Electronic Supplementary Material (ESI) for Chemical Communications.


# Iron-Mediated C-H Coupling of Arenes and Unactivated Terminal Alkenes Directed by Sulfur

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## Contents

## General Experimental

THF was distilled from sodium/benzophenone and $CH_2Cl_2$ was distilled from $CaH_2$. All other solvents and reagents were purchased from commercial sources and used as supplied.

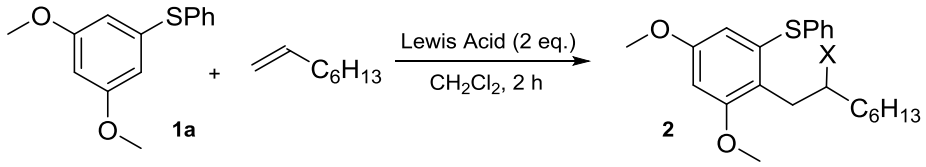
Crude yields were determined by $^1H$ NMR using $MeNO_2$ standard. $^1H$ NMR spectra were recorded on a 300, 400 or 500 MHz spectrometer, $^{13}C$ NMR spectra were recorded on a 75, 100 or 125 MHz spectrometer. All chemical shift values are reported in parts per million (ppm) relative to the solvent signal and were determined in $CDCl_3$, with coupling constant (*J*) values reported in Hz. The notation of signals is: Proton: δ *chemical shift in ppm (number of protons, multiplicity, J value (s), proton assignment*). Carbon: δ *chemical shift in ppm (carbon assignment)*.

Column chromatography was carried out using 35 – 70 μm, 60A silica gel. Routine TLC analysis was carried out on silica gel 60 Å F254 coated aluminium sheets of 0.2 mm thickness. Plates were viewed using a 254 nm ultraviolet lamp.

Low resolution and high resolution mass spectra were obtained using either positive and/or negative electrospray ionisation (ES), electron impact ionisation (EI) and chemical ionisation (CI) techniques.

IR spectra were recorded on a FTIR spectrometer as evaporated films (from $CH_2Cl_2$) using sodium chloride windows or neat.

## Lewis Acid Screen




The corresponding Lewis acid (0.40 mmol) was added to a stirred mixture of **1a** (50.0 mg, 0.20 mmol) and 1-octene (160 μL, 1 mmol) in $CH_2Cl_2$ (2 mL) under $N_2$ atmosphere. The mixture was stirred for 2 h. The reaction mixture was then quenched with $H_2O$ (2 ml) and diluted with $CH_2Cl_2$ (2 mL). The organic layer was then washed twice more with $H_2O$ (2 ml). The aqueous layer was extracted with $CH_2Cl_2$ (3 × 2 mL). The combined organic extracts were dried with $Na_2SO_4$, filtered and solvent removed *in vacuo*.

**Table 1 Screen of Lewis Acids with 1a and 1-octene**

| Lewis Acid | Yield[a] |
|---|---|
| $InCl_3$ | >95% **1a** |
| $Sc(OTf)_3$ | >95% **1a** |
| $BF_3{\cdot}Et_2O$ | >95% **1a** |
| $In(OTf_3)$ | >95% **1a** |
| $CeCl_3$ | >95% **1a** |

[a]**Yield by NMR**

## Cyclic Voltammetry

All voltammetry was performed in a 5 mL water jacketed glass cell at 25°C under Ar, following purging with Ar (MeCN saturated with Ar for MeCN solutions), using CH Instruments CHI600B Electrochemical Analyser with 3 mm diameter glassy carbon working electrode and platinum wire counter electrode . Reference electrodes used were Ag/AgCl 3 M KCl(aq) and a pseudo-reference electrode consisting of Ag wire coated in AgCl (Ag wire dipped in concentrated HCl for a few minutes) in 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP) separated from the analyte solution via a glass frit.

The condition of the Ag/AgCl 3 M KCl(aq) reference electrode was tested by measuring the formal potential of 1mM $K_4Fe(CN)_6.3H_2O$ in 0.1 M KCl at pH 7. The pseudo-reference electrode was calibrated by measuring the formal potential of 1 mM ferrocene in 0.1M TBAHFP MeCN vs. Ag/AgCl 3 M KCl(aq) then measuring the formal potential of 1 mM ferrocene in 0.1 M TBAHFP in MeCN vs. the pseudo-reference electrode. The stability of the pseudo-reference electrode was checked by repeating the ferrocene formal potential measurement after measurement of analyte solutions had been completed.

Potassium ferrocyanide and ferrocene formal potentials were calculated by taking the value at the mid-point between reduction and oxidation peaks. The formal potentials of (3,5-dimethoxyphenyl)(phenyl)sulfide and (3-methoxyphenyl)(phenyl)sulfide were calculated by fitting an EC mechanism model to the experimental data and finding the best fit over all scan rates investigated (using 'sensible' values for the EC model parameters).

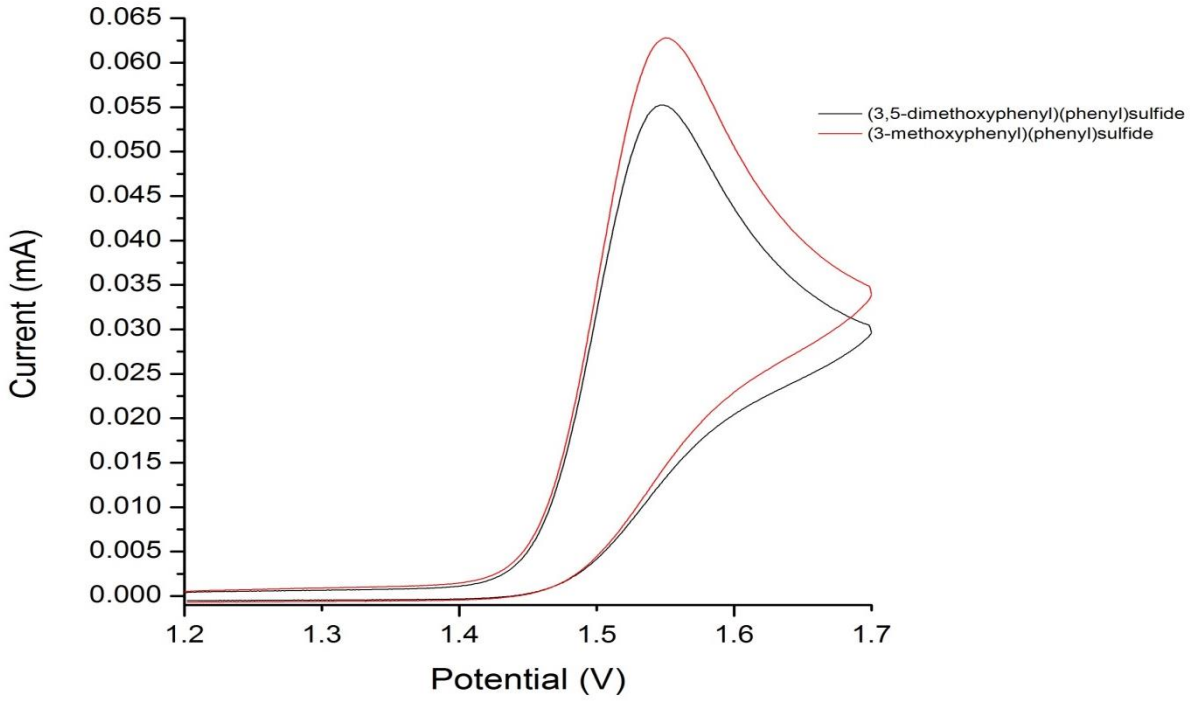
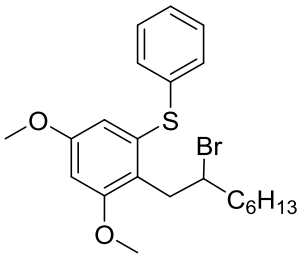



**Figure 1 Voltammogram for sulfides vs reference electrode**

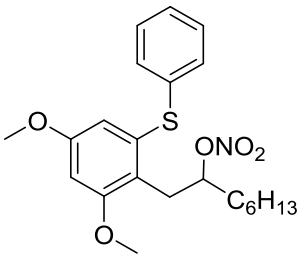
## Products Using $FeBr_3$ and CAN As Oxidants

*(2-(2-Bromooctyl)-3,5-dimethoxyphenyl)(phenyl)sulfide*




$FeBr_3$ (130 mg, 0.44 mmol) was added to a stirred mixture of **1a** (50.0 mg, 0.20 mmol) and 1-octene (160 μL, 1 mmol) in $CH_2Cl_2$ (2 mL) under $N_2$ atmosphere. The mixture was stirred for 1.5 h. The reaction mixture was then quenched with $H_2O$ (2 ml) and diluted with $CH_2Cl_2$ (2 mL). The organic layer was then washed twice more with $H_2O$ (2 ml) and the combined aqueous washes extracted with $CH_2Cl_2$ (3 × 2 mL). The combined organic extracts were dried with $Na_2SO_4$, filtered and the solvent removed *in vacuo*. The crude mixture was then passed through a silica plug with $CHCl_3$ eluent. The crude product was purified by column chromatography on silica gel (30% $CHCl_3$ in hexanes) to give (2-(2-bromooctyl)-3,5-dimethoxyphenyl)(phenyl)sulfide (17.4 mg, 20 %) as a clear oil; $\delta_H$ (500 MHz, $CDCl_3$) 0.89 (3 H, t, *J* 6.9 Hz, $CH_2CH_3$), 1.20 - 1.43 (7 H, m, $CH_2$), 1.56 - 1.67 (1 H, m, $CH_2$), 1.72 - 1.81 (1 H, m, $CH_2$), 1.81 - 1.89 (1 H, m, $CH_2$), 3.37 (1 H, dd, *J* 13.9, 7.6 Hz, $ArCH_2CHBr$), 3.47 (1 H, dd, *J* 13.9, 7.3 Hz, $ArCH_2CHBr$), 3.69 (3 H, s, $OCH_3$), 3.84 (3 H, m, $OCH_3$), 4.38 - 4.45 (1 H, m, $CH_2CHBrCH_2$), 6.42 (1 H, d, *J* 2.5 Hz, aryl H), 6.45 (1 H, d, *J* 2.2 Hz, aryl H), 7.20 - 7.32 (5 H, m, aryl H); $\delta_C$ (125 MHz, $CDCl_3$) 14.1 ($CH_3$), 22.6 ($CH_2$), 27.8 ($CH_2$), 28.6 ($CH_2$), 31.7 ($CH_2$), 37.0 ($ArCH_2CHBr$), 38.1 ($CH_2$), 55.3 ($OCH_3$), 55.6 ($OCH_3$), 57.4 (*C*HBr), 98.3 (aryl *C*-H), 108.9 (aryl *C*-H), 121.9 (aryl C), 126.7 (aryl *C*-H), 129.1 (aryl *C*-H), 130.0 (aryl *C*-H), 136.3 (aryl C), 136.5 (aryl C), 159.0 (aryl C), 159.3 (aryl C); $\nu_{max}$ (thin film/$cm^{-1}$) 1047 (s), 1156 (s), 1196 (s), 1459 (w), 1596 (s), 2856 (w), 2920 (w); MS ($ES^+$) *m/z* 437.3 (M+H); HRMS $C_{22}H_{30}O_2BrS$ (M+H) Expected 437.1144, Found 437.1143.

