

**Elusive ethynyl azides:  
trapping by 1,3-dipolar cycloaddition and  
decomposition to cyanocarbenes**

Klaus Banert,<sup>\*a</sup> Manfred Hagedorn,<sup>a</sup> Jens Wutke,<sup>a</sup> Petra Ecorchard,<sup>b</sup> Dieter Schaarschmidt<sup>b</sup>  
and Heinrich Lang<sup>b</sup>

<sup>a</sup> *Chemnitz University of Technology, Organic Chemistry, Strasse der Nationen 62, 09111 Chemnitz, Germany. Fax: 0049 371 531 21229; e-mail: [klaus.banert@chemie.tu-chemnitz.de](mailto:klaus.banert@chemie.tu-chemnitz.de).*

<sup>b</sup> *Chemnitz University of Technology, Inorganic Chemistry, Strasse der Nationen 62, 09111 Chemnitz, Germany. (single crystal X-ray diffraction analysis)*

**SUPPLEMENTARY INFORMATION**

**TABLE OF CONTENTS**

GENERAL .....	2
EXPERIMENTAL PROCEDURES .....	3
CHARACTERISATION DATA .....	16
REFERENCES .....	37
COPIES OF <sup>1</sup> H/ <sup>13</sup> C NMR SPECTRA OF ALL NEW COMPOUNDS .....	38

## GENERAL

### Safety

Azides should always be handled with care. Organic azides, particularly those of low molecular weight or with high nitrogen content, are potentially explosive.<sup>[S1]</sup> Heat, light and pressure can cause decomposition under loss of dinitrogen. Furthermore, the azide ion is toxic and the use of gloves is highly recommended when working with ionic azides ( $\text{NaN}_3$ ,  $\text{LiN}_3$ ).

### Equipment

**IR spectra** have been measured using a BRUKER FT-IR spectrometer IFS 28 or a machine PERKIN ELMER "Spektrum 1000", respectively. The intensity of the peaks is given in brackets using the following abbreviations: br = broad, vs = very strong, s = strong, m = medium, w = weak and vw = very weak.

**NMR spectra** have been recorded using a VARIAN UNITY INOVA 400 spectrometer. The measuring frequency was 399.93 MHz ( $^1\text{H}$  NMR measurements) or 100.56 MHz ( $^{13}\text{C}$  NMR measurements), respectively. Chemical shift values are reported in ppm with the solvent resonance as internal standard ( $\text{CDCl}_3$ : 7.26 ppm for  $^1\text{H}$  and 77.0 ppm for  $^{13}\text{C}$ ,  $\text{DMSO-d}_6$ : 2.50 ppm for  $^1\text{H}$  and 39.50 ppm for  $^{13}\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ : 5.30 ppm for  $^1\text{H}$  and 53.73 ppm for  $^{13}\text{C}$ ). The multiplicity is described using the following abbreviations and their combination: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet and m = multiplet. The prefix *pseudo* indicates coupling patterns resulting from highly coupled spin systems which are apparently evaluable as first order multiplicities. The  $^{13}\text{C}$  NMR data comprise the information from the DEPT experiment. As long as nothing else is mentioned, all spectra were recorded at ambient temperature.

**Elemental analyses** have been performed using a machine Elementanalysator VARIO EL of ELEMENTAR ANALYSENSYSTEME GmbH Hanau or with a machine VARIO MICRO CUBE of ELEMENTAR, respectively.

**Mass spectra** have been recorded using a APPLIED BIOSYSTEMS spectrometer MARINER 5229 or a Bruker micrOTOF-QII spectrometer, respectively. For both spectrometers ionisation was realized by electrospray ionisation (ESI). The  $m/z$  values of the high resolution (HR) mass spectra were determined by comparison with internal standards.

**Melting points** were measured with a Boetius apparatus of PENTAKON Dresden. The received values are not corrected.

**Flash chromatography** was performed using the method of Still<sup>[S2]</sup> with silica gel 60 M (size 0.04–0.063 mm / 230–400 mesh ASTM for column chromatography) of the company Macherey-Nagel. TLC analyses were performed on Macherey-Nagel precoated silica gel Polygram Sil G/UV<sub>254</sub> plates and visualized by UV or oxidation ( $\text{KMnO}_4$ ), respectively.

**Single crystal X-ray diffraction analyses** were made with a machine Oxford Gemini S at the Inorganic Chemistry at the Chemnitz University of Technology.

## EXPERIMENTAL PROCEDURES

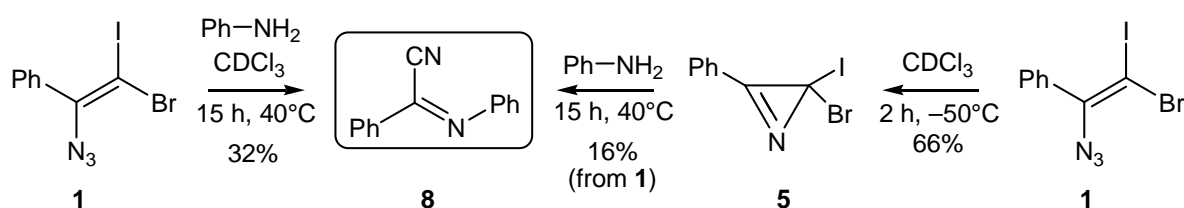
<i>Synthesis of literature-known compounds</i> .....	4
<i>Reactions of vinyl azide 1</i> .....	4
<i>Reaction of vinyl azide 1 under thermal conditions in DMSO (analogue to Hassner<sup>[6b]</sup>) [1 → 6]</i> .....	4
<i>Reaction of vinyl azide 1 with cyclooctyne [1 → 2]</i> .....	4
<i>Reaction of vinyl azide 1 with aniline [1 → 8]</i> .....	5
<i>Photolysis of vinyl azide 1 [1 → 5]</i> .....	5
<i>Reaction of azirine 5 with aniline [5 → 8]</i> .....	5
<i>Synthesis of the (chloroethynyl)arenes 10 and 19</i> .....	6
<i>Reaction of the (chloroethynyl)arenes with NaN<sub>3</sub>/LiN<sub>3</sub> in DMSO [10/19 → 14/20]</i> .....	7
<i>Control experiment to the formation of 14 starting from diazirine 16 [16 → 14]</i> .....	8
<i>Reaction of (chloroethynyl)benzene (10) with LiN<sub>3</sub> and cyclooctyne in DMSO [10 → 15 + 17]</i> .....	8
<i>Reaction of (chloroethynyl)benzene (10) with LiN<sub>3</sub> and cyclooctyne in DMF [10 → 15 + 17]</i> .....	9
<i>Reaction of (chloroethynyl)benzene (10) with NaN<sub>3</sub> and cyclooctyne in HMPTA [10 → 15 + 17]</i> .....	10
<i>Control experiments to the formation of 17</i> .....	11
<i>Reaction of (chloroethynyl)benzene (10) with NaN<sub>3</sub> and toluene in DMF [10 → 18]</i> .....	11
<i>Reaction of vinyl azide 13 with cyclooctyne [13 → 15]</i> .....	12
<i>Reaction of (chloroethynyl)biphenyl (19b) with LiN<sub>3</sub> and cyclooctyne in DMF</i> .....	12
<i>Intramolecular trapping of ethynyl azides</i> .....	13
<i>Reaction of (chloroethynyl)benzyl alcohol (19h) with NaN<sub>3</sub> in sulfolane [19h → 23]</i> .....	13
<i>Synthesis of heterocycle 23 from aldehyde 24 and hydrogen cyanide [24 → 23]</i> .....	13
<i>Reactions of (chloroethynyl) propyl thioether (25b)</i> .....	14
<i>Synthesis of 25b</i> .....	14
<i>Attempt to reproduce the described<sup>[18]</sup> reaction starting from 25b and NaN<sub>3</sub></i> .....	14
<i>Reaction of 25b with NaN<sub>3</sub> and cyclooctyne in DMF [25b → 26b]</i> .....	15

### Synthesis of literature-known compounds

The literature-known compounds have been synthesized according to the literature given in the following table and obtained in the mentioned yields.

Compound	Literature	Yield (%)
<b>1</b>	[6b]	45 %
<b>16</b>	analogue to [S3]	3.4 % (over 2 steps)
<b>24</b>	[S4]	49 %

### Reactions of vinyl azide **1**



Scheme 1.

### Reaction of vinyl azide **1** under thermal conditions in DMSO (analogue to Hassner<sup>[6b]</sup>)

Dimethyl sulfoxide (20 mL, 22 g, 282 mmol, 60 °C) was heated to 150 °C and vinyl azide **1** (1.65 g, 4.7 mmol, 1 eq) was added dropwise over about three minutes. The reaction mixture was stirred for another two minutes at the same temperature, then the hot mixture was poured into chilled aqueous sodium thiosulfate (2 % m/V, 3.00 g Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> diluted into 100 mL of water and top up to 150 mL with ice). After extraction with methylene chloride (3x 50 mL) the combined organic layers were dried over magnesium sulfate and the solvent was removed with a rotary evaporator at room temperature. Thereafter, the DMSO was removed *in vacuo* at 10<sup>-3</sup> Torr and the residue (500 mg) was chromatographed on silica gel. Using a mixture chloroform/*n*-hexane = 1:1 as eluent, 149 mg of (*E*)-**6** (27 %) and, after solvent change to diethyl ether, 118 mg of (*Z*)-**6** (22 %) could be isolated but no sulfoxonium ylide **14** was observed.

### Reaction of vinyl azide **1** with cyclooctyne

Vinyl azide **1** (1.00 g, 2.86 mmol, 1 eq) was diluted in anhydrous tetrahydrofuran (5 mL) and cyclooctyne (467 mg, 4.32 mmol, 1.5 eq) was added dropwise under vigorously stirring. The mixture was reacted for 5 hours at room temperature. After removing of the cyclooctyne excess and the solvent in vacuum (10<sup>-2</sup> mbar, 30 °C), the residue was purified by flash chromatography on silica gel (4x 20 cm, eluent: Et<sub>2</sub>O/*n*-hexane = 2:1) to yield 1.20 g of cyclooctatriazole **2** (100 %).

### ***Reaction of vinyl azide 1 with aniline***

Vinyl azide **1** (103 mg, 0.294 mmol, 1 eq) was placed in CDCl<sub>3</sub> (0.5 mL) in an NMR tube and 1,4-dioxane (20 mg, 0.227 mmol, 0.8 eq) was added as internal standard. Freshly distilled aniline (69 mg, 0.741 mmol, 2.5 eq) was given to the solution in a single portion and the closed tube was heated to 40 °C for 15½ hours. The formed solid was filtered off, washed with chloroform and dried in vacuum to give aniline hydrobromide (17 mg, 33 %). The filtrate was evaporated using a rotary evaporator (ambient temperature) and the residue (52 mg, orange-brown oil) was purified by chromatography on silica gel (2x 31 cm, eluent: CHCl<sub>3</sub>) to give 16 mg of **1** (*R*<sub>f</sub> = 0.94, 16 %) and 19 mg of **8** (*R*<sub>f</sub> = 0.77, 32 %).

### ***Photolysis of vinyl azide 1***

Photolysis was performed using a 150 W mercury high pressure burner of Quarzlampengesellschaft Hanau. Cooling of lamp and photolysis sample was realized with ethanol using a machine Ultra-Kryomat® of MGW Lauda.

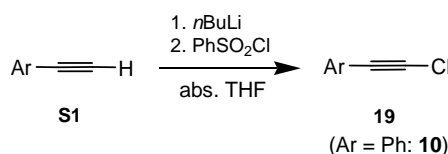
Freshly purified (chromatography on silica gel) vinyl azide **1** (30 mg, 0.086 mmol, 1 eq) was placed in CD<sub>2</sub>Cl<sub>2</sub> (0.8 mL, 99.6 %) in an NMR tube. The mixture was frozen using liquid nitrogen and the tube was melted down. Then, the solution was photolysed at –70 °C over 2 hours, carried at –65 °C to the NMR spectrometer and measured at ambient temperature. Using the solvent signal as internal standard, 2*H*-azirine **5** was obtained in 90 % yield.

Subsequently, the sample was stored for 17 hours at room temperature in which azirine **5** decomposed completely to give a complex mixture. Thereafter, the NMR tube was heated to 85 °C until no significant changes could be observed anymore. After 4 days the mixture was converted completely into the dicyanostilbenes **6** (*cis*-**6** / *trans*-**6** = 1:2.4). The *E* isomer was obtained in 77 % yield (using the solvent signal as internal standard), the *Z* isomer could not be determined exactly (about 30 %) caused by overlapping of the proton signals.

### ***Reaction of azirine 5 with aniline***

Vinyl azide **1** (93 mg, 0.266 mmol, 1 eq) was placed in CDCl<sub>3</sub> (0.5 mL) in an NMR tube and 1,4-dioxane (14 mg, 0.159 mmol, 0.6 eq) was added as internal standard. The resulting mixture was photolysed at –50 °C over 2 hours to yield 66 % 2*H*-azirine **5** as shown by low temperature <sup>1</sup>H NMR measurement (–50 °C). Freshly distilled aniline (62 mg, 0.666 mmol, 2.5 eq) was added and the sealed NMR tube was heated to 40 °C for 15½ hours. The formed solid was filtered off, washed with chloroform and dried in vacuum to give aniline hydrobromide (40 mg, 87 %). The filtrate was evaporated using a rotary evaporator (ambient temperature) and the residue (70 mg, orange-red viscous oil) was purified by chromatography on silica gel (3x 22 cm, eluent: CHCl<sub>3</sub>) to give 9 mg of **1** (*R*<sub>f</sub> = 0.93, 9 %) and 9 mg of **8** (*R*<sub>f</sub> = 0.82, 16 %).

## Synthesis of the (chloroethynyl)arenes **10** and **19**



**Scheme 2.**

The alkyne precursor **S1** (1 eq) was dissolved in anhydrous THF in an inert nitrogen atmosphere which was maintained throughout the reaction. The mixture was cooled down (see Table 1) and a solution of 2.5 M *n*-butyllithium (in anhydrous *n*-hexane), diluted by THF in some cases (see Table 1), was added dropwise over 15–30 minutes maintaining the temperature. After vigorously stirring for 15–30 minutes, benzenesulfonyl chloride (diluted by THF or pure) was added at the same temperature over 15–30 minutes. The reaction mixture was allowed to warm up to room temperature under vigorously stirring, still maintaining the inert atmosphere. Then, water (about the same amount as THF) was added dropwise and the mixture was extracted with an organic solvent. The combined organic layers were dried over magnesium sulfate and evaporated to dryness using a rotary evaporator (room temperature). Purification of the crude product was realized by vacuum distillation or column chromatography, respectively.

Isolated yields and the exact reaction parameters can be found in Table 1.

**Table 1.** Reaction conditions for the conversion **S1**→**19**.

<sup>1</sup> the temperature ±10 °C was maintained throughout the complete addition of *n*BuLi and PhSO<sub>2</sub>Cl

<sup>2</sup> means the volume of tetrahydrofuran in which the alkyne precursor **S1** is placed

<sup>3</sup> means the volume of tetrahydrofuran in which the *n*BuLi or the PhSO<sub>2</sub>Cl is dissolved

<sup>4</sup> reaction time in which the reaction mixture is allowed to warm up to room temperature

<sup>5</sup> the workup contains the solvent used for extraction and the purification method: a) vacuum distillation, b) flash-chromatography on silica gel, the eluent as well as the *R<sub>f</sub>* value is given at the substance characterisation

<sup>6</sup> **S1i** fits to phenylacetylene, in all other cases the small formula letter is in accordance with scheme 3 of the communication article

Starting material		Temperature <sup>1</sup> / V(THF) <sup>2</sup>	<i>n</i> -BuLi / V(THF) <sup>3</sup>	PhSO <sub>2</sub> Cl / V(THF) <sup>3</sup>	Time <sup>4</sup> / Workup <sup>5</sup>	Product
<b>S1i</b> <sup>6</sup>	245 mmol	−40 °C / 200 mL	1.02 eq / without solvent	1.02 eq / 60 mL	26 h / <i>n</i> -pentane, a	58 % <b>10</b>
<b>S1a</b>	10 mmol	−30 °C / 15 mL	1.05 eq / without solvent	1.2 eq / without solvent	overnight / <i>n</i> -pentane, a	89 % <b>19a</b>
<b>S1b</b>	20 mmol	−60 °C / 35 mL	1.02 eq / 20 mL	1.02 eq / without solvent	45 h / Et <sub>2</sub> O, b	26 % <b>19b</b> +37% <b>S1b</b>
<b>S1c</b>	3.7 mmol	−60 °C / 5 mL	1.02 eq / 3 mL	1.02 eq / without solvent	47 h / Et <sub>2</sub> O, b	63 % <b>19c</b>
<b>S1d</b>	7.1 mmol	−60 °C / 10 mL	1.7 eq / 5 mL	1.2 eq / 10 mL	22 h / Et <sub>2</sub> O, b	45 % <b>19d</b> +31% <b>S2d</b>
<b>S1e</b>	12 mmol	−85 °C / 20 mL	1.5 eq / 6 mL	1.5 eq / without solvent	45 h / Et <sub>2</sub> O, b	61 % <b>19e</b>
<b>S1g</b>	3.2 mmol	−50 °C / 10 mL	1.5 eq / without solvent	1.2 eq / 5 mL	overnight / Et <sub>2</sub> O, b	45 % <b>19g</b>

The alcohol **19h** was prepared from the tetrahydropyran **19g** using a modified literature procedure<sup>[S5]</sup> as follows:

1.44 mL concentrated sulfuric acid (96 %) was carefully diluted in methanol (25 mL) and the tetrahydropyran derivative **19g** was added dropwise at ambient temperature. After stirring overnight, aqueous sodium hydroxide was slowly added until the pH indicated complete neutralisation of the acid. Water was added and the mixture was extracted with diethyl ether. The combined organic layers were washed twice with water, twice with brine and dried over magnesium sulfate. After evaporation of the solvent at room temperature, the residue was chromatographed using a silica gel column (eluent: methylene chloride). Because **19h** was prepared in a three-step synthesis starting from commercially available alcohol **S1h** → **S1g** → **19g** → **19h**, no exact yield for the last step can be given. Starting with 1.00 g 2-ethynylbenzyl alcohol (**S1h**), yields of 31–69 % over all three steps could be obtained for **19h**.

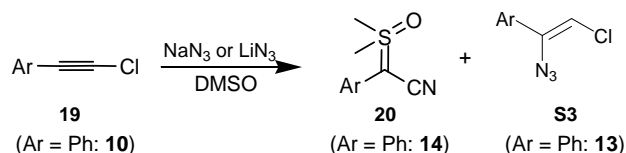
The chloroacetylene **19f** was prepared from the alcohol **19h** in an esterification reaction as follows:

The alcohol **19h** (250 mg, 1.5 mmol, 1 eq) and triethylamine (304 mg, 3.0 mmol, 2 eq) were placed in methylene chloride (5 mL), cooled down to 0 °C and acryloyl chloride (2 eq) was added dropwise within one minute. The mixture was allowed to warm up to room temperature over 17½ hours, the solvent was removed using a rotary evaporator (ambient temperature) and the residue was purified by column chromatography on silica gel (eluent: Et<sub>2</sub>O/*n*-hexane = 1:10). The ester **19f** was obtained in 90 % yield (298 mg).

For reasons of completeness the synthesis of **S1g**<sup>[S6]</sup> should be described on this spot. **S1g** was prepared analogous to a literature procedure starting from propargyl alcohol<sup>[S7]</sup> with a modified workup:

Dihydropyran (1.73 mL, 1.6 g, 19 mmol, 2.5 eq) was heated to 60 °C, some crystals of *p*-toluenesulfonic acid were added and 2-ethynylbenzyl alcohol (**S1h**) (1.00 g, 7.6 mmol, 1 eq), dissolved in dest. methylene chloride (10 mL), was added dropwise over 15 minutes. After complete addition, the mixture was refluxed for 45 minutes and thereafter allowed to cool down for another 45 minutes. Sodium bicarbonate (0.5 g, 6 mmol) was added and the mixture was stirred for an additional hour. The solid was separated by filtration, washed with methylene chloride and the filtrate was dried over magnesium sulfate. The solvent was evaporated at room temperature and the residue (**S1g**, orange oil) was supposed to be pure enough for further conversion to **19g** as described above.

### Reaction of the (chloroethynyl)arenes with NaN<sub>3</sub>/LiN<sub>3</sub> in DMSO



**Scheme 3.** The Z configuration of **S3** was confirmed using nOe experiments.

The (chloroethynyl)arene **10** or **19**, respectively, was dissolved in DMSO and the azide was added to the vigorously stirred solution in portions over about 3–5 minutes. The mixture was stirred for about three days, and after addition of water it was extracted with an organic

solvent, or the DMSO and all volatile compounds were removed in vacuum ( $10^{-3}$  Torr, room temperature), respectively. In the first case, the combined organic layers were washed with water, dried over magnesium sulfate and evaporated to dryness at room temperature. In both cases, the residue was purified using column chromatography on silica gel. First of all, unreacted starting material **19** and the vinyl azides **S3** were isolated using *n*-hexane as eluent. Then, the sulfoxonium ylide **20** was eluted with ethanol or ethyl acetate, respectively. For the reaction of **19h**, the chromatography was performed with the eluents methylene chloride, Et<sub>2</sub>O/*n*-hexane = 1:3 and ethyl acetate in the given order. The *R<sub>f</sub>* values as well as the used solvent are given at the substance characterisation. Isolated yields and reaction conditions can be found in Table 2.

**Table 2.** Reaction parameters for the reaction of (chloroethynyl)arenes with LiN<sub>3</sub>/NaN<sub>3</sub> in DMSO

<sup>1</sup> The reaction mixture was extracted with *n*-pentane, diethyl ether and benzene in the given order and each extract was worked up by chromatography separately.

Educt		Azide	time / V(DMSO) / extraction	Yield of 14 / 20	Yield of 13 / S3	re-isola- ted Educt
<b>10</b>	14.6 mmol	NaN <sub>3</sub> (1.5 eq)	3 d / 20 mL / see note <sup>1</sup>	10 % <b>14</b>	13 % <b>13</b>	<1 % <b>10</b>
<b>10</b>	7.3 mmol	LiN <sub>3</sub> (1 eq)	73 h / 5 mL / chloroform	9 % <b>14</b>	15 % <b>13</b>	18 % <b>10</b>
<b>19a</b>	8.0 mmol	NaN <sub>3</sub> (1.05 eq)	3 d / 35 mL / see note <sup>1</sup>	4.2 % <b>20a</b>	16 % <b>S3a</b>	-
<b>19b</b>	2.4 mmol	NaN <sub>3</sub> (1.05 eq)	69 h / 15 mL / vacuum	12 % <b>20b</b>	11 % <b>S3b</b>	19 % <b>19b</b>
<b>19c</b>	2.9 mmol	NaN <sub>3</sub> (1.5 eq)	75 h / 15 mL / vacuum	17 % <b>20c</b>	6.4 % <b>S3c</b>	-
<b>19d</b>	3.0 mmol	LiN <sub>3</sub> (2 eq)	71 h / 5 mL / chloroform	14 % <b>20d</b>	-	-
<b>19e</b>	3.6 mmol	NaN <sub>3</sub> (1.5 eq)	69 h / 15 mL / chloroform	19 % <b>20e</b>	-	-
<b>19f</b>	0.54 mmol	NaN <sub>3</sub> (1.5 eq)	4 d / 5 mL / chloroform	18 % <b>20f</b>	-	-
<b>19g</b>	1.8 mmol	NaN <sub>3</sub> (1.5 eq)	71 h / 15 mL / vacuum	25 % <b>20g</b>	-	20 % <b>19g</b>
<b>19h</b>	2.4 mmol	NaN <sub>3</sub> (1.5 eq)	66 h / 15 mL / vacuum	3.9 % <b>20h</b>	1.8 % <b>S3h</b>	22 % <b>19h</b> +0.9 % <b>23</b>

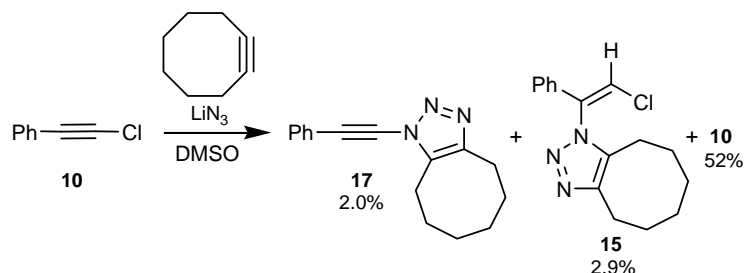
#### **Control experiment to the formation of 14 starting from diazirine 16**

Diazirine **16** (80 mg, 0.41 mmol, 1 eq) was placed in dimethyl sulfoxide (5 mL) and tetrabutylammonium cyanide (220 mg, 0.82 mmol, 2 eq) was added under vigorously stirring. The colour of the previously colourless mixture changed into yellow but no gas evolution was observed. Another 2 mL of DMSO (total: 7 mL, 7.7 g, 99 mmol, 241 eq) were added and the mixture was stirred for 47 hours at ambient temperature. After addition of water (20 mL), the



mixture was saturated with sodium chloride and extracted with benzene (5x 20 mL). The combined organic layers were washed with water (2x 30 mL), dried over magnesium sulfate and the solvent was evaporated at room temperature. The residue (orange-brown oil, 48 mg) was chromatographed on silica gel to yield 11 mg of **14** (14 %) and, after flushing of the column with ethanol, 21 mg of tetrabutylammonium bromide (16 %).

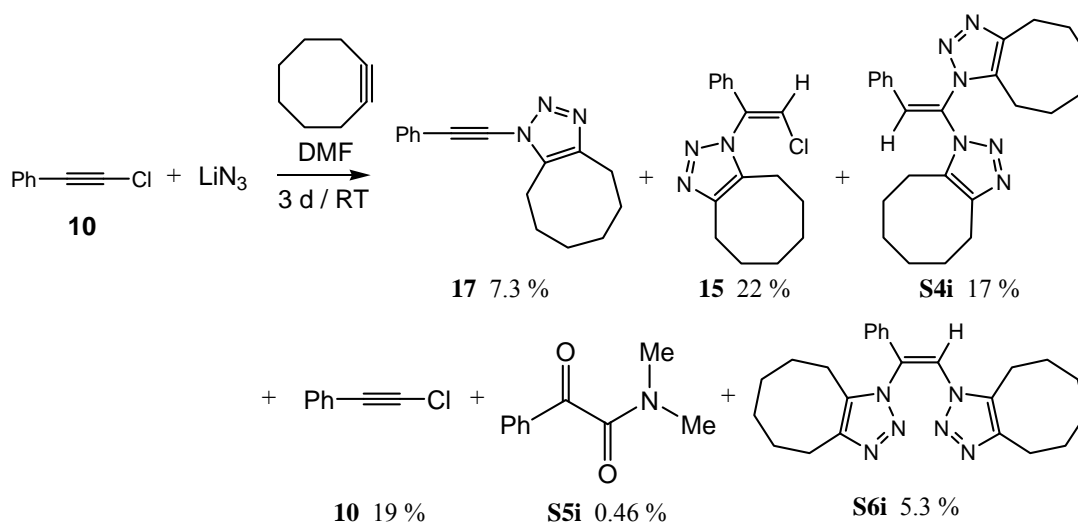
**Reaction of (chloroethynyl)benzene (**10**) with LiN<sub>3</sub> and cyclooctyne in DMSO**



**Scheme 4.**

Lithium azide (810 mg, 16.5 mmol, 1.5 eq) was given to DMSO (2.4 mL) under vigorously stirring and cyclooctyne (3.57 g, 33 mmol, 3 eq) was added in a single portion. (Chloroethynyl)benzene (**10**) (1.50 g, 11 mmol, 1 eq) was added dropwise over 2 minutes and the mixture was stirred at ambient temperature for 72 hours. Thereafter, water (15 mL) was added and the mixture was extracted with chloroform (3x 50 mL). The combined organic layers were washed with water (2x 200 mL), dried over magnesium sulfate and the solvent was evaporated using a rotary evaporator (room temperature). The residue (3.41 g, yellow liquid) still contained a higher amount of DMSO. Thereupon, the DMSO was removed in vacuum (10<sup>-3</sup> Torr) at room temperature. 52 % of unreacted starting material **10** were also re-condensed with the DMSO as shown by <sup>1</sup>H NMR spectrum of the condensate. The new residue was purified by column chromatography on silica gel (eluent: ethyl acetate/*n*-hexane = 1:3) to give 55 mg of **17** (2.0 %) and 92 mg of **15** (2.9 %).

**Reaction of (chloroethynyl)benzene (**10**) with LiN<sub>3</sub> and cyclooctyne in DMF**



**Scheme 5.** We have been able to show the  $\alpha$ -oxo amide **S5i** also to be a product resulting from carbene **4** and we have been able to obtain such  $\alpha$ -oxo amides in significantly higher yields in other experiments. Because this result is more difficult to explain, it will be published separately, soon.<sup>[S8]</sup>

Lithium azide (0.49 g, 10 mmol, 1.5 eq) was placed in dry dimethylformamide (15 mL) and dissolved completely under vigorously stirring. Immediately following each other, cyclooctyne (3.56 g, 33 mmol, 5 eq) and (chloroethynyl)benzene (**10**) (0.9 g, 6.6 mmol, 1 eq), diluted in anhydrous dimethylformamide (5 mL), were added in single portions to the azide solution. After stirring for three days in an inert atmosphere, the mixture was given to ice/water (50 mL) and extracted with *n*-pentane, diethyl ether and methylene chloride in the given order. Each extract was washed with water thoroughly, dried over magnesium sulfate and the solvent was removed using a rotary evaporator (room temperature). The respective residue was chromatographed on silica gel as described below.

The *n*-pentane extract (3.27 g) still contained a higher amount of DMSO. Thereupon, the DMSO was removed in vacuum ( $10^{-3}$  Torr) at room temperature. 19 % of unreacted starting material **10** have also been re-condensed with the DMSO as determined from  $^1\text{H}$  NMR spectrum of the condensate. The remaining residue was pre-fractionized by column chromatography (eluent: ethyl acetate/*n*-hexane = 3:1) to give two mixture fractions. From the first fraction 129 mg crude cyclooctatriazole **17** was isolated using a mixture EtOAc/*n*-hexane = 2:1 as eluent. Purification of **17** could be realized with additional chromatography (eluent: ethyl acetate/*n*-hexane = 1:3) and washing of the product with a small amount of cold diethyl ether to give 106 mg of pure **17** (6.4 %). Additional 228 mg of **15** (12 %), 123 mg of a mixture of **17** and **15** as well as another multi-compound-fraction (370 mg) could be obtained from the silica gel column. The mixture was separated using diethyl ether/*n*-hexane = 5:1 as eluent to give 6 mg of **17** (0.34 %) and 100 mg of **15** (5.3 %). From the multi-component-fraction 36 mg of **15** (1.9 %) and 308 mg of **S4i** (15 %) were isolated by flash chromatography (eluent: Et<sub>2</sub>O/*n*-hexane = 5:1). The second of the previously mentioned mixture fractions (83 mg) contained mainly the alkene **S6i**.

The diethyl ether extract (0.25 g) could be separated by chromatography into 9 mg of **17** (0.53 %,  $\Sigma$  = 7.3 %), 46 mg of **15** (2.4 %), 5 mg of **S5i** (2.4 %) and 64 mg of an impure fraction using an Et<sub>2</sub>O/*n*-hexane = 3:1 solvent mixture. Last-named fraction was taken in *n*-hexane and treated in an ultrasonic bath until a white solid precipitated. The solid was filtered off, washed with *n*-hexane and a small amount of cold diethyl ether and identified as **S4i** (26 mg, 1.3 %). From the previously mentioned column 47 mg of crude alkene **S6i** were isolated after changing the chromatography solvent to pure diethyl ether. These 47 mg were combined with the 83 mg of **S6i** for purification reasons. Silica chromatography with diethyl ether as eluent gave 106 mg of pure **S6i** (5.3 %).

Last of all, the methylene chloride extract (27 mg) was worked-up by chromatography with an eluent mixture ethyl acetate/*n*-hexane = 3:1 to give 6 mg of **15** (0.32 %,  $\Sigma$  = 22 %) as the only pure isolable compound. Consequently, the last extraction with methylene chloride is not necessary when repeating the experiment.

#### **Reaction of (chloroethynyl)benzene (**10**) with NaN<sub>3</sub> and cyclooctyne in HMPTA**

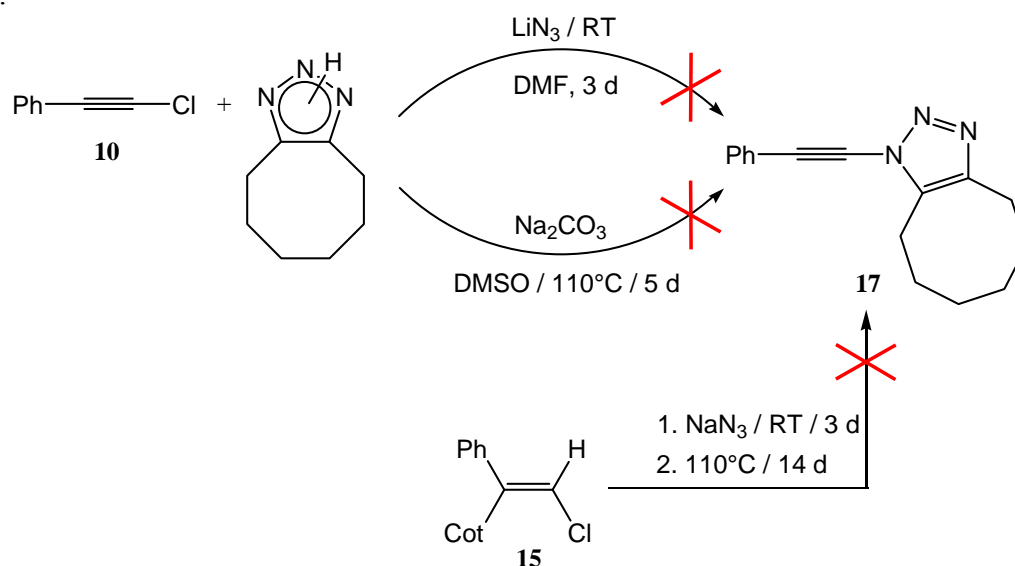
**Note: Hexamethylphosphoric triamide (HMPTA) is highly carcinogenic! The usage of gloves is highly recommended when working with this compound!**

(Chloroethynyl)benzene (**10**) (1.00 g, 7.32 mmol, 1 eq) was placed in HMPTA (5 mL), cooled down to 0 °C and sodium azide (714 mg, 11 mmol, 1.5 eq) was added in portions to the vigorously stirred solution. The resulting suspension was stirred at 0 °C for 30 minutes, distilled water (0.5 mL) was added and the mixture was stirred for another 90 minutes at the same temperature. Afterwards, cyclooctyne (1.60 g, 14.6 mmol, 2 eq) was added and the

mixture was allowed to warm up to room temperature over 20 hours. After addition of chloroform (100 mL), the mixture was washed with brine (5x 50 mL, removal of NaN<sub>3</sub>), diluted aqueous hydrochloric acid (3.7 %, 2x 50 mL) and water (1x 50 mL) in the given order. Unreacted starting material **10** (70 % as determined by <sup>1</sup>H NMR) and cyclooctyne were re-condensed *in vacuo* (10<sup>-3</sup> Torr) at ambient temperature and the residue (brown viscous oil, 889 mg) was chromatographed on silica gel (4x 36 cm, eluent: diethyl ether/*n*-hexane = 3:1) to give 212 mg of **17** (12 %, *R*<sub>f</sub> = 0.64), 215 mg of **15** (10 %, *R*<sub>f</sub> = 0.52) and 165 mg of **S4i** (5.6 %, *R*<sub>f</sub> = 0.32).

### Control experiments to the formation of **17**

Several control experiments have been realized to exclude possible reaction mechanism with formation of **17** without involving an ethynyl azide. These experiments were realized on NMR scale and without any chromatographic workup. It was only examined whether compound **17** was formed or not using the known NMR data of this structure. For that reason, we are able to summarize the received results in Scheme 6 without giving further experimental details.



**Scheme 6.** Both reaction of **10** with 4,5,6,7,8,9-hexahydrocycloocta-1*H*-1,2,3-triazole and Fritsch-Buttenberg-Wiechell-rearrangement-like reaction starting from **15** could be excluded as reaction pathways to **17**.

### Reaction of (chloroethynyl)benzene (**10**) with NaN<sub>3</sub> and tolane in DMF

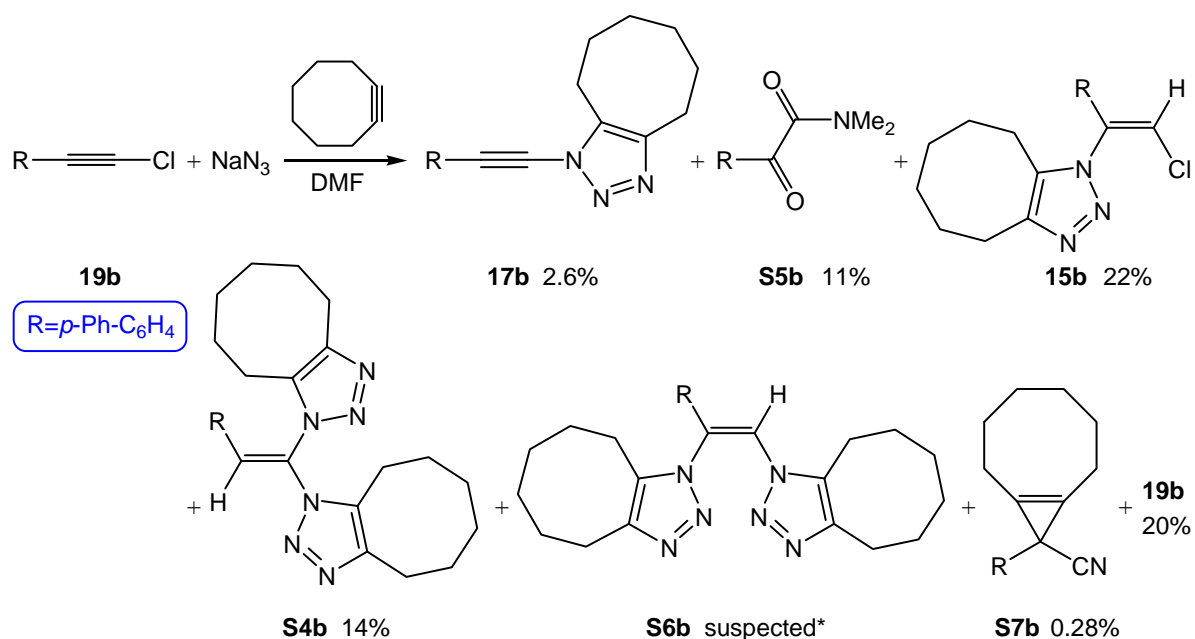
Sodium azide (1.90 g, 29 mmol, 2 eq) was placed in dry dimethylformamide (20 mL) in an inert argon atmosphere and stirred at ambient temperature for 30 minutes. Tolane (5.21 g, 29 mmol, 2 eq) was added in a single portion and immediately afterwards (chloroethynyl)benzene (**10**) (2.00 g, 15 mmol, 1 eq) was given to the vigorously stirred mixture, which was stirred at room temperature for 122 hours (5 days) maintaining the inert atmosphere. The mixture was poured into ice/water (50 mL) and extracted with methylene chloride (5x 50 mL). From the aqueous layer, 182 mg of  $\alpha$ -oxo amide **S5i** (7.0 %) could be isolated after evaporating the solvent and removal of all chloroform-insoluble components. The combined organic layers were washed with water (5x 50 mL), dried over magnesium sulfate and the solvent was removed using a rotary evaporator (room temperature). All volatile compounds were removed *in vacuo* (10<sup>-3</sup> Torr) at ambient temperature and the remaining residue was chromatographed on silica gel (6x 12 cm). Starting with *n*-hexane as eluent unreacted tolane (5.05 g, *R*<sub>f</sub> = 0.21, contained small impurities, about 97 % of the used amount) was recovered.

After solvent change to diethyl ether another 362 mg of **S5i** (14 %,  $R_f$  = 0.45) and a mixture (266 mg,  $R_f$  = 0.75–0.91, brown oil, almond-like smell) were isolated. The mixture was purified by flash-chromatography (eluent: Et<sub>2</sub>O/*n*-hexane = 1:3) to give 50 mg of cyclopropene **18** (1.2 %).

### Reaction of vinyl azide **13** with cyclooctyne

Vinyl azide **13** (15 mg, 0.084 mmol, 1 eq) was dissolved in CDCl<sub>3</sub> (0.75 mL) and placed in an NMR tube. Using a syringe cyclooctyne (10 mg, 0.092 mmol, 1.1 eq) was added at ambient temperature and the components were mixed thoroughly. The tube was stored at room temperature and the reaction was observed by NMR spectroscopy until complete conversion. After 4½ hours the solvent was removed using a rotary evaporator and the excess of cyclooctyne was re-condensed *in vacuo* (10<sup>-3</sup> Torr) to give pure **15** (100%) quantitatively.

### Reaction of (chloroethynyl)biphenyl (**19b**) with LiN<sub>3</sub> and cyclooctyne in DMF



**Scheme 7.** The formation of **S4b** was only supposed based on an obtained mixture fraction, but the compound could be isolated in a pure form in a later experiment using HMPTA instead of DMF as solvent. For **S5b** see also the comment given at Scheme 5.

Sodium azide (160 mg, 2.5 mmol, 1.05 eq) was placed in dimethylformamide (10 mL) and a mixture of cyclooctyne (508 mg, 4.7 mmol, 2 eq) and (chloroethynyl)biphenyl (**19b**) (0.5 g, 2.4 mmol, 1 eq) in dimethylformamide (10 mL) was added dropwise over 25 minutes under vigorously stirring. Another 5 mL of DMF were added and the mixture was stirred for 69 hours at room temperature. Then, the solvent was evaporated at 40 °C and the residue was worked up by chromatography on silica gel using diethyl ether/*n*-hexane = 1:6, diethyl ether/*n*-hexane = 1:1 and ethyl acetate as eluents in the given order.

From the 1:6 eluent mixture 102 mg of starting material **19b** (20 %) and a mixture were obtained which gave 2 mg of **S7b** (0.28 %) using a second column chromatography (eluent: chloroform/ *n*-hexane = 1:2). From the 1:1 eluent mixture 34 mg of crude **17b**, 190 mg of **15b** (22 %) and 194 mg of a mixture of **S5b** and **S4b** were isolated. **17b** was purified by chromatography (eluent: methylene chloride/diethyl ether = 10:1) yielding 20 mg pure compound (2.6 %). The mixture was separated into 85 mg of **S4b** (14 %) and 65 mg of **S5b**

(11 %) using an eluent mixture chloroform/diethyl ether = 1:1 (impurities were previously flushed through the column with pure diethyl ether). From the ethyl acetate a mixture (51 mg,  $R_f$  = 0.73) was obtained which was subjected to another flash chromatography (eluent: diethyl ether/*n*-hexane = 5:1) to give 28 mg of an oil ( $R_f$  = 0.17). Treatment of this oil in *n*-hexane with ultrasonic gave a solid which was suspected to be (still impure) **S6b**, what was confirmed later on (see comment to Scheme 7).

### **Intramolecular trapping of a cyanocarbene\***

#### ***Reaction of (chloroethynyl)benzyl alcohol (19h) with NaN<sub>3</sub> in sulfolane***

To a vigorously stirred suspension of sodium azide (3.00 g, 46 mmol, 29 eq) in sulfolane (150 mL) (chloroethynyl)benzyl alcohol (**19h**) (265 mg, 1.6 mmol, 1 eq) was added dropwise and the dropping funnel was flushed with another 50 mL of sulfolane after complete addition. To avoid solidification of the sulfolane (mp 20–26 °C) the reaction flask was placed into a metal tin closed with aluminium foil which was able to keep the waste heat of the stirring motor. The mixture was stirred at 25–30 °C for 68 hours, then chloroform (200 mL) was added and the mixture was washed thoroughly with water (20x 100 mL). The organic layer was dried over magnesium sulfate and the chloroform was evaporated at room temperature. Because the residue still contained about 25 mL sulfolane, it was dissolved in chloroform (50 mL) and washed another time with water (10x 350 mL). The organic layer was dried again (MgSO<sub>4</sub>) and the chloroform was removed with a rotary evaporator at ambient temperature. The residue (272 mg) was purified by flash chromatography on silica gel (eluent: diethyl ether/*n*-hexane = 1:1) to give 11 mg of **23** (4.8 %) and 96 mg of starting material **19h** (36 %).

#### ***Synthesis of heterocycle 23 from aldehyde 24 and hydrogen cyanide***

Sodium cyanide (634 mg, 12.9 mmol, 10 eq) was placed in DMSO (90 mL) and the aldehyde **24** (200 mg, 1.3 mmol, 1 eq) was added under vigorously stirring. After addition of further 10 mL of DMSO, the mixture was heated to 60 °C and concentrated sulfuric acid (634 mg, 96 %, 6.2 mmol, 4.8 eq) was added dropwise through a septum using a syringe. The reaction flask was directly connected to a cooling finger (about –100 °C) to avoid the HCN leaving the reaction vessel. After complete addition the mixture was heated further 30 minutes and allowed to cool down to room temperature overnight (after removal of the cooling trap). Chloroform (150 mL) was added and the mixture was washed thoroughly with water (5x 250 mL). The organic layer was dried over magnesium sulfate and the solvent was evaporated at ambient temperature. The residue (197 mg) was purified by flash chromatography on silica gel (eluent: methylene chloride) to yield 97 mg of **23** (52 %).

---

\*We started also to prepare (2-chloroethynyl)benzenes bearing an appropriate group in the *ortho* position to trap intramolecularly the corresponding ethynyl azides instead of the cyanocarbenes. But the synthesis of such compounds will require a sequence of several steps.



attempt to purify the compound by chromatography failed what might be caused by decomposition of the compound on the column.

The chloroform extract (229 mg) was chromatographed on silica gel using ethyl acetate/*n*-hexane = 1:2 as eluent to give 35 mg of **S14** (2.8 %) and, after changing the solvent to acetone, another 70 mg of crude **S14** ( $R_f$  = 0.90). Purification was performed using flash chromatography (eluent: ethyl acetate) to yield 35 mg of pure **S14** (2.8 %,  $\Sigma$  = 5.6 %).

Other products, explicitly **S9** or **S10**, have not been isolated.

