# Supporting Information for

# Visible-Light-Driven Synthesis of Alkenyl Thiocyanates: Novel Building Blocks for Diverse Sulfur-Containing Molecular Assembly

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**CONTENTS**

## 1. General considerations

All of the vinyl bromides **1** were prepared following previously reported methodologies.[1] The different reagents employed during the development of this work are commercially available from Sigma Aldrich Chemical co., Acros Organics Chemical co. and Alfa Aesar Chemical co. Dry DMSO stored with molecular sieves acquired from Sigma Aldrich Chemical co. was used for the photochemical reactions.

A Kessil® PR160 Rig equipped with different lamps (PR160-366nm, PR160-390nm, PR160-427nm, PR160-440nm and PR160-456nm) and a cooling fan was used as the photochemistry setup. A PR time controller was additionally used to select the irradiation time. 5 mL glass vials purchased in VWR® were used to run the photochemical reactions. The vials were sealed with a cap after adding the chemicals and solvent and placed at a distance of approximately 5 cm away from the lamp prior to irradiation at maximum intensity (100% power) of the Kessil lamp. Figures SI-1 to SI-3 illustrate relevant photophysical properties of the lamps.

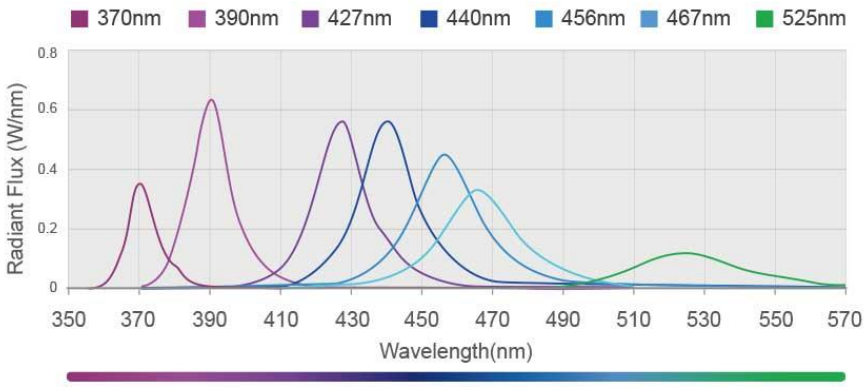



**Figure SI-1.** Emission spectrums of the different Kessil® lamps.

| | |
|---|---|
| Power Consumption | 370nm (max 43W), 390nm (max 52W), 427nm & 440nm (max 45W), 456nm (max 50W), 467nm (max 44W), 525nm (max 44W) |
| Input Voltage | 100-240 VAC |
| Operating Temperature | 0 - 40°C / 32 - 104°F |
| Beam Angle | 56° |
| Wavelength Options | 370nm, 390nm, 427nm, 440nm, 456nm, 467nm, 525nm |
| Average Intensity of PR160 series | 352mW/cm2 (measured from 1 cm distance) |
| Dimensions (H x D) | 4.49" x 2.48" / 11.4cm x 6.3cm |

**Figure SI-2.** Technical specifications of the Kessil® lamps.

[1] For the synthesis of the vinyl bromides **1**, we followed a two-step sequence based on a dibromoolefination reaction of the corresponding aldehyde precursor (A. R. Silva, E. C. Polo, N. C. Martins, Correia, D. C. Roque. *Adv. Synth. Catal.* **2018**, *360*, 346.) followed by a dehalogenation reaction (Y. Ye, H. Chen, K. Yao, H. Gong. *Org. Lett.* **2020**, *22*, 2070.).

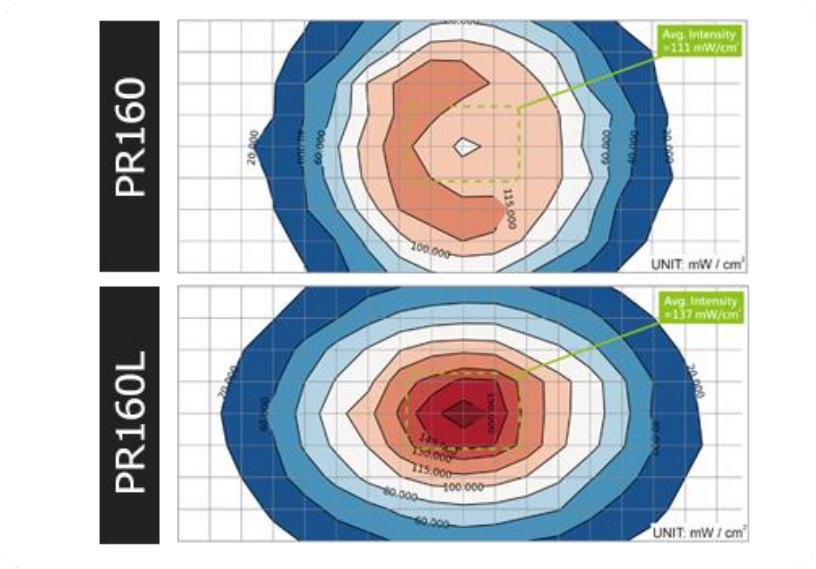



**Figure SI-3.** Intensity map of the Kessil® lamps.

NMR spectra were recorded in $CDCl_3$ at 600 MHz and 300 MHz for $^{1}H$, 75 MHz, 100 MHz and 150 MHz for $^{13}C$ and 282 MHz for $^{19}F$, with tetramethylsilane as internal standard for $^{1}H$ and the residual solvent signals as standard for $^{13}C$. The data is being reported as s = singlet, bs = broad singlet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, q = quatriplet, p = quintuplet and m = multiplet or unresolved, chemical shifts in ppm and coupling constant(s) in Hz. The values of the chemical shift of the signals in the NMR reports are in ppms. HRMS were measured in ESI, EI or APCI mode, and the mass analyser of the HRMS was TOF (Bruker model Impact II).

Melting points were measured in a Gallenkamp apparatus.

## 2. Continuous flow protocol

### The Photochemical flow reactor

The flow reactor was constructed using 0.8 mm internal diameter PTFE tubing wound around a transparent, colourless polystyrene sheet measuring 10cm x 10cm. Two different panels connected in tandem were employed having a total volume of 10 mL, utilizing 20 meters of PTFE tubing. The end of the photoreactor was attached to a 20 psi back pressure regulator (BPR) through a flangeless fitting. The BPR's exit was linked to a collector flask. The initial end of the PTFE tubing in the flow reactor was connected via a flangeless fitting to a syringe containing the solution. This syringe pump was used to push the reaction solution through the reactor to the collector flask.

To provide lighting for the flow reactor, two Kessil® PR160L lamps (with either 390 nm or 427 nm wavelength) were positioned at a distance of 3-7 cm from the photoreactor. These lamps were attached to a PR160 Rig with Fan Kit by Kessil to prevent overheating of the reaction due to radiation (refer to figures SI-4 and SI-5 for details).

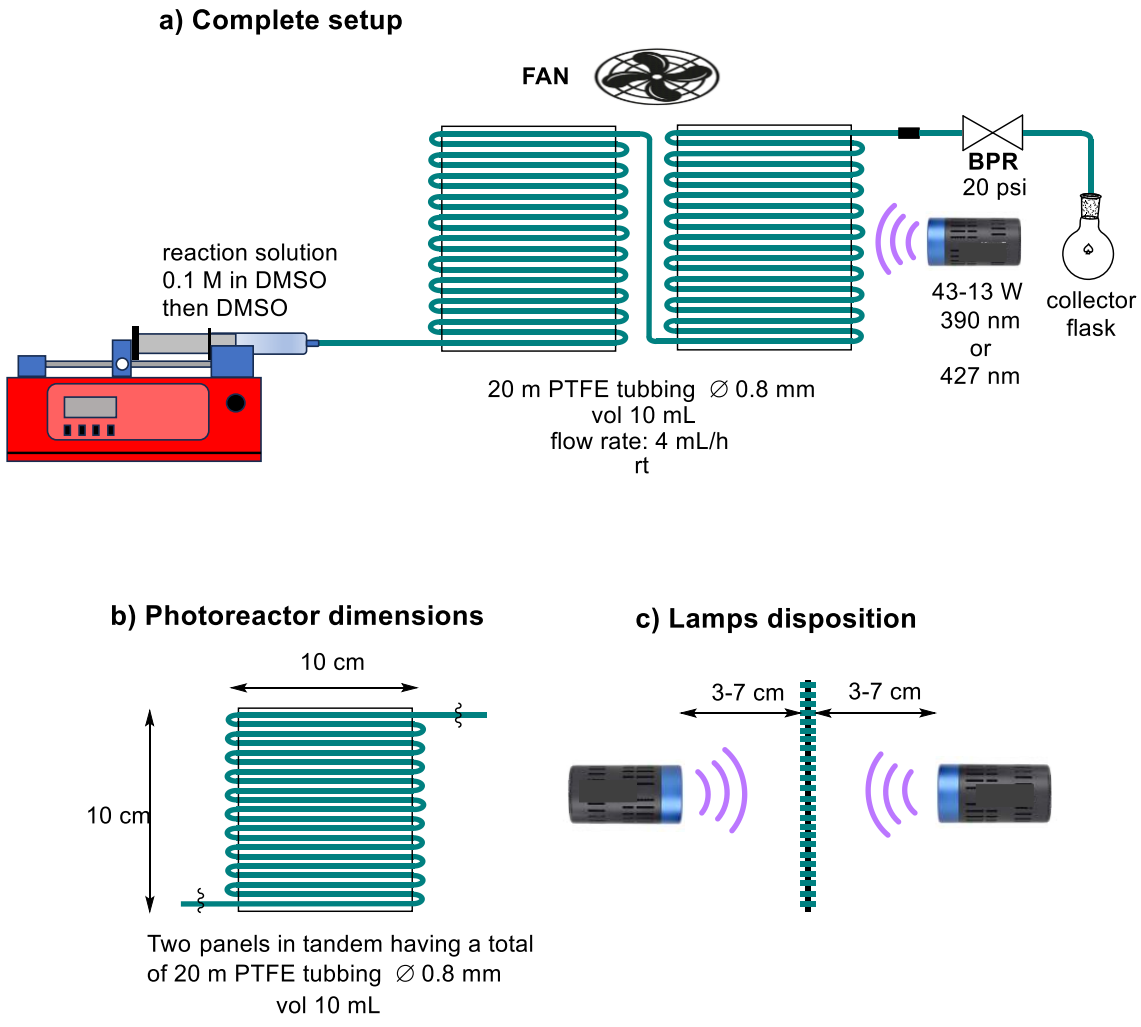



**Figure SI-4.** Scheme of the set up for the continuous flow reactions.

- Materials:

PTFE tubing: Ø 0.8 mm from BOLA (ref. S 1810-10)

Back pressure regulator: P-763 BPR Cartridge from IDEX health and science

LED lamps: PR160L 390 nm and PR160L 427 nm.

Fan kit: Kessil PR160 Rig with Fan Kit

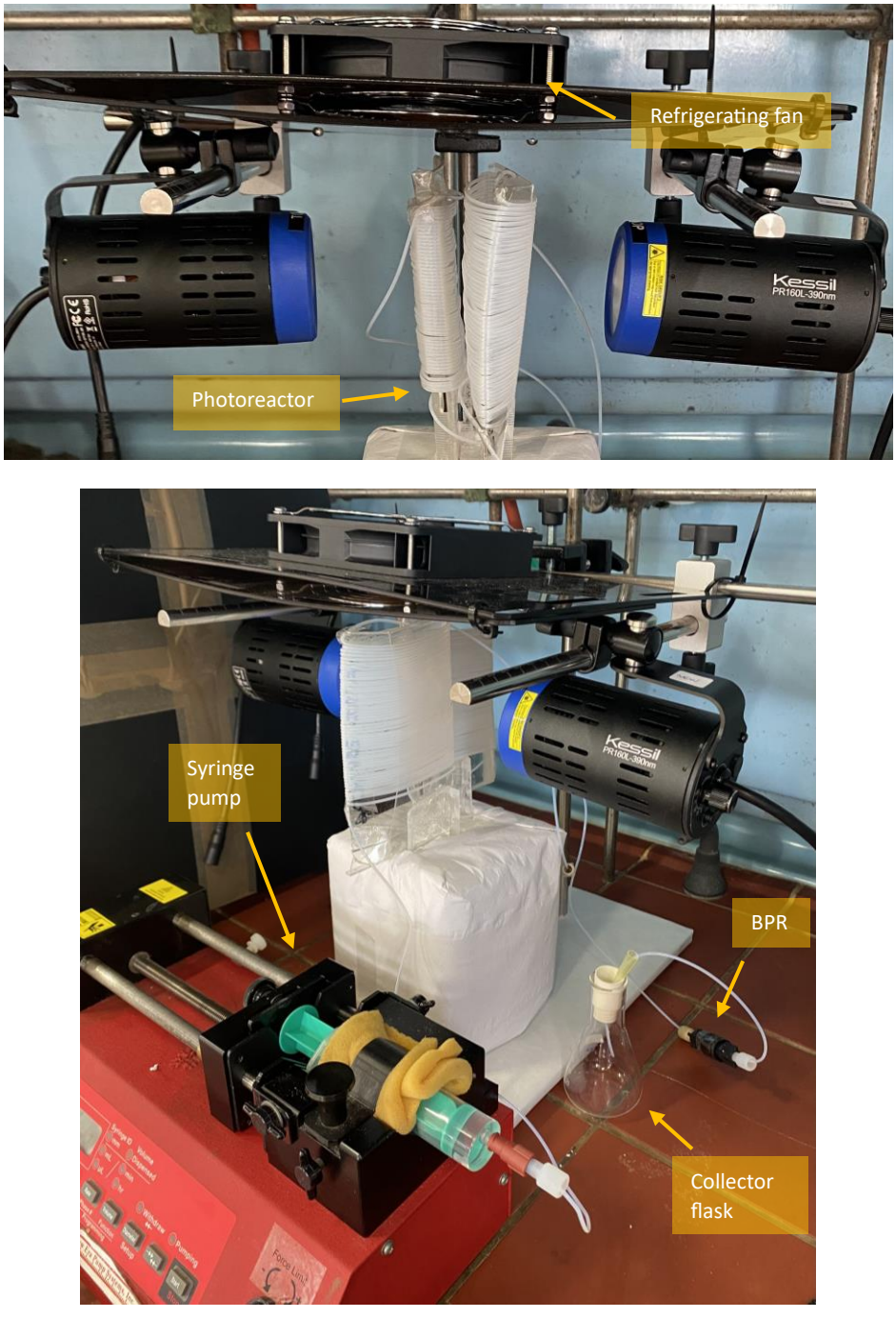



**Figure SI-5.** Pictures of the setup used.

## 3. General procedures for the synthesis and characterization data for the compounds 3.

### General procedure A (under batch conditions)

A 5 mL glass vial was prepared with vinyl bromide **1** (0.2 mmol), potassium thiocyanate **2a** (1 mmol) and 2 mL of dry DMSO. The vial was sealed and placed 5 cm from a 390 nm Kessil lamp. The lamp and its cooling fan were turned on, and the mixture was stirred at room temperature for 3 hours to achieve complete conversion. The reaction was stopped by adding 2 mL of water. The mixture, now heterogeneous, was diluted with 5 mL of diethyl ether ($Et_2O$) and transferred to a separating funnel. The aqueous phase was extracted three times with 5 mL portions of $Et_2O$. The combined organic layers were washed with 10 mL of brine and dried over $Na_2SO_4$. Solvents were removed first by rotary evaporation and then under high vacuum. The crude product was analysed by $^1$H-NMR or GC/MS to determine the trans/cis ratio and then purified by flash chromatography (Hex/EtOAc) to obtain pure thiocyanate **3**.

### General procedure B (under batch conditions)

A 5 mL glass vial was prepared with vinyl bromide **1** (0.2 mmol), potassium thiocyanate **2a** (1 mmol) and 2 mL of dry DMSO. The vial was sealed and placed 5 cm from a 427 nm Kessil lamp. The lamp and its cooling fan were turned on, and the mixture was stirred at room temperature for 3 hours to achieve complete conversion. The reaction was stopped by adding 2 mL of water. The mixture, now heterogeneous, was diluted with 5 mL of diethyl ether ($Et_2O$) and transferred to a separating funnel. The aqueous phase was extracted three times with 5 mL portions of $Et_2O$. The combined organic layers were washed with 10 mL of brine and dried over $Na_2SO_4$. Solvents were removed first by rotary evaporation and then under high vacuum. The crude product was analysed by $^1$H-NMR or GC/MS to determine the trans/cis ratio and then purified by flash chromatography (Hex/EtOAc) to obtain pure thiocyanate **3**.

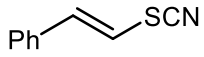
### General procedure C (under continuous flow conditions)

A solution containing vinyl bromide **1** (0.4 mmol) and potassium thiocyanate **2a** (1.6 mmol) in dry DMSO (4 mL) was loaded into a syringe, placed within a high-pressure syringe pump, and connected to the photoreactor. The reaction was conducted by pumping it through the system at a rate of 4 mL/h, with two 390 nm Kessil lamps PRL160 activated. Once the solution entered the reactor, DMSO was employed to propel the

reaction through the system into a collector flask. Following the collection of the reaction, it was quenched by adding 15 mL of water, resulting in a heterogeneous mixture. This mixture was subsequently diluted with 15 mL of diethyl ether ($Et_2O$) and transferred to a separation funnel. The aqueous phase underwent two extractions, each with 15 mL of $Et_2O$, while the combined organic phases underwent a 20 mL brine wash and was then dried using $Na_2SO_4$. The solvents were removed under reduced pressure, and the crude reaction was purified through flash chromatography (Hexane/EtOAc) to obtain product **3**.

**Characterization data for the compounds 3**

**(*E*)-(2-thiocyanatovinyl)benzene (3a)**




Batch reaction: Following the general procedure **A**, a 10.0:1 *trans/cis* mixture of vinyl bromide **1a** (26 µL, 0.2 mmol) and potassium thiocyanate **2a** (97 mg, 1 mmol) were dissolved in 2 mL of dry DMSO. After purification by column chromatography (20:1 Hex/EtOAc), the product **3c** was obtained as a yellow oil (26 mg, 80% isolated yield, *d.r.*: 10.3:1 *trans/cis*).

Continuous flow reaction: Using procedure **C**, a 10:1 *trans/cis* mixture of vinyl bromide **1a** (51 µL, 0.4 mmol) and potassium thiocyanate **2a** (155 mg, 1.6 mmol) were dissolved in 4 mL of dry DMSO. After purification by column chromatography (20:1 Hex/EtOAc), the product was obtained as a yellow oil (50 mg, 77% isolated yield, *d.r.*: 4:1 *trans/cis*).

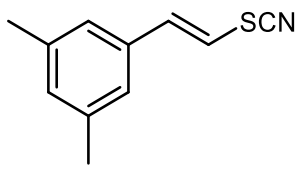
Rf = 0.30 (20:1 Hex/EtOAc) [UV] [$KMnO_4$]

A 10.0:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed. All of the characterization data is in accordance with the previously reported one in literature. [2]

**$^{1}$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.49 – 7.29 (m, 5H), 7.02 (d, *J* = 15.1 Hz, 1H), 6.50 (d, *J* = 15.1 Hz, 1H), 6.33 (d, J = 10.0 Hz, *cis isom.*).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 138.3 (CH), 134.9 (CH, *cis isom.*), 134.4 (C), 129.4 (CH), 129.0 (CH), 128.8 (CH, *cis isom.*), 128.5 (CH, *cis isom.*), 126.7 (CH), 113.7 (CH, *cis isom.*), 109.9 (C), 109.7 (CH).

**(*E*)-1,3-dimethyl-5-(2-thiocyanatovinyl)benzene (3b)**




Batch reaction: Following the general procedure **A**, a 8.6:1 *trans/cis* mixture of vinyl bromide **1b** (55 mg, 0.2 mmol) and potassium thiocyanate **2a** (97 mg, 1 mmol) were dissolved in 2 mL of dry DMSO. After purification by column chromatography (20:1

[2] D. Jaiswal, J. Tiwari, S. Singh, Kartikey, J. Singh, J. Singh, *Catal. Lett.*, **2021**, *151*, 1738

Hex/EtOAc), the product **3b** was obtained as a colourless oil (39 mg, 80% isolated yield, *d.r.*: 2.9:1 *trans/cis*).

Continuous flow reaction: Using procedure **C**, a 8.6:1 *trans/cis* mixture of vinyl bromide **1b** (84 mg, 0.4 mmol) and potassium thiocyanate **2a** (155 mg, 1.6 mmol) were dissolved in 4 mL of dry DMSO. After purification by column chromatography (20:1 Hex/EtOAc), the product **3b** was obtained as a colourless oil (45 mg, 60% isolated yield, *d.r.*: 2.3:1 *trans/cis*).

Rf = 0.25 (0:1 Hex/EtOAc) [UV] [$KMnO_4$]

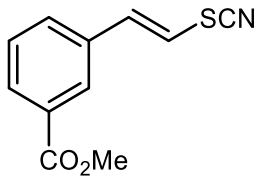
A 2.9:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 6.99 (s, 2H), 6.93 (d, J = 15.1 Hz, 1H), 6.90 – 6.86 (m, 1H + *cis isom.*), 6.45 (d, *J* = 15.1 Hz, 1H), 6.26 (d, *J* = 10.1 Hz, *cis isom.*), 2.34 (s, *cis isom.*), 2.32 (s, 6H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 138.9 (CH), 138.5 (CH), 135.0 (C), 134.3 (C), 133.7 (C, *cis isom.*), 131.1 (CH), 130.5 (CH, *cis isom.*), 126.2 (CH, *cis isom.*), 124.6 (CH), 113.2 (C), 110.9 (CH, *cis isom.*), 110.0 (C, *cis isom.*), 109.1 (CH), 21.3 ($CH_3$, *cis isom.*), 21.2 ($CH_3$).

**HRMS** [ESI (+)]: calcd. for ($[C_{11}H_{11}NS + H]^+$): 190.0685, found: 190.0686.

**Methyl (*E*)-3-(2-thiocyanatovinyl)benzoate (3c)**




Following the general procedure **A**, a 5.7:1 *trans/cis* mixture of vinyl bromide **1c** (48.2 mg, 0.2 mmol) and potassium thiocyanate **2a** (97 mg, 1 mmol) were dissolved in 2 mL of dry DMSO. After purification by column chromatography (20:1 Hex/EtOAc), the product **3c** was obtained as a yellow oil (17 mg, 40% isolated yield, *d.r.*: 5.6:1 *trans/cis*).

Rf = 0.11 (20:1 Hex/EtOAc) [UV] [Vanillin]

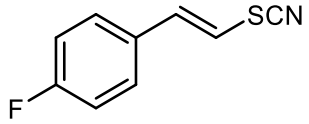
A 5.6:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 8.10 – 7.92 (m, 2H + *cis isom.*), 7.59 – 7.40 (m, 2H + *cis isom.*), 7.02 (d, *J* = 15.1 Hz, 1H + *cis isom.*), 6.58 (d, *J* = 15.2 Hz, 1H), 6.40 (d, *J* = 10.0 Hz, *cis isom.*), 3.94 (s, 3H + *cis isom.*).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 166.5 (C), 136.5 (CH), 134.7 (C), 134.0 (C), 130.9 (CH), 130.2 (CH), 129.2(CH), 127.6 (CH), 111.6 (CH), 109.4 (C), 52.4 ($CH_3$).

**HRMS** [GC-Q-TOF]: calcd. for ([$C_{11}H_9NO_2S$]): 219.0354, found: 219.0357.

**(*E*)-1-fluoro-4-(2-thiocyanatovinyl)benzene (3d)**




Following the general procedure **A**, a 7:1 *trans/cis* mixture of vinyl bromide **1d** (52 mg, 0.2 mmol) and potassium thiocyanate **2a** (97 mg, 1 mmol) were dissolved in 2 mL of dry DMSO. After purification by column chromatography (20:1 Hex/EtOAc), the product **3d** was obtained as a yellow oil (70 mg, 87% isolated yield, *d.r.:* 6.7:*1 trans/cis*).

Rf = 0.20 (20:1 Hex/EtOAc) [UV] [$KMnO_4$]

A 6.7:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed. All of the characterization data is in accordance with the previously reported one in literature.[3]

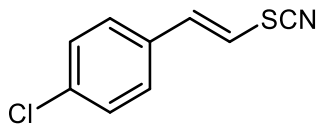
**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.40 – 7.27 (m, 2H), 7.15 – 7.02 (m, 2H), 6.96 (d, *J* = 15.1 Hz, 1H), 6.40 (d, *J* = 15.1 Hz, 1H), 6.30 (d, *J* = 9.9 Hz, *cis isom.*).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 163.2 (d, *J* = 250.1 Hz, C), 137.2 (CH), 134.1 (CH, *cis isom.*), 130.7 (d, *J* = 3.3 Hz), 130.4 (d, *J* = 8.4 Hz, *cis isom.*), 128.53 (d, J = 8.3 Hz, CH), 116.11 (d, J = 22.0 Hz, CH), 116. 0 (d, *J* = 22.5 Hz, *cis isom.*), 109.8 (C), 109.51 (d, *J* = 2.5 Hz, CH).

**$^{19}$F NMR** (282 MHz, $CDCl_3$, 300K) δ -106.0, -109.9.

[3] R. Kapoor, R. Chawla, L. D. S. Yadav, *Tetrahedron Lett.*, **2020**, *61*, 152505

**(*E*)-1-chloro-4-(2-thiocyanatovinyl)benzene (3e)**




Following the general procedure **A**, a 8.9:1 *trans/cis* mixture of vinyl bromide **1e** (43 mg, 0.2 mmol) and potassium thiocyanate **2a** (97 mg, 1 mmol) were dissolved in 2 mL of dry DMSO. After purification by column chromatography (20:1 Hex/EtOAc), the product **3e** was obtained as a colourless oil (26 mg, 66% isolated yield, *d.r.*: 12:1 *trans/cis*).

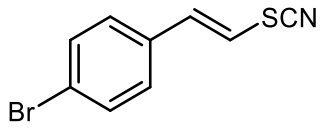
Rf = 0.17 (20:1 Hex/EtOAc) [UV] [$KMnO_4$]

A 12:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding cis isomer have also been analysed. All of the characterization data is in accordance with the previously reported one in literature.[2]

**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.43 – 7.18 (m, 4H + *cis isom.*), 6.94 (d, *J* = 15.2 Hz, 1H + *cis isom.*), 6.47 (d, *J* = 15.2 Hz, 1H), 6.34 (d, *J* = 10.0 Hz, *cis isom.*).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 136.6 (CH), 135.2 (C), 132.9 (C), 129.8 (CH), 127.9 (CH), 110.7 (CH), 109.5 (C).

**(*E*)-1-bromo-4-(2-thiocyanatovinyl)benzene (3f)**




Batch reaction: Following the general procedure **A**, a 5.3:1 *trans/cis* mixture of vinyl bromide **1f** (52.4 mg, 0.26 mmol) and potassium thiocyanate **2a** (97 mg, 1 mmol) were dissolved in 2 mL of dry DMSO. After purification by column chromatography (20:1 Hex/EtOAc), the product **3f** was obtained as a yellow oil (40 mg, 65% isolated yield, *d.r.*: 1.6:1 *trans/cis*).

Continuous flow reaction: Using procedure **C**, a 5.3:1 *trans/cis* mixture of vinyl bromide **1j** (104.7 mg, 0.4 mmol) and potassium thiocyanate **2a** (155 mg, 1.6 mmol) were dissolved in 4 mL of dry DMSO. After purification by column chromatography (20:1 Hex/EtOAc), the product **3j** was obtained as a yellow oil (45 mg, 47% isolated yield, *d.r.*: 6.2:1 *trans/cis*).

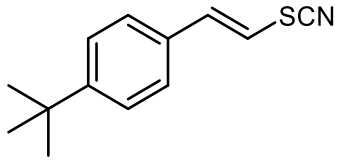
Rf = 0.20 (20:1 Hex/EtOAc) [UV] [Vanillin]

A 1.6:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed. All of the characterization data is in accordance with the previously reported one in literature.[2]

**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.60 – 7.46 (m, 2H + *cis isom.*), 7.25 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, *cis isom.*), 6.94 (d, *J* = 15.2 Hz, 1H), 6.89 (d, *J* = 10.0 Hz, *cis isom.*), 6.50 (d, *J* = 15.2 Hz, 1H), 6.37 (d, *J* = 10.0 Hz, 1H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 136.5 (CH), 133.8 (CH, *cis isom.*), 133.3 (C, *cis isom.*), 132.6 (C), 132.2 (CH), 132.0 (CH, *cis isom.*), 130.0 (CH, *cis isom.*), 128.1 (CH), 123.4 (C), 123.0 (C, *cis isom.*), 114.6 (CH, *cis isom.*), 110.8 (CH), 110.2 (C, *cis isom.*), 109.4 (C).

**(*E*)-1-(tert-butyl)-4-(2-thiocyanatovinyl)benzene (3g)**




Following the general procedure **A**, a 10.6:1 *trans/cis* mixture of vinyl bromide **1g** (48 mg, 0.2 mmol) and potassium thiocyanate **2a** (97 mg, 1 mmol) were dissolved in 2 mL of dry DMSO. After purification by column chromatography (20:1 Hex/EtOAc), the product **3g** was obtained as a colourless oil (21 mg, 48% isolated yield, *d.r.*: 4.4:1 *trans/cis*).

Rf = 0.25 (20:1 Hex/EtOAc) [UV] [$KMnO_4$]

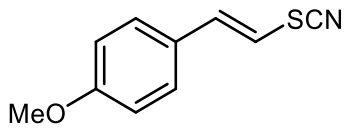
A 4.4:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding cis isomer have also been analysed.

**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.45 – 7.34 (m, 2H + *cis isom.*), 7.35 – 7.20 (m, 2H + *cis isom.*), 6.99 (d, *J* = 15.1 Hz, 1H), 6.91 (d, *J* = 9.9 Hz, *cis isom.*), 6.45 (d, *J* = 15.0 Hz, 1H), 6.25 (d, *J* = 9.9 Hz, *cis isom.*), 1.32 (s, 9H + *cis isom.*).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 152.9 (C), 138.7 (CH), 131.7 (C), 126.5 (CH), 125.9 8 (CH), 110.2 (C), 108.6 (CH), 34.8 (C), 31.2 ($CH_3$).

**HRMS** [ESI (+)]: calcd. for ($[C_{13}H_{14}NS + H]^+$): 218.1000, found: 218.0998.

**(*E*)-1-methoxy-4-(2-thiocyanatovinyl)benzene (3h)**




Following the general procedure **A**, a 9:1 *trans/cis* mixture of vinyl bromide **1h** (56 mg, 0.2 mmol) and potassium thiocyanate **2a** (97 mg, 1 mmol) were dissolved in 2 mL of dry DMSO. After purification by column chromatography (20:1 Hex/EtOAc), the product **3h** was obtained as a yellow oil (43 mg, 85% isolated yield, *d.r.*: 2.3:1 *trans/cis*).

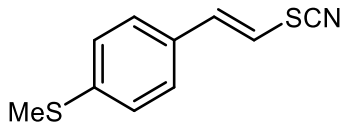
Rf = 0.15 (0:1 Hex/EtOAc) [UV] [$KMnO_4$]

A 2.3:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed. All of the characterization data is in accordance with the previously reported one in literature.[2]

**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.40 – 7.21 (m, 2H), 7.02 – 6.83 (m, 3H), 6.35 (d, *J* = 15.0 Hz, 1H), 6.18 (d, *J* = 9.9 Hz, *cis isom.*), 3.85 (s, *cis isom.*), 3.84 (s, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 160.6 (C), 159.9 (C, *cis isom.*), 139.2 (CH), 134.9 (C), 130.2 (CH *cis isom.*), 128.2 (CH), 127.2 (C), 126.4 (C, *cis isom.*), 114.3 (CH), 114.2 (CH, *cis isom.*), 110.9 (C, *cis isom.*), 110.8 (CH, *cis isom.*), 110.4 (C), 106.4 (CH), 55.3 ($CH_3$).

**(*E*)-methyl(4-(2-thiocyanatovinyl)phenyl)sulfane (3i)**




Following the general procedure **A**, a 8.2:1 *trans/cis* mixture of vinyl bromide **1i** (60 mg, 0.2 mmol) and potassium thiocyanate **2a** (97 mg, 1 mmol) were dissolved in 2 mL of dry DMSO. After purification by column chromatography (20:1 Hex/EtOAc), the product **3i** was obtained as a colourless oil (30 mg, 56% isolated yield, *d.r.*: 1.8:1 *trans/cis*).

Rf = 0.10 (20:1 Hex/EtOAc) [UV] [$KMnO_4$]

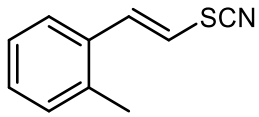
A 1.8:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.33 – 7.17 (m, 4H), 6.96 (d, J = 15.1 Hz, 1H), 6.89 (d, J = 9.9 Hz, *cis isom.*), 6.44 (d, J = 15.1 Hz, 1H), 6.26 (d, J = 9.9 Hz, *cis isom.*), 2.52 (s, *cis isom.*), 2.51 (s, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 140.7 (C), 140.2 (C, *cis isom.*), 138.1 (CH), 134.5 (CH, *cis isom.*), 131.0 (C), 130.2 (C, *cis isom.*), 128.9 (CH, *cis isom.*), 127.0 (CH), 126.2 (CH), 126.0 (CH, *cis isom.*), 112.6 (CH, *cis isom.*), 110.6 (CH, *cis isom.*), 110.0 (C), 108.5 (CH), 15.3 ($CH_3$), 15.2 ($CH_3$, *cis isom.*).

**HRMS** [ESI (+)]: calcd. for ($[C_{10}H_9NS_2 + Na]^+$): 230.0069, found: 230.0073.

**(*E*)-1-methyl-2-(2-thiocyanatovinyl)benzene (3j)**




Following the general procedure **A**, a 4.8:1 *trans/cis* mixture of vinyl bromide **1j** (51 mg, 0.2 mmol) and potassium thiocyanate **2a** (97 mg, 1 mmol) were dissolved in 2 mL of dry DMSO. After purification by column chromatography (20:1 Hex/EtOAc), the product **3j** was obtained as a colourless oil (35 mg, 76% isolated yield, *d.r.*: 4:1 *trans/cis*).

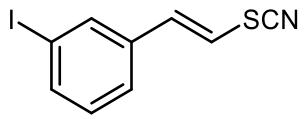
Rf = 0.35 (20:1 Hex/EtOAc) [UV] [Vanillin]

A 4:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding cis isomer have also been analysed. All of the characterization data is in accordance with the previously reported one in literature.[2]

**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.40 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.33 – 7.11 (m, 4H), 7.07 (d, *J* = 9.5 Hz, *cis isom.*), 6.42 (d, J = 15.0 Hz, 1H + *cis isom.*), 2.40 (s, 3H), 2.31 (s, *cis isom.*).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 136.6 (CH), 135.9 (CH, *cis isom.*), 134.5 (C, *cis isom.*), 133.6 (C), 130.7 (CH), 130.6 (CH, *cis isom.*), 129.3 (CH), 129.1 (CH, *cis isom.*), 127.8 (C), 126.4 (CH), 126.0 (CH, *cis isom.*), 125.9 (CH), 115.5 (C), 110.8 (CH), 110.0 (CH, *cis isom.*), 19.7 ($CH_3$), 19.7 ($CH_3$, *cis isom.*).

