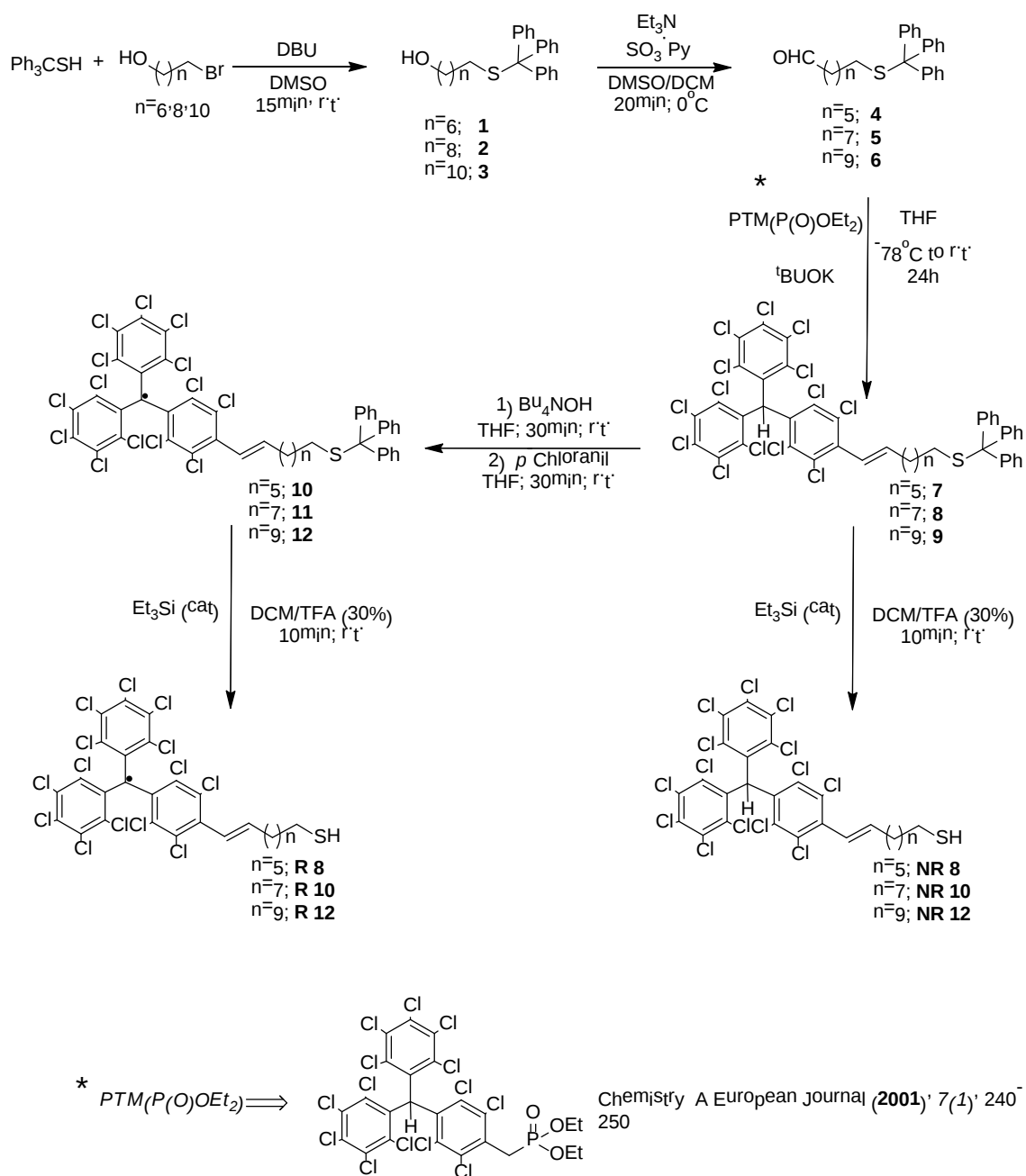
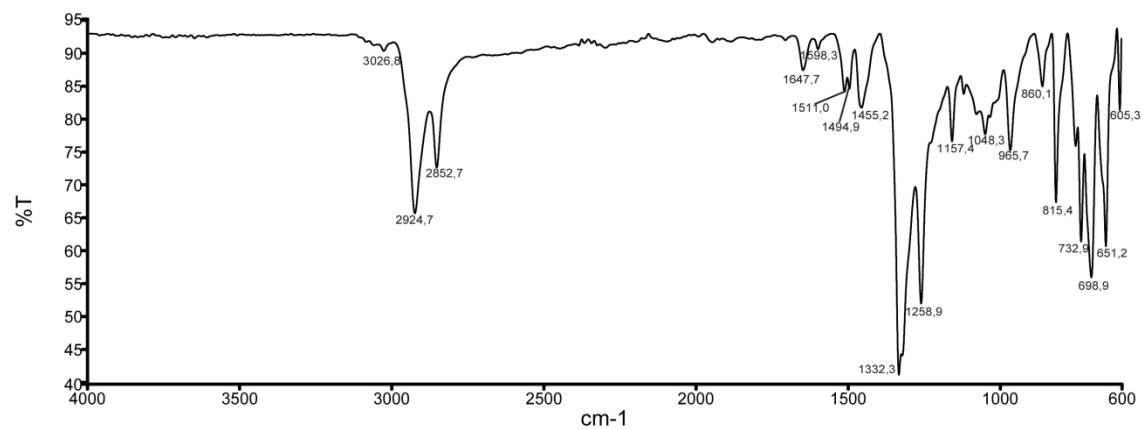
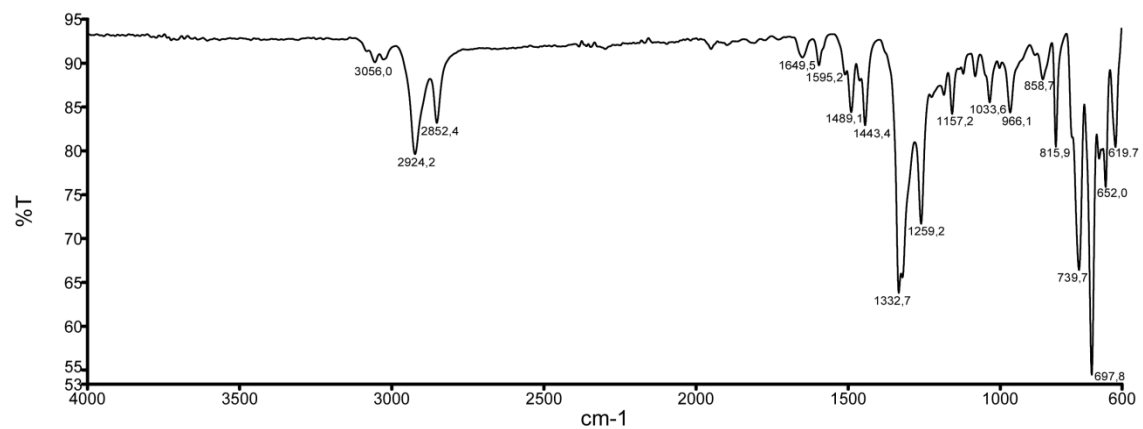




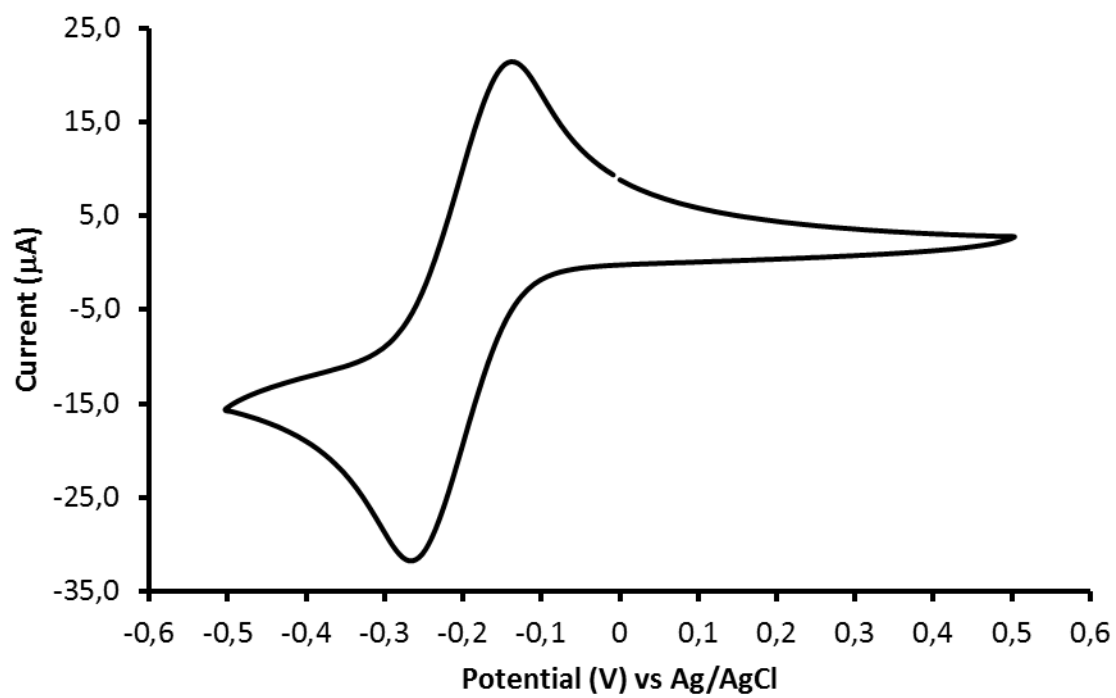
Supplementary Figure 1. General procedure for the synthesis of PTMC_xStrityl and PTMC_xSH.



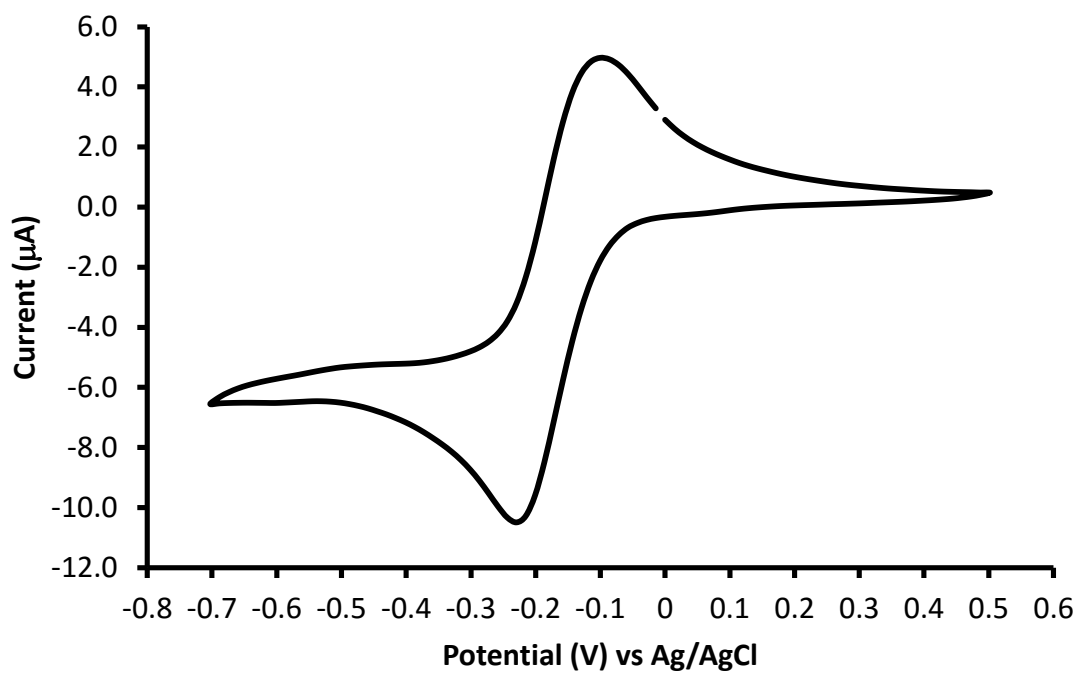
Supplementary Figure 2. IR-ATR spectrum of compound **R10**.



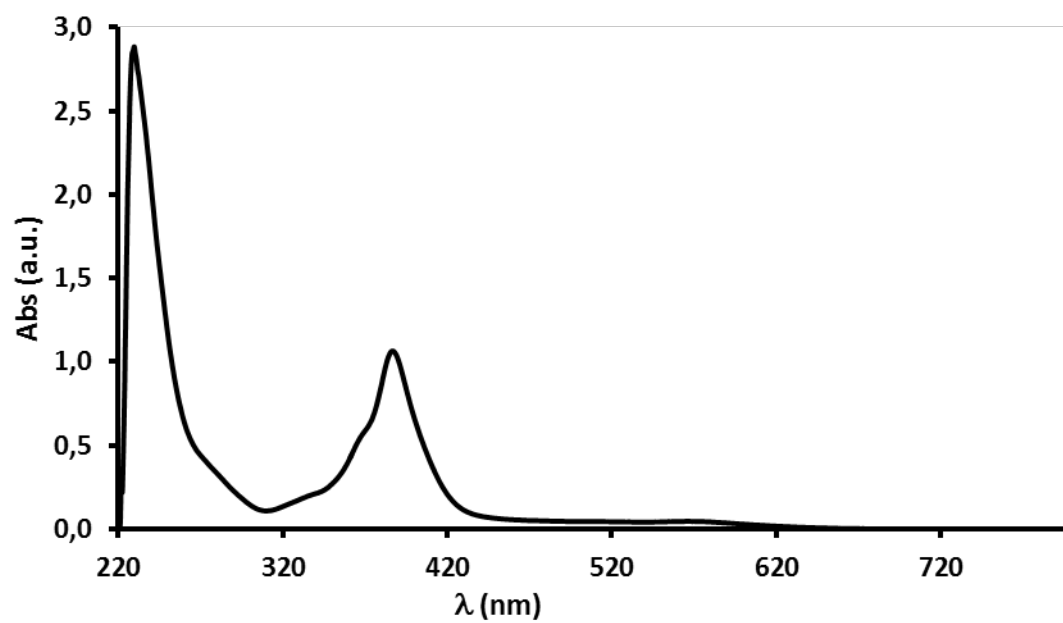
Supplementary Figure 3. IR-ATR spectrum of compound **11**.



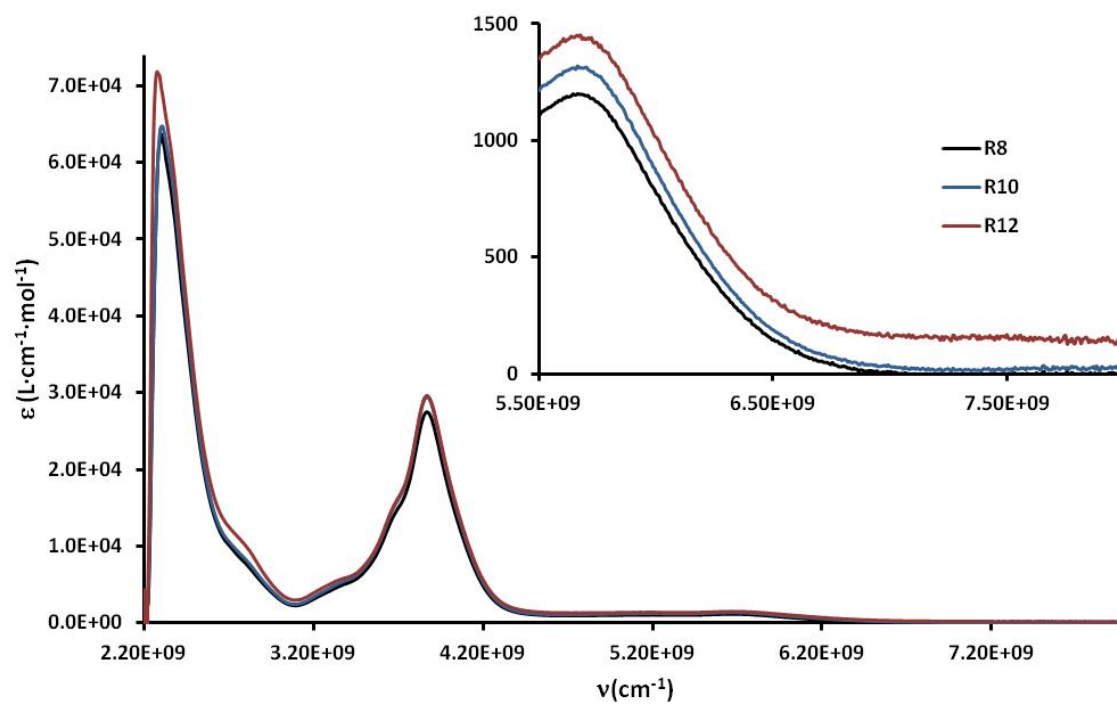
Supplementary Figure 4. Cyclic voltammogram of compound **R8**.



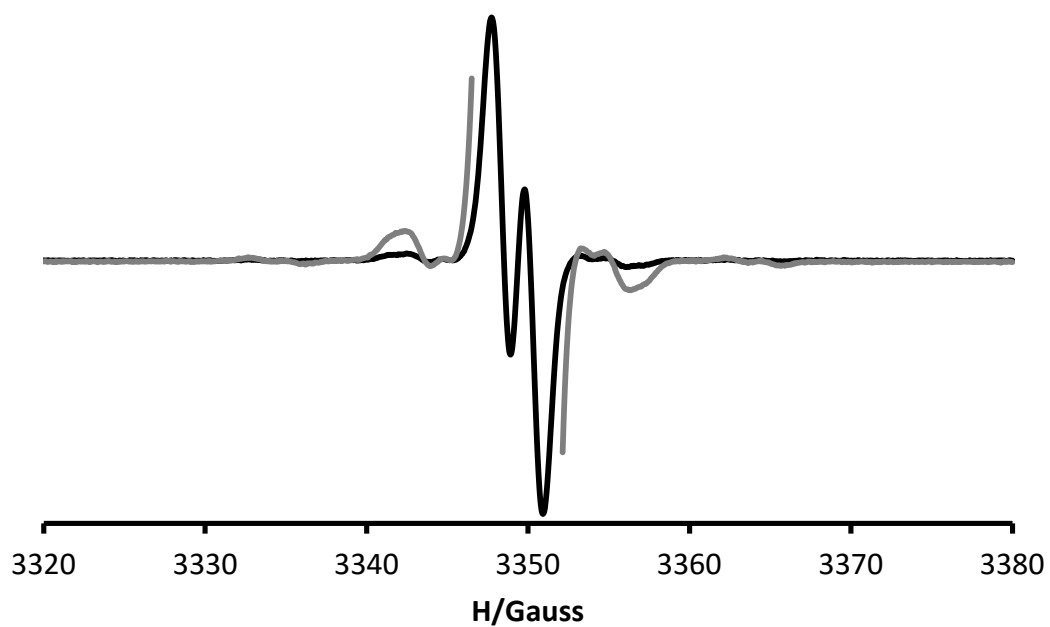
Supplementary Figure 5. Cyclic voltammogram of compound **11**.



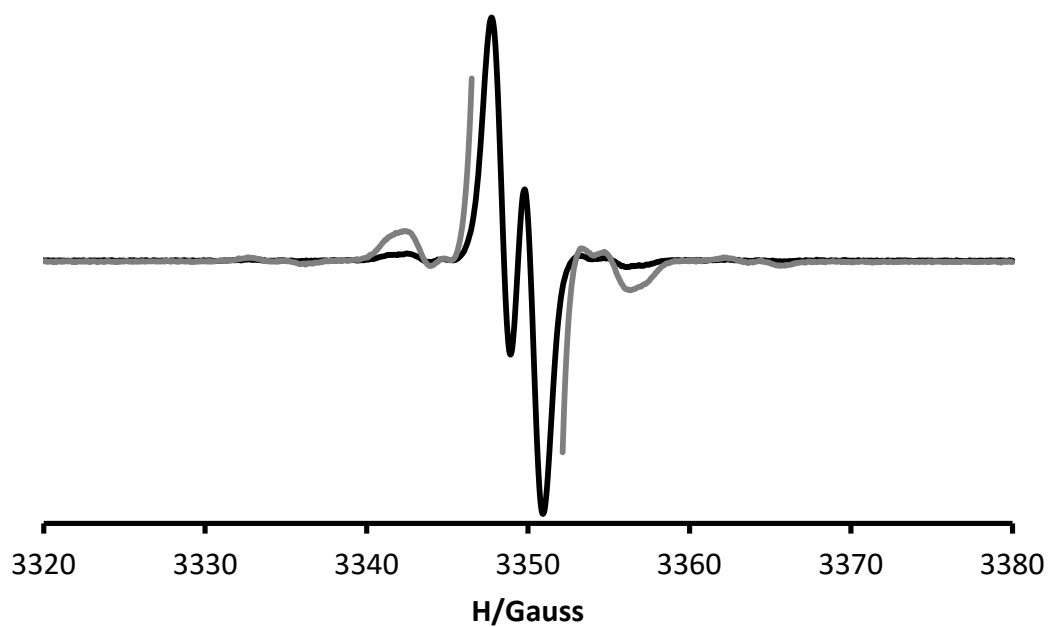
Supplementary Figure 6. UV-Vis spectrum of compound **10** in CH_2Cl_2 solution.



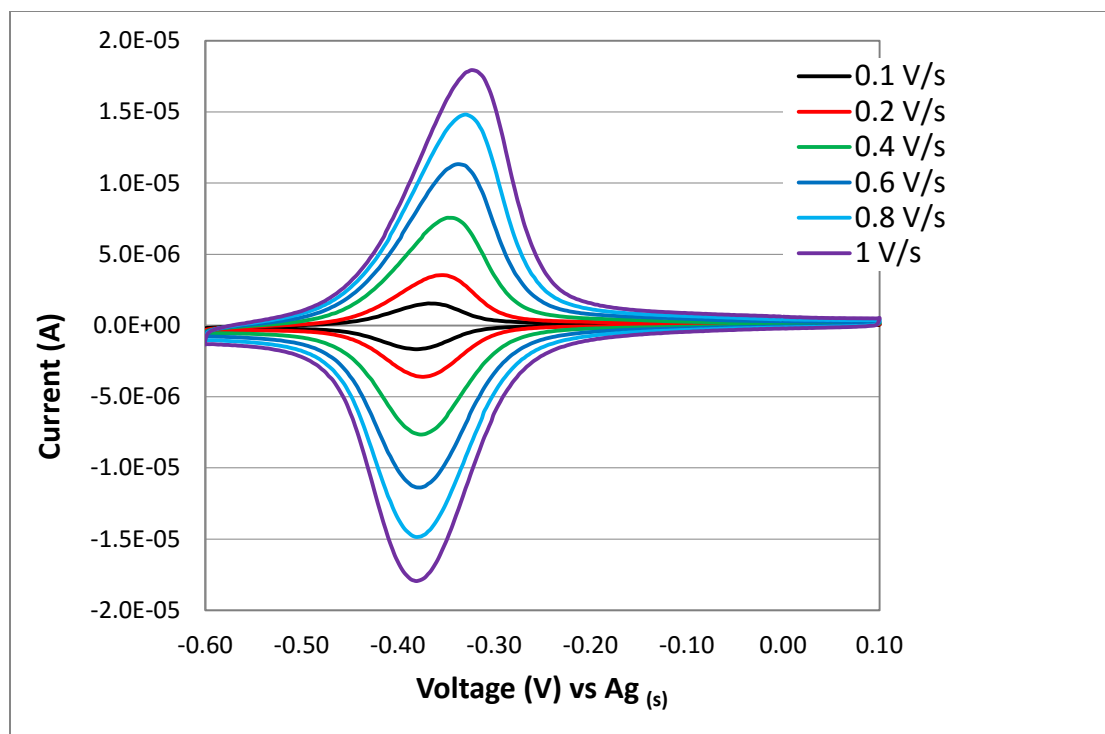
Supplementary Figure 7. UV-Vis spectra of radicals **R8**, **R10** and **R12** in CH_2Cl_2 .