*1-(2,4-Dimethoxy-6-(phenylsulfanyl)phenyl)octan-2-yl nitrate*




Ceric ammonium nitrate (223 mg, 0.40 mmol) was added to a stirred mixture of **1a** (50.0 mg, 0.20 mmol) and 1-octene (160 μL, 1 mmol) in MeCN (2 mL) and stirred for 2 h. The reaction mixture was

then quenched with $H_2O$ (2 ml) and diluted with EtOAc (5 mL). The organic layer was then washed twice more with $H_2O$ (2 ml). The aqueous layer was extracted with EtOAc (3 × 2 mL). The combined organic extracts were dried with $Na_2SO_4$, filtered and solvent removed *in vacuo*. The crude product was then purified by column chromatography on silica gel (50% $CHCl_3$ in hexanes) to give 1-(2,4-dimethoxy-6-(phenylthio)phenyl)octan-2-yl nitrate (39.8 mg, 47%) as a clear oil; $\delta_H$ (500 MHz, $CDCl_3$) 0.88 (3 H, t, *J* 6.9 Hz, C*H*$_3$), 1.19 - 1.38 (7 H, m, C*H*$_2$), 1.43 (1 H, m, C*H*$_2$), 1.63 - 1.70 (2 H, m, C*H*$_2$), 3.14 (1 H, dd, *J* 14.2, 5.4 Hz, ArC*H*$_2$CH(ONO$_2$)), 3.21 (1 H, dd, *J* 14.2, 7.6 Hz, ArC*H*$_2$CH(ONO$_2$)CH$_2$), 3.68 (3 H, s, OC*H*$_3$), 3.83 (3 H, s, OC*H*$_3$), 5.31 - 5.39 (1 H, m, C*H*(ONO$_2$)), 6.40 (1 H, d, *J* 2.2 Hz, aryl H), 6.42 (1 H, d, *J* 2.2 Hz, aryl H), 7.19 - 7.32 (5 H, m, aryl H); $\delta_C$ (500 MHz, $CDCl_3$) 14.0 (*C*H$_3$), 22.5 (*C*H$_2$), 25.3 (*C*H$_2$), 29.0 (*C*H$_2$), 30.6 (Ar*C*H$_2$CH(ONO$_2$)), 31.7 (*C*H$_2$), 32.5 (*C*H$_2$), 55.3 (O*C*H$_3$), 55.6 (O*C*H$_3$), 84.5 (*C*H(ONO$_2$)), 98.2 (aryl *C*-H), 108.9 (aryl *C*-H), 119.2 (aryl C), 126.7 (aryl *C*-H), 129.2 (aryl *C*-H), 130.1 (aryl *C*-H), 136.0 (aryl C), 136.7 (aryl C), 159.3 (aryl C), 159.5 (aryl C); $\nu_{max}$ (thin film/cm$^{-1}$) 1046 (s), 1147 (s), 1196 (m), 1274 (s), 1459 (m), 1571 (s), 1596 (s), 1620 (s), 2857 (w), 2930 (w); MS (ES$^+$) *m/z* 420.4 (M+H); HRMS $C_{22}H_{29}O_2S$ (M-$NO_3$) Expected 357.1888, Found 357.1879.

## Sulfide Synthesis

### *General Procedure A: Pd-catalysed sulfide formation*[1]

Tetrakis(triphenylphosphine)palladium(0) (58.0 mg, 0.05 mol), (S)-BINAP (62 mg, 0.10 mmol), potassium hydroxide (1.12 g, 20.0 mmol), arylbromide (10.0 mmol), 2-propanol (10.3 mL) and thiol (10.0 mmol) were charged to a metal-capped, oven-dried test tube with Teflon-lined septum, pre-flushed with $N_2$ at room temperature. The mixture was heated to 80 °C and stirred for 24 h. The reaction mixture was then allowed to cool to rt before the addition of $H_2O$ (5 mL) and dilution with EtOAc (5 mL). The organic layer was separated and washed twice more with $H_2O$ (2 × 5 mL). The combined aqueous extracts were then further extracted with EtOAc (2 × 10 mL) and the combined aqueous layer washed with brine (5 mL), dried over $Na_2SO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with 50:1 petroleum ether : EtOAc to yield the product.

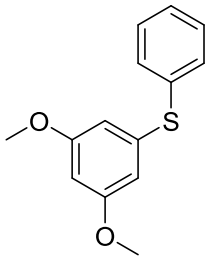
### *General Procedure B: Cu-catalysed sulfide formation*[2]

Cu(I) iodide (19.0 mg, 0.10 mmol), potassium carbonate (553 mg, 4.00 mmol) and aryl iodide (2.00 mmol) were charged to a metal-capped, over-dried test tube with Teflon-lined septum. The tube was then evacuated and backfilled with argon three times. 2-Propanol (2 mL), ethylene glycol (220 μL, 4.00 mmol) and thiol (1 mmol) were added and the mixture heated to 80 °C for 24 h with stirring. The

[1] T. Norris and K. Leeman, *Org. Process Res. Dev.*, 2008, **12**, 869.
[2] F. Y. Kwong and S. L. Buchwald, *Org. Lett.*, 2002, **4**, 3517.

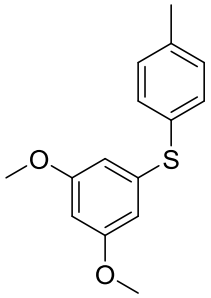
mixture was then cooled, passed through a plug of Celite® 545 with EtOAc eluent and concentrated *in vacuo*. The crude product was purified by column chromatography.

### *(3,5-Dimethoxyphenyl)(phenyl)sulfide* ***1a***




As described in general procedure A, 1-bromo-3,5-dimethoxybenzene (2.19 g, 10.0 mmol) and thiophenol (1 mL, 10.0 mmol), after purification by column chromatography (50:1 hexanes:EtOAc) gave **1a** (2.21 g, 90% yield) as a colourless oil; $\delta_H$ (400 MHz, $CDCl_3$) 3.74 (6 H, s, OC*H*$_3$), 6.34 (1 H, t, *J* 2.3, aryl H), 6.47 (1 H, d, *J* 2.3, aryl H), 7.25 - 7.36 (3 H, m, aryl H), 7.38 - 7.43 (2 H, m, aryl H); $\delta_C$ (100 MHz, $CDCl_3$) 55.8 (O*C*H$_3$), 99.6 (aryl *C*-H), 108.4 (aryl *C*-H), 127.6 (aryl *C*-H), 129.4 (aryl *C*-H), 122.1 (aryl *C*-H), 135.3 (aryl C), 138.3 (aryl C), 161.4 (aryl C).[3]

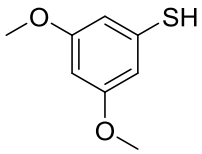
### *(3,5-Dimethoxyphenyl)(p-tolyl)sulfide* ***1b***




As described in general procedure A, 1-bromo-3,5-dimethoxybenzene (2.19 g, 10.0 mmol) and *p*-thiocresol (1.24 g, 10.0 mmol), after purification by column chromatography (50:1 hexanes:EtOAc) gave **1b** (2.53 g, 91 %) as a white solid; m.p. 64.7-67.4 °C, $\delta_H$ (400 MHz, $CDCl_3$) 2.37 (3 H, s, ArC*H*$_3$), 3.74 (6 H, s, OC*H*$_3$), 6.30 (1 H, t, *J* 2.3 Hz, aryl H), 6.40 (2 H, d, *J* 2.3 Hz, aryl H), 7.17 (2 H, d, *J* 7.8 Hz, aryl H), 7.36 (2 H, d, *J* 7.8 Hz, aryl H); $\delta_C$ (100 MHz, $CDCl_3$) 21.1 (Ar*C*H$_3$), 55.3 (O*C*H$_3$), 98.6 (aryl *C*-H), 107.0 (aryl *C*-H), 130.0 (aryl *C*-H), 130.2 (aryl C), 132.9 (aryl *C*-H), 138.0 (aryl C), 139.5 (aryl C), 161.0 (aryl C); $\nu_{max}$ (thin film/cm$^{-1}$) 1044 (s), 1103 (s), 1203 (s), 1280.2 (w), 1418 (m), 1581 (s), 2833 (w), 2936 (s); MS (ES$^+$) *m/z* 261.1 (M+H); HRMS $C_{15}H_{17}O_2S$ (M+H) Expected 261.0949, Found 261.0945.

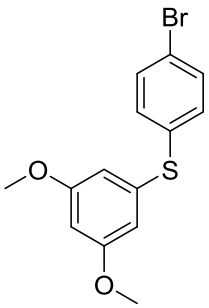
[3] H. Wang, L. Jiang, T. Chen and Y. Li, *Eur. J. Org. Chem.*, 2010, **12**, 2324.

