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Supporting Information

Photoredox Catalytic α-Alkoxypentafluorosulfanylation of α-methyl- and α-phenylstyrene using SF_6

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Materials and Methods

All chemicals were purchased from *Sigma Aldrich, Fluka, Alfa Aesar, ABCR* or *Tokyo Chemical Industry (TCI)*. The chemicals were used as received if not otherwise stated. Benchmark experiments were carried out using Acros Sureseal solvents. If the solvent was stored over molecular sieves the solvent prior to use was filtered by syringe filter to remove particles of residual molecular sieves.

NMR spectroscopic data was recorded using the following spectrometer hardware.

Bruker Ascend 500

^{1}H-NMR (500 MHz), ^{13}C-NMR-spectra (126 MHz), ^{19}F-NMR-Spektren (470 MHz).

Bruker Ascend 400

^{1}H-NMR (400 MHz), ^{13}C-NMR-spectra (100 MHz), ^{19}F-NMR-Spektren (376 MHz).

Chemical shifts of the ^{1}H-,^{13}C- and ^{19}F-NMR spectra are reported in parts per million (*ppm*) relative to the solvent as an internal standard and was converted to the TMS-reference system by applying frequency correction using the values of Fulmer *et al.* [S1]. Routine ^{13}C-NMR spectroscopy was recorded while applying broadband ^{1}H-decoupling. The chemical shifts of ^{19}F-NMR experiments are reported relative to CCl_3F as standard, which was added to the NMR sample. Coupling constants (J) are given in Hertz (*Hz*) and the multiplicity of signals are reported as followed: s (singlet), d (doublet), t (triplet), q (quadruplet), p (pentet), sext (sextet), m (multiplet), br. s (broad singlet), dt (doublet of triplets), td (triplet of doublets), dp (doublet of pentets), ddp (doublet of doublet of pentets).

The calculation of NMR-yields was carried out as follows. To the crude reaction mixture the standard was added in the following way. A mixture of 20 µL α,α,α-trifluorotoluene and 2000 µL acetonitrile was prepared. To the reaction mixture 200 µL of the stock solution was given and the mixture was vigorously shaken. Then a volume of ~

100 µL of the resulting solution was transferred to an NMR tube and 300 µL of $CDCl_3$ was added.

The concentration in general was determined as follows: The ratio of integrals of the axial fluorine signal in the SF_5 compound and the CF_3 moiety of the standard was determined. The number of moles included in one reaction mixture was calculated as follows, dependent on the scale of reaction given in mL(V_0) with 0.200 mmol/mL. The volume of α,α,α-trifluorotoluene in one shot (200 µL/mL(V_0)) contained {200 µL/mL(V_0)} /(2020 µL)}*20 µL α,α,α-trifluorotoluene. This is 1.98 µL/mL(V_0) of standard per batch. Calculation the mass using a density of 1.19 g/cm^3 (*Sigma Aldrich*) yields a number of moles of 0.0161 mmol/mL(V_0) experiment. The total number of moles in the tube was referenced against the internal standard integral. Routine NMR screenings to find best conditions were carried out applying a *zgflqn* pulse sequence, using D1 = 1s, O1P = 0 ppm, SW1 = 250 ppm. Integration of the signals was done separately to adjust the proper phase and get proper absolute integrals. Quantification of product concentrations was done using modified ^{19}F-NMR Parameters. To ensure sufficient relaxation of the nuclei the D1 time was modified to D1 = 5 s. We warmly thank Frau Pia Lang for their support with recording NMR spectra. Control experiments by preparative isolation of **9** as well as quantifying **8** by using an internal standard indicated a total accuracy of +/- 10% of the chosen quantification protocol for the model compounds **8**, **9** and **31**.

Irradiation of the photochemical reaction was carried out using a setup which was designed and manufactured by the University of Regensburg and the workshop of the Institute for Physical Chemistry at KIT Karlsruhe. We warmly thank Dieter Waltz and Klaus Stree for their kind support with manufacturing the irradiation hardware. High-power LEDs of the following types were used to irradiate the samples. 365 nm irradiation was applied using a *Nichia NVSU233A* LED. The temperature during the reaction time was controlled by using a *LAUDA Alpha R8* thermostat. (see Figure S1, right).

High resolution mass spectrometry was performed on a *Finnigan Modell MAT 95* using an electron impact ionization source. GC/MS coupling was recorded by using a

Varian 431 GC using a capillary column *FactorFourTM VF-5 ms* (30 m × 0.25 mm × 0.25 µm) and a *Varian* 210 ion trap mass detector or using a *Agilent Technologies 6890N* GC coupled to a *Agilent Technologies 5975B VL MSD* mass detector. Thin layer chromatography was performed using *Fluka silica gel 60 F254* coated aluminum foil. Flash chromatography was carried out on silica gel 60 supplied by *Sigma Aldrich* (43-60 µm). GC-FID quantification was performed using a *Bruker-430 GC* and a *FactorFourTM VF-5 ms (30 m × 0,25 mm × 0,25 µm)* stationary phase against trifluorotoluene as internal standard.

Small quantities of products were purified using a glass pipet or conventional column chromatography glassware. High purity grade solvents were used for purification of the characterized compounds. Sulfur hexafluoride was purchased from *Linde* in high purity grade (5.0). The gas was not further purified before use. Gas volumes were dosed using a four-necked glass cylinder of a volume of 68 mL (including tube) to control the amount of gas applied to the reaction mixture. The reaction was carried out using precisely manufactured glass tubes sealed with a Young-type screwing valve.

Single crystals of $C_{15}H_{15}F_5OS$ (**9**) were colorless needles and have been grown by crystallization from water/acetonitrile. A suitable crystal was selected, and the crystal was mounted on a MITIGEN holder in perfluoroalkylether oil on a Stoe IPDS II diffractometer. The crystal was kept at 200 K during data collection. Using Olex2[S2], the structure was solved with the ShelXT[S3] structure solution program using Intrinsic Phasing and refined with the ShelXL[S4] refinement package using Least Squares minimisation. We kindly thank M. Sc. Bernhard Birenheide and Prof. Dr. Frank Breher for solving the crystal structure of **9**.

Gas measure apparatus and calculation of pressure inside the reaction vessels

Sulfur hexafluoride is known not being able to be described by the ideal gas model due to non-negligible intermolecular interactions. Therefore, the *van-der-Waals* equation[S5] has to be used to calculate the pressure inside of the reaction vessel. The van-der-Waals coefficients were used as reported to be a = 0.7857 Pa m^6 mol^{-2} and b = 8.79 · 10^{-5} m^3 mol^{-1}.[S6]

$$p + \left(\frac{n^2 a}{V^2}\right) * (V - n * b) = n * R * T$$

The calculation of the pressure inside the reaction vessels using 1 volume of gas measure glassware is as follows. The relevant volumes were

V(gas dosage apparatur) = 68 mL
V(Youngvalve-Tube) = 26 mL

Spring loaded overpressure valve is equipped with spring for building up 1.1 bar or 0.1 bar overpressure. Therefore, the pressure of SF_6 in tube under standard conditions (0.200 mmol scale) is calculated by solving the van-der-Waals equation.

The resulting number of moles was calculated to be

$$n = 3.01\ mmol$$

For standard reaction a Young-valve tube was used fitting a volume of 26 mL. These tubes were sealed using a Teflon screw. Therefor the pressure inside the vessel was calculated to be

$$p(26mL) = \mathbf{2.8\ bar}$$

The upscaling reactions (1.00 mmol) were carried out using two volumes of the apparatus with 6.10 mmol resulting in a pressure of the vessel of 5.5 bar. The amount of gas used

for the reactions was measured using a glass cylinder having four ground glass joints connected to (i) a Schlenk line, (ii) the gas cylinder, (iii) an overpressure valve and (iv) to a tubing going to the reaction mixture containing Young-type tube (Figure S1, left). After degassing the reaction mixture by freeze-pump-thaw the whole reaction setup including the reaction tube was evacuated after freezing the reaction mixture at -196°C. Then valves **V5** and **V1** were closed. After refilling the apparatus with SF_6 until the overpressure valve indicated a pressure of 1.1 bar valve **V3** and **V2** have been closed. The remaining gas containing volume of the glass cylinder and the tubing (connecting **V4** and **V5**) was measured to be 68 mL. Now valve **V5** was open to sublime the measured gas volume into the reaction tube at -196°C. Finally, the reaction tube was sealed and was let come to room temperature.

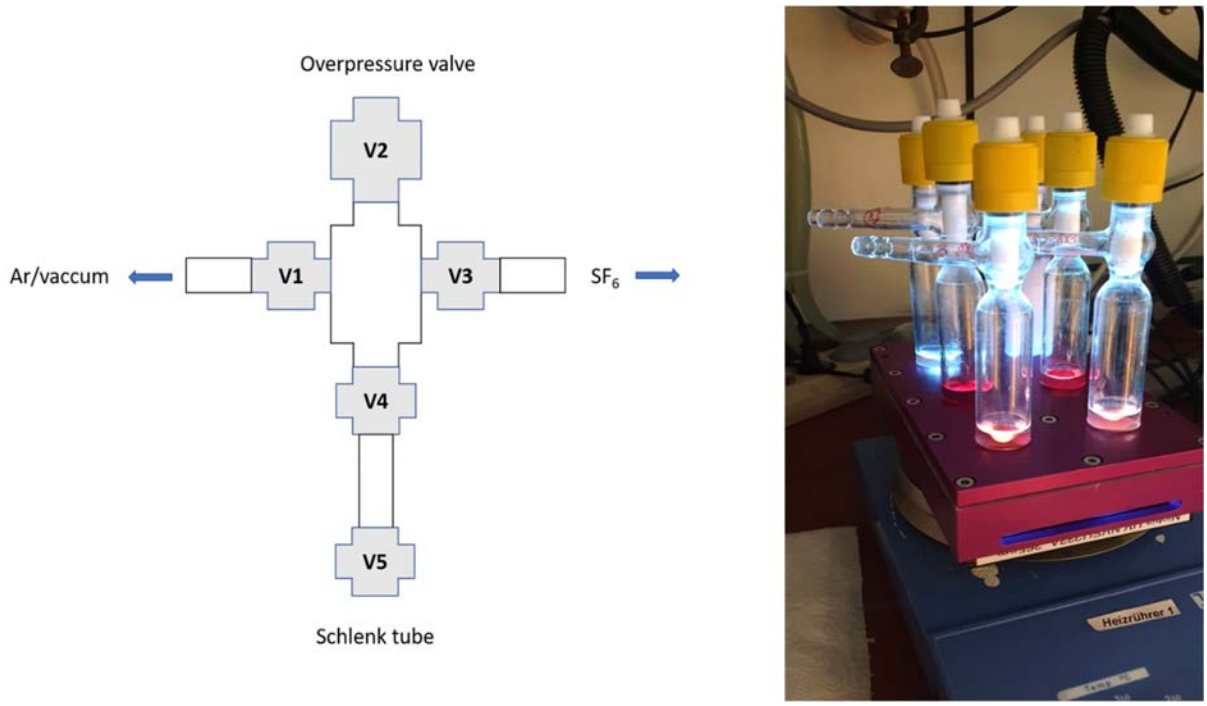


Fig. S1

Left: Scheme of the gas measure apparatus. Right: Setup for irradiation of the samples by high-power LEDs under stirring and temperature control.

High power LED-emission spectra

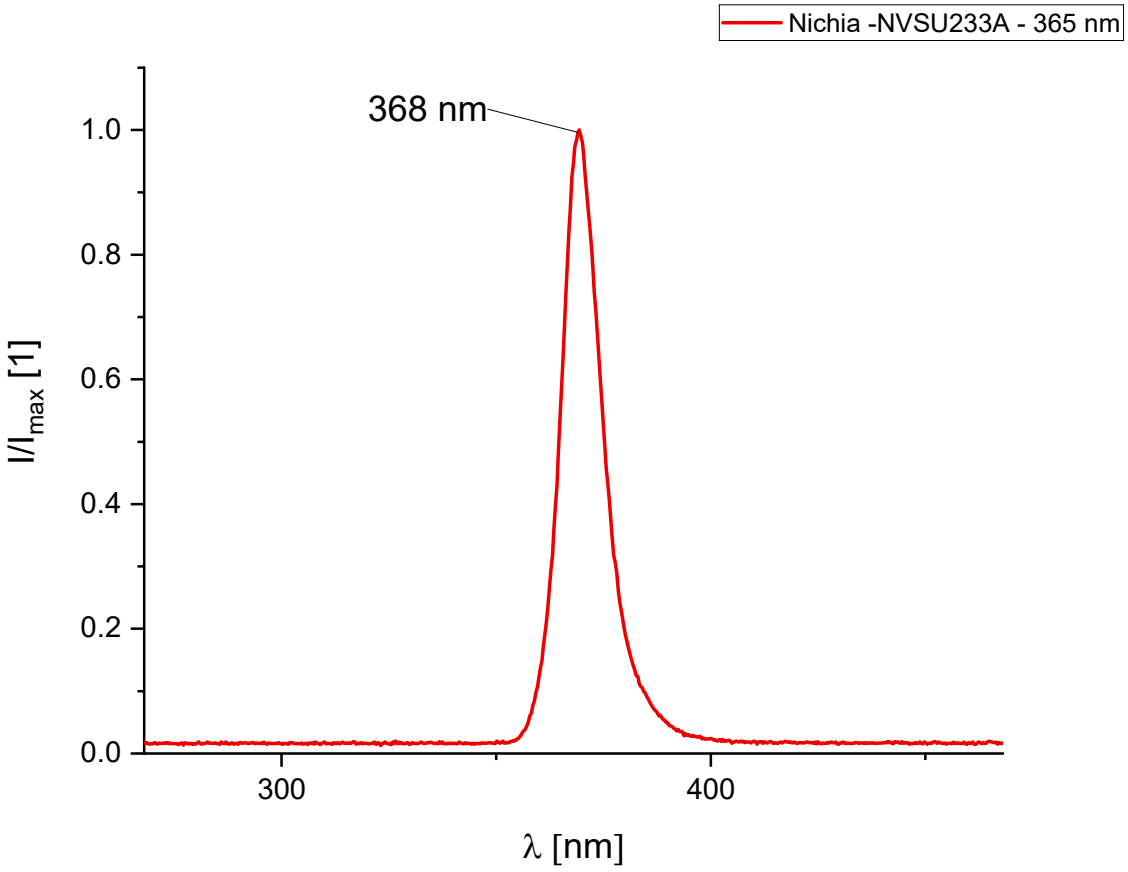


Fig. S2

LED emission spectra of Nichia NVSU233A ($\lambda_{max,supplier}$ = 365 nm).

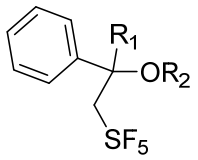
Experimental part

Preparation of the catalysts

Photoredox catalyst **3** was prepared by Buchwald-Hartwig coupling starting from phenothiazine and bromobenzene as described previously.[S7,S8] NMR data given below.

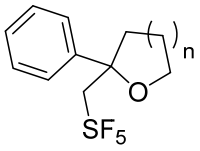
Preparation of α-alkoxypentafluorosulfanyl compounds **8** and **9** and **12** to **32**.

General procedure A: Preparation of open chain α-alkoxypentafluorosulfanyl compounds.



In a Young-type glass tube 0.20 mmol (1.00 eq.) of the alkene were added to 1 mL of acetonitrile (Sureseal grade stored over molecular sieves, filtered). Then 2.00 mmol (10.0 eq.) of the alcohol as well as 5.50 mg (0.02 mmol, 10 mol%) of the photoredox catalyst **3** were added. Finally, 20 µL (0.02 mmol, 10 mol%) of BEt_3 (1.0 M in hexanes) were added to the reaction mixture. The reaction mixture was degassed by three freeze-pump-thaw cycles and was refilled with sulfur hexafluoride (2.8 bar, 15 eq.). The reaction mixture was stirred at room temperature under irradiation at 368 nm by a high-power LED at 20 °C for 22 h. The yield was determined by ^{19}F-NMR spectrocopy using α,α,α-trifluorotoluene as an internal standard. The compounds were purified by means of column chromatography using silica as stationary phase and dichloromethane in hexanes as eluent.

General procedure B: Preparation of cyclic α-alkoxypentafluorosulfanyl compounds.

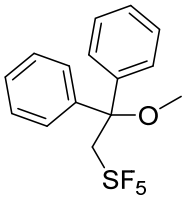


In a Young-type glass tube 0.33 mmol (1.00 eq.) of the alkenol were added to 1 mL of acetonitrile (Sureseal®, filtered). Then 5.50 mg (0.02 mmol, 6 mol%) of the photoredox catalyst **3** were added. Finally, 20 µL (0.02 mmol, 6 mol%) of BEt_3 (1.0 M in hexanes) were added to the reaction mixture. The reaction mixture was degassed by three freeze-pump-thaw cycles and was refilled with sulfur hexafluoride (2.8 bar, 15 eq.). The reaction mixture was stirred at room temperature under irradiation at 368 nm by a high-power LED at 20 °C for 22 h. The yield was determined by ^{19}F-NMR spectrocopy using α,α,α-trifluorotoluene as an internal standard. The compounds were purified by means of column chromatography using silica as stationary phase and dichloromethane in hexanes as eluent.

Individual experimental procedures

The assignment of NMR ^{1}H-, ^{13}C- and ^{19}F-NMR resonances was done by analysis of ^{1}H, ^{13}C, ^{19}F-1D NMR spectra as well as 2D-experiments as far as necessary. Therefore in general $HSQC_{ed}$, HMBC, COSY or advanced experiments have been run on the compounds.

Pentafluoro-(2-methoxy-2,2-diphenylethyl)-λ^6-sulfane (9)



$C_{15}H_{15}F_5OS$
338,0764

The compound was prepared according to a modified *general procedure A* using 20 mol% BEt_3. In a Young-type reaction tube 35.3 µL (0.200 mmol, 1.00 eq.) of diphenylethylene **2** as well as 81.1 µL (64.1 mg, 2.00 mmol, 10.0 eq.) of MeOH and 40 µL (0.040 mmol, 20 mol%) of BEt_3 in hexanes (1 M) were used. The compound was purified by column chromatography (silica, 5% DCM in cyclohexane). The yield of the product was determined by analyzing the crude reaction mixture by means of GC-FID (53%). The product was obtained as colorless solid.

Scale-up: The reaction was also run on a 1.00 mmol scale using the *general procedure A* using 5.5 bar of SF_6 (6.0 eq.). The yield was 45% determined by NMR spectroscopy (40% isolated yield).

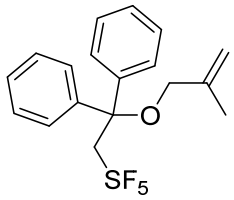
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 8H, Ar**H**), 7.26 – 7.22 (m, 2H, Ar**H**), 4.72 (p, *J* = 7.9 Hz, 2H, **CH_2**-SF_5), 3.18 (s, 3H, **CH_3**).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.90 ($\mathbf{C}_{q,Ar}$), 128.37 (**C**H_{Ar}), 127.52(**C**H_{Ar}), 126.60 (**C**H_{Ar}), 81.34 ($\mathbf{C}_{q,bridge}$), 74.80 (p, *J* = 10.7 Hz, **C**H_2SF_5), 51.36 (O**C**H_3).

^{19}F NMR (471 MHz, Chloroform-*d*) δ 84.36 (p, *J* = 148 Hz, 1F, $\mathbf{F_{ax}}$), 71.89 (dt, *J* = 149, 8.1 Hz, 4F, $\mathbf{F_{eq}}$).

HR-EI-MS m/z (calc.) = 338.0764 [$M^{\bullet+}$]; m/z (found) = 338.0765 [$M^{\bullet+}$] ($C_{15}H_{15}F_5OS$).

Pentafluoro-(2-((2-methylallyl)-oxy)-2,2-diphenylethyl)-λ^6-sulfane (10)



$C_{18}H_{19}F_5OS$
378,1077

The compound was prepared according to general procedure A. In a Young-type reaction tube 35.3 µL (0.200 mmol, 1.00 eq.) of diphenylethylene **2** as well as 168 µL (144 mg, 2.00 mmol, 10.0 eq.) of 2-methyl-2-propen-1-ol were used. The compound was purified by column chromatography (silica, 5% DCM in hexanes, TLC: R_f = 0.3). The yield of the product was determined by analyzing the crude reaction mixture by means of ^{19}F-NMR spectroscopy (26%). The product was obtained as colorless solid.

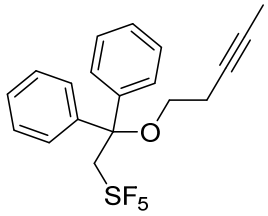
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 – 7.28 (m, 8H), 7.27 – 7.21 (m, 2H), 5.21 – 5.01 (m, 1H), 4.90 (p, *J* = 1.3 Hz, 1H), 4.73 (p, *J* = 7.8 Hz, 2H), 3.65 (s, 2H), 1.75 (t, *J* = 1.2 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.86 (**C**$_{q,Ar}$), 141.79 (**C**$_{q,vinyl}$), 128.37 (**C**H$_{Ar}$), 127.62 (**C**H$_{Ar}$), 126.76 (**C**H$_{Ar}$), 111.51 (**C**H$_{2,vinyl}$), 81.02 (**C**$_{q,Bridge}$), 75.91 (**C**H$_2$SF$_5$), 67.08 (**C**H$_2$O), , 19.99 (**C**H$_3$).

^{19}F NMR (471 MHz, Chloroform-*d*) δ 84.31 (p, *J* = 150 Hz, 1F, **F$_{ax}$**), 72.07 (dt, *J* = 149, 8.1 Hz, 4F, **F$_{eq}$**).

HR-EI-MS m/z (calc.) = 378.1077 [M$^{\bullet+}$]; m/z (found) = 378.1079 [M$^{\bullet+}$] ($C_{18}H_{19}F_5OS$).

Pentafluoro-(2-(pent-3-yn-1-yloxy)-2,2-diphenylethyl)-λ^6-sulfane (11)



$C_{19}H_{19}F_5OS$
390,1077

The compound was prepared according to general procedure A. In a Young-type reaction tube 35.3 µL (0.200 mmol, 1.00 eq.) of diphenylethylene **2** as well as 187 µL (168 mg, 2.00 mmol, 10.0 eq.) of 3-pentynol were used to prepare the compound. The compound was purified by preparative TLC (silica, 1% Et_2O in hexanes). The yield of the product was determined by analyzing the crude reaction mixture by means of ^{19}F-NMR spectroscopy (33%).

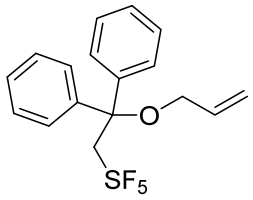
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.33 – 7.27 (m, 8H, C**H**$_{Ar}$), 7.23 (m, 2H, C**H**$_{Ar}$), 4.72 (p, *J* = 7.8 Hz, 2H, **CH$_2$**-SF_5), 3.31 (t, *J* = 7.4 Hz, 2H, **O-CH$_2$**), 2.48 (tq, *J* = 7.4, 2.6 Hz, 2H, **CH$_2$**-C≡C), 1.75 (t, *J* = 2.5 Hz, 3H, C≡C-**CH$_3$**).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.04 (**C**$_{q,Ar}$) , 128.36 (**CH**$_{Ar}$), 127.56 (**CH**$_{Ar}$), 126.57 (**CH**$_{Ar}$), 80.76 (**C**$_{q,Bridge}$) , 76.96 (**C**$_{C≡C}$), 75.64 (**C**$_{C≡C}$) , 75.21 (p, *J* = 11.4 Hz, **CH$_2$**-SF_5), 62.14 (O-**CH$_2$**) , 20.22 (-**CH$_2$**-C≡C), 3.57 (C≡C-**CH$_3$**) .

^{19}F NMR (471 MHz, Chloroform-*d*) δ 84.30 (p, *J* = 149 Hz, 1F, **F$_{ax}$**), 72.12 (dt, *J* = 149, 8.0 Hz, 4F, **F$_{eq}$**).

HR-EI-MS m/z (calc.) = 390.1077 [$M^{\bullet+}$]; m/z (found) = 390.1075 [$M^{\bullet+}$] ($C_{19}H_{19}F_5OS$).

(2-(Allyloxy)-2,2-diphenylethyl)-pentafluoro-λ^6-sulfane (12)



$C_{17}H_{17}F_5OS$
364,0920

The compound was prepared according to general procedure A. In a Young-type reaction tube 35.3 µL (0.200 mmol, 1.00 eq.) of diphenylethylene **2** as well as 137 µL (116 mg, 2.00 mmol, 10.0 eq.) of allyl alcohol were used. The compound was purified by column chromatography (silica, hexanes). The yield of the product was determined by analyzing the crude reaction mixture by means of ^{19}F-NMR spectroscopy (32%). The product was obtained as a colorless oil.

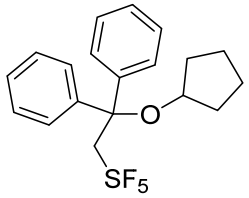
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 – 7.19 (m, 10H, C**H**$_{Ar}$), 5.92 (ddd, *J* = 17.3, 10.2, 5.0 Hz, 1H, C=**CH$_2$**), 5.39 (dq, *J* = 17.3, 1.9 Hz, 1H, C=**CH$_2$**), 5.18 (dq, *J* = 10.5, 1.7 Hz, 1H, **CH**=CH$_2$), 4.73 (p, *J* = 7.9 Hz, 2H, **CH$_2$**-SF$_5$), 3.76 (dt, *J* = 5.0, 1.7 Hz, 2H, O-**CH$_2$**).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.81 (**C**$_{q,Ar}$), 134.22 (**CH**=CH$_2$), 128.38 (**CH**$_{Ar}$), 127.63 (**CH**$_{Ar}$), 126.69 (**CH**$_{Ar}$), 116.27 (CH=**CH$_2$**), 81.06 (**C**$_{q,bridge}$), 75.69 (p, *J* = 11.2 Hz, **CH$_2$**-SF$_5$), 64.50 (O-**CH$_2$**).

^{19}F NMR (471 MHz, Chloroform-*d*) δ 84.26 (p, *J* = 149 Hz, 1F, **F$_{ax}$**), 72.06 (dt, *J* = 149, 8.1 Hz, 4F, **F$_{eq}$**).

HR-EI-MS m/z (calc.) = 364.0920 [M$^{\bullet+}$]; m/z (found) = 364.0919 [M$^{\bullet+}$] ($C_{17}H_{17}F_5OS$).

(2-(Cyclopentyloxy)-2,2-diphenylethyl)-pentafluoro-λ^6-sulfane (13)



$C_{19}H_{21}F_5OS$
392,1233

The compound was prepared according to general procedure A. In a Young-type reaction tube 35.3 µL (0.200 mmol, 1.00 eq.) of diphenylethylene **2** as well as 181 µL (172 mg, 2.00 mmol, 10.0 eq.) of cyclopentanol were used. The compound was purified by column chromatography (silica, 5% DCM in hexanes). The yield of the product was determined by analyzing the crude reaction mixture by means of ^{19}F-NMR spectroscopy (31%). The product was obtained as colorless oil.

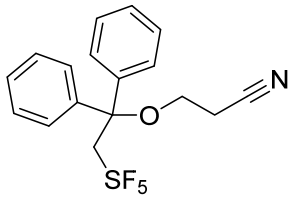
^{1}H NMR (500 MHz, CDCl3) δ = 7.28 – 7.20 (m, 10H, C**H**$_{Ar}$), , 4.69 (p, J=7.8, 2H, **CH$_2$**-SF_5), 3.93 (p, J=6.1, 1H, **O-CH**), 1.66 – 1.54 (m, 2H, **CH$_2$**$_{,cProp}$), 1.49 – 1.39 (m, **CH$_2$**$_{,cProp}$).

^{13}C NMR (126 MHz, CDCl3) δ 143.65 (**C**$_{q,Ar}$), 127.94 (**CH**$_{Ar}$), 127.83 (**CH**$_{Ar}$), 127.61 (**CH**$_{Ar}$), 81.15 (**C**$_{q,Bridge}$), 77.0 (p, *J* = 9.8 Hz, **CH$_2$**-SF_5), 76.41 (O-**CH**), 33.79 **(CH$_2$)**, 23.54 (**CH$_2$)**.

^{19}F NMR (471 MHz, Chloroform-*d*) δ 85.14 (p, *J* = 150 Hz, 1F, **F$_{ax}$**), 72.64 (dt, *J* = 149 Hz, 8.0 Hz, 4F, **F$_{eq}$**).

HR-EI-MS m/z (calc.) = 392.1233 [M$^{\bullet+}$]; m/z (found) = 392.1235 [M$^{\bullet+}$] ($C_{19}H_{21}OF_5S$).

3-(2-(Pentafluoro-λ^6-sulfaneyl)-1,1-diphenylethoxy)-propanenitrile (14)



$C_{17}H_{16}F_5NOS$
377,0873

The compound was prepared according to general procedure A. In a Young-type reaction tube 35.3 µL (0.200 mmol, 1.00 eq.) of diphenylethylene **2** as well as 137 µL (142 mg, 2.00 mmol, 10.0 eq.) of 3-hydroxypropionitrile were used. The compound was purified by column chromatography (silica, 50% DCM in hexanes). The yield of the product was determined by analyzing the crude reaction mixture by means of ^{19}F-NMR spectroscopy (29%). The product was obtained as colorless needles.

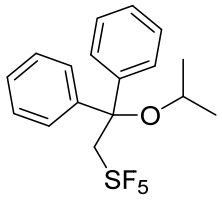
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.33 (m, 8H, **CH$_{Ar}$**), 7.27 (m, 2H, **CH$_{Ar}$**), 4.73 (p, *J* = 7.7 Hz, 2H, **CH$_2$**SF$_5$), 3.46 (t, *J* = 6.4 Hz, 2H, O**CH$_2$**), 2.66 (t, *J* = 6.4 Hz, 2H, **CH$_2$**CN).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.11 (**C$_{q,Ar}$**), 128.64 (**CH$_{Ar}$**), 127.97(**CH$_{Ar}$**), 126.44 (**CH$_{Ar}$**), 117.58 (**C**≡N), 81.30 (**C**$_{q,bridge}$), 74.95 (p, *J* = 11.2 Hz, **CH$_2$**SF$_5$), 58.28 (O-**CH$_2$**), 19.02 (**CH$_2$**CN).

^{19}F NMR (471 MHz, Chloroform-*d*) δ 83.91 (p, *J* = 148 Hz, 1F, **F$_{ax}$**), 72.03 (dt, *J* = 149, 8.0 Hz, 4F, **F$_{eq}$**).

HR-EI-MS m/z (calc.) = 377.0873 [M$^{\bullet+}$]; m/z (found) = 377.0873 [M$^{\bullet+}$] ($C_{17}H_{16}F_5NOS$).

Pentafluoro-(2-isopropoxy-2,2-diphenylethyl)-λ^6-sulfane (15)



$C_{17}H_{19}F_5OS$
366,1077

The compound was prepared according to general procedure A. In a Young-type reaction tube 35.3 µL (0.200 mmol, 1.00 eq.) of diphenylethylene **2** as well as 154 µL (120 mg, 2.00 mmol, 10.0 eq.) of *i*-PrOH were used. The compound was purified by column chromatography (silica, 5% DCM in hexanes). The yield of the product was determined by analyzing the crude reaction mixture by means of ^{19}F-NMR spectroscopy (20%). The product was obtained as colorless oil.

Scale-up: The reaction was also run on a 1.00 mmol scale using 5.5 bar of SF_6. The yield was determined to be 29% NMR.

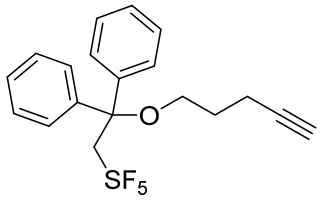
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.7 Hz, 2H, C**H**$_{Ar}$), 7.36 (t, *J* = 7.4 Hz, 2H, C**H**$_{Ar}$), 7.31 (t, *J* = 7.3 Hz, 1H, C**H**$_{Ar}$), 4.00 – 3.89 (m, 1H, **CH$_2$**SF_5), 3.89 – 3.75 (m, 1H,**CH$_2$**SF_5), 3.55 (h, *J* = 6.1 Hz, 1H,C**H**iPr), 1.91 (s, 3H, **CH$_3$**), 1.15 (d, *J* = 6.1 Hz, 3H, CH**CH$_3$**), 0.93 (d, *J* = 6.1 Hz,3H, CH**CH$_3$**).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.06 (**C**$_{q,Ar}$), 128.32 (**CH**$_{Ar}$), 128.19 (**CH**$_{Ar}$, 127.05 (**CH**$_{Ar}$) , 77.88 (**C$_q$**$_{,Bridge}$) , 66.09 (**CH$_2$**-SF5) , 24.88 (**CH$_3$**-iPr) , 24.36 (**CH$_3$**-iPr) , 22.00 (**CH$_3$**).

^{19}F NMR (471 MHz, Chloroform-*d*) δ 85.77 (p, *J* = 151 Hz, 1F, **F$_{ax}$**), 72.69 (dt, *J* = 149, 8.2 Hz, 4F, **F$_{eq}$**).

HR-EI-MS m/z (calc.) = 366.1077 [M$^{\bullet+}$]; m/z (found) = 366.1076 [M$^{\bullet+}$] ($C_{17}H_{19}OF_5S$).

Pentafluoro-(2-(pent-4-yn-1-yloxy)-2,2-diphenylethyl)-λ^6-sulfane (16)



$C_{19}H_{19}F_5OS$
390,1077

The compound was prepared according to general procedure A. In a Young-type reaction tube 35.3 µL (0.200 mmol, 1.00 eq.) of diphenylethylene **2** as well as 55.6 µL (50.5 mg, 0.600 mmol, 3.00 eq.) of 4-pentynol were used. The compound was prepurified by IPLC (Puriflash, RP-C18, 60% to 78% MeCN in water) and the product containing fraction was purified by column chromatography (silica, 15% DCM in hexanes) as well as final consecutive purification by column chromatography (silica, 5% DCM in cyclohexanes, R_f (40% DCM in cyclohexanes = 0.5). The yield of the product was determined by analyzing the crude reaction mixture by means of ^{19}F-NMR spectroscopy (26%).

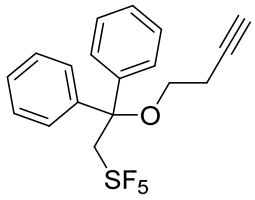
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.32-7.13 (m, 10H, C**H**$_{Ar}$) 4.74 (p, *J* = 7.8 Hz, 1H, **CH$_2$**-SF_5), 3.31 (t, *J* = 5.9 Hz, 1H, O-**CH$_2$**), 2.39 (td, *J* = 7.3, 2.7 Hz, 2H,**CH$_2$**-C≡C), 1.91 (t, *J* = 2.7 Hz, 1H, C≡C-**H**), 1.89 – 1.83 (m, 2H, CH_2**CH$_2$**CH_2).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.04 (**C**$_{q,Ar}$) , 128.36 (**CH**$_{Ar}$), 127.56 (**CH**$_{Ar}$), 126.57 (**CH**$_{Ar}$), 80.76 (**C**$_{q,Bridge}$) , 76.96 (**C**$_{C≡C}$), 75.64 (**C**$_{C≡C}$) , 75.21 (p, *J* = 11.4 Hz, **CH$_2$**-SF_5), 62.14 (O-**CH$_2$**) , 20.22 (-**CH$_2$**-C≡C), 3.57 (C≡C-**CH$_3$**).

^{19}F NMR (471 MHz, Chloroform-*d*) δ 84.40 (p, *J* = 149 Hz, 1F, **F$_{ax}$**), 72.08 (dt, *J* = 149, 8.0 Hz, 4F, **F$_{eq}$**).

HR-EI-MS m/z (calc.) = 390.1077 [$M^{\bullet+}$]; m/z (found) = 390.1077 [$M^{\bullet+}$] ($C_{19}H_{19}F_5OS$).

(2-(But-3-yn-1-yloxy)-2,2-diphenylethyl)-pentafluoro-λ^6-sulfane (17)



$C_{18}H_{17}F_5OS$
376,0920

The compound was prepared according to general procedure A. In a Young-type reaction tube 35.3 µL (0.200 mmol, 1.00 eq.) of diphenylethylene **2** as well as 151 µL (140 mg, 2.00 mmol, 10.00 eq.) of 3-butyn-1-ol were used to prepare the compound. The compound was prepurified by IPLC (Puriflash, RP-C18, 75% to 95% MeCN in water) and the product containing fraction was purified by column chromatography (silica, 15% DCM in hexanes) as well as final consecutive purification by column chromatography (silica, 5% DCM in cyclohexanes, R_f (20% DCM in cyclohexanes = 0.2). The yield of the product was determined by analyzing the crude reaction mixture by means of ^{19}F-NMR spectroscopy (17%). The product was isolated as colorless oil.

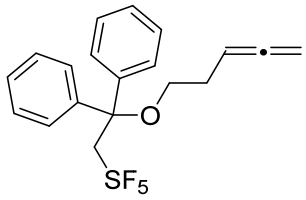
^{1}H NMR (500 MHz, CDCl3) δ = 7.35 – 7.21 (m, 10H, C**H**$_{Ar}$), 4.73 (p, J=7.8, 2H, **CH$_2$**-SF_5), 3.36 (t, J=7.1, 2H, O-**CH$_2$**), 2.54 (td, J=7.1, 2.7, 2H, **CH$_2$-**C≡C), 1.97 (t, J=2.7, 1H, C≡C-**H**).

^{13}C NMR (126 MHz, CDCl3) δ = 142.88 (**C**$_{q,Ar}$), 128.41 (**CH**$_{Ar}$), 127.63 (**CH**$_{Ar}$), 126.54 (**CH**$_{Ar}$), 81.08 (C≡**C**-H**)**, 80.82 (**C**$_{q,Bridge}$), 75.14 (p, *J* = 12.0 Hz, **CH$_2$**-SF_5), 69.55 (C≡**C**-H**)**, 61.48 (**O-CH$_2$**), 19.99 (**CH$_2$**-C≡C).

^{19}F NMR (471 MHz, $CDCl_3$) δ = 84.25 (p, *J* = 151 Hz, 1F, **F$_{ax}$**), 72.07 (dt, J=148.4 Hz, 7.4 Hz, 4F, **F$_{eq}$**).

HR-EI-MS m/z (calc.) = 376.0920 [M$^{\bullet+}$]; m/z (found) = 376.0921 [M$^{\bullet+}$] ($C_{18}H_{17}F_5OS$).

Pentafluoro-(2-(penta-3,4-dien-1-yloxy)-2,2-diphenylethyl)-λ^6-sulfane (18)



$C_{19}H_{19}F_5OS$
390,1077

The compound was prepared according to a modified procedure of the general procedure A. In a Young-type reaction tube 26.0 µL (26.5 mg, 0.148 mmol, 1.00 eq.) of diphenylethylene **2** as well as 188 µL (168 mg, 2.00 mmol, 13.6 eq.) of 3,4-pentadien-1-ol were used. The compound was purified by column chromatography (silica, 5% DCM in hexanes, R_f = 0.3 in 10% DCM in hexanes). The yield of the product was determined by analyzing the crude reaction mixture by means of ^{19}F-NMR spectroscopy (19%). The product was obtained as colorless oil.

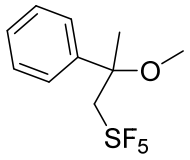
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.33 – 7.27 (m, 8H, **CH$_{Ar}$**), 7.23 (ddt, *J* = 6.3, 5.3, 2.6 Hz, 2H, **CH$_{Ar}$**), 5.16 (p, *J* = 7.0 Hz, 1H, CH_2**CH**=C=), 4.73 (p, *J* = 7.9 Hz, 2H, **CH$_2$**SF_5), 4.69 – 4.63 (m, 2H, CH_2CH=**CH$_2$**), 3.28 (t, *J* = 6.6 Hz, 2H, O**CH$_2$**), 2.44 – 2.24 (m, 2H, **CH$_2$**CH=C=).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 209.19 (**C**$_{q,allene}$), 143.26 (**C**$_{q,Ar}$), 128.32 (**C**H$_{Ar}$), 127.50 (**C**H$_{Ar}$), 126.62 (**C**H$_{Ar}$), 86.79 (C**C**H=CH_2), 75.26 (p, *J* = 10.7 Hz, **C**H_2SF_5), 74.93 (**C**H_2=C), 62.56 (O**C**H_2), 29.23 (OCH_2**C**H_2).

^{19}F NMR (471 MHz, Chloroform-*d*) δ 84.45 (p, *J* = 149 , 1F, **F$_{ax}$**), 72.10 (dt, *J* = 149.1, 8.0 Hz, 4F, **F$_{eq}$**).

HR-EI-MS m/z (calc.) = 263.1436 [M-$SF_5^{\bullet+}$]; m/z (found) = 263.1435 [M-$SF_5^{\bullet+}$] ($C_{19}H_{19}O$); m/z (calc.) = 249.1279 [M-$CH_2SF_5^{\bullet+}$]; m/z (found) = 249.1278 [M-$CH_2SF_5^{\bullet+}$] ($C_{18}H_{17}O$).

Pentafluoro-(2-methoxy-2-phenylpropyl)-λ^6-sulfane (8)



$C_{10}H_{13}F_5OS$
276,0607

The compound was prepared according to general procedure A. In a Young-type reaction tube 26.0 µL (0.200 mmol, 1.00 eq.) of α-methylstyrene **1** as well as 81.1 µL (64.1mg, 2.00 mmol, 10.0 eq.) of MeOH were used to prepare the compound. The compound was purified by column chromatography (silica, hexanes to 2% DCM in hexanes). The product was obtained as volatile oil. The yield of the product was determined by analyzing the crude reaction mixture by means of ^{19}F-NMR spectroscopy (37%).

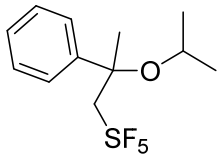
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45 – 7.36 (m, 4H, **CH**$_{Ar}$), 7.34 – 7.30 (m, 1H, **CH**$_{Ar}$), 3.94 (dp, *J* = 14.2, 8.8 Hz, 1H, **CH$_{2,dia}$**SF$_5$), 3.81 (dp, *J* = 14.2, 8.7 Hz, 1H, **CH$_{2,dia}$**SF$_5$), 3.12 (s, 3H, **OCH$_3$**), 1.85 (s, 3H, **CH$_3$**).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.02 (**C**$_{q,Ar}$), 128.78 (**CH**$_{Ar}$), 128.23 (**CH**$_{Ar}$), 126.54 (**CH**$_{Ar}$), 81.13 (p, *J* = 10.0 Hz, **CH$_{2,dia}$**-SF$_5$), 78.33 (p, *J* = 2.3 Hz, **C**$_{q,bridge}$), 50.64 (O**CH$_3$**), 21.13 (p, *J* = 2.2 Hz, **CH$_3$**).

^{19}F NMR (471 MHz, Chloroform-*d*) δ 85.10 (p, *J* = 148 Hz, 1F, **F$_{ax}$**), 70.01 (dt, *J* = 147, 8.8 Hz, 4F, **F$_{eq}$**).

HR-EI-MS m/z (calc.) = 276.0607 [M$^{\bullet+}$]; m/z (found) = 276.0608 [M$^{\bullet+}$] ($C_{10}H_{13}OF_5S$).

Pentafluoro-(2-isopropoxy-2-phenylpropyl)-λ^6-sulfane (19)



$C_{12}H_{17}F_5OS$
304,0920

The compound was prepared according to a modified general procedure A. In a Young-type reaction tube 23.1 µL (0.178 mmol, 1.00 eq.) of α-methylstyrene **1** as well as 154 µL (120 mg, 2.00 mmol, 11.3 eq.) of isopropanol were used to prepare the compound. The compound was purified by column chromatography (silica, 10% DCM in hexanes). The yield of the product was determined by analyzing the crude reaction mixture by means of ^{19}F-NMR spectroscopy (38%). The product was isolated as colorless oil.

Scale up: The reaction was also scaled up to 1.00 mmol following the general procedure A. The yield was determined by ^{19}F-NMR-spectrocopy to be 40%.

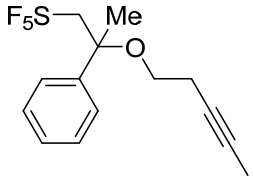
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.7 Hz, 2H, **CH**$_{Ar}$), 7.36 (t, *J* = 7.4 Hz, 2H, **CH**$_{Ar}$), 7.31 (t, *J* = 7.3 Hz, 1H, **CH**$_{Ar}$), 4.05 – 3.89 (m, 1H, **CH$_{2,dia}$**-SF_5), 3.89 – 3.75 (m, 1H, **CH$_{2,dia}$**-SF_5), 3.55 (p, *J* = 6.1 Hz, 1H, **CH**-$(CH_3)_2$), 1.91 (s, 3H,**CH$_3$**), 1.15 (d, *J* = 6.1 Hz, 3H,CH-**CH$_{3,dia}$**), 0.93 (d, *J* = 6.1 Hz,3H, CH-**CH$_{3,dia}$**).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.06 (**C**$_{q,Ar}$), 128.32 (**CH**$_{Ar}$), 128.19 (**CH**$_{Ar}$) , 127.05 (**CH**$_{Ar}$) , 82.11 (p, *J* = 9.6 Hz, **CH$_2$**-SF_5), 77.88 (**C**$_{q,Bridge}$), 66.09 (O-**CH**$(CH_3)_2$) , 24.88 (CH-**CH$_{3,dia}$**) , 24.36 (CH-**CH$_{3,dia}$**) , 22.00 (**CH$_3$**).

^{19}F NMR (471 MHz, Chloroform-*d*) δ 86.10 (p, *J* = 148 Hz, 1F, **F$_{ax}$**), 70.05 (dt, *J* = 147, 8.9 Hz, 4F, **F$_{eq}$**).

HR-EI-MS m/z (calc.) = 303.0842 [M-H$^{\bullet+}$]; m/z (found.) = 303.0842 [M-H$^{\bullet+}$] ($C_{12}H_{16}F_5OS$); m/z (calc.) = 245.0423 [M-OiPr$^{\bullet+}$]; m/z (found) = 245.0424 [M-OiPr$^{\bullet+}$] ($C_9H_{10}F_5S$).

Pentafluoro-(2-(pent-3-yn-1-yloxy)-2-phenylpropyl)-λ^6-sulfane (20)



$C_{14}H_{17}F_5OS$
328.3410

The compound was prepared according to general procedure A. In a Young-type reaction tube 26.0 µL (23.6 mg, 0.20 mmol, 1.00 eq.) of α-methylstyrene **1** as well as 186 µL (168 mg, 2.00 mmol,10.0 eq.) of 3-pentynol were used to prepare the compound. The compound was purified by column chromatography (silica, 5% DCM in hexanes). The yield of the product was determined by analyzing the crude reaction mixture by means of ^{19}F-NMR spectroscopy (34%). The product was obtained as colorless oil.

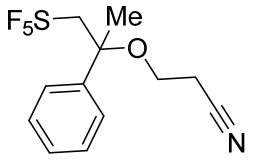
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 7.1 Hz, 2H, **CH**$_{Ar}$), 7.38 (t, *J* = 7.6 Hz, 2H, **CH**$_{Ar}$), 7.34 – 7.29 (m, 1H, **CH**$_{Ar}$), 3.95 (dp, *J* = 14.1, 8.7 Hz, 1H, **CH$_2$**-SF$_5$), 3.82 (dp, *J* = 14.2, 8.5 Hz, 1H, **CH$_2$**-SF$_5$), 3.40 (dt, *J* = 7.5 Hz, 1H, O-**CH$_{2,dia}$**), 3.16 (dt, *J* = 7.7 Hz, 2H, O-**CH$_{2,dia,}$**), 2.38 (tq, *J* = 7.3, 2.6 Hz, 2H, **CH$_2$**), 1.86 (s, 1H, **CH$_3$**), 1.76 (t, *J* = 2.6 Hz, 1H, **CH$_3$**).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.16 (**C**$_{q,Ar}$), 128.71 (**CH**$_{Ar}$), 128.26 (**CH**$_{Ar}$), 126.52 (**CH**$_{Ar}$), 81.22 (p, J_{CF} = 9.9 Hz, **CH$_2$**-SF$_5$), 78.02 (C≡C), 77.37 (C$_{q,Bridge}$), 75.90 (C≡C), 61.71 (O-**CH$_2$**), 21.60 (C-**CH$_3$**), 20.51 (**CH$_2$**-C≡C), 3.56 (C≡C-**CH$_3$**).

^{19}F NMR (471 MHz, Chloroform-*d*) δ 85.08 (p, *J* = 148 Hz, 1F, **F$_{ax}$**), 70.12 (dt, *J* = 147, 8.8 Hz, 4F, **F$_{eq}$**).

HR-EI-MS m/z (calc.) = 328.0920 [M$^{\bullet+}$]; m/z (found) = 328.0923 [M$^{\bullet+}$] ($C_{14}H_{17}OF_5S$).

3-((1-(Pentafluoro-λ^6-sulfaneyl)-2-phenylpropan-2-yl)-oxy)-propanenitrile (21)



$C_{12}H_{14}F_5NOS$
315,0716

The compound was prepared according to general procedure A. In a Young-type reaction tube 26.0 µL (0.200 mmol, 1.00 eq.) of α-methylstyrene **1** as well as 137 µL (142 mg, 2.00 mmol, 10.0 eq.) of 3-hydroxypropionitrile were used to prepare the compound. The compound was purified by column chromatography (silica, 20% DCM in hexanes). The yield of the product was determined by analyzing the crude reaction mixture by means of ^{19}F-NMR spectroscopy (35%). The product was obtained as colorless solid.

Scale-up: The reaction was also run on a 1.00 mmol scale. The yield was determined to be 31% by ^{19}F-NMR.

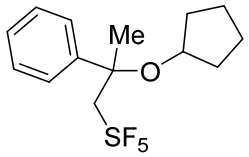
^{1}H NMR (500 MHz, CDCl3) δ = 7.46 (d, J=7.7, 2H, C**H**$_{Ar}$), 7.41 (t, J=7.6, 2H, C**H**$_{Ar}$), 7.35 (t, J=7.1, 1H, C**H**$_{Ar}$), 3.99 (dt, J=14.2, 8.6, 1H, **CH$_2$**SF$_5$), 3.82 (dt, J=14.2, 8.4, **CH$_2$**SF$_5$), 3.54 (dt, J=8.8, 6.1, 1H, O-**CH$_2$**), 3.36 – 3.22 (m, 1H, O-**CH$_2$**), 2.68 – 2.46 (m, 2H, **CH$_2$**), 1.91 (s, 3H, **CH$_3$**).

^{13}C NMR (126 MHz, CDCl3) δ = 141.03 (**C**$_{q,Ar}$), 129.06 (**CH**$_{Ar}$), 128.77 (**CH**$_{Ar}$), 126.43 (**CH**$_{Ar}$), 117.78 (**CN**), 80.89 (p, *J* = 11.0 Hz, **CH**$_2$-SF$_5$), 78.59 (C$_{q,Bridge}$), 57.76 (O-**CH$_2$**), 21.32 (**CH**$_3$), 19.24 (**CH$_2$**-CN).

^{19}F NMR (471 MHz, CDCl3) δ = 84.59 (p, *J* = 147 Hz, 1F, **F$_{ax}$**), 70.13 (dt, *J* = 147, 9.1, 4F, **F$_{eq}$**).

HR-EI-MS m/z (calc.) = 315.0716 [M$^{\bullet+}$]; m/z (found) = 315.0715 [M$^{\bullet+}$] ($C_{12}H_{14}F_5NOS$).

(2-(Cyclopentyloxy)-2-phenylpropyl)-pentafluoro-λ^6-sulfane (22)



$C_{14}H_{19}F_5OS$
330,1077

The compound was prepared according to general procedure A. In a Young-type reaction tube 26.0 µL (0.20 mmol, 1.0 eq.) of α-methylstyrene **1** as well as 181 µL (172 mg, 2.00 mmol, 10.0 eq.) of cyclopentanol were used. The compound was purified by column chromatography (silica, hexanes). The yield of the product was determined by analyzing the crude reaction mixture by means of ^{19}F-NMR spectroscopy (22%). The product was obtained as a colorless oil.

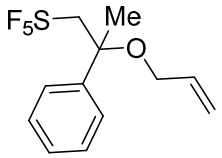
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.46 (d, J=7.7, 2H, C**H**$_{Ar}$), 7.37 (t, J=7.6, 2H, C**H**$_{Ar}$), 7.31 (t, J=7.3, 1H, C**H**$_{Ar}$), 3.91 (dp, J=14.1, 8.8, 1H,**CH$_{2,dia}$**-SF_5), 3.82 – 3.64 (m, 2H, **CH$_{2,dia}$**-SF_5 und O-**CH**$(CH_3)_2$), 1.87 (s, 3H, **CH$_3$**), 1.77 – 1.31 (m, 8H, 4 x **CH$_{2,cProp,dia}$**).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 143.66 (**C**$_{q,Ar}$), 128.52 (**CH$_{Ar}$**), 128.06 (**CH$_{Ar}$**), 126.87 (**CH$_{Ar}$**), 82.01 (p, J = 9.4 Hz, **CH$_2$**-SF_5), 78.29 (**C**$_{q,Bridge}$), 75.76 (O-**CH**$(CH_3)_2$), 34.65 (**CH$_{2,dia}$**), 34.22 (**CH$_{2,dia}$**), 23.96 (**CH$_{2,dia}$**), 23.44 (**CH$_{2,dia}$**), 22.58 (**CH$_3$**).

^{19}F NMR (471 MHz, CDCl3) δ = 85.57 (p, J=148, 1F, **F$_{ax}$**), 70.15 (dt, J=146, 9.3, 4F, **F$_{ax}$**).

HR-EI-MS m/z (calc.) = 315.0842 [M-Me$^{\bullet+}$]; m/z (found) = 315.0842 [M-Me$^{\bullet+}$] ($C_{13}H_{16}F_5OS$); m/z (calc.) = 245.0423 [M-cycPentO$^{\bullet+}$]; m/z (found) = 245.0425 [M-cycPentO$^{\bullet+}$] ($C_9H_{10}F_5S$); m/z (calc.) = 203.1436 [M-$SF_5^{\bullet+}$]; m/z (found) = 203.1436 [M-$SF_5^{\bullet+}$] ($C_{14}H_{19}O$).

(2-(Allyloxy)-2-phenylpropyl)-pentafluoro-λ^6-sulfane (23)



$C_{12}H_{15}F_5OS$
302,0764

The compound was prepared according to the modified general procedure A. In a Young-type reaction tube 11.6 µL (10.6 mg, 0.893 mmol, 1.00 eq.) of α-methylstyrene **1** as well as 68.3 µL (58.3 mg, 1.00 mmol, 11.2 eq.) of allyl alcohol were used. The compound was purified by column chromatography (silica, cyclohexane). The yield of the product was determined by analyzing the crude reaction mixture by means of ^{19}F-NMR spectroscopy (20%). The product was obtained as colorless oil.

Scale-up: The reaction could also be run on a 1.00 mmol scale following the general procedure A. The yield was determined to be 31% by NMR spectroscopy.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 7.6 Hz, 2H, C**H**$_{Ar}$), 7.31 (t, *J* = 7.6 Hz, 2H, C**H**$_{Ar}$), 7.25 (t, *J* = 7.2 Hz, 1H, C**H**$_{Ar}$), 5.81 (ddt, *J* = 17.3, 10.1, 4.9 Hz, 1H,**HC**=CH$_2$), 5.26 (dq, *J* = 17.2, 1.9 Hz, 1H, HC=**CH$_2$**), 5.08 (dt, *J* = 10.5, 1.8 Hz, 1H, HC=**CH$_2$**), 3.97 (dq, J=17.6, 8.7, 1H, **CH$_{2,dia}$**-SF$_5$), 3.85 (m, 2H, **CH$_{2,dia}$**-SF$_5$ und **CH$_{2,\ dia}$**-CH=CH$_2$), 3.64 (dd, J=12.8, 4.7, 1H, **CH$_{2,\ dia}$**-CH=CH$_2$),1.81 (s, 3H, **CH$_3$**).

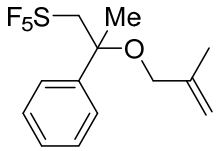
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.15 (**C**$_{q,Ar}$), 134.71 (**CH**=CH$_2$) , 128.78 (**CH**$_{Ar}$), 128.30 (**CH**$_{Ar}$), 126.47 (**CH**$_{Ar}$), 115.89 (CH=**CH$_2$**), 81.34 (p, *J* = 10.1 Hz, **CH$_2$**-SF$_5$), 78.27 (C$_{q,Bridge}$), 63.78 (O-**CH$_2$**), 21.71 (**CH$_3$**).

^{19}F NMR (471 MHz, Chloroform-*d*) δ 85.04 (p, *J* = 147 Hz, 1F, **F$_{ax}$**), 70.15 (dt, *J* = 147, 8.9 Hz, 4F, **F$_{eq}$**).

HR-EI-MS m/z (calc.) = 287.0529 [M-Me$^{\bullet+}$]; m/z (found) = 287.0529 [M-Me$^{\bullet+}$] ($C_{11}H_{12}OFS_5$); m/z (calc.) = 246.0502 [M-OiPr+H$^{\bullet+}$]; m/z (found) = 287.0503 [M-OiPr+H$^{\bullet+}$]

($C_9H_{11}OFS_5$); m/z (calc.) = 161.0966 [M-SF_5-$Me^{\bullet+}$]; m/z (found) = 161.0966 [M-SF_5-$Me^{\bullet+}$] ($C_{11}H_{13}O$).

Pentafluoro-(2-((2-methylallyl)-oxy)-2-phenylpropyl)-λ^6-sulfane (24)



$C_{13}H_{17}F_5OS$
316,0920

The compound was prepared according to general procedure A. In a Young-type reaction tube 26.0 µL (23.6 mg, 0.200 mmol, 1.00 eq.) of α-methylstyrene **1** as well as 168 µL (144 mg, 2.00 mmol, 10.0 eq.) of 2-methyl-2-propen-1-ol were used. The compound was purified by column chromatography (silica, cyclohexane). The yield of the product was determined by analyzing the crude reaction mixture by means of ^{19}F-NMR spectroscopy (31%). The product was obtained as colorless oil.

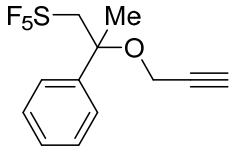
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.47 – 7.42 (m, 2H, C**H**$_{Ar}$), 7.41 – 7.36 (m, 2H, C**H**$_{Ar}$), 7.35 – 7.30 (m, 1H, C**H**$_{Ar}$), 5.04 (s, 1H, **=CH$_a$**H$_b$), 4.87 (s, 1H, **=C**H$_a$**H$_b$**), 3.98 (dp, *J* = 14.2, 8.7 Hz, 1H, **CH$_{2,dia}$**-SF$_5$), 3.82 (dp, *J* = 14.1, 8.6 Hz, 1H, **CH$_{2,dia}$**-SF$_5$), 3.74 (d, *J* = 12.0 Hz, 1H, O**CH$_{2,dia}$**), 3.51 (d, *J* = 12.0 Hz, 1H, O**CH$_{2,dia}$**), 1.89 (s, 3H, **CH$_3$**), 1.72 (s, 3H, **CH$_3$**).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.15 (**C**=CH$_2$), 142.21 (**C**$_{q,Ar}$), 128.79 (**CH**$_{Ar}$), 128.29 (**CH**$_{Ar}$), 126.50 (**CH**$_{Ar}$), 111.09 (C=**CH$_2$**)., 81.46 (p, *J* = 10.0 Hz, **CH$_2$**SF$_5$), 78.20 (**C**$_{q,bridge}$), 66.51 (O**CH$_2$**), 21.55 (p, *J* = 2.1 Hz, C**CH$_3$**), 19.79 (C(C=CH$_2$)**CH$_3$**).

^{19}F NMR (471 MHz, Chloroform-*d*) δ 85.10 (p, *J* = 147 Hz, 1F, **F$_{ax}$**), 70.17 (dt, *J* = 147, 8.8 Hz, 4F, **F**$_{eq}$).

HR-EI-MS m/z (calc.) = 301.0686 [M-Me$^{\bullet+}$]; m/z (found) = 301.0686 [M-Me$^{\bullet+}$] ($C_{12}H_{14}OF_5S$); m/z (calc.) = 245.0423 [M-OMeAllyl$^{\bullet+}$]; m/z (found) = 245.0422 [M-OMeAllyl$^{\bullet+}$] ($C_9H_{10}F_5S$).

Pentafluoro(2-phenyl-2-(prop-2-yn-1-yloxy)propyl) - λ^6-sulfane (25)



$C_{12}H_{13}F_5OS$
300,0607

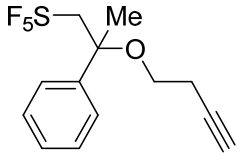
The compound was prepared according to general procedure A. In a Young-type reaction tube 26.0 µL (23.6 mg, 0.200 mmol, 1.00 eq.) of α-methylstyrene **1** as well as 35.5 µL (34.2 mg, 0.610 mmol, 3.04 eq.) of propargylic alcohol were used. The compound was prepurified by IPLC (Puriflash, RP-C18, 65% to 72% MeCN in water) and the product containing fraction was purified by column chromatography (silica, cyclohexane to 10% DCM in cyclohexane, R_f (50% DCM in cyclohexanes = 0.76). The yield of the product was determined by analyzing the crude reaction mixture by means of ^{19}F-NMR spectroscopy (20%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 – 7.44 (m, 2H, **CH**$_{Ar}$), 7.40 (ddd, *J* = 7.8, 6.7, 1.3 Hz, 2H, **CH**$_{Ar}$), 7.37 – 7.31 (m, 1H, **CH**$_{Ar}$), 4.06 – 3.77 (m, 4H, **CH$_2$**SF5, O**CH$_2$**), 2.39 (t, *J* = 2.4 Hz, 1H, C≡**CH**), 1.93 (s, 3H, **CH$_3$**).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.15 (**C$_{q,Ar}$**), 128.93 (**CH**$_{Ar}$), 128.65 (**CH**$_{Ar}$), 126.64 (**CH**$_{Ar}$), 81.12 (p, *J* = 10.7 Hz, **CH$_2$**SF$_5$), 80.34 (**C**≡CH),, 79.30 (**C$_q$**$_{,bridge}$), 73.94 (C≡**CH**), 51.68 (O**CH$_2$**), 21.45 (**CH$_3$**).

^{19}F NMR (471 MHz, Chloroform-*d*) δ 84.66 (p, *J* = 148 Hz, 1F, **F$_{ax}$**), 70.16 (dt, *J* = 147, 8.7 Hz, 4F, **F$_{eq}$**).
HR-EI-MS m/z (calc.) = 300.0607 [M$^{\bullet+}$]; m/z (found) = 300.0607 [M$^{\bullet+}$]; ($C_{12}H_{13}OF_5S$).

(2-(But-3-yn-1-yloxy)-2-phenylpropyl)-pentafluoro-λ^6-sulfane (26)



$C_{13}H_{15}F_5OS$
314,0764

The compound was prepared according to a modified general procedure A. In a Young-type reaction tube 26.0 µL (0.200 mmol, 1.00 eq.) of α-methylstyrene **1** as well as 45.4 µL (42.1 mg, 0.600 mmol, 3.00 eq.) of 3-butynol were used to prepare the compound. The compound was prepurified by IPLC (Puriflash, RP-C18, 65% to 73% MeCN in water) and the product containing fraction was purified by column chromatography (silica, cyclohexane to 10% DCM in cyclohexane, R_f (50% DCM in cyclohexanes = 0.61). The yield of the product was determined by analyzing the crude reaction mixture by means of ^{19}F-NMR spectroscopy (19%).

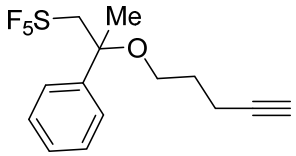
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 – 7.43 (m, 2H, **CH**$_{Ar}$), 7.42 – 7.36 (m, 2H, **CH**$_{Ar}$), 7.35 – 7.30 (m, 1H, **CH**$_{Ar}$), 3.96 (dp, *J* = 14.1, 8.8 Hz, 1H, **CH$_{2,dia}$**SF$_5$), 3.82 (dp, *J* = 14.2, 8.6 Hz, 1H, **CH$_{2,dia}$**SF$_5$), 3.45 (dt, *J* = 8.5, 6.9 Hz, 1H, O**CH$_{2,dia}$**), 3.22 (dt, *J* = 8.5, 7.2 Hz, 1H, O**CH$_{2,dia}$**), 2.45 (td, *J* = 7.1, 2.7 Hz, 2H, **CH$_2$**), 1.96 (t, *J* = 2.7 Hz, 1H, C≡**C-H**), 1.88 (s, 3H, **CH$_3$**).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.98 (**C$_{q,Ar}$**), 128.78 (**CH**$_{,Ar}$), 128.35 (**CH**$_{,Ar}$), 126.50 (**CH**$_{,Ar}$), 81.30 (**C**≡CH),, 81.16 (p, *J* = 10.2 Hz, **CH$_2$**SF$_5$), 78.10 (p, *J* = 2.0 Hz, **C**$_{q,bridge}$), 69.47 (C≡**CH**), 61.06 (O**CH$_2$)**, 21.56 (p, *J* = 1.9 Hz, C**CH$_3$**), 20.26 (CH$_2$**CH$_2$**).

^{19}F NMR (471 MHz, Chloroform-*d*) δ 85.01 (p, *J* = 147 Hz, 1F, **F$_{ax}$**), 70.14 (dt, *J* = 147, 8.7 Hz, 4F, **F$_{eq}$**).

HR-EI-MS m/z (calc.) = 314.0764 [M$^{\bullet+}$]; m/z (found) = 314.0766 [M$^{\bullet+}$]; ($C_{13}H_{15}OF_5S$).

Pentafluoro-(2-(pent-4-yn-1-yloxy)-2-phenylpropyl)-λ^6-sulfane (27)



$C_{14}H_{17}F_5OS$
328,0920

The compound was prepared according to general procedure A. In a Young-type reaction tube 26.0 µL (0.200 mmol, 1.00 eq.) of α-methylstyrene **1** as well as 55.8 µL (50.5 mg, 0.600 mmol, 3.00 eq.) of 4-pentynol were used to prepare the compound. The compound was prepurified by IPLC (Puriflash, RP-C18, 60% to 78% MeCN in water) and the product containing fraction was purified by column chromatography (hexanes to 15% DCM in hexanes, R_f (30% DCM in hexanes) = 0.5). The yield of the product was determined by analyzing the crude reaction mixture by means of ^{19}F-NMR spectroscopy (24%). The product was obtained as colorless liquid.

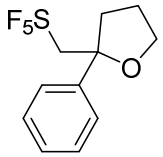
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.8 Hz, 2H, **CH_{Ar}**), 7.38 (dd, *J* = 8.3, 6.7 Hz, 2H, **CH_{Ar}**), 7.34 – 7.29 (m, 1H, **CH_{Ar}**), 3.92 (dq, J=17.5, 8.6, 1H, **$CH_{2,dia}$**-SF_5), 3.78 (dq, J=14.9, 8.3, 1H, **$CH_{2,dia}$**-SF_5), 3.41 (q, J=7.3, 1H, O-**$CH_{2,dia}$**), 3.17 (q, J=6.3, 1H, O-**$CH_{2,dia}$**), 2.34 (t, J=7.4, 2H, **CH_2**-C≡CH), 1.92 (t, *J* = 2.5 Hz, 1H, C≡C-**H**), 1.87 (s, **CH_3**), 1.84 – 1.69 (m, 2H, -CH_2-**CH_2**-CH_2).

^{13}C NMR (126 MHz, CDCl3) δ 142.36 (**$C_{q,Ar}$**), 128.75 (**CH_{Ar}**), 128.21 (**CH_{Ar}**), 126.45 (**CH_{Ar}**), 84.12 (**C**≡C), 81.34 (p, *J* = 9.5 Hz, **CH_2**-SF_5), 77.78 (**$C_{q,Bridge}$**), 68.58 (C≡**CH**), 60.65 (O-**CH_2**), 29.03 (CH_2), 21.56 (**CH_3**), 15.33 (CH_2-**CH_2**-CH_2).

^{19}F-NMR (471 MHz, CDCl3) δ = 85.21 (p, J=148, 1F, **F_{ax}**), 70.13 (dt, J = 147, 8.3 Hz, 4F, **F_{eq}**).

HR-EI-MS m/z (calc.) = 328.0920 [$M^{\bullet+}$]; m/z (found) = 328.0920 [$M^{\bullet+}$] ($C_{14}H_{17}OF_5S$).

2-((Pentafluoro-λ^6-sulfaneyl)-methyl)-2-phenyltetrahydrofuran (28)



$C_{11}H_{13}F_5OS$
288,0607

The compound was prepared according to general procedure B. In a Young-type reaction tube 50.0 µL (53.5 mg, 0.31 mmol, 1.00 eq.) of 3-phenylbut-3-en-1-ol was used. The compound was purified by column chromatography (silica, hexanes). The yield of the product was determined by analyzing the crude reaction mixture by means of ^{19}F-NMR spectroscopy (26%).

Comment: 3-Phenylbut-3-en-1-ol was prepared by Pd-catalyzed addition of phenylboronic acid to 4-pentynol. The product could was contaminated by 18% of non-separatable but unreactive 4-phenylpent-3-en-1-ol (internal alkene). The given yield was corrected by the molar ratio of both species.

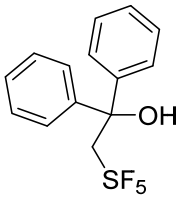
^{1}H NMR (500 MHz, CDCl3) δ = 7.40 (d, J=7.4, 2H, **CH**$_{Ar}$), 7.35 (dd, J=8.6, 6.7, 2H, **CH**$_{Ar}$), 7.28 (d, J=7.1, 1H, **CH**$_{Ar}$), 4.24 – 3.92 (m, 4H, **CH$_2$**SF_5 und O-**CH$_2$**), 2.29 (dd, J=8.1, 6.5, 2H, CH_2-**CH$_2$**-CH_2), 2.07 – 1.90 (m, 1H, C_q-**CH$_{2,dia}$**), 1.87 – 1.78 (m, 1H, C_q-**CH$_{2,dia}$**).

^{13}C NMR (126 MHz, CDCl3) δ = 143.69 (**C**$_{q,Ar}$), 128.40 (**CH**$_{Ar}$), 127.48 (**CH**$_{Ar}$), 125.44 (**CH**$_{Ar}$), 85.04 (**C**$_{q,Bridge}$)78.93 (q, *J* = 10.0, **CH$_2$**-SF_5), 68.65 (O-**CH$_2$**), 38.75 (**CH$_2$**), 25.14 (C_q-**CH$_2$**).

^{19}F NMR (471 MHz, Chloroform-*d*) δ 84.56 (p, *J* = 148 Hz, 1F, **F$_{ax}$**), 69.86 (dt, *J* = 147, 8.2 Hz, 4F, **F$_{eq}$**).).

HR-EI-MS m/z (calc.) = 288.0796 [M$^{\bullet+}$]; m/z (found) = 288.0794 [M$^{\bullet+}$] ($C_{11}H_{13}F_5OS$).

2-(Pentafluoro-λ^6-sulfaneyl)-1,1-diphenylethan-1-ol (29)



$C_{14}H_{13}F_5OS$
324,0607

The compound was prepared according to a modified general procedure A. In a Young-type reaction tube 26.0 µL (26.5 mg, 0.148 mmol, 1.00 eq.) of diphenylethylene **2** as well as 229 µL (220 mg, 2.00 mmol, 13.6 eq.) of 1-ethinylcyclopentanol were used. The compound was purified by column chromatography (silica, hexanes to DCM). The yield of the product was determined by analyzing the crude reaction mixture by means of ^{19}F-NMR spectroscopy (13%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53 – 7.44 (m, 4H, CH_{Ar}), 7.41 – 7.33 (m, 4H, CH_{Ar}), 7.32 – 7.26 (m, 2H, CH_{Ar}), 4.49 (p, *J* = 8.2 Hz, 2H, **CH2**-SF5), 3.04(s, 1H, OH).

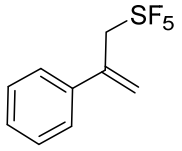
^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.60 ($C_{q,Ar}$), 128.74 (CH_{Ar}), 128.03 (CH_{Ar}), 125.70 (CH_{Ar}), 79.89 (p, *J* = 8.0 Hz), 78.22.

^{19}F NMR (471 MHz, Chloroform-*d*) δ 85.06 (p, *J* = 150 Hz, 1F, $\mathbf{F_{ax}}$), 71.41 (dt, *J* = 147, 8.3 Hz, 4F, $\mathbf{F_{eq}}$).

HR-EI-MS m/z (calc.) = 324.0607 [$M^{\bullet+}$]; m/z (found) = 324.0606 [$M^{\bullet+}$] ($C_{14}H_{13}OF_5S$).

Elimination of ROH by **8** and **9** to prepare **30** and **31**

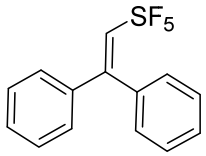
Pentafluoro-(2-phenylallyl)-λ^6-sulfane (30)



$C_9H_9F_5S$
244,2230

In a borosilicate NMR tube 5.2 mg (19 µmol, 1.00 eq.) of **8** were suspended in 400 µL $CDCl_3$. Then 23.8 µL (188 µmol, 10.0 eq.) of $BF_3 \cdot OEt$ were added. The tube was sealed with parafilm and the reaction mixture was shaken vigorously. Then the reaction progress was monitored by ^{19}F-NMR over a period of 27 min when the starting material was fully converted to the product. The yield of the product was determined by means of ^{19}F-NMR spectrocopy (>98%). The identity of the product was confirmed by means of ^{1}H-NMR, ^{19}F-NMR as well as $HSQC_{ed}$ and ^{1}H-^{13}C-HMBC spectroscopy and corresponds to **30** which NMR spectroscopic data after purification previously was reported by our group and is given below.[S7]

(2,2-Diphenylvinyl)pentafluoro-λ^6-sulfane (31)



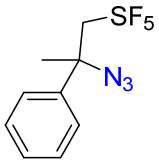
$C_{14}H_{11}F_5S$
306,2940

In a borosilicate NMR tube 6.4 mg (19 µmol, 1.00 eq.) of **9** was suspended in 400 µL $CDCl_3$. Then 23.8 µL (188 µmol, 10.0 eq.) of $BF_3 \cdot OEt$ were added. The tube was sealed with parafilm and the reaction mixture was shaken vigorously. Then the reaction progress was monitored by ^{19}F-NMR over a period of 17 min when the starting material was fully converted to the product. The yield of the product was determined by means of ^{19}F-NMR spectrocopy (>99%). The identity of the product was confirmed by means of ^{1}H-NMR and ^{19}F-NMR as well as $HSQC_{ed}$ and ^{1}H-^{13}C-HMBC spectroscopy and corresponds to **31** as previously reported.[S7]

Preparation of the (2-azido-2-phenylpropyl)pentafluoro-λ^6-sulfane (**32**)

Caution: TMS-CN and TMS-N_3 are highly toxic compounds and can lead to serious injury or fatality. All manipulations have been carried out under a well ventilated fumehood or have been handled in a sealed container. Gold cyanide compounds are potentially explosive compounds. While having an huge excess of TMSCN present in the reaction mixture, formation of the relatively stable $Au(N_3)_4^-$ anion was likely in the case of formation of azide complexes. The reactions have been carried out behind a blast shield as far as possible. The solutions have never been concentrated to dryness but have been distributed between 1 M potassium hydroxide solution and diethyl ether or dichloromethane. The aqueous phases finally have been disposed by treatment with freshly prepared nitrous acid as soon as possible while the organic phase has been concentrated under reduced pressure and purified by column chromatography.

(2-azido-2-phenylpropyl)pentafluoro-λ^6-sulfane (32)



$C_9H_{10}F_5N_3S$
287,0516

In a borosilicate NMR tube 6.8 mg (25 µmol, 1.00 eq.) of **8** were suspended in 500 µL CD_2Cl_2. Then 5.4 mg of $HAuCl_4 \cdot 3H_2O$ (17 µmol, 71 mol%) ere added. Finally 50.0 µL (377 µmol, 15.1 eq.) of TMS-N_3 were added while the reaction mixture turned orange. The tube was sealed with parafilm and the reaction mixture was shaken vigorously. Then the reaction progress was monitored by ^{19}F-NMR over a period of 5 h. A control NMR analysis was finally performed after additional 12 h. The yield of the reaction product was purified by column chromatography (silica, cyclohexane, R_f = 0.5). The product was obtained as colorless oil and was characterized by NMR spectroscopy.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.52 – 7.44 (m, 2H,**CH**$_{Ar}$), 7.45 – 7.38 (m, 2H,**CH**$_{Ar}$), 7.38 – 7.32 (m, 1H,**CH**$_{Ar}$), 3.92 (p, *J* = 8.4 Hz, 2H,**CH$_2$**SF_5), 1.96 (s, 3H,**CH$_3$**).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.86 (**C**$_{q,Ar}$), 129.11 (**CH**$_{Ar}$), 128.64 (**CH**$_{Ar}$), 125.70 (**CH**$_{Ar}$), 79.10 (p, *J* = 11.2 Hz, **CH$_2$**SF_5), 64.95 (**C**$_q$$N_3$), 24.36 (p, *J* = 2.2 Hz, **CH$_3$**).

^{19}F NMR (471 MHz, Chloroform-*d*) δ 83.52 (p, *J* = 147 Hz, 1F, **F$_{ax}$**), 69.60 (dt, *J* = 147, 8.6 Hz, 4F, **F$_{eq}$**).

GC-EI-MS m/z (calc.) = 287.1 [$M^{\bullet+}$]; m/z (found) = 287.0 [$M^{\bullet+}$].

HR-EI-MS m/z (calc.) = 287.0516 [$M^{\bullet+}$]; m/z (found) = 287.0513 [$M^{\bullet+}$]; m/z (calc.) = 245.0423 [M-$N_3^{\bullet+}$] ($C_9H_{10}F_5N_3S$); m/z (found) = 245.0422 [M-$N_3^{\bullet+}$] ($C_9H_{10}F_5S$).

NMR kinetics of elimination reactions

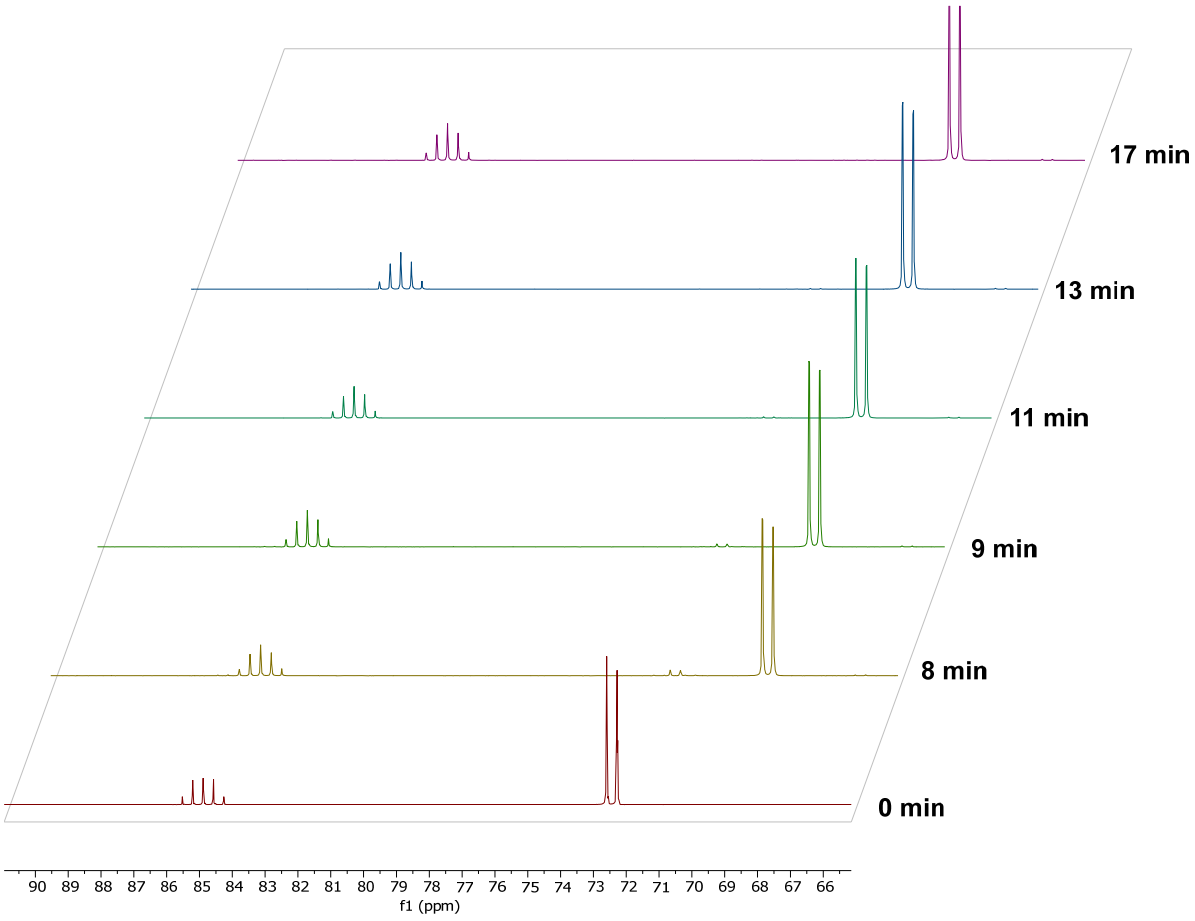


Fig. S3

Time resolved ^{19}F-NMR spectra of elimination reaction of **9** to **31**.

