SUPPORTING INFORMATION

Too Short-Lived or Not Existing Species: *N*-Azidoamines Reinvestigated

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Apparatus for the isolation of **6**:

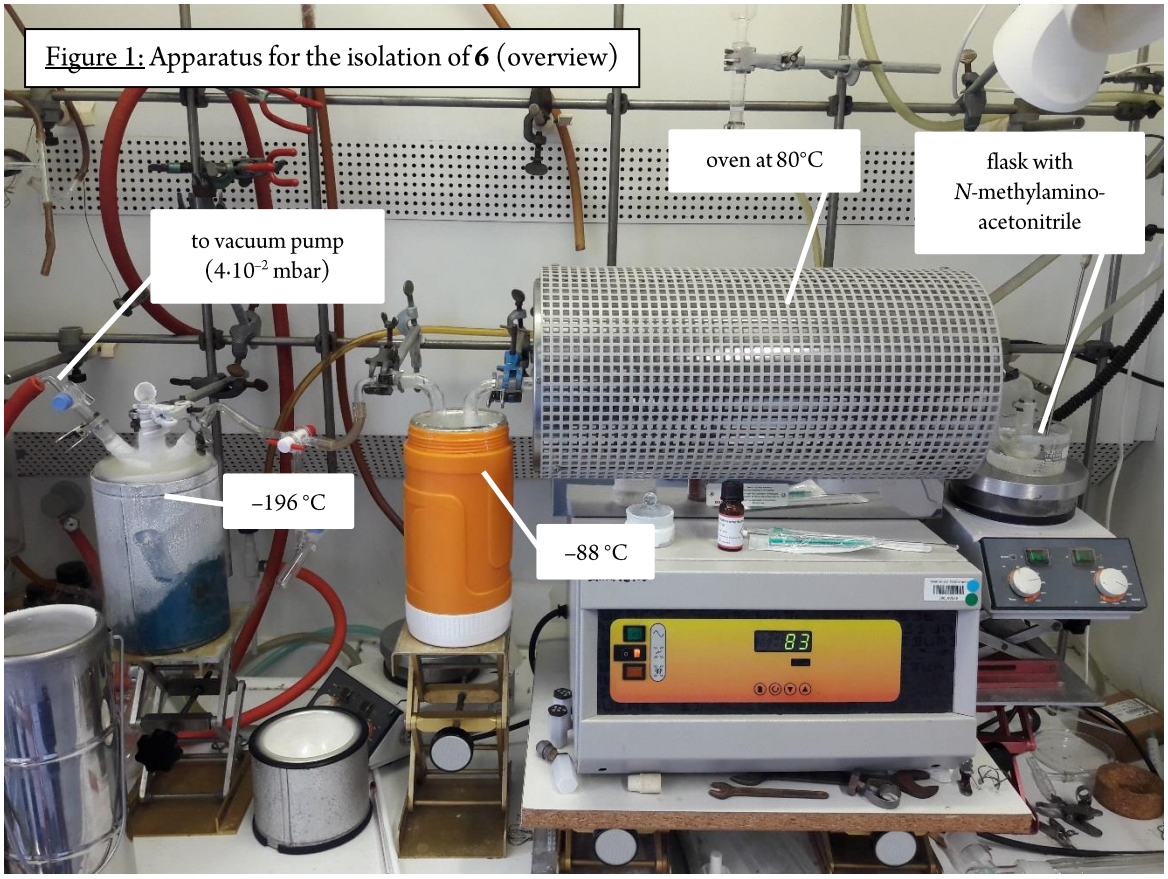


Figure 1: Apparatus for the isolation of **6** (overview)

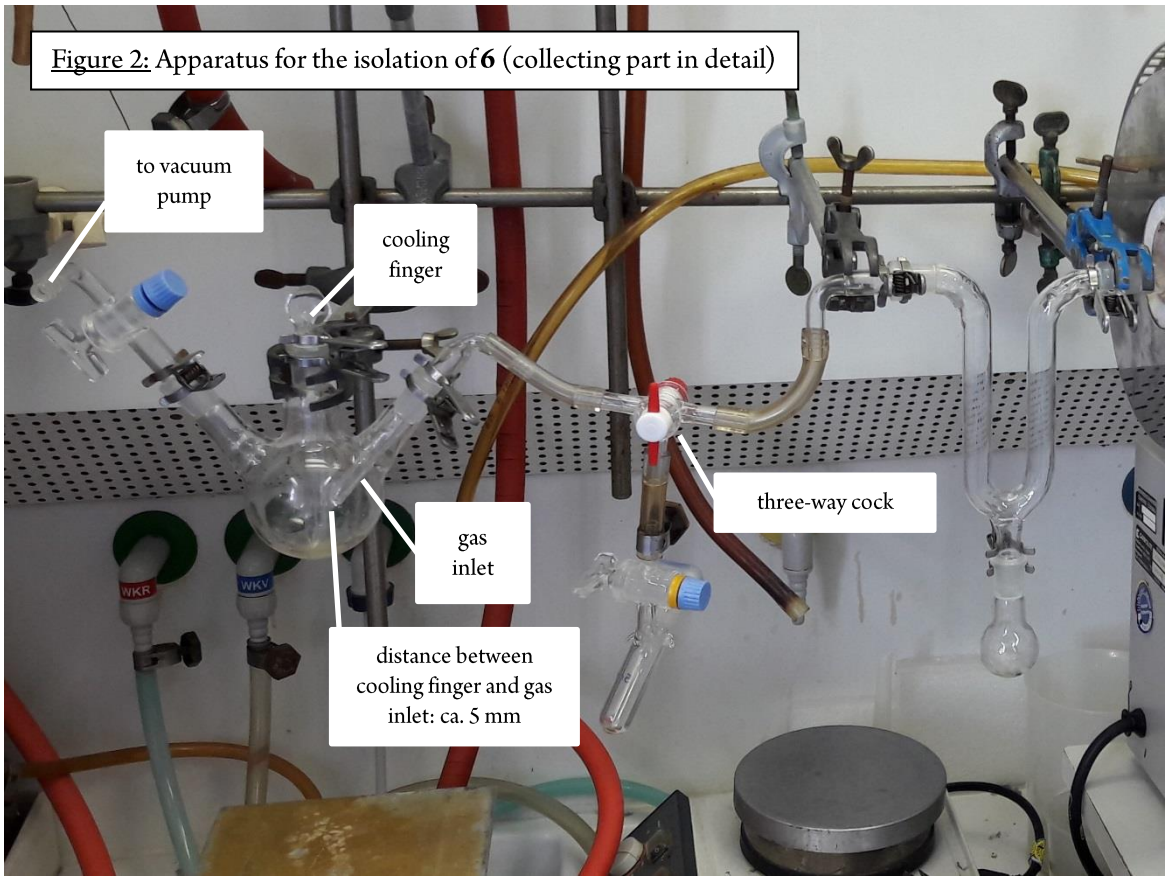


Figure 2: Apparatus for the isolation of **6** (collecting part in detail)

(Photos by T. Pester)

Procedures, observed phenomena, spectra, analysis of the reaction products, and control experiments for the reactions described by Bock *et al.* [9] and Anselme *et al.* [10] and repeated now.

1) Bock *et al.* [9]

Procedures: [9]

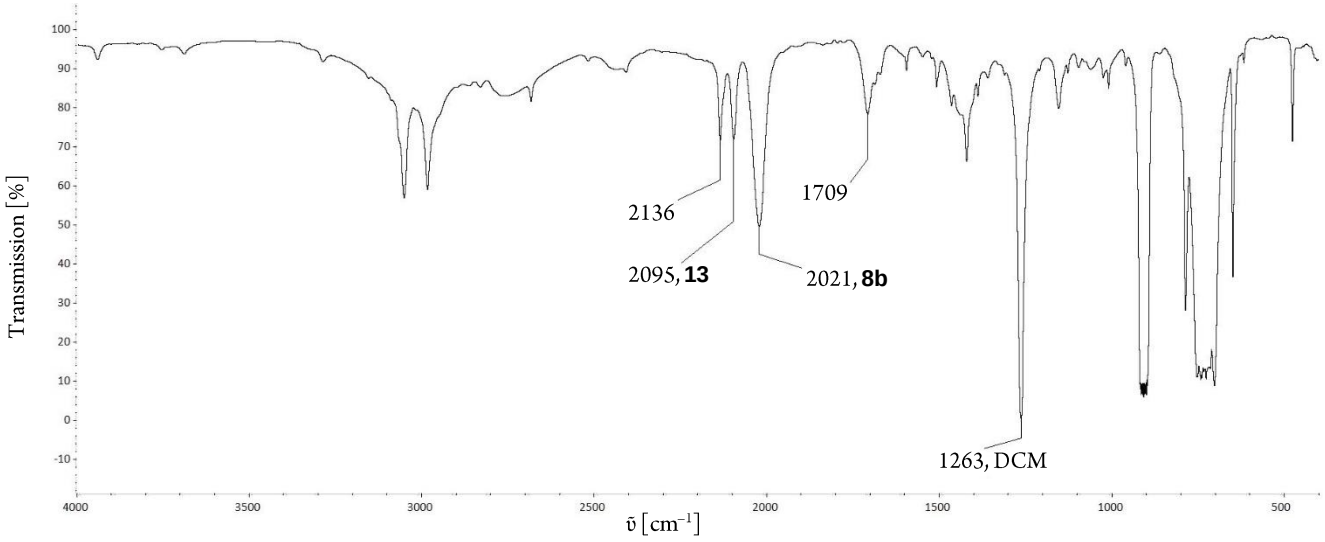
To a solution of *N*-chloro-*N*,*N*-dimethylamine (**1b**) in DCM (2.9%, 1 g, 12.6 mmol **1b**) was added sodium azide (0.8 g, 12.6 mmol, 1 eq.) in a flask connected with a pneumatic apparatus. The mixture was stirred for 24 h cooled by water bath at RT. After 24 h the reaction mixture was filtered and analyzed.

Observed phenomena:

We were able to observe all the phenomena described in literature.[9] Nitrogen evolution was ca. 16 mol% based on **1b**. It started directly after addition of sodium azide and then continued with a slow flow over nearly the whole reaction time. Without tempering via water-bath the reaction vessel is warming up to ca. 30 °C.

Spectra:

- IR:



- NMR spectra: See pages S9–S12.

Analysis the reaction products

The verification of all reaction products was done by comparing the NMR signals with the signals of the pure compounds, prepared by alternative procedures. Further verification was done by comparing the NMR signals of the trapping products with cyclooctyne and finally by NMR adding experiments.

Control experiments

a) confirming **13** as the only volatile compound

For confirming **13** as the only volatile compound, two reaction mixtures were recondensed with the help of a U-tube-apparatus at different pressures (details see page S8).
Our NMR data of obtained **13** in toluene correspond with those reported in literature.[19c,d]

b) trapping with cyclooctyne

For trapping with cyclooctyne, the reaction mixture was cooled with ice/water bath to 0 °C and treated with 4 eq. of cyclooctyne (NMR spectra: See pages S8–S10; ^{13}C NMR spectrum is divided into two parts for better clarity).

c) reaction of Bock *et al.* in [D_2]-DCM

To exclude any solvent incorporation, the reaction was repeated in [D_2]-DCM. In case of an interaction, multiplets should be observable in ^{13}C NMR spectrum (see page S10).

d) reaction of **7** with **1b**

To a solution of **7** (2.5 mL, 2.3 g, 17.8 mmol) in DCM (5 mL) was added **1b** (14% in DCM, 1.42 g, 17.8 mmol, 1 eq.). The reaction mixture was cooled with water bath to RT. After stirring the solution overnight, the reaction products were analyzed without further purification (1,3,5-trimethyl-2,3,4,5-tetrahydro-1,3,5-triazin-1-ium chloride: 0.275 g, 1.68 mmol, yield: 10%; dimethylamine hydrochloride: 1.1 g, 13.5 mmol, yield: 19%, analyzed by NMR spectroscopy with internal naphthalene-standard).

Hint: NMR spectrum shows besides the known products 1,3,5-trimethyl-2,3,4,5-tetrahydro-1,3,5-triazin-1-ium chloride and dimethylamine hydrochloride other signals from currently unknown oxidation products (NMR spectra: see page S11).

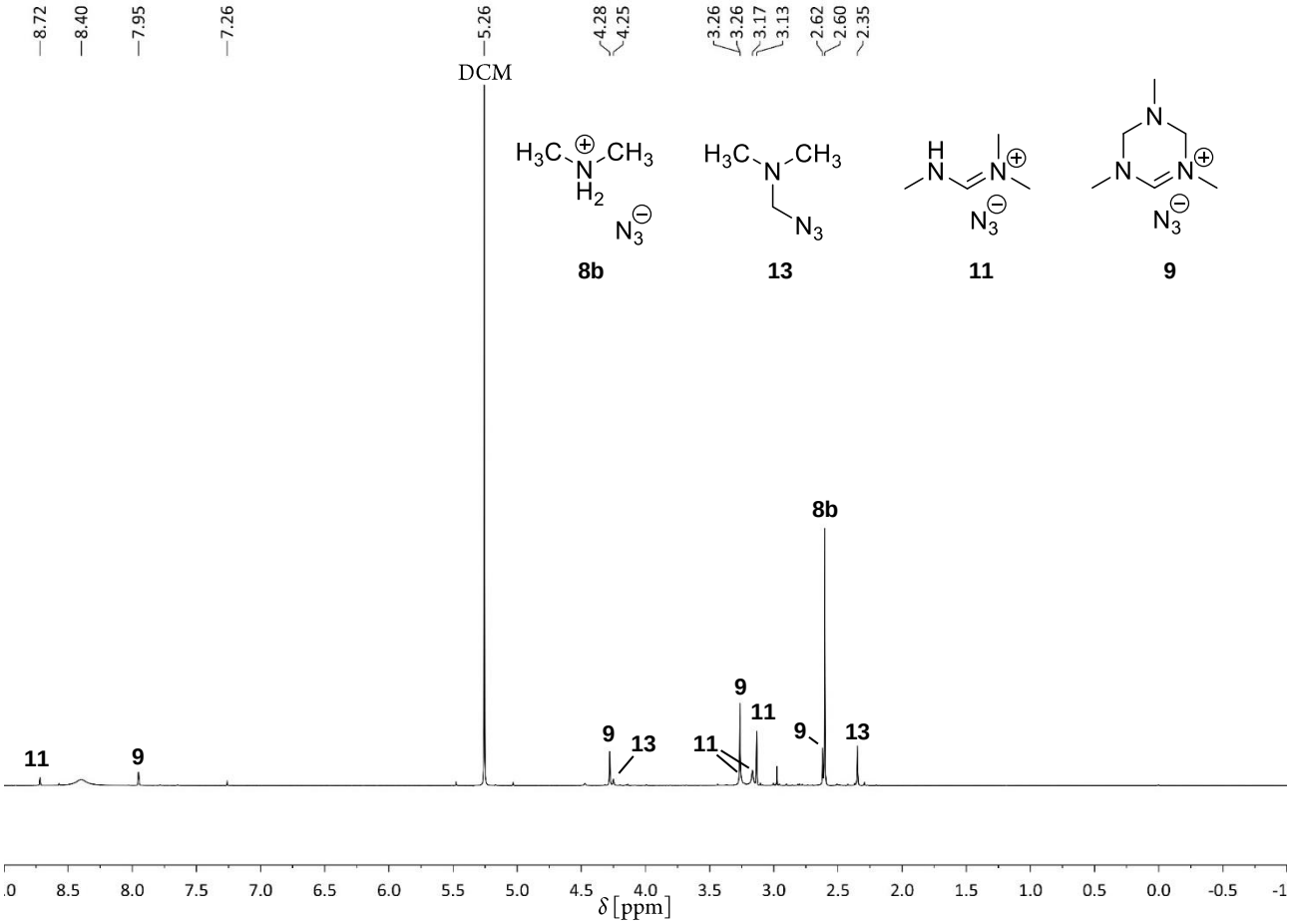
e) reaction of **7** with **8b**

To a solution of **7** (0.22 mL, 0.2 g, 1.55 mmol) in DCM (5 mL), was added **8b** (0.55 g, 6.9 mmol, 4 eq.). The reaction mixture was cooled with a water bath to RT. After stirring the solution for 24 h, the reaction products were analyzed without further purification (**13**: 37 mg, 0.37 mmol, yield: 8%, analyzed by NMR spectroscopy with internal naphthalene-standard) (NMR spectra: See page S11).

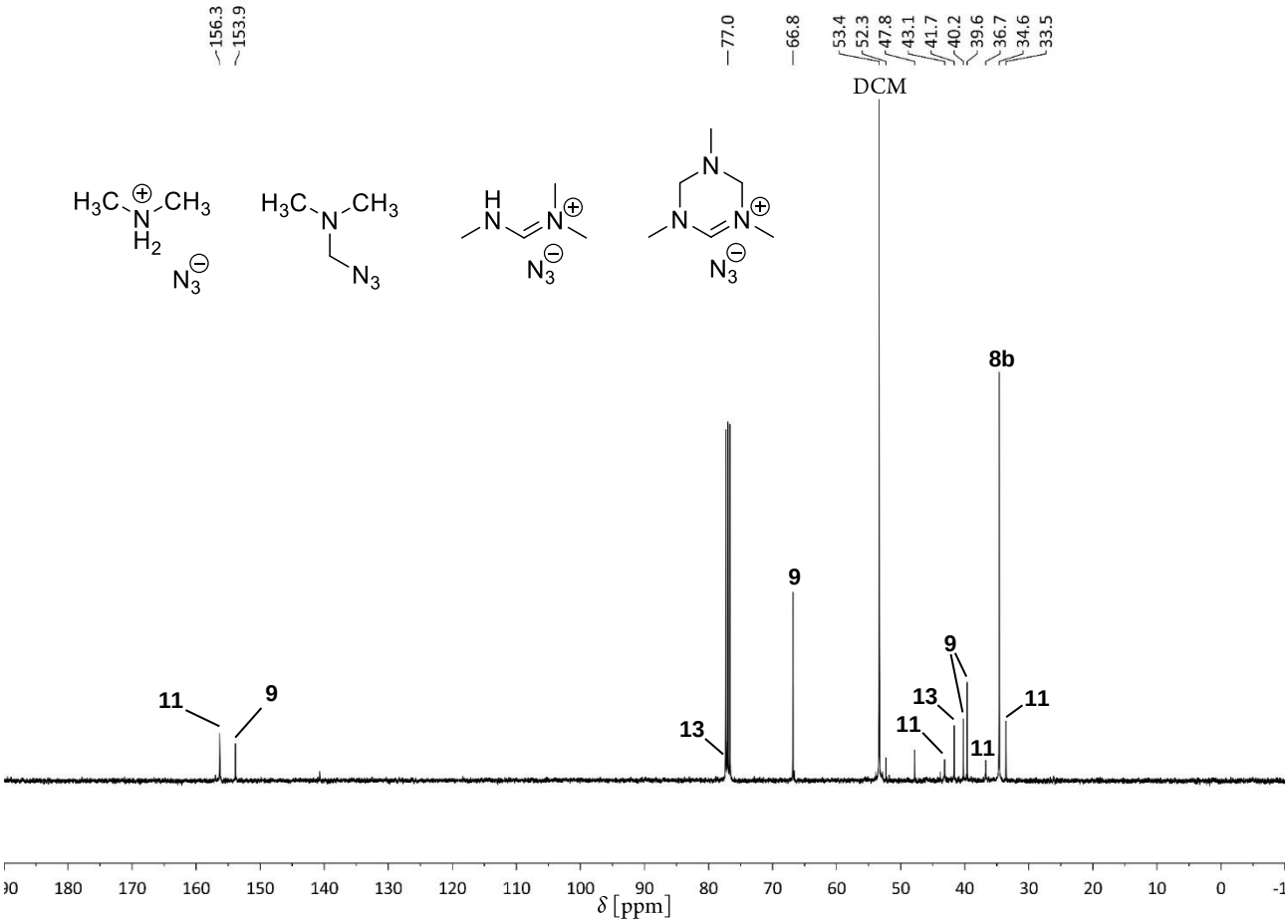
f) reaction of **6** with **8b**

To a solution of **6** in DCM, prepared as described above, was added **8b** (0.5 g, 5.67 mmol, 1 eq.) at –80 °C. The solution was stirred for 1 h at low temperature and was then allowed, while stirring overnight, to warm up to RT. The reaction products were analyzed without further purification (**13**: 0.162 g, 1.62 mmol, yield: 7% based on used *N*-methylaminoacetonitrile, analyzed by NMR spectroscopy with internal naphthalene-standard) (NMR spectra: see page S11).