*3,5-Dimethoxybenzenethiol*




Dimethylthiocarbamoyl chloride (7.90 g, 64 mmol) in DMF (10 mL) was added slowly to a mixture of 3,5-dimethoxyphenol (5.00 g, 32 mmol) and 1,4-diazabicylco[2.2.2]octane (7.18 g, 64 mmol) in DMF (30 mL). The mixture was stirred at room temperature overnight and 10 % aqueous solution LiCl (40 mL) and ether (150 mL) were added. The organic layer was separated and washed with 10 % aqueous solution LiCl (3 × 40 mL) and brine (20 mL). The combined organic layers were dried with $Na_2SO_4$, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (4:1 hexanes:EtOAc) to give O-3,5-dimethoxyphenyl dimethylcarbamothioate (7.54 g, 98 %) as a white solid; $\delta_H$ (500 MHz, $CDCl_3$) 3.33 (3 H, s, C(O)N(C*H*$_3$)$_2$), 3.46 (3 H, s, C(O)N(C*H*$_3$)$_2$), 3.79 (6 H, s, OC*H*$_3$), 6.26 (2 H, d, *J* 2.5 Hz, aryl H), 6.37 (1 H, t, *J* 2.2 Hz, aryl H). The solid was heated to 260 °C for 3 h under nitrogen to give a brown oil after cooling, which was dissolved in MeOH (100 mL). KOH (11.60 g, 0.2 mol) was added and the mixture was refluxed for 2 h with stirring. After cooling, the mixture was concentrated and EtOAc (150 mL) and 1N HCl (30 mL) were added. The organic layer was washed with brine (3 × 40 mL), dried with $Na_2SO_4$, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (10 % EtOAc in hexanes) to give 3,5-dimethoxybenzenethiol (3.48 g, 64 % over 3 steps) as a colourless oil; $\delta_H$ (400 MHz, $CDCl_3$) 3.47 (1 H, s, S*H*), 3.77 (6 H, s, OC*H*$_3$), 6.27 (1 H, t, *J* 2.3 Hz, aryl H), 6.43 (2 H, d, *J* 2.3 Hz, aryl H).[4]

*(4-Bromophenyl)(3,5-dimethoxyphenyl)sulfide* ***1c***

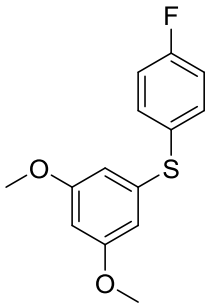



As described in general procedure B, 1-bromo-4-iodobenzene (566 mg, 2.00 mmol) and 3,5-dimethoxybenzenethiol (340 mg, 2 mmol), after purification by column chromatography (50:1 hexanes:EtOAc) gave **1c** (534 mg, 80 %) as a white solid; m.p. 54.2-56.2 °C $\delta_H$ (400 MHz, $CDCl_3$) 3.76 (6 H, s, OC*H*$_3$), 6.37 (1 H, t, *J* 2.1 Hz, aryl H), 6.48 (2 H, d, *J* 2.1 Hz, aryl H), 7.23 (2 H, d, *J* 8.5

[4] M, Lloyd; Aquinox Pharmaceuticals Inc., U.S. Patent, US20110136802, 2011.

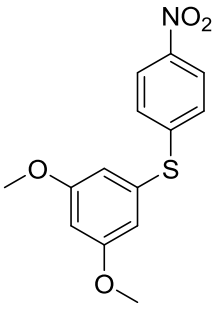
Hz, aryl H), 7.43 (2 H, d, *J* 8.5 Hz, aryl H); $\delta_C$ (100 MHz, $CDCl_3$) 55.4 (O*C*$H_3$), 99.7 (aryl *C*-H), 108.7 (aryl *C*-H), 121.3 (aryl C), 132.3 (aryl *C*-H), 132.7 (aryl *C*-H), 134.5 (aryl C), 137.0 (aryl C), 161.1 (aryl C); $\nu_{max}$ (thin film/$cm^{-1}$) 1044 (m), 1154 (s), 1204 (m), 1281 (w), 1418 (m), 1581 (s), 2833 (w), 2936 (w), 3001 (w); MS ($ES^+$) *m/z* 325.0 (M+H); HRMS $C_{14}H_{14}BrO_2S$ (M+H) Expected 325.9878, Found 325.9886.

### *(3,5-Dimethoxyphenyl)(4-fluorophenyl)sulfide* ***1d***




As described in general procedure B, 1-bromo-3,5-dimethoxybenzene (2.19 g, 10.0 mmol) and 4-fluorobenzenethiol (1.10 mL, 10.0 mmol), after purification by column chromatography (50:1 hexanes:EtOAc) gave **1d** (1.40 g, 53 %) as a colourless oil; $\delta_H$ (400 MHz, $CDCl_3$) 3.74 (6 H, s, OC$H_3$), 6.31 (1 H, t, *J* 2.3 Hz, aryl H), 6.38 (2 H, d, *J* 2.3 Hz, aryl H), 7.06 (2 H, t, *J* 8.8 Hz, aryl H), 7.44 (2 H, dd, *J* 8.8, 5.3 Hz, aryl H); $\delta_C$ (100 MHz, $CDCl_3$) 55.3 (O*C*$H_3$), 98.8 (aryl *C*-H), 107.1 (aryl *C*-H), 116.4 (d, *J* 22.1 Hz, aryl *C*-H), 129.2 (d, *J* 3.7 Hz, aryl C), 134.8 (d, *J* 8.1 Hz, aryl *C*-H), 139.0 (aryl C), 161.1 (aryl C), 163.0 (d, *J* 248.4 Hz, *C*-F); $\nu_{max}$ (thin film/$cm^{-1}$) 1043 (m), 1152 (s), 1203 (s), 1281 (w), 1418 (m), 1453 (m), 1488 (s), 1581 (s), 2834 (w), 2938 (w); MS ($ES^+$) *m/z* 265.2 (M+H); HRMS $C_{14}H_{14}FO_2S$ (M+H) Expected 265.0699, Found 265.0711.

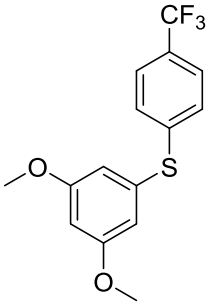
### *(3,5-Dimethoxyphenyl)(4-nitrophenyl)sulfide* ***1e***




As described in general procedure B, 1-iodo-4-nitrobenzene (498 mg, 2.00 mmol) and 3,5-dimethoxybenzenethiol (340 mg, 2.00 mmol), after purification by column chromatography (10 % EtOAc in hexanes) gave **1e** (591 mg, 93 %) as a yellow solid; $\delta_H$ (400 MHz, $CDCl_3$) 3.80 (6 H, s, OC$H_3$), 6.53 (1 H, t, *J* 2.3 Hz, aryl H), 6.68 (2 H, d, *J* 2.3 Hz, aryl H), 7.24 (2 H, d, *J* 8.8 Hz, aryl H),

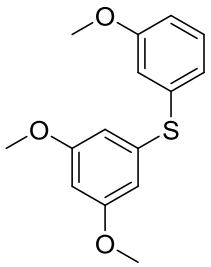
8.09 (2 H, d, *J* 8.8 Hz, aryl H); $\delta_C$ (100 MHz, $CDCl_3$) 55.6 ($OCH_3$), 101.9 (aryl *C*-H), 112.0 (aryl *C*-H), 124.0 (aryl *C*-H), 127.0 (aryl *C*-H), 132.0 (aryl C), 145.4 (aryl C), 148.0 (aryl C), 161.6 (aryl C).[5]

### *(3,5-Dimethoxyphenyl)(4-(trifluoromethyl)phenyl)sulfide* ***1f***




As described in general procedure B, 4-iodobenzotrifluoride (295 μL, 2.00 mmol) and 3,5-dimethoxybenzenethiol (340 mg, 2.00 mmol), after purification by column chromatography (50:1 hexanes:EtOAc) gave **1f** (465 mg, 68 %) as a colourless oil; $\delta_H$ (500 MHz, $CDCl_3$) 3.78 (6 H, m, $OCH_3$), 6.47 (1 H, t, *J* 2.4 Hz, aryl H), 6.62 (2 H, d, *J* 2.2 Hz, aryl H), 7.34 (2 H, d, *J* 8.2 Hz, aryl H), 7.51 (2 H, d, *J* 8.2 Hz, aryl H); $\delta_C$ (125 MHz, $CDCl_3$) 55.5 ($OCH_3$), 100.9 (aryl *C*-H), 110.7 (aryl *C*-H), 124.1 (q, *J* 271.6 Hz, $CF_3$), 125.8 (q, *J* 4.5 Hz, aryl *C*-H), 128.5 (q, *J* 32.7 Hz, aryl C), 128.8 (aryl *C*-H), 134.4 (aryl C), 142.2 (aryl C), 161.3 (aryl C); $\nu_{max}$ (thin film/$cm^{-1}$) 1013 (s), 1043 (s), 1061 (s), 1061 (s), 1088 (s), 1119 (s), 1154 (s), 1205 (m), 1321 (s), 1419 (w), 1581 (s), 2940 (w); MS ($ES^+$) *m/z* 315.3 (M+H); HRMS $C_{15}H_{14}F_3O_2S$ (M+H) Expected 315.0667, Found 315.0671.

### *(3,5-Dimethoxyphenyl)(3-methoxyphenyl)sulfide* ***1g***

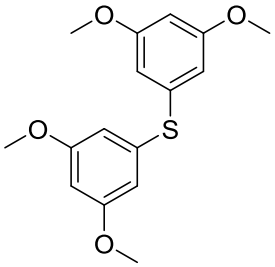



As described in general procedure A, 1-bromo-3,5-dimethoxybenzene (2.19 g, 10 mmol) and 3-methoxythiophenol (1.2 mL, 10 mmol), after purification by column chromatography (50:1 hexanes:EtOAc) gave **1g** (2.39 g, 86% yield) as a colourless oil; $\delta_H$ (500 MHz, $CDCl_3$) 3.75 (6 H, s), 3.78 (3 H, s), 6.35 (1 H, t, *J* 2.2 Hz), 6.50 (2 H, d, *J* 2.2 Hz), 6.81 (1 H, ddd, *J* 8.4, 2.5, 0.8 Hz), 6.94 (1 H, t, *J* 1.9 Hz), 6.98 (1 H, dt, *J* 7.6, 0.8 Hz), 7.24 (1 H, t, *J* 7.9 Hz); $\delta_C$ (125 MHz, $CDCl_3$) 55.3 ($OCH_3$), 55.4 ($OCH_3$), 99.6 (aryl *C*-H), 108.5 (aryl *C*-H), 113.2 (aryl *C*-H), 116.6 (aryl *C*-H), 123.7 (aryl *C*-H), 130.0 (aryl *C*-H), 136.2, 138.7, 160.0, 161.05; $\nu_{max}$ (thin film/$cm^{-1}$) 1039 (s), 1152 (s),

[5] B, Michael; Hoffman-La Roche Inc., U.S. Patent, US005990105A.