#### ***Reaction of 25b with NaN<sub>3</sub> and cyclooctyne in DMF***

In an inert argon atmosphere sodium azide (809 mg, 12.4 mmol, 1.7 eq) was stirred into anhydrous dimethylformamide (10 mL) and cyclooctyne (1.35 g, 12.4 mmol, 1.7 eq) was added in a single portion. After complete addition, chloroalkyne **25b** (1.00 g, 7.4 mmol, 1 eq) was added in portions over 25 minutes maintaining the temperature at 20–25 °C (exothermic reaction, gas evolution observable). The mixture was reacted at ambient temperature for 4 days and then poured into ice/water (30 mL), stirred over 20 minutes and extracted with diethyl ether (5x 50 mL). The combined organic layers were washed with water (3x 50 mL), dried over magnesium sulfate and the solvent was evaporated at ambient temperature to yield 1.22 g of a brown oil. This crude product was purified by flash-chromatography on silica gel.

First, a pre-separation was performed using chloroform as eluent to get four main fractions (fraction 1: 328 mg,  $R_f$  = 0.95–0.98; fraction 2: 21 mg,  $R_f$  = 0.80–0.90; fraction 3: 75 mg,  $R_f$  = 0.68–0.75; fraction 4 after solvent change to ethyl acetate: 294 mg,  $R_f$  = 0.83–0.93). Fraction 3 was chromatographically separated (diethyl ether/*n*-hexane = 1:3) into 6 mg of **S12** (0.8%), 37 mg of **26b** (2.3 %) and an otherwise pure mixture of **S12** and **26b** (25 mg). Fraction 4 was chromatographed as well (diethyl ether/*n*-hexane = 3:1) to give 19 mg of **S13** (0.93 %) and 54 mg of crude **S11**. The cyclooctatriazole **S11** was purified using a silica gel column and diethyl ether as eluent to yield 2.3 % pure compound (48 mg).

## CHARACTERISATION DATA

### COMPOUNDS MENTIONED IN THE COMMUNICATION

<i>Characterisation of vinyl azide 1 and the corresponding cyclooctatriazole 2</i> .....	17
<i>Characterisation of 2H-azirine 5</i> .....	17
<i>Characterisation of the stilbenes 6</i> .....	18
<i>Characterisation of nitrile 8</i> .....	18
<i>Characterisation of the (chloroethynyl)arenes 10, 19 and the alkylsulfanylethyne 25b</i> .....	18
<i>Characterisation of vinyl azide 13 and the corresponding cyclooctatriazole 15</i> .....	21
<i>Characterisation of the sulfoxonium ylides 14 and 20</i> .....	22
<i>Characterisation of diazirine 16</i> .....	26
<i>Characterisation of the cyclooctatriazoles 17</i> .....	26
<i>Characterisation of cyclopropene 18</i> .....	27
<i>Characterisation of heterocycle 23</i> .....	28
<i>Characterisation of aldehyde 24</i> .....	28
<i>Characterisation of cyclopropene 26b</i> .....	28

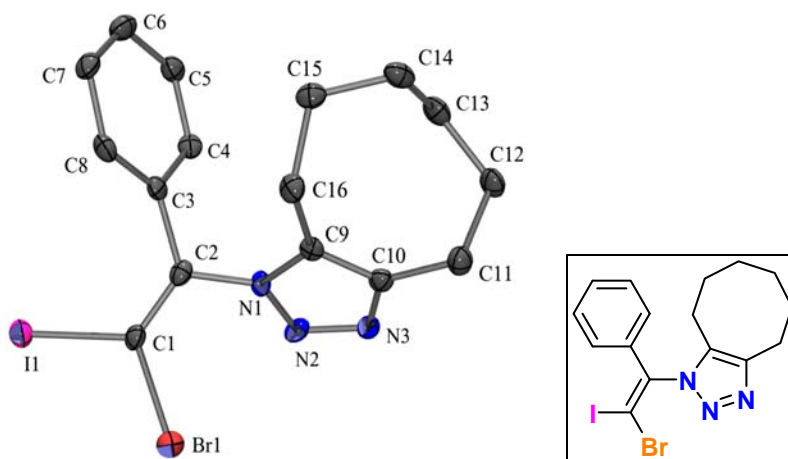
### COMPOUNDS ONLY MENTIONED IN THIS SUPPLEMENT

<i>Characterisation of cyclooctatriazole 15b</i> .....	29
<i>Characterisation of side-product S2d</i> .....	29
<i>Characterisation of the vinyl azides S3</i> .....	30
<i>Characterisation of the bis(cyclooctatriazoles) S4 and S6</i> .....	31
<i>Characterisation of the <math>\alpha</math>-oxo amides S5</i> .....	33
<i>Characterisation of cyclopropene S7</i> .....	34
<i>Characterisation of the thiopropyl compounds S8–S15</i> .....	34



## 1. Characterisation of vinyl azide 1 and the corresponding cyclooctatriazole 2

**(E)-(1-Azido-2-bromo-2-iodovinyl)benzene (1):**<sup>[6a]</sup> orange-yellow oil, darkened at standing. – <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.34–7.36 (m, 2 H, *o*-Ph), 7.47–7.52 (m, 3 H, *m*-Ph, *p*-Ph). – <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 41.23 (s, =C(I)Br), 128.65 (d, *o*-Ph), 129.14 (d, *m*-Ph), 130.16 (d, *p*-Ph), 134.96 (s, *i*-Ph), 143.19 (s, =CN<sub>3</sub>). – IR (CCl<sub>4</sub>):  $\tilde{\nu}$  = 704 cm<sup>-1</sup> (m), 1214 (w), 1292 (m), 2120 (vs, N<sub>3</sub>). – *R*<sub>f</sub> (*n*-pentane): 0.29.



ORTEP plot of 2, H atoms are omitted for clarity.

**(E)-1-(2-Bromo-2-iodo-1-phenylvinyl)-4,5,6,7,8,9-hexahydro-1H-cycloocta[d][1,2,3]triazole (2):** yellow solid. – mp: 129–133 °C. – <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.39 (m, 4 H, H-6, H-7), 1.52 (m, 2 H, H-8), 1.72 (*pseudo* quint, *J* = 6.0 Hz, 2 H, H-5), 2.59 (*pseudo* t, *J* = 6.4 Hz, 2 H, H-9), 2.88 (*pseudo* t, *J* = 6.4 Hz, 2 H, H-4), 7.32–7.39 (m, 3 H, *m*-Ph, *p*-Ph), 7.45–7.51 (m, 2 H, *o*-Ph). – <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 21.68 (t, C-9), 24.20 (t, C-4), 24.73 (t, C-6 or C-7), 25.68 (t, C-6 or C-7 or C-8), 25.83 (t, C-6 or C-7 or C-8), 27.72 (t, C-5), 61.99 (s, =C(I)Br), 128.59 (d, *m*-Ph), 128.95 (d, *o*-Ph), 129.96 (d, *p*-Ph), 133.46 (s, C-9a), 135.96 (s, *i*-Ph), 142.22 (s, =C(Ph)Cot), 144.31 (s, C-3a). – IR (CCl<sub>4</sub>):  $\tilde{\nu}$  = 602 cm<sup>-1</sup> (w), 696 (s), 1053 (w), 1243 (w), 1444 (s), 1456 (m), 2856 (s), 2933 (vs). – C<sub>16</sub>H<sub>17</sub>BrIN<sub>3</sub> (458.14 g/mol): calc. (%): C 41.95, H 3.74, N 9.17; found (%): C 42.21, H 3.68, N 9.24. – *R*<sub>f</sub> (Et<sub>2</sub>O/*n*-hexane=2:1): 0.52. – **Crystal data:** C<sub>16</sub>H<sub>17</sub>BrIN<sub>3</sub>, *MW* = 458.14, *T* = 105 K, λ = 0.71073 Å, orthorhombic, space group P2(1)2(1)2(1), *a* = 7.4385(3) Å, *b* = 11.2805(4) Å, *c* = 19.1852(8) Å, α = 90 °, β = 90 °, γ = 90 °, *V* = 1609.83(11) Å<sup>3</sup>, *Z* = 4, *D* = 1.890 Mg/m<sup>3</sup>, μ = 4.468 mm<sup>-1</sup>, *F*(000) = 888. Crystallographic data for structure 2 have been deposited at the Cambridge Crystallographic Data Center under the number CCDC 766228.

## 2. Characterisation of 2H-azirine 5

**2-Bromo-2-iodo-3-phenyl-2H-azirine (5):** The compound decomposes rapidly at standing in solution at room temperature. – <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, –55 °C): δ = 7.67 (*pseudo* t, *J* = 7.6 Hz, 2 H, *m*-Ph), 7.80 (*pseudo* t, *J* = 7.6 Hz, 1 H, *p*-Ph), 8.01 (*pseudo* d, *J* = 7.2 Hz, 2 H, *o*-Ph). – <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, –55 °C): δ = –24.18 (s, C(I)Br), 119.08 (s, *i*-Ph), 129.58 (d, *o*-Ph oder *m*-Ph), 130.30 (d, *o*-Ph oder *m*-Ph), 135.81 (d, *p*-Ph), 178.67 (s, PhC=N).

### 3. Characterisation of the stilbenes 6

**trans-Dicyanostilbene (E)-6:**<sup>[S9]</sup> pale yellow solid. – **mp:** 156–157.5 °C (ref.<sup>[S9]</sup>: 156 °C). – <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.52–7.58 (m, 6 H, *m*-Ph, *p*-Ph), 7.82–7.87 (m, 4 H, *o*-Ph). – <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 116.66 (s, CN), 125.58 (s, CCN), 128.68 (d, *o*-Ph), 129.28 (d, *m*-Ph), 131.70 (d, *p*-Ph), 131.97 (s, *i*-Ph). – **IR (CCl<sub>4</sub>):**  $\tilde{\nu}$  = 692 cm<sup>-1</sup> (s), 1447 (m), 2222 (w, CN), 3065 (w). – **MS (ESI):** *m/z* (100): 231.1 [M+H<sup>+</sup>], 303.2 (100). – **C<sub>16</sub>H<sub>10</sub>N<sub>2</sub> (230.27 g/mol):** calc. (%): C 83.46, H 4.38, N 12.17; found (%): C 82.70, H 4.28, N 12.29. – **R<sub>f</sub> (CHCl<sub>3</sub>/*n*-hexane = 1:1):** 0.23. – **R<sub>f</sub> (*n*-hexane/CH<sub>2</sub>Cl<sub>2</sub>=1:1):** 0.50.

**cis-Dicyanostilbene (Z)-6:**<sup>[S10]</sup> pale yellow solid. – **mp:** 129–131 °C (ref.<sup>[S10]</sup>: 132–133 °C). – <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.29–7.35 (m, 8 H, *o*-Ph, *m*-Ph), 7.38–7.43 (m, 2 H, *p*-Ph). – <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 116.78 (s, CN), 125.97 (s, =CCN), 129.13 (d, *m*-Ph oder *o*-Ph), 129.28 (d, *m*-Ph oder *o*-Ph), 130.46 (s, *i*-Ph), 131.12 (*p*-Ph). – **IR (CCl<sub>4</sub>):**  $\tilde{\nu}$  = 694 cm<sup>-1</sup> (vs), 1303 (m), 1447 (m), 1491 (w), 2222 (w, CN), 3065 (w). – **R<sub>f</sub> (*n*-hexane/CH<sub>2</sub>Cl<sub>2</sub>=1:1):** 0.35.

### 4. Characterisation of nitrile 8

**2-Phenyl-2-(phenylimino)acetonitrile (8)**<sup>[S11]</sup>: yellow solid. – **mp:** 57–59 °C. – <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.20 (*pseudo* d, *J* = 8.0 Hz, 2 H, *o*-Ph-N), 7.33 (*pseudo* t, *J* = 7.6 Hz, 1 H, *p*-Ph-N), 7.49 (*pseudo* t, *J* = 7.6 Hz, 2 H, *m*-Ph-N), 7.55 (*pseudo* t, *J* = 7.6 Hz, 2 H, *m*-Ph-C), 7.61 (*pseudo* t, *J* = 7.6 Hz, 1 H, *p*-Ph-C), 8.17 (*pseudo* d, *J* = 7.6 Hz, 2 H, *o*-Ph-C). – <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 110.83 (s, CN), 120.30 (d, *o*-Ph-N), 127.30 (d, *p*-Ph-N), 128.21 (d, *o*-Ph-C), 129.03 (d, *m*-Ph-C), 129.27 (d, *m*-Ph-N), 132.86 (d, *p*-Ph-C), 133.57 (s, *i*-Ph-C), 139.79 (s, C(CN)Ph), 149.08 (s, *i*-Ph-N). No significant nOe effects between the phenyl substituents have been found irradiating at the *ortho*-protons. Consequently, the *Z* isomer may be supposed. – **IR (CCl<sub>4</sub>):**  $\tilde{\nu}$  = 689 cm<sup>-1</sup> (vs), 720 (w), 1007 (m), 1201 (m), 1273 (m), 1451 (m), 1485 (m), 1576 (m), 1589 (m), 1606 (m), 2220 (vw, CN), 3069 (vw, arom. CH). – **C<sub>14</sub>H<sub>10</sub>N<sub>2</sub> (206.25 g/mol):** ber. (%): C 81.53, H 4.89, N 13.58; gef. (%): C 81.41, H 4.88, N 13.32. – **MS (EI):** *m/z* (%): 206 [M<sup>+</sup>], 180, 77 (100), 51. – **R<sub>f</sub> (CHCl<sub>3</sub>):** 0.73.

### 5. Characterisation of the (chloroethynyl)arenes 10, 19 and the alkylsulfanylethyne 25b

**(Chloroethynyl)benzene (10):**<sup>[S12]</sup> colourless liquid, darkened at standing. – <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.29–7.36 (m, 3 H, Ph), 7.44–7.47 (m, 2 H, Ph). – <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 67.99 (s, ≡C), 69.34 (s, ≡C), 122.12 (s, *i*-Ph), 128.35 (d), 128.57 (d), 131.95 (d). – **IR (CCl<sub>4</sub>):**  $\tilde{\nu}$  = 689 cm<sup>-1</sup> (s), 1489 (m), 2225 (m, C≡C), 3084 (w). – **MS (ESI):** *m/z* (%): 137.08 [M+H<sup>+</sup>], 207.09 (100), 272.06 [2M<sup>+</sup>]. – **C<sub>8</sub>H<sub>5</sub>Cl (136.58 g/mol):** ber. (%): C 70.35, H 3.69; gef. (%): C 69.12, H 3.66. – **R<sub>f</sub> (*n*-hexane):** 0.62.

**2-(4-Methylphenyl)chloroacetylene (19a):**<sup>[S15]</sup> colourless liquid. – <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 2.35 (s, 3 H, Me), 7.12 (*pseudo* d, *J* = 8.0 Hz, 2 H, Ar), 7.33 (*pseudo* d, *J* = 8.0 Hz, 2 H, Ar). – <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 21.40 (q, Me), 67.11 (s, ≡C), 69.47 (s, ≡C), 118.99 (s, ≡CC), 129.06 (d, CH), 131.79 (d, CH), 138.69 (s, CMe). – **IR (CCl<sub>4</sub>):**  $\tilde{\nu}$  = 889 cm<sup>-1</sup> (s), 1040 (m), 1451 (m), 1508 (s), 1903 (m), 2222 (s, C≡C), 2868 (m), 2923 (s), 3031 (m). – **C<sub>9</sub>H<sub>7</sub>Cl (150.61 g/mol):** ber. (%): C 71.78, H 4.68; gef. (%): C 70.61, H 4.87. – **R<sub>f</sub> (*n*-hexane):** 0.51.

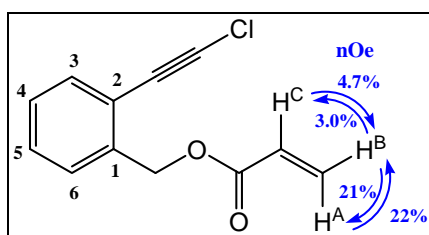
**4-(Chloroethynyl)biphenyl (19b):**<sup>[S14]</sup> white solid. – **mp:** 85–87 °C. – <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.37 (*pseudo* t, *J* = 7.2 Hz, 1 H, H-4'), 7.46 (*pseudo* t, *J* = 7.2 Hz, 2 H, H-3'), 7.52 (*pseudo* d, *J* = 8.4 Hz, 2 H, H-3), 7.56 (*pseudo* d, *J* = 8.4 Hz, 2 H, H-2), 7.59 (*pseudo* d, *J* =

7.2 Hz, 2 H, H-2'). –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 68.57 (s,  $\equiv\text{CCl}$ ), 69.26 (s,  $\equiv\text{CAr}$ ), 120.98 (s, C-4), 127.00 (d, C-2'), 127.01 (d, C-2), 127.70 (d, C-4'), 128.85 (d, C-3'), 132.36 (d, C-3), 140.17 (s, C-1'), 141.32 (s, C-1). – IR ( $\text{CCl}_4$ ):  $\tilde{\nu}$  = 555  $\text{cm}^{-1}$  (m), 696 (s), 840 (s), 890 (m), 1487 (s), 2222 (m,  $\text{C}\equiv\text{C}$ ), 3033 (m) und 3062 (w,  $\text{CH}_{\text{Ar}}$ ). – MS (ESI):  $m/z$  (%): 212.9 [ $\text{M}^+$ ], 370.9. –  $\text{C}_{14}\text{H}_9\text{Cl}$  (212.68 g/mol): calc. (%): C 79.07, H 4.27; found (%): C 78.95, H 4.25. –  $R_f$  (*n*-hexane): 0.50.

**1-Chloro-4-(chloroethynyl)benzene (19c).**<sup>[S13]</sup> white solid, prominent, medicine-like odour. – mp: 70–71 °C. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 7.29 (*pseudo* d,  $J$  = 8.8 Hz, 2 H, ClCCH), 7.36 (*pseudo* d,  $J$  = 8.8 Hz, 2 H, ClCCHCH). –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 68.31 (s,  $\equiv\text{CCl}$ ), 69.12 (s,  $\equiv\text{CAr}$ ), 120.58 (s,  $\equiv\text{CC}$ ), 128.71 (d, ClCCH), 133.17 (d, ClCCHCH), 134.67 (s, CCl). – IR ( $\text{CCl}_4$ ):  $\tilde{\nu}$  = 494  $\text{cm}^{-1}$  (m), 829 (m), 887 (m), 1093 (m), 1488 (s), 2224 (m,  $\text{C}\equiv\text{C}$ ). – MS (ESI):  $m/z$  (%): 169.9, 171.9 [ $\text{M}^+$ ]. –  $\text{C}_8\text{H}_4\text{Cl}_2$  (171.03 g/mol): calc. (%): C 56.18, H 2.36; found (%): C 56.22, H 2.40. –  $R_f$  (*n*-hexane): 0.71.

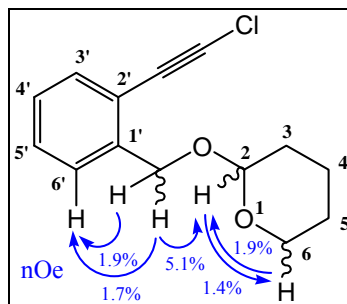
**1,3-Dichloro-2-(chloroethynyl)benzene (19d):** white solid. – mp: 41–44 °C. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 7.16 (t,  $^3J$  = 7.6 Hz, 1 H, CHCHCCl), 7.30 (d,  $^3J$  = 7.6 Hz, 2 H, CHCCl). –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 63.83 (s,  $\equiv\text{CAr}$ ), 78.56 (s,  $\equiv\text{CCl}$ ), 122.15 (s,  $\equiv\text{CC}$ ), 127.46 (d, CHCCl), 129.26 (d, CHCHCCl), 137.82 (s,  $\text{C}_{\text{Ar}}\text{Cl}$ ). – IR ( $\text{CCl}_4$ ):  $\tilde{\nu}$  = 718  $\text{cm}^{-1}$  (m), 896 (m), 1108 (m), 1195 (m), 1432 (s), 1446 (m), 2226 (s,  $\text{C}\equiv\text{C}$ ). –  $\text{C}_8\text{H}_3\text{Cl}_3$  (205.47 g/mol): calc. (%): C 46.76, H 1.47; found (%): C 45.07, H 2.01. The compound still contained traces of impurities but was further converted, notwithstanding. – MS (EI):  $m/z$  (%): 206.1 (11) [ $\text{M}+\text{H}^+$ ], 49.0 (50), 47.0 (61), 37.0 (85), 35.0 (100), 26.1 (50). –  $R_f$  (*n*-hexane): 0.63.

**(Chloro)-2-pyridylacetylene (19e).**<sup>[S15]</sup> brown oil. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 7.44 (ddd,  $^3J$  = 7.6 Hz, 5.2 Hz,  $^4J$  = 1.2 Hz, 1 H, H-5), 7.62 (*pseudo* dt,  $J$  = 8.0 Hz, 1.2 Hz, 1 H, H-3), 7.84 (*pseudo* dd,  $J$  = 8.0 Hz, 1.6 Hz, 1 H, H-4), 8.76 (*pseudo* dq,  $J$  = 4.8 Hz, 0.8 Hz, 1 H, H-6). –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 68.84 (s,  $\equiv\text{C}$ ), 69.01 (s,  $\equiv\text{C}$ ), 123.19 (d, C-5), 127.30 (d, C-3), 136.20 (d, C-4), 142.24 (s, C-2), 150.02 (d, C-6). – IR ( $\text{CCl}_4$ ):  $\tilde{\nu}$  = 679  $\text{cm}^{-1}$  (m), 905 (m), 991 (m), 1428 (s), 1464 (vs), 1566 (m), 1583 (s), 2231 (vs,  $\text{C}\equiv\text{C}$ ), 3010 (w), 3056 (w). – MS (ESI):  $m/z$  (%): 138.0 [ $\text{M}+\text{H}^+$ ]. –  $R_f$  (EtOAc/*n*-hexane = 1:4): 0.31.



**2-(2-Chloroethynyl)benzyl acrylate (19f):** pale yellow liquid. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 5.35 (s, 2 H,  $\text{OCH}_2$ ), 5.88 (dd,  $^3J_{\text{cis}}$  = 10.4 Hz,  $^2J$  = 1.6 Hz, 1 H,  $\text{H}^{\text{B}}$ ), 6.20 (dd,  $^3J_{\text{trans}}$  = 17.6 Hz,  $^3J_{\text{cis}}$  = 10.4 Hz, 1 H,  $\text{H}^{\text{C}}$ ), 6.48 (dd,  $^3J_{\text{trans}}$  = 17.6 Hz,  $^2J$  = 1.6 Hz, 1 H,  $\text{H}^{\text{A}}$ ), 7.28 (*pseudo* td,  $J$  = 7.6 Hz, 1.6 Hz, 1 H, H-4), 7.35 (*pseudo* td,  $J$  = 7.6 Hz, 1.6 Hz, 1 H, H-5), 7.41 (*pseudo* d,  $J$  = 7.6 Hz, 1 H, H-6), 7.48 (*pseudo* dd,  $J$  = 7.6 Hz, 0.8 Hz, 1 H, H-3). –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 64.46 (t,  $\text{OCH}_2$ ), 66.75 (s,  $\equiv\text{CAr}$ ), 72.78 (s,  $\equiv\text{CCl}$ ), 121.42 (s, C-2), 128.07 (d, C-4 or  $\text{C}(\text{O})\text{CH}$ ), 128.12 (d, C-4 or  $\text{C}(\text{O})\text{CH}$ ), 128.23 (d, C-6), 128.78 (d, C-5), 131.28 (t,  $=\text{CH}_2$ ), 132.79 (d, C-3), 138.08 (s, C-1), 165.88 (s,  $\text{C}=\text{O}$ ). – IR ( $\text{CCl}_4$ ):  $\tilde{\nu}$  = 654  $\text{cm}^{-1}$  (m), 896 (m), 949 (m), 967 (s), 985 (s), 1023 (m), 1050 (s), 1185 (s), 1269 (s), 1295 (s), 1371 (m), 1407 (m), 1452 (m), 1487 (m), 1635 (m), 1739 (vs,  $\text{C}=\text{O}$ ), 1926 (w), 1956 (w), 2220 (s,  $\text{C}\equiv\text{C}$ ), 2893

(w), 2961 (w), 3033 (w, =CH), 3070 (w, =CH). – **C<sub>12</sub>H<sub>9</sub>ClO<sub>2</sub> (220.66 g/mol)**: calc. (%): C 65.32, H 4.11; found (%): C 64.90, H 4.12. – **R<sub>f</sub> (Et<sub>2</sub>O/*n*-hexane=1:10)**: 0.41.

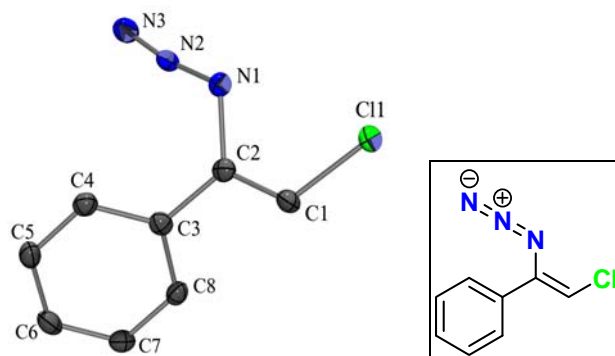


**2-[2-(Chloroethynyl)benzyloxy]tetrahydro-2H-pyran (19g)**: viscous yellow oil. – **<sup>1</sup>H NMR (CDCl<sub>3</sub>)**: δ = 1.52–1.65 (m, 3 H, H-4, H-5), 1.67–1.73 (m, 1 H, H-3, diastereotope protons), 1.74–1.82 (m, 1 H, H-3, diastereotope protons), 1.85–1.95 (m, 1 H, H-5, diastereotope protons), 3.59 (m, 1 H, H-6, diastereotope protons), 3.95 (m, 1 H, H-6, diastereotope protons), 4.65 (d, <sup>2</sup>J = 12.8 Hz, 1 H, ArCH<sub>2</sub>, diastereotope protons), 4.78 (*pseudo* t, J = 3.2 Hz, 1 H, H-2), 4.90 (d, <sup>2</sup>J = 12.8 Hz, 1 H, ArCH<sub>2</sub>, diastereotope protons), 7.23 (*pseudo* t, J = 7.6 Hz, 1 H, H-4'), 7.35 (*pseudo* td, J = 7.6 Hz, J = 1.2 Hz, 1 H, H-5'), 7.45 (*pseudo* dd, J = 7.6 Hz, J = 1.2 Hz, 1 H, H-3'), 7.49 (*pseudo* d, J = 7.6 Hz, 1 H, H-6'). – **<sup>13</sup>C NMR (CDCl<sub>3</sub>)**: δ = 19.30 (t, C-5), 25.46 (t, C-4), 30.52 (t, C-3), 62.06 (t, C-6), 67.28 (t, ArCH<sub>2</sub>), 67.30 (s, ≡CAr), 72.04 (s, ≡CCl), 98.48 (d, C-2), 120.66 (s, C-2'), 127.20 (d, C-4'), 127.58 (d, C-6'), 128.73 (d, C-5'), 132.57 (d, C-3'), 140.96 (s, C-1'). – **IR (CCl<sub>4</sub>)**:  $\tilde{\nu}$  = 871 cm<sup>-1</sup> (w), 908 (m), 976 (w), 1035 (s), 1060 (m), 1201 (w), 1350 (w), 1453 (w), 2219 (w, C≡C), 2851 (w), 2873 (m), 2944 (s). – **C<sub>14</sub>H<sub>15</sub>ClO<sub>2</sub> (250.72 g/mol)**: calc. (%): C 67.07, H 6.03; found (%): C 66.68, H 6.00. – **R<sub>f</sub> (CHCl<sub>3</sub>)**: 0.50–0.57.

**2-(Chloroethynyl)benzyl alcohol (19h)**: white solid. – **mp**: 76–82 °C. – **<sup>1</sup>H NMR (CDCl<sub>3</sub>)**: δ = 1.92 (s, 1 H, OH), 4.82 (s, 2 H, CH<sub>2</sub>OH), 7.25 (*pseudo* t, J = 7.6 Hz, 1 H, H-4), 7.36 (*pseudo* t, J = 7.6 Hz, 1 H, H-5), 7.45–7.47 (m, 2 H, H-2, H-3, H-6). – **<sup>13</sup>C NMR (CDCl<sub>3</sub>)**: δ = 63.60 (t, CH<sub>2</sub>OH), 67.04 (s, ≡CAr), 72.37 (s, ≡CCl), 120.17 (s, C-2), 127.20 (d, C-6), 127.45 (d, C-4), 129.00 (d, C-5), 132.73 (d, C-3), 143.09 (s, C-1). – **IR (CCl<sub>4</sub>)**:  $\tilde{\nu}$  = 655 cm<sup>-1</sup> (m), 947 (m), 1015 (s), 1040 (vs), 1191 (m), 1378 (m), 1450 (m), 1484 (m), 2218 (s, C≡C), 2878 (w), 2929 (w), 3071 (w), 3458 (br.), 3616 (m). – **MS (ESI)**: *m/z*: 167.0 [M+H<sup>+</sup>]. – **C<sub>9</sub>H<sub>7</sub>ClO (166.61 g/mol)**: calc. (%): C 64.89, H 4.23; found (%): C 65.28, H 4.43. – **R<sub>f</sub> (CHCl<sub>3</sub>)**: 0.19.

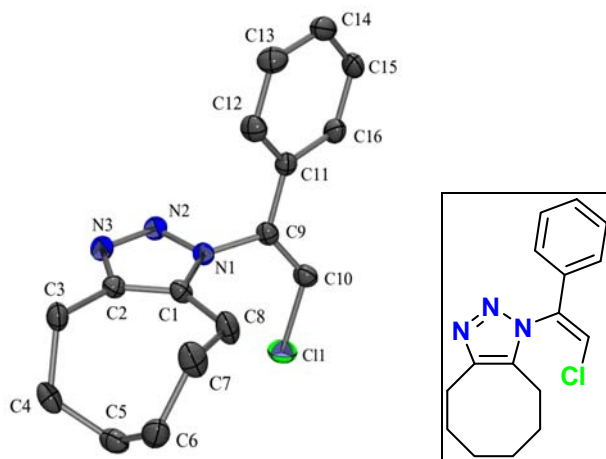
**(Chloroethynyl) propyl thioether (25b)**:<sup>[S16]</sup> colourless liquid, darkened rapidly at standing (room temperature). – **<sup>1</sup>H NMR (CDCl<sub>3</sub>)**: δ = 1.02 (*pseudo* t, J = 7.2 Hz, 3 H, Me), 1.76 (*pseudo* qt, J<sub>Me,CH<sub>2</sub></sub> = 7.2 Hz, J = 7.2 Hz, 2 H, CH<sub>3</sub>CH<sub>2</sub>), 2.69 (*pseudo* t, J = 7.2 Hz, 2 H, SCH<sub>2</sub>). – **<sup>1</sup>H NMR (DMSO-d<sub>6</sub>)**: δ = 0.97 (*pseudo* t, J = 7.2 Hz, 3 H, Me), 1.68 (*pseudo* sext, J = 7.2 Hz, 2 H, MeCH<sub>2</sub>), 2.77 (*pseudo* t, J = 7.2 Hz, 2 H, SCH<sub>2</sub>). – **<sup>13</sup>C NMR (CDCl<sub>3</sub>)**: δ = 12.82 (q, Me), 22.70 (t, MeCH<sub>2</sub>), 37.01 (t, SCH<sub>2</sub>), 59.83 (s, ≡C), 68.94 (s, ≡C). – **<sup>13</sup>C NMR (DMSO-d<sub>6</sub>)**: δ = 12.43 (q, Me), 22.25 (t, MeCH<sub>2</sub>), 36.13 (t, SCH<sub>2</sub>), 60.34 (s, ≡C), 68.61 (s, ≡C). – **IR (CCl<sub>4</sub>)**:  $\tilde{\nu}$  = 897 cm<sup>-1</sup> (m), 911 (m), 952 (m), 1236 (s), 1292 (s), 1333 (s), 1379 (m), 1461 (s), 2147 (s, C≡C), 2875 (s), 2933 (s), 2963 (s). – **C<sub>5</sub>H<sub>7</sub>ClS (134.63 g/mol)**: calc. (%): C 44.61, H 5.24, S 23.82; found (%): C 43.79, H 5.18, S 24.66.

## 6. Characterisation of vinyl azide **13** and the corresponding cyclooctatriazole **15**



ORTEP plot of **13**, H atoms are omitted for clarity.

**(Z)-(1-Azido-2-chloroethenyl)benzene (13):**<sup>[9]</sup> yellow solid. – **mp:** 23–26 °C. – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 5.82 (s, 1 H, =C(Cl)H), 7.38–7.45 (m, 5 H, Ph). – <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 105.94 (d, =C(Cl)H), 127.01 (d), 128.92 (d), 129.72 (d, *p*-Ph), 132.57 (s, *i*-Ph), 139.11 (s, *C*Ph). – **IR (CCl<sub>4</sub>):**  $\tilde{\nu}$  = 698 cm<sup>-1</sup> (s), 838 (s), 1322 (s), 1614 (w), 2119 (vs, N<sub>3</sub>), 3093 (w). – **MS (ESI):**  $m/z$  (%): 152.05 [M–N<sub>2</sub>+H<sup>+</sup>]. – **C<sub>8</sub>H<sub>6</sub>ClN<sub>3</sub> (179.61 g/mol):** calc. (%): C 53.50, H 3.37, N 23.40; found (%): C 53.38, H 3.32, N 23.08. – **R<sub>f</sub> (CHCl<sub>3</sub>/*n*-hexane = 1:1):** 0.82. – **Crystal data:** C<sub>8</sub>H<sub>6</sub>ClN<sub>3</sub>, *MW* = 179.61, *T* = 100 K,  $\lambda$  = 1.54184 Å, orthorhombic, space group Pbca, *a* = 9.13600(10) Å, *b* = 7.63310(10) Å, *c* = 23.2493(3) Å,  $\alpha$  = 90 °,  $\beta$  = 90 °,  $\gamma$  = 90 °, *V* = 1621.31(3) Å<sup>3</sup>, *Z* = 8, *D* = 1.472 Mg/m<sup>3</sup>,  $\mu$  = 3.692 mm<sup>-1</sup>, *F*(000) = 736. Crystallographic data for structure **13** have been deposited at the Cambridge Crystallographic Data Center under the number CCDC 766233.

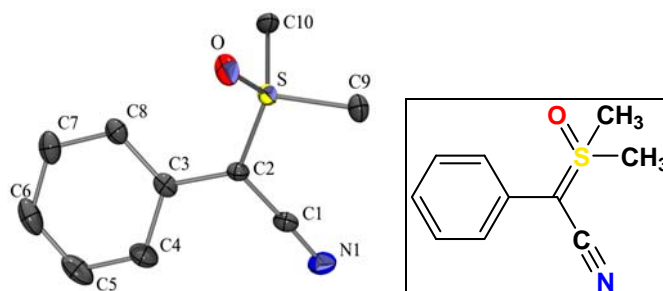


ORTEP plot of **15**, H atoms are omitted for clarity.

**(Z)-1-(2-Chloro-1-phenylvinyl)-4,5,6,7,8,9-hexahydro-1H-cycloocta[d][1,2,3]triazole (15):** white solid. – **mp:** 75–78. – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.49 (m, 4 H, H-6, H-7), 1.62 (m, 2 H, H-8), 1.80 (m, 2 H, H-5), 2.58 (m, 2 H, H-9), 3.00 (m, 2 H, H-4), 7.03 (s, 1 H, =C(Cl)H), 7.09–7.13 (m, 2 H, *o*-Ph), 7.31–7.36 (m, 3 H, *p*-Ph, *m*-Ph). – <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 21.54 (t, C-9), 24.32 (t, C-4), 24.84 (t, C-6 or C-7), 25.76 (t, C-6 or C-7), 26.05 (t, C-8), 27.92 (t, C-5), 119.21 (d, =C(Cl)H), 125.11 (d, *o*-Ph), 129.04 (d, *m*-Ph), 129.80 (d, *p*-Ph), 133.63 (s, *i*-Ph), 134.70 (s, C-9a), 137.77 (s, *C*=C(Cl)H), 144.50 (s, C-3a). – **IR (CCl<sub>4</sub>):**  $\tilde{\nu}$  = 1243 cm<sup>-1</sup> (m), 1456 (s), 1496 (m), 1619 (m), 2856 (s), 2933 (vs, CH<sub>2</sub>), 3087. – **HR-MS (ESI):**  $m/z$ : 288.1221 [M+H<sup>+</sup>, calc.: 288.1262], 575.4 [2M+H<sup>+</sup>]. – **C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>Cl (287.79 g/mol):** calc. (%): C 66.78, H 6.30, N 14.60, Cl 12.32; found (%): C 67.16, H 6.34, N 14.48. – **R<sub>f</sub> (Et<sub>2</sub>O):** 0.74.

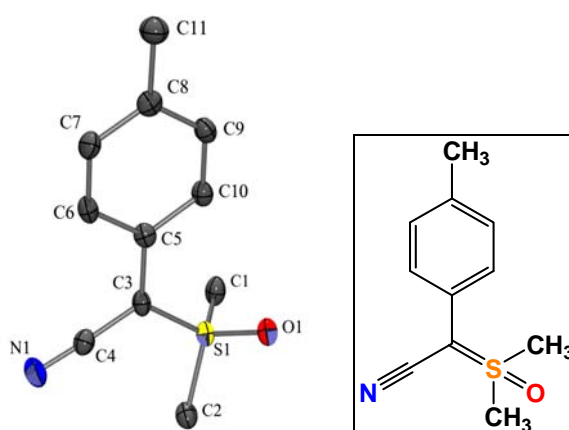
– **Crystal data** ( $\text{Et}_2\text{O}/n\text{-pentane}$ ):  $\text{C}_{16}\text{H}_{18}\text{ClN}_3$ ,  $MW = 287.78$ ,  $T = 120 \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , monoclinic, space group  $P2(1)/a$ ,  $a = 11.51210(10) \text{ \AA}$ ,  $b = 10.10690(10) \text{ \AA}$ ,  $c = 12.42760(10) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 93.6380(10)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 1443.06(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $D = 1.325 \text{ Mg/m}^3$ ,  $\mu = 2.275 \text{ mm}^{-1}$ ,  $F(000) = 608$ . Crystallographic data for structure **15** have been deposited at the Cambridge Crystallographic Data Center under the number CCDC 766234.

## 7. Characterisation of the sulfoxonium ylides **14** and **20**



ORTEP plot of **14**, H atoms are omitted for clarity.

**Dimethylsulfoxonium- $\alpha$ -cyanobenzylide (**14**)**: orange solid. – **mp**:  $97\text{--}99^\circ\text{C}$ . –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 3.51$  (s, 6 H, Me),  $7.09$  (m, 1 H, *p*-Ph),  $7.27\text{--}7.32$  (m, 4 H, *o*-Ph, *m*-Ph). –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 41.73$  (q, Me),  $51.24$  (s,  $\text{C}=\text{S}$ ),  $119.96$  (s, CN),  $124.08$  (d, *m*-Ph),  $124.22$  (d, *p*-Ph),  $129.09$  (d, *o*-Ph),  $132.06$  (s, *i*-Ph). – **IR** ( $\text{CCl}_4$ ):  $\tilde{\nu} = 1026 \text{ cm}^{-1}$  (m),  $1200$  (s,  $\text{C}=\text{S}$ ),  $1494$  (m),  $2163$  (s, CN),  $2915$  (w),  $2994$  (w),  $3009$  (w). – **HR-MS** (ESI):  $m/z$ :  $194.0658$  [ $\text{M}+\text{H}^+$ , calc.:  $194.0634$ ]. –  **$\text{C}_{10}\text{H}_{11}\text{NOS}$  (**193.27 g/mol**)**: calc. (%): C 62.15, H 5.74, N 7.24, S 16.59, O 8.28; found (%): C 62.24, H 5.53, N 7.27, S 16.36. –  **$R_f$  (EtOH)**: 0.64. –  **$R_f$  (EtOAc)**: 0.50. – **Crystal data**:  $\text{C}_{10}\text{H}_{12}\text{NOS}$ ,  $MW = 193.27$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 0.71073 \text{ \AA}$ , orthorhombic, space group  $\text{Pbca}$ ,  $a = 10.1145(7) \text{ \AA}$ ,  $b = 8.6150(7) \text{ \AA}$ ,  $c = 22.2122(16) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 1935.5(2) \text{ \AA}^3$ ,  $Z = 8$ ,  $D = 1.333 \text{ Mg/m}^3$ ,  $\mu = 0.292 \text{ mm}^{-1}$ ,  $F(000) = 824$ . Crystallographic data for structure **14** have been deposited at the Cambridge Crystallographic Data Center under the number CCDC 766236.

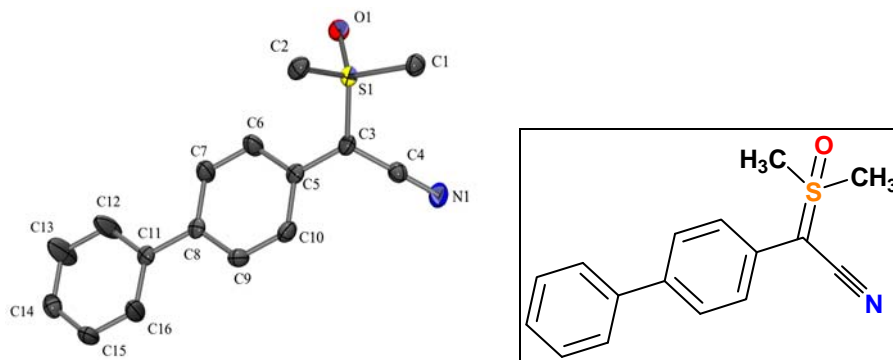


ORTEP plot of **20a**, H atoms are omitted for clarity.

**Dimethylsulfoxonium- $\alpha$ -cyano(4-methylphenyl)methylide (**20a**)**: yellow solid. – **mp**:  $125\text{--}128^\circ\text{C}$ . –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 2.31$  (s, 3 H,  $\text{C}_6\text{H}_4\text{CH}_3$ ),  $3.48$  (s, 6 H, SMe),  $7.12$  (*pseudo* d,  $J = 8.2 \text{ Hz}$ , 2 H, MeCCH),  $7.22$  (*pseudo* d,  $J = 8.2 \text{ Hz}$ , 2 H, MeCCHCH). –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 20.91$  (q,  $\text{C}_6\text{H}_4\text{CH}_3$ ),  $41.67$  (q, SCH<sub>3</sub>),  $50.50$  (s,  $\text{C}=\text{S}$ ),  $120.22$  (s, CN),  $124.88$  (d, MeCCHCH),  $128.62$  (s, MeCCHCHC),  $129.80$  (d, MeCCH),  $134.35$  (MeC). – **IR** ( $\text{CCl}_4$ ):

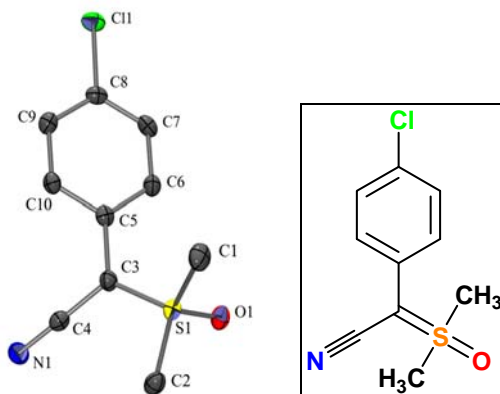


$\tilde{\nu}$  = 689 cm<sup>-1</sup> (m), 1024 (m), 1202 (s), 1296 (w), 1325 (w), 1356 (w), 1510 (m), 1613 (w), 1689 (s), 2168 (s, CN), 2927 (w), 3024 (w). – **HR-MS (ESI):**  $m/z$ : 208.0807 [M+H<sup>+</sup>, calc.: 208.0791]. – **C<sub>11</sub>H<sub>13</sub>NSO (207.29 g/mol):** calc. (%): C 63.74, H 6.32, N 6.75, S 15.47, O 7.72; found (%): C 63.47, H 6.67, N 6.77, S 15.41. – **R<sub>f</sub> (EtOAc):** 0.34. – **Crystal data** (THF/*n*-hexane): C<sub>11</sub>H<sub>13</sub>NOS,  $MW$  = 207.28,  $T$  = 100 K,  $\lambda$  = 1.54184 Å, monoclinic, space group P 1 21/c 1,  $a$  = 10.1586(10) Å,  $b$  = 10.9459(8) Å,  $c$  = 10.0846(10) Å,  $\alpha$  = 90 °,  $\beta$  = 108.164(11) °,  $\gamma$  = 90 °,  $V$  = 1065.48(17) Å<sup>3</sup>,  $Z$  = 4,  $D$  = 1.292 Mg/m<sup>3</sup>,  $\mu$  = 2.419 mm<sup>-1</sup>,  $F(000)$  = 440. Crystallographic data for structure **20a** have been deposited at the Cambridge Crystallographic Data Center under the number CCDC 766224.



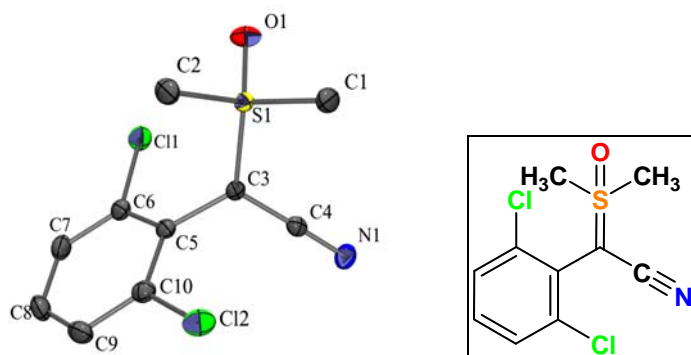
ORTEP plot of **20b**, H atoms are omitted for clarity.

**Dimethylsulfoxonium- $\alpha$ -cyano(4-biphenyl)methylide (20b):** yellow solid, prominent sweet odour. – **mp:** 164–167 °C. – **<sup>1</sup>H NMR (CDCl<sub>3</sub>):**  $\delta$  = 3.55 (s, 6 H, Me), 7.33 (*pseudo* t,  $J$  = 7.6 Hz, 1 H, H-4'), 7.39 (*pseudo* d,  $J$  = 8.4 Hz, 2 H, H-3), 7.43 (*pseudo* t,  $J$  = 7.6 Hz, 2 H, H-3'), 7.55 (*pseudo* d,  $J$  = 8.4 Hz, 2 H, H-2), 7.57 (*pseudo* d,  $J$  = 7.6 Hz, 2 H, H-2'). – **<sup>13</sup>C NMR (CDCl<sub>3</sub>):**  $\delta$  = 41.88 (q, Me), 51.28 (s, C=S), 119.84 (s, CN), 124.35 (d, C-3), 126.68 (d, C-2'), 127.09 (d, C-4'), 127.72 (d, C-2), 128.79 (d, C-3'), 131.21 (s, C-4), 137.00 (s, C-1), 140.45 (s, C-1'). – **IR (CDCl<sub>3</sub>):**  $\tilde{\nu}$  = 791 cm<sup>-1</sup> (s), 1018 (w), 1192 (m), 1311 (w), 1487 (m), 1605 (w), 2166 (s, CN), 2360 (w), 2930 (w), 3031 (w). – **HR-MS (ESI):**  $m/z$ : 270.0954 [M+H<sup>+</sup>, calc.: 270.0947]. – **C<sub>16</sub>H<sub>15</sub>NSO (269.36 g/mol):** calc. (%): C 71.35, H 5.61, N 5.20, S 11.90, O 5.94; found (%): C 71.17, H 5.70, N 5.44, S 11.23. – **R<sub>f</sub> (EtOAc):** 0.48. – **Crystal data** (THF/*n*-hexane): C<sub>16</sub>H<sub>15</sub>NOS,  $MW$  = 269.35,  $T$  = 100 K,  $\lambda$  = 1.54184 Å, monoclinic, space group P 1 21/c 1,  $a$  = 8.2481(5) Å,  $b$  = 5.3260(2) Å,  $c$  = 30.6598(13) Å,  $\alpha$  = 90 °,  $\beta$  = 94.469(5) °,  $\gamma$  = 90 °,  $V$  = 1342.77(11) Å<sup>3</sup>,  $Z$  = 4,  $D$  = 1.332 Mg/m<sup>3</sup>,  $\mu$  = 2.054 mm<sup>-1</sup>,  $F(000)$  = 568. Crystallographic data for structure **20b** have been deposited at the Cambridge Crystallographic Data Center under the number CCDC 766223.