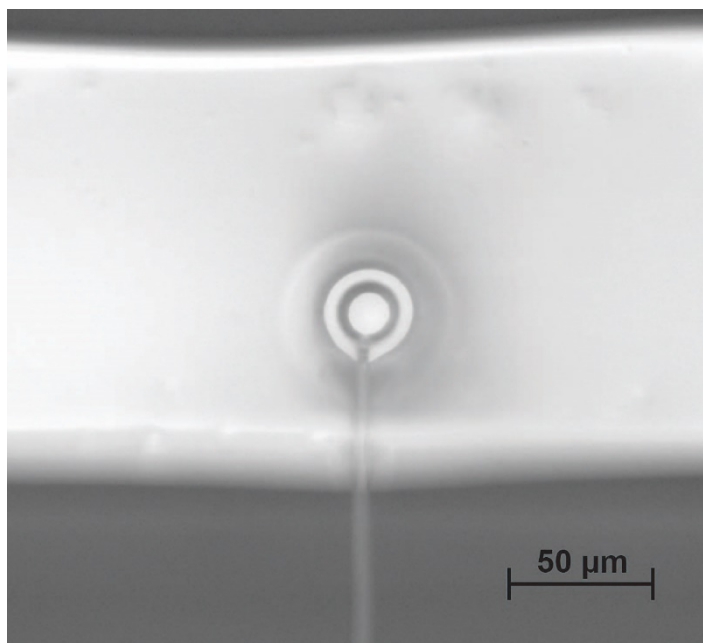
Supplementary Figure 8. EPR spectrum of compound **R10** in CH_2Cl_2 solution, at room temperature.



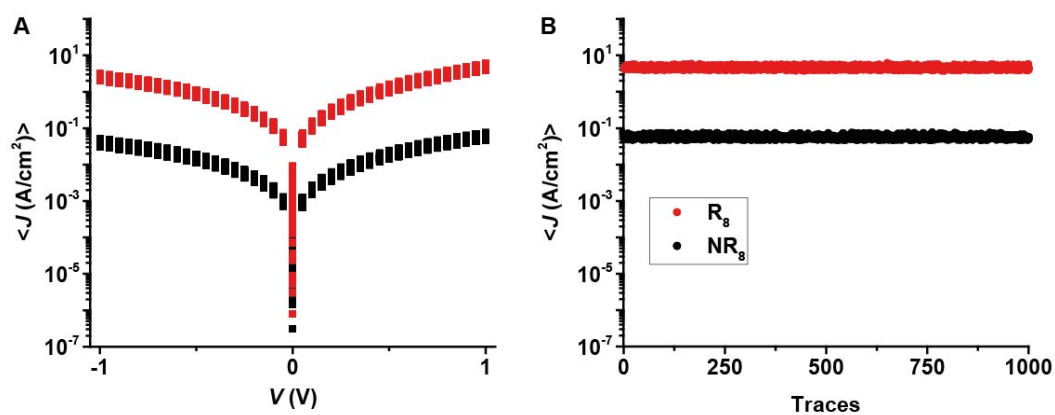
Supplementary Figure 9. EPR spectrum of compound **10** in CH_2Cl_2 solution, at room temperature.



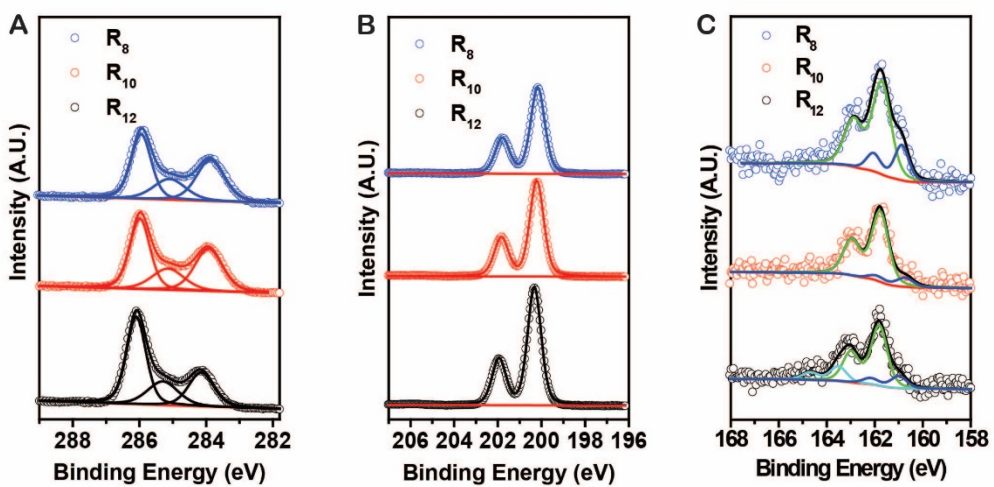
Supplementary Figure 10. Cyclic voltammogram of the R_{10} SAM on Au (111)/mica.



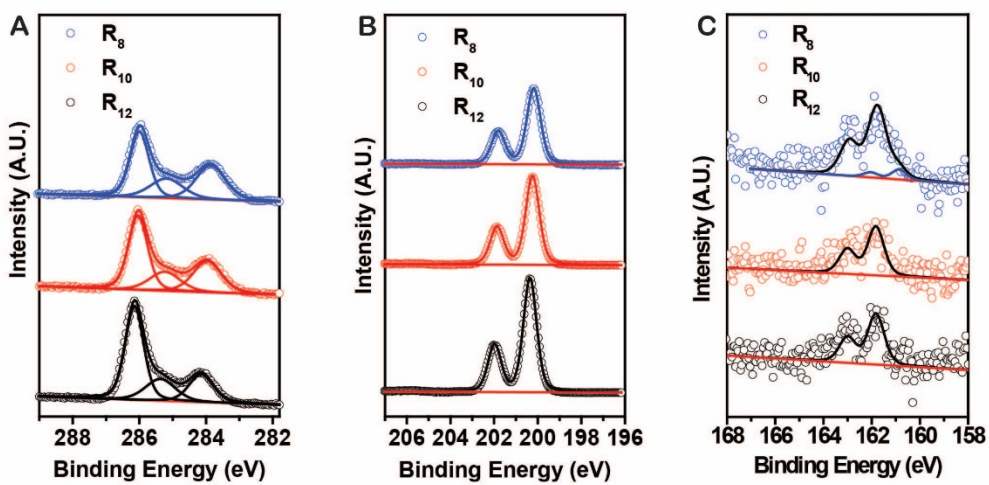
Supplementary Figure 11. Optical microscope image of the through-hole filled with Ga₂O₃/EGaIn.



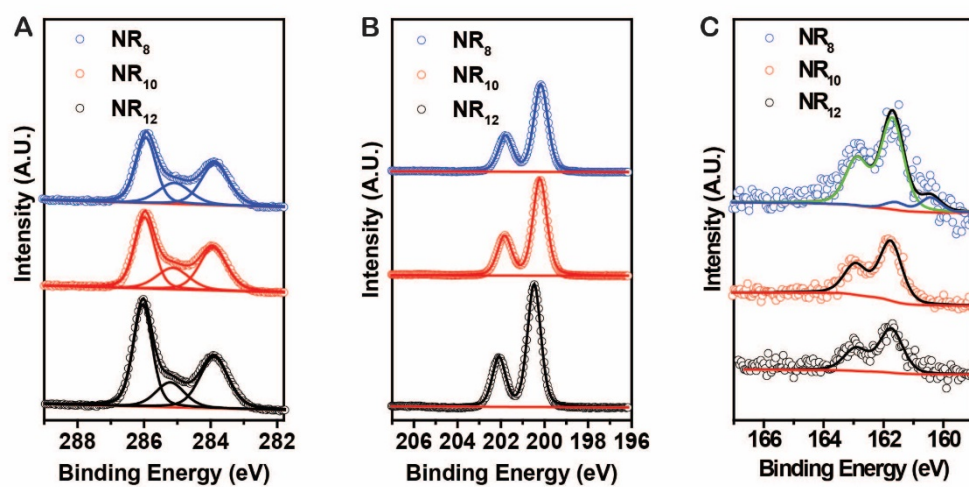
Supplementary Figure 12. A) The 1000 $J(V)$ traces of $\text{Au}^{\text{TS}}\text{-SC}_8\text{PTM}^{\text{R/NR}}//\text{GaO}_x^{\text{cond}}/\text{EGaIn}$ junctions. B) The values of J as a function of trace number with R_8 and NR_8 SAMs at +1.0 V.



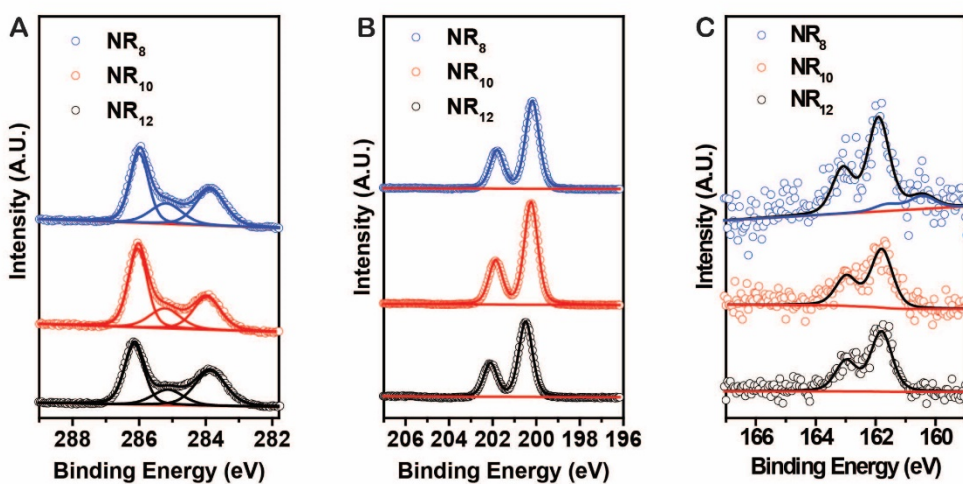
Supplementary Figure 13. The C 1s (A), Cl 2p (B), and S 2p (C) spectra of Au^{TS}-SC_nPTM^R (n= 8, 10, 12; R₈, R₁₀ and R₁₂ as indicated in the panels) with a take-off angle of 90°.



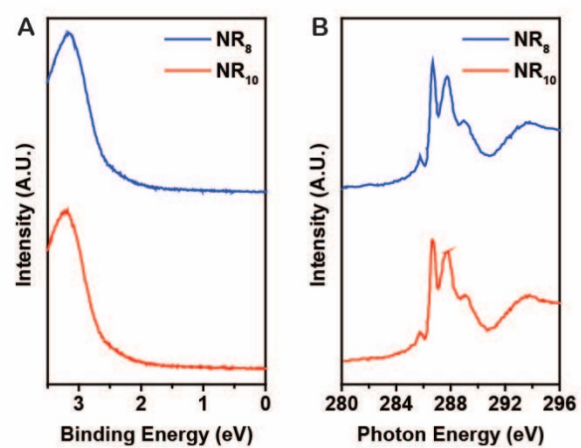
Supplementary Figure 14. The C 1s (A), Cl 2p (B), and S 2p (C) spectra of Au^{TS}-SC_nPTM^R (n= 8, 10, 12; R₈, R₁₀ and R₁₂ as indicated in the panels) with a take-off angle of 40°.



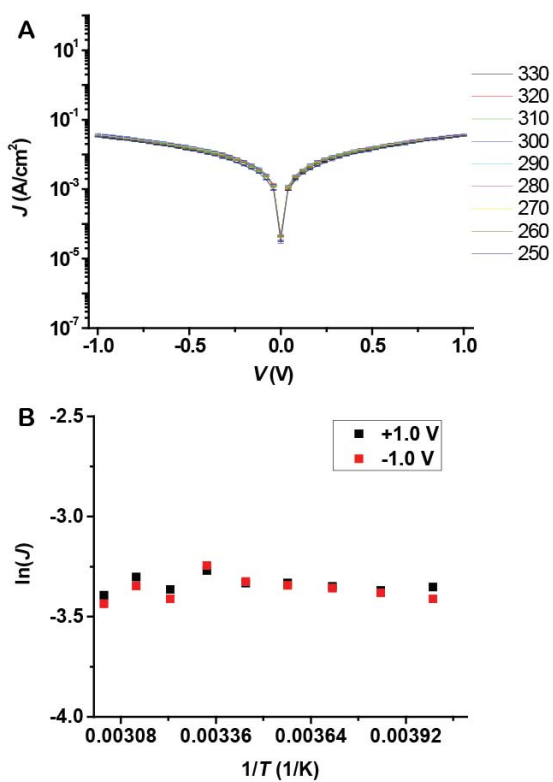
Supplementary Figure 15. The C 1s (A), Cl 2p (B), and S 2p (C) spectra of Au^{TS}-SC_nPTM^{NR} (n= 8, 10, 12; NR₈, NR₁₀ and NR₁₂ as indicated in the panels) with a take-off angle of 90°.



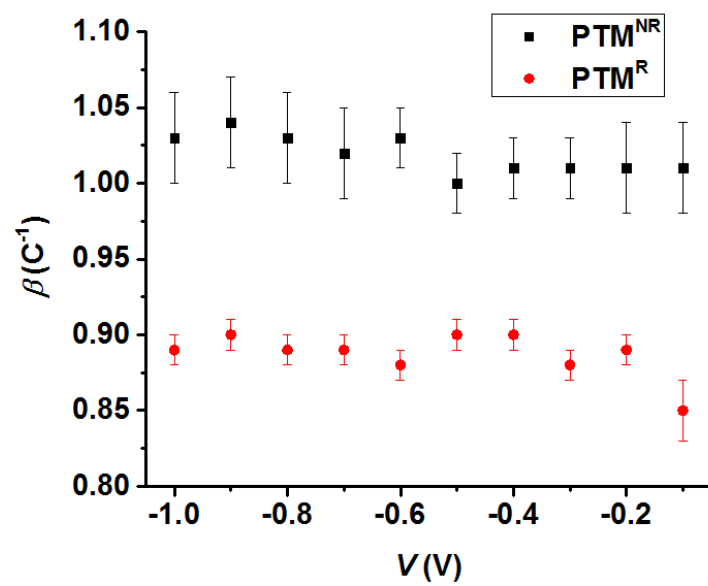
Supplementary Figure 16. The C 1s (A), Cl 2p (B), and S 2p (C) spectra of Au^{TS}-SC_nPTM^{NR} (n= 8, 10, 12; NR₈, NR₁₀ and NR₁₂ as indicated in the panels) with a take-off angle of 40°.



Supplementary Figure 17. UPS and NEXAFS spectra of Au^{TS}-SC_nPTM^{NR} (n= 8 and 10; NR₈ and NR₁₀ respectively in the figures).



Supplementary Figure 18. Temperature dependent $J(V)$ curves and the corresponding Arrhenius plot at $V = \pm 1.0$ V over the range of temperatures of 250 to 330 K of a junctions with a SAMs of NR₈.



Supplementary Figure 19. The plot of tunneling decay coefficient (β) against V .

Supplementary Table 1. The values of I_{Cl} , relative surface coverage and absolute surface coverage.

SAMs	I_{Cl} at 90° take-off angle	Relative surface coverage ^a	Absolute surface coverage ($\times 10^{-9}$ mol/cm ²)
R ₈	47997	0.13	0.14
R ₁₀	49774	0.13	0.15
R ₁₂	52305	0.14	0.16
NR ₈	49225	0.13	0.15
NR ₁₀	50556	0.14	0.15
NR ₁₂	52907	0.14	0.16
SC ₁₁ Cl	26450	1	1.10

^a The relative surface coverage is calculated from $I_{\text{Cl}}(\text{SC}_{11}\text{Cl}) / (I_{\text{Cl}}(\text{PTM}^{\text{R/NR}}) / 14)$.

Supplementary Table 2. The elemental ratios calculated from the high-resolution XPS spectra

SAM	C 1s at 90°		C 1s at 40°		Cl/C ₃	
	C ₁ /C ₃	C ₂ /C ₃	C ₁ /C ₃	C ₂ /C ₃	At 90°	At 40°
R ₈	0.87	0.52	0.80	0.52	3.69	4.03
R ₁₀	0.73	0.49	0.62	0.47	3.70	4.09
R ₁₂	0.54	0.49	0.40	0.44	3.69	4.12
NR ₈	0.87	0.51	0.80	0.51	3.68	4.06
NR ₁₀	0.72	0.48	0.60	0.47	3.70	4.11
NR ₁₂	0.57	0.51	0.39	0.44	3.68	4.20

Supplementary Table 3. The ratio of (I_{θ}) of S 2*p* between take-off angles of 90° and 40° of R-based SAMs on Au^{TS}.

	$I_{\theta}(90^{\circ})$ (%)	$I_{\theta}(40^{\circ})$ (%)	d (nm)
Au ^{TS} -SC ₈ PTM ^R	69.6	30.4	1.83
Au ^{TS} -SC ₁₀ PTM ^R	73.2	26.8	2.05
Au ^{TS} -SC ₁₂ PTM ^R	75.1	24.9	2.20
Au ^{TS} -SC ₈ PTM ^{NR}	68.9	31.1	1.79
Au ^{TS} -SC ₁₀ PTM ^{NR}	73.5	26.5	2.08
Au ^{TS} -SC ₁₂ PTM ^{NR}	75.2	24.8	2.22

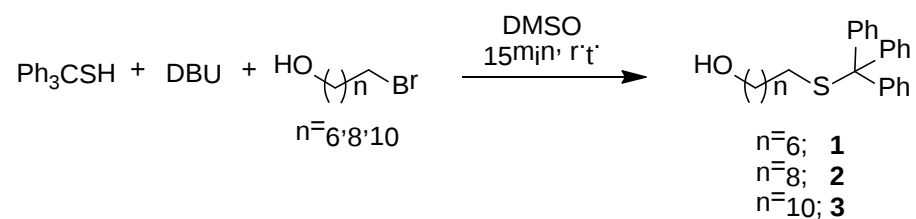
Supplementary Methods

Synthesis and characterization of PTM derivatives

General procedure

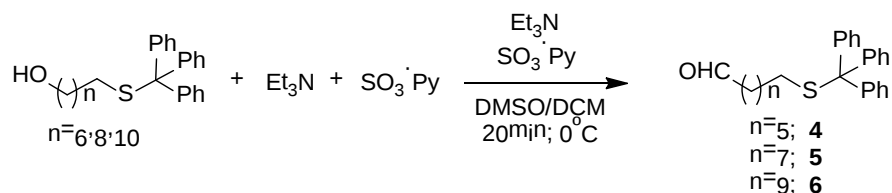
Elemental analyses were performed on the CID (CSIC) services. NMR spectra were recorded on a Bruker Avance 400 MHz. EPR spectra were recorded in a Bruker ELEXYS E500 X-band spectrometer. The simulation of the EPR spectra was realised with software Simfonia. Electrochemical experiments were performed with a potentiostat/galvanostat Autolab/PGSTAT204 from Metrohm Autolab B.V. in a standard three-electrode cell, by using a platinum wire as working and counter electrode and Ag/AgCl as reference electrode. Tetrabutylammonium hexafluorophosphate (Fluka, 99%) was used as the supporting electrolyte. UV-Vis spectra were recorded on a Varian Carey 5000 in double-beam mode. Mass Spectra were recorded with a Bruker Ultraflex LDI-TOF mass spectrometer. The liquid chromatography were performed in an Agilent 1100 series HPLC (Agilent Technologies) connected to with two (in parallel) detectord, a photodiode array working into 200nm and 800nm and a mass spectrometer (Esquire 3000 MS Trap (Bruker Daltonik) equipped with Electrospray source ionisation), the methodology used was a binary gradient of acetonitrile (with 5% of formic acid) and chloroform, from 90/10 to 60/40. The IR spectra were recorded with an ATR-IR Perkin Elmer Spectrum One. The manipulation of the radicals in solution was performed under red light.

General procedure for the synthesis of compounds tritylthio-alcohols 1, 2 and 3.



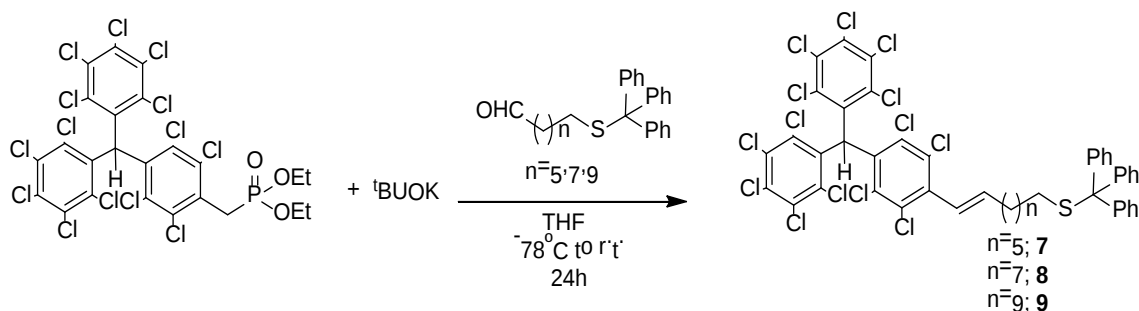
Triphenylmethane thiol (1Eq) was suspended in DMSO and DBU (1.14 Eq,) was added. After stirring at room temperature for 5 min, the corresponding bromo-alcohol derivative (1.08 Eq, 0.96 mmol) was added, and the mixture was stirred for 10 min. The reaction mixture was diluted with ethyl acetate, quenched with 0.1M HCl (5 ml), extracted with ethyl acetate, dried over MgSO₄ and dried in vacum. The crude product was purified by flash chromatography (SiO₂, heptane/AcOEt 1/1).

General procedure for the synthesis of compounds tritylthio- aldehydes 4, 5 and 6.



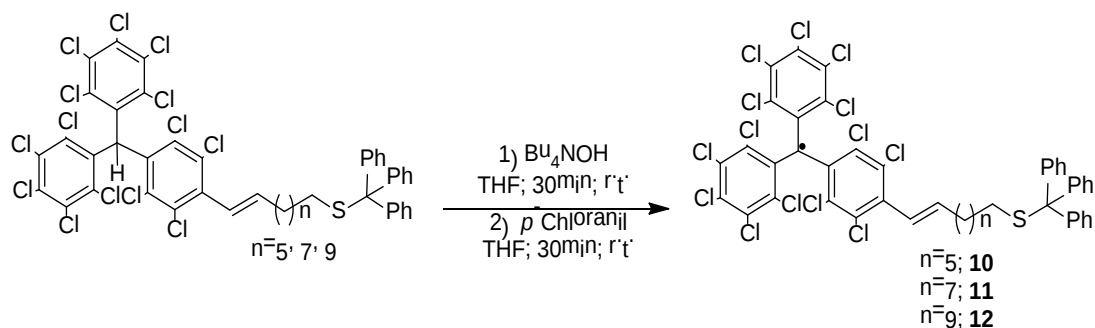
The corresponding Triphenylmercapto-*n*-ol (1 Eq.) and triethylamine (3.5 Eq.) were dissolved in dichloromethane and DMSO, cooled to 0°C and added a suspension of sulfur trioxide pyridine complex (2.07 Eq, 408 mg, 2.57 mmol) in DMSO (400 μL). At the same temperature, the mixture was then stirred for 20 min at 0°C and after diluted with dichloromethane and quenched with 0.1M HCl (5ml) and extracted with dichloromethane. The combined organic phases were washed with brine and dried (MgSO_4) The crude product was purified by flash chromatography (heptane/AcOEt 1/1).

General procedure for the synthesis of PTM derivatives 7, 8 and 9.



