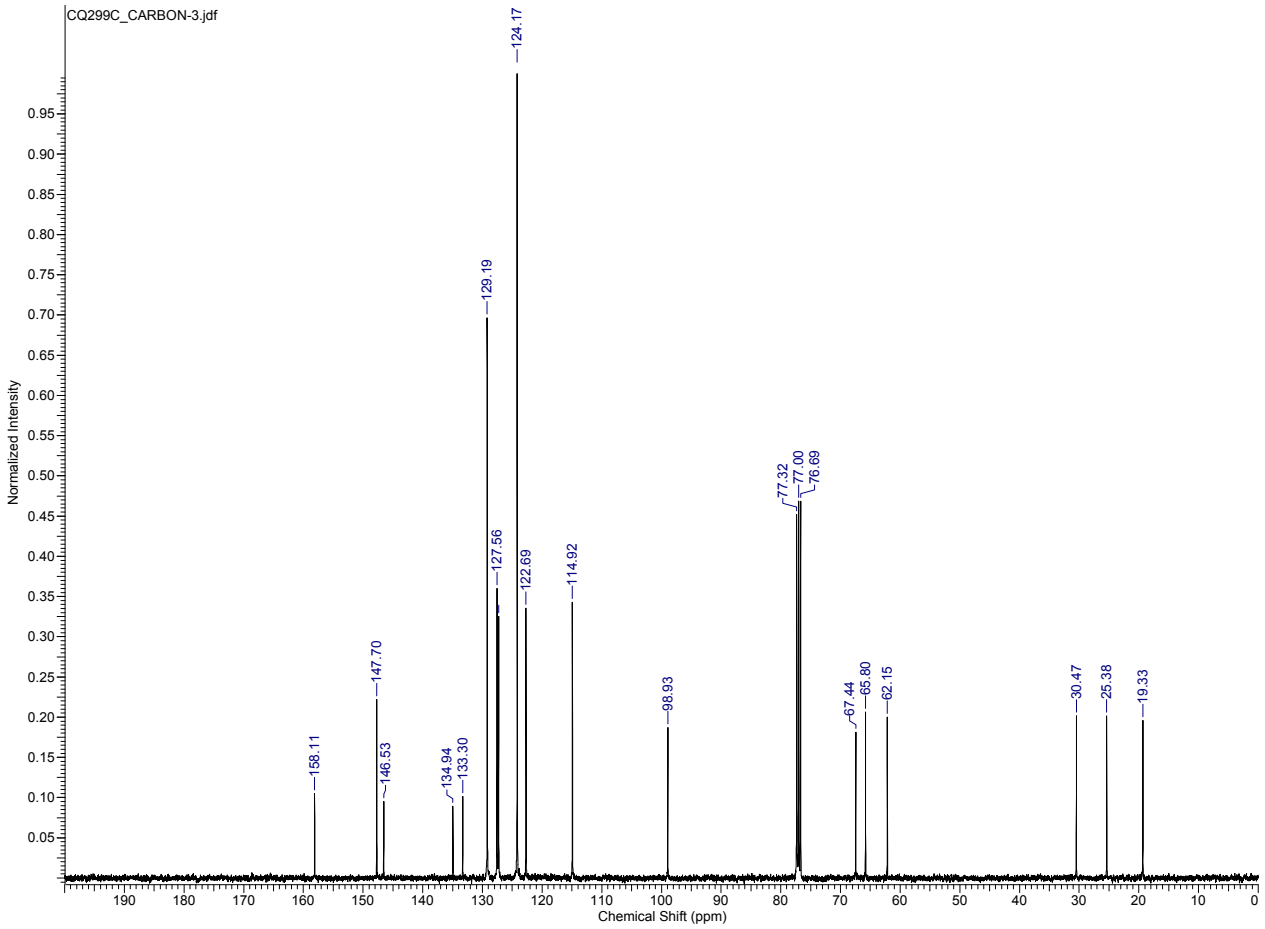


Figure S 37 ^{13}C NMR of **13** in $CDCl_3$

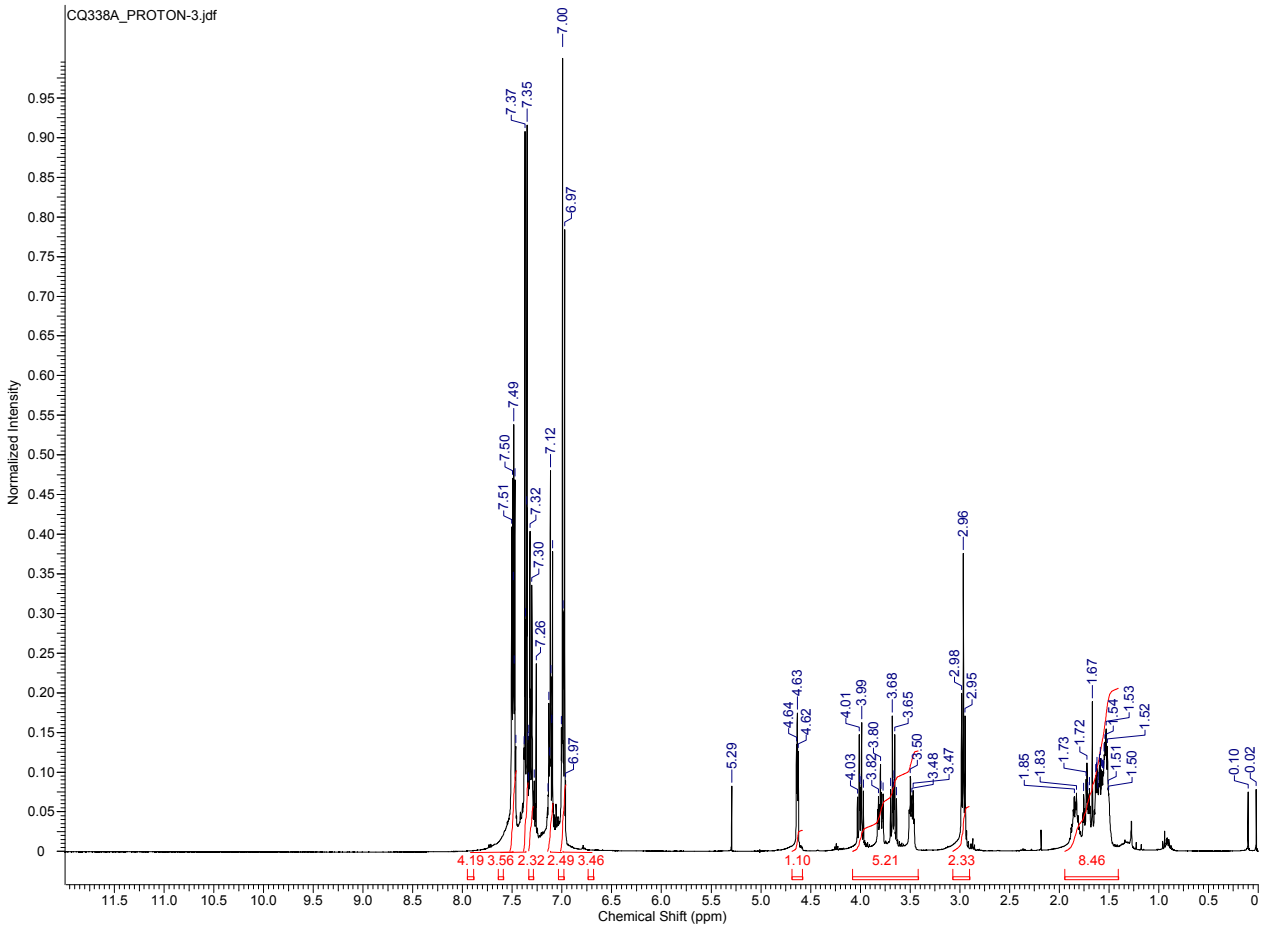


Figure S 38 ^{1}H NMR of **14** in $CDCl_3$

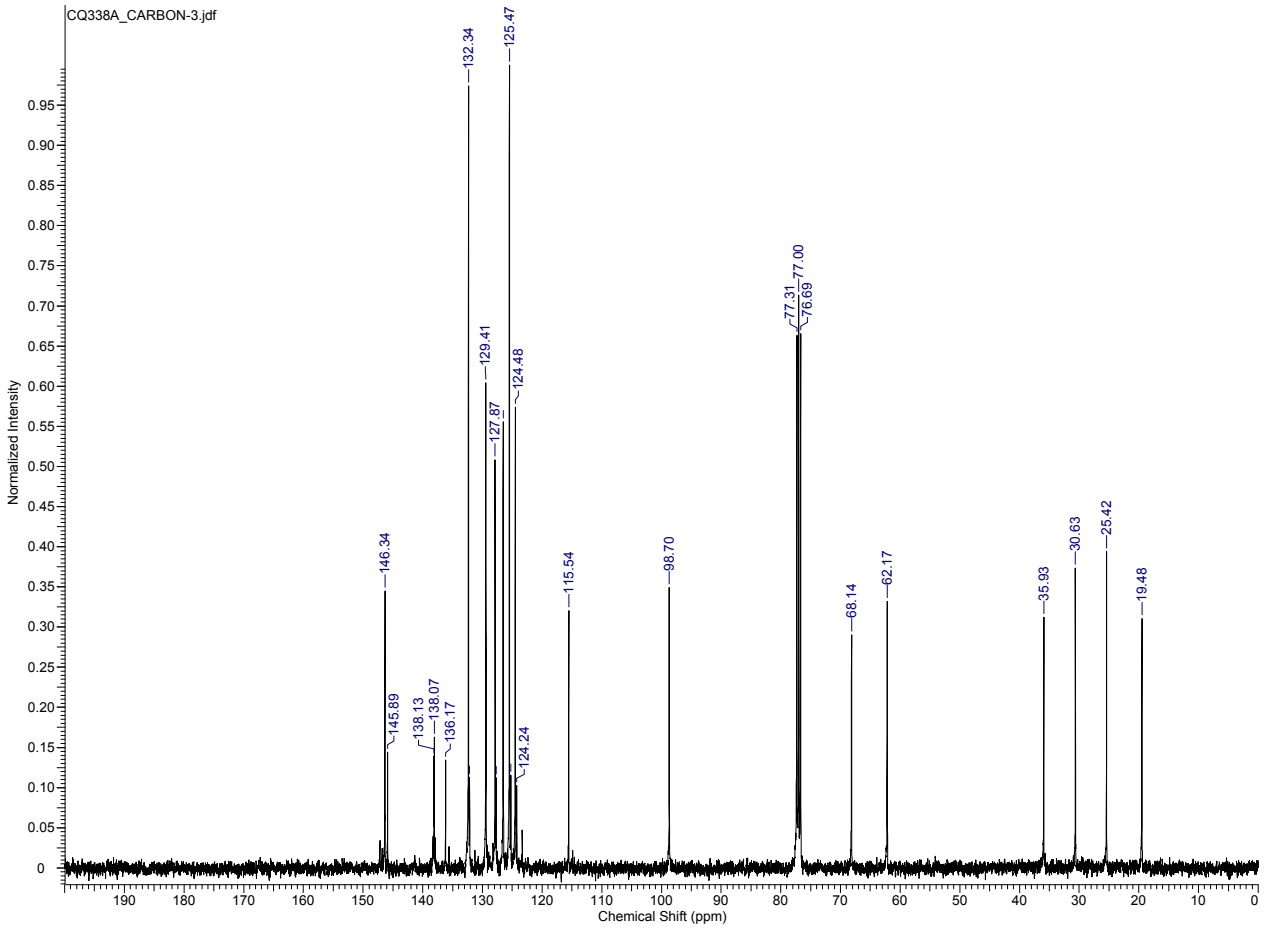


Figure S 39 ^{13}C NMR of **14** in $CDCl_3$

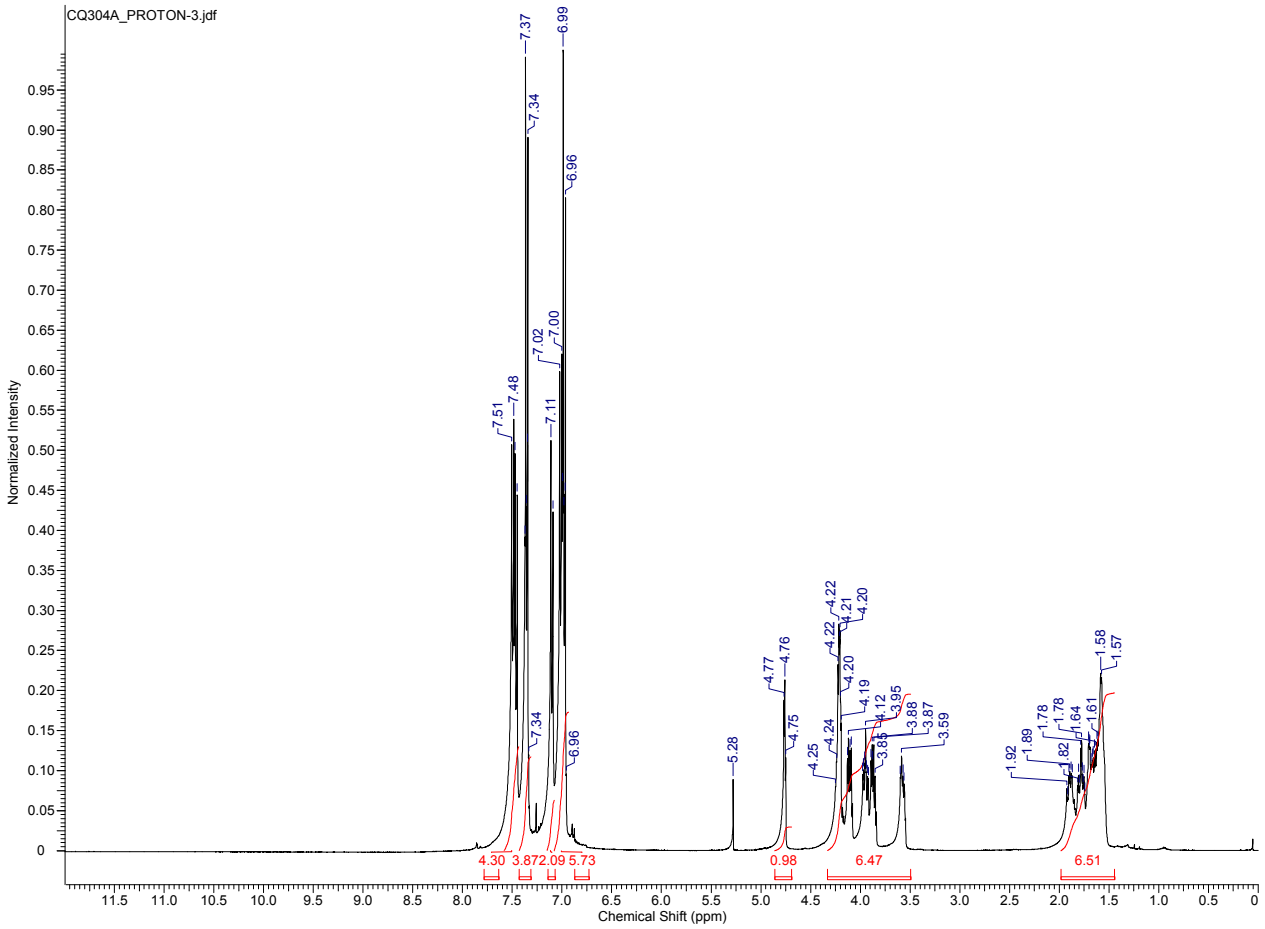


Figure S 40 ^{1}H NMR of **15** in $CDCl_3$

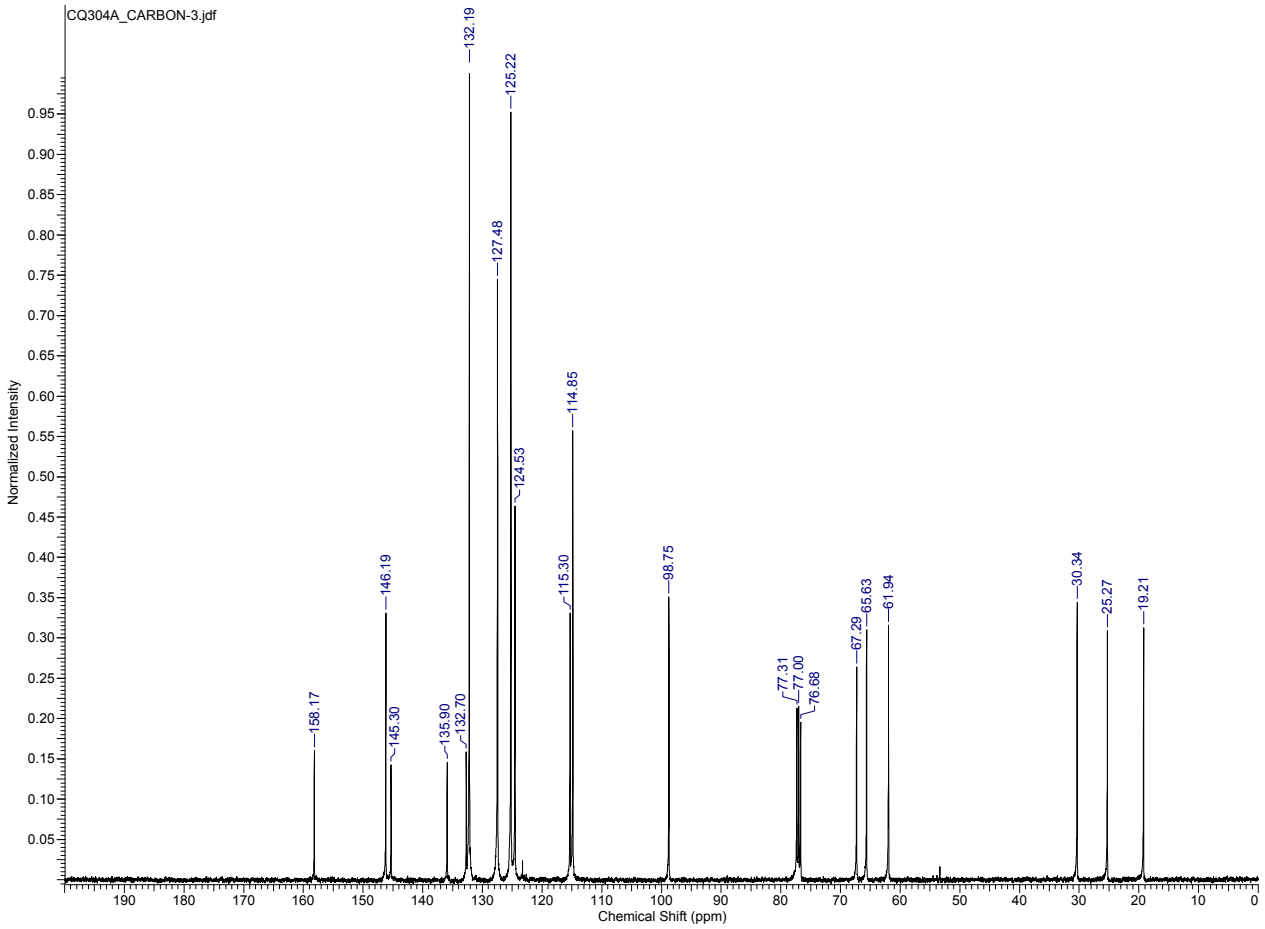