**(*E*)-1-iodo-3-(2-thiocyanatovinyl)benzene (3k)**




Following the general procedure **A**, a 6.5:1 *trans/cis* mixture of vinyl bromide **1k** (80 mg, 0.2 mmol) and potassium thiocyanate **2a** (97 mg, 1 mmol) were dissolved in 2 mL of dry DMSO. After purification by column chromatography (20:1 Hex/EtOAc), the product **3k** was obtained as a yellow oil (30 mg, 41% isolated yield, *d.r.*: 3.4:1 *trans/cis*).

Rf = 0.40 (20:1 Hex/EtOAc) [UV] [$KMnO_4$]

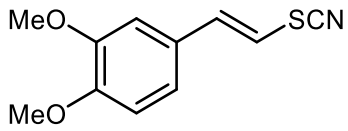
A 3.4:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding cis isomer have also been analysed.

**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.76 – 7.61 (m, 2H + *cis isom.*), 7.38 – 7.24 (m, 1H + *cis isom.*), 7.18 (d, J = 7.8 Hz, *cis isom.*), 7.13 (t, J = 7.8 Hz, 1H), 6.90 (d, *J* = 15.2 Hz, 1H + *cis isom.*), 6.51 (d, *J* = 15.2 Hz, 1H), 6.39 (d, *J* = 10.0 Hz, *cis isom.*).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 138.1 (CH), 137.7 (CH, *cis isom.*), 137.3 (CH, *cis isom.*), 136.4 (C), 135.7 (CH), 135.4 (CH), 133.2 (CH, *cis isom.*), 130.6 (CH), 130.4 (CH, *cis isom.*), 127.4 (CH, *cis isom.*), 125.8 (CH), 115.5 (C), 111.7 (CH), 94.8 (C).

**HRMS** [ESI (+)]: calcd. for ($[C_9H_6NIS + H]^+$): 287.9338, found: 287.9339.

**(*E*)-1,2-dimethoxy-4-(2-thiocyanatovinyl)benzene (3l)**




Following the general procedure **A**, a 12:1 *trans/cis* mixture of vinyl bromide **1l** (63 mg, 0.2 mmol) and potassium thiocyanate **2a** (97 mg, 1 mmol) were dissolved in 2 mL of dry DMSO. After purification by column chromatography (20:1 Hex/EtOAc), the product **3l** was obtained as a yellow oil (30 mg, 53% isolated yield, *d.r.*: 1.3:1 *trans/cis*).

Rf = 0.10 (20:1 Hex/EtOAc) [UV] [$KMnO_4$]

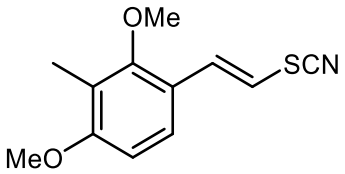
A 1.3:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding cis isomer have also been analysed.

**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 6.93 (d, *J* = 14.9 Hz, 1H), 6.87 (s, 1H), 6.55 – 6.39 (m, 2H + *cis isom.*), 6.32 (d, *J* = 9.9 Hz, *cis isom.*), 3.82 (s, 6H + *cis isom.*).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 161.1 (CH, *cis isom.*), 161.0 (CH), 138.0 (CH, *cis isom.*), 136.2 (C, *cis isom.*), 135.6 (C), 134.5 (CH), 114.6 (CH), 110.7 (C), 110.4 (CH, *cis isom.*), 109.7 (C, *cis isom.*), 106.4 (CH), 104.7 (CH, *cis isom.*), 101.4 (CH, *cis isom.*), 100.8 (CH), 55.4 ($CH_3$ + *cis isom.*).

**HRMS** [ESI (+)]: calcd. for ($[C_{11}H_{11}NO_2S + H]^+$): 222.0583, found: 222.0586.

**(*E*)-1,3-dimethoxy-2-methyl-4-(2-thiocyanatovinyl)benzene (3m)**




Following the general procedure **A**, a 15.5:1 *trans/cis* mixture of vinyl bromide **1m** (51 mg, 0.2 mmol) and potassium thiocyanate **2a** (97 mg, 1 mmol) were dissolved in 2 mL of dry DMSO. After purification by column chromatography (20:1 Hex/EtOAc), the product **3m** was obtained as a colourless oil (24 mg, 51% isolated yield, *d.r.*: 8:1 *trans/cis*).

Rf = 0.10 (20:1 Hex/EtOAc) [UV] [$KMnO_4$]

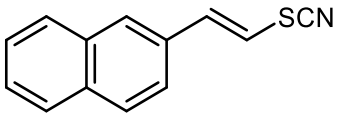
A 8:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding cis isomer have also been analysed. All of the characterization data is in accordance with the previously reported one in literature.[2]

**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.22 (d, *J* = 8.1 Hz, 1H), 7.16 (d, *J* = 15.2 Hz, 1H), 7.10 – 6.98 (m, *cis isom.*), 6.65 (d, *J* = 8.6 Hz, 1H + *cis isom.*), 6.51 (d, *J* = 15.1 Hz, 1H), 6.33 (d, *J* = 10.7 Hz, *cis isom.*), 6.23 (d, *J* = 9.8 Hz, *cis isom.*), 3.85 (s, 3H + *cis isom.*), 3.71 (s, 3H + *cis isom.*), 3.63 (s, *cis isom.*), 2.15 (s, 3H + *cis isom.*).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 159.9 (C), 157.3 (C), 135.5 (CH), 125.4 (CH), 121.7, 120.7 (C), 120.3 (C), 110.7 (C), 107.8 (CH), 106.5 (CH), 61.1 ($CH_3$), 55.7 ($CH_3$), 8.9 ($CH_3$).

**HRMS** [APCI (+)]: calcd. for ($[C_{12}H_{12}NO_2S + H]^+$): 236.0736, found: 236.0740.

**(*E*)-2-(2-thiocyanatovinyl)naphthalene (3n)**




Following the general procedure **B**, a 8.7:1 *trans/cis* mixture of vinyl bromide **1n** (47 mg, 0.2 mmol) and potassium thiocyanate **2a** (97 mg, 1 mmol) were dissolved in 2 mL of dry DMSO. After purification by column chromatography (20:1 Hex/EtOAc), the product **3n** was obtained as a yellow oil (17 mg, 40% isolated yield, *d.r.*: 2:1 *trans/cis*).

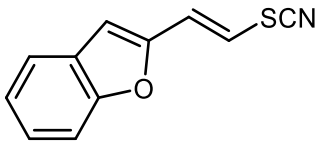
Rf = 0.35 (20:1 Hex/EtOAc) [UV] [Vanillin]

A 2:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding cis isomer have also been analysed. All of the characterization data is in accordance with the previously reported one in literature.[4]

**$^{1}$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.89 – 7.79 (m, 3H + *cis isom.*), 7.77 – 7.70 (m, 1H + *cis isom.*), 7.60 – 7.35 (m, 3H + *cis isom.*), 7.14 (d, *J* = 15.1 Hz, 1H), 7.08 (d, *J* = 10.0 Hz, *cis isom.*), 6.58 (d, *J* = 15.1 Hz, 1H), 6.38 (d, *J* = 10.0 Hz, *cis isom.*).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 138.4 (CH), 133.6 (C), 133.3 (C), 133.0 (C), 131.8 (C), 128.9 (CH), 128.4 (CH), 127.8 (CH), 127.6 (CH), 127.0 (CH), 126.9 (CH), 122.8 (CH), 109.9 (CH).

**(*E*)-2-(2-thiocyanatovinyl)benzofuran (3o)**




Following the general procedure **A**, a 2.8:1 *trans/cis* mixture of vinyl bromide **1o** (58 mg, 0.2 mmol) and potassium thiocyanate **2a** (97 mg, 1 mmol) were dissolved in 2 mL of dry DMSO. After purification by column chromatography (20:1 Hex/EtOAc), each of the isomers *cis*-**3o** and *trans*-**3o** could be isolated with stereochemical purity ,both as a yellow oil (13 mg *cis*-**3o**, 25% isolated yield, 13 mg *trans*-**3o**, 25% isolated yield).

- *Cis* isomer (*cis*-**3o**)

Rf = 0.15 (20:1 Hex/EtOAc) [UV] [Vanillin]

[4] C. Jiang, Y. Zhu, H. Li, P. Liu, P. Sun. *J. Org. Chem.*, **2022**, *87*, 10026.

**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.60 (ddd, *J* = 7.7, 1.4, 0.7 Hz, 1H), 7.52 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.37 (ddd, *J* = 8.3, 7.2, 1.4 Hz, 1H), 7.27 (ddd, *J* = 8.3, 7.2, 1.4 Hz, 1H), 6.79 (s, 1H), 6.76 (d, J = 10.4 Hz, 1H), 6.37 (d, J = 10.4 Hz, 1H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 155.0 (C), 151.5 (C), 127.8 (C), 125.8 (CH), 123.6 (CH), 121.6 (CH), 120.2 (CH), 115.6 (CH), 111.5 (C), 111.4 (CH), 108.5 (CH).

**HRMS** [ESI (+)]: calcd. for ($[C_{11}H_7NOS + H]^+$): 202.0321, found: 202.0321.

- *Trans* isomer (*trans*-**3o**)

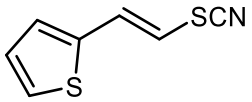
Rf = 0.20 (20:1 Hex/EtOAc) [UV] [Vanillin]

**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.59 (ddd, *J* = 7.6, 1.4, 0.7 Hz, 1H), 7.47 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.35 (ddd, *J* = 8.3, 7.2, 1.4 Hz, 1H), 7.30 – 7.17 (ddd, *J* = 8.3, 7.2, 1.4 Hz, 1H), 6.92 (d, *J* = 14.7 Hz, 1H), 6.72 (s, 1H), 6.70 (d, *J* = 14.7 Hz, 1H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 155.1 (C), 151.5 (C), 128.2 (C), 125.8 (CH), 124.2 (CH), 123.3 (CH), 121.6 (CH), 111.3 (CH), 111.1 (CH), 108.9 (C), 107.2 (CH).

**HRMS** [ESI (+)]: calcd. for ($[C_{11}H_7NOS + H]^+$): 202.0321, found: 202.0321.

**(*E*)-2-(2-thiocyanatovinyl)thiophene (3p)**




Following the general procedure **A**, a 2.2:1 *trans/cis* mixture of vinyl bromide **1p** (49 mg, 0.2 mmol) and potassium thiocyanate **2a** (97 mg, 1 mmol) were dissolved in 2 mL of dry DMSO. After purification by column chromatography (20:1 Hex/EtOAc), the product **3p** was obtained as a yellow oil (30 mg, 70% isolated yield, *d.r.*: 2.3:1 *trans/cis*).

Continuous flow reaction: Using procedure **C**, a 2.2:1 *trans/cis* mixture of vinyl bromide **1p** (75.6 mg, 0.4 mmol) and potassium thiocyanate **2a** (155 mg, 1.6 mmol) were dissolved in 4 mL of dry DMSO. After purification by column chromatography (20:1 Hex/EtOAc), the product **3p** was obtained as a yellow oil (42 mg, 63% isolated yield, *d.r.*: 2.2:1 *trans/cis*).

Rf = 0.25 (20:1 Hex/EtOAc) [UV] [Vanillin]

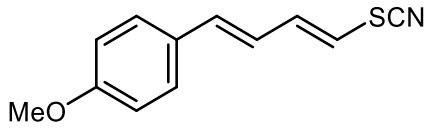
A 2.3:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.49 (d, *J* = 5.1 Hz, *cis isom.*), 7.32 (d, *J* = 5.1 Hz, 1H), 7.22 – 7.16 (m, 1H + *cis isom.*), 7.15 – 7.07 (m, 2H + *cis isom.*), 7.06 – 7.00 (m, 1H + *cis isom.*), 6.32 (d, *J* = 14.9 Hz, 1H), 6.16 (d, *J* = 9.7 Hz, *cis isom.*).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 138.7 (C), 136.8 (C, *cis isom.*), 132.2 (CH), 130.9 (CH, *cis isom.*), 129.4 (CH, *cis isom.*), 128.8 (CH, *cis isom.*), 128.2 (CH), 127.8 (CH), 127.3 (CH, *cis isom.*), 127.0 (CH), 109.8 (C), 109.0 (CH, *cis isom.*), 107.8 (CH).

**HRMS** [ESI (+)]: calcd. for ($[C_7H_5N_2S + Na]^+$): 189.9757, found: 189.9762.

**1-methoxy-4-((1*E*,3*E*)-4-thiocyanatobuta-1,3-dien-1-yl)benzene (3q)**




Following the general procedure **B**, a 1.8:1 *trans/cis* mixture of 1,3-dienyl bromide **1q** (62 mg, 0.2 mmol) and potassium thiocyanate **2a** (97 mg, 1 mmol) were dissolved in 2 mL of dry DMSO. After purification by column chromatography (10:1 Hex/EtOAc), the product **3q** was obtained as an orange oil (25 mg, 45% isolated yield, *d.r.*: 2:1 *trans/cis*).

Rf = 0.2 (10:1 Hex/EtOAc) [UV] [KMnO4]

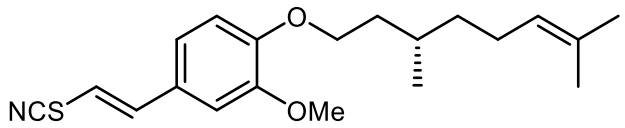
A 2:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding cis isomer have also been analysed.

**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.44 (d, *J* = 8.7 Hz, *cis isom.*), 7.38 (d, J = 8.8 Hz, 2H), 6.97 – 6.59 (m, 5H + *cis isom.*), 6.04 (d, *J* = 14.1 Hz, 1H), 5.97 (d, *J* = 9.6 Hz, *cis isom.*), 3.86 (s, *cis isom*.), 3.85 (s, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 160.1 (C, *cis isom.*), 139.8 (C), 138.6 (CH), 138.6 (CH, *cis isom.*), 136.2 (CH, *cis isom.*), 128.7 (CH, *cis isom.*), 128.6 (CH), 128.2 (CH), 123.0 (CH), 119.3 (CH, *cis isom.*), 114.3 (CH), 114.2 (CH), 110.1 (C), 109.7 (CH), 108.8 (CH, *cis isom.*), 55.3 ($CH_3$ + *cis isom.*).

**HRMS** [ESI (+)]: calcd. for ($[C_{12}H_{11}NOS + H]^+$): 218.0634, found: 218.0631.

**(*S,E*)-1-((3,7-dimethyloct-6-en-1-yl)oxy)-2-methoxy-4-(2-thiocyanatovinyl)benzene (3r)**




Following the general procedure **A**, a 9.6:1 *trans/cis* mixture of vinyl bromide **1r** (73.4 mg, 0.2 mmol) and potassium thiocyanate **2a** (97 mg, 1 mmol) were dissolved in 2 mL of dry DMSO. After purification by column chromatography (20:1 Hex/EtOAc), the product **3m** was obtained as a yellow oil (35 mg, 50% isolated yield, *d.r.*: 5:1 *trans/cis*).

Rf = 0.16 (20:1 Hex/EtOAc) [UV] [Vanillin]

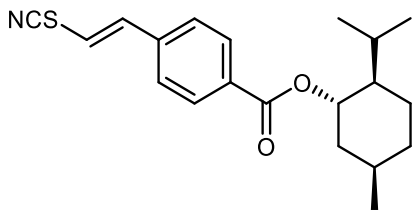
A 5:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding cis isomer have also been analysed.

**$^{1}$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.02 – 6.76 (m, 3H + *cis isom.*), 6.34 (d, *J* = 15.1 Hz, 1H), 6.17 (d, *J* = 9.9 Hz, *cis isom.*), 5.15 – 5.04 (m, 1H + *cis isom.*), 4.14 – 3.99 (m, 2H + *cis isom.*), 3.88 (s, 3H + *cis isom.*), 2.13 – 1.81 (m, 4H + *cis isom.*), 1.73 – 1.63 (m, 3H + *cis isom.*), 1.60 (s, 3H + *cis isom.*), 1.45 – 1.14 (m, 3H + *cis isom.*), 0.96 (d, *J* = 6.0 Hz, 3H + *cis isom.*).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 150.0 (C), 149.6 (C), 139.5 (CH), 131.4 (C), 127.3 (C), 124.6 (CH), 120.6 (CH), 112.5 (CH), 109.3 (CH), 106.6 (CH), 67.4 ($CH_2$), 56.1 ($CH_3$), 37.1 ($CH_2$), 35.9 ($CH_2$), 29.6 (CH), 25.8 ($CH_3$), 25.4 ($CH_2$), 19.6 ($CH_3$), 17.7 ($CH_3$).

**HRMS** [GC-Q-TOF]: calcd. for ([$C_{20}H_{27}NO_2S$]): 345.1762, found: 345.1769.

**(1*R*,2*S*,5*S*)-2-isopropyl-5-methylcyclohexyl 4-((*E*)-2-thiocyanatovinyl)benzoate (3s)**




Following the general procedure **A**, a 8.3:1 *trans/cis* mixture of vinyl bromide **1s** (73 mg, 0.2 mmol) and potassium thiocyanate **2a** (97 mg, 1 mmol) were dissolved in 2 mL of dry

DMSO. After purification by column chromatography (20:1 Hex/EtOAc), the product **3s** was obtained as a colourless oil (15 mg, 22% isolated yield, *d.r.*: 2.8:1 *trans/cis*).

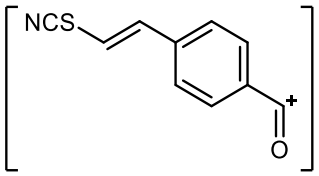
Rf = 0.13 (20:1 Hex/EtOAc) [UV] [$KMnO_4$]

A 2.8:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding cis isomer have also been analysed.

**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 8.08 (d, *J* = 8.4 Hz, *cis isom.*), 8.04 (d, *J* = 8.3 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H + *cis isom.*), 7.35 (d, *J* = 8.2 Hz, *cis isom.*), 7.01 (d, *J* = 15.2 Hz, 1H + *cis isom.*), 6.59 (d, *J* = 15.2 Hz, 1H), 6.43 (d, *J* = 10.1 Hz, *cis isom.*), 5.31 (td, *J* = 6.2, 3.3 Hz, 1H + *cis isom.*), 2.02 – 1.88 (m, 1H + *cis isom.*), 1.90 – 1.41 (m, 6H + *cis isom.*), 1.34 – 1.18 (m, 2H + *cis isom.*), 0.99 (d, *J* = 6.7 Hz, 3H + *cis isom.*), 0.96 (d, *J* = 6.8 Hz, 3H + *cis isom.*), 0.89 (d, *J* = 6.7 Hz, 3H + *cis isom.*).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 165.3 (C), 138.3 (C), 136.0 (CH), 131.5 (C), 130.2 (CH), 126.5 (CH), 112.8 (CH), 109.2 (C), 72.8 (CH), 45.7 (CH), 35.7 ($CH_2$), 29.9 ($CH_2$), 27.7 (CH), 26.4 (CH), 21.3 ($CH_2$), 21.0 ($CH_3$), 20.8 ($CH_3$), 19.4 ($CH_3$).

**HRMS** [GC-Q-TOF]: Molecular fragmentation observed at the C-O ester bond. calcd. for ([$C_{10}H_6NOS$]): 188.0165, found: 188.0167.



## 4. UV-Vis spectra

All measurements were conducted by dissolving the corresponding reagents in DMSO at a concentration of [1.3 mM].

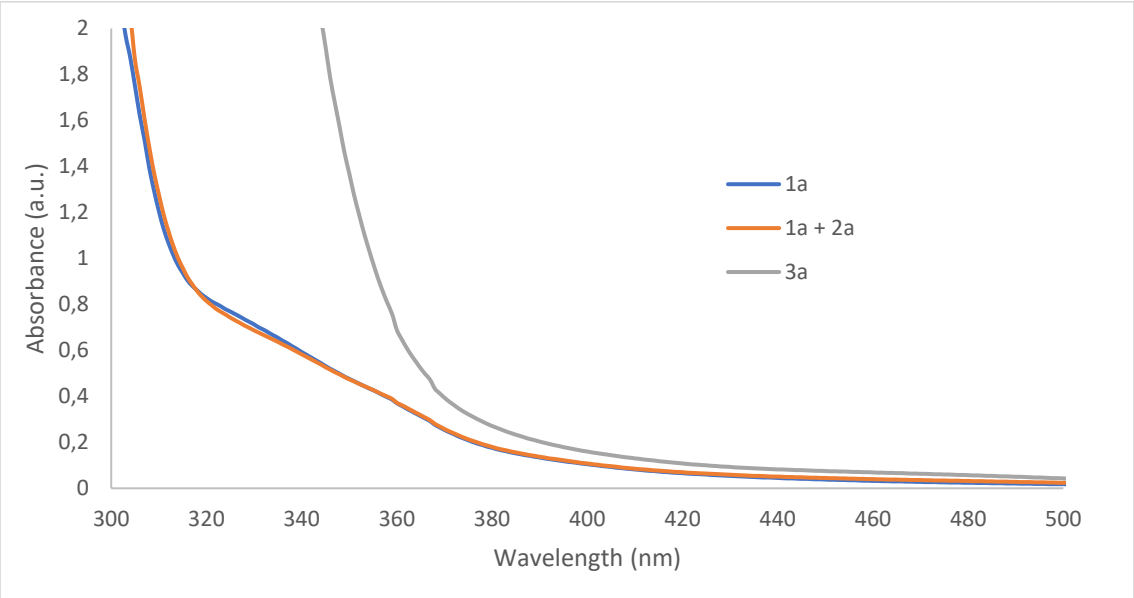


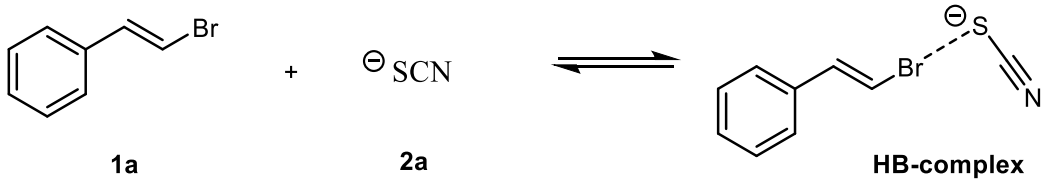

**Figure SI-6.** UV-Vis spectra of compounds **1a** (blue line), an equimolar mixture of **1a** + **2a** (orange line) and **3a** (grey line).

## 5. Computational studies

To perform the computational calculations, Gaussian 09 was used. For the geometry optimizations the wB97x-D functional was employed as it incorporates dispersion corrections and has been demonstrated to consistently produce reliable results for non-covalent interactions.[5] Moreover, all calculation were carried out using Def2-TZVPP basis set with polarization correction. To confirm the optimized structures were energy minima in the potential energy surface, frequency calculations were also performed. Finally, single point energy calculations on the optimized structures considering solvation effects were achieved by using the CMCD (DMSO) model at the same theoretical level.

The three-dimensional model was showed using Cylview 2.0.[6] To represent the electrostatic potential map, Gaussview 5.0 was employed based on a model derived from Gaussian 09 at the wB97x-D/Def2-TZVPP level. The electrostatic potential was mapped over a $4x10^{-4}$ atomic units (au) isodensity surface. The modelling studies support the presence of a potential energy surface minimum, signifying the existence of a halogen-bonded complex (HB-complex) between vinyl bromide **1a** and potassium thiocyanate **2a**. The halogen bond interaction between the bromine and sulfur atoms exhibits notable directionality, illustrated by a dihedral angle of 179.3° between the $Csp^2$-Br-S bonds. Remarkably, the electrostatic potential surface reveals that the positively charged bromine σ-hole region is situated close to the centre of the C-Br axis. This linear geometry, with dihedral angles ranging from 160° to 180° for the HB complex, aligns with previously reported findings on similar complexes. Additionally, our results suggest that the distance between the bromine and sulfur atoms in the halogen-bonding complex is 3.33 Å, which is shorter than the sum of the Van der Waals radii of sulfur and bromine atoms (3.65 Å). This observation provides further evidence of a non-covalent weak interaction between these atoms, likely arising from the formation of a halogen bond.

Based on the calculations, the complexation process is determined to be exothermic, with a ΔH of -2.96 kcal·mol$^{-1}$, but endergonic, with a ΔG of 3.34 kcal·mol$^{-1}$. Nevertheless, the ΔG value overestimates the entropic effects in the complexation process.




**1a** **2a** **HB-complex**

[5] Y.-S. Lin, G.-D. Li, S. P. Maohhh, J.-D. Chai. *J. Chem. Theory Comput.* **2013**, *9*, 263.

[6] CYLview20; Legault, C. Y., Université de Sherbrooke, 2020 (http://www.cylview.org).

$$\Delta H = -2.96\ kcal \cdot mol^{-1};\ \Delta G(solv) = 3.34\ kcal \cdot mol^{-1}$$

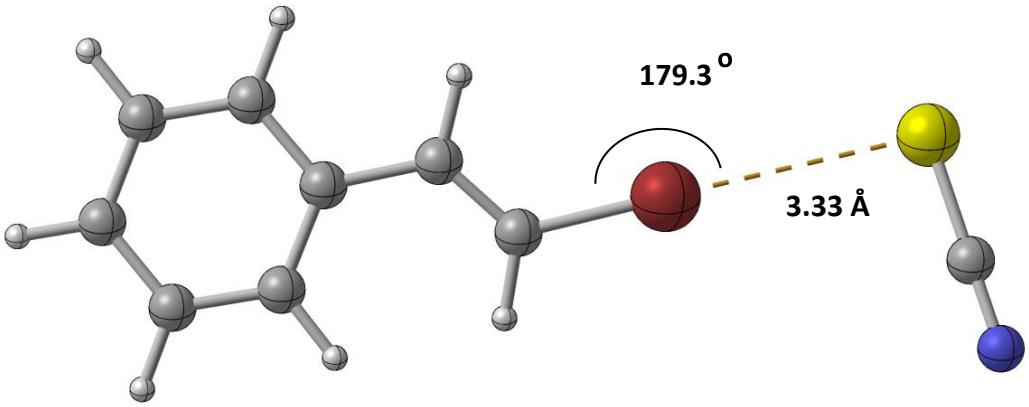



**Figure SI-7.** HB complex between **1a** and thiocyanate **2a** calculated at the wB97x-D/Def2TZVPP.

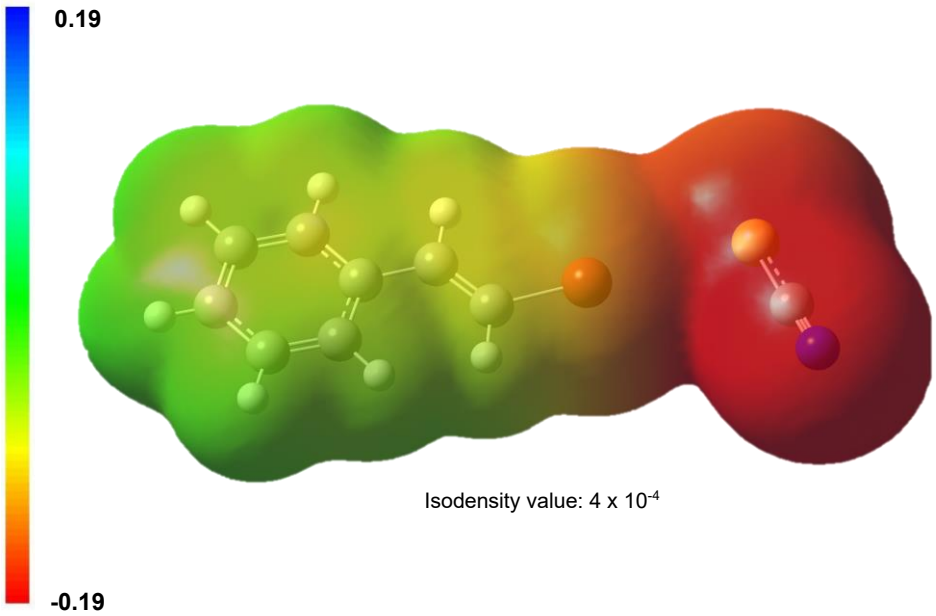



**Figure SI-8.** Calculated electrostatic potential map (red = negative electrostatic potential) on the 0.0004 au isodensity surface.

**Cartesian Coordinates and energy data**

- β-bromostyrene **1a**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| C | 1.116212 | 0.422628 | -0.083875 | C | -1.818751 | 1.096414 | 0.078922 |
| H | 0.947304 | 1.465540 | -0.304211 | C | -1.286418 | -0.194123 | 0.063024 |
| C | 0.156670 | -0.469797 | 0.108556 | H | -1.772349 | -2.279987 | -0.001711 |
| H | 0.434454 | -1.500492 | 0.298317 | H | -4.204599 | -1.922099 | -0.109210 |
| C | -2.168599 | -1.272043 | 0.002422 | H | -5.120251 | 0.376006 | -0.105328 |
| C | -3.537899 | -1.071388 | -0.060133 | H | -3.579771 | 2.305043 | 0.030530 |
| C | -4.051699 | 0.215036 | -0.056933 | H | -1.162563 | 1.953432 | 0.154356 |
| C | -3.185249 | 1.297610 | 0.015405 | Br | 2.946062 | -0.015527 | -0.010488 |

SCF energy: -2883.26439080 Hartree

Gibbs free energy: -2883.174132 Hartree

SCF energy (CPCM-dmso): -2883.26882569 Hartree

Gibbs free energy (CPCM-dmso): -2883.17413 Hartree

- Thiocyanate **2a**

| | | | |
|---|---|---|---|
| C | 0.000000 | 0.000000 | -0.633627 |
| N | -0.000000 | 0.000000 | -1.800860 |
| S | -0.000000 | -0.000000 | 1.025487 |

SCF energy: -491.116712802 Hartree

Gibbs free energy: -491.130266 Hartree

SCF energy (CPCM-dmso): -491.208889044 Hartree

Gibbs free energy (CPCM-dmso): -491.222442 Hartree

- HB complex

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.454705 | 0.363761 | -0.105135 | H | 3.452566 | -2.228724 | 0.167326 |
| H | 0.617117 | 1.415966 | -0.296111 | H | 5.872598 | -1.792006 | 0.114628 |
| C | 1.452950 | -0.493117 | 0.079706 | H | 6.712697 | 0.533183 | -0.025011 |
| H | 1.212081 | -1.536721 | 0.251140 | H | 5.095211 | 2.406657 | -0.098276 |
| C | 3.813276 | -1.209033 | 0.107051 | H | 2.691960 | 1.973695 | -0.033805 |
| C | 5.176688 | -0.963513 | 0.077458 | Br | -1.362883 | -0.113457 | -0.073609 |
| C | 5.648822 | 0.336789 | -0.000629 | C | -5.153376 | 0.625035 | 0.110325 |
| C | 4.739534 | 1.385528 | -0.043379 | N | -5.548434 | 1.716577 | 0.215752 |
| C | 3.379258 | 1.138674 | -0.012010 | S | -4.593617 | -0.932366 | -0.039701 |
| C | 2.885410 | -0.167327 | 0.056843 | | | | |

SCF energy: -3374.38705375 Hartree

Gibbs free energy: -3374.299880 Hartree

SCF energy (CPCM-dmso): -3374.47842715 Hartree

Gibbs free energy (CPCM-dmso): -3374.39125315 Hartree

## 6. NMR titration experiments.

To conduct these experiments, we made various solutions containing escalating quantities of potassium thiocyanate **2a** while keeping the amount of vinyl bromide **1a** consistent across all solutions. All samples were prepared in $d^6$-DMSO to facilitate immediate NMR analysis. Throughout the titration process, a progressive downfield shift of the carbon signal in the α position to the phenyl group adjacent to vinyl bromide **1a** (highlighted by a light pink dot) and of the carbon signal in the thiocyanate (highlighted by a dark purple dot) were observed. Details regarding the composition of each sample along with their respective $^{13}$C-NMR spectra will be presented.

- Sample 1

Preparation: **1a** (34 µL, 0.26 mmol) was dissolved in 0.6 mL of $d^6$-DMSO in a 5 mL vial.

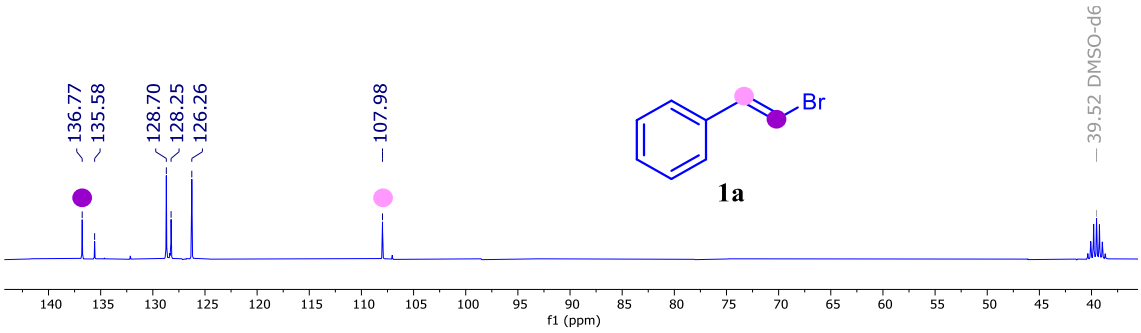



**Figure SI-9.** $^{13}$C-NMR spectra recorded for the Sample 1 in $d^6$-DMSO.

Chemical shift ( ● ) = 136.77 ppm; ( ● ) = 107.98 ppm.

- Sample 2

Preparation: **1a** (34 µL, 0.26 mmol) and **2a** (26.3 mg, 0.26 mmol) were dissolved in 0.6 mL of $d^6$-DMSO in a 5 mL vial.

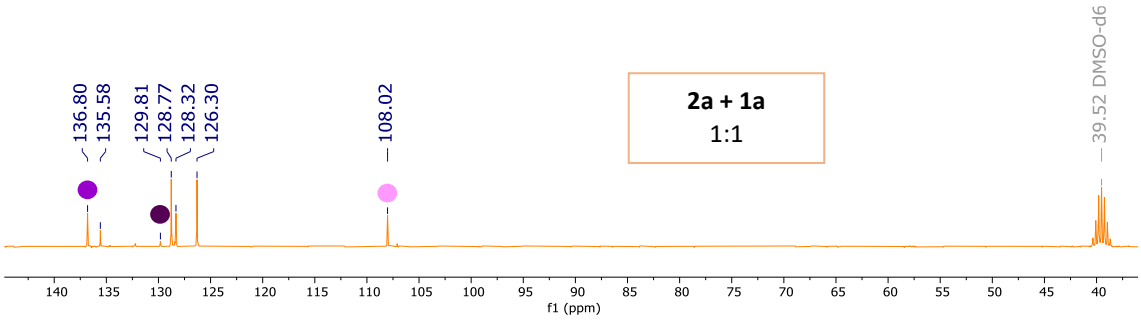



**Figure SI-10.** $^{13}$C-NMR spectra recorded for the Sample 2 in $d^6$-DMSO.

Chemical shift ( ● ) = 136.80 ppm; ( ● ) = 129.81 ppm; ( ● ) = 108.02 ppm.

- Sample 3

Preparation: **1a** (34 µL, 0.26 mmol) and **2a** (50.5 mg, 0.52 mmol) were dissolved in 0.6 mL of $d^6$-DMSO in a 5 mL vial.