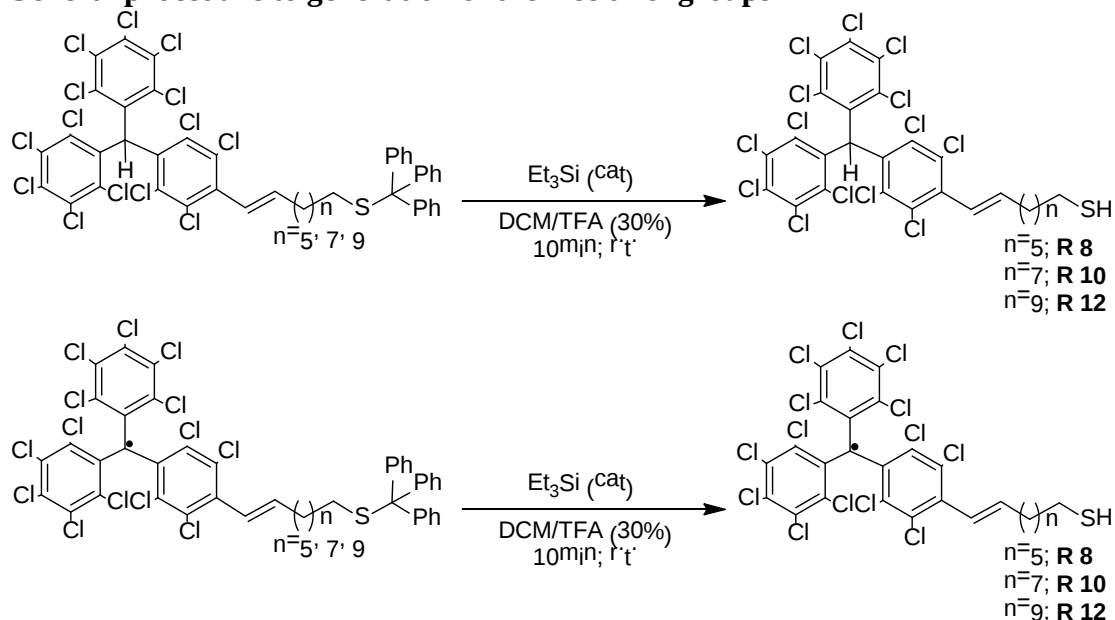
Under Argon, potassium tert-butoxide (1.5 Eq) was added to a stirred solution of PTM- P(O)(OEt)_2 (1 Eq) in dry tetrahydrofuran (THF) at -78°C and the mixture was stirred at this temperature for 10min, then a solution of the corresponding triphenylmercapto-*n*-al (2 Eq) in dry THF was added and the mixture was allowed to warm to room temperature. The resulting mixture was stirred in the dark at room temperature for 24h. After evaporation of the solvent the crude was purified by column chromatography (SiO_2 , Hexane/ CH_2Cl_2 80/20).

General procedure for the synthesis of PTM radical derivatives 10, 11 and 12.



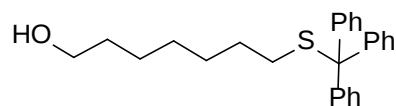
To a solution of the corresponding α H PTM triphenylmercapto derivative in THF, 1.3 Eq of Bu_4NOH (1M in methanol) was added. The initial colorless solution turned to intense violet and the reaction mixture was stirred at room temperature for 30 min. and then, 1.5 Eq of *p*-chloranil was added. The color of the reaction mixture changed to red. After 30 min the solvent was removed under vacuum and the crude product was purified by flash chromatography (SiO_2 , Hexane/ CH_2Cl_2 80/20). The resulting waxy compounds were washed with methanol to give a red solid in almost quantitative yield (96-98%).

General procedure to generation of the free thiol groups

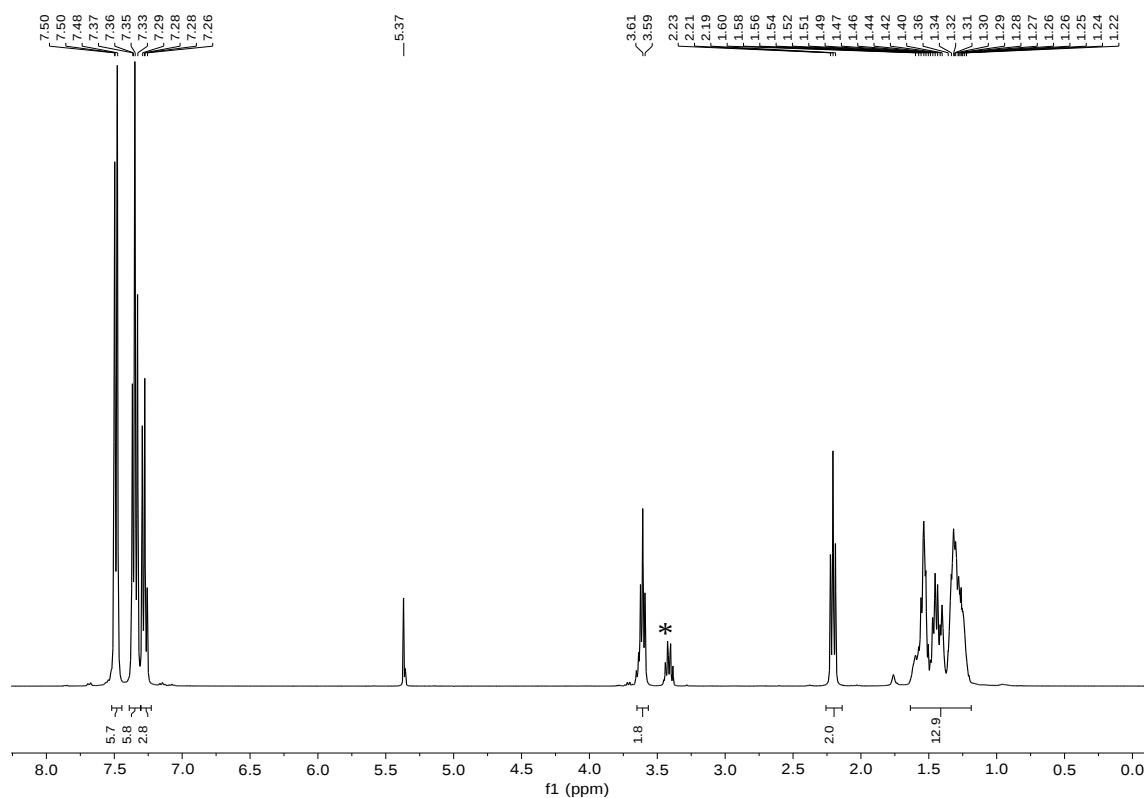


To a solution of trifluoroacetic acid (TFA) in DCM (30%) triethylsilyl (cat) was added under argon, and then the PTM triphenylmercapto derivative (either radical or α H) was added to the mixture. The solution was stirred at room temperature in the dark for 10 min. Then the solvent was evaporated in vacuum, and the crude product was purified by flash chromatography (silica gel, Hexane/ CH_2Cl_2 80/20). The product was washed with methanol in a sonicated bath and filtered several time, to yield a solid (red for radicals and white for α Hs) in almost quantitative yield (95%-97%).

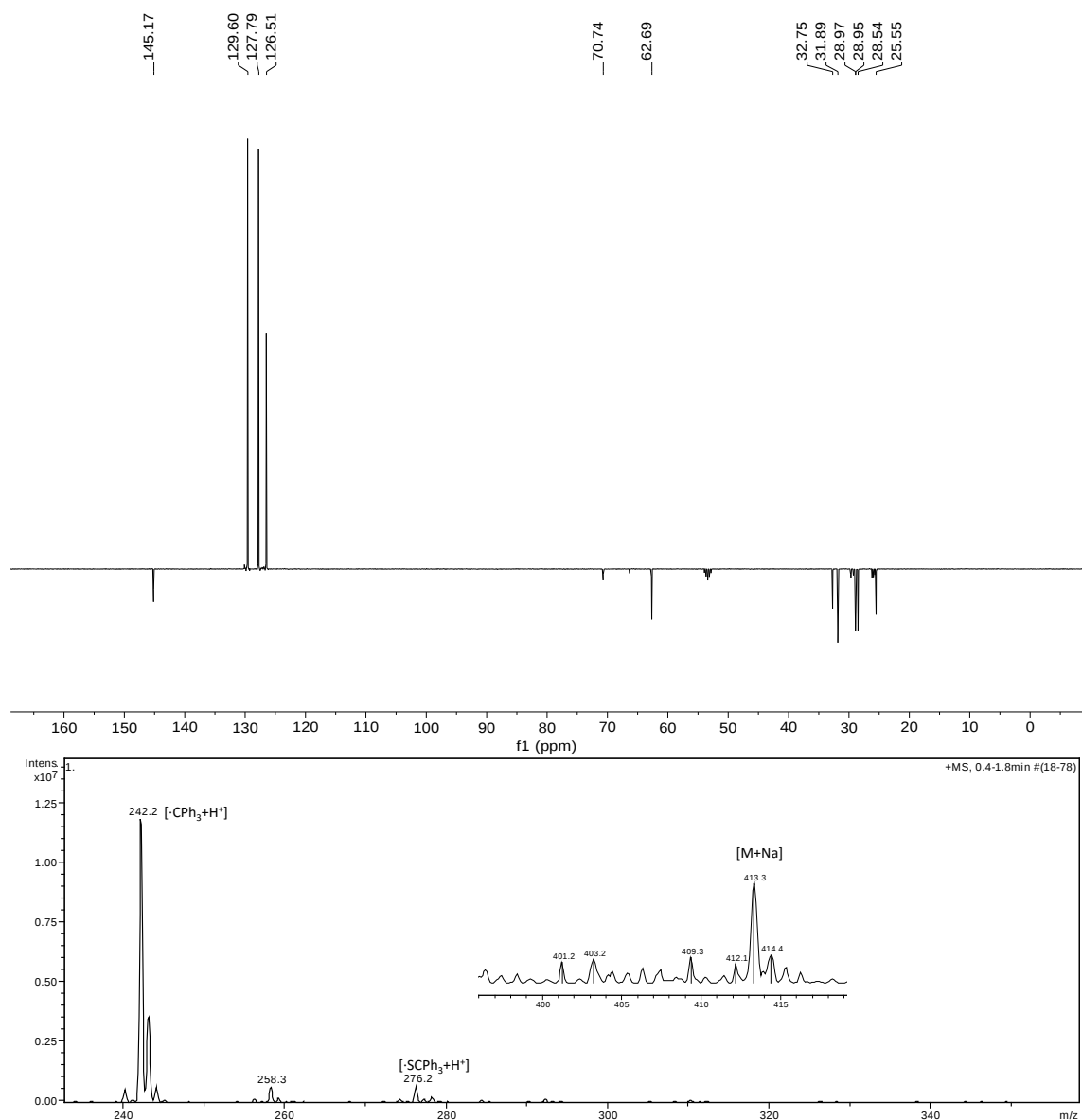
7-(tritylthio)heptan-1-ol (1)



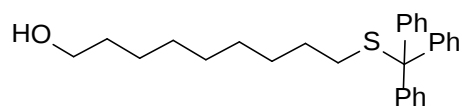
According to the general procedure, from triphenylmethane thiol (247 mg, 0.89 mmol), DBU (1.14 Eq, 152 μ L, 1.02 mmol) and 7bromo-heptanol (187 mg, 0.96 mmol) in DMSO (1 mL), the compound **1** was obtained as a transparent oil (yield, 84%). **$^1\text{H-NMR}$** (400 MHz, CD_2Cl_2) δ /ppm: 7.49 (m, 6H), 7.35 (m, 6H), 7.28(m, 3H), 3.61 (t, $J = 6.6$ Hz, 2H), 2.21 (t, $J = 7.4$ Hz, 2H), 1.64 – 1.14 (m, 11H); **$^{13}\text{C-NMR}$** (101 MHz, CD_2Cl_2) δ /ppm: 145.17, 129.60, 127.79, 126.51, 70.74, 62.69, 32.75, 31.89, 28.97, 28.95, 28.54, 25.55. **FT-IR** ν/cm^{-1} : 3345.9, 3085.0, 3055.8, 3024.1, 2927.5, 2853.9, 1594.7, 1488.5, 1443.4, 1183.3, 1079.6, 1054.8, 1033.9, 1001.6, 884.2, 850.1, 764.7, 741.3, 697.8, 676.3, 617.1; **EM (m/z)** (ESI): calculated for $\text{C}_{26}\text{H}_{30}\text{OS}$: 390.2; found: 413.2 ($\text{M}+\text{Na}$), 276.2 ($\cdot\text{SCPh}_3+\text{H}^+$), 243.11 ($\cdot\text{CPh}_3+\text{H}^+$).



* Impurity that does not affect to the rest of the synthesis. Probably a fragment of the alkyl chain.

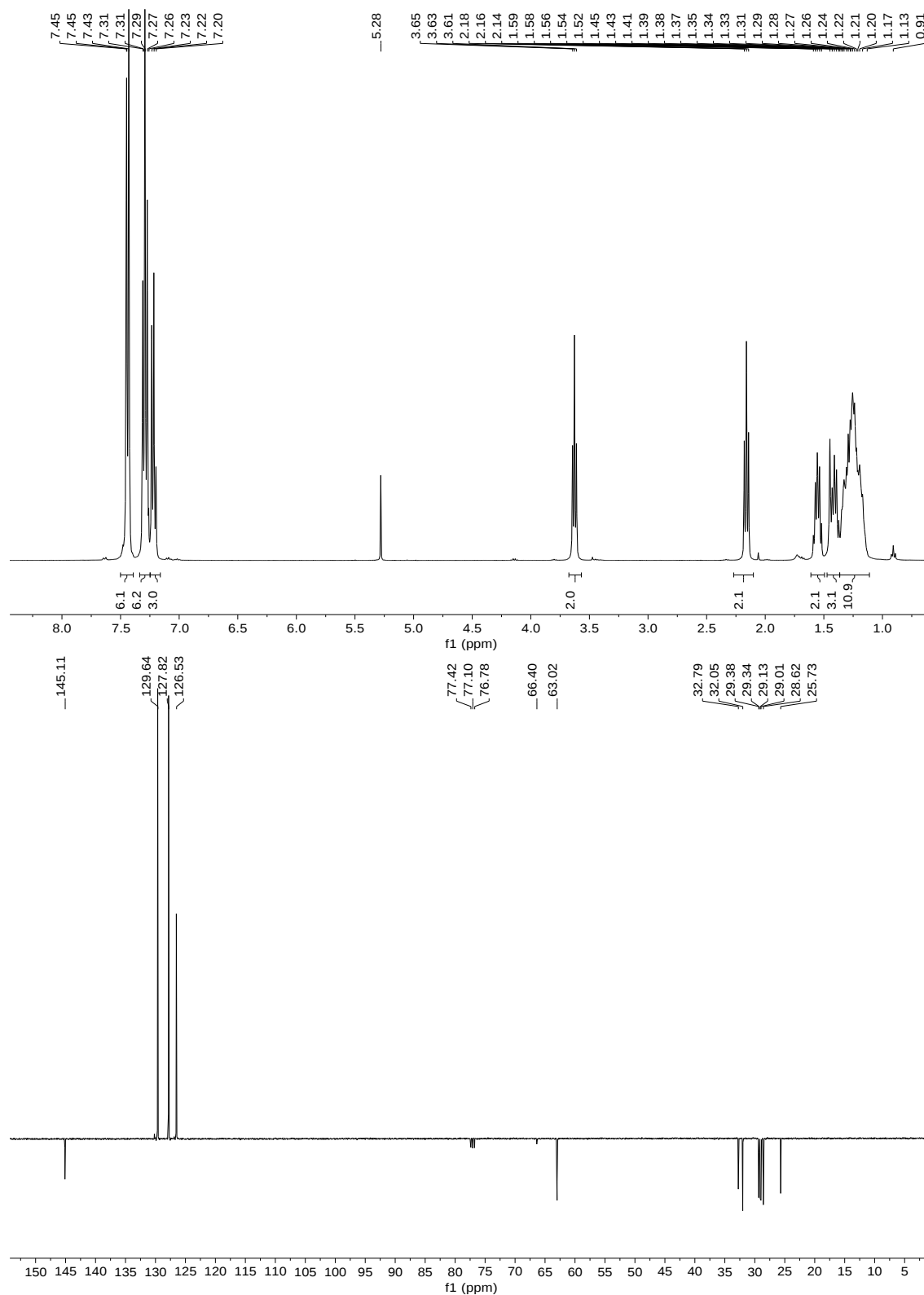


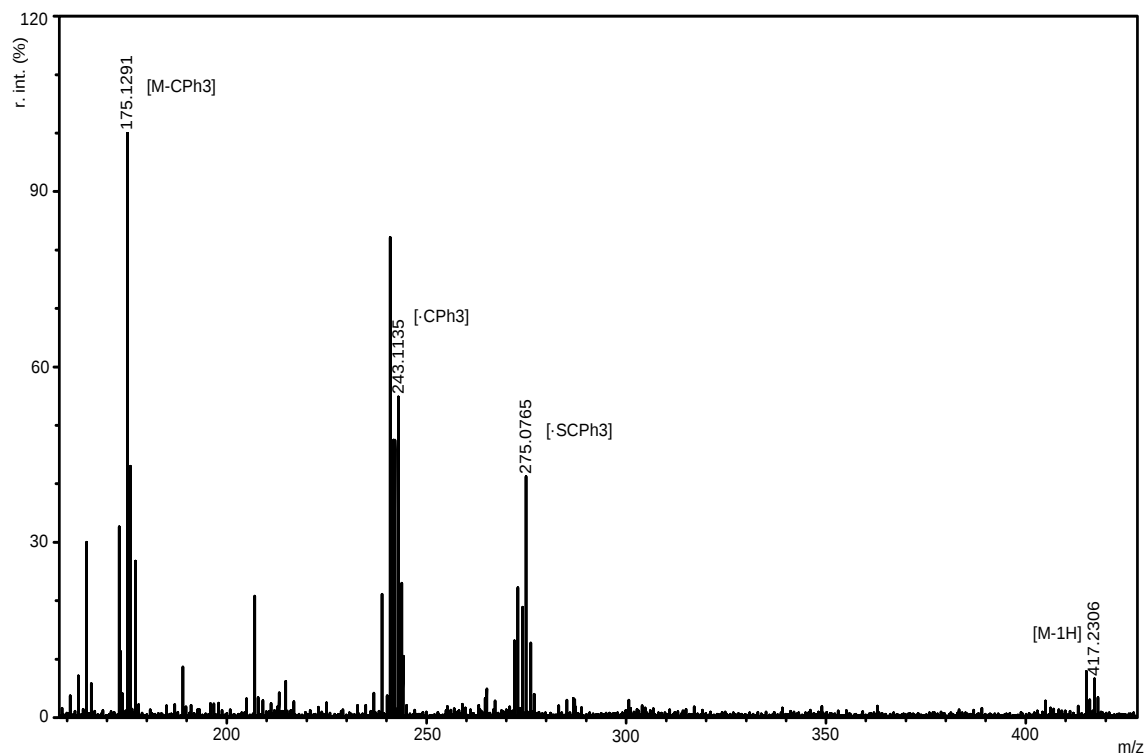
9-(tritylthio)nonan-1-ol (2)



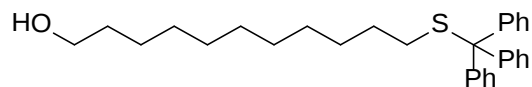
According to the general procedure, from triphenylmethane thiol (247 mg, 0.89 mmol), DBU (152 μL , 1.02 mmol) and 9-bromo-nonan-1-ol (214 mg, 0.96 mmol) in DMSO (1 mL) the compound **2** was obtained as a transparent oil (yield, 85%), ^1H -NMR (400 MHz, CDCl_3) δ /ppm: 7.49 – 7.39 (m, 6H), 7.34 – 7.25 (m, 6H), 7.22 (t, $J = 7.2$ Hz, 3H), 3.63 (t, $J = 6.6$ Hz, 2H), 2.16 (t, $J = 7.3$ Hz, 2H), 1.56 (p, $J = 6.6$ Hz, 2H), 1.45 (s, 1H, OH), 1.40 (q, $J = 7.5$ Hz, 2H), 1.37 – 1.11 (m, 10H). ^{13}C -NMR (101 MHz, CDCl_3) δ /ppm: 145.11, 129.64, 127.82, 126.53, 77.42, 77.10, 76.78, 66.40, 63.02, 32.79, 32.05, 29.38, 29.34, 29.13, 29.01, 28.62, 25.73; FT-IR ν/cm^{-1} : 338.0, 3083.3, 3057.8, 3026.7, 2927.7, 2851.3, 1595.0, 1488.6, 1443.1, 1179.7, 1076.3, 1054.1,

1034.1, 1001.9, 885.2, 850.8, 765.2, 740.8, 697.5, 677.4. **EM (m/z)** (MALDI-TOF): calculated for $C_{28}H_{34}OS$: 418.23; found: 417.23 (M-H), 275.08 ($\cdot$ SCPh₃), 243.11 ($\cdot$ CPh₃) and 175.13 (M-CPh₃).

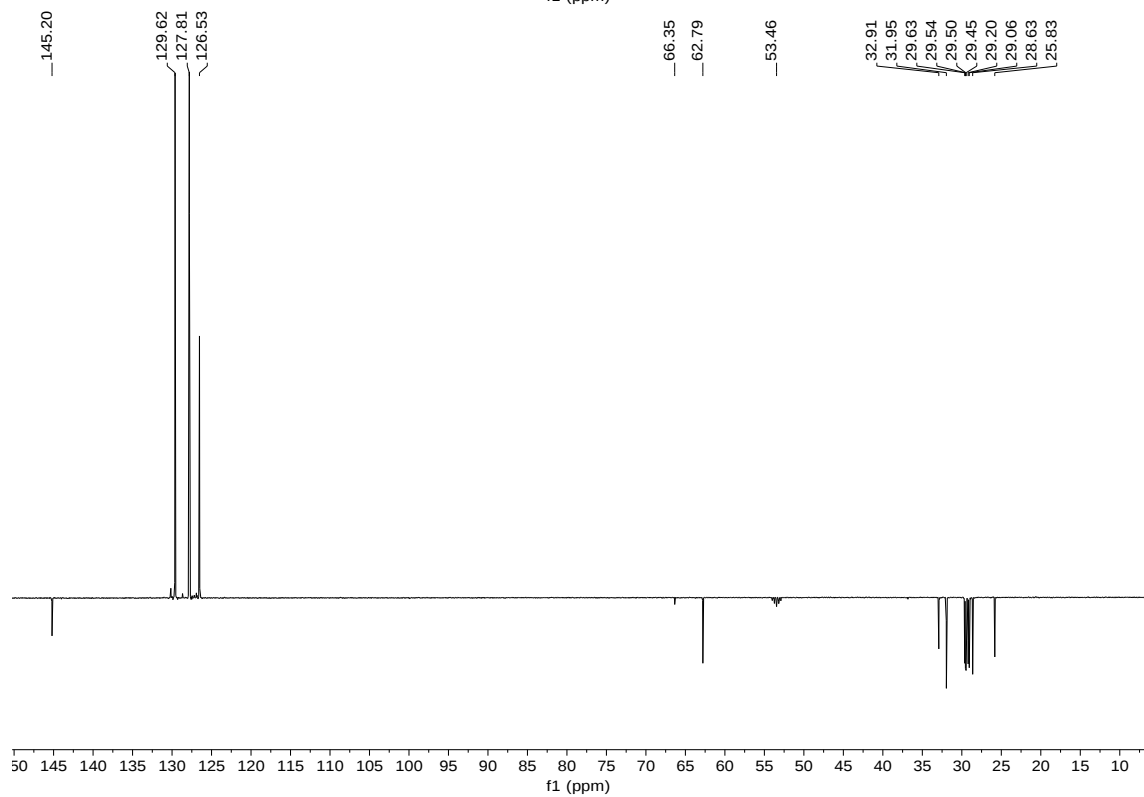
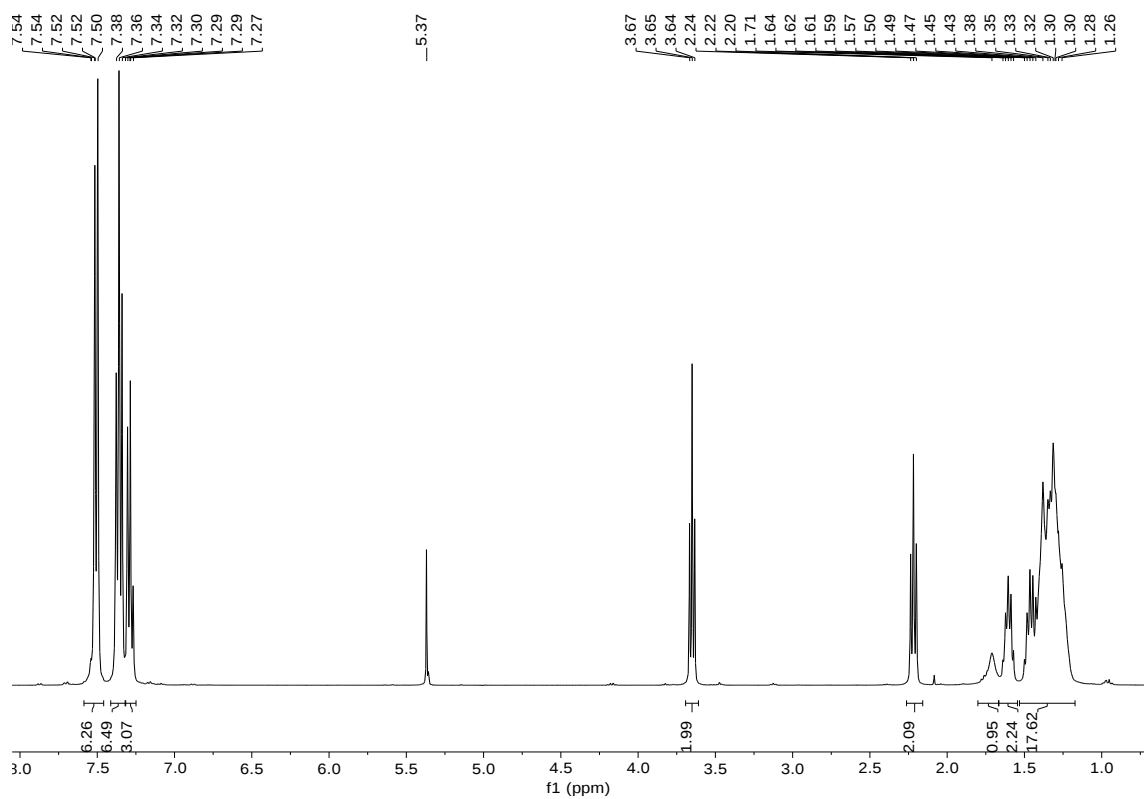