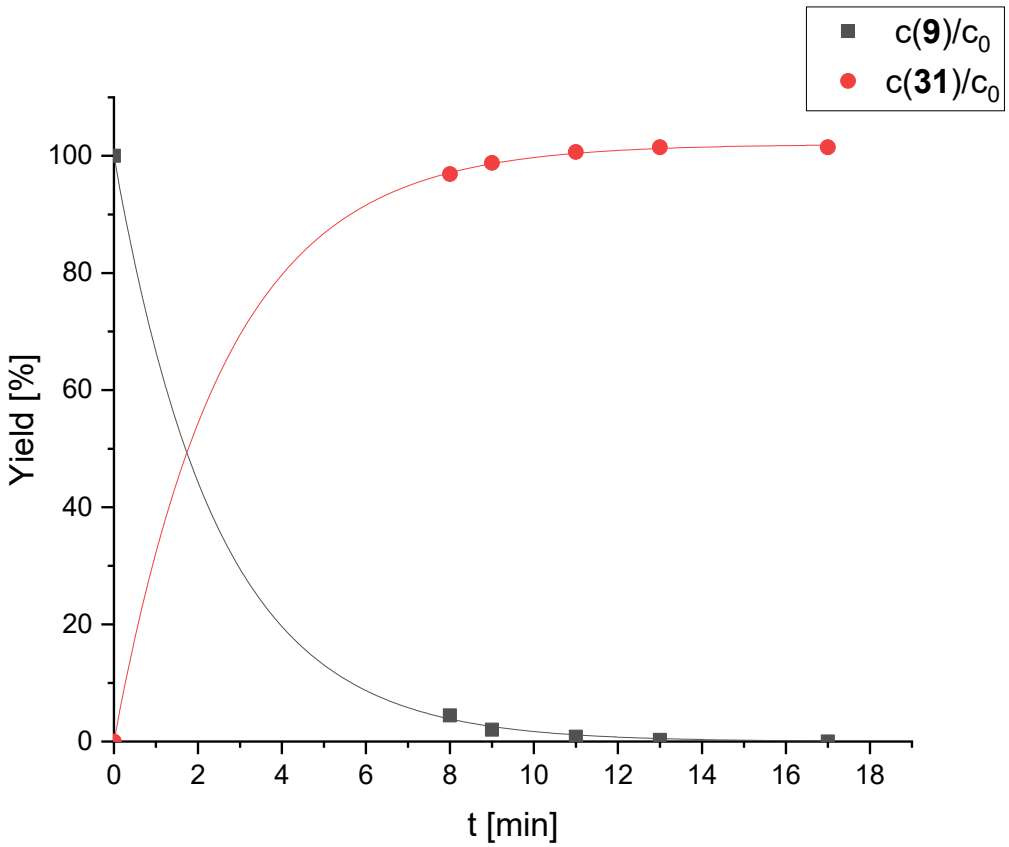


Fig. S4

Plot of the ^{19}F-NMR integrals of product **9** and **31** vs. time.

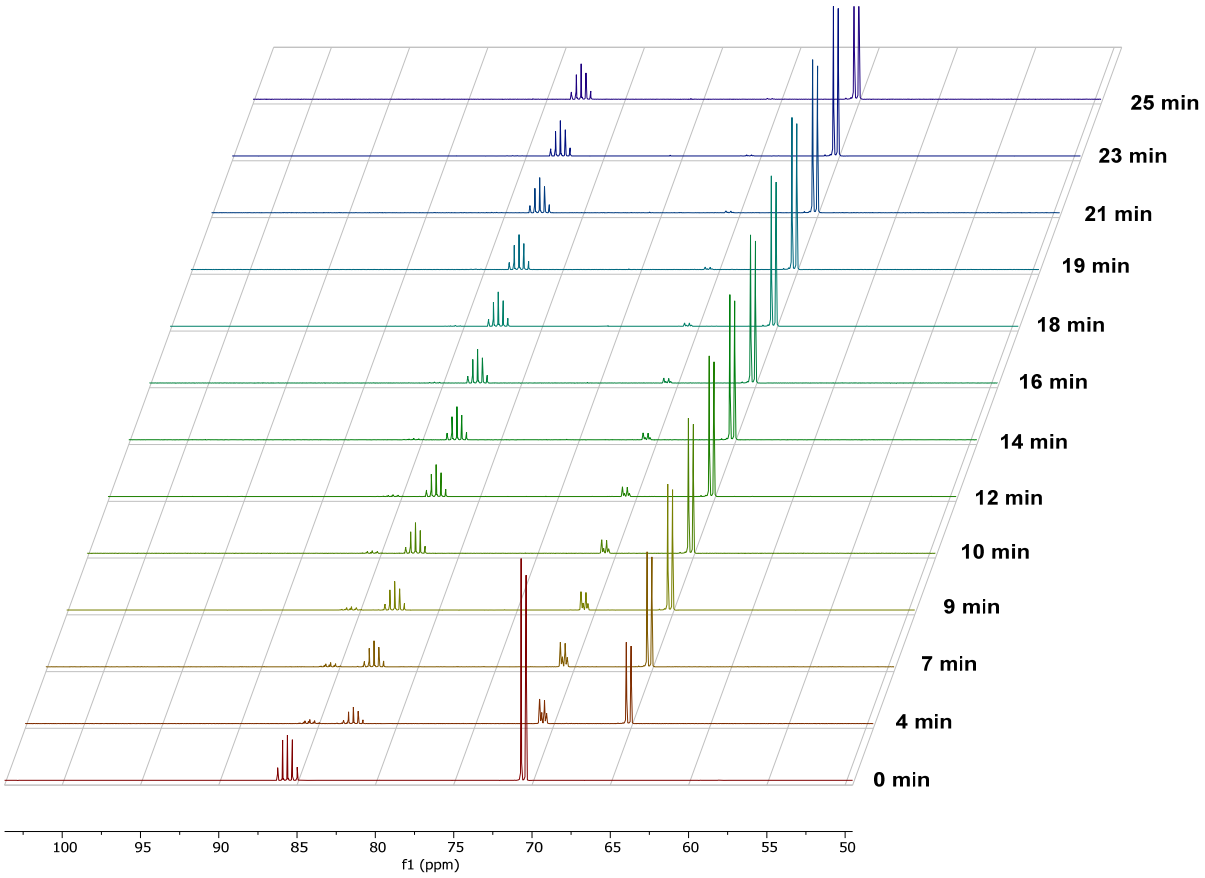


Fig. S5

Time resolved ^{19}F-NMR spectra of elimination reaction of **8** to **30**.

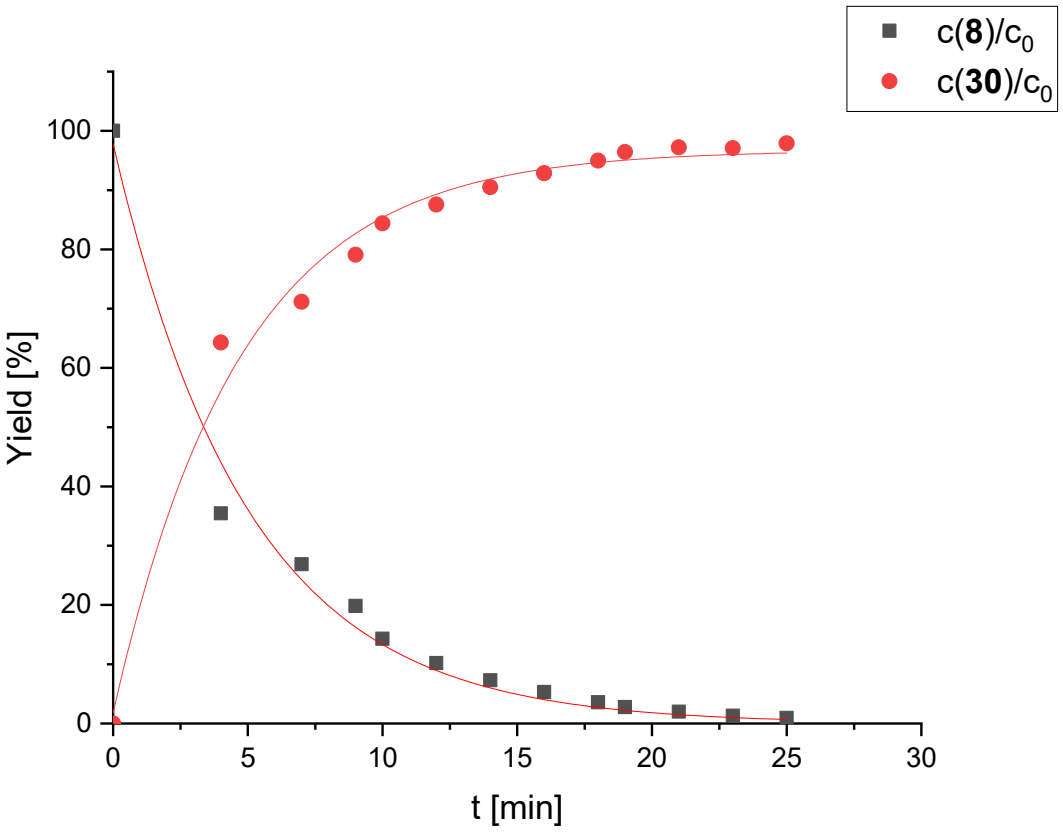


Fig. S6

Plot of the ^{19}F-NMR integrals of product **8** and **30** vs. time.

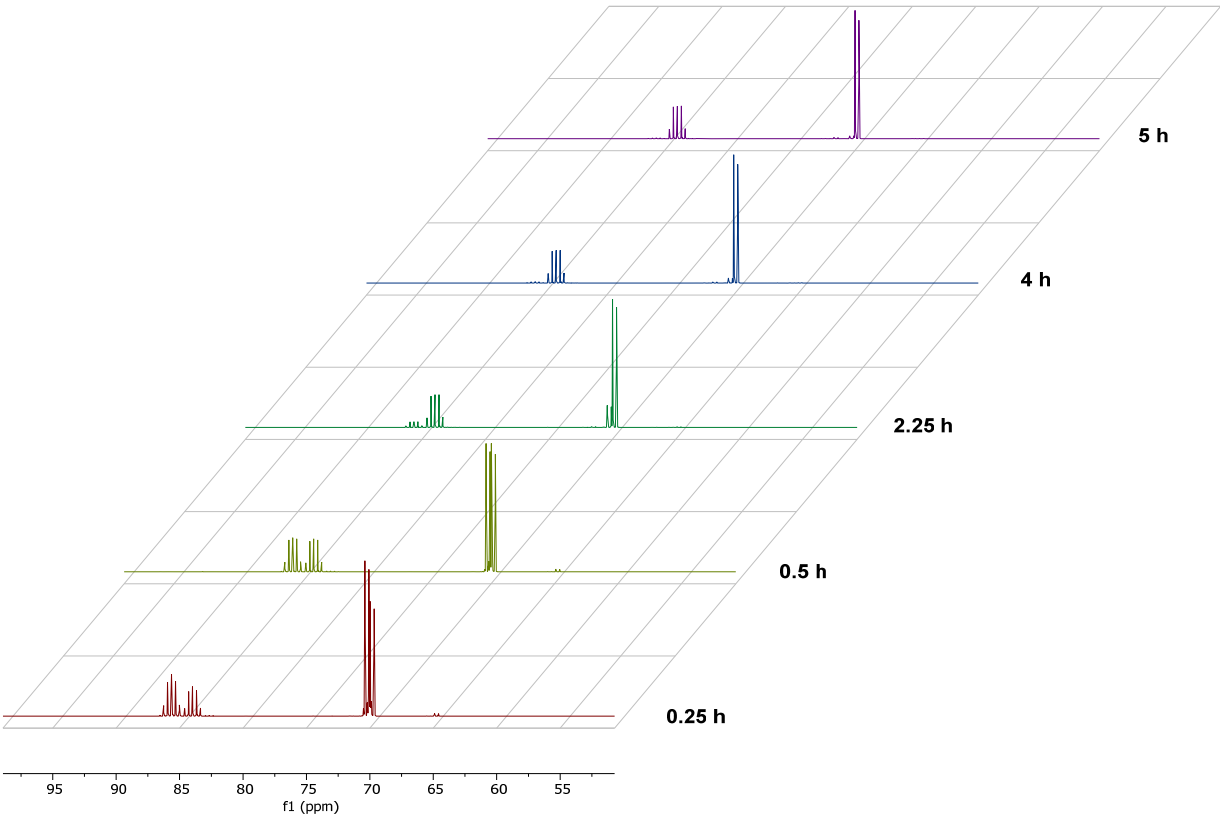


Fig. S7

Time resolved ^{19}F-NMR spectra of azidation reaction of **8** to **32**.

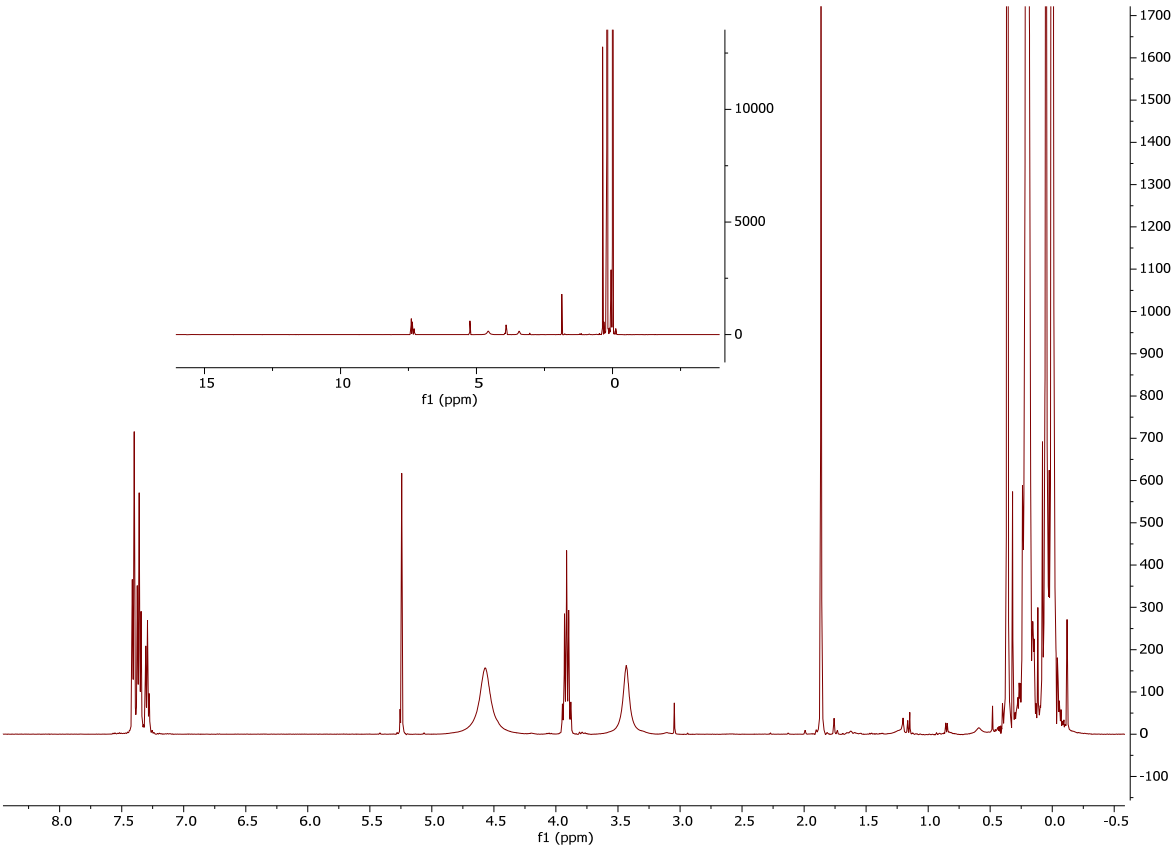


Fig. S8

^{1}H-NMR of the crude reaction mixture of the azidation reaction of **8** to **32** after 17h.

NMR spectroscopic characterisations

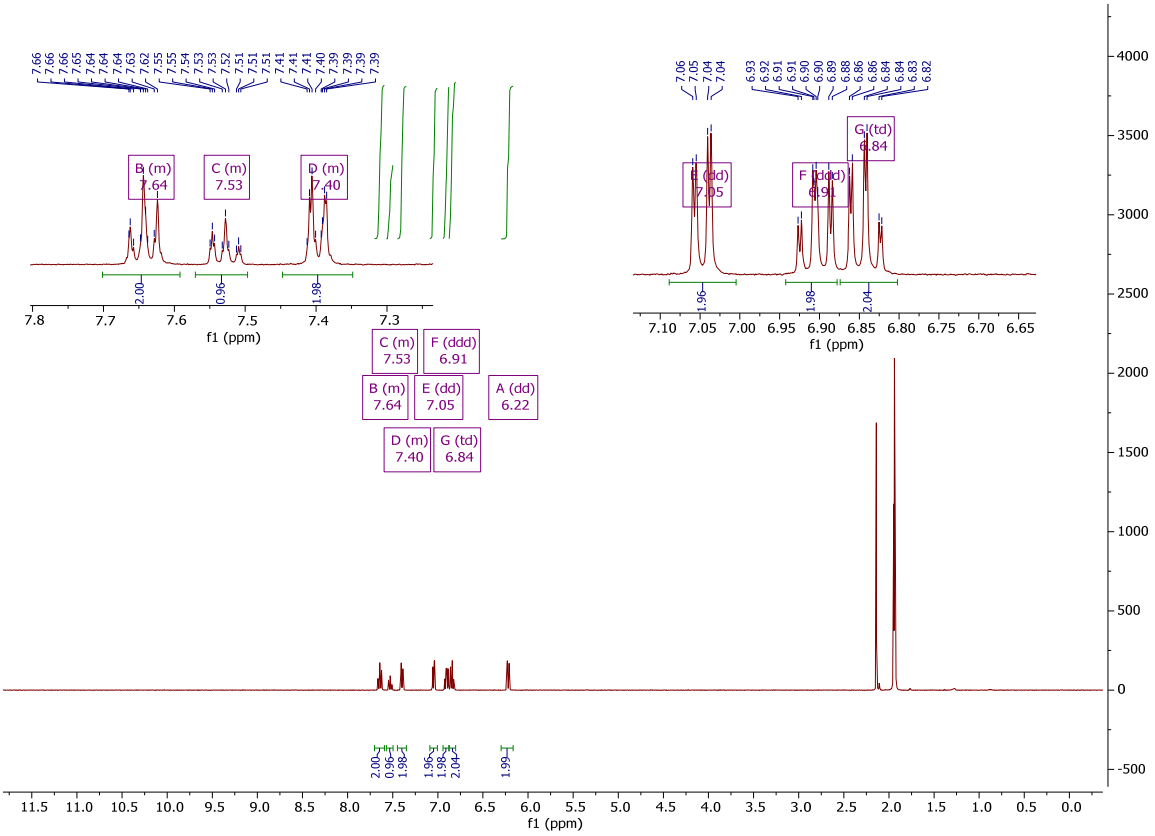


Fig. S9

^{1}H-NMR spectrum of 10-phenyl-10*H*-phenothiazine (**3**) in MeCN-d^{3}.

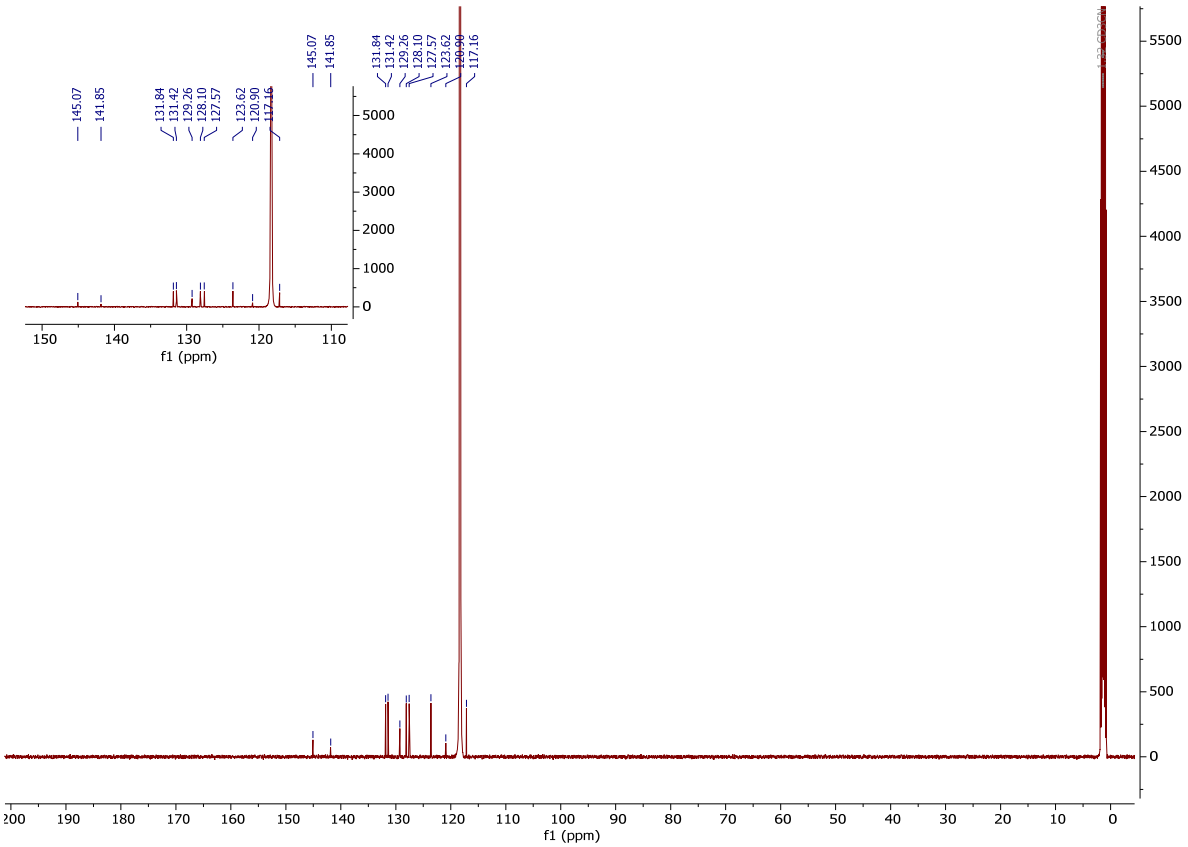


Fig. S10

^{13}C-NMR spectrum of 10-phenyl-10*H*-phenothiazine (**3**) in MeCN-d^{3}.

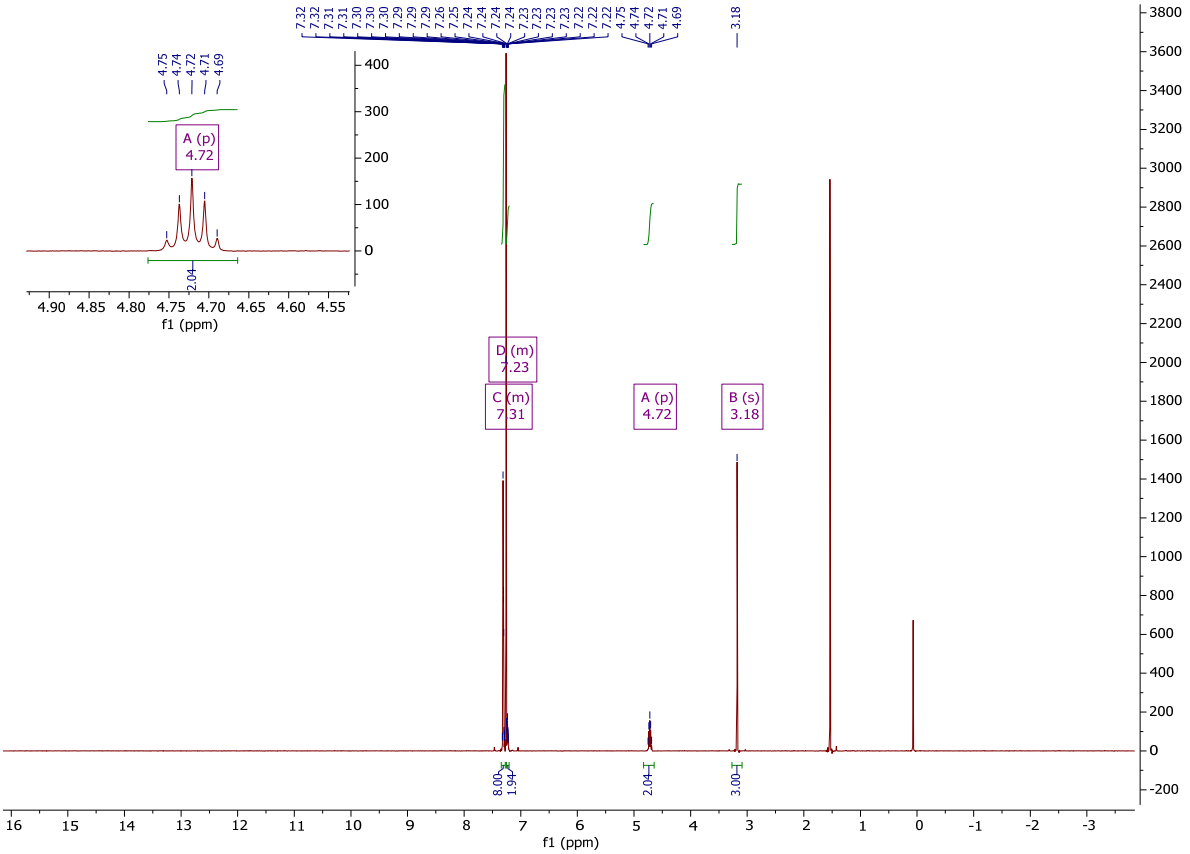


Fig. S11

^{1}H-NMR spectrum of pentafluoro(2-methoxy-2,2-diphenylethyl)-λ^{6}-sulfane (**9**) in $CDCl_3$.

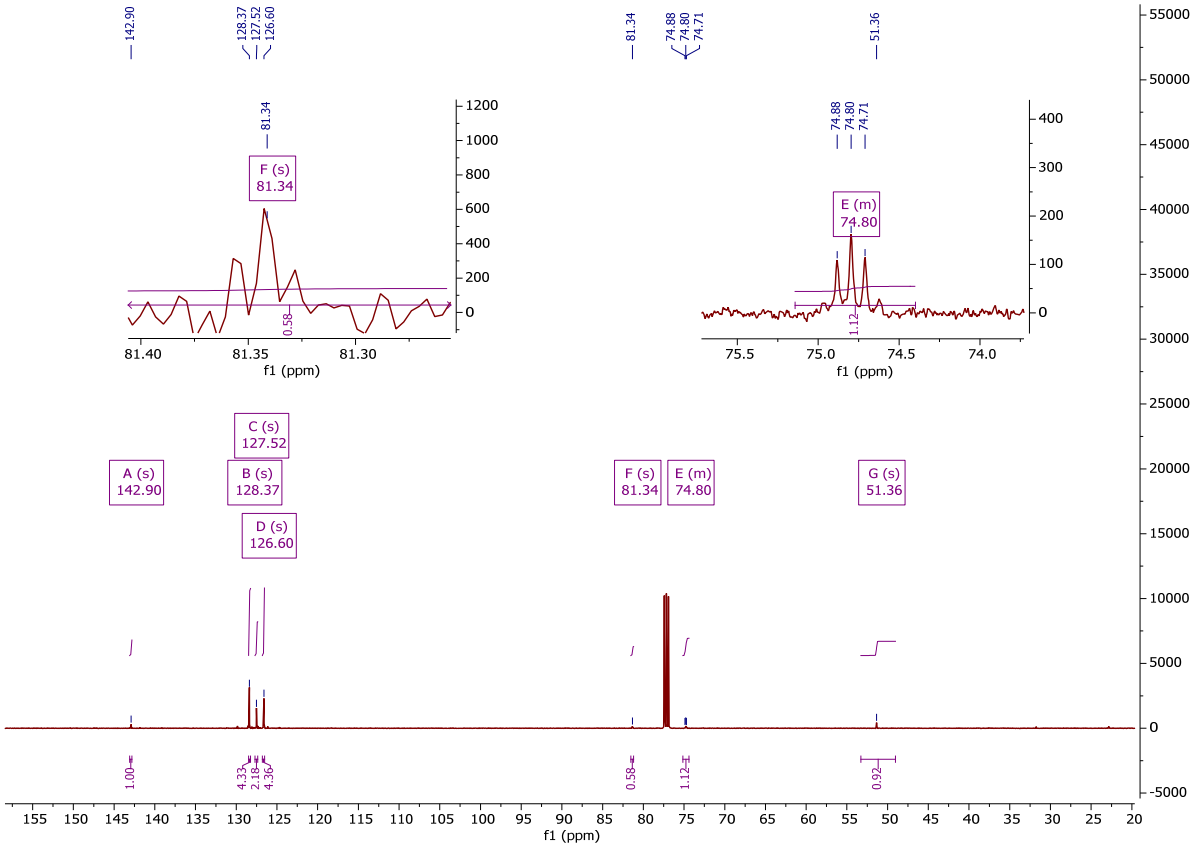


Fig. S12

^{13}C-NMR spectrum of pentafluoro(2-methoxy-2,2-diphenylethyl)-λ^6-sulfane (**9**) in $CDCl_3$.

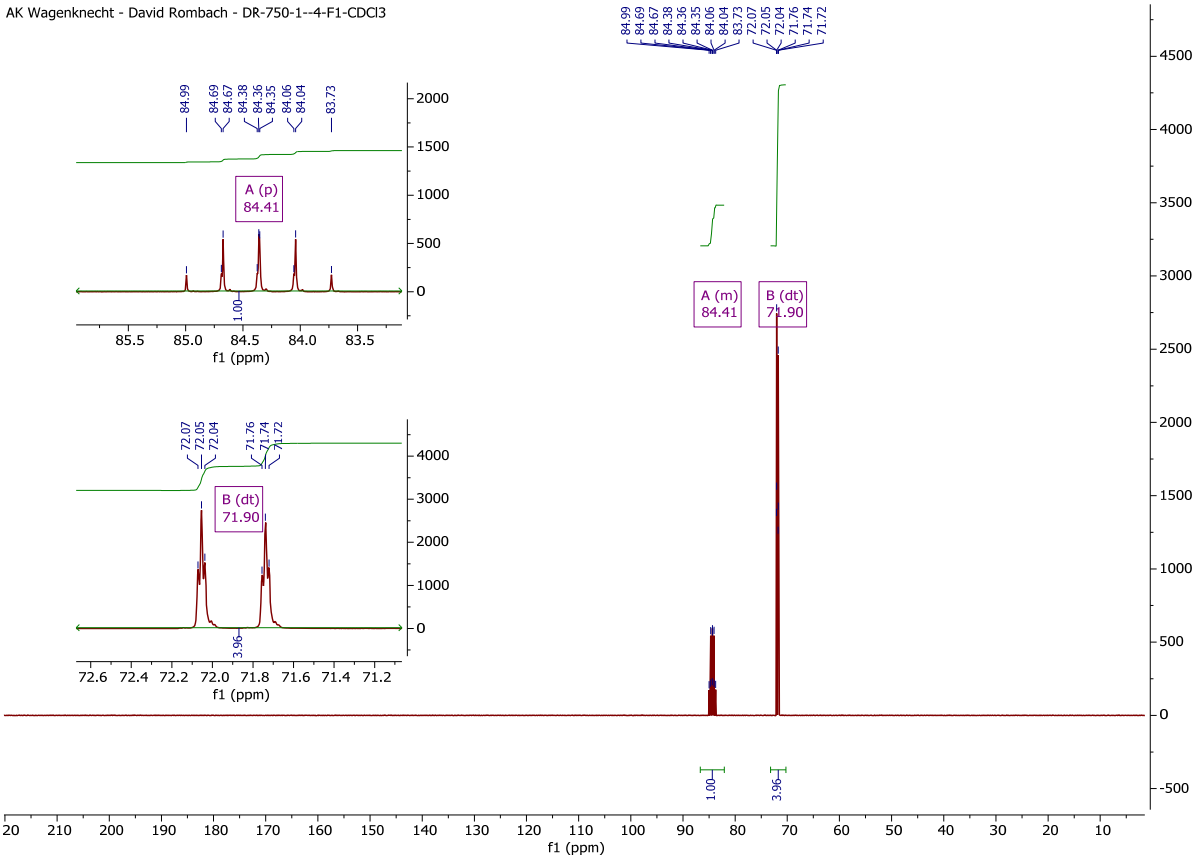


Fig. S13

^{19}F-NMR spectrum of pentafluoro(2-methoxy-2,2-diphenylethyl)-λ^6-sulfane (**9**) in $CDCl_3$

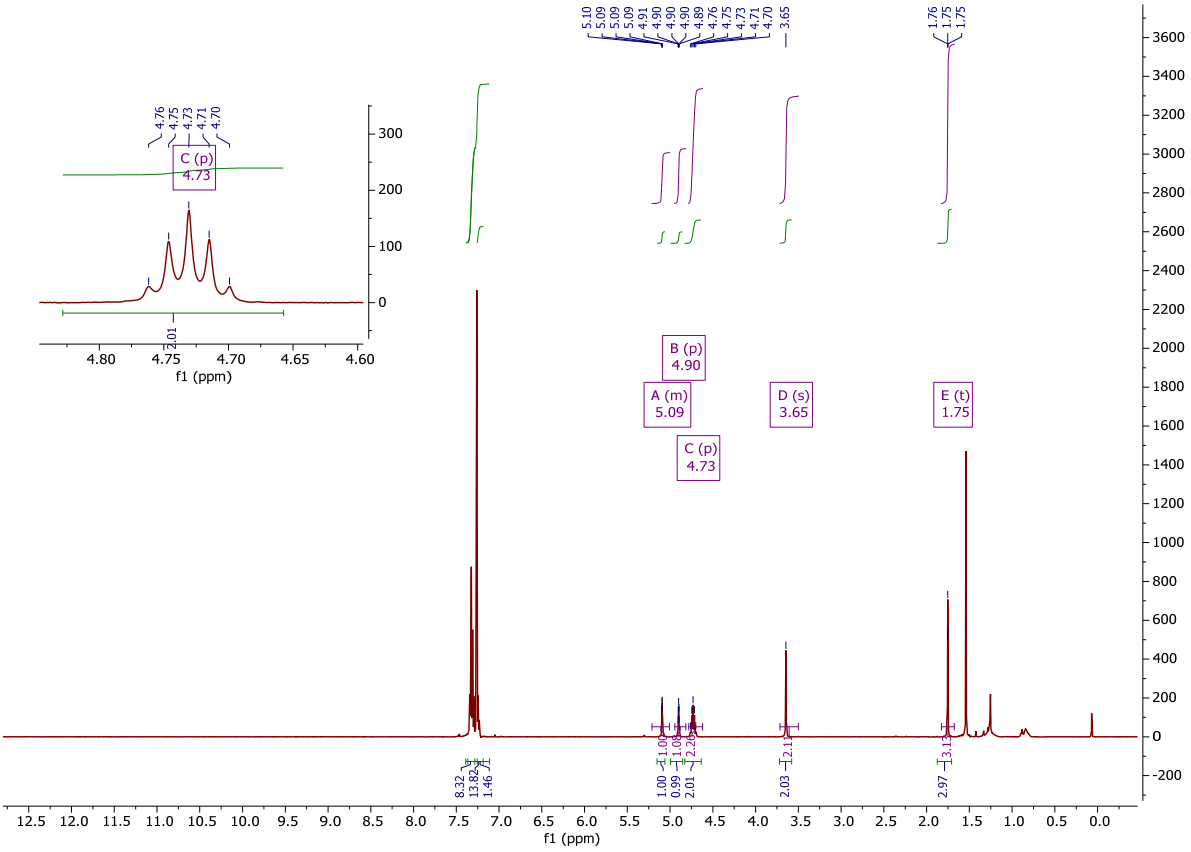


Fig. S14

^{1}H - NMR spectrum of (2,2-diphenyl-2-(prop-1-en-2-yloxy)ethyl)pentafluoro-λ^{6}-sulfane (**10**) in $CDCl_3$.

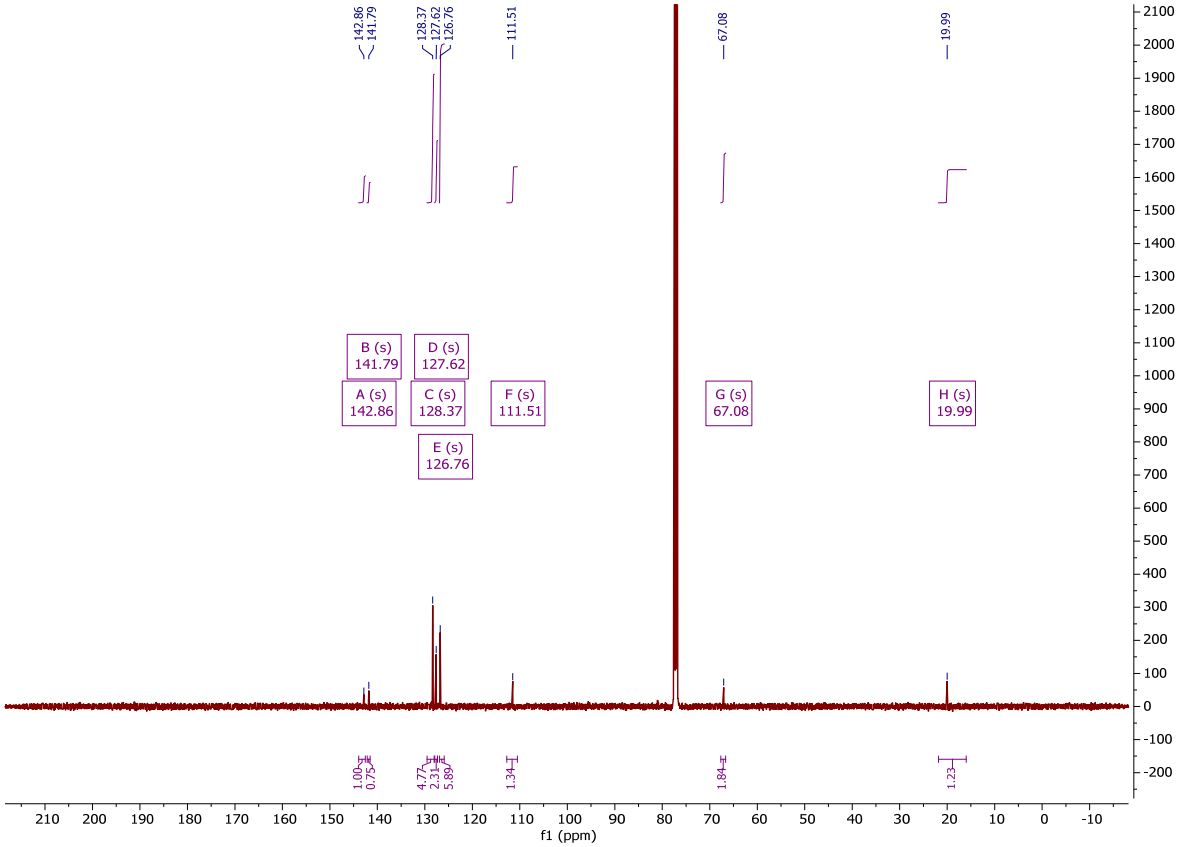


Fig. S15

^{13}C - NMR spectrum of (2,2-diphenyl-2-(prop-1-en-2-yloxy)ethyl)pentafluoro-λ^6-sulfane (**10**) in $CDCl_3$.

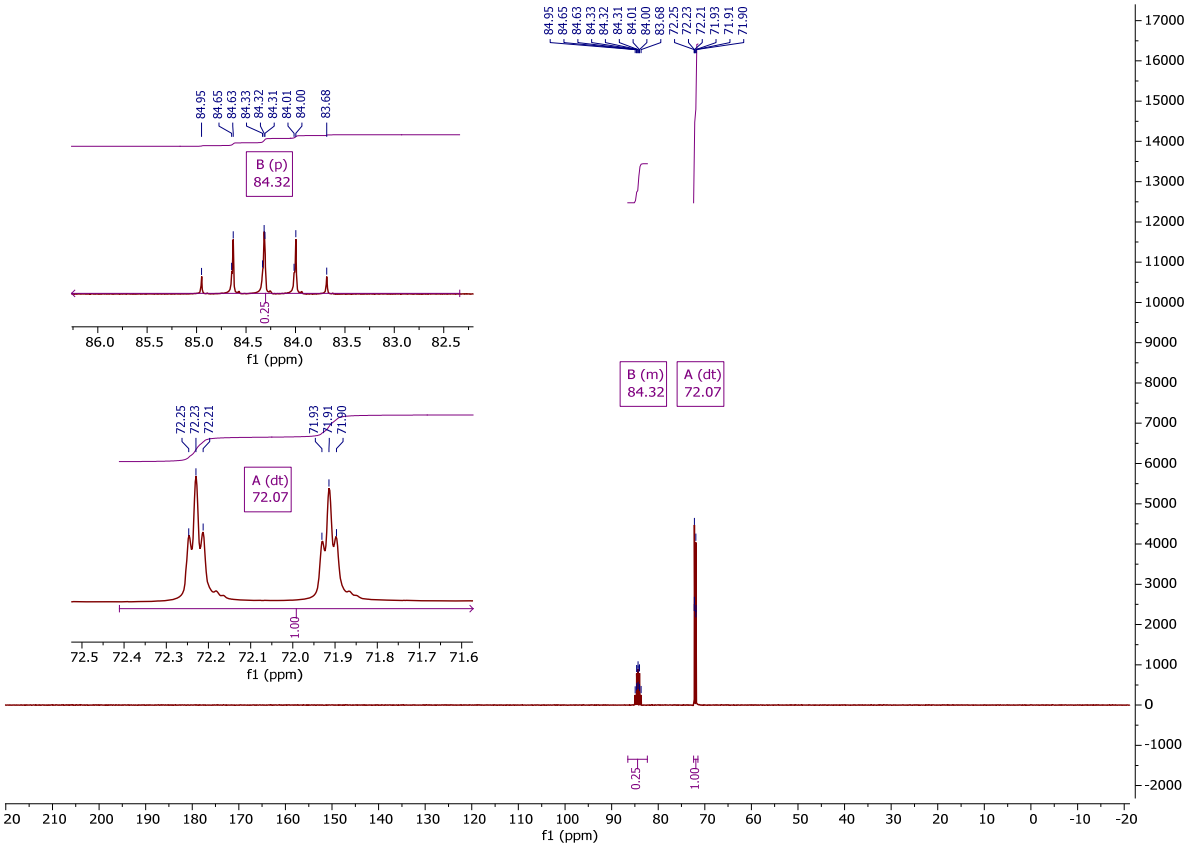


Fig. S16

^{19}F-NMR spectrum of (2,2-diphenyl-2-(prop-1-en-2-yloxy)ethyl)pentafluoro-λ^6-sulfane (**10**) in $CDCl_3$.

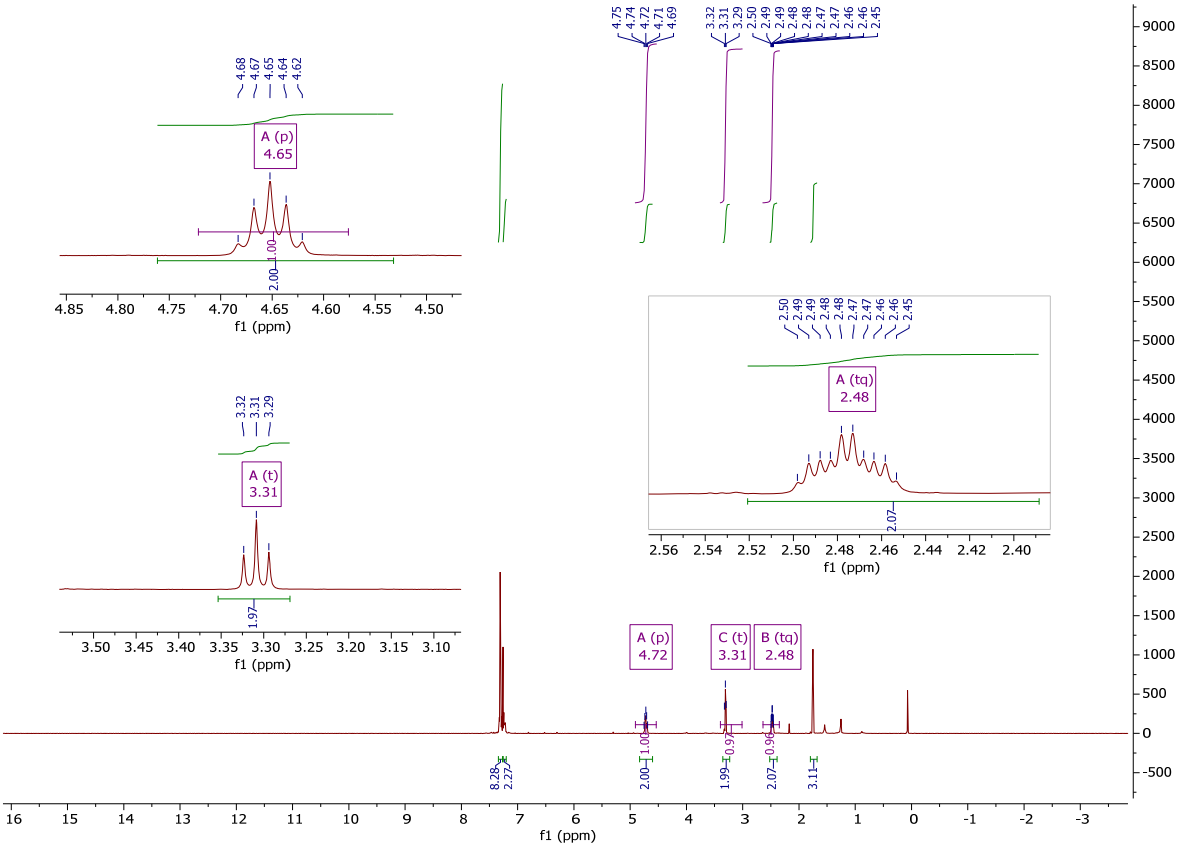


Fig. S17

^{1}H-NMR spectrum of pentafluoro(2-(pent-3-yn-1-yloxy)-2,2-diphenylethyl)-λ^{6}-sulfane (**11**) in $CDCl_3$.

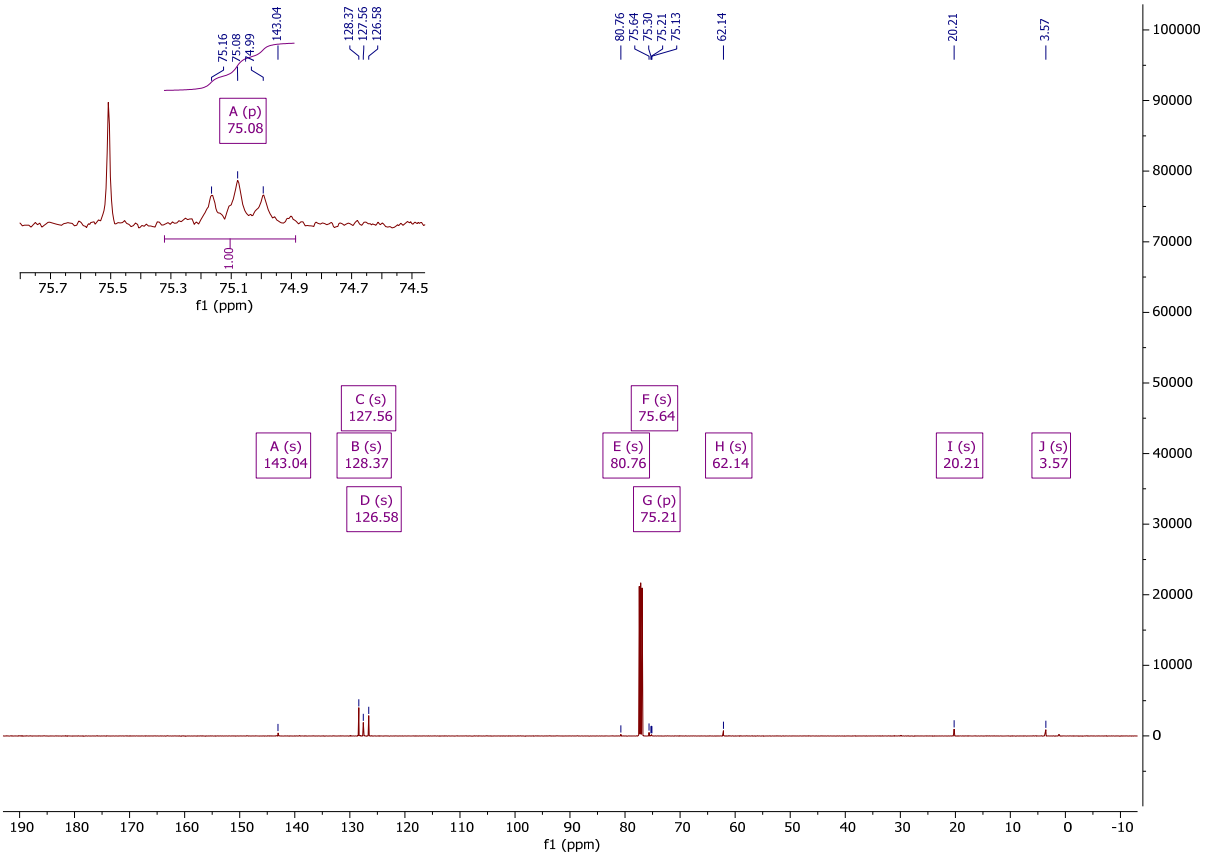


Fig. S18

^{13}C-NMR spectrum of pentafluoro(2-(pent-3-yn-1-yloxy)-2,2-diphenylethyl)-λ^6-sulfane (**11**) in $CDCl_3$.

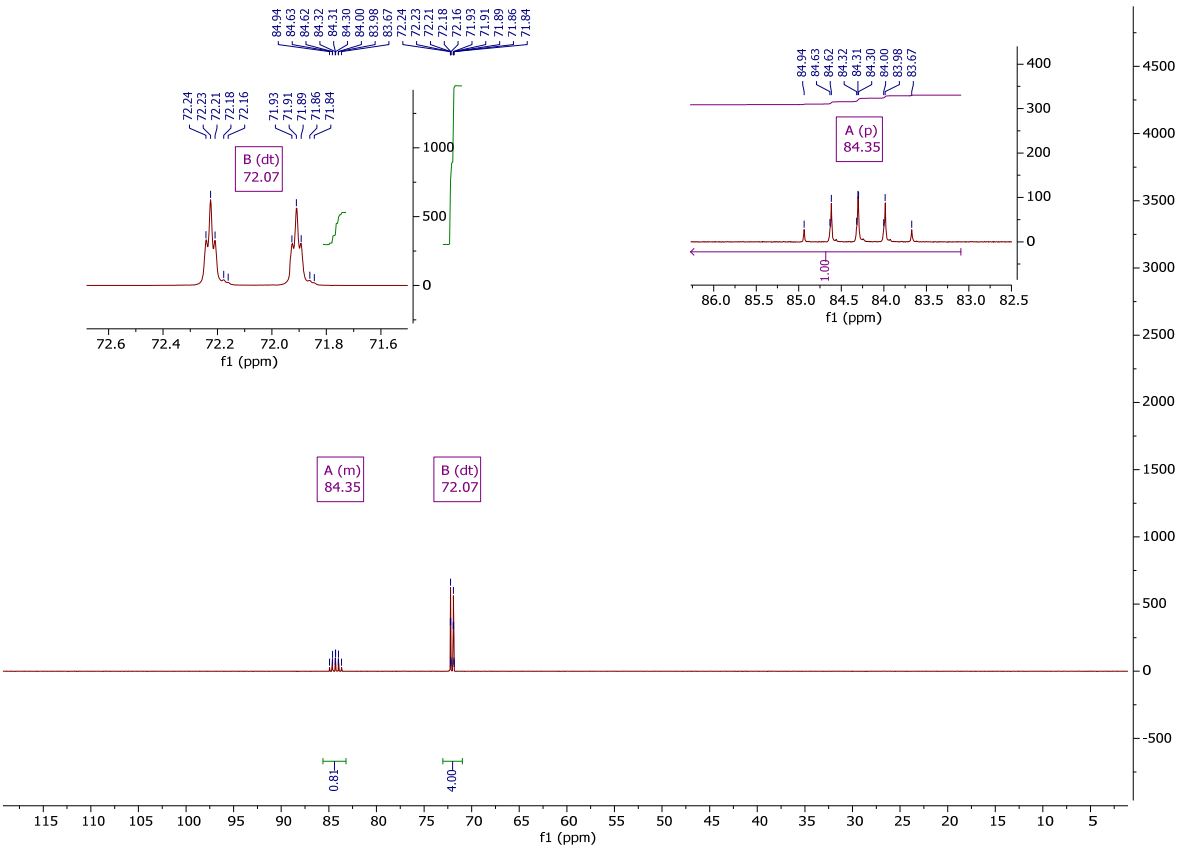


Fig. S19

^{19}F-NMR spectrum of pentafluoro(2-(pent-3-yn-1-yloxy)-2,2-diphenylethyl)-λ^6-sulfane (**11**) in $CDCl_3$.

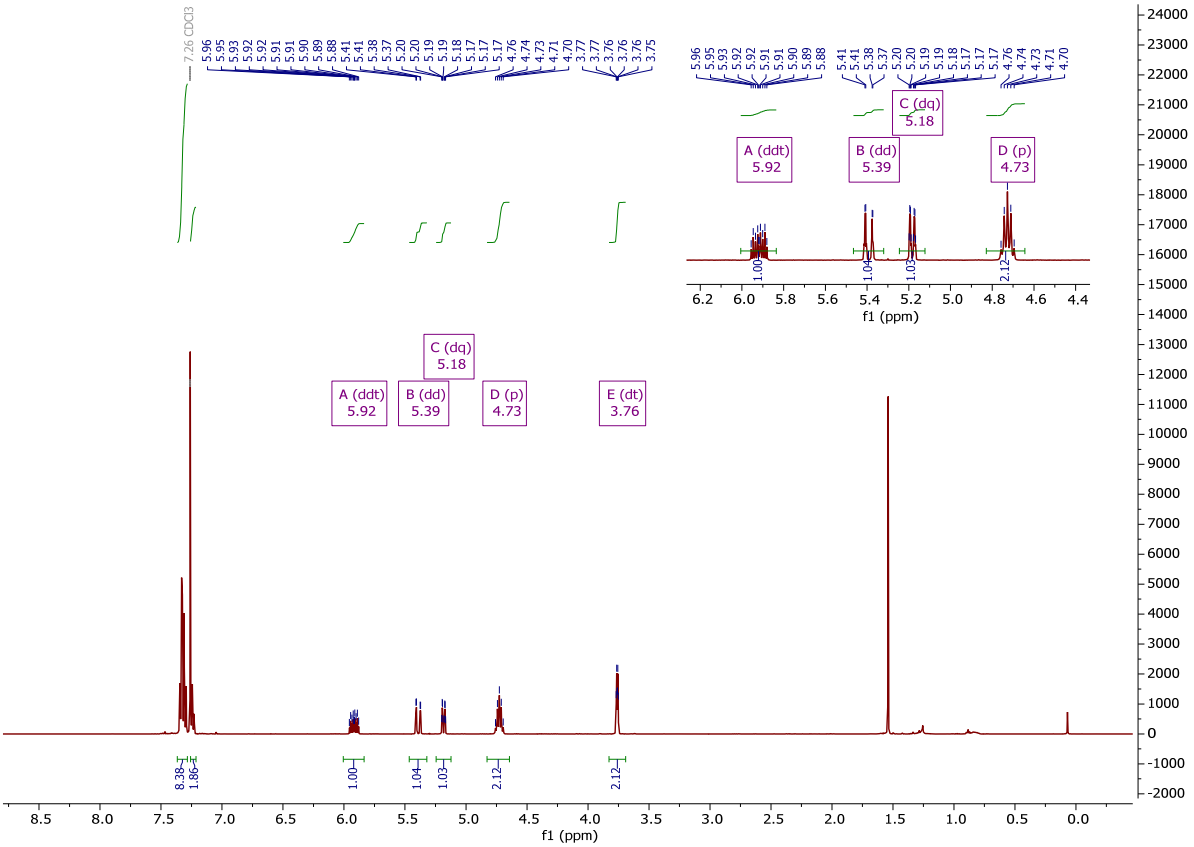


Fig. S20

^{1}H-NMR spectrum of (2-(allyloxy)-2,2-diphenylethyl)pentafluoro-λ^{6}-sulfane (**12**) in $CDCl_3$.

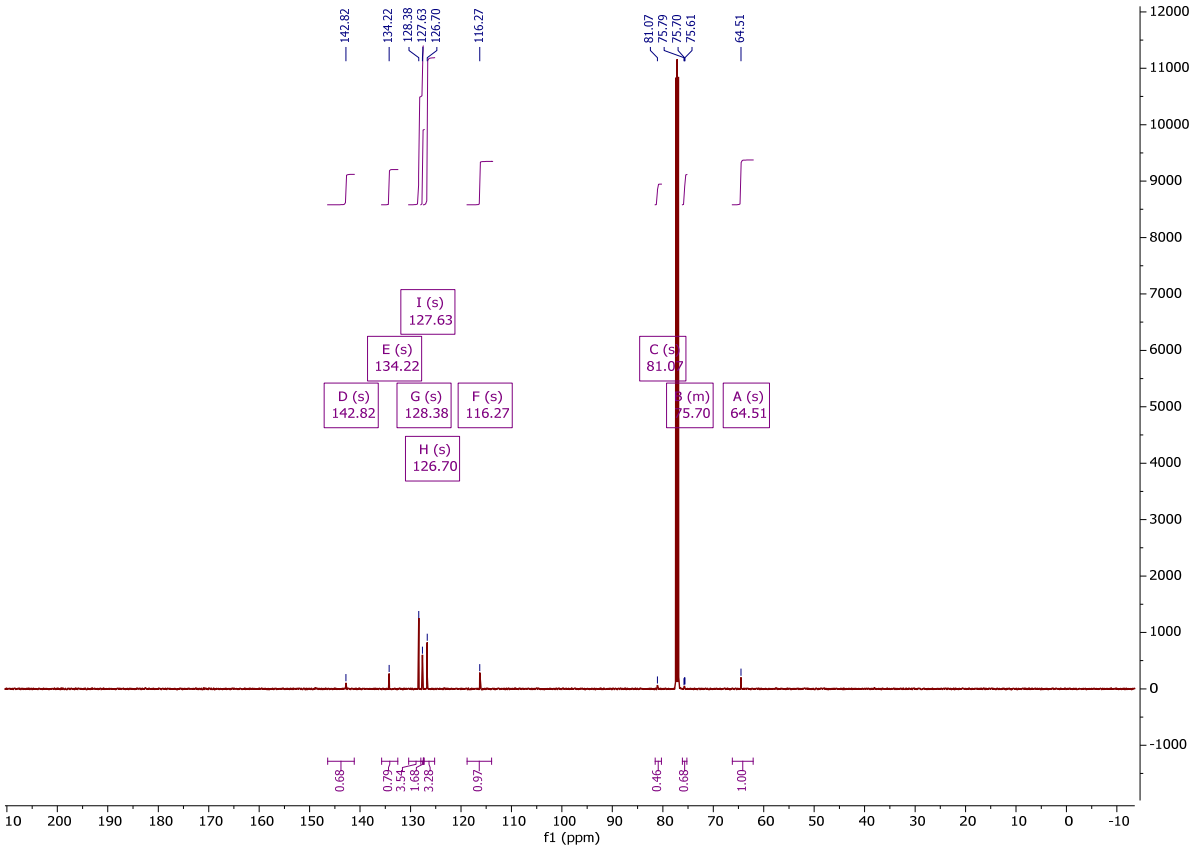


Fig. S21

^{13}C-NMR spectrum of (2-(allyloxy)-2,2-diphenylethyl)pentafluoro-λ^6-sulfane (**12**) in $CDCl_3$.

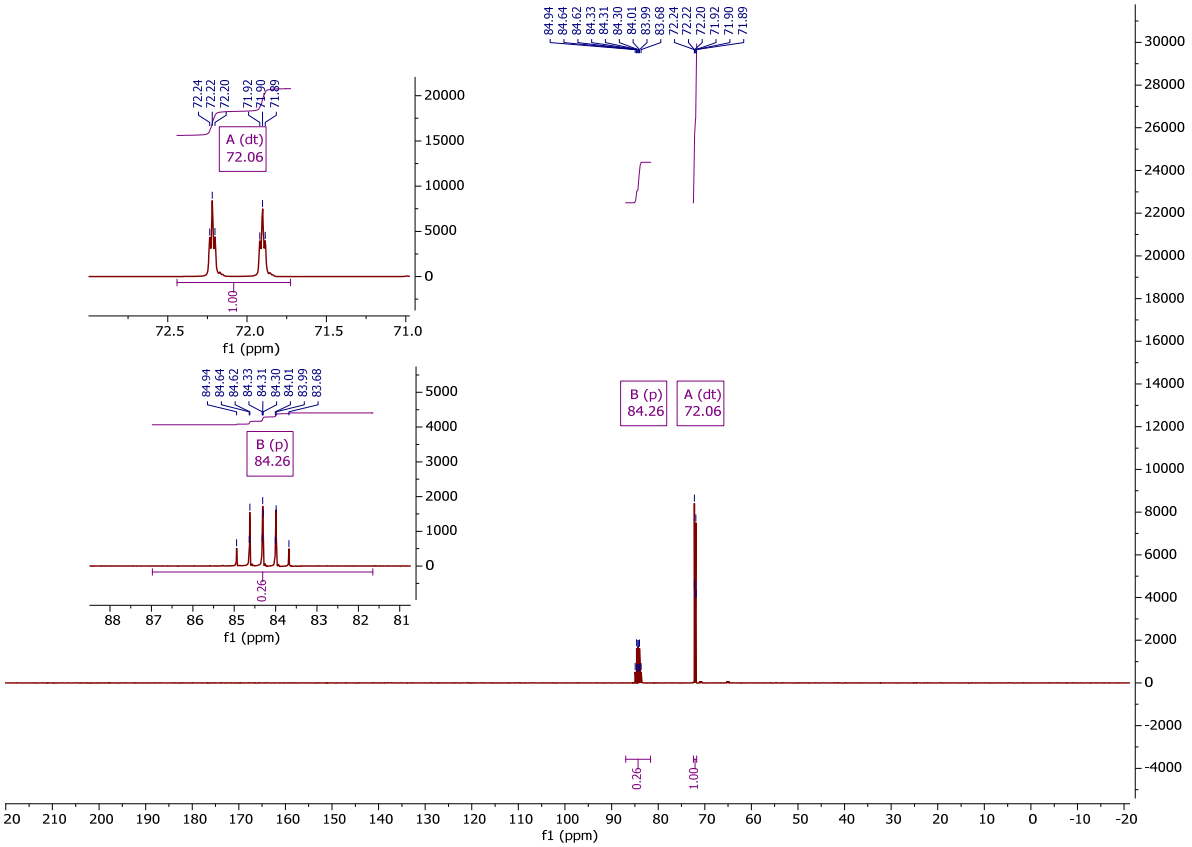


Fig. S22

^{19}F-NMR spectrum of (2-(allyloxy)-2,2-diphenylethyl)pentafluoro-λ^6-sulfane (**12**) in $CDCl_3$.

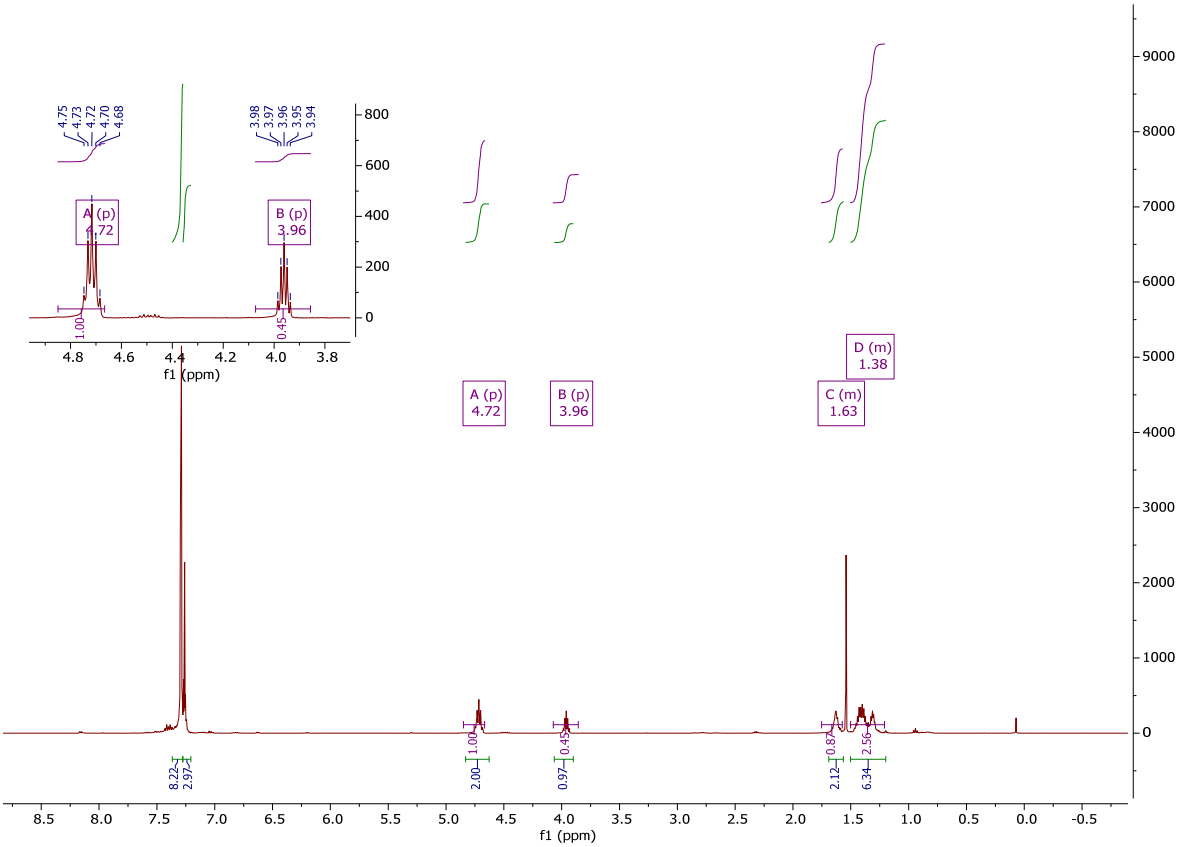


Fig. S23

^{1}H-NMR spectrum of (2-(cyclopentyloxy)-2,2-diphenylethyl)pentafluoro-λ^{6}-sulfane (**13**) in $CDCl_3$.

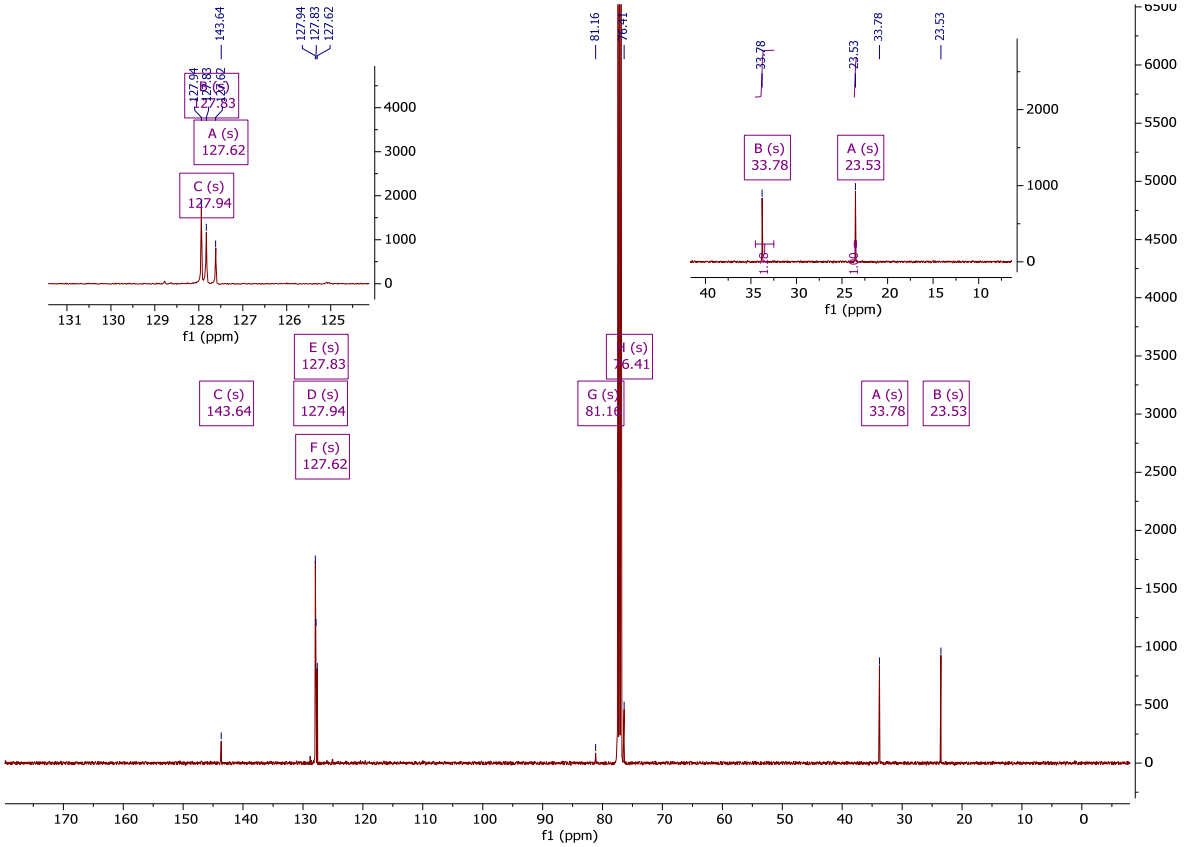


Fig. S24

^{13}C-NMR spectrum of (2-(cyclopentyloxy)-2,2-diphenylethyl)pentafluoro-λ^6-sulfane (**13**) in $CDCl_3$.

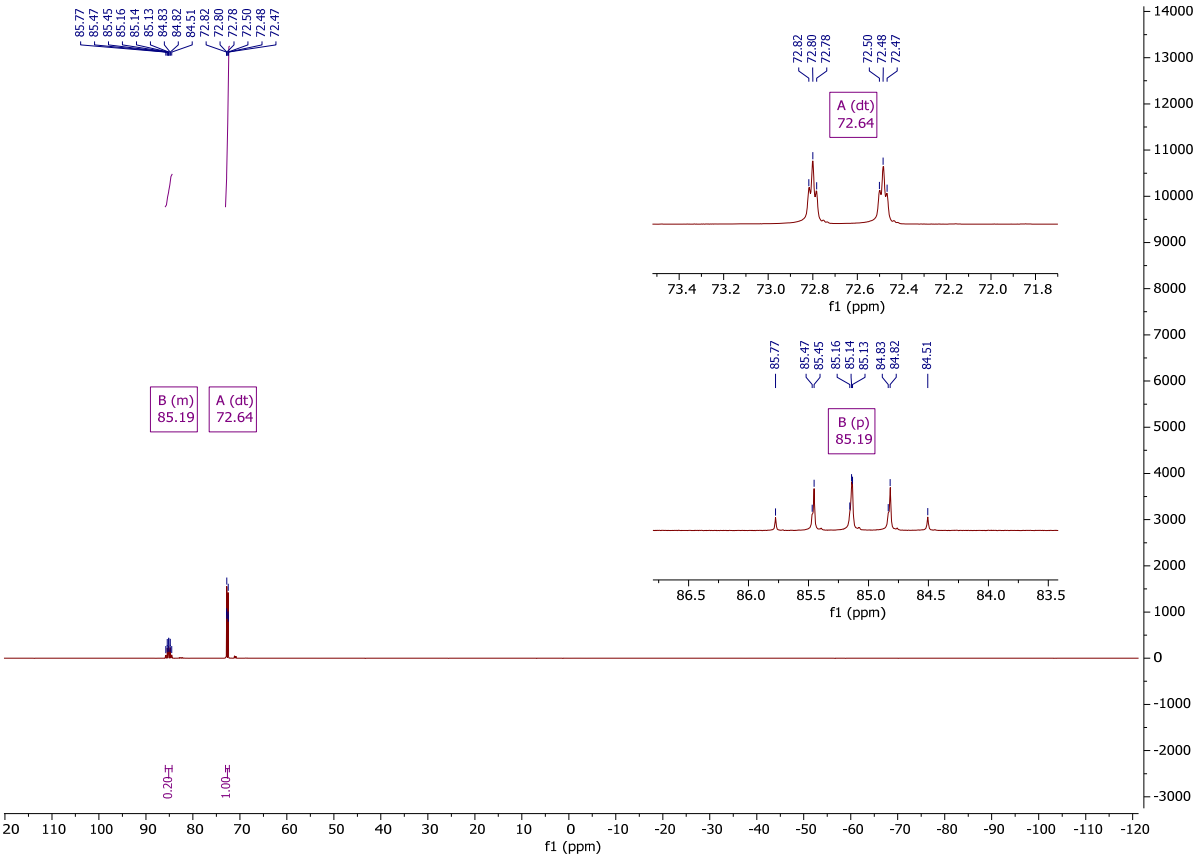


Fig. S25

^{19}F-NMR spectrum of (2-(cyclopentyloxy)-2,2-diphenylethyl)pentafluoro-λ^6-sulfane (**13**) in $CDCl_3$.

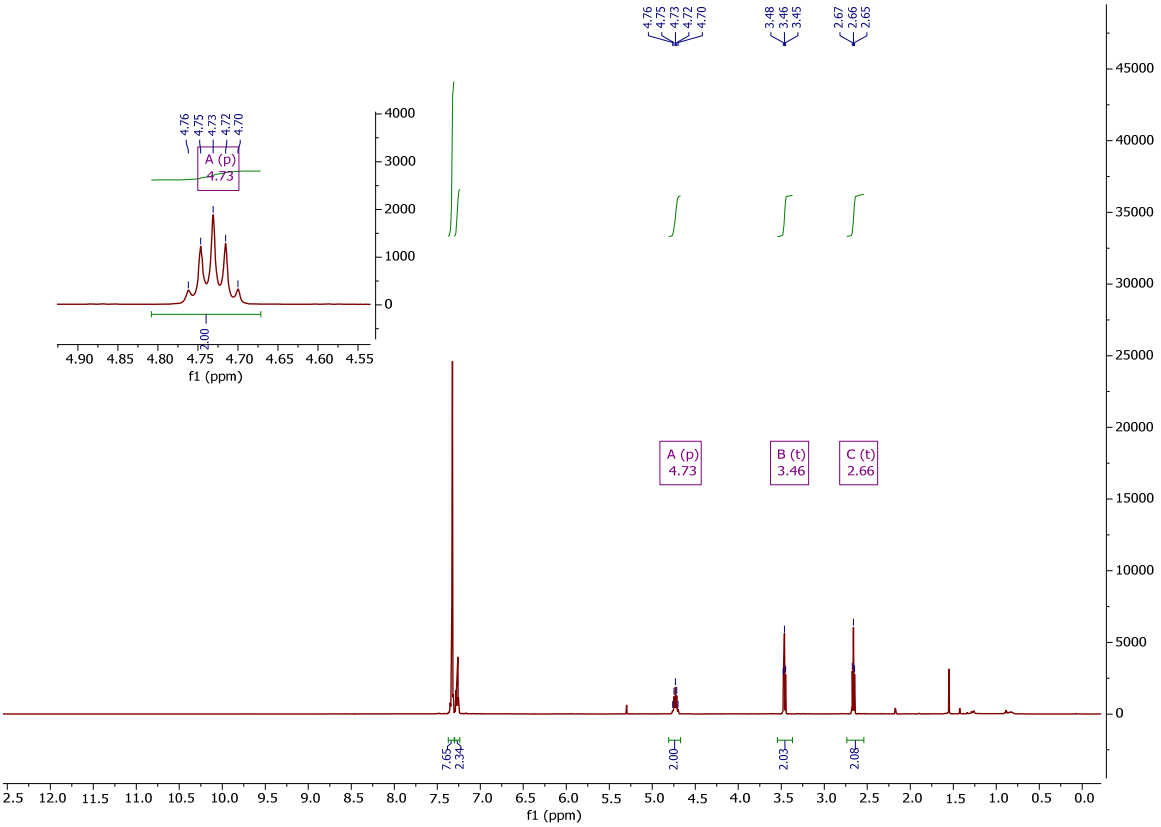


Fig. S26

^{1}H-NMR spectrum of 3-(2-(pentafluoro-λ^{6}-sulfaneyl)-1,1-diphenylethoxy)propanenitrile (**14**) in $CDCl_3$.

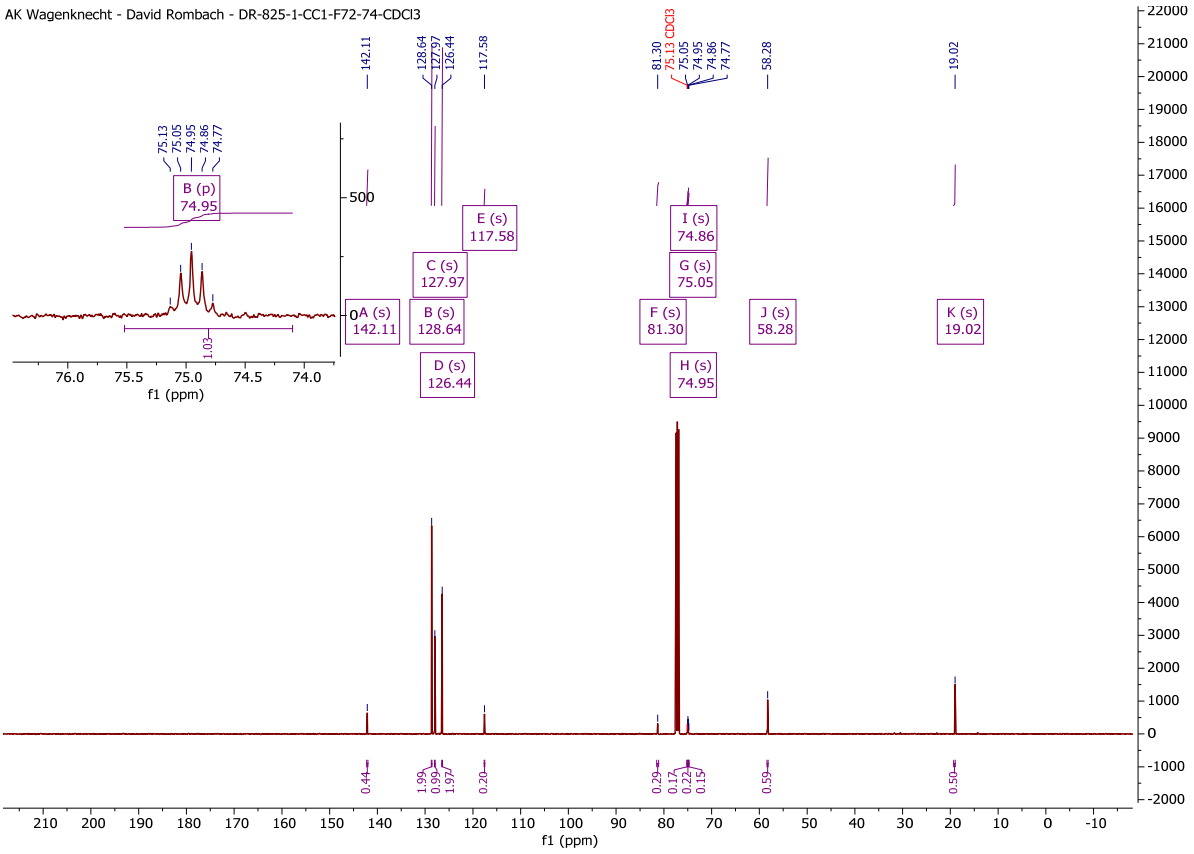


Fig. S27

^{13}C-NMR spectrum of 3-(2-(pentafluoro-λ^6-sulfaneyl)-1,1-diphenylethoxy)propanenitrile (**14**) in $CDCl_3$.

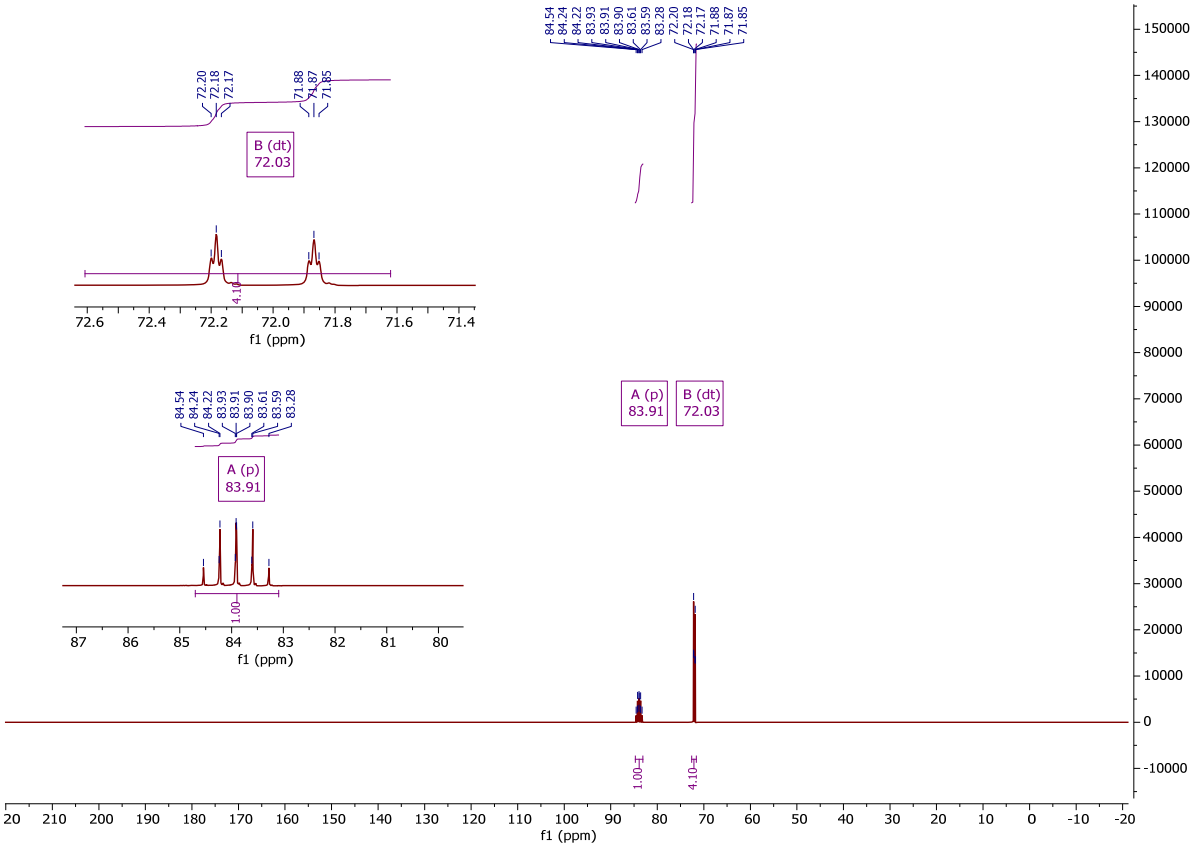


Fig. S28

^{19}F-NMR spectrum of 3-(2-(pentafluoro-λ^6-sulfaneyl)-1,1-diphenylethoxy)propanenitrile (**14**) in $CDCl_3$.

