Supporting Information

Turn-on Phosphorescent Sensor of Pb^{2+} in Water by formation of a coordination polymer

Marco Villa, Myriam Roy, Giacomo Bergamini, Marc Gingras and Paola Ceroni

1. Experimental procedures and methodologies

Materials and General Procedures

All reagents, solvents and chemicals were purchased from Sigma-Aldrich, Fisher, or Alfa-Aesar and used directly unless otherwise stated (purity: reagent or analytical grade). Solvents were stored for several days over freshly activated 3 Å molecular sieves (activated for 3 h at 250 °C). All the reactions were monitored by TLC or LCMS or FT-IR (ATR)

Photophysical Measurements

The experiments were carried out in air-equilibrated tetrahydrofuran or water solution at 298 K unless otherwise noted. Luminescence measurements at 77 K were performed in dichloromethane/methanol (1:1 v/v). UV–vis absorption spectra were recorded with a PerkinElmer λ40 spectrophotometer using quartz cells with path length of 1.0 cm. Luminescence spectra were performed with a PerkinElmer LS-50 or an Edinburgh FLS920 spectrofluorimeter equipped with a Hamamatsu R928 phototube. Lifetimes shorter than 10 µs were measured by the above-mentioned Edinburgh FLS920 spectrofluorimeter equipped with a TCC900 card for data acquisition in time-correlated single-photon counting experiments (0.5 ns time resolution) with a D_2 lamp. Longer lifetimes were measured by the PerkinElmer LS-50. Emission quantum yields were measured following the method of Demas and Crosby[2] (standard used: $[Ru(bpy)_3]^{2+}$ in aqueous solution)[3]. For solid samples, the emission quantum yield was calculated from corrected emission spectra registered by an Edinburgh FLS920 spectrofluorimeter equipped with a barium sulfate coated integrating sphere (4 in.), a 450W Xe lamp (λ excitation tunable by a monochromator supplied with the instrument) as light source, and a R928 photomultiplayer tube, following the procedure described by De Mello et al.[4] Global fitting of absorption and emission spectra has been performed by Specfit software. The estimated experimental errors are 2 nm on the band maximum, 5% on the molar absorption coefficient, luminescence lifetime and log *K* values, 10% on the emission quantum yield in solution, and 20% on the emission quantum yield in solid.

Thin-Layer chromatography (TLC): TLC analyses were performed on precoated silica gel (Alugram® SilG/UV254gel) aluminium plates from Macherey-Nagel. Compounds were visualized with UV-light (254 or 365 nm)

Flash chromatography was performed over silica gel 60, Merck type 230-400 mesh (40-63µm).

NMR spectra ^{1}H (400 MHz) and ^{13}C (100.53 MHz) were recorded on JEOL ECX-400 spectrometer signals of the residual protic solvent $CHCl_3$ at 7.26 ppm and DMSO-d_6 at 2.50 ppm were used as internal references, along with TMS. As for ^{13}C NMR spectra, the central resonance of the triplet for $CDCl_3$ at 77.16 ppm and the signal for DMSO-d_6 at 39.52 ppm were used as internal references.[1] The resonance multiplicities in the ^{1}H NMR spectra are described as "s" (singlet), "d"(doublet), "t" (triplet), "q" (quarted), "sept" (septet) "m" (multiplet) or "b" (broad).

LC-MS (APCI and ESI): Analyses were performed with a C18 Phenomenex Luna (3µm; 100 x 2 mm) column on a Shimadzu LCMS-2020 fitted with two LC-20AD prominence pumps equipped with a DGU-20AD prominence line degasser, a SIL-20AHT prominence auto-sampler, a CTO-20A prominence column oven, a SPD-20A prominence UV/Vis detector, a FCV-20AH valve unit, a Parker NitroFloLab nitrogen generator and either an APCI SET or an ESI SET detector. Positive or negative modes were used for both APCI and ESI mode.

HRMS (ESI): High resolution mass spectra were recorded at the Spectropôle of Marseille (France) in triplicate with double internal standards. Oligomers of poly(propylene glycol) were used as internal standards. Ionization was facilitated by some adducts with Ag+ , NH_4+ or Na+ ions. Two spectrometers were used: a) SYNAPT G2 HDMS (Waters) instrument equipped with an ESI source and a TOF analyzer in a positive mode. b) QStar Elite (Applied Biosystems SCIEX) instrument equipped with an atmospheric ionization source (API). The samples were ionized under ESI with an electrospray voltage of 5500 V; orifice voltage: 10V, and air pressure of the nebulizer at 20 psi. A TOF analyzer was used in a positive mode.

FT-IR: Infrared absorption spectra were directly recorded on solids or neat liquids on a Perkin-Elmer Spectrum 100 FT-IR Spectrometer equipped with a universal ATR accessory (contact crystal: diamond).

Elemental analysis: Elemental analyses were performed by the Spectropôle of Marseille on a Thermo Finnigan EA 1112 equipped with an autosampler and Eager Xperience software.

2. Photophysical measurements

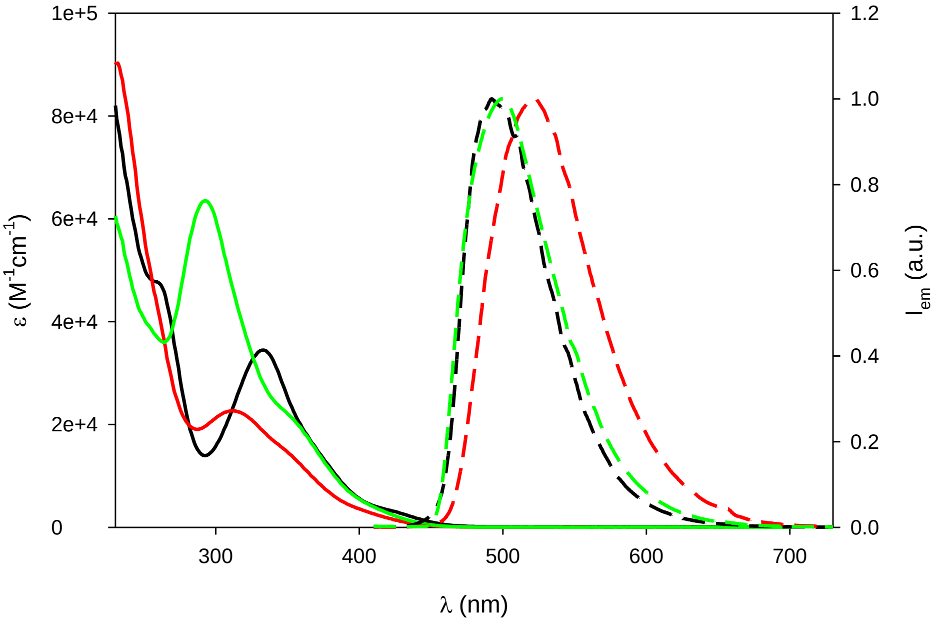


Figure S1 Absorption spectra (solid lines) in CH_2Cl_2 and phosphorescence spectra (dashed lines) in CH_2Cl_2 /MeOH 1:1 at 77 K (delay 0.05ms, λ_{exc}= 350 nm) of **1P** (green), **1M** (red) and **1O** (black).

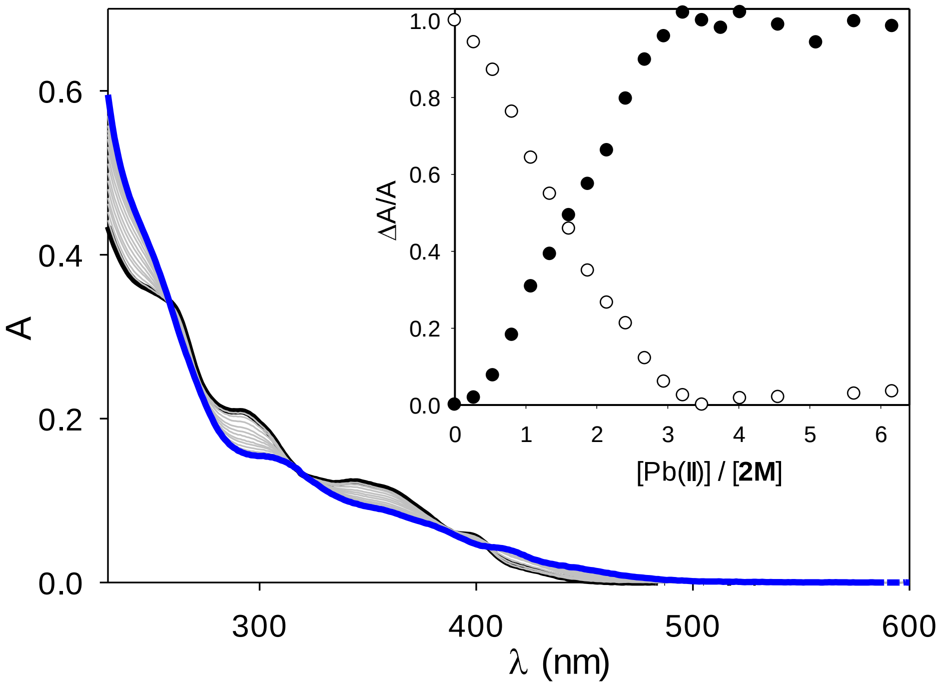


Figure S2 Absorption of a 5.6 x 10^{-6} M solution of **2M** in air-equilibrated aqueous solution (pH=8) upon titration with a 3.73 mM an aqueous solution of $Pb(NO_3)_2$: black line (0 eq), blue line (3.0 eq). Inset shows the normalized absorption changes at 290 nm (empty circles) and 423 nm (solid circles).

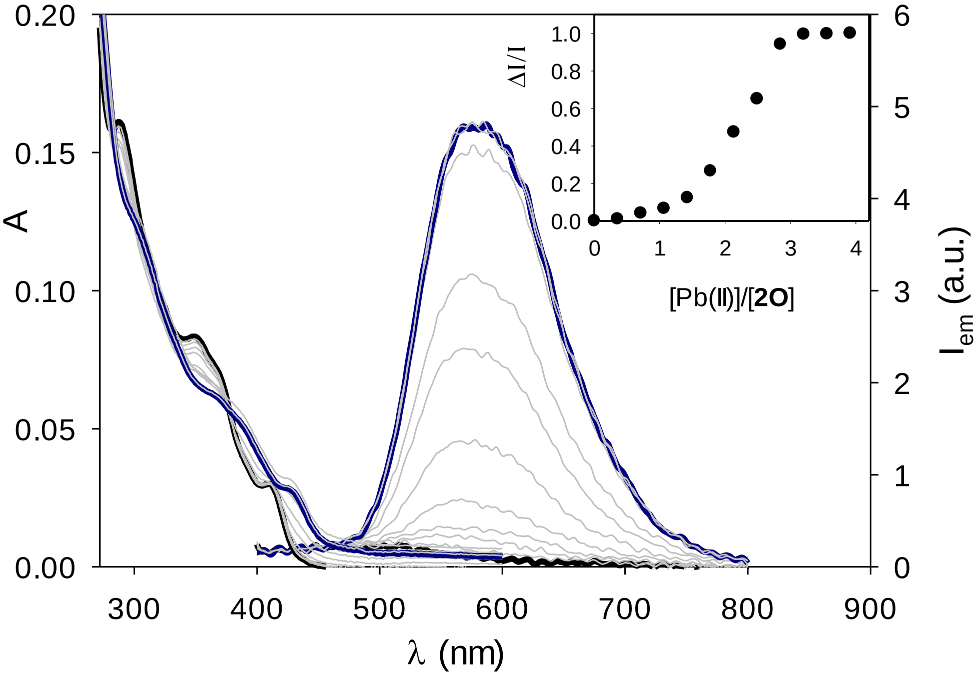


Figure S3

Figure S3. Absorption (left) and phosphorescence (right) of a 6.7 x 10^{-6} M solution of **2O** in air-equilibrated aqueous solution (pH=8) upon titration with a 3.73 mM an aqueous solution of $Pb(NO_3)_2$: black line (0 eq), blue line (2.9eq). Inset show the normalized emission intensity changes at 560 nm. Delay 0.05 ms, λ_{em} = 320 nm (isosbestic point).

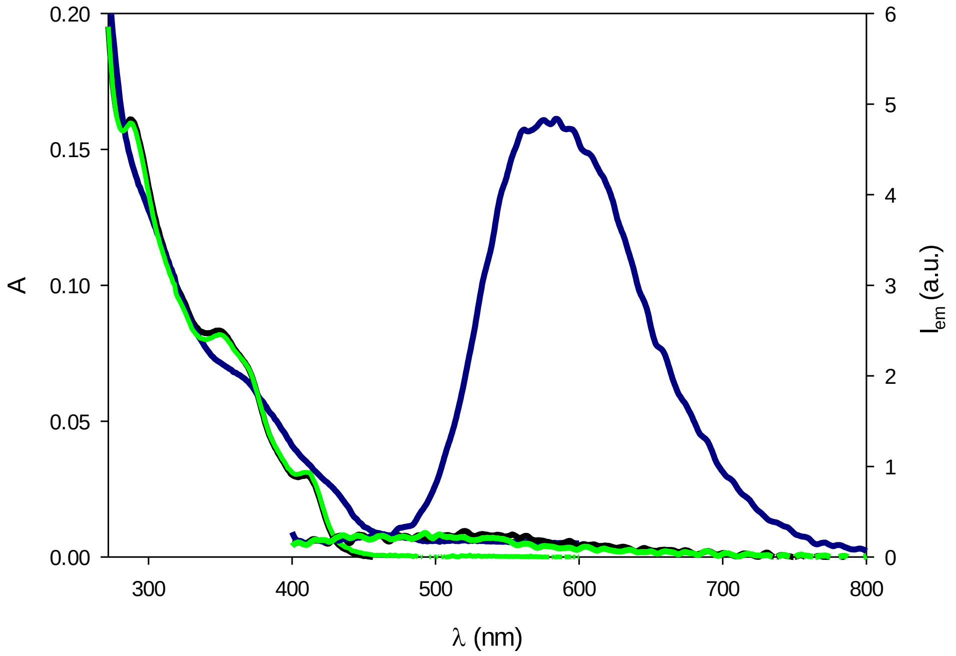


Figure S4 Absorption (left) and phosphorescence (right) of a 6.7 x 10^{-6} M solution of **2O** in air-equilibrated aqueous solution (pH=8) (black line) upon addition of 3.5 eq of $Pb(NO_3)_2$ (blue line) and 5 eq of EDTA (green line). Delay 0.05 ms, λ_{em} = 320 nm.

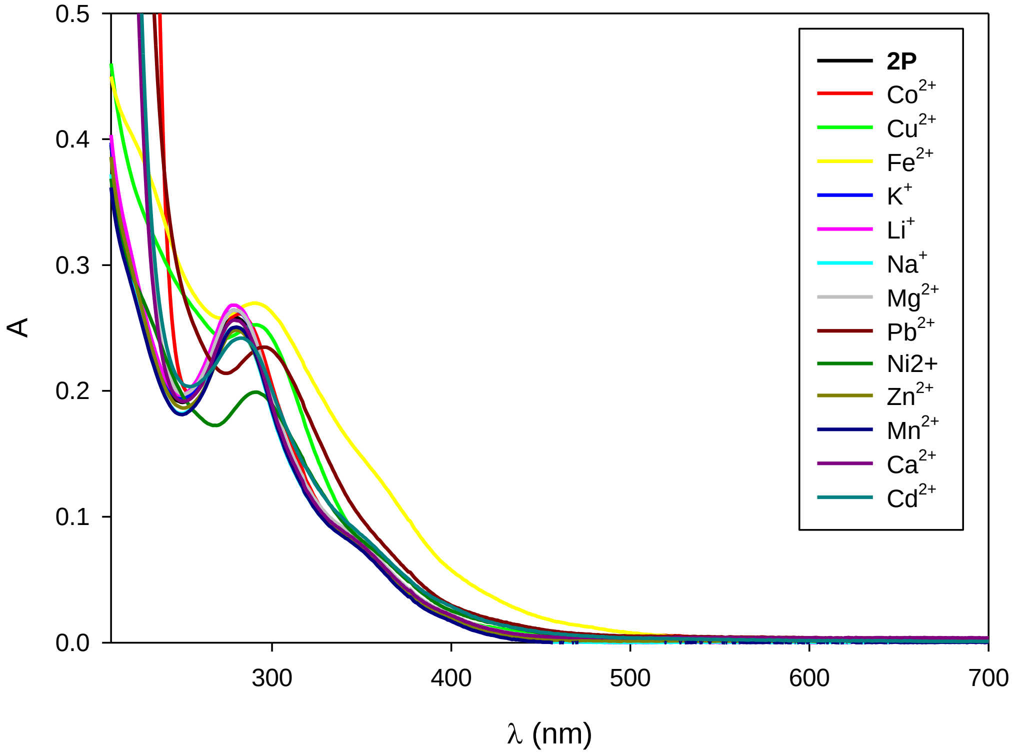


Figure S5a Absorption spectra of a 5.0×10^{-6} M solution of **2P** in aqueous solution (pH=8) upon addition of 15 eq of $Co(NO_3)_2$, $Ni(NO_3)_2$, $FeCl_2$, $CuSO_4$, $MgSO_4$, $Pb(NO_3)_2$, $Cd(NO_3)_2$, $CaCl_2$, $Mn(NO_3)_2$ $Zn(CF_3SO_3)_2$, KCl, NaCl and LiCl.

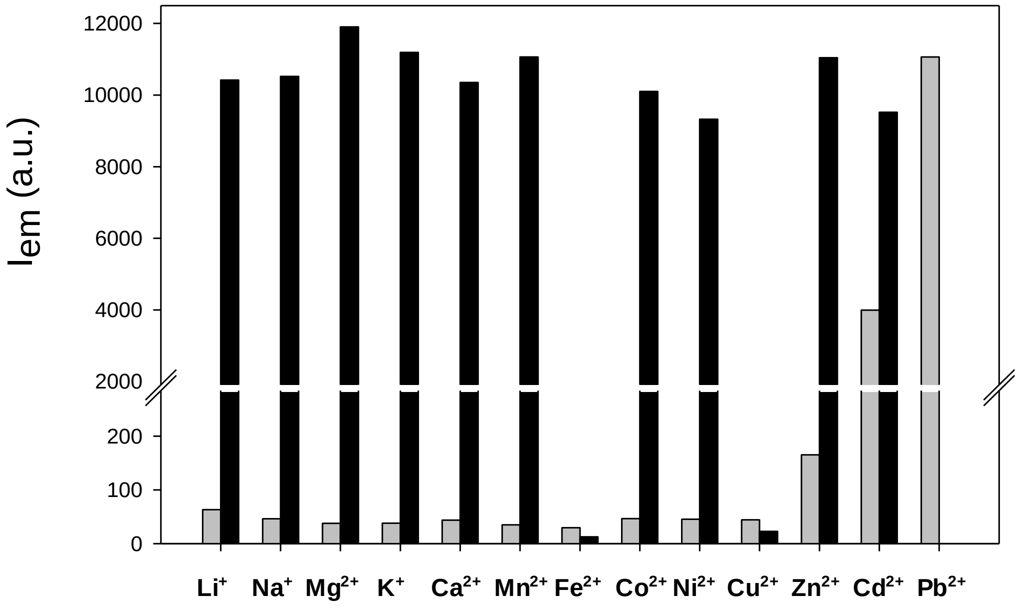


Figure S5b Relative phosphorescence quantum yields of **2P** 4.8 µM in water at pH=8 upon addition of different metal ions (75 µM for K^+, Na^+ and Li^+, 75 µM for all other metal ion) (grey bar). Delay 0.05 ms, λ_{ex} = 300 nm and subsequent addition of 75 µM of $Pb(NO_3)_2$ (black bar).

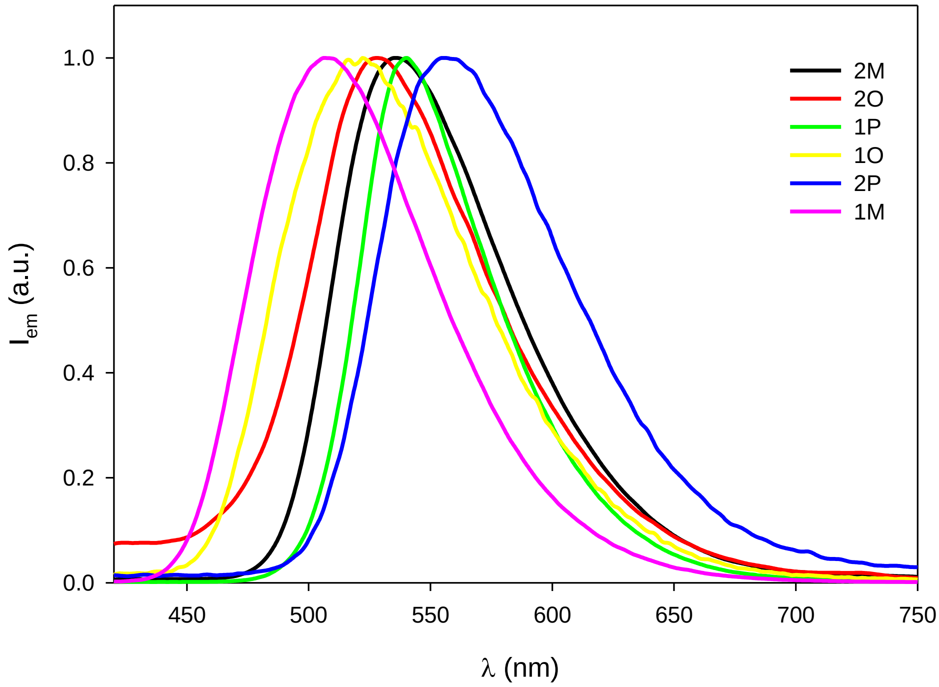
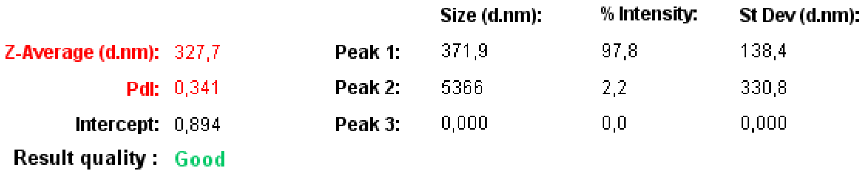


Figure S6. Normalized phosphorescence spectra of **2M, 2O, 2P, 1M, 1O, 1P** as powder. Delay (0.04 ms), λ_{em}= 350 nm.



			Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm):	327,7	Peak 1:	371,9	97,8	138,4
PdI:	0,341	Peak 2:	5366	2,2	330,8
Intercept:	0,894	Peak 3:	0,000	0,0	0,000
Result quality :	Good				

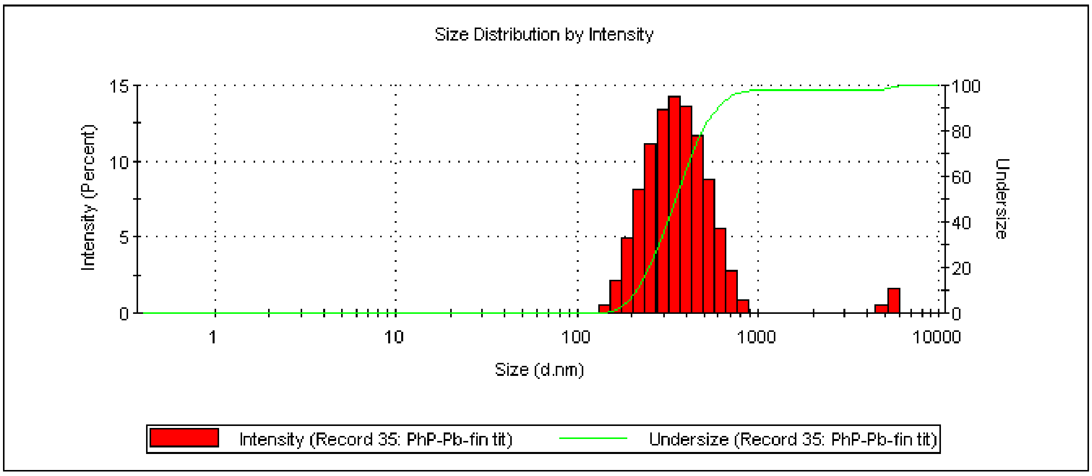


Figure S7. Size distribution by DLS analysis on a 4.9 x 10^{-6} M solution of **2P** in aqueous solution (pH=8) upon addition of 3 equiv of $Pb(NO_3)_2$ per ligand.

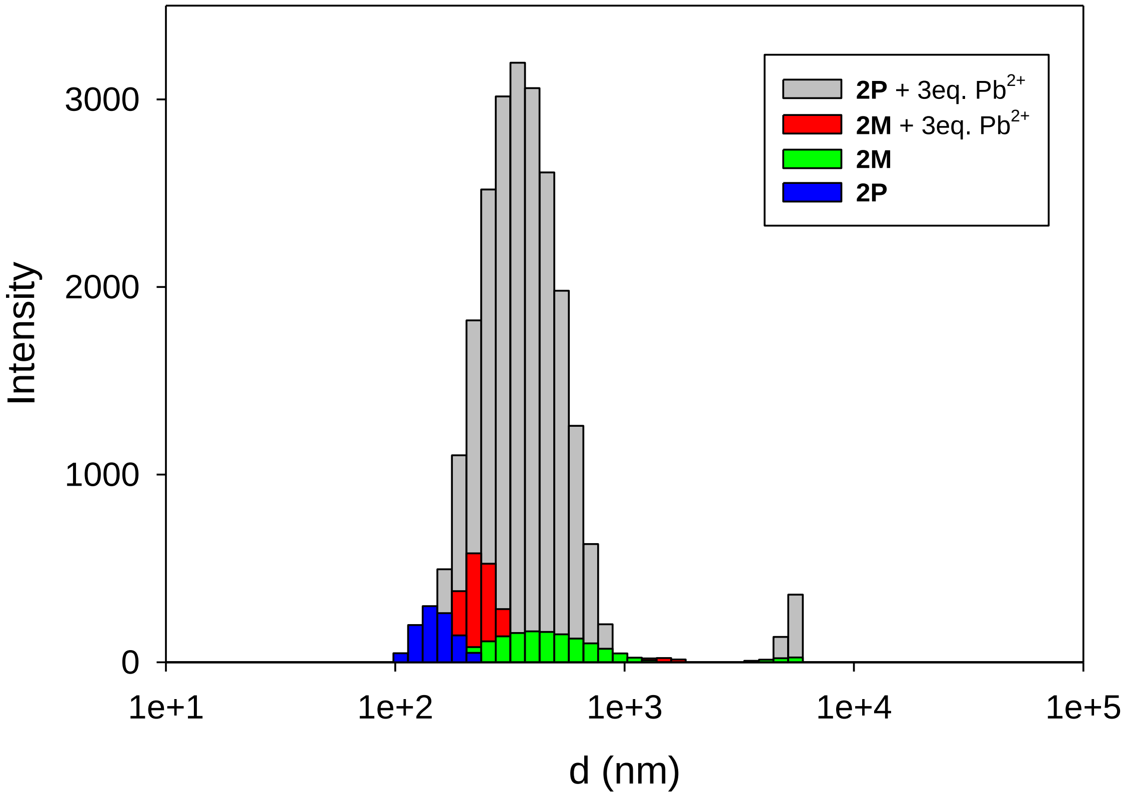


Figure S8. Size distribution by DLS analysis of scattered intensity on a 4.9 x 10^{-6} M solution of **2P** and **2M** in aqueous solution (pH=8) before (blue for **2P** and green for **2M**) and after addition of 3 equiv. of $Pb(NO_3)_2$ per ligand (gray for **2P** and red for **2M**). The reported intensity values are directly comparable. The presence of scattered light for the pristine solution of **2P** and **2M** is due to a small fraction of non-solubilized ligand

3. Synthetic protocols and characterization of compounds

Diisopropyl 3,3'-dithiobisbenzoate: To a solution of 3-mercaptobenzoic acid (2.080 g, 13.51 mmol, 1.0 eq) in isopropanol (120 ml, 1.57 mol, 116.0 eq) was added dropwise $SOCl_2$ (13 mL, 174.84 mmol, 13.0 eq) at 0°C under an argon atmosphere. The reaction was heated at 80°C for 1 day. Upon completion of the reaction, isopropanol was evaporated under reduced pressure. The crude solid was dissolved in 200 mL of ethyl acetate and extracted with 400 mL of sat. Na_2CO_3 (aq.). The aqueous phase was further extracted thrice with ethyl acetate (3x40 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. A mixture of disulfide and trisulfide (1.8:1 mol-eq) with minor other compounds of mixed sulfur oxidation state was obtained as a brown oil (2.64 g, 6.74 mmol, crude yield 97%). The mixture of products was used without further purification.

Disulfide characterization:

TLC (8:2 cyclohexane-dichloromethane) R_f :0.4; **^{1}H NMR (399.78 MHz, $CDCl_3$, ppm)** : δ = 8.15 (dd, 2H, *J* = 1.7, 1.7 Hz), 7.90 (ddd, 2H, *J* = 7.8, 1.3, 1.3 Hz), 7.68 (br d, 2H, *J* = 7.8 Hz), 7.38 (dd, 2H, *J* = 7.8, 7.8 Hz), 5.25 (sept, 2H, *J* = 6.3 Hz), 1.34 (d, 12H, *J* = 6.3 Hz); **^{13}C NMR (100.53 MHz, $CDCl_3$ ppm)** δ = 165.29, 148.21, 137.61, 131.86, 131.69, 129.91, 129.11, 69.13, 22.24; **FT- IR (cm^{-1})** ν = 2979, 2935, 1714, 1571, 1373, 1352, 1280, 1258, 1105, 1072, 923, 748, 679. **LC-MS** Acetonitrile/water APCI: 391 *m/z* $[M+H]^+$.