Figure S 41 ^{13}C NMR of **15** in $CDCl_3$

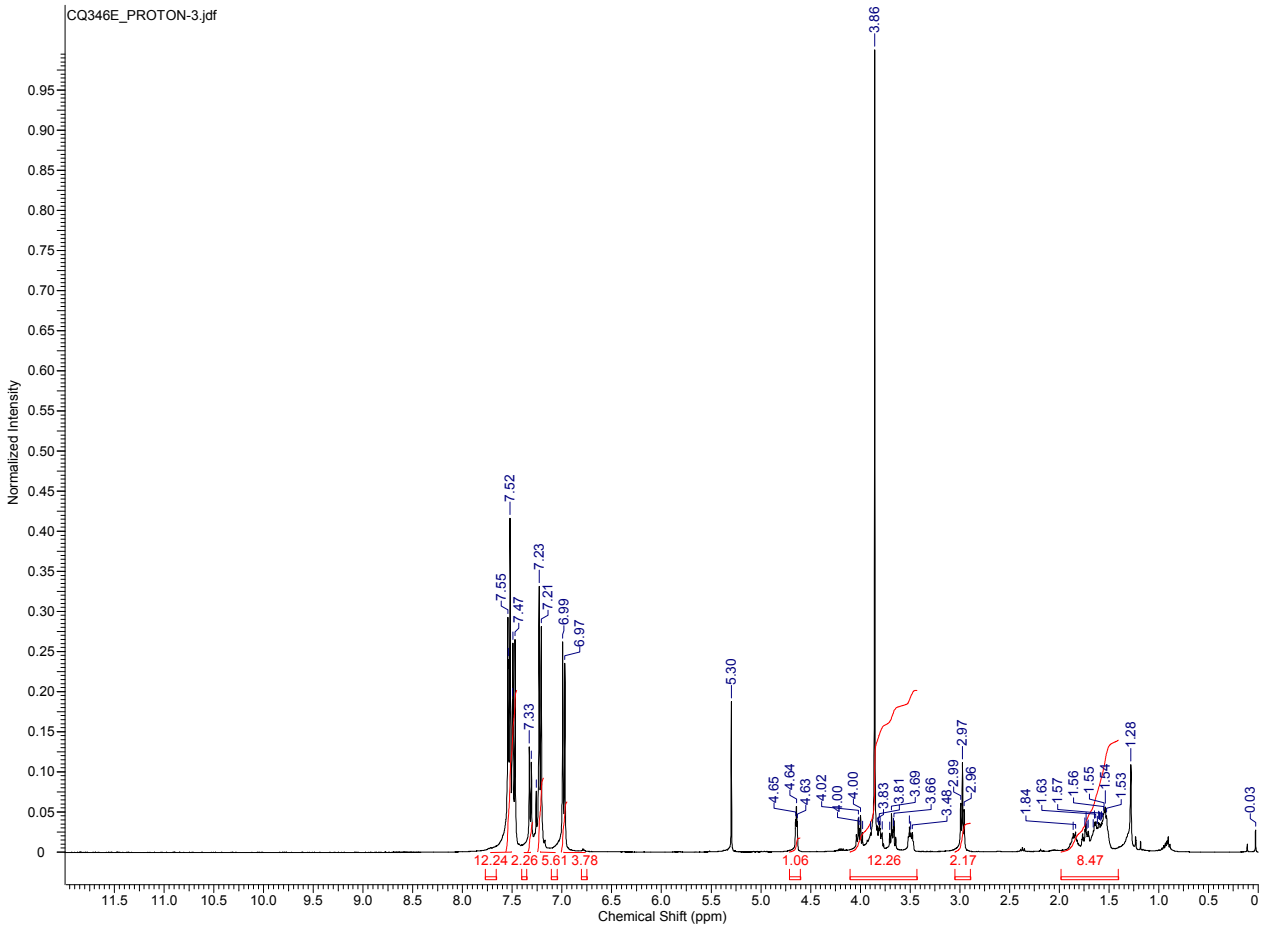


Figure S 42 ^{1}H NMR of **16** in $CDCl_3$

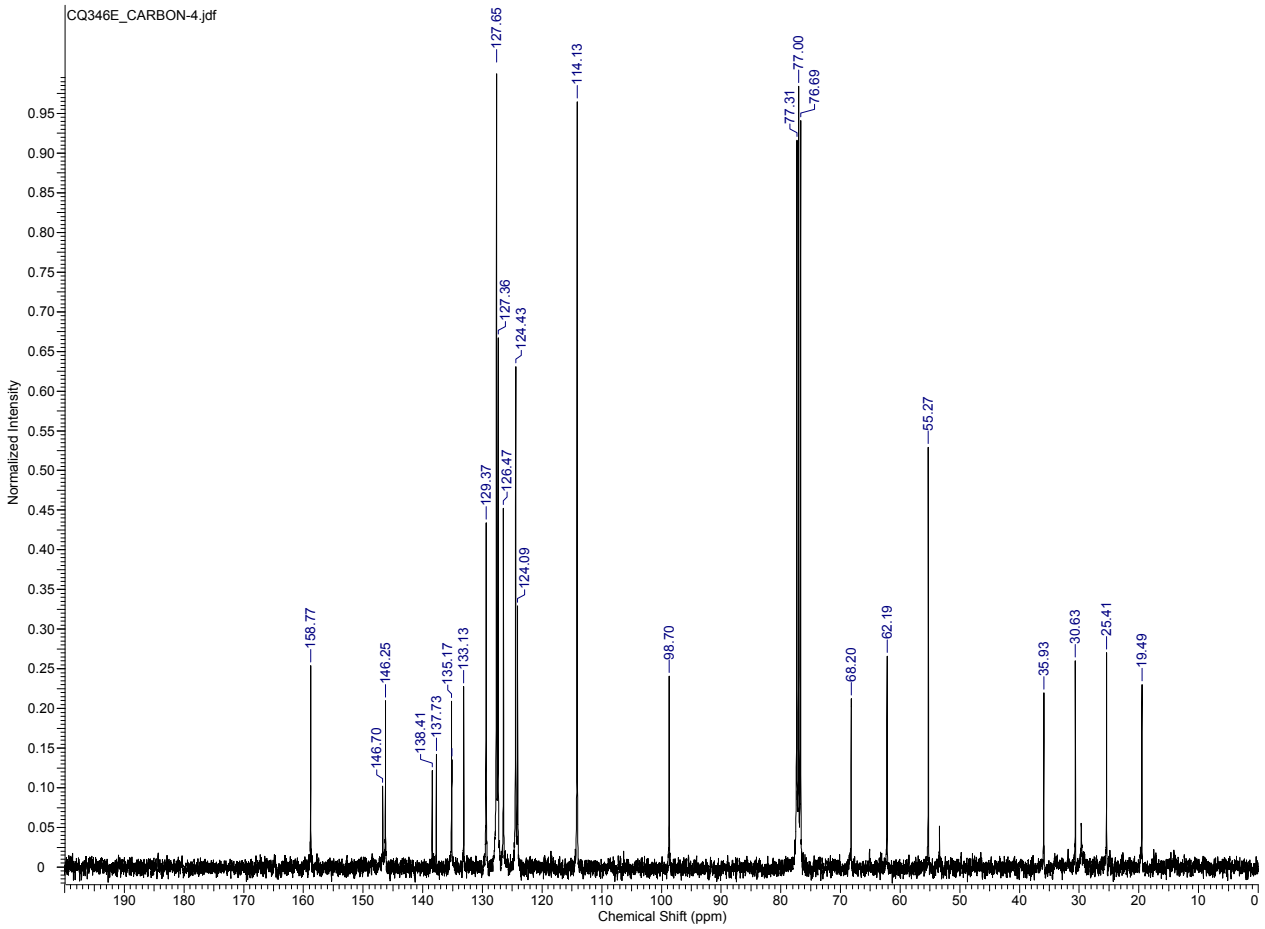


Figure S 43 ^{13}C NMR of **16** in $CDCl_3$

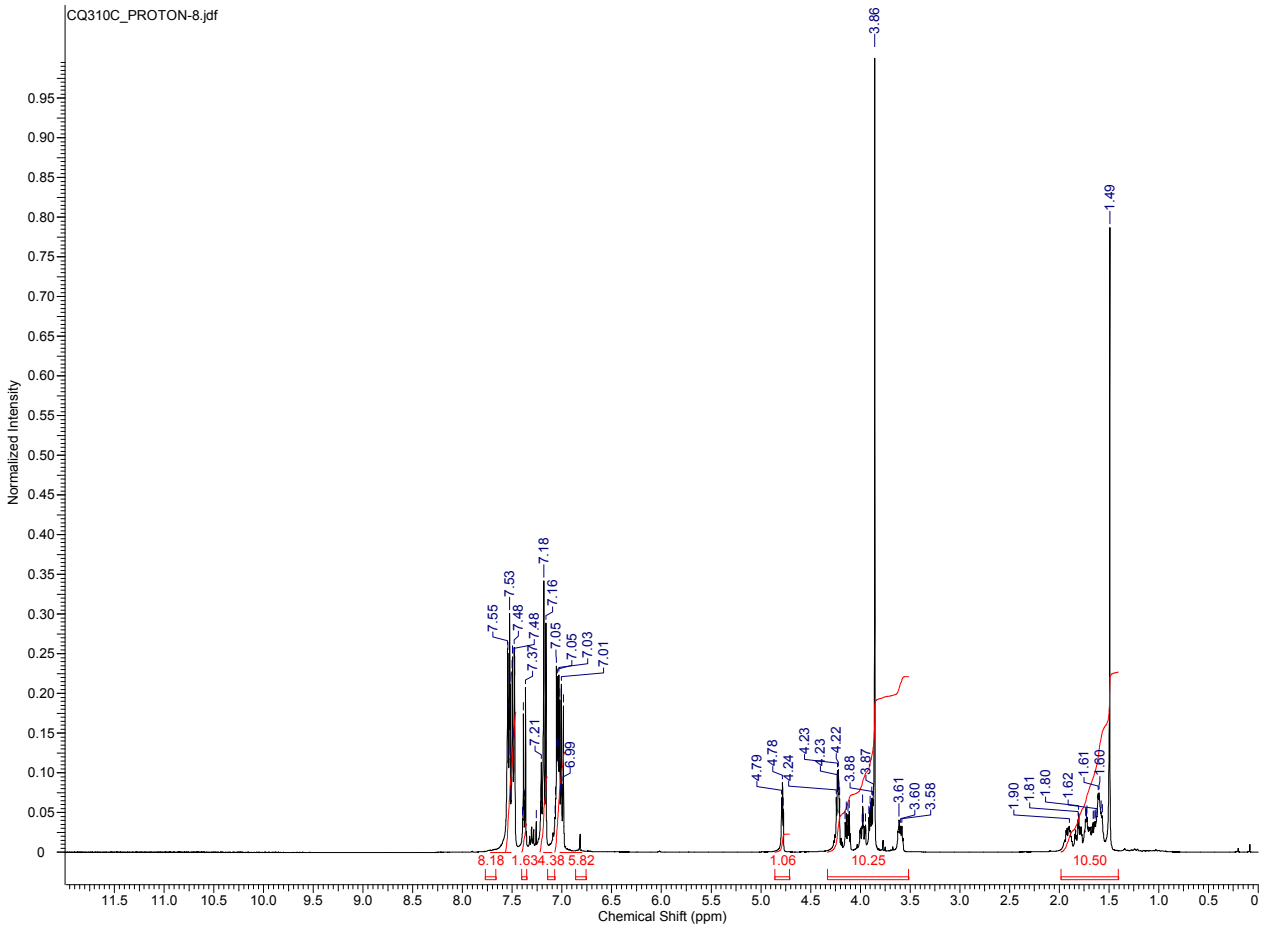


Figure S 44 ^{1}H NMR of **17** in $CDCl_3$

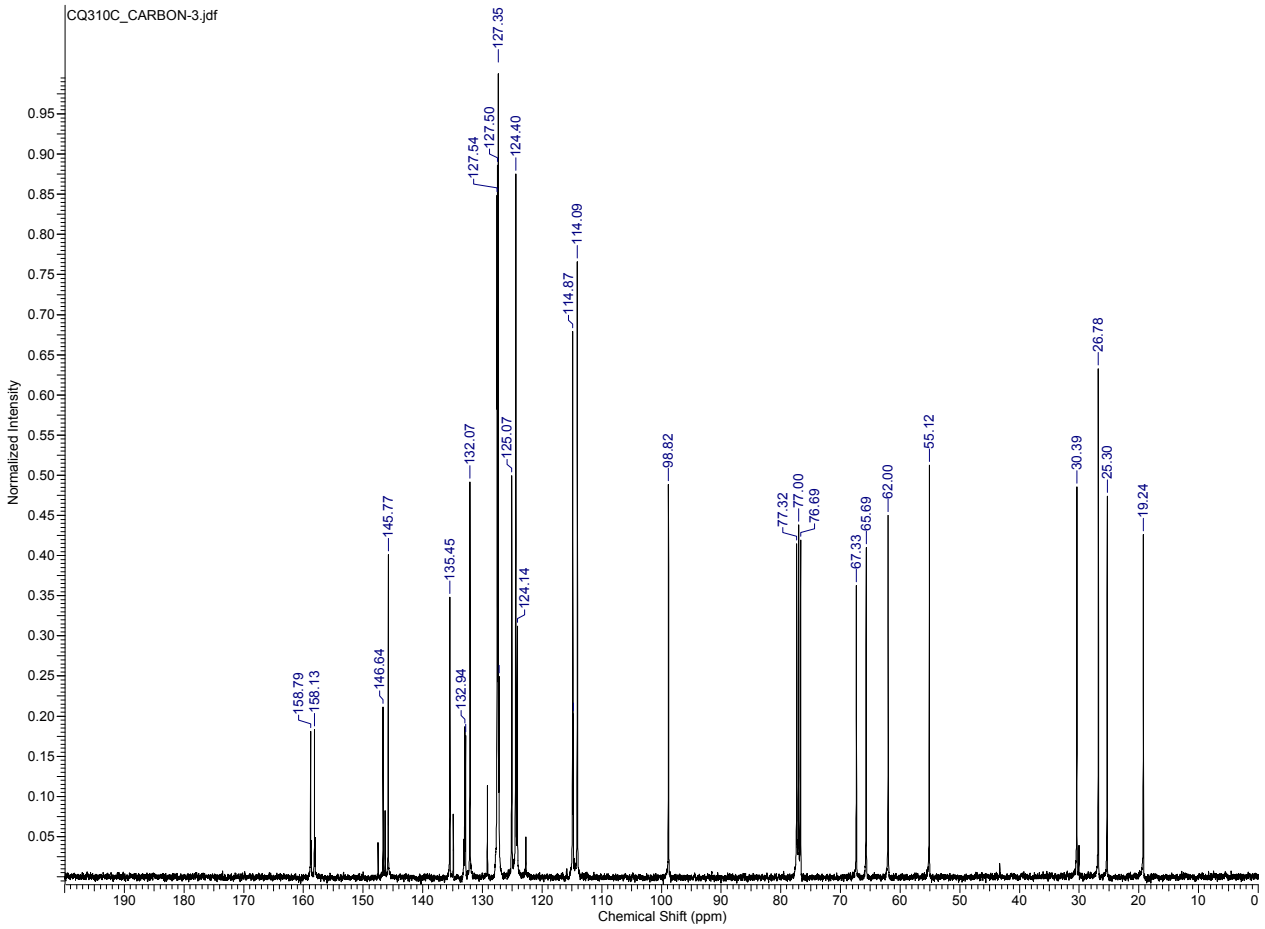