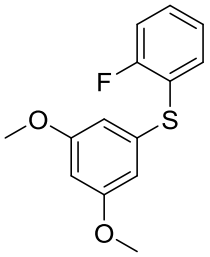
1203 (m), 1281 (m), 1417 (m), 1574 (s), 2832 (w), 2936 (w), 3000 (w); MS ($ES^+$) *m/z* 277.2 (M+H); HRMS $C_{15}H_{17}O_3S$ (M+H) Expected 277.0898, Found 277.0903.

*Bis(3,5-dimethoxyphenyl)sulfide* ***1h***



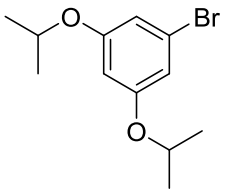
As described in General Procedure A, 1-bromo-3,5-dimethoxybenzene (2.19 g, 10 mmol) and 3,5-dimethoxybenzenethiol (1.70 g, 10 mmol), after purification by column chromatography (50:1 Hexanes:EtOAc) gave **1h** (2.25 g, 74%) as a white solid; $\delta_H$ (400 MHz, $CDCl_3$) 3.76 (12 H, s, OC*H*$_3$), 6.36 (2 H, t, *J* 2.3 Hz, aryl H), 6.53 (4 H, d, *J* 2.3 Hz, aryl H); $\delta_C$ (100 MHz, $CDCl_3$) 55.4 (O*C*H$_3$), 99.7 (aryl *C*-H), 108.8 (aryl *C*-H), 137.0 (aryl C), 161.0 (aryl C).[5]

*(3,5-Dimethoxyphenyl)(2-fluorophenyl)sulfide* ***1i***



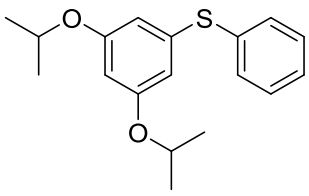
As described in general procedure A, 1-bromo-3,5-dimethoxybenzene (2.19 g, 10 mmol) and 2-fluorothiophenol (1.49 mL, 10 mmol), after purification by column chromatography (50:1 hexanes:EtOAc) gave **1i** (1.53 g, 58% yield) as a colourless oil; $\delta_H$ (500 MHz, $CDCl_3$) 3.78 (6 H, s, OC*H*$_3$), 6.40 (1 H, t, *J* 2.2 Hz, aryl H), 6.51 (2 H, d, *J* 2.2 Hz, aryl H), 7.10 - 7.19 (2 H, m, aryl H), 7.28 - 7.42 (2 H, m, aryl H); $\delta_C$ (125 MHz, $CDCl_3$) 55.3 (O*C*H$_3$), 99.4 (aryl *C*-H), 108.0 (aryl *C*-H), 115.9 (d, *J* 22.7 Hz, aryl *C*-H), 121.7 (d, *J* 18.2 Hz, aryl C), 124.7 (d, *J* 3.6 Hz, aryl *C*-H), 129.7 (d, *J* 8.2 Hz, aryl *C*-H), 134.0 (aryl *C*-H), 136.3 (aryl C), 161.0 (aryl C), 161.2 (d, *J* 247 Hz, aryl C-F); $\nu_{max}$ (thin film/$cm^{-1}$) 1042 (m), 1153 (s), 1203 (s), 1281 (w), 1418 (m), 1454 (m), 1471 (s), 1581 (s), 2834 (w), 2938 (w); MS ($ES^+$) *m/z* 265.2 (M+H); HRMS $C_{14}H_{14}FO_2S$ (M+H) Expected 265.0699, Found 265.0705.

*1-Bromo-3,5-diisopropoxybenzene*



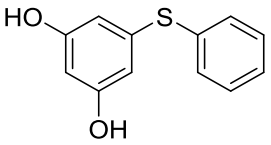

A solution of 1-bromo-3,5-dimethoxybenzene (2.50 g, 0.012 mol) in $CH_2Cl_2$ (7 ml) was cooled to 0 °C and a 1 M $BBr_3$ solution in $CH_2Cl_2$ (25 mL) was added dropwise. The ice bath was removed and the reaction was stirred at room temperature for 18 h. The reaction was quenched with MeOH and concentrated *in vacuo*. The residue was dissolved in EtOAc (100 mL) and washed with $H_2O$ (50 mL). The organic layer was separated, dried over $Na_2SO_4$ and concentrated to give 5-bromobenzene-1,3-diol as an orange oil; $\delta_H$ (400 MHz, $CDCl_3$) 5.10 (2 H, br s), 6.30 (1 H, t, *J* 2.1 Hz), 6.60 (2 H, d, *J* 2.3 Hz). 5-bromobenzene-1,3-diol (2 g) was dissolved in DMF (40 mL) and $K_2CO_3$ (6 g, 0.044 mol) was added at room temperature, followed by 2-bromopropane (4 mL, 0.044 mol). The mixture was heated to 60 °C and stirred for 18 h. The reaction was cooled to room temperature, quenched with water (120 mL) and extracted with EtOAc (3 × 50 mL). The organic layer was separated, dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (10:1 Hexanes:EtOAc) to give 1-bromo-3,5-diisopropoxybenzene (2.48 g, 85%) as a colourless oil; $\delta_H$ (500 MHz, $CDCl_3$) 1.25 (12 H, d, *J* 6.0 Hz), 4.40 (2 H, sept., *J* 6.0 Hz), 6.27 (1 H, t, *J* 2.2 Hz), 6.54 (2 H, d, *J* 2.2 Hz).[4]

*(3,5-Diisopropoxyphenyl)(phenyl)sulfide* ***1j***



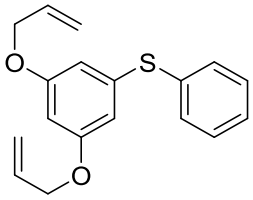

As described in general procedure A, 1-bromo-3,5-diisopropoxybenzene (2.19 g, 8.00 mmol) and thiophenol (0.80 mL, 8.00 mmol), after purification by column chromatography (50:1 hexanes:EtOAc) gave **1j** (1.84 g, 76% yield) as a colourless oil; $\delta_H$ (500 MHz, $CDCl_3$) 1.31 (12 H, d, *J* 6.0 Hz, (OCH($CH_3$)$_2$), 4.46 (2 H, sept, *J* 6.0 Hz, OC*H*($CH_3$)$_2$)), 6.33 (1 H, t, *J* 2.2 Hz, aryl H), 6.46 (2 H, d, *J* 2.2 Hz, aryl H), 7.25 - 7.29 (1 H, m, aryl H), 7.31 - 7.36 (2 H, m, aryl H), 7.39 - 7.43 (2 H, m, aryl H); $\delta_C$ (125 MHz, $CDCl_3$) 22.0 (OCH(*C*$H_3$)$_2$), 70.0 (O*C*H($CH_3$)$_2$), 102.8 (aryl *C*-H), 109.9 (aryl *C*-H), 127.2 (aryl *C*-H), 129.1 (aryl *C*-H), 131.5 (aryl *C*-H), 135.2 (aryl C), 137.6 (aryl C), 159.3 (aryl C); $\nu_{max}$ (thin film/cm$^{-1}$) 1033 (m), 1112 (s), 1151 (s), 1182 (m), 1277 (w), 1428 (w), 1575 (s), 2931 (w), 2975 (w); MS (ES$^+$) *m/z* 303.3 (M+H); HRMS $C_{18}H_{23}O_2S$ (M+H) Expected 303.1419, Found 303.1425.

*5-(Phenylsulfanyl)benzene-1,3-diol*




A 1 M $BBr_3$ solution in $CH_2Cl_2$ (10 mL, 10.0 mmol) was added dropwise to a solution of **1a** (0.62 g, 2.5 mmol) in dichloromethane (6 mL) at 0 °C under $N_2$. When addition was complete, the mixture was warmed to room temperature and stirred for 2 h. This was then quenched with MeOH (4 mL) and concentrated *in vacuo*. The residue was dissolved in EtOAc (5 mL) and extracted with $H_2O$ (2 × 5 mL). The combined organic layers were then washed with brine (5 mL), dried over $Na_2SO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (30% EtOAc in hexanes) to give 5-(phenylsulfanyl)benzene-1,3-diol (0.45 g, 82%) as an off-white crystalline solid; m.p. 136.0 – 140.0 °C (from $CHCl_3$); $\delta_H$ (400 MHz, $CDCl_3$) 4.68 (2 H, s, O*H*), 6.20 (1 H, t, *J* 2.2 Hz, aryl H), 6.32 (2 H, d, *J* 2.2 Hz, aryl H), 7.29 - 7.38 (3 H, m, aryl H), 7.42 - 7.46 (2 H, m, aryl H); $\delta_C$ (100 MHz, $CDCl_3$) 101.2 (aryl *C*-H), 108.9 (aryl *C*-H), 127.9 (aryl *C*-H), 129.4 (aryl *C*-H), 132.7 (aryl *C*-H), 133.9 (aryl C), 139.3 (aryl C), 156.9 (aryl C); $\nu_{max}$ (thin film/$cm^{-1}$) 996 (s), 1066 (w), 1155 (s), 1200 (w), 1265 (w), 1300 (w), 1328 (w), 1344 (w), 1439 (w), 1471 (s), 1587 (s), 1620 (s), 2853 (w), 2923 (w), 2956 (w), 3055 (w), 3233 (w, br); MS ($ES^-$) *m/z* 217 (M−H); HRMS $C_{12}H_{10}O_2S$ (M−H) Expected 217.0323 Found 217.0324.