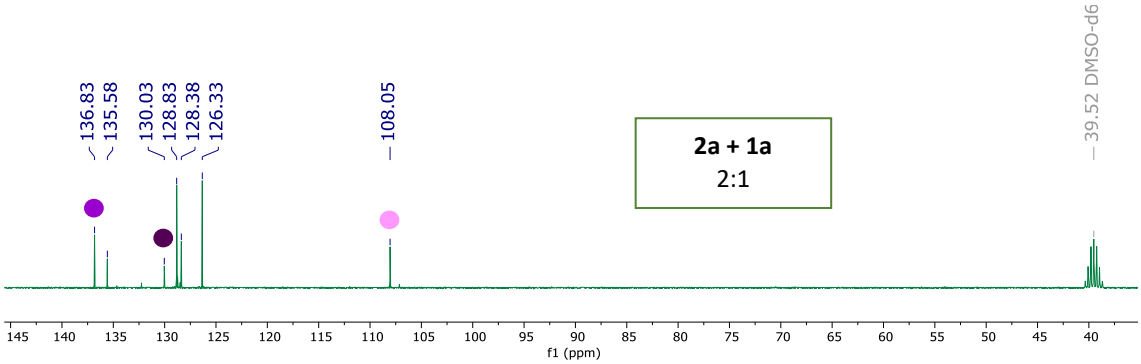



**Figure SI-11.** $^{13}$C-NMR spectra recorded for the Sample 3 in d$^6$-DMSO.

Chemical shift ( ● ) = 136.83 ppm; ( ● ) = 130.03 ppm; ( ● ) = 108.05 ppm.

- Sample 4

Preparation: **1a** (34 µL, 0.26 mmol) and **2a** (126.3 mg, 1.30 mmol) were dissolved in 0.6 mL of d$^6$-DMSO in a 5 mL vial.

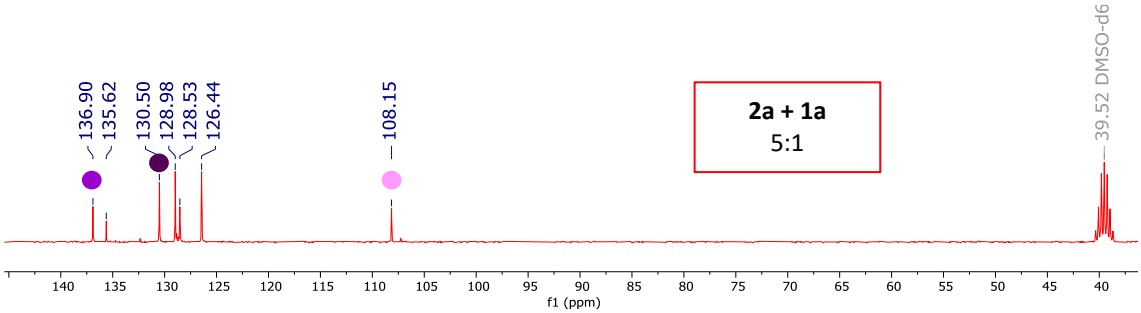



**Figure SI-12.** $^{13}$C-NMR spectra recorded for the Sample 3 in d$^6$-DMSO.

Chemical shift ( ● ) = 136.90 ppm; ( ● ) = 130.50 ppm; ( ● ) = 108.15 ppm.

- Sample 5

Preparation: **1a** (34 µL, 0.26 mmol) and **2a** (252.7 mg, 2.60 mmol) were dissolved in 0.6 mL of d$^6$-DMSO in a 5 mL vial.

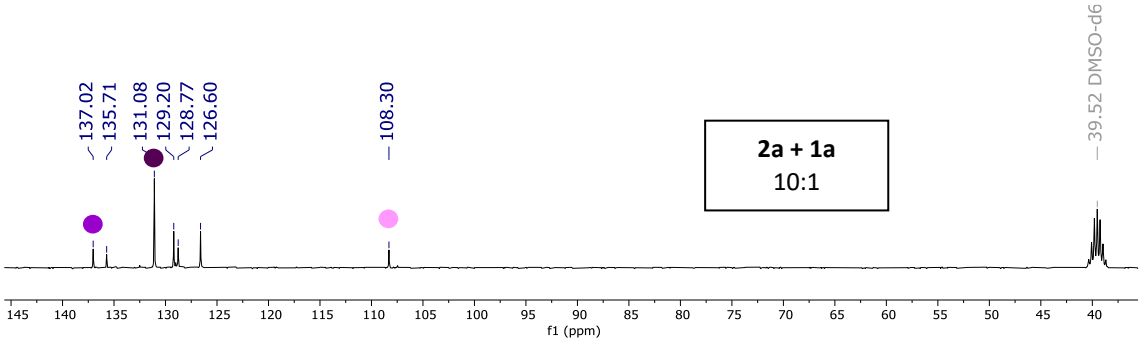



**Figure SI-13.** $^{13}$C-NMR spectra recorded for the Sample 4 in d$^6$-DMSO.

Chemical shift ( ● ) = 137.02 ppm; ( ● ) = 131.08 ppm; ( ● ) = 108.30 ppm.

## 7. Binding constant calculation.

Based on these measurements, we calculated the thermodynamic binding constant associated to the formation of the halogen-bonding complex between **1a** and **2a**. For this purpose, we utilized the *Bindfit* application, which is available online free of charge and open-access.[7] Following the instructions in the website, we first prepared an excel document with the necessary data to perform the calculations: Concentrations of the host (sulfinate salt **2a**) /gest (alkenyl bromide **1a**) solutions and the observed NMR chemical shifts measured in the titration experiments (**Figure SI-14**)

| Host concentration / M | Guest concentration / M | 13C (C2, 1a) |
|---|---|---|
| 0,43 | 0 | 107,98 |
| 0,43 | 0,43 | 108,02 |
| 0,43 | 0,86 | 108,05 |
| 0,43 | 2,15 | 108,15 |
| 0,43 | 10,3 | 108,3 |

**Figure SI-14**. Host/guest concentration of the different NMR samples and observed chemical shift for the signal of **1a**.

With all the raw data, the instructions in the previously described website were followed step by step in order to calculate the desired binding constant (K).

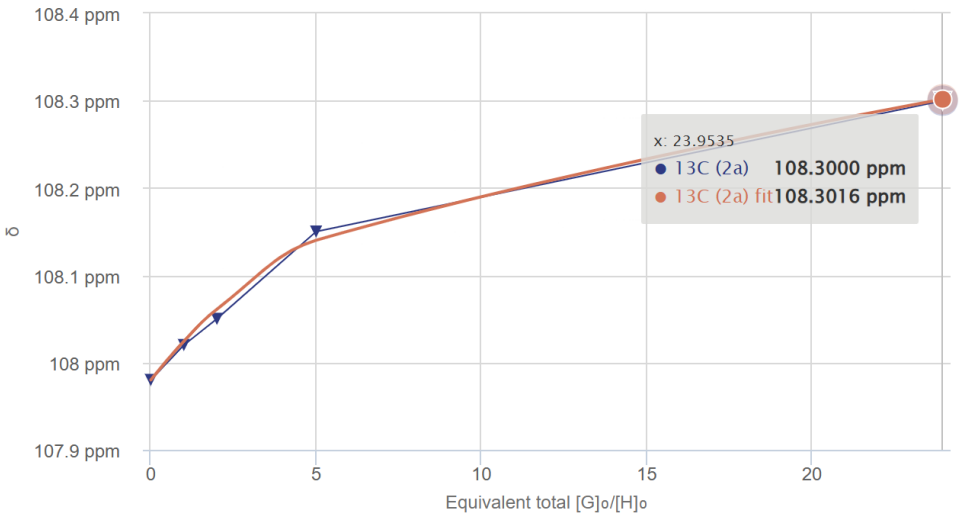



**Figure SI-15**. Representation of the $^{1}$H-NMR chemical shift (y axis) versus $[G]_0/[H]_0$

[7] The website tool Bindfit is open access and available to a general public through the following link: https://urldefense.com/v3/__http://supramolecular.org/__;!!D9dNQwwGXtA!W8BJfdU5UufikVjU0daGfmcAH1DBbku2p2znhU7Ag_rmjTKY1eemU2vSQA660Iux8uGICmHS6PROv8I7orosp7e7Mjnag7qe$

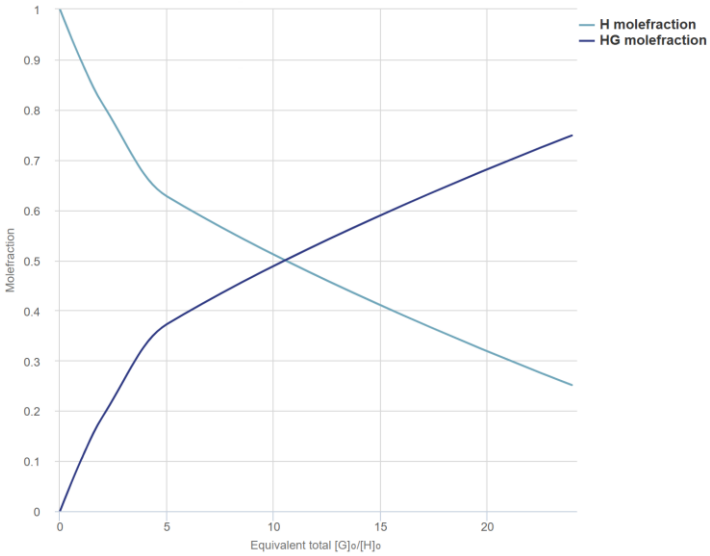



**Figure SI-16**. Molefraction representation

## Details

| | |
|---|---|
| **Time to fit** | 0.2826 s |
| **SSR** | 2.4176e-4 |
| **Fitted datapoints** | 5 |
| **Fitted params** | 2 |

## Parameters

| Parameter (bounds) | Optimised | Error | Initial |
|---|---|---|---|
| **K** ( 0 → ∞ ) | 0.30 $M^{-1}$ | ± 24.4139 % | 0.60 $M^{-1}$ |

**Figure SI-17**. Output data from Bindfit. Calculation of the binding constant K.

## 8. Quantum yield measurement

- Determination of the photon flux

The quantum yield measurements were performed following the procedures described by Dell' Amico and Xia.[8,9] This method involves a ferrioxalate actinometry solution where the decomposition of ferric ions to ferrous ions, by irradiation at a particular wavelength, is measured. To achieve this, the ferrous ions are complexed with 1,10-phenanthroline and its absorbance at 510 nm by UV/Vis is determined. Finally, the moles of iron-phenanthroline complex formed are associated to the moles of photons absorbed.

The photon flux of the lamp was calculated to be $6.058 \times 10^{-7}$ einstein $s^{-1}$.

- Determination of the quantum yield

Following the general procedure A, a 10:1 trans/cis mixture of vinyl bromide **1a** (26 µL, 0.2 mmol) and the potassium thiocyanate **2a** (78 mg, 0.8 mmol) were dissolved in 2 mL of dry DMSO. The moles of product formed (compound **3a**) were determined following conversion via $^1$H-NMR after 7 hours.

$$\varphi = \frac{\text{moles of product}}{\text{moles of photons}} = \frac{5.56\ x\ 10^{-5}}{1.53\ x\ 10^{-2}} = \mathbf{0.004}$$

[8] S. Cuadros, C. Rosso, G. Barison, P. Costa, M. Kurbasic, M. Bonchio, M. Prato, G. Filippini and L. Dell'Amico, *Org. Lett.*, **2022**, *24*, 2961.

[9] T. Li, K. Liang , J. Tang , Y. Ding , X. Tong and C. Xia , *Chem. Sci.*, **2021**, *12* , 15655

## 9. Light on/off studies

For the light on/off studies, a mixture of vinyl bromide **1a** and potassium thiocyanate **2a** was prepared in DMSO following general procedure **A**. The first aliquot was collected after 30 minutes of continuous irradiation with the lamp turned on. Following this, the lamp was turned off, and the reaction mixture was allowed to rest in the dark. After 30 minutes, the second aliquot was collected. This on/off cycle of 30 minutes of light exposure followed by 30 minutes of darkness was repeated two more times, resulting in a total of three on/off cycles.

Each aliquot was analysed to determine the conversion of **3a**. The data obtained from these aliquots indicated that the reaction did not proceed in the absence of light and resumed upon re-irradiation. This behaviour corroborated the calculated quantum yield and provided evidence that the reaction mechanism is not a chain propagation.

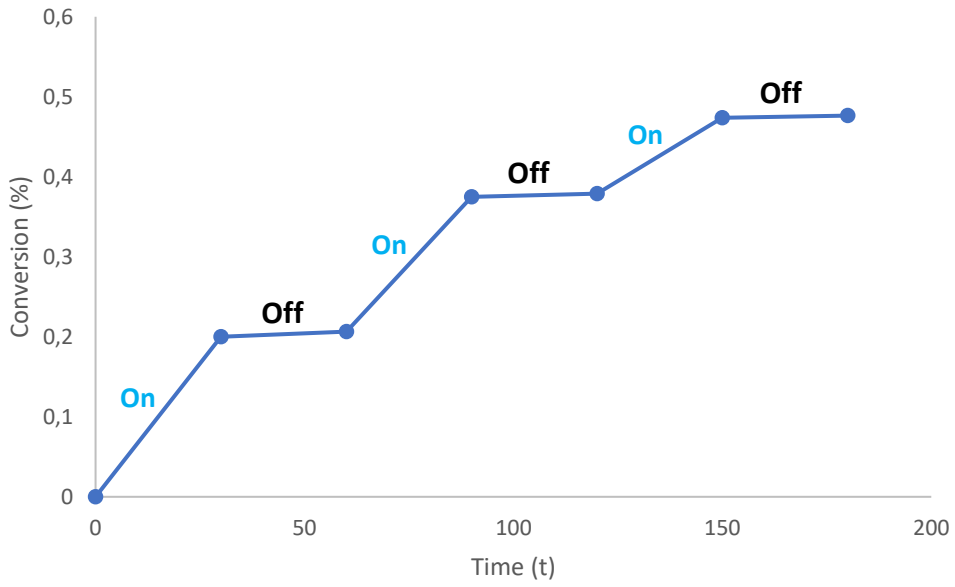
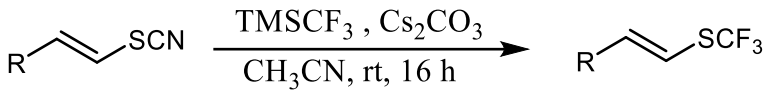



**Figure SI-18.** Light on/off studies. Conversion to **3a** monitored by $^{1}$H-NMR: 30 min ON / 30 min OFF.

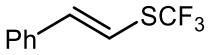
**10. General procedure for the preparation of compounds 7, 8, 9, 10, 11 and 12.**

**General procedure D**




Under argon atmosphere, **3** (1 equiv.), $Cs_2CO_3$ (2 equiv.) and $CH_3CN$ were introduced into a Schlenk flask. To this solution, $TMSCF_3$ (1.2 equiv.) was added, and the mixture was stirred for 16 h at room temperature. After adding diethyl ether (10 mL), the organic solution underwent successive washes with water (2x10 mL) and brine (10 mL). The organic layer was dried using $MgSO_4$ and concentrated by rotatory evaporation. Purification was achieved by dissolving the crude of the reaction in pentane, followed by filtration through a celite obtaining compound **7**.

**(*E*)-(2-thiocyanatovinyl)benzene (7a)**




Following general procedure **D**, **3a** (50 mg, 0.31 mmol), $Cs_2CO_3$ (202.1 mg, 0.62 mmol). $TMSCF_3$ (55 µL, 0.37 mmol) and 2 ml of $CH_3CN$ were used. Purification was achieved by dissolving the crude of the reaction in pentane, followed by filtration through a celite obtaining compound **7a** as a colourless oil (45 mg, 71% yield, *d.r.*: 2.2:1 *trans/cis*).

A 2.2:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding cis isomer have also been analysed.

**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.47 – 7.32 (m, 5H + *cis isom.*), 7.04 (d, *J* = 15.3 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, *cis isom.*), 6.77 (d, *J* = 15.4 Hz, 1H).

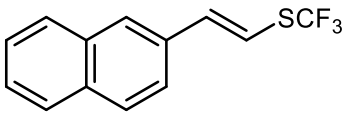
**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) 141.2 (CH), 135.8 (C), 129.2 (q, *J* = 308.2 Hz, C), 129.2 (CH), 128.9 (CH), 126.8 (CH), 111.7 (q, *J* = 3.2 Hz, CH)

**$^{19}$F NMR** (235 MHz, $CDCl_3$,300K) -42.7.

The data matched those reported in the literature. [10]

[10] S. Pan, Y. Huang, F. Qing. *Chem. Asian J.*, **2016**, *11*, 2854.

**(*E*)-(2-(naphthalen-2-yl)vinyl)(trifluoromethyl)sulfane (7b)**




Following general procedure **D**, **3n** (56 mg, 0.26 mmol), $Cs_2CO_3$ (173 mg, 0.53 mmol). $TMSCF_3$ (47 µL, 0.32 mmol) and 2 ml of $CH_3CN$ were used. Purification was achieved by dissolving the crude of the reaction in pentane, followed by filtration through a celite obtaining compound **7b** as a white solid (45 mg, 68% yield, *d.r.*: 13.5:1 *trans/cis*).

A 13.5:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding cis isomer have also been analysed.

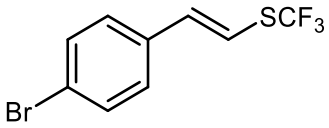
**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.91 – 7.79 (m, 3H + *cis isom.*), 7.76 (s, 1H + *cis isom.*), 7.62 – 7.46 (m, 3H + *cis isom.*), 6.99 (d, J = 10.5 Hz, *cis isom.*), 7.16 (d, J = 15.3 Hz, 1H), 6.87 (d, J = 15.3 Hz, 1H), 6.49 (d, J = 10.5 Hz, *cis isom.*).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 141.2 (CH), 133.6 (C), 133.4 (CH), 132.5 (CH), 131.7 (q, *J* = 306.2 Hz), 128.7 (CH), 128.3 (CH), 127.8 (CH), 127.6 (CH), 126.8 (CH), 126.7 (CH), 123.1 (CH), 111.9 (d, *J* = 2.9 Hz, CH)

**$^{19}$F NMR** (235 MHz, $CDCl_3$, 300K) δ -42.6, -43.1.

The data matched those reported in the literature. [11]

**(*E*)-(4-Bromophenyl)(trifluoromethyl)sulfane (7c)**




Following general procedure **D**, **3f** (35 mg, 0.15 mmol), $Cs_2CO_3$ (98 mg, 0.3 mmol). $TMSCF_3$ (25 µL, 0.18 mmol) and 1 ml of $CH_3CN$ were used. Purification was achieved by dissolving the crude of the reaction in pentane, followed by filtration through a celite obtaining compound **7c** as a yellow oil (19 mg, 45% yield).

**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.49 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 15.4 Hz, 1H), 6.74 (d, *J* = 15.3 Hz, 1H).

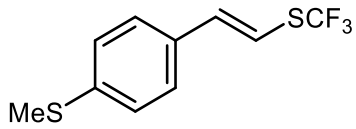
[11] C. Zheng, S. Huang, Y. Liu, C. Jiang, W. Zhang, G. Fang, J. Hong. *Org. Lett.*, **2020**, *22*, 4868

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 139.2 (CH), 133.9 (C), 132.0 (CH), 129.5 (q, *J* = 308.0 Hz, C) 128.2 (CH), 123.2 (C), 112.8 (q, *J* = 3.2 Hz, CH).

**$^{19}$F NMR** (235 MHz, $CDCl_3$, 300K) δ -42.6.

The data matched those reported in the literature.[10]

**(*E*)-(4-methoxystyryl)(trifluoromethyl)sulfane (7d)**




Following general procedure **D**, **3i** (84 mg, 0.4 mmol), $Cs_2CO_3$ (261 mg, 0.8 mmol). $TMSCF_3$ (71 µL, 0.48 mmol) and 3 ml of $CH_3CN$ were used. Purification was achieved by dissolving the crude of the reaction in pentane, followed by filtration through a celite obtaining compound **7d** as a yellow oil (60 mg, 60% yield, *d.r.*: 2.1:1 *trans/cis*).

A 2.1:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding cis isomer have also been analysed.

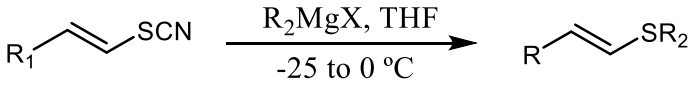
**$^{1}$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.69 – 7.59 (m, 1H), 7.29 – 7.15 (m, 3H), 7.05 (d, J = 14.0 Hz, 1H), 6.72 (d, J = 13.9 Hz, 1H), 6.39 (d, J = 8.1 Hz, *cis isom.*), 2.48 (s, 4H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 141.0 (C), 136.5 (CH), 136.1 (q, *J* = 477.6 Hz), 131.7 (CH), 129.4 (CH), 126.5 (CH), 125.8 (CH), 105.9 (CH), 15.6 ($CH_3$).

**$^{19}$F NMR** (235 MHz, $CDCl_3$,300K) δ -42.8, -43.1.

The data matched those reported in the literature. [11]

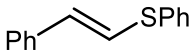
**General procedure E**




In a Schlenk flask under argon atmosphere, **3** (1 equiv.) was dissolved in THF and the solution was cooled down to -25 ºC. To this mixture the organomagnesium compound (1.2 equiv.) was added dropwise and the solution was stirred overnight while the temperature reached 0 ºC. Once the reaction was completed, it was extracted using EtOAc (10 mL) and the organic solution was washed with brine (10 mL). The organic

layer was dried using $MgSO_4$, concentrated by rotatory evaporation and the product was purified by column chromatography. Finally, product **8** was obtained.

**(*E*)-phenyl(styryl)sulfane (8a)**



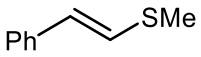

Following general procedure **E**, phenylmagnesium bromide (0.3 mmol) was added dropwise to a solution of **3a** (40.3 mg, 0.25 mmol) in 2 ml of THF. Product **8a** was obtained as a colourless oil (48 mg, 90% isolated yield, *d.r.:* 6.3:1 *trans/cis*).

**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.68 – 7.18 (m, 10H + *cis isom.*), 6.92 (d, *J* = 15.5 Hz, 1H), 6.77 (d, *J* = 15.5 Hz, 1H), 6.63 (d, J = 10.8 Hz, *cis isom.*), 6.53 (d, *J* = 10.7 Hz, *cis isom.*).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 136.6 (C), 135.3 (C), 131.9 (CH), 129.9 (CH), 129.2 (CH), 128.7 (CH), 127.7 (CH), 127.0 (CH), 126.1 (CH), 123.4 (CH).

The data matched those reported in the literature. [12]

**(*E*)-methyl(styryl)sulfane (8b)**




Following general procedure **E**, methylmagnesium bromide (0.3 mmol) was added dropwise to a solution of **3a** (40.3 mg, 0.25 mmol) in 2 ml of THF. Product **8b** was obtained as a yellow oil (35 mg, 92% isolated yield, *d.r.:* 5.9:1 *trans/cis*).

**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.54 – 7.18 (m, 5H + *cis isom.*), 6.84 (d, *J* = 15.5 Hz, 1H), 6.49 (d, *J* = 10.9 Hz, *cis isom.*), 6.36 (d, *J* = 15.4 Hz, 1H), 6.26 (d, J = 10.9 Hz, *cis isom.*), 2.43 (s, 3H).

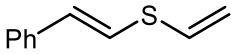
**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 137.2 (C), 128.7 (CH), 126.7 (CH), 125.8 (CH), 125.4 (CH), 124.7 (CH), 14.8 ($CH_3$).

The data matched those reported in the literature. [13]

[12] H. F. Piedra, M. Plaza. *Chem. Sci.,* **2023**, *14*, 650

[13] Y. Uetake, M. Isoda, T. Niwa, T. Hosoya. *Org. Lett.*, **2019**, *21*, 4933

**(*E*)-styryl(vinyl)sulfane (8c)**



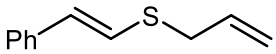

Following general procedure **E**, vinylmagnesium bromide (0.3 mmol) was added dropwise to a solution of **3a** (40.3 mg, 0.25 mmol) in 2 ml of THF. Product **8c** was obtained as a yellow oil (38 mg, 93% isolated yield, *d.r.:* 4:1 *trans/cis*).

Rf = 0.17 (hexane) [UV] [Vanillin]

**$^{1}$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.54 – 7.18 (m, 5H + *cis isom.*), 6.84 (d, *J* = 15.5 Hz, 1H), 6.49 (d, *J* = 10.9 Hz, *cis isom.*), 6.36 (d, *J* = 15.4 Hz, 1H), 6.26 (d, J = 10.9 Hz, 1H).) δ 7.49 – 7.19 (m, 5H + *cis isom.*), 6.79 (d, *J* = 15.6 Hz, 1H + *cis isom.*), 6.69 (d, *J* = 15.6 Hz, 1H), 6.52 (dd, *J* = 16.7, 9.8 Hz, 1H + *cis isom.*), 5.43 – 5.33 (m, 2H + *cis isom.*)

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 136.5 (C), 131.1 (CH), 130.3 (CH), 128.7 (CH), 127.6 (CH), 126.0 (CH), 121.3 (CH), 114.6 ($CH_2$).

**(*E*)-styryl(vinyl)sulfane (8d)**




Following general procedure **E**, allylmagnesium bromide (0.3 mmol) was added dropwise to a solution of **3a** (40.3 mg, 0.25 mmol) in 2 ml of THF. Product **8d** was obtained as a colourless oil (38 mg, 85% isolated yield).

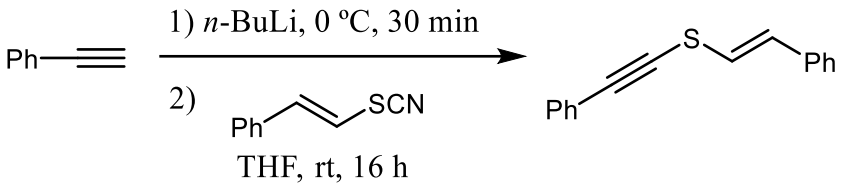
**$^{1}$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.30 (d, *J* = 4.3 Hz, 4H), 6.71 (d, *J* = 15.6 Hz, 1H), 6.55 (d, *J* = 15.6 Hz, 1H), 5.92 (ddt, *J* = 16.9, 10.0, 6.9 Hz, 1H), 5.33 – 5.15 (m, 1H), 3.44 (dt, *J* = 7.0, 1.2 Hz, 2H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 137.0 (C), 133.6 (CH), 128.7 (CH), 128.0 (CH), 127.0 (CH), 125.6 (CH), 124.1 (CH), 117.9 ($CH_2$), 35.8 ($CH_2$).

The data matched those reported in the literature. [14]

[14] L. Castoldi, E. M. Di Tommaso, M. Reitti, B. Gräfen, B. Olofsson. *Angew. Chem. Int. Ed.*, **2020**, *59*, 15512

**Procedure for the synthesis of 9a**



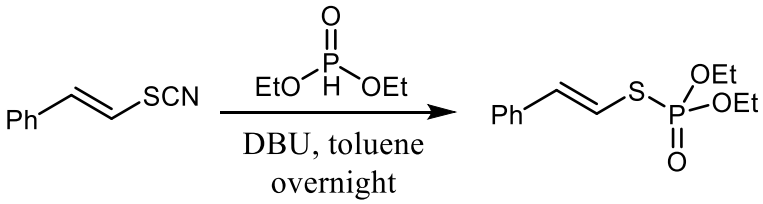

Under inert atmosphere, phenylacetylene (77 µL, 0.70 mmol) was dissolved in 1.5 mL of dry THF and cooled to –78°C. Then, *n*-BuLi (0.28 mL, 0.70 mmol, 2.5 M in n-hexane) was added dropwise. After 30 min, **3a** (106 mg, 0.65 mmol) was introduced slowly, and the mixture was allowed to gradually warm to room temperature overnight. Once the reaction was complete, water (10 ml) was added to quench the reaction and it was extracted using EtOAc (10 mL) and the organic solution was washed with brine (10 mL). The organic layer was dried using $MgSO_4$, concentrated by rotatory evaporation and the product was purified by column chromatography obtaining compound **9a** (79 mg, 52% yield).

**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.63 – 7.49 (m, 2H), 7.44 – 7.18 (m, 8H), 6.89 (d, *J* = 15.1 Hz, 1H), 6.61 (d, *J* = 15.1 Hz, 1H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 136.0 (C), 131.7 (CH), 129.6 (CH), 128.7 (CH), 128.6 (CH), 128.4 (CH), 127.7 (CH), 126.1 (CH), 122.7 (C), 118.7 (CH), 98.8 (C), 74.6 (C).

The data matched those reported in the literature. [15]

**Procedure for the synthesis of 10a**




To a solution of **3a** (60 mg, 0.37 mmol) and diethyl phosphite (71 µL, 0.55 mmol) in dry toluene (1.0 mL), DBU (83 µL, 0.55 mmol) was added dropwise. The reaction was stirred at room temperature overnight. Once the reaction was completed, the mixture was

[15] C. C. Silveira, F. Rinaldi, R. C. Guadagnin, A. L. Braga, *Synth*., **2009**, *3*, 469

concentrated in vacuo and the product was purified by column chromatography (1:1 Hex/EtOAc). Product **10a** was obtained as an orange oil (30 mg, 30% yield).

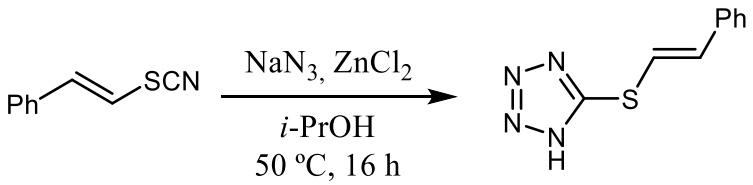
**$^{1}$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.43 – 7.29 (m, 5H), 6.88 (dd, *J* = 15.5, 2.1 Hz, 1H), 6.68 (dd, *J* = 15.5, 8.4 Hz, 1H), 4.38 – 4.14 (m, 4H), 1.40 (t, *J* = 0.9 Hz, 6H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 137.0 (d, $^{2}J_{C\text{-}P}$ = 12.4 Hz, CH), 135.8 (C), 128.7 (CH), 128.4 (CH), 126.3 (CH), 114.8 (CH) (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, CH), 64.0 (d, $^{2}J_{C\text{-}P}$ = 5.8 Hz, $CH_2$), 16.1 (d, $^{3}J_{C\text{-}P}$ = 7.2 Hz, $CH_3$).

**$^{31}$P NMR** (121 MHz, $CDCl_3$, 300K) δ 23.1.

The data matched those reported in the literature.[16]

**Procedure for the synthesis of 11a**[7]




To a solution of **3a** (132 mg, 0.82 mmol) in 2.5 mL of isopropanol, sodium azide (61 mg, 0.94 mmol), and zinc chloride (111 mg, 0.82 mmol) were added. The mixture was stirred at 50 °C overnight. Then, the solvent was evaporated under vacuum and 5% NaOH solution (11 mL) was added. The mixture was stirred for 20 minutes until the initial precipitate dissolved and a $Zn(OH)_2$ suspension formed. This suspension was filtered, and the solid was washed with 10 mL of 5% NaOH. The pH of the filtrate was adjusted to 1.0 using concentrated HCl, resulting in the precipitation of the tetrazole product. The tetrazole was filtered, washed with 2 portions of 10 mL of 9% HCl, and dried under vacuum, obtaining product **11a** (142 mg, 85% yield).

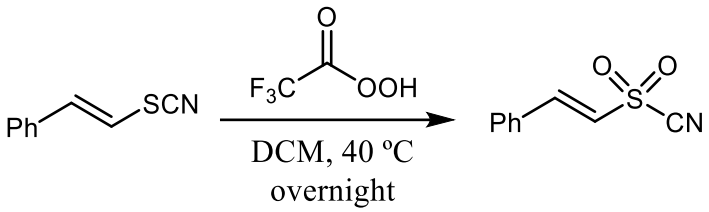
**$^{1}$H NMR** (300 MHz, d$^{6}$-DMSO, 300K) δ 7.57 – 7.20 (m, 6H), 7.04 (d, *J* = 15.6 Hz, 1H), 6.94 (bs, 1H).

**$^{13}$C NMR** (75 MHz, d$^{6}$-DMSO, 300K) δ 153.5 (C), 135.8 (C), 135.3 (CH), 129.2 (CH), 128.9 (CH), 127.0 (CH), 116.8 (CH).

**HRMS** [ESI (+)]: calcd. for ($[C_9H_8N_4S + Na]^+$): 205.0542, found: 205.0543.

[16] H. F. Piedra, V. Gebler, C. Valdes, M. Plaza. *Chem. Sci.*, **2023**, *14*, 12767.

**Procedure for the synthesis of 12a**




A 50 wt.% solution of hydrogen peroxide (10 eq.) was slowly added drop by drop at 0°C to a solution of trifluoroacetic anhydride (10 eq.) in dichloromethane. After stirring for 40 minutes at 0°C, thiocyanate **3a** (60 mg, 0.37 mmol) was introduced dropwise. The reaction mixture was then stirred at 40°C overnight. The reaction was quenched with water at 0°C. The aqueous layer was extracted with dichloromethane, and the combined organic layers were subsequently washed with water and brine. The resulting solution was dried over $MgSO_4$ and concentrated under reduced pressure. The colourless sulfonyl cyanide **12a** was obtained (28 mg, 39% yield).

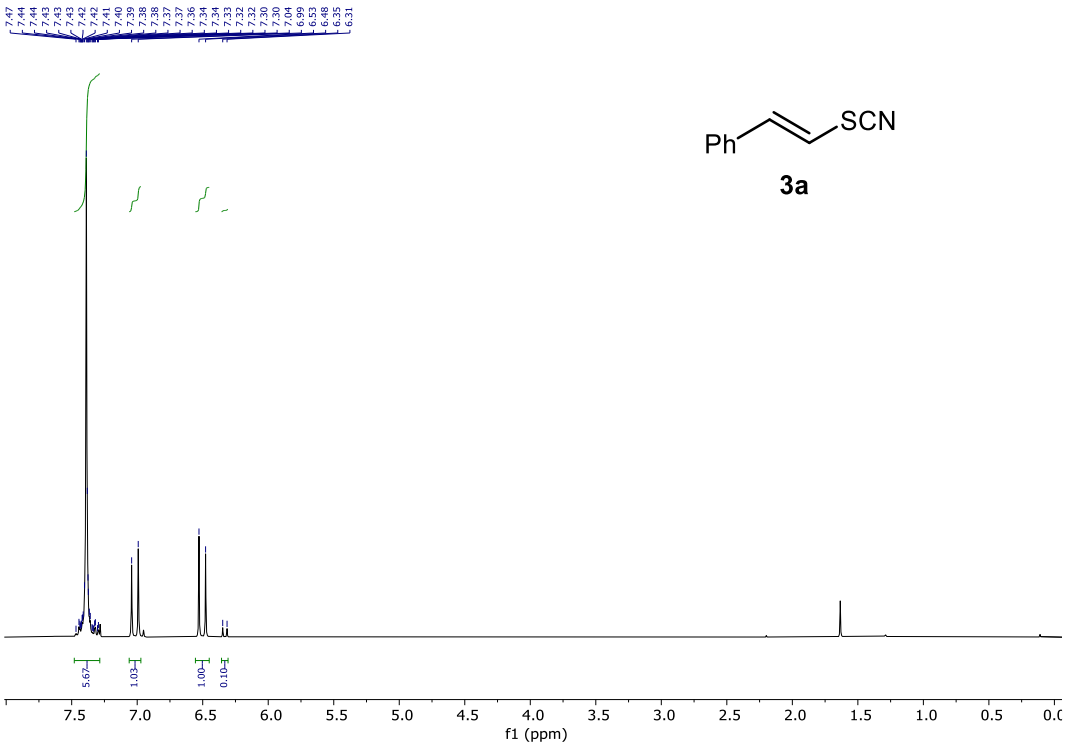
**$^1$H NMR** (300 MHz, $CDCl_3$, 300K) δ 7.94 (d, *J* = 15.3 Hz, 1H), 7.70 – 7.47 (m, 5H), 7.06 (d, *J* = 15.3 Hz, 1H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K) δ 152.9 (CH), 133.9 (CH), 130.5 (C), 129.9 (CH), 129.7 (CH), 122.8 (CH), 114.0 (C).