Figure S 45 ^{13}C NMR of **17** in $CDCl_3$

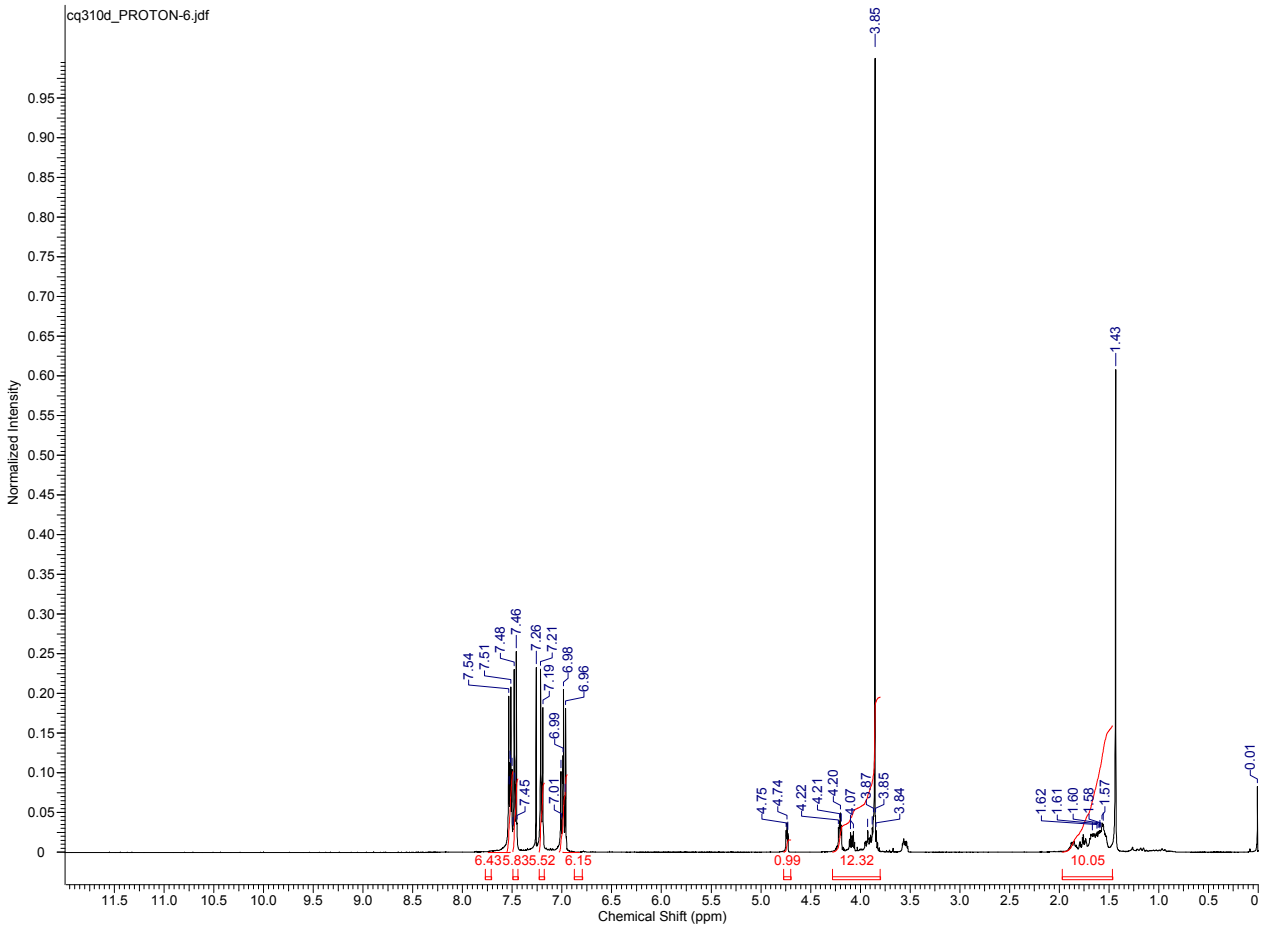


Figure S 46 ^{1}H NMR of **18** in $CDCl_3$

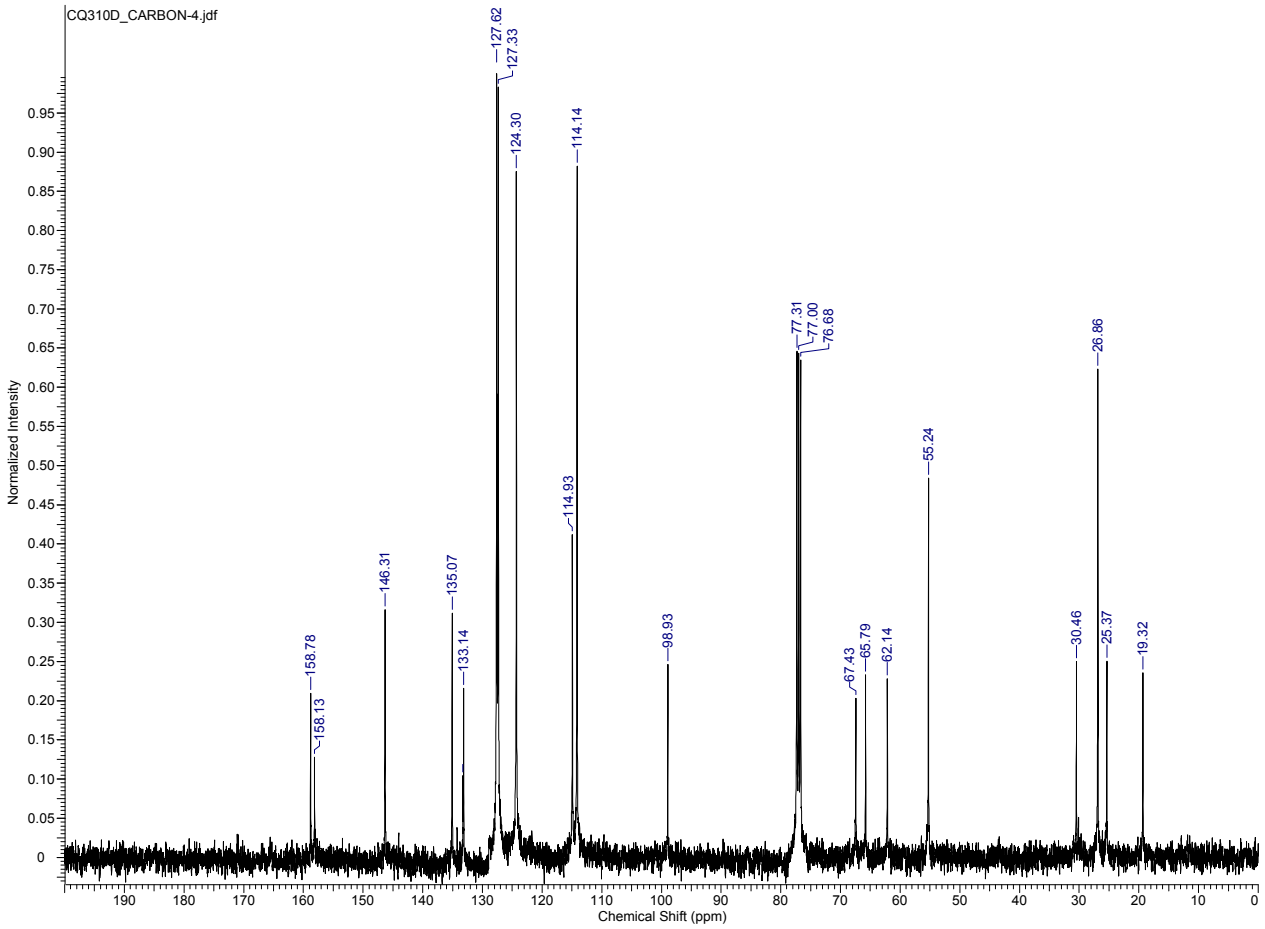


Figure S 47 ^{13}C NMR of **18** in $CDCl_3$

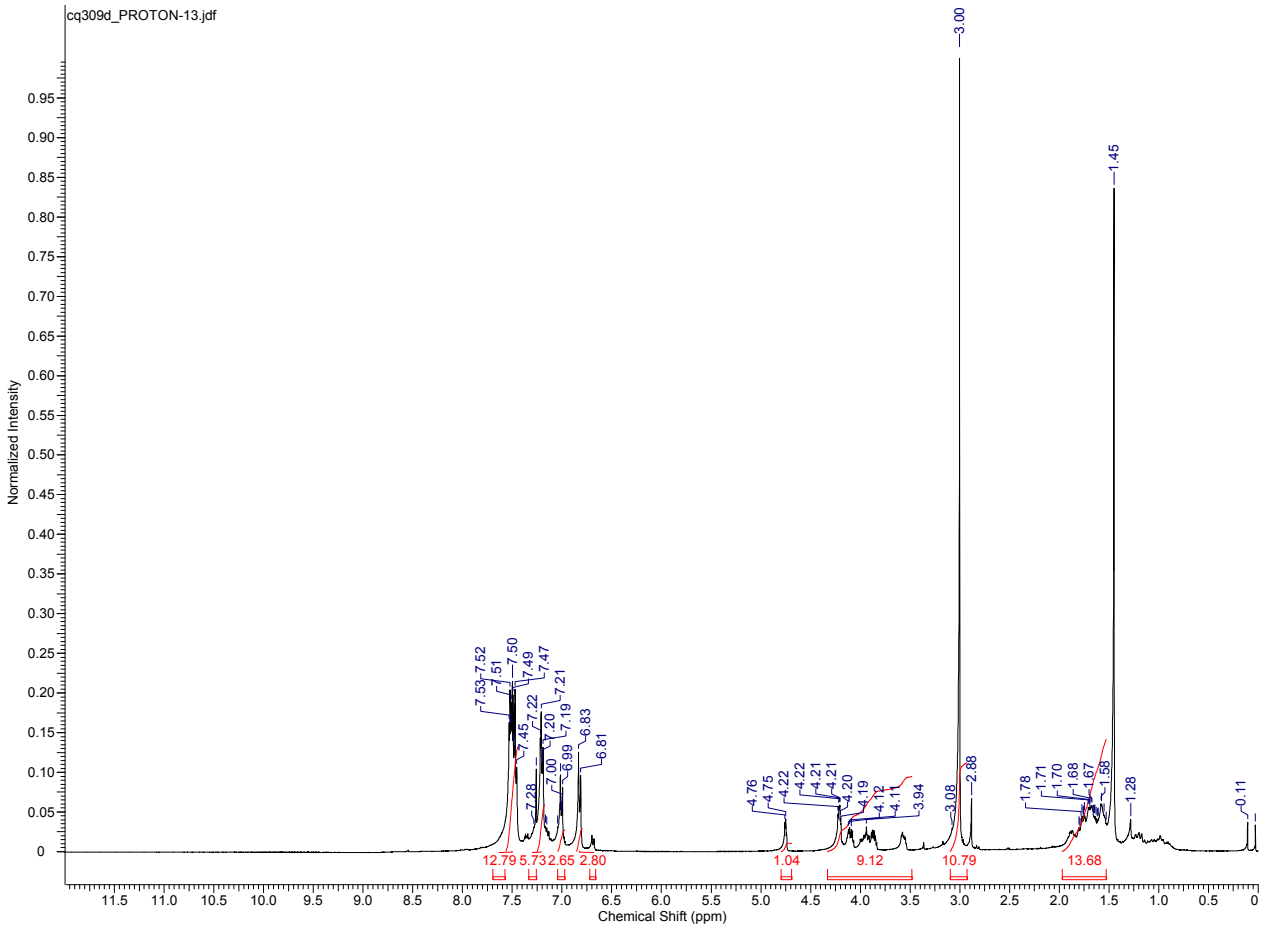


Figure S 48 ^{1}H NMR of **19** in $CDCl_3$

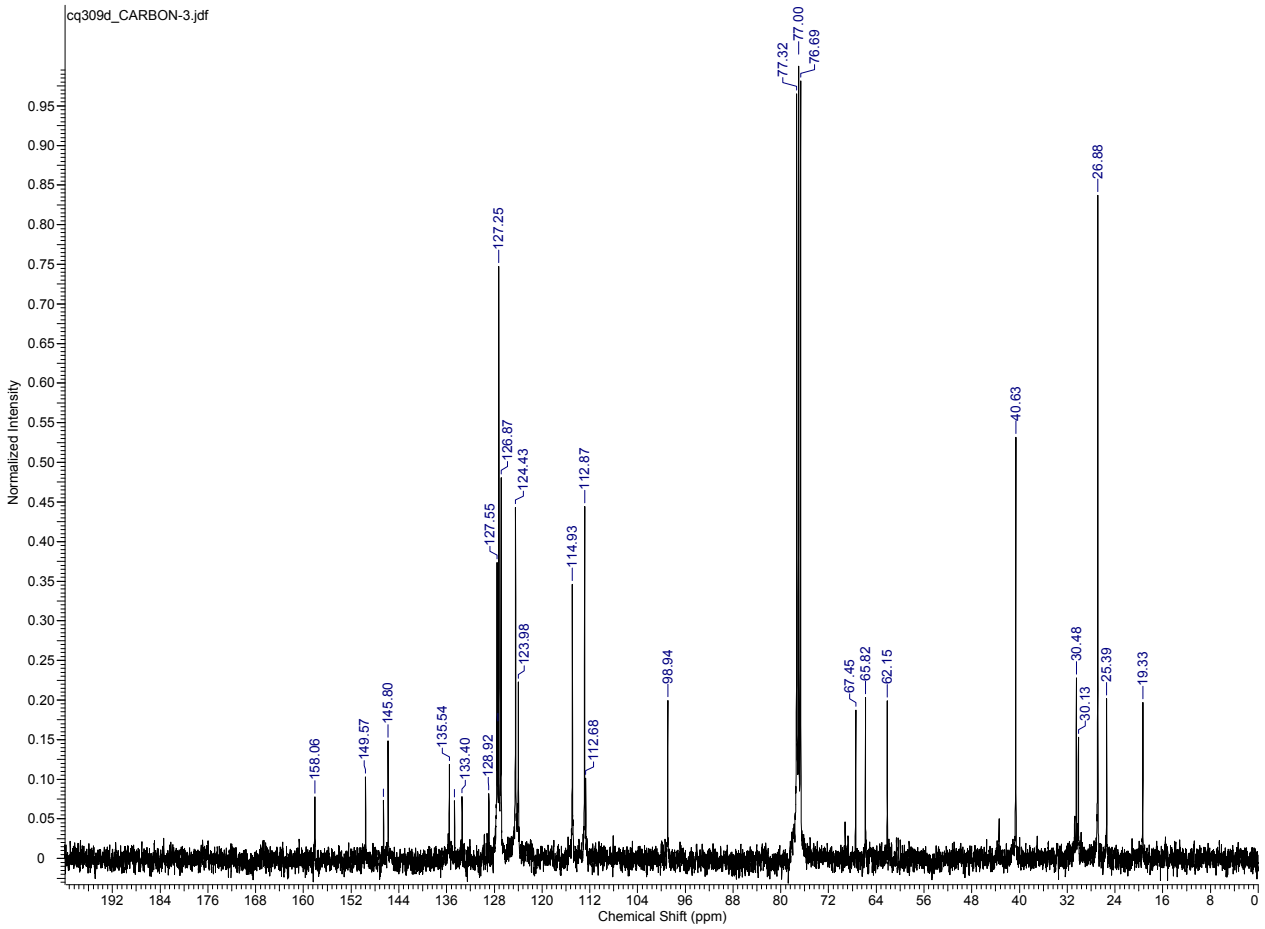


Figure S 49 ^{13}C NMR of **19** in $CDCl_3$

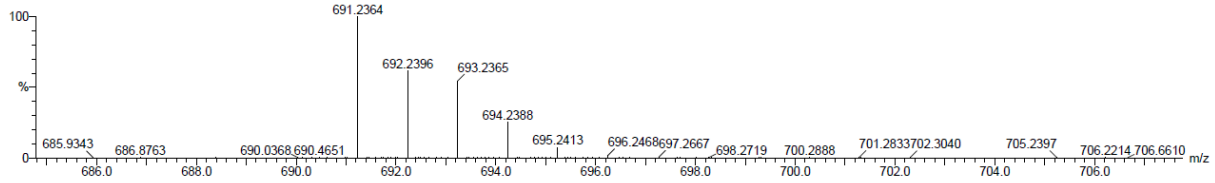
HRMS characterizations

Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Odd Electron Ions
860 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 1-100 H: 1-150 N: 0-10 O: 0-10 Cl: 1-1

05-Nov-2012 12:50:24 CH3CN+CH2Cl2 LCT Premier XE KE483
PPSM_CQ348A 23 (0.608) Cm (19:28) 1: TOF MS ES+
9.56e+003



Minimum:				-1.5			
Maximum:		5.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
691.2364	691.2390	-2.6	-3.8	32.0	552.4	0.1	C47 H34 N3 O Cl
	691.2350	1.4	2.0	28.0	555.5	3.2	C42 H34 N5 O3 Cl
	691.2337	2.7	3.9	23.0	556.9	4.6	C41 H38 N O7 Cl
	691.2369	-0.5	-0.7	15.0	561.4	9.0	C30 H38 N7 O10 Cl

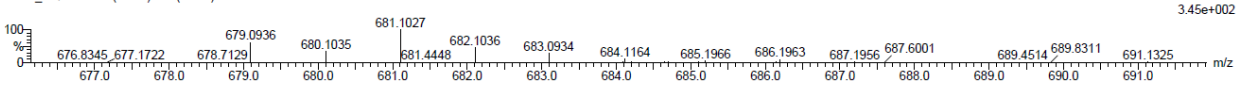
Figure S 50 HRMS of **1**

Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
