Supporting Information

Indium(III)-catalyzed Tandem Synthesis of 2-Alkynyl-3,3-dichloropyrrolidines and their Conversion to 3-Chloropyrroles

Khushbu Kushwaha,[a] Chandi C. Malakar,[a] Sara Stas,[a] Filip Lemière[b] and Kourosch Abbaspour Tehrani[a]*

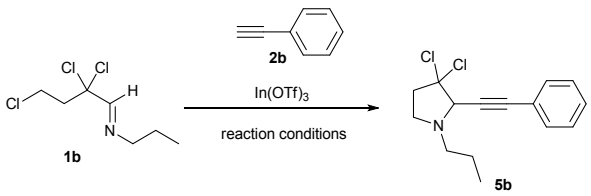
[a] *Organic Synthesis, Department of Chemistry, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium. Fax: (+32)32653233; phone: (+32)32653226.*

[b] *Biomolecular & Analytical Mass Spectrometry and Center for Proteomics, Department of Chemistry, University of Antwerp, B-2020 Antwerp, Belgium.*

E-mail: kourosch.abbaspourtehrani@uantwerpen.be

Table of Contents

1. Optimization of the Reaction Conditions for the Synthesis of 5b using $In(OTf)_3$[a]



Entry	Catalyst/[mol%]	**2b** [equiv]	Solvent	*t* [°C]	Yield **5b** [%]
1	$In(OTf)_3$/25	1.0	DCM	50	60[b]
2	$In(OTf)_3$/25	1.0	DCE	70	5[c]
3	$In(OTf)_3$/25	1.0	DCM/HFIP	rt	0
4	$In(OTf)_3$/25	1.0	THF	70	SM
5	$In(OTf)_3$/40	1.0	DCM	50	64[b]
6	$In(OTf)_3$/10	1.0	DCM	50	34[b]
7	$In(OTf)_3$/25	1.5	DCM	50	74[d]
8	**$In(OTf)_3$/25**	**2.0**	**DCM**	**50**	**80**[d]
9	$In(OTf)_3$/25	2.5	DCM	50	81[d]

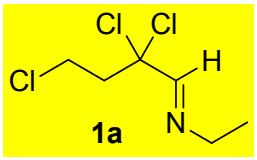
[a]All reactions were performed using 0.5 mmol **1b** in DCM (4 mL) in a sealed vial under air for 18h, unless otherwise stated. [b]Yield after chromatography using a short column of silica gel.[c]Yield calculated from ^{1}H NMR. [d] Isolated yield after basic workup.

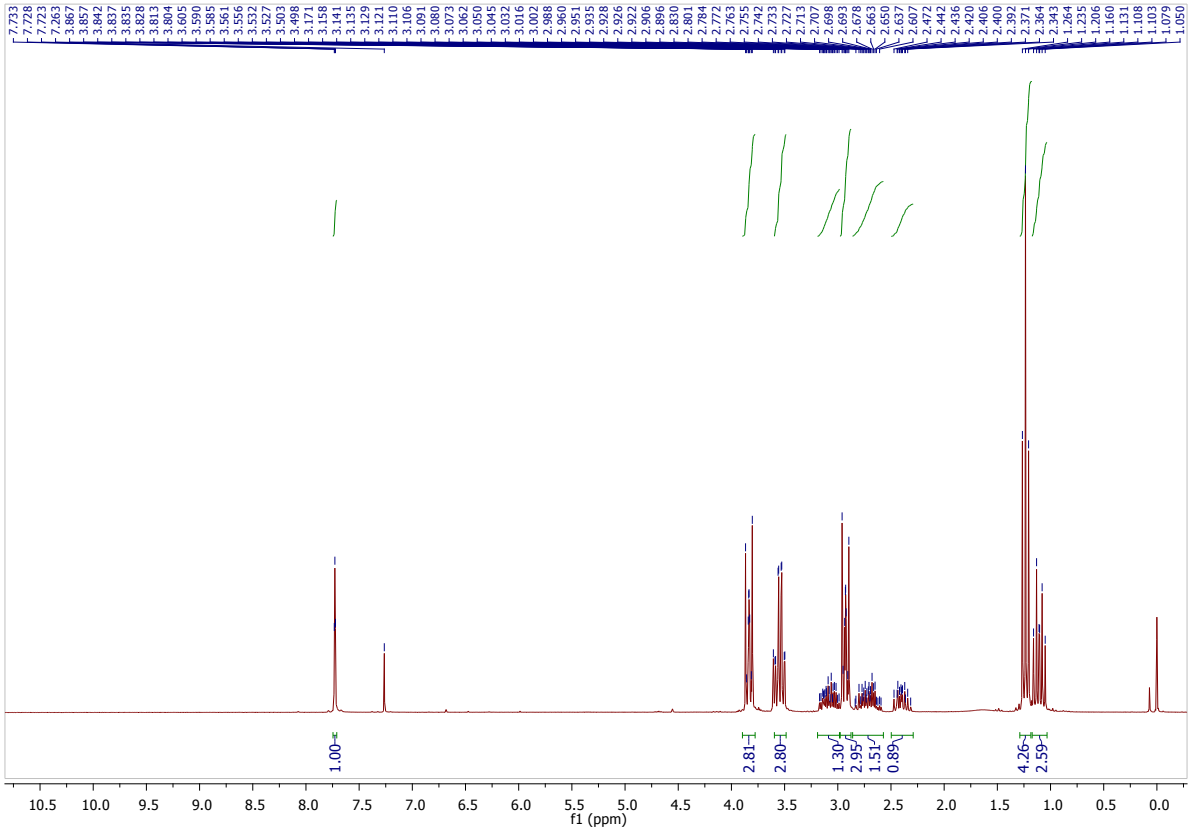
First of all, we tried to isolate the product **5b**, obtained under the optimized reaction conditions, by means of column chromatography on silica gel, which resulted in a reasonably good yield of 60% (entry 1). The more convenient acid base workup yielded a more complex mixture and required still further column chromatography which reduced the yield even more. Replacing dichloromethane with 1,2-dichloroethane as solvent and heating the reaction mixture at 70 °C resulted in a complex mixture and yielded **5b** only in 5% yield (entry 2). Since there have been precedents[1] that the use of fluorinated solvents can result in extraordinary effects on the efficiency, regioselectivity and stereoselectivity of several chemical reactions, we also used hexafluoroisopropanol (HFIP) as co-solvent. This reaction gave a complex mixture with multiple unidentifiable side products. More polar solvents such as THF did not result in any reaction and only starting materials were recovered (entries 3 and 4). An increase in the amount of $In(OTf)_3$ from 25 mol% to 40 mol%, did not show a relevant improvement and product **5b** was isolated in 64% yield. Decreasing the amount of $In(OTf)_3$ to 10 mol% decreased the yield to 34% (entries 5 and 6). When the reaction was conducted with an excess of phenylacetylene (**2b**) (1.5 equiv) a 74% yield was obtained

(entry 7). Further improvement in the reaction was made by using 2 equivalents of phenylacetylene which delivered the product **5b** in 80% yield (entry 8). Under this condition the crude reaction mixture was purer and the formation of hemiaminal side product **5b'** could be completely avoided as it was not observed in the ^{1}H NMR. With 2.5 equivalents of phenylacetylene 81% yield was obtained, which is not a substantial improvement compared to that from the previous reaction (entry 9).

1. Copies of ^{1}H and ^{13}C spectra of starting imines

N-(2,2,4-Trichloro-1-butylidene)ethylamine (1a)





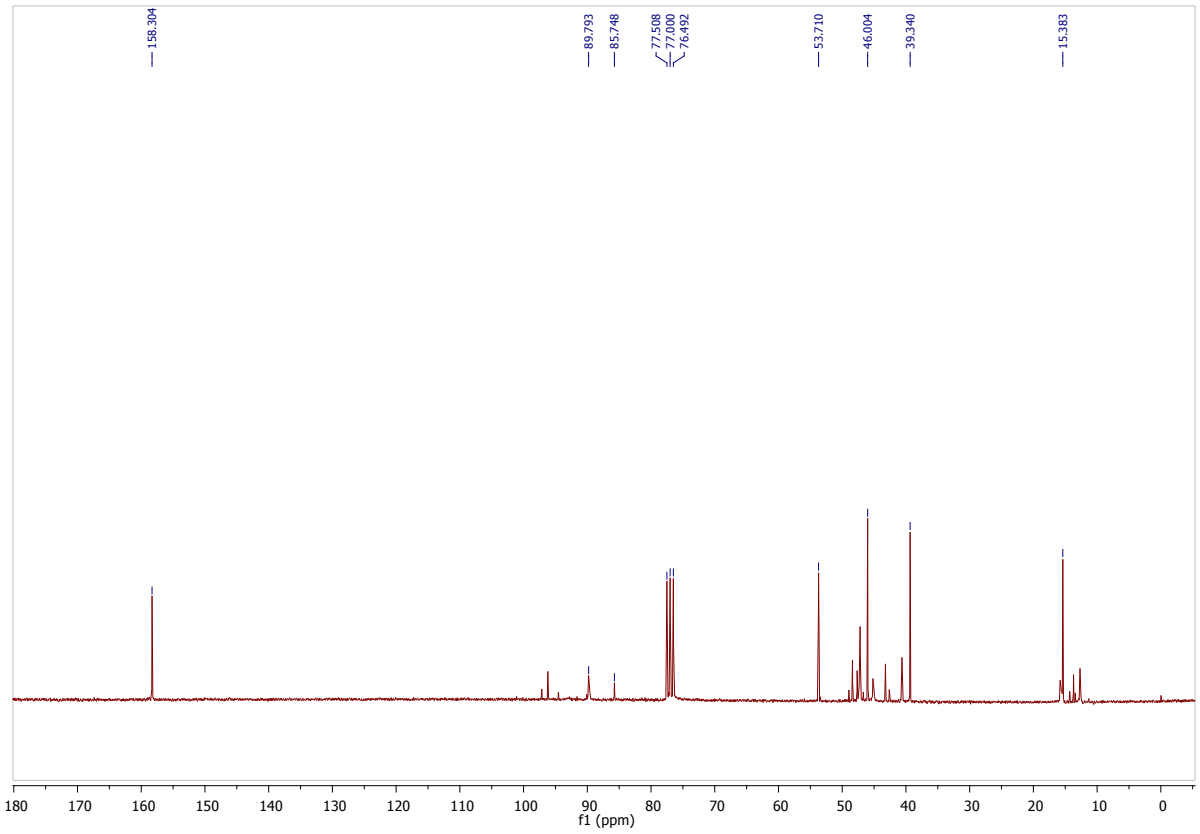
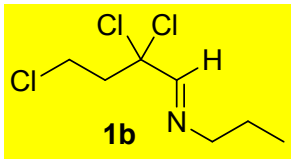


Figure 1. ^{1}H (250 MHz) and ^{13}C (62.90 MHz) NMR spectra of **1a** in $CDCl_3$.

N-(2,2,4-Trichlorobutylidene)propan-1-amine (1b)



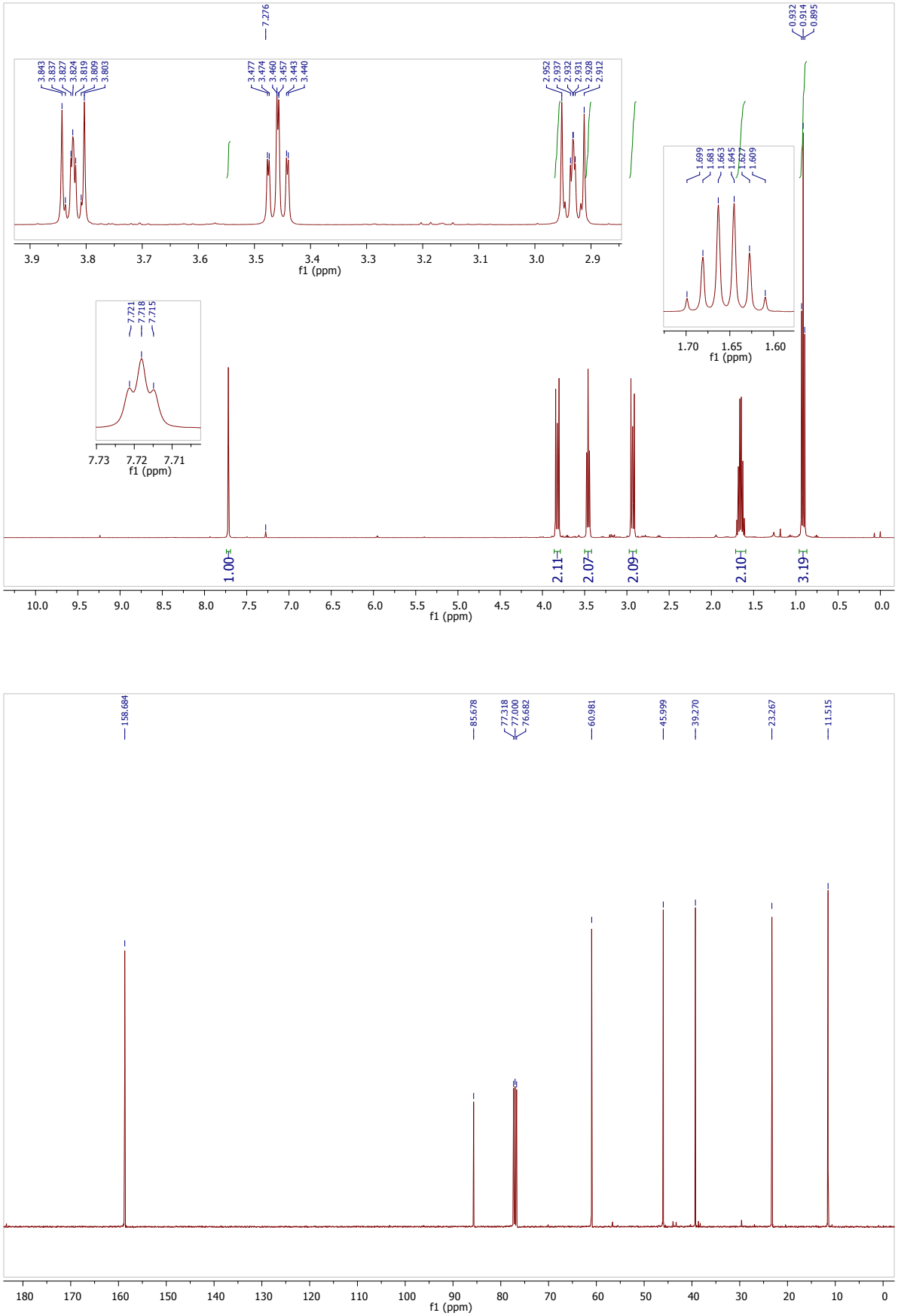
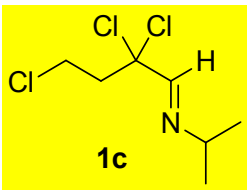
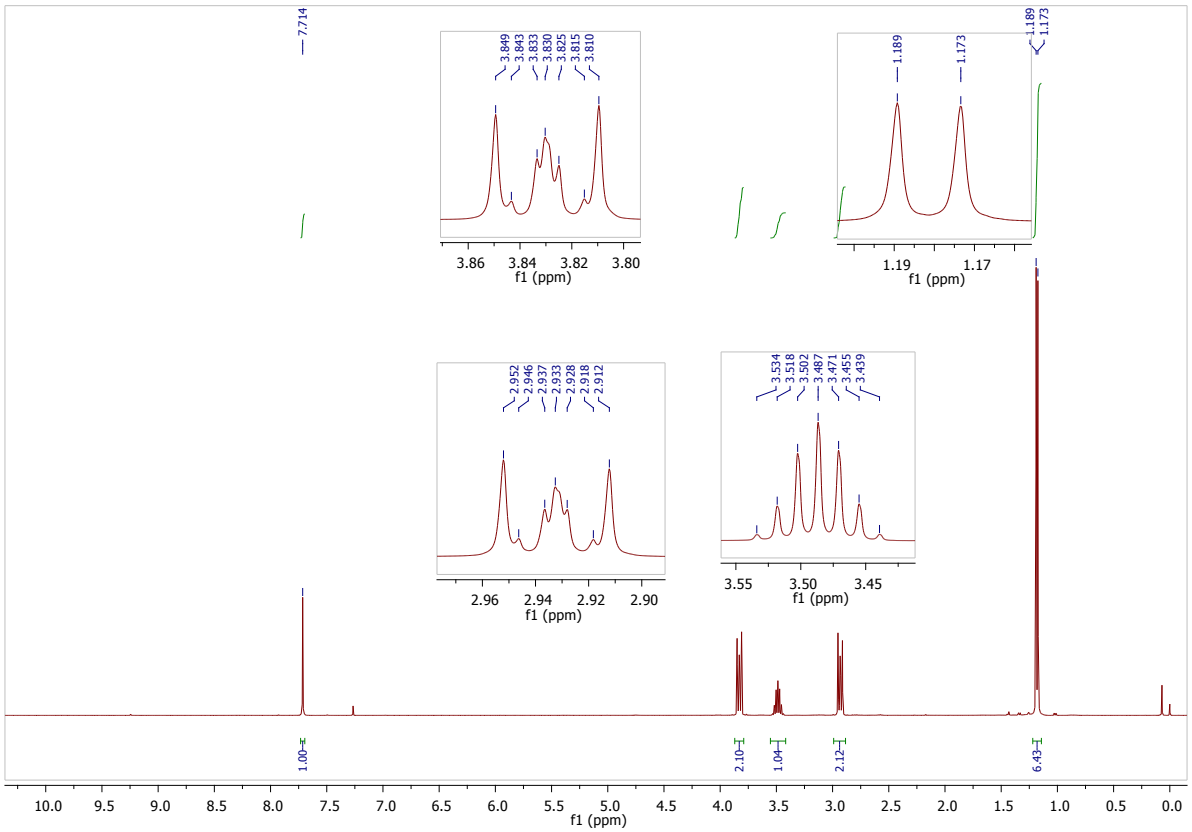


Figure 2. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **1b** in $CDCl_3$.

N-(2,2,4-Trichlorobutylidene)propan-2-amine (1c)





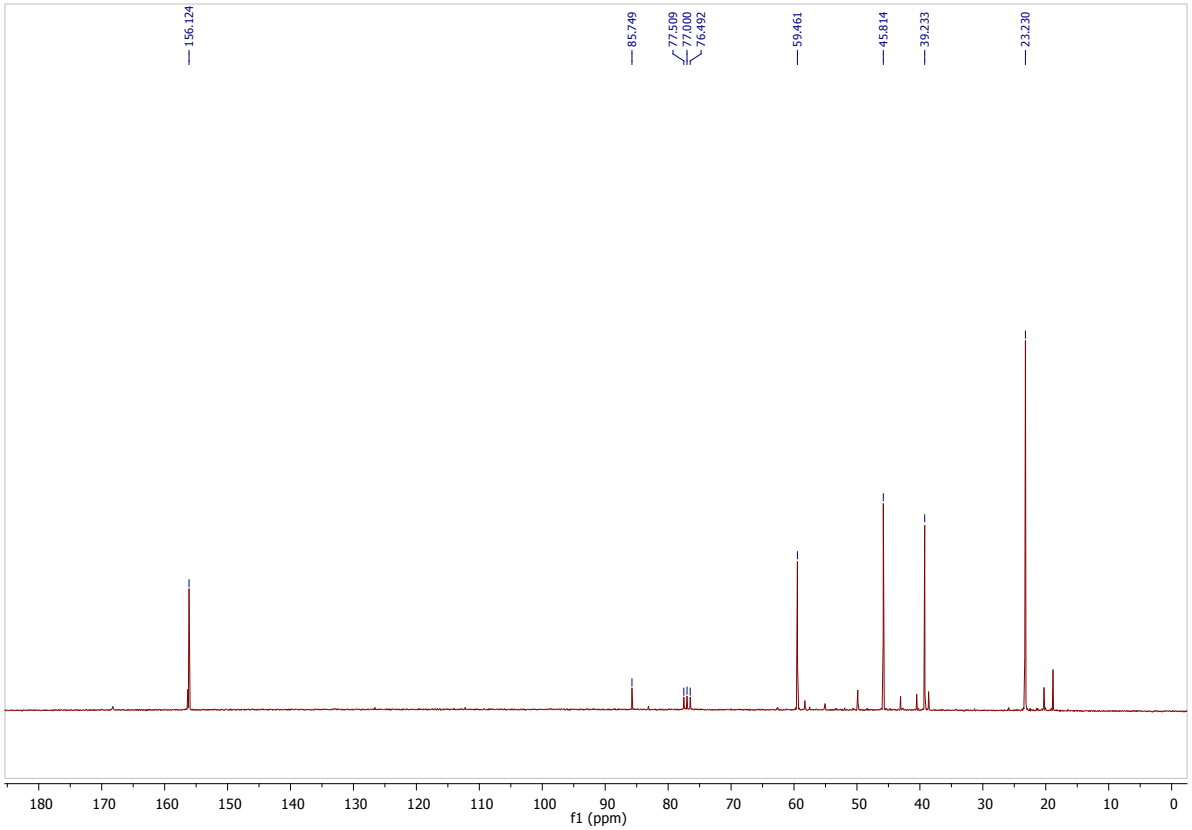
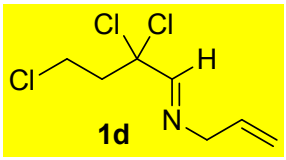


Figure 3. ^{1}H (400 MHz) and ^{13}C (62.90 MHz) NMR spectra of **1c** in $CDCl_3$.

_N_-(2,2,4-Trichlorobutylidene)prop-2-en-1-amine (1d)



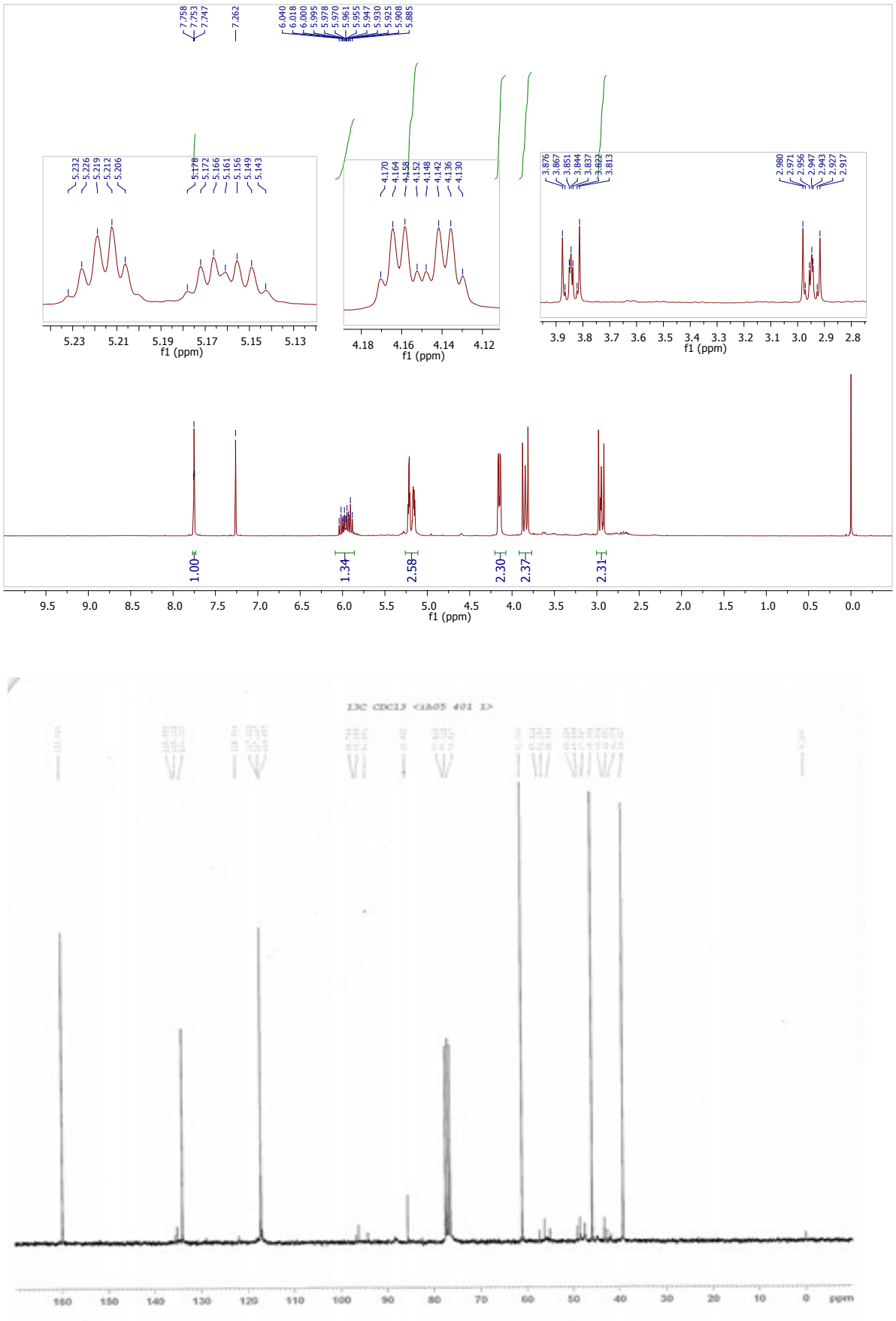
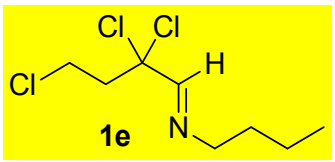
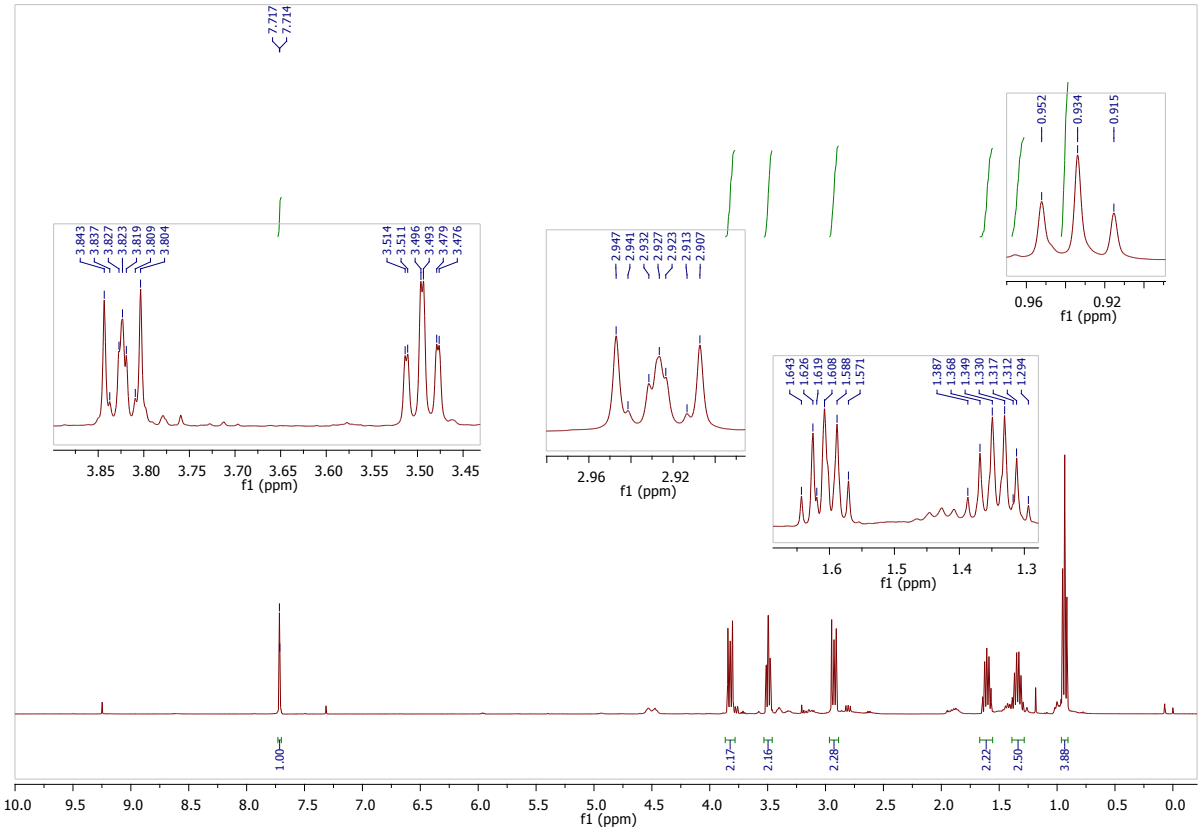


Figure 4. ^{1}H (250 MHz) and ^{13}C (62.90 MHz) NMR spectra of **1d** in $CDCl_3$.

N-(2,2,4-Trichlorobutylidene)butan-1-amine (1e)





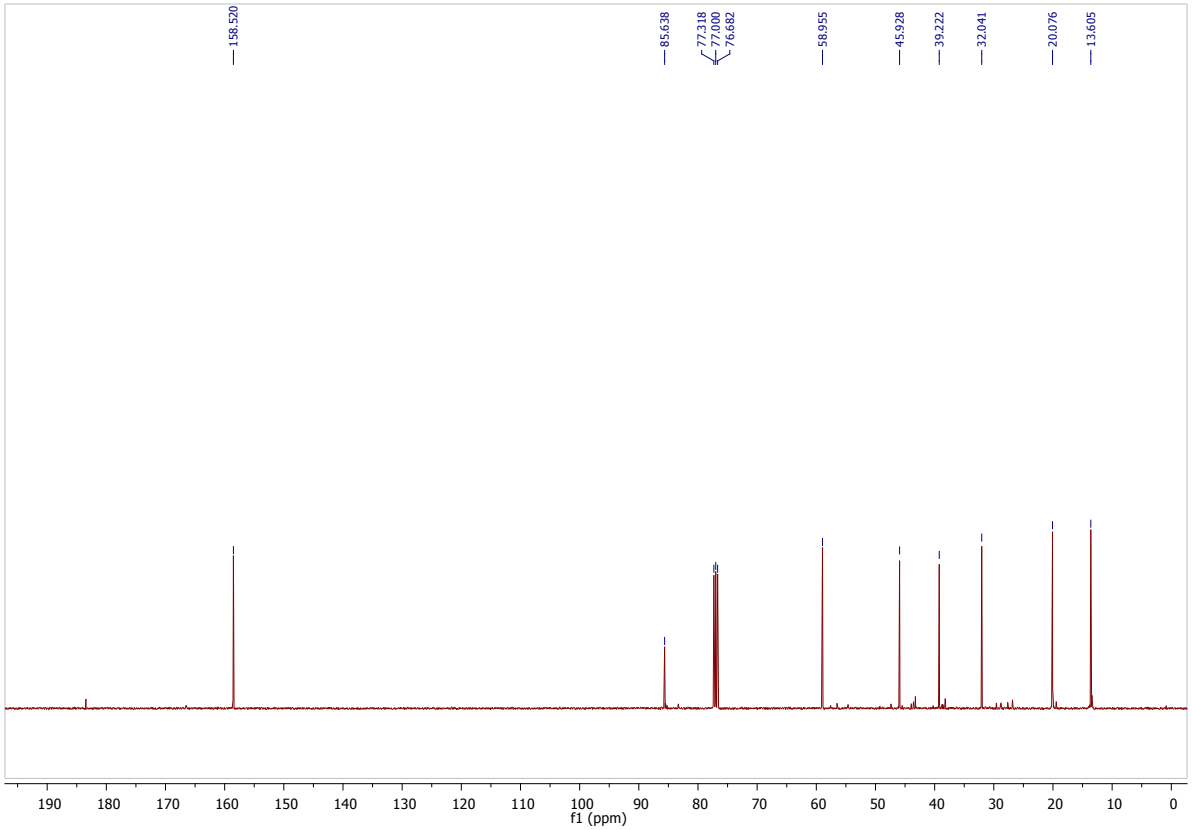
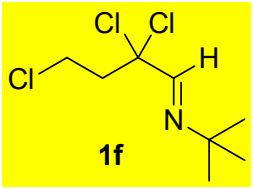


Figure 5. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **1e** in $CDCl_3$.