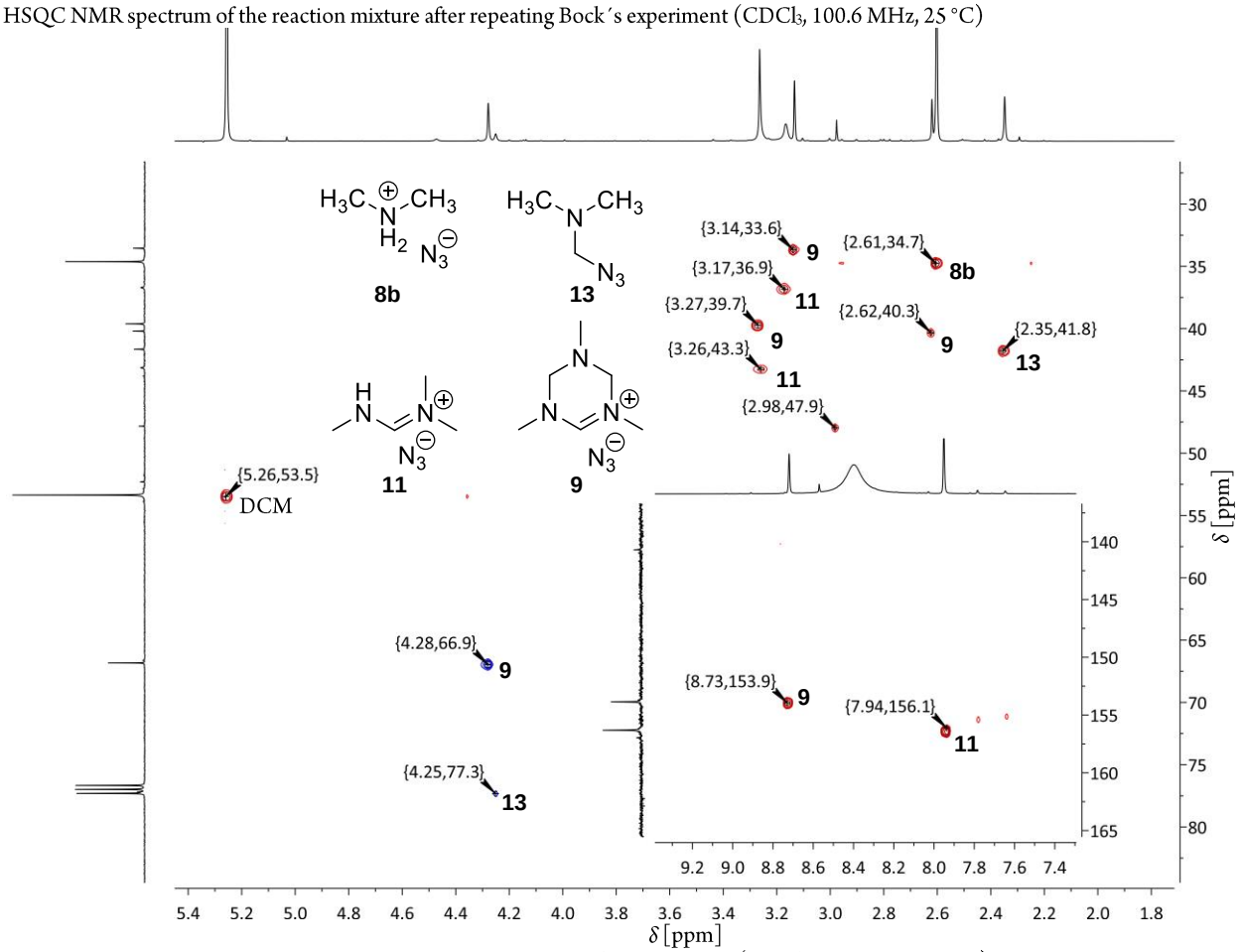
^{1}H NMR spectrum of the reaction mixture after repeating Bock´s experiment (CDCl$_3$, 400 MHz, 25 °C)



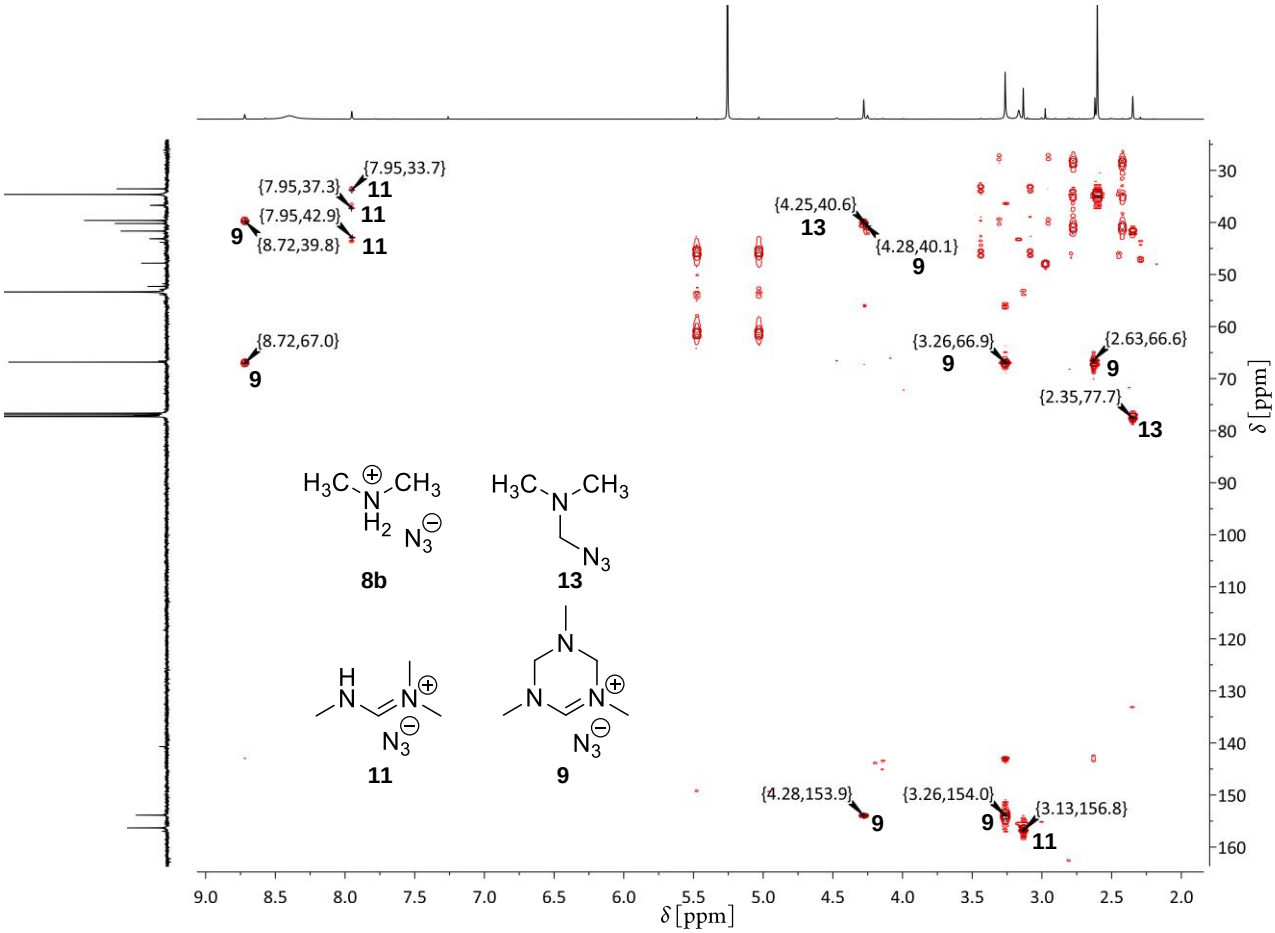
^{13}C{^{1}H} NMR spectrum of the reaction mixture after repeating Bock´s experiment (CDCl$_3$, 100.6 MHz, 25 °C)

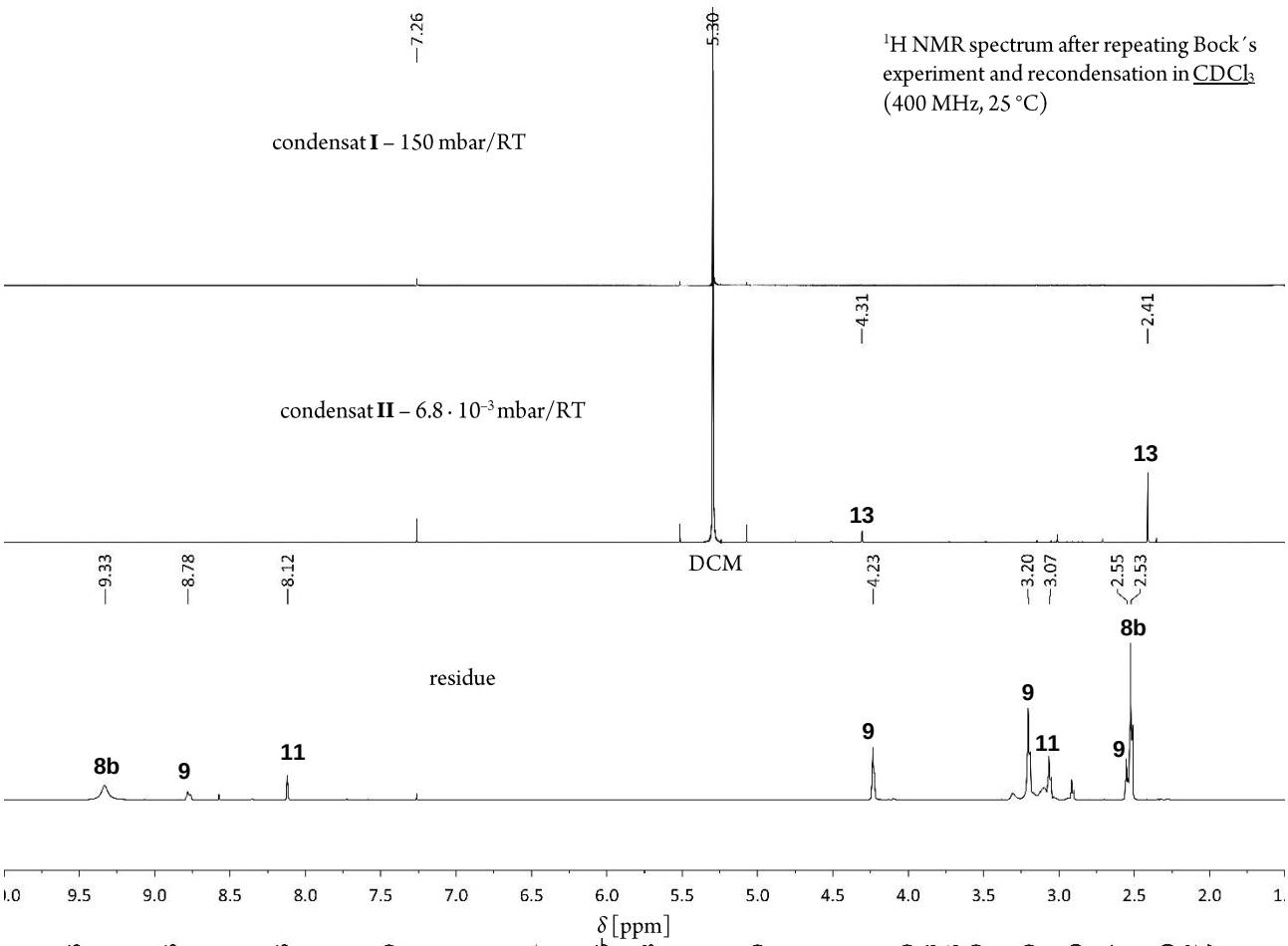


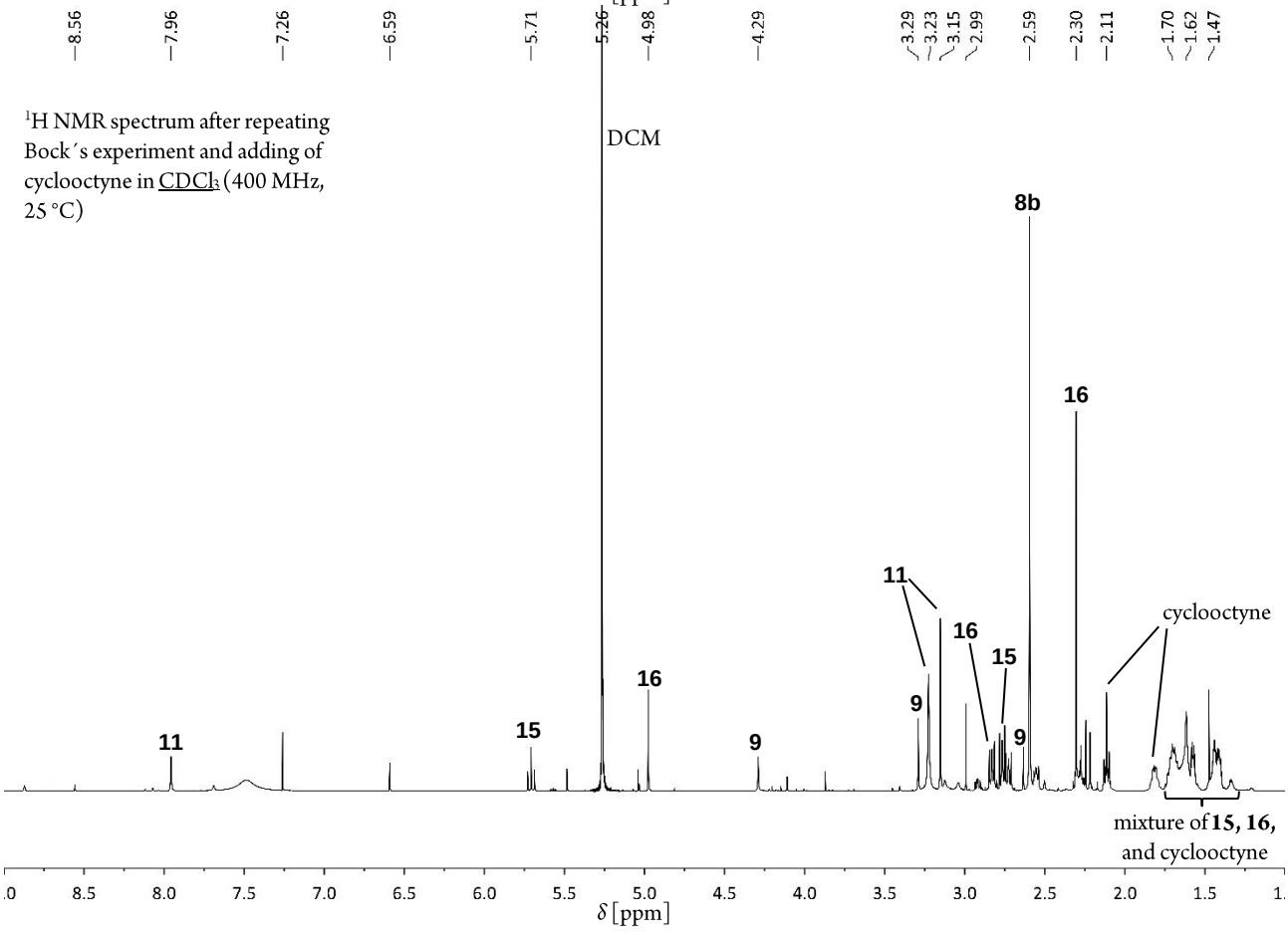
HSQC NMR spectrum of the reaction mixture after repeating Bock´s experiment ($CDCl_3$, 100.6 MHz, 25 °C)