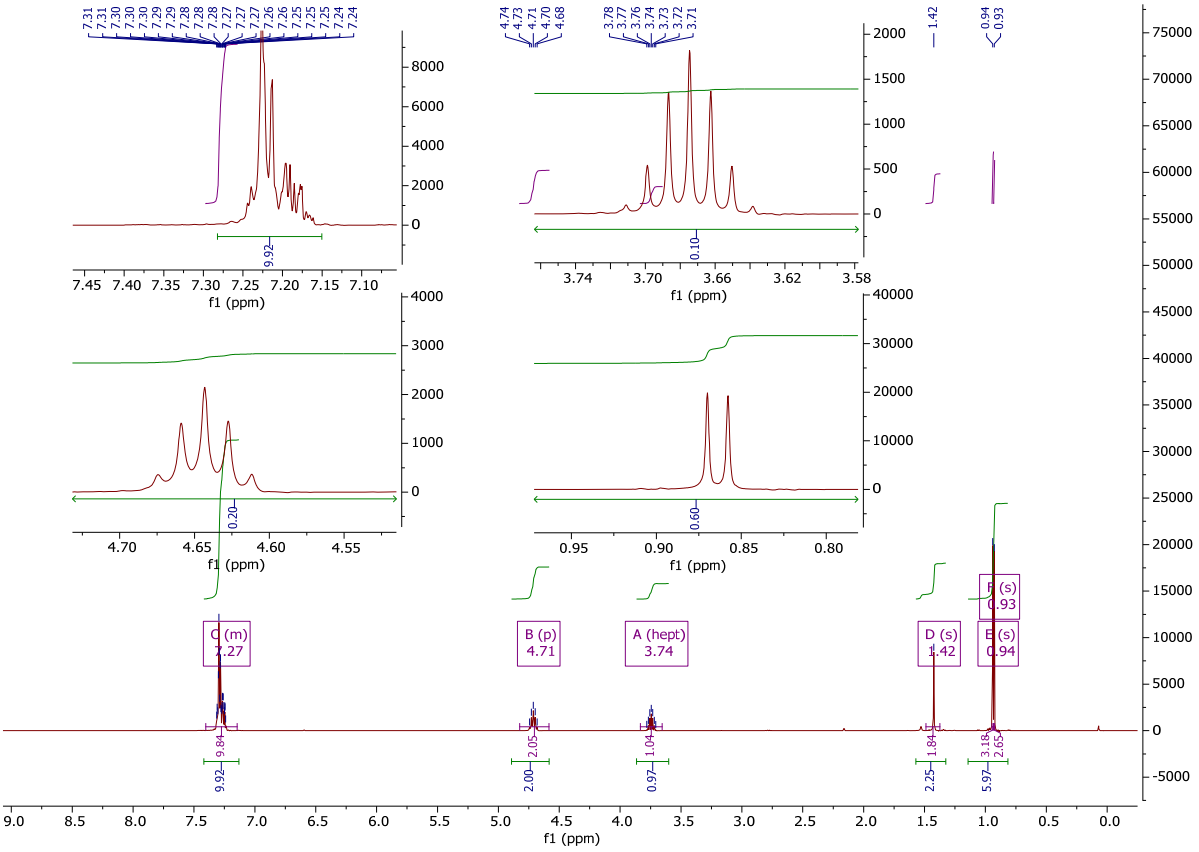


Fig. S29

^{1}H-NMR spectrum of pentafluoro-(2-isopropoxy-2,2-diphenylethyl)-λ^{6}-sulfane (**15**) in $CDCl_3$.

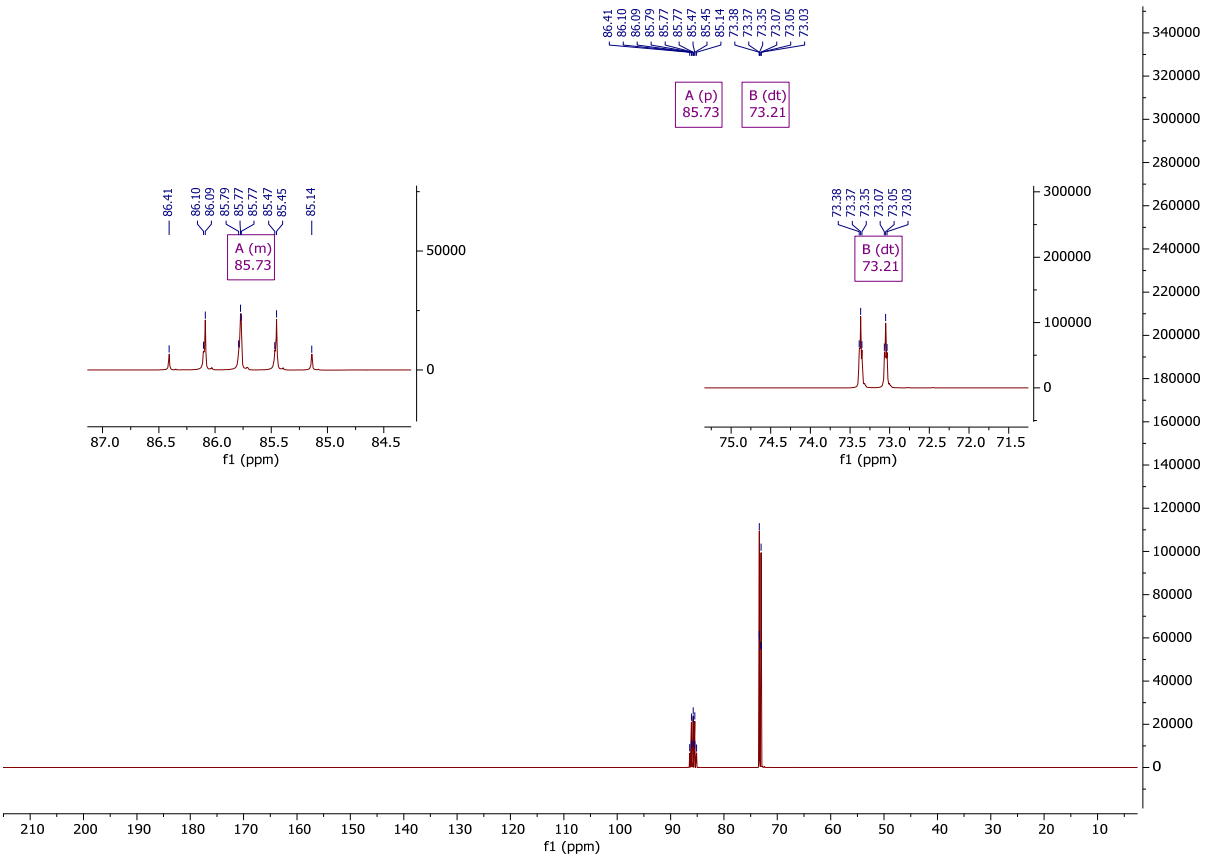


Fig. S30

^{19}F-NMR spectrum of pentafluoro-(2-isopropoxy-2,2-diphenylethyl)-λ^6-sulfane (**15**) in $CDCl_3$.

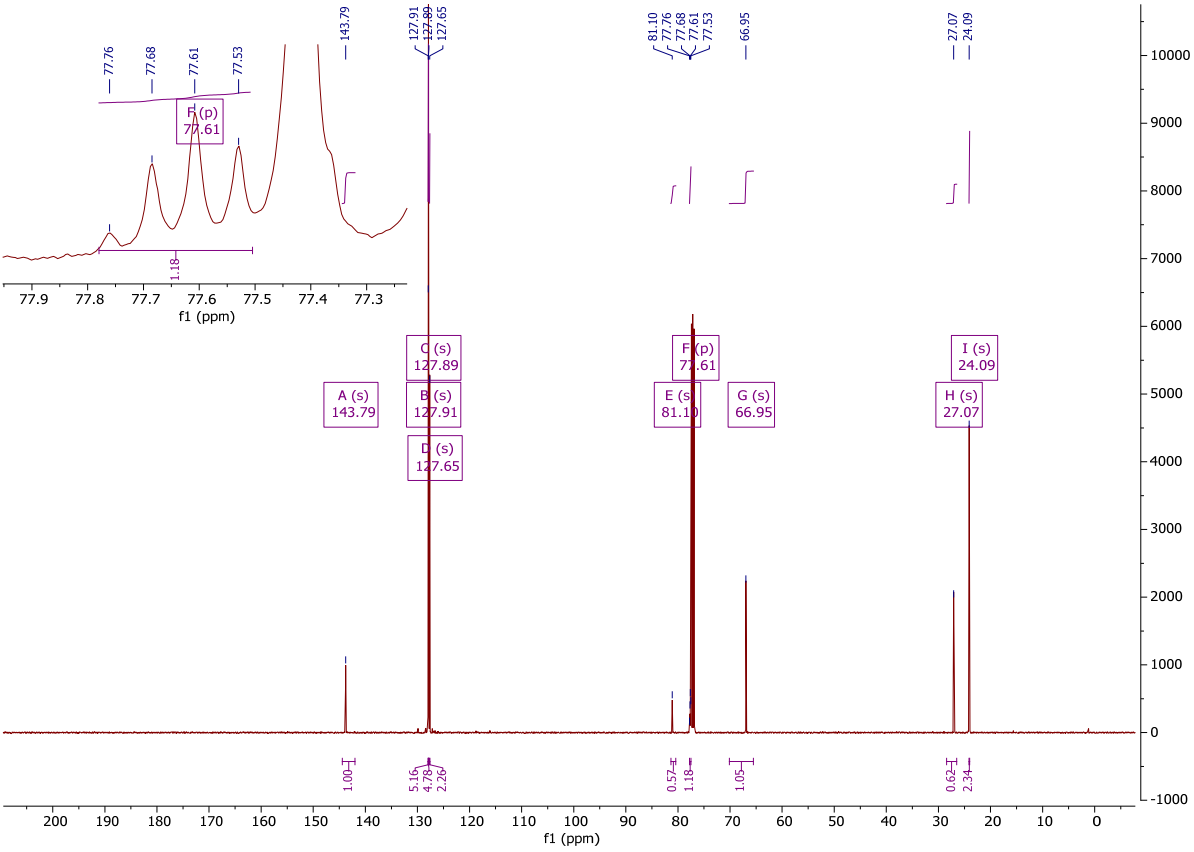


Fig. S31

^{13}C-NMR spectrum of pentafluoro-(2-isopropoxy-2,2-diphenylethyl)-λ^6-sulfane (**15**) in $CDCl_3$.

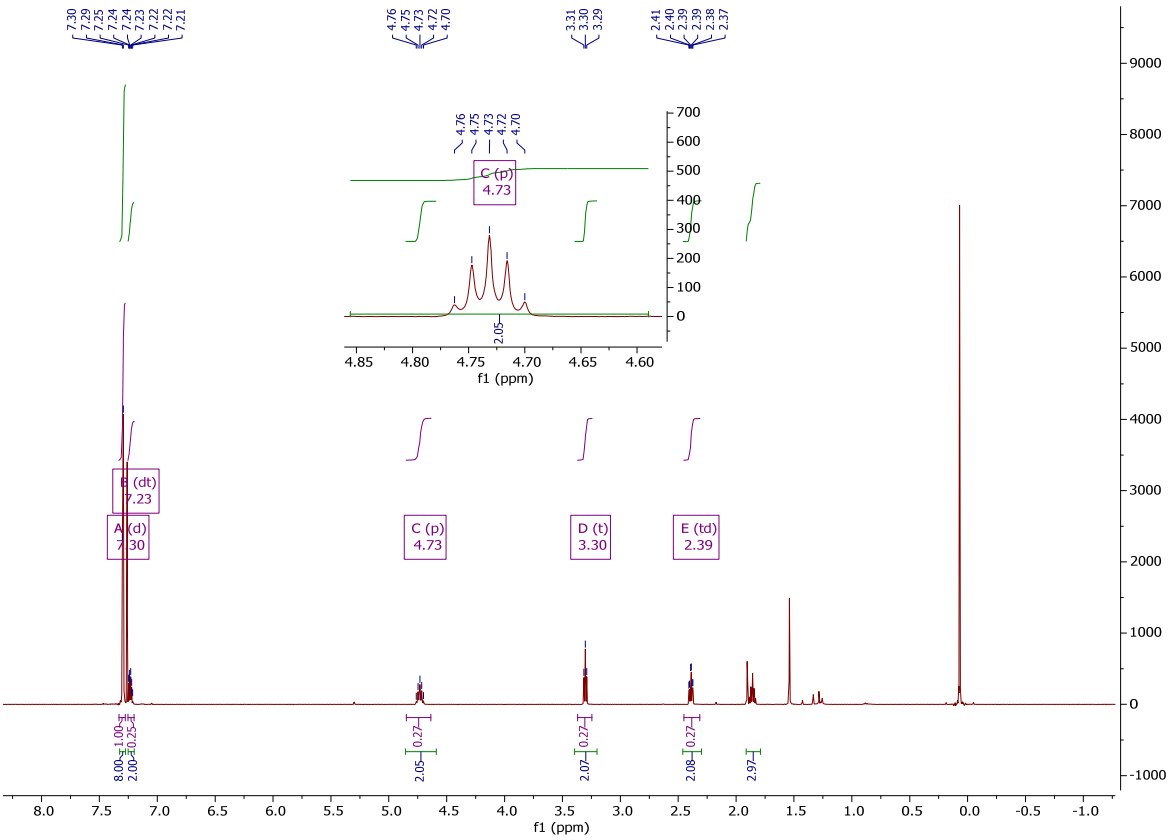


Fig. S32

^{1}H-NMR spectrum of pentafluoro(2-(pent-4-yn-1-yloxy)-2,2-diphenylethyl)-λ^{6}-sulfane (**16**) in $CDCl_3$.

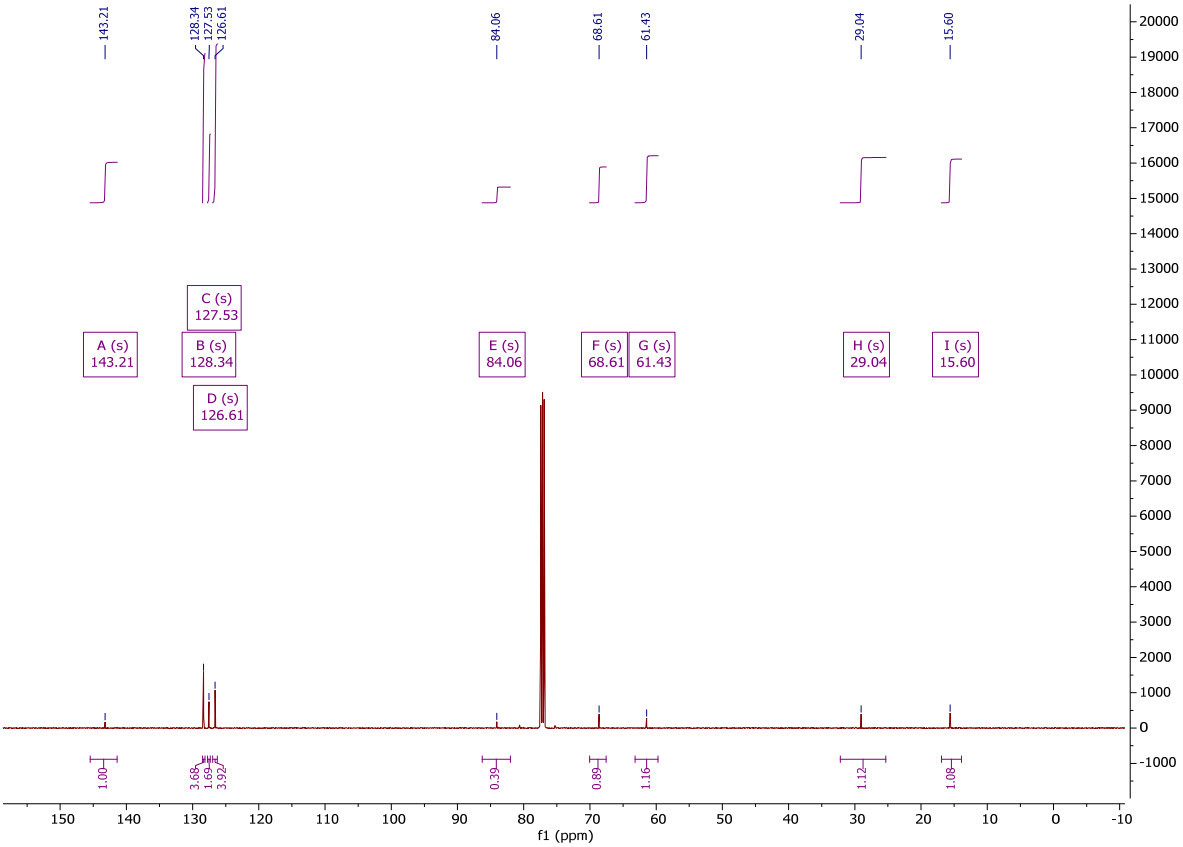


Fig. S33

^{13}C-NMR spectrum of pentafluoro(2-(pent-4-yn-1-yloxy)-2,2-diphenylethyl)-λ^6-sulfane (**16**) in $CDCl_3$.

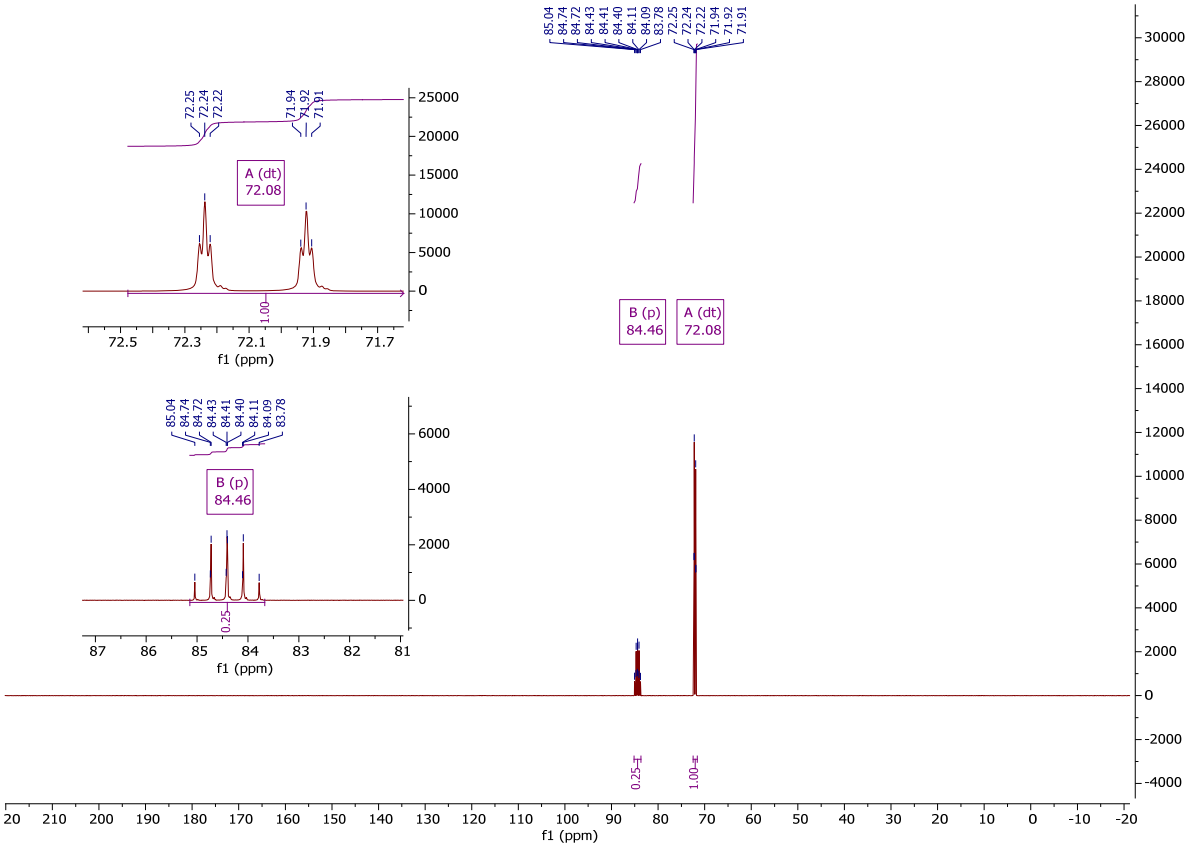


Fig. S34

^{19}F-NMR spectrum of pentafluoro(2-(pent-4-yn-1-yloxy)-2,2-diphenylethyl)-λ^6-sulfane (**16**) in $CDCl_3$.

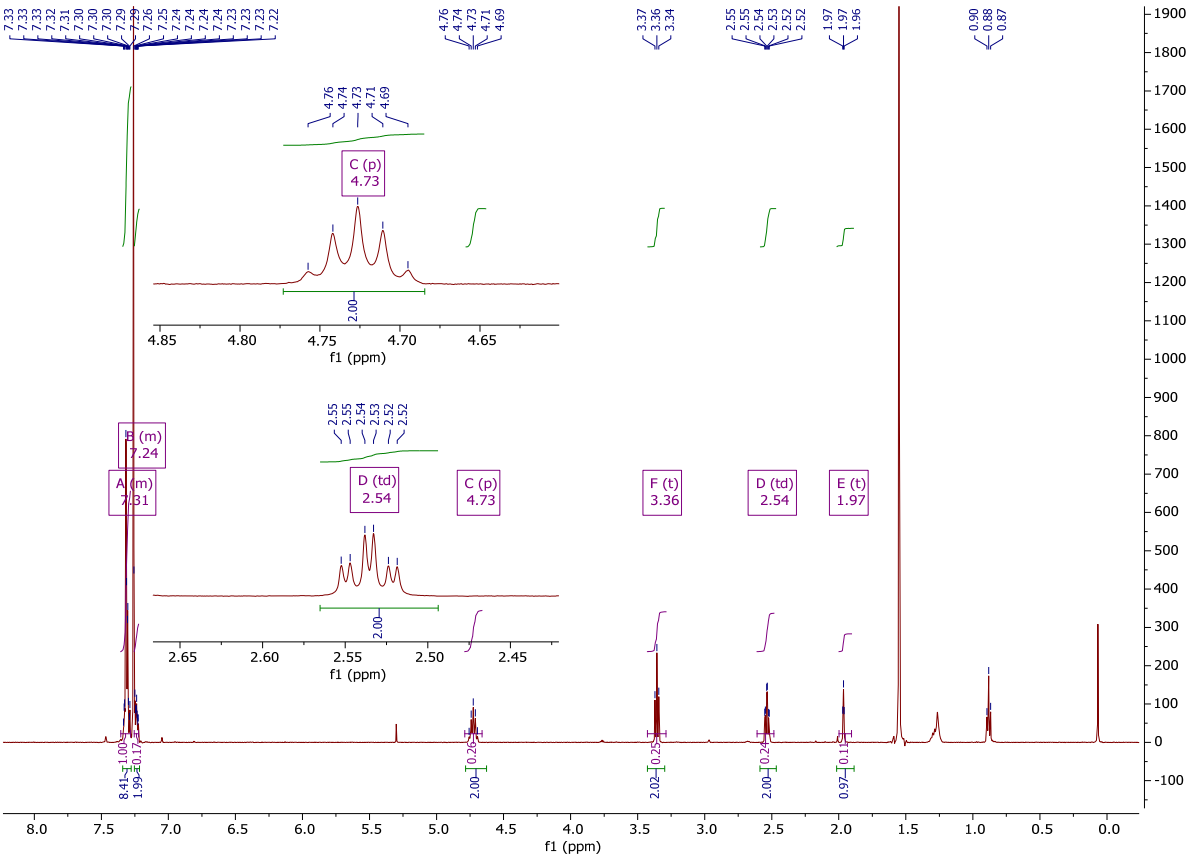


Fig. S35

^{1}H-NMR spectrum of (2-(but-3-yn-1-yloxy)-2,2-diphenylethyl)pentafluoro-λ^{6}-sulfane (**17**) in $CDCl_3$.

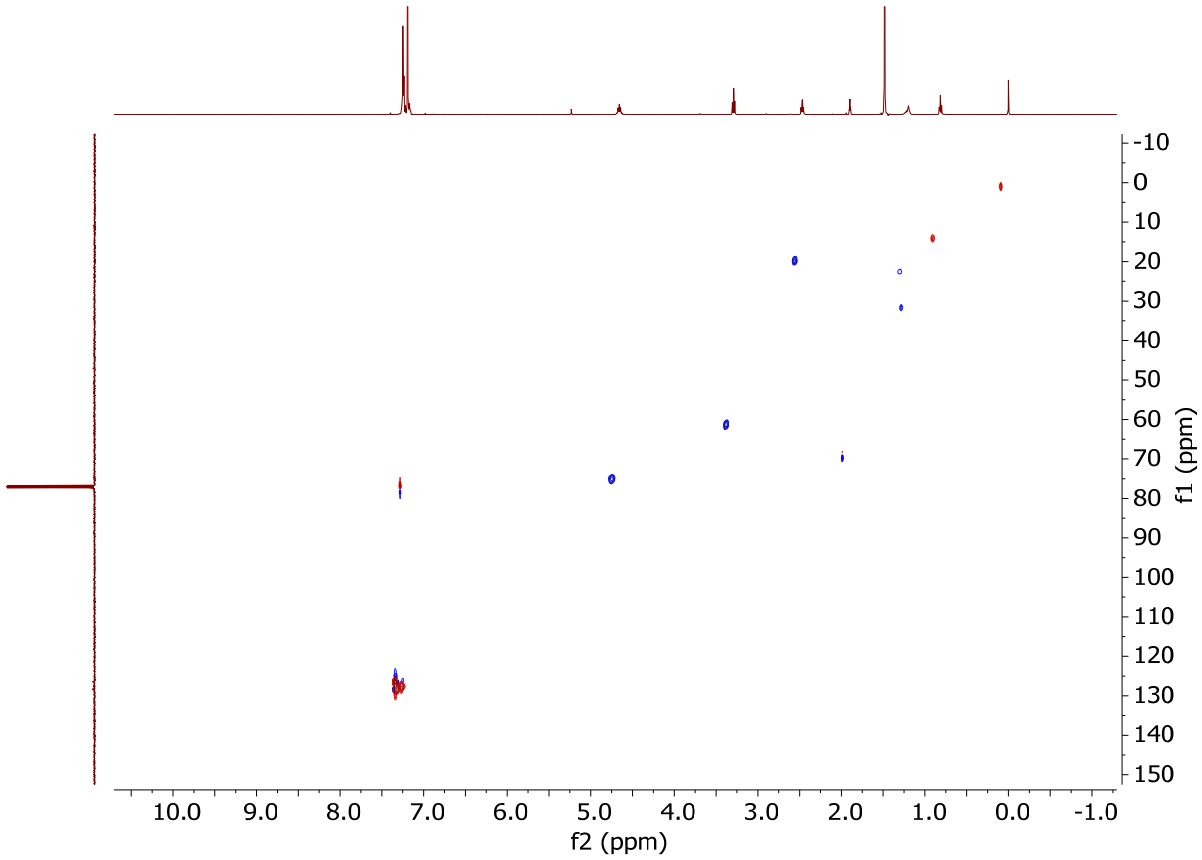


Fig. S36

^{1}H-^{13}C-HSQC$_{ed}$-NMR spectrum of (2-(but-3-yn-1-yloxy)-2,2-diphenylethyl)pentafluoro-λ^{6}-sulfane (**17**) in $CDCl_3$.

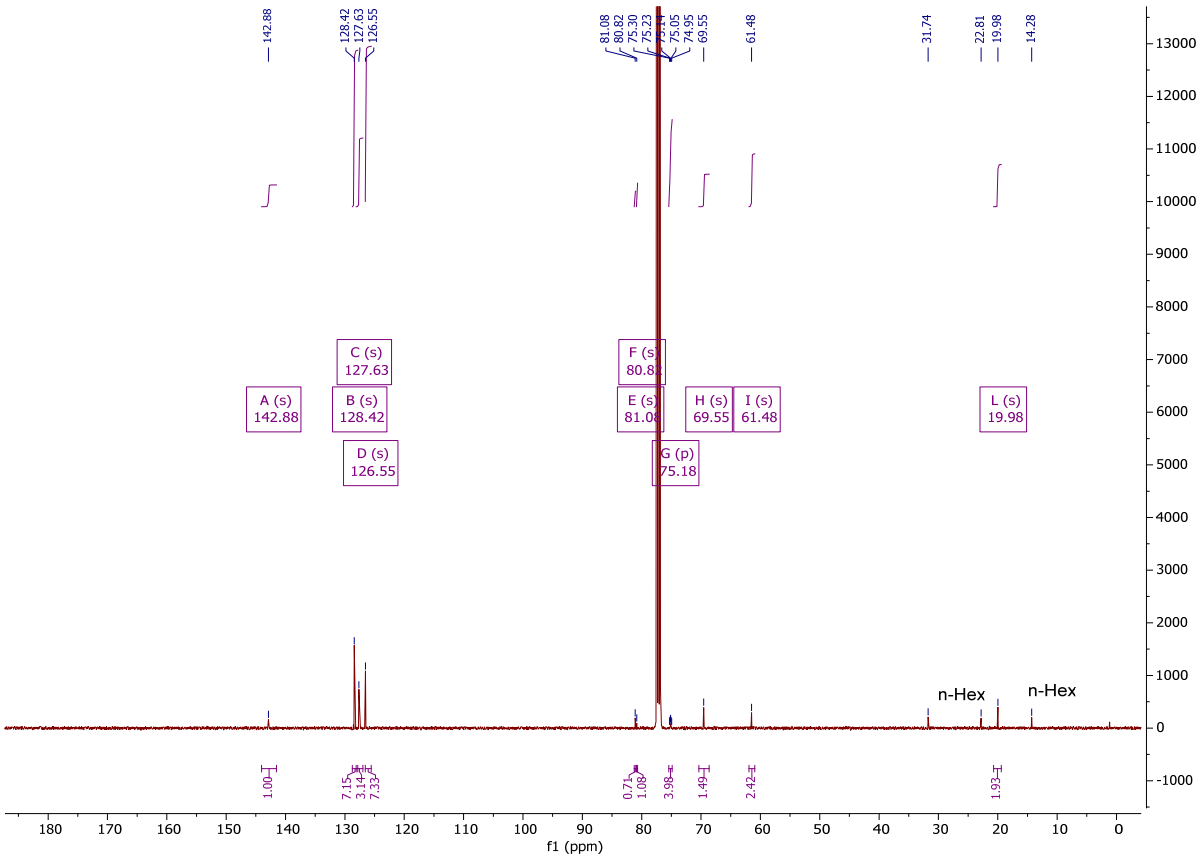


Fig. S37

^{13}C-NMR spectrum of (2-(but-3-yn-1-yloxy)-2,2-diphenylethyl)pentafluoro-λ^6-sulfane (**17**) in $CDCl_3$.

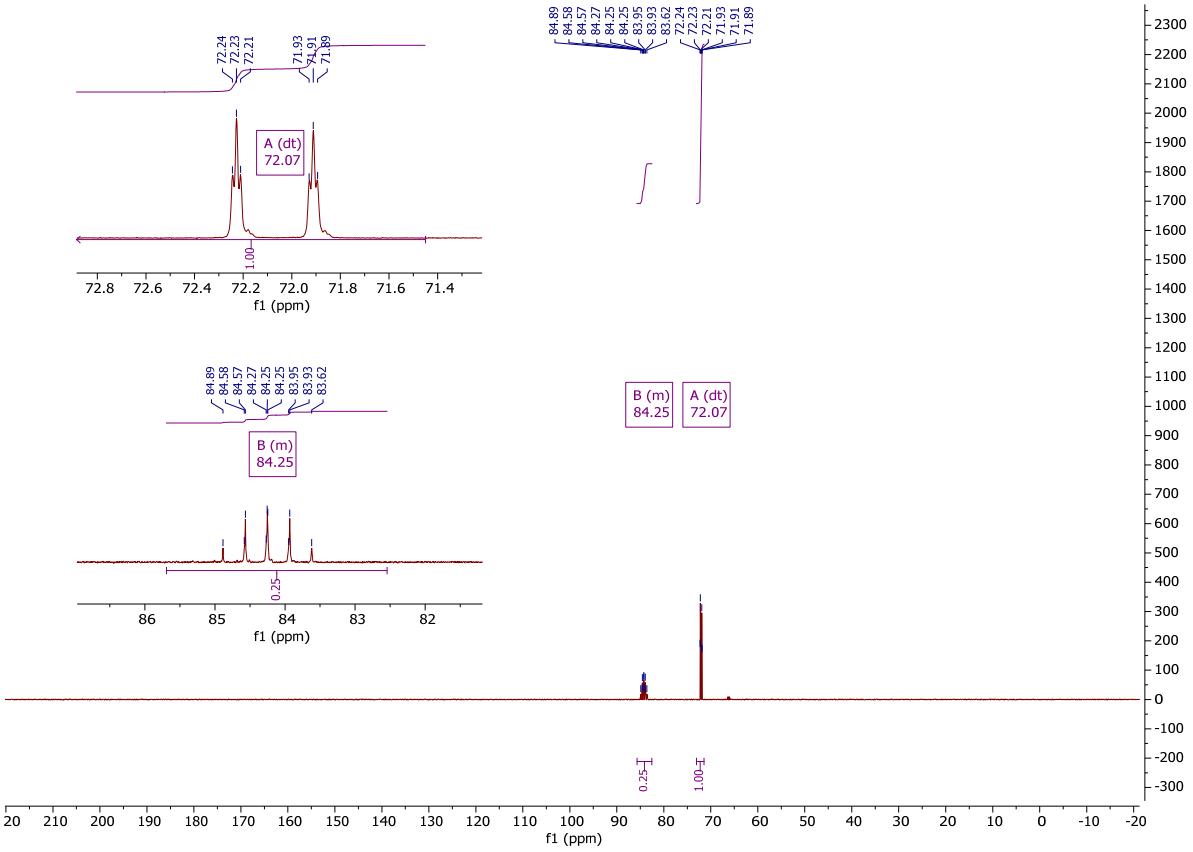


Fig. S38

^{19}F-NMR spectrum of (2-(but-3-yn-1-yloxy)-2,2-diphenylethyl)pentafluoro-λ^6-sulfane (**17**) in $CDCl_3$.

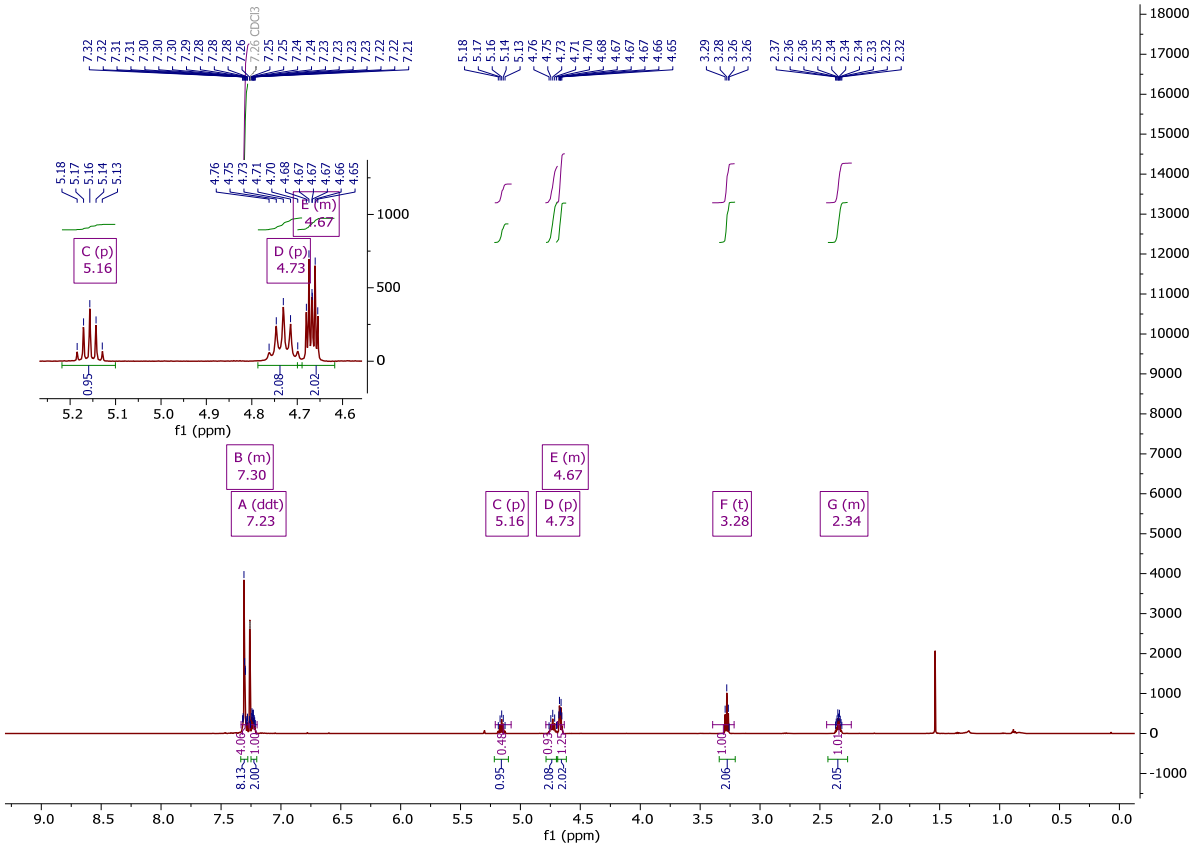


Fig. S39

^{1}H-NMR spectrum of pentafluoro(2-(penta-3,4-dien-1-yloxy)-2,2-diphenylethyl)-□^{6}-sulfane (**18)** in $CDCl_3$.

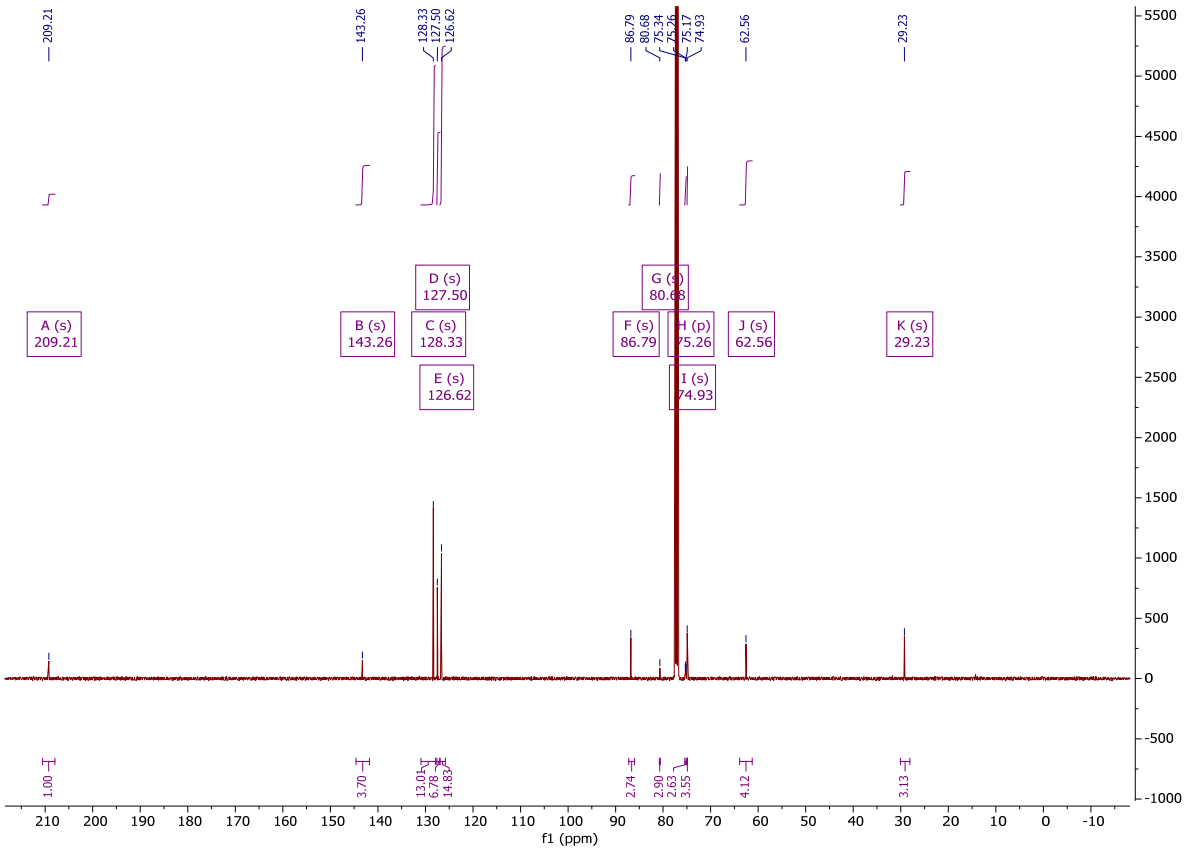


Fig. S40

^{13}C-NMR spectrum of pentafluoro(2-(penta-3,4-dien-1-yloxy)-2,2-diphenylethyl)-λ^6-sulfane (**18)** in $CDCl_3$.

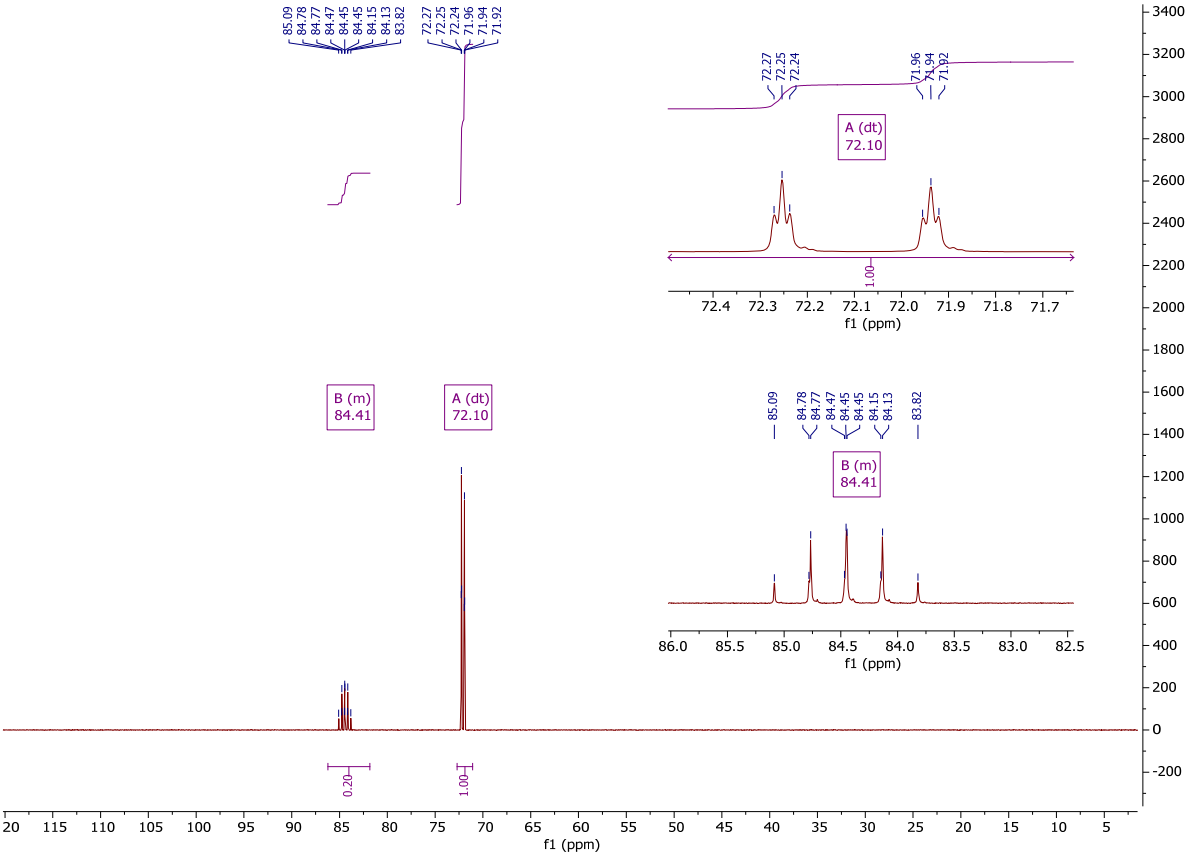


Fig. S41

^{19}F-NMR spectrum of pentafluoro(2-(penta-3,4-dien-1-yloxy)-2,2-diphenylethyl)-λ^6-sulfane (**18**) in $CDCl_3$.

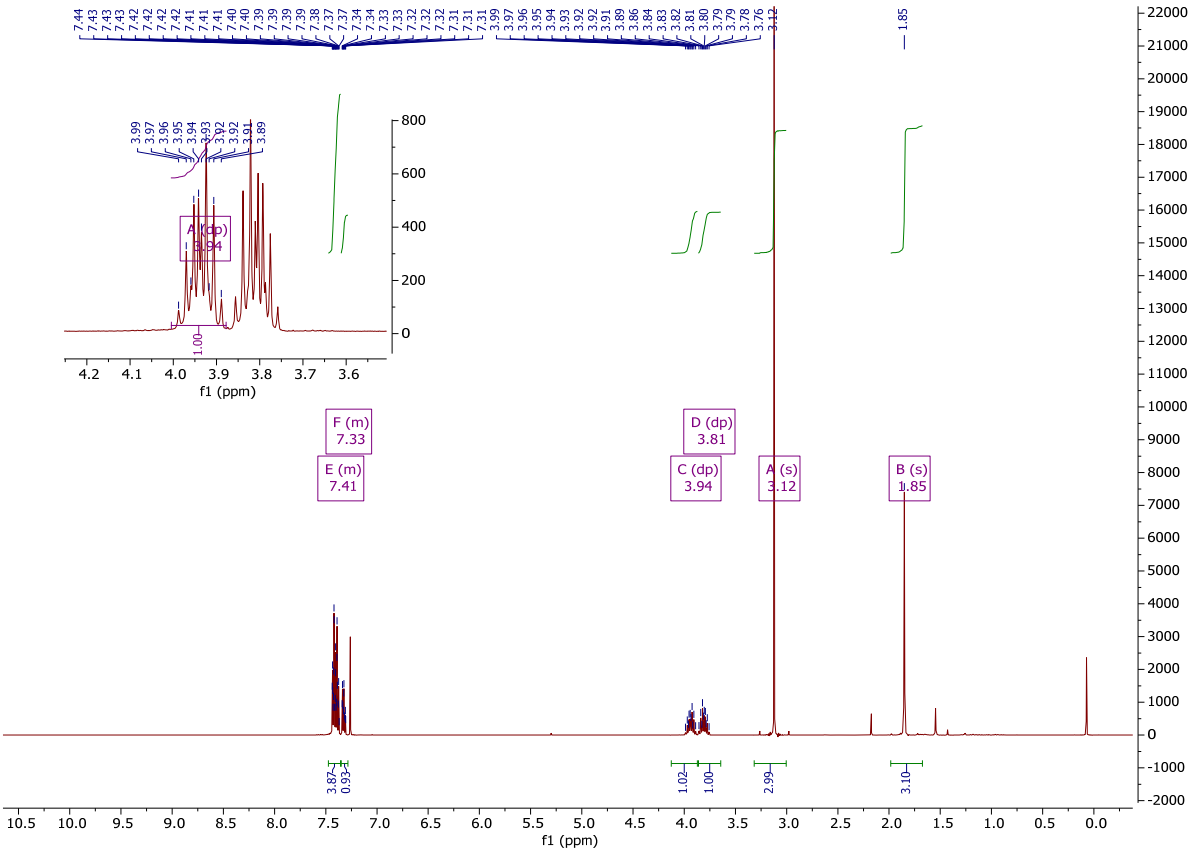


Fig. S42

^{1}H-NMR spectrum of pentafluoro(2-methoxy-2-phenylpropyl)-λ^{6}-sulfane (**8**) in $CDCl_3$.

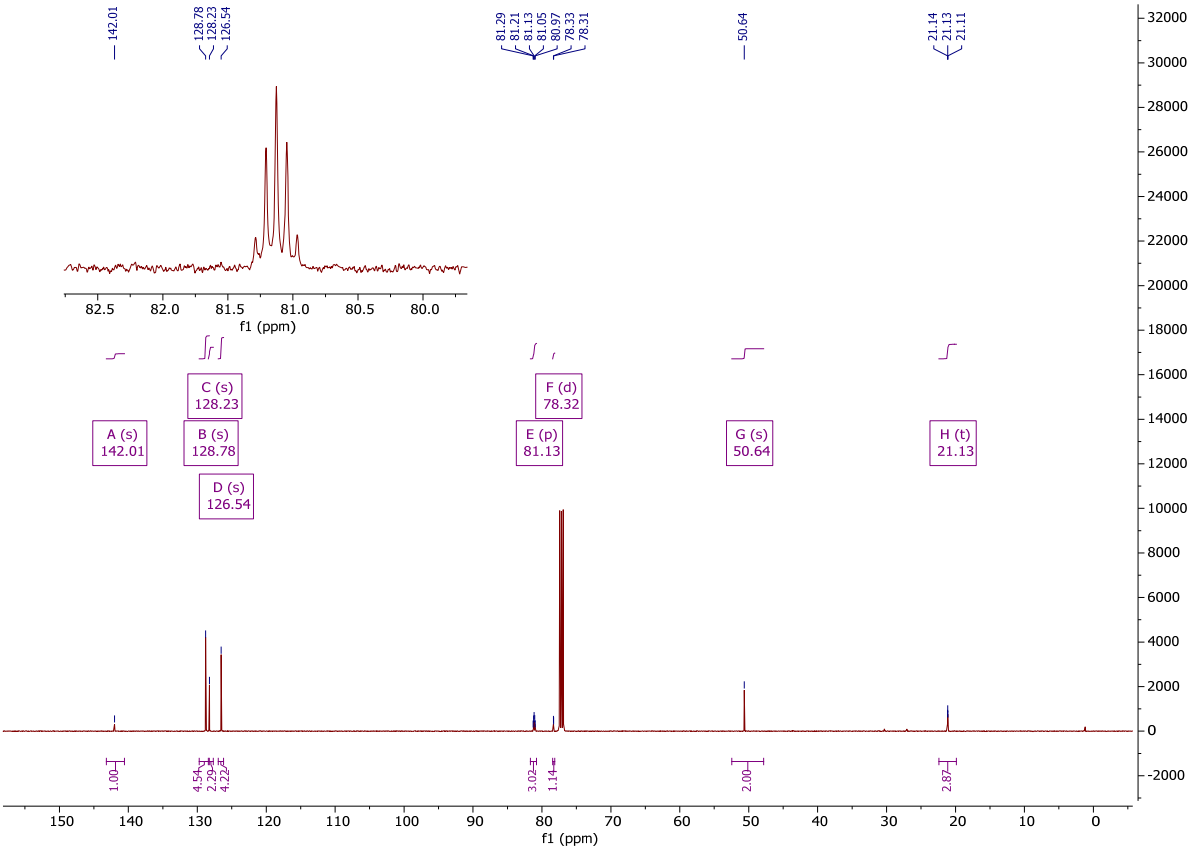


Fig. S43

^{13}C-NMR spectrum of pentafluoro(2-methoxy-2-phenylpropyl)-λ^6-sulfane (**8**) in $CDCl_3$.

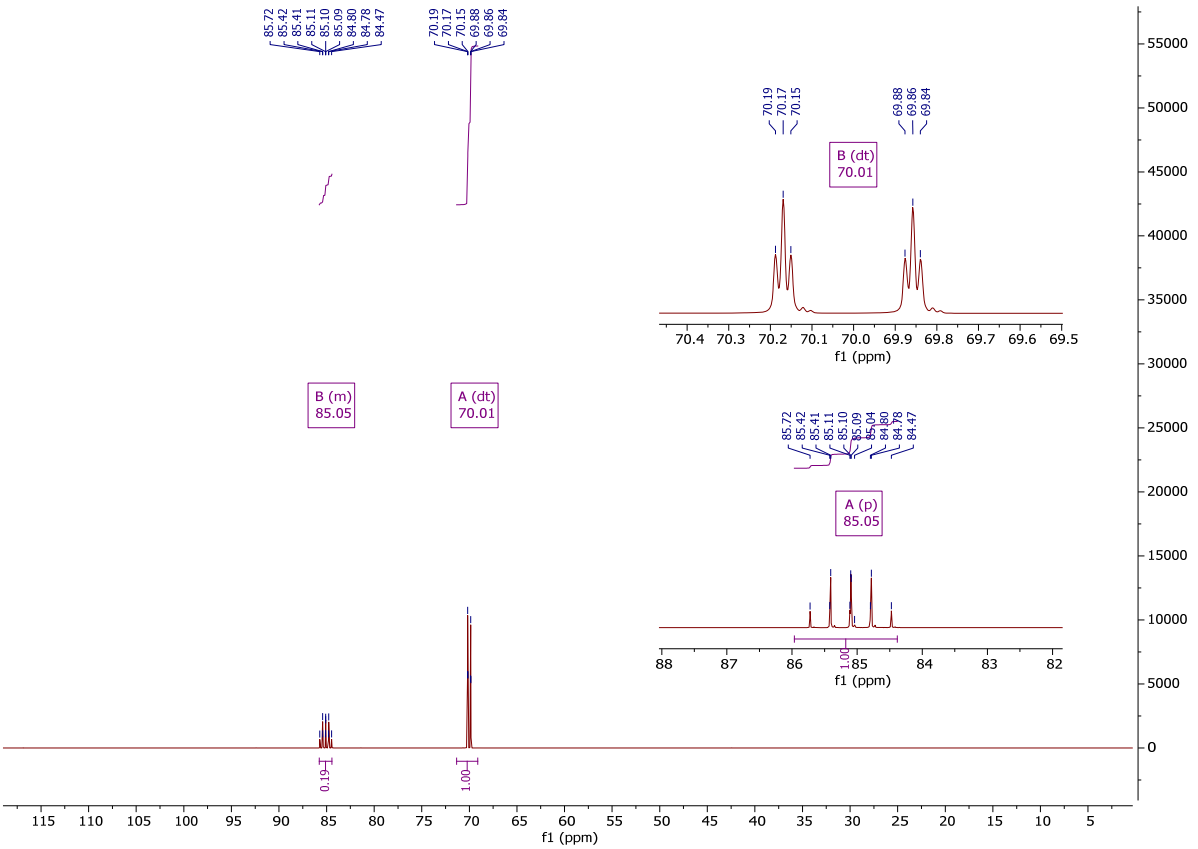


Fig. S44

^{19}F-NMR spectrum of pentafluoro(2-methoxy-2-phenylpropyl)-λ^6-sulfane (**8**) in $CDCl_3$.

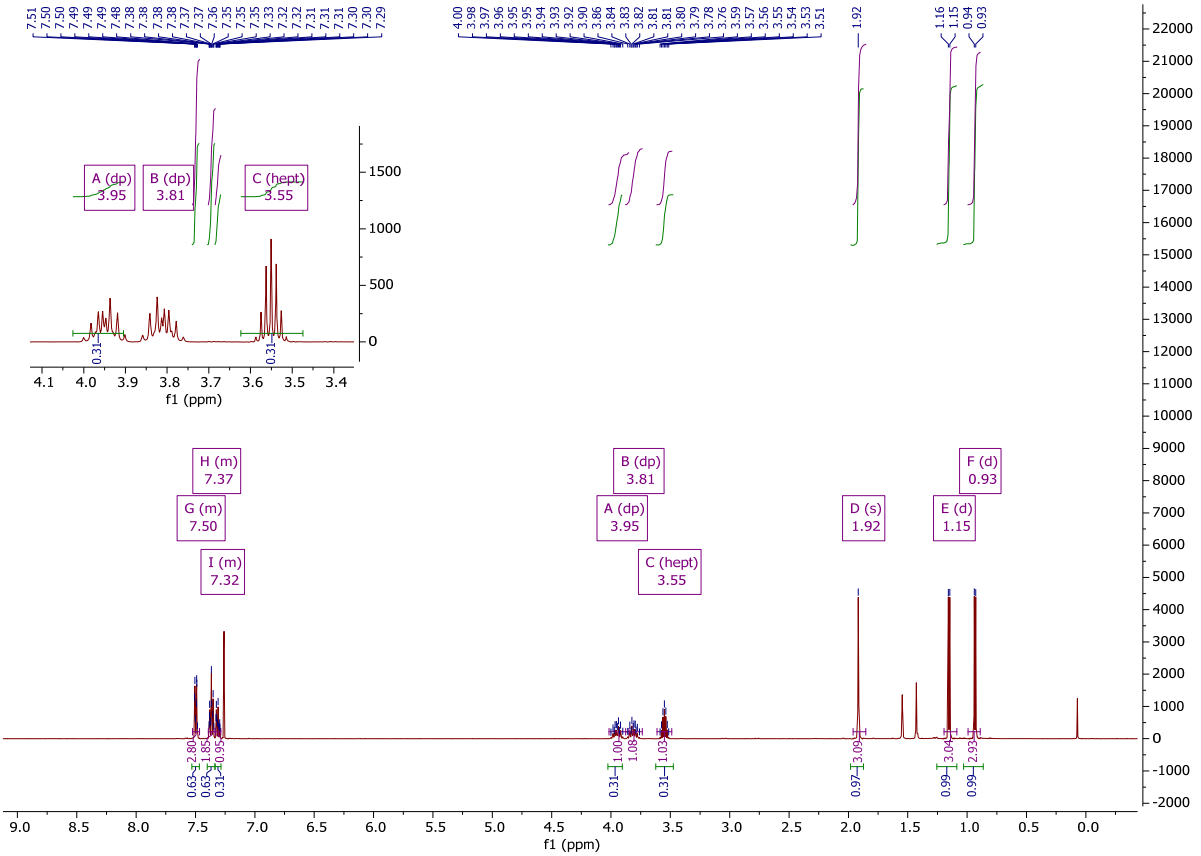


Fig. S45

^{1}H - NMR spectrum of pentafluoro(2-isopropoxy-2-phenylpropyl)-λ^{6}-sulfane (**19**) in $CDCl_3$.

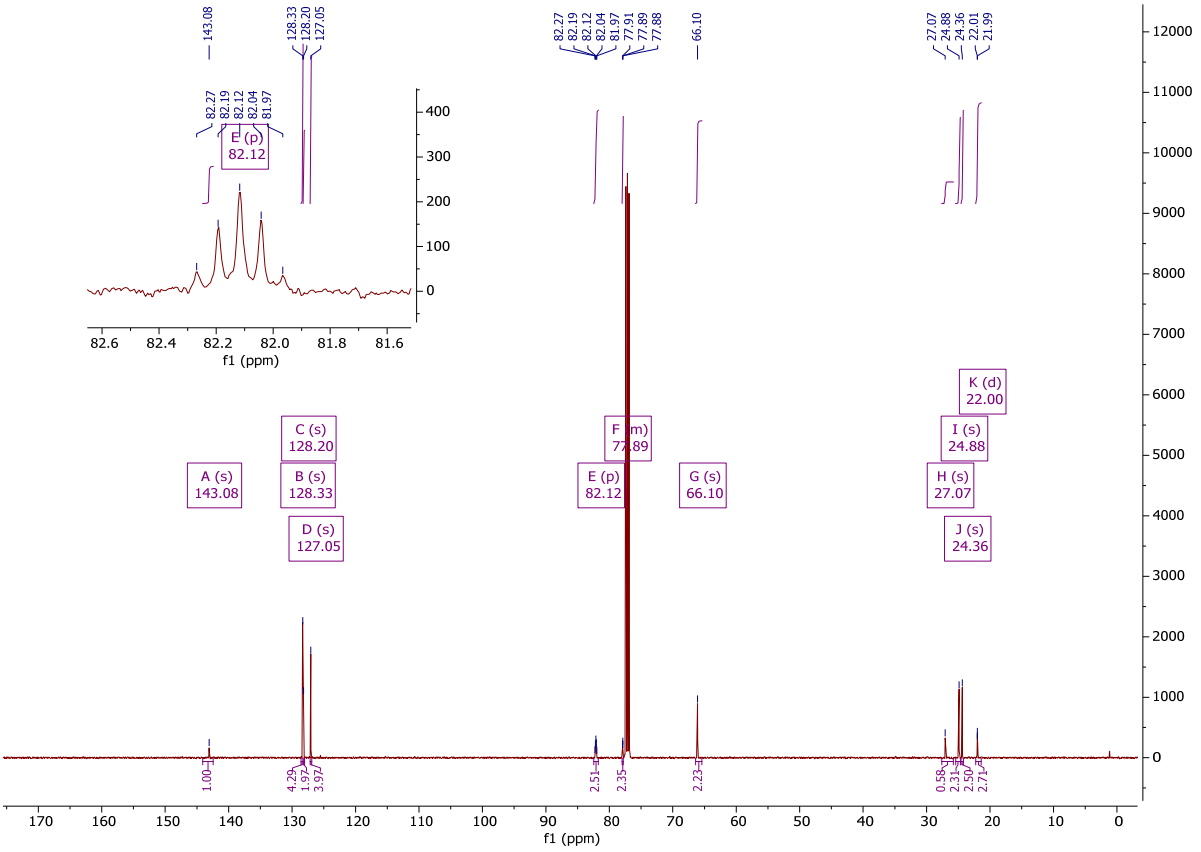


Fig. S46

^{13}C-NMR spectrum of pentafluoro(2-isopropoxy-2-phenylpropyl)-λ^6-sulfane (**19**) in $CDCl_3$.

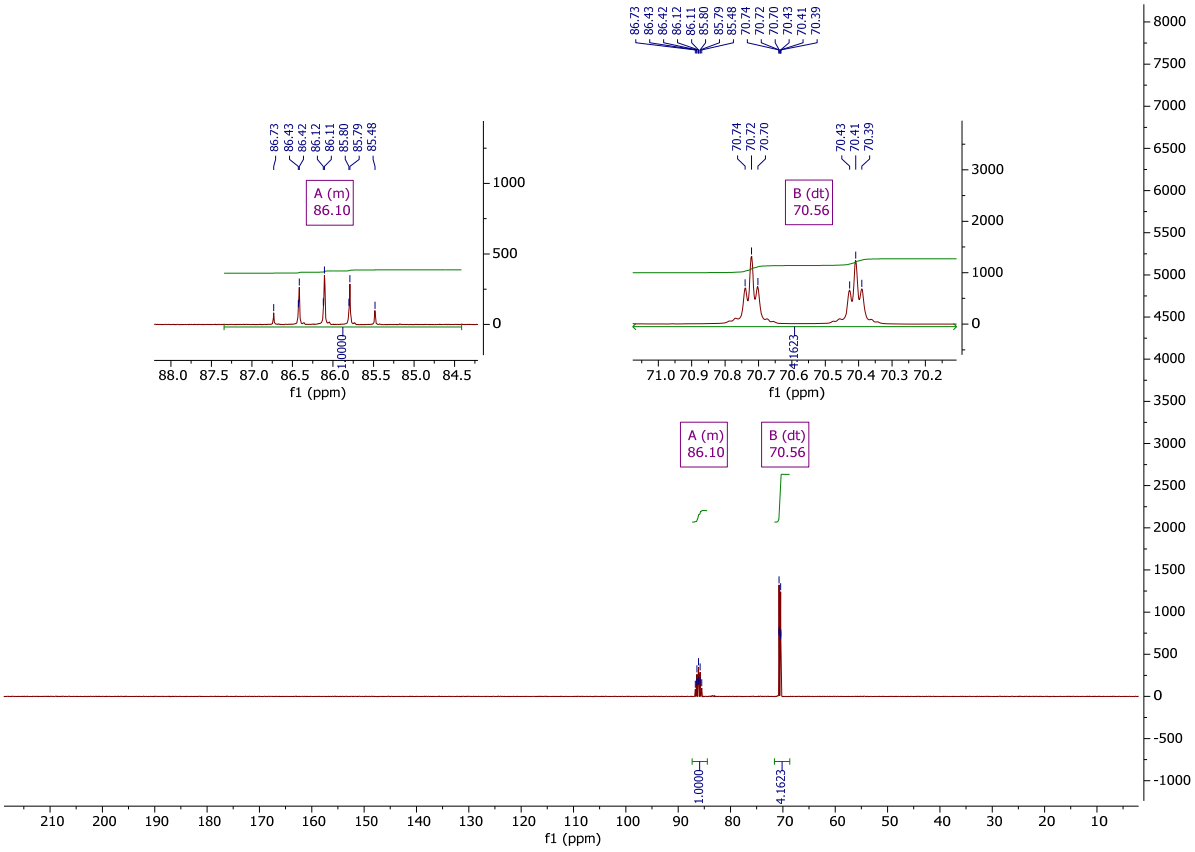


Fig. S47

^{19}F-NMR spectrum of pentafluoro(2-isopropoxy-2-phenylpropyl)-λ^6-sulfane (**19**) in $CDCl_3$.

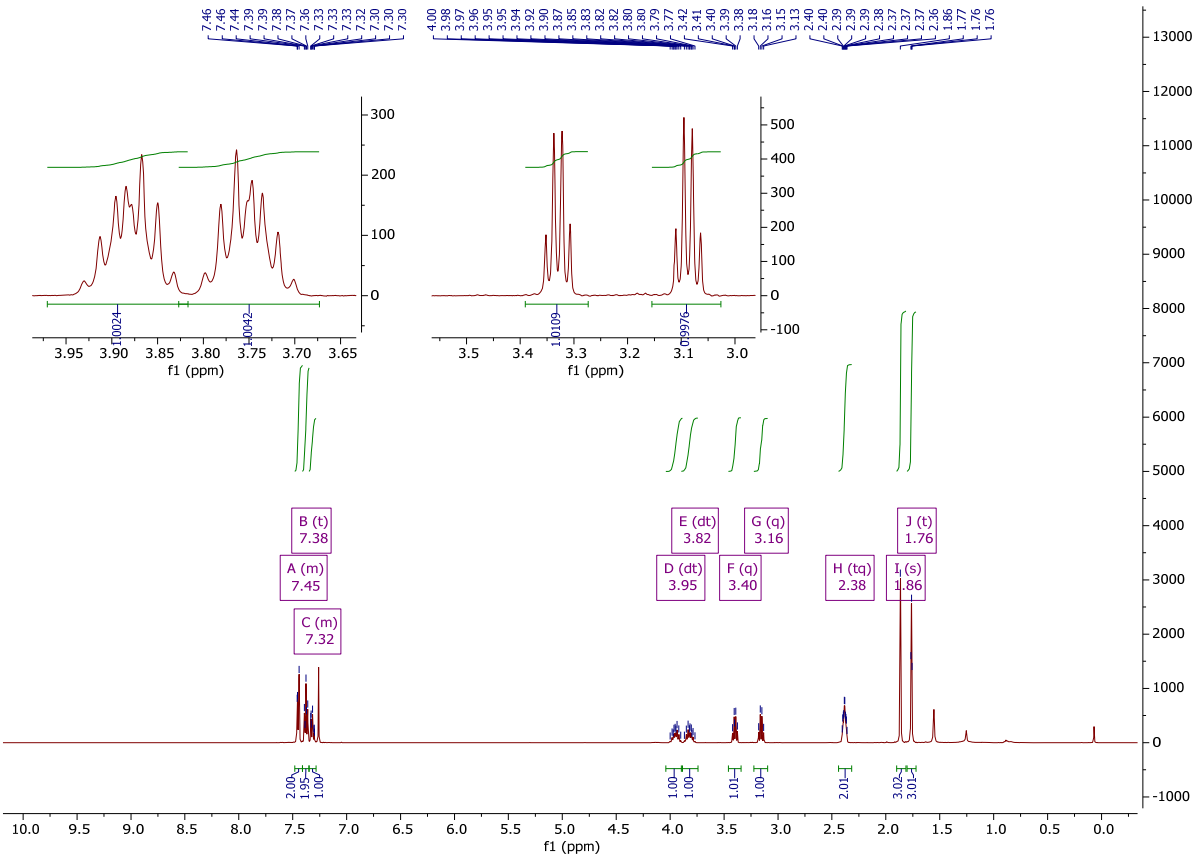


Fig. S48

^{1}H-NMR spectrum of pentafluoro(2-(pent-3-yn-1-yloxy)-2-phenylpropyl)-λ^{6}-sulfane (**20**) in $CDCl_3$.

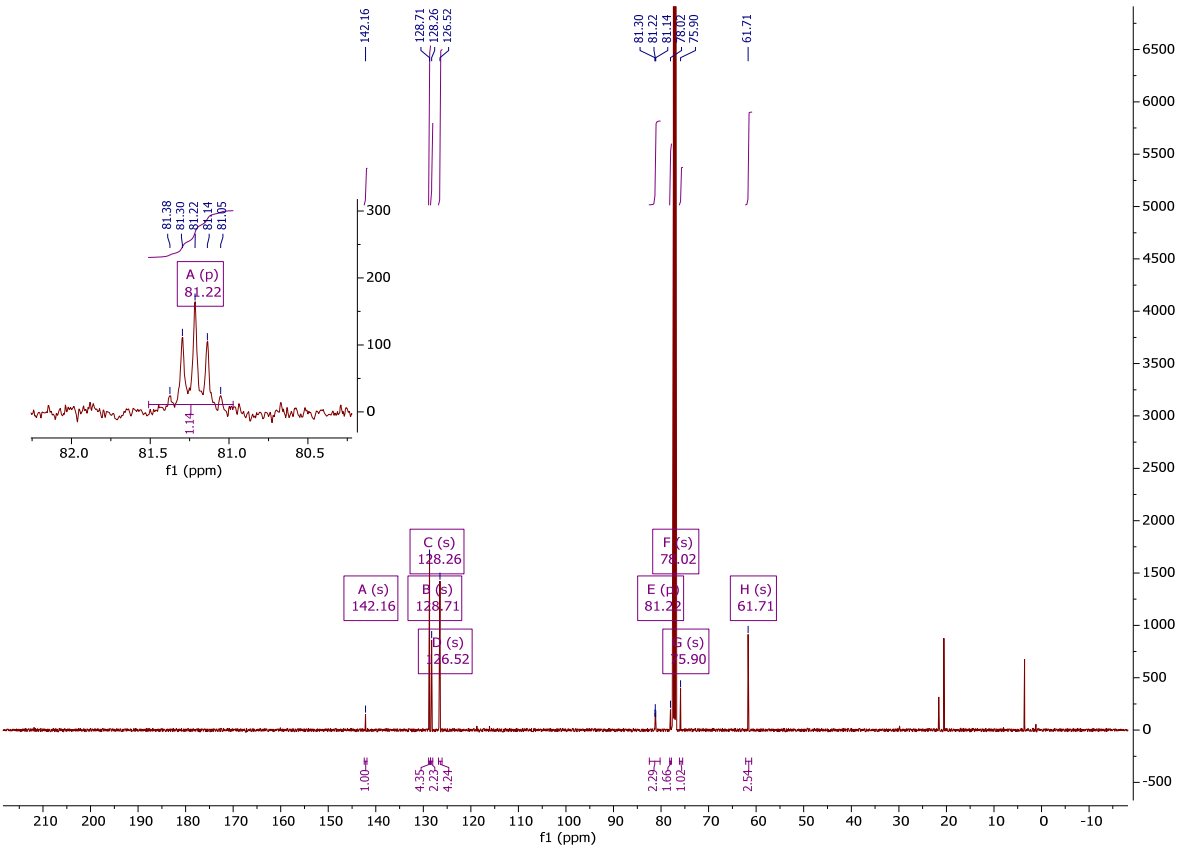


Fig. S49

^{13}C-NMR spectrum of pentafluoro(2-(pent-3-yn-1-yloxy)-2-phenylpropyl)-λ^6-sulfane (**20**) in $CDCl_3$.

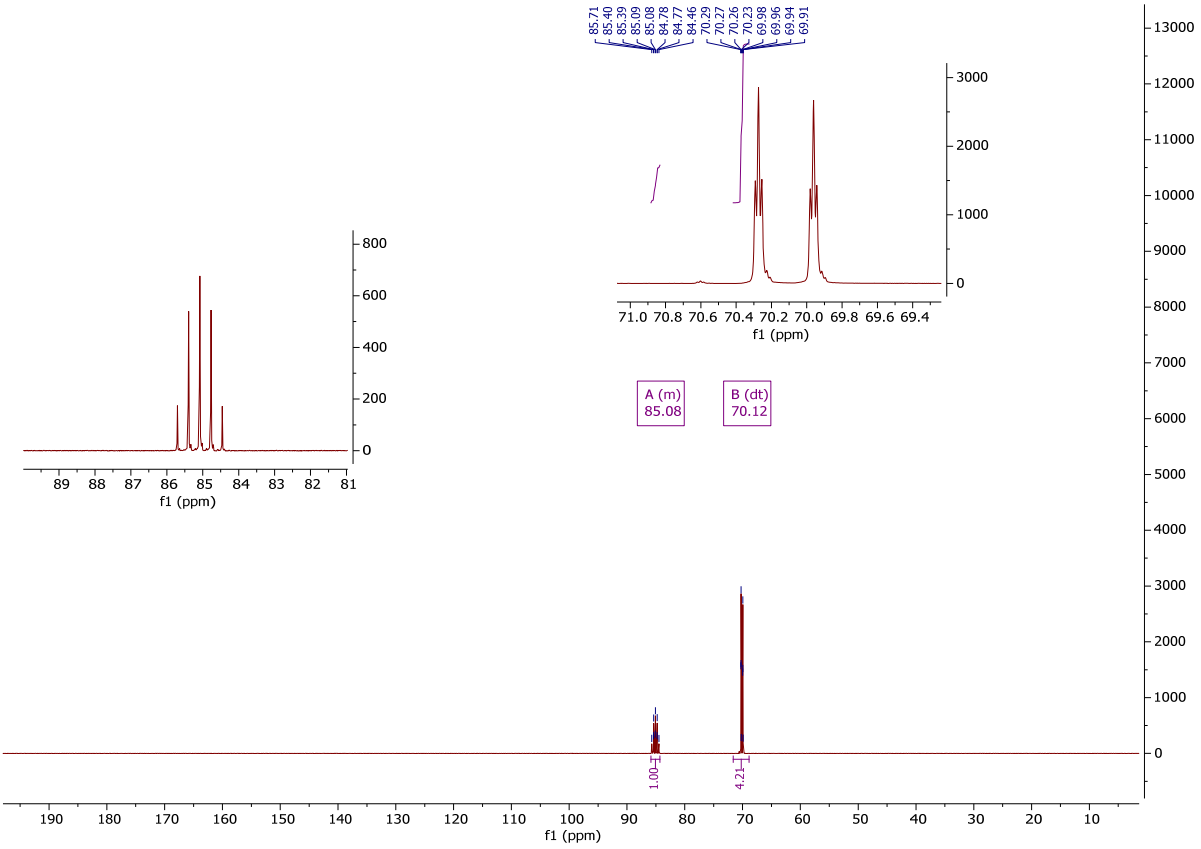


Fig. S50

^{19}F-NMR spectrum of pentafluoro(2-(pent-3-yn-1-yloxy)-2-phenylpropyl)-λ^6-sulfane (**20**) in $CDCl_3$.

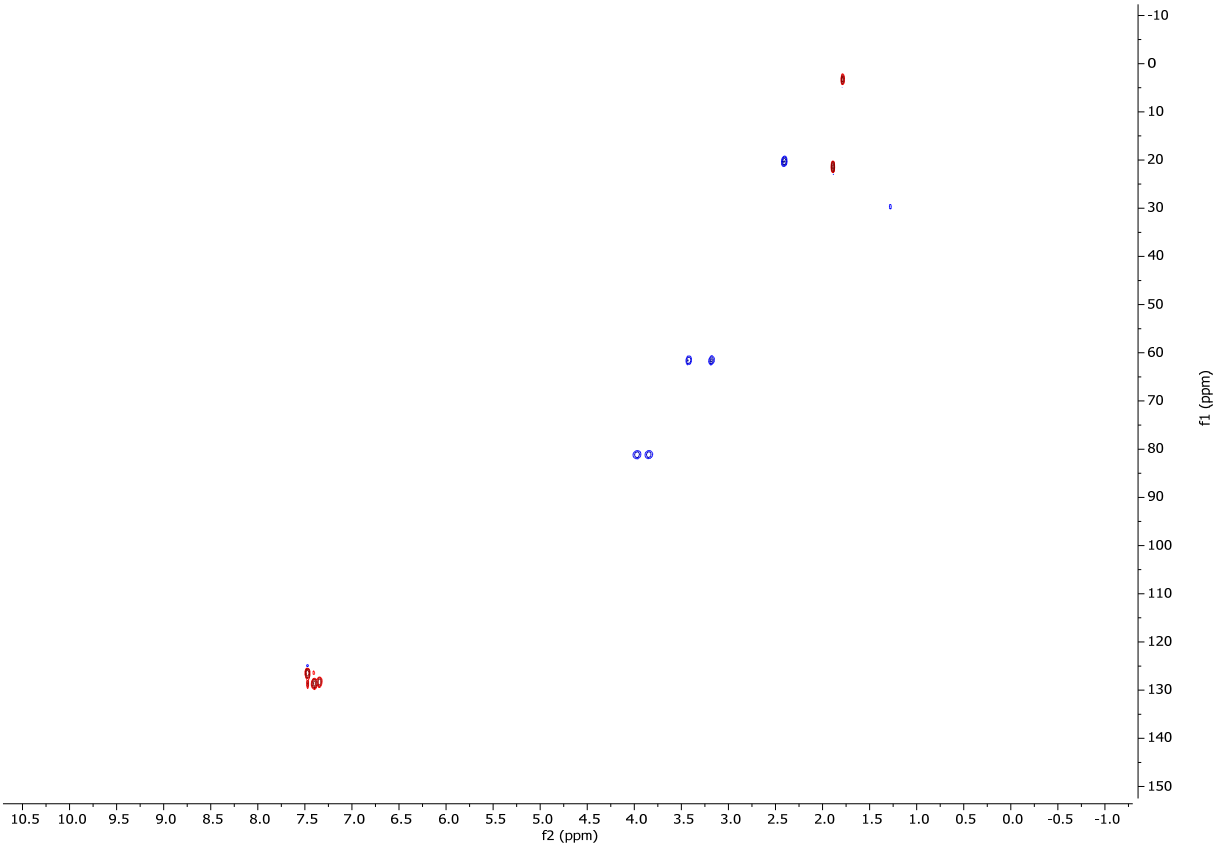


Fig. S51

^{1}H-^{13}C-HSQC$_{ed}$-NMR spectrum of pentafluoro(2-(pent-3-yn-1-yloxy)-2-phenylpropyl)-λ^{6}-sulfane (**20**) in $CDCl_3$.

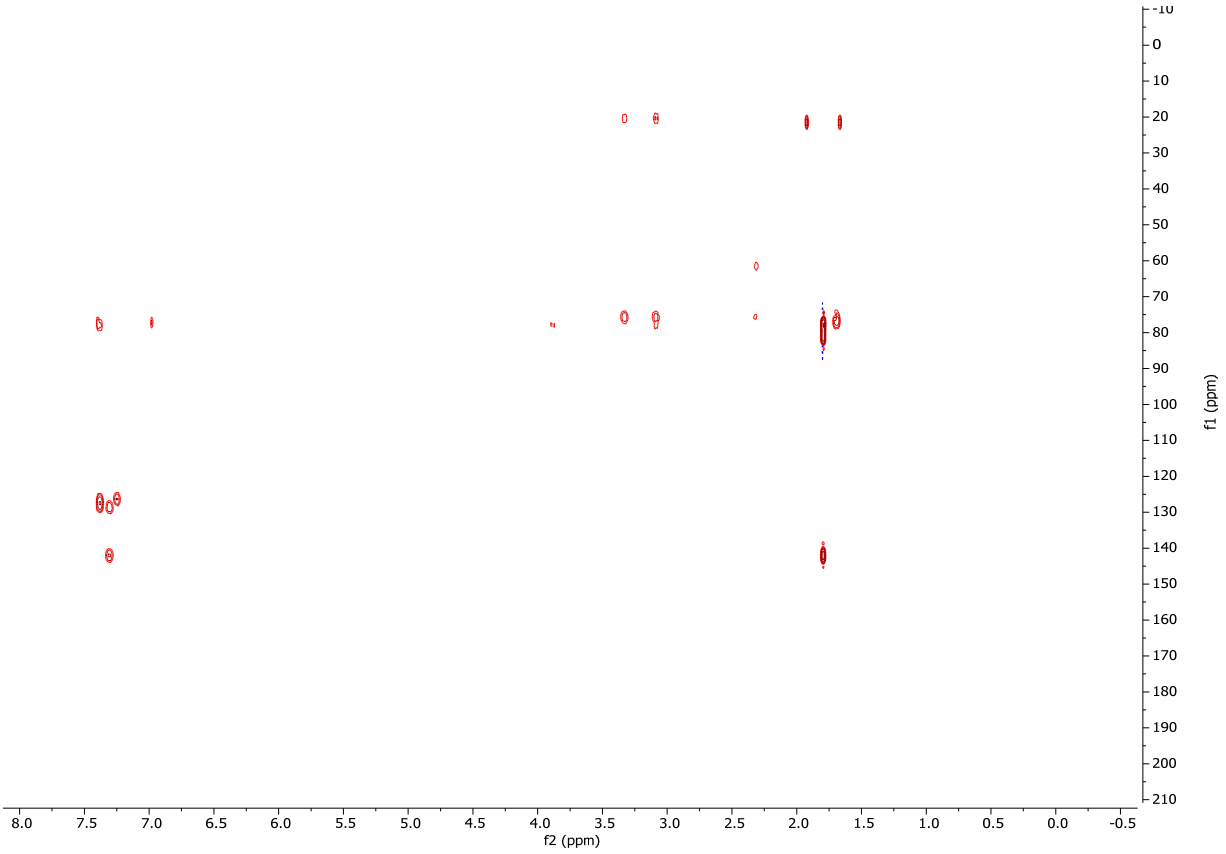


Fig. S52

^{1}H-^{13}C-HMBC-NMR spectrum of pentafluoro(2-(pent-3-yn-1-yloxy)-2-phenylpropyl)-λ^{6}-sulfane (**20**) in $CDCl_3$.