***N-tert*-Butyl-(2,2,4-trichloro-1-butylidene)amine (1f)**



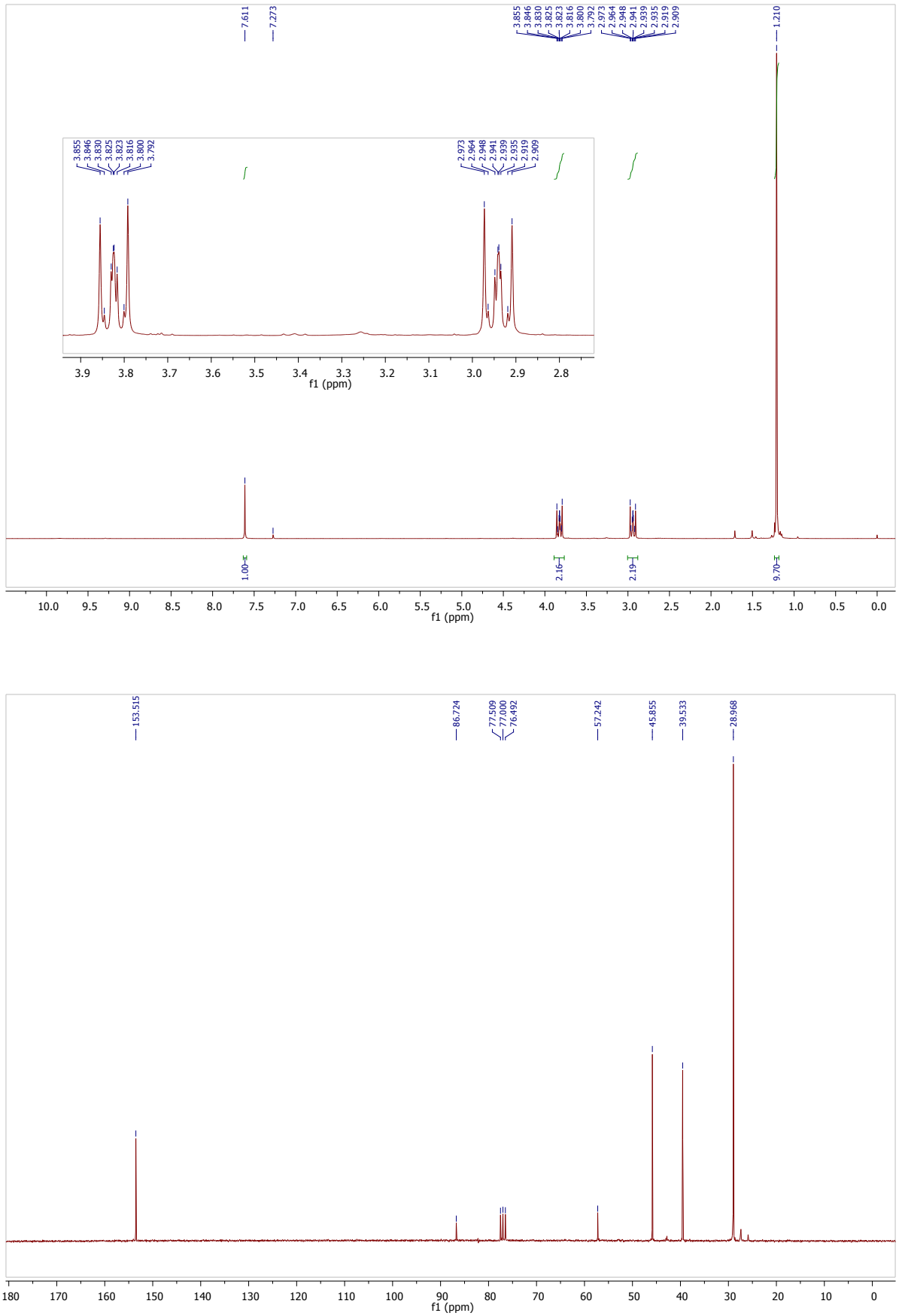
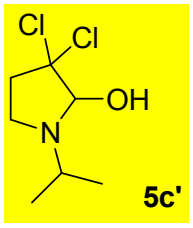
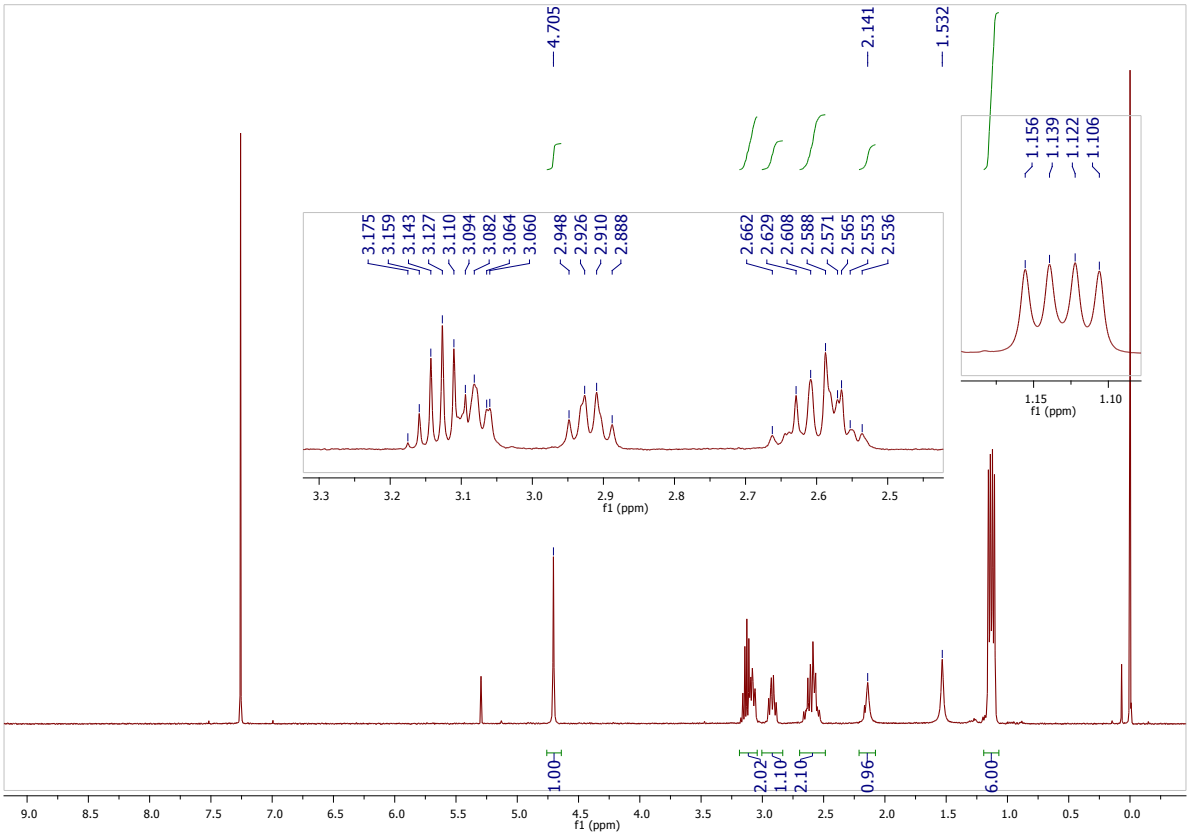


Figure 6. ^{1}H (250 MHz) and ^{13}C (62.90 MHz) NMR spectra of **1f** in $CDCl_3$.

2. Formation of side products

3,3-Dichloro-1-isopropylpyrrolidin-2-ol (5c')





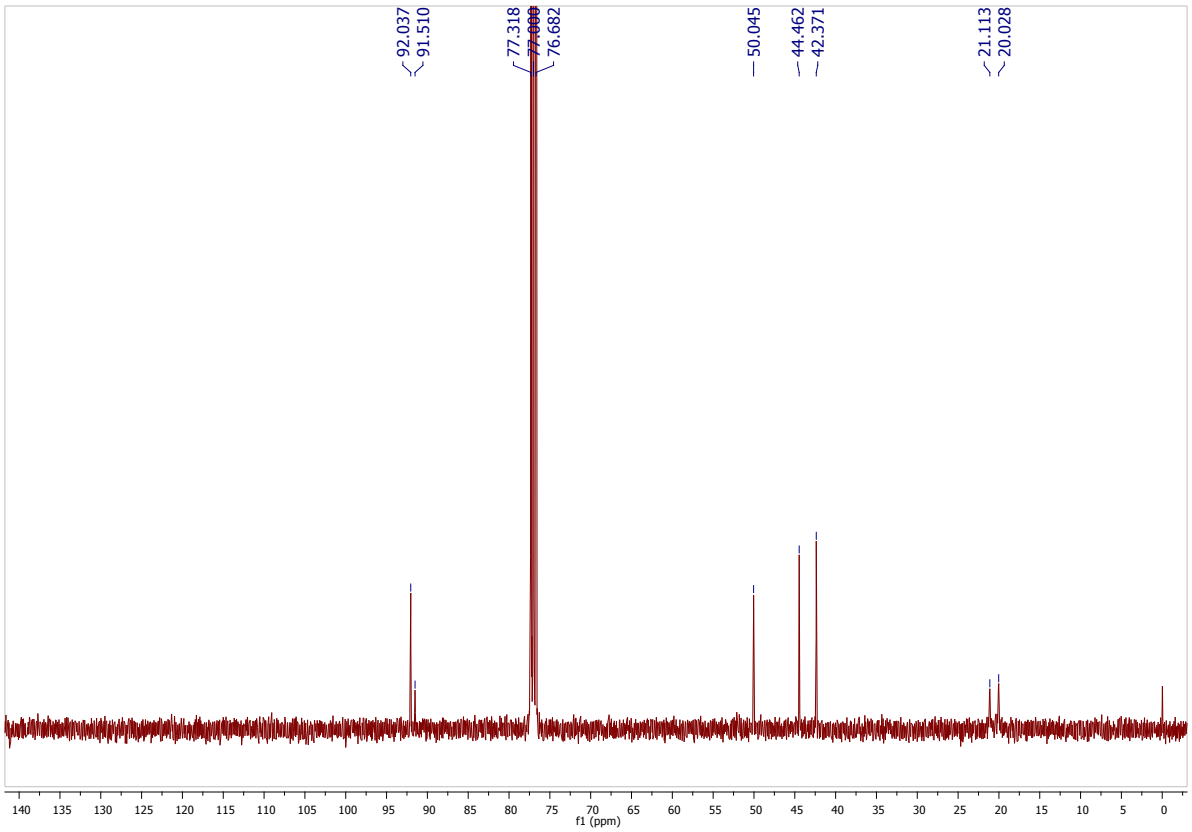
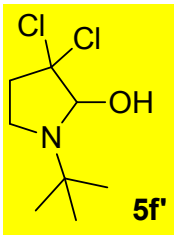


Figure 7. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **5c'** in $CDCl_3$.

1-*tert*-Butyl-3,3-dichloro-2-hydroxypyrrolidine (5f')



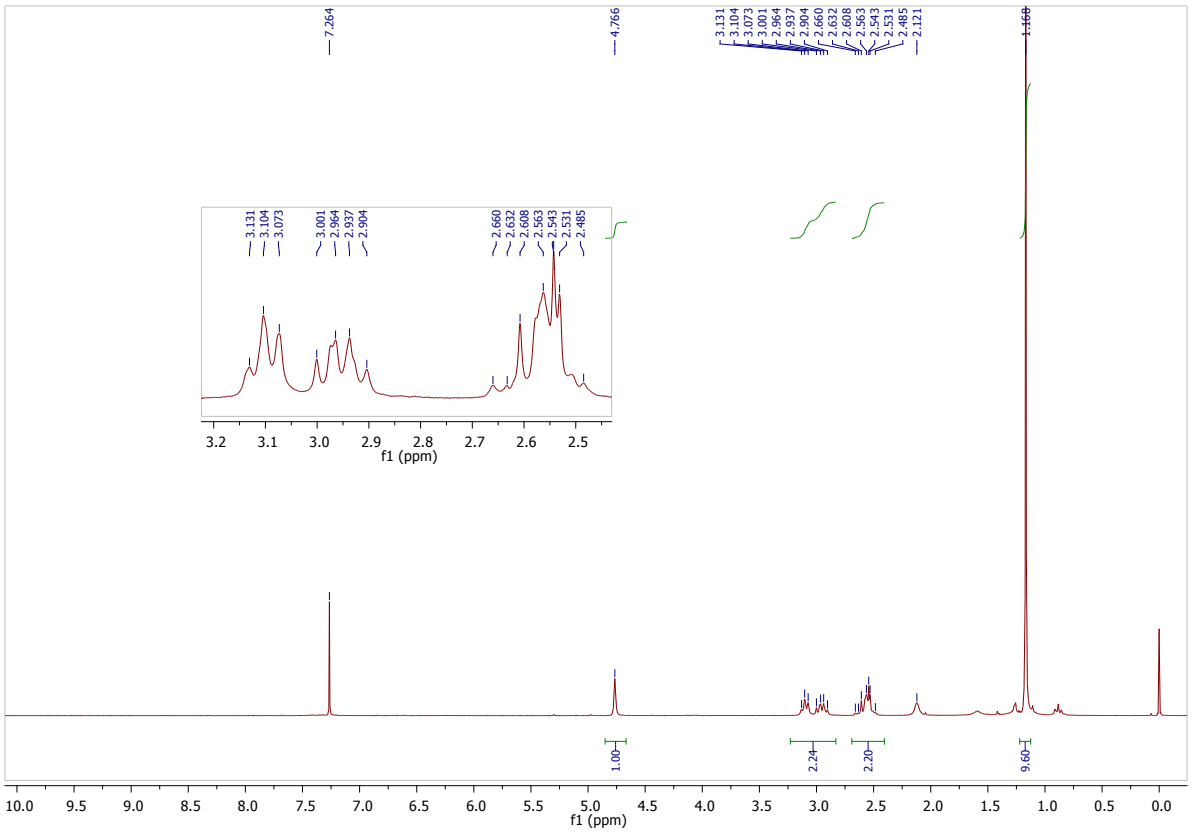
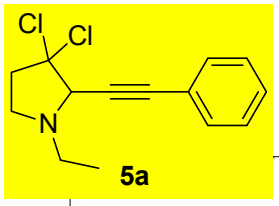
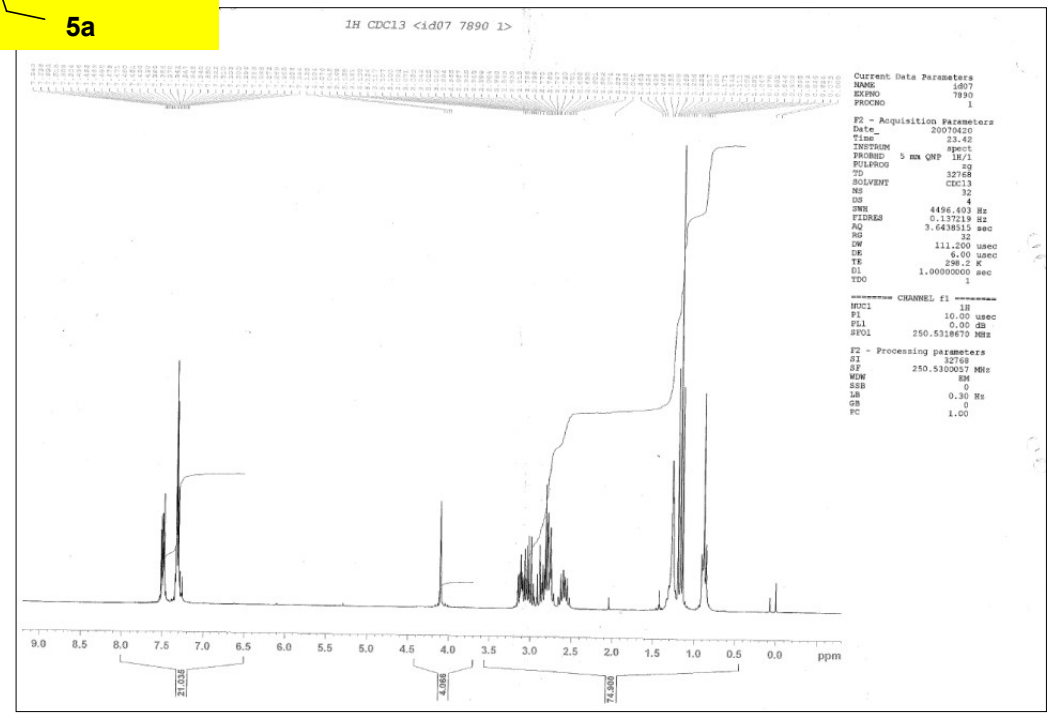


Figure 8. ^{1}H (400 MHz) NMR spectrum of **5f'** in $CDCl_3$.

3. Copies of ^{1}H and ^{13}C spectra of 2-alkynylpyrrolidines 5a-q

3,3-Dichloro-1-ethyl-2-(phenylethynyl)pyrrolidine (5a)





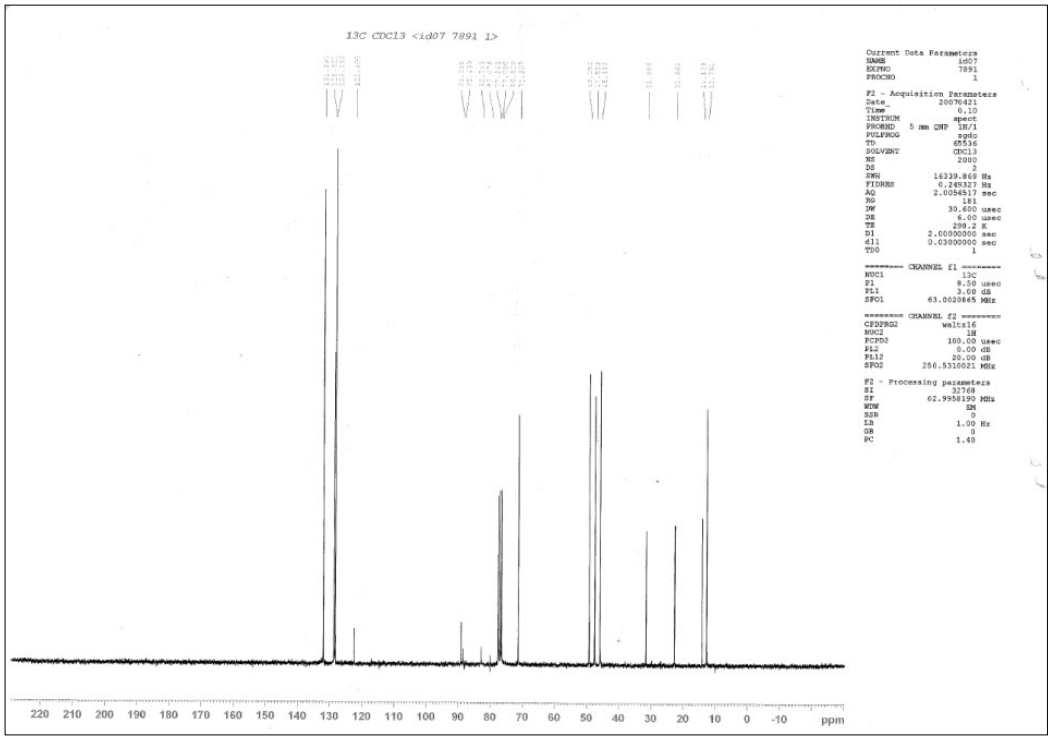
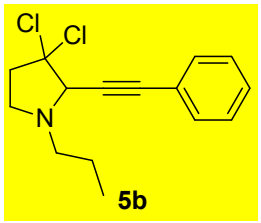


Figure 9. ^{1}H (250 MHz) and ^{13}C (63 MHz) NMR spectra of **5a** in $CDCl_3$.

3,3-Dichloro-1-propyl-2-(phenylethynyl)pyrrolidine (5b)



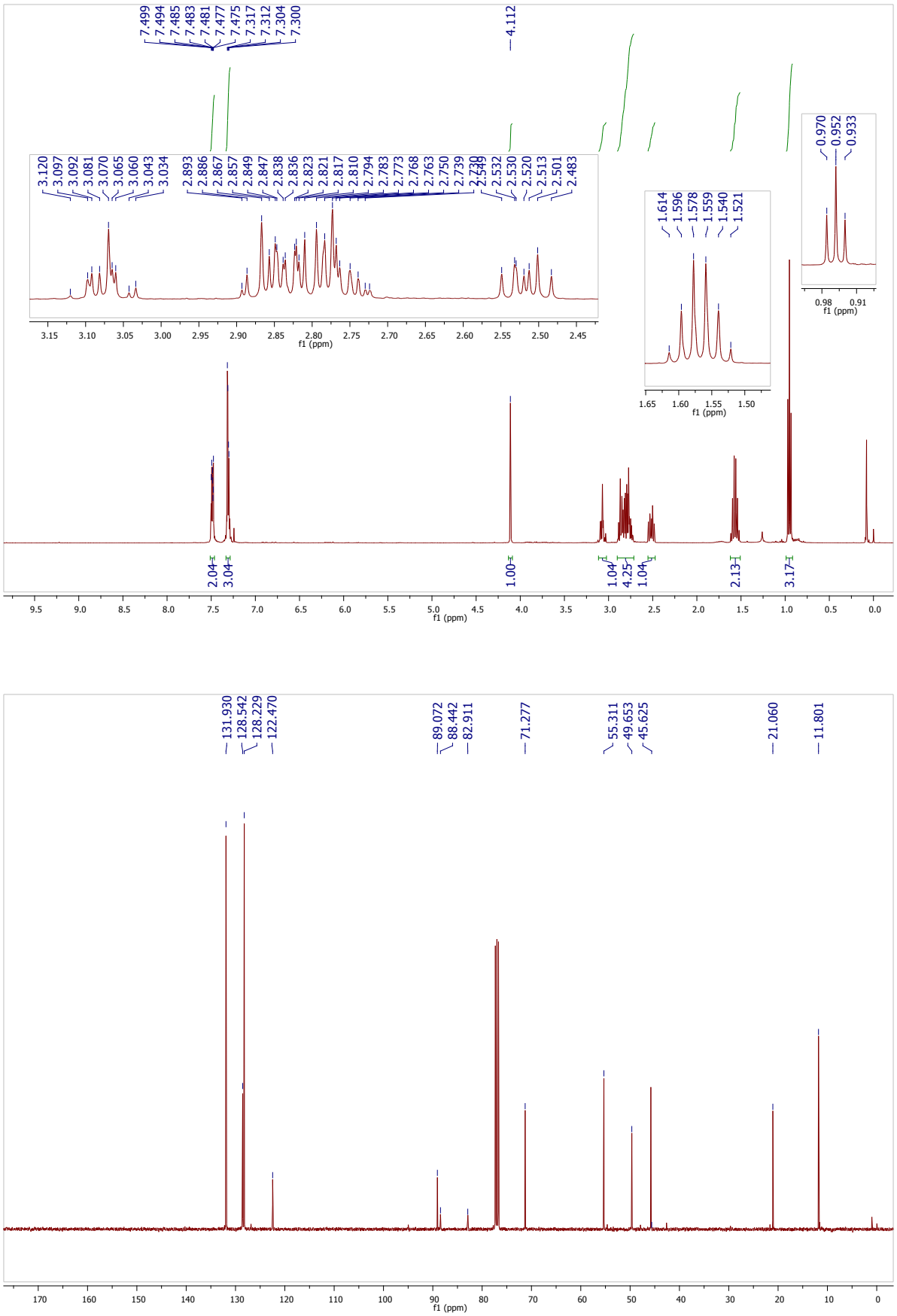
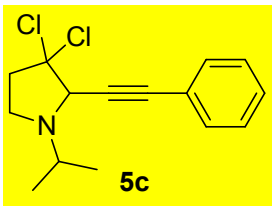
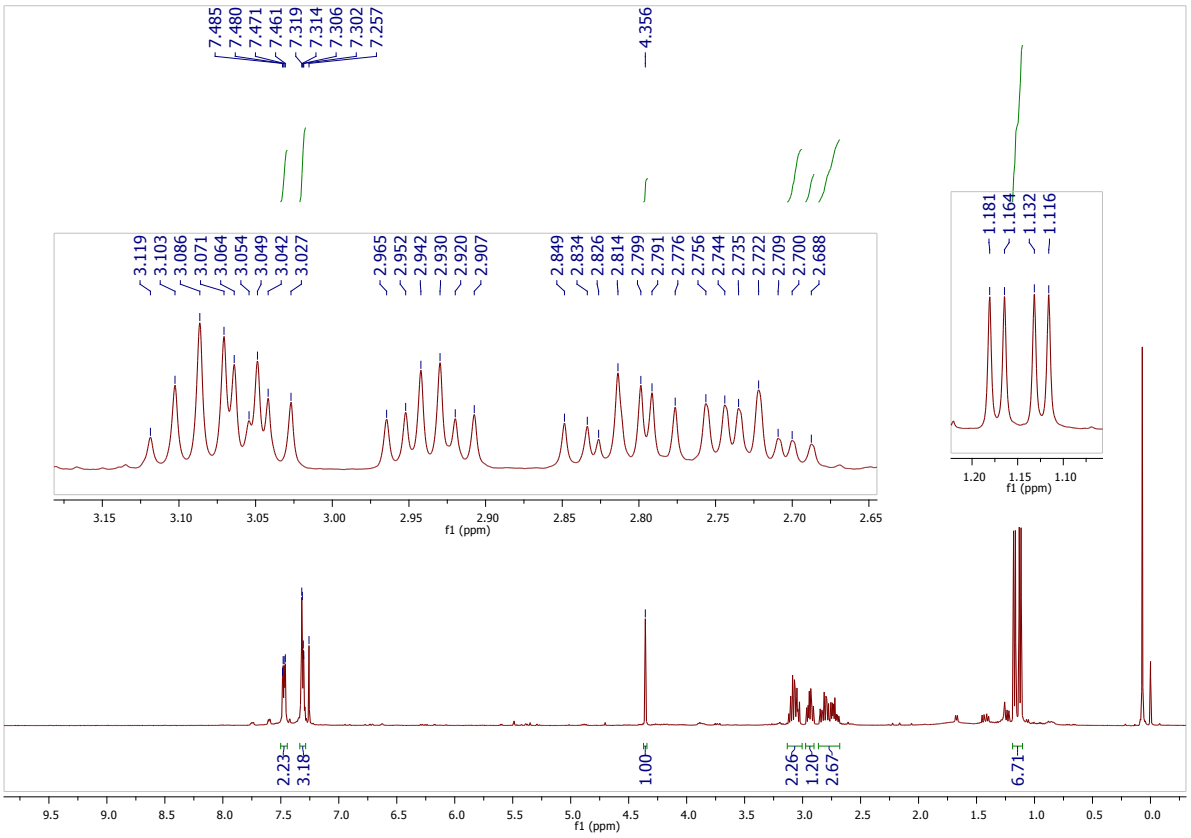


Figure 10. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **5b** in $CDCl_3$.

3,3-Dichloro-1-isopropyl-2-(phenylethynyl)pyrrolidine (5c)





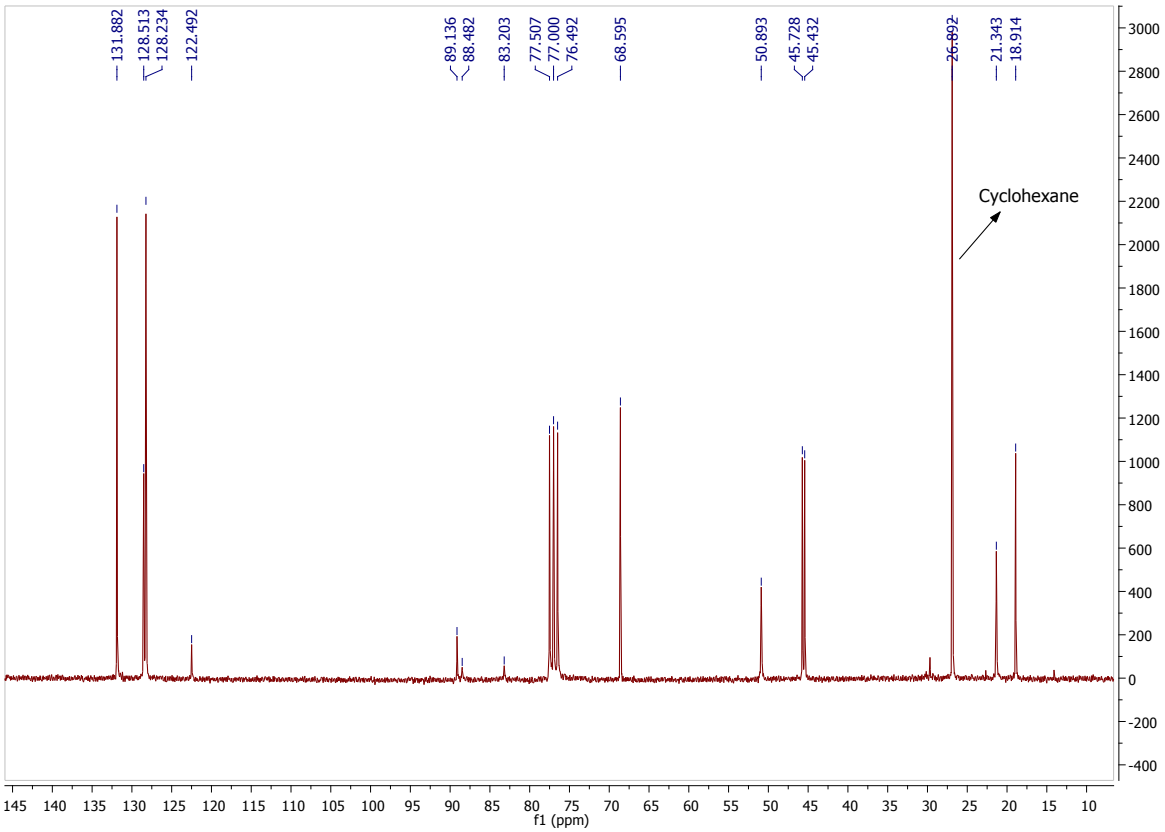
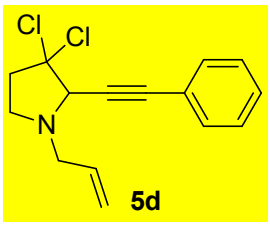


Figure 11. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **5c** in $CDCl_3$.

1-Allyl-3,3-dichloro-2-(phenylethynyl)pyrrolidine (5d)