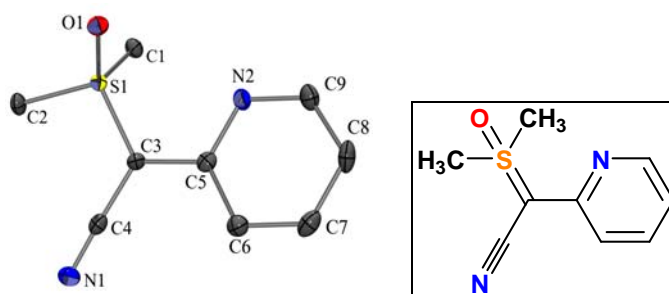
ORTEP plot of **20c**, H atoms are omitted for clarity.

**Dimethylsulfoxonium- $\alpha$ -cyano(4-chlorophenyl)methylide (20c):** yellow solid. – **mp:** 129–133 °C. –  **$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):**  $\delta$  = 3.51 (s, 6 H, Me), 7.23–7.28 (m, 4 H, Ph). –  **$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):**  $\delta$  = 41.77 (q, Me), 50.83 (s, C=S), 119.54 (s, CN), 125.19 (d, ClCCHCH), 129.17 (s, ClCCH), 129.73 (s, CCl or  $\text{C}_{\text{Ar}}\text{C}=\text{S}$ ), 130.68 (s, CCl or  $\text{C}_{\text{Ar}}\text{C}=\text{S}$ ). – **IR ( $\text{CHCl}_3$ ):**  $\tilde{\nu}$  = 546  $\text{cm}^{-1}$  (w), 826 (m), 1020 (s), 1184 (w), 1295 (m), 1313 (m), 1326 (m), 1492 (s), 1711 (w), 2167 (vs, CN), 2343 (w), 2934 (w), 3006 (w). – **HR-MS (ESI):**  $m/z$ : 228.0222 [ $\text{M}+\text{H}^+$ , calc.: 228.0244]. –  **$\text{C}_{10}\text{H}_{10}\text{ClNSO}$  (227.71 g/mol):** calc. (%): C 52.74, H 4.43, N 6.15, S 14.08; found (%): C 52.61, H 4.48, N 6.20, S 14.02. –  **$R_f$  (EtOAc):** 0.57. – **Crystal data** (slow evaporation of  $\text{CHCl}_3/\text{CCl}_4$ ):  $\text{C}_{10}\text{H}_{10}\text{ClNSO}$ ,  $MW = 227.70$ ,  $T = 100\text{ K}$ ,  $\lambda = 1.54184\text{ \AA}$ , monoclinic, space group  $P\ 1\ 21/c\ 1$ ,  $a = 12.6494(2)\text{ \AA}$ ,  $b = 8.25640(10)\text{ \AA}$ ,  $c = 10.09780(10)\text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 98.4520(10)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 1043.15(2)\text{ \AA}^3$ ,  $Z = 4$ ,  $D = 1.450\text{ Mg/m}^3$ ,  $\mu = 4.829\text{ mm}^{-1}$ ,  $F(000) = 472$ . Crystallographic data for structure **20c** have been deposited at the Cambridge Crystallographic Data Center under the number CCDC 766231.



ORTEP plot of **20d**, H atoms are omitted for clarity.

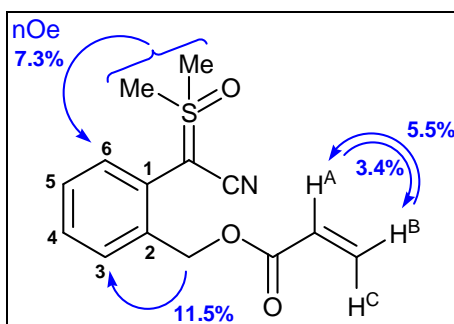
**Dimethylsulfoxonium- $\alpha$ -cyano(2,6-dichlorophenyl)methylide (20d):** white solid. – **mp:** 183–185 °C. –  **$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):**  $\delta$  = 3.40 (s, 6 H,  $\text{CH}_3$ ), 7.25 (t,  $^3J = 8.0\text{ Hz}$ , 1 H,  $p$ -Ph), 7.41 (d,  $^3J = 8.0\text{ Hz}$ , 2 H,  $m$ -Ph). –  **$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):**  $\delta$  = 41.65 (q,  $\text{CH}_3$ ), 43.81 (s, C=S), 119.07 (br. s, CN), 126.82 (s,  $i$ -Ph), 128.62 (d,  $m$ -Ph), 131.01 (d,  $p$ -Ph), 141.43 (s, CCl). – **IR ( $\text{CHCl}_3$ ):**  $\tilde{\nu}$  = 554  $\text{cm}^{-1}$  (m), 1022 (s), 1190 (m), 1428 (s), 1440 (m), 1556 (m), 2166 (vs, CN), 2930 (w,  $\text{CH}_3$ ), 3005 (m, arom. CH). – **HR-MS (ESI):**  $m/z$ : 261.9841 [ $\text{M}^+$ , calc.: 261.9855]. –  **$\text{C}_{10}\text{H}_9\text{Cl}_2\text{NSO}$  (262.16 g/mol):** calc. (%): C 45.82, H 3.46, N 5.34, S 12.23; found (%): C 45.70, H 3.50, N 5.43, S 11.57. –  **$R_f$  (EtOAc):** 0.48. – **Crystal data** (THF/ $n$ -hexane):  $\text{C}_{10}\text{H}_9\text{Cl}_2\text{NSO}$ ,  $MW = 262.14$ ,  $T = 110(2)\text{ K}$ ,  $\lambda = 0.71073\text{ \AA}$ , orthorhombic, space group  $\text{Pbca}$ ,  $a = 10.0743(2)\text{ \AA}$ ,  $b = 10.8754(2)\text{ \AA}$ ,  $c = 20.7109(3)\text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 2269.13(7)\text{ \AA}^3$ ,  $Z = 8$ ,  $D = 1.535\text{ Mg/m}^3$ ,  $\mu = 0.727\text{ mm}^{-1}$ ,  $F(000) = 1072$ . Crystallographic data for structure **20d** have been deposited at the Cambridge Crystallographic Data Center under the number CCDC 766230.



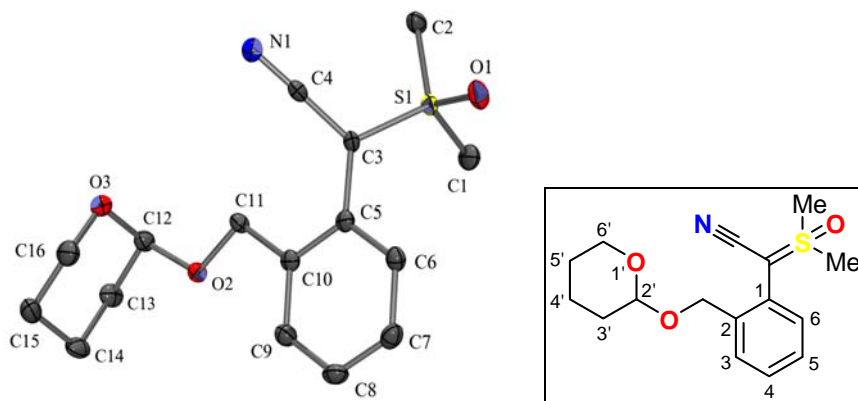
ORTEP plot of **20e**, H atoms are omitted for clarity.



**Dimethylsulfoxonium- $\alpha$ -cyano(2-pyridyl)methylide (20e):** red-orange solid. – **mp:** 122–125 °C. –  **$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):**  $\delta$  = 3.70 (s, 6 H, Me), 6.78 (*pseudo* t,  $J$  = 6.4 Hz, 1 H, H-5), 7.04 (*pseudo* dd,  $J$  = 8.0 Hz, 1.2 Hz, 1 H, H-3), 7.50 (*pseudo* td,  $J$  = 7.2 Hz, 1.2 Hz, 1 H, H-4), 8.26 (*pseudo* dt,  $J$  = 4.8 Hz, 0.8 Hz, 1 H, H-6). –  **$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):**  $\delta$  = 42.80 (q, Me), 56.61 (s, C=S), 116.18 (d, C-3), 116.47 (d, C-5), 118.60 (s, CN), 136.77 (d, C-4), 147.77 (d, C-6), 154.61 (s, C-2). – **IR ( $\text{CHCl}_3$ ):**  $\tilde{\nu}$  = 533  $\text{cm}^{-1}$  (m), 1024 (s), 1052 (m), 1291 (s), 1335 (s), 1428 (m), 1471 (s), 1560 (m), 1591 (s), 2172 (vs, CN), 2931 (w,  $\text{CH}_3$ ), 3004 (w, arom. CH). – **HR-MS (ESI):**  $m/z$ : 195.0681 [ $\text{M}+\text{H}^+$ , calc.: 195.0587]. –  **$\text{C}_9\text{H}_{10}\text{N}_2\text{OS}$  (194.25 g/mol):** calc. (%): C 55.65, H 5.19, N 14.42, S 16.50; found (%): C 55.62, H 5.21, N 14.17, S 16.18. –  **$R_f$  (EtOAc):** 0.46. – **Crystal data** (THF/*n*-hexane):  $\text{C}_9\text{H}_{10}\text{N}_2\text{OS}$ ,  $MW$  = 194.25,  $T$  = 100 K,  $\lambda$  = 0.71073 Å, monoclinic, space group P 1 21 1,  $a$  = 6.9633(2) Å,  $b$  = 5.10970(10) Å,  $c$  = 13.5723(4) Å,  $\alpha$  = 90°,  $\beta$  = 104.691(3)°,  $\gamma$  = 90°,  $V$  = 467.12(2) Å<sup>3</sup>,  $Z$  = 2,  $D$  = 1.381 Mg/m<sup>3</sup>,  $\mu$  = 0.305 mm<sup>-1</sup>,  $F(000)$  = 204. Crystallographic data for structure **20e** have been deposited at the Cambridge Crystallographic Data Center under the number CCDC 766225.



**Dimethylsulfoxonium- $\alpha$ -cyano[2-(ethenyloxo)oxymethyl]benzylide (20f):** yellow oil. –  **$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):**  $\delta$  = 3.40 (s, 6 H, Me), 5.29 (s, 2 H,  $\text{OCH}_2$ ), 5.84 (dd,  $^3J_{\text{cis}}$  = 10.4 Hz,  $^2J$  = 1.6 Hz, 1 H, H<sup>B</sup>), 6.14 (dd,  $^3J_{\text{trans}}$  = 17.2 Hz,  $^3J_{\text{cis}}$  = 10.4 Hz, 1 H, H<sup>A</sup>), 6.41 (dd,  $^3J_{\text{trans}}$  = 17.2 Hz,  $^2J$  = 1.6 Hz, 1 H, H<sup>C</sup>), 7.30 (symm. m, 2 H, H-4, H-5), 7.43 (dd,  $^3J$  = 7.2 Hz,  $^4J$  = 2.0 Hz, 1 H, H-3), 7.47 (dd,  $^3J$  = 6.8 Hz,  $^4J$  = 2.4 Hz, 1 H, H-6). –  **$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):**  $\delta$  = 41.14 (q, Me), 46.70 (s, C=S), 63.70 (t,  $\text{OCH}_2$ ), 119.98 (s, CN), 128.07 (d,  $=\text{C}(\text{H})\text{CO}$ ), 128.17 (s, C-1), 128.33 (d, C-4 or C-5), 128.57 (d, C-4 or C-5), 128.84 (d, C-3), 131.26 (t,  $=\text{CH}_2$ ), 132.19 (d, C-6), 137.41 (s, C-2), 165.79 (s, C=O). – **IR ( $\text{CHCl}_3$ ):**  $\tilde{\nu}$  = 553  $\text{cm}^{-1}$  (m), 877 (m), 984 (m), 1024 (s), 1047 (s), 1178 (m), 1267 (s), 1297 (s), 1372 (m), 1408 (m), 1450 (m), 1487 (m), 1724 (vs, C=O), 2162 (vs, CN), 2895 (m), 2931 (m), 2975 (m,  $\text{CH}_2$ ), 3621 (m). – **HR-MS (ESI):**  $m/z$ : 278.0863 [ $\text{M}+\text{H}^+$ , calc.: 278.0845]. –  **$R_f$  (EtOAc):** 0.30.



ORTEP plot of **20g**, H atoms are omitted for clarity.

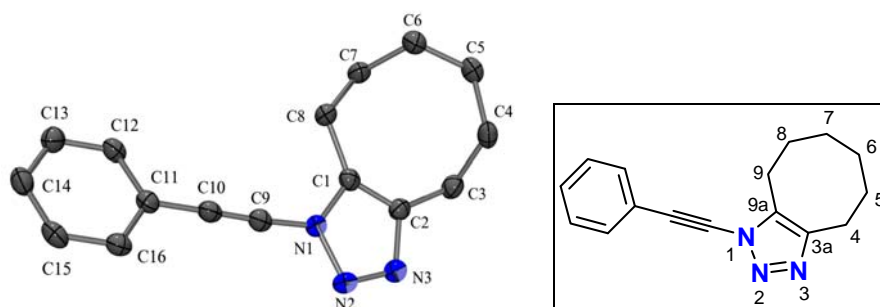
**Dimethylsulfoxonium- $\alpha$ -cyano[2-(tetrahydro-2H-pyran-2-yl)oxymethyl]benzylide (20g):** yellow solid. – **mp:** 90–94 °C. –  **$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):**  $\delta$  = 1.48–1.60 (m, 4 H, H-3', H-4', H-4' H-5'), 1.69–1.77 (m, 1 H, H-3', diastereotope protons), 1.80–1.86 (m, 1 H, H-5', diastereotope protons), 3.33 (s, 3 H, Me), 3.38 (s, 3 H, Me), 3.49–3.55 (m, 1 H, H-6'), 3.89 (m, 1 H, H-6'), 4.59 (d,  $^2J$  = 12 Hz, 1 H,  $\text{ArCH}_2$ , diastereotope protons), 4.69 (m, 1 H, H-2'), 4.85 (d,  $^2J$  = 12 Hz, 1 H,  $\text{ArCH}_2$ , diastereotope protons), 7.26 (*pseudo* td,  $J$  = 7.6 Hz,  $J$  = 1.2 Hz, 1 H, H-5), 7.32 (*pseudo* td,  $J$  = 7.6 Hz,  $J$  = 1.2 Hz, 1 H, H-4), 7.43 (*pseudo* dd,  $J$  = 7.6 Hz,  $J$  = 1.2 Hz, 1 H, H-6), 7.50 (*pseudo* dd,  $J$  = 7.6 Hz,  $J$  = 1.2 Hz, 1 H, H-3). –  **$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):**  $\delta$  = 19.73 (t, C-5'), 25.29 (t, C-4'), 30.68 (t, C-3'), 40.89 (q, Me), 41.09 (q, Me), 46.73 (s, C=S), 62.74 (t, C-6'), 66.89 (t,  $\text{ArCH}_2$ ), 98.58 (d, C-2'), 120.07 (s, CN), 127.83 (s, C-1), 128.13 (d, C-5), 128.41 (d, C-4), 129.41 (d, C-3), 132.67 (d, C-6), 139.66 (s, C-2). – **IR ( $\text{CCl}_4$ ):**  $\tilde{\nu}$  = 552  $\text{cm}^{-1}$  (m), 870 (m), 907 (m), 976 (m), 1028 (s), 1059 (m), 1077 (m), 1129 (m), 1191 (s), 1312 (m), 1350 (m), 1453 (m), 1485 (m), 2158 (s, CN), 2871 (m), 2944 (s). – **HR-MS (ESI):**  $m/z$ : 308.1305 [ $\text{M}+\text{H}^+$ , calc.: 308.1315]. –  **$\text{C}_{16}\text{H}_{21}\text{NO}_3\text{S}$  (307.41 g/mol):** calc. (%): C 62.51, H 6.89, N 4.56, S 10.43; found (%): C 62.46, H 6.69, N 5.02, S 10.23. –  **$R_f$  (EtOAc):** 0.20. – **Crystal data** ( $\text{CH}_2\text{Cl}_2/n$ -pentane):  $\text{C}_{16}\text{H}_{21}\text{NO}_3\text{S}$ ,  $MW$  = 307.40,  $T$  = 100 K,  $\lambda$  = 1.54184 Å, monoclinic, space group P1 21/c 1,  $a$  = 16.2018(4) Å,  $b$  = 8.2340(2) Å,  $c$  = 12.3791(3) Å,  $\alpha$  = 90°,  $\beta$  = 108.596(3)°,  $\gamma$  = 90°,  $V$  = 1565.22(7) Å<sup>3</sup>,  $Z$  = 4,  $D$  = 1.304  $\text{Mg/m}^3$ ,  $\mu$  = 1.918  $\text{mm}^{-1}$ ,  $F(000)$  = 656. Crystallographic data for structure **20g** have been deposited at the Cambridge Crystallographic Data Center under the number CCDC 766226.

**Dimethylsulfoxonium- $\alpha$ -cyano(2-hydroxymethyl)benzylide (20h):** highly viscous yellow oil. –  **$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):**  $\delta$  = 3.00–6.00 (br. s, 1 H, OH), 3.38 (s, 6 H,  $\text{CH}_3$ ), 4.75 (s, 2 H,  $\text{CH}_2\text{OH}$ ), 7.28 (*pseudo* td,  $J$  = 7.6 Hz,  $J$  = 1.6 Hz, 1 H, H-5), 7.34 (*pseudo* td,  $J$  = 7.6 Hz,  $J$  = 1.6 Hz, 1 H, H-4), 7.41 (*pseudo* dd,  $J$  = 7.6 Hz,  $J$  = 1.6 Hz, 1 H, H-6), 7.49 (*pseudo* d,  $J$  = 7.6 Hz, 1 H, H-3). –  **$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):**  $\delta$  = 41.16 (q,  $\text{CH}_3$ ), 46.37 (s, C=S), 62.87 (t,  $\text{CH}_2\text{OH}$ ), 120.63 (s, CN), 127.04 (s, C-1), 128.35 (d, C-5), 128.88 (d, C-4), 129.59 (d, C-3), 132.99 (d, C-6), 142.55 (s, C-2). – **IR ( $\text{CHCl}_3$ ):**  $\tilde{\nu}$  = 552  $\text{cm}^{-1}$  (m), 806 (m), 1005 (s), 1022 (s), 1181 (m), 1312 (w), 1382 (w), 1452 (w), 1485 (w), 1565 (w), 2162 (vs, CN), 2930 (w), 3004 (w). – **HR-MS (ESI):**  $m/z$ : 224.0725 [ $\text{M}+\text{H}^+$ , calc.: 224.0740]. –  **$R_f$  (EtOH):** 0.60.

## 8. Characterisation of diazirine 16

**3-Bromo-3-phenyl-3H-diazirine (16):**<sup>[S17]</sup> yellow liquid. –  **$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):**  $\delta$  = 7.12–7.17 (m, 2 H, *o*-Ph), 7.35–7.41 (m, 3 H, *m*-Ph, *p*-Ph). –  **$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):**  $\delta$  = 37.99 (s, CBr), 126.65 (d, *o*-Ph), 128.48 (d, *m*-Ph), 129.37 (d, *p*-Ph), 136.65 (s, *i*-Ph). –  **$R_f$  (*n*-hexane):** 0.70.

## 9. Characterisation of the cyclooctatriazoles 17

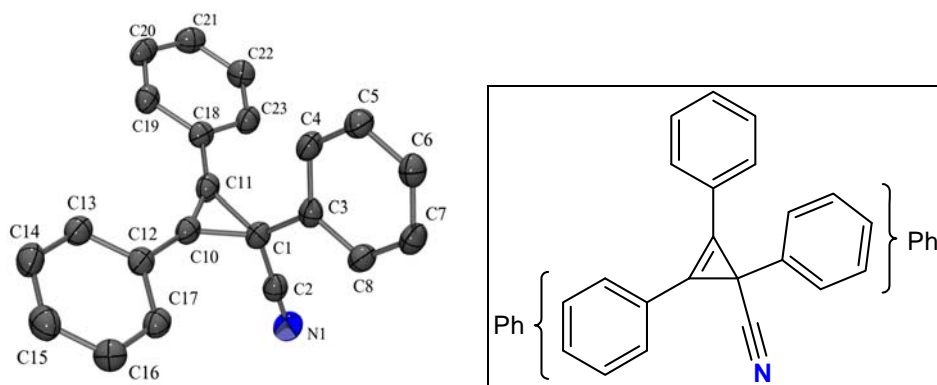


ORTEP plot of 17, H atoms are omitted for clarity.

**1-(2-Phenylethynyl)-4,5,6,7,8,9-hexahydro-1H-cycloocta[d][1,2,3]triazole (17):** white solid. – **mp:** 54–60 °C. –  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 1.47–1.60 (m, 4 H, H-6 and H-7), 1.80 (m, 2 H, H-5), 1.90 (m, 2 H, H-8), 2.96 (m, 4 H, H-4 and H-9), 7.36–7.44 (m, 3 H, *m*-Ph, *p*-Ph), 7.54–7.59 (m, 2 H, *o*-Ph). –  $^1\text{H NMR}$  ( $\text{DMSO}-d_6$ ):  $\delta$  = 1.40–1.51 (m, 4 H), 1.70 (m, 2 H), 1.83 (m, 2 H), 2.89 (m, 2 H), 2.96 (m, 2 H), 7.47–7.54 (m, 3 H, *m*-Ph, *p*-Ph), 7.65–7.69 (m, 2 H, *o*-Ph). –  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 22.10 (t, C-9), 24.28 (t, C-4), 24.72 (t, C-6 or C-7), 25.69 (t, C-8), 25.93 (t, C-6 or C-7), 27.57 (t, C-5), 76.11 (s, Ph–C $\equiv$ C), 78.54 (s, Ph–C $\equiv$ C), 120.55 (s, *i*-Ph), 128.56 (d, *m*-Ph), 129.45 (d, *p*-Ph), 131.81 (d, *o*-Ph), 137.46 (s, C-9a), 142.82 (s, C-3a). Numbering appropriate to IUPAC. –  $^{13}\text{C NMR}$  ( $\text{DMSO}-d_6$ ):  $\delta$  = 21.35 (t), 23.50 (t), 24.16 (t), 25.11 (t), 25.52 (t), 27.34 (t), 75.94 (s), 78.10 (s), 119.53 (s), 129.00 (d), 130.03 (d, *p*-Ph), 131.76 (d), 137.95 (s), 142.27 (s). – **IR** ( $\text{CCl}_4$ ):  $\tilde{\nu}$  = 689  $\text{cm}^{-1}$  (s), 1023 (s), 1264 (s), 1273 (s), 1445 (s), 1456 (m), 2259 (m, –C $\equiv$ C–), 2857 (m), 2935 (s, CH<sub>2</sub>), 3063 (w). – **HR-MS** (ESI):  $m/z$ : 252.1490 [ $\text{M}+\text{H}^+$ , calc.: 252.1495]. – **C<sub>16</sub>H<sub>17</sub>N<sub>3</sub>** (251.33 g/mol): calc. (%): C 76.46, H 6.82, N 16.72; found (%): C 76.30, H 6.52, N 16.63. – **R<sub>f</sub>** ( $\text{Et}_2\text{O}$ ): 0.88. – **Crystal data:** C<sub>16</sub>H<sub>17</sub>N<sub>3</sub>,  $MW$  = 251.33,  $T$  = 100 K,  $\lambda$  = 1.54184 Å, orthorhombic, space group Pbcn,  $a$  = 14.44590(10) Å,  $b$  = 7.55580(10) Å,  $c$  = 24.0084(2) Å,  $\alpha$  = 90°,  $\beta$  = 90°,  $\gamma$  = 90°,  $V$  = 2620.52(4) Å<sup>3</sup>,  $Z$  = 8,  $D$  = 1.274 Mg/m<sup>3</sup>,  $\mu$  = 0.601 mm<sup>−1</sup>,  $F(000)$  = 1072. Crystallographic data for structure **17** have been deposited at the Cambridge Crystallographic Data Center under the number CCDC 766232.

**1-[2-(4-Biphenyl)ethynyl]-4,5,6,7,8,9-hexahydro-1H-cycloocta[d][1,2,3]triazole (17b):** Colourless oil. –  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 1.49–1.60 (m, 4 H, H-6, H-7), 1.81 (m, 2 H, H-5), 1.91 (m, 2 H, H-8), 2.97 (m, 4 H, H-4, H-9), 7.38 (*pseudo* t,  $J$  = 7.2 Hz, 1 H, H-4''), 7.47 (*pseudo* t,  $J$  = 7.2 Hz, 2 H, H-3''), 7.61 (*pseudo* d,  $J$  = 7.2 Hz, 2 H, H-2''), 7.63 (*pseudo* s, 4 H, H-2', H-3'). –  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 22.09 (t, C-9), 24.25 (t, C-4), 24.66 (t, C-6 or C-7), 25.65 (t, C-8), 25.90 (t, C-6 or C-7), 27.54 (t, C-5), 76.62 (s,  $\equiv\text{C}-\text{N}$ ), 78.48 (s,  $\equiv\text{C}-\text{Ar}$ ), 119.28 (s, C-4'), 127.03 (d, C-2' or C-3' or C-2''), 127.20 (d, C-2' or C-3' or C-2''), 127.90 (d, C-4''), 128.90 (d, C-3''), 132.21 (d, C-2' or C-3'), 137.47 (s, C-9a), 139.94 (s, C-1''), 142.20 (s, C-1'), 142.80 (s, C-3a). – **HR-MS** (ESI):  $m/z$ : 328.1821 [ $\text{M}+\text{H}^+$ , calc.: 328.1808]. – **R<sub>f</sub>** ( $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  = 10:1): 0.83.

## 10. Characterisation of cyclopropene 18



ORTEP plot of **18**, H atoms are omitted for clarity.

**3-Cyano-1,2,3-triphenylcycloprop-1-ene (18):**<sup>[7b]</sup> orange-yellow solid. – **mp:** 123–126 °C (ref.<sup>[7b]</sup>: 145–146 °C). –  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 7.26 (*pseudo* t,  $J$  = 7.2 Hz, 1 H, *p*-Ph'), 7.33 (*pseudo* t,  $J$  = 7.2 Hz, 2 H, *m*-Ph'), 7.45 (*pseudo* d,  $J$  = 6.8 Hz, 2 H, *o*-Ph'), 7.47 (*pseudo* t,  $J$  = 6.8 Hz, 2 H, *p*-Ph), 7.50 (*pseudo* t,  $J$  = 6.8 Hz, 4 H, *m*-Ph), 7.72 (*pseudo* d,  $J$  = 6.8 Hz, 4 H, *o*-Ph). Determination of the signal pattern at 7.44–7.52 ppm was realized using irradiation

experiments (HOMODEC pulse sequence). –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 21.46 (s, CCN), 107.79 (s,  $=\text{C}_{\text{Dreiring}}$ ), 121.28 (s, CN), 124.39 (s, *i*-Ph), 125.41 (d, *o*-Ph'), 127.15 (d, *p*-Ph'), 128.68 (d, *m*-Ph'), 129.25 (d, *m*-Ph), 129.97 (d, *o*-Ph), 130.38 (d, *p*-Ph), 136.98 (s, *i*-Ph'). – IR ( $\text{CCl}_4$ ):  $\tilde{\nu}$  = 687  $\text{cm}^{-1}$  (vs), 698 (s), 935 (w), 1310 (w), 1448 (m), 1495 (m), 2226 (w,  $\text{C}\equiv\text{N}$ ), 3031 (w), 3065 (w) und 3085 (w, 3x arom. C–H). –  $\text{C}_{22}\text{H}_{15}\text{N}$  (293.37 g/mol): calc. (%): C 90.07, H 5.15, N 4.78; found (%): C 88.67, H 5.15, N 5.08. – MS (EI):  $m/z$  (%): 293.3 (30.7)  $[\text{M}^+]$ , 77.1 (54.8)  $[\text{Ph}^+]$ , 51.1 (98.2), 39.1 (56.4), 27.1 (100)  $[\text{HCN}]$ . –  $R_f$  ( $\text{Et}_2\text{O}/n\text{-hexane}$  = 1:3): 0.41. – Crystal data (slow evaporation of  $\text{CDCl}_3$ ):  $\text{C}_{22}\text{H}_{15}\text{N}$ ,  $MW$  = 293.35,  $T$  = 105 K,  $\lambda$  = 1.54184 Å, monoclinic, space group C 1 2/c 1,  $a$  = 15.2276(5) Å,  $b$  = 11.8186(4) Å,  $c$  = 19.2336(7) Å,  $\alpha$  = 90°,  $\beta$  = 110.067(4)°,  $\gamma$  = 90°,  $V$  = 3251.31(19) Å<sup>3</sup>,  $Z$  = 8,  $D$  = 1.199  $\text{Mg}/\text{m}^3$ ,  $\mu$  = 0.532  $\text{mm}^{-1}$ ,  $F(000)$  = 1232. Crystallographic data for structure **18** have been deposited at the Cambridge Crystallographic Data Center under the number CCDC 766227.

## 11. Characterisation of heterocycle 23

**1,3-Dihydroisobenzofuran-1-carbonitrile (23)**: orange-yellow solid. – mp: 31–32 °C. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 5.18 (*pseudo* d,  $J$  = 12.4 Hz, 1 H, H-3, diastereotope protons), 5.30 (*pseudo* dd,  $J$  = 12.4 Hz,  $J$  = 2.4 Hz, 1 H, H-3, diastereotope protons), 5.92 (m, 1 H, H-1), 7.31 (*pseudo* d,  $J$  = 8.0 Hz, 1 H, H-4), 7.38–7.45 (m, 3 H, H-5, H-6, H-7). –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 71.28 (d, C-1), 74.22 (t, C-3), 117.51 (s, CN), 121.48 (d, C-4), 121.81 (d), 128.49 (d), 129.66 (d), 134.01 (s), 138.53 (s). – IR ( $\text{CCl}_4$ ):  $\tilde{\nu}$  = 915  $\text{cm}^{-1}$  (m), 1048 (s), 1248 (w), 1356 (w), 1463 (m), 1640 (w), 2214 (w, CN), 2359 (w), 2871 (w,  $\text{CH}_2$ ), 2957 (w), 3084 (w). –  $\text{C}_9\text{H}_7\text{NO}$  (145.16 g/mol): calc. (%): C 74.47, H 4.86, N 9.65; found (%): C 74.53, H 4.92, N 9.58. –  $R_f$  ( $\text{CH}_2\text{Cl}_2$ ): 0.55.

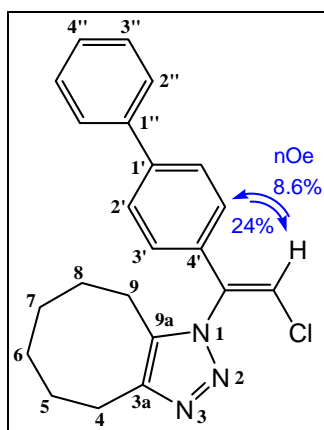
## 12. Characterisation of aldehyde 24

**2-(Chloromethyl)benzaldehyde (24)**:<sup>[16]</sup> pale yellow liquid. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 5.05 (s, 2 H,  $\text{CH}_2\text{Cl}$ ), 7.53 (*pseudo* td,  $J$  = 7.2 Hz,  $J$  = 1.6 Hz, 1 H, H-4 or H-5), 7.56–7.58 (m, 1 H, H-3), 7.61 (*pseudo* td,  $J$  = 7.2 Hz,  $J$  = 1.2 Hz, 1 H, H-4 or H-5), 7.85 (*pseudo* dd,  $J$  = 7.2 Hz,  $J$  = 1.6 Hz, 1 H, H-6), 10.22 (s, 1 H, CHO). –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 42.95 (t,  $\text{CH}_2\text{Cl}$ ), 128.93 (d, C-4 or C-5), 130.73 (d, C-3), 133.25 (s, C-1 or C-2), 133.68 (d, C-6), 134.00 (d, C-4 oder C-5), 138.63 (s, C-1 oder C-2), 192.19 (d, CHO). – IR ( $\text{CCl}_4$ ):  $\tilde{\nu}$  = 682  $\text{cm}^{-1}$  (m), 865 (m), 1195 (m), 1265 (m), 1288 (s), 1308 (m), 1453 (w), 1578 (w), 1601 (m), 1704 (vs, CO), 2738 (m), 2834 (m,  $\text{CH}_2$ ), 3074 (w).

## 13. Characterisation of cyclopropene 26b

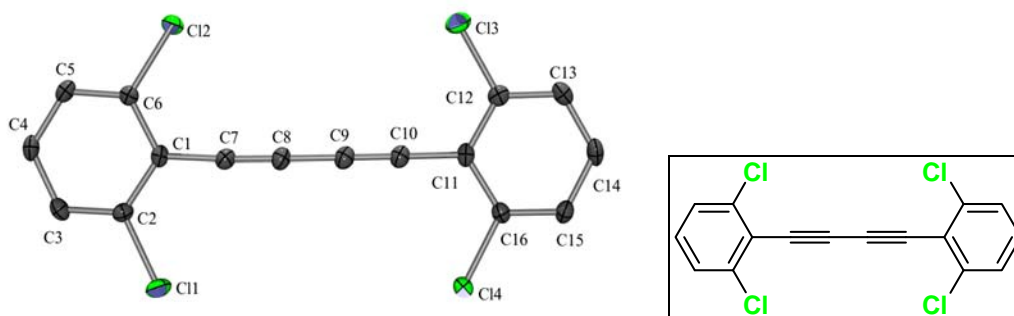
**9-(Propylthio)bicyclo[6.1.0]non-1(8)-en-9-carbonitrile (26b)**: viscous yellow oil. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.01 (*pseudo* t,  $J$  = 7.2 Hz, 3 H, Me), 1.61 (m, 4 H,  $\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 1.66 (*pseudo* qt,  $J_{\text{Me},\text{CH}_2}$  = 7.2 Hz,  $J_{\text{CH}_2,\text{CH}_2}$  = 7.2 Hz, 2 H,  $\text{CH}_2\text{CH}_3$ ), 1.77 (m, 4 H,  $\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 2.44 (m, 4 H,  $\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 2.73 (*pseudo* t,  $J$  = 7.2 Hz, 2 H,  $\text{SCH}_2$ ). –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 13.39 (q, Me), 21.82 (s,  $\text{PrSC}$ ), 23.24 (t,  $\text{CH}_2\text{CH}_3$ ), 23.93 (t,  $\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 24.56 (t,  $\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 26.86 (t,  $\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 34.16 (t,  $\text{SCH}_2$ ), 118.37 (s,  $=\text{C}$ ), 121.24 (s, CN). – IR ( $\text{CCl}_4$ ):  $\tilde{\nu}$  = 1426  $\text{cm}^{-1}$  (m), 1460 (m), 1890 (w), 2218 (m, CN), 2873 (m), 2934 (s,  $\text{CH}_2$ ), 2964 (m). – HR-MS (ESI):  $m/z$ : 222.1314  $[\text{M}+\text{H}^+]$ , calc.: 222.1311]. – MS:  $m/z$  (%): 222.1  $[\text{M}+\text{H}]^+$  ( $\cong 1$ ), 195.1  $[\text{M}-\text{CN}]^+$  ( $\cong 4$ ), 146.1  $[\text{M}-\text{PrS}]^+$  (100 %). –  $\text{C}_{13}\text{H}_{19}\text{NS}$  (221.37 g/mol): calc. (%): C 70.54, H 8.65, N 6.33, S 14.48; found (%): C 70.05, H 8.20, N 6.07, S 14.54. –  $R_f$  ( $\text{Et}_2\text{O}/n\text{-hexane}$ =1:3): 0.51.

#### 14. Characterisation of cyclooctatriazole 15b



**(Z)-1-[1-(4-Biphenyl)-2-chlorovinyl]-4,5,6,7,8,9-hexahydro-1H-cycloocta[d][1,2,3]triazole (15b):** orange solid. – **mp:** 94–95 °C. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.50 (m, 4 H, H-6, H-7), 1.67 (m, 2 H, H-8), 1.83 (m, 2 H, H-5), 2.61 (m, 2 H, H-9), 3.02 (m, 2 H, H-4), 7.09 (s, 1 H,  $\text{CH}_{\text{alkene}}$ ), 7.17 (*pseudo* dt,  $J$  = 8.4 Hz,  $J$  = 2.0 Hz, 2 H, H-3'), 7.35 (*pseudo* t,  $J$  = 7.2 Hz, 1 H, H-4''), 7.43 (*pseudo* t,  $J$  = 7.2 Hz, 2 H, H-3''), 7.54–7.57 (m, 4 H, H-2', H-2''). –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 21.57 (t, C-9), 24.31 (t, C-4), 24.84 (t, C-6 or C-7), 25.78 (t, C-6 or C-7), 26.06 (t, C-8), 27.90 (t, C-5), 119.04 (d, =CCl), 125.48 (d, C-3'), 126.88 (d, C-2' or C-2''), 127.60 (d, C-2' or C-2''), 127.84 (d, C-4''), 128.83 (d, C-3''), 132.46 (s, C-4'), 134.75 (s, C-9a), 137.46 (s, =CAr), 139.64 (s, C-1''), 142.50 (s, C-1'), 144.47 (s, C-3a). – **IR** ( $\text{CCl}_4$ ):  $\tilde{\nu}$  = 696  $\text{cm}^{-1}$  (s), 840 (m), 1242 (m), 1446 (m), 1456 (m), 1488 (m), 1615 (m), 2361 (w), 2856 (s) and 2933 (vs,  $\text{CH}_2$ ), 3033 (w) and 3084 (w, =C–H). – **HR-MS** (ESI):  $m/z$ : 364.1594 [ $\text{M}+\text{H}^+$ , calc.: 364.1575]. –  **$\text{C}_{22}\text{H}_{22}\text{N}_3\text{Cl}$  (363.89 g/mol):** calc. (%): C 72.62, H 6.09, N 11.55; found (%): C 72.74, H 6.15, N 11.44. –  **$R_f$  ( $\text{Et}_2\text{O}/n\text{-Hexan}$  = 1:1):** 0.33.

#### 15. Characterisation of side-product S2d

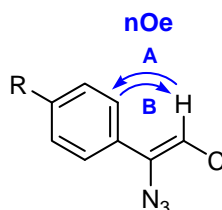


ORTEP plot of S2d, H atoms are omitted for clarity.

**1,4-Bis(2,6-dichlorophenyl)-buta-1,3-diyne (S2d):** Pale yellow solid. – **mp:** 191–195 °C. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 7.23 (t,  $^3J$  = 8.0 Hz, 1 H,  $\text{CHCHCCl}$ ), 7.35 (d,  $^3J$  = 8.0 Hz, 2 H,  $\text{CHCCl}$ ). –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 77.76 (s,  $\text{ArC}\equiv$ ), 82.90 (s,  $\equiv\text{C}$ ), 121.96 (s,  $\equiv\text{CC}$ ), 127.67 (d,  $\text{CHCCl}$ ), 130.10 (d,  $\text{CHCHCCl}$ ), 138.55 (s, CCl). – **IR** ( $\text{CHCl}_3$ ):  $\tilde{\nu}$  = 877  $\text{cm}^{-1}$  (m), 1046 (s), 1431 (s), 1553 (m), 2156 (w,  $\text{C}\equiv\text{C}$ ). –  **$\text{C}_{16}\text{H}_6\text{Cl}_4$  (340.04 g/mol):** calc. (%): C 56.52, H 1.78; found (%): C 56.43, H 2.02. –  **$R_f$  ( $n\text{-hexane}$ ):** 0.30. – **Crystal data:**  $\text{C}_{16}\text{H}_6\text{Cl}_4$ ,  $MW$  = 340.01,  $T$  = 110 K,  $\lambda$  = 0.71073 Å, monoclinic, space group  $P1\ 21/n\ 1$ ,  $a$  = 8.0811(2) Å,  $b$  = 13.0846(4) Å,  $c$  = 13.8754(4) Å,  $\alpha$  = 90°,  $\beta$  = 103.347(3)°,  $\gamma$  = 90°,  $V$  = 1427.53(7) Å<sup>3</sup>,  $Z$  = 4,  $D$  = 1.582  $\text{Mg/m}^3$ ,  $\mu$  = 0.813  $\text{mm}^{-1}$ ,  $F(000)$  = 680. Crystallographic data for structure S2d

have been deposited at the Cambridge Crystallographic Data Center under the number CCDC 766229.

### 16. Characterisation of the vinyl azides S3

			
		<b>A</b>	<b>B</b>
	<b>a</b> R = CH <sub>3</sub>	1.0 %	3.5 %
	<b>a</b> R = Ph	1.9 %	3.8 %
	<b>a</b> R = Cl	2.1 %	6.7 %

**(Z)-1-(1-Azido-2-chlorovinyl)-4-methylbenzene (S3a):** yellow liquid. – <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 2.39 (s, 3 H, Me), 5.75 (s, 1 H, =C(Cl)H), 7.23 (*pseudo* d, *J* = 8.4 Hz, 2 H, MeCCH), 7.28 (*pseudo* d, *J* = 8.4 Hz, 2 H, MeCCHCH). – <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 21.22 (q, Me), 105.15 (d, =C(Cl)H), 126.93 (d, MeCCHCH), 129.57 (d, MeCCH), 129.64 (s, CMe), 139.11 (s, =C(N<sub>3</sub>)C<sub>Ar</sub>), 139.37 (s, =C(Ar)N<sub>3</sub>). – IR (CDCl<sub>3</sub>):  $\tilde{\nu}$  = 512 cm<sup>-1</sup> (w), 797 (m), 813 (s), 847 (m), 1211 (m), 1225 (m), 1241 (m), 1280 (w), 1320 (s), 1510 (m), 1609 (m), 2130 (vs, N<sub>3</sub>), 2925 (w, CH<sub>3</sub>), 3032 (vw), 3095 (vw). – C<sub>9</sub>H<sub>8</sub>ClN<sub>3</sub> (193.64 g/mol): calc. (%): C 55.83, H 4.16, N 21.70; found (%): C 56.15, H 4.23, N 21.76. – MS (EI): *m/z* (%): 165 [M<sup>+</sup>–N<sub>2</sub>] (87), 130 (69), 103 (100), 91 (52), 65 (56), 51 (58).

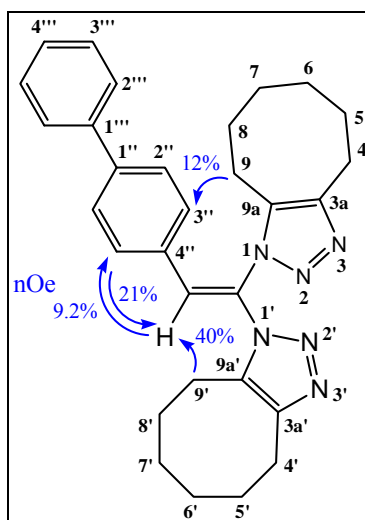
**(Z)-1-(4-Biphenyl)-2-chlorovinyl azide (S3b):** white solid. – mp: 97–99 °C. – <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 5.89 (s, 1 H, =C(Cl)H), 7.39 (*pseudo* t, *J* = 7.2 Hz, 1 H, H-4'), 7.47 (*pseudo* d, *J* = 8.4 Hz, 2 H, H-3), overlaying 7.47 (m, 2 H, H-3'), 7.61 (*pseudo* d, *J* = 7.2 Hz, 2 H, H-2'), 7.65 (*pseudo* d, *J* = 8.4 Hz, 2 H, H-2). – <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 106.07 (d, =C(Cl)H), 127.05 (d, C-2'), 127.38 (d, C-3 or C-3'), 127.59 (d, C-2), 127.86 (d, C-4'), 128.90 (d, C-3 or C-3'), 131.45 (s, C-4), 138.82 (s, =CN<sub>3</sub>), 139.91 (s, C-1'), 142.58 (s, C-1). – IR (CCl<sub>4</sub>):  $\tilde{\nu}$  = 696 cm<sup>-1</sup> (m), 857 (m), 1225 (w), 1323 (s), 1487 (m), 1606 (w), 2120 (vs, N<sub>3</sub>), 3033 (w) and 3091 (w, =C–H). – C<sub>14</sub>H<sub>10</sub>ClN<sub>3</sub> (255.71 g/mol): calc. (%): C 65.76, H 3.94, N 16.43; found (%): C 66.14, H 4.08, N 16.10. – R<sub>f</sub> (*n*-hexane): 0.17.

**(Z)-1-(4-Chlorophenyl)-2-chlorovinyl azide (S3c):** Pale yellow liquid. – <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 5.87 (s, 1 H, vinyl-H), 7.34 (*pseudo* d, *J* = 8.8 Hz, 2 H, ClCCHCH), 7.40 (*pseudo* d, *J* = 8.8 Hz, 2 H, ClCCH). – <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 106.77 (d, =C(Cl)H), 128.22 (d, ClCCHCH), 129.23 (d, ClCCH), 131.14 (s, ClCCHCHC), 135.84 (s, ClC), 138.01 (s, CN<sub>3</sub>). – IR (CCl<sub>4</sub>):  $\tilde{\nu}$  = 853 cm<sup>-1</sup> (w), 1321 (m), 1490 (w), 2118 (s, N<sub>3</sub>), 3089 (w). – R<sub>f</sub> (*n*-hexane): 0.48.