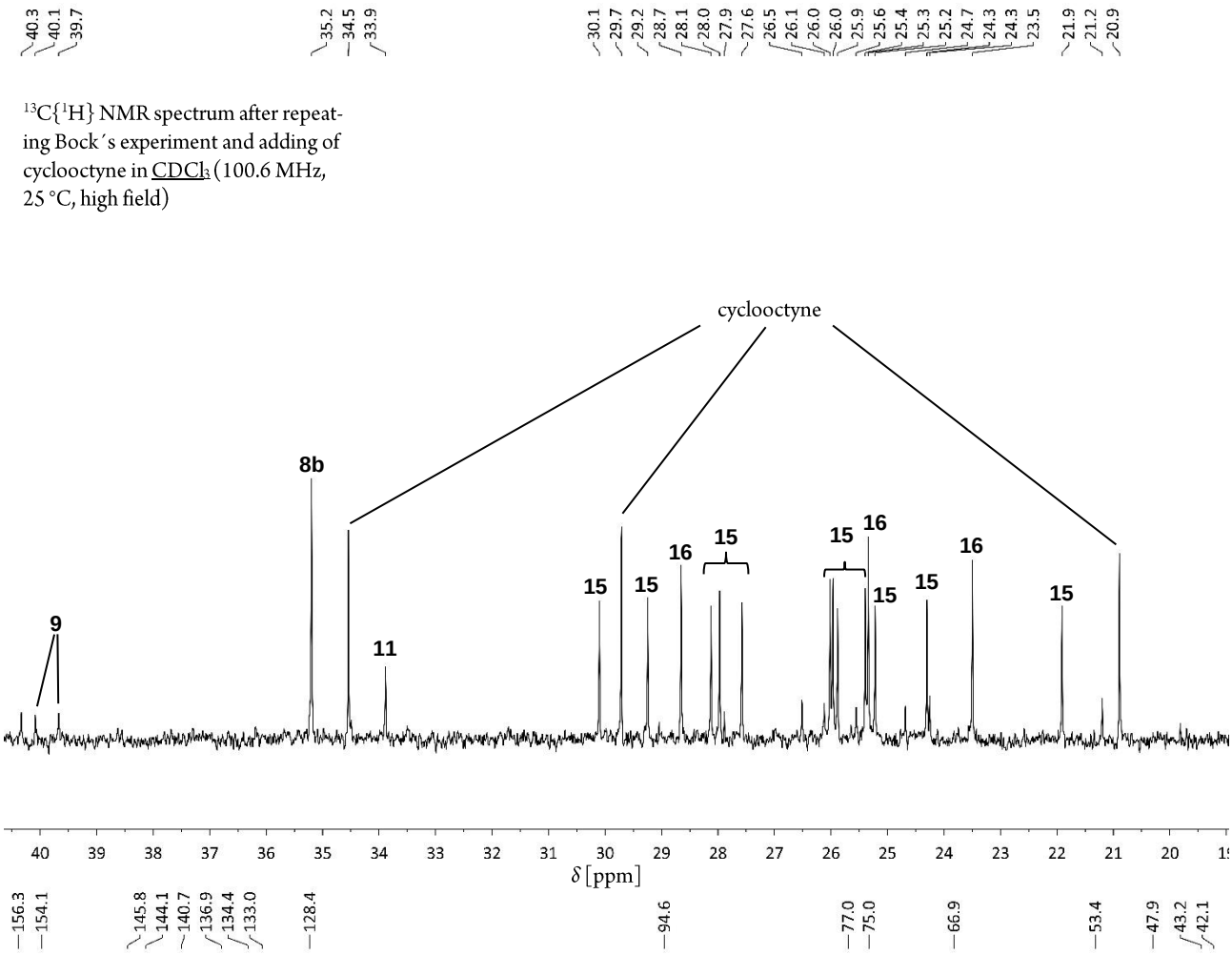


CIGAR NMR spectrum of the reaction mixture after repeating Bock´s experiment ($CDCl_3$, 100.6 MHz, 25 °C)

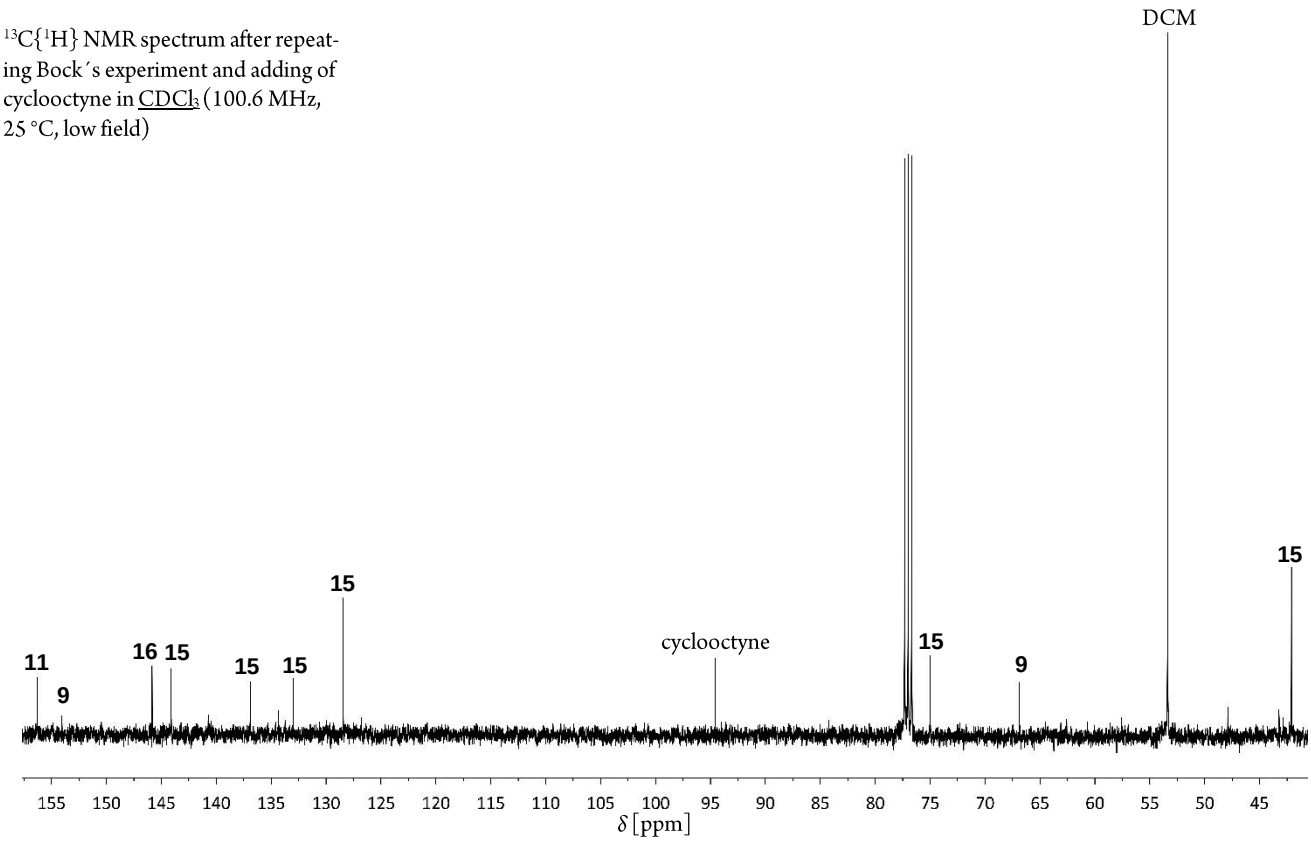



7.26
5.30
condensat I – 150 mbar/RT
1H NMR spectrum after repeating Bock´s experiment and recondensation in CDCl3 (400 MHz, 25 °C)
4.31
2.41
condensat II – 6.8 · 10−3 mbar/RT
13
13
9.33
8.78
8.12
DCM
4.23
3.20
3.07
2.55
2.53
8b
residue
9
8b
9
11
9
11
9
δ [ppm]


8.56
7.96
7.26
6.59
5.71
5.26
4.98
4.29
3.29
3.23
3.15
2.99
2.59
2.30
2.11
1.70
1.62
1.47
1H NMR spectrum after repeating Bock´s experiment and adding of cyclooctyne in CDCl3 (400 MHz, 25 °C)
DCM
8b
16
11
16
15
16
cyclooctyne
9
15
9
11
9
9
mixture of 15, 16, and cyclooctyne
δ [ppm]

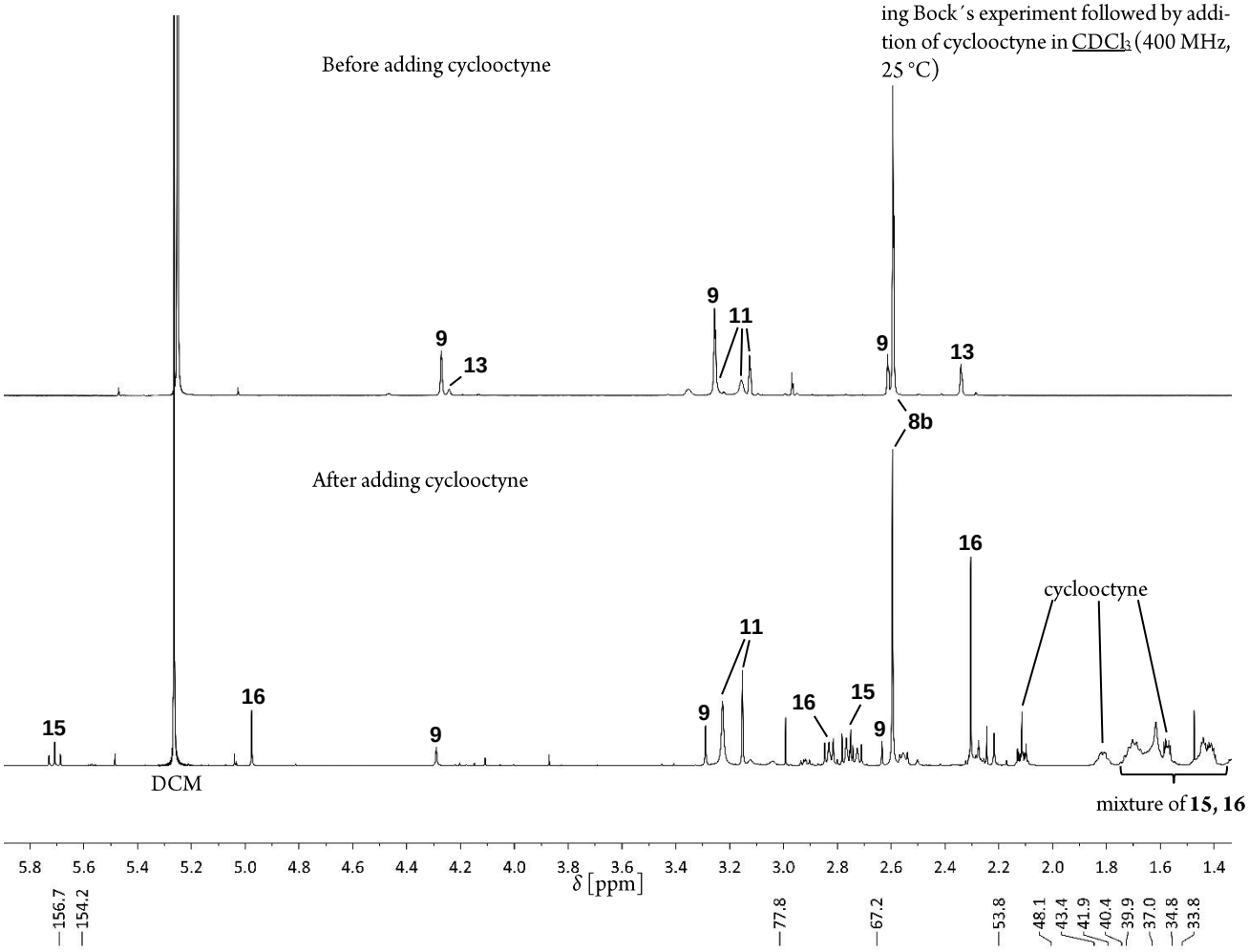


$^{13}C\{^{1}H\}$ NMR spectrum after repeating Bock´s experiment and adding of cyclooctyne in $CDCl_3$ (100.6 MHz, 25 °C, high field)

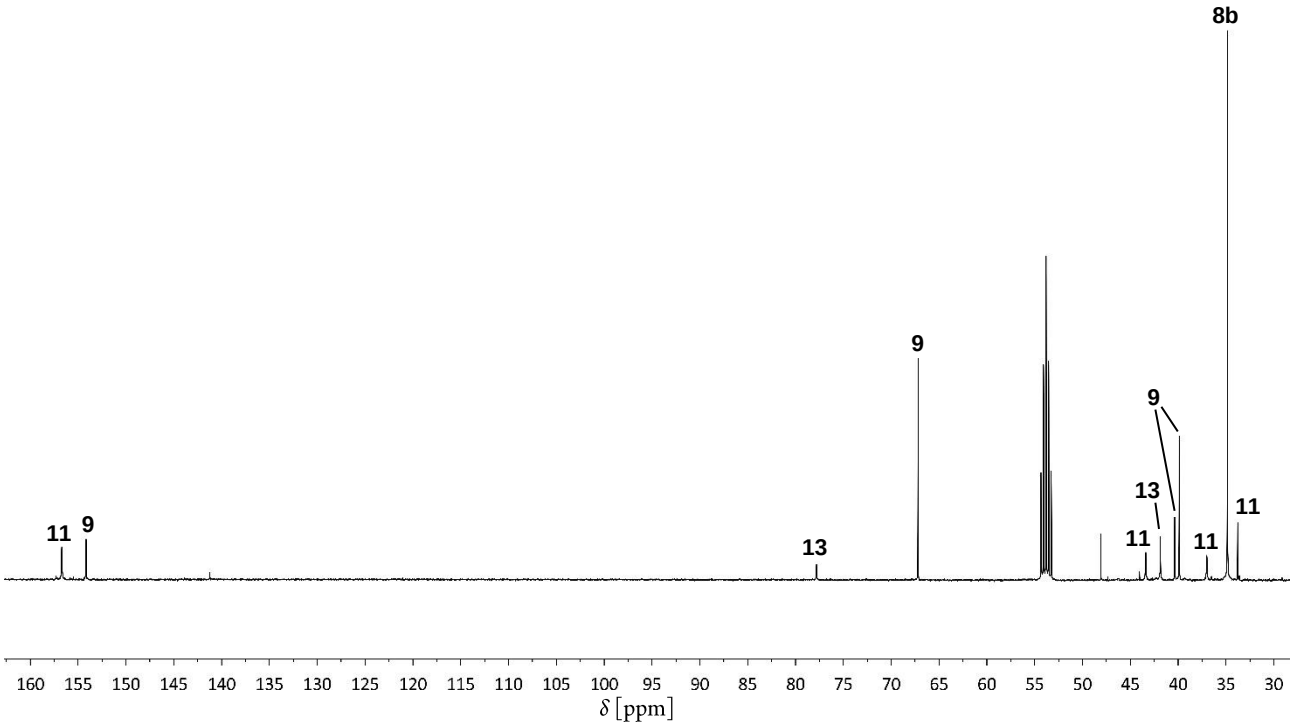


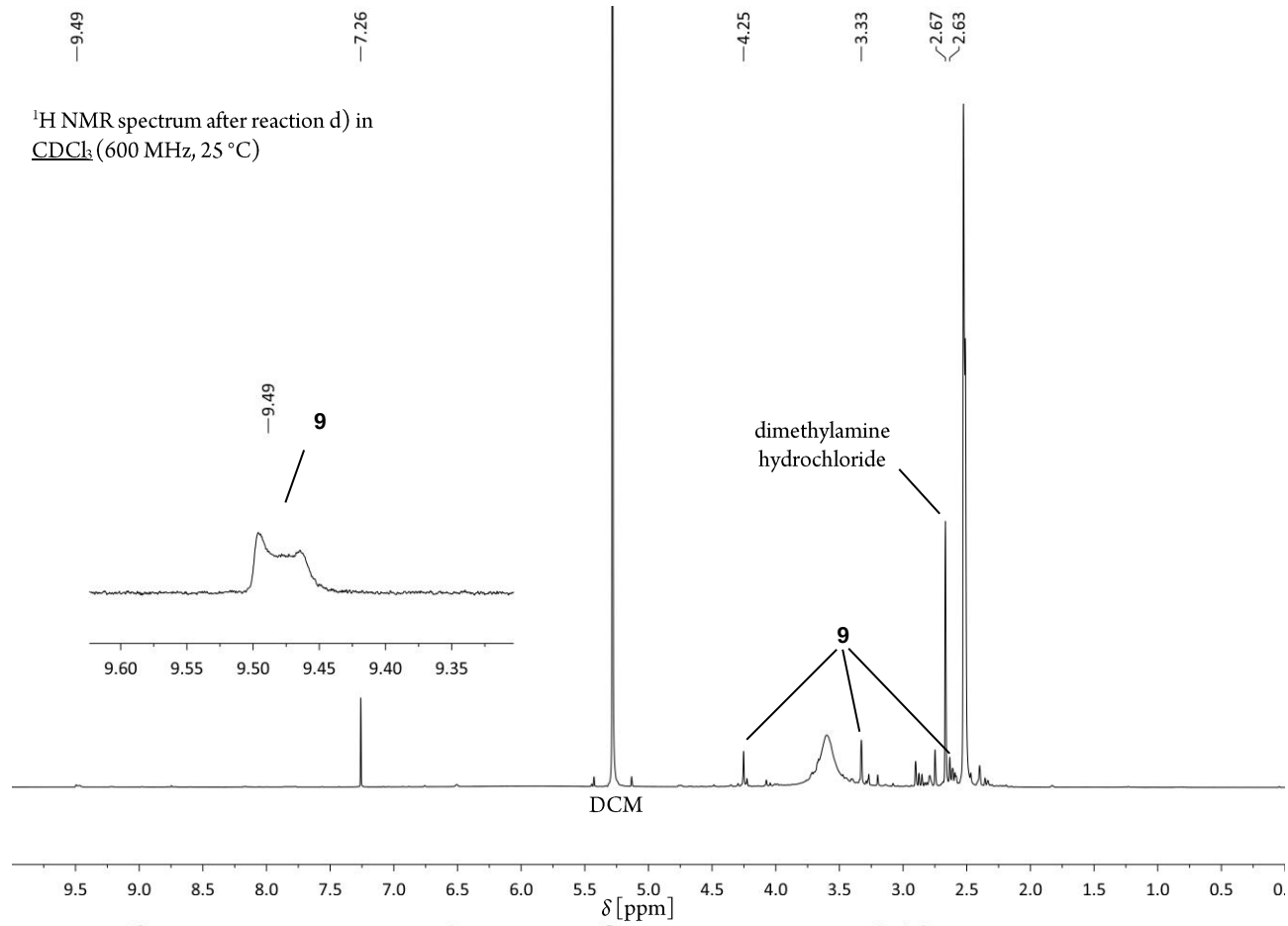
$^{13}C\{^{1}H\}$ NMR spectrum after repeating Bock´s experiment and adding of cyclooctyne in $CDCl_3$ (100.6 MHz, 25 °C, low field)

Comparing ^{1}H NMR spectra after repeating Bock´s experiment followed by addition of cyclooctyne in CDCl$_3$ (400 MHz, 25 °C)

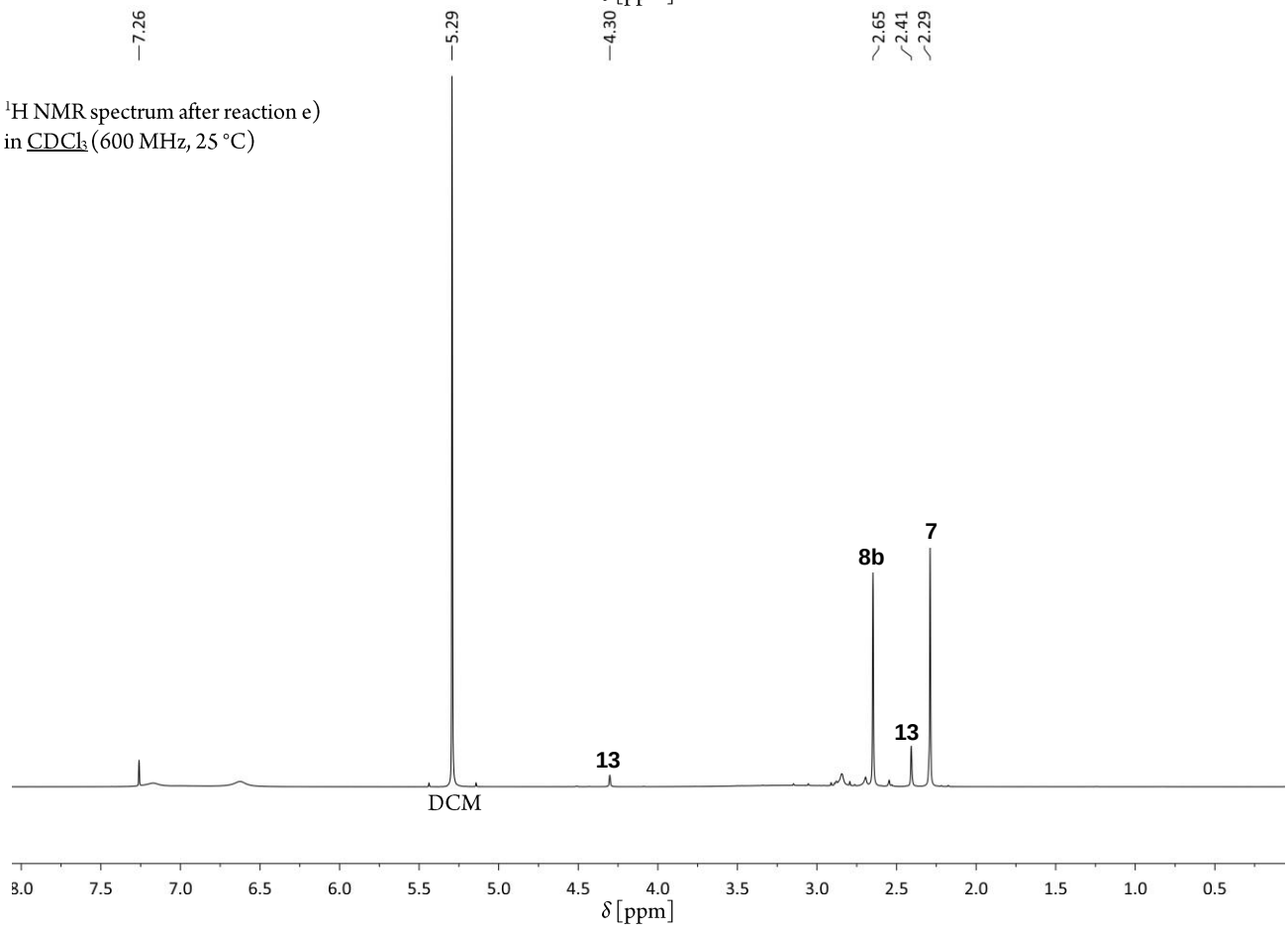


^{13}C{^{1}H} NMR spectrum after repeating Bock´s experiment in [D$_2$]-DCM (100.6 MHz, 25 °C)

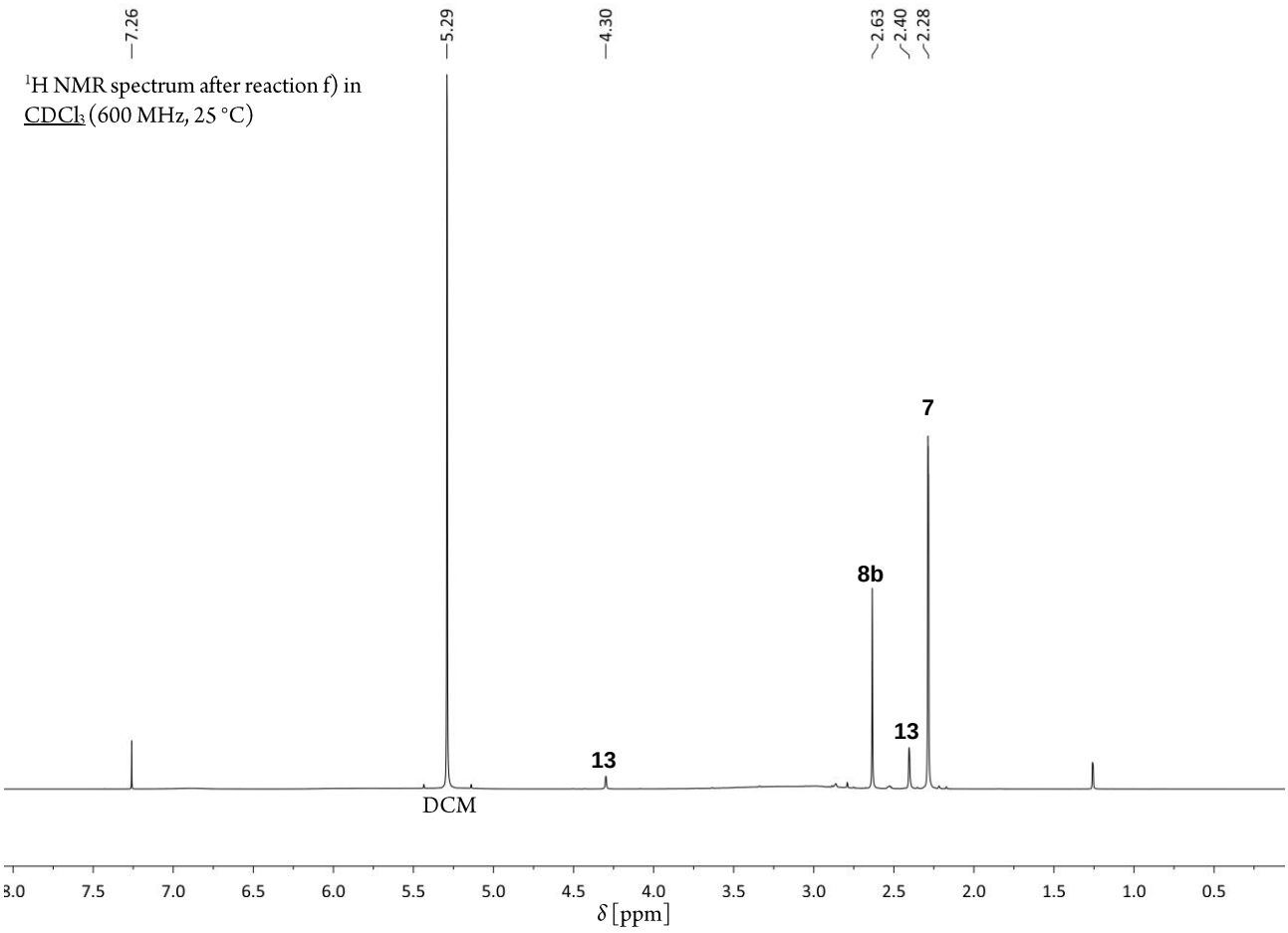




^{1}H NMR spectrum after reaction d) in $CDCl_3$ (600 MHz, 25 °C)



^{1}H NMR spectrum after reaction e) in $CDCl_3$ (600 MHz, 25 °C)


7.26
5.29
4.30
2.63
2.40
2.28
^{1}H NMR spectrum after reaction f) in
CDCl$_3$ (600 MHz, 25 °C)
7
8b
13
13
DCM
3.0
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
δ [ppm]

2) Anselme *et al.* [10]

Procedures:[10]

To a solution of **3c** (1.08 g, 5.1 mmol) in dry THF (10 mL) was added under nitrogen atmosphere at –78 °C ^{n}BuLi (2.5 M in hexanes, 2.03 mL, 5.1 mmol, 1 eq.). The mixture was stirred for 1 h, and then TsN_3 (1 g, 5.1 mmol, 1 eq.) in dry THF (10 mL) was added under nitrogen atmosphere at –78 °C and stirred for additional 1 h. The mixture was then pureed into 30 mL ice/water and extracted with Et_2O (3 x 20 mL), followed by drying over $MgSO_4$ and removing the solvent with a rotary evaporator.

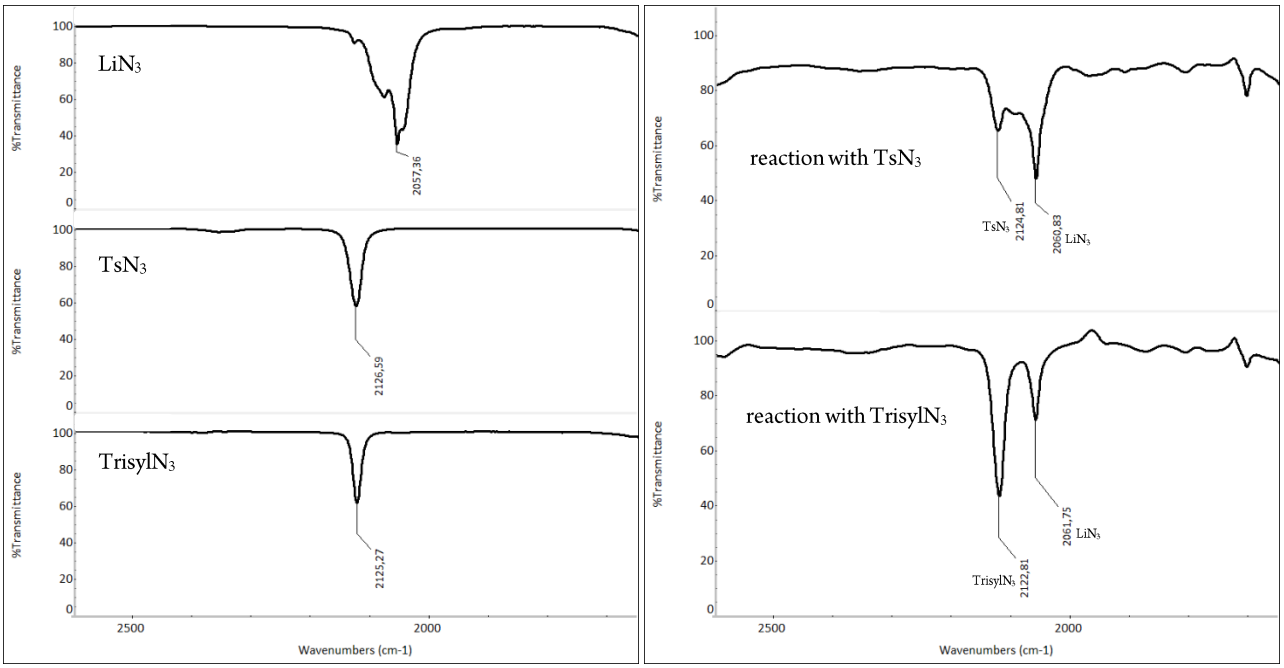
Hint: For trapping experiments were used 2-3 eq. of cyclooctyne.

Observed phenomena:

We were able to observe all the phenomena described in literature.[10] After addition of ^{n}BuLi the solution turns deep red, and color changes after addition of TsN_3 and warming up to ca. –30 °C. The evolution of nitrogen started directly after the addition of TsN_3, first slowly, then when mixture temperature reaches –30 °C, fast and as described under changing color.

IR:

For comparism, the IR spectra of LiN_3, TsN_3, $TrisylN_3$ and reaction solutions resulting from the conversion with TsN_3 and $TrisylN_3$ were depicted. It is observable that, as described, the yield of LiN_3 decreases with increasing the steric hinderance of the sulfonyl azide.



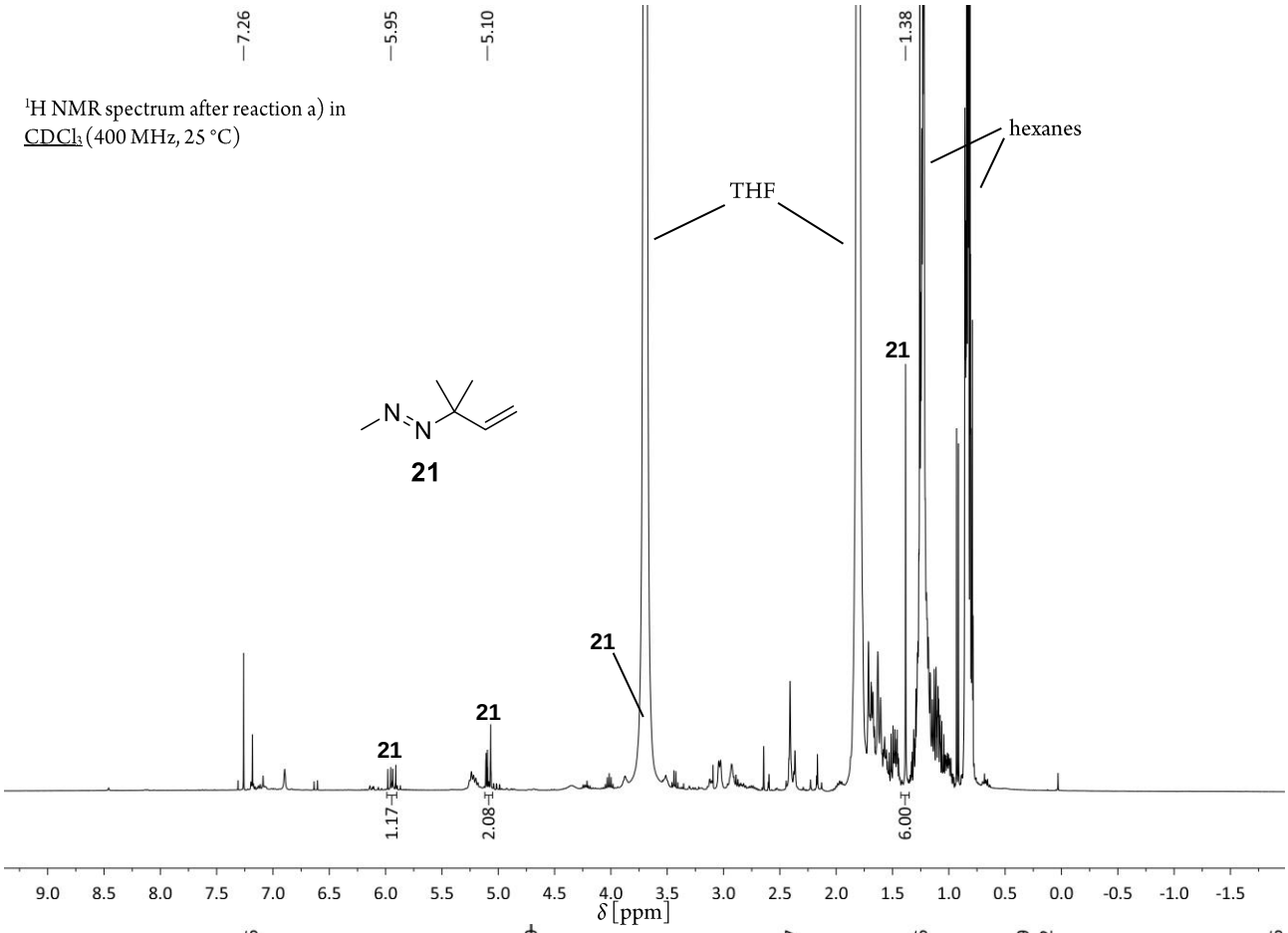
Further attempts to generate *N*-azidoamines via diazo group transfer or nucleophilic substitution

a) further diazo group transfer reactions

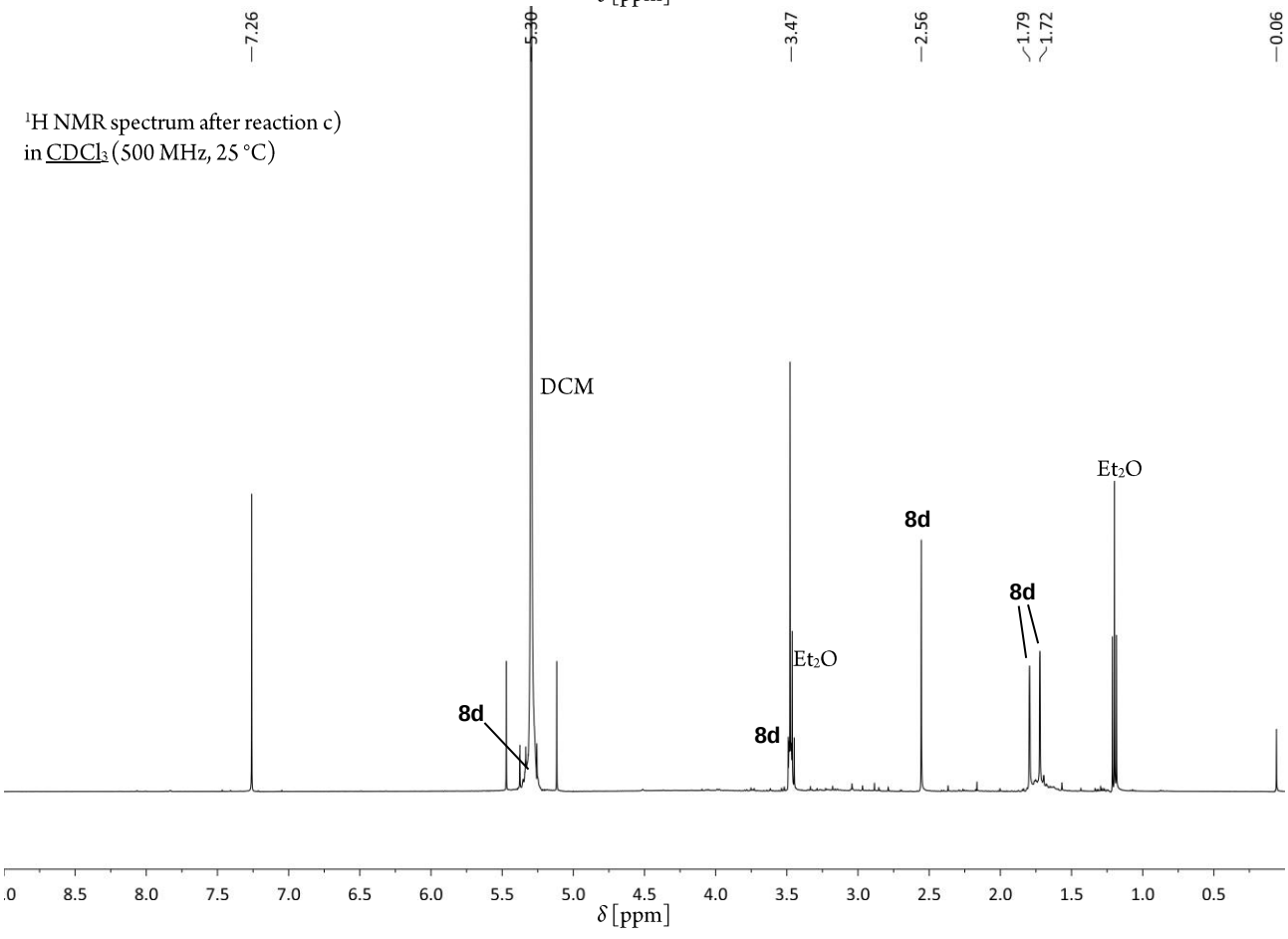
Further diazo group transfer reactions were performed as described in the procedure of synthesizing **21**. Trapping experiments were realized by adding at least 3 eq. of cyclooctyne to the reaction mixture.

b) reaction of **1d** with NaN_3

To a solution of **1d** in DCM (1.75%, 250 mg **1d**, 1.87 mmol) was added NaN_3 (123 mg, 1.87 mmol, 1 eq.) while cooling with ice-water. The mixture was stirred for 2 h, was then allowed to warm up to RT and then stirred for additional 22 h. After filtration, the mixture was directly analyzed.

