Electronic Supplementary Material (ESI) for CrystEngComm

# Electronic Supplementary Information

## Modified Ene-Yne Compounds: A Novel Functional Material with Nonlinear Optical Properties

Daniel Lumpi,[*,a] Berthold Stöger,[b] Christian Hametner,[a] Frank Kubel,[b] Georg Reider,[c] Hans Hagemann,[d] Alfred Karpfen,[e] and Johannes Fröhlich[a]

[a] Institute of Applied Synthetic Chemistry, [b] Institute of Chemical Technologies and Analytics, [c] Photonics Institute, Vienna University of Technology, Austria; [d] Département de Chimie Physique, Université de Genève, Switzerland; [e] Institute for Theoretical Chemistry, University of Vienna, Austria.

### Table of contents:

1. Synthetic Part -2-
2. Optical Transmission Studies -7-
3. Thermal Analysis -8-
4. Crystallographic Part -9-
5. Computational Methods -11-
6. Polarized Single Crystal Spectroscopy -11-
7. Powder SHG Studies -12-
8. References -12-

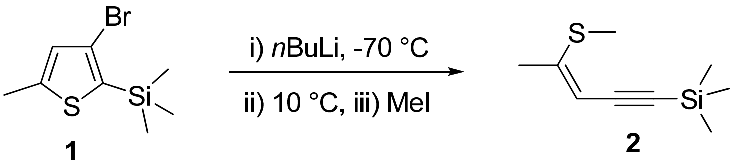
# 1. Synthetic Part

## 1.1. General procedures and methods.

All reactions were performed in oven-dried glassware. Reagents were purchased from commercial sources and used without prior purification. Anhydrous solvents were obtained by filtration through drying columns. Column chromatography was performed on silica 60 (Merck, 40-63 µm) using distilled solvents as given. Melting points were recorded on an OptiMelt Automated Melting Point System (Stanfort Research Systems) and are corrected. Experiments under microwave irradiation were performed in a Biotage Initiator Sixty microwave reactor. The syntheses of (3-bromo-5-methyl-2-thienyl)-trimethylsilane **1**[1] and azidobenzene **4**[2] were performed according to literature.

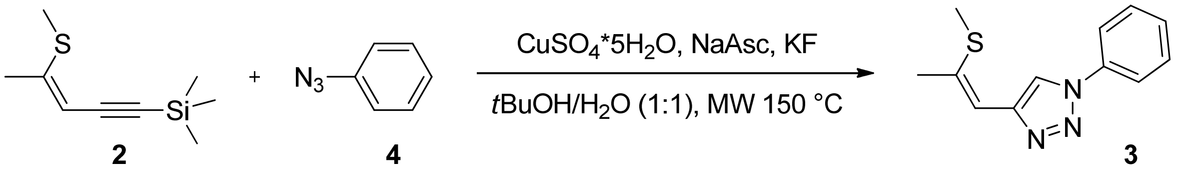
NMR spectra were recorded at 400 MHz for $^1$H and 100 MHz for $^{13}$C on a Bruker Avance DRX-400 Spectrometer. Data for $^1$H NMR are reported as follows: chemical shift in parts per million from TMS with the residual solvent signal as an internal reference ($CDCl_3$ $\delta$ = 7.26 ppm, $CD_2Cl_2$ $\delta$ = 5.32 ppm) multiplicity (s = singlet, d = doublet, t = triplet and m = multiplet), coupling constant in Hz and integration. $^{13}$C NMR spectra are reported in ppm from TMS using the central peak of the solvent as reference ($CDCl_3$ $\delta$ = 77.0 ppm, $CD_2Cl_2$ $\delta$ = 54.0 ppm); multiplicity with respect to proton (deduced from APT experiments, s = quaternary C, d = CH, t = $CH_2$, q = $CH_3$).