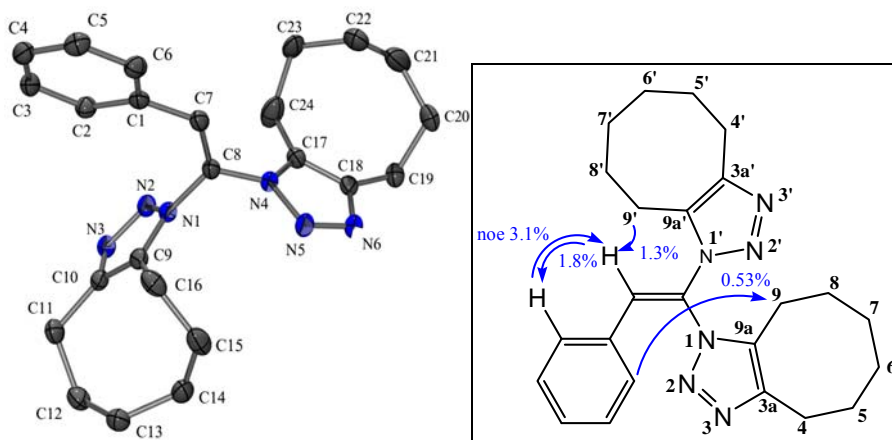
**2-(1-Azido-2-chlorovinyl)benzyl alcohol (S3h):** colourless viscous oil. – <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.77 (s, 1 H, OH), 4.74 (s, 2 H, CH<sub>2</sub>OH), 5.58 (s, 1 H, =C(Cl)H), 7.30 (*pseudo* dd, *J* = 7.2 Hz, *J* = 1.6 Hz, 1 H, H-3), 7.39 (*pseudo* td, *J* = 7.2 Hz, *J* = 1.6 Hz, 1 H, H-4), 7.48 (*pseudo* td, *J* = 7.6 Hz, *J* = 1.2 Hz, 1 H, H-5), 7.58 (*pseudo* dm, *J* = 7.6 Hz, 1 H, H-6). – <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 62.62 (t, CH<sub>2</sub>OH), 105.67 (d, =C(Cl)H), 128.21 (d, C-4), 128.79 (d, C-6), 129.98 (d, C-3), 130.47 (d, C-5), 130.94 (s, C-2), 137.62 (s, =CN<sub>3</sub>), 139.45 (s, C-1). – R<sub>f</sub> (Et<sub>2</sub>O/*n*-Hexan=1:3): 0.10. The compound was significantly less stable compared to analogue structures and decomposed completely during the NMR measurement overnight (at room temperature). For that reason no complete characterisation data of this side-product can be given.



## 17. Characterisation of the bis(cyclooctatriazoles) S4 and S6



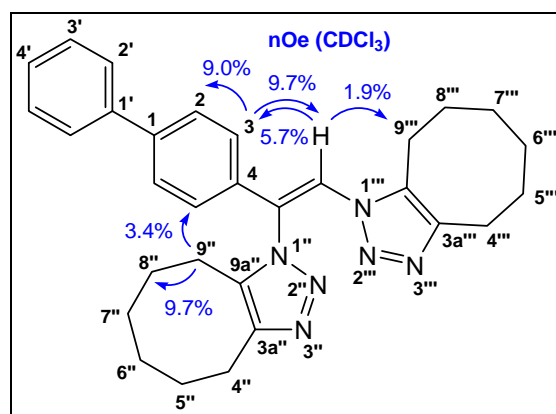
**1,1-Bis(4,5,6,7,8,9-hexahydro-1H-cycloocta[d]triazole-1-yl)-2-(4-biphenyl)ethene (S4b):** Colourless viscous oil. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.34–1.48 (m, 10 H, H-6, H-6', H-7, H-7', H-8), 1.57 (m, 2 H, H-8'), 1.77 (m, 4 H, H-5, H-5'), 2.73 (m, 2 H, H-9), 2.83 (m, 2 H, H-9'), 2.92 (m, 2 H, H-4'), 2.97 (m, 2 H, H-4), 6.91 (*pseudo* d,  $J$  = 8.4 Hz, 2 H, H-3''), 7.24 (s, 1 H, =CH<sub>Alken</sub>), 7.36 (*pseudo* t,  $J$  = 7.6 Hz, 1 H, H-4''), 7.43 (*pseudo* t,  $J$  = 7.6 Hz, 2 H, H-3''), 7.50 (*pseudo* d,  $J$  = 8.4 Hz, 2 H, H-2''), 7.54 (*pseudo* d,  $J$  = 7.6 Hz, 2 H, H-2''). –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 21.47 (t, C-9), 21.58 (t, C-9'), 24.32 (t, C-4), 24.36 (t, C-4'), 24.75 (t, C-6 or C-6' or C-7 or C-7'), 24.95 (t, C-6 or C-6' or C-7 or C-7'), 25.62 (t, C-6 or C-6' or C-7 or C-7'), 25.65 (t, C-6 or C-6' or C-7 or C-7'), 25.79 (t, C-8), 26.45 (t, C-8'), 27.67 (t, C-5), 28.02 (t, C-5'), 124.49 (s, =C(Cot)<sub>2</sub>), 126.96 (d, C-2''), 127.54 (d, C-2'), 127.98 (d, C-4''), 128.87 (d, C-3''), 129.42 (s, C-4'), 129.67 (d, C-3'), 131.28 (d, =CH<sub>Alken</sub>), 135.33 (s, C-9a), 135.36 (s, C-9a'), 139.67 (s, C-1''), 143.02 (s, C-1'), 145.23 (s, C-3a'), 145.54 (s, C-3a). Numbering according to IUPAC. Assignment is based on C-3a lying at lowest field.<sup>[S18]</sup> – IR ( $\text{CCl}_4$ ):  $\tilde{\nu}$  = 696  $\text{cm}^{-1}$  (s), 928 (m), 1052 (m), 1247 (m), 1315 (m), 1397 (m), 1445 (s), 1457 (s), 1487 (m), 1606 (w), 2856 (s) und 2933 (vs,  $\text{CH}_2$ ). – HR-MS (ESI):  $m/z$ : 479.2918 [ $\text{M}+\text{H}^+$ , calc.: 479.2918]. –  $R_f$  ( $\text{CHCl}_3/\text{Et}_2\text{O}$  = 1:1): 0.79. Several attempts to crystallise the compound failed.



ORTEP plot of S4i, H atoms are omitted for clarity.

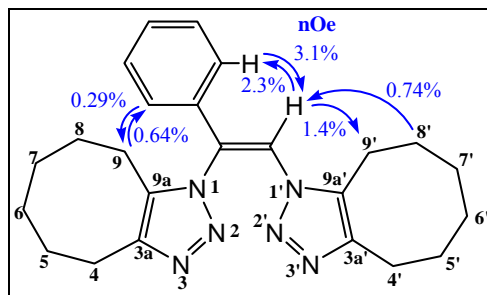
**1,1-Bis(4,5,6,7,8,9-hexahydro-1H-cycloocta[d][1,2,3]triazole-1-yl)-2-phenylethene (S4i):** white solid. – mp: 140–143 °C. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.35 (m, 4 H, H-6, H-7), 1.43 (m,

6 H, H-6', H-7', H-8), 1.57 (m, 2 H, H-8'), 1.76 (m, 4 H, H-5, H-5'), 2.70 (m, 2 H, H-9), 2.83 (m, 2 H, H-9'), 2.91 (m, 2 H, H-4'), 2.95 (m, 2 H, H-4), 6.84–6.87 (m, 2 H, *o*-Ph), 7.21 (s, 1 H, PhCH), 7.25–7.38 (m, 3 H, *m*-Ph, *p*-Ph). –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 21.47 (t, C-9), 21.60 (t, C-9'), 24.32 (t, C-4), 24.38 (t, C-4'), 24.75 (t, C-6 or C-7), 24.97 (t, C-6' or C-7'), 25.63 (t, C-6 or C-7), 25.67 (t, C-6' or C-7' or C-8), 25.78 (t, C-6' or C-7' or C-8), 26.47 (t, C-8'), 27.68 (t, C-5), 28.03 (t, C-5'), 124.76 (s, =C(Cot)<sub>2</sub>), 129.01 (d, *m*-Ph), 129.18 (d, *o*-Ph), 130.38 (d, *p*-Ph), 130.57 (s, *i*-Ph), 131.69 (d, PhCH), 135.27 (s, C-9a'), 135.33 (s, C-9a), 145.23 (s, C-3a'), 145.48 (s, C-3a). – IR ( $\text{CCl}_4$ ):  $\tilde{\nu}$  = 690  $\text{cm}^{-1}$  (w), 1247 (w), 1457 (m), 2856 (m), 2933 (s). – HR-MS (ESI):  $m/z$ : 403.2587 [ $\text{M}+\text{H}^+$ , calc.: 403.2605]. –  $\text{C}_{24}\text{H}_{30}\text{N}_6$  (402.54 g/mol): calc. (%): C 71.61, H 7.51, N 20.88; found (%): C 71.68, H 7.14, N 20.81. –  $R_f$  ( $\text{Et}_2\text{O}/n\text{-hexane}=5:1$ ): 0.45. – Crystal data (slow evaporation of  $\text{CDCl}_3$  at ambient temperature):  $\text{C}_{24}\text{H}_{30}\text{N}_6$ ,  $MW = 402.54$ ,  $T = 100$  K,  $\lambda = 1.54184$  Å, triclinic, space group P-1,  $a = 8.2407(19)$  Å,  $b = 9.125(2)$  Å,  $c = 14.745(5)$  Å,  $\alpha = 94.66(2)^\circ$ ,  $\beta = 103.07^\circ$ ,  $\gamma = 95.21(2)^\circ$ ,  $V = 1069.6(5)$  Å<sup>3</sup>,  $Z = 2$ ,  $D = 1.250$  Mg/m<sup>3</sup>,  $\mu = 0.601$  mm<sup>-1</sup>,  $F(000) = 432$ . Crystallographic data for structure **S4i** have been deposited at the Cambridge Crystallographic Data Center under the number CCDC 767175.



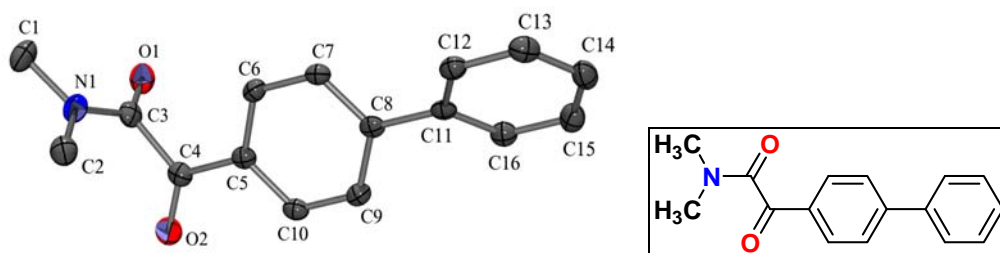
(*Z*)-1,2-Bis(4,5,6,7,8,9-hexahydro-1*H*-cycloocta[*d*][1,2,3]triazole-1-yl)-1-(4-biphenyl)-ethene (**S6b**): orange solid. – mp: 73–76 °C. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.42 (m, 2 H, H-6'' or H-6'''), 1.48 (m, 6 H, H-7'', H-7''', H-6'' or H-6'''), 1.63 (m, 2 H, H-8''), 1.69 ("quint",  $J = 6.4$  Hz, 2 H, H-5''), 1.76 ("quint",  $J = 6.4$  Hz, 2 H, H-5'''), 1.85 ("quint",  $J = 6.4$  Hz, 2 H, H-8'''), 2.60 ("t",  $J = 6.0$  Hz, 2 H, H-9''), 2.81 ("t",  $J = 6.4$  Hz, 2 H, H-9'''), 2.83 ("t",  $J = 6.4$  Hz, 2 H, H-4''), 2.93 ("t",  $J = 6.4$  Hz, 2 H, H-4'''), 7.29 ("d",  $J = 8.0$  Hz, 2 H, H-3), 7.36 ("t",  $J = 7.6$  Hz, 1 H, H-4'), 7.44 ("t",  $J = 7.6$  Hz, 2 H, H-3'), 7.49 (s, 1 H, vinyl-H), 7.58 ("d",  $J = 8.0$  Hz, 2 H, H-2'), 7.62 ("d",  $J = 8.0$  Hz, 2 H, H-2). –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 21.80 (t, C-9'''), 21.98 (t, C-9''), 24.19 (t, C-4''), 24.21 (t, C-4'''), 24.33 (t, C-6''), 24.39 (t, C-6'''), 25.48 (t, C-8''), 25.61 (t, C-8'''), 25.97 (t, C-7'''), 26.00 (t, C-7''), 27.75 (t, C-5'''), 27.88 (t, C-5''), 118.70 (d, vinyl-CH), 126.35 (d, C-3), 126.94 (d, C-2'), 127.71 (d, C-2), 127.98 (d, C-4'), 128.88 (d, C-3'), 132.45 (s, C-4), 133.33 (s, =CBiphenyl), 134.80 (s, C-9a''), 136.13 (s, C-9a'''), 139.55 (s, C-1'), 143.20 (s, C-1), 143.92 (s, C-3a''), 144.55 (s, C-3a'''). – IR ( $\text{CCl}_4$ ):  $\tilde{\nu}$  = 696  $\text{cm}^{-1}$  (s), 909 (s), 1048 (m), 1243 (m), 1267 (m), 1379 (m), 1445 (s), 1457 (s), 1471 (m), 1488 (m), 2855 (s, CH<sub>2</sub>), 2931 (vs, CH<sub>2</sub>), 3033 (w, =CH), 3062 (w, =CH). – HR-MS (ESI):  $m/z$ : 479.2858 [ $\text{M}+\text{H}^+$ , calc.: 479.2919]. –  $R_f$  (diethyl ether): 0.38.





**1,2-Bis(4,5,6,7,8,9-hexahydro-1H-cycloocta[d][1,2,3]triazole-1-yl)-1-phenylethene (S6i):** white fluffy solid. – **mp:** 64–66 °C. – **<sup>1</sup>H NMR (CDCl<sub>3</sub>):**  $\delta$  = 1.39–1.54 (m, 8 H, H-6, H-6', H-7, H-7'), 1.60 (m, 2 H, H-8), 1.70 (m, 2 H, H-5'), 1.75 (m, 2 H, H-5), 1.85 (m, 2 H, H-8'), 2.56 (m, 2 H, H-9), 2.81 (m, 2 H, H-9'), 2.84 (m, 2 H, H-4'), 2.91 (m, 2 H, H-4), 7.22–7.25 (m, 2 H, *o*-Ph), 7.39–7.47 (m, 4 H, *m*-Ph, *p*-Ph) overlaying 7.42 (s, 1 H, CH<sub>alkene</sub>). – **<sup>13</sup>C NMR (CDCl<sub>3</sub>):**  $\delta$  = 21.83 (t, C-9'), 21.95 (t, C-9), 24.24 (t, C-4'), 24.26 (t, C-4), 24.37 (t, C-6 or C-6' or C-7 or C-7'), 24.44 (t, C-6 or C-6' or C-7 or C-7'), 25.52 (t, C-8), 25.65 (t, C-8'), 25.98 (t, C-6 or C-6' or C-7 or C-7'), 26.04 (t, C-6 or C-6' or C-7 or C-7'), 27.80 (t, C-5), 27.92 (t, C-5'), 118.97 (d, CH<sub>Alken</sub>), 126.00 (d, *o*-Ph), 129.17 (d, *m*-Ph), 130.47 (d, *p*-Ph); 133.72 (s, *i*-Ph oder PhC), 133.88 (s, *i*-Ph oder PhC), 134.78 (s, C-9a'), 136.07 (s, C-9a), 143.97 (s, C-3a'), 144.58 (s, C-3a). Assignment of the methylene signals to the two eight-membered rings was realized by TOCSY spectrum and nOe irradiating experiments. – **IR (CCl<sub>4</sub>):**  $\tilde{\nu}$  = 692 cm<sup>-1</sup> (m), 1457 (m), 2855 (m), 2933 (s), 3066 (w). – **HR-MS (ESI):** *m/z*: 403.2592 [M+H<sup>+</sup>, calc.: 403.2605]. – **C<sub>24</sub>H<sub>30</sub>N<sub>6</sub> (402.54 g/mol):** calc. (%): C 71.61, H 7.51, N 20.88; found (%): C 70.01, H 7.01, N 19.96. The large differences between calculated and measured values might be caused by complexation of solvent molecules due to the *cis*-connected triazole rings. – **R<sub>f</sub> (Et<sub>2</sub>O):** 0.24.

### 18. Characterisation of the $\alpha$ -oxo amides S5



ORTEP plot of S5b, H atoms are omitted for clarity.

**N,N-Dimethyl-2-oxo-2-(4-biphenyl)acetamide (S5b):** white solid. – **mp:** 109–111 °C. – **<sup>1</sup>H NMR (CDCl<sub>3</sub>):**  $\delta$  = 2.99 (s, 3 H, Me), 3.14 (s, 3 H, Me), 7.42 (*pseudo t*, *J* = 7.2 Hz, 1 H, H-4''), 7.48 (*pseudo t*, *J* = 7.2 Hz, 2 H, H-3''), 7.63 (*pseudo d*, *J* = 7.2 Hz, 2 H, H-2''), 7.72 (*pseudo d*, *J* = 8.8 Hz, 2 H, H-2'), 8.02 (*pseudo d*, *J* = 8.8 Hz, 2 H, H-3'). – **<sup>13</sup>C NMR (CDCl<sub>3</sub>):**  $\delta$  = 34.00 (q, Me), 37.07 (q, Me), 127.31 (d, C-2''), 127.61 (d, C-2'), 128.54 (d, C-4''), 128.99 (d, C-3''), 130.22 (d, C-3'), 131.72 (s, C-4'), 139.51 (s, C-1''), 147.39 (s, C-1'), 167.02 (s, C-1), 191.34 (s, C-2). – **IR (CDCl<sub>3</sub>):**  $\tilde{\nu}$  = 696 (m), 853 (m), 884 (m), 993 (m), 1145 (m), 1253 (m), 1275 (m), 1404 (m), 1604 (m), 1656 (s) und 1682 (s, C=O), 2934 (w), 3033 (w) and 3063 (w, =C–H), 3461 (br.). – **HR-MS (ESI):** *m/z*: 254.1242 [M+H<sup>+</sup>, calc.: 254.1176]. – **C<sub>16</sub>H<sub>15</sub>NO<sub>2</sub> (253.30 g/mol):** calc. (%): C 75.87, H 5.97, N 5.53, O 12.63; found (%): C 75.49, H 5.99, N 5.73. – **R<sub>f</sub> (CHCl<sub>3</sub>/Et<sub>2</sub>O = 1:1):** 0.66. – **Crystal data:** C<sub>16</sub>H<sub>15</sub>NO<sub>2</sub>,

$MW = 253.29$ ,  $T = 100\text{ K}$ ,  $\lambda = 1.54184\text{ \AA}$ , monoclinic, space group  $P2(1)/n$ ,  $a = 6.14680(10)\text{ \AA}$ ,  $b = 6.99200(10)\text{ \AA}$ ,  $c = 30.0286(4)\text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 91.2010(10)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 1290.30(3)\text{ \AA}^3$ ,  $Z = 4$ ,  $D = 1.304\text{ Mg/m}^3$ ,  $\mu = 0.691\text{ mm}^{-1}$ ,  $F(000) = 536$ . Crystallographic data for structure **S5b** have been deposited at the Cambridge Crystallographic Data Center under the number CCDC 766235.

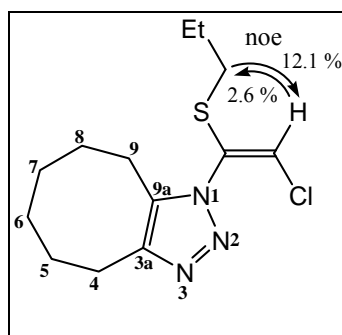
***N,N*-Dimethyl-2-oxo-2-phenylacetamide (S5i):**<sup>[S19]</sup> Colourless viscous oil. – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 2.97$  (s, 3 H, NMe), 3.13 (s, 3 H, NMe), 7.51 (*pseudo* t,  $J = 7.6\text{ Hz}$ , 2 H, *m*-Ph), 7.65 (*pseudo* t,  $J = 7.6\text{ Hz}$ , 1 H, *p*-Ph), 7.95 (*pseudo* d,  $J = 7.6\text{ Hz}$ , 2 H, *o*-Ph). – <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 34.01$  (q, Me), 37.06 (q, Me), 129.00 (d, *m*-Ph), 129.66 (d, *o*-Ph), 133.05 (s, *i*-Ph), 134.71 (d, *p*-Ph), 167.02 (s, CONMe<sub>2</sub>), 191.77 (s, C=O). – IR (CCl<sub>4</sub>):  $\tilde{\nu} = 1656$  (s), 1684 (m), 2932 (w). – MS (ESI):  $m/z$  (%): 178.1 [M+H<sup>+</sup>], 355.2 [2M+H<sup>+</sup>]. –  $R_f(\text{Et}_2\text{O}/n\text{-hexane}=5:1)$ : 0.36.

### 19. Characterisation of cyclopropene **S7b**

**9-(4-Biphenyl)bicyclo[6.1.0]non-1(8)-en-9-carbonitrile (15b):** yellow viscous oil. – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.76$  (m, 4 H, H-4, H-5 diastereotope protons), 1.88 (m, 4 H, H-3, H-6 diastereotope protons), 2.39–2.56 (m, 4 H, H-2, H-7 diastereotope protons), 7.32 (*pseudo* d,  $J = 8.4\text{ Hz}$ , 2 H, H-3'), 7.35 (*pseudo* t,  $J = 7.2\text{ Hz}$ , 1 H, H-4''), 7.44 (*pseudo* t,  $J = 7.2\text{ Hz}$ , 2 H, H-3''), 7.55–7.58 (m, 4 H, H-2', H-2''). – <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 22.86$  (t, C-2, C-7), 23.93 (s, C(CN)), 25.32 (t, C-3, C-6), 27.37 (t, C-4, C-5), 112.88 (s, =CCH<sub>2</sub>), 122.73 (s, CN), 125.68 (d, C-3'), 127.01 (d, C-2' oder C-2''), 127.27 (d, C-2' oder C-2''), 127.31 (d, C-4''), 128.80 (d, C-3''), 138.20 (s, C-1' oder C-4'), 139.68 (s, C-1' oder C-4'), 140.54 (s, C-1''). Both the nitrile carbon as well as the sp<sup>3</sup> carbon of the three-membered ring have proved to be very low in intensity. No significant nOe effects between the phenyl protons and the methylene protons have been found. – IR (CCl<sub>4</sub>):  $\tilde{\nu} = 696\text{ cm}^{-1}$  (m), 1487 (m), 1707 (w), 2224 (w), 2341 und 2359 (s, CN), 2934 (s). – MS (ESI):  $m/z$ : 301.1 [M+H<sup>+</sup>]. –  $R_f(\text{CHCl}_3/n\text{-hexane}=1:2)$ : 0.08.

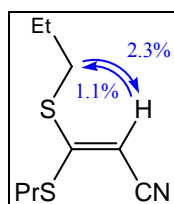
### 20. Characterisation of the thiopropyl compounds **S8–S15**

**2,2-Dichlorovinyl propyl thioether (S8):**<sup>[S20]</sup> Colourless liquid. – <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 12.98$  (q, Me), 23.72 (t, MeCH<sub>2</sub>), 35.82 (t, SCH<sub>2</sub>), 113.71 (s), 126.09 (s).

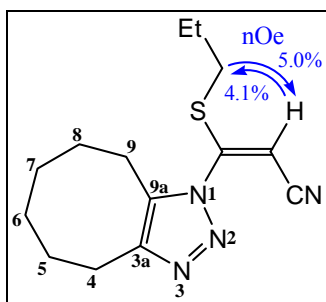


**(E)-1-[2-Chloro-1-(propylthio)vinyl]-4,5,6,7,8,9-hexahydro-1H-cycloocta[d][1,2,3]triazole (S11):** foul-smelling orange viscous oil. – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 0.95$  (*pseudo* t,  $J = 7.2\text{ Hz}$ , 3 H, Me), 1.43–1.55 (m, 4 H, H-6, H-7), 1.64 (*pseudo* qt,  $J_{\text{Me,CH}_2} = 7.2\text{ Hz}$ ,  $J_{\text{CH}_2,\text{CH}_2} = 7.2\text{ Hz}$ , 2 H, CH<sub>3</sub>CH<sub>2</sub>), 1.76 (m, 2 H, H-5), 1.84 (m, 2 H, H-8), 2.68 (*pseudo* t,  $J = 7.2\text{ Hz}$ , 2 H, SCH<sub>2</sub>), 2.77 (m, 2 H, H-9), 2.92 (m, 2 H, H-4), 6.74 (s, 1 H, =C(Cl)H). – <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 12.85$  (q, Me), 21.49 (t, C-9), 23.54 (t, MeCH<sub>2</sub>), 24.21 (t, C-4), 24.79 (t, C-6),

25.75 (t, C-7), 26.16 (t, C-8), 27.76 (t, C-5), 36.14 (t, SCH<sub>2</sub>), 114.61 (s, =CSP<sub>rop</sub>), 131.39 (d, =C(Cl)H), 134.32 (s, C-9a), 144.28 (s, C-3a). – **IR (CCl<sub>4</sub>)**:  $\tilde{\nu}$  = 918 cm<sup>-1</sup> (s), 1457 (m), 2856 (m), 2934 (s), 2965 (m). – **HR-MS (ESI)**:  $m/z$ : 286.1105 [M+H<sup>+</sup>, calc.: 286.1139]. – **R<sub>f</sub> (Et<sub>2</sub>O/*n*-hexane = 6:1)**: 0.69.



**3,3-Bis(propylthio)acrylnitrile (S12)**: orange liquid. – **<sup>1</sup>H NMR (CDCl<sub>3</sub>)**:  $\delta$  = 1.03 (*pseudo* t,  $J$  = 7.2 Hz, 3 H, *E*-Me), 1.04 (*pseudo* t,  $J$  = 7.2 Hz, 3 H, *Z*-Me), 1.65–1.76 (m, 4 H, *E*-CH<sub>2</sub>CH<sub>3</sub>, *Z*-CH<sub>2</sub>CH<sub>3</sub>), 2.86 (*pseudo* t,  $J$  = 7.2 Hz, 2 H, *E*-SCH<sub>2</sub>), 3.01 (*pseudo* t,  $J$  = 7.2 Hz, 2 H, *Z*-SCH<sub>2</sub>), 5.19 (s, 1 H, =CH). The geminal constitution of the propylthio-substituents was confirmed by <sup>3</sup> $J$  coupling of the SCH<sub>2</sub> protons to the same alkene carbon (gHMBC pulse sequence). – **<sup>13</sup>C NMR (CDCl<sub>3</sub>)**:  $\delta$  = 13.12 (q, *Z*-Me), 13.42 (q, *E*-Me), 21.33 (t, *E*-CH<sub>2</sub>CH<sub>3</sub>), 23.03 (t, *Z*-CH<sub>2</sub>CH<sub>3</sub>), 35.82 (t, SCH<sub>2</sub>), 35.97 (t, SCH<sub>2</sub>), 90.60 (d, =CH), 116.45 (s, CN), 162.58 (s, =C(SPr)<sub>2</sub>). – **IR (CCl<sub>4</sub>)**:  $\tilde{\nu}$  = 1460 cm<sup>-1</sup> (m), 1535 (m), 1643 (w), 2211 (s, CN), 2875 (w), 2934 (m), 2968 (s, CH<sub>2</sub>). – **HR-MS (ESI)**:  $m/z$ : 202.0727 [M+H<sup>+</sup>, calc.: 202.0719]. – **C<sub>9</sub>H<sub>15</sub>NS<sub>2</sub> (201.34 g/mol)**: calc. (%): C 53.69, H 7.51, N 6.96, S 31.84; found (%): C 54.22, H 7.18, N 6.53, S 30.82. – **R<sub>f</sub> (Et<sub>2</sub>O/*n*-hexane=1:3)**: 0.41.



**(*E*)-1-[2-Cyano-1-(propylthio)vinyl]-4,5,6,7,8,9-hexahydro-1*H*-cycloocta[*d*][1,2,3]triazole (S13)**: orange-brown oil. – **<sup>1</sup>H NMR (CDCl<sub>3</sub>)**:  $\delta$  = 1.02 (*pseudo* t,  $J$  = 7.2 Hz, 3 H, Me), 1.46–1.57 (m, 4 H, H-6, H-7), 1.73 (*pseudo* qt,  $J_{Me,CH_2}$  = 7.2 Hz,  $J_{CH_2,CH_2}$  = 7.2 Hz, 2 H, MeCH<sub>2</sub>), 1.79 (m, 2 H, H-5), 1.85 (m, 2 H, H-8), 2.70 (*pseudo* t,  $J$  = 7.2 Hz, 2 H, SCH<sub>2</sub>), 2.84 (m, 2 H, H-9), 2.95 (m, 2 H, H-4), 5.59 (s, 1 H, =CH). – **<sup>13</sup>C NMR (CDCl<sub>3</sub>)**:  $\delta$  = 13.28 (q, Me), 21.48 (t, MeCH<sub>2</sub>), 21.77 (t, C-9), 24.23 (t, C-4), 24.83 (t, C-6), 25.65 (C-7), 26.54 (C-8), 27.77 (C-5), 34.90 (SCH<sub>2</sub>), 94.15 (d, =CH), 113.45 (s, CN), 134.55 (s, C-9a), 145.23 (s, C-3a), 154.90 (=CSP<sub>rop</sub>). – **IR (CCl<sub>4</sub>)**:  $\tilde{\nu}$  = 942 cm<sup>-1</sup> (m), 1382 (m), 1444 (m), 1453 (m), 1592 (m), 2221 (m, CN), 2857 (m), 2934 (s), 2966 (m). – **HR-MS (ESI)**:  $m/z$ : 277.1515 [M+H<sup>+</sup>, calc.: 277.1481]. – **R<sub>f</sub> (Et<sub>2</sub>O/*n*-hexane = 3:1)**: 0.43.

**4-Cyano-5-propylthio-1*H*-1,2,3-triazole (S14)**: brown foul-smelling oil. – **<sup>1</sup>H NMR (CDCl<sub>3</sub>)**:  $\delta$  = 1.04 (*pseudo* t,  $J$  = 7.2 Hz, 3 H, Me), 1.73 (*pseudo* qt,  $J_{Me,CH_2}$  = 7.2 Hz,  $J_{CH_2,CH_2}$  = 7.2 Hz, 2 H, CH<sub>2</sub>CH<sub>2</sub>), 3.10 (*pseudo* t,  $J$  = 7.2 Hz, 2 H, SCH<sub>2</sub>), 11.18 (br. s, 1 H, NH). – **<sup>13</sup>C NMR (CDCl<sub>3</sub>)**:  $\delta$  = 12.99 (q, Me), 22.82 (t, MeCH<sub>2</sub>), 35.56 (t, SCH<sub>2</sub>), 111.09 (s, CN), 121.59 (s, CCN), 147.10 (s, PropSC). – **IR (CCl<sub>4</sub>)**:  $\tilde{\nu}$  = 978 cm<sup>-1</sup> (m), 1107 (m), 1381 (m), 1432 (m), 1461 (m), 2248 (m, CN), 2875 (m), 2934 (s), 2969 (s), 3207 (br.), 3430 (m). – **HR-MS (ESI)**:  $m/z$ : 169.0530 [M+H<sup>+</sup>, calc.: 169.0542]. – **R<sub>f</sub> (EtOAc)**: 0.85. – **R<sub>f</sub> (Et<sub>2</sub>O/*n*-hexane = 1:2)**: 0.17.

**Dimethylsulfoxonium- $\alpha$ -cyano(propylthio)methylide (S15):** The compound was only identified from a mixture, attempts to isolate **S15** failed. –  **$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):**  $\delta$  = 0.99 (*pseudo* t,  $J$  = 7.6 Hz, 3 H,  $\text{CH}_3\text{CH}_2$ ), 1.70 (*pseudo* qt,  $J_{\text{Me,CH}_2}$  = 7.6 Hz,  $J_{\text{CH}_2,\text{CH}_2}$  = 7.2 Hz, 2 H,  $\text{MeCH}_2$ ), 2.57 (*pseudo* t,  $J$  = 7.2 Hz, 2 H,  $\text{SCH}_2$ ), 3.45 (s, 6 H, =SMe). –  **$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):**  $\delta$  = 13.15 (q,  $\text{CH}_3\text{CH}_2$ ), 22.02 (t,  $\text{CH}_3\text{CH}_2$ ), 36.87 (s, C=S), 40.98 (q, =SMe), 41.40 (t,  $\text{SCH}_2$ ), 120.60 (s, CN). – **HR-MS (ESI):**  $m/z$ : 192.0530 [ $\text{M}+\text{H}^+$ , calc.: 192.0511].

## REFERENCES

- [S1] (a) S. Bräse, C. Gil, K. Knepper and V. Zimmermann, *Angew. Chem.*, 2005, **117**, 5320–5374; *Angew. Chem. Int. Ed.*, 2005, **44**, 5188–5240; (b) P. A. S. Smith, *Open Chain Nitrogen Compounds*, Bd. 2, Benjamin, New York, 1966, 211–256; (c) J. H. Boyer, R. Moriarty, B. de Darwent and P. A. S. Smith, *Chem. Eng. News*, 1964, **42**, 6.
- [S2] W. C. Still, M. Kahn and A. Mitra, *J. Org. Chem.*, 1978, **43**, 2923–2925.
- [S3] X. Creary and A. F. Sky, *J. Am. Chem. Soc.*, 1990, **112**, 368–374.
- [S4] N. Iqbal, C.-A. McEwen and E. E. Knaus, *Drug Dev. Res.*, 2000, **51**, 177–186.
- [S5] L. F. Tietze and Th. Eicher, *Reaktionen und Synthesen im organisch-chemischen Praktikum und Forschungslaboratorium*, 2. Aufl., Georg Thieme Verlag, Stuttgart, New York, 1991, 413.
- [S6] D. Sun, P. Lai, W. Xie, J. Deng and Y. Jiang, *Synth. Commun.*, 2007, **37**, 2989–2994.
- [S7] R. A. Earl and L. B. Townsend, *Org. Synth., Coll.*, 1990, **7**, 334; 1980, **60**, 81.
- [S8] J. Wutke and K. Banert, Poster presentation within the 12<sup>th</sup> JCF-Frühjahrssymposium, Göttingen, 2010.
- [S9] L. Feng, A. Zhang and S. M. Kerwin, *Org. Lett.*, 2006, **8**, 1983–1986 (supporting information).
- [S10] M. V. Sargent and C. J. Timmons, *J. Chem. Soc.*, 1964, 2222–2225.
- [S11] (a) Synthesis: Sh.-I. Murahashi, T. Naota and H. Taki, *J. Chem. Soc., Chem. Commun.*, 1985, 613–614; (b) Spectral data: P. Fontaine, A. Chiaroni, G. Masson and J. Zhu, *Org. Lett.*, 2008, **10**, 1509–1512 (supporting information).
- [S12] M. A. P. Martins, D. J. Emmerich, C. M. P. Pereira, W. Cunico, M. Rossato, N. Zanatta and H. G. Bonaccorso, *Tetrahedron Lett.*, 2004, **45**, 4935–4938.
- [S13] Sh.-T. Lin, Ch.-Ch. Lee and D. W. Liang, *Tetrahedron*, 2000, **56**, 9619–9623.
- [S14] S. Huppe, H. Rezaei and S. Z. Zard, *Chem. Commun.*, 2001, 1894–1895.
- [S15] (a) É. Abele, M. Fleisher, K. Rubina, R. Abele and E. Lukevics, *J. Mol. Catal. A: Chemicals*, 2001, **165**, 121–126; (b) É. Abele, R. Abele, K. Rubina and E. Lukevics, *Chem. Heterocycl. Comp.*, 1998, **34**, 122–123.
- [S16] A. N. Mirskova, S. G. Seredkina, I. D. Kalikhman and M. G. Voronkov, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Trans.)*, 1985, **34**, 2614–2617.
- [S17] R. A. Thompson, J. S. Francisco and J. B. Grutzner, *Phys. Chem. Chem. Phys.*, 2004, **6**, 756–765.
- [S18] K. Banert, M. Hagedorn, C. Liedtke, A. Melzer and C. Schöffler, *Eur. J. Org. Chem.*, 2000, 257–267.
- [S19] R. F. Cunico and J. Chen, *J. Org. Chem.*, 2004, **69**, 5509–5511.
- [S20] E. Nagashima, K. Suzuki and M. Sekiya, *Chem. Pharm. Bull.*, 1981, **29**, 1274–1279.

## COPIES OF $^1\text{H}/^{13}\text{C}$ NMR SPECTRA OF ALL NEW COMPOUNDS

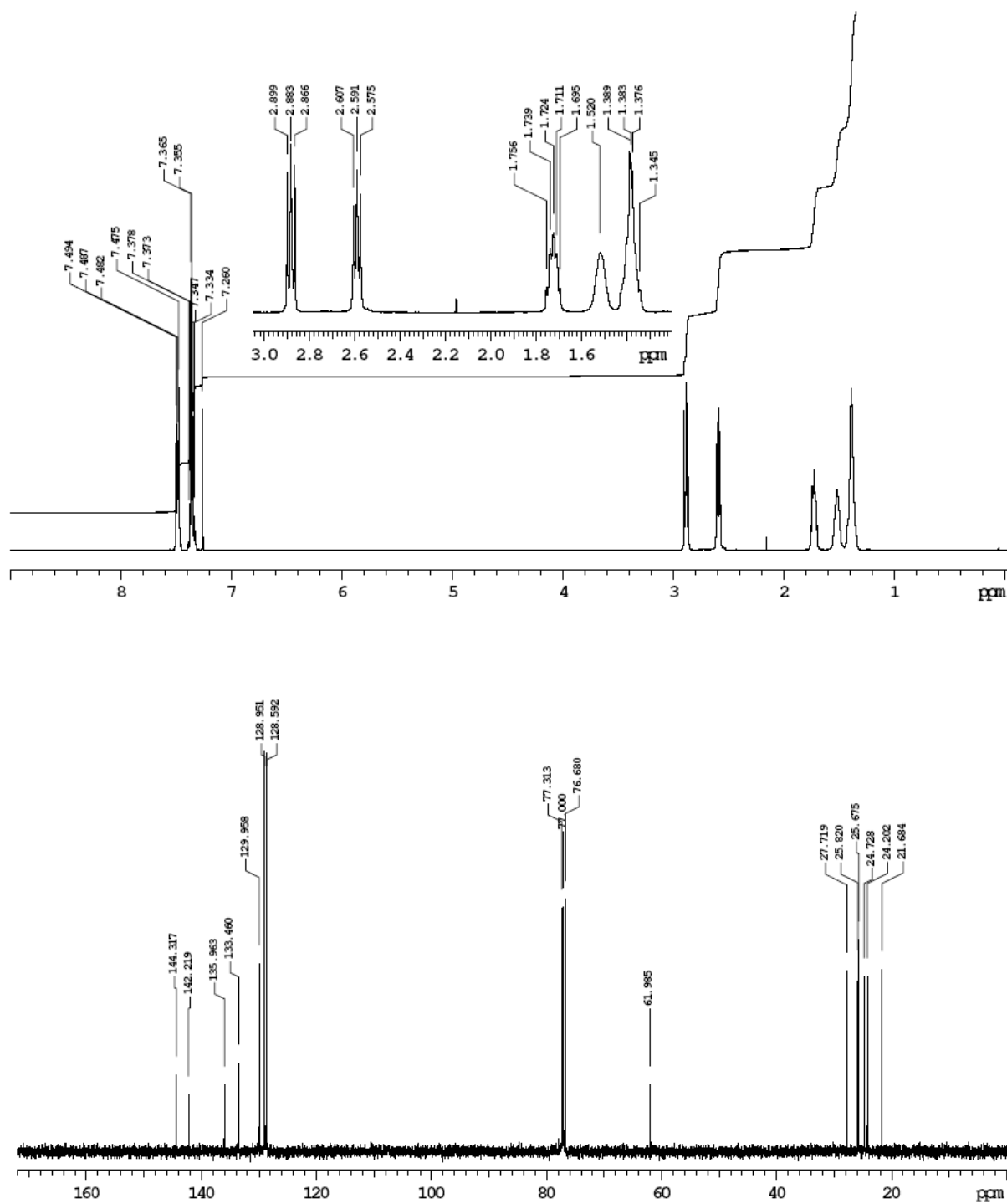
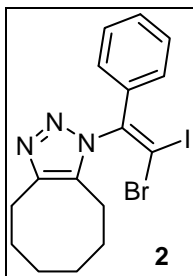
### COMPOUNDS MENTIONED IN THE COMMUNICATION

$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>2</b> .....	39	$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>20a</b> .....	49
$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>5</b> .....	40	$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>20b</b> .....	50
$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>14</b> .....	41	$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>20c</b> .....	51
$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>15</b> .....	42	$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>20d</b> .....	52
$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>17</b> .....	43	$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>20e</b> .....	53
$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>17b</b> .....	44	$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>20f</b> .....	54
$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>19d</b> .....	45	$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>20g</b> .....	55
$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>19f</b> .....	46	$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>20h</b> .....	56
$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>19g</b> .....	47	$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>23</b> .....	57
$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>19h</b> .....	48	$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>26b</b> .....	58

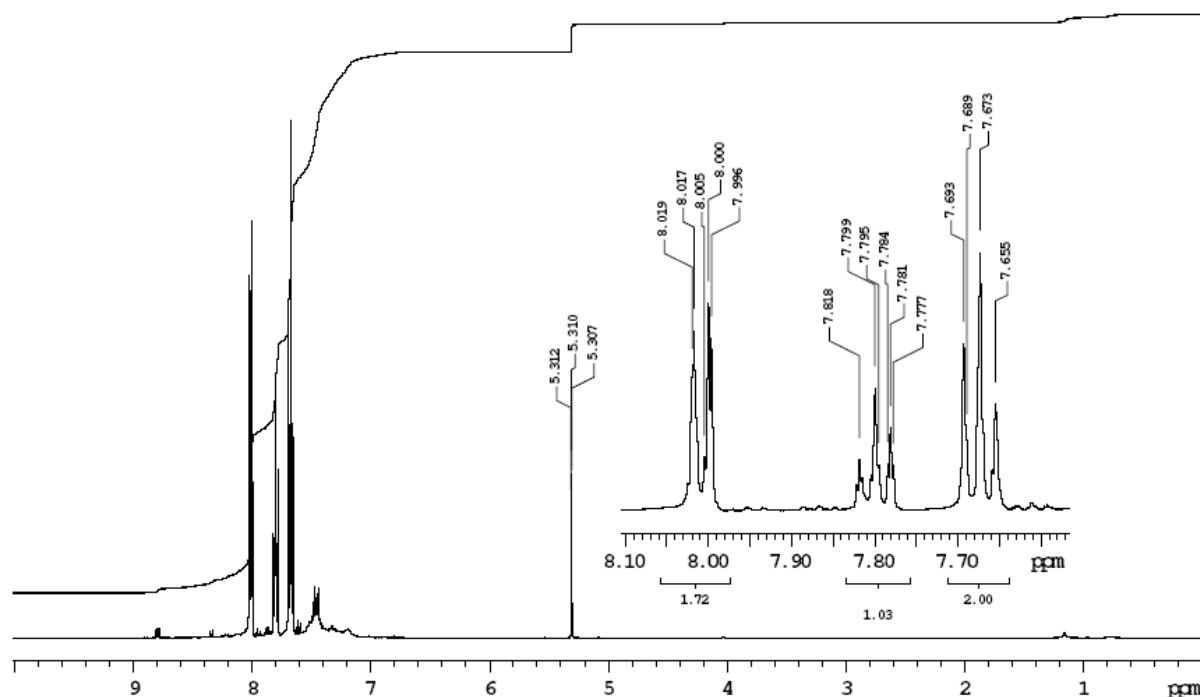
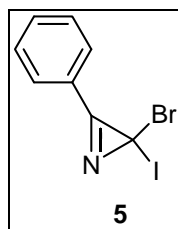
### COMPOUNDS ONLY MENTIONED IN THIS SUPPLEMENT

$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>15b</b> .....	59	$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>S6b</b> .....	68
$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>S2d</b> .....	60	$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>S6i</b> .....	69
$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>S3a</b> .....	61	$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>S7b</b> .....	70
$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>S3b</b> .....	62	$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>S11</b> .....	71
$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>S3c</b> .....	63	$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>S12</b> .....	72
$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>S3h</b> .....	64	$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>S13</b> .....	73
$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>S4b</b> .....	65	$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>S14</b> .....	74
$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>S4i</b> .....	66	$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>S15</b> .....	75
$^1\text{H}/^{13}\text{C}$ NMR spectra of compound <b>S5b</b> .....	67		

**$^1\text{H}/^{13}\text{C}$  NMR spectra of compound 2**



**$^1\text{H}/^{13}\text{C}$  NMR spectra of compound 5**

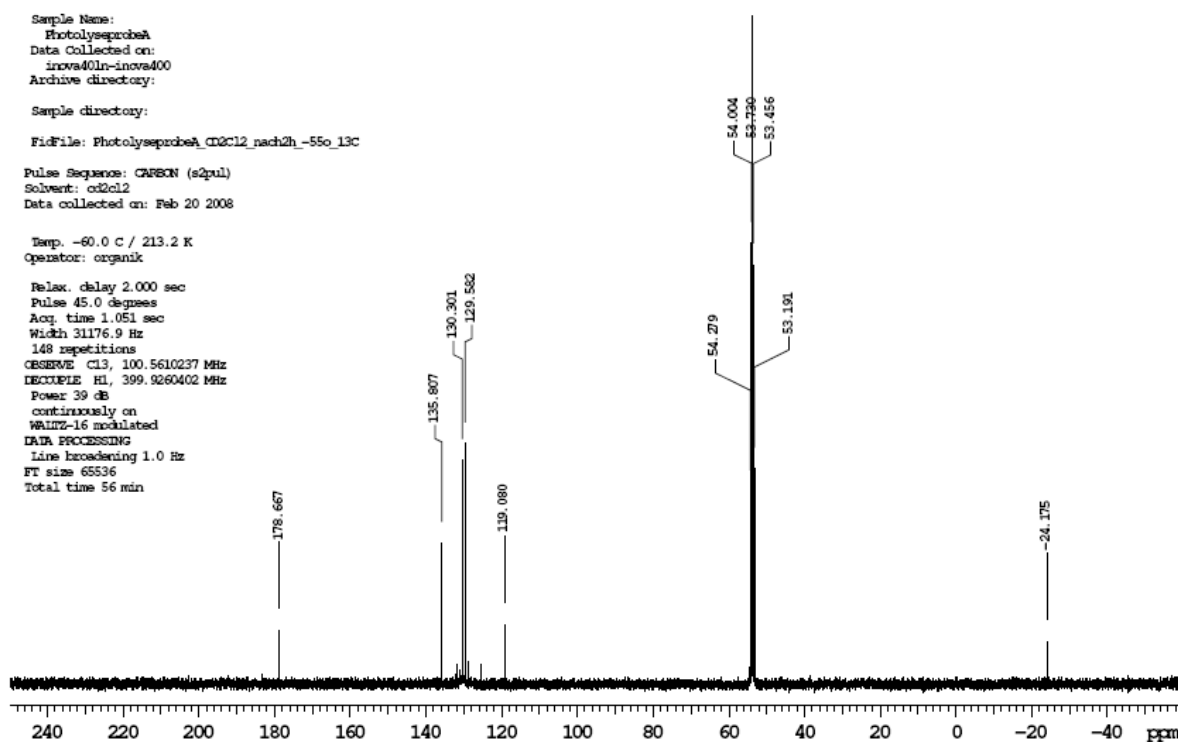


Sample Name:  
PhotolysprobeA  
Data Collected on:  
inova401n-inova400  
Archive directory:  
Sample directory:  
Fidfile: PhotolysprobeA\_CDCl2\_nach2h\_-55o\_13C