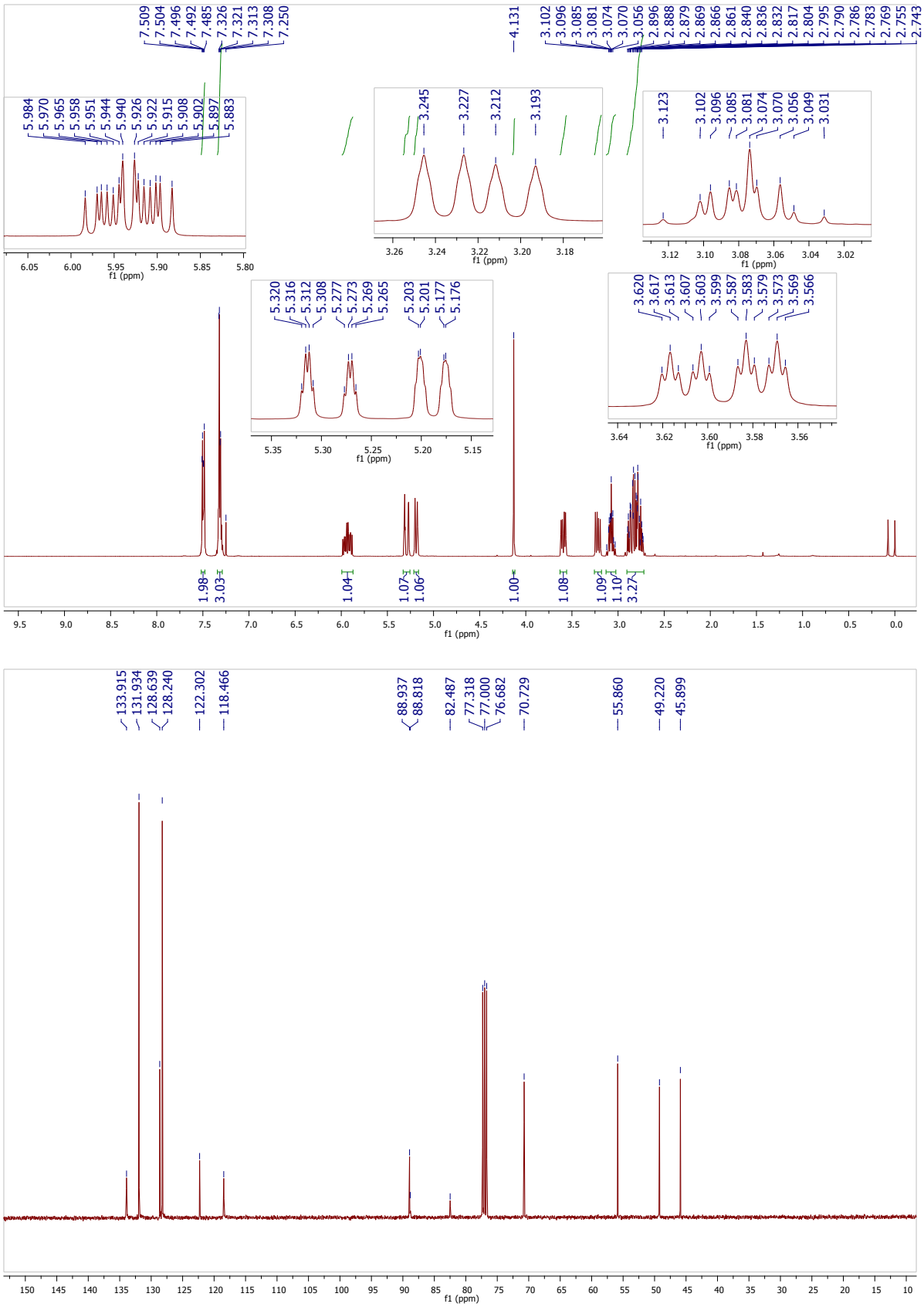
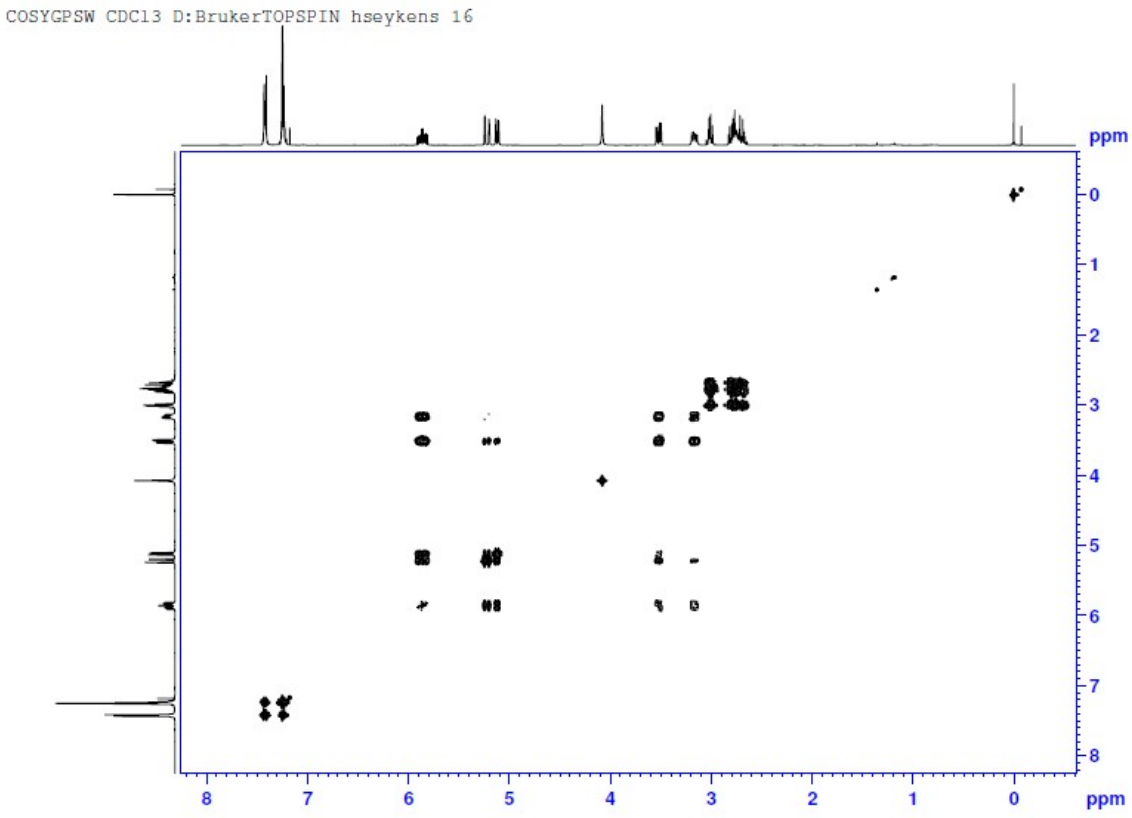
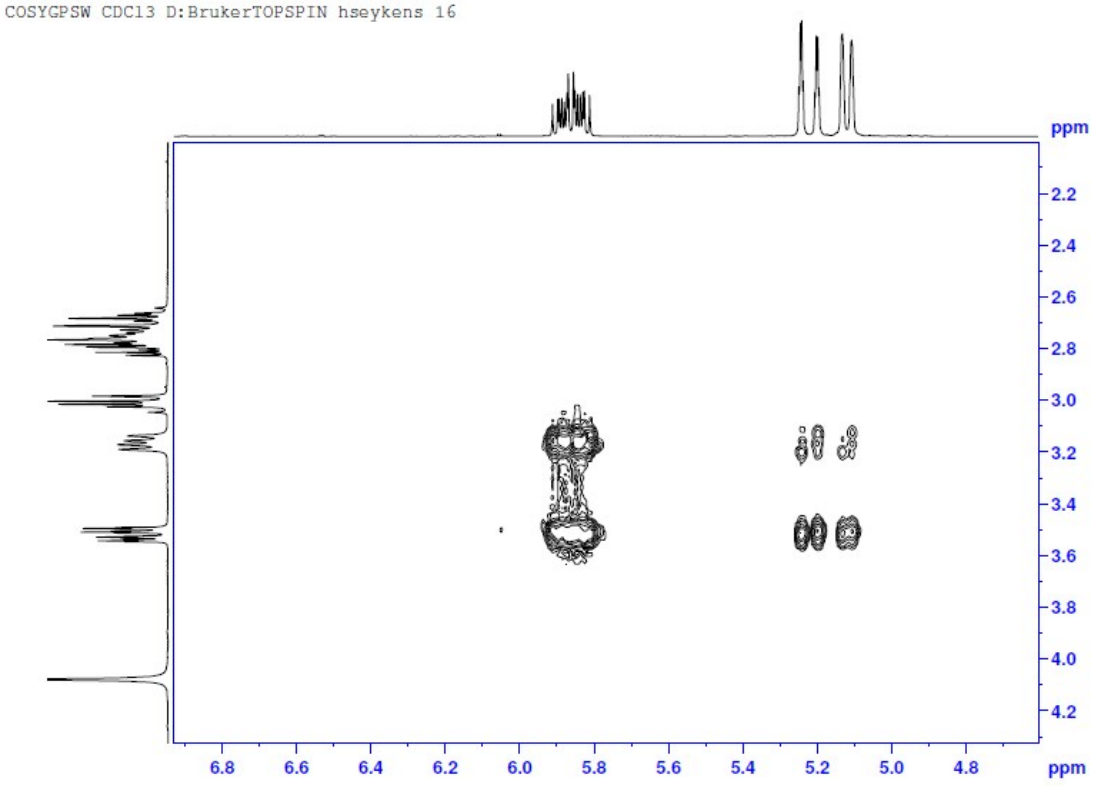
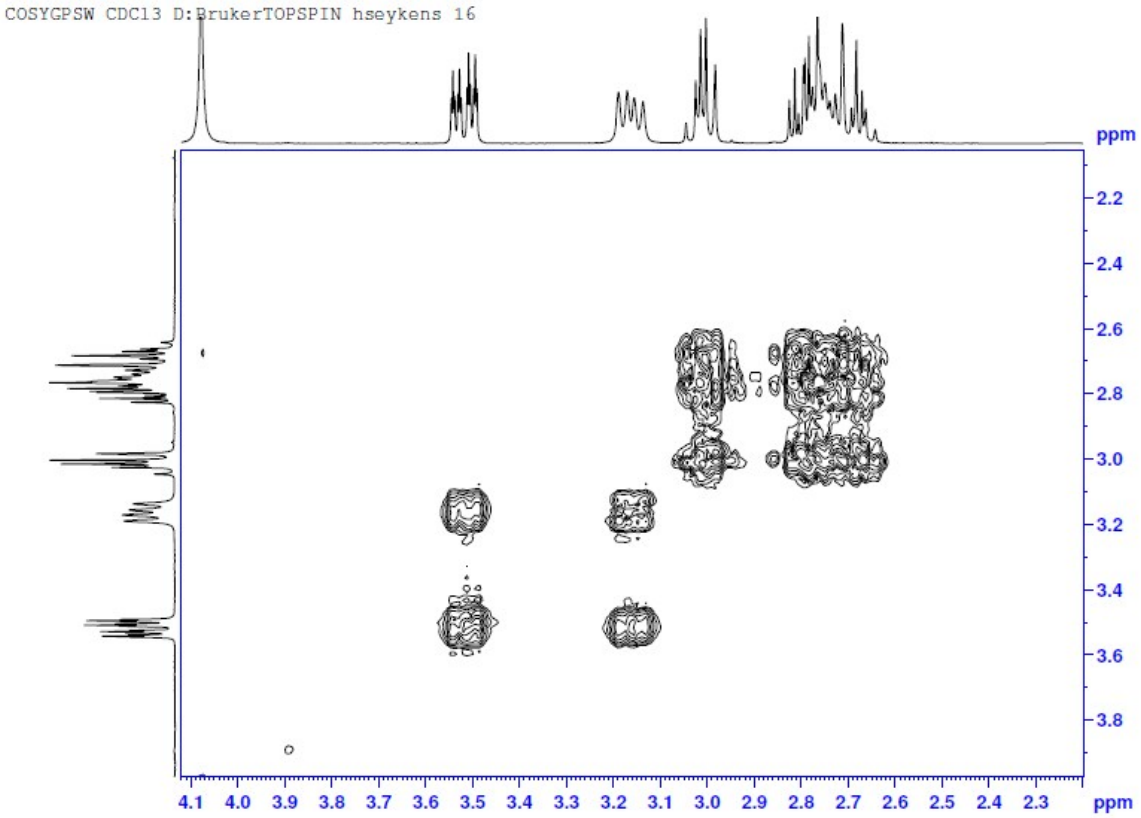
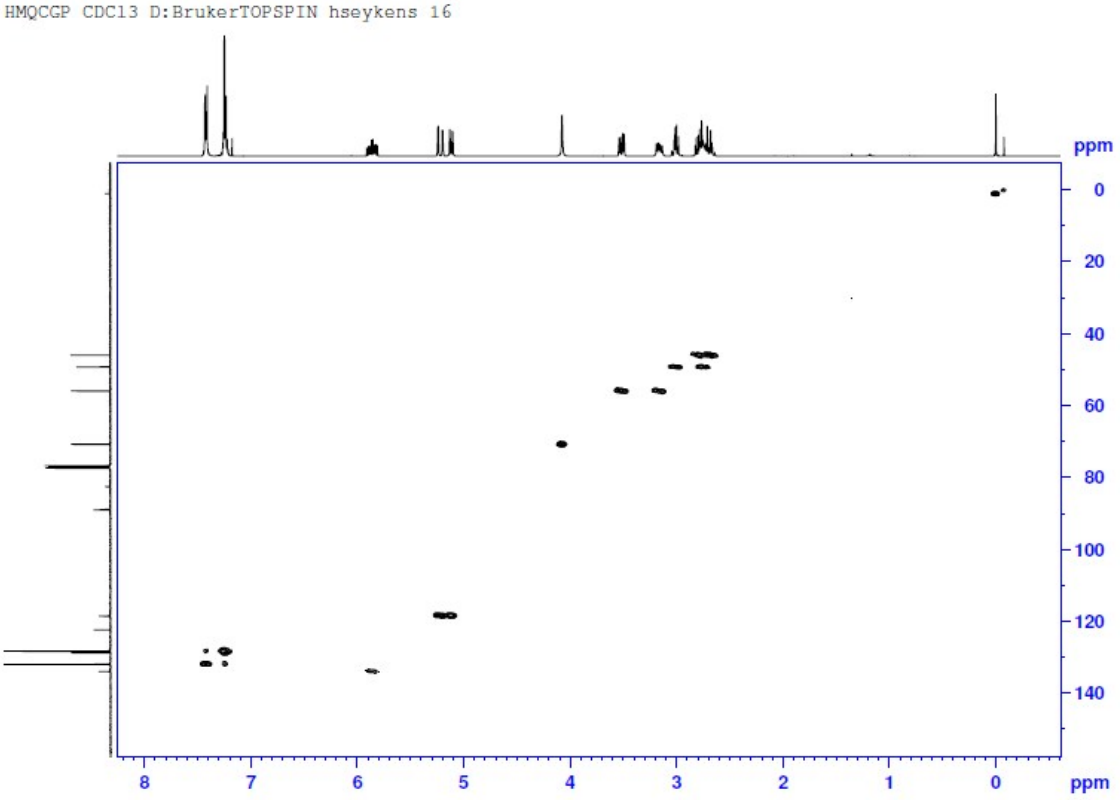


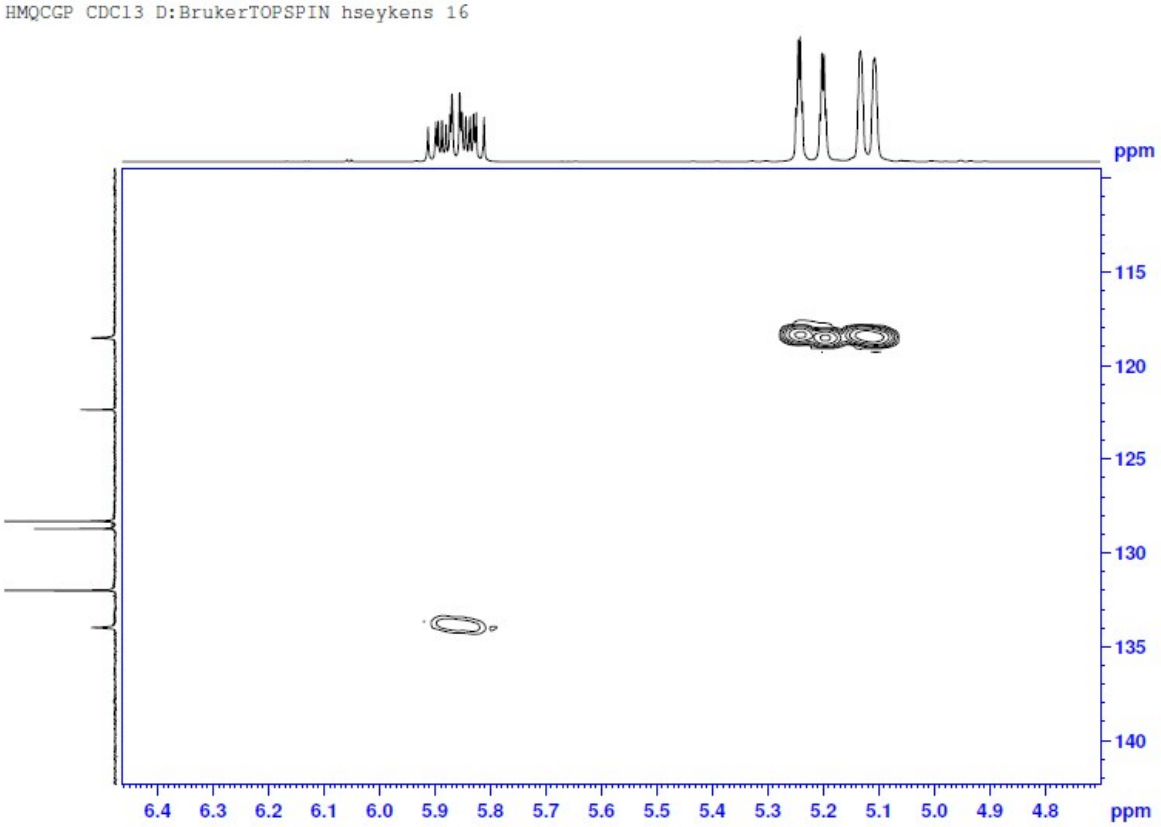
Figure 12. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **5d** in $CDCl_3$.

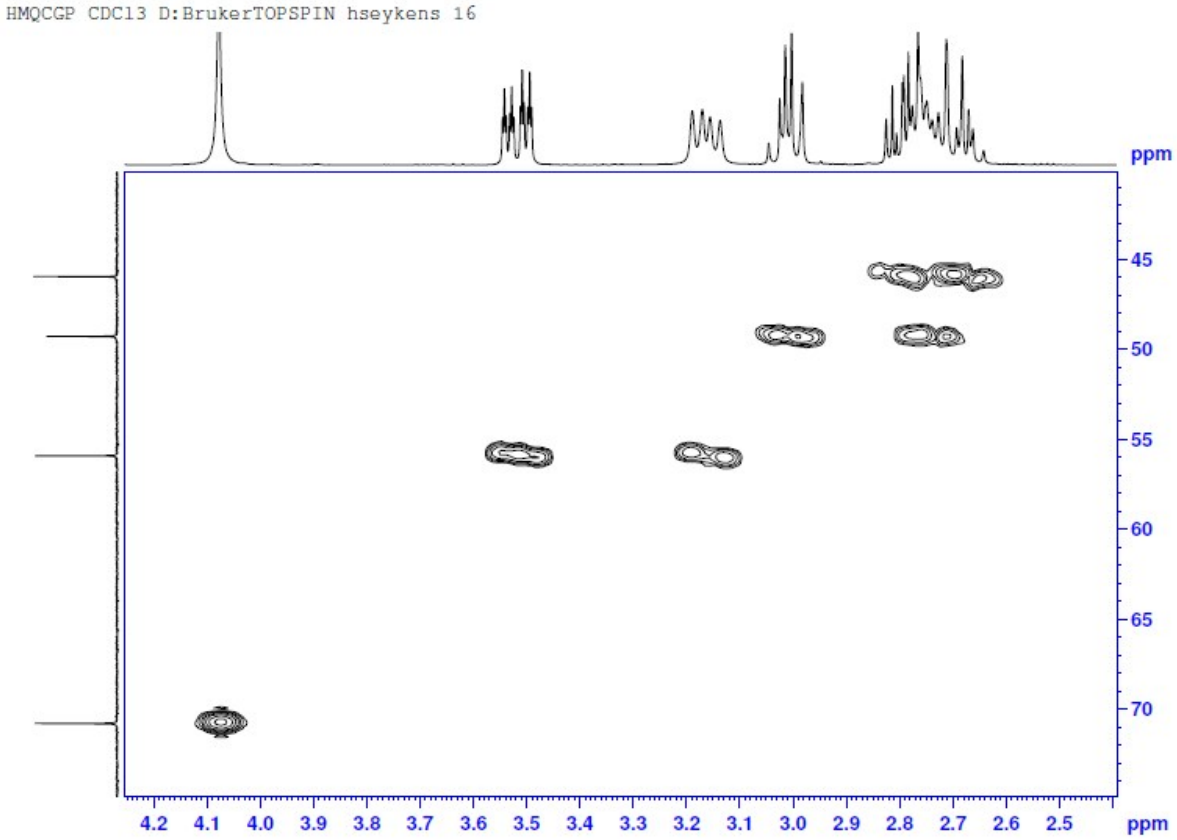

COSYGPSW CDC13 D:BrukerTOPSPIN hseykens 16
ppm
0
1
2
3
4
5
6
7
8
8
7
6
5
4
3
2
1
0
ppm

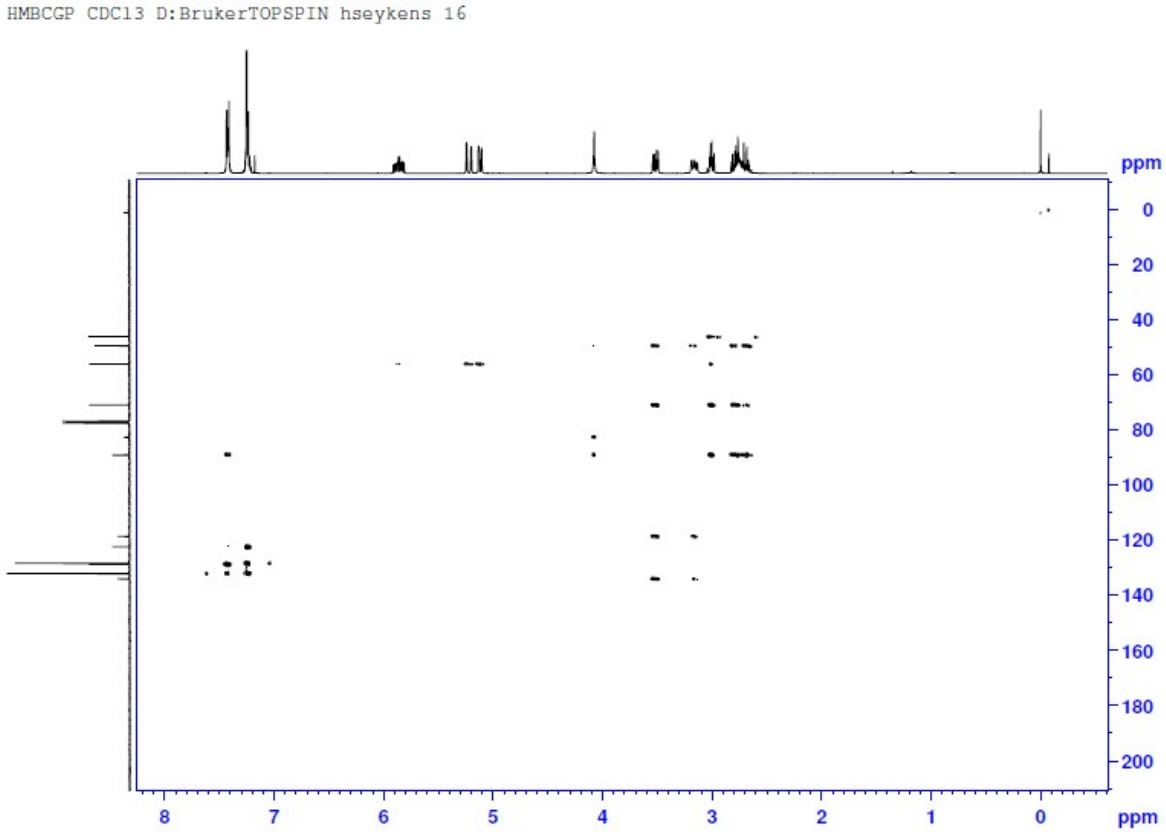

COSYGPSW CDC13 D:BrukerTOPSPIN hseykens 16
ppm
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
ppm

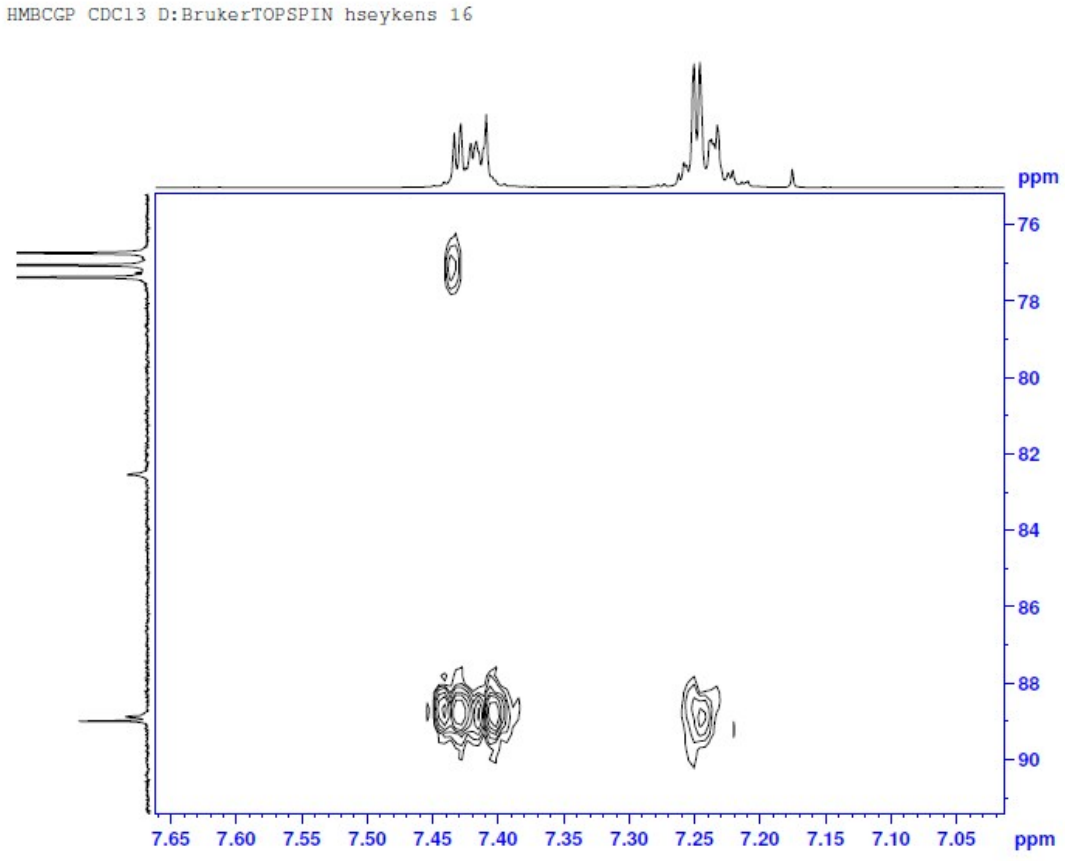

COSYGPSW CDC13 D:BrukerTOPSPIN hseykens 16
ppm
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3
ppm


HMQCGP CDC13 D:BrukerTOPSPIN hseykens 16
ppm
0
20
40
60
80
100
120
140
8 7 6 5 4 3 2 1 0
ppm


HMQCGP CDCl3 D:BrukerTOPSPIN hseykens 16
ppm
115
120
125
130
135
140
6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8
ppm


HMQCGP CDCl3 D:BrukerTOPSPIN hseykens 16
ppm
45
50
55
60
65
70
4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5
ppm


HMBCGP CDCl3 D:BrukerTOPSPIN hseykens 16
ppm
0
20
40
60
80
100
120
140
160
180
200
8
7
6
5
4
3
2
1
0
ppm


HMBCGP CDCl3 D:BrukerTOPSPIN hseykens 16
ppm
76
78
80
82
84
86
88
90
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
ppm

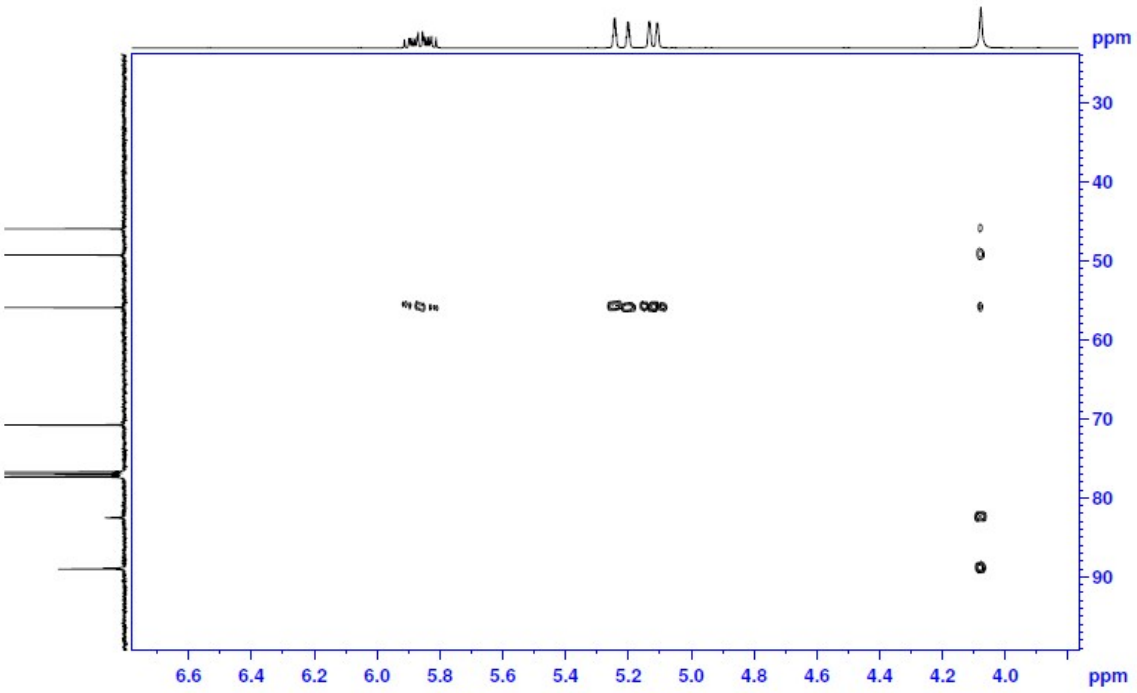
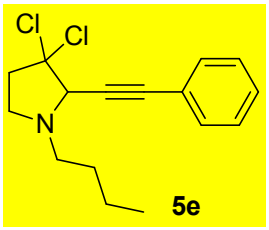


Figure 13. COSY, HMQC and HMBC spectra of **5d** in $CDCl_3$.

1-Butyl-3,3-dichloro-2-(phenylethynyl)pyrrolidine (5e)



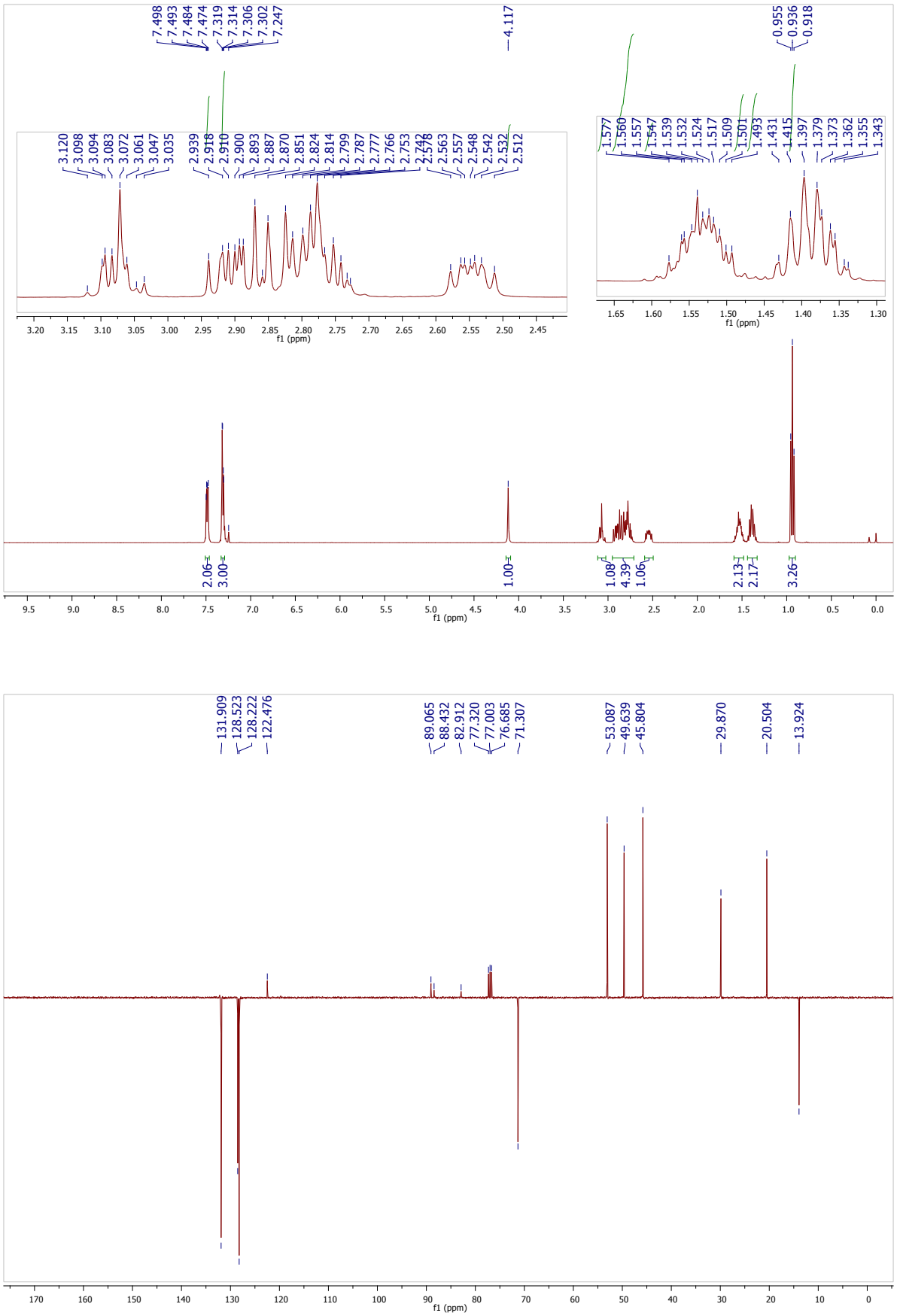
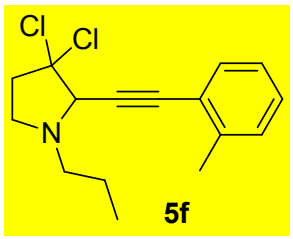
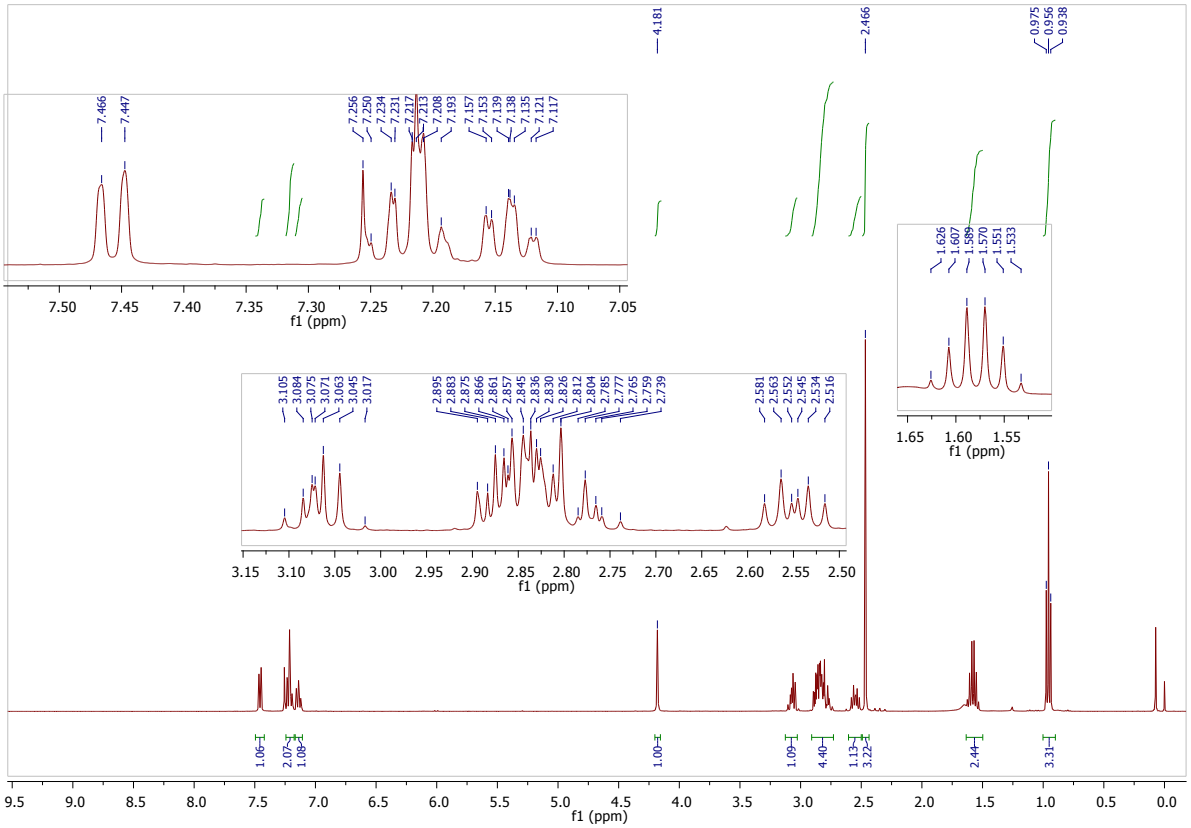


Figure 14. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **5e** in $CDCl_3$.