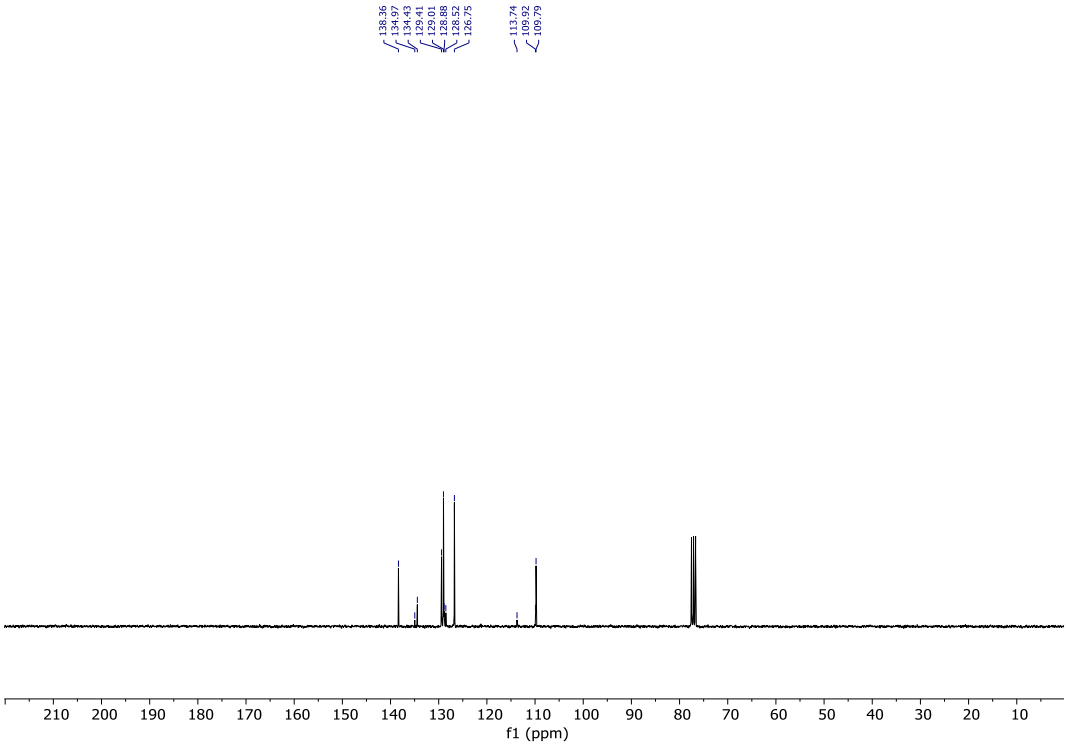
## 11. Copies of the NMR spectra

### (*E*)-(2-thiocyanatovinyl)benzene (3a)

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

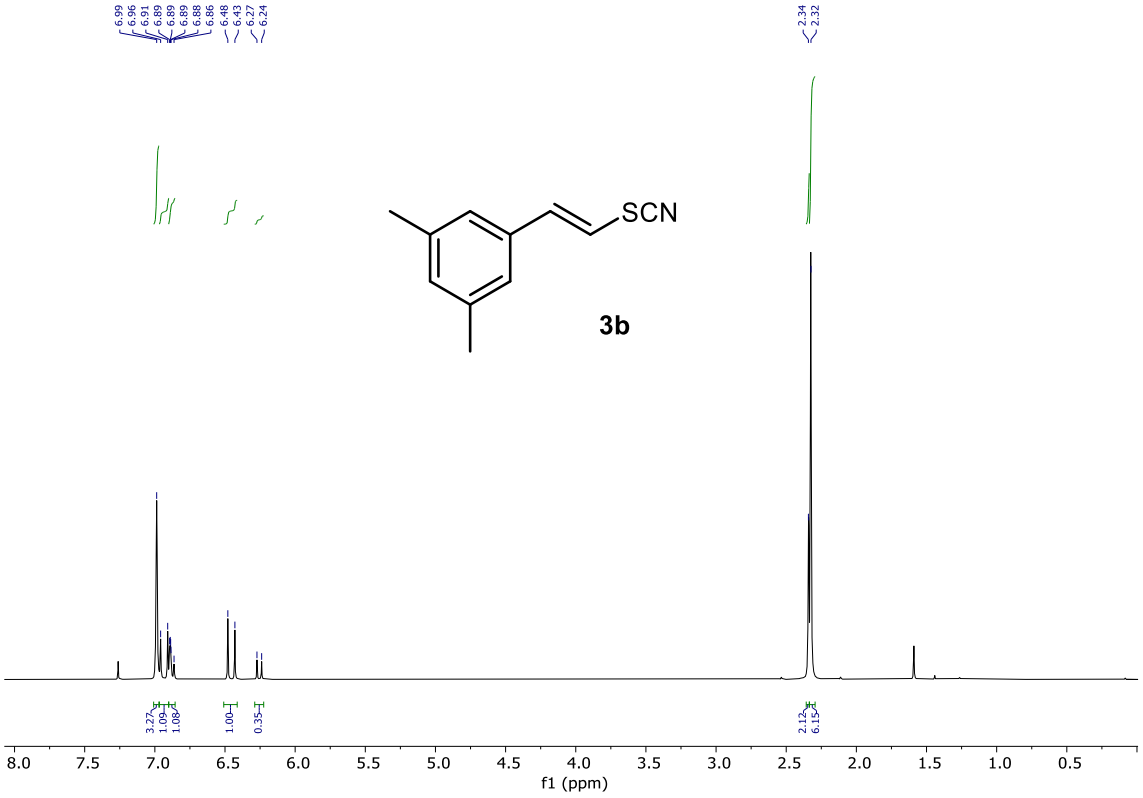



**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

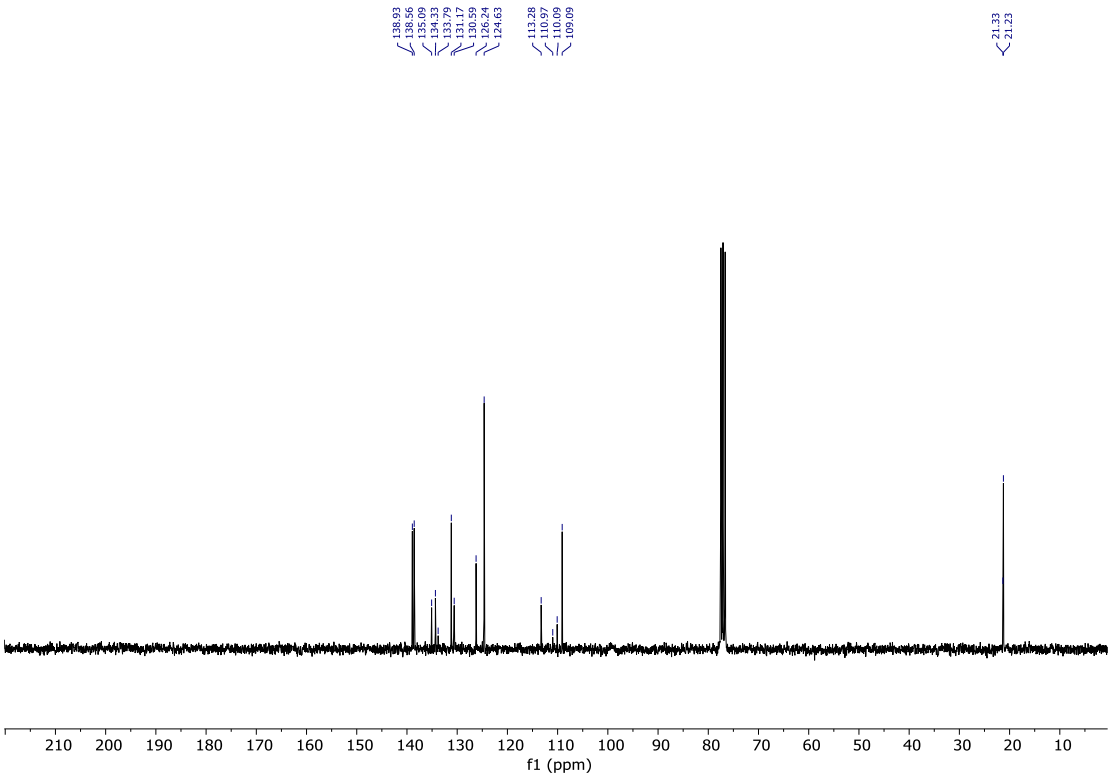


**(*E*)-1,3-dimethyl-5-(2-thiocyanatovinyl)benzene (3b)**

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

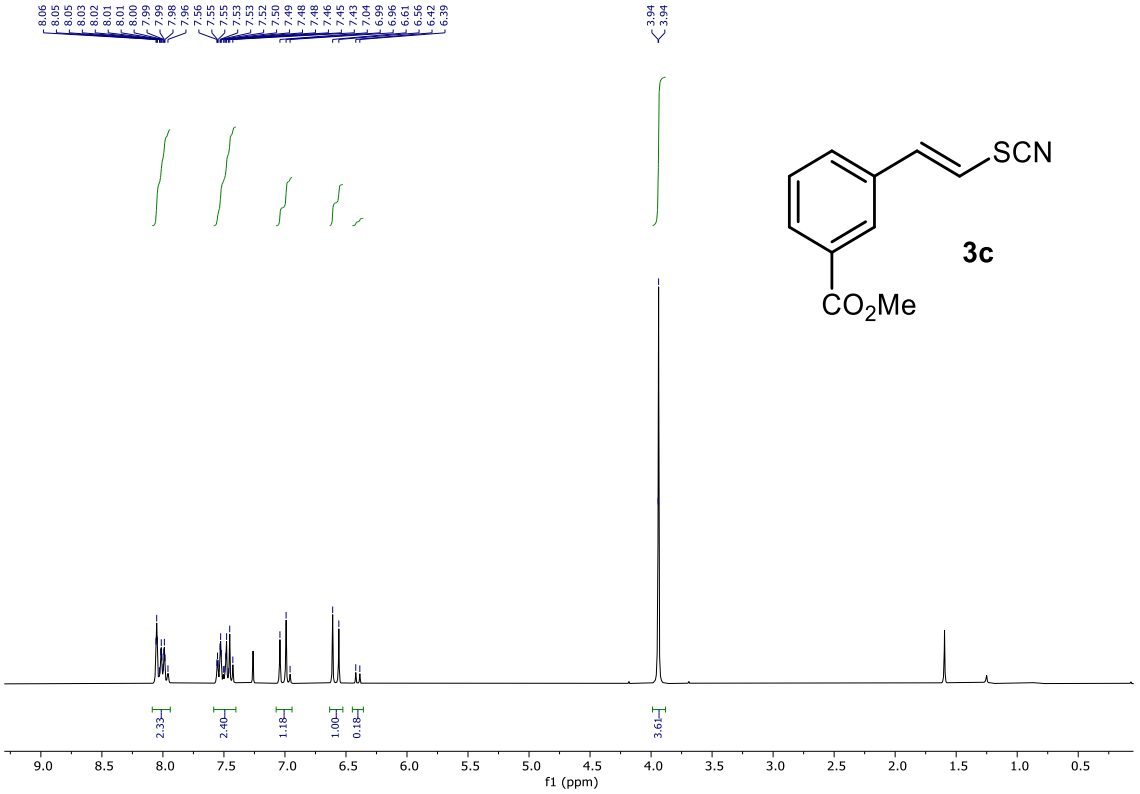



**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

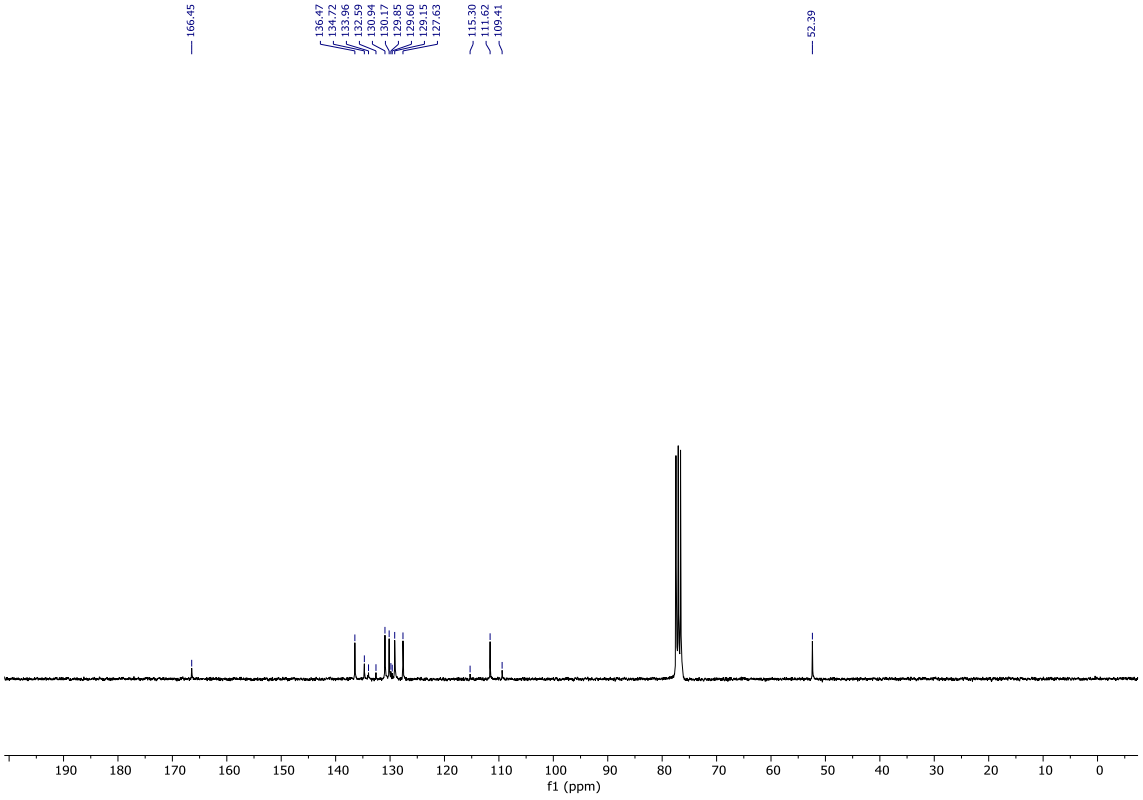


**Methyl (*E*)-3-(2-thiocyanatovinyl)benzoate (3c)**

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

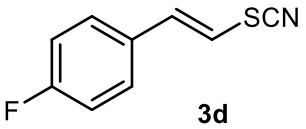



**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

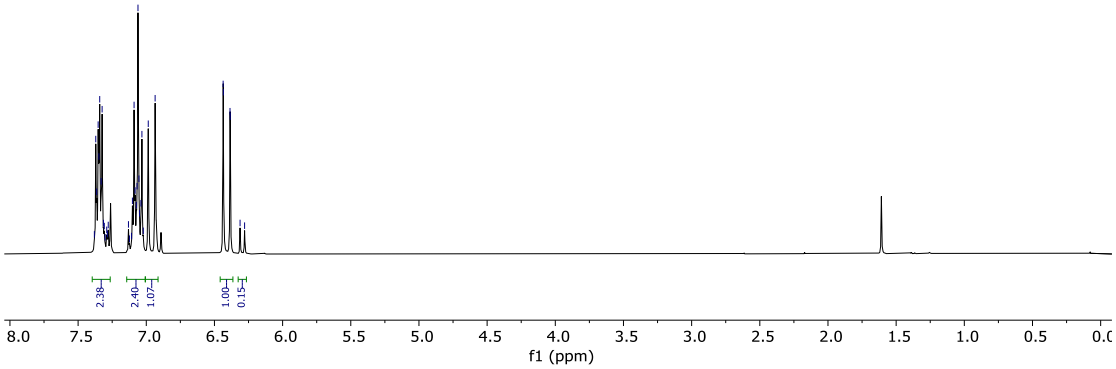


## (*E*)-1-fluoro-4-(2-thiocyanatovinyl)benzene (3d)

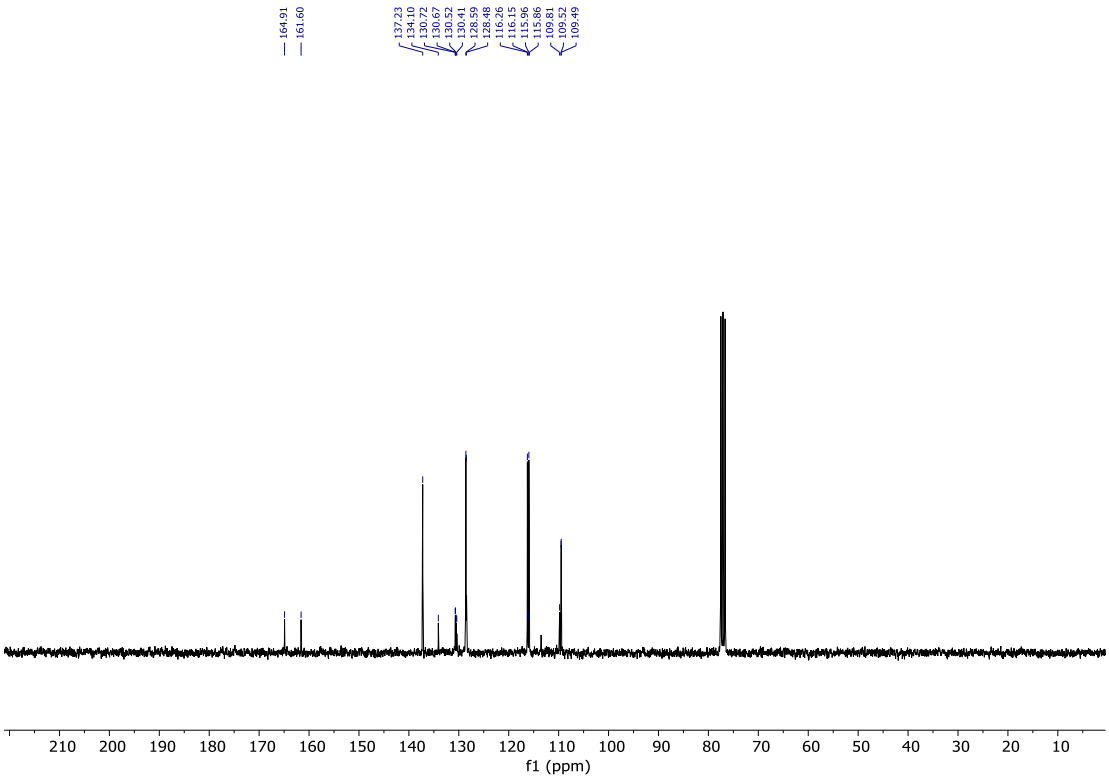
**$^{1}$H NMR** (300 MHz, $CDCl_3$, 300K)

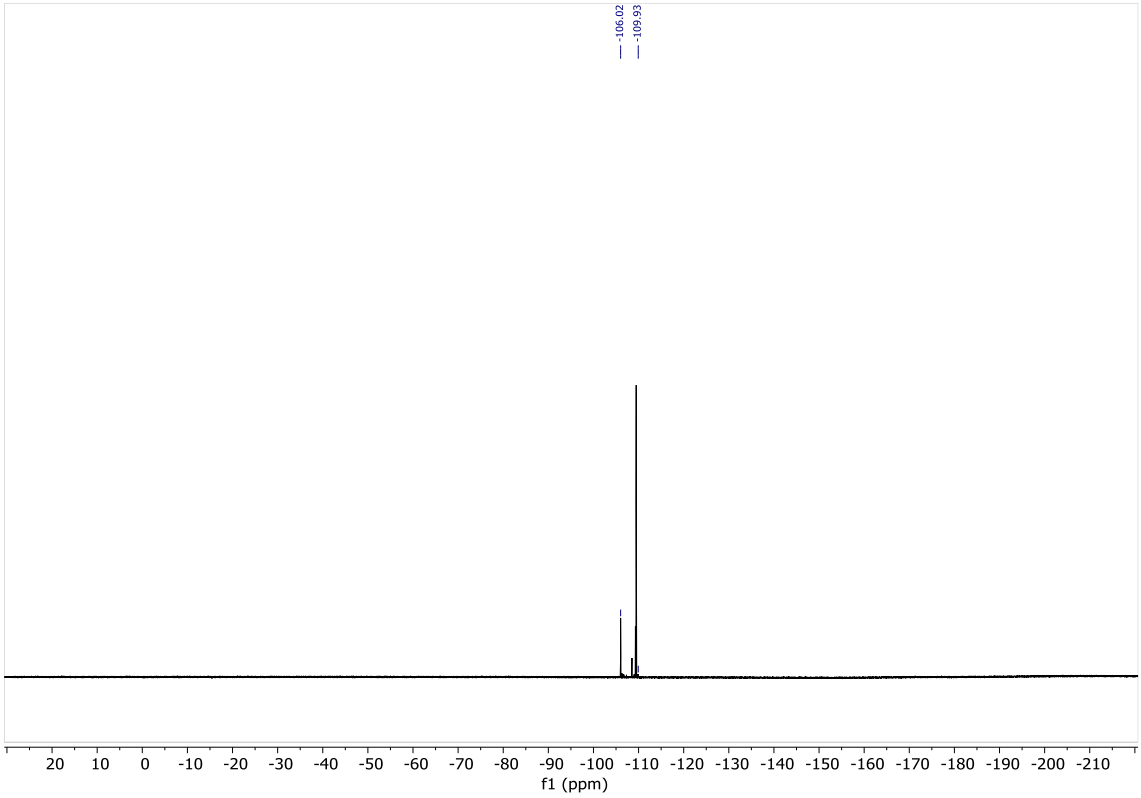

**3d**




**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

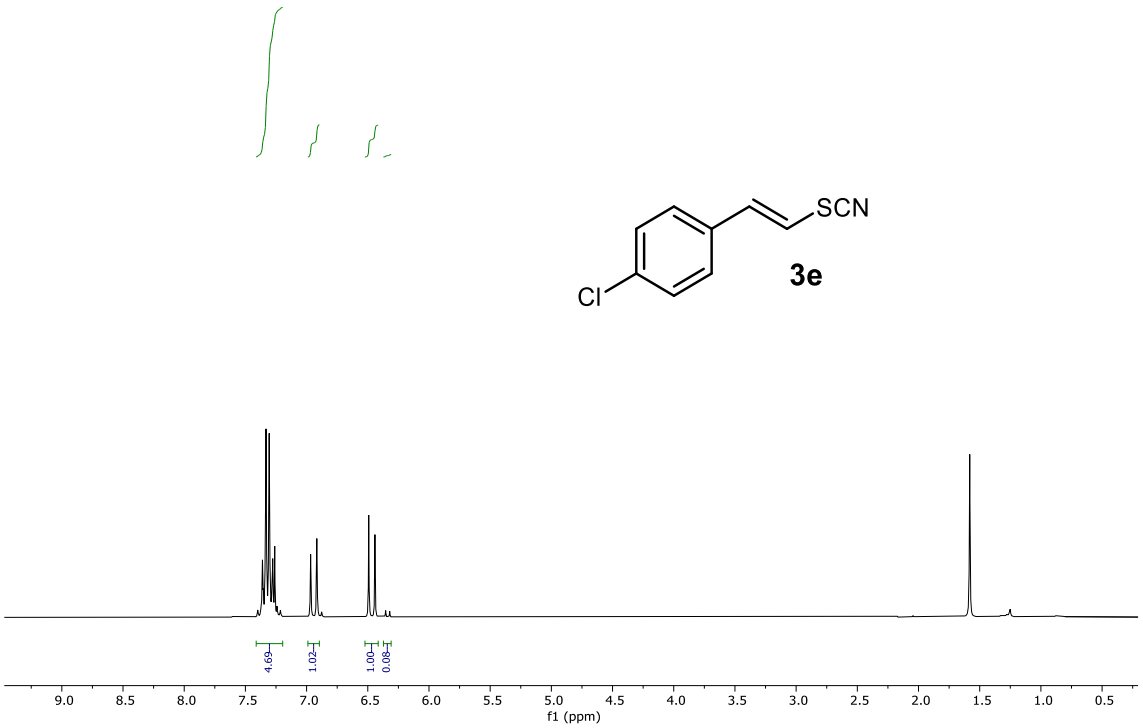


**$^{19}$F NMR** (282 MHz, $CDCl_3$, 300K)

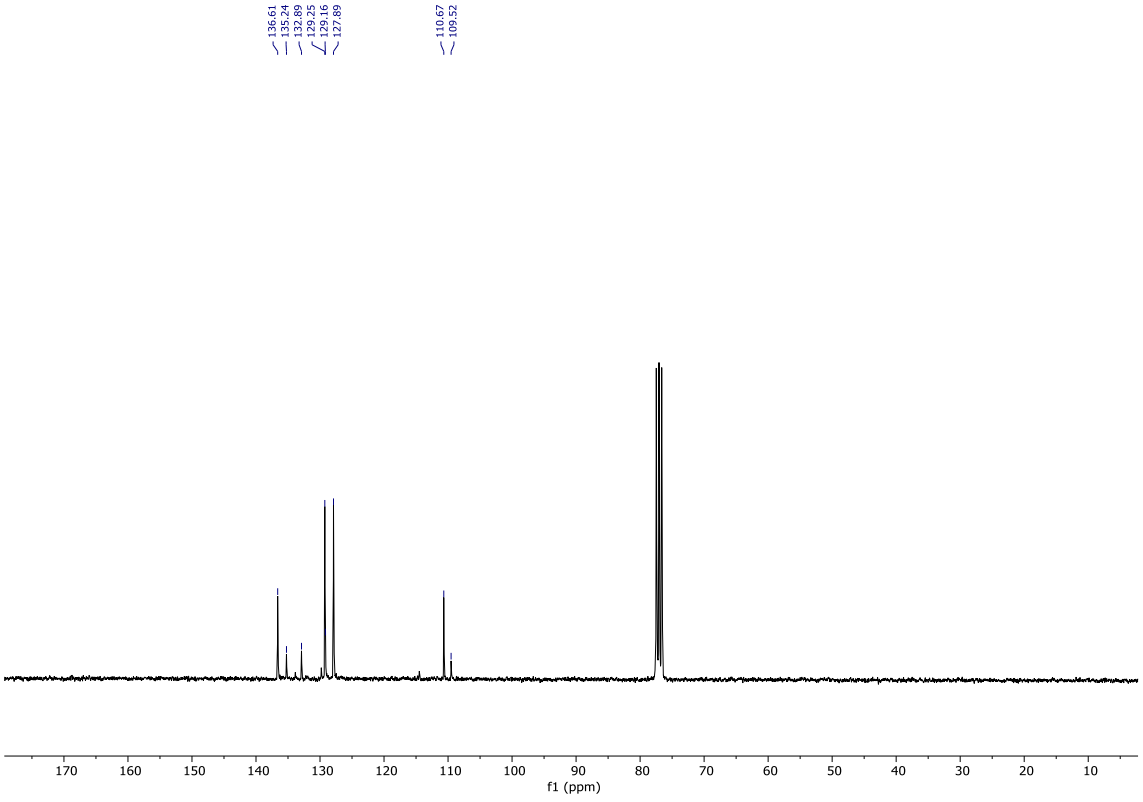


**(*E*)-1-chloro-4-(2-thiocyanatovinyl)benzene (3e)**

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

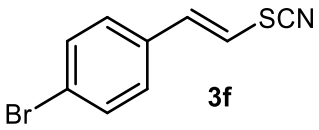


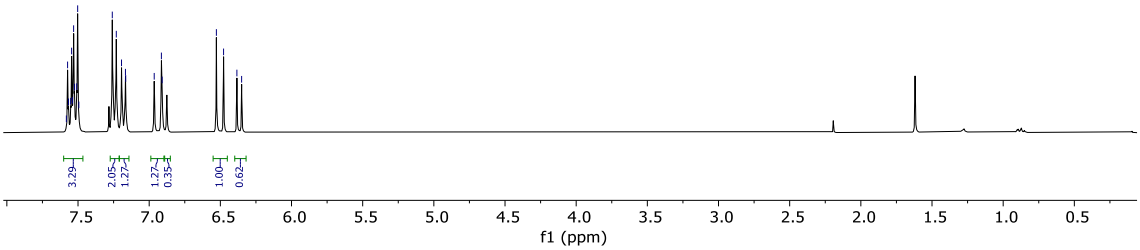

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)



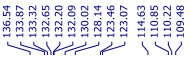
## (*E*)-1-bromo-4-(2-thiocyanatovinyl)benzene (3f)

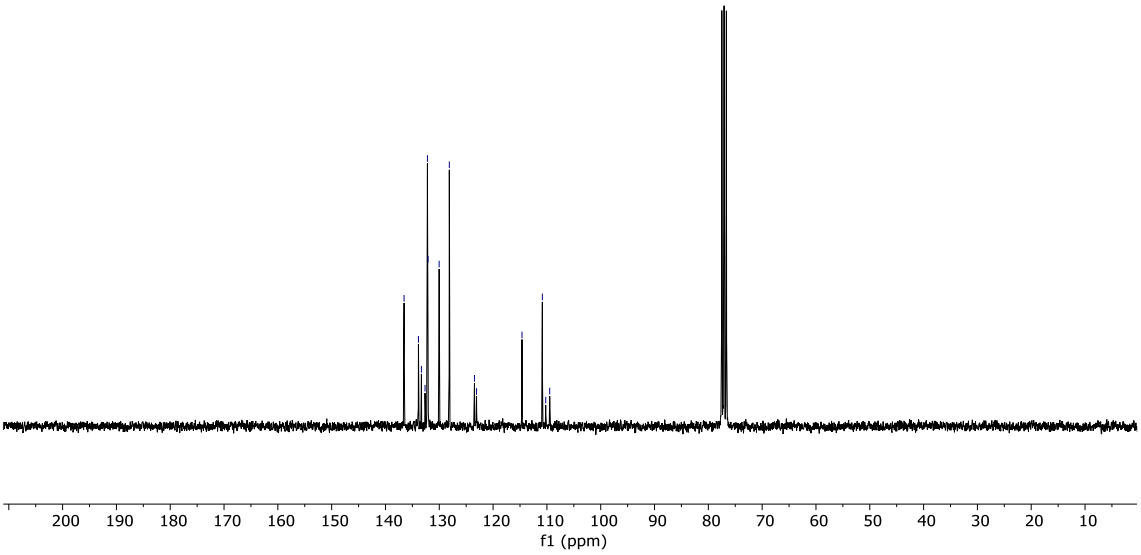
**$^{1}$H NMR** (300 MHz, $CDCl_3$, 300K)

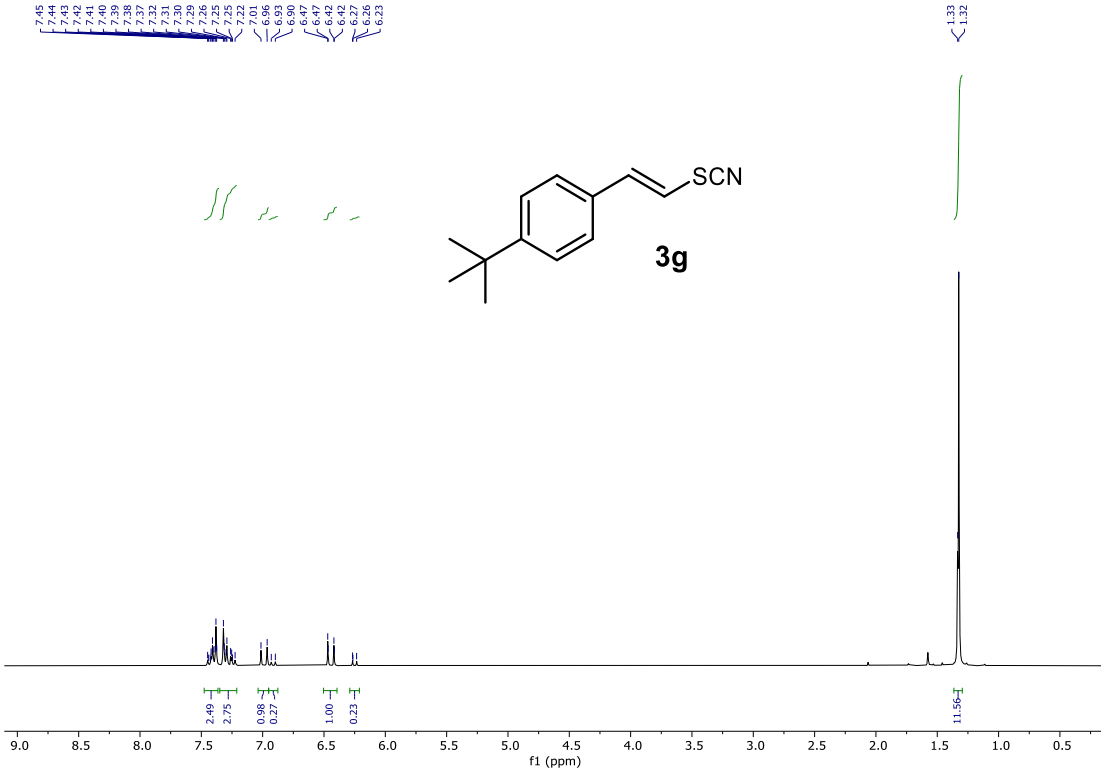

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)