Pulse Sequence: CARBON (s2pul)  
Solvent: cdcl2  
Data collected on: Feb 20 2008

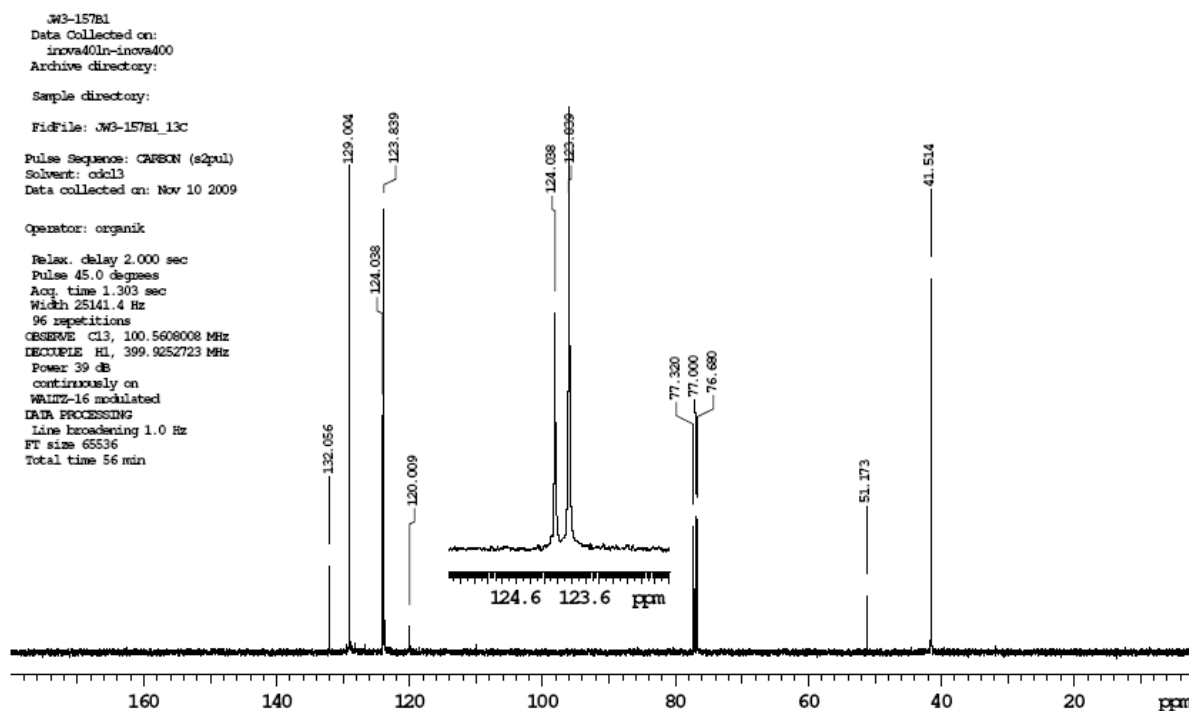
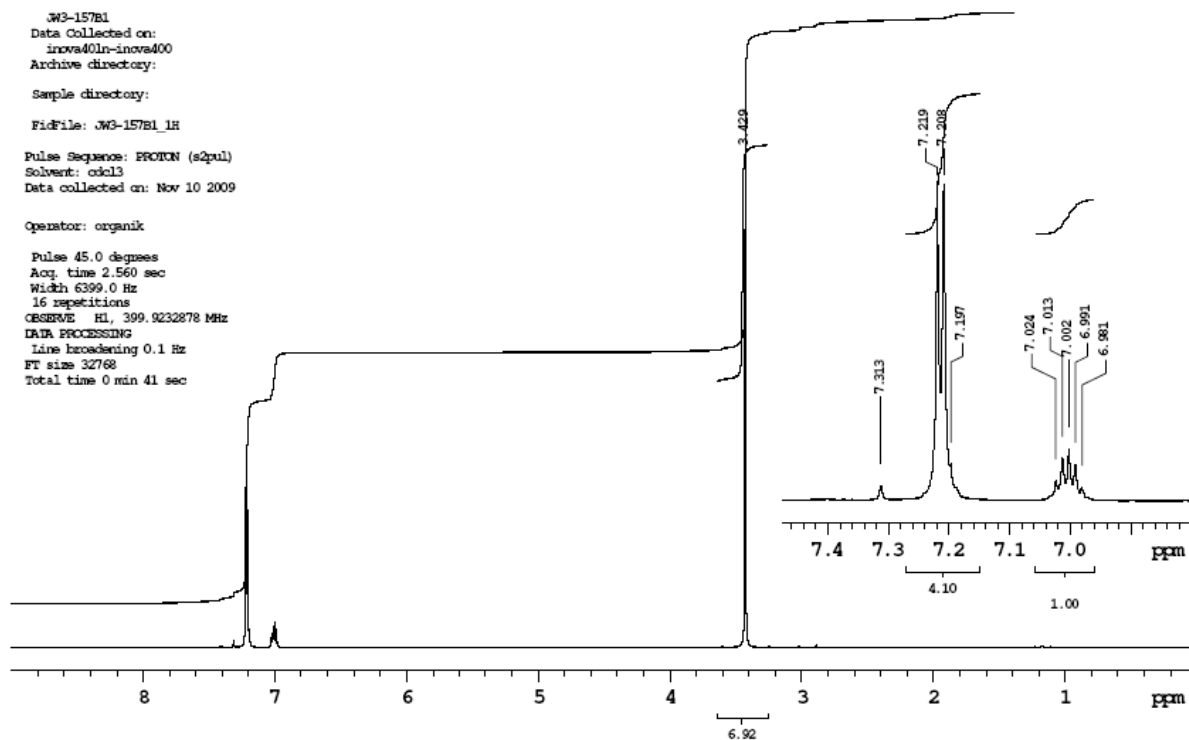
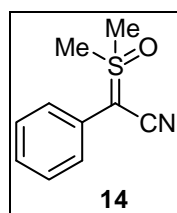
Temp. -60.0 C / 213.2 K  
Operator: organik

Relax. delay 2.000 sec  
Pulse 45.0 degrees  
Acq. time 1.051 sec  
Width 31176.9 Hz  
148 repetitions  
OBSERVE C13, 100.5610237 MHz  
DECOUPLE H1, 399.9260402 MHz  
Power 39 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 65536  
Total time 56 min

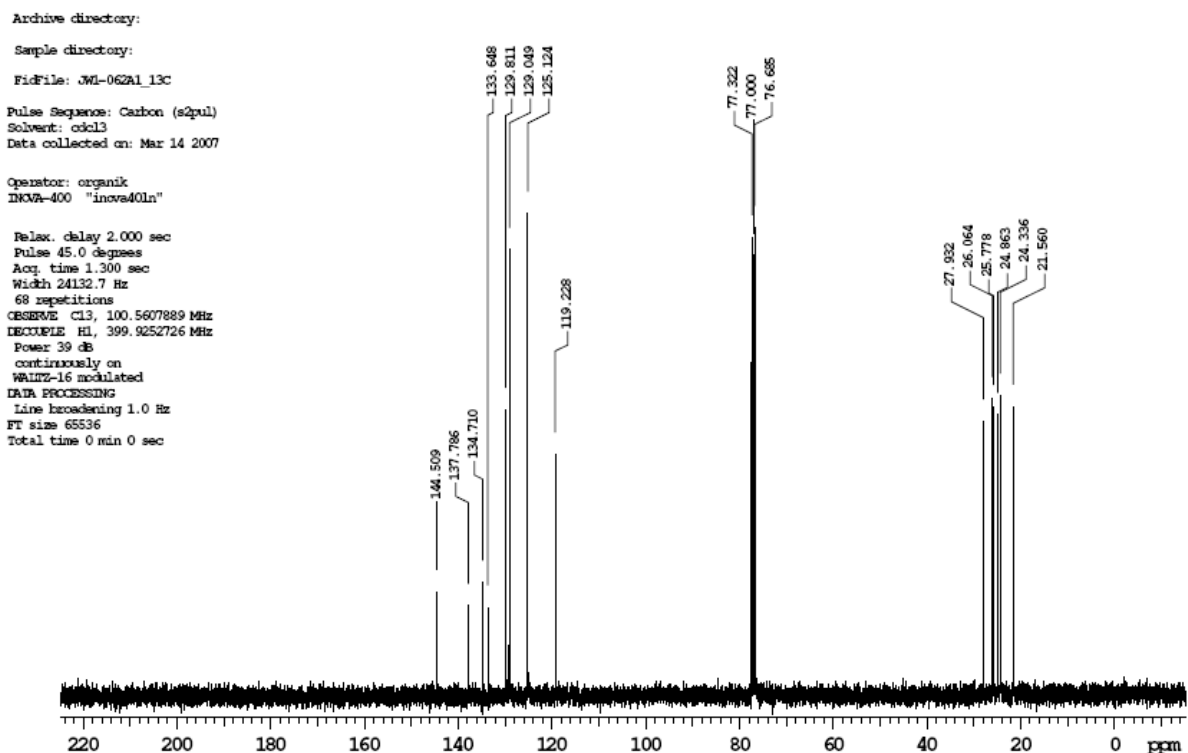
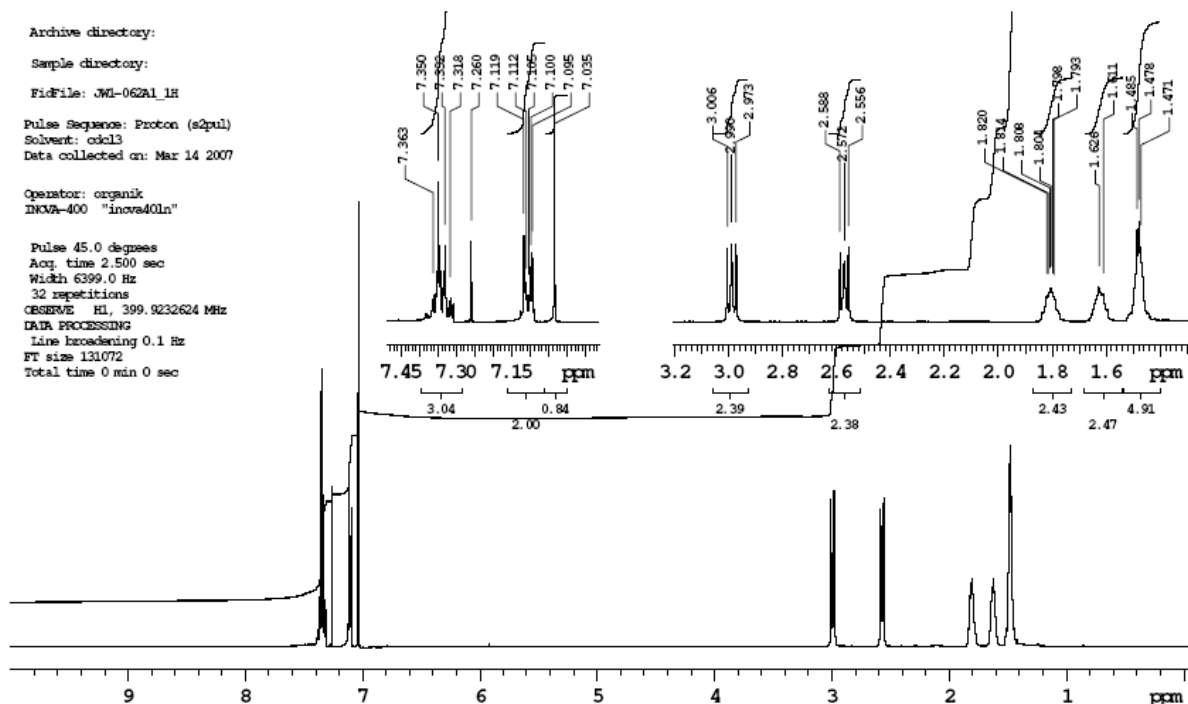
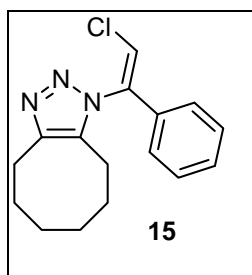




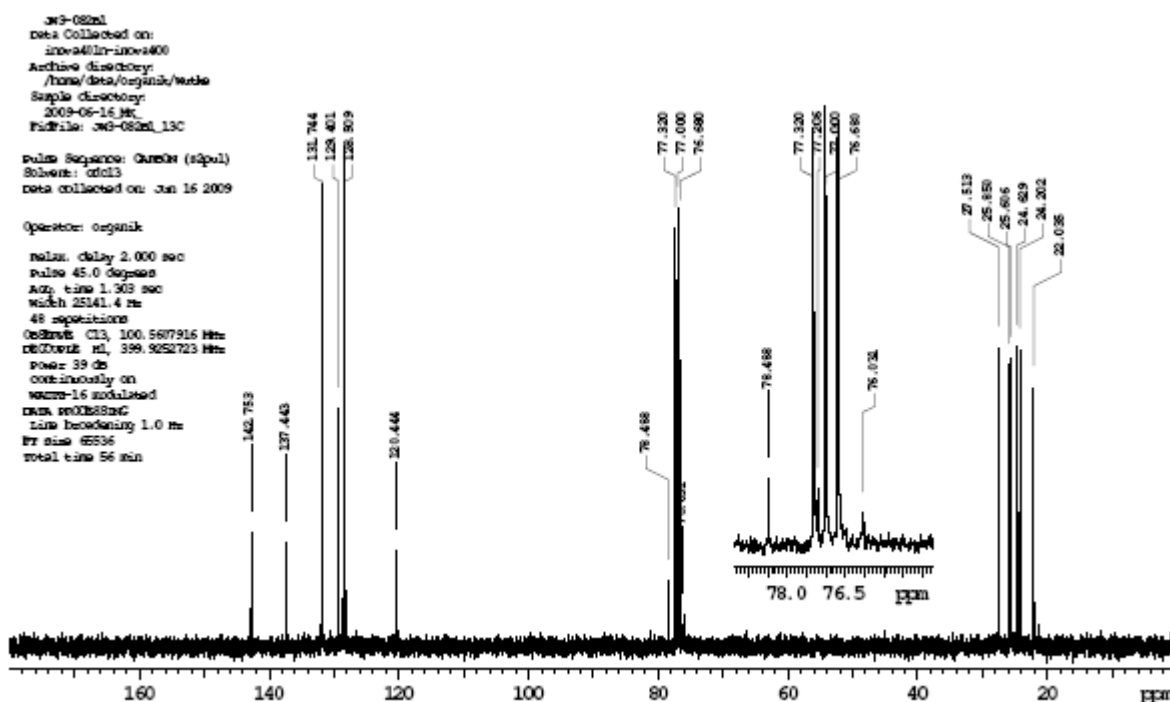
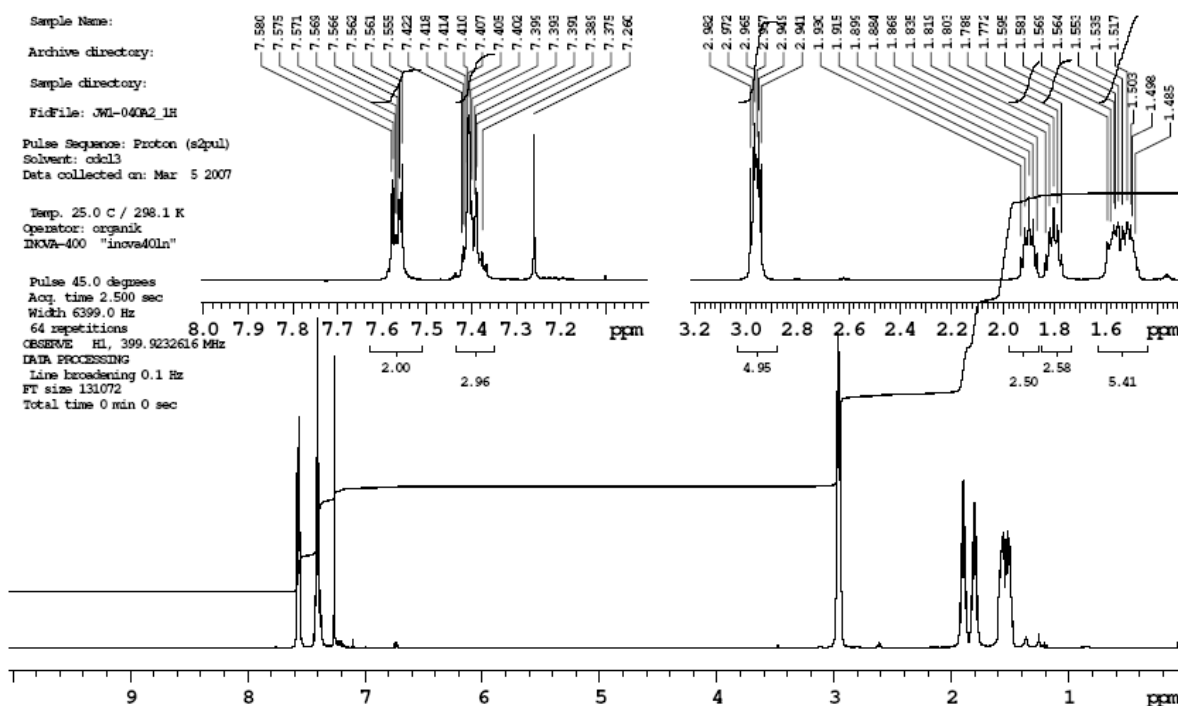
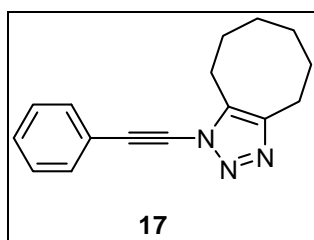
**$^1\text{H}/^{13}\text{C}$  NMR spectra of compound 14**



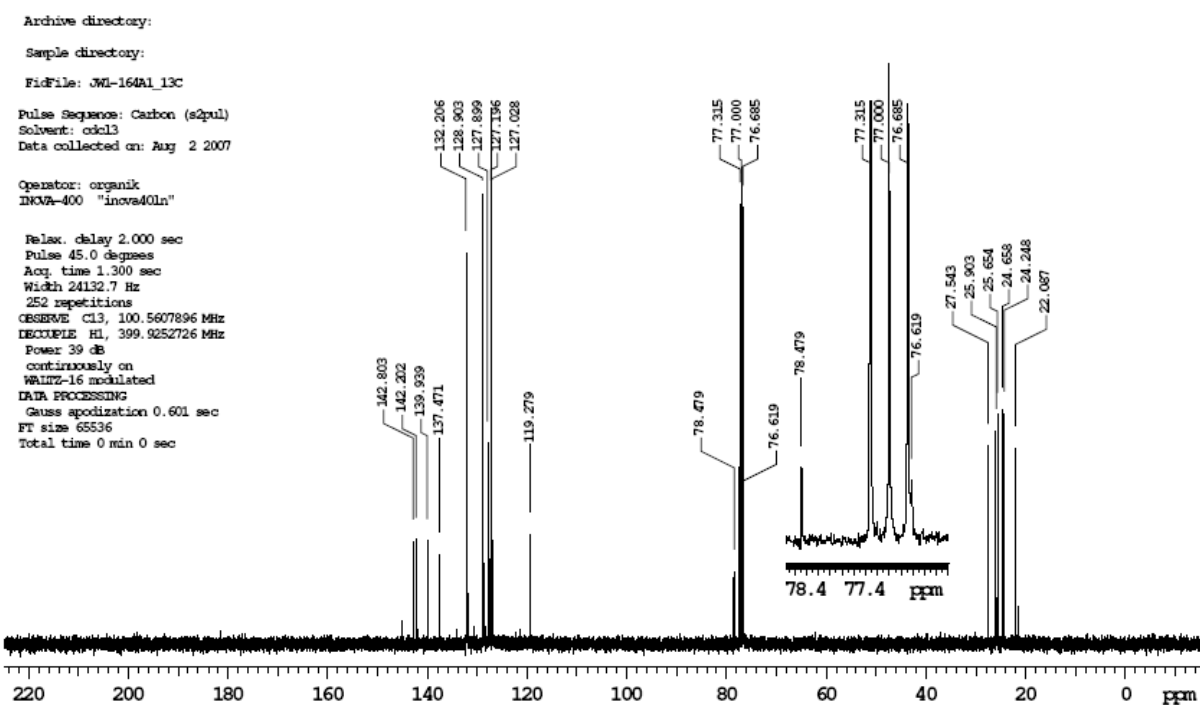
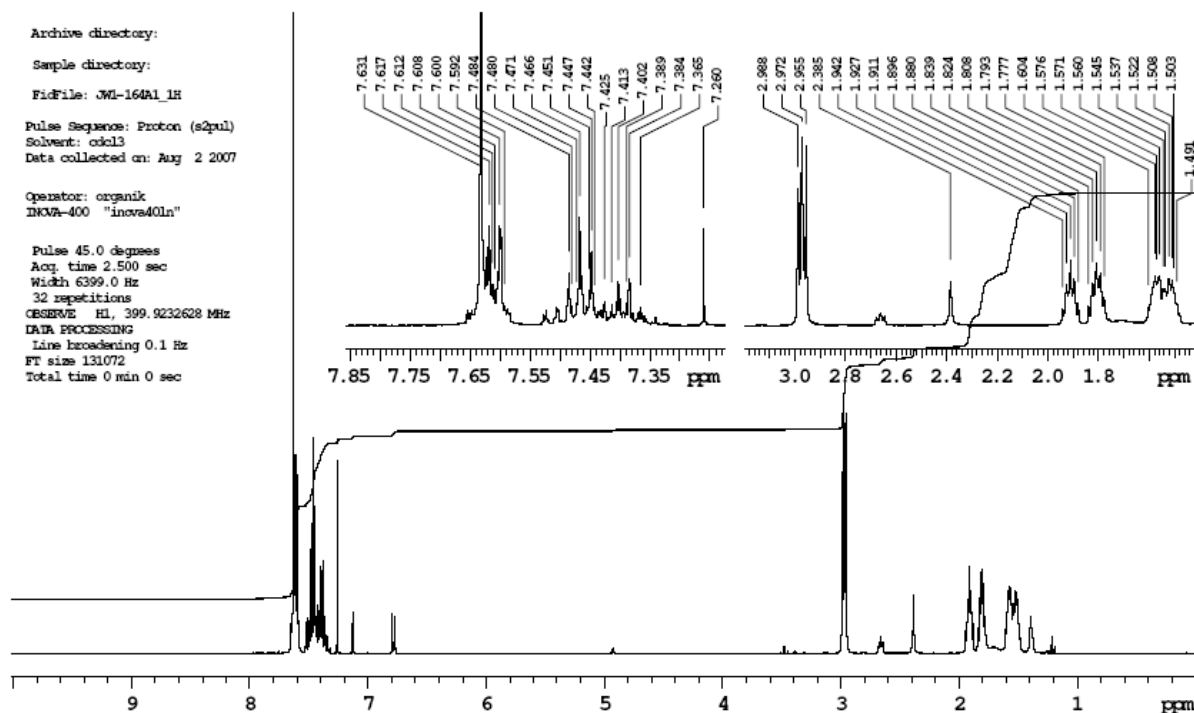
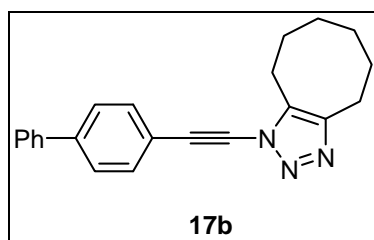
**$^1\text{H}/^{13}\text{C}$  NMR spectra of compound 15**



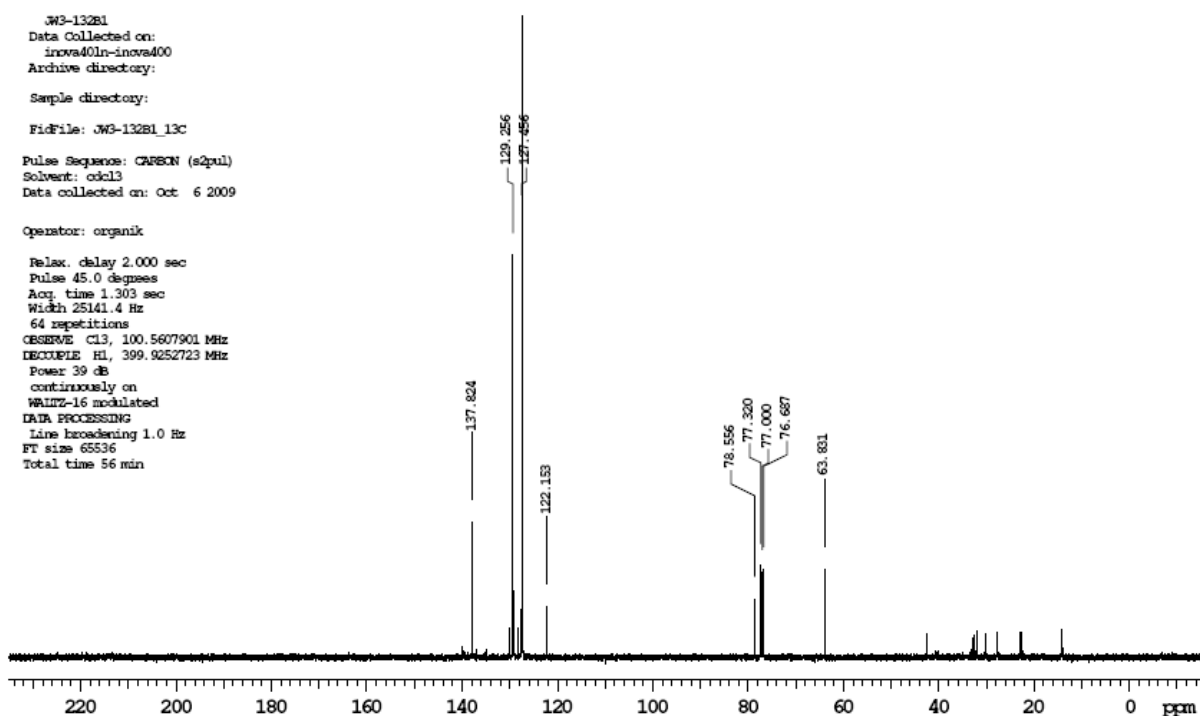
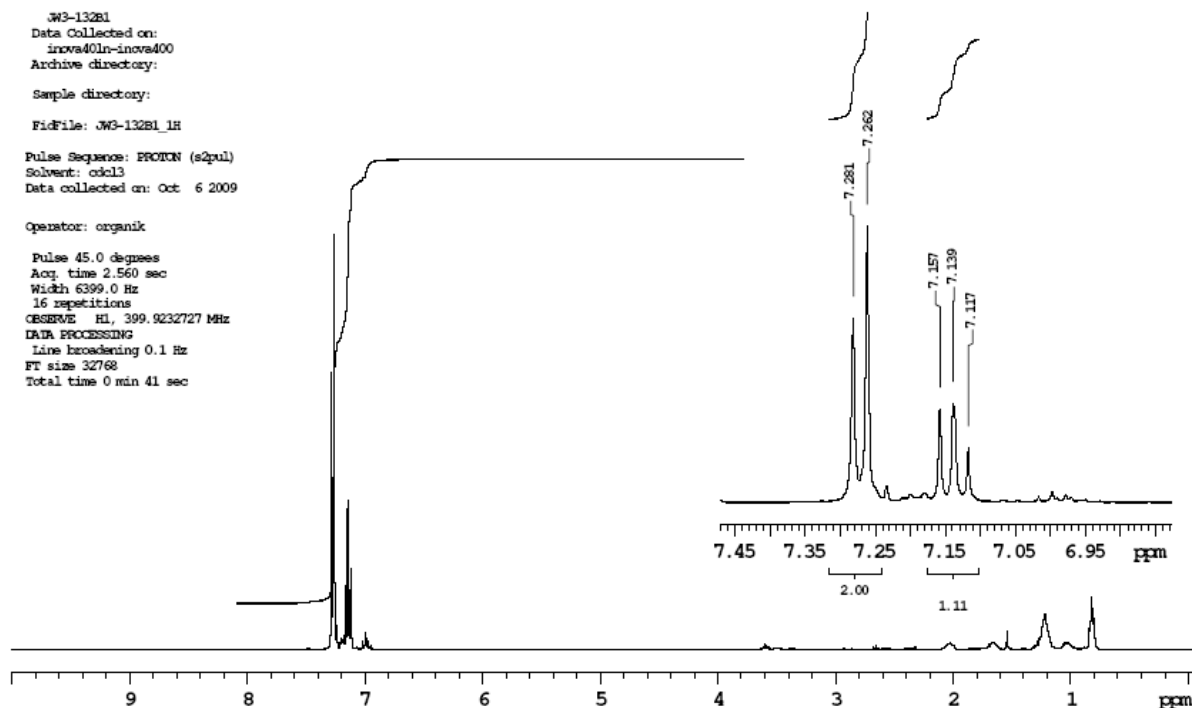
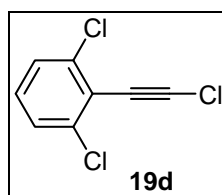
**$^1\text{H}/^{13}\text{C}$  NMR spectra of compound 17**



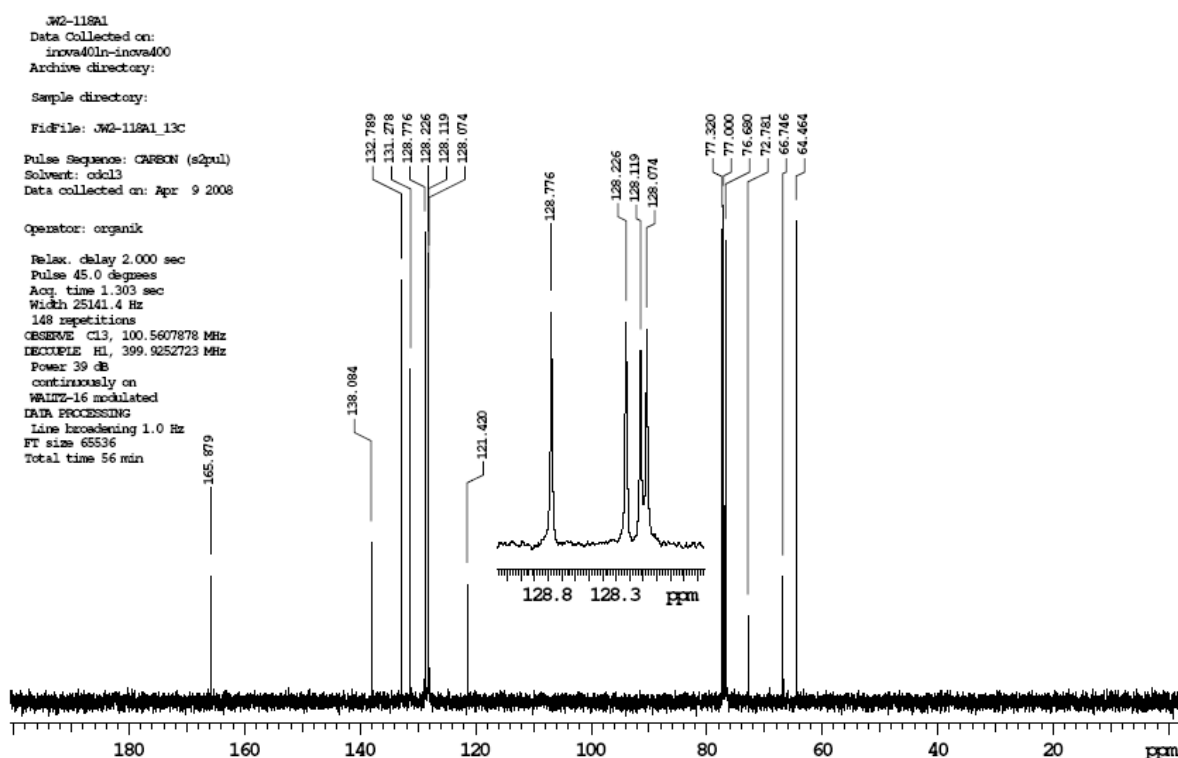
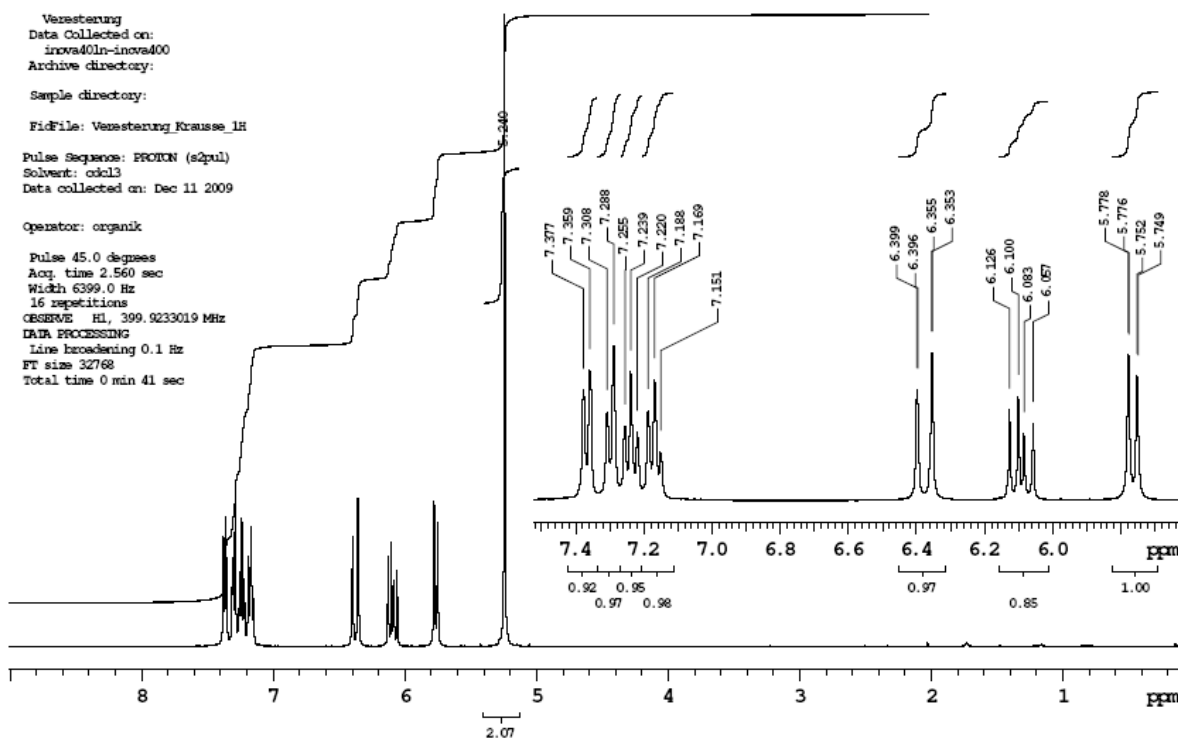
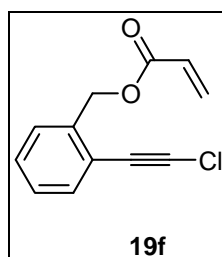
**$^1\text{H}/^{13}\text{C}$  NMR spectra of compound 17b**



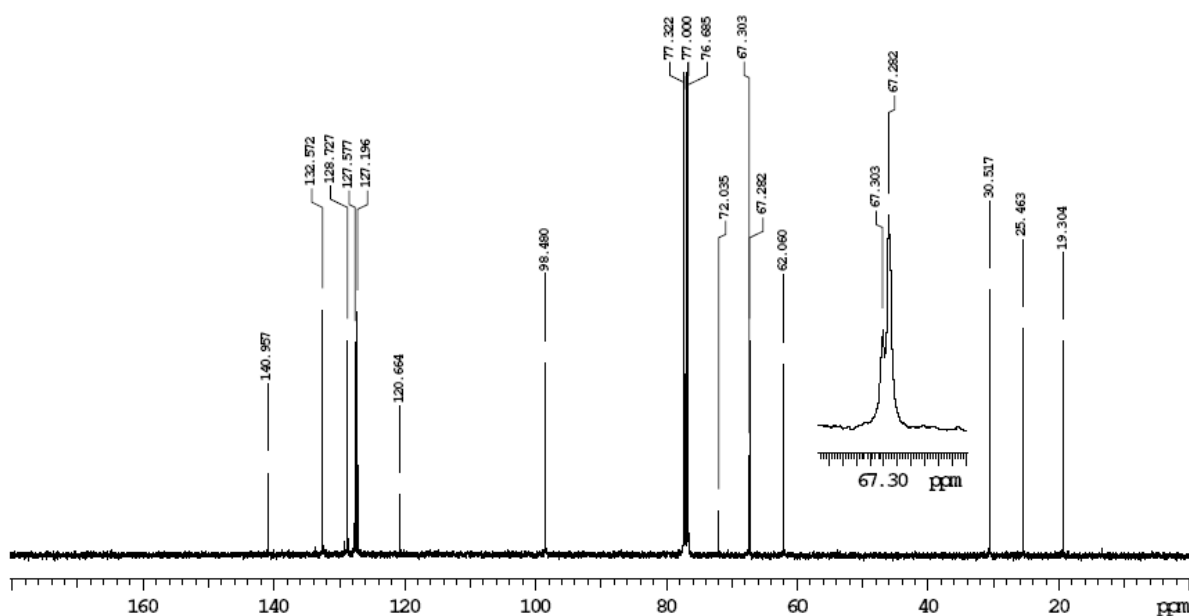
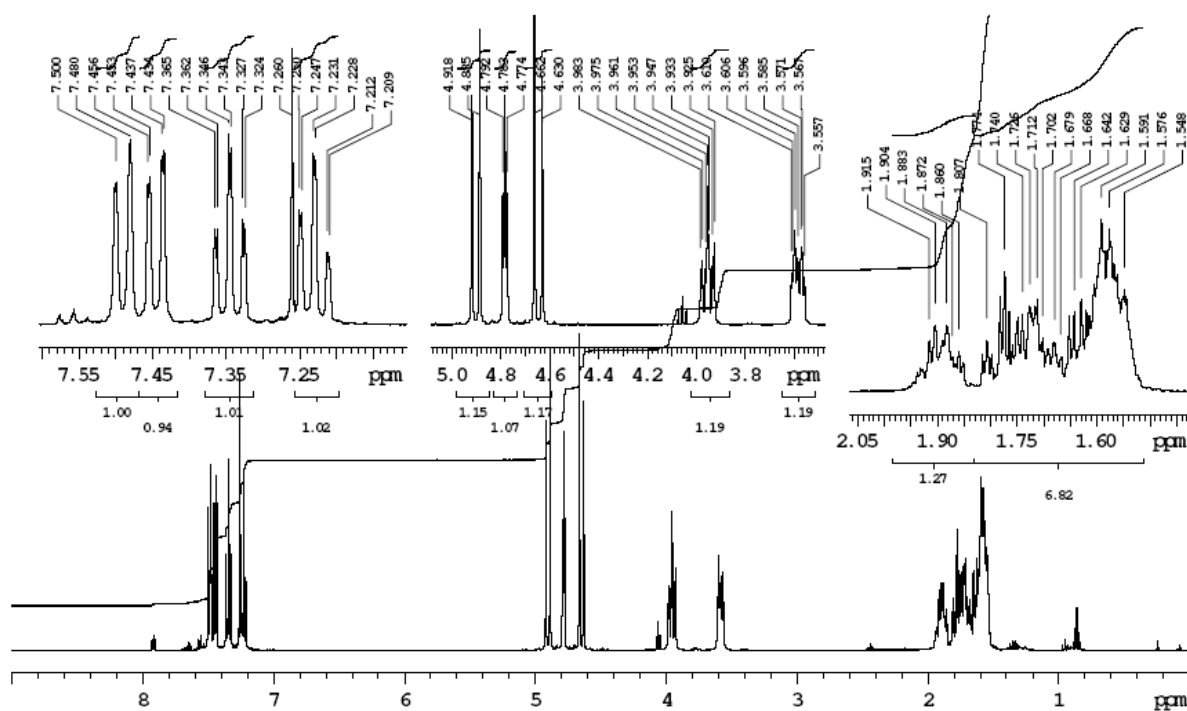
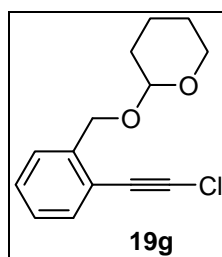
**$^1\text{H}/^{13}\text{C}$  NMR spectra of compound 19d**



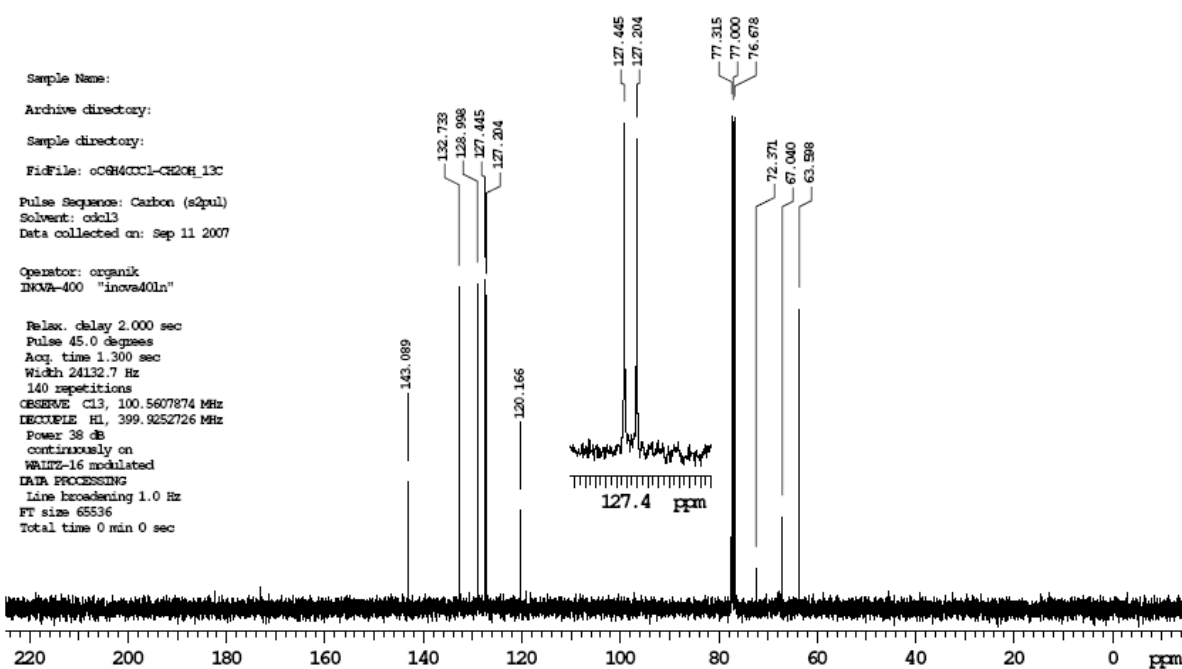
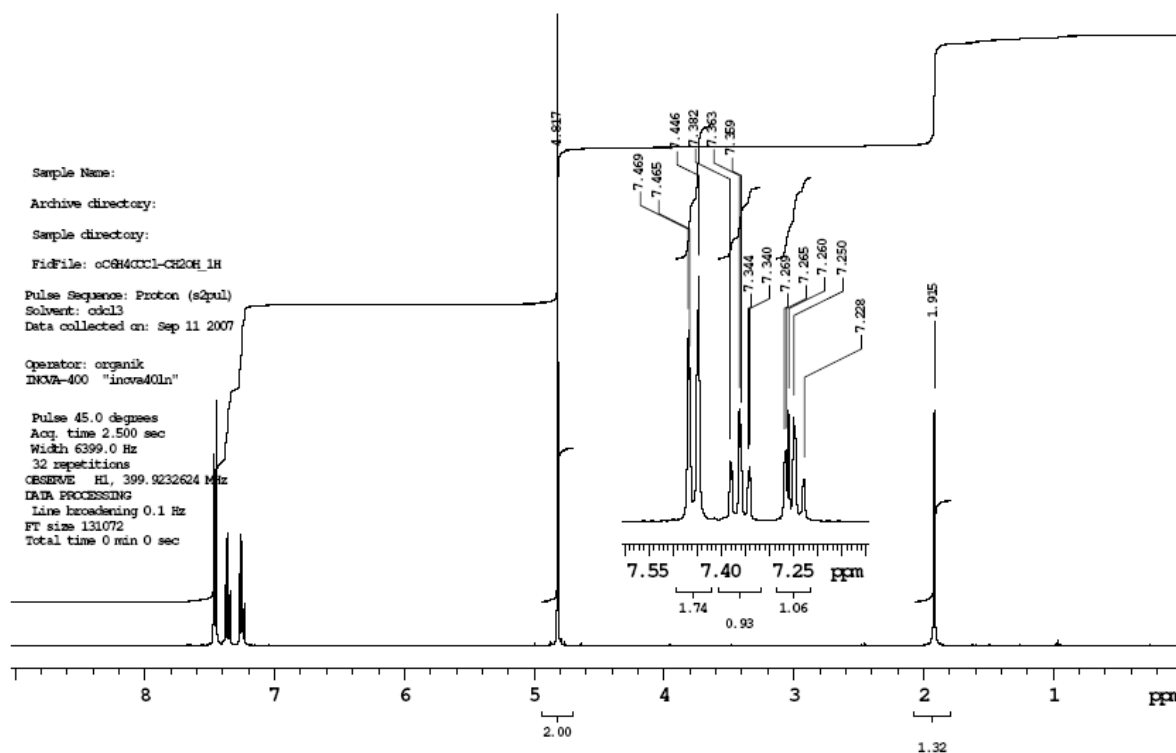
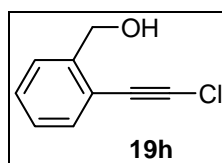
$^1\text{H}/^{13}\text{C}$  NMR spectra of compound **19f**