3,3-Dichloro-1-propyl-2-(*ortho*-tolylethynyl)pyrrolidine (5f)





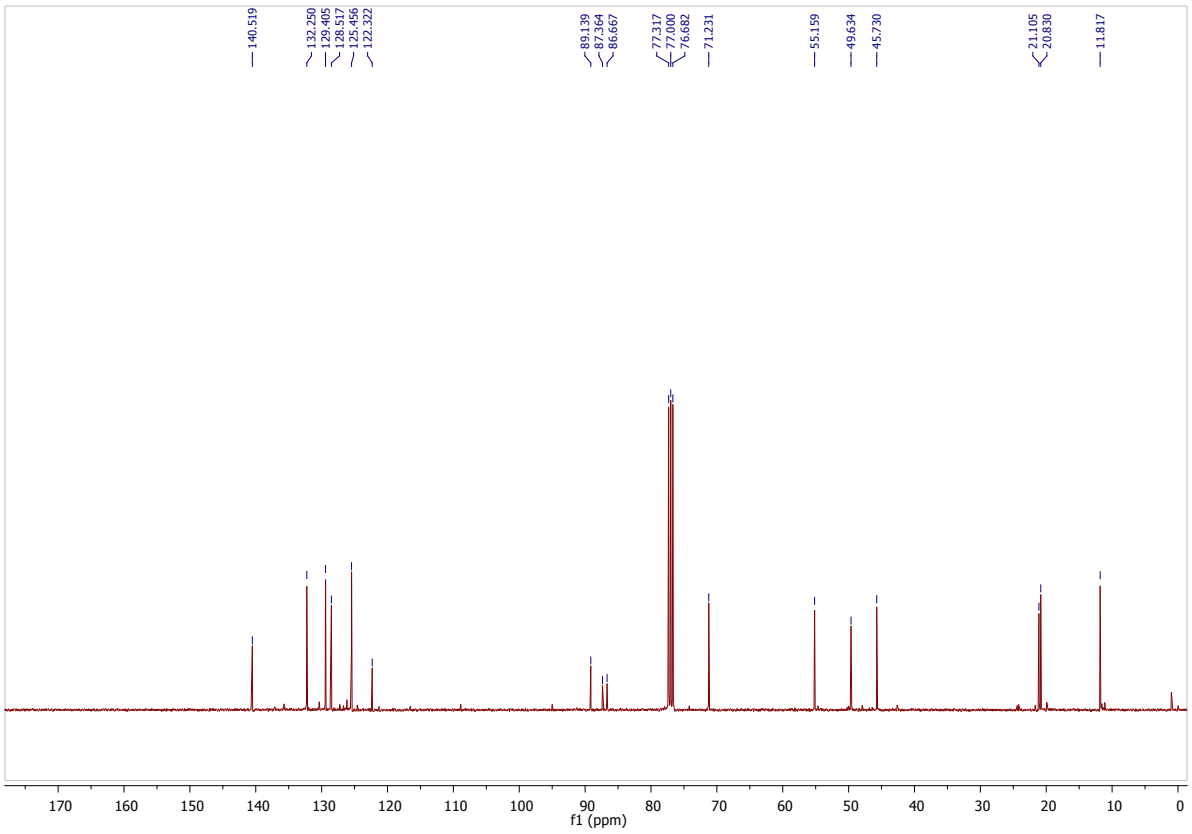
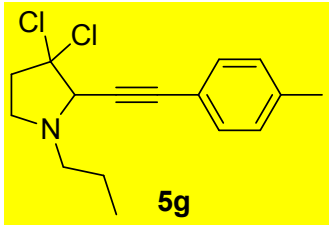


Figure 15. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **5f** in $CDCl_3$.

3,3-Dichloro-1-propyl-2-(*para*-tolylethynyl)pyrrolidine (5g)



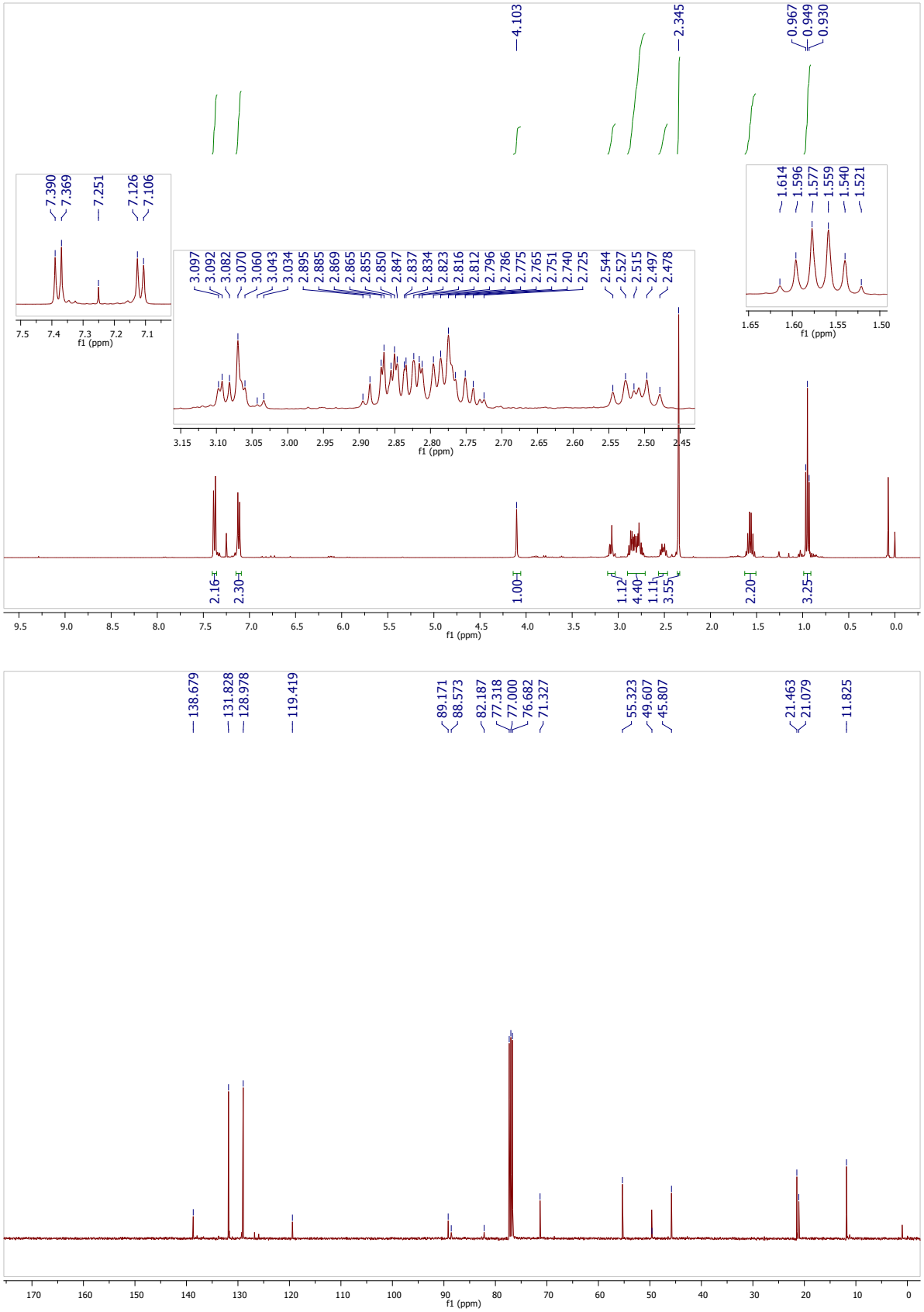
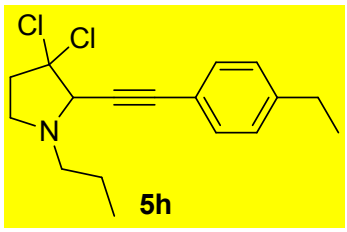
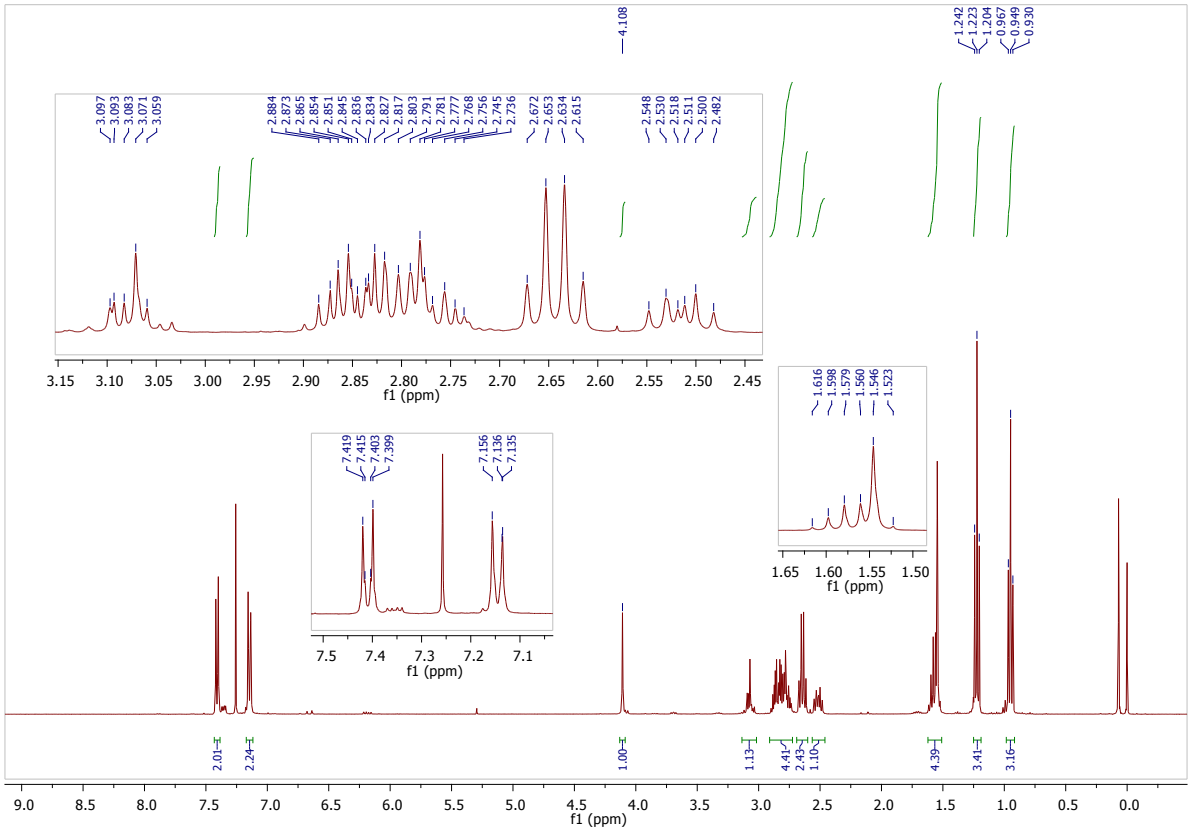


Figure 16. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **5g** in $CDCl_3$.

3,3-Dichloro-2-((4-ethylphenyl)ethynyl)-1-propylpyrrolidine (5h)





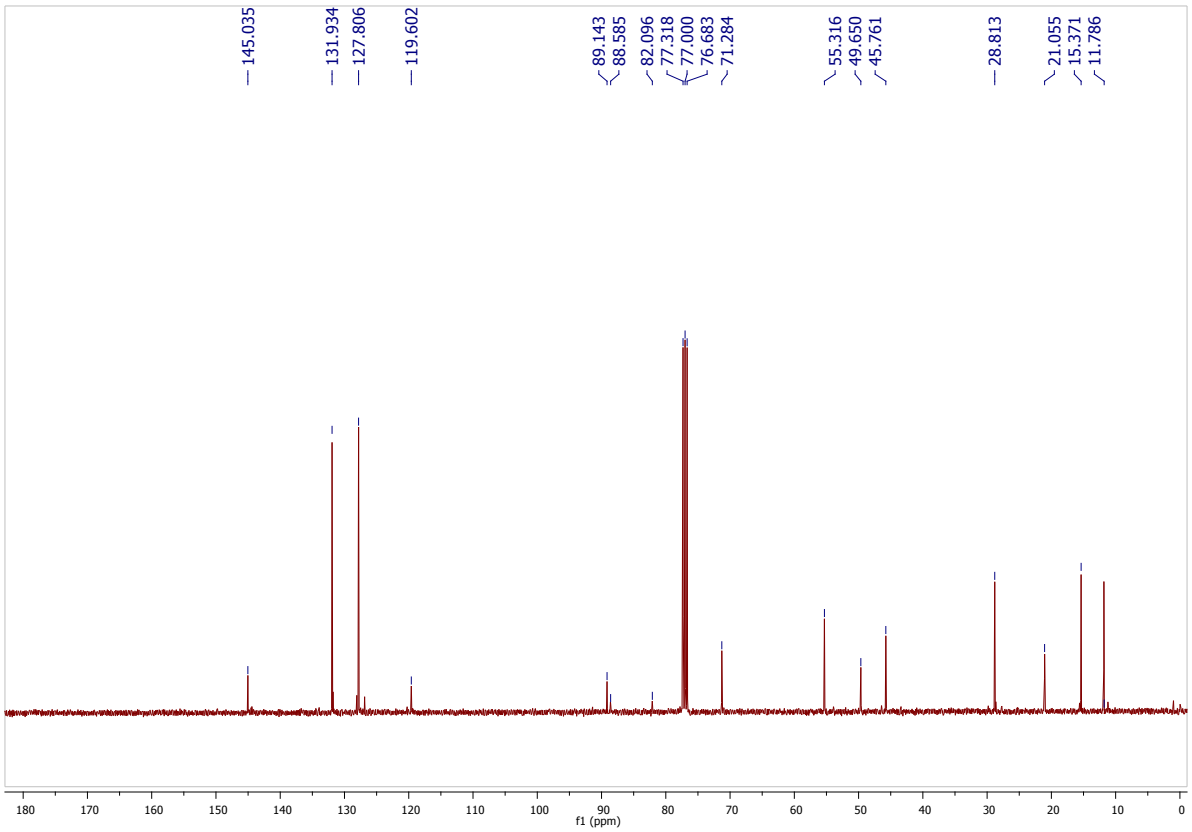
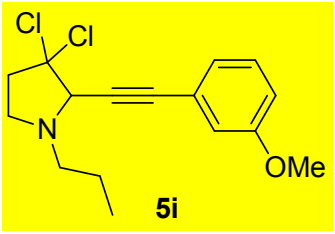


Figure 17. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **5h** in $CDCl_3$.

3,3-Dichloro-2-((3-methoxyphenyl)ethynyl)-1-propylpyrrolidine (5i)



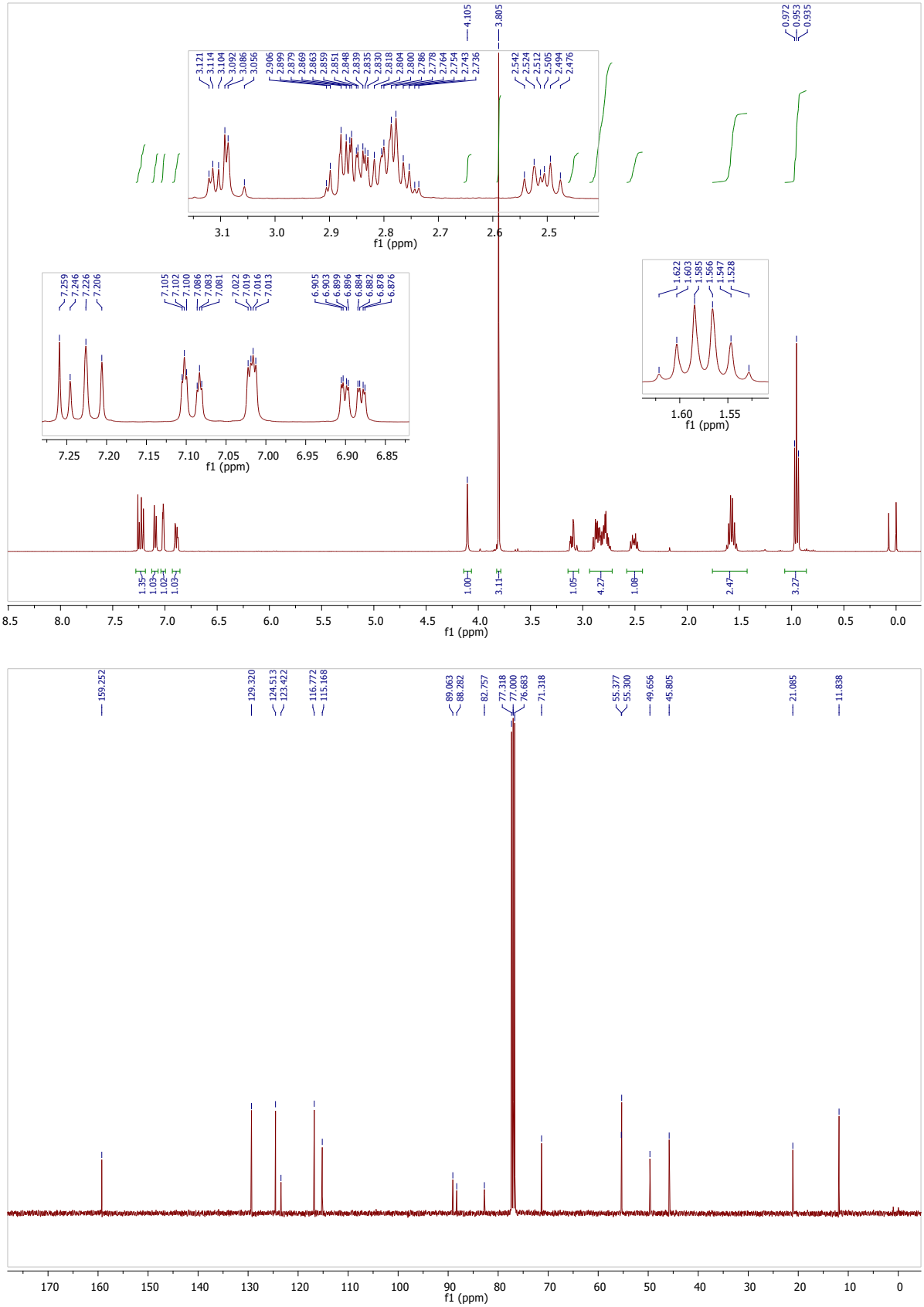
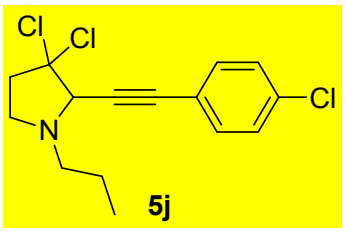
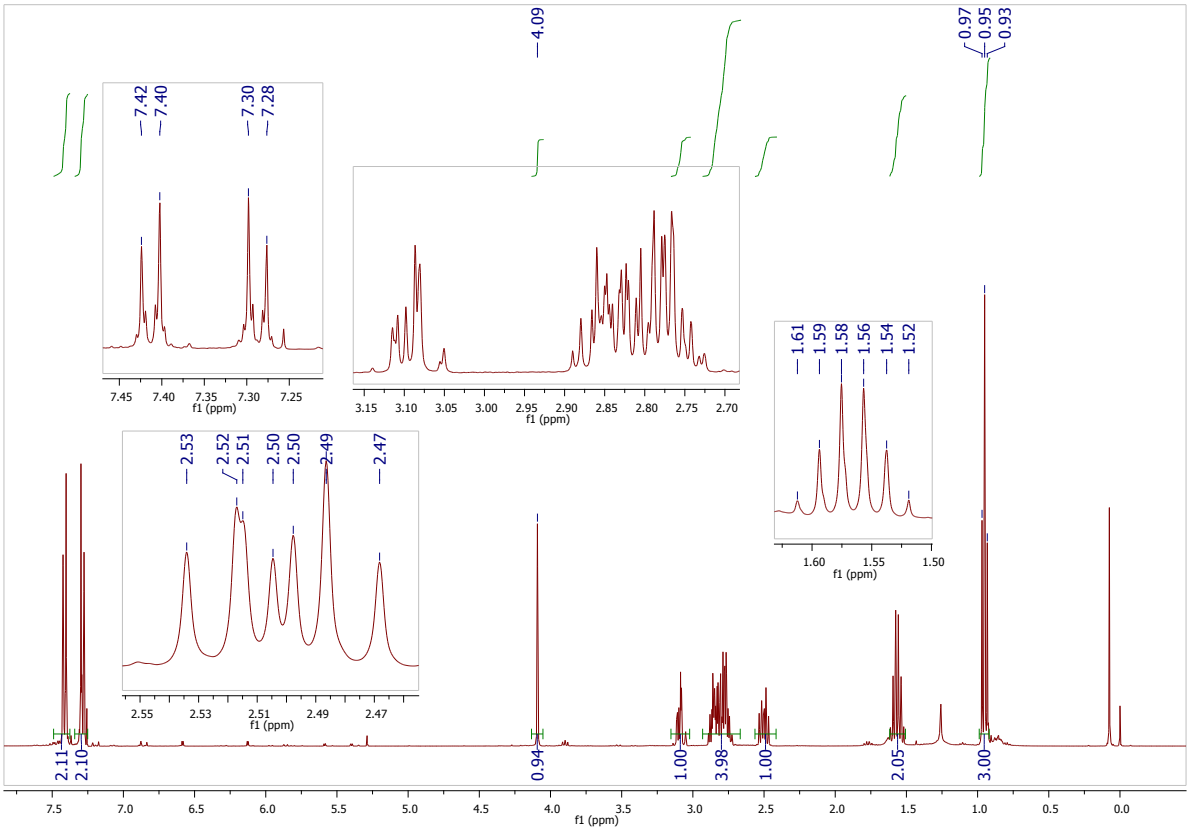


Figure 18. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **5i** in $CDCl_3$.

3,3-Dichloro-2-((4-chlorophenyl)ethynyl)-1-propylpyrrolidine (5j)





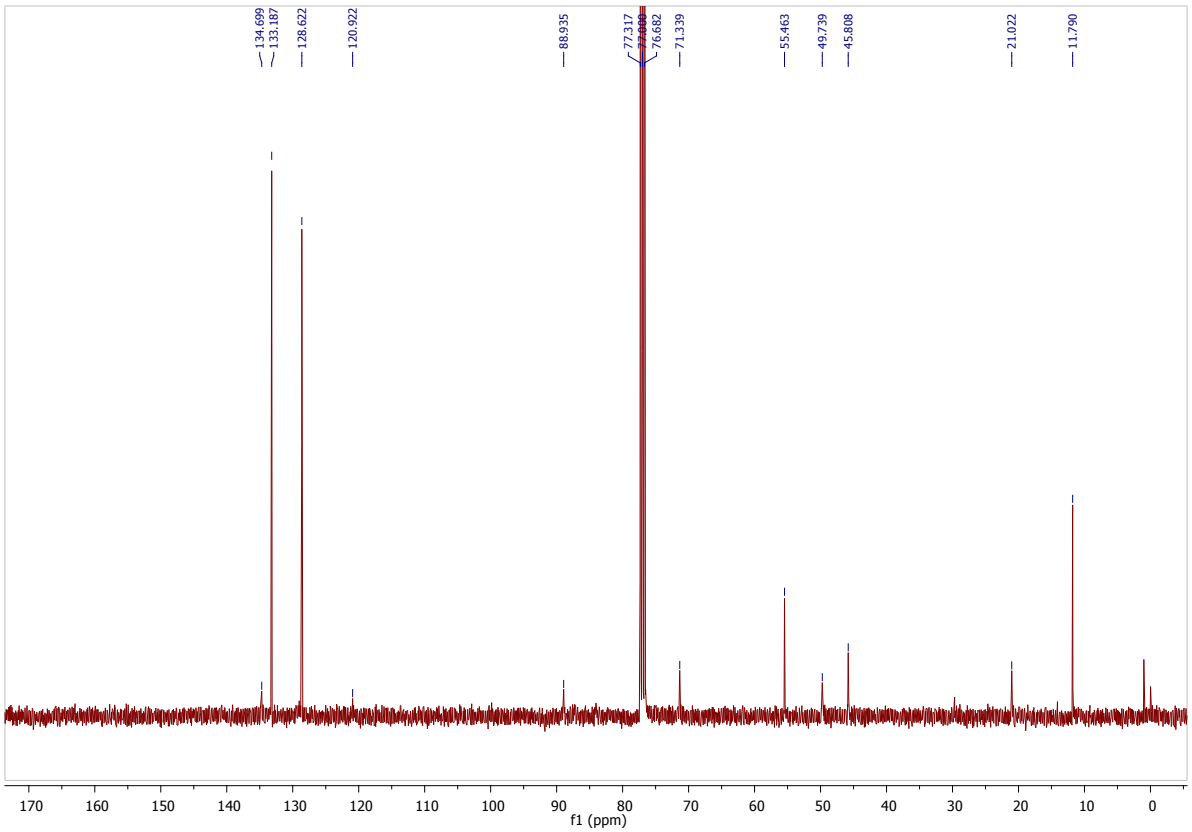
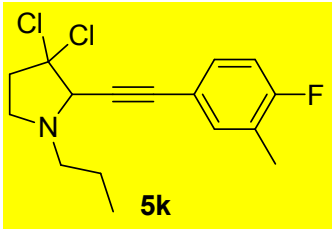


Figure 19. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **5j** in $CDCl_3$.

3,3-Dichloro-2-((4-fluoro-3-methylphenyl)ethynyl)-1-propylpyrrolidine (5k)



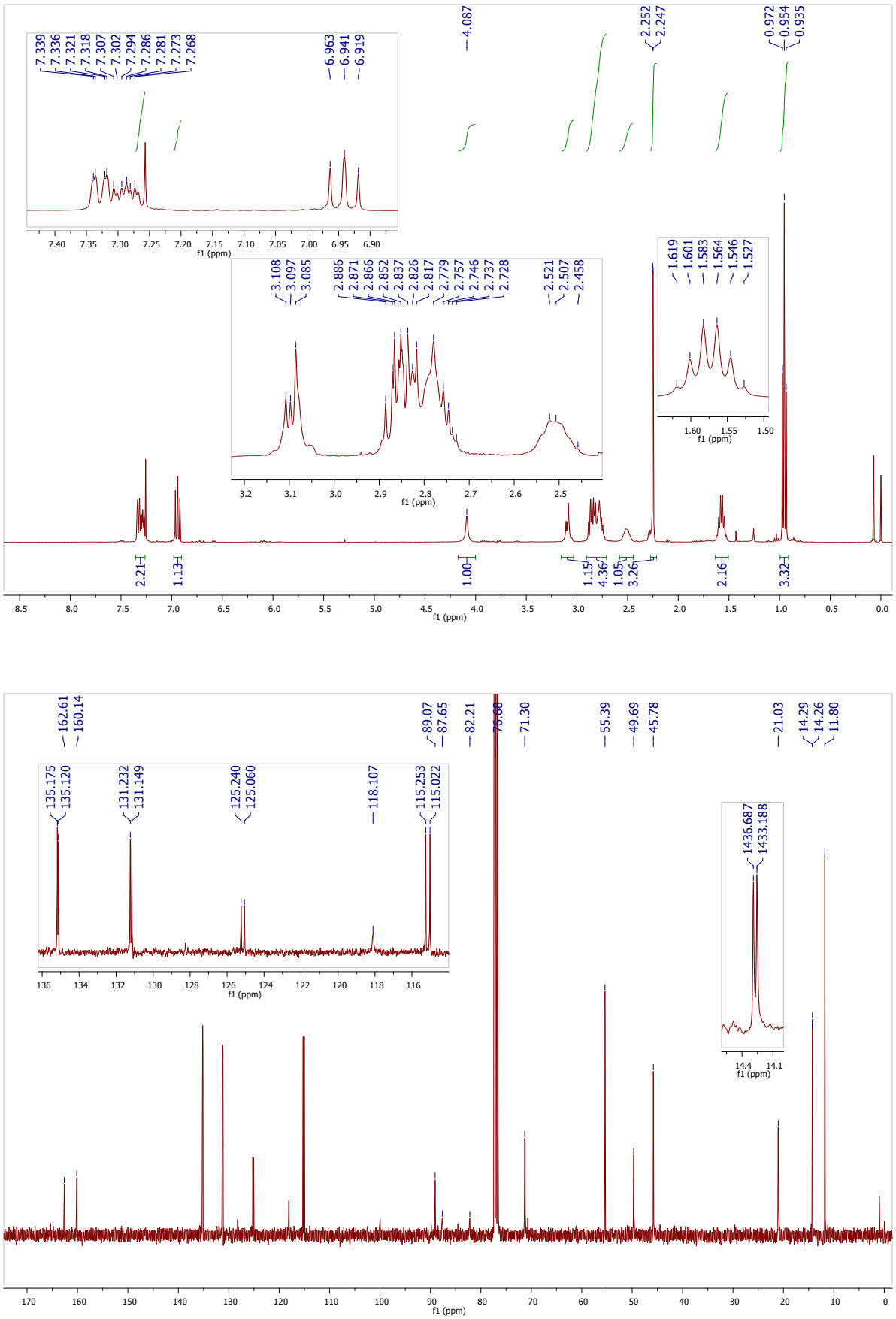
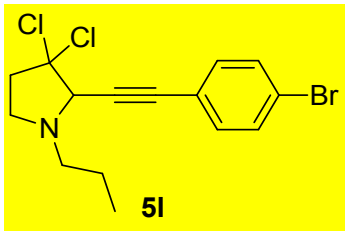
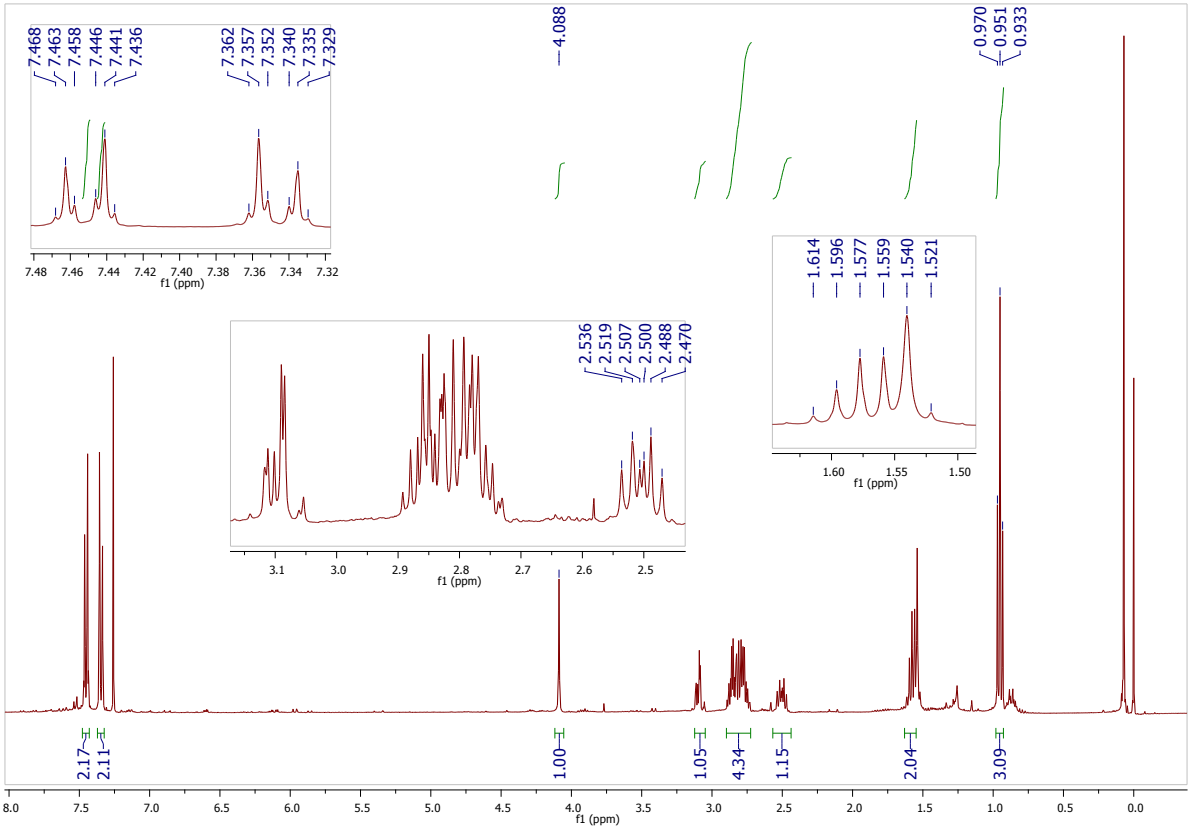


Figure 20. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **5k** in $CDCl_3$.

3,3-Dichloro-2-((4-bromophenyl)ethynyl)-1-propylpyrrolidine (5l)





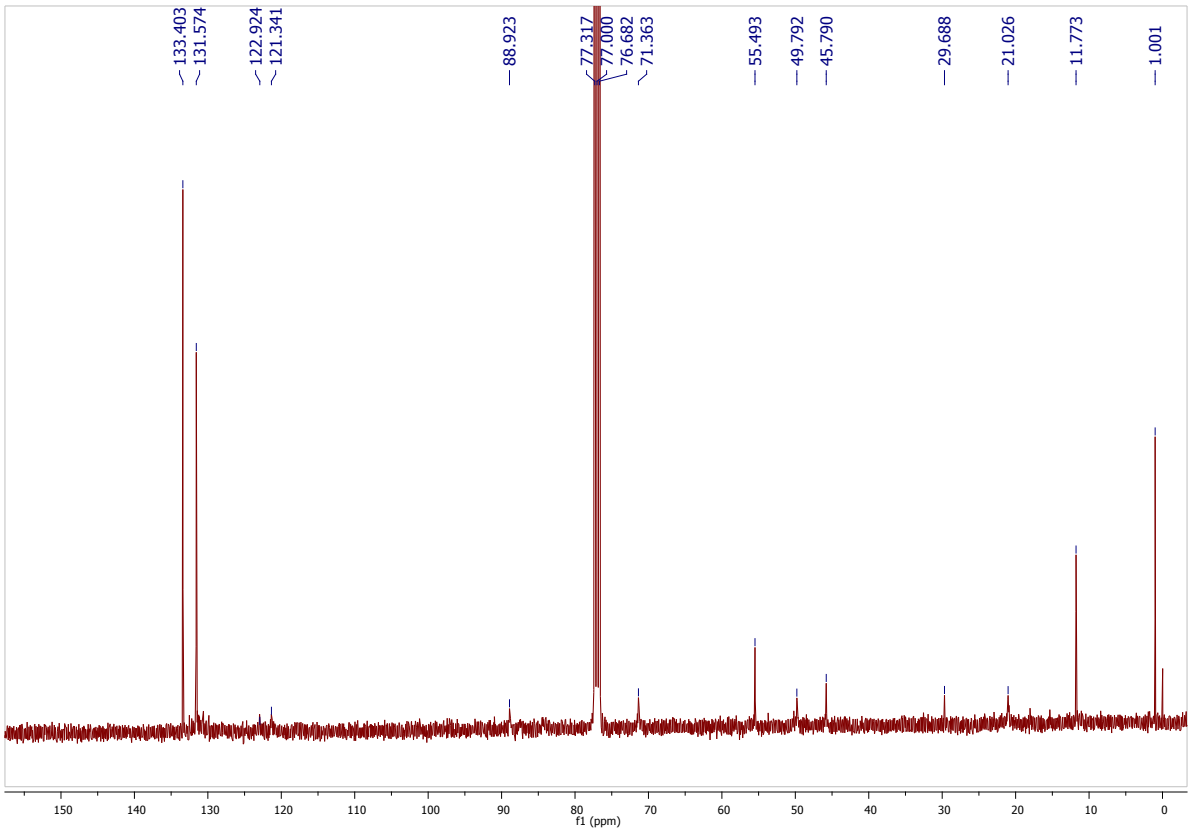
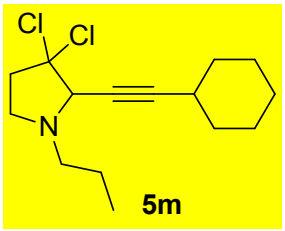


Figure 21. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **5l** in $CDCl_3$.