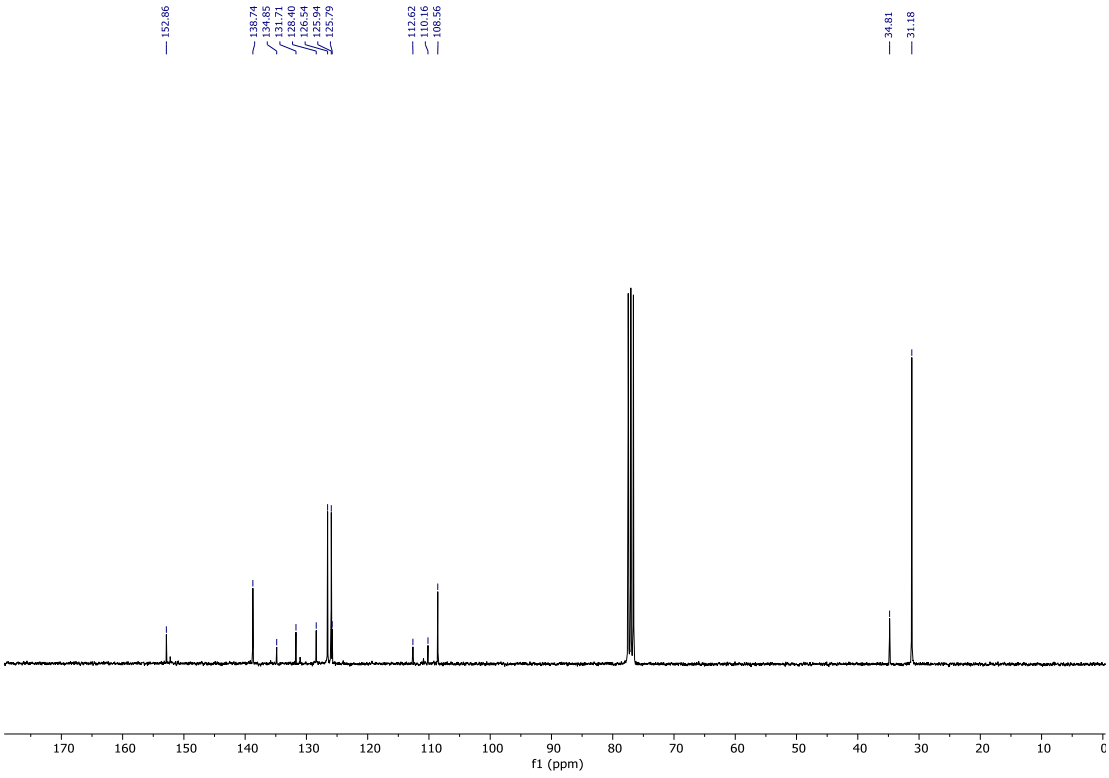



## (*E*)-1-(tert-butyl)-4-(2-thiocyanatovinyl)benzene (3g)

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

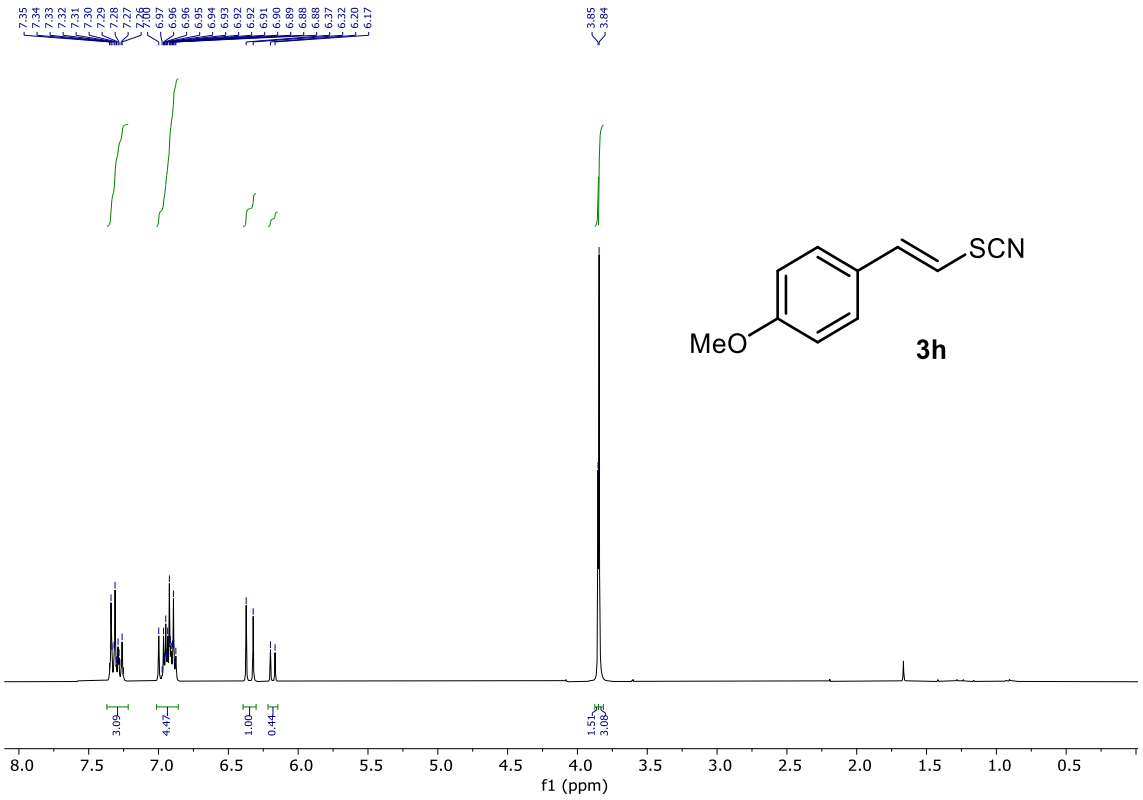



**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

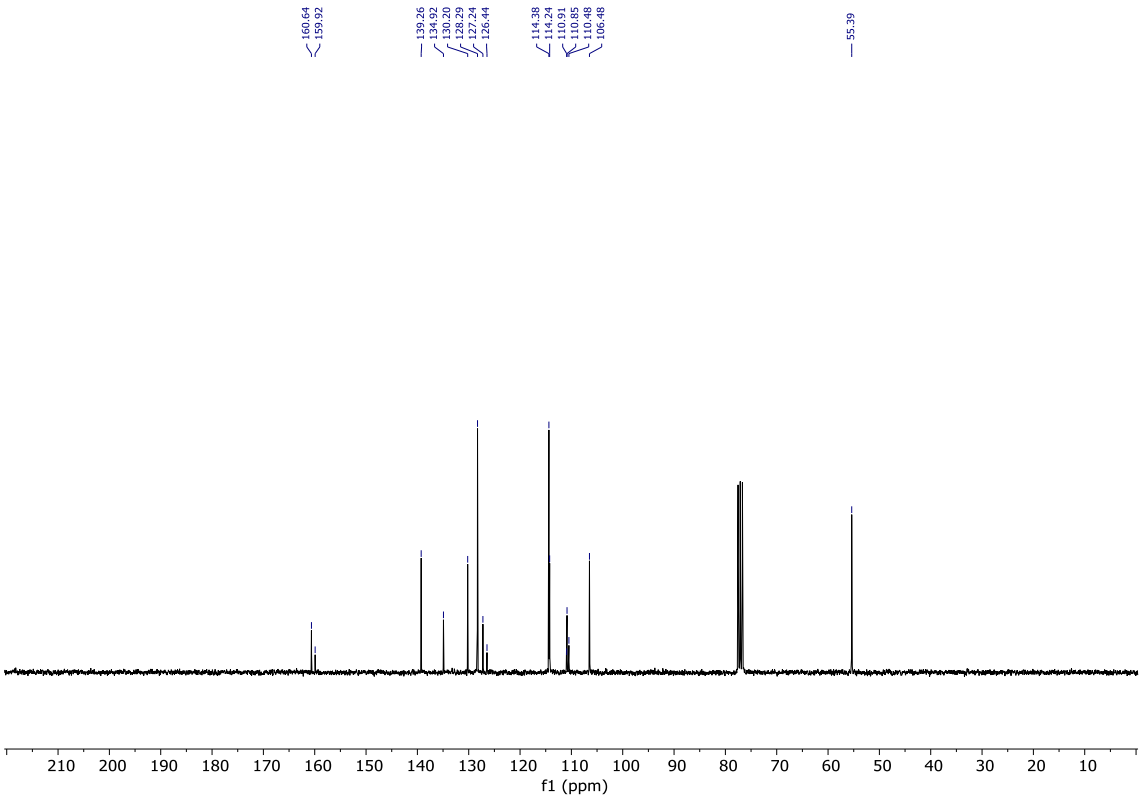


## (*E*)-1-methoxy-4-(2-thiocyanatovinyl)benzene (3h)

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

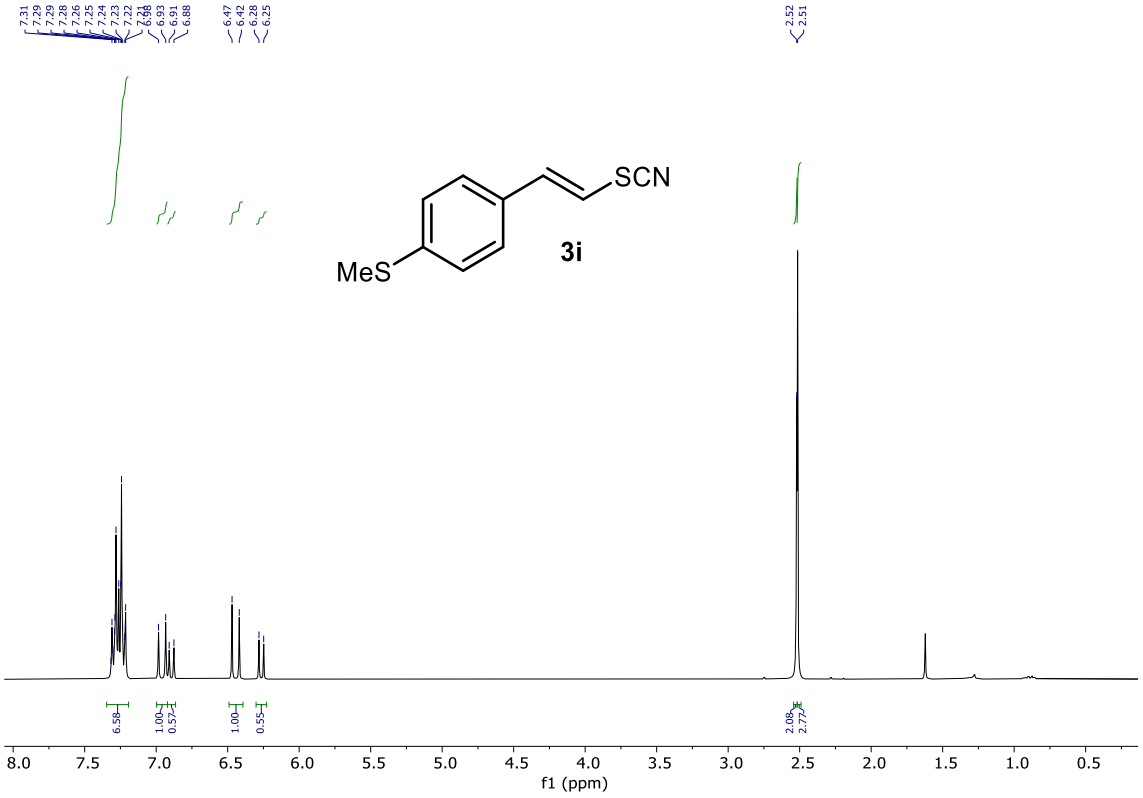



**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

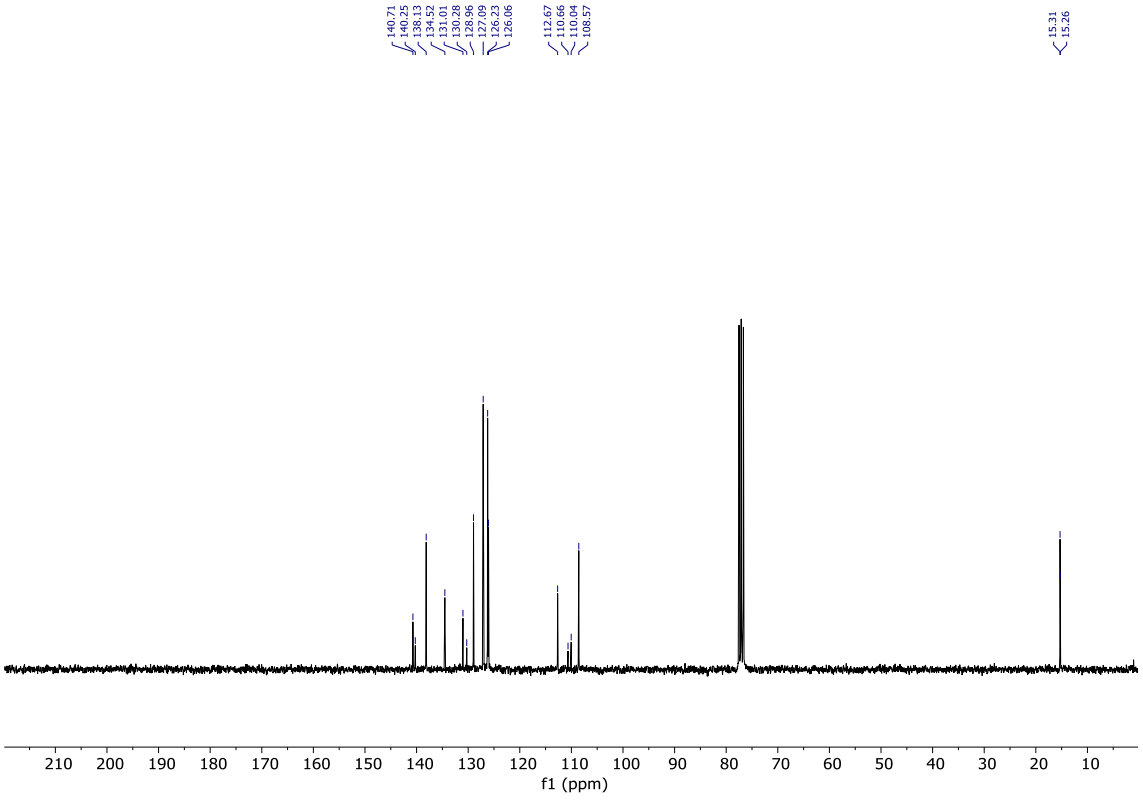


## (*E*)-methyl(4-(2-thiocyanatovinyl)phenyl)sulfane (3i)

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

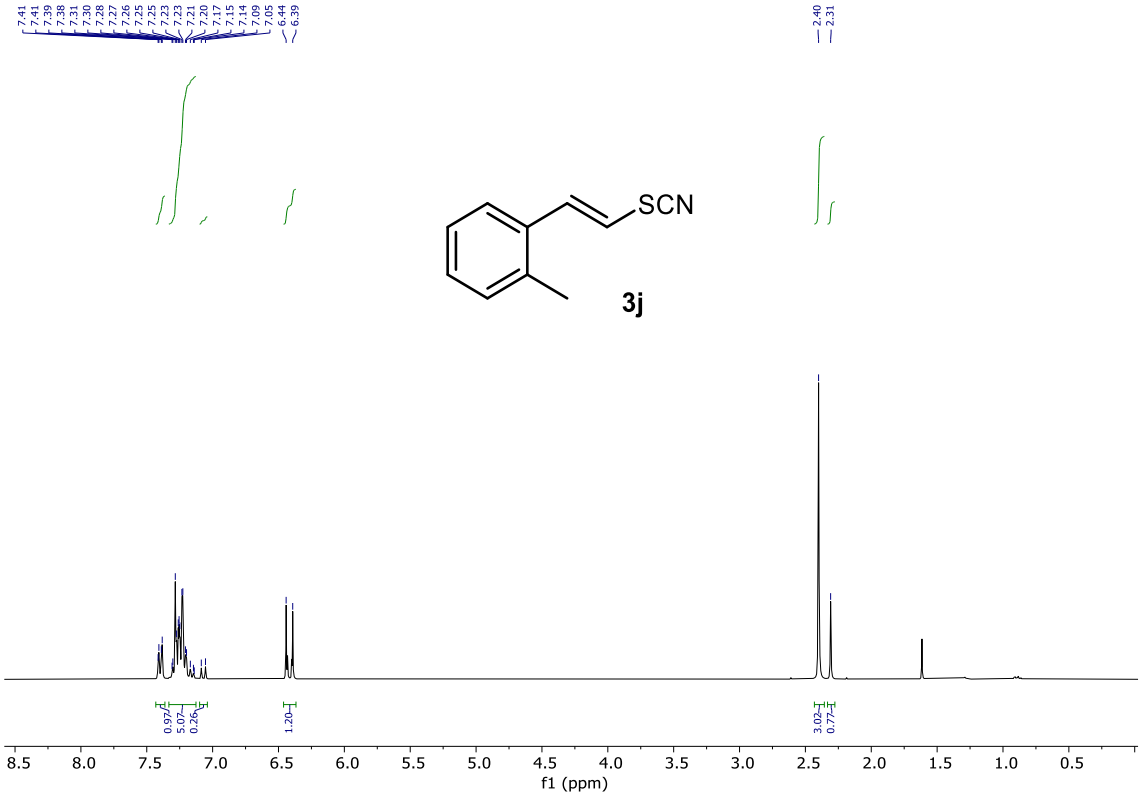



**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

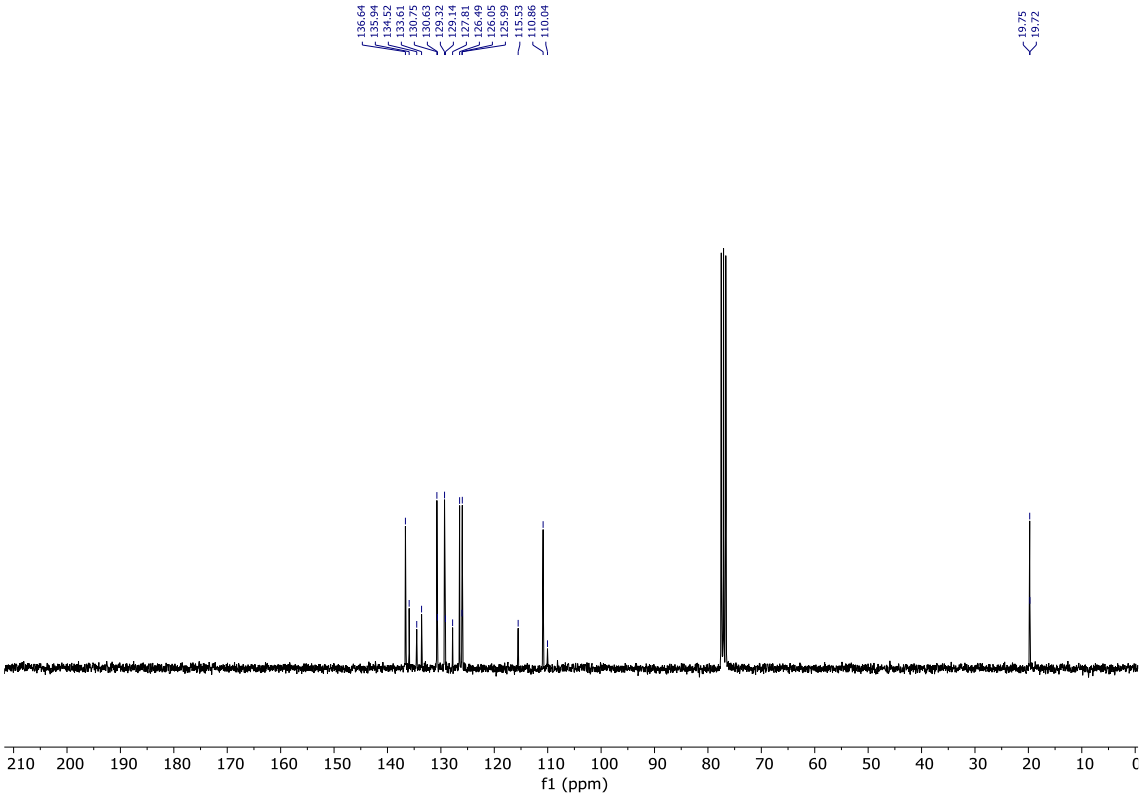


## (*E*)-1-methyl-2-(2-thiocyanatovinyl)benzene (3j)

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

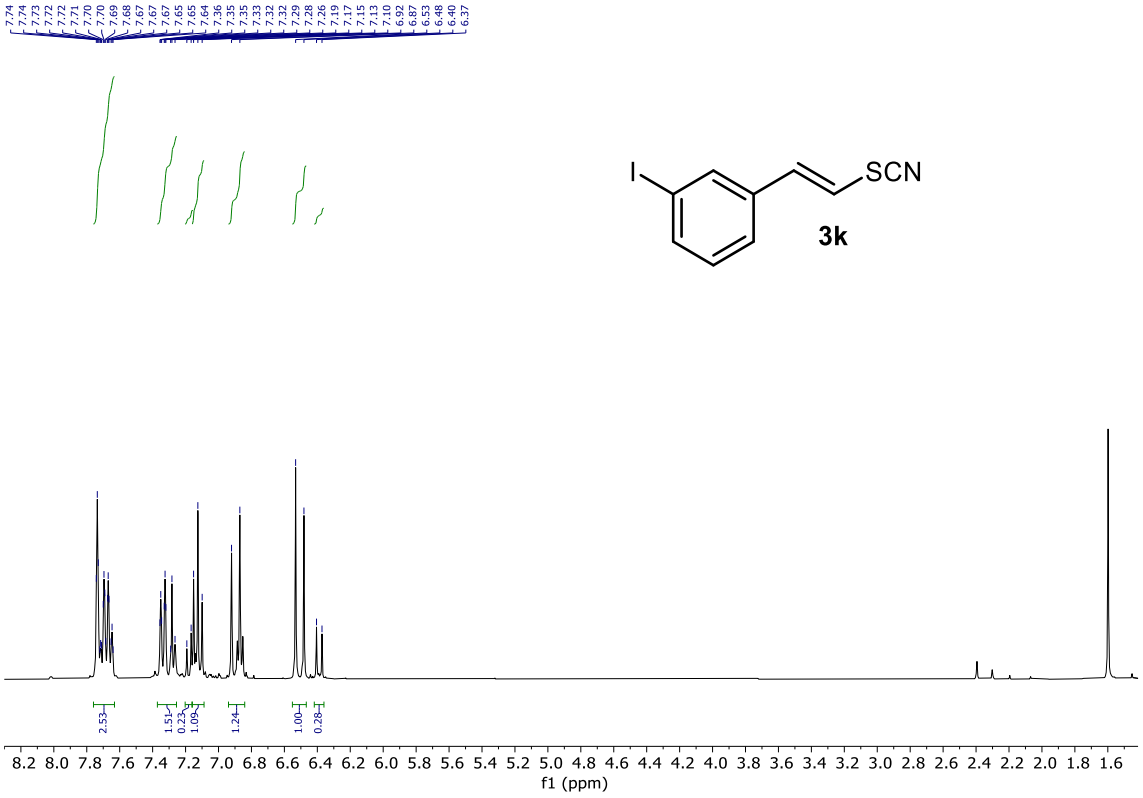



**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

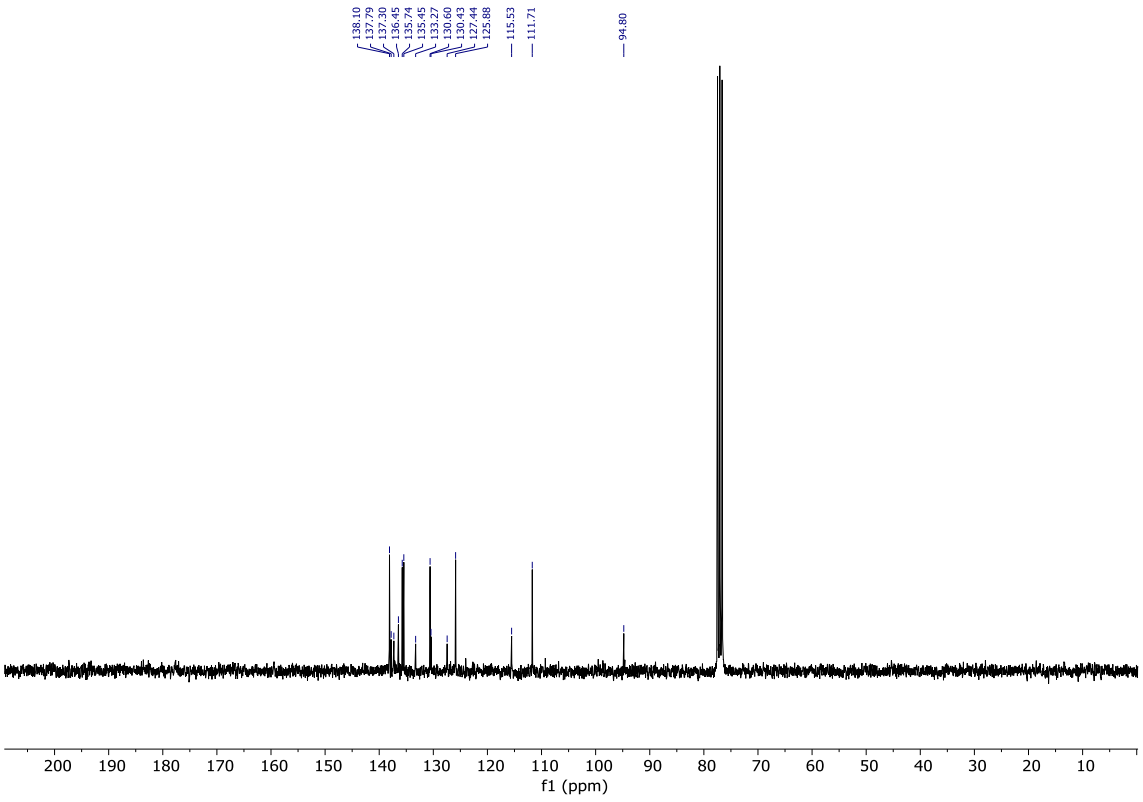


## (*E*)-1-iodo-3-(2-thiocyanatovinyl)benzene (3k)

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

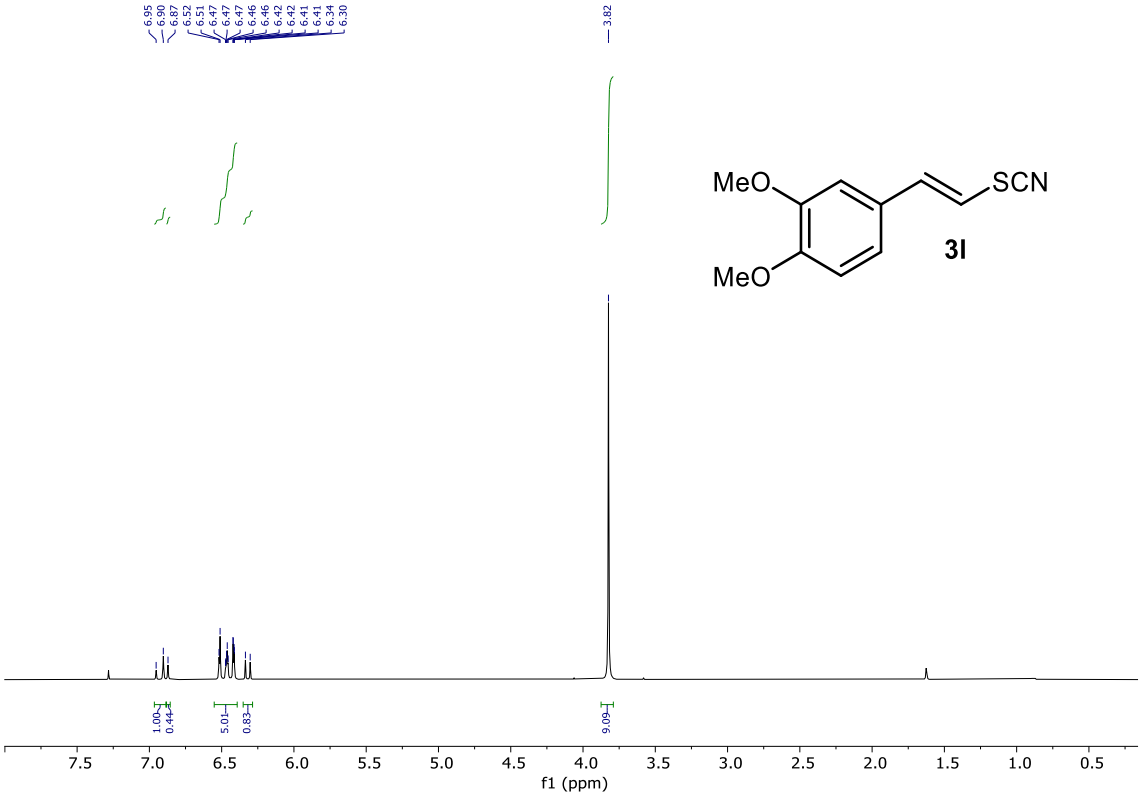



**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

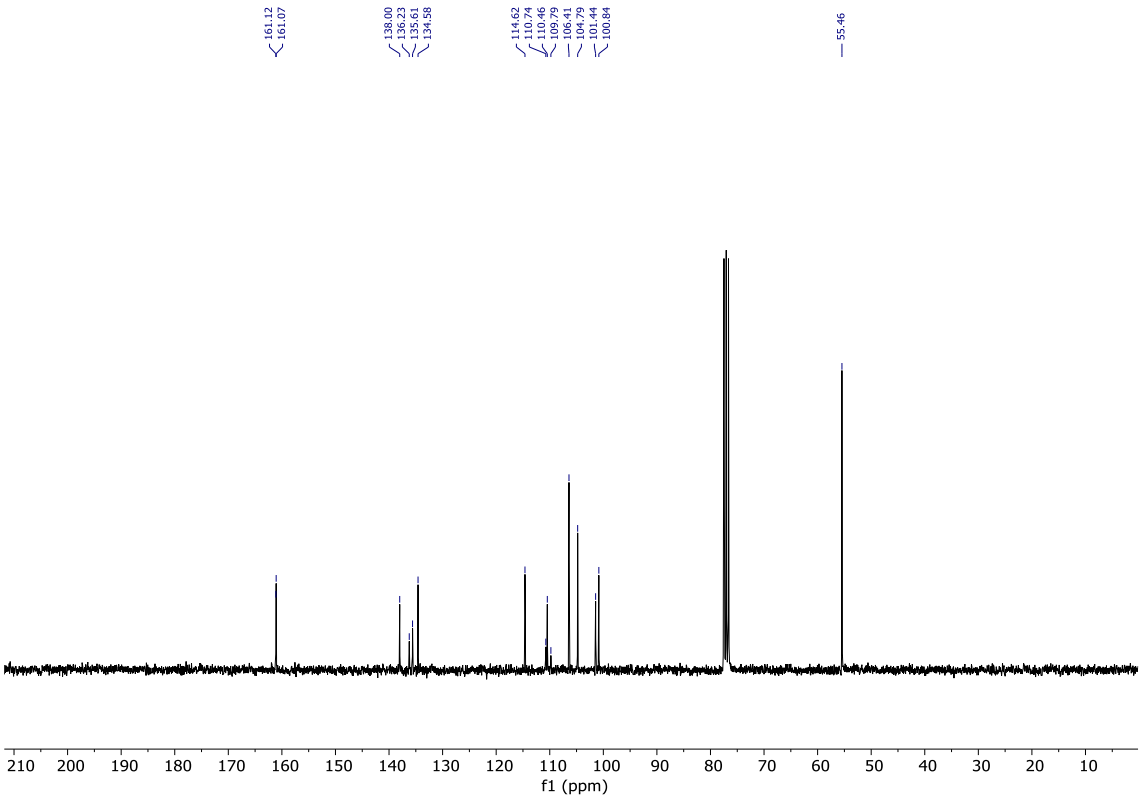


## (*E*)-1,2-dimethoxy-4-(2-thiocyanatovinyl)benzene (3l)

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

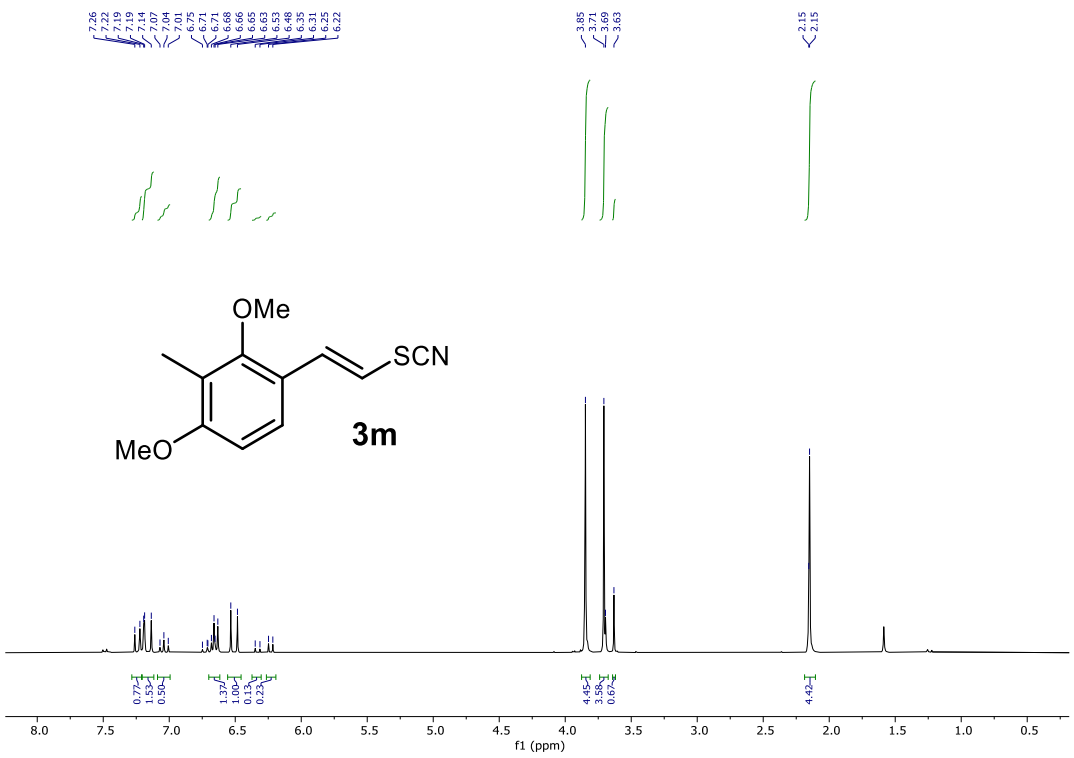



**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

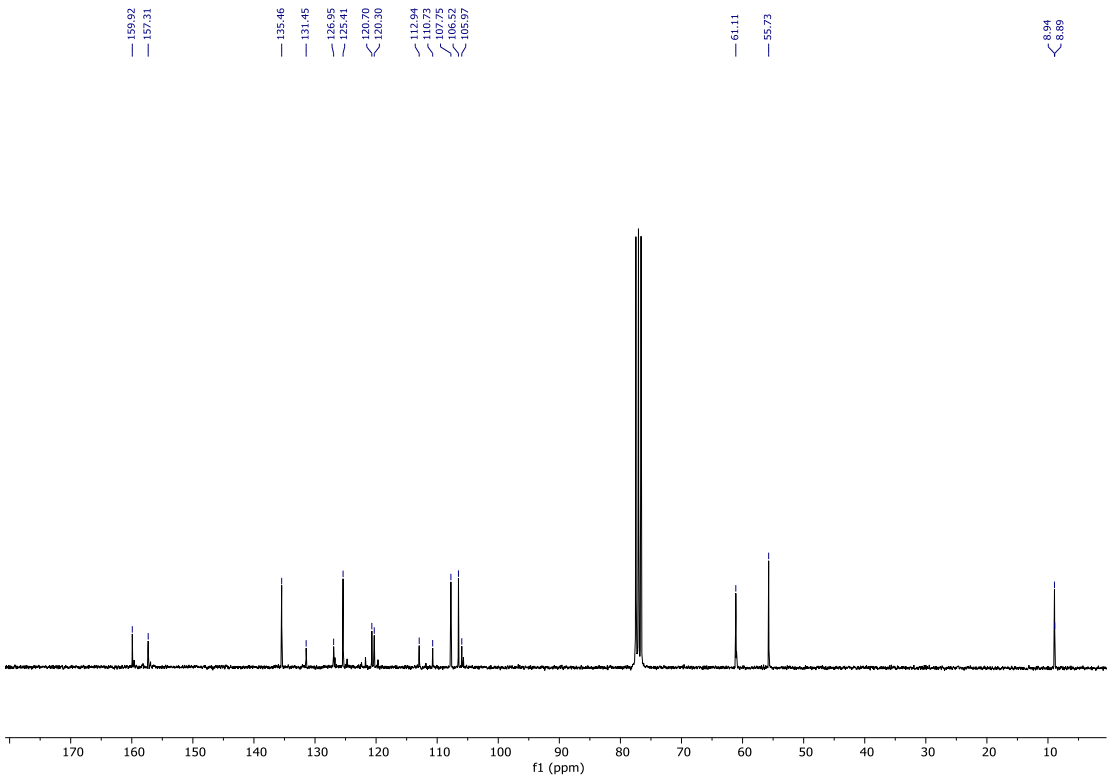


## (*E*)-1,3-dimethoxy-2-methyl-4-(2-thiocyanatovinyl)benzene (3m)

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

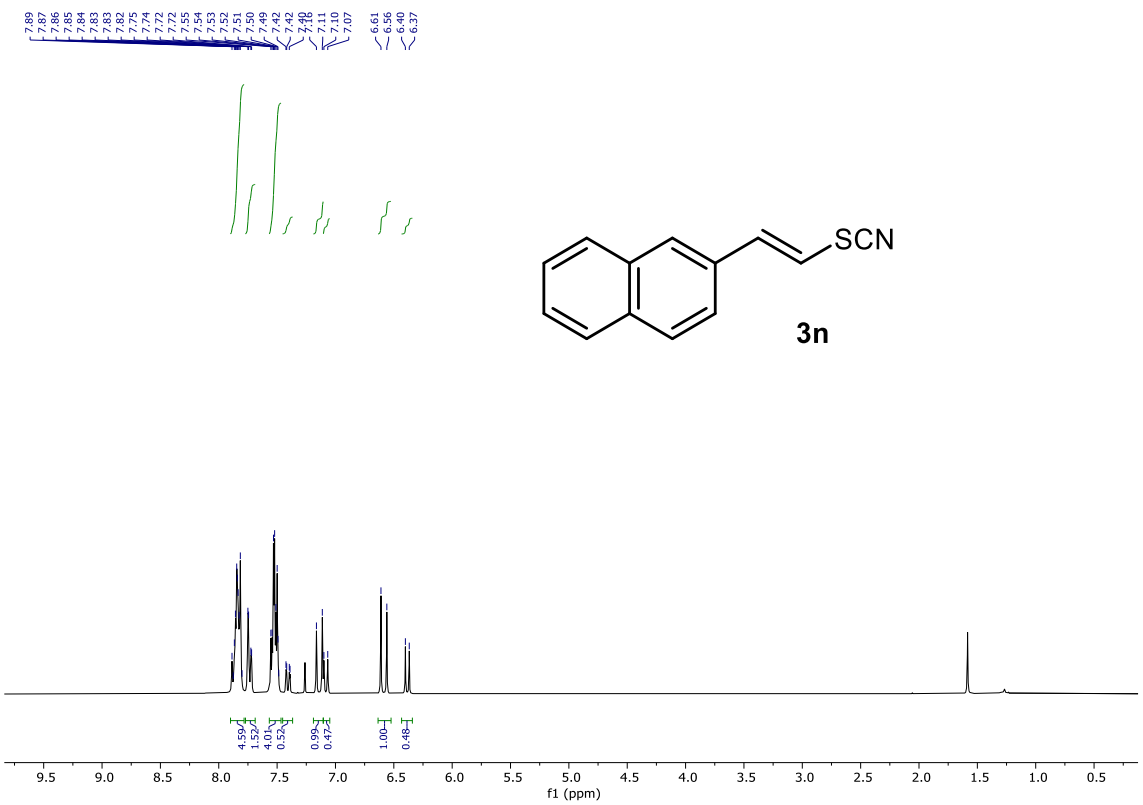



**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

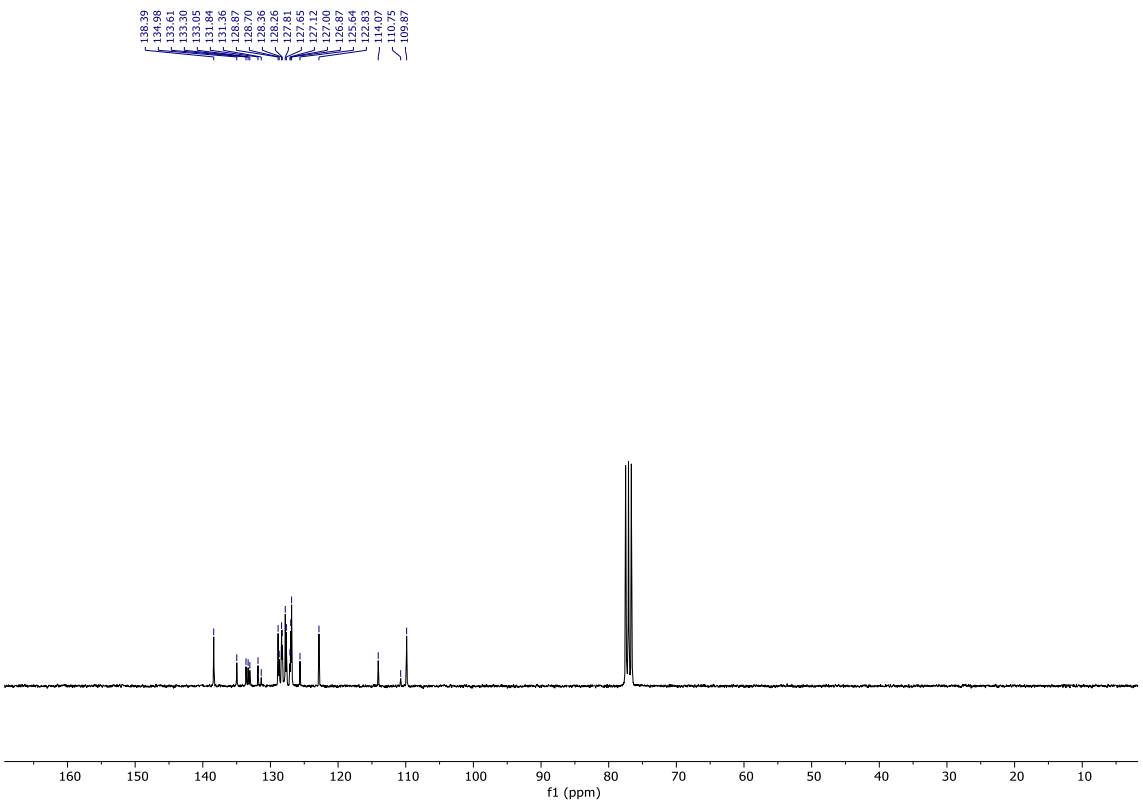


## (*E*)-2-(2-thiocyanatovinyl)naphthalene (3n)

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

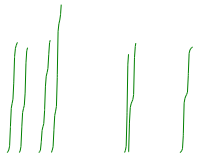


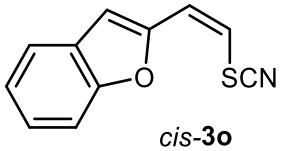

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)



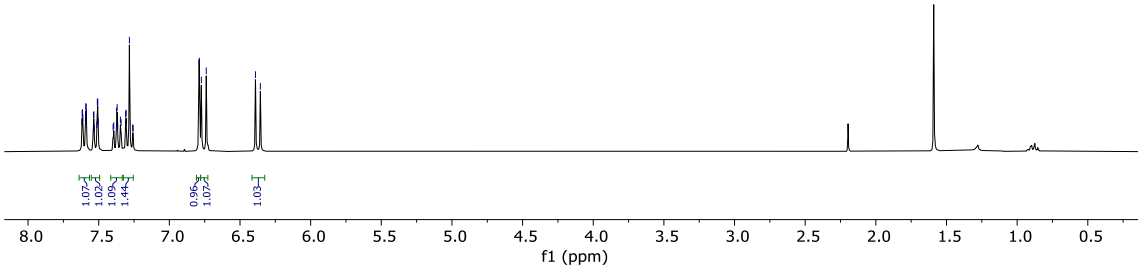
## (*Z*)-2-(2-thiocyanatovinyl)benzofuran (*cis*-**3o**)