**$^1\text{H}/^{13}\text{C}$  NMR spectra of compound 19g**

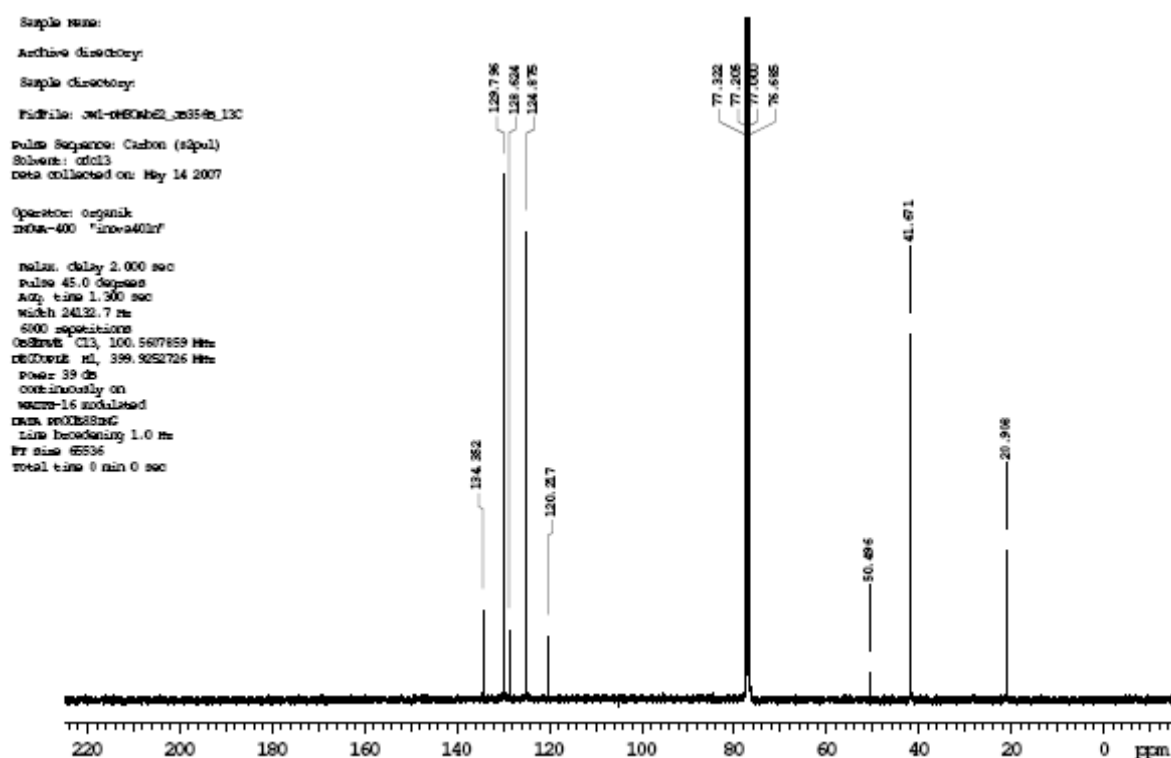
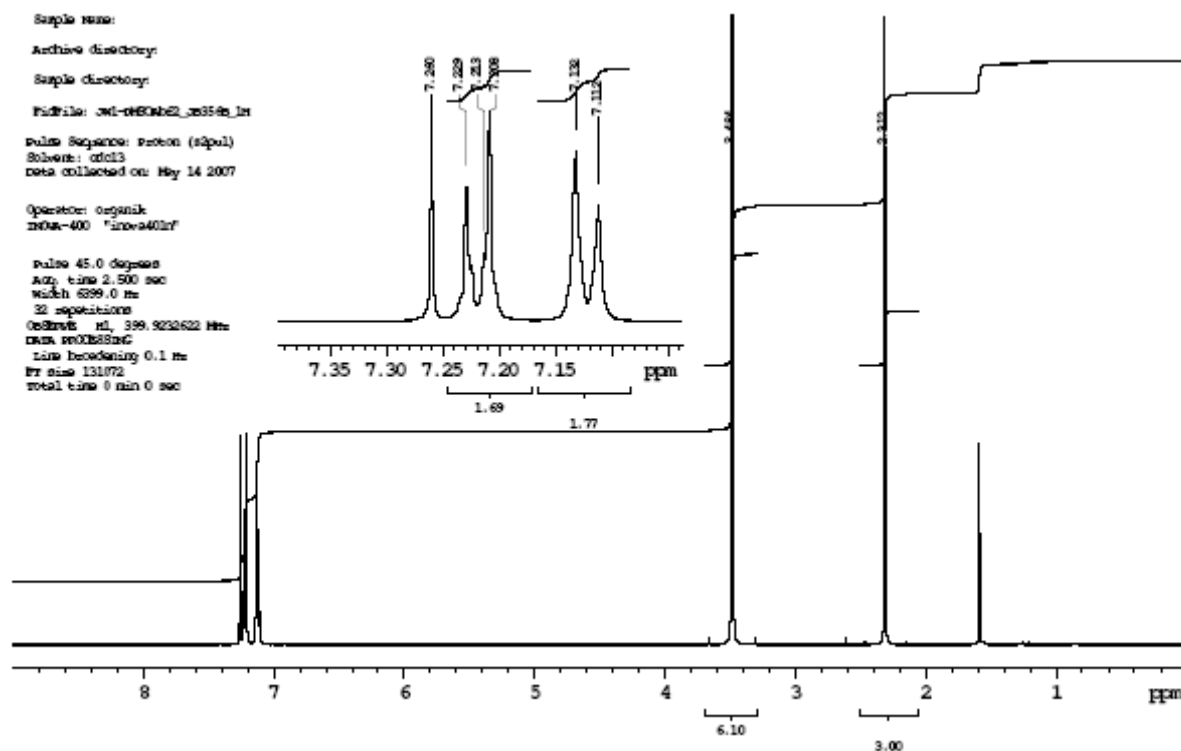
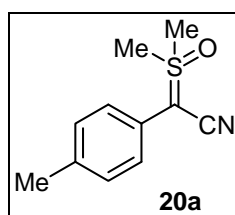


**$^1\text{H}/^{13}\text{C}$  NMR spectra of compound 19h**

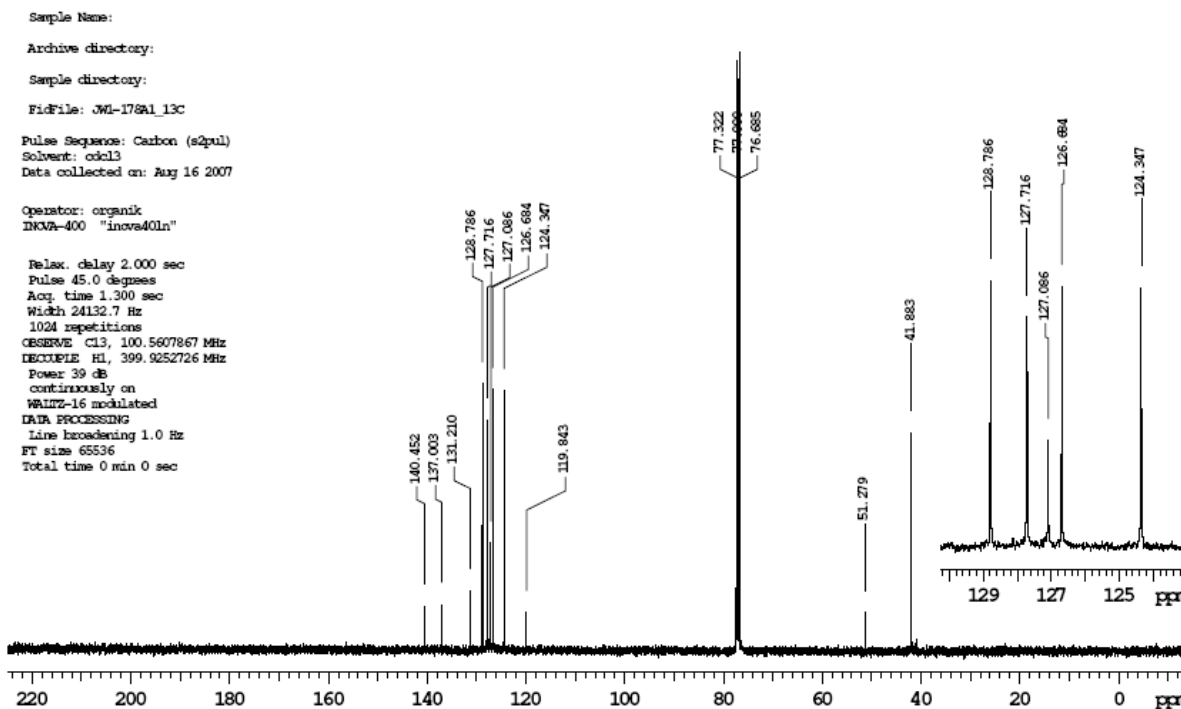
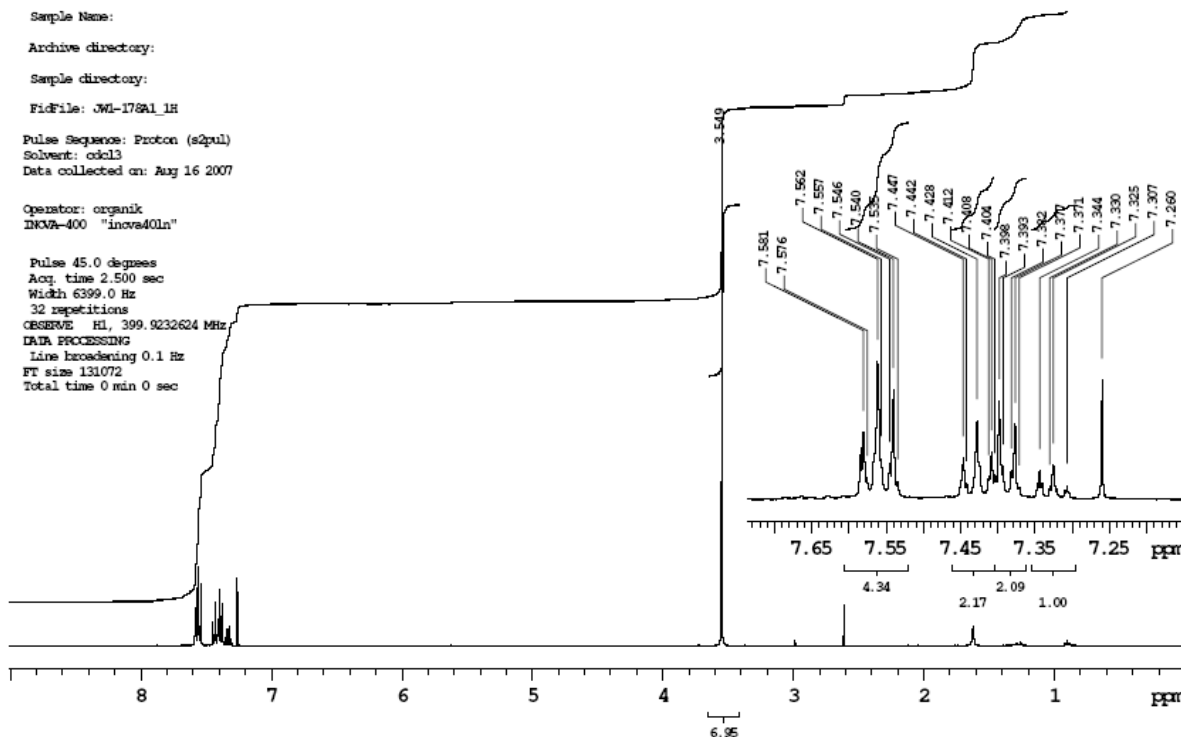
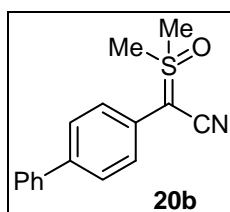




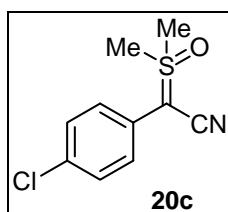
**$^1\text{H}/^{13}\text{C}$  NMR spectra of compound 20a**



**$^1\text{H}/^{13}\text{C}$  NMR spectra of compound 20b**



**$^1\text{H}/^{13}\text{C}$  NMR spectra of compound 20c**



Archive directory:

Sample directory:

FidFile: JWL-177B1\_1H

Pulse Sequence: Proton (s2pul)

Solvent: cdcl3

Data collected on: Aug 16 2007

Operator: organik

INMVA-400 "inova400n"

Pulse 45.0 degrees

Acq. time 2.500 sec

Width 6399.0 Hz

32 repetitions

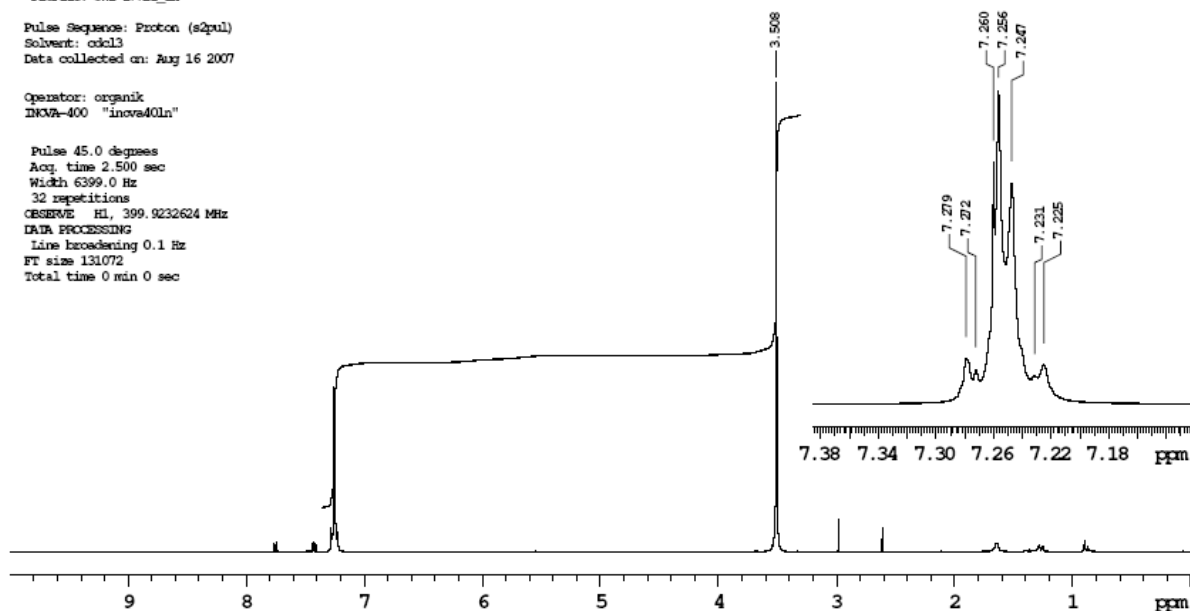
OBSERVE H1, 399.9232624 MHz

DATA PROCESSING

Line broadening 0.1 Hz

FT size 131072

Total time 0 min 0 sec



Archive directory:

Sample directory:

FidFile: JWL-177B1\_13C

Pulse Sequence: Carbon (s2pul)

Solvent: cdcl3

Data collected on: Aug 16 2007

Operator: organik

INMVA-400 "inova400n"

Relax. delay 2.000 sec

Pulse 45.0 degrees

Acq. time 1.300 sec

Width 24132.7 Hz

328 repetitions

OBSERVE C13, 100.5607874 MHz

DECOUPLE H1, 399.9252726 MHz

Power 39 dB

continuously on

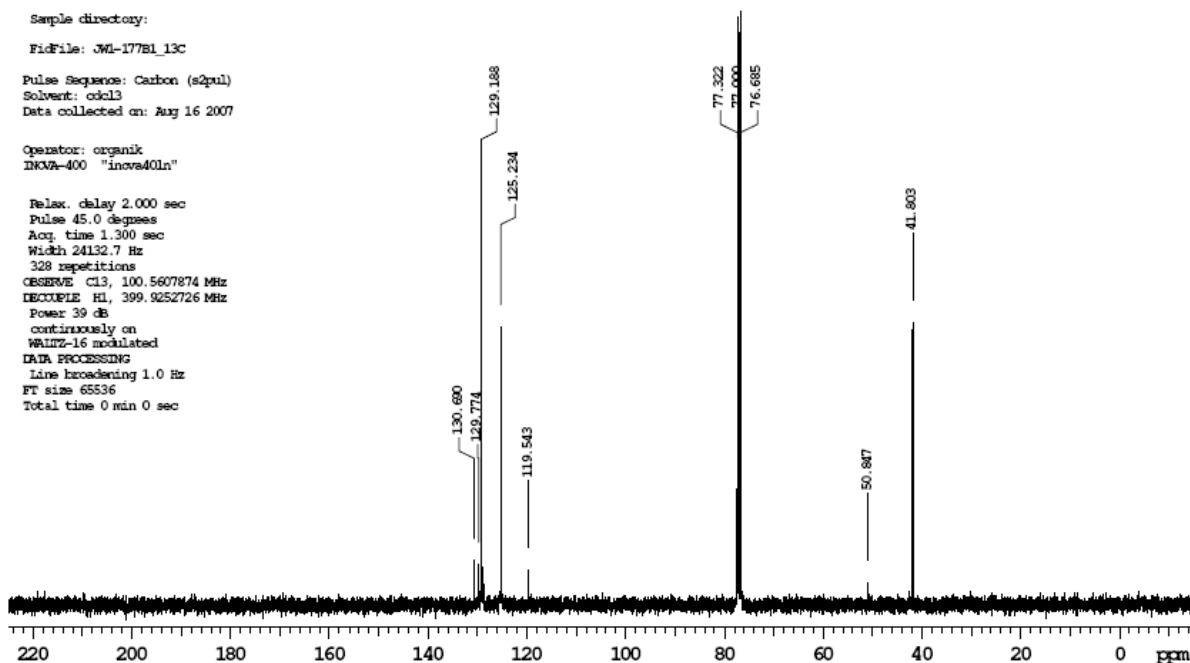
WALTZ-16 modulated

DATA PROCESSING

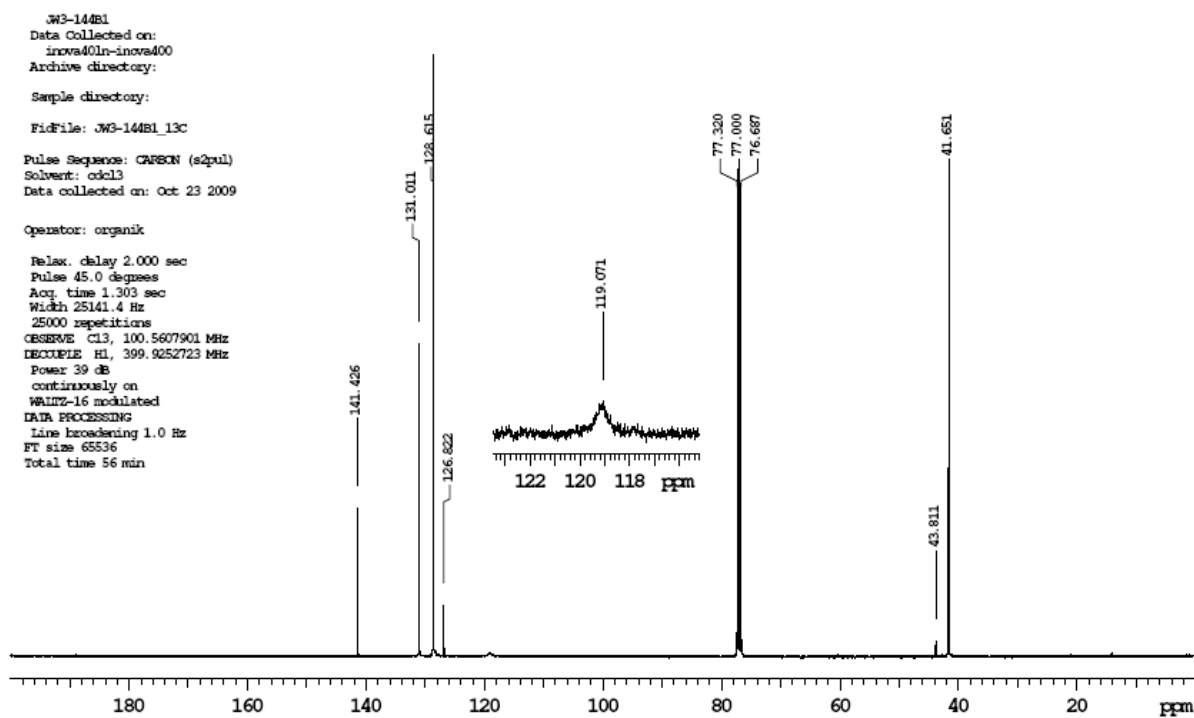
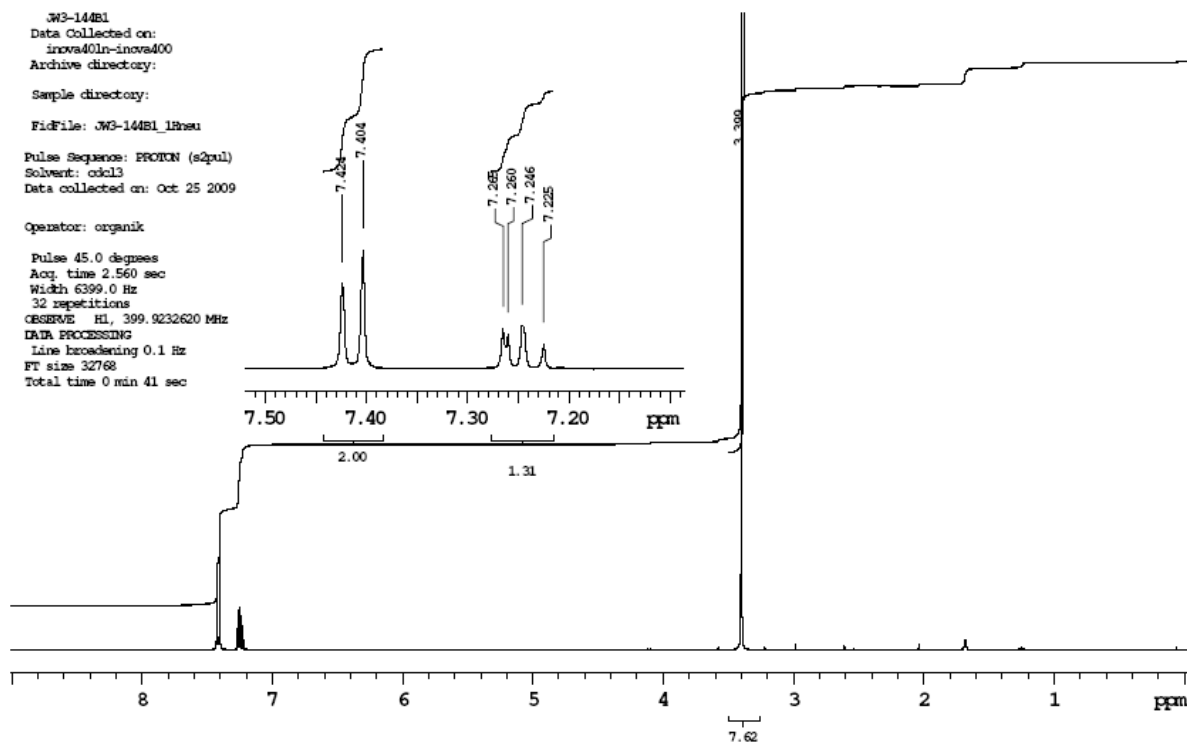
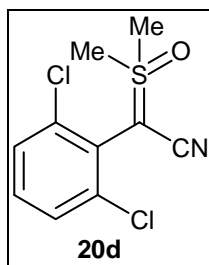
Line broadening 1.0 Hz

FT size 65536

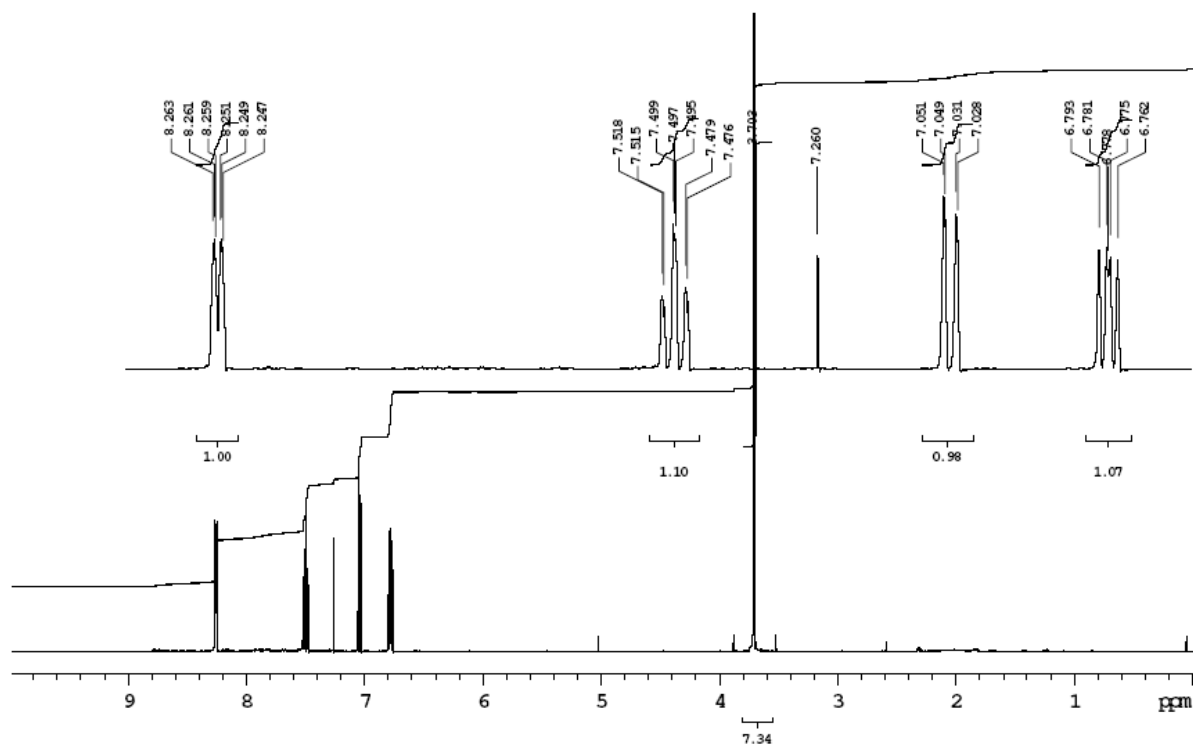
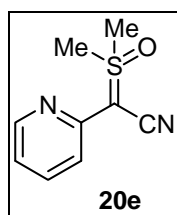
Total time 0 min 0 sec



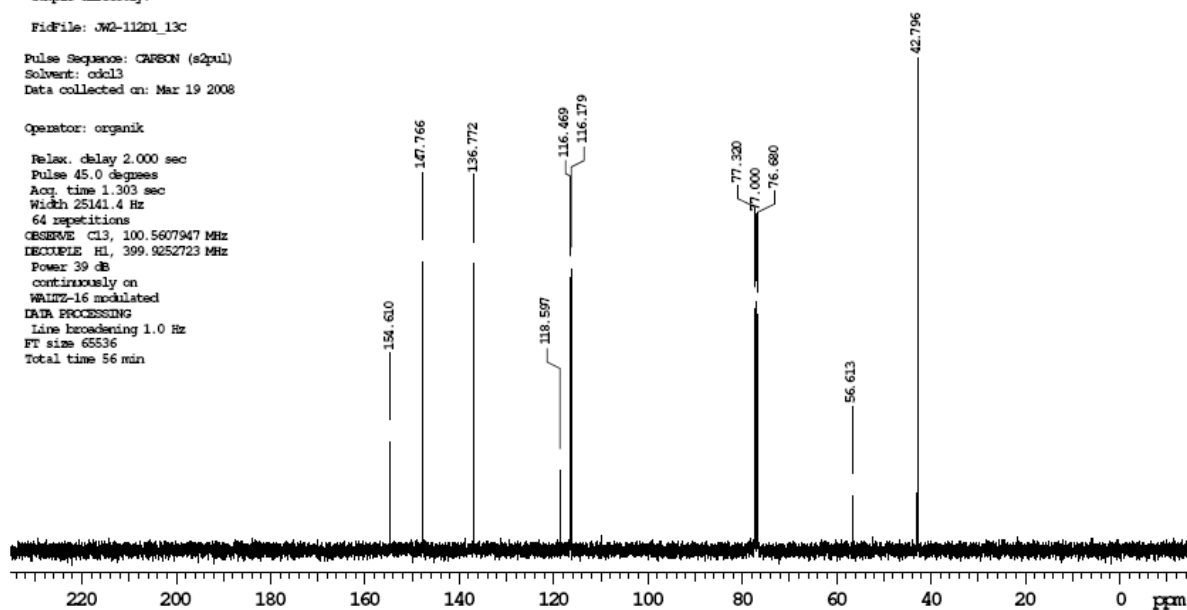
**$^1\text{H}/^{13}\text{C}$  NMR spectra of compound 20d**



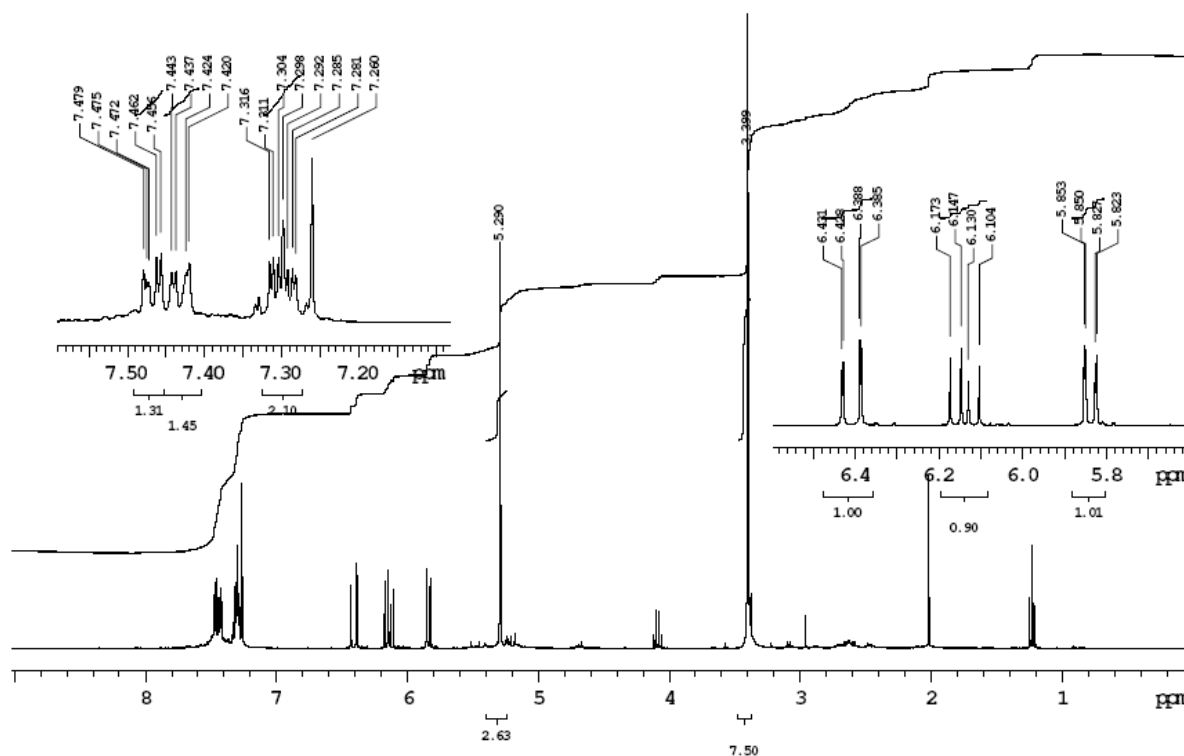
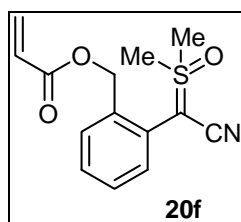
**$^1\text{H}/^{13}\text{C}$  NMR spectra of compound 20e**



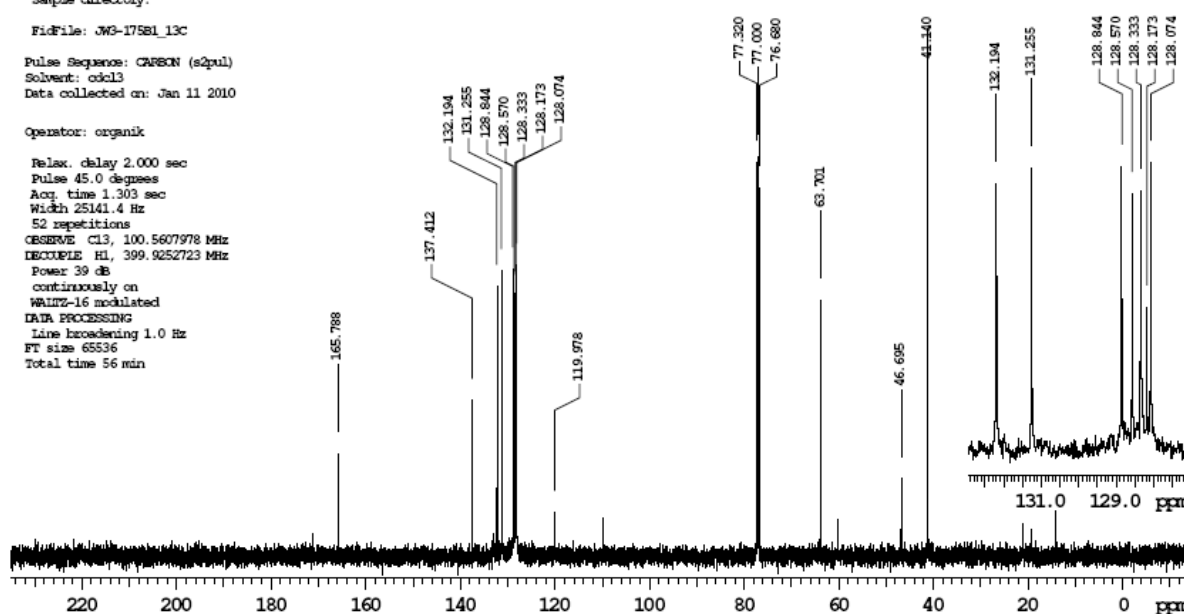
JW2-112D1  
 Data Collected on:  
 inova400n-inova400  
 Archive directory:  
 Sample directory:  
 FIDFile: JW2-112D1\_13C  
 Pulse Sequence: CARBON (s2pul)  
 Solvent: cdcl3  
 Data collected on: Mar 19 2008  
 Operator: organik  
 Relax. delay 2.000 sec  
 Pulse 45.0 degrees  
 Acq. time 1.303 sec  
 Width 25141.4 Hz  
 64 repetitions  
 OBSERVE C13, 100.5607947 MHz  
 DECOUPLE H1, 399.9252723 MHz  
 Power 39 dB  
 continuously on  
 WALTZ-16 modulated  
 DATA PROCESSING  
 Line broadening 1.0 Hz  
 FT size 65536  
 Total time 56 min



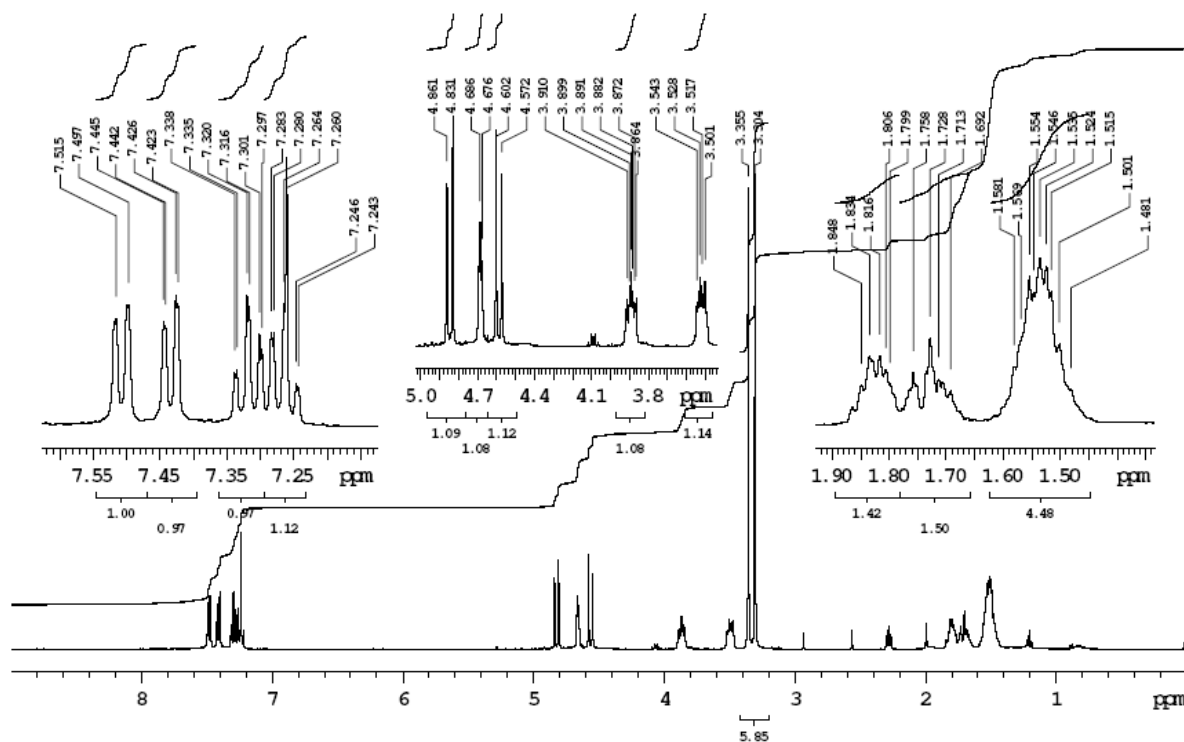
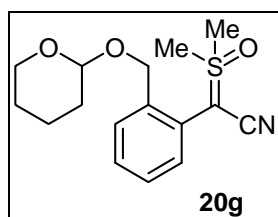
**$^1\text{H}/^{13}\text{C}$  NMR spectra of compound 20f**



JWS-17581  
 Data Collected on:  
 inova400n-inova400  
 Archive directory:  
 Sample directory:  
 FIDFile: JWS-17581\_13C  
 Pulse Sequence: CARBON (s2pul)  
 Solvent: cdcl3  
 Data collected on: Jan 11 2010  
 Operator: organik  
 Relax. delay 2.000 sec  
 Pulse 45.0 degrees  
 Acq. time 1.303 sec  
 Width 25141.4 Hz  
 52 repetitions  
 OBSERVE C13, 100.5607978 MHz  
 DECOUPLE H1, 399.9252723 MHz  
 Power 39 dB  
 continuously on  
 WALTZ-16 modulated  
 DATA PROCESSING  
 Line broadening 1.0 Hz  
 FT size 65536  
 Total time 56 min



**$^1\text{H}/^{13}\text{C}$  NMR spectra of compound 20g**



Archive directory:

Sample directory:

FidFile: JW2-02MB1\_13C

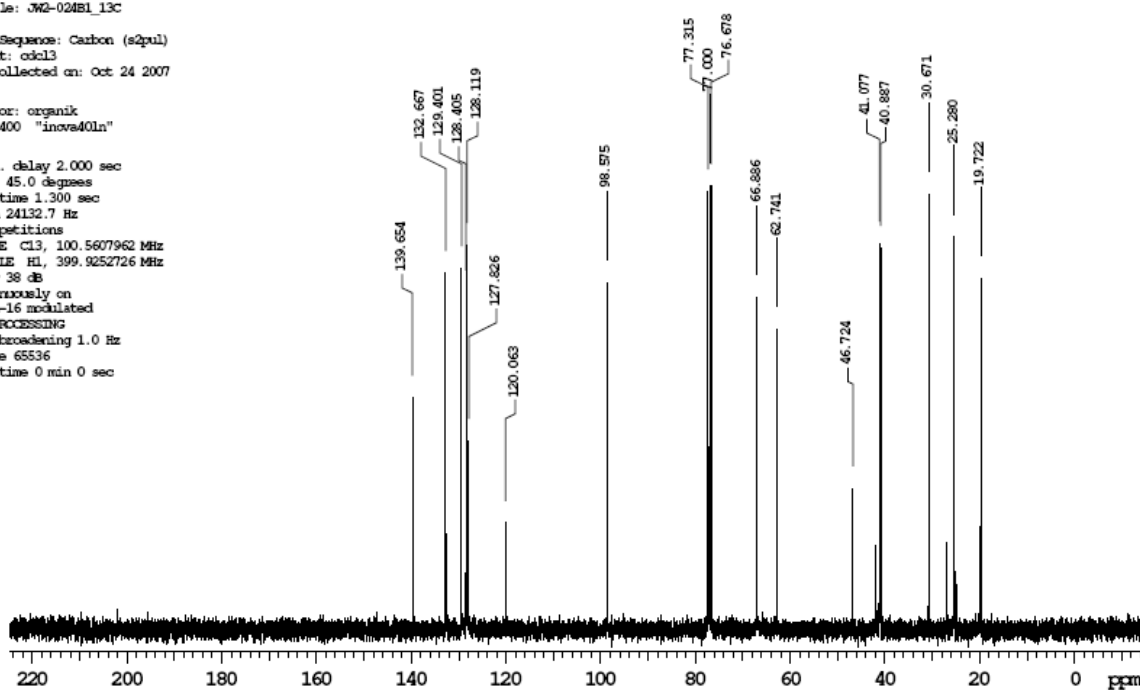
Pulse Sequence: Carbon (s2pul)

Solvent: cdcl3

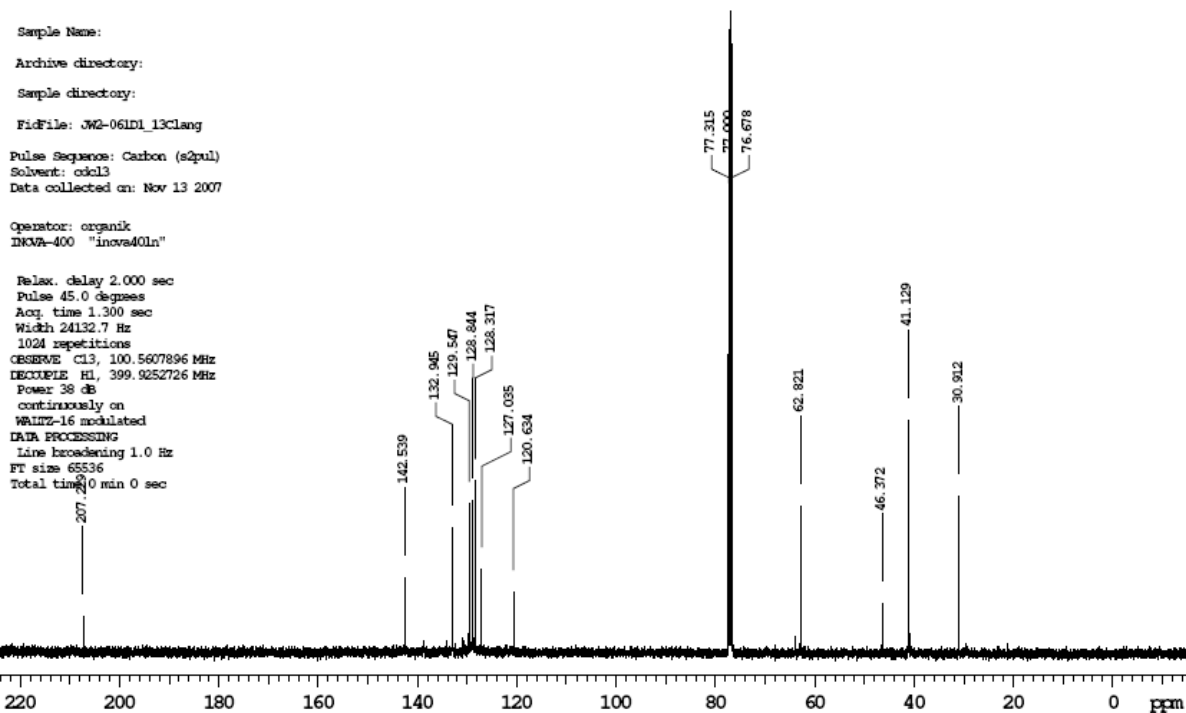
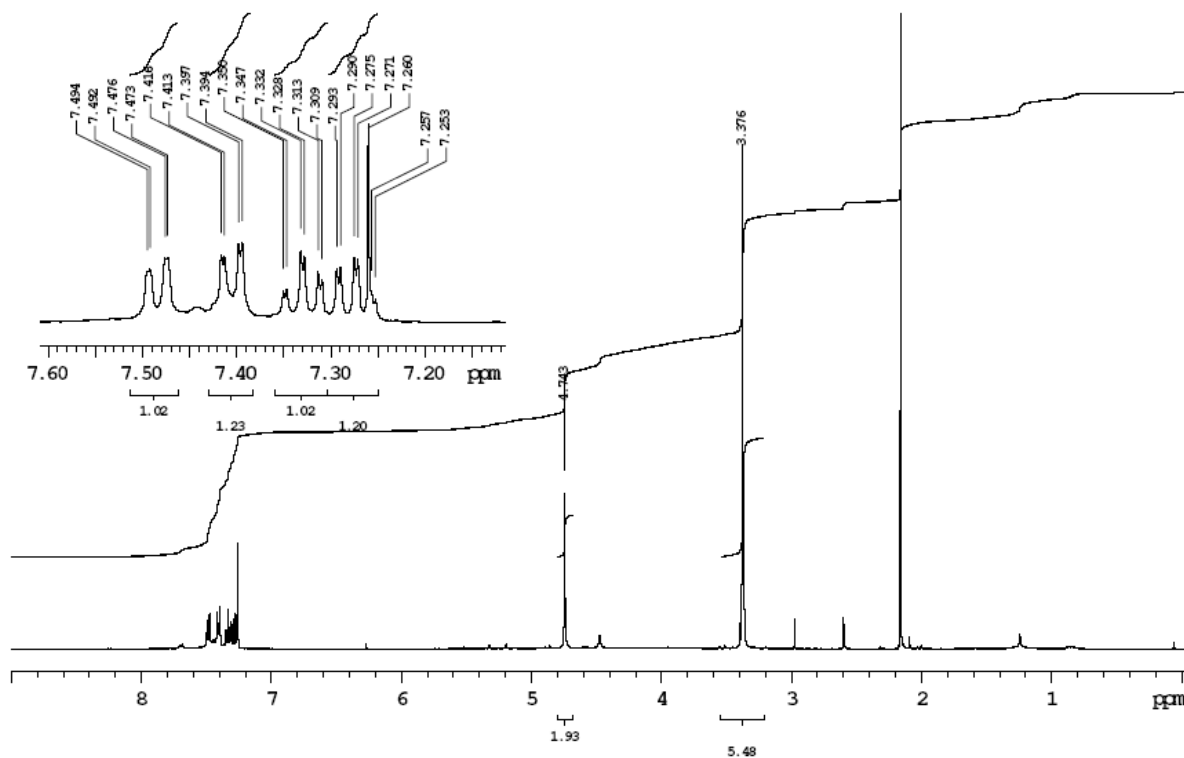
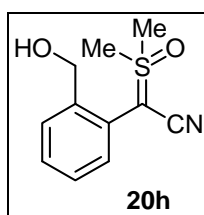
Data collected on: Oct 24 2007