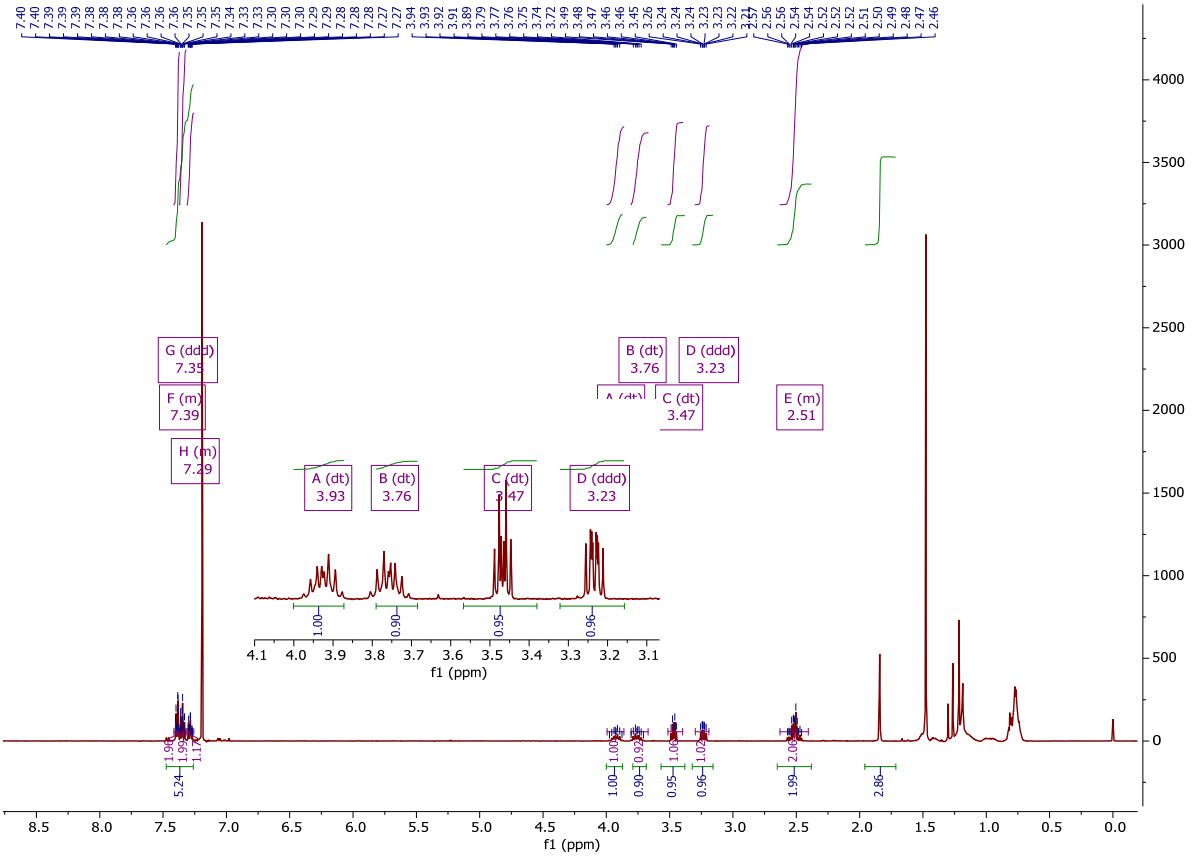


Fig. S53

^{1}H - NMR spectrum of 3-((1-(pentafluoro-λ^{6}-sulfaneyl)-2-phenylpropan-2-yl)oxy)-propanenitrile (**21**) in $CDCl_3$. Residual alkyl impurities in high field between 0.5 and 1.4 ppm.

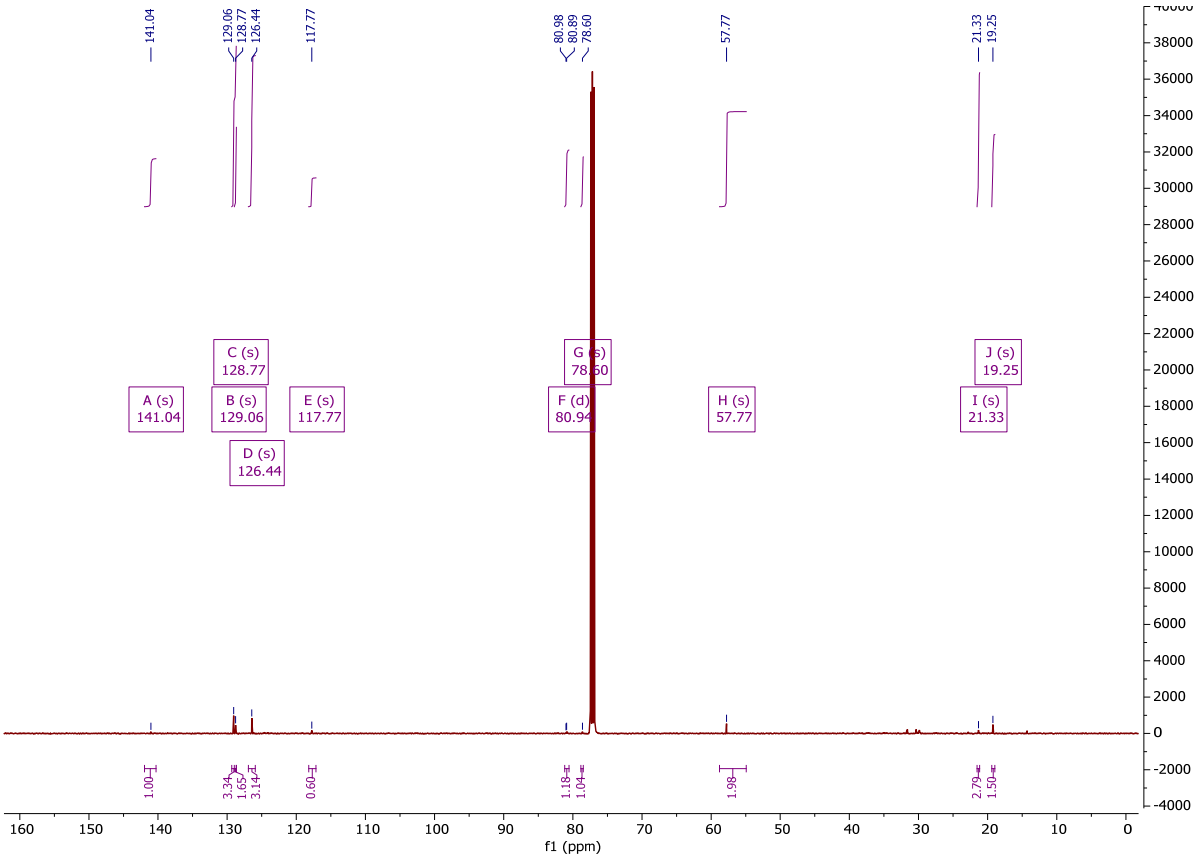


Fig. S54

^{13}C-NMR spectrum of 3-((1-(pentafluoro-λ^6-sulfaneyl)-2-phenylpropan-2-yl)oxy)propanenitrile (**21**) in $CDCl_3$.

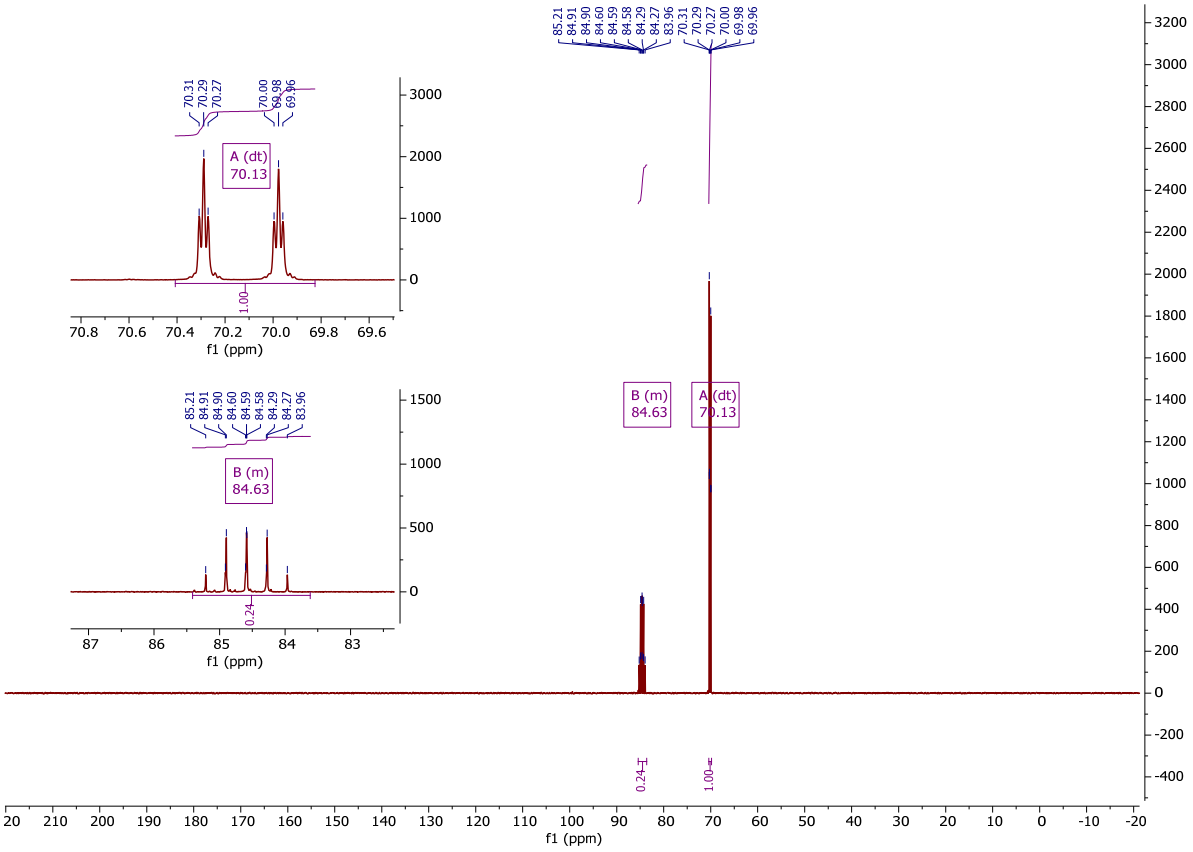


Fig. S55

^{19}F-NMR spectrum of 3-((1-(pentafluoro-λ^6-sulfaneyl)-2-phenylpropan-2-yl)oxy)propanenitrile (**21**) in $CDCl_3$.

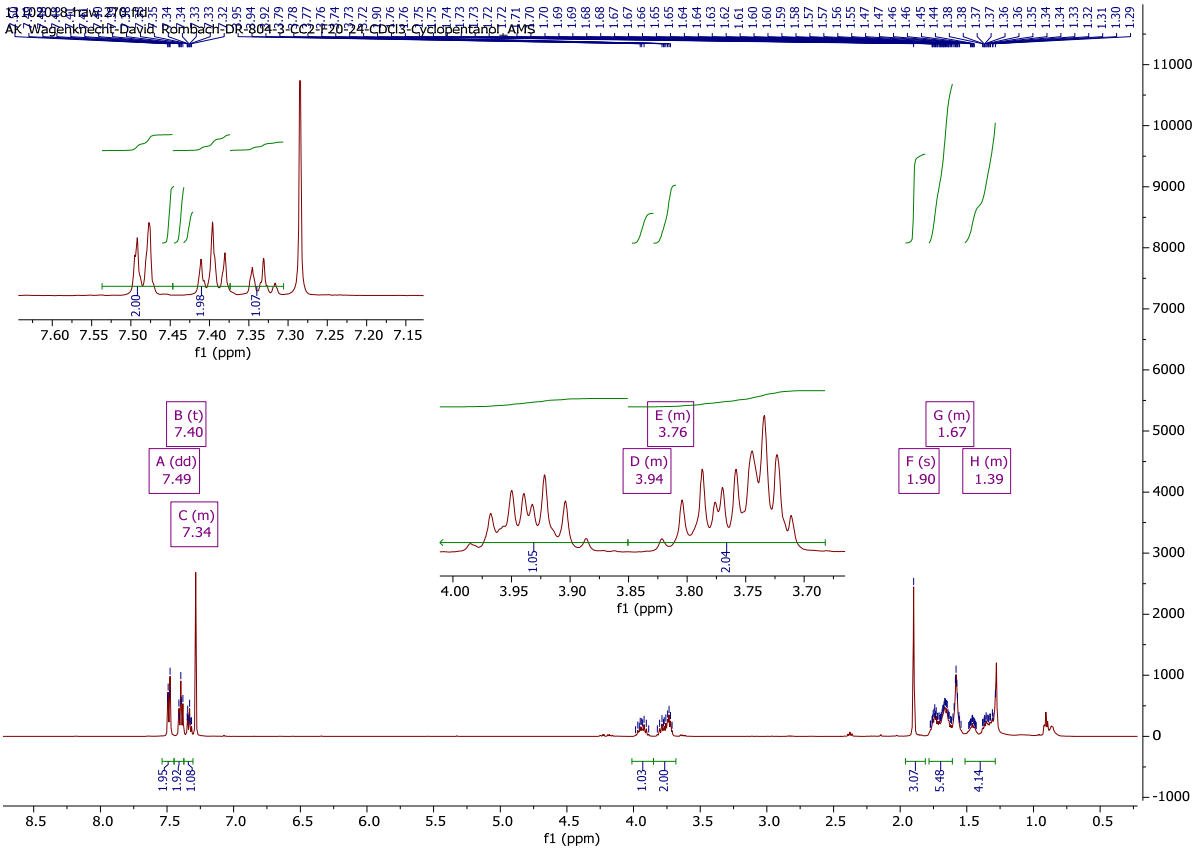


Fig. S56

^{1}H-NMR spectrum of (2-(cyclopentyloxy)-2-phenylpropyl)pentafluoro-λ^{6}-sulfane (**22**) in $CDCl_3$.

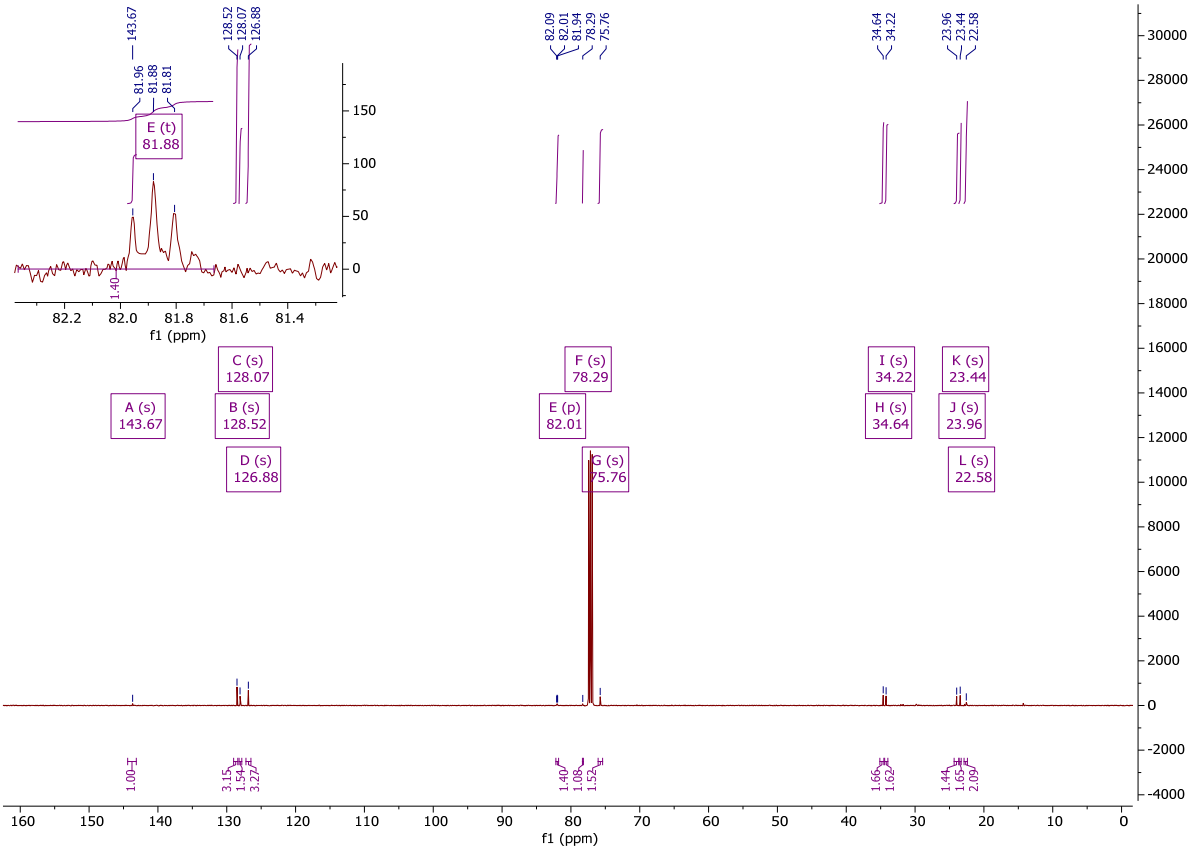


Fig. S57

^{13}C-NMR spectrum of (2-(cyclopentyloxy)-2-phenylpropyl)pentafluoro-λ^6-sulfane (**22**) in $CDCl_3$.

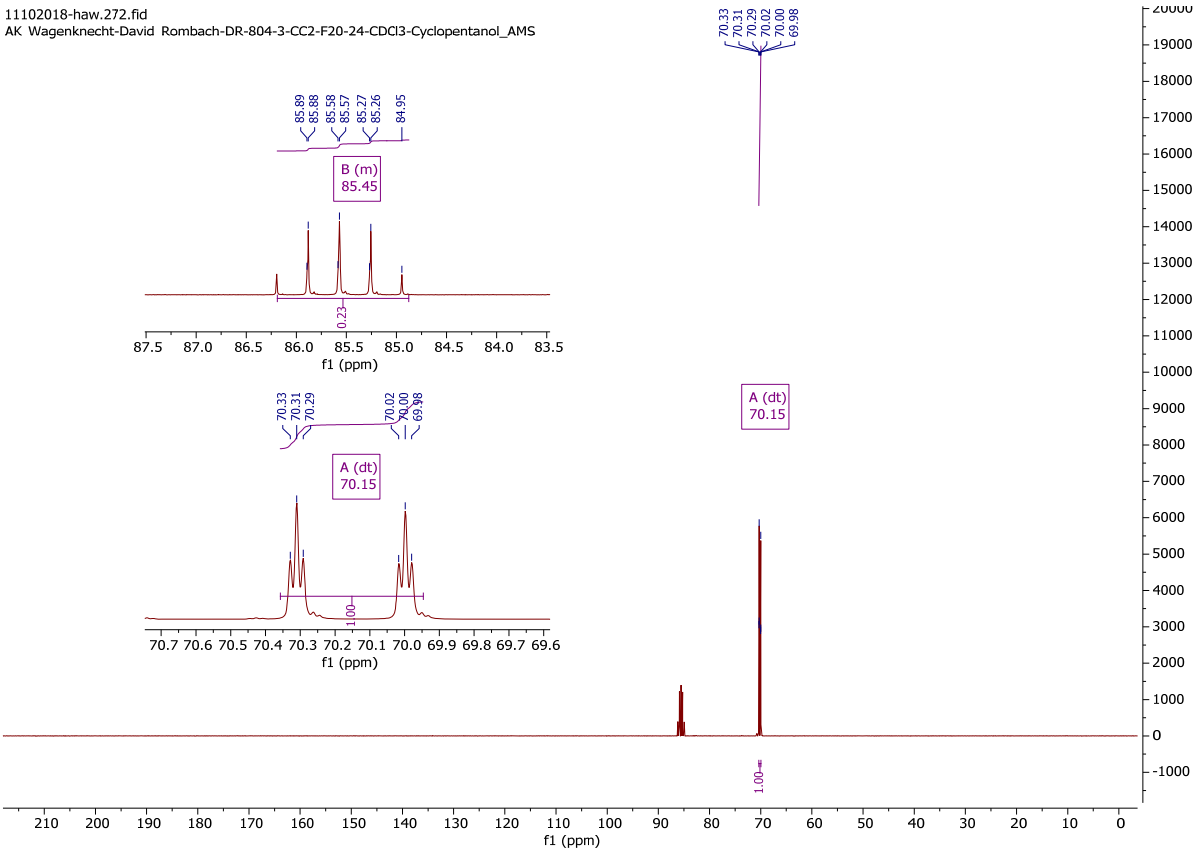


Fig. S58

^{19}F-NMR spectrum of (2-(cyclopentyloxy)-2-phenylpropyl)pentafluoro-λ^6-sulfane (**22**) in $CDCl_3$.

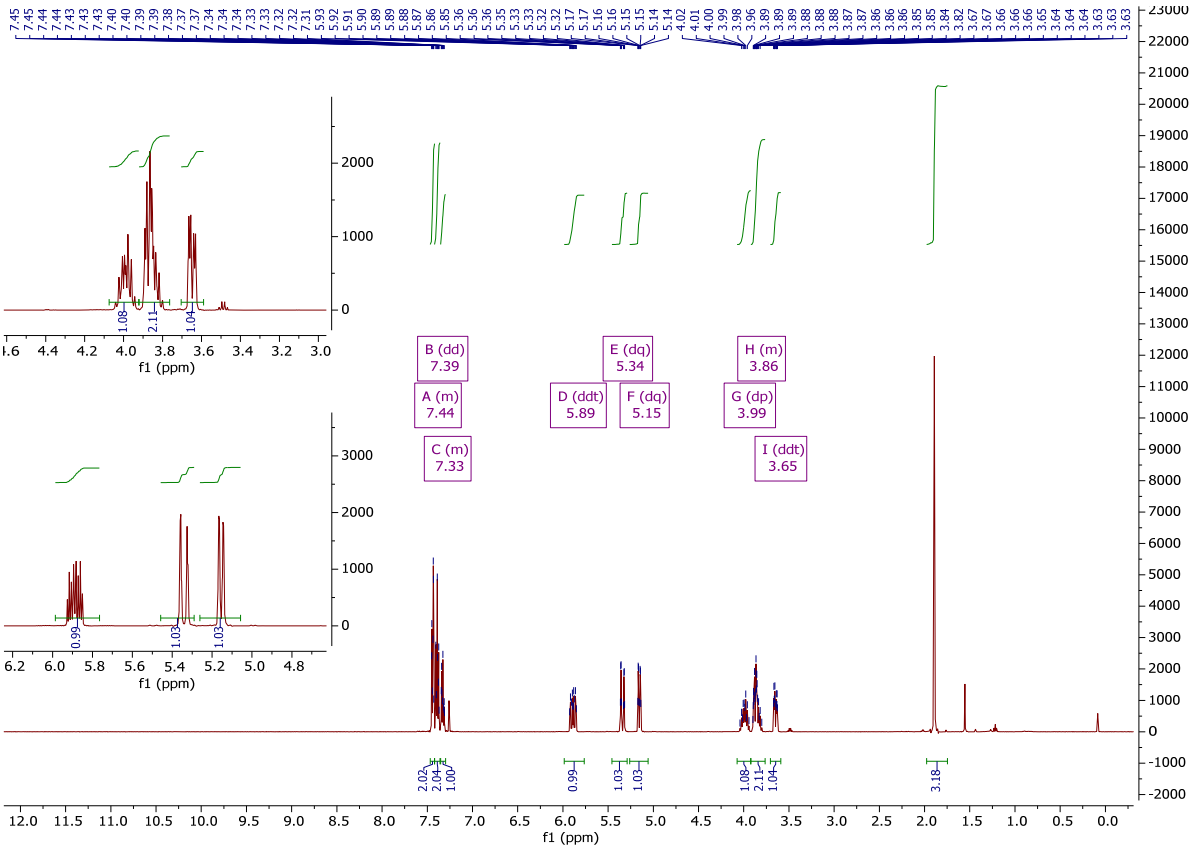


Fig. S59

^{1}H-NMR spectrum of (2-(allyloxy)-2-phenylpropyl)pentafluoro-λ^{6}-sulfane (**23**) in $CDCl_3$.

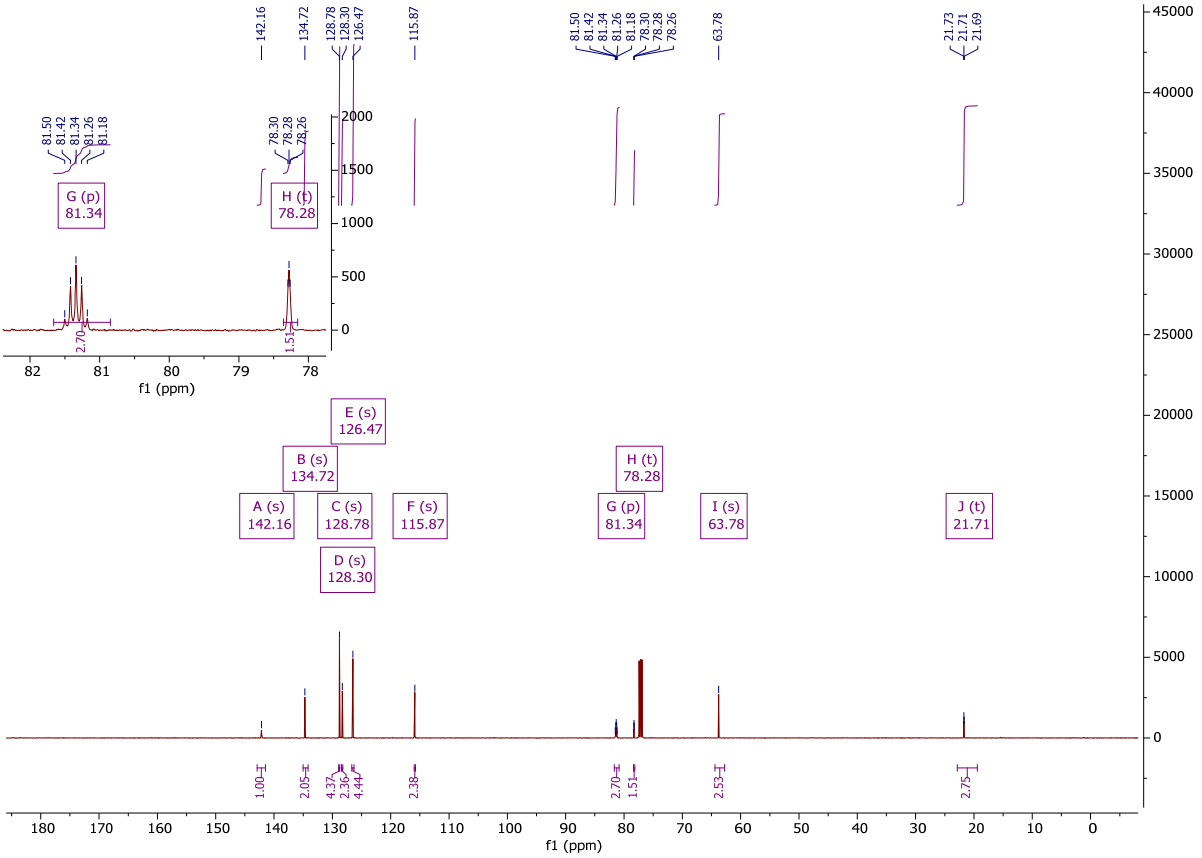


Fig. S60

^{13}C-NMR spectrum of (2-(allyloxy)-2-phenylpropyl)pentafluoro-λ^6-sulfane (**23**) in $CDCl_3$.

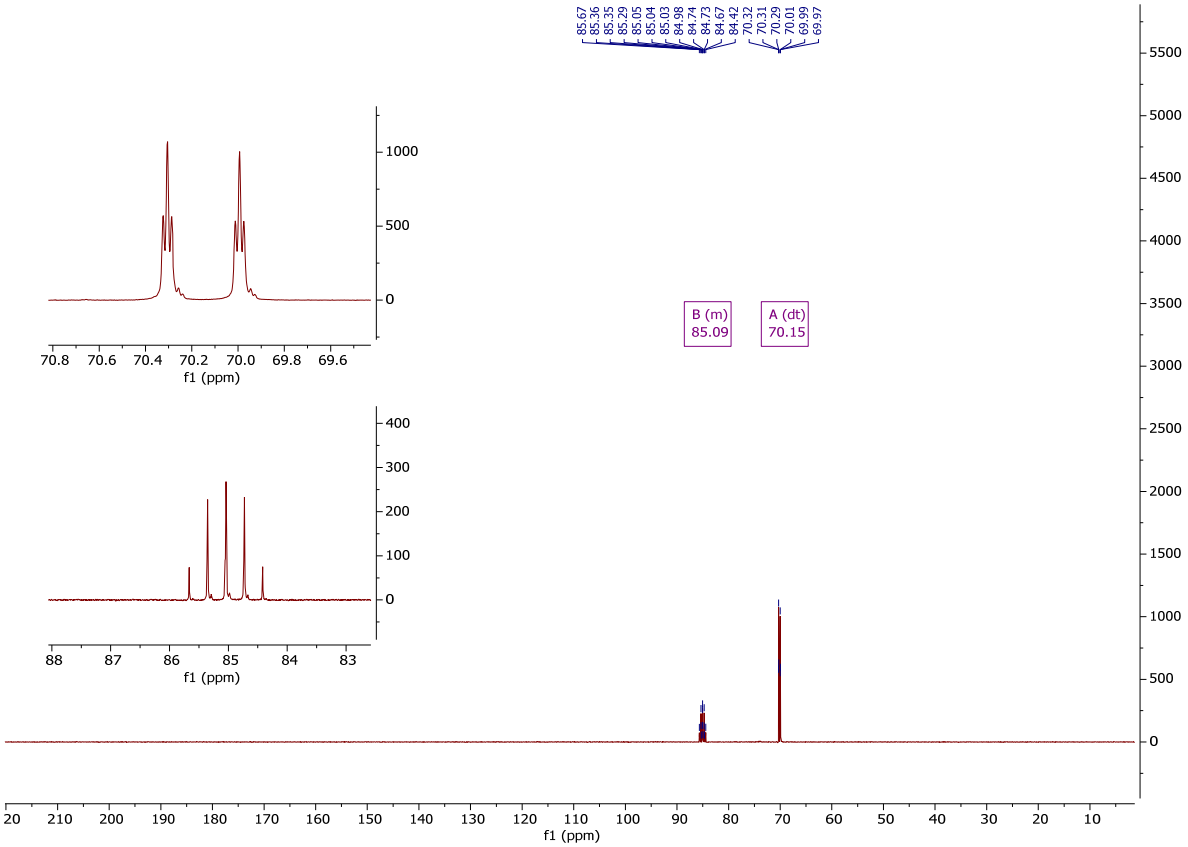


Fig. S61

^{19}F-NMR spectrum of (2-(allyloxy)-2-phenylpropyl)pentafluoro-λ^6-sulfane (**23**) in $CDCl_3$.

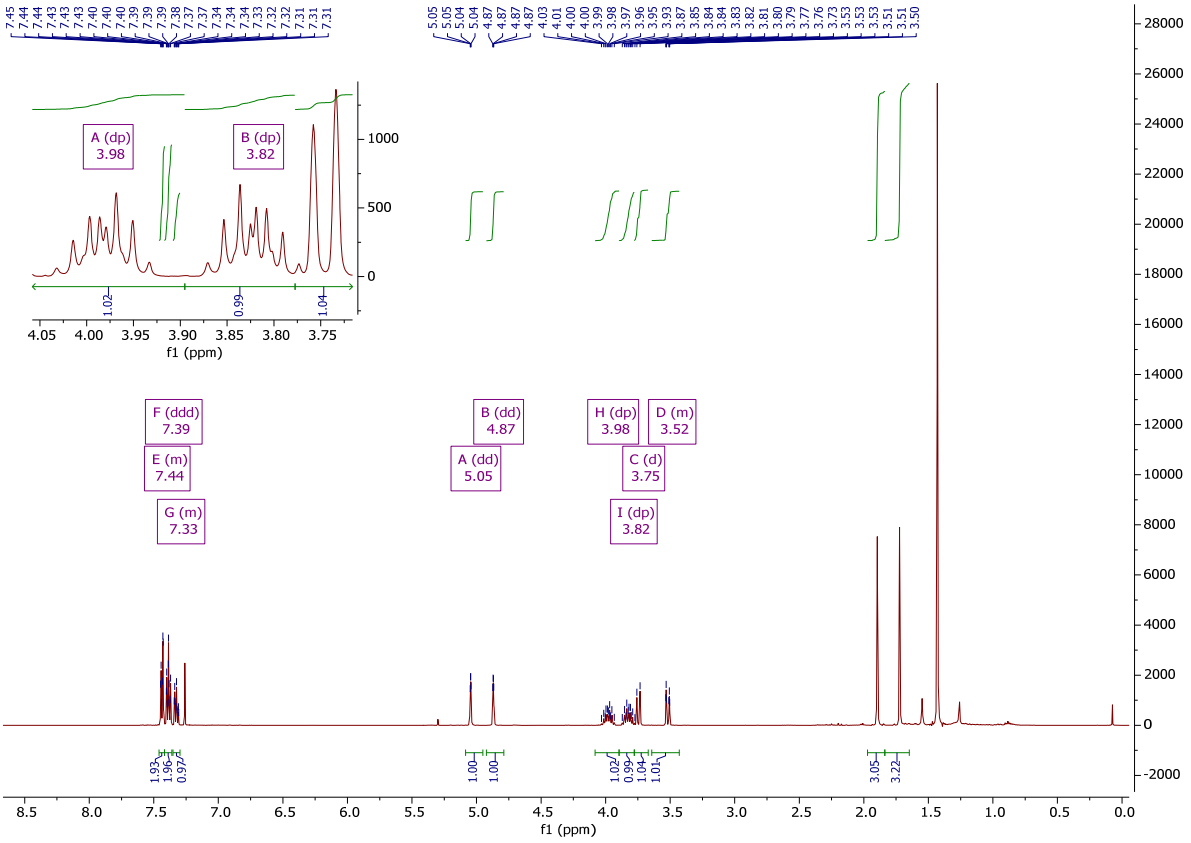


Fig. S62

^{1}H - NMR spectrum of pentafluoro(2-((2-methylallyl)oxy)-2-phenylpropyl)-λ^{6}-sulfane (**24**) in $CDCl_3$.

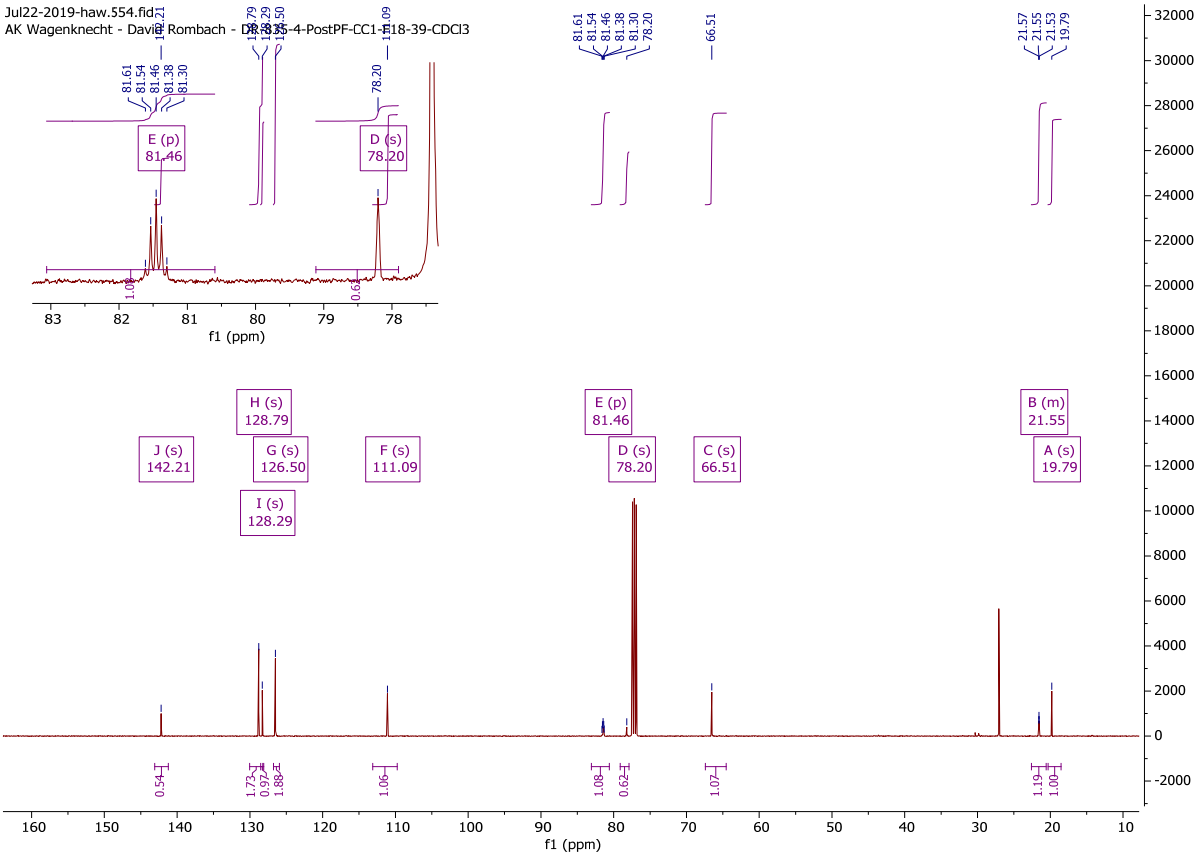


Fig. S63

^{13}C-NMR spectrum of pentafluoro(2-((2-methylallyl)oxy)-2-phenylpropyl)-λ^6-sulfane (**24**) in $CDCl_3$.

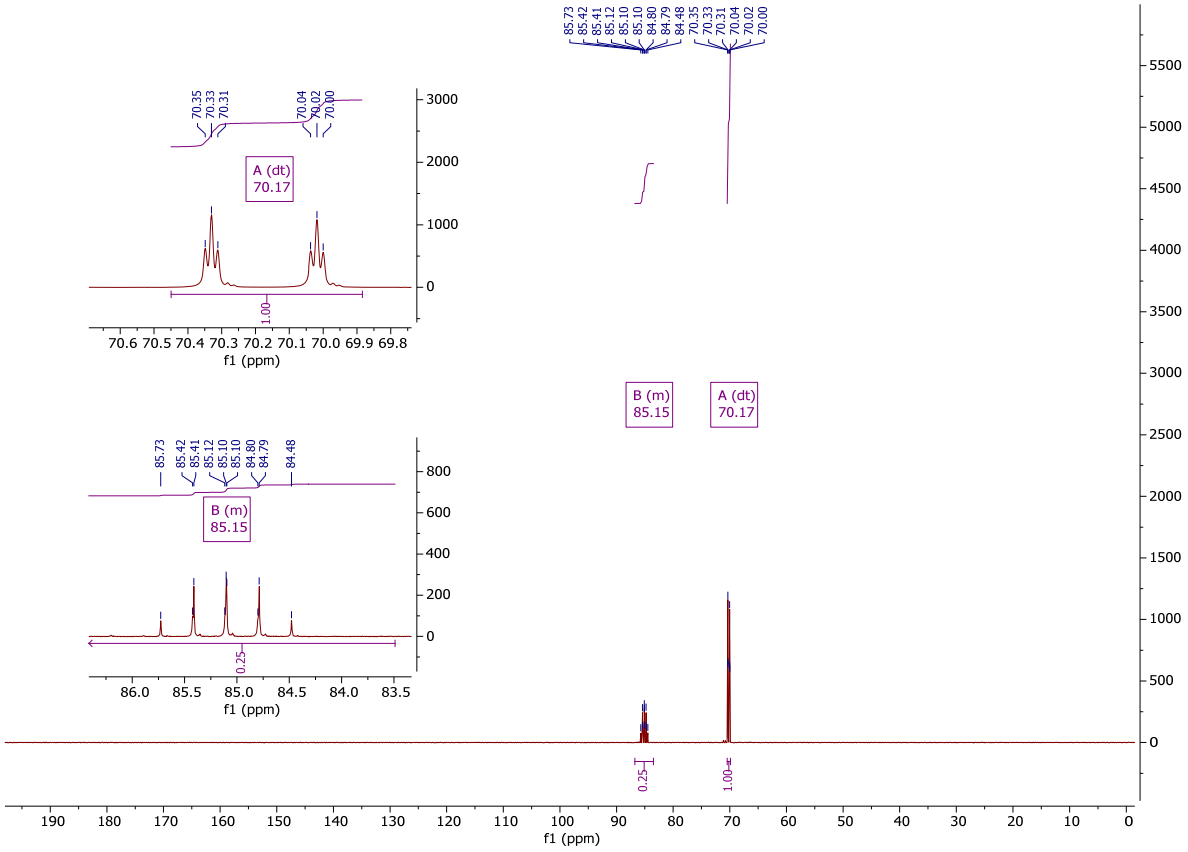


Fig. S64

^{19}F-NMR spectrum of pentafluoro(2-((2-methylallyl)oxy)-2-phenylpropyl)-λ^6-sulfane (**24**) in $CDCl_3$.

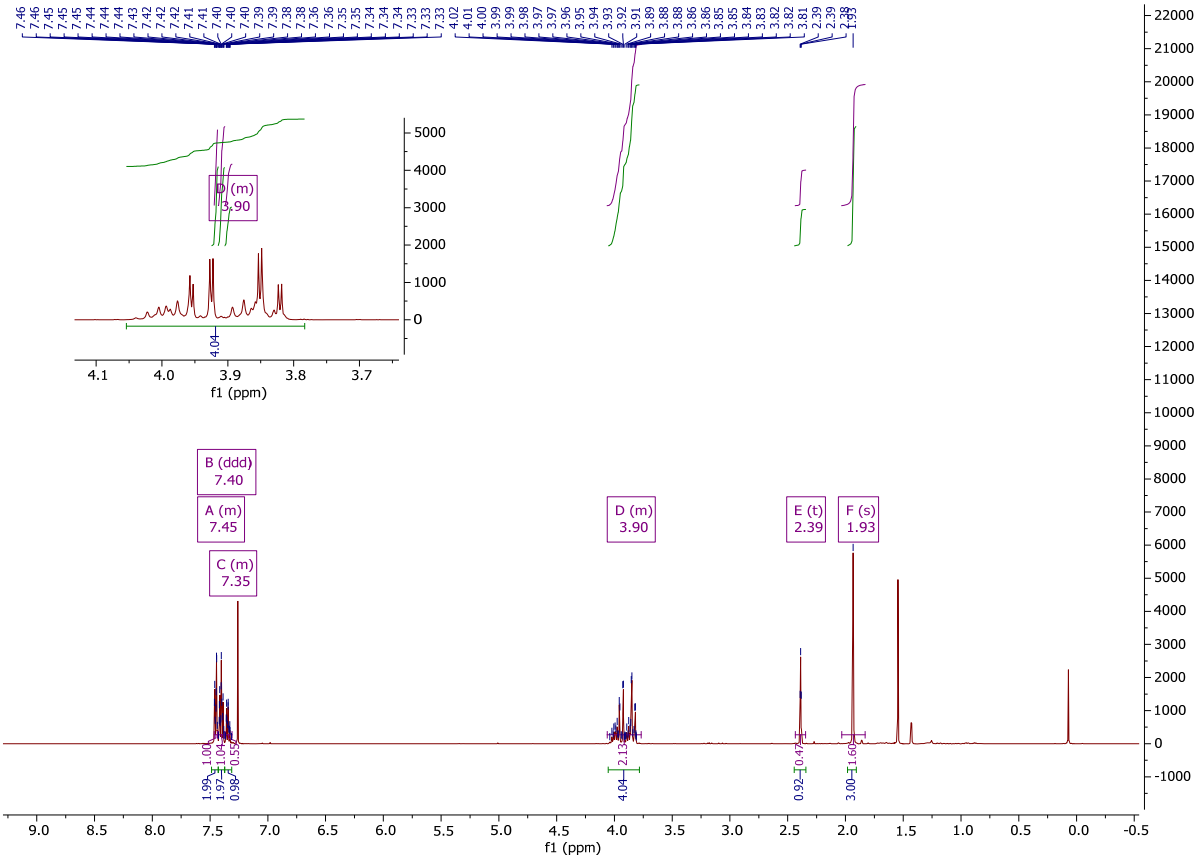


Fig. S65

^{1}H - NMR spectrum of pentafluoro(2-phenyl-2-(prop-2-yn-1-yloxy)propyl)-λ^{6}-sulfane (**25**) in $CDCl_3$.

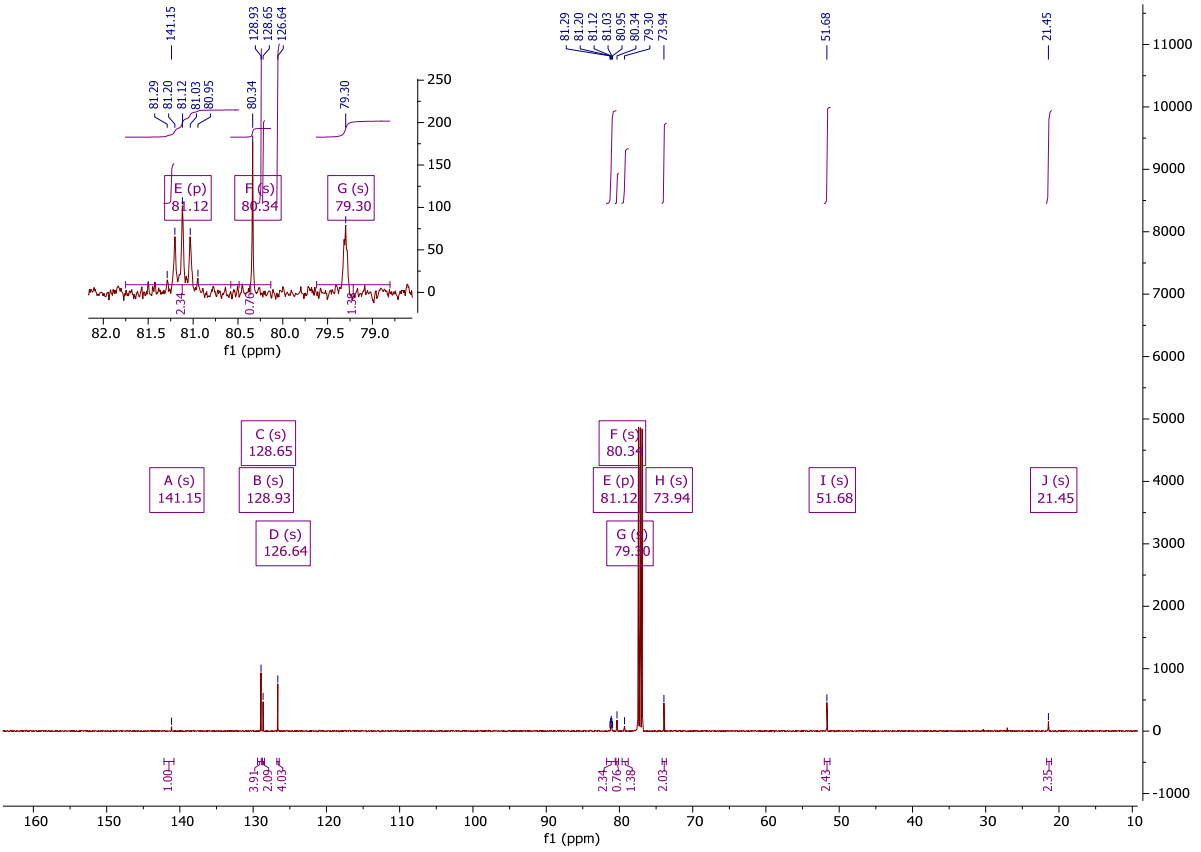


Fig. S66

^{13}C-NMR spectrum of pentafluoro(2-phenyl-2-(prop-2-yn-1-yloxy)propyl)-λ^6-sulfane (**25**) in $CDCl_3$.

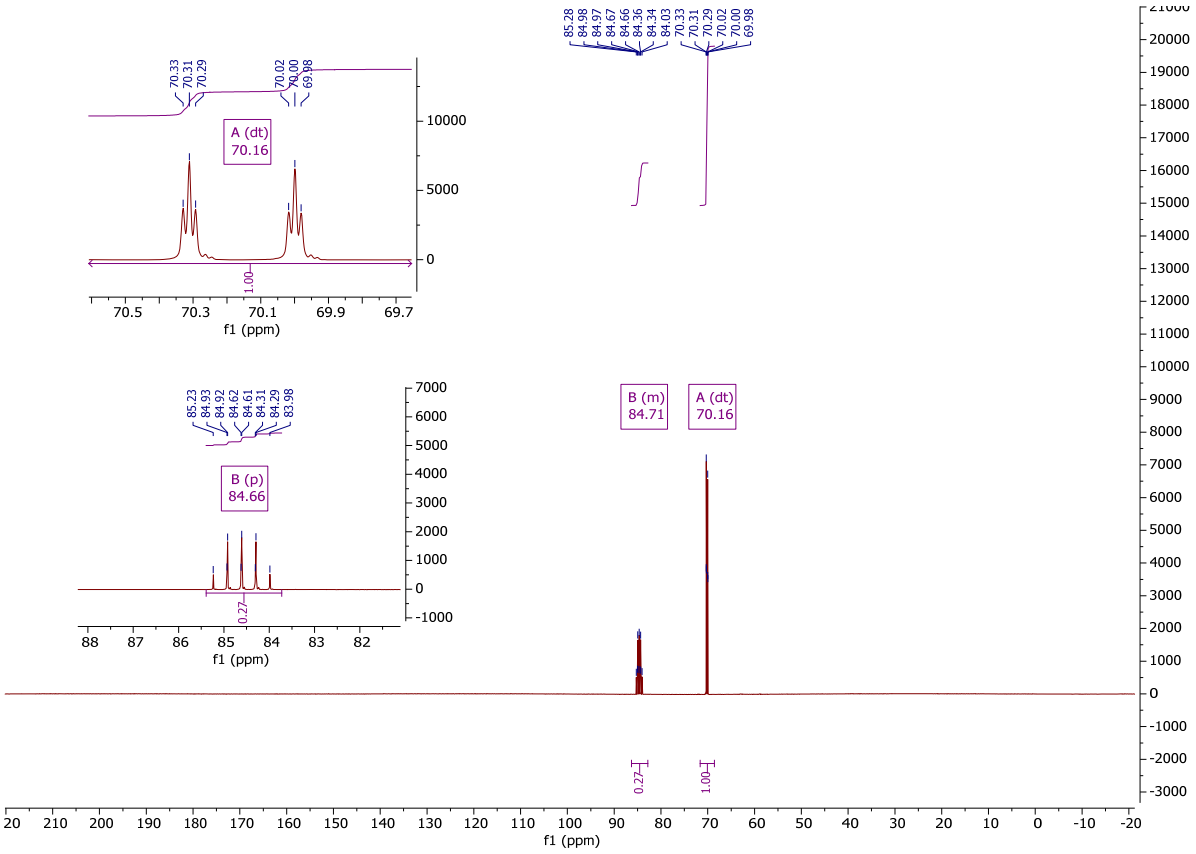


Fig. S67

^{19}F-NMR spectrum of pentafluoro(2-phenyl-2-(prop-2-yn-1-yloxy)propyl)-λ^6-sulfane (**25**) in $CDCl_3$.

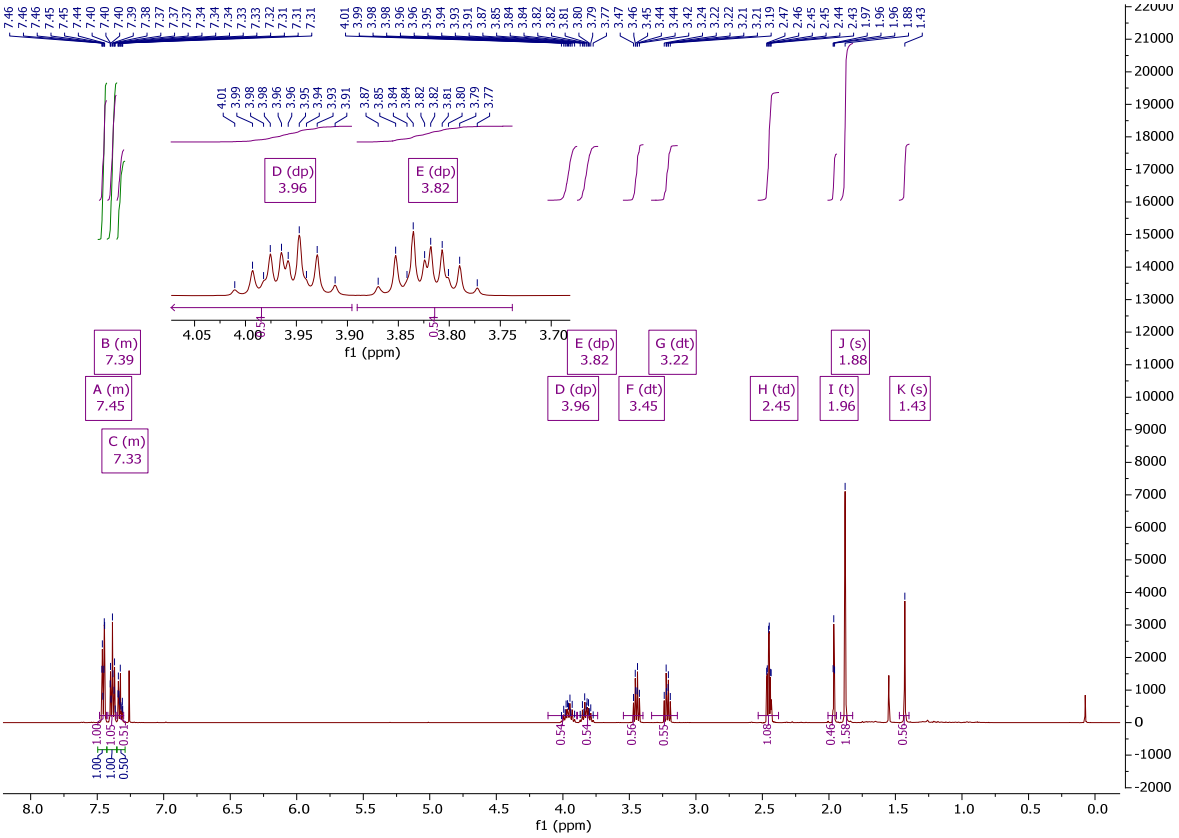


Fig. S68

^{1}H-NMR spectrum of (2-(but-3-yn-1-yloxy)-2-phenylpropyl)pentafluoro-λ^{6}-sulfane (**26**) in $CDCl_3$.

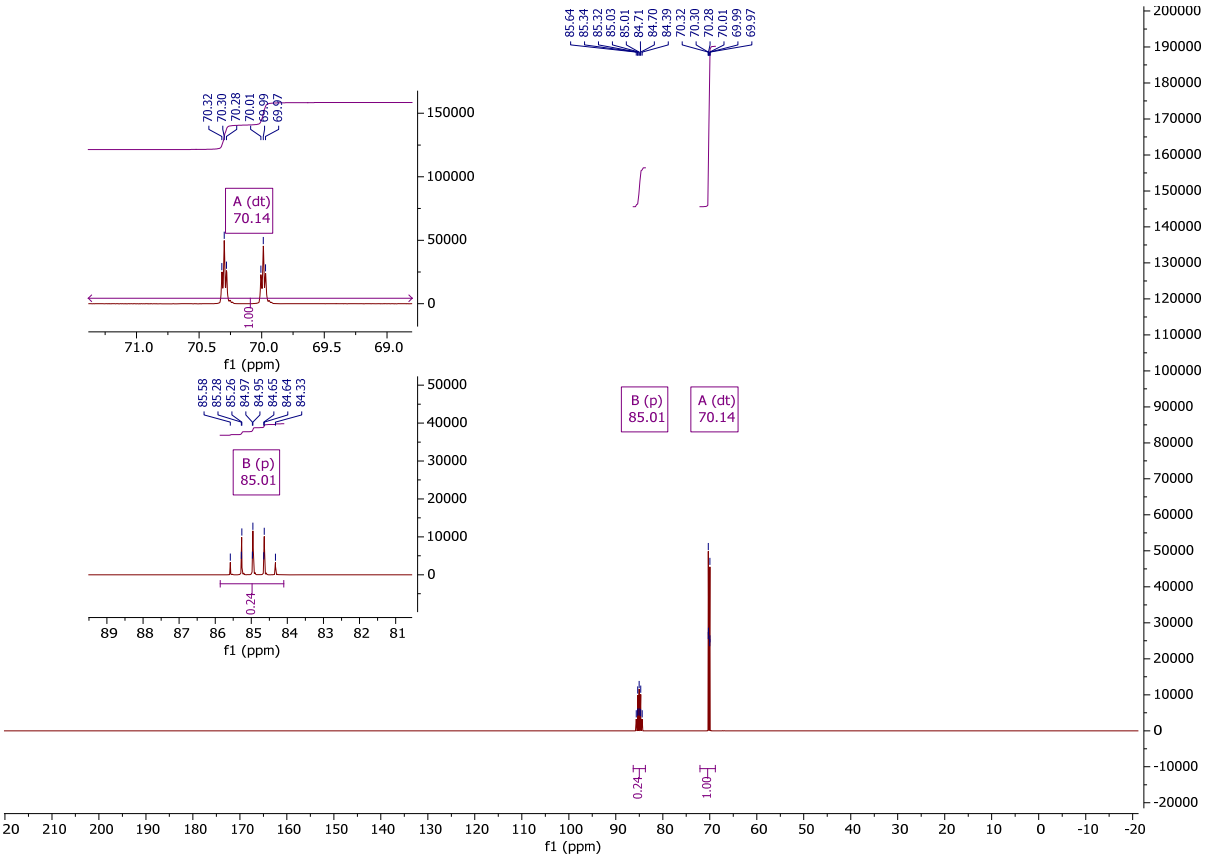


Fig. S69

^{19}F-NMR spectrum of (2-(but-3-yn-1-yloxy)-2-phenylpropyl)pentafluoro-λ^6-sulfane (**26**) in $CDCl_3$.

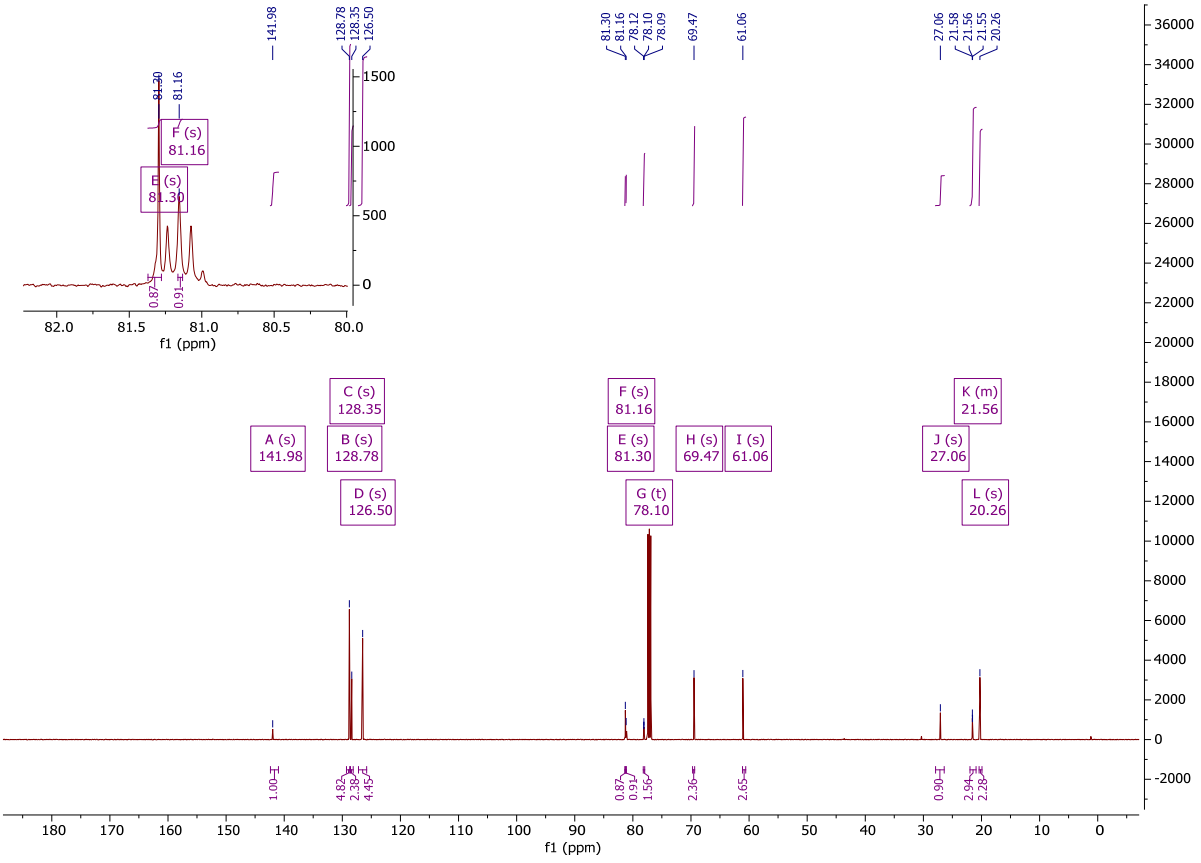


Fig. S70

^{13}C-NMR spectrum of (2-(but-3-yn-1-yloxy)-2-phenylpropyl)pentafluoro-λ^6-sulfane (**26**) in $CDCl_3$.

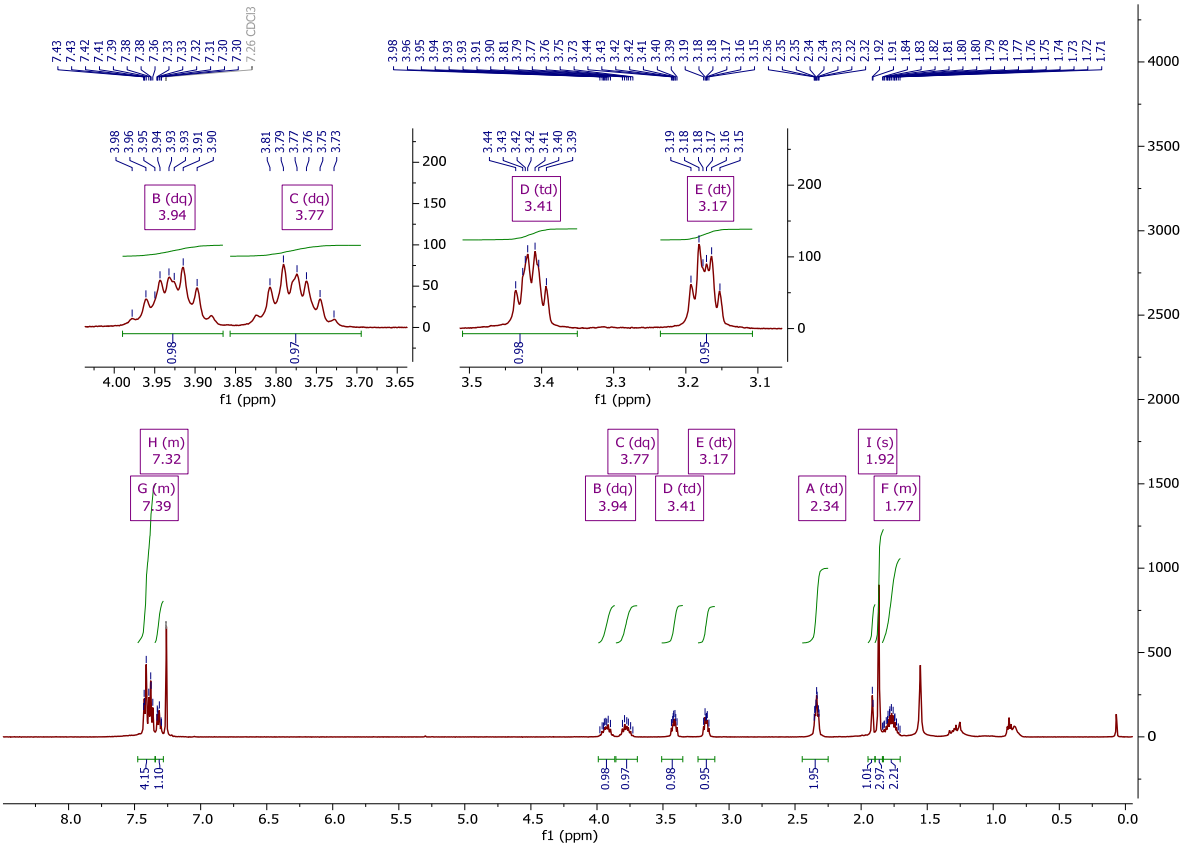


Fig. S71

^{1}H - NMR of spectrum pentafluoro(2-(pent-4-yn-1-yloxy)-2-phenylpropyl)-λ^{6}-sulfane (**27**) in $CDCl_3$.

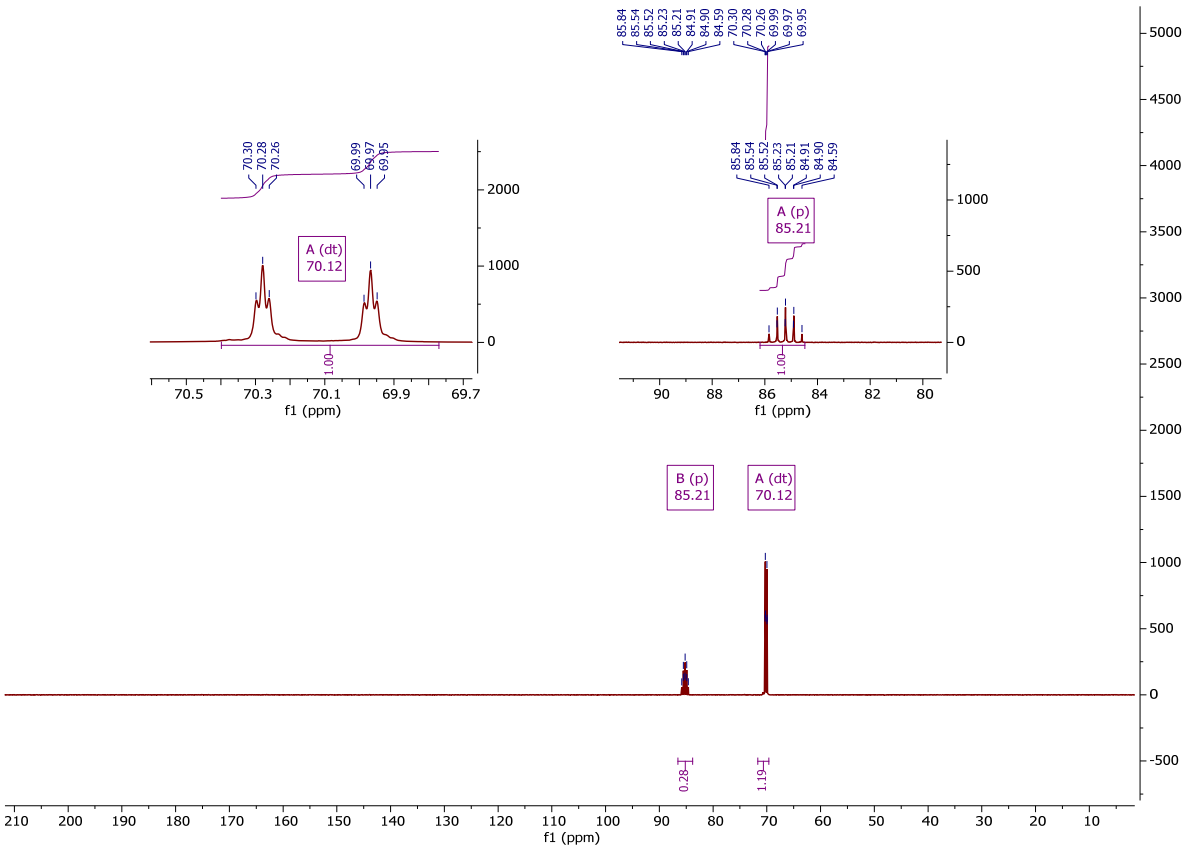


Fig. S72

^{19}F-NMR of spectrum pentafluoro(2-(pent-4-yn-1-yloxy)-2-phenylpropyl)-λ^6-sulfane (**27**) in $CDCl_3$.

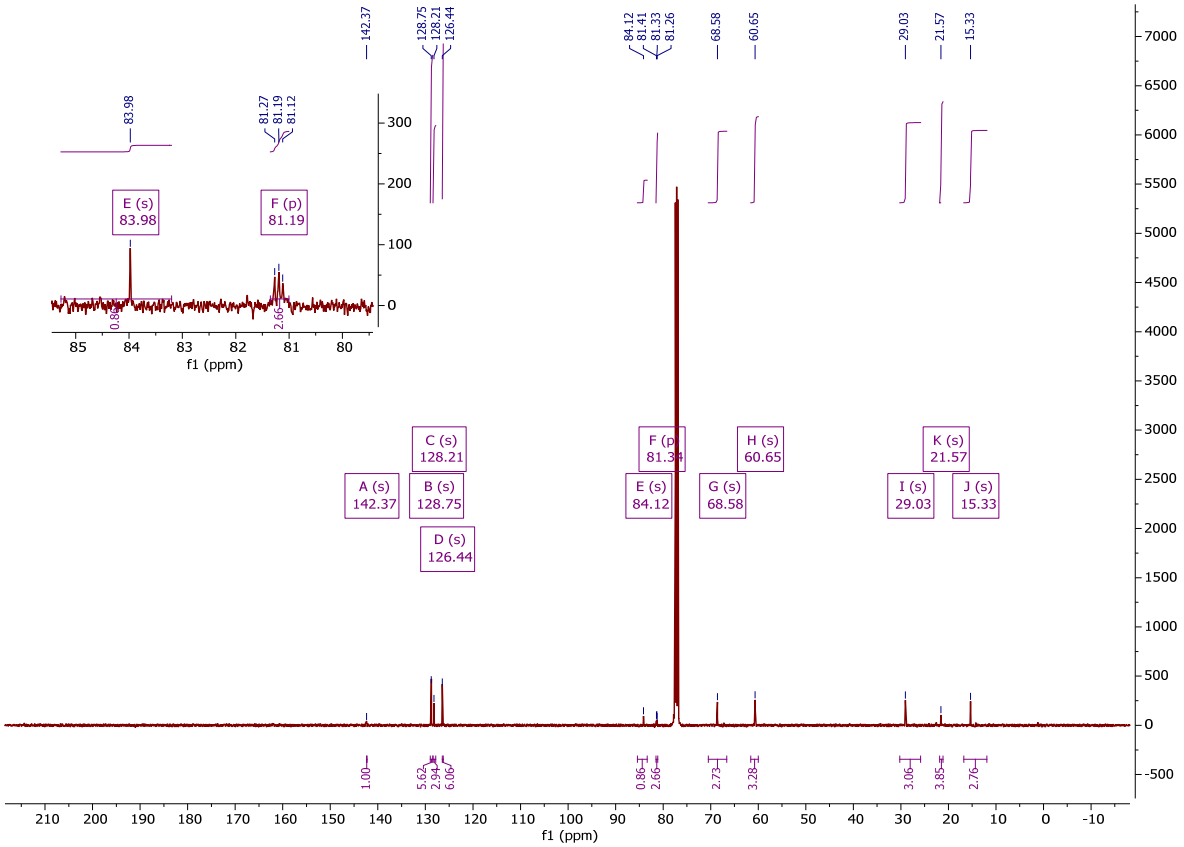


Fig. S73

^{13}C-NMR of spectrum pentafluoro(2-(pent-4-yn-1-yloxy)-2-phenylpropyl)-λ^6-sulfane (**27**) in $CDCl_3$.

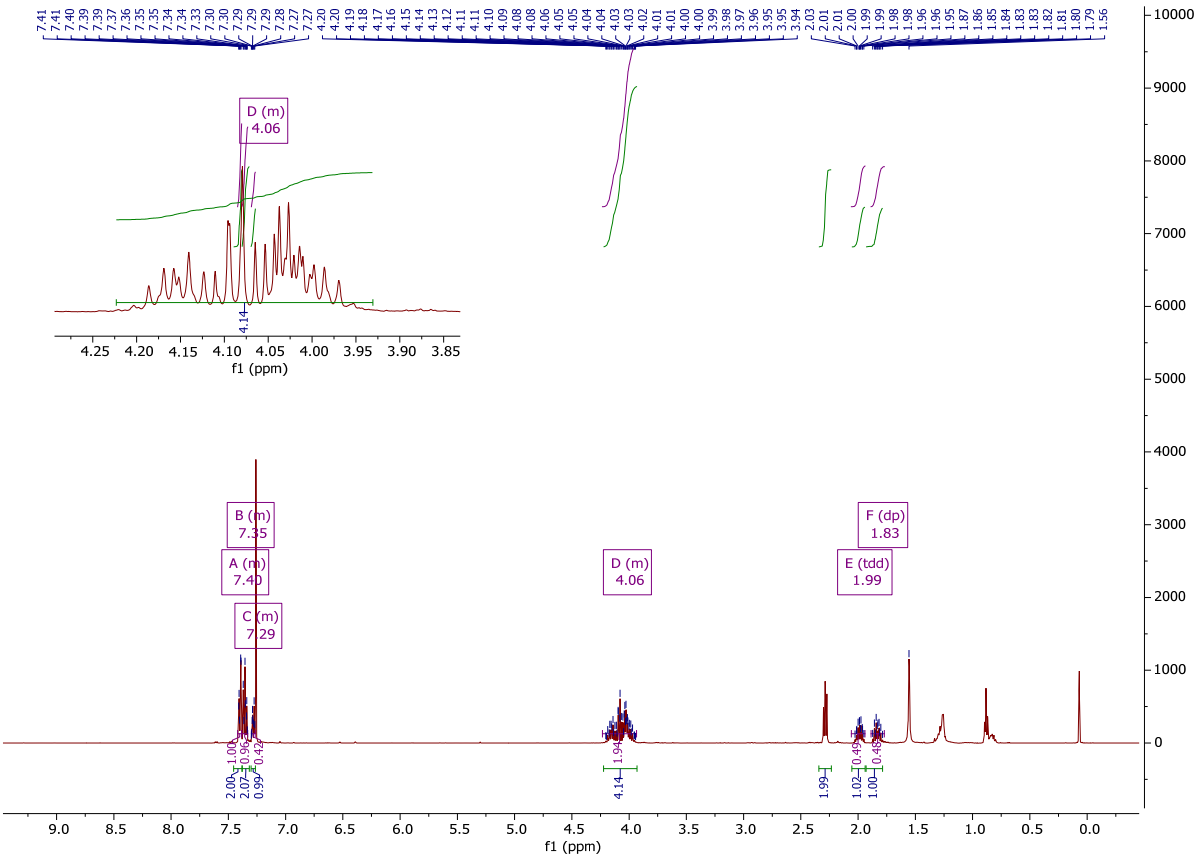


Fig. S74

^{1}H - NMR spectrum of 2-((pentafluoro-λ^{6}-sulfaneyl)methyl)-2-phenyltetrahydrofuran (**28**) in $CDCl_3$.

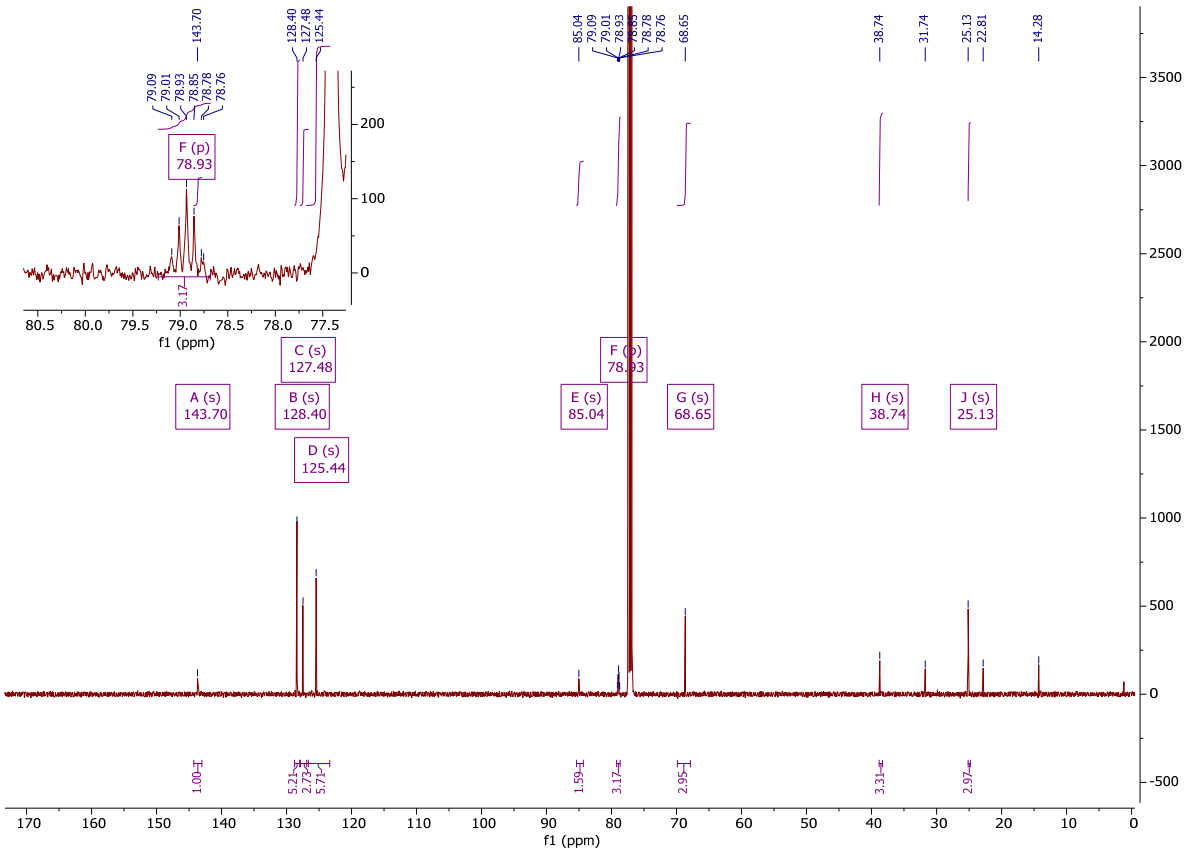


Fig. S75

^{13}C - NMR spectrum of 2-((pentafluoro-λ^6-sulfaneyl)methyl)-2-phenyltetrahydrofuran (**28**) in $CDCl_3$.

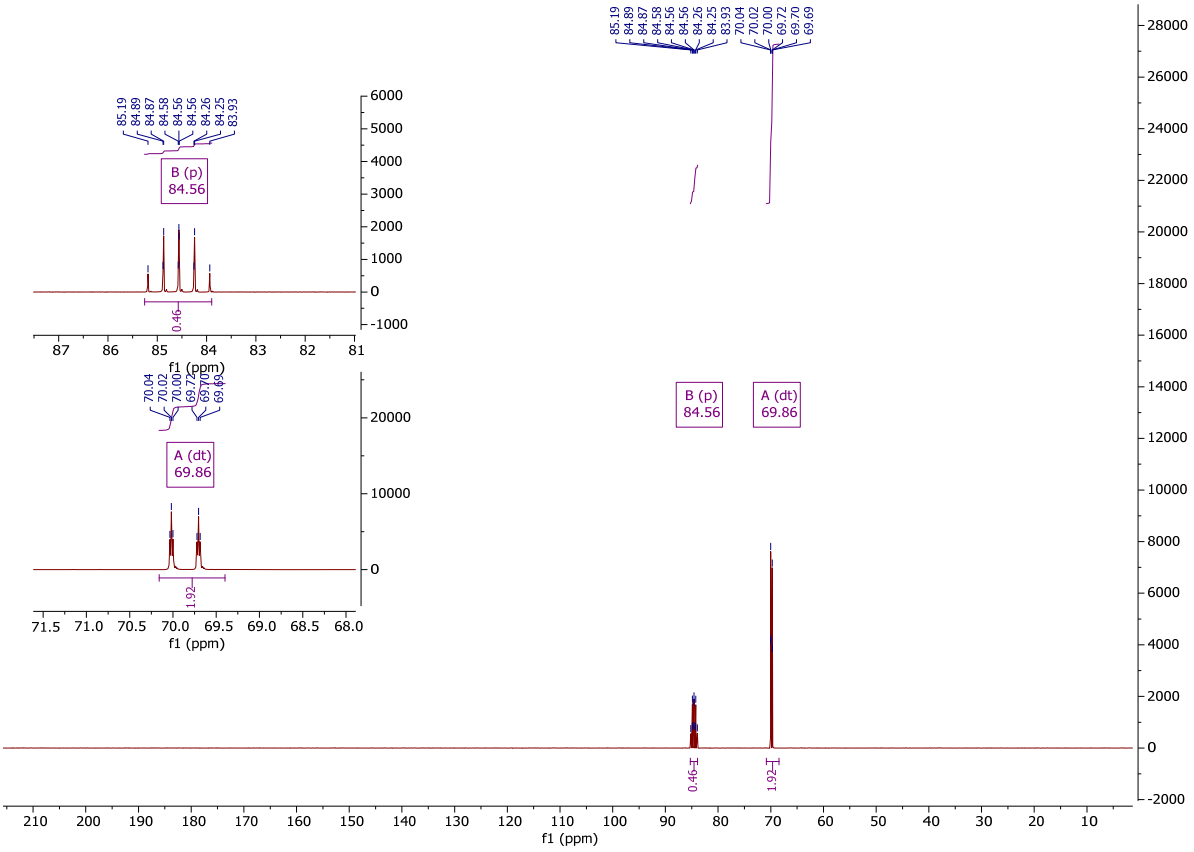


Fig. S76

^{19}F - NMR spectrum of 2-((pentafluoro-λ^6-sulfaneyl)methyl)-2-phenyltetrahydrofuran (**28**) in $CDCl_3$.