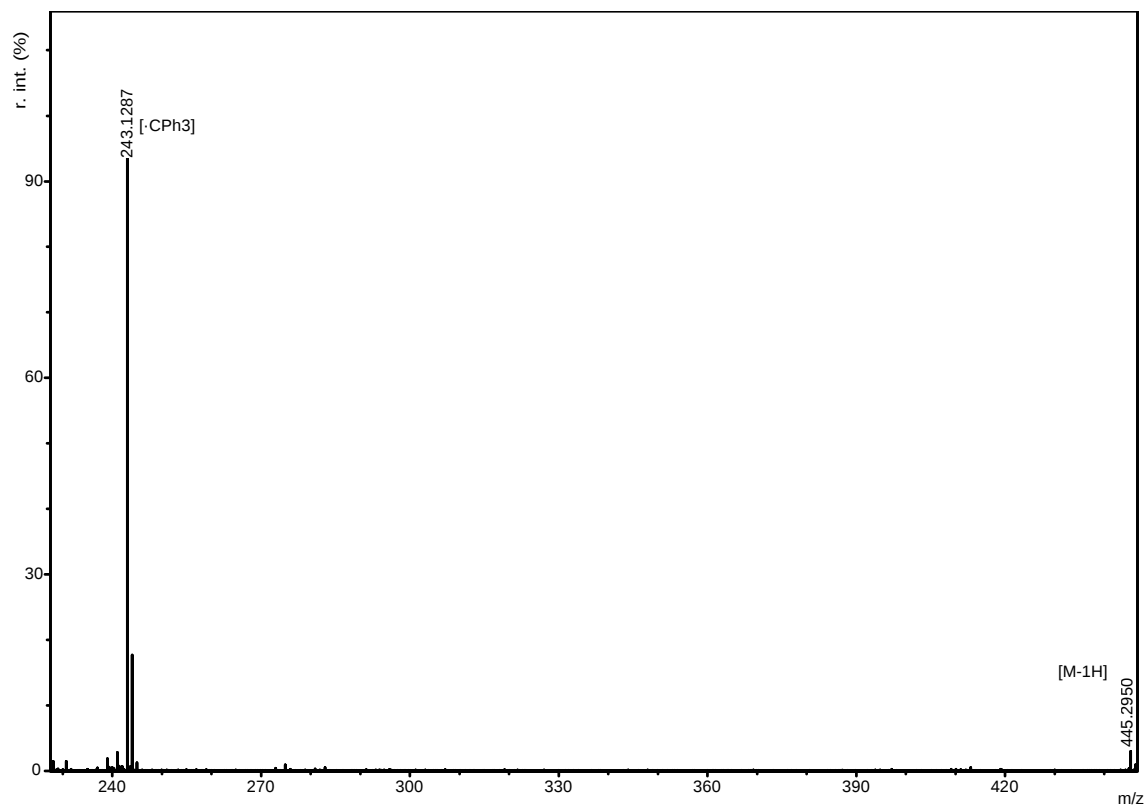


11-(tritylthio)undecan-1-ol (**3**)

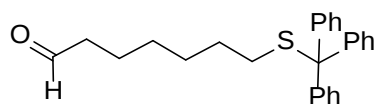


According to general procedure, from triphenylmethane thiol (247 mg, 0.89 mmol), DBU (152 μ L, 1.02 mmol) and 11-bromo-undecanol (241 mg, 0.96 mmol) in DMSO (1 mL), the compound **3** was obtained as a transparent oil (yield, 79%). **$^1\text{H-NMR}$** (400 MHz, CD_2Cl_2) δ /ppm: 7.54 – 7.47 (m, 6H), 7.36 (t, $J = 7.5$ Hz, 6H), 7.29 (t, $J = 7.2$ Hz, 3H), 3.65 (t, $J = 6.6$ Hz, 2H), 2.22 (t, $J = 7.4$ Hz, 2H), 1.71 (s, 1H), 1.61 (q, $J = 6.7$ Hz, 2H), 1.53 – 1.16 (m, 16H); **$^{13}\text{C-NMR}$** (101 MHz, CD_2Cl_2) δ /ppm: 145.20, 129.62, 127.81, 126.53, 66.35, 62.79, 53.46, 32.91, 31.95, 29.63, 29.54, 29.50, 29.45, 29.20, 29.06, 28.63, 25.83. **FT-IR** ν/cm^{-1} : 3327.5, 3085.2, 3058.0, 3023.0, 2923.9, 2852.6, 1595.1, 1488.9, 1443.8, 1183.5, 1077.4, 1055.3, 1033.9, 1001.7, 884.7, 852.1, 741.4, 967.8, 676.2, 617.3; **EM (m/z)** (MALDI-TOF): calculated for $\text{C}_{30}\text{H}_{38}\text{OS}$: 446.22; found: 445.29 (M-1H) and 243.13 ($\cdot\text{CPh}_3$).

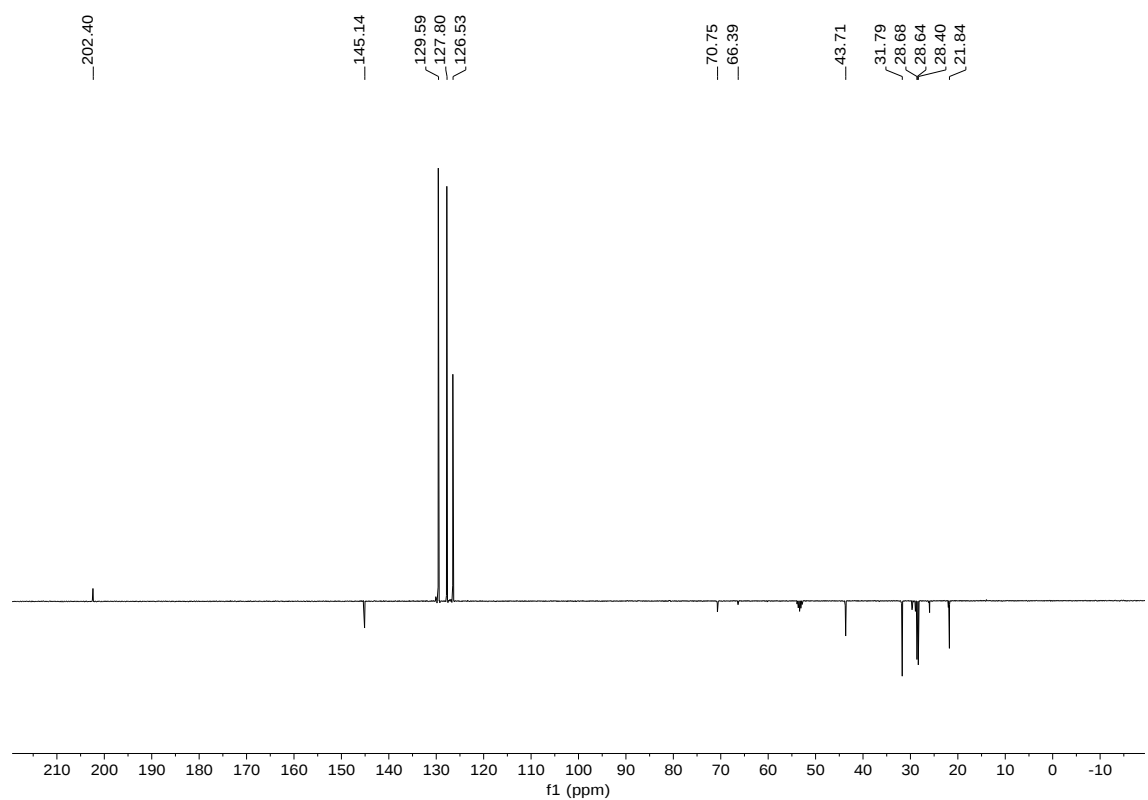
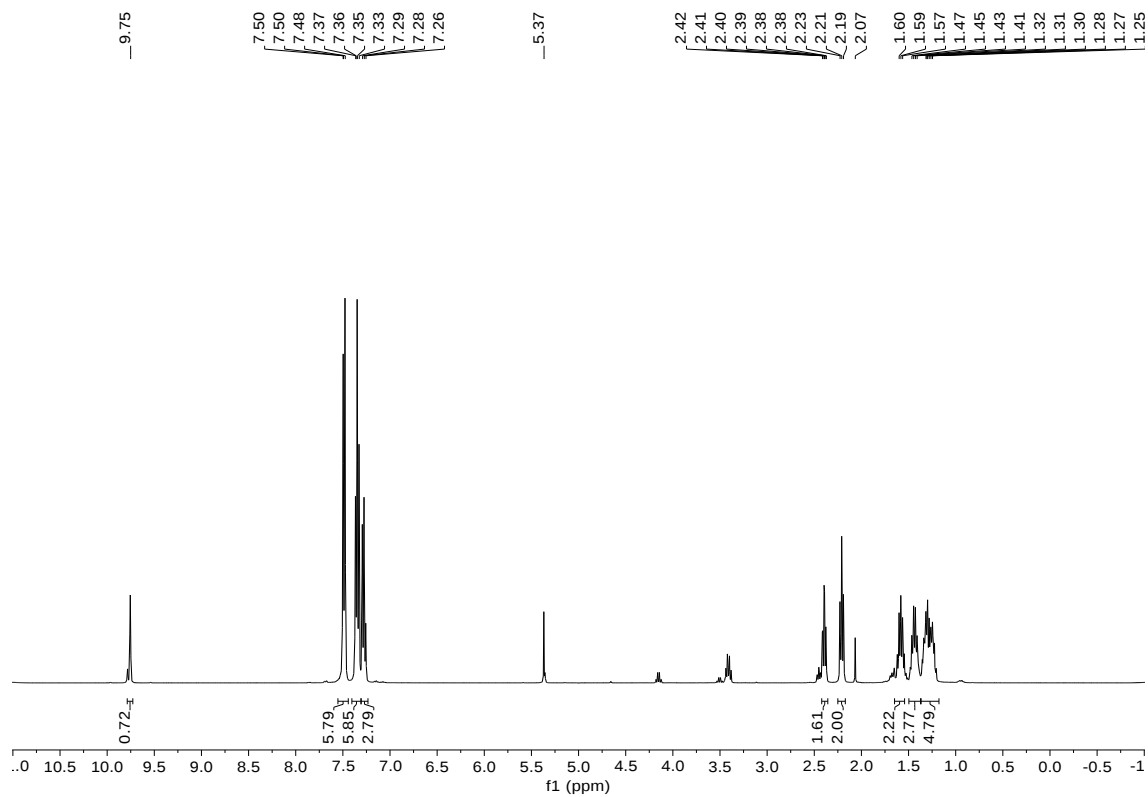


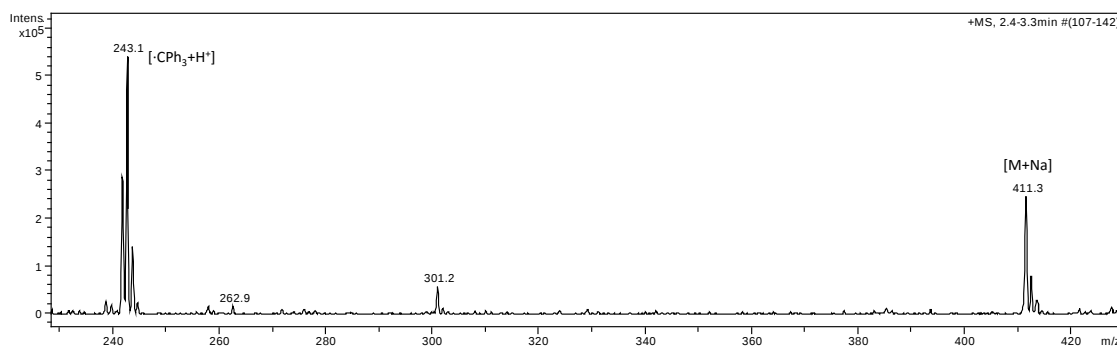


7-(tritylthio)heptanal (**4**)

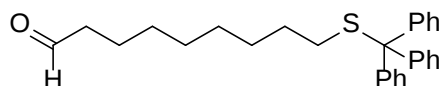


According to general procedure, from 7-triphenylmercapto-1-ol (**1**) (484 mg, 1.24 mmol) triethylamine (600 μ L, 4.34 mmol) and sulfur trioxide pyridine complex (408 mg, 2.57 mmol) in mixture of DCM (3.5 mL) and DMSO (500 μ L), the compound **4** was obtained as a transparent oil (yield, 66%). **¹H-NMR** (400 MHz, CD₂Cl₂) δ /ppm: 9.75 (t, J = 1.7 Hz, 1H), 7.56 – 7.43 (m, 6H), 7.35 (t, J = 7.5 Hz, 7H), 7.28 (t, J = 7.2 Hz, 3H), 2.40 (td, J = 7.4, 1.7 Hz, 2H), 2.21 (t, J = 7.3 Hz, 2H), 1.59 (p, J = 7.4 Hz, 2H), 1.51 – 1.38 (m, 2H), 1.38 – 1.19 (m, 4H). **¹³C-NMR** (101 MHz, CD₂Cl₂) δ /ppm: 202.40, 145.14, 129.59, 127.80, 126.53, 70.75, 70.62, 43.71, 31.79, 28.68, 28.64, 28.40, 21.84; **FT-IR** ν /cm⁻¹: 3083.7, 3056.6, 3028.8, 2929.2, 2855.5, 2721.2, 1721.9, 1593.5, 1485.6, 1440.8, 1238.1, 1079.6, 1033.9, 742.2, 698.3, 674.5, 625.5. **EM (m/z)** (ESI): calculated for C₂₆H₂₈OS: 388.2; found: 411.2 (M+Na), 243.11 ($\cdot$ CPh₃+1H⁺).

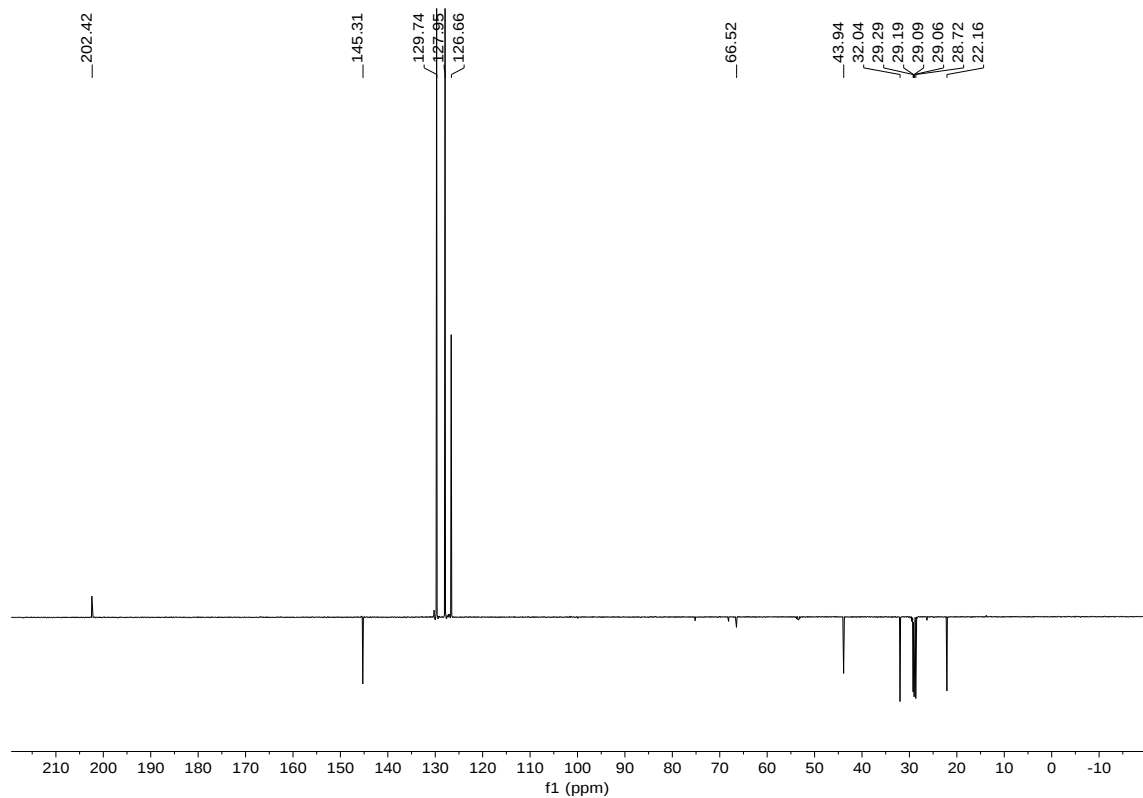
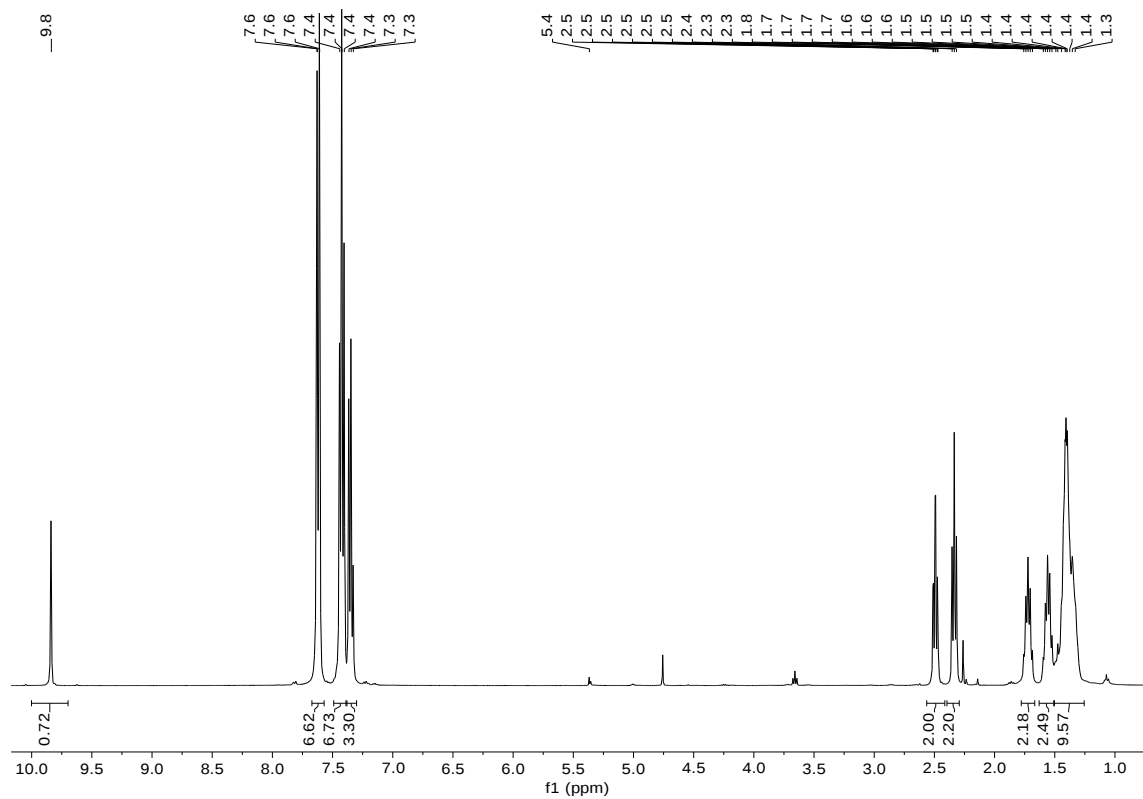


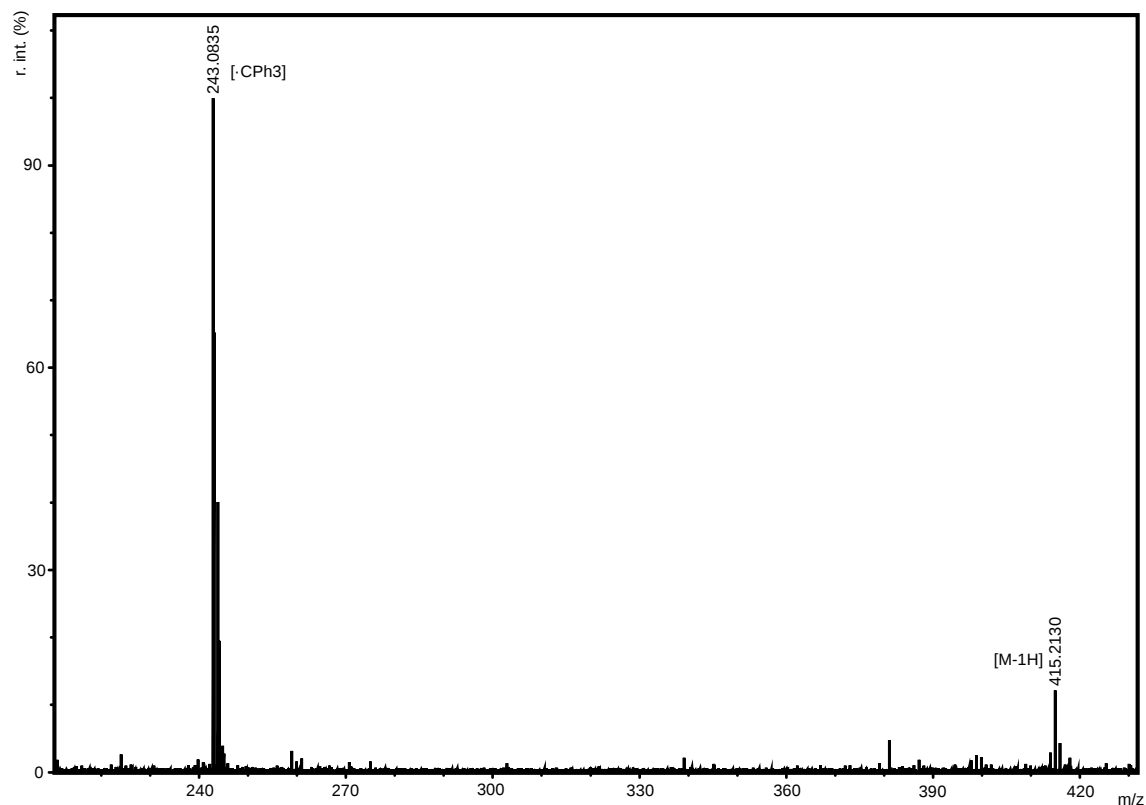


9-(tritylthio)nonanal (5)

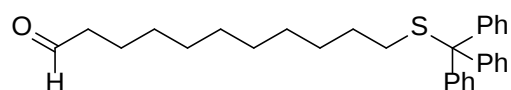


According to the general procedure, from 9-triphenylmercapto-1-ol (**2**) (1.24 mmol, 519 mg), triethylamine (600 μ L, 4.34 mmol) and sulfur trioxide pyridine complex (408 mg, 2.57 mmol) in a mixture of DCM (3.5 mL) and DMSO (500 μ L), the compound **5** was obtained as a transparent oil (yield, 71%). **¹H-NMR** (400 MHz, CDCl₃) δ /ppm: 9.84 (t, J = 1.6 Hz, 1H), 7.67 – 7.57 (m, 6H), 7.42 (t, J = 7.5 Hz, 6H), 7.35 (t, J = 7.2 Hz, 3H), 2.49 (td, J = 7.4, 1.6 Hz, 2H), 2.34 (t, J = 7.3 Hz, 2H), 1.72 (q, J = 7.2 Hz, 2H), 1.56 (q, J = 7.1 Hz, 2H), 1.50 – 1.26 (m, 8H); **¹³C-NMR** (101 MHz, CD₂Cl₂) δ /ppm: 202.42, 145.31, 129.74, 127.95, 126.66, 66.52, 43.94, 32.04, 29.29, 29.19, 29.09, 29.06, 28.72, 22.16; **FT-IR** ν /cm⁻¹: 3086.5, 3057.1, 3032.2, 2922.8, 2852.5, 1722.9, 1594.7, 1488.7, 1444.3, 155.5, 10841.1, 1034.1, 952.9, 887.2, 850.2, 164.3, 742.4, 697.8, 676.7; **EM (m/z)** (MALDI-TOF): calculated for C₂₈H₃₂OS: 416.22; found: 415.21 (M-H) and 243.08 (M-CPh₃).

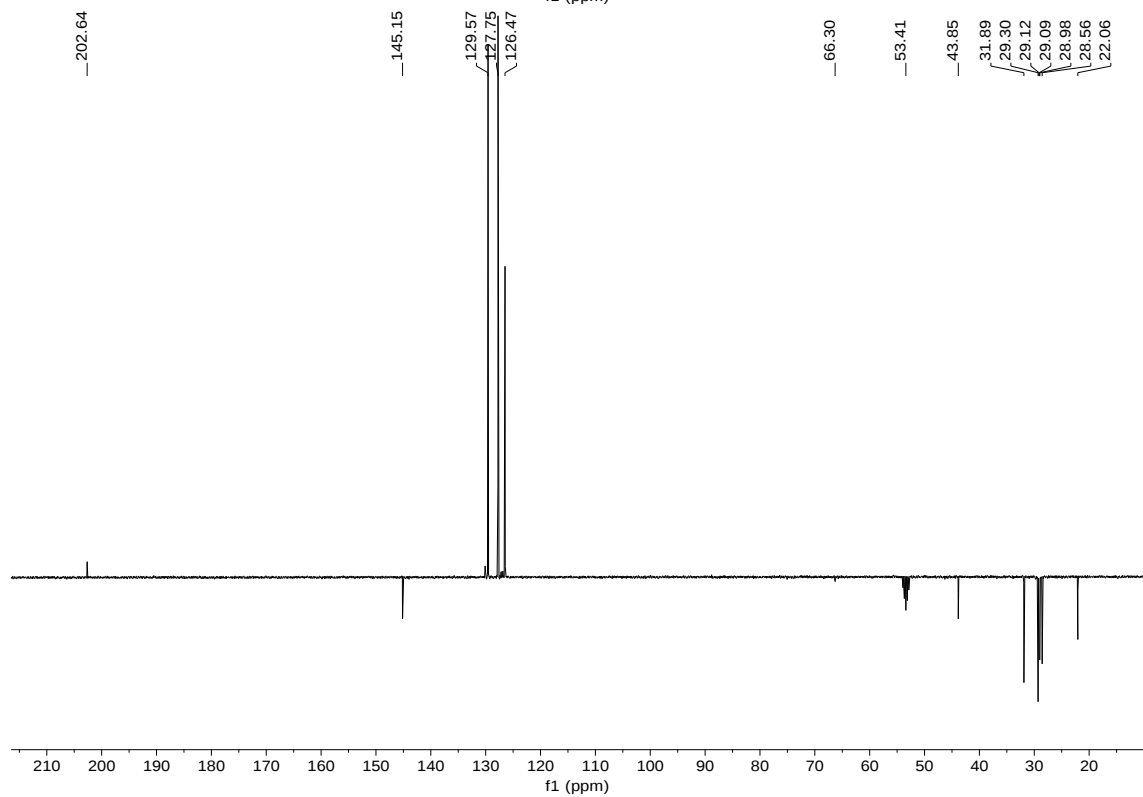
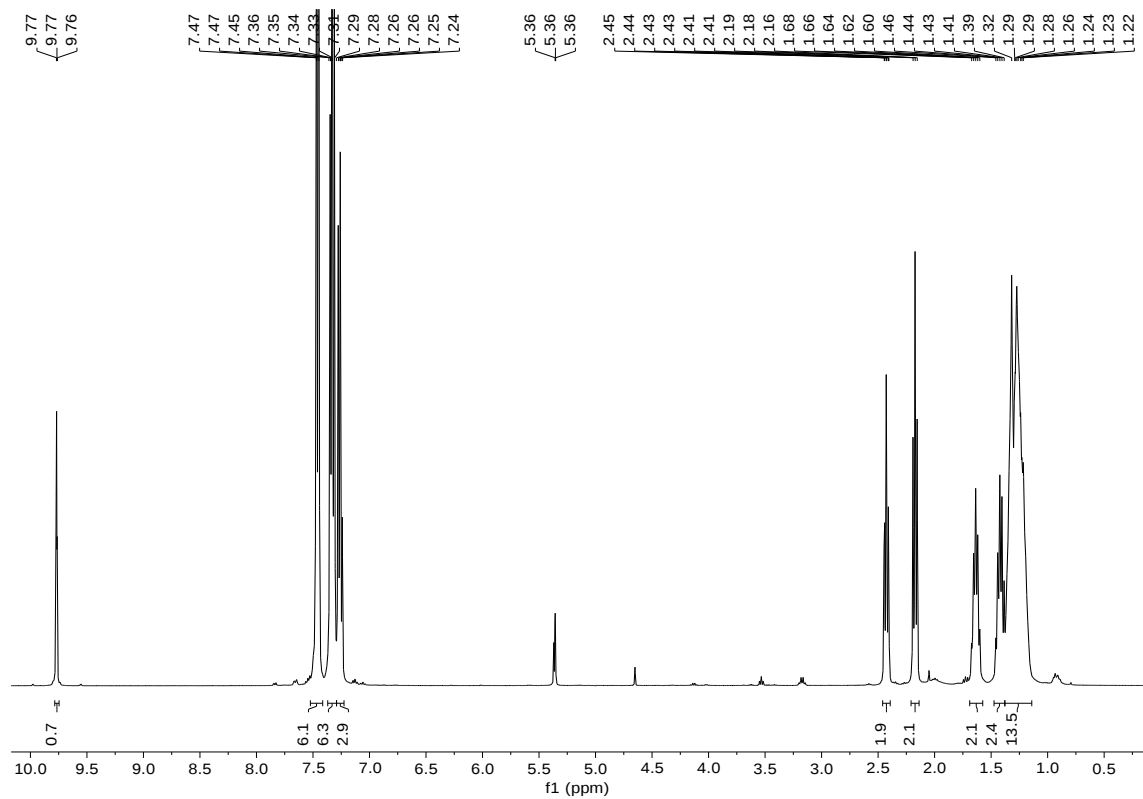


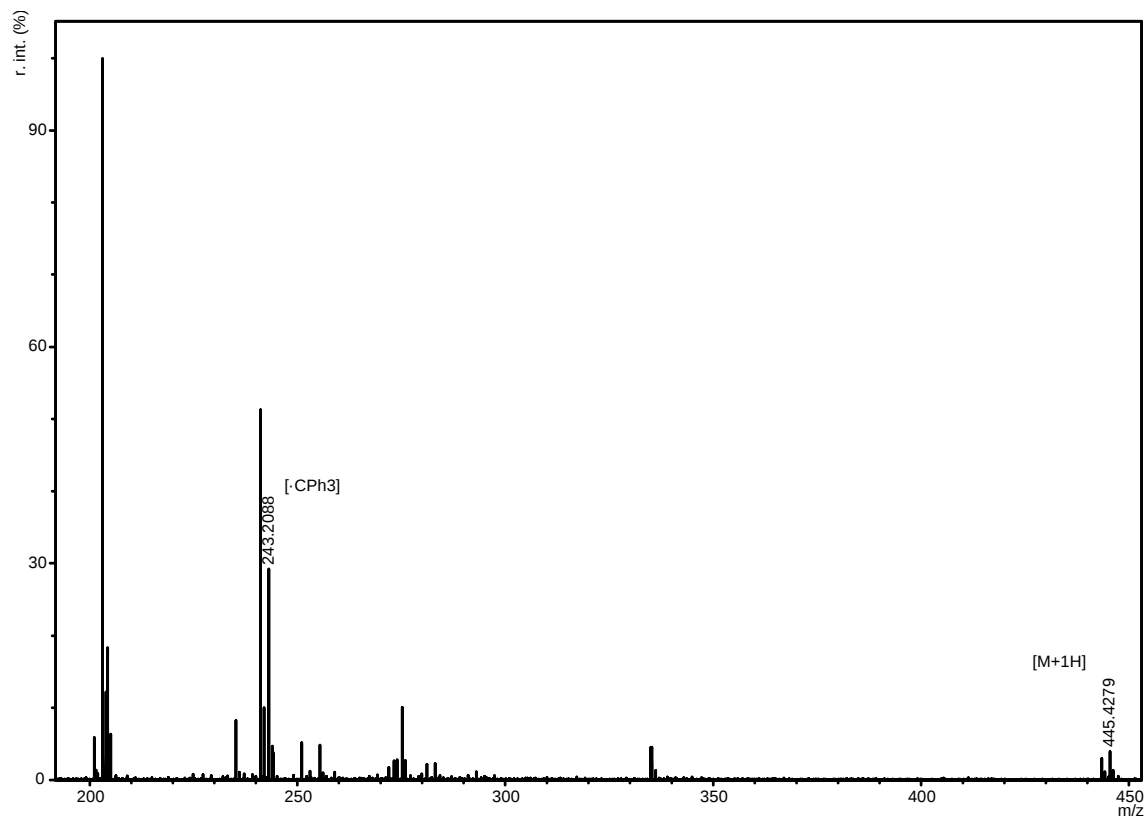


11-(tritylthio)undecanal (**6**)

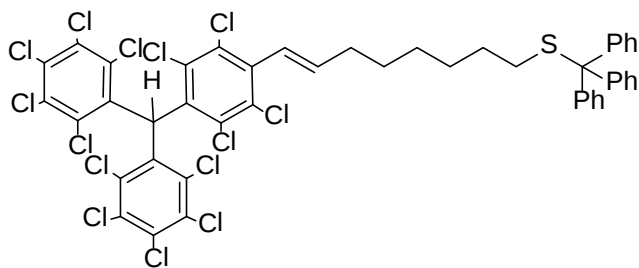


According to the general procedure, from 11-triphenylmercapto-1-ol (**3**) (1.24 mmol, 553 mg), triethylamine (600 μ L, 4.34 mmol) and sulfur trioxide pyridine complex (408 mg, 2.57 mmol) in a mixture of DCM (3.5 mL) and DMSO (500 μ L), the compound **6** was obtained as a transparent oil (yield, 68%). **¹H-NMR** (400 MHz, CD₂Cl₂) δ /ppm: 9.77 (t, J = 1.8 Hz, 1H), 7.50 – 7.41 (m, 6H), 7.33 (t, J = 7.5 Hz, 6H), 7.26 (t, J = 7.2 Hz, 3H), 2.43 (td, J = 7.4, 1.8 Hz, 2H), 2.18 (t, J = 7.4 Hz, 2H), 1.64 (q, J = 7.3 Hz, 2H), 1.43 (q, J = 7.3 Hz, 2H), 1.38 – 1.12 (m, 12H). **¹³C-NMR** (101 MHz, CD₂Cl₂) δ /ppm: 202.64, 145.15, 129.57, 127.75, 126.47, 66.30, 53.41, 43.85, 31.89, 29.30, 29.12, 29.09, 28.98, 28.56, 22.06; **FT-IR** (ν /cm⁻¹): 3058.1, 2924.9, 2853.2, 1723.2, 1595.5, 1489.3, 1444.1, 1276.2, 1262.1, 1081.4, 1033.4, 908.6, 851.1, 743.3; **EM (m/z)**: (MALDI-TOF): calculated for C₃₀H₃₆OS: 444.25; found: 445.43 (M+1H) and 243.21 ($\cdot$ CPh₃).



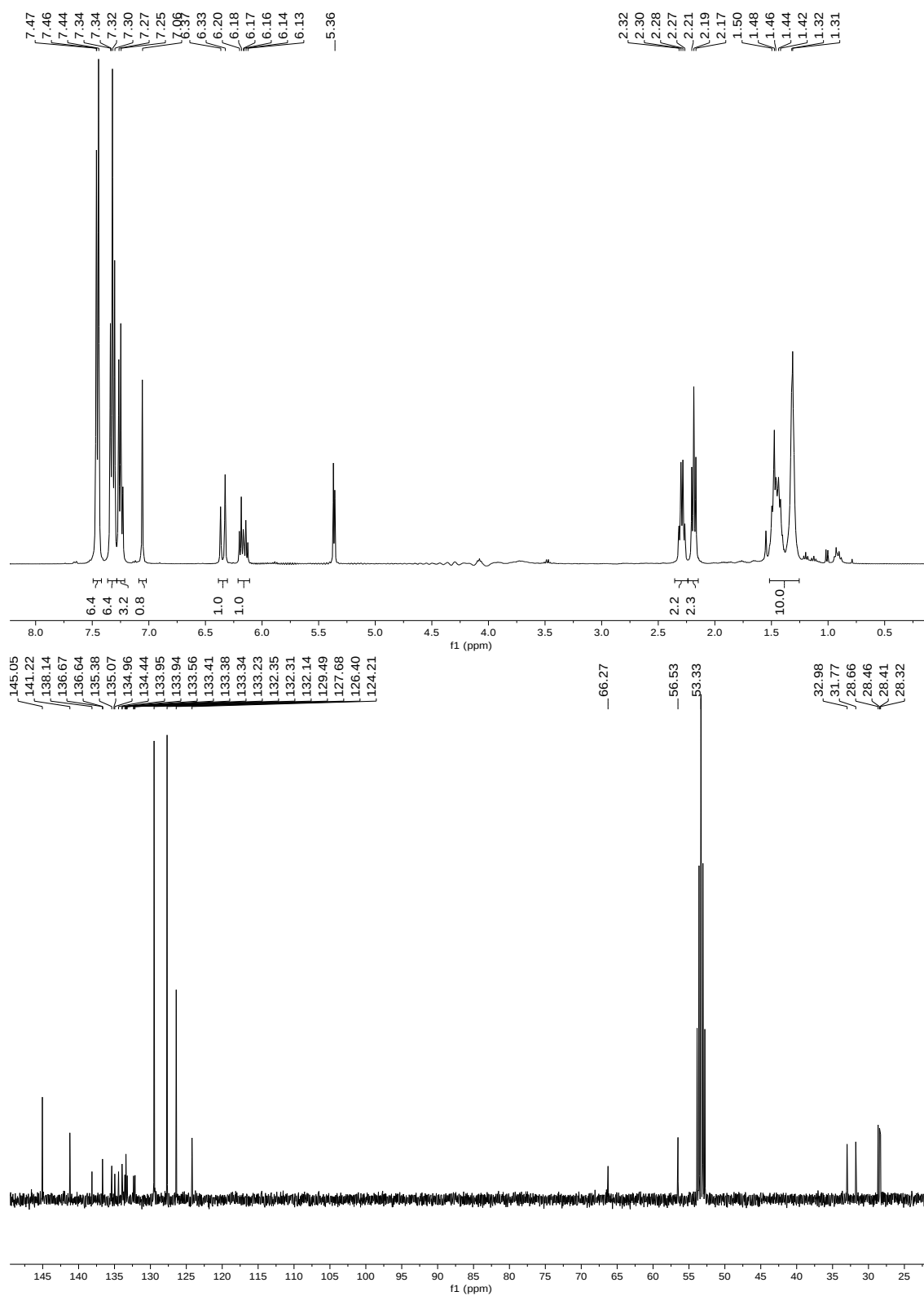


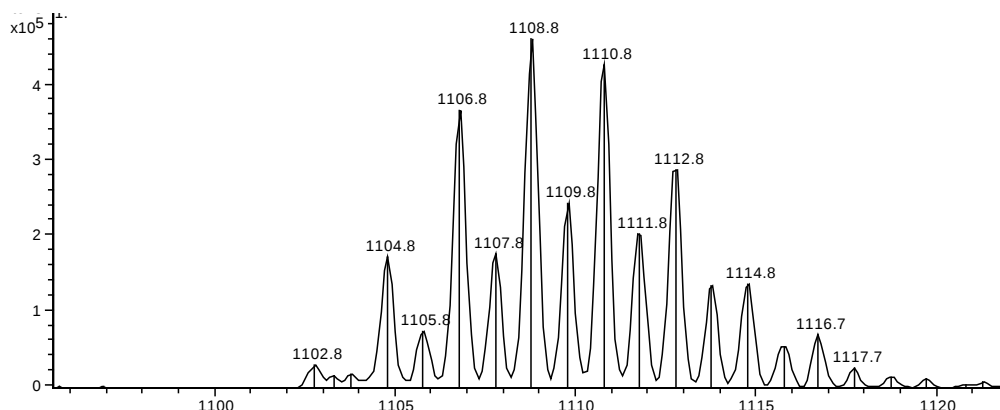
(E)-(8-(4-(bis(perchlorophenyl)methyl)-2,3,5,6-tetrachlorophenyl)oct-7-en-1-yl)(trityl)sulfane (7)



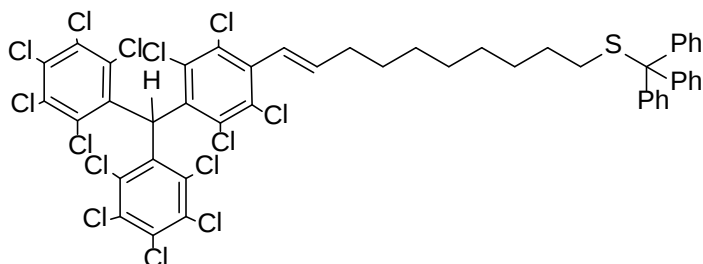
According to the general procedure, from potassium tert-butoxide (58 mg 0.51 mmol), PTM-P(O)(OEt)₂ (300 mg, 0.34 mmol) and 7-(tritylthio)heptanal (**4**) (263 mg, 0.68 mmol) in THF (10 mL), the compound **7** was obtained as a white powder (yield, 67%). ¹H-NMR (400 MHz, CD₂Cl₂) δ/ppm: 7.49 – 7.42 (m, 6H), 7.32 (t, *J* = 7.5 Hz, 6H), 7.25 (t, *J* = 7.2 Hz, 3H), 7.06 (s, 1H), 6.35 (d, *J* = 16.1 Hz, 1H), 6.16 (dt, *J* = 16.1, 6.9 Hz, 1H), 2.29 (q, *J* = 6.8 Hz, 2H), 2.19 (t, *J* = 7.3 Hz, 2H), 1.53 – 1.20 (m, 8H); ¹³C-NMR (101 MHz, CD₂Cl₂) δ/ppm: 145.05, 141.22, 138.14, 136.67, 136.64, 135.38, 135.07, 134.96, 134.44, 133.95, 133.94, 133.56, 133.41, 133.38, 133.34, 133.23, 132.35, 132.31, 132.14, 129.49, 127.68, 126.40, 124.21, 66.27, 56.53, 53.33, 32.98, 31.77, 28.66, 28.46, 28.41, 28.32; FT-IR (ν/cm⁻¹): 3057.4, 2926.1, 2852.6, 1594.5, 1488.4, 1442.7, 1362.6, 1334.9, 1295.2, 1238.3, 1137.8, 1238.3, 1137.8, 1032.6, 966.2, 852.7,

807.2, 741.5, 696.9. **EM (m/z)** (ESi): calculated for $C_{46}H_{30}Cl_{14}S$: 1109.76; found: 1108.8 (M-1H).