*(3,5-bis(Allyloxy)phenyl)(phenyl)sulfide* ***1k***




Allyl bromide (0.7 mL, 8.0 mmol) was added to a solution of 5-(phenylsulfanyl)benzene-1,3-diol (0.42 g, 2.0 mmol) and potassium carbonate (0.82 g, 6.0 mmol) in acetone (2 mL) at room temperature under $N_2$. The resulting mixture was stirred for 48 h, before adding $H_2O$ until the disappearance of the precipitate. The crude product was then extracted with diethyl ether (3 × 5 mL). The combined organic extracts were washed with $H_2O$ (2 × 5 mL) and brine (5 mL), dried over magnesium sulfate, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (25% $CH_2Cl_2$ in hexanes) to give **1k** (0.32 g, 58%) as a colourless oil; $\delta_H$ (500 MHz, $CDCl_3$) 4.45 (4 H, dt, *J* 5.4, 1.5 Hz, O$CH_2$), 5.27 (2 H, dq, *J* 10.5, 1.5 Hz, CH=C$H_2$), 5.37 (2 H, dq, *J* 17.3, 1.5 Hz, CH=C$H_2$), 6.00 (2 H, ddt, *J* 17.3, 10.5, 5.4 Hz, C*H*=$CH_2$), 6.37 (1 H, t, *J* 2.2 Hz, aryl H), 6.47 (2 H, d, *J* 2.2 Hz, aryl H), 7.28 - 7.36 (3 H, m, aryl H), 7.38 - 7.42 (2 H, m, aryl H); $\delta_C$ (100 MHz, $CDCl_3$) 68.9 ($CH_2$), 100.7 (*C*H=$CH_2$), 108.9 (aryl *C*-H), 118.1 (C=*C*$H_2$), 127.5 (aryl *C*-

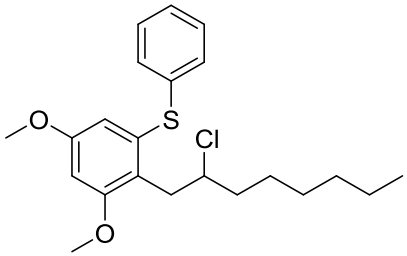
H), 129.3 (aryl *C*-H), 131.9 (aryl *C*-H), 132.9 (aryl *C*-H), 134.6 (aryl C), 138.1 (aryl C), 159.9 (aryl C); $\nu_{max}$ (thin film/$cm^{-1}$) 924 (w), 997 (w), 1023 (w), 1084 (w), 1149 (s), 1278 (w), 1419 (w), 1439 (s), 1578 (s), 2862 (w), 2918 (w), 2983 (w), 3019 (w), 3076 (w); MS ($ES^+$) *m/z* 299 (M+H); HRMS $C_{18}H_{18}O_2SNa$ (M+Na) Expected 321.0925 Found 321.0921.

## Fe(III)-Mediated C-H Coupling of Arylsulfides and Terminal Alkenes

*General Procedure C*

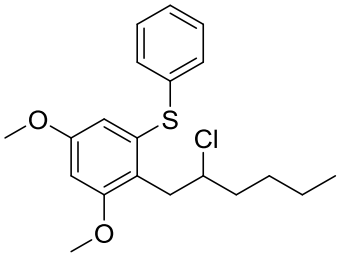
A solution of $FeCl_3$ (0.8 mmol) in $MeNO_2$ (1 mL) was added dropwise over 1 h to a stirred solution of the corresponding sulphide (0.2 mmol) and alkene (1.0 mmol) in $CH_2Cl_2$ (1 mL). The mixture was then left to stir for 1 h. The reaction mixture was then quenched with $H_2O$ (2 ml), diluted with $CH_2Cl_2$ (2 mL) and 2,2'-bipyridine (127 mg, 0.8 mmol) was added. The organic layer was then washed with $H_2O$ (2 × 2 ml) and the combined aqueous was extracted with $CH_2Cl_2$ (3 × 2 mL). The combined organic extracts were dried with $Na_2SO_4$, filtered and solvent removed *in vacuo*. The crude mixture was then passed through a silica plug with $CHCl_3$ eluent.

*(2-(2-Chlorooctyl)-3,5-dimethoxyphenyl)(phenyl)sulfide* ***2a***



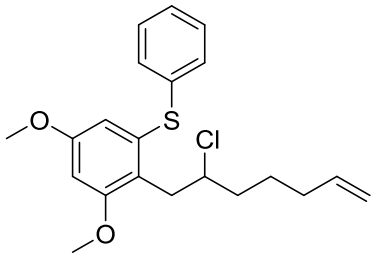

As described in general procedure C, **1a** (50 mg, 0.2 mmol), octene (160 µl, 1 mmol) and $FeCl_3$ (131 mg, 0.8 mmol), after purification by column chromatography (30 % $CHCl_3$ in hexanes) gave **2a** (51.2 mg, 64%) as a colourless oil; $\delta_H$ (500 MHz, $CDCl_3$) 0.79 (3 H, t, *J* 6.9, $CH_2CH_3$), 1.11 - 1.34 (7 H, m, $CH_2$), 1.44 - 1.56 (1 H, m, $CH_2$), 1.60 - 1.68 (2 H, m, $CH_2$), 3.14 (1 H, dd, *J* 13.9, 7.3, $ArCH_2CHCl$), 3.24 (1 H, dd, *J* 13.9, 7.3 Hz, $ArCH_2CHCl$), 3.59 (3 H, s, $OCH_3$), 3.74 (3 H, s, $OCH_3$), 4.18 (1 H, dt, *J* 12.9, 7.3, $CH_2CHClCH_2$), 6.32 (1 H, d, *J* 2.5, aryl H), 6.35 (1 H, d, *J* 2.5, aryl H), 7.09 - 7.22 (5 H, m, aryl H); $\delta_C$ (125 MHz, $CDCl_3$) 14.1 ($CH_3$), 22.6 ($CH_2$), 26.7 ($CH_2$), 28.8 ($CH_2$), 31.7 ($CH_2$), 36.3 ($ArCH_2CHCl$), 37.7 ($CH_2$), 55.3 ($OCH_3$), 55.6 ($OCH_3$), 63.4 (*C*HCl), 98.3 (aryl *C*-H), 108.8 (aryl *C*-H), 121.3 (aryl C), 126.6 (aryl *C*-H), 129.1 (aryl *C*-H), 130.0 (aryl *C*-H), 136.4 (aryl C), 136.6 (aryl C), 159.1 (aryl C), 159.3 (aryl C); $\nu_{max}$ (thin film/$cm^{-1}$) 1046 (s), 1163 (s), 1198, 1459 (w), 1570 (s), 1596 (s), 2856 (w), 2929 (w), 2954 (w); MS ($ES^+$) *m/z* 393.3 (M+H); HRMS $C_{22}H_{30}O_2ClS$ (M+H) Expected 393.1650 Found 393.1651.

*(2-(2-Chlorohexyl)-3,5-dimethoxyphenyl)(phenyl)sulfide* ***2b***




As described in general procedure C, **1a** (50 mg, 0.2 mmol), hexene (127 µl, 1 mmol) and $FeCl_3$ (131 mg, 0.8 mmol), after purification by column chromatography (30 % $CHCl_3$ in hexanes) gave **2b** (46.0 mg, 62%) as a colourless oil; $\delta_H$ (500 MHz, $CDCl_3$) 0.90 (3 H, t, *J* 7.3 Hz, $CH_2CH_3$), 1.23 - 1.43 (3 H, m, $CH_2$), 1.54 - 1.65 (1 H, m, $CH_2$), 1.71 - 1.78 (2 H, m, $CH_2$), 3.24 (1 H, dd, *J* 13.9, 7.3 Hz, $ArCH_2CHCl$), 3.34 (1 H, dd, *J* 13.9, 7.3 Hz, $ArCH_2CHCl$), 3.69 (3 H, s, $OCH_3$), 3.84 (3 H, m, $OCH_3$), 4.28 (1 H, m, $CH_2CHClCH_2$), 6.42 (1 H, d, *J* 2.2 Hz, aryl H), 6.45 (1 H, d, *J* 2.2 Hz, aryl H), 7.20 - 7.32 (5 H, m, aryl H); $\delta_C$ (125 MHz, $CDCl_3$) 14.0 ($CH_3$), 22.2 ($CH_2$), 28.9 ($CH_2$), 36.3 ($ArCH_2CHCl$), 37.5 ($CH_2$), 55.3 ($OCH_3$), 55.6 ($OCH_3$), 63.3 (*C*HCl), 98.3 (aryl *C*-H), 108.9 (aryl *C*-H), 121.3 (aryl C), 126.6 (aryl *C*-H), 129.1 (aryl *C*-H), 130.1 (aryl *C*-H), 136.4 (aryl C), 136.7 (aryl C), 159.2 (aryl C), 159.3 (aryl C); $\nu_{max}$ (thin film/$cm^{-1}$) 1048 (s), 1156 (s), 1198, 1459 (w), 1581 (s), 1598 (s), 2856 (w), 2935 (w); MS ($ES^+$) *m/z* 365.2 (M+H); HRMS $C_{20}H_{26}O_2ClS$ (M+H) Expected 365.1337 Found 365.1334

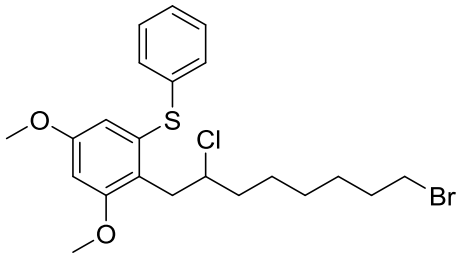
*(2-(2-Chlorohept-6-en-1-yl)-3,5-dimethoxyphenyl)(phenyl)sulfide* ***2c***




As described in general procedure C, **1a** (50 mg, 0.2 mmol), 1,6-heptadiene (138 µl, 1 mmol) and $FeCl_3$ (131 mg, 0.8 mmol), after purification by column chromatography (30 % $CHCl_3$ in hexanes) gave **2c** (42.2 mg, 55%) as a colourless oil; $\delta_H$ (500 MHz, $CDCl_3$) 1.43 - 1.54 (1 H, m, $CH_2$), 1.67 - 1.80 (3 H, m, $CH_2$), 1.96 - 2.12 (2 H, m. $CH_2CH_2CH=CH_2$), 3.24 (1 H, dd, *J* 13.6, 7.3 Hz, $ArCH_2CHCl$), 3.34 (1 H, dd, *J* 13.6, 7.3 Hz, $ArCH_2CHCl$), 3.69 (3 H, s, $OCH_3$), 3.84 (3 H, s, $OCH_3$), 4.29 (1 H, m, $CH_2CHClCH_2$), 4.93 - 4.97 (1 H, m, $CH=CH_2$), 5.00 (1 H, dq, *J* 17.1, 1.8 Hz, $CH=CH_2$), 5.79 (1 H, ddt, *J* 17.1, 10.4, 6.6 Hz, $CH_2CH=CH_2$), 6.42 (1 H, d, *J* 2.2 Hz, aryl H), 6.44 (1 H, d, *J* 2.2 Hz, aryl H), 7.21 - 7.32 (5 H, m, aryl H); $\delta_C$ (125 MHz, $CDCl_3$) 25.9 ($CH_2$), 33.2 ($CH_2CH_2CH=CH_2$), 36.3 ($ArCH_2CHCl$), 37.1 ($CH_2$), 55.3 ($OCH_3$), 55.6 ($OCH_3$), 63.0 (*C*HCl), 98.3 (aryl *C*-H), 108.9 (aryl *C*-H), 114.7 ($CH=CH_2$), 121.2 (aryl C), 126.6 (aryl *C*-H), 129.1 (aryl *C*-H), 130.1 (aryl *C*-H), 136.3

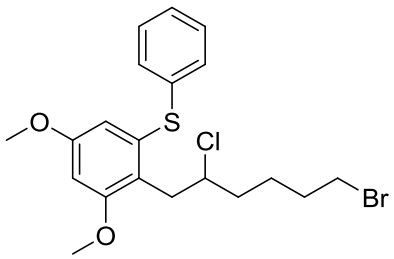
(aryl C), 136.7 (aryl C), 138.5 (*C*H=$CH_2$), 159.1 (aryl C), 159.3 (aryl C); $\nu_{max}$ (thin film/$cm^{-1}$) 1047 (s), 1144 (s), 1198 (s), 1295 (w), 1460 (m), 1571 (s), 1597 (s), 2835 (w), 2936 (w); MS ($ES^+$) *m/z* 377 (M+H); HRMS $C_{21}H_{26}O_2ClS$ (M+H) Expected 377.1337, Found 377.1339.