3,3-Dichloro-2-(cyclohexylethynyl)-1-propylpyrrolidine (5m)



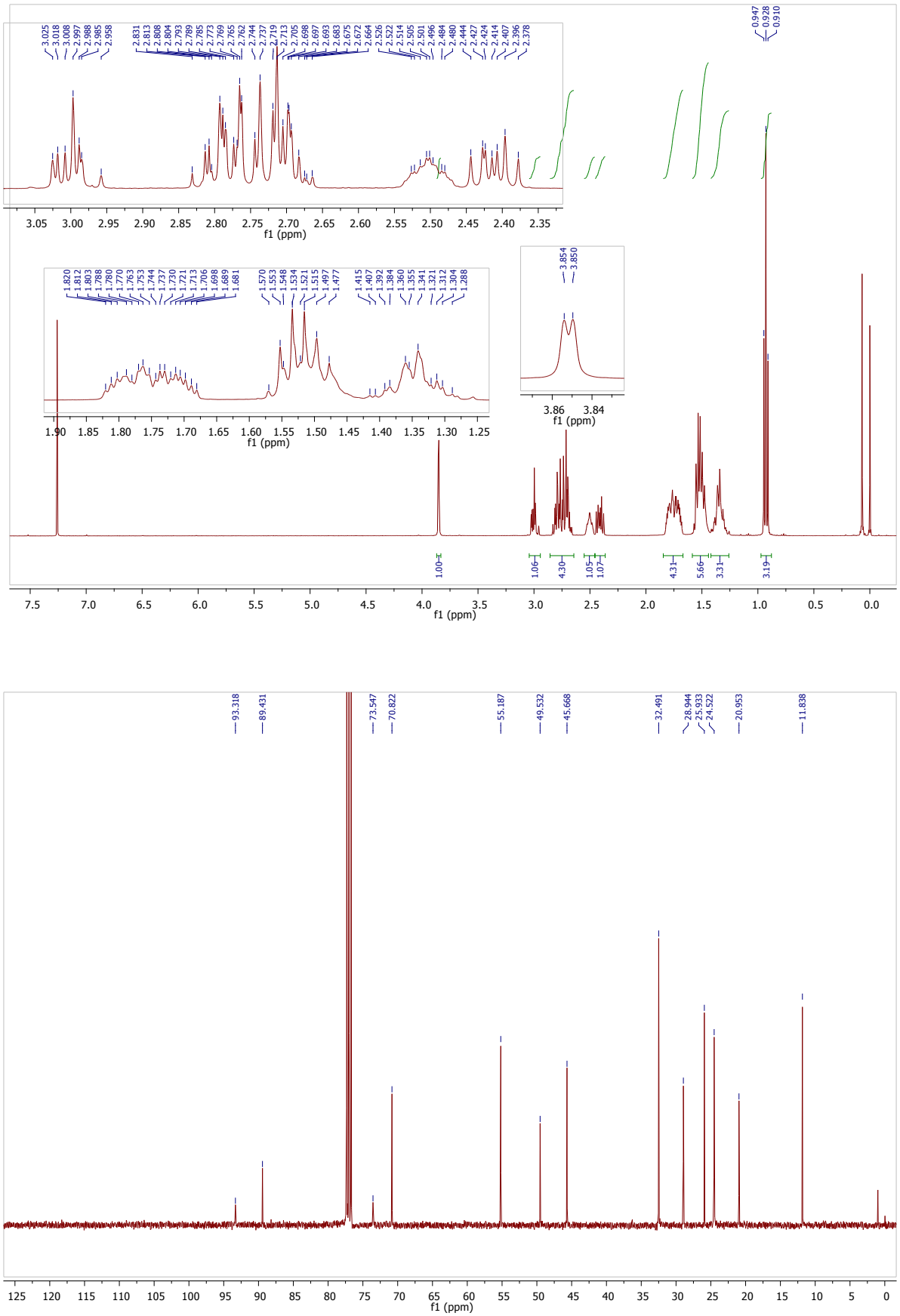
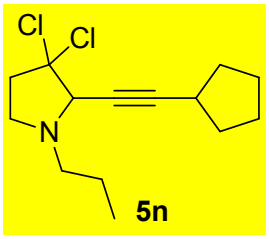
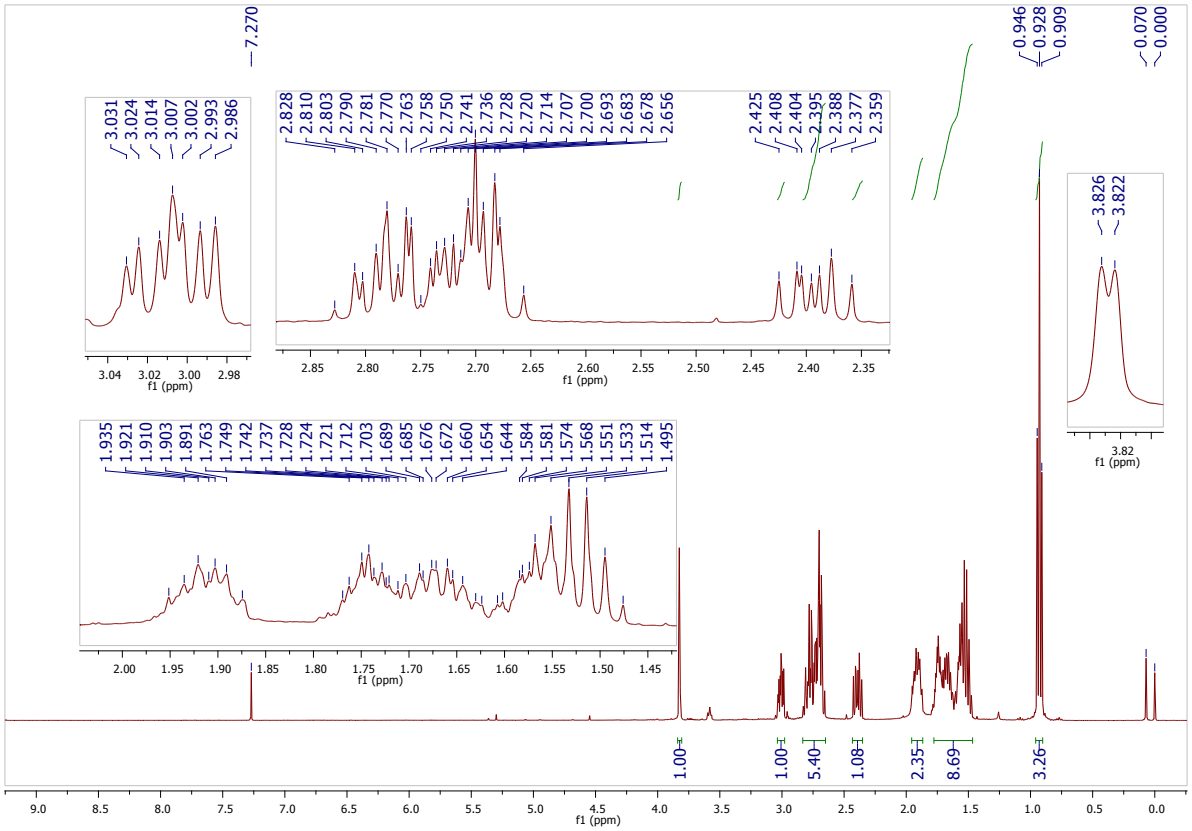


Figure 22. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **5m** in $CDCl_3$.

3,3-Dichloro-2-(cyclopentylethynyl)-1-propylpyrrolidine (5n)





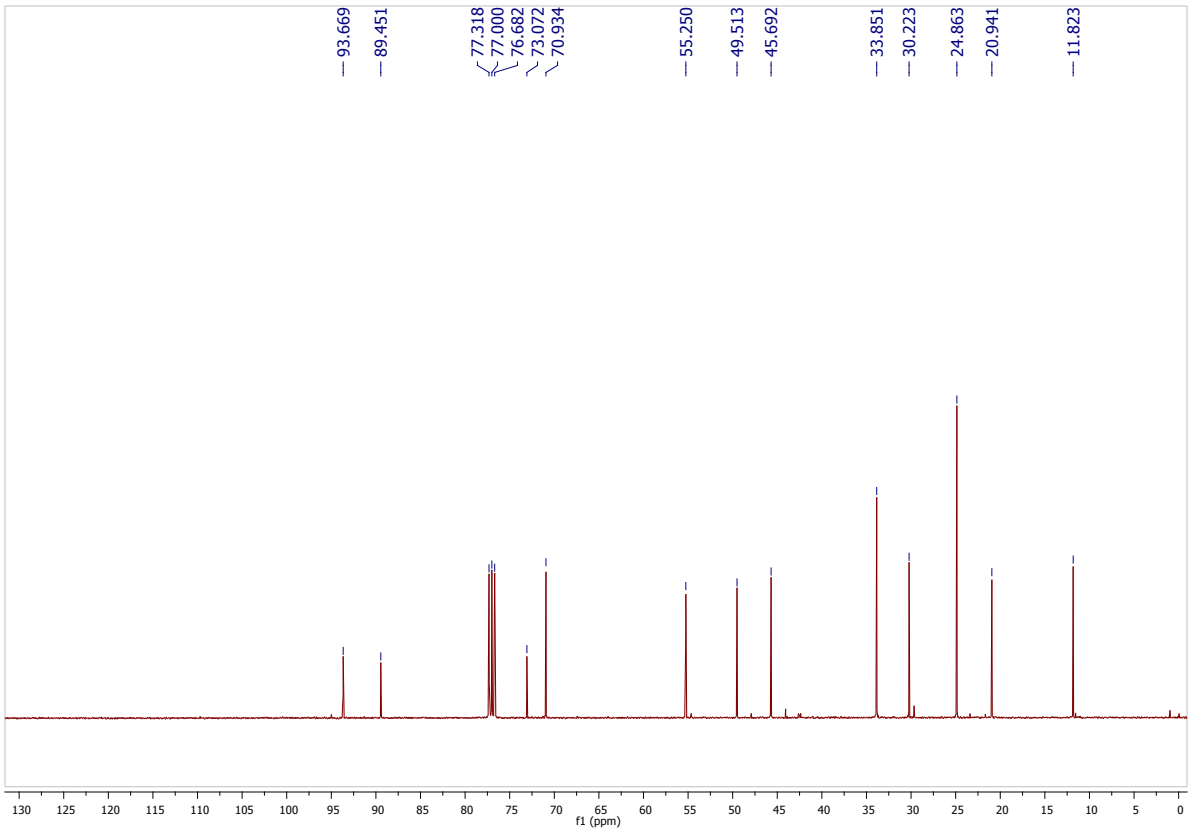
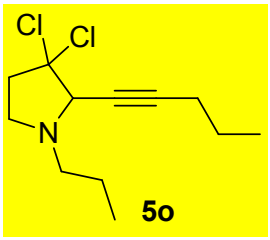


Figure 23. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **5n** in $CDCl_3$.

3,3-Dichloro-2-(pent-1-ynyl)-1-propylpyrrolidine (5o)



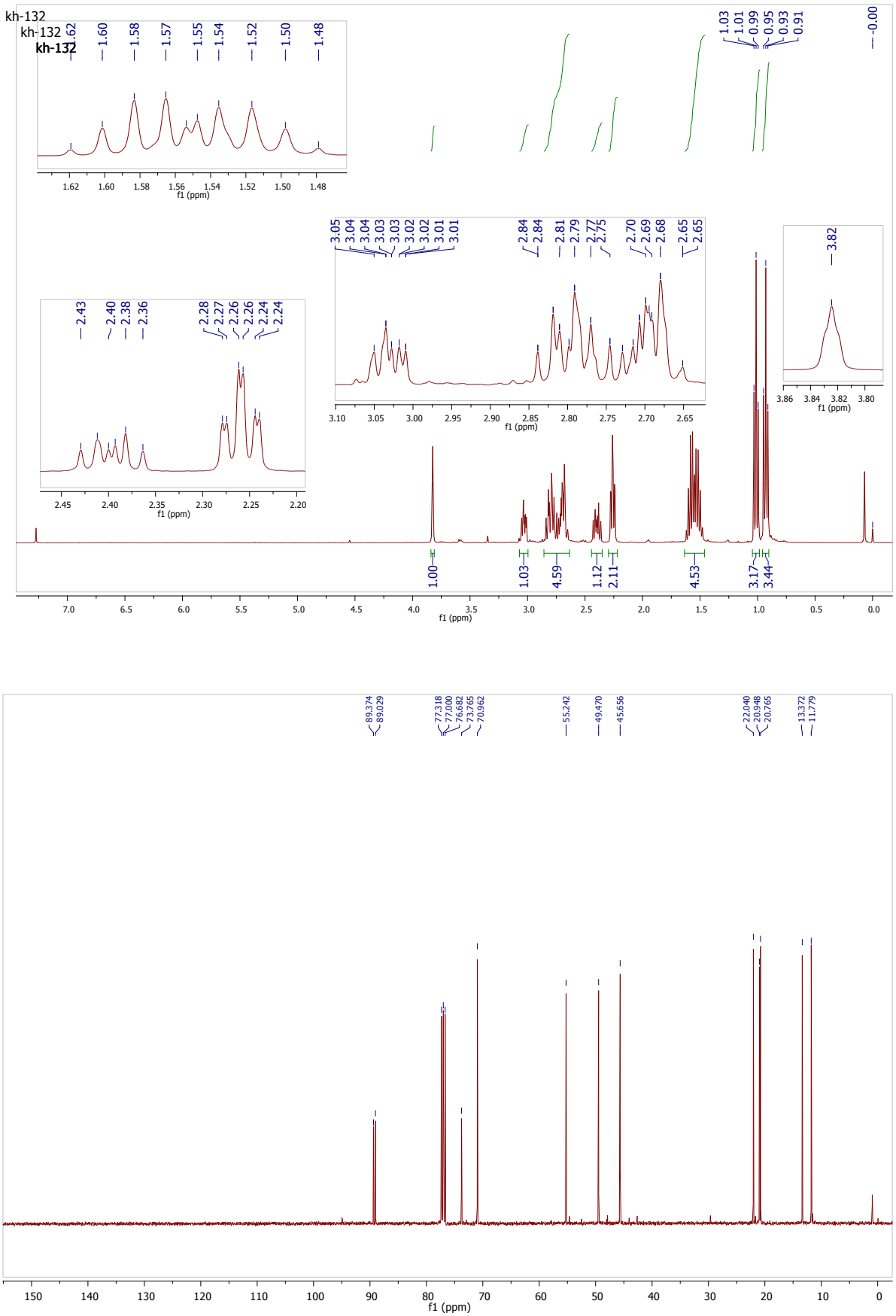
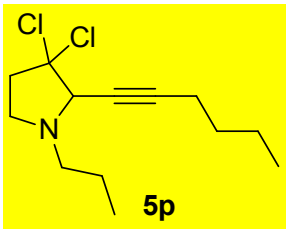
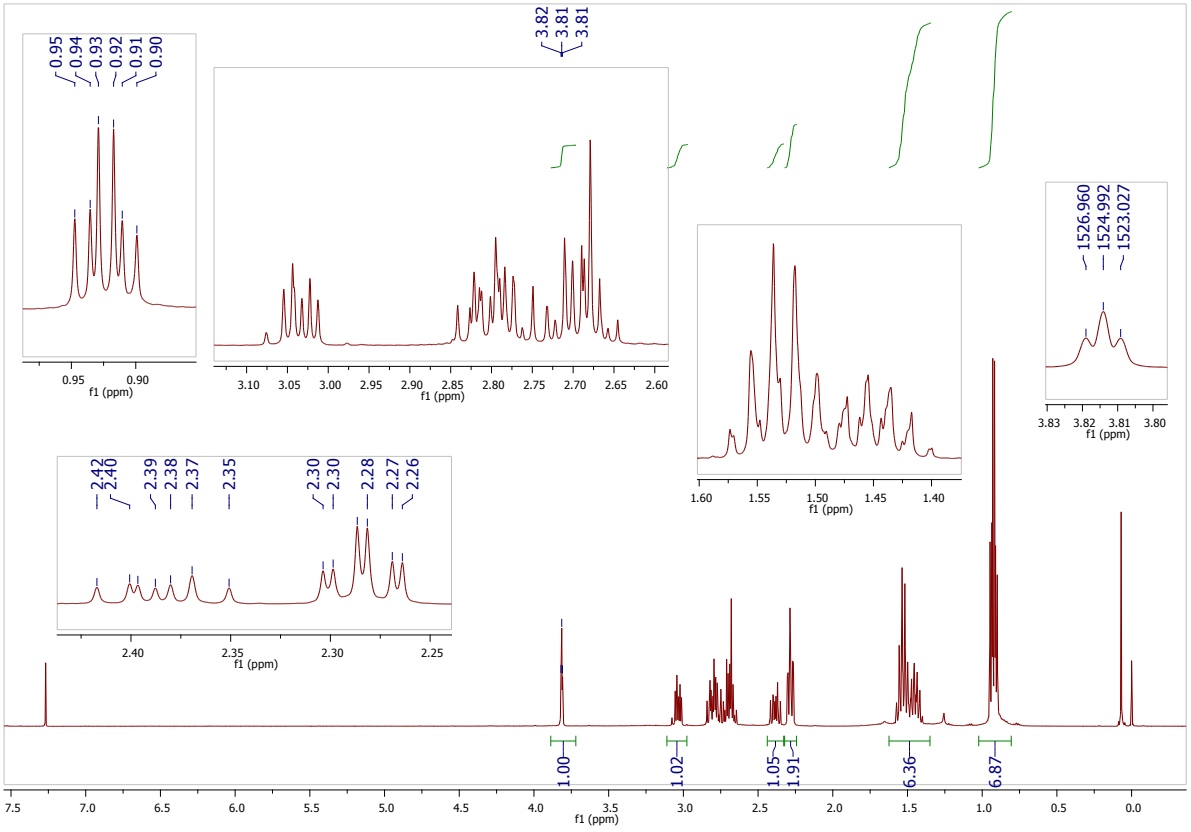


Figure 24. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **5o** in $CDCl_3$.

3,3-Dichloro-2-(hex-1-ynyl)-1-propylpyrrolidine (5p)





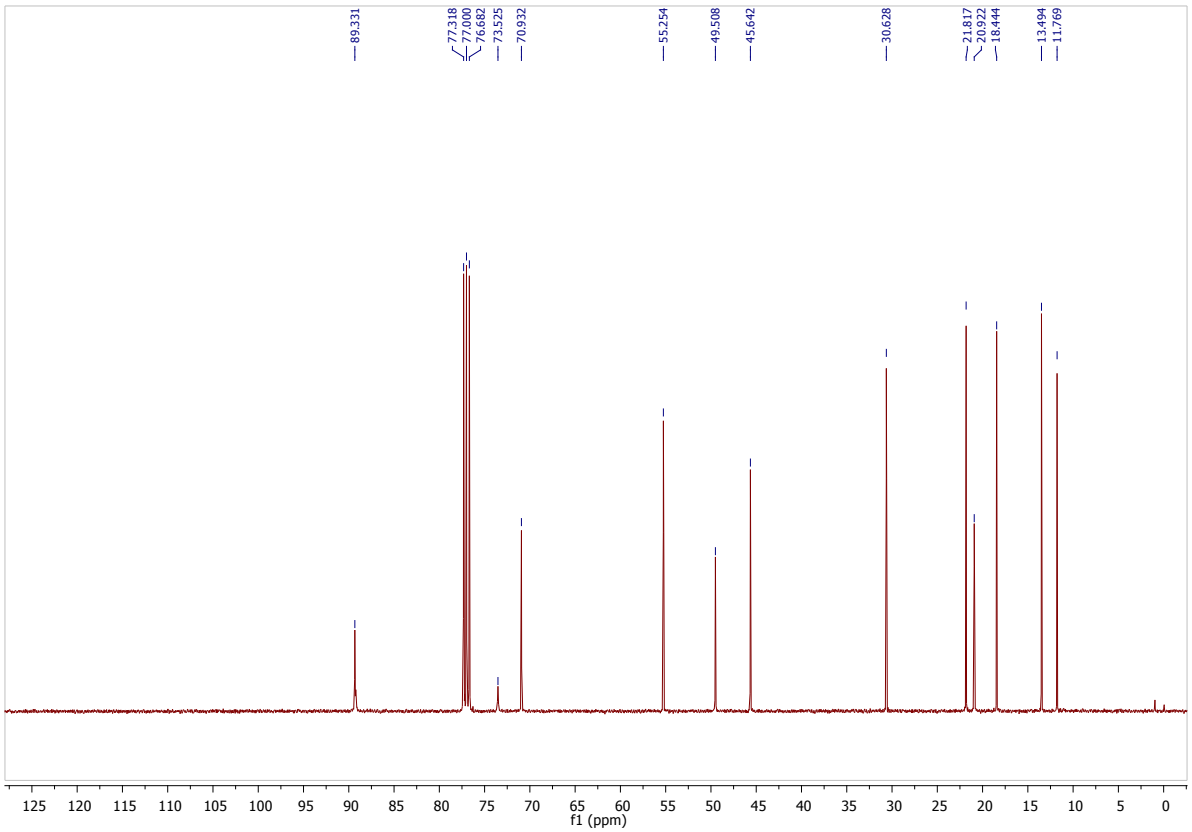
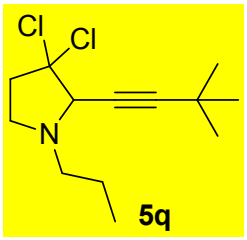


Figure 25. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **5p** in $CDCl_3$.

3,3-Dichloro-2-(3,3-dimethylbut-1-ynyl)-1-propylpyrrolidine (5q)



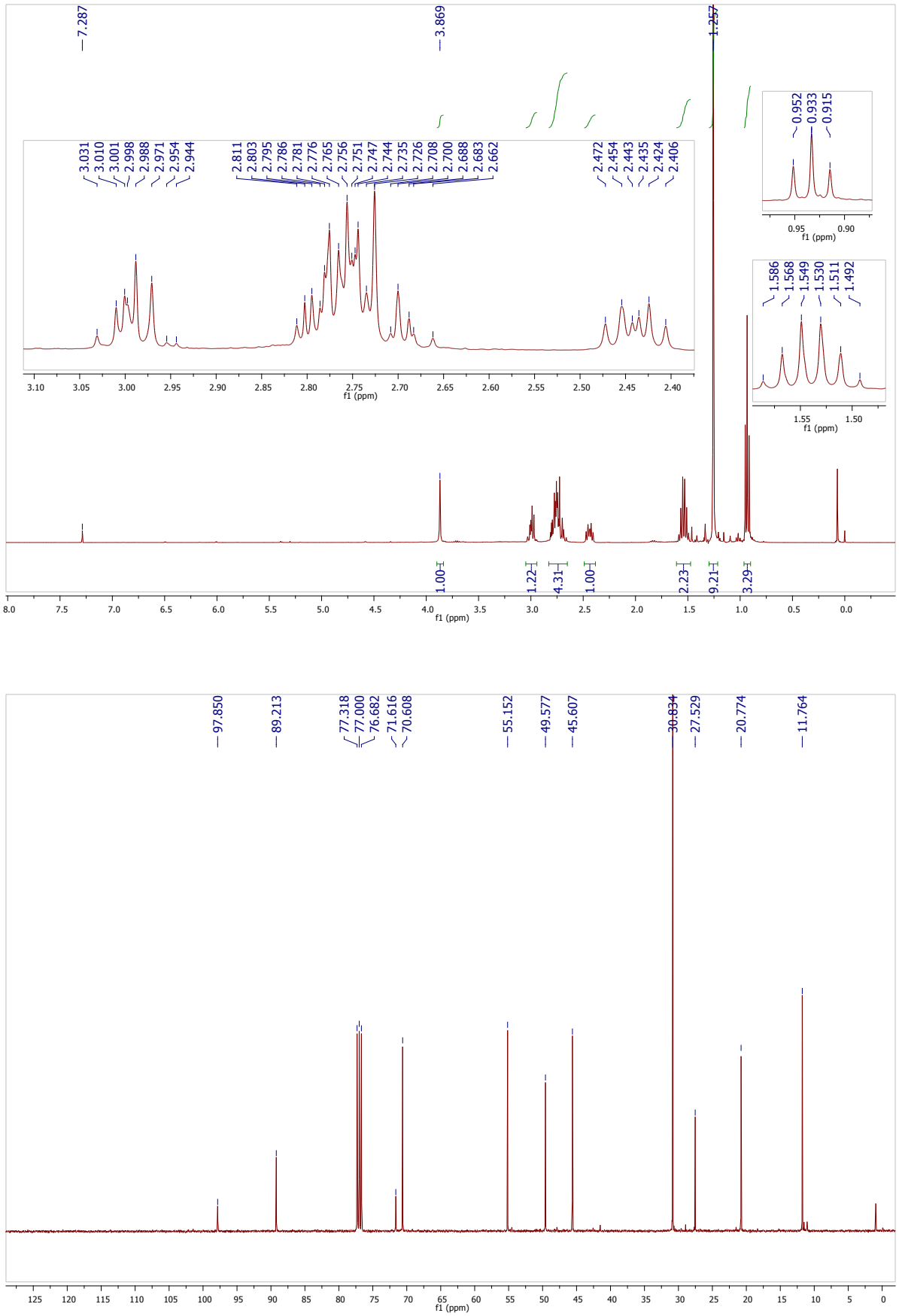
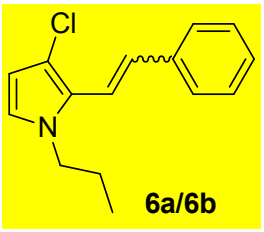


Figure 26. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **5q** in $CDCl_3$.

4. Copies of ^{1}H and ^{13}C spectra of 2-alkenylpyrroles 6a-f and 7

(*E/Z*)-3-Chloro-1-propyl-2-styryl-1*H*-pyrrole (6a)/(6b)



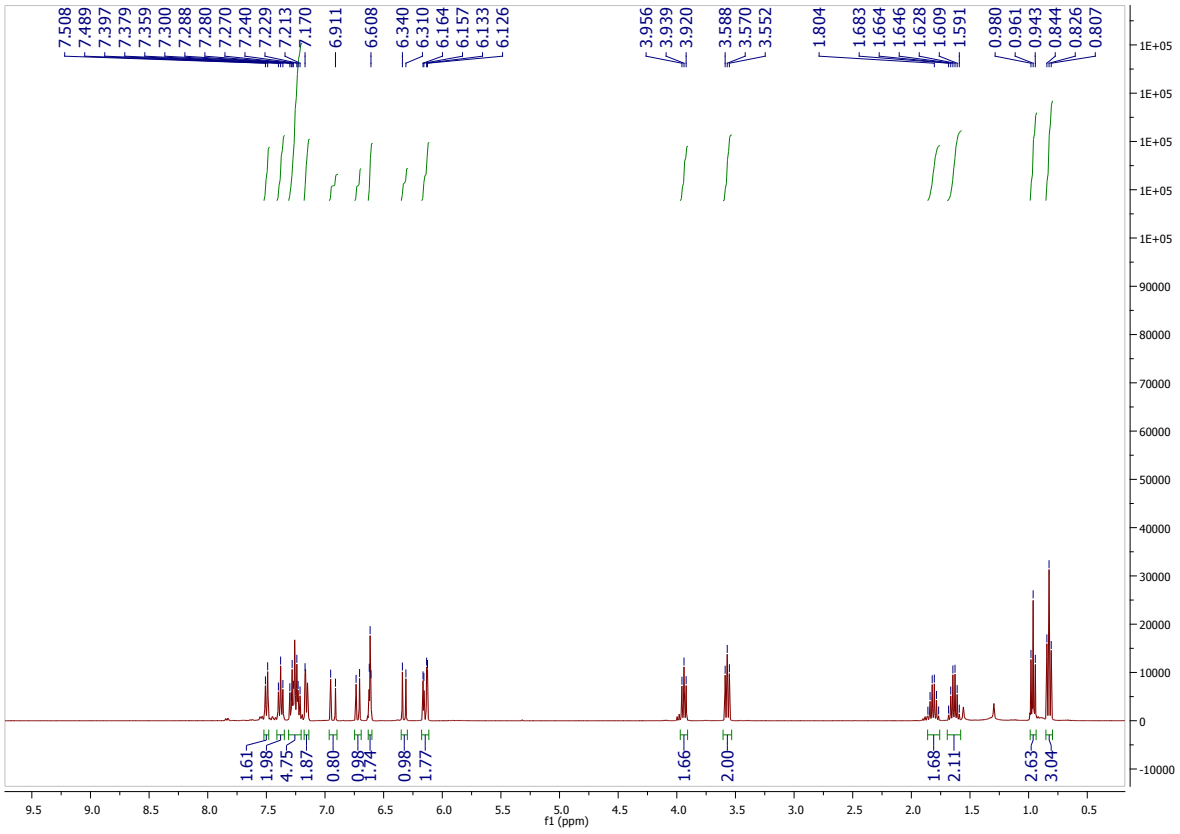
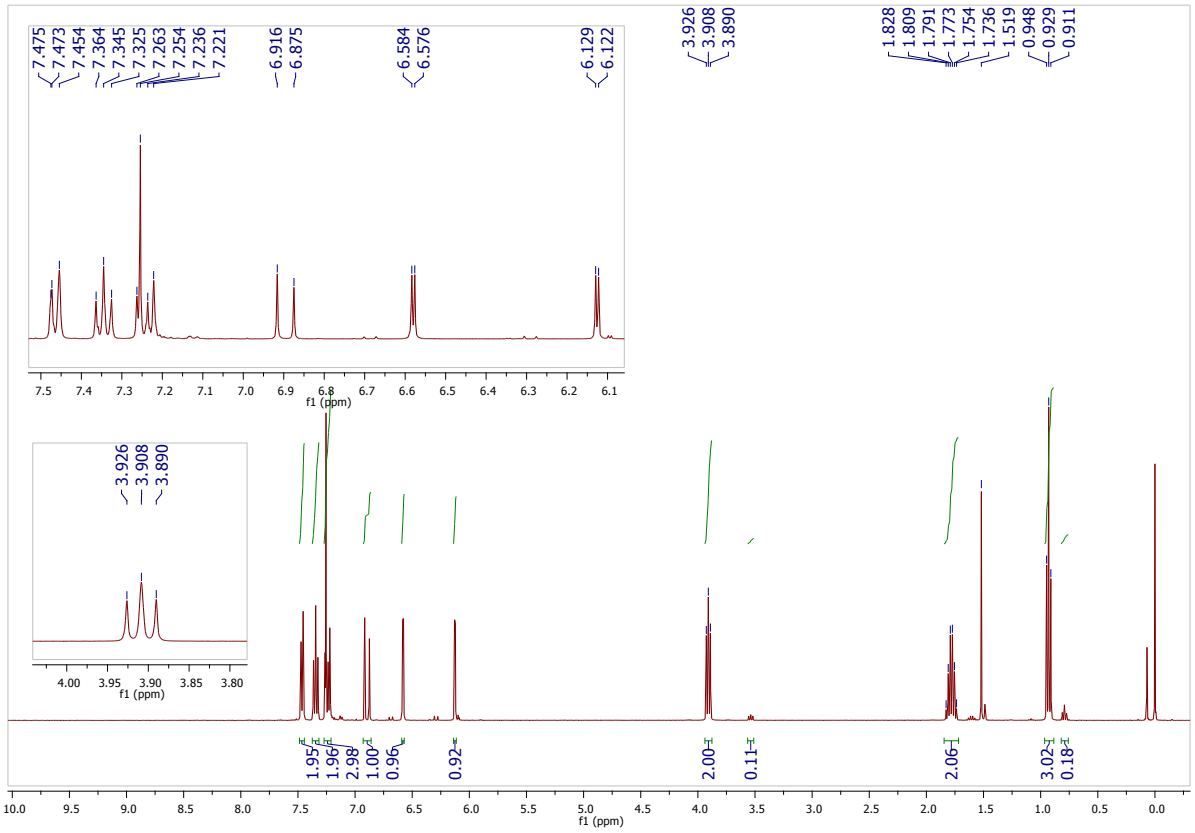


Figure 27. ^{1}H (400 MHz) NMR spectra of **6a/6b** (mixture of *E* and *Z*) in $CDCl_3$.