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

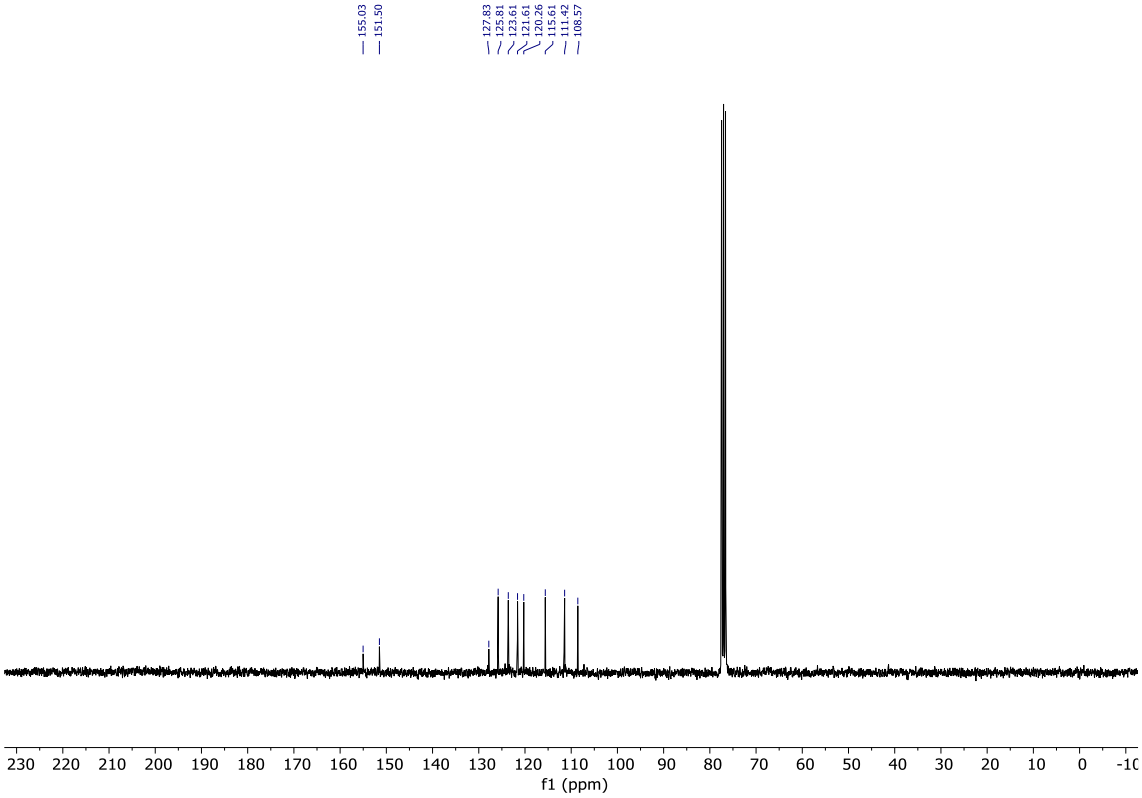






*cis*-**3o**

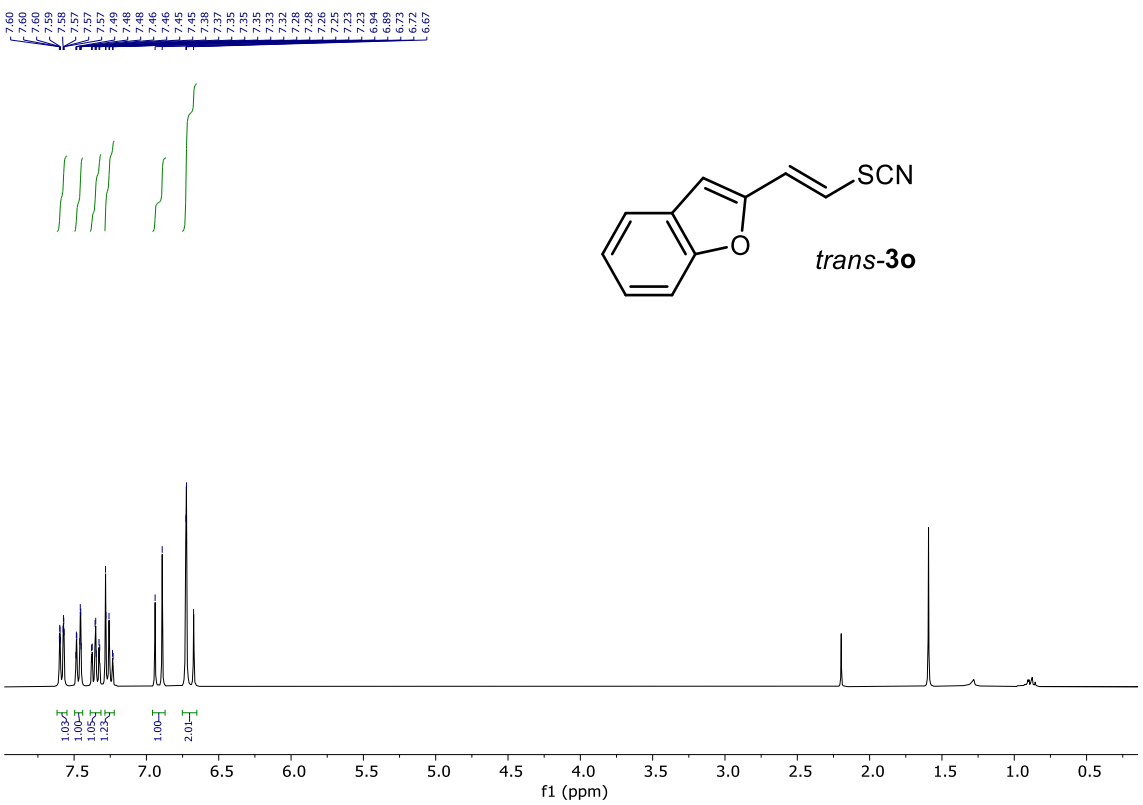



**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

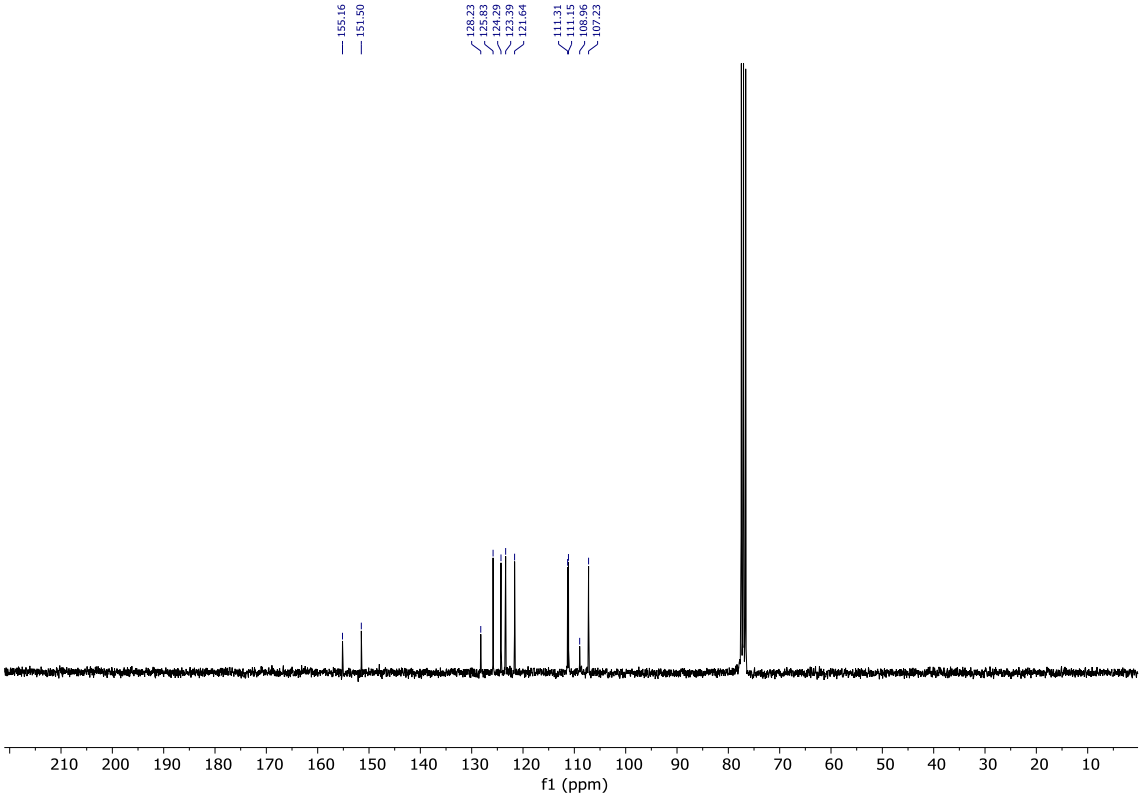


## (*E*)-2-(2-thiocyanatovinyl)benzofuran (*trans*-3o)

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

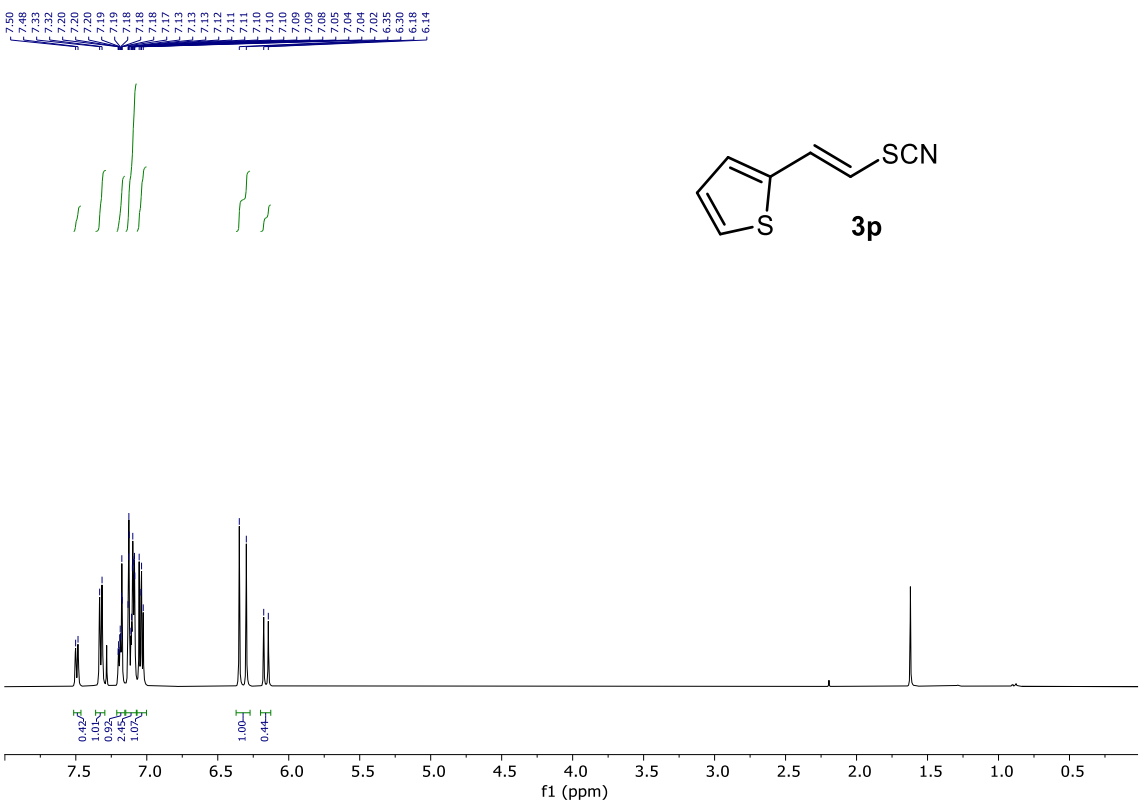



**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

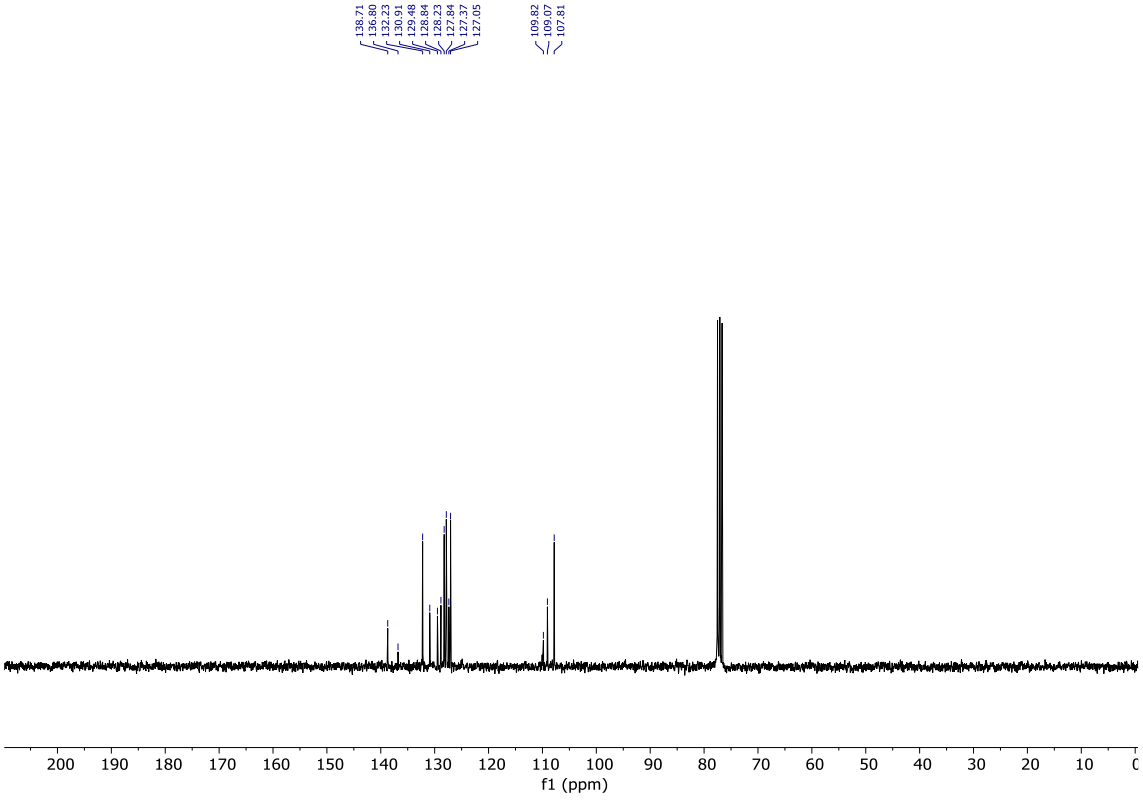


## (*E*)-2-(2-thiocyanatovinyl)thiophene (3p)

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

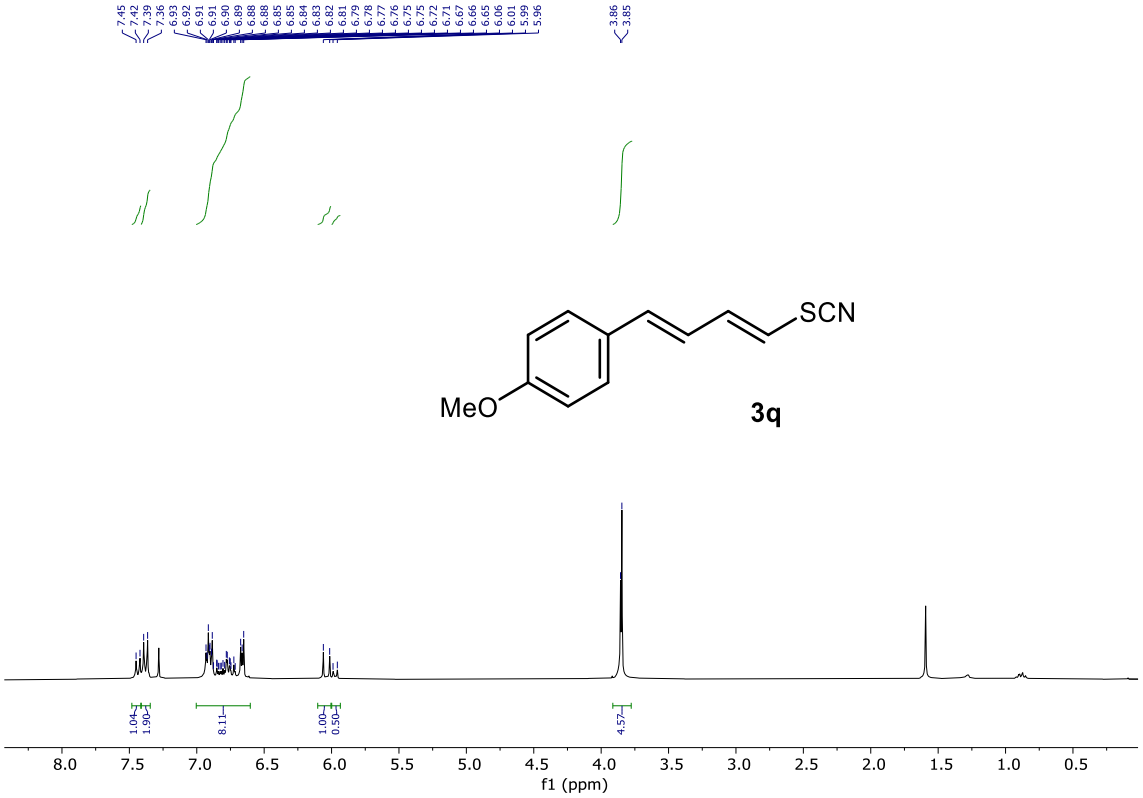



**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

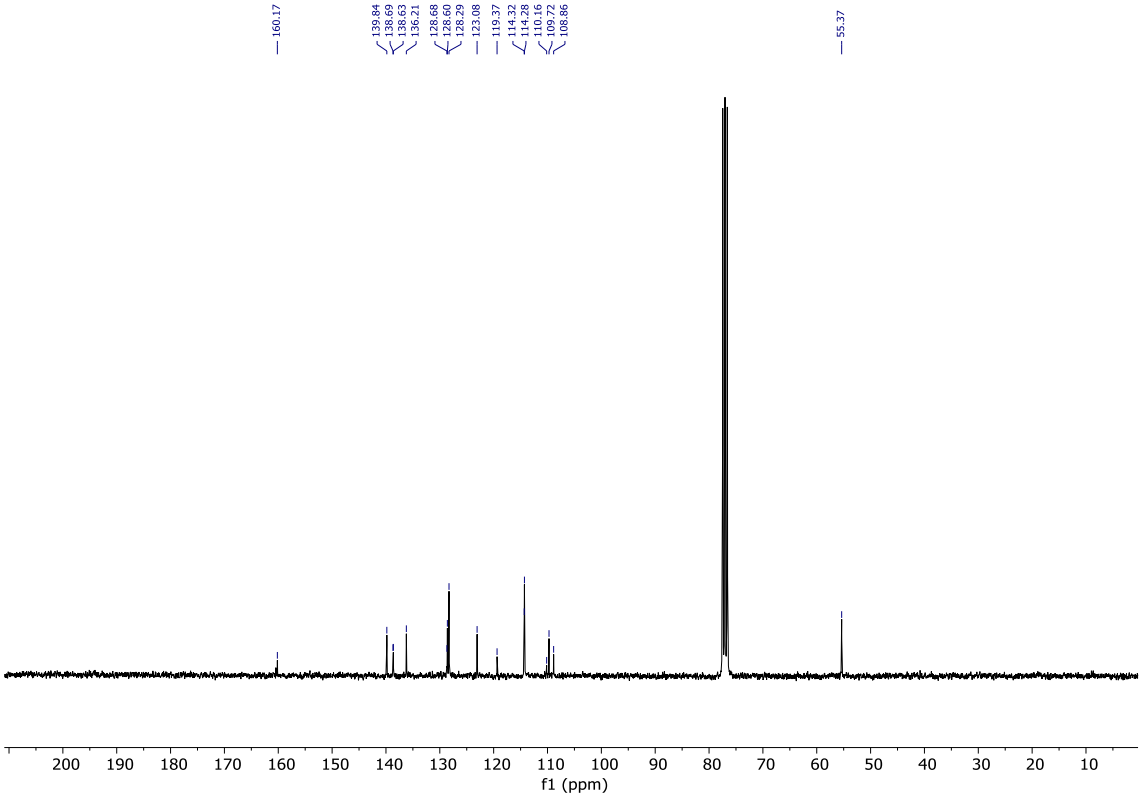


**1-methoxy-4-((1*E*,3*E*)-4-thiocyanatobuta-1,3-dien-1-yl)benzene (3q)**

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

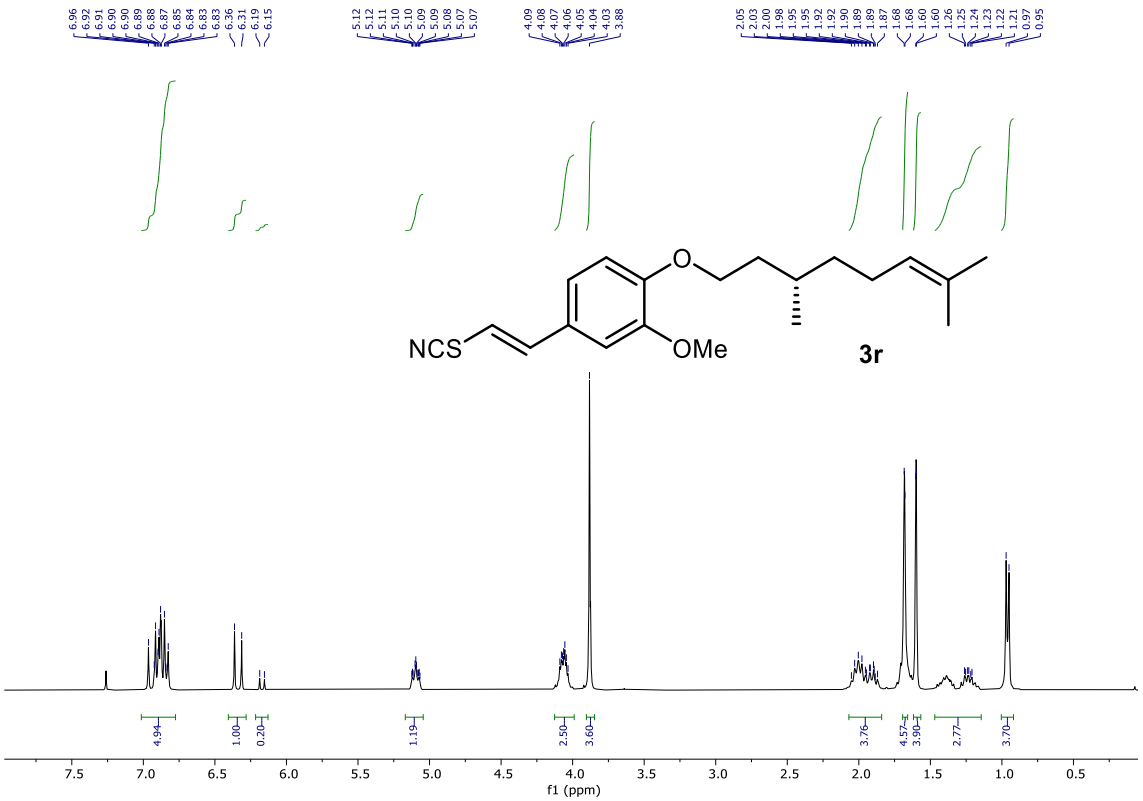



**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

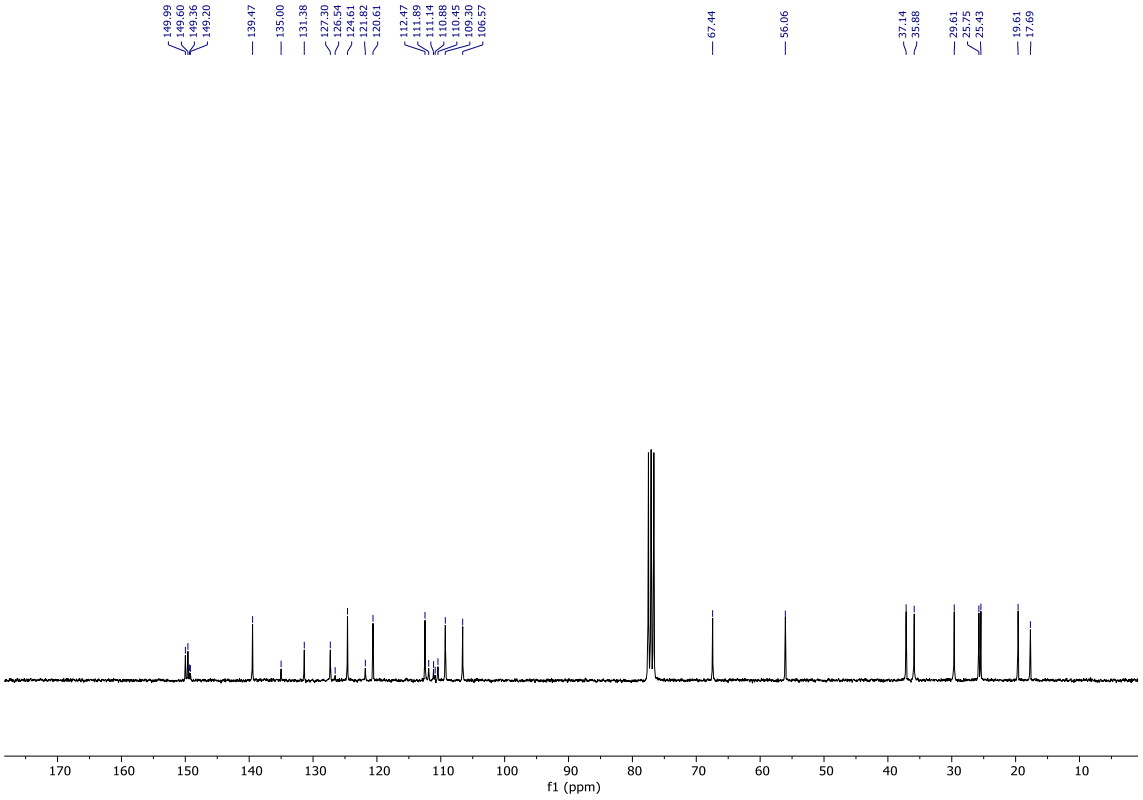


**(*S,E*)-1-((3,7-dimethyloct-6-en-1-yl)oxy)-2-methoxy-4-(2-thiocyanatovinyl)benzene (3r)**

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

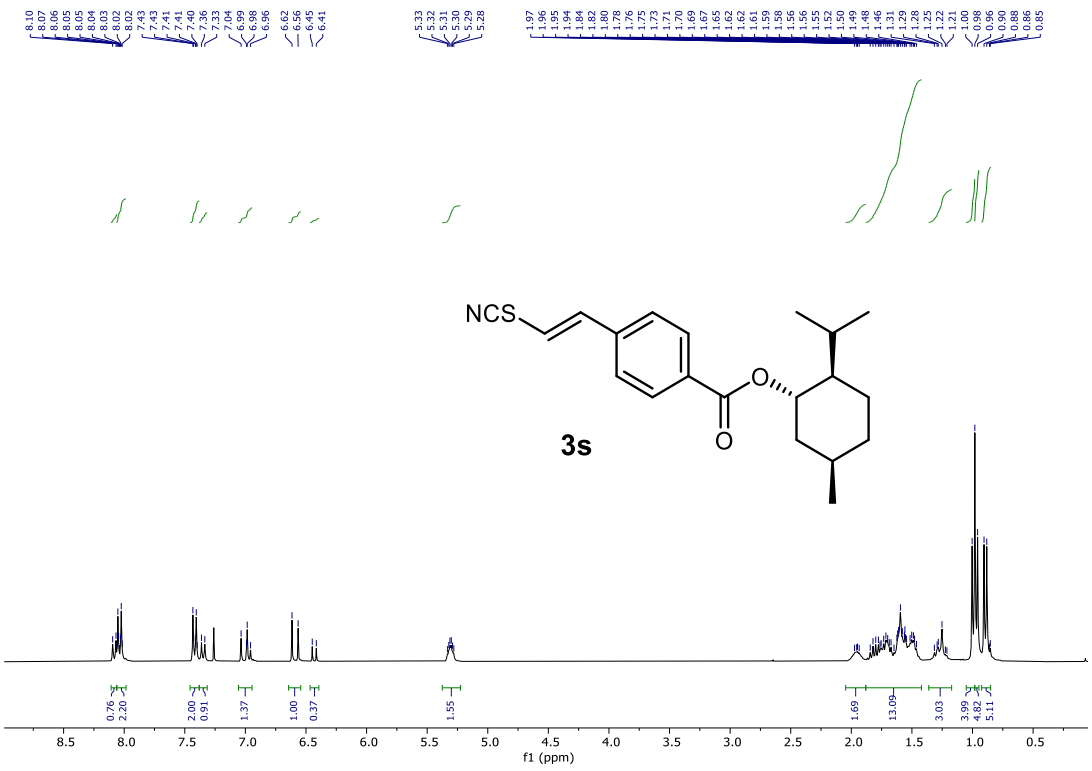



**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

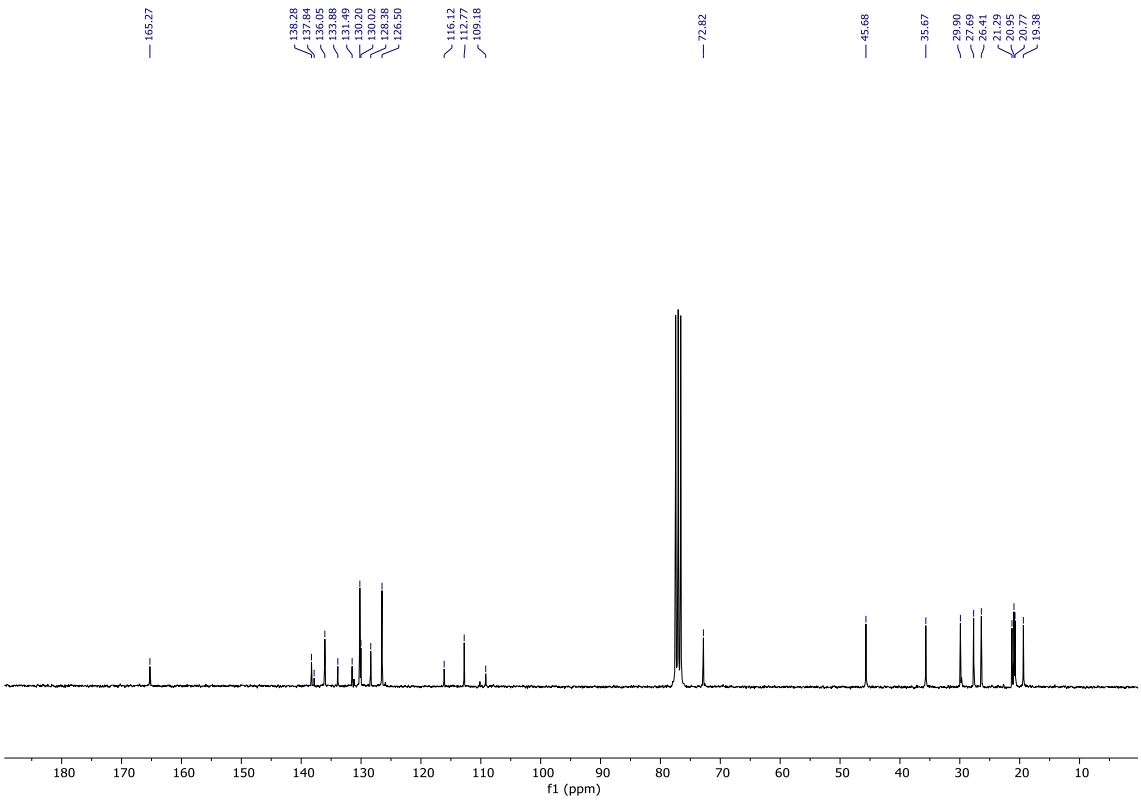


**(1*R*,2*S*,5*S*)-2-isopropyl-5-methylcyclohexyl 4-((*E*)-2-thiocyanatovinyl)benzoate (3s)**

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

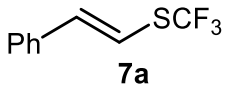



**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

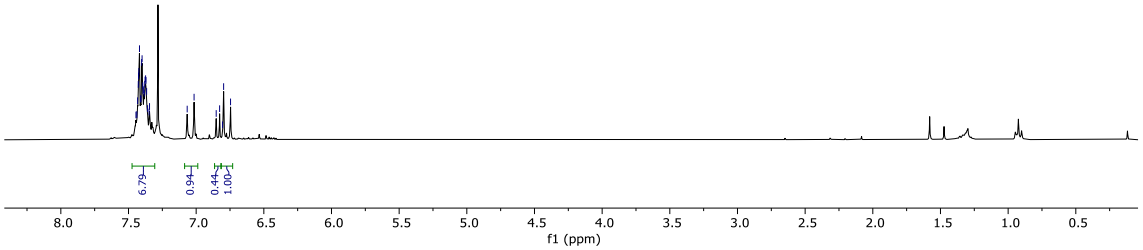