*(2-(8-Bromo-2-chlorooctyl)-3,5-dimethoxyphenyl)(phenyl)sulfide* ***2d***




As described in General Procedure C, **1a** (50 mg, 0.2 mmol), 8-bromo-1-octene (171 μL, 1 mmol) and $FeCl_3$ (131 mg, 0.8 mmol), after purification by column chromatography (30% $CHCl_3$ in hexanes) gave **2d** (53.8 mg, 56%) as a colourless oil; $\delta_H$ (400 MHz, $CDCl_3$) 1.19 - 1.47 (5 H, m, C$H_2$), 1.58 - 1.67 (1 H, m, C$H_2$), 1.68 - 1.76 (2 H, m, C$H_2$), 1.84 (2 H, quin, *J* 7.1 Hz, $CH_2CH_2CH_2Br$), 3.23 (1 H, dd, *J* 13.8, 7.3 Hz, ArC$H_2$CHCl), 3.33 (1 H, dd, *J* 13.8, 7.3 Hz ArC$H_2$CHCl), 3.40 (2 H, t, *J* 7.1 Hz, $CH_2CH_2Br$), 3.68 (3 H, s, OC$H_3$), 3.83 (3 H, s, OC$H_3$), 4.20 - 4.31 (1 H, m, C*H*Cl), 6.42 (2 H, m, aryl H), 7.18 - 7.32 (5 H, m, aryl H); $\delta_C$ (100 MHz, $CDCl_3$) 26.5 ($CH_2$), 28.0 ($CH_2$), 28.2 ($CH_2$), 32.7 ($CH_2CH_2Br$), 34.0 ($CH_2Br$), 36.2 (Ar$CH_2$CHCl), 37.4 (C$H_2$), 55.3 (O$CH_3$), 55.6 (O$CH_3$), 63.1 (*C*HCl), 98.3 (aryl *C*-H), 108.8 (aryl *C*-H), 121.1 (aryl C), 126.6 (aryl *C*-H), 129.1 (aryl *C*-H), 130.0 (aryl *C*-H), 136.3 (aryl C), 136.5 (aryl C), 159.1 (aryl C), 159.3 (aryl C); $\nu_{max}$ (thin film/$cm^{-1}$) 1046 (s), 1146 (s), 1198 (s), 1296 (w), 1461 (m), 1571 (s), 1596 (s), 2856 (w), 2933.67 (w); MS ($ES^+$) *m/z* 471 (M+H); HRMS $C_{22}H_{28}BrO_2S$ (M-Cl) Expected 435.0993, Found 435.1008.

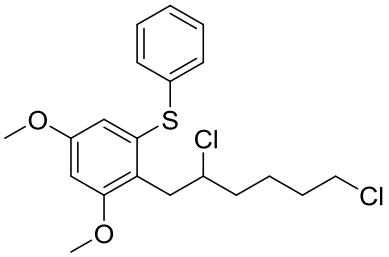
*(2-(6-Bromo-2-chlorohexyl)-3,5-dimethoxyphenyl)(phenyl)sulfide* ***2e***




As described in General Procedure C, **1a** (50 mg, 0.2 mmol), 6-bromo-1-octene (136 μL, 1 mmol) and $FeCl_3$ (131 mg, 0.8 mmol), after purification by column chromatography (30 % $CHCl_3$ in hexanes) gave **2e** (47.9 mg, 53%) as a colourless oil; $\delta_H$ (500 MHz, $CDCl_3$) 1.46 - 1.56 (1 H, m, C$H_2$), 1.69 - 1.91 (5 H, m, C$H_2$), 3.24 (1 H, dd, *J* 13.6, 7.3 Hz, ArC$H_2$CHCl), 3.33 (1 H, dd, *J* 13.9, 7.3 Hz, ArC$H_2$CHCl), 3.38 (2 H, t, *J* 6.8 Hz, $CH_2CH_2Br$), 3.69 (3 H, s, OC$H_3$), 3.83 (3 H, s, OC$H_3$), 4.22 - 4.30 (1 H, m, C*H*Cl), 6.41 (1 H, d, *J* 2.2 Hz, aryl H), 6.44 (1 H, d, *J* 2.2 Hz, aryl H), 7.20 - 7.32 (5 H,

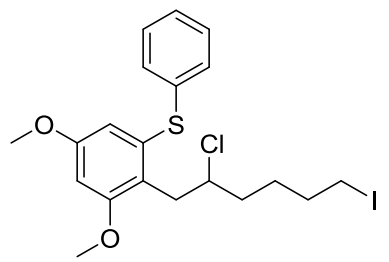
m, aryl H); $\delta_C$ (125 MHz, $CDCl_3$) 25.5 (*C*$H_2$), 32.3 (*C*$H_2$), 33.5 ($CH_2$*C*$H_2$Br), 36.2 (Ar*C*$H_2$CHCl), 36.6 (*C*$H_2$), 55.3 (O*C*$H_3$), 55.6 (O*C*$H_3$), 62.6 (*C*HCl), 98.3 (aryl *C*-H), 108.9 (aryl *C*-H), 120.9 (aryl C), 126.7 (aryl *C*-H), 129.2 (aryl *C*-H), 130.0 (aryl *C*-H), 136.2 (aryl C), 136.6 (aryl C), 159.1 (aryl C), 159.4 (aryl C); $\nu_{max}$ (thin film/$cm^{-1}$) 1046 (s), 1146 (s), 1197 (s), 1295 (w), 1459 (m), 1571 (s), 1596 (s), 2835 (w), 2937 (w), 3001 (w); MS ($ES^+$) *m/z* 442.8 (M+H); HRMS $C_{20}H_{24}O_2BrS$ (M-Cl) Expected 407.0680 Found 407.0663.

### *(2-(2,6-Dichlorohexyl)-3,5-dimethoxyphenyl)(phenyl)sulfide* ***2f***




As described in general procedure C, **1a** (50 mg, 0.2 mmol), 6-chloro-1-hexene (135 µl, 1 mmol) and $FeCl_3$ (131 mg, 0.8 mmol), after purification by column chromatography (30 % $CHCl_3$ in hexanes) gave **2f** (36.8 mg, 45%) as a colourless oil; $\delta_H$ (500 MHz, $CDCl_3$) 1.39 - 1.46 (1 H, m, C*H*$_2$) 1.61 - 1.73 (5 H, m, C*H*$_2$), 3.16 (1 H, dd, *J* 13.6, 7.3 Hz, ArC*H*$_2$CHCl), 3.25 (1 H, dd, *J* 13.6, 7.3 Hz, ArC*H*$_2$CHCl), 3.42 (2 H, t, *J* 6.3 Hz, $CH_2$C*H*$_2$Cl), 3.60 (3 H, s, OC*H*$_3$), 3.75 (3 H, m, OC*H*$_3$), 4.18 (1 H, m, $CH_2$C*H*ClCH$_2$), 6.33 (1 H, d, *J* 2.5 Hz, aryl H), 6.35 (1 H, d, *J* 2.5 Hz, aryl H), 7.11 - 7.23 (5 H, m, aryl H); $\delta_C$ (125 MHz, $CDCl_3$) 24.2 (*C*$H_2$), 32.2 (C*H*$_2$), 36.2 (Ar*C*$H_2$CHCl), 36.8 (C*H*$_2$), 44.8 (*C*$H_2$Cl), 55.3 (O*C*$H_3$), 55.7 (O*C*$H_3$), 62.6 (*C*HCl), 98.4 (aryl *C*-H), 109.0 (aryl *C*-H), 121.0 (aryl C), 126.7 (aryl *C*-H), 129.2 (aryl *C*-H), 130.0 (aryl *C*-H), 136.3 (aryl C), 136.6 (aryl C), 159.1 (aryl C), 159.4 (aryl C); $\nu_{max}$ (thin film/$cm^{-1}$) 1046 (s), 1148 (s), 1198 (s), 1295 (w), 1460 (m), 1477 (m), 1571 (s), 1596 (s), 2835 (w), 2938 (w); MS ($ES^+$) *m/z* 399.2 (M+H); HRMS $C_{20}H_{24}O_2ClS$ (M-Cl) Expected 363.1186, Found 363.1201.

