

# Chemistry–A European Journal

Supporting Information

## **“The Sulfur Dance” Around Arenes and Heteroarenes - the Reversible Nature of Nucleophilic Aromatic Substitutions**

Sapna Gahlot, Jean-Louis Schmitt,\* Aline Chevalier, Marco Villa, Myriam Roy, Paola Ceroni, Jean-Marie Lehn,\* and Marc Gingras\*

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#### 1.0 General Information

**Materials and General Procedures:** All reagents, solvents and chemicals were purchased from Sigma-Aldrich, Fisher, Alfa-Aesar or TCI Europe and used directly unless otherwise stated (purity: reagent or analytical grade). Solvents were stored for several days over freshly activated 3Å or 4Å molecular sieves (activated for 3 hours at 250°C). Reactions were monitored by TLC,  $^1H$ ,  $^{19}F$ ,  $^{13}C$  NMR spectroscopy or LC-MS and LC-HRMS.

**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 spectroscopy

**NMR (CINaM, Aix-Marseille Univ.):** most spectra  $^1H$  (399.78 MHz),  $^{13}C$  (100.53 MHz) and  $^{19}F$  (376.17 MHz) were recorded on JEOL ECX-400 spectrometer with internal reference signals from residual protic solvent  $CHCl_3$  at 7.26 ppm and  $DMSO-d_6$  at 2.50 ppm, 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.<sup>[1]</sup> As for  $^{19}F$  NMR spectra, the internal

reference was C<sub>6</sub>F<sub>6</sub> signal at -164.90 ppm relative to CFC<sub>3</sub> (0 ppm). The resonance multiplicities in the <sup>1</sup>H NMR spectra are described as “s” (singlet), “d”(doublet), “t” (triplet), “q” (quarted), “sept” (septet) “m” (multiplet) or “b” (broad).

**NMR (Univ. of Bologna):** a Varian ARX Inova 400 NMR spectrometer was used in a few cases for recording <sup>1</sup>H NMR (400.72 MHz) and <sup>13</sup>C NMR (100.76 MHz) spectra.

(1) Gottlieb, H.E., Kotlyar, V., Nudelman, A., "NMR Chemical shifts of common laboratory solvents as trace impurities", *J. Org. Chem.* **1997**, 62, 7512-7515.

### Mass spectroscopy

**LC-MS (APCI and ESI+) (CINaM, Aix-Marseille Univ.):** 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.

**GC-MS (CINaM, Aix-Marseille Univ.):** Low resolution mass spectra (LRMS-EI) were recorded on a Shimadzu GC-MS QP2010SE instrument equipped with a DI2010 direct introduction unit with an electronic impact ionization source at 70eV. Direct introduction of the sample in the electronic impact (EI) detector.

**LC-HRMS (ESI+) (ISIS, Univ. of Strasbourg):** Analyses were performed using a Dionex RSLC U3000HPLC system (Thermo) with a chromatography column Acclaim Phenyl-1, (3µm; 150 x 2.1 mm). The mobile phase was water with 0.1% formic acid (method A) or acetonitrile with 0.1% formic acid (method B). Full MS spectra were acquired using Exactive series 2.9 sp4 software in a positive ion mode at a 3.5 kV spray voltage setting on a Thermo Scientific Exactive Plus EMR. Resolution of full MS and HCD scans were 140,000 and data were acquired in profile mode and processed using Xcalibur 4.3.

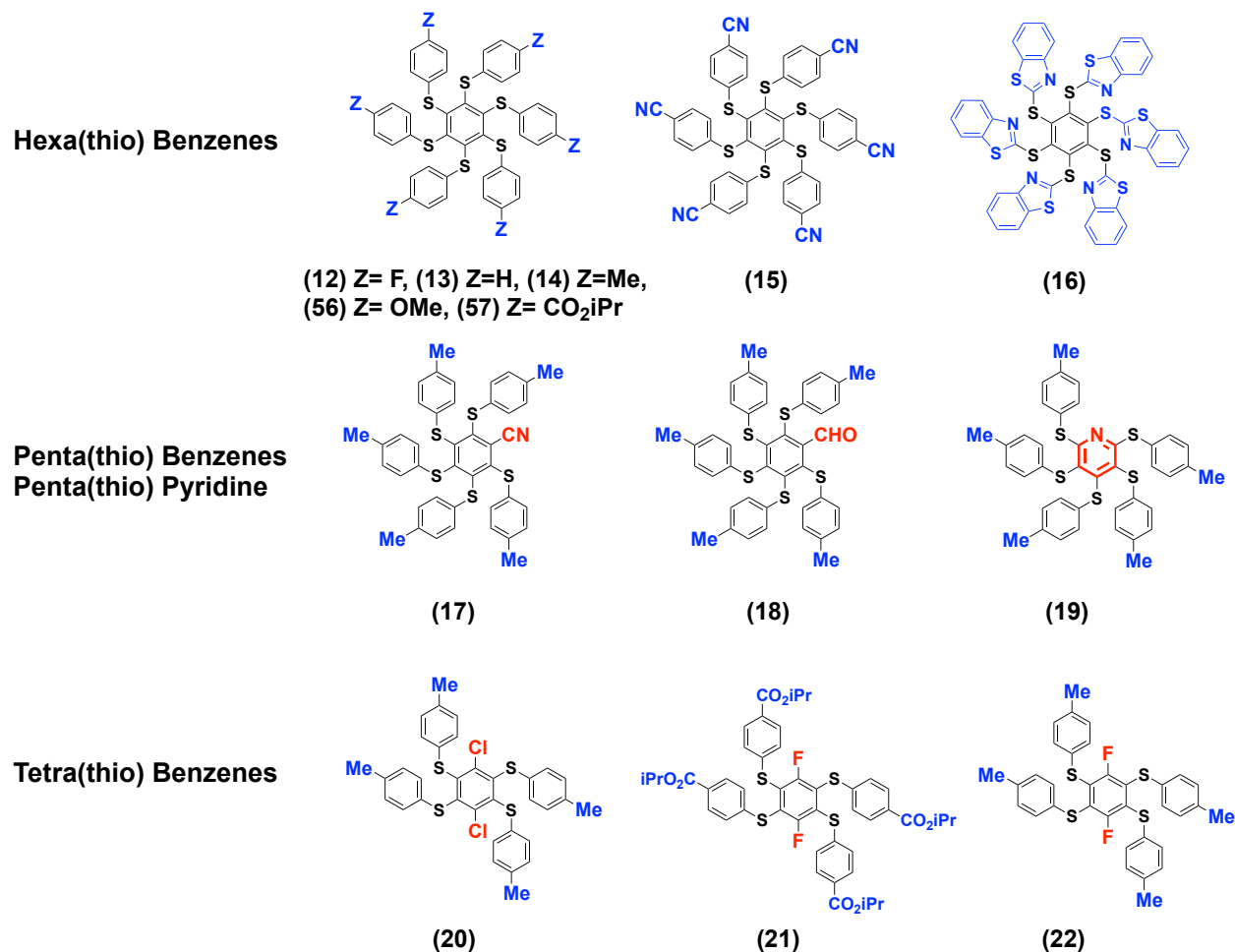
**HRMS (ESI+) (Spectropôle of Marseille):** High resolution mass spectra were recorded at the Spectropôle of Marseille (France) in triplicate with double internal standards. Oligomers of poly(propylene glycol) were used as internal standards. Ionization was facilitated by some adducts with Ag<sup>+</sup>, NH<sub>4</sub><sup>+</sup> or Na<sup>+</sup> 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. Most high-resolution mass spectra (ESI+) were recorded in triplicate using double internal standards at the Spectropole (<https://fr-chimie.univ-amu.fr/spectropole/>).

**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).

**Melting points** (uncorrected) were recorded with an Electrothermal 9200 digital melting point apparatus with a ramp rate temperature (rate increase of temperature) using samples in glass capillaries.

## 2.0 Synthesis and characterization of reference asterisks, thiols and disulfides

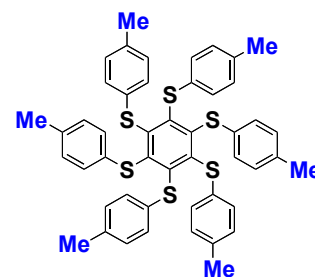
List of reference asterisks for LC-MS and NMR analyses:



### 2.1 Hexa(thio) benzene asterisks

#### Hexakis(4-methylphenylthio)benzene (14)<sup>1-8</sup>

Hexachlorobenzene (4.506 g, 15.82 mmol, 1.00 mol-eq.), dry potassium carbonate (19.66 g, 142.2 mmol; 8.99 mol-eq.) and *p*-thiocresol (18.06 g, 145.4 mmol; 9.19 mol-eq.) were added into a round bottom flask capped with a septum under an argon atmosphere. Dry DMF (100 mL) was injected via a syringe and the mixture was stirred at 60°C for 40 h. It turned yellow and the completion of the reaction was monitored by TLC (SiO<sub>2</sub>, *n*-hex./EtOAc 85:15 v/v; R<sub>f</sub> = 0.74). An aqueous solution of NaOH (2 M, 100 mL) was poured into the flask while stirring, and a yellow precipitate appeared. After collecting the solid by filtration, the crude product was triturated with a solution of ethanol/H<sub>2</sub>O (85:15 v/v; 50 mL) while stirring at reflux for 3 h. After cooling at RT, a filtration left a yellow solid, which was rinsed with ethanol (10 mL), with diethyl ether (20 mL), and then

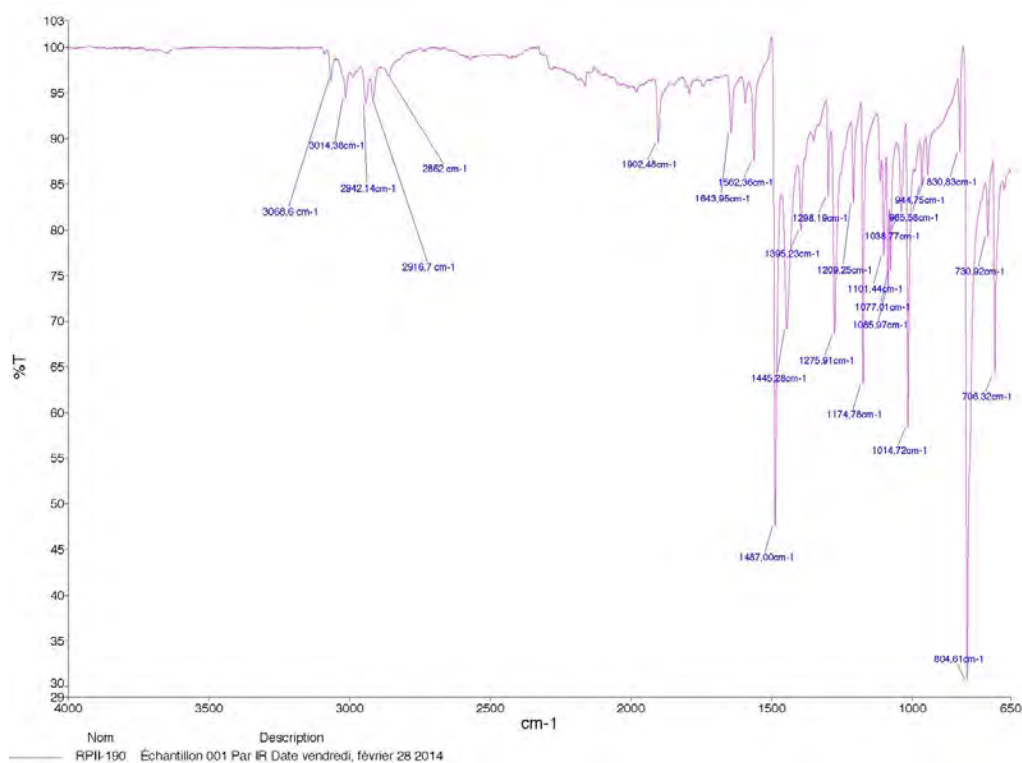


dried under high vacuum (11.55 g, 14.24 mmol, 90%). For analytical purity, it was recrystallized from warm toluene to afford bright yellow crystals.

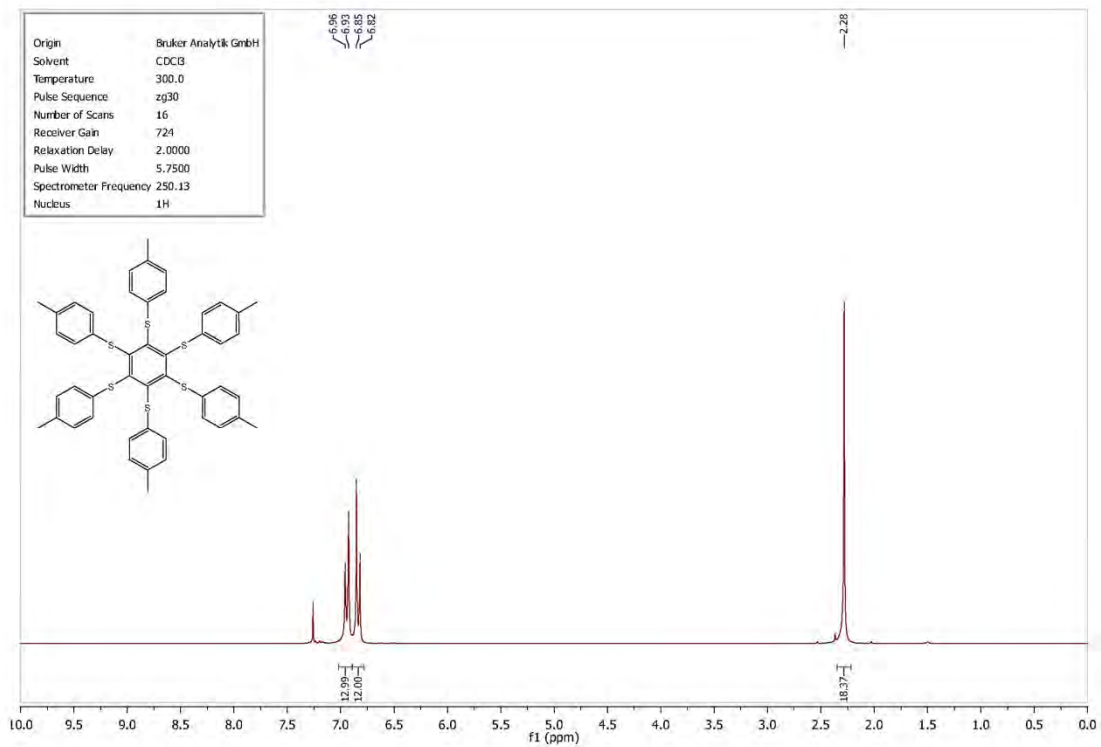
**M.p.:** 201.9-202.3°C (lit. 197-8°C<sup>6</sup>; 197-200°C<sup>7</sup>); **TLC** (SiO<sub>2</sub>, *n*-hex/EtOAc 85:15 v/v) R<sub>f</sub> = 0.74; **FT-IR** (ATR, diamond contact, neat, cm<sup>-1</sup>)  $\nu$  = 3069 (CH arom), 3014 (CH arom), 2942 (CH<sub>3</sub>), 2862 (CH<sub>3</sub>), 1487, 1445, 1276, 1174, 1015 (CH arom), 805 (strong, CH arom); **<sup>1</sup>H NMR (250.13 MHz, CDCl<sub>3</sub>, ppm):**  $\delta$  = 6.94 (d<sub>app</sub>, *J* = 8.1 Hz, 12H), 6.83 (d<sub>app</sub>, *J* = 8.2 Hz, 12H); 2.28 (s, 18H); **<sup>13</sup>C NMR (62.90 MHz, CDCl<sub>3</sub>, ppm):**  $\delta$  = 147.9; 135.80, 134.42, 129.56, 128.52, 21.03; **LC-MS** (acetonitrile/water/0.1% formic acid; ESI+): 811 *m/z* [M+H]<sup>+</sup>, 833 *m/z* [M+Na]<sup>+</sup>; **Elemental analysis:** calculated %C 71.07 %H 5.22 %S 23.72, found %C 71.48 %H 5.39 %S 23.10.

#### References:

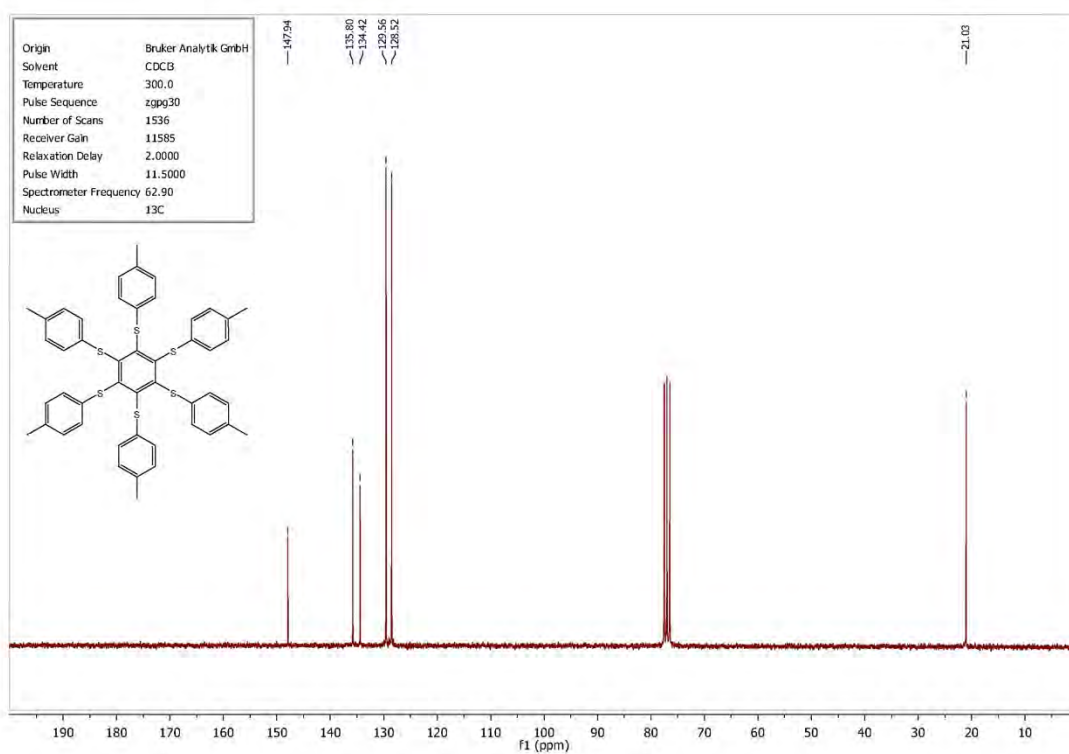
1. A. Fermi, G. Bergamini, R. Peresutti, E. Marchi, Roy, Myriam; P. Ceroni, M. Gingras, *Dyes and Pigments* (2014), 110, 113-122.
2. A. Fermi, G. Bergamini, M. Roy; M. Gingras, P. Ceroni, *J. Am. Chem. Soc.* (2014), 136, 6395-6400.
3. G. Bergamini, A. Fermi, C. Botta, U. Giovanella, S. Di Motta, F. Negri, R. Peresutti, M. Gingras, P. Ceroni, *J. Mater. Chem. C* (2013), 1(15), 2717-2724.
4. M. Arisawa, T. Suzuki, T. Ishikawa, M. Yamaguchi, *J. Am. Chem. Soc.* (2008), 130, 12214-12215
5. Y. Suenaga, K. Kitamura, T. Kuroda-Sowa, M. Maekawa, M. Munakata, *Inorg. Chim. Acta* (2002), 328, 105-110.
6. J.H.R. Tucker, M. Gingras, H. Brand, J.-M. Lehn, *J. Chem. Soc., Perkin Trans. 2: Physical Organic Chemistry* (1997), 7, 1303-1307.
7. A. D.U. Hardy, D.D. MacNicol, D.R. Wilson, *J. Chem. Soc., Perkin Trans. 2: Physical Organic Chemistry* (1979), 7, 1011-19.
8. B.F. Malichenko, L.P. Robota, *Zhurnal Organicheskoi Khimii* (1975), 11, 778-82.



FT-IR-ATR spectrum of (14)



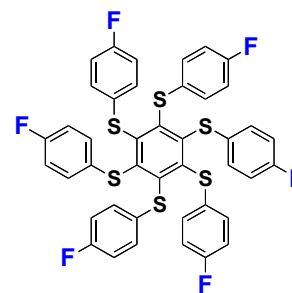
<sup>1</sup>H-NMR spectrum of **(14)** (CDCl<sub>3</sub>, 250.13 MHz)



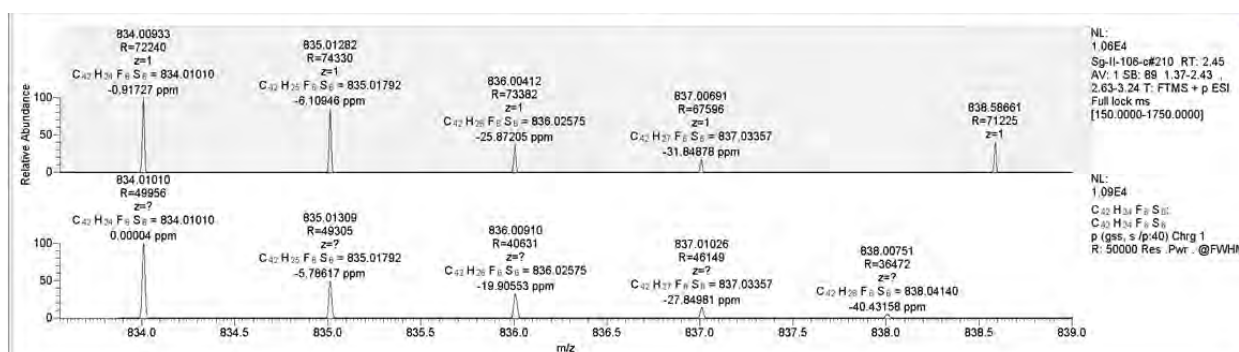
<sup>13</sup>C-NMR spectrum of **(14)** (CDCl<sub>3</sub>, 62.90 MHz)

## Hexakis(4-fluorophenylthio)benzene (**12**)

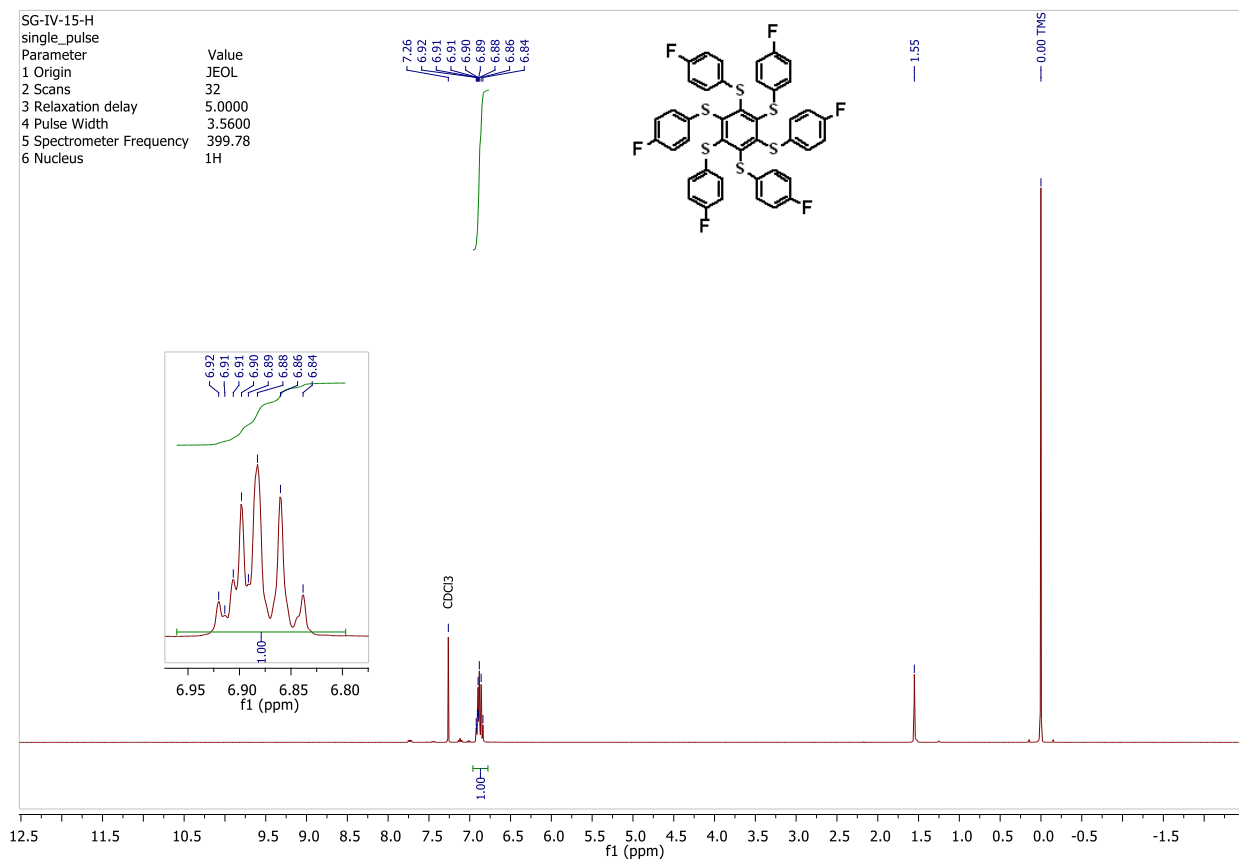
In an oven-dried sealed tube, purged with argon, was added hexachlorobenzene (0.447 g, 1.57 mmol, 1.00 mol-eq.), dried potassium carbonate (1.945 g, 14.07 mmol, 8.96 mol-eq.), *p*-fluorothiophenol (1.804 g, 14.08 mmol, 1.50 mL, 8.97 mol-eq.) and dry DMF (6.0 mL, dried and kept over activated molecular sieves 3Å). Argon was bubbled through the mixture for 5-10 minutes. The tube was sealed and the reaction was stirred at 27°C for 3 days. Most DMF was removed on a rotary evaporator under reduced pressure. To the reaction mixture was added EtOH (30 mL) and H<sub>2</sub>O (30 mL) at 25°C while stirring vigorously. A solid was formed and stirring was continued for 3 hrs. After filtration, the solid was dried *in vacuo* to afford a pure yellow solid (1.230 g, 1.473 mmol, 94% yield).



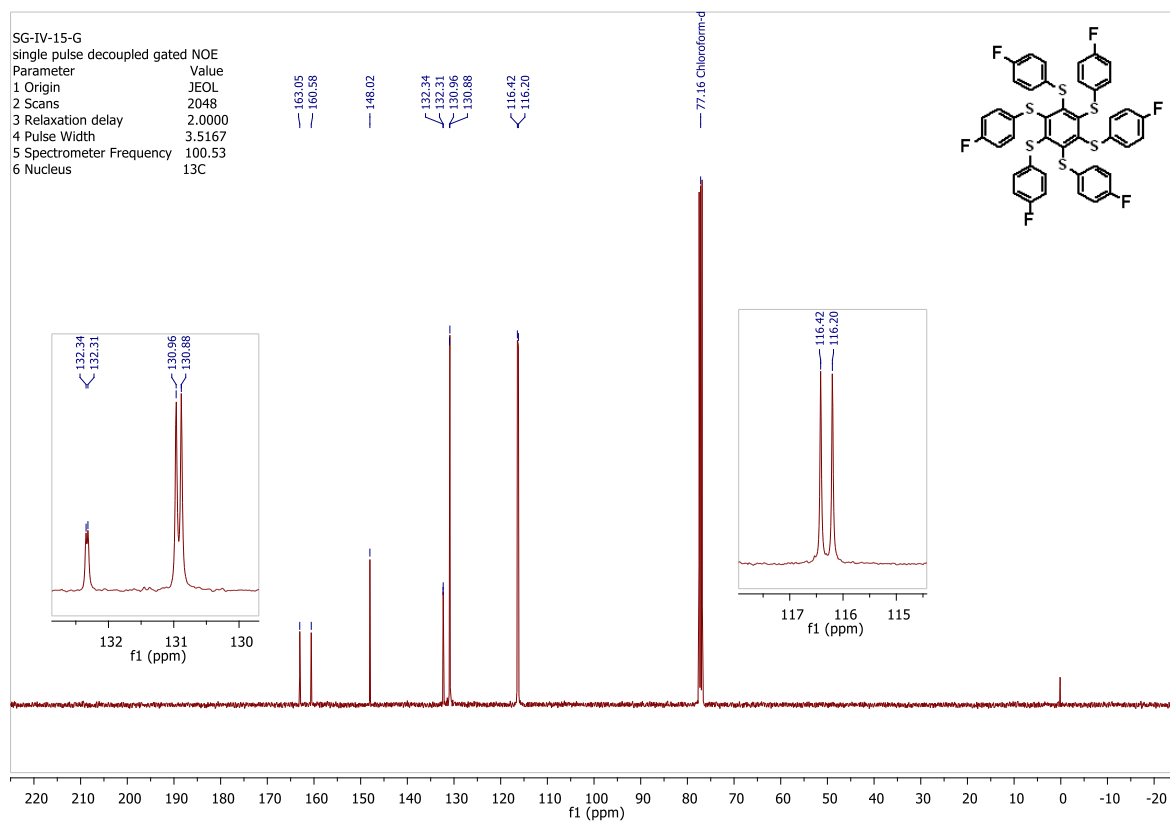
**M.p.** 117-118°C; **TLC** (SiO<sub>2</sub>, tol./*n*-hex. 50:50 v/v) R<sub>f</sub> = 0.33; **<sup>1</sup>H NMR** (399.78 MHz, CDCl<sub>3</sub>, ppm): δ = 6.82-6.94 (m, 24H); **<sup>13</sup>C NMR** (100.53 MHz, CDCl<sub>3</sub> ppm): δ = 161.8 (d, <sup>1</sup>J<sub>C-F</sub> = 248,0 Hz), 148.0, 132.3, <sup>4</sup>J<sub>C-F</sub>=3.3 Hz), 130.9 (d, <sup>3</sup>J<sub>C-F</sub>= 7.9 Hz), 116.2 (d, <sup>2</sup>J<sub>C-F</sub>= 22.2 Hz); **<sup>19</sup>F NMR** (376.17 MHz, CDCl<sub>3</sub>) : -114.16 (s); **MS** (EI, 70 eV) calculated for [C<sub>42</sub>H<sub>24</sub>F<sub>6</sub>S<sub>6</sub>]: 834 Da, found [M<sup>+</sup>] 834 *m/z*, [M - (F-Ph-SH)] 707 *m/z*; **HRMS (ESI+)** calculated for [C<sub>42</sub>H<sub>24</sub>F<sub>6</sub>S<sub>6</sub>]: 834.010 Da, found [M<sup>+</sup>] 834.009 *m/z*.



HRMS (ESI positive mode) of (**12**)

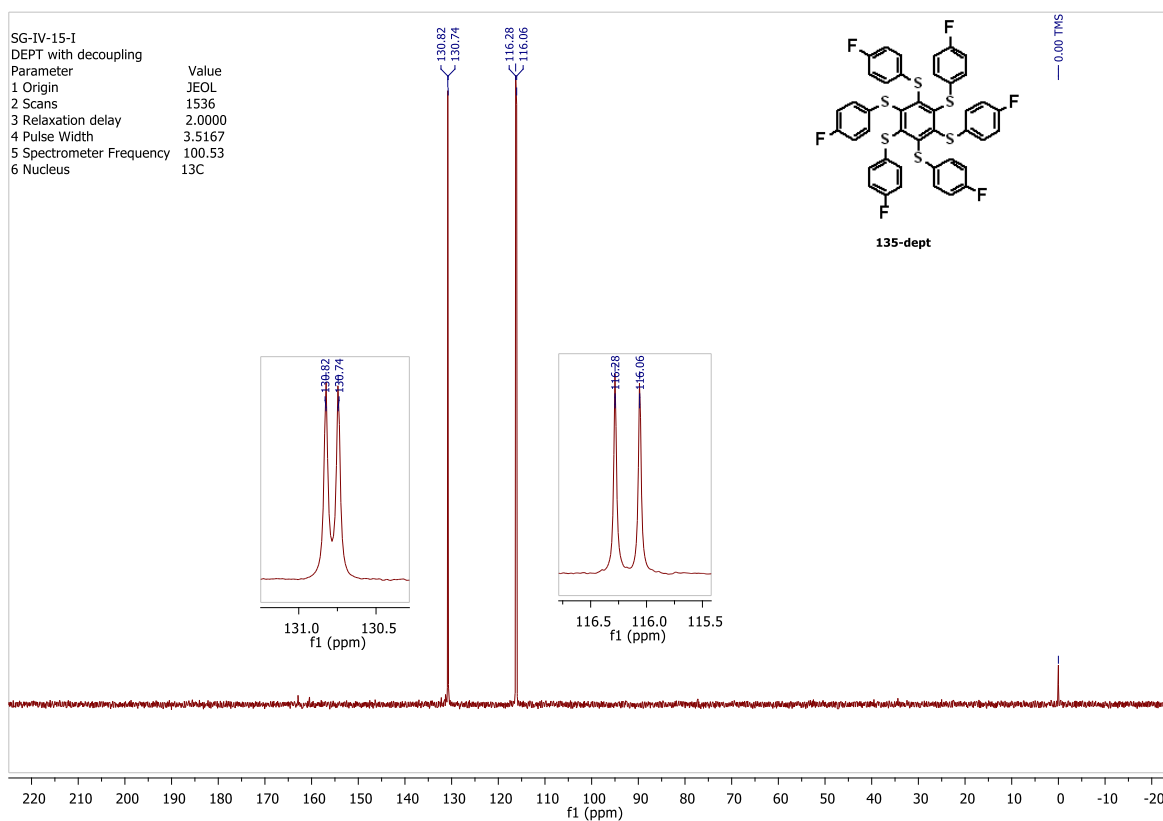


<sup>1</sup>H-NMR spectrum of (**12**) (CDCl<sub>3</sub>, 399.78 MHz)

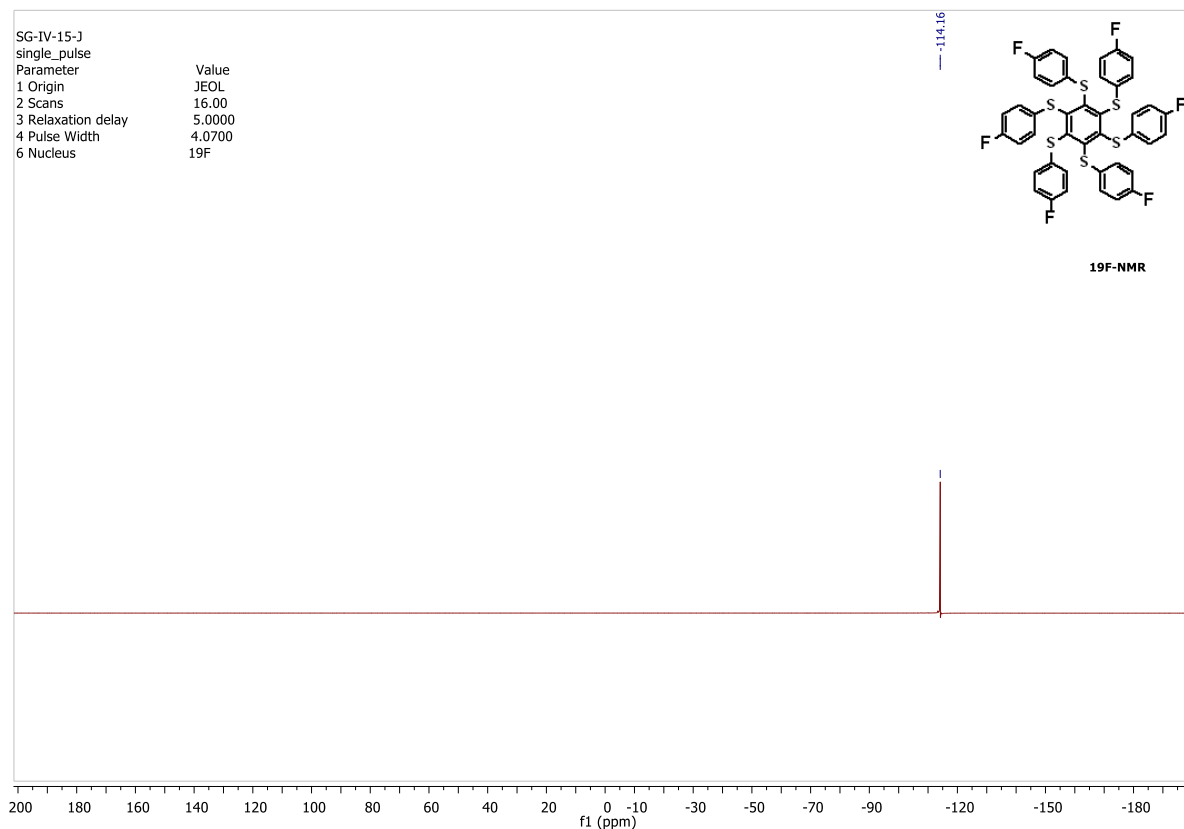


<sup>13</sup>C-NMR {H} spectrum of (**12**) (CDCl<sub>3</sub>, 100.53 MHz)





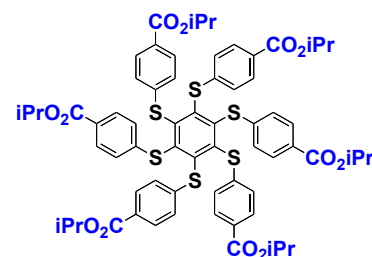
<sup>13</sup>C-NMR DEPT 135 spectrum of (**12**) (CDCl<sub>3</sub>, 100.53 MHz)



<sup>19</sup>F-NMR spectrum of (**12**) (CDCl<sub>3</sub>, 376,17 MHz)

### Hexakis (4-isopropoxy carbonylphenylthio)benzene (57) <sup>1</sup>

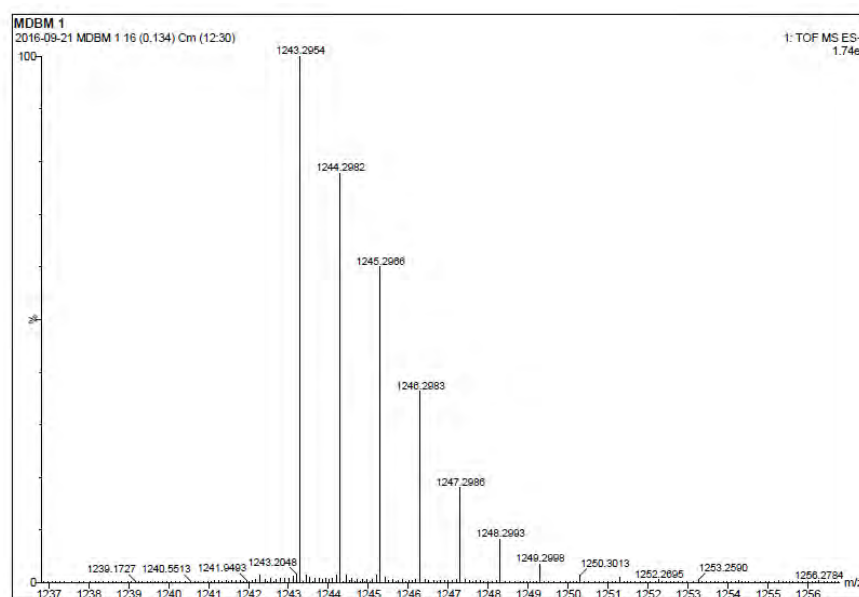
Hexachlorobenzene (676 mg, 2.37 mmol, 1.00 mol-eq), isopropyl-4-mercaptobenzoate (4.082 g, 20.83 mmol, 8.79 mol-eq) and dry potassium carbonate (3.809 g, 27.6 mmol, 11.7 mol-eq) were dried under high vacuum for 30 min. before being introduced into an oven-dried sealed tube. Under an argon atmosphere, dry DMF (10 mL, kept over activated 3Å molecular sieves) 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<sub>4</sub>, filtered and concentrated *in vacuo*. The crude yellow-orange solid was purified by trituration in ethanol (70 mL) under vigorous stirring and filtration. The collected solid was then recrystallized in warm isopropanol to give the desired compound as a yellow solid (2.830 g, 2.27 mmol, 96% yield).



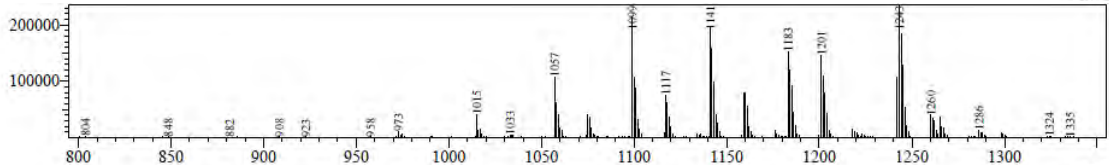
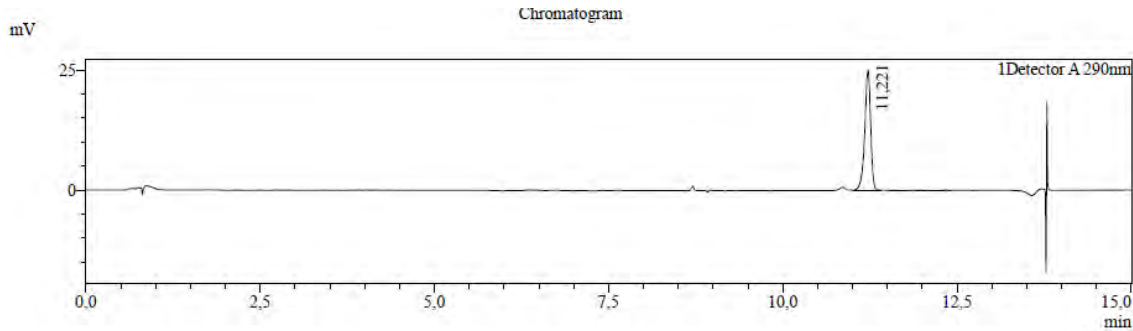
**TLC** (*n*-hept./EtOAc; 80:20 v/v) R<sub>f</sub> = 0.2; **FT-IR** (ATR, diamond contact, neat, cm<sup>-1</sup>) ν = 2977, 2940, 1708, 1592, 1270, 1179, 1091, 1012, 917, 852, 755, 687; **<sup>1</sup>H NMR** (399.78 MHz, CDCl<sub>3</sub>, ppm): δ = 7.85 (d<sub>app</sub>, J = 8.5 Hz, 12H), 6.93 (d<sub>app</sub>, J = 8.4 Hz, 12H), 5.22 (sept, J = 6.3 Hz, 6H), 1.36 (d, J = 6.3 Hz, 36H); **<sup>13</sup>C NMR** (100.53 MHz, CDCl<sub>3</sub> ppm): δ = 165.33, 148.11, 142.64, 130.42, 129.12, 126.97, 68.70, 22.06; **LC-MS** (acetonitrile/water/ 0.1% formic acid; APCI: 1243 m/z [M+H]<sup>+</sup>); **HRMS (ESI+)** calculated for [C<sub>66</sub>H<sub>66</sub>O<sub>12</sub>S<sub>6</sub> + H<sup>+</sup>]: 1243.2954 Da, found [M+H]<sup>+</sup> 1243.2954 m/z; **Elemental analysis**: calculated: %C 63.74 %H 5.35 %S 15.47, found: %C 63.31 %H 5.19 %S 15.45.

### Reference:

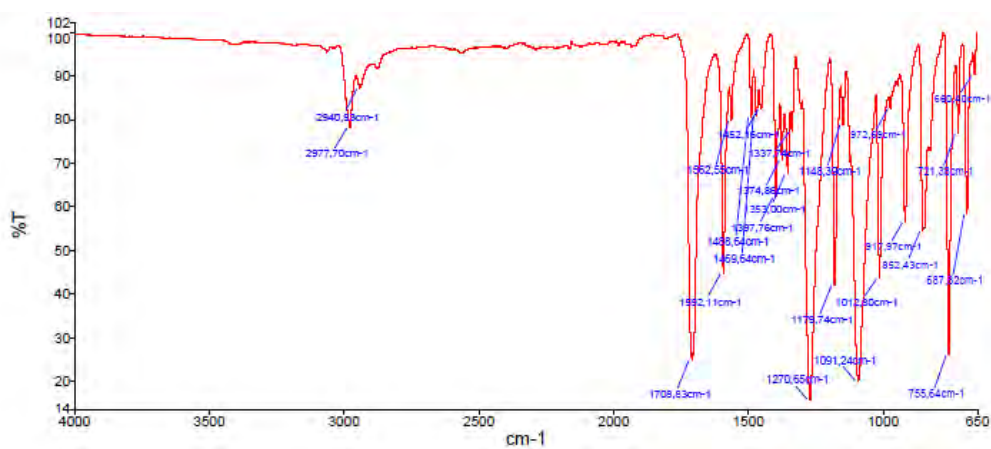
1. M. Villa, M. Roy, G. Bergamini, M. Gingras, P. Ceroni *Dalton Trans.* (2019), 48, 3815-3818.



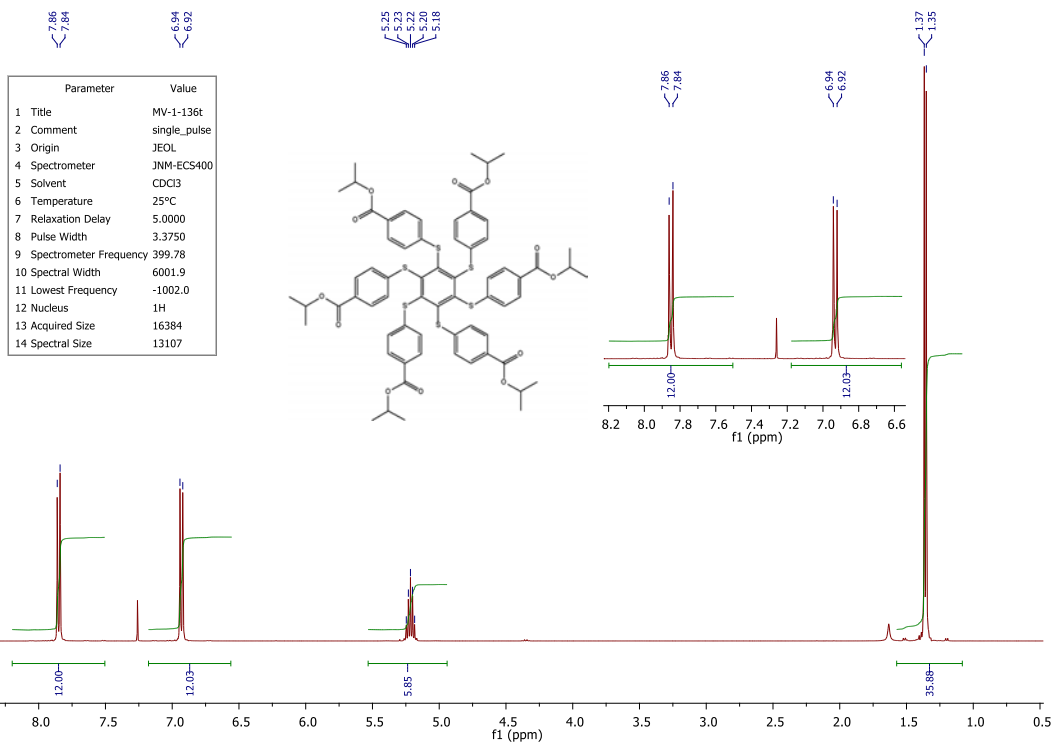
HRMS (ESI, positive mode) of (57)



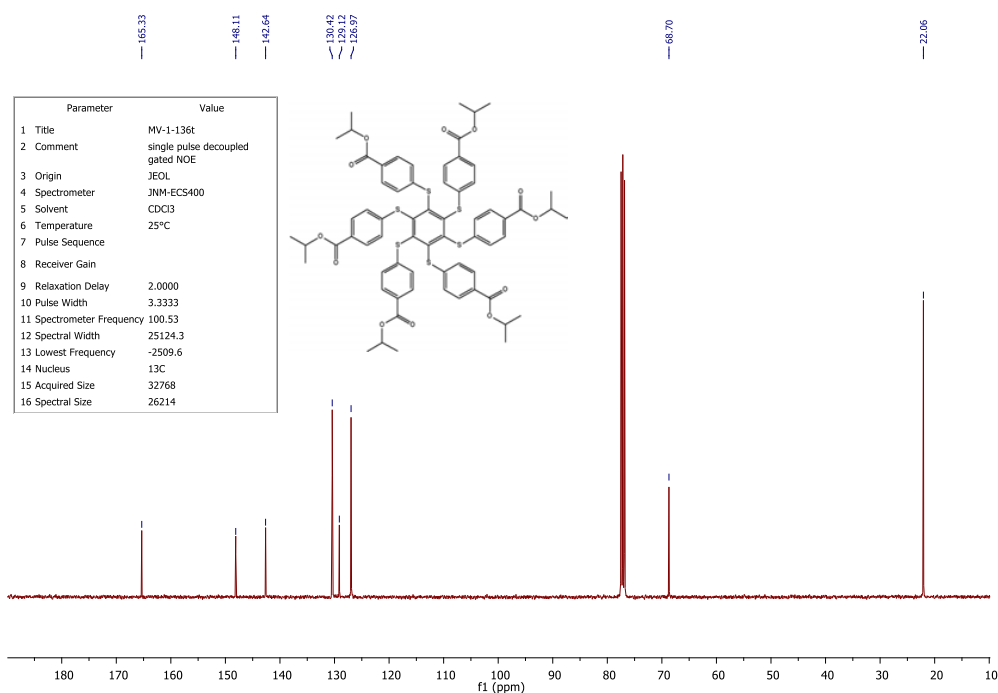
LC-MS: Reverse phase HPLC chromatogram of (**57**) and MS-APCI



FT-IR (ATR diamond contact) spectrum of (**57**)



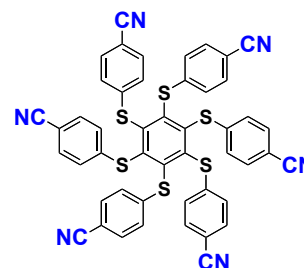
<sup>1</sup>H-NMR spectrum of (**57**) (CDCl<sub>3</sub>, 399.78 MHz)



$^{13}\text{C}$ -NMR spectrum of (**57**) ( $\text{CDCl}_3$ , 100.53 MHz)

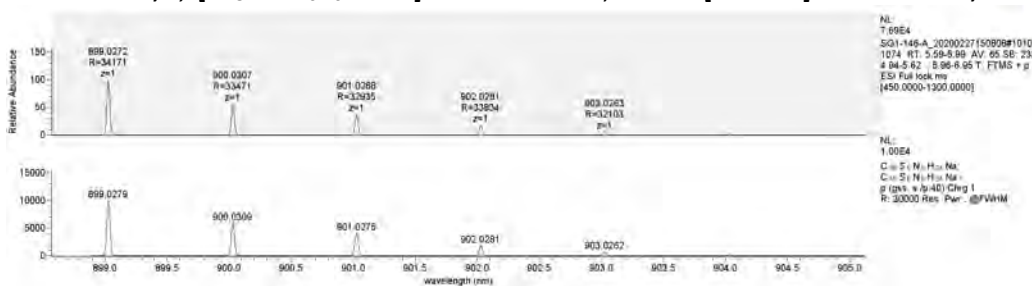
### Hexakis(4-cyanophenylthio)benzene (**15**).

Hexachlorobenzene (100 mg, 0.351 mmol, 1.00 eq.), 4-mercaptobenzonitrile (285 mg, 2.106 mmol, 6.00 eq.) and dry potassium carbonate (292 mg, 2.112 mmol, 6.02 eq.) were introduced into an oven-dried sealed tube. Under an argon atmosphere, dry DMF (0.5 mL, kept over  $3\text{\AA}$  molecular sieves) was injected via a syringe and the tube was purged with argon for 15-20 minutes before being sealed. The heterogeneous mixture was stirred at  $40^\circ\text{C}$  in an oil bath for 16h.

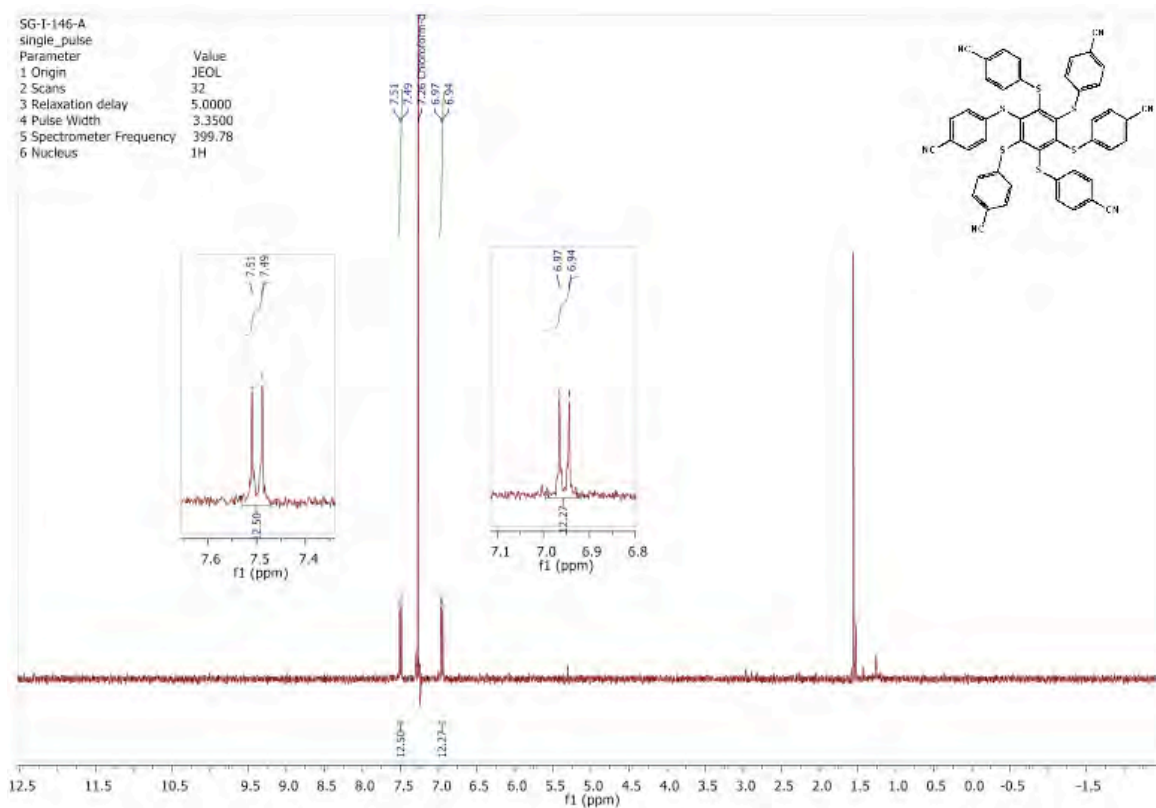


It turned from colorless to a bright yellow color in a few minutes. After cooling to  $25^\circ\text{C}$  and adding a solution of ethanol/water (50:50 v/v; 10 mL) a bright yellow solid precipitated. After filtration and drying under vacuum, the corresponding product (**15**) was obtained as a bright yellow solid (284 mg.; 0.324 mmol; 92% yield).

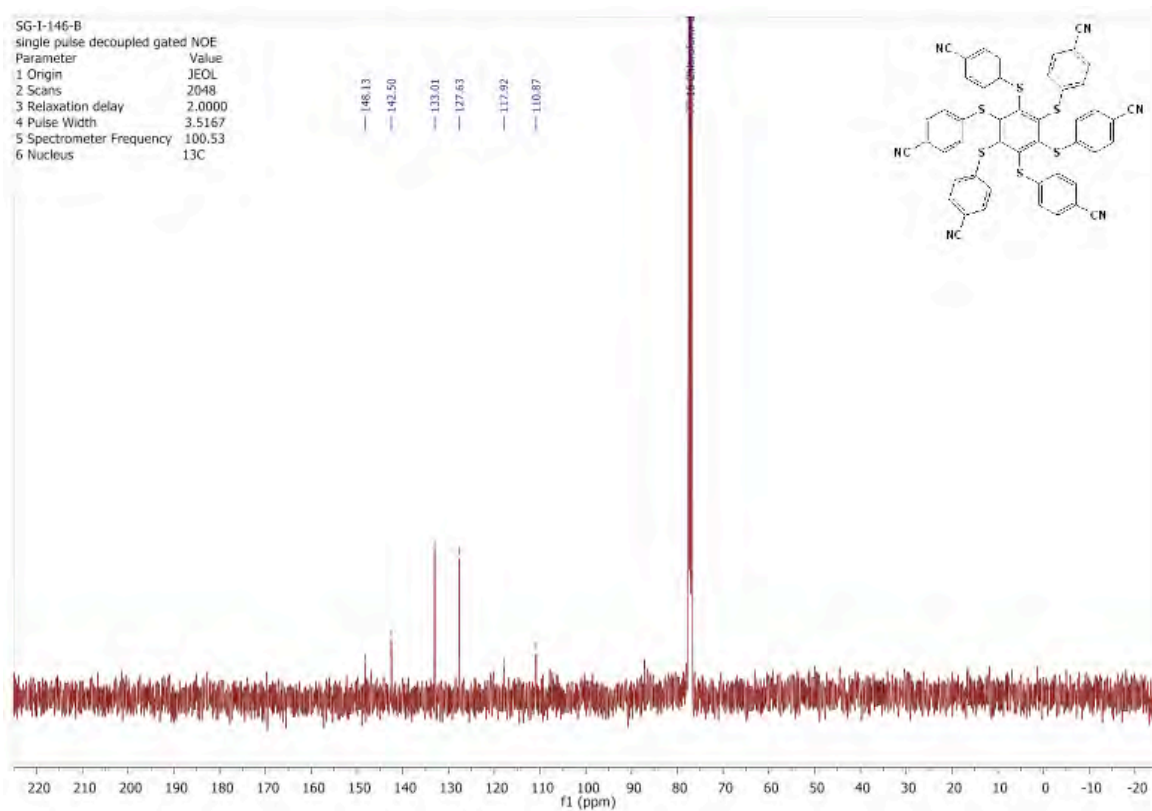
**M.p.:**  $282\text{--}286^\circ\text{C}$ ; **TLC** ( $\text{SiO}_2$ , *n*-hex/EtOAc: 70/30 v/v)  $R_f = 0.29$ ;  $^1\text{H NMR}$  (399.78 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.50$  ( $d_{\text{app}}$ ,  $J = 8.4$  Hz, 12H),  $6.95$  ( $d_{\text{app}}$ ,  $J = 8.5$  Hz, 12H);  $^{13}\text{C NMR}$  (100.53 MHz,  $\text{CDCl}_3$  ppm):  $\delta = 148.1$ ,  $142.5$ ,  $133.0$ ,  $127.6$ ,  $117.9$ ,  $110.9$ ;  $^1\text{H NMR}$  (200.13 MHz,  $\text{DMSO-d}_6$ , ppm):  $\delta = 7.30$  ( $d_{\text{app}}$ ,  $^3J = 8.2$  Hz, 12H),  $7.76$  ( $d_{\text{app}}$ ,  $^3J = 8.2$  Hz, 12H);  $^{13}\text{C NMR}$  (50.32 MHz,  $\text{DMSO-d}_6$  ppm):  $\delta = 147.9$ ,  $144.3$ ,  $133.8$ ,  $128.1$ ,  $119.4$ ,  $109.4$ ; **HRMS (ESI+)** calculated for  $[\text{C}_{48}\text{H}_{24}\text{N}_6\text{S}_6 + \text{H}^+]$ : 877.0459 Da, found  $[\text{M} + \text{H}^+]$  877.0447  $m/z$ ;  $[\text{C}_{48}\text{H}_{24}\text{N}_6\text{S}_6 + \text{Na}^+]$ : 899.0279 Da, found  $[\text{M} + \text{Na}^+]$  899.0272  $m/z$ .



HRMS (ESI positive mode) of (**15**)



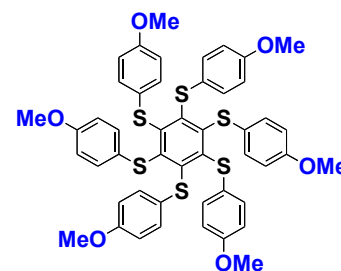
<sup>1</sup>H-NMR spectrum of (**15**) (CDCl<sub>3</sub>, 399.78 MHz)



<sup>13</sup>C-NMR spectrum of (**15**) (CDCl<sub>3</sub>, 100.53 MHz)

**Hexakis(4-methoxyphenylthio)benzene (56)** <sup>1-6</sup> (procedure taken from the PhD thesis of A. Pinchart)<sup>6</sup>

Into a two-necked 100 mL flask, fitted with a condenser, taken out of the oven and cooled under nitrogen, hexachlorobenzene (3.00 g.; 10.5 mmol) was added. 4-Methoxythiophenol (11.66 mL; 13.29 g.; 94.81 mmol) and dry 1,3-dimethyl-2-imidazolidinone (DMI, 30.0 mL) were injected via a syringe. Powdered NaH 95% (2.74 g., 114 mmol) was weighed in a dry flask taken out of the oven, which is then fixed with an elbow on the second neck of the flask containing the solution. The reaction medium is cooled by an ice bath. Oxygen

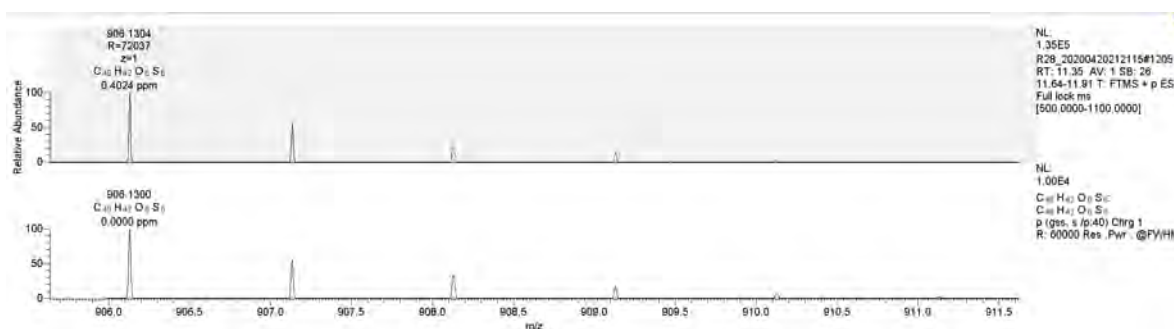


was removed by the use of vacuum and successive purges of nitrogen – freeze-thaw cycles (3 x 10 min). Sodium hydride was added carefully in small portions over 60 minutes. During the addition, a foam forms and the color of the solution became successively yellow, orange and red. At the end of the addition, the reaction medium was left for one hour at room temperature, with magnetic stirring. The flask was immersed in an oil bath at 80 ° C. After one hour, heating was stopped and the reaction was left at room temperature for two hours. A yellow precipitate formed on addition of 1M NaOH aqueous solution (1.25L). This solid is extracted with DCM (3 x 200 mL). The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was evaporated off. A yellow oil was collected. After one night on the vacuum pump, the product solidified. Trituration in ethanol (150 mL) while stirring for two hours, filtration, and drying afforded a yellow solid (8.40 g.; 9.26 mmol; 88%).

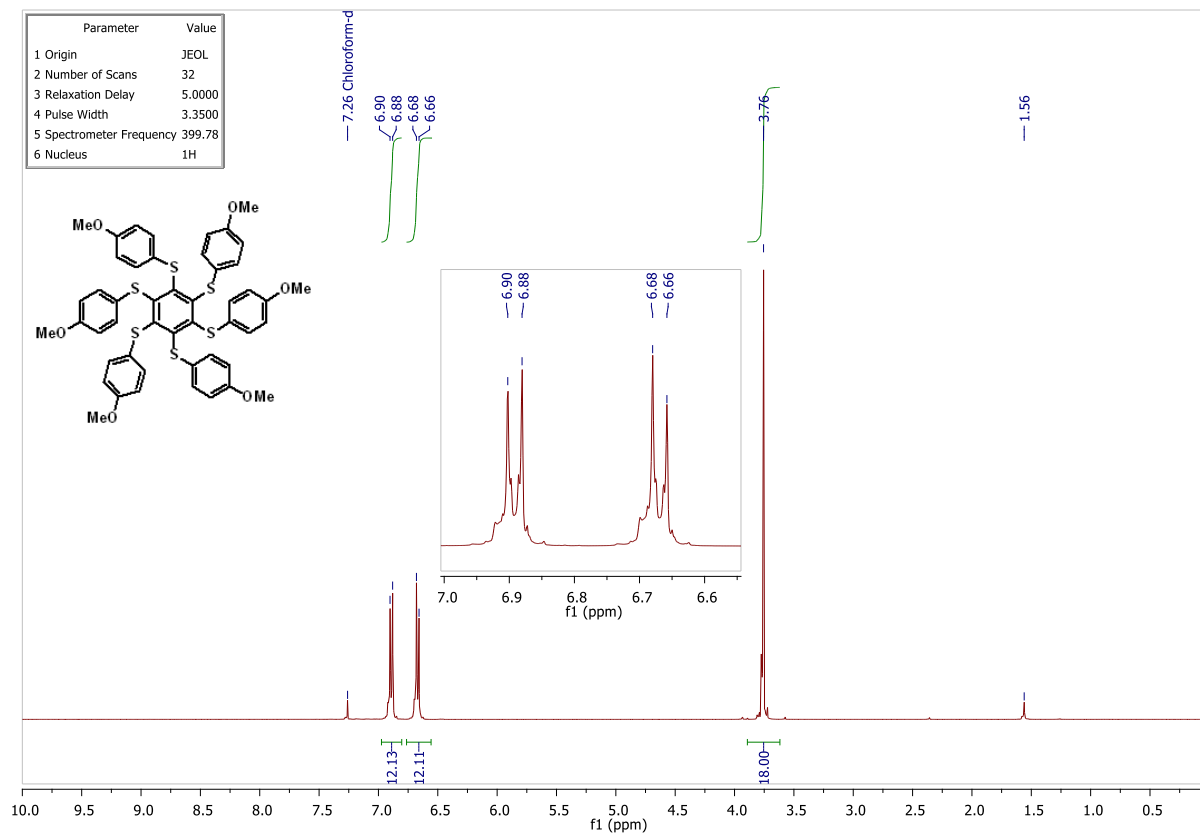
**M.p.:** 161-162°C (lit. 161-163°C<sup>5</sup>; 158-159°C<sup>4</sup>); **TLC** (SiO<sub>2</sub>, DCM/acetone 95:5 v/v) R<sub>f</sub> = 0.84; **<sup>1</sup>H NMR** (399.78 MHz, CDCl<sub>3</sub>, ppm): δ = 6.89 (d<sub>app</sub>, J = 8.7 Hz, 12H), 6.67 (d<sub>app</sub>, J = 8.7 Hz, 12H), 3.76 (s, 18H); **<sup>13</sup>C NMR** (100.53 MHz, CDCl<sub>3</sub> ppm): δ = 158.5, 147.8, 131.0, 128.7, 114.5, 55.4; **HRMS (ESI+)** calculated for [C<sub>48</sub>H<sub>42</sub>O<sub>6</sub>S<sub>6</sub> + H<sup>+</sup>]: 907.1378 Da, found [M+H<sup>+</sup>] 907.1376 m/z.

#### References:

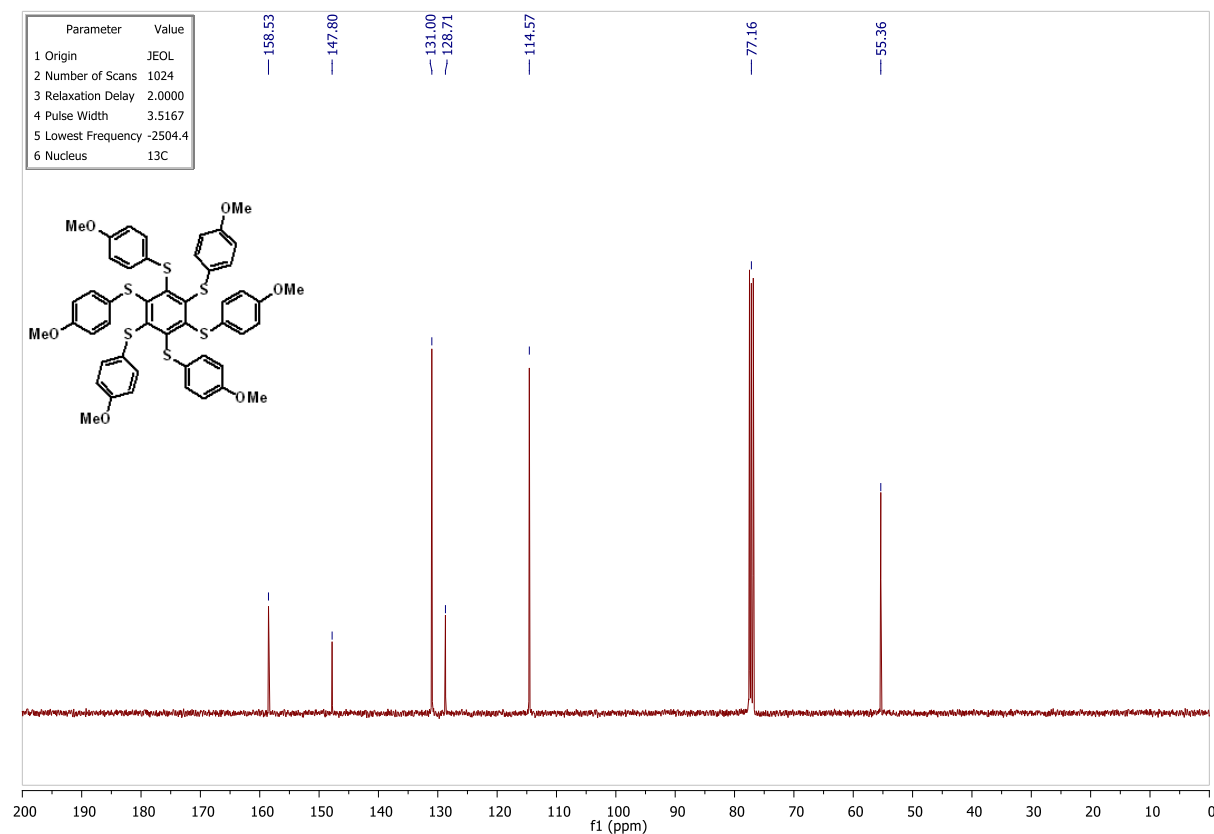
1. C. Aubert, C. Dallaire, G. Pepe, E. Levillain, G. Felix, M. Gingras, *Eur.J.Org.Chem.* (2012), 6145-6154.
2. C. Aubert, C. Dallaire, M. Gingras, *Tetrahedron Lett.* (2008), 49, 5355-5358.
3. J. N. Lowe, D.A. Fulton, S.-H. Chiu, A.M. Elizarov, S.J. Cantrill, S.J. Rowan, J.F. Stoddart, *J.Org. Chem.* (2004), 69, 4390-4402.
4. J.H.R. Tucker, M. Gingras, H. Brand, J.-M. Lehn, *J.Chem.Soc., Perkin Trans. 2: Physical Organic Chemistry* (1997), 7, 1303-1307.
5. T.D.P. Stack, R.H. Holm, *J.Am.Chem.Soc.* (1988), 110, 2484-94.
6. A. Pinchart, PhD dissertation, Université Libre de Bruxelles and Université de Paris-Sud Orsay, "Synthèse d'architectures moléculaires de sulfures de phénylène et de noyaux aromatiques persulfurés", sept. 26, 2000.



HRMS (ESI, positive mode) for (56)



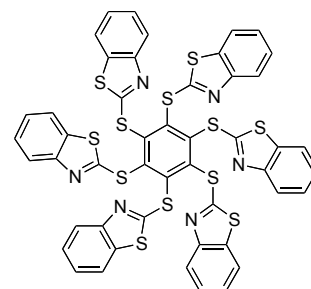
<sup>1</sup>H-NMR spectrum of (**56**) (CDCl<sub>3</sub>, 399.78 MHz)



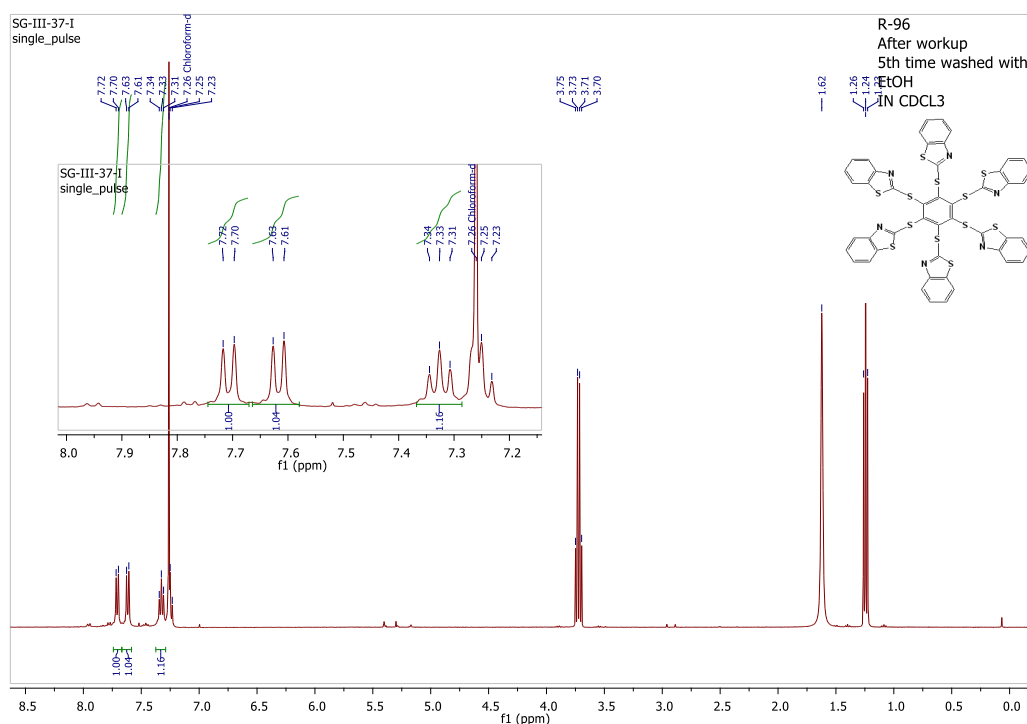
<sup>13</sup>C-NMR spectrum of (**56**) (CDCl<sub>3</sub>, 100.53 MHz)

## Hexakis(2-benzothiazolylthio)benzene (16)

In an oven-dried sealed tube, purged with argon, was added hexachlorobenzene (0.200 g, 0.702 mmol, 1.00 mol-eq.), dried potassium carbonate (1.163 g, 8.415 mmol, 11.99 mol-eq.), 2-mercaptobenzothiazole (1.000 g, 5.979 mmol, 8.517 mol-eq.) and dry DMF (3.5 mL, dried and kept over activated molecular sieves 3Å). Argon was bubbled through the mixture for 5-10 min.. The color changed from yellow to orange. The tube was sealed and the reaction was stirred at 60°C for 5 days in an oil bath. Most DMF was removed on a rotary evaporator under reduced pressure. To the reaction mixture was added DCM (15 mL) and the organic layer was washed with H<sub>2</sub>O (2×15mL) to remove remaining DMF. The organic phase was dried over anhydrous MgSO<sub>4</sub>, filtered and DCM evaporated to afford a yellow-orange solid. It was triturated with EtOH (5×10 mL) at 25°C with a strong stirring for several minutes, and the supernatant was removed. It was repeated four times. The solid was then dried *in vacuo* to afford a pure yellow solid (0.634 g, 5.93 mmol, 84% yield).

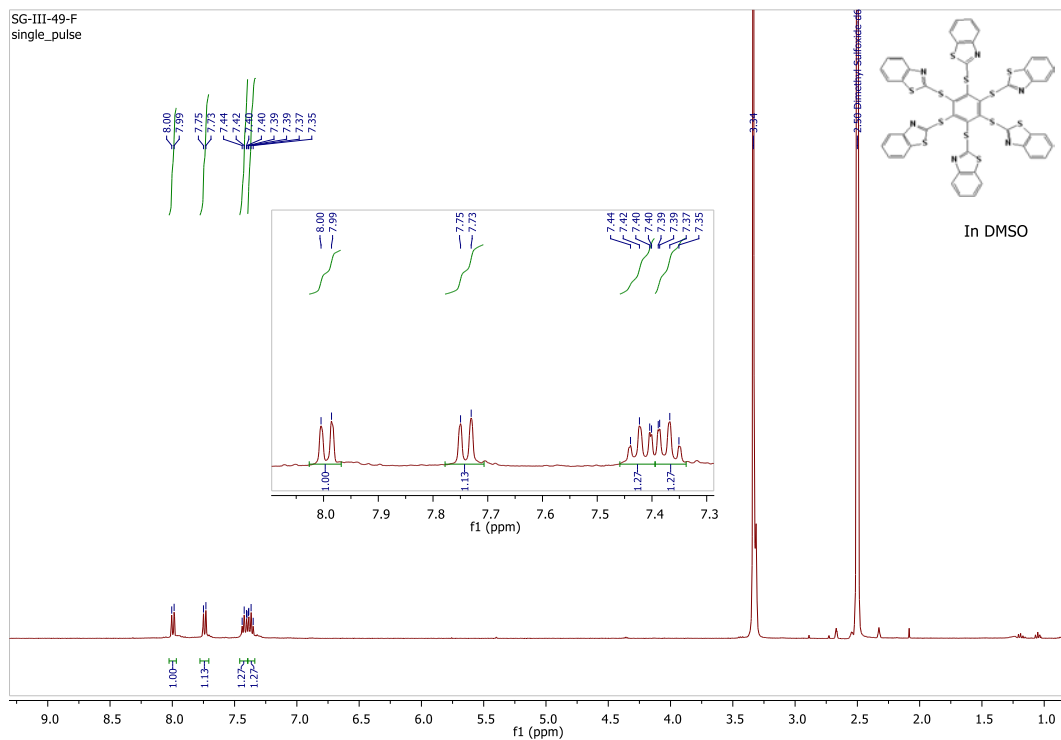


**M.p.:** 218-234°C (dec.); **TLC** (SiO<sub>2</sub>, EtOAc/cyclohex. 10:90 v/v) R<sub>f</sub> = 0.43; (SiO<sub>2</sub>, DCM 100%) R<sub>f</sub> = 0.23; **<sup>1</sup>H NMR** (SGIII49G, 399.78 MHz, DMSO-d<sub>6</sub>, ppm): δ = 7.99 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.42 (ddd, J = 7.9, 7.3, 1.3 Hz, 1H), 7.36 (dd, J = 7.6, 7.5, 1.2 Hz, 1H); **<sup>1</sup>H NMR** (SGIII49E, 399.78 MHz, CDCl<sub>3</sub>, ppm): δ = 7.71 (d, J = 8.0 Hz, 1H); 7.62 (d, J = 7.8 Hz, 1H), 7.32 (dd, J = 7.8, 7.5 Hz, 1H), 7.24 (dd, J = 7.8, 7.5 Hz, 1H); **<sup>13</sup>C NMR** (SGIII37K, 100.53 MHz, DMSO-d<sub>6</sub>, ppm): δ = 164.4, 152.3, 148.1, 135.3, 126.6, 125.1, 122.0, 121.7; **<sup>13</sup>C NMR** (SGIII49E, 100.53 MHz, CDCl<sub>3</sub>, ppm): δ = 164.8, 153.0, 148.8, 135.9, 126.3, 124.9, 122.3, 121.1. **MS (MALDI-TOF)** calculated for [C<sub>48</sub>H<sub>24</sub>N<sub>6</sub>S<sub>12</sub> + H<sup>+</sup>]: 1068.87 Da, found 1068.70; **HRMS (ESI+)** calculated for [C<sub>48</sub>H<sub>24</sub>N<sub>6</sub>S<sub>12</sub> + H<sup>+</sup>]: 1068.8789 Da; for [C<sub>48</sub>H<sub>24</sub>N<sub>6</sub>S<sub>12</sub> + Na<sup>+</sup>]: 1090.8609 Da; for [C<sub>48</sub>H<sub>24</sub>N<sub>6</sub>S<sub>12</sub> + K<sup>+</sup>]: 1106.8348 Da, found [M + H<sup>+</sup>] 1068.8791; [M + Na<sup>+</sup>] 1090.8610; [M + K<sup>+</sup>] 1106.8349.