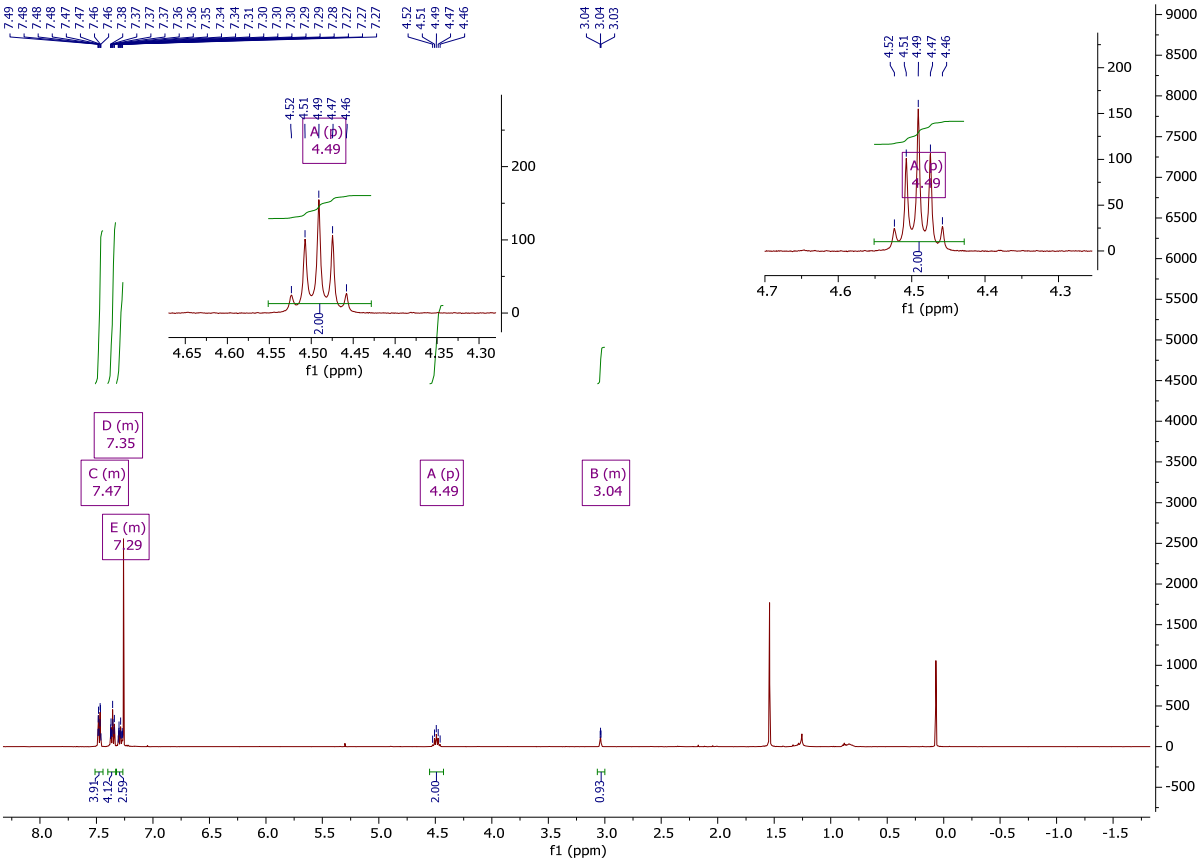


Fig. S77

^{1}H - NMR spectrum of 2-(pentafluoro-λ^{6}-sulfaneyl)-1,1-diphenylethan-1-ol (**29**) in $CDCl_3$.

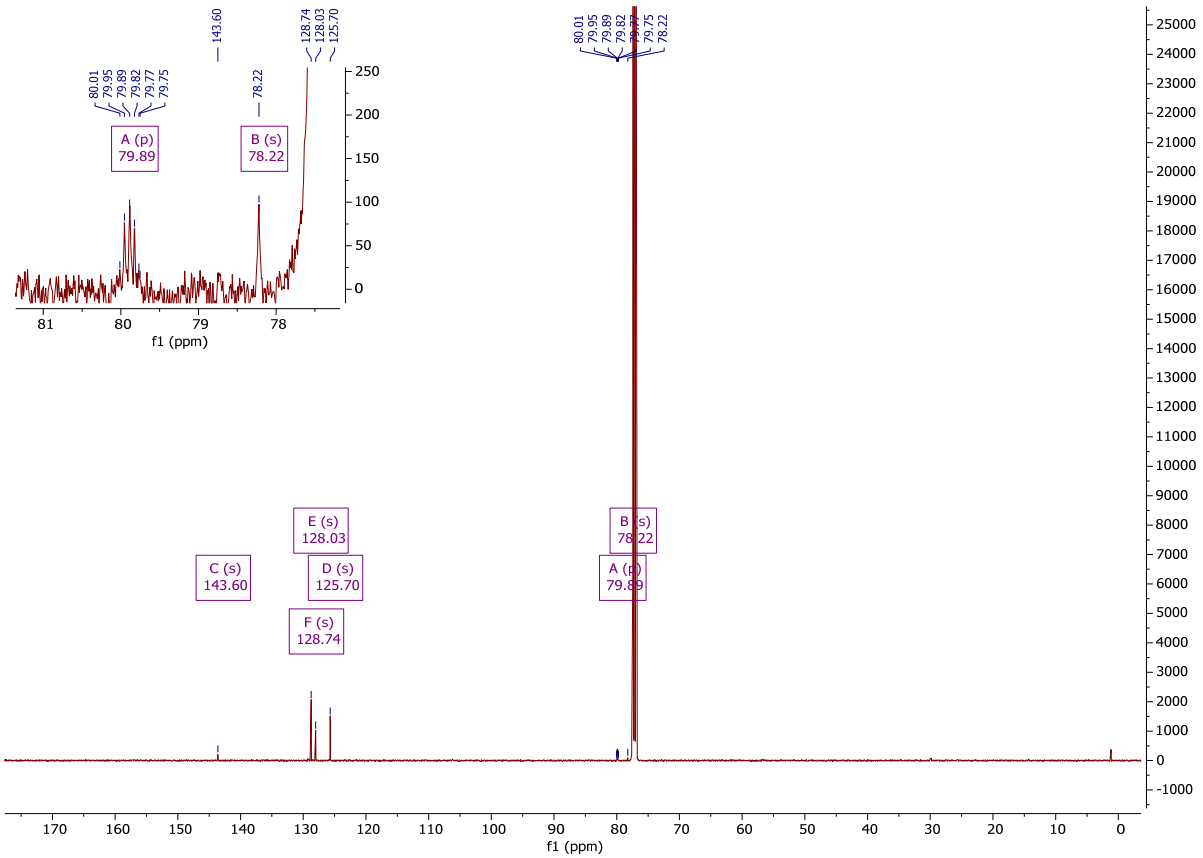


Fig. S78

^{13}C-NMR spectrum of 2-(pentafluoro-λ^6-sulfaneyl)-1,1-diphenylethan-1-ol (**29**) in $CDCl_3$.

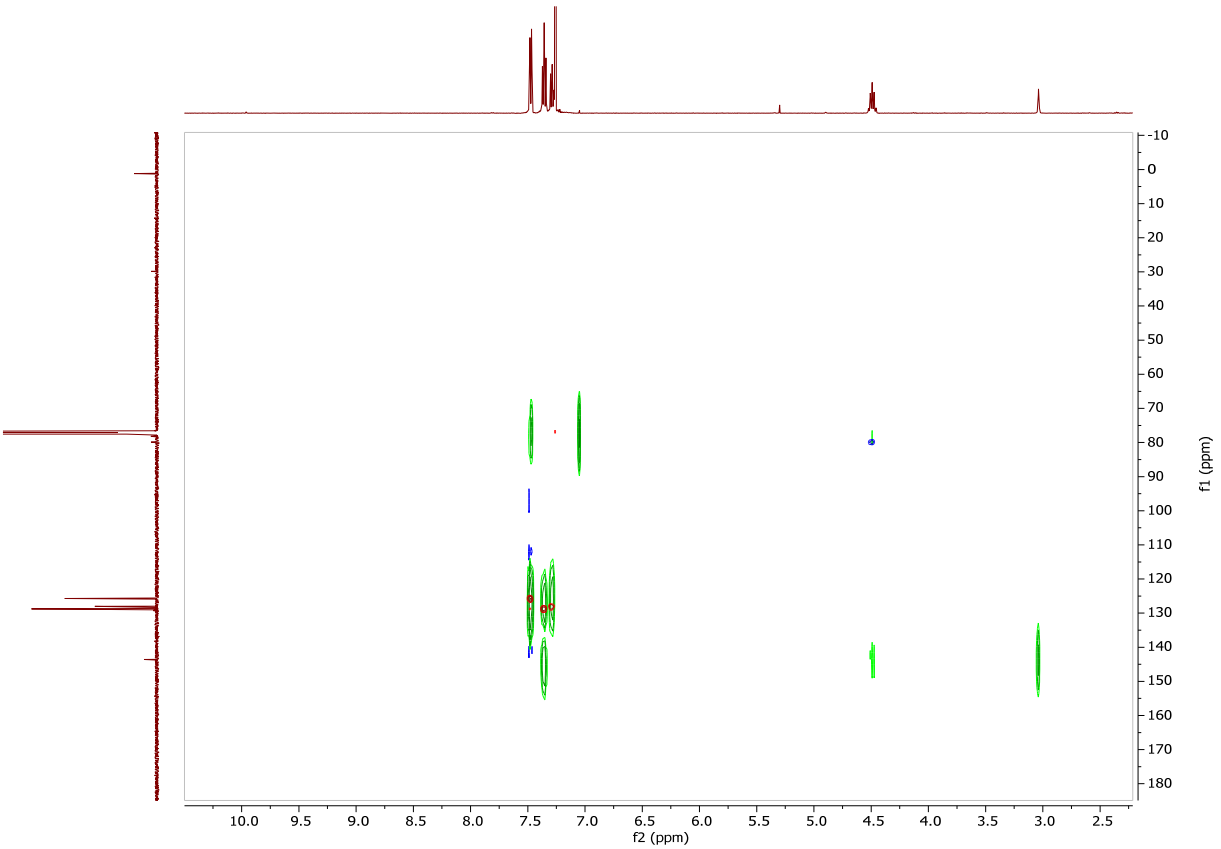


Fig. S79

Stacked ^{1}H -^{13}C- HSQCed/HMBC spectra of 2-(pentafluoro-λ^{6}-sulfaneyl)-1,1-diphenylethan-1-ol (**29**) in $CDCl_3$.

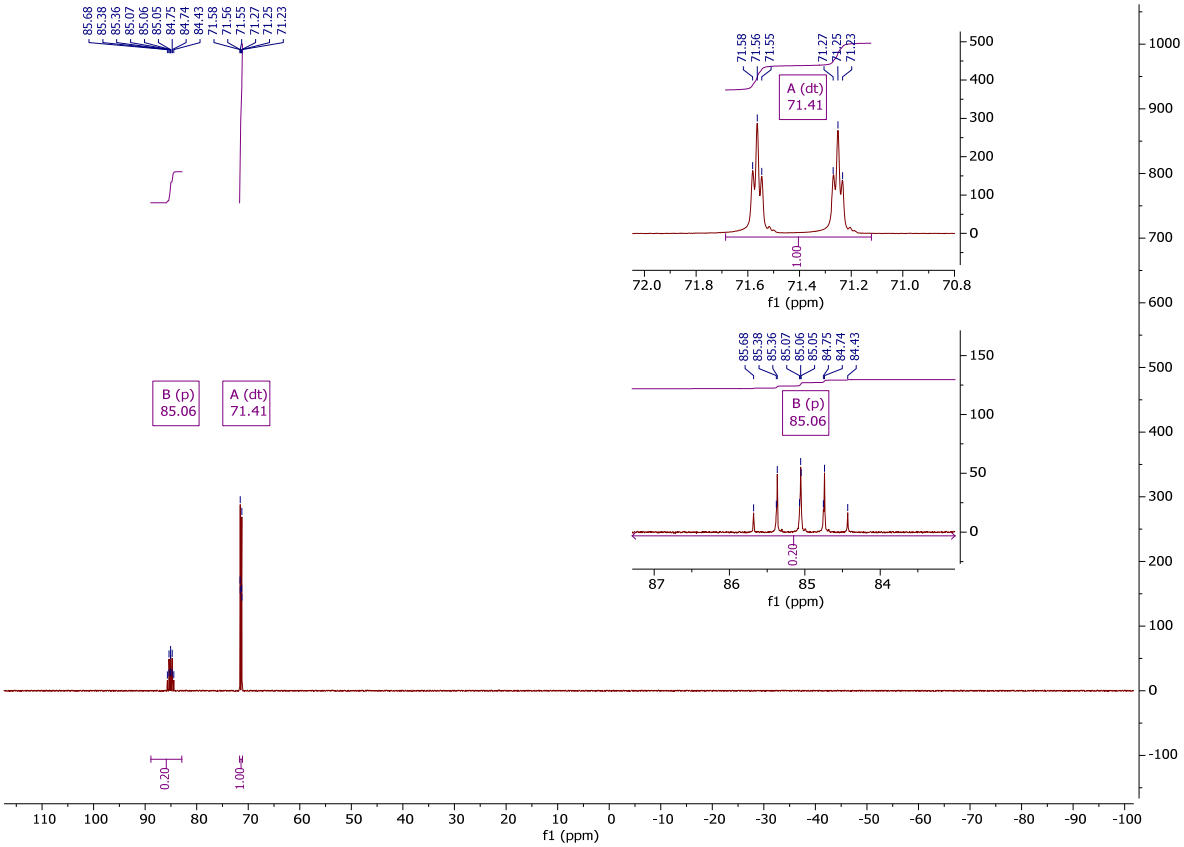


Fig. S80

^{19}F-NMR spectrum of 2-(pentafluoro-λ^6-sulfaneyl)-1,1-diphenylethan-1-ol (**29**) in $CDCl_3$.

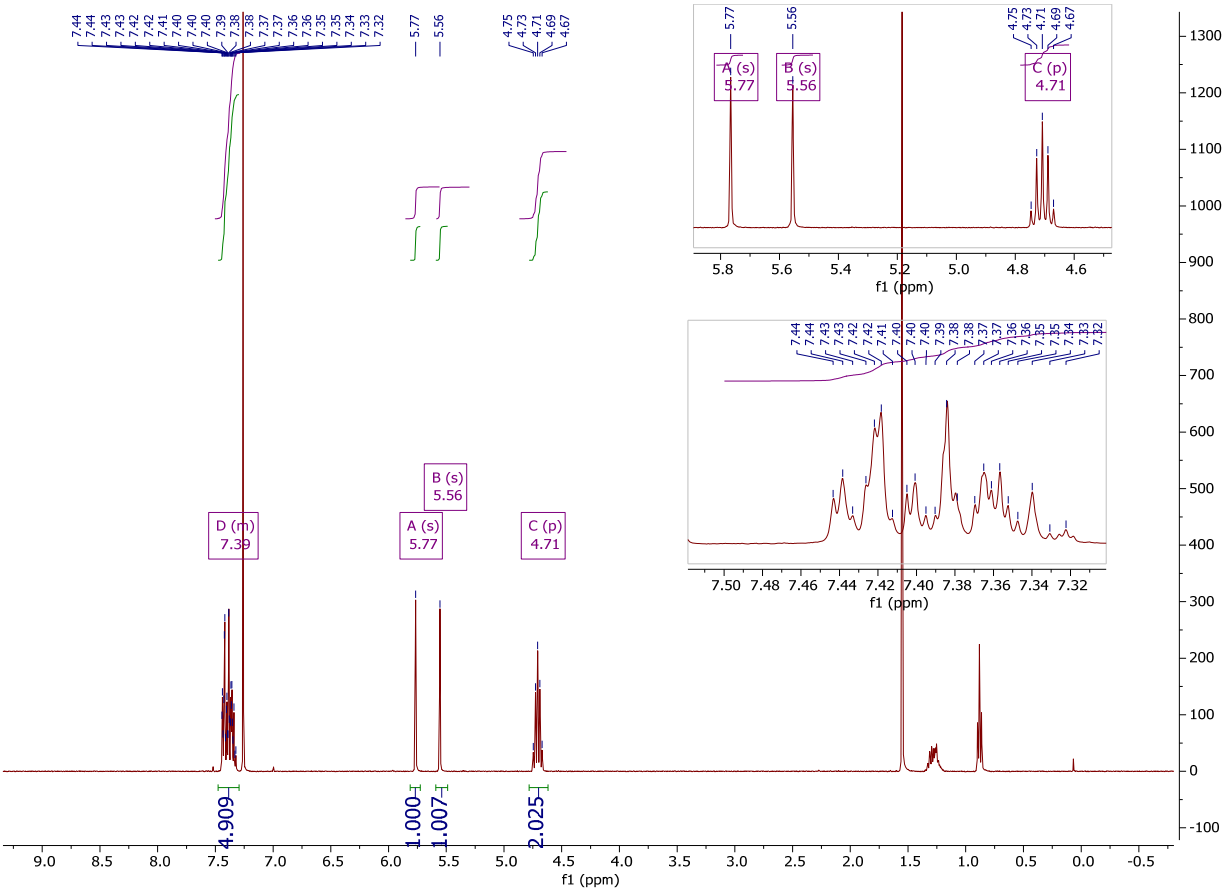


Fig. S81

^{1}H-NMR spectrum of pentafluoro-(2-phenylallyl)-λ^{6}-sulfane (**30)** in $CDCl_3$ as previously reported.[S7]

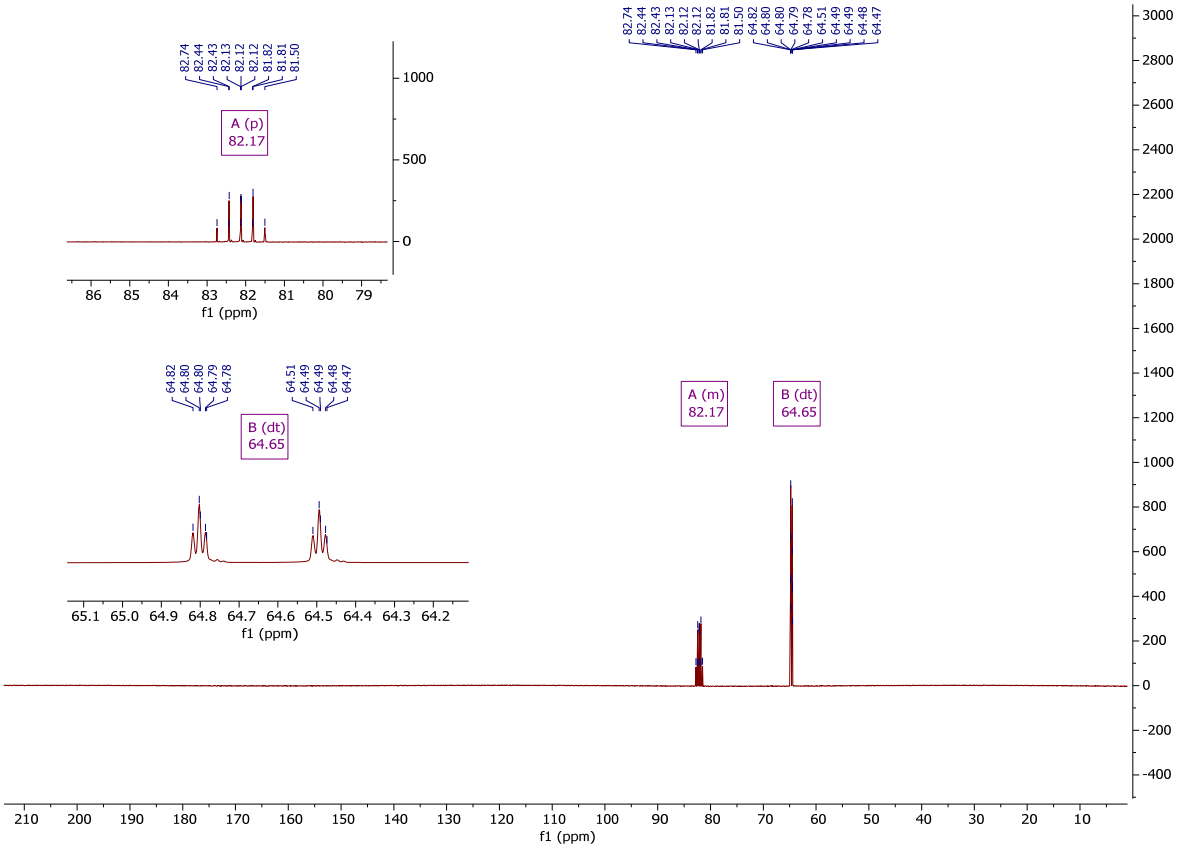


Fig. S82

^{19}F-NMR spectrum of pentafluoro-(2-phenylallyl)-λ^6-sulfane (**30)** in $CDCl_3$ as previously reported.[S7]

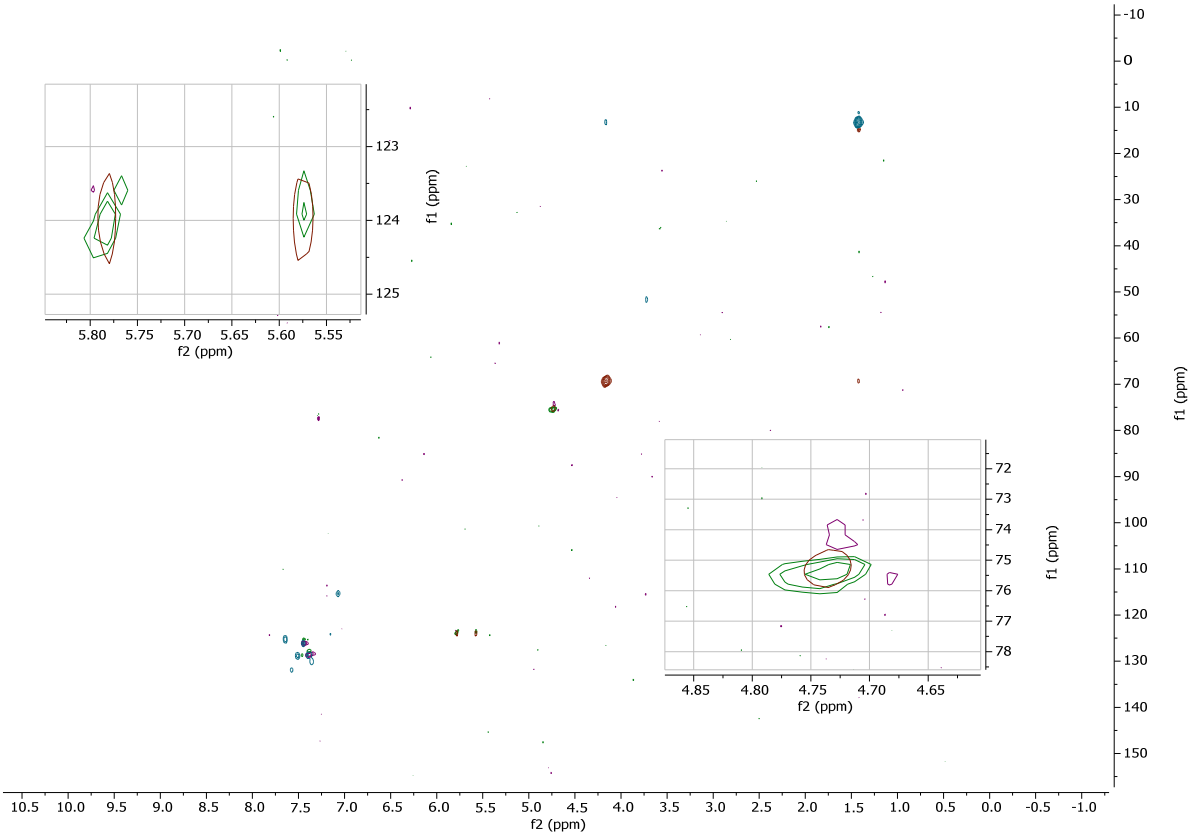


Fig. S83

Stacked ^{1}H-^{13}C-HSQC spectra of isolated pentafluoro-(2-phenylallyl)-λ^{6}-sulfane (**30**) and the crude reaction mixture of the demethoxylation reaction of **8** in $CDCl_3$. The relevant CH_2SF_5 group as well as the $C{=}CH_2$ groups are highlighted. The mixture contains fluorobenzene and α,α,α-trifluorotoluene which was added as standard to the reaction mixture.

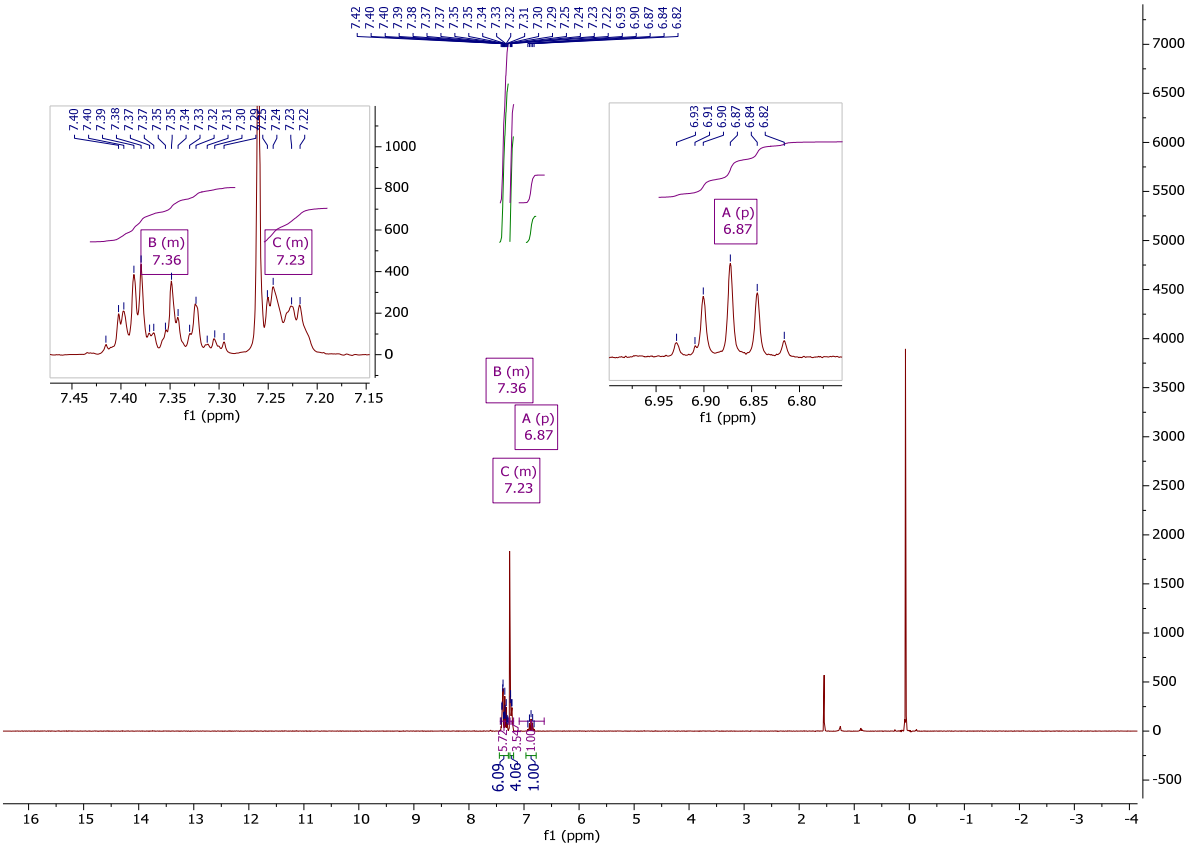


Fig. S84

^{1}H-NMR spectrum of (2,2-Diphenylvinyl)-pentafluoro-λ^{6}-sulfane (**31**) in $CDCl_3$ as previously reported[S7].

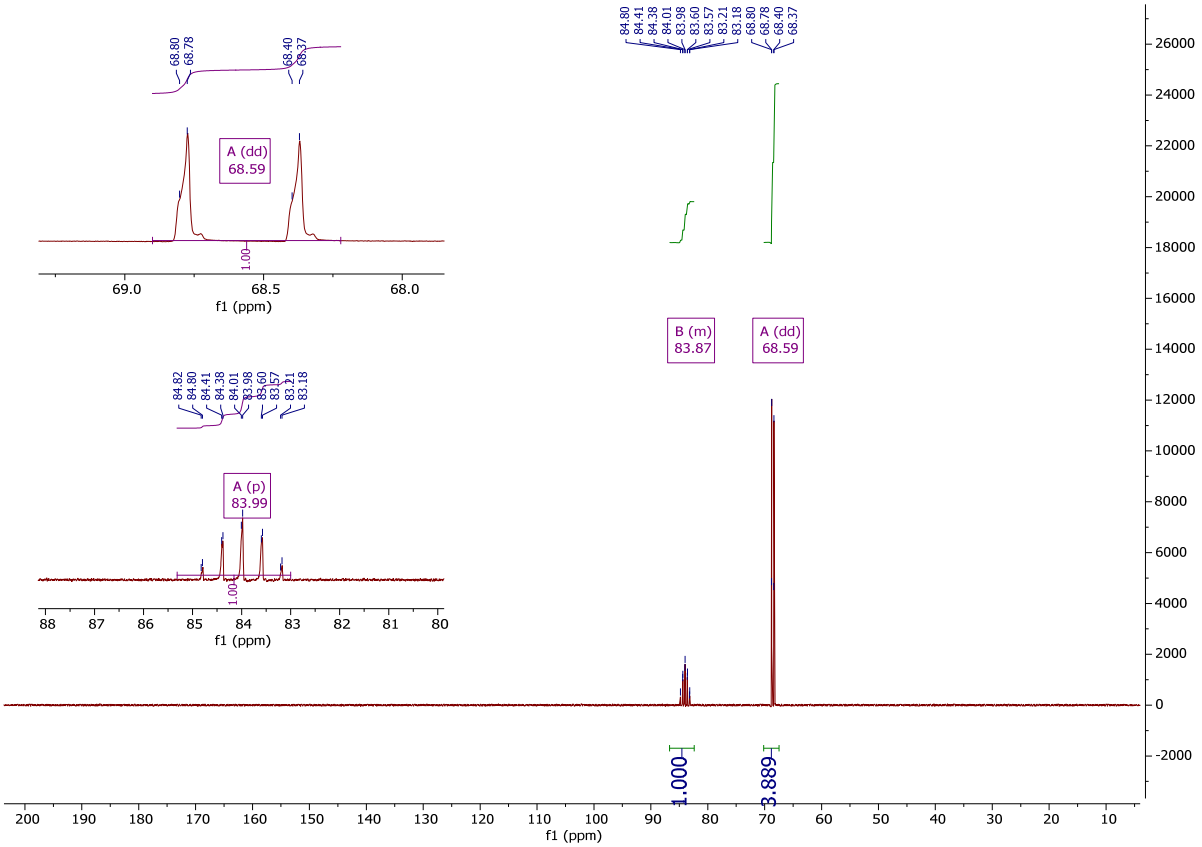


Fig. S85

^{19}F-NMR spectrum of (2,2-Diphenylvinyl)-pentafluoro-λ^6-sulfane (**31**) in $CDCl_3$ as previously reported[S7].

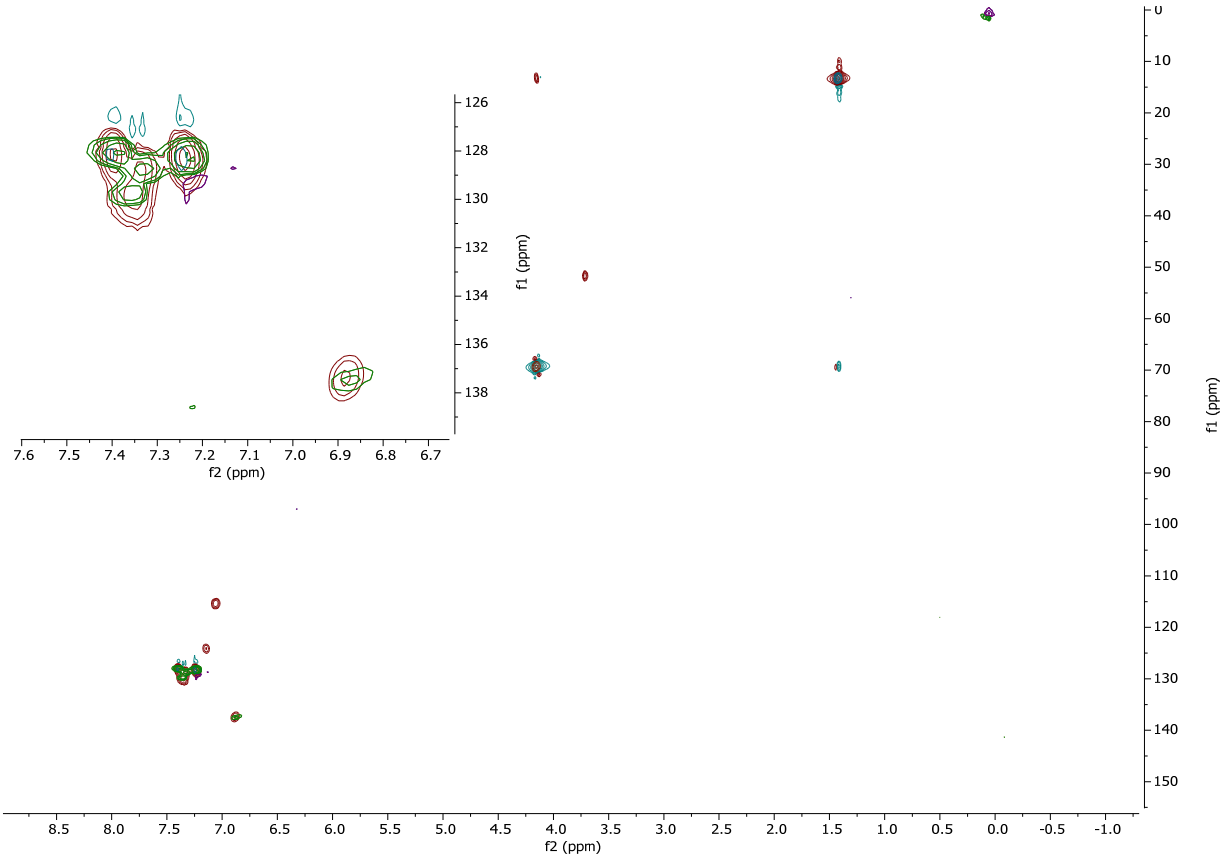


Fig. S86

Stacked ^{1}H-^{13}C-HSQC spectra of isolated (2,2-Diphenylvinyl)-pentafluoro-λ^{6}-sulfane (**31**) and the crude reaction mixture of the demethoxylation of **9** by BF_3 in $CDCl_3$. The relevant $=CHSF_5$ group as well as the arene region is highlighted. The mixture contains fluorobenzene which was added as standard to the reaction mixture.

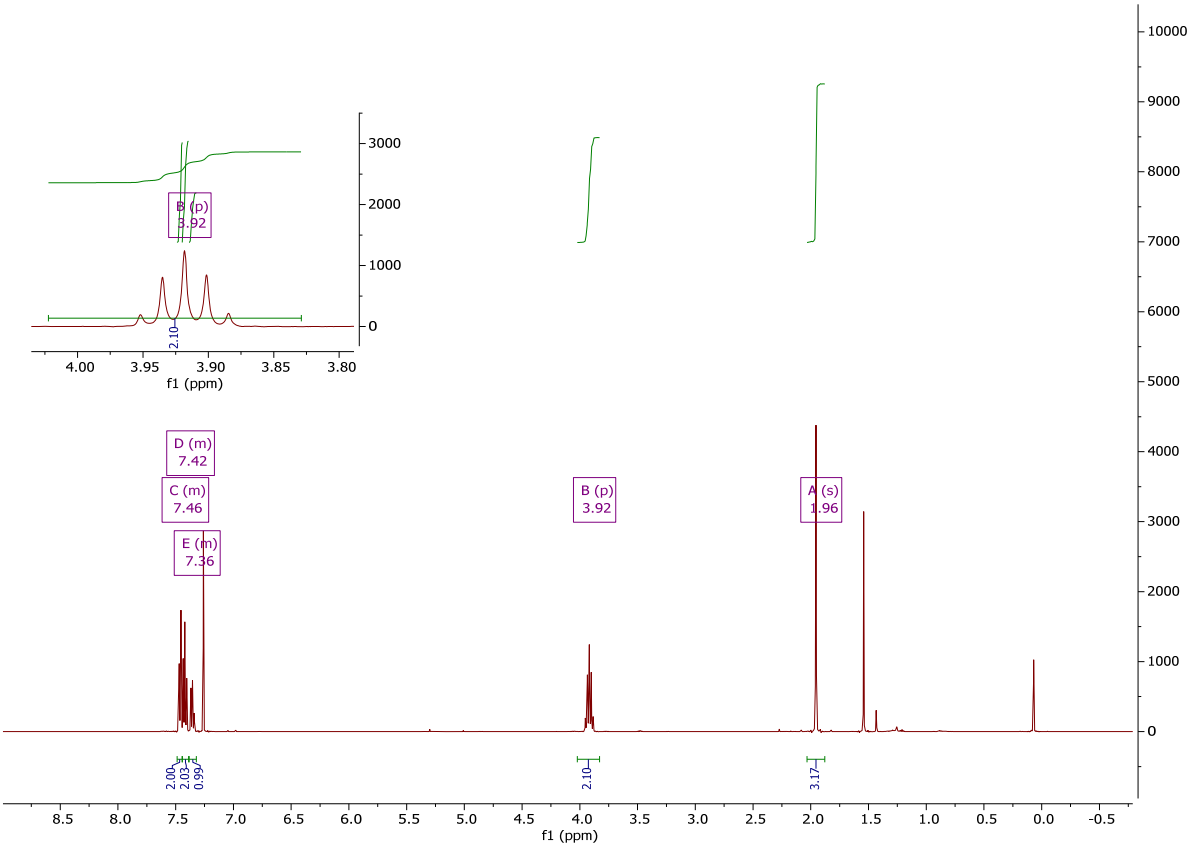


Fig. S87

^{1}H-NMR spectrum of (2-azido-2-phenylpropyl)pentafluoro-λ^{6}-sulfane (**32**) in $CDCl_3$.

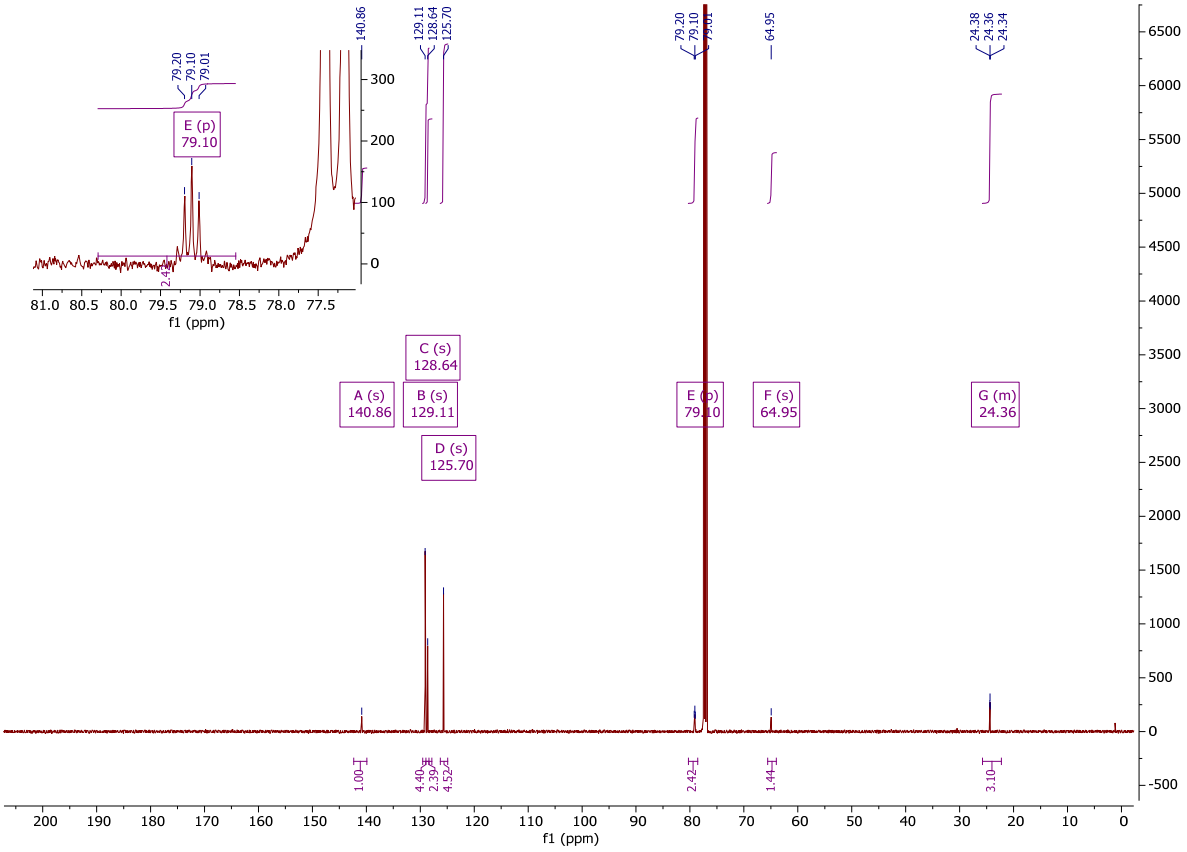


Fig. S88

^{13}C-NMR spectrum of (2-azido-2-phenylpropyl)pentafluoro-λ^6-sulfane (**32**) in $CDCl_3$.

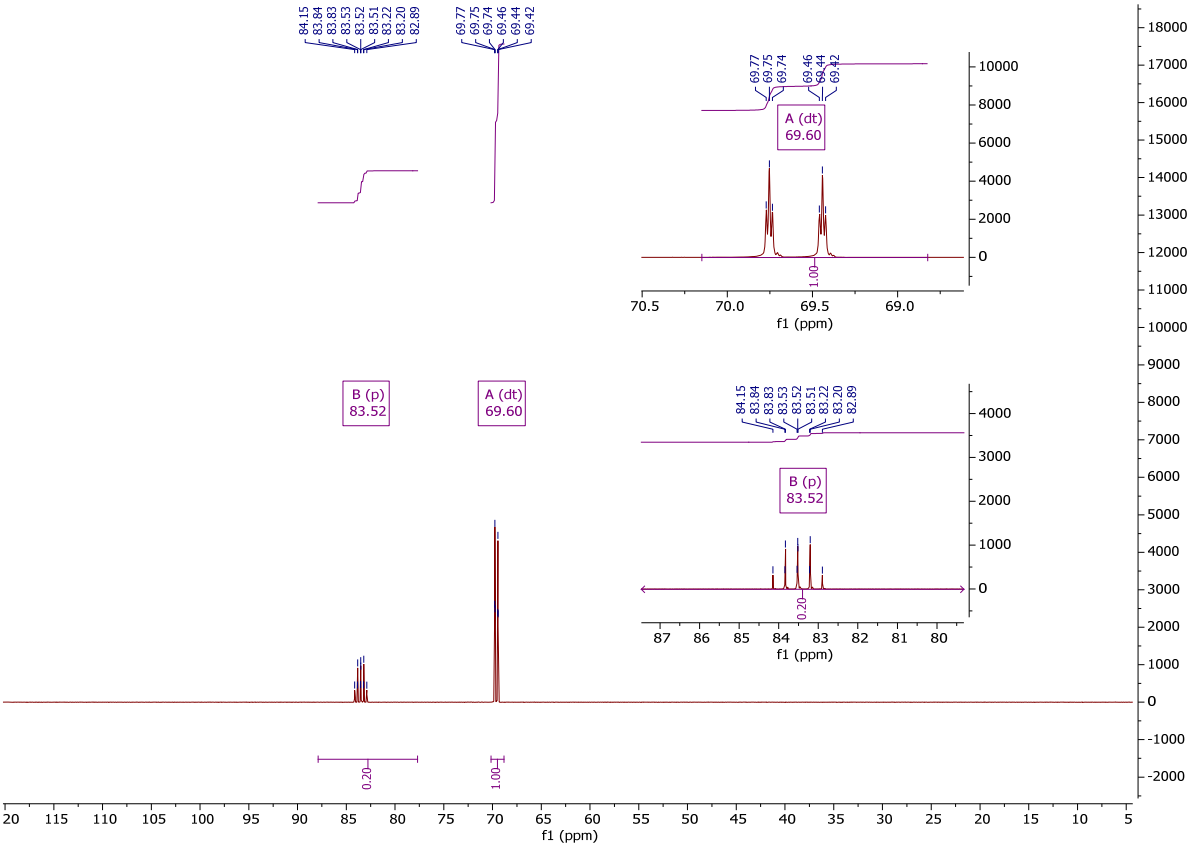


Fig. S89

^{19}F-NMR spectrum of (2-azido-2-phenylpropyl)pentafluoro-λ^6-sulfane (**32**) in $CDCl_3$.

Mass spectrometric characterisations

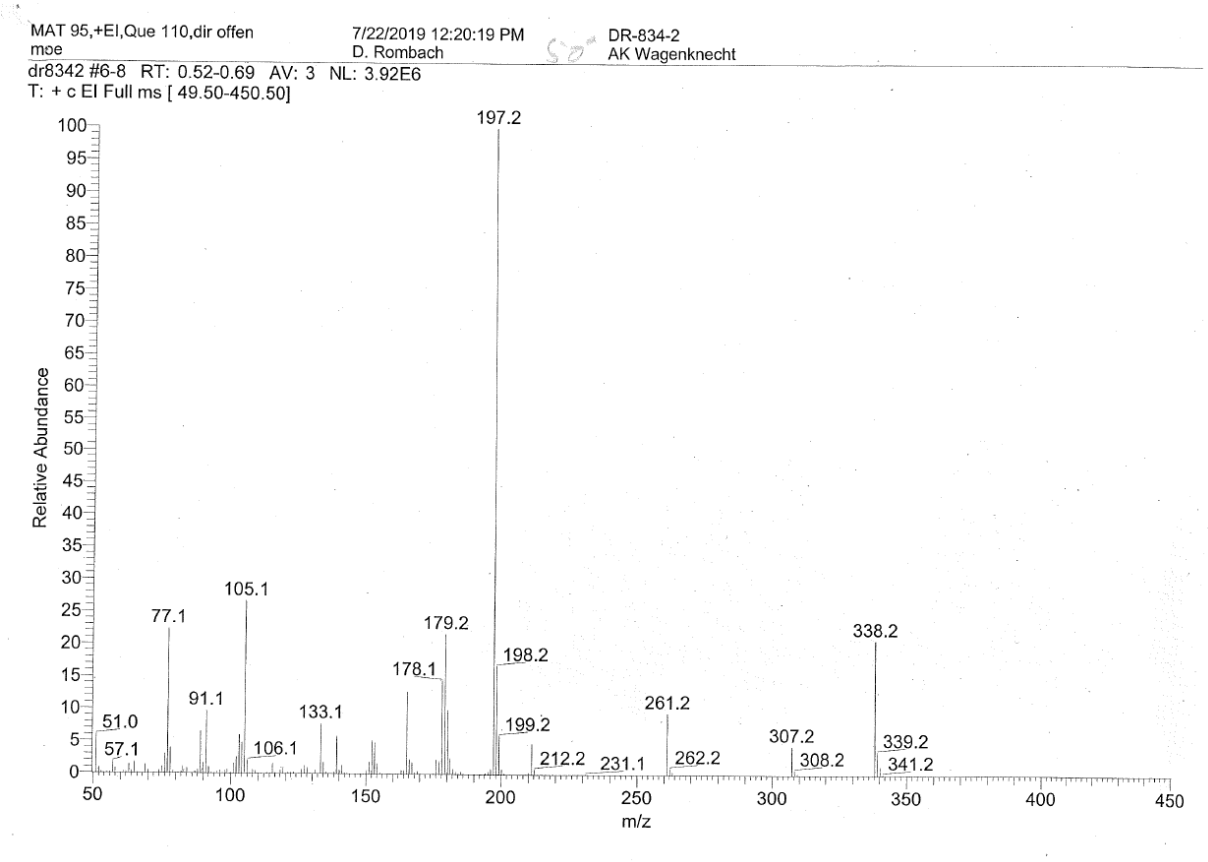


Fig. S90

HR-EI-MS spectrum of pentafluoro(2-methoxy-2,2-diphenylethyl)-λ^6-sulfane (**9**).

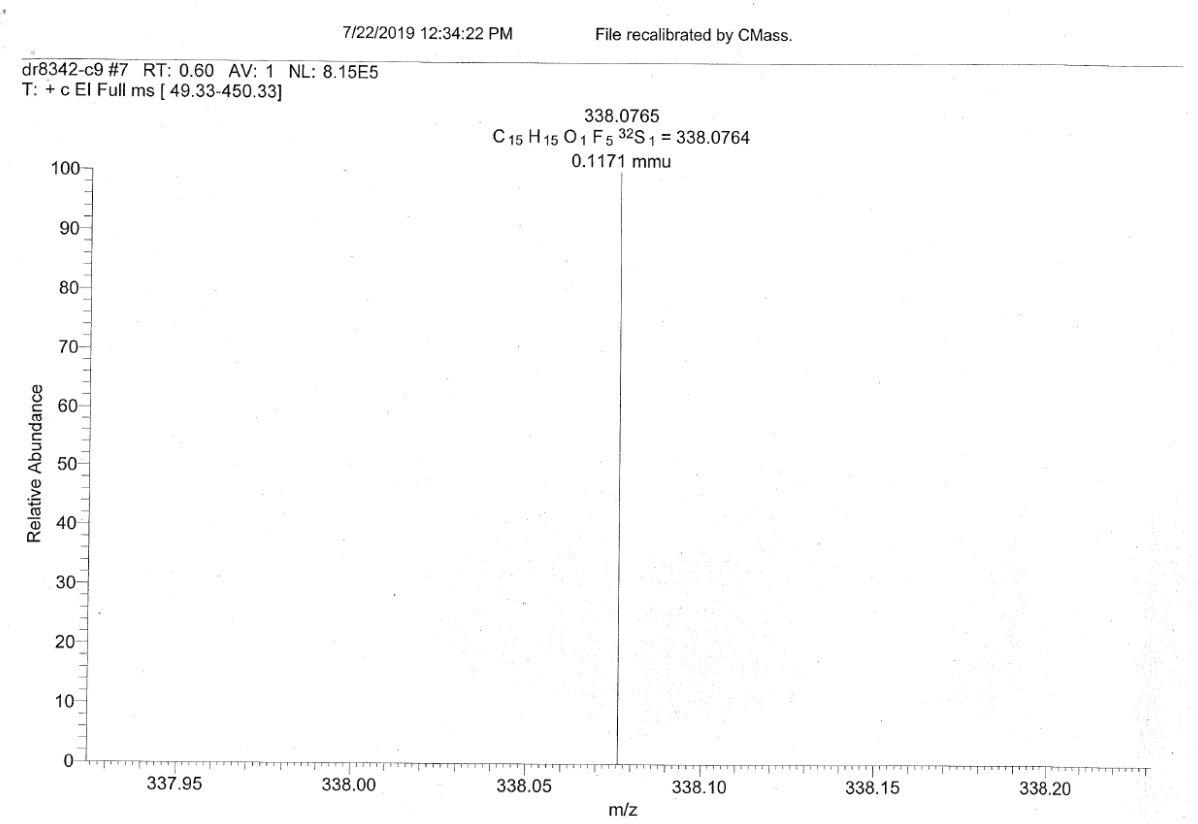


Fig. S91

HR-EI-MS spectrum of pentafluoro(2-methoxy-2,2-diphenylethyl)-λ^6-sulfane (**9**).

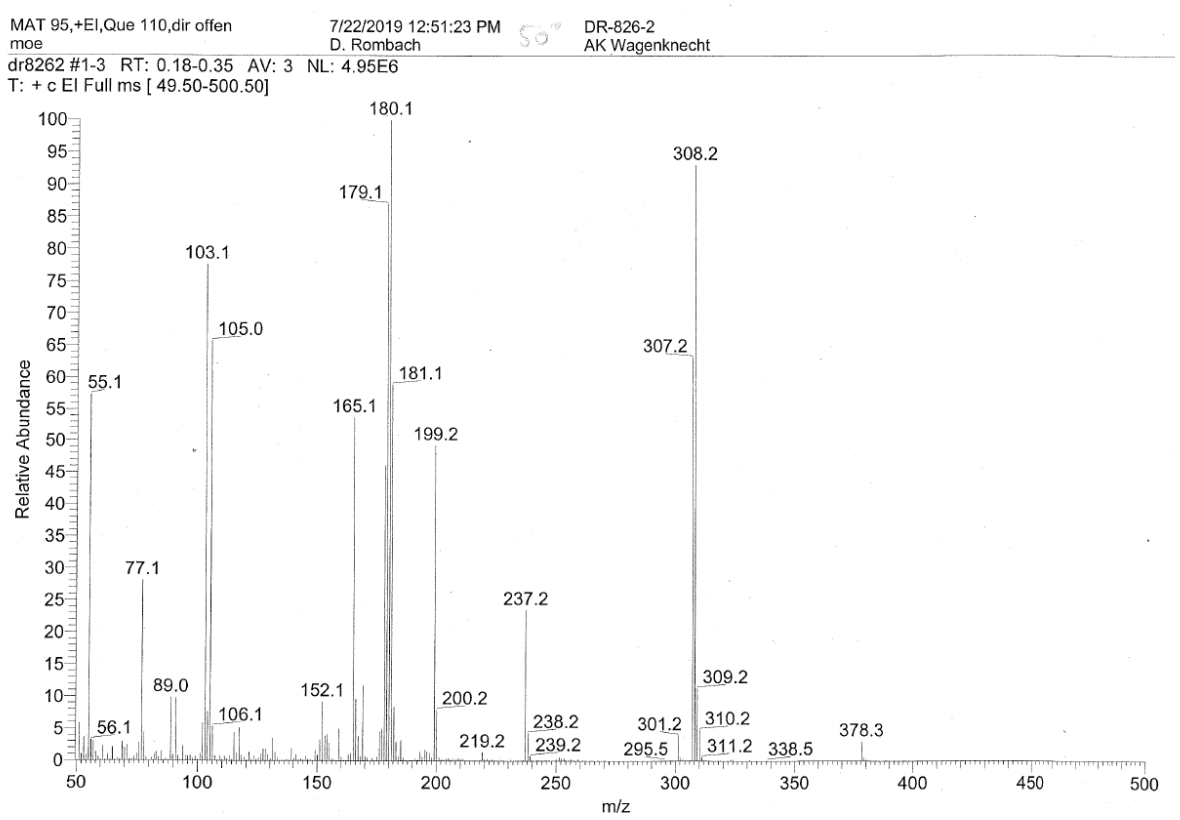


Fig. S92

EI-MS spectrum of pentafluoro(2-((2-methylallyl)oxy)-2,2-diphenylethyl)-λ^6-sulfane (**10**).

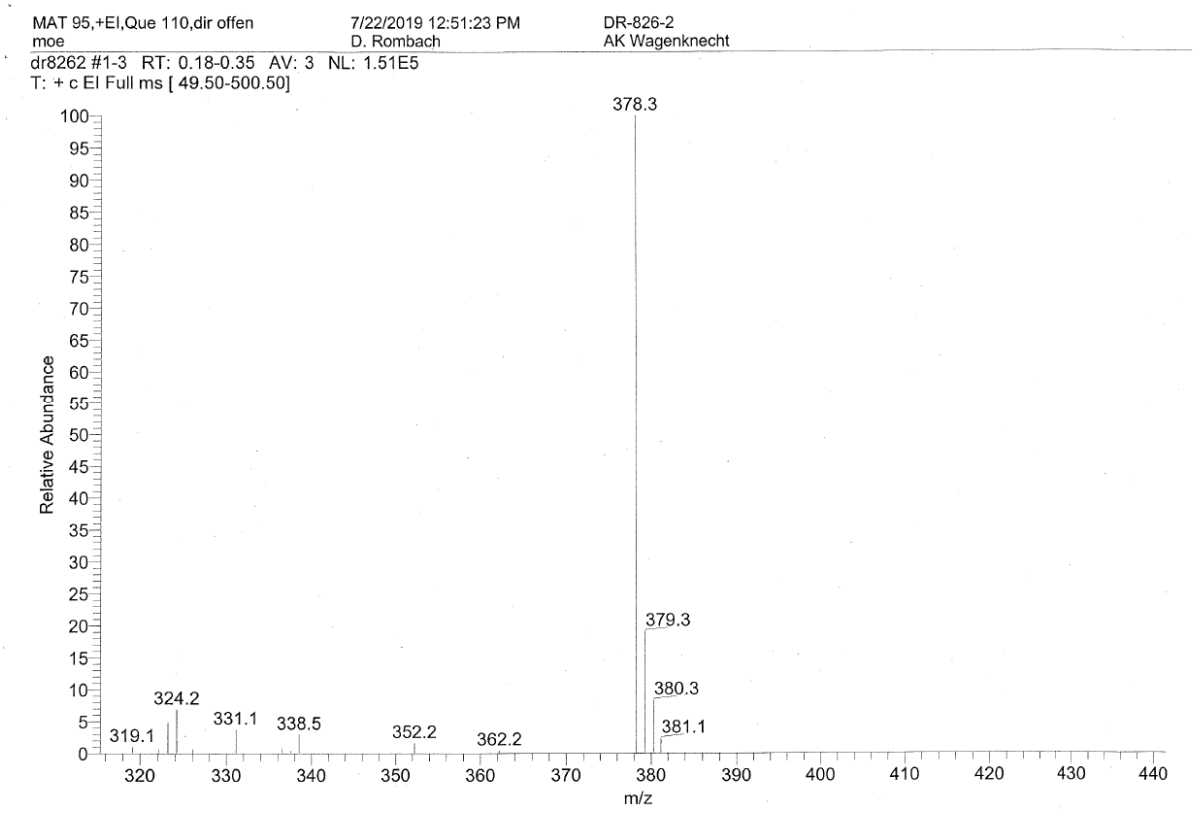


Fig. S93

HR-EI-MS spectrum of pentafluoro(2-((2-methylallyl)oxy)-2,2-diphenylethyl)-λ^6-sulfane (**10**).

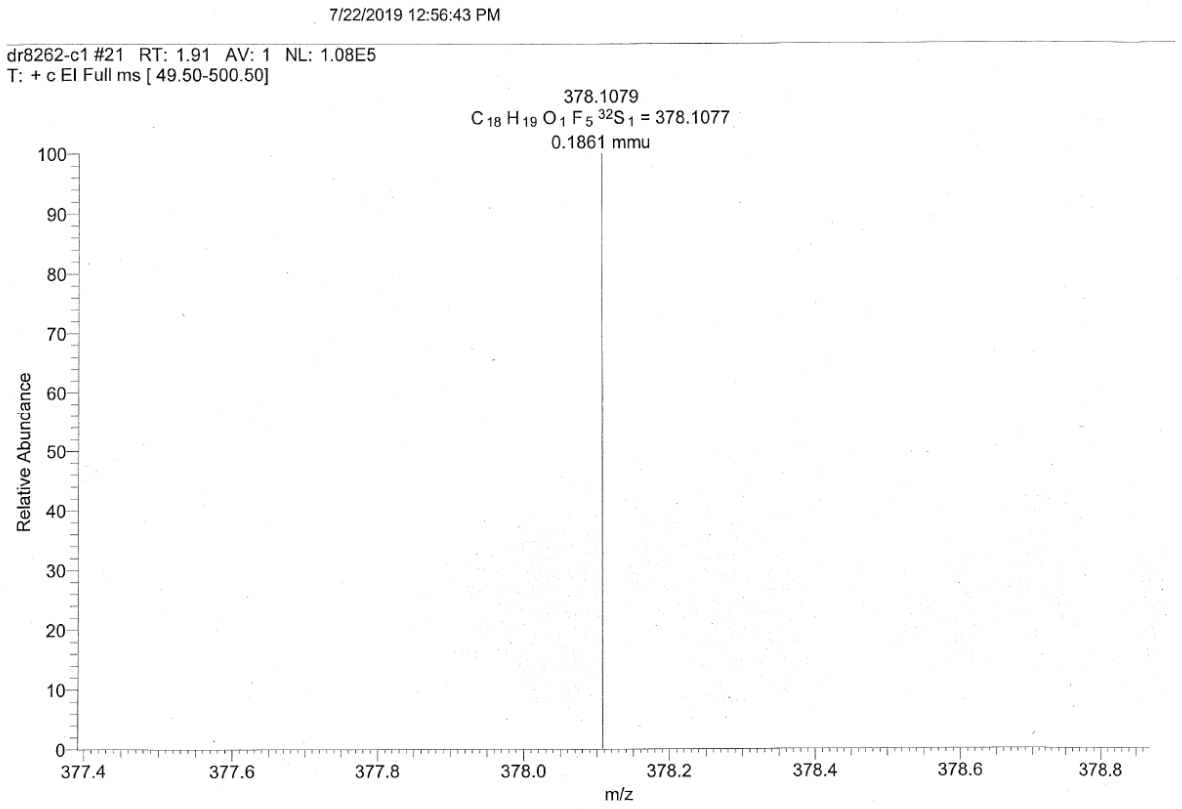


Fig. S94

HR-EI-MS spectrum of pentafluoro(2-((2-methylallyl)oxy)-2,2-diphenylethyl)-λ^6-sulfane (**10**).

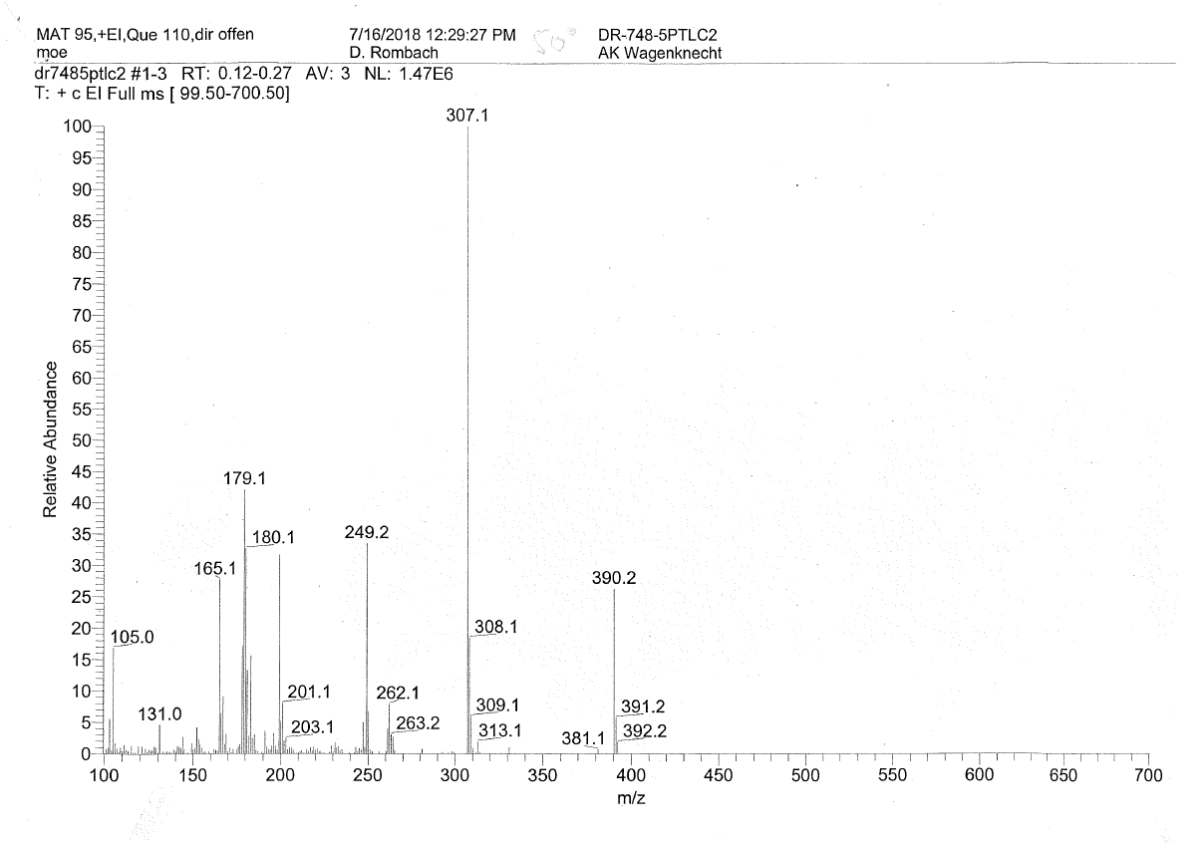


Fig. S95

EI-MS spectrum of pentafluoro(2-(pent-3-yn-1-yloxy)-2,2-diphenylethyl)-λ^6-sulfane (**11**).

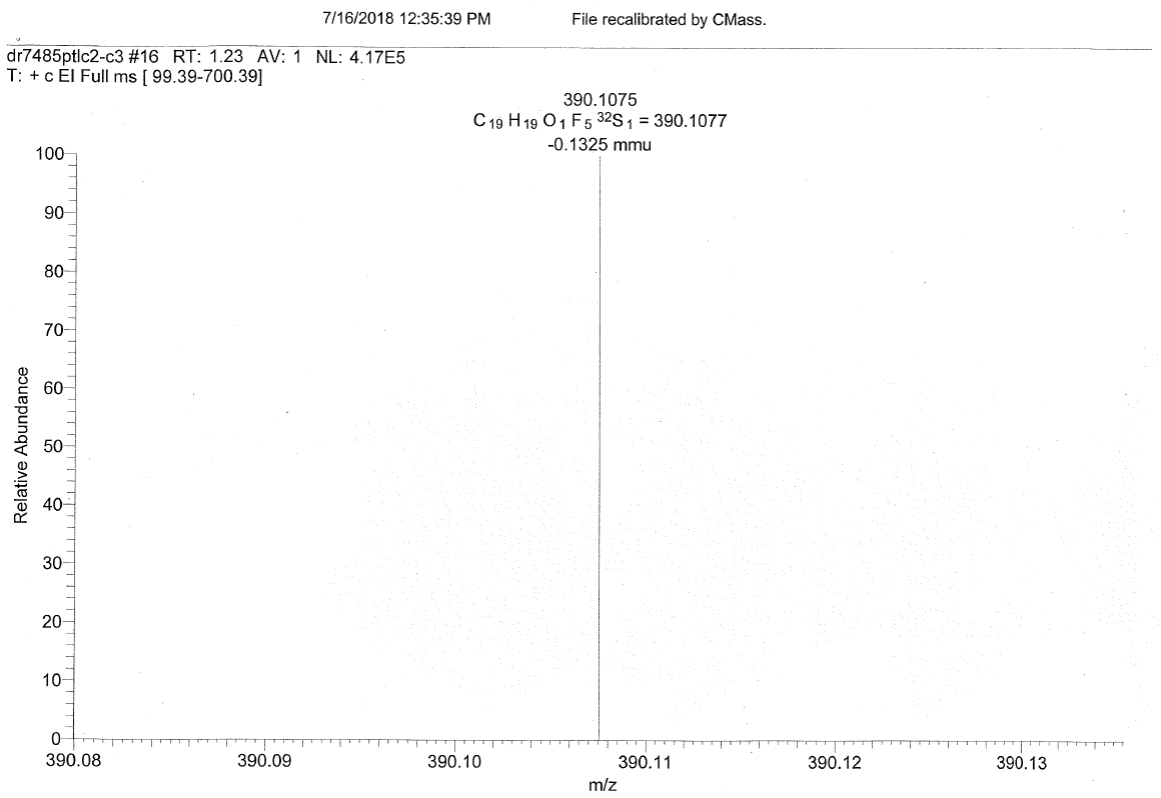


Fig. S96

HR-EI-MS spectrum of pentafluoro(2-(pent-3-yn-1-yloxy)-2,2-diphenylethyl)-λ^6-sulfane (**11**).

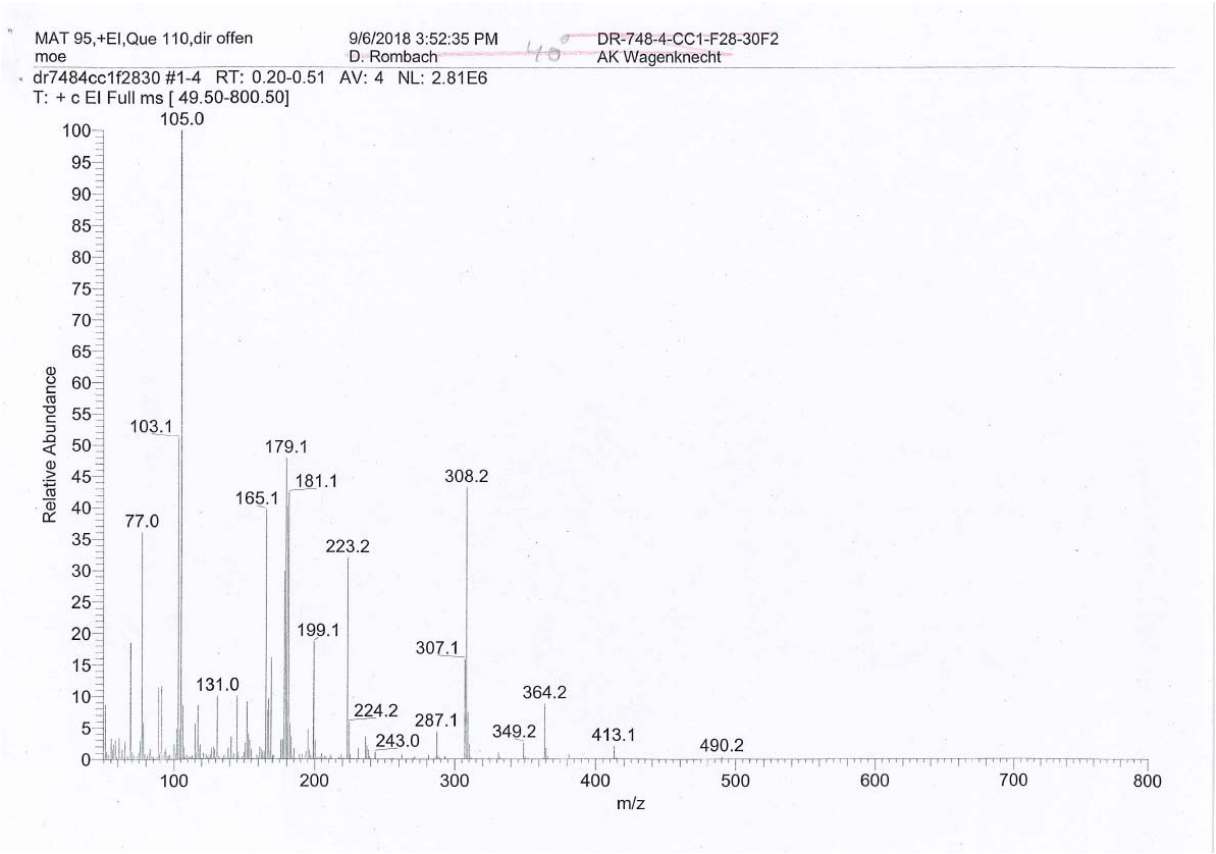


Fig. S97

EI-MS spectrum of (2-(allyloxy)-2,2-diphenylethyl)pentafluoro-λ^6-sulfane (**12**).

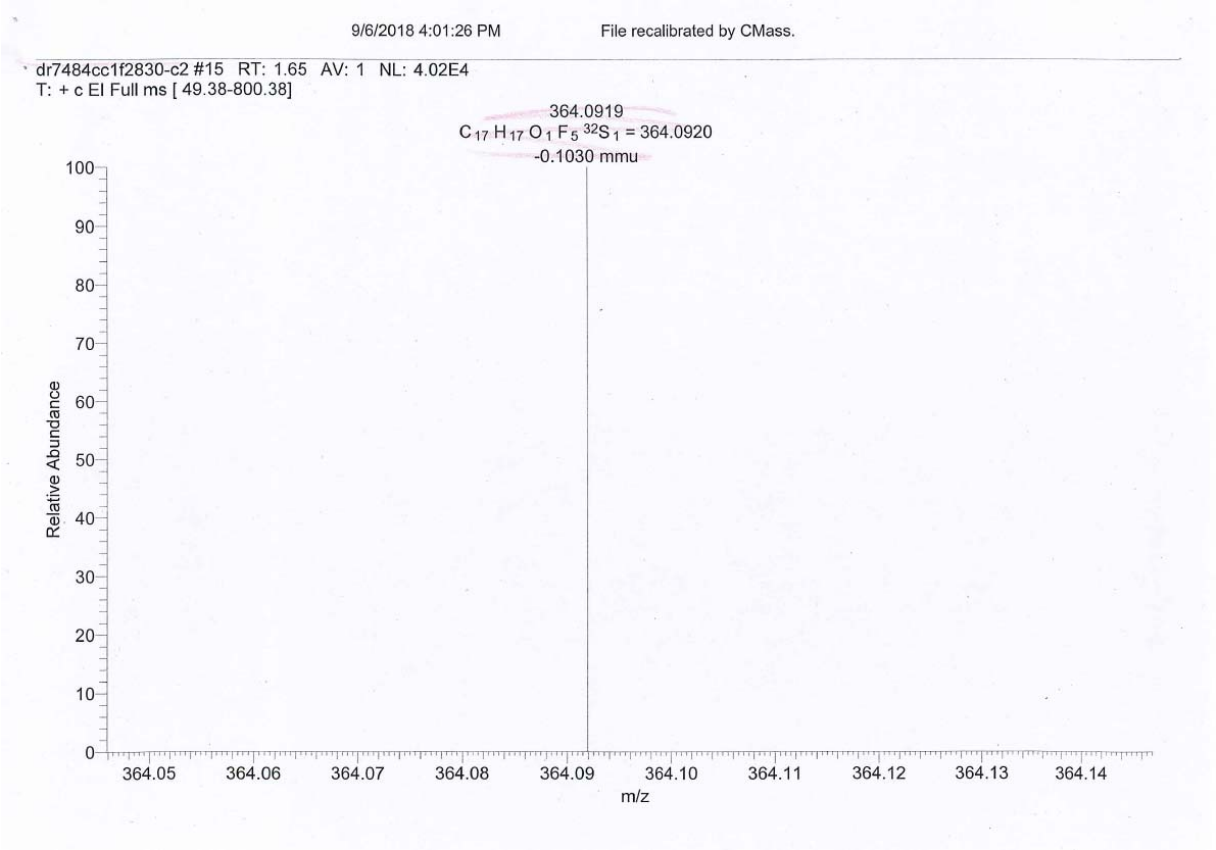


Fig. S98

HR-EI-MS spectrum of (2-(allyloxy)-2,2-diphenylethyl)pentafluoro-λ^6-sulfane (**12**).

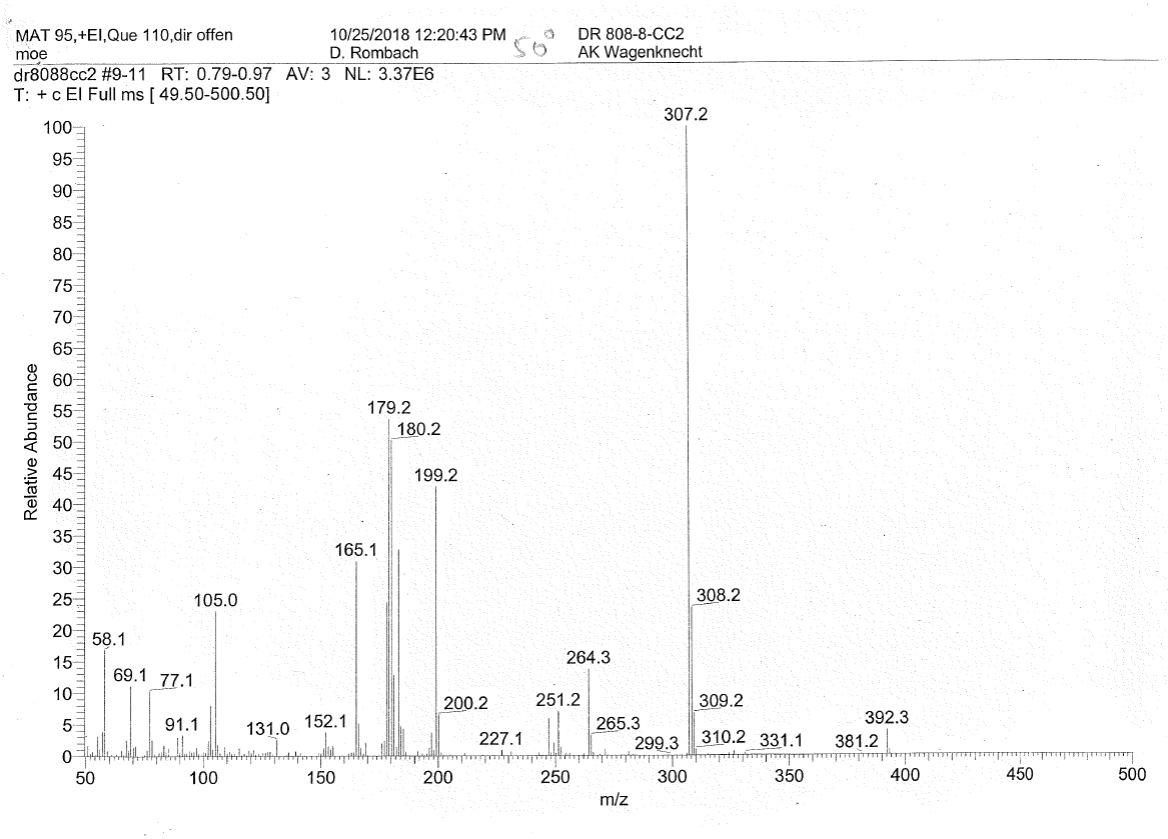


Fig. S99

EI-MS spectrum of (2-(cyclopentyloxy)-2,2-diphenylethyl)pentafluoro-λ^6-sulfane (**13**).

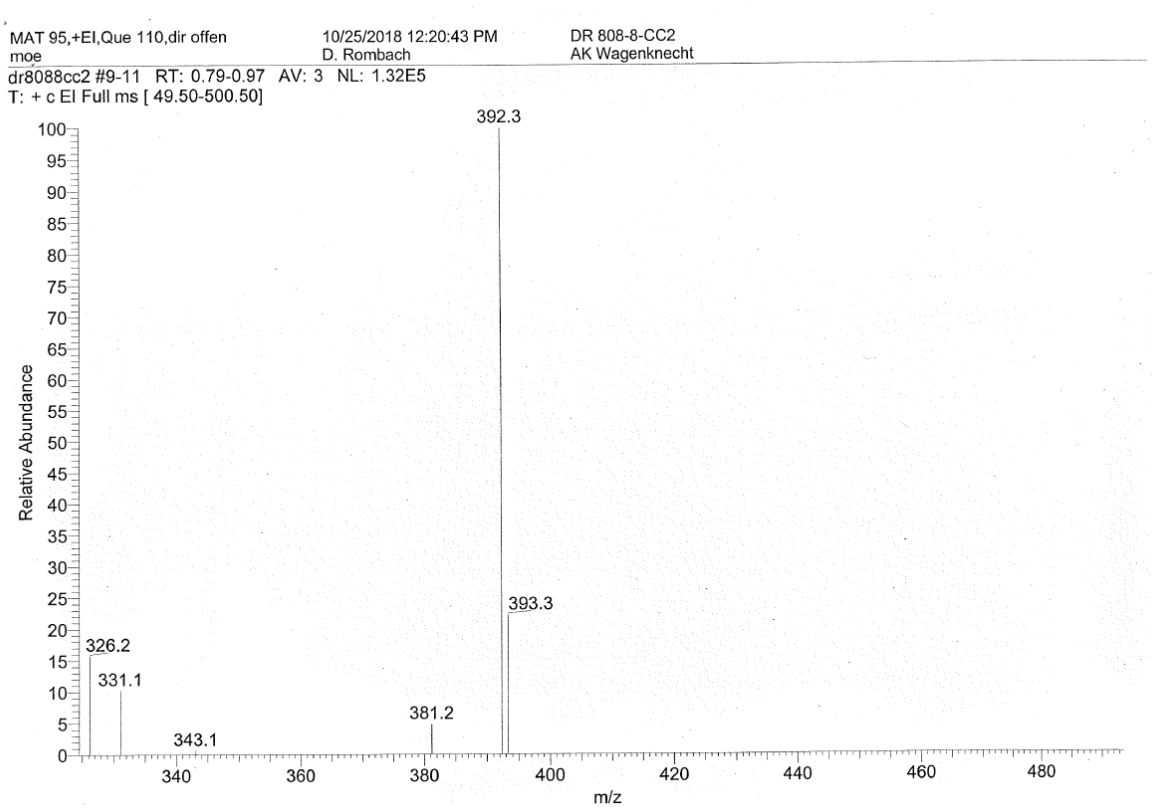


Fig. S100

EI-MS spectrum of (2-(cyclopentyloxy)-2,2-diphenylethyl)pentafluoro-λ^6-sulfane (**13**).

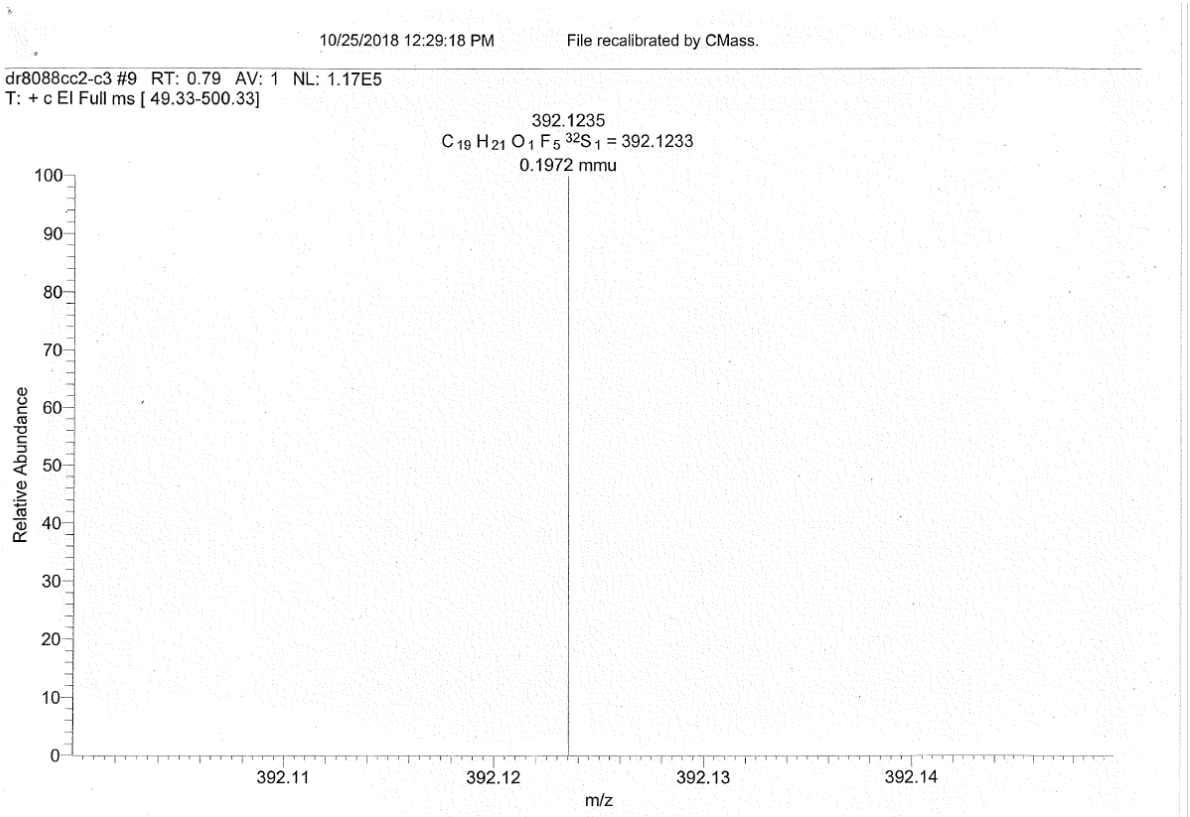


Fig. S101

HR-EI-MS spectrum of (2-(cyclopentyloxy)-2,2-diphenylethyl)pentafluoro-λ^6-sulfane (**13**).

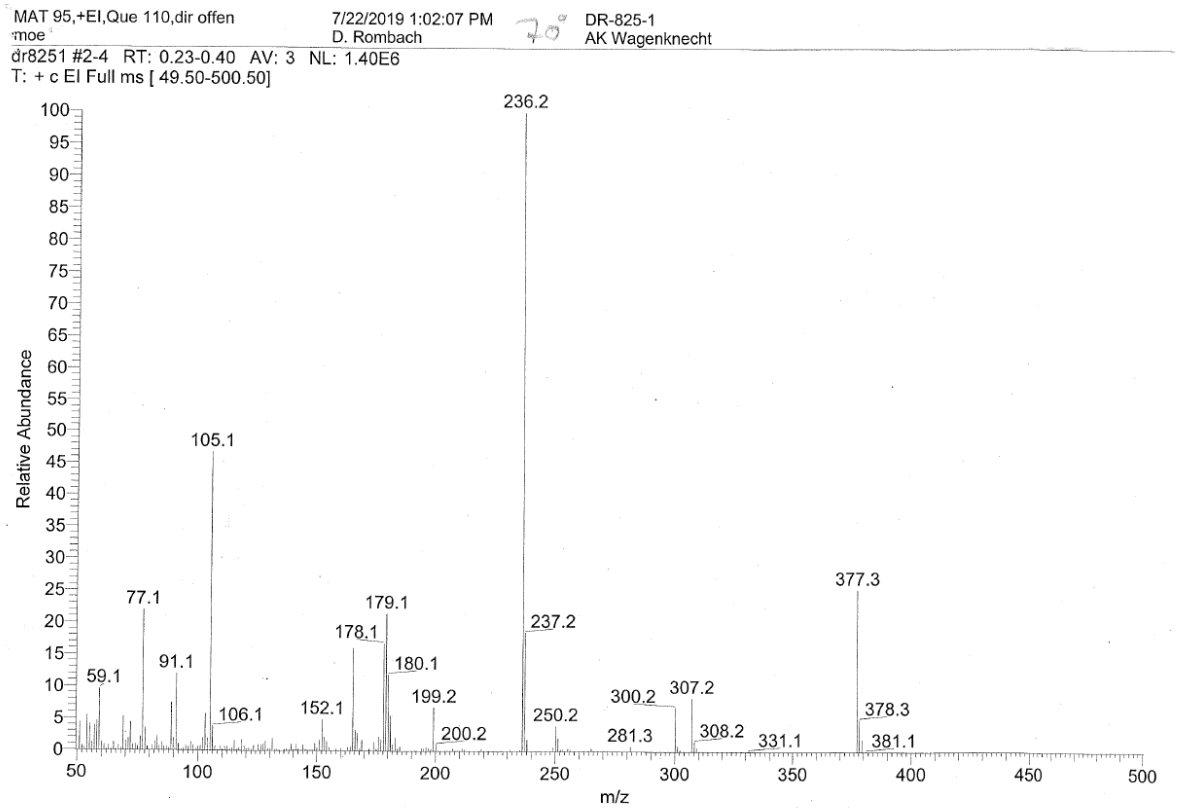


Fig. S102

EI-MS spectrum of 3-(2-(pentafluoro-λ^6-sulfaneyl)-1,1-diphenylethoxy)propanenitrile (**14**).

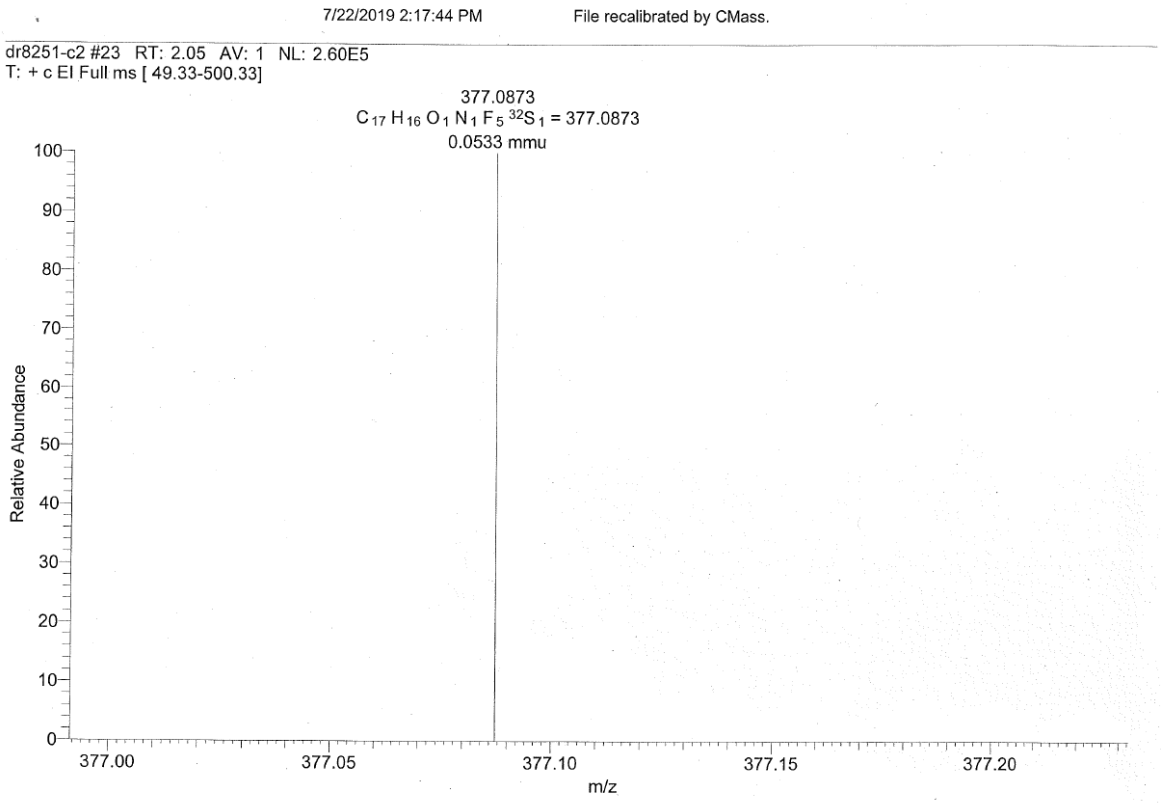


Fig. S103

HR-EI-MS spectrum of 3-(2-(pentafluoro-λ^6-sulfaneyl)-1,1-diphenylethoxy)propanenitrile (**14**).

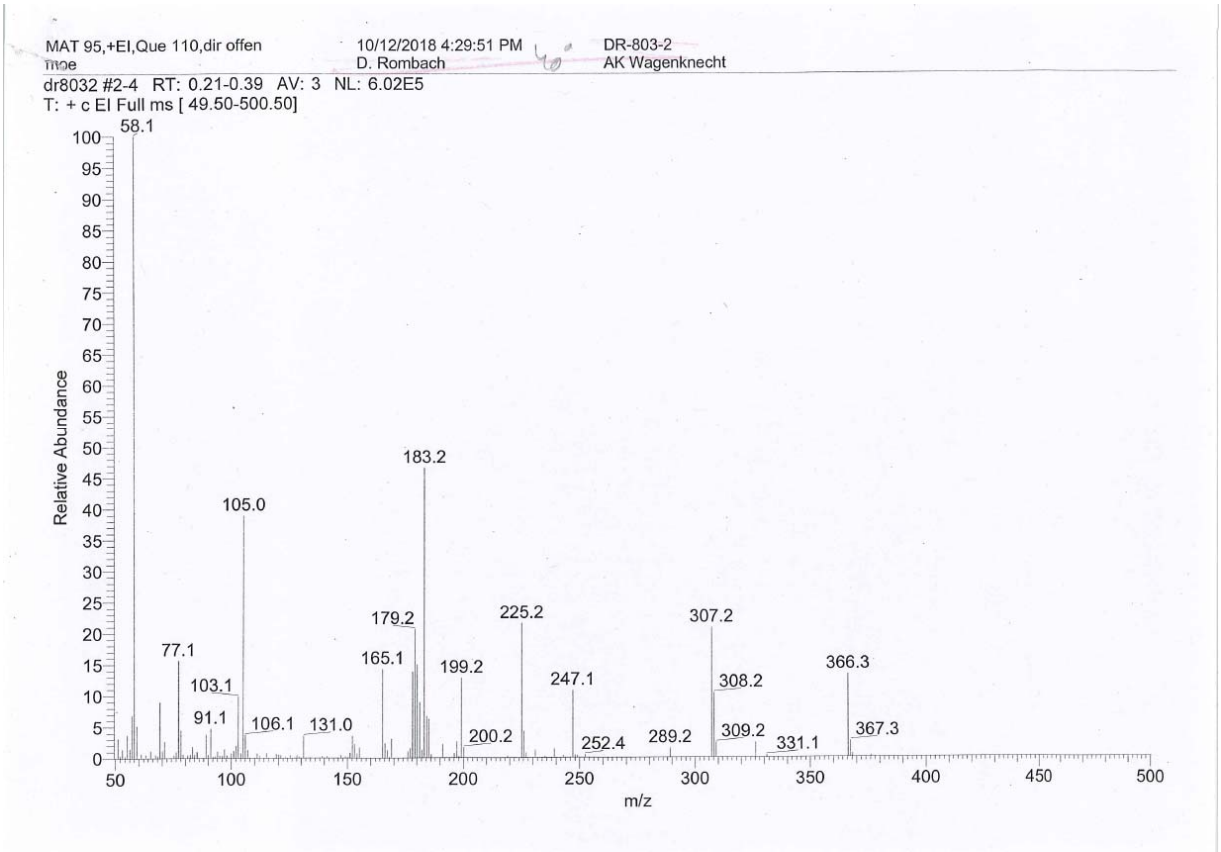


Fig. S104

EI-MS spectrum of pentafluoro(2-isopropoxy-2,2-diphenylethyl)-λ^6-sulfane (**15**).

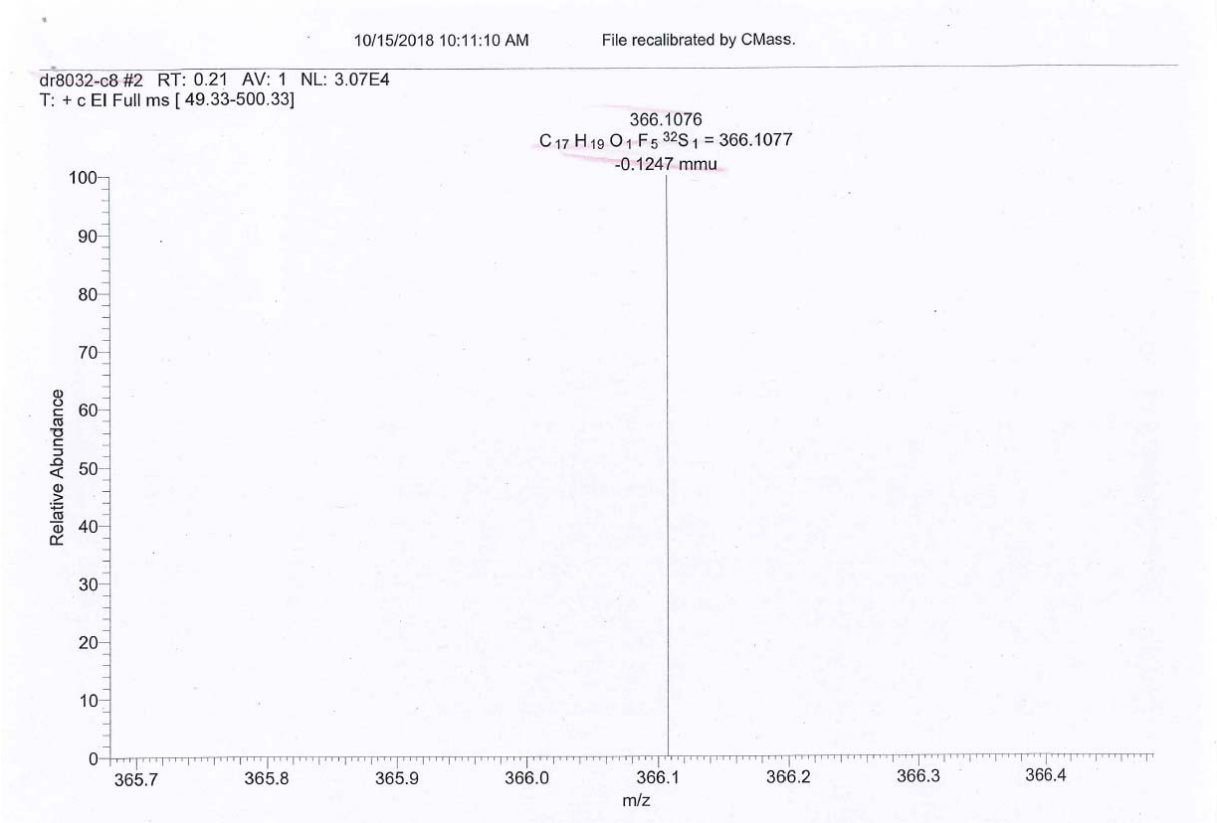


Fig. S105

HR-EI-MS spectrum of pentafluoro(2-isopropoxy-2,2-diphenylethyl)-λ^6-sulfane (**15**).

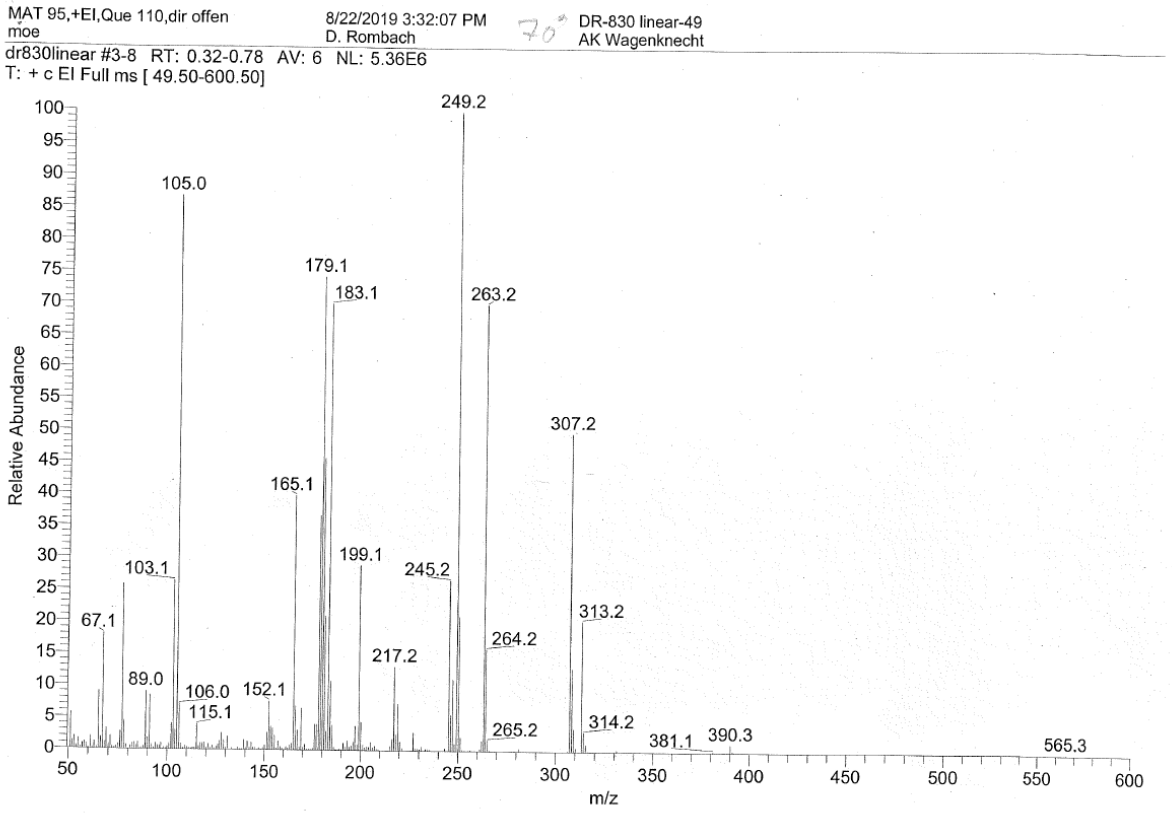


Fig. S106

EI-MS spectrum of pentafluoro(2-(pent-4-yn-1-yloxy)-2,2-diphenylethyl)-λ^6-sulfane (**16**).

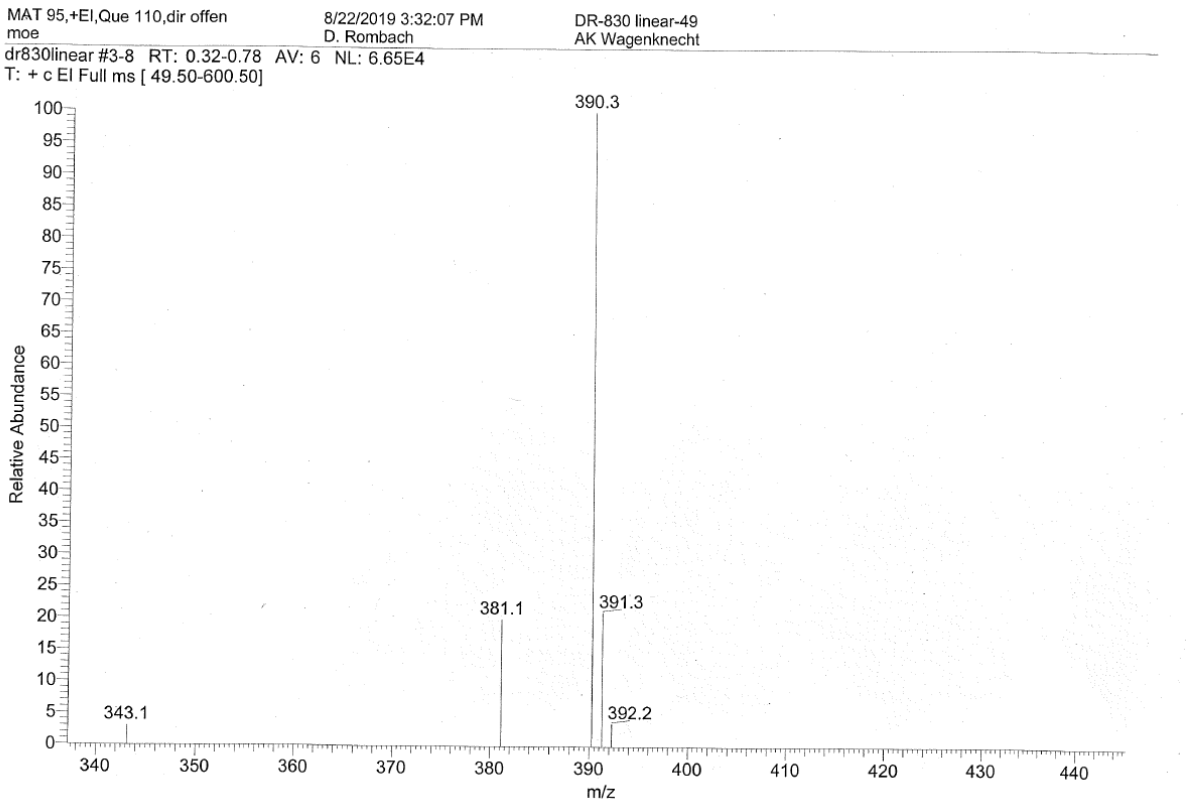


Fig. S107

EI-MS spectrum of pentafluoro(2-(pent-4-yn-1-yloxy)-2,2-diphenylethyl)-λ^6-sulfane (**16**).

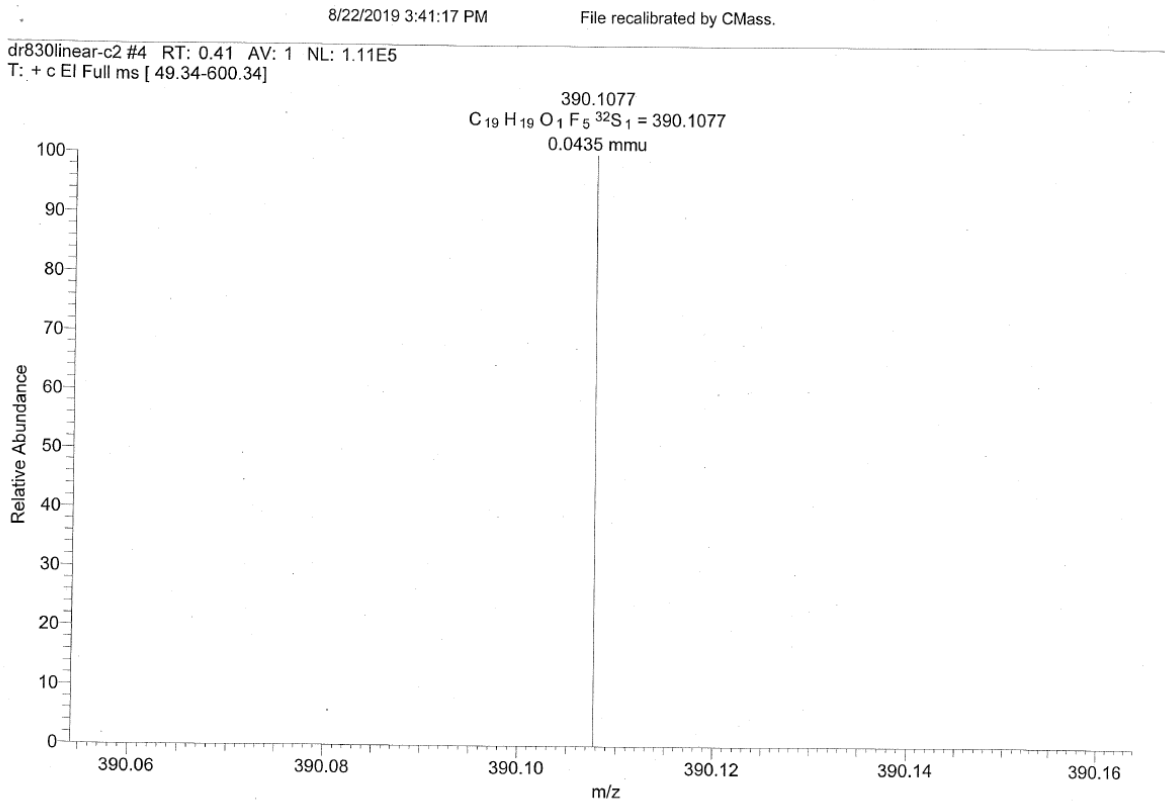


Fig. S108

HR-EI-MS spectrum of pentafluoro(2-(pent-4-yn-1-yloxy)-2,2-diphenylethyl)-λ^6-sulfane (**16**).

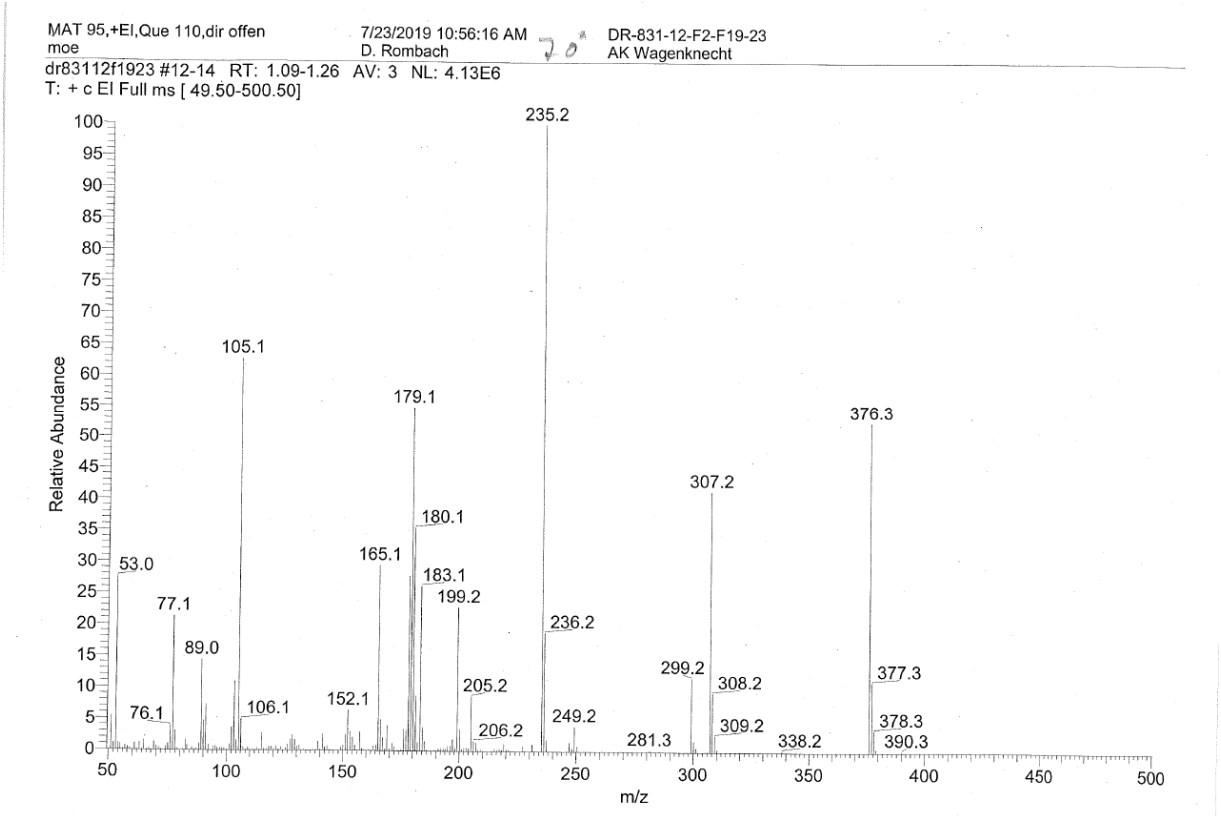


Fig. S109

EI-MS spectrum of (2-(but-3-yn-1-yloxy)-2,2-diphenylethyl)pentafluoro-λ^6-sulfane (**17**).

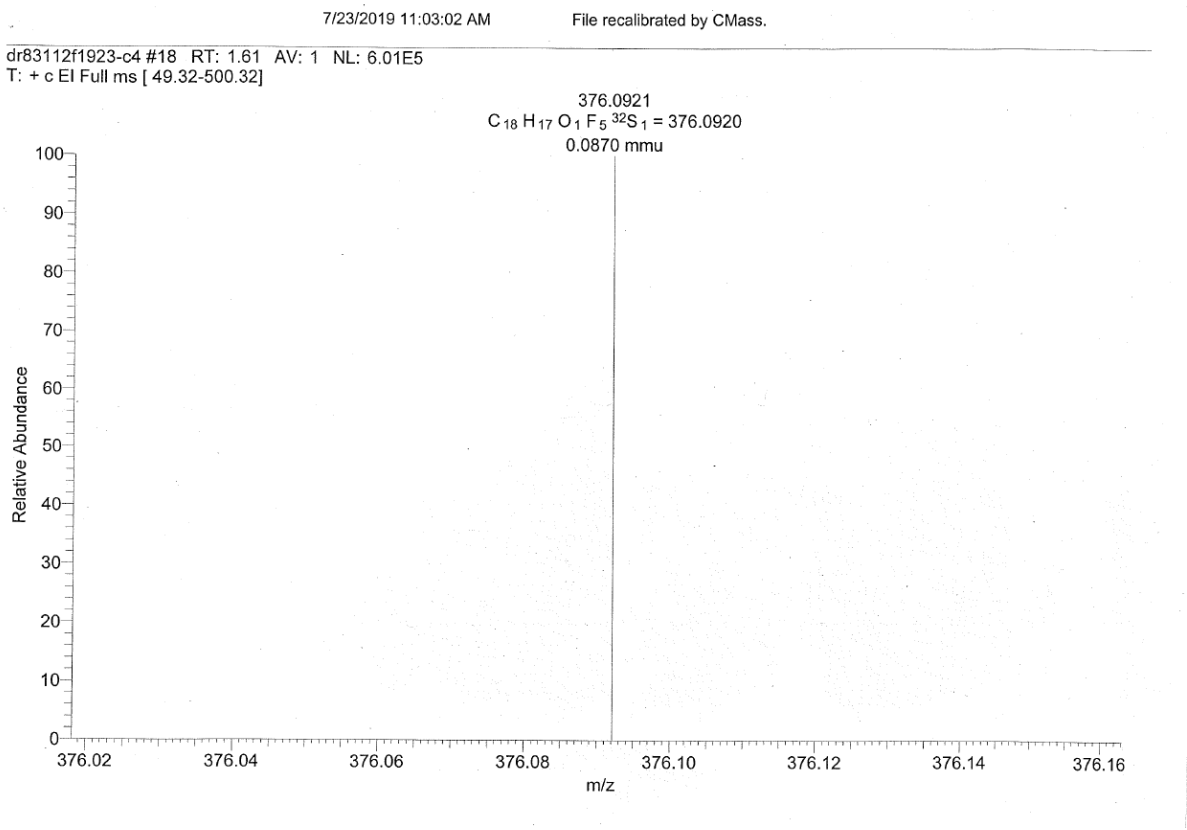


Fig. S110

HR-EI-MS spectrum of (2-(but-3-yn-1-yloxy)-2,2-diphenylethyl)pentafluoro-λ^6-sulfane (**17**).

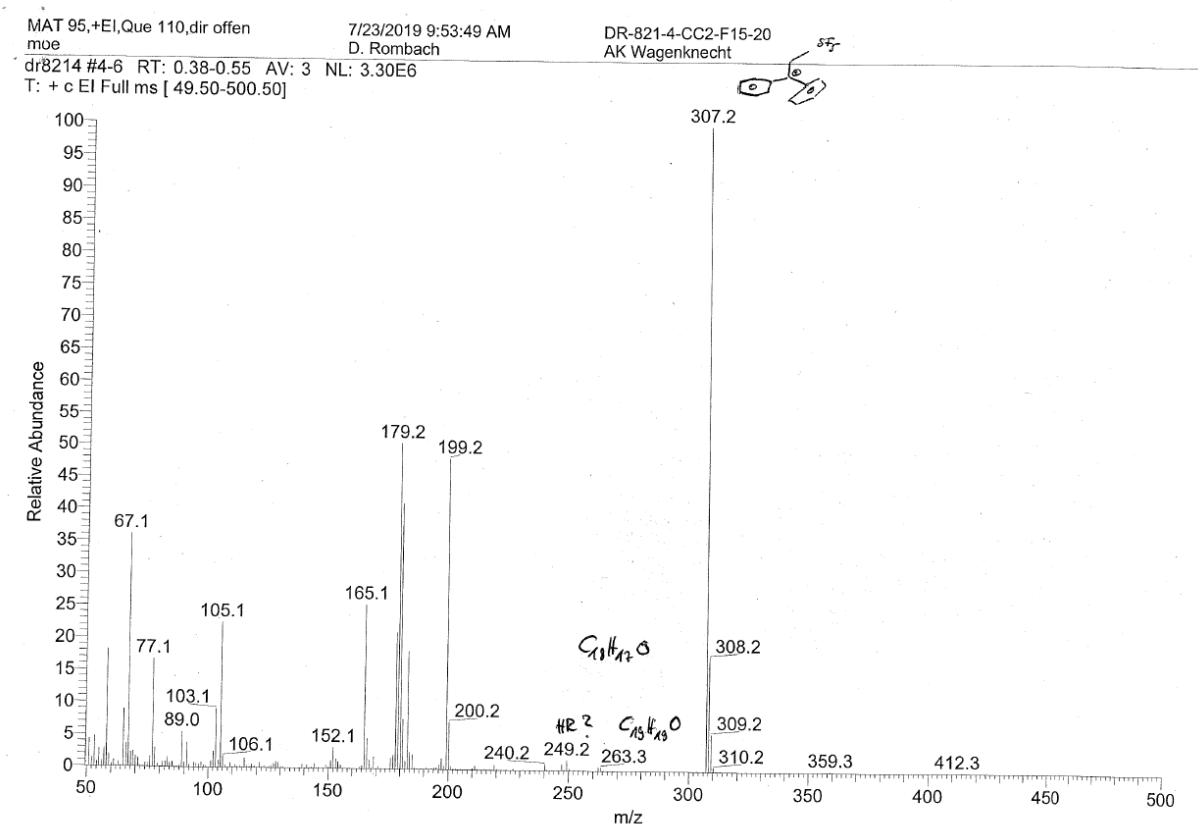


Fig. S111

EI-MS spectrum of pentafluoro(2-(penta-3,4-dien-1-yloxy)-2,2-diphenylethyl)-λ^6-sulfane (**18**).

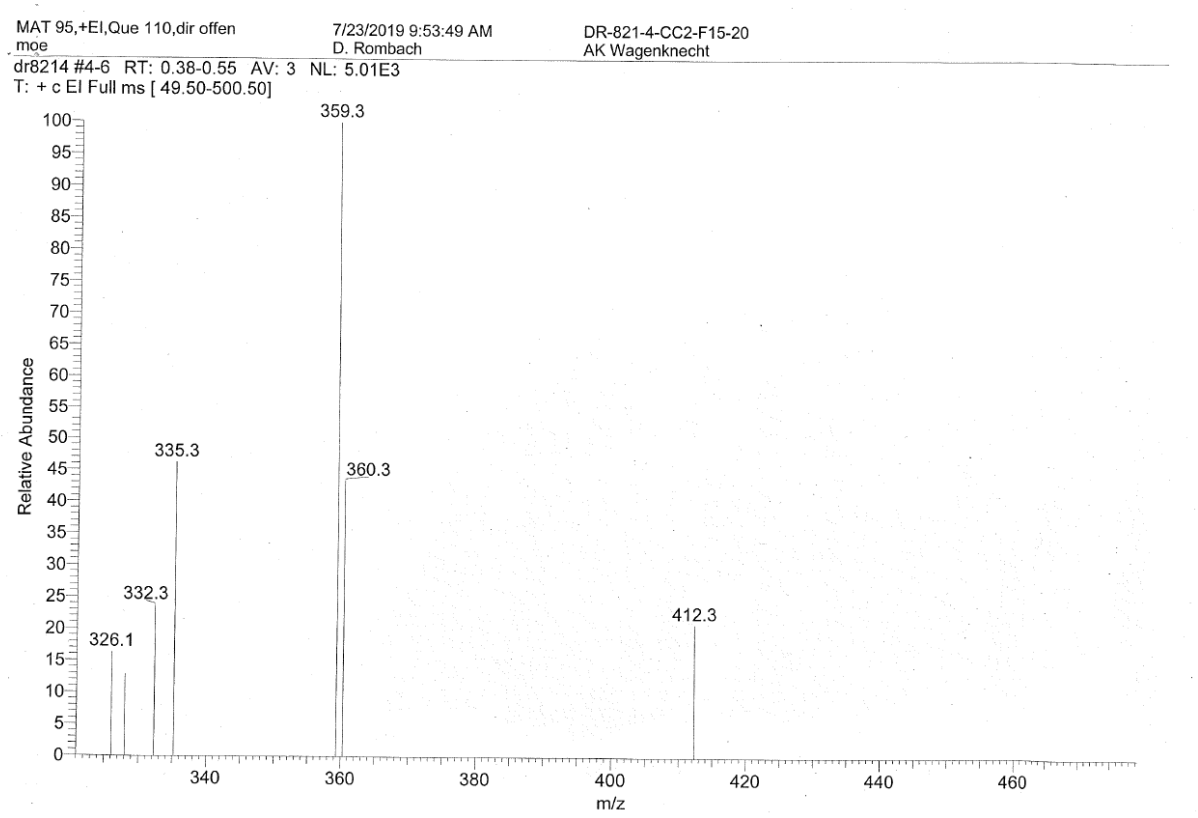


Fig. S112

EI-MS spectrum of pentafluoro(2-(penta-3,4-dien-1-yloxy)-2,2-diphenylethyl)-λ^6-sulfane (**18**).

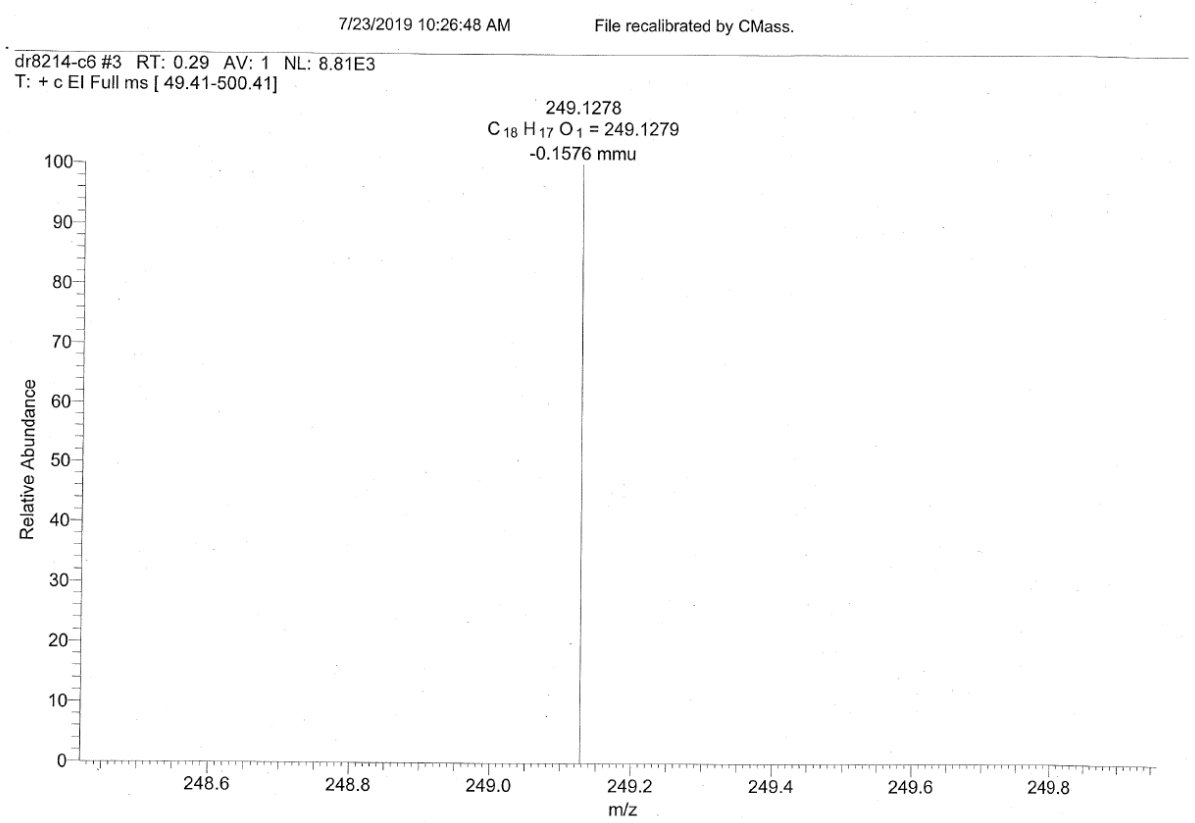


Fig. S113

HR-EI-MS spectrum of pentafluoro(2-(penta-3,4-dien-1-yloxy)-2,2-diphenylethyl)-λ^6-sulfane (**18**).

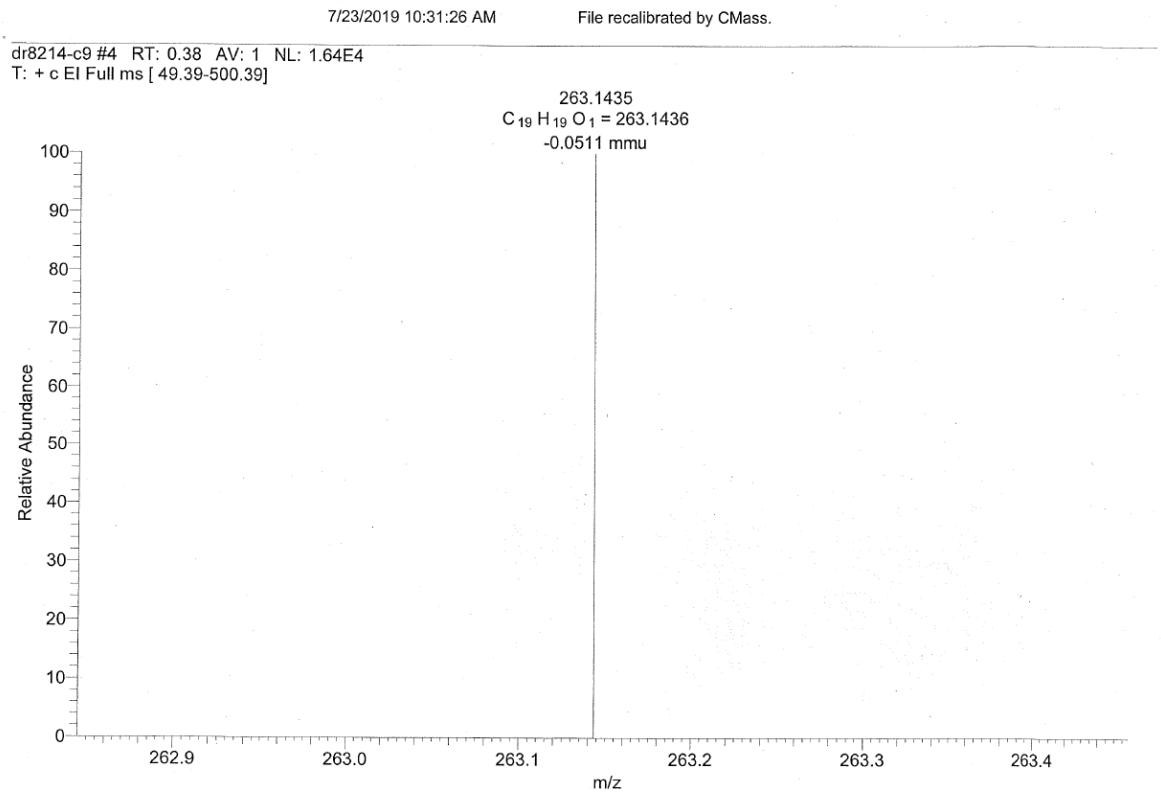


Fig. S114

HR-EI-MS spectrum of pentafluoro(2-(penta-3,4-dien-1-yloxy)-2,2-diphenylethyl)-λ^6-sulfane (**18**).

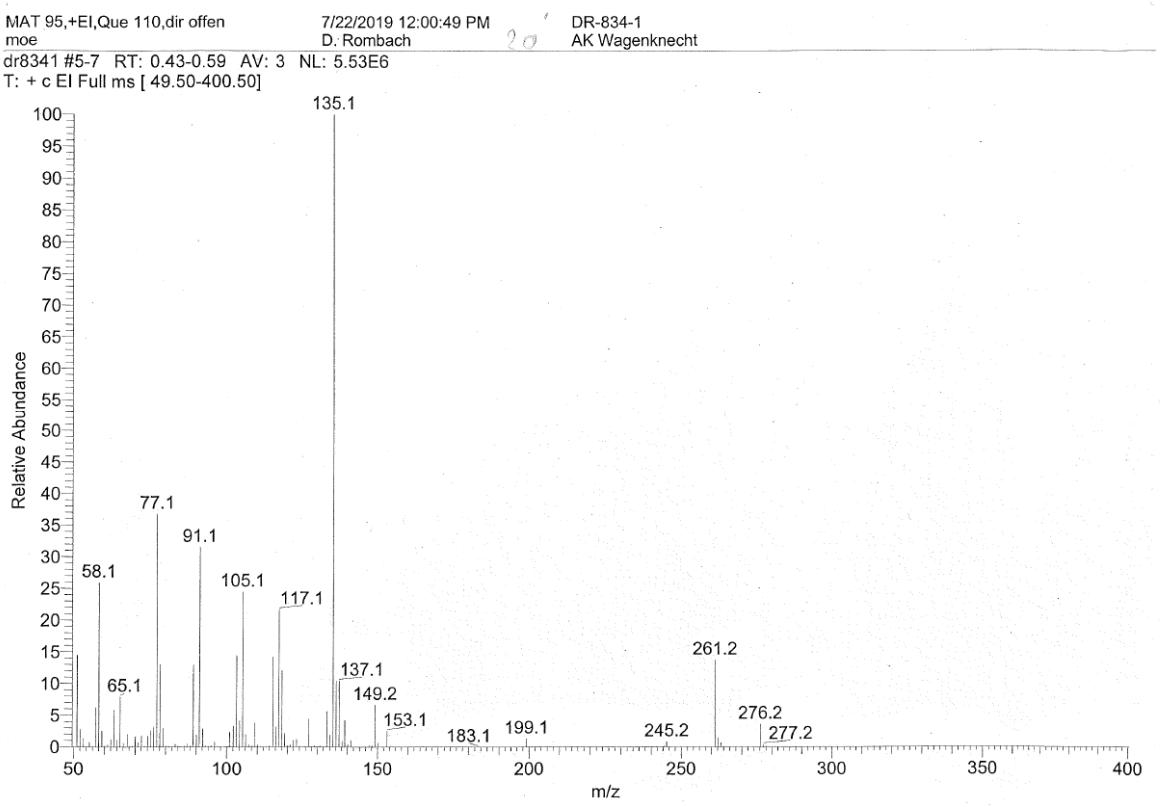


Fig. S115

HR-EI-MS spectrum of pentafluoro(2-methoxy-2-phenylpropyl)-λ^6-sulfane (**8**).

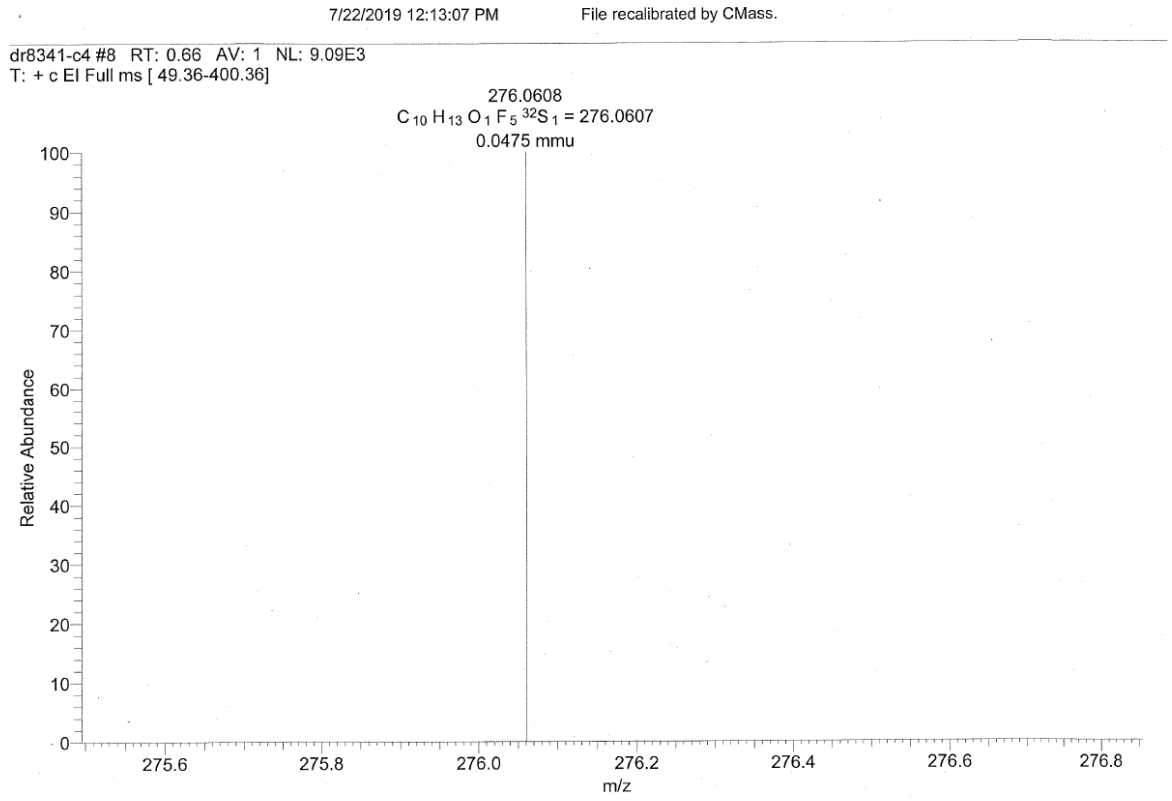


Fig. S116

HR-EI-MS spectrum of pentafluoro(2-methoxy-2-phenylpropyl)-λ^6-sulfane (**8**).

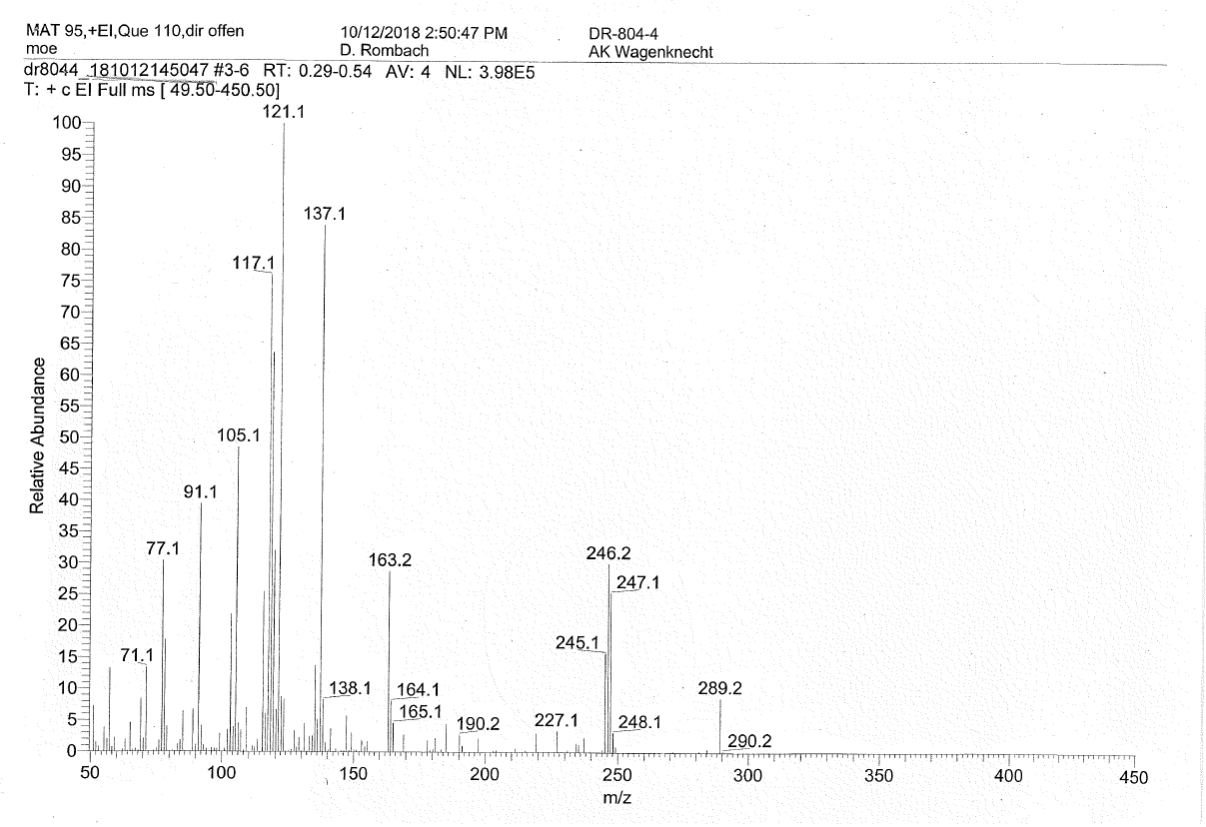


Fig. S117

EI-MS spectrum of pentafluoro(2-isopropoxy-2-phenylpropyl)-λ^6-sulfane (**19**).

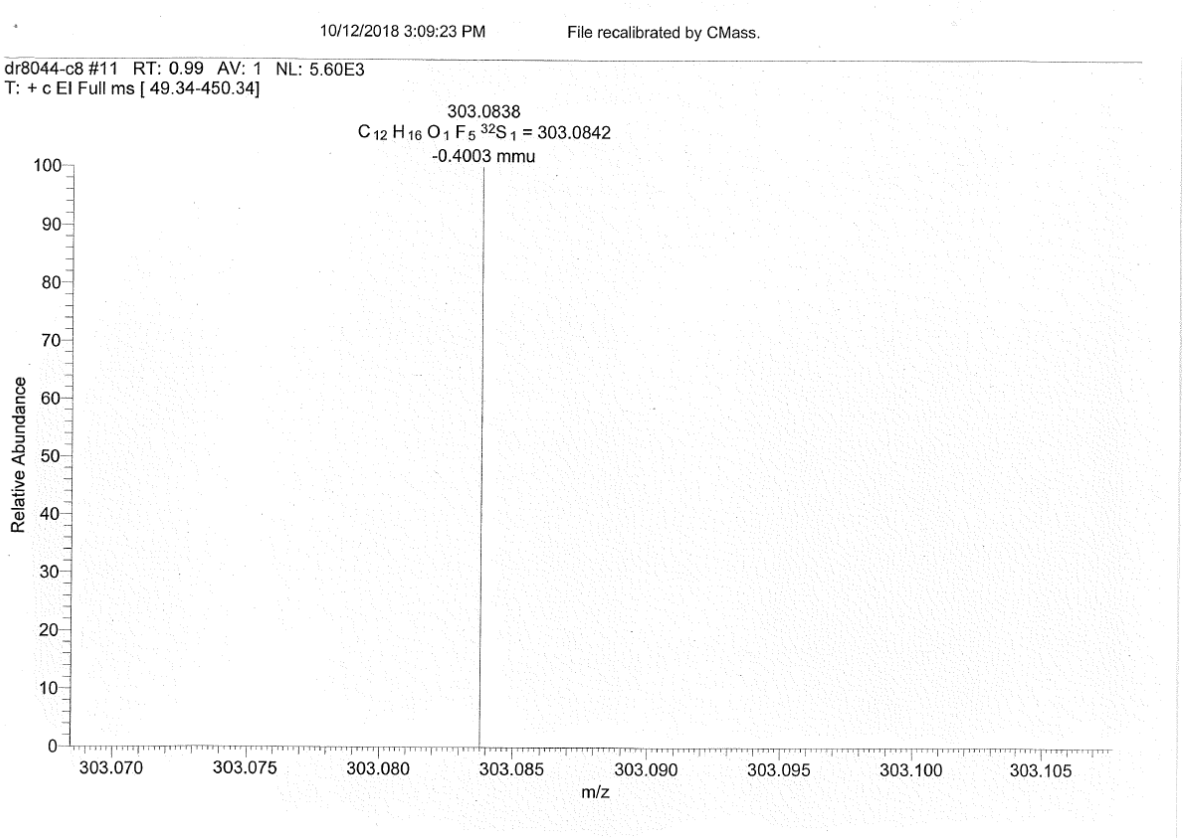


Fig. S118

HR-EI-MS spectrum of pentafluoro(2-isopropoxy-2-phenylpropyl)-λ^6-sulfane (**19**).

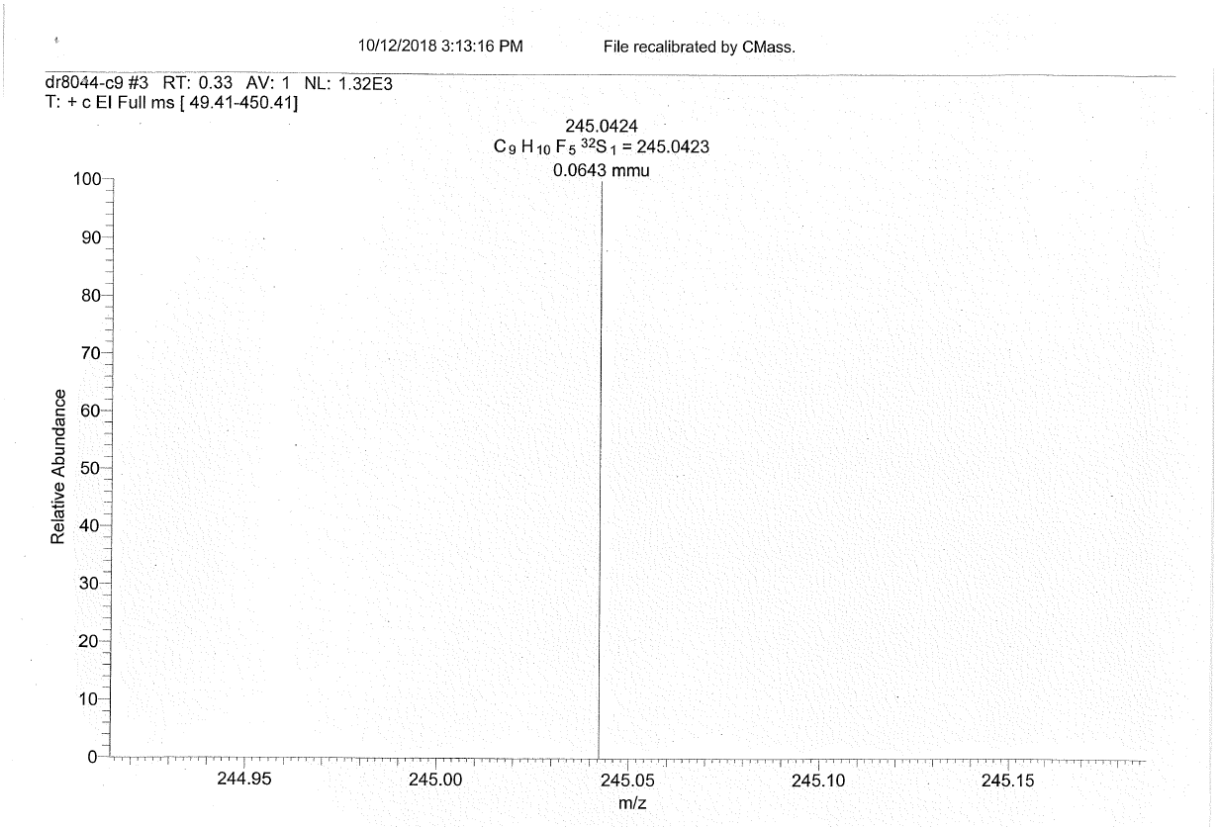


Fig. S119

HR-EI-MS spectrum of pentafluoro(2-isopropoxy-2-phenylpropyl)-λ^6-sulfane (**19**).

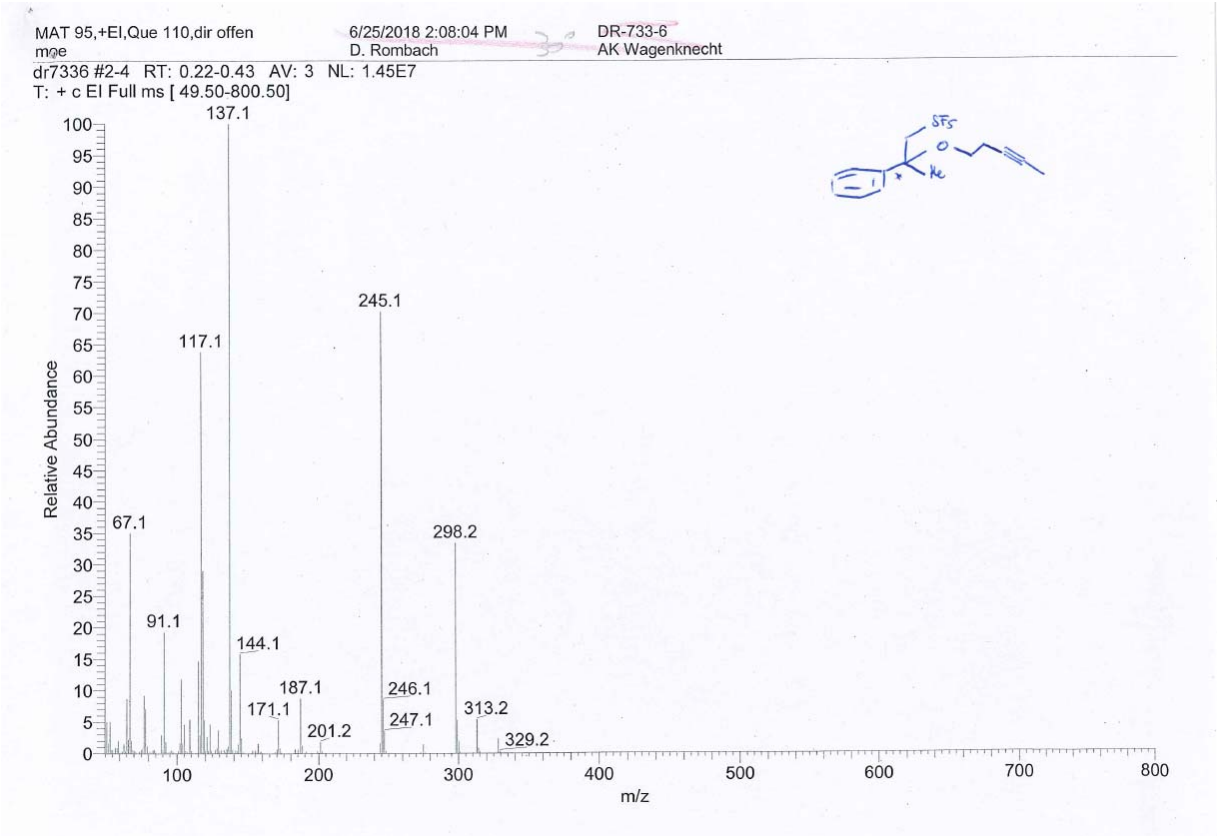


Fig. S120

EI-MS spectrum of pentafluoro(2-(pent-3-yn-1-yloxy)-2-phenylpropyl)-λ^6-sulfane (**20**).

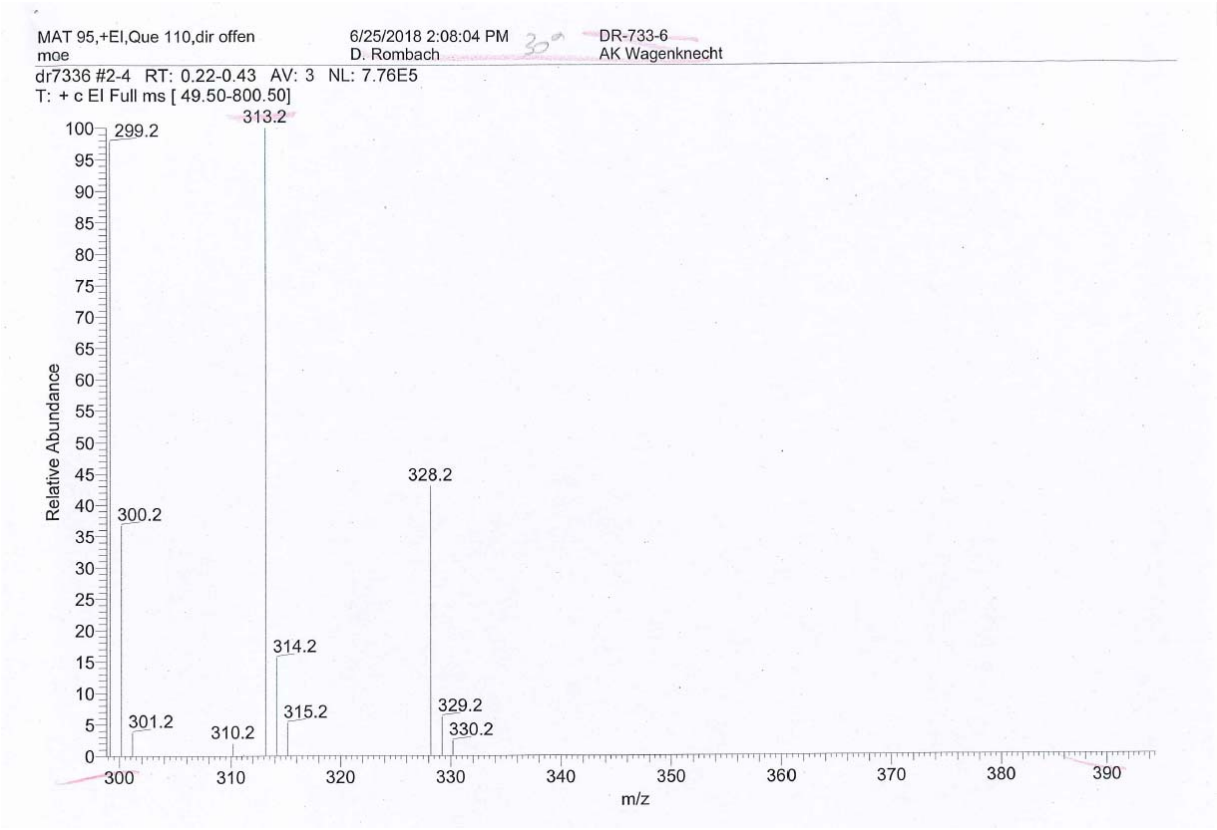


Fig. S121

EI-MS spectrum of pentafluoro(2-(pent-3-yn-1-yloxy)-2-phenylpropyl)-λ^6-sulfane (**20**).

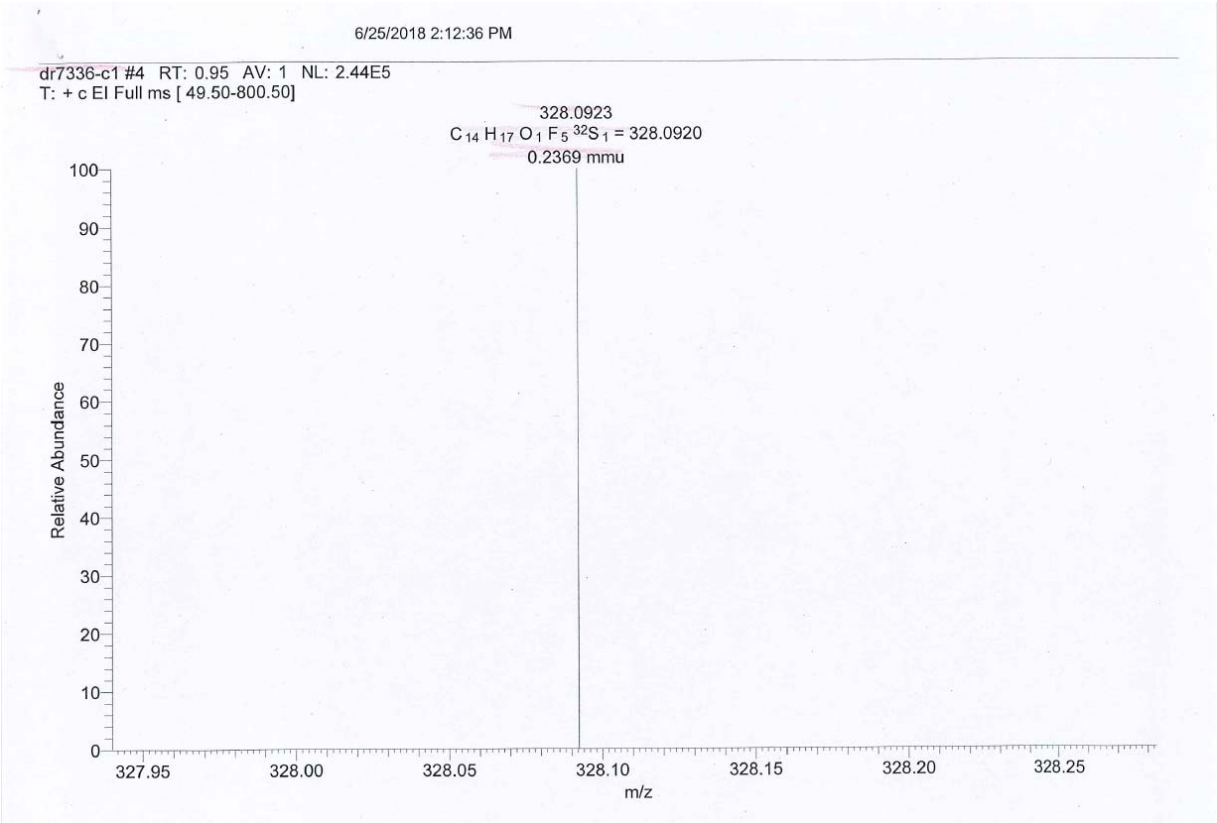


Fig. S122

HR-EI-MS spectrum of pentafluoro(2-(pent-3-yn-1-yloxy)-2-phenylpropyl)-λ^6-sulfane (**20**).

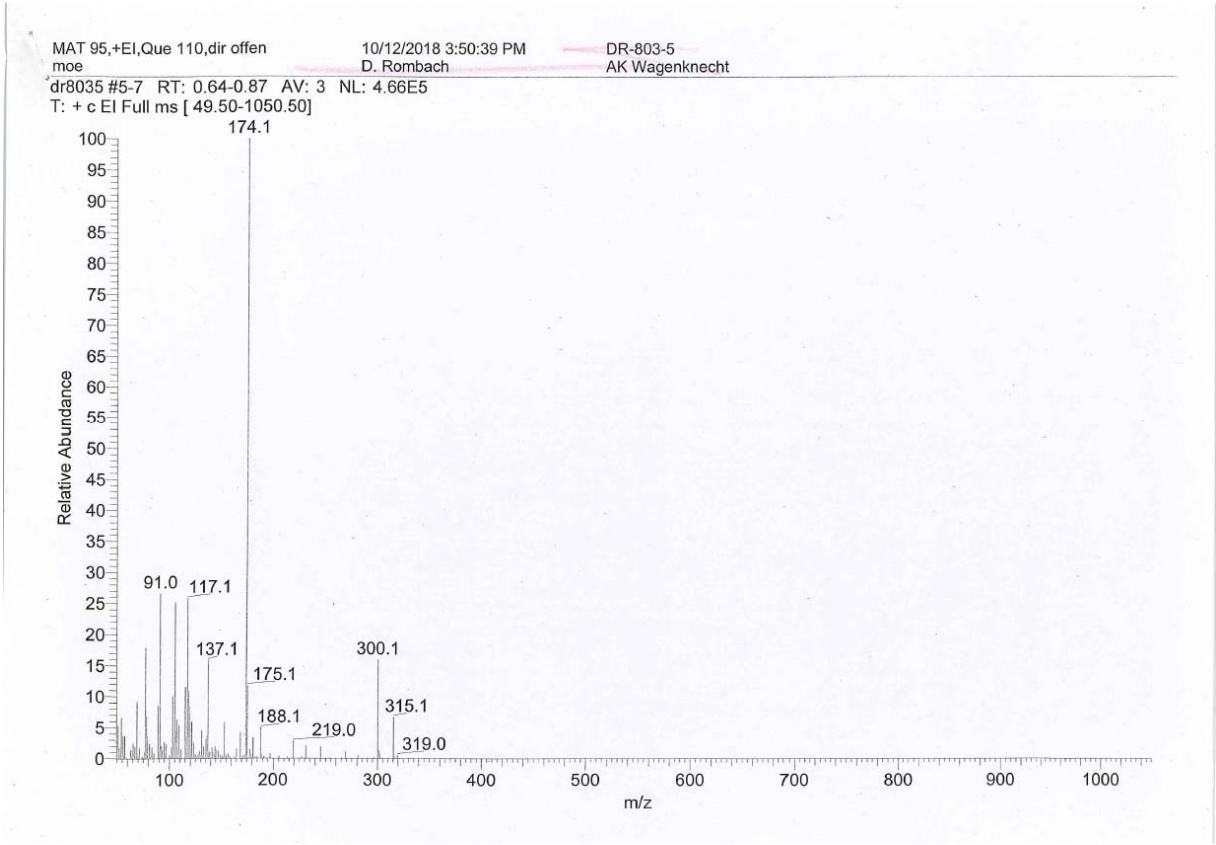


Fig. S123

EI-MS spectrum of 3-((1-(pentafluoro-λ^6-sulfaneyl)-2-phenylpropan-2-yl)oxy)propane-nitrile (**21**).

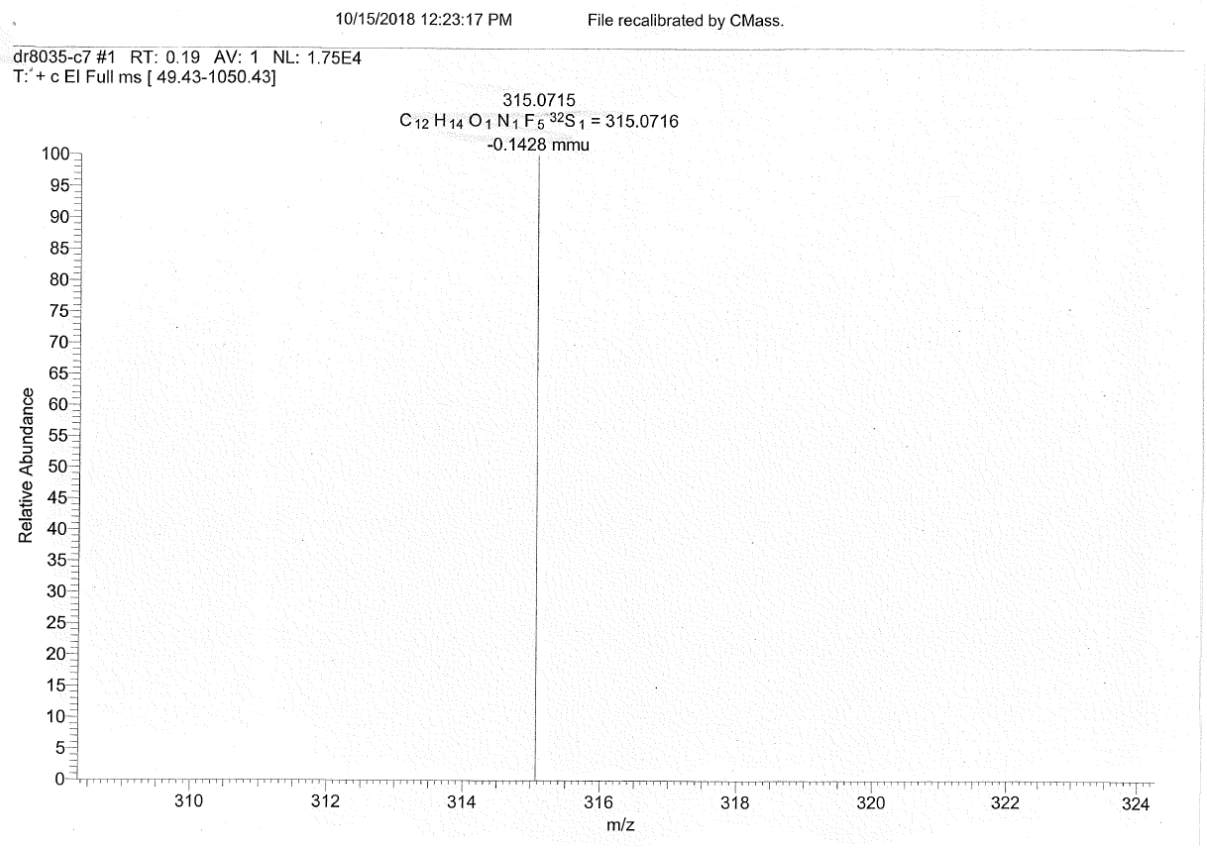


Fig. S124

HR-EI-MS spectrum of 3-((1-(pentafluoro-λ^6-sulfaneyl)-2-phenylpropan-2-yl)oxy)propanenitrile (**21**).

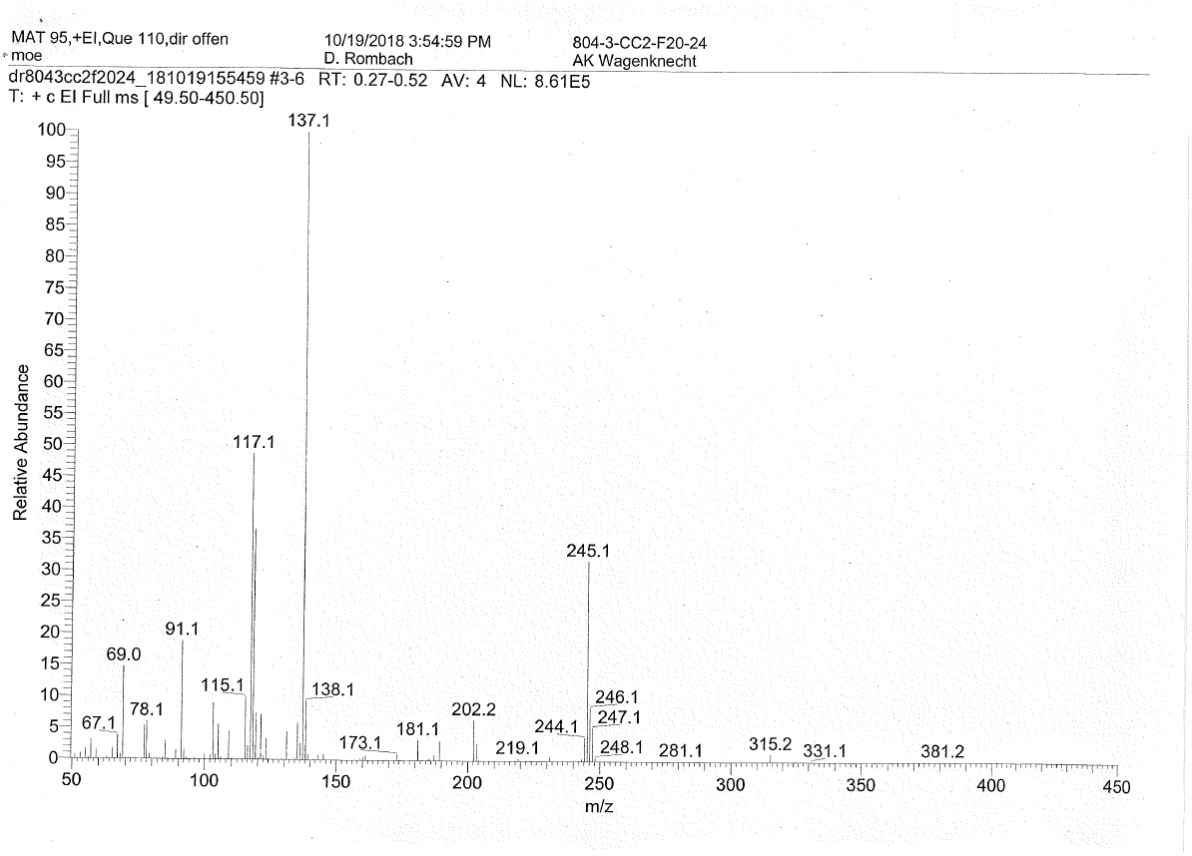


Fig. S125

EI-MS spectrum of (2-(cyclopentyloxy)-2-phenylpropyl)pentafluoro-λ^6-sulfane (**22**).

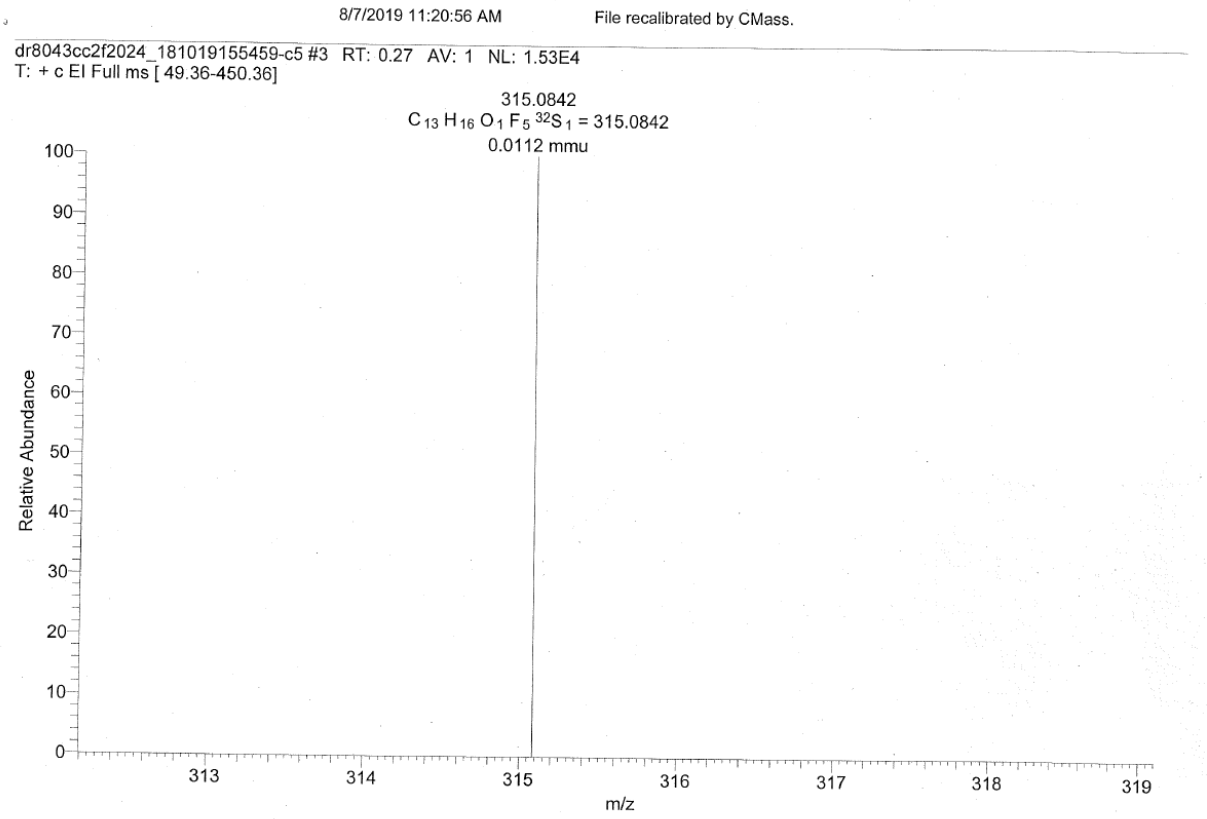


Fig. S126

HR-EI-MS spectrum of (2-(cyclopentyloxy)-2-phenylpropyl)pentafluoro-λ^6-sulfane (**22**).

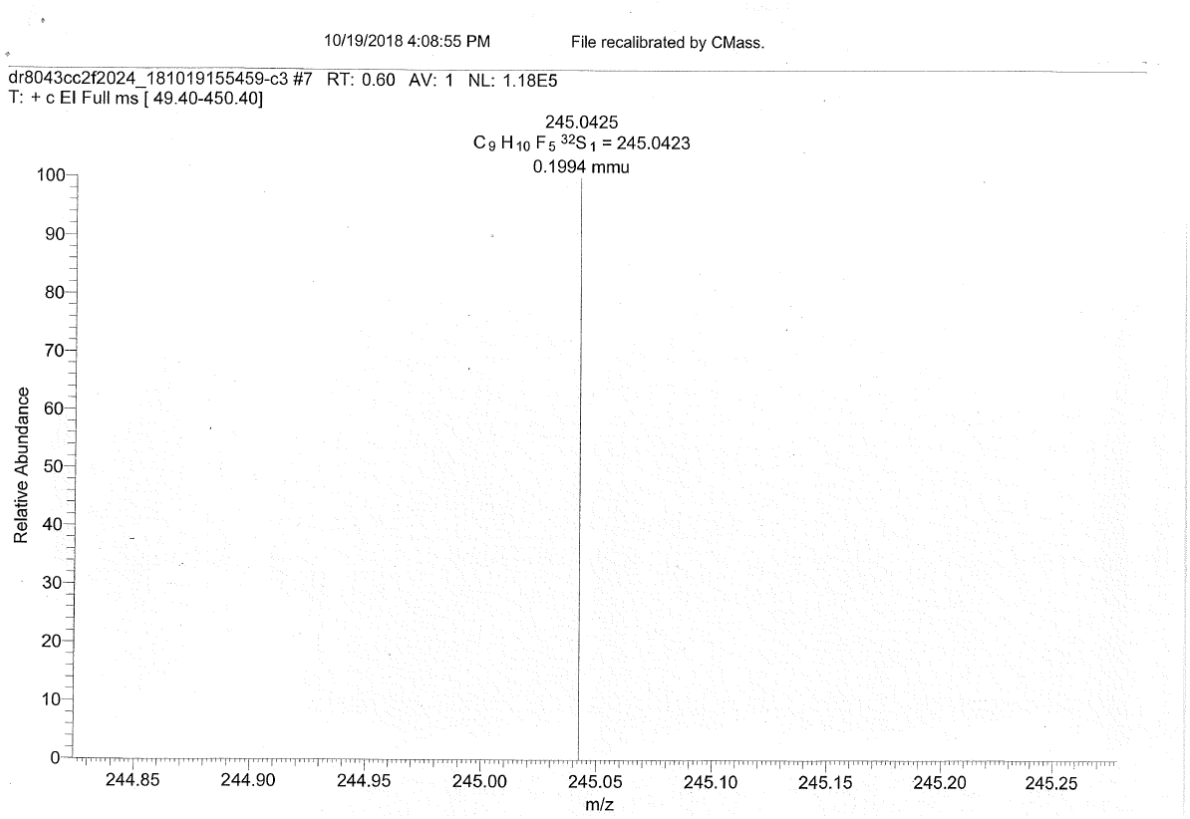


Fig. S127

HR-EI-MS spectrum of (2-(cyclopentyloxy)-2-phenylpropyl)pentafluoro-λ^6-sulfane (**22**).

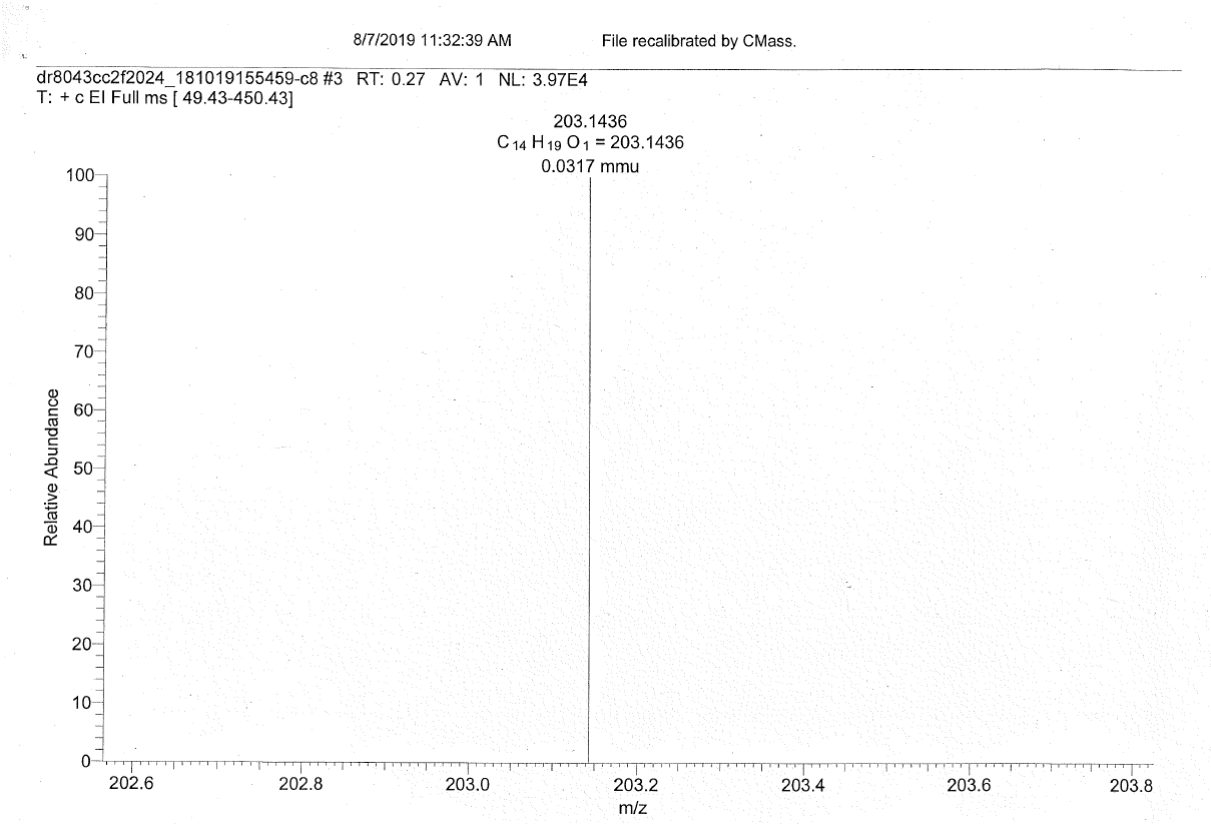


Fig. S128

HR-EI-MS spectrum of (2-(cyclopentyloxy)-2-phenylpropyl)pentafluoro-λ^6-sulfane (**22**).

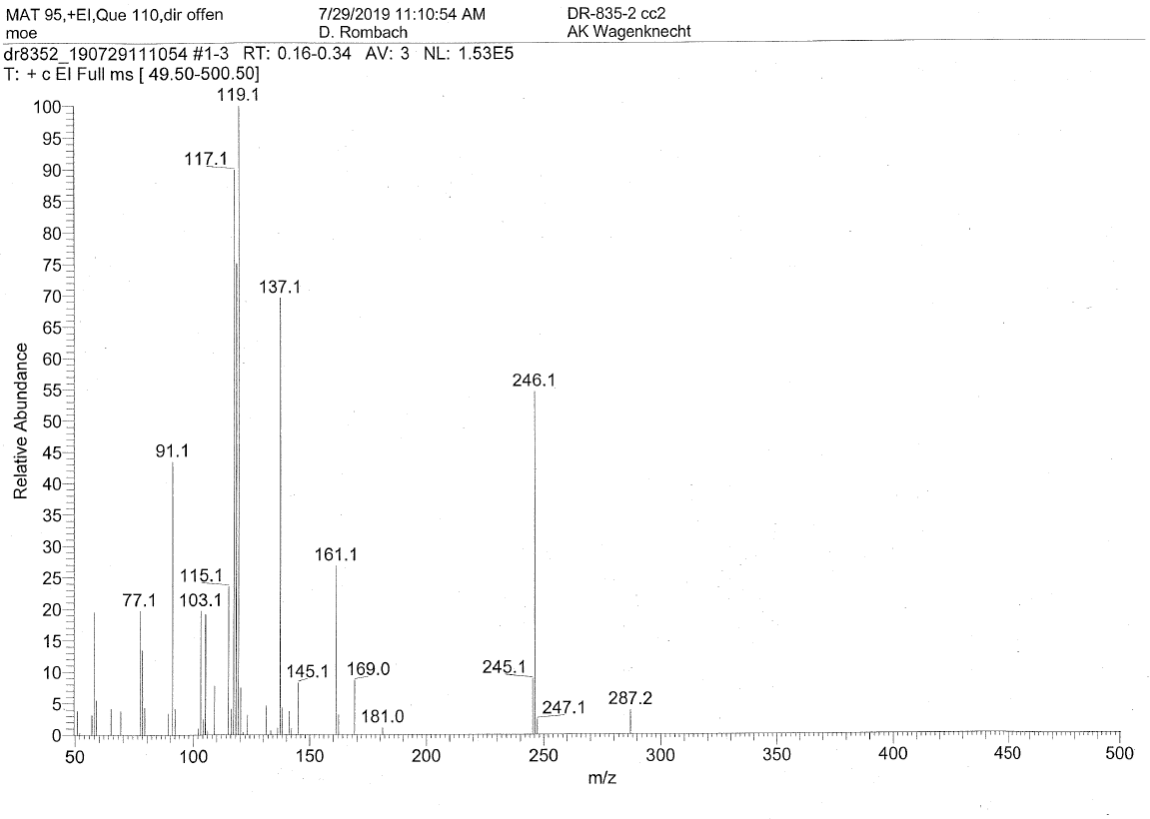


Fig. S129

EI-MS spectrum of (2-(allyloxy)-2-phenylpropyl)pentafluoro-λ^6-sulfane (**23**).

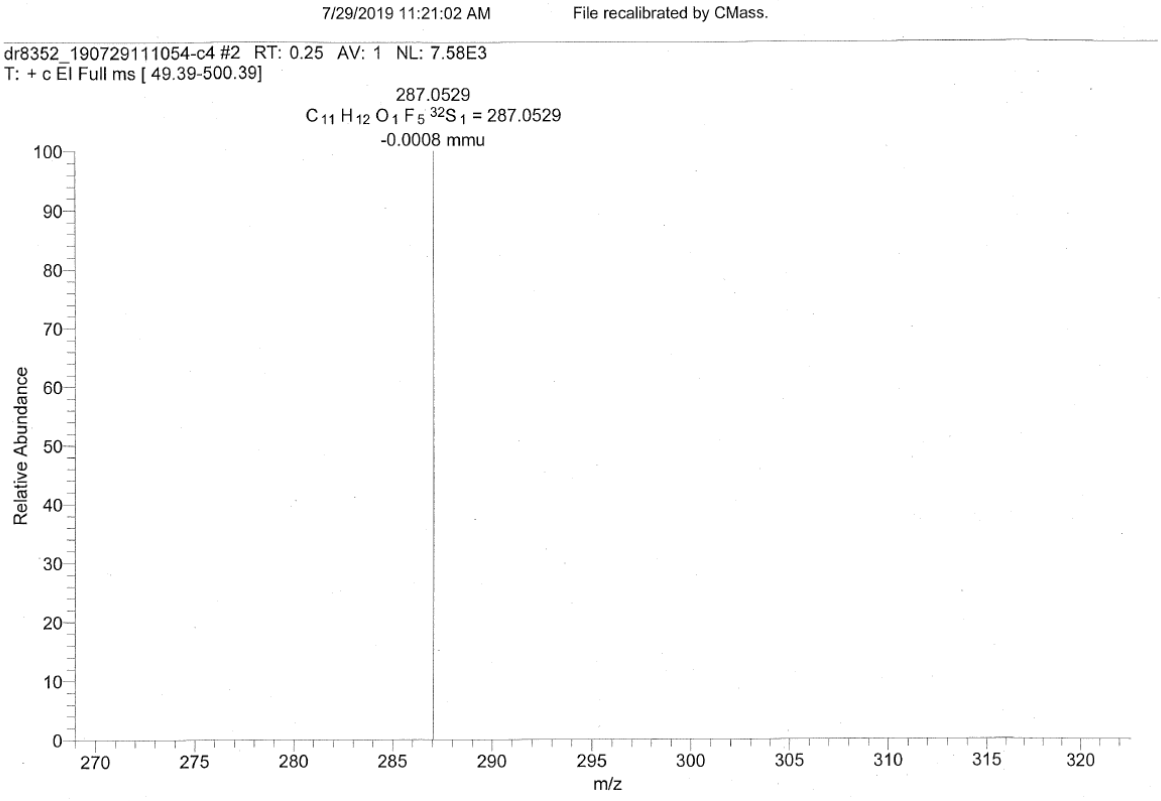


Fig. S130

EI-MS spectrum of (2-(allyloxy)-2-phenylpropyl)pentafluoro-λ^6-sulfane (**23**).

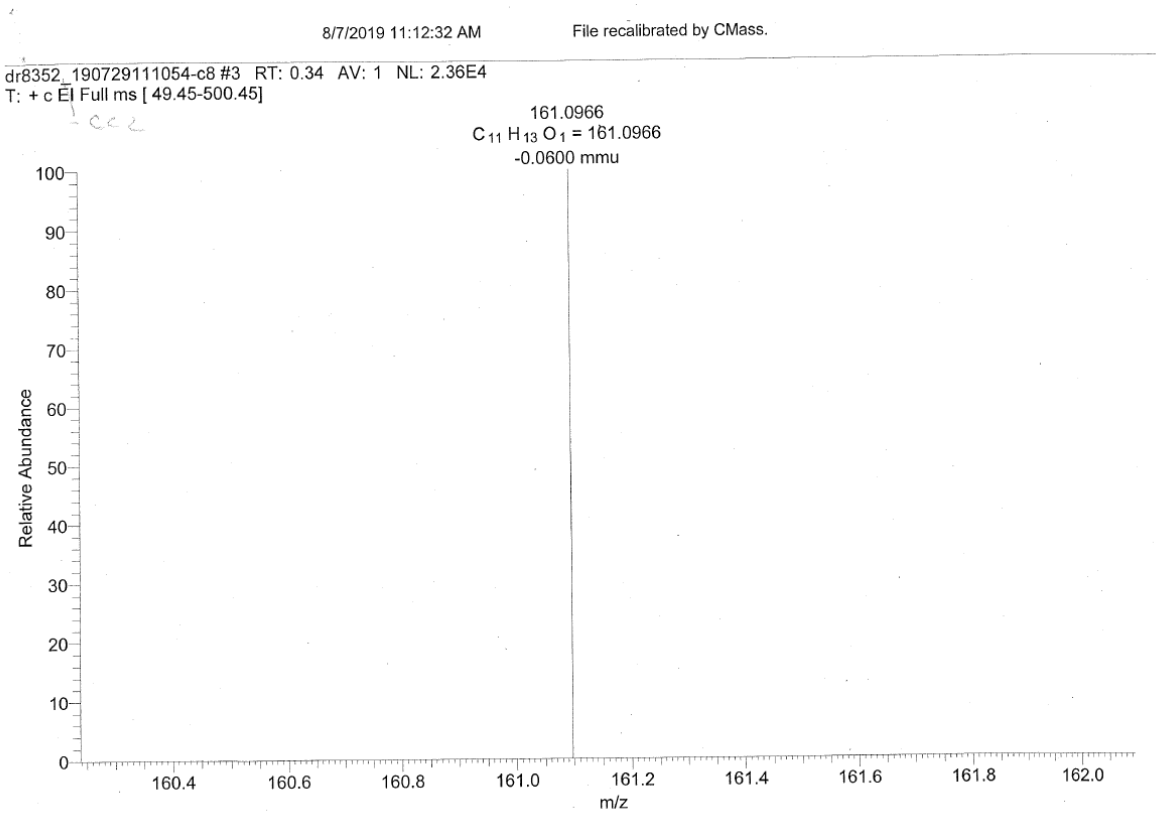


Fig. S131

EI-MS spectrum of (2-(allyloxy)-2-phenylpropyl)pentafluoro-λ^6-sulfane (**23**).

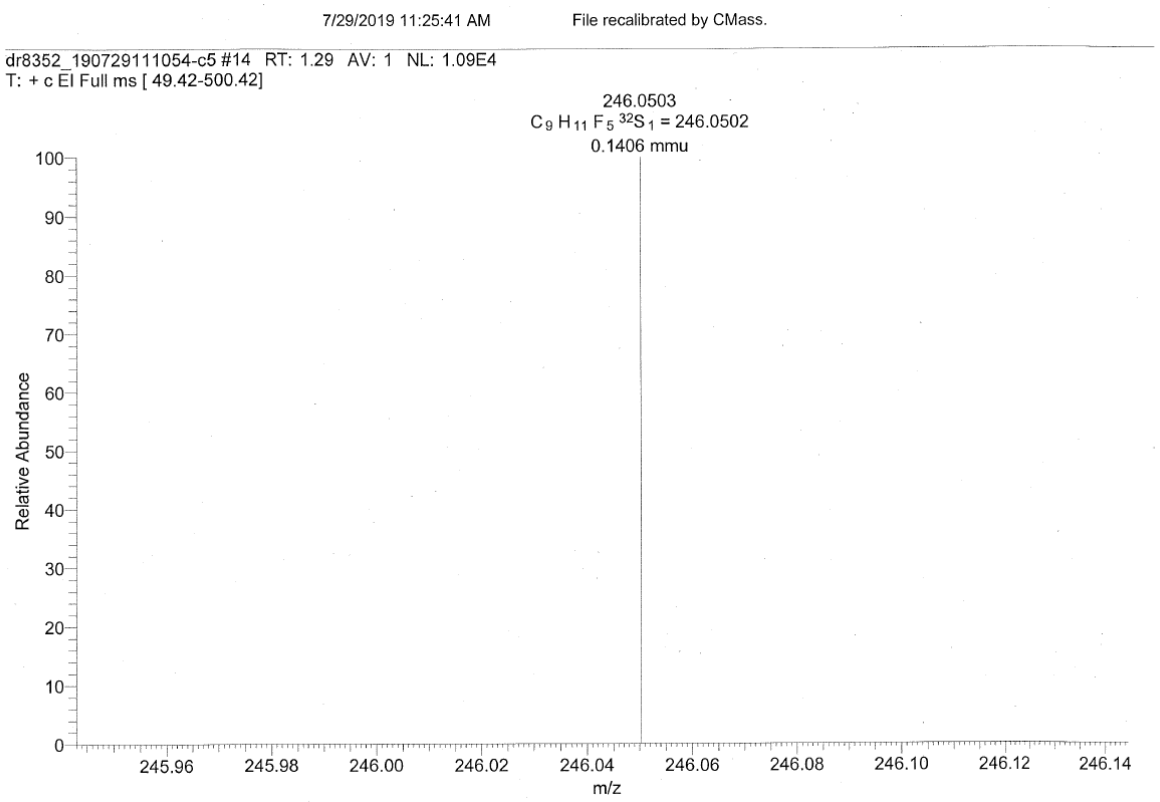


Fig. S132

EI-MS spectrum of (2-(allyloxy)-2-phenylpropyl)pentafluoro-λ^6-sulfane (**23**).

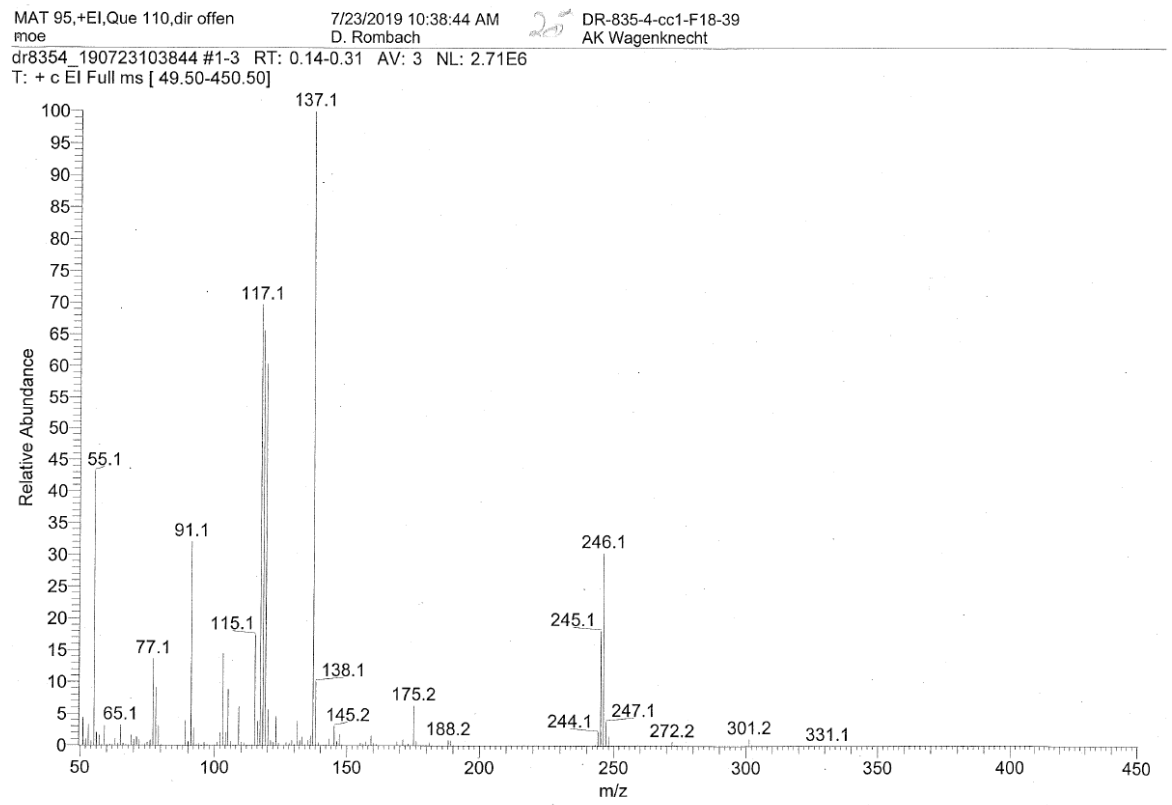


Fig. S133

EI-MS spectrum of pentafluoro(2-((2-methylallyl)oxy)-2-phenylpropyl)-λ^6-sulfane (**24**).

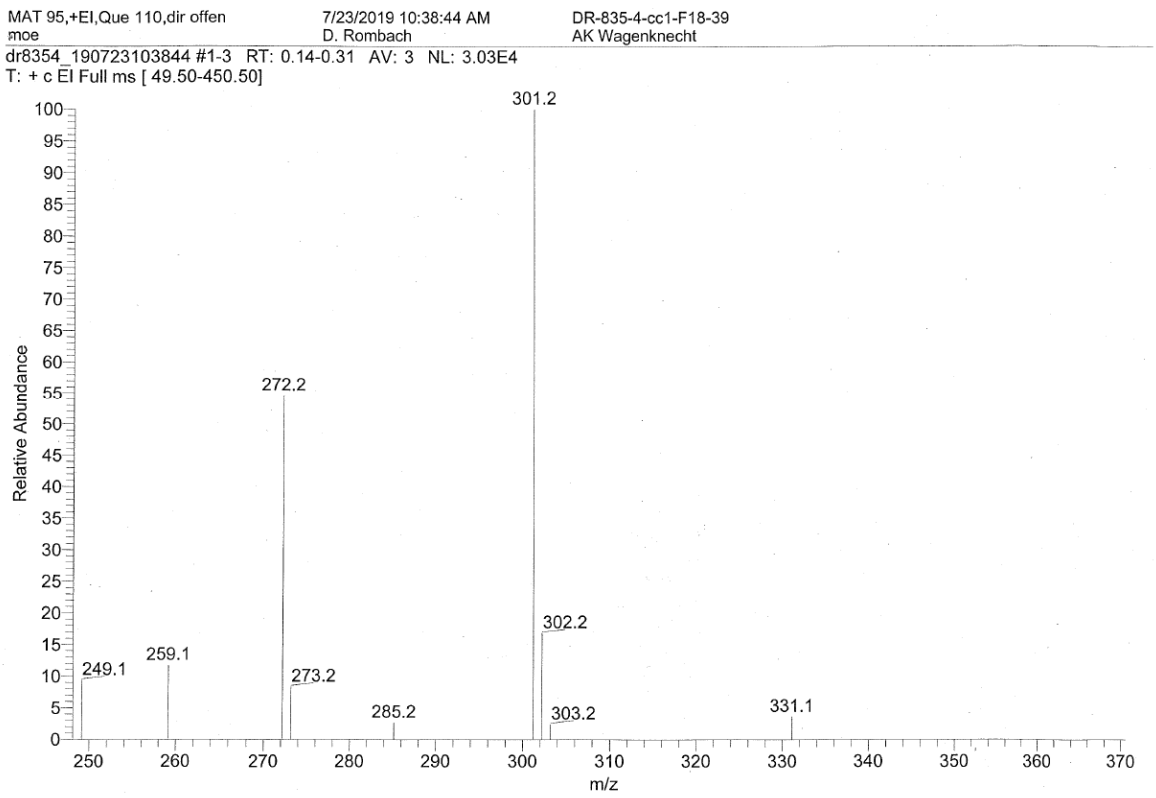


Fig. S134

EI-MS spectrum of pentafluoro(2-((2-methylallyl)oxy)-2-phenylpropyl)-λ^6-sulfane (**24**).

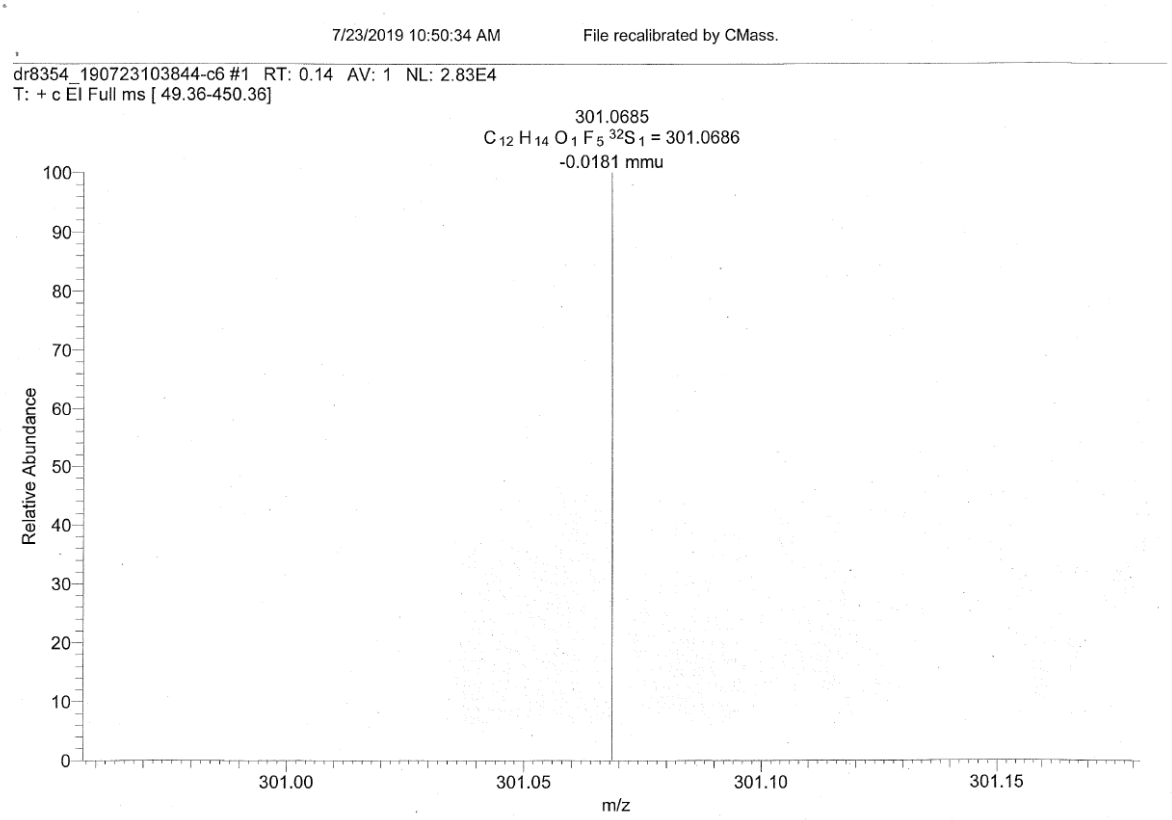


Fig. S135

HR-EI-MS spectrum of pentafluoro(2-((2-methylallyl)oxy)-2-phenylpropyl)-λ^6-sulfane (**24**).

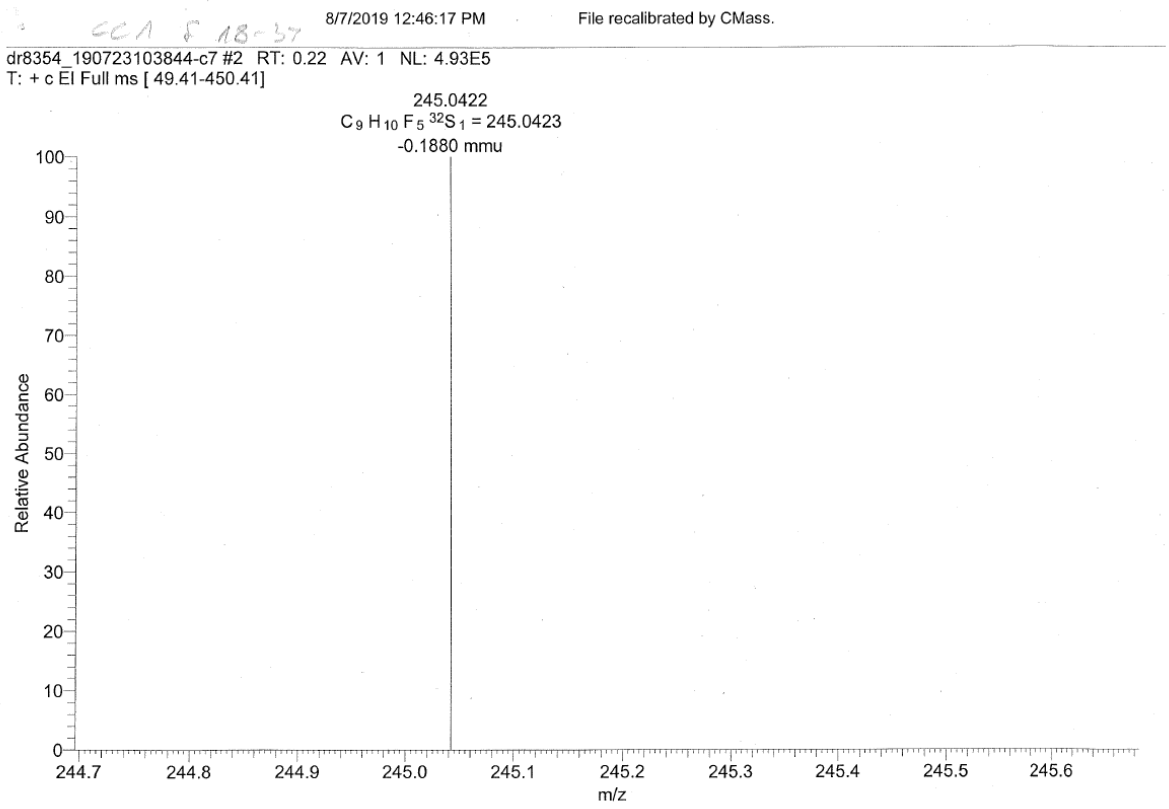


Fig. S136

HR-EI-MS spectrum of pentafluoro(2-((2-methylallyl)oxy)-2-phenylpropyl)-λ^6-sulfane (**24**).

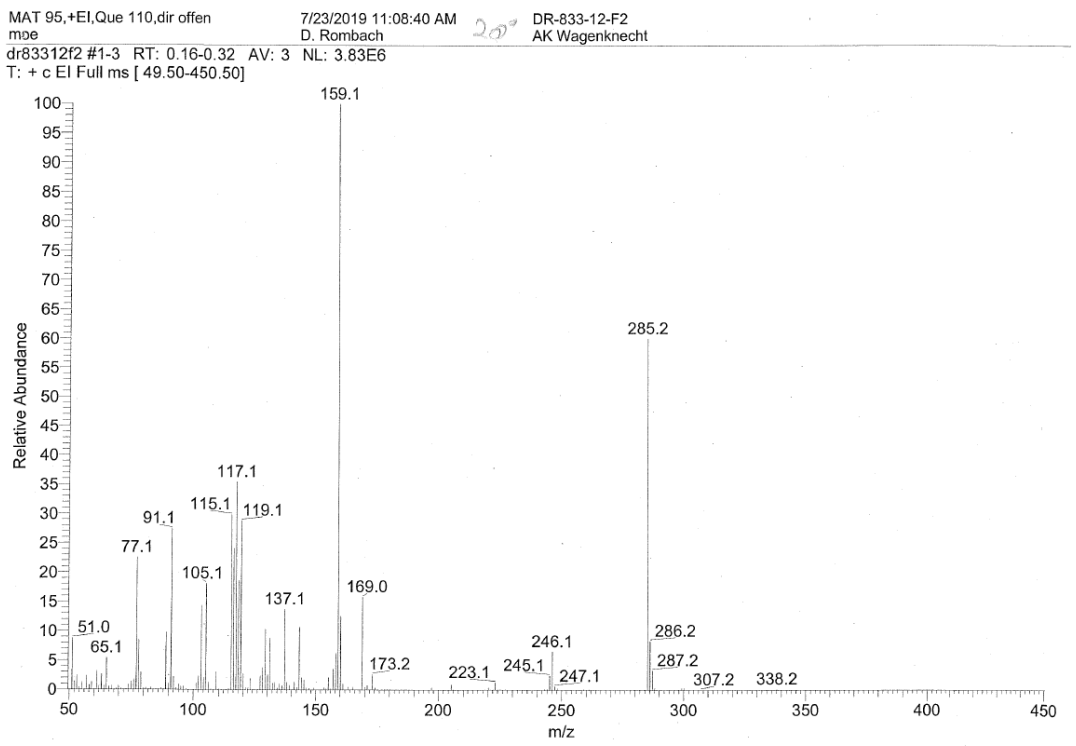


Fig. S137

EI-MS spectrum of pentafluoro(2-phenyl-2-(prop-2-yn-1-yloxy)propyl)-λ^6-sulfane (**25**).

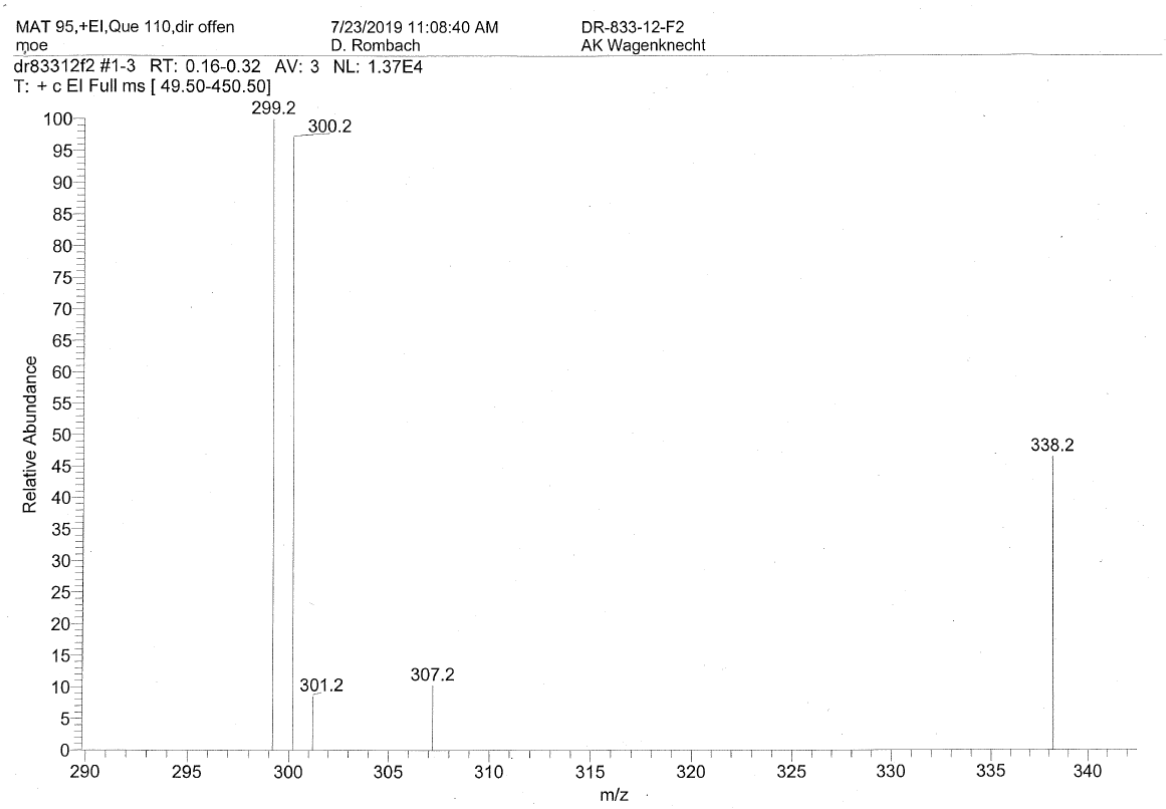


Fig. S138

EI-MS spectrum of pentafluoro(2-phenyl-2-(prop-2-yn-1-yloxy)propyl)-λ^6-sulfane (**25**).

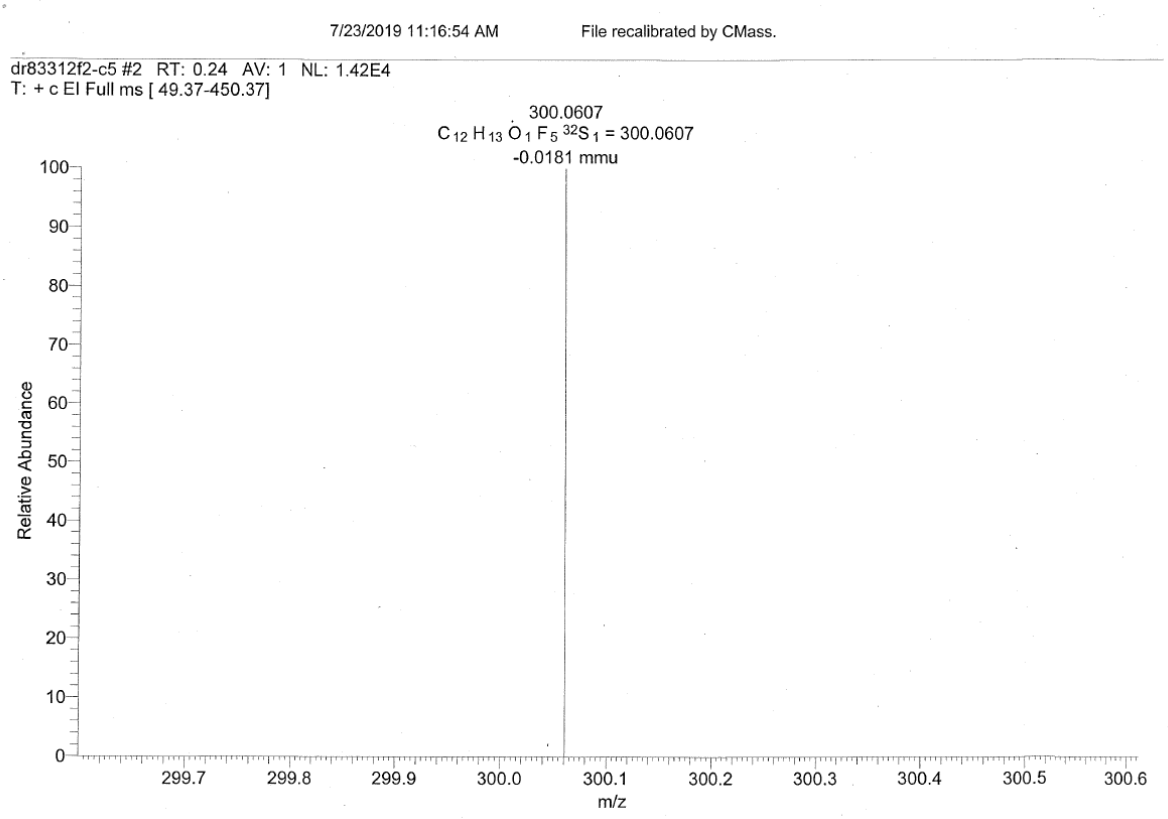


Fig. S139

HR-EI-MS spectrum of pentafluoro(2-phenyl-2-(prop-2-yn-1-yloxy)propyl)-λ^6-sulfane (**25**).

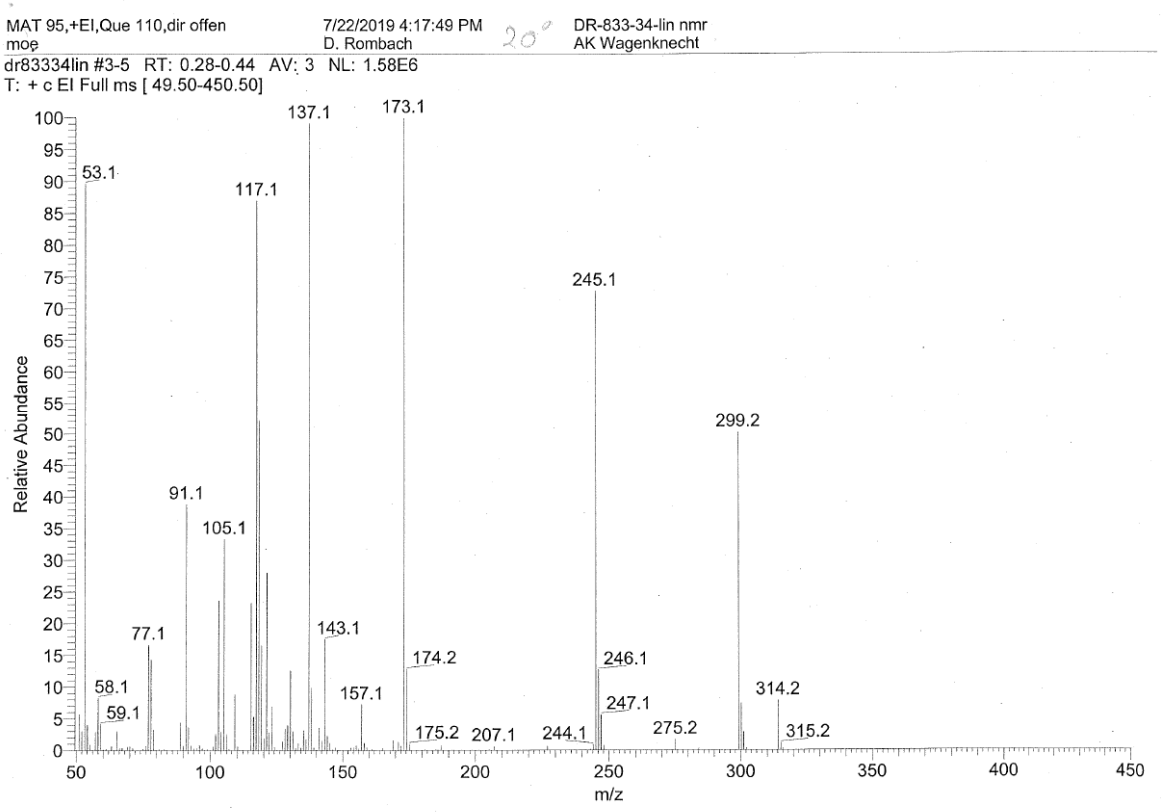


Fig. S140

HR-EI-MS spectrum of (2-(but-3-yn-1-yloxy)-2-phenylpropyl)pentafluoro-λ^6-sulfane (**26**).

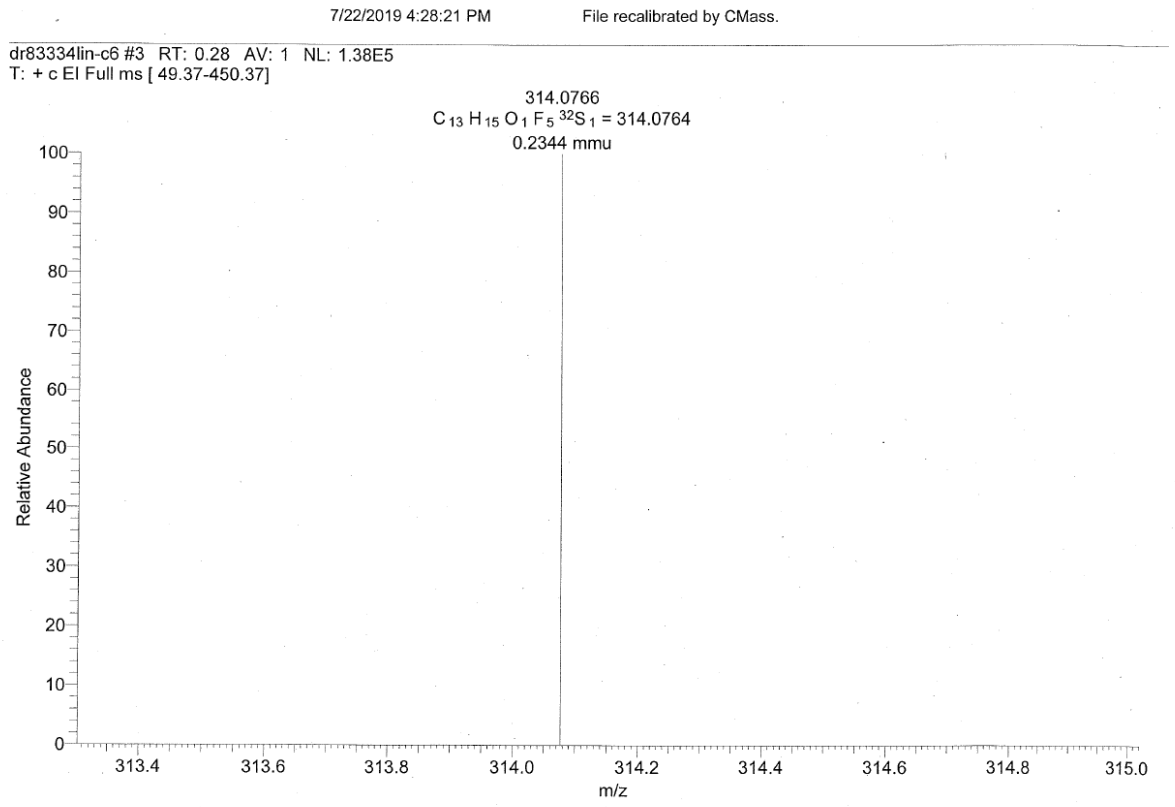


Fig. S141

HR-EI-MS spectrum of (2-(but-3-yn-1-yloxy)-2-phenylpropyl)pentafluoro-λ^6-sulfane (**26**).

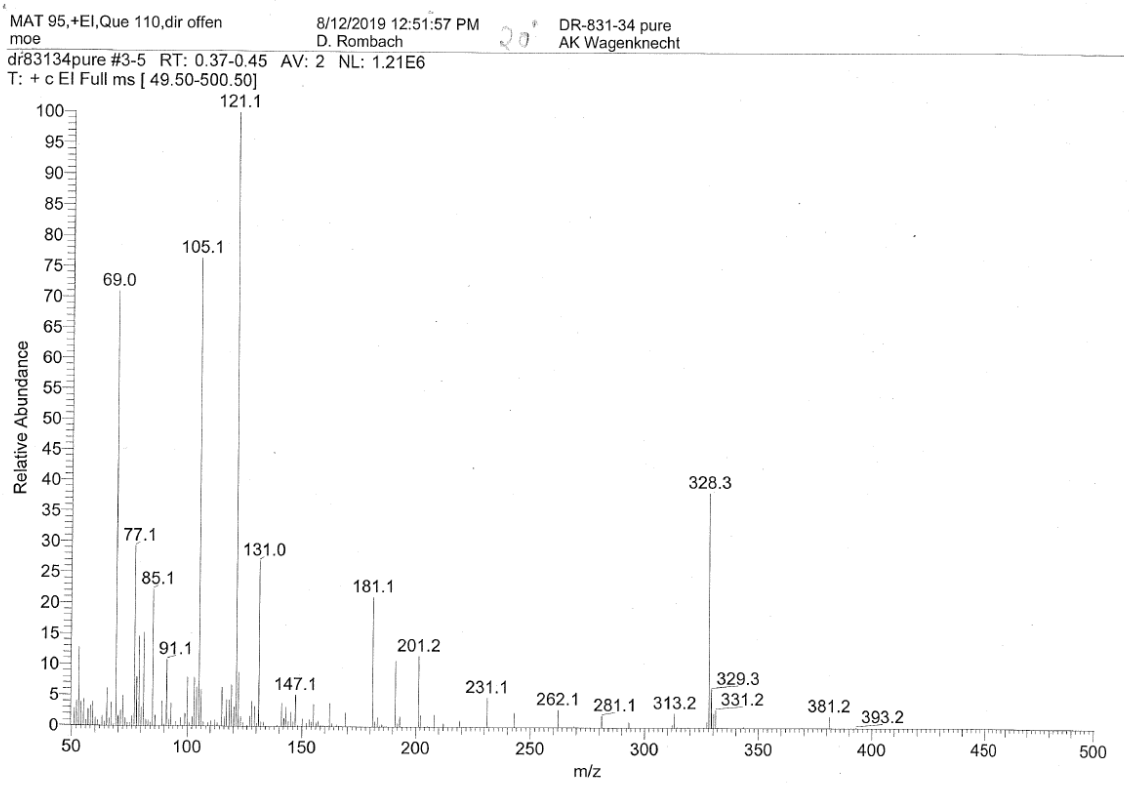


Fig. S144

EI-MS spectrum of pentafluoro(2-(pent-4-yn-1-yloxy)-2-phenylpropyl)-λ^6-sulfane (**27**).

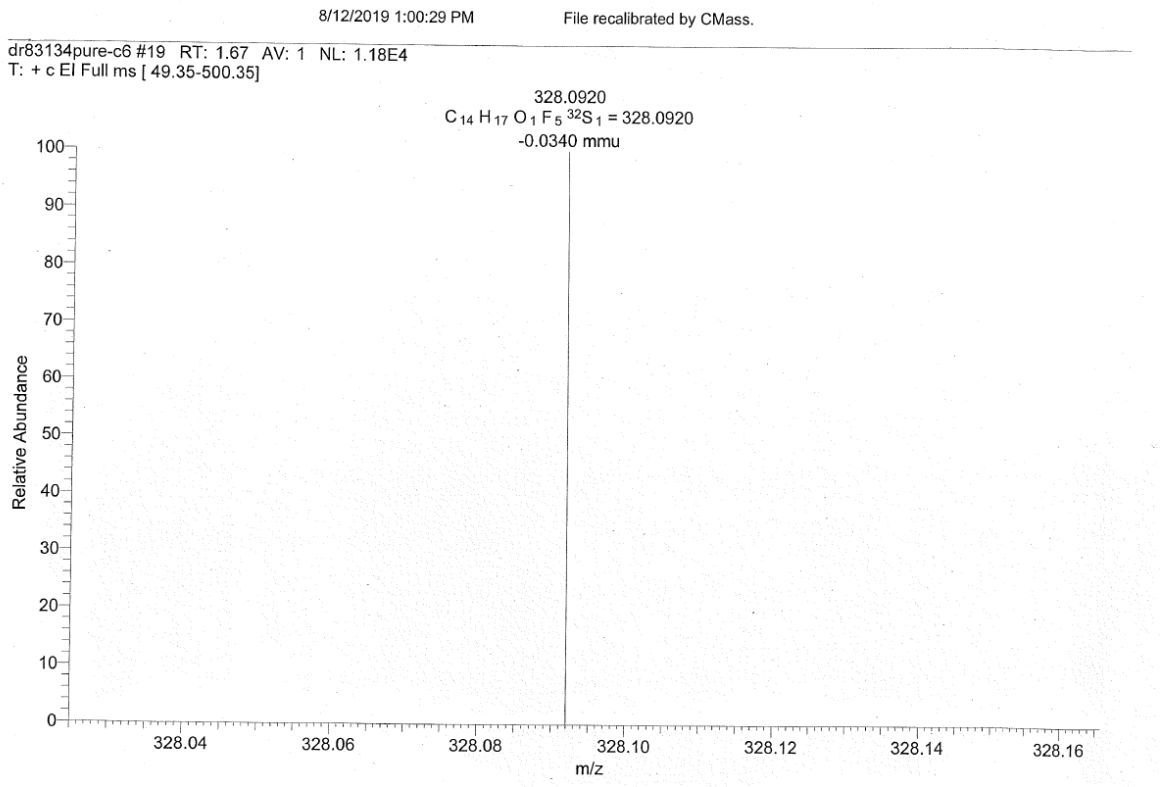


Fig. S145

HR-EI-MS spectrum of pentafluoro(2-(pent-4-yn-1-yloxy)-2-phenylpropyl)-λ^6-sulfane (**27**).

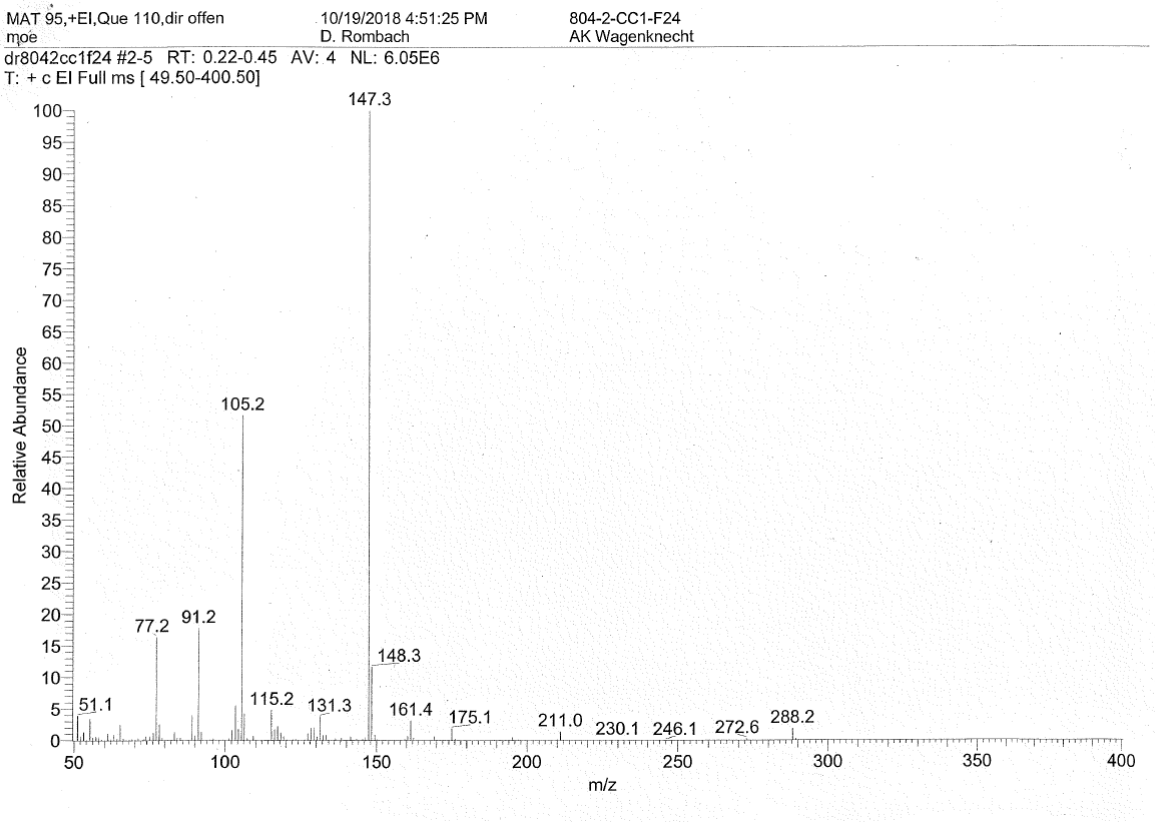


Fig. S146

EI-MS spectrum of 2-((pentafluoro-λ^6-sulfaneyl)methyl)-2-phenyltetrahydrofuran (**28**).

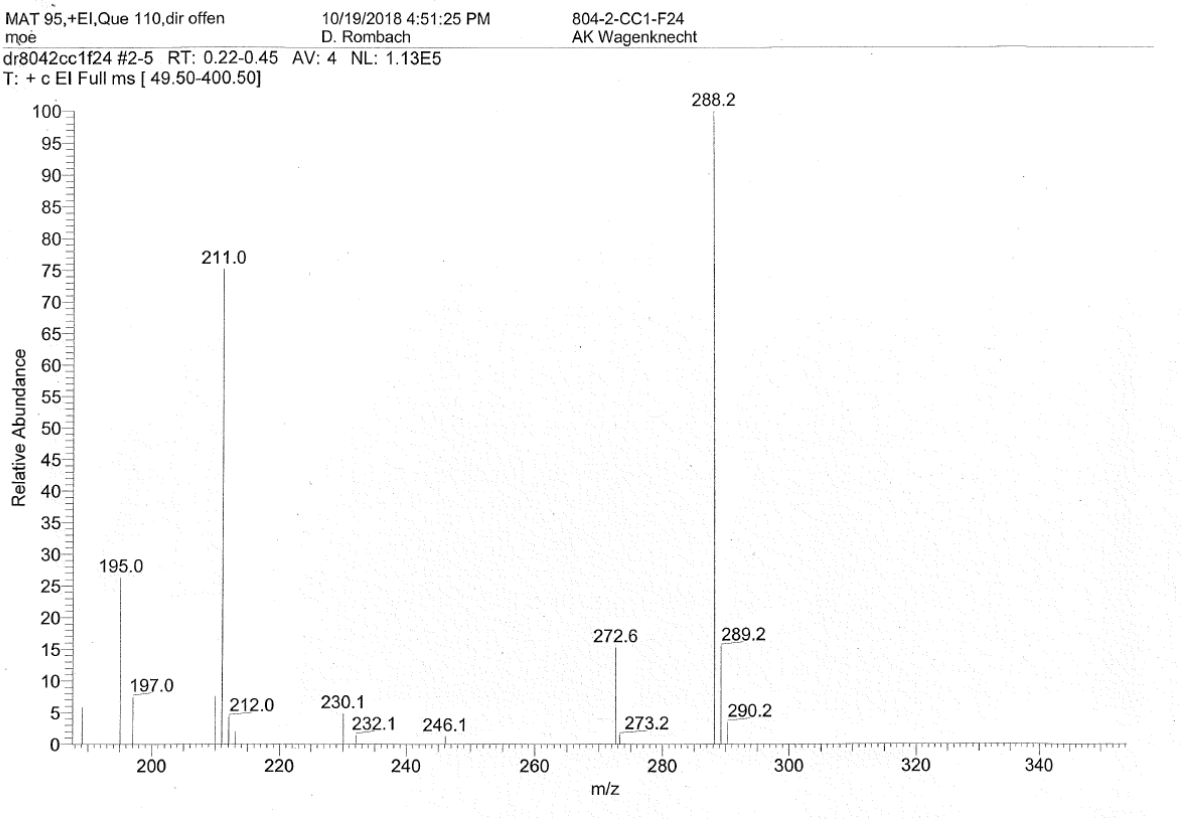


Fig. S147

EI-MS spectrum of 2-((pentafluoro-λ^6-sulfaneyl)methyl)-2-phenyltetrahydrofuran (**28**).

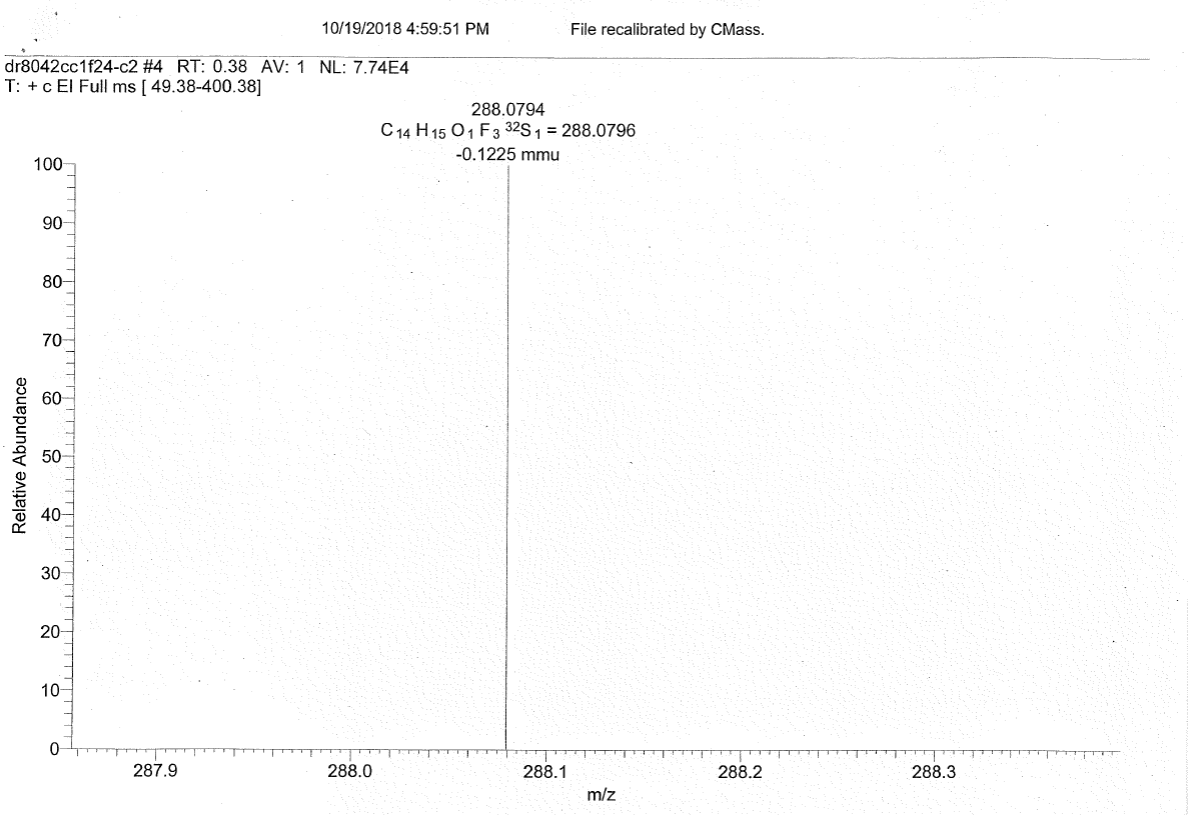


Fig. S148

HR-EI-MS spectrum of 2-((pentafluoro-λ^6-sulfaneyl)methyl)-2-phenyltetrahydrofuran (**28**).

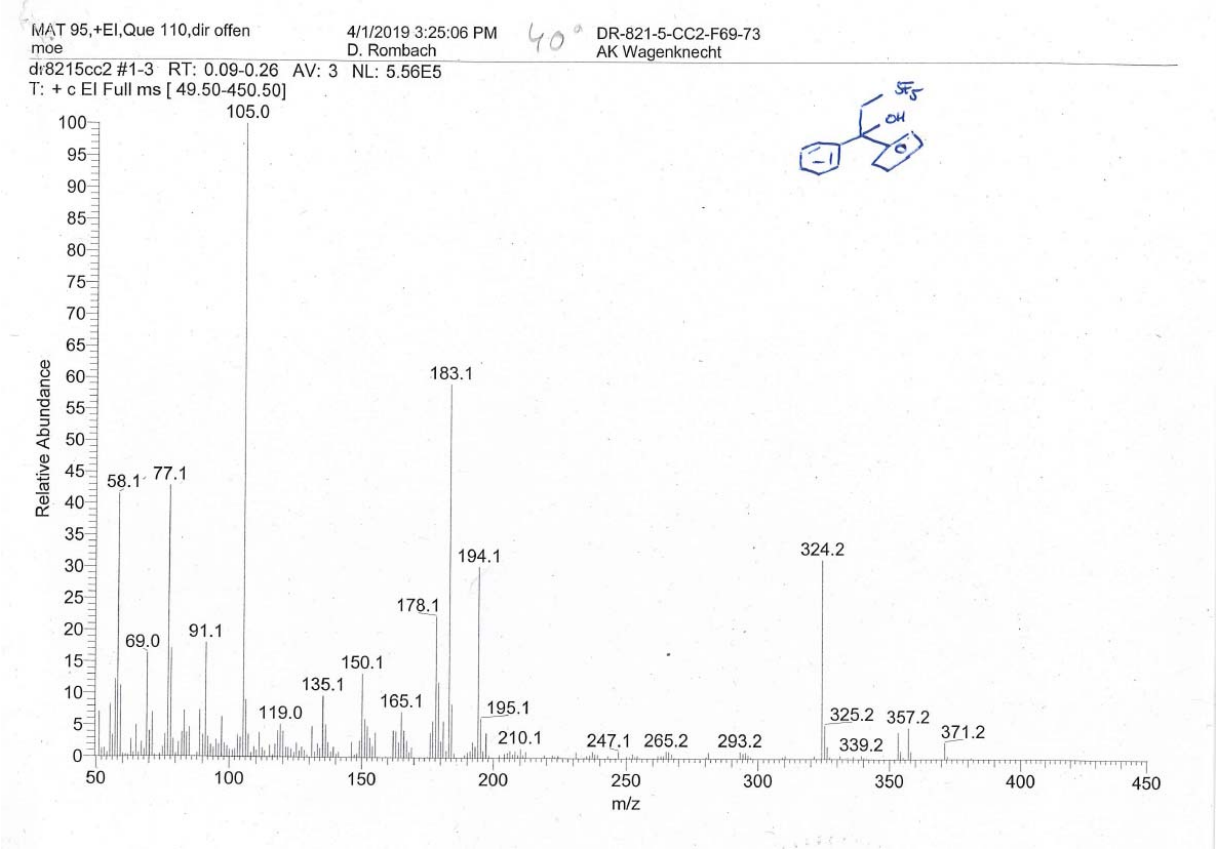


Fig. S149

EI-MS spectrum of 2-(pentafluoro-λ^6-sulfaneyl)-1,1-diphenylethan-1-ol (**29**).

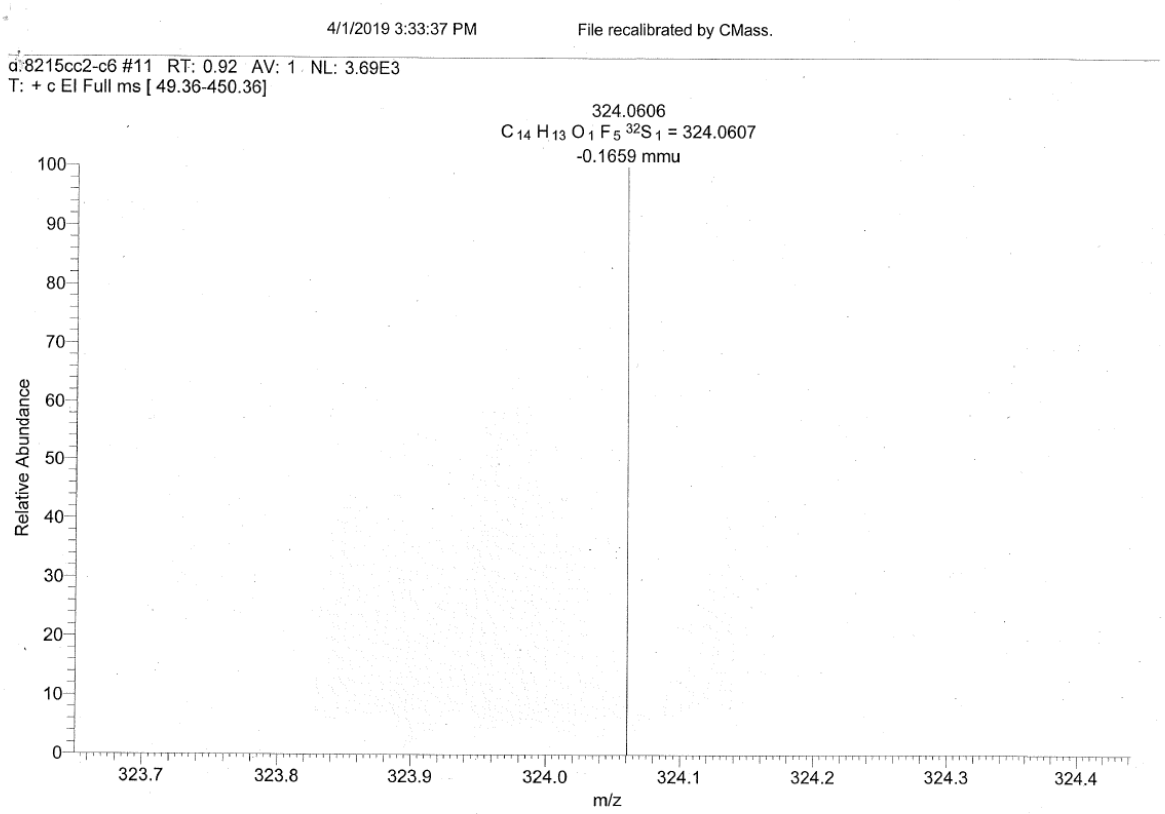


Fig. S150

HR-EI-MS spectrum of 2-(pentafluoro-λ^6-sulfaneyl)-1,1-diphenylethan-1-ol (**29**).

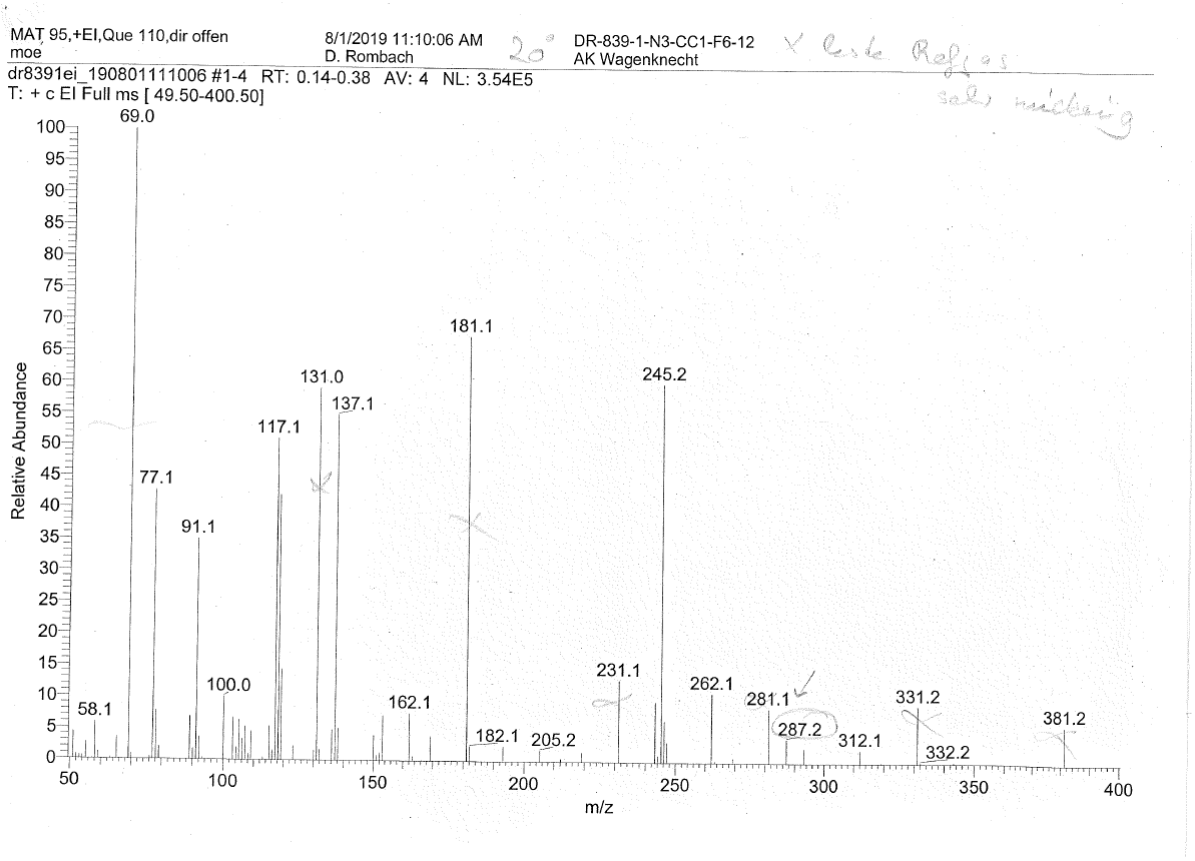


Fig. S151

EI-MS spectrum of (2-azido-2-phenylpropyl)pentafluoro-λ^6-sulfane (**32**). Crossed peaks belong to reference gas.

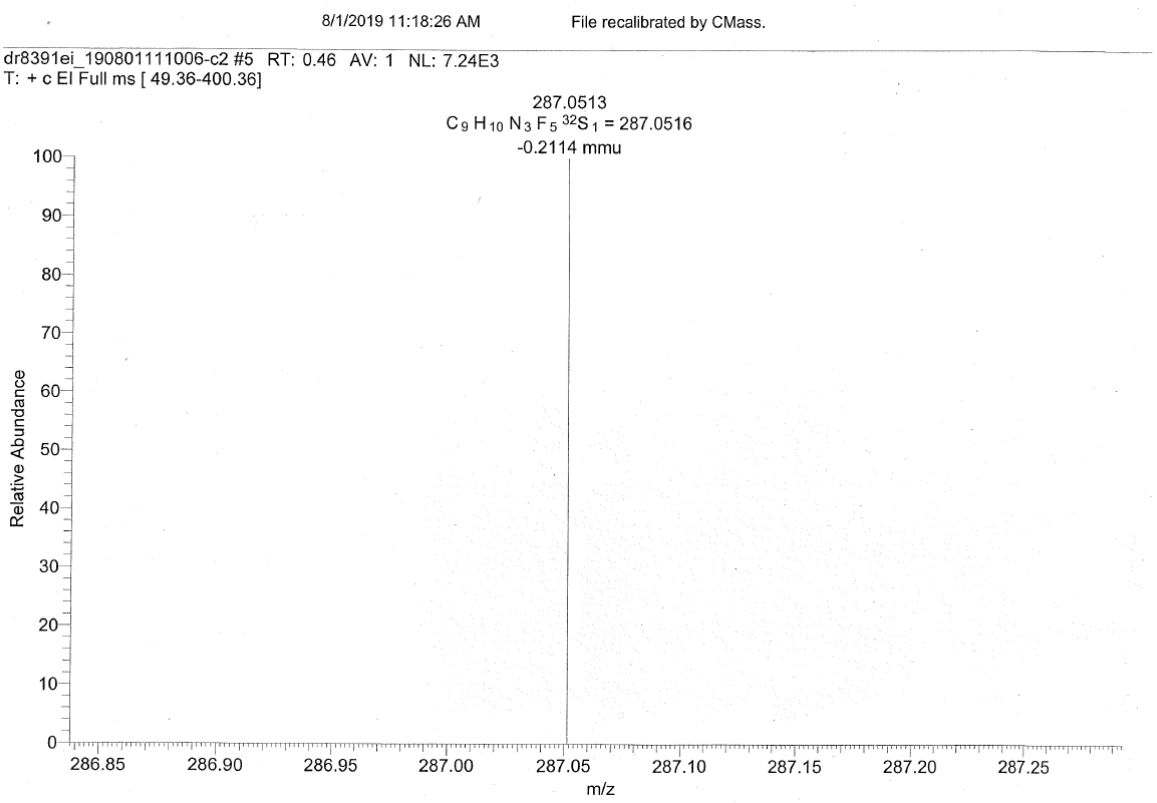


Fig. S152

EI-MS spectrum of (2-azido-2-phenylpropyl)pentafluoro-λ^6-sulfane (**32**).

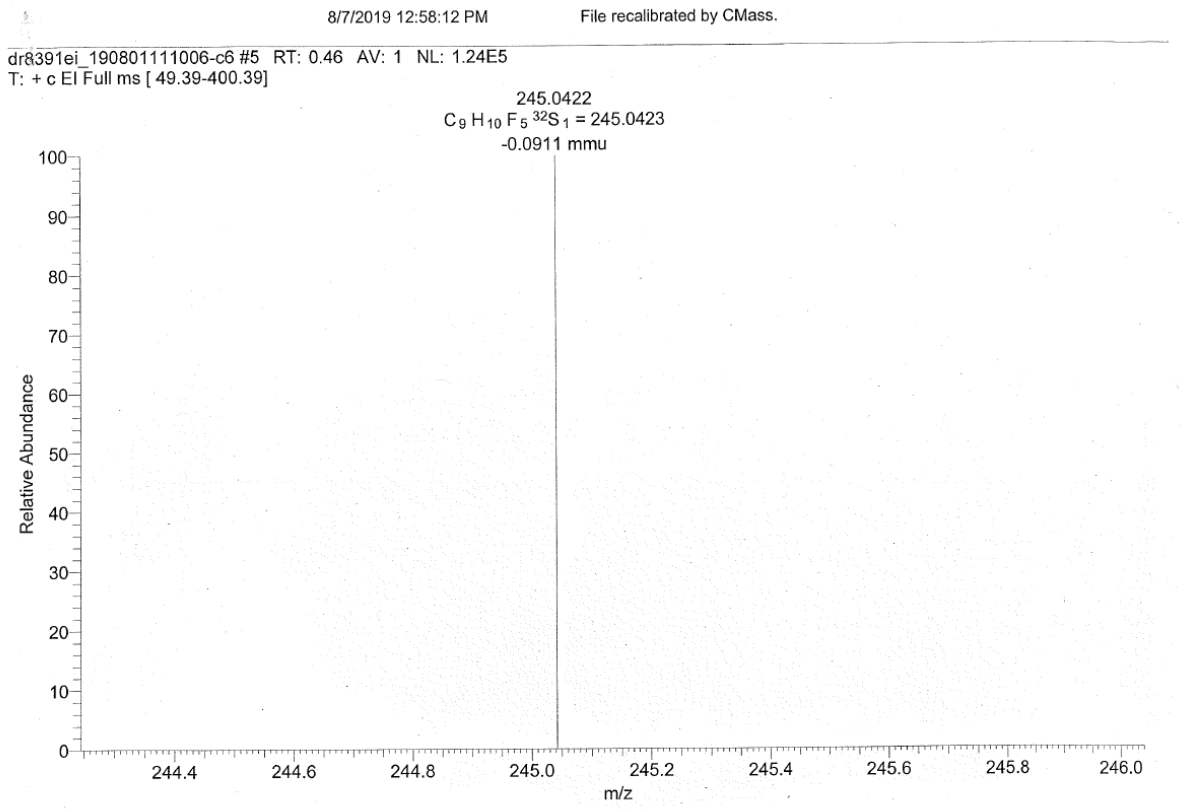


Fig. S153

EI-MS spectrum of (2-azido-2-phenylpropyl)pentafluoro-λ^6-sulfane (**32**).

Infrared spectroscopic characterisation

Infrared spectroscopic characterisations of **8**, **9** and **32.**

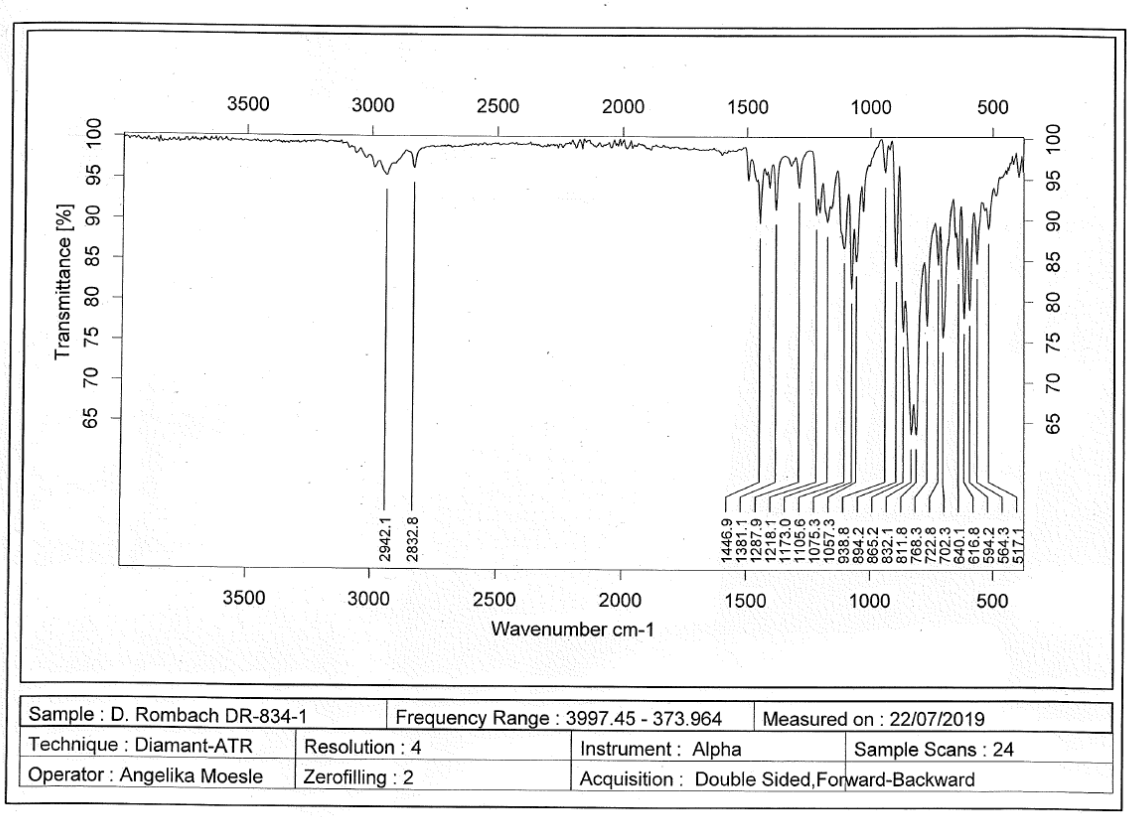


Fig. S154

FT-IR spectrum of pentafluoro(2-methoxy-2-phenylpropyl)-λ^6-sulfane (**8**).