741 formula(e) evaluated with 4 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-150 H: 0-130 N: 0-10 O: 0-10 Cl: 1-1 Br: 1-1

QUINTON CH2Cl2+ACN 07-May-2012 2::3::2
PPSM_CQ-314A 29 (0.754) Cm (29:32) 1: TOF MS ES+
3.45e+002

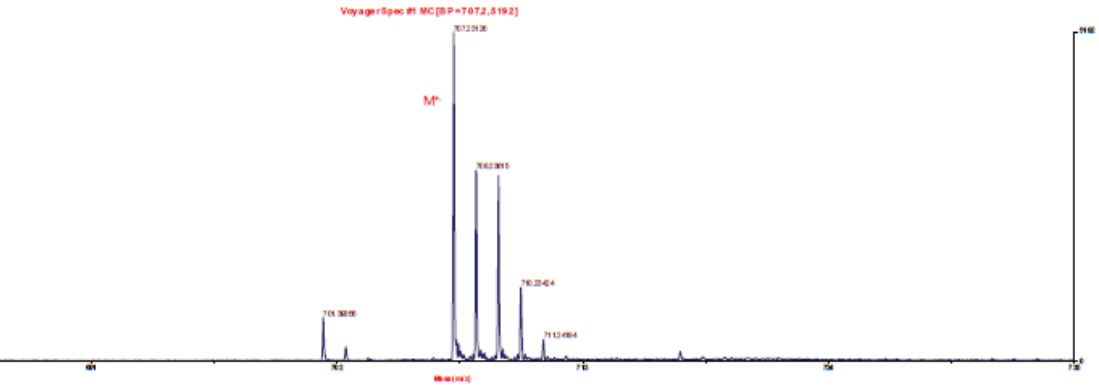


Minimum:				-1.5			
Maximum:		5.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
680.1035	680.1064	-2.9	-4.3	23.5	81.2	1.5	C35 H28 N5 O3 Cl Br
	680.1051	-1.6	-2.4	18.5	81.1	1.4	C34 H32 N O7 Cl Br
	680.1024	1.1	1.6	19.5	81.0	1.3	C30 H28 N7 O5 Cl Br
	680.1010	2.5	3.7	14.5	81.1	1.4	C29 H32 N3 O9 Cl Br

Figure S 51 HRMS of **2**

80-735

n positif



File Name: CQ321A-HRMS_+_0001

Trace: Voyager Spec #1 MC[BP = 707.2, 5192]

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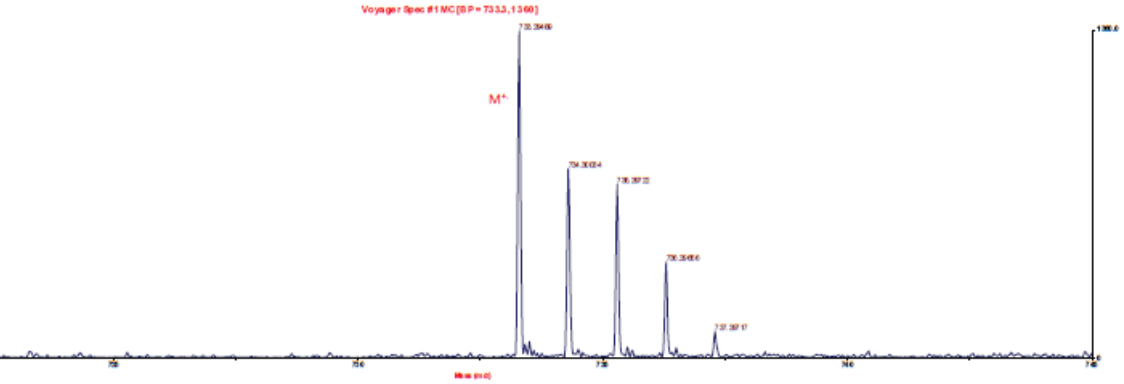
1	707.23126	707.22938	1.87590	2.65245	28.00	C42 H34 N5 O4 Cl	0.99122

Figure S 52 HRMS of **3**

z 720-745

tron positif



File Name: CQ323C-HRMS_+_0001

Trace: Voyager Spec #1 MC[BP = 733.3, 1360]

Index	Input m/z	Mass	Error (mDa)	Error (ppm)	DBE	Formula	Score
1	733.29489	733.29265	2.23692	3.05050	28.00	C44 H40 N7 O2 Cl	0.99346

Figure S 53 HRMS of **4**