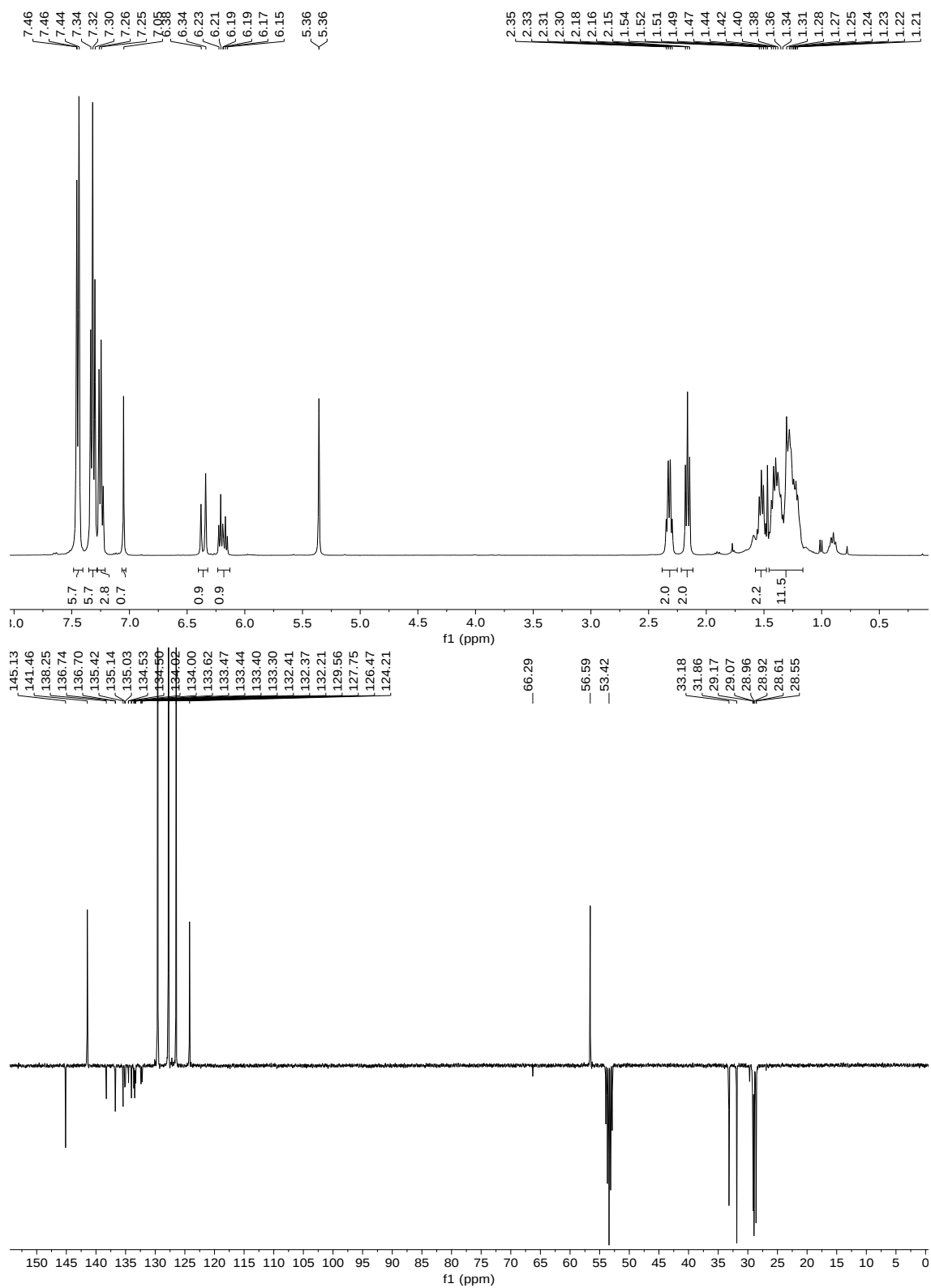


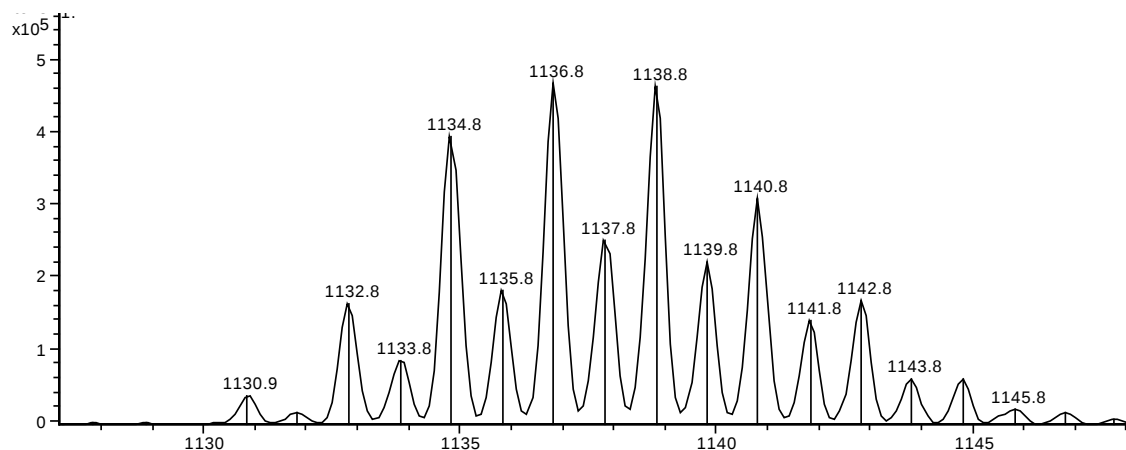


(E)-(10-(4-(bis(perchlorophenyl)methyl)-2,3,5,6-tetrachlorophenyl)dec-9-en-1-yl)(trityl)sulfane (8)

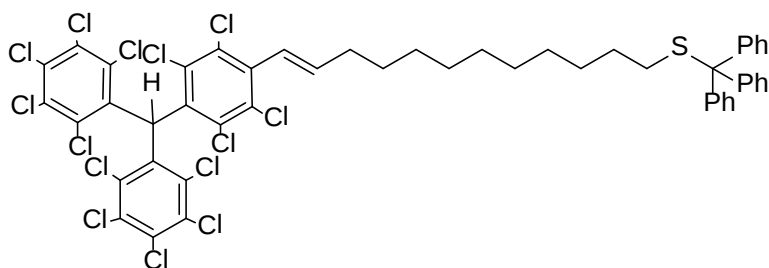


According to the general procedure, from potassium tert-butoxide (58 mg 0.51 mmol), PTM- $\text{P}(\text{O})(\text{OEt})_2$ (300 mg, 0.34 mmol) and 9-(tritylthio)nonanal (**5**) (283 mg, 0.68 mmol) in THF (10 mL), the compound **8** was obtained as a white powder (yield, 65%). **$^1\text{H-NMR}$** (400 MHz, CD_2Cl_2) δ /ppm: 7.48 – 7.41 (m, 6H), 7.32 (t, $J = 7.5$ Hz, 6H), 7.25 (t, $J = 7.2$ Hz, 3H), 7.05 (s, 1H), 6.36 (d, $J = 16.1$ Hz, 1H), 6.19 (dt, $J = 16.1, 6.9$ Hz, 1H), 2.32 (q, $J = 6.8$ Hz, 2H), 2.16 (t, $J = 7.4$ Hz, 2H), 1.52 (p, $J = 7.2$ Hz, 2H), 1.46 – 1.16 (m, 10H); **$^{13}\text{C-NMR}$** (101 MHz, CD_2Cl_2) δ /ppm: 145.13, 141.46, 138.25, 136.74, 136.70, 135.42, 135.14, 135.03, 134.53, 134.50, 134.02, 134.00, 133.62, 133.47, 133.44, 133.40, 133.30, 132.41, 132.37, 132.21, 129.56, 127.75, 126.47, 124.21, 66.29, 56.59, 53.42, 33.18, 31.86, 29.17, 29.07, 28.96, 28.92, 28.61, 28.55; **FT-IR** (ν/cm^{-1}): 3061.7, 2923.7, 2851.4, 1593.4, 1488.3, 1443.0, 1365.1, 1334.7, 1295.9, 1238.3, 1137.9, 1033.1, 965.1, 852.9, 807.5, 741.5, 967.7. **EM (m/z)** (ESI): calculated for $\text{C}_{48}\text{H}_{34}\text{Cl}_{14}\text{S}$: 1137.79; found: 1136.8 (M-1H).

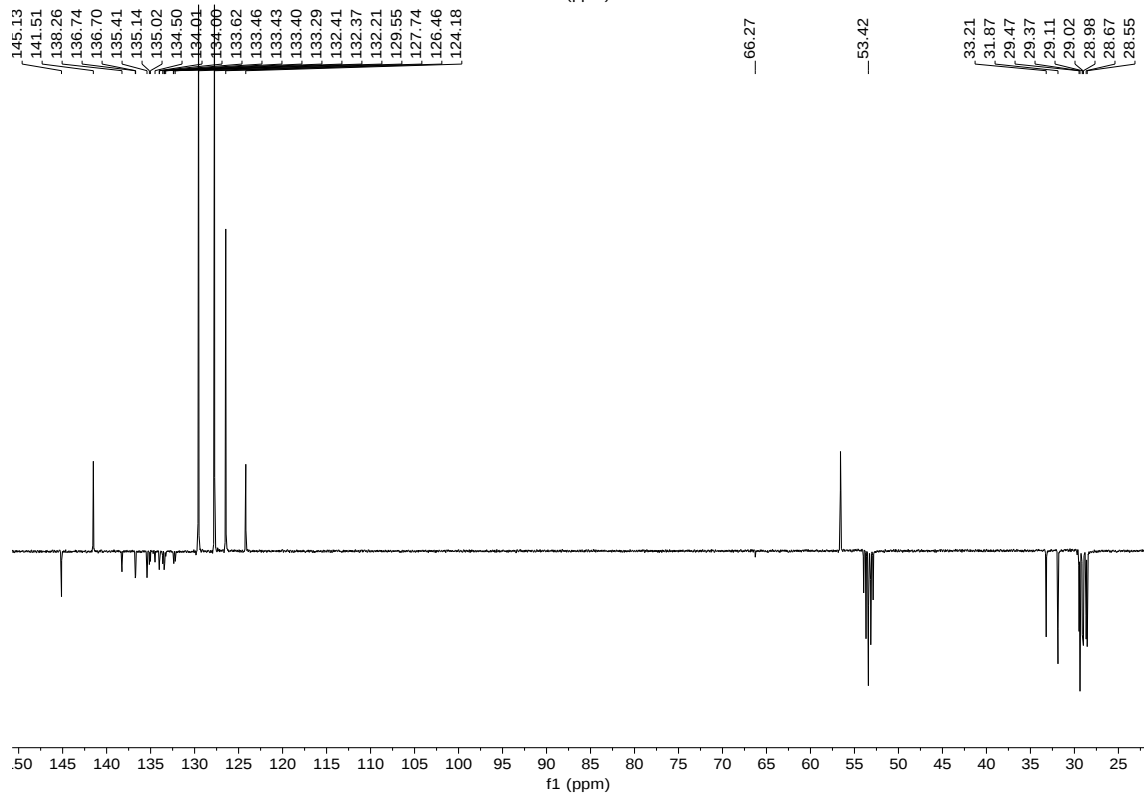
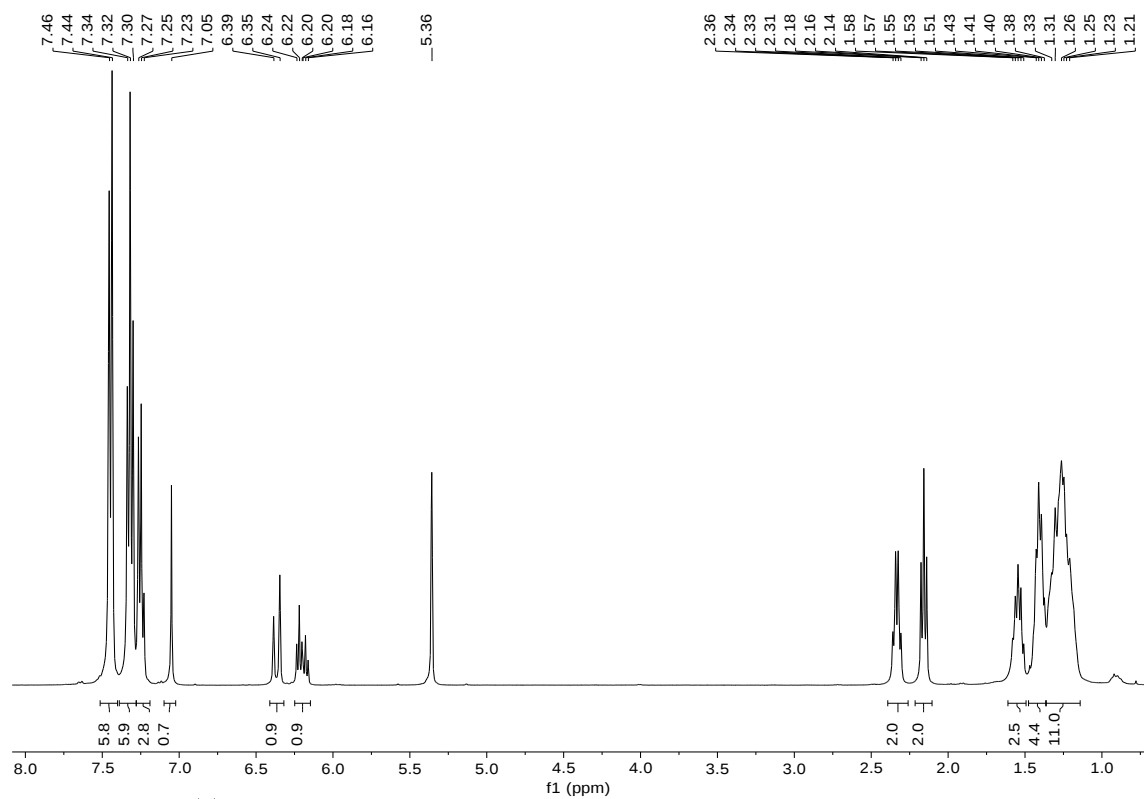


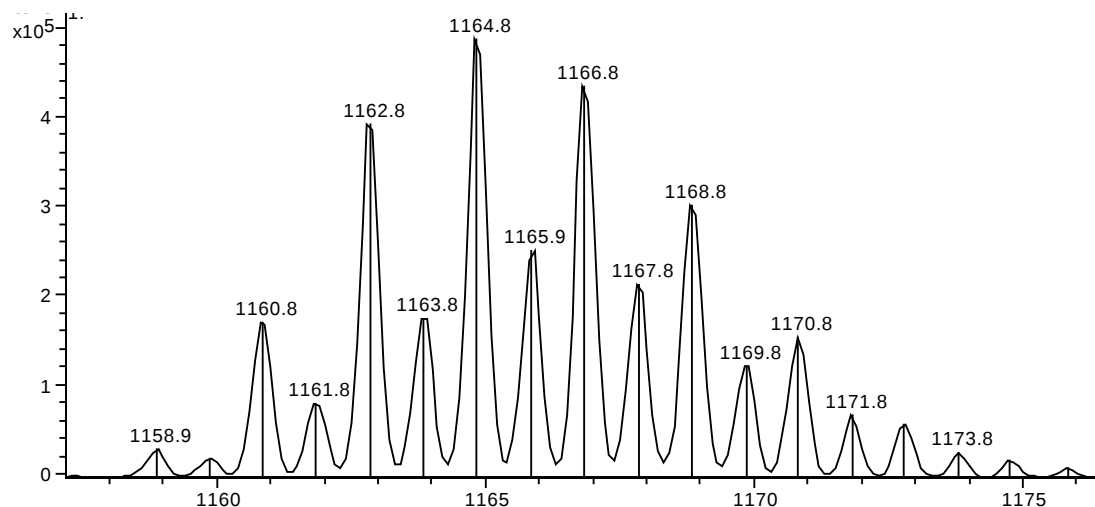


(E)-(12-(4-(bis(perchlorophenyl)methyl)-2,3,5,6-tetrachlorophenyl)dodec-11-en-1-yl)(trityl)sulfane (9)

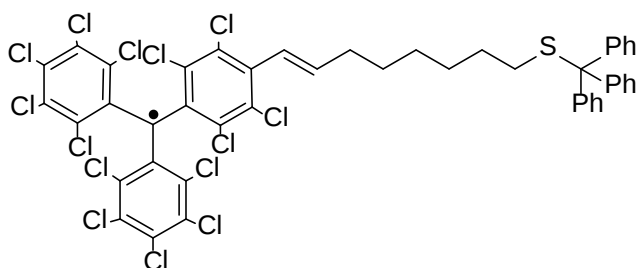


According to the general procedure, from potassium tert-butoxide (58 mg 0.51 mmol), PTM- $\text{P}(\text{O})(\text{OEt})_2$ (300 mg, 0.34 mmol) and 11-(tritylthio)undecanal (**6**) (302 mg, 0.68 mmol) in THF (10 mL), the compound **9** was obtained as a white powder (yield, 71%). $^1\text{H-NMR}$ (400 MHz, CD_2Cl_2) δ /ppm: 7.45 (d, $J = 7.6$ Hz, 6H), 7.32 (t, $J = 7.5$ Hz, 6H), 7.25 (t, $J = 7.2$ Hz, 3H), 7.05 (s, 1H), 6.37 (d, $J = 16.1$ Hz, 1H), 6.20 (dt, $J = 16.1, 6.8$ Hz, 1H), 2.33 (q, $J = 6.8$ Hz, 2H), 2.16 (t, $J = 7.4$ Hz, 2H), 1.55 (p, $J = 7.3$ Hz, 2H), 1.48 – 1.11 (m, 14H); $^{13}\text{C-NMR}$ (101 MHz, CD_2Cl_2) δ /ppm: 145.13, 141.51, 138.26, 136.74, 136.70, 135.41, 135.14, 135.02, 134.50, 134.01, 134.00, 133.62, 133.46, 133.43, 133.40, 133.29, 132.41, 132.37, 132.21, 129.55, 127.74, 126.46, 124.18, 66.27, 53.42, 33.21, 31.87, 29.47, 29.37, 29.11, 29.02, 28.98, 28.67, 28.55. **EM (m/z)** (ESI): calculated for $\text{C}_{50}\text{H}_{38}\text{Cl}_{14}\text{S}$: 1165.82; found: 1164.8 (M-1H).

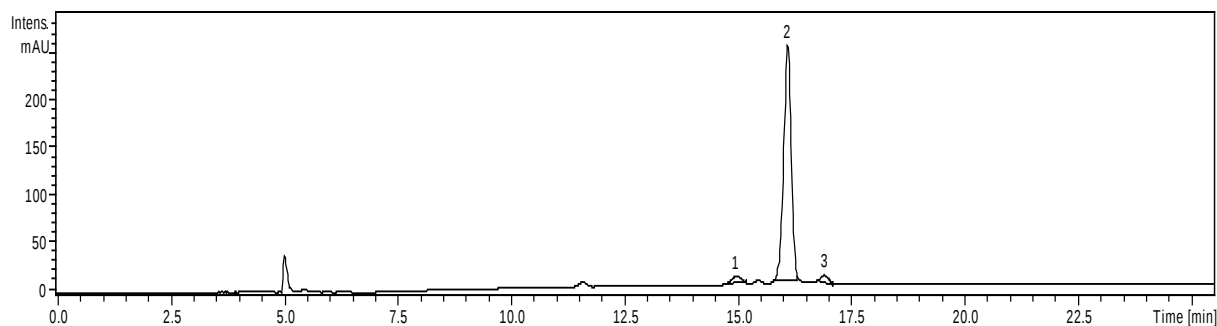


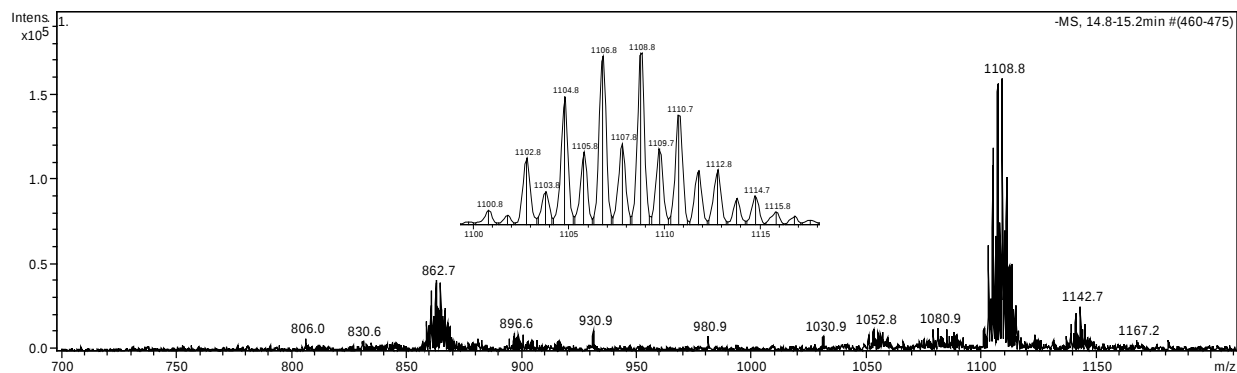


(E)-(8-(4-(bis(perchlorophenyl)methyl)-2,3,5,6-tetrachlorophenyl)oct-7-en-1-yl)(trityl)sulfane (radical) (10)

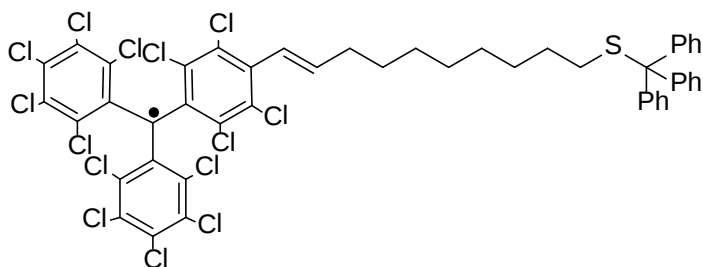


According to the general procedure, the compound **10** was obtained as a red powder in quantitative yield. **HPLC**: retention time: 14.9 (2.5% of cis isomer), 15.5min (95% of trans isomer), 16.9 (2.5% α H); **UV/Vis** (CH_2Cl_2): $\lambda(\text{nm})$ ($\log\epsilon$)= 388 (4.46), 515 (3.08), 567 (3.10). **CV**: $E^{1/2} = -0.16$ V (PTM reduction); **FT-IR** (v/cm^{-1}): 3057.1, 2924.2, 2853.2, 1653.5, 1596.1, 1489.5, 144.4, 1333.0, 1259.6, 1157.3, 1081.6, 1033.9, 857.7, 816.4, 738.1, 697.9, 652.3, 620.5; **EPR** (CH_2Cl_2 , r.t.): $g = 2.002804$; $\Delta H_{\text{PP}} = 1.3$ G, $a_{13\text{C}\alpha} = 29.6$ G; $a_{13\text{C}\beta} = 13.2$ G; $a_{13\text{C}\gamma} = 10.3$ G; $a_{1\text{H}} = 1.8$ G; **EM (m/z)** (ESI): calculated for $\text{C}_{46}\text{H}_{29}\text{Cl}_{14}\text{S}^{\cdot-}$: 1108.75; found: 1108.8 ($\text{M}^{\cdot-}$).

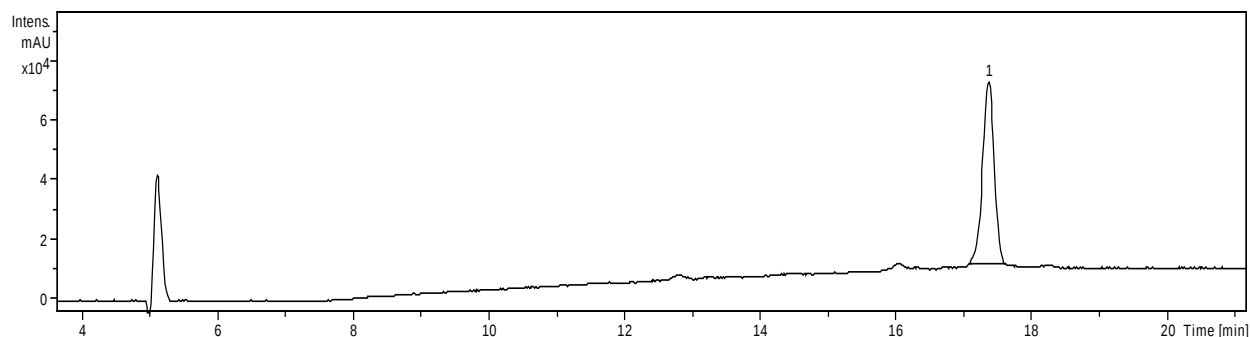


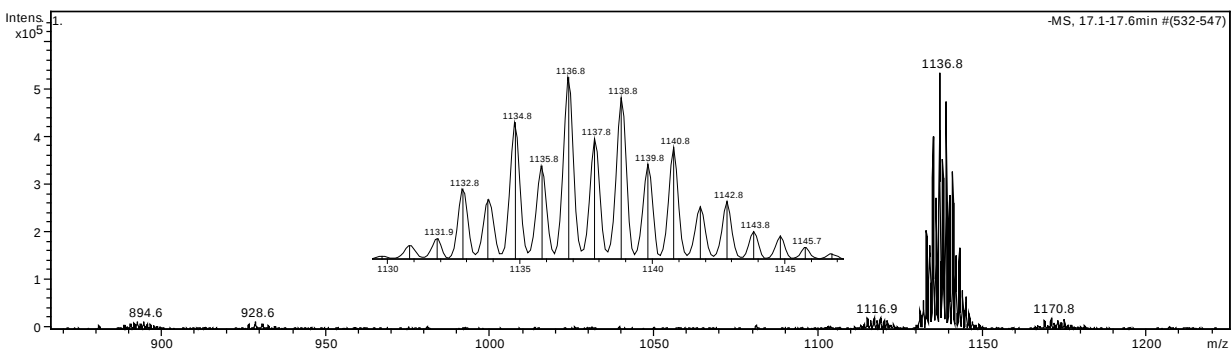


(E)-(10-(4-(bis(perchlorophenyl)methyl)-2,3,5,6-tetrachlorophenyl)dec-9-en-1-yl)(trityl)sulfane (radical) (11**)**

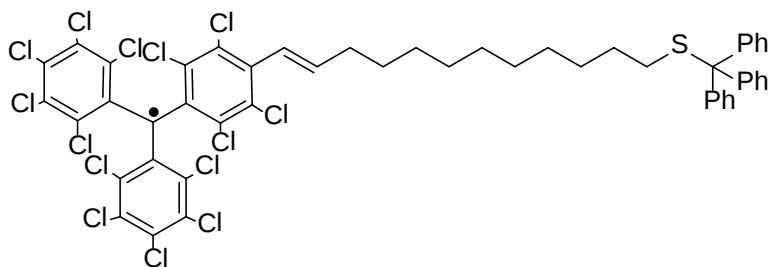


According to the general procedure, the compound **11** was obtained as a red powder in quantitative yield. **HPLC**, retention time: 17.4min (98% of trans isomer); **UV/Vis** (CH_2Cl_2): $\lambda(\text{nm})$ ($\log \epsilon$) = 387 (4.49), 515 (3.11), 566 (3.13); **CV**: $E^{1/2} = -0.16$ V (PTM reduction); **FT-IR** (ν/cm^{-1}): 3056.0, 2924.2, 2852.4, 1649.5, 1595.2, 1489.1, 1443.4, 1332.7, 1259.2, 1157.2, 1033.6, 966.06, 858.7, 815.9, 739.7, 697.8, 651.9, 619.7; **EPR** (CH_2Cl_2 , r.t.): $g = 2.002840$; $\Delta H_{\text{pp}} = 1.1$ G, $a_{13\text{C}\alpha} = 29.6$ G; $a_{13\text{C}\beta} = 13.2$ G; $a_{13\text{Cm}} = 10.2$ G; $a_{1\text{H}} = 1.8$ G; **EM (m/z)** (Electrospray): calculated for $\text{C}_{48}\text{H}_{33}\text{Cl}_{14}\text{S}^+$: 1136.78; found: 1136.8 (M^+).

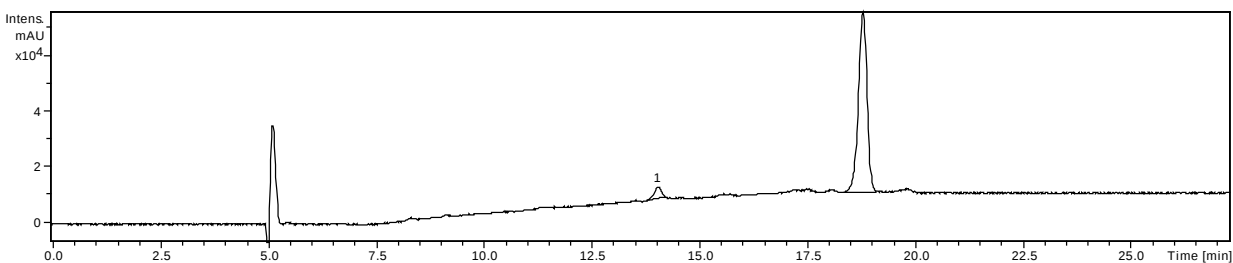


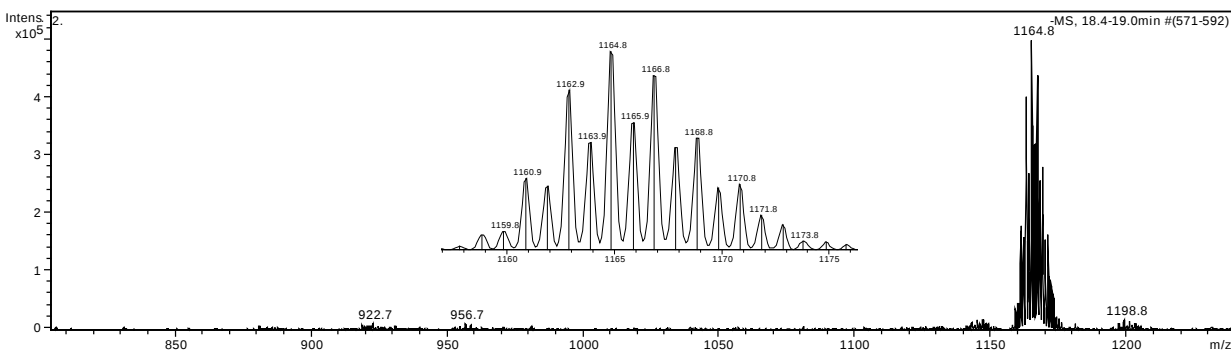


(E)-(12-(4-(bis(perchlorophenyl)methyl)-2,3,5,6-tetrachlorophenyl) dodec-11-en-1-yl)(trityl)sulfane (radical) (12)

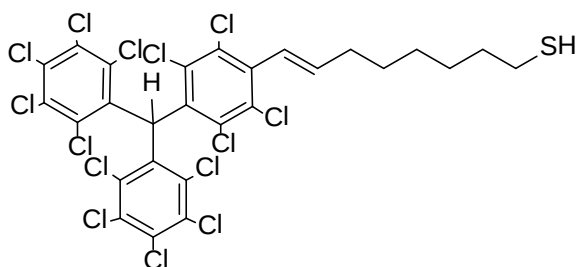


According to the general procedure, the compound **12** was obtained as a red powder in quantitative yield. **HPLC**, retention time: 18.8min (96% of trans isomer); **UV/Vis** (CH_2Cl_2): $\lambda(\text{nm})$ ($\log \epsilon$) = 388 (4.49), 515 (3.12), 566 (3.14); **CV**: $E^{1/2} = -0.16$ V (PTM reduction); **FT-IR** (v/cm^{-1}): 3055.7, 2924.2, 2852.3, 1658.5, 1595.6, 1489.5, 1444.0, 1332.8, 1259.4, 1156.9, 1080.9, 1033.4, 967.2, 858.5, 816.0, 738.6, 697.8, 673.2, 651.8, 620.1; **EPR** (CH_2Cl_2 , r.t.): $g = 2.002945$; $\Delta H_{\text{PP}} = 1.4$ G, $a_{13\text{C}\alpha} = 29.6$ G; $a_{13\text{C}\beta} = 13.2$ G; $a_{13\text{Cm}} = 10.1$ G; $a_{1\text{H}} = 1.8$ G; **EM (m/z)** (Electrospray): calculated for $\text{C}_{48}\text{H}_{32}\text{Cl}_{14}\text{S}^{\cdot}$: 1164.81; found: 1164.8 ($\text{M}^{\cdot}$).

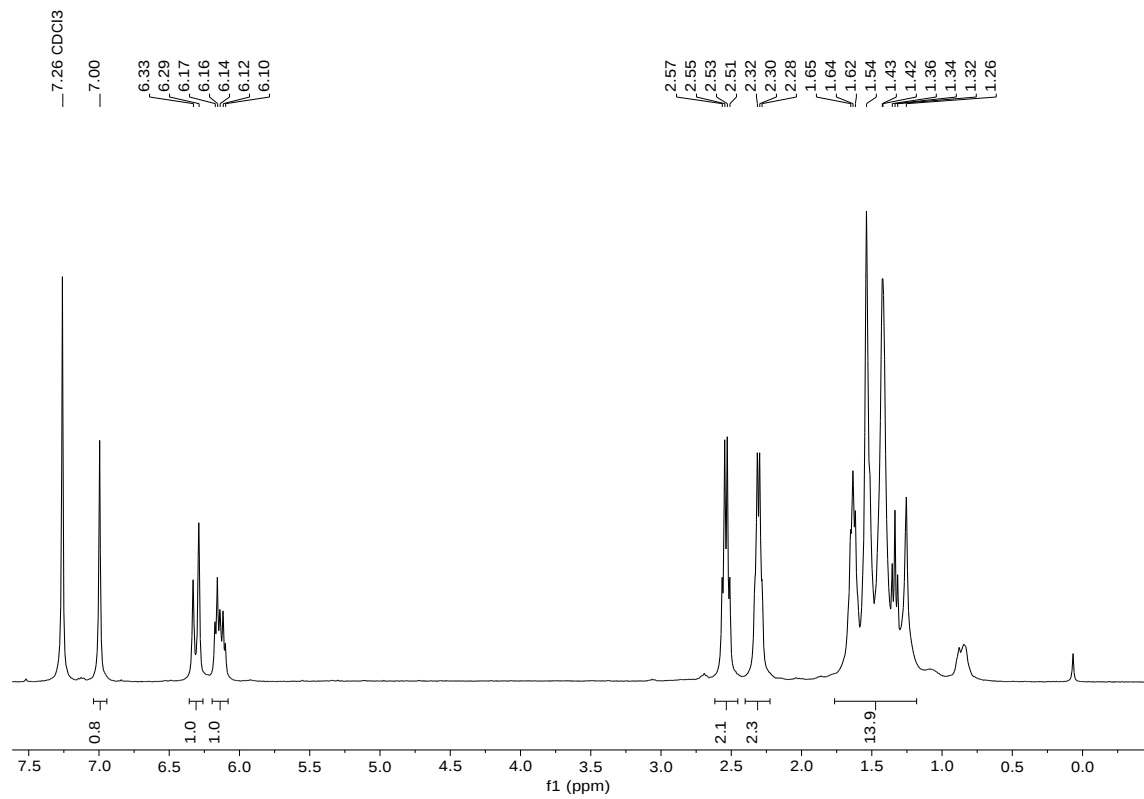
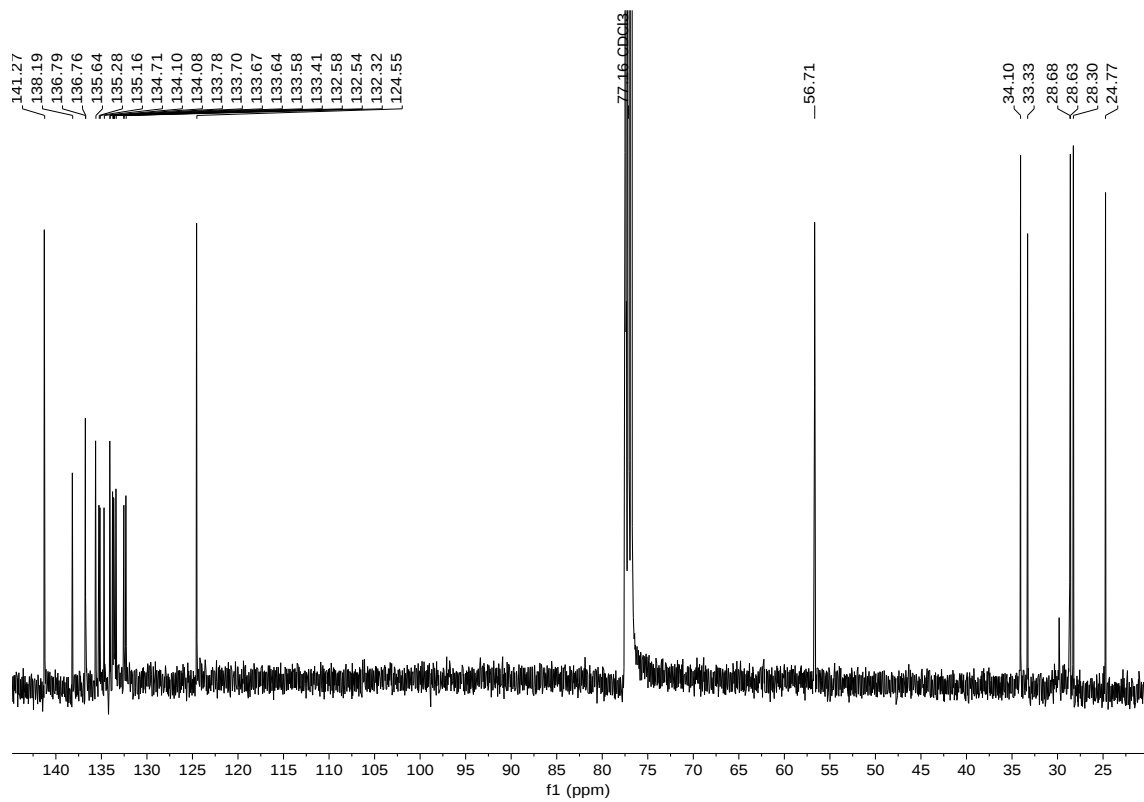


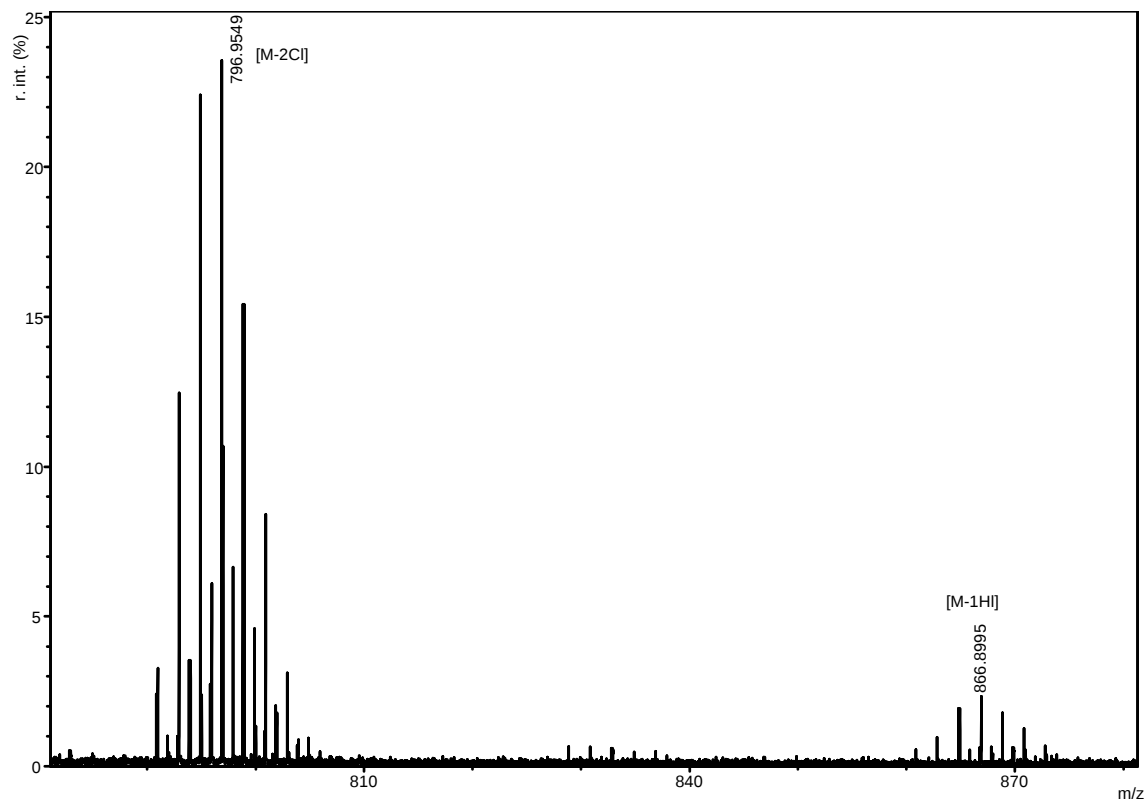


(E)-8-(4-(bis(perchlorophenyl)methyl)-2,3,5,6-tetrachlorophenyl)oct-7-ene-1-thiol (NR8)

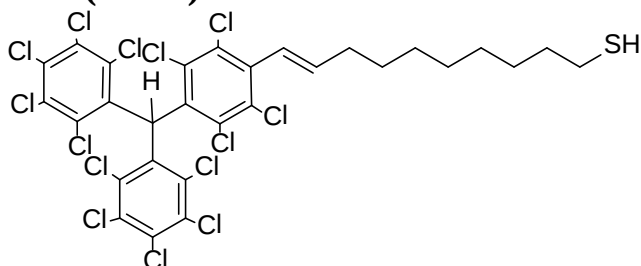


The compound **NR8** was obtained as white powder in quantitative yield, using the general methodology described for the generation of free thiols. ¹H-NMR (400 MHz, CD₂Cl₂) δ/ppm: 7.00 (s, 1H), 6.31 (d, *J* = 16.1 Hz, 1H), 6.14 (dt, *J* = 15.7, 6.7 Hz, 1H), 2.54 (q, *J* = 7.2 Hz, 2H), 2.31 (q, *J* = 6.3 Hz, 2H), 1.71 – 1.17 (m, 9H); ¹³C-NMR (101 MHz, CDCl₃) δ/ppm: 141.27, 138.19, 136.79, 136.76, 135.64, 135.28, 135.16, 134.71, 134.10, 134.08, 133.78, 133.70, 133.67, 133.64, 133.58, 133.41, 132.58, 132.54, 132.32, 124.55, 77.16, 56.71, 34.10, 33.33, 28.68, 28.63, 28.30, 24.77. FT-IR (ν/cm⁻¹): 2927.0, 2853.9, 2343.8, 1654.2, 1533.8, 1461.7, 1363.7, 1335.5, 1298.7, 1241.0, 1139.2, 963.9, 855.3, 807.2, 752.8, 717.0, 675.2, 692.5. EM (m/z) (MALDI-TOF): calculated for C₂₇H₁₆Cl₁₄S: 867.65; found: 866.90 (M-1H) and 796.95 (M-2Cl).

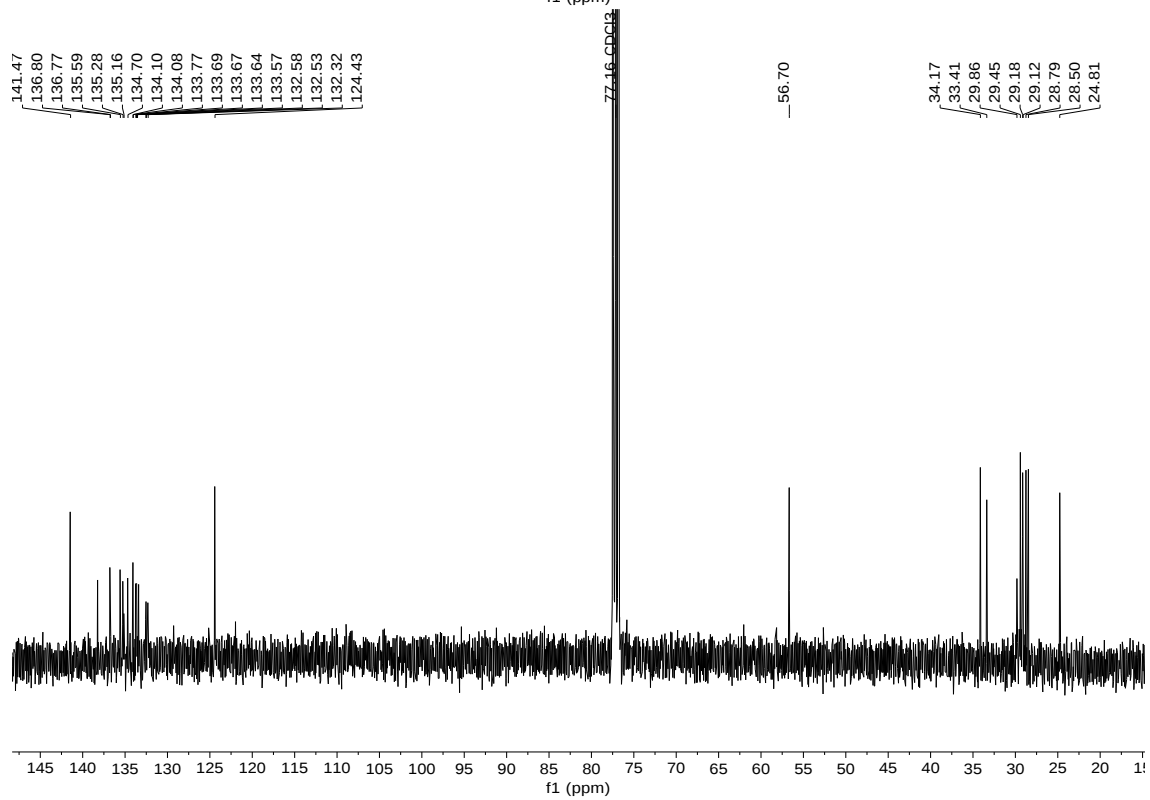
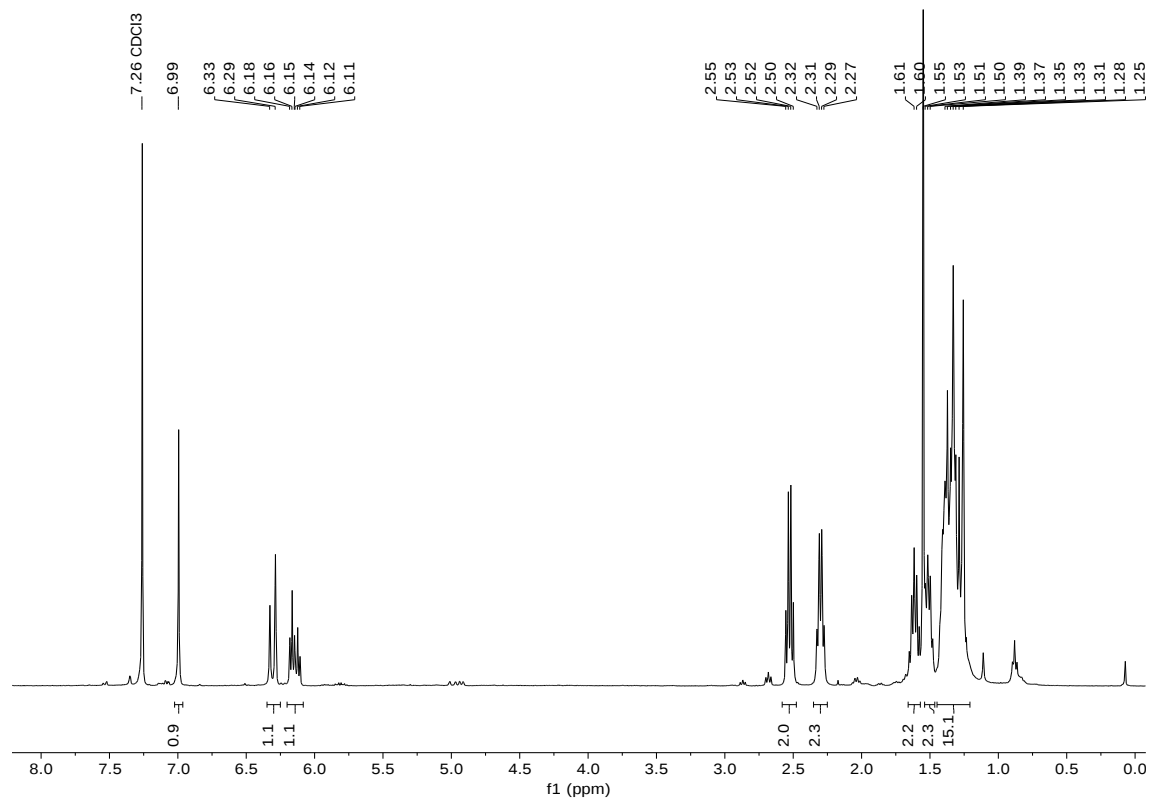


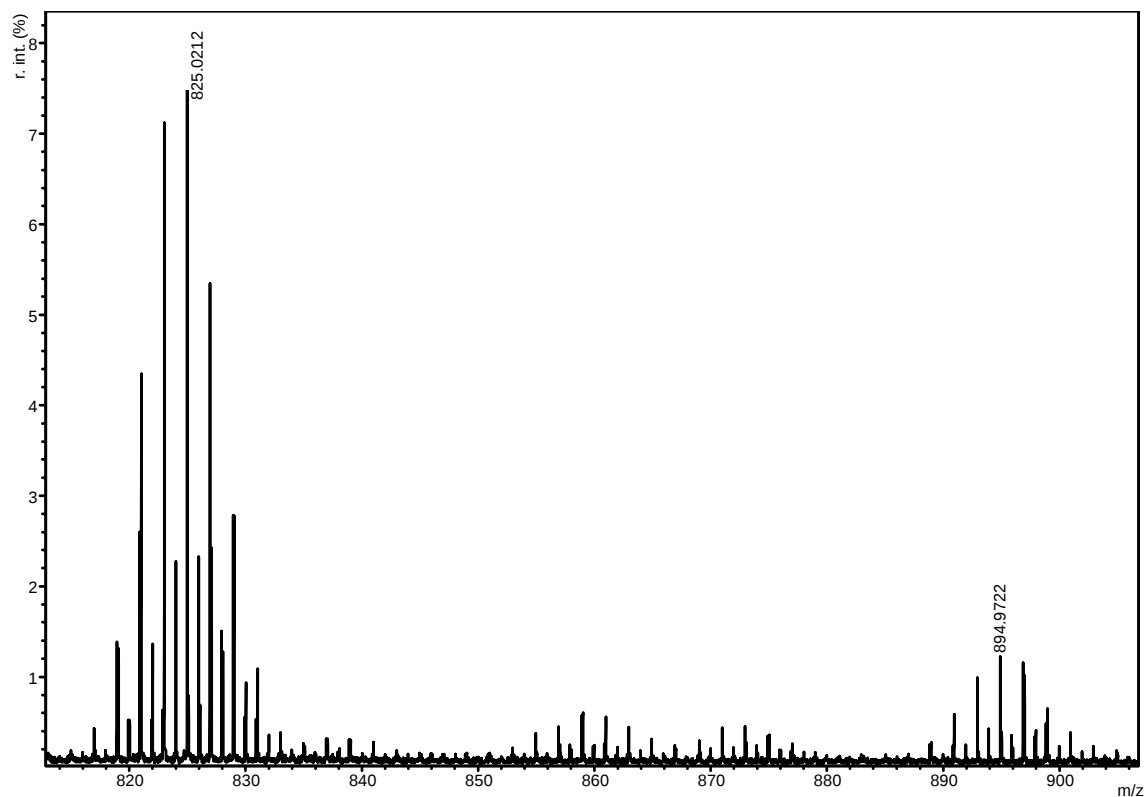


(E)-10-(4-(bis(perchlorophenyl)methyl)-2,3,5,6-tetrachlorophenyl)dec-9-ene-1-thiol (NR10).

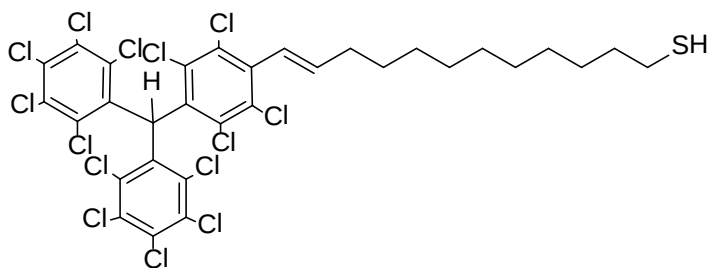


The compound **NR10** was obtained as white powder in quantitative yield, using the general methodology described for the generation of free thiols. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ /ppm: 6.99 (s, 1H), 6.31 (d, $J = 16.1$ Hz, 1H), 6.14 (dt, $J = 16.1, 6.8$ Hz, 1H), 2.52 (q, $J = 7.4$ Hz, 2H), 2.30 (q, $J = 6.8$ Hz, 2H), 1.61 (p, $J = 7.2$ Hz, 2H), 1.51 (p, $J = 7.2$ Hz, 2H), 1.43 – 1.21 (m, 9H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ /ppm: 141.47, 136.80, 136.77, 135.59, 135.28, 135.16, 134.70, 134.10, 134.08, 133.77, 133.69, 133.67, 133.64, 133.57, 132.58, 132.53, 132.32, 124.43, 77.16, 56.70, 34.17, 33.41, 29.86, 29.45, 29.18, 29.12, 28.79, 28.50, 24.81.; **FT-IR** (ν/cm^{-1}): 2926.5, 2854.0, 1710.0, 1653.9, 1461.1, 1365.2, 1337.0, 1296.8, 1239.7, 1193.0, 1137.7, 1042.9, 966.8, 899.9, 855.2, 808.4, 739.0, 690.1, 648.4, 609.9; **EM (m/z)** (MALDI-TOF): calculated for $\text{C}_{29}\text{H}_{20}\text{Cl}_{14}\text{S}$: 895.68; found: 894.97 (M-1H) and 825.02 (M-2Cl).

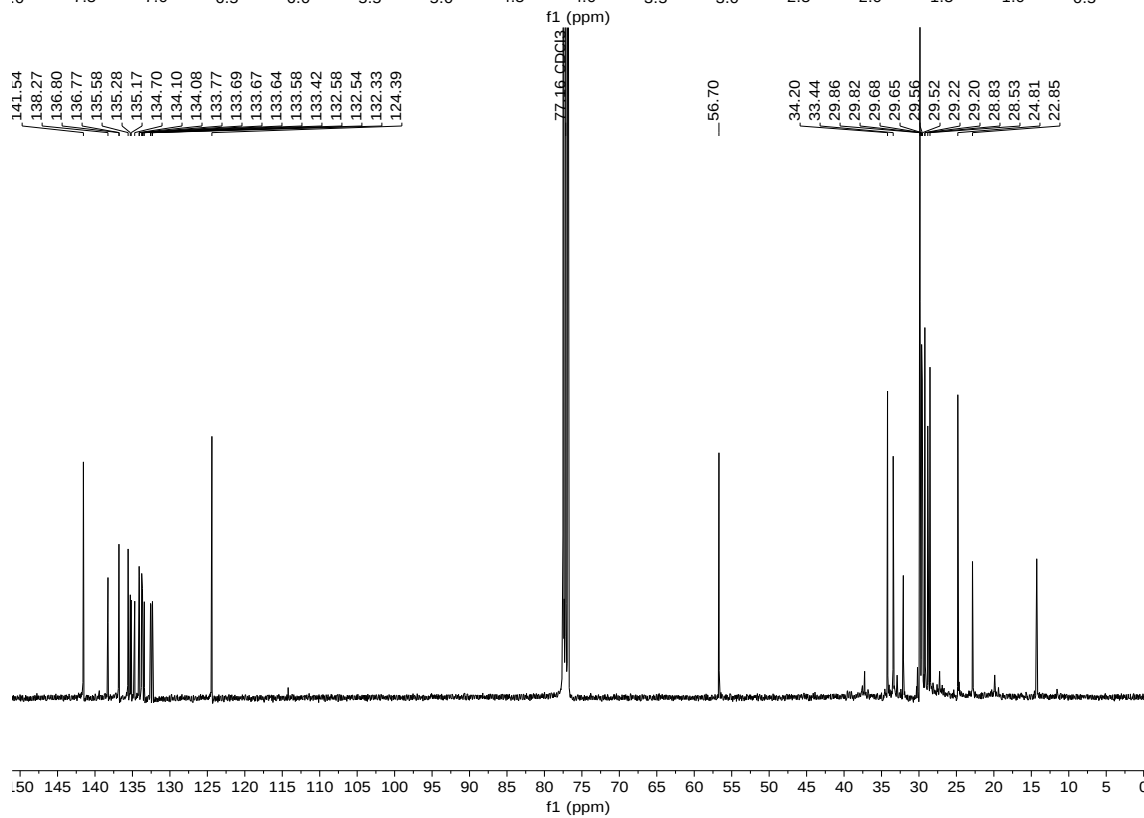
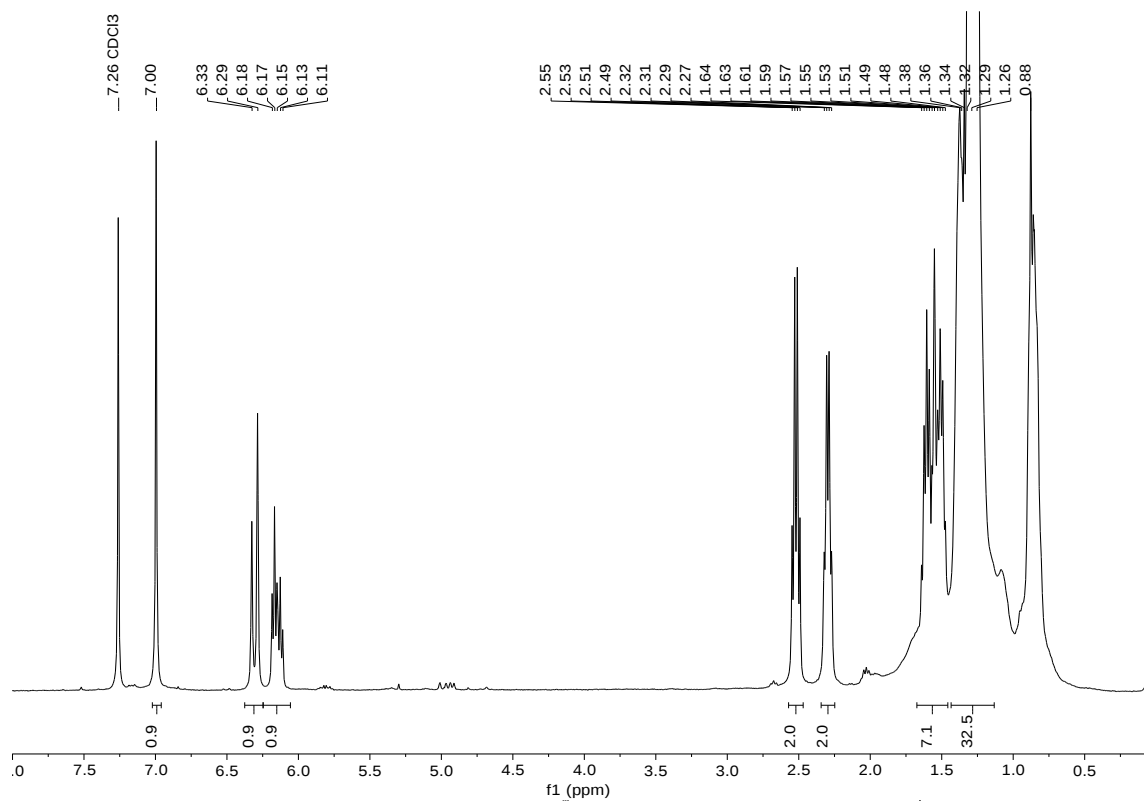


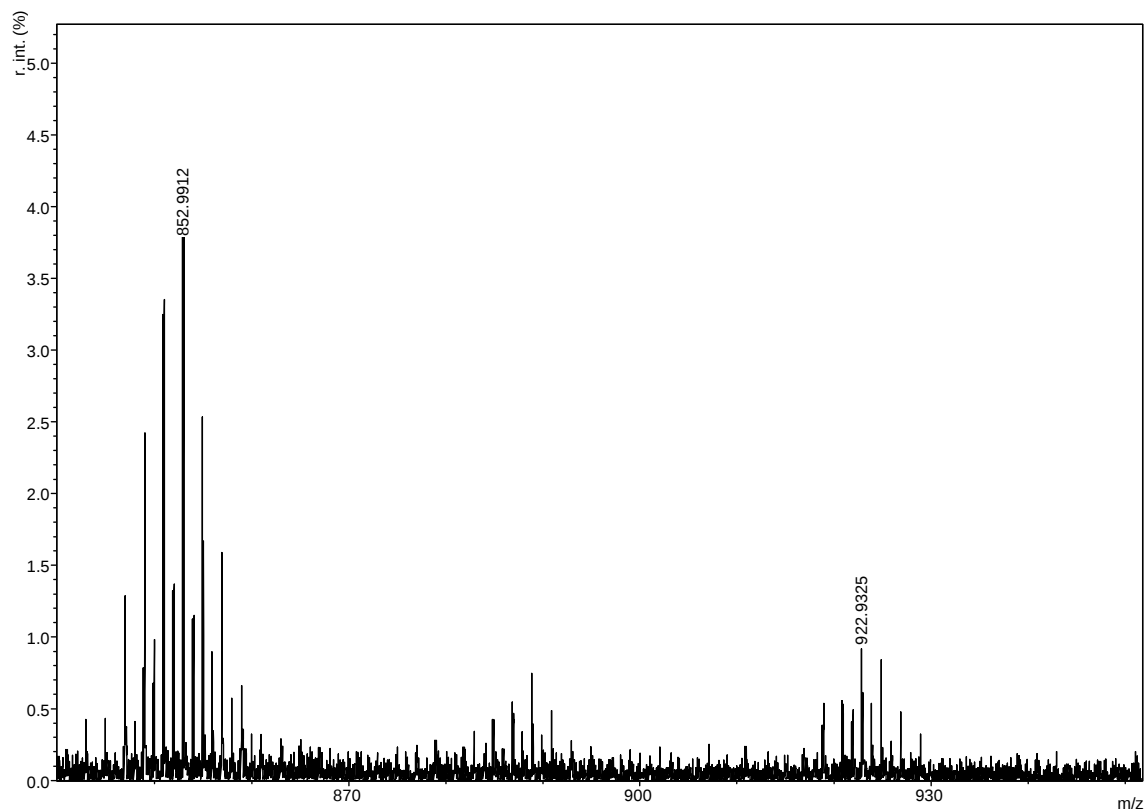


(E)-12-(4-(bis(perchlorophenyl)methyl)-2,3,5,6-tetrachlorophenyl) dodec-11-ene-1-thiol (NR12)

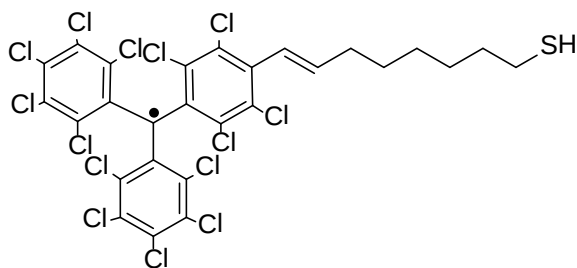


The compound **NR12** was obtained as white powder in quantitative yield, using the general methodology described for the generation of free thiols. ¹H-NMR (400 MHz, CDCl₃) δ/ppm: 7.00 (s, 1H), 6.31 (d, *J* = 16.2 Hz, 1H), 6.15 (dt, *J* = 16.1, 6.9 Hz, 1H), 2.52 (q, *J* = 7.4 Hz, 2H), 2.30 (q, *J* = 6.7 Hz, 2H), 1.67 – 1.45 (m, 5H), 1.45 – 1.12 (m, 16H); ¹³C-NMR (101 MHz, CDCl₃) δ/ppm: 141.54, 138.27, 136.80, 136.77, 135.58, 135.28, 135.17, 134.70, 134.10, 134.08, 133.77, 133.69, 133.67, 133.64, 133.58, 133.42, 132.58, 132.54, 132.33, 124.39, 77.16, 56.70, 34.20, 33.44, 29.86, 29.82, 29.68, 29.65, 29.56, 29.52, 29.22, 29.20, 28.83, 28.53, 24.81, 22.85; FT-IR (ν/cm⁻¹): 2924.5, 2852.6, 1717.8, 1653.2, 1532.6, 1461.2, 1365.3, 1336.1, 1296.1, 1263.7, 1238.8, 1137.4, 966.7, 854.8, 807.6, 737.8, 717.6, 700.1, 674.9, 648.0, 606.9; EM (m/z) (MALDI-TOF): calculated for C₃₁H₂₄Cl₁₄S: 923.71; found: 922.93 (M-1H) and 852.99 (M-2Cl).

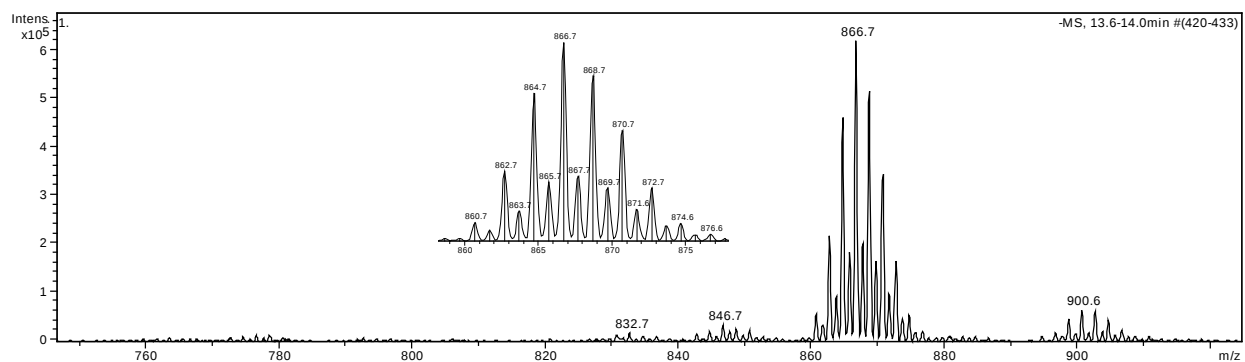
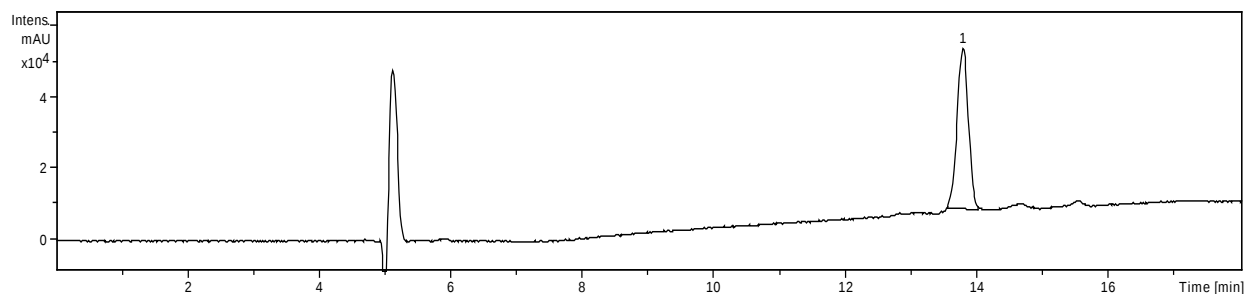




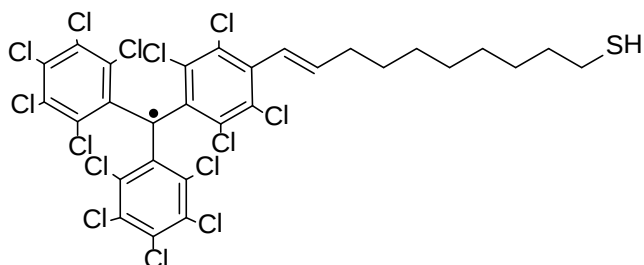
(E)-8-(4-(bis(perchlorophenyl)methyl)-2,3,5,6-tetrachlorophenyl)oct-7-ene-1-thiol radical (R8)



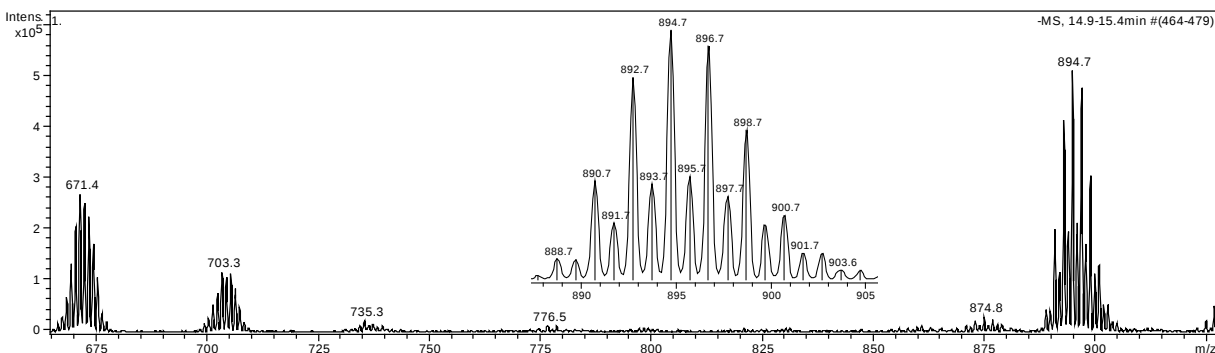
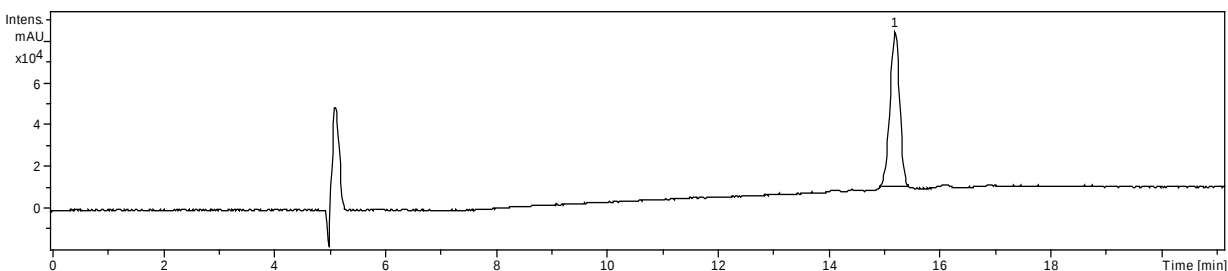
The compound **R8** was obtained as a red powder in quantitative yield, using the general methodology described for the generation of the free thiol groups. **HPLC**, retention time 13.8min: (97% of trans isomer); **UV/Vis** (CH_2Cl_2): $\lambda(\text{nm})$ ($\log \epsilon$) = 387 (4.43), 515 (3.10), 566 (3.14); **CV**: $E^{1/2} = -0.18$ V (PTM reduction); **FT-IR** (v/cm^{-1}): 3025.5, 2926.1, 2853.6, 1647.8, 1597.7, 1511.2, 1494.2, 1450.8, 1332.3, 12594.4, 1157.4, 1120.1, 1078.6, 1049.1, 1031.4, 966.1, 860.2, 815.8, 752.9, 732.7, 698.1, 651.7, 605.1; **EPR** (CH_2Cl_2 , r.t.): $g = 2.002552$; $\Delta H_{\text{pp}} = 1.4$ G, $a_{13\text{C}\alpha} = 29.8$ G; $a_{13\text{C}\beta} = 13.1$ G; $a_{13\text{Cm}} = 10.1$ G; $a_{1\text{H}} = 1.8$ G; **EM** (m/z) (**ESI**): calculated for $\text{C}_{27}\text{H}_{15}\text{Cl}_{14}\text{S}^{\cdot}$: 866.6; found: 866.7 ($M^{\cdot}$).



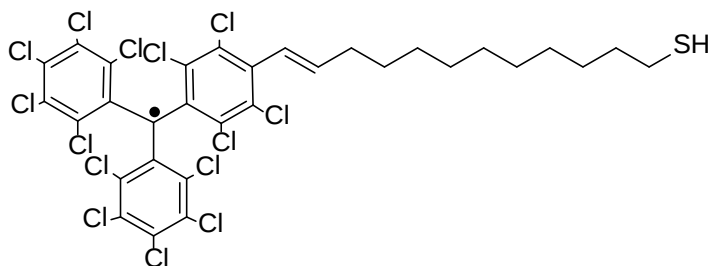
(E)-10-(4-(bis(perchlorophenyl)methyl)-2,3,5,6-tetrachlorophenyl)dec-9-ene-1-thiol radical (R10)



The compound **R10** was obtained as a red powder in quantitative yield, using the general methodology described for the generation of the free thiol groups. **HPLC** retention time: 15.2min (98% of trans isomer); **UV/Vis** (CH₂Cl₂): λ (nm) (log ϵ) = 388 (4.46), 515 (3.08), 566 (3.12); **CV**: $E^{1/2}$ = -0.18 V (PTM reduction); **FT-IR** (v/cm⁻¹): 3026.8, 2924.7, 2852.7, 1647.37, 1598.3, 1511.0, 1494.9, 1455.2, 1332.3, 1258.9, 1157.4, 1118.9, 1048.3, 965.7, 860.1, 815.4, 750.7, 732.9, 698.9; **EPR** (CH₂Cl₂, r.t.): g = 2.002431; ΔH_{pp} = 1.4 G, $a_{13C\alpha}$ = 29.5 G; $a_{13C\beta}$ = 13.0 G; a_{13Cm} = 10.0 G; a_{1H} = 1.8 G; **EM (m/z)** (ESI): calculated for C₂₉H₁₉Cl₁₄S[•]: 894.7; found: 894.7 (M[•]).



(E)-12-(4-(bis(perchlorophenyl)methyl)-2,3,5,6-tetrachlorophenyl) dodec-11-ene-1-thiol radical (R12)



The compound **R12** was obtained as a red powder in quantitative yield, using the general methodology described for the generation of the free thiol groups. **HPLC** retention time: 21.1min (92% of trans isomer), 22.8 (8% of α H derivative); **UV/Vis** (CH_2Cl_2): $\lambda(\text{nm})$ ($\log \epsilon$) = 387 (4.50), 515 (3.13), 566 (3.16); **CV**: $E^{1/2} = -0.18$ V (PTM reduction); **FT-IR** (v/cm^{-1}): 2924.4, 2852.4, 1648.6, 1510.6, 1460.7, 1332.3, 1259.1, 1157.1, 1119.7, 1048.3, 966.4, 860.2, 815.7, 752.1, 733.9, 707.0, 651.4, 606.1; **EPR** (CH_2Cl_2 , r.t.): $g = 2.002803$; $\Delta H_{\text{pp}} = 1.2$ G, $a_{13\text{C}\alpha} = 29.8$ G; $a_{13\text{C}\beta} = 13.2$ G; $a_{13\text{Cm}} = 10.3$ G; $a_{1\text{H}} = 1.8$ G; **EM** (m/z) (ESI): calculated for $\text{C}_{31}\text{H}_{23}\text{Cl}_{14}\text{S}^+$: 922.7; found: 922.7 (M^+).