Operator: organik  
DKVA-400 "inova400n"

Relax. delay 2.000 sec  
Pulse 45.0 degrees  
Acq. time 1.300 sec  
Width 24132.7 Hz  
80 repetitions  
OBSERVE C13, 100.5607962 MHz  
DECOUPLE H1, 399.9252726 MHz  
Power 38 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 65536  
Total time 0 min 0 sec



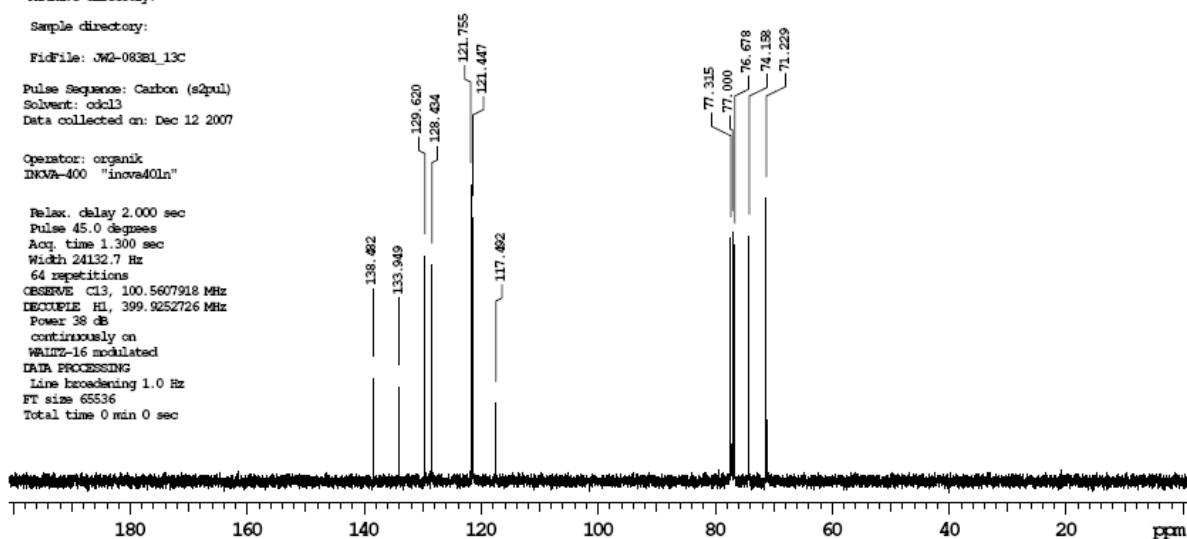
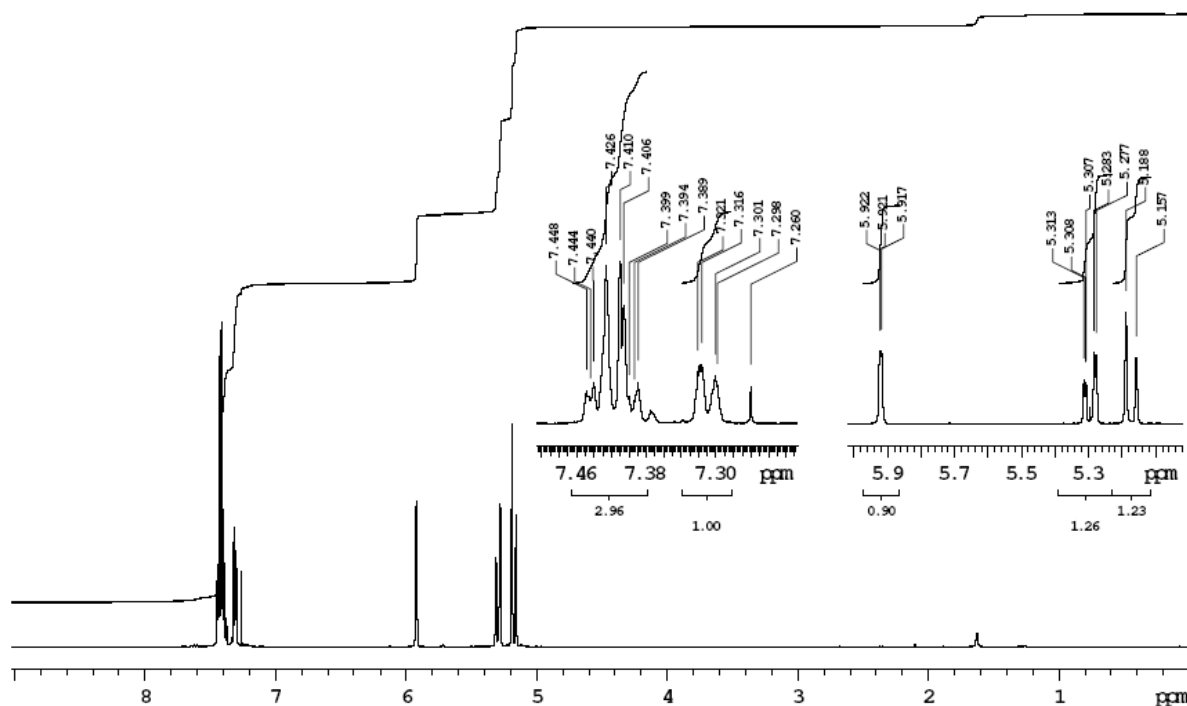
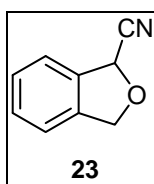
**$^1\text{H}/^{13}\text{C}$  NMR spectra of compound 20h**



Sample Name:  
Archive directory:  
Sample directory:  
FidFile: JWG-061D1\_13Clang  
Pulse Sequence: Carbon (s2pul)  
Solvent: cdcl3  
Data collected on: Nov 13 2007  
  
Operator: organik  
INOVA-400 "inova400n"  
  
Relax. delay 2.000 sec  
Pulse 45.0 degrees  
Acq. time 1.300 sec  
Width 24132.7 Hz  
1024 repetitions  
OBSERVE C13, 100.5607896 MHz  
DECOUPLE H1, 399.9252726 MHz  
Power 38 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 65536  
Total time 0 min 0 sec

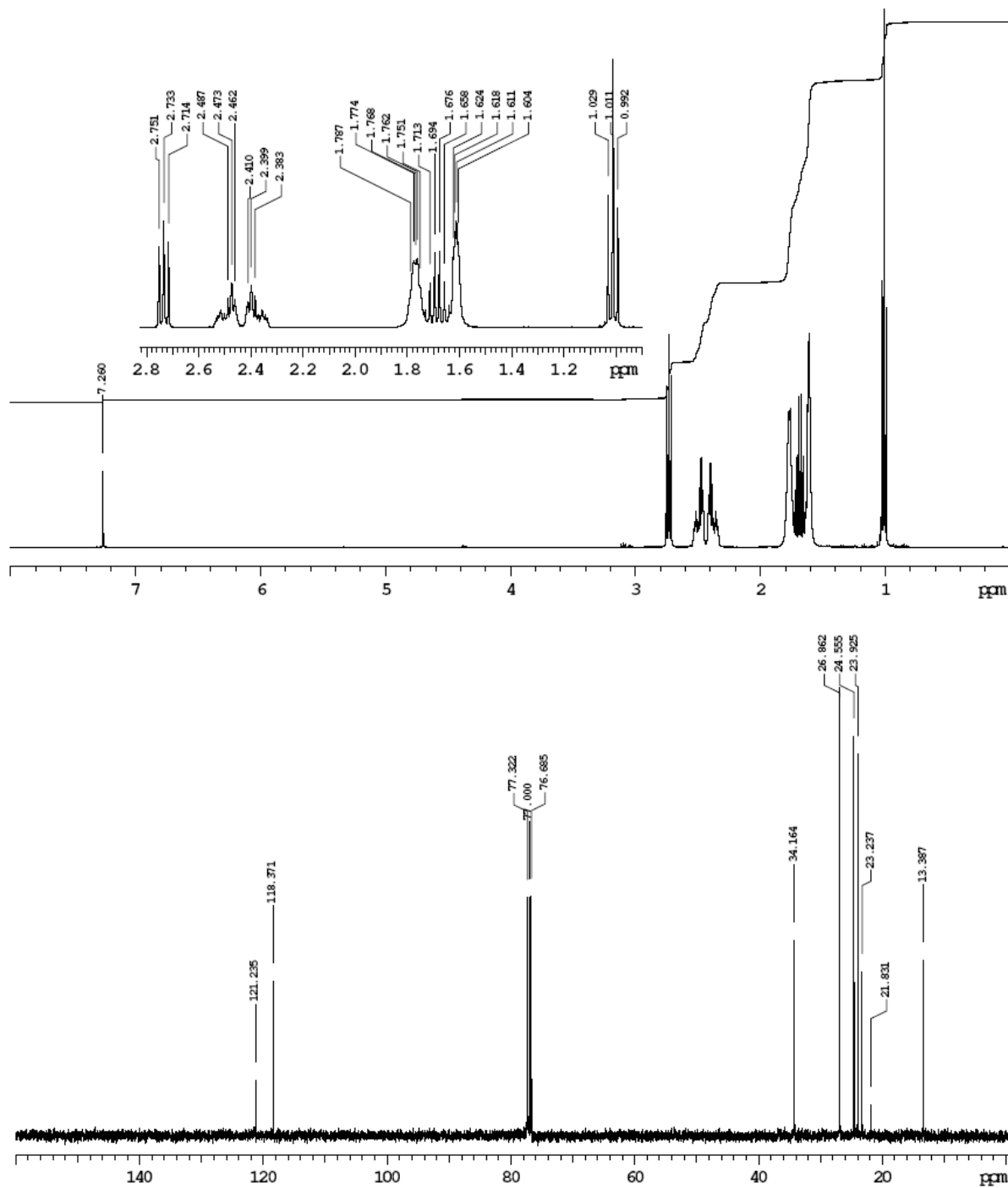
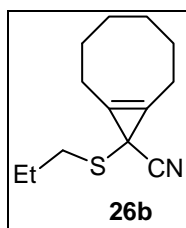


**$^1\text{H}/^{13}\text{C}$  NMR spectra of compound 23**

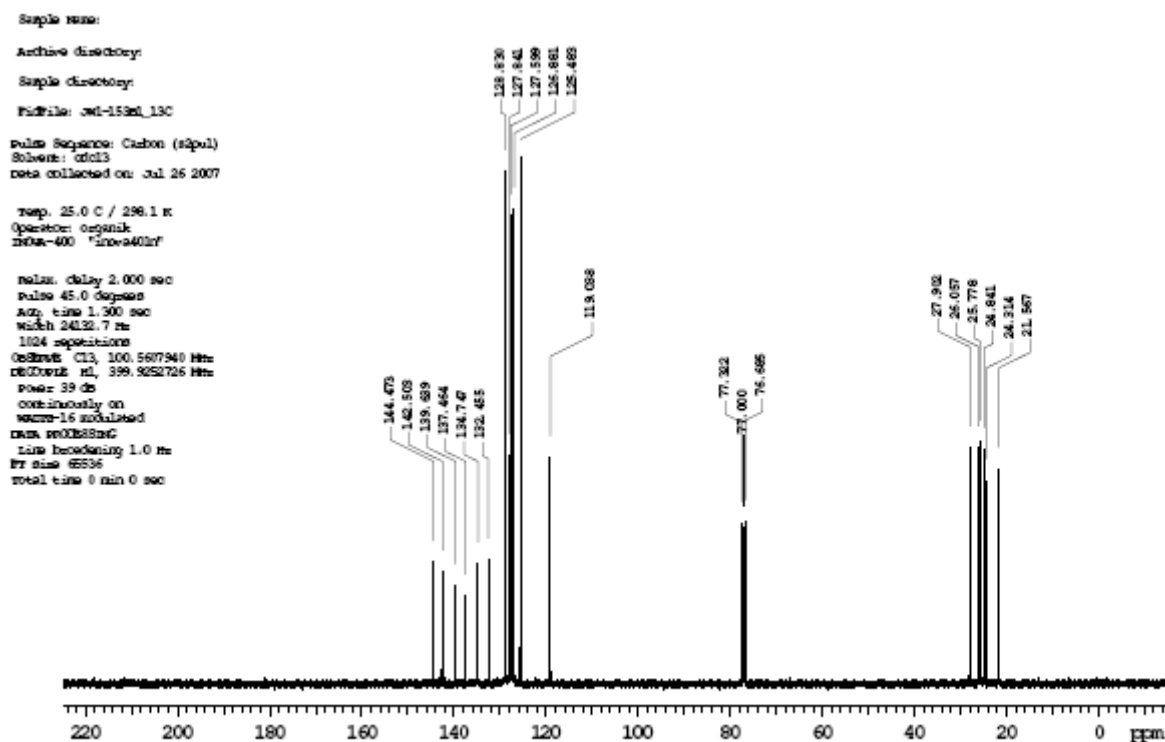
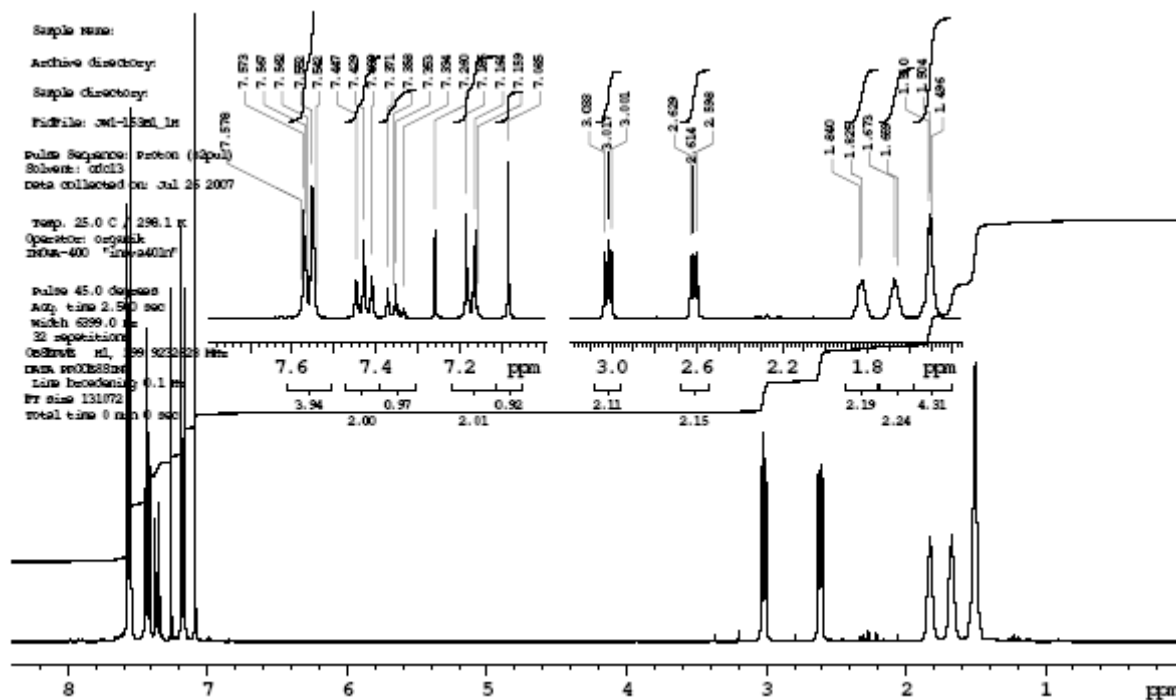
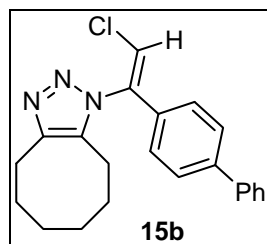


Sample Name:  
Archive directory:  
Sample directory:  
FidFile: JMW-08381\_13C  
Pulse Sequence: Carbon (s2pul)  
Solvent: cdcl3  
Data collected on: Dec 12 2007  
Operator: organik  
INOVA-400 "nova401n"  
Relax. delay 2.000 sec  
Pulse 45.0 degrees  
Acq. time 1.300 sec  
Width 24132.7 Hz  
64 repetitions  
OBSERVE C13, 100.5607918 MHz  
DECOUPLE H1, 399.9252726 MHz  
Power 38 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 65536  
Total time 0 min 0 sec

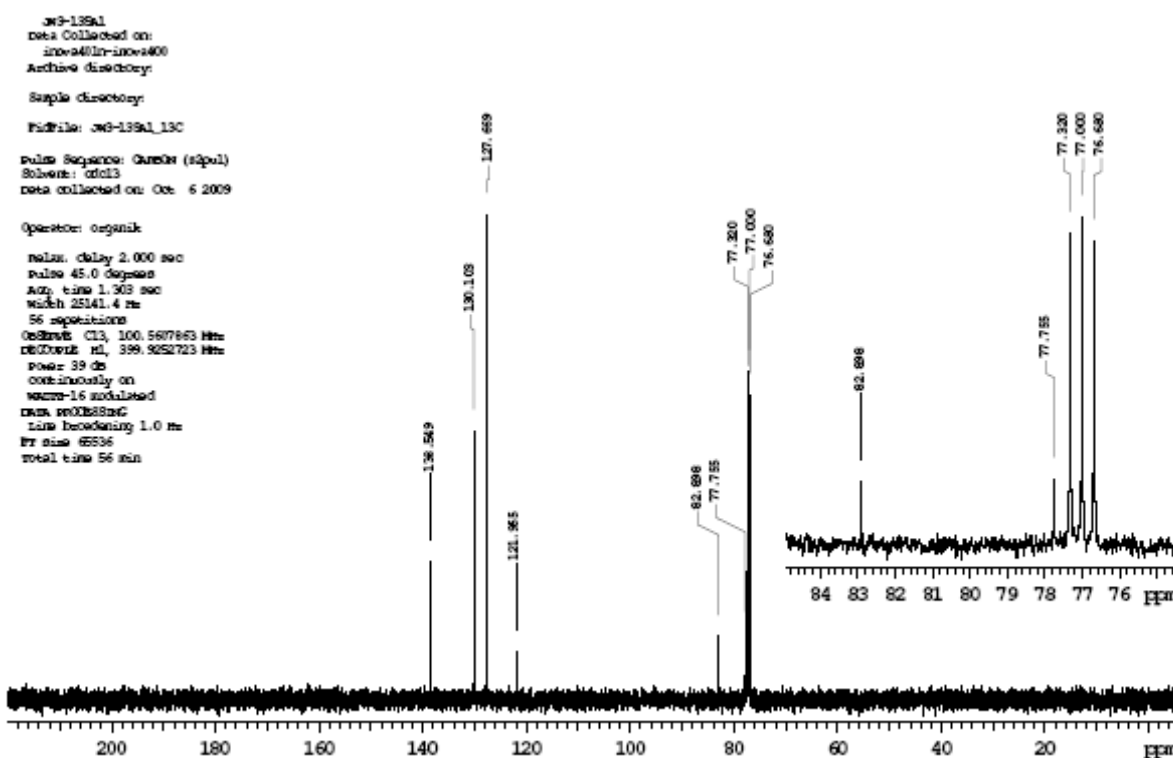
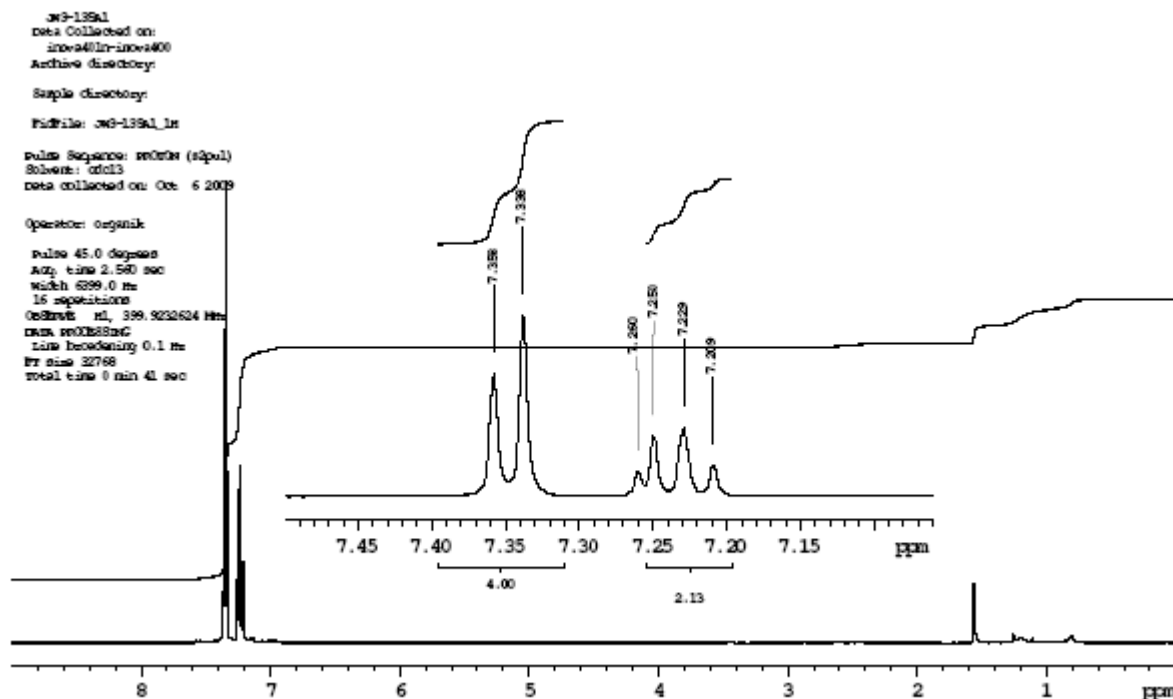
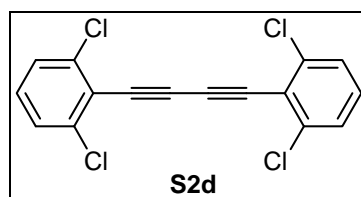
**$^1\text{H}/^{13}\text{C}$  NMR spectra of compound 26b**



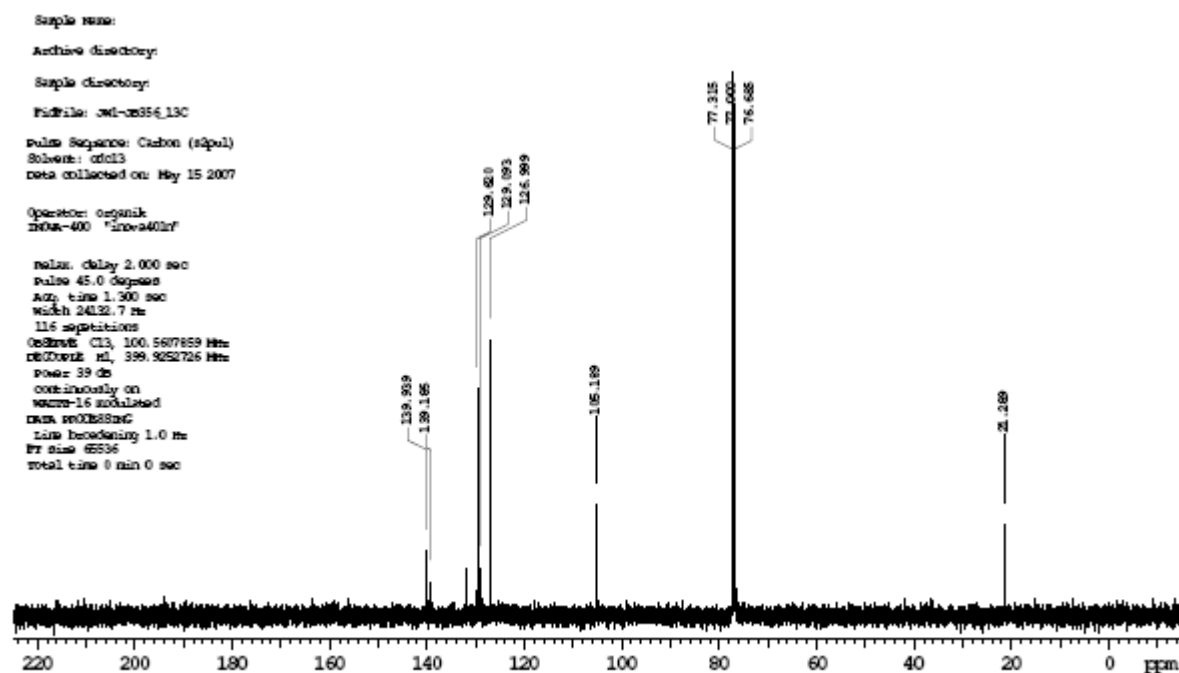
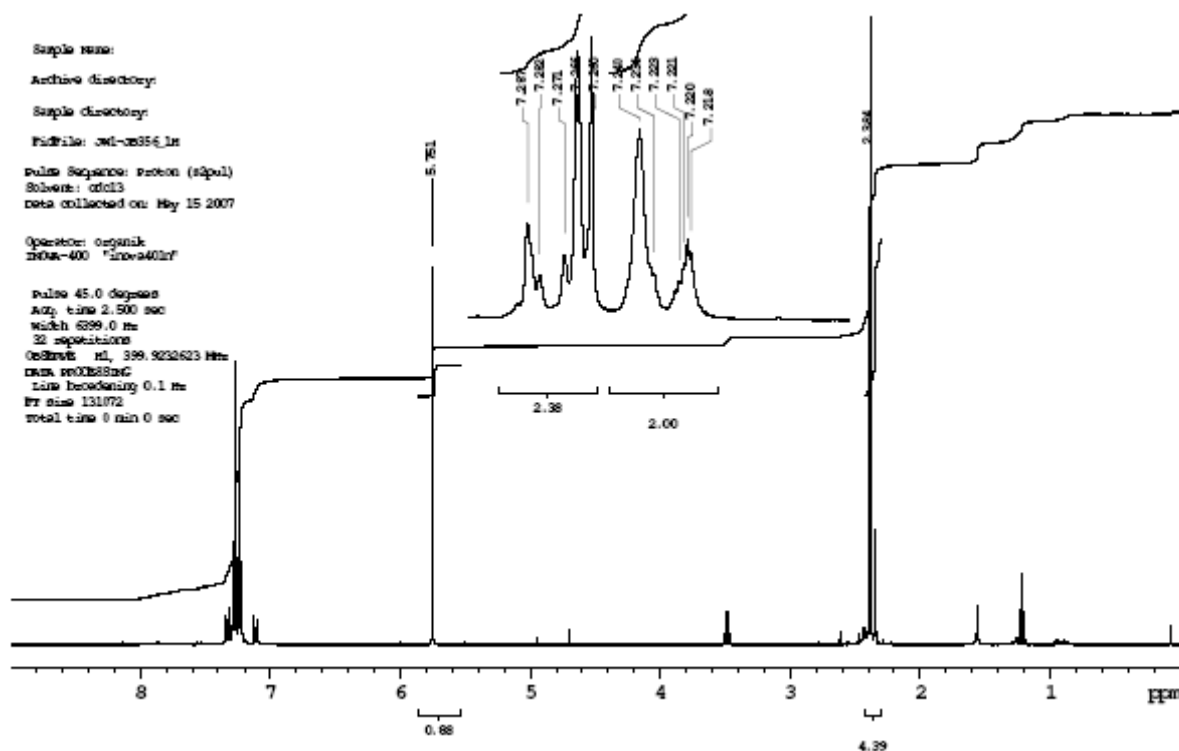
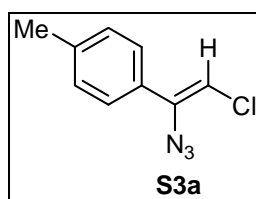
$^1\text{H}/^{13}\text{C}$  NMR spectra of compound **15b**



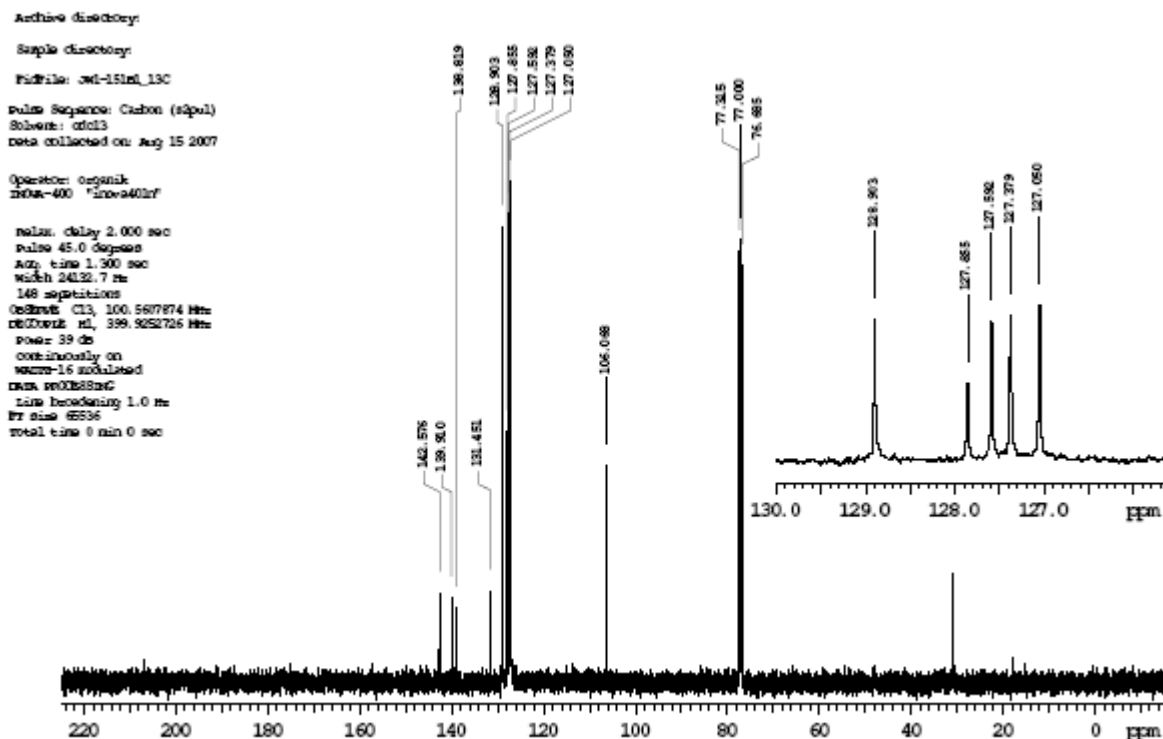
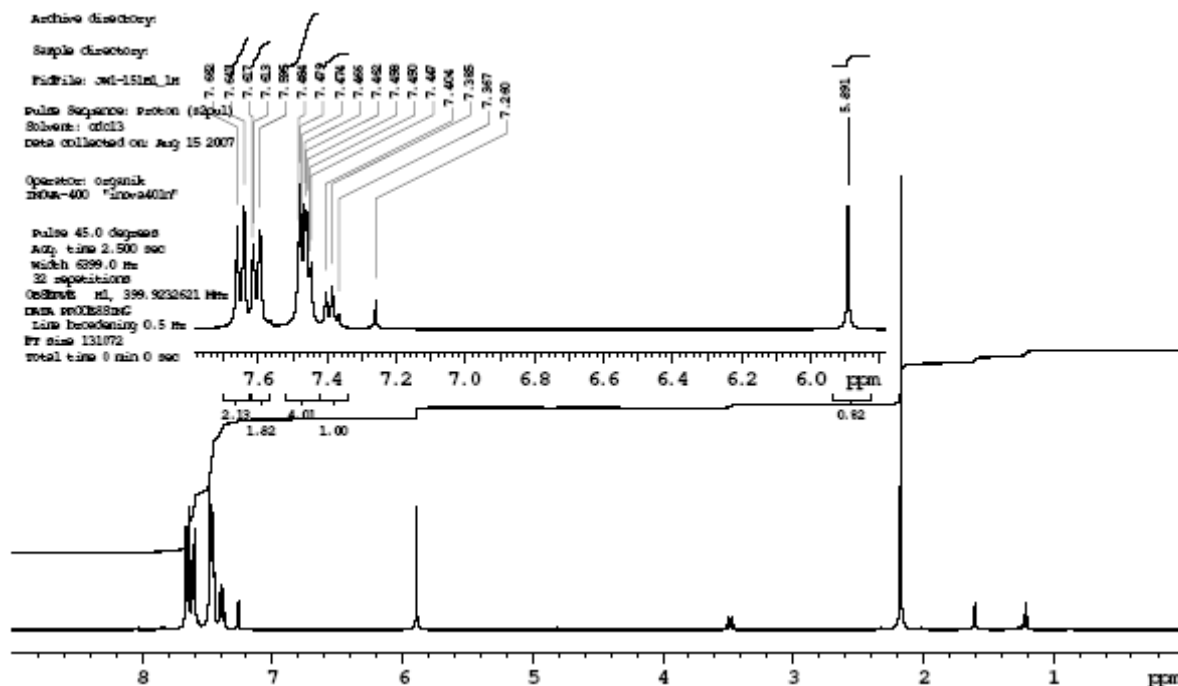
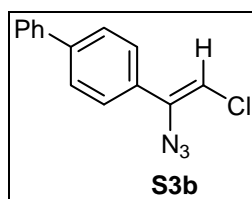
$^1\text{H}/^{13}\text{C}$  NMR spectra of compound **S2d**



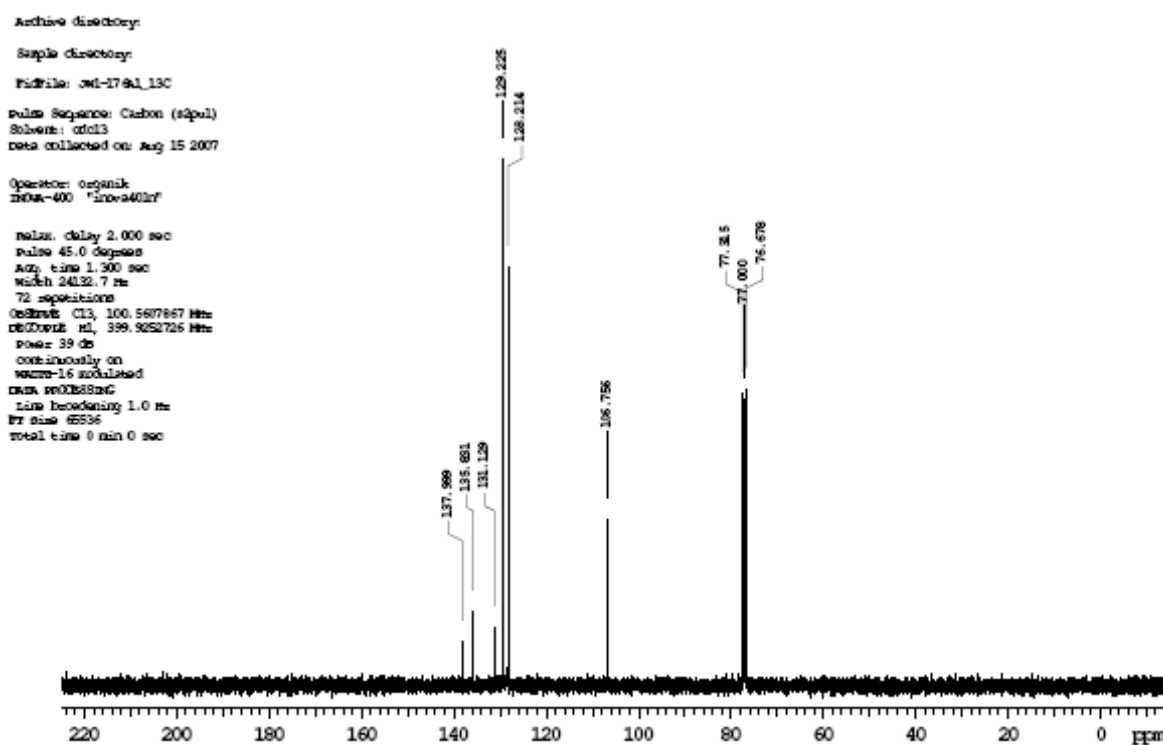
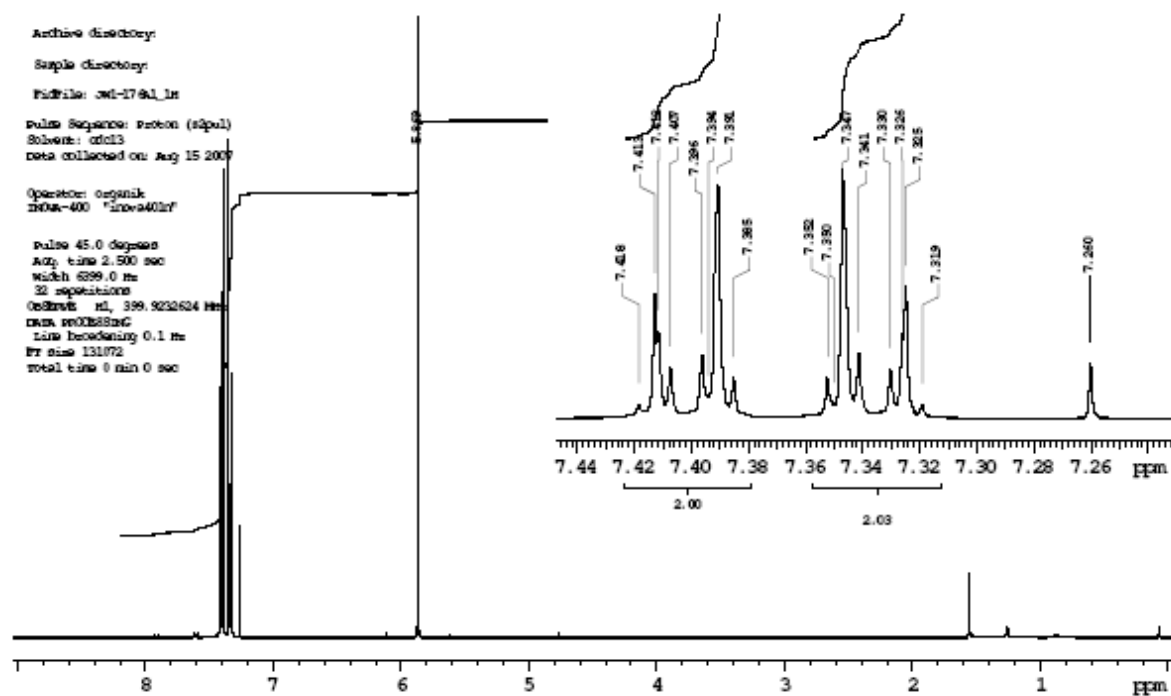
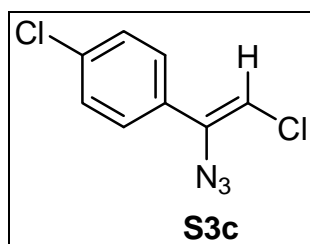
$^1\text{H}/^{13}\text{C}$  NMR spectra of compound **S3a**



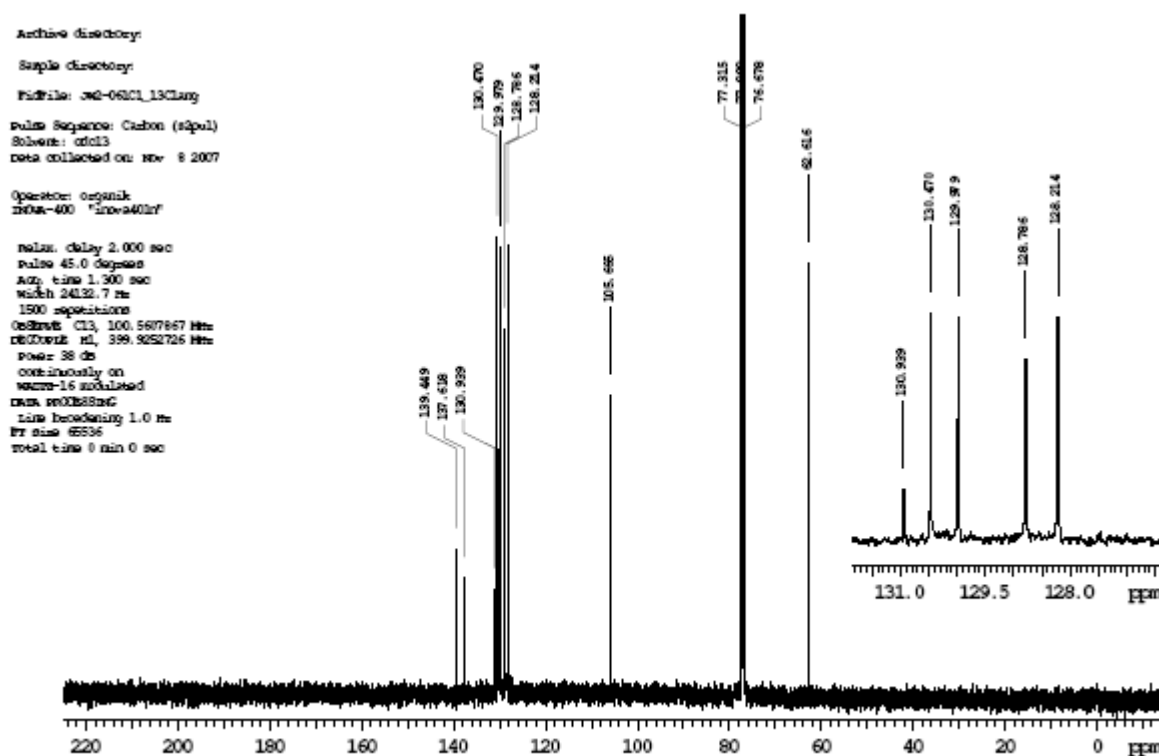
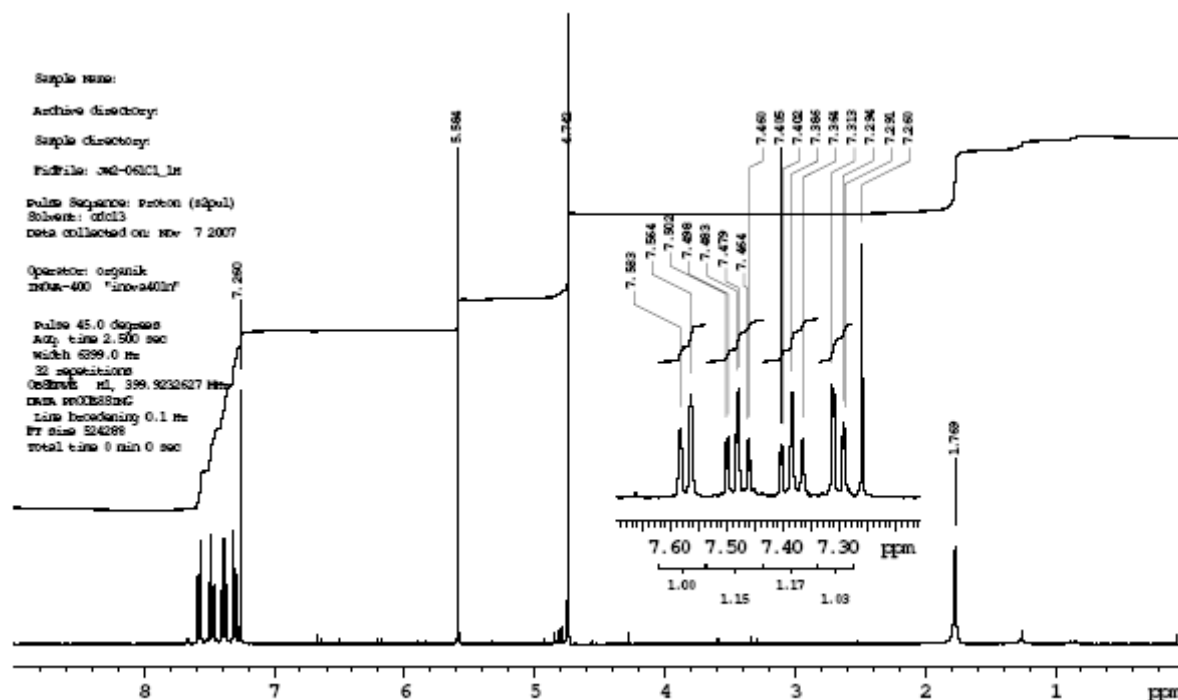
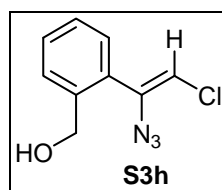
$^1\text{H}/^{13}\text{C}$  NMR spectra of compound **S3b**



$^1\text{H}/^{13}\text{C}$  NMR spectra of compound **S3c**

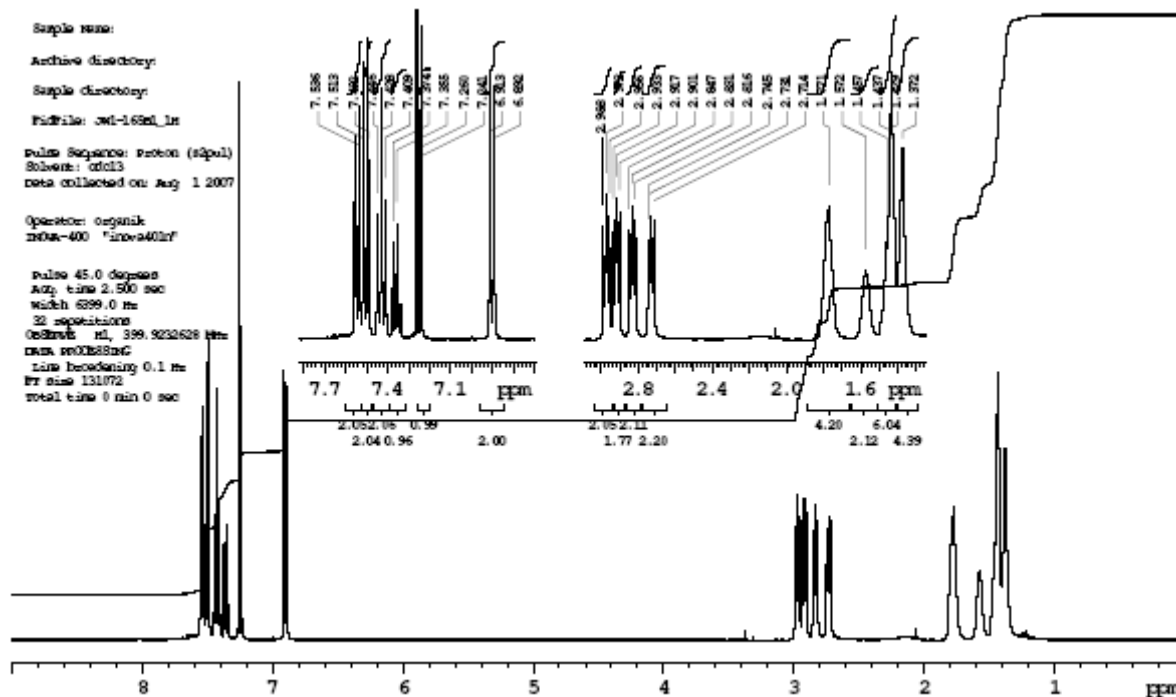
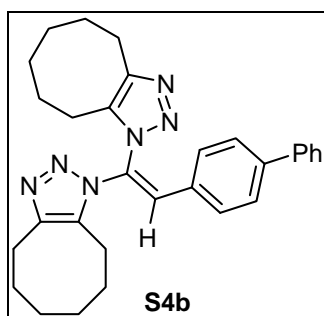