## 1.2. Synthesis of 2.



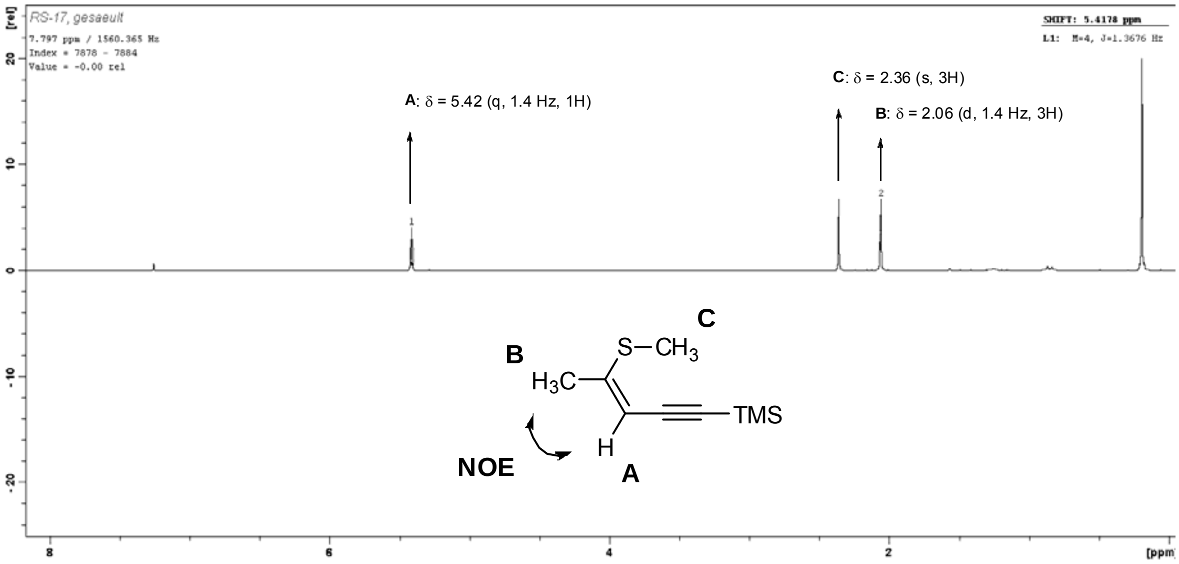
**(Z)-Trimethyl(4-(methylthio)pent-3-en-1-inyl)silane 2.** To a solution of **1** (6.23 g, 25.0 mmol, 1.00 equiv.) in dry $Et_2O$ (85 mL, 0.3 M) under argon atmosphere at -80 °C *n*-BuLi (11.0 mL, 27.5 mmol, 1.10 equiv.; 2.5 M solution in hexanes) was added over 10 min. The mixture was then allowed to warm to 10 °C and stirred for 45 min, again cooled to -50 °C and MeI (5.33 g, 37.5 mmol, 1.5 eq.) added. After a reaction time of 30 min at room temperature the mixture was poured on water and extracted with $Et_2O$. The organic layer was washed with brine, dried over anhydrous $Na_2SO_4$ and concentrated. Column chromatography (light petroleum) resulted in 3.73 g (81 %) **2** as a slightly yellow liquid. BP: 83.0-84.5 °C (4 mbar), $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.42 (q, J = 1.4 Hz, 1H), 2.36 (s, 3H), 2.06 (d, J = 1.4 Hz, 3H), 0.20 (s, 9H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 149.3 (s), 102.9 (d), 101.7 (s), 101.1 (s), 22.3 (q), 14.0 (q), 0.0 (q) ppm. Anal Calcd for $C_9H_{16}SSi$: *m/z* 185.0815 [M + H]+. Found: MS (APCI): *m/z* 185.0843 [M + H]+.

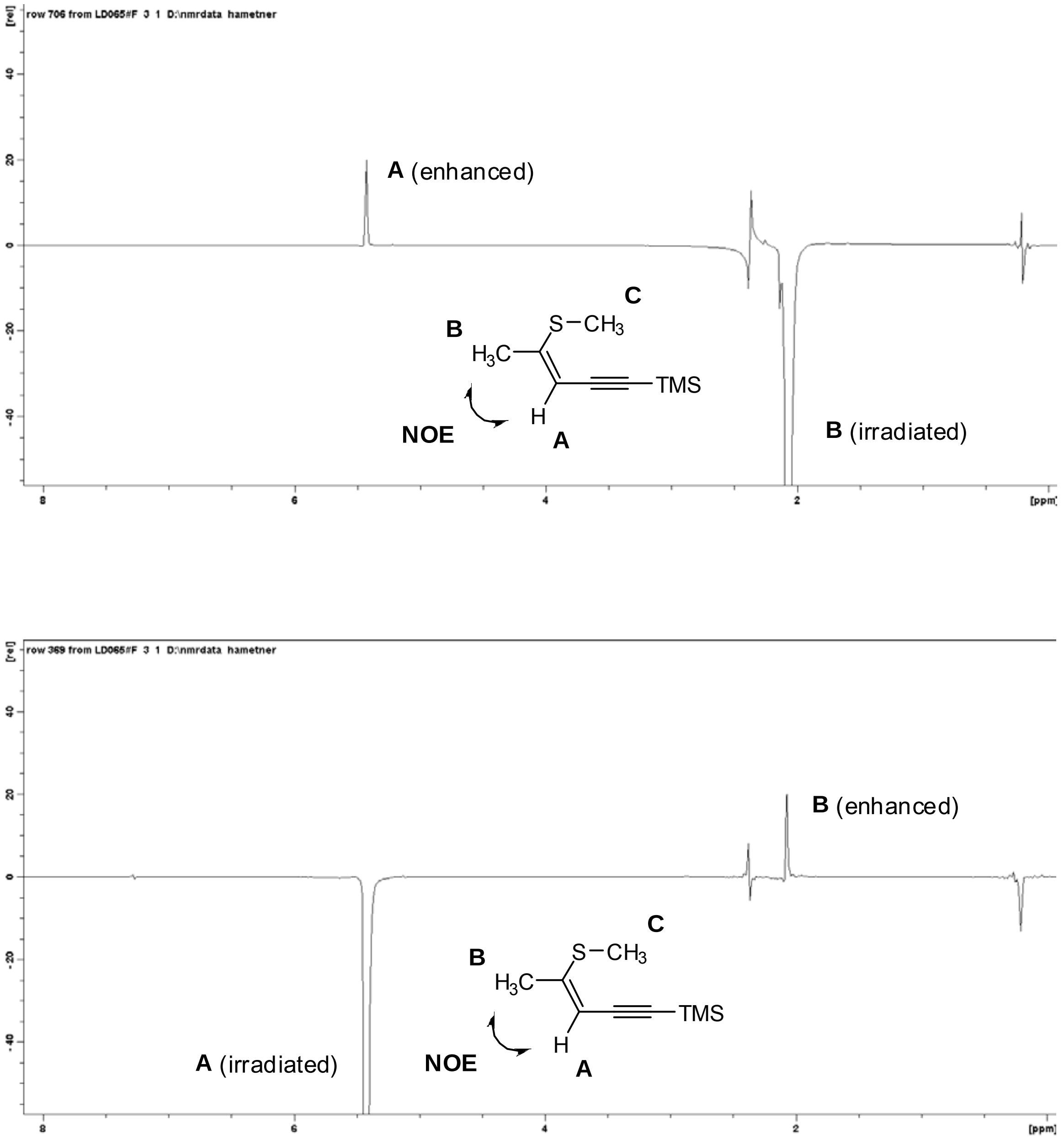
## 1.3. Synthesis of 3.