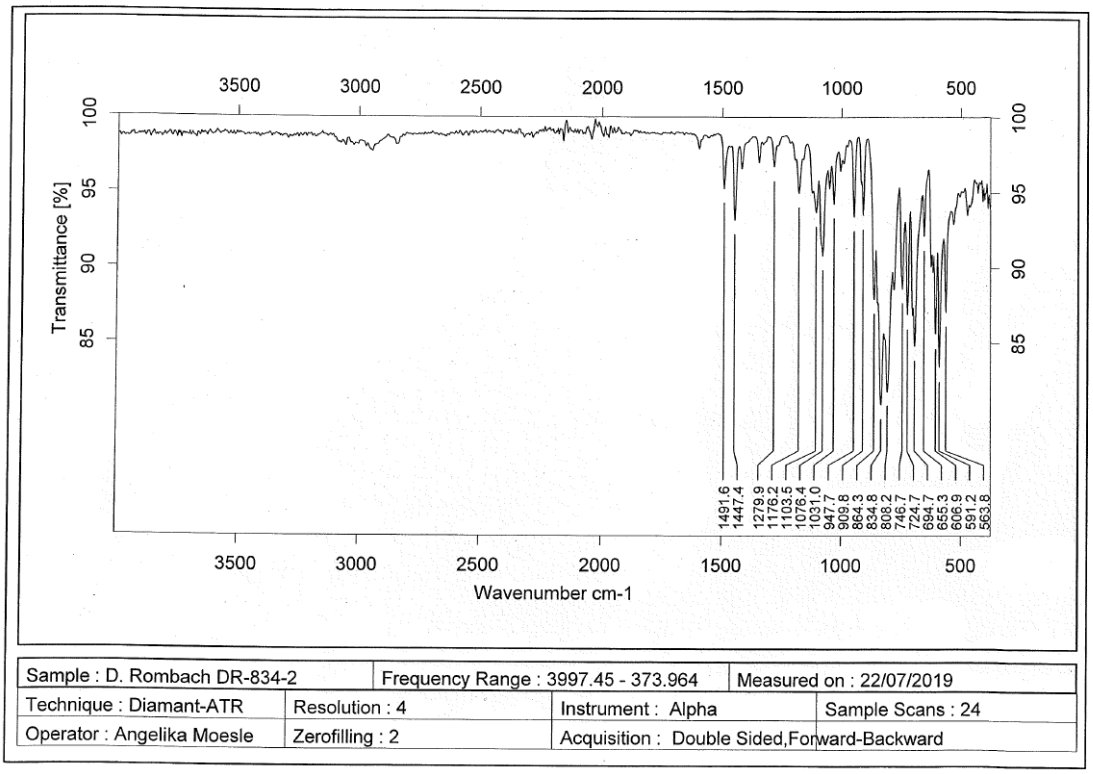


Fig. S155

FT-IR spectrum of pentafluoro(2-methoxy-2,2-diphenylethyl)-λ^6-sulfane (**9**).

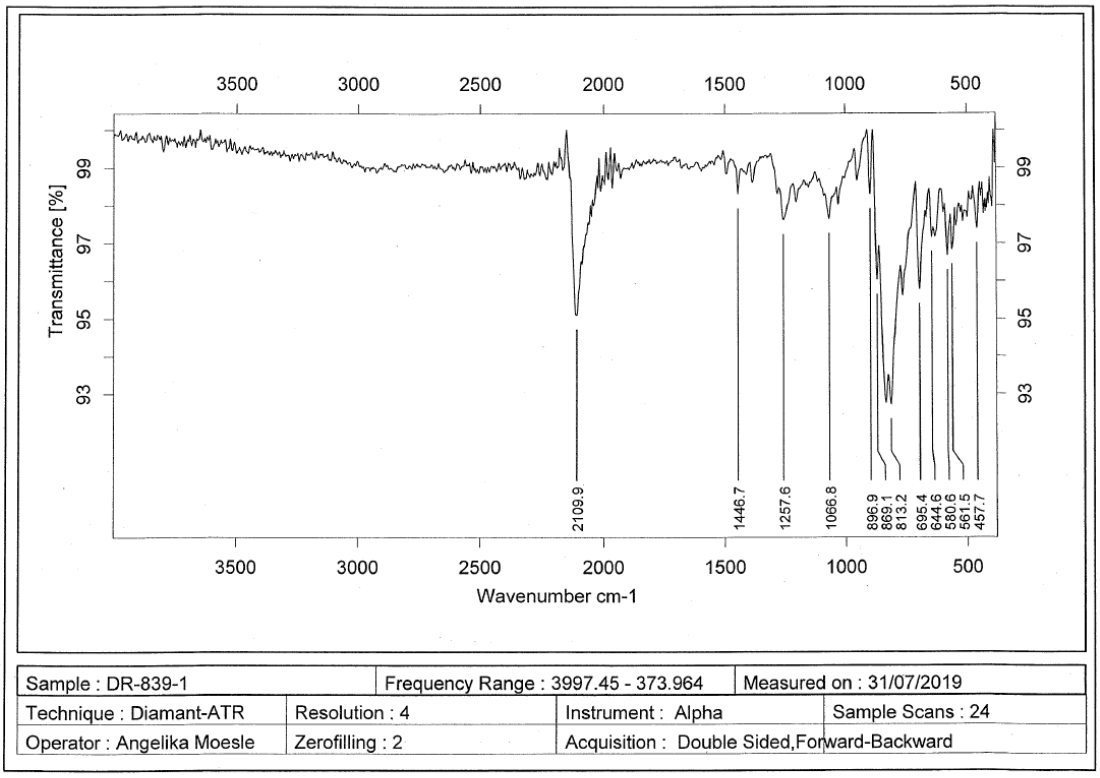


Fig. S156

FT-IR spectrum of (2-azido-2-phenylpropyl)pentafluoro-λ^6-sulfane (**32**).

XRD-data

XRD-data of **9**

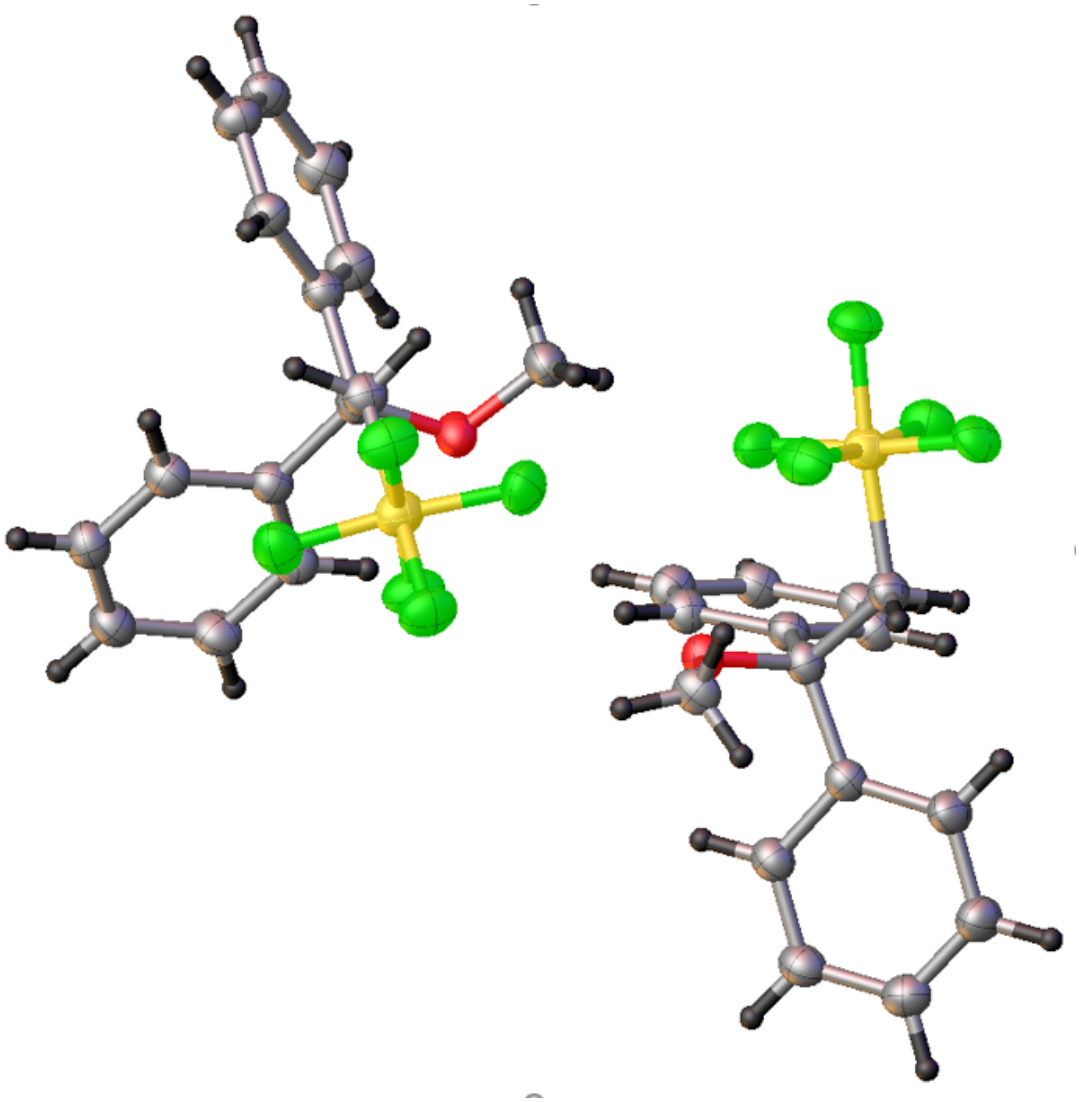


Fig. S157
Plot of the XRD-structure of **9**.

Table 1 - Crystal data and structure refinement for **9**.	
Identification code	1948906
Empirical formula	$C_{15}H_{15}F_5OS$
Formula weight	338.33
Temperature/K	200
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.865(2)
b/Å	15.146(3)
c/Å	19.988(4)
α/°	90
β/°	101.03(3)
γ/°	90
Volume/Å^3	2931.3(11)
Z	8
ρ_{calc}g/cm^3	1.533
μ/mm^{-1}	0.274
F(000)	1392.0
Crystal size/mm^3	0.8 × 0.2 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.398 to 51.996
Index ranges	-9 ≤ h ≤ 12, -16 ≤ k ≤ 18, -24 ≤ l ≤ 24
Reflections collected	15063
Independent reflections	5756 [R_{int} = 0.0758, R_{sigma} = 0.0605]
Data/restraints/parameters	5756/0/400
Goodness-of-fit on F^2	0.988
Final R indexes [I>=2σ (I)]	R_1 = 0.0603, wR_2 = 0.1541
Final R indexes [all data]	R_1 = 0.0954, wR_2 = 0.1811
Largest diff. peak/hole / e Å^{-3}	0.42/-0.29

Table 2 - Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **9**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1A	11024.0(8)	1625.0(6)	4112.0(4)	54.9(3)
S1B	7163.0(8)	3940.8(6)	2317.3(4)	60.4(3)
F1A	12542.4(18)	1394.7(14)	4504.8(11)	66.2(5)
F4A	10479(2)	731.0(14)	4381.1(10)	68.0(5)
F5A	11372(2)	1067.9(14)	3492.8(10)	71.2(6)
F2A	11611(2)	2460.5(14)	3786.9(11)	72.7(6)
O1A	9064(2)	3342.7(14)	4323.3(11)	52.2(5)
F3A	9566.7(19)	1793.6(16)	3669.8(10)	70.7(6)
F4B	8281(2)	4097.3(16)	1855.5(11)	76.1(6)
F2B	6125(2)	3852.7(16)	2818.8(11)	76.8(6)
F1B	8154(2)	3255.4(16)	2762.1(11)	76.9(6)
F5B	7922(2)	4693.0(16)	2804.3(11)	77.7(6)
O1B	5302(2)	2135.9(16)	2463.8(11)	56.5(6)
F3B	6236(2)	4694.6(14)	1915.3(11)	76.8(6)
C4A	8136(3)	2073(2)	4754.6(15)	47.0(7)
C10A	9421(3)	3158(2)	5553.1(15)	48.6(7)
C10B	3851(3)	3231(2)	1844.9(16)	50.1(7)
C5A	6979(3)	2221(2)	4245.5(15)	51.0(7)
C3B	5060(3)	2603(2)	1832.1(15)	50.9(7)
C4B	4616(3)	1954(2)	1235.1(15)	51.2(7)
C2A	10750(3)	2235(2)	4857.6(15)	50.4(7)
C3A	9363(3)	2708(2)	4855.9(15)	47.8(7)
C9A	8121(3)	1374(2)	5199.0(16)	52.3(7)
C1A	10030(3)	4050(2)	4341.6(18)	56.5(8)
C7A	5839(3)	967(2)	4626.8(18)	56.2(8)
C9B	4924(3)	2058(2)	592.5(16)	55.6(8)
C2B	6371(3)	3094(2)	1717.3(16)	54.1(8)
C8A	6991(3)	813(2)	5134.6(17)	53.9(8)
C11A	8356(3)	3750(2)	5605.9(17)	53.8(8)
C11B	3419(3)	3807(2)	1307.1(17)	54.8(8)
C8B	4464(3)	1459(2)	78.9(18)	60.3(8)
C15B	3119(3)	3214(2)	2373.6(17)	57.0(8)
C6A	5840(3)	1661(2)	4191.1(17)	56.9(8)
C5B	3825(3)	1228(2)	1346.0(19)	62.5(9)
C13B	1573(3)	4336(2)	1822.4(18)	61.4(9)
C1B	6329(3)	1453(2)	2539.7(18)	63.9(9)
C13A	9283(4)	3993(2)	6784.5(18)	60.4(8)
C12A	8291(3)	4161(2)	6208.5(17)	58.4(8)
C14A	10318(4)	3407(3)	6743.8(18)	63.8(9)
C15A	10395(3)	2995(3)	6135.5(17)	60.6(9)
C12B	2302(3)	4359(2)	1296.1(17)	58.6(8)
C7B	3701(4)	739(2)	199.0(19)	64.1(9)
C14B	1987(3)	3764(3)	2365.3(19)	65.4(9)
C6B	3375(4)	623(3)	834(2)	69.8(10)

Table 3 - Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **9**.						
Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
S1A	48.4(4)	57.3(5)	59.8(5)	-2.7(4)	12.4(3)	2.9(4)
S1B	50.2(5)	68.8(6)	61.6(5)	-7.3(4)	9.0(4)	-6.6(4)
F1A	46.5(10)	71.9(13)	79.5(13)	-8.1(10)	10.3(9)	10.8(9)
F4A	70.3(12)	56.8(12)	79.3(13)	-8.4(10)	20.1(10)	-9.8(9)
F5A	67.3(12)	76.9(15)	72.8(13)	-15.5(11)	21.7(10)	7.6(10)
F2A	87.9(14)	65.0(14)	73.8(13)	3.3(10)	36.6(11)	-2.8(11)
O1A	48.3(11)	49.2(13)	58.4(12)	8.1(10)	8.9(9)	-3.0(9)
F3A	56.9(11)	90.5(16)	60.4(11)	-14.1(11)	0.3(9)	15.9(10)
F4B	57.5(11)	93.7(17)	80.4(14)	-15.1(12)	21.5(10)	-23.9(11)
F2B	70.0(13)	95.7(17)	69.7(13)	-23.9(12)	25.7(10)	-17.7(12)
F1B	67.4(12)	86.4(16)	68.7(13)	-0.5(11)	-8.0(10)	2.8(11)
F5B	67.6(12)	88.2(17)	75.0(13)	-22.1(12)	7.7(10)	-17.9(11)
O1B	53.8(12)	64.6(15)	52.5(12)	6.7(11)	14.0(9)	10.1(11)
F3B	73.9(13)	62.1(14)	87.6(14)	-6.5(11)	-1.5(11)	1.0(11)
C4A	42.8(15)	46.4(17)	52.0(16)	-3.0(13)	9.7(12)	-0.5(13)
C10A	44.2(15)	46.7(17)	55.2(17)	0.0(13)	10.1(13)	-2.3(13)
C10B	43.7(15)	51.7(18)	55.2(17)	-1.8(14)	10.3(13)	-0.6(13)
C5A	42.9(15)	55.2(19)	55.9(17)	2.4(14)	12.3(13)	-1.4(14)
C3B	43.3(15)	56.8(19)	53.6(17)	3.6(14)	11.7(12)	1.9(14)
C4B	42.8(15)	55.4(19)	55.5(18)	0.0(14)	9.6(13)	1.8(14)
C2A	41.6(15)	54.0(19)	54.9(17)	-0.9(14)	7.8(12)	3.2(13)
C3A	41.3(15)	47.3(17)	54.4(17)	3.9(13)	8.4(12)	0.9(13)
C9A	46.6(16)	51.0(18)	60.0(18)	1.0(15)	12.0(13)	0.2(14)
C1A	55.9(18)	44.6(18)	71(2)	2.2(15)	17.0(15)	-7.0(14)
C7A	43.9(16)	54.9(19)	71(2)	-6.4(16)	12.8(15)	-5.6(14)
C9B	56.9(18)	53.6(19)	56.6(19)	-1.1(15)	11.2(14)	-6.5(15)
C2B	43.8(15)	60(2)	59.2(18)	-1.8(15)	12.3(13)	-4.1(14)
C8A	48.4(16)	49.2(18)	67(2)	1.7(15)	18.2(14)	-4.0(14)
C11A	49.5(17)	52.5(19)	60.7(19)	2.8(15)	13.9(14)	3.2(14)
C11B	50.8(17)	56(2)	59.7(18)	1.3(15)	15.4(14)	-3.5(15)
C8B	57.5(19)	65(2)	58.3(19)	-6.8(16)	11.0(15)	-6.2(16)
C15B	53.3(17)	61(2)	58.2(19)	1.4(16)	15.3(14)	1.5(15)
C6A	42.5(16)	68(2)	59.6(19)	-0.6(17)	8.2(14)	-5.4(15)
C5B	53.6(18)	67(2)	68(2)	-0.8(18)	15.4(16)	-11.6(17)
C13B	51.6(18)	60(2)	73(2)	-2.1(17)	13.3(16)	6.9(16)
C1B	63(2)	64(2)	64(2)	4.3(17)	12.2(16)	16.2(17)
C13A	66(2)	58(2)	59.7(19)	-6.7(16)	17.4(16)	-3.2(16)

C12A	58.2(18)	57(2)	64(2)	-1.4(16)	21.2(15)	4.9(15)
C14A	57.1(19)	72(2)	59(2)	-6.9(17)	3.8(15)	3.0(17)
C15A	50.8(17)	68(2)	61(2)	-6.8(17)	5.2(14)	9.7(16)
C12B	53.9(18)	55(2)	65(2)	4.0(16)	6.8(15)	2.2(15)
C7B	57.7(19)	58(2)	74(2)	-11.1(17)	6.7(17)	-1.4(16)
C14B	56.8(19)	72(2)	73(2)	-2.3(19)	24.2(17)	6.6(17)
C6B	60(2)	69(2)	81(2)	-2(2)	14.4(18)	-14.2(18)

Table 4 - Bond Lengths for **9**.

Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
S1A	F1A	1.5911(19)		C10B	C11B	1.386(5)
S1A	F4A	1.588(2)		C10B	C15B	1.390(4)
S1A	F5A	1.589(2)		C5A	C6A	1.395(4)
S1A	F2A	1.582(2)		C3B	C4B	1.544(4)
S1A	F3A	1.558(2)		C3B	C2B	1.547(4)
S1A	C2A	1.817(3)		C4B	C9B	1.384(4)
S1B	F4B	1.586(2)		C4B	C5B	1.390(5)
S1B	F2B	1.569(2)		C2A	C3A	1.544(4)
S1B	F1B	1.578(2)		C9A	C8A	1.388(4)
S1B	F5B	1.589(2)		C7A	C8A	1.391(4)
S1B	F3B	1.583(2)		C7A	C6A	1.365(5)
S1B	C2B	1.826(3)		C9B	C8B	1.379(4)
O1A	C3A	1.423(4)		C11A	C12A	1.368(5)
O1A	C1A	1.430(4)		C11B	C12B	1.380(5)
O1B	C3B	1.427(4)		C8B	C7B	1.372(5)
O1B	C1B	1.436(4)		C15B	C14B	1.391(5)
C4A	C5A	1.394(4)		C5B	C6B	1.383(5)
C4A	C3A	1.528(4)		C13B	C12B	1.383(5)
C4A	C9A	1.385(4)		C13B	C14B	1.388(5)
C10A	C3A	1.543(4)		C13A	C12A	1.385(5)
C10A	C11A	1.400(4)		C13A	C14A	1.366(5)
C10A	C15A	1.383(4)		C14A	C15A	1.382(5)
C10B	C3B	1.529(4)		C7B	C6B	1.378(5)

Table 5 - Bond Angles for **9**.								
Atom	**Atom**	**Atom**	**Angle/˚**		**Atom**	**Atom**	**Atom**	**Angle/˚**
F1A	S1A	C2A	88.87(12)		C11B	C10B	C15B	118.3(3)
F4A	S1A	F1A	89.64(12)		C15B	C10B	C3B	121.4(3)
F4A	S1A	F5A	87.06(12)		C4A	C5A	C6A	119.6(3)
F4A	S1A	C2A	92.46(13)		O1B	C3B	C10B	107.0(2)
F5A	S1A	F1A	86.83(11)		O1B	C3B	C4B	110.1(3)
F5A	S1A	C2A	175.68(13)		O1B	C3B	C2B	111.5(2)
F2A	S1A	F1A	89.66(12)		C10B	C3B	C4B	107.6(2)
F2A	S1A	F4A	174.42(13)		C10B	C3B	C2B	112.3(3)
F2A	S1A	F5A	87.37(12)		C4B	C3B	C2B	108.3(2)
F2A	S1A	C2A	93.06(14)		C9B	C4B	C3B	124.4(3)
F3A	S1A	F1A	174.45(12)		C9B	C4B	C5B	117.9(3)
F3A	S1A	F4A	89.80(12)		C5B	C4B	C3B	117.7(3)
F3A	S1A	F5A	87.63(11)		C3A	C2A	S1A	120.3(2)
F3A	S1A	F2A	90.36(13)		O1A	C3A	C4A	106.2(2)
F3A	S1A	C2A	96.67(12)		O1A	C3A	C10A	110.1(3)
F4B	S1B	F5B	87.19(12)		O1A	C3A	C2A	111.8(2)
F4B	S1B	C2B	88.87(13)		C4A	C3A	C10A	106.8(2)
F2B	S1B	F4B	174.78(13)		C4A	C3A	C2A	112.9(3)
F2B	S1B	F1B	89.65(13)		C10A	C3A	C2A	108.9(2)
F2B	S1B	F5B	87.59(12)		C4A	C9A	C8A	121.1(3)
F2B	S1B	F3B	90.07(13)		C6A	C7A	C8A	119.6(3)
F2B	S1B	C2B	96.35(13)		C8B	C9B	C4B	121.1(3)
F1B	S1B	F4B	90.08(13)		C3B	C2B	S1B	120.3(2)
F1B	S1B	F5B	87.61(13)		C9A	C8A	C7A	119.6(3)
F1B	S1B	F3B	174.89(13)		C12A	C11A	C10A	121.3(3)
F1B	S1B	C2B	92.82(15)		C12B	C11B	C10B	121.3(3)
F5B	S1B	C2B	176.04(13)		C7B	C8B	C9B	120.3(3)
F3B	S1B	F4B	89.74(14)		C10B	C15B	C14B	120.9(3)
F3B	S1B	F5B	87.28(13)		C7A	C6A	C5A	121.2(3)
F3B	S1B	C2B	92.28(14)		C6B	C5B	C4B	121.1(3)
C3A	O1A	C1A	116.4(2)		C12B	C13B	C14B	119.5(3)
C3B	O1B	C1B	116.5(2)		C14A	C13A	C12A	119.1(3)
C5A	C4A	C3A	120.9(3)		C11A	C12A	C13A	120.2(3)
C9A	C4A	C5A	118.9(3)		C13A	C14A	C15A	120.9(3)
C9A	C4A	C3A	120.1(3)		C14A	C15A	C10A	120.9(3)
C11A	C10A	C3A	116.9(3)		C11B	C12B	C13B	120.2(3)
C15A	C10A	C3A	125.5(3)		C8B	C7B	C6B	119.6(3)
C15A	C10A	C11A	117.5(3)		C13B	C14B	C15B	119.9(3)
C11B	C10B	C3B	120.2(3)		C7B	C6B	C5B	119.9(3)

Table 6 - Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **9**.				
Atom	***x***	***y***	***z***	**U(eq)**
H5A	6966.44	2700.05	3937.5	61
H2AA	10900.93	1819.05	5246.58	60
H2AB	11486.63	2687.4	4956.12	60
H9A	8896.39	1276.16	5553.71	63
H1AA	9589.04	4541.89	4063.26	85
H1AB	10830.91	3845.13	4160.85	85
H1AC	10332.57	4248.93	4813.17	85
H7A	5056.14	590.98	4583.17	67
H9B	5460.41	2549.2	503.66	67
H2BA	6147.54	3373.81	1261.72	65
H2BB	7085.98	2642.18	1695.2	65
H8A	7003.55	326.29	5435.79	65
H11A	7665.86	3869.33	5215.34	65
H11B	3900.77	3821.33	938.77	66
H8B	4677.1	1546.23	-360.2	72
H15B	3395.08	2821.54	2745.44	68
H6A	5051.99	1764.52	3844.84	68
H5B	3589.91	1146.76	1781.06	75
H13B	796.03	4709.81	1812.29	74
H1BA	6237.94	1119.84	2113.01	96
H1BB	6200.46	1053.8	2908.33	96
H1BC	7250.93	1718.74	2649.43	96
H13A	9245.14	4280.92	7202.67	73
H12A	7561.63	4562.23	6231.96	70
H14A	10993.22	3281.86	7138.97	77
H15A	11127.47	2593.35	6117.24	73
H12B	2032.97	4755.39	926.24	70
H7B	3398.43	322.97	-153.52	77
H14B	1497.59	3747.89	2730.79	78
H6B	2842.15	127.97	918.88	84

Crystal Data for $C_{15}H_{15}F_5OS$ (*M* =338.33 g/mol)

Monoclinic, space group $P2_1/c$ (no. 14), *a* = 9.865(2) Å, *b* = 15.146(3) Å, *c* = 19.988(4) Å, *β* = 101.03(3)°, *V* = 2931.3(11) Å^3, *Z* = 8, *T* = 200 K, μ(MoKα) = 0.274 mm^{-1}, *Dcalc* = 1.533 g/cm^3, 15063 reflections measured (3.398° ≤ 2Θ ≤ 51.996°), 5756 unique (R_{int} = 0.0758, R_{sigma} = 0.0605) which were used in all calculations. The final R_1 was 0.0603 (I > 2σ(I)) and wR_2 was 0.1811 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso
   At 1.2 times of:
   All C(H) groups, All C(H,H) groups
   At 1.5 times of:
   All C(H,H,H) groups

2. *2.a Secondary CH2 refined with riding coordinates:*
   C2A(H2AA,H2AB), C2B(H2BA,H2BB)

   2.b Aromatic/amide H refined with riding coordinates:
   C5A(H5A), C9A(H9A), C7A(H7A), C9B(H9B), C8A(H8A), C11A(H11A), C11B(H11B),
   C8B(H8B), C15B(H15B), C6A(H6A), C5B(H5B), C13B(H13B), C13A(H13A), C12A(H12A),
   C14A(H14A), C15A(H15A), C12B(H12B), C7B(H7B), C14B(H14B), C6B(H6B)

   2.c Idealised Me refined as rotating group:
   C1A(H1AA,H1AB,H1AC), C1B(H1BA,H1BB,H1BC)

Stability measurements of 8 and 9

DSC-Measurements of **8** and **9**

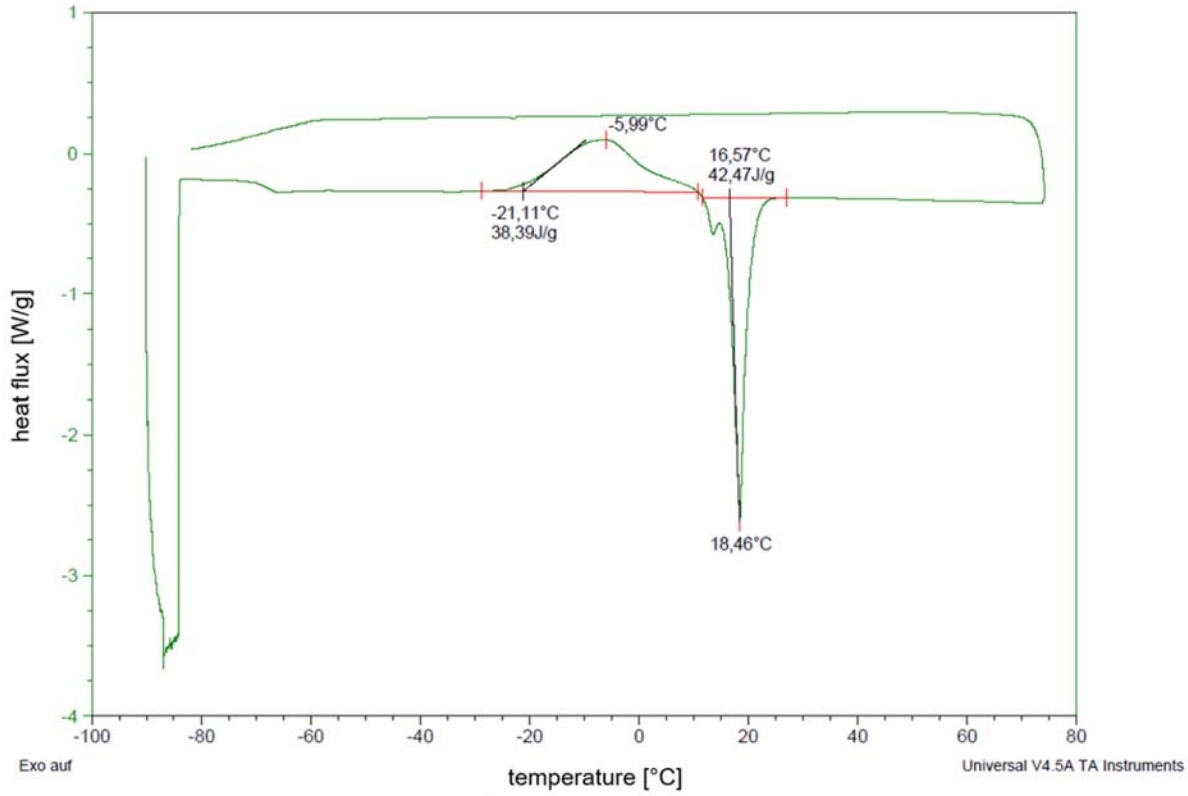


Fig. S158

DSC measurement of **8** in the range of -90°C – 70°C. The feature at -6°C could not be assigned. However, the assignment to a decomposition reaction was excluded due to the storability of the neat liquid **8** without any indication of decomposition at 2°C in the fridge over weeks or for hours at ambient temperature. Further a solution of the product could be heated to 75°C for 60 min under air without any sign of decomposition.

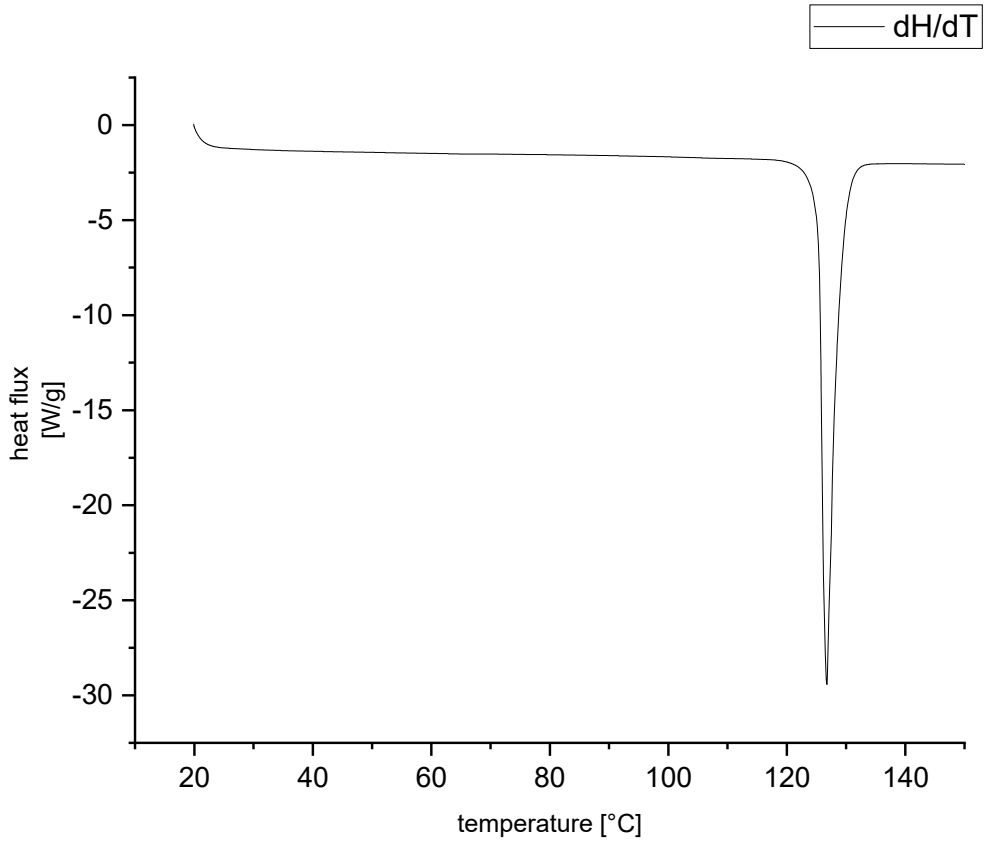


Fig. S159
DSC measurement of **9** in the range of 20°C – 150°C.

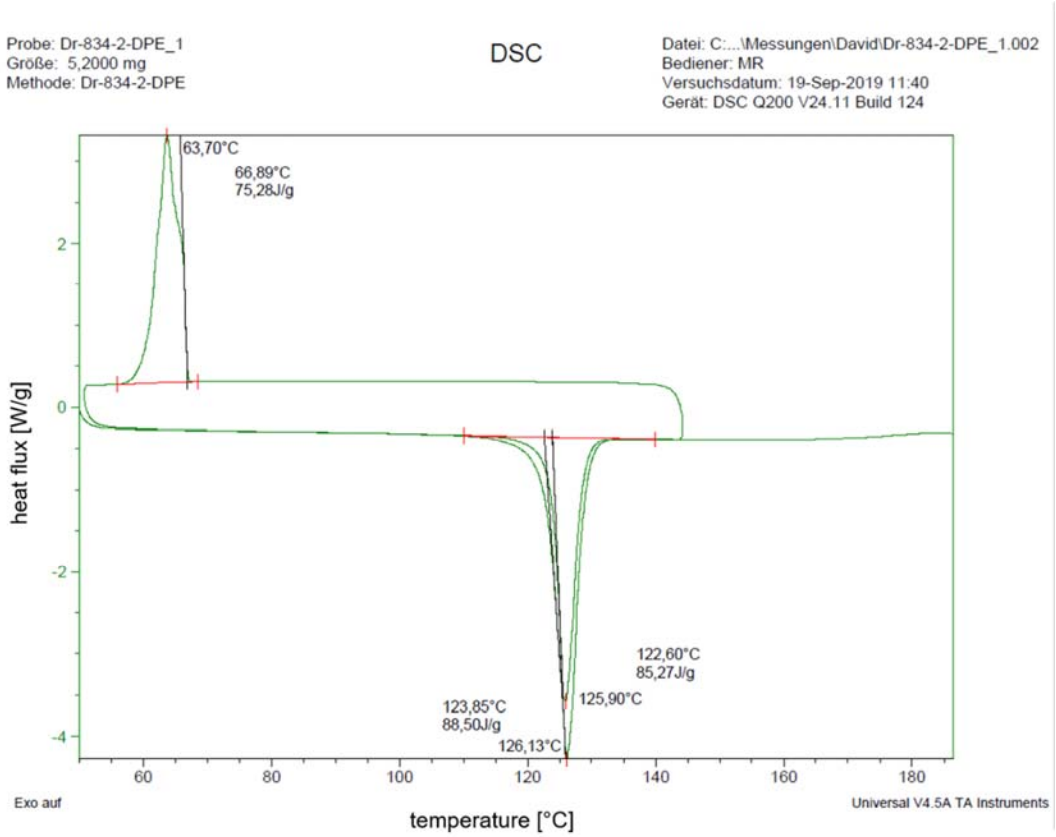


Fig. S160
DSC reversibility measurement of **9** in the range of 20°C – 150°C and final heating to 190°C.

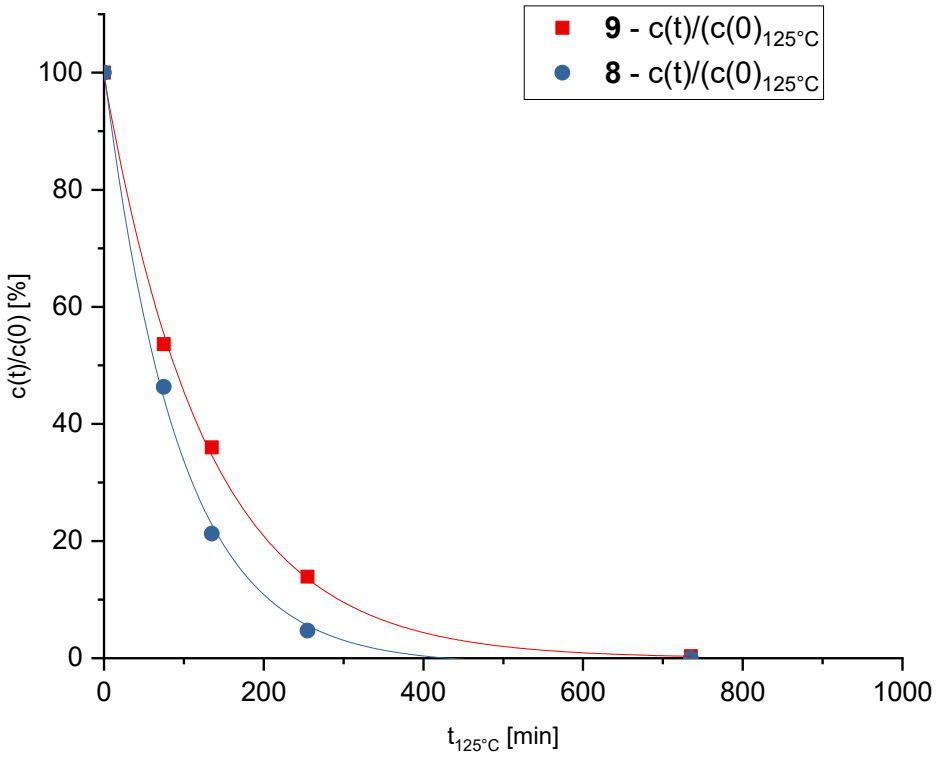


Fig. S161
Kinetics of the degradation of **8** and **9** under heating (125°C in DMSO) under ambient atmosphere.

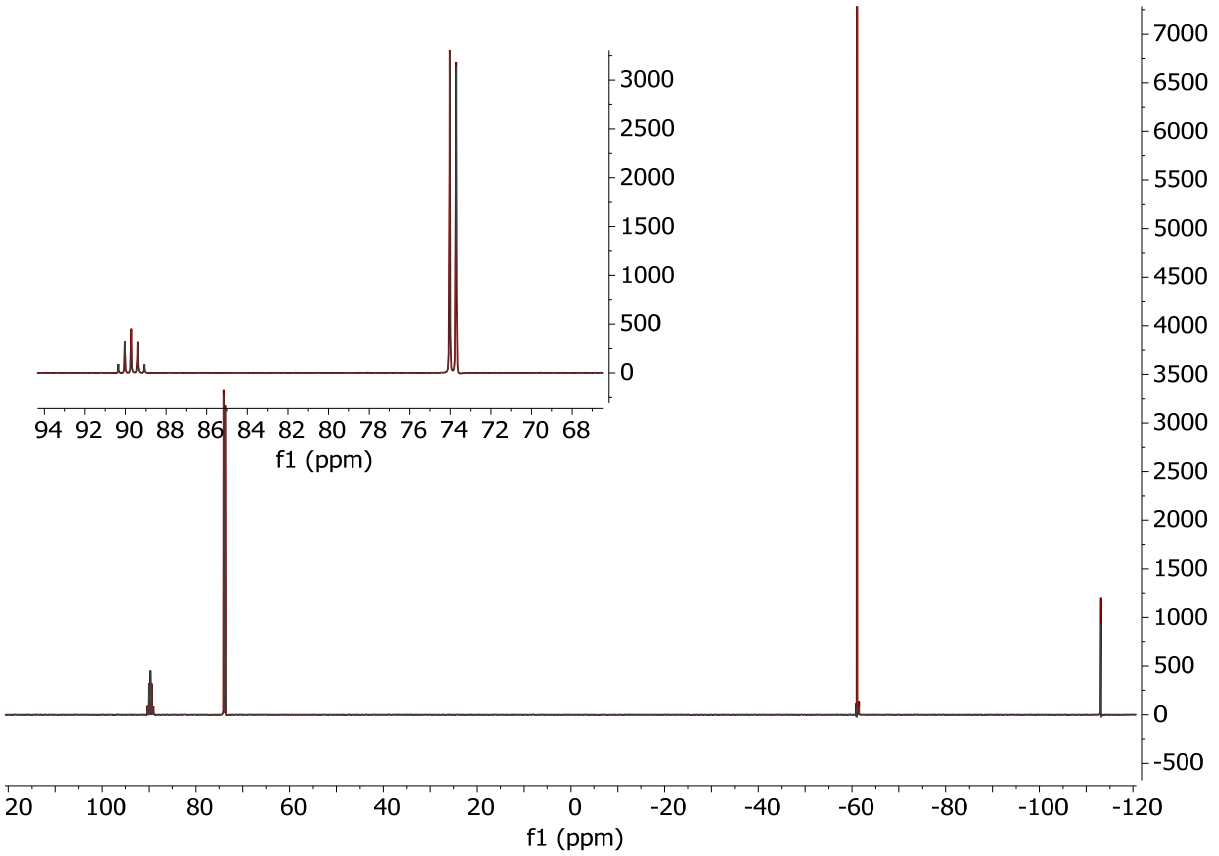


Fig. S162

^{19}F-NMR investigation of photostability of a solution of **9** (24 mM in DMSO) over 15h under irradiation at 365 nm at 20°C under air. Red: ^{19}F-NMR spectrum at t = 0. Green: ^{19}F-NMR Spectrum at t = 15h. Benzotrifluoride as well as fluorobenzene have been added as internal standard.

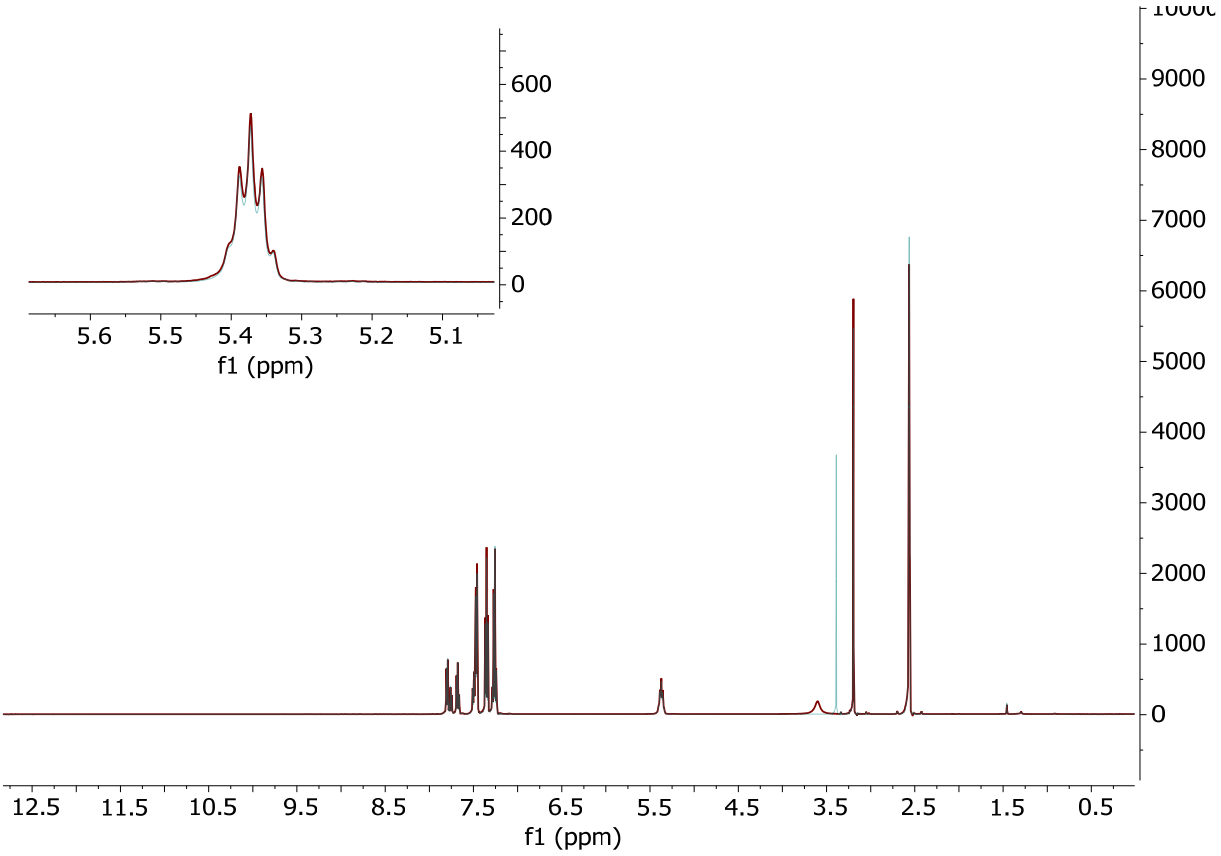


Fig. S163

^{1}H-NMR investigation of photostability of a solution of **9** (24 mM in DMSO) over 62h under irradiation at 365 nm at 20°C under air. Green: ^{1}H-NMR Spectrum at t = 62h. Red: ^{1}H-NMR spectrum at t = 0. Benzotrifluoride as well as fluorobenzene have been added as internal standard.

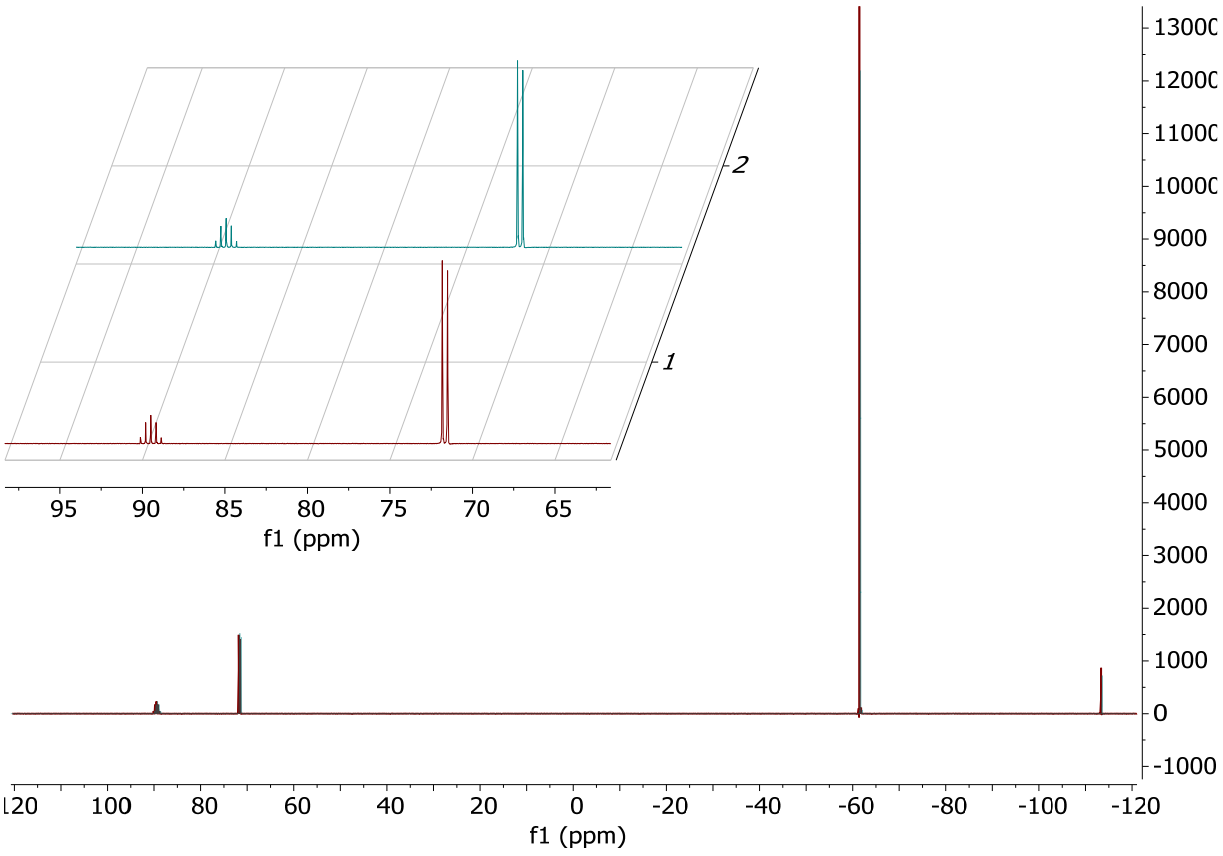


Fig. S164

^{19}F-NMR investigation of photostability of a solution of **8** (24 mM in DMSO) after 15h under irradiation at 365 nm at 20°C under air. Red: ^{19}F-NMR spectrum at t = 0. Green: ^{19}F-NMR Spectrum at t = 15h. Benzotrifluoride as well as fluorobenzene have been added as internal standard.

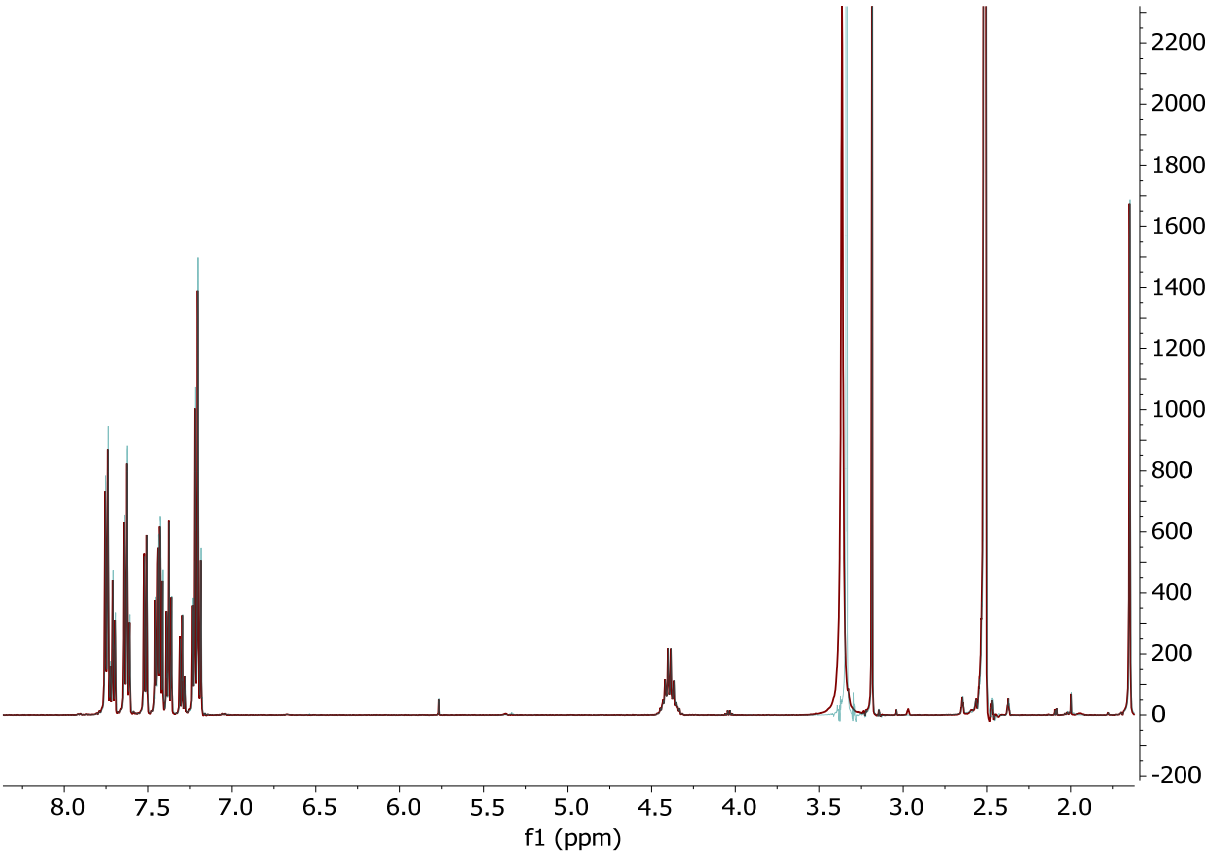
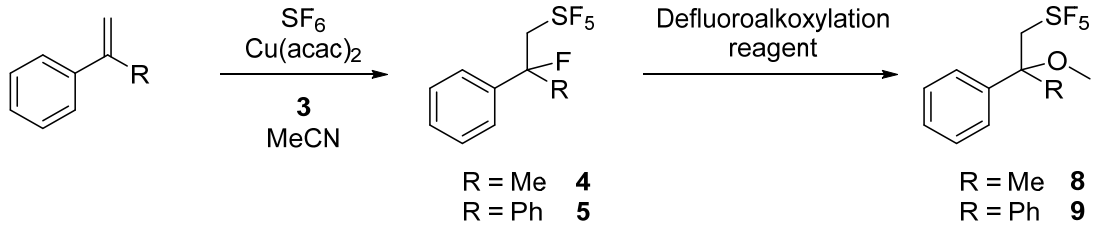


Fig. S165

^{1}H-NMR investigation of photostability of a solution of **8** (24 mM in DMSO) over 62h under irradiation at 365 nm at 20°C. Red: ^{1}H-NMR spectrum at t = 0. Green: ^{1}H-NMR Spectrum at t = 62h. Benzotrifluoride as well as fluorobenzene have been added as internal standard.

Two-step reaction procedure

While investigating the alkoxylation reaction we also investigated the idea of a two-step access to the compounds **8** and **9**. Therefore the addition products **4** and **5** have been prepared according to the previously reported procedure.[S7] The products have been subjected to the reaction with different alkoxy salts in THF-d^8 as well as to BEt_3 in the presence of MeOH in MeCN-d^3



General reaction using metal methoxide and substrate **4**:

In a borosilicate NMR tube 100 µmol (38.9 eq., 196 mM) of the metal hydride was suspended in 350 µL THF-d^8. Then 10 µL (246 µmol, 95.7 eq., 482 mM) of anhydrous MeOH were added to the reaction vessel and the mixture was vigorously shaken for 1 min while hydrogen evolution was observed. After 5 min 150 µL (2.57 µmol, 5.03 mM, 1.00 eq.) of a stock solution of **4** (17.1 mM in pentanes) were added to the reaction mixture. In case of CaH_2 the base was reacted for 18 h under inert conditions with the MeOH before the substrate was added to ensure the kinetically hampered formation of the alcoholate. The reaction mixture was vigorously shaken for 1 min and then monitored by ^1H and ^{19}F-NMR.

Procedure using triethylborane and substrate **4**:

In a borosilicate NMR tube 150 µL (2.57 µmol, 4.85 mM, 1.00 eq.) of a stock solution of **4** (17.1 mM in pentanes) have been suspended in 350 µL MeCN-d^3. Then 10 µL

(246 µmol, 95.7 eq., 482 mM) of anhydrous MeOH were added to the reaction vessel and the mixture was vigorously shaken for 1 min. Finally 20.0 µmol (20.0 µmol, 37.7 mM, 7.78 eq.) of triethylborane (1 M in hexanes) was added to the reaction mixture. The reaction mixture was vigorously shaken for 1 min and then monitored by ^{1}H and ^{19}F-NMR.

General reaction using metal methoxide and substrate **5**:

In a borosilicate NMR tube 100 µmol (22.6 eq., 244 mM) of the metal hydride was suspended in 350 µL THF-d^8. Then 10 µL (246 µmol, 55.6 eq., 600 mM) of anhydrous MeOH were added to the reaction vessel and the mixture was vigorously shaken for 1 min while hydrogen evolution was observed. After 5 min 50.0 µL (4.43 µmol, 10.8 mM, 1.00 eq.) of a stock solution (88.6 mM in cyclohexane) of **5** were added to the reaction mixture. In case of CaH_2 the base was reacted for 18 h under inert conditions with the MeOH before the substrate was added to ensure the kinetically hampered formation of the alcoholate. The reaction mixture was vigorously shaken for 1 min and then monitored by ^{1}H and ^{19}F-NMR.

Procedure using triethylborane and substrate **5**:

In a borosilicate NMR tube 50.0 µL (4.43 µmol, 10.3 mM, 1.00 eq.) of a stock solution of **5** (88.6 mM in cyclohexane) have been suspended in 350 µL MeCN-d^3. Then 10.0 µL (246 µmol, 55.5 eq., 572 mM) of anhydrous MeOH were added to the reaction vessel and the mixture was vigorously shaken for 1 min. Finally, 20.0 µL (20.0 µmol, 46.5 mM, 4.51 eq.) of triethylborane (1 M in hexanes) was added to the reaction mixture. The reaction mixture was vigorously shaken for 1 min and then monitored by ^{1}H and ^{19}F-NMR.

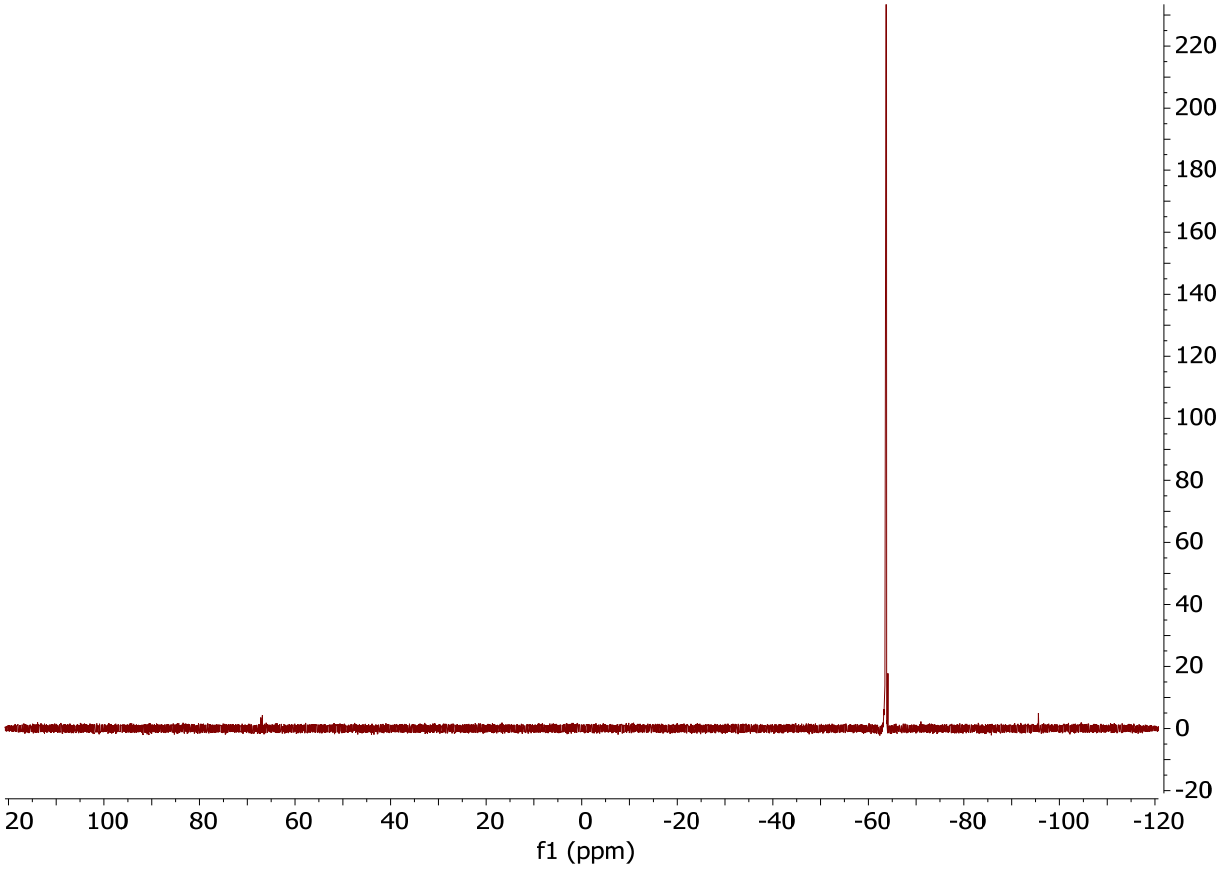


Fig. S166

^{19}F-NMR spectra of the reaction of **4** with KOMe in THF-d^{8} after 15 min. Full decomposition of the pentafluorosulfanyl substituent was indicated after 15 min.

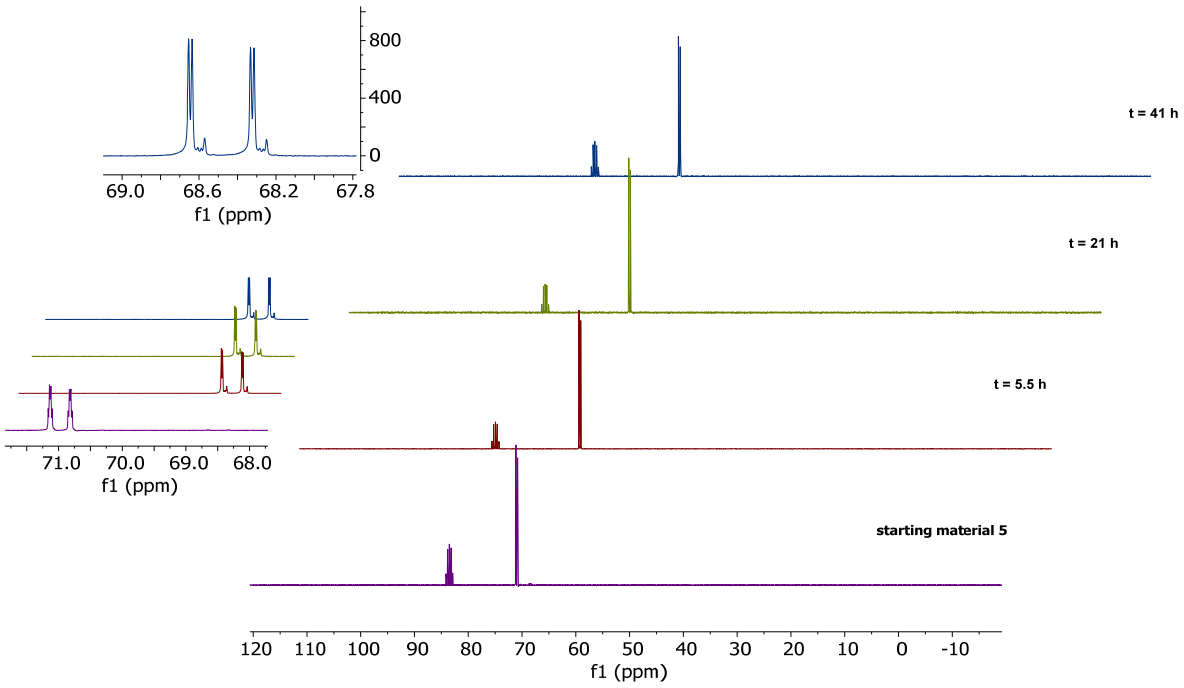


Fig. S167

Time resolved ^{19}F-NMR spectra of the reaction of **5** with KOMe in THF-d^{8}.

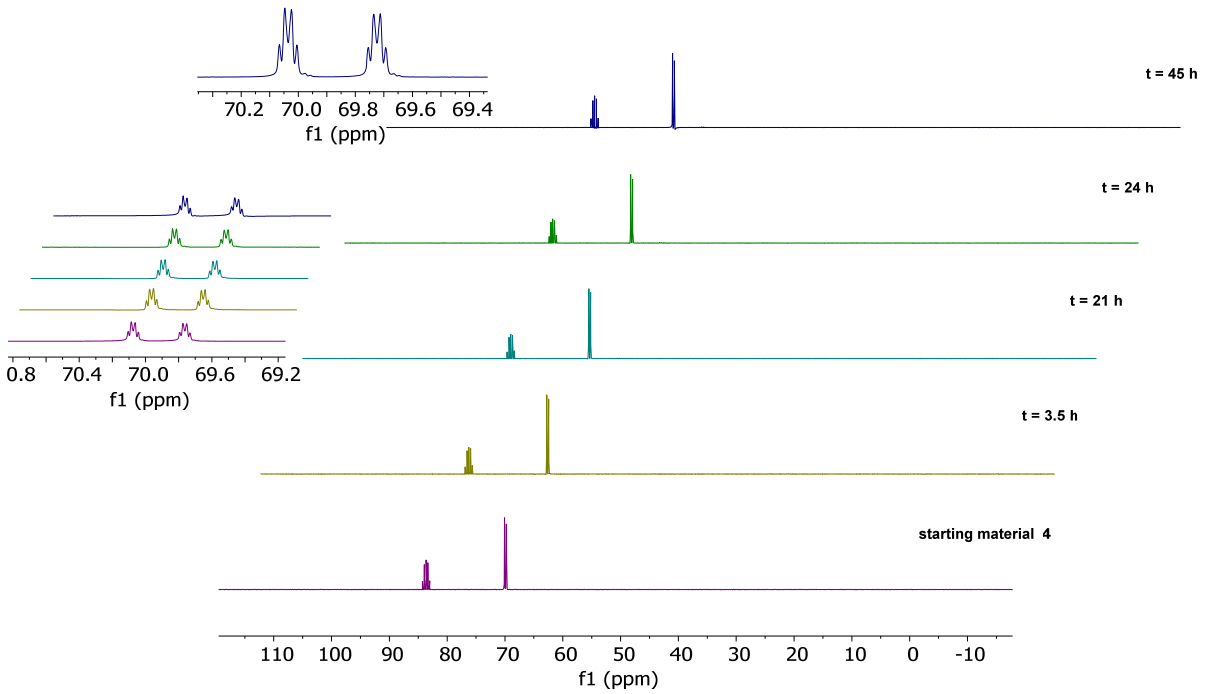


Fig. S168

Time resolved ^{19}F-NMR spectra of the reaction of **4** with LiOMe in THF-d^{8}.

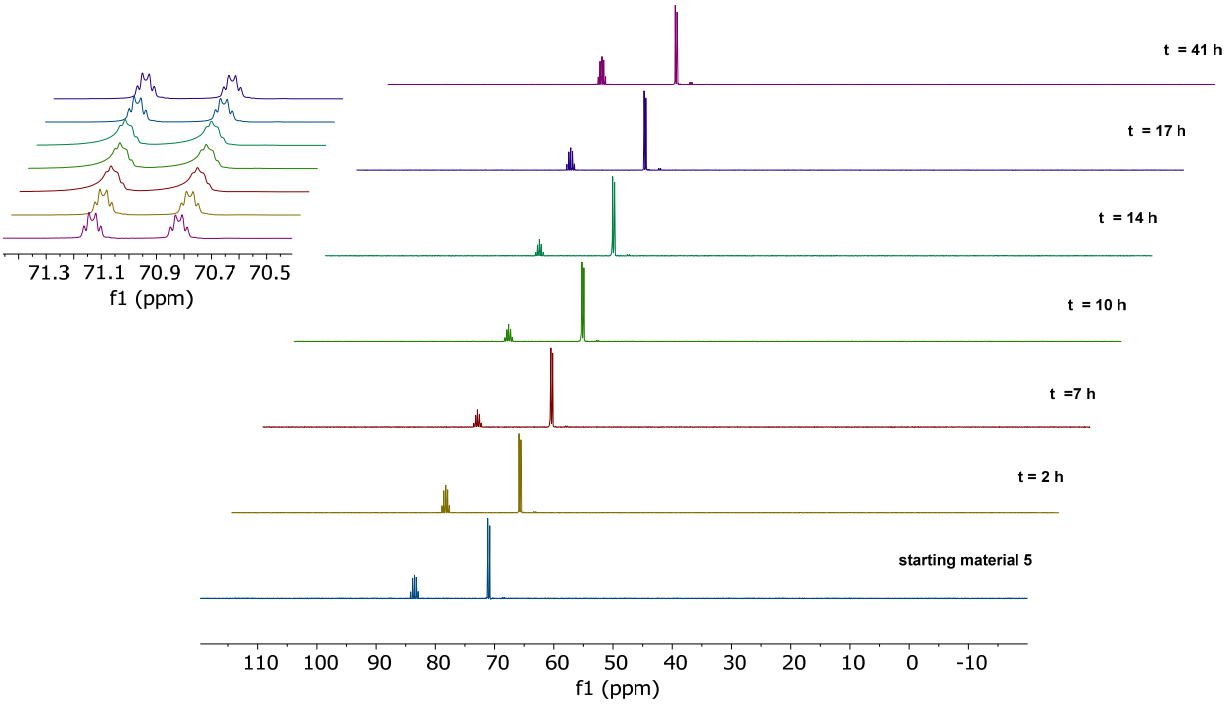


Fig. S169

Time resolved ^{19}F-NMR spectra of the reaction of **5** with LiOMe in THF-d^{8}.

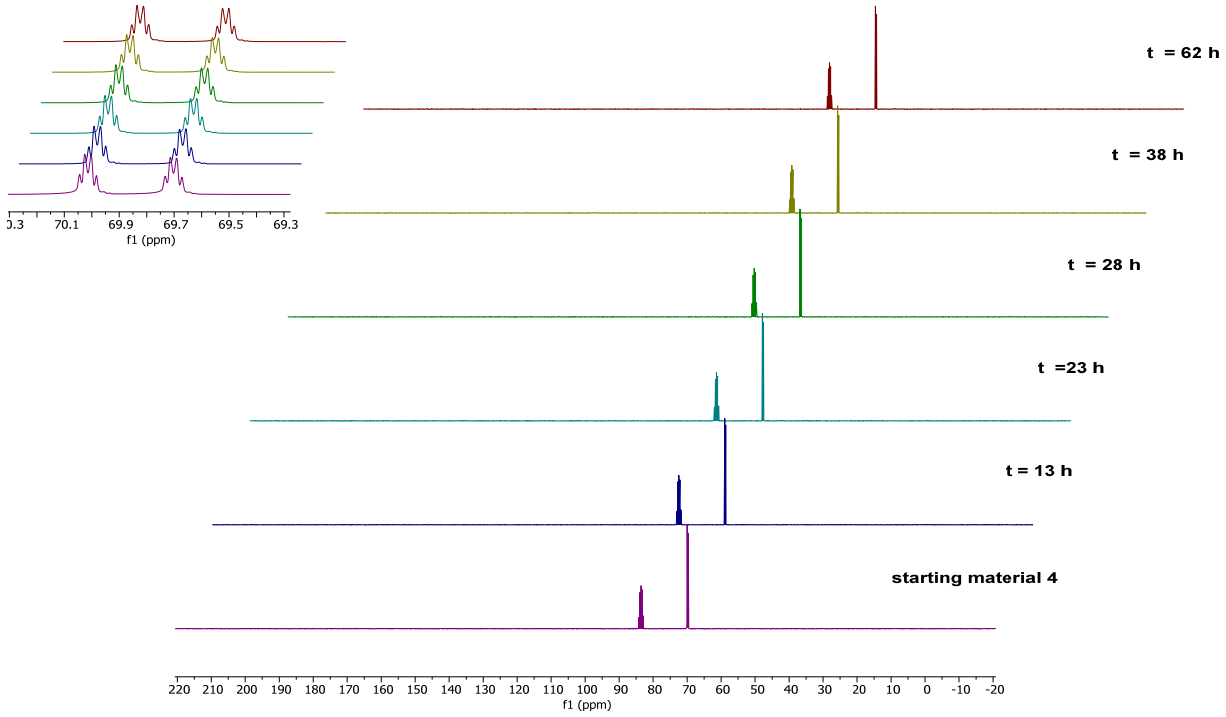


Fig. S170

Time resolved ^{19}F-NMR spectra of the reaction of **4** with CaH_2 in THF-d^8.

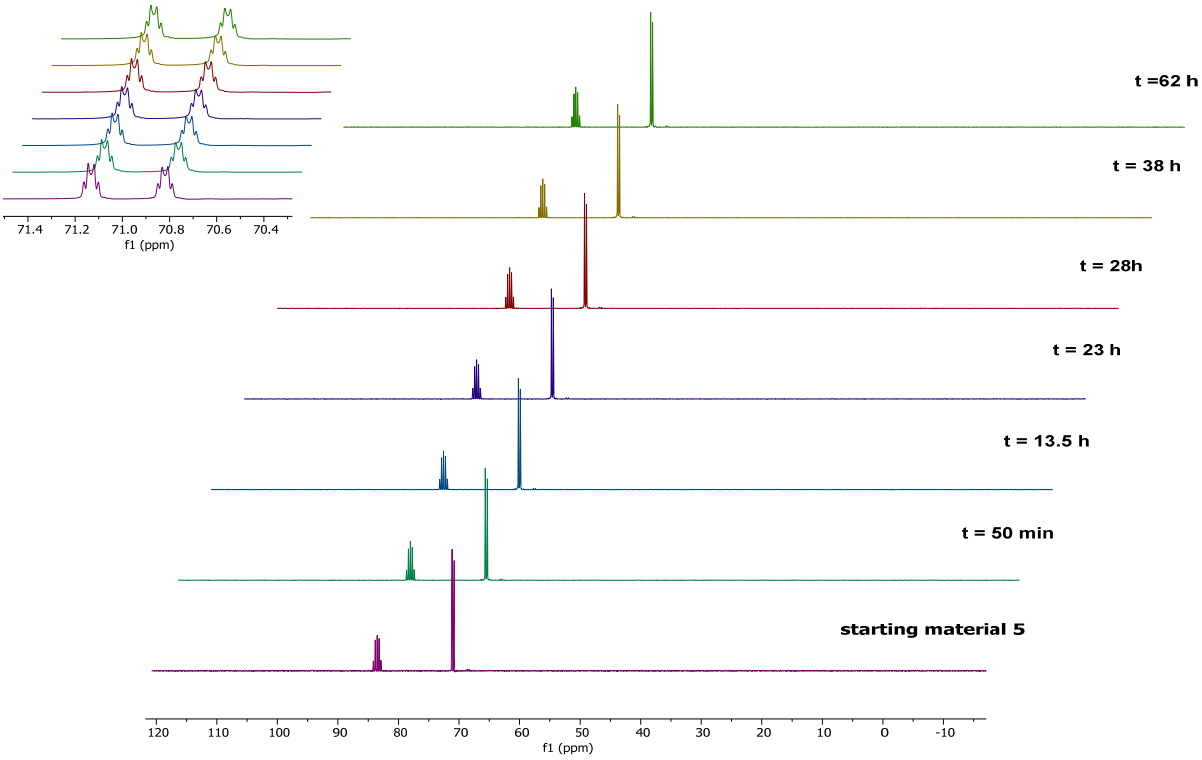


Fig. S171

Time resolved ^{19}F-NMR spectra of the reaction of **5** with CaH_2 in THF-d^8.

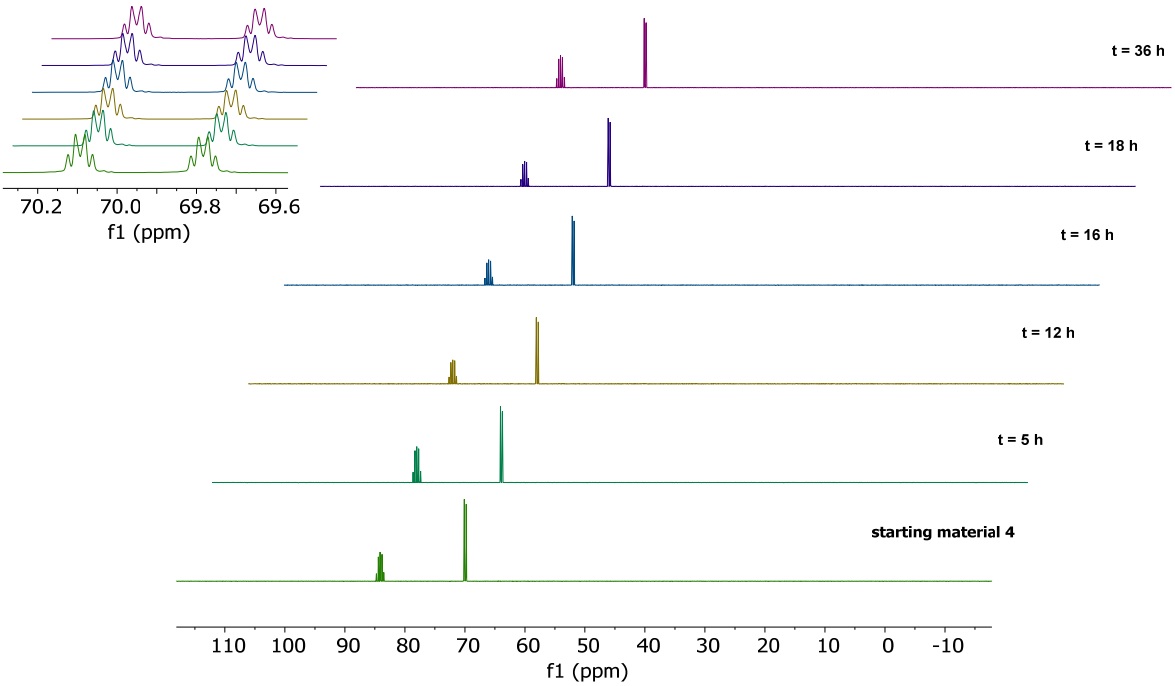


Fig. S172

Time resolved ^{19}F-NMR spectra of the reaction of **4** with BEt_3 and MeOH in MeCN-d^3.

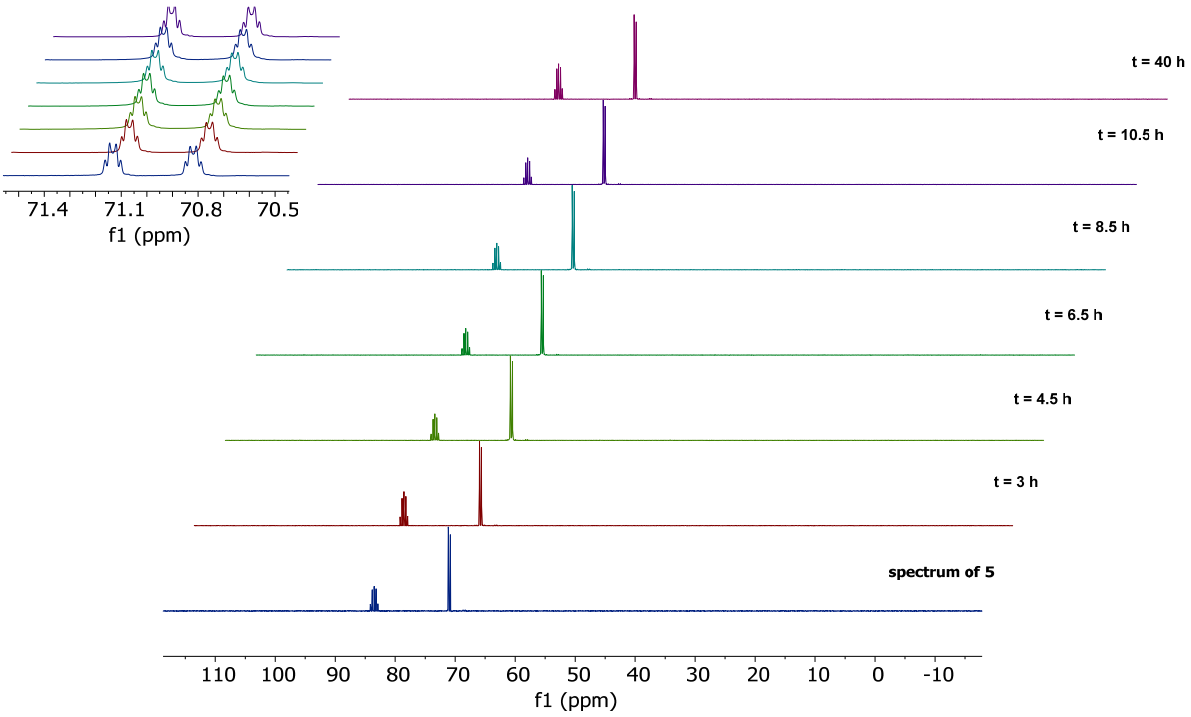


Fig. S173
Time resolved ^{19}F-NMR spectra of the reaction of **5** with BEt_3 and MeOH in MeCN-d^3.

References:

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