$^1\text{H}/^{13}\text{C}$  NMR spectra of compound **S3h**

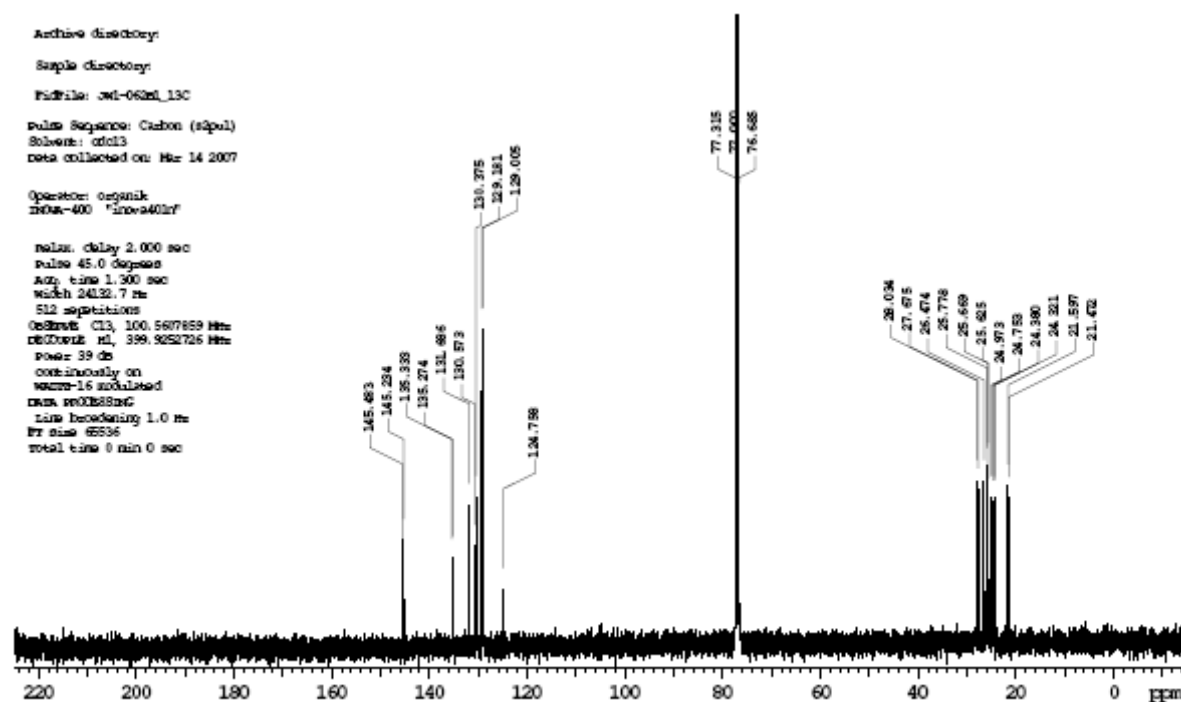
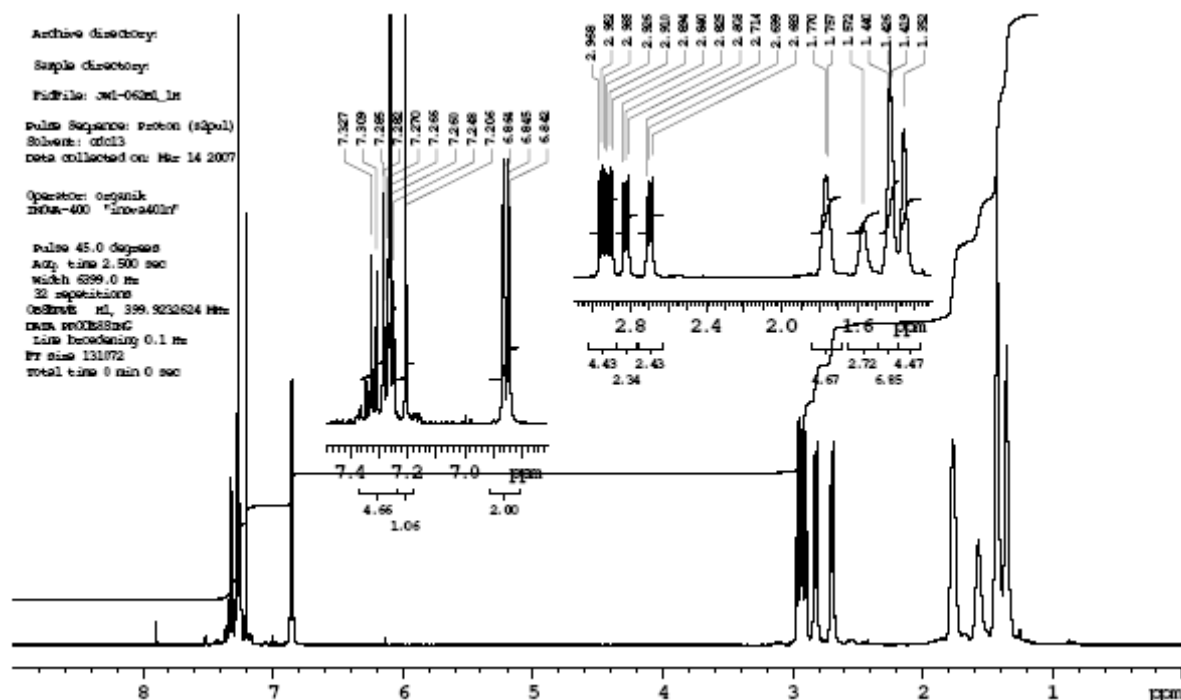
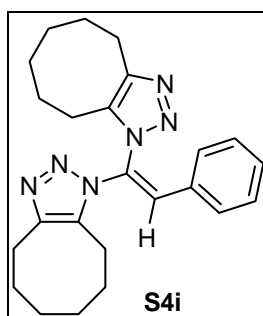




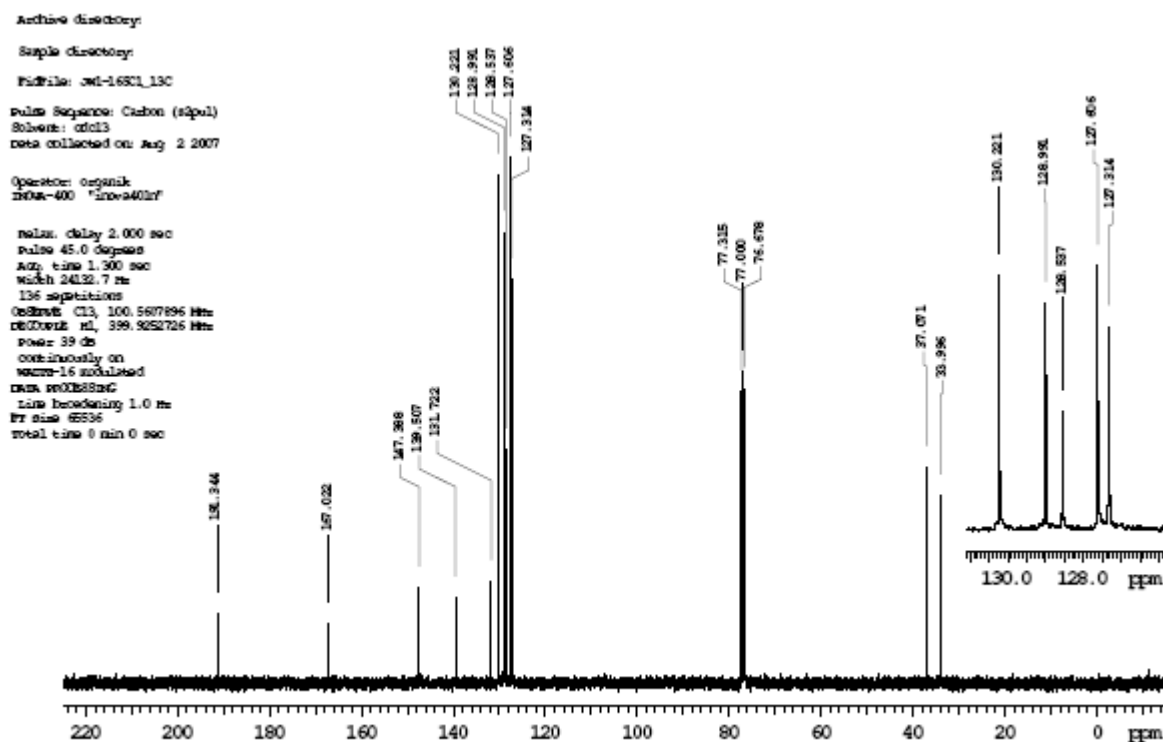
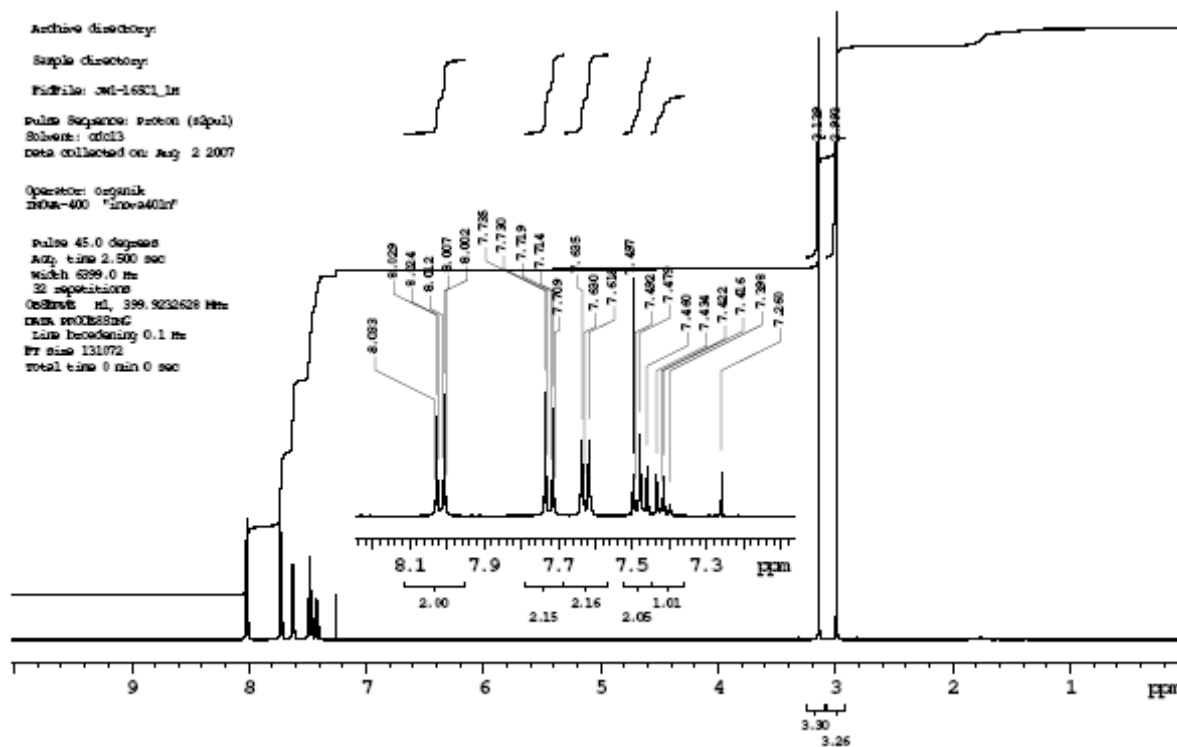
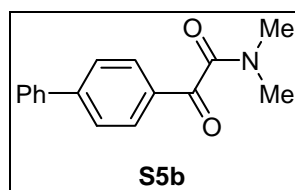
$^1\text{H}/^{13}\text{C}$  NMR spectra of compound **S4b**



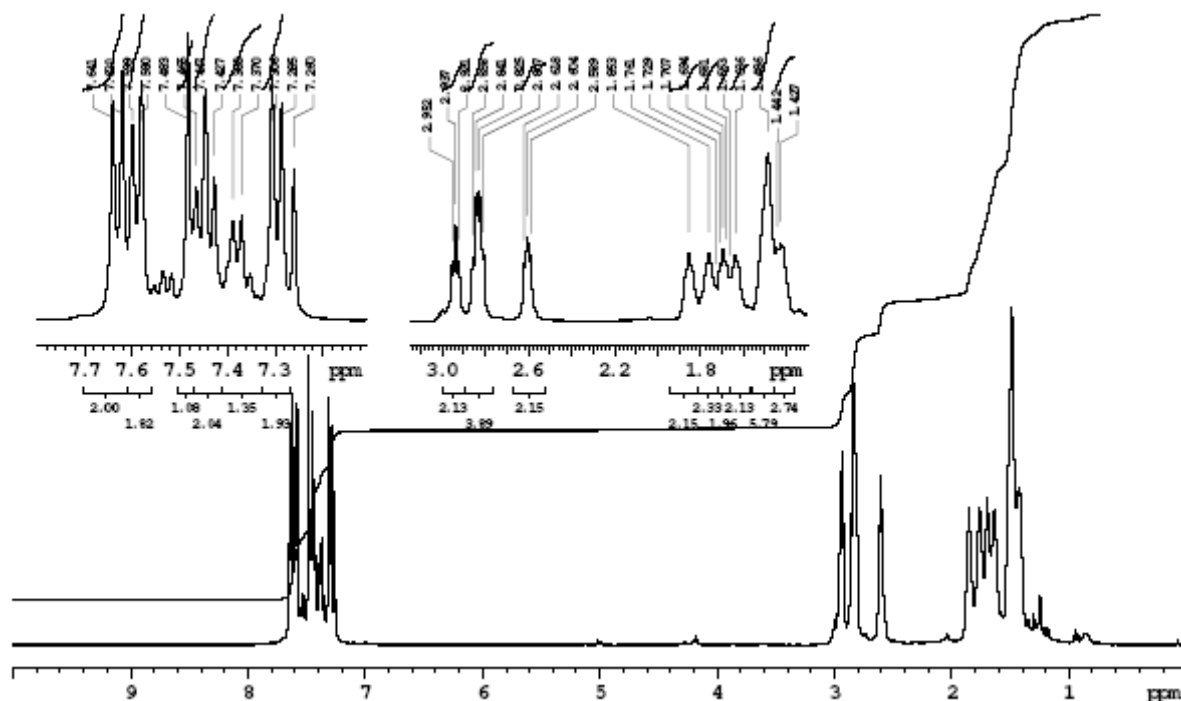
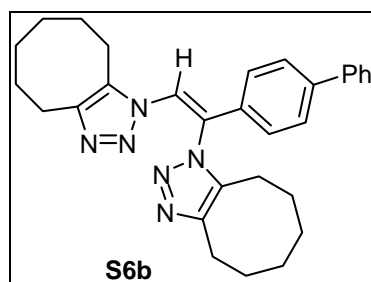
$^1\text{H}/^{13}\text{C}$  NMR spectra of compound **S4i**



$^1\text{H}/^{13}\text{C}$  NMR spectra of compound **S5b**

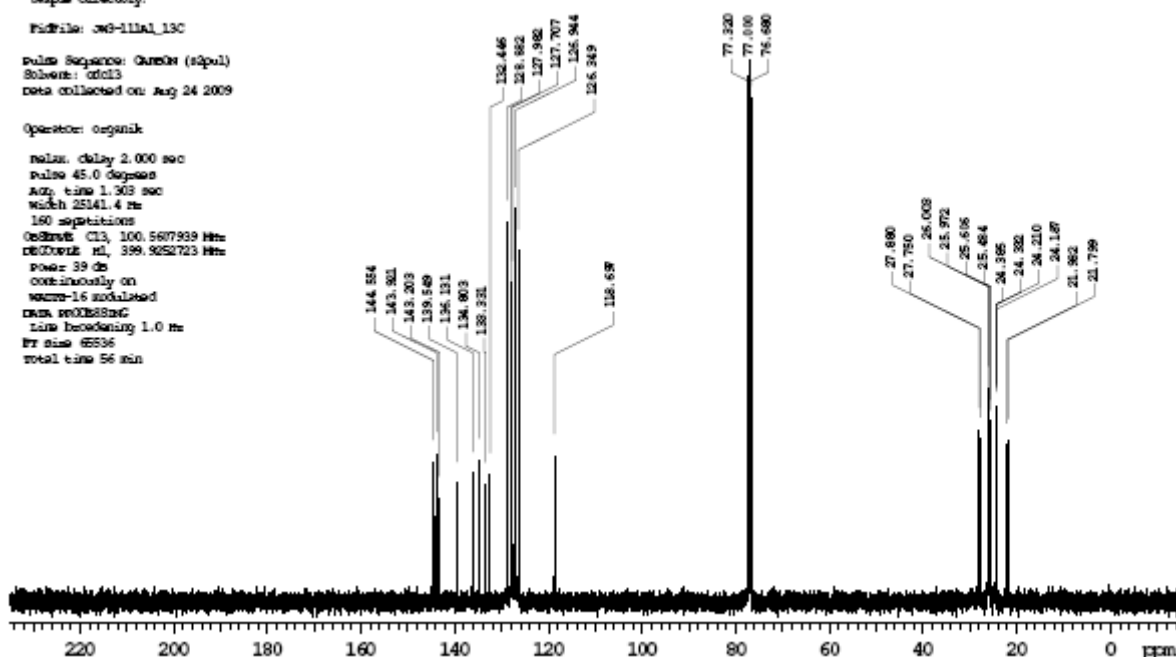


$^1\text{H}/^{13}\text{C}$  NMR spectra of compound **S6b**

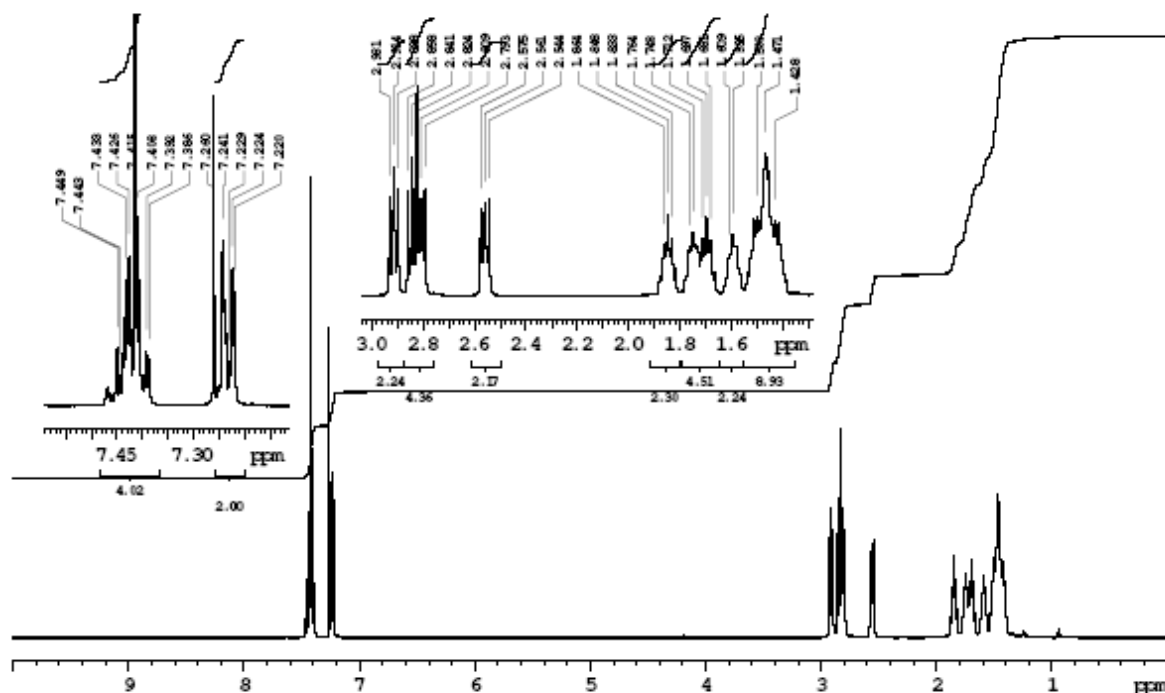
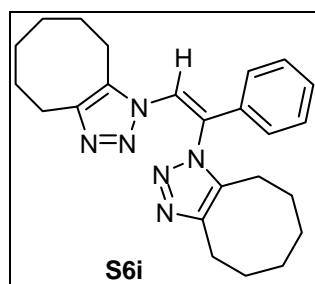


JG-111A1  
 Data Collected on:  
 inova400  
 Archive directory:  
 Sample directory:  
 File: JG-111A1\_13C  
 Pulse Sequence: zgpg30 (zgpg30)  
 Solvent: cdcl3  
 Data collected on: Aug 24 2009

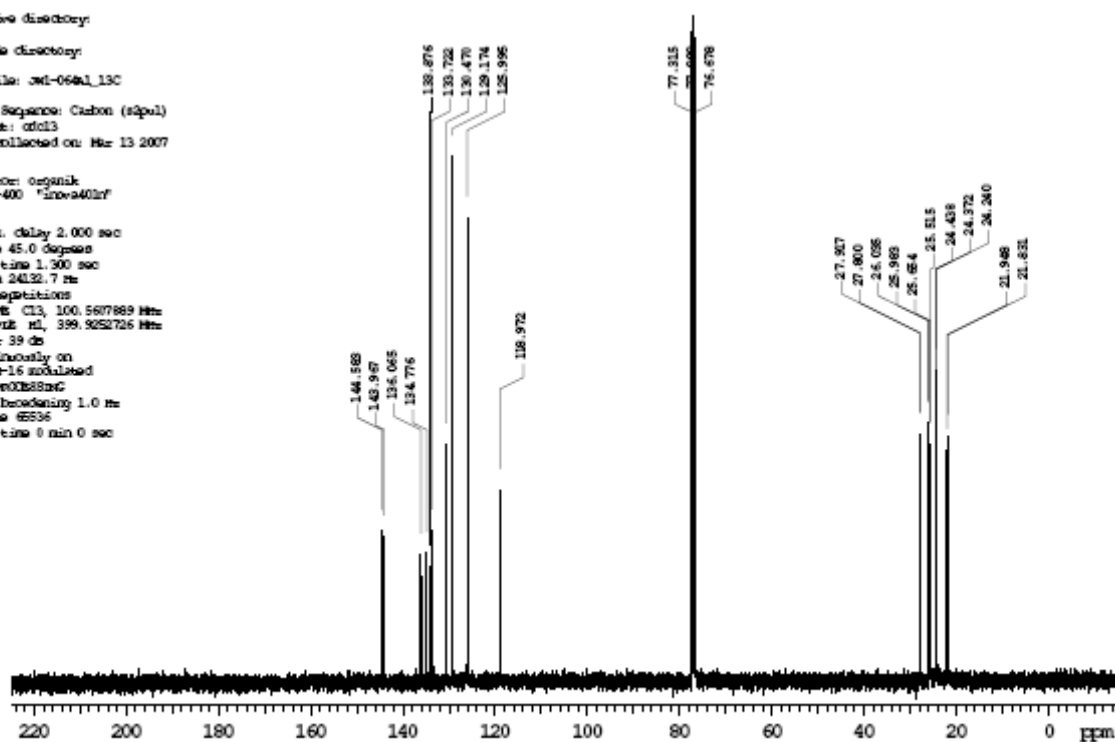
Operator: organic  
 Relax: delay 2.000 sec  
 Pulse: 45.0 degrees  
 Acq. time 1.305 sec  
 Width 25141.4 Hz  
 160 repetitions  
 Offset: 113.100 567939 Hz  
 RF Drive: 113.100 567939 Hz  
 Power: 39 dB  
 Continuously on  
 WALTZ-16 modulated  
 DATA: zgpg30  
 Line broadening 1.0 Hz  
 F2 size 65536  
 Total time 56 min



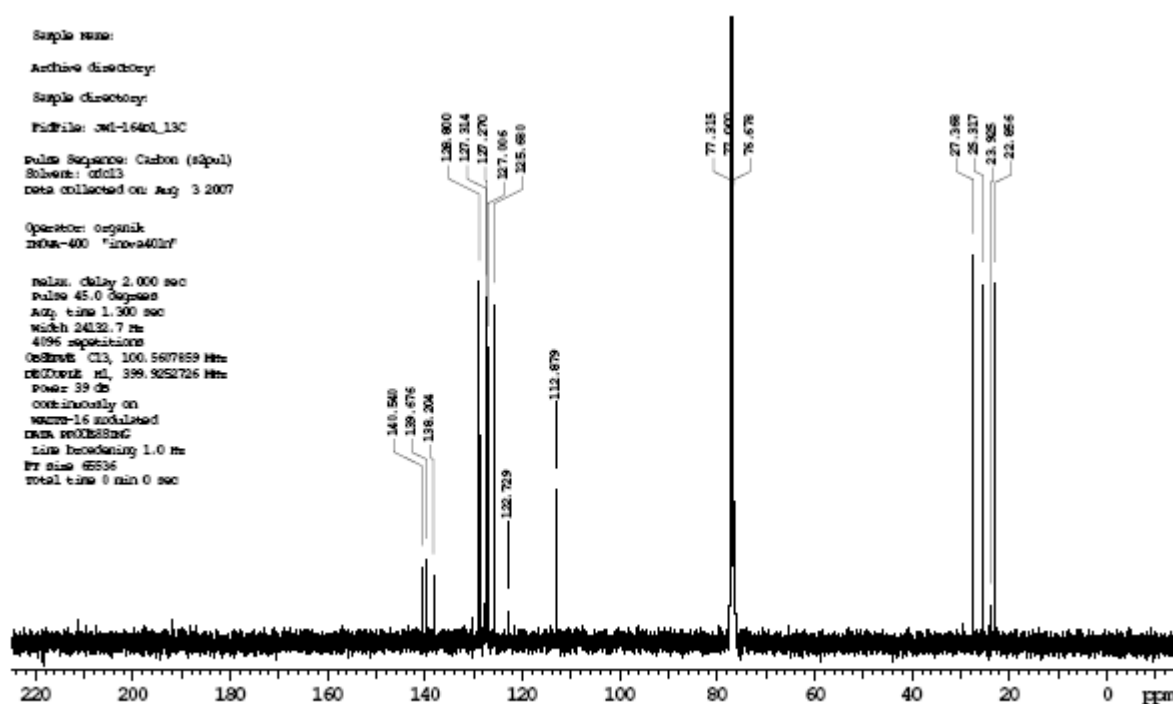
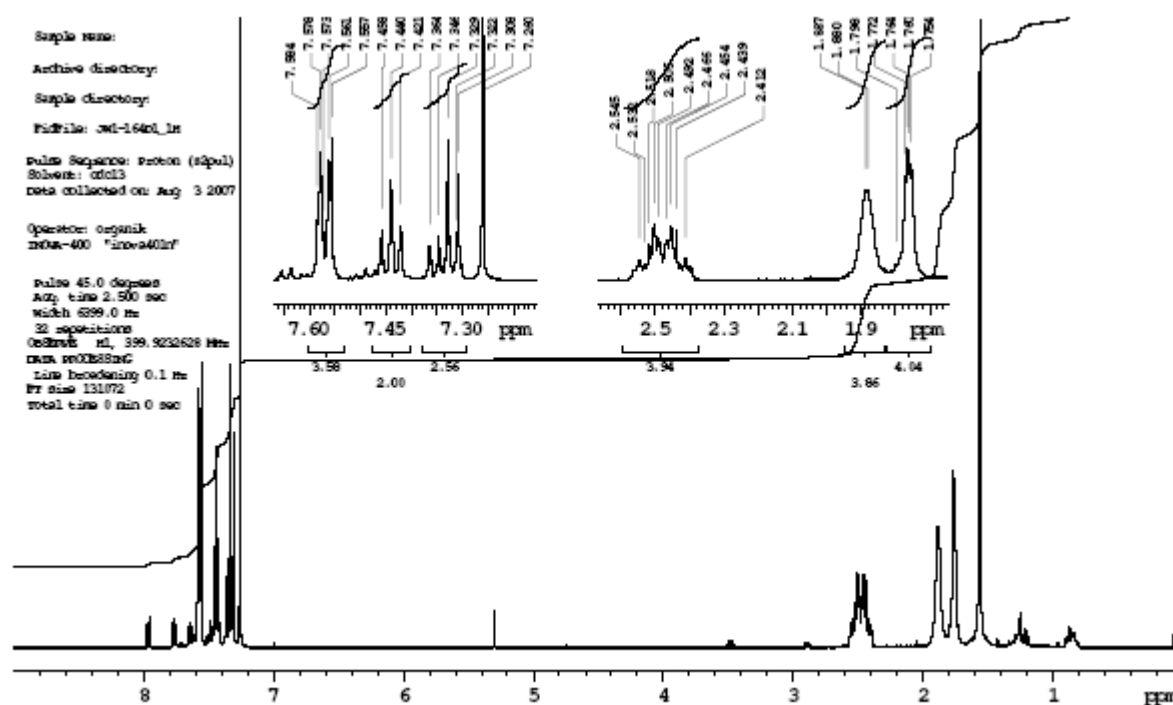
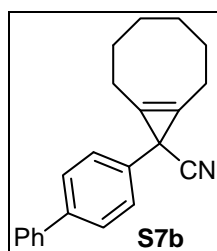
$^1\text{H}/^{13}\text{C}$  NMR spectra of compound **S6i**



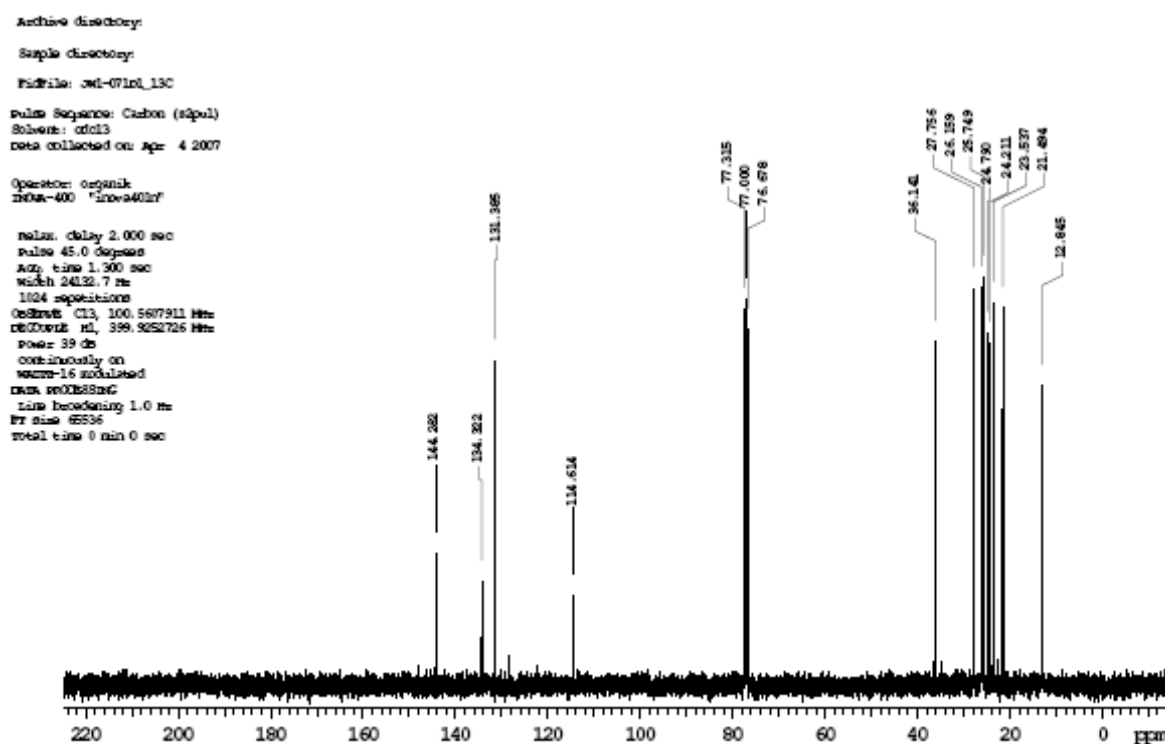
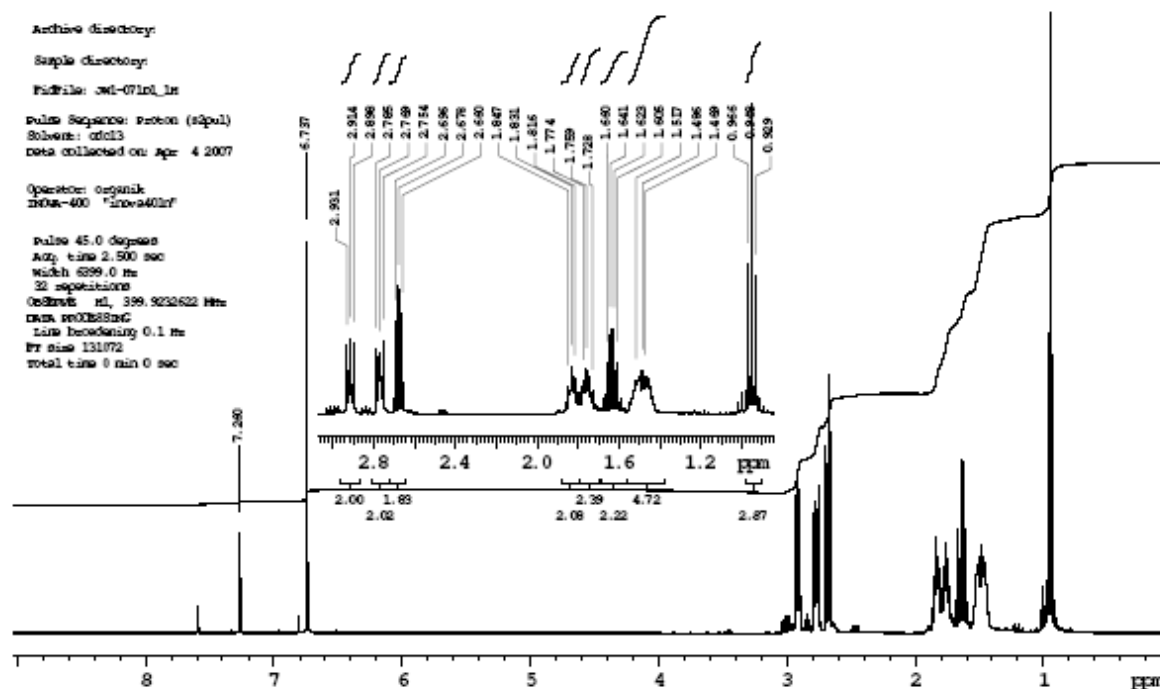
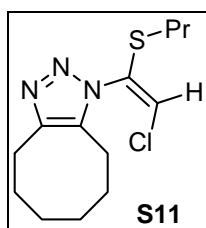
Archive directory:  
Sample directory:  
Filename: s6i-06ad\_130  
Pulse Sequence: Carbon (zgpg3)  
Solvent: cdcl3  
Data collected on: Mar 13 2007  
Operator: organic  
Inova-400 "Inova400m"  
relax. delay 2.000 sec  
pulse 45.0 degrees  
acq. time 1.300 sec  
width 24132.7 Hz  
312 repetitions  
ObsF1: C13, 100.627889 MHz  
nucl1: C13, 100.627889 MHz  
Power 39 dB  
continuously on  
wzr-16 modulated  
data resolution 1.0 Hz  
F2 time 00:00:00  
total time 0 min 0 sec



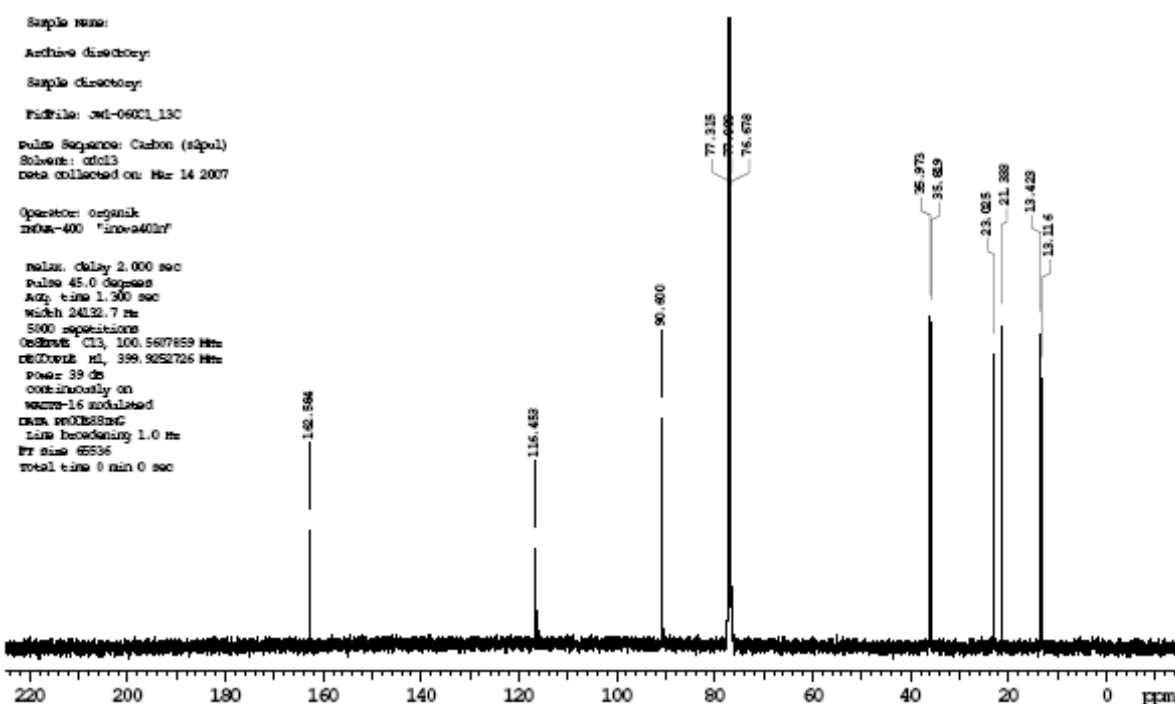
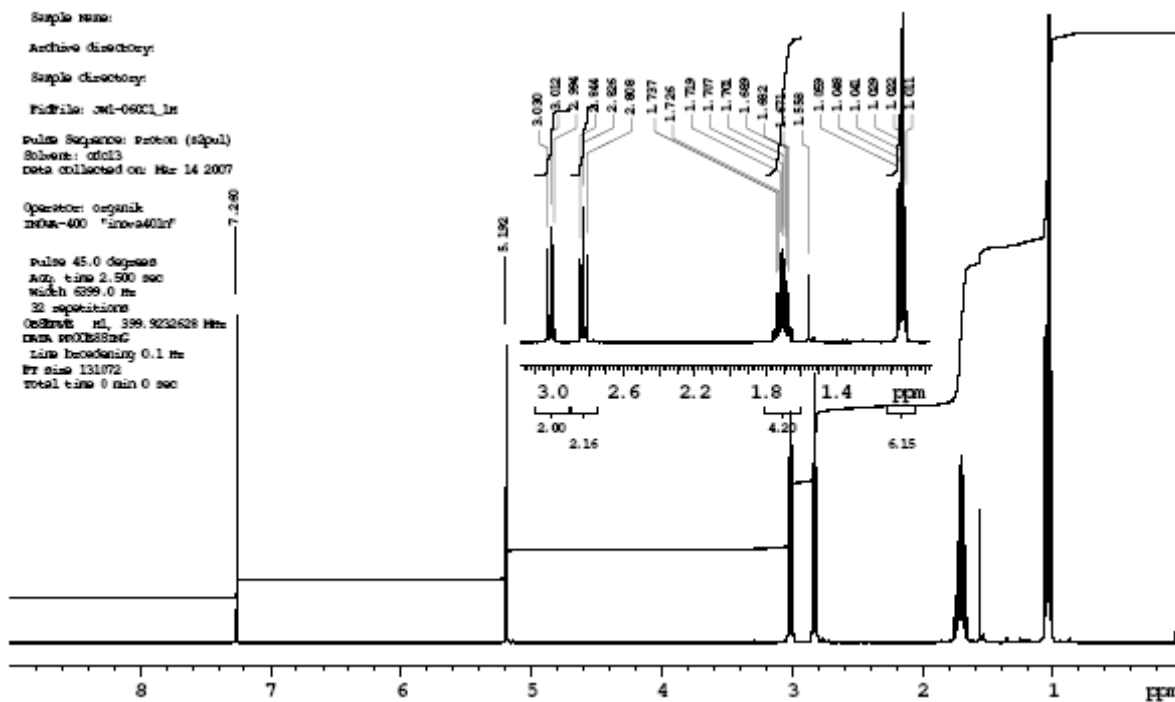
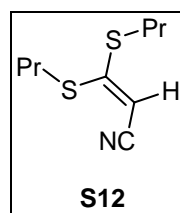
$^1\text{H}/^{13}\text{C}$  NMR spectra of compound **S7b**



$^1\text{H}/^{13}\text{C}$  NMR spectra of compound **S11**

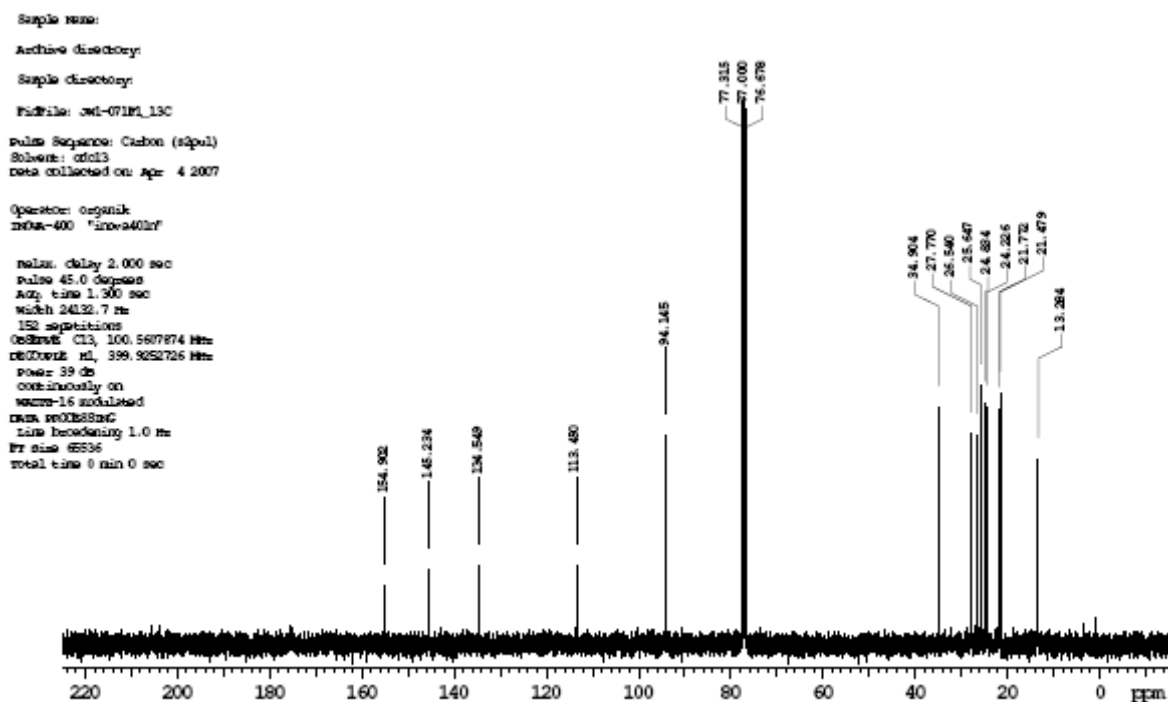
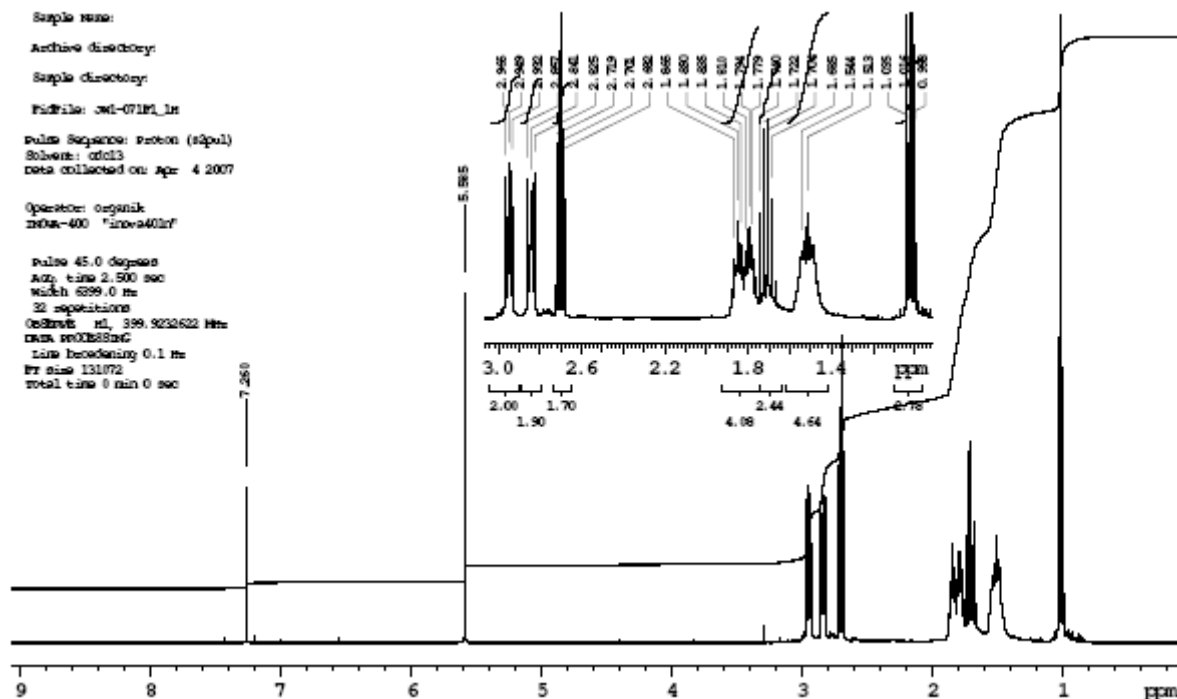
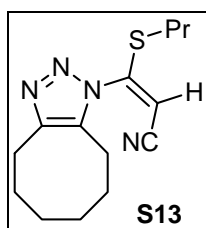


$^1\text{H}/^{13}\text{C}$  NMR spectra of compound **S12**





$^1\text{H}/^{13}\text{C}$  NMR spectra of compound **S13**





$^1\text{H}/^{13}\text{C}$  NMR spectra of compound **S15**