(*E*)-3-Chloro-1-propyl-2-styryl-1*H*-pyrrole (6a)



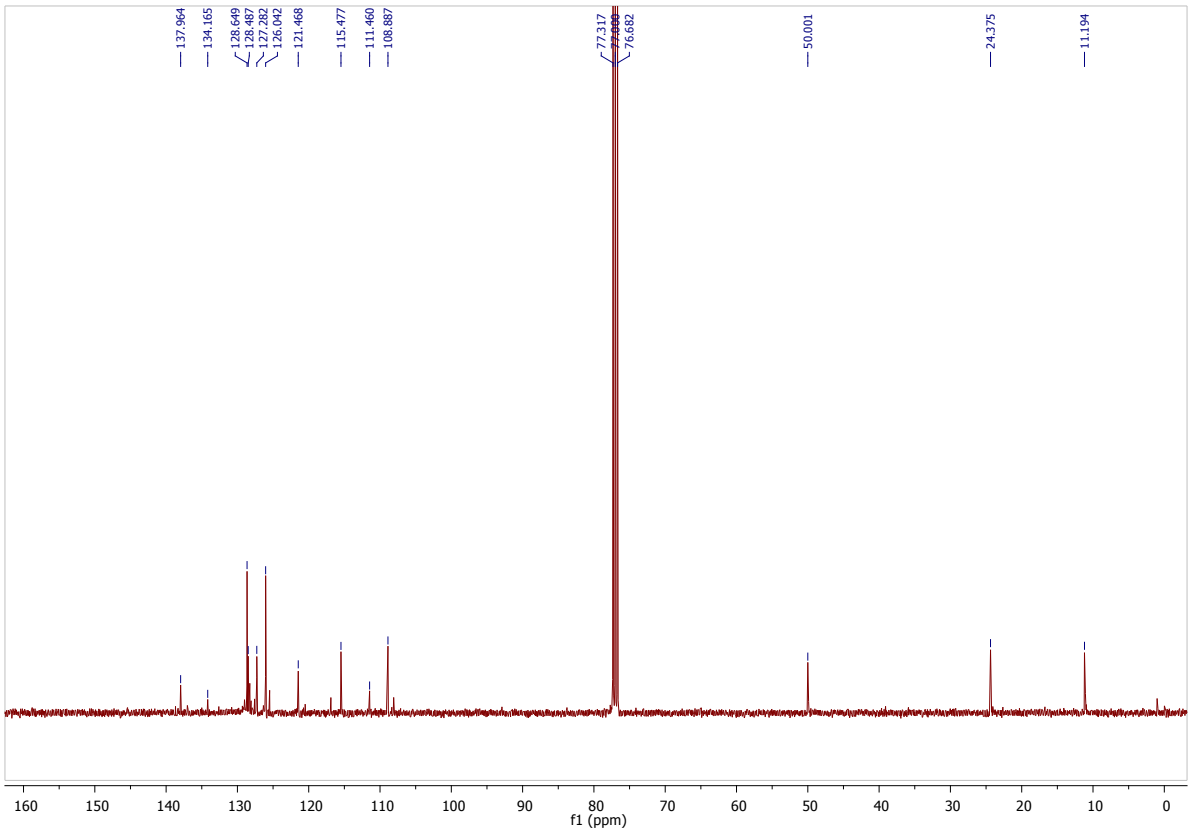
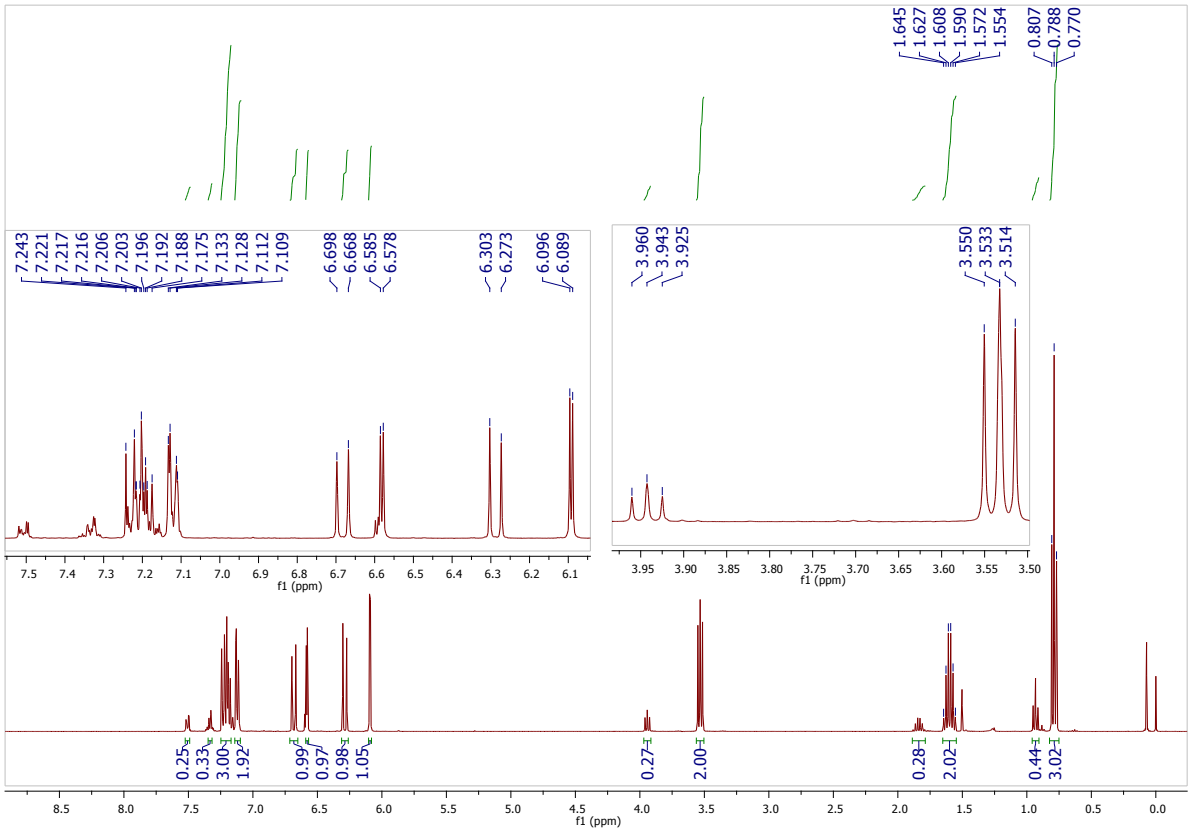


Figure 28. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **6a** in $CDCl_3$.

(*Z*)-3-Chloro-1-propyl-2-styryl-1*H*-pyrrole (6b)



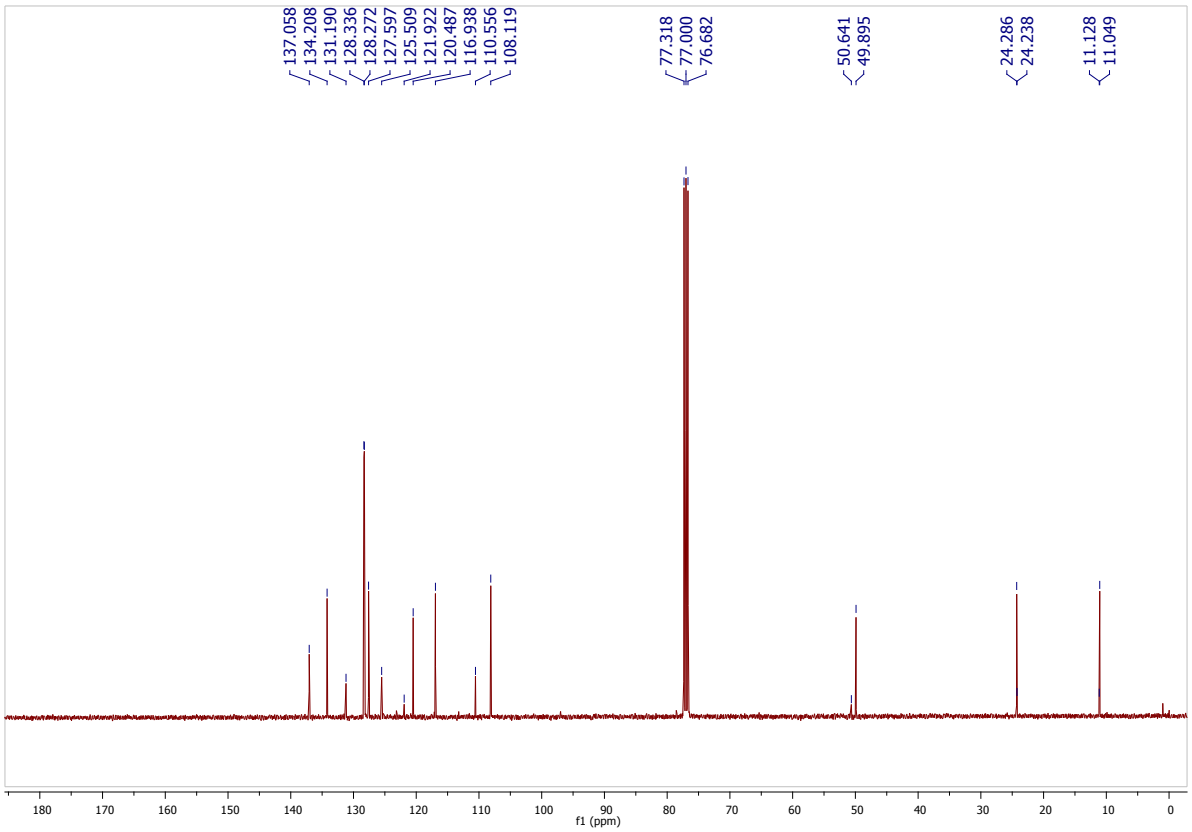
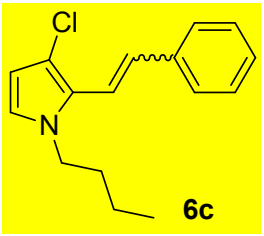
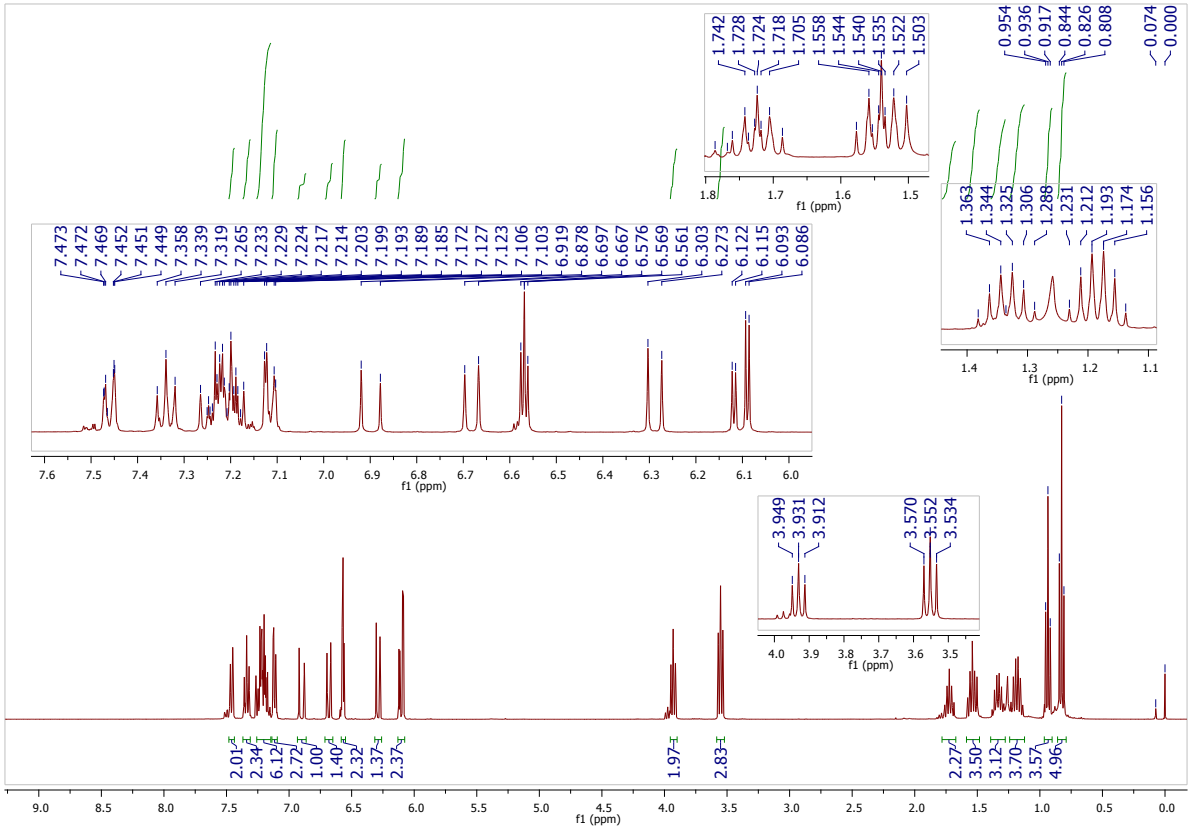


Figure 29. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **6b** in $CDCl_3$.

(*E/Z*)-1-Butyl-3-chloro-2-styryl-1*H*-pyrrole (6c)




7.473 7.472 7.469 7.452 7.451 7.449 7.358 7.339 7.319 7.265 7.233 7.229 7.224 7.217 7.214 7.203 7.199 7.193 7.189 7.185 7.172 7.127 7.123 7.106 7.103 6.919 6.878 6.697 6.667 6.576 6.569 6.561 6.303 6.273 6.122 6.115 6.093 6.086
1.742 1.728 1.724 1.718 1.705 1.558 1.544 1.540 1.535 1.522 1.503
0.954 0.936 0.917 0.844 0.826 0.808 0.074 0.000
1.363 1.344 1.325 1.306 1.288 1.231 1.212 1.193 1.174 1.156
3.949 3.931 3.912 3.570 3.552 3.534
2.01 2.34 6.12 2.72 1.00 1.40 2.32 1.37 2.37 1.97 2.83 2.27 3.50 3.12 3.70 3.57 4.96
f1 (ppm)

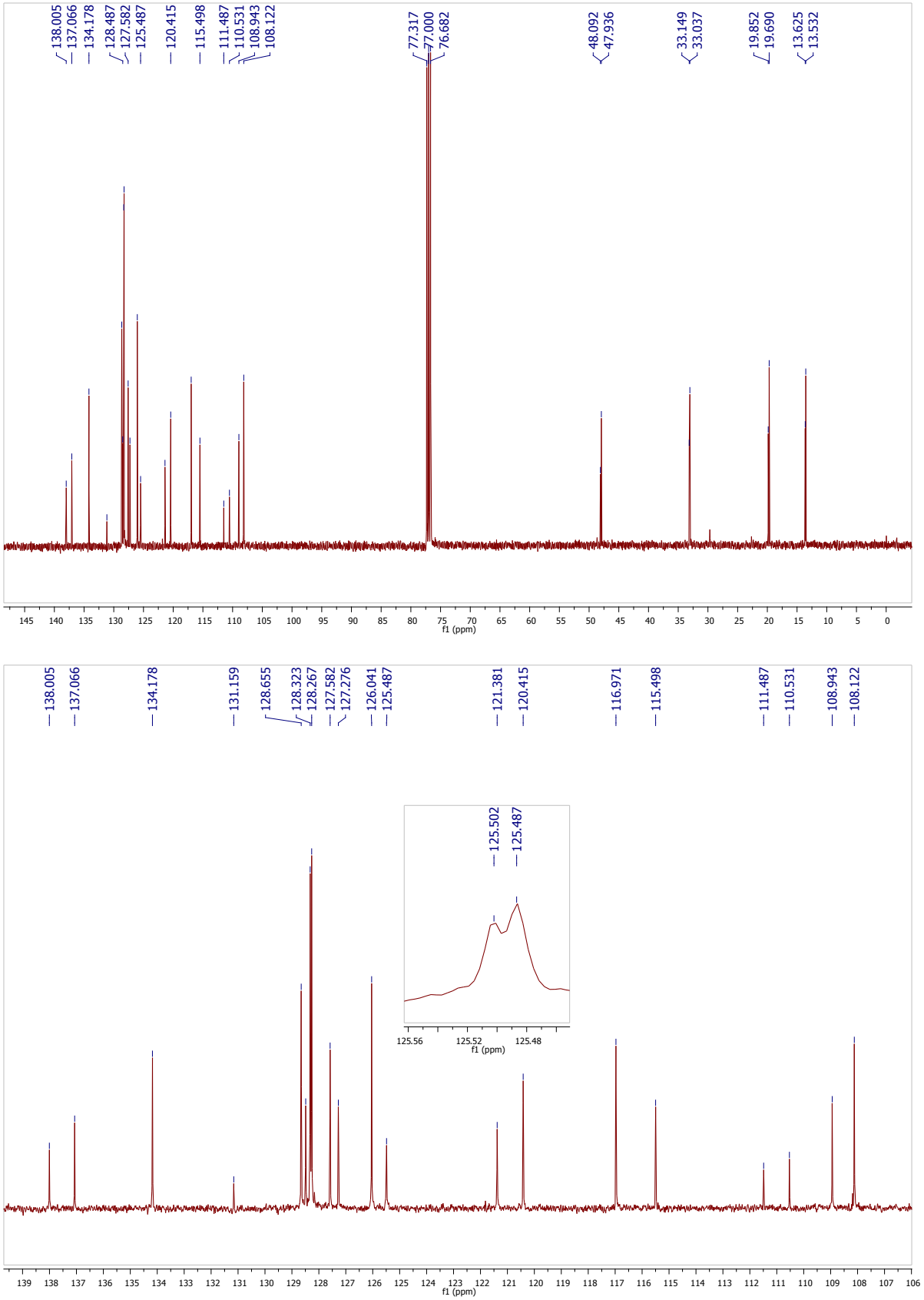
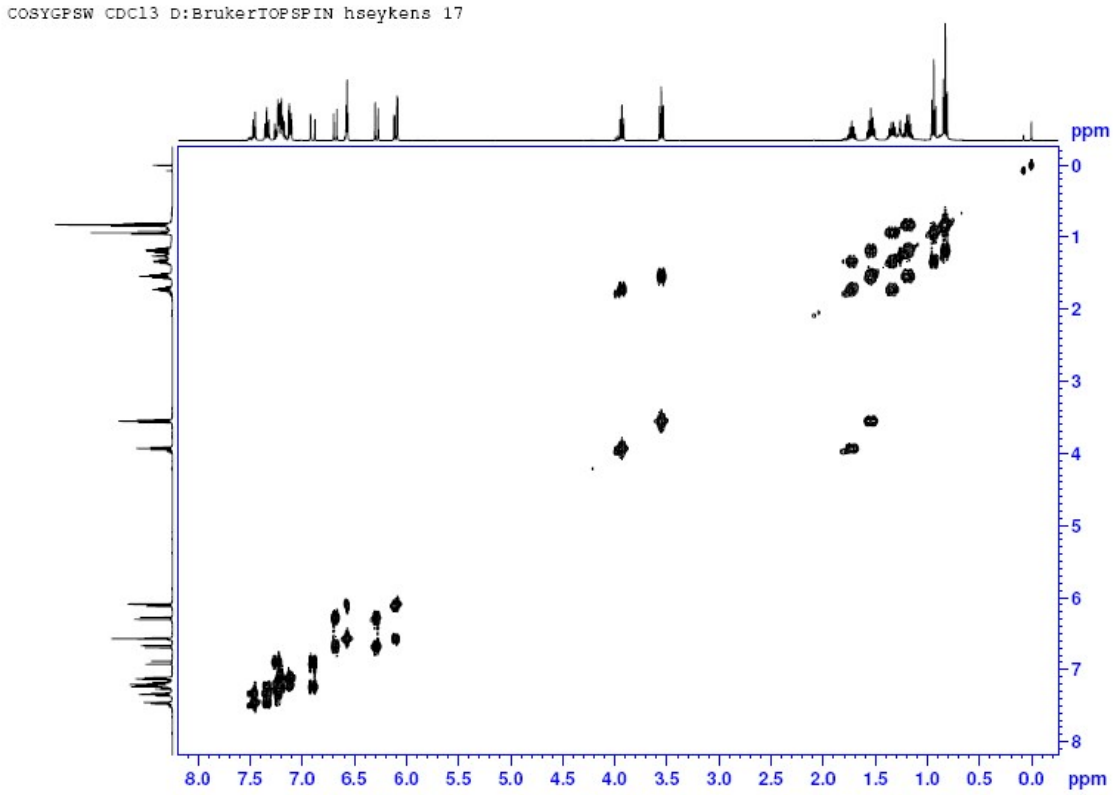
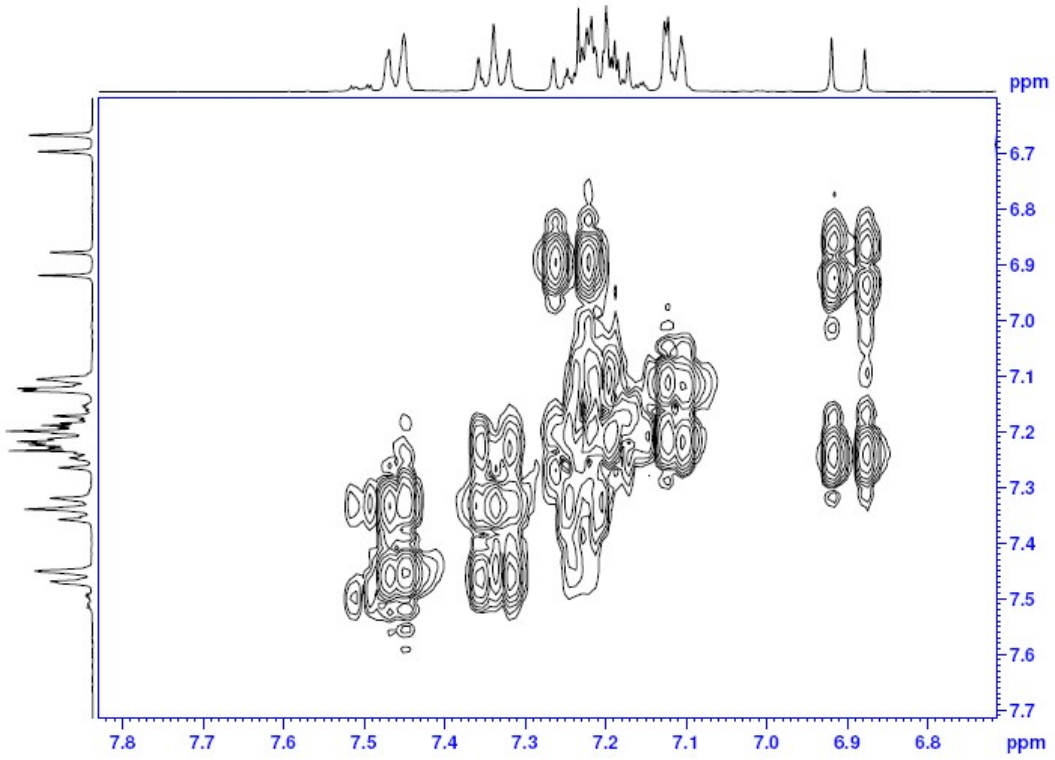


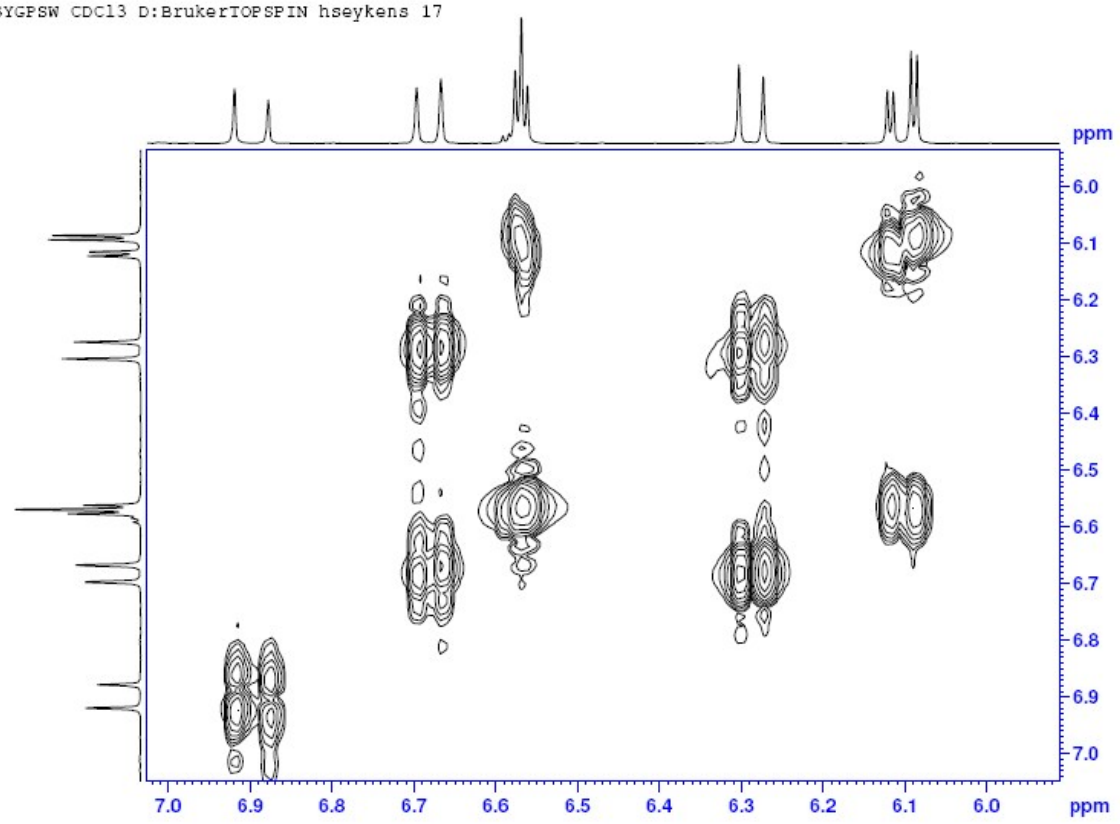
Figure 30. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **6c** (mixture of *E* and *Z*) in $CDCl_3$.


COSYGPSW CDCl3 D:BrukerTOPSPIN hseykens 17
ppm
0
1
2
3
4
5
6
7
8
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

COSYGPSW CDCl3 D:BrukerTOPSPIN hseykens 17



COSYGPSW CDCl3 D:BrukerTOPSPIN hseykens 17



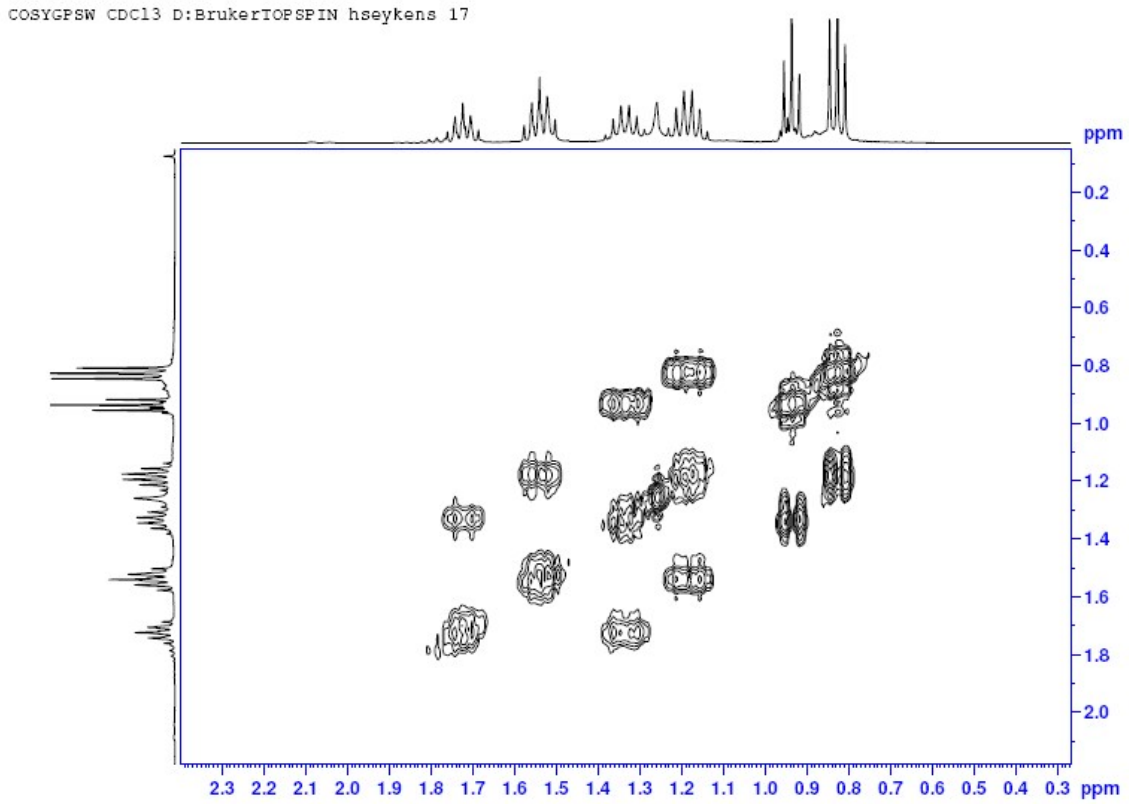
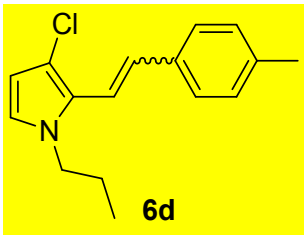
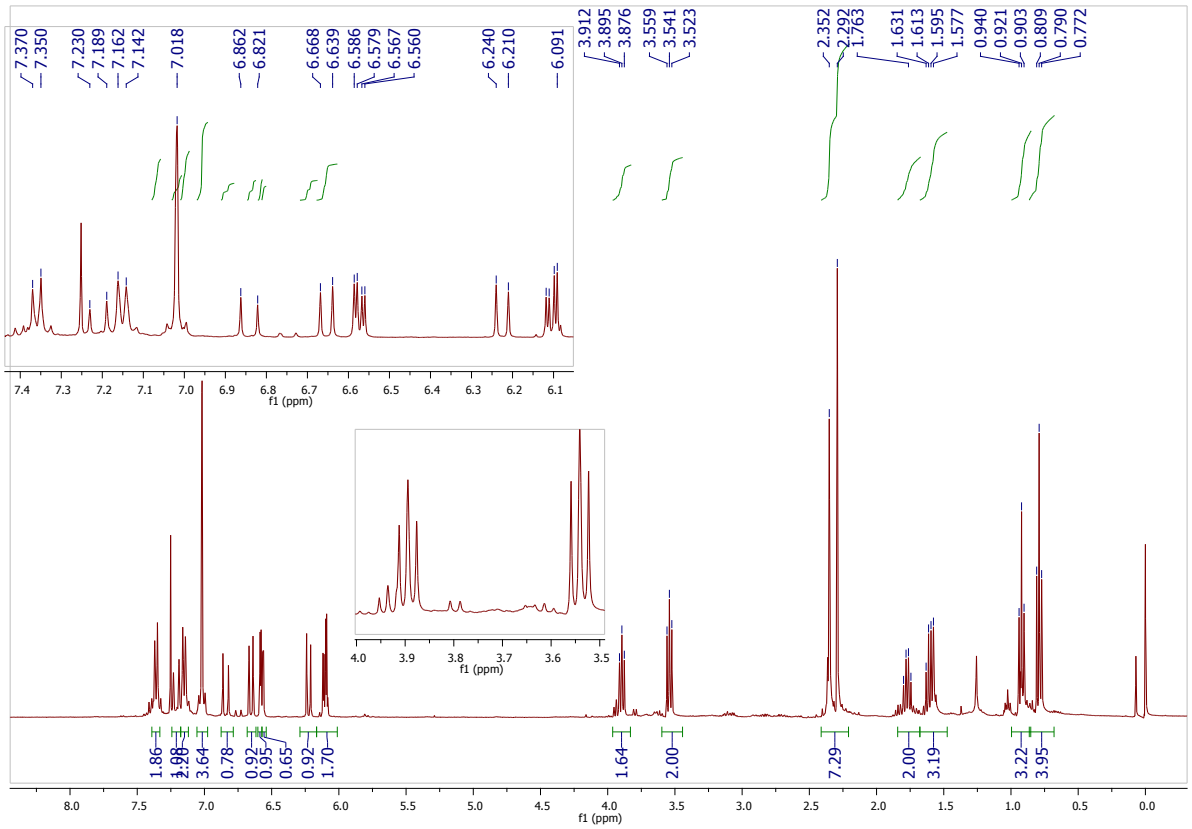
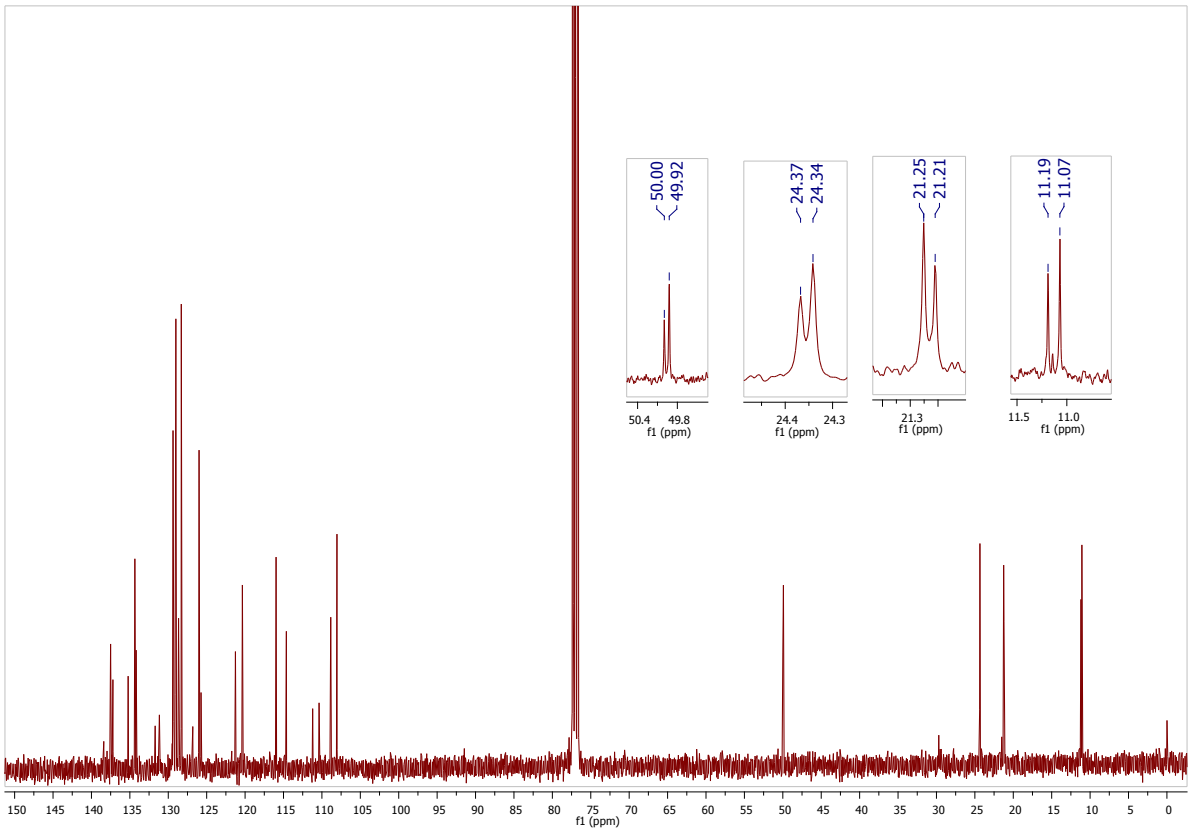


Figure 31. 2D-NMR spectra of **6c** in $CDCl_3$.

(*E/Z*)-3-Chloro-2-(4-methylstyryl)-1-propyl-1*H*-pyrrole (6d)




7.370
7.350
7.230
7.189
7.162
7.142
7.018
6.862
6.821
6.668
6.639
6.586
6.579
6.567
6.560
6.240
6.210
6.091
3.912
3.895
3.876
3.559
3.541
3.523
2.352
2.292
1.763
1.631
1.613
1.595
1.577
0.940
0.921
0.903
0.809
0.790
0.772
1.86
1.08
3.64
0.78
0.92
0.95
0.65
0.92
1.70
1.64
2.00
7.29
2.00
3.19
3.22
3.95
f1 (ppm)


50.00
49.92
24.37
24.34
21.25
21.21
11.19
11.07
f1 (ppm)

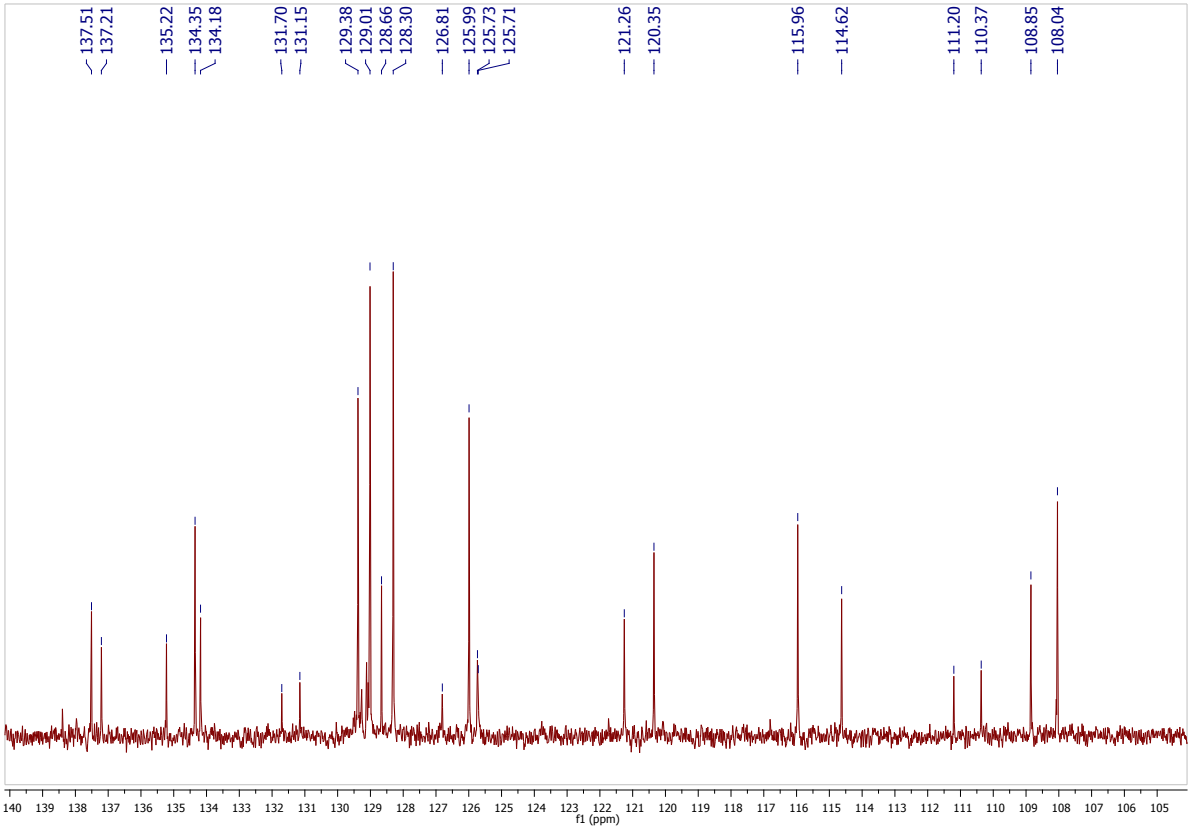
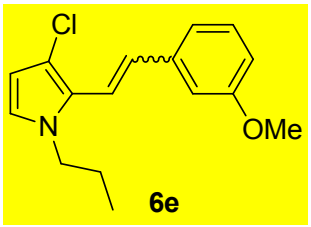
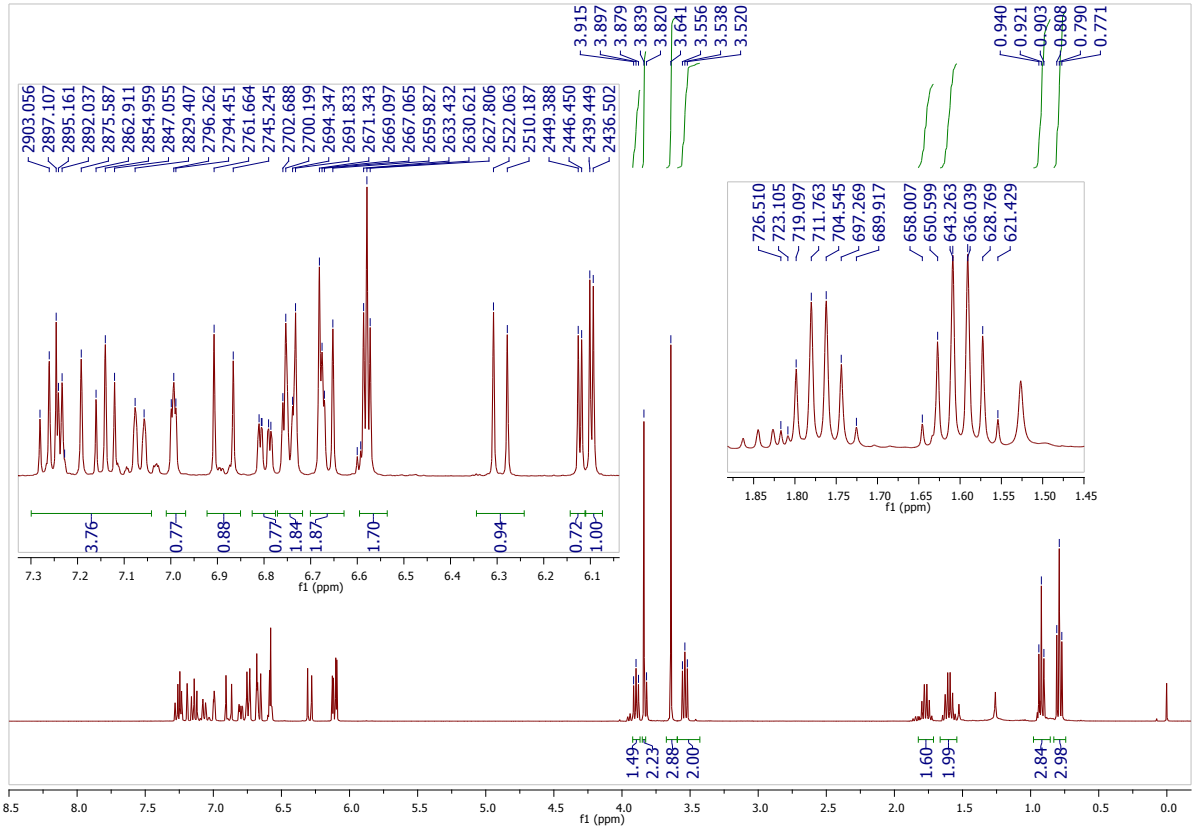
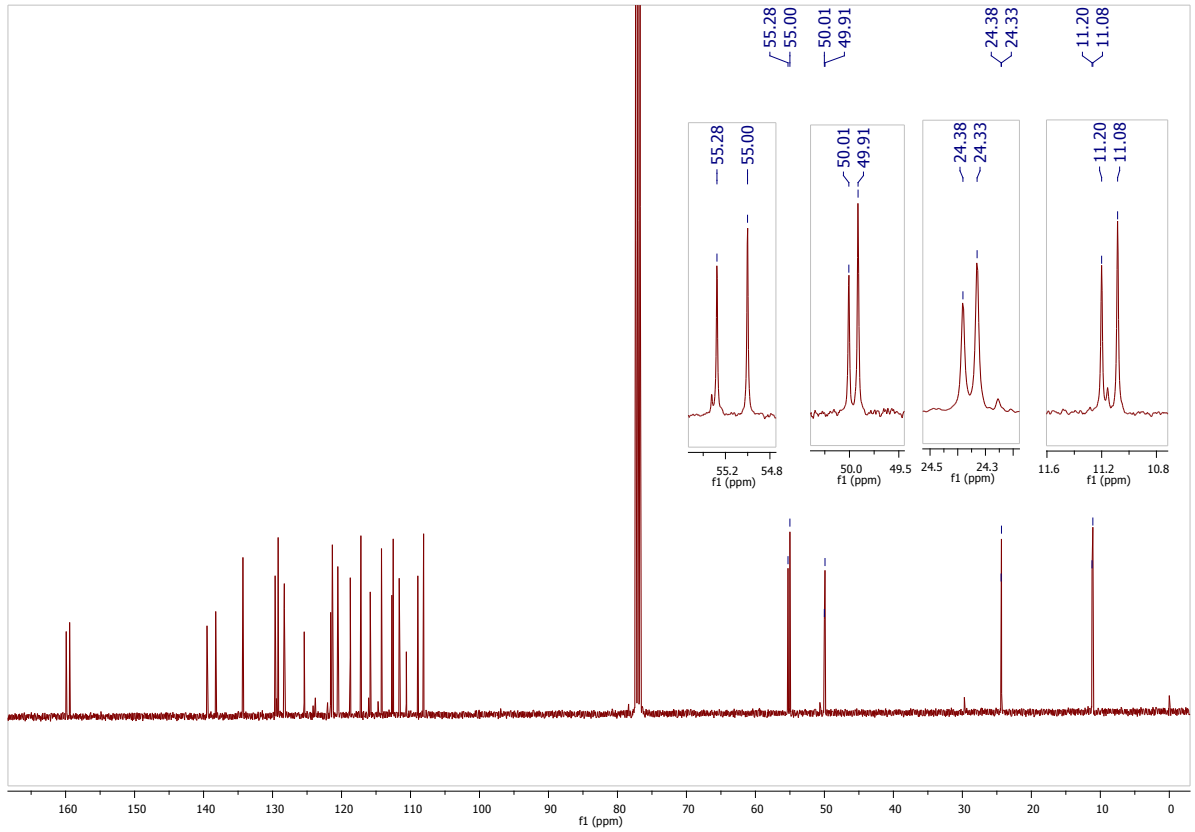


Figure 32. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **6d** in $CDCl_3$.

(*E/Z*)-3-Chloro-2-(3-methoxystyryl)-1-propyl-1*H*-pyrrole (6e)




3.915
3.897
3.879
3.839
3.820
3.641
3.556
3.538
3.520
0.940
0.921
0.903
0.808
0.790
0.771
2903.056
2897.107
2895.161
2892.037
2875.587
2862.911
2854.959
2847.055
2829.407
2796.262
2794.451
2761.664
2745.245
2702.688
2700.199
2694.347
2691.833
2671.343
2669.097
2667.065
2659.827
2633.432
2630.621
2627.806
2522.063
2510.187
2449.388
2446.450
2439.449
2436.502
726.510
723.105
719.097
711.763
704.545
697.269
689.917
658.007
650.599
643.263
636.039
628.769
621.429
3.76
0.77
0.88
0.77
1.84
1.87
1.70
0.94
0.72
1.00
1.49
2.23
2.88
2.00
1.60
1.99
2.84
2.98
f1 (ppm)


55.28
55.00
50.01
49.91
24.38
24.33
11.20
11.08
f1 (ppm)

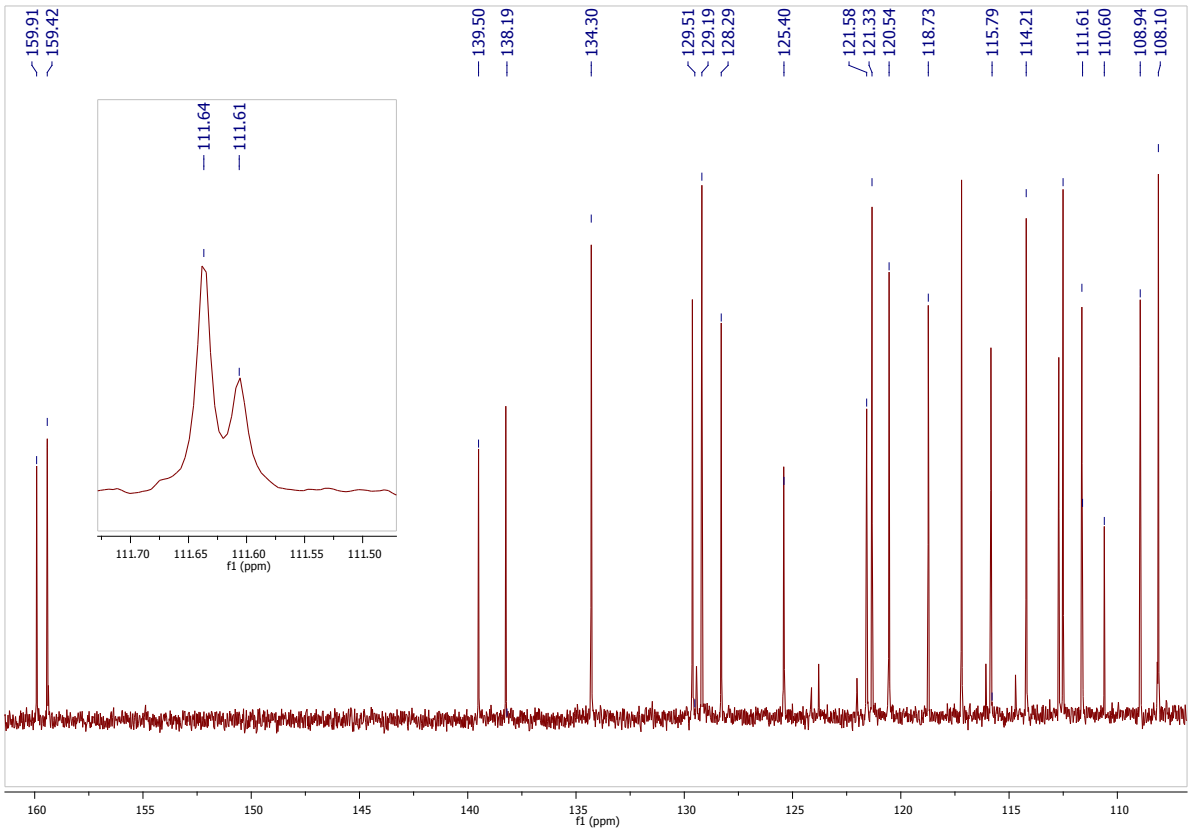
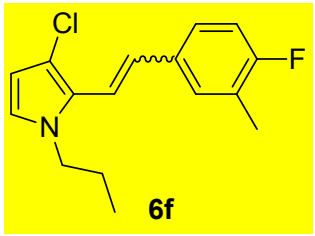
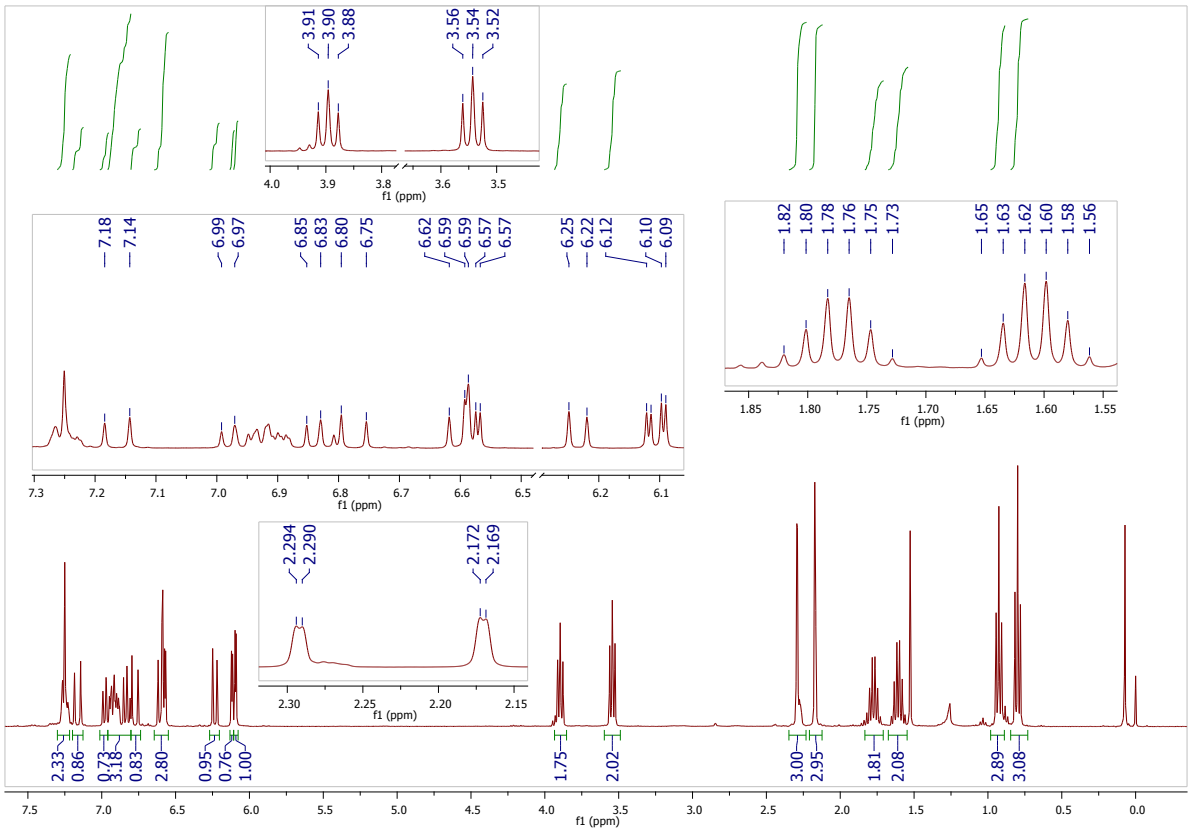
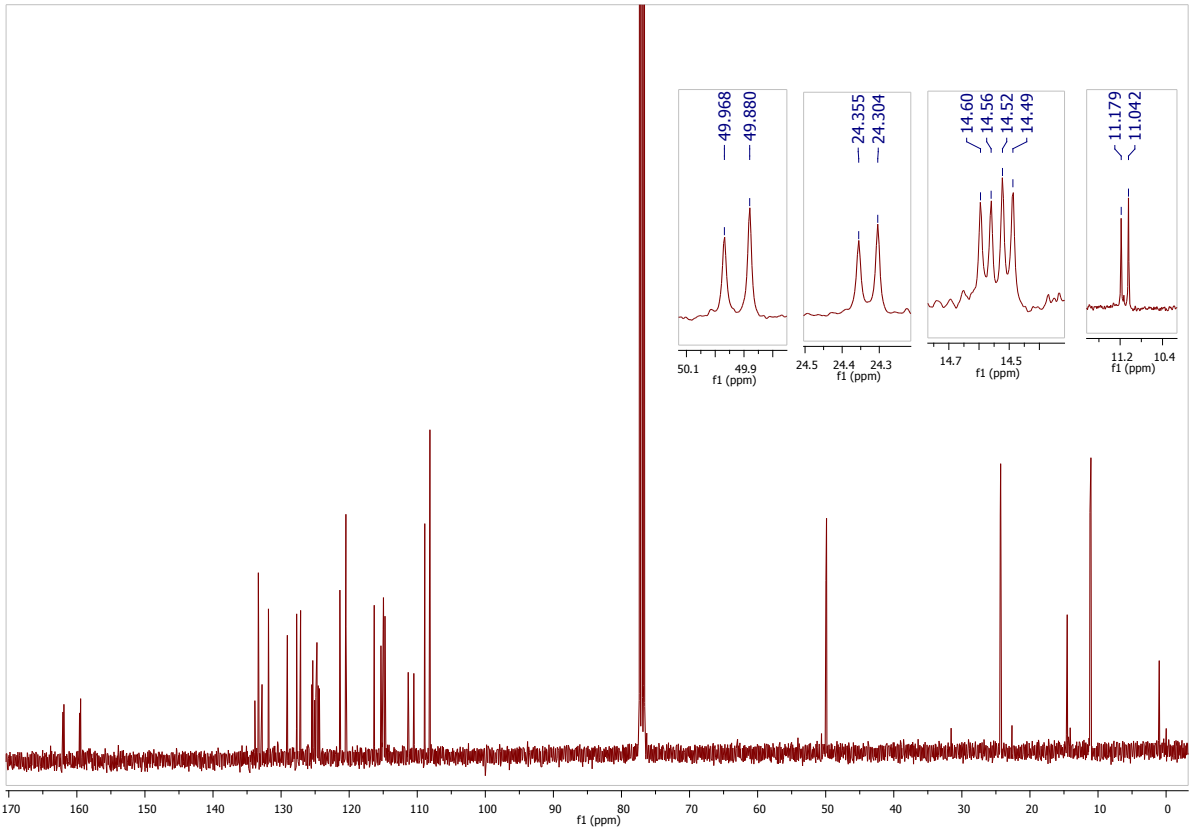


Figure 33. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **6e** in $CDCl_3$.

***E/Z*-(3-Chloro-2-(4-fluoro-3-methylstyryl)-1-propyl-1*H*-pyrrole (6f)**




3.91
3.90
3.88
3.56
3.54
3.52
7.18
7.14
6.99
6.97
6.85
6.83
6.80
6.75
6.62
6.59
6.59
6.57
6.57
6.25
6.22
6.12
6.10
6.09
1.82
1.80
1.78
1.76
1.75
1.73
1.65
1.63
1.62
1.60
1.58
1.56
2.294
2.290
2.172
2.169
2.33
0.86
0.73
3.18
0.83
2.80
0.95
0.76
1.00
1.75
2.02
3.00
2.95
1.81
2.08
2.89
3.08
f1 (ppm)


49.968
49.880
24.355
24.304
14.60
14.56
14.52
14.49
11.179
11.042
f1 (ppm)

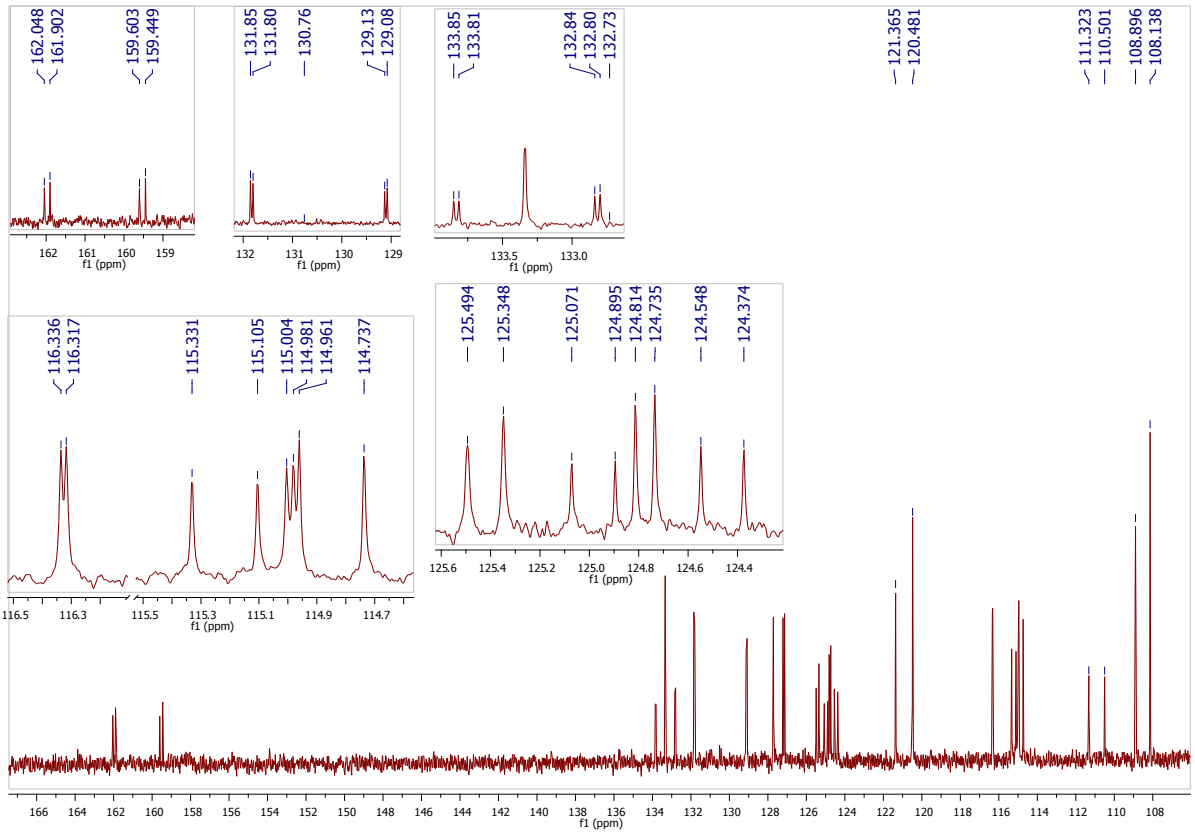
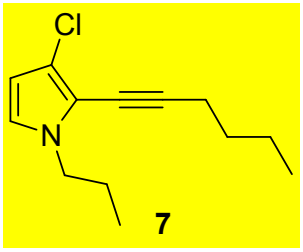


Figure 34. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **6f** in $CDCl_3$.

3-Chloro-2-(hex-1-ynyl)-1-propyl-1*H*-pyrrole (7)



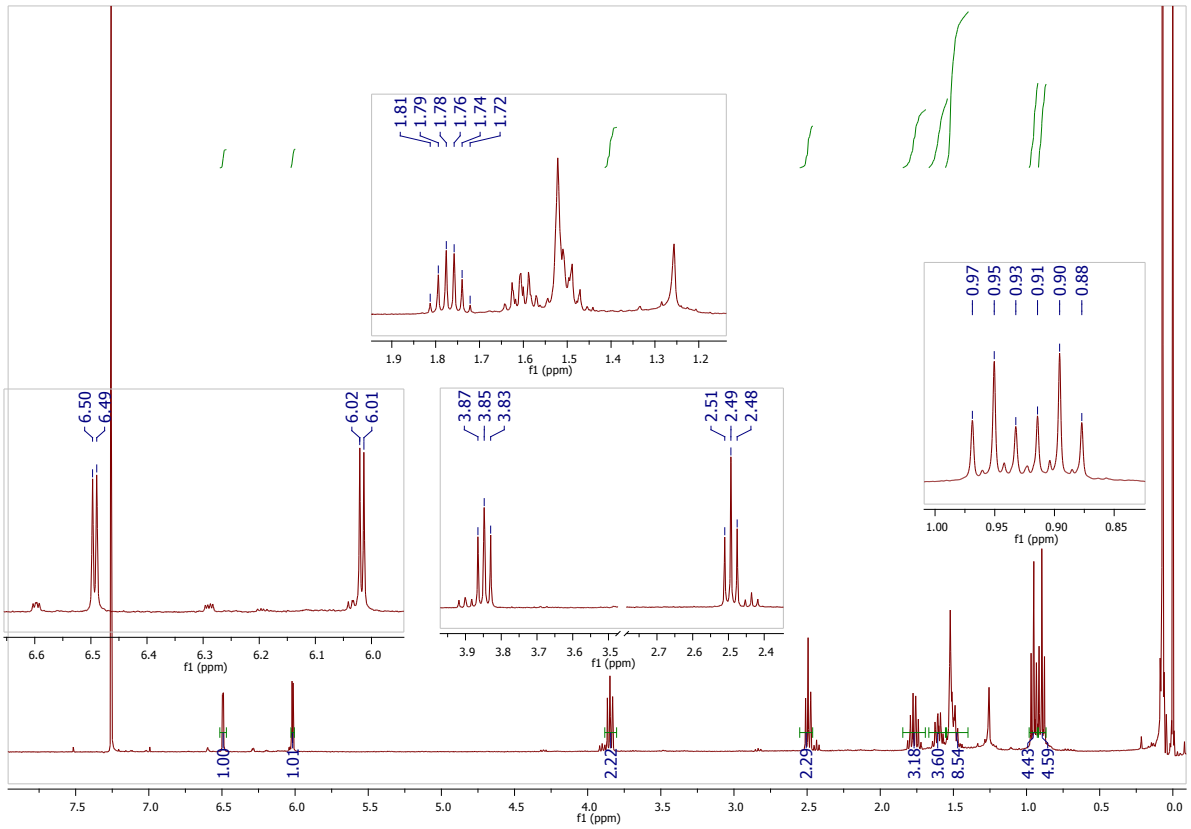
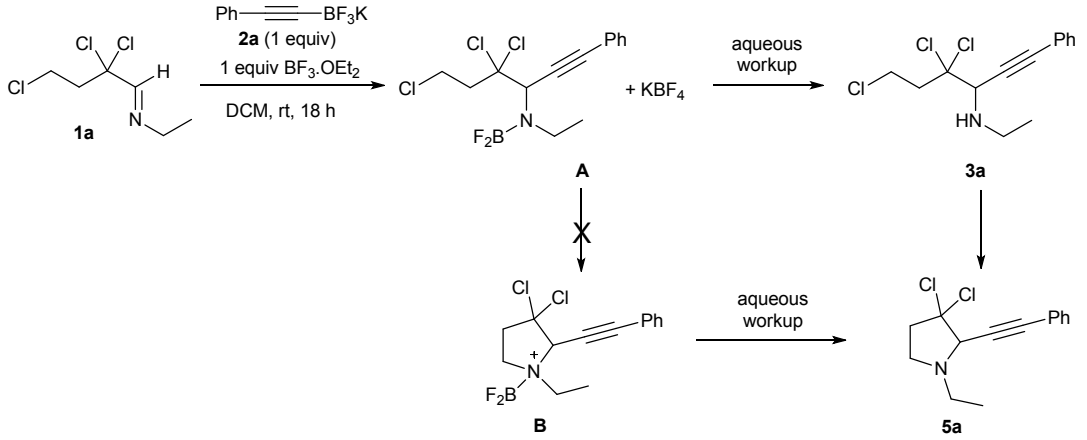


Figure 35. ^{1}H (400 MHz) NMR spectrum of **7** in $CDCl_3$.

5. Mechanistic study for the borontrifluoride mediated reaction of imine with potassium alkynyltrifluoroborate



Scheme 1. Reaction mechanism of the Lewis acid promoted Petasis type reaction of *α,α,ω*-trichloroaldimines with organotrifluoroborates.

In a previous paper from our lab[1] it was established that the reaction of α,α-dichloroaldimines with potassiumtrifluoroborates results in an aminodifluoroborane intermediate which upon aqueous workup gives the *β,β*-dichloroamine. Because a ring closure takes place in the Petasis reaction of *α,α,ω*-trichloroaldimines with trifluoroborates, it would be valuable to establish if the ring closure either occurs during the reaction itself or during the aqueous workup. Since the aminodifluoroborane nitrogen atom is less nucleophilic it is expected that ring closure cannot take place after the addition of the alkyne moiety to the imino carbon. As a consequence the ring closure must occur during the aqueous workup. In order to prove the existence of an intermediate aminodifluoroborane, the reaction mixture obtained after Petasis reaction of *N*-(2,2,4-trichloro-1-butylidene)ethylamine (**1a**), potassium phenylethynyl-trifluoroborate (**2a**) and $BF_3 \cdot OEt_2$, was filtered, evaporated and analysed by ^{1}H, ^{19}F and ^{11}B NMR. The solid, which was filtered off prior to evaporation was shown to be KBF_4 by comparison with a commercially available reference sample. The signals in the ^{1}H NMR ($CDCl_3$) of the filtrate after evaporation were shifted downfield compared to the signals of 3,3-dichloro-2-phenylethynylpyrrolidine (**5a**), pointing to the existence of an aminodifluoroborane intermediate **A**. Especially, the signal at 3.78 ppm is characteristic for a Cl$C\underline{H_2}$ and not a N$C\underline{H_2}$, indicating the presence of non-ring closed Mannich product. These results confirm the earlier stated assumption that first aminodifluoroborane **A** is formed and that ring closure takes only place during aqueous workup. A second experiment was executed to confirm the obtained results. The NMR sample of the filtrate was treated with a few drops

of water and the ^{1}H NMR was recorded again to check if trichlorinated Mannich product **3a** was present. In this case the formation of pyrrolidine **5a** (18%) and **3a** (82%) was observed. The presence of the latter was interpreted by an upfield shift of all the NMR-signals compared to the signals of aminodifluoroborane **A** (striking shift for CCl_2CHN from 5.00 ppm (**A**) to 4.80 ppm (**3a**)). Scheme 1 depicts the reaction mechanism of the Lewis acid mediated borono Mannich type reaction of α,α,ω-trichloroaldimines **1** with organotrifluoroborates **2**. First, aminodifluorborane **A** is formed which after aqueous workup is turned into the trichlorinated propargylic amine **3a**. Subsequently, an intramolecular nucleophilic substitution of the ω-chloro atom by the amine nitrogen atom of **3a** leads to pyrrolidine **5a**.