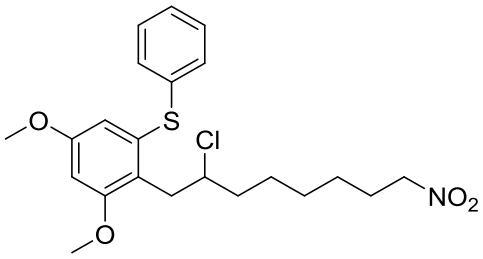
### *(2-(2-Chloro-6-iodohexyl)-3,5-dimethoxyphenyl)(phenyl)sulfide* ***2g***




As described in general procedure C, **1a** (50 mg, 0.2 mmol), 6-iodo-1-hexene (135 µl, 1 mmol) and $FeCl_3$ (131 mg, 0.8 mmol), after purification by column chromatography (30 % $CHCl_3$ in hexanes) gave **2b** (49.1 mg, 49%) as a yellow oil; $\delta_H$ (500 MHz, $CDCl_3$) 1.49 (1 H, m, C*H*$_2$), 1.66 - 1.89 (5 H,

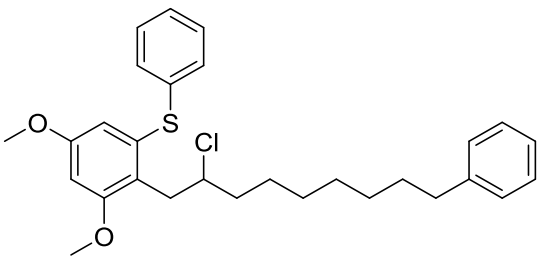
m, C$H_2$), 3.15 (2 H, m, $CH_2CH_2I$), 3.24 (1 H, dd, *J* 13.6, 7.3 Hz, ArC$H_2$CHCl), 3.33 (1 H, dd, *J* 13.6, 7.3 Hz, ArC$H_2$CHCl), 3.69 (3 H, s, OC$H_3$), 3.84 (3 H, m, OC$H_3$), 4.26 (1 H, dt, *J* 12.3, 7.3 Hz, $CH_2CHClCH_2$), 6.42 (1 H, d, *J* 2.5 Hz, aryl H), 6.44 (1 H, d, *J* 2.5 Hz, aryl H), 7.20 - 7.32 (5 H, m, aryl H); $\delta_C$ (125 MHz, $CDCl_3$) 6.4 ($CH_2I$), 27.8 ($CH_2$), 33.1 ($CH_2$), 36.3 (Ar$CH_2$CHCl), 36.4 (C$H_2$), 55.3 (O$CH_3$), 55.7 (O$CH_3$), 62.3 (CHCl), 98.4 (aryl *C*-H), 109.0 (aryl *C*-H), 121.0 (aryl C), 126.7 (aryl *C*-H), 129.2 (aryl *C*-H), 130.0 (aryl *C*-H), 136.3 (aryl C), 136.6 (aryl C), 159.1 (aryl C), 159.4 (aryl C); $\nu_{max}$ (thin film/$cm^{-1}$) 1045 (s), 1147 (s), 1198 (s), 1295 (w), 1437 (m), 1458 (m), 1478 (m), 1571 (s), 1595 (s), 2834 (w), 2936 (w), 3000 (w); MS ($ES^+$) *m/z* 491.2 (M+H); HRMS $C_{20}H_{25}IO_2ClS$ (M+H) Expected 491.0303 Found, 491.0298.

### *(2-(2-Chloro-8-nitrooctyl)-3,5-dimethoxyphenyl)(phenyl)sulfide* ***2h***



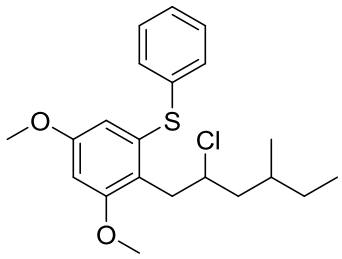

As described in general procedure C, **1a** (50 mg, 0.2 mmol), 6-nitro-1-octene (160.4 mg, 1 mmol) and $FeCl_3$ (131 mg, 0.8 mmol), after purification by column chromatography (10% EtOAc in hexanes) gave **2h** (42.1 mg, 47%) as a yellow oil; $\delta_H$ (500 MHz, $CDCl_3$) 1.23 - 1.44 (5 H, m, C$H_2$), 1.56 - 1.66 (1 H, m, C$H_2$), 1.67 - 1.77 (2 H, m, C$H_2$), 1.99 (2 H, quin, *J* 7.2 Hz, $CH_2CH_2CH_2NO_2$), 3.23 (1 H, dd, *J* 13.6, 7.3 Hz, ArC$H_2$CHCl), 3.33 (1 H, dd, *J* 13.6, 7.3 Hz, ArC$H_2$CHCl), 3.69 (3 H, s, OC$H_3$), 3.83 (3 H, s, OC$H_3$), 4.26 (1 H, m, $CH_2CHClCH_2$), 4.36 (2 H, t, *J* 7.2 Hz, $CH_2CH_2NO_2$), 6.41 (1 H, d, *J* 2.2 Hz, aryl H), 6.44 (1 H, d, *J* 2.2 Hz, aryl H), 7.19 - 7.32 (5 H, m, aryl H); $\delta_C$ (125 MHz, $CDCl_3$) 26.1 ($CH_2$), 26.3 ($CH_2$), 27.3 ($CH_2CH_2NO_2$), 28.3 ($CH_2$), 36.3 (Ar$CH_2$CHCl), 37.3 ($CH_2$), 55.3 (O$CH_3$), 55.7 (O$CH_3$), 62.9 (CHCl), 75.6 ($CH_2NO_2$), 98.4 (aryl *C*-H), 108.9 (aryl *C*-H), 121.1 (aryl C), 126.7 (aryl *C*-H), 129.2 (aryl *C*-H), 130.0 (aryl *C*-H), 136.3 (aryl C), 136.6 (aryl C), 159.1 (aryl C), 159.4 (aryl C); $\nu_{max}$ (thin film/$cm^{-1}$) 1046 (s), 1144 (s), 1198 (s), 1295 (w), 1390 (m), 1458 (m), 1560 (s), 2844 (w), 2926 (m); MS ($ES^+$) *m/z* 438.2 (M+H); HRMS $C_{22}H_{28}NO_4S$ (M-Cl) Expected 402.1739, Found 402.1741.

### *(2-(2-Chloro-9-phenylnonyl)-3,5-dimethoxyphenyl)(phenyl)sulfide* ***2i***



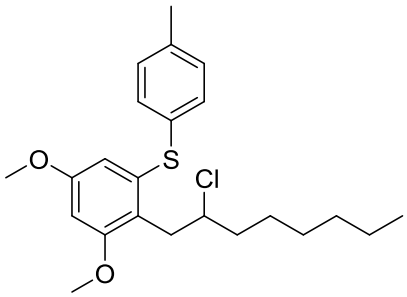
As described in general procedure C, **1a** (50 mg, 0.2 mmol), 9-phenyl-1-nonene (206.4 mg, 1 mmol) and $FeCl_3$ (131 mg, 0.8 mmol), after purification by column chromatography (30 % $CHCl_3$ in hexanes) gave **2i** (61.9 mg, 63%) as a colourless oil; $\delta_H$ (400 MHz, $CDCl_3$) 1.18 - 1.44 (7 H, m, C$H_2$), 1.59 - 1.67 (3 H, m, C$H_2$), 1.69 - 1.78 (2 H, m, C$H_2$), 2.61 (2 H, t, *J* 7.5 Hz, $CH_2CH_2$Ph), 3.24 (1 H, dd, *J* 13.8, 7.5 Hz, ArC$H_2$CHCl), 3.34 (1 H, dd, *J* 13.8, 7.5 Hz, ArC$H_2$CHCl), 3.69 (3 H, s, OC$H_3$), 3.83 (3 H, s, OC$H_3$), 4.28 (1 H, m, $CH_2CH$ClC$H_2$), 6.42 (1 H, d, *J* 2.3 Hz, aryl H), 6.45 (1 H, d, *J* 2.3 Hz, aryl H), 7.16 - 7.33 (10 H, m, aryl H); $\delta_C$ (100 MHz, $CDCl_3$) 26.8 (*C*$H_2$), 29.1 (*C*$H_2$), 29.3 (*C*$H_2$), 29.4 (*C*$H_2$), 31.6 (*C*$H_2$), 36.0 ($CH_2$*C*$H_2$Ph), 36.3 (Ar*C*$H_2$CHCl), 37.7 (*C*$H_2$), 55.4 (O*C*$H_3$), 55.7 (O*C*$H_3$), 63.4 (*C*HCl), 98.3 (aryl *C*-H), 108.8 (aryl *C*-H), 121.3 (aryl C), 125.6 (aryl *C*-H), 126.6 (aryl *C*-H), 128.3 (aryl *C*-H), 128.5 (aryl *C*-H), 129.2 (aryl *C*-H), 130.0 (aryl *C*-H), 136.4 (aryl C), 136.6 (aryl C), 142.9 (aryl C), 159.1 (aryl C), 159.3 (aryl C); $\nu_{max}$ (thin film/$cm^{-1}$) 1047 (s), 1146 (s), 1198 (s), 1296 (w), 1454 (m), 1495 (m), 1571 (s), 1596 (s), 2854 (m), 2928 (s); MS ($ES^+$) *m/z* 483.4 (M+H); HRMS $C_{29}H_{35}O_2S$ (M-Cl) Expected 447.2358, Found 447.2323.

### *(2-(2-Chloro-4-methylpentyl)-3,5-dimethoxyphenyl)(phenyl)sulfide* ***2j***



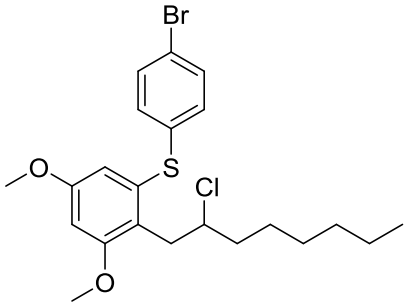

As described in general procedure C, **1a** (50 mg, 0.2 mmol), 4-methyl-1-hexene (142 μL, 1 mmol) and $FeCl_3$ (131 mg, 0.8 mmol), after purification by column chromatography (30 % $CHCl_3$ in hexanes) gave **2j** (35.7 mg, 46% as a 1:1 mixture of diastereomers) as a colourless oil; $\delta_H$ (400 MHz, $CDCl_3$) 0.75 - 0.93 (6 H, m, C$H_3$), 0.98 - 1.58 (3 H, m, C$H_2$), 1.60 - 1.88 (2 H, m, C$H_2$), 3.17 - 3.40 (2 H, m, ArC$H_2$CHCl), 3.69 (3 H, s, OC$H_3$), 3.83 (3 H, s, OC$H_3$), 4.31 - 4.44 (1 H, m, $CH_2CH$ClC$H_2$), 6.42 (1 H, app. s, aryl H), 6.45 (1 H, app. s, aryl H), 7.17 - 7.32 (5 H, m, aryl H); $\delta_C$ (100 MHz, $CDCl_3$) 10.7 + 11.4 (*C*$H_3$), 18.0 + 19.4 (*C*$H_3$), 27.9, 30.0, 31.5, 31.7, 36.3 + 36.8 (Ar*C*$H_2$CHCl), 44.7 + 45.2 (alkyl H), 55.3 (O*C*$H_3$), 55.6 (O*C*$H_3$), 61.3 + 61.4 (*C*HCl), 98.4 (aryl *C*-H), 109.0 (aryl *C*-H), 121.4 + 121.5 (aryl C), 126.5 (aryl *C*-H), 129.1 (aryl *C*-H), 129.8 (aryl *C*-H), 136.4 (aryl C), 136.5 + 136.6 (aryl C), 159.1 (aryl C), 159.2 (aryl C); $\nu_{max}$ (thin film/$cm^{-1}$) 1047 (s), 1146 (s), 1199 (s), 1296 (w), 1461 (m), 1477 (m), 1571 (s), 1597 (s), 2931 (m), 2959 (m); MS ($ES^+$) *m/z* 379.3 (M+H); HRMS $C_{21}H_{27}O_2S$ (M-Cl) Expected 343.1732, Found 343.1729.