**(Z)-4-(2-(methylthio)-1-propenyl)-1-phenyl-1,2,3-triazole 3.** To a *t*BuOH/$H_2O$ (1:1, 12.5 mL, 0.4 M) suspension of **2** (0.922 g, 5.00 mmol, 1.00 equiv.), azidobenzene **4** (0.745 g, 6.25 mmol, 1.25 equiv.), $CuSO_4$*$5H_2O$ (0.250 g, 1.00 mmol, 20 mol%) and sodium ascorbate (0.396 g, 2.00 mmol, 40 mol%) in a microwave vessel potassium fluoride (0.349 g, 6.00 mmol, 1.20 equiv.) was added at room temperature. Subsequently the vessel was sealed and heated to 150 °C for 20 min under microwave irradiation. The reaction mixture was diluted with water and extracted with $Et_2O$. The combined organic layers were washed with brine and dried over anhydrous $Na_2SO_4$. Suction filtration and evaporation of the solvent followed by column chromatography (light petroleum/$Et_2O$ (3:1)) afforded **3** (0.869 g, 75 %) as a white solid. Single crystals were obtained by crystallization from saturated solution in *n*-hexane. MP: 83.5 - 84.2 °C. $^1H$ NMR (400 MHz, $CD_2Cl_2$): δ 8.39 (s, 1H), 7.77 (d, J = 8.1 Hz, 2H), 7.54 (t, J = 7.8 Hz, 2H), 7.44 (t, J = 7.4 Hz, 1H), 6.63 (s, 1H), 2.42 (s, 3H), 2.27 (s, 3H). $^{13}C$ NMR (100 MHz, $CD_2Cl_2$): δ 145.7 (s), 137.7 (s), 136.3 (s), 130.2 (d), 129.0 (d), 120.9 (d), 120.4 (d), 114.9 (d), 23.8 (q), 14.7 (q). Anal Calcd for $C_{12}H_{13}N_3S$: *m/z* 232.0903 [M + H]+. Found: MS (ESI): *m/z* 232.0903 [M + H]+. Anal Calcd for $C_{12}H_{13}N_3S$: C, 62.31; H, 5.66; N, 18.17; S, 13.86. Found: C, 62.38; H, 5.47; N, 17.70; S, 13.65.

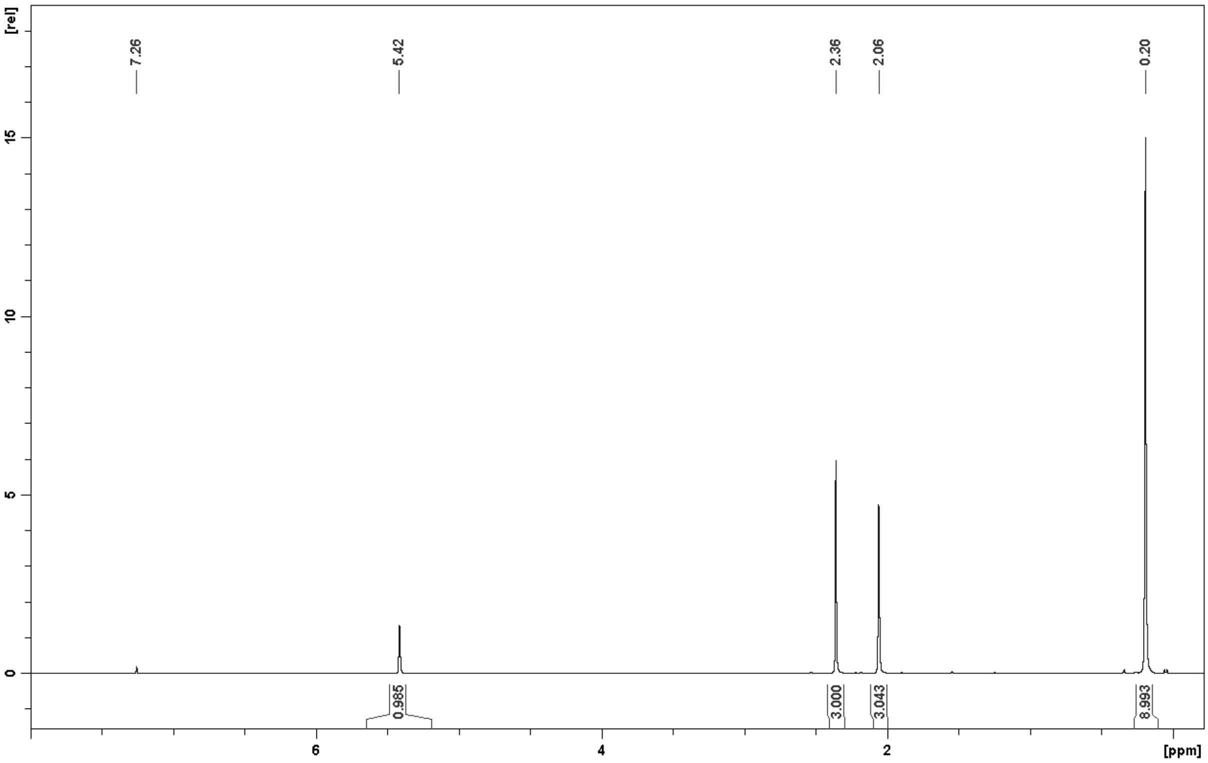
## 1.4. NOE Experiments (structure confirmation of 2).



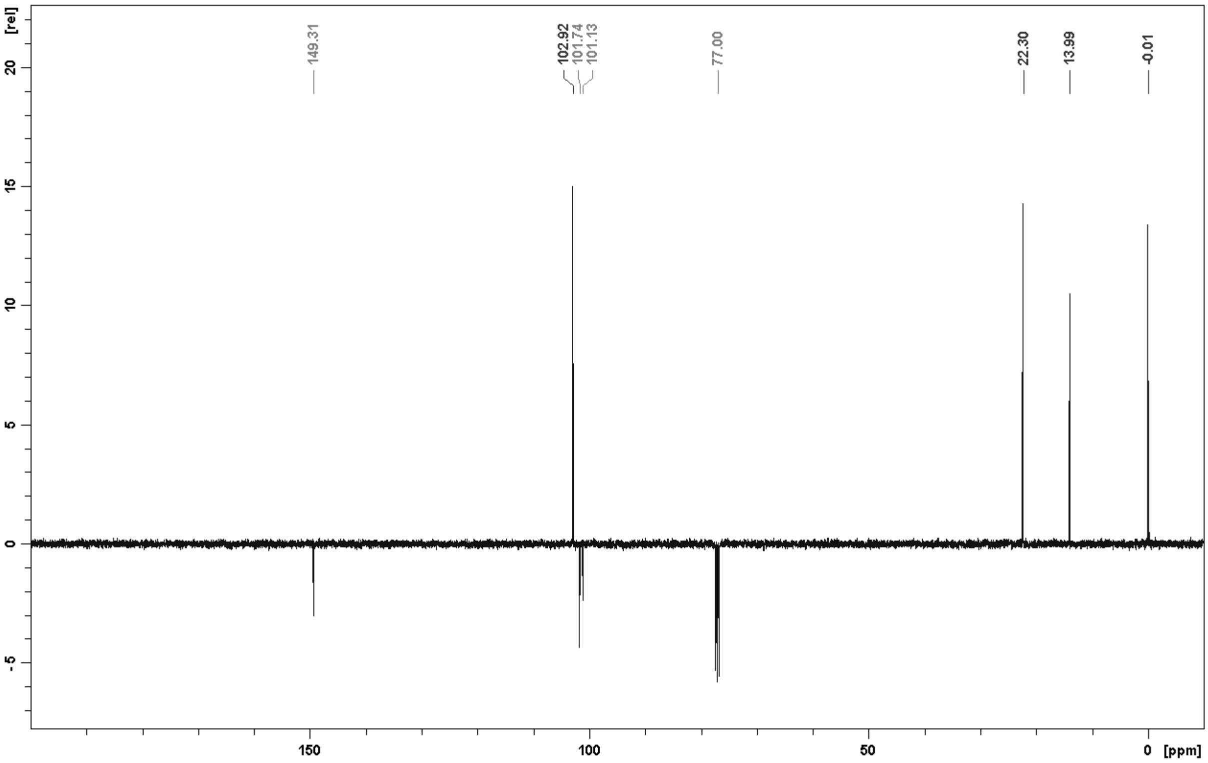


**Figures 1.1. – 1.3.** Elucidation of double bond configuration in **2**: original 400 MHz 1H spectrum (1.1), irradiation of the $CH_3$ signal enhances the olefinic proton (1.2) and vice versa (1.3).

### 1.5. Spectral Data for 2 ($^1$H-, APT NMR spectra).

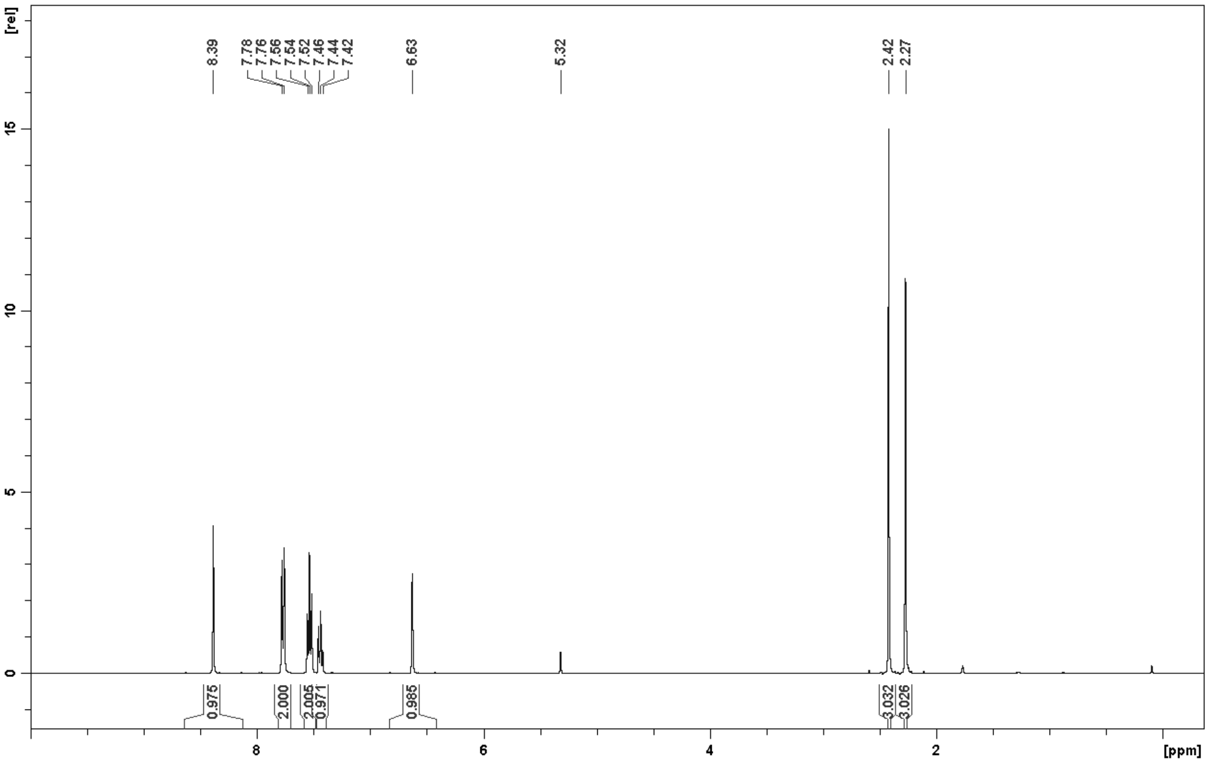


**Spectrum 1.1.** $^1$H NMR (400 MHz, $CDCl_3$) of compound **2**.

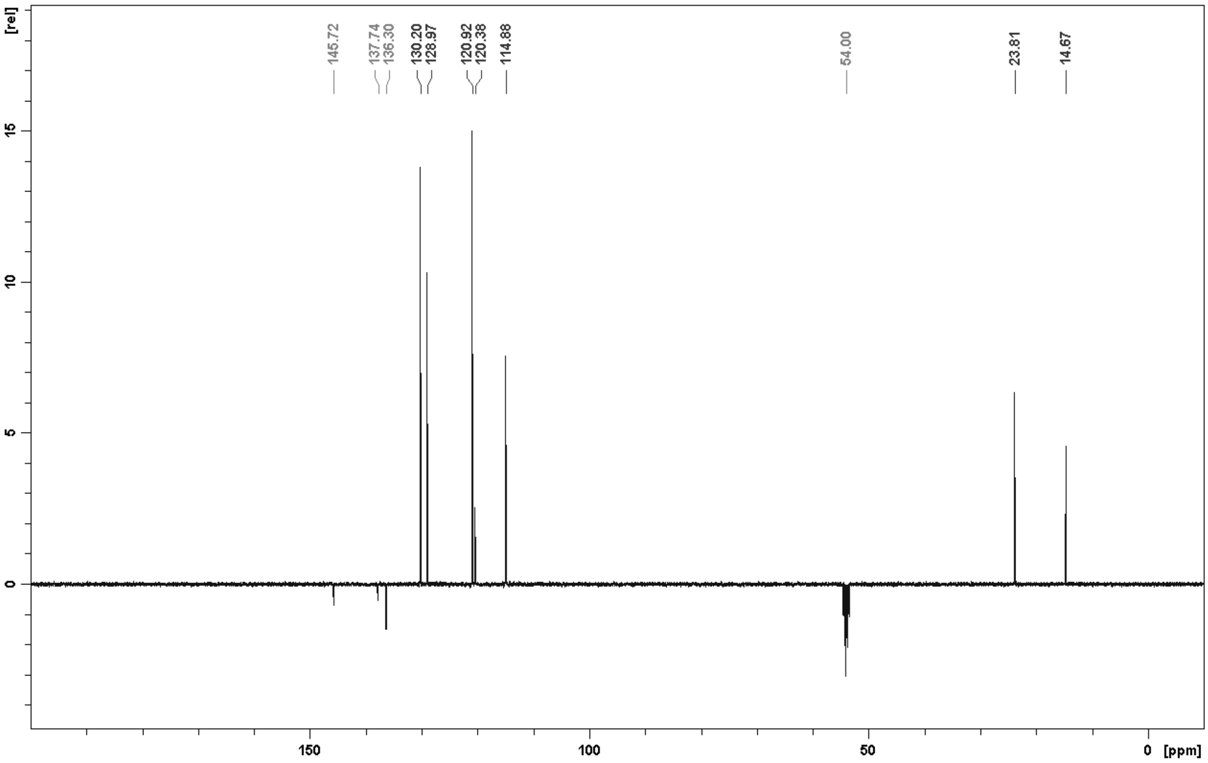


**Spectrum 1.2.** $^{13}$C NMR (100 MHz, $CDCl_3$) of compound **2**.

## 1.6. Spectral Data for 3 ($^1$H-, APT NMR spectra).



**Spectrum 1.3.** $^1$H NMR (400 MHz, $CD_2Cl_2$) of compound **3**.



**Spectrum 1.4.** $^{13}$C NMR (100 MHz, $CD_2Cl_2$) of compound **3**.

## 2. Optical Transmission Studies.

The measurements were conducted on a Perkin Elmer Lambda 750 using Suprasil glass slides as a sample holder. Measurement window ranges from 250 to 750 nm; the resulting % transmission values are normalized to 1.0.

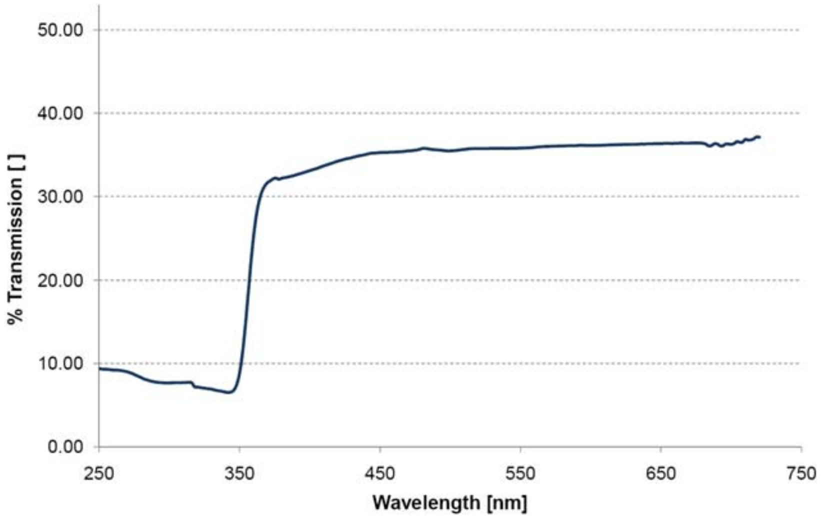


**Figure 2.1.** Optical transmission spectra of a single crystalline probe of **3**.

## 3. Thermal Analysis.

TGA analysis was conducted on a NETZSCH TG 209 T3 Taurus thermobalance in $Al_2O_3$ crucibles; DSC measurements were performed on a NETZSCH DSC 200 F3 calorimeter in Al crucibles. An endothermic effect is observed at 83.5 °C, the melting point. The corresponding exothermic recrystallization effect shows strong hysteresis and appears at ~ 40 °C (cooling of 1.0 K/min). Measurements under dry nitrogen indicate the compound to be thermally stable up to ~ 180 °C, subsequently decomposition evidenced by a mass loss of 67 % and an endothermic effect over a wide temperature range was observed; measurement under synthetic air revealed the same results for both TGA and DSC analysis.

### 3.1. TGA Measurement.

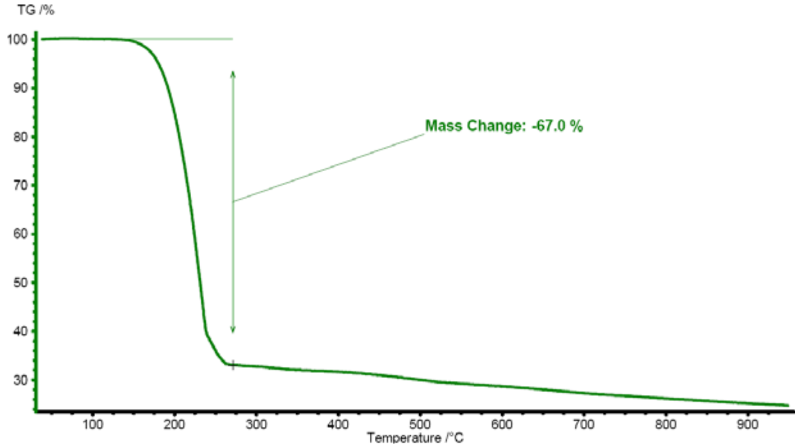


**Figure 3.1.** Thermogravimetric analysis of **3** in the temperature range 30-900°C under a dry stream of nitrogen with a heating rate of 5 K/min.

### 3.2. DSC Analysis.

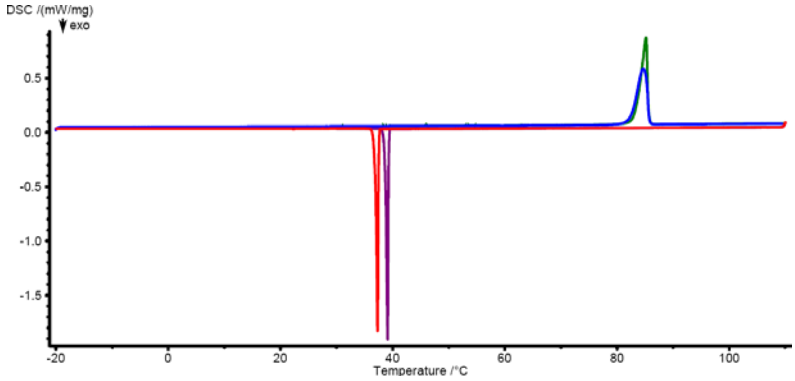


**Figure 3.2.** Two DSC heating/cooling cycles in the temperature range -20-120°C under a dry stream of nitrogen with a heating/cooling rate of 1 K/min. The heating/cooling curves of the first cycle are green and purple, of the second cycle blue and red.

## 4. Crystallographic Part.

### 4.1. Data Collection.

A suitable crystal of the title compound was mounted on a Bruker APEX II diffractometer equipped with a CCD detector. Intensity data was recorded at 100 K in a dry stream of nitrogen. Five independent sets were collected in ω- and φ-scan modes with 0.5° rotation width optimized for completeness and redundancy. In total 1865 frames were recorded. More details of the data collection are summarized in Table 4.1..

**Table 4.1.** Details of single crystal data collection and structure refinement.

| | |
|---|---|
| Diffractometer | Bruker SMART APEX II |
| Radiation; $\lambda$ / Å | Mo K$\alpha$; 0.71073 |
| Temperature / °C | -173 |
| Crystal dimensions / mm | 0.25; 0.07; 0.05 |
| Crystal colour; shape | clear colorless rod |
| Space group, no. | $P2_12_12_1$, 19 |
| Formula units $Z$ | 4 |
| $a$ / Å | 4.8314(2) |
| $b$ / Å | 15.4009(6) |
| $c$ / Å | 15.6421(5) |
| $V$ / Å$^3$ | 1163.90(8) |
| Sum formula | $C_{12}H_{13}N_3S$ |
| Formula weight | 231.3 |
| $\mu$ / mm$^{-1}$ | 0.253 |
| X-ray density / g·cm$^{-3}$ | 1.3197 |
| Range $\theta_{min}$- $\theta_{max}$ | 1.9-30.1 |
| Range $h$ | -4→6 |
| $k$ | -21→21 |
| $l$ | -22→22 |
| Measured reflections | 21682 |
| Independent reflections | 3390 |
| Obs. Reflections [$I>3\sigma(I)$] | 2525 |
| $R_i$ | 0.064 |
| Absorption correction | SADABS |
| Trans. Coef. $T_{min}$; $T_{max}$ | 0.9415; 0.9879 |
| Number of parameters | 198 |
| Diff. elec. dens. max; min [e-· Å$^{-3}$] | 0.21; -0.14 |
| $R[F>3\sigma(F)]$ | 0.03 |
| $wR(F^2$ all) | 0.03 |
| GooF | 1.25 |
| Flack Parameter | 0.00(6) |

## 4.2. Structure Solution and Refinement.

Frames were integrated using SAINT PLUS[3] and absorption correction was performed using a multi-scan approach with SADABS.[3] The lattice parameters and systematic extinctions clearly indicated orthorhombic space group $P2_12_12_1$. The crystal structure was solved by charge-flipping using SUPERFLIP.[4] All C, N and S atoms were located in the resulting electron density map. The structure was refined with JANA2006.[5] The protons were located in subsequent difference Fourier maps and refined without restraints or constraints. In the final refinement steps, all non-H atoms were refined anisotropically.

## 4.3. Additional Information.

The geometry of the intra- and intermolecular hydrogen bonds is summarized in Table 4.3..

**Table 4.3.** Non classical intra- and intermolecular hydrogen bonds.

| D–H…A | Type | D–H / Å | H…A / Å | D…A / Å | D–H…A / ° |
|---|---|---|---|---|---|
| C7–H7…S1 | intramolecular | 0.966(14) | 2.691(14) | 3.1567(16) | 110.2(10) |
| C3–H3…N3 | intermolecular | 0.898(14) | 2.518(14) | 3.3983(19) | 166.8(12) |
| C11–H113…N2 | intermolecular | 1.00(2) | 2.599(15) | 3.448(2) | 142.1(11) |

## 4.4. Czochralski process.

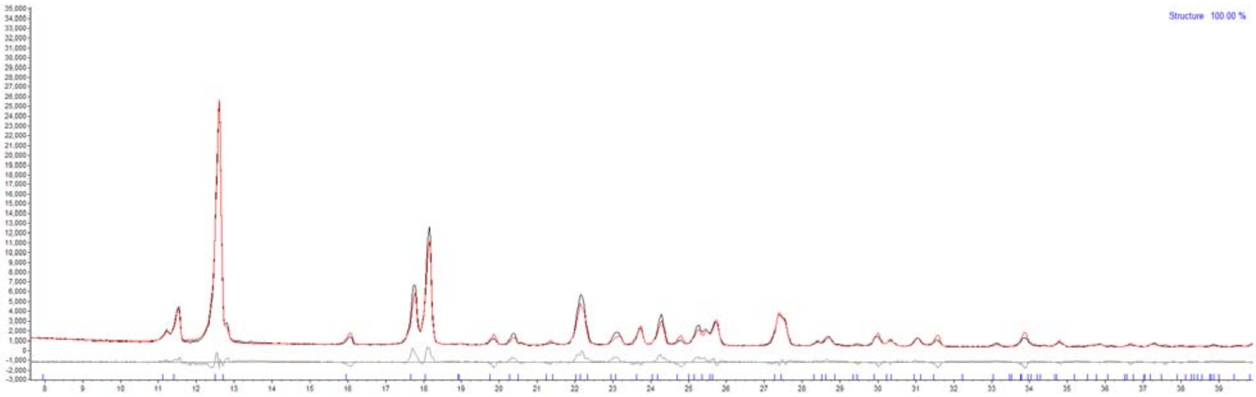


**Figure 4.1.** Powder diffraction measurement in the 2θ-range between 7 - 60°. Parameters: Cu(LFF)-anode, λ(Kα1) = 1.5406, λ(Kα2) = 1.5444 Å; Bragg-Brentano-goniometer, tube power 40 kV, 40 mA, θ/θ - scans, with 4 s/rot.; X'Celerator-multi-channel detector, Scan-length 2.456°, measuring time 30 min, divergence slit ½°, secondary Ni-Kß-filter.

The powder diffraction refinements on data acquired from a PANanlytical X'pert PRO diffractometer were performed using the Topas[6] program package (24 variables for pattern refinement, fixed structural data except lattice parameters). A $R_{Bragg}$ of 8.0% was found which is in excellent agreement with data from the single crystal refinement. Refined lattice parameters in (Å) are: a: 4.9100(6), b: 15.4907(17), c: 15.9089(20). Figure 4.1. shows calculated (red) measured (black) and difference pattern (grey).

## 5. Computational Methods.

All calculations on the torsional potentials were performed with the recently developed hybrid density functional M06-2X[7] in conjunction with the Dunning-type basis set cc-pVDZ[8] using the *GAUSSIAN 09* suite of programs.[9] This computational level is certainly sufficient for our purposes.

## 6. Polarized Single Crystal Spectroscopy.

Raman spectroscopy: Raman spectra were obtained at room temperature in the backscattering geometry using a 50mW 488 nm laser in conjunction with a Kaiser Optical Holospec monochromator equipped with a liquid nitrogen cooled CCD detector.

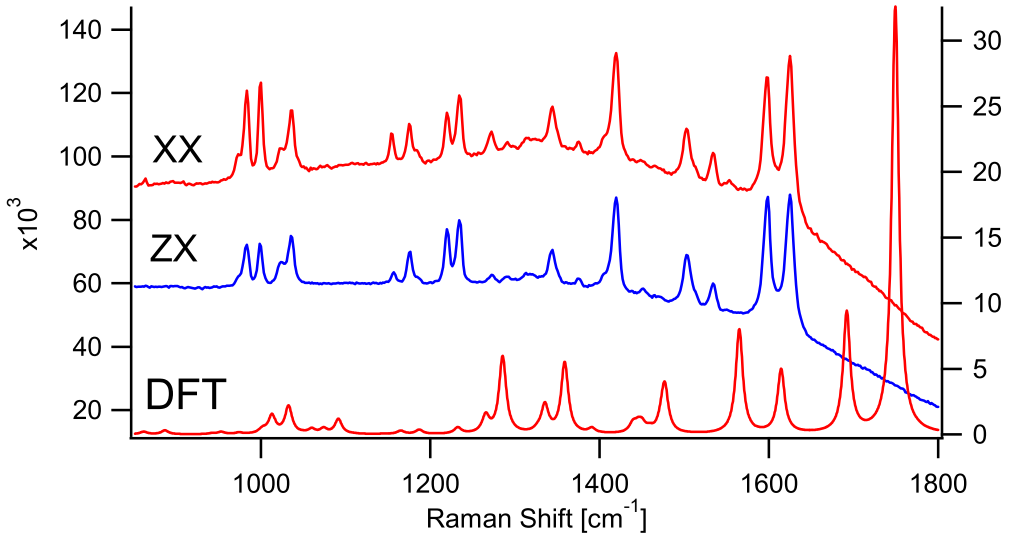


**Figure 6.1.** Comparison of experimental and theoretical Raman spectra between 800 and 1800 $cm^{-1}$.

## 7. Powder SHG Studies

Microcrystalline material was prepared from originally synthesized single crystal needles with an agate mortar, placed between two glass slides, and exposed to pulses from a Q-switched Nd:YAG Laser (wavelength 1064 nm, 10 ns pulse duration and 10 Hz repetition rate, focal area approximately 1 mm$^2$). The SH radiation transmitted through the 0.2 mm thick sample was separated from the fundamental radiation by glass filters and analyzed by a monochromator, photomultiplier tube and boxcar averager.

## 8. References

[1] Froehlich, J.; Hametner, C.; Kalt, W. *Monatshefte fuer Chemie* **1996**, *127(3)*, 325-330.

[2] Cwiklicki, A.; Rehse, K. Arch. *Pharm. Pharm. Med. Chem.* **2004**, *337*, 156-163.

[3] Bruker Analytical X-ray Instruments, Inc., Madinson, WI, USA: SAINT and SADABS 2008.

[4] Palatinus, L; Chapuis, G. *J. Appl. Cryst.* **2007**, *40*, 786-790.

[5] Petříček, V.; Dušek, M.; Palatinus, L.; **2006**: Jana2006. The crystallographic computing system. Institute of Physics, Praha, Czech Republic.

[6] Coelho, A. A. Topas **2002**.

[7] Zhao, Y.; Truhlar, D. G. *Theor. Chem. Account* **2008**, *120*, 215-241.

[8] (a) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007-1023; (b) Woon, D.E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *98*, 1358-1371.

[9] Gaussian 09, Revision A.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.