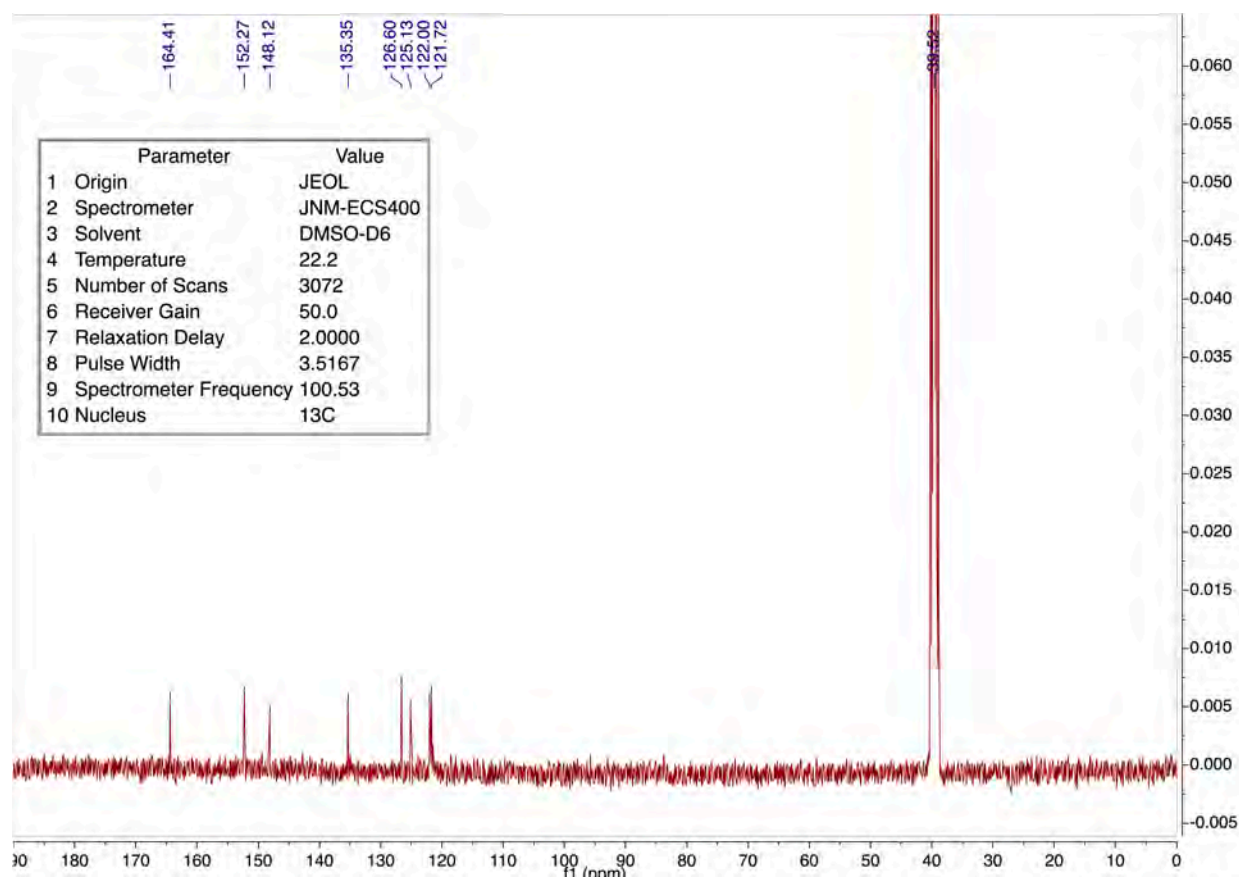


<sup>1</sup>H-NMR spectrum of (16) (CDCl<sub>3</sub>, 399.78 MHz)





$^1\text{H-NMR}$  spectrum of **(16)** (DMSO- $d_6$ , 399.78 MHz)



$^{13}\text{C-NMR}$  spectrum of **(16)** (DMSO- $d_6$ , 100.53 MHz)

## 2.2 Penta(thio) benzene asterisks

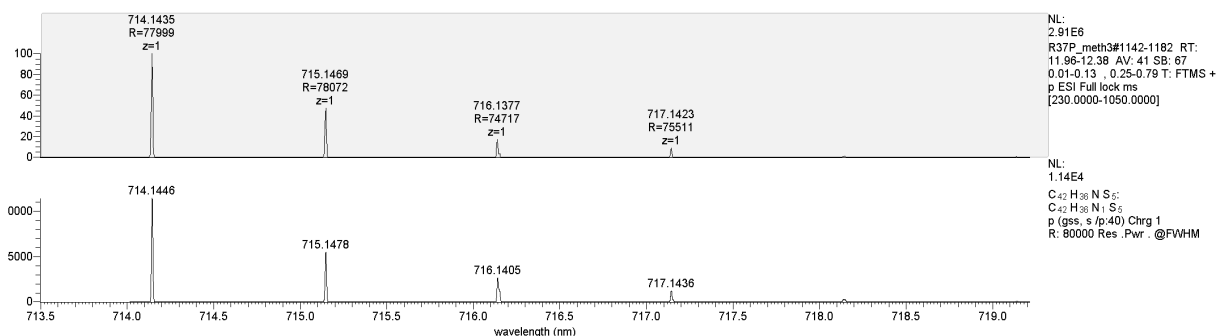
### 2,3,4,5,6-pentakis(4-methylphenylthio)benzonitrile (**17**)<sup>1,2</sup>

To a solution of 2,3,4,5,6-pentafluorobenzonitrile (106 mg, 0.549 mmol, 1.00 eq.) in dry DMF (4.0 mL, kept over activated 3Å molecular sieves) was added dry potassium carbonate (572 mg, 4.14 mmol, 7.54 mol-eq.). The mixture was purged with argon for several minutes. 4-Methylbenzenethiol (482 mg, 3.88 mmol, 7.07 mol-eq.) was added and the reaction mixture was stirred at 20°C for 12 hours while changing color to bright yellow. Upon completion of the reaction (absence of <sup>19</sup>F NMR signal), an aqueous solution of NaOH (2M, 50 mL) was added, and the mixture was extracted with DCM (3x30 mL). The organic layers were combined, dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated *in vacuo*. The crude product was then purified by column chromatography over silica gel using petroleum ether/DCM (80:20 v/v) as eluent. A bright yellow solid (**17**) was obtained (370 mg, 0,518 mmol, 94 % yield).

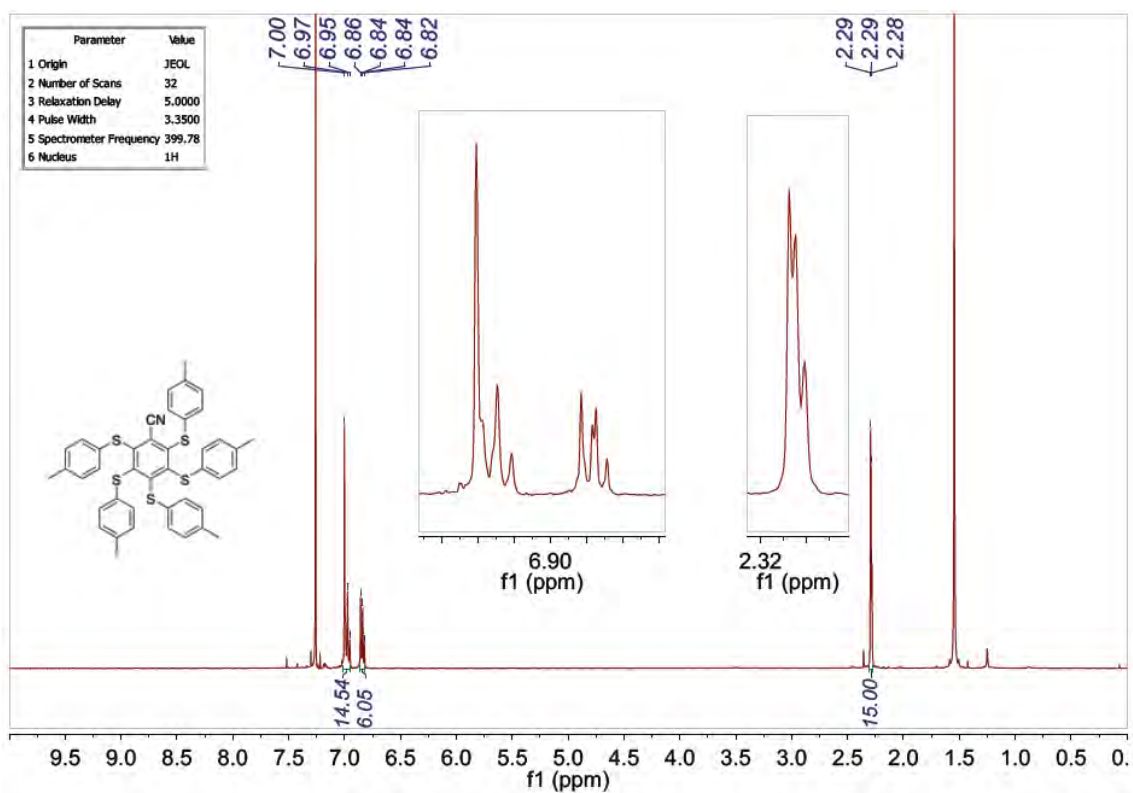
**M.p.:** 170.6-173.3°C; **TLC** (SiO<sub>2</sub>, petroleum ether/DCM; 80:20 v/v) R<sub>f</sub> = 0.16; **<sup>1</sup>H NMR** (399.78 MHz, CDCl<sub>3</sub>, ppm) δ = 7.01-6.94 (m, 14H), 6.84 (d, *J* = 8.2 Hz, 4H), 6.82 (d, *J* = 8.0 Hz, 2H), 2.295 (s, 6H), 2.290 (s, 6H), 2.28 (s, 3H); **<sup>13</sup>C NMR** (100.53 MHz, CDCl<sub>3</sub>, ppm) δ = 153.24, 146.83, 146.76, 137.45, 136.94, 136.71, 133.61, 133.31, 131.98, 130.53, 130.07, 130.00, 129.97, 129.39, 128.96, 124.76, 115.39, 21.28, 21.27, 21.23; **HRMS (API+)** calculated for [C<sub>42</sub>H<sub>35</sub>NS<sub>5</sub> + NH<sub>4</sub>]<sup>+</sup>: 731.1717 Da, found [M+NH<sub>4</sub>]<sup>+</sup> 731.1712 *m/z*. **HRMS (ESI+)** calculated for [C<sub>42</sub>H<sub>35</sub>N<sub>1</sub>S<sub>5</sub> + H]<sup>+</sup>: 714.1446 Da, found [M+H]<sup>+</sup> 714.1435 *m/z*.

#### Reference:

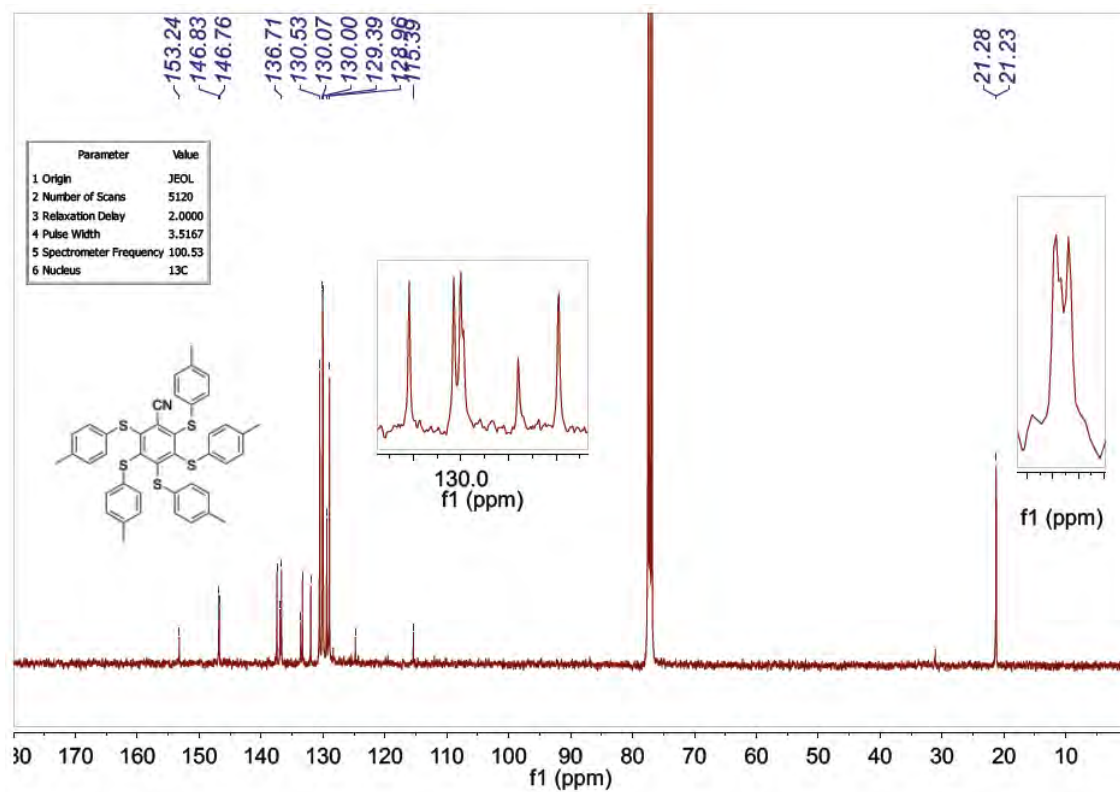
1. M. Villa; S. D'Agostino; P. Sabatino; R. Noel; J. Busto; M. Roy; M. Gingras; P. Ceroni; *New J. Chem.* (2020), 44, 3249-3254.
2. R. Noel, *Étude et développement de substrats microporeux pour l'adsorption du radon et son application en physique du neutrino*, doctoral dissertation, Aix-Marseille Université, Déc. 13, 2015; <https://tel.archives-ouvertes.fr/tel-01521979>.



HRMS (ESI, positive mode) of (**17**)



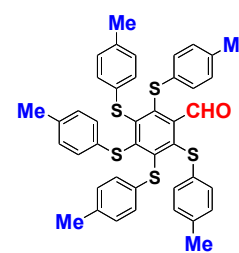
<sup>1</sup>H-NMR spectrum of **(17)** (CDCl<sub>3</sub>, 399.78 MHz)



<sup>13</sup>C-NMR spectrum of **(17)** (CDCl<sub>3</sub>, 100.53 MHz)

### 2,3,4,5,6-pentakis(4-methylphenylthio)benzaldehyde (**18**)<sup>1</sup>

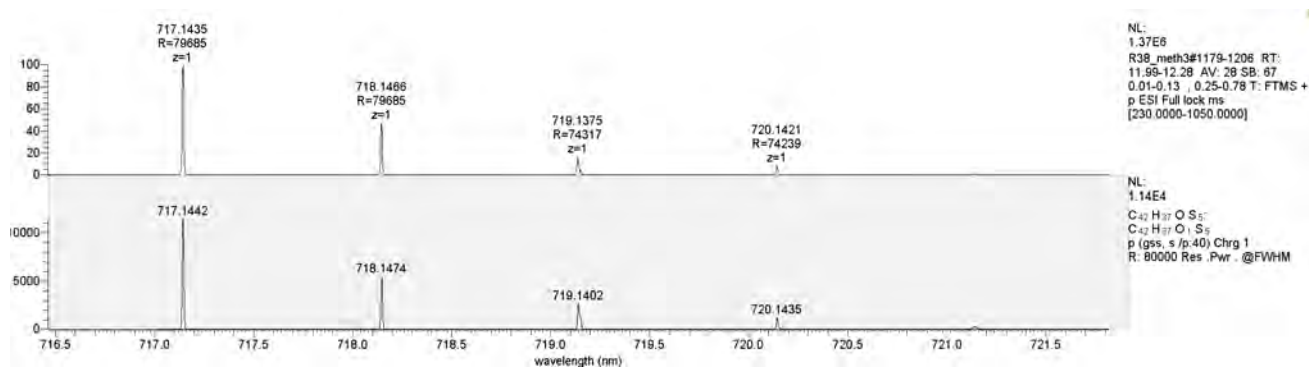
Pentafluorobenzaldehyde (500 mg, 2.55 mmol, 1.00 mol-eq.), was dissolved in dry DMI (6.0 mL), and potassium carbonate (2.82 g, 20.4 mmol, 8.00 mol-eq.) was added. The mixture was purged with argon for several minutes. The color of the mixture turned yellow. 4-Methyl-benzenethiol (2.37 g, 19.1 mmol, 7.49 mol-eq.) was added and the color changed to orange at 20°C. It was then heated to 40 °C (oil bath) and stirred overnight (12 hrs). Upon completion of the reaction (absence of <sup>19</sup>F NMR signal), the mixture was treated with a saturated NaCl aqueous brine solution (100 mL) and extracted with Et<sub>2</sub>O (4 x 30 mL). The organic layers were combined, dried over anhydrous MgSO<sub>4</sub> and filtered. After evaporating the solvent, a dark yellow oil was purified by column chromatography over silica gel using cyclohexane/DCM (90:10 v/v) as eluent. A yellow solid (**18**) was obtained (1.655 g, 2.32 mmol, 91% yield).



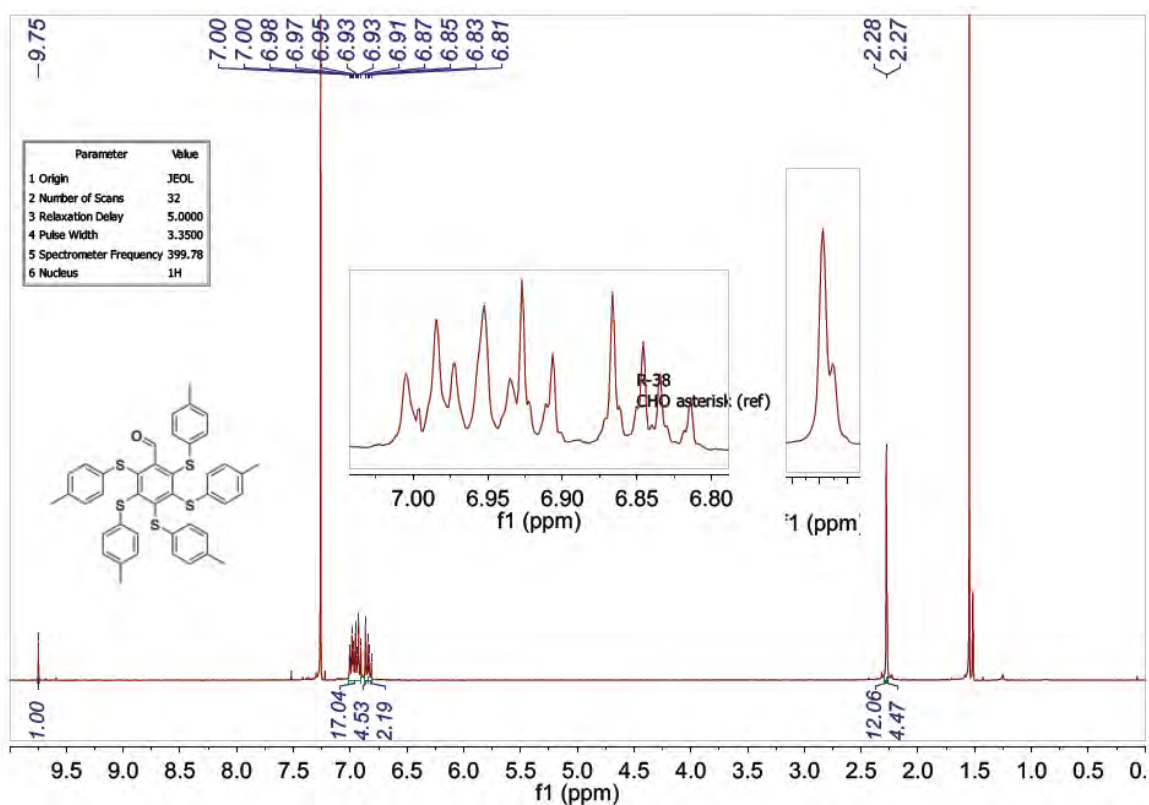
**M.p.:** 133.6-141.0°C; **TLC** (SiO<sub>2</sub>, tol/cyclohex. 50:50 v/v ) R<sub>f</sub> = 0.47; **FT-IR** (ATR, diamond contact, neat, cm<sup>-1</sup>) ν = 3018 (w), 2917 (w), 2862 (w), 1889 (w) 1698 (m), 1566 (w), 1489 (s), 1447(m), 1286 (m), 1162 (m), 1083 (m), 1015 (m), 926 (m), 796 (s), 734(m), 700 (m); **<sup>1</sup>H NMR** (399.78 MHz, CDCl<sub>3</sub>, ppm) δ = 9.75 (s, 1H), 6.99 (d, J = 8.3 Hz, 4H), 6.96 (d, J = 8.2 Hz, 4H), 6.94 (d, J = 8.3 Hz, 2H), 6.92 (d, J = 8.3 Hz, 4H), 6.86 (d, J = 8.3 Hz, 4H), 6.82 (d, J = 8.3 Hz, 2H), 2.28 (s, 12H), 2.27 (s, 3H); **<sup>13</sup>C NMR** (100.53 MHz, CDCl<sub>3</sub>, ppm) δ = 190.69, 150.97, 147.28, 145.94, 141.46, 137.00, 136.39, 136.31, 134.12, 133.78, 133.15, 130.16, 129.87, 129.81, 129.49, 129.04, 128.72, 21.22 (3C); **HRMS (ESI+)** calculated for [C<sub>42</sub>H<sub>36</sub>O<sub>1</sub>S<sub>5</sub>+H<sup>+</sup>]: 717.1442 Da, found [M+H<sup>+</sup>] 717.1435 m/z.

#### Reference:

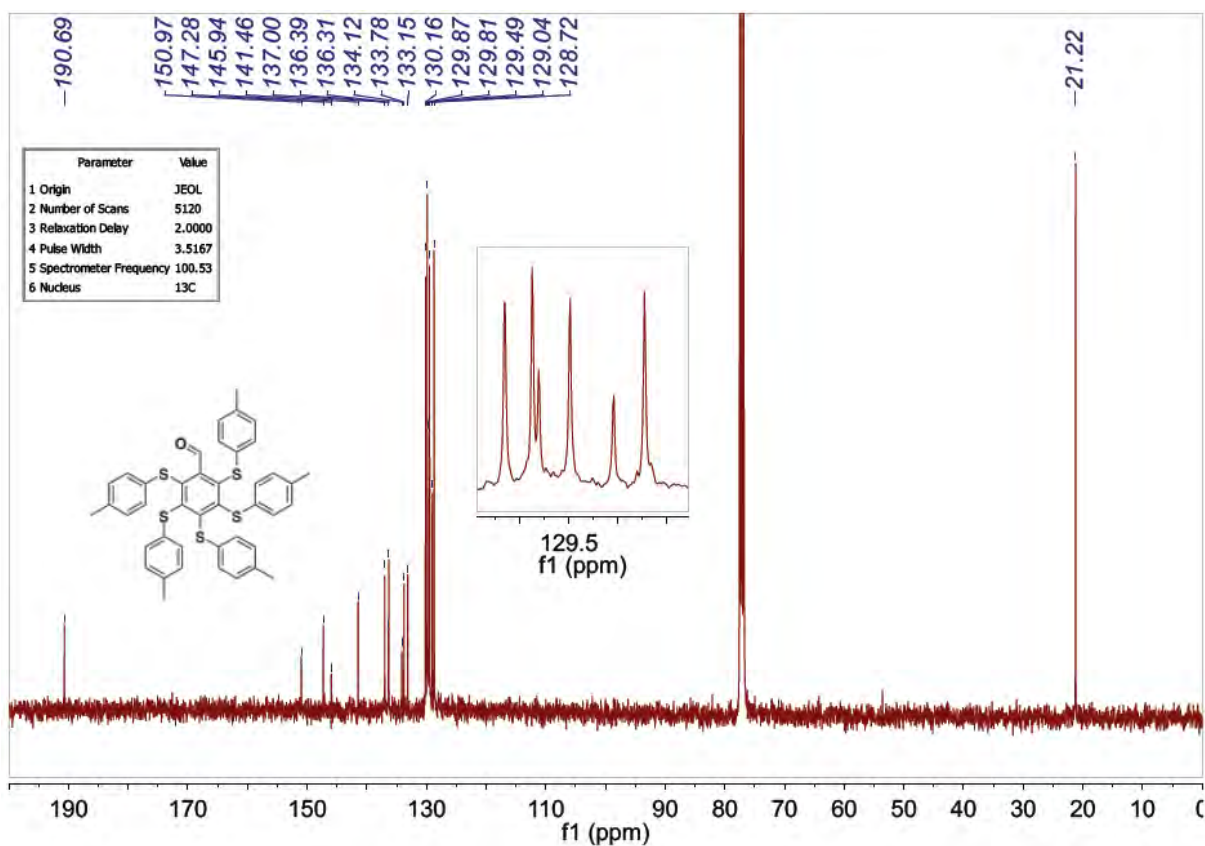
1. M. Villa; S. D'Agostino; P. Sabatino; R. Noel; J. Busto; M. Roy; M. Gingras; P. Ceroni, *New J. Chem.* (2020), 44, 3249-3254.



HRMS (ESI, positive mode) of (**18**)



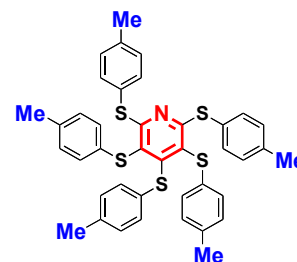
<sup>1</sup>H-NMR spectrum of **(18)** (CDCl<sub>3</sub>, 399.78 MHz)



<sup>13</sup>C-NMR spectrum of **(18)** (CDCl<sub>3</sub>, 100.53 MHz)

## 2,3,4,5,6-pentakis(4-methylphenylthio)pyridine (**19**)<sup>1</sup>

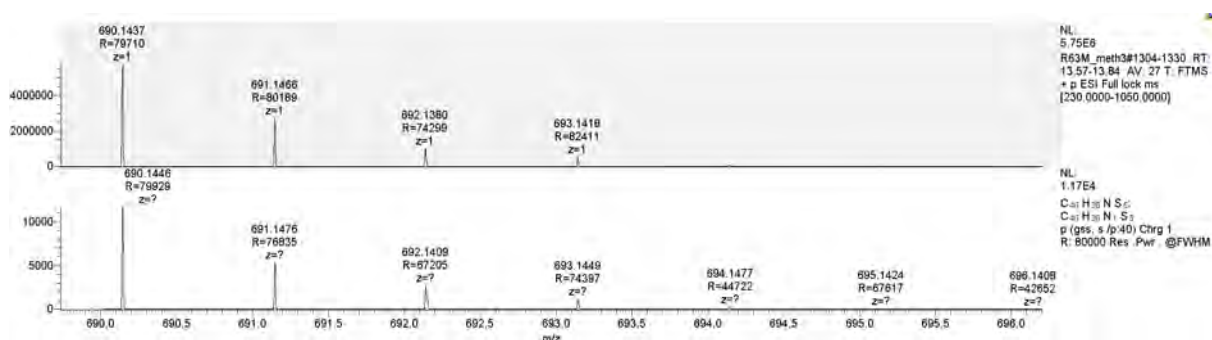
Under an argon atmosphere, pentafluoropyridine (128 mg, 0.757 mmol, 1.00 mol-eq.) and 4-methylbenzenethiol (930 mg, 7.49 mmol, 9.89 mol-eq.) were added in a 50 ml two-necked flask, followed by injection of DMI (5.0 ml, dried over activated 4Å molecular sieves) via a syringe. The mixture was cooled in an ice-bath (3°C) and powdered NaH (183 mg, 7.63 mmol, 10.0 mol-eq.) was slowly added. Upon addition of NaH, the mixture became light yellow and hydrogen was evolved. The reaction mixture was allowed to reach room temperature and it was stirred for six days. Ethanol (20 mL) was slowly added to the flask while stirring, and the resulting precipitate was collected by filtration under vacuum. TLC indicated that the crude product contained a slight impurity. A trituration in EtOH while stirring vigorously for 30 min. was carried out, and the solid was again collected by vacuum filtration. The pale-yellow powder (**19**) was then dried under high vacuum to afford a pure solid (510 mg; 0.739 mmol, 98% yield).



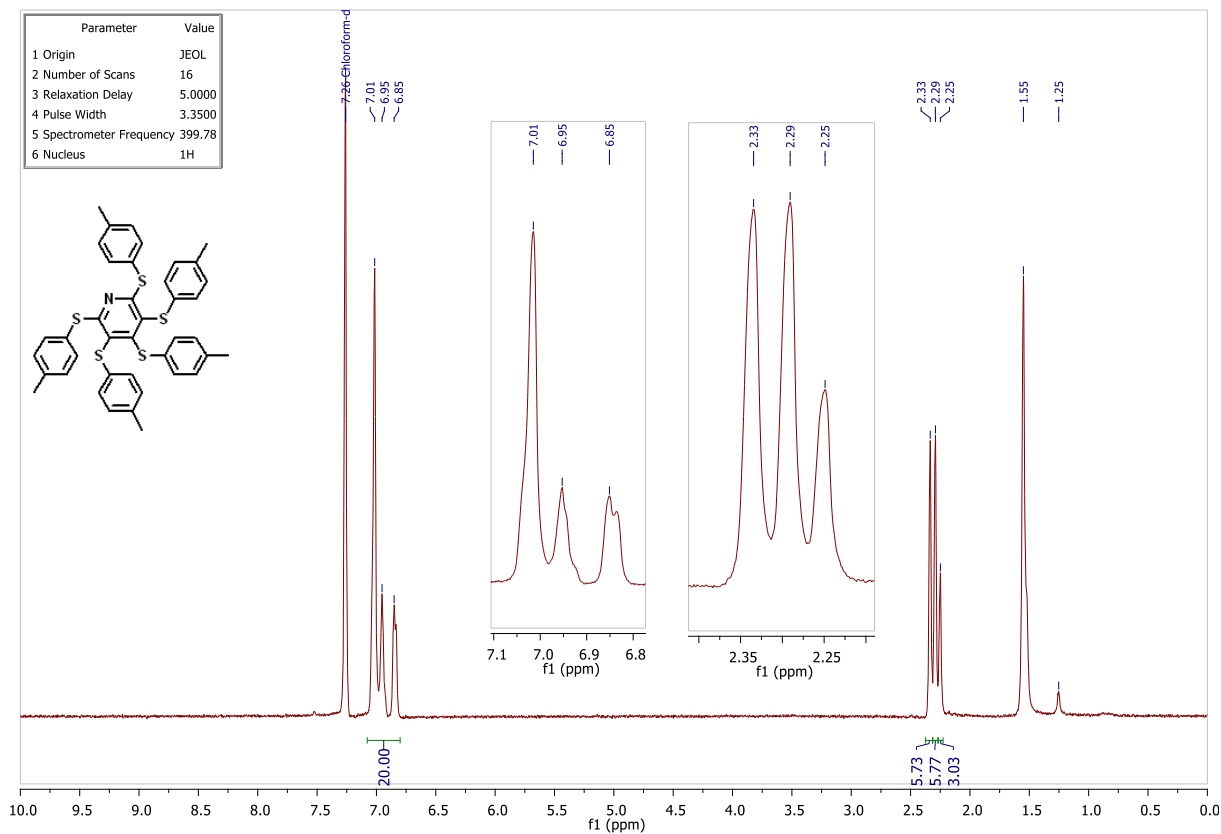
**M.p.:** 147-149°C (lit. 147-149°C)<sup>1</sup>; **TLC** (SiO<sub>2</sub>, acetone/cyclohex. 30:70 v/v) R<sub>f</sub> = 0.70; (SiO<sub>2</sub>, petroleum ether/DCM 50:50 v/v) R<sub>f</sub> = 0.80; **<sup>1</sup>H NMR** (399.78 MHz, CDCl<sub>3</sub>, ppm) δ = 6.80-7.10 (m, 20H), 2.33 (s, 6H), 2.29 (s, 6H), 2.25 (s, 3H); **<sup>13</sup>C NMR** (100.53 MHz, CDCl<sub>3</sub>, ppm) δ = 168.18, 158.66, 138.41, 137.17, 136.36, 135.22, 132.94, 132.64, 130.48, 130.15 (2C), 129.77, 128.11, 127.20, 126.05, 21.94, 21.50 (2C); **<sup>13</sup>C NMR** (125.77 MHz, CDCl<sub>3</sub>, ppm) δ = 21.38, 21.41, 21.81, 125.98, 127.14, 128.03, 130.07, 130.25, 130.39, 132.55, 132.85, 135.04, 135.11, 136.26, 137.07, 138.30, 158.55, 168.07; **MS (MALDI-TOF)** calculated for [C<sub>40</sub>H<sub>35</sub>N<sub>1</sub>S<sub>5</sub>+H<sup>+</sup>]: 690.14 Da, found 690.10 m/z; **HRMS (ESI+)** calculated for [C<sub>40</sub>H<sub>35</sub>N<sub>1</sub>S<sub>5</sub>+H<sup>+</sup>]: 690.1446 Da, found [M+H<sup>+</sup>] 690.1437 m/z.

### Reference:

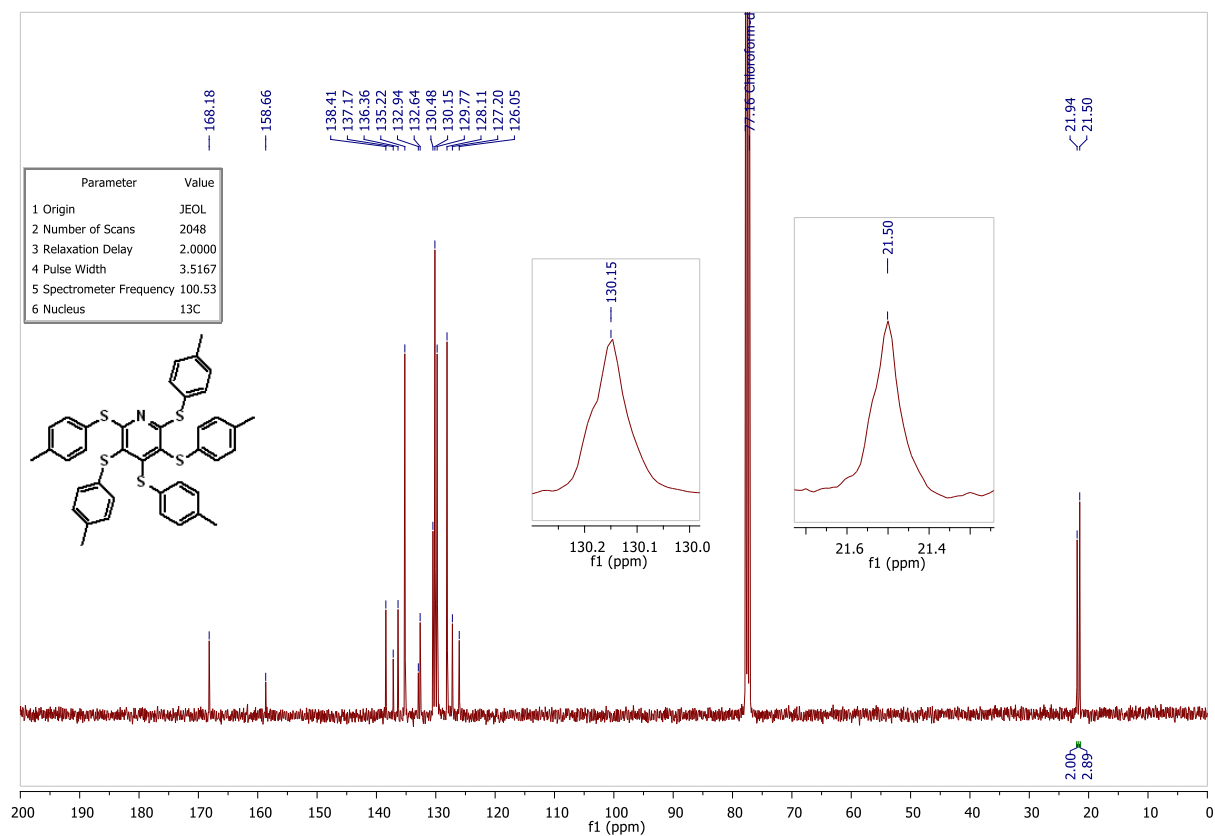
1. J.H.R. Tucker; M. Gingras; H. Brand; J.-M. Lehn, *J. Chem. Soc. Perkin Trans. 2: Physical Organic Chemistry* (1997), 7, 1303-1307.



HRMS (ESI, positive mode) of (**19**)



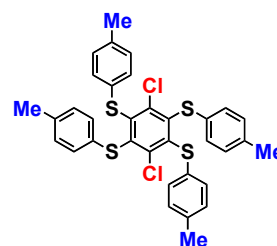
<sup>1</sup>H-NMR spectrum of **(19)** (CDCl<sub>3</sub>, 399.78 MHz)



<sup>13</sup>C-NMR spectrum of **(19)** (CDCl<sub>3</sub>, 100.53 MHz)

## 2.3 Tetrathio benzene and pyridine asterisks

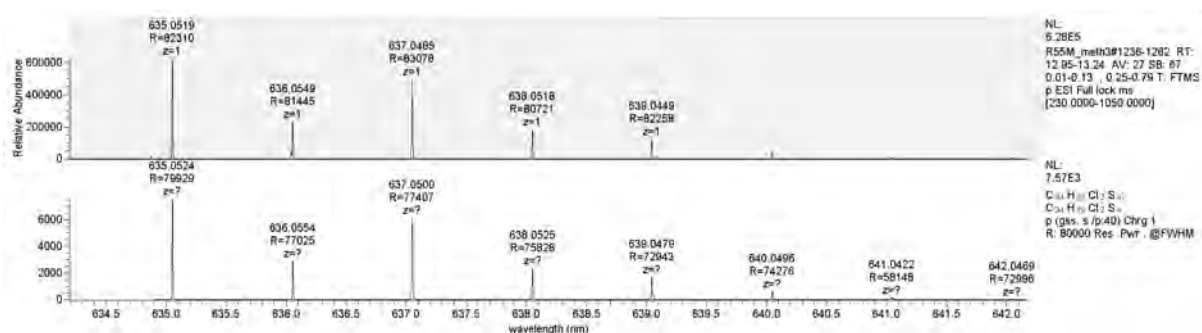
**1,4-dichoro-2,3,5,6-tetrakis(4-methylphenylthio)benzene (20).**<sup>1</sup> In a 50 mL two-necked flask, taken out of the oven and cooled under argon, hexachlorobenzene (100 mg, 0.351 mmol) and *p*-methylbenzenethiol (4.22 eq., 179 mg, 1.48 mmol) were added. DMI (5.0 mL) was injected. Powdered sodium hydride 95% (41 mg, 1.7 mmol) was weighed in a Gooch tube installed at a neck. Oxygen was removed by the use of high vacuum and successive purges of nitrogen – freeze-thaw cycles. The hydride was slowly added at 3°C (ice-bath temperature). The reaction mixture was stirred at room temperature for 3 hours. After cooling, EtOAc (20 ml) was added and a pale yellow solid precipitated. It was filtered, recovered and dried. After two triturations in ethanol while stirring vigorously and filtration, a pale yellow solid (**20**) was obtained (147 mg, 0.231 mmol, 66% yield).



**M.p.:** 235-239°C (pale yellow solid); **TLC** (SiO<sub>2</sub>, EtOAc/*n*-hex 10:90 v/v) : R<sub>f</sub> = 0.50; **<sup>1</sup>H NMR** (399.78 MHz, CDCl<sub>3</sub>, ppm): δ = 7.00 (d<sub>app</sub>, J = 8.2 Hz, 8H), 6.95 (d<sub>app</sub>, J = 8.3 Hz, 8H), 2.28 (s, 12H); **<sup>13</sup>C NMR** (100.53 MHz, CDCl<sub>3</sub>, ppm): δ = 144.8, 142.8, 136.6, 132.7, 130.0, 128.7, 21.19; **MS (EI)** m/e 635 (M<sup>+</sup>, 52%); **HRMS (ESI+)** calculated for [C<sub>34</sub>H<sub>28</sub>Cl<sub>2</sub>S<sub>4</sub> +H<sup>+</sup>]: 635.0524 Da, found [M+H<sup>+</sup>] 635.0519 m/z.

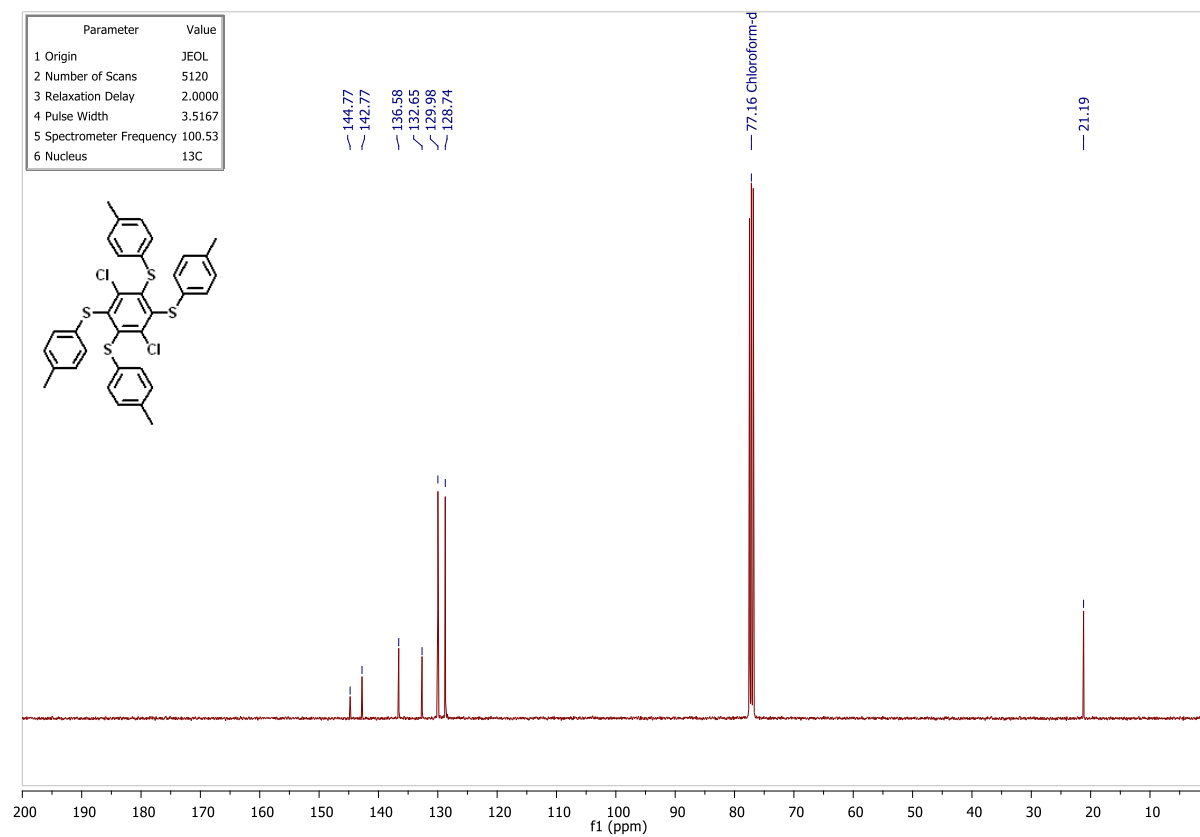
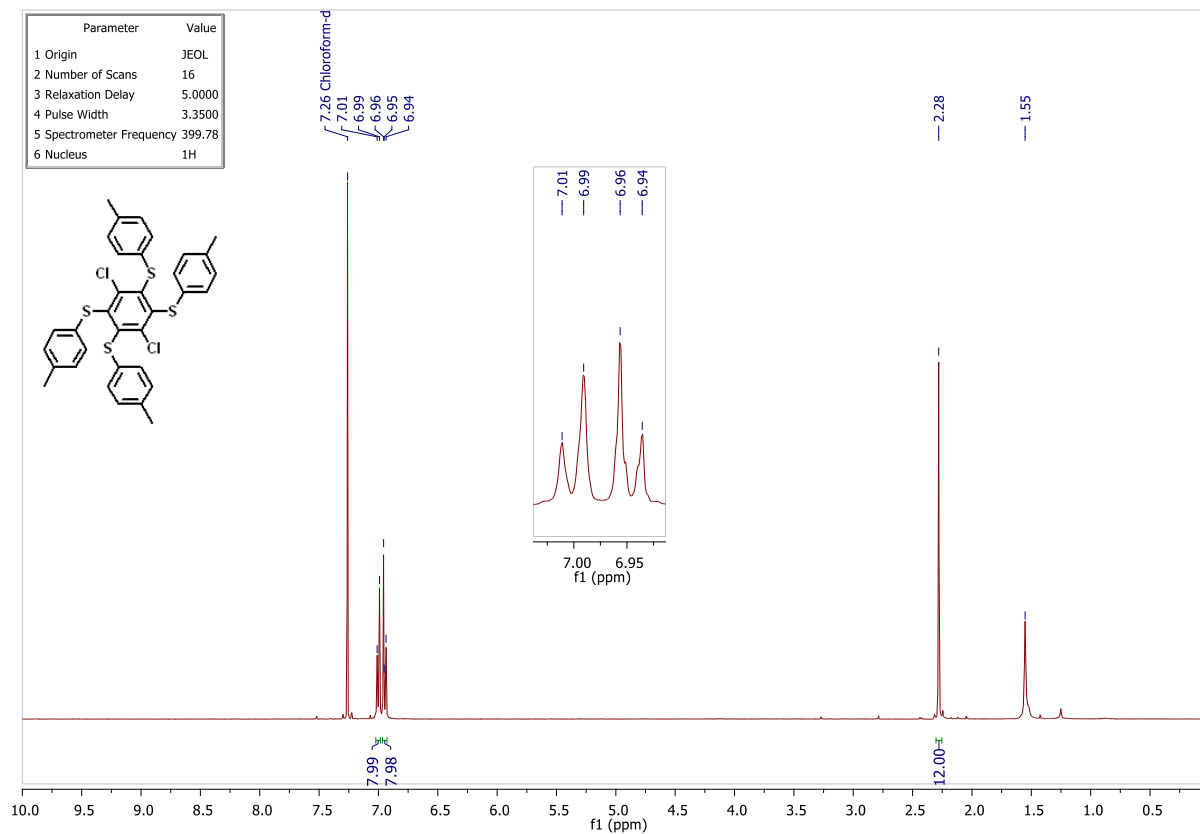
### Reference:

1. Pinchart, A. *Synthèses d'architectures moléculaires de sulfure de phénylène et de noyaux aromatiques persulfurés* PhD dissertation, Université Libre de Bruxelles et Université de Paris XI Orsay, Sept. 26 **2000**.



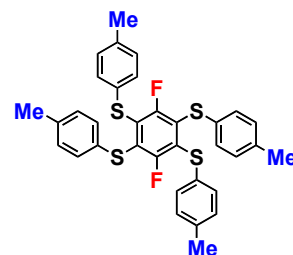
HRMS (ESI, positive mode) of (**20**)





### 1,4-difluoro-2,3,5,6-tetrakis(4-methylphenylthio)benzene (**22**)<sup>1,2,3</sup>

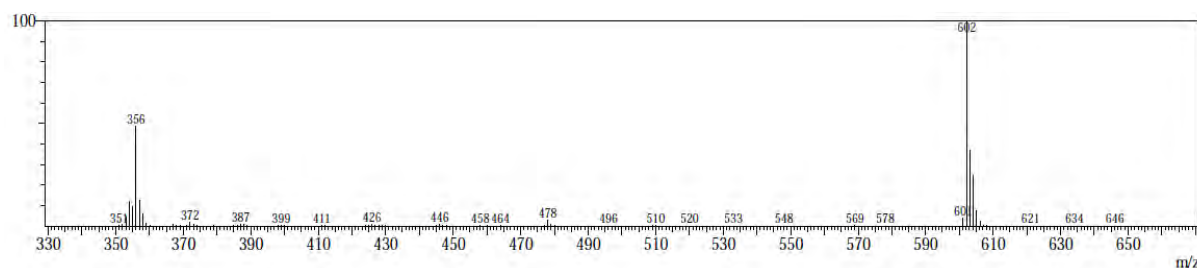
In a reaction tube, hexafluorobenzene (220 mg, 1.18 mmol, 1.00 mol-eq.) was dissolved in a solution of dry DMF and absolute EtOH (DMF/EtOH: 50:50 v/v, 2.0 mL). Dry potassium carbonate (817 mg, 5.91 mmol, 5.00 mol-eq.) was added. The mixture was purged with argon for several minutes. 4-Methyl-1-benzenethiol (587 mg, 4.73 mmol, 4.00 mol-eq.) was added. The tube was sealed and the reaction mixture was heated to 40°C and stirred 2 days. After completion of the reaction, the mixture was treated with an aqueous solution of NaOH (2M, 50 mL) and extracted with DCM (5x10 mL). The organic layers were combined, dried over anhydrous MgSO<sub>4</sub> and filtered. After removal the solvent *in vacuo*, the crude was purified by column chromatography over silica gel using cyclohexane/DCM as eluent to separate the disulfurated benzene molecule from the tetrasulfurated one. Crystallization by a slow evaporation of DCM provided transparent colorless needles of (**21**) (299 mg, 0.496 mmol, 42% yield).



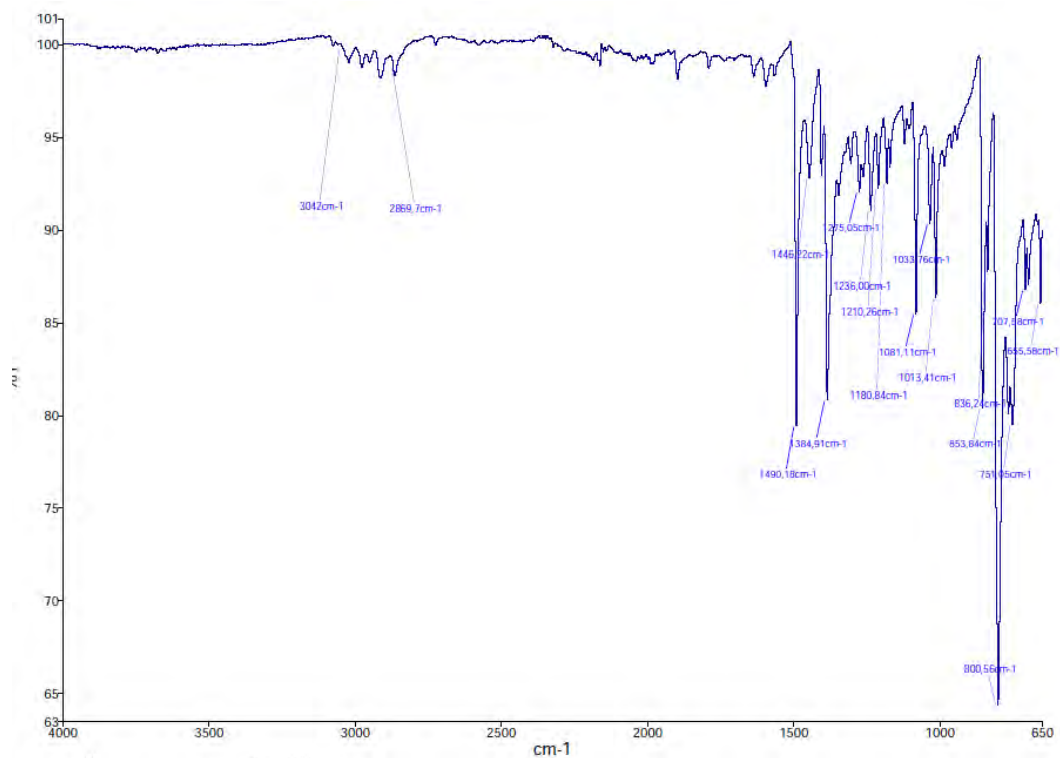
**M.p.:** 189.2-191.0°C (CH<sub>2</sub>Cl<sub>2</sub>); **FT-IR** (ATR, diamond contact, neat, cm<sup>-1</sup>)  $\nu$  = 3059 (w), 1579 (s), 1475 (s), 1440 (s), 1391 (s), 1378 (s), 1174 (m), 1081 (m), 1022 (m), 965 (m), 850 (s), 736 (s), 686 (s); **<sup>1</sup>H NMR** (399.78 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 7.08 (d<sub>app</sub>, *J* = 8.2, 8H), 7.01 (d<sub>app</sub>, *J* = 8.4, 8H), 2.30 (s, 12H); **<sup>13</sup>C NMR** (100.53 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 159,18 (dd, *J* = 251, 4 Hz), 137.15, 131.31, 130.06, 129.89, 129.23-129.01 (m, AA'XX' second order system), 21.17; **<sup>19</sup>F NMR** (376.17 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = -94.81; **MS** (EI, direct introduction GC-MS): 602 m/z [M]<sup>+</sup>.

#### Reference:

1. M. Arisawa; T. Suzuki; T. Ishikawa; M. Yamaguchi, *J. Am. Chem. Soc.* (2008), 130, 12214-12215.
2. B. F. Malichenko; L. P. Robota, *Zhurnal Organicheskoi Khimii* (1975), 11, 778-82.
3. Marco Villa, PhD thesis, University of Bologna and Aix-Marseille Université, december 14 (2018).

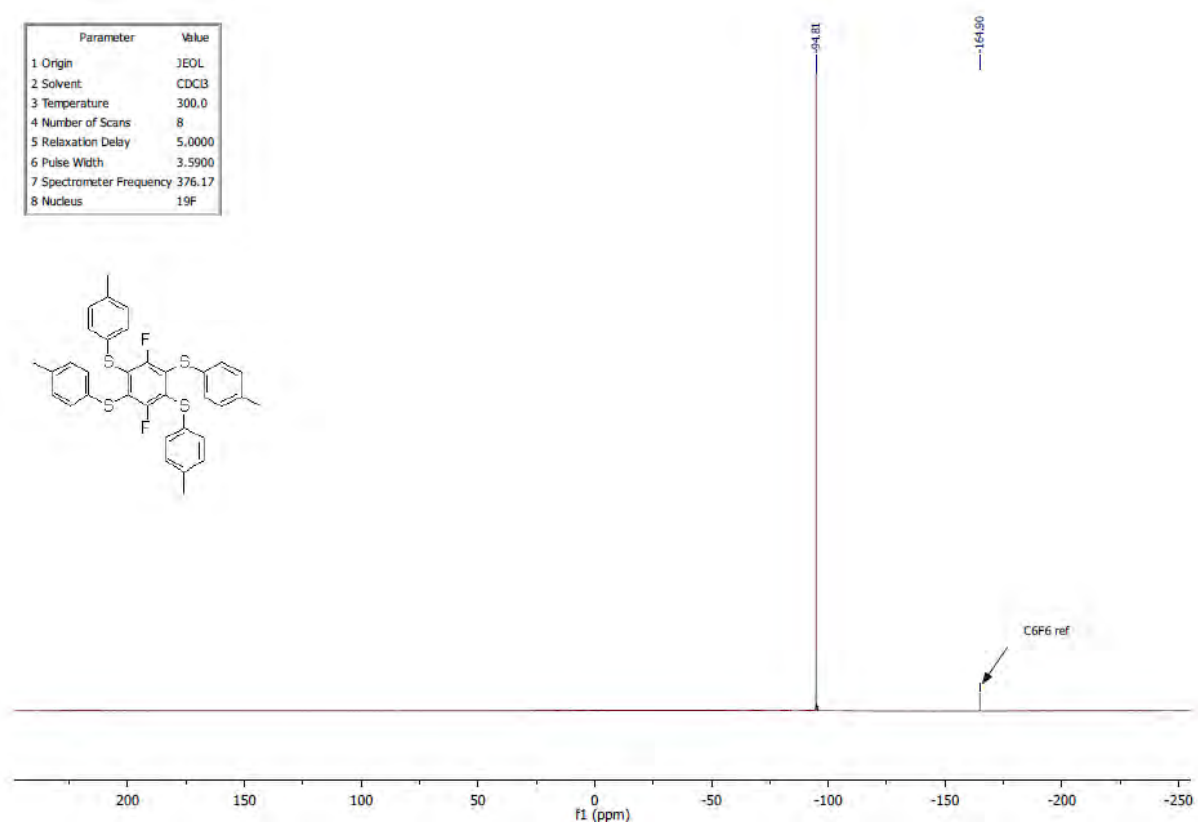


Reverse phase HPLC chromatogram of (**22**) and MS-APCI

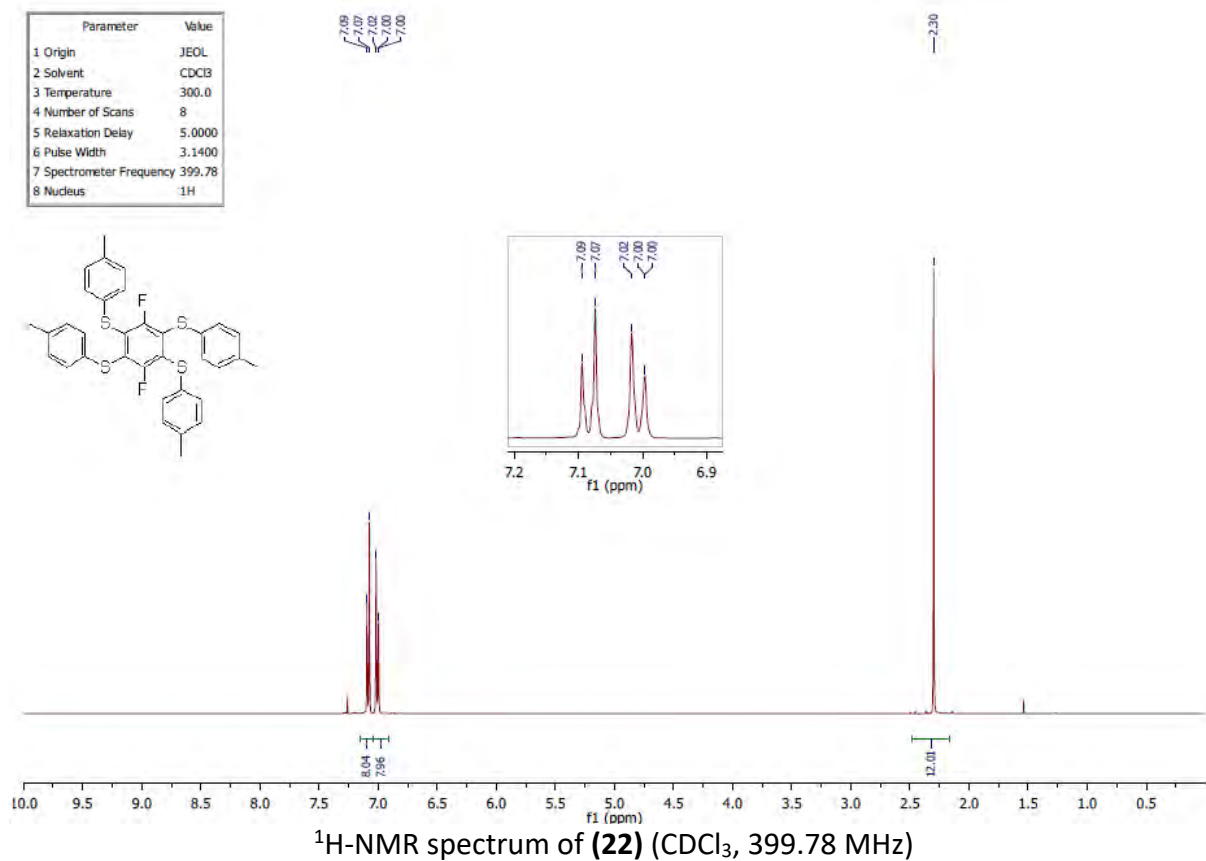
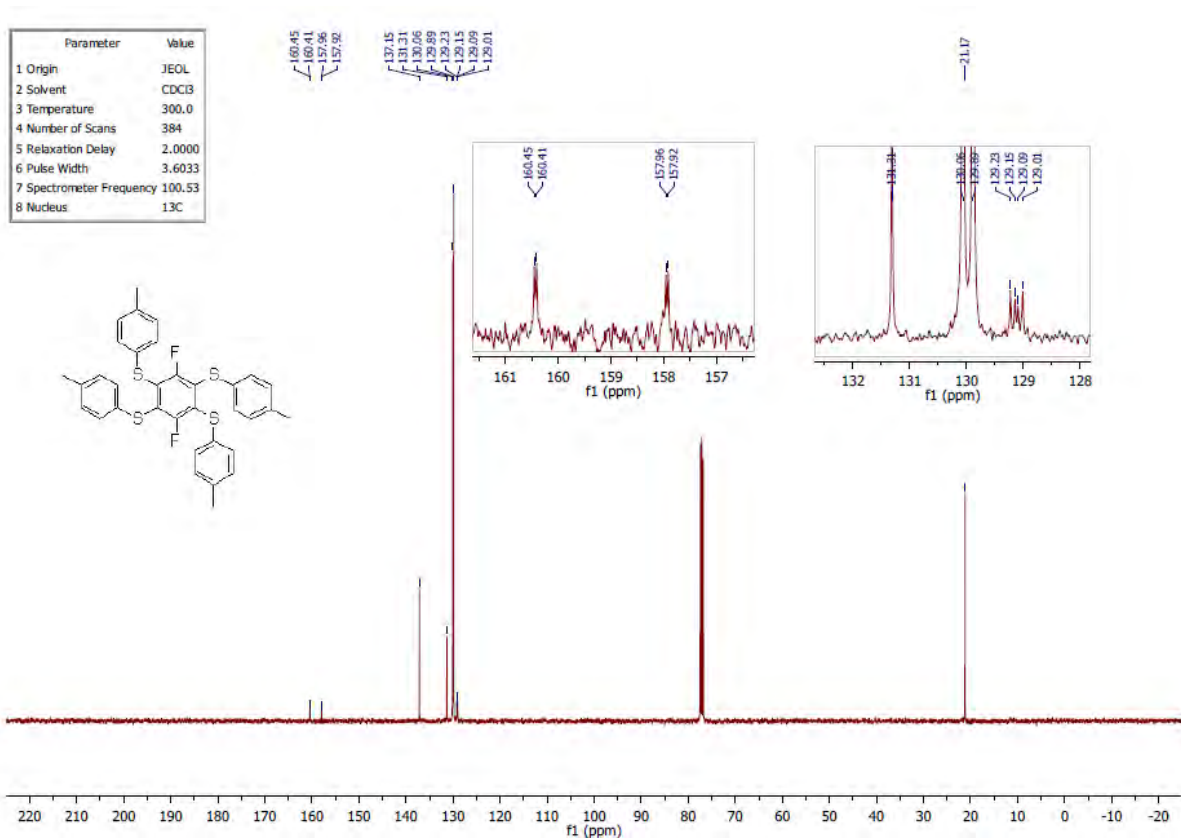


FT-IR spectrum of **(22)**

Parameter	Value
1 Origin	JEOL
2 Solvent	CDCl <sub>3</sub>
3 Temperature	300.0
4 Number of Scans	8
5 Relaxation Delay	5.0000
6 Pulse Width	3.5900
7 Spectrometer Frequency	376.17
8 Nucleus	<sup>19</sup> F

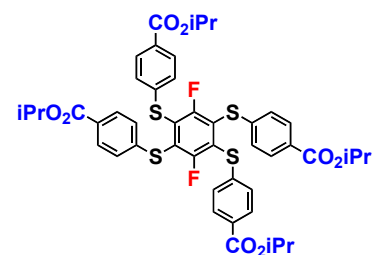


<sup>19</sup>F-NMR spectrum of **(22)** (CDCl<sub>3</sub>, 376.17 MHz)



### 1,4-difluoro-2,3,5,6-tetrakis(4-isopropylcarbonyloxy-phenylthio)benzene (**21**).

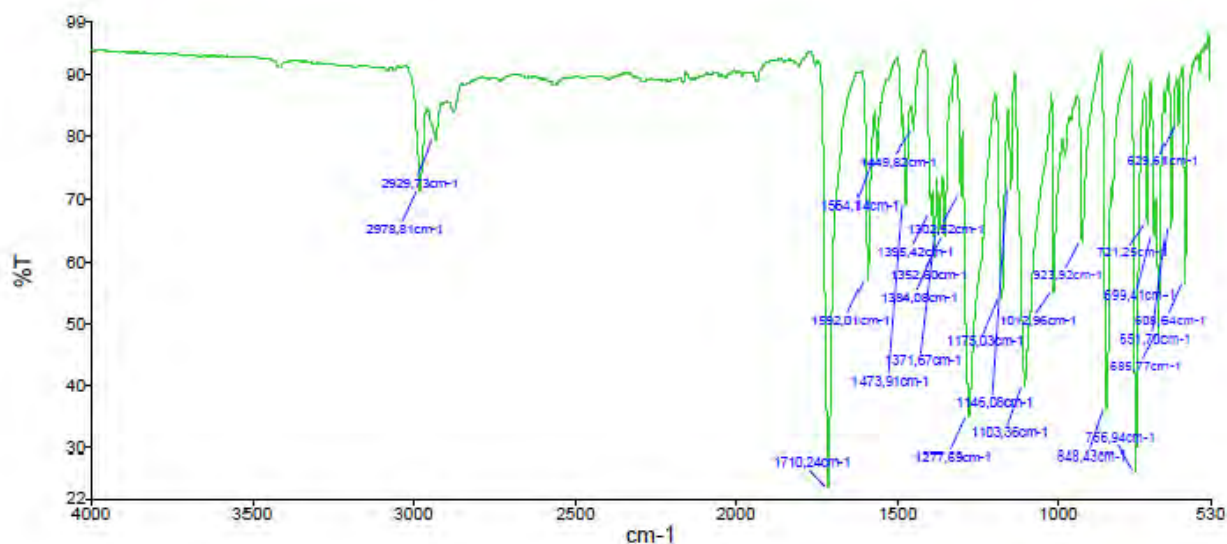
In an oven-dried glass tube were placed hexafluorobenzene (200 mg, 1.07 mmol, 1.00 mol-eq.), isopropyl-4-mercaptobenzoate (880 mg, 4.48 mmol, 4.19 mol-eq.) and dry potassium carbonate (623 mg, 4.51 mmol, 4.21 mol-eq.). All reagents were freshly dried under vacuum for about 30 min prior to use them. Under an argon atmosphere, dry DMF (5.5 mL) was injected via a syringe at 20°C and the mixture was vigorously stirred at 60°C (oil bath temperature) for 1 day. After cooling down to room temperature, an aqueous solution of HCl (1M, 100mL) was added, and the reaction mixture was extracted with toluene (3x25 mL). The combined organic phases were washed with water (5x25 mL), dried over anhydrous MgSO<sub>4</sub>. After filtration and removal of solvents in vacuo, a brown-yellow crude product (**21**) was purified by chromatography over silica gel (eluent: *n*-hept./EtOAc: 90:10 v/v) to yield a pale yellow solid (855 mg, 0.96 mmol, 89% yield).



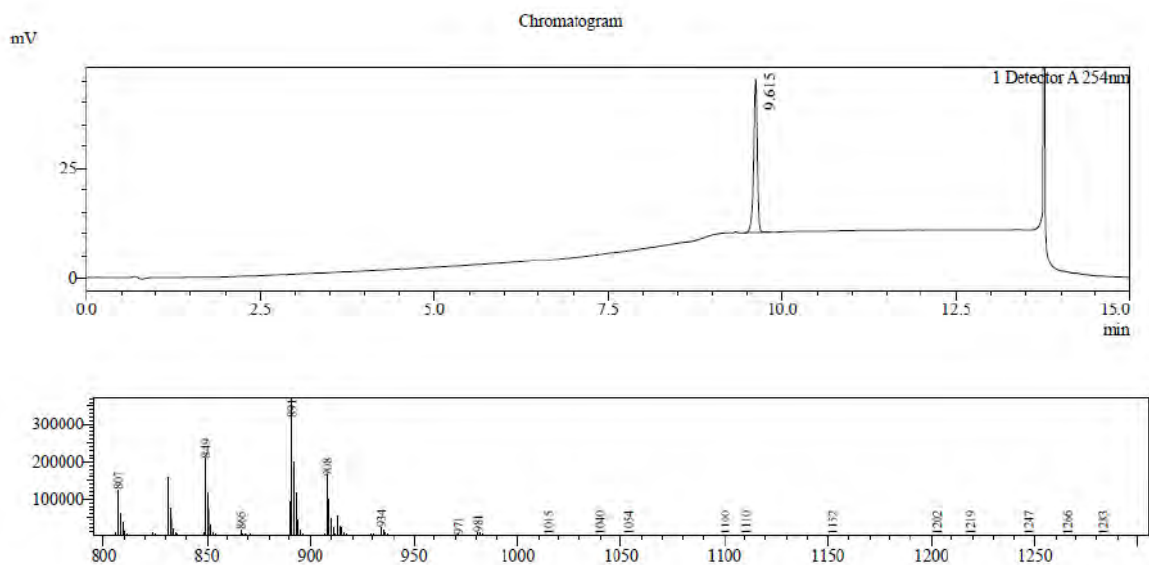
**FT-IR** (ATR, diamond contact, neat, cm<sup>-1</sup>)  $\nu$  = 2978, 2929, 1710, 1592, 1277, 1175, 1103, 848, 756, 685. **<sup>1</sup>H NMR** (399.78 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 7.88 (d<sub>app</sub>, *J* = 8.5 Hz, 8H), 7.14 (d<sub>app</sub>, *J* = 8.5 Hz, 8H), 5.22 (hept, *J* = 6.3 Hz, 4H), 1.35 (d, *J* = 6.2 Hz, 24H); **<sup>13</sup>C NMR** (100.53 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 165.37, 159.65 (dd, *J*<sub>C-F</sub> = 253, 4 Hz), 140.20, 130.43, 129.62, 128.62-128.64 (m, AA'XX' second order system), 128.03, 68.75, 22.05; **<sup>19</sup>F NMR** (376.17 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = - 89.31; **MS** (LC-MS acetonitrile/water/0.1% formic acid; APCI) 891 m/z [M+H]<sup>+</sup>.