*(2-(2-Chlorooctyl)-3,5-dimethoxyphenyl)(p-tolyl)sulfide* ***2k***




As described in general procedure C, **1b** (52.9 mg, 0.2 mmol), octene (160 μL, 1 mmol) and $FeCl_3$ (131 mg, 0.8 mmol), after purification by column chromatography (30 % $CHCl_3$ in hexanes) gave **2k** (43.6 mg, 53%) as a colourless oil; $\delta_H$ (500 MHz, $CDCl_3$) 0.89 (3 H, t, *J* 6.9 Hz, $CH_2CH_3$), 1.20 - 1.43 (7 H, m, $CH_2$), 1.60 (1 H, m, $CH_2$), 1.70 - 1.77 (2 H, m, $CH_2$), 2.34 (3 H, s, $ArCH_3$), 3.24 (1 H, dd, *J* 13.6, 7.3 Hz, $ArCH_2CHCl$), 3.32 (1 H, dd, *J* 13.6, 7.3 Hz, $ArCH_2CHCl$), 3.66 (3 H, s, $OCH_3$), 3.82 (3 H, m, $OCH_3$), 4.29 (1 H, m, $CH_2CHClCH_2$), 6.34 (1 H, d, *J* 2.5 Hz, aryl H), 6.36 (1 H, d, *J* 2.5 Hz, aryl H), 7.12 (2 H, d, *J* 7.9 Hz, aryl H), 7.21 (2 H, d, *J* 7.9 Hz, aryl H); $\delta_C$ (125 MHz, $CDCl_3$) 14.1 ($CH_2CH_3$), 21.1 ($ArCH_3$), 22.6 ($CH_2$), 26.7 ($CH_2$), 28.8 ($CH_2$), 31.7 ($CH_2$), 36.2 ($ArCH_2CHCl$), 37.7 ($CH_2$), 55.3 ($OCH_3$), 55.6 ($OCH_3$), 63.3 (*C*HCl), 97.6 (aryl *C*-H), 107.9 (aryl *C*-H), 120.3 (aryl C), 130.0 (aryl *C*-H), 131.3 (aryl *C*-H), 131.9 (aryl C), 137.1 (aryl C), 138.0 (aryl C), 159.0 (aryl C), 159.2 (aryl C); $\nu_{max}$ (thin film/$cm^{-1}$) 1048 (s), 1145 (s), 1199 (s), 1295 (w), 1460 (m), 1572 (s), 1596 (s), 2867 (w), 2929 (m); MS ($ES^+$) *m/z* 407.3 (M+H); HRMS $C_{23}H_{32}O_2ClS$ (M+H) Expected 407.1808, Found 407.1806.

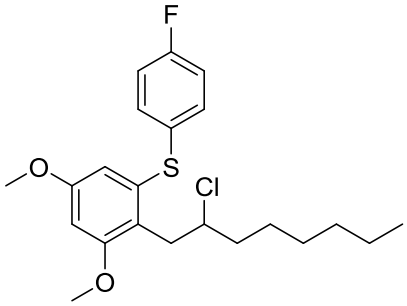
*(4-Bromophenyl)(2-(2-chlorooctyl)-3,5-dimethoxyphenyl)sulfide* ***2l***




As described in general procedure C, **1c** (66 mg, 0.2 mmol), octene (160 μL, 1 mmol) and $FeCl_3$ (131 mg, 0.8 mmol), after purification by column chromatography (30 % $CHCl_3$ in hexanes) gave **2l** (62.7 mg, 65%) as a colourless oil; $\delta_H$ (400 MHz, $CDCl_3$) 0.88 (3 H, t, *J* 6.8 Hz, $CH_2CH_3$) 1.17 - 1.43 (7 H, m, $CH_2$), 1.51 - 1.64 (1 H, m, $CH_2$), 1.65 - 1.77 (2 H, m, $CH_2$), 3.20 (1 H, dd, *J* 13.7, 6.7 Hz, $ArCH_2CHCl$), 3.30 (1 H, dd, *J* 13.7, 7.7 Hz, $ArCH_2CHCl$), 3.71 (3 H, s, $OCH_3$), 3.83 (3 H, s, $OCH_3$), 4.24 (1 H, m, $CH_2CHClCH_2$), 6.44 (1 H, d, *J* 2.2 Hz, aryl H), 6.45 (1 H, d, *J* 2.2 Hz, aryl H), 7.08 (2 H, d, *J* 8.4 Hz, aryl H), 7.39 (2 H, d, *J* 8.4 Hz, aryl H); $\delta_C$ (100 MHz, $CDCl_3$) 14.1 ($CH_2CH_3$), 22.6

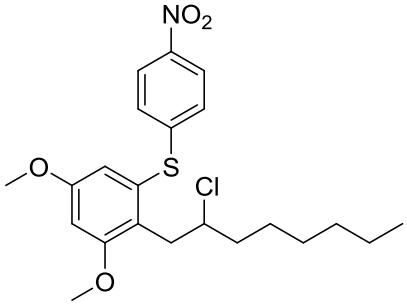
($CH_2$), 26.7 ($CH_2$), 28.8 ($CH_2$), 31.8 ($CH_2$), 36.3 (Ar$CH_2$CHCl), 37.8 ($CH_2$), 55.4 (O$CH_3$), 55.7 (O$CH_3$), 63.3 ($CH$Cl), 98.8 (aryl *C*-H), 109.3 (aryl *C*-H), 120.2 (aryl C), 121.9 (aryl C), 130.9 (aryl *C*-H), 132.1 (aryl *C*-H), 135.6 (aryl C), 136.2 (aryl C), 159.2 (aryl C), 159.4 (aryl C); $\nu_{max}$ (thin film/$cm^{-1}$) 1007 (s), 1047 (s), 1144 (s), 1198 (s), 1295 (m), 1434 (m), 1471 (s), 1570 (s), 1596 (s), 2856 (w), 2929 (m); MS ($ES^+$) *m/z* 471.1 (M+H); HRMS $C_{22}H_{29}BrO_2ClS$ (M+H) Expected 471.0755, Found 471.0751.

### *(2-(2-Chlorooctyl)-3,5-dimethoxyphenyl)(4-fluorophenyl)sulfide* ***2m***



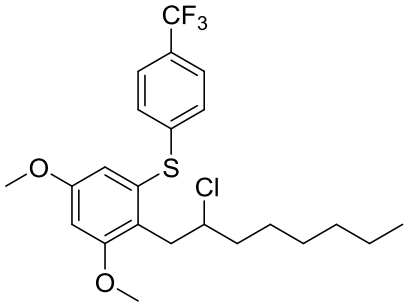

As described in general procedure C, **1d** (53.7 mg, 0.2 mmol), octene (160 µL, 1 mmol) and $FeCl_3$ (131 mg, 0.8 mmol), after purification by column chromatography (30 % $CHCl_3$ in hexanes) gave **2m** (55.9 mg, 66%) as a colourless oil; $\delta_H$ (400 MHz, $CDCl_3$) 0.89 (3 H, t, *J* 6.8 Hz, $CH_2CH_3$), 1.20 - 1.45 (7 H, m, $CH_2$), 1.54 - 1.67 (1 H, m, $CH_2$), 1.68 - 1.78 (2 H, m, $CH_2$), 3.22 (1 H, dd, *J* 13.8, 6.8 Hz, Ar$CH_2$CHCl), 3.31 (1 H, dd, *J* 13.8, 7.5 Hz, Ar$CH_2$CHCl), 3.67 (3 H, s, O$CH_3$), 3.83 (3 H, s, O$CH_3$), 4.28 (1 H, m, $CH_2CHClCH_2$), 6.30 (1 H, d, *J* 2.3 Hz, aryl H), 6.38 (1 H, d, *J* 2.3 Hz, aryl H), 7.02 (2 H, t, *J* 8.7 Hz, aryl H), 7.25 - 7.33 (2 H, dd, *J* 8.7, 5.3 Hz, aryl H); $\delta_C$ (100 MHz, $CDCl_3$) 14.1 ($CH_3$), 22.6 ($CH_2$), 26.7 ($CH_2$), 28.8 ($CH_2$), 31.7 ($CH_2$), 36.2 (Ar$CH_2$CHCl), 37.8 ($CH_2$), 55.3 (O$CH_3$), 55.6 (O$CH_3$), 63.3 ($CH$Cl), 97.7 (aryl *C*-H), 107.8 (aryl *C*-H), 116.4 (d, *J* 22.0 Hz, aryl *C*-H), 120.3 (aryl C), 130.8 (d, *J* 2.9 Hz, aryl C), 133.2 (d, *J* 8.1 Hz, aryl *C*-H), 137.7 (aryl C), 159.1 (aryl C), 159.3 (aryl C), 162.2 (d, *J* 247.2 Hz, *C*-F); $\nu_{max}$ (thin film/$cm^{-1}$) 1047 (s), 1145 (s), 1198 (m), 1226 (m), 1295 (w), 1460 (w), 1488 (s), 1571 (m), 1590 (m), 2856 (w), 2929 (w); MS ($ES^+$) *m/z* 411.2 (M+H); HRMS $C_{22}H_{29}O_2ClFS$ (M+H) Expected 411.1555, Found 411.1556.

### *(2-(2-Chlorooctyl)-3,5-dimethoxyphenyl)(4-nitrophenyl)sulfide* ***2n***



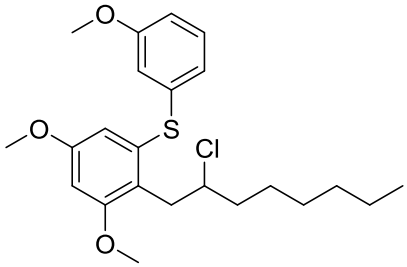
As described in general procedure C, **1e** (59.1 mg, 0.2 mmol), octene (160 μL, 1 mmol) and $FeCl_3$ (131 mg, 0.8 mmol), after purification by column chