Access to *N*-Thioalkenyl and *N*-(*o*-Thio)aryl-benzimidazol-2-ones by Ring Opening of Thiazolobenzimidazolium or Benzimidazobenzothiazolium Salts and C-O Bond Cleavage of an Alkoxide

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Supporting Information

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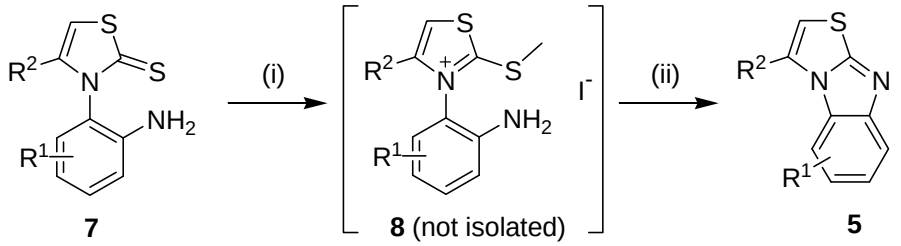
Sequence leading to thiazolobenzimidazoles **5** starting from thiazoline-2-thiones **7**

Thiazoline-2-thiones **7** were treated with an excess of iodomethane in acetone to afford quantitatively the corresponding thiazolium salts **8**. At this stage, it is interesting to note that due to the very high nucleophilicity of the sulphur atom, no methylation occurred on the amino group. After evaporation of solvent and unreacted methyl iodide, the crude was refluxed in methanol. The intramolecular nucleophilic attack of the amino group at the thiazolium moiety led to the cyclization into thiazolo[3,2-a]benzimidazolium iodide by elimination of methanethiol. The free thiazolo[3,2-a]benzimidazoles **5** were then isolated after treatment with an aqueous solution of $NaHCO_3$ and extraction in dichloromethane (Table A).



7 **5**

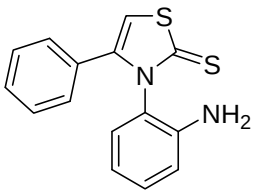
Entry	**5**	R^1	R^2	Overall yield (%)
1	**5a**[1]	H	Me	100
2	**5i**[1]	H	*t*Bu	100
3	**5k**	H	Ph	69
4	**5l**	H	4-fluorophenyl	91
5	**5m**	H	4-chlorophenyl	86
6	**5n**	H	4-methoxyphenyl	55
7	**5o**	H	2-naphthyl	33
8	**5p**[2]	7-fluoro	Me	73
9	**5q**[2]	6-trifluoromethyl	Me	83

[a] Reagents and conditions: (i) MeI, acetone, r.t.; (ii) MeOH, reflux.

Table A. Synthesis of thiazolo[3,2-a]benzimidazoles **5**[a]

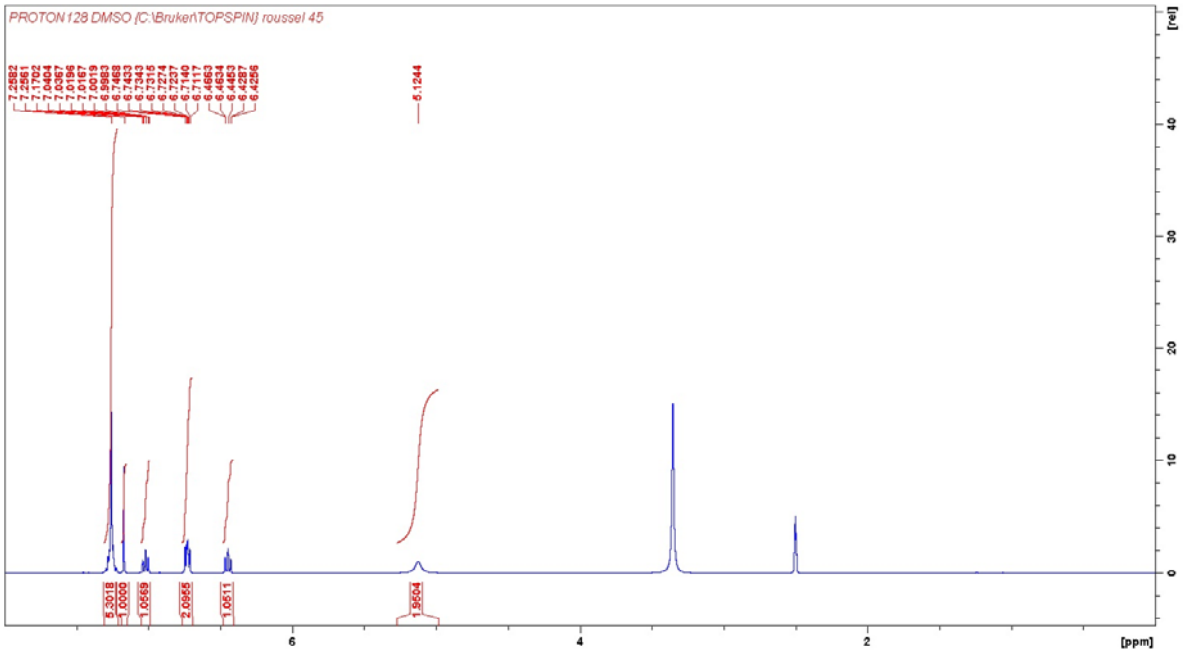
[1] Roussel, C.; Andreoli, F.; Roman, M.; Hristova, M.; Vanthuyne, N. *Molecules* **2005**, *10*, 327.
[2] For experimental procedures and characterization data see: Roussel, C.; Andreoli, F.; Vanthuyne, N. International Patent WO 2010/052670 A1, May 14, 2010. Copies of ^{1}H NMR and ^{13}C NMR spectra for compounds **5p-q** and **7p-q** are given latter in this supporting information.

NMR analyses

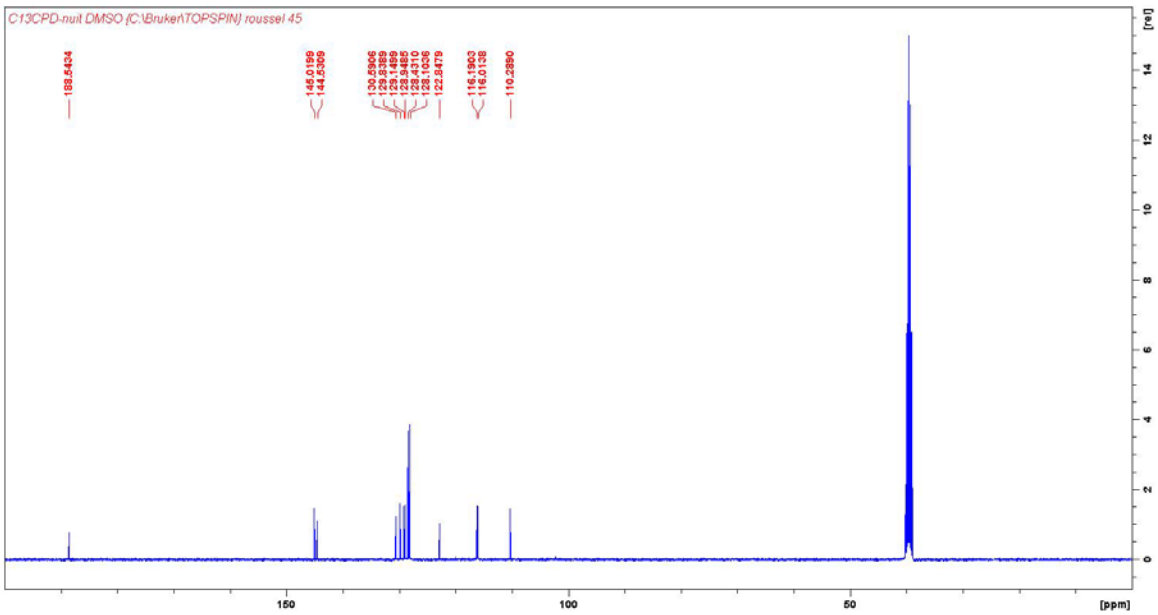


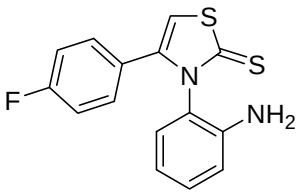
3-(2-Aminophenyl)-4-phenyl-1,3-thiazole-2(3*H*)-thione **7k**

^{1}H NMR (DMSO-*d6*, 400 MHz) spectrum



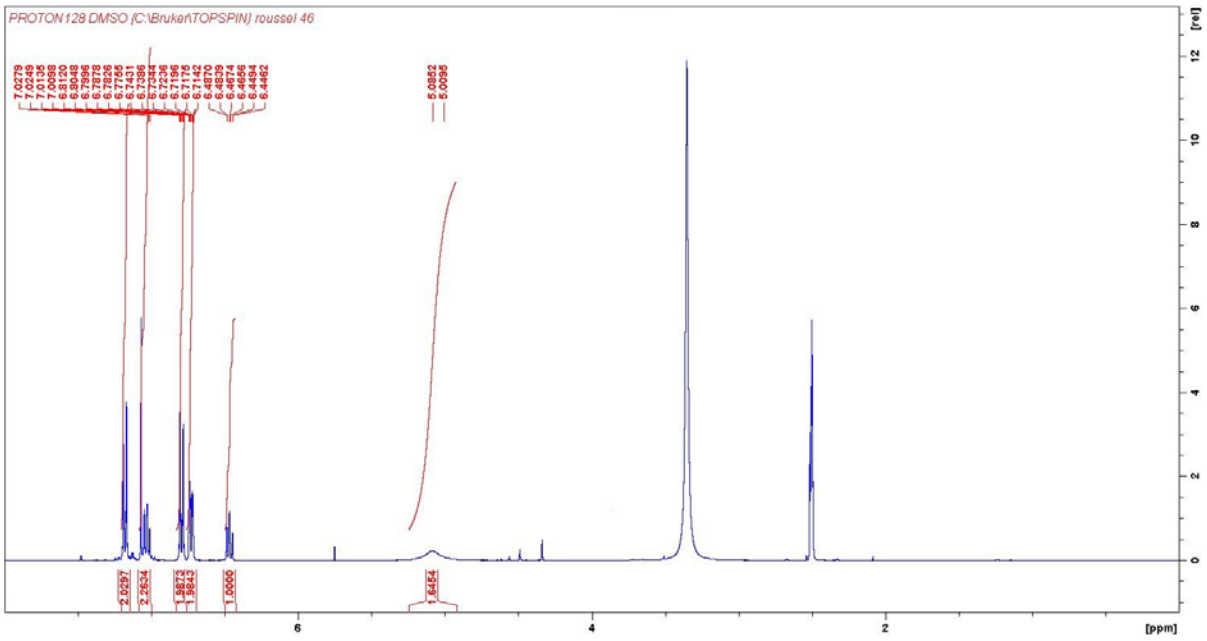
^{13}C NMR (DMSO-*d6*, 100 MHz) spectrum



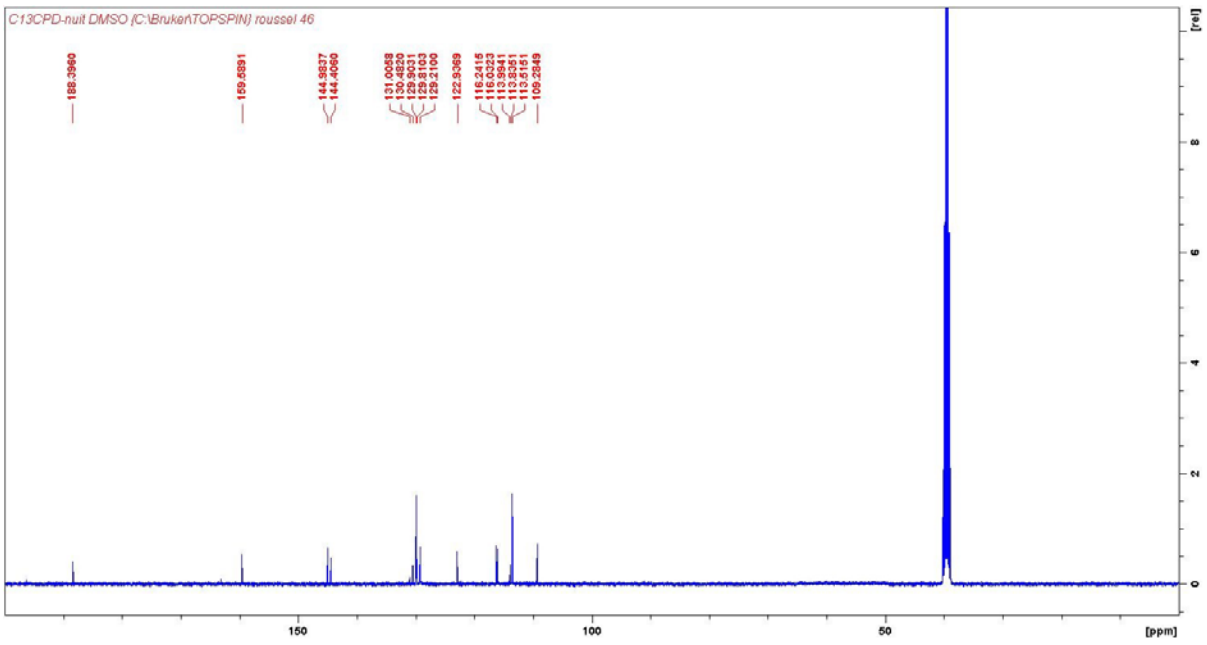


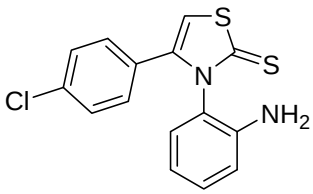
3-(2-Aminophenyl)-4-(4-fluorophenyl)-1,3-thiazole-2(3*H*)-thione **7l**

^{1}H NMR (DMSO-*d6*, 400 MHz) spectrum



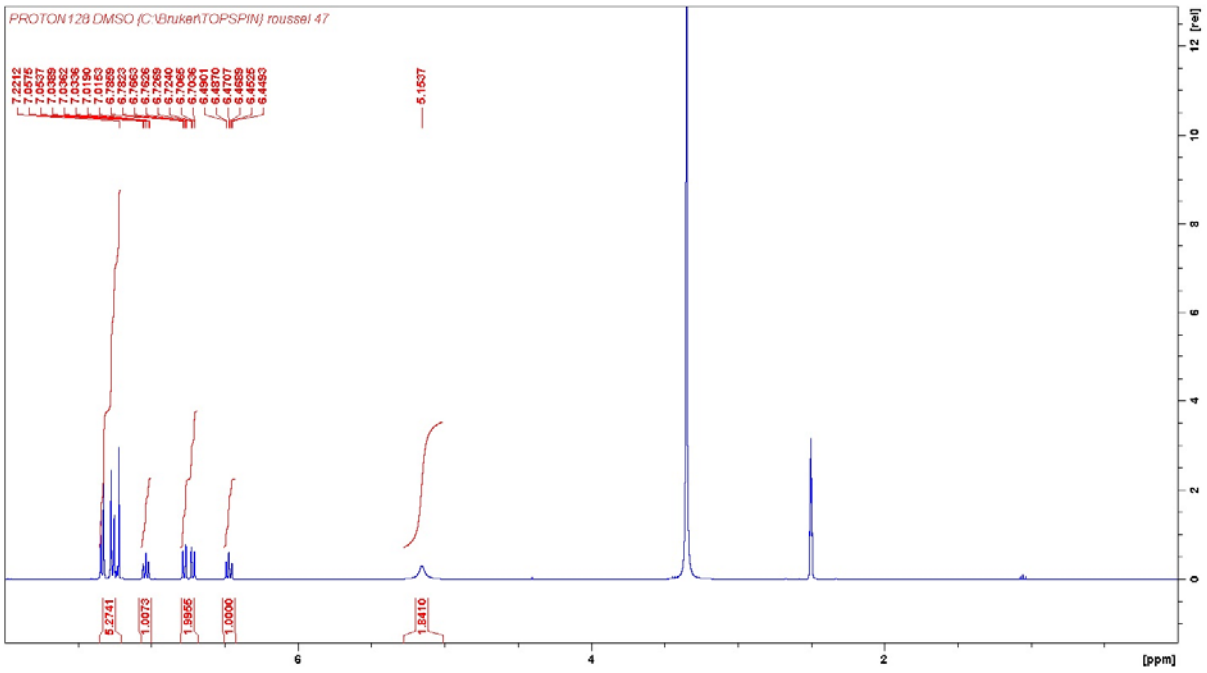
^{13}C NMR (DMSO-*d6*, 100 MHz) spectrum



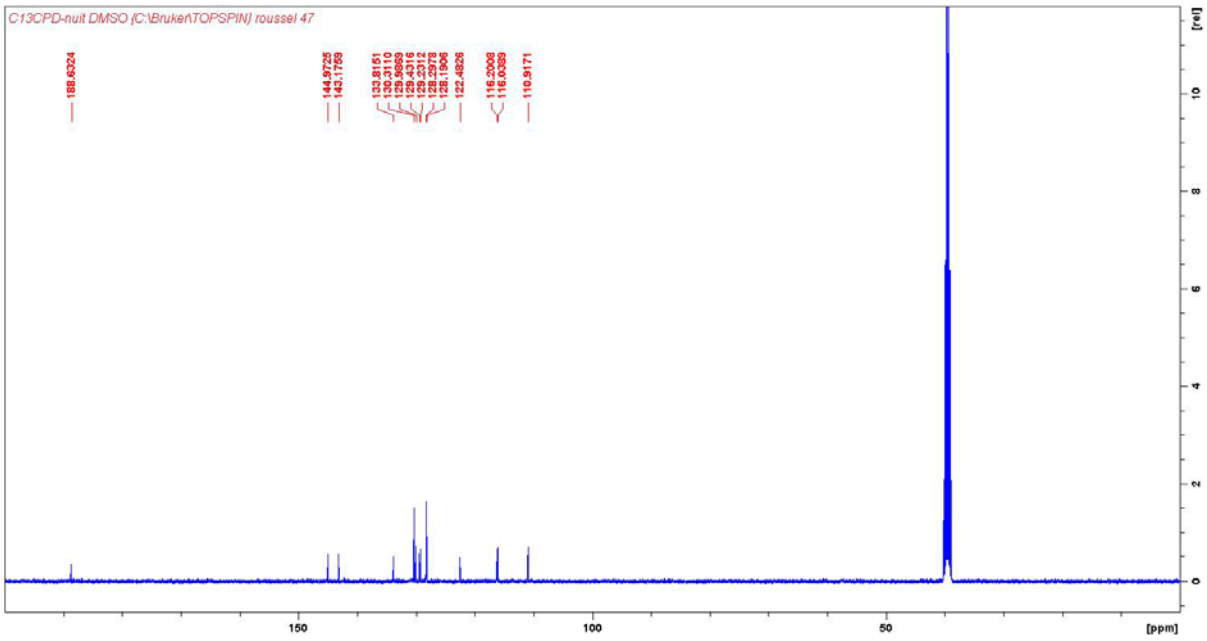


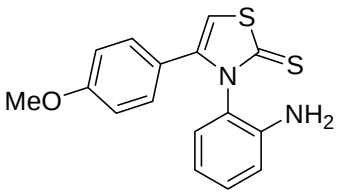
3-(2-Aminophenyl)-4-(4-chlorophenyl)-1,3-thiazole-2(3*H*)-thione **7m**

^{1}H NMR (DMSO-*d6*, 400 MHz) spectrum



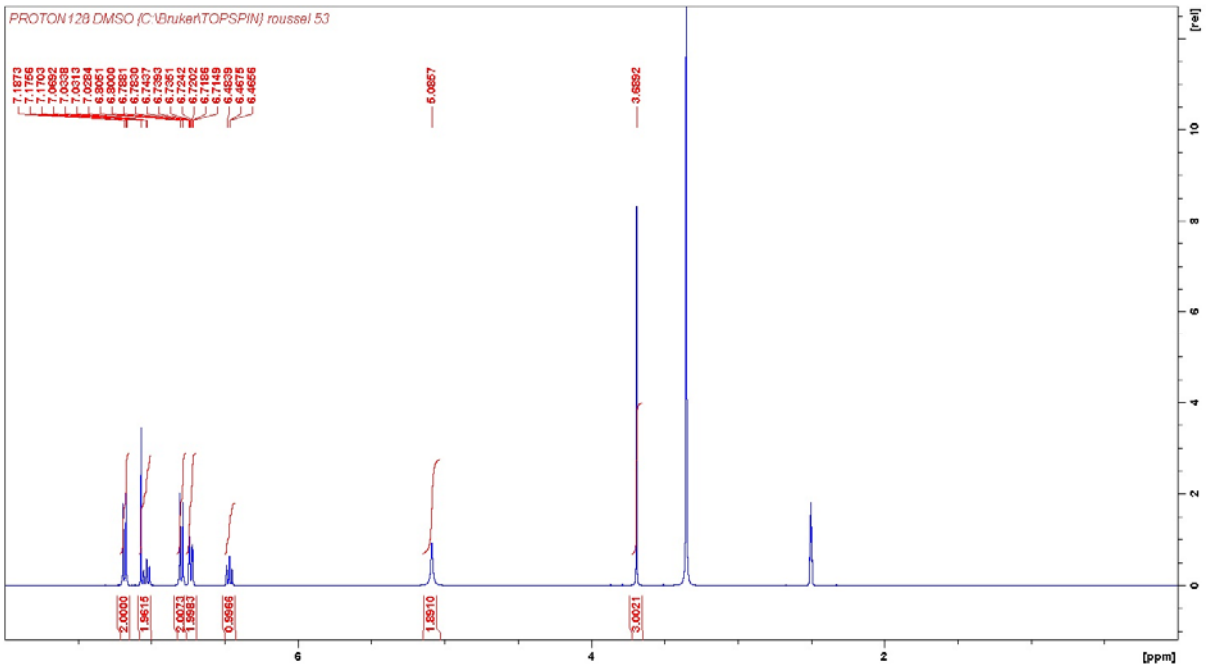
^{13}C NMR (DMSO-*d6*, 100 MHz) spectrum



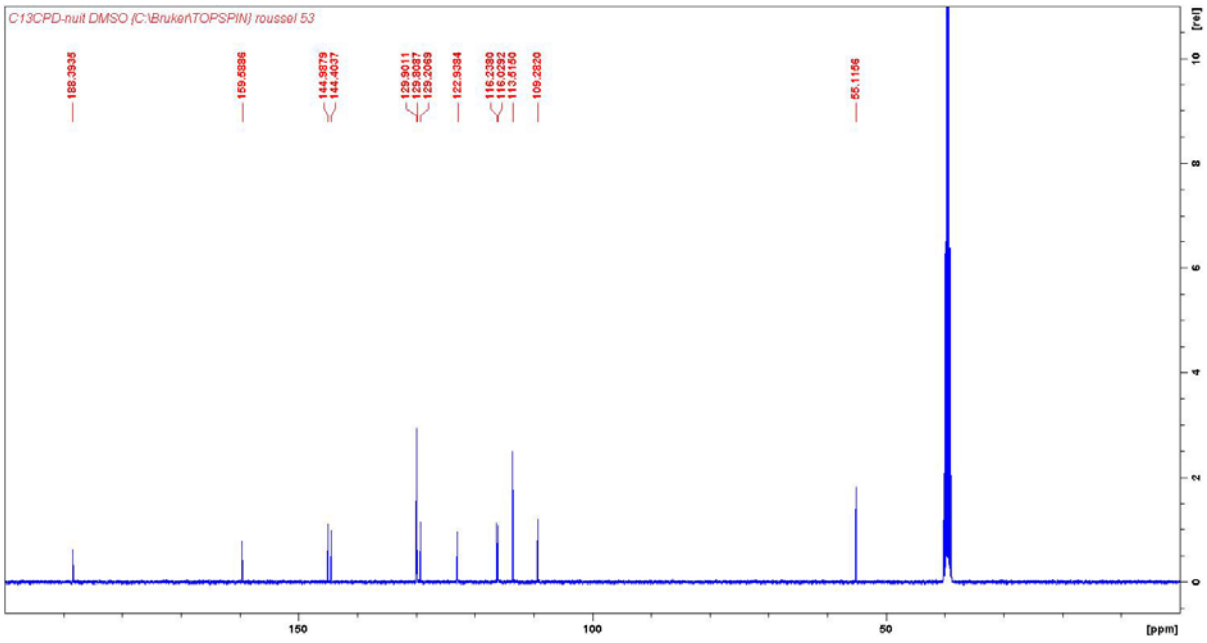


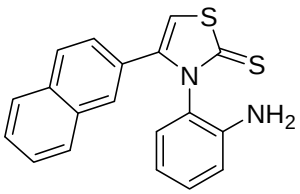
3-(2-Aminophenyl)-4-(4-methoxyphenyl)-1,3-thiazole-2(3*H*)-thione **7n**

^{1}H NMR (DMSO-*d6*, 400 MHz) spectrum



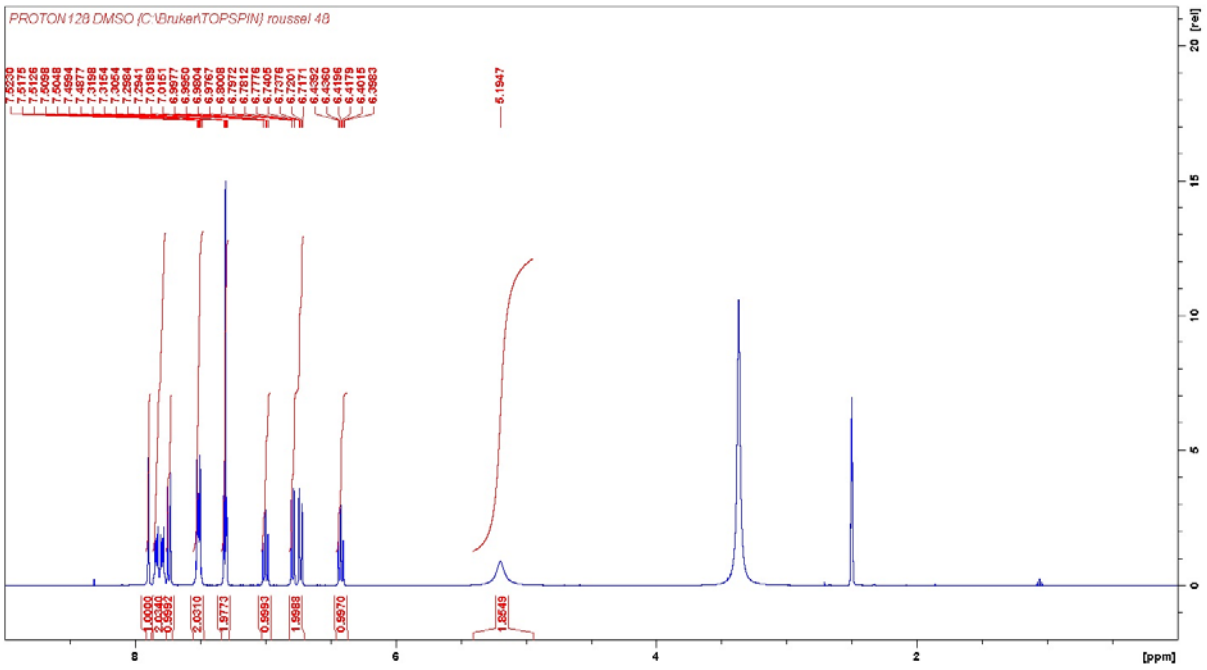
^{13}C NMR (DMSO-*d6*, 100 MHz) spectrum



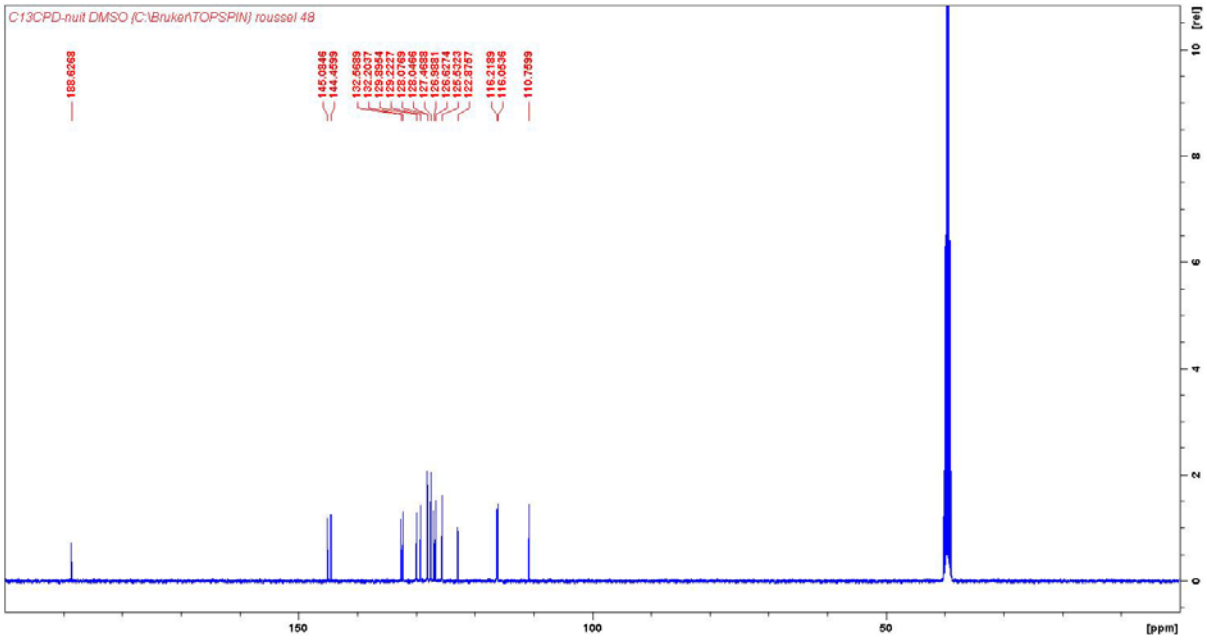


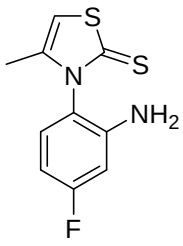
3-(2-Aminophenyl)-4-(naphthalen-2-yl)-1,3-thiazole-2(3*H*)-thione **7o**

^{1}H NMR (DMSO-*d6*, 400 MHz) spectrum



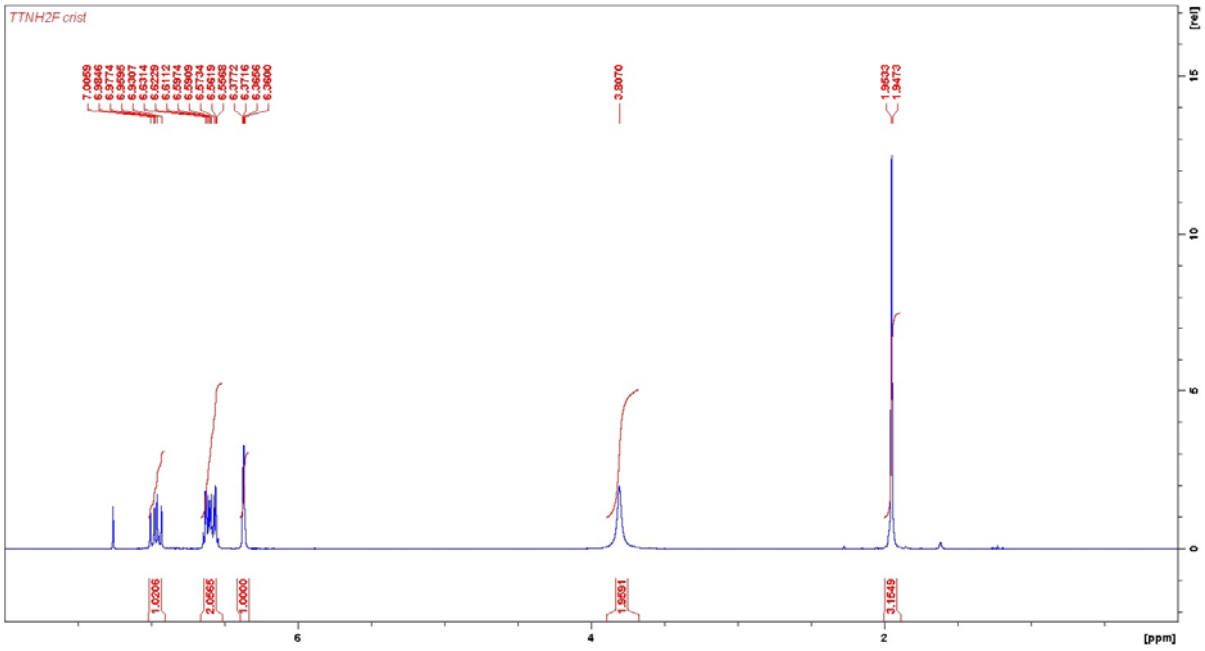
^{13}C NMR (DMSO-*d6*, 100 MHz) spectrum



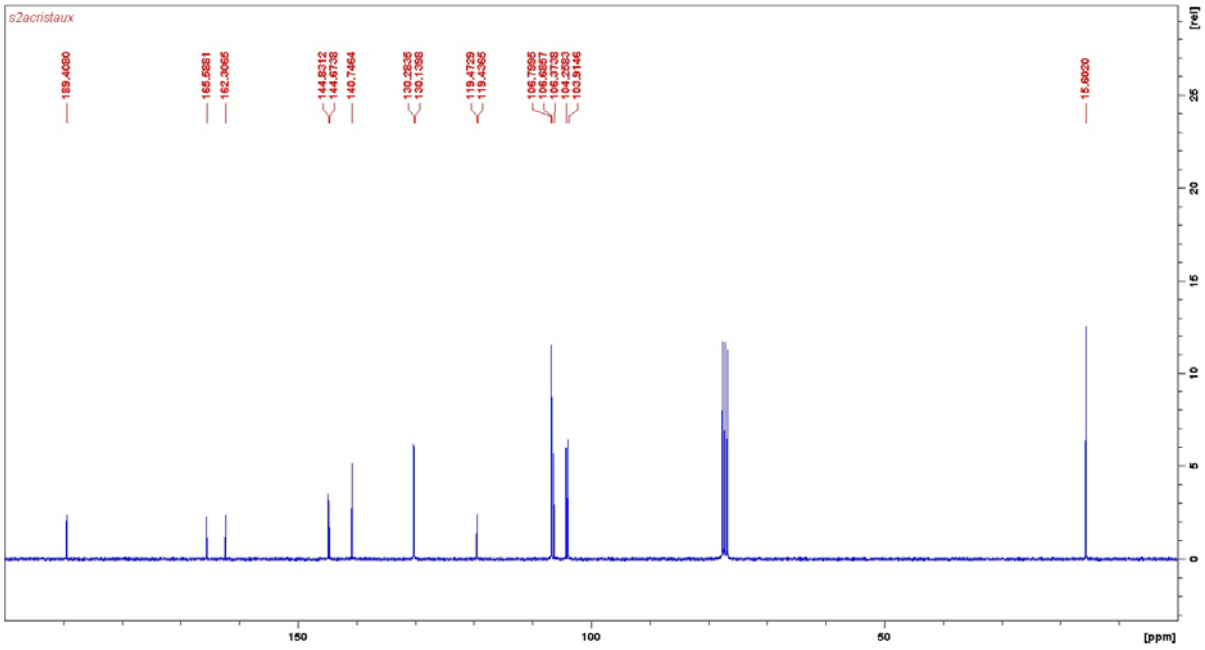


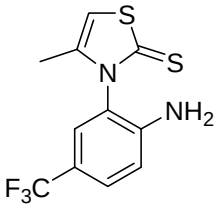
3-(2-Amino-4-fluorophenyl)-4-methyl-1,3-thiazole-2(3*H*)-thione **7p**

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



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

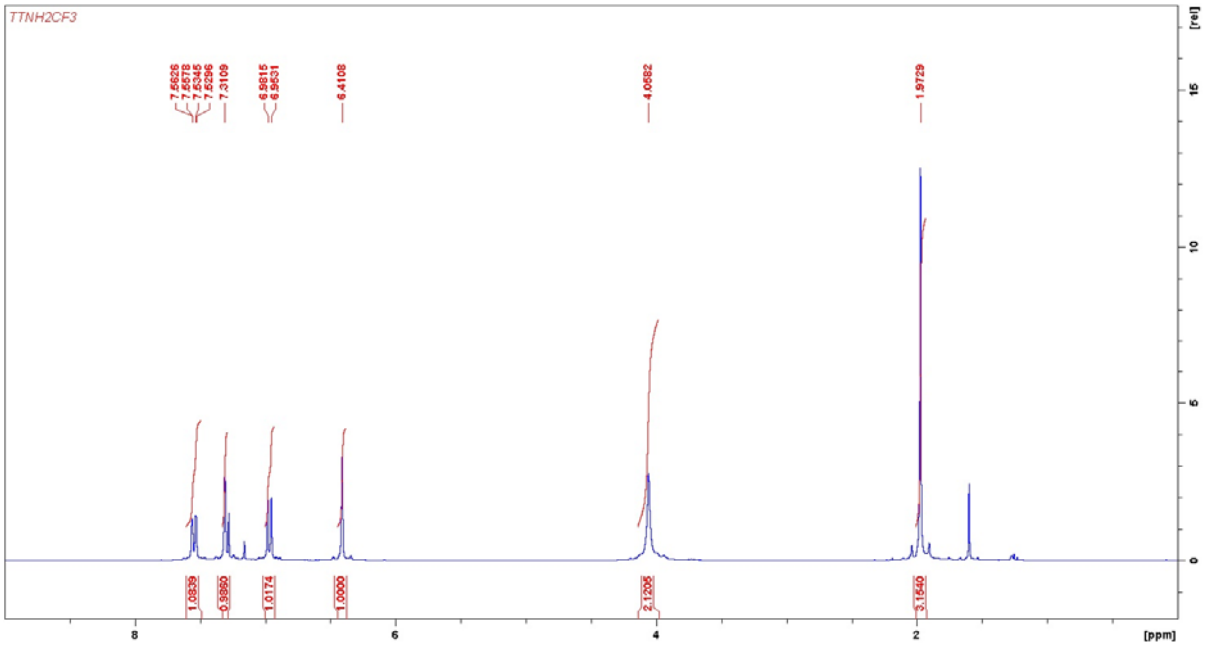




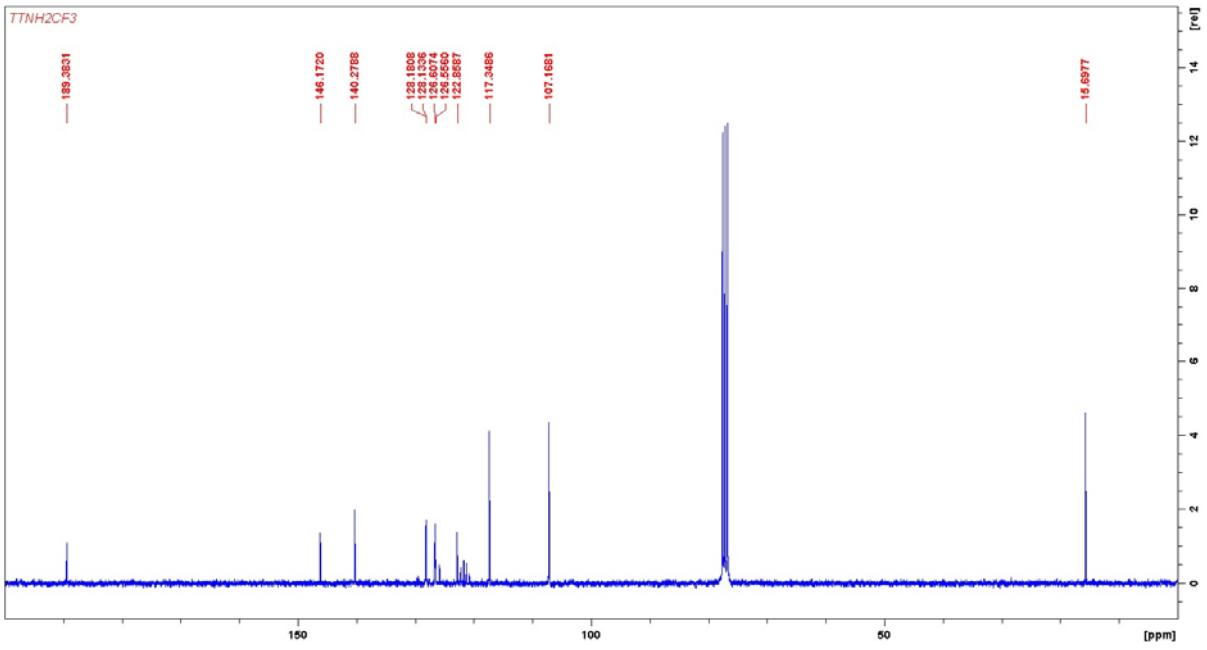
3-[2-Amino-5-(trifluoromethyl)phenyl]-4-methyl-1,3-thiazole-2(3*H*)-thione

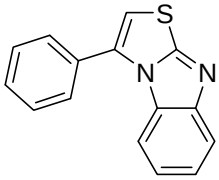
7q

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



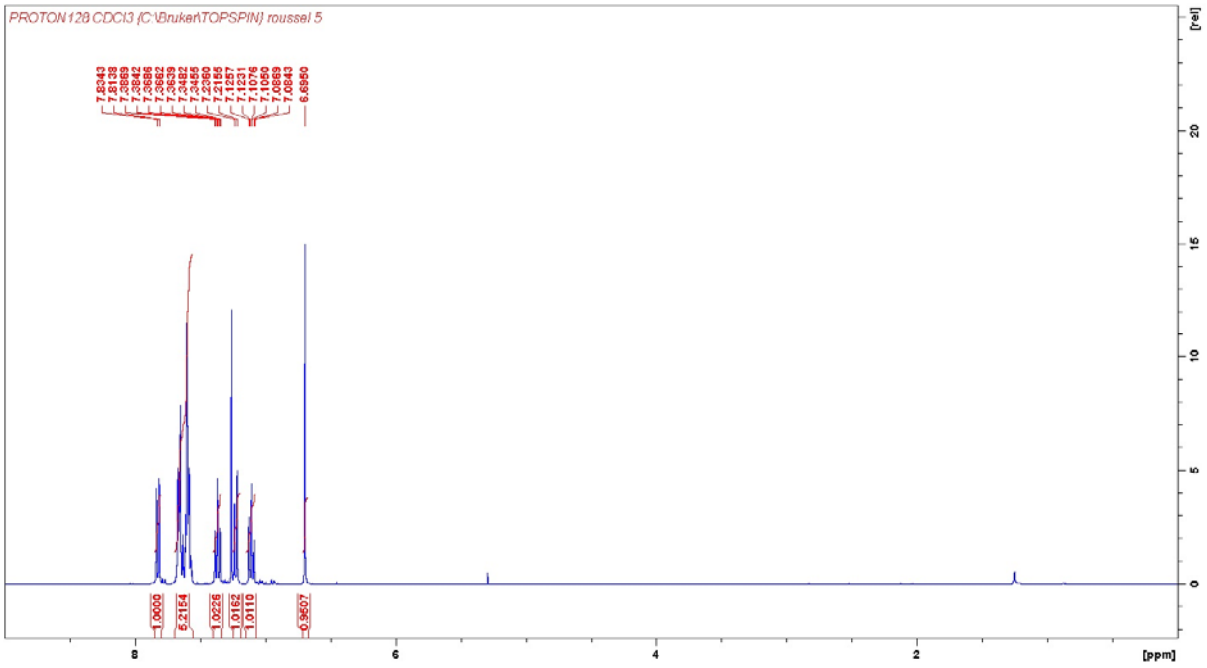
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum



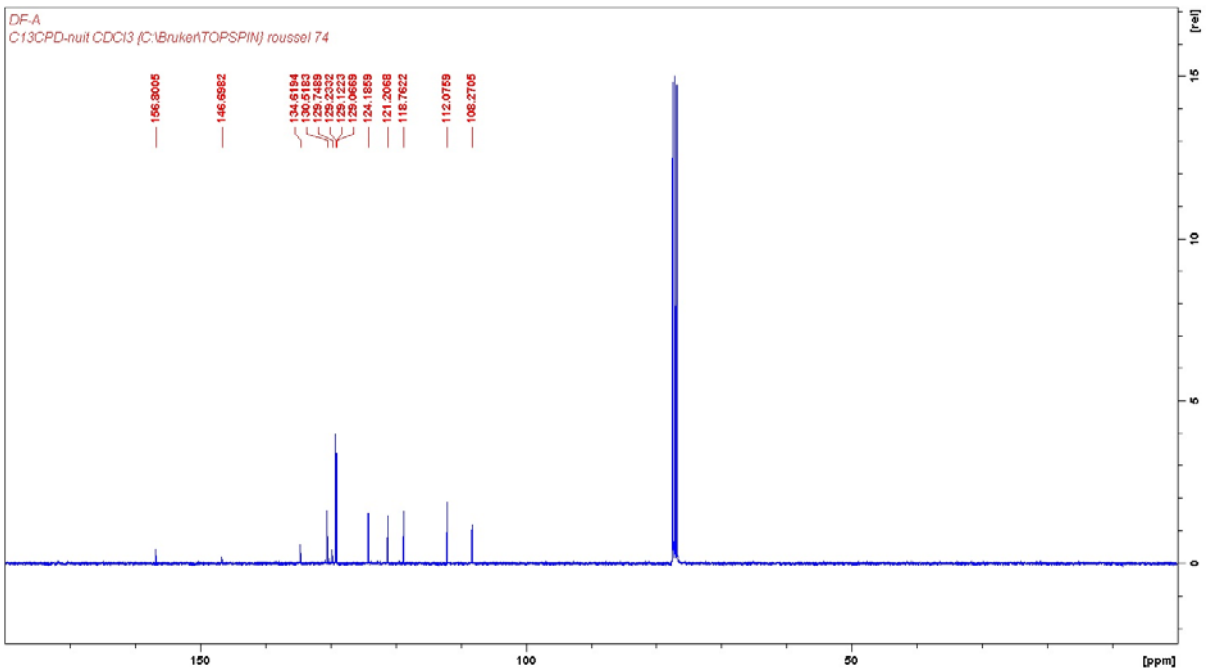


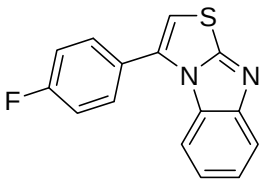
3-Phenyl[1,3]thiazolo[3,2-*a*]benzimidazole **5k**

^{1}H NMR ($CDCl_3$, 400 MHz) spectrum



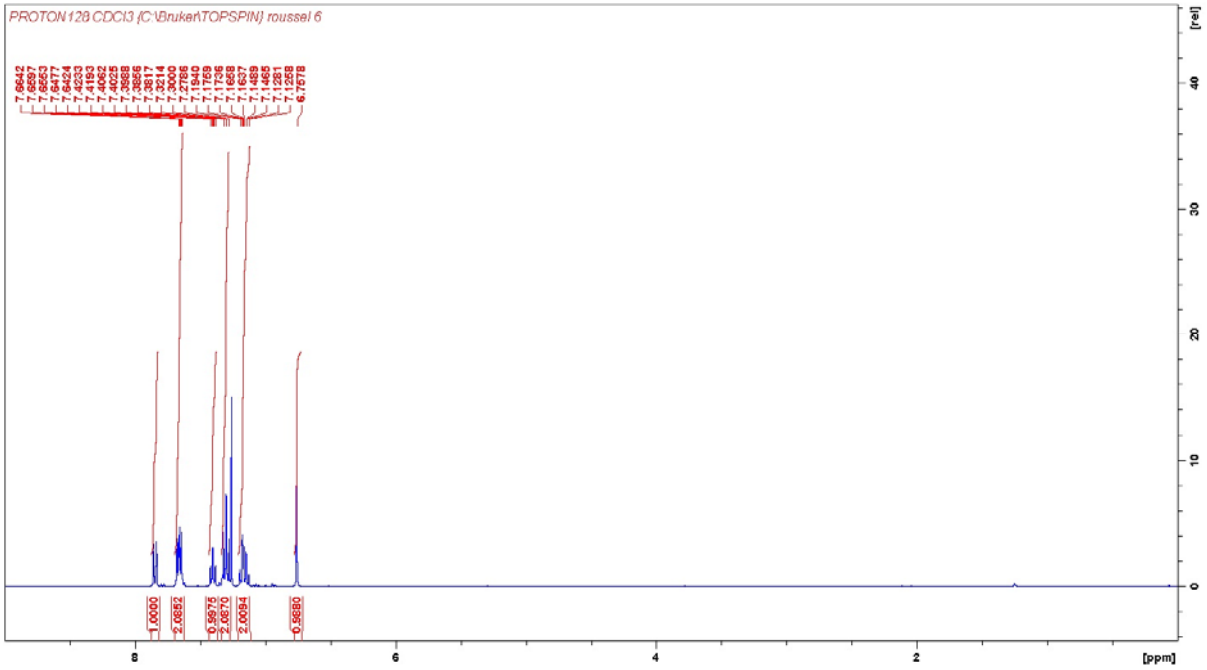
^{13}C NMR ($CDCl_3$, 100 MHz) spectrum



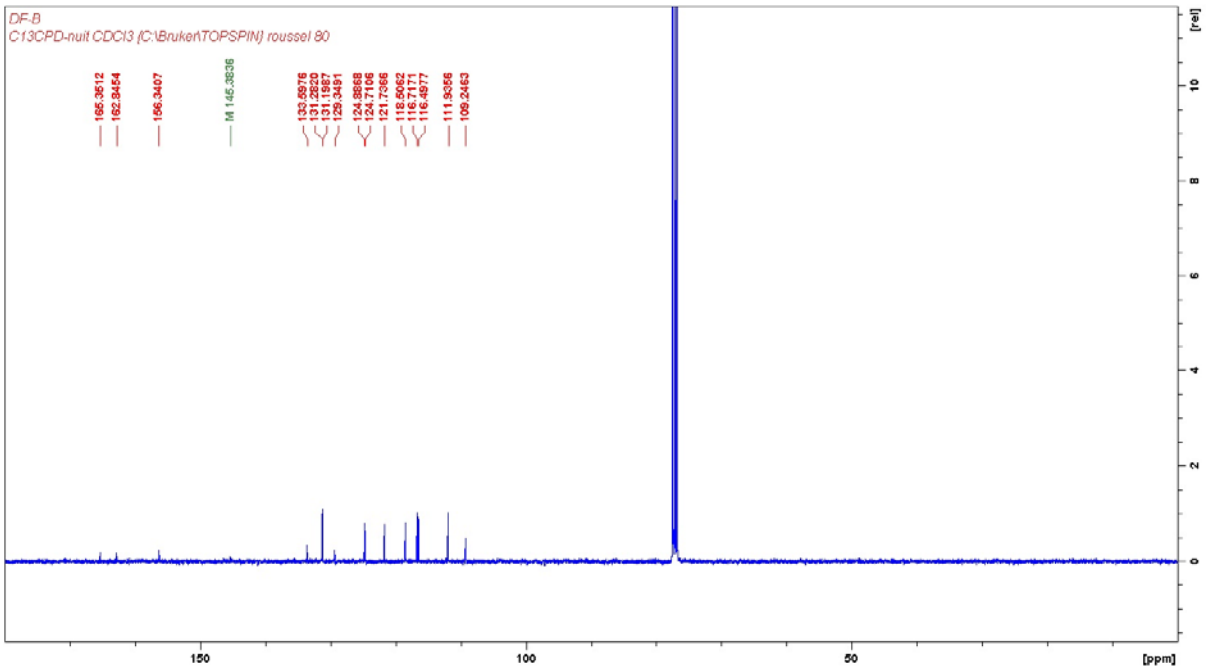


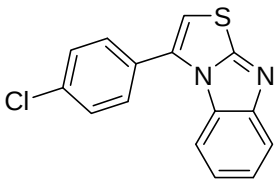
3-(4-Fluorophenyl)[1,3]thiazolo[3,2-*a*]benzimidazole **5l**

^{1}H NMR ($CDCl_3$, 400 MHz) spectrum



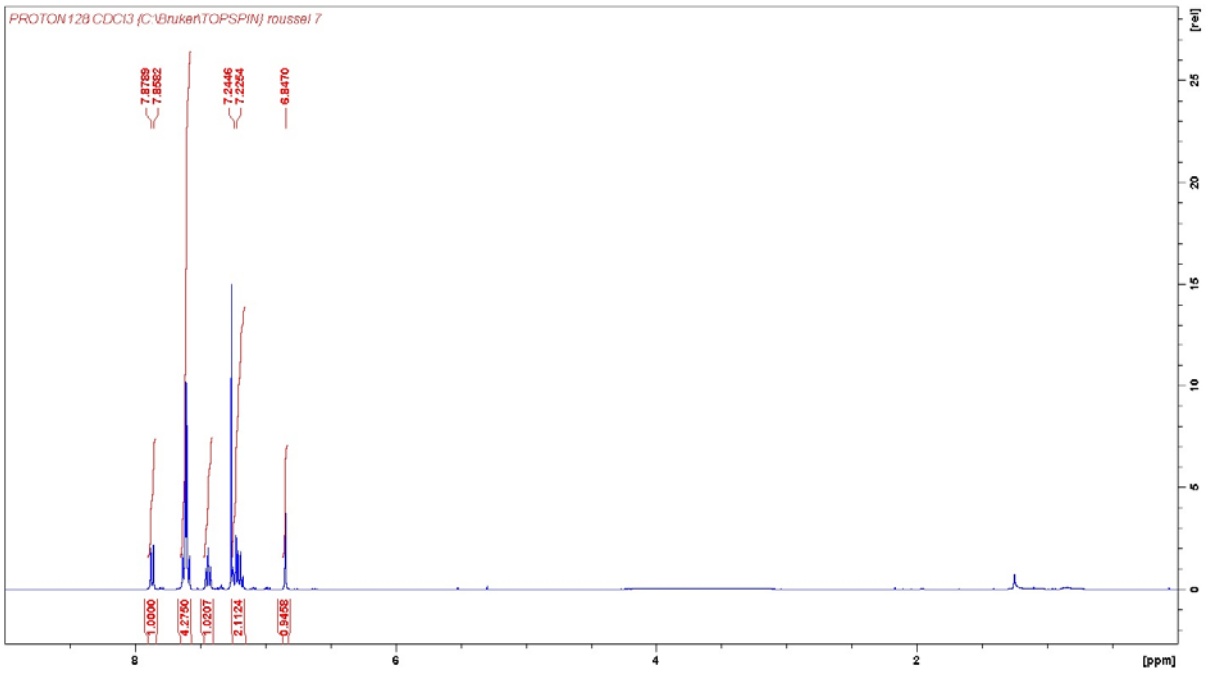
^{13}C NMR ($CDCl_3$, 100 MHz) spectrum



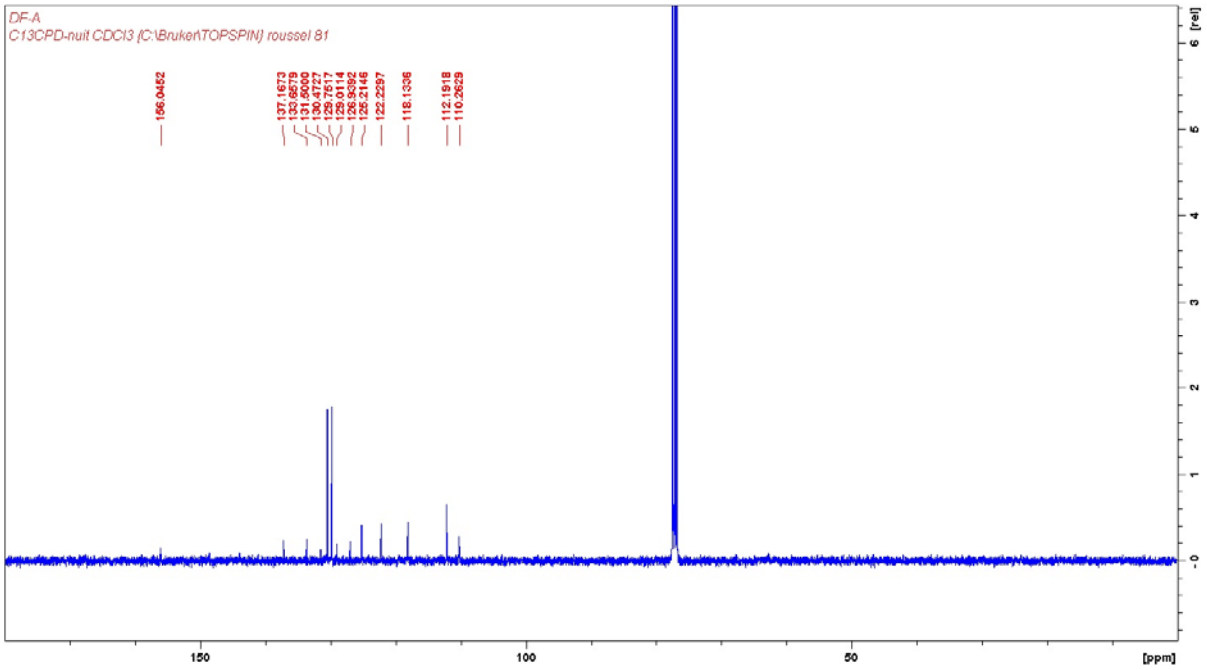


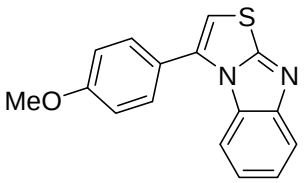
3-(4-Chlorophenyl)[1,3]thiazolo[3,2-*a*]benzimidazole **5m**

^{1}H NMR ($CDCl_3$, 400 MHz) spectrum



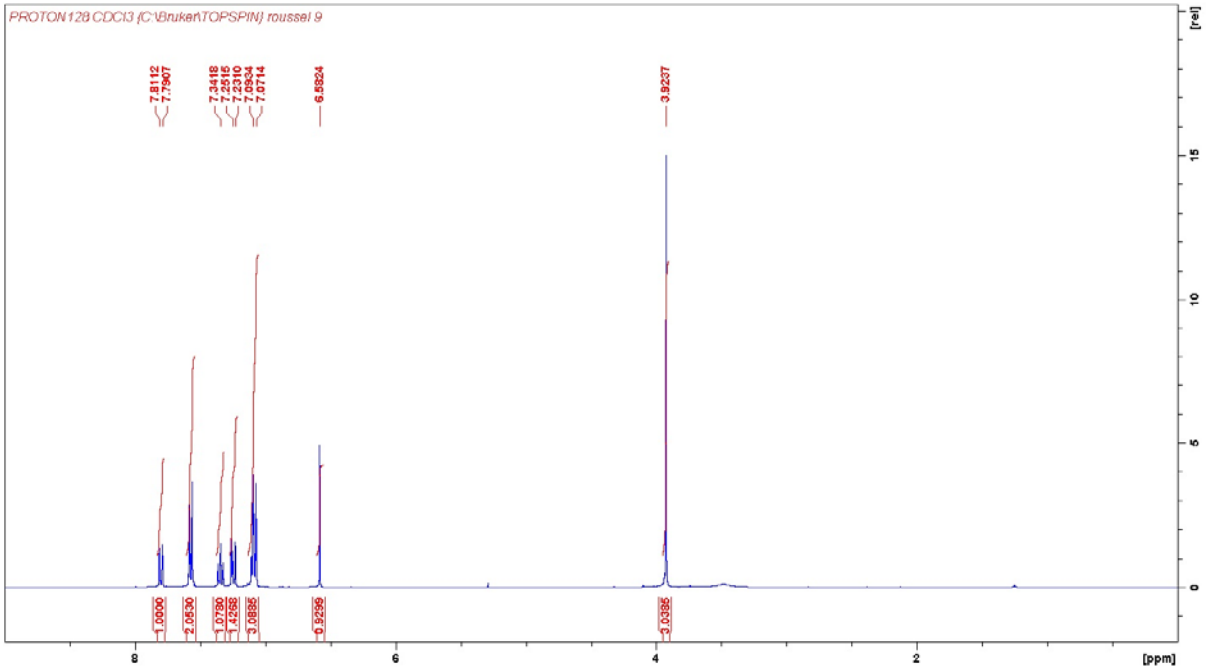
^{13}C NMR ($CDCl_3$, 100 MHz) spectrum



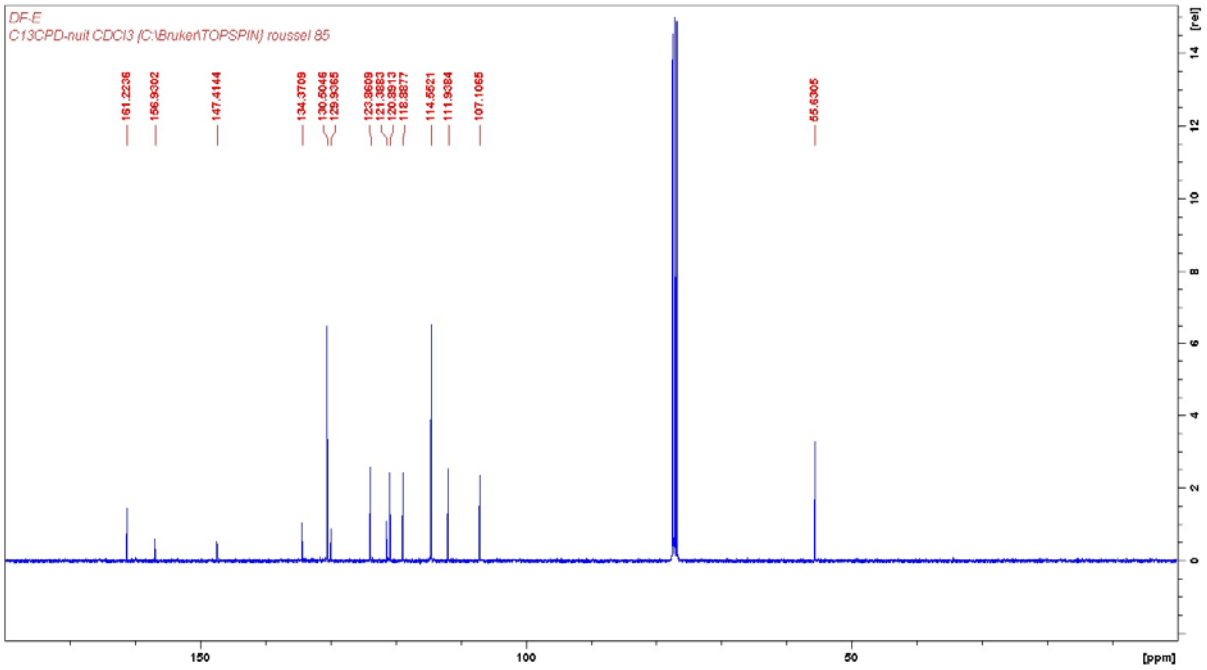


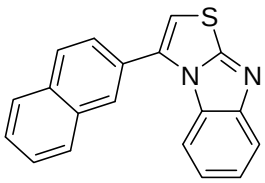
3-(4-Methoxyphenyl)[1,3]thiazolo[3,2-*a*]benzimidazole **5n**

^{1}H NMR ($CDCl_3$, 400 MHz) spectrum



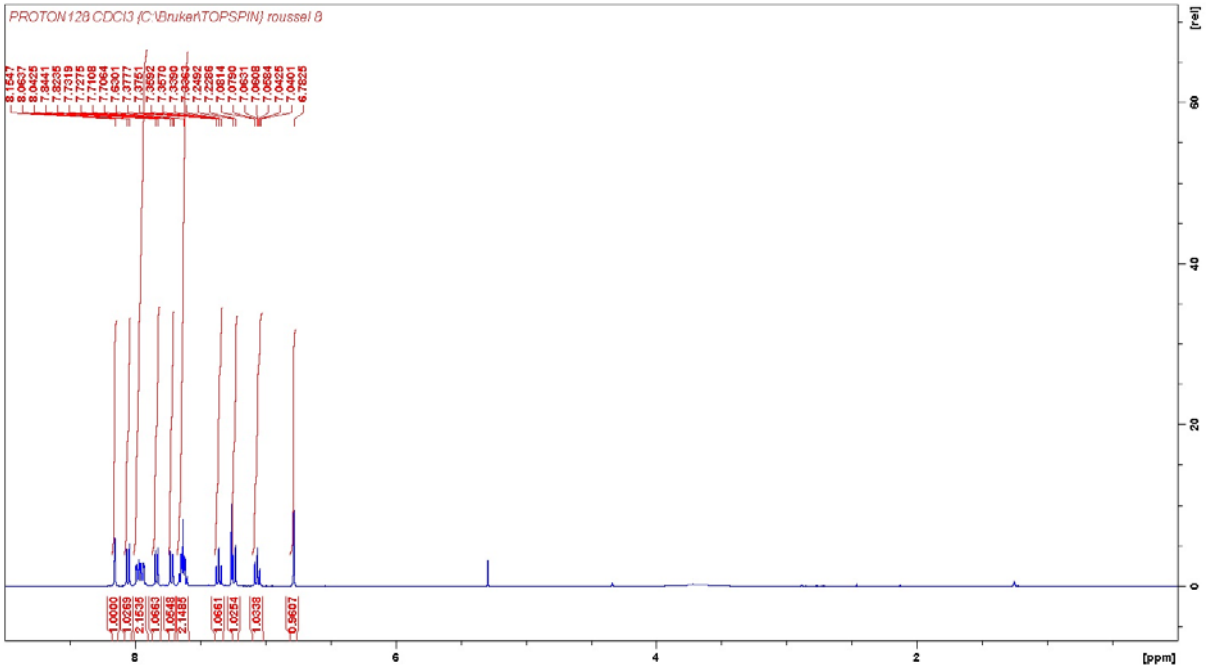
^{13}C NMR ($CDCl_3$, 100 MHz) spectrum



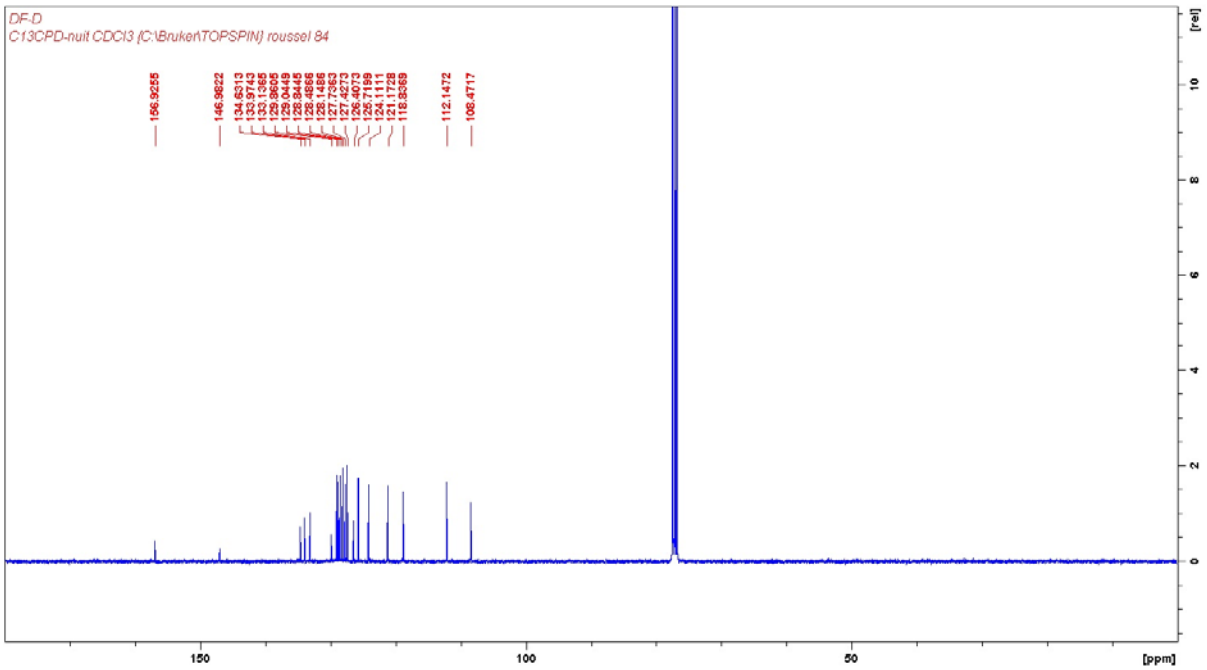


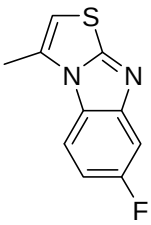
3-(Naphthalen-2-yl)[1,3]thiazolo[3,2-*a*]benzimidazole **5o**

^{1}H NMR ($CDCl_3$, 400 MHz) spectrum



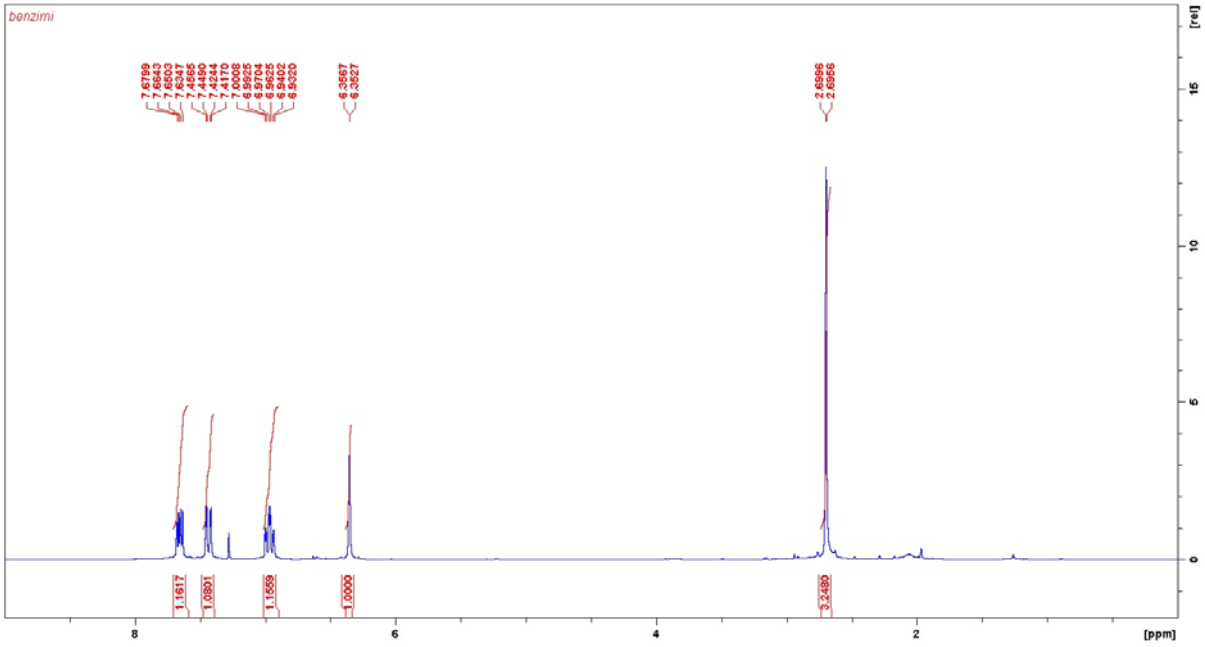
^{13}C NMR ($CDCl_3$, 100 MHz) spectrum



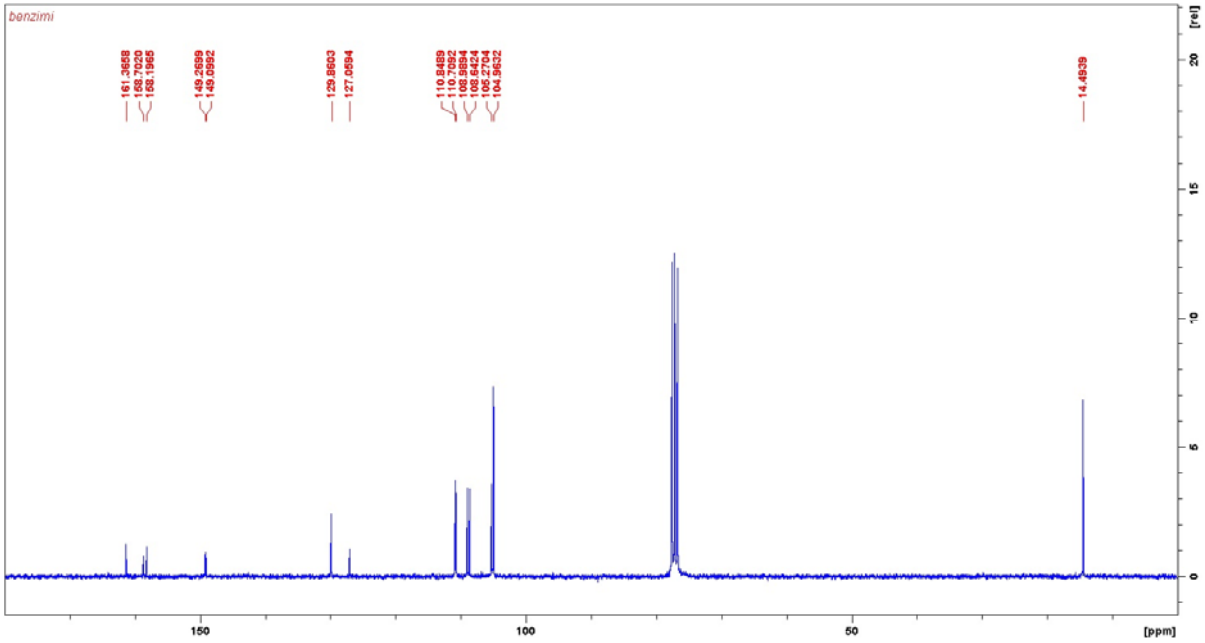


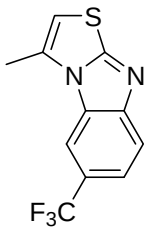
7-Fluoro-3-methyl[1,3]thiazolo[3,2-*a*]benzimidazole **5p**

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



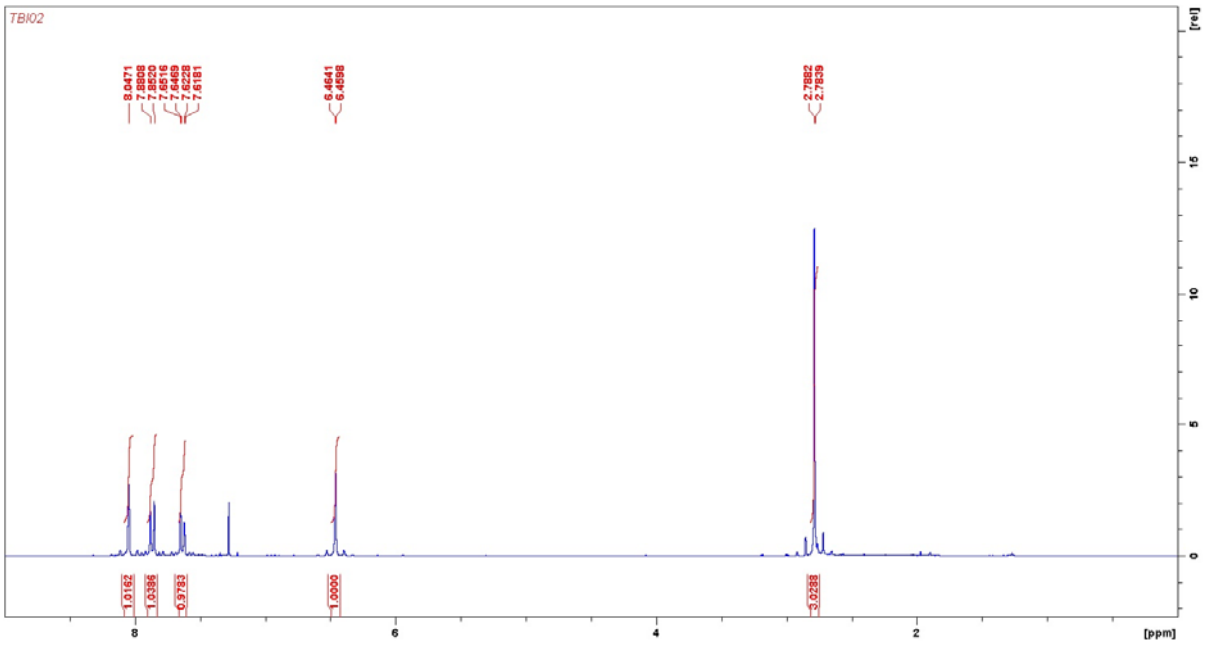
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum



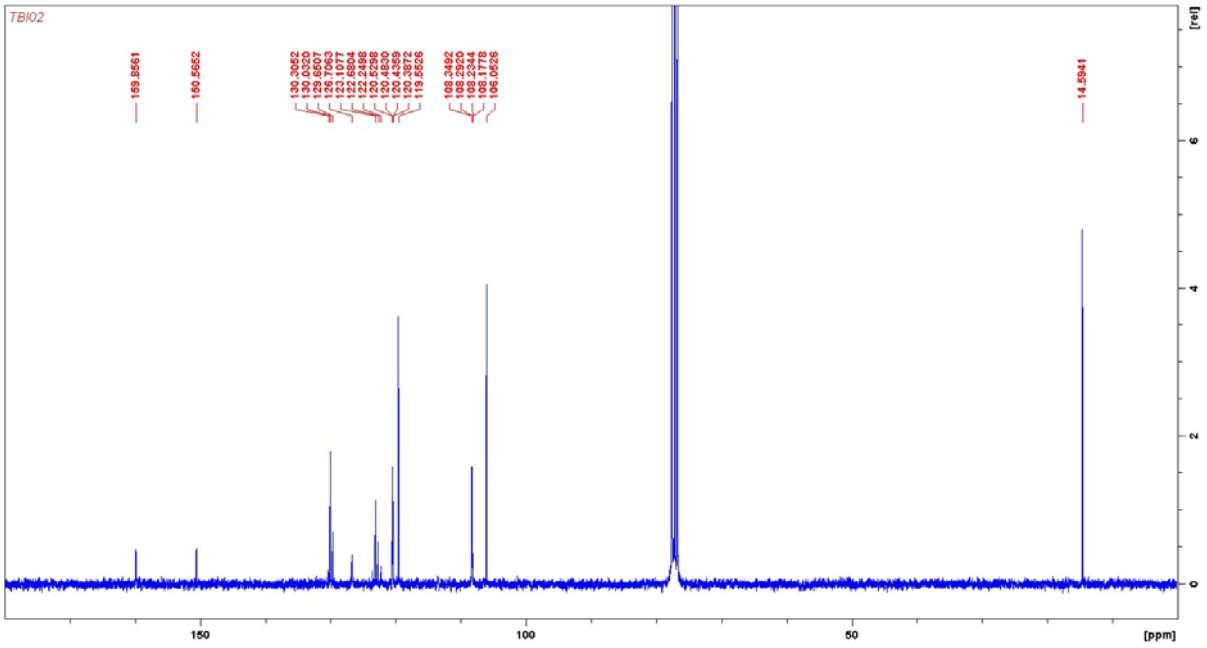


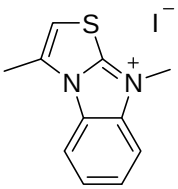
3-Methyl-6-(trifluoromethyl)[1,3]thiazolo[3,2-*a*]benzimidazole **5q**

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



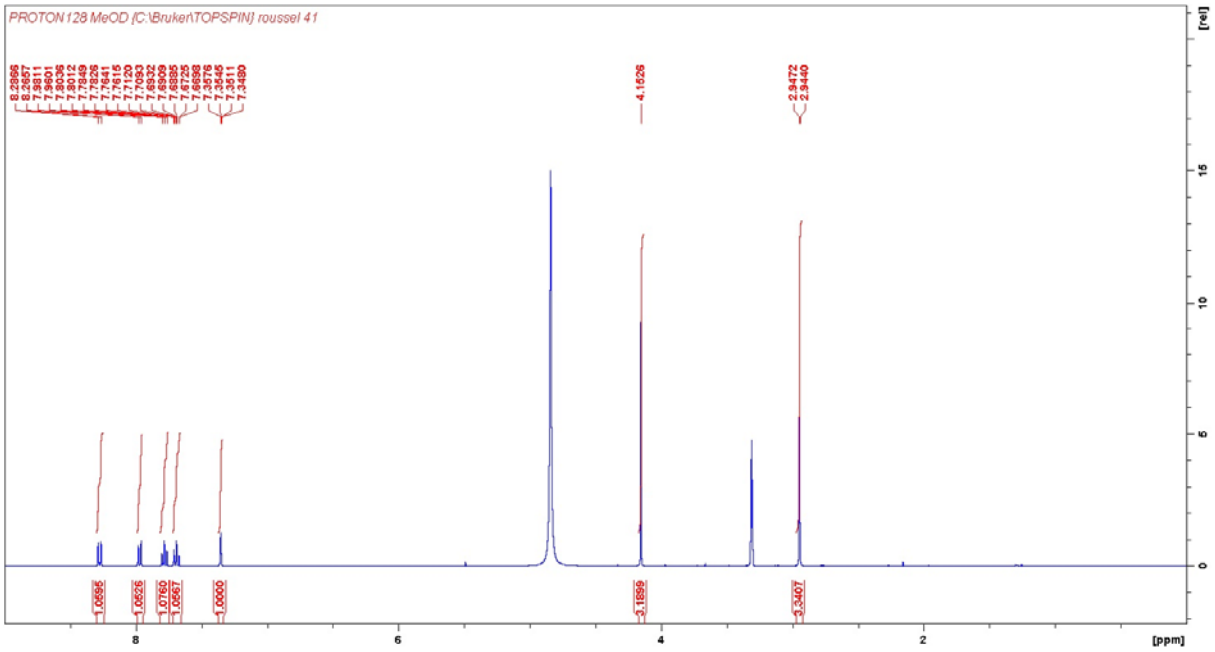
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum



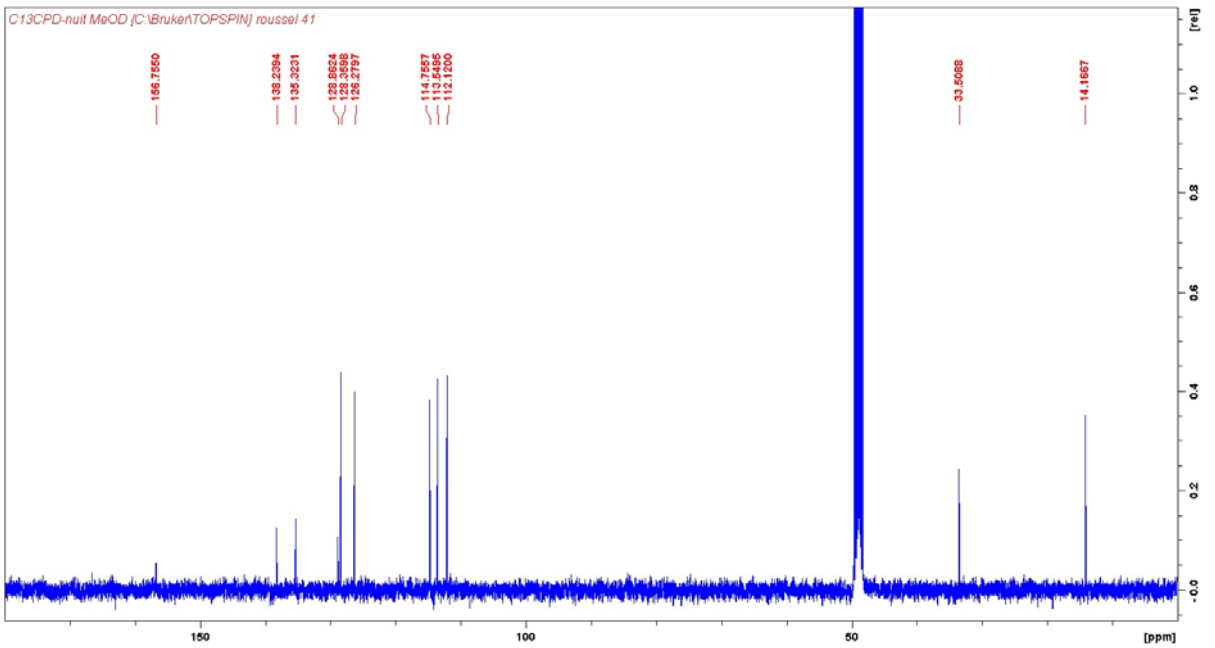


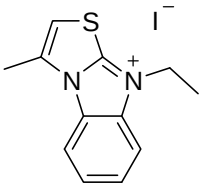
3,9-Dimethyl[1,3]thiazolo[3,2-*a*]benzimidazol-9-ium iodide **3a**

^{1}H NMR (CD_3OD, 300 MHz) spectrum



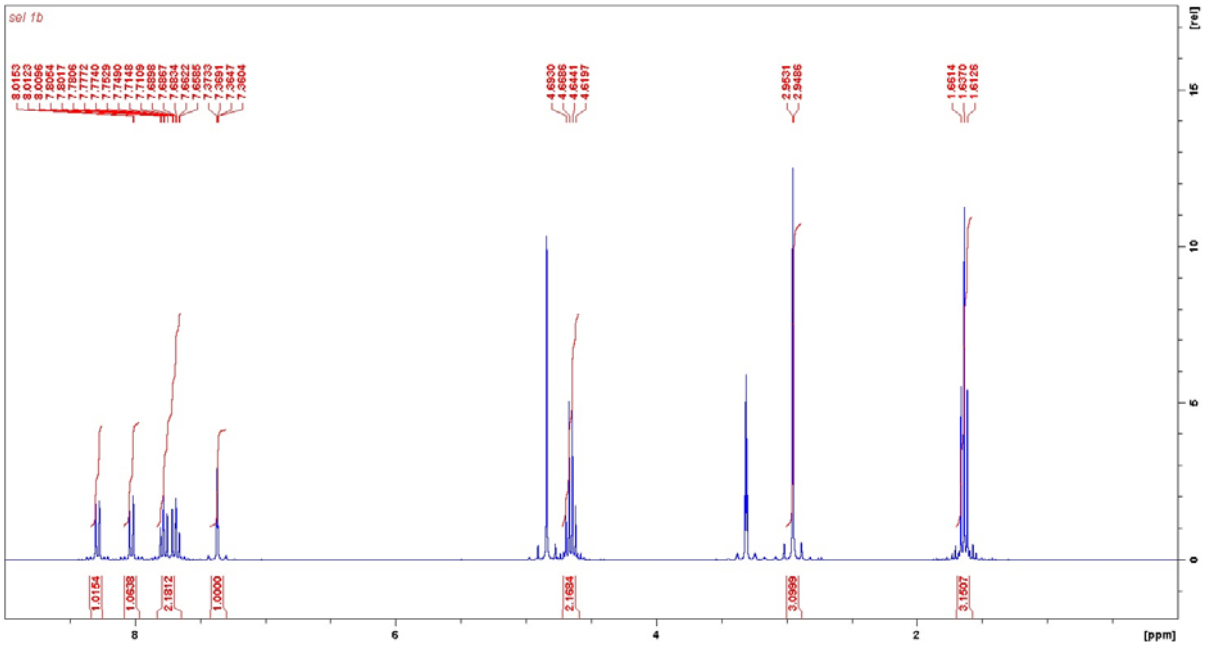
^{13}C NMR (CD_3OD, 75 MHz) spectrum



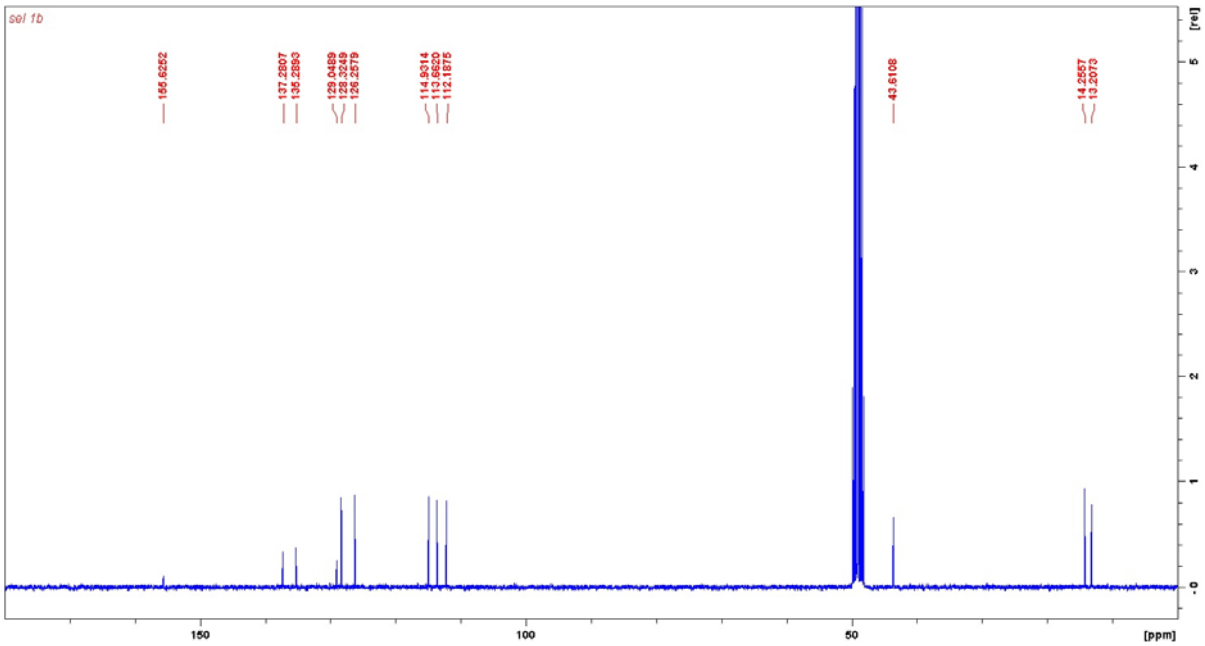


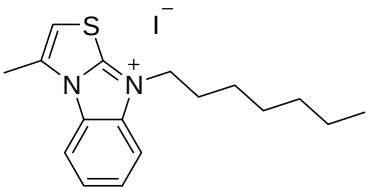
9-Ethyl-3-methyl[1,3]thiazolo[3,2-*a*]benzimidazol-9-ium iodide **3b**

^{1}H NMR (CD_3OD, 300 MHz) spectrum



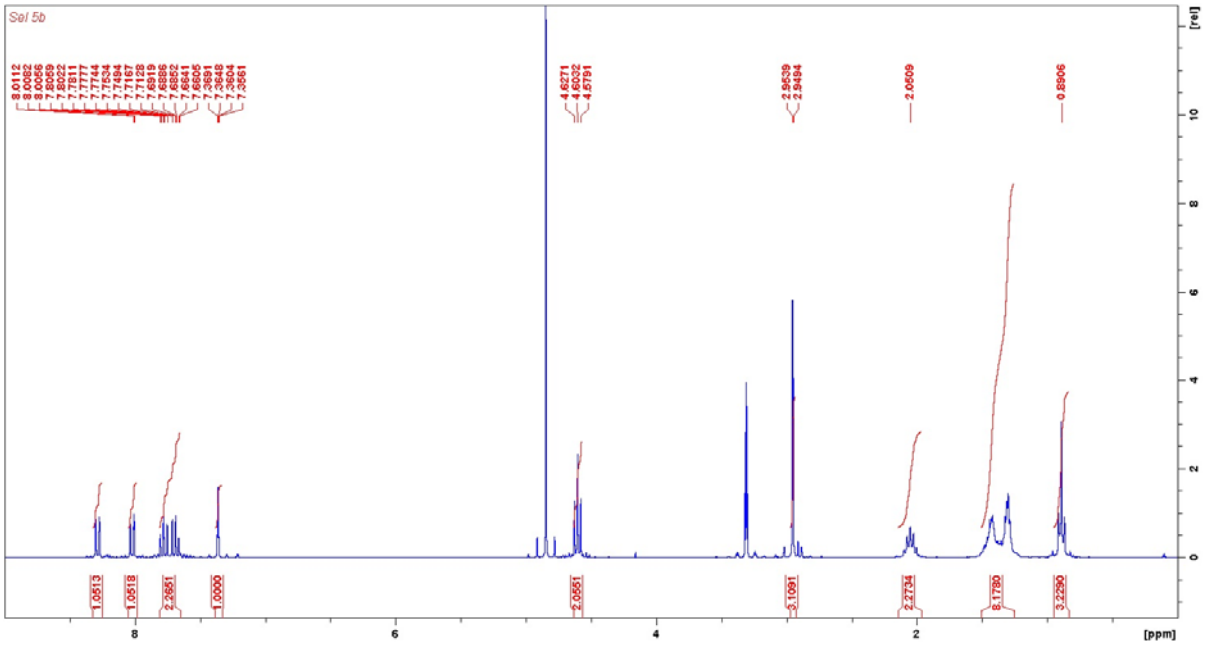
^{13}C NMR (CD_3OD, 75 MHz) spectrum



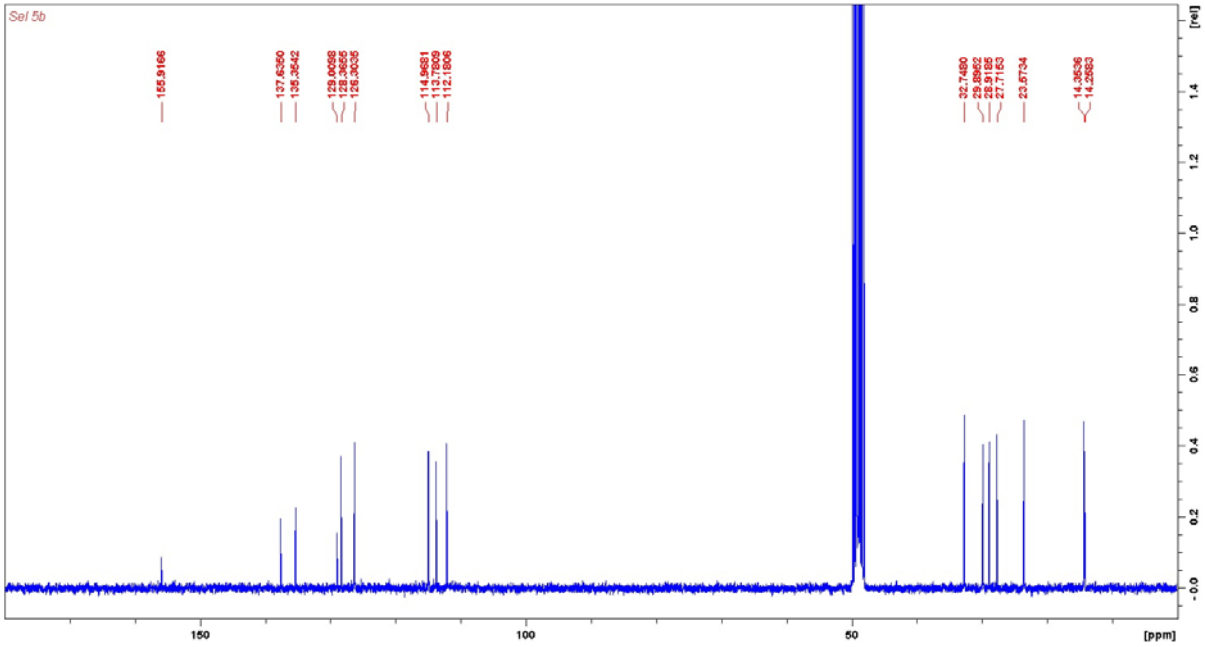


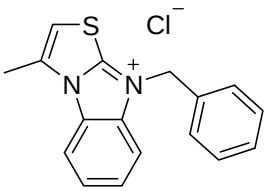
9-Heptyl-3-methyl[1,3]thiazolo[3,2-*a*]benzimidazol-9-ium iodide **3c**

^{1}H NMR (CD_3OD, 300 MHz) spectrum



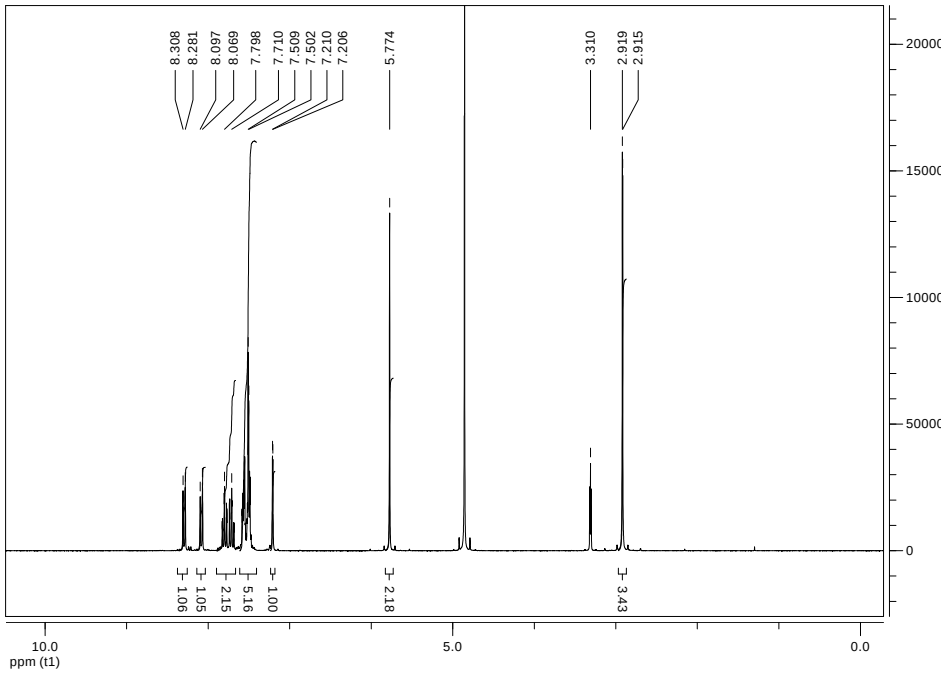
^{13}C NMR (CD_3OD, 75 MHz) spectrum



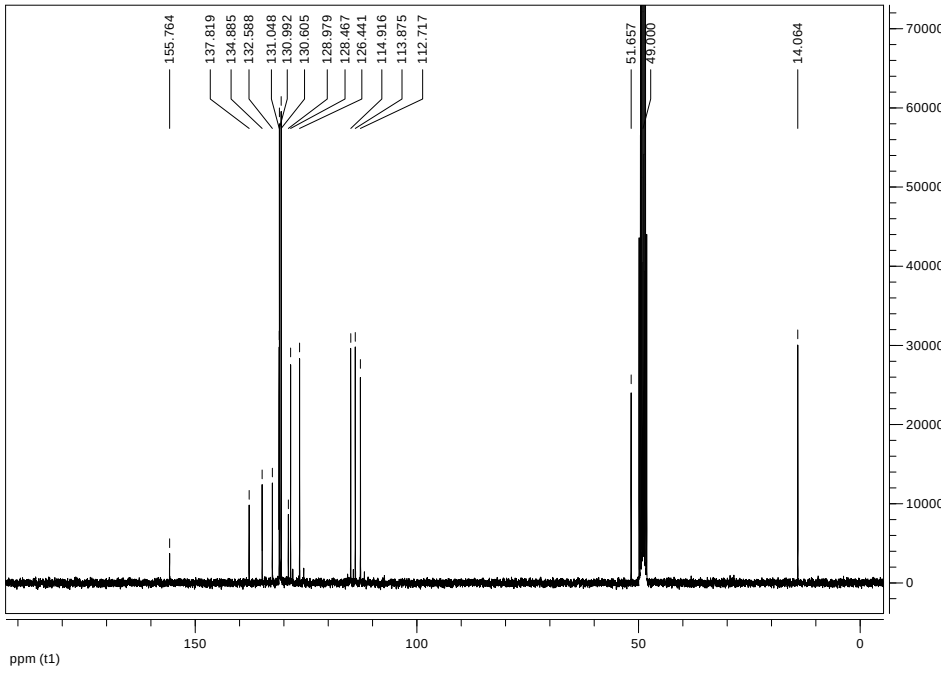


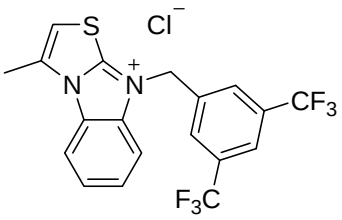
9-Benzyl-3-methyl[1,3]thiazolo[3,2-*a*]benzimidazol-9-ium chloride **3d**

^{1}H NMR (CD_3OD, 300 MHz) spectrum



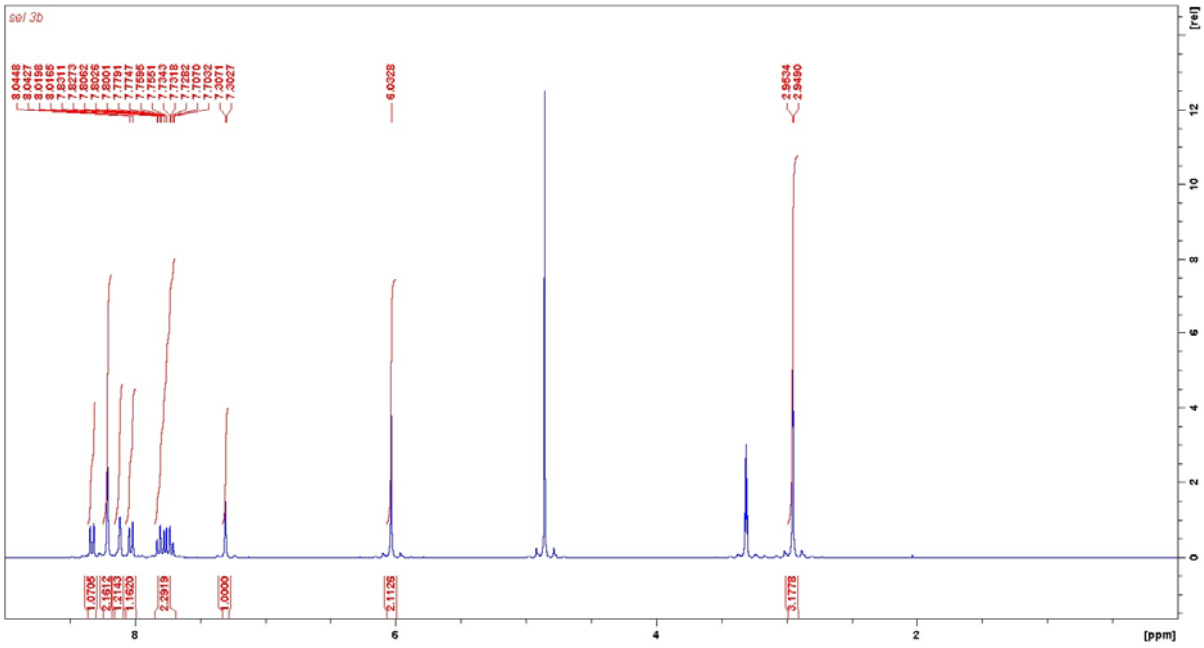
^{13}C NMR (CD_3OD, 75 MHz) spectrum



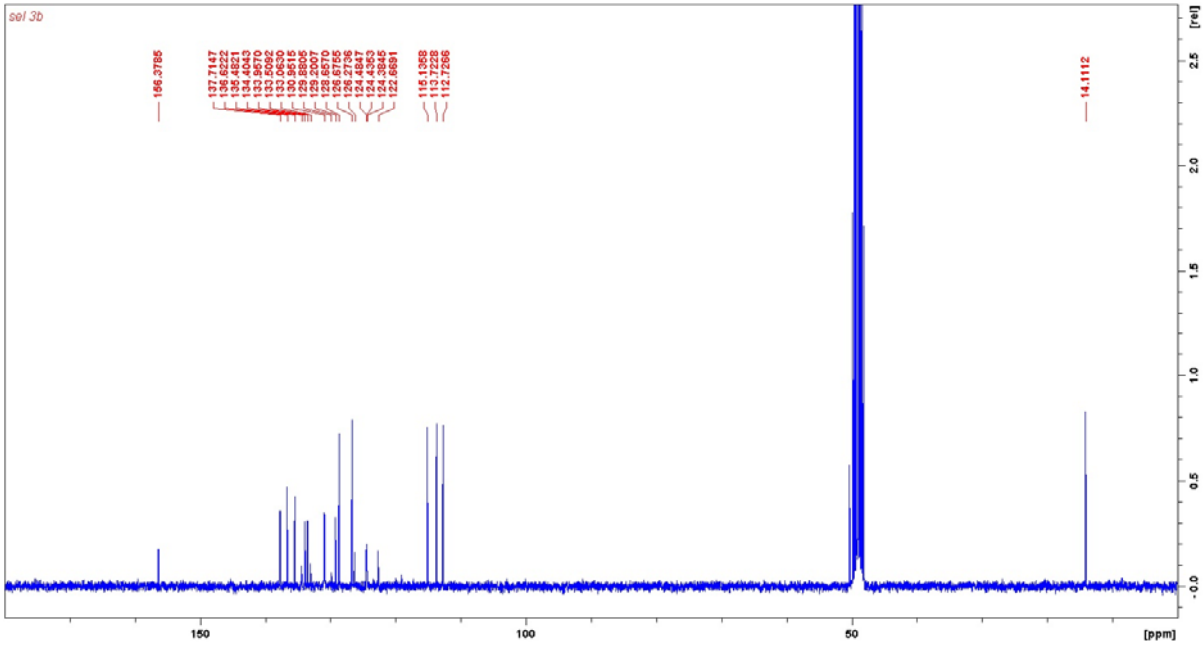


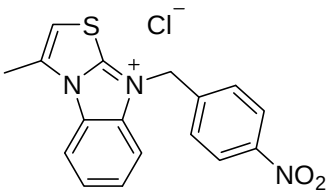
9-[3,5-Bis(trifluoromethyl)benzyl]-3-methyl[1,3]thiazolo[3,2-*a*]benzimidazol-9-ium chloride **3e**

^{1}H NMR (CD_3OD, 300 MHz) spectrum



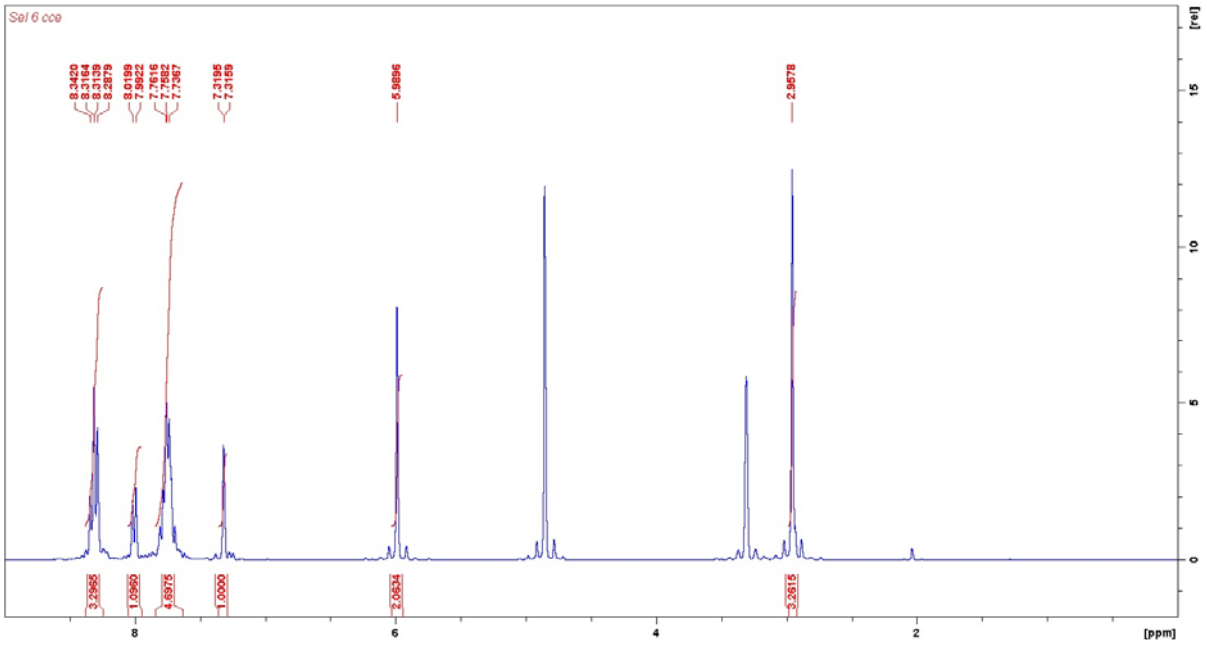
^{13}C NMR (CD_3OD, 75 MHz) spectrum



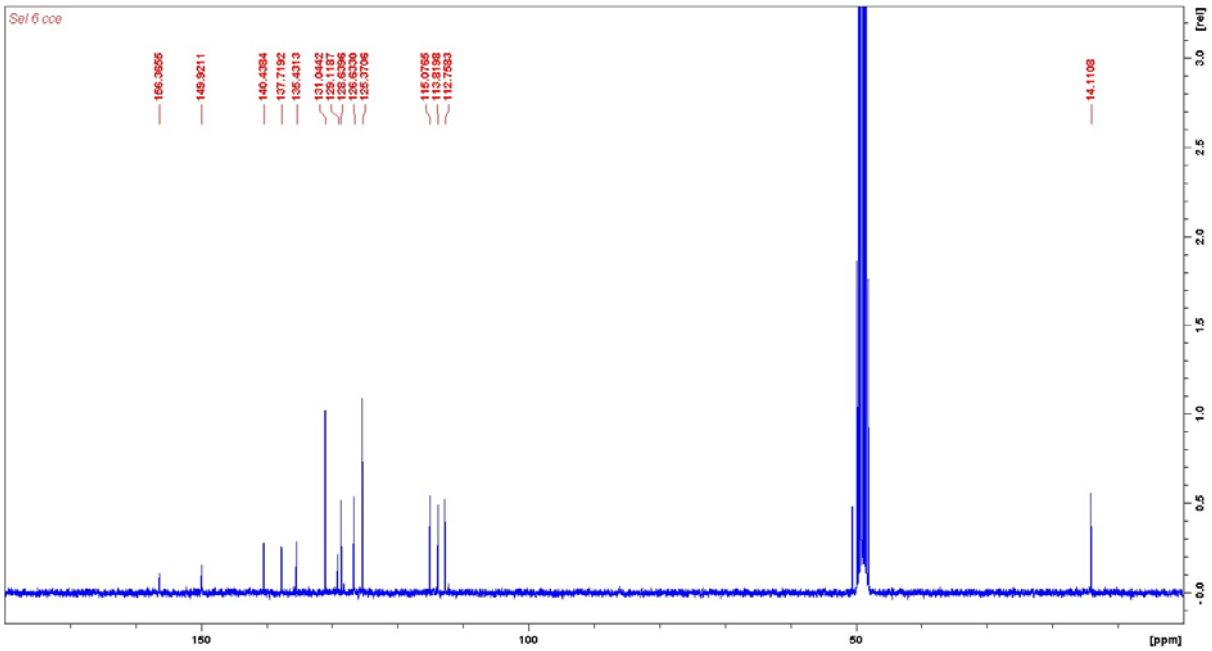


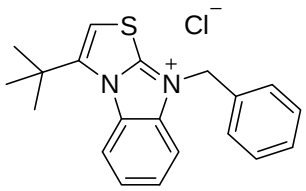
3-Methyl-9-(4-nitrobenzyl)[1,3]thiazolo[3,2-*a*]benzimidazol-9-ium chloride **3f**

^{1}H NMR (CD_3OD, 300 MHz) spectrum



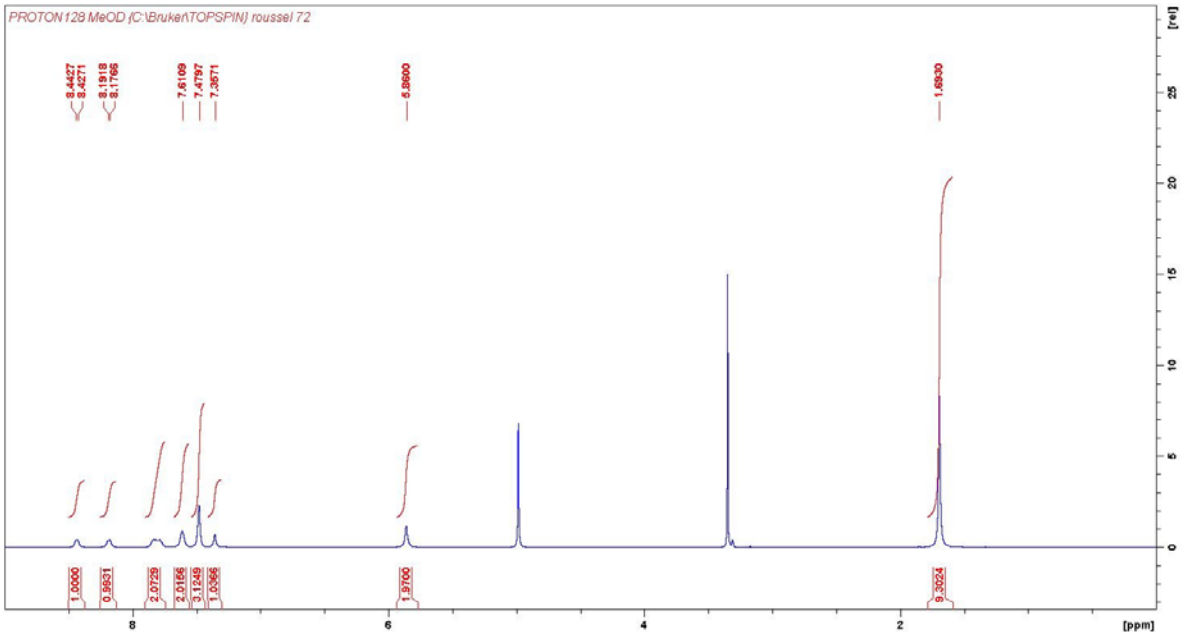
^{13}C NMR (CD_3OD, 75 MHz) spectrum



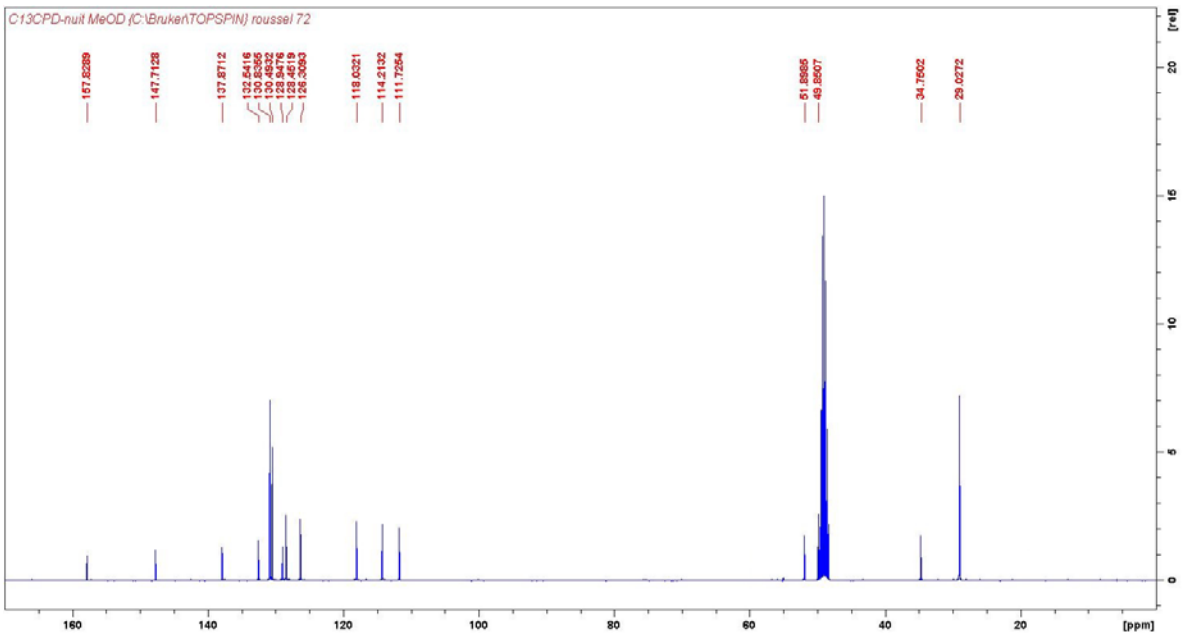


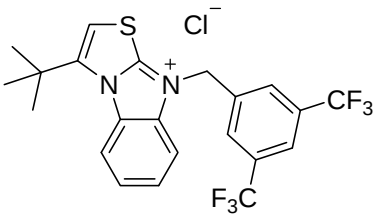
9-Benzyl-3-*tert*-butyl[1,3]thiazolo[3,2-*a*]benzimidazol-9-ium chloride **3i**

^{1}H NMR (CD_3OD, 400 MHz) spectrum



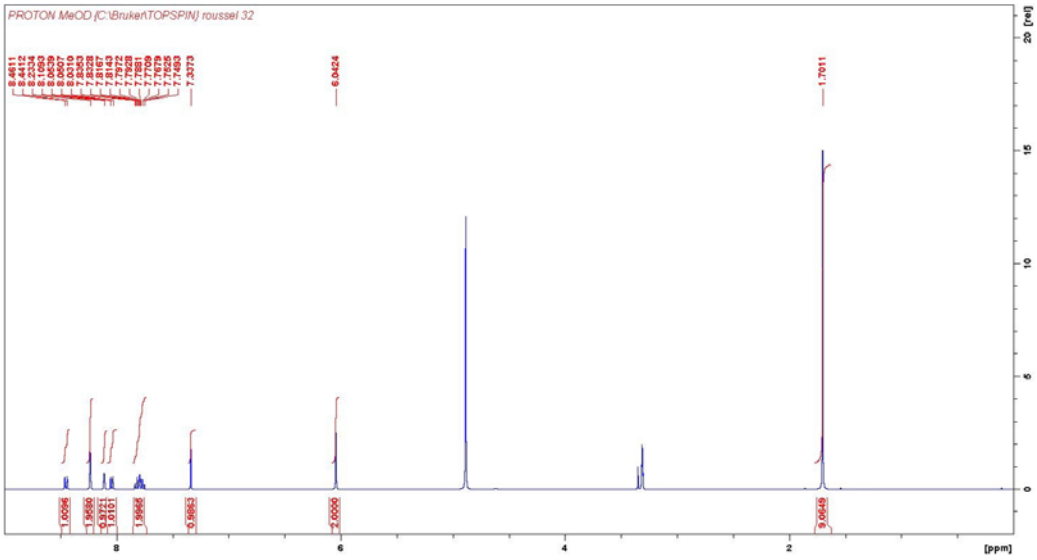
^{13}C NMR (CD_3OD, 100 MHz) spectrum



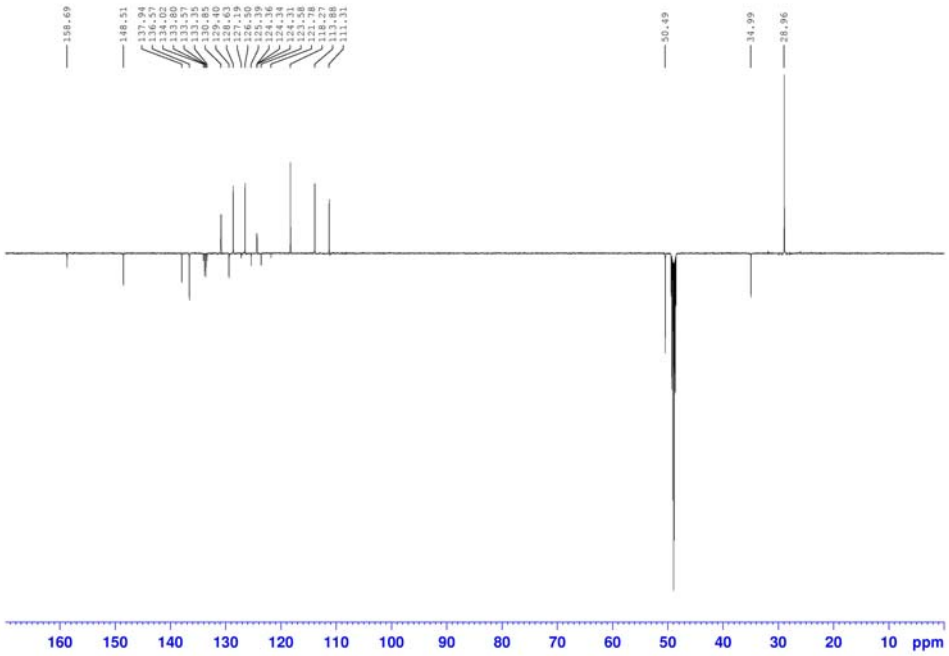


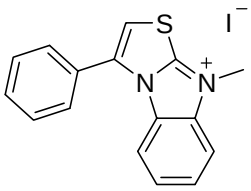
9-[3,5-Bis(trifluoromethyl)benzyl]-3-*tert*-butyl[1,3]thiazolo[3,2-*a*]benzimidazol-9-ium chloride **3j**

^{1}H NMR (CD_3OD, 400 MHz) spectrum



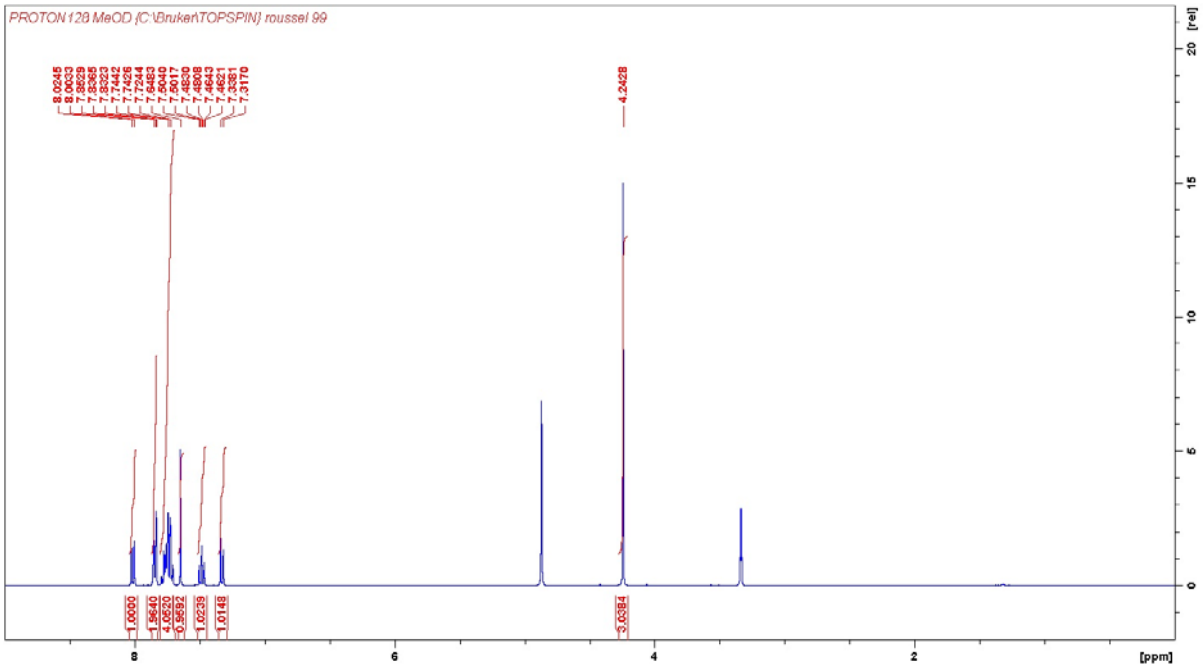
^{13}C NMR (CD_3OD, 150 MHz) spectrum



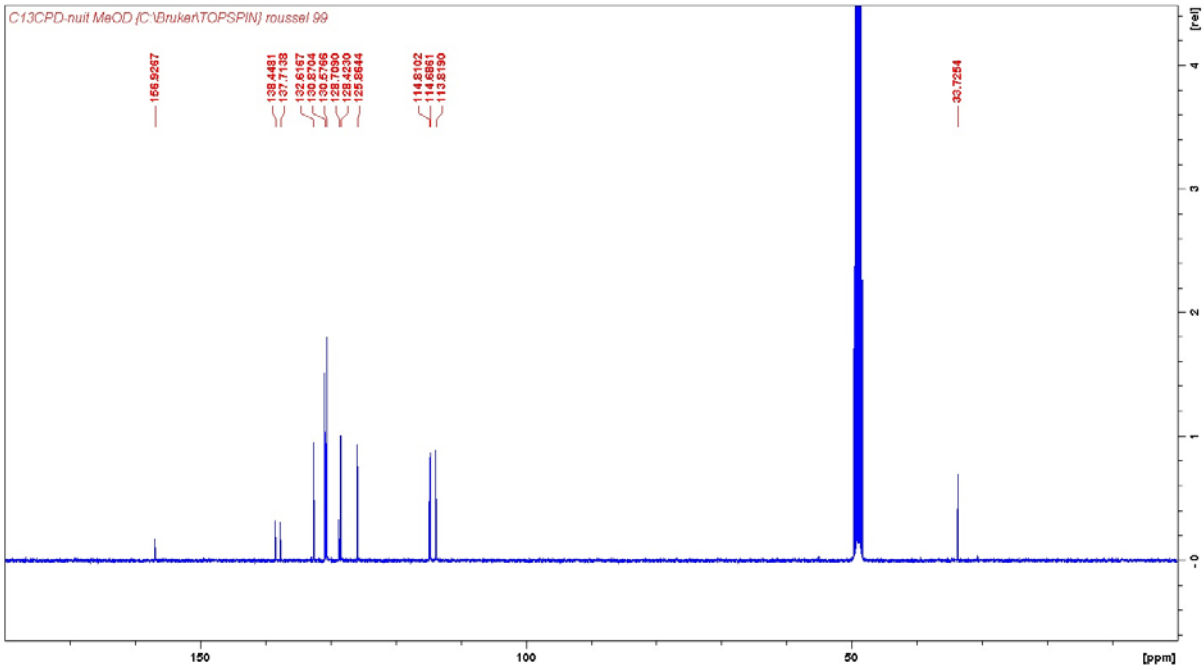


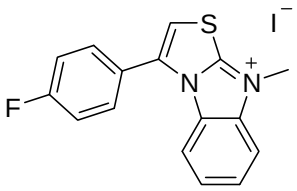
9-Methyl-3-phenyl[1,3]thiazolo[3,2-*a*]benzimidazol-9-ium iodide **3k**

^{1}H NMR (CD_3OD, 400 MHz) spectrum



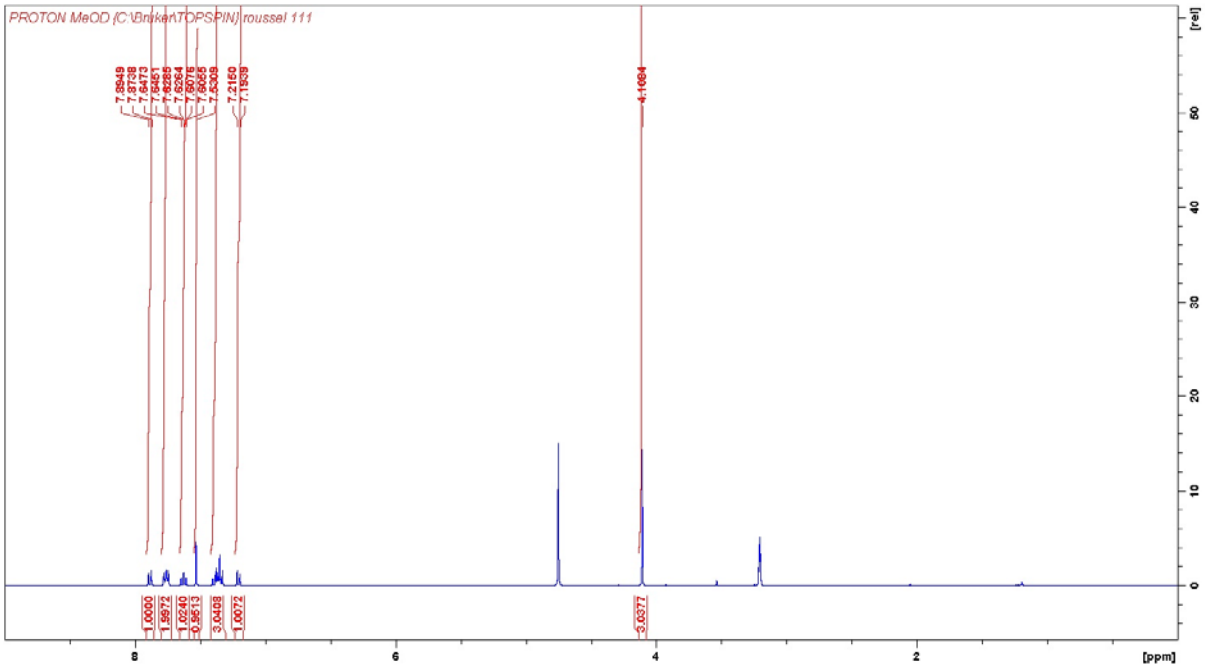
^{13}C NMR (CD_3OD, 100 MHz) spectrum



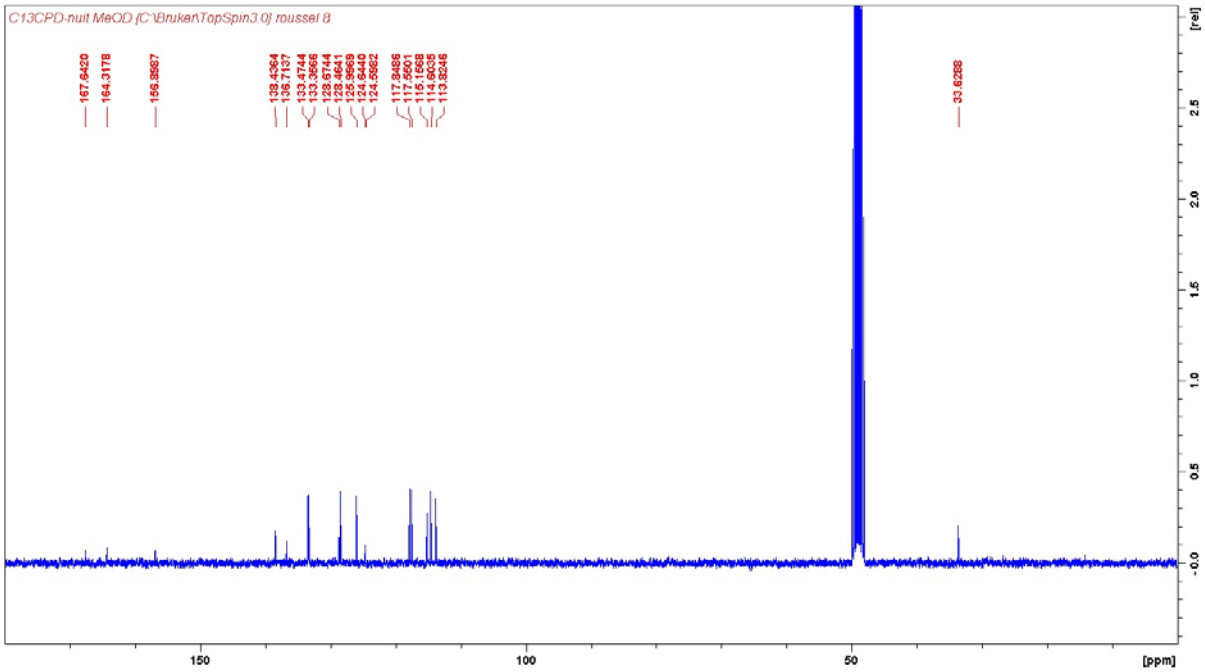


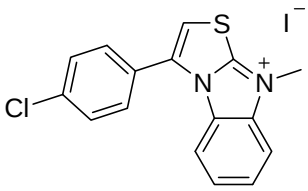
3-(4-Fluorophenyl)-9-methyl[1,3]thiazolo[3,2-*a*]benzimidazol-9-ium iodide **3l**

^{1}H NMR (CD_3OD, 400 MHz) spectrum



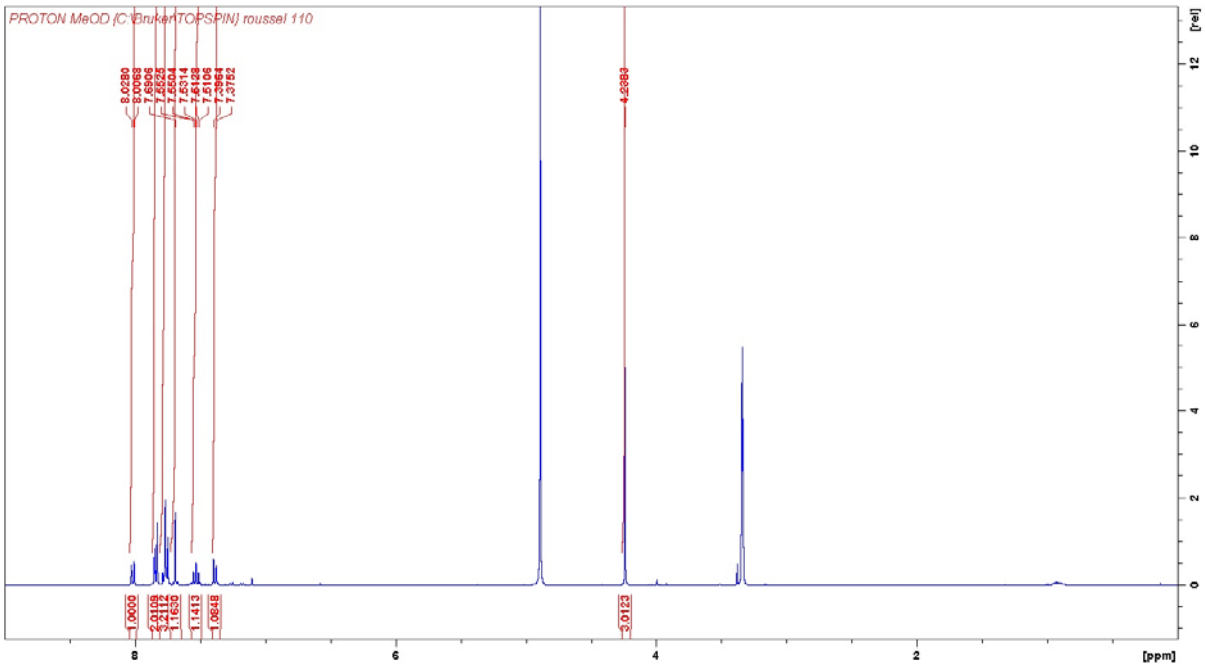
^{13}C NMR (CD_3OD, 75 MHz) spectrum



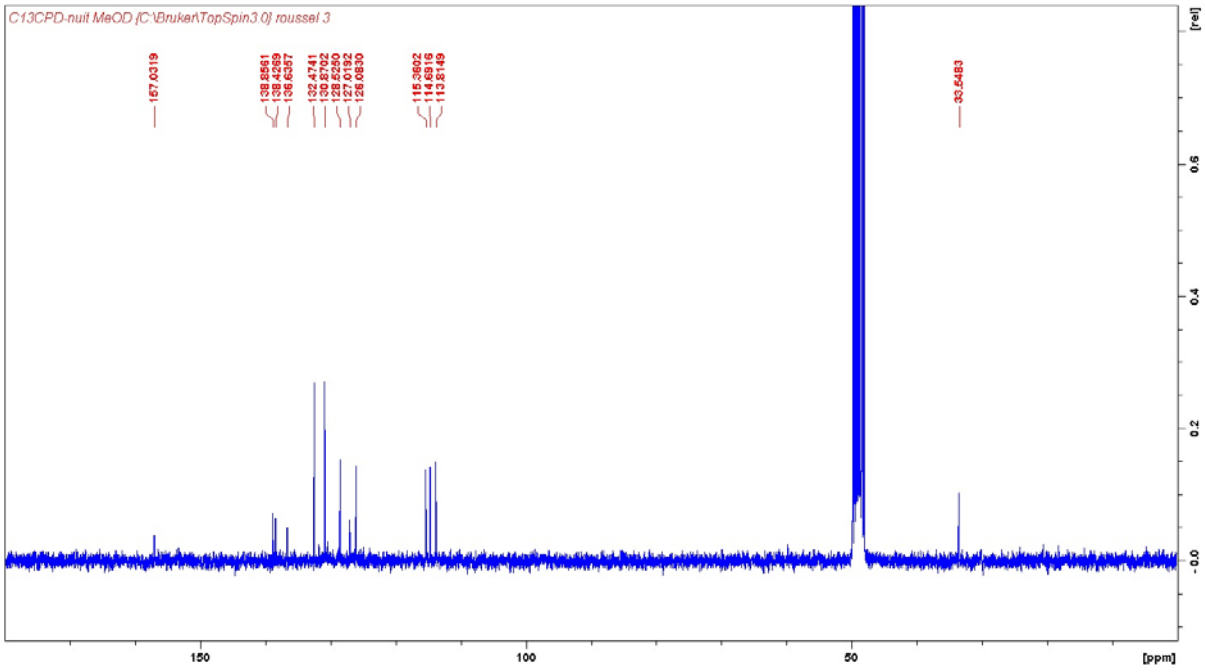


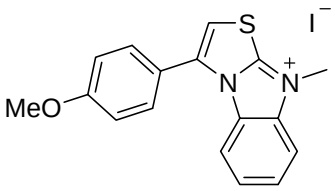
3-(4-Chlorophenyl)-9-methyl[1,3]thiazolo[3,2-*a*]benzimidazol-9-ium iodide **3m**

^{1}H NMR (CD_3OD, 400 MHz) spectrum



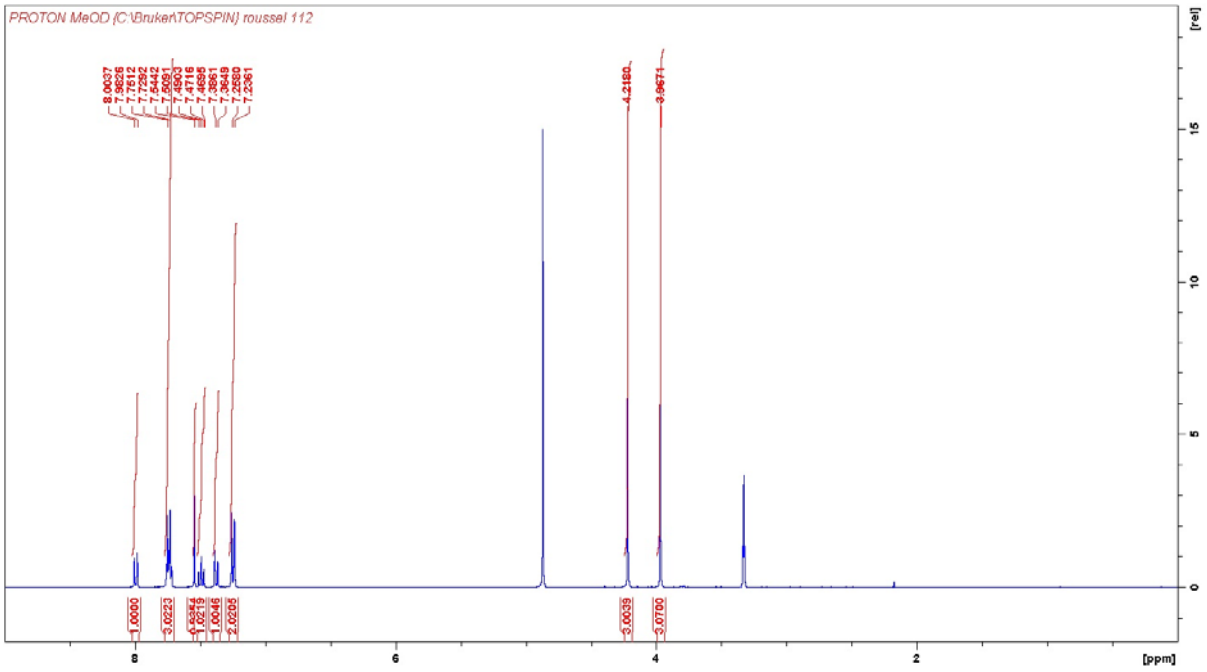
^{13}C NMR (CD_3OD, 75 MHz) spectrum



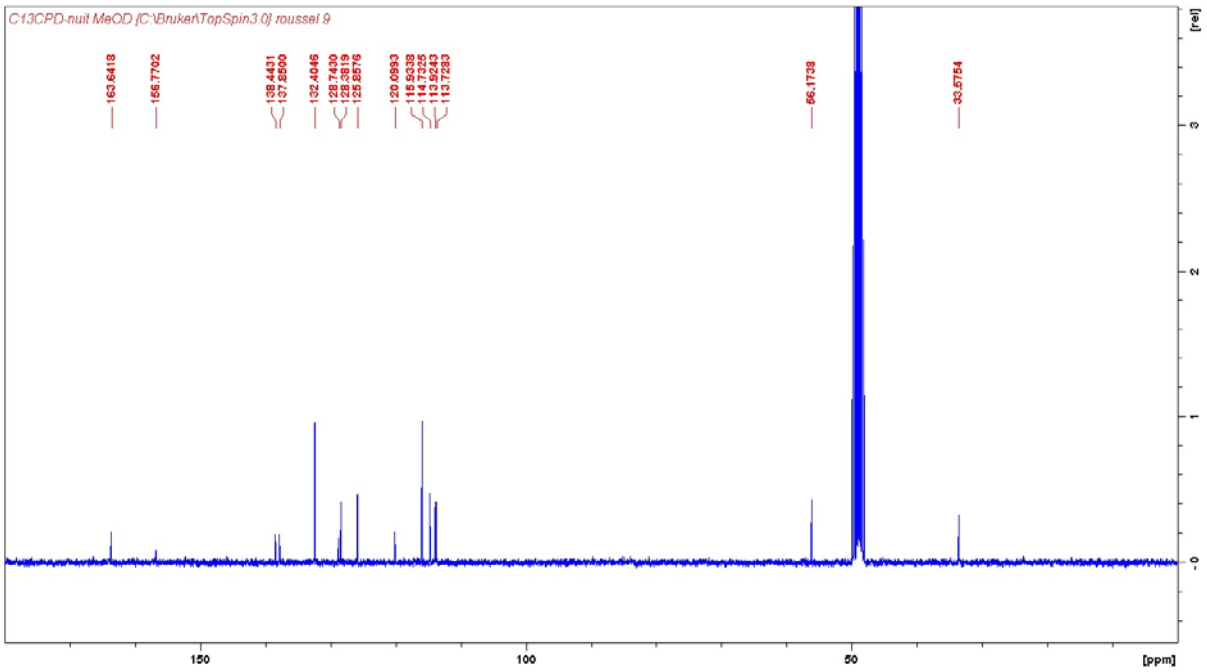


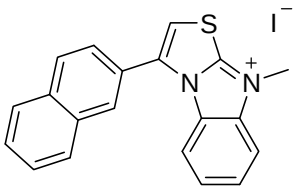
3-(4-Methoxyphenyl)-9-methyl[1,3]thiazolo[3,2-*a*]benzimidazol-9-ium iodide **3n**

^{1}H NMR (CD_3OD, 400 MHz) spectrum



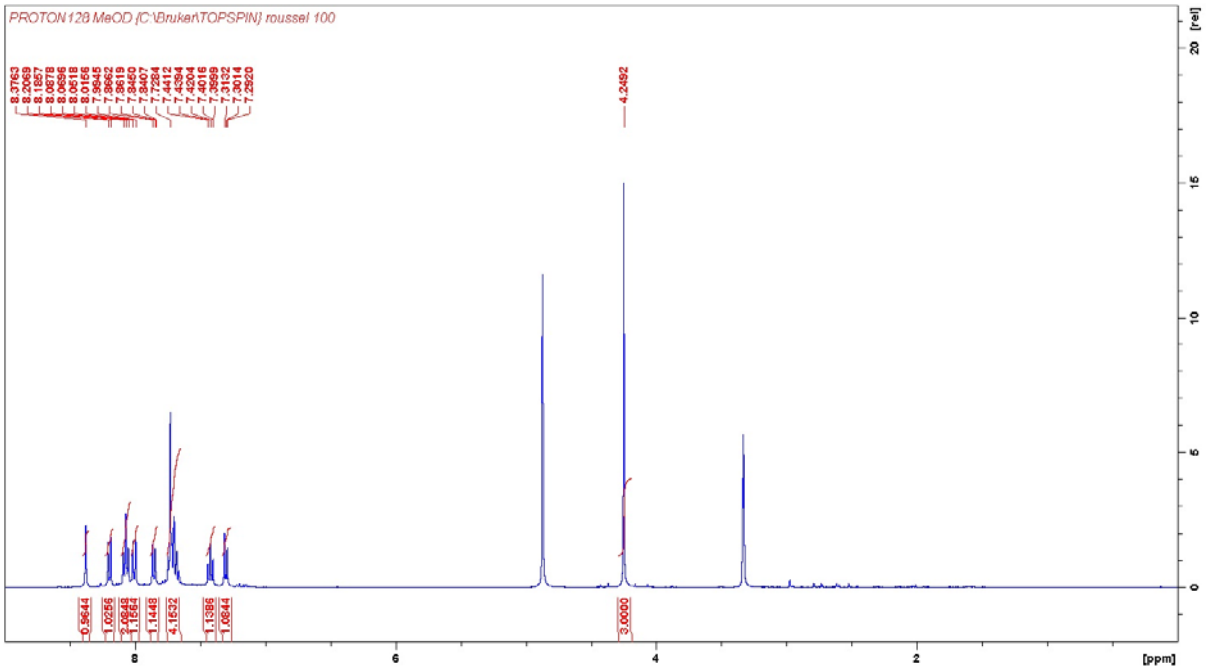
^{13}C NMR (CD_3OD, 75 MHz) spectrum



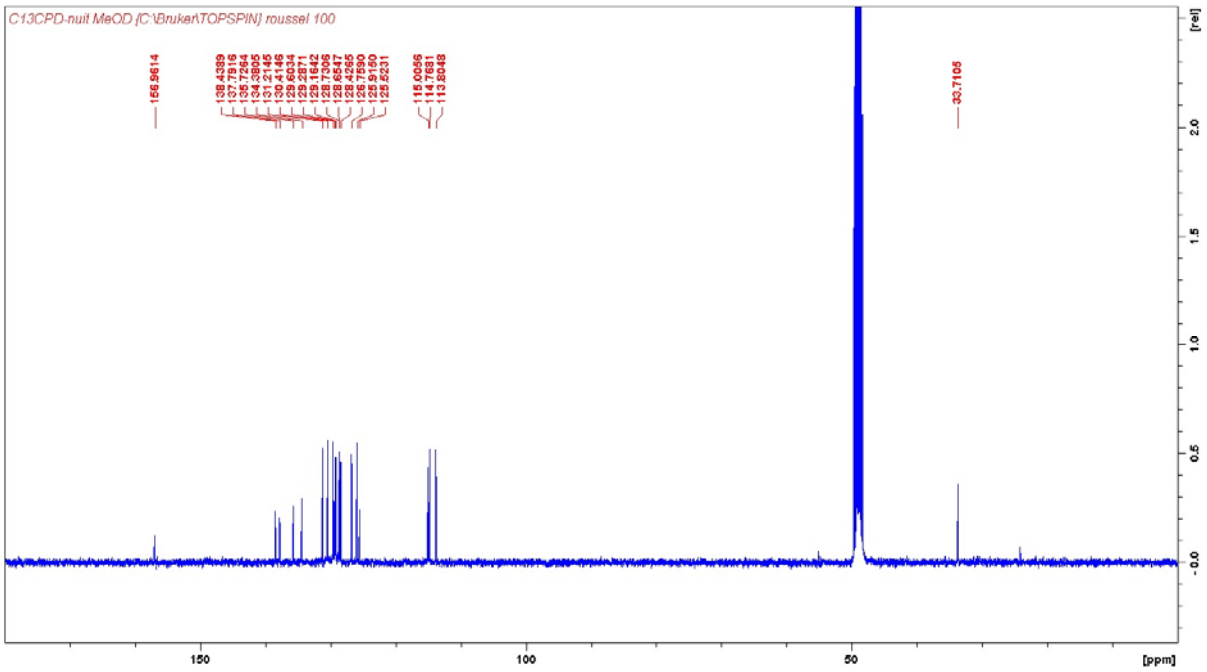


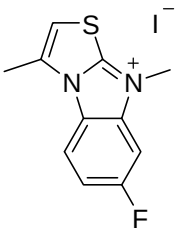
9-Methyl-3-(naphthalen-2-yl)[1,3]thiazolo[3,2-*a*]benzimidazol-9-ium iodide **3o**

^{1}H NMR (CD_3OD, 400 MHz) spectrum



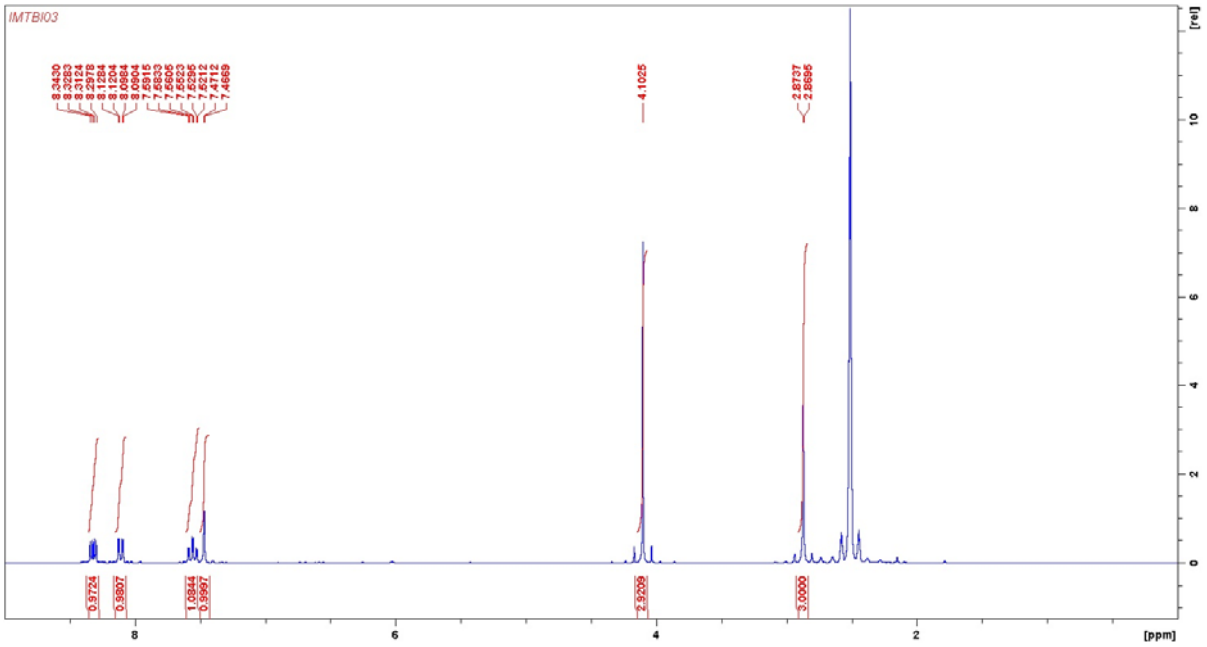
^{13}C NMR (CD_3OD, 100 MHz) spectrum



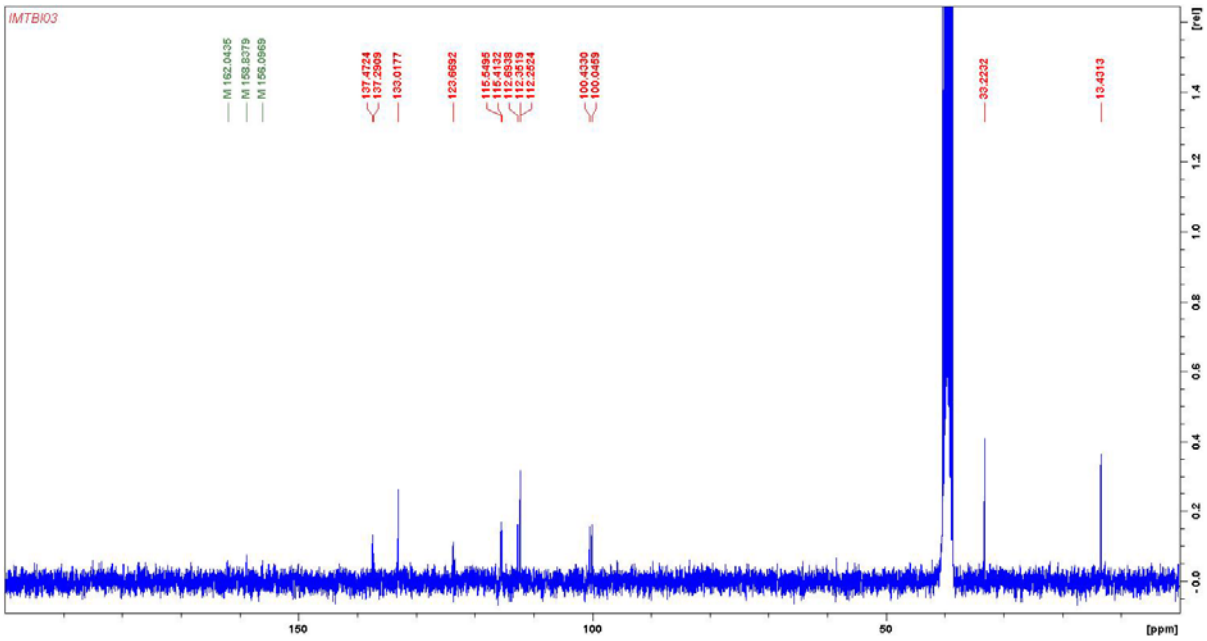


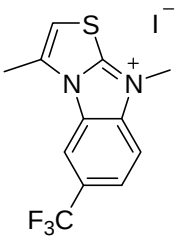
7-Fluoro-3,9-dimethyl[1,3]thiazolo[3,2-*a*]benzimidazol-9-ium iodide **3p**

^{1}H NMR (DMSO-*d6*, 300 MHz) spectrum



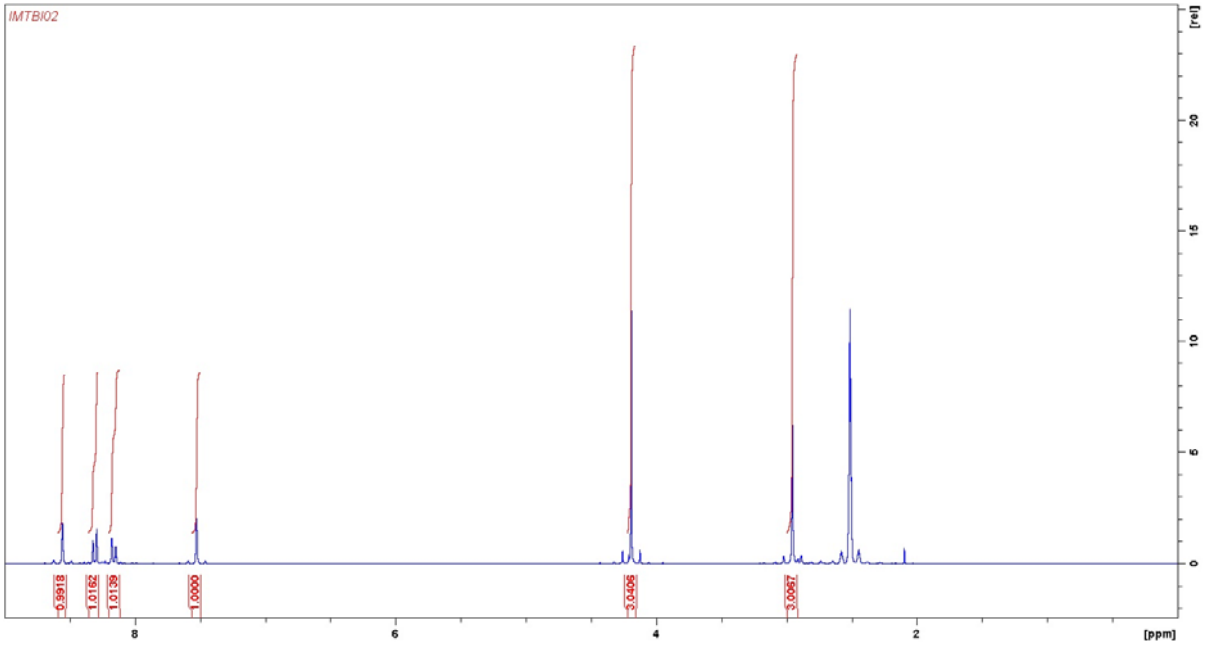
^{13}C NMR (DMSO-*d6*, 75 MHz) spectrum



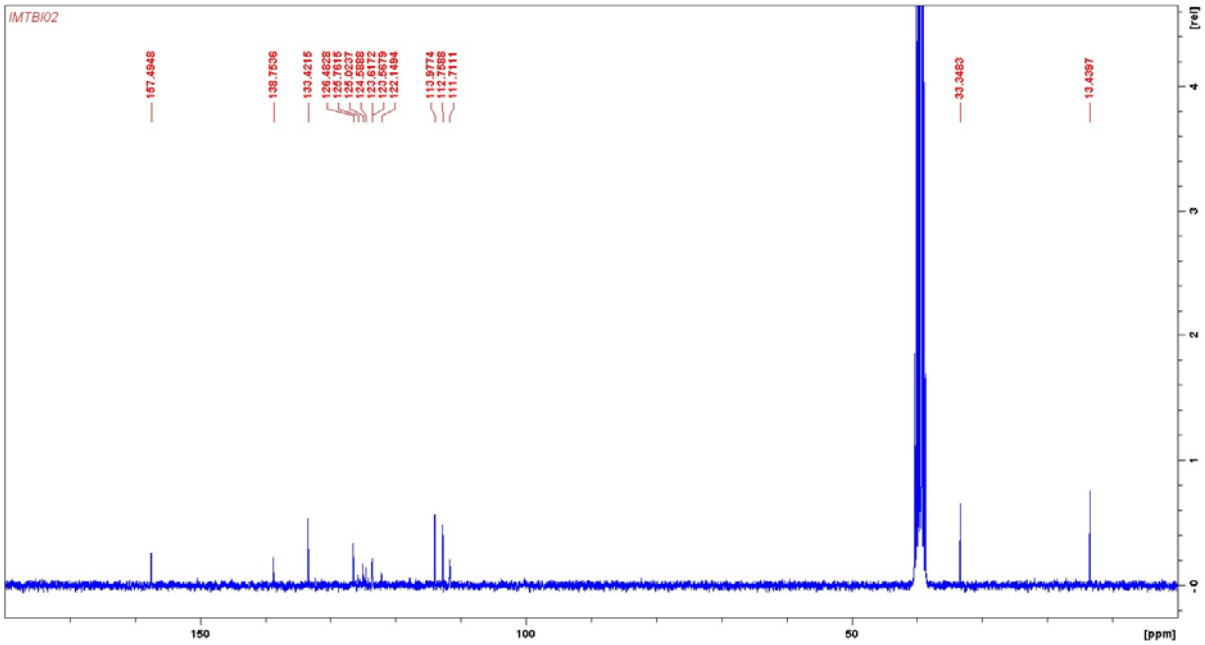


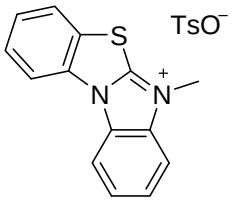
3,9-Dimethyl-6-(trifluoromethyl)[1,3]thiazolo[3,2-*a*]benzimidazol-9-ium iodide **3q**

^{1}H NMR (DMSO-*d6*, 300 MHz) spectrum



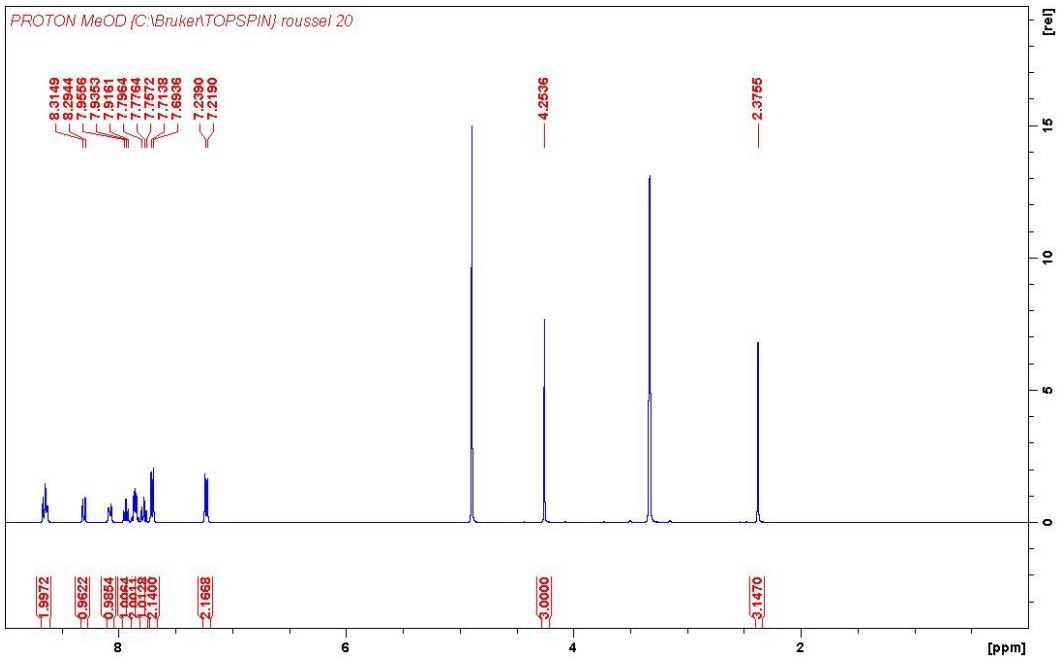
^{13}C NMR (DMSO-*d6*, 75 MHz) spectrum



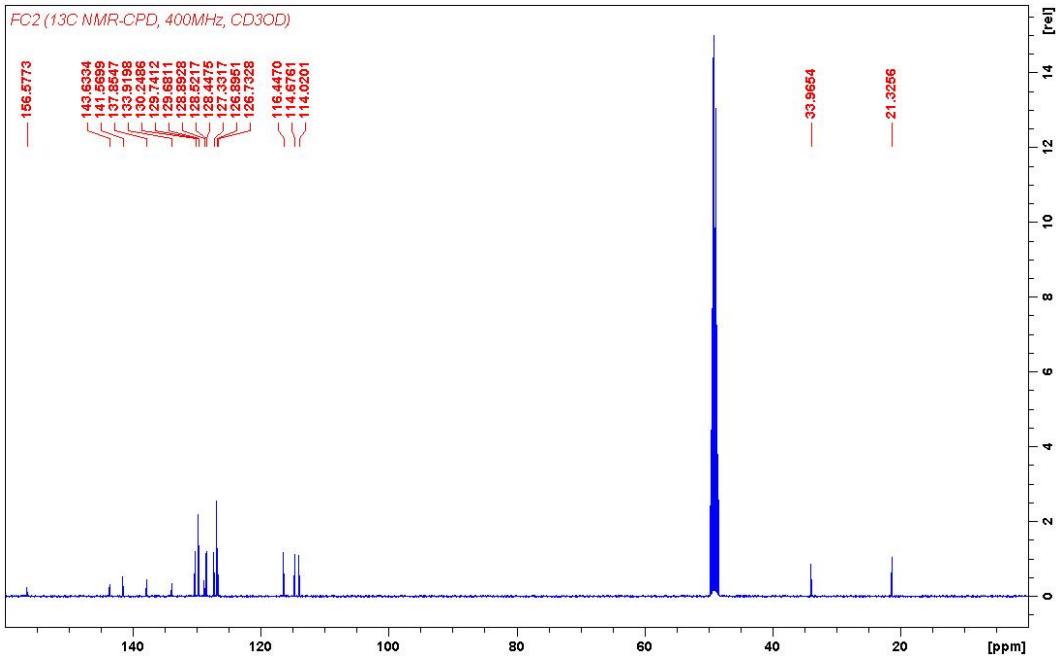


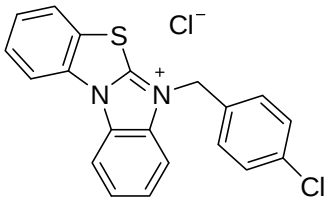
6-methyl[3,1]benzimidazo[2,1-*b*][1,3]benzothiazol-6-ium 4-methylbenzenesulfonate **4a**

^{1}H NMR (CD_3OD, 400 MHz) spectrum



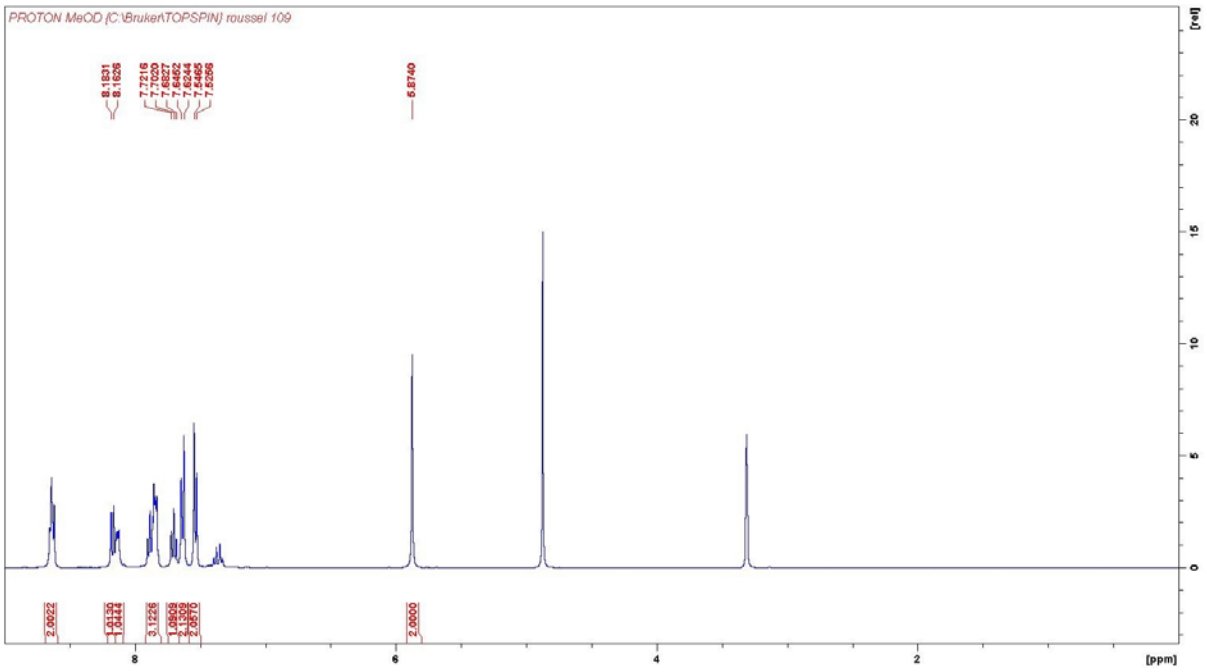
^{13}C NMR (CD_3OD, 100 MHz) spectrum



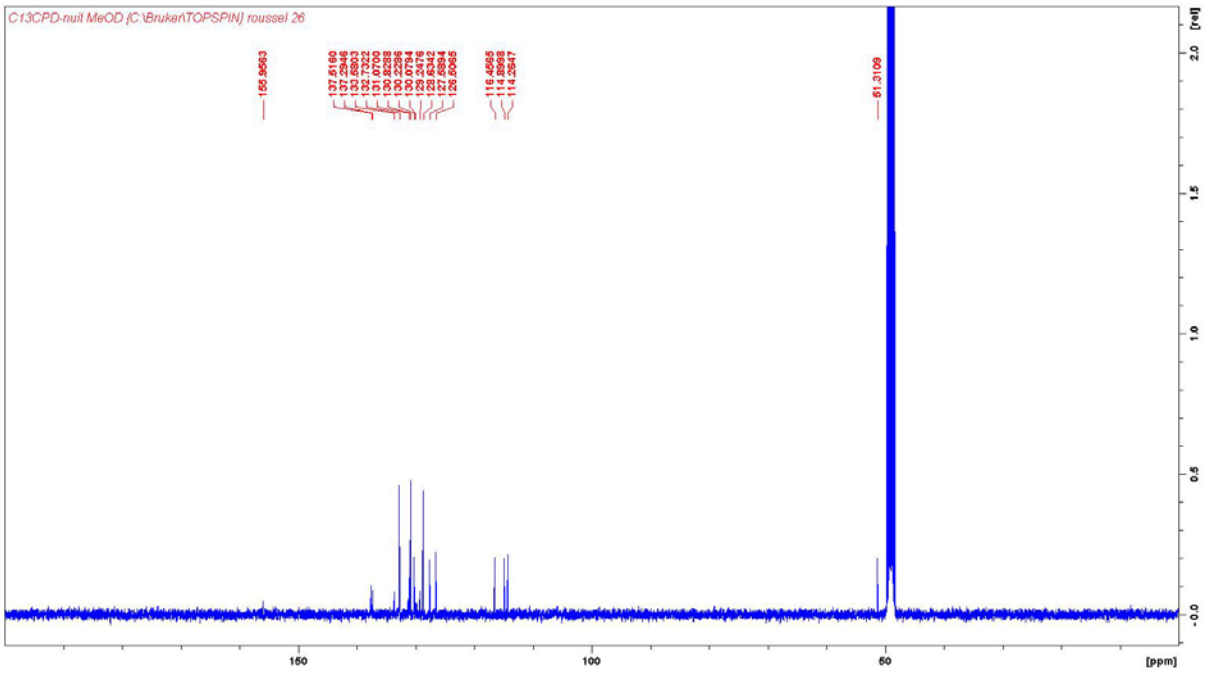


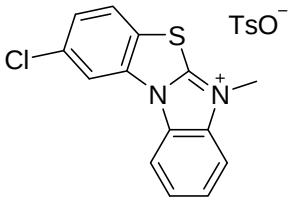
6-(4-chlorobenzyl)[3,1]benzimidazo[2,1-*b*][1,3]benzothiazol-6-ium chloride **4b**

^{1}H NMR (CD_3OD, 400 MHz) spectrum



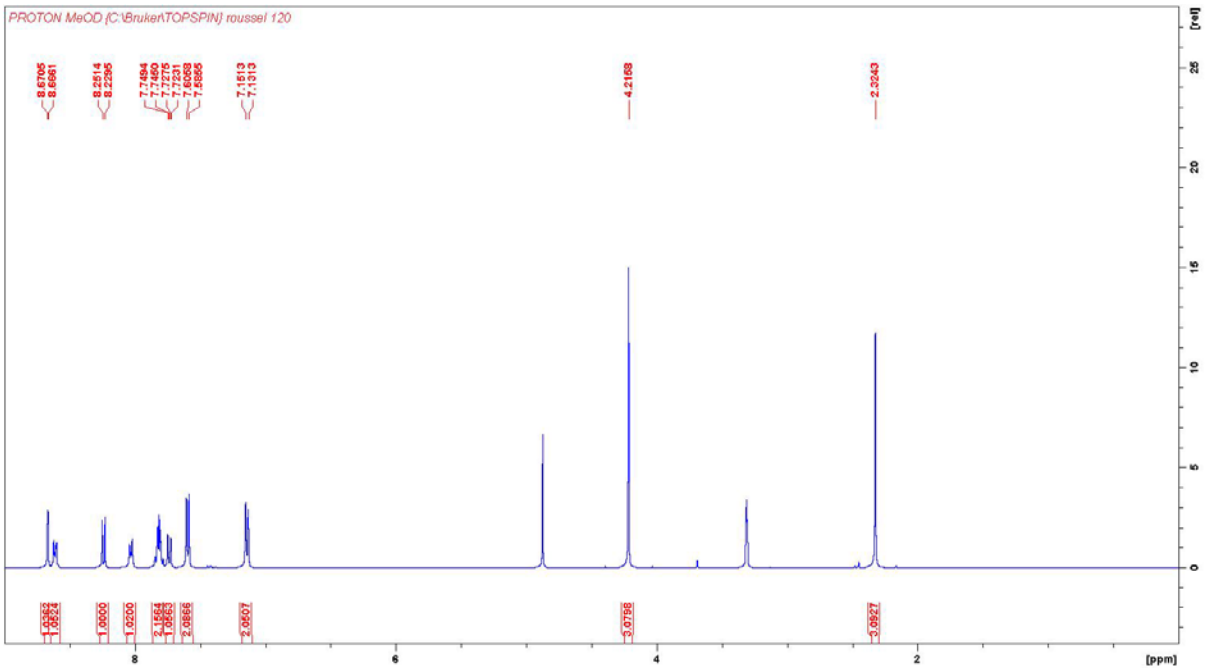
^{13}C NMR (CD_3OD, 100 MHz) spectrum



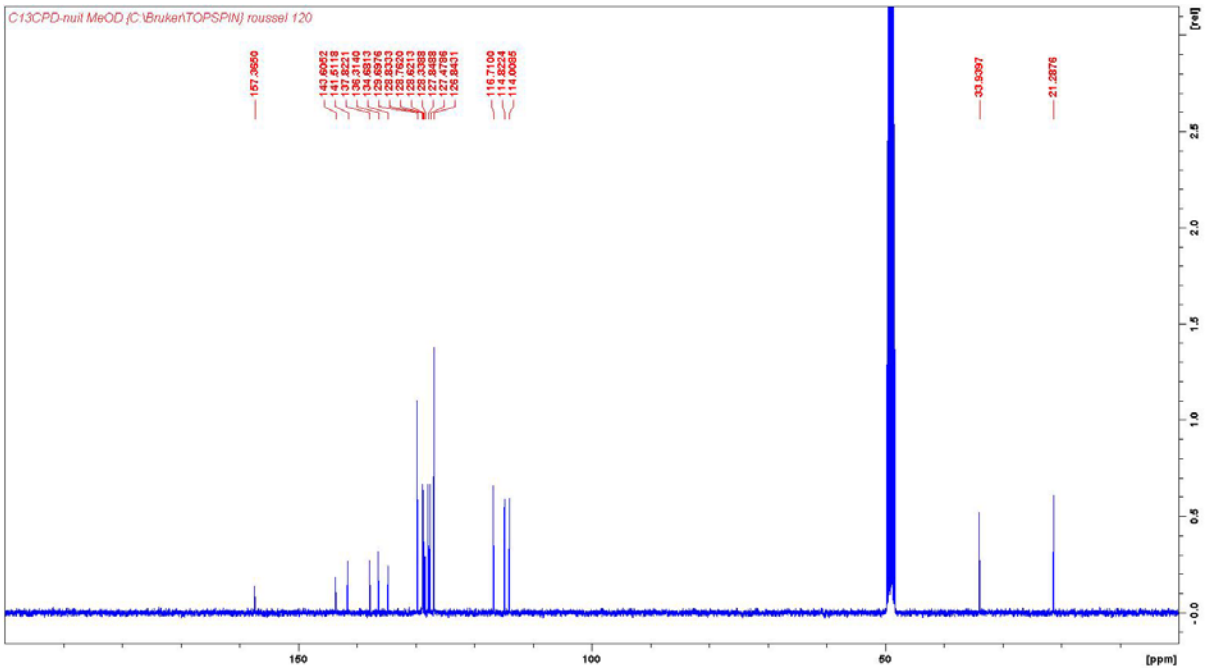


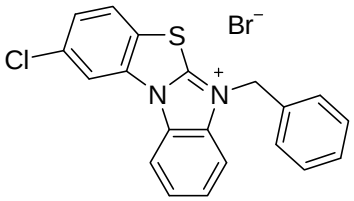
2-chloro-6-methyl[3,1]benzimidazo[2,1-*b*][1,3]benzothiazol-6-ium 4-methylbenzenesulfonate **4c**

^{1}H NMR (CD_3OD, 400 MHz) spectrum



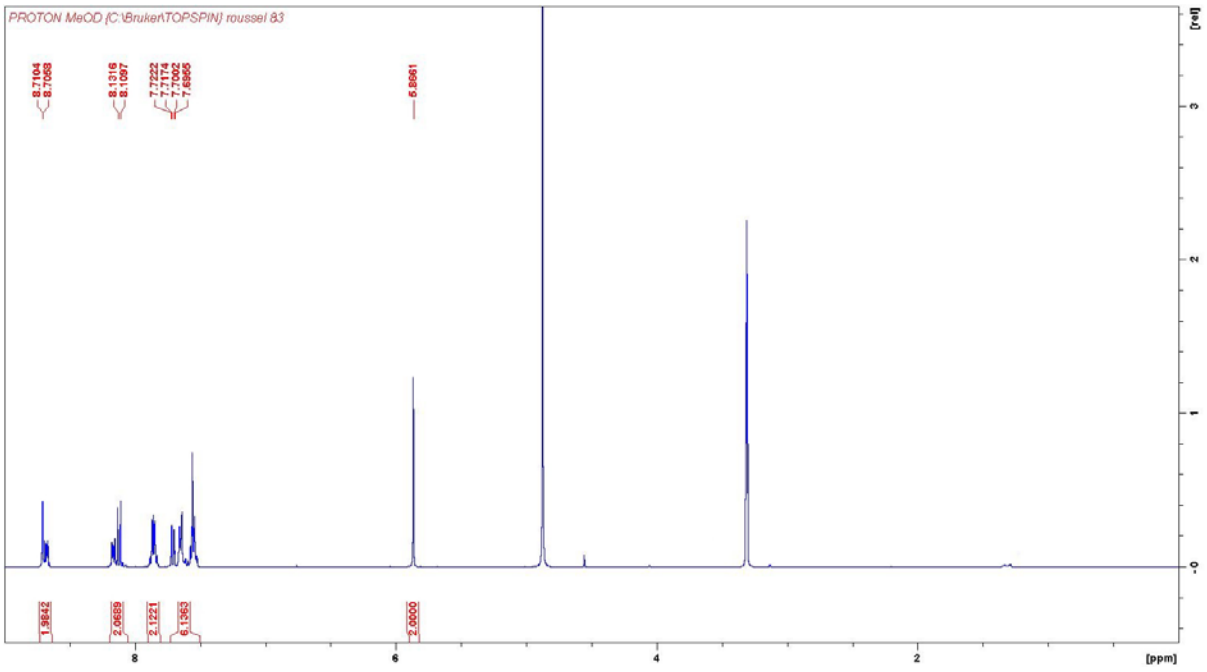
^{13}C NMR (CD_3OD, 100 MHz) spectrum



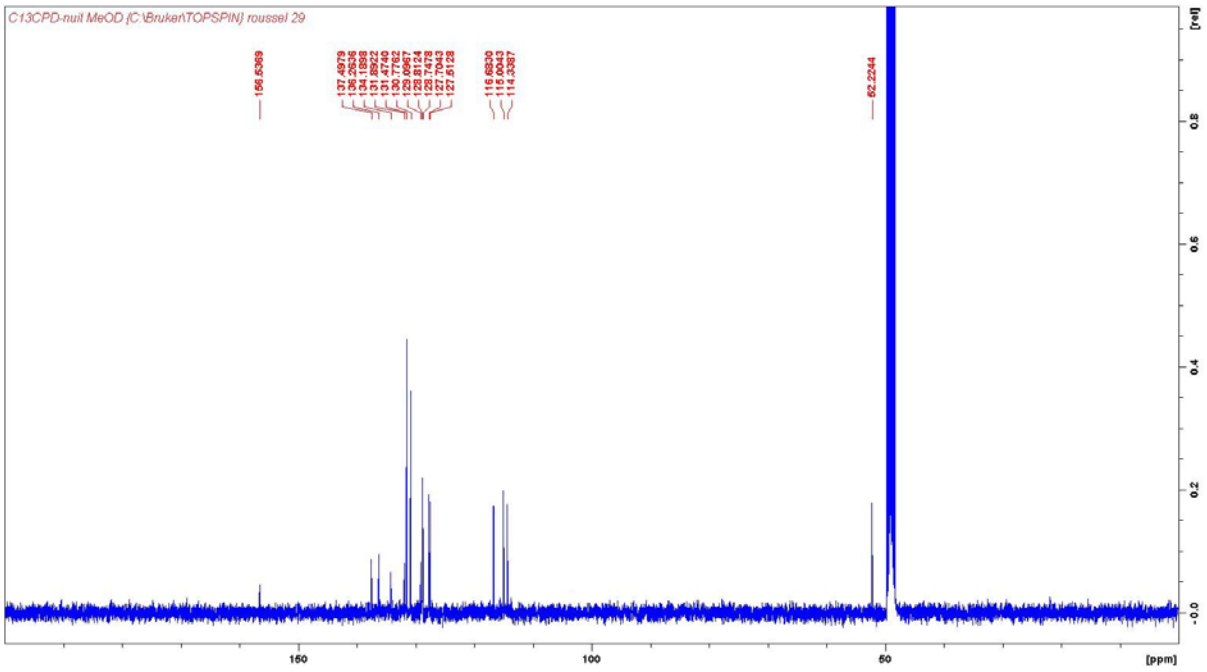


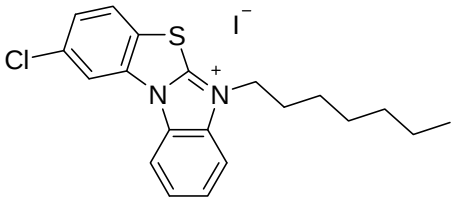
6-benzyl-2-chloro[3,1]benzimidazo[2,1-*b*][1,3]benzothiazol-6-ium bromide **4e**

^{1}H NMR (CD_3OD, 400 MHz) spectrum



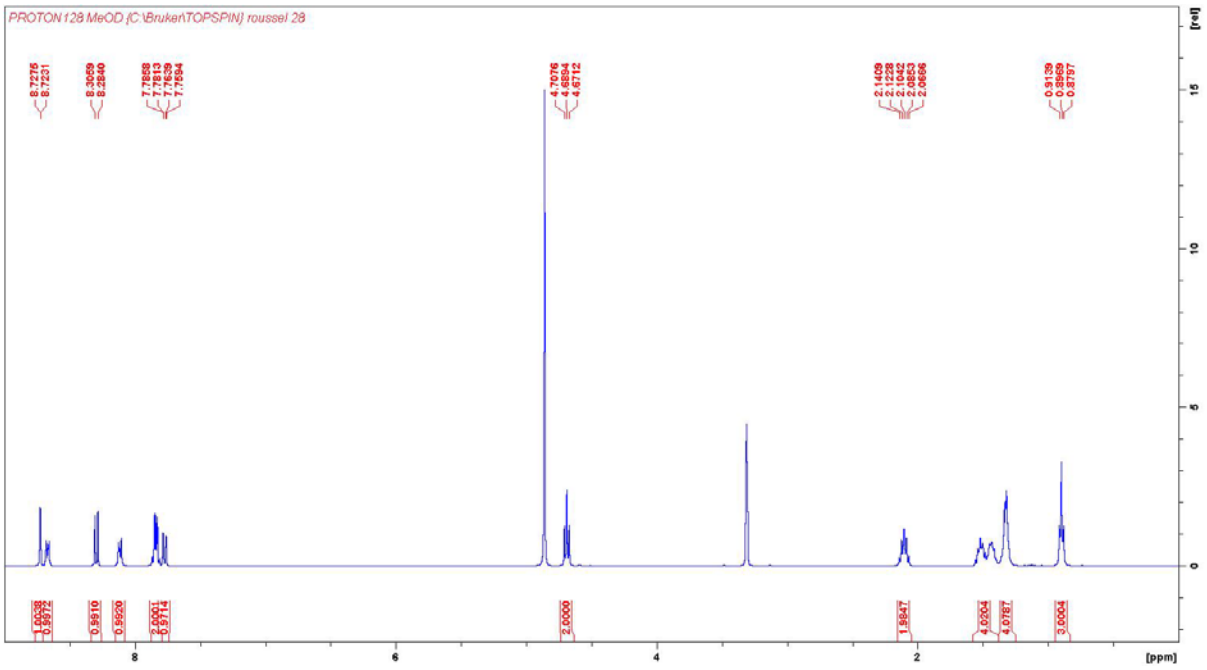
^{13}C NMR (CD_3OD, 100 MHz) spectrum



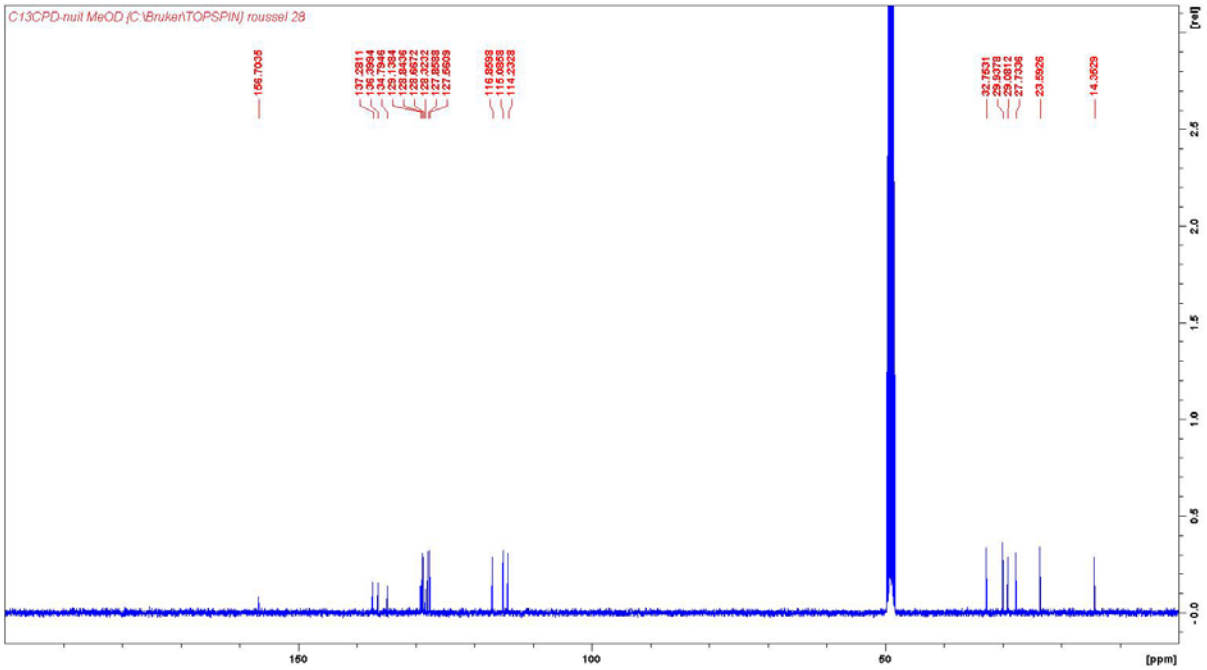


2-chloro-6-hepty[3,1]benzimidazo[2,1-*b*][1,3]benzothiazol-6-ium iodide **4g**

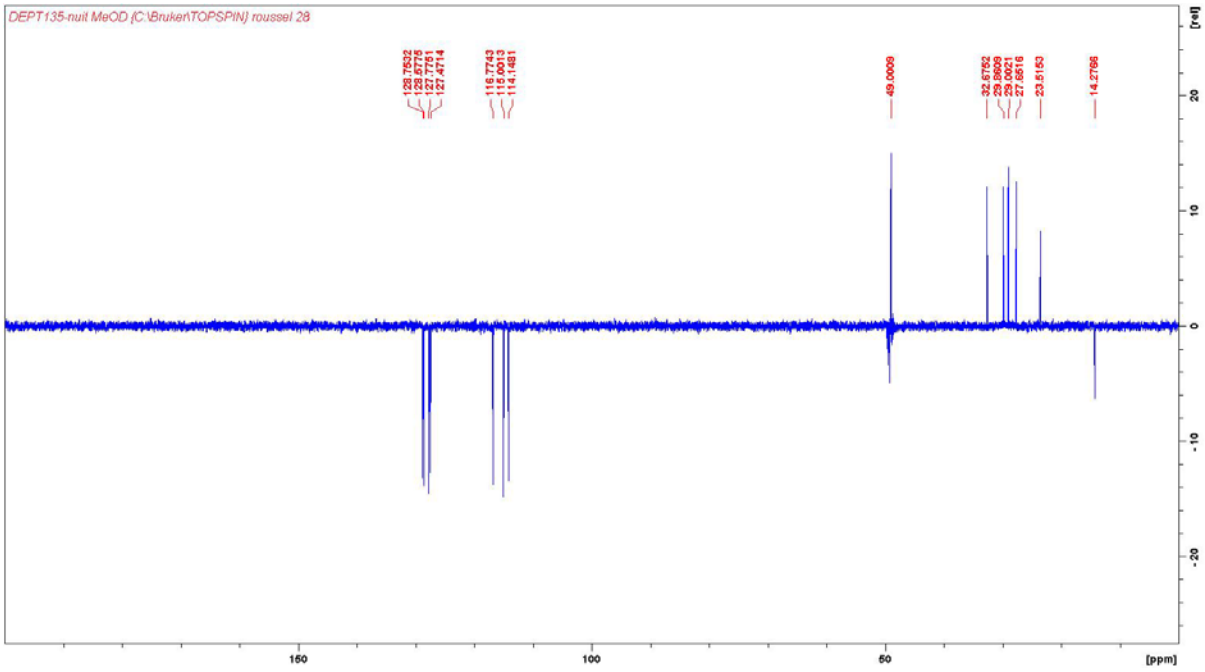
^{1}H NMR (CD_3OD, 400 MHz) spectrum

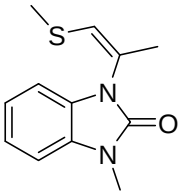


^{13}C NMR (CD_3OD, 100 MHz) spectrum



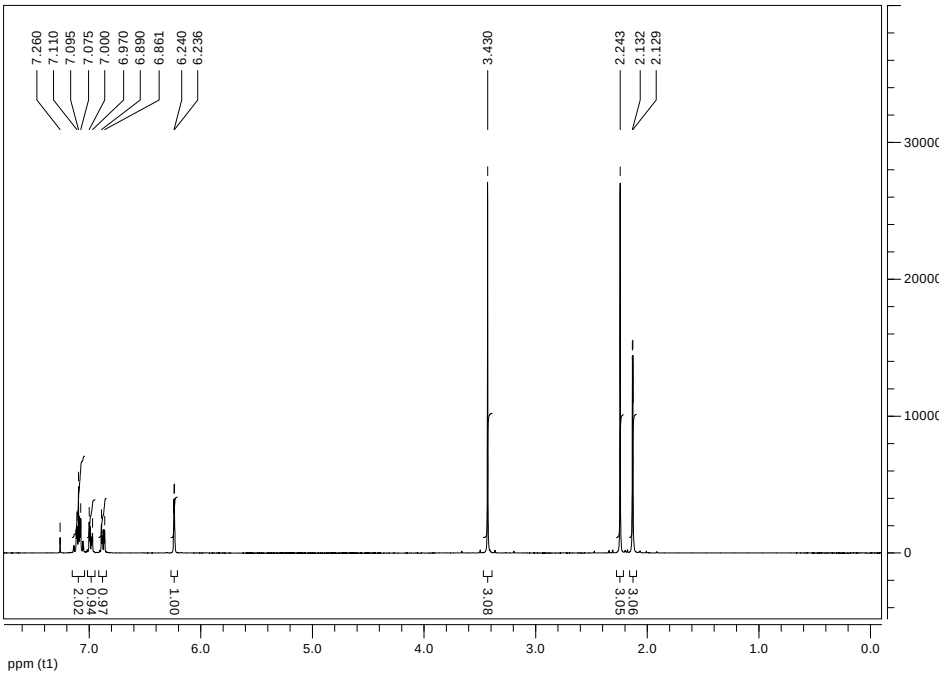
DEPT 135 (CD_3OD, 100 MHz) spectrum



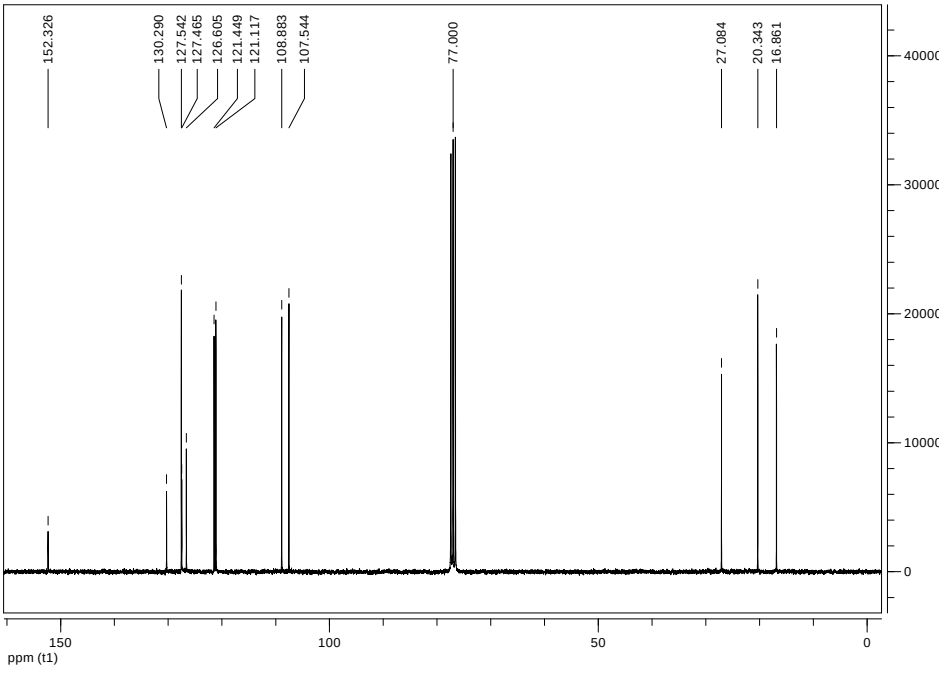


1-Methyl-3-[(1*Z*)-1-(methylsulfanyl)prop-1-en-2-yl]-1,3-dihydro-2*H*-benzimidazol-2-one **1a**

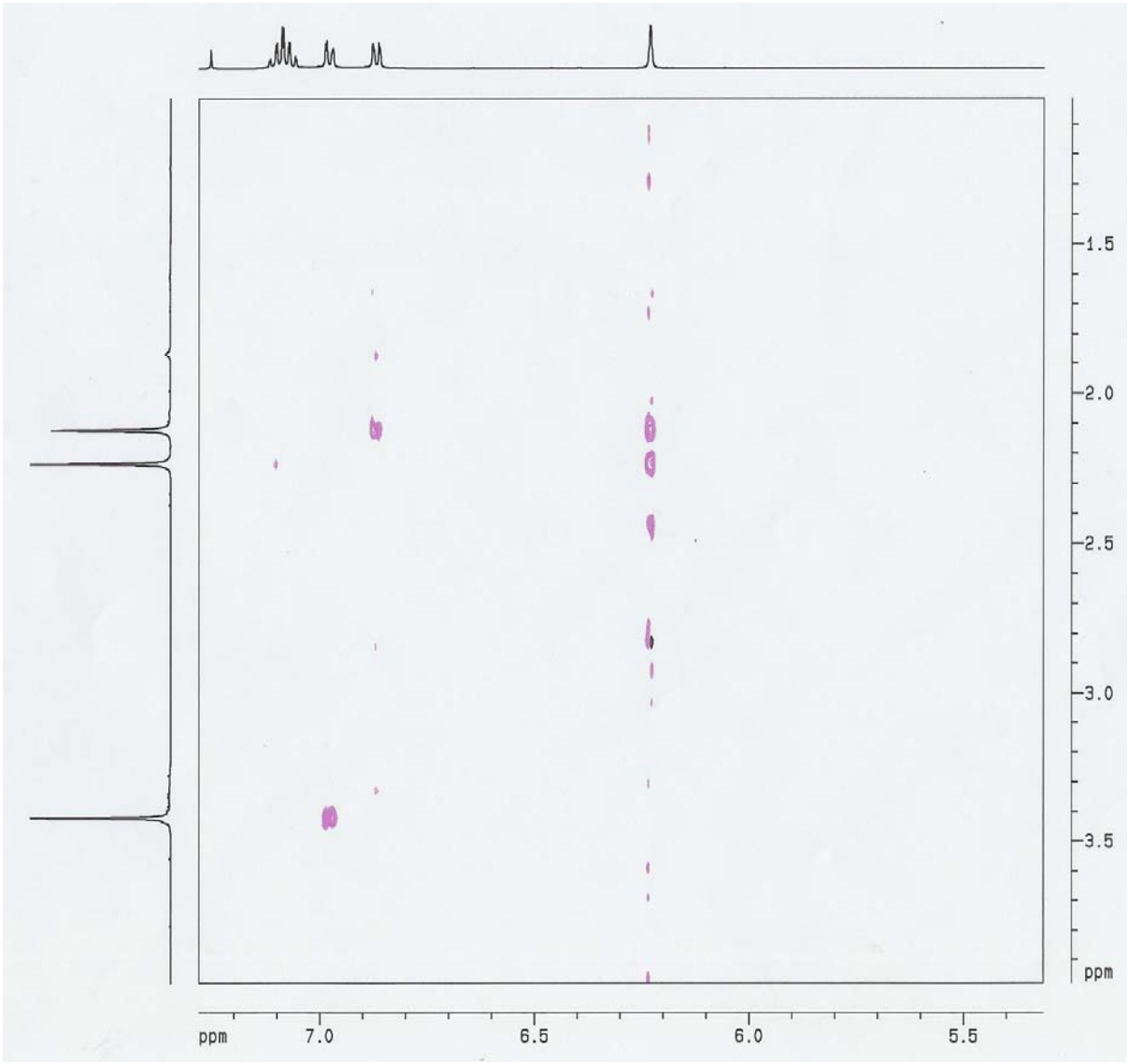
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum



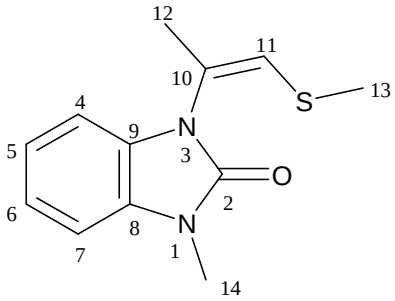
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum

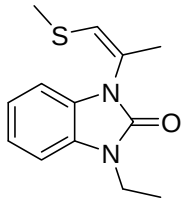


NOESY experiment ($CDCl_3$, 500 MHz) spectrum



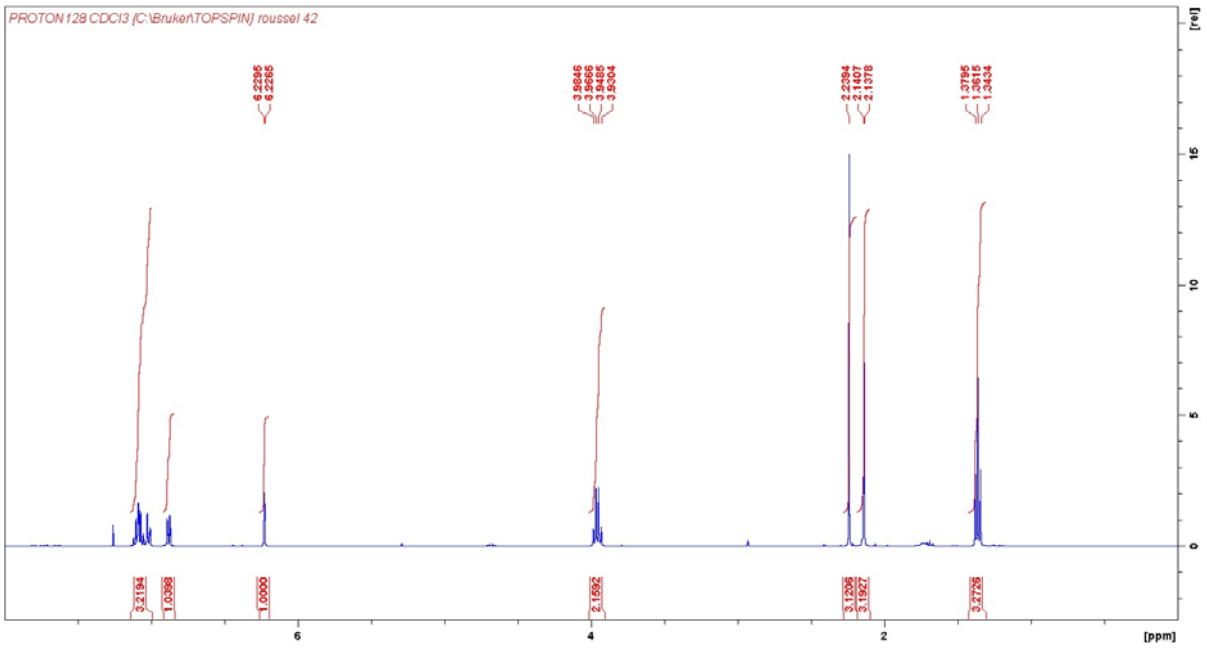
The (*Z*) configuration of **1a** has been established by NOESY study which shows a strong interaction between the hydrogen atom on carbon 11 and the hydrogen atoms on carbon 12.



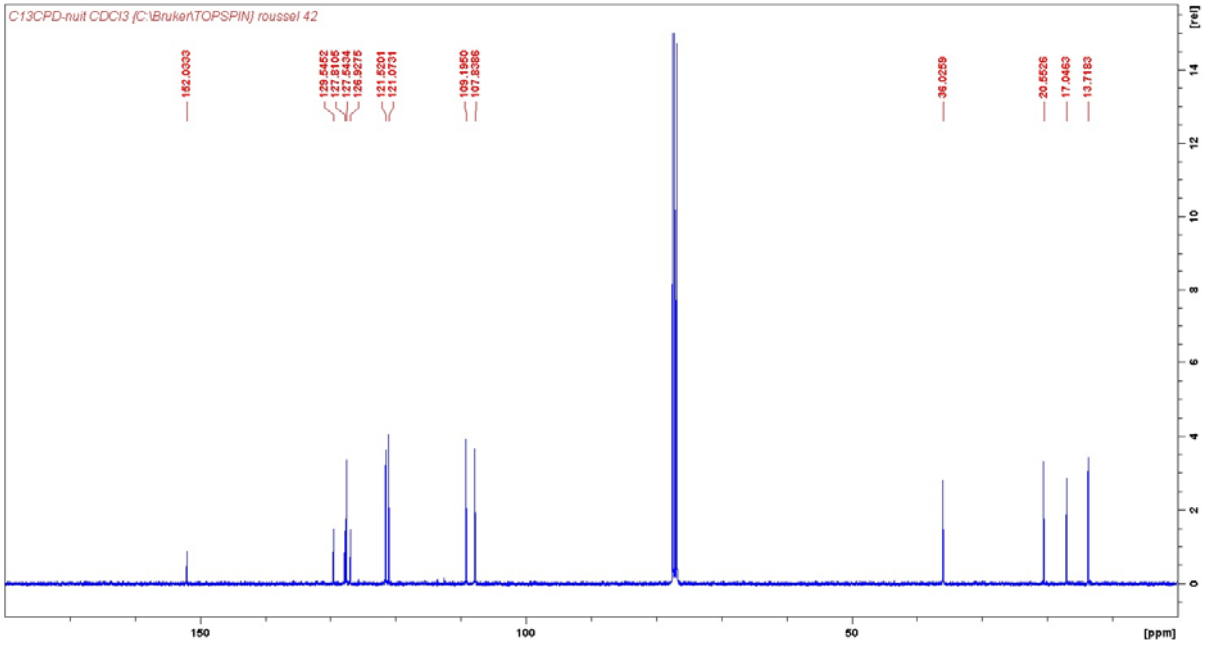


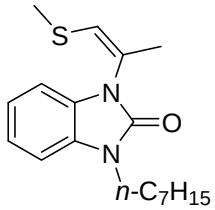
1-Ethyl-3-[(1*Z*)-1-(methylsulfanyl)prop-1-en-2-yl]-1,3-dihydro-2*H*-benzimidazol-2-one **1b**

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



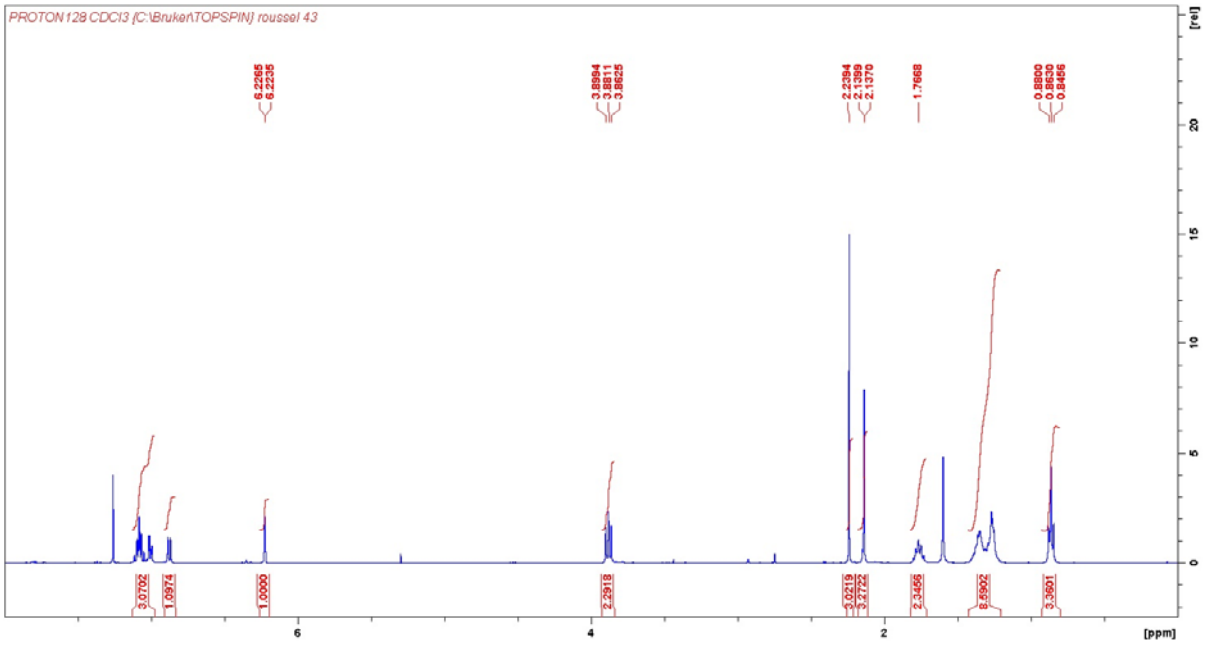
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum



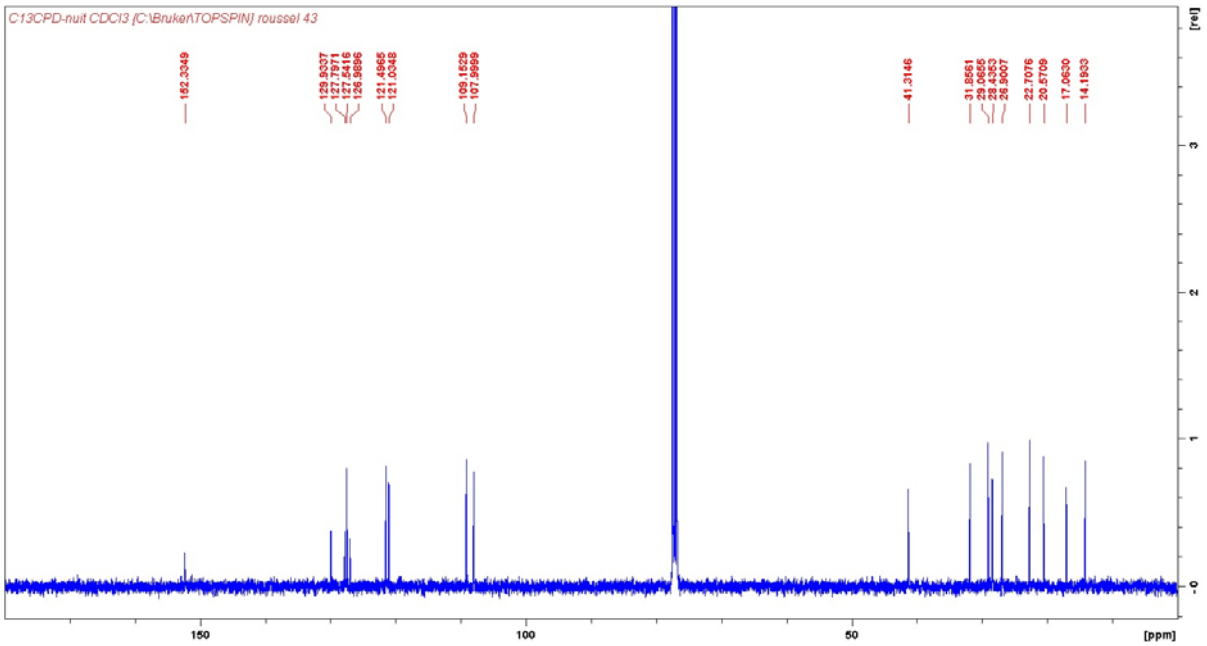


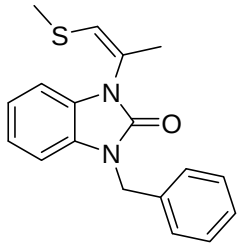
1-Heptyl-3-[(1*Z*)-1-(methylsulfanyl)prop-1-en-2-yl]-1,3-dihydro-2*H*-benzimidazol-2-one **1c**

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



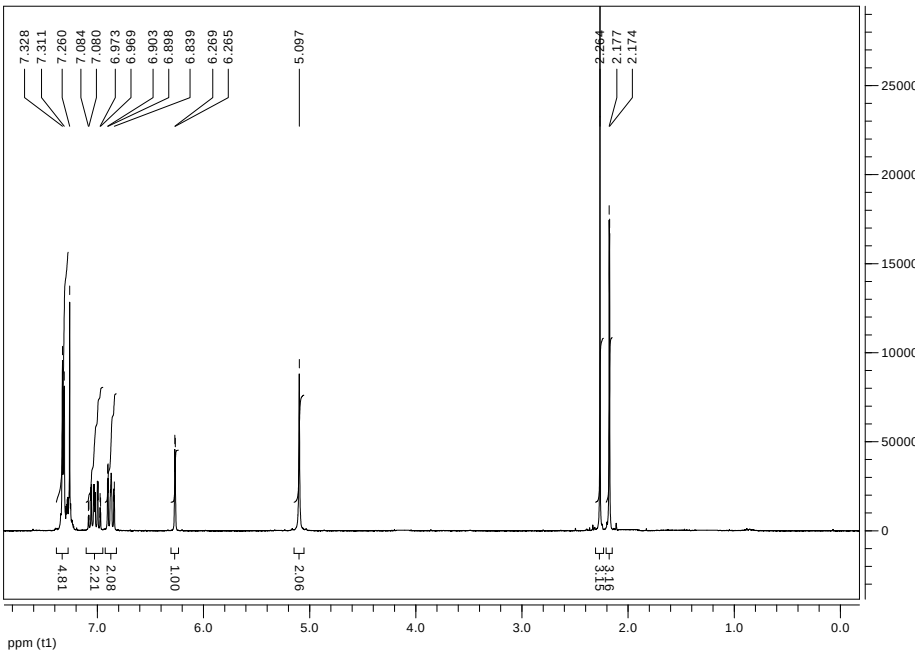
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum



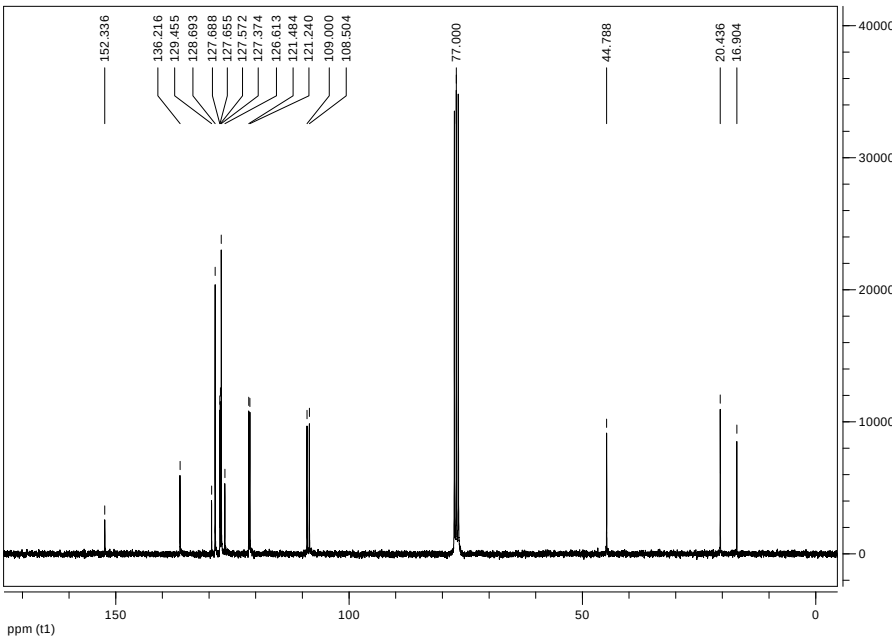


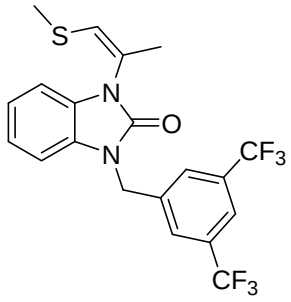
1-Benzyl-3-[(1*Z*)-1-(methylsulfanyl)prop-1-en-2-yl]-1,3-dihydro-2*H*-benzimidazol-2-one **1d**

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



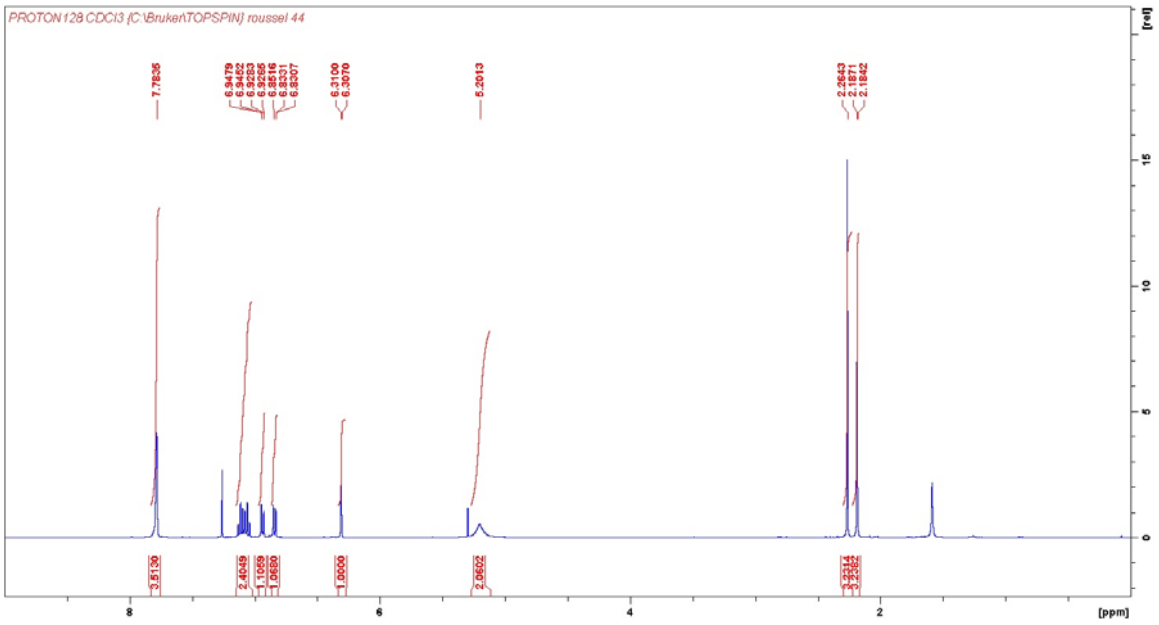
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum



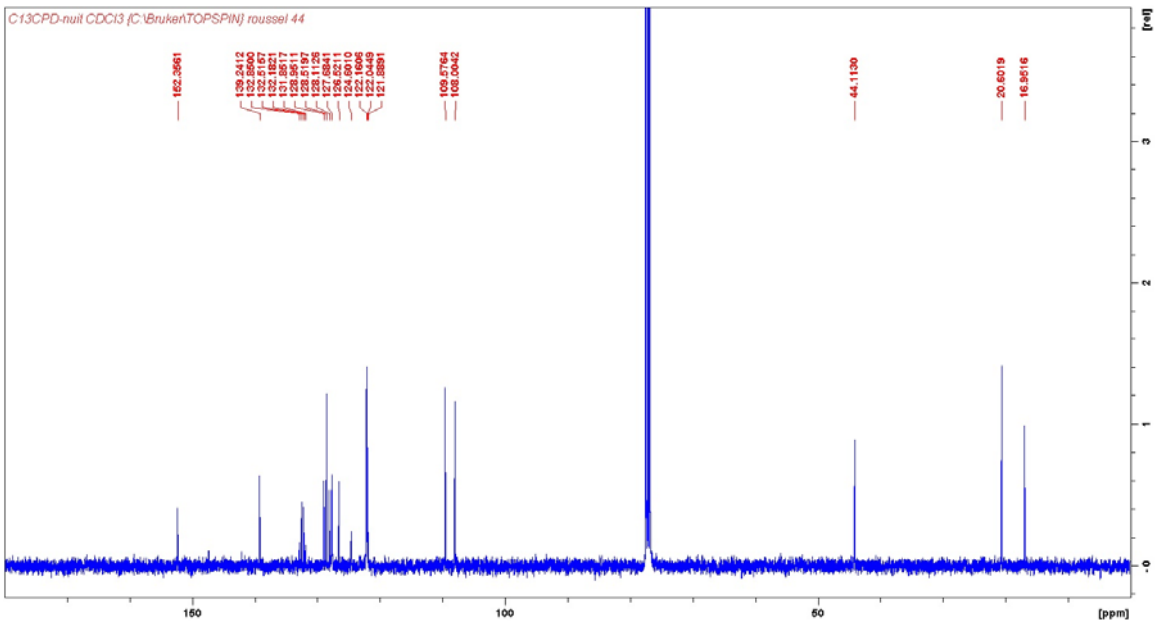


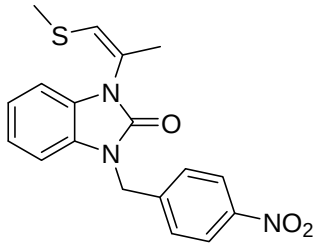
1-[3,5-Bis(trifluoromethyl)benzyl]-3-[(1*Z*)-1-(methylsulfanyl)prop-1-en-2-yl]-1,3-dihydro-2*H*-benzimidazol-2-one **1e**

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



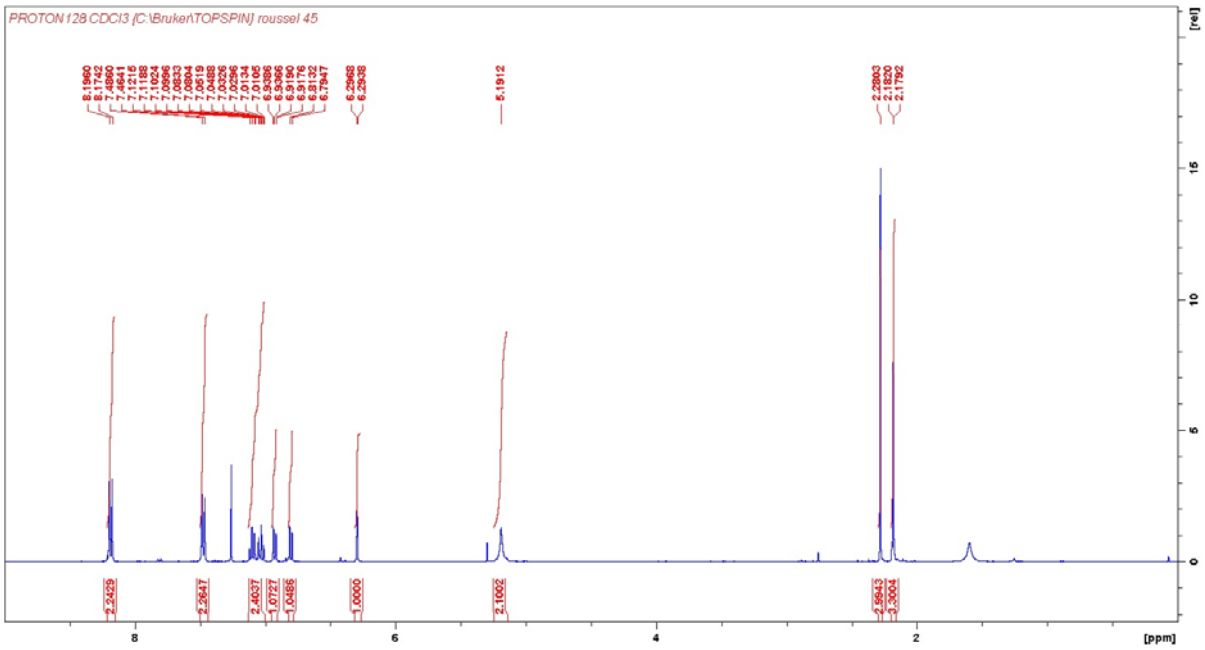
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum



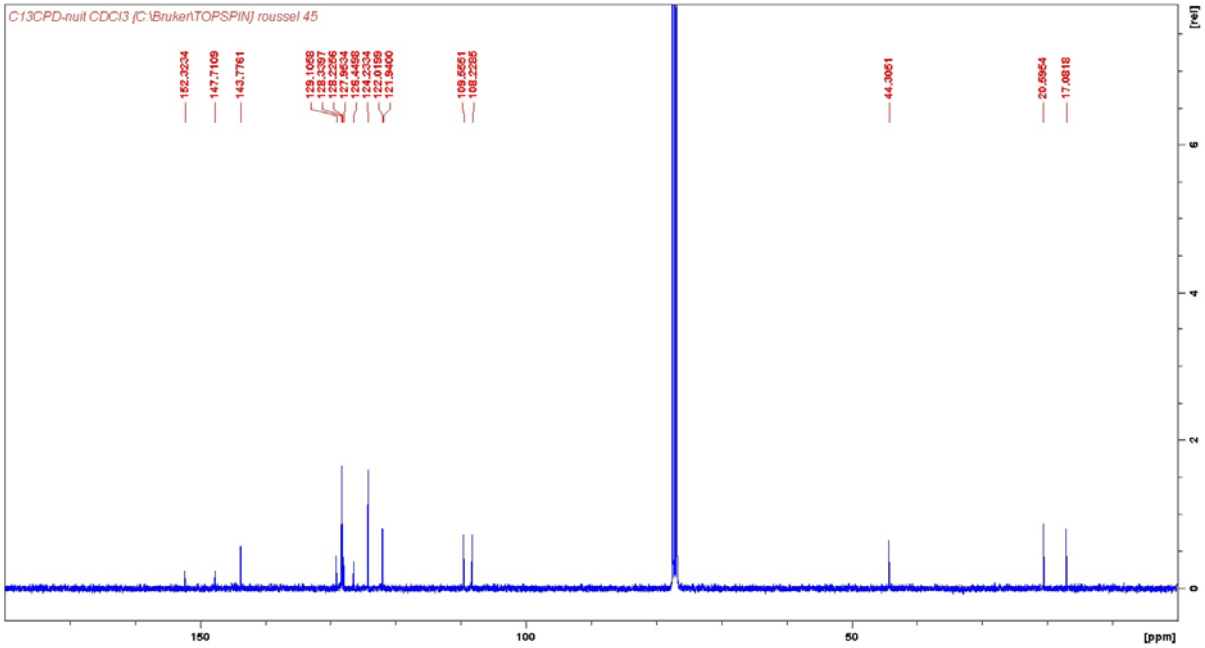


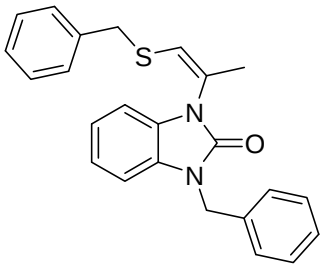
1-[(1*Z*)-1-(Methylsulfanyl)prop-1-en-2-yl]-3-(4-nitrobenzyl)-1,3-dihydro-2*H*-benzimidazol-2-one **1f**

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



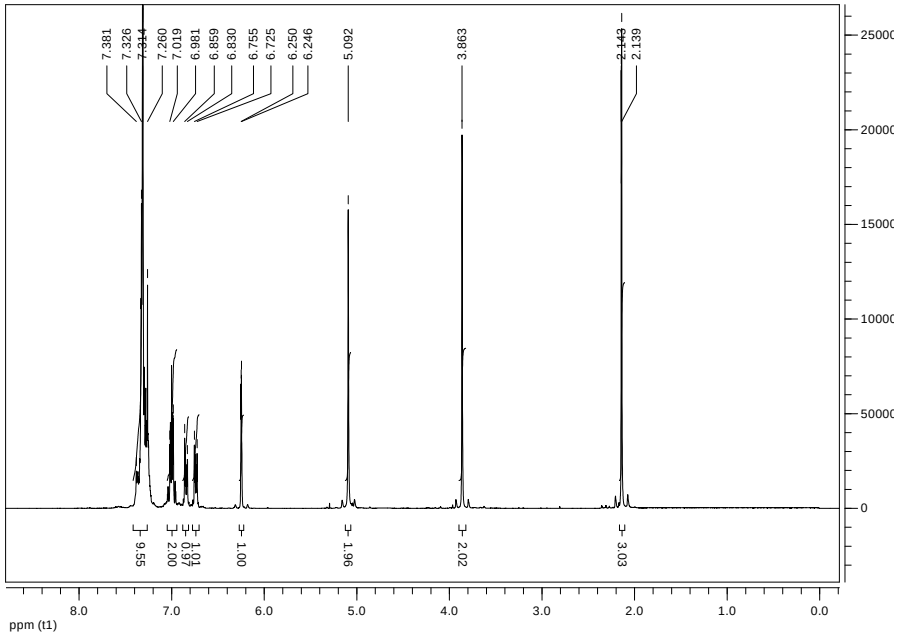
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum



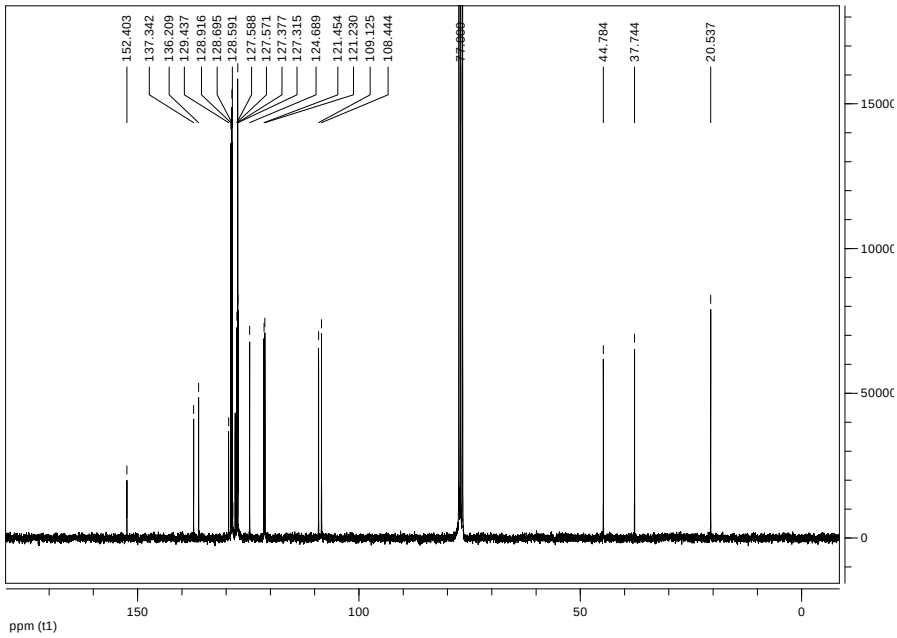


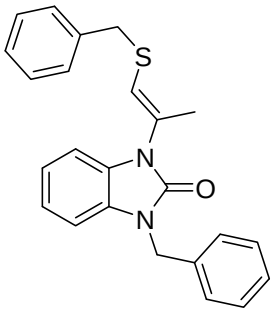
1-Benzyl-3-[(1*Z*)-1-(benzylsulfanyl)prop-1-en-2-yl]-1,3-dihydro-2*H*-benzimidazol-2-one **1g$_1$**

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



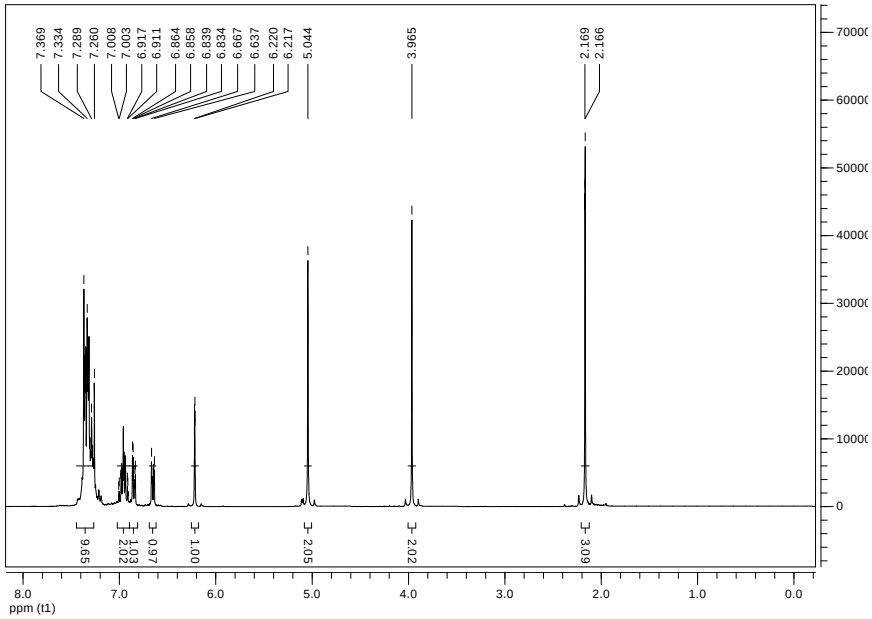
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum



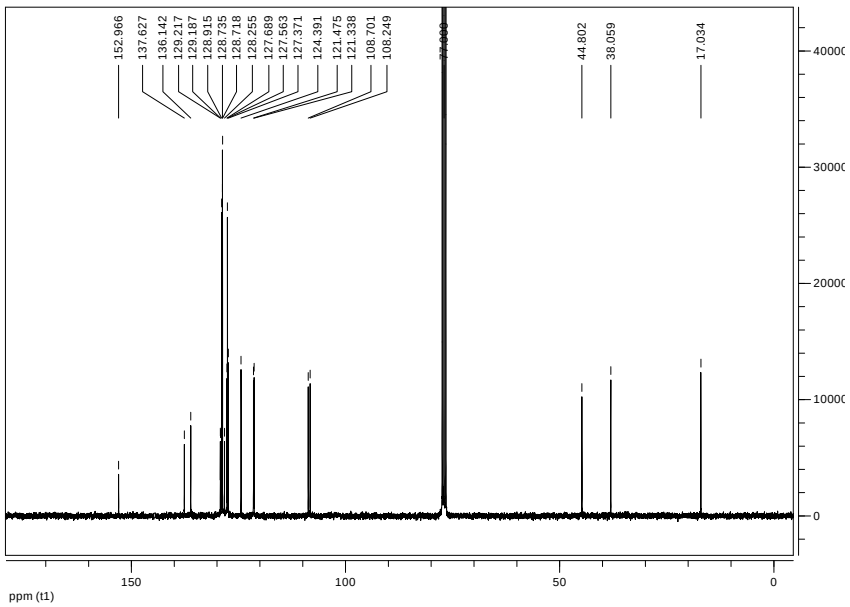


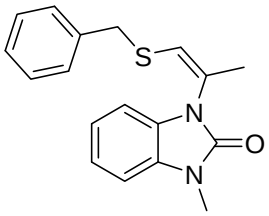
1-Benzyl-3-[(1*E*)-1-(benzylsulfanyl)prop-1-en-2-yl]-1,3-dihydro-2*H*-benzimidazol-2-one **1g$_2$**

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



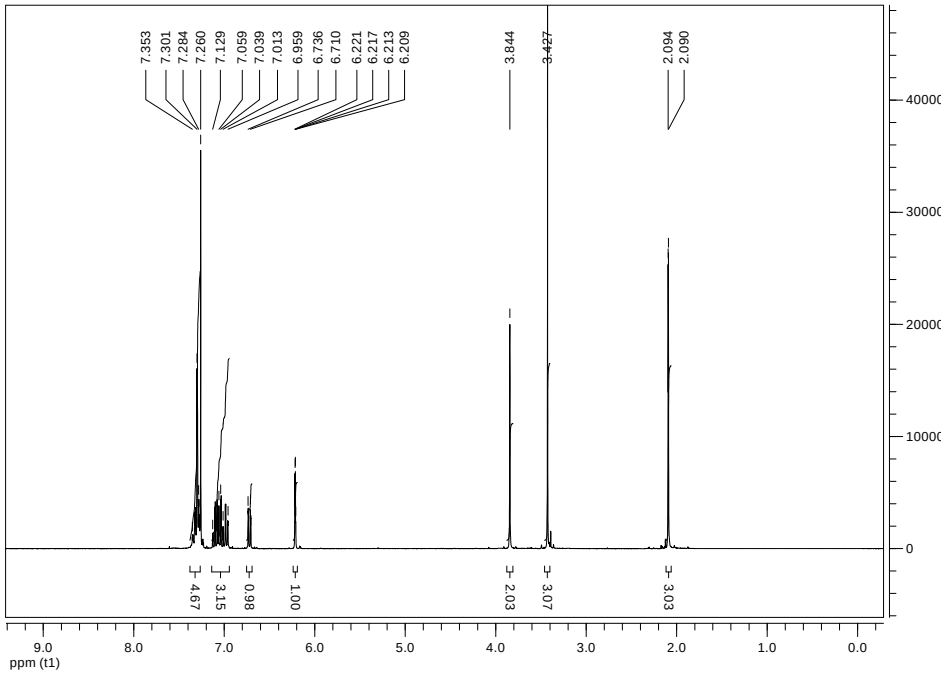
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum



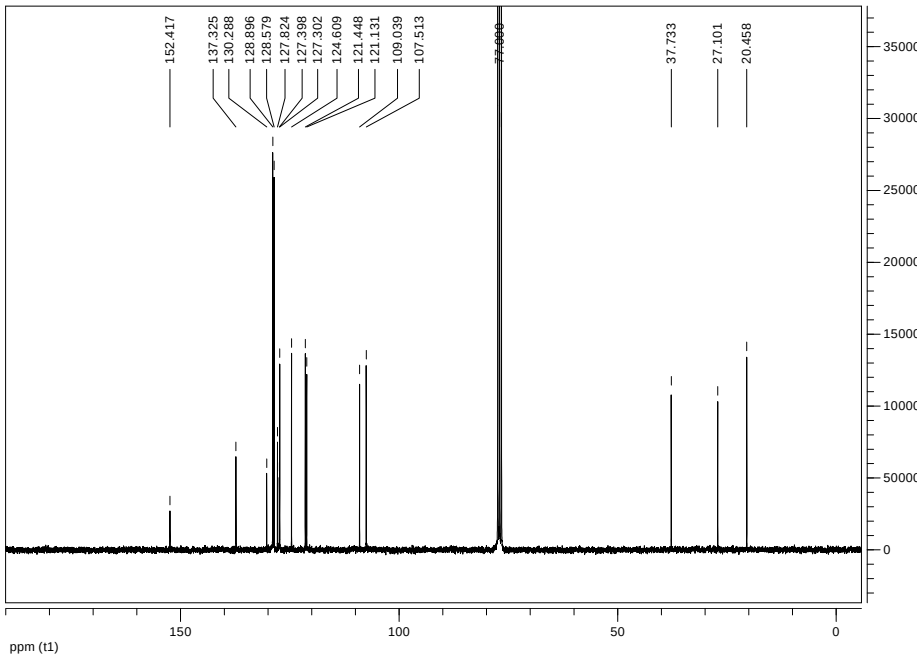


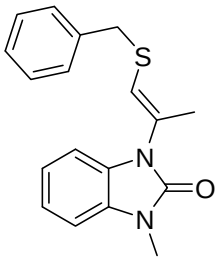
1-[(1*Z*)-1-(Benzylsulfanyl)prop-1-en-2-yl]-3-methyl-1,3-dihydro-2*H*-benzimidazol-2-one **1h$_1$**

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



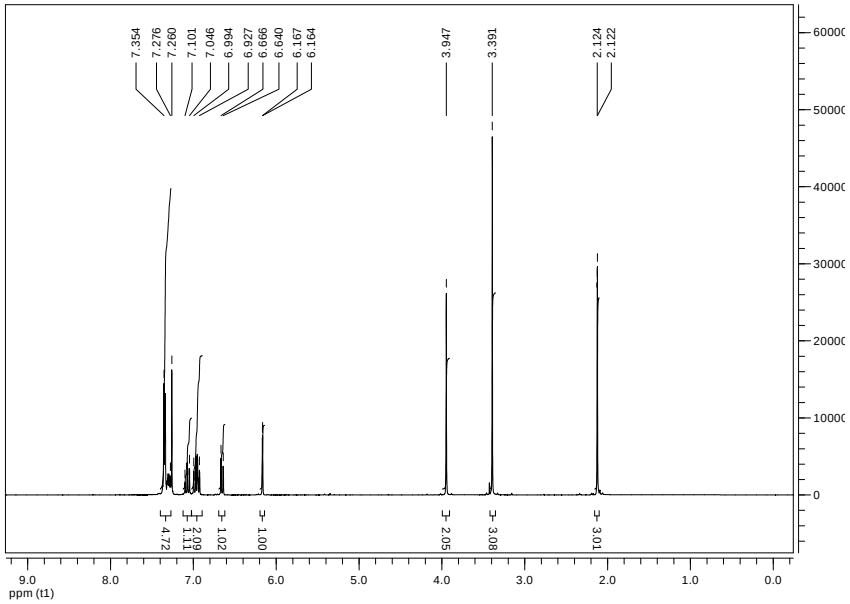
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum



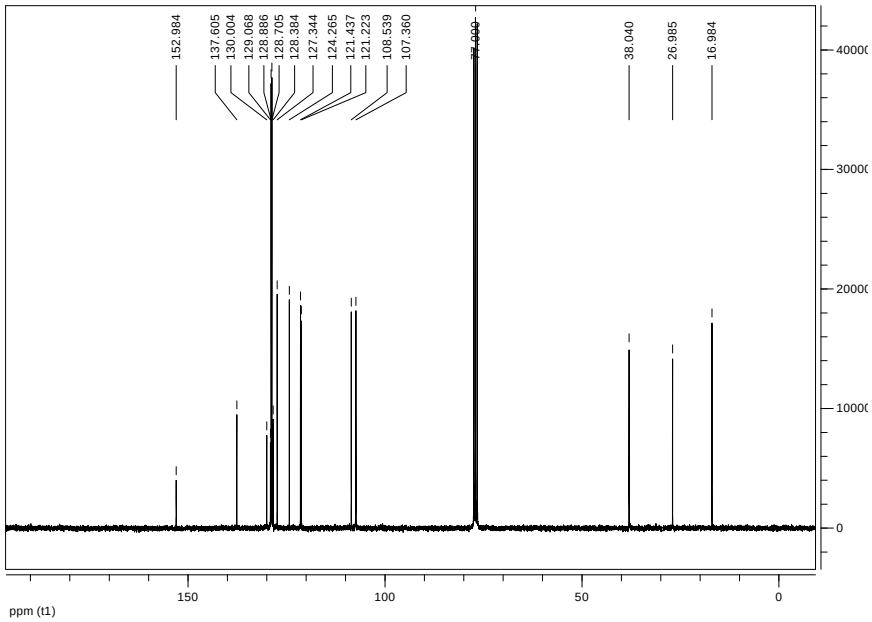


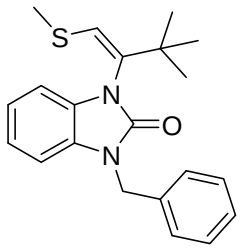
1-[(1*E*)-1-(Benzylsulfanyl)prop-1-en-2-yl]-3-methyl-1,3-dihydro-2*H*-benzimidazol-2-one **1h$_2$**

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



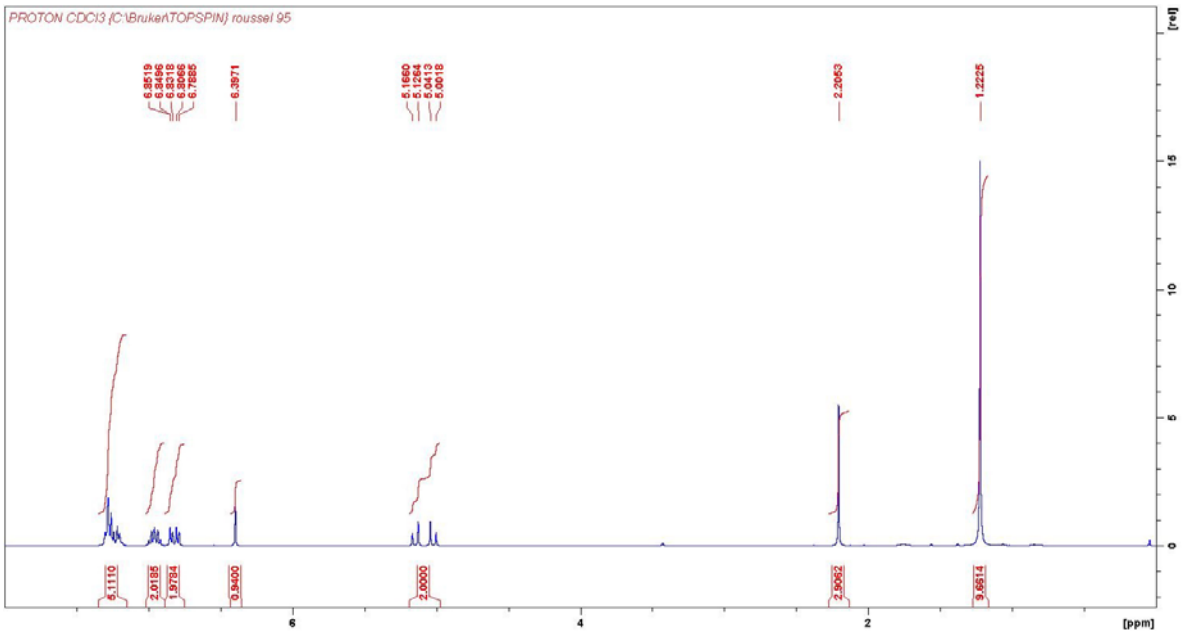
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum



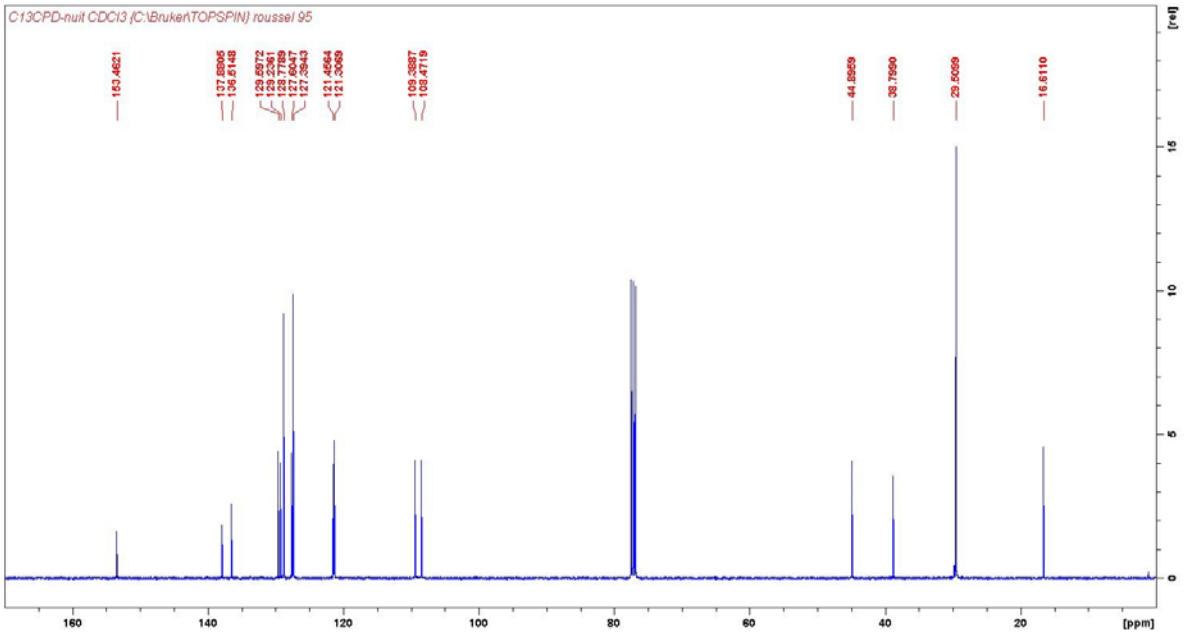


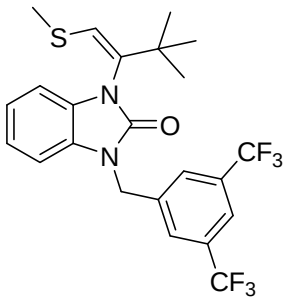
1-Benzyl-3-[(1*Z*)-3,3-dimethyl-1-(methylsulfanyl)but-1-en-2-yl]-1,3-dihydro-2*H*-benzimidazol-2-one **1i**

^{1}H NMR ($CDCl_3$, 400 MHz) spectrum



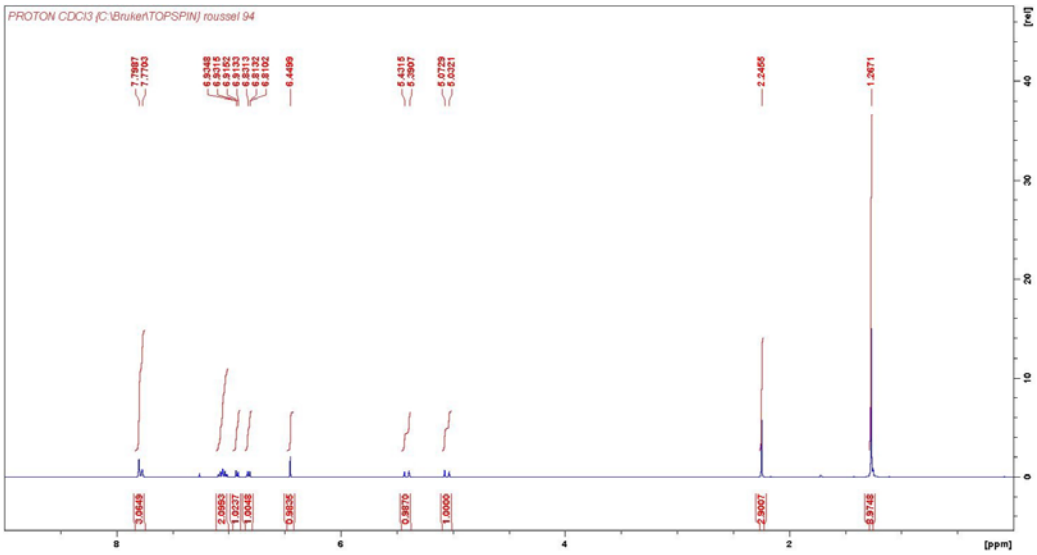
^{13}C NMR ($CDCl_3$, 100 MHz) spectrum



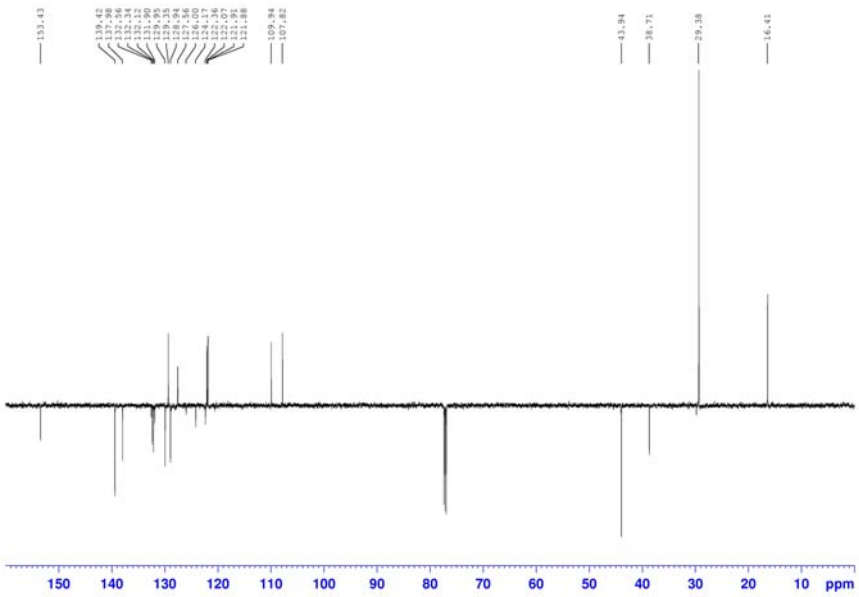


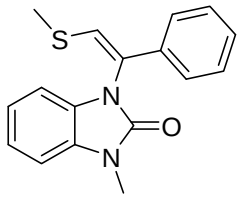
1-[3,5-Bis(trifluoromethyl)benzyl]-3-[(1*Z*)-3,3-dimethyl-1-(methylsulfanyl)but-1en-2-yl]-1,3-dihydro-2*H*-benzimidazol-2-one **1j**

^{1}H NMR ($CDCl_3$, 400 MHz) spectrum



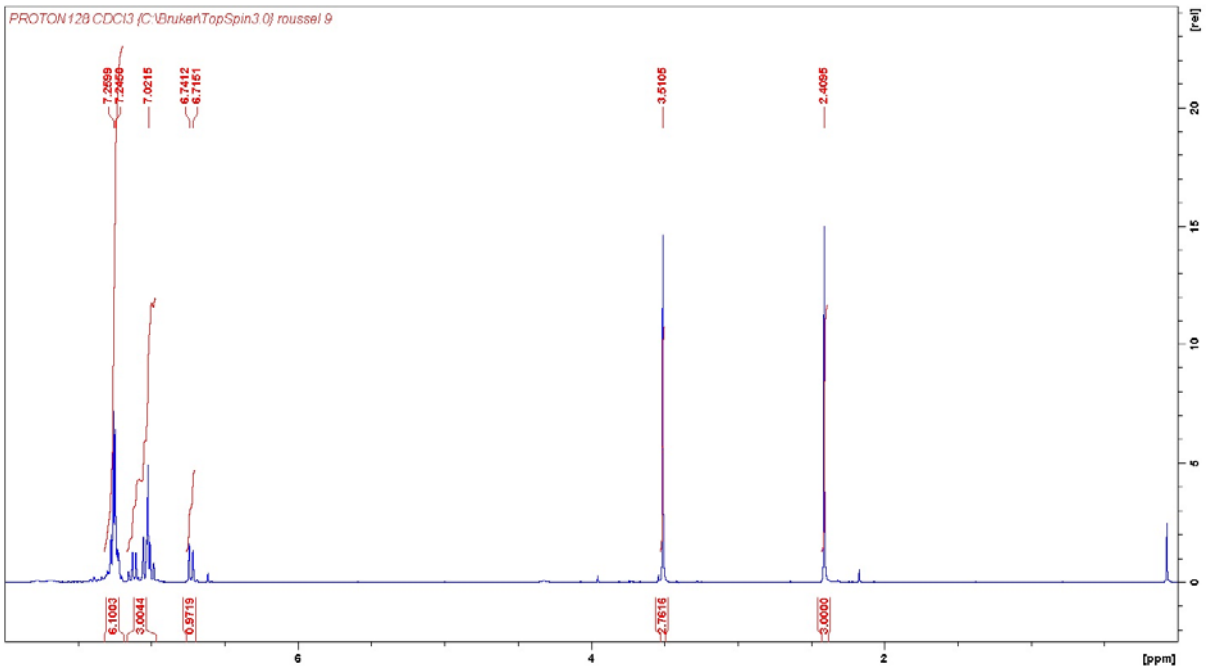
^{13}C NMR ($CDCl_3$, 150 MHz) spectrum



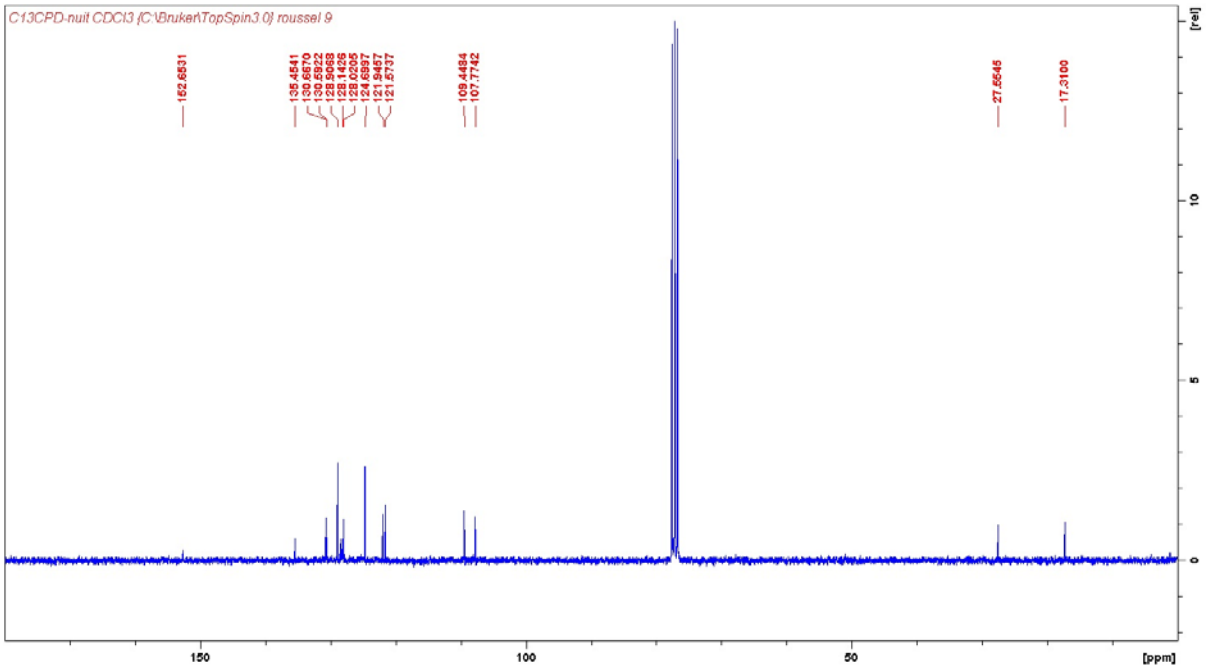


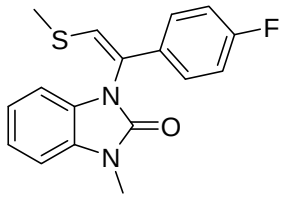
1-Methyl-3-[(*Z*)-2-(methylsulfanyl)-1-phenylethenyl]-1,3-dihydro-2*H*-benzimidazol-2-one **1k**

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



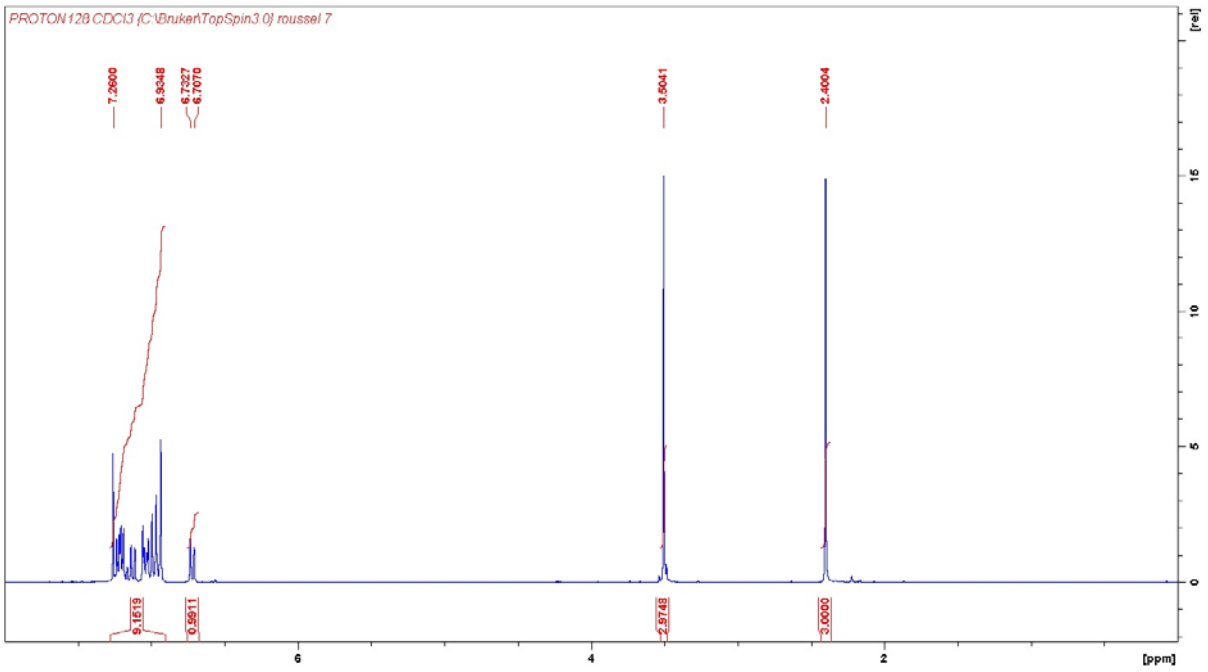
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum



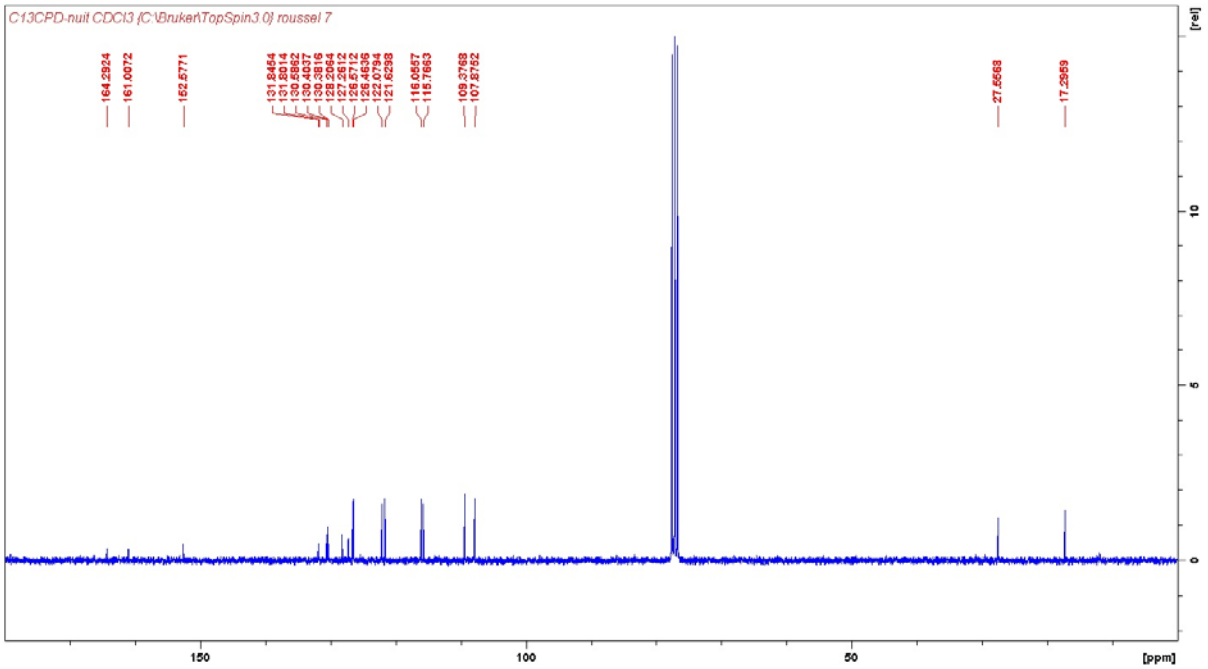


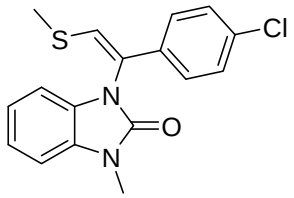
1-[(*Z*)-1-(4-Fluorophenyl)-2-(methylsulfanyl)ethenyl]-3-methyl-1,3-dihydro-2*H*-benzimidazol-2-one **1l**

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



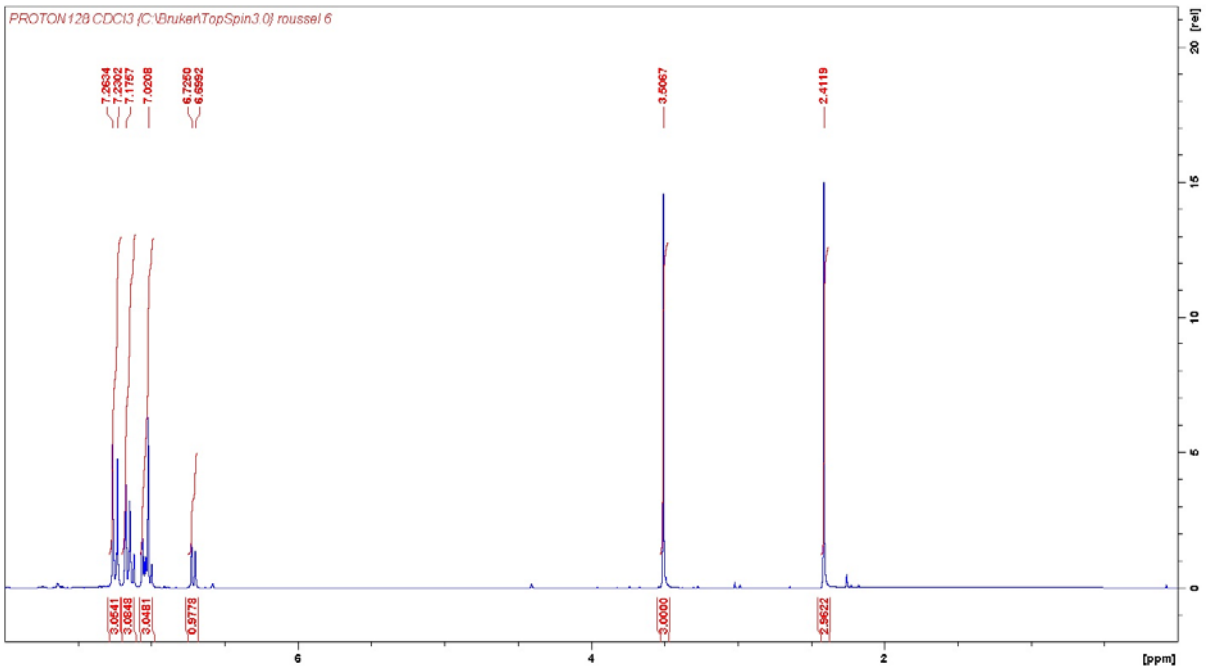
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum



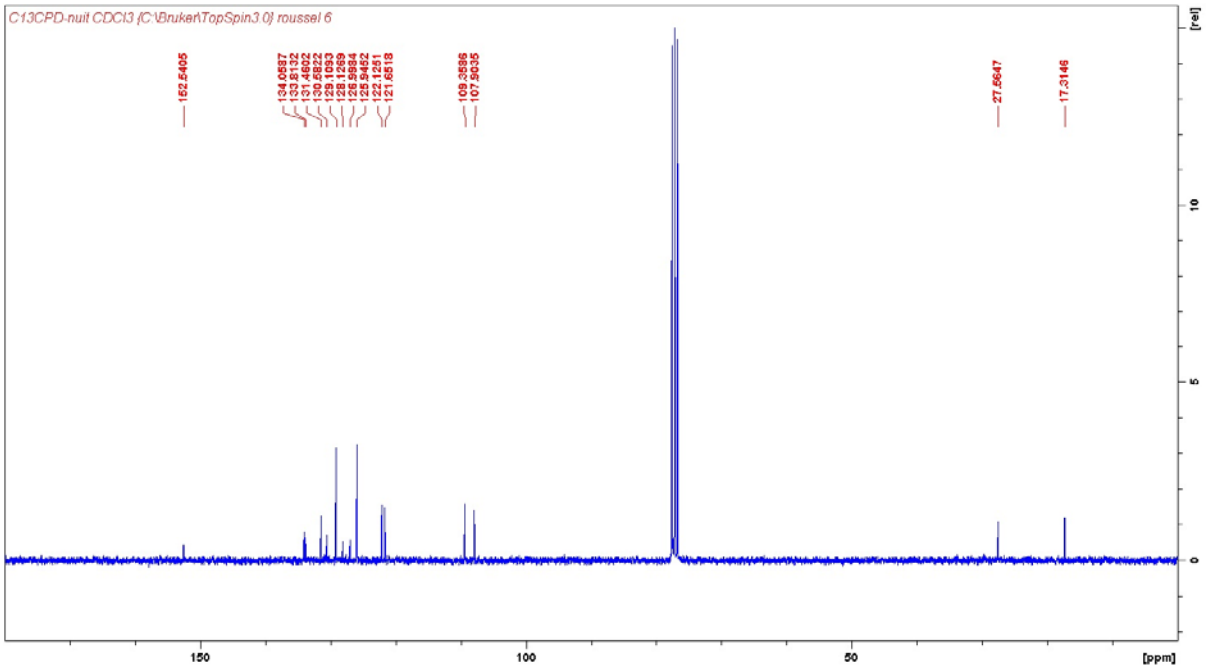


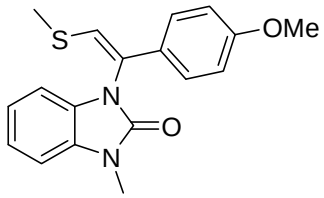
1-[(*Z*)-1-(4-Chlorophenyl)-2-(methylsulfanyl)ethenyl]-3-methyl-1,3-dihydro-2*H*-benzimidazol-2-one **1m**

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



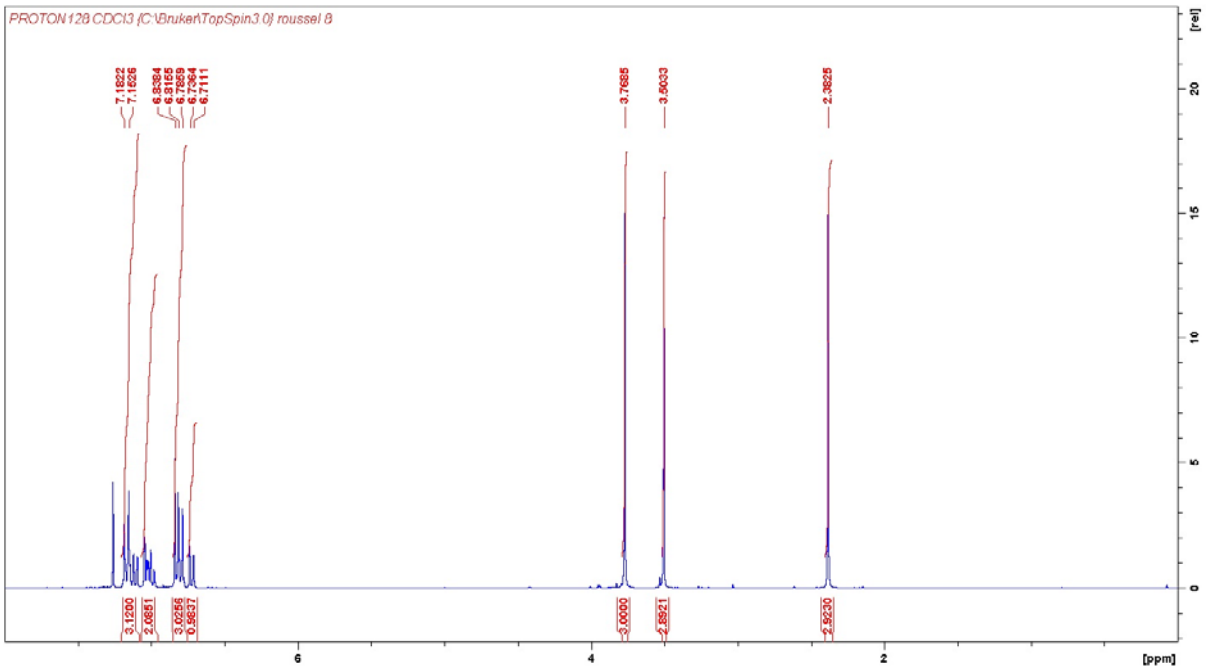
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum



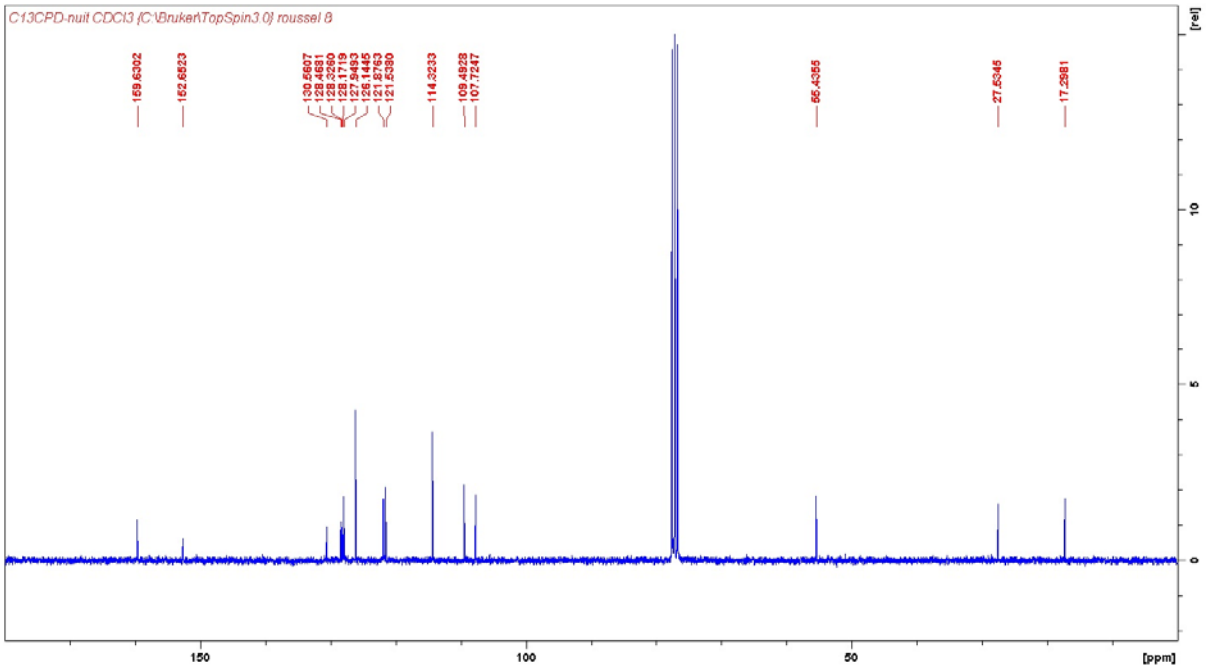


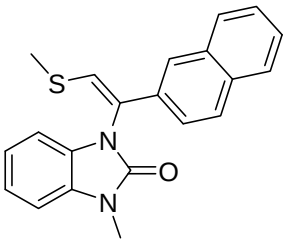
1-[(*Z*)-1-(4-Methoxyphenyl)-2-(methylthio)vinyl]-3-methyl-1,3-dihydro-2*H*-benzimidazol-2-one **1n**

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



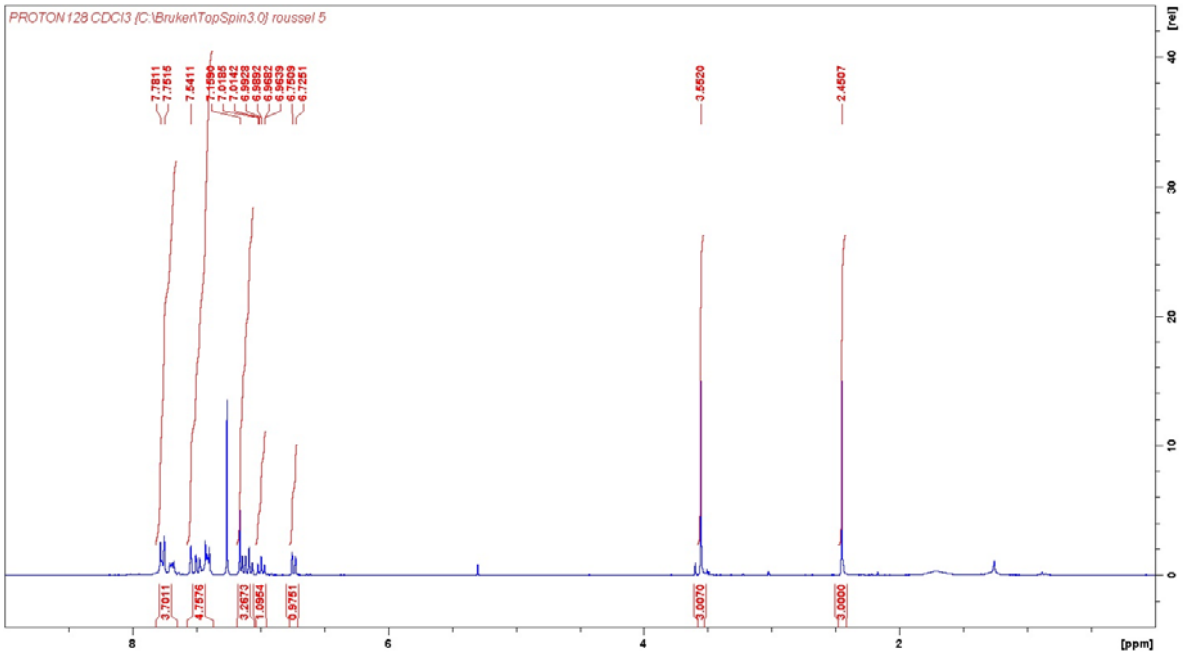
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum



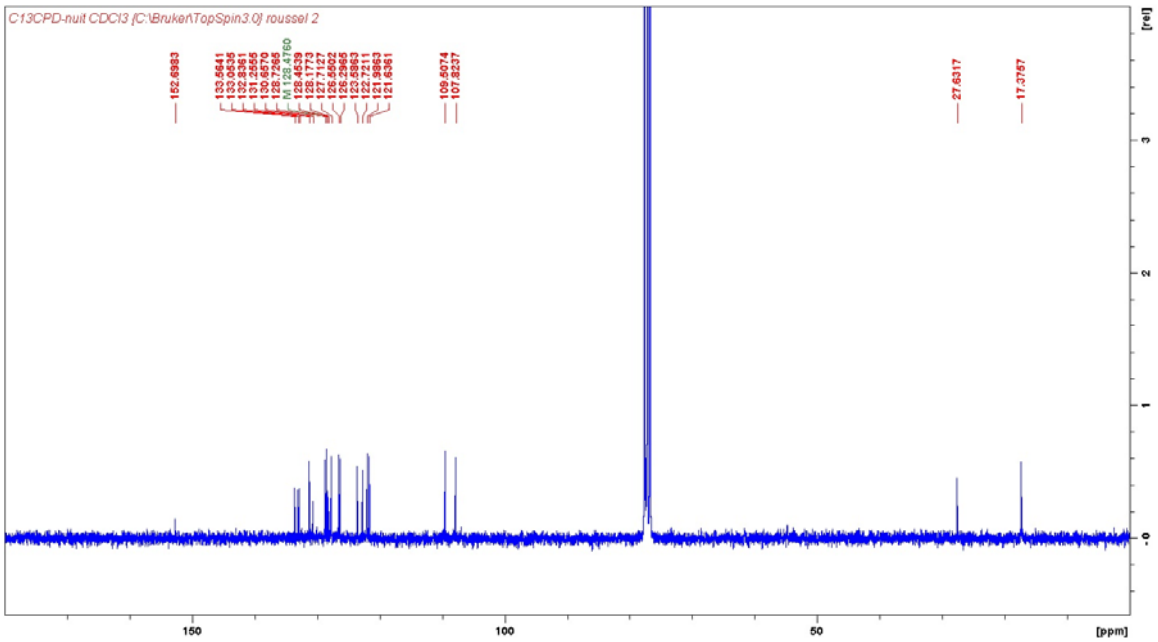


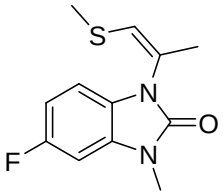
1-Methyl-3-[(*Z*)-2-(methylsulfanyl)-1-(naphthalen-2-yl)ethenyl]-1,3-dihydro-2*H*-benzimidazol-2-one **1o**

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



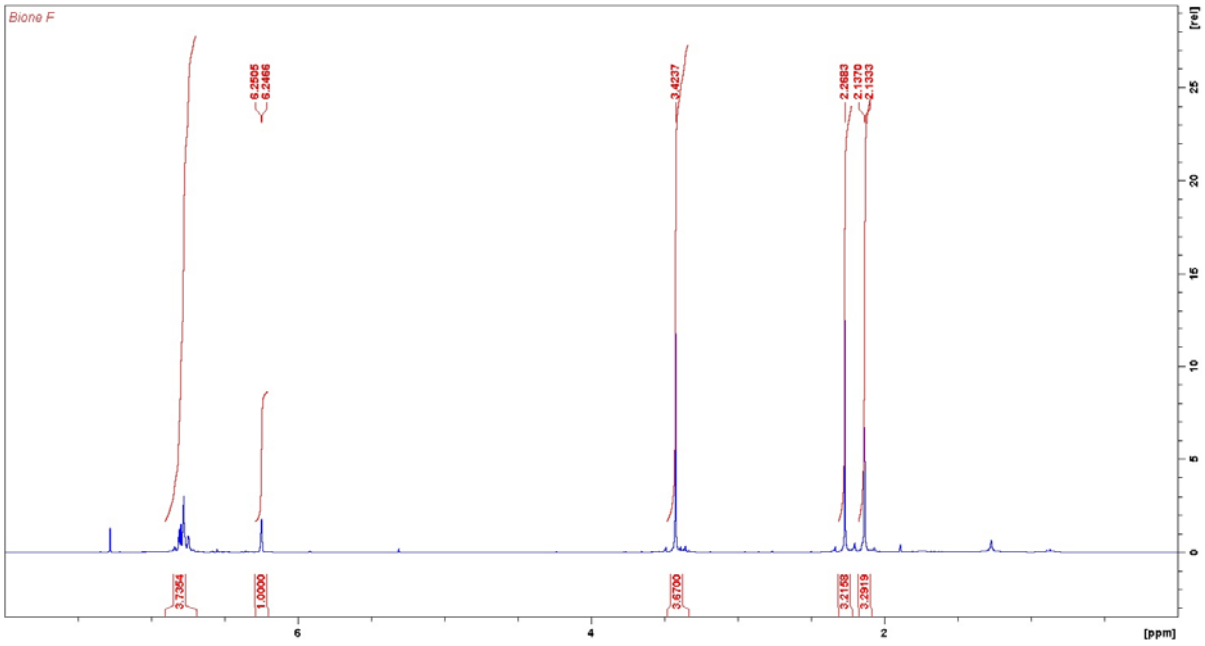
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum



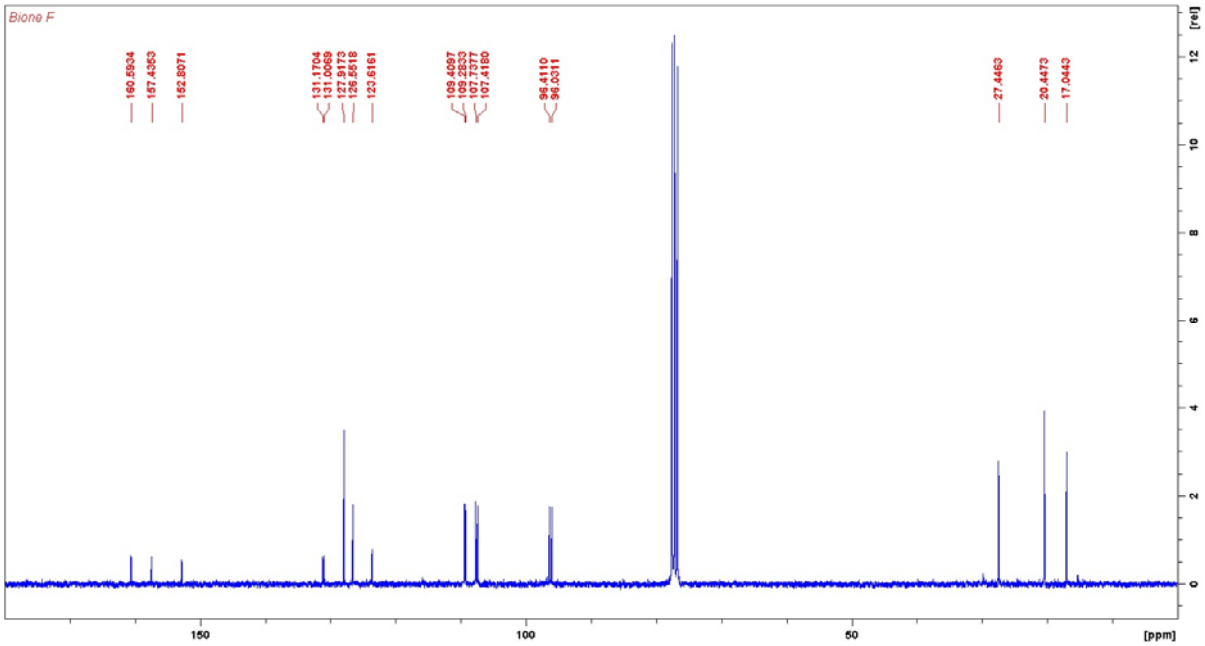


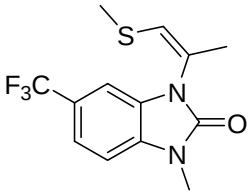
5-Fluoro-3-methyl-1-[(1*Z*)-1-(methylsulfanyl)prop-1-en-2-yl]-1,3-dihydro-2*H*-benzimidazol-2-one **1p**

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



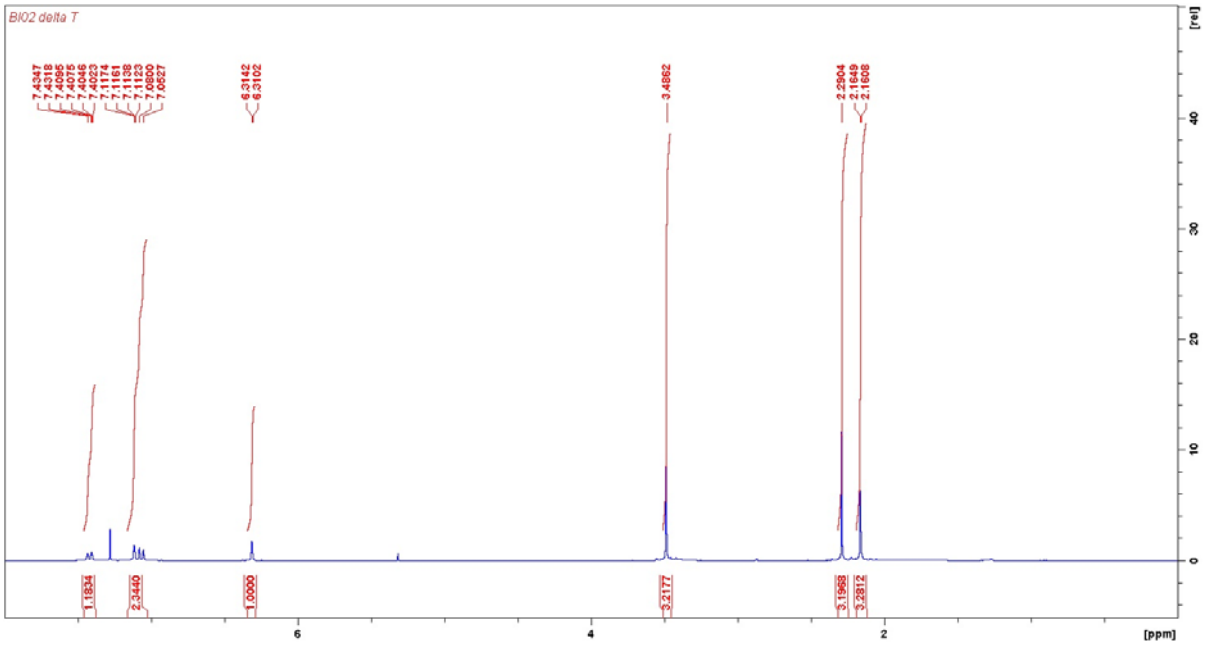
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum



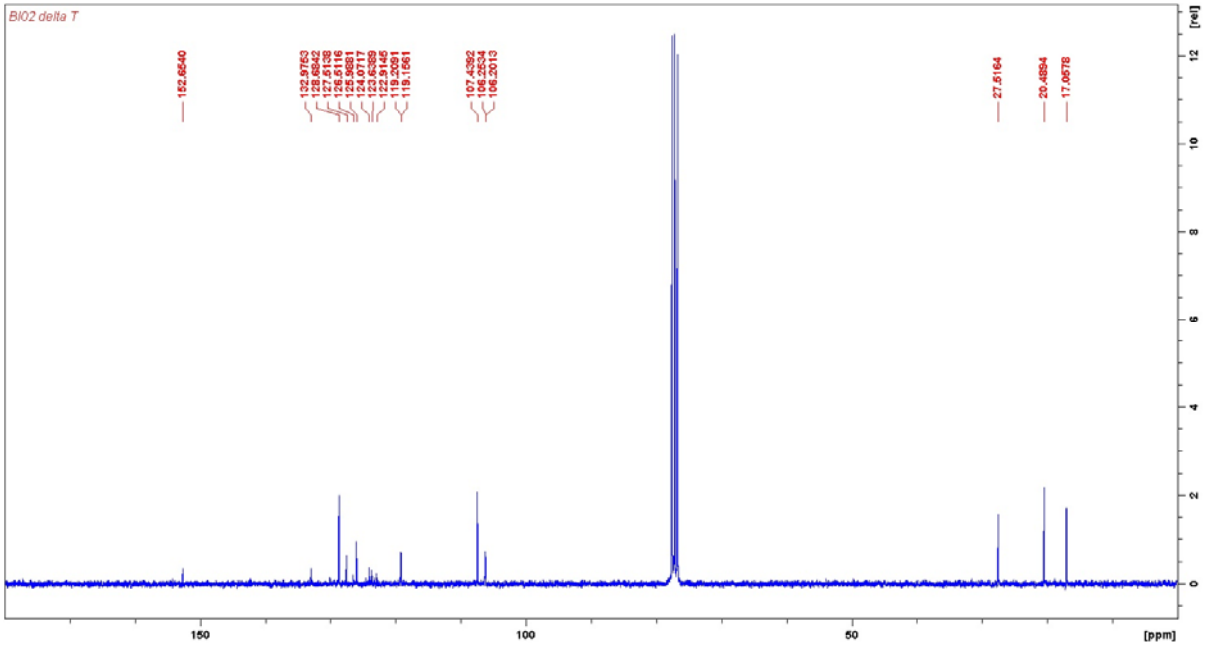


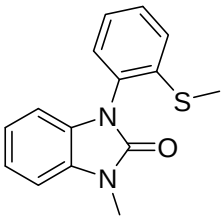
1-Methyl-3-[(1*Z*)-1-(methylsulfanyl)prop-1-en-2-yl]-5-(trifluoromethyl)-1,3-dihydro-2*H*-benzimidazol-2-one **1q**

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



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

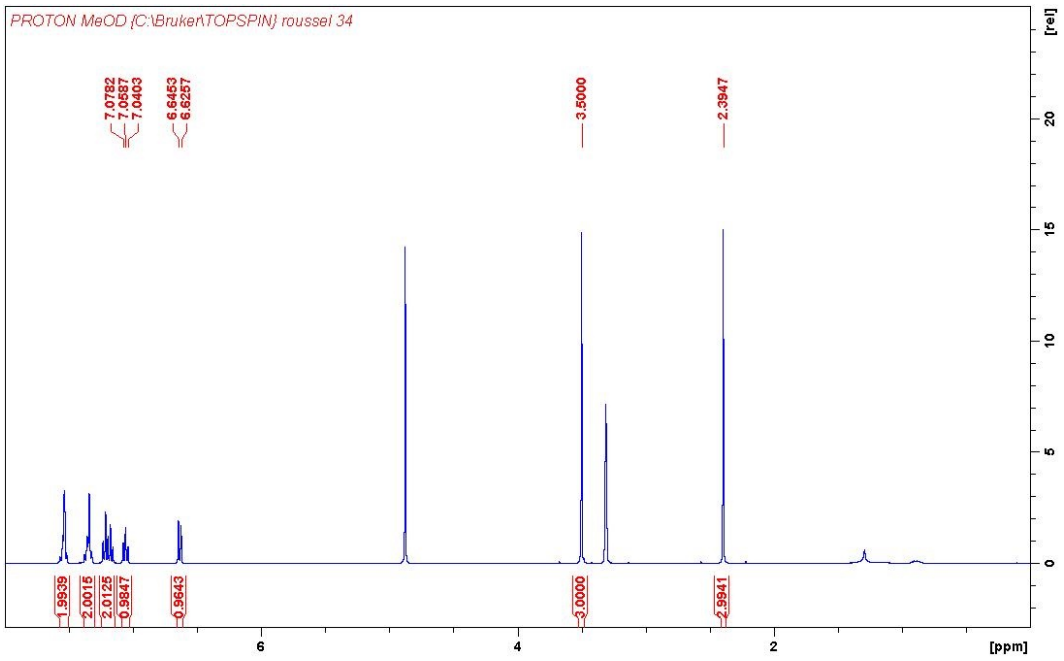




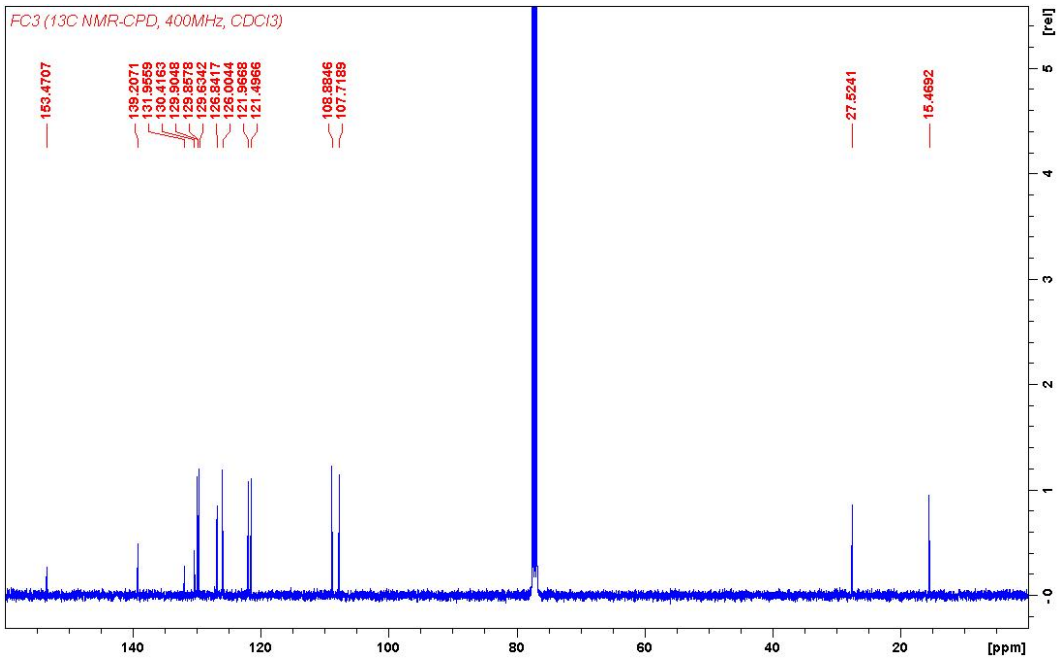
1-methyl-3-[2-(methylsulfanyl)phenyl]-1,3-dihydro-2*H*-benzimidazol-2-one

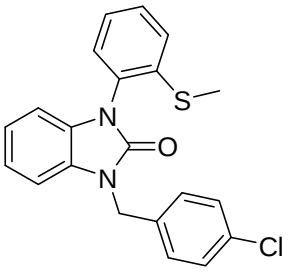
2a

^{1}H NMR (CD_3OD, 400 MHz) spectrum



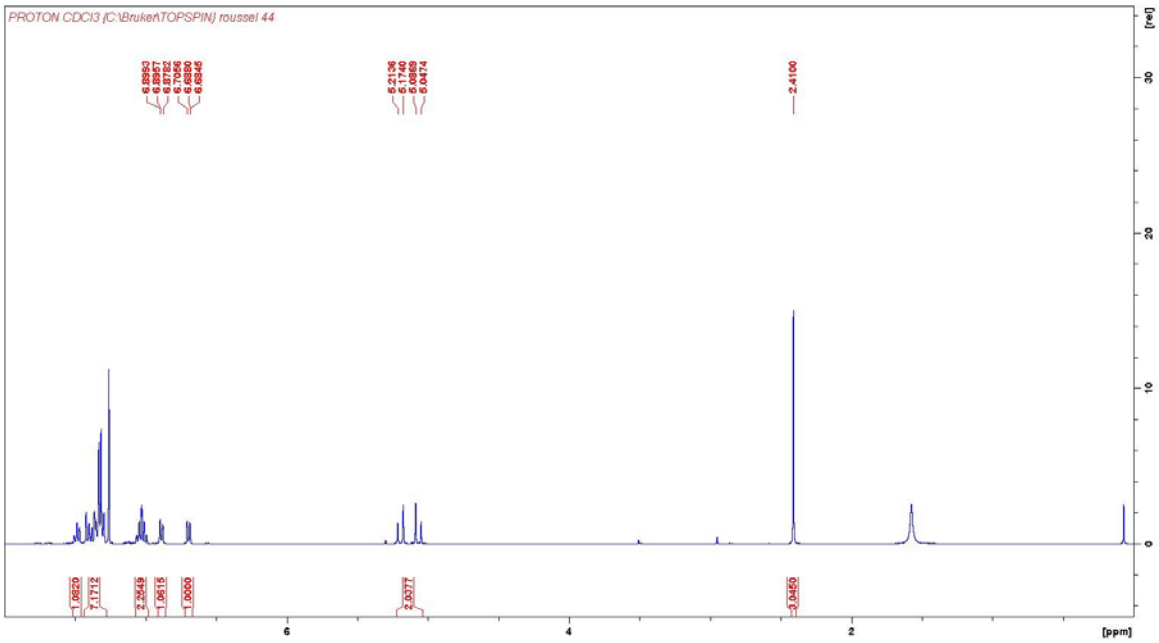
^{13}C NMR ($CDCl_3$, 100 MHz) spectrum



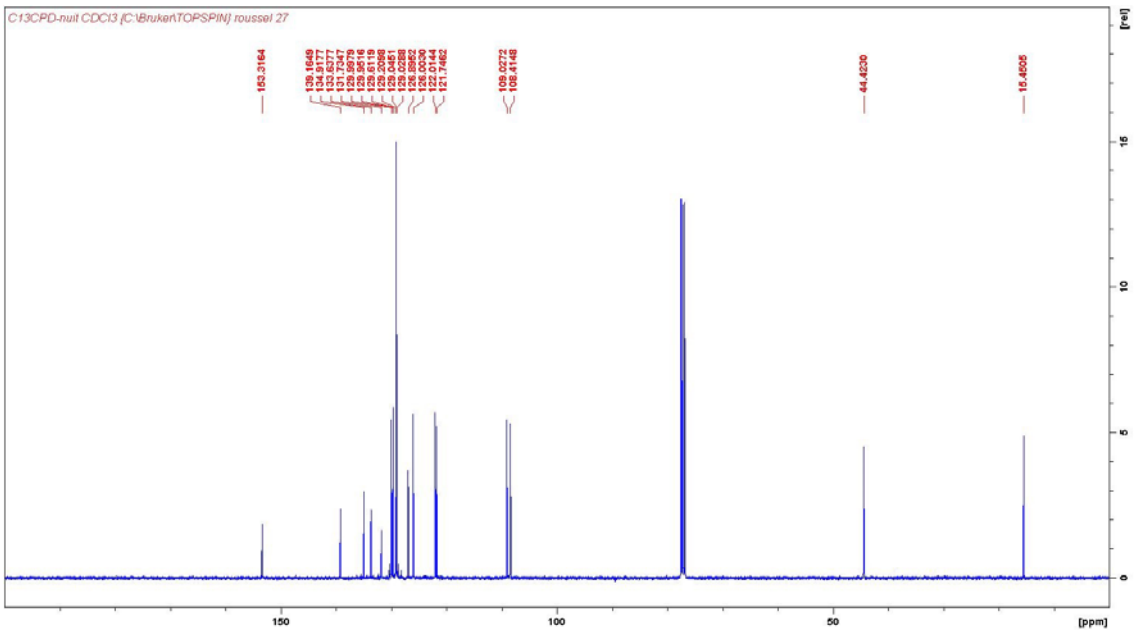


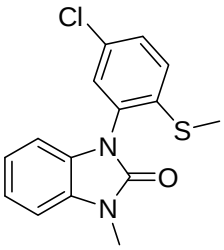
1-(4-chlorobenzyl)-3-[2-(methylsulfanyl)phenyl]-1,3-dihydro-2*H*-benzimidazol-2-one **2b**

^{1}H NMR ($CDCl_3$, 400 MHz) spectrum



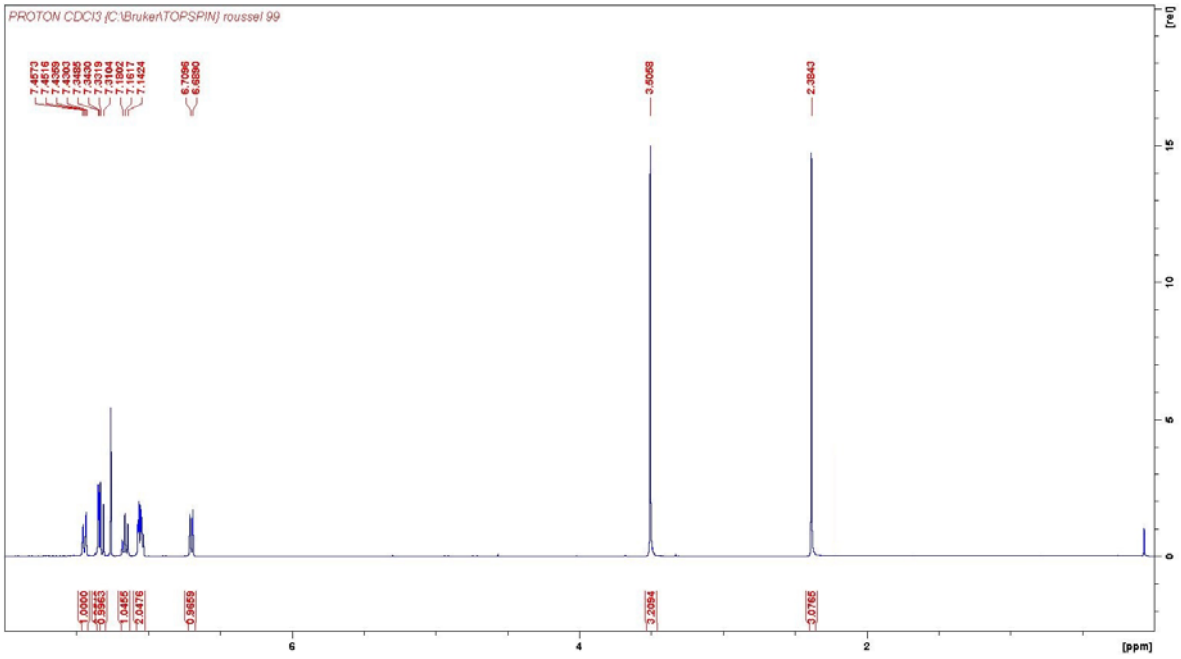
^{13}C NMR ($CDCl_3$, 100 MHz) spectrum



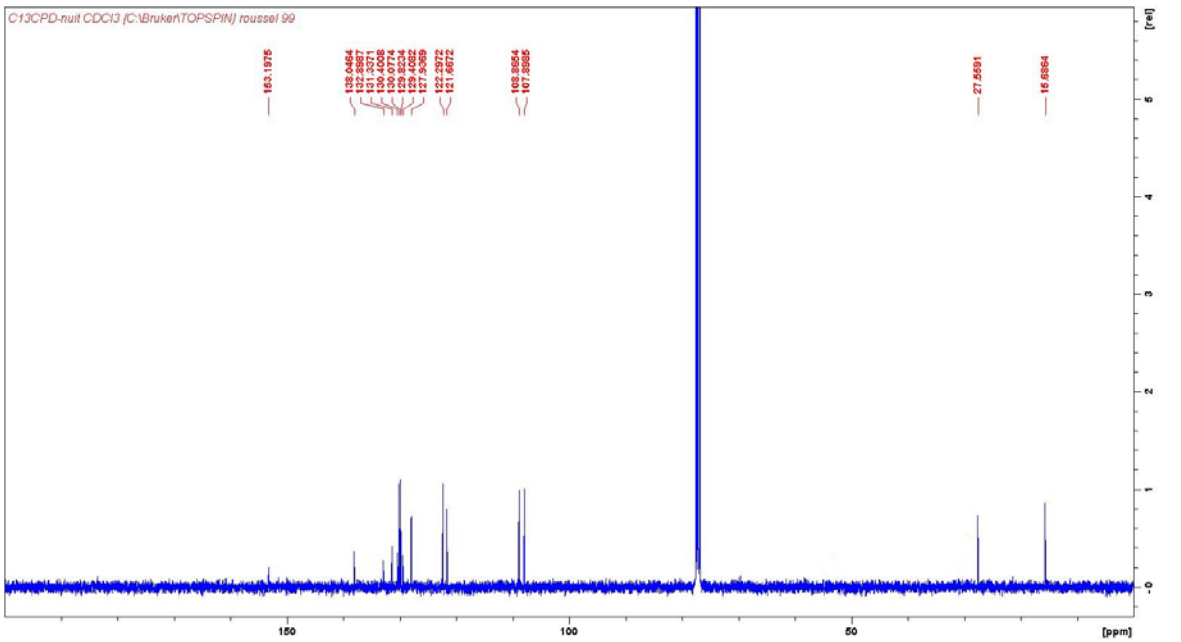


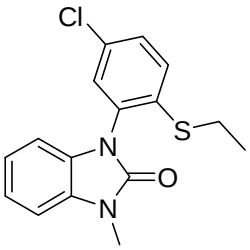
1-[5-chloro-2-(methylsulfanyl)phenyl]-3-methyl-1,3-dihydro-2*H*-benzimidazol-2-one **2c**

^{1}H NMR ($CDCl_3$, 400 MHz) spectrum



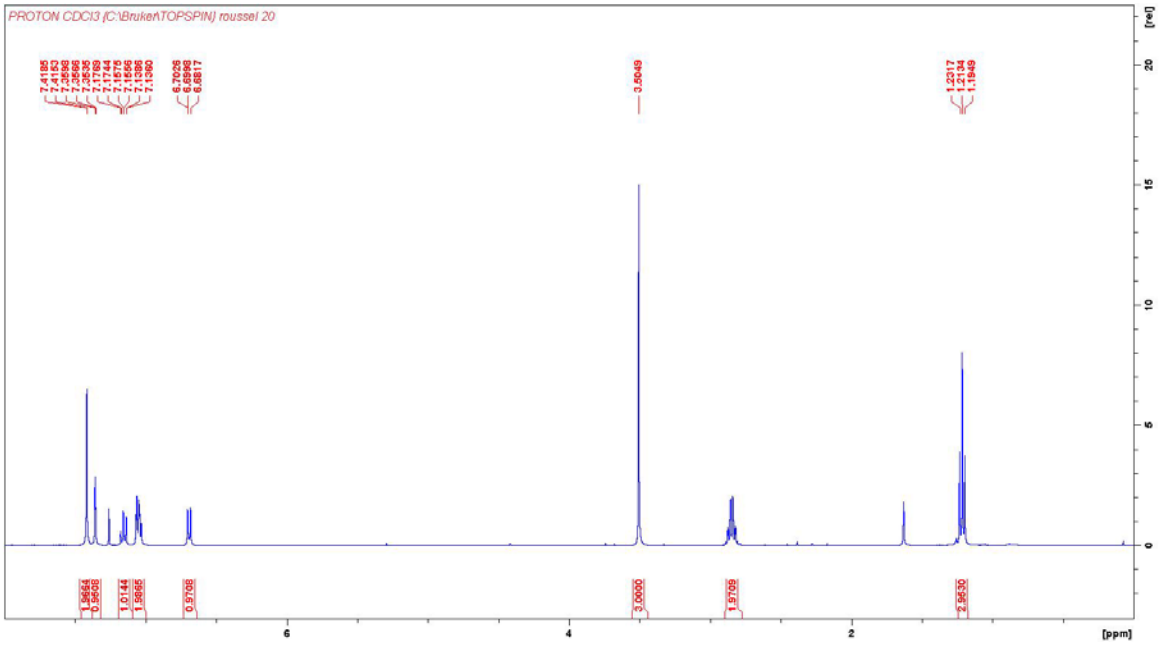
^{13}C NMR ($CDCl_3$, 100 MHz) spectrum



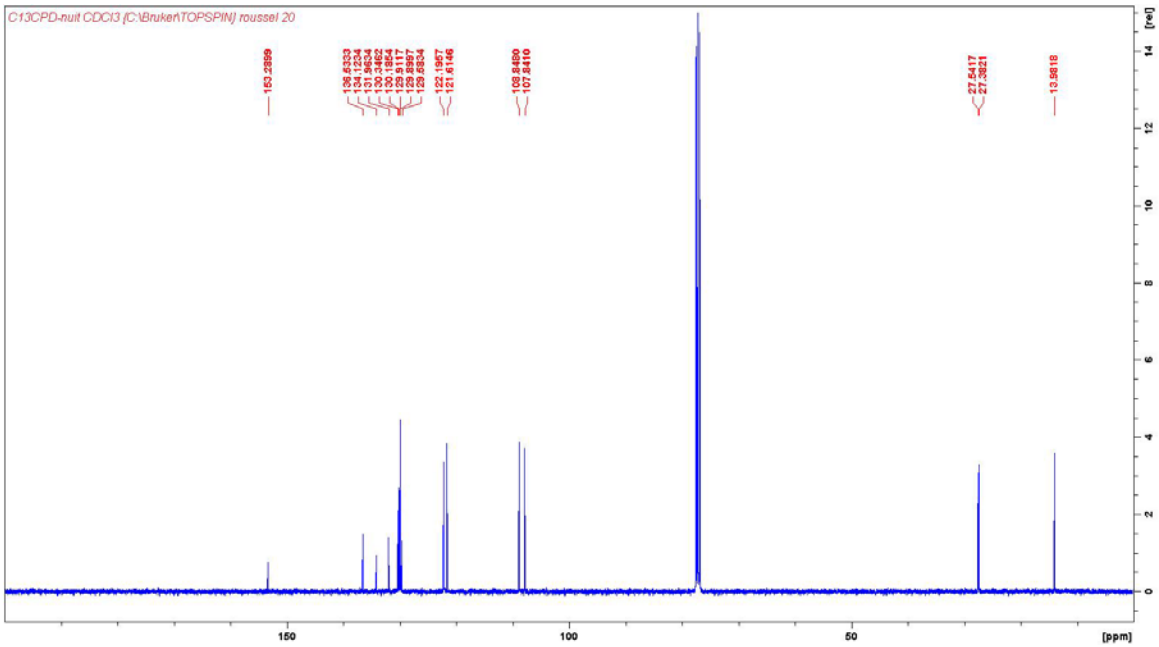


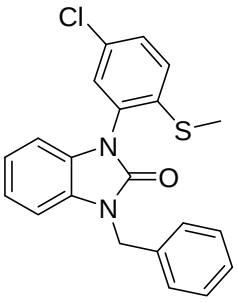
1-[5-chloro-2-(ethylsulfanyl)phenyl]-3-methyl-1,3-dihydro-2*H*-benzimidazol-2-one **2d**

^{1}H NMR ($CDCl_3$, 400 MHz) spectrum



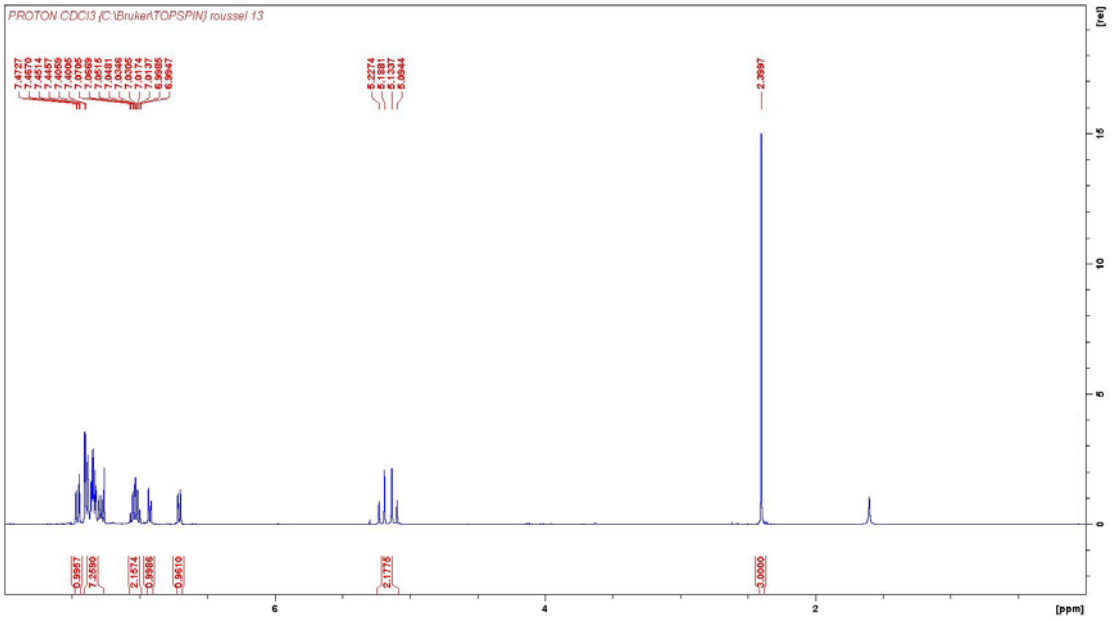
^{13}C NMR ($CDCl_3$, 100 MHz) spectrum



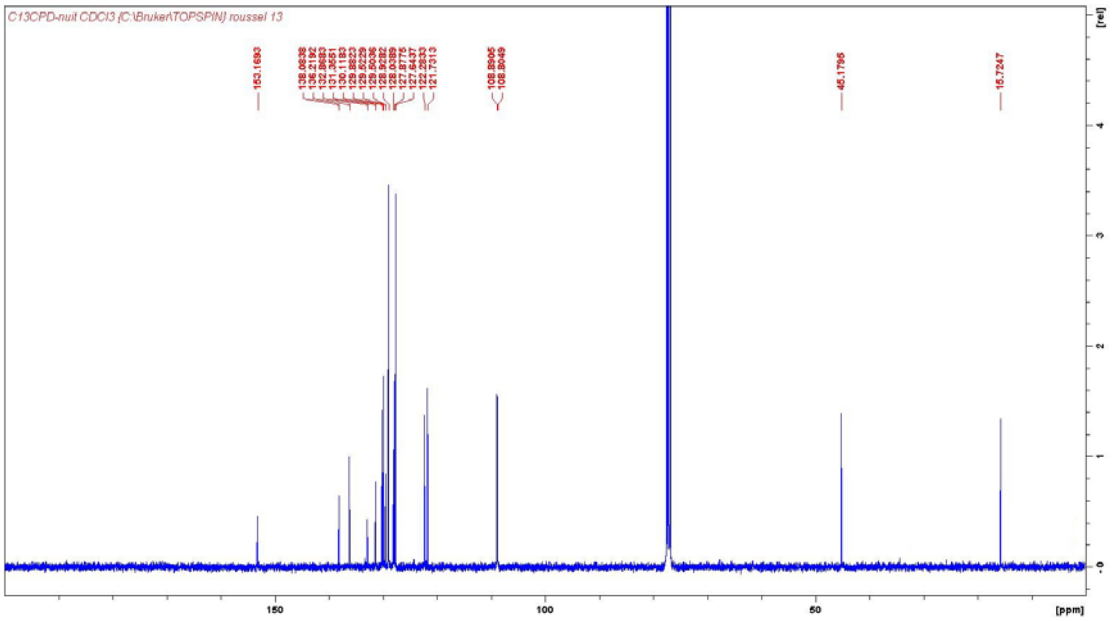


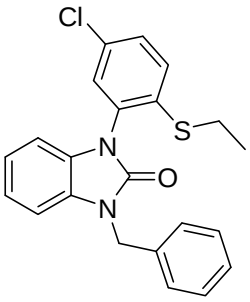
1-benzyl-3-[5-chloro-2-(methylsulfanyl)phenyl]-1,3-dihydro-2*H*-benzimidazol-2-one **2e**

^{1}H NMR ($CDCl_3$, 400 MHz) spectrum



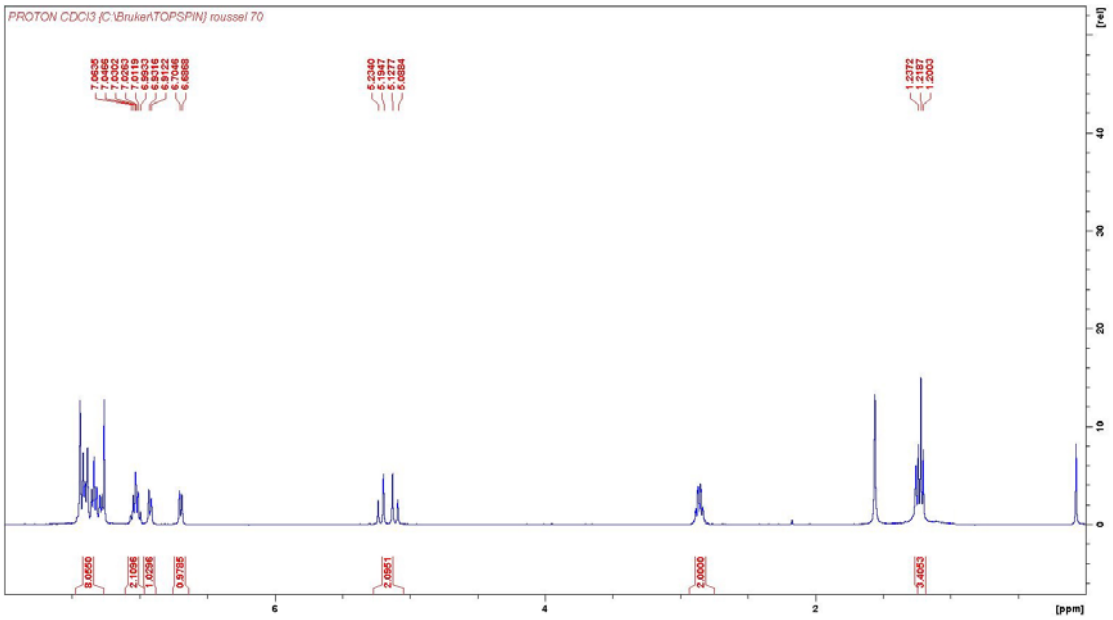
^{13}C NMR ($CDCl_3$, 100 MHz) spectrum



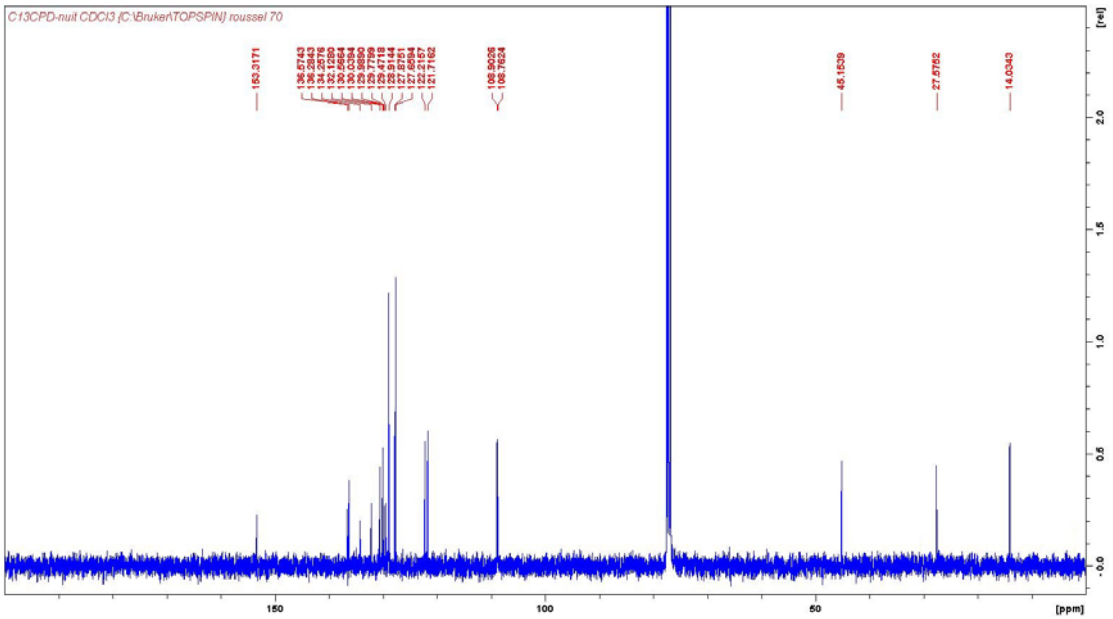


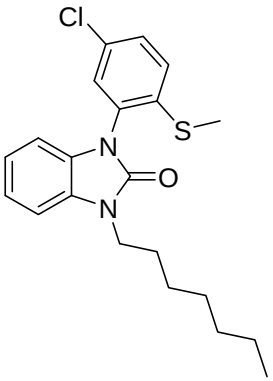
1-benzyl-3-[5-chloro-2-(ethylsulfanyl)phenyl]-1,3-dihydro-2*H*-benzimidazol-2-one **2f**

^{1}H NMR ($CDCl_3$, 400 MHz) spectrum



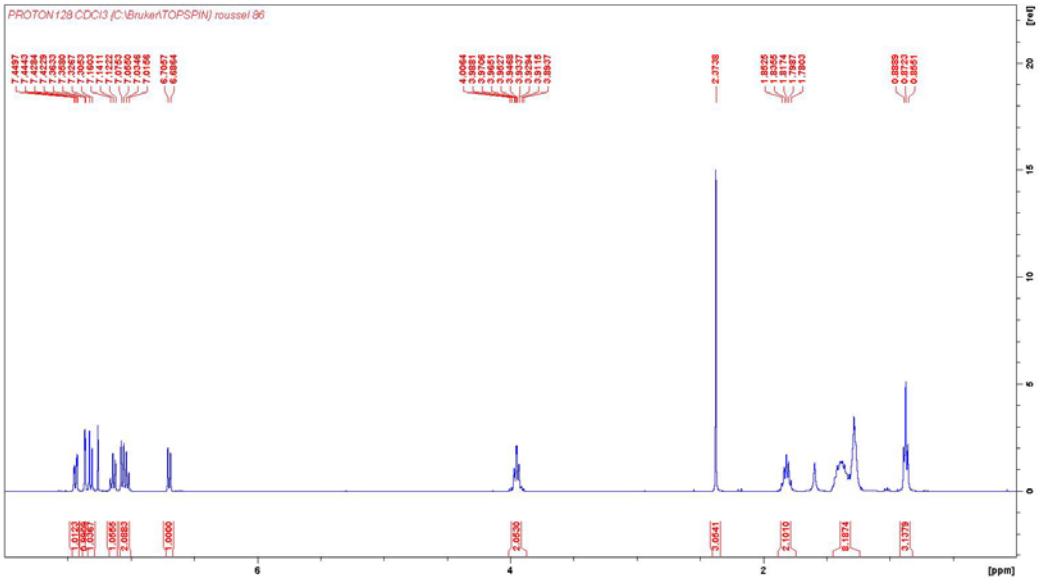
^{13}C NMR ($CDCl_3$, 100 MHz) spectrum



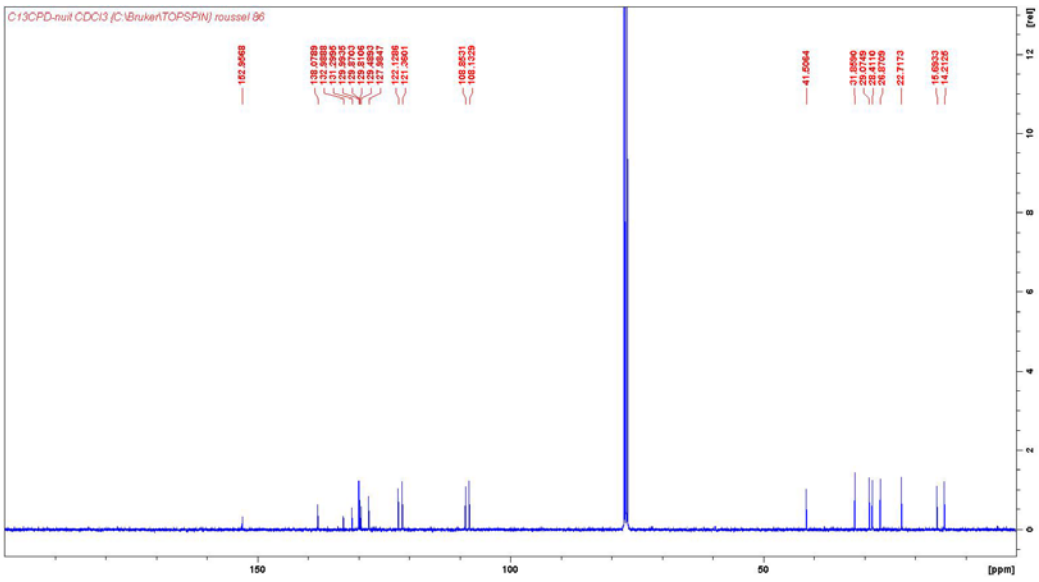


1-[5-chloro-2-(methylsulfanyl)phenyl]-3-heptyl-1,3-dihydro-2*H*-benzimidazol-2-one **2g**

^{1}H NMR ($CDCl_3$, 400 MHz) spectrum



^{13}C NMR ($CDCl_3$, 100 MHz) spectrum



Crystal packing of the two frozen atropisomers **1k**