Trisulfide characterization:

^{1}H NMR (399.78 MHz, $CDCl_3$, ppm) : δ = 8.15 (dd, 2H, *J* = 1.7, 1.7 Hz), 7.89 (br d, 2H, *J* = 7.8 Hz), 7.69 (br d, 2H, *J* = 7.7 Hz), 7.32 (dd, 2H, *J* = 7.8, 7.8 Hz), 5.23 (sept, 2H, *J* = 6.3 Hz), 1.36 (d, 12H, *J* = 6.3 Hz). **LC-MS** Acetonitrile/water APCI: 423 *m/z* $[M+H]^+$. $]^+$, **HRMS (ESI+)** calculated for $[C_{20}H_{22}O_4S_3 + H^+]$: 440.1019 Da, found $[M+H^+]$ 440.1026 *m/z.*

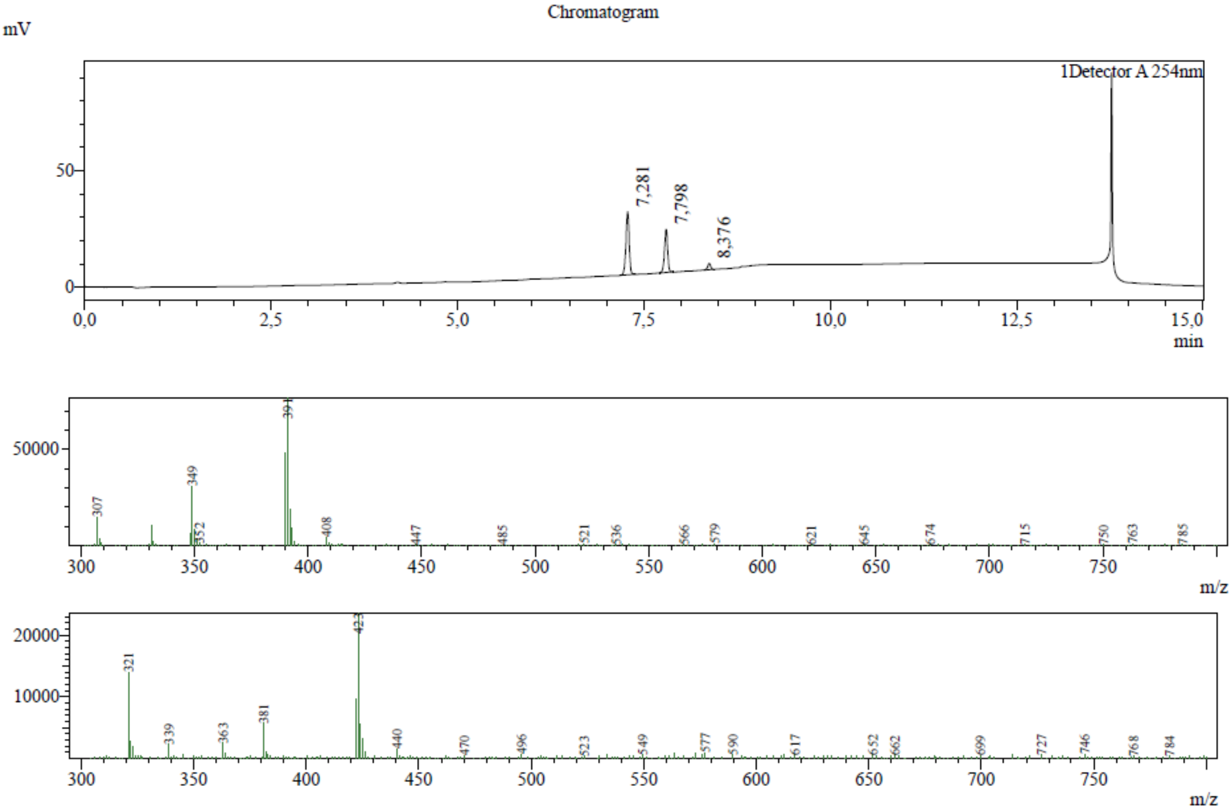


Figure S9 reversed-phase HPLC chromatogram of diisopropyl 3,3'-dithiobisbenzoate and MS-APCI of different peaks**.**

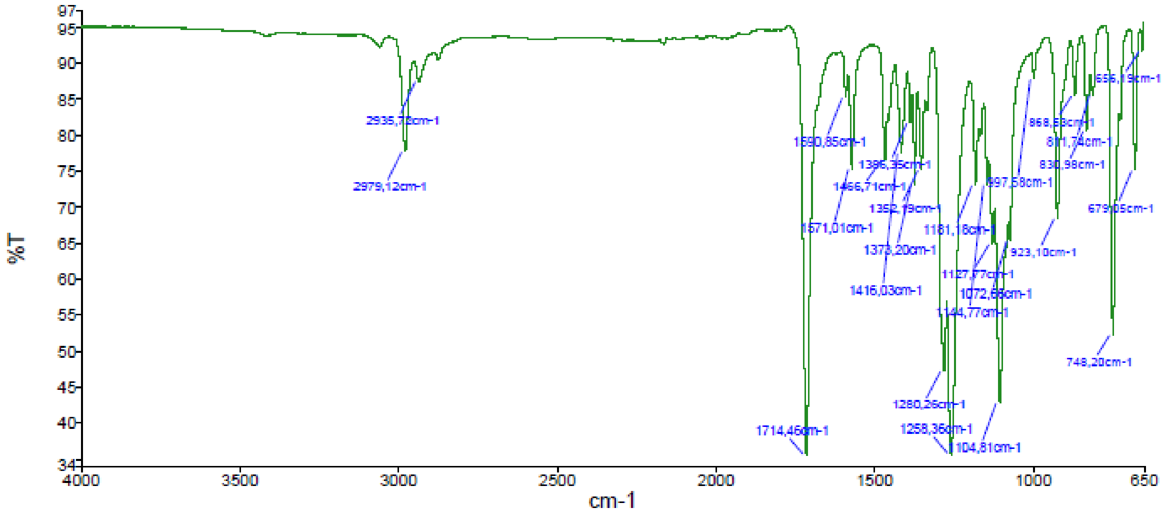
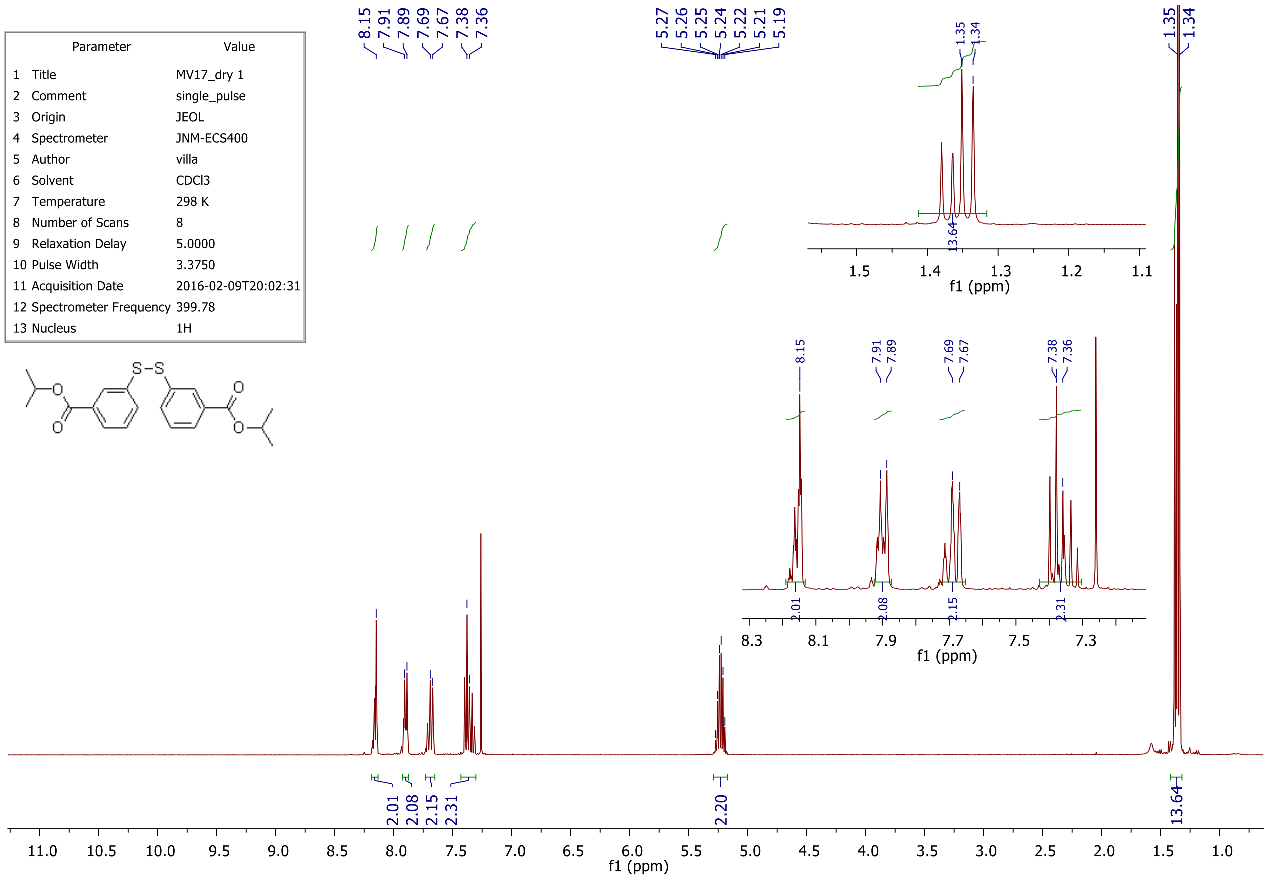


Figure S10 FT-IR (ATR) spectrum of diisopropyl 3,3'-dithiobis benzoate



	Parameter	Value
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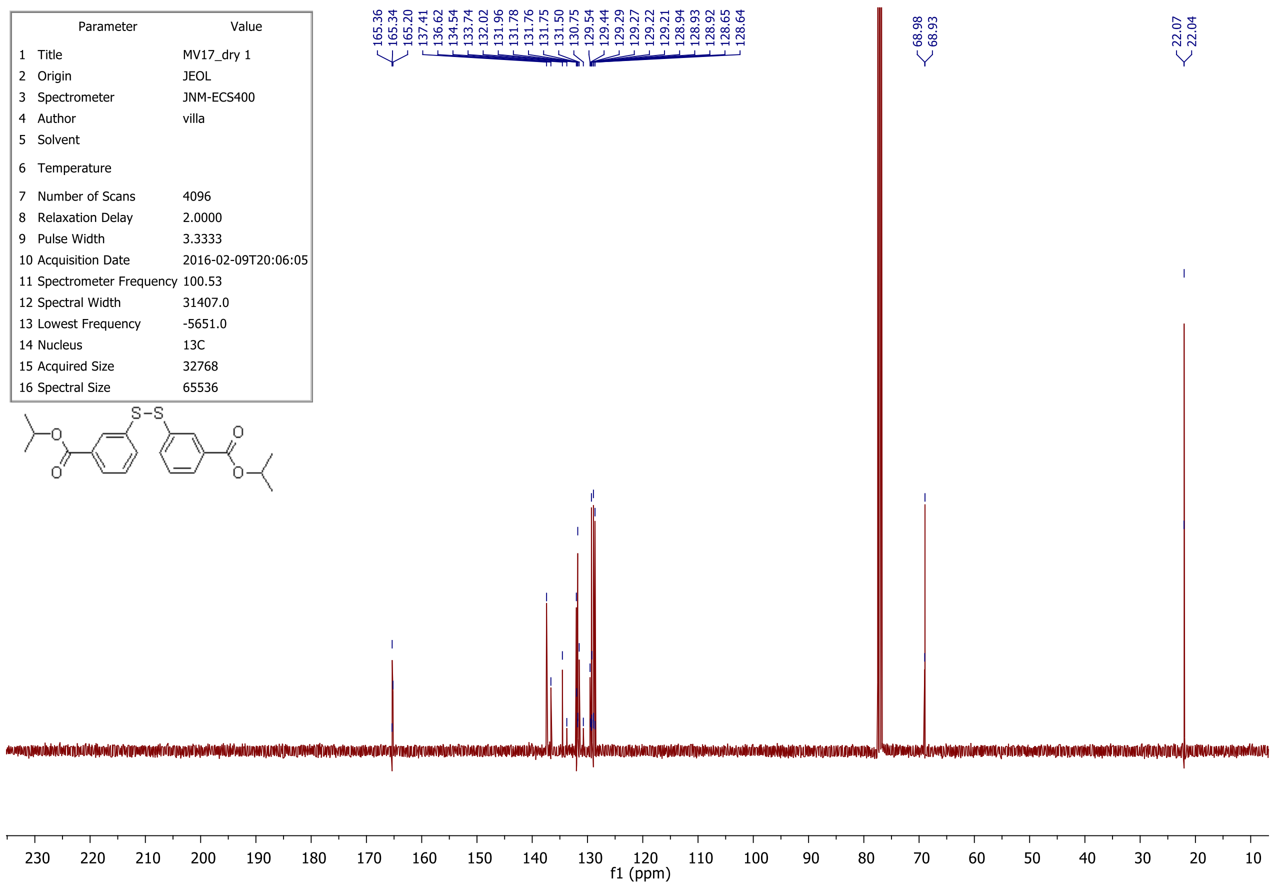
4	Spectrometer	JNM-ECS400
5	Author	villa
6	Solvent	CDCl3
7	Temperature	298 K
8	Number of Scans	8
9	Relaxation Delay	5.0000
10	Pulse Width	3.3750
11	Acquisition Date	2016-02-09T20:02:31
12	Spectrometer Frequency	399.78
13	Nucleus	1H

Figure S11 ^{1}H-NMR spectrum of diisopropyl 3,3'-dithiobisbenzoate ($CDCl_3$, 399.78 MHz)



	Parameter	Value
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3	Spectrometer	JNM-ECS400
4	Author	villa
5	Solvent	
6	Temperature	
7	Number of Scans	4096
8	Relaxation Delay	2.0000
9	Pulse Width	3.3333
10	Acquisition Date	2016-02-09T20:06:05
11	Spectrometer Frequency	100.53
12	Spectral Width	31407.0
13	Lowest Frequency	-5651.0
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536

Figure S12 ^{13}C-NMR spectrum of diisopropyl 3,3'-dithiobisbenzoate ($CDCl_3$, 100.53 MHz)

Diisopropyl 2,2’-dithiobisbenzoate: To a solution of thiosalicylic acid (5.095 g, 33.08 mmol, 1.0 eq) in isopropanol (300 mL, 3.92 mol, 118.0 eq) was added dropwise $SOCl_2$ (30 mL, 0.41 mol, 12.4 eq) at 0°C under an argon atmosphere. The reaction was heated at 80°C for 10 days. Upon completion of the reaction, isopropanol was evaporated under reduced pressure. The crude solid was dissolved in 400 mL of ethyl acetate and extracted with 500 mL of sat. Na_2CO_3 (aq.). The aqueous phase was further extracted thrice with ethyl acetate (3x100 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. A mixture of disulfide and trisulfide (6:1 mol eq.) with minor other compounds of mixed sulfur oxidation state was obtained as a brown oil (4.012 g, 10.28 mmol, crude yield 60%). The mixture of products was used without further purification.

Disulfide characterization:

TLC (8:2 cyclohexane-dichloromethane) R_f :0.4; **^{1}H NMR (399.78 MHz, $CDCl_3$ ppm)** δ = 8.06 (dd, 2H, *J* = 7.8, 1.5 Hz), 7.75 (d, 2H, *J* = 8.3 Hz), 7.39 (ddd, 2H, *J* = 8.3, 8.3, 1.5 Hz), 7.22 (ddd, 2H, *J* = 7.5, 7.5, 1.0 Hz), 5.33 (sept, 2H, *J* = 6.2 Hz), 1.42 (d, 12H, *J* = 6.3 Hz); **^{13}C NMR (100.53 MHz, $CDCl_3$ ppm)** δ = 166.39, 140.58, 133.20, 131.70, 128.39, 126.18, 125.72, 69.64, 22.35.; **FT-IR (cm^{-1})** ν = 2979, 2935, 1714, 1571, 1373, 1352, 1280, 1258, 1105, 1072, 923, 748, 679; **LC-MS** acetonitrile/water APCI: 391 *m/z* [M+H]$^+$. **HRMS (ESI+)** calculated for [$C_{20}H_{22}O_4S_2$ + H$^+$]: 391.1032 Da, found [M+H$^+$] 391.1031 *m/z*

Trisulfide characterization: **LC-MS** Acetonitrile/water APCI: 423 *m/z* $[M+H]^+$. **HRMS (ESI+)** calculated for $[C_{20}H_{22}O_4S_3 + NH^+]$: 440.1019 Da, found $[M+H^+]$ 440.1019 *m/z*

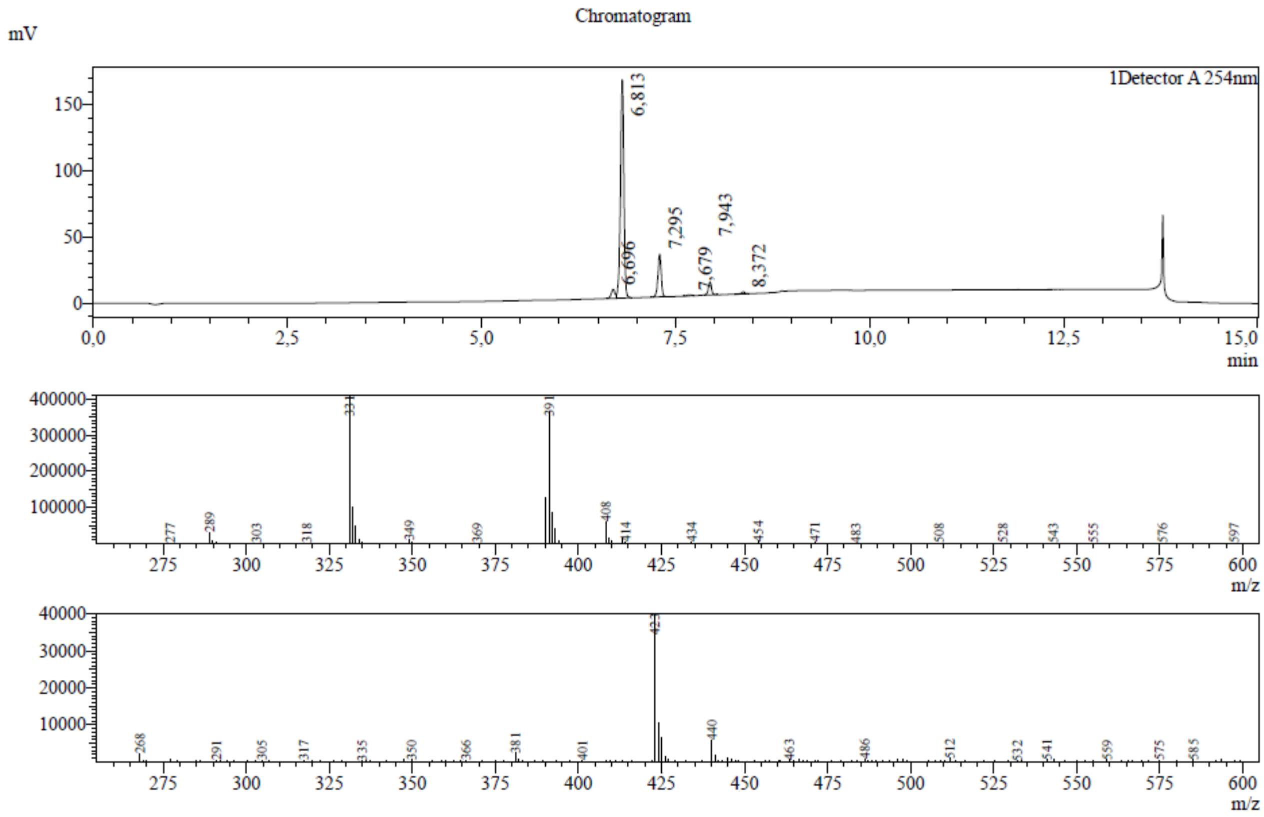


Figure S13 reversed-phase HPLC chromatogram of diisopropyl 2,2’-dithiobisbenzoate and MS-APCI of different peaks.

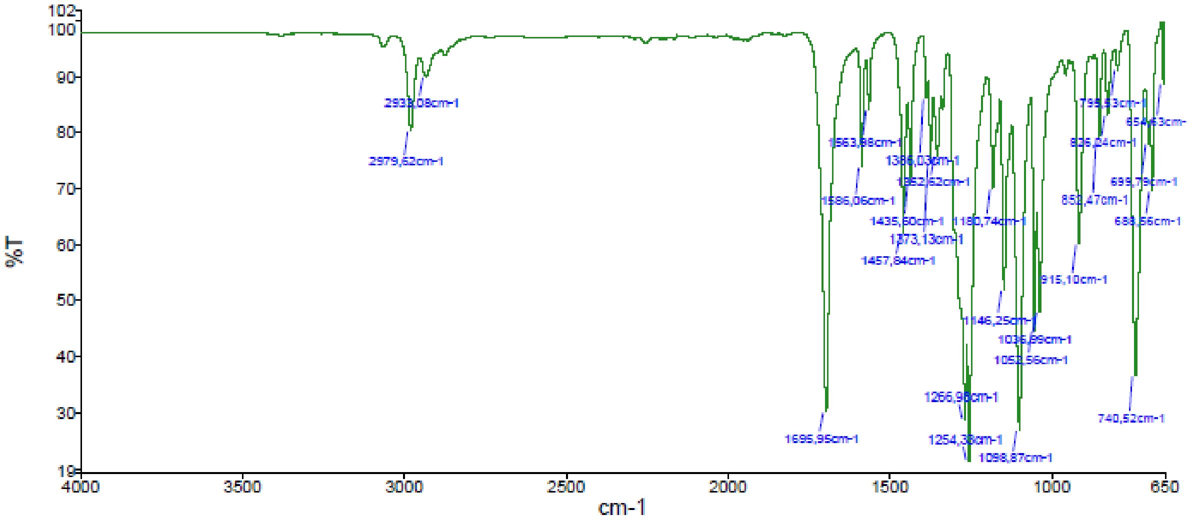
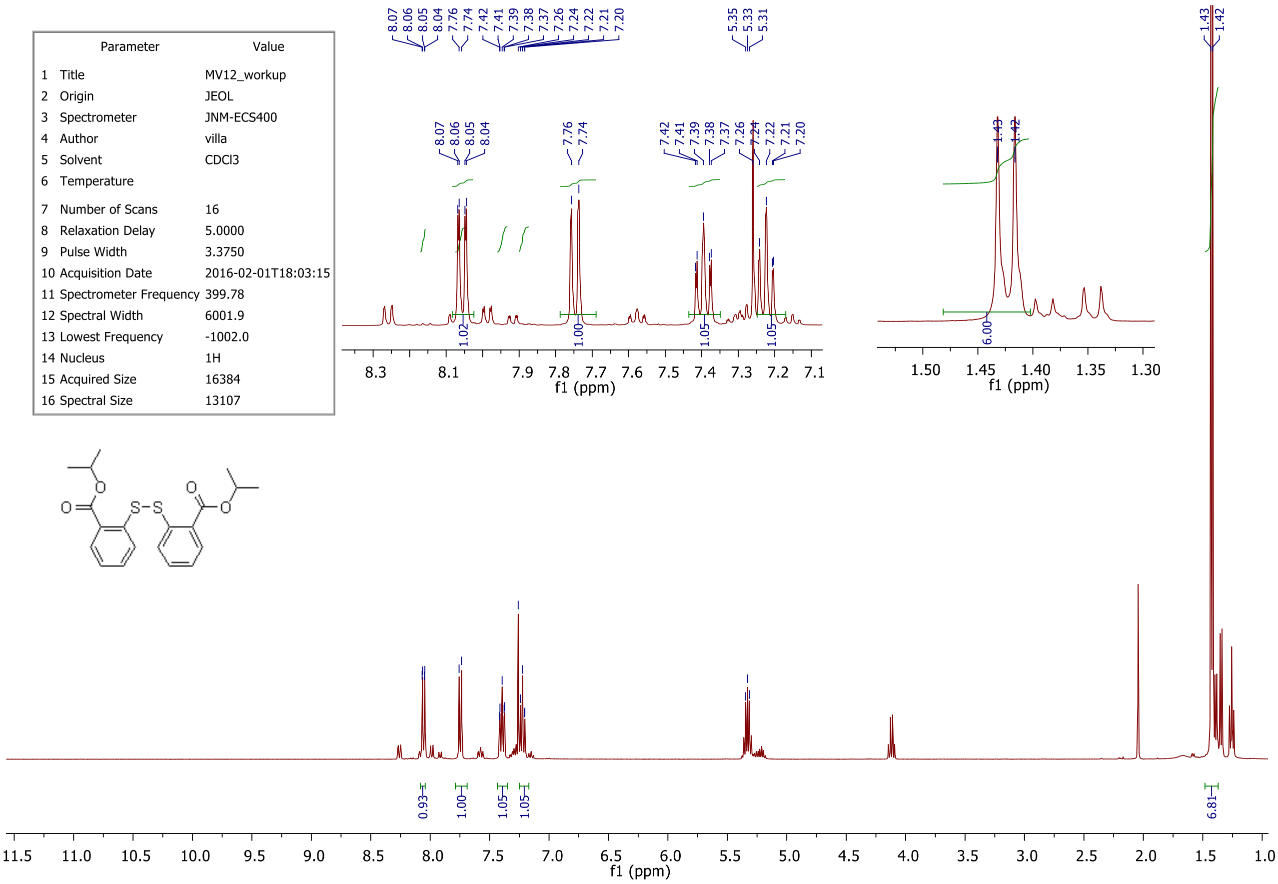


Figure S14 FT-IR (ATR) spectrum of diisopropyl 2,2'-dithiobisbenzoate



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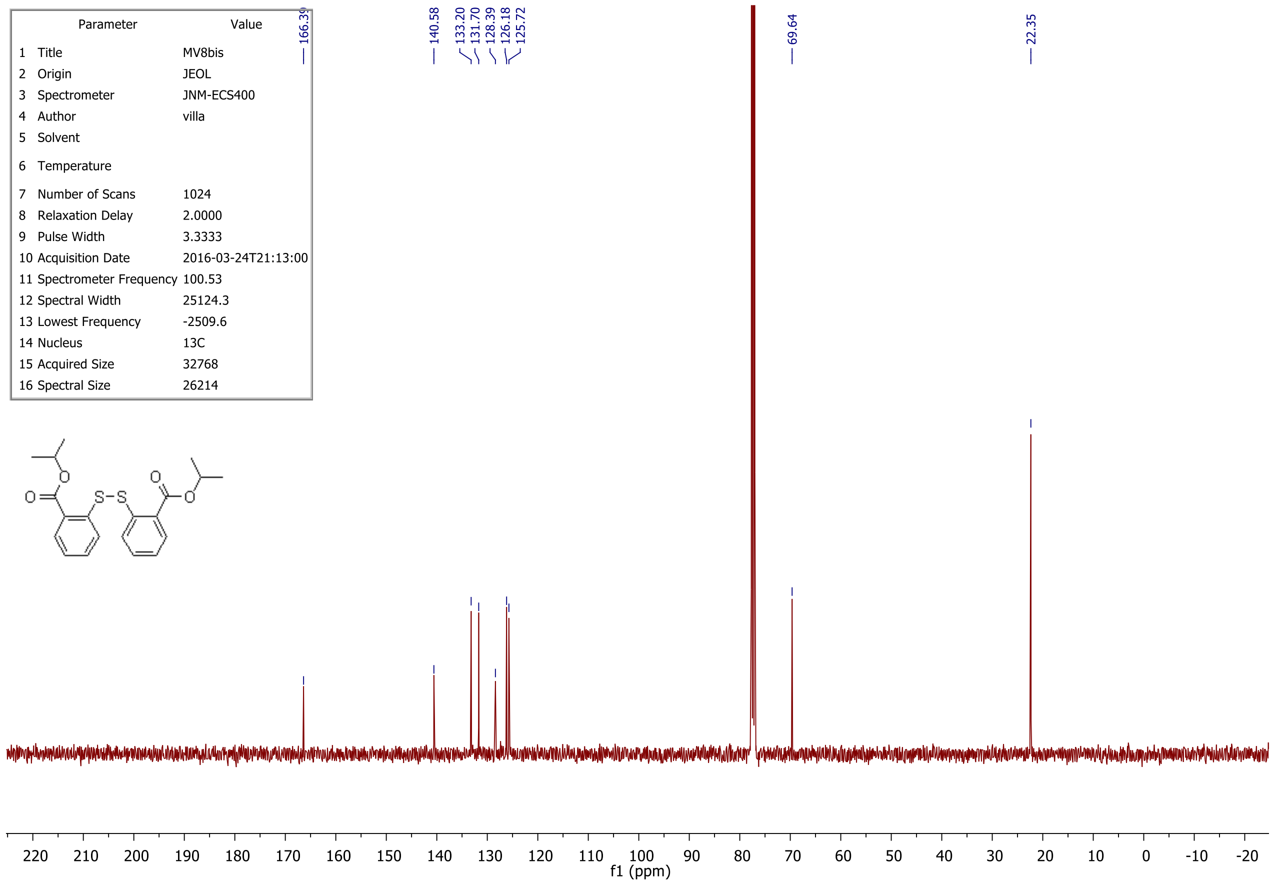
4	Author	villa
5	Solvent	CDCl3
6	Temperature	
7	Number of Scans	16
8	Relaxation Delay	5.0000
9	Pulse Width	3.3750
10	Acquisition Date	2016-02-01T18:03:15
11	Spectrometer Frequency	399.78
12	Spectral Width	6001.9
13	Lowest Frequency	-1002.0
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	13107

Figure S15 ^{1}H-NMR spectrum of diisopropyl 2,2'-dithiobisbenzoate ($CDCl_3$, 399.78 MHz)



	Parameter	Value
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4	Author	villa
5	Solvent	
6	Temperature	
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8	Relaxation Delay	2.0000
9	Pulse Width	3.3333
10	Acquisition Date	2016-03-24T21:13:00
11	Spectrometer Frequency	100.53
12	Spectral Width	25124.3
13	Lowest Frequency	-2509.6
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	26214

Figure S16 ^{13}C-NMR spectrum of diisopropyl 2,2'-dithiobisbenzoate ($CDCl_3$, 100.53 MHz)

Diisopropyl 4,4'-dithiobisbenzoate: To a solution of 4-mercaptobenzoic acid (1.980 g, 33.08 mmol, 1.00 eq) in isopropanol (120ml, 1.57 mol, 122.0 eq) was added dropwise $SOCl_2$ (13 mL, 0.18 mol, 13.0 eq) at 0°C under an argon atmosphere. The reaction was heated at 80°C for 7 days. Upon completion of the reaction, isopropanol was evaporated under reduced pressure. The crude solid was dissolved in 200 mL of ethyl acetate and extracted with 400 mL of sat. Na_2CO_3 (aq.). The aqueous phase was further extracted thrice with ethyl acetate (3x100 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. A mixture of disulfide and trisulfide (4:1 mol eq) with minor other compound of mixed sulfur oxidation state was obtained as a brown oil (2.501g, 10.16 mmol, 97 % yield). The mixture of products was used without further purification.

Disulfide characterization:

TLC (8:2 cyclohexane-dichloromethane) R_f :0.4; **^{1}H NMR (399.78 MHz, $CDCl_3$ ppm)** δ = 7.96 (d, 4H, *J* = 8.6 Hz), 7.51 (d, 4H, *J* = 8.5 Hz), 5.22 (sept, 2H, *J* = 6.2 Hz), 1.34 (d, 12H, *J* = 6.3 Hz); **^{13}C NMR (100.53 MHz, $CDCl_3$ ppm)** δ = 165.55, 141.95, 130.37, 130.29, 129.74, 129.02, 126.13, 68.70, 22.07; **FR- IR (cm^{-1})** : ν = 2979, 2935, 1714, 1571, 1373, 1352, 1280, 1105, 1072, 923, 748, 679; **LC-MS** acetonitrile/water, APCI: 391 *m/z* $[M+H]^+$.

Trisulfide characterization: **LC-MS** Acetonitrile/water APCI: 423 *m/z* $[M+H]^+$. **HRMS (ESI+)** calculated for $[C_{20}H_{22}O_4S_3 + NH^+]$: 440.1019 Da, found $[M+H^+]$ 440.1034 *m/z*

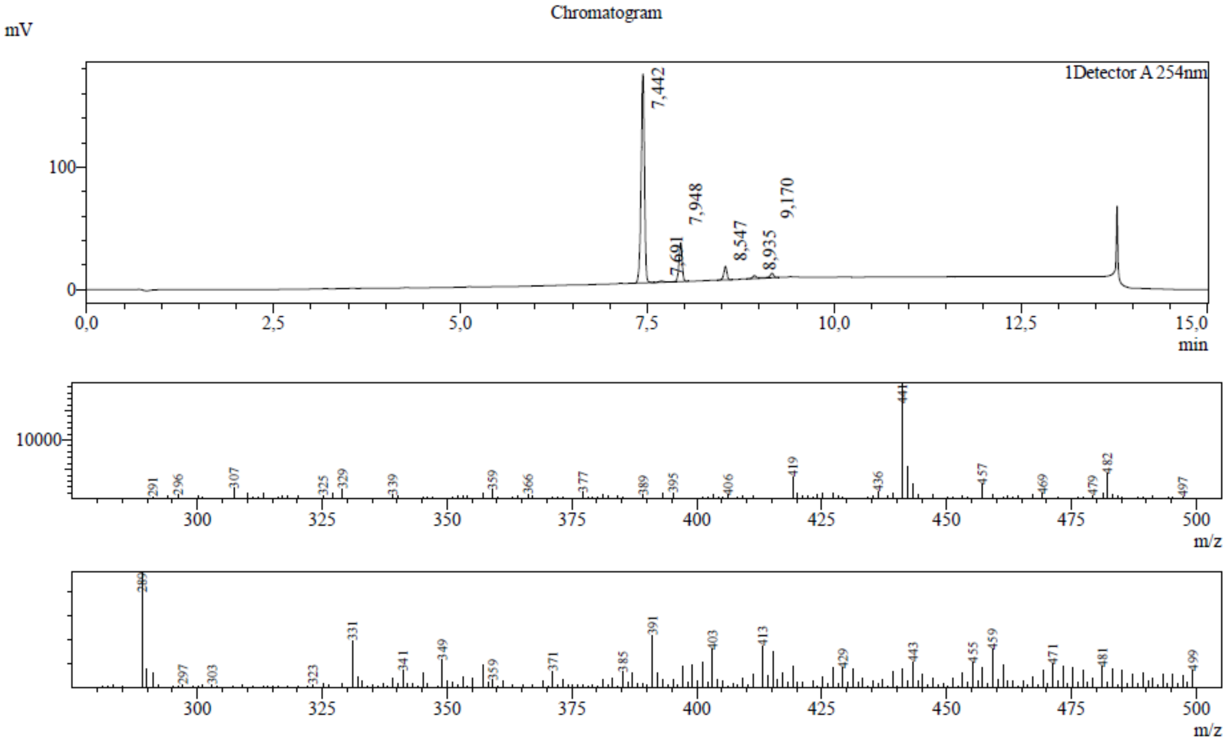


Figure S17 reversed-phase HPLC chromatogram of Diisopropyl 4,4'-dithiobisbenzoate and MS-APCI of different peaks.

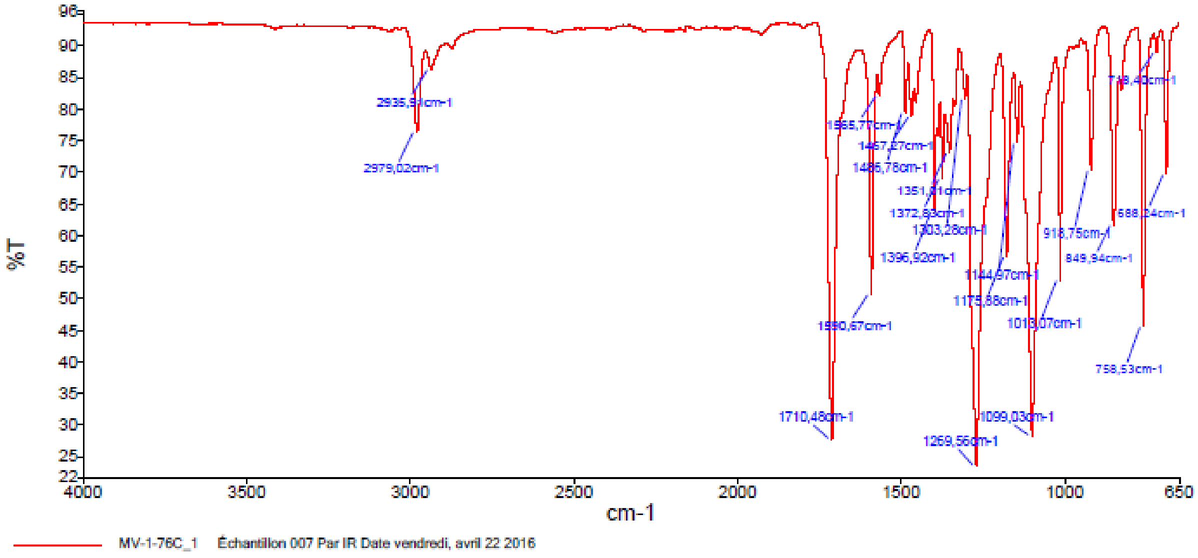
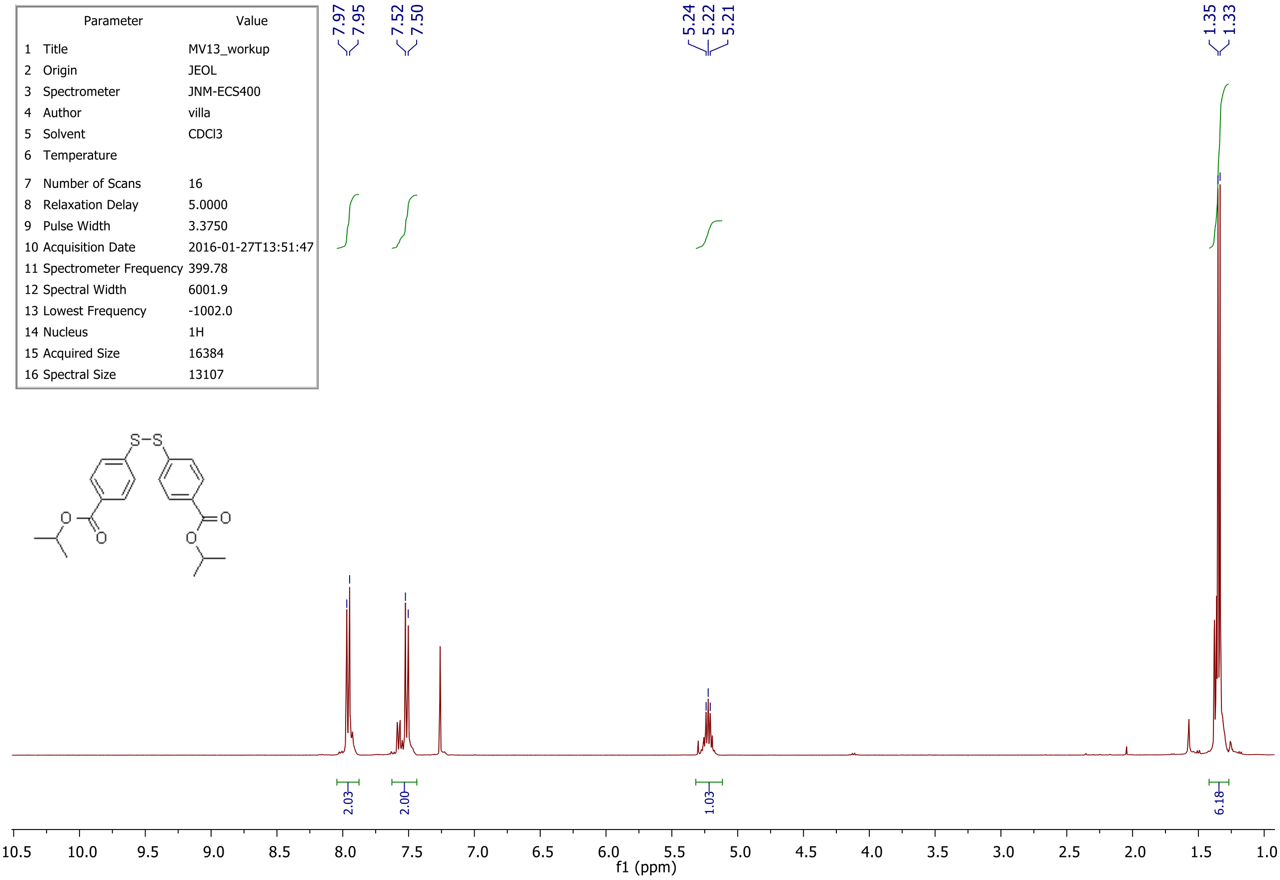


Figure S18 FT-IR (ATR) spectrum of diisopropyl 4,4'-dithiobisbenzoate



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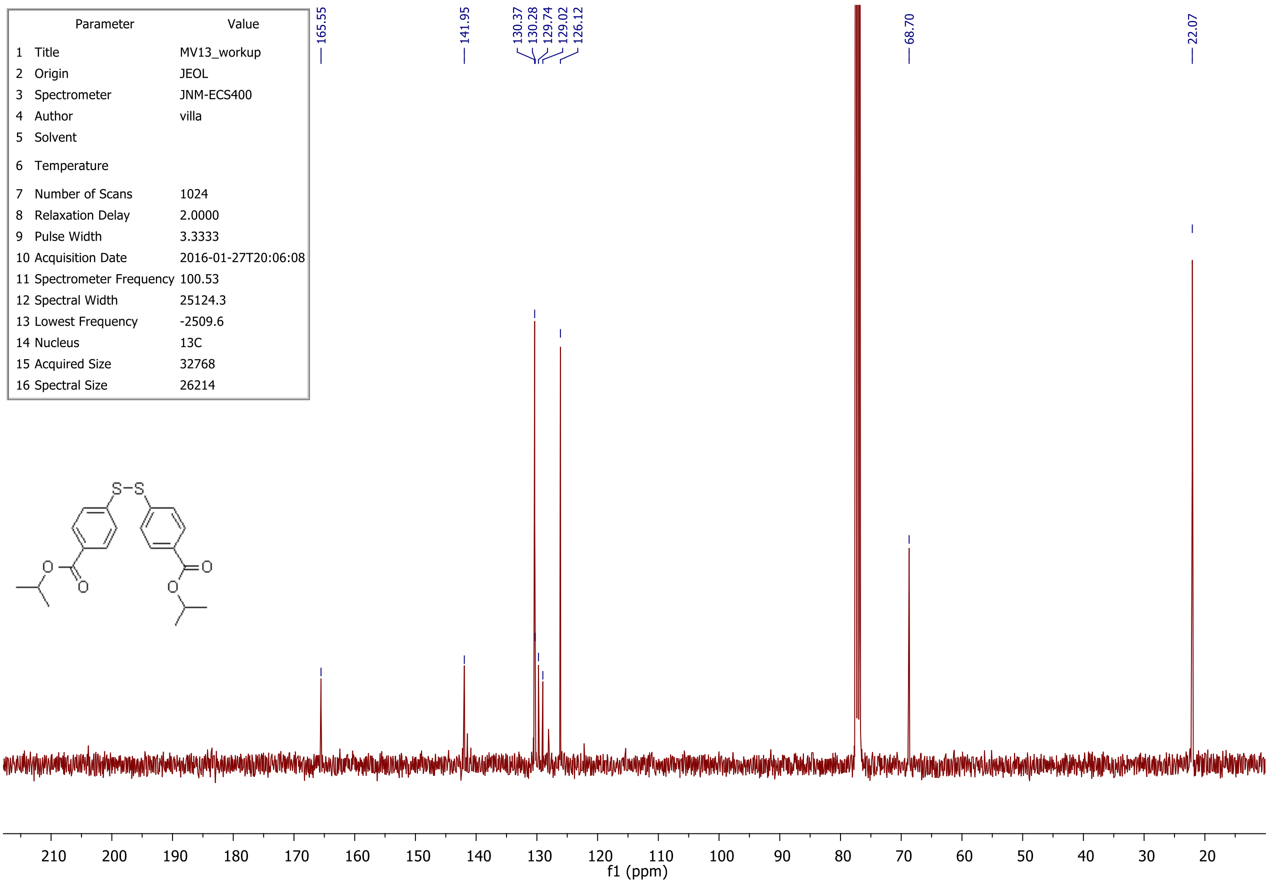
4	Author	villa
5	Solvent	CDCl3
6	Temperature	
7	Number of Scans	16
8	Relaxation Delay	5.0000
9	Pulse Width	3.3750
10	Acquisition Date	2016-01-27T13:51:47
11	Spectrometer Frequency	399.78
12	Spectral Width	6001.9
13	Lowest Frequency	-1002.0
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	13107

Figure S19 ^{1}H-NMR spectrum of diisopropyl 4,4'-dithiobisbenzoate ($CDCl_3$, 399.78 MHz)



	Parameter	Value
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3	Spectrometer	JNM-ECS400
4	Author	villa
5	Solvent	
6	Temperature	
7	Number of Scans	1024
8	Relaxation Delay	2.0000
9	Pulse Width	3.3333
10	Acquisition Date	2016-01-27T20:06:08
11	Spectrometer Frequency	100.53
12	Spectral Width	25124.3
13	Lowest Frequency	-2509.6
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	26214

Figure S20 ^{13}C-NMR spectrum of diisopropyl 4,4'-dithiobisbenzoate ($CDCl_3$, 100.53 MHz)

Isopropyl 3-mercaptobenzoate: A solution of diisopropyl 3,3'-dithiobisbenzoate (0.512 g, 1.31 mmol, 1.00 eq) and grinded dried zinc powder (1.295 g, 19.92 mmol, 15.0 eq) in acetic acid (15 mL) was heated overnight at 90°C under an argon atmosphere. Upon completion of the reaction, the reaction mixture was diluted with 100 mL of 1 N HCl (aq.) and extracted thrice with dichloromethane (3x40 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The desired thiol was obtained as a brown oil (504 mg, 2.57 mmol, 98% yield) and used without further purification.

^{1}H NMR (399.78 MHz, $CDCl_3$ ppm) δ = 7.94 (dd, 1H, *J* = 1.6, 1.6 Hz), 7.82 (ddd, 1H, *J* = 7.8, 1.2, 1.2 Hz), 7.43 (br d, 1H, *J* = 7.8 Hz), 7.30 (dd, 1H, *J* = 7.8, 7.8 Hz), 5.24 (sept, 1H, *J* = 6.2 Hz), 3.55 (s, 1H), 1.36 (d, 6H, *J* = 6.3 Hz); **^{13}C NMR (100.53 MHz, $CDCl_3$ ppm)** δ = 165.55, 133.36, 131.92, 131.63, 130.24, 129.13, 126.90, 68.84, 22.07; **FT-IR (cm^{-1})** ν = 2980, 2560, 1712, 1573, 1373, 1281, 1261, 1105, 921, 830, 746, 678; **LC-MS** acetonitrile/water APCI: 195 *m/z* [M-H]$^-$.

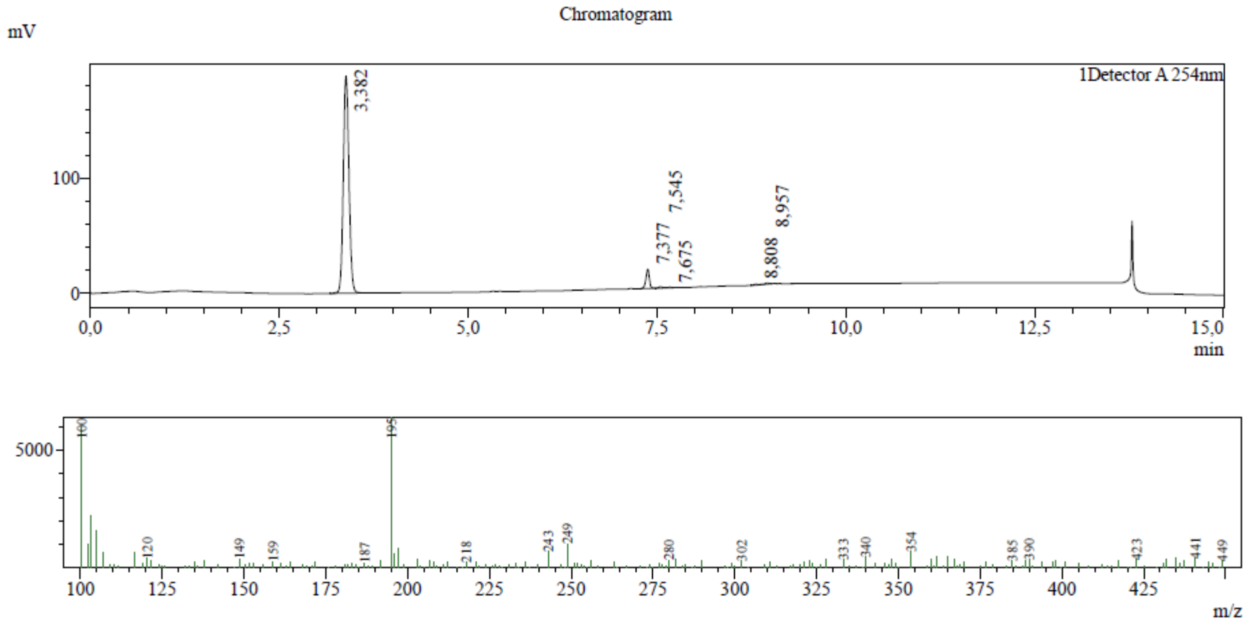


Figure S21 reversed-phase HPLC chromatogram of Isopropyl 3-mercaptobenzoate and MS-ESI of different peaks (negative ionization upper spectrum, positive ionization lower spectrum)**.**

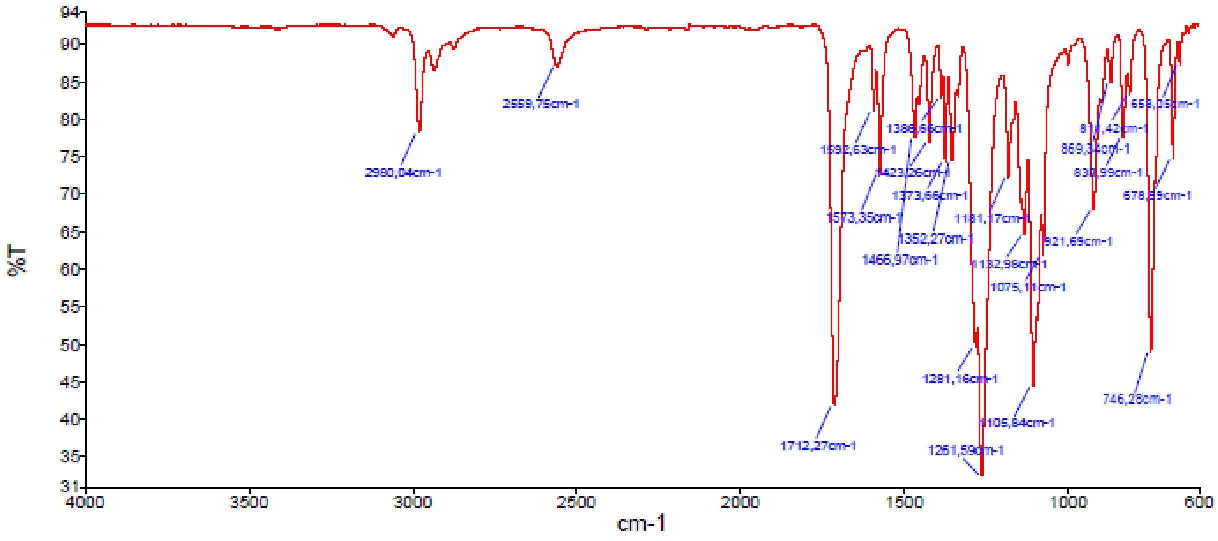
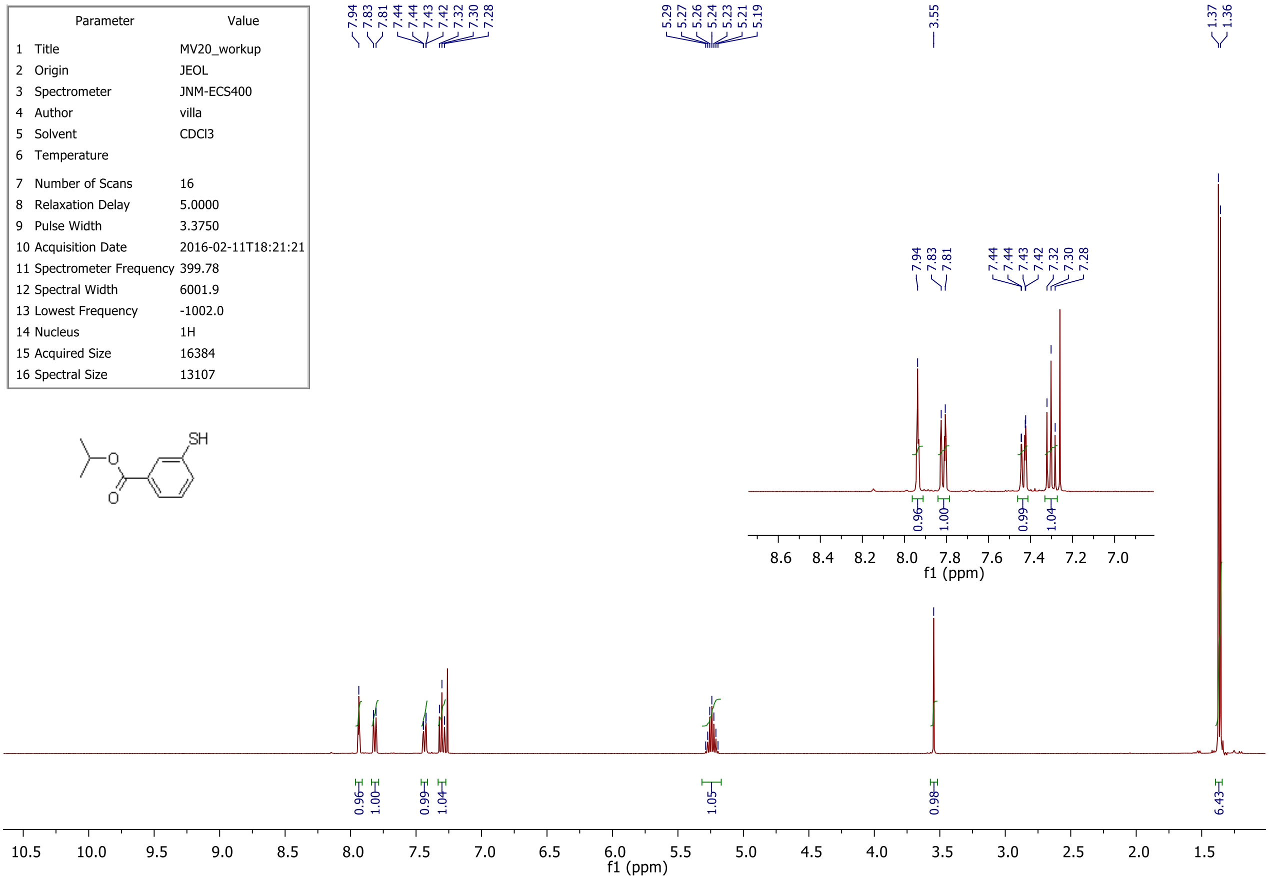
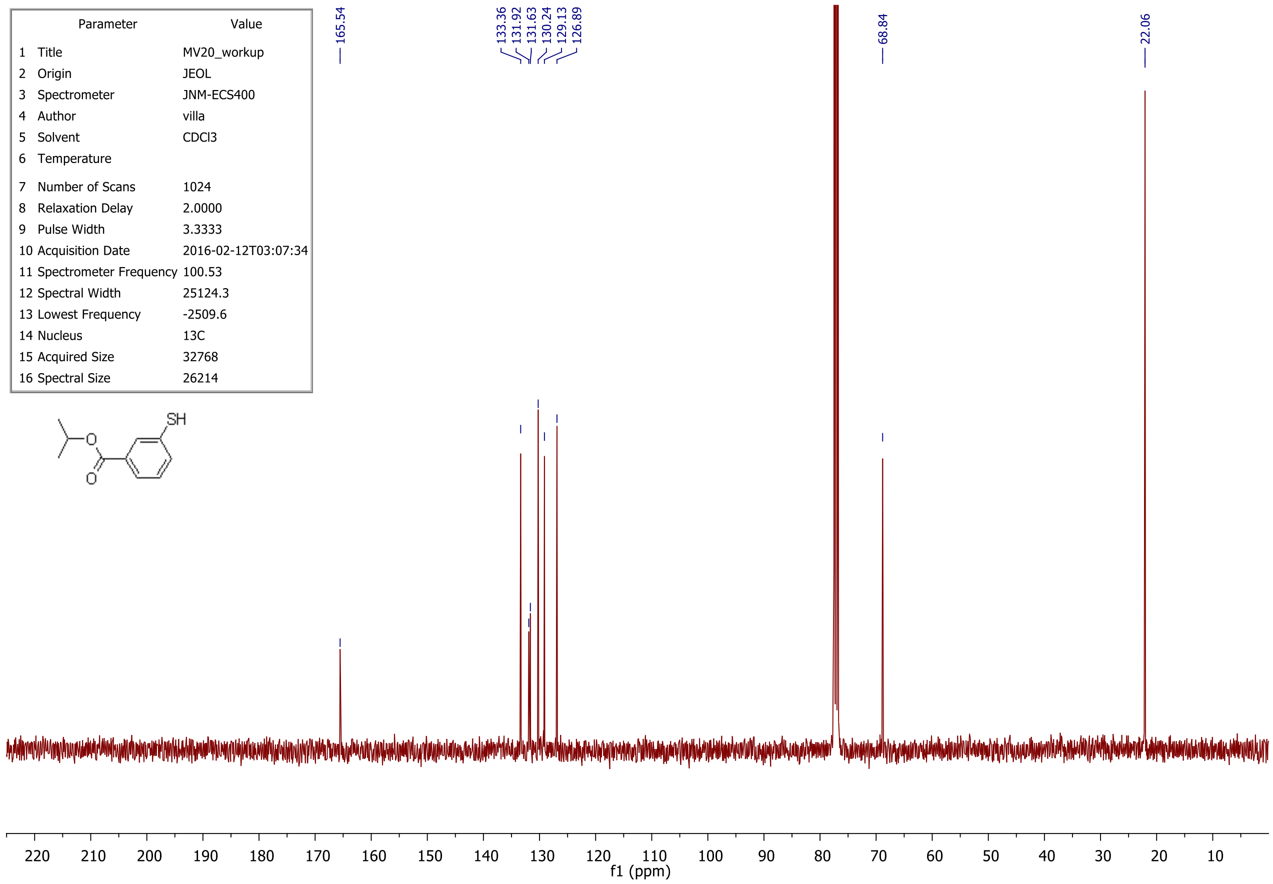


Figure S22 FT-IR (ATR) spectrum of Isopropyl 3-mercaptobenzoate



	Parameter	Value
1	Title	MV20_workup
2	Origin	JEOL
3	Spectrometer	JNM-ECS400
4	Author	villa
5	Solvent	CDCl3
6	Temperature	
7	Number of Scans	16
8	Relaxation Delay	5.0000
9	Pulse Width	3.3750
10	Acquisition Date	2016-02-11T18:21:21
11	Spectrometer Frequency	399.78
12	Spectral Width	6001.9
13	Lowest Frequency	-1002.0
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	13107

Figure S23 ^{1}H-NMR spectrum of Isopropyl 3-mercaptobenzoate ($CDCl_3$, 399.78 MHz)



	Parameter	Value
1	Title	MV20_workup
2	Origin	JEOL
3	Spectrometer	JNM-ECS400
4	Author	villa
5	Solvent	CDCl3
6	Temperature	
7	Number of Scans	1024
8	Relaxation Delay	2.0000
9	Pulse Width	3.3333
10	Acquisition Date	2016-02-12T03:07:34
11	Spectrometer Frequency	100.53
12	Spectral Width	25124.3
13	Lowest Frequency	-2509.6
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	26214

Figure S24 ^{13}C-NMR spectrum of Isopropyl 3-mercaptobenzoate ($CDCl_3$, 100.53 MHz)

Isopropyl 2-mercaptobenzoate: A solution of Diisopropyl 2,2' dithiobisbenzoate (4.012 g, 10.29 mmol, 1.0 eq) and and grinded dried zinc powder (12.980 g, 198.53 mmol, 19.0 eq) in acetic acid (120 mL) was heated overnight at 90°C under an argon atmosphere. Upon completion of the reaction, the reaction mixture was diluted with 300 mL of 1 N HCl (aq.) and extracted thrice with dichloromethane (3x150 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The desired thiol was obtained as a brown oil (3.809 g , 19.43 mmol, 94.4% yield) and used without further purification.