### Reference:

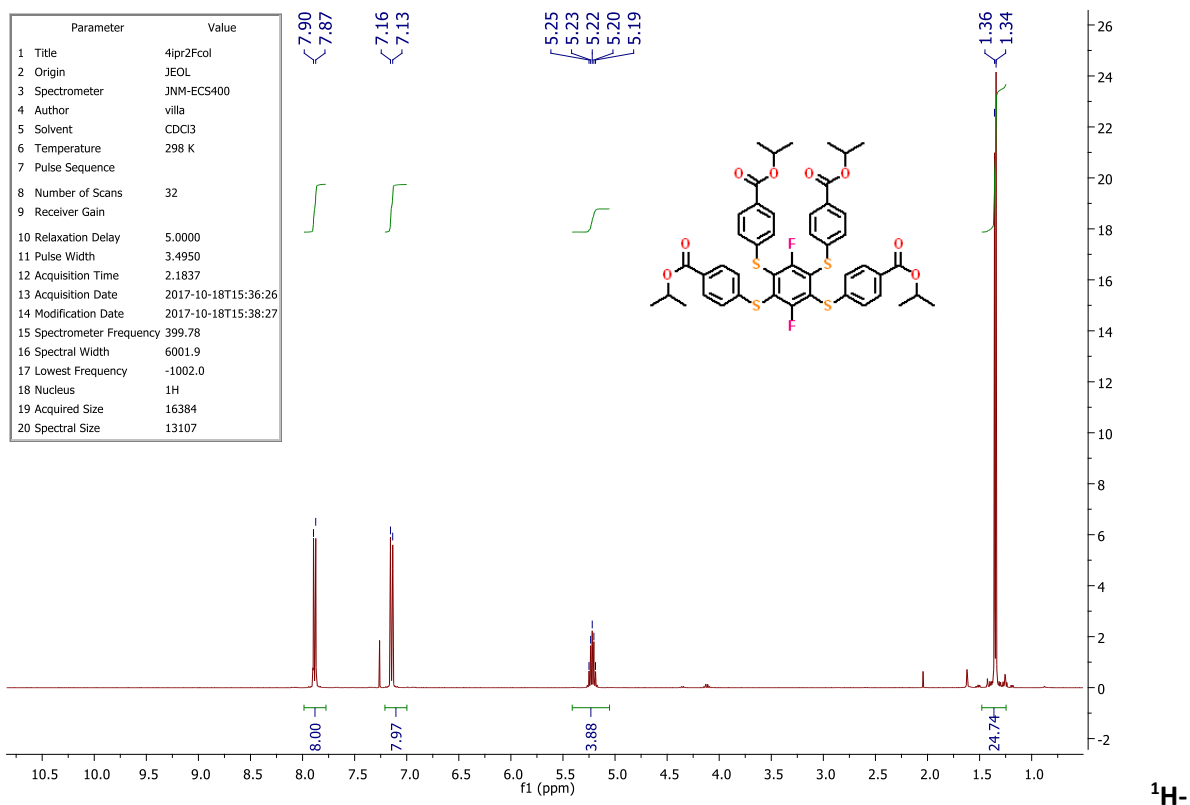
1. M. Villa; B. Del Secco; L. Ravotto; M. Roy; E. Rampazzo; N. Zaccheroni; L. Prodi; M. Gingras; S. Vinogradov; P. Ceroni, *J. Phys. Chem. C* 2019, 123, 29884-29890



FT-IR spectrum of (**21**)

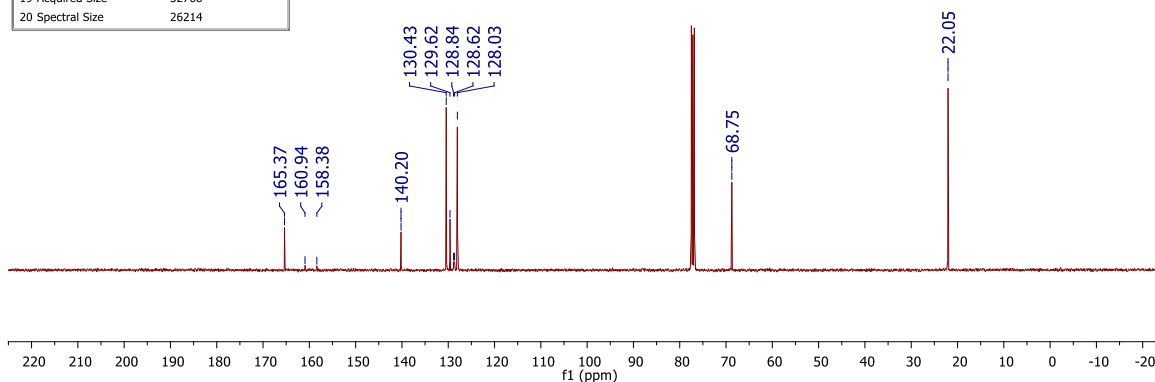
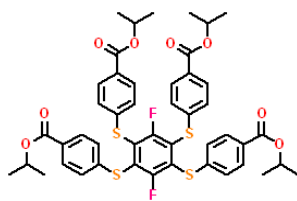


Reversed-phase HPLC chromatogram of **(21)** and MS-APCI



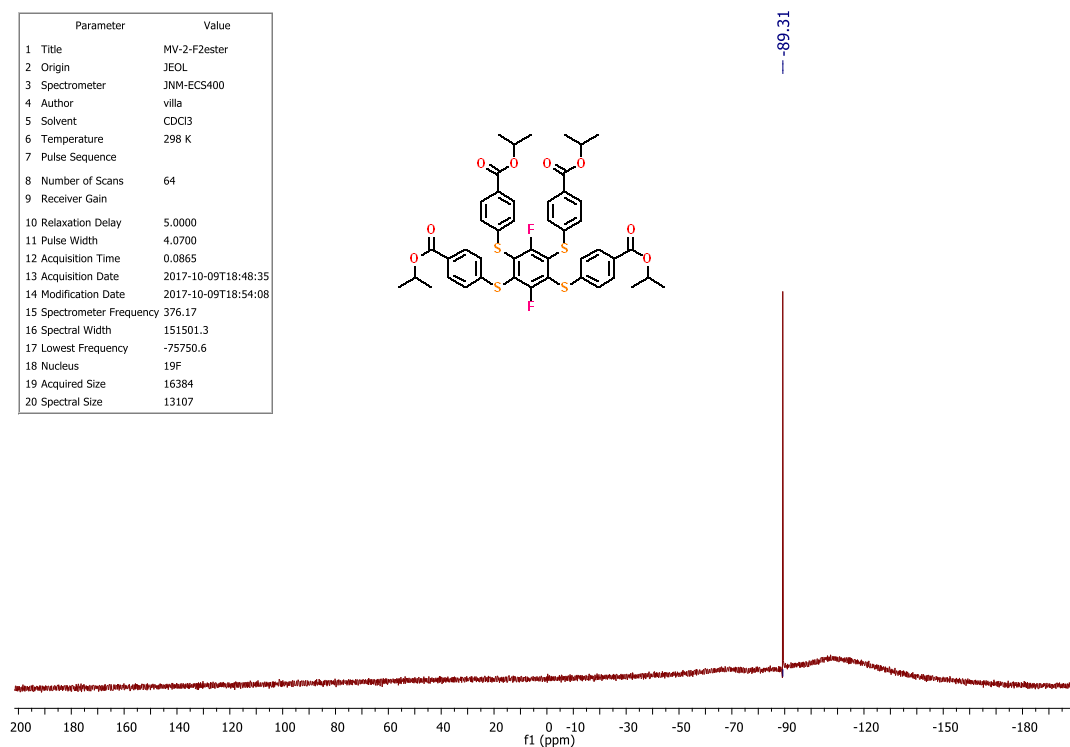
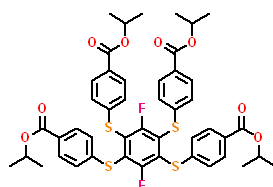
NMR spectrum of **(21)** (CDCl<sub>3</sub>, 399.78 MHz)

Parameter	Value
1 Title	4ipr2Fcol
2 Origin	JEOL
3 Spectrometer	JNM-ECS400
4 Author	villa
5 Solvent	CDCl3
6 Temperature	298 K
7 Pulse Sequence	
8 Number of Scans	1024
9 Receiver Gain	
10 Relaxation Delay	2.0000
11 Pulse Width	3.5333
12 Acquisition Time	1.0433
13 Acquisition Date	2017-10-19T03:24:23
14 Modification Date	2017-10-19T04:16:36
15 Spectrometer Frequency	100.53
16 Spectral Width	25124.3
17 Lowest Frequency	-2509.6
18 Nucleus	13C
19 Acquired Size	32768
20 Spectral Size	26214



$^{13}\text{C}$ -NMR spectrum of **(21)** ( $\text{CDCl}_3$ , 100.53 MHz)

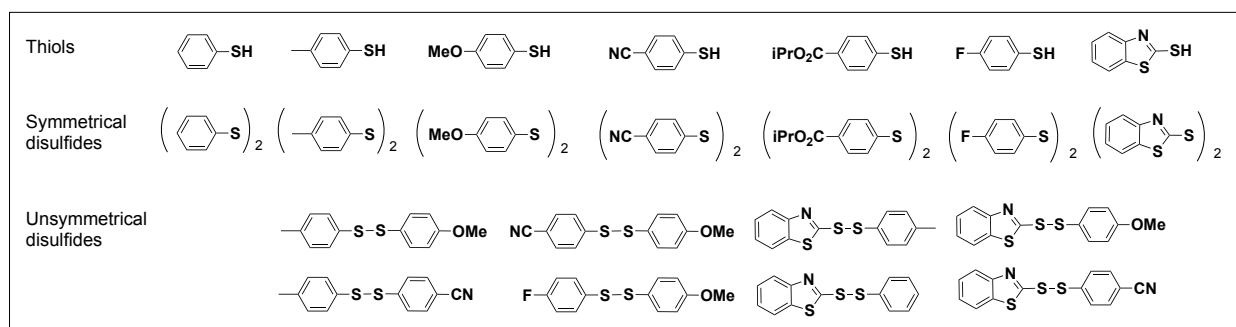
Parameter	Value
1 Title	MV-2-Fzester
2 Origin	JEOL
3 Spectrometer	JNM-ECS400
4 Author	villa
5 Solvent	CDCl3
6 Temperature	298 K
7 Pulse Sequence	
8 Number of Scans	64
9 Receiver Gain	
10 Relaxation Delay	5.0000
11 Pulse Width	4.0700
12 Acquisition Time	0.0865
13 Acquisition Date	2017-10-09T18:48:35
14 Modification Date	2017-10-09T18:54:08
15 Spectrometer Frequency	376.17
16 Spectral Width	151501.3
17 Lowest Frequency	-75750.6
18 Nucleus	19F
19 Acquired Size	16384
20 Spectral Size	13107



$^{19}\text{F}$ -NMR spectrum of **(21)** ( $\text{CDCl}_3$ , 376.17 MHz)

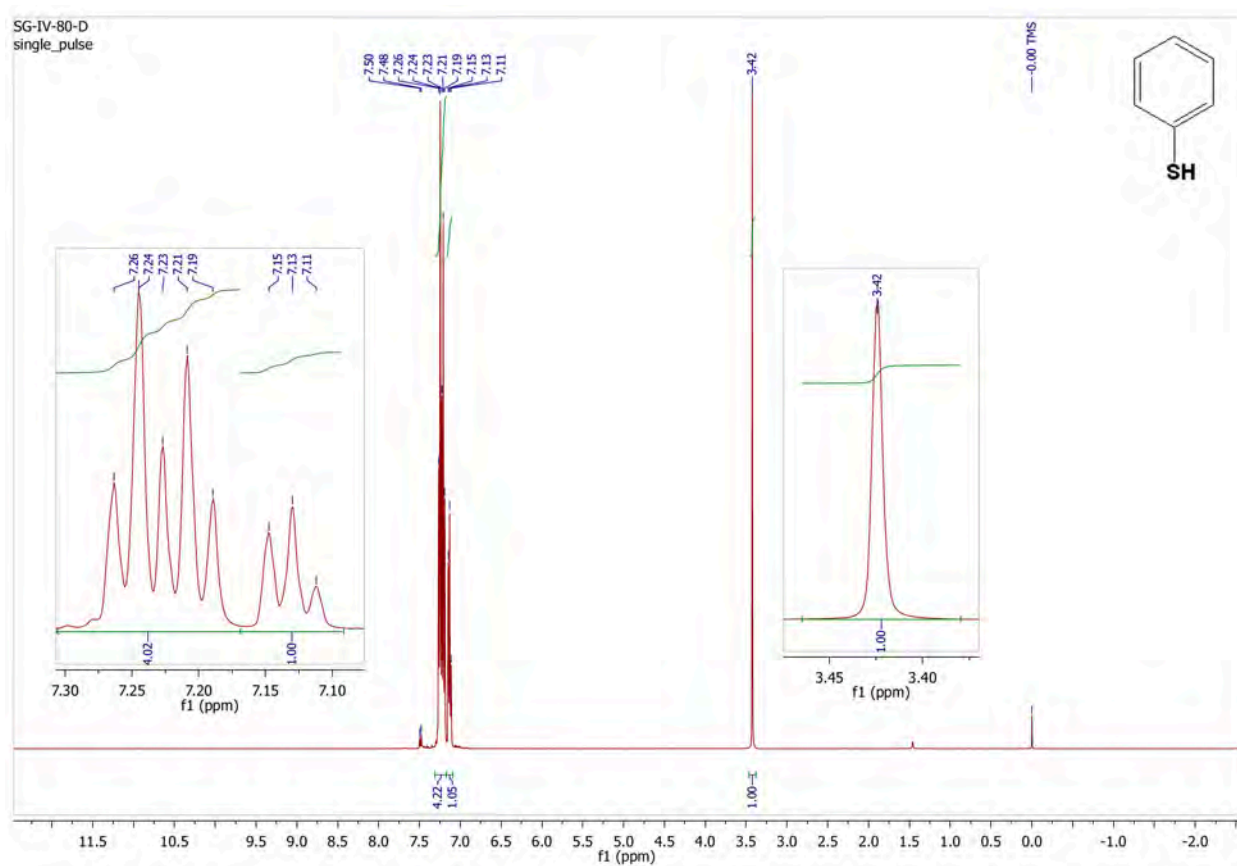
## 2.4 Reference thiols, symmetrical and mixed disulfides

### List of thiols and disulfides as reference compounds in this work



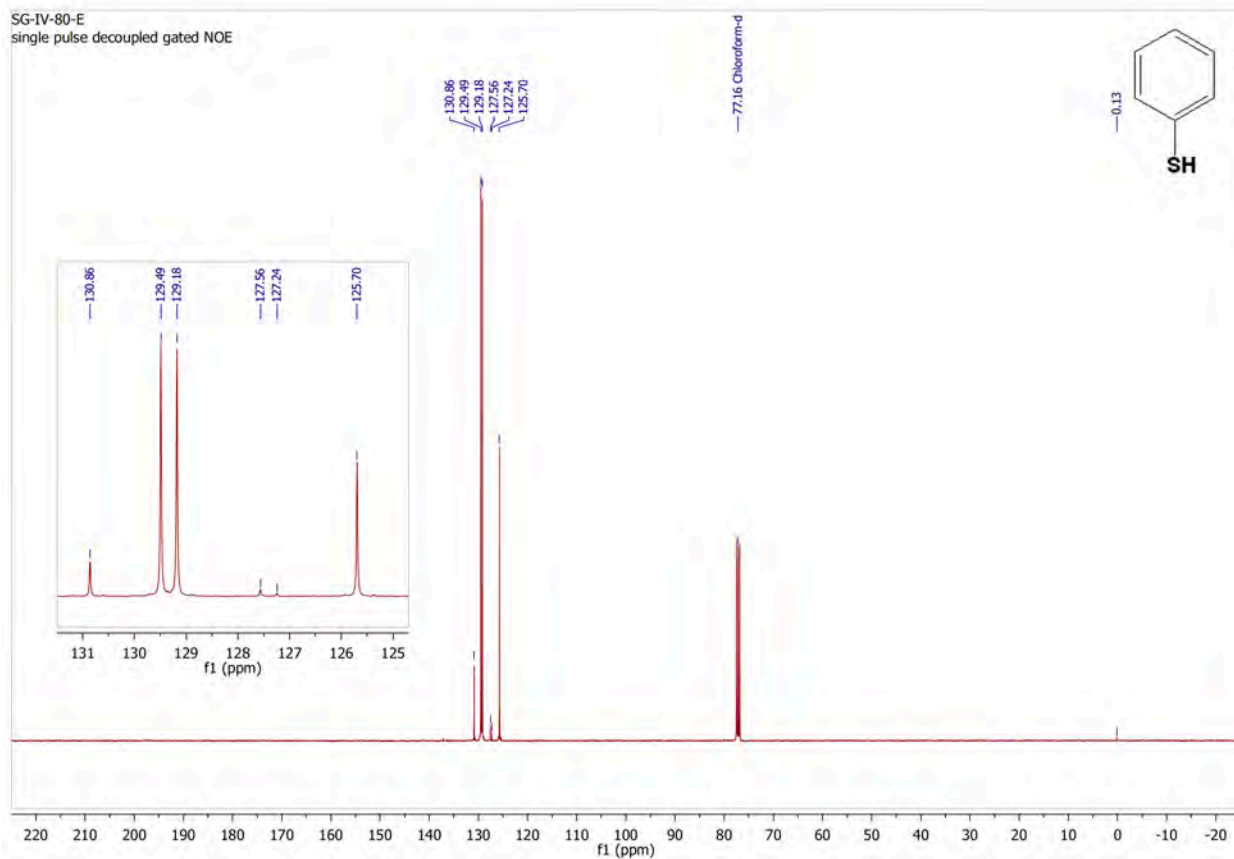
### List of references thiols

#### Thiophenol (commercial)

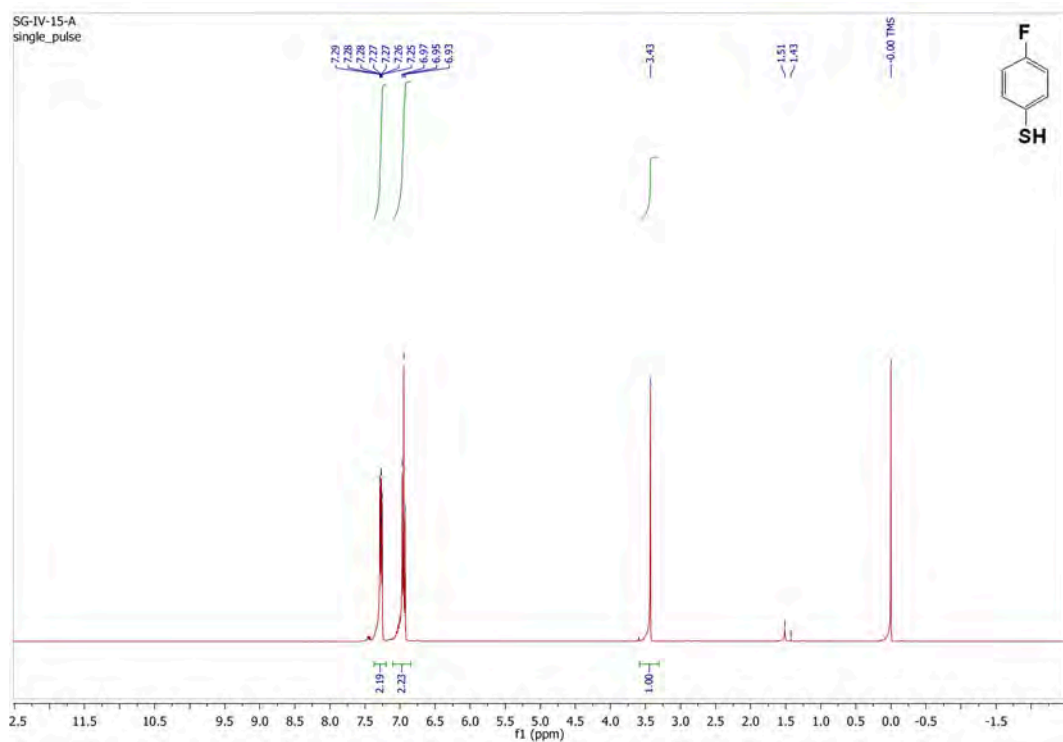


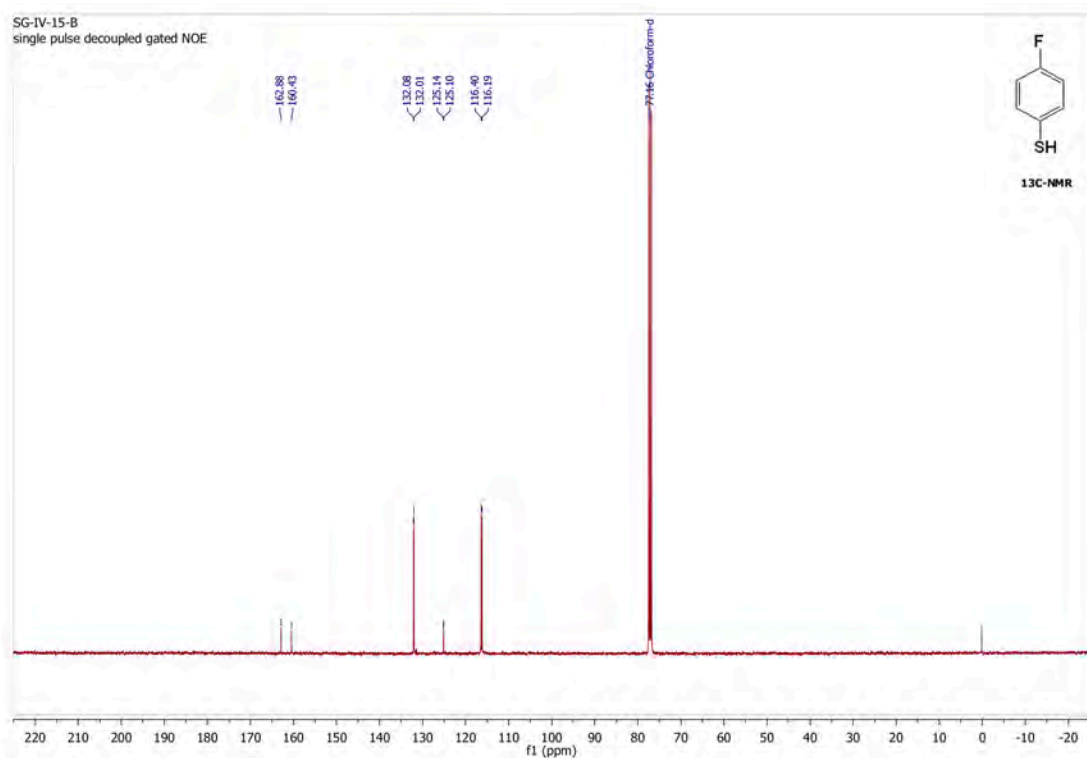
$^1\text{H-NMR}$  of thiophenol ( $\text{CDCl}_3$ , 399.78 MHz)



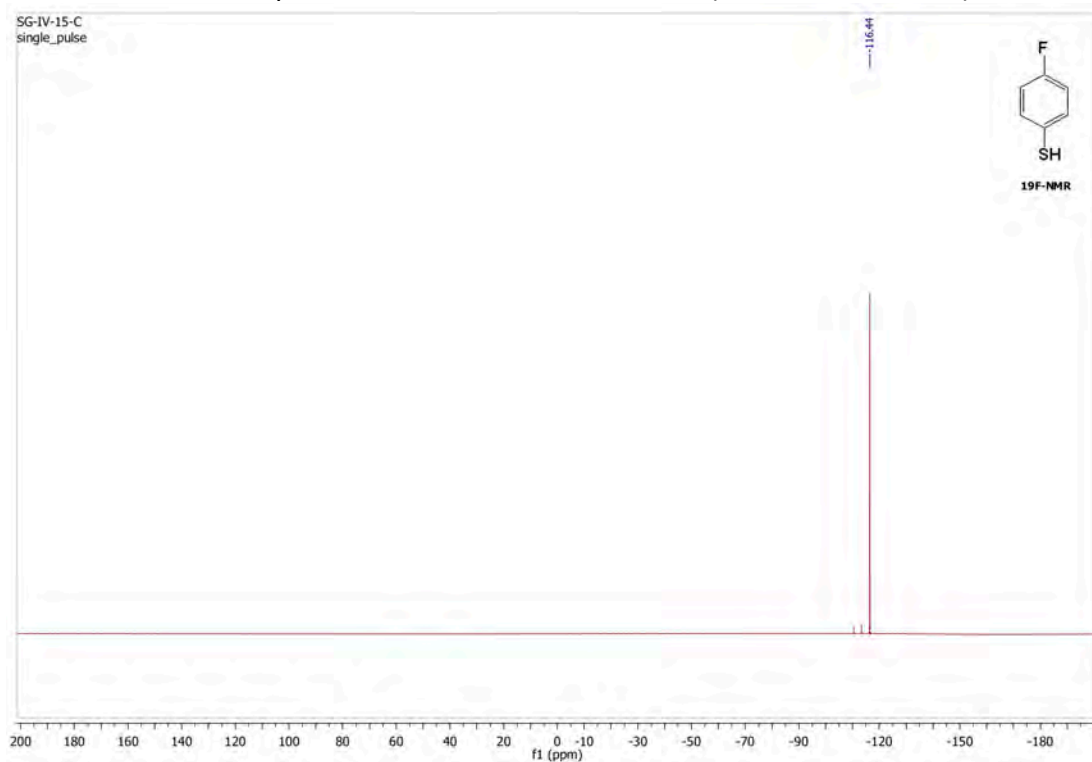


#### 4-Fluorobenzenethiol (commercial)





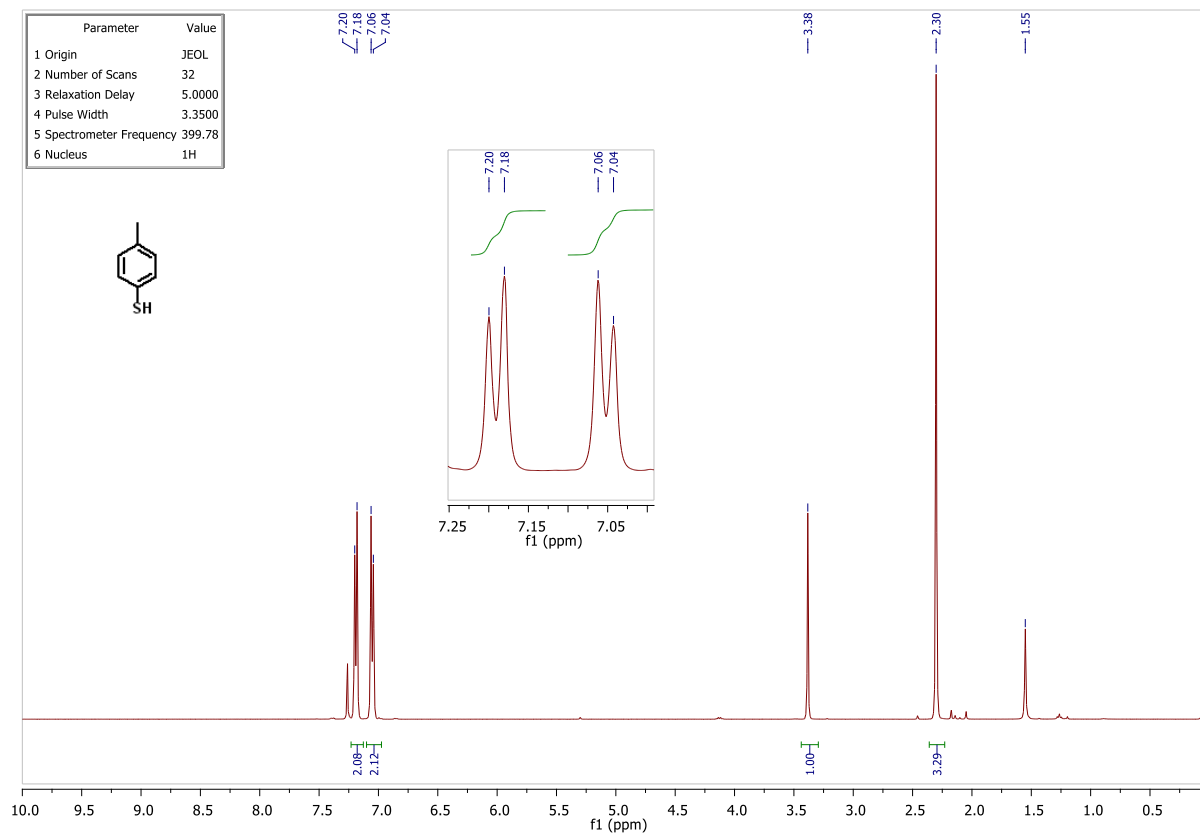
$^{13}\text{C}$ -NMR spectrum of 4-fluorobenzenethiol ( $\text{CDCl}_3$ , 100.53 MHz)



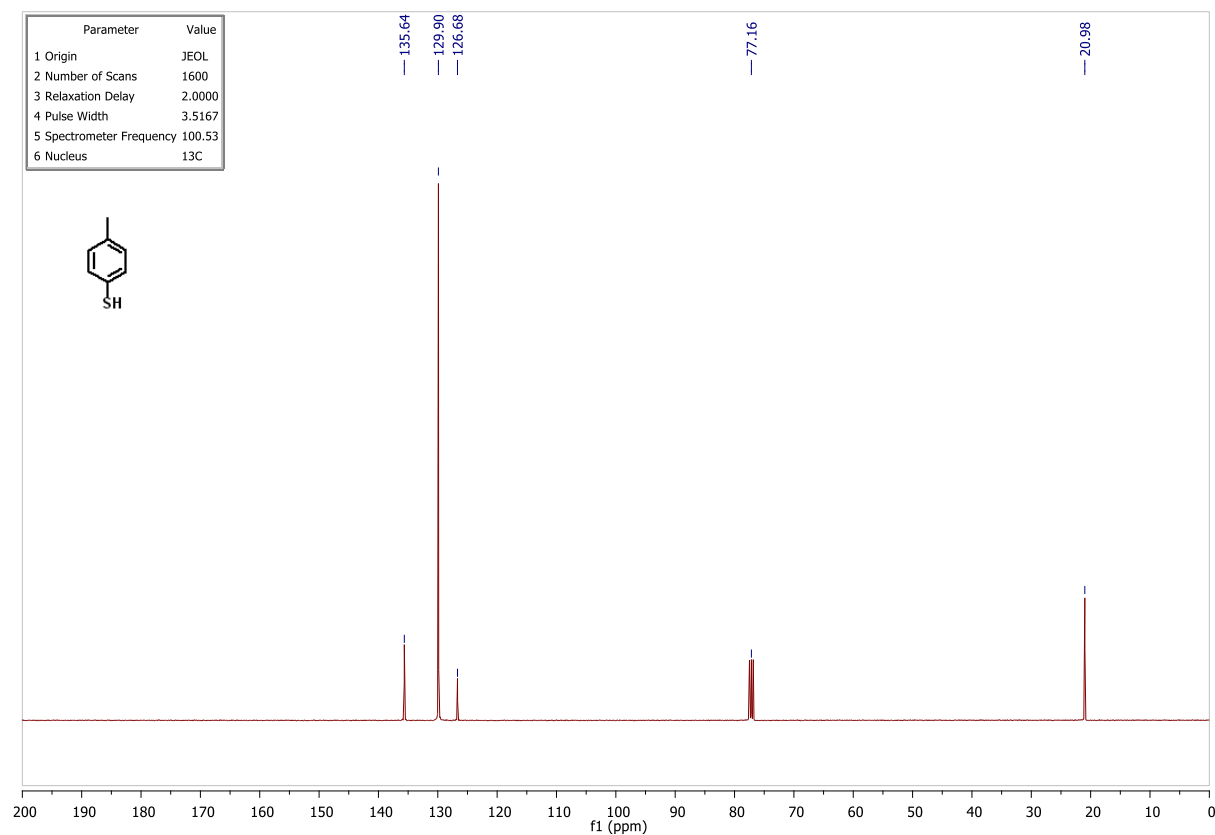
$^{19}\text{F}$ -NMR of 4-fluorobenzenethiol ( $\text{CDCl}_3$ , 376.17 MHz)

**4-Methylbenzenethiol (commercial)**

$^1\text{H}$  NMR (399.78 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.19 (d,  $J$  = 7.8 Hz, 2H), 7.05 (d,  $J$  = 7.7 Hz, 2H), 2.38 (s, 3H);  $^{13}\text{C}$  NMR (100.53 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 135.64, 129.90 (2C), 126.68, 20.98.



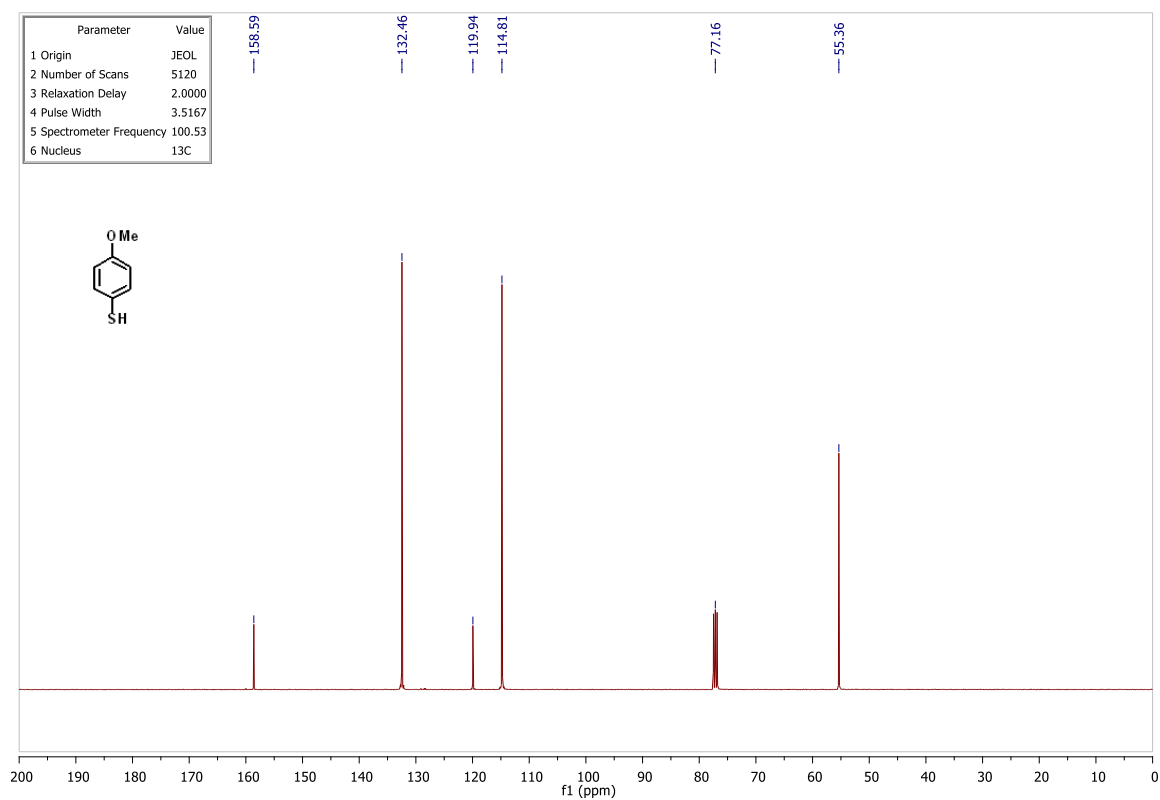
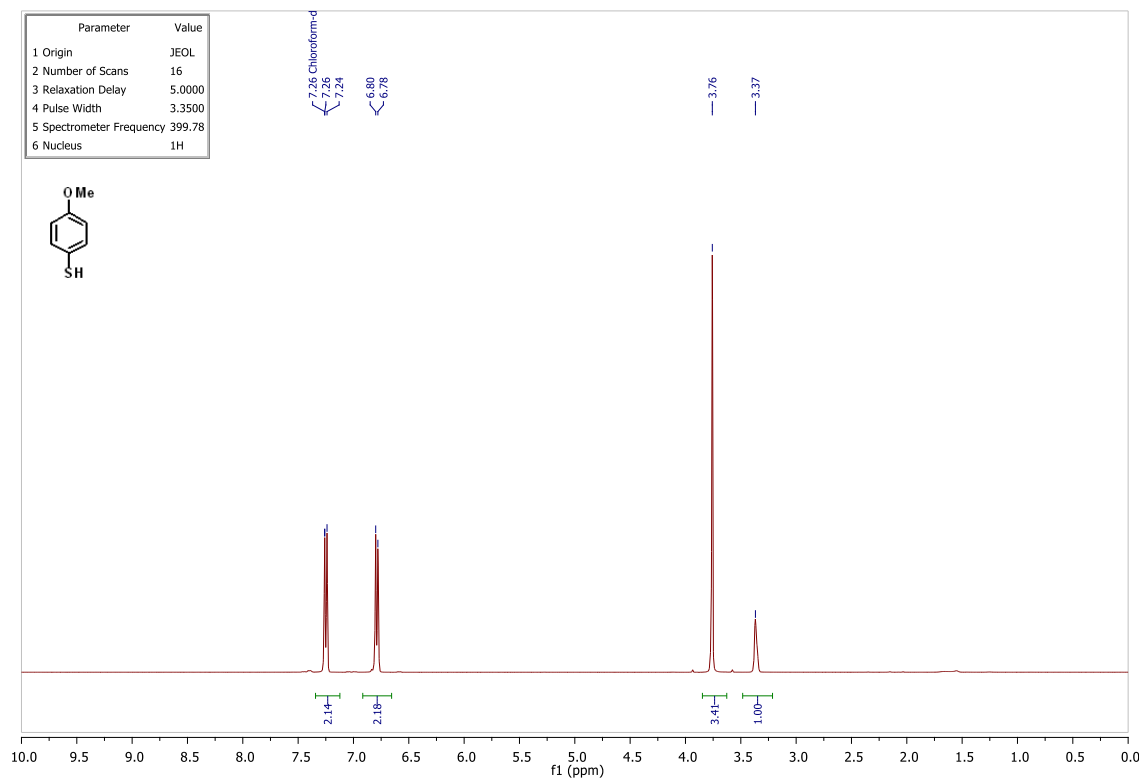
<sup>1</sup>H-NMR of 4-methylbenzenethiol (CDCl<sub>3</sub>, 399.78 MHz)



<sup>13</sup>C-NMR spectrum of 4-methylbenzenethiol (CDCl<sub>3</sub>, 100.53 MHz)

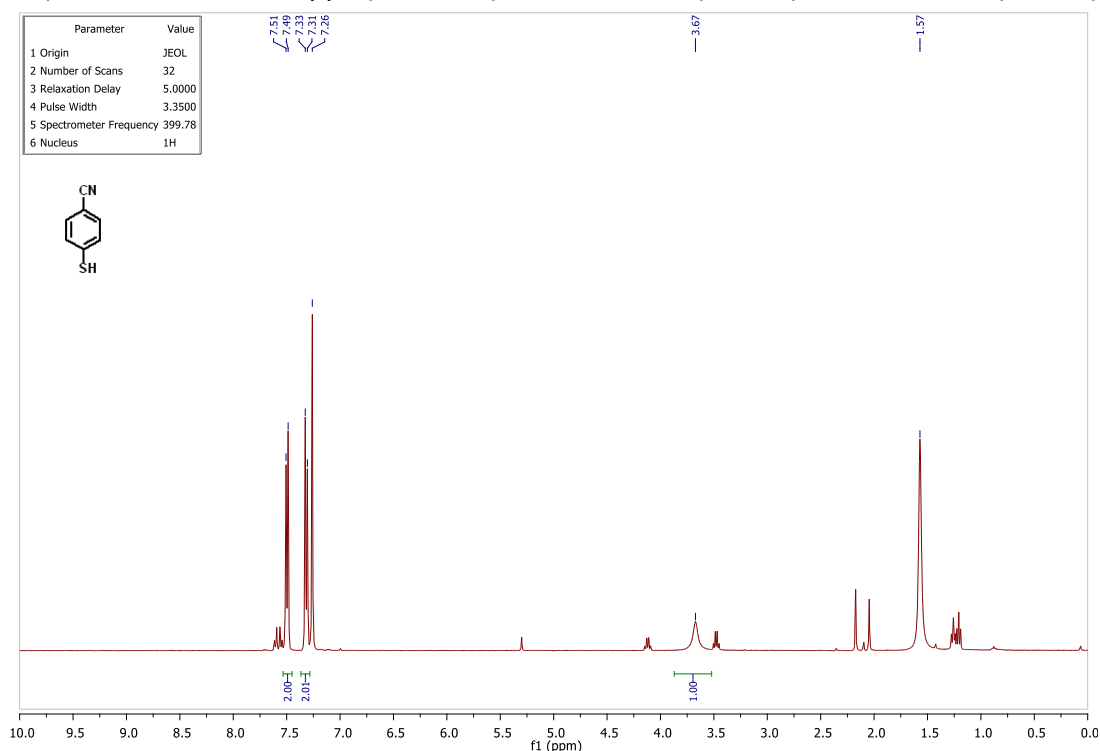
### 4-Methoxybenzenethiol (commercial)

$^1\text{H}$  NMR (399.78 MHz,  $\text{CDCl}_3$ , ppm)  $\delta = 7.25$  (d,  $J = 8.2$  Hz, 2H),  $6.79$  (d,  $J = 8.0$  Hz, 2H),  $3.76$  (s, 3H);  $^{13}\text{C}$  NMR (100.53 MHz,  $\text{CDCl}_3$ , ppm)  $\delta = 158.59$ ,  $132.46$ ,  $119.94$ ,  $114.81$ ,  $55.36$ .



#### 4-Cyanobenzenethiol (commercial)

$^1\text{H NMR}$  (399.78 MHz,  $\text{CDCl}_3$ , ppm)  $\delta = 7.50$  (d,  $J = 8.0$  Hz, 2H), 7.32 (d,  $J = 7.9$  Hz, 2H), 3.67 (s, 1H).



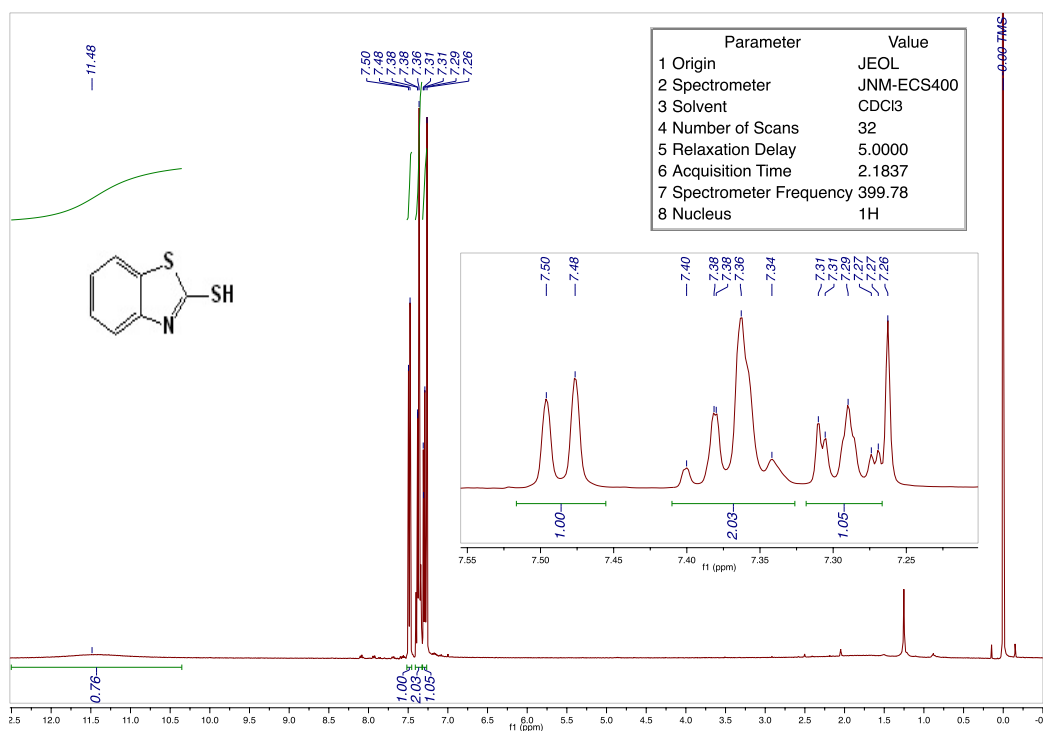
$^1\text{H-NMR}$  of 4-cyanobenzenethiol ( $\text{CDCl}_3$ , 399.78 MHz)

#### Among some references:

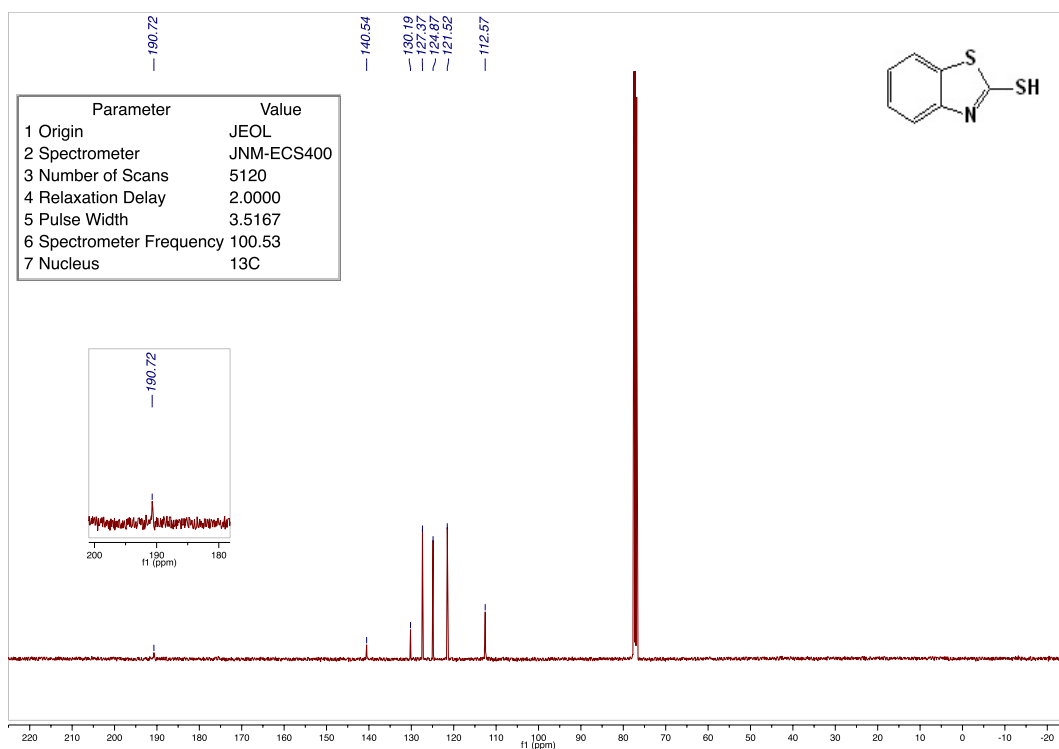
- 1) Z.-B. Dong; M. Balkenhohl; E. Tan; P. Knochel *Org. Lett.* (2018), 20, 7581-7584.
- 2) E. W. McClelland; L.A. Warren *J. Chem. Soc.* (1930), 1095-1102.
- 3) S. Krishnamurthy; D. Aimino *J. Org. Chem.* (1989), 54, 4458-62.
- 4) C. Combellas; S. Dellerue; G. Mathey; A. Thiebault *Tetrahedron Lett.* (1997), 38, 539-542.
- 5) S. Antonello; K. Daasbjerg; H. Jensen; F. Taddei; F. Maran *J. Am. Chem. Soc.* (2003), 125, 14.
- 6) J. Tobias; P. Knochel *Synlett* (2005), 1185-1187.

#### 2-Mercaptobenzothiazole (commercial)

$^1\text{H NMR}$  (399.78 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.49$  (d,  $J = 8.0$  Hz, 1H), 7.33-7.41 (m, 2H), 7.29 (ddd,  $J = 8.1, 6.3, 1.9$  Hz, 1H), 11.43 (br s, 1H, NH);  $^{13}\text{C NMR}$  (100.53 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 190.7, 140.5, 130.2, 127.4, 124.9, 121.5, 112.6$ .



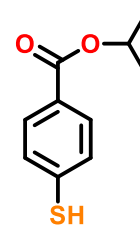
<sup>1</sup>H-NMR of 2-mercaptobenzothiazole (CDCl<sub>3</sub>, 399.78 MHz)



<sup>13</sup>C-NMR spectrum of 2-mercaptobenzothiazole (CDCl<sub>3</sub>, 100.53 MHz)

### Isopropyl 4-mercaptobenzoate: (31)

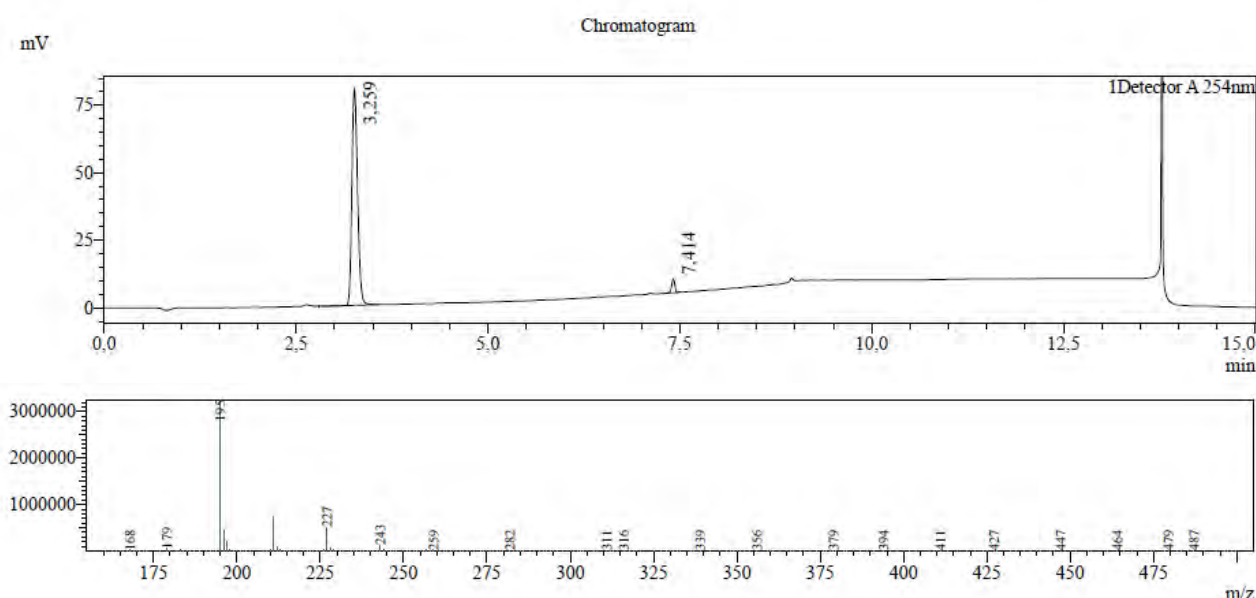
A solution of diisopropyl 4,4'-dithiobisbenzoate (**35**) (610 mg, 1.56 mmol, 1.00 mol-eq) and ground zinc powder (1.85 g, 28.29 mmol, 18.1 mol-eq) in acetic acid (10 mL) was heated to 90°C under an argon atmosphere. Upon completion of the reaction (about 12 hrs), the mixture was cooled to 20°C while stirring. To the mixture was added a 1 M HCl aqueous solution (50 mL), and the thiol was extracted with dichloromethane (3x20 mL). The combined organic phases were dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. After drying under high vacuum, an oil was recovered as the desired thiol (596 mg, 3.04 mmol, yield 97%).



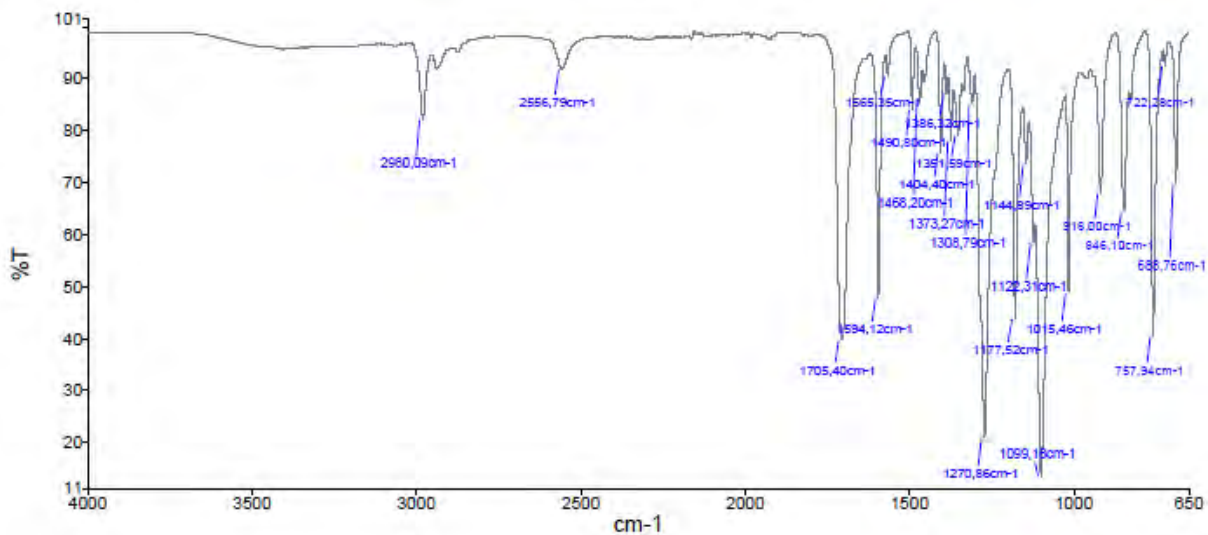
**IR** ( $\nu$ , cm<sup>-1</sup>): 2980, 2556, 1705, 1594, 1404, 1270, 1177, 1099, 1015, 918, 846, 757, 688; **<sup>1</sup>H NMR** ( $\delta$ , 400 MHz, CDCl<sub>3</sub>): 7.87 (d, 2H, J=8.5), 7.26 (d, 2H, J=8.6), 5.25-5.18 (sept, 1H, J=6.2), 3.58 (s, 1H), 1.35 (d, 6H, J=6.3). **<sup>13</sup>C NMR** ( $\delta$ , 100 MHz, CDCl<sub>3</sub>): 165.73, 138.02, 130.26, 128.13, 127.98, 68.47, 22.03. **MS** (LC-MS, acetonitrile/water APCI): 195 m/z [M-H]<sup>-</sup>.

### References:

- 1) M. Villa, M. Roy, G. Bergamini, P. Ceroni, M. Gingras *Chem Plus Chem* (2020), *85*, 1481-1486.
- 2) M. Villa; B. Del Secco; L. Ravotto; M. Roy; E. Rampazzo; N. Zaccheroni; L. Prodi; M. Gingras; S.A. Vinogradov; P. Ceroni *J. Phys. Chem. C* (2019), *123*, 29884-29890.
- 3) X. Yan; C. Li; X. Xu; Q. He; X. Zhao; Y. Pan, *Tetrahedron* (2019), *75*, 3081-3087.
- 4) M. Villa; M. Roy; G. Bergamini; M. Gingras; P. Ceroni *Dalton Trans.* (2019), *48*, 3815-3818.

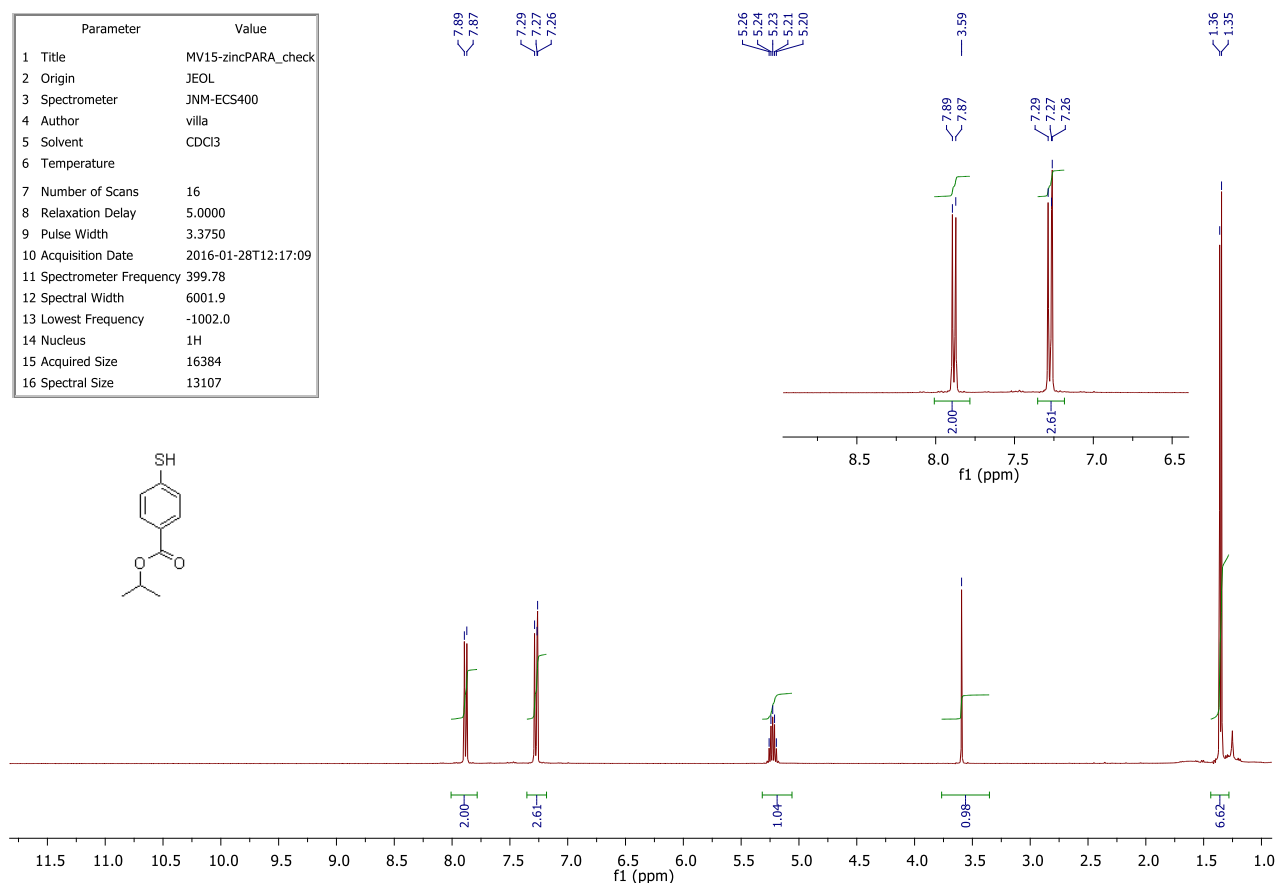


Reversed-phase HPLC chromatogram of Isopropyl 4-mercaptobenzoate and MS-APCI of different peaks (negative ionization).



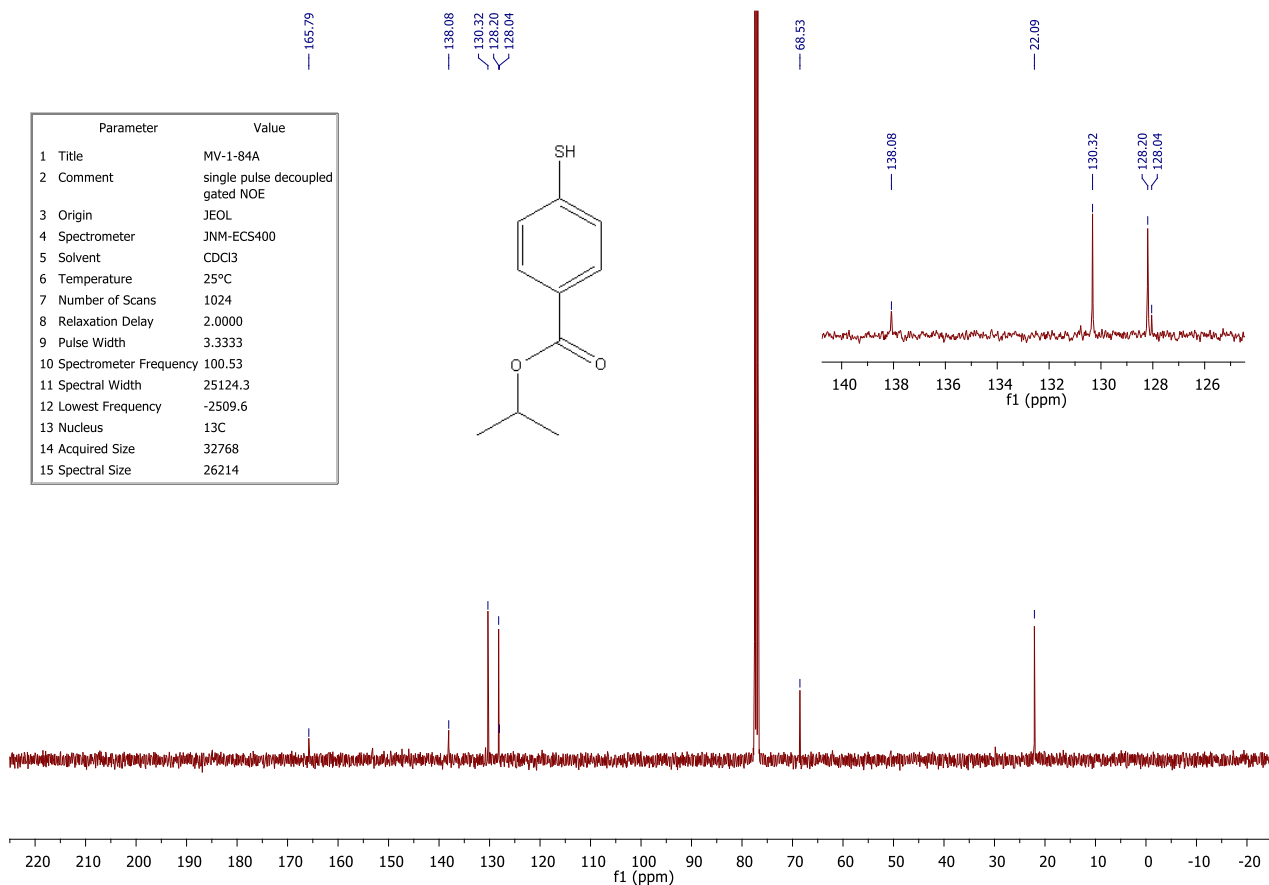
FT-IR spectrum of Isopropyl 4-mercaptobenzoate

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



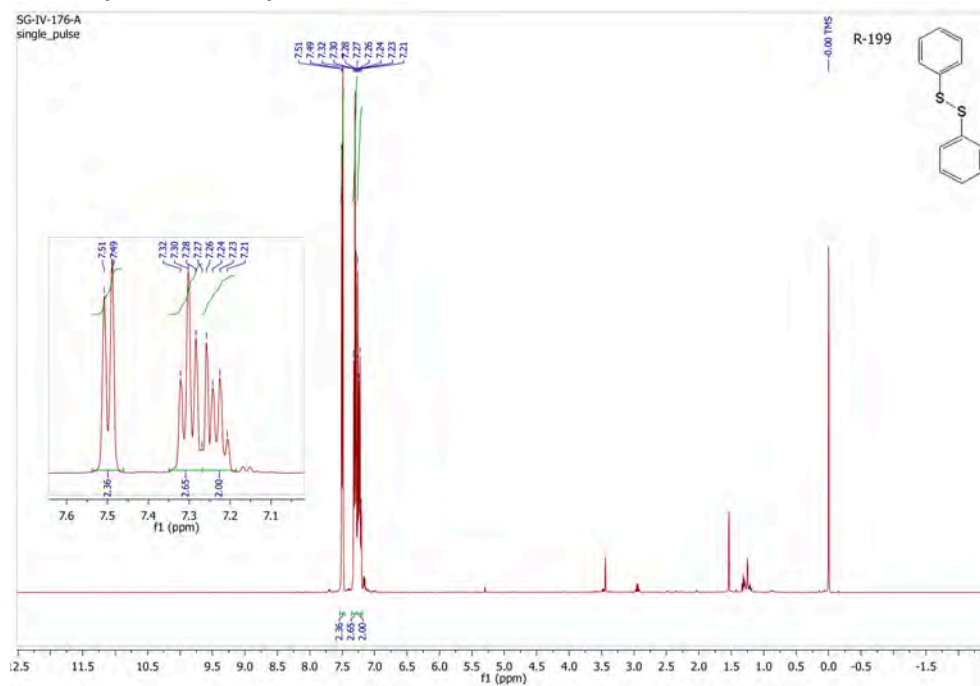
<sup>1</sup>H-NMR spectrum of Isopropyl 4-mercaptobenzoate (CDCl<sub>3</sub>, 399.78 MHz)

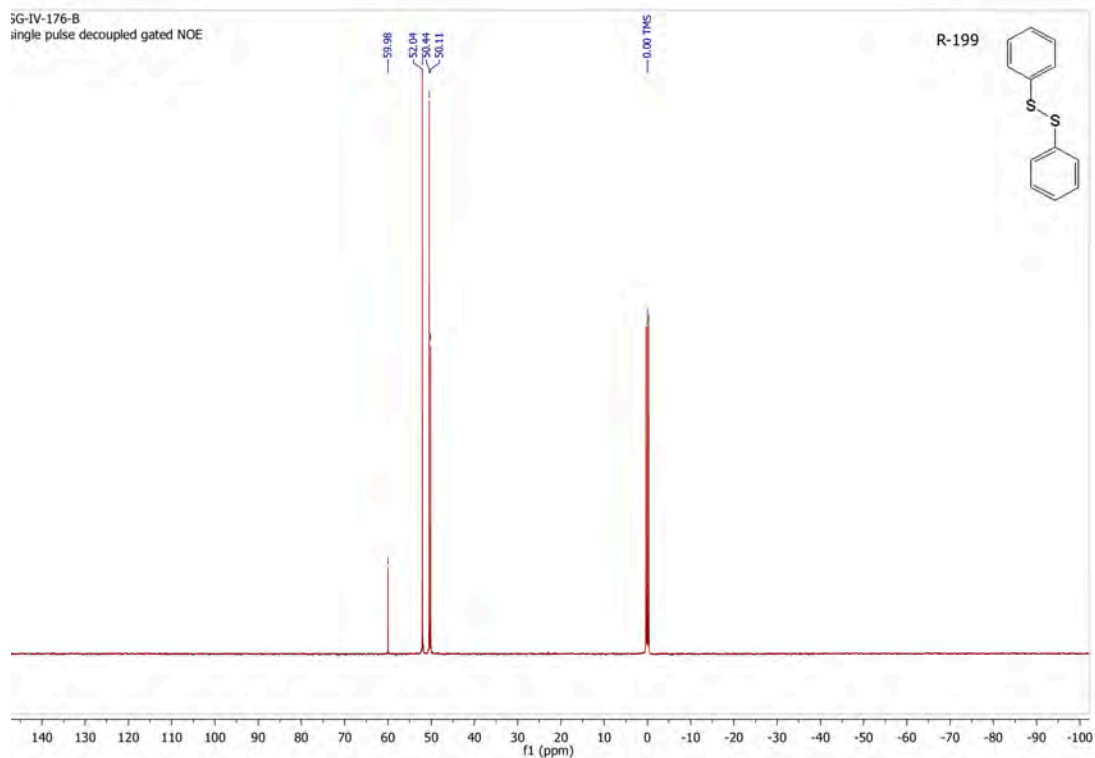




## List of reference disulfides

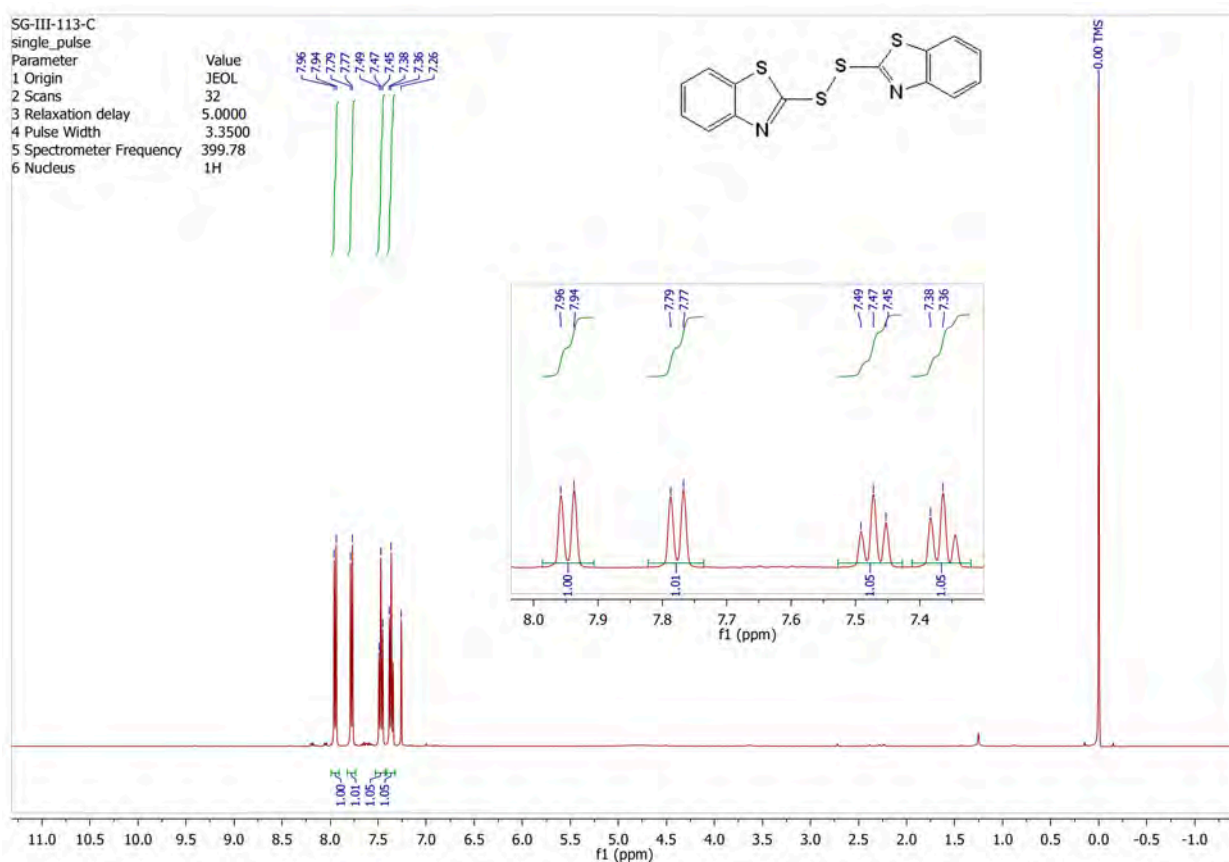
### Phenyl disulfide (commercial)



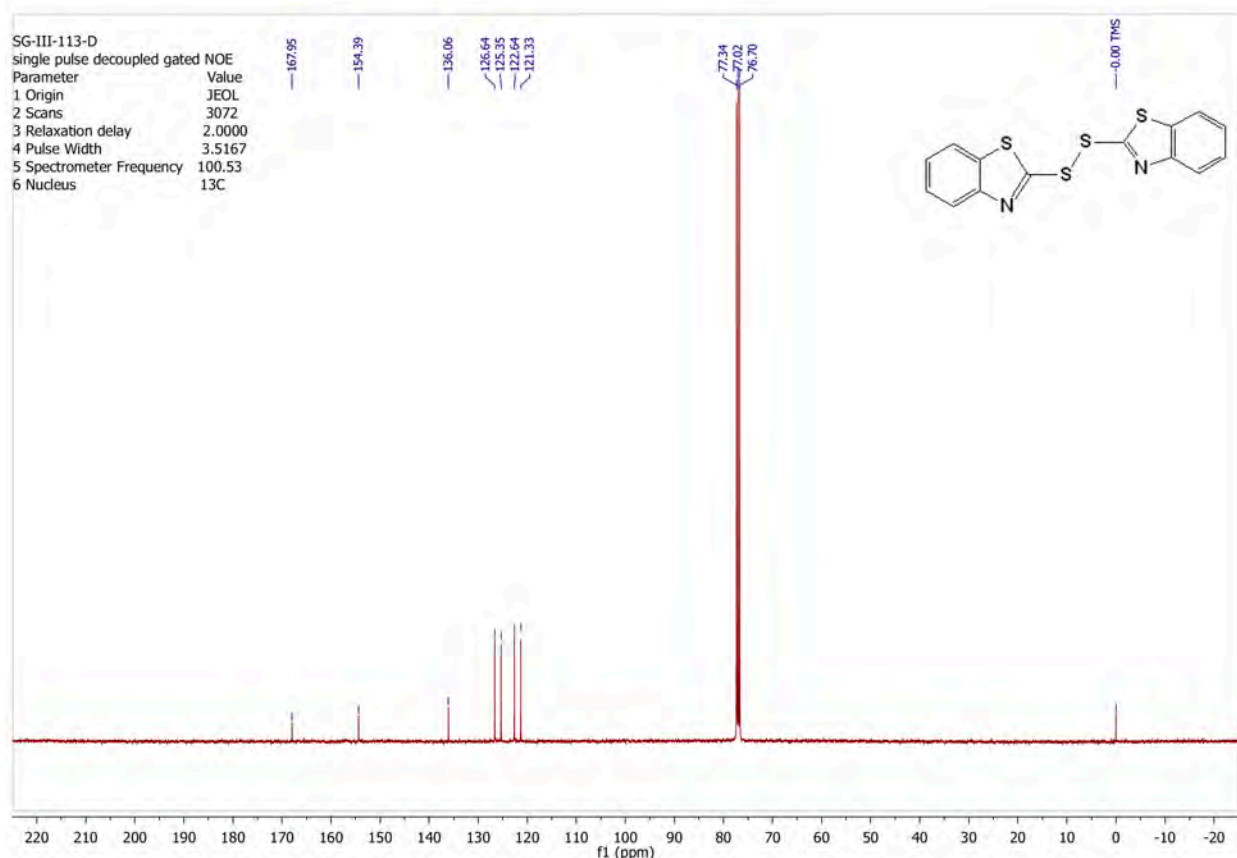


$^{13}\text{C}$ -NMR spectrum of phenyl disulfide ( $\text{CDCl}_3$ , 100.53 MHz)

## 2,2'-Dibenzothiazolyl disulfide (**44**) (commercial)



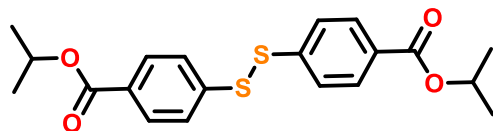
$^1\text{H}$ -NMR spectrum of (**44**) ( $\text{CDCl}_3$ , 399.78 MHz)



$^{13}\text{C}$ -NMR spectrum of (**44**) ( $\text{CDCl}_3$ , 100.53 MHz)

### Diisopropyl 4,4'-dithiobisbenzoate (**35**)

To a solution of 4-mercaptobenzoic acid (1.980 g, 33.08 mmol, 1.00 mol-eq) in isopropanol (120 ml, 1.57 mol, 47.5 mol-eq) was added in a dropwise manner  $\text{SOCl}_2$  (13.0 mL, 178 mmol, 5.38 mol-eq) at  $0^\circ\text{C}$  (ice-bath)



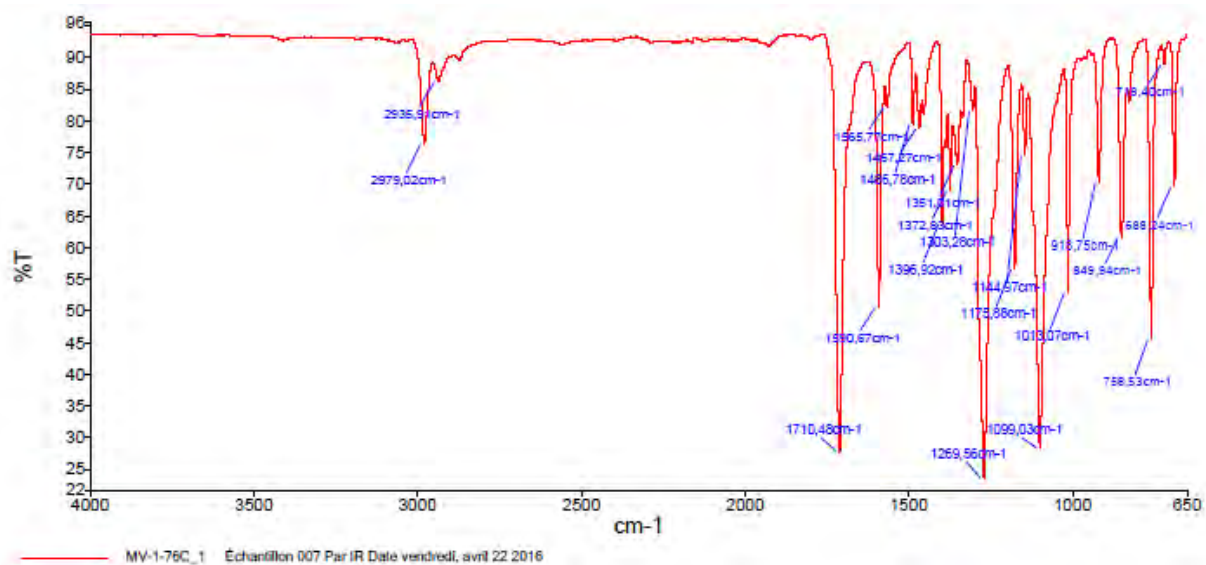
under an argon atmosphere. After removal of the bath, the mixture reached  $20^\circ\text{C}$  and then it was heated at  $80^\circ\text{C}$  for 7 days. Residual isopropanol was removed from the reaction mixture under reduced pressure, and the crude solid was dissolved in ethyl acetate and washed with an aqueous solution of  $\text{Na}_2\text{CO}_3$ . The aqueous phase was extracted further with ethyl acetate (3x100 mL). The combined organic phases were dried over anhydrous  $\text{MgSO}_4$ , filtered and evaporated under reduced pressure. The brown oil obtained was a mixture of disulfide and trisulfide (4:1 molar ratio) (2.501 g., 10.16 mmol, approximate yield of 97%).

**TLC** ( $\text{SiO}_2$ , cyclohex/dichloromethane 80:20 v/v)  $R_f = 0.4$ ; **FT-IR** (ATR, diamond contact, neat,  $\text{cm}^{-1}$ )  $\nu = 2979, 2935, 1714, 1571, 1373, 1352, 1280, 1105, 1072, 923, 748, 679$ ;  **$^1\text{H}$  NMR** (399.78 MHz,  $\text{CDCl}_3$ , ppm)  $\delta = 7.96$  (d,  $J = 8.6$  Hz, 4H),  $7.51$  (d,  $J = 8.5$  Hz, 4H),  $5.22$  (sept,  $J = 6.2$  Hz, 2H),  $1.34$  (d,  $J = 6.3$  Hz, 12H);  **$^{13}\text{C}$  NMR** (100.53 MHz,  $\text{CDCl}_3$ , ppm)  $\delta = 165.55, 141.95, 130.37, 130.29, 129.74, 129.02, 126.13, 68.70, 22.07$ ; **LC-MS** (acetonitrile/water, 0.1% formic acid), APCI:  $391\ m/z$   $[\text{M}+\text{H}]^+$ .

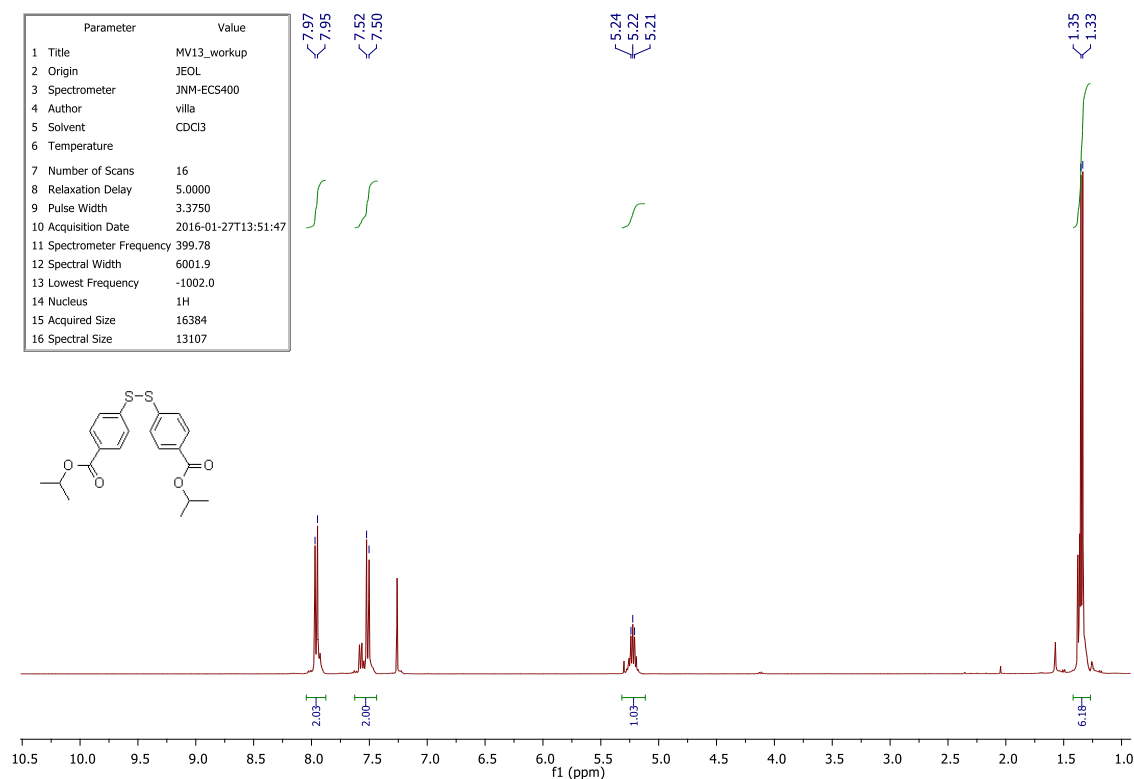
### References:

- 1) M. Villa, M. Roy, G. Bergamini, P. Ceroni, M. Gingras *Chem Plus Chem* (2020), *85*, 1481-1486.

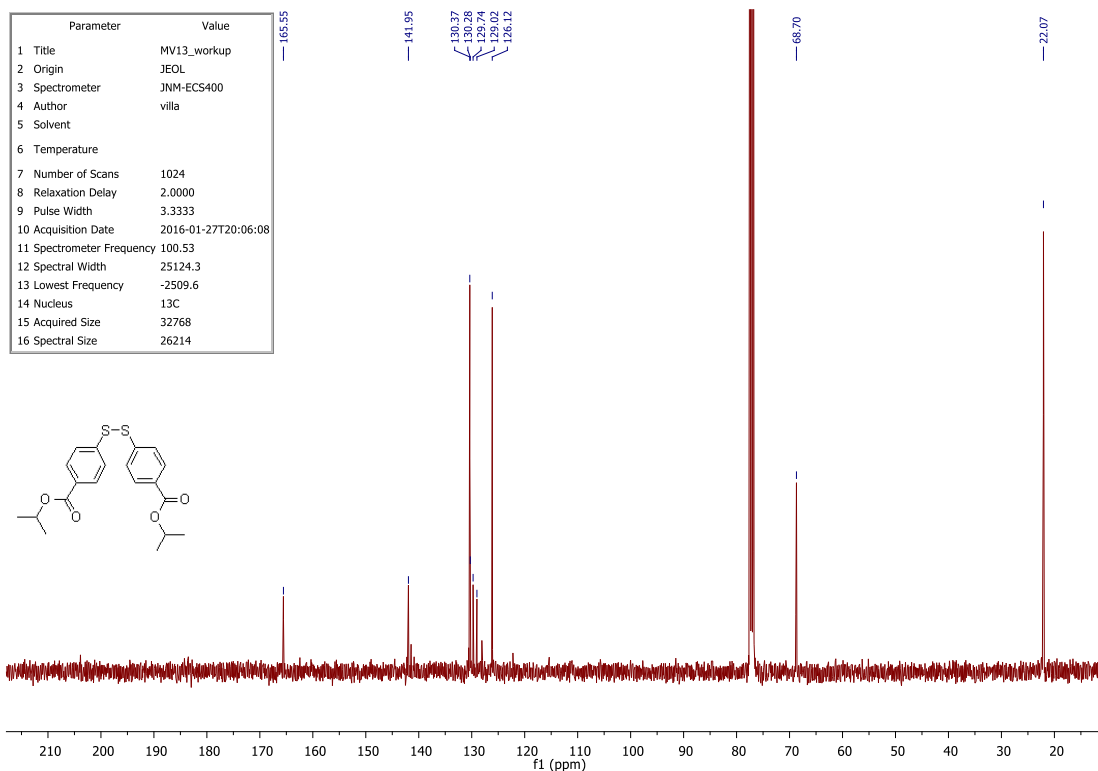
- 2) M. Villa; B. Del Secco; L. Ravotto; M. Roy; E. Rampazzo; N. Zaccheroni; L. Prodi; M. Gingras; S.A. Vinogradov; P. Ceroni *J. Phys. Chem. C* (2019), 123, 29884-29890.
- 3) X. Yan; C. Li; X. Xu; Q. He; X. Zhao; Y. Pan *Tetrahedron* (2019), 75, 3081-3087.
- 4) M. Villa; M. Roy; G. Bergamini; M. Gingras; P. Ceroni *Dalton Trans.* (2019), 48, 3815-3818.



FT-IR (ATR) spectrum of diisopropyl 4,4'-dithiobisbenzoate (**35**)



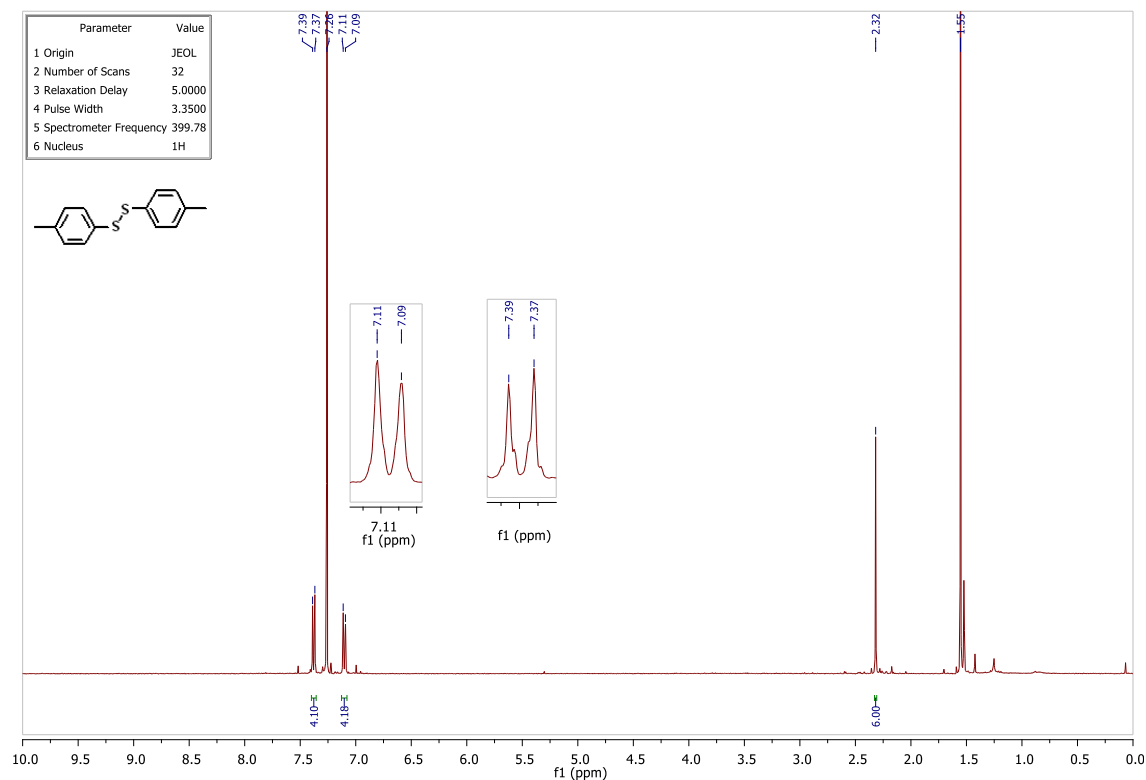
<sup>1</sup>H-NMR spectrum of diisopropyl 4,4'-dithiobisbenzoate (**35**) (CDCl<sub>3</sub>, 399.78 MHz)



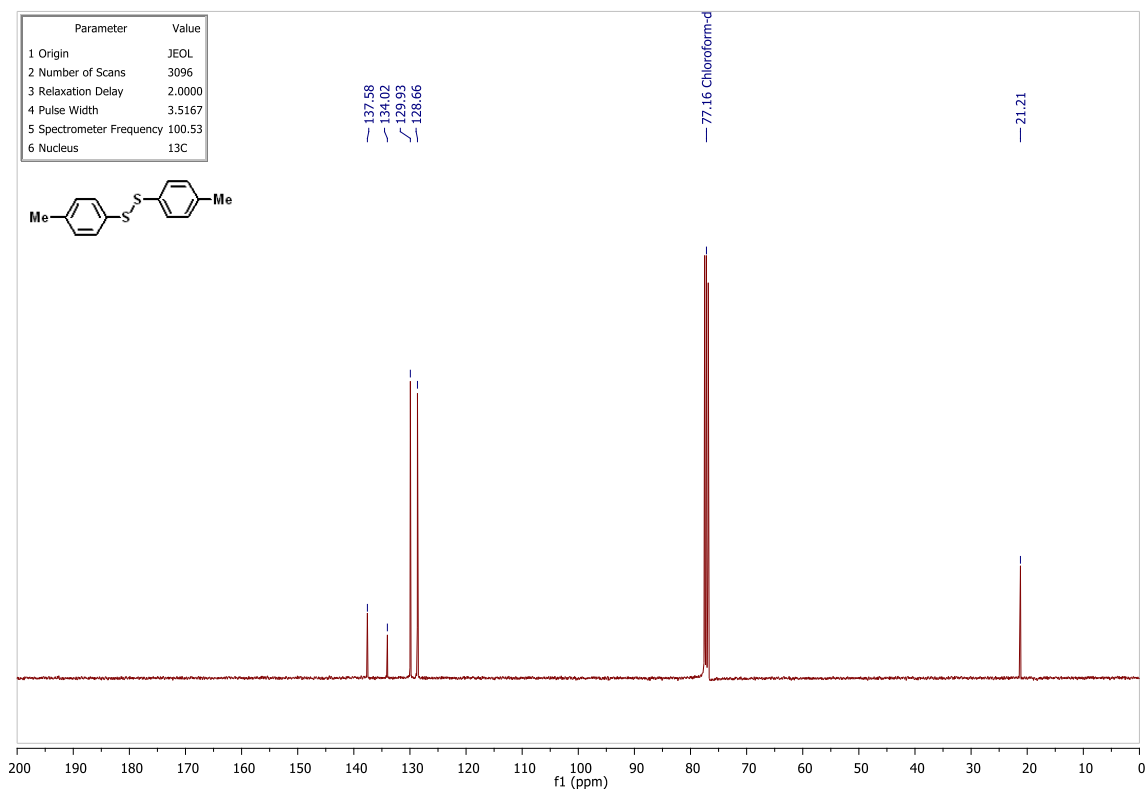
$^{13}\text{C}$ -NMR spectrum of diisopropyl 4,4'-dithiobisbenzoate (**35**) ( $\text{CDCl}_3$ , 100.53 MHz)

### Bis(4-methylphenyl) disulfide (**33**) (commercial)

$^1\text{H}$  NMR (399.78 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.38 (d<sub>app</sub>,  $J$  = 8.1 Hz, 4H), 7.09 (d<sub>app</sub>,  $J$  = 8.1 Hz, 4H), 2.32 (s, 6H);  $^{13}\text{C}$  NMR (100.53 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 137.58, 134.02, 129.93, 128.66, 21.21.



$^1\text{H}$ -NMR of bis(4-methylphenyl) disulfide ( $\text{CDCl}_3$ , 399.78 MHz)



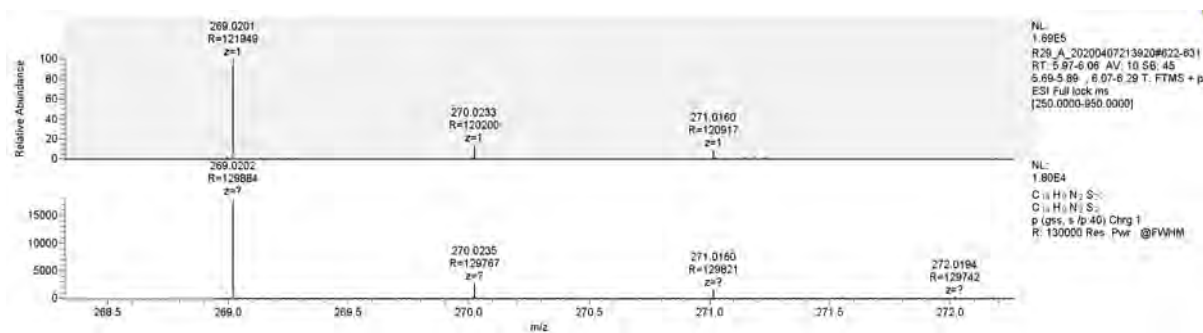
<sup>13</sup>C-NMR spectrum of bis(4-methylphenyl) disulfide (CDCl<sub>3</sub>, 100.53 MHz)

### Bis(4-cyanophenyl) disulfide (47)

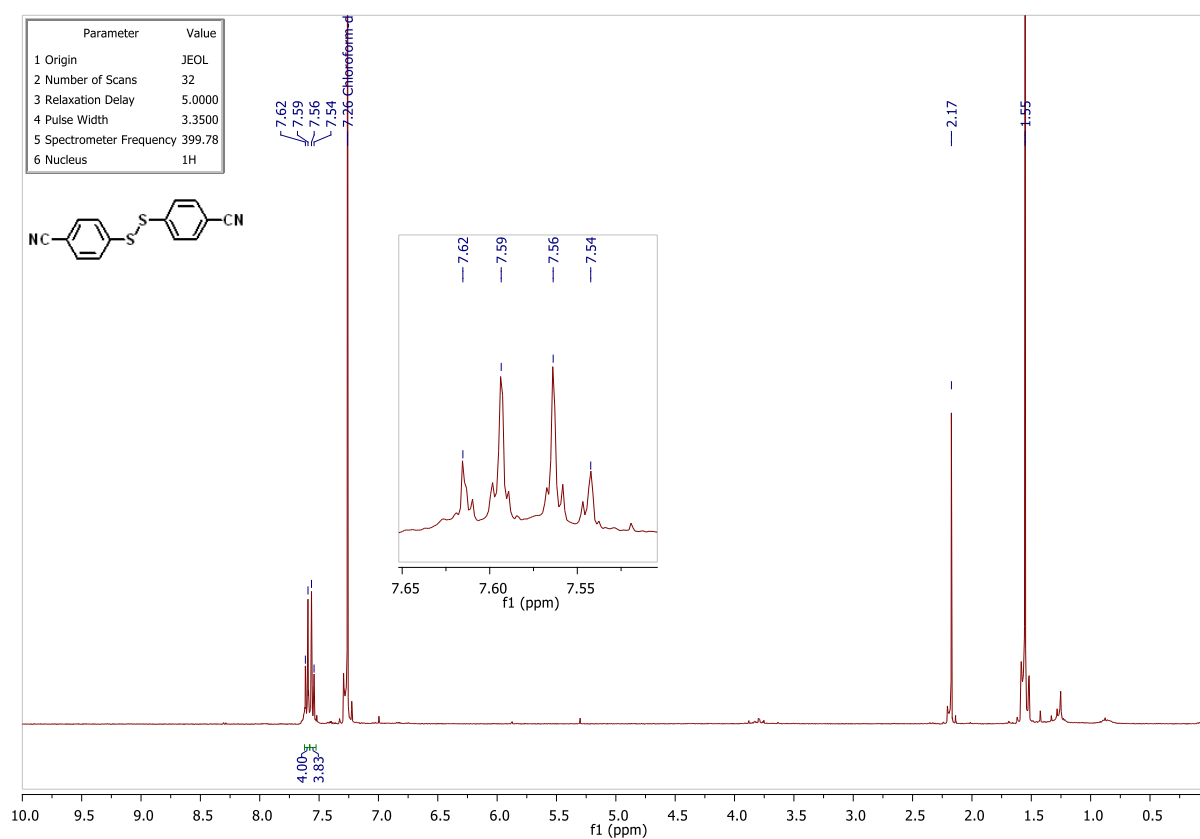
<sup>1</sup>H NMR (399.78 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 7.60 (d,  $J$  = 8.9 Hz, 4H), 7.55 (d,  $J$  = 8.8 Hz, 4H); <sup>13</sup>C NMR (100.53 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 139.33, 132.36, 128.52, 118.60, 108.43; HRMS (ESI+) calculated for [C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>S<sub>2</sub> +H<sup>+</sup>]: 269.0202 Da, found [M+H<sup>+</sup>] 269.0201 m/z;

### References:

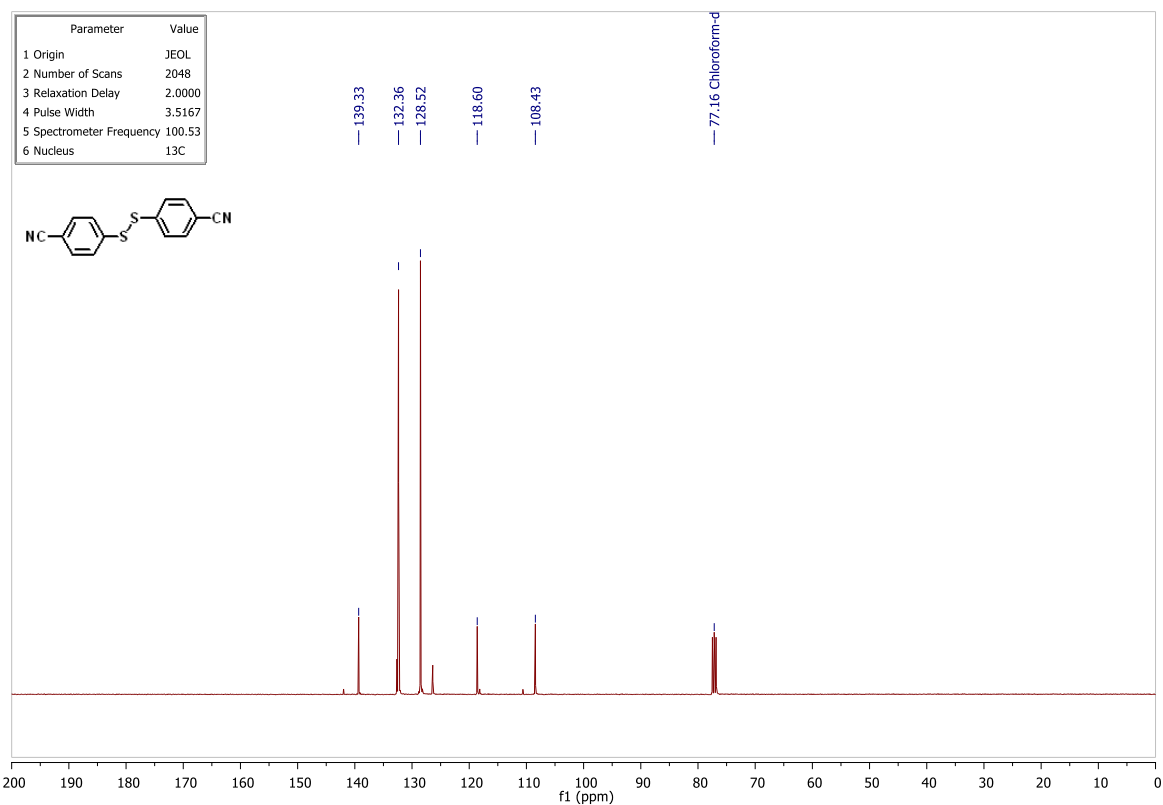
- 1) E. W. McClelland; L.A. Warren *J. Chem. Soc.* (1930), 1095-1102.
- 2) L. Bauer; J. Cymerman *J. Chem. Soc.* (1949), 3434.
- 3) L. Bauer; J. Cymerman *J. Chem. Soc.* (1950), 109-14.
- 4) J. Cymerman; J.B. Willis *J. Chem. Soc.* (1951), 1332-7.
- 5) R. Sato; S. Takizawa; S. Oae *Phosphorus, Sulfur Silicon Rel. Elem.* (1979), 7, 229-34.
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- 7) C. Combellas; S. Dellerue; G. Mathey; A. Thiebault *Tetrahedron Lett.* (1997), 38, 539-542.
- 8) S. Antonello; K. Daasbjerg; H. Jensen; F. Taddei; F. Maran *J. Am. Chem. Soc.* (2003), 125, 14.
- 9) J. Tobias; P. Knochel *Synlett* (2005), 1185-1187.
- 10) H.-Y. Chen; W.-T. Peng; Y.-H. Lee; Y.-L. Chang; Y.-J. Chen; Y.-C. Lai; N.-Y. Jheng; H.-Y. Chen *Organometallics* (2013), 32, 5514-5522.
- 11) J.-T. Yu; H. Guo; Y. Yi; H. Fei; Y. Jiang *Adv. Synth. & Catal.* (2014), 356, 749-752.
- 12) M. Abbasi; N. Nowrouzi; H. Latifi *J. Organomet. Chem.* (2016), 822, 112-117.
- 13) Y. Zheng; F.-L. Qing; Y. Huang; X.-H. Xu *Adv. Synth. & Catal.* (2016), 358, 3477-3481.



HRMS (ESI, positive mode) of (47)



<sup>1</sup>H-NMR of (47) (CDCl<sub>3</sub>, 399.78 MHz)

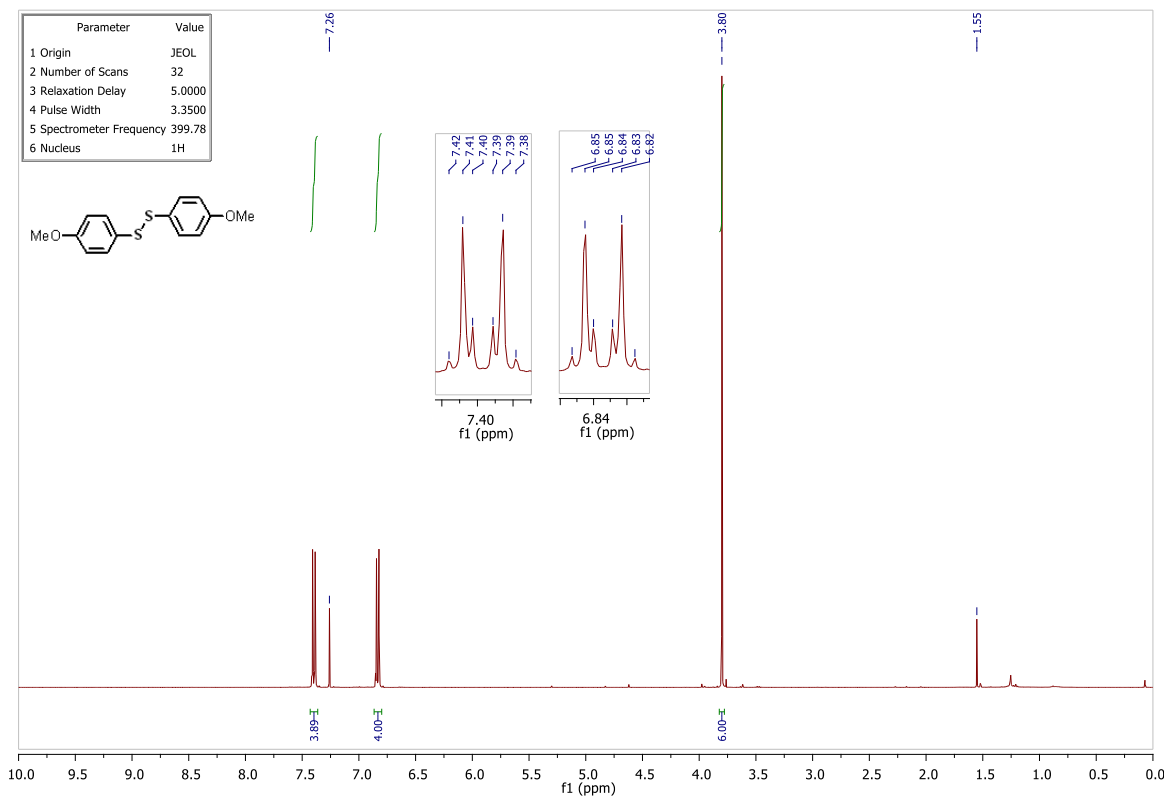


<sup>13</sup>C-NMR spectrum of **(47)** (CDCl<sub>3</sub>, 100.53 MHz)

**Bis(4-methoxyphenyl) disulfide (commercial)**

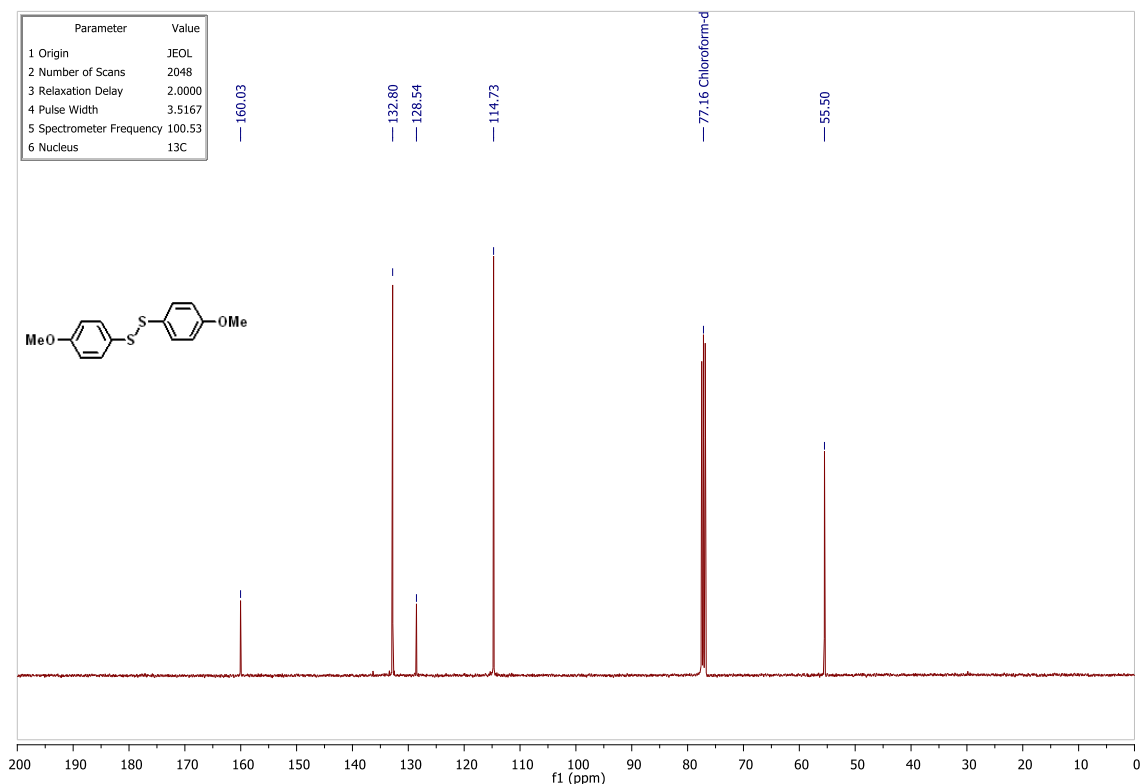
<sup>1</sup>H NMR (399.78 MHz, CDCl<sub>3</sub>, ppm) δ = 7.40 (d, *J* = 9.0 Hz, 4H), 6.83 (d, *J* = 8.8 Hz, 4H), 3.80 (s, 6H);

<sup>13</sup>C NMR (100.53 MHz, CDCl<sub>3</sub>, ppm) δ = 160.03, 132.80, 128.54, 114.73, 55.50; HRMS (ESI+) calculated for [C<sub>14</sub>H<sub>14</sub>O<sub>2</sub>S<sub>2</sub> + H<sup>+</sup>]: 279.0508 Da, found [M+H<sup>+</sup>] 279.0509 m/z;



<sup>1</sup>H-NMR of bis(4-methoxyphenyl) disulfide (CDCl<sub>3</sub>, 399.78 MHz)



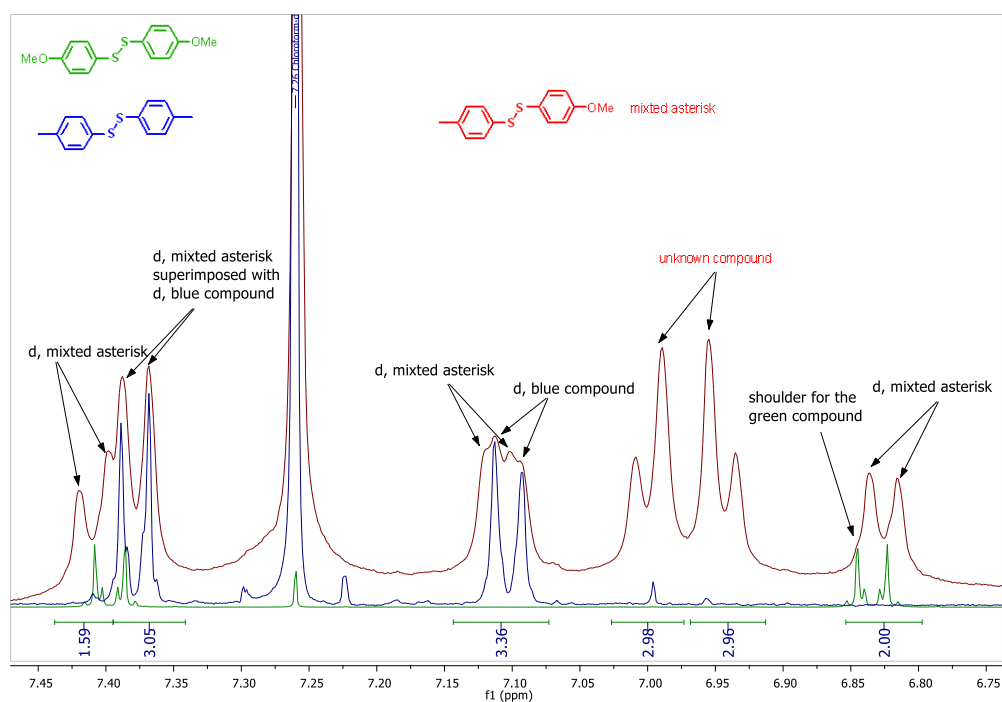


$^{13}\text{C}$ -NMR spectrum of bis(4-methoxyphenyl) disulfide ( $\text{CDCl}_3$ , 100.53 MHz)

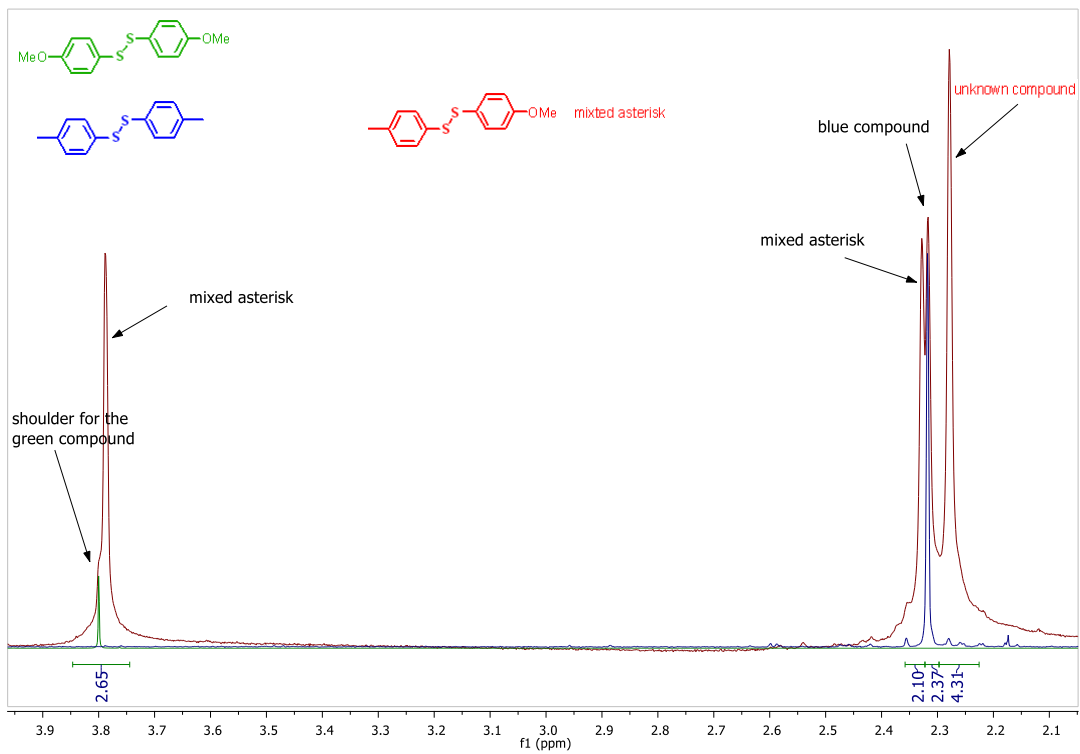
### List of mixed disulfides

#### 4-Methylphenyl-4-methoxyphenyl disulfide (58)

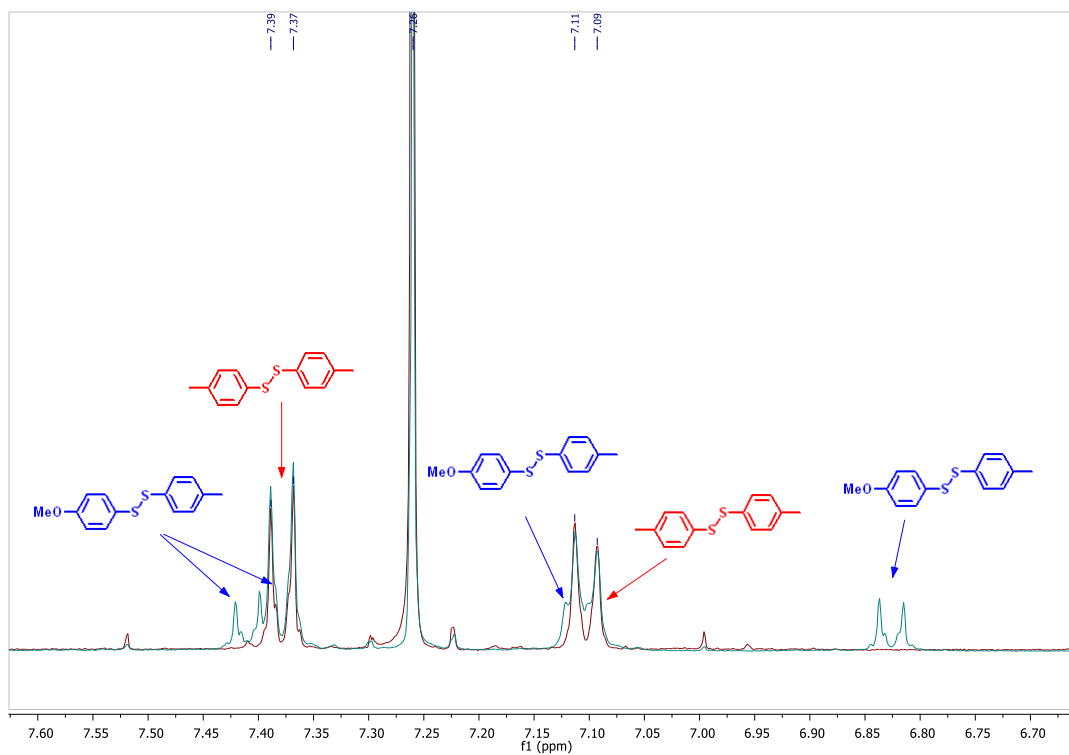
$^1\text{H}$  NMR (399.78 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.41 (d,  $J$  = 8.2 Hz, 2H), 7.38 (d,  $J$  = 7.8 Hz, 2H), 7.11 (d,  $J$  = 7.4 Hz, 2H), 6.83 (d,  $J$  = 8.3 Hz, 2H), 3.79 (s, 3H), 2.33 (s, 3H).



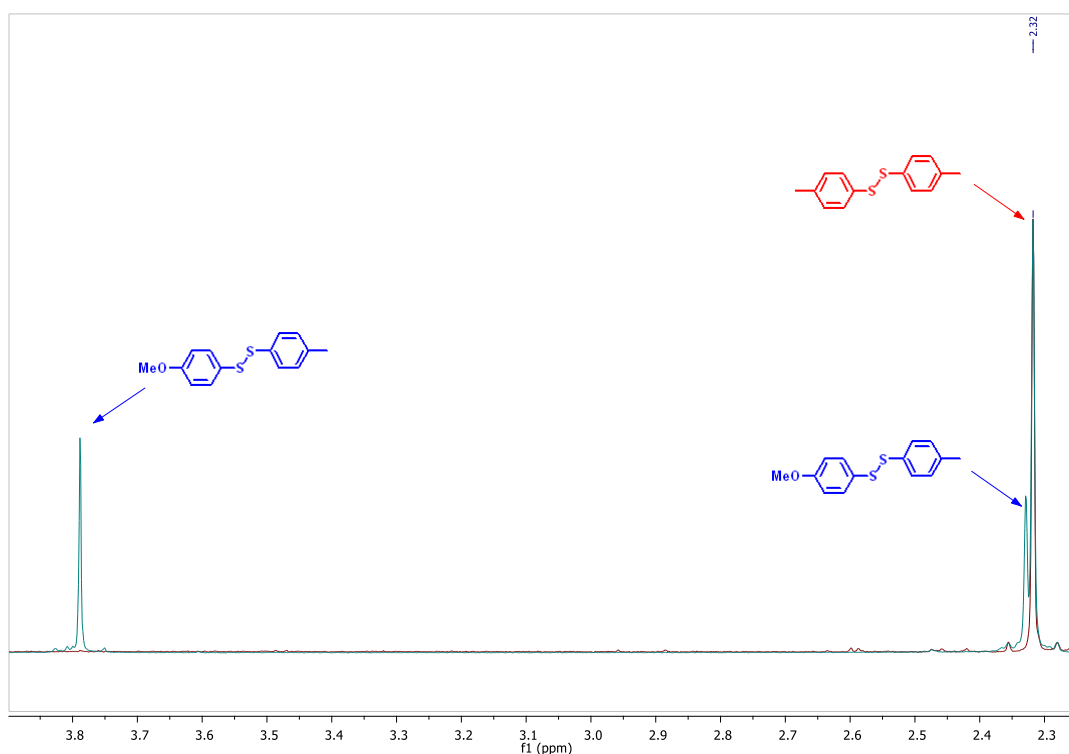
$^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 399.78 MHz)



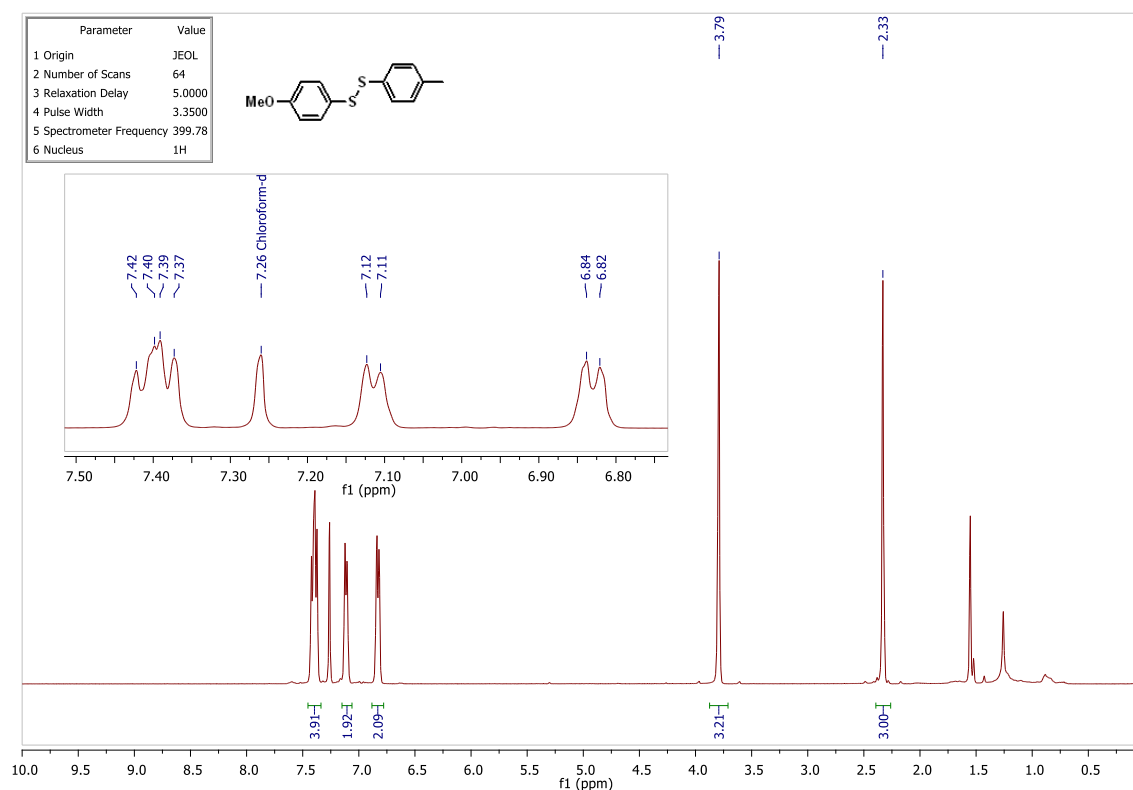
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 399.78 MHz)



$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 399.78 MHz)



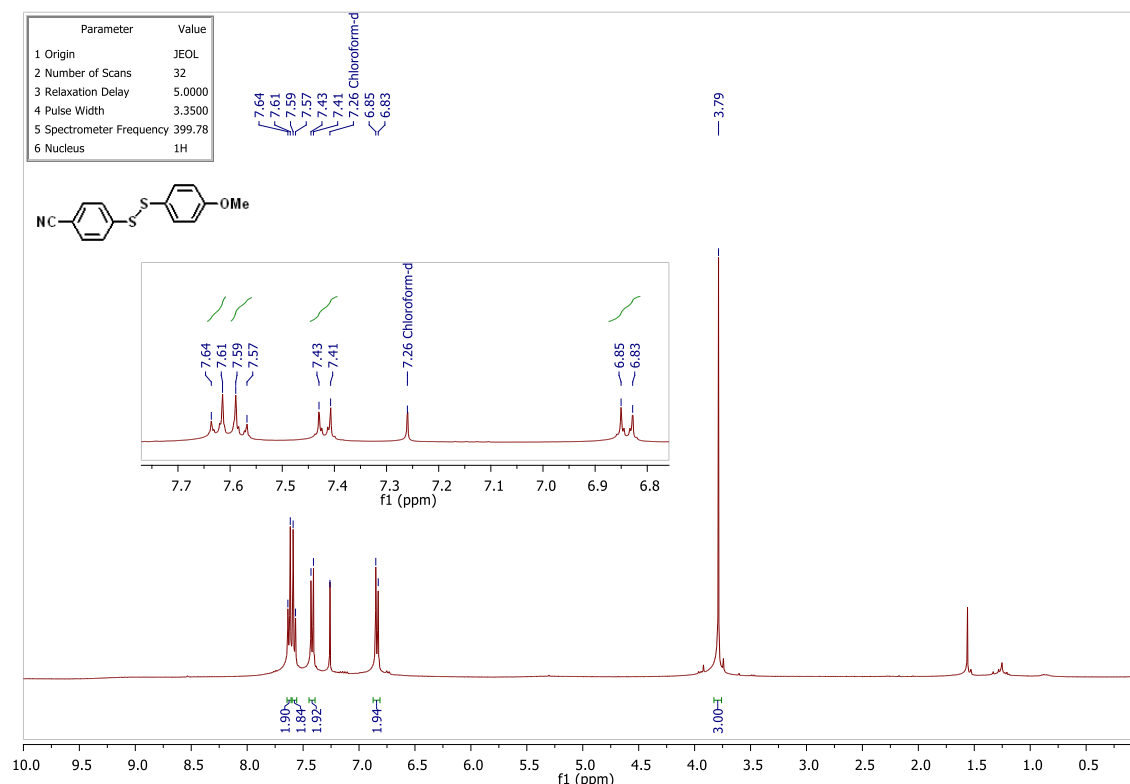
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 399.78 MHz)



$^1\text{H-NMR}$  of 4-methylphenyl-4-methoxyphenyl disulfide (**58**) ( $\text{CDCl}_3$ , 399.78 MHz)

#### 4-Methoxyphenyl-4-cyanophenyl disulfide (**59**)

$^1\text{H NMR}$  (399.78 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.63 (d,  $J$  = 8.6 Hz, 2H), 7.58 (d,  $J$  = 8.7 Hz, 2H), 7.42 (d,  $J$  = 8.8 Hz, 2H), 6.84 (d,  $J$  = 8.9 Hz, 2H), 3.79 (s, 3H).



<sup>1</sup>H-NMR of 4-methoxyphenyl-4-cyanophenyl disulfide (**59**) (CDCl<sub>3</sub>, 399.78 MHz)

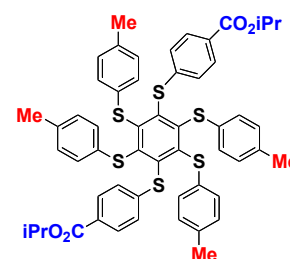
## References:

- 1) D. Wang; X. Liang; M. Xiong; H. Zhu; Y. Zhou; Y. Pan, *Org. & Biomol. Chem.* (2020), 18, 4447-4451.
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- 3) N. Taniguchi *Tetrahedron* (2017), 73, 2030-2035
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- 5) N. Stellenboom; R. Hunter; M. R. Caira *Tetrahedron* (2010), 66, 3228-3241.
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## 2.5 Mixed hexa(thio) benzene asterisks

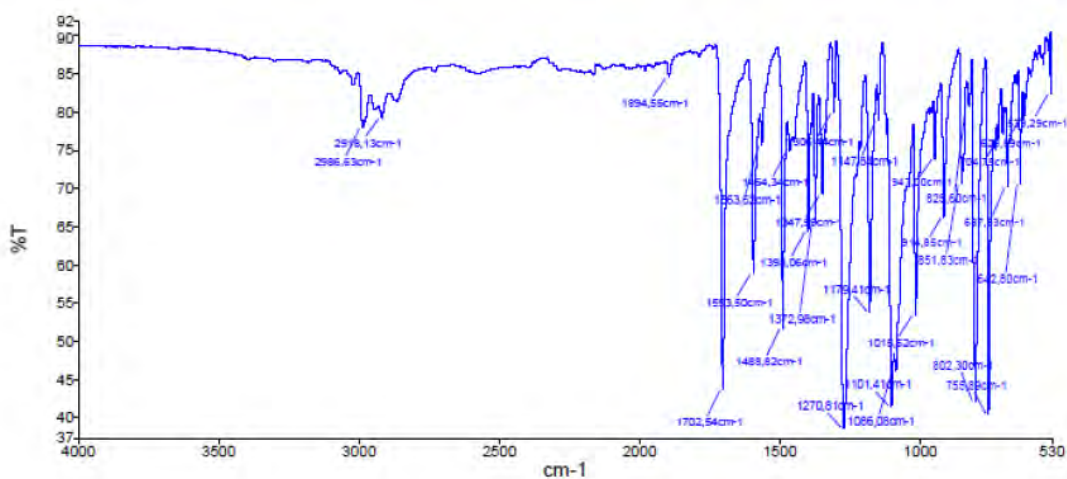
### 1,4-Bis(4-isopropoxycarbonyl-phenylthio)-2,3,5,6-tetrakis(4-methylphenylthio)benzene (**32**, n= 2)

In an oven-dried glass tube were placed 2,3,5,6-tetrafluoro-1,2-bis(4-isopropoxycarbonyl-phenylthio) benzene (400 mg, 0.743 mmol, 1.00 mol-eq), *p*-methylbenzenethiol (372 mg, 3.00 mmol, 4.04 mol-eq) and dry potassium carbonate (614 mg, 4.44 mmol, 5.98 mol-eq) under an argon atmosphere. All reagents were freshly dried under vacuum for about 30 min prior to use them. Under argon, dry DMF (3.7 mL, kept over activated 3Å molecular sieves) was then injected, the tube was sealed and the mixture was vigorously stirred at 20°C for 45 min.. An aqueous HCl solution (1M, 100 mL) was added and a yellow-brown solution was extracted with toluene (3x25 mL). The

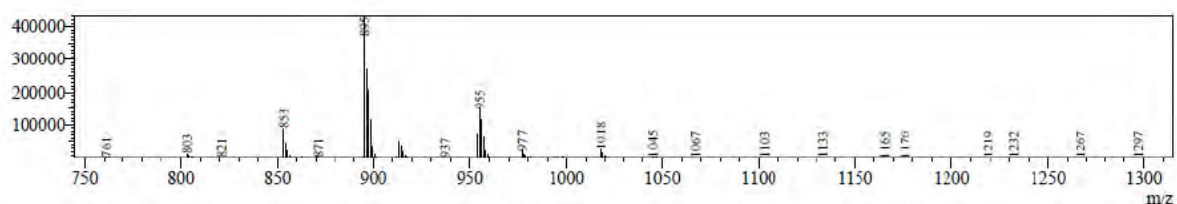
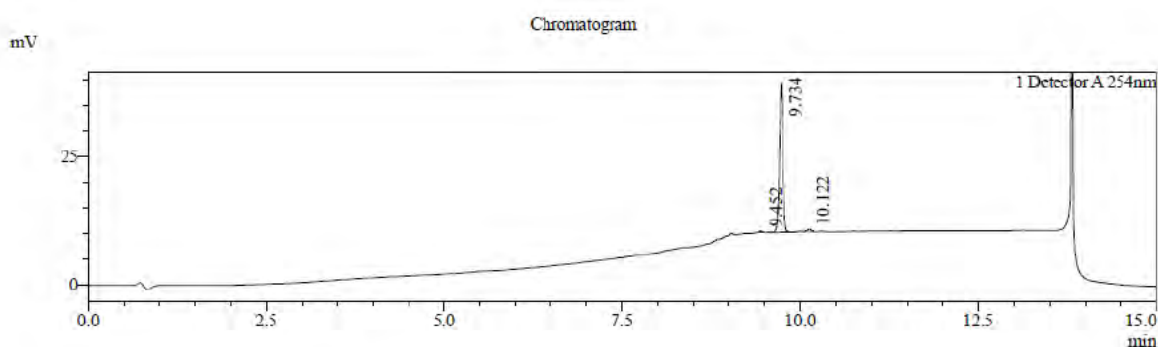


combined organic phases were washed with water (5x25 mL), and dried over anhydrous MgSO<sub>4</sub>. After filtration, and evaporation of solvents, a yellow-brown solid was obtained and a purification by column chromatography on silica gel (eluent: toluene/DCM: 80/20) afforded a yellow solid (453 mg, 0.474 mmol, 64 % yield).

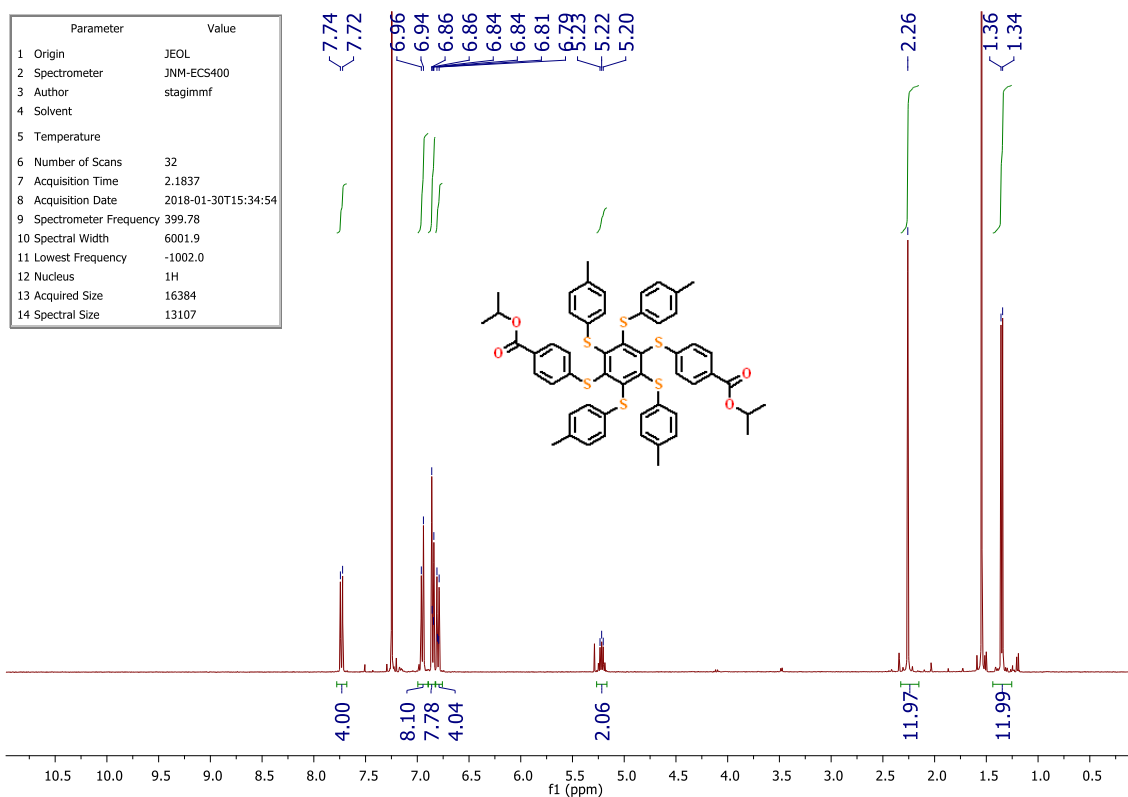
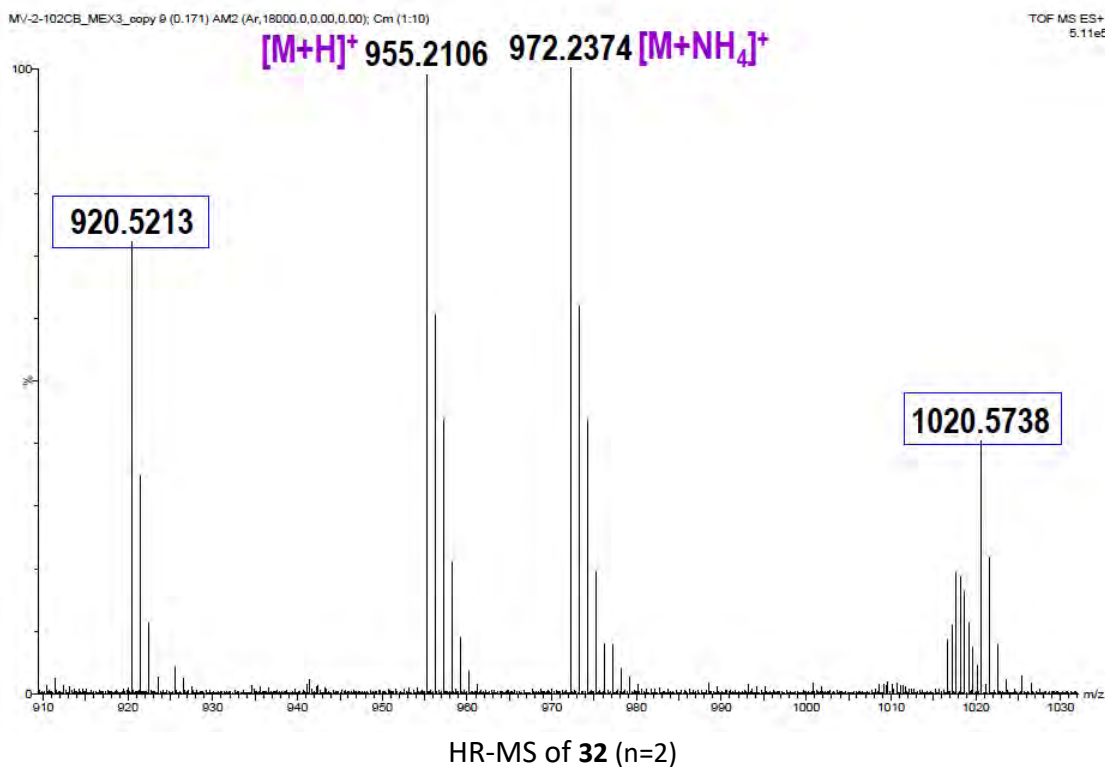
**TLC** (toluene/DCM : 80/20) R<sub>f</sub> = 0.25; **FT-IR** (ATR, diamond contact, neat, cm<sup>-1</sup>) ν = 2986, 2918, 1702, 1593, 1488, 1270, 1179, 1101, 1085, 914, 802, 755; **<sup>1</sup>H NMR** (399.78 MHz, CDCl<sub>3</sub>, ppm): δ = 7.74 (d, J = 8.5 Hz, 4H), 6.96 (d, J = 8.0 Hz, 8H), 6.86 (d, J = 8.0 Hz, 8H), 6.81 (d, J = 8.5 Hz, 4H), 5.23 (sept, J = 6.3 Hz, 2H), 2.27 (s, 12H) 1.36 (d, J = 6.3 Hz, 12H); **<sup>13</sup>C NMR** (100.53 MHz, CDCl<sub>3</sub>, ppm): δ = 165.74, 148.78, 146.41, 143.89, 136.67, 133.90, 130.07, 129.92, 129.13, 128.01, 126.35, 68.46, 22.15, 21.22; **MS** (LC-MS acetonitrile/water, 0.1% formic acid; APCI) 955 m/z [M+H]<sup>+</sup>; **HRMS (ESI+)** calculated for [C<sub>54</sub>H<sub>50</sub>O<sub>4</sub>S<sub>6</sub> + NH<sub>4</sub><sup>+</sup>]: 972.2377 Da, found 972.2374 m/z [M+NH<sub>4</sub>]<sup>+</sup>; **HRMS (ESI+)** calculated for [C<sub>54</sub>H<sub>50</sub>O<sub>4</sub>S<sub>6</sub> + H<sup>+</sup>]: 955.2106 Da, found [M+H]<sup>+</sup> 955.2106 m/z.

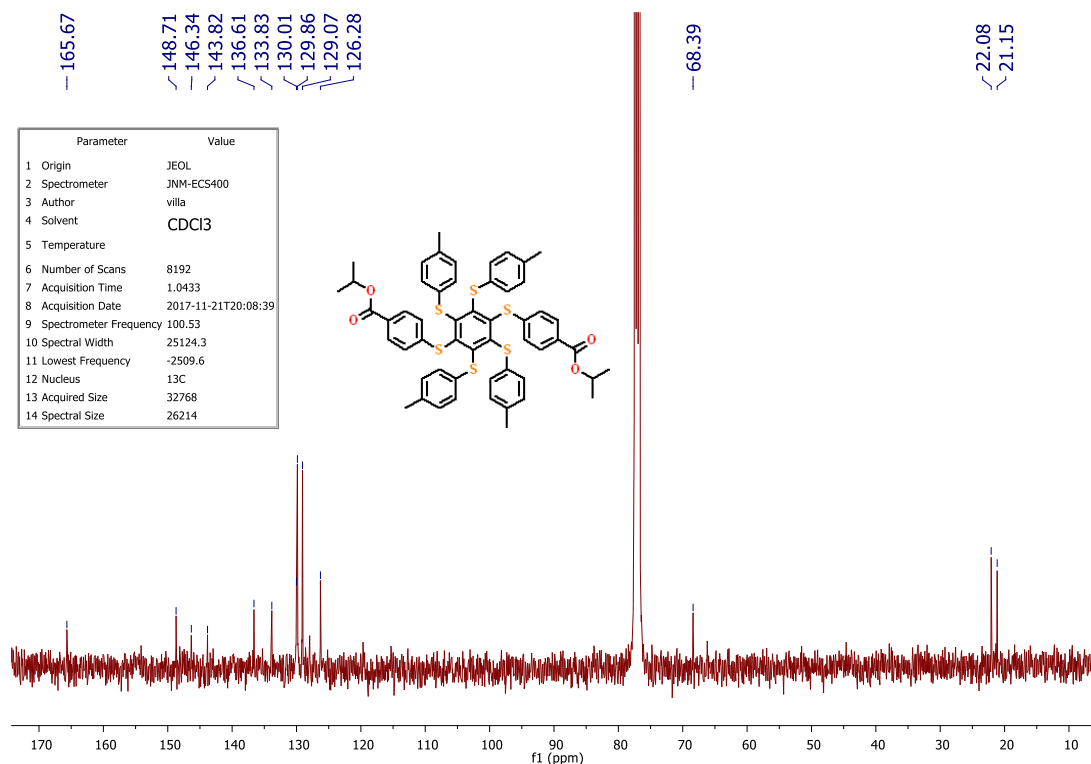


FT-IR spectrum of **32** (n=2)



Reverse phase HPLC chromatogram and MS-APCI of **32** (n=2)





$^{13}\text{C}$ -NMR of **32** (n=2) ( $\text{CDCl}_3$ , 100.53 MHz)

### 2,3,5,6-Tetrakis(4-isopropoxyxycarbonyl-phenylthio)-1,4-bis(4-methylphenylthio)benzene (**60**)<sup>1</sup>

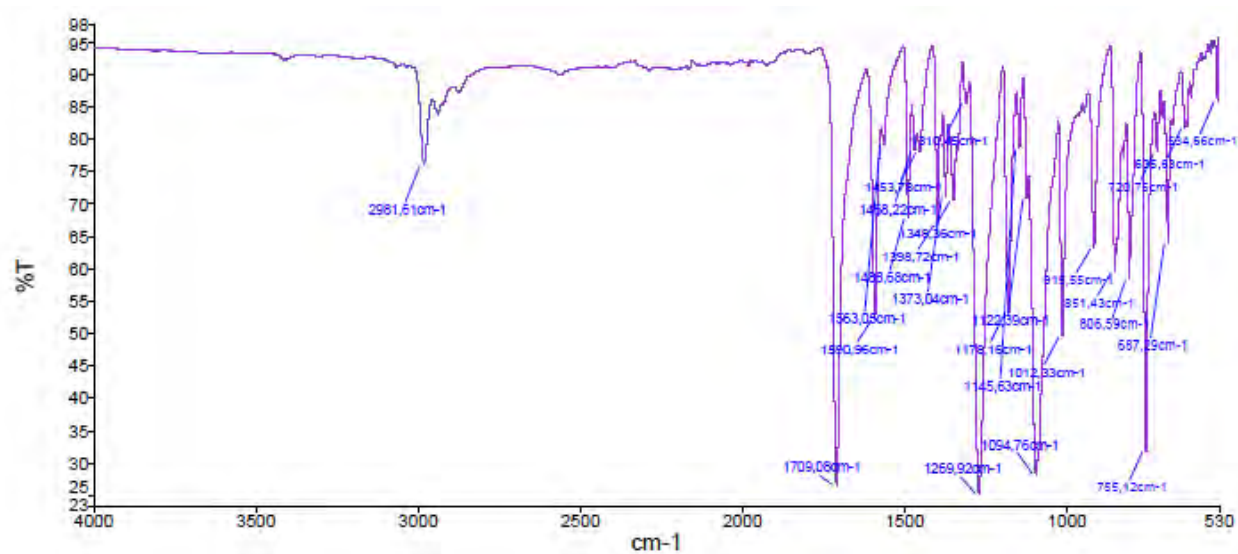
In an oven-dried tube were placed 1,4-difluoro-2,3,5,6-tetrakis(4-isopropoxyxycarbonyl-phenylthio)benzene (400 mg, 0.449 mmol, 1.00 mol-eq), *p*-methylbenzenethiol (114.1 mg, 0.919 mmol, 2.05 mol-eq) and dry potassium carbonate (198.2 mg, 1.44 mmol, 3.21 mol-eq) under an argon atmosphere. All reagents were freshly dried under vacuum for about 30 min prior to use them. Under argon, dry DMF (3.7 mL, kept over molecular sieves 3A) was injected, the tube was sealed, and the mixture was vigorously stirred at 80°C (oil bath temperature) for 4 days. After cooling down to room temperature, an aqueous HCl solution (1M, 100 mL) was added and it was extracted with toluene (3x25 mL). The combined organic phases were washed with water (5x25 mL), and dried over anhydrous  $\text{MgSO}_4$ . After filtration, and evaporation of solvents, a yellow-brown solid was obtained. A purification by a chromatography column over silica gel (eluent: toluene/DCM: 80:20 v/v) afforded a yellow solid (370 mg, 0.337 mmol, 75 %).



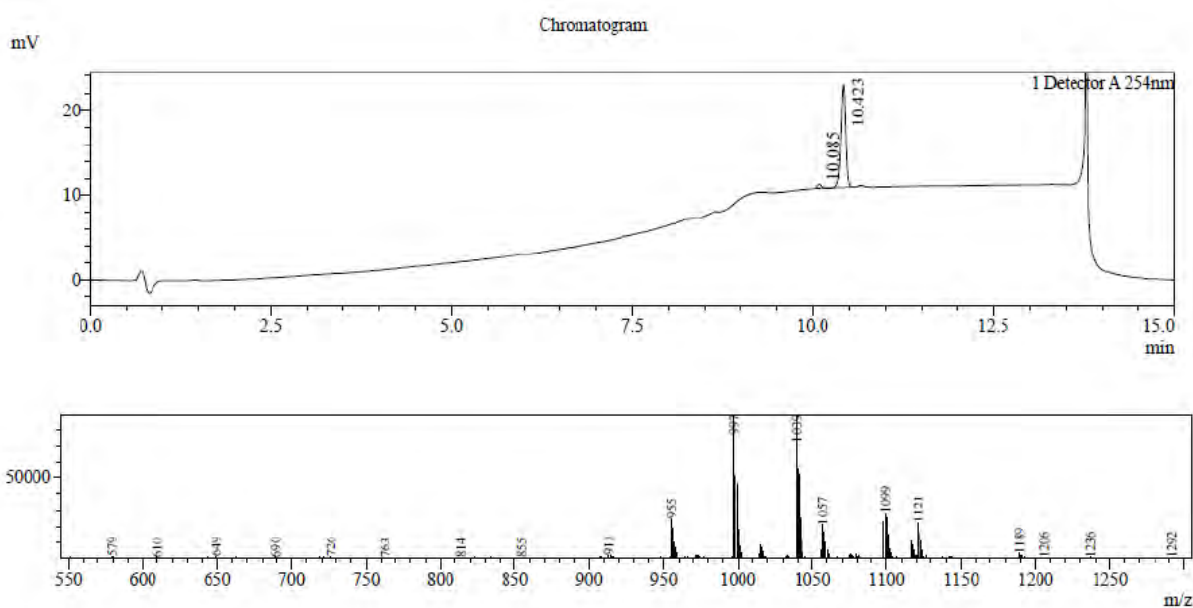
**TLC** (tol/DCM: 80/20 v/v)  $R_f = 0.5$ ; **FT-IR** (ATR, diamond contact, neat,  $\text{cm}^{-1}$ )  $\nu = 2981, 1709, 1590, 1488, 1269, 1178, 1094, 1012, 915, 851, 806, 755, 687$ ;  **$^1\text{H}$  NMR** (400.72 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.82$  (d,  $J = 8.2$  Hz, 8H),  $6.97$  (d,  $J = 8.0$  Hz, 4H),  $6.90$  (d,  $J = 8.3$  Hz, 8H),  $6.87$  (d,  $J = 8.2$  Hz, 4H),  $5.23$  (sept,  $J = 6.3$  Hz, 4H),  $2.26$  (s, 6H),  $1.37$  (d,  $J = 6.3$  Hz, 24H);  **$^{13}\text{C}$  NMR** (100.77 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 165.55, 149.83, 147.09, 143.30, 137.21, 133.31, 130.27, 130.09, 129.42, 128.64, 126.77, 68.60, 22.12, 21.18$ ; **MS** (LC-MS acetonitrile/water, 0.1% formic acid; APCI) 1099  $[\text{M}+\text{H}]^+$ .

## Reference

- 1) M. Villa; B. Del Secco; L. Ravotto; M. Roy; E. Rampazzo; N. Zaccheroni; L. Prodi; M. Gingras; S. Vinogradov; P. Ceroni *J. Phys. Chem. C* (2019), 123, 29884-29890.



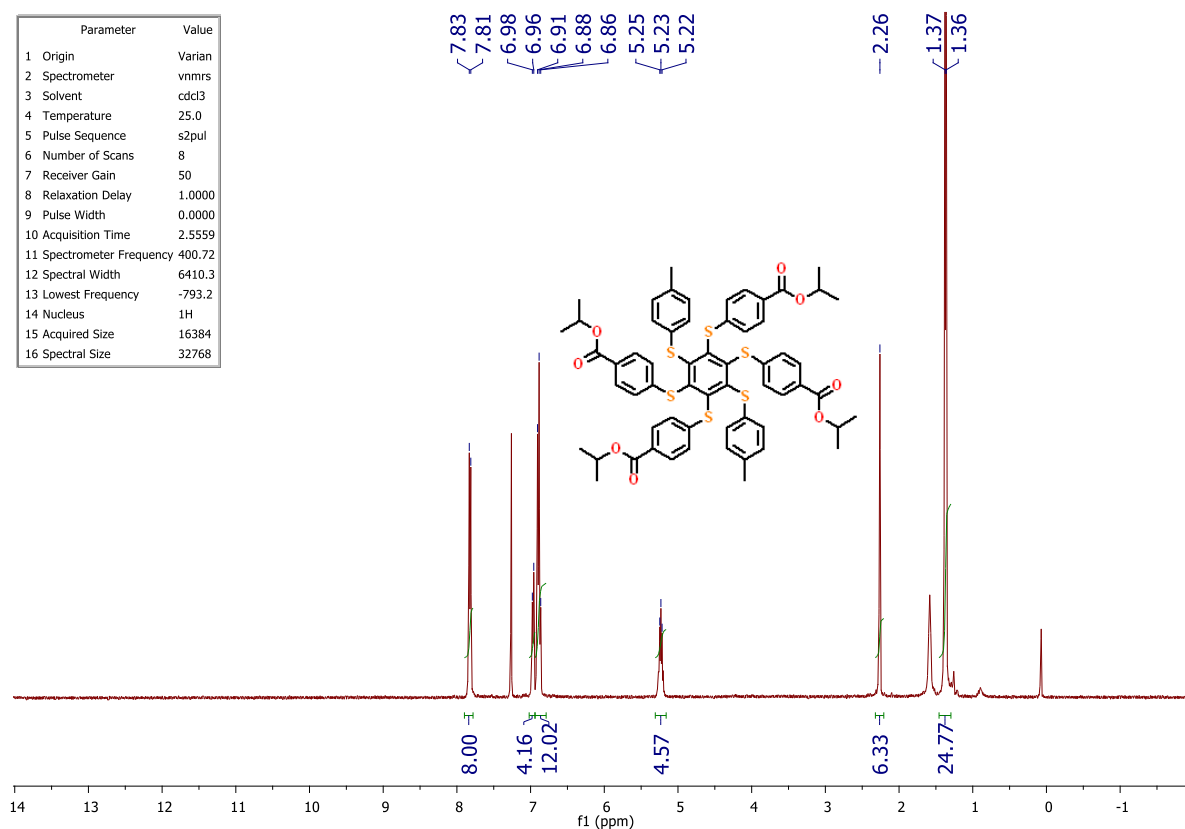
FT-IR spectrum of (60)



Reverse-phase HPLC chromatogram of (60) and MS-APCI

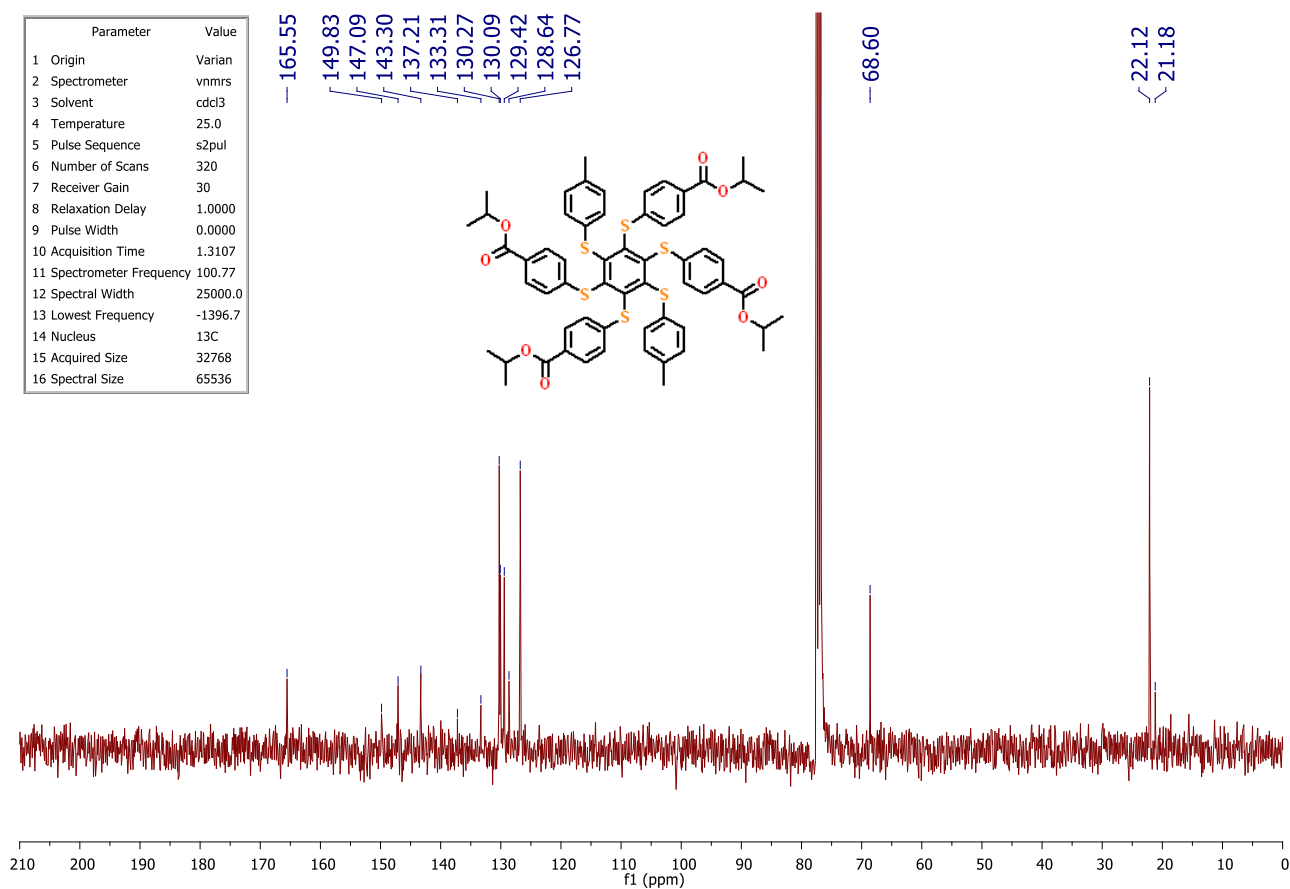


Parameter	Value
1 Origin	Varian
2 Spectrometer	nmrs
3 Solvent	cdcl3
4 Temperature	25.0
5 Pulse Sequence	s2pul
6 Number of Scans	8
7 Receiver Gain	50
8 Relaxation Delay	1.0000
9 Pulse Width	0.0000
10 Acquisition Time	2.5559
11 Spectrometer Frequency	400.72
12 Spectral Width	6410.3
13 Lowest Frequency	-793.2
14 Nucleus	1H
15 Acquired Size	16384
16 Spectral Size	32768



<sup>1</sup>H-NMR of (60) (CDCl<sub>3</sub>, 400.72 MHz, Varian)

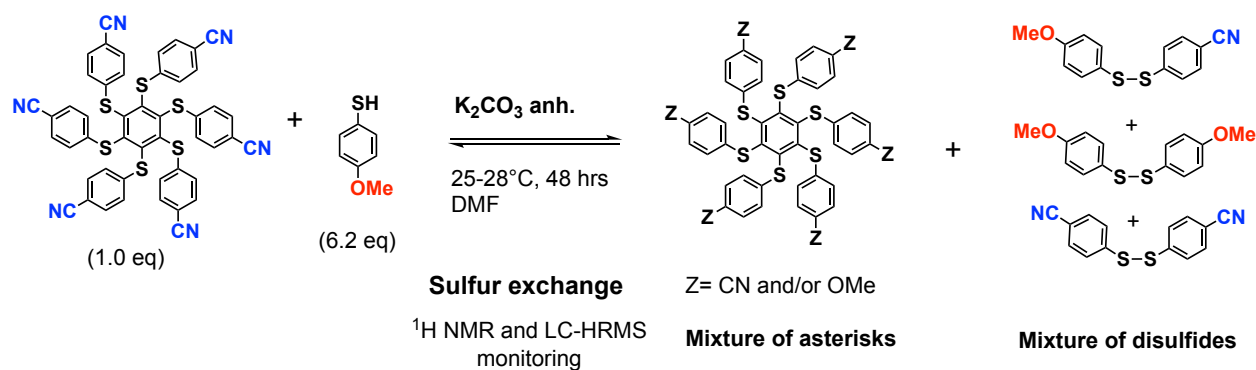
Parameter	Value
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2 Spectrometer	nmrs
3 Solvent	cdcl3
4 Temperature	25.0
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6 Number of Scans	320
7 Receiver Gain	30
8 Relaxation Delay	1.0000
9 Pulse Width	0.0000
10 Acquisition Time	1.3107
11 Spectrometer Frequency	100.77
12 Spectral Width	25000.0
13 Lowest Frequency	-1396.7
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536



<sup>13</sup>C-NMR of (60) (CDCl<sub>3</sub>, 100.77 MHz, Varian ARX Inova 400 NMR)

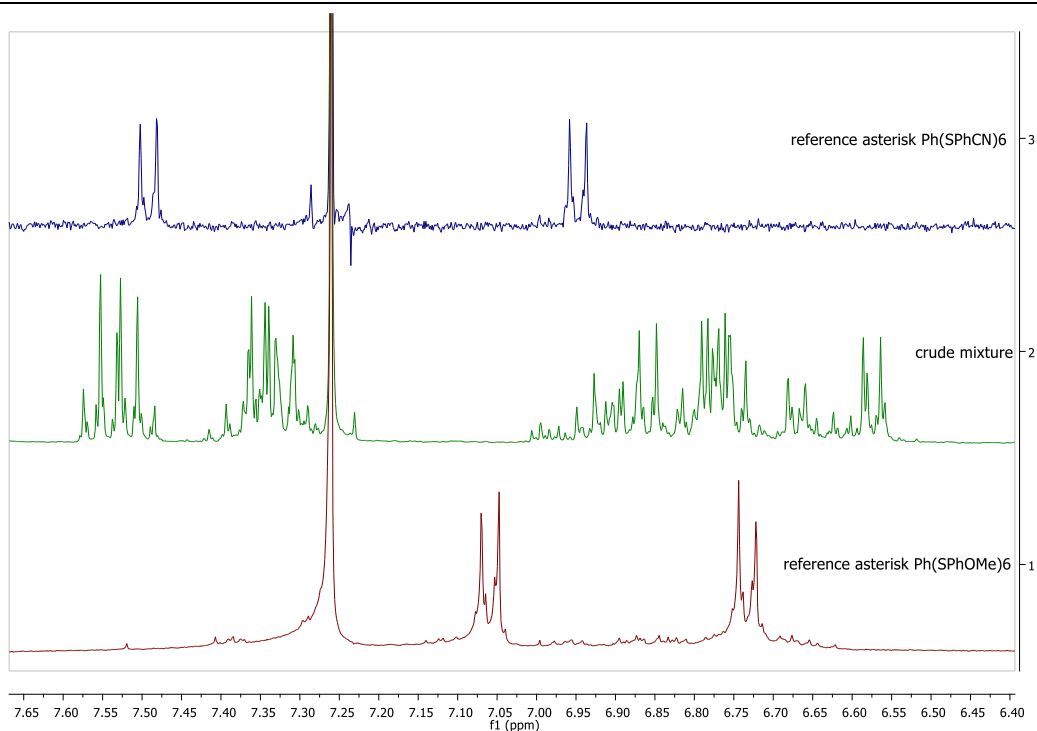
### 3.0 Sulfur exchange reactions on hexa(thio) benzene asterisks

#### SULFUR EXCHANGE REACTIONS WITH HEXAKIS(4-CYANOPHENYLTHIO)BENZENE.

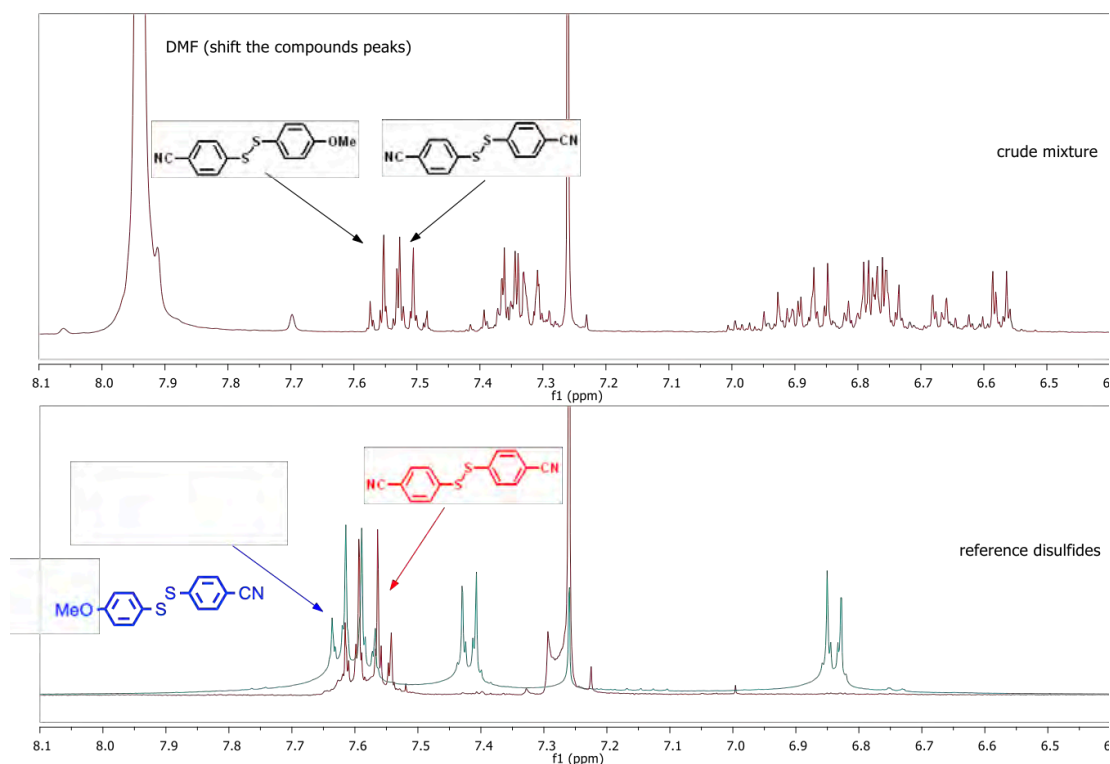


**(R-29) Procedure.** In an oven-dried glass tube were placed hexakis(4-cyanophenylthio)benzene (40 mg, 0.046 mmol, 1.00 mol-eq.) and dried potassium carbonate (39.7 mg, 0.287 mmol, 6.24 mol-eq.) under a flow of argon. 4-Methoxythiophenol (39.9 mg, 0.285 mmol, 35 $\mu$ L, 6.2 mol-eq.) in dry DMF (0.5mL, kept over activated molecular sieves 3 $\text{\AA}$ ) was injected via a syringe. Argon was bubbled through the mixture for 5-10 min.. The tube was sealed, and the reaction was stirred at room temperature (25-28 $^{\circ}$ C) for 2 days. It was monitored by TLC (SiO<sub>2</sub>, 10% to 30% EtOAc/*n*-hept or 80% tol/*n*-hept). After one day, TLC (30% ETOAc/*n*-hept) indicated under UV-vis lamp two less polar spots corresponding to some disulfides. The two more polar spots were yellow. One corresponded to hexakis (4-cyanophenylthio)benzene. After collecting a small aliquot, addition of H<sub>2</sub>O and extraction with CHCl<sub>3</sub>, the reaction was monitored by <sup>1</sup>H NMR (**SG-I-152-A**). It indicated some ligand exchanges after 16 hrs. The reaction mixture reacted for two days and it was stopped by adding water (5 mL) and CHCl<sub>3</sub> (5 mL). The organic phase was separated and washed further with H<sub>2</sub>O (2x5mL) for removing DMF. It was dried over anhydrous MgSO<sub>4</sub>, filtered and evaporated. The crude product was purified by column chromatography over SiO<sub>2</sub> while using an increasing polarity of eluent from 5% EtOAc to 30% EtOAc in cyclohexane. Some fractions and the crude were analyzed by LC-HRMS.

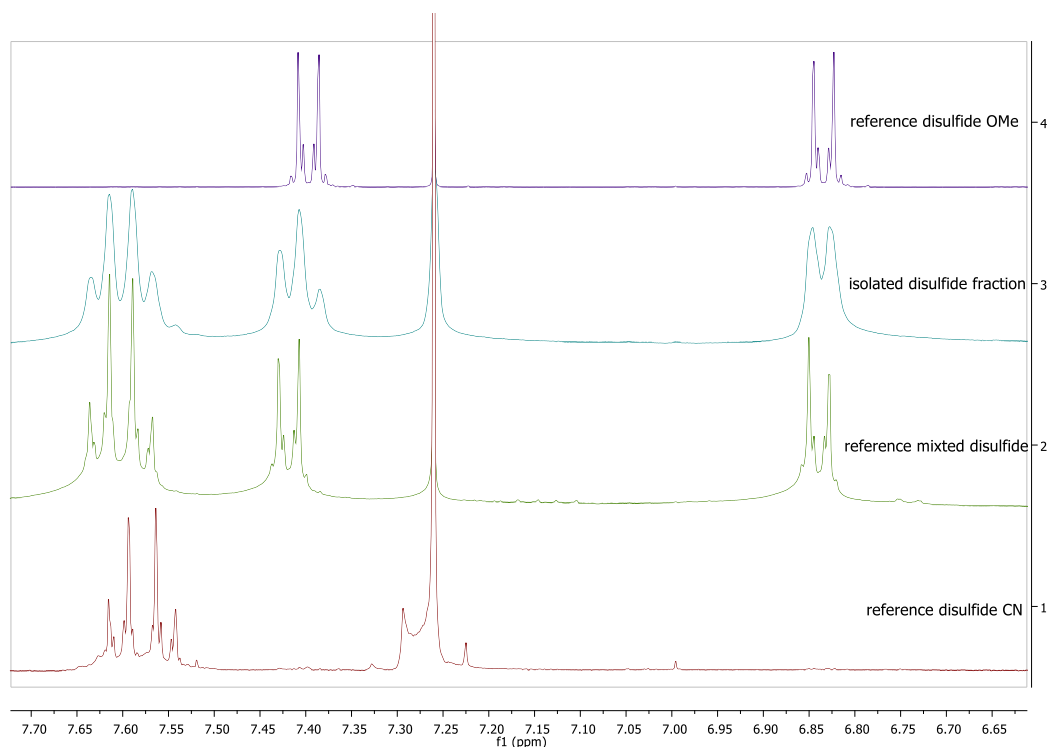
## $^1\text{H}$ NMR monitoring and analysis of the mixture



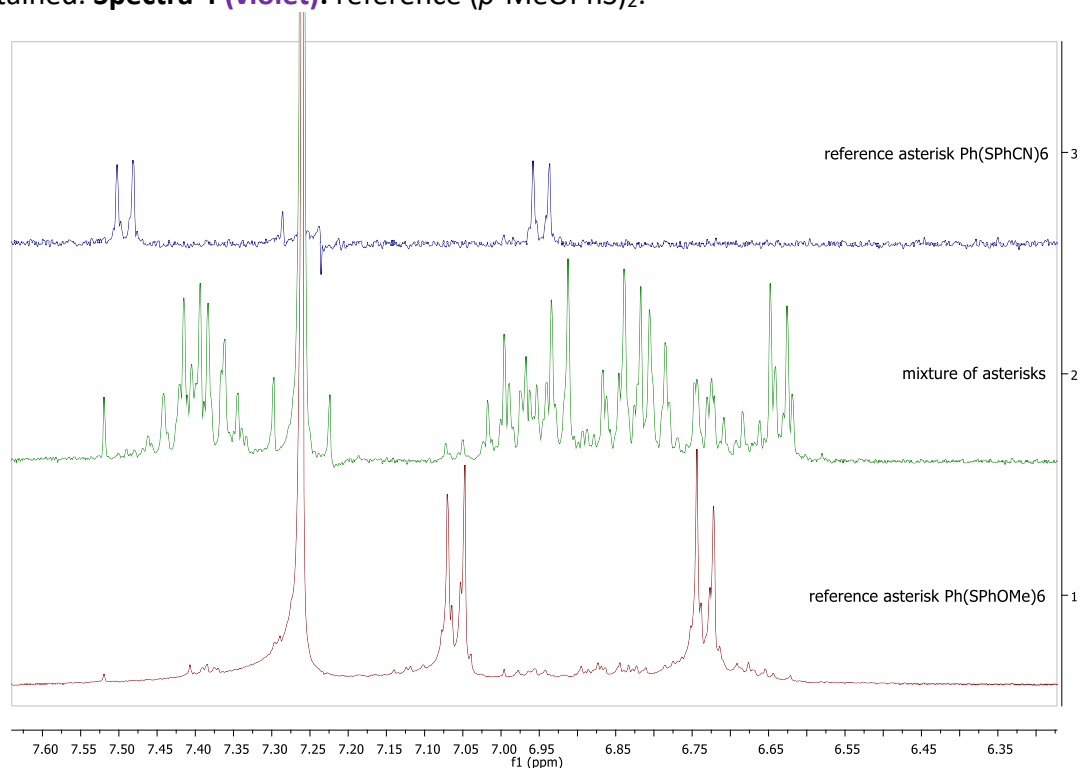
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 399.78 MHz) of the two reference hexathiobenzene asterisks (**blue**:  $\text{Ph}(\text{SPhCN})_6$  and **red**:  $\text{Ph}(\text{SPhOMe})_6$ ) and the crude mixture (**green**: middle spectrum) after 16 hrs at 25–28°C. **Conclusion:** the starting asterisk  $\text{Ph}(\text{SPhCN})_6$  fully reacted after 16 hrs at 25–28°C.



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 399.78 MHz). Above: crude mixture after 16 hrs at room temperature. Below: two reference disulfides superimposed. The presence of the mixed disulfides proves that some thiol exchange reactions occurred.

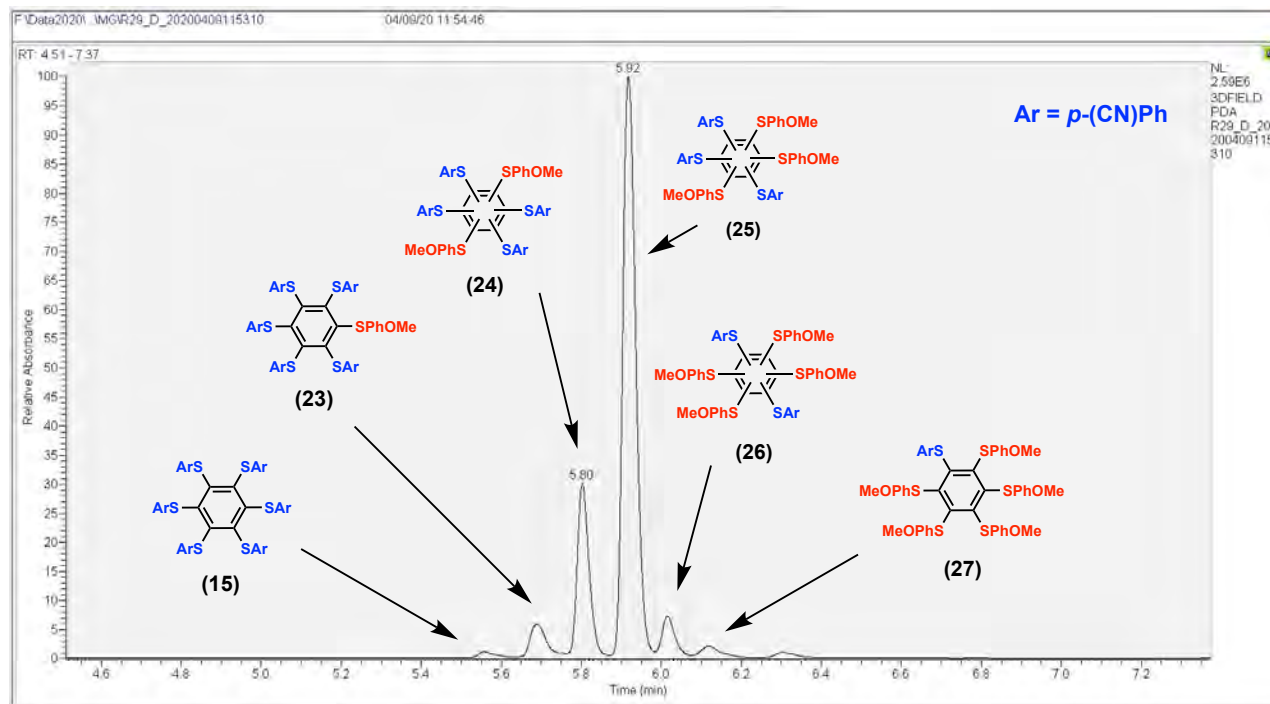


<sup>1</sup>H NMR (CDCl<sub>3</sub>, 399.78 MHz). **Spectra 1 (red):** reference (*p*-CNPhS)<sub>2</sub>. **Spectra 2 (green):** reference mixed disulfide (*p*-CNPhS-*p*-MeOPh). **Spectra 3 (blue):** one of the column fraction containing a mixture of disulfides (less polar fractions) from a comparison to reference spectra of symmetrical and mixed disulfides. The presence of *p*-CNPhS-*p*-MeOPh and (*p*-MeOPhS)<sub>2</sub> can be clearly ascertained. **Spectra 4 (violet):** reference (*p*-MeOPhS)<sub>2</sub>.



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 399.78 MHz) **Spectrum 1 (red):** reference Ph(SPhOMe)<sub>6</sub>. **Spectrum 2 (green):** one of the column fraction containing a mixture of mixed asterisks. The column fraction might contain a small amount of Ph(PhOMe)<sub>6</sub> and several mixed asterisks. No starting material could be found in any column fractions. **Spectrum 3 (blue):** reference Ph(SPhCN)<sub>6</sub>.

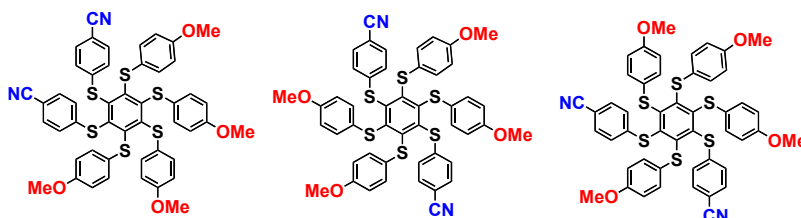
## LC-HRMS analysis of the crude mixture



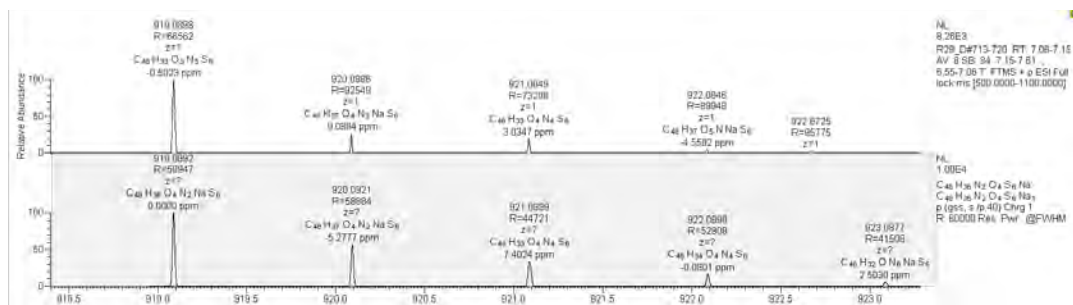
**LC-Chromatogram (R-29)**

### 4 Substitutions with *p*-MeOPhSH:

**HRMS (ESI+)** calculated for  $[C_{48}H_{36}O_4N_2+Na^+]$ : 919.0892 Da, found  $[M+Na^+]$  919.0898 m/z;  
Possible isomers:



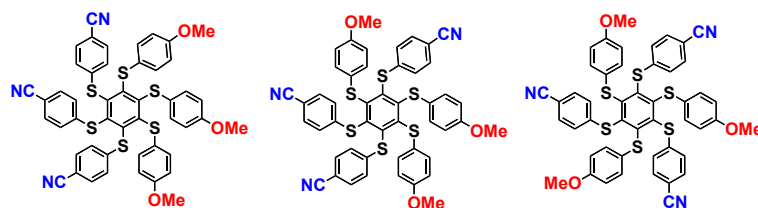
### 4 substitutions of *p*-MeOPhSH ( $C_{48}H_{36}O_4N_2NaS_6$ )



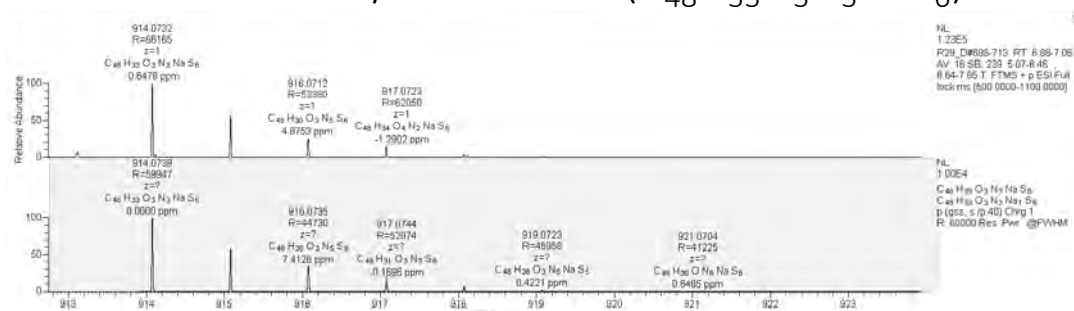
### 3 Substitutions with *p*-MeOPhSH:

**HRMS (ESI+)** calculated for  $[C_{48}H_{33}O_3N_3+Na^+]$ : 914.0738 Da, found  $[M+Na^+]$  914.0732 m/z

Possible isomers:



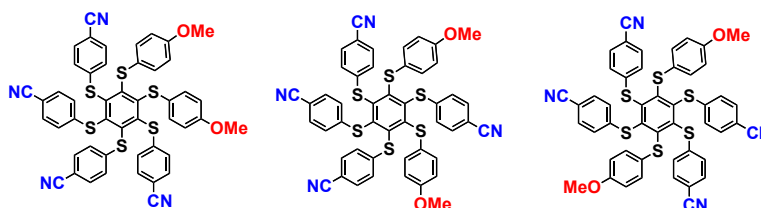
3 substitutions of *p*-MeOPhSH ( $C_{48}H_{33}O_3N_3NaS_6$ )



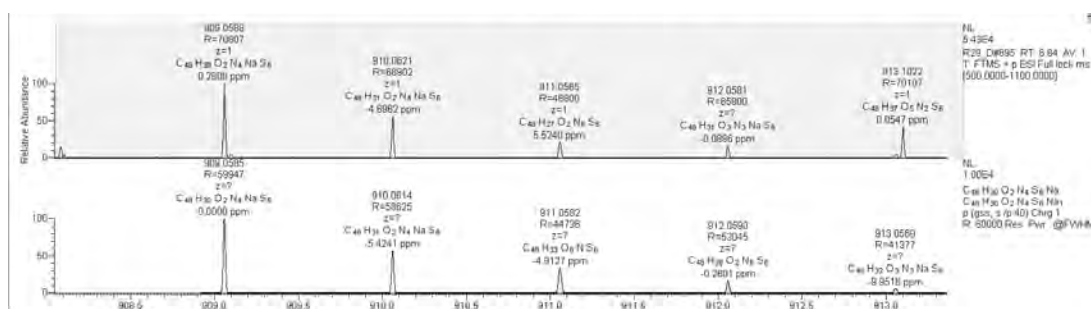
**2 Substitutions with *p*-MeOPhSH:**

**HRMS (ESI+)** calculated for  $[C_{48}H_{33}O_2N_4+Na^+]$ : 909.0585 Da, found  $[M+Na^+]$  909.0588 m/z.

Possible isomers:

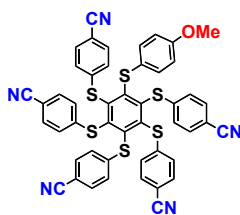


2 substitutions of *p*-MeOPhSH ( $C_{48}H_{30}O_2N_4NaS_6$ )

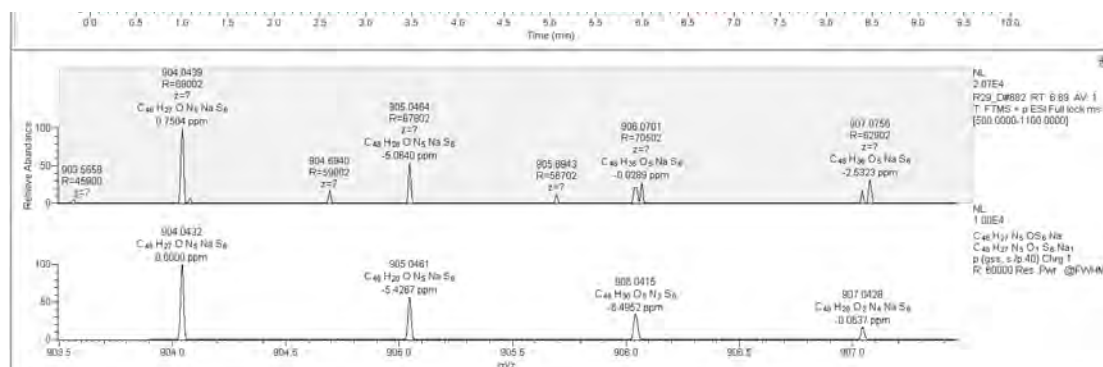


**1 Substitution with *p*-MeOPhSH:**

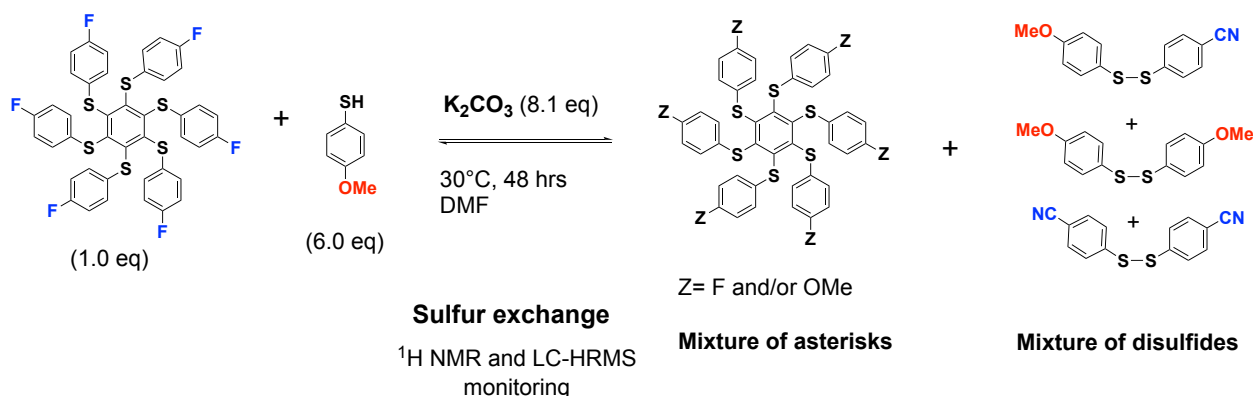
**HRMS (ESI+)** calculated for  $[C_{48}H_{33}O_1N_5+Na^+]$ : 904.0432 Da, found  $[M+Na^+]$  904.0439 m/z;



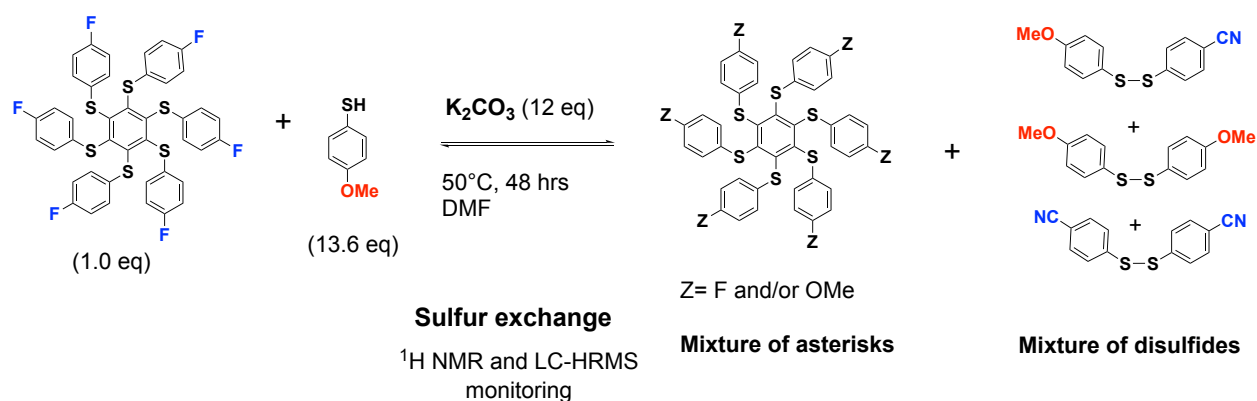
1 substitution of *p*-MeOPhSH ( $C_{48}H_{27}ON_5NaS_6$ )



### SULFUR EXCHANGE REACTIONS WITH HEXAKIS(4-FLUOROPHENYLTHIO)BENZENE



**(R-66) Procedure.** In an oven-dried tube, purged with argon, was added hexakis (4-fluorophenylthio)benzene (15.1 mg, 0.0181 mmol, 1.00 mol-eq.), dried potassium carbonate (20.3 mg, 0.0147 mmol, 8.12 mol-eq.) and 4-methoxythiophenol (15.1 mg, 0.108 mmol, 13.2  $\mu$ L, 5.97 mol-eq.) in dry DMF (0.6 mL, dried and kept over 3Å molecular sieves). Argon was bubbled through the mixture for 5-10 min.. The tube was sealed and the reaction was vigorously stirred at 30°C (water bath temperature) for 43 hrs. The reaction was monitored by TLC ( $SiO_2$ , 50% and 80% tol/cyclohex). After 43 hrs, 4 spots were observed under UV-vis lamp on TLC plates (eluent: 50% and 80% tol/cyclohex). To the reaction mixture was added toluene (20 mL) and water (20 mL). The organic phase was kept and further washed with  $H_2O$  (3×20 mL) for removing DMF. It was dried over anhydrous  $MgSO_4$ , filtered and evaporated. The crude product was analyzed. The components of the mixture were separated by column chromatography over  $SiO_2$  by using an increasing polarity of eluent from 10% toluene in cyclohexane (v/v) to 100% toluene.

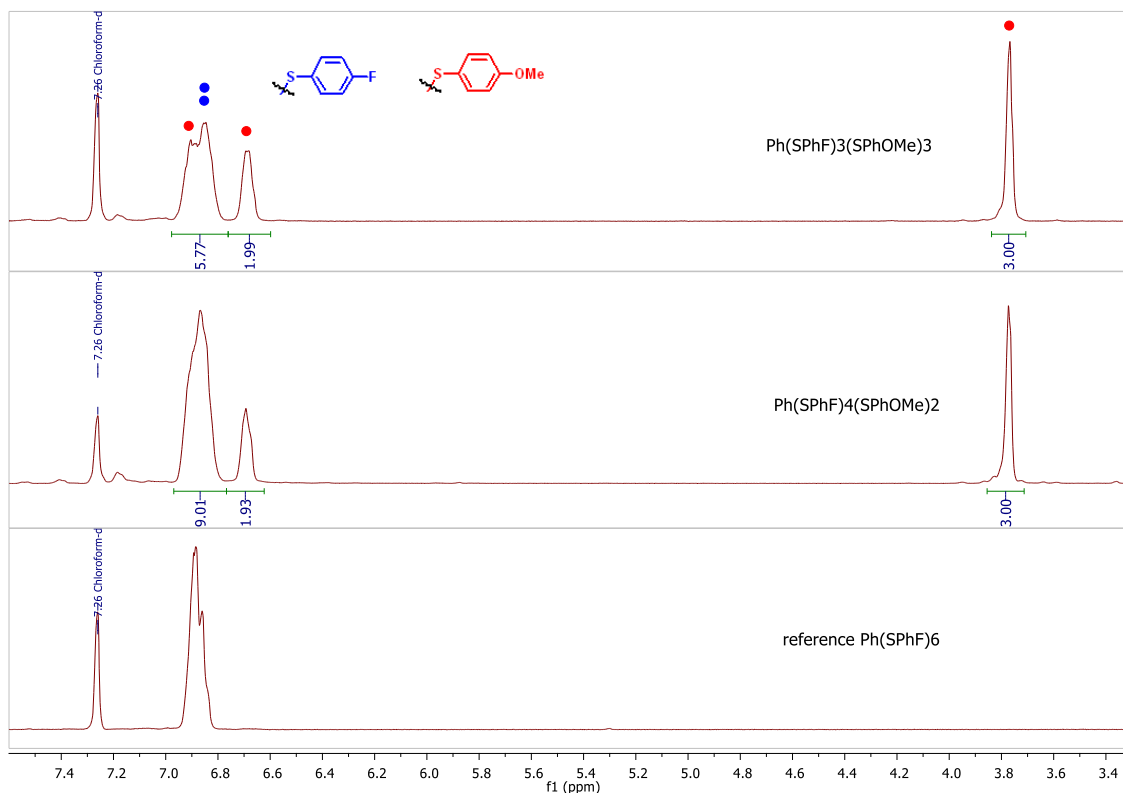


**(R-74) Procedure.** In an oven-dried tube, purged with argon, was added hexakis (4-fluorophenylthio)benzene (10.0 mg, 0.0119 mmol, 1.00 mol-eq.), dried potassium carbonate (20.0 mg, 0.0144 mmol, 12 mol-eq.) and 4-methoxythiophenol (22.8 mg, 0.163 mmol, 20  $\mu\text{L}$ , 13.6 mol-eq) in dry DMF (0.25 mL, dried and kept over 3Å molecular sieves). Argon was bubbled through the mixture for 5-10 min.. The tube was sealed and the reaction was vigorously stirred at 50°C for 48 hrs. The reaction was monitored by TLC ( $\text{SiO}_2$ , 50% and 80% tol/cyclohex). After 48 hrs 7 spots were observed under UV-vis lamp (eluent: 80% tol/cyclohex). To the reaction mixture was added toluene (20 mL) and water (20 mL). The organic phase was kept and further washed with  $\text{H}_2\text{O}$  (3×20 mL) for removing DMF. It was dried over anhydrous  $\text{MgSO}_4$ , filtered and evaporated. The crude product was analyzed. Mass obtained: 8.6 mg. The components of the mixture were separated by column chromatography over  $\text{SiO}_2$  by using an increasing polarity of eluent from 10% toluene in cyclohexane (v/v) to 100% toluene.

### $^1\text{H}$ NMR monitoring and analysis of the mixture

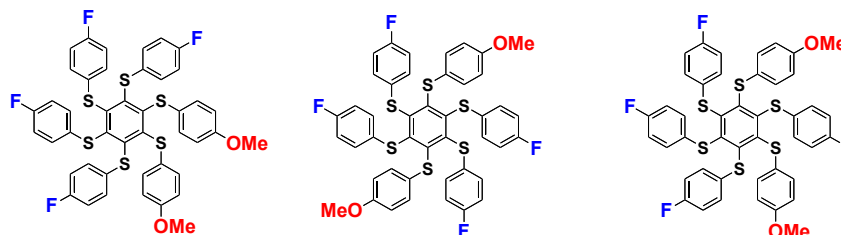
Although no mixed disulfide could be isolated from this reaction, the starting hexakis(4-fluorophenylthio)benzene was consumed and two mixed asterisks were isolated. A tentative structural assignment is proposed from the NMR integration area in the aromatic region as well as in the aliphatic region. The low resolution does not allow to ascertain the number of regioisomers per fraction nor the symmetry of the molecules. In short, we observed two and three substitutions with *p*-MeOPhSH:





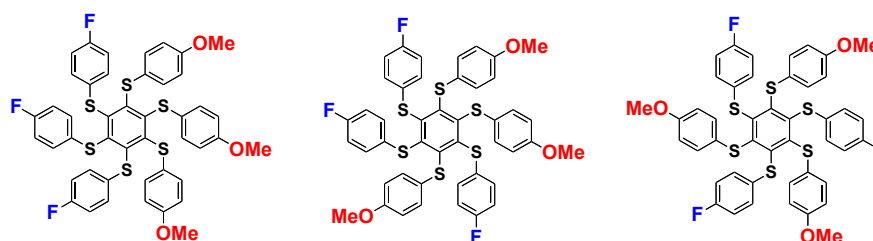
## 2 substitutions of *p*-MeOPhSH

Possible regioisomers:



## 3 substitutions of *p*-MeOPhSH

Possible regioisomers:

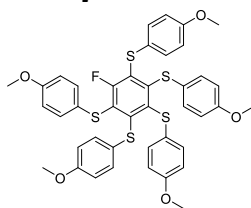


## LC-HRMS analysis of the crude mixture

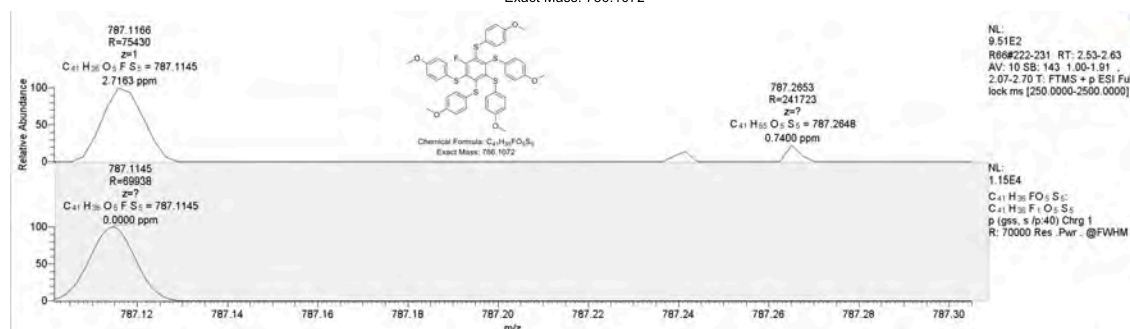
R-66 Sulfur exchanges at 30°C with *p*-OMePhSH:  
LC-Chromatogram

## 5 Substitutions with *p*-MeOPhSH:

HRMS (ESI+) calculated for  $[C_{41}H_{35}O_5FS_5 + H^+]$ : 787.1145 Da, found  $[M+H^+]$  787.1166 m/z;



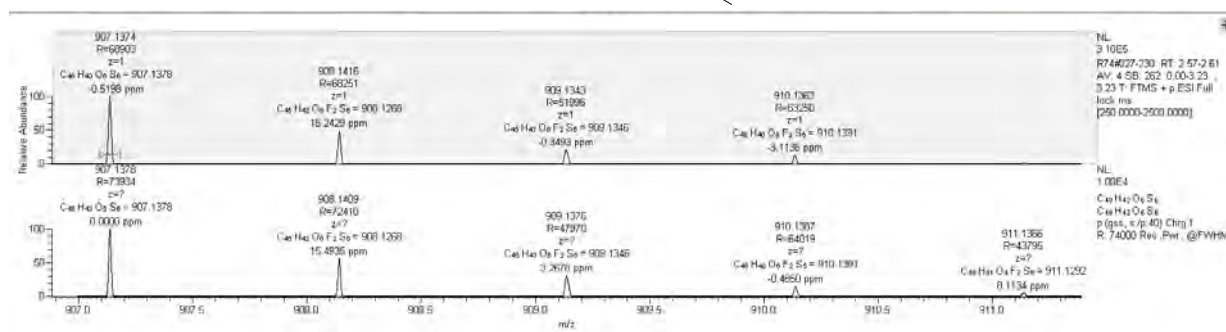
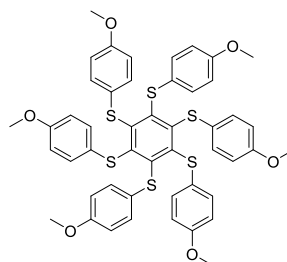
Chemical Formula:  $C_{41}H_{35}FO_5S_5$   
Exact Mass: 786.1072



## R-74 Sulfur exchanges at 50°C : LC-Chromatogram

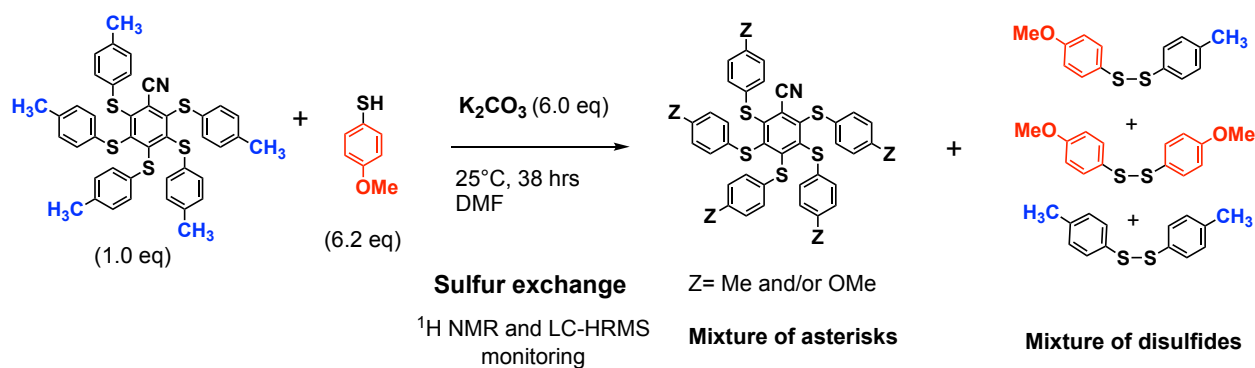
## 6 Substitutions with *p*-MeOPhSH:

HRMS (ESI+) calculated for  $[C_{48}H_{42}O_6S_6 + H^+]$ : 907,1378 Da, found  $[M+H^+]$  907,1374 m/z;



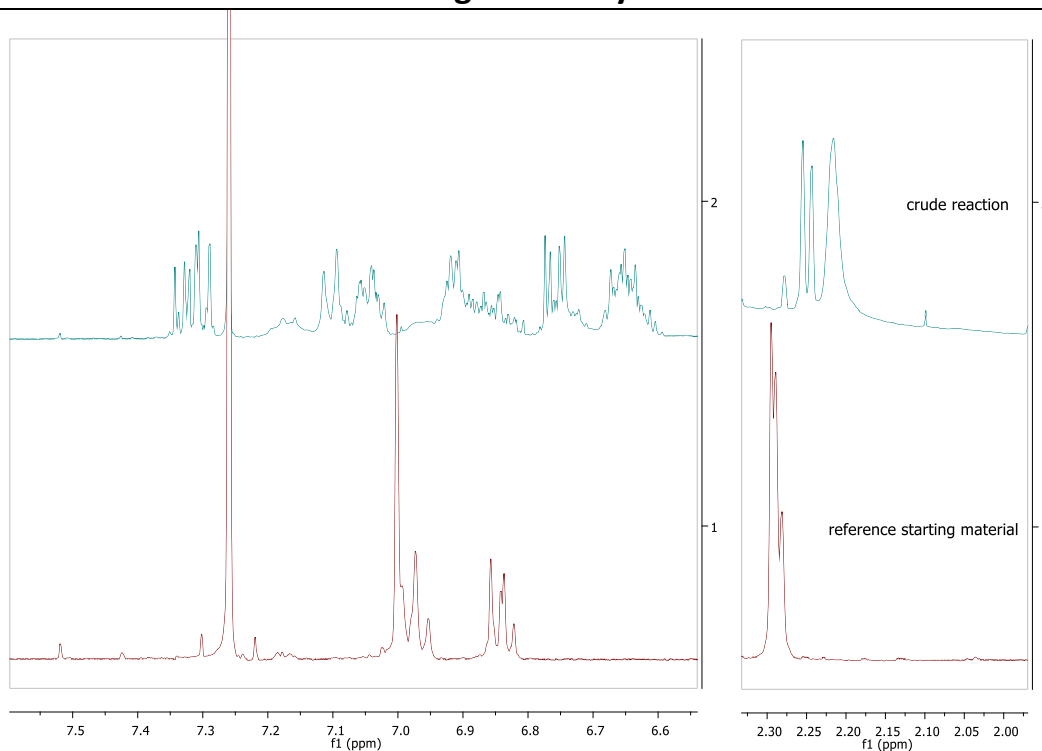
## 4.0 Sulfur exchange reactions on penta(thio) benzene asterisks

### SULFUR EXCHANGE REACTIONS WITH 1-CYANO-2,3,4,5,6-PENTAKIS(4-PHENYLTHIO) BENZENE



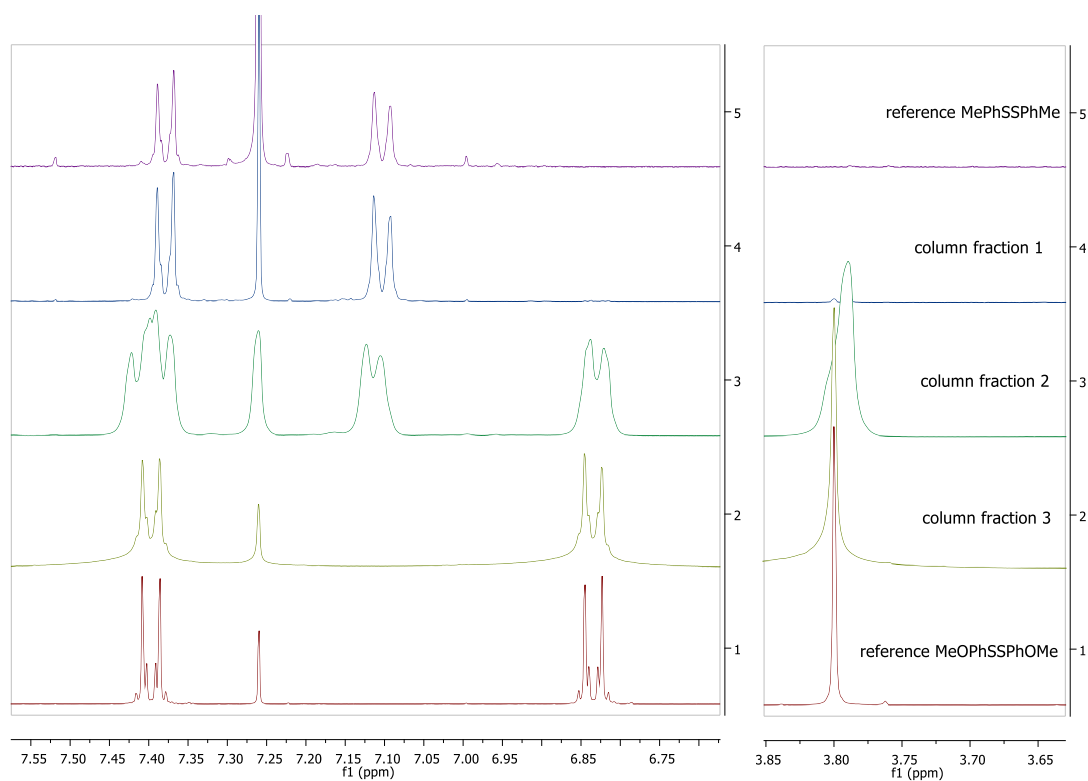
**(R-37) Procedure.** In an oven-dried tube, purged with argon, was added 1-cyano-2,3,4,5,6-pentakis(4-phenylthio)benzene (40.9 mg, 0.0573 mmol, 1.00 mol-eq.), dried potassium carbonate (47.9 mg, 0.346 mmol, 6.03 mol-eq.) and 4-methoxybenzenethiol (49 mg, 0.35mmol, 43 $\mu$ L, 6.2 mol-eq.) in dry DMF (0.5 mL dried with molecular sieves 3 $\text{Å}$ ). Argon was bubbled through the mixture for 5-10 min.. The tube was sealed and the reaction was vigorously stirred at 25°C for 38 hrs. Six TLC spots (SiO<sub>2</sub>, eluent: tol/cyclohex. 80:20 v/v) were observed by UV-vis. The three less polar spots correspond to disulfides. The fourth yellow spot which was slightly more polar, and other polar spots, correspond to some asterisks. The mixture was taken up in toluene (10 mL) and water (10 mL). The organic phase was separated and further washed with water (4x10mL). The organic phase was dried over anhydrous MgSO<sub>4</sub>, filtered and evaporated; mass of the crude mixture: 56.7 mg. Separation of the components in the crude mixture was achieved by column chromatography over silica gel, by using an increasing polarity of the eluent, starting from 30% toluene/70% cyclohexane to 100% toluene, and then to 5% EtOAc in toluene.

### <sup>1</sup>H NMR monitoring and analysis of the mixture



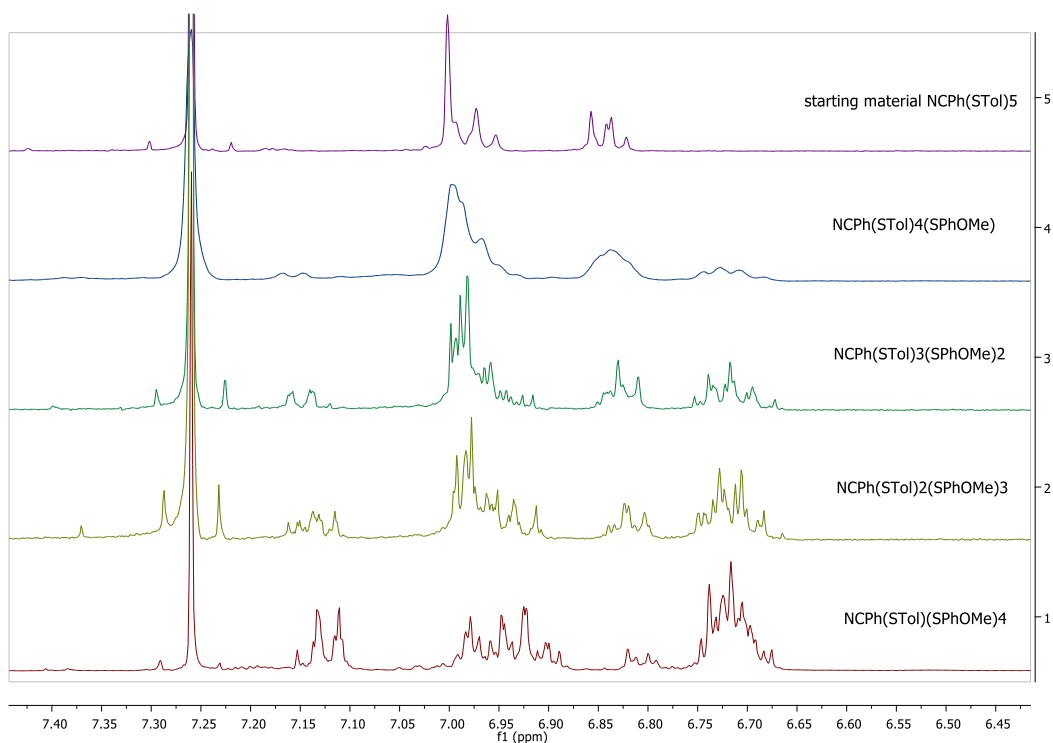
<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 399.78 MHz). **Spectrum 1 (red):** reference 1-cyano-pentakis(4-phenylthio)benzene. **Spectrum 2 (blue):** crude reaction mixture; all the starting material was

consumed after 38 hrs at 25°C. However, the presence of DMF in the crude mixture might induce some chemical shifts.



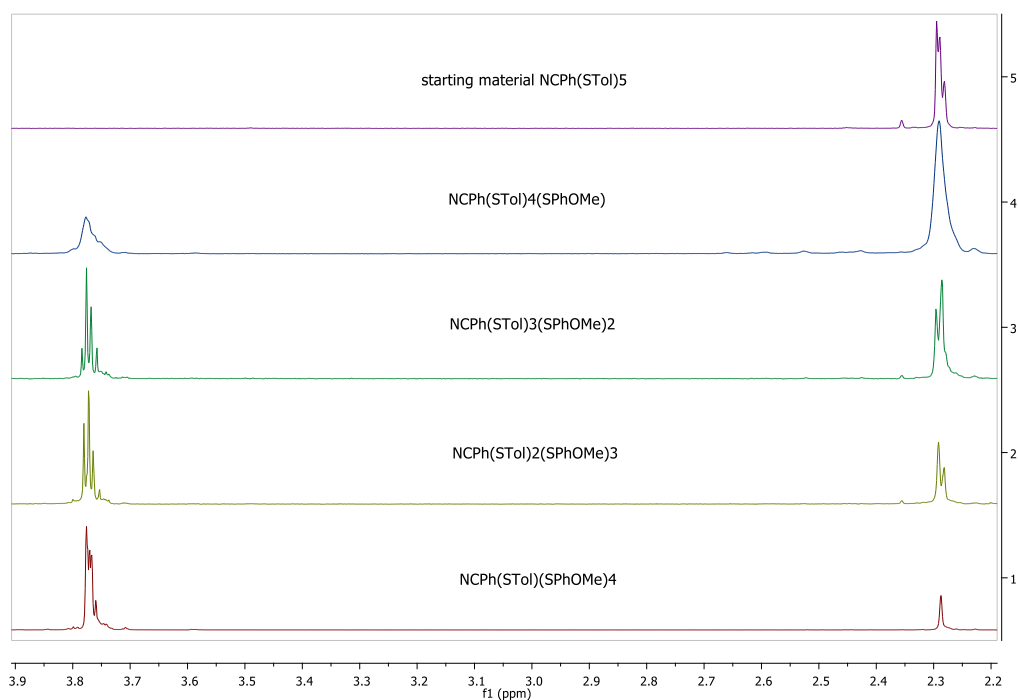
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 399.78 MHz). **Spectrum 1 (red)**: reference disulfide (*p*-MeOPhS)<sub>2</sub>. **Spectrum 2 (brown)**: column fraction 3 (more polar). **Spectrum 3 (green)**: column fraction 3 corresponds to the unsymmetrical disulfide (*p*-MePhS)-(S-*p*-MeOPh). **Spectrum 4 (blue)**: column fraction 4. **Spectrum 5 (violet)**: reference disulfide (*p*-MePhS)<sub>2</sub>. The first three fractions correspond to the disulfides. The first fraction contains only symmetrical (*p*-MePhS)<sub>2</sub> while the third one contains only the symmetrical (*p*-MeOPhS)<sub>2</sub>. The second fraction corresponds to the mixed disulfide (*p*-MePhS)-(S-*p*-MeOPh) with some symmetrical (*p*-MeOPhS)<sub>2</sub> as can be seen, thanks to the shoulder of the methoxy signal (CH<sub>3</sub>O).

**Conclusion:** The presence of the mixed disulfide (*p*-MePhS)-(S-*p*-MeOPh) as well as the symmetrical (*p*-MePhS)<sub>2</sub> disulfide demonstrates the exchange of sulfur substituents on the starting material 1-cyano-pentakis(4-phenylthio)benzene at 25°C.



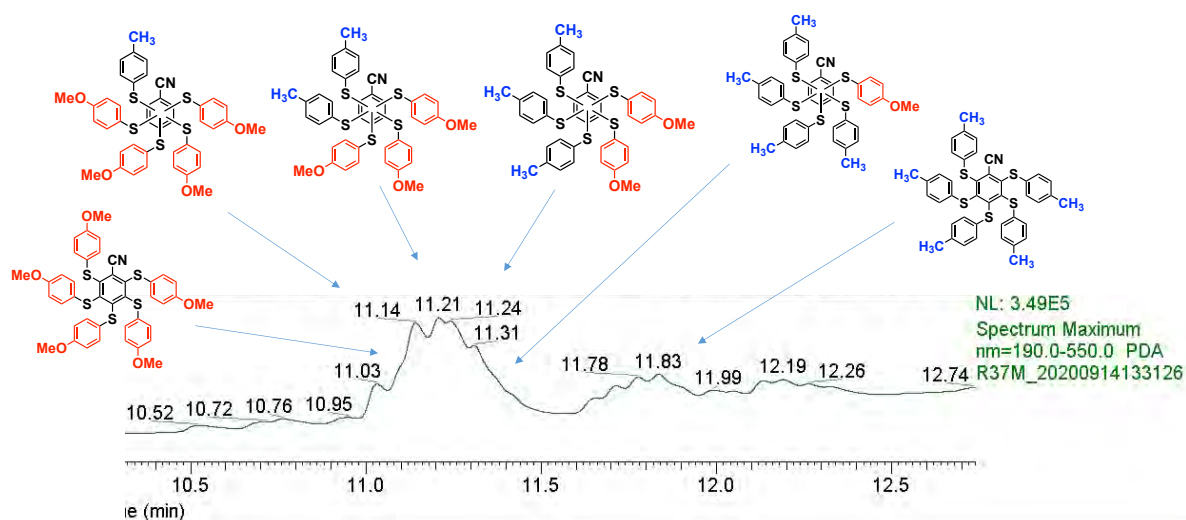
**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 399.78 MHz). <sup>1</sup>H-NMR spectra of the aromatic region of many isolated fractions indicated a complex mixture of asterisks incorporating various number of SPhOMe substituents. **Spectrum 1 (red)**: four SPhOMe substituents. **Spectrum 2 (yellow-green)**: three SPhOMe substituents. **Spectrum 3 (green)**: two SPhOMe substituents. **Spectrum 4 (blue)**: one SPhOMe substituent. **Spectrum 5 (violet)**: starting 1-cyano-pentakis(4-phenylthio)benzene.

**Conclusion:** even though the exact isomeric structure of some asterisk compounds cannot be proposed with certainty, these spectra clearly and unambiguously demonstrate sulfur exchange reactions occurring with starting 1-cyano-pentakis(4-phenylthio)benzene at 25°C leading to a library of asterisks containing various ratio of SPhOMe substituents.



<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 399.78 MHz). <sup>1</sup>H-NMR of the methyl and methoxy groups of different isolated fractions. The assignment is attempted thanks to the relative integration of these <sup>1</sup>H NMR signals. **Conclusion:** even though the exact isomeric structure of some asterisk compounds cannot be proposed with certainty, these spectra clearly and unambiguously demonstrate sulfur ligands exchange reactions occurring with starting 1-cyano-pentakis(4-phenylthio)benzene at 25°C as a penta(thio) benzene asterisk.

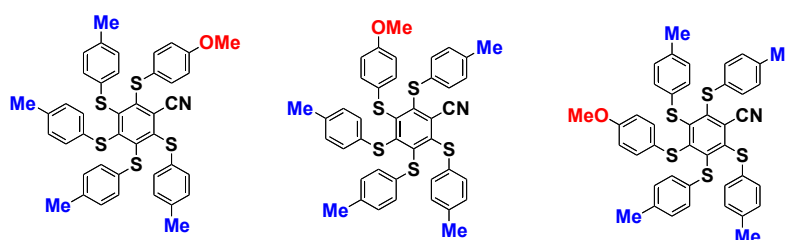
### LC-HRMS analysis of the crude mixture



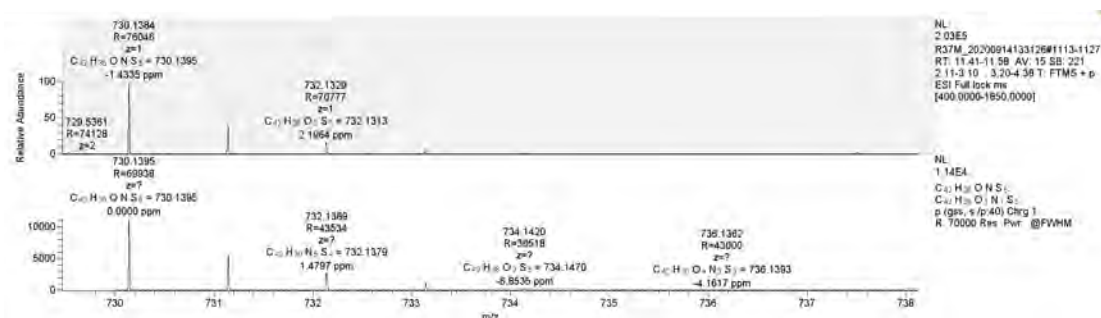
### LC-Chromatogram of the crude (R-37)

#### 1 Substitution with *p*-MeOPhSH:

HRMS (ESI+) calculated for [C<sub>42</sub>H<sub>35</sub>ONS<sub>5</sub> + H<sup>+</sup>]: 730.1395 Da, found [M+H<sup>+</sup>] 730.1384 m/z;  
Possible isomers:



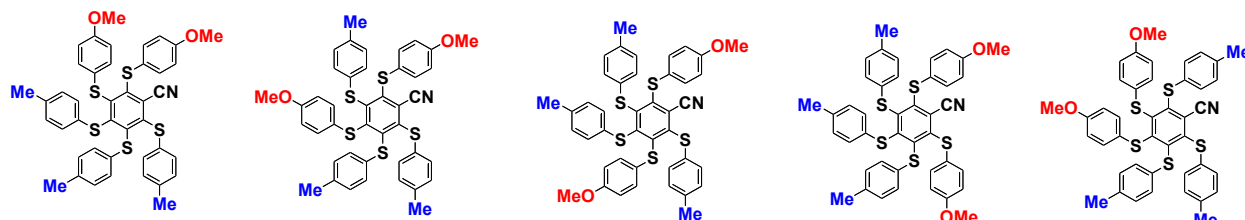
#### 1 substitution by *p*-MeOPhSH (C<sub>42</sub>H<sub>36</sub>ONS<sub>5</sub>)



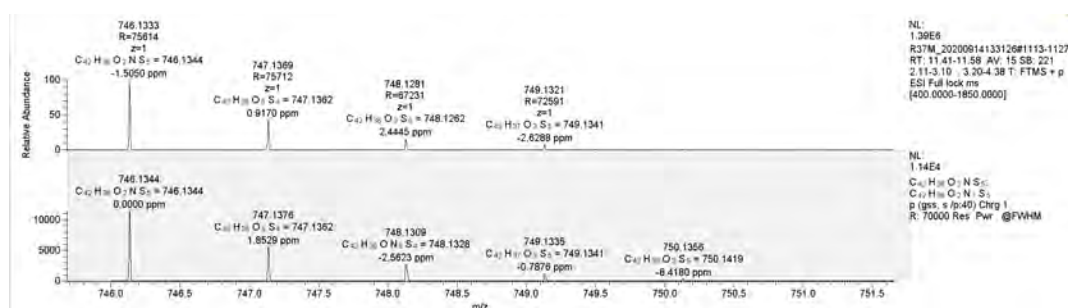
## 2 Substitutions with *p*-MeOPhSH:

HRMS (ESI+) calculated for  $[C_{42}H_{35}O_2NS_5 + H^+]$ : 746.1344 Da, found  $[M+H^+]$  746.1333 m/z;

Possible isomers:



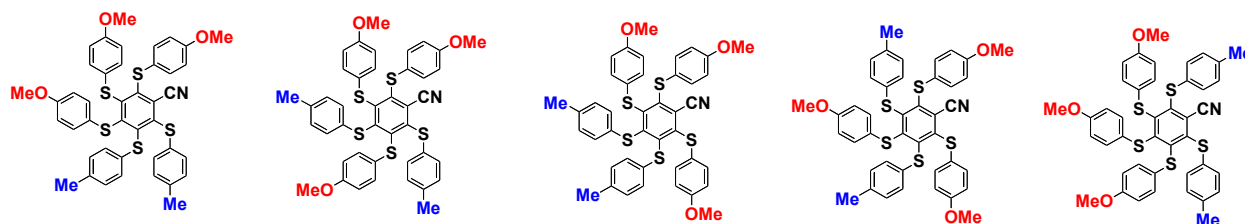
## 2 substitutions by *p*-MeOPhSH ( $C_{42}H_{36}O_2NS_5$ )



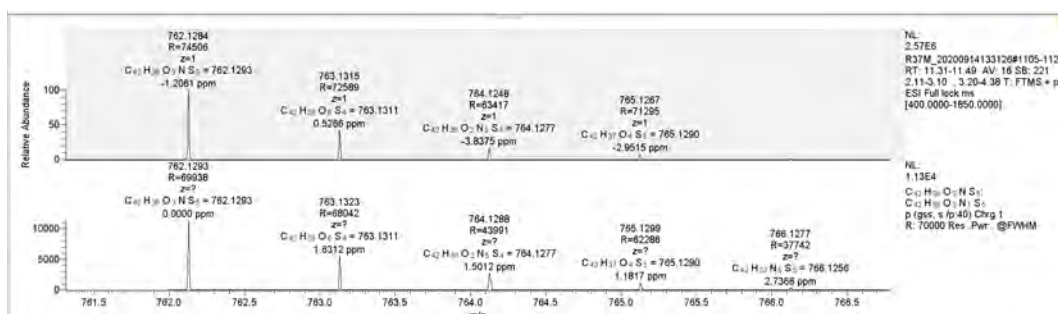
## 3 Substitutions with *p*-MeOPhSH:

HRMS (ESI+) calculated for  $[C_{42}H_{35}O_3NS_5 + H^+]$ : 762.1293 Da, found  $[M+H^+]$  762.1284 m/z;

Possible isomers:

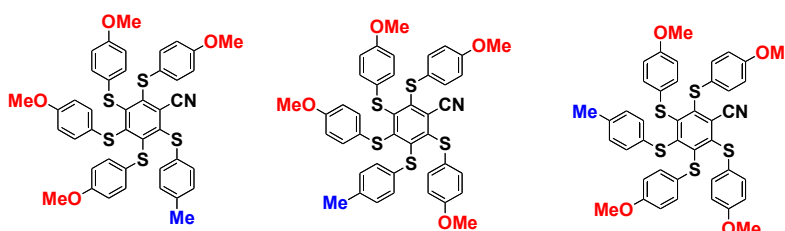


## 3 substitutions by *p*-MeOPhSH ( $C_{42}H_{36}O_3NS_5$ )

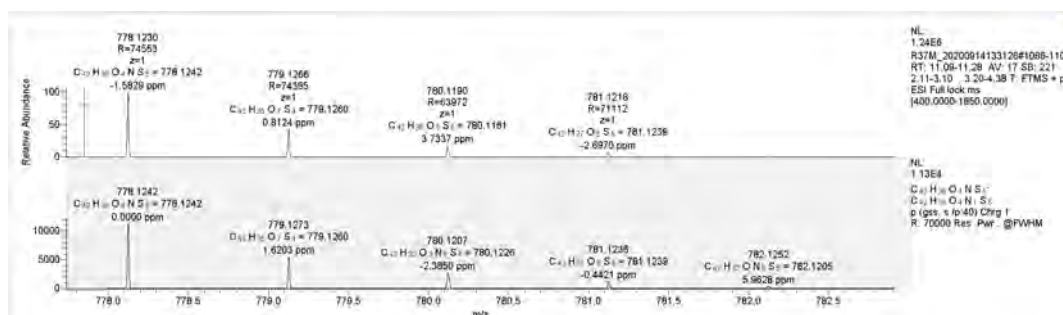


#### 4 Substitutions with *p*-MeOPhSH:

HRMS (ESI+) calculated for  $[C_{42}H_{35}O_4NS_5 + H^+]$ : 778.1242 Da, found  $[M+H^+]$  778.1230 m/z;  
Possible isomers:

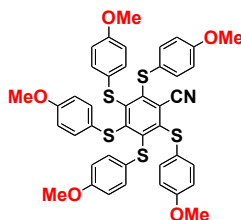


4 substitutions by *p*-MeOPhSH ( $C_{42}H_{36}O_4NS_5$ )

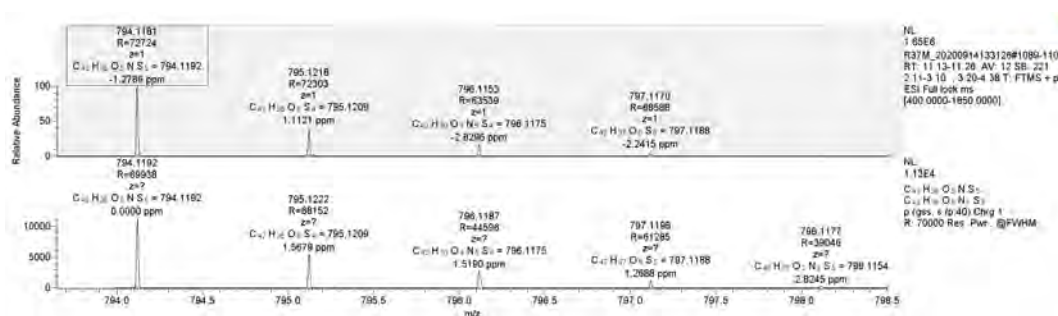


#### 5 Substitutions with *p*-MeOPhSH:

HRMS (ESI+) calculated for  $[C_{42}H_{35}O_5NS_5 + H^+]$ : 794.1192 Da, found  $[M+H^+]$  794.1181 m/z;  
Possible isomers:

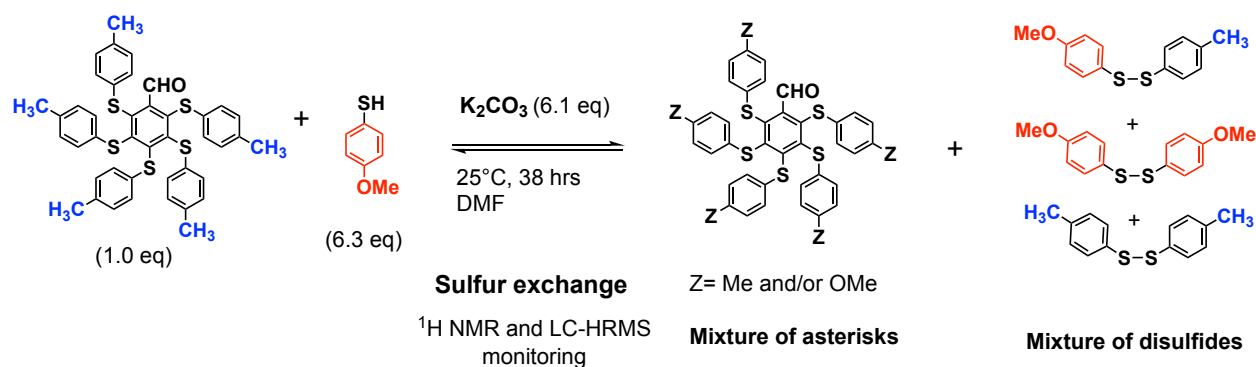


5 substitutions by *p*-MeOPhSH ( $C_{42}H_{36}O_5NS_5$ )



**SULFUR EXCHANGE REACTIONS WITH PENTAKIS (4-METHYL-PHENYLTHIO) BENZALDEHYDE**

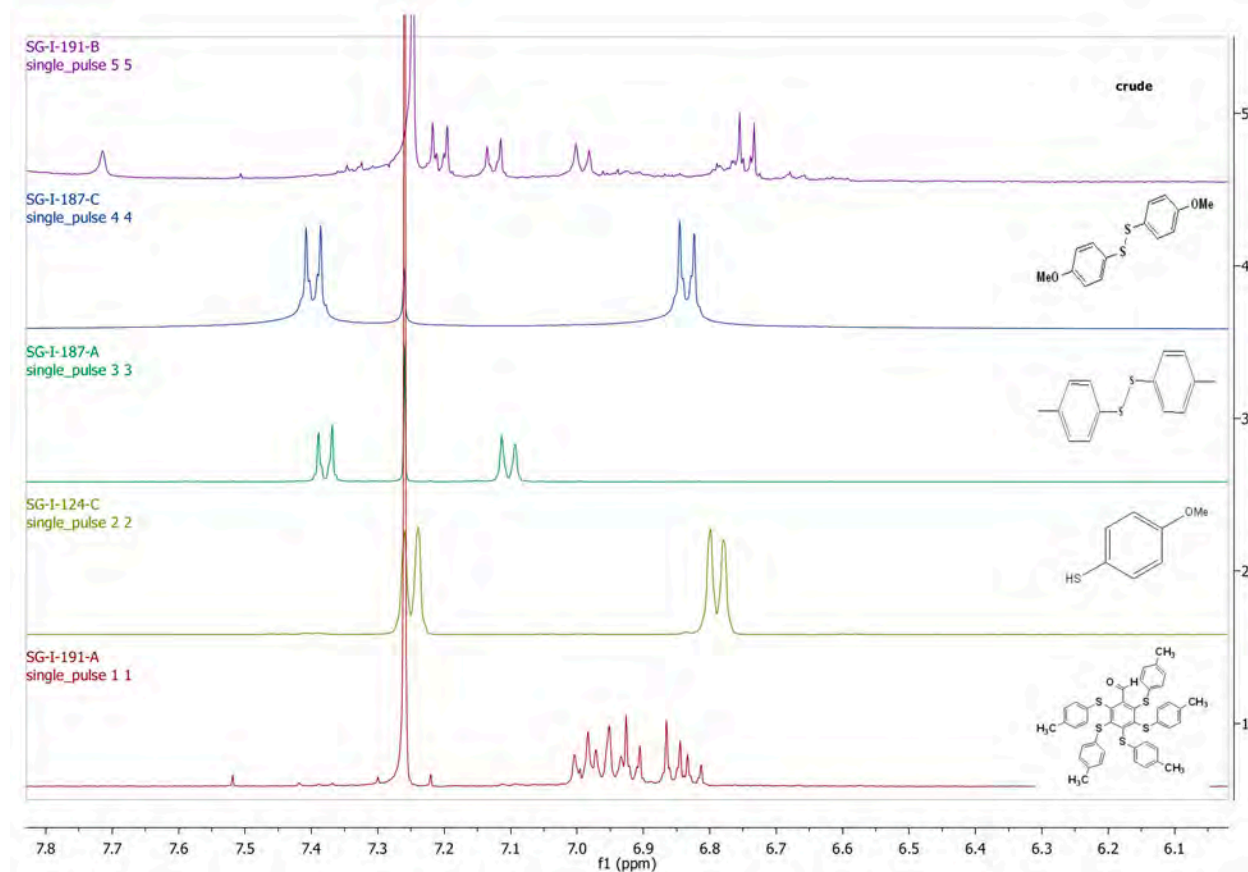




**(R-38) Procedure.** In an oven-dried tube, purged with argon, was added pentakis(4-methylphenylthio)benzaldehyde (40.0 mg, 0.0558 mmol, 1.00 mol-eq.), dried potassium carbonate (46.9 mg, 0.340 mmol, 6.09 mol-eq.) and 4-methoxythiophenol (49.0 mg, 0.349 mmol, 43  $\mu\text{L}$ , 6.3 mol-eq.) in dry DMF (0.5 mL, dried and kept over activated 3 $\text{\AA}$  molecular sieves). Argon was bubbled through the mixture for 5-10 min.. The tube was sealed and the reaction was vigorously stirred at 25 $^{\circ}\text{C}$  for 38 hrs. The consistency of the original mixture changed quickly over time. The mixture was taken up in toluene (10 mL) and water (10 mL). The organic phase was separated and further washed with water (3 $\times$ 10 mL). The organic phase was dried over anhydrous  $\text{MgSO}_4$ , filtered and evaporated; mass of the crude product: 60.9 mg.

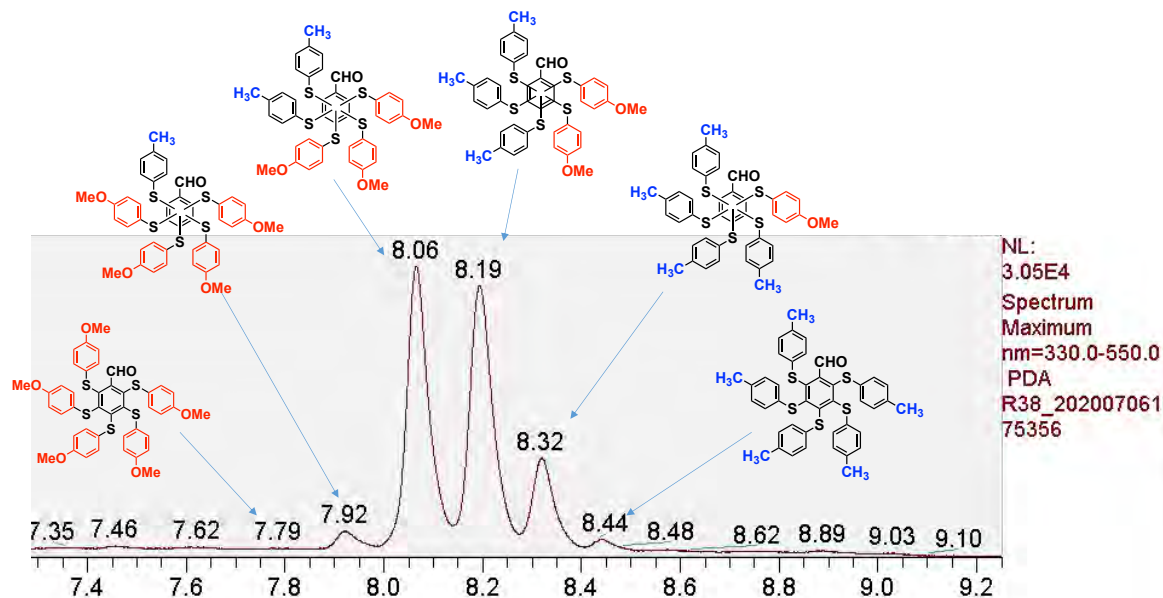
**NMR results:**  $^1\text{H}$  NMR (399.78 MHz,  $\text{CDCl}_3$ , **SG-I-191-B**) indicates many exchanges of ligands at 25 $^{\circ}\text{C}$  in DMF. A mixture of asterisks containing OMe and Me groups was formed.

**Reference NMR:**  $^1\text{H}$  NMR (**SG-I-191-A**):  $^{13}\text{C}$  NMR (**SG-I-191-C**)



$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 399.78 MHz)

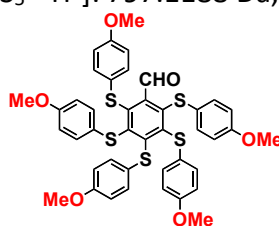
### LC-HRMS analysis of the crude mixture



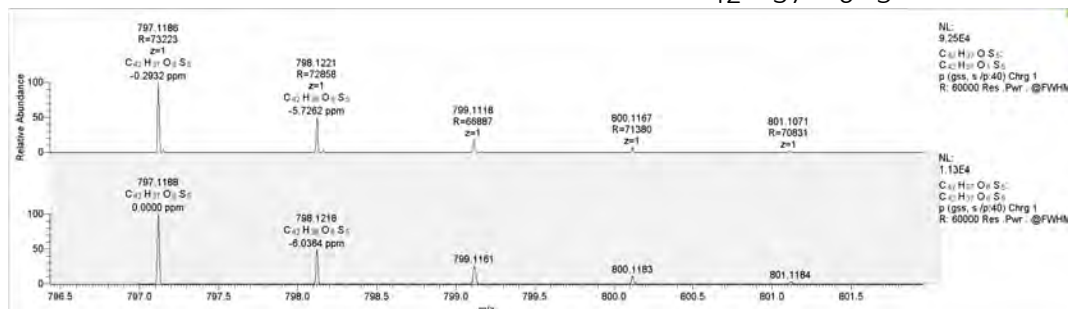
### LC-Chromatogram (R-38)

#### 5 Substitutions:

HRMS (ESI+) calculated for  $[\text{C}_{42}\text{H}_{36}\text{O}_6\text{S}_5 + \text{H}^+]$ : 797.1188 Da, found  $[\text{M} + \text{H}^+]$  797.1186 m/z;



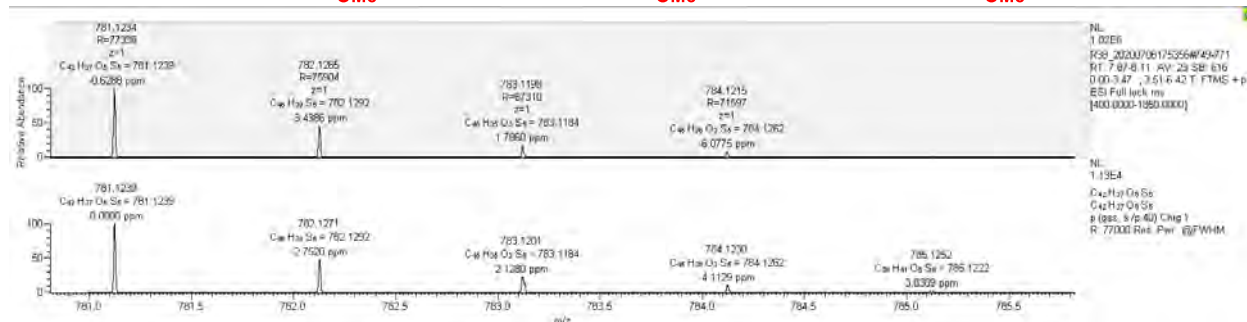
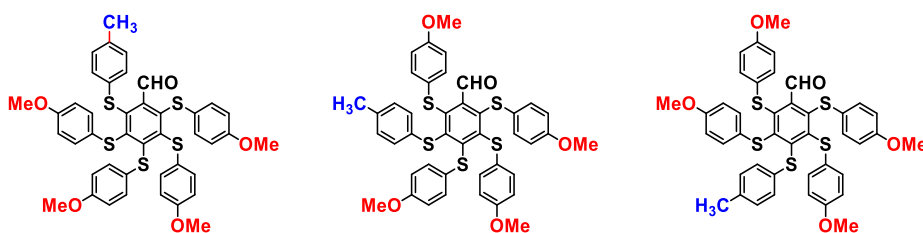
5 substitutions with *p*-MeOPhSH ( $\text{C}_{42}\text{H}_{37}\text{O}_6\text{S}_5$ )



#### 4 substitutions :

HRMS (ESI+) calculated for  $[\text{C}_{42}\text{H}_{36}\text{O}_5\text{S}_5 + \text{H}^+]$ : 781.1239 Da, found  $[\text{M} + \text{H}^+]$  781.1234 m/z;

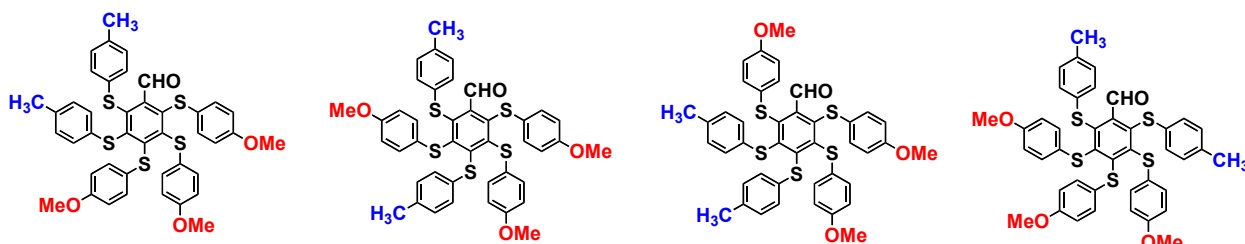
Possible isomers:



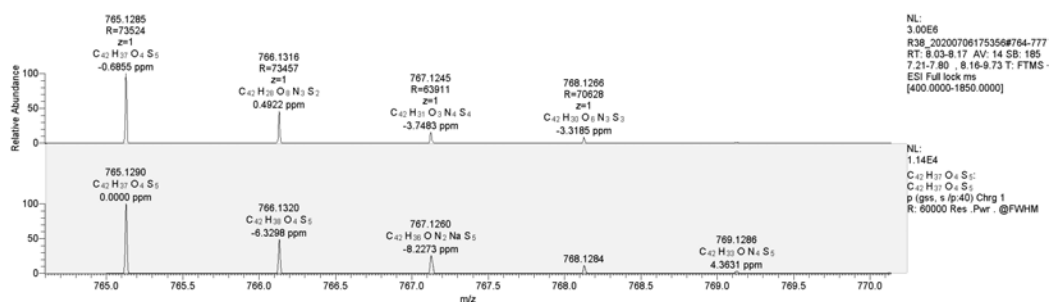
**3 Substitutions:**

**HRMS (ESI+)** calculated for  $[C_{42}H_{36}O_4S_5 + H^+]$ : 765.1290 Da, found  $[M+H^+]$  765.1285 m/z;

Possible isomers:



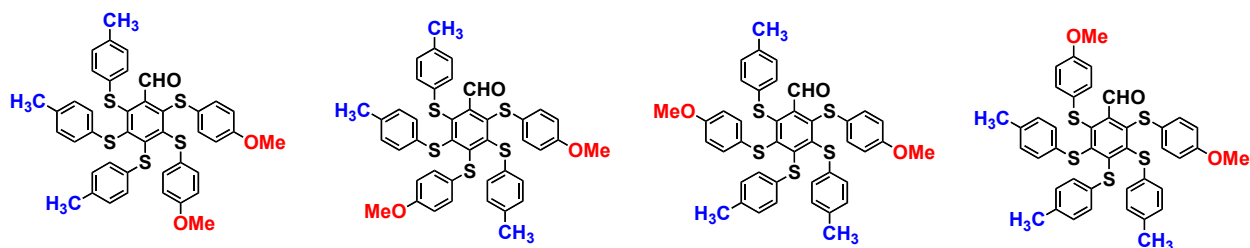
3 substitutions with *p*-MeOPhSH ( $C_{42}H_{37}O_4S_5$ )



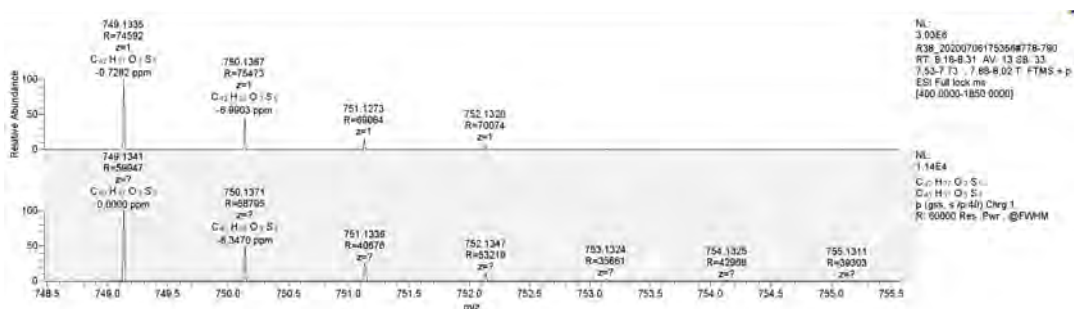
**2 Substitutions:**

**HRMS (ESI+)** calculated for  $[C_{42}H_{36}O_3S_5 + H^+]$ : 749.1341 Da, found  $[M+H^+]$  749.1335 m/z;

Possible isomers:



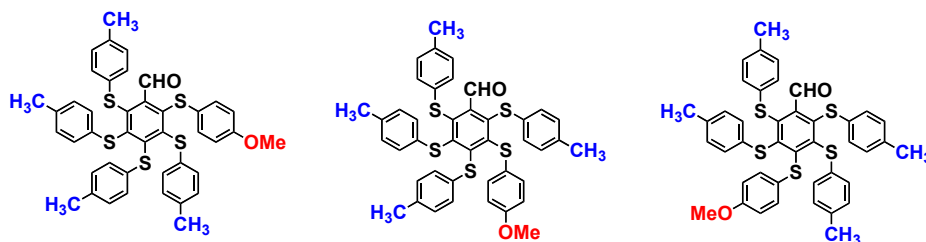
2 substitutions with *p*-MeOPhSH (C<sub>42</sub>H<sub>37</sub>O<sub>3</sub>S<sub>5</sub>)



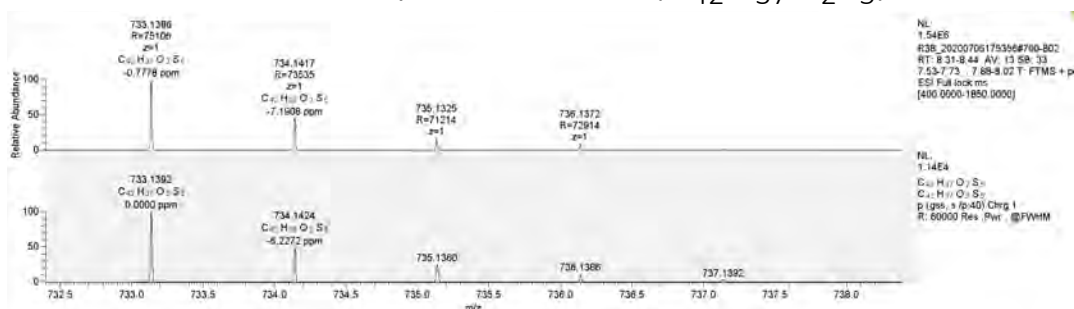
1 substitution:

HRMS (ESI+) calculated for [C<sub>42</sub>H<sub>36</sub>O<sub>2</sub>S<sub>5</sub> + H<sup>+</sup>]: 733.1392 Da, found [M+H<sup>+</sup>] 733.1386 m/z;

Possible isomers:

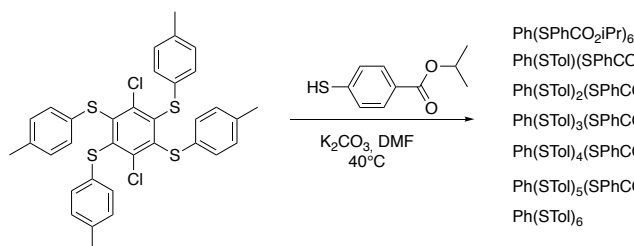


1 substitution with *p*-MeOPhSH (C<sub>42</sub>H<sub>37</sub>O<sub>2</sub>S<sub>5</sub>)



## 5.0 Sulfur exchange reactions on tetra(thio) benzene asterisks

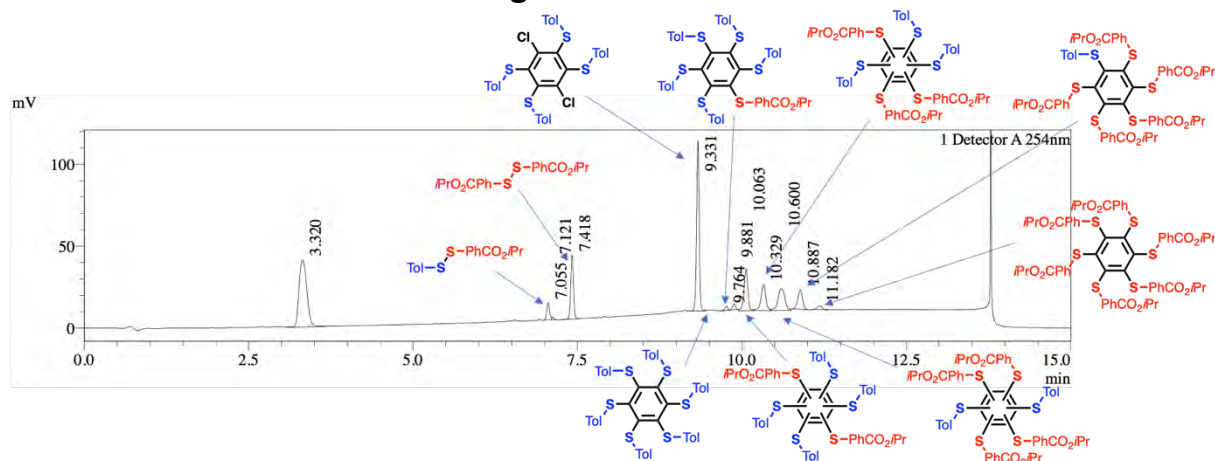
### SULFUR EXCHANGE REACTIONS WITH 1,4-DICHOHO-2,3,5,6-TETRAKIS(4-METHYLPHENYLTHIO)BENZENE



**MV-II-36 Procedure.** In an oven-dried glass tube were placed 1,4-dichloro-2,3,5,6-tetrakis(4-methylphenylthio)benzene (112 mg, 0.176 mmol, 1.00 mol-eq.), isopropyl-4-mercaptobenzoate (73.0 mg, 0.372 mmol, 2.11 mol-eq.) and dry potassium carbonate (77.0 mg, 0.558 mmol, 3.17 mol-eq.) under an argon atmosphere. All reagents were freshly dried under vacuum for about 30 min prior to use them. Under argon, dry DMF (1.0 mL, kept over 3Å molecular sieves) was injected and argon was bubbled through the mixture for about 20 min.. The tube was sealed and the mixture was vigorously stirred at 40°C for 22 hrs. An aqueous HCl solution (1M, 100 mL) was added and it was extracted with toluene (3x25 mL). The combined organic phases were washed with water (5x25 mL), and dried over anhydrous  $\text{MgSO}_4$ . After filtration and evaporation of solvents, a yellow-brown solid was obtained.

### LC-MS analysis of the mixture

#### LC-Chromatogram of the crude mixture

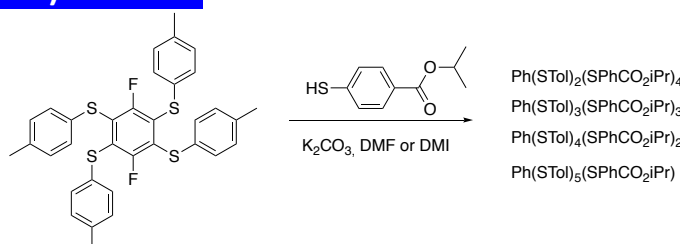


Retention Time	m/z	Formula	Structure	UV %
7.055	318	$[\text{M}]^+ = \text{C}_{17}\text{H}_{18}\text{O}_2\text{S}_2$	$\text{CH}_3\text{PhSSPhCO}_2\text{iPr}$	N/A
7.418	390	$[\text{M}]^+ = \text{C}_{20}\text{H}_{22}\text{O}_4\text{S}_2$	$(\text{CO}_2\text{iPrPhS})_2$	N/A
9.331	635	$[\text{M}+\text{H}]^+ = \text{C}_{34}\text{H}_{28}\text{Cl}_2\text{S}_4$	$\text{PhCl}_2(\text{SPhCH}_3)_4$	44%
9.492	811	$[\text{M}+\text{H}]^+ = \text{C}_{48}\text{H}_{42}\text{S}_6$	$\text{Ph}(\text{SPhCH}_3)_6$	traces
9.764	883	$[\text{M}+\text{H}]^+ = \text{C}_{51}\text{H}_{46}\text{O}_2\text{S}_6$	$\text{Ph}(\text{SPhCH}_3)_5(\text{SPhCO}_2\text{iPr})$	1%
10.063	955	$[\text{M}+\text{H}]^+ = \text{C}_{54}\text{H}_{50}\text{O}_4\text{S}_6$	$\text{Ph}(\text{SPhCH}_3)_4(\text{SPhCO}_2\text{iPr})_2$	15%
10.329	1027	$[\text{M}+\text{H}]^+ = \text{C}_{57}\text{H}_{54}\text{O}_6\text{S}_6$	$\text{Ph}(\text{SPhCH}_3)_3(\text{SPhCO}_2\text{iPr})_3$	12%
10.600	1099	$[\text{M}+\text{H}]^+ = \text{C}_{60}\text{H}_{58}\text{O}_8\text{S}_6$	$\text{Ph}(\text{SPhCH}_3)_2(\text{SPhCO}_2\text{iPr})_4$	14%

10.887	1171	$[M+H]^+ = C_{63}H_{62}O_{10}S_6$	$Ph(SPhCH_3)_1(SPhCO_2iPr)_5$	9%
11.182	1183	$[M-OiPr]^+ = C_{63}H_{59}O_{11}S_6$	$Ph(SPhCO_2iPr)_6$	2%

**Conclusion:** LC-MS data of the mixture indicated a series of mixed asterisks formed with one to six SPhCO<sub>2</sub>iPr substituents (the remaining ones are SPhMe). Some ligand exchanges occur under mild conditions at 40°C. It should be noted that some *p*-MePhS ligands make some exchanges to provide asterisks with five and six *p*-MePhS substituents, clearly demonstrating a "sulfur dance" around the central benzene core.

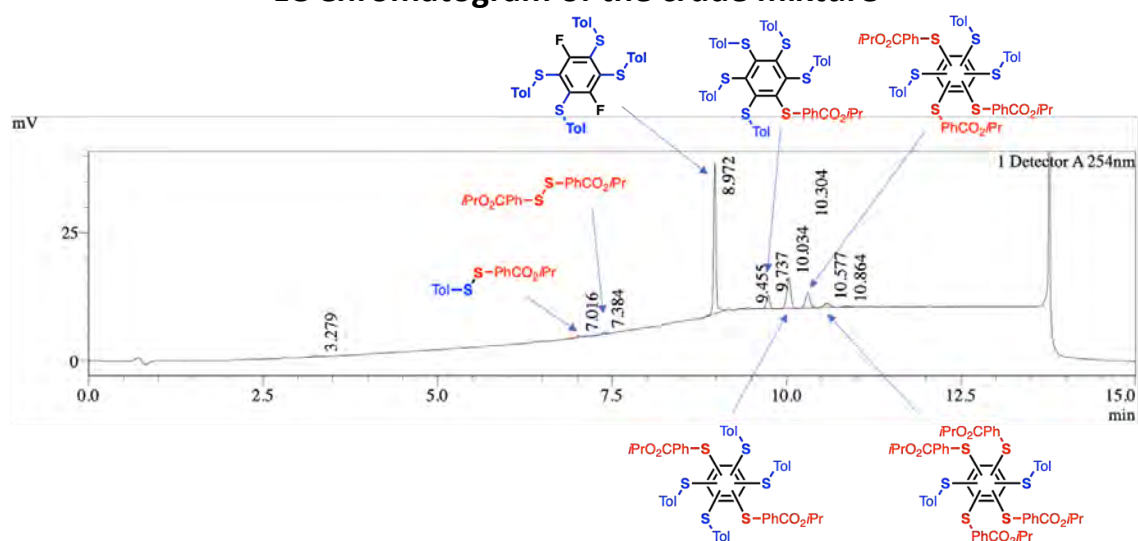
## SULFUR EXCHANGE REACTIONS WITH 1,4-DIFLUORO-2,3,5,6-TETRAKIS(4-METHYLPHENYLTHIO)BENZENE



**Procedure.** In an oven-dried glass tube were placed 1,4-difluoro-2,3,5,6-tetrakis(4-methylphenylthio) benzene (400 mg, 0.66 mmol, 1.00 mol-eq), isopropyl-4-mercaptobenzoate (273 mg, 1.39 mmol, 2.09 mol-eq) and dry potassium carbonate (230 mg, 1.67 mmol, 2.51 mol-eq) under an argon atmosphere. All reagents were freshly dried under vacuum for about 30 min prior to use them. Under argon, dry DMF (5.5 mL, kept over 3Å molecular sieves) was then injected, the tube was sealed and the mixture was vigorously stirred at 40°C for 22 hours. An aqueous HCl solution (1M, 100 mL) was added and it was extracted with toluene (3 x 25 mL). The combined organic phases were washed with water (5 x 25 mL), and dried over anhydrous MgSO<sub>4</sub>. After filtration and evaporation of solvents, a yellow-brown solid was obtained.

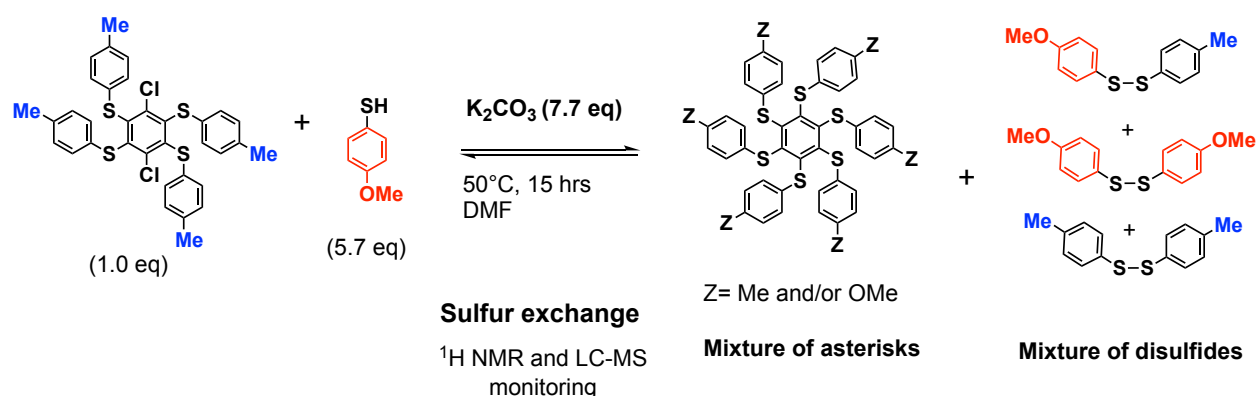
## LC-MS analysis of the mixture

### LC Chromatogram of the crude mixture



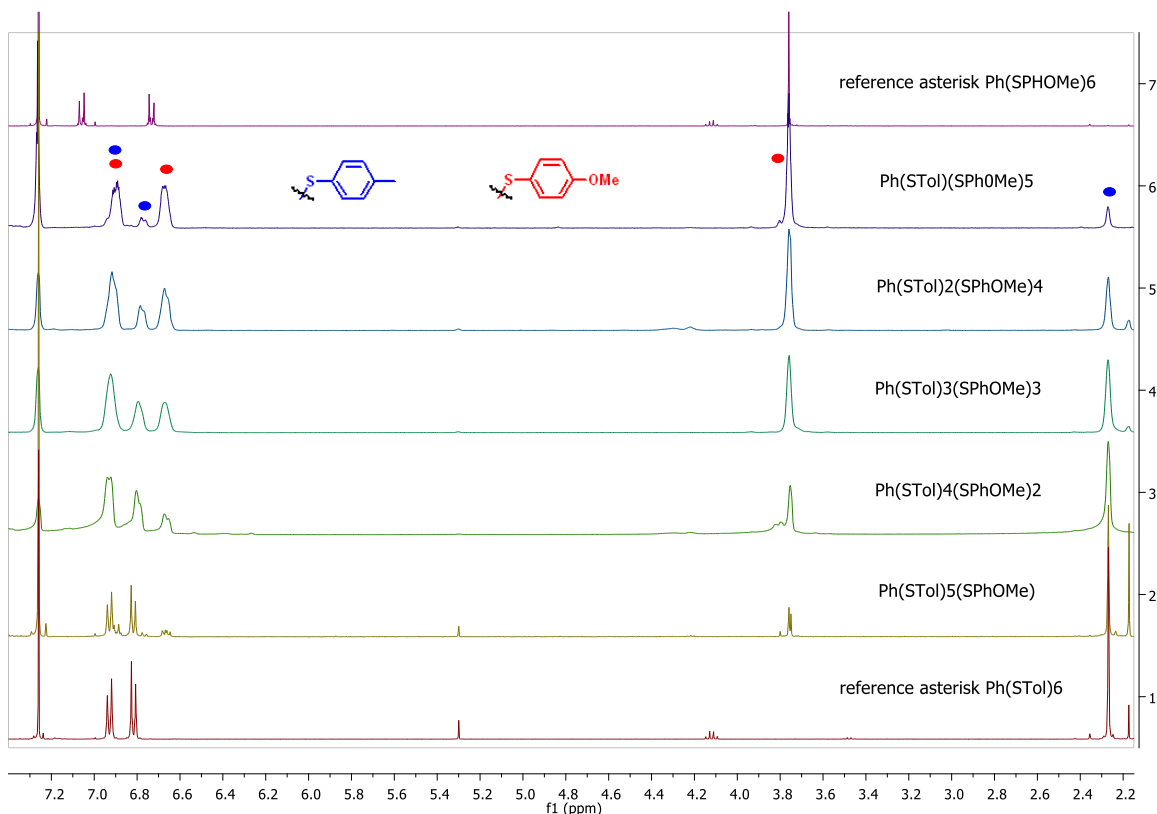
Retention Time	m/z	Formula	Structure	UV %
7.016	318	[M] <sup>+</sup> = C <sub>17</sub> H <sub>18</sub> O <sub>2</sub> S <sub>2</sub>	CH <sub>3</sub> PhSSPhCO <sub>2</sub> iPr	N/A
7.384	390	[M] <sup>+</sup> = C <sub>20</sub> H <sub>22</sub> O <sub>4</sub> S <sub>2</sub>	(CO <sub>2</sub> iPrPhS) <sub>2</sub>	N/A
8.972	603	[M+H] <sup>+</sup> = C <sub>34</sub> H <sub>28</sub> F <sub>2</sub> S <sub>4</sub>	PhF <sub>2</sub> (SPhCH <sub>3</sub> ) <sub>4</sub>	54%
9.737	883	[M+H] <sup>+</sup> = C <sub>51</sub> H <sub>46</sub> O <sub>2</sub> S <sub>6</sub>	Ph(SPhCH <sub>3</sub> ) <sub>5</sub> (SPhCO <sub>2</sub> iPr)	6%
10.034	955	[M+H] <sup>+</sup> = C <sub>54</sub> H <sub>50</sub> O <sub>4</sub> S <sub>6</sub>	Ph(SPhCH <sub>3</sub> ) <sub>4</sub> (SPhCO <sub>2</sub> iPr) <sub>2</sub>	17%
10.304	1027	[M+H] <sup>+</sup> = C <sub>57</sub> H <sub>54</sub> O <sub>6</sub> S <sub>6</sub>	Ph(SPhCH <sub>3</sub> ) <sub>3</sub> (SPhCO <sub>2</sub> iPr) <sub>3</sub>	10%
10.577	1099	[M+H] <sup>+</sup> = C <sub>60</sub> H <sub>58</sub> O <sub>8</sub> S <sub>6</sub>	Ph(SPhCH <sub>3</sub> ) <sub>2</sub> (SPhCO <sub>2</sub> iPr) <sub>4</sub>	4%

## SULFUR EXCHANGE REACTIONS WITH 1,4-DICHLORO-2,3,5,6-TETRAKIS(4-METHYLPHENYLTHIO)BENZENE



**(R-62) Procedure.** In an oven-dried tube, purged with argon, was added 1,4-dichloro-2,3,5,6-tetrakis(*p*-tolylthio) benzene (20.1 mg, 0.0330 mmol, 1.00 mol-eq.), dried potassium carbonate (35.1 mg, 0.254 mmol, 7.70 mol-eq.) and 4-methoxythiophenol (26.4 mg, 0.188 mmol, 23  $\mu$ L, 5.70 mol-eq.) in dry DMF (1.0 mL, dried with 3 $\text{\AA}$  molecular sieves). Argon was bubbled through the mixture for 5-10 min.. The tube was sealed under argon and the reaction was vigorously stirred at 50°C for 15 hrs. To the reaction mixture was added H<sub>2</sub>O (20 mL) and the mixture was extracted with toluene (5 $\times$ 15 mL). The collected organic phases were dried over anhydrous MgSO<sub>4</sub>, filtered and the solvent evaporated. The crude product was analyzed by <sup>1</sup>H NMR and LC-MS.

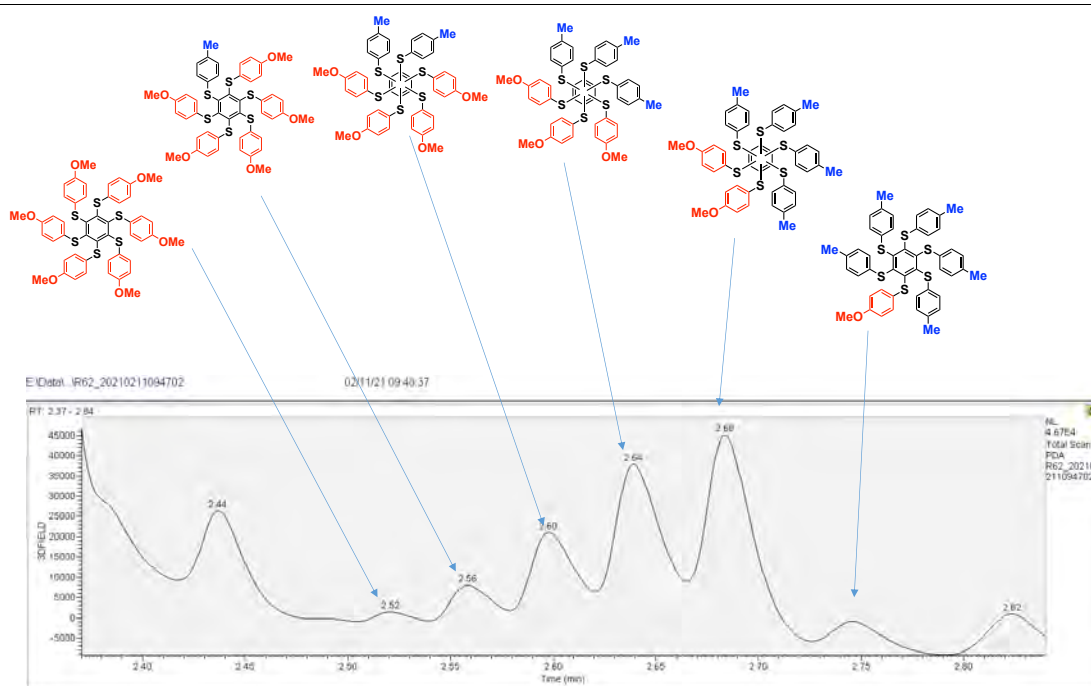
### <sup>1</sup>H NMR monitoring and analysis of the mixture



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 399.78 MHz)

**Conclusion:** 5 constitutional asterisk isomers with mixed ligands were isolated. The assignment was established by area integration in the aromatic region as well as in the aliphatic region. The low resolution does not allow ascertaining the number of regioisomers per fraction or the symmetry of the molecules.

### LC-HRMS analysis of the crude mixture

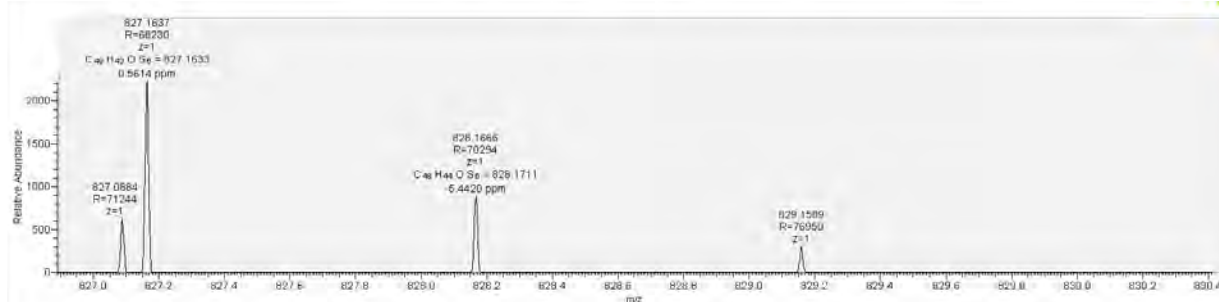


LC Chromatogram of the crude mixture (R-62)



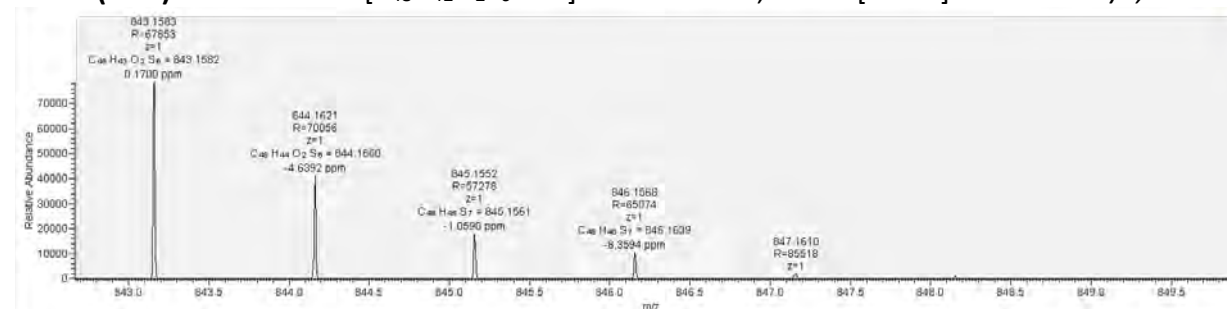
### 1 Substitution by MeOPhSH:

HRMS (ESI+) calculated for  $[C_{48}H_{42}OS_6 + H^+]$ : 827.1637 Da, found  $[M+H^+]$  827.1633 m/z;



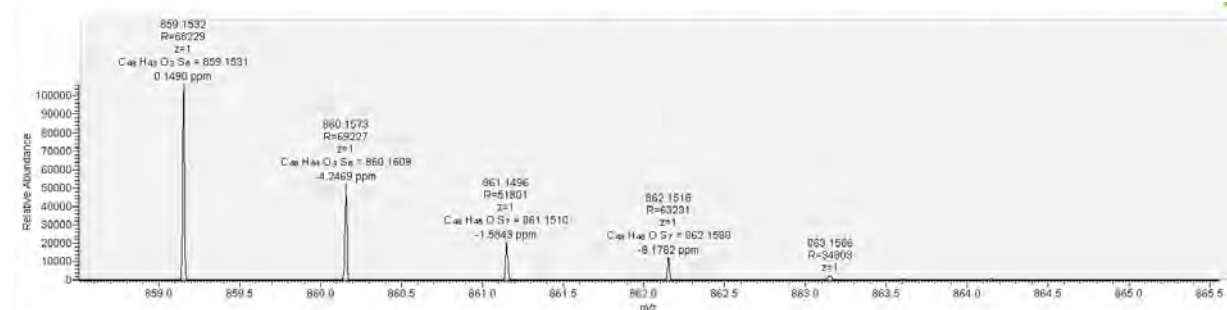
### 2 Substitutions by MeOPhSH:

HRMS (ESI+) calculated for  $[C_{48}H_{42}O_2S_6 + H^+]$ : 843.1583 Da, found  $[M+H^+]$  843.1582 m/z;



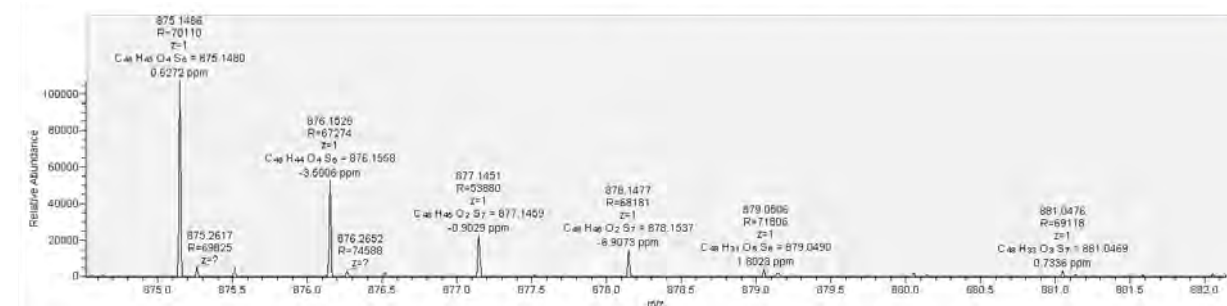
### 3 Substitutions by MeOPhSH:

HRMS (ESI+) calculated for  $[C_{48}H_{42}O_3S_6 + H^+]$ : 859.1532 Da, found  $[M+H^+]$  859.1531 m/z;



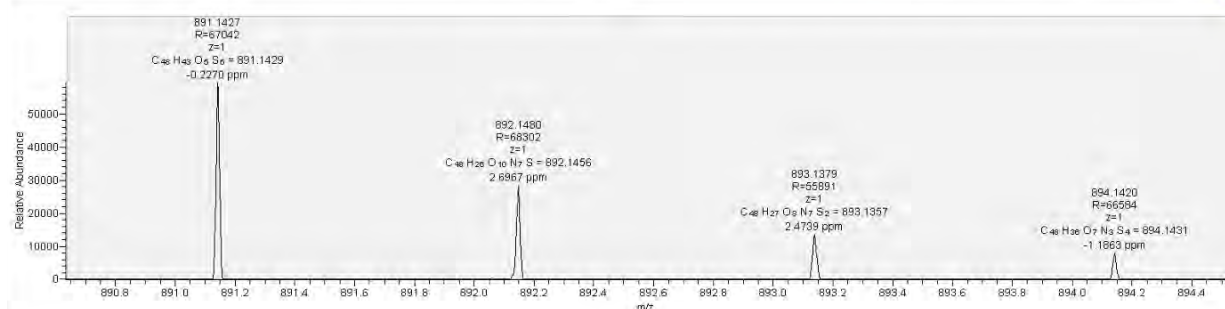
### 4 Substitutions by MeOPhSH:

HRMS (ESI+) calculated for  $[C_{48}H_{42}O_4S_6 + H^+]$ : 875.1486 Da, found  $[M+H^+]$  875.1480 m/z;

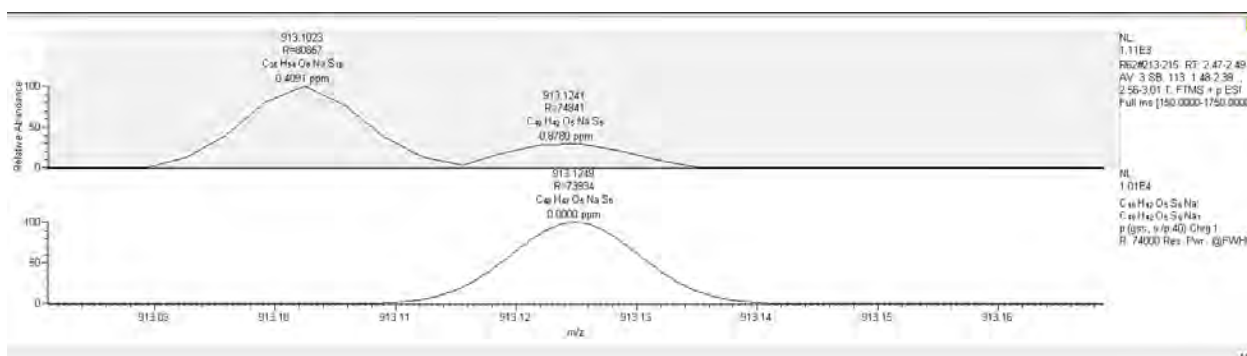


## 5 Substitutions by MeOPhSH:

HRMS (ESI+) calculated for  $[C_{48}H_{42}O_5S_6 + H^+]$ : 891.1429 Da, found  $[M + H^+]$  891.1427 m/z;

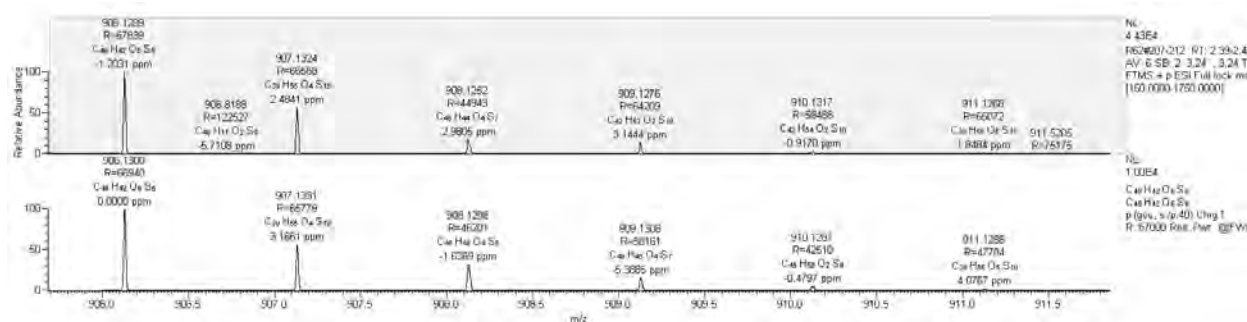


HRMS (ESI+) calculated for  $[C_{48}H_{43}O_5S_6 + Na^+]$ : 913.1249 Da, found  $[M + Na^+]$  913.1241 m/z;



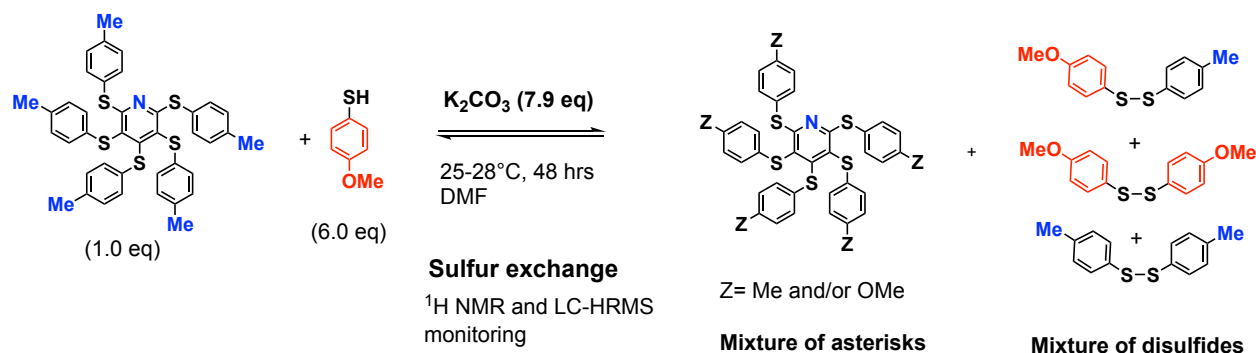
## 6 Substitutions by MeOPhSH:

HRMS (ESI+) calculated for  $[C_{48}H_{42}O_6S_6]$ : 906.1300 Da, found  $[M^+]$  891.1289 m/z;



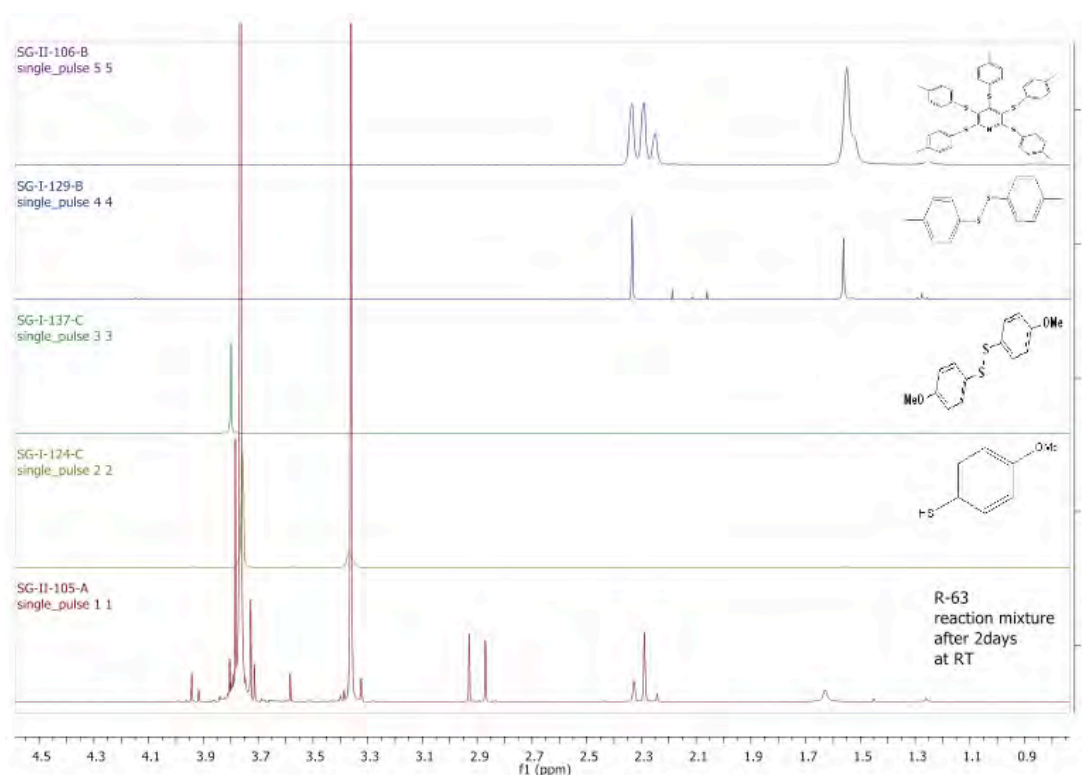
## 6.0 Sulfur exchange reactions on tetra(thio)pyridine asterisks

### SULFUR EXCHANGE REACTIONS WITH 2,3,4,5,6-PENTAKIS(P-TOLYLTHIO)PYRIDINE AT 25-28°C



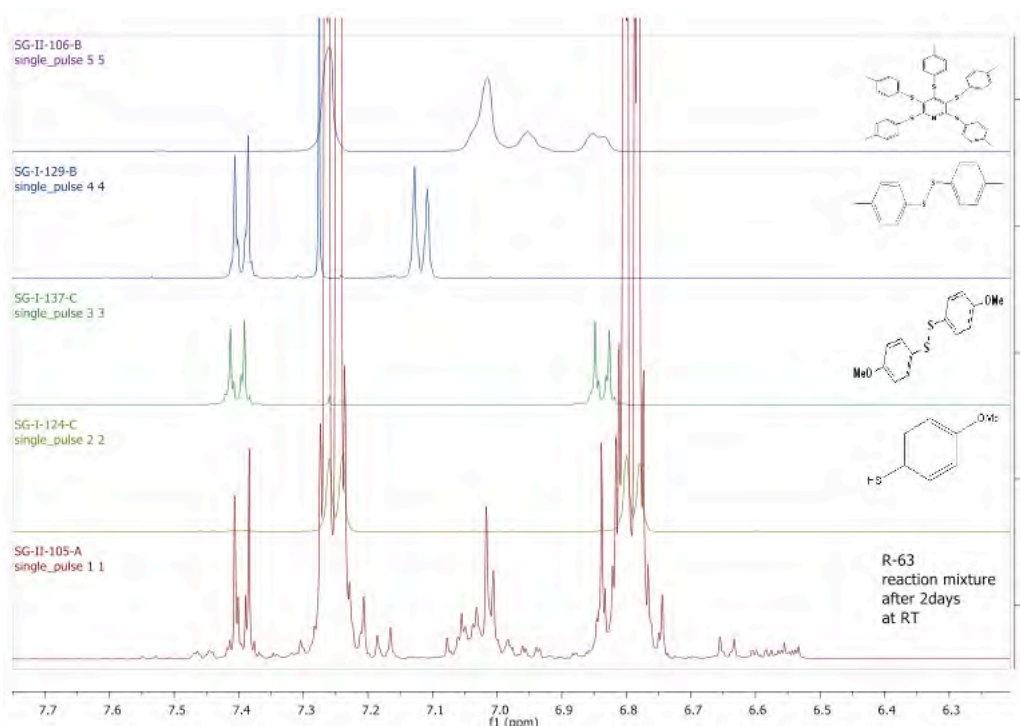
**(R-63M) Procedure:** In an oven-dried tube, purged with argon, was added 2,3,4,5,6-pentakis(*p*-tolylthio)pyridine (20.6 mg, 0.0299 mmol, 1.00 mol-eq.), dried potassium carbonate (32.8 mg, 0.237 mmol, 7.93 mol-eq.) and 4-methoxythiophenol (24.3 mg, 0.173 mmol, 21  $\mu$ L, 5.79 mol-eq.) in dry DMF (1.0 mL, dried and kept over 3Å molecular sieves). Argon was bubbled through the mixture for 5-10 min.. The tube was sealed and the reaction was vigorously stirred at 25-28°C for 48 hrs. The color turned from white to dark brown within a few seconds. After two days, the color turned to yellow. The reaction mixture was monitored by TLC (SiO<sub>2</sub>, 10% and 80% tol/cyclohex). After 2 days, no starting material was detected by TLC, and mainly 3 spots were observed by UV-vis. To the reaction mixture was added H<sub>2</sub>O (20 mL) and extracted with toluene (4× 20 mL ). The collected organic phases were dried over anhydrous MgSO<sub>4</sub>, filtered and the solvent evaporated; mass of crude: 396.2 mg.

### <sup>1</sup>H NMR monitoring and analysis of the mixture



**<sup>1</sup>H NMR (399.78 MHz, CDCl<sub>3</sub>) spectra 1 (SG-II-105A):** indicates that the pattern of CH<sub>3</sub> signals between 2.20 to 2.35 ppm for **spectra 1** changed relative to the composition of CH<sub>3</sub> signals of the pyridine asterisk reference in **spectra 5**. These signals do not correspond to a significant amount of *p*-methylphenyl disulfide (when looking at the aromatic CH region).

**Conclusion:** From the CH<sub>3</sub> signals, we can conclude that other asterisks were formed by ligand exchanges with *p*-MeOPhSH.

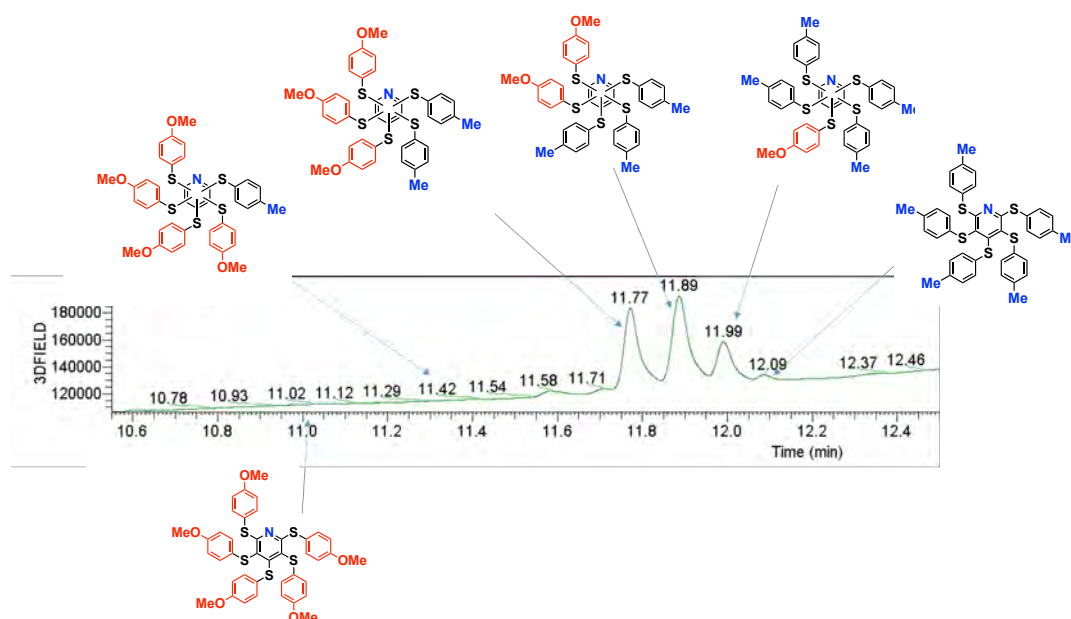


**$^1\text{H}$  NMR (399.78 MHz,  $\text{CDCl}_3$ ) spectra 1 (SG-II-105A) of the reaction mixture indicates a drastic change of the pattern of aromatic C-H signals from 7.00 to 7.05 ppm relative to the C-H aromatic signals of the reference pyridine asterisk in spectra 5 (starting material).**

**Conclusion:** From the C-H aromatic signals, we can conclude that other asterisks were formed by sulfur exchanges with *p*-MeOPhSH.

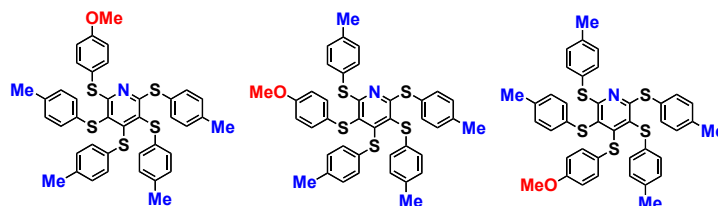
**General conclusion:**  $^1\text{H}$  NMR (399.78 MHz,  $\text{CDCl}_3$ , SG-II-105-A) monitoring after stirring for 48 hrs at 25-28°C indicated many sulfur exchange reactions at 25-28°C in DMF. A mixture of asterisks containing OMe and Me groups was formed.

### LC-HRMS analysis of the crude mixture

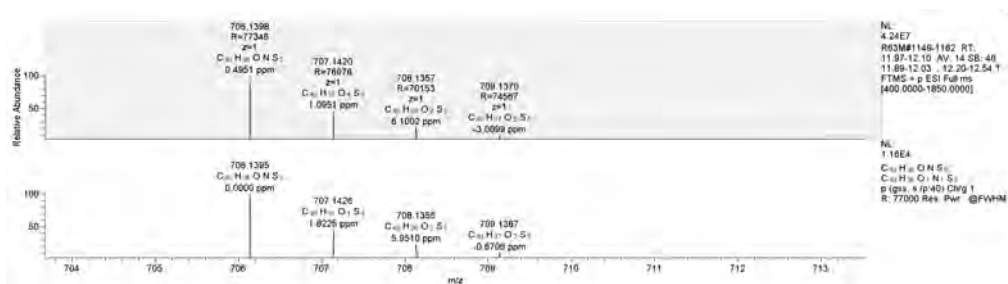


### 1 Substitution:

HRMS (ESI+) calculated for  $[C_{40}H_{35}ONS_5 + H^+]$ : 706.1395 Da, found  $[M+H^+]$  706.1398 m/z;  
Possible isomers:

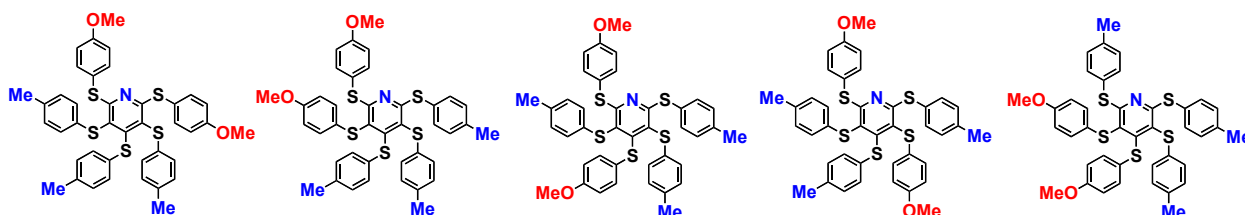


1 substitution by *p*-OMePhSH ( $C_{40}H_{36}ONS_5$ )

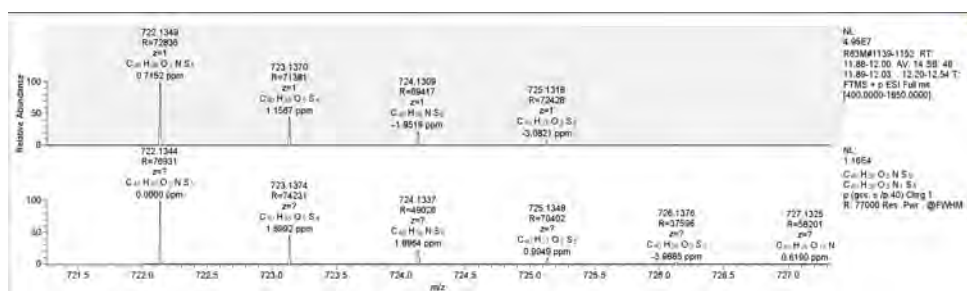


### 2 Substitutions:

HRMS (ESI+) calculated for  $[C_{40}H_{35}O_2NS_5 + H^+]$ : 722.1344 Da, found  $[M+H^+]$  722.1349 m/z;  
Possible isomers:

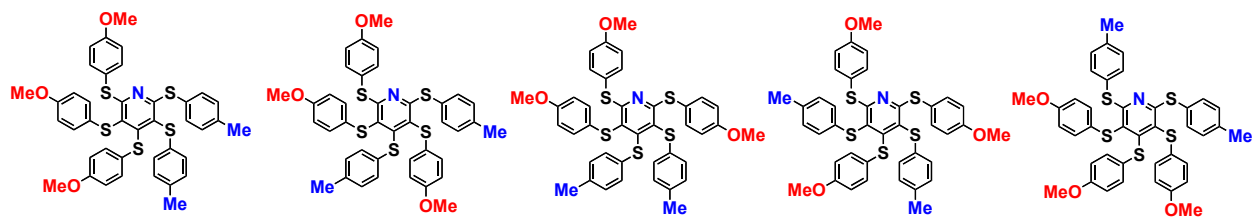


2 substitutions by *p*-OMePhSH ( $C_{40}H_{36}O_2NS_5$ )

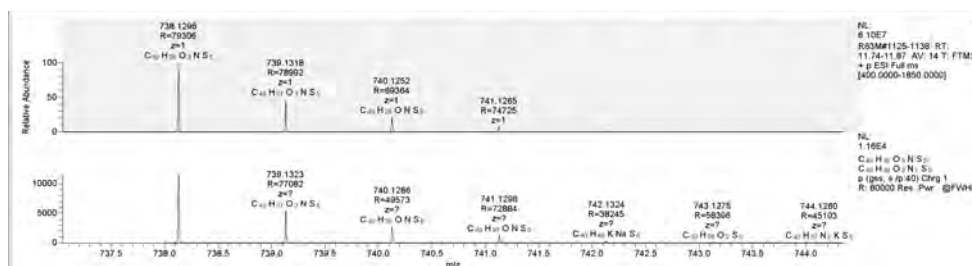


### 3 Substitutions:

HRMS (ESI+) calculated for  $[C_{40}H_{35}O_3NS_5 + H^+]$ : 738.1299 Da, found  $[M+H^+]$  738.1296 m/z;  
Possible isomers:

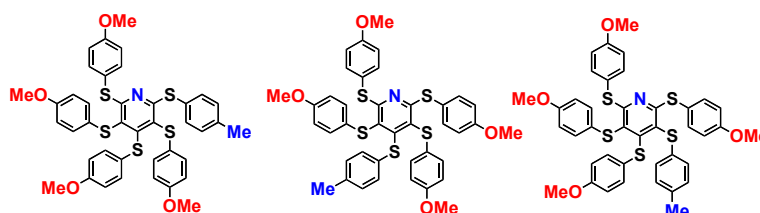


3 substitutions by *p*-OMePhSH ( $C_{40}H_{36}O_3NS_5$ )

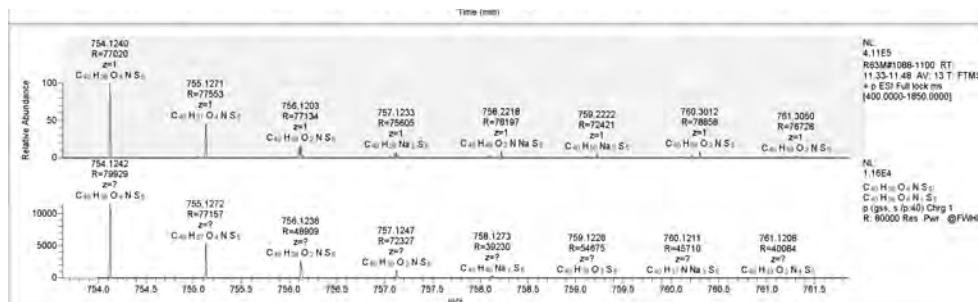


#### 4 Substitutions:

HRMS (ESI+) calculated for  $[C_{40}H_{35}O_4NS_5 + H^+]$ : 754.1242 Da, found  $[M+H^+]$  754.1240 m/z;  
Possible isomers:

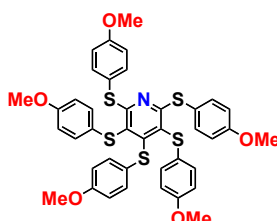


4 substitutions by *p*-OMePhSH ( $C_{40}H_{36}O_4NS_5$ )

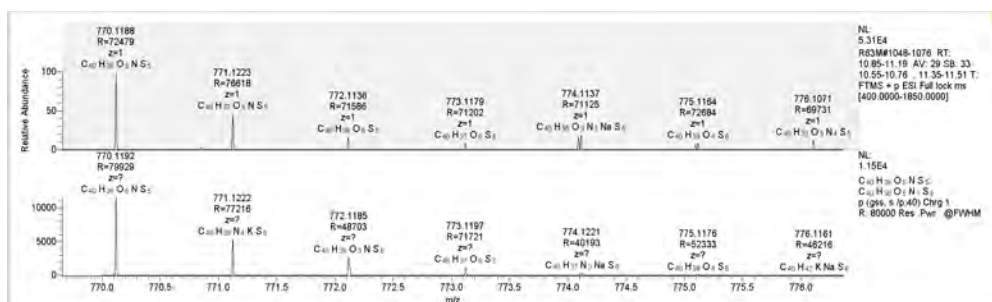


#### 5 Substitutions:

HRMS (ESI+) calculated for  $[C_{40}H_{35}O_5NS_5 + H^+]$ : 770.1192 Da, found  $[M+H^+]$  770.1188 m/z;  
Possible isomers:

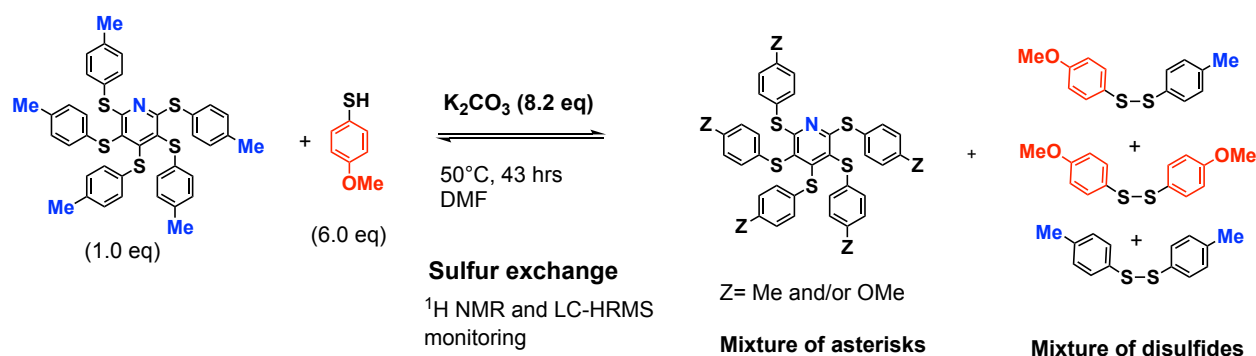


## 5 substitutions by *p*-OMePhSH (C<sub>40</sub>H<sub>36</sub>O<sub>5</sub>NS<sub>5</sub>)



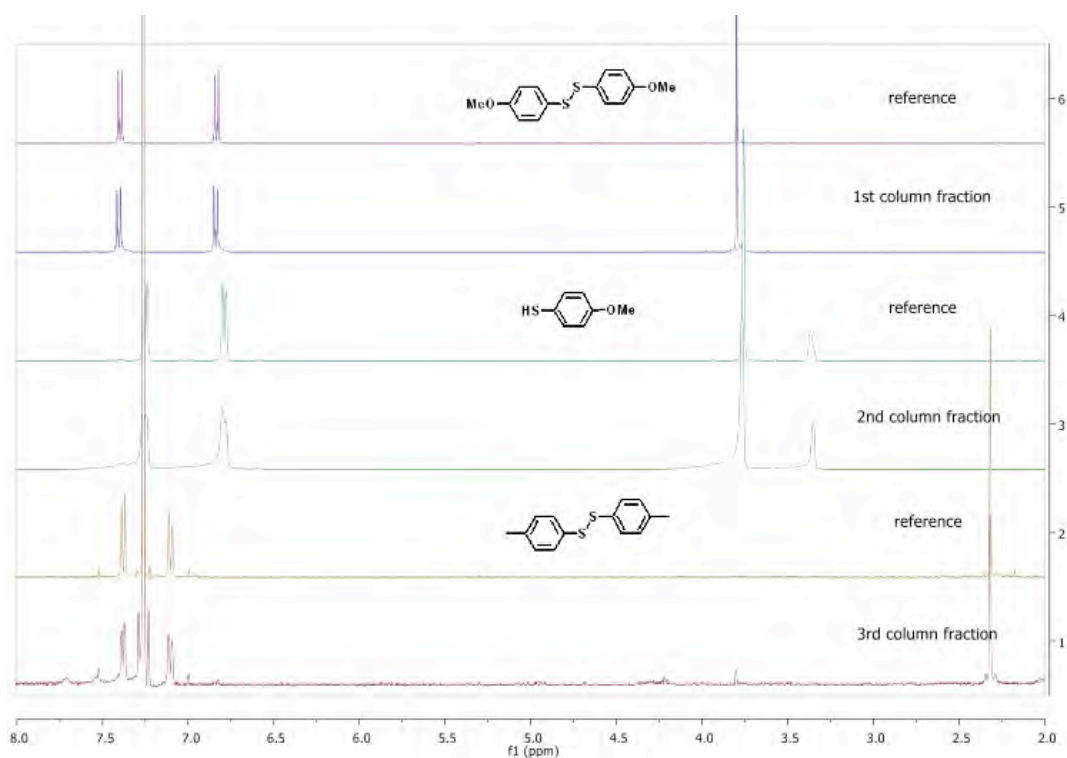
**Conclusion:** Some ligand exchanges occur in DCC under mild conditions at 25°C with 2,3,4,5,6-pentakis(*p*-tolylthio)pyridine. Up to five substitutions by *p*-MeOPhSH are noticed. Some selectivity is observed from the UV-vis integration of the signals in the chromatogram, for producing asterisks with disubstituted and trisubstituted *p*-MeOPhS groups, as the major products, even if 6 mol-eq. of *p*-MeOPhSH are used. Details of the exact structure of some possible regioisomers are not available at this stage.

### SULFUR EXCHANGE REACTIONS WITH 2,3,4,5,6-PENTAKIS(*p*-METHYLPHENYLTHIO) PYRIDINE AT 50°C



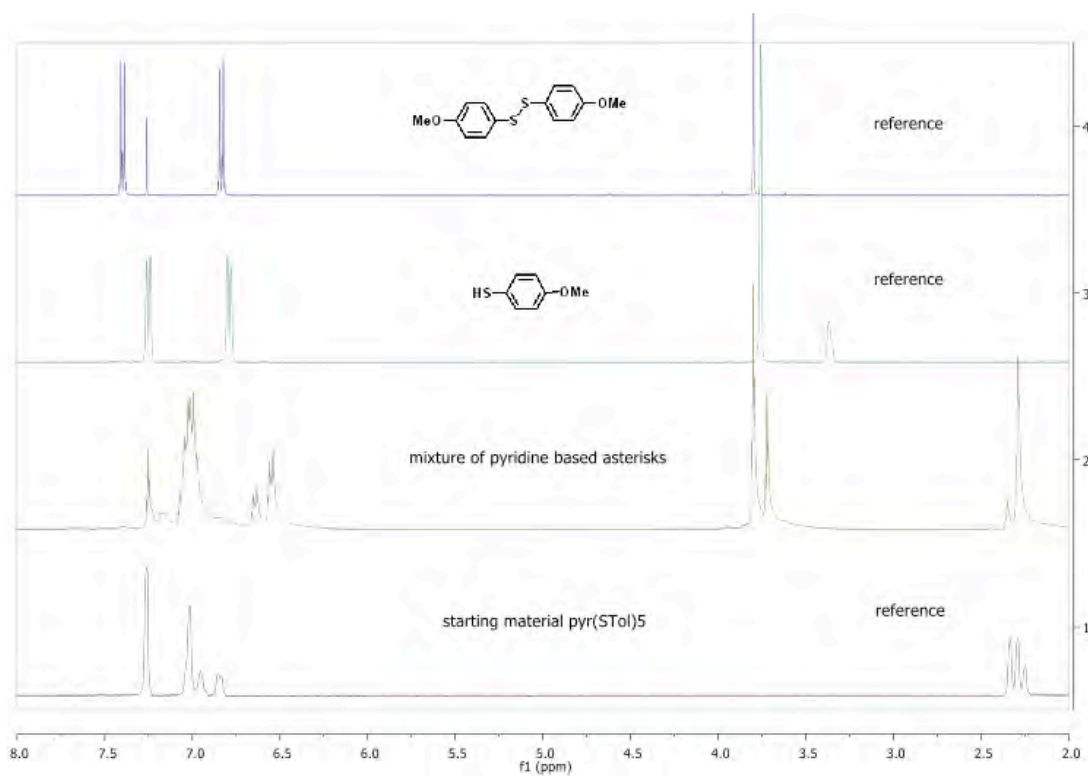
**(R-64) Procedure:** In an oven-dried tube, purged with argon, was added 2,3,4,5,6-pentakis(*p*-tolylthio)pyridine (20.1 mg, 0.0291 mmol, 1.00 mol-eq.), dried potassium carbonate (32.9 mg, 0.238 mmol, 8.18 mol-eq.) and 4-methoxythiophenol (24.3 mg, 0.173 mmol, 21  $\mu$ L, 5.96 mol-eq) in dry DMF (0.6 mL, dried and kept over 3Å molecular sieves). Argon was bubbled through the mixture for 5-10 min.. The tube was sealed and the mixture was vigorously stirred at 50°C The reaction was monitored by TLC (SiO<sub>2</sub>, eluent: tol/cyclohex. 80:20 v/v). After 43 hrs. no starting material was found by TLC (UV-vis) and four spots were detected (eluent: toluene/cyclohex. 80:20 v/v). The reaction mixture was taken-up in toluene (20 mL) and water (20 mL). The aqueous phase was discarded and the organic phase was further washed with water (3×20 mL). It was then dried over anhydrous MgSO<sub>4</sub>, filtered and evaporated; mass of crude to be analyzed : 349.7 mg. The components of the crude were separated by chromatography over silica gel, by using an increasing polarity of the eluent from 10% toluene in cyclohexane to 100% toluene.

### <sup>1</sup>H NMR monitoring and analysis of the mixture



<sup>1</sup>H NMR (399.78 MHz, CDCl<sub>3</sub>, R-64)

**Conclusion. NMR signals between 2.0-4.0 ppm (CH<sub>3</sub>Ph and MeOPh region):** among thiols and disulfides isolated, a small amount of *p*-tolyl disulfide (3<sup>rd</sup> column fraction, *vide infra*) could be identified. This clearly demonstrates the displacement of *p*-tolylthio groups in pentakis(*p*-tolylthio)pyridine.

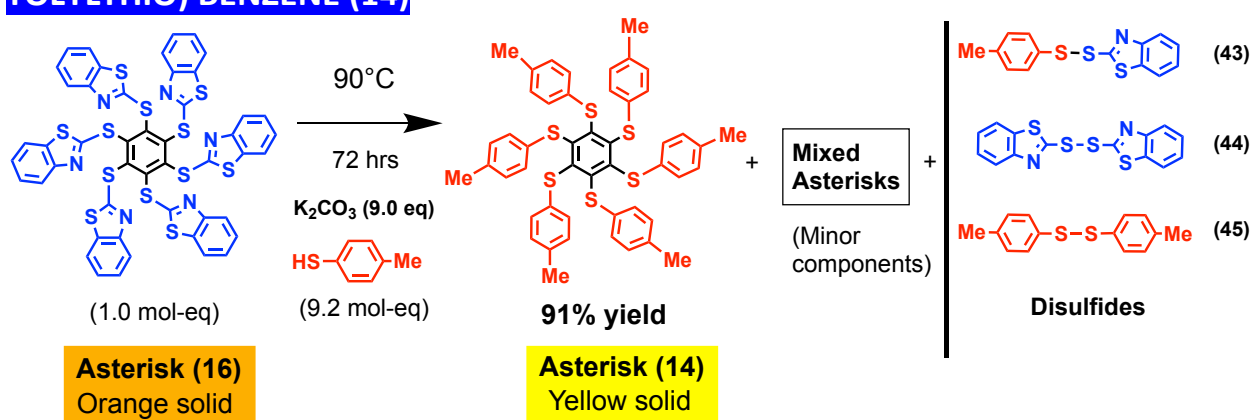




**Conclusion: NMR signals between 6.0-7.0 ppm (aromatic region):** the different pyridine-based methoxylated asterisks could not be separated. Methoxylated and methylated units can be easily identified by  $^1\text{H}$  NMR of the mixture. The methoxy signals do not come from remaining *p*-methoxyphenyl disulfide or from *p*-methoxybenzenethiol as can be seen in the figure above. Thus, it confirms the sulfur exchange reactions on the pyridine ring.

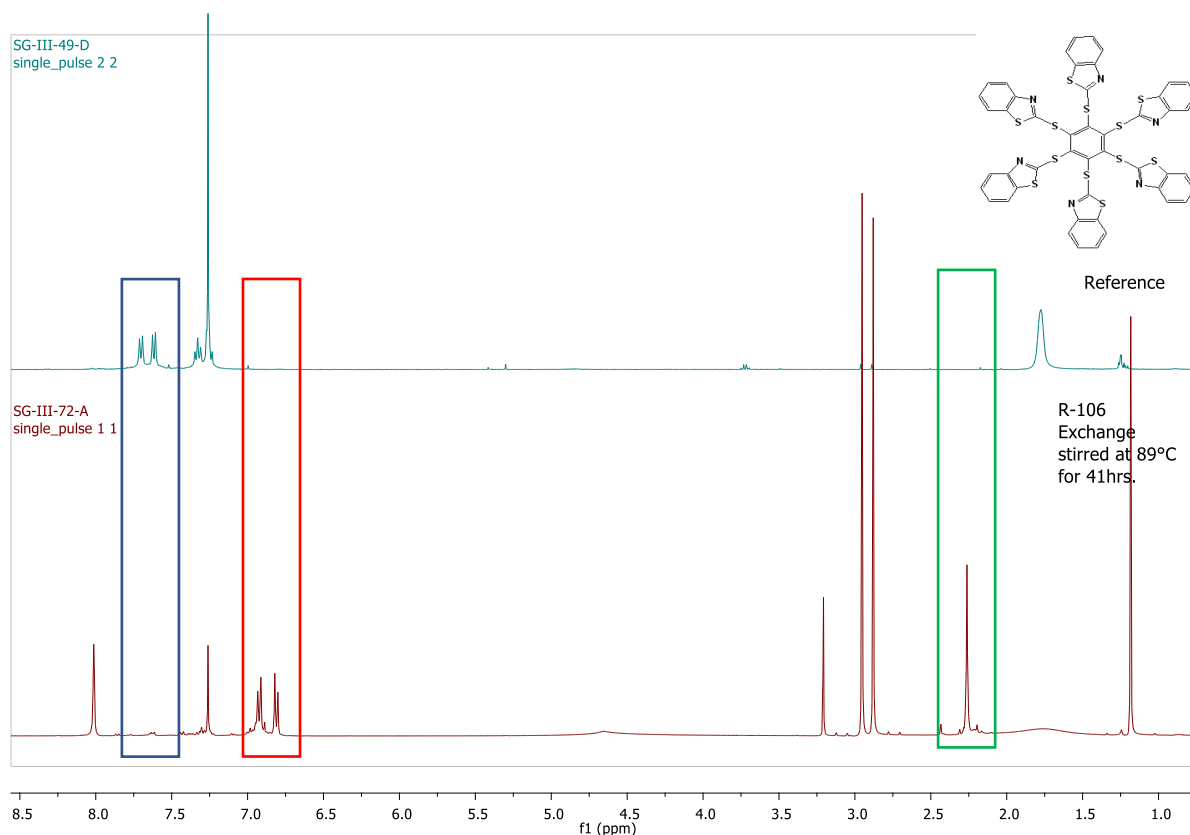
## 7.0 Conversion between two hexa(thio)benzene asterisks

### CONVERSION OF HEXAKIS(BENZOTHIAZOLYLTHIO) BENZENE (16) TO HEXAKIS (*p*-TOLYLTHIO) BENZENE (14)



**(R-106) Procedure:** In an oven-dried tube, purged with argon, was added hexakis (benzothiazolyl-2-thio) benzene (**16**) (100.0 mg, 0.0935 mmol, 1.00 mol-eq.), dried potassium carbonate (116.3 mg, 0.841 mmol, 9.00 mol-eq.), 4-methylthiophenol (106.8 mg, 0.860 mmol, 9.20 mol-eq.) in dry DMF (1.0 mL, dried over activated 3Å molecular sieves). Argon was bubbled through the mixture for 5-10 min.. The tube was sealed under argon and the reaction was stirred at 90°C in an oil bath for 3 days. After cooling to 20°C, water (30 mL) was added to the mixture, and the product was extracted with toluene (5 x 30 mL). The combined organic phases were dried over anhydrous  $\text{MgSO}_4$ , filtered and evaporated to dryness. TLC ( $\text{SiO}_2$ , acetone/cyclohexane 10:90 v/v) indicated six spots under a UV-vis lamp, among which one intense luminescent yellow spot. The mixture of compounds was separated by column chromatography over silica gel (eluent: acetone/cyclohexane 10:90 v/v) as eluent. The luminescent yellow spot corresponded to hexakis (*p*-tolylthio)benzene (69.1 mg, 0.0852 mmol, 91% yield).

## $^1\text{H}$ NMR monitoring and analysis of the mixture



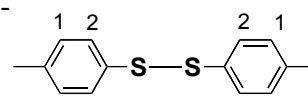
$^1\text{H}$ -NMR (399.78 MHz,  $\text{CDCl}_3$ ) monitoring after stirring for 41 hrs at 90°C.

a) **Green spectra:** hexakis(benzenethiazolyl-2-thio)benzene; b) **Red spectra:** reaction mixture after 41 hrs at 90°C.

**Conclusion:** Comparison of  $^1\text{H}$  NMR spectra of hexakis(benzenethiazolyl-2-thio)benzene (green spectra) with  $^1\text{H}$  NMR spectra of the reaction mixture (red spectra) after sulfur exchanges with 4-methylbenzenethiol indicates an excellent conversion of hexakis(benzenethiazolyl-2-thio)benzene (see blue rectangle) to hexakis(4-methylphenylthio)benzene (see red rectangle). It was observed over time some new signals at 6.93 ppm (doublet), 6.84 ppm (doublet) (red rectangle), and a singlet at 2.29 ppm (green rectangle). Thus, 4-methylbenzenethiol promoted the exchange of ligands to make hexakis(4-methylphenylthio)benzene in a 91% isolated yield.

After column chromatography ( $\text{SiO}_2$ , eluent: acetone/cyclohexane 10:90 v/v) several components were separated, including disulfides. The release of benzenethiazolyl-2-thio groups for making mixed or symmetrical disulfides is also confirmed by  $^1\text{H}$  NMR.

**a) Fraction [12-17] (1<sup>st</sup> less polar spot on top of TLC):**  $^1\text{H}$ -NMR (SG-III-72-B) indicates *p*-tolyl disulfide as a major component;  $^1\text{H}$  NMR (399.78 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.38 ( $d_{\text{app}}$ ,  $J$  = 8.1 Hz, 4H), 7.10 ( $d_{\text{app}}$ ,  $J$  = 8.1 Hz, 4H), 2.32 (s, 6H). Mass: 3.7 mg.



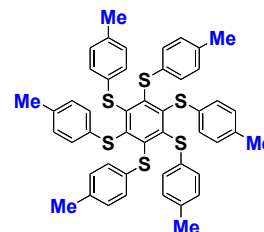
**b) Fraction [40] (2<sup>nd</sup> spot** from the top of TLC): <sup>1</sup>H-NMR (SG-III-72-C) indicates a methyl and a benzothiazole group corresponding to the mixed disulfide: *p*-tolyl-2-benzothiazolyl disulfide;. Mass: 0.4 mg.

**c) Fraction [42] (mixture of 1<sup>st</sup> and 2<sup>nd</sup> spot on TLC).** Mass: 1.8 mg

**d) Fraction [43-47] (mixture of 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> spot on TLC).** Mass: 10.5 mg

**e) Fraction [48] (mixture of 2<sup>nd</sup> and 3<sup>rd</sup> spot on TLC)**

**f) Fraction [50-58] (3<sup>rd</sup> spot on TLC, asterisk (14)):** <sup>1</sup>H NMR (SG-III-72-D) indicates an excellent sulfur exchange to hexakis(*p*-tolylthio) benzene; <sup>1</sup>H NMR (399.78 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 6.93 (d<sub>app</sub>, *J* = 8.1 Hz, 12H), 6.82 (d<sub>app</sub>, *J* = 8.2 Hz, 12H), 2.29 (s, 18H); <sup>13</sup>C NMR (100.53 MHz, CDCl<sub>3</sub>, ppm) (SG-III-72-H)  $\delta$  = 148.03, 135.97, 134.53, 129.73, 128.65, 21.22. Mass: 69.1 mg.



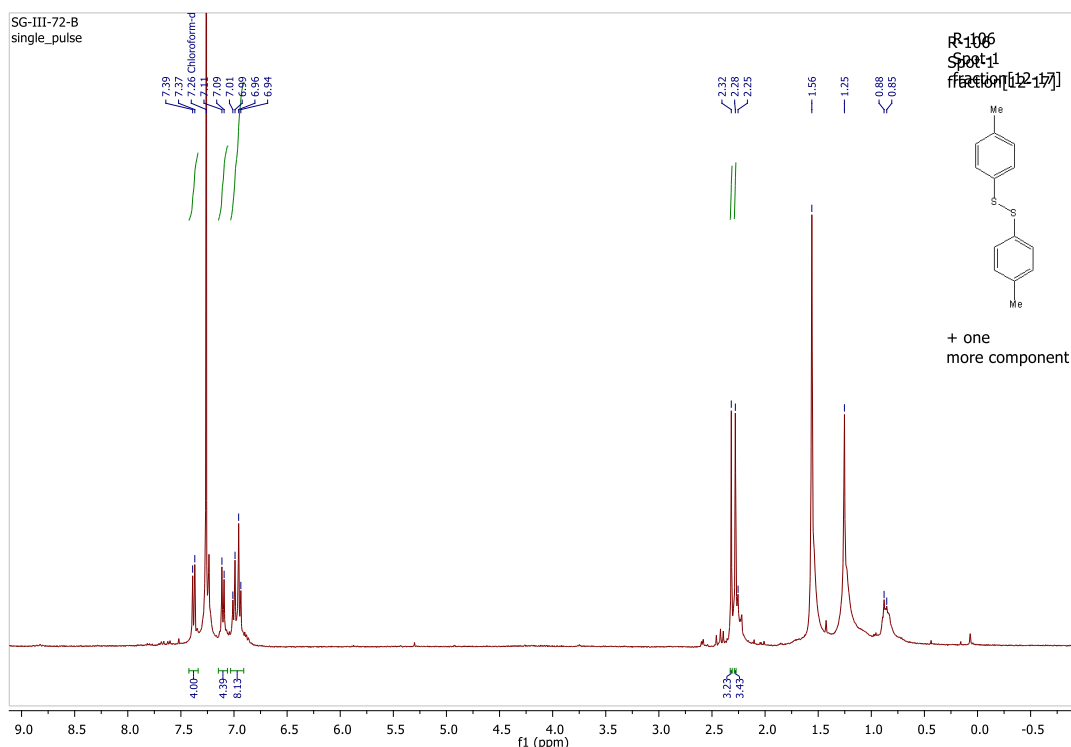
**g) Fraction [59-60] (mixture of 3<sup>rd</sup> and 4<sup>th</sup> spot on TLC).** Mass: 3.7 mg.

**Fraction [61-63] (4<sup>th</sup> spot on TLC, yellow):** <sup>1</sup>H NMR (SG-III-72-E) indicates a mixture of asterisks. Mass: 0.9 mg.

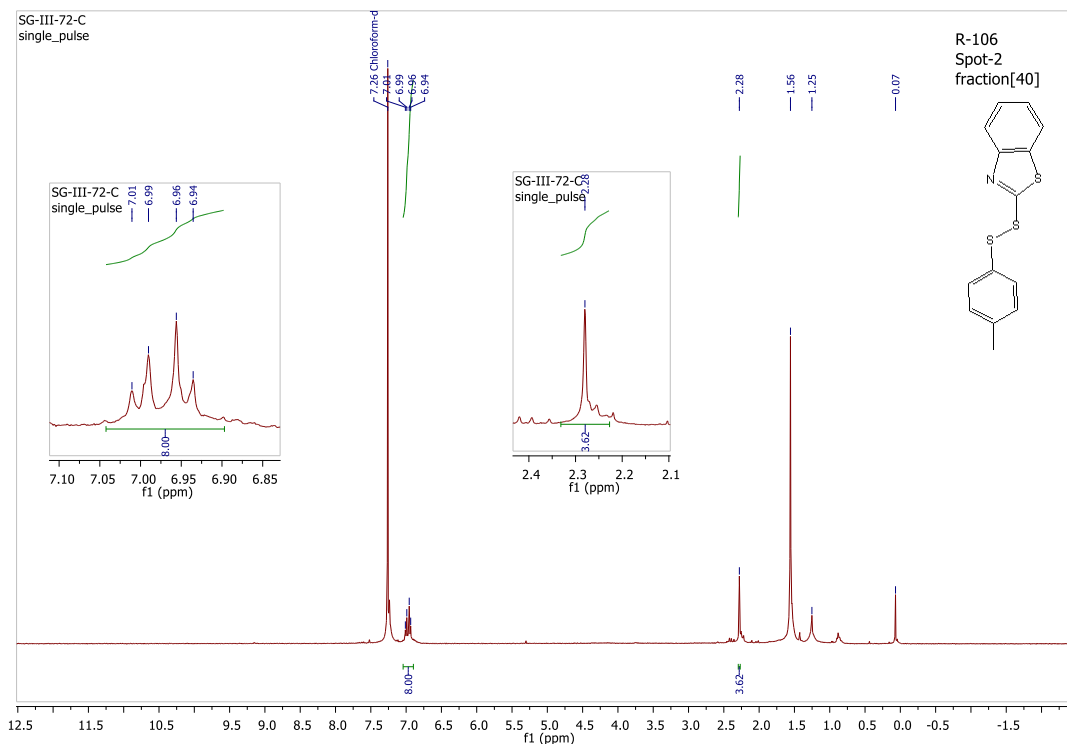
**h) Fraction [72-80] (5<sup>th</sup> spot on TLC, yellow):** <sup>1</sup>H NMR (SG-III-72-F) indicates a mixture of asterisks. Mass: 19.8 mg.

**i) Fraction [95] (6<sup>th</sup> spot on TLC):** <sup>1</sup>H NMR indicates a mixture of 2- mercaptobenzothiazole and asterisks. Mass: 14.3 mg.

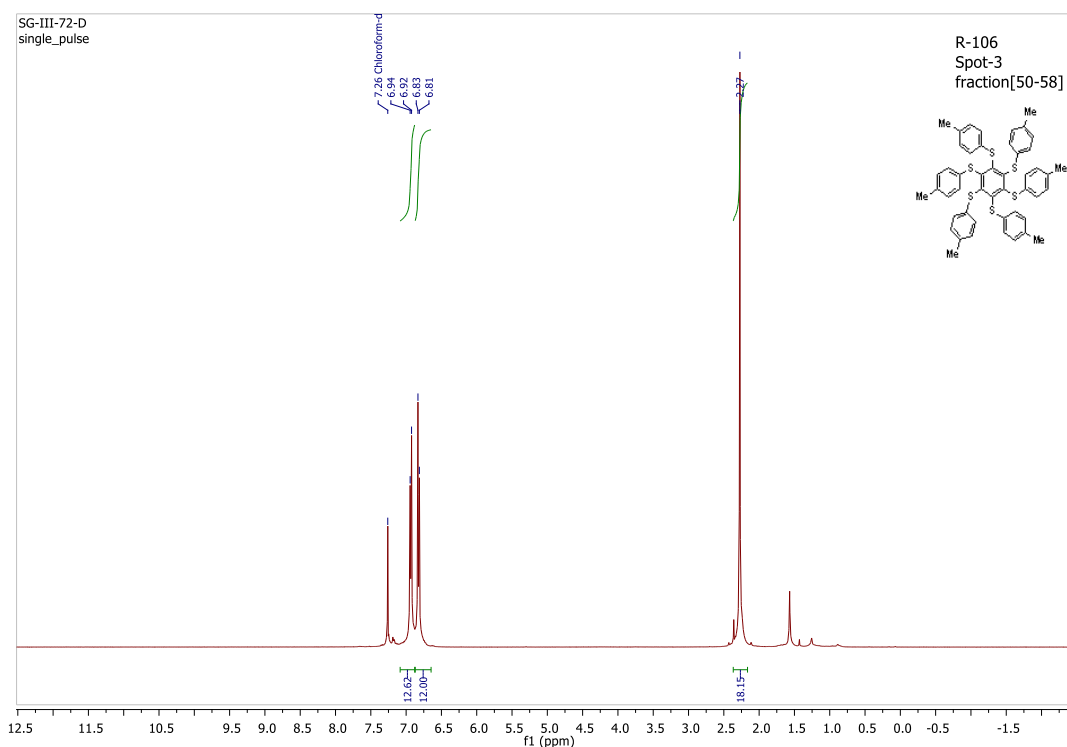
### List of corresponding <sup>1</sup>H- and <sup>13</sup>C-NMR spectra



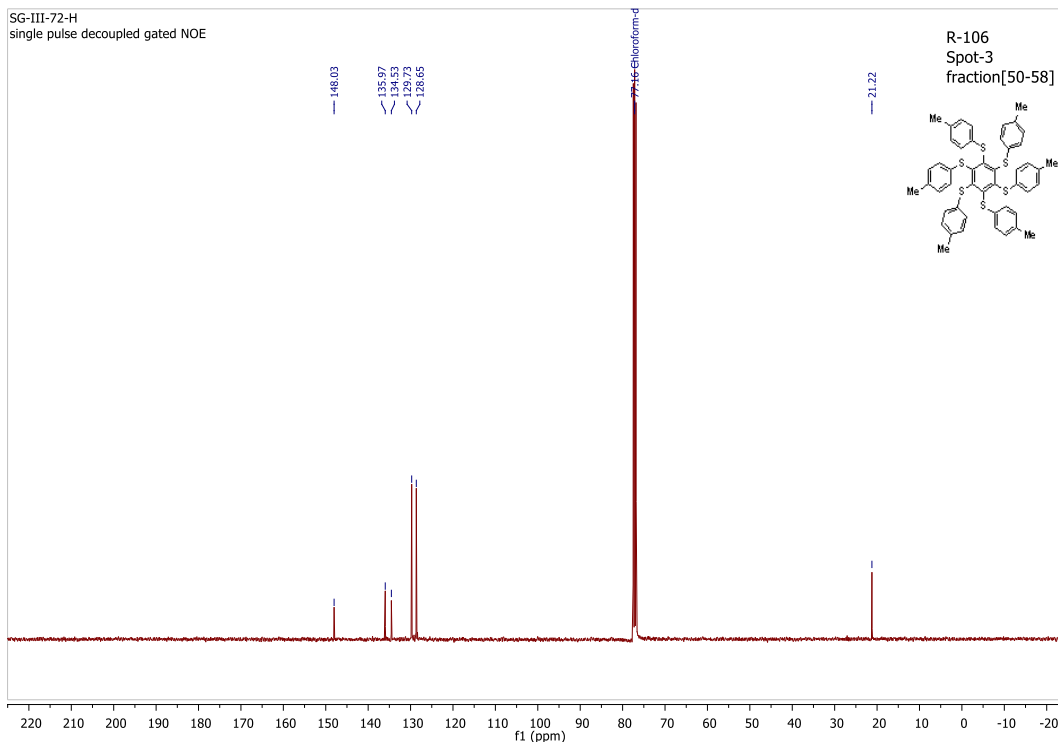
<sup>1</sup>H-NMR (399.78 MHz, CDCl<sub>3</sub>) - SG-III-72B (fractions 12-17)



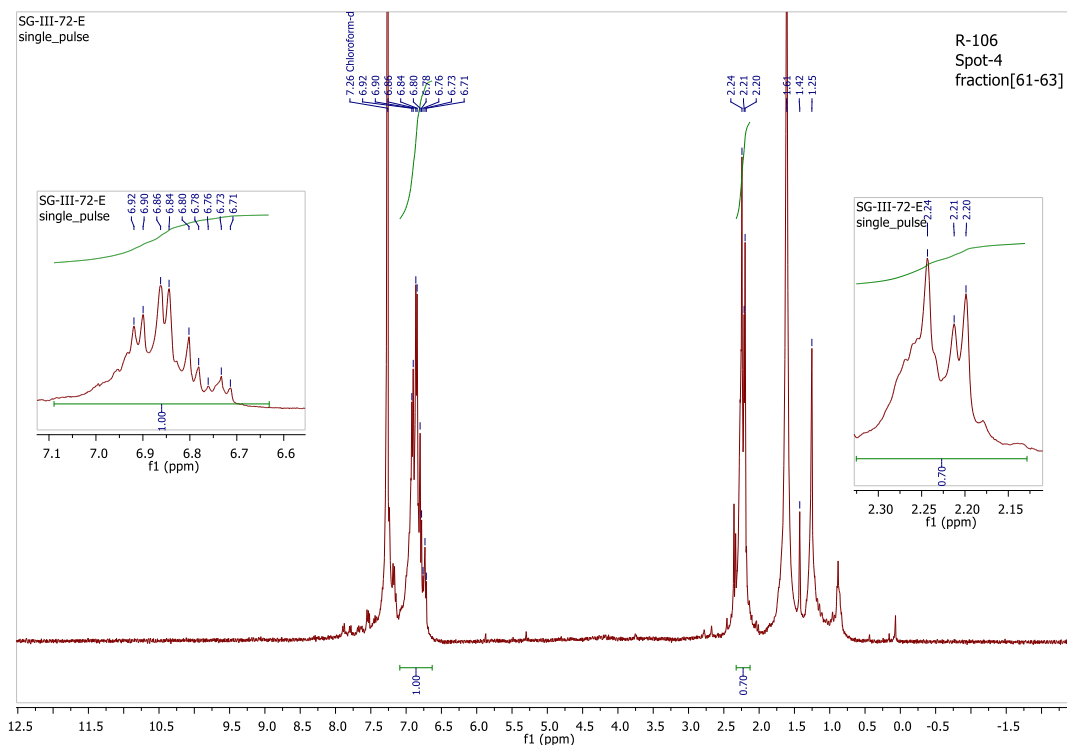
**<sup>1</sup>H-NMR (399.78 MHz, CDCl<sub>3</sub>) - SG-III-72C (fraction 40)**



**<sup>1</sup>H-NMR (399.78 MHz, CDCl<sub>3</sub>) - SG-III-72D (fractions 50-58)**



<sup>1</sup>H-NMR (399.78 MHz, CDCl<sub>3</sub>) - SG-III-72H (fractions 50-58)

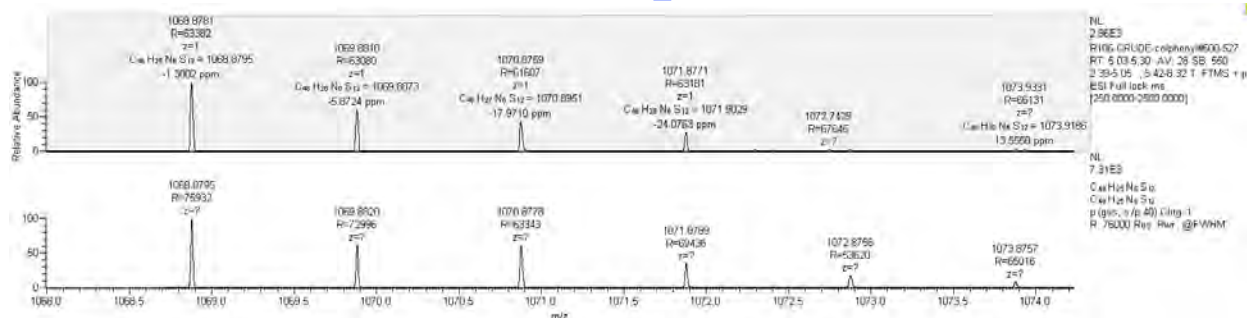
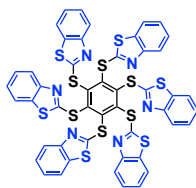


<sup>1</sup>H-NMR (399.78 MHz, CDCl<sub>3</sub>) - SG-III-72E (fractions 61-63)



### 0 Substitution: Asterisk (16) hexakis(benzenethiazolyl-2-thio) benzene

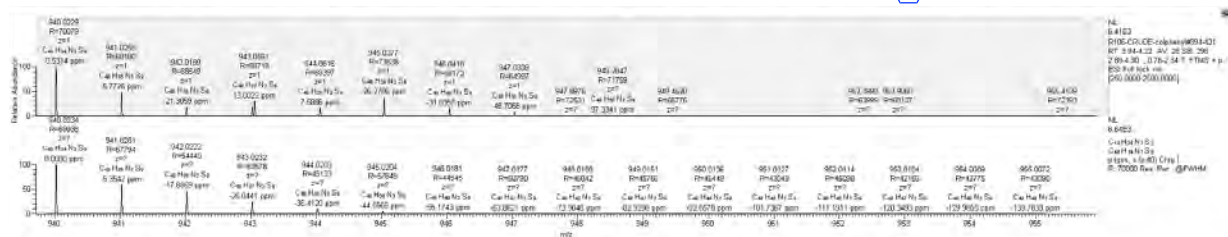
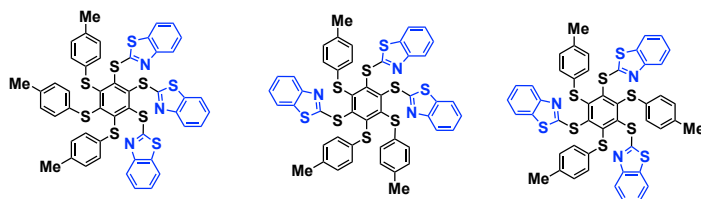
HRMS (ESI+) calculated for  $[C_{48}H_{24}N_6S_{12} + H^+]$ : 1068.8795 Da, found  $[M+H^+]$  1068.8781 m/z;



### 3 Substitutions by MePhSH (minor component):

HRMS (ESI+) calculated for  $[C_{48}H_{33}N_3S_9 + H^+]$ : 940.0234 Da, found  $[M+H^+]$  940.0229 m/z;

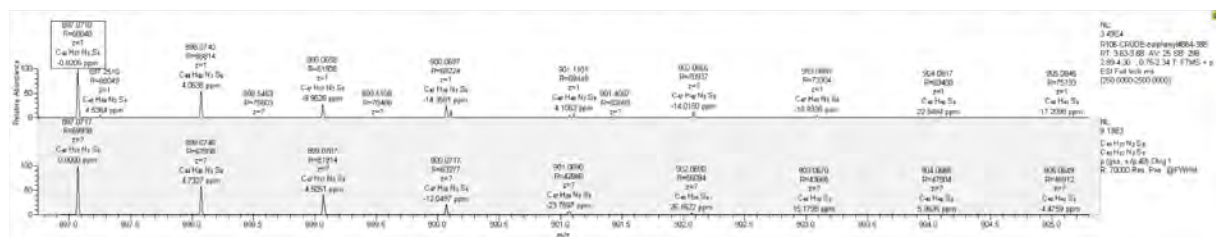
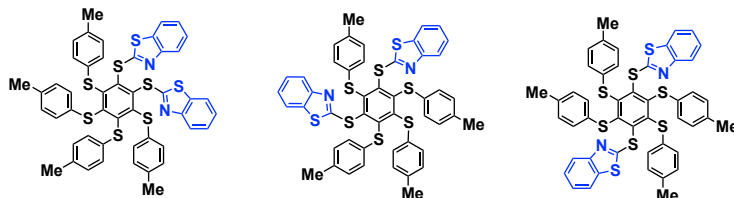
Possible isomers:



### 4 Substitutions by MePhSH (minor component):

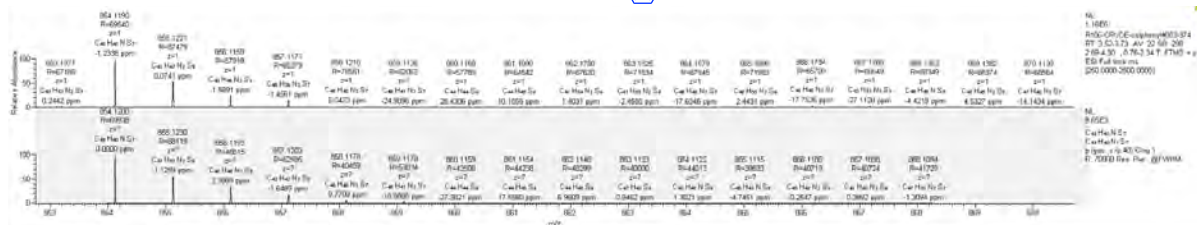
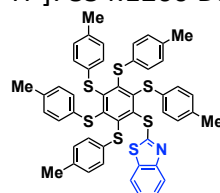
HRMS (ESI+) calculated for  $[C_{48}H_{36}N_2S_8 + H^+]$ : 897.0717 Da, found  $[M+H^+]$  897.0710 m/z;

Possible isomers:



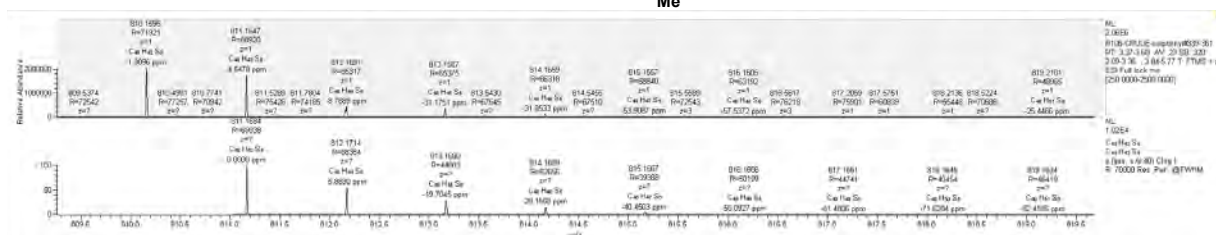
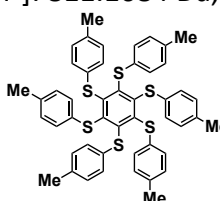
### 5 Substitutions by MePhSH (minor component):

HRMS (ESI+) calculated for  $[C_{48}H_{39}NS_7 + H^+]$ : 854.1200 Da, found  $[M+H^+]$  854.1190 m/z;

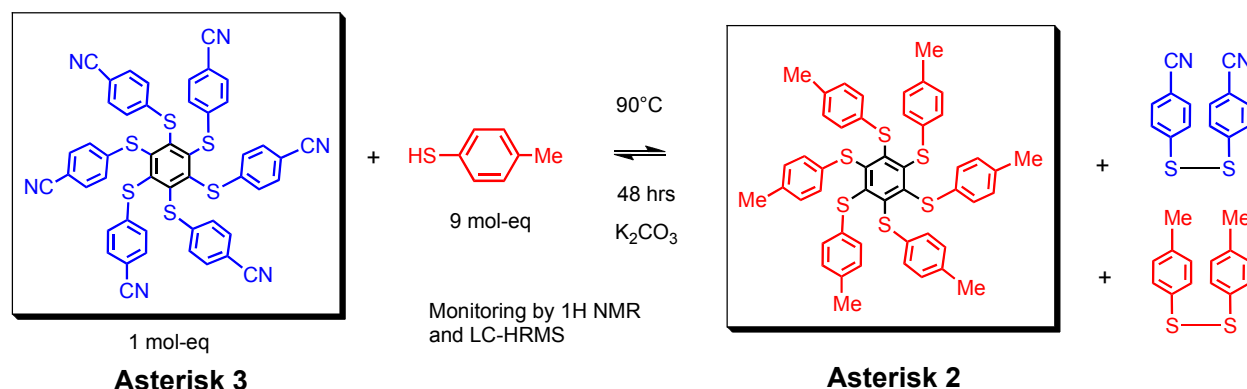


### 6 Substitutions by MePhSH. (Asterisk (14) is the major compound isolated):

HRMS (ESI+) calculated for  $[C_{48}H_{42}S_6 + H^+]$ : 811.1684 Da, found  $[M+H^+]$  811.1647 m/z;



## (R109) CONVERSION OF HEXAKIS(4-CYANOPHENYLTHIO)BENZENE TO HEXAKIS(4-METHYLPHENYLTHIO) BENZENE



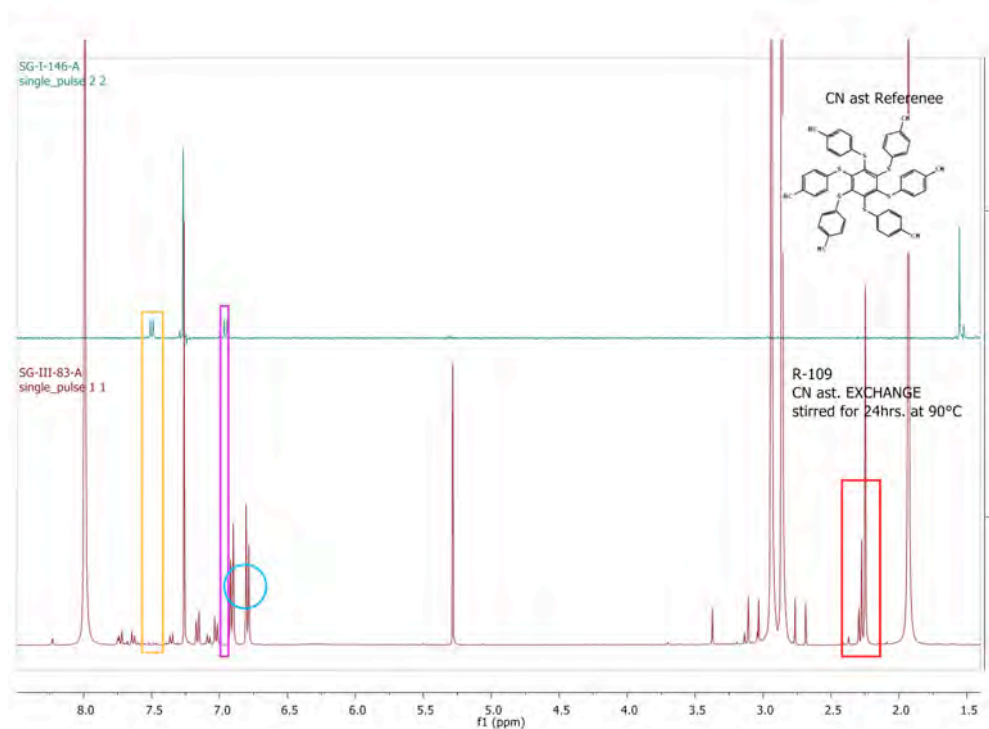
**Procedure.** In an oven-dried tube, purged with argon, was added hexakis(4-cyanophenylthio)benzene (30.2 mg, 0.034 mmol, 1.00 mol-eq.), dried potassium carbonate (42.6 mg, 0.308 mmol, 9.00 mol-eq.) and 4-methylthiophenol (39.7 mg, 0.319 mmol, 9.00 mol-eq.) in dry DMF (0.5mL, dried with activated 3Å molecular sieves). Argon was bubbled through the mixture for 5-10minutes in the tube. The tube was sealed under argon, and the reaction was



stirred in an oil bath at 90°C for 2 days. The reaction mixture was monitored by TLC (SiO<sub>2</sub>, eluent: 100% cyclohex. and tol/cyclohex. 80:20 v/v). Mainly two spots were observed by UV-vis in 100% cyclohexane and only one spot in tol/cyclohex (80:20 v/v). DMF was removed from the reaction mixture under reduced pressure on a rotary evaporator. To the crude mixture was added water (30 mL) and it was extracted with toluene (4 × 25mL). The collected organic phases were dried over anhydrous MgSO<sub>4</sub>, filtered, and the solvent evaporated. The products were separated by column chromatography over silica gel using toluene/cyclohex. (5:95 v/v) as eluent. Hexakis(*p*-tolylthio)benzene was isolated as a major product (25.1 mg, 90% yield).

### **<sup>1</sup>H NMR monitoring and analysis of the mixture**

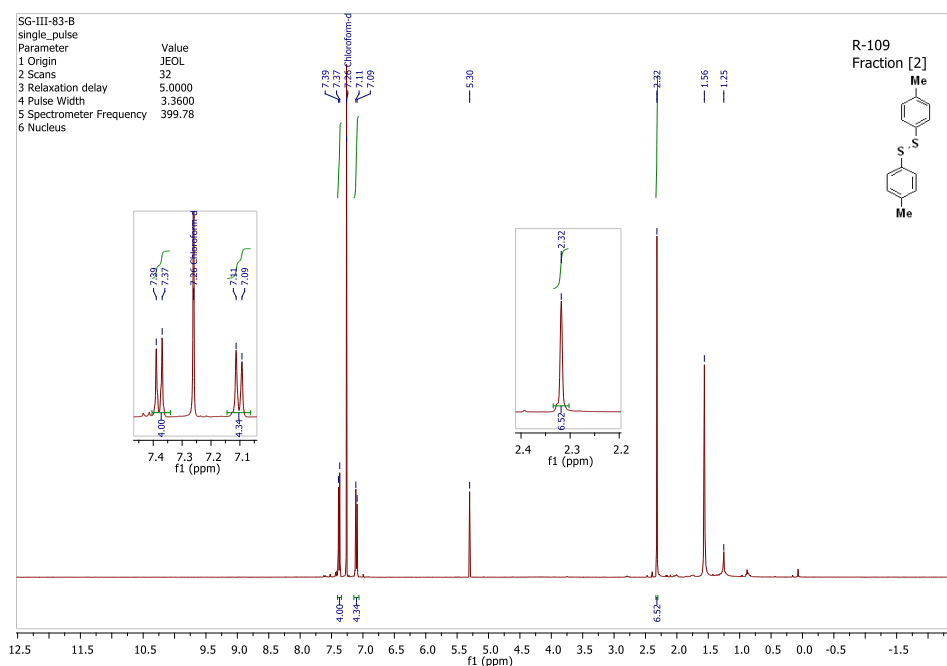
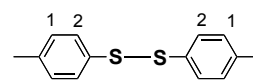
Comparison of <sup>1</sup>H NMR spectra of starting hexakis(4-cyanophenylthio)benzene with <sup>1</sup>H NMR spectra of the reaction mixture after sulfur ligand exchanges with 4-methylbenzenethiol indicated an excellent conversion to hexakis(4-methylphenylthio)benzene. It was observed over time some new signals at 6.93 ppm (doublet), 6.84 ppm (doublet), and 2.29 ppm. Finally, 4-methylbenzenethiol promoted the exchange of ligands to make hexakis (4-methylphenylthio) benzene in a 90% yield after 2 days at 90°C.



**<sup>1</sup>H-NMR** (399.78 MHz, CDCl<sub>3</sub>, SG-III-83A) monitoring after stirring for 24 hrs at 90°C. Comparison of <sup>1</sup>H-NMR spectra of starting hexakis (4-cyanophenylthio)benzene (spectra 2, blue) with its characteristic signals at 6.96 ppm (d<sub>app</sub>), 7.50 ppm (d<sub>app</sub>) and the spectra from reaction mixture (spectra 1, red) indicated that most starting asterisk was consumed (see orange and pink boxes for changes of signals), which is also confirmed by TLC. Some new methyl signals appear between 2.25-2.30 ppm (shown in red box), corresponding to hexakis(4-methylphenylthio)benzene.

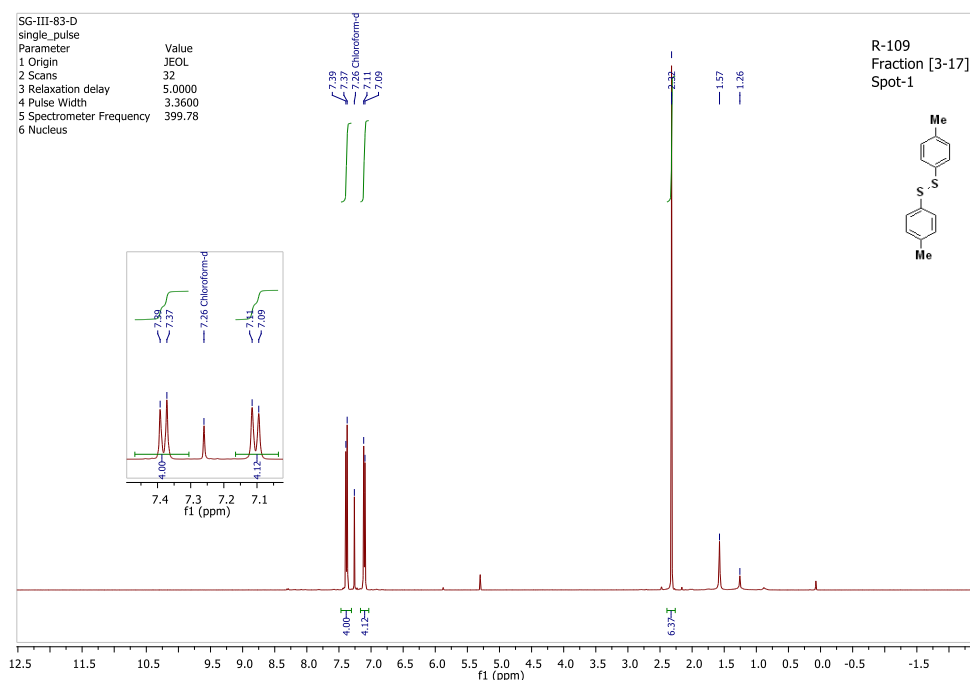
After column chromatography over silica gel, several compounds were separated.

**Fraction [2]** (1<sup>st</sup> less polar spot on TLC): <sup>1</sup>H NMR (**SG-III-83-B**) indicates the formation of *p*-tolyl disulfide: <sup>1</sup>H NMR (399.78 MHz, CDCl<sub>3</sub>, ppm) δ = 7.38 (d<sub>app</sub>, *J* = 8.1 Hz), 7.10 (d<sub>app</sub>, *J* = 8.1 Hz), 2.32 (s, 6H), when compared to an authentic sample.



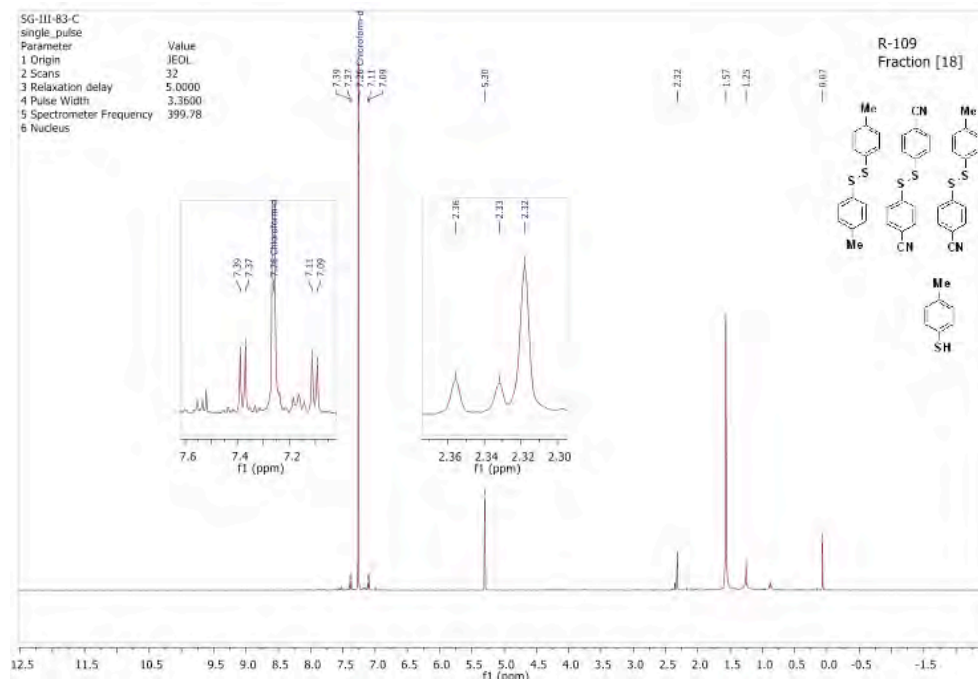
<sup>1</sup>H-NMR (399.78 MHz, CDCl<sub>3</sub>) SG-III-83B (fraction 2)

**Fraction [3-17]** (1<sup>st</sup> less polar spot on TLC): <sup>1</sup>H-NMR SG-III-83-D indicates disulfide containing Me groups (MePhSSPhMe). <sup>1</sup>H NMR (399.78 MHz, CDCl<sub>3</sub>, ppm) δ = 7.38 (d<sub>app</sub>, *J* = 8.1 Hz), 7.10 (d<sub>app</sub>, *J* = 8.1 Hz), 2.32 (s, 6H). Mass: 0.7 mg.



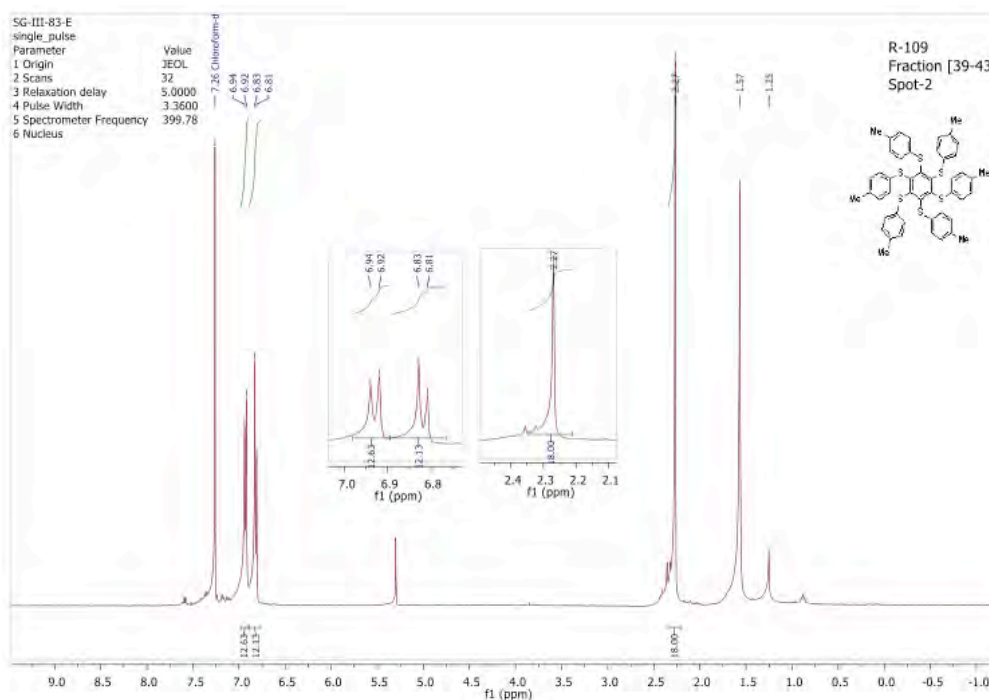
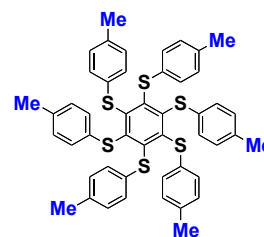
<sup>1</sup>H-NMR (399.78 MHz, CDCl<sub>3</sub>) SG-III-83D (fractions 3-17)

**Fraction [18]:**  $^1\text{H-NMR}$  SG-III-83-C product indicates mixture of disulfides. Mass: 0.2 mg.

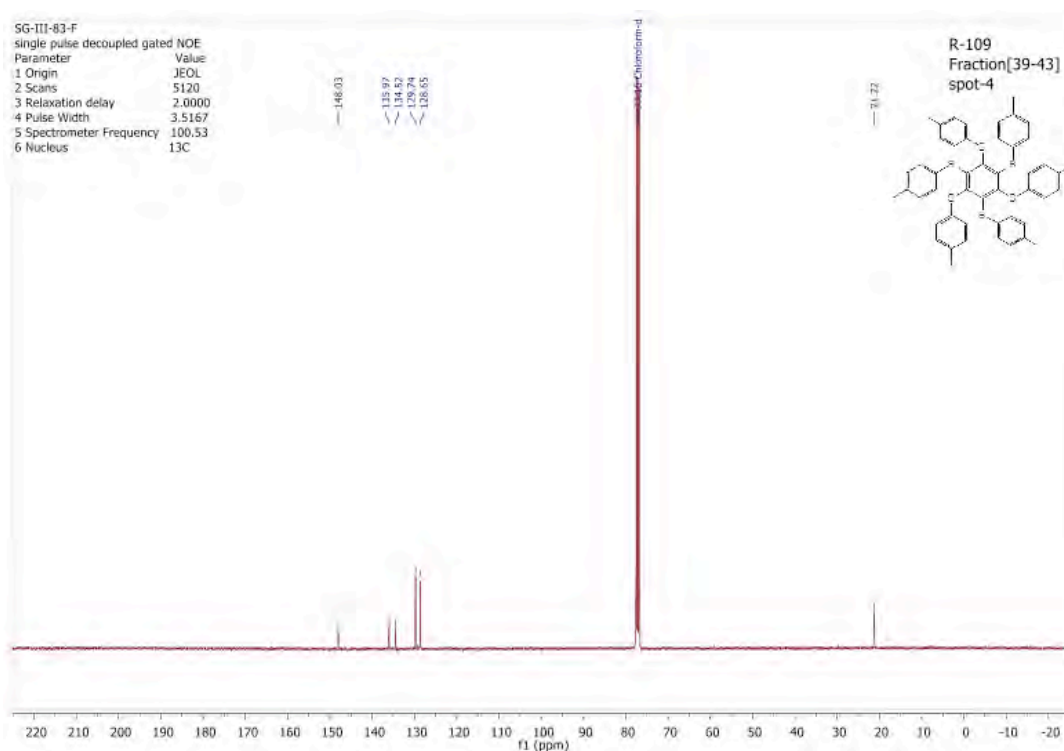


$^1\text{H-NMR}$  (399.78 MHz,  $\text{CDCl}_3$ ) SG-III-83C (fraction 18)

**Fraction [39-43]** (2<sup>nd</sup> spot on TLC):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , SG-III-83-E) indicates excellent exchange of sulfur ligands to provide hexakis (*p*-tolylthio)benzene.  $^1\text{H NMR}$  (399.78 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 6.93 (d<sub>app</sub>,  $J$  = 8.1 Hz, 12H), 6.82 (d<sub>app</sub>,  $J$  = 8.2 Hz, 12H), 2.29 (s, 18H);  $^{13}\text{C NMR}$  (100.53 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 148.03, 135.97, 134.53, 129.73, 128.65, 21.22. Mass: 25.1 mg.

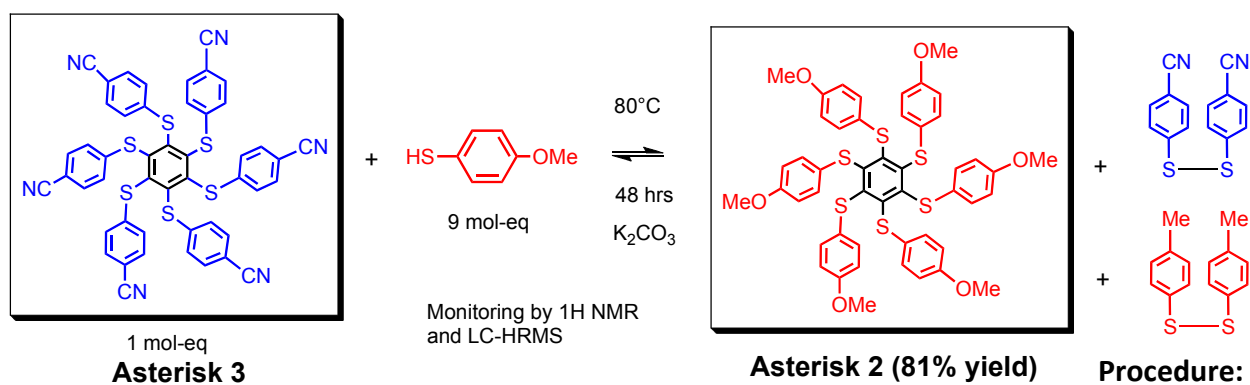


$^1\text{H-NMR}$  (399.78 MHz,  $\text{CDCl}_3$ ) SG-III-83E (fraction 39-43)



<sup>13</sup>C-NMR (399.78 MHz, CDCl<sub>3</sub>) SG-III-83E (fraction 39-43)

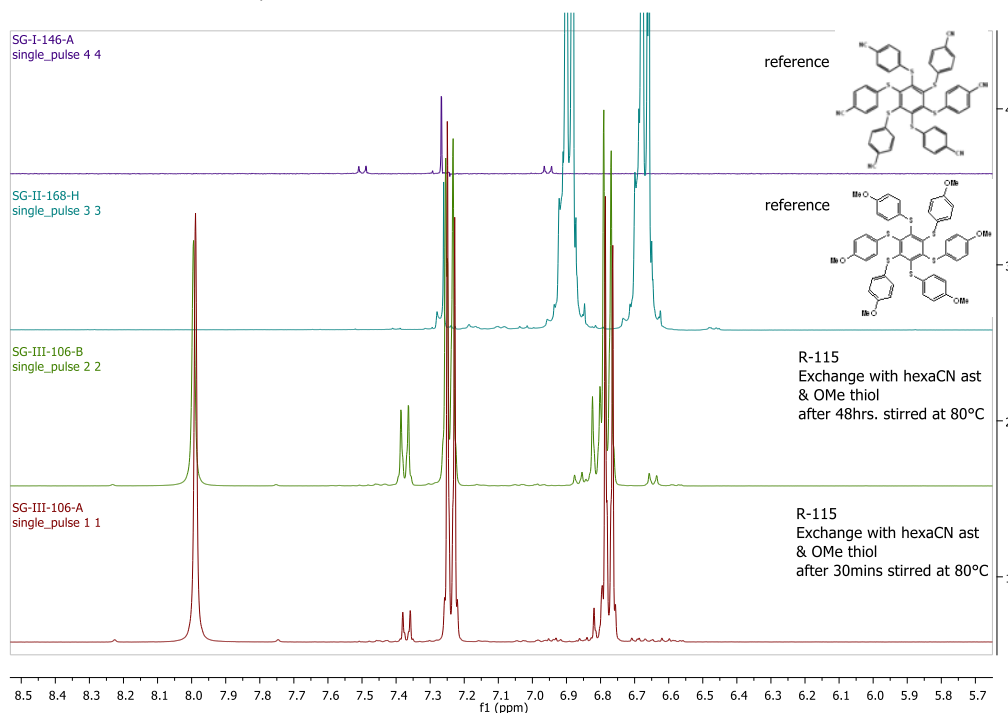
**(R-115) CONVERSION OF HEXAKIS(4-CYANOPHENYLTHIO)BENZENE TO HEXAKIS(4-METHOXYPHENYLTHIO) BENZENE**



**Procedure.** In an oven-dried tube, purged with argon, was added hexakis(4-cyanophenylthio)benzene (10.04 mg, 0.011 mmol, 1.00 mol-eq.), dried potassium carbonate (14.4 mg, 0.104 mmol, 9.45 mol-eq.) and 4-methoxybenzenethiol (14.8 mg, 0.105 mmol, 13 μL, 9.55 mol-eq.) in dry DMF (1.0 mL, dried and kept over activated 3 Å molecular sieves). Argon was bubbled through the mixture for 5-10 min.. The tube was sealed, and the reaction was stirred in an oil bath at 80°C for 2 days. DMF was removed from the reaction mixture on a rotary evaporator under reduced pressure. To the crude mixture was added water (30 mL) and it was extracted with toluene (4 × 30 mL). The collected organic phases were dried over anhydrous MgSO<sub>4</sub>, filtered, and the solvent evaporated. The products were separated by column chromatography over silica gel using acetone/cyclohex. (30:70 v/v) as eluent. Hexakis(*p*-tolylthio)benzene was isolated as a major product (8.1 mg, 81% yield).

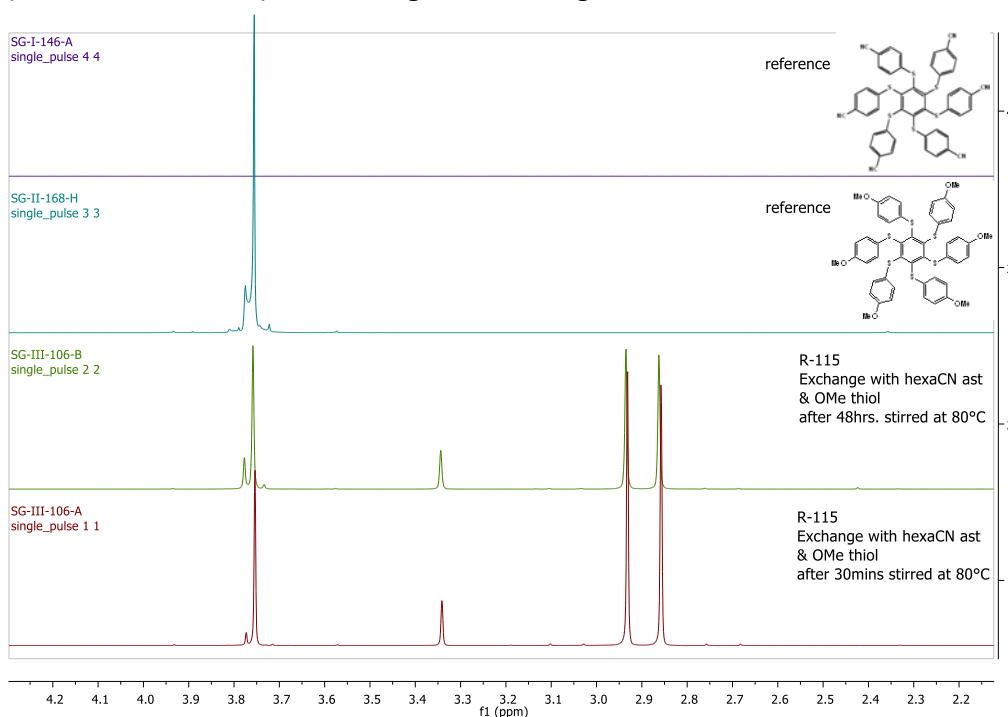
## **$^1\text{H}$ NMR monitoring and analysis of the mixture**

**$^1\text{H}$  NMR (399.78 MHz,  $\text{CDCl}_3$ , SG-III-106-A) monitoring after stirring for 30 min. at  $80^\circ\text{C}$  below.**



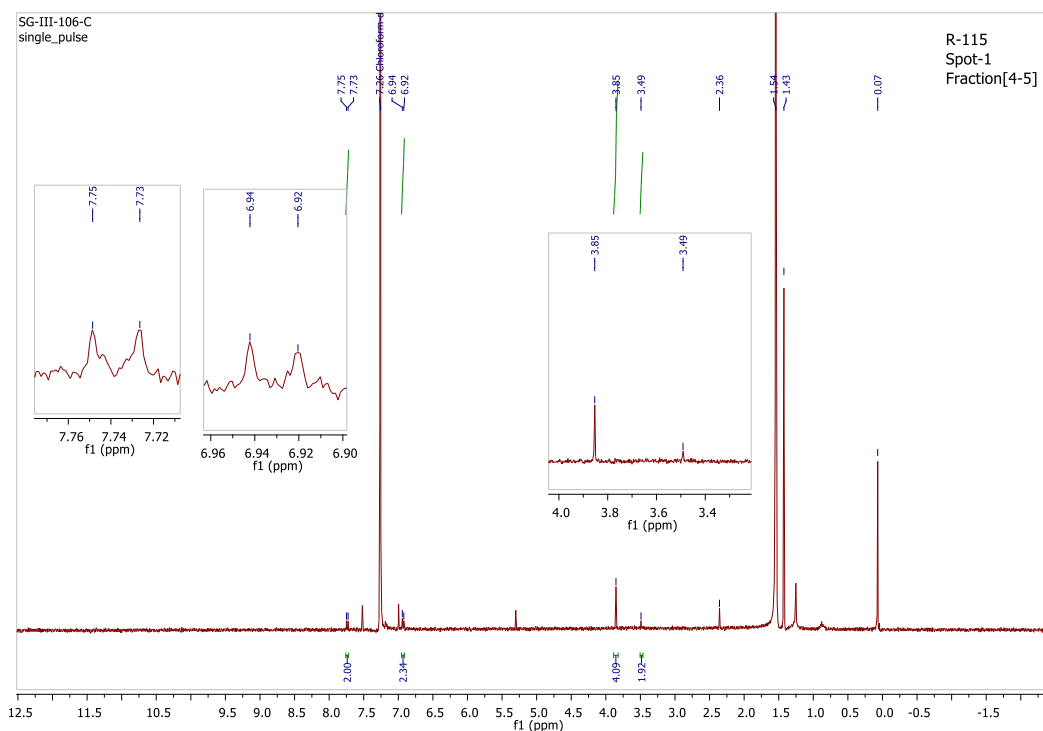
**$^1\text{H}$  NMR (399.78 MHz,  $\text{CDCl}_3$ , SG-III-106-A)**

**$^1\text{H}$  NMR (399.78 MHz,  $\text{CDCl}_3$ ) monitoring after stirring for 48 hrs at  $80^\circ\text{C}$  below.**



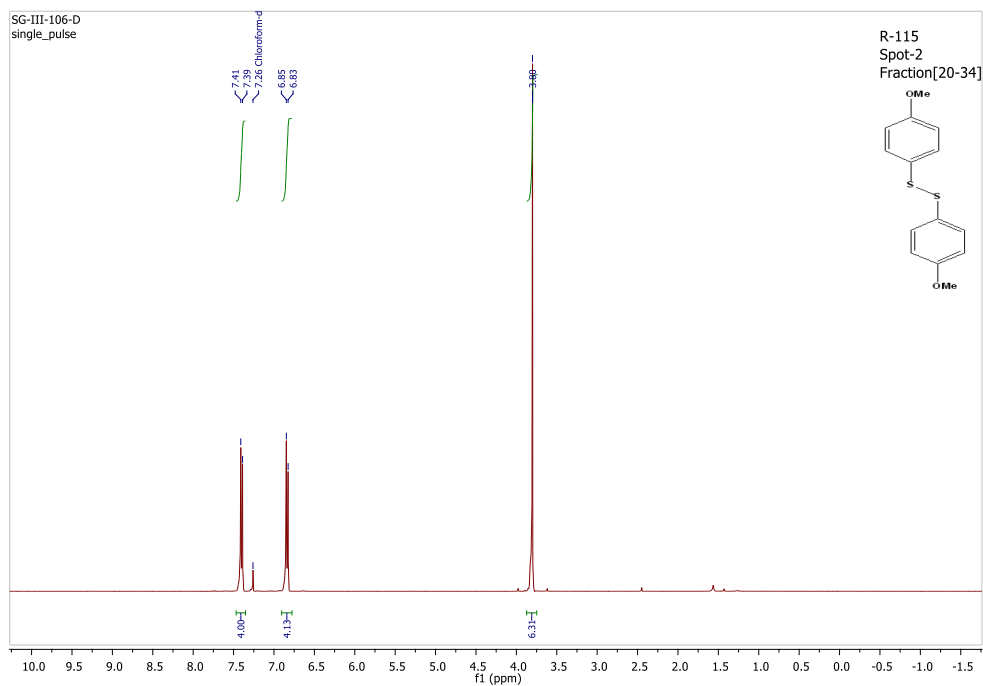
**$^1\text{H}$  NMR (399.78 MHz,  $\text{CDCl}_3$ , SG-III-106-B)**

**Fraction [4-5]** (1<sup>st</sup> spot on TLC, SG-III-106-C): Mass: 0.6 mg.



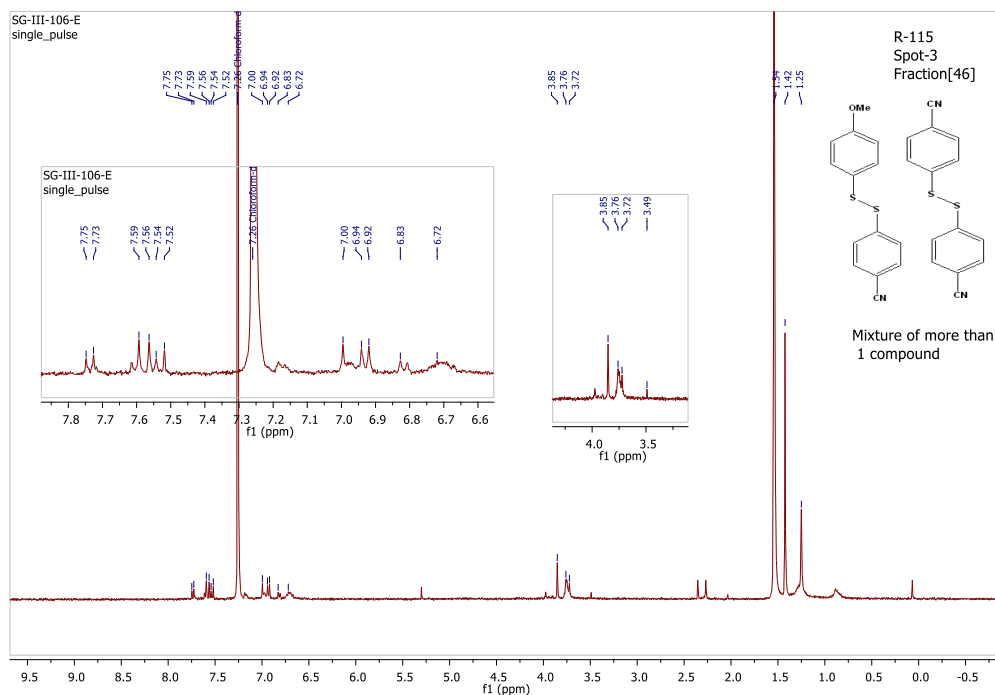
**Fraction [6-19]** (mixture of 1<sup>st</sup> and 2<sup>nd</sup> spot on TLC)

**Fraction [20-34]** (2<sup>nd</sup> spot on TLC): <sup>1</sup>H NMR (399.78 MHz, CDCl<sub>3</sub>, SG-III-106-D) indicates disulfide containing OMe groups for **MeOPhSSPhOMe**, as compared to the reference disulfide. <sup>1</sup>H NMR (399.78 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 7.40 (d,  $J$  = 9.0 Hz, 4H), 6.84 (d,  $J$  = 8.8 Hz, 4H), 3.78 (s, 6H). Mass: 87.7 mg.



<sup>1</sup>H NMR (399.78 MHz, CDCl<sub>3</sub>, SG-III-106-D)

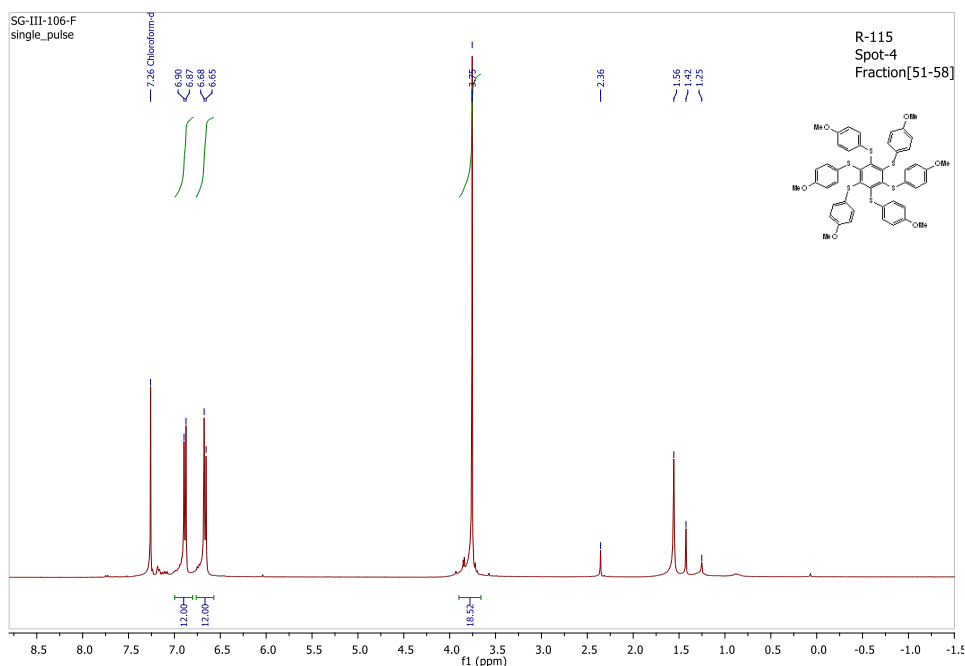
**Fraction [46]** (3<sup>rd</sup> spot on TLC): <sup>1</sup>H NMR (SG-III-106-E) indicates a mixture of disulfides containing OMe and CN groups (**MeOPhSSPhOMe**, **MeOPhSSPhCN**, **NCPHSSPhCN**). Mass: 0.1 mg.



<sup>1</sup>H NMR (399.78 MHz, CDCl<sub>3</sub>, SG-III-106-E)

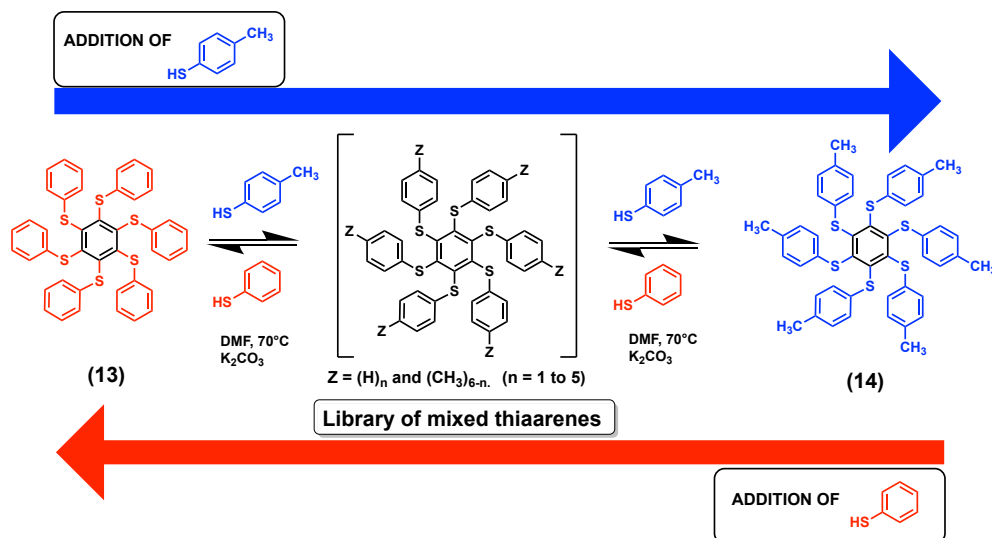
**Fraction [47-50]** (mixture of 3<sup>rd</sup> and 4<sup>th</sup> spot on TLC). Mass: 2.0 mg

**Fraction [51-58]** (4<sup>th</sup> spot on TLC): <sup>1</sup>H-NMR (SG-III-106-F) indicates **hexakis(p-methoxyphenylthio) benzene**, as compared to the reference asterisk. <sup>1</sup>H NMR (399.78 MHz, CDCl<sub>3</sub>, ppm) δ = 6.89 (d<sub>app</sub>, J = 8.7 Hz, 12H), 6.67 (d<sub>app</sub>, J = 8.7 Hz, 12H), 3.76 (s, 18H). Mass: 8.1 mg.



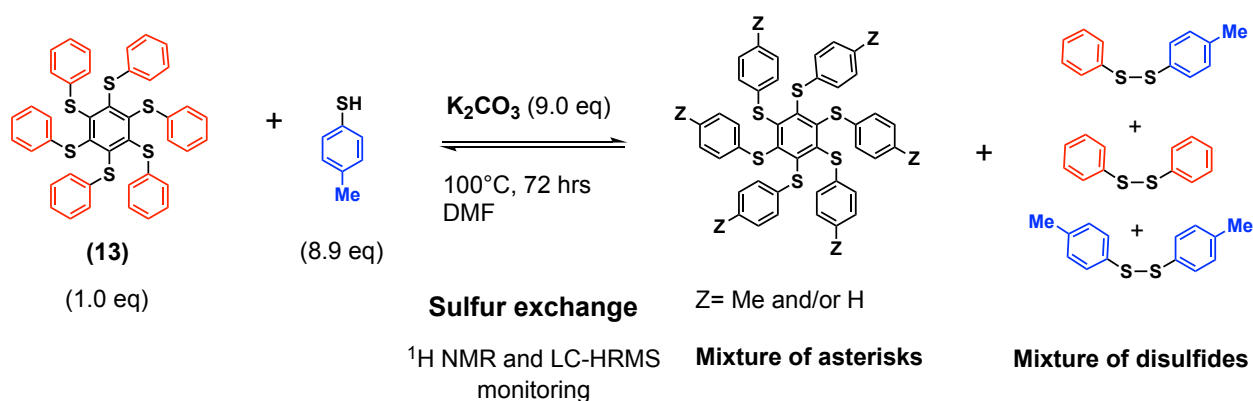
<sup>1</sup>H NMR (399.78 MHz, CDCl<sub>3</sub>, SG-III-106-F)

## 8.0 Demonstration of reversibility in $S_NAr$



**Conclusion:** Asterisk (**13**) reacted with *p*-thiocresol (8.9 mol-eq) to provide a library of mixed thiaarenes and (**14**) (Figure 4, reaction from left to right – **blue arrow**). When asterisk (**14**) reacted with thiophenol (9 mol-eq.), a similar library of mixed asterisks and (**13**) was produced (Figure 4 reaction from right to left – **red arrow**). The convergence of the product distribution in the two processes points to the reversible nature of the  $S_NAr$  process. It was monitored by  $^1\text{H}$  NMR and LC-HRMS, as shown below.

### SULFUR EXCHANGE REACTIONS WITH HEXAKIS(PHENYLTHIO)BENZENE AND 4-METHYLBENZENETHIOL



**(R-124) Procedure:** In an oven-dried sealed tube, purged with argon, was added hexakis(phenylthio)benzene (50.1 mg, 0.0689 mmol, 1.00 mol-eq), dried potassium carbonate (85.7 mg, 0.620 mmol, 9.00 mol-eq.) and 4-methylbenzenethiol (76.4 mg, 0.615 mmol, 8.93 mol-eq.) in dry DMF (0.9 mL, dried with molecular sieves  $3\text{\AA}$ ). Argon was bubbled through the mixture for 5-10 minutes in the tube. The tube was sealed under argon, and the reaction was stirred at  $100^\circ\text{C}$  in an oil bath for 3 days. DMF was removed from reaction mixture by evaporation under vacuum. To the crude mixture was added  $\text{H}_2\text{O}$  (20 mL), and the aqueous phase was extracted with toluene (4 $\times$ 20 mL). The collected organic phases were dried over anhydrous  $\text{MgSO}_4$ , filtered,



and evaporated. TLC (SiO<sub>2</sub>; acetone/cyclohexane 3:7 V/V and 60% toluene/cyclohexane (60:40 V/V) indicated two spots, the more polar was yellow. The solid was triturated with EtOH (5 mL) and filtered. A yellow solid was obtained: mass: 43.9 mg

## **<sup>1</sup>H NMR monitoring and analysis of the mixture**

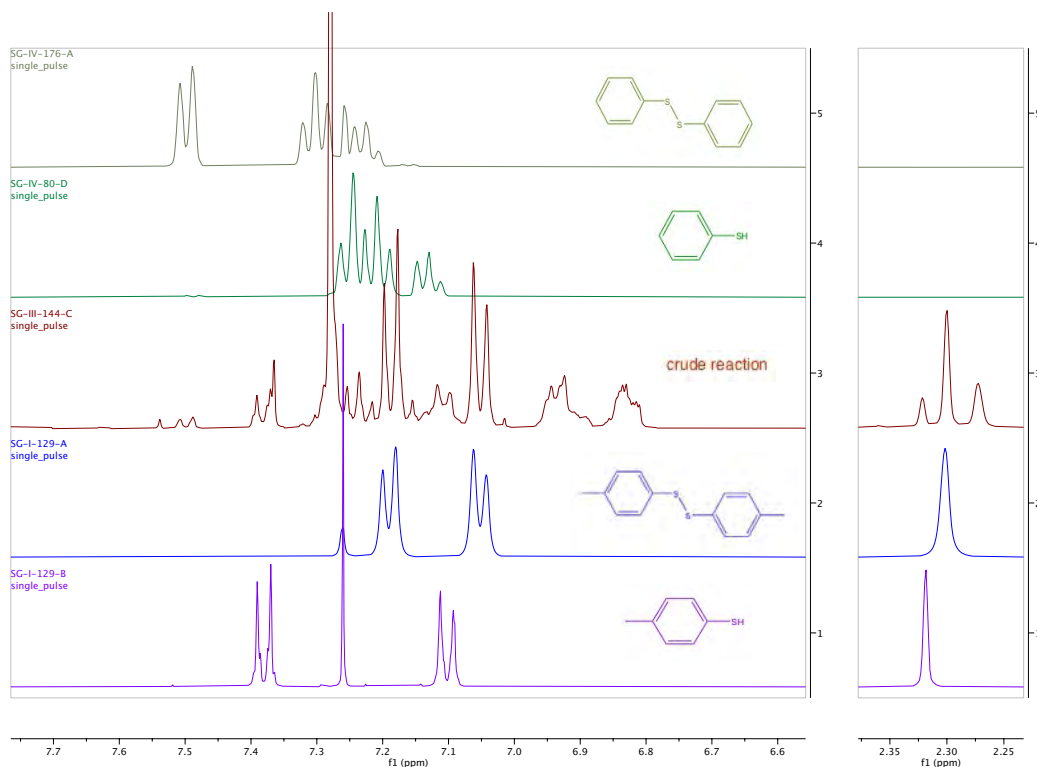
### **RESULTS**

<sup>1</sup>H NMR **SG-III-144-A** (CDCl<sub>3</sub>, 400MHz): reference asterisk (**13**)

<sup>1</sup>H NMR **SG-III-144-B** (CDCl<sub>3</sub>, 400MHz): reference asterisk (**14**)

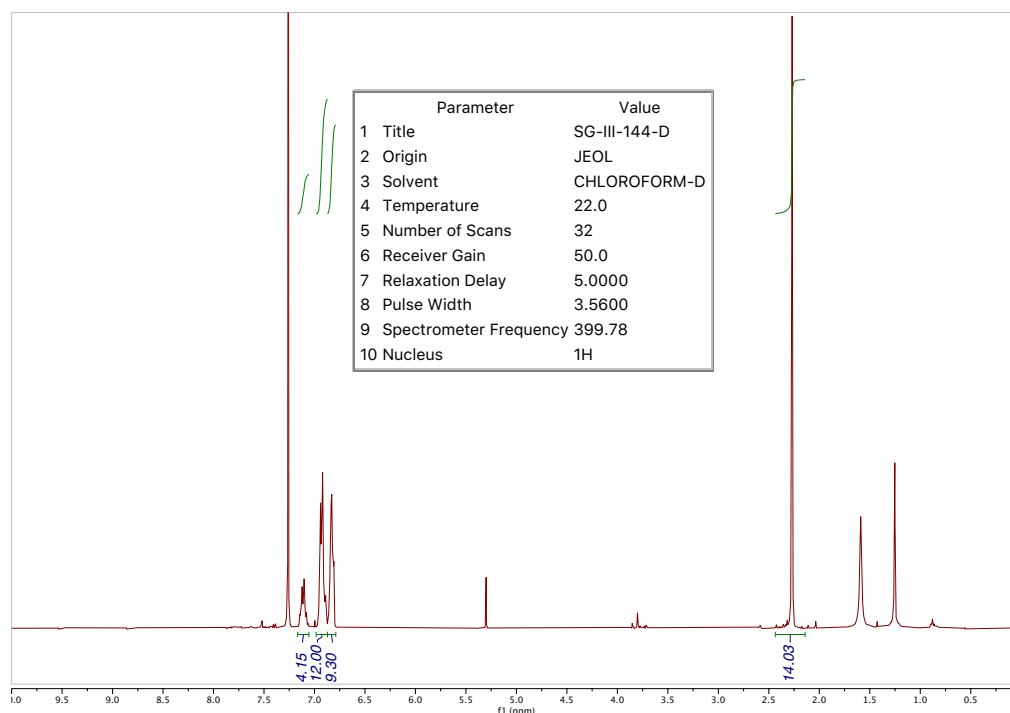
<sup>1</sup>H NMR **SG-III-144-C** (CDCl<sub>3</sub>, 400MHz): Small workup, after stirred for 48hrs. at 100°C

<sup>1</sup>H NMR **SG-III-144-D** (CDCl<sub>3</sub>, 400MHz): crude solid triturated with EtOH.

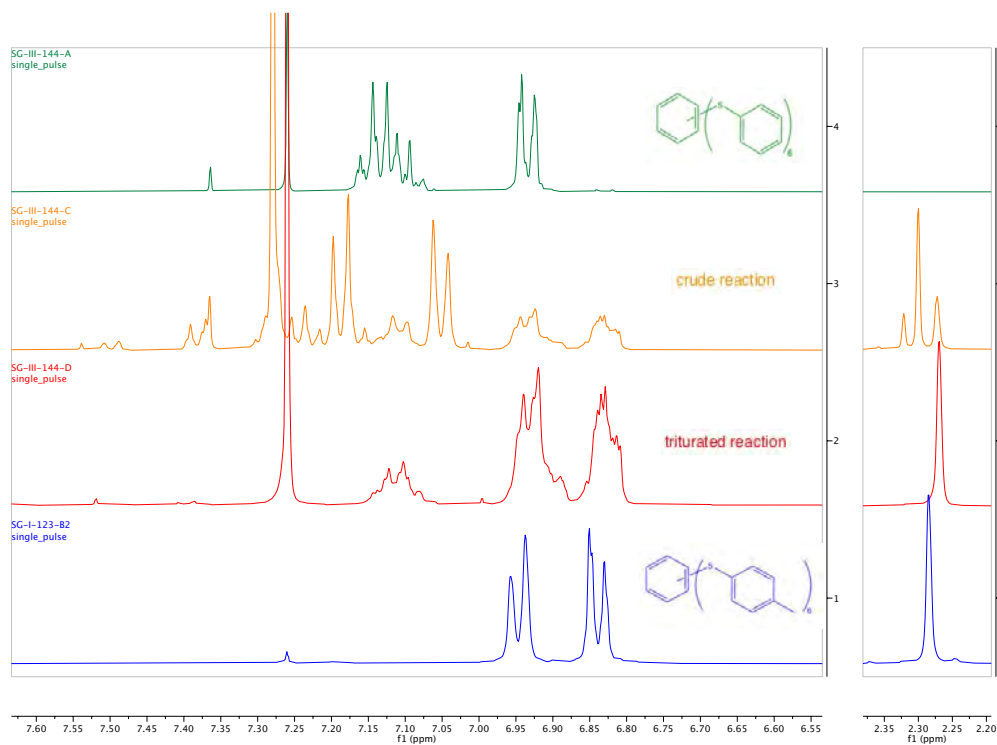


**(R-124) <sup>1</sup>H NMR** (399.78 MHz, CDCl<sub>3</sub>): **Spectra 1 (violet)**: reference spectra of 4-methylbenzenethiol. **Spectra 2 (blue)**: reference spectra of *p*-tolyl disulfide. **Spectra 3 (red)**: spectra of the crude reaction. **Spectra 4 (green)**: reference spectra of benzenethiol. **Spectra 5 (yellow-green)**: reference spectra of phenyl disulfide.

**Conclusion:** <sup>1</sup>H NMR indicated the presence of *p*-tolyl disulfide and *p*-thiocresol, as expected. Traces of phenyl disulfide and benzenethiol can also be seen. These species can only come from the displacement of the phenylthio groups from starting hexakis(phenylthio)benzene (**13**).



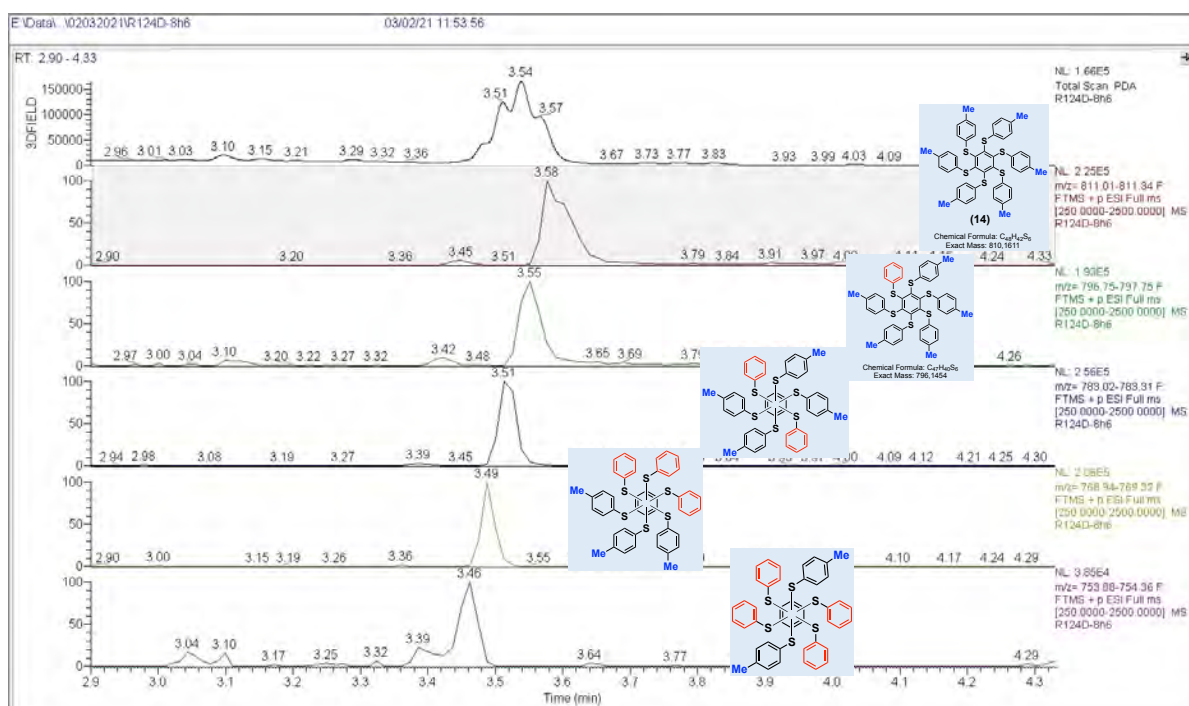
(R-124)  $^1\text{H}$  NMR (399.78 MHz,  $\text{CDCl}_3$ ): A trituration with EtOH removed most disulfides and thiols leaving mainly a mixture of asterisks. Most of the asterisks signals (6.8-7.0 ppm) of the crude and trituated reaction do not correspond to the reference spectra of asterisk (**13**) and (**14**), and additional signals are observed.



(R-124)  $^1\text{H}$  NMR (399.78 MHz,  $\text{CDCl}_3$ ): **Spectra 1 (blue)**: reference spectra of hexakis(*p*-tolylthio)benzene (**14**). **Spectra 2 (red)**: spectra after trituration with EtOH. **Spectra 3 (orange)**: spectra of the crude reaction. **Spectra 4 (green)**: reference spectra of hexakis(phenylthio)benzene (**13**).

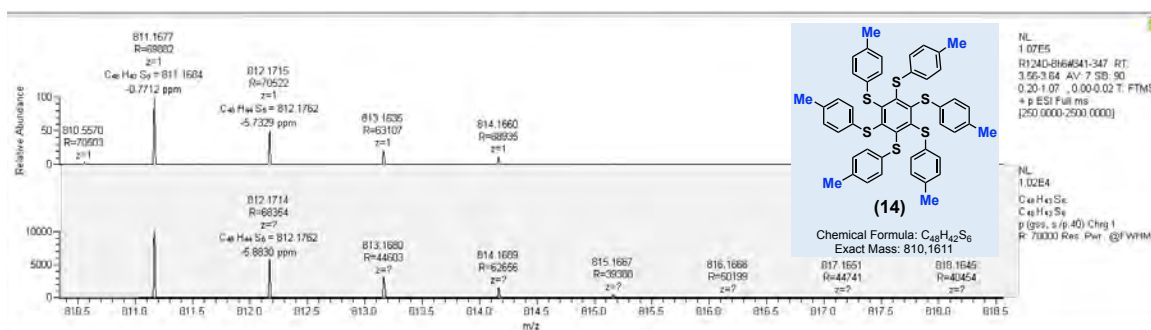
**Conclusion:** Sulfur components exchanges were clearly demonstrated by  $^1\text{H}$  NMR in that direction of exchange. A mixture of asterisks incorporating phenyl and *p*-tolylthio groups was formed. The presence of benzenethiol and phenyl disulfide in the crude mixture confirmed the release of benzenethiol from (13). A relative integration in the aromatic region shows an average of 4.6 tolyl groups incorporated into the structures of the asterisks, as a mixture.

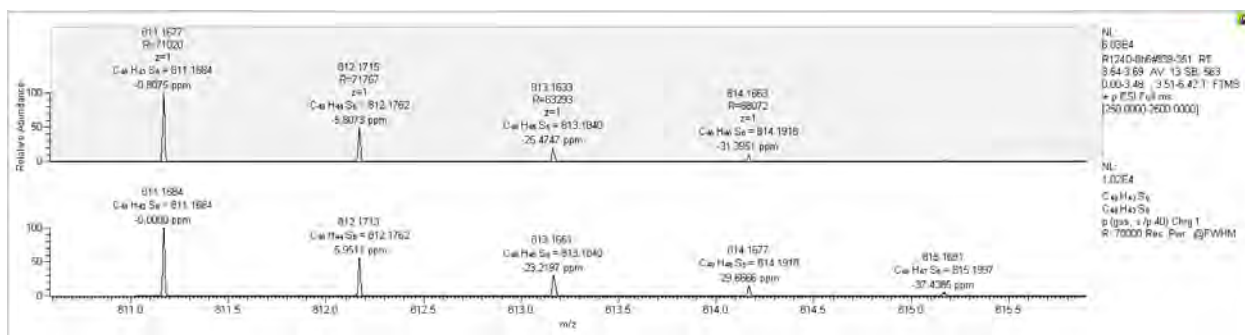
### LC-HRMS analysis of the crude mixture



### 6 Substitutions by 4-MePhSH:

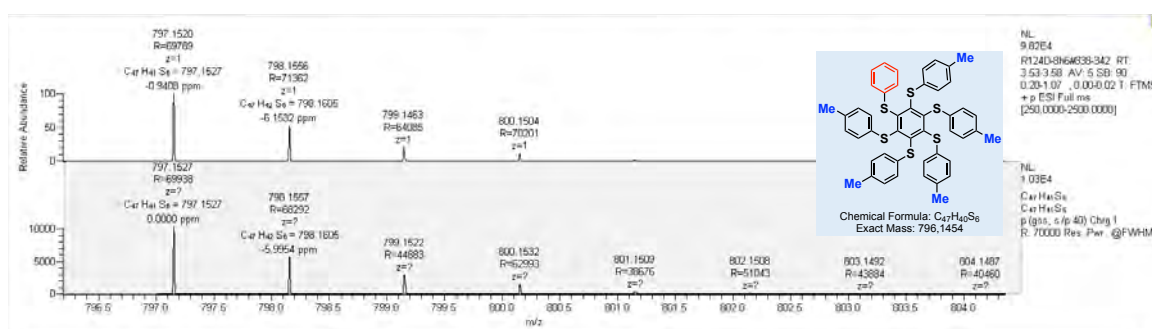
HRMS (ESI+) calculated for  $[\text{C}_{48}\text{H}_{42}\text{S}_6 + \text{H}^+]$ : 811.1684 Da, found  $[\text{M} + \text{H}^+]$  811.1677 m/z;





### 5 Substitutions by 4-MePhSH:

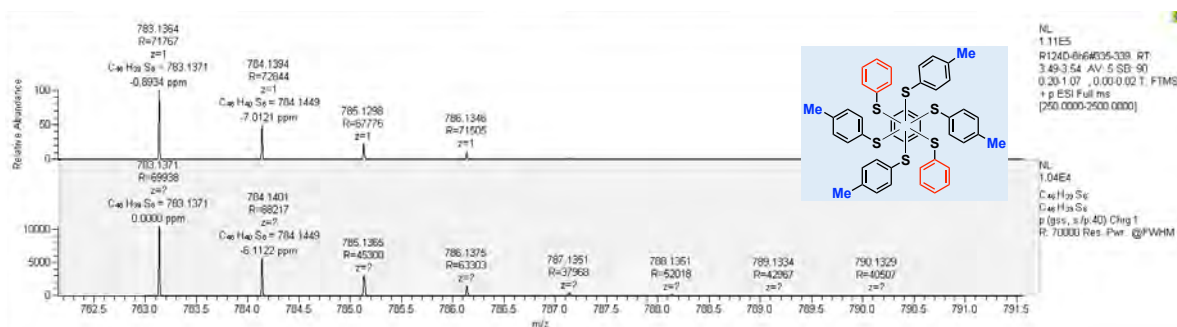
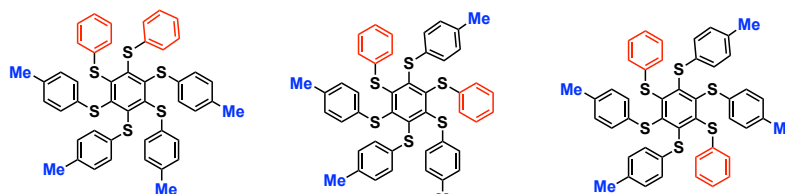
HRMS (ESI+) calculated for [C<sub>47</sub>H<sub>40</sub>S<sub>6</sub> + H<sup>+</sup>]: 797.1527 Da, found [M+H<sup>+</sup>] 797.1520 m/z;



### 4 Substitutions by 4-MePhSH:

HRMS (ESI+) calculated for [C<sub>46</sub>H<sub>38</sub>S<sub>6</sub> + H<sup>+</sup>]: 783.1371 Da, found [M+H<sup>+</sup>] 783.1364 m/z;

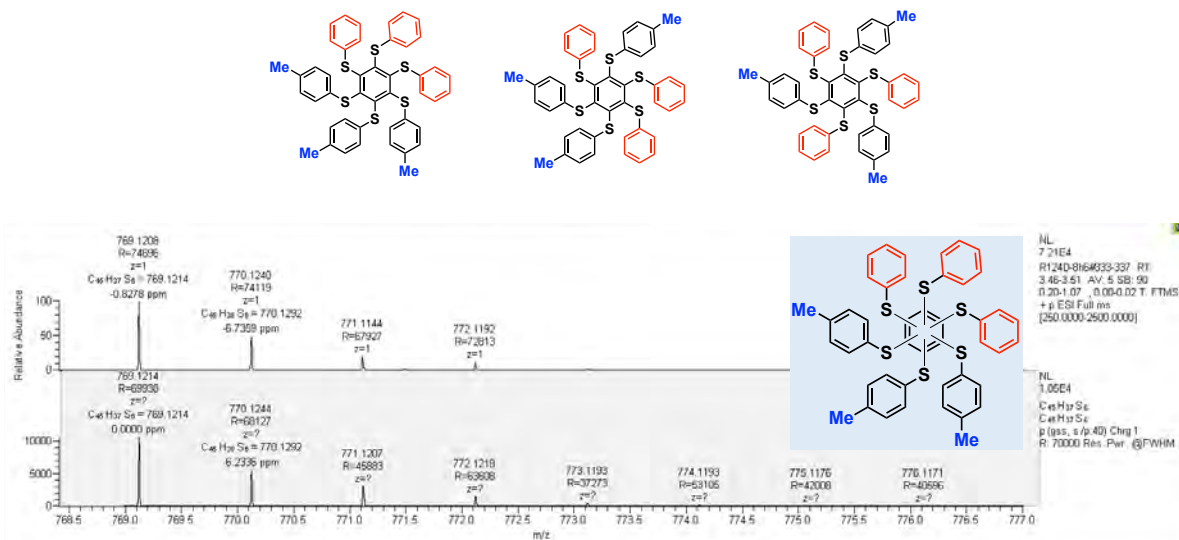
Possible isomers:



### 3 Substitutions by 4-MePhSH:

HRMS (ESI+) calculated for [C<sub>45</sub>H<sub>36</sub>S<sub>6</sub> + H<sup>+</sup>]: 769.1214 Da, found [M+H<sup>+</sup>] 769.1208 m/z;

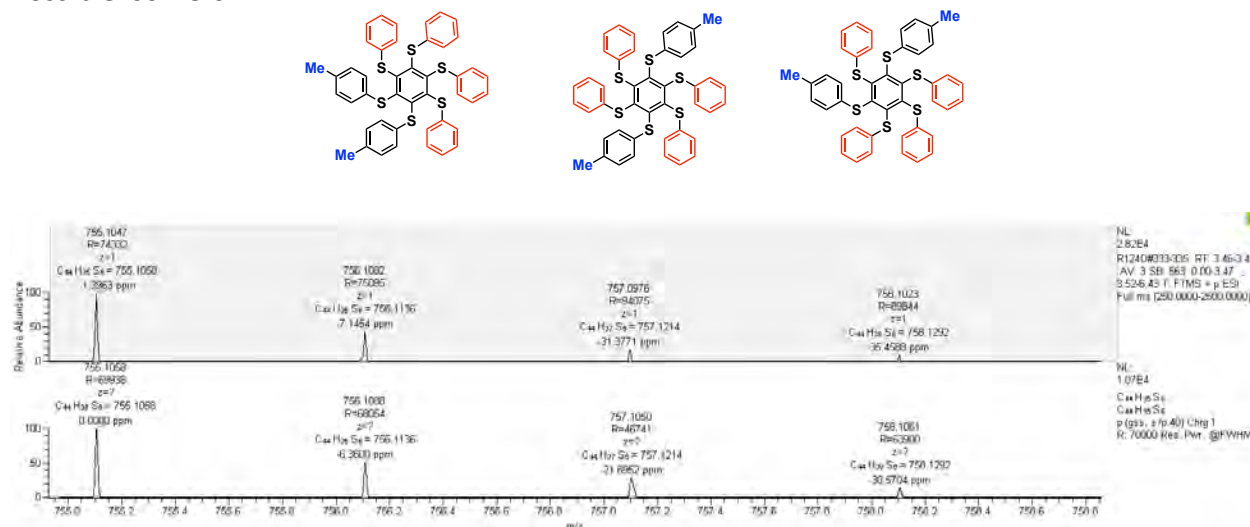
Possible isomers:



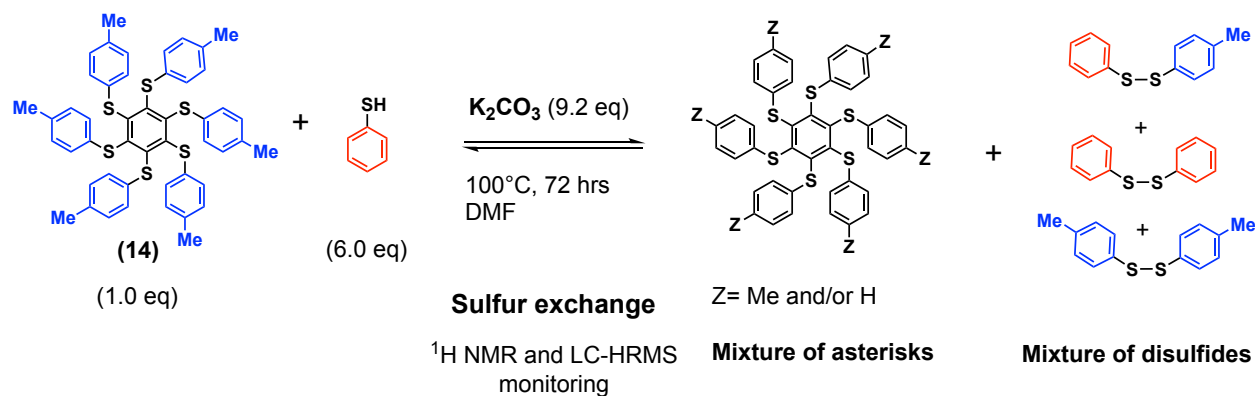
## 2 Substitutions by 4-MePhSH:

HRMS (ESI+) calculated for  $[C_{44}H_{34}S_6 + H^+]$ : 755.1058 Da, found  $[M+H^+]$  755.1407 m/z;

Possible isomers:



## Sulfur exchange with hexakis(4-tolylthio)benzene and 4-methylbenzenethiol

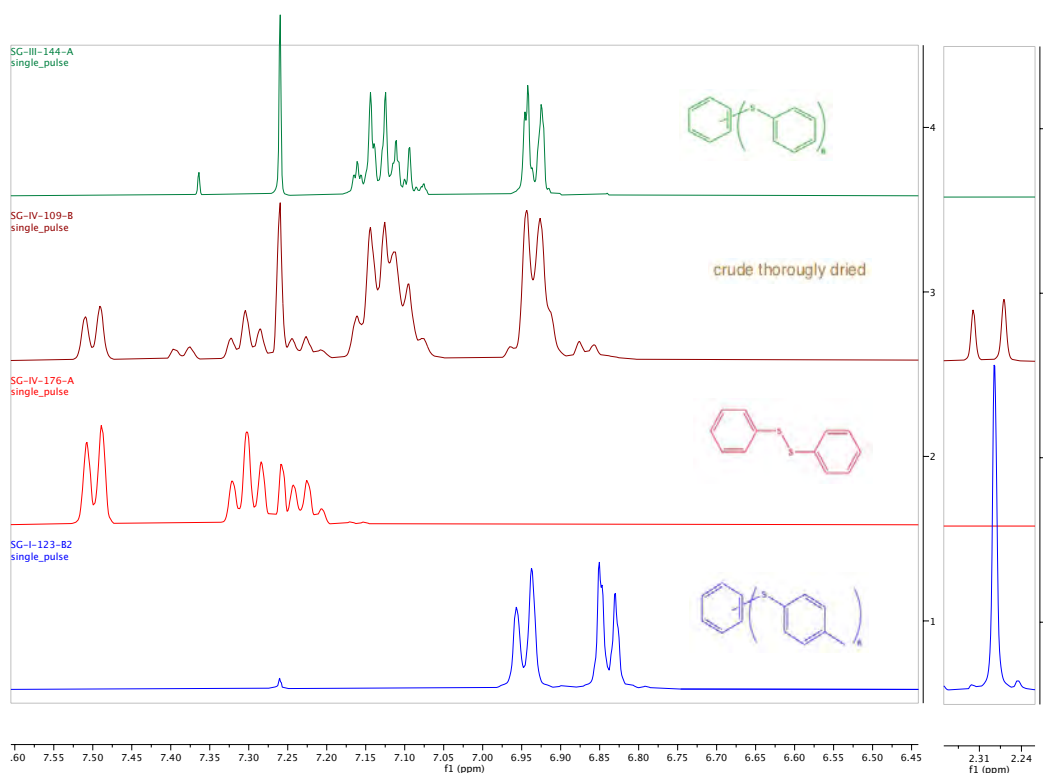


**(R-177) Procedure:** In an oven-dried sealed tube, purged with argon, was added hexakis(4-methylphenylthio) benzene (**14**) (50.4 mg, 0.0621 mmol, 1.00 mol-eq.), dried potassium carbonate (78.5 mg, 0.568 mmol, 9.15 mol-eq.) and thiophenol (41.0 mg, 0.372 mmol, 38  $\mu$ L, 6.0 mol-eq.) in dry DMF (1.0 mL, dried with molecular sieves 3 $\text{Å}$ ). Argon was bubbled through the mixture for 5-10 minutes in the tube. It was sealed under argon, and the reaction was stirred at 100 $^{\circ}$ C in an oil bath for 3 days. To the crude mixture was added H<sub>2</sub>O (20 mL), and the aqueous phase was extracted with toluene (3 $\times$ 20 mL). The collected organic phases were dried over anhydrous MgSO<sub>4</sub>, filtered, and evaporated. Mass: 53.1 mg.

### **$^1\text{H}$ NMR monitoring and analysis of the mixture**

**$^1\text{H}$ -NMR SG-IV-109-A:** small workup, after 3 days at 100 $^{\circ}$ C

**$^1\text{H}$ -NMR SG-IV-109-B:** after final workup, 3 days at 100 $^{\circ}$ C



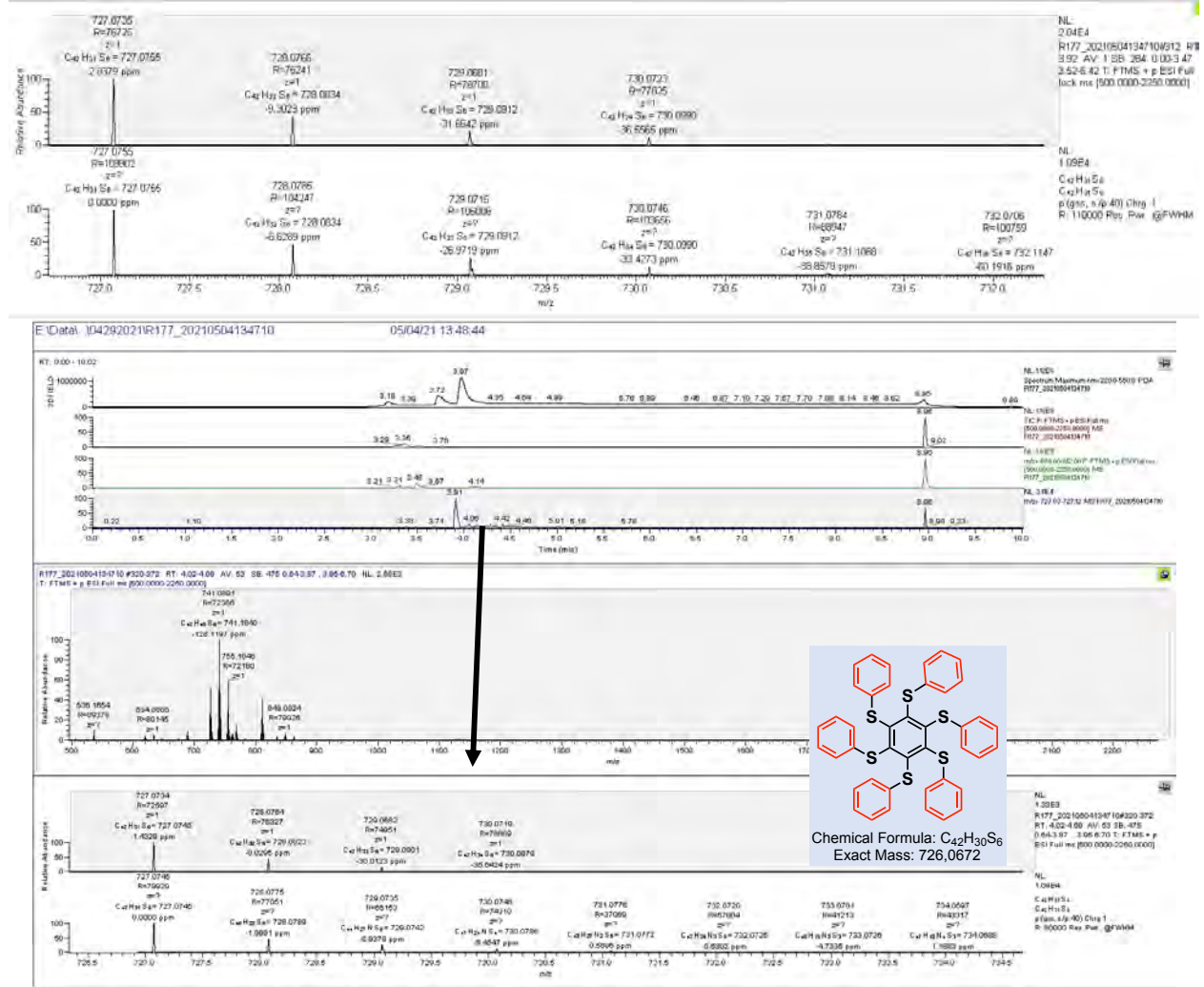
**(R-177)  $^1\text{H}$  NMR (399.78 MHz, CDCl<sub>3</sub>):** **Spectra 1 (blue):** reference spectra of hexakis (*p*-tolylthio) benzene (**14**). **Spectra 2 (red):** reference spectra of phenyl disulfide. **Spectra 3 (dark red):** spectra of the crude reaction. **Spectra 4 (green):** reference spectra of hexakis (phenylthio)benzene (**13**).

**Conclusion:** In the crude spectrum, as expected, phenyl disulfide can be clearly identified. The starting asterisk hexakis(*p*-tolylthio)benzene (**14**) had mostly reacted, and a mixture of new asterisks were generated, likely to be hexakis(phenylthio)benzene (**13**) as a major component, as well as mixed asterisks and/or a mixed disulfide.

### **LC-HRMS analysis of the crude mixture**

### 6 Substitutions by PhSH:

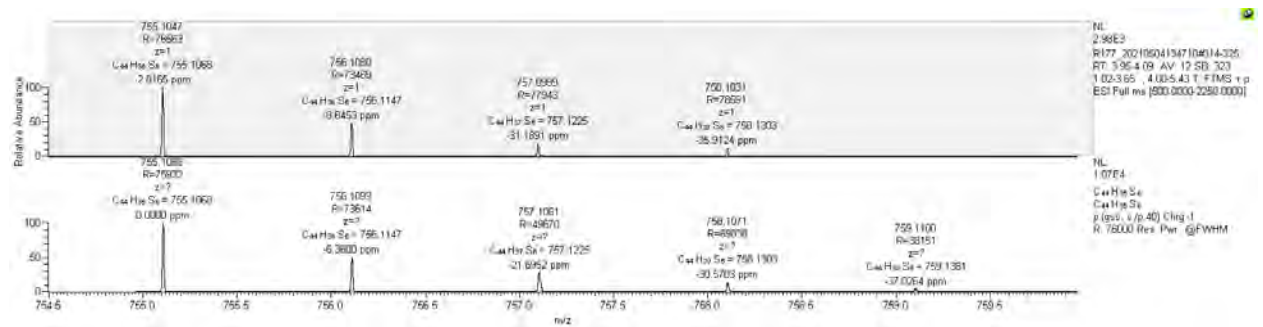
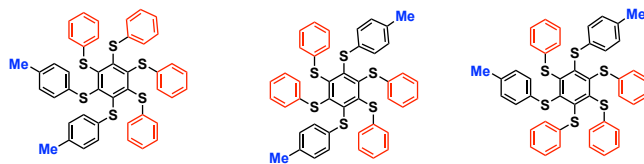
HRMS (ESI+) calculated for  $[C_{42}H_{30}S_6 + H^+]$ : 727.0755 Da, found  $[M+H^+]$  727.0735 m/z;



### 4 Substitutions by PhSH:

HRMS (ESI+) calculated for  $[C_{44}H_{34}S_6 + H^+]$ : 755.1068 Da, found  $[M+H^+]$  755.1047 m/z;

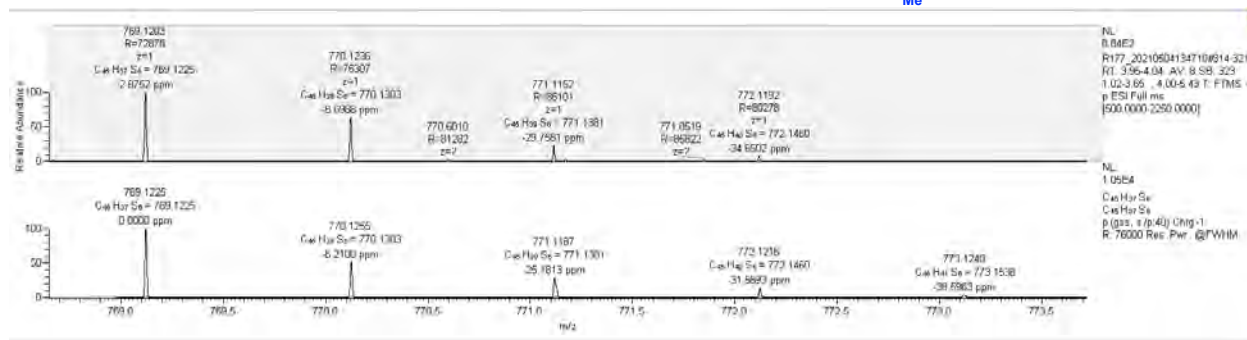
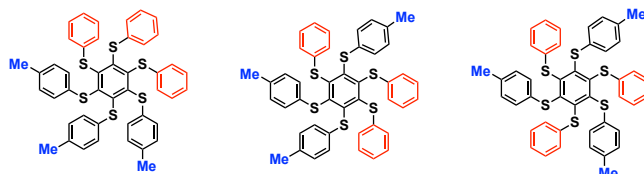
Possible isomers:



### 3 Substitutions by PhSH:

HRMS (ESI+) calculated for  $[C_{45}H_{36}S_6 + H^+]$ : 769.1225 Da, found  $[M+H^+]$  769.1203 m/z;

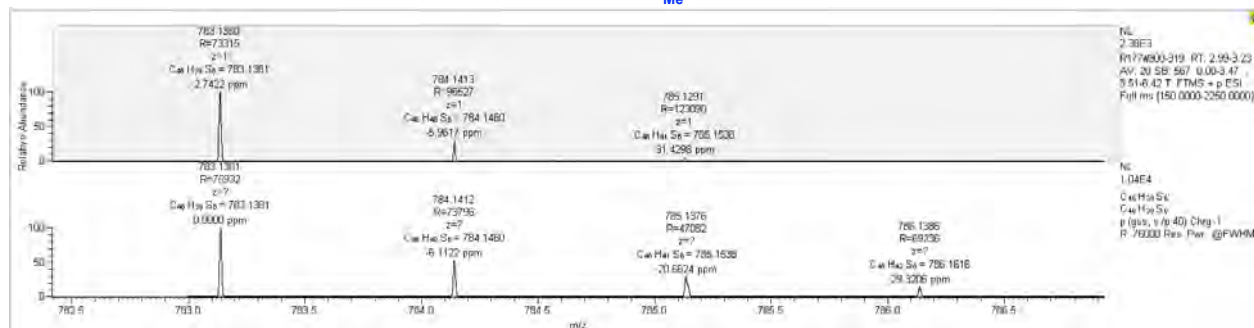
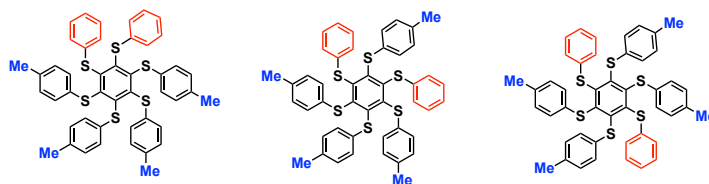
Possible isomers:



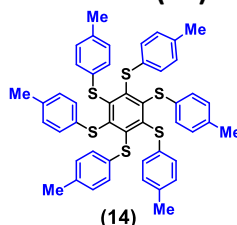
### 2 Substitutions by PhSH:

HRMS (ESI+) calculated for  $[C_{46}H_{38}S_6 + H^+]$ : 783.1381 Da, found  $[M+H^+]$  783.1360 m/z;

Possible isomers:



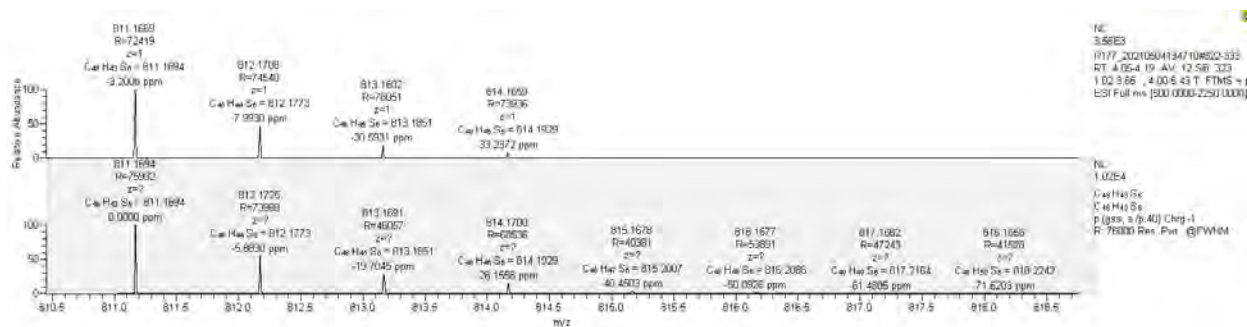
### Asterisk (14)



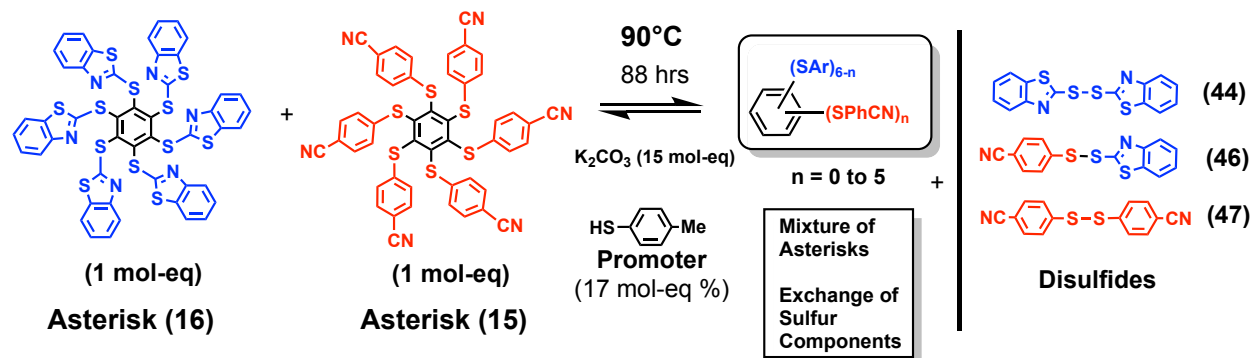
### 0 Substitution by PhSH:

HRMS (ESI+) calculated for  $[C_{48}H_{42}S_6 + H^+]$ : 811.1694 Da, found  $[M+H^+]$  811.1669 m/z;





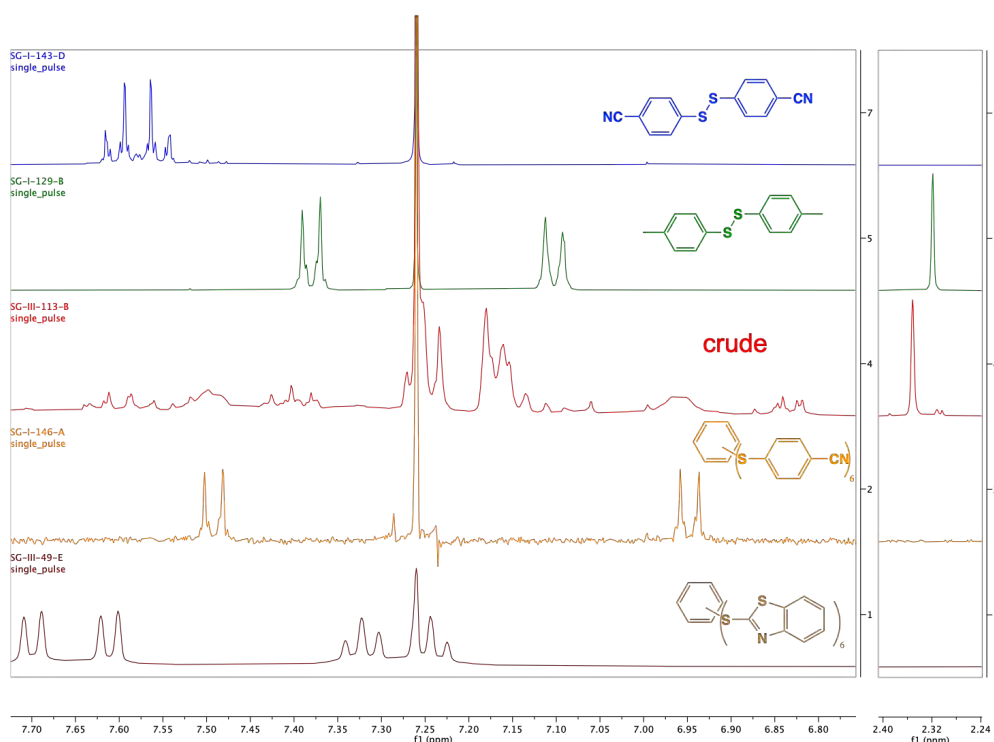
## 9.0 Exchange of sulfur components between two asterisks with a thiol as a promoter (demonstration of reversibility)



**(R-114) Procedure:** In an oven-dried sealed tube, purged with argon, was added hexakis(4-cyano-phenylthio)benzene asterisk **(15)** (8.23 mg, 0.0094 mmol, 1,00 mol-eq.), dried potassium carbonate (20.0 mg, 0.144 mmol, 20 mol%, 15,3 mol-eq.) and hexakis(benzenethiazolyl-2-thio)benzene **(16)** (10.0 mg, 0.0093 mmol, 1,00 mol-eq.), 4-methylbenzenethiol (0.2 mg, 0.0016 mmol, 17 mol% relative to **15** or **16**) in dry DMF (0.9 mL - dried with molecular sieves 3Å). Argon was bubbled through the mixture for 5-10 minutes in the tube. It was sealed, and the reaction was stirred at 90°C in an oil bath for 88 hrs. Most of DMF was removed from reaction mixture in vacuo. To the crude mixture was added H<sub>2</sub>O (30 mL), and the aqueous phase was extracted with toluene (4×30 mL). The collected organic phases were dried over anhydrous MgSO<sub>4</sub>, filtered, and evaporated. TLC (30% acetone/70% cyclohexane V/V) indicated several spots and the mass obtained was 2.4 mg.

### <sup>1</sup>H NMR monitoring and analysis of the mixture

Results: <sup>1</sup>H-NMR **SG-III-113-B** (CDCl<sub>3</sub>, 400MHz): After workup and drying.



**(R-114)  $^1\text{H}$  NMR** (399.78 MHz,  $\text{CDCl}_3$ ): **Spectra 1 (brown)**: reference spectra hexakis(benzenethiazolyl-2-thio)benzene (**16**). **Spectra 2 (orange)**: reference spectra of hexakis(*p*-cyanophenylthio)benzene (**15**). **Spectra 3 (red)**: spectra of crude reaction mixture. **Spectra 4 (green)**: reference spectra of *p*-tolyl disulfide. **Spectra 5 (blue)**: reference spectra of *p*-cyanophenyl disulfide (**47**)

**Conclusion:** According to  $^1\text{H}$ -NMR, there is no *p*-tolyl disulfide in the crude reaction (nor thiol). The signals of hexakis(benzenethiazolyl-2-thio)benzene (**16**) asterisk disappeared, but we cannot rule out the presence of hexakis(4-cyanophenylthio)benzene asterisk (**15**). From a comparison to the reference spectra of 4-cyanophenyl disulfide (spectra 5, blue), we can conclude to the presence in the crude of 4-cyanophenylthio groups, either from mixed disulfides (**46**), from some mixed cyano-containing asterisks or from 4-cyanophenyl disulfide (**47**). Overall, we can conclude for some sulfur component exchanges, as confirmed by LC-HRMS (next section).

### LC-HRMS analysis of the crude mixture

**Conclusion:** Exchange of sulfur components between asterisks (**15**) and (**16**) through reversible  $\text{S}_\text{N}\text{Ar}$  in the “sulfur dance” is promoted by *p*-thiocresol. Products resulting from reversible exchange of sulfur components from asterisks (**15**) and (**16**) are observed, as determined by LC-HRMS (below, Figure 5b and LC-HRMS chromatogram)

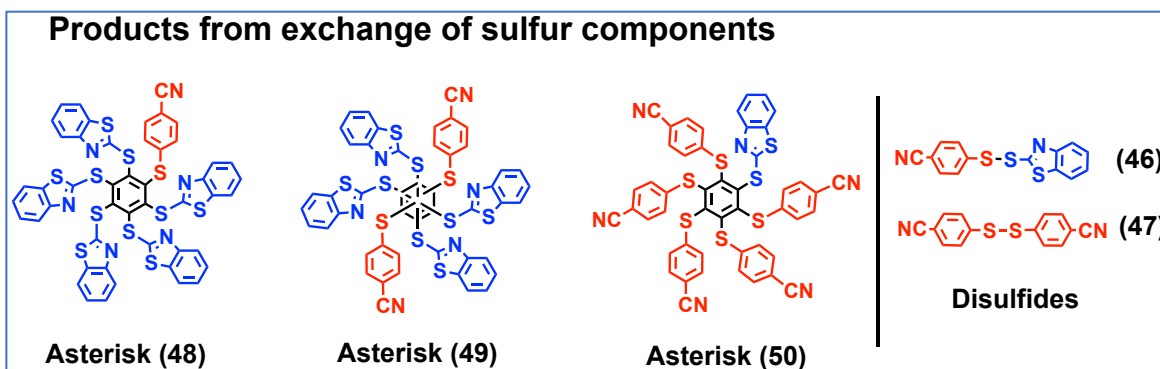
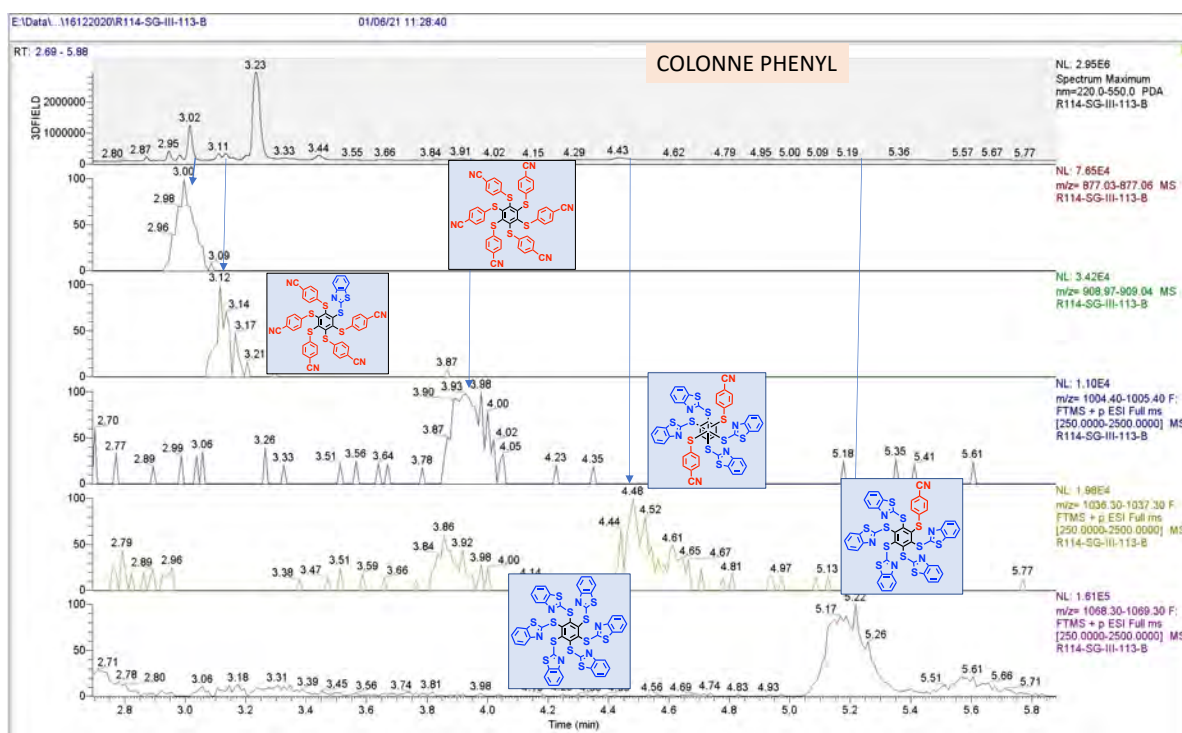


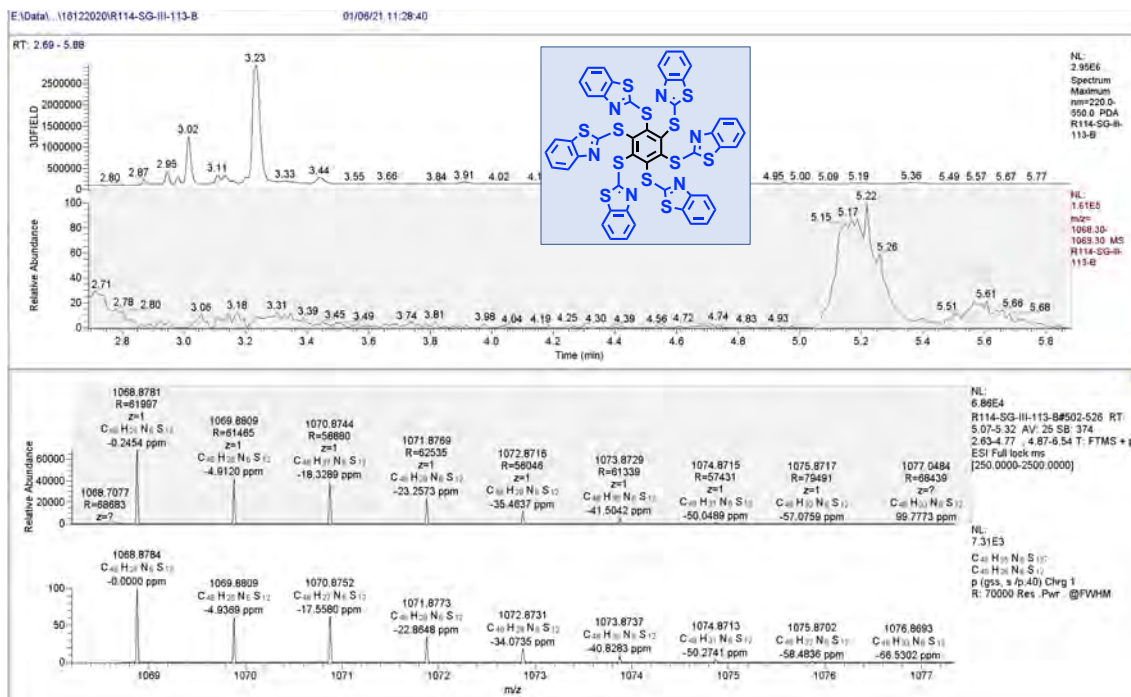
Figure 5b: products detected by LC-HRMS

**LC-HRMS Chromatogram of the mixture (R-113):  
sulfur component exchanges**



**Asterisk (16)**

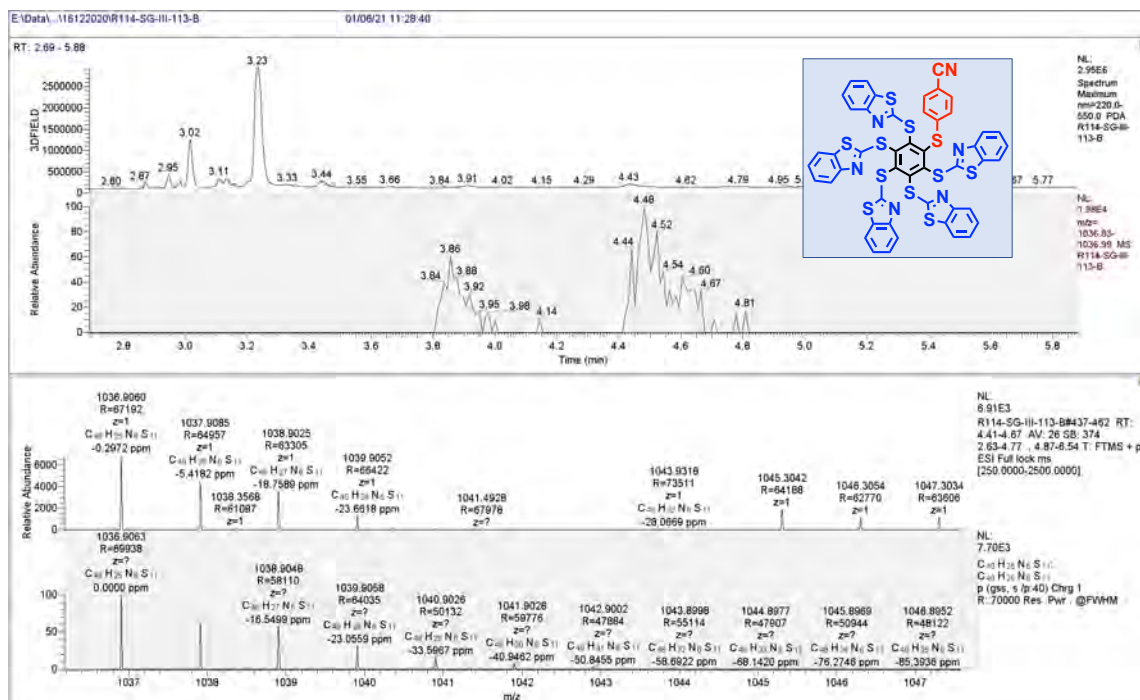
HRMS (ESI+) calculated for  $[C_{48}H_{24}N_6S_{12} + H^+]$ : 1068.8784 Da, found  $[M+H^+]$  1068.8781 m/z;



**Asterisk (48):**

**1 Substitution by 4-CNPhSh:**

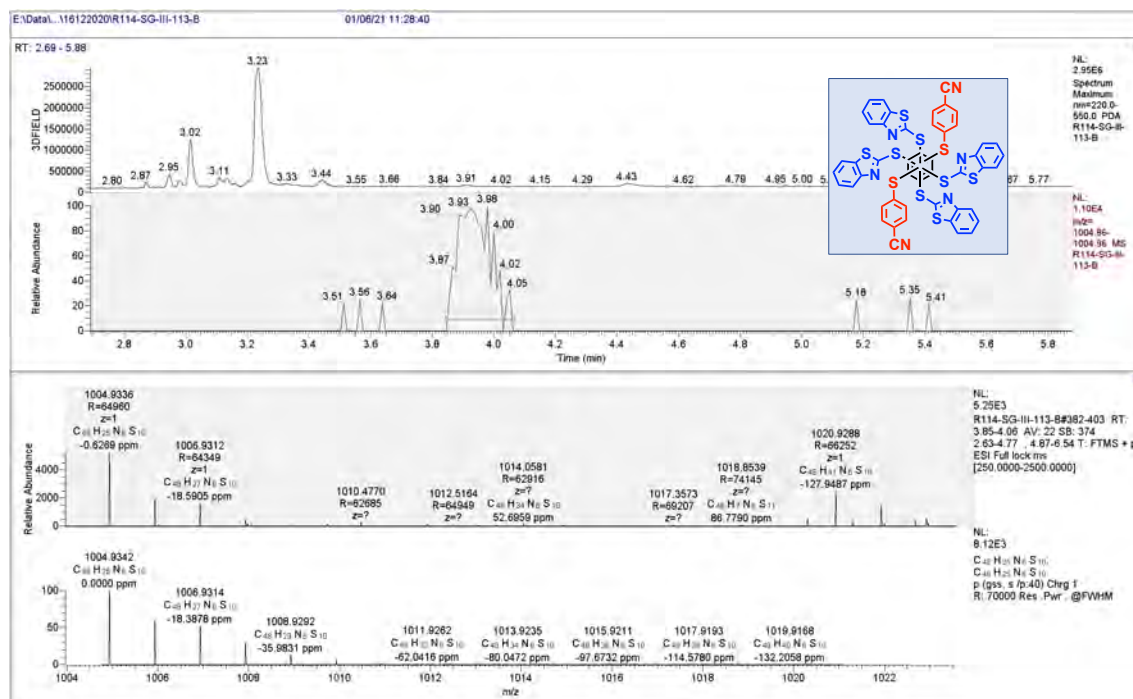
**HRMS (ESI+) calculated for [C<sub>48</sub>H<sub>24</sub>N<sub>6</sub>S<sub>11</sub> + H<sup>+</sup>]: 1036.9063 Da, found [M+H<sup>+</sup>] 1036.9060 m/z;**



### Asterisk (49)

#### 2 Substitutions by 4-CNPhSH:

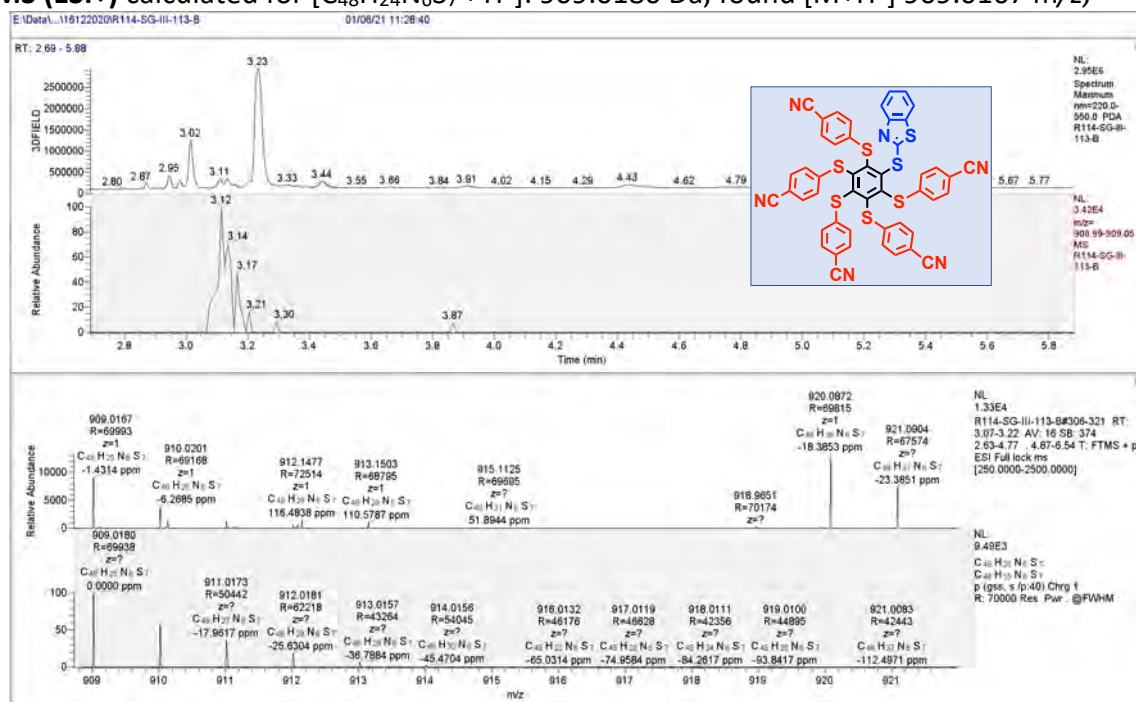
HRMS (ESI+) calculated for  $[C_{48}H_{24}N_6S_{10} + H^+]$ : 1004.9432 Da, found  $[M+H^+]$  1004.9336 m/z;



### Asterisk (50)

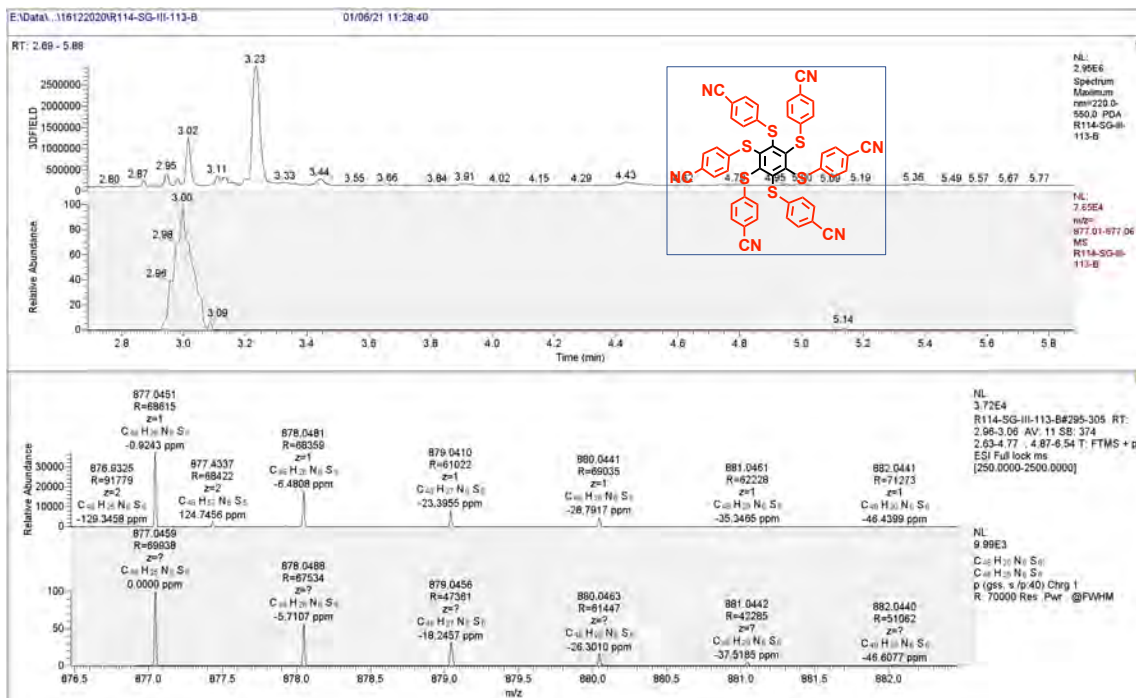
#### 4 Substitutions by 4-CNPhSH:

HRMS (ESI+) calculated for  $[C_{48}H_{24}N_6S_7 + H^+]$ : 909.0180 Da, found  $[M+H^+]$  909.0167 m/z;

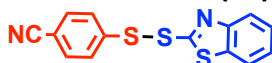


### Asterisk (15)

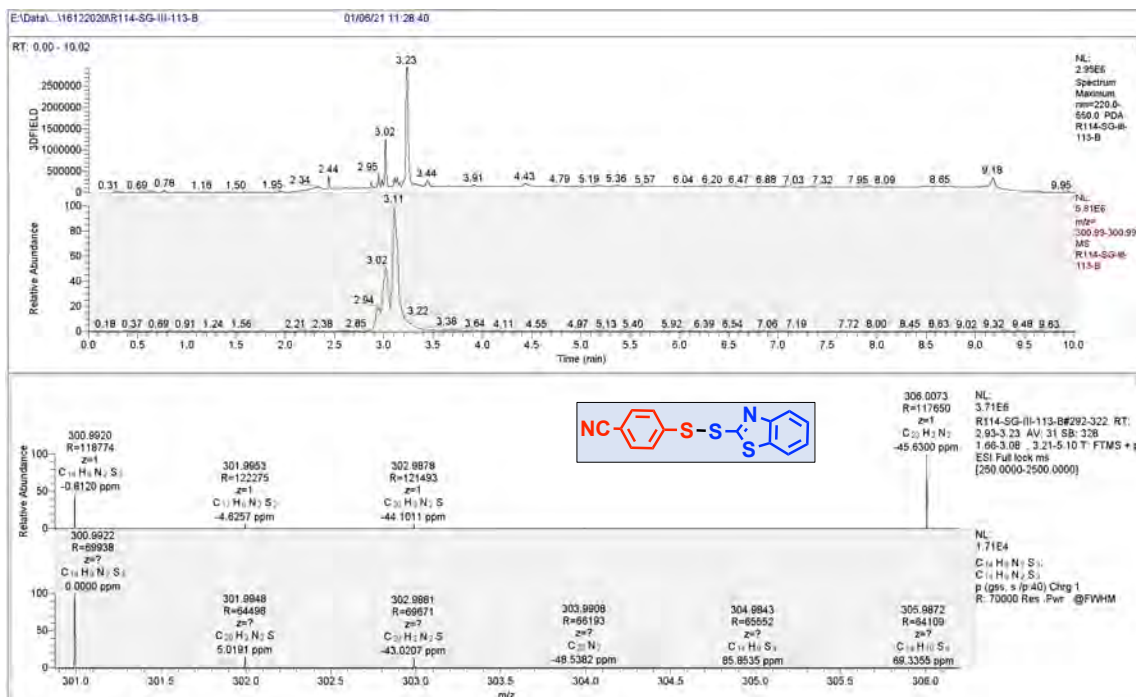
HRMS (ESI+) calculated for  $[C_{48}H_{24}N_6S_6 + H^+]$ : 877.0459 Da, found  $[M+H^+]$  877.0451 m/z;



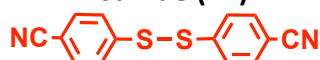
### Mixed Disulfide (46):



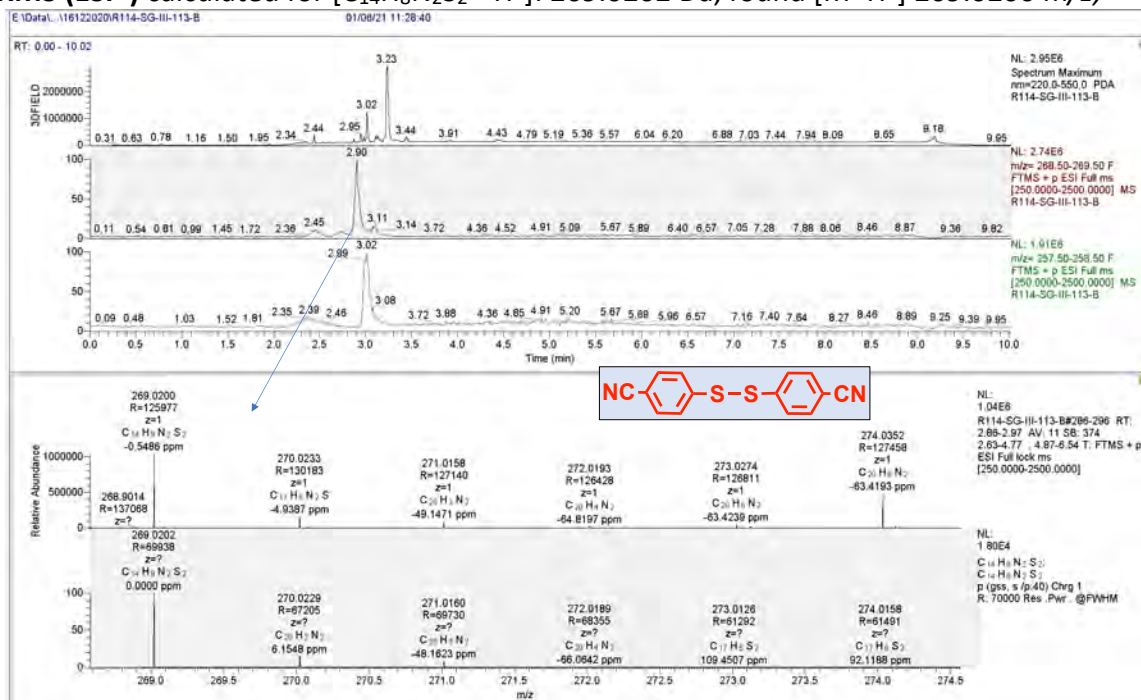
HRMS (ESI+) calculated for  $[C_{14}H_8N_2S_3 + H^+]$ : 300.9922 Da, found  $[M+H^+]$  300.9920 m/z;



Disulfide (47):



HRMS (ESI+) calculated for [C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>S<sub>2</sub> + H<sup>+</sup>]: 269.0202 Da, found [M+H<sup>+</sup>] 269.0200 m/z;



LC-HRMS Chromatogram of the mixture (R-114):  
***p*-thiocresol promoter incorporated into asterisks (15) and (16)**

Products resulting from the **incorporation** of *p*-thiocresol as a promoter into asterisks (15) and (16), as determined by LC-HRMS. Compounds (44) to (55) were identified after work-up (below, Figure 5c).

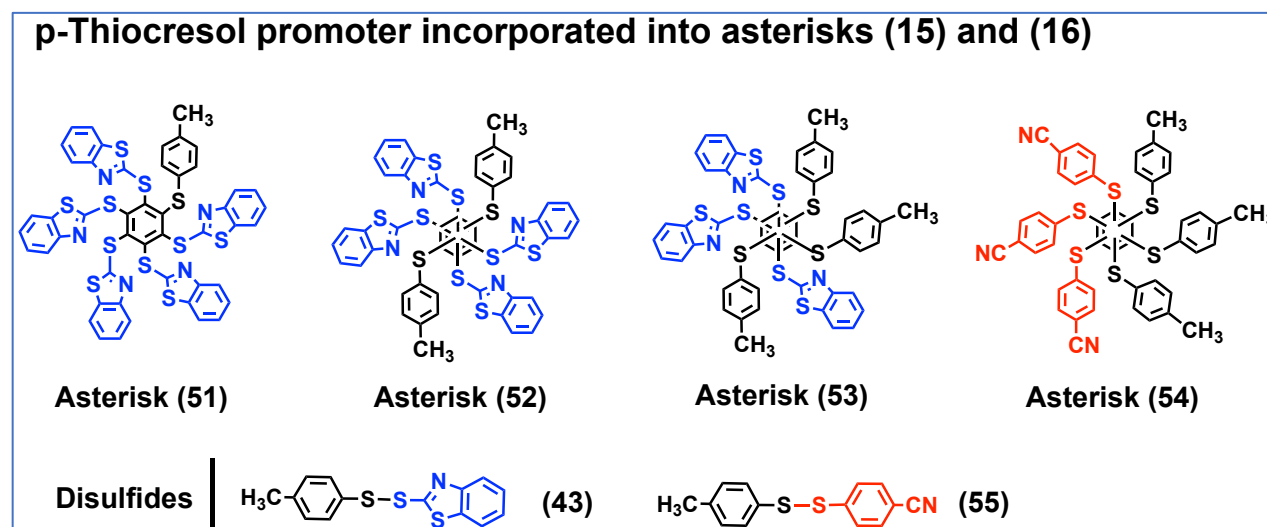
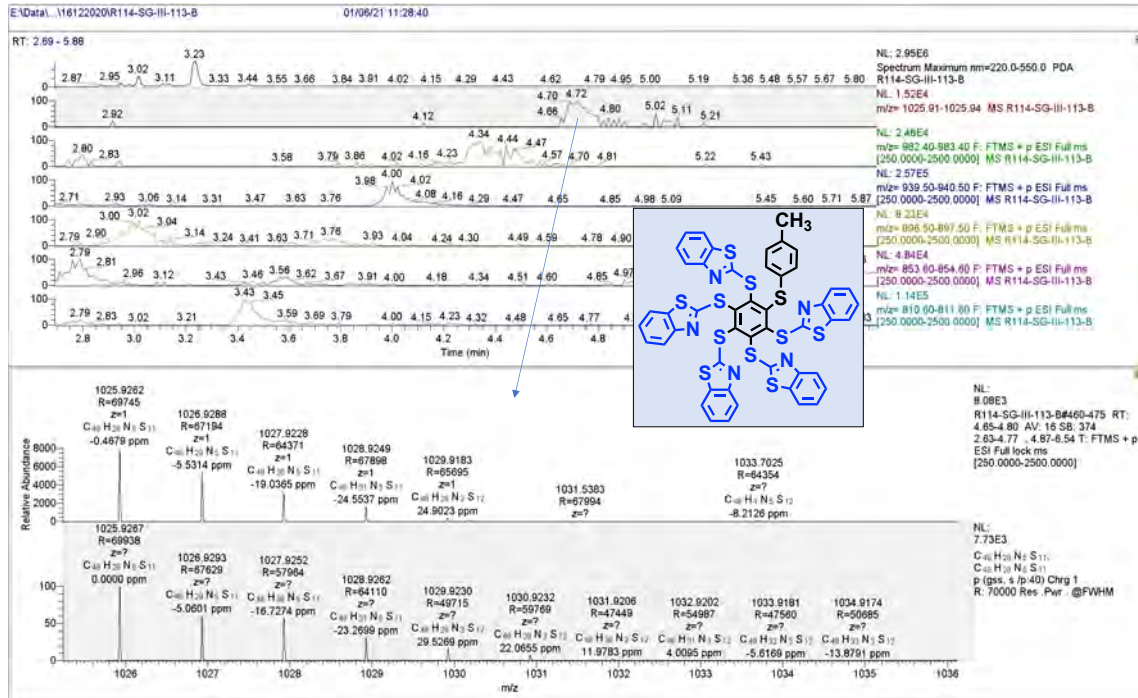


Figure 5c

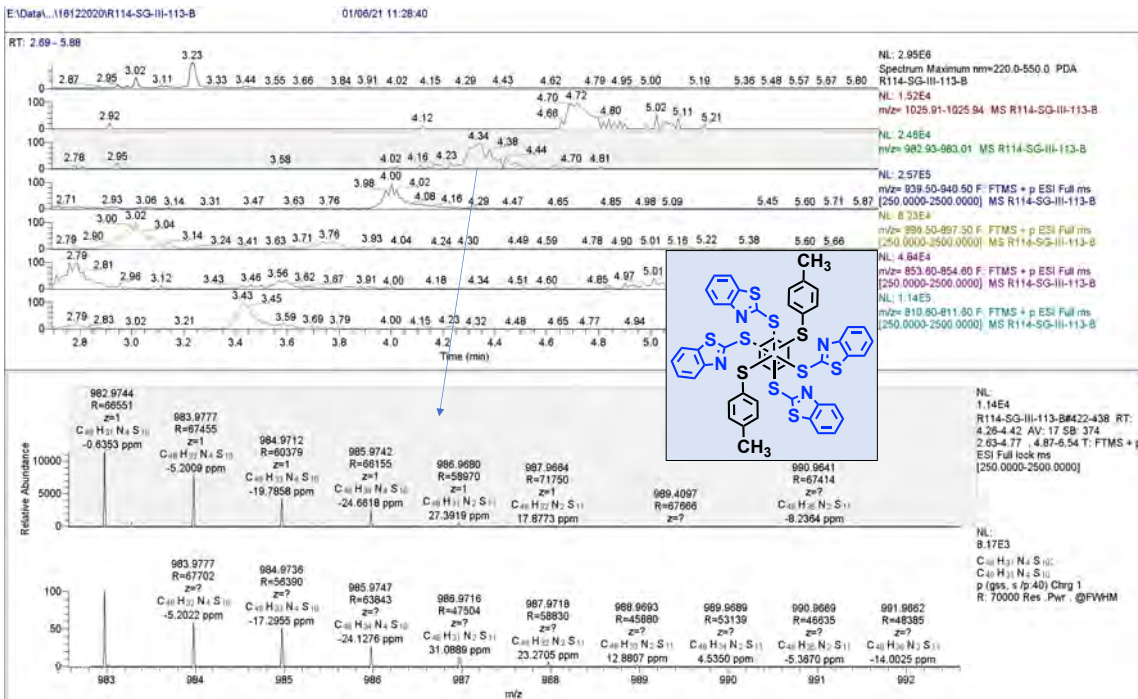
### Asterisk (51)

HRMS (ESI+) calculated for  $[C_{48}H_{27}N_5S_{11} + H^+]$ : 1025.9267 Da, found  $[M+H^+]$  1025.9262 m/z;



### Asterisk (52)

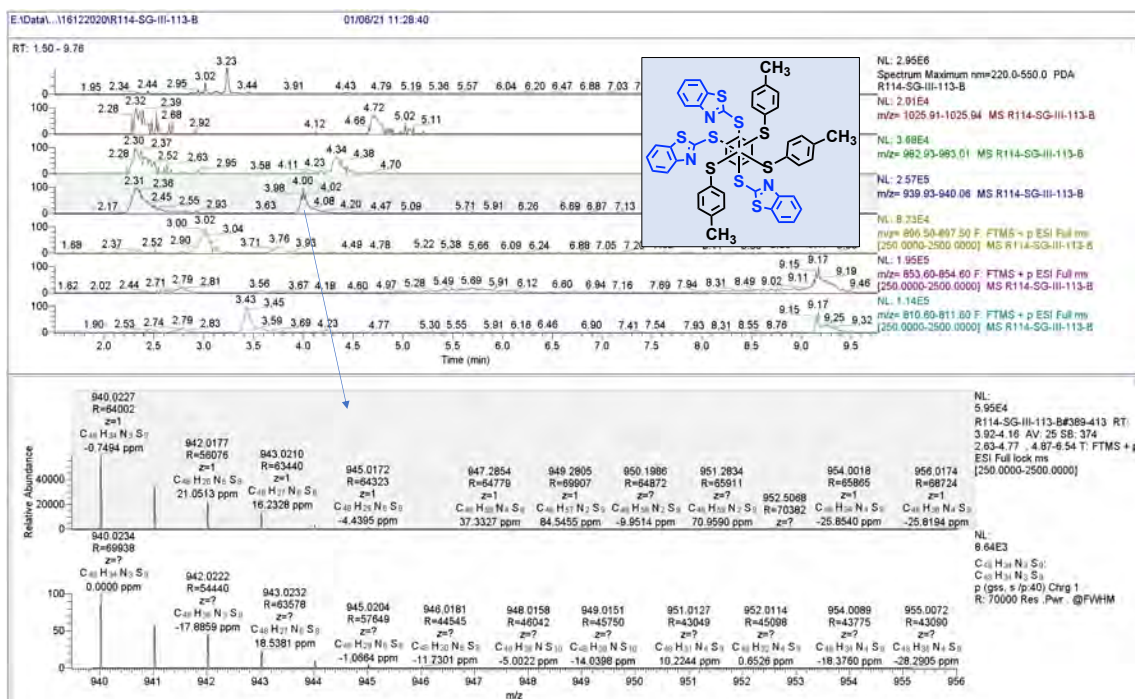
HRMS (ESI+) calculated for  $[C_{48}H_{30}N_4S_{10} + H^+]$ : 982.9750 Da, found  $[M+H^+]$  982.9744 m/z;





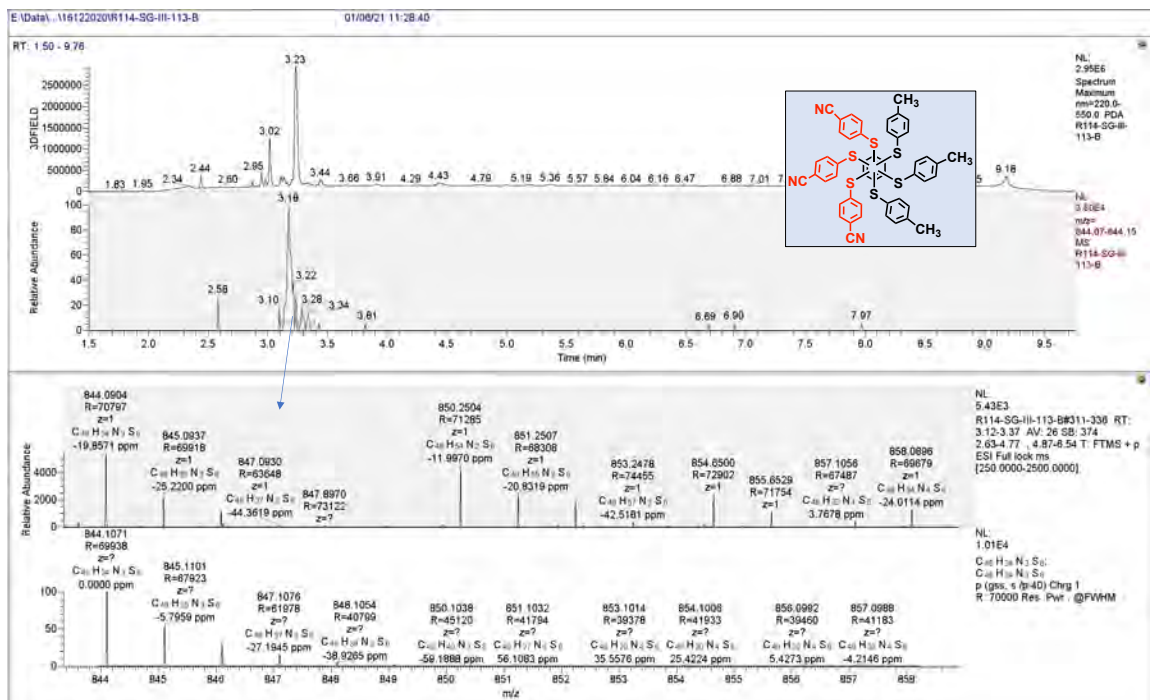
### Asterisk (53)

HRMS (ESI+) calculated for [C<sub>48</sub>H<sub>33</sub>N<sub>3</sub>S<sub>9</sub> + H<sup>+</sup>]: 940.0234 Da, found [M+H<sup>+</sup>] 940.0227 m/z;

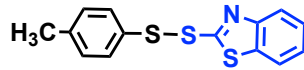


### Asterisk (54)

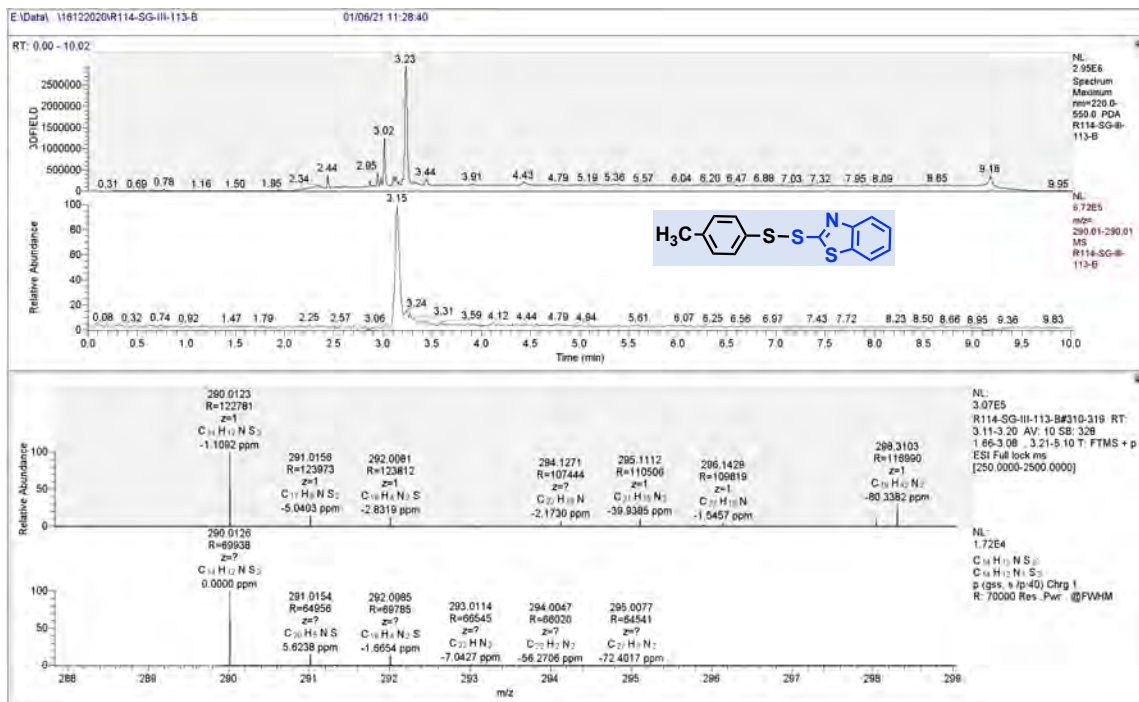
HRMS (ESI+) calculated for [C<sub>48</sub>H<sub>34</sub>N<sub>3</sub>S<sub>6</sub> + H<sup>+</sup>]: 844.1071 Da, found [M+H<sup>+</sup>] 844.0904 m/z;



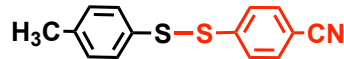
### Mixed Disulfide (43)



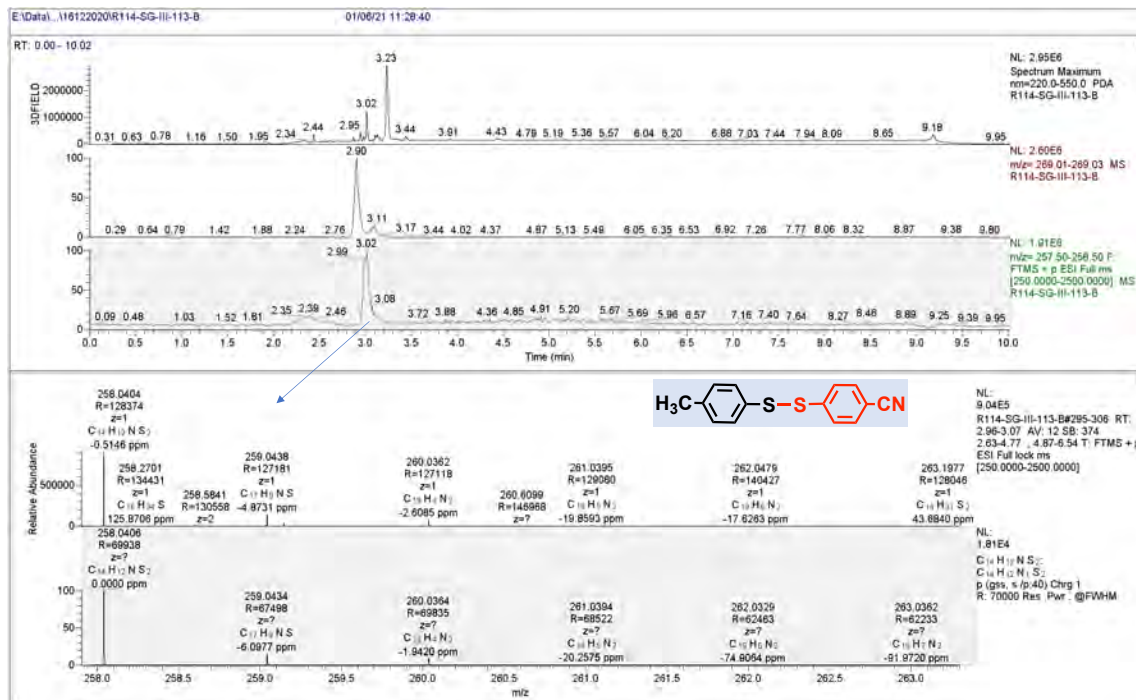
HRMS (ESI+) calculated for [C<sub>14</sub>H<sub>11</sub>N<sub>1</sub>S<sub>3</sub> + H<sup>+</sup>]: 290.126 Da, found [M+H<sup>+</sup>] 290.0123 m/z;



### Mixed Disulfide (55)



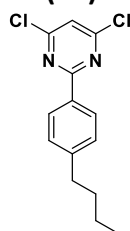
HRMS (ESI+) calculated for [C<sub>14</sub>H<sub>11</sub>N<sub>1</sub>S<sub>2</sub> + H<sup>+</sup>]: 258.0406 Da, found [M+H<sup>+</sup>] 258.0404 m/z;



## 10.0 Four-Component DCC System with Macrocycles

**Microwave oven set up :** Microwave-assisted reactions were carried out using a microwave apparatus CEM SP Discover. The instrument consists of a focused microwave power delivery system with a variable power output from 0-300 W and variable temperature. In all experiments, the power is pulsed over time to maintain the set temperature. Reactions were performed in glass vessels of 30 mL. The temperature control is achieved by means of a thermocouple and a digital temperature regulator during each experiment. The specified reaction time corresponds to the total irradiation time.

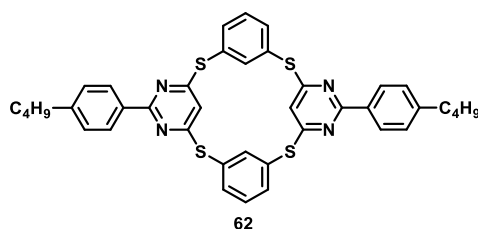
### 2-(4-butylphenyl)-4,6-dichloropyrimidine (56)



CAS N°442127-97-1

Fully characterized in *J. Org. Chem.* 2008, 73, 7, 2481–2495

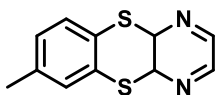
### 12,52-bis(4-butylphenyl)-2,4,6,8-tetrathia-1,5(4,6)-dipyrimidina-3,7(1,3)-dibenzenacyclooctaphane (62)



Potassium carbonate (2.10 eq., 80.59 mg, 0.373 mmol), 2-(4-butylphenyl)-4,6-dichloropyrimidine (1.00 eq., 51.7 mg, 0.178 mmol) were placed in a 5-ml microwave flask and DMF (3.0 mL) was injected via a syringe. The solution was degassed under a nitrogen flow for 5 minutes and toluene-3,4-dithiol (1.05 eq., 26.5 mg, 21  $\mu$ L, 0.186 mmol) was added. The vessel was placed into the microwave cavity and its source was then turned on. The reaction mixture was irradiated under a constant microwave emission for about 60 minutes with the reaction temperature controlled at 150 °C. After cooling at RT, a filtration left a yellow solid, which was rinsed with cold water (10 mL), ethanol (10 mL) and with diethyl ether (20 mL), then dried under high vacuum (27 mg, 38.9 mmol, 43.6%).

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  8.35 (d,  $J$  = 8.3 Hz, 4H), 7.79 (t,  $J$  = 1.6 Hz, 2H), 7.61 (dd,  $J$  = 7.7, 1.8 Hz, 4H), 7.46 (dd,  $J$  = 8.3, 7.2 Hz, 2H), 7.29 (d,  $J$  = 8.2 Hz, 4H), 5.60 (s, 2H), 3.48 (q,  $J$  = 7.0 Hz, residual EtOH), 2.72 – 2.64 (m, 4H), 1.64 (p,  $J$  = 7.6 Hz, 4H), 1.38 (h,  $J$  = 7.6 Hz, 4H), 1.23 (dt,  $J$  = 14.1, 7.0 Hz, residual EtOH), 0.94 (t,  $J$  = 7.3 Hz, 6H); **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  173.00, 163.06, 146.74, 143.68, 138.30, 133.58, 131.11, 130.28, 128.75, 128.66, 108.19, 35.68, 33.44, 22.38, 13.99. **HRMS (ESI+)** calc. for [C<sub>40</sub>H<sub>36</sub>N<sub>4</sub>S<sub>4</sub>+H<sup>+</sup>]: 701.1896 Da; found [M+H<sup>+</sup>]: 701.1891 Da.

### 7-methyl-4a,10a-dihydrobenzo[5,6][1,4]dithiino[2,3-b]pyrazine (63).



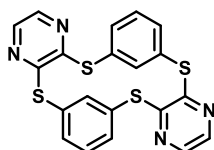
Potassium carbonate (2.20 eq., 104 mg, 0.738 mmol), 2,3-dichloropyrazine (1.00 eq., 50 mg, 0.335 mmol) were placed in a 5-ml microwave flask and DMF (3.0 mL) was injected via a syringe. The solution was degassed under a nitrogen flow for 5 minutes and toluene-3,4-dithiol (1.10 eq., 96 mg, 81  $\mu$ L, 0.369 mmol) was added. The vessel was placed into the microwave cavity and its source was then turned on. The reaction mixture was irradiated under a constant microwave emission for about 60 minutes with the reaction temperature controlled at 150 °C. After cooling at RT, a filtration left a yellow solid, which was rinsed with cold water (10 mL), ethanol (10 mL) and with diethyl ether (20 mL), then dried under high vacuum (27.2 mg, 38.9  $\mu$ mol, 43.6%).

NMR:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (s, 2H), 7.33 (d,  $J$  = 8.0 Hz, 1H), 7.28 (d,  $J$  = 1.7 Hz, 1H), 7.09 (ddd,  $J$  = 7.9, 1.8, 0.8 Hz, 1H), 2.33 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.75, 153.57, 141.59, 141.58, 138.78, 132.04, 129.41, 129.32, 128.61, 128.55, 20.89.

HRMS (ESI+) calc. for  $[\text{C}_{11}\text{H}_9\text{N}_2\text{S}_2+\text{H}^+]$ : 233.0202 Da ; found  $[\text{M}+\text{H}^+]$ : 233.0213 Da

### 2,4,6,8-tetrathia-1,5(2,3)-dipyrazina-3,7(1,3)-dibenzenacyclooctaphane (61)

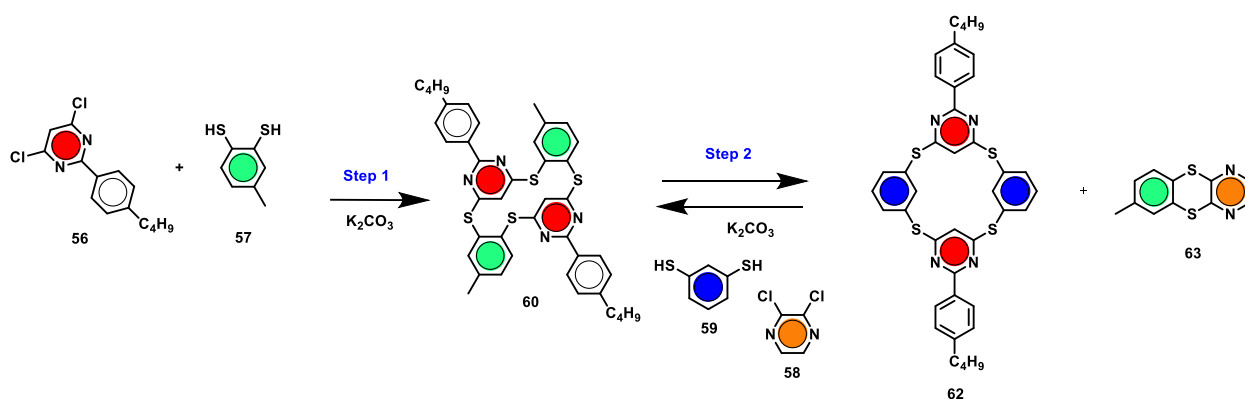


This product is not fully characterized because the  $^1\text{H}$  NMR spectrum and the HRMS indicate a complex mixture due to its chemical instability.

HRMS (MS,  $m/z$ ):  $[\text{M}+\text{H}^+]$  calc. for  $\text{C}_{20}\text{H}_{13}\text{N}_4\text{S}_4$ : 437.0018; found: 437.0033

### Dynamic exchange of sulfur components through reversible $\text{S}_{\text{N}}\text{Ar}$ reactions in the formation of macrocycles 62 and 63

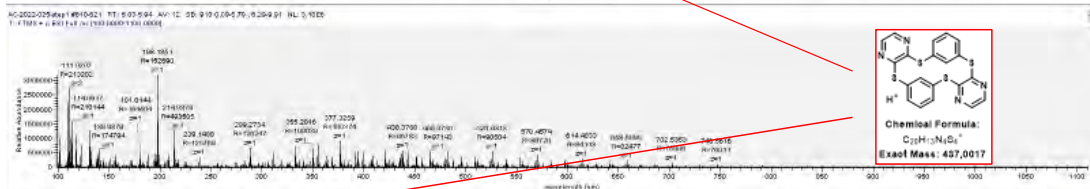
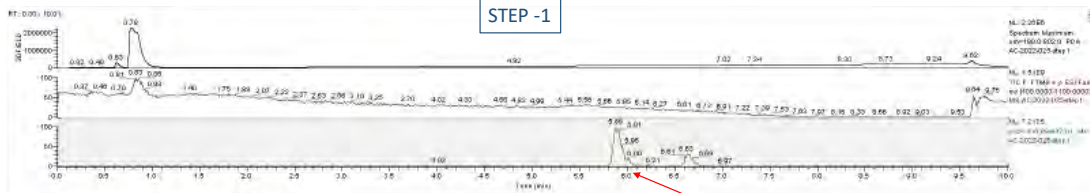
Conditions 1 : Starting from a mixture of compounds 56 and 57

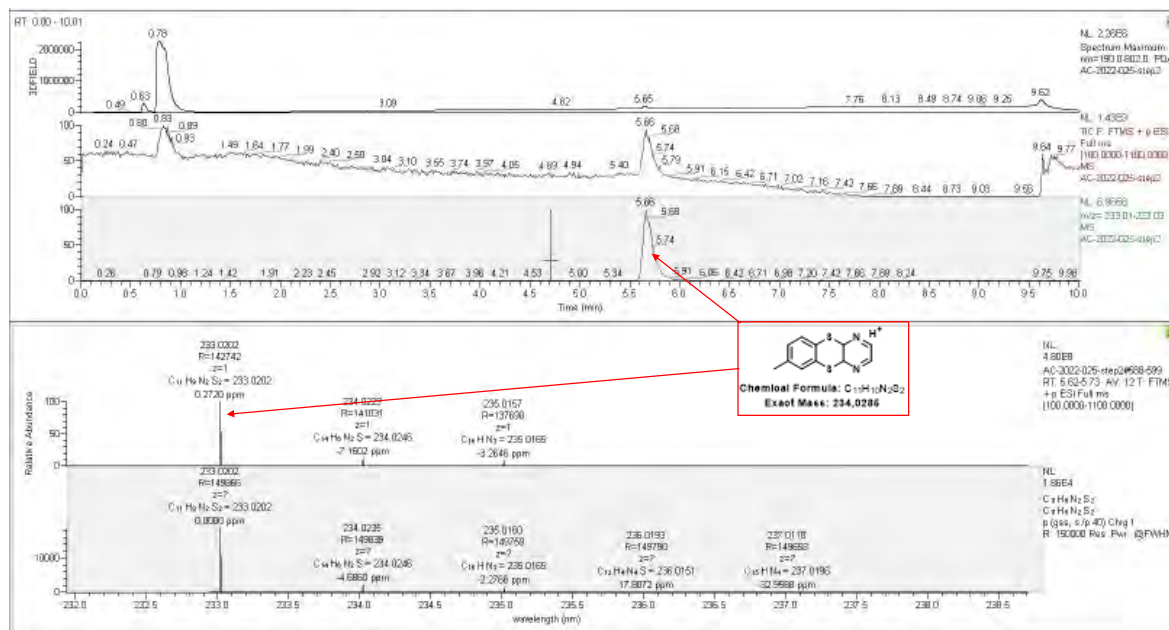




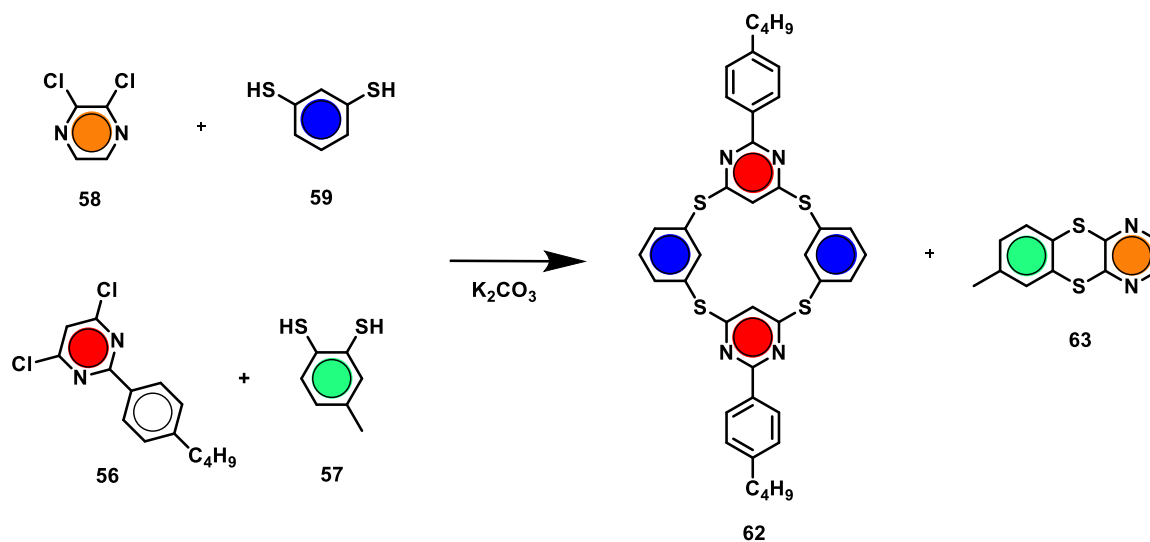


STEP -1





### Conditions 3: Starting from a mixture of compounds 56, 57, 58 and 59



In a 5-mL vessel were introduced potassium carbonate (4.81 eq., 71 mg, 0.512 mmol), 2-(4-butylphenyl)-4,6-dichloropyrimidine (1.00 eq., 29.9 mg, 0.106 mmol) and 2,3-dichloropyrimidine (1.00 eq., 16 mg, 0.107 mmol). DMF (3 mL) was injected in the microwave flask. A nitrogen flow was bubbled through the solution in the vessel for 5 minutes and then toluene-3,4-dithiol (1.21 eq., 20.0 mg, 17  $\mu$ L, 0.13 mmol) and benzene-1,3-dithiol (1.21 eq., 18 mg, 14.7  $\mu$ L, 0.128 mmol) were added. The vessel was placed into the microwave cavity and its source was then turned on. The reaction mixture was irradiated under a constant microwave emission for 15 minutes with the reaction temperature kept at 150 °C. The reaction was monitored by <sup>1</sup>H NMR and LC-HRMS.