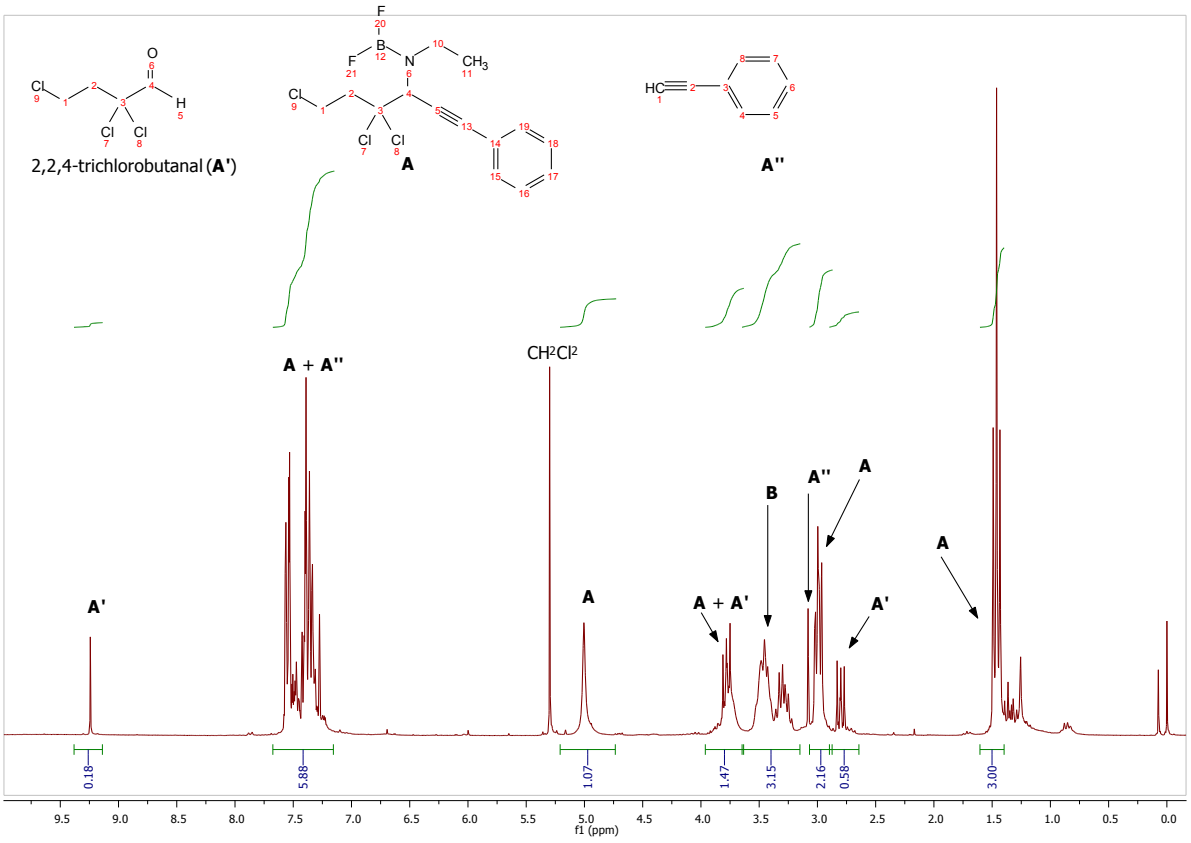


Figure 36. ^{1}H (400 MHz) NMR spectra of intermediate A in $CDCl_3$.

6. Mechanistic study for the In(OTf)$_3$ catalyzed reaction of imine with phenylacetylene

To prove that ring closure takes place during the alkynylation, a reaction was carried out between imine (**1b**) and phenylacetylene (2 equiv) in the presence of In(OTf)$_3$ (0.25 equiv) in CH_2Cl_2 at 50 °C for 18 h. This reaction mixture was evaporated *in vacuo* and its ^{1}H NMR was measured. The mass spectrum of the reaction mixture showed a [M+H$^+$] peak at 282 indicating the formation of the pyrrolidine ring during the reaction, while the absence of a

peak at 318 excludes the trichlorinated open chain intermediate (Figure 37). The ^{1}H NMR spectrum (Figure 38) also suggests the formation of a pyrrolidine ring, either complexed with the Lewis acid or in the form of a hydrochloride salt (X = H or $In(OTf)_3$; Figure 39, triplet at 1.03, multiplet at 1.94-1.83, multiplets at 2.96-3.13 & 3.45 ppm). A very broad peak around 5 ppm accounts for the NC*H*CCl_2 proton and this downfield shift, compared to the NC*H*CCl_2 proton (4.11 ppm) of **5b** (Figure 10) is indicative for a positively charged nitrogen atom. A comparison was made of this spectrum with the ^{1}H NMR of an independently prepared sample of the hydrochloride of pyrrolidine **5b** (Figure 39). Since both spectra are not the same, it can be concluded that most probably pyrrolidine **5b** formed a complex with $In(OTf)_3$ during the reaction.

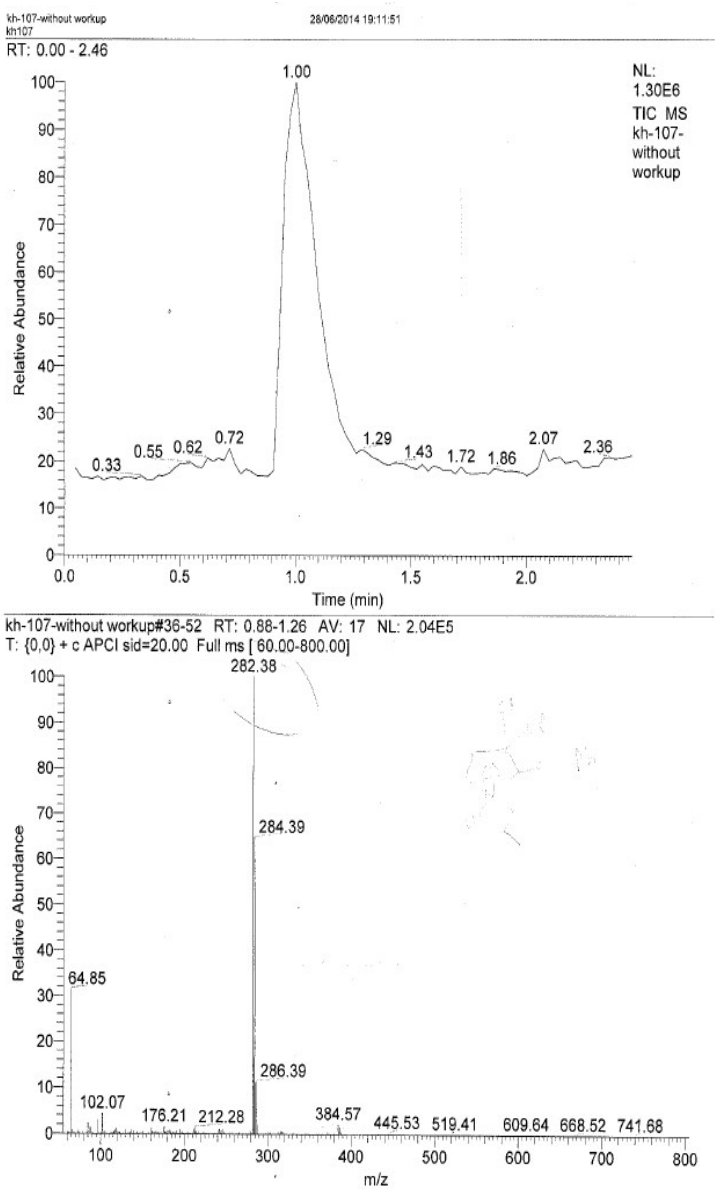


Figure 37. Mass spectrum of reaction mixture.

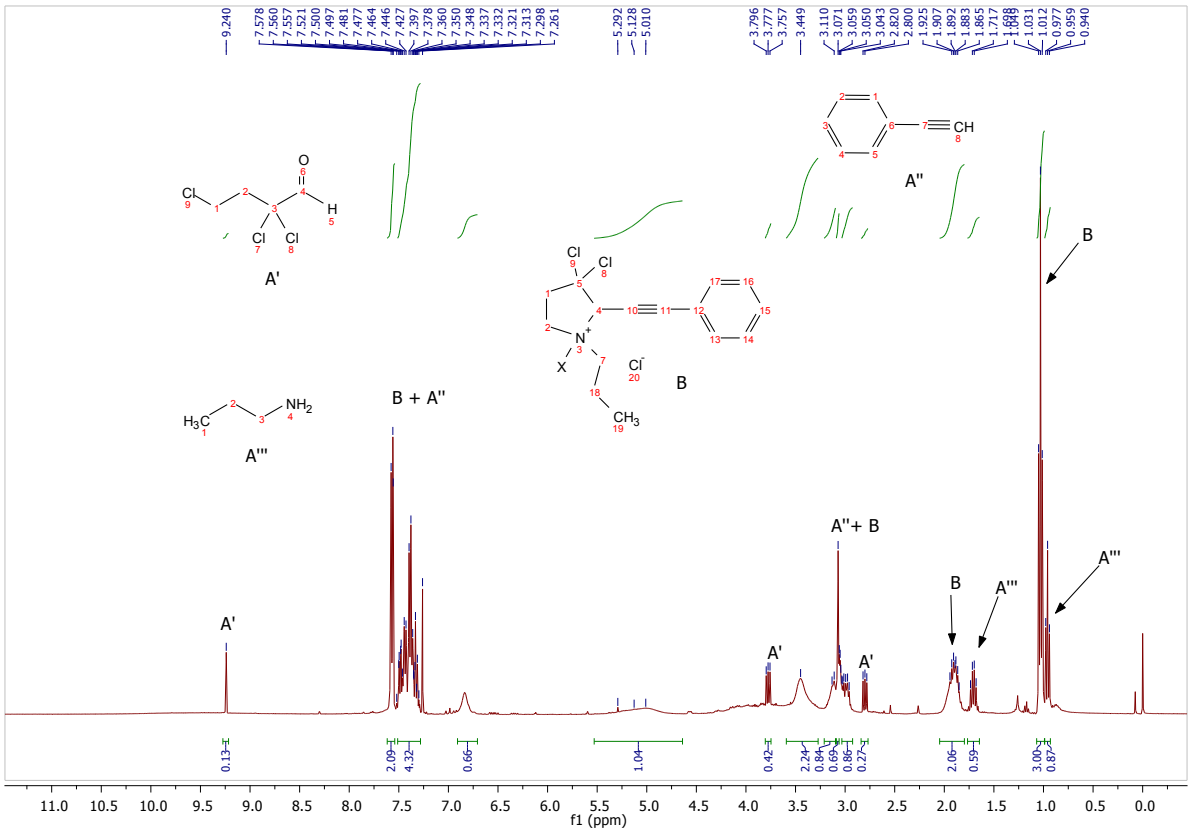


Figure 38. ^{1}H (400 MHz) NMR spectra of reaction mixture in $CDCl_3$.

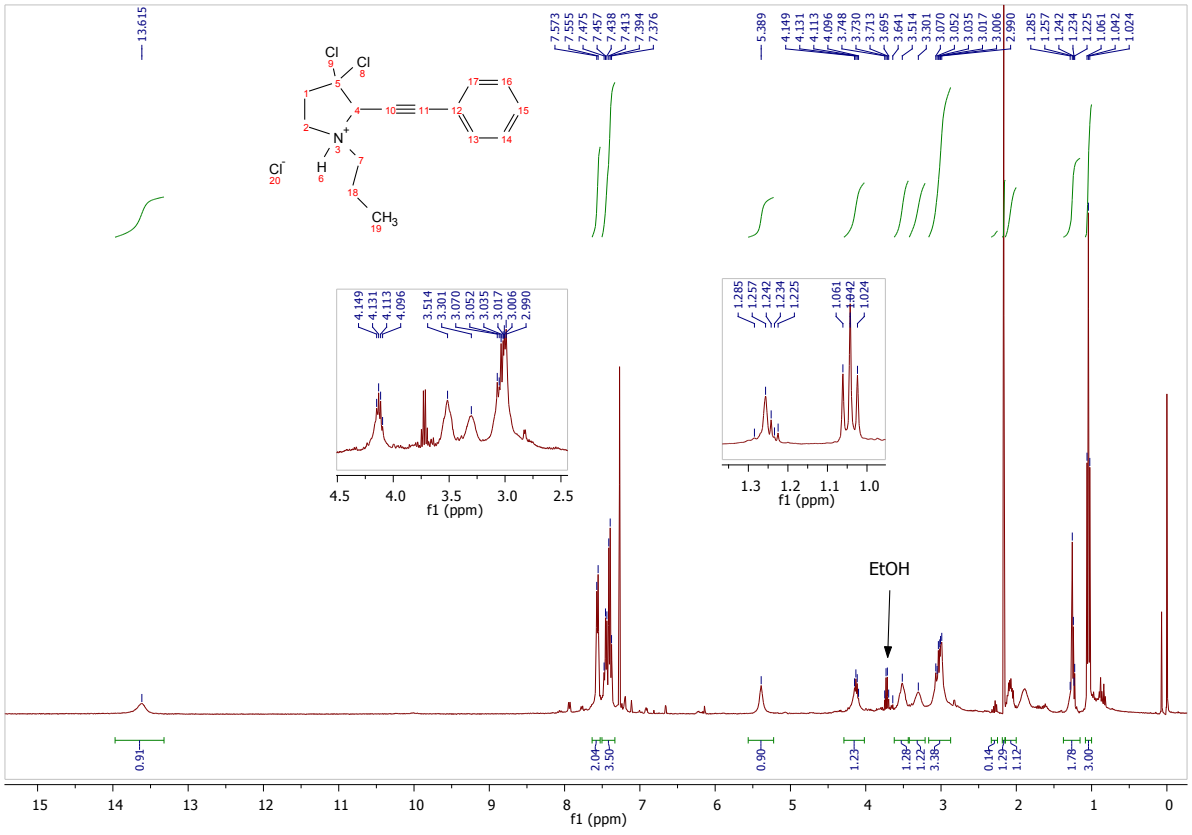
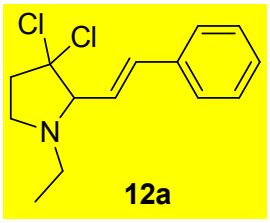
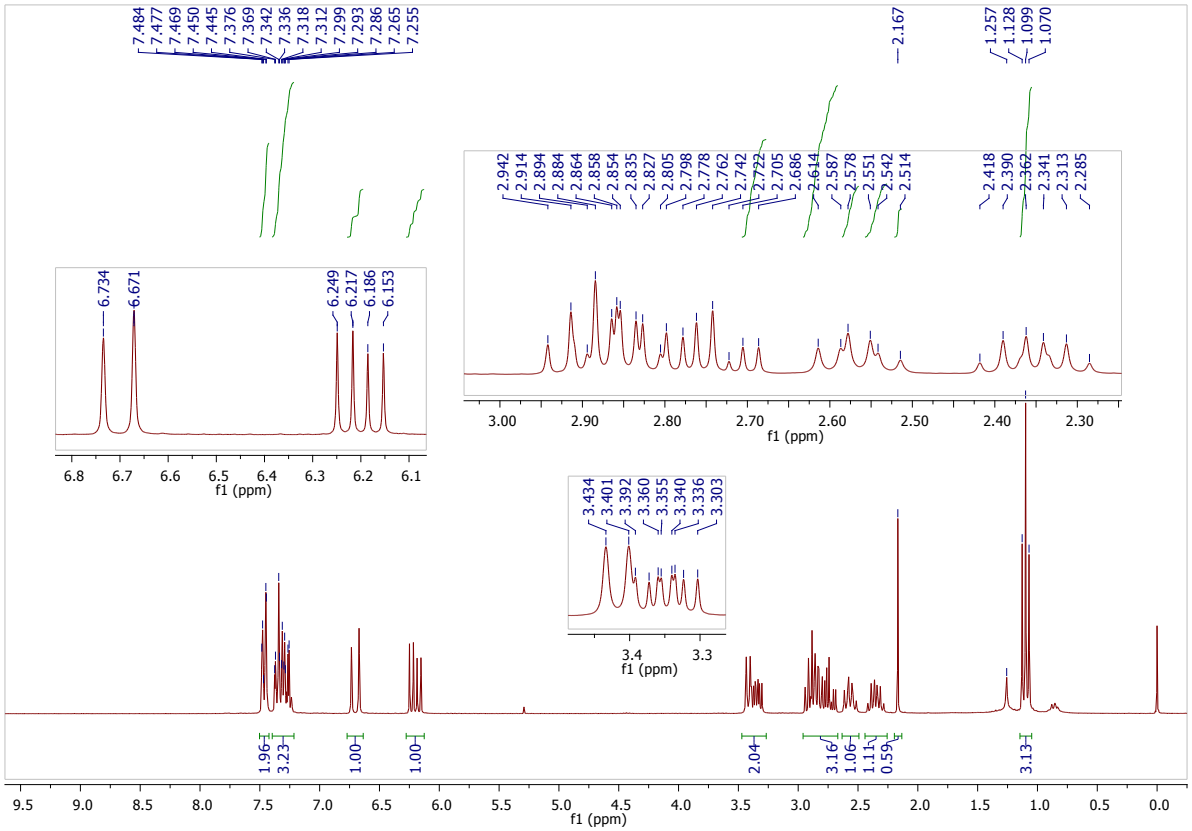


Figure 39. ^{1}H (400 MHz) NMR spectra of hydrochloride salt of pyrrolidine **5b** in $CDCl_3$.

7. Copies of ^{1}H and ^{13}C spectra of 3,3-dichloro-1-ethyl-2-(2-phenylvinyl)pyrrolidine (12a)





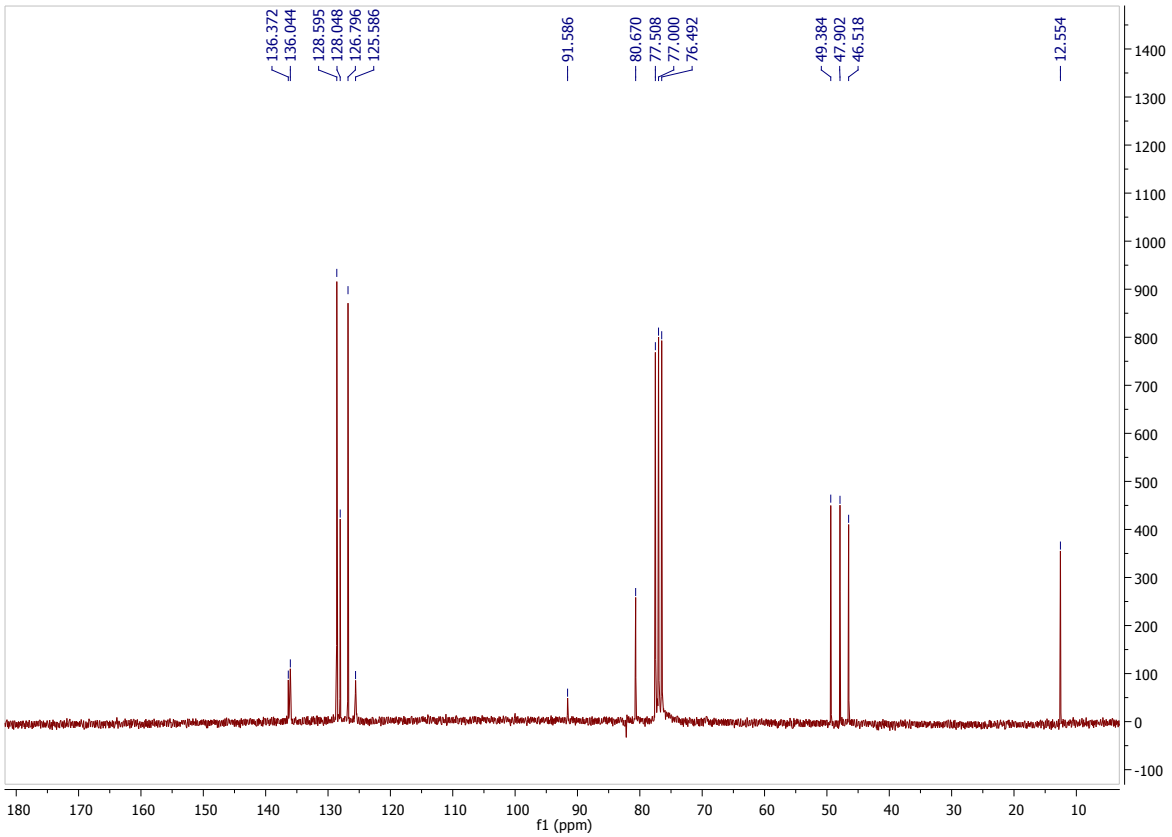
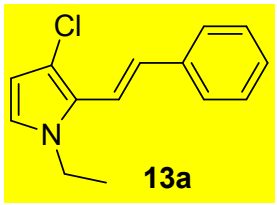


Figure 40. ^{1}H (250 MHz) and ^{13}C (63 MHz) NMR spectra of **12a** in $CDCl_3$.

8. Copies of ^{1}H and ^{13}C Spectra of 13a and 14a

3-Chloro-1-ethyl-2-(2-phenylvinyl)-1*H*-pyrrole (13a)



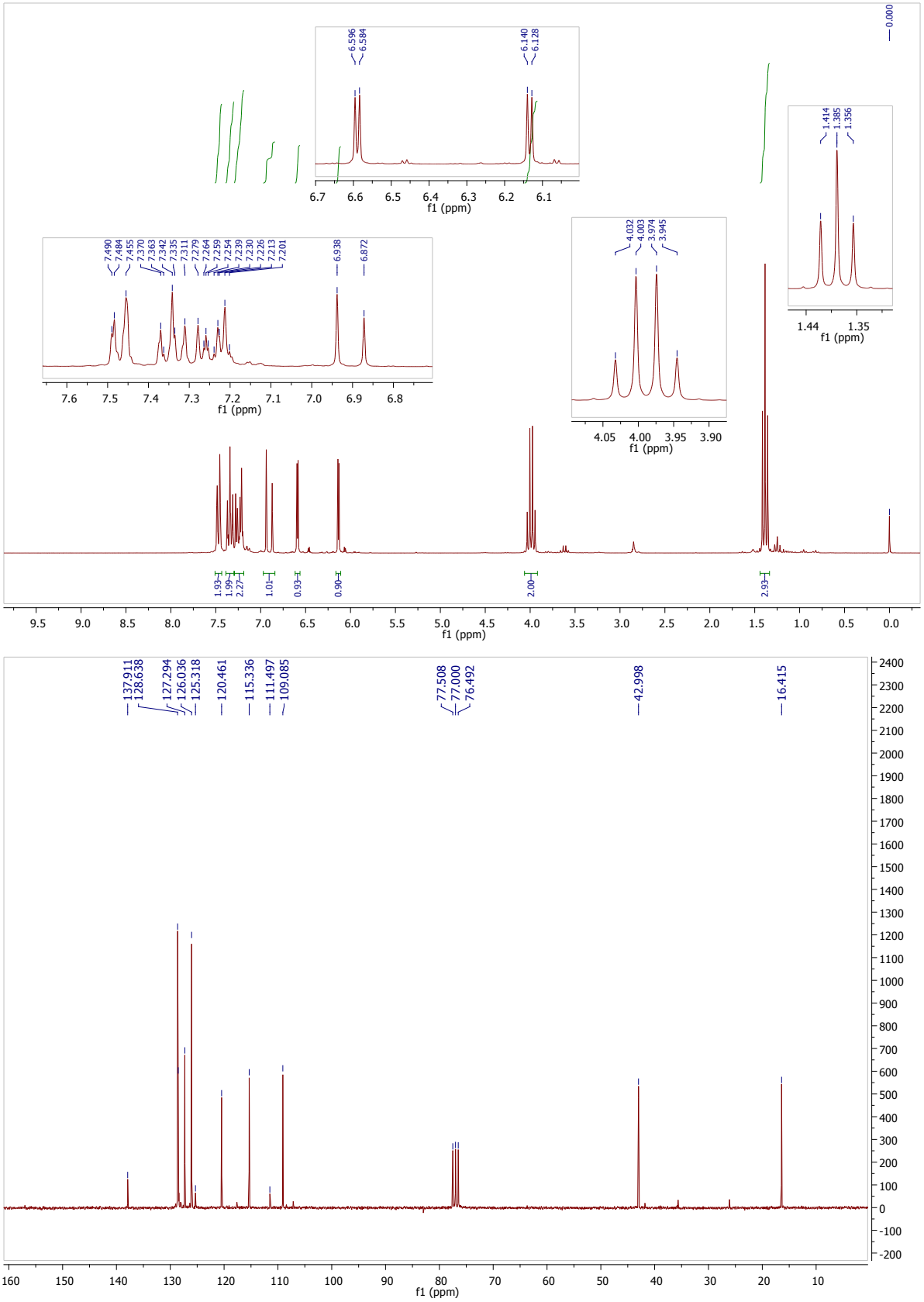
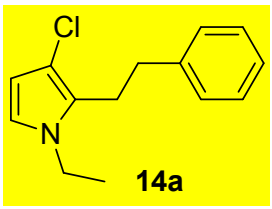
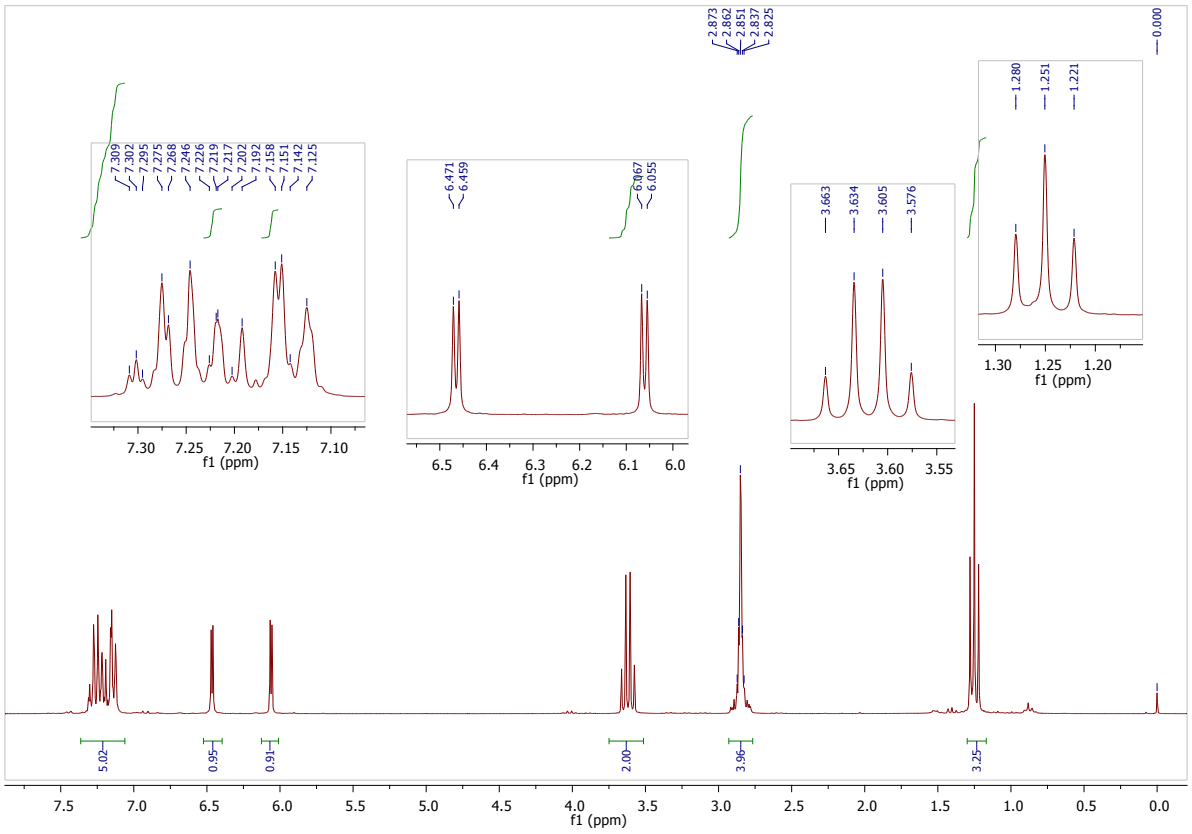


Figure 41. ^{1}H (250 MHz) and ^{13}C (63 MHz) NMR spectra of **13a** in $CDCl_3$.

3-Chloro-1-ethyl-2-(2-phenylethyl)-1*H*-pyrrole (14a)





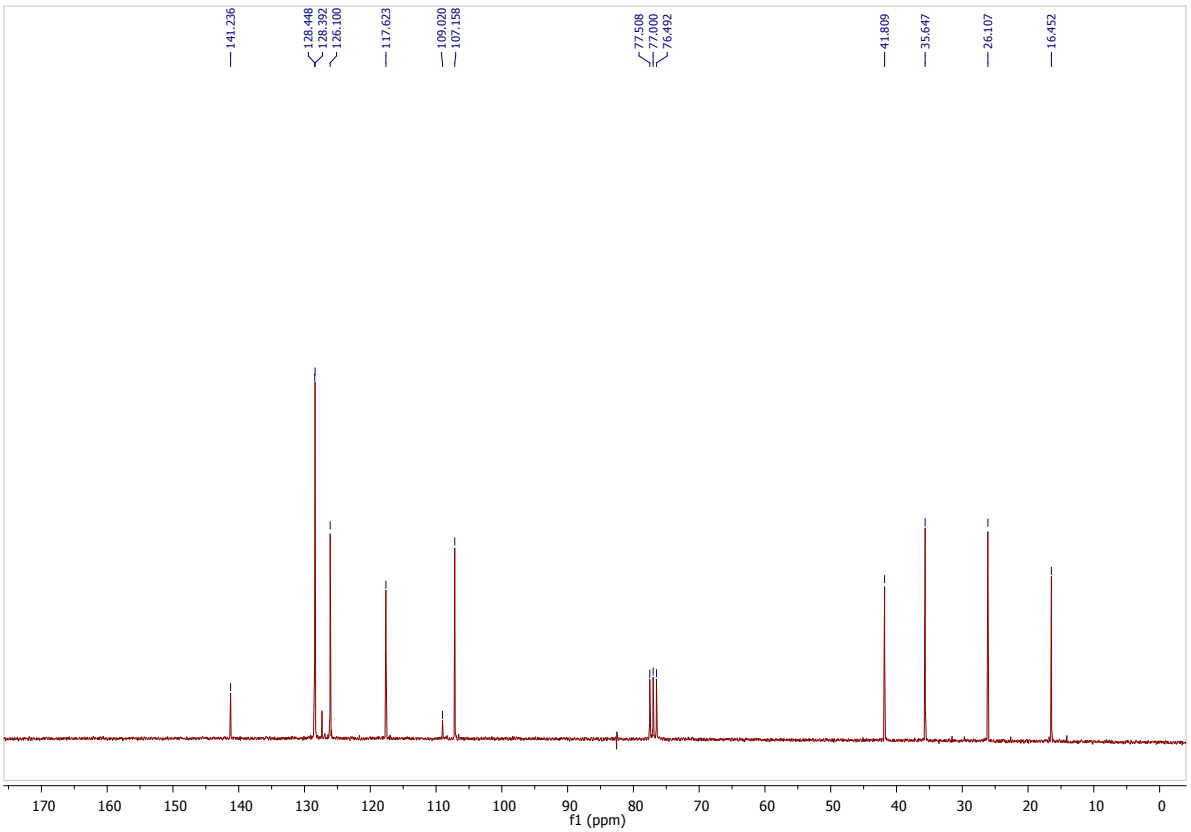


Figure 42. ^{1}H (250 MHz) and ^{13}C (63 MHz) NMR spectra of **14a** in $CDCl_3$.

9. References

1. (a) K. K. Nanda and B. W. Trotter, *Tetrahedron Lett.*, 2005, **46**, 2025; (b) C. Cativiella, J. I. García, J. A. Mayoral and L. Salvatella, *Can. J. Chem.*, 1994, **72**, 308. (c) H. C. Brown, E. J. Mead and C. J. Shoaf, *J. Am. Chem. Soc.*, 1956, **78**, 3613; (d) D. Vuluga, J. Legros, B. Crousse, A. M. Z. Slawin, C. Laurence, P. Nicolet and D. Bonnet-Delpon, *J. Org. Chem.*, 2011, **76**, 1126-1133; (e) C. C. Malakar, S. Stas, W. Herrebout and K. Abbaspour Tehrani, *Chem. Eur. J.*, 2013, **19**, 14263; (f) G. A. Price, A. K. Brisdon, K. R. Flower, R. G. Pritchard and P. Quayle, *Tetrahedron Lett.*, 2014, **55**, 151.
2. C. C. Malakar, B. U. W. Maes and K. Abbaspour Tehrani, *Adv. Synth. Catal.*, 2012, **354**, 3461.