^{1}H NMR (399.78 MHz, $CDCl_3$ ppm) δ = 8.01 (d, 1H, *J* = 7.9 Hz), 7.31-7.28 (m, 2H), 7.15 (m, 1H), 5.26 (sept, 1H, *J* = 6.2 Hz), 4.66 (s, 1H), 1.38 (d, 6H, *J* = 6.4 Hz); **^{13}C NMR (100.53 MHz, $CDCl_3$ ppm)** δ = 166.39, 138.14, 132.39, 131.76, 131.00, 126.72, 124.73, 69.06, 22.09; **IR (cm^{-1})** : ν = 3359, 3207, 2979, 1659, 1619, 1463, 1304, 1255, 1103, 1055, 915, 744, 696; **LC-MS** Acetonitrile/water APCI: 195 *m/z* [M-H]$^-$.

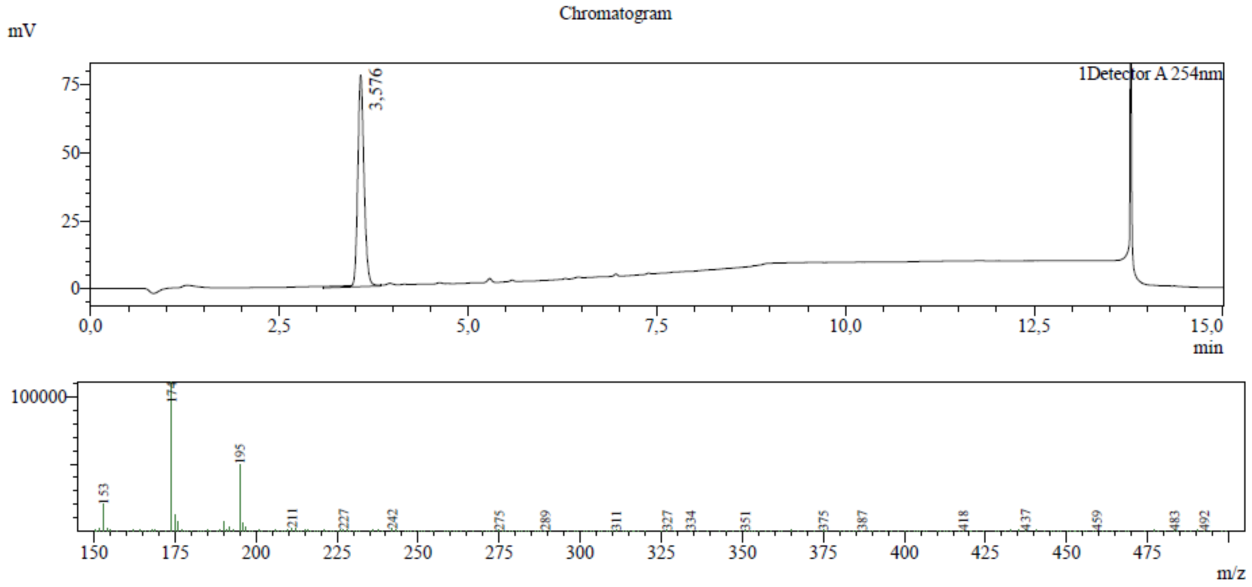


Figure S25 reversed-phase HPLC chromatogram of Isopropyl 2-mercaptobenzoate and MS-APCI (negative ionization).

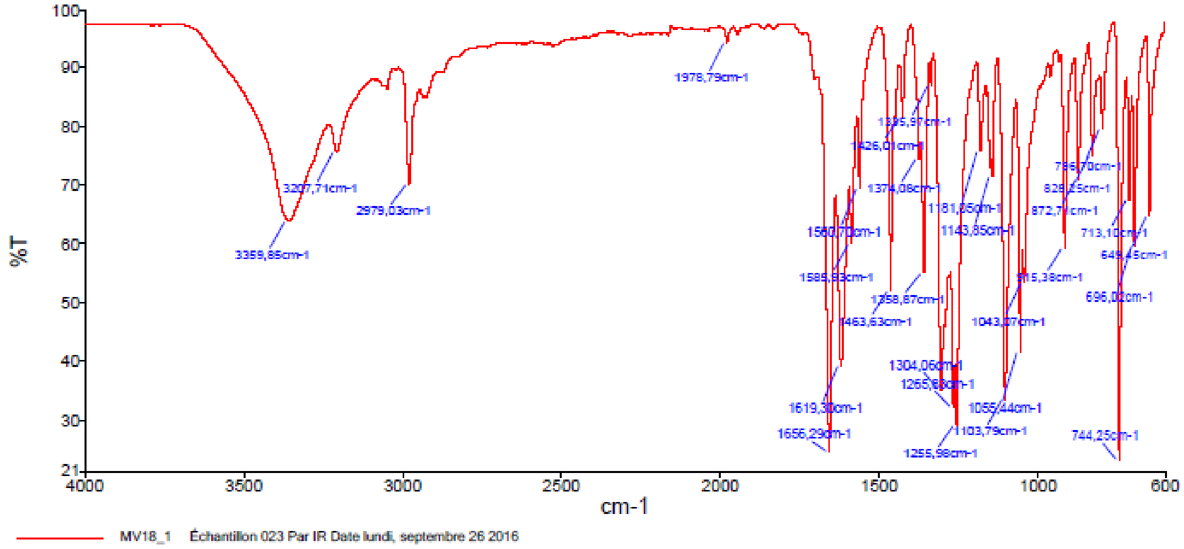
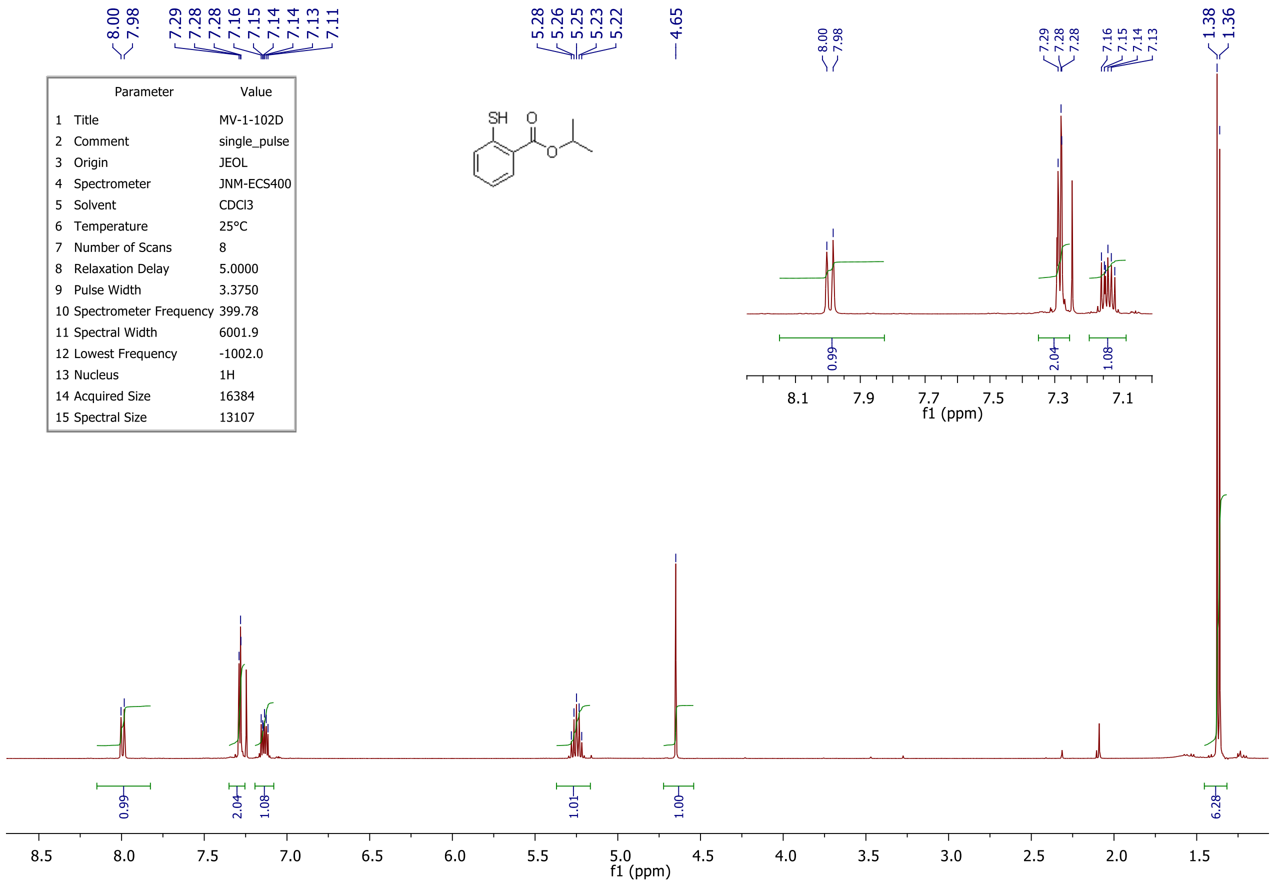
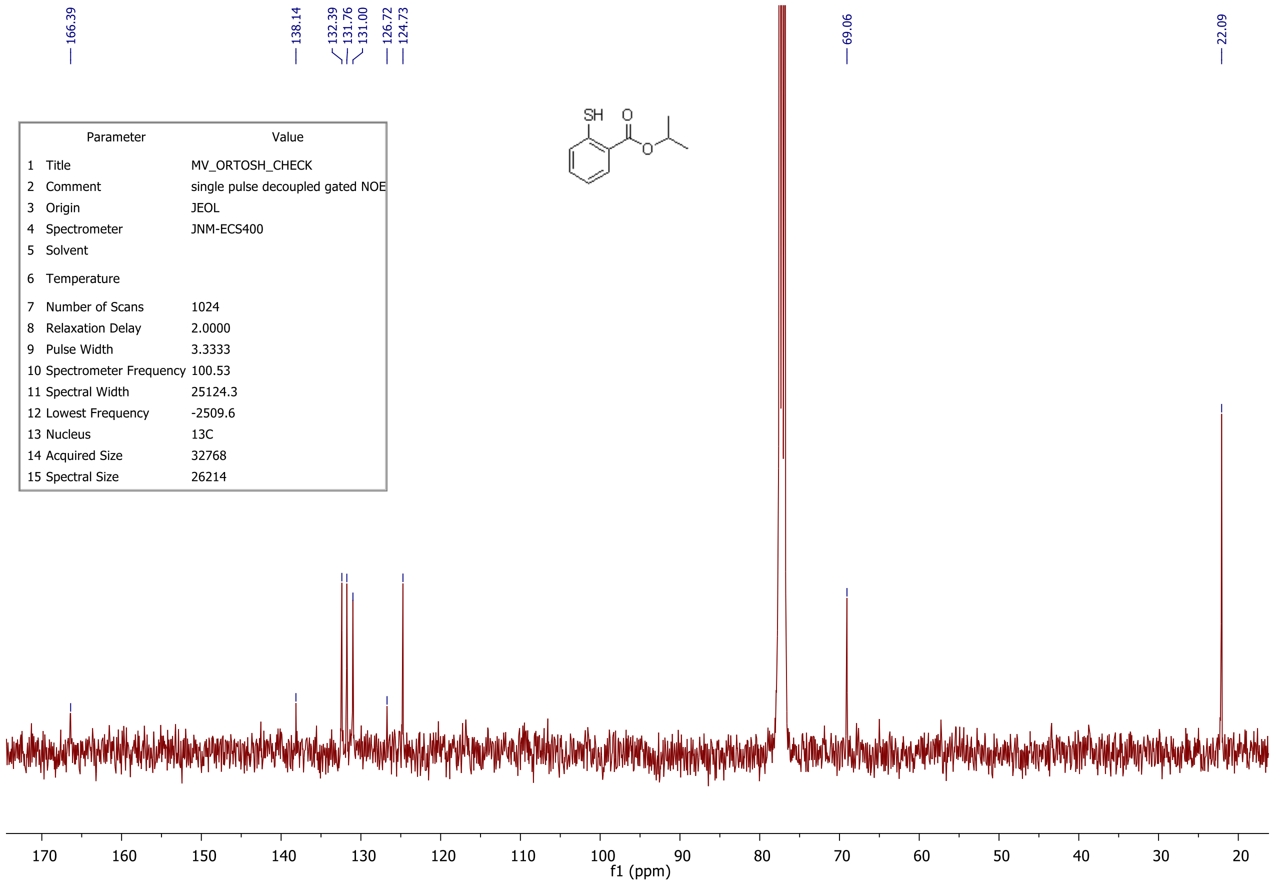


Figure S26 FT-IR (ATR) spectrum of Isopropyl 2-mercaptobenzoate



	Parameter	Value
1	Title	MV-1-102D
2	Comment	single_pulse
3	Origin	JEOL
4	Spectrometer	JNM-ECS400
5	Solvent	CDCl3
6	Temperature	25°C
7	Number of Scans	8
8	Relaxation Delay	5.0000
9	Pulse Width	3.3750
10	Spectrometer Frequency	399.78
11	Spectral Width	6001.9
12	Lowest Frequency	-1002.0
13	Nucleus	1H
14	Acquired Size	16384
15	Spectral Size	13107

Figure S27 ^{1}H-NMR spectrum of isopropyl 2-mercaptobenzoate (CDCl$_3$, 399.78 MHz)

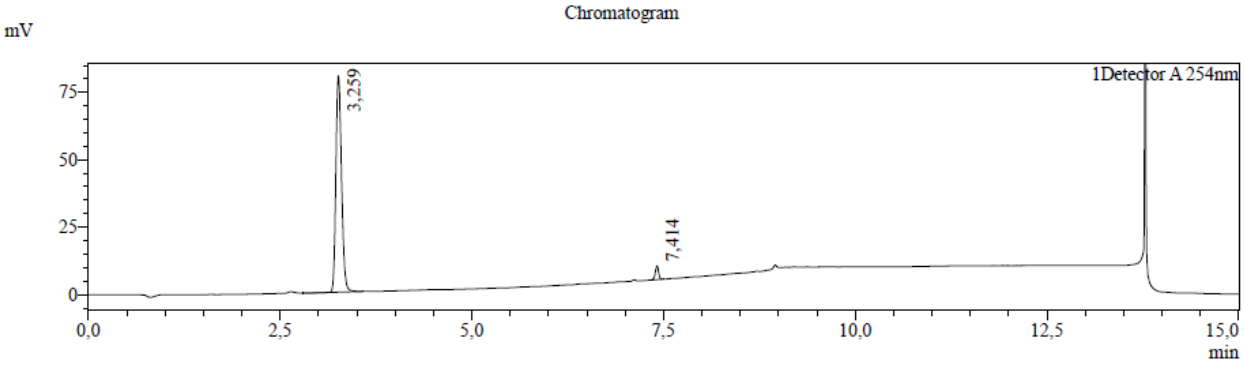


	Parameter	Value
1	Title	MV_ORTOSH_CHECK
2	Comment	single pulse decoupled gated NOE
3	Origin	JEOL
4	Spectrometer	JNM-ECS400
5	Solvent	
6	Temperature	
7	Number of Scans	1024
8	Relaxation Delay	2.0000
9	Pulse Width	3.3333
10	Spectrometer Frequency	100.53
11	Spectral Width	25124.3
12	Lowest Frequency	-2509.6
13	Nucleus	13C
14	Acquired Size	32768
15	Spectral Size	26214

Figure S28 ^{13}C-NMR spectrum of Isopropyl 2-mercaptobenzoate ($CDCl_3$, 100.53 MHz)

Isopropyl 4-mercaptobenzoate: A solution of diisopropyl 4,4'-dithiobisbenzoate (610 mg, 1.56 mmol, 1.00 eq) and grinded dried zinc powder (1.85 g, 28.29 mmol, 18.0 eq) in acetic acid (10 mL) was heated overnight at 90°C under argon atmosphere. Upon completion of the reaction, the reaction mixture was diluted with 50 mL of 1 N HCl (aq.) and extracted thrice with dichloromethane (3x20 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The desired thiol was obtained as a brown oil (596 mg, 3.04 mmol, 97% yield) and used without further purification.

^{1}H NMR (399.78 MHz, $CDCl_3$ ppm) δ = 7.88 (ddd, 2H, *J* = 8.5, 1.8, 1.8 Hz), 7.27 (ddd, 2H, *J* = 8.6, 1.8, 1.8 Hz), 5.23 (sept, 1H, *J* = 6.3 Hz), 3.59 (s, 1H), 1.35 (d, 6H, *J* = 6.3 Hz); **^{13}C NMR (100.53 MHz, $CDCl_3$ ppm)** δ = 165.80, 138.09, 130.33, 128.20, 128.05, 68.54, 22.10; **IR (cm^{-1})** ν = 2980, 2556, 1705, 1594, 1404, 1270, 1177, 1099, 1015, 918, 846, 757, 688; **LC-MS**, acetonitrile/water APCI: 195 *m/z* [M-H]$^{-}$.



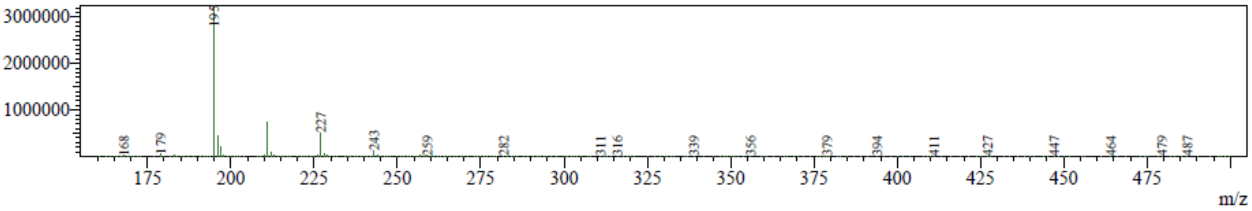


Figure S29 reversed-phase HPLC chromatogram of Isopropyl 4-mercaptobenzoate and MS-APCI of different peaks (negative ionization).

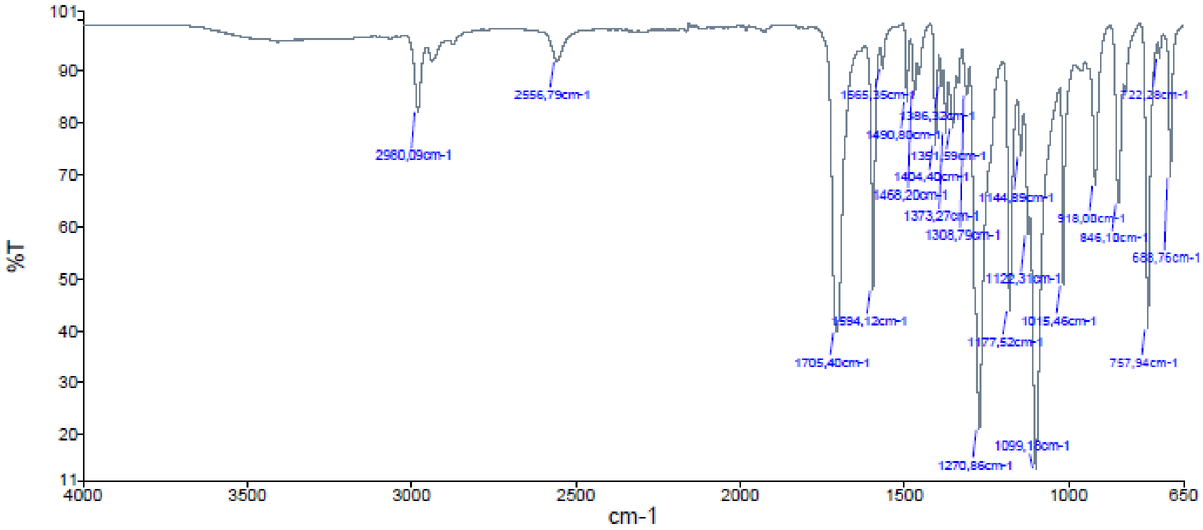
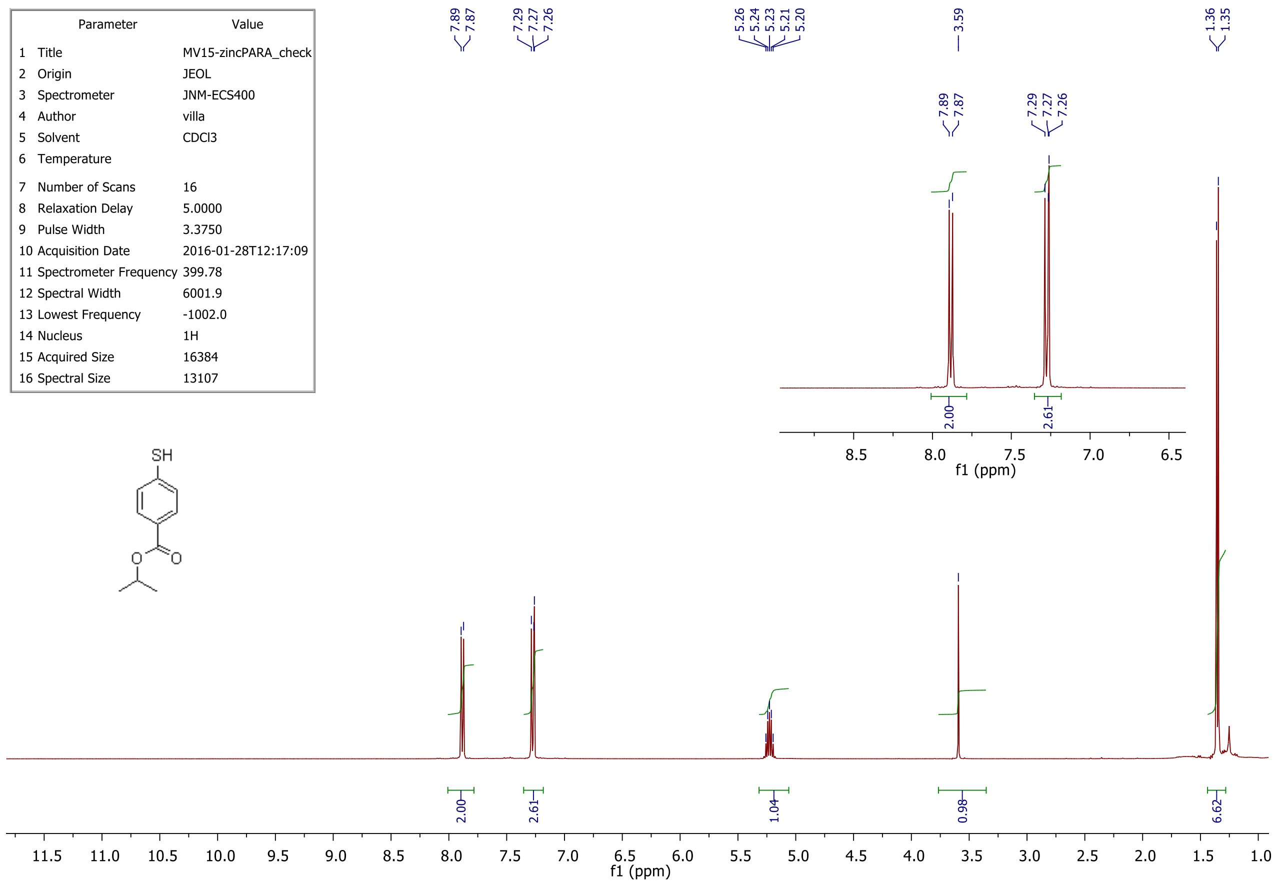
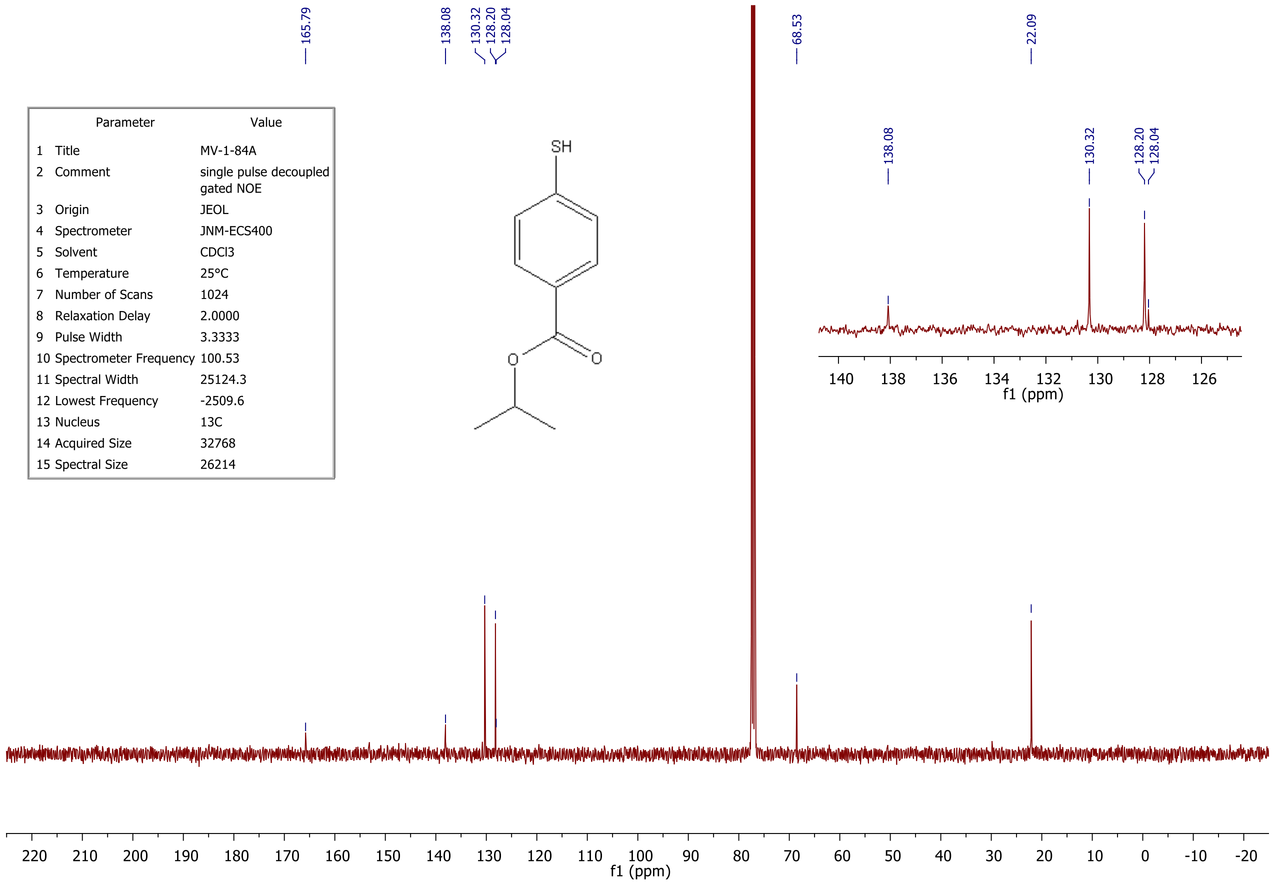


Figure S30 FT-IR (ATR) spectrum of isopropyl 4-mercaptobenzoate



	Parameter	Value
1	Title	MV15-zincPARA_check
2	Origin	JEOL
3	Spectrometer	JNM-ECS400
4	Author	villa
5	Solvent	CDCl3
6	Temperature	
7	Number of Scans	16
8	Relaxation Delay	5.0000
9	Pulse Width	3.3750
10	Acquisition Date	2016-01-28T12:17:09
11	Spectrometer Frequency	399.78
12	Spectral Width	6001.9
13	Lowest Frequency	-1002.0
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	13107

Figure S31 1H-NMR spectrum of isopropyl 4-mercaptobenzoate (CDCl$_3$, 399.78 MHz)



	Parameter	Value
1	Title	MV-1-84A
2	Comment	single pulse decoupled gated NOE
3	Origin	JEOL
4	Spectrometer	JNM-ECS400
5	Solvent	CDCl3
6	Temperature	25°C
7	Number of Scans	1024
8	Relaxation Delay	2.0000
9	Pulse Width	3.3333
10	Spectrometer Frequency	100.53
11	Spectral Width	25124.3
12	Lowest Frequency	-2509.6
13	Nucleus	13C
14	Acquired Size	32768
15	Spectral Size	26214

Figure S32 ^{13}C-NMR spectrum of isopropyl 4-mercaptobenzoate (CDCl$_3$, 100.53 MHz)

Hexaisopropyl 3,3',3'',3''',3'''',3'''''-(benzene-1,2,3,4,5,6-hexaylhexakis(sulfanediyl))hexabenzoate (1M):

Hexafluorobenzene (57 µL, 0.49 mmol, 1.0 eq), isopropyl-3-mercaptobenzoate (1.517 g, 7.74 mmol, 15.7 eq) and dry Cs$_2$CO$_3$ (3.402 g, 10.30 mmol, 21.0 eq) were dried under high vacuum for 30 min before being introduced into an oven-dried sealed tube. Under an argon atmosphere, dry 1,3- dimethyl-2-imidazolidone (DMI, 3.5 mL) was added and the mixture was vigorously stirred at 30°C (oil bath temperature) for 6 days. Upon completion of the reaction, the reaction mixture was cooled down to room temperature and diluted with 70 mL of 1N HCl (aq.). A yellow-brown solid precipitated and the reaction mixture was extracted four times with toluene (4 x 20 mL). The combined organic phases were washed four times with water (4x20 mL), dried over anhydrous MgSO$_4$, filtered and concentrated *in vacuo*. The crude yellow-orange solid was purified by trituration in ethanol/water (8:2 v/v) (20 mL) under vigorous stirring and then was recrystallized in isopropanol to give the desired compound as yellow crystals (602 mg, 0.49 mmol, 99% yield).

TLC (8:2 Heptane-ethyl acetate) R$_f$:0.2; **^{1}H NMR (399.78 MHz, CDCl$_3$, ppm)**: δ = 7.73 (d, 6H, *J* = 7.8 Hz), 7.69 (s, 6H), 7.21 (dd, 6H, *J* = 7.8, 7.8 Hz), 7.03 (d, 6H, *J* = 7.9 Hz), 5.20 (sept, 6H, *J* = 6.2 Hz), 1.34 (d, 36H, *J* = 6.2 Hz); **^{13}C NMR (100.53 MHz, CDCl$_3$, ppm)**: δ = 165.30, 148.23, 138.04, 131.87, 131.71, 129.32, 129.12, 127.43, 68.80, 22.07; **LC-MS** acetonitrile, ESI: 1265 [M+Na]$^+$, **HRMS (ESI+)** calculated for [C$_{66}$H$_{66}$O$_{12}$S$_6$ + H$^+$]: 1243.2954 Da, found [M+H$^+$] 1243.2953 *m/z*; **FT- IR (cm^{-1})** ν = 2983, 2935, 1705, 1570, 1371, 1352, 1284, 1258, 1103, 1074, 918, 749, 682; **Elemental analysis:** calculated %C 63.74 %H 5.35 %S 15.47, found %C 63.77 %H 5.26 %S 15.24.

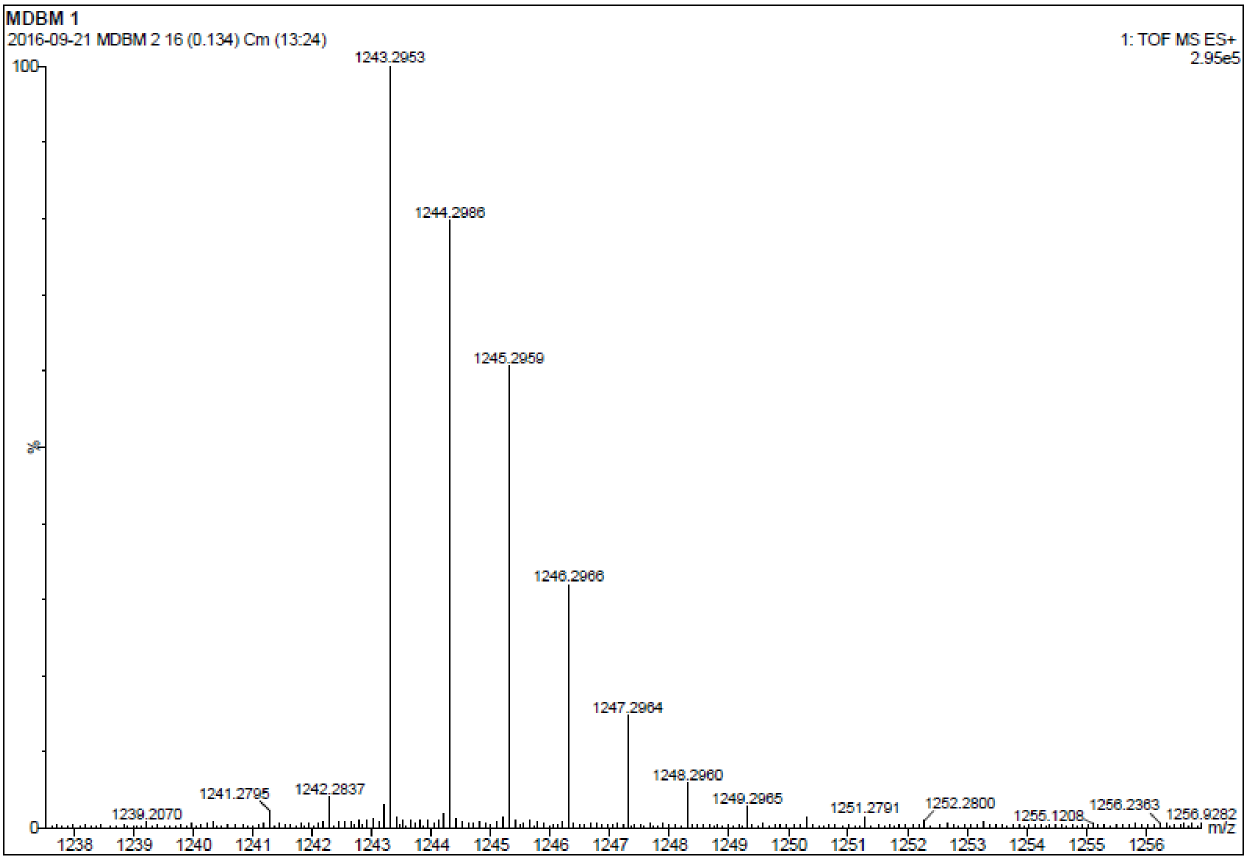


Figure S33 HR-MS of 1M

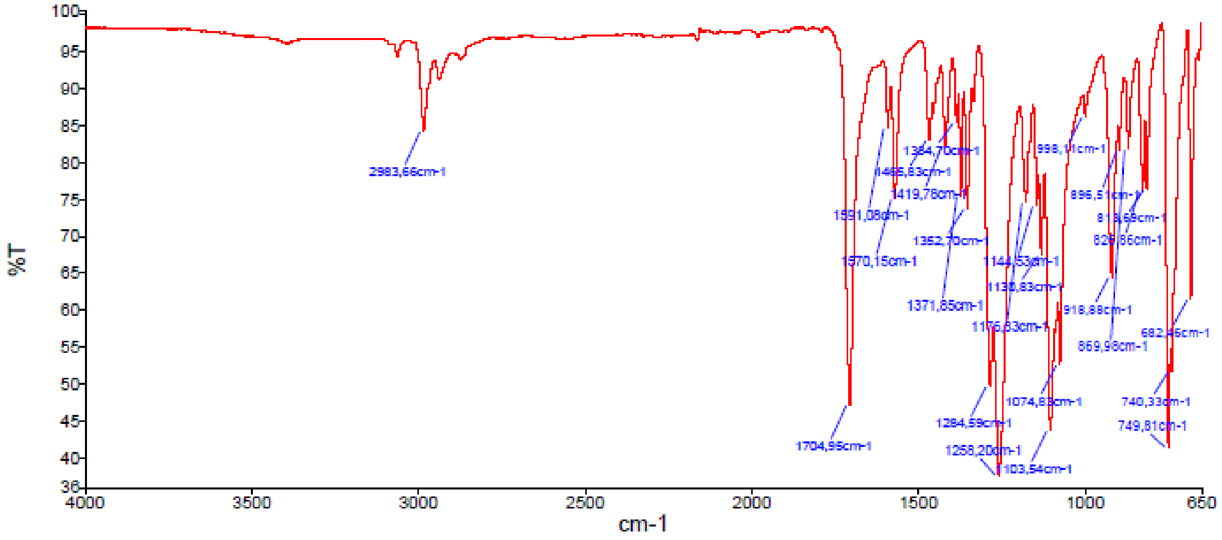


Figure S34 FT-IR (ATR) spectrum of 1M

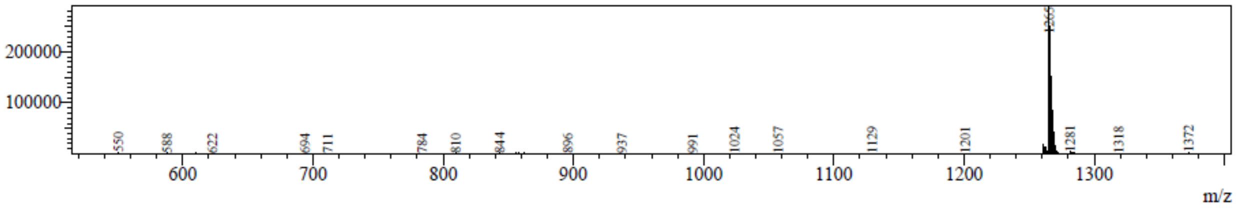
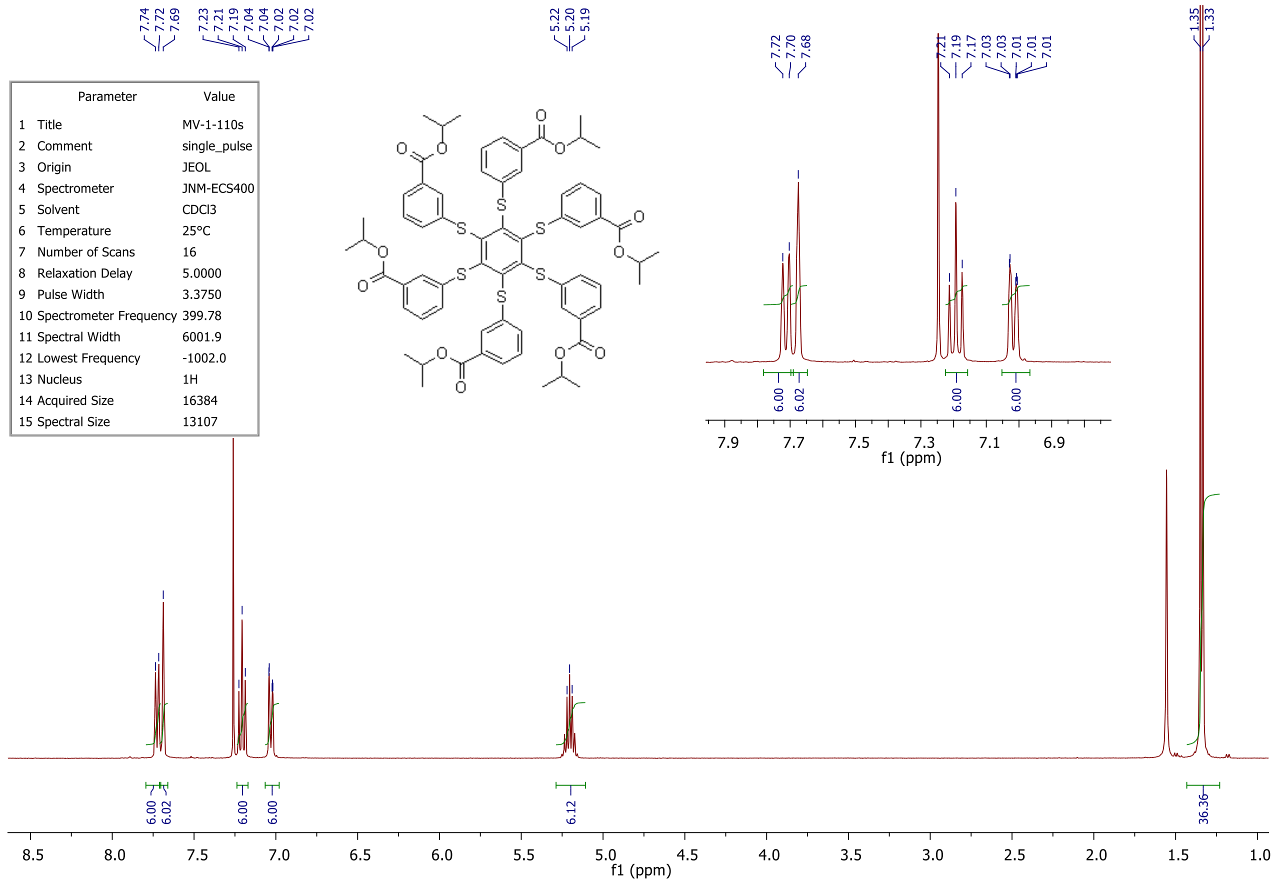
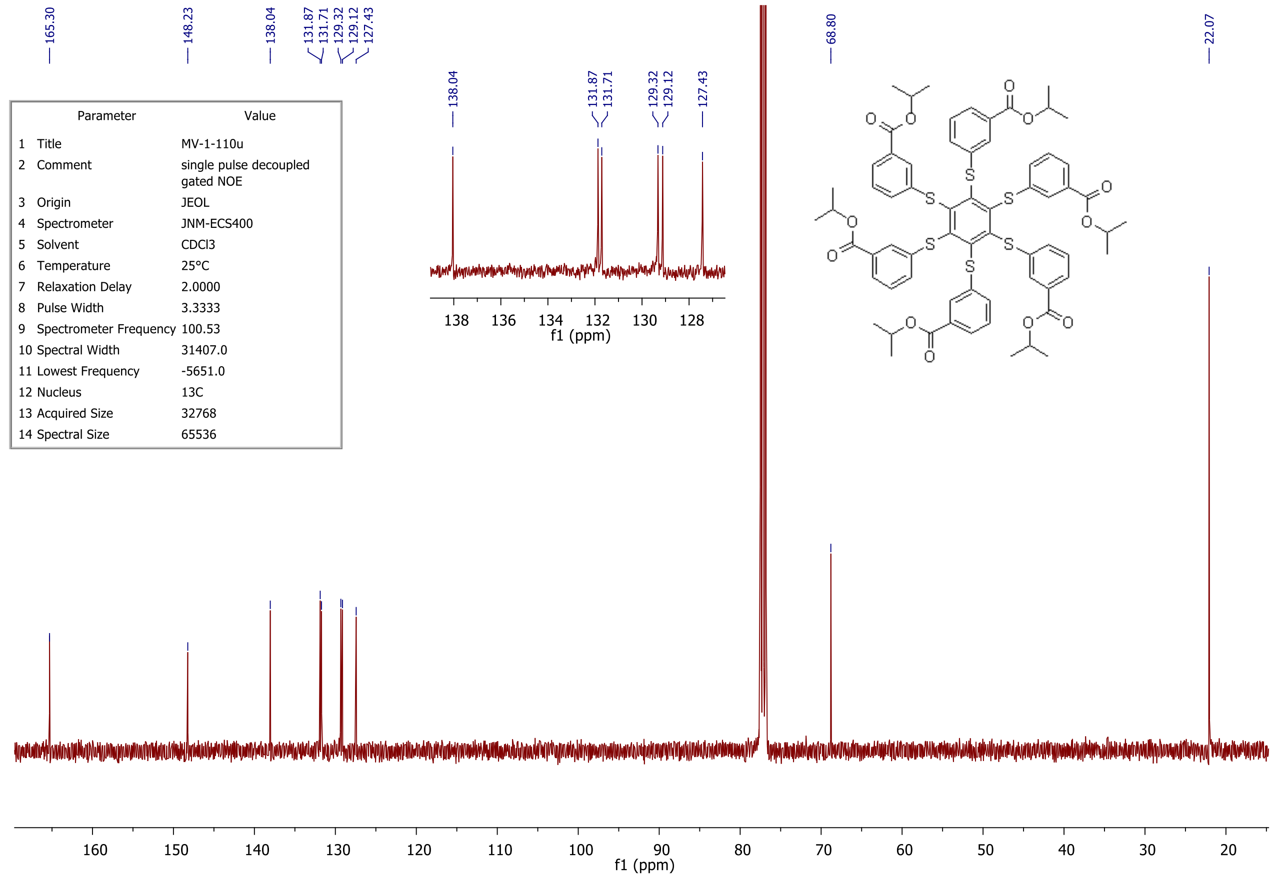


Figure S35 MS-ESI of **1M**



	Parameter	Value
1	Title	MV-1-110s
2	Comment	single_pulse
3	Origin	JEOL
4	Spectrometer	JNM-ECS400
5	Solvent	CDCl3
6	Temperature	25°C
7	Number of Scans	16
8	Relaxation Delay	5.0000
9	Pulse Width	3.3750
10	Spectrometer Frequency	399.78
11	Spectral Width	6001.9
12	Lowest Frequency	-1002.0
13	Nucleus	1H
14	Acquired Size	16384
15	Spectral Size	13107

Figure S36 ^{1}H-NMR spectrum of 1M (CDCl$_3$, 399.78 MHz)



Parameter	Value
1 Title	MV-1-110u
2 Comment	single pulse decoupled gated NOE
3 Origin	JEOL
4 Spectrometer	JNM-ECS400
5 Solvent	CDCl3
6 Temperature	25°C
7 Relaxation Delay	2.0000
8 Pulse Width	3.3333
9 Spectrometer Frequency	100.53
10 Spectral Width	31407.0
11 Lowest Frequency	-5651.0
12 Nucleus	13C
13 Acquired Size	32768
14 Spectral Size	65536

Figure S37 ^{13}C-NMR spectrum of 1M ($CDCl_3$, 100.53 MHz)

```
Composé              Temps   rét         Elément  %          Facteur
                     (min)               %                   K
-------------------- ------------------- ------------------- -------------------
Carbon               1.39                63.77               4714468
Hydrogen             3.82                5.26                13391050
Sulphur              7.51                15.24               2024149
                                         _____
                                         84.27
```

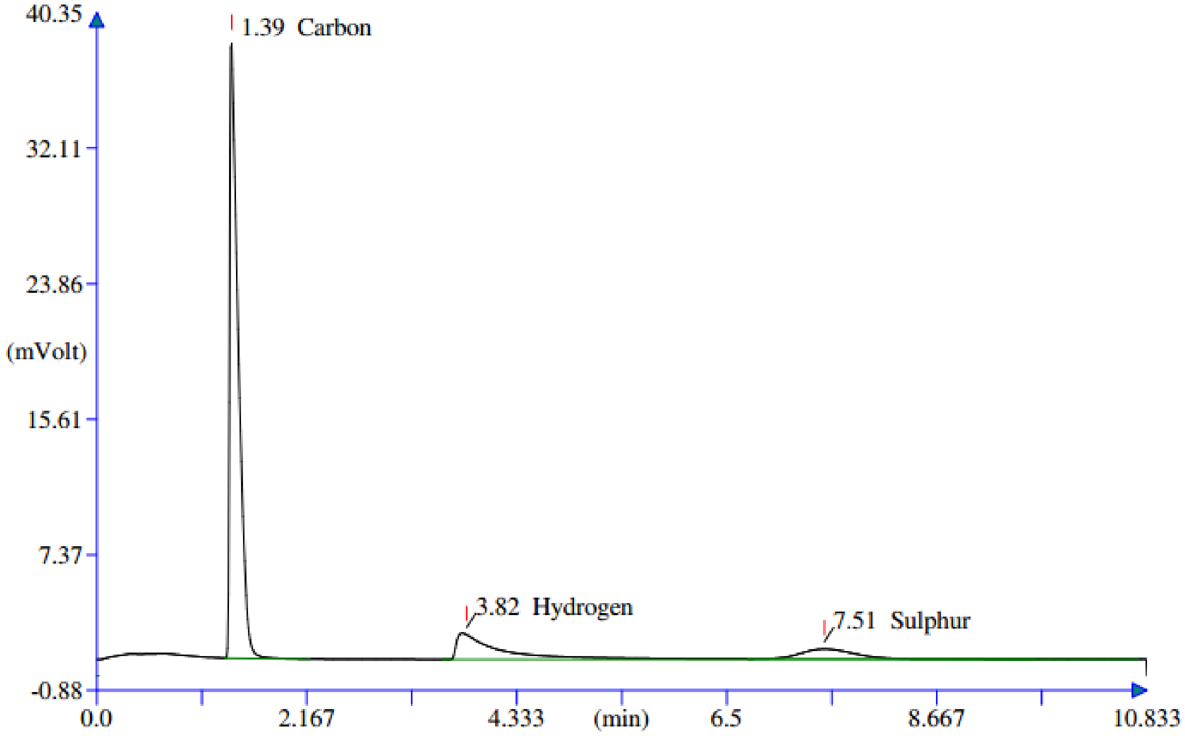


Figure S38 Elemental analysis for 1M

Hexaisopropyl 2,2',2'',2''',2'''',2'''''-(benzene-1,2,3,4,5,6-hexaylhexakis(sulfanediyl))hexabenzoate (1O):

Hexafluorobenzene (130 µL, 1.11 mmol, 1.00 eq), isopropyl-2-mercaptobenzoate (2.097 g, 10.70 mmol, 9.6 eq) and dry Cs_2CO_3 (4.407 g, 13.56 mmol, 12.2 eq) were dried under high vacuum for 30 min before being introduced into an oven-dried sealed tube. Under an argon atmosphere, dry 1,3-dimethyl-2-imidazolidone (DMI, 4 mL) was added and the mixture was vigorously stirred at 50°C (oil bath temperature) for 2 days. The reaction mixture was cooled down to room temperature and diluted with 100 mL of 1N HCl (aq.). A yellow-brown solid precipitated and the reaction mixture was extracted thrice with toluene (3x25 mL). The combined organic phases were washed five times with water (5x25 mL), dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude yellow-orange solid containing the tetrasubstituted and hexasubstituted products was purified by trituration in ethanol/water (8:2 v/v) (15 mL) under vigorous stirring. The two compounds were separated on isocratic column chromatography (SiO_2, eluent heptane/ethyl acetate (8/2 v/v)) and further purified by recrystallization in isopropanol to give pure tetrasubstituted (389.0 mg, 0.44 mmol, yield 39%) and hexasubstituted products (796.0 mg, 0.64 mmol, 58% yield).

TLC (8:2 Heptane-ethyl acetate) R_f :0.2; **^{1}H NMR (399.78 MHz, $CDCl_3$, ppm)**: δ = 7.81 (dd, 6H, *J* = 7.8, 1.5 Hz), 7.17 (ddd, 6H, *J* = 7.5, 7.5, 1.5 Hz), 7.04 (ddd, 6H, *J* = 7.7, 7.7, 1.1 Hz), 6.73 (dd, 6H, *J* = 7.7, 1.0 Hz), 5.04 (sept, 6H, *J* = 6.2 Hz), 1.14 (d, 36H, *J* = 6.3 Hz); **^{13}C NMR (100.53 MHz, $CDCl_3$, ppm)**: δ = 165.37, 150.55, 142.02, 131.83, 131.24, 128.03, 127.44, 124.61, 68.99, 21.86; **LC-MS** Acetonitrile/water ESI: 1265 *m/z* [M+H]$^+$; **HRMS (ESI+)** calculated for [$C_{66}H_{66}O_{12}S_6$ + H$^+$]: 1243.2954 Da, found [M+H$^+$] 1243.2952 *m/z*; **FT- IR (cm^{-1})** ν = 2980, 2935, 1700, 1460, 1587, 1435, 1285, 1249, 1145, 1099, 1039, 931, 736; **Elemental analysis:** calculated %C 63.74 %H 5.35 %S 15.47, found %C 63.90 %H 5.31 %S 15.65.

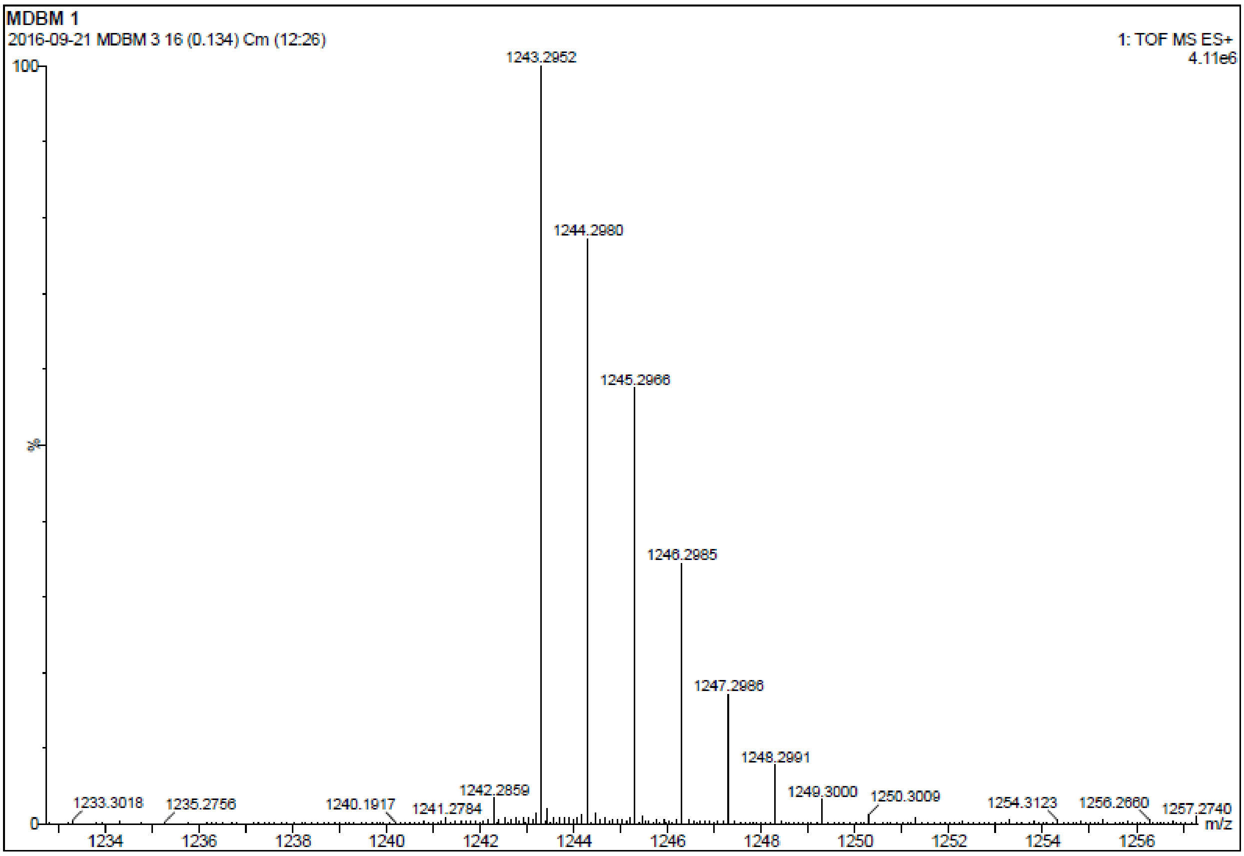


Figure S39 HR-MS of 1O

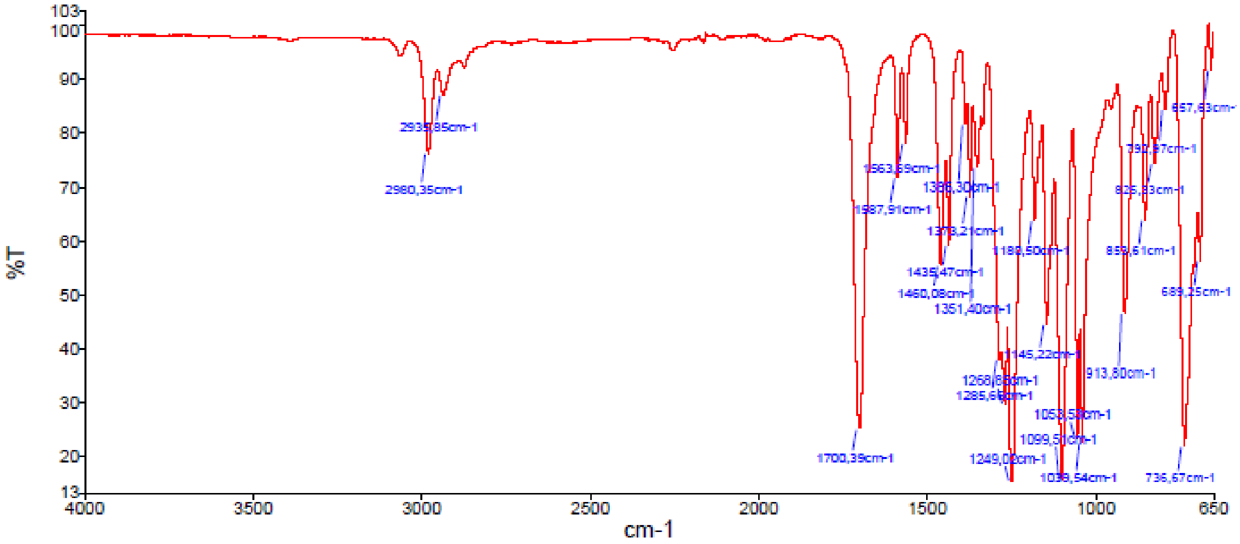


Figure S40 FT-IR (ATR) spectrum of **1O**

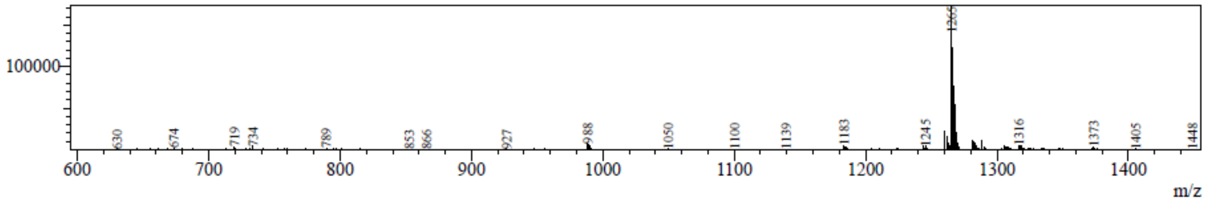
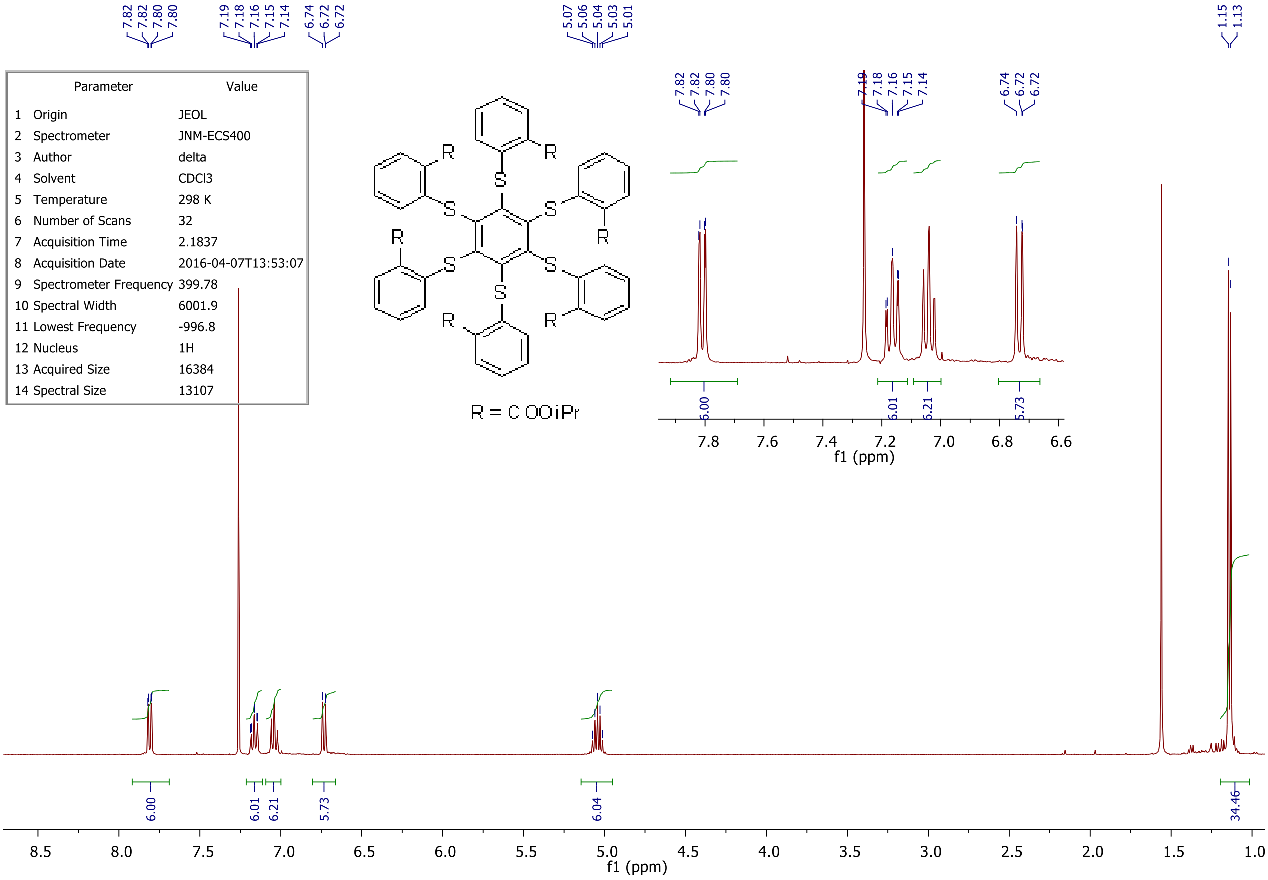


Figure S41 MS-ESI spectrum of **1O**



Parameter	Value
1 Origin	JEOL
2 Spectrometer	JNM-ECS400
3 Author	delta
4 Solvent	CDCl3
5 Temperature	298 K
6 Number of Scans	32
7 Acquisition Time	2.1837
8 Acquisition Date	2016-04-07T13:53:07
9 Spectrometer Frequency	399.78
10 Spectral Width	6001.9
11 Lowest Frequency	-996.8
12 Nucleus	1H
13 Acquired Size	16384
14 Spectral Size	13107

Figure S42 ^{1}H-NMR spectrum of 1O (CDCl$_3$, 399.78 MHz)

```
Composé            Temps   rét        Elément  %         Facteur
                   (min)              %                  K
---------------    ---------------    ---------------    ---------------
Carbon             1.39               63.90              4696704
Hydrogen           3.93               5.31               13494920
Sulphur            7.69               15.65              2019452
                                      -----
                                      84.86
```

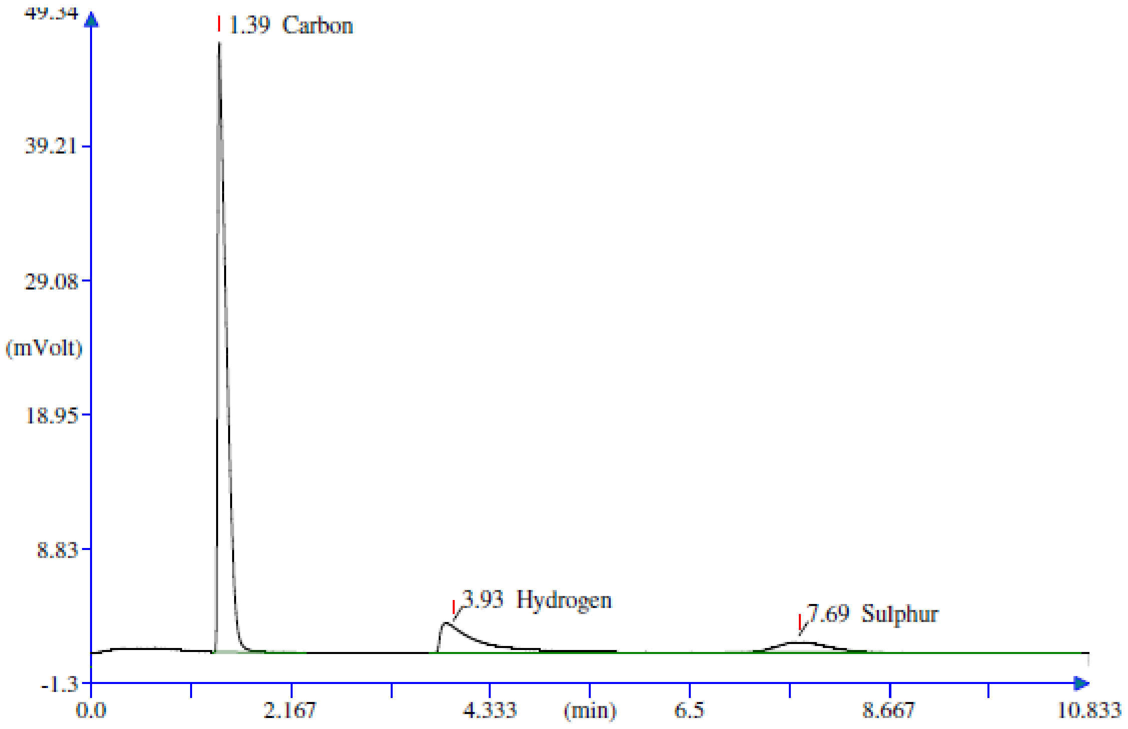
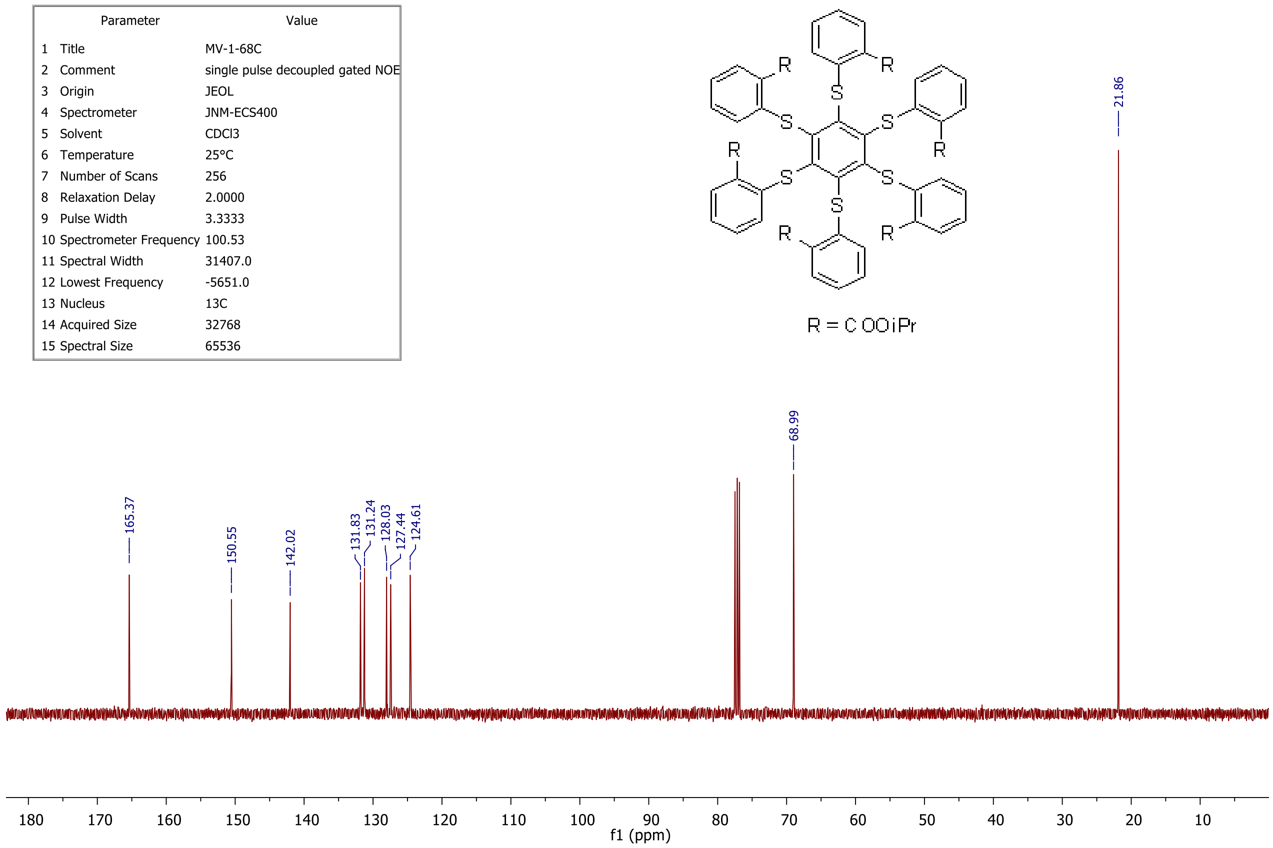


Figure S43 Elemental analysis of **1O**



Parameter	Value
1 Title	MV-1-68C
2 Comment	single pulse decoupled gated NOE
3 Origin	JEOL
4 Spectrometer	JNM-ECS400
5 Solvent	CDCl3
6 Temperature	25°C
7 Number of Scans	256
8 Relaxation Delay	2.0000
9 Pulse Width	3.3333
10 Spectrometer Frequency	100.53
11 Spectral Width	31407.0
12 Lowest Frequency	-5651.0
13 Nucleus	13C
14 Acquired Size	32768
15 Spectral Size	65536

Figure S44 ^{13}C-NMR spectrum of **1O** ($CDCl_3$, 100.53 MHz)

Hexaisopropryl 4,4',4'',4''',4'''',4'''''-(benzene-1,2,3,4,5,6-hexaylhexakis(sulfanediyl))hexabenzoate (1P):

Hexachlorobenzene (676.0 mg, 2.37 mmol, 1.00 eq), isopropyl-4-mercaptobenzoate (4.082 g, 20.83 mmol, 9.0 eq) and dry K_2CO_3 (3809 mg, 27.6 mmol, 11.7 eq) were dried under high vacuum for 30 min before being introduced into an oven-dried sealed tube. Under an argon atmosphere, dry N,N-dimethylformamide (DMF, 10 mL) was added and the mixture was vigorously stirred at 60°C (oil bath temperature) for 4 days. Upon completion of the reaction, the reaction mixture was cooled down to room temperature and diluted with 150 mL of 1N HCl (aq.). A yellow-brown solid precipitated and the reaction mixture was extracted four times with toluene (4x50 mL). The combined organic phases were washed thrice with water (3x100 mL), dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude yellow-orange solid was purified by trituration in ethanol (70 mL) under vigorous stirring and then was recrystallized in isopropanol to give the desired compound as a yellow solid (2.830 g, 2.27 mmol, 96% yield).

TLC (8:2 Heptane-ethyl acetate) R_f :0.2; **^{1}H NMR (399.78 MHz, $CDCl_3$, ppm)**: δ = 7.85 (d, 12H, *J* = 8.5 Hz), 6.93 (d, 12H, *J* = 8.4 Hz), 5.22 (sept, 6H, *J* = 6.3 Hz), 1.36 (d, 36H, *J* = 6.3 Hz); **^{13}C NMR (100.53 MHz, $CDCl_3$ ppm):** δ = 165.33, 148.11, 142.64, 130.42, 129.12, 126.97, 68.70, 22.06; **LC-MS** Acetonitrile/water APCI: 1243 *m/z* $[M+H]^+$ **HRMS (ESI+)** calculated for $[C_{66}H_{66}O_{12}S_6 + H^+]$: 1243.2954 Da, found $[M+H^+]$ 1243.2954 *m/z*; **FT- IR (cm^{-1})** ν = 2977, 2940, 1708, 1592, 1270, 1179, 1091, 1012, 917, 852, 755, 687; **Elemental analysis:** calculated %C 63.74 %H 5.35 %S 15.47, found %C 63.31 %H 5.19 %S 15.45.

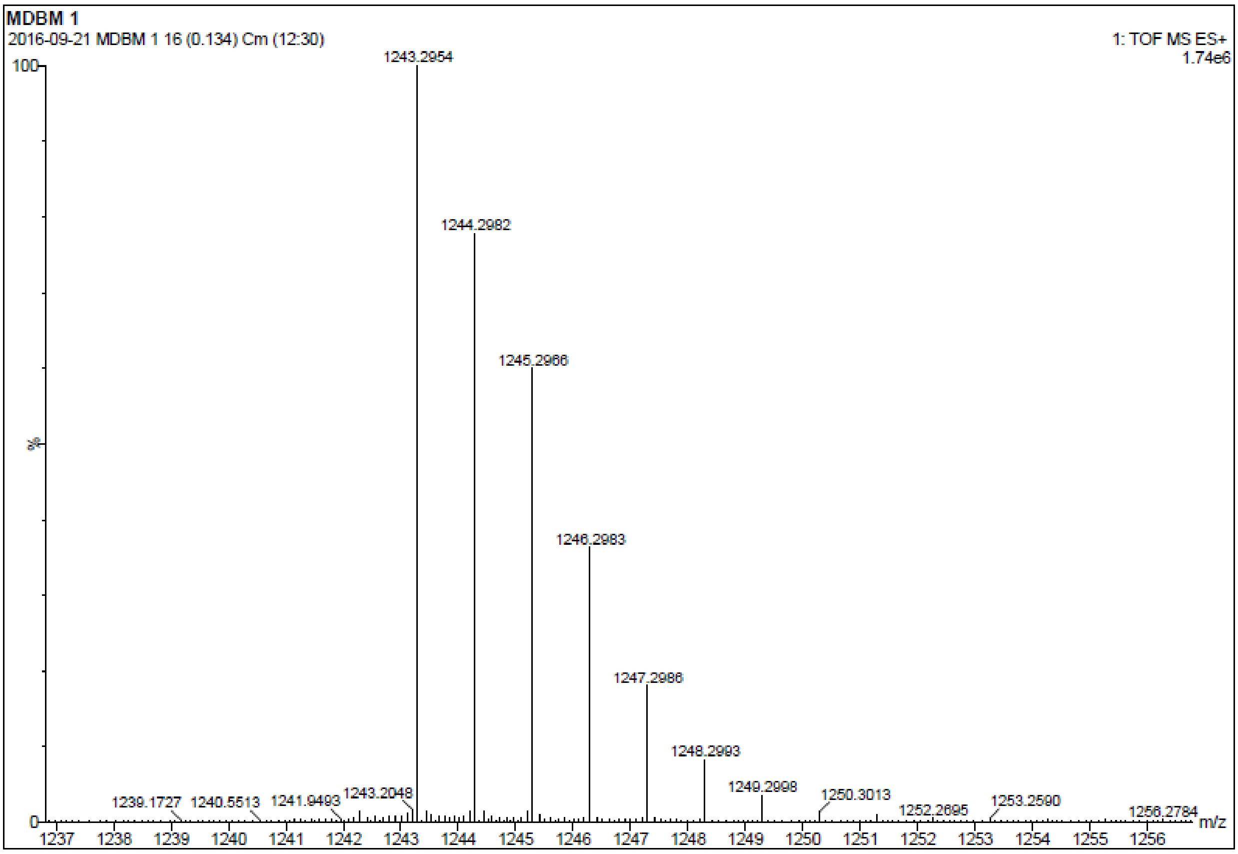


Figure S45 HR-MS of **1P**

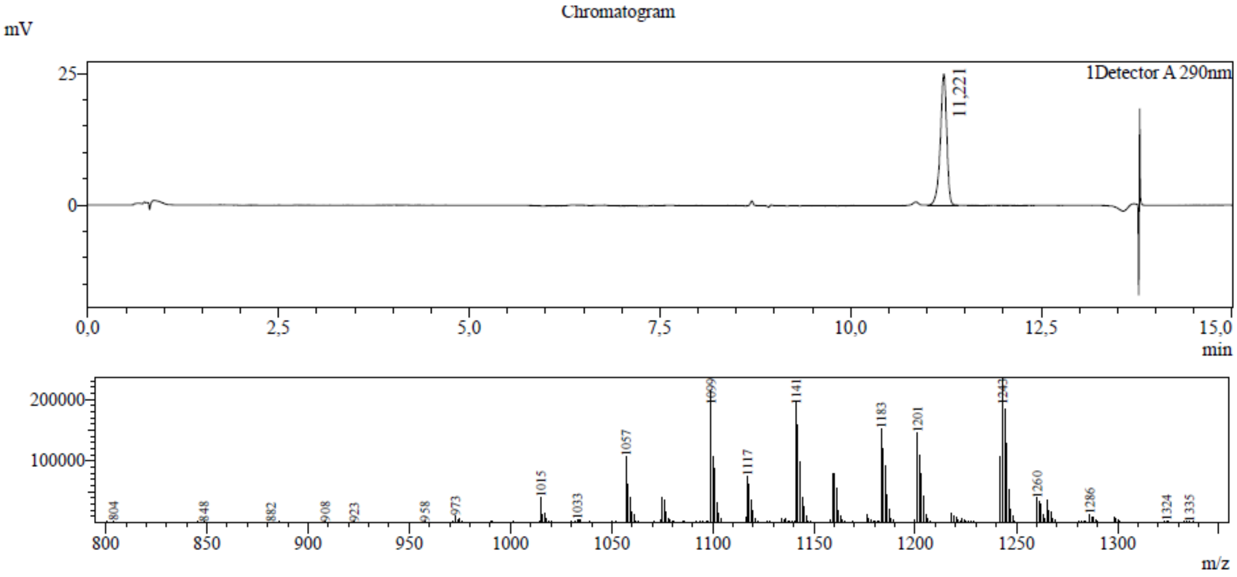


Figure S46 reversed-phase HPLC chromatogram of **1P** and MS-APCI

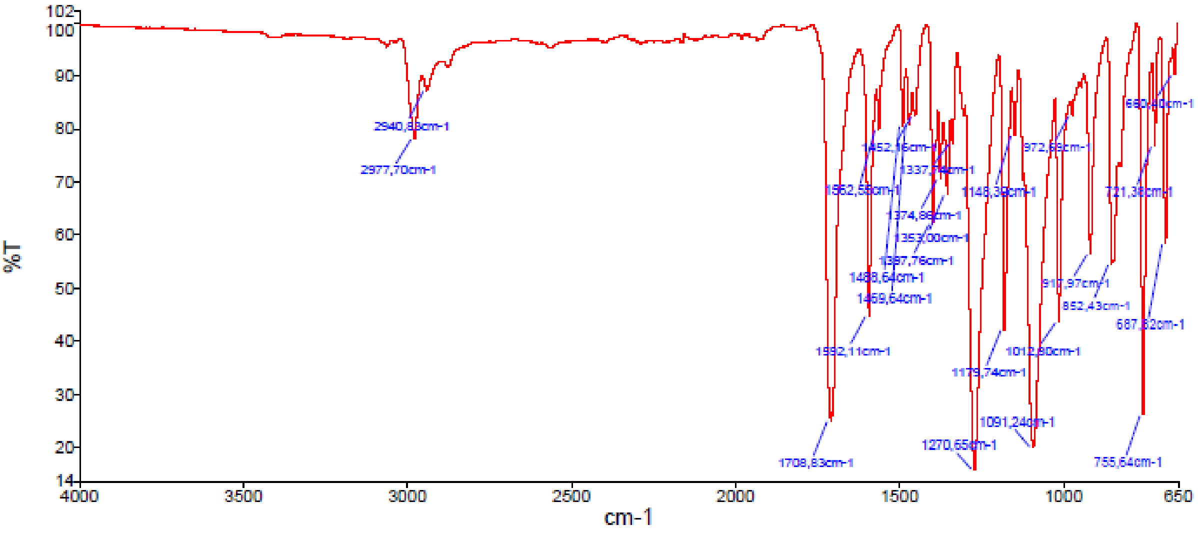
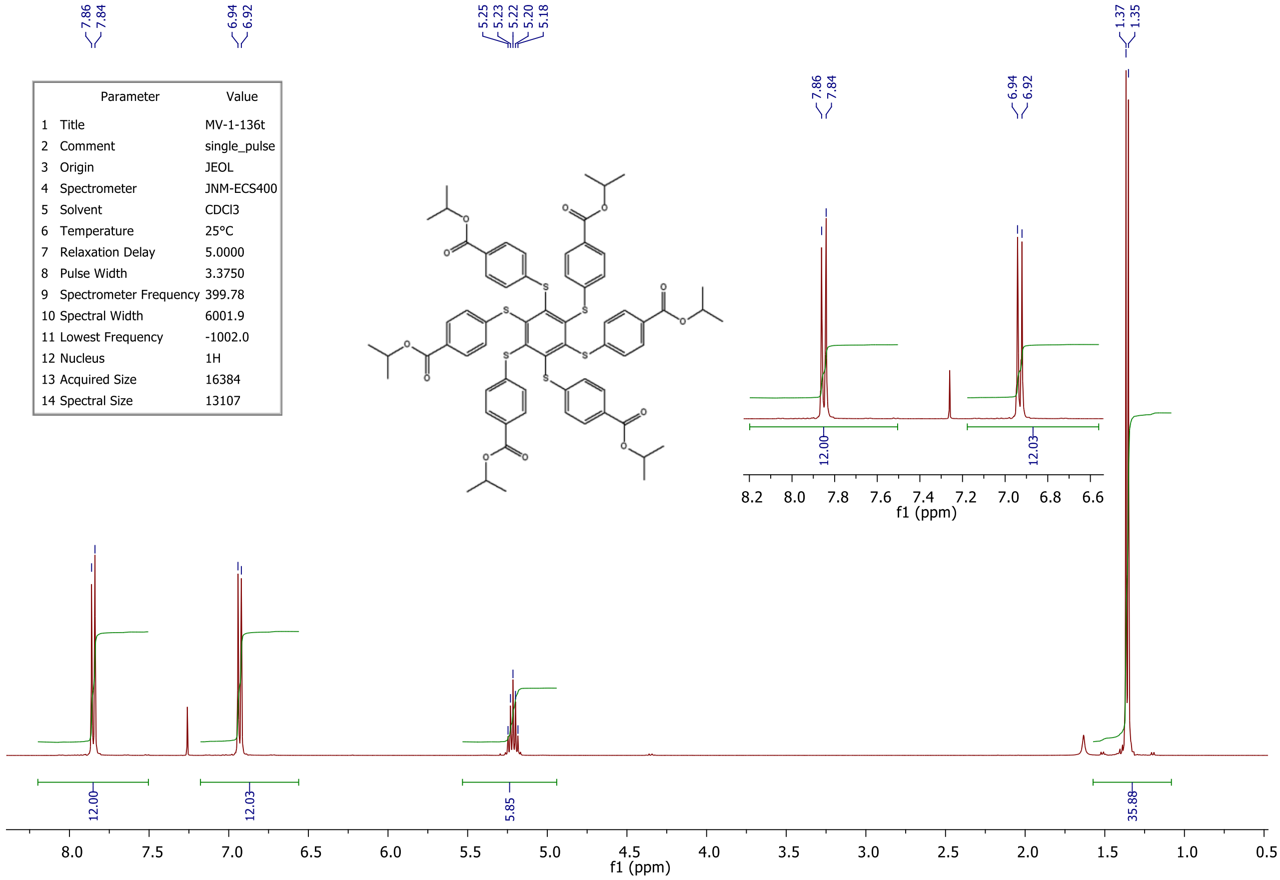
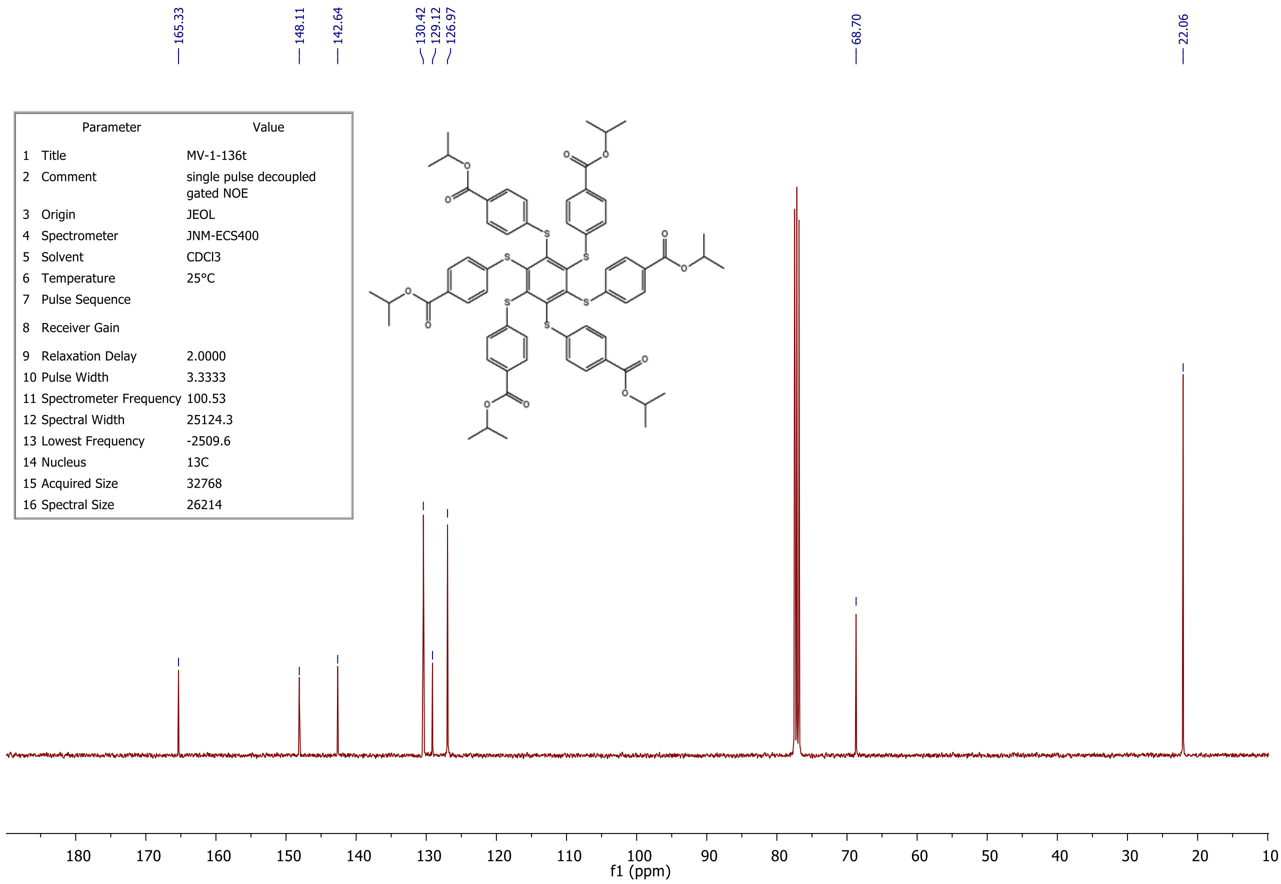


Figure S47 FT-IR spectrum of **1P**



	Parameter	Value
1	Title	MV-1-136t
2	Comment	single_pulse
3	Origin	JEOL
4	Spectrometer	JNM-ECS400
5	Solvent	CDCl3
6	Temperature	25°C
7	Relaxation Delay	5.0000
8	Pulse Width	3.3750
9	Spectrometer Frequency	399.78
10	Spectral Width	6001.9
11	Lowest Frequency	-1002.0
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	13107

Figure S48 ^{1}H-NMR spectrum of **1P** ($CDCl_3$, 399.78 MHz)



	Parameter	Value
1	Title	MV-1-136t
2	Comment	single pulse decoupled gated NOE
3	Origin	JEOL
4	Spectrometer	JNM-ECS400
5	Solvent	CDCl3
6	Temperature	25°C
7	Pulse Sequence	
8	Receiver Gain	
9	Relaxation Delay	2.0000
10	Pulse Width	3.3333
11	Spectrometer Frequency	100.53
12	Spectral Width	25124.3
13	Lowest Frequency	-2509.6
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	26214

Figure S49 ^{13}C-NMR spectrum of **1P** ($CDCl_3$, 100.53 MHz)

```
Composé              Temps    rét        Elément  %          Facteur
                     (min)               %                   K
-------------------  -------------------  -------------------  -------------------
Carbon               1.39                 63.31                4714468
Hydrogen             3.82                 5.19                 13391050
Sulphur              7.50                 15.45                2024149
                                          _____
                                          83.95
```

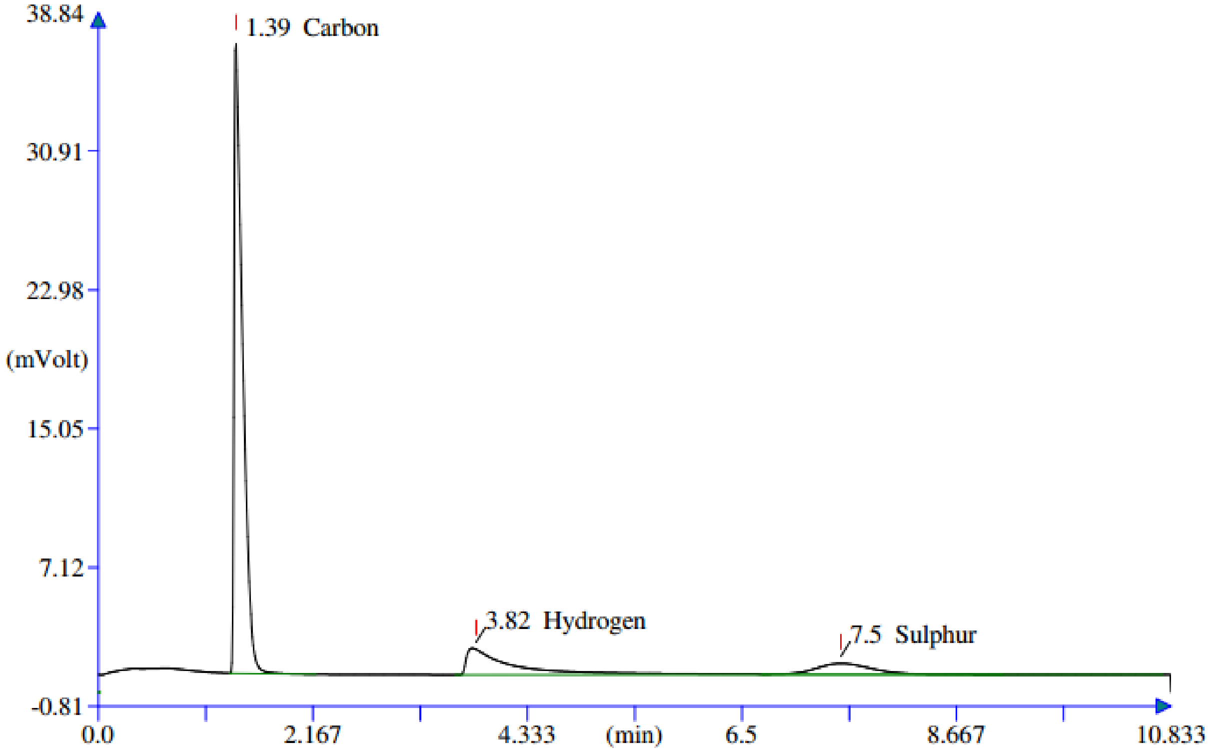


Figure S50 Elemental analysis for **1P**

3,3',3'',3''',3'''',3'''''-(benzene-1,2,3,4,5,6-hexaylhexakis(sulfanediyl))hexabenzoic acid (2M):

A solution of **1M** (205.0 mg, 0.16 mmol, 1.0 eq) and LiOH*H2O (125.0 mg, 10.00 mmol, 63.0 eq) in absolute ethanol (50 mL) was heated under argon atmosphere at 70°C (oil bath temperature) for 16h. The reaction was monitored by IR. Upon completion of the reaction, the reaction mixture was cooled down to room temperature and diluted with 50 mL of 1N HCl (aq.). A yellow solid precipitated providing a suspension. The solid was filtered and dried under vacuum at 60°C for 3 days to yield the desired product as a yellow-green solid (160.0 mg, 0.16 mmol, 98% yield).

^{1}H NMR (399.78 MHz, DMSO-d$_6$, ppm): δ = 7.67 (d, 6H, *J* = 7.7 Hz), 7.54 (s, 6H), 7.31 (dd, 6H, *J* = 7.9, 7.9 Hz), 7.11 (d, 6H, *J* = 7.9 Hz); **^{13}C NMR (100.53 MHz, DMSO-d$_6$, ppm)**: δ = 166.47, 147.71, 137.40, 132.15, 130.98, 129.61, 127.94, 127.19; **HRMS (ESI+)** calculated for [$C_{48}H_{30}O_{12}S_6$ + H$^+$]: 991.0156 Da, found [M+H$^+$] 991.0157 *m/z*; **FT-IR (cm^{-1})** ν = 3500-2500, 1681, 1570, 1408, 1295, 1259, 1151, 1071, 742, 711, 670; **Elemental analysis:** calculated %C 58.17 %H 3.05 %S 19.37, found %C 58.32 %H 2.88 %S 20.70.

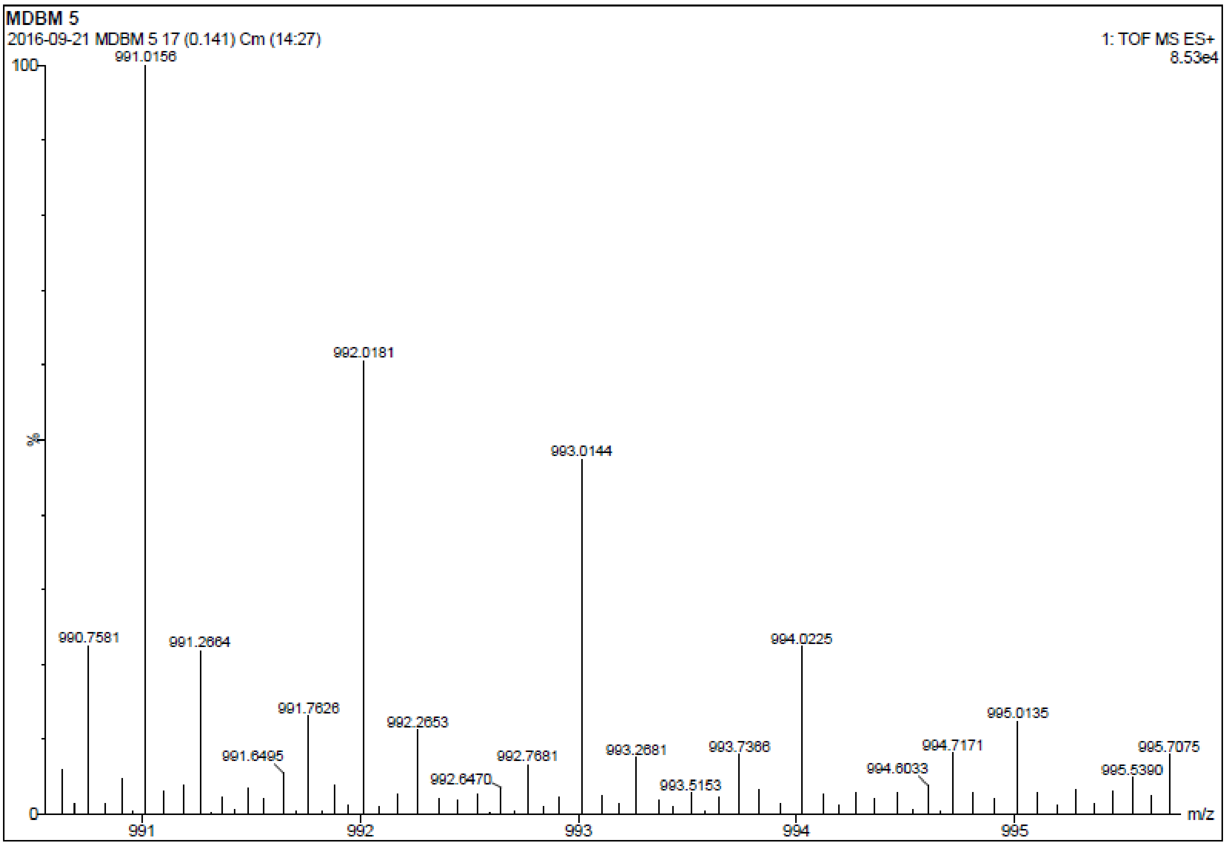


Figure S51 HR-MS of **2M**

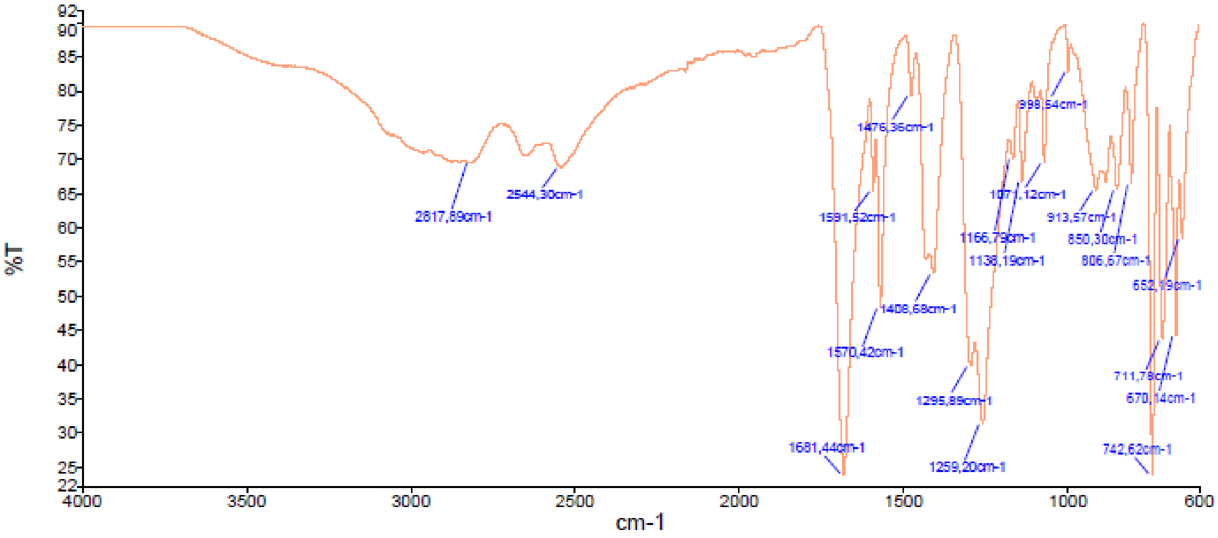
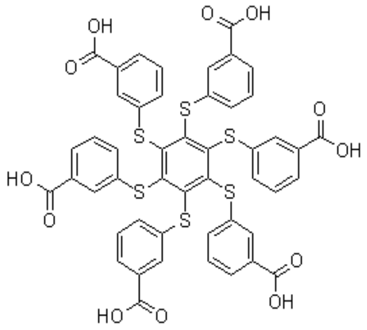
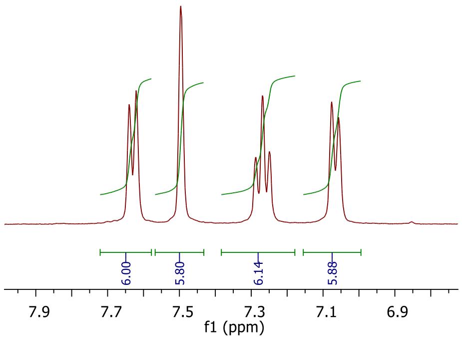


Figure S52 FT-IR spectrum of 2M

	Parameter	Value
1	Title	MV-1-128u
2	Comment	single_pulse
3	Origin	JEOL
4	Spectrometer	JNM-ECS400
5	Solvent	DMSO-d6
6	Temperature	25°C
7	Relaxation Delay	5.0000
8	Pulse Width	3.3750
9	Spectrometer Frequency	399.78
10	Spectral Width	7503.0
11	Lowest Frequency	-1752.6
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768





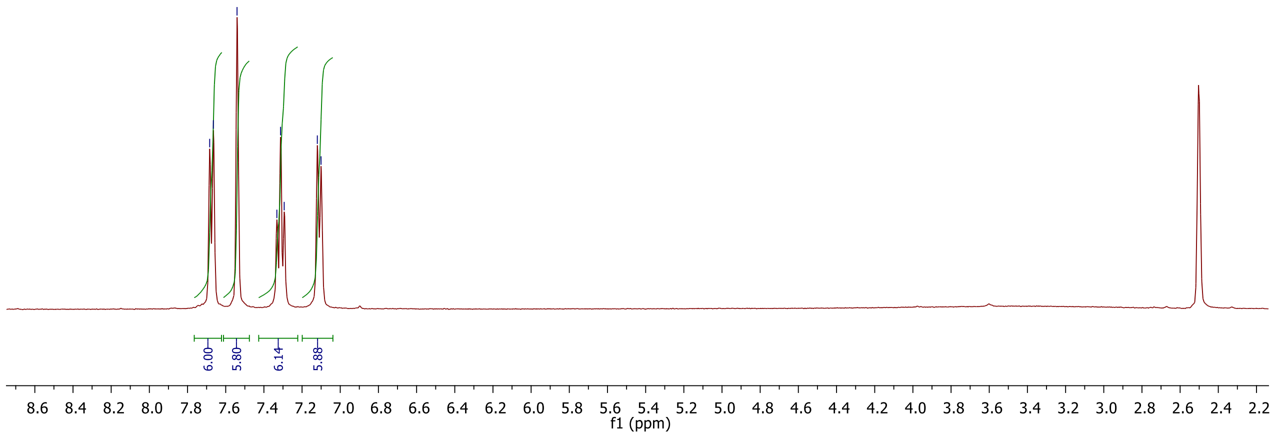
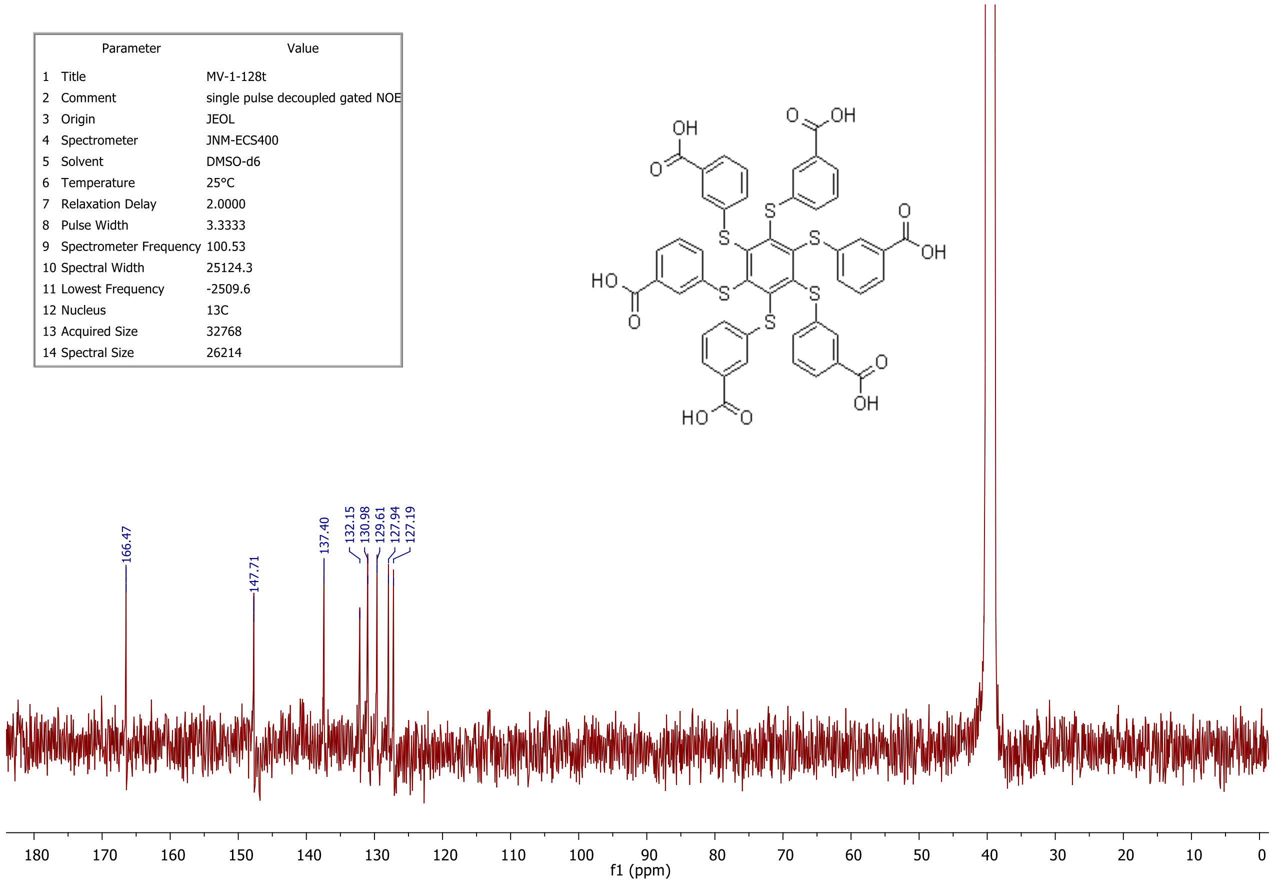


Figure S53 ^{1}H-NMR spectrum of **2M** (DMSO-d_6, 399.78 MHz)



	Parameter	Value
1	Title	MV-1-128t
2	Comment	single pulse decoupled gated NOE
3	Origin	JEOL
4	Spectrometer	JNM-ECS400
5	Solvent	DMSO-d6
6	Temperature	25°C
7	Relaxation Delay	2.0000
8	Pulse Width	3.3333
9	Spectrometer Frequency	100.53
10	Spectral Width	25124.3
11	Lowest Frequency	-2509.6
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	26214

Figure S54 ^{13}C-NMR spectrum of **2M** (DMSO-d_6, 100.53 MHz)

Composé	Temps rét (min)	Elément % %	Facteur K
Carbon	1.39	58.32	4714468
Hydrogen	3.86	2.88	13391050
Sulphur	7.46	20.70	2024149
		81.90	

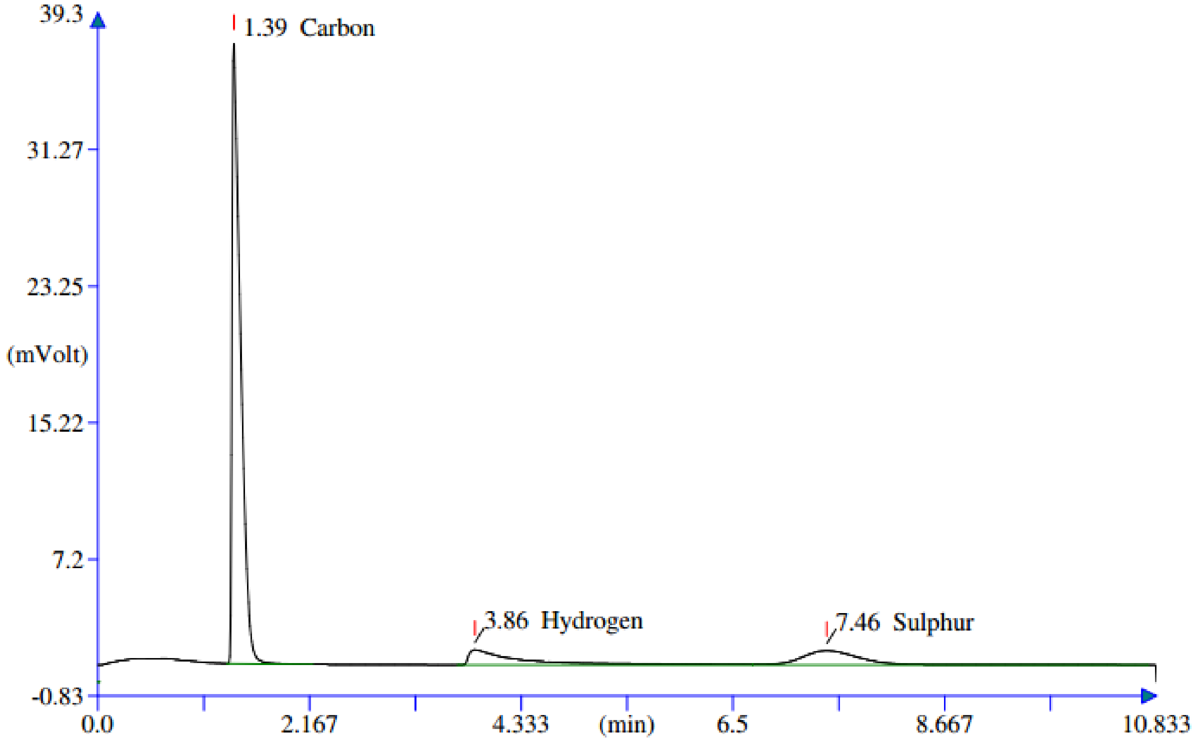


Figure S55 Elemental analysis for **2M**

2,2',2'',2''',2'''',2'''''-(benzene-1,2,3,4,5,6-hexaylhexakis(sulfanediyl))hexabenzoic acid (2O):

A solution of **1O** (500.0 mg, 0.40 mmol, 1.0 eq) and LiOH*H_2O (1.025 g, 24.44 mmol, 61.1 eq) in absolute ethanol (85 mL) was heated under argon atmosphere at 70°C (oil bath temperature) for 3 days. The reaction was monitored by IR. Upon completion of the reaction, the reaction mixture was cooled down to room temperature and diluted with 150 mL of 1N HCl (aq.). A yellow solid precipitated providing a suspension. The solid was filtered and dried under vacuum at 60°C for 3 days to yield the desired product as a yellow solid (379.0 mg, 0.38 mmol, 95 % yield).

^{1}H NMR (399.78 MHz, DMSO-d$_6$, ppm): δ = 7.81 (d, 6H, *J* = 7.7 Hz), 7.40 (br dd, 6H, *J* = 7.0, 7.0 Hz), 7.16 (dd, 6H, *J* = 7.5, 7.5 Hz), 6.81 (d, 6H, *J* = 7.9 Hz); **^{13}C NMR (100.53 MHz, DMSO-d$_6$, ppm)**: 166.91, 150.72, 142.09, 132.64, 130.94, 126.76, 126.73, 124.68. **HRMS (ESI+)** calculated for [$C_{48}H_{30}O_{12}S_6$ + Li^+]: 997.0217 Da, found [M+Li^+] 997.0157; $[M+H]^+$ 991.0157 *m/z*; **FT- IR (cm^{-1})** ν = 3500-2500, 1673, 1562, 1463, 1403, 1254, 1151, 1055, 1039, 740, 696; **Elemental analysis:** calculated $C_{48}H_{30}O_{12}S_6$*H_2O %C 57.13 %H 3.20 %S 19.06, found %C 57.19 %H 2.94 %S 19.26.

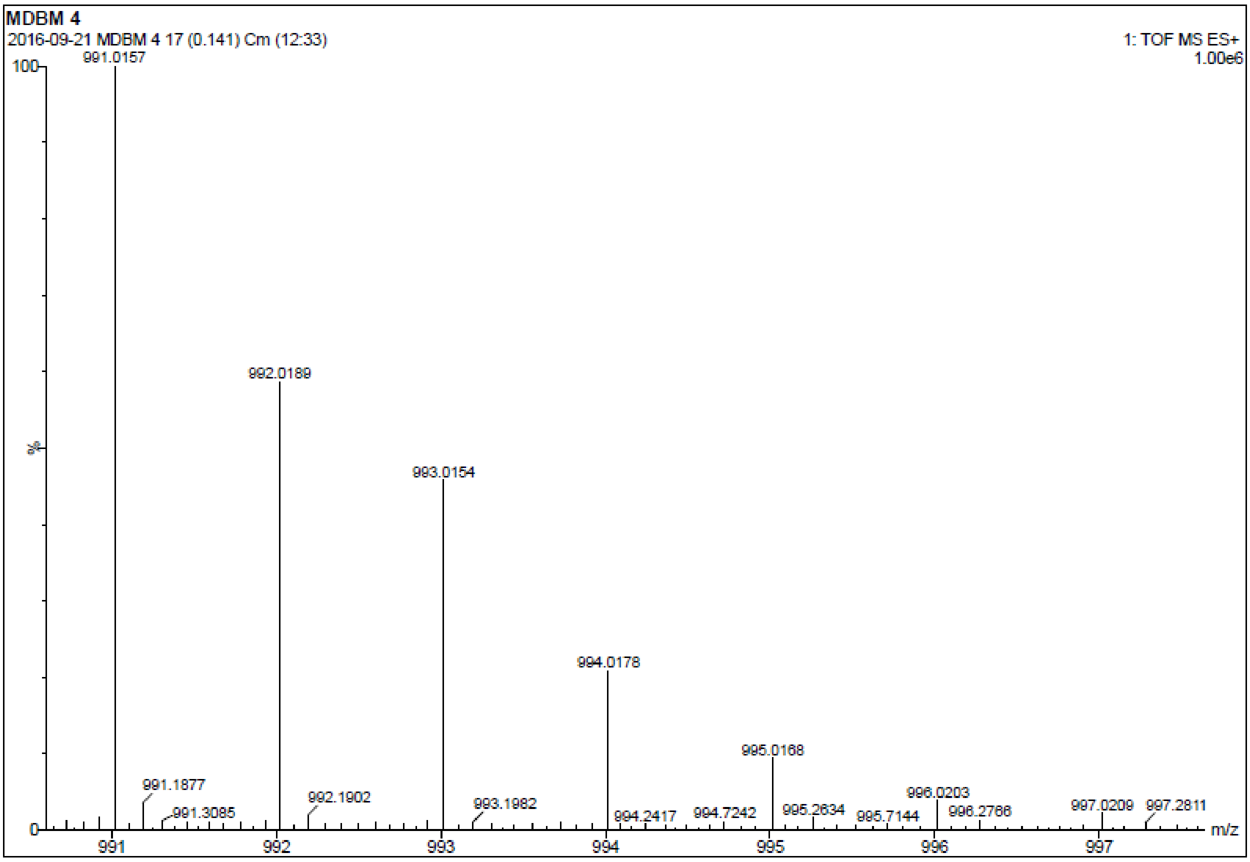


Figure S56 HR-MS of **2O**

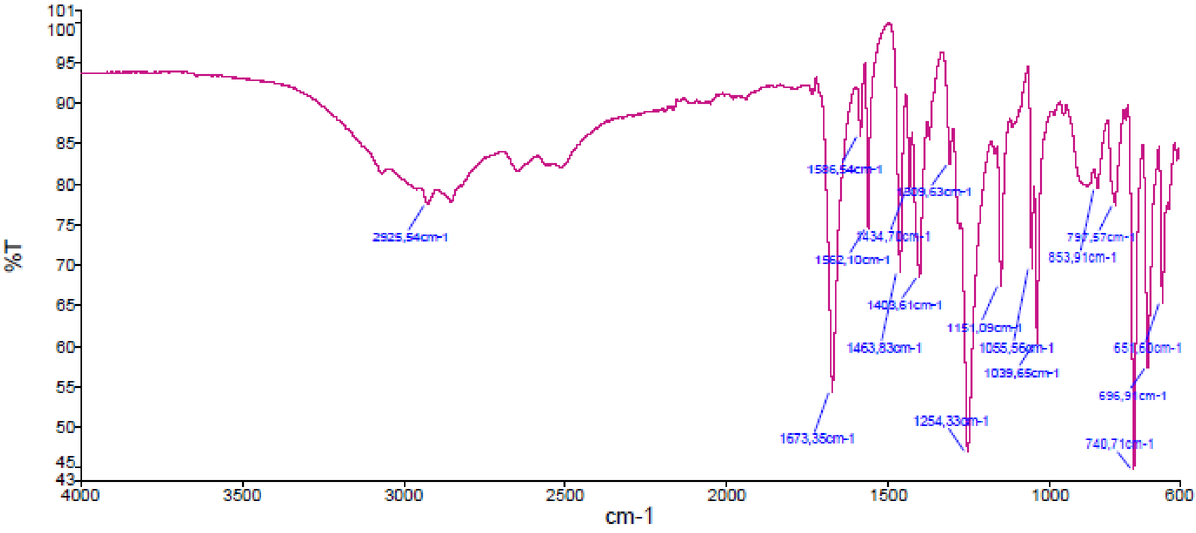
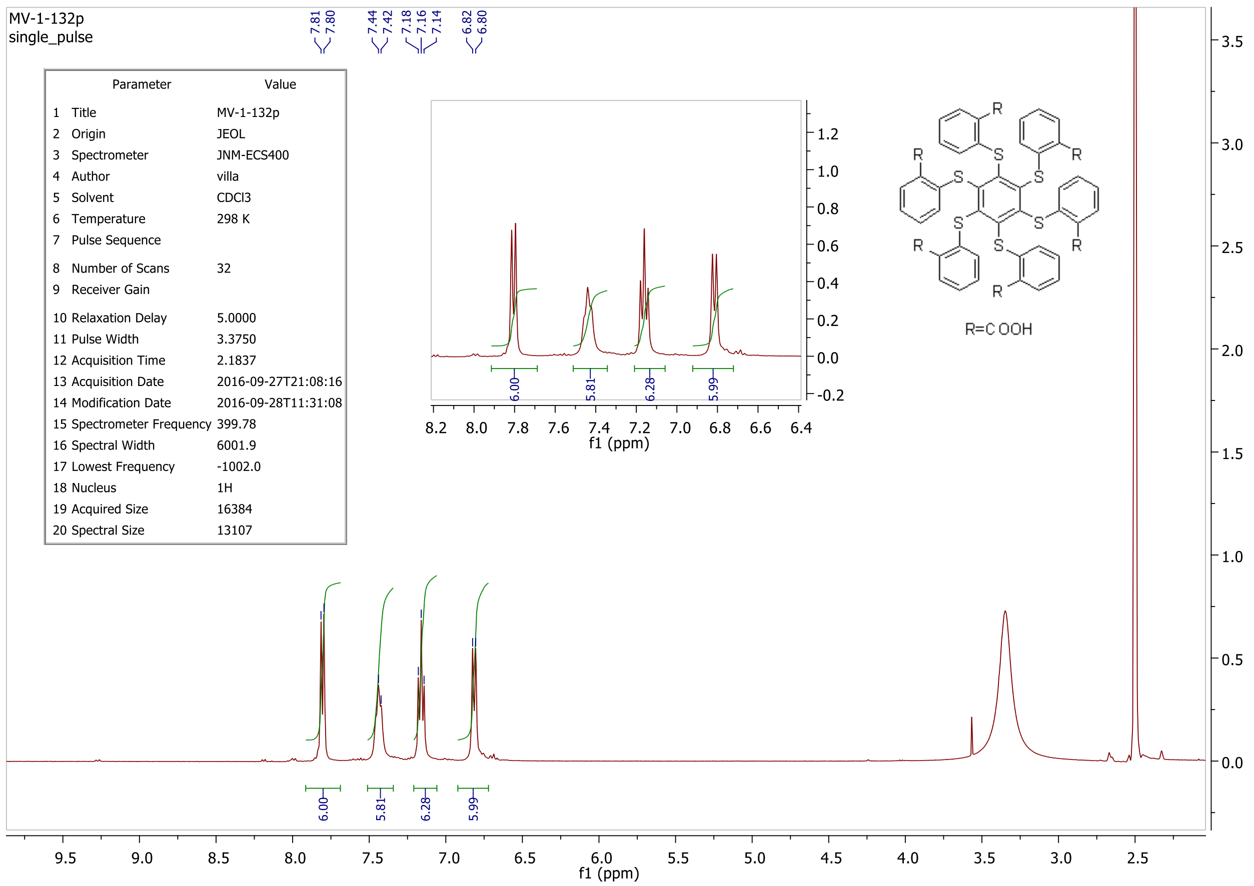
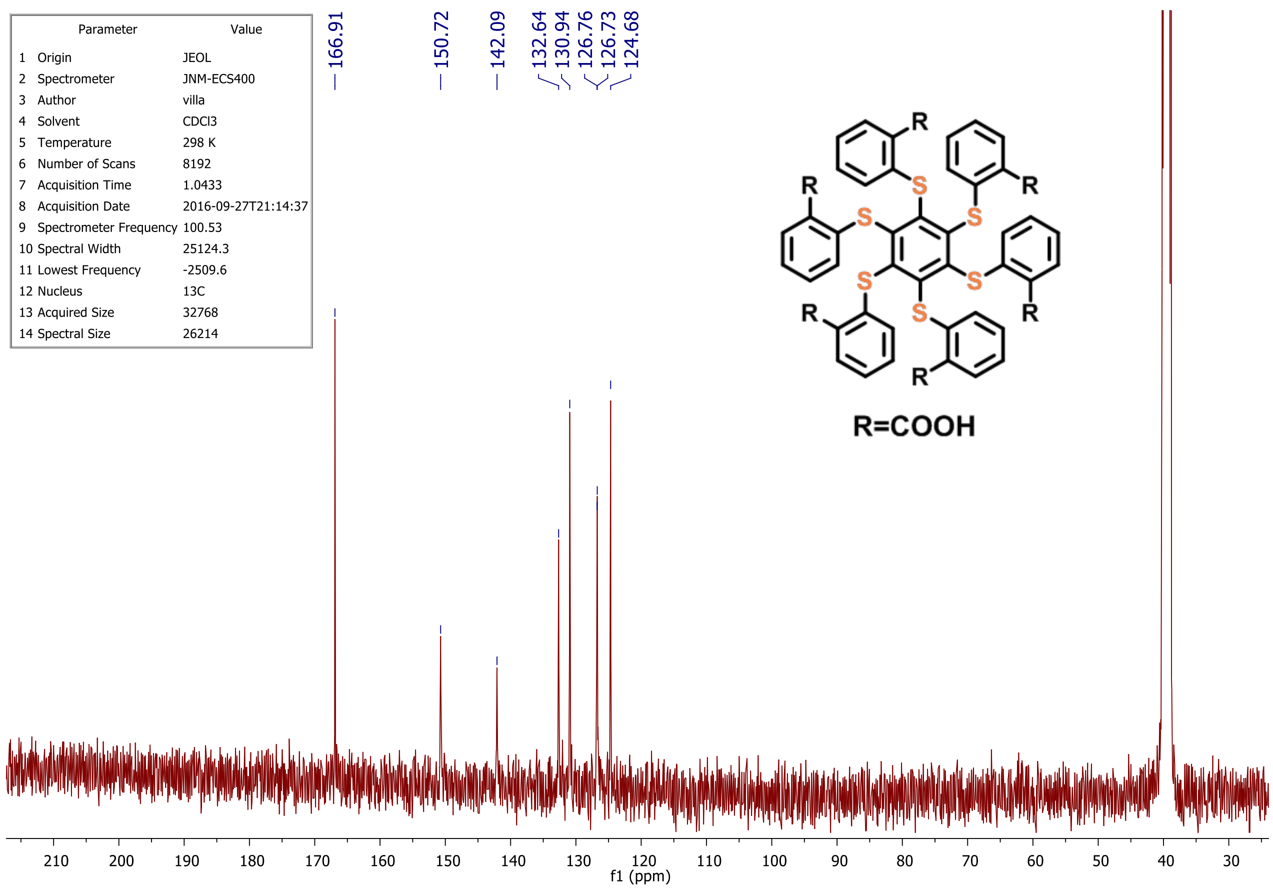


Figure S57 FT-IR spectrum of **2O**



	Parameter	Value
1	Title	MV-1-132p
2	Origin	JEOL
3	Spectrometer	JNM-ECS400
4	Author	villa
5	Solvent	CDCl3
6	Temperature	298 K
7	Pulse Sequence	
8	Number of Scans	32
9	Receiver Gain	
10	Relaxation Delay	5.0000
11	Pulse Width	3.3750
12	Acquisition Time	2.1837
13	Acquisition Date	2016-09-27T21:08:16
14	Modification Date	2016-09-28T11:31:08
15	Spectrometer Frequency	399.78
16	Spectral Width	6001.9
17	Lowest Frequency	-1002.0
18	Nucleus	1H
19	Acquired Size	16384
20	Spectral Size	13107

Figure S58 ^{1}H-NMR of **2O**



	Parameter	Value
1	Origin	JEOL
2	Spectrometer	JNM-ECS400
3	Author	villa
4	Solvent	CDCl3
5	Temperature	298 K
6	Number of Scans	8192
7	Acquisition Time	1.0433
8	Acquisition Date	2016-09-27T21:14:37
9	Spectrometer Frequency	100.53
10	Spectral Width	25124.3
11	Lowest Frequency	-2509.6
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	26214

Figure S59 ^{13}C-NMR of **2O**

```
Composé          Temps   rét      Elément  %       Facteur
                 (min)            %                K
---------------  ---------------  ---------------  ---------------
Carbon           1.40             57.19            4696704
Hydrogen         3.96             2.94             13494920
Sulphur          7.68             19.26            2019452
                                  _____
                                  79.39
```

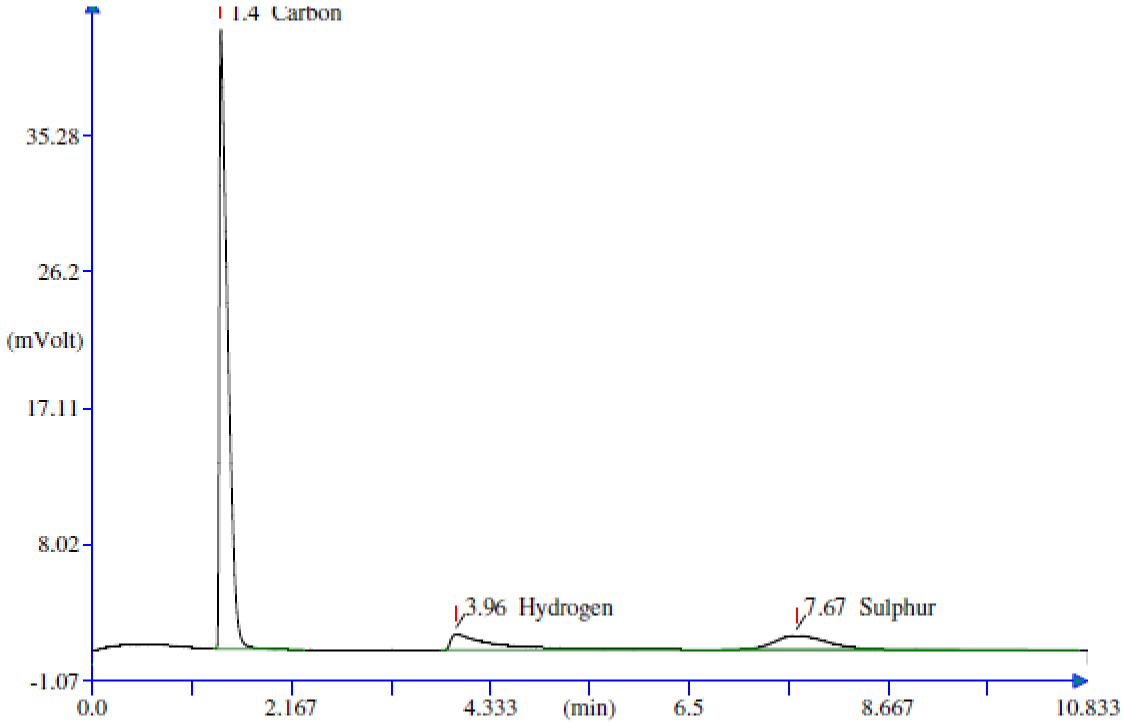


Figure S60 Elemental analysis of **2O**

4,4',4'',4''',4'''',4'''''-(benzene-1,2,3,4,5,6-hexaylhexakis(sulfanediyl))hexabenzoic acid (2P):

A solution of **1P** (1.504 g, 1.21 mmol, 1.0 eq) and LiOH*H_2O (2.884 g, 68.70 mmol, 57 eq) in absolute ethanol (200 mL) was heated under argon atmosphere at 70°C (oil bath temperature) for 48h. The reaction was monitored by IR. Upon completion of the reaction, the reaction mixture was cooled down to room temperature and diluted with 200 mL of 1N HCl (aq.). A yellow solid precipitated providing a suspension. The solid was filtered and dried under vacuum at 60°C for 3 days to yield the desired product as a yellow solid (1.174 g, 1.18 mmol, 98% yield).

^{1}H NMR (399.78 MHz, DMSO-d$_6$, ppm): δ = 7.79 (d, 12H, J = 8.6 Hz), 7.12 (d, 12H, J = 8.5 Hz); **^{13}C NMR (100.53 MHz, DMSO-d$_6$, ppm)**: δ = 166.65, 147.21, 142.45, 130.16, 128.52, 126.41; **HRMS (ESI+)** calculated for [$C_{48}H_{30}O_{12}S_6$ + Li$^+$]: 997.0217 Da, found [M+Li$^+$] 997.0217 *m/z*; **FT- IR (cm^{-1})** ν = 3500-2500, 1684, 1590, 1399, 1261, 1177, 1080, 1012, 757; **Elemental analysis:** calculated for **2P***3H_2O %C 55.16 %H 3.47 %S 18.40, found %C 54.99 %H 3.09 %S 18.42.

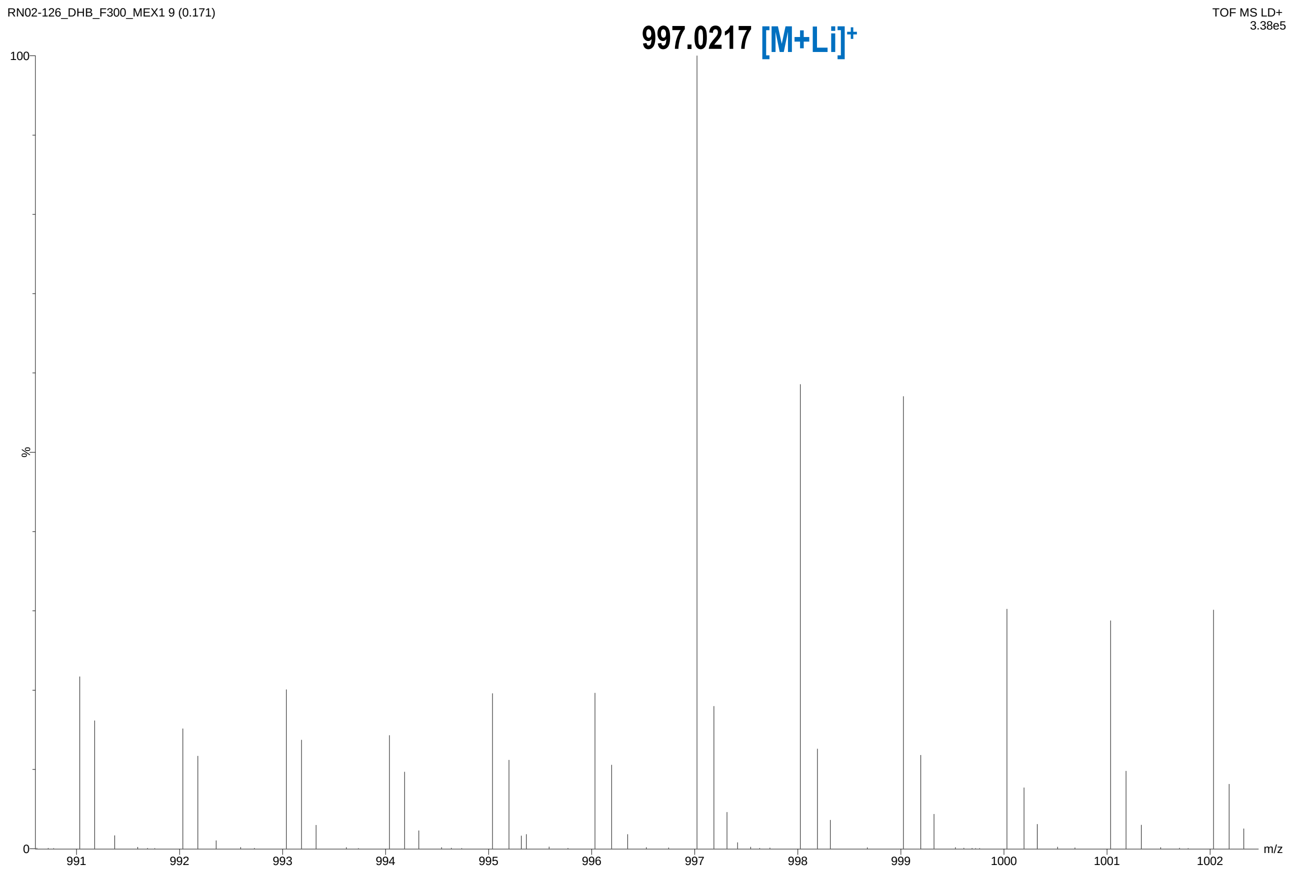


Figure S61 HR-MS of **2P**

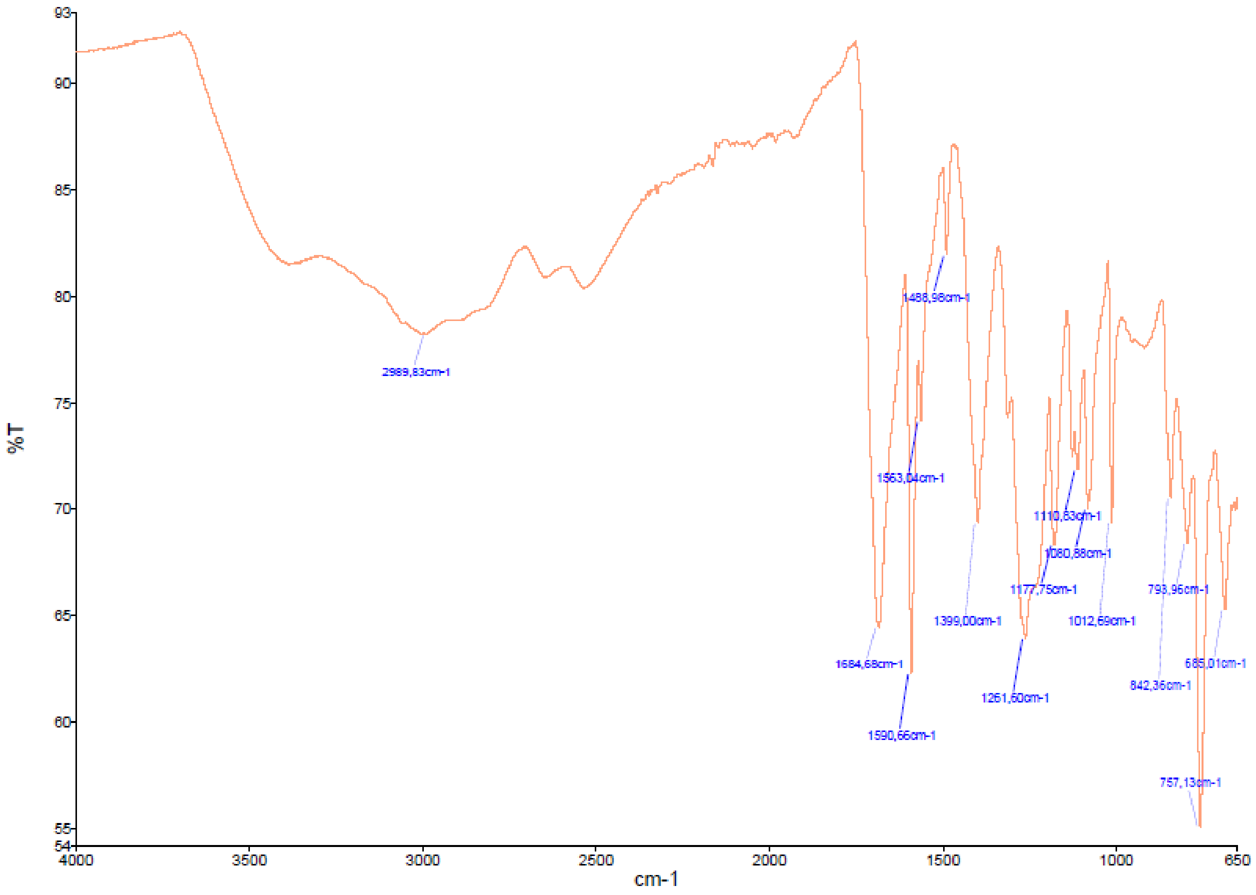


Figure S62 FT-IR spectrum of **2P**

```
Composé           Temps   rét       Elément  %        Facteur
                  (min)             %                 K
---------------   ---------------   ---------------   ---------------
Carbon            1.40              54.99             4720749
Hydrogen          3.93              3.09              13344700
Sulphur           7.53              18.42             2018954
                                    _____
                                    76.51
```

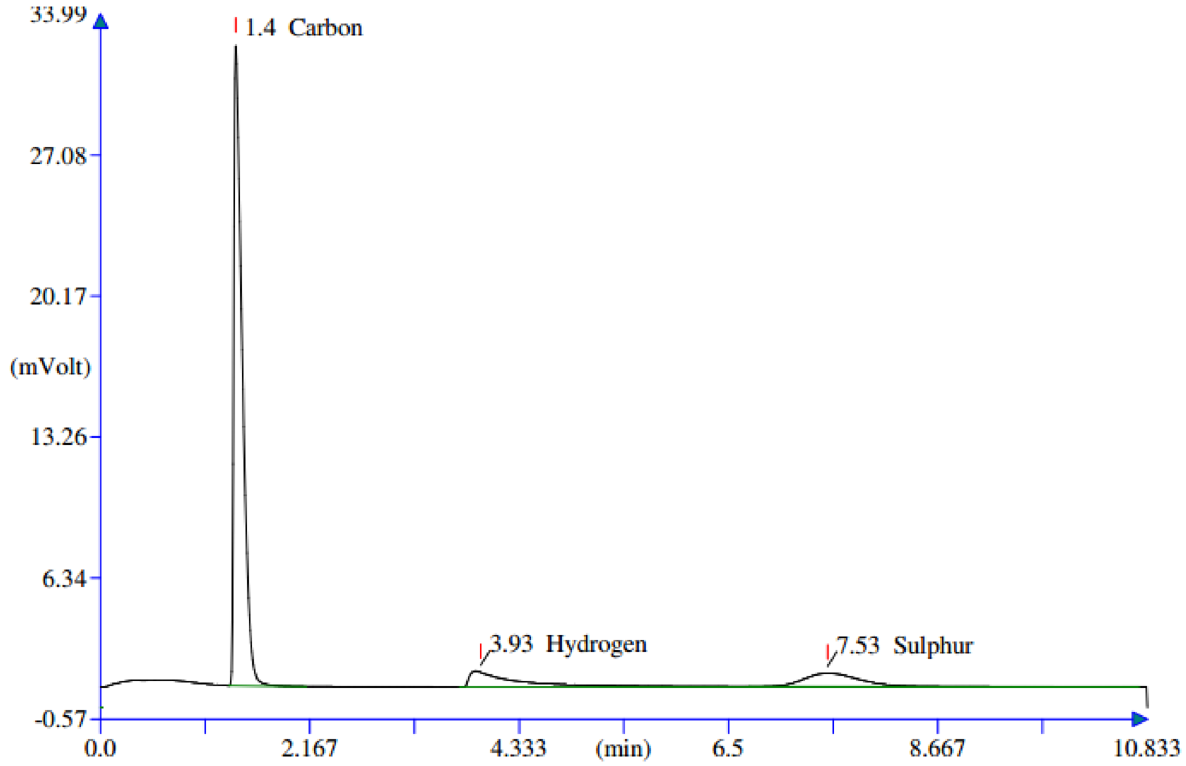
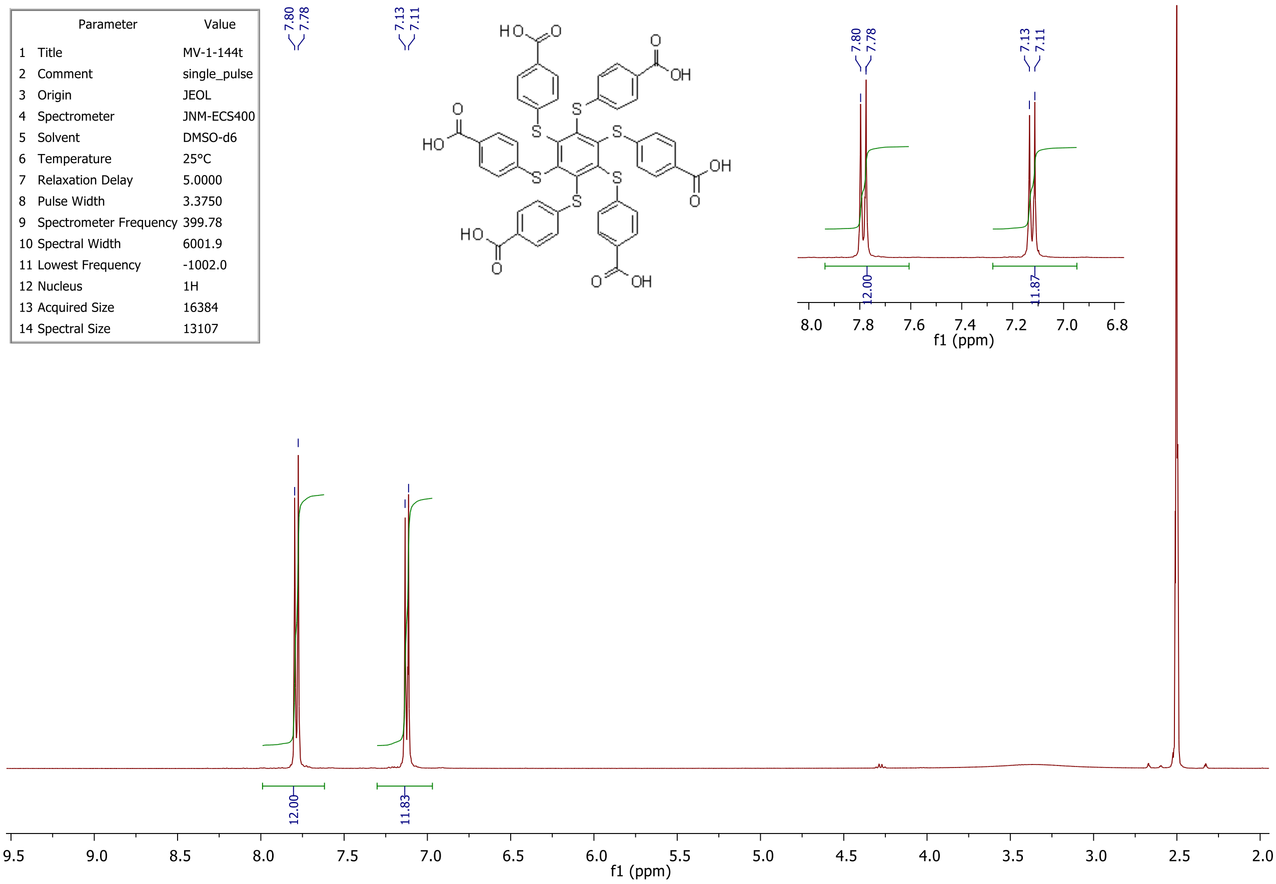
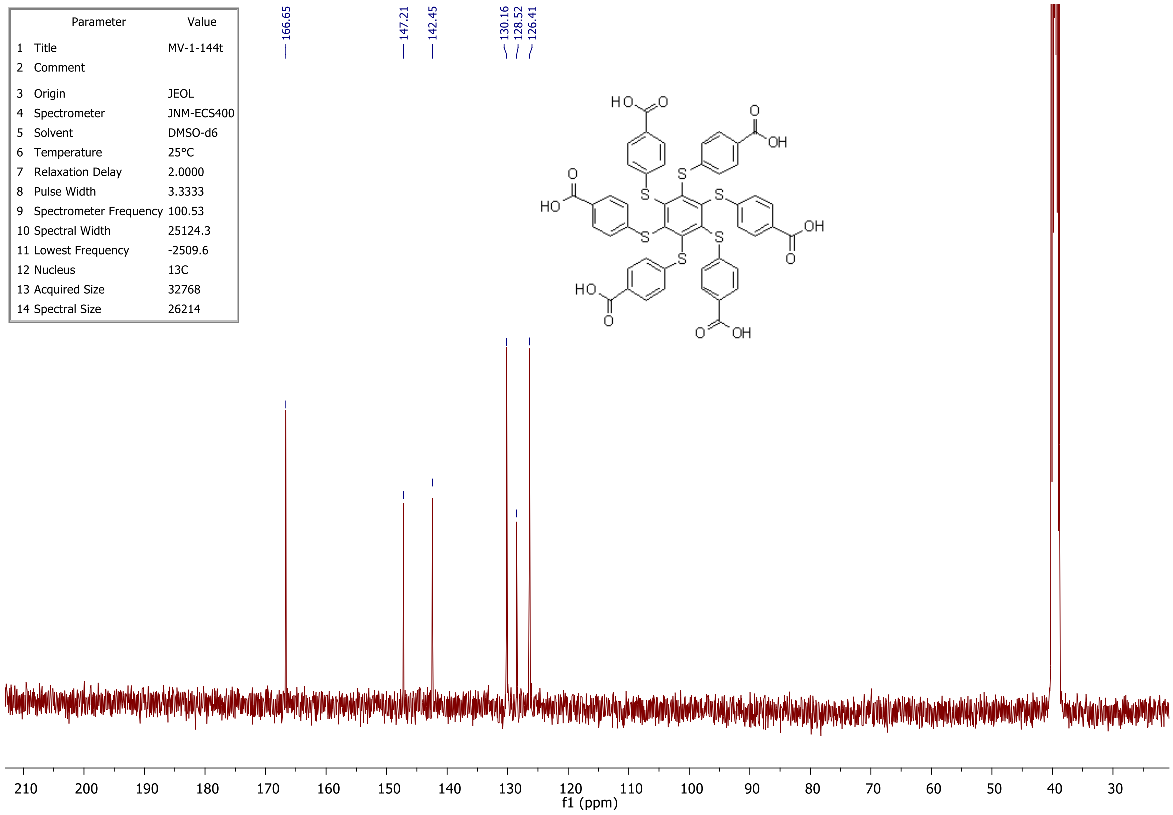


Figure S63 Elemental analysis for **2P**



	Parameter	Value
1	Title	MV-1-144t
2	Comment	single_pulse
3	Origin	JEOL
4	Spectrometer	JNM-ECS400
5	Solvent	DMSO-d6
6	Temperature	25°C
7	Relaxation Delay	5.0000
8	Pulse Width	3.3750
9	Spectrometer Frequency	399.78
10	Spectral Width	6001.9
11	Lowest Frequency	-1002.0
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	13107

Figure S64 ^{1}H-NMR spectrum of **2P** (DMSO-*d*$_6$, 399.78 MHz)



	Parameter	Value
1	Title	MV-1-144t
2	Comment	
3	Origin	JEOL
4	Spectrometer	JNM-ECS400
5	Solvent	DMSO-d6
6	Temperature	25°C
7	Relaxation Delay	2.0000
8	Pulse Width	3.3333
9	Spectrometer Frequency	100.53
10	Spectral Width	25124.3
11	Lowest Frequency	-2509.6
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	26214

Figure 65 ^{13}C-NMR spectrum of **2P** (DMSO-*d*$_6$, 100.53 MHz)

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