## (*E*)-(2-thiocyanatovinyl)benzene (7a)

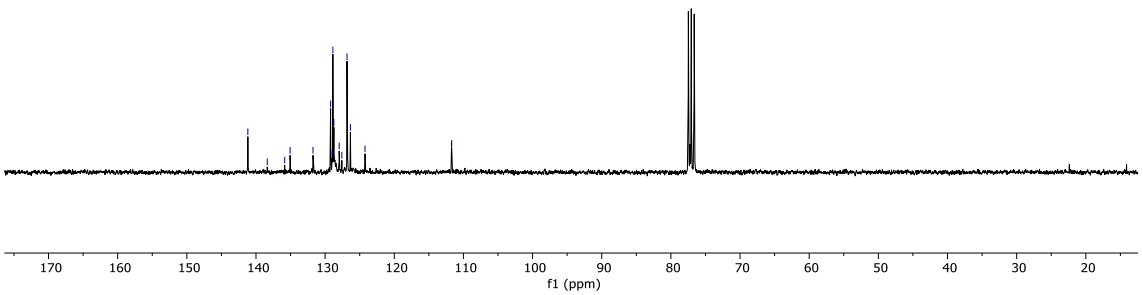
**$^{1}$H NMR** (300 MHz, $CDCl_3$, 300K)

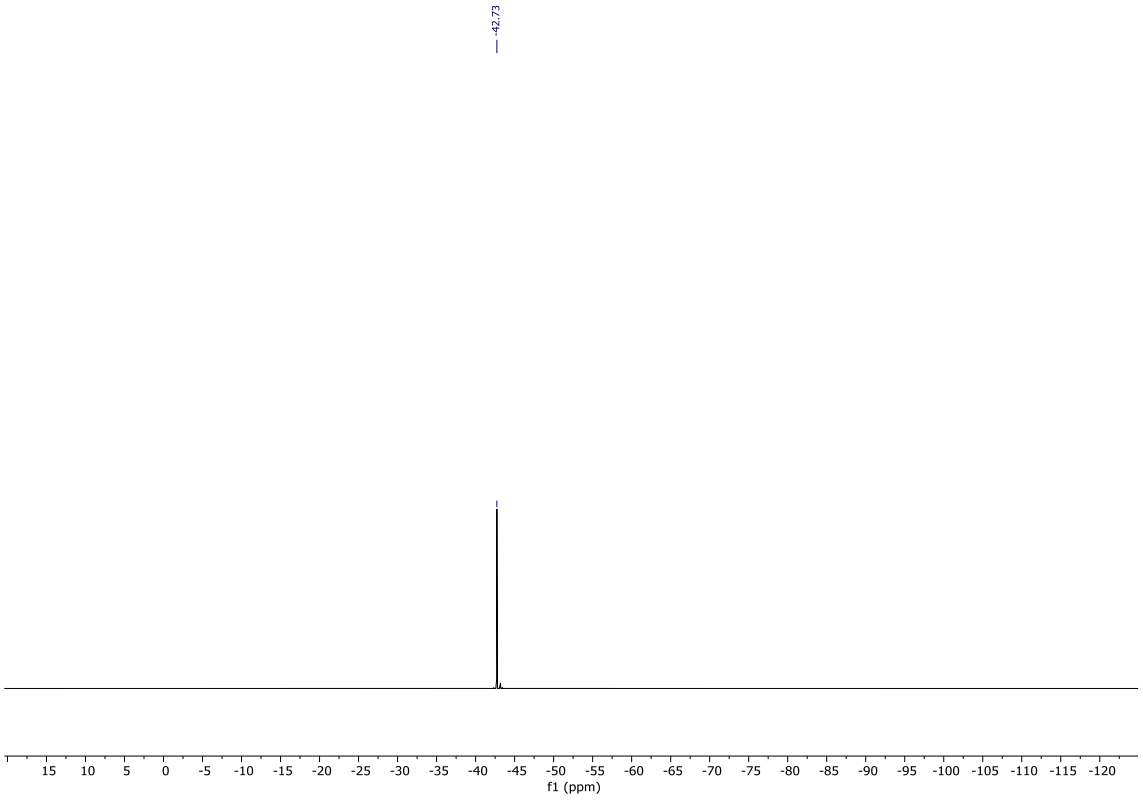

**7a**




**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

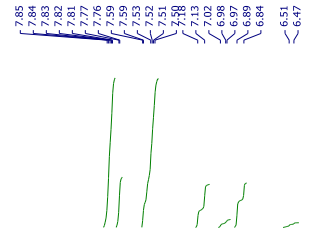



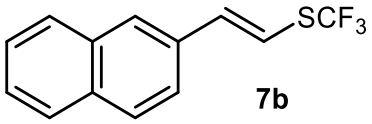
**$^{19}$F NMR** (235 MHz, $CDCl_3$, 300K)



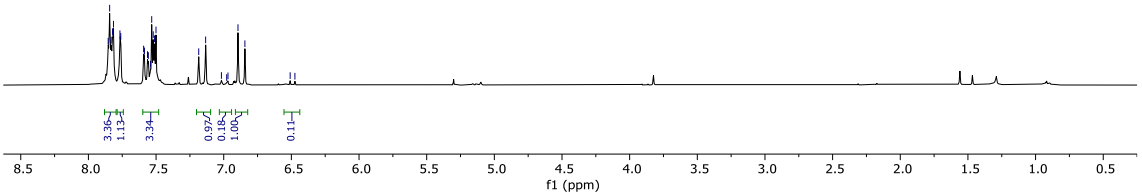
## (*E*)-(2-(naphthalen-2-yl)vinyl)(trifluoromethyl)sulfane (7b)

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

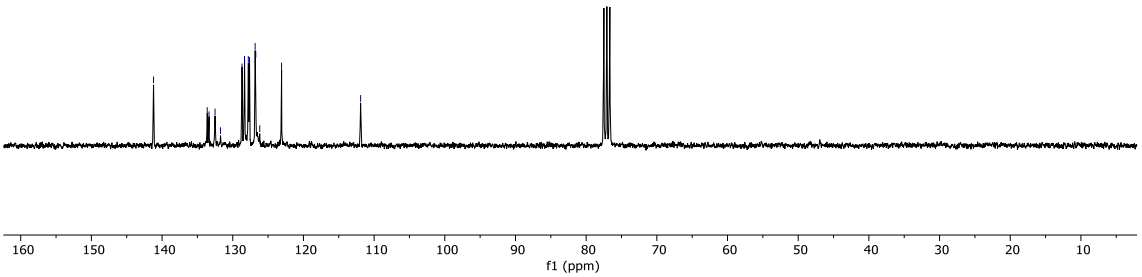


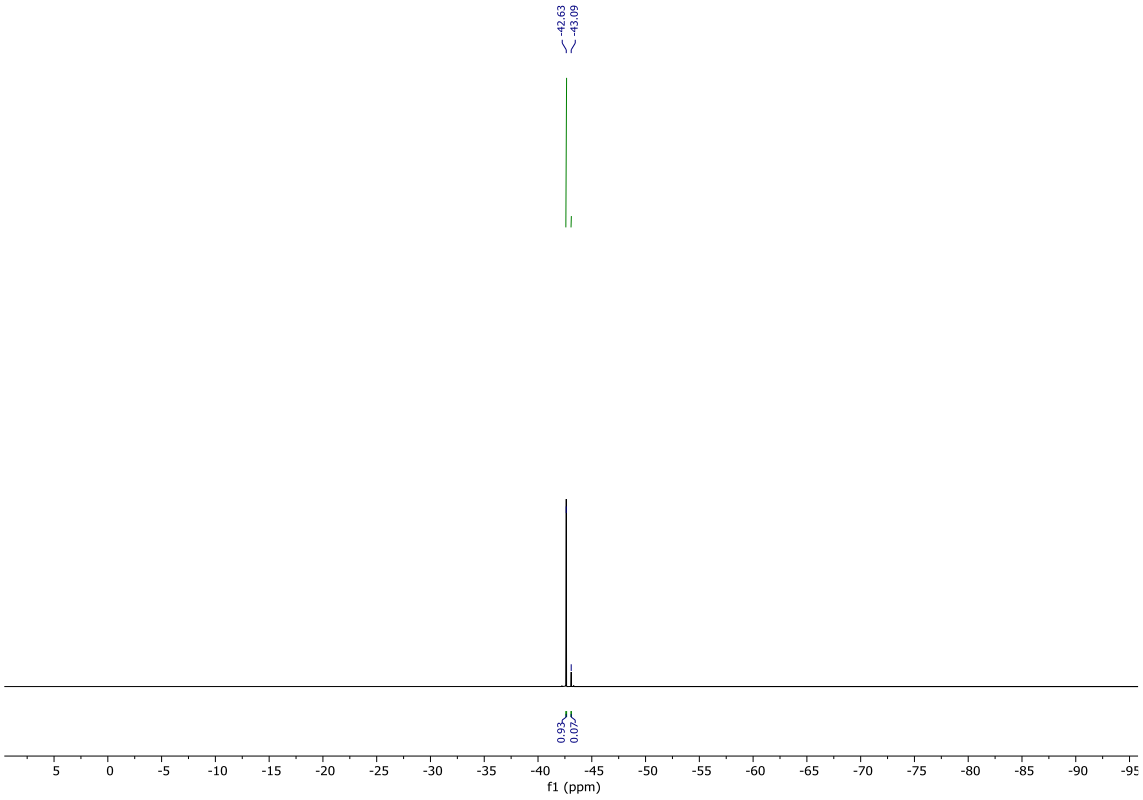

**7b**




**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

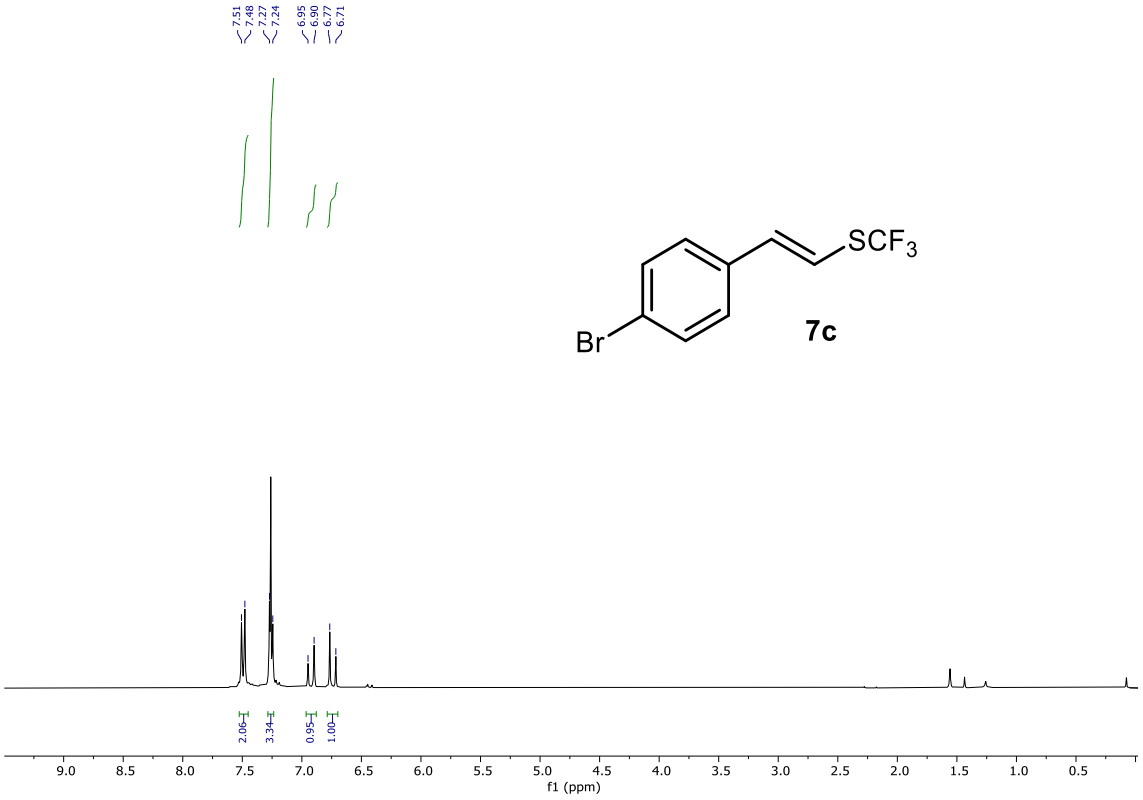



**$^{19}$F NMR** (235 MHz, $CDCl_3$, 300K)

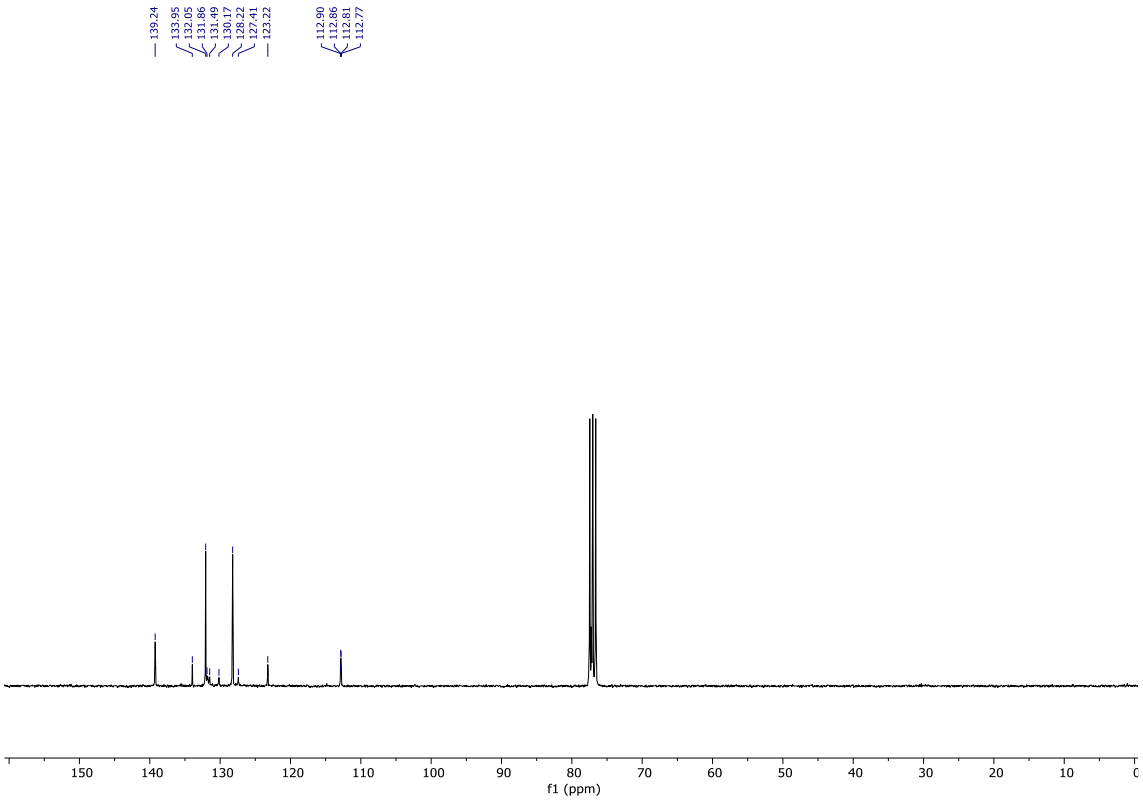


## (*E*)-(4-Bromophenyl)(trifluoromethyl)sulfane (7c)

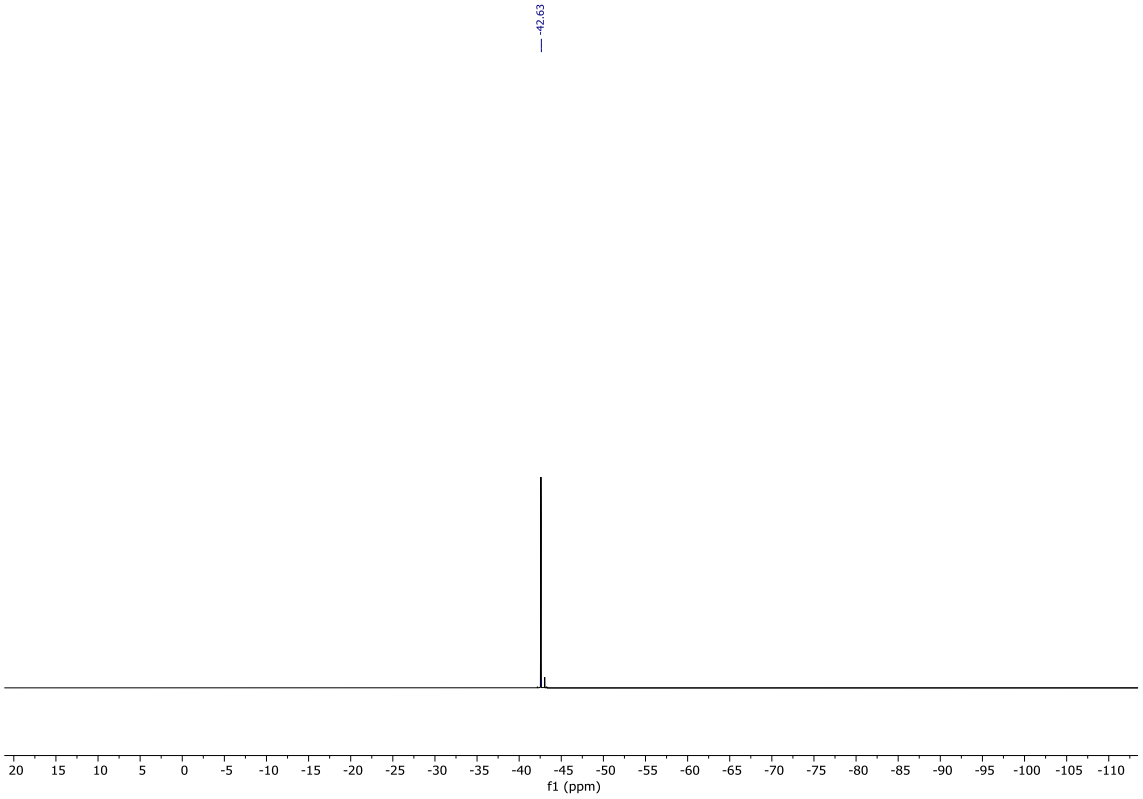
**$^{1}$H NMR** (300 MHz, $CDCl_3$, 300K)




**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

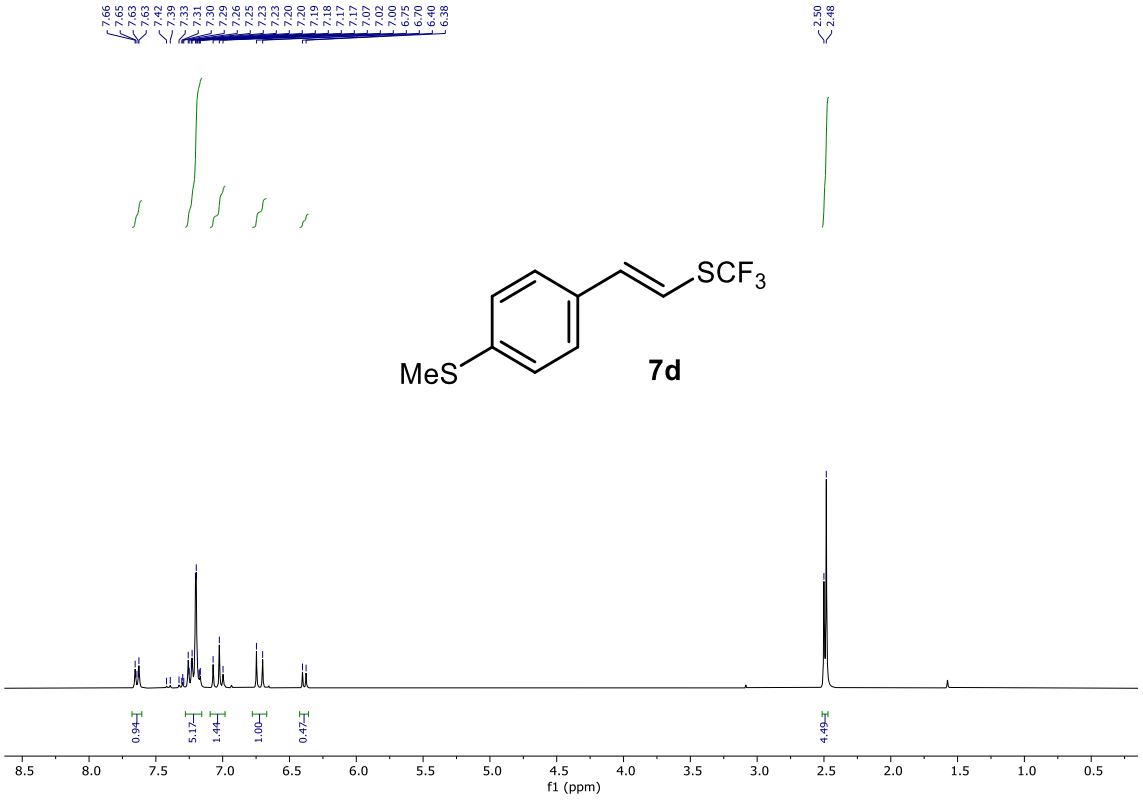


**$^{19}$F NMR** (235 MHz, $CDCl_3$, 300K)

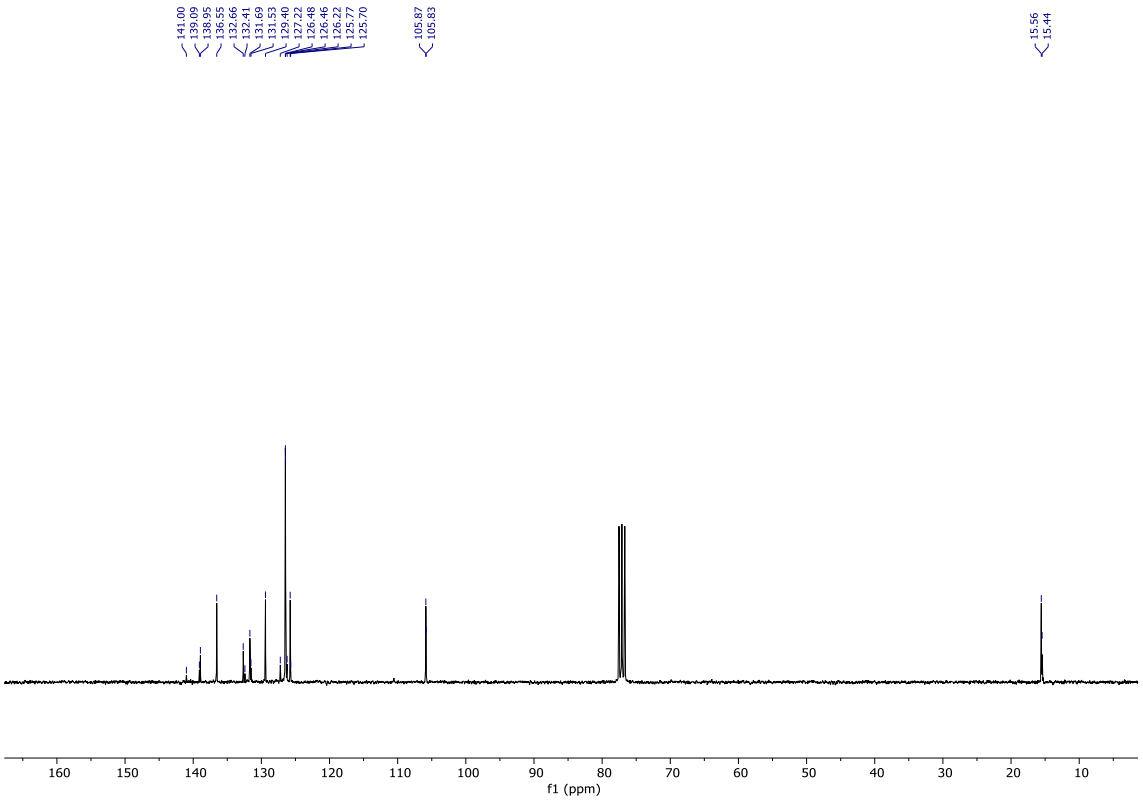


**(*E*)-(4-methoxystyryl)(trifluoromethyl)sulfane (7d)**

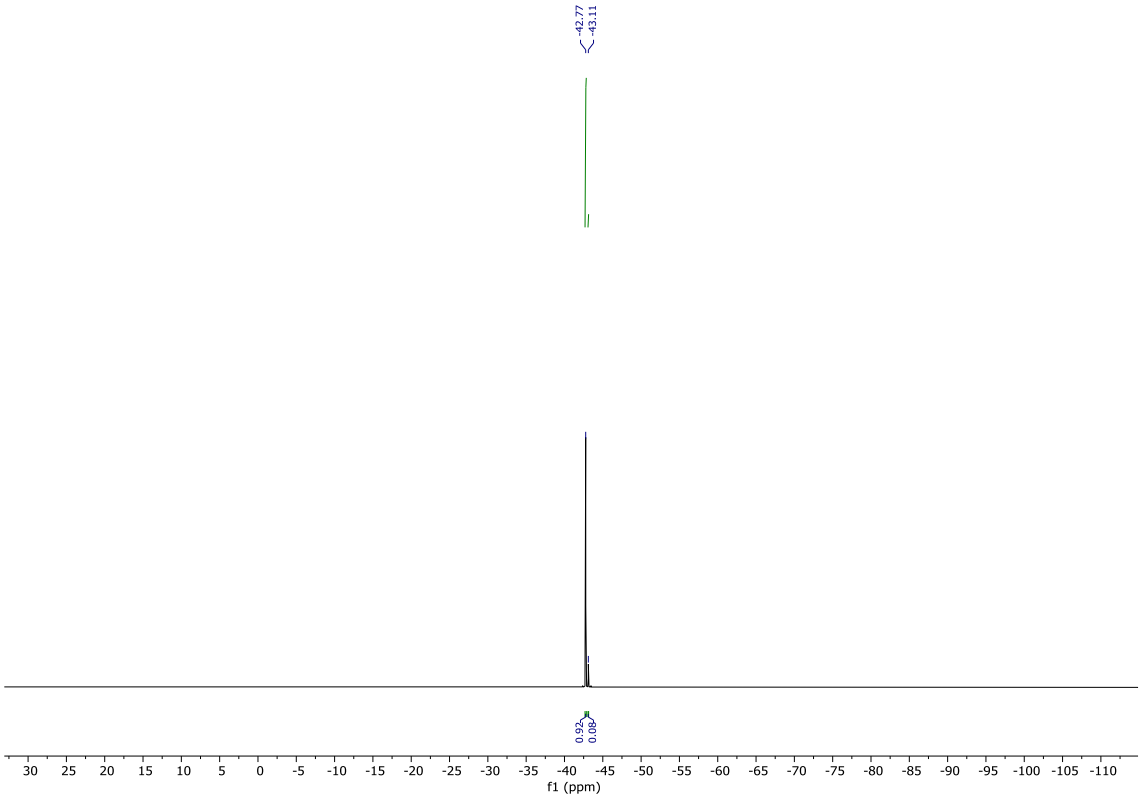
**$^{1}$H NMR** (300 MHz, $CDCl_3$, 300K)




**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

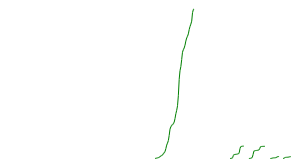


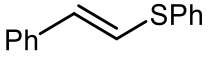
**$^{19}$F NMR** (235 MHz, $CDCl_3$, 300K)



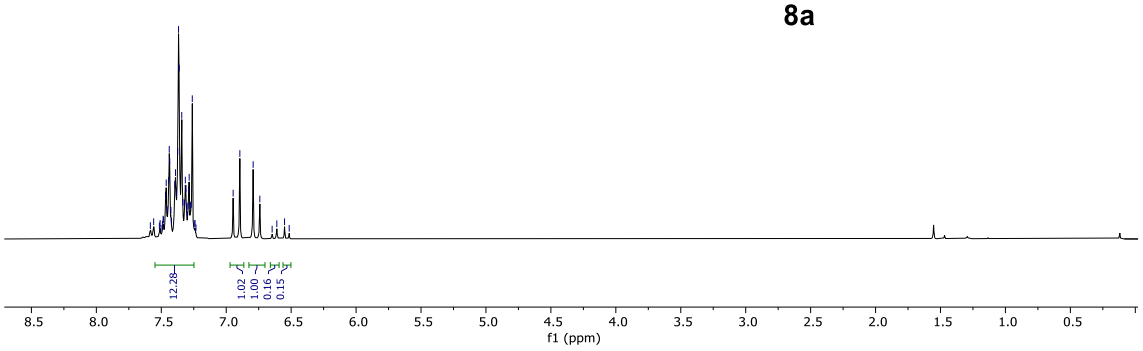
## (*E*)-phenyl(styryl)sulfane (8a)

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

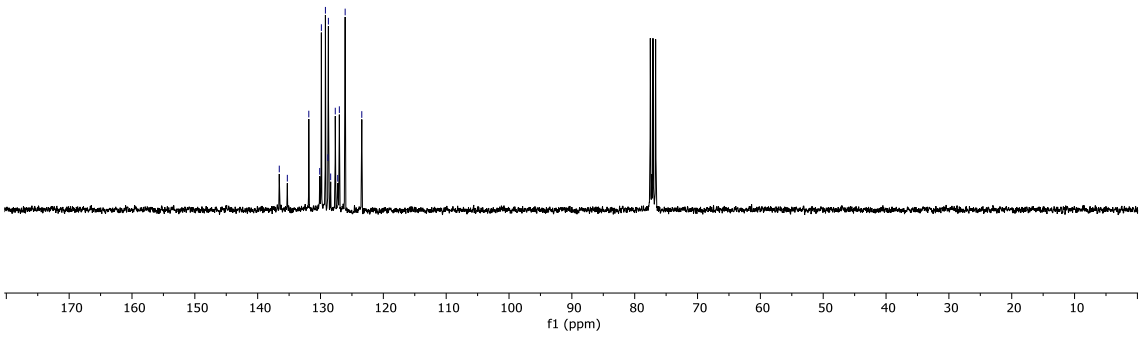






**8a**

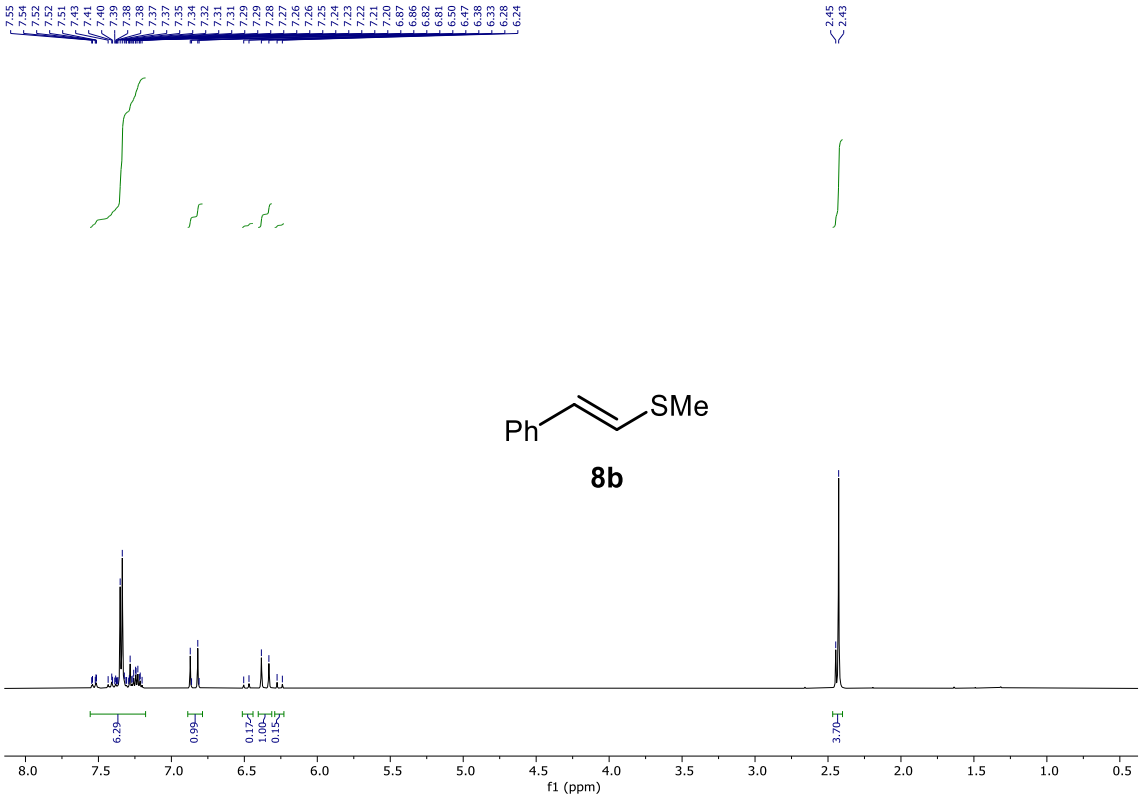



**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

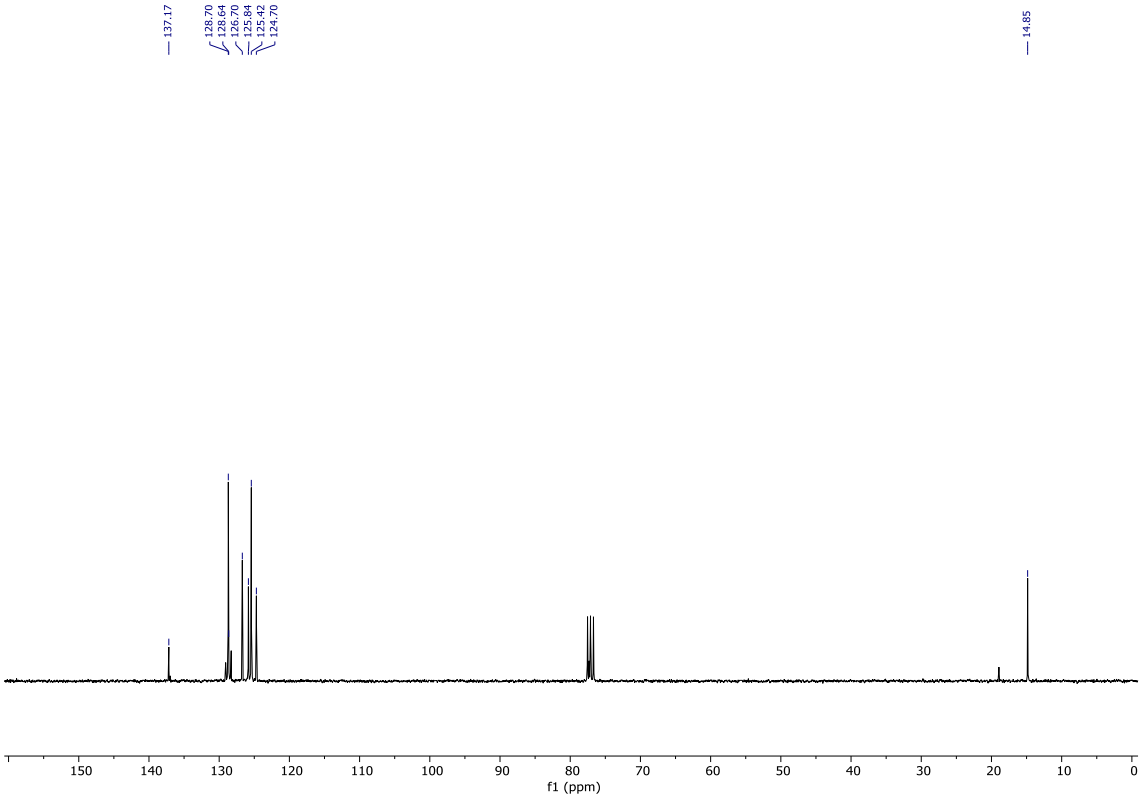



## (*E*)-methyl(styryl)sulfane (8b)

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

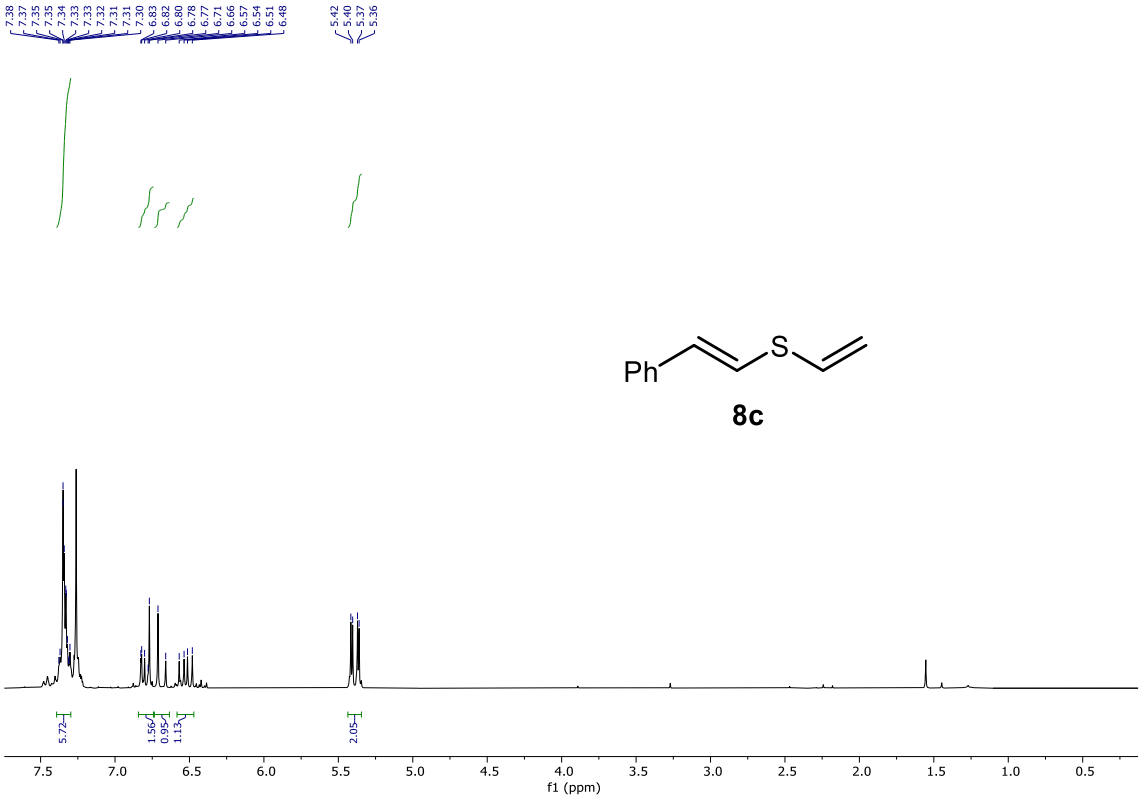



**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

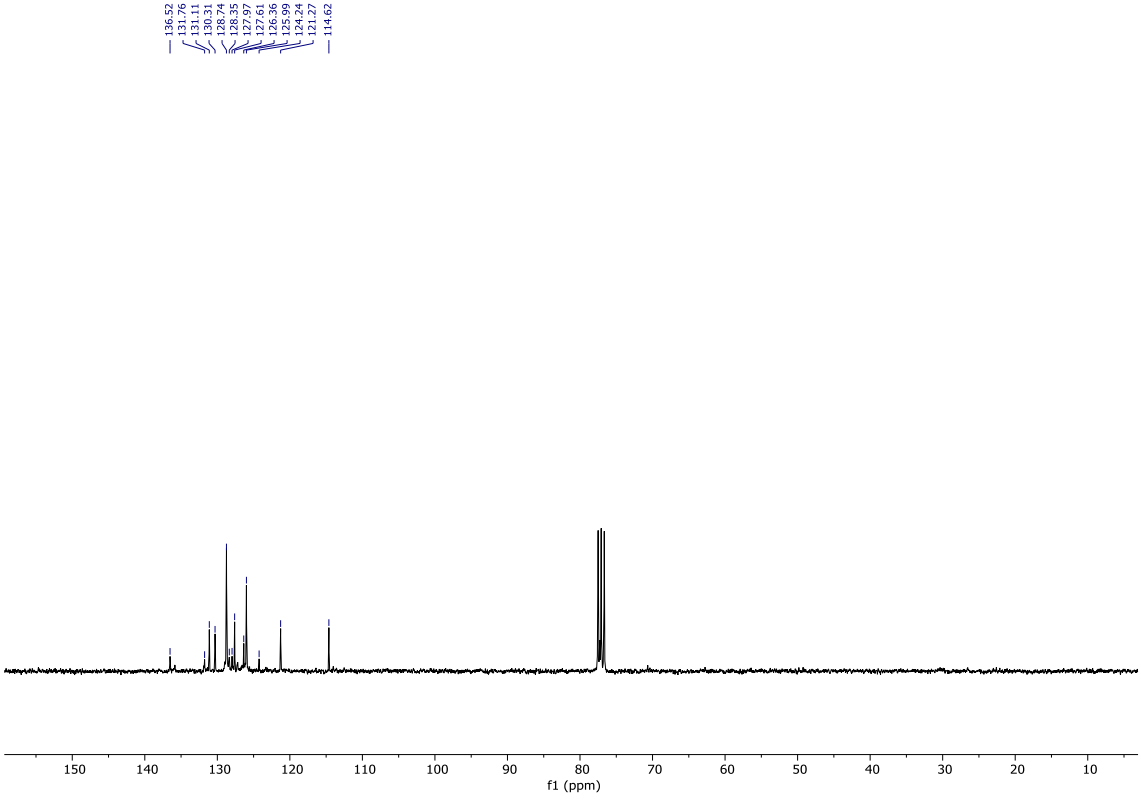


## (*E*)-styryl(vinyl)sulfane (8c)

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

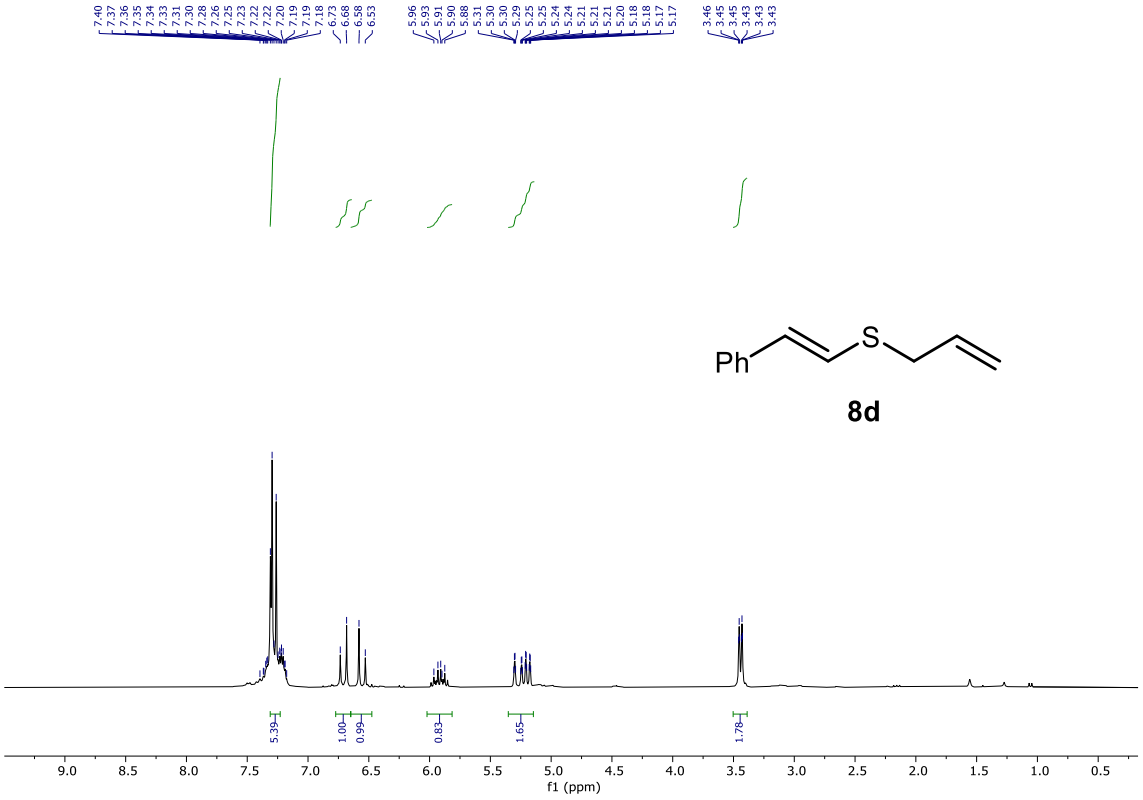



**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

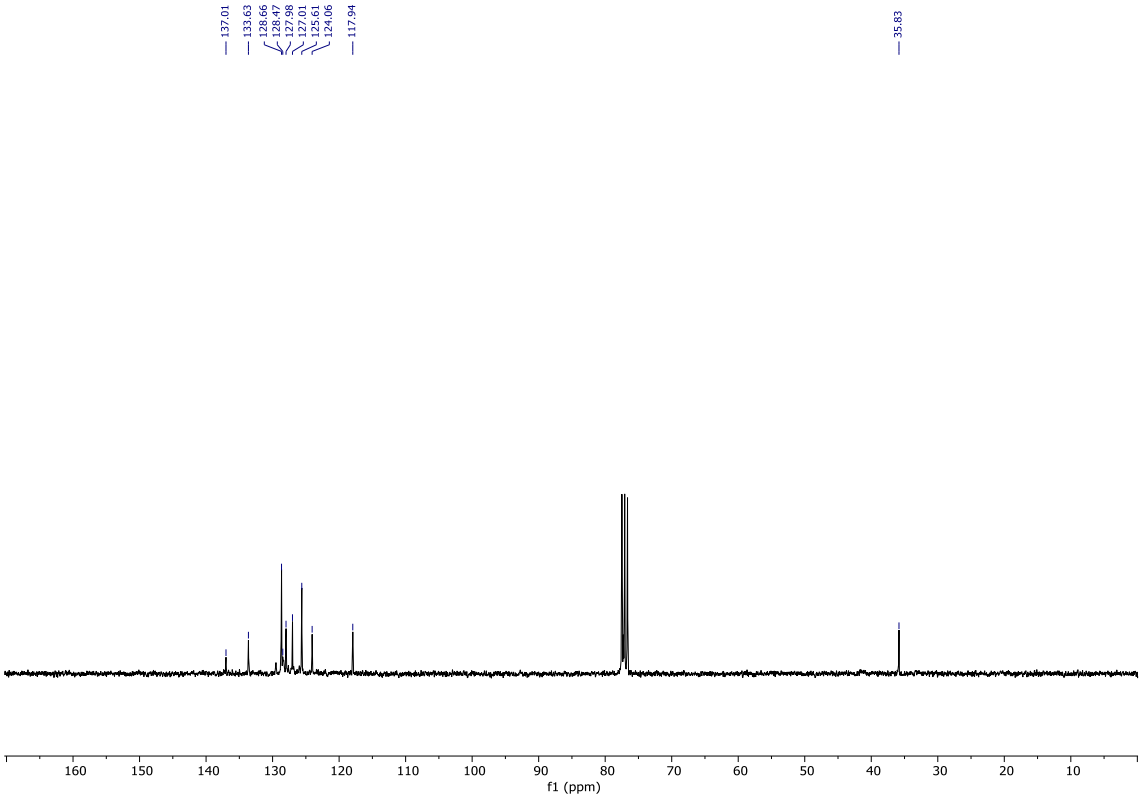


## (*E*)-styryl(vinyl)sulfane (8d)

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

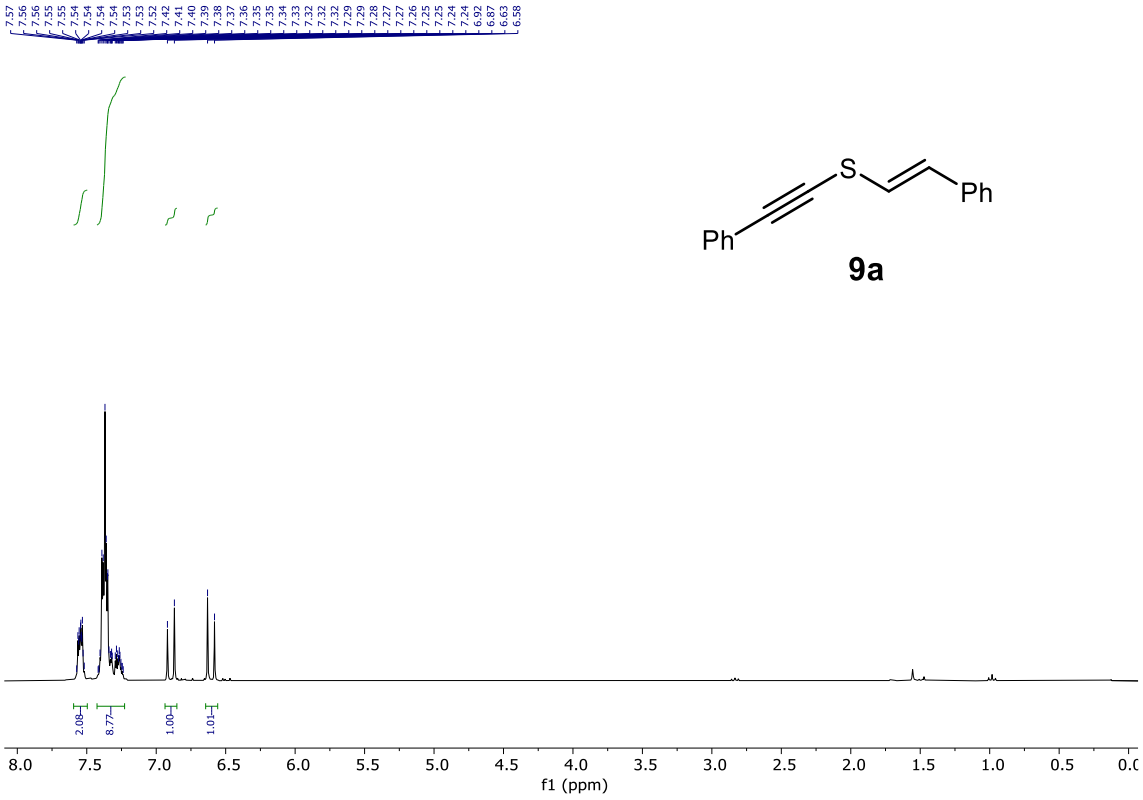



**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)



## (*E*)-(phenylethynyl)(styryl)sulfane (9a)

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

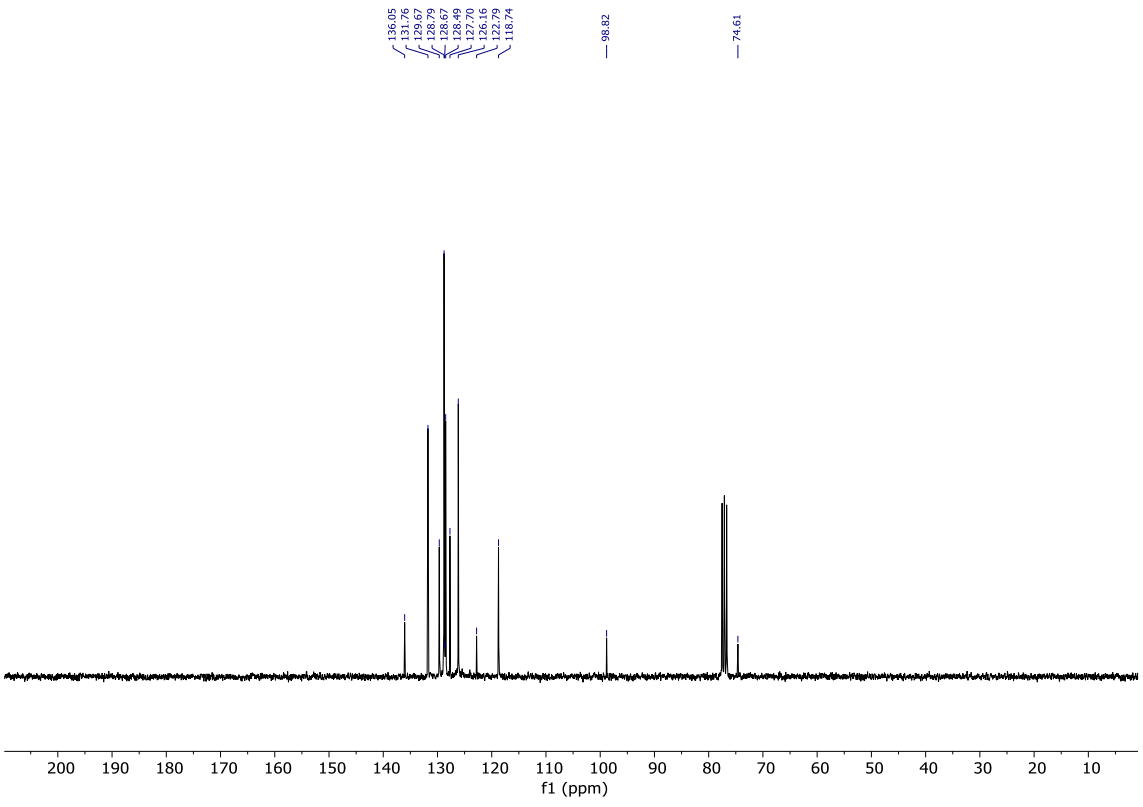






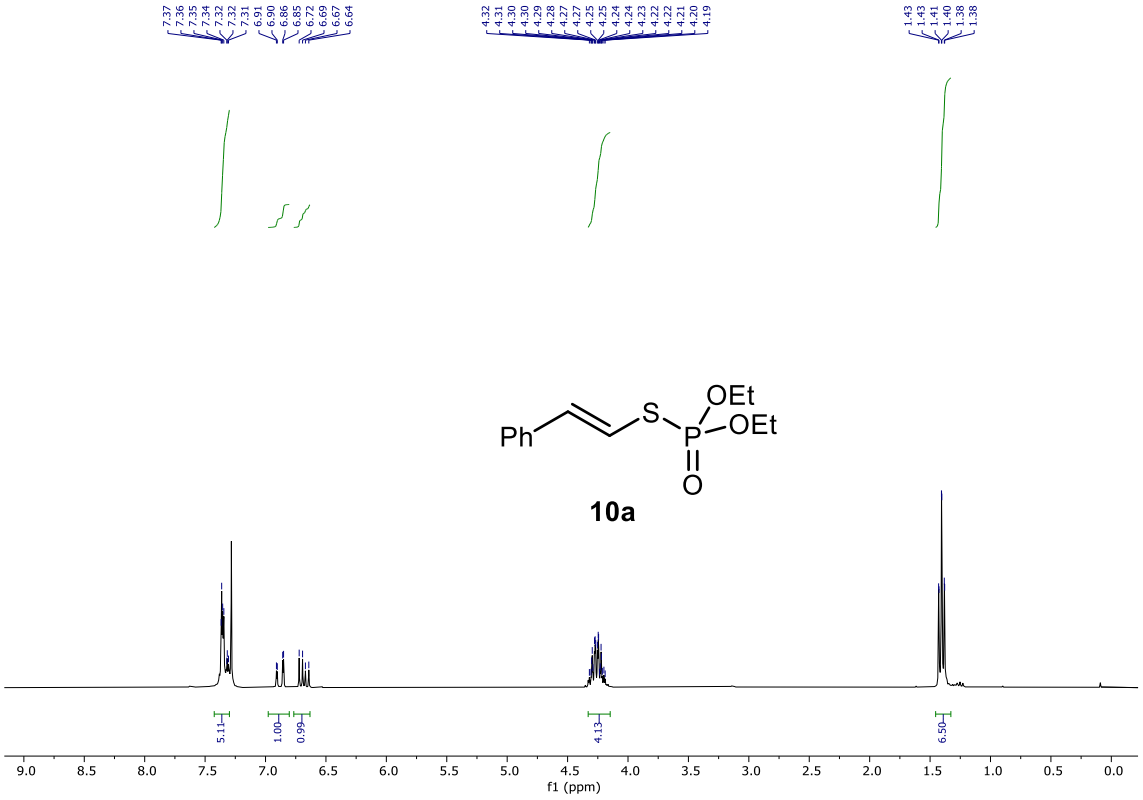
**9a**

**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

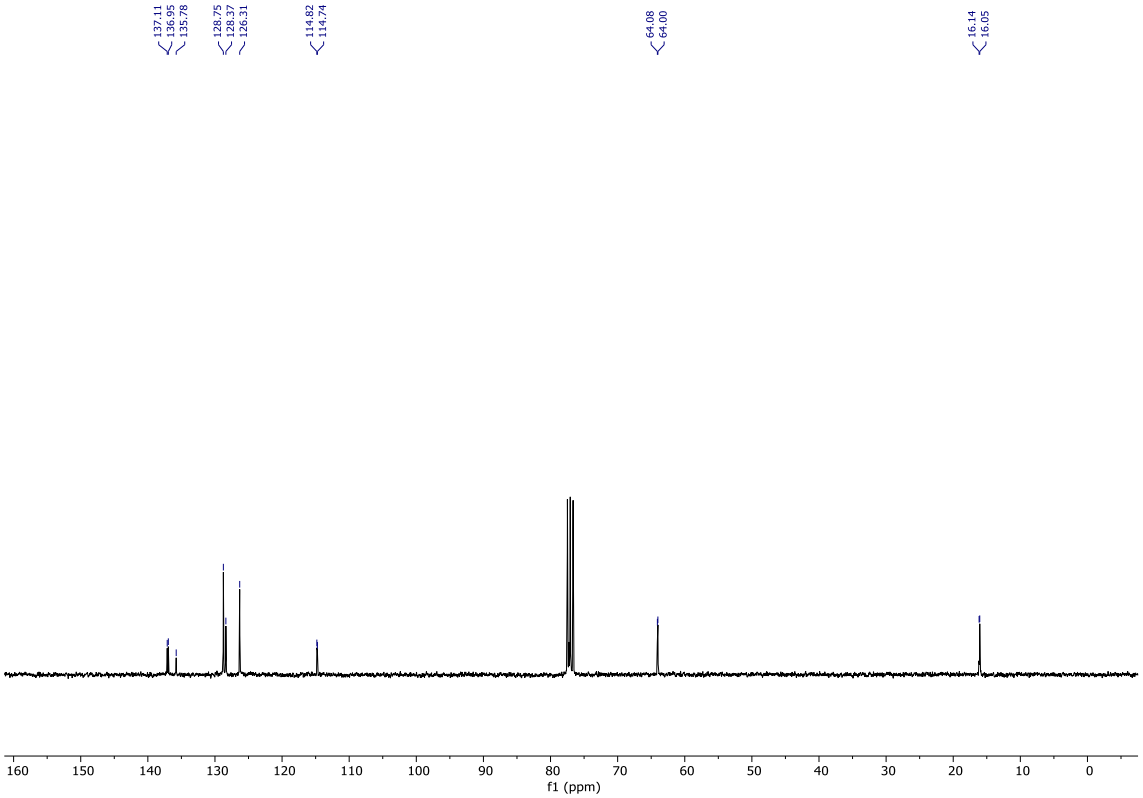


## (*E*)-*O,O*-diethyl *S*-styryl phosphorothioate (10a)

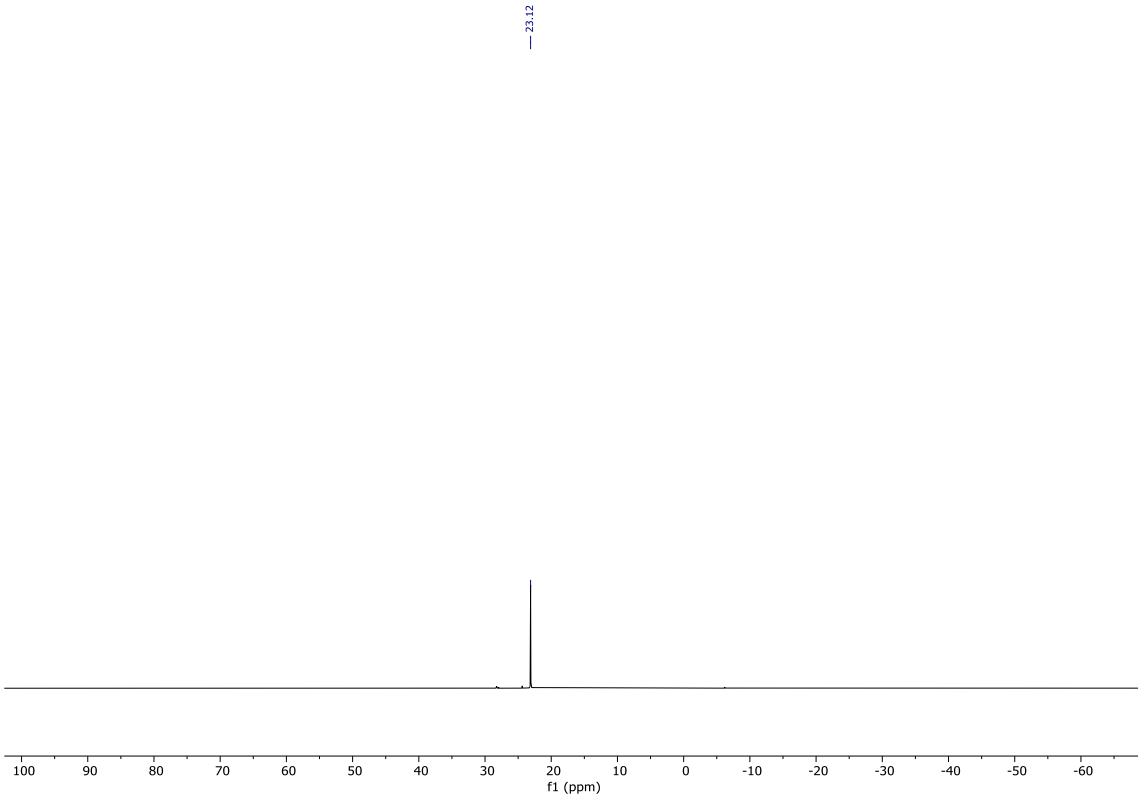
**$^{1}$H NMR** (300 MHz, $CDCl_3$, 300K)




**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

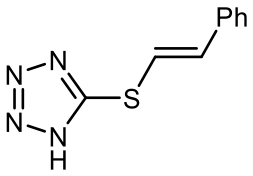


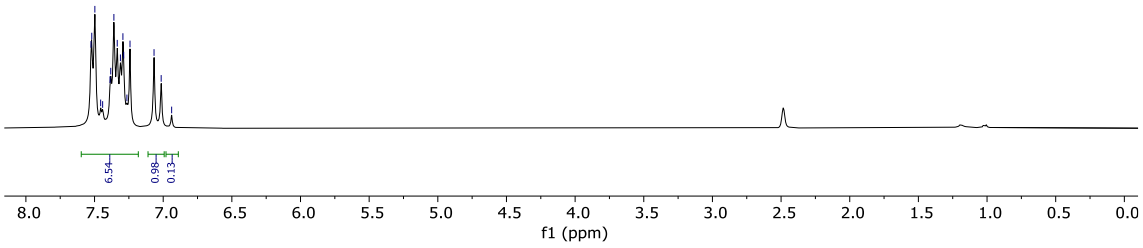
**$^{31}$P NMR** (121 MHz, $CDCl_3$, 300K)



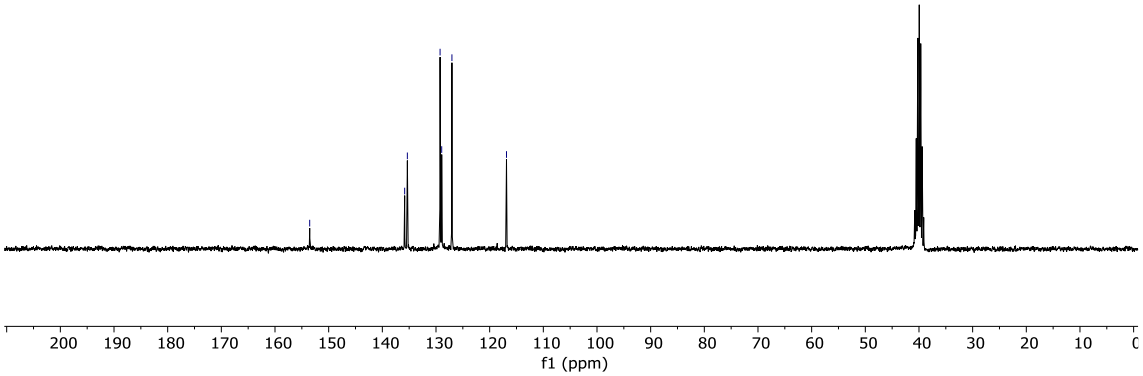
## (*E*)-5-(styrylthio)-1H-tetrazole (11a)

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

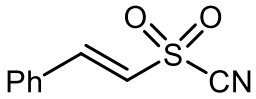




**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)

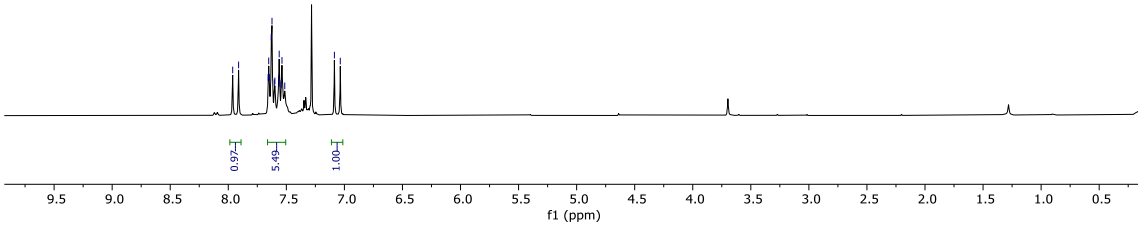



## (*E*)-2-phenylethene-1-sulfonyl cyanide (12a)

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


**12a**




**$^{13}$C NMR** (75 MHz, $CDCl_3$, 300K)