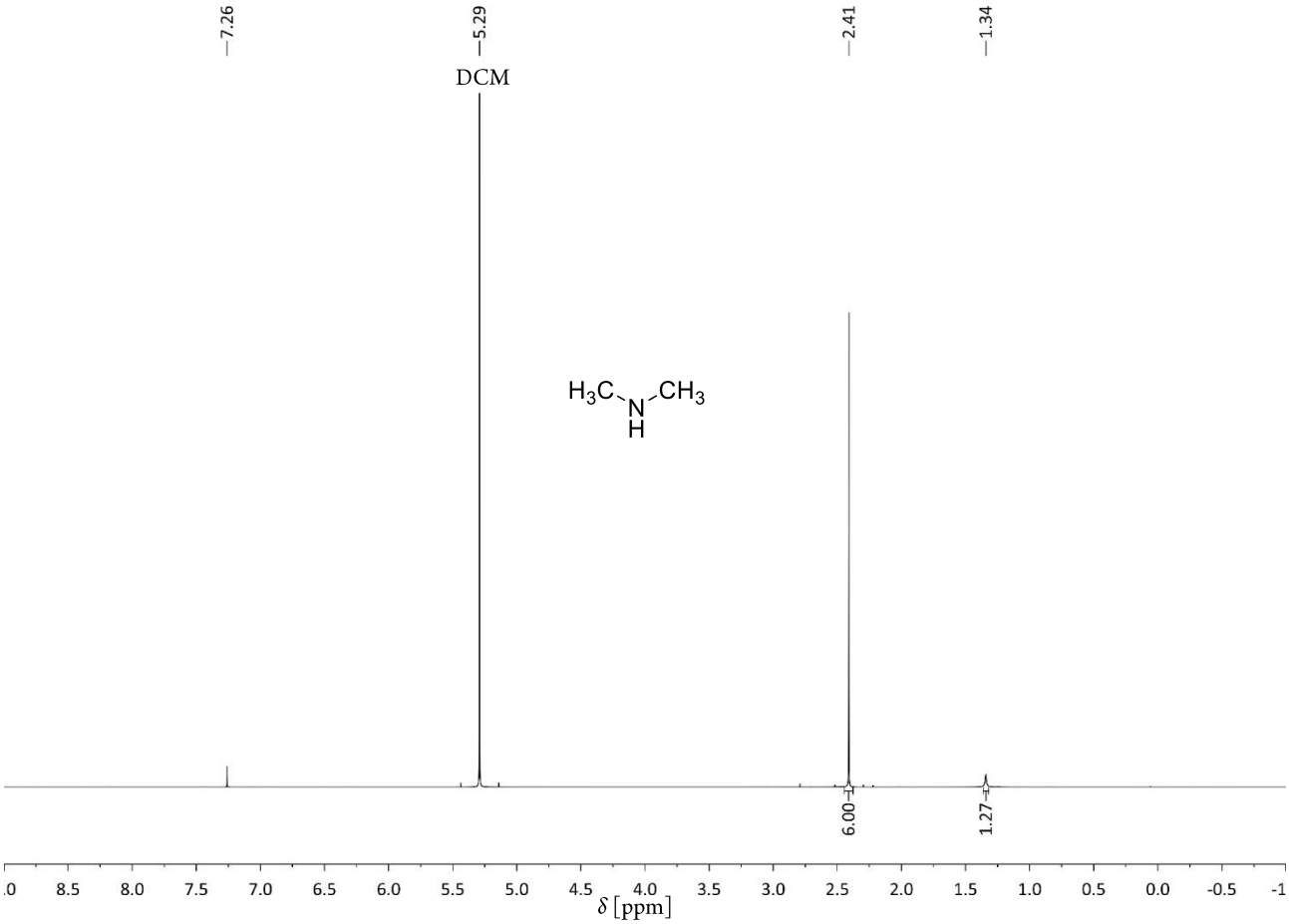


^{1}H NMR spectrum after reaction a) in $\underline{CDCl_3}$ (400 MHz, 25 °C)

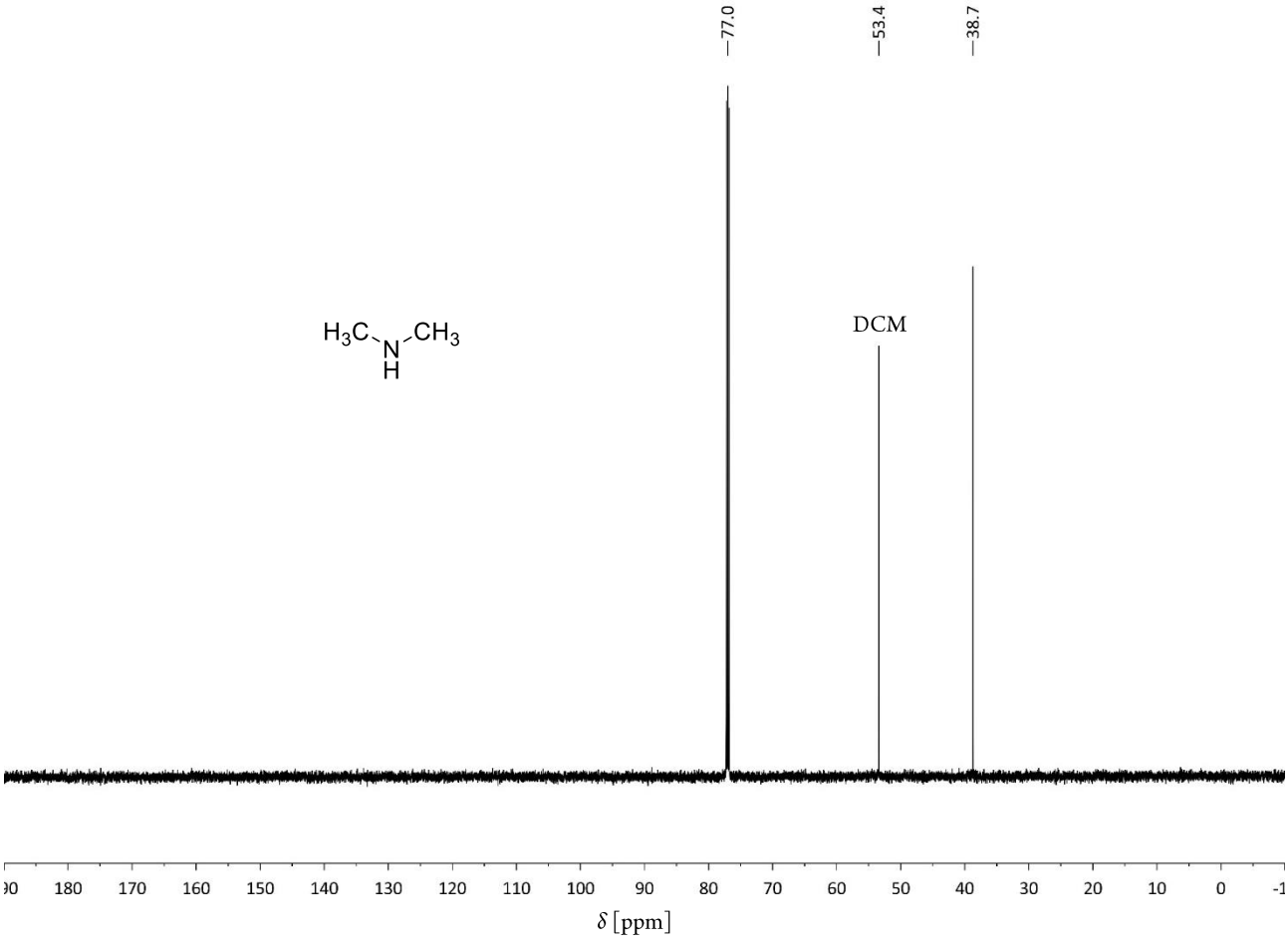


^{1}H NMR spectrum after reaction c) in $\underline{CDCl_3}$ (500 MHz, 25 °C)

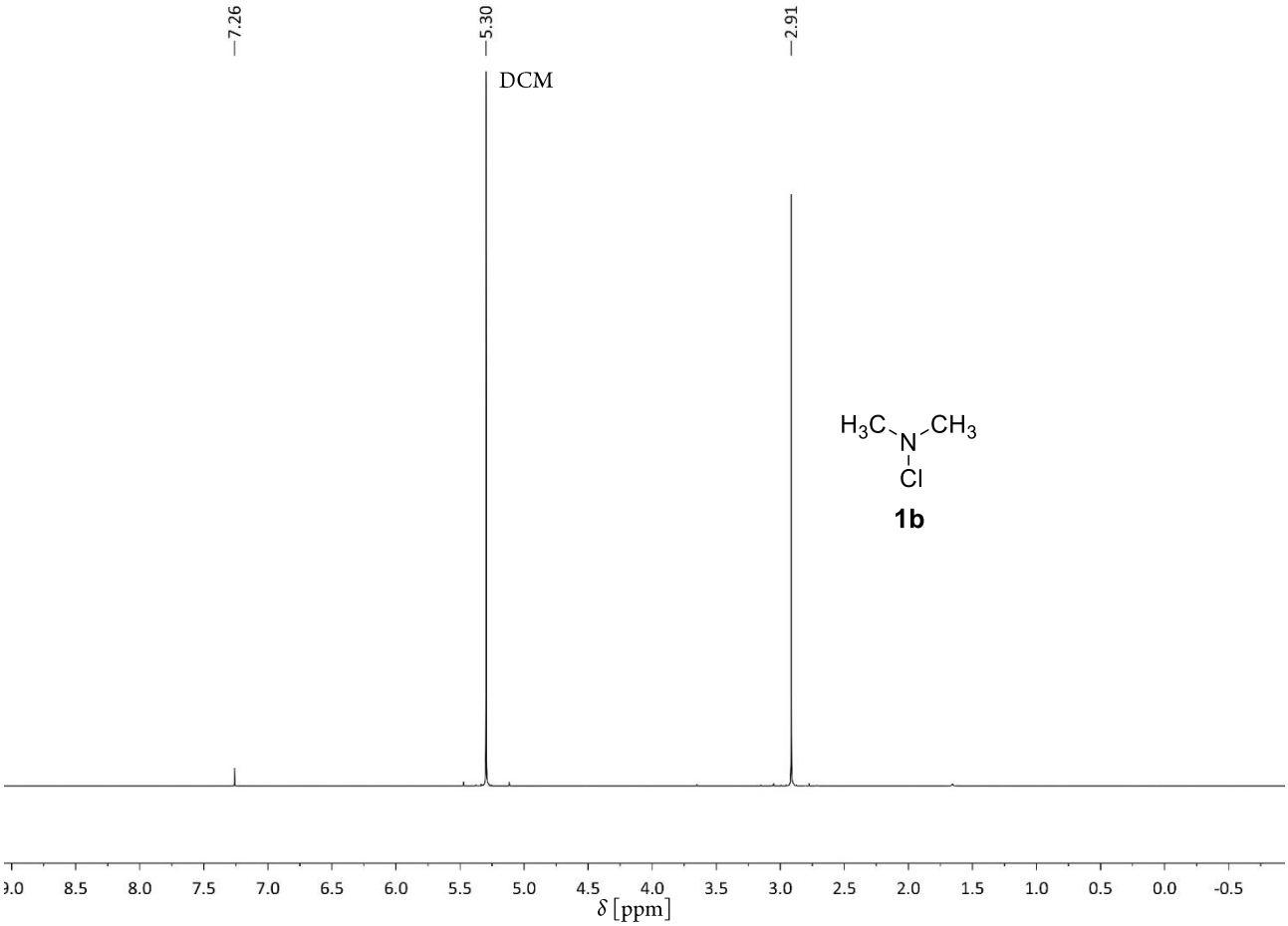
^{1}H NMR spectrum of *N,N*-dimethylamine in $CDCl_3$ (600 MHz, 25 °C)



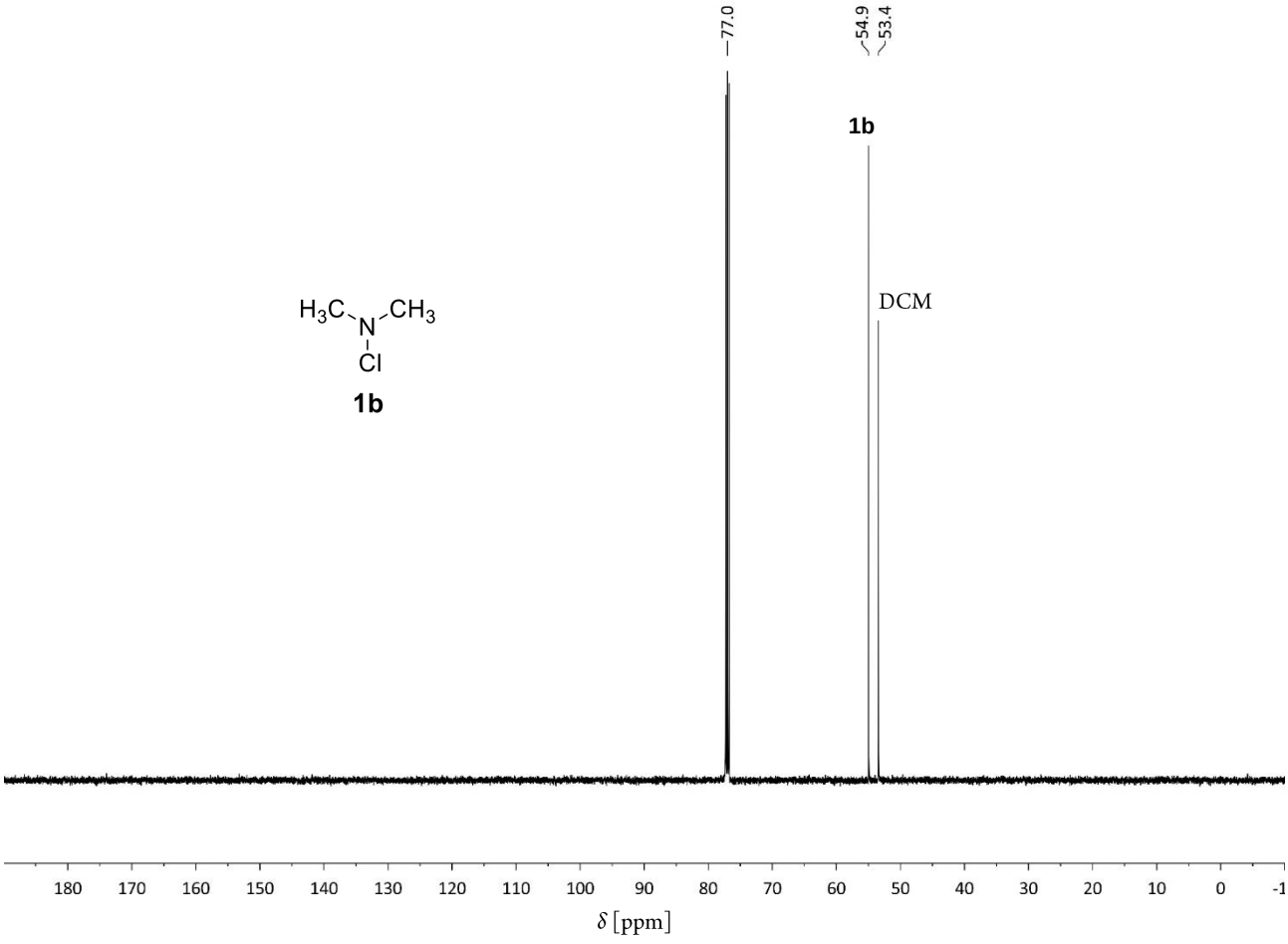
^{13}C{^{1}H} NMR spectrum of *N,N*-dimethylamine in $CDCl_3$ (150.9 MHz, 25 °C)



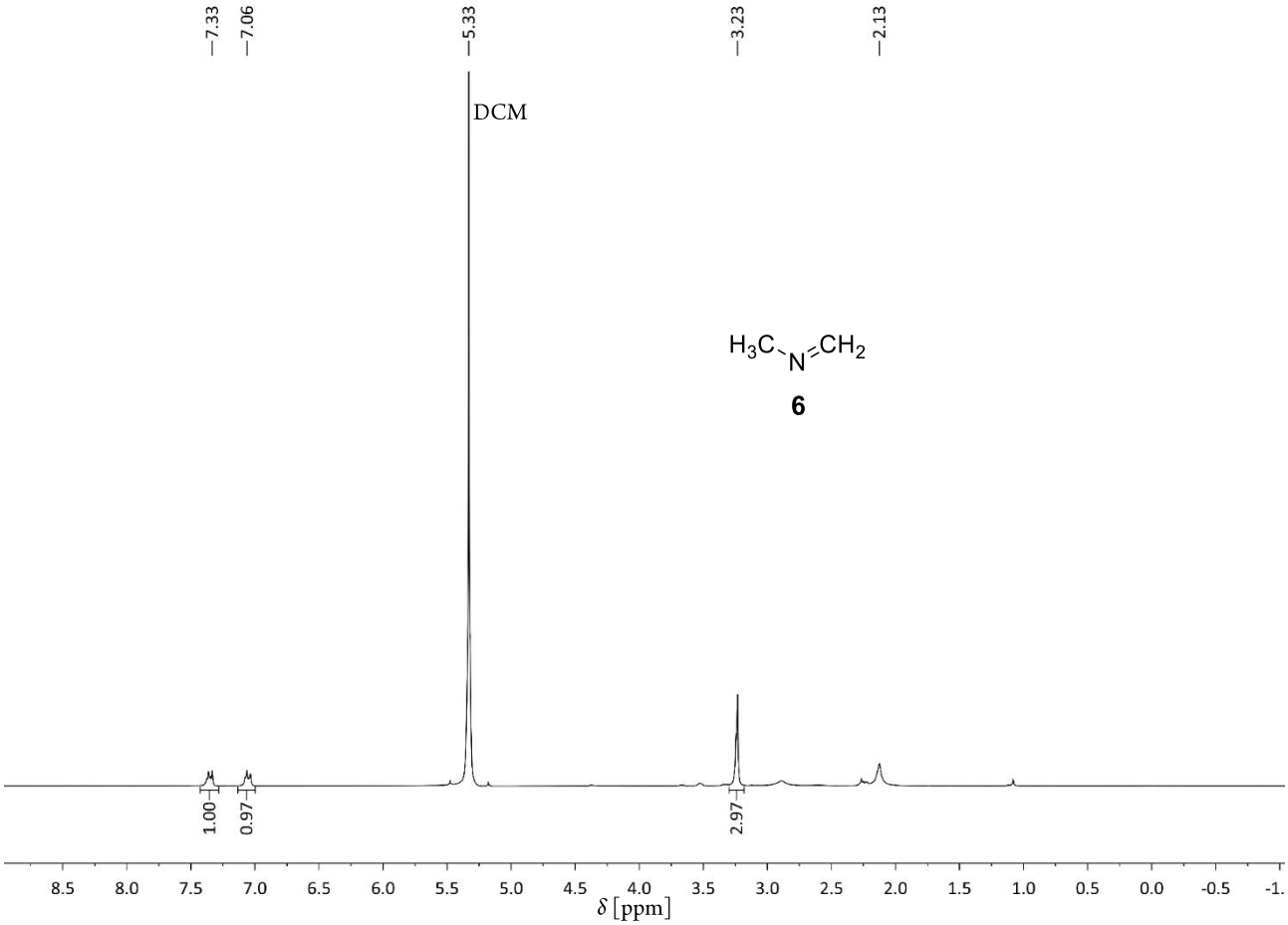
^{1}H NMR spectrum of **1b** in $CDCl_3$ (500 MHz, 25 °C)



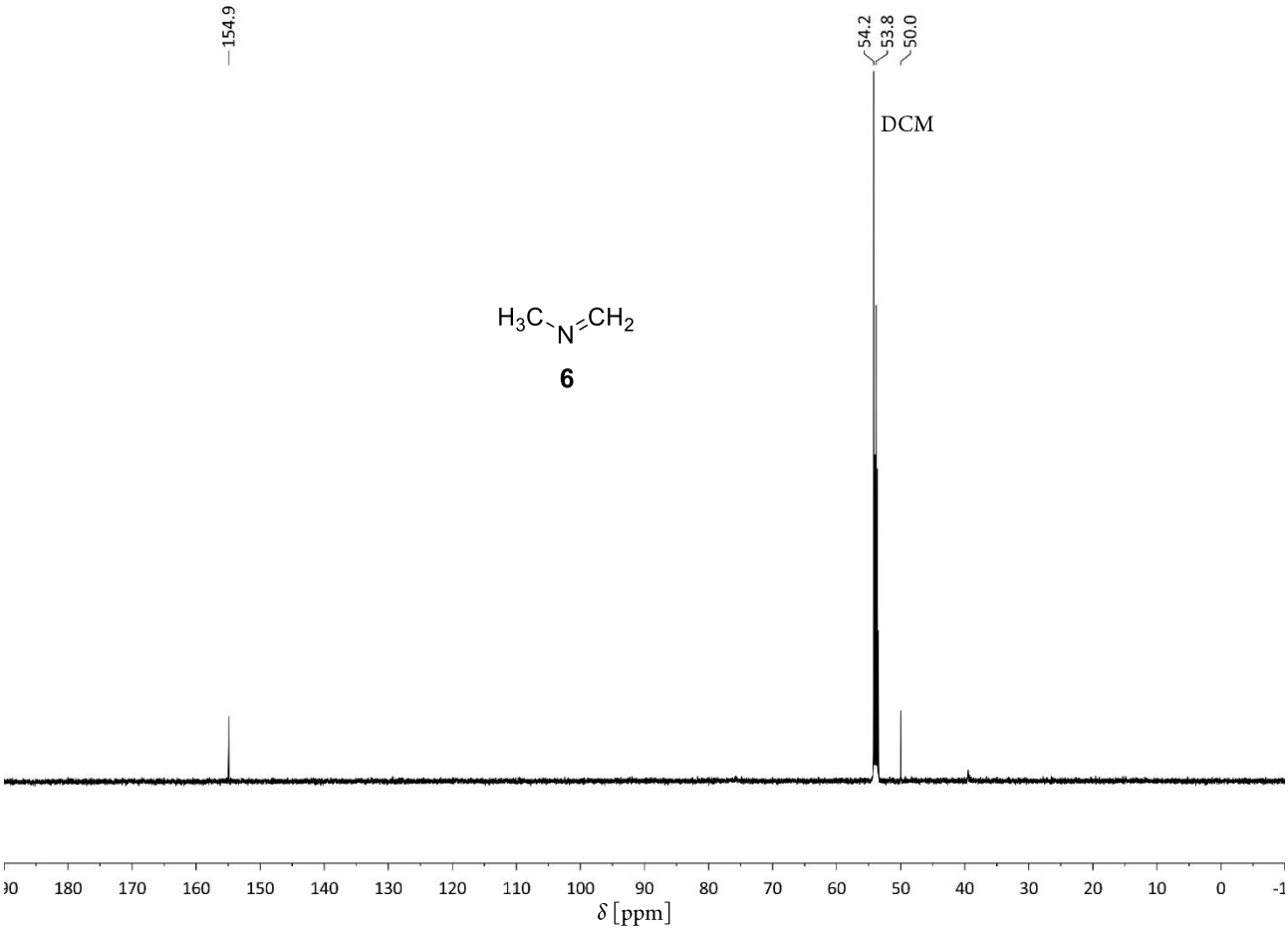
^{13}C{^{1}H} NMR spectrum of **1b** in $CDCl_3$ (125.8 MHz, 25 °C)



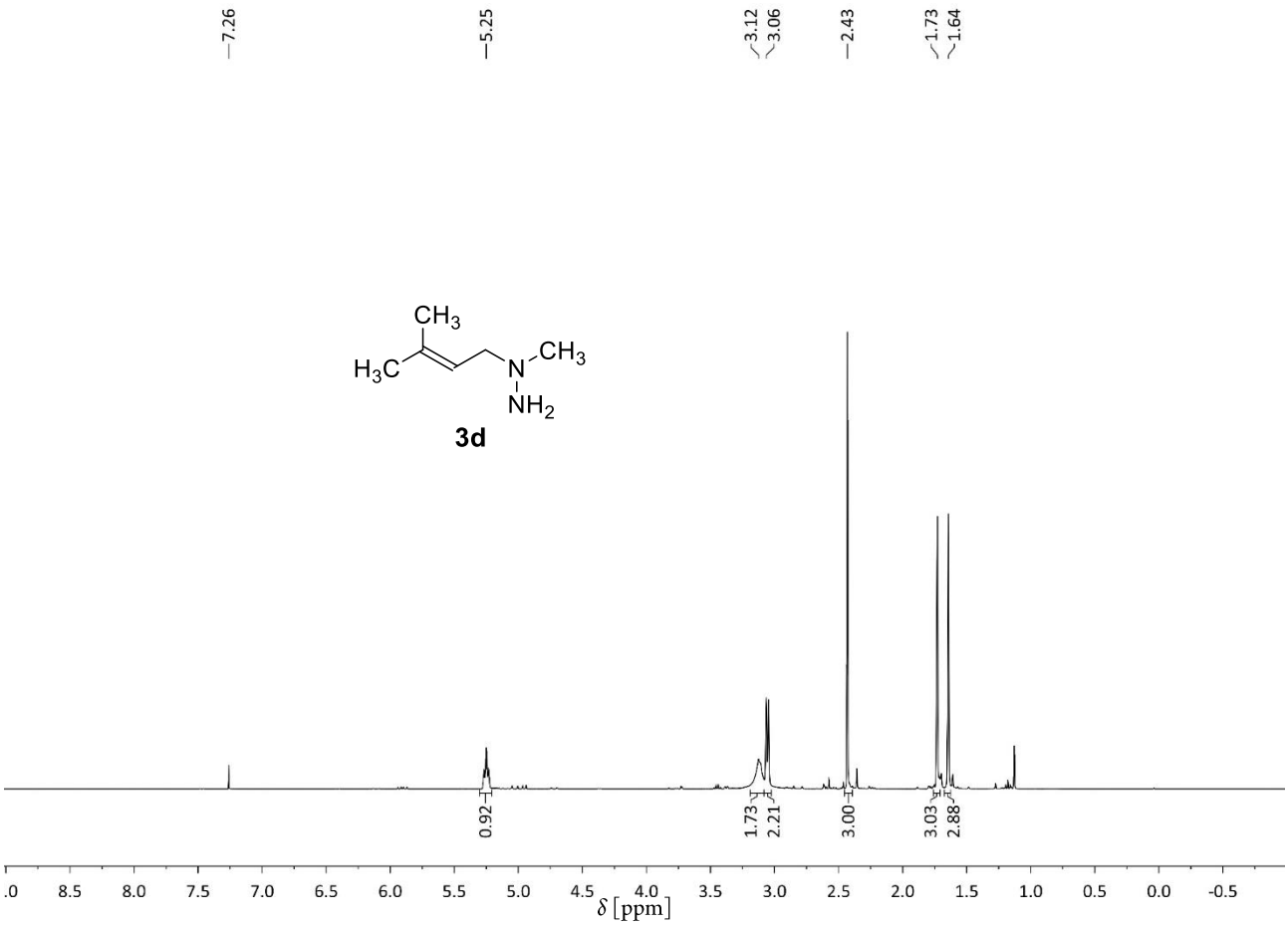
^{1}H NMR spectrum of **6** in [D$_2$]-DCM (600 MHz, –80 °C)



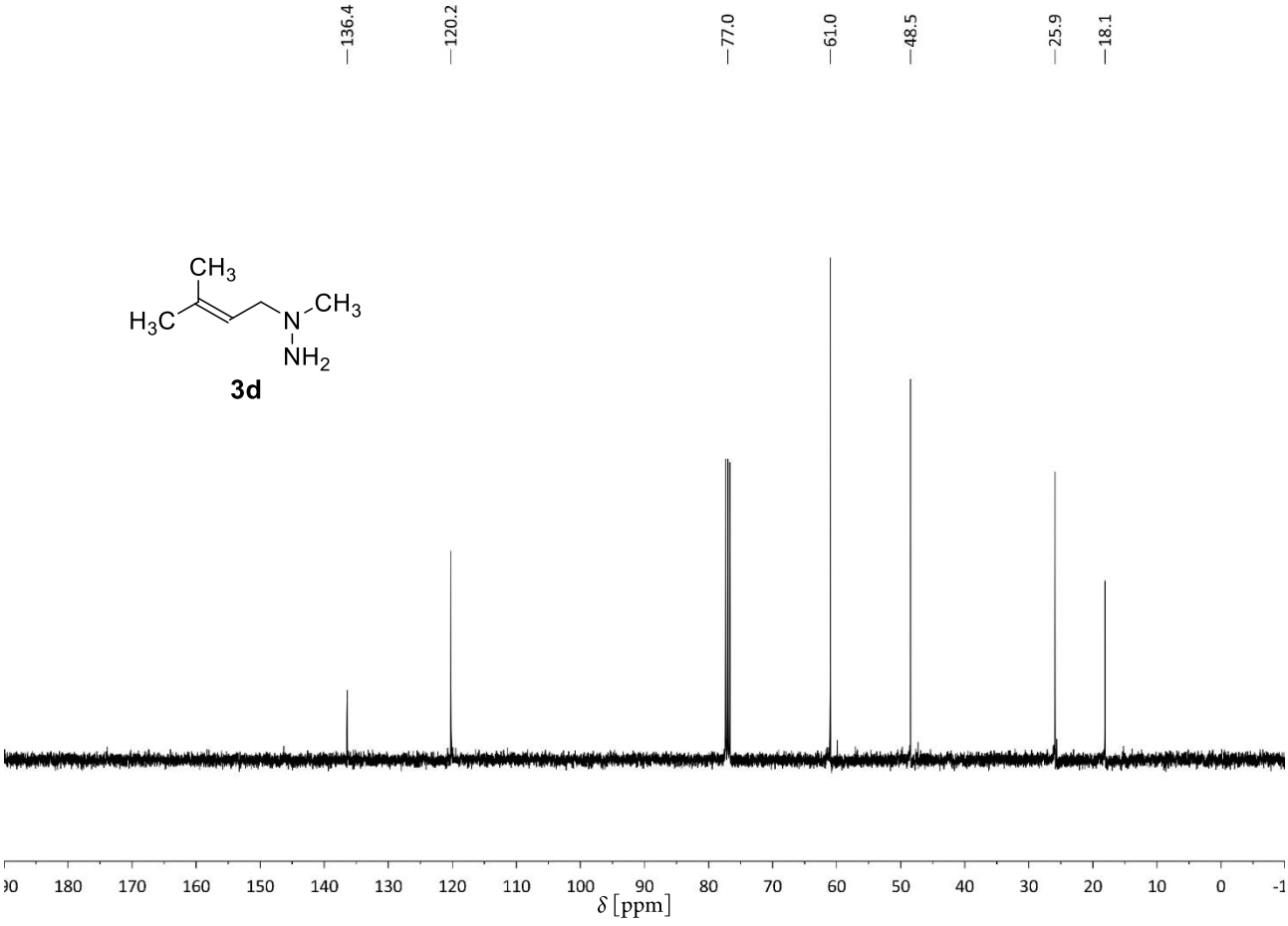
^{13}C{^{1}H} NMR spectrum of **6** in [D$_2$]-DCM (150.9 MHz, –80 °C)



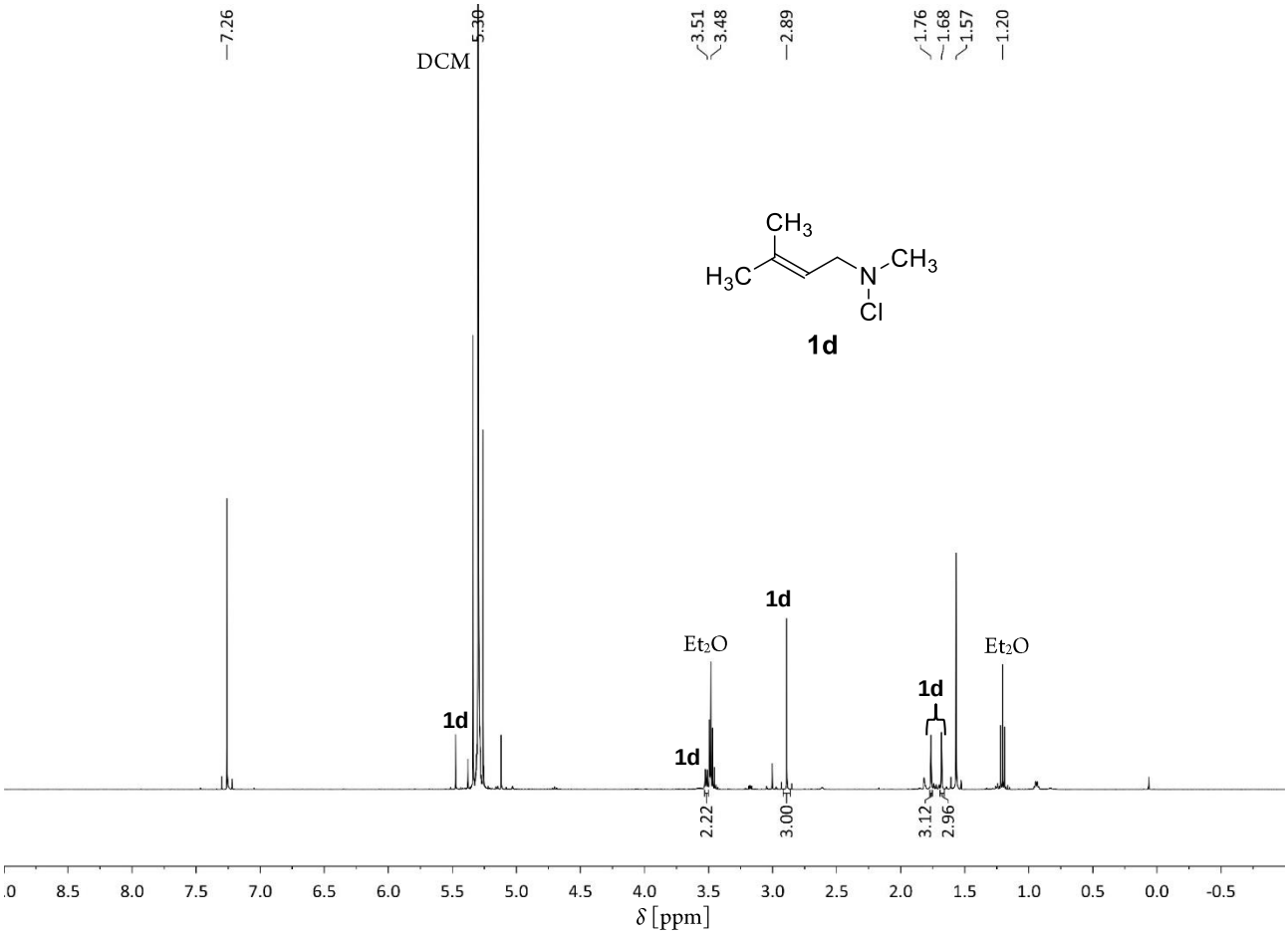
^{1}H NMR spectrum of **3d** in $CDCl_3$ (400 MHz, 25 °C)



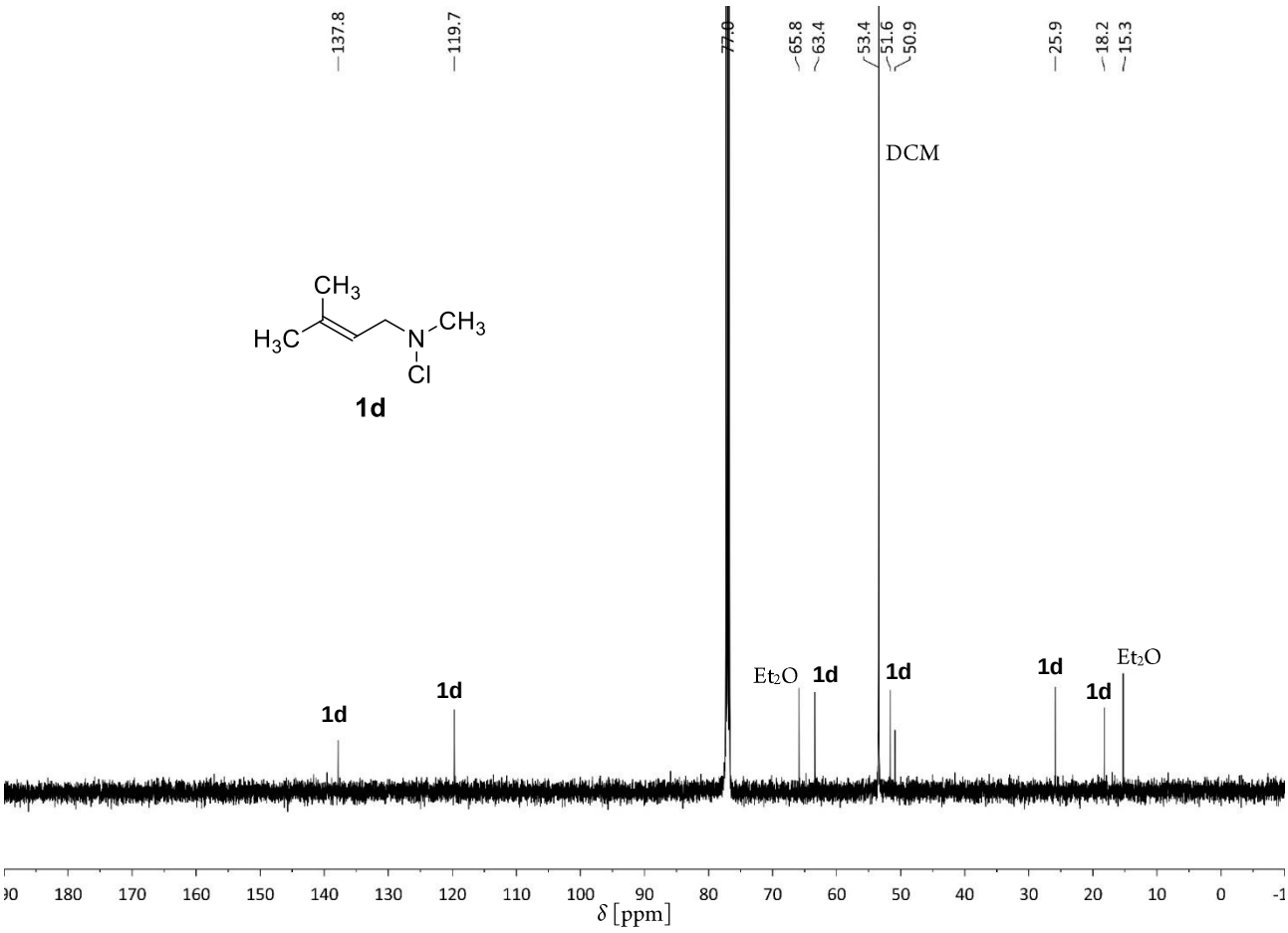
^{13}C{^{1}H} NMR spectrum of **3d** in $CDCl_3$ (100.6 MHz, 25 °C)



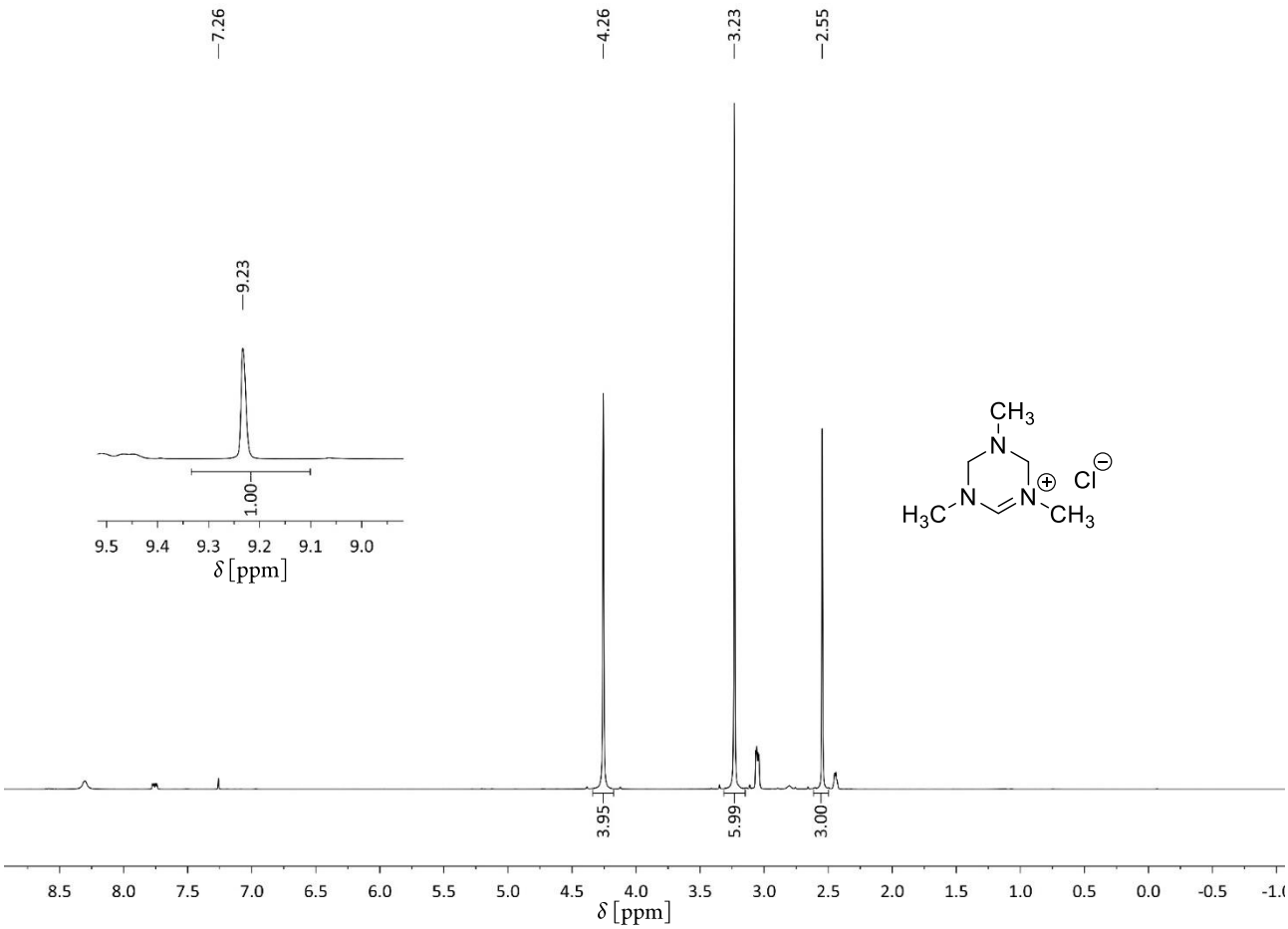
^{1}H NMR spectrum of **1d** in $CDCl_3$ (500 MHz, 25 °C)



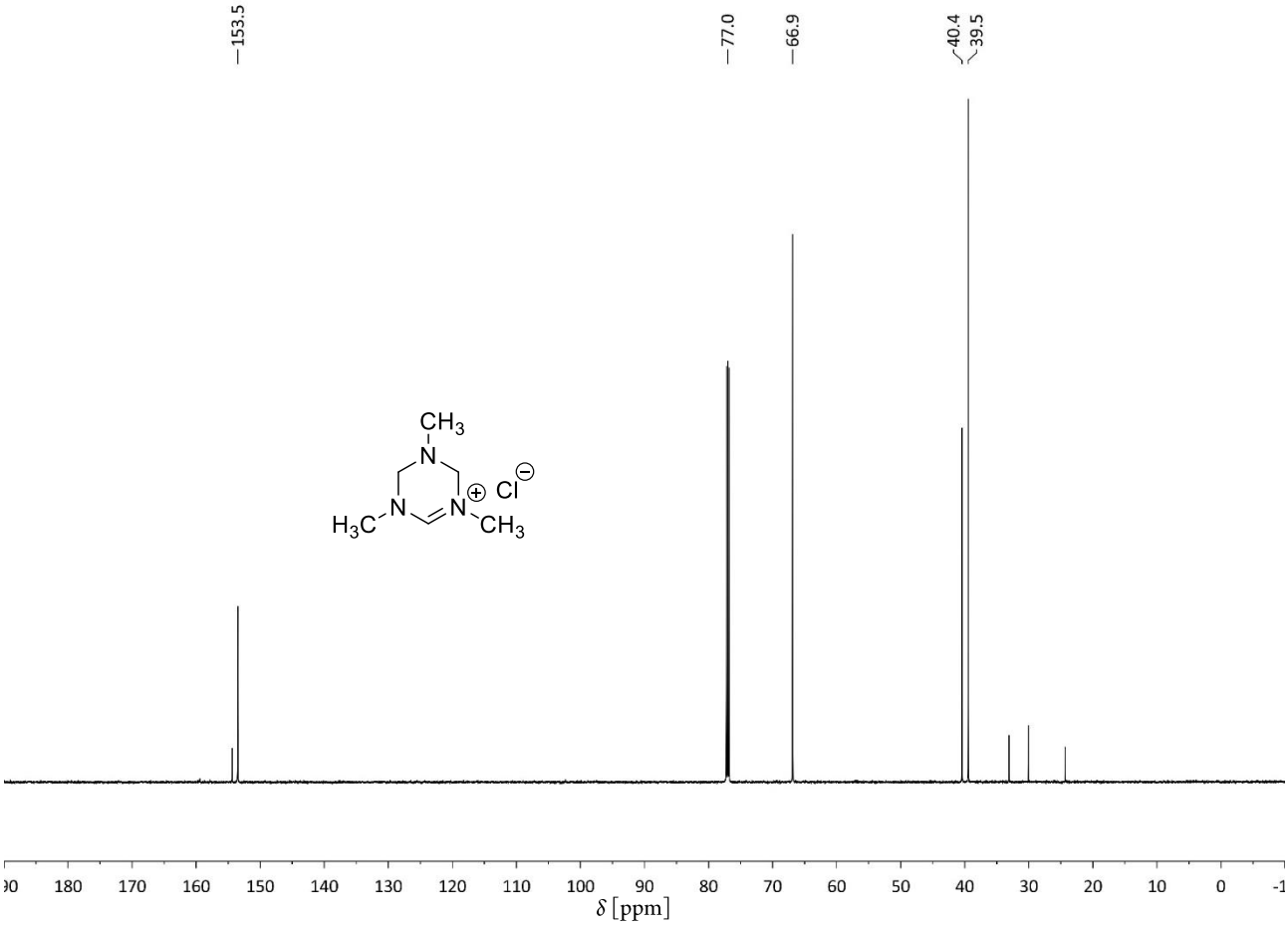
^{13}C{^{1}H} NMR spectrum of **1d** in $CDCl_3$ (125.8 MHz, 25 °C)



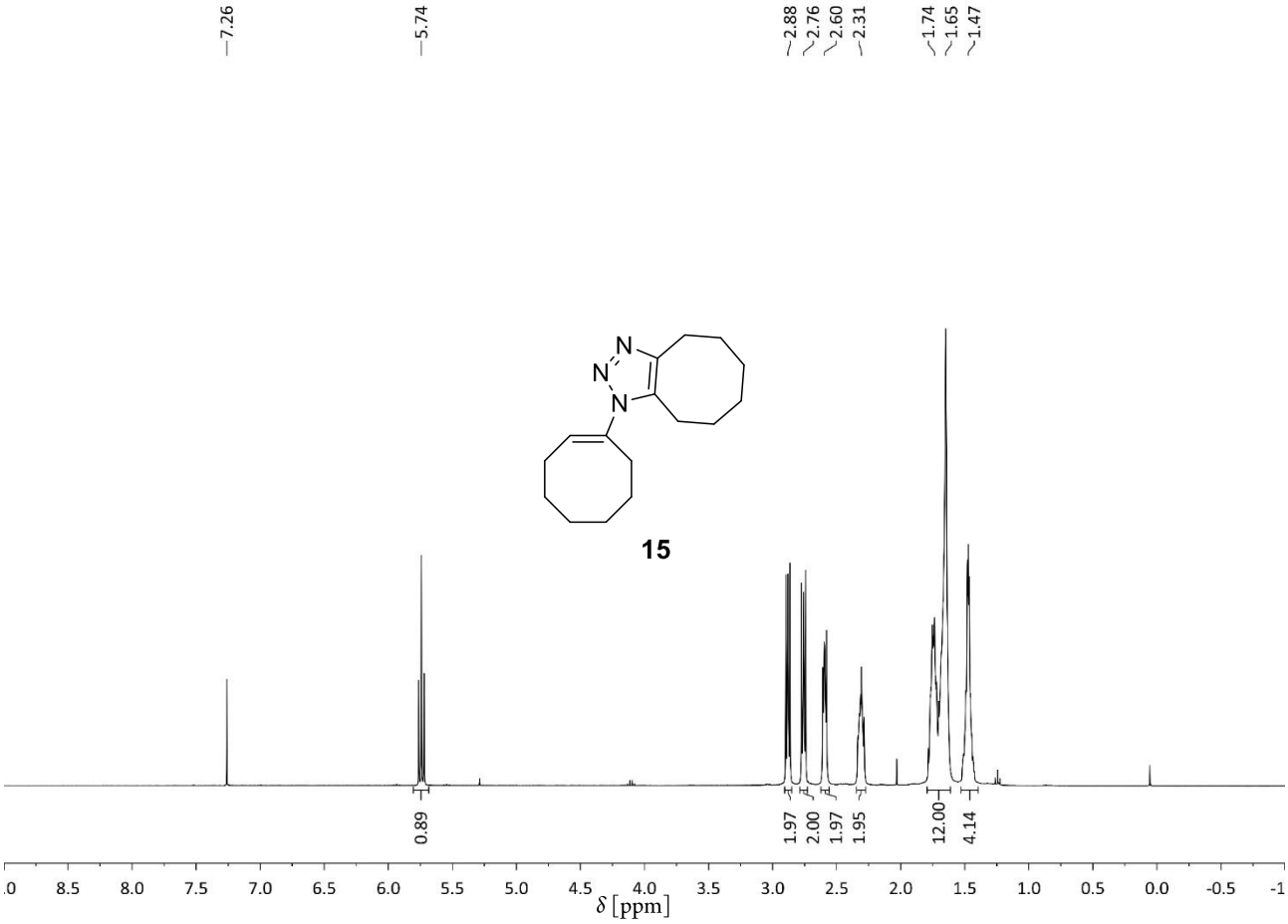
^{1}H NMR spectrum of 1,3,5-trimethyl-2,3,4,5-tetrahydro-1,3,5-triazin-1-ium chloride in $CDCl_3$ (600 MHz, 25 °C)



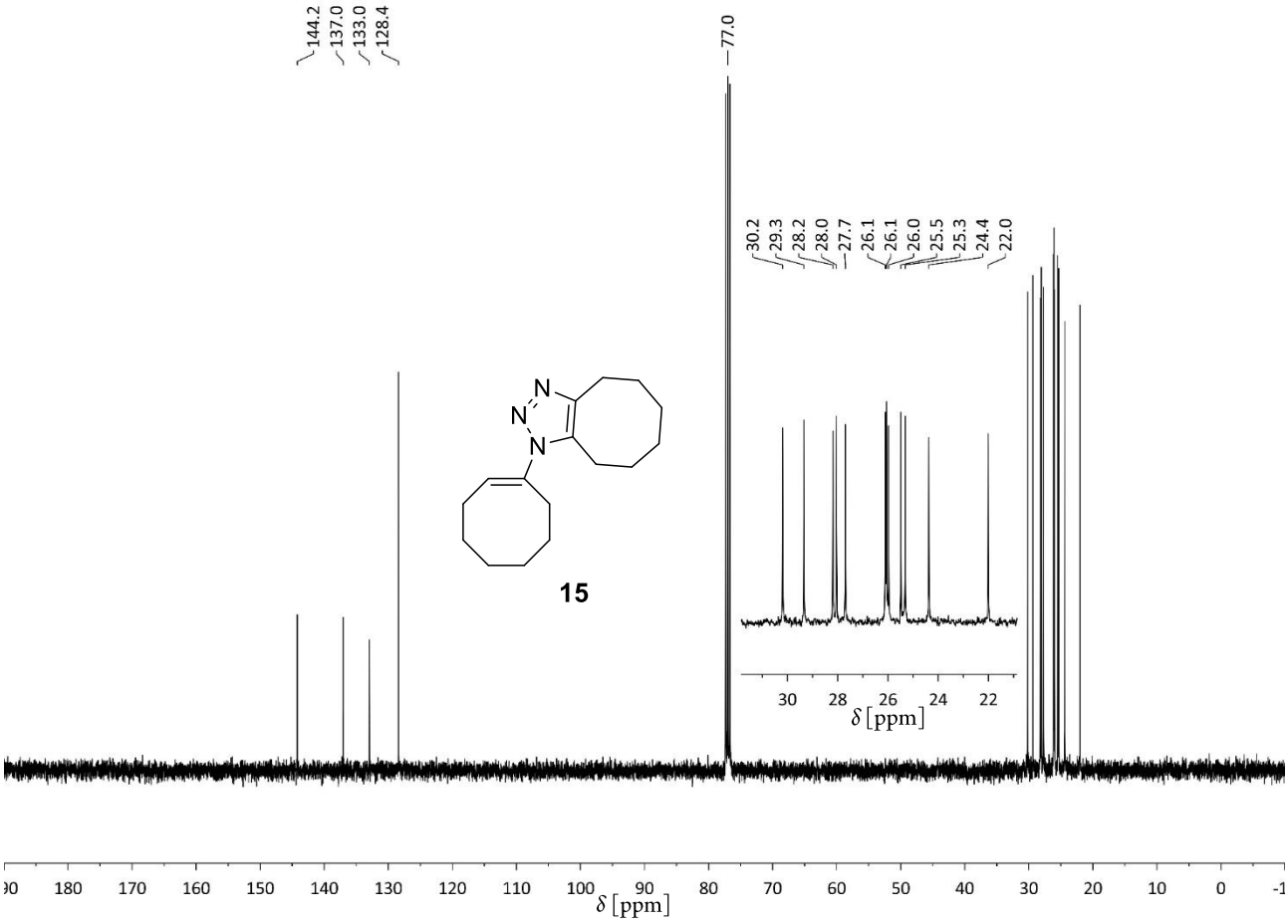
^{13}C{^{1}H} NMR spectrum of 1,3,5-trimethyl-2,3,4,5-tetrahydro-1,3,5-triazin-1-ium chloride in $CDCl_3$ (150.9 MHz, 25 °C)



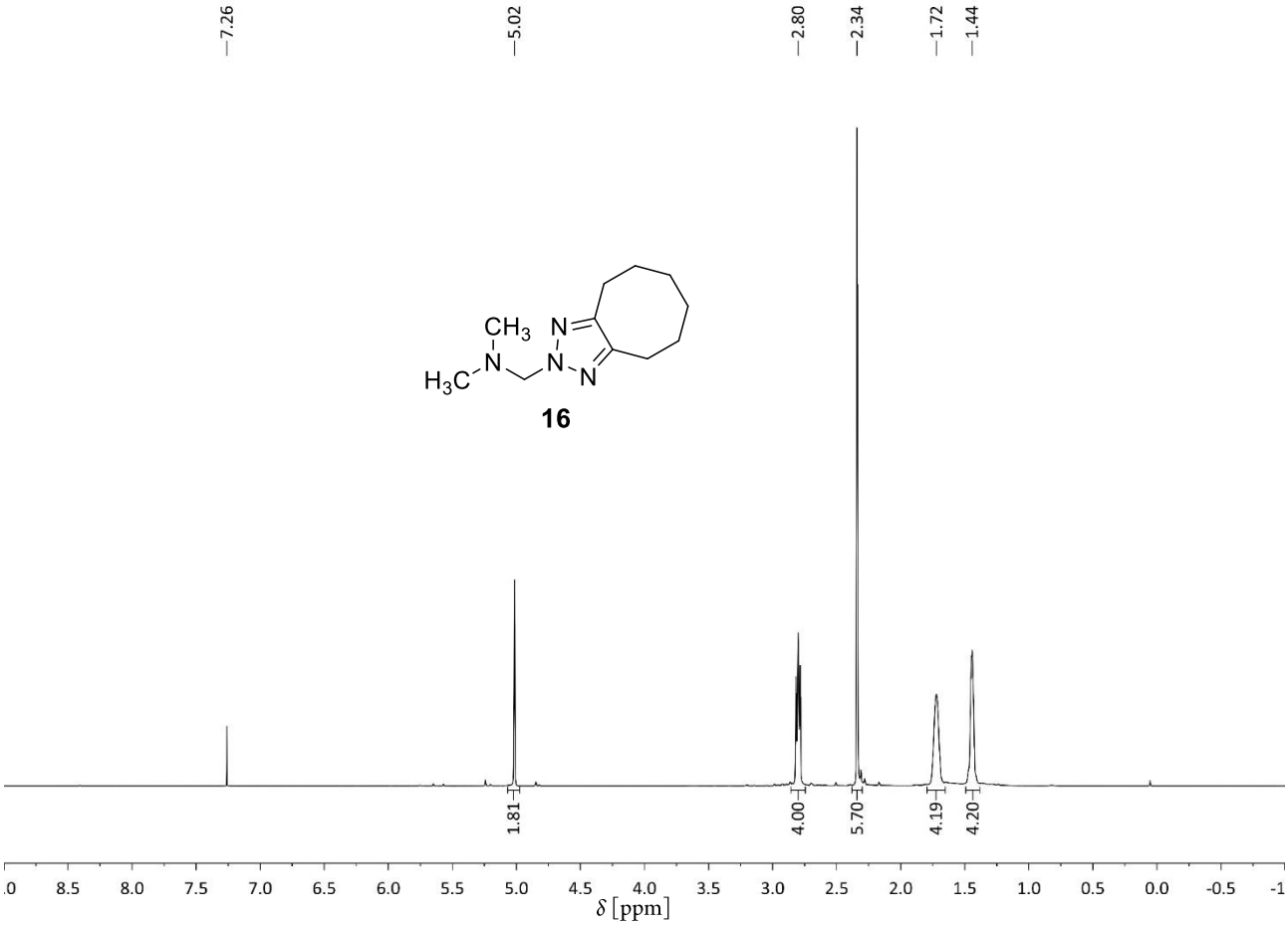
^{1}H NMR spectrum of **15** in $CDCl_3$ (400 MHz, 25 °C)



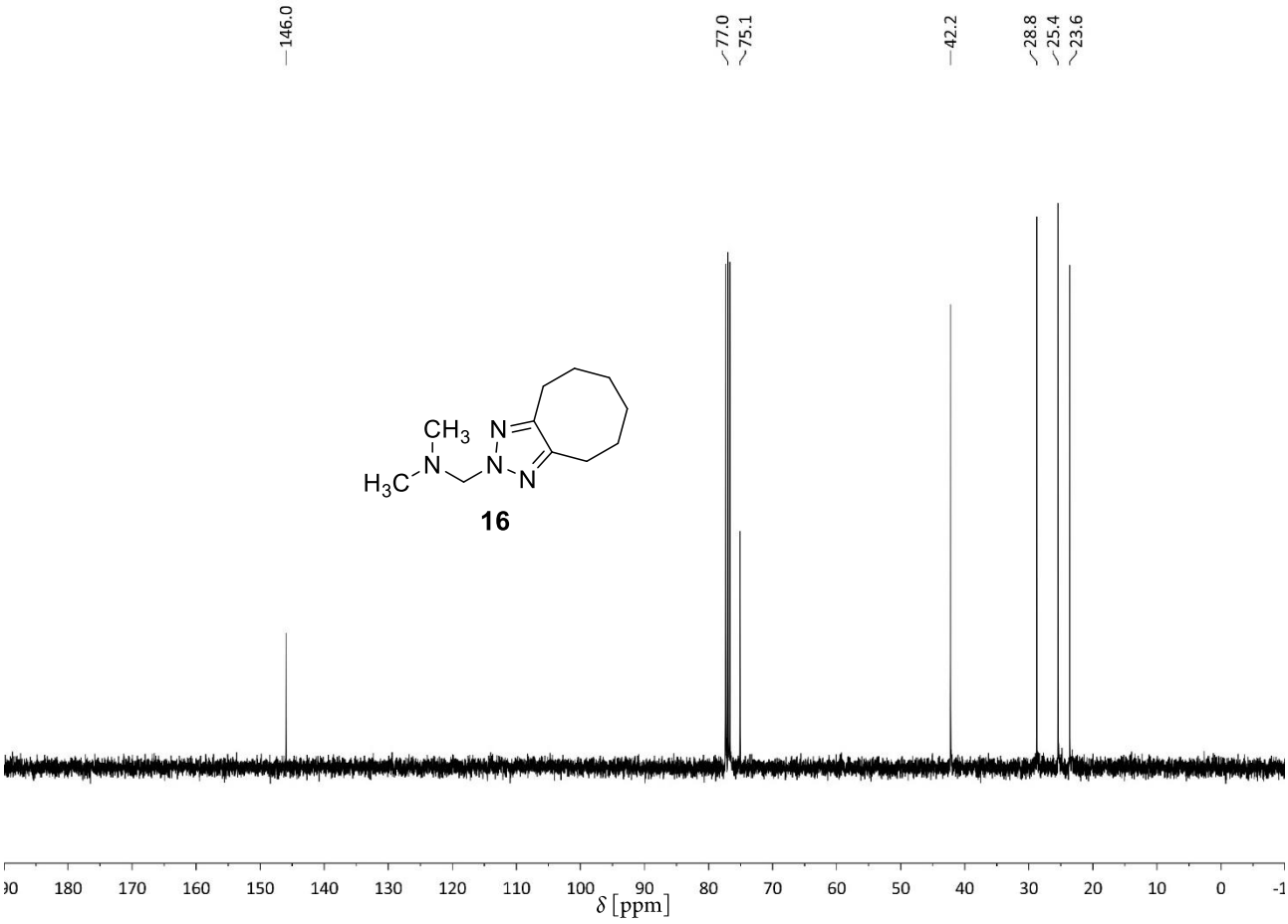
^{13}C{^{1}H} NMR spectrum of **15** in $CDCl_3$ (100.6 MHz, 25 °C)



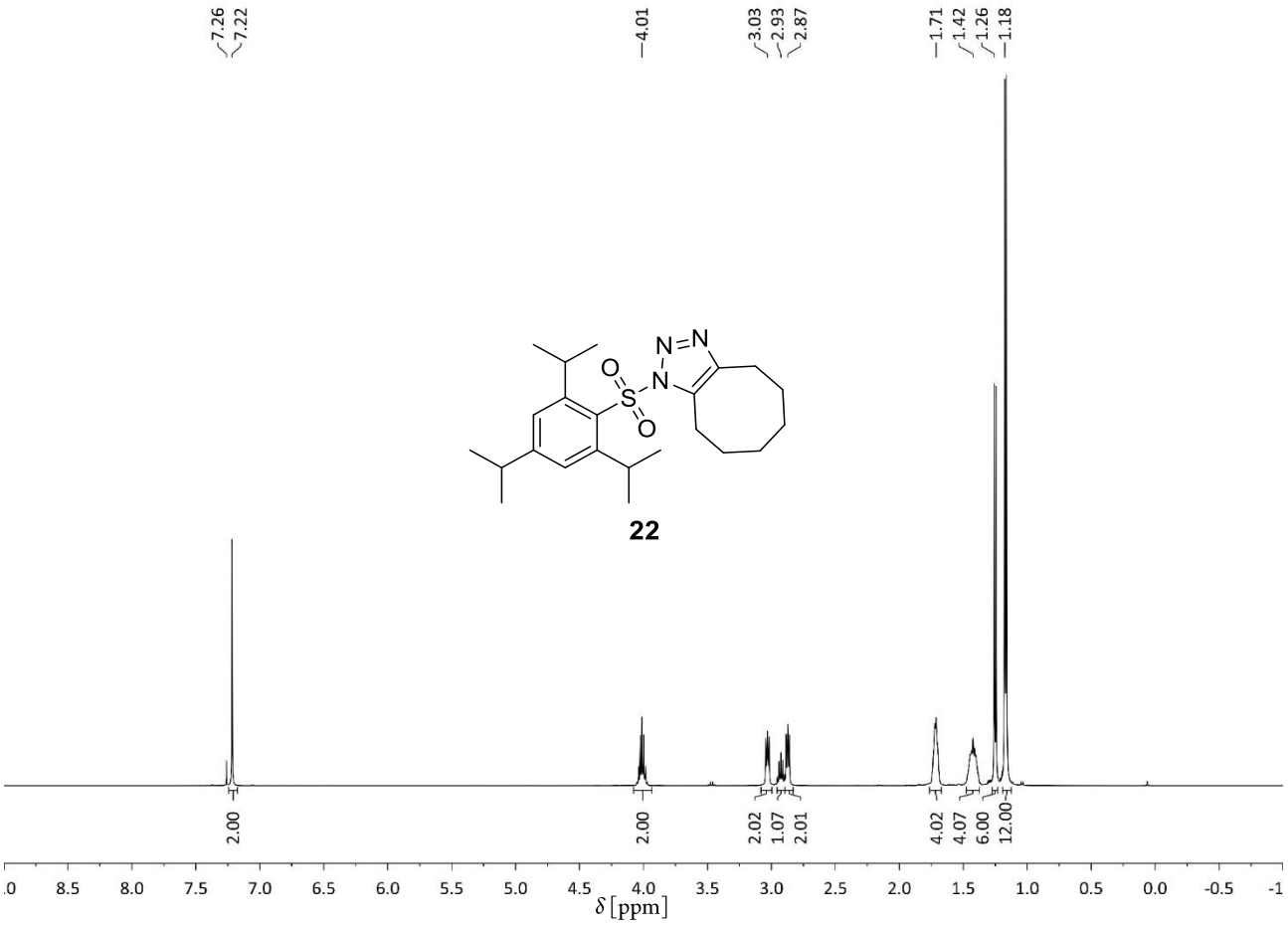
^{1}H NMR spectrum of **16** in $CDCl_3$ (400 MHz, 25 °C)



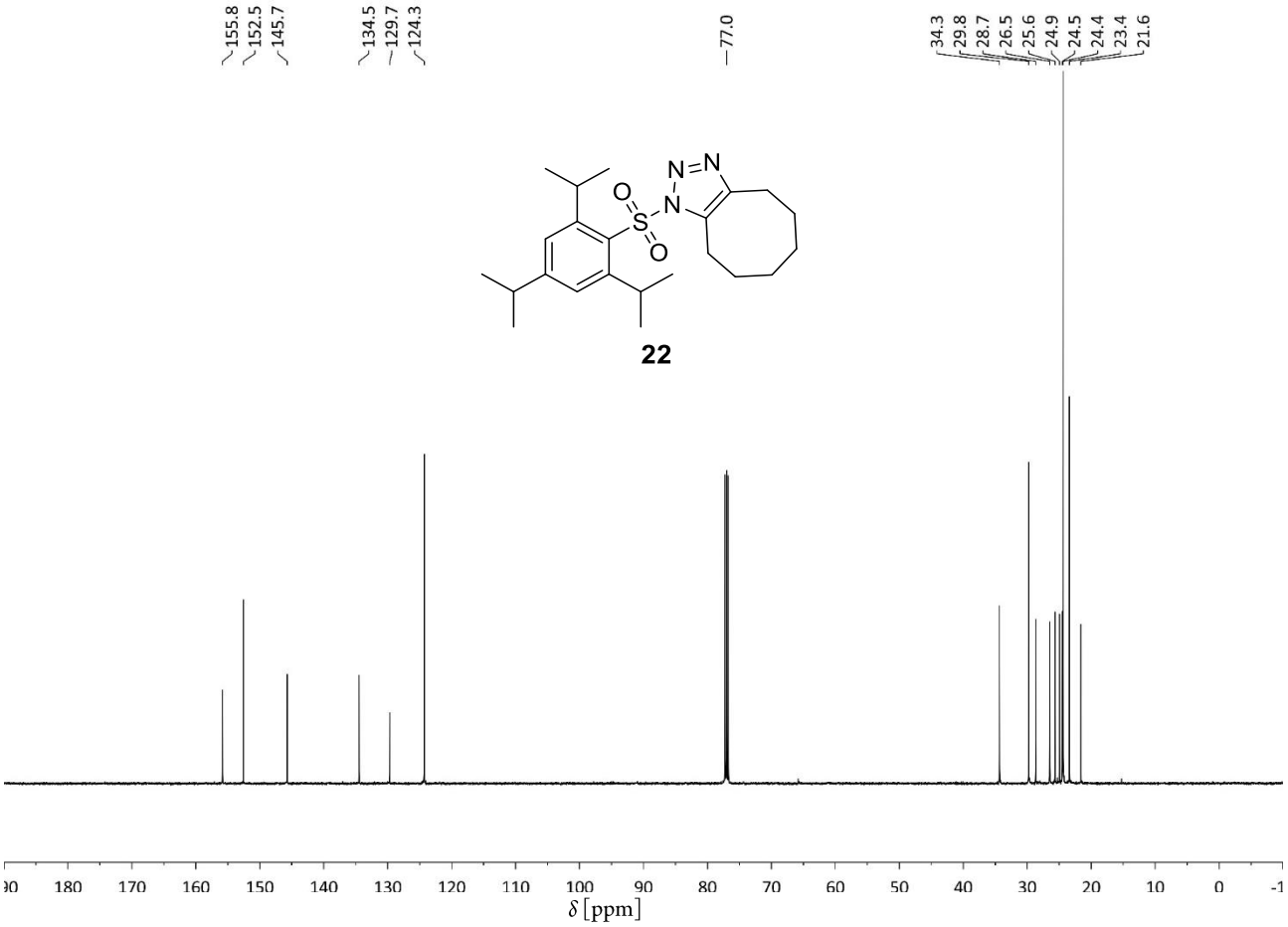
^{13}C{^{1}H} NMR spectrum of **16** in $CDCl_3$ (100.6 MHz, 25 °C)



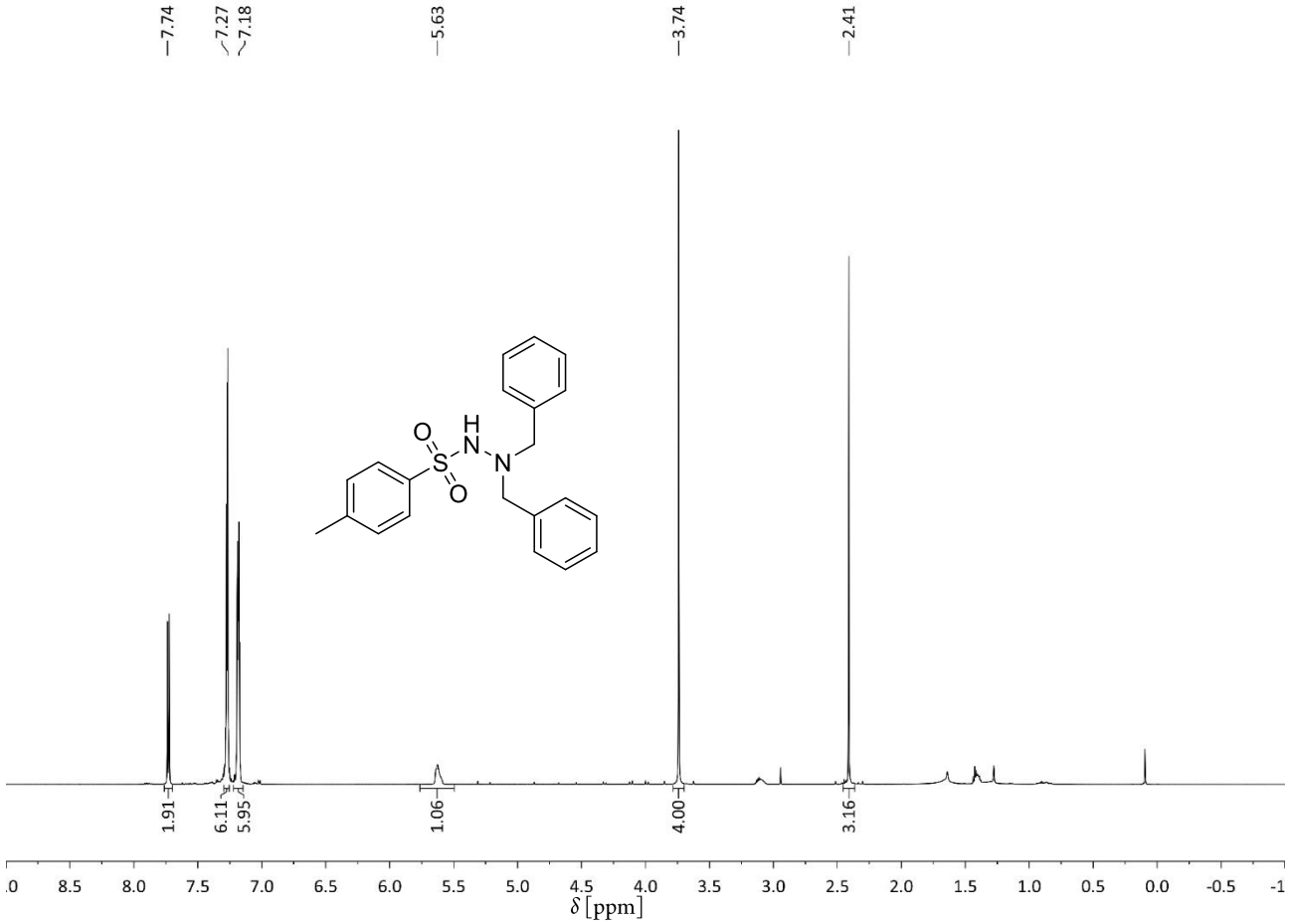
^{1}H NMR spectrum of **22** in $CDCl_3$ (600 MHz, 25 °C)



^{13}C{^{1}H} NMR spectrum of **22** in $CDCl_3$ (150.9 MHz, 25 °C)



^{1}H NMR spectrum of *N′,N′*-dibenzyl-4-methylbenzenesulfonohydrazide in $CDCl_3$ (600 MHz, 25 °C)



^{13}C{^{1}H} NMR spectrum of *N′,N′*-dibenzyl-4-methylbenzenesulfonohydrazide in $CDCl_3$ (150.9 MHz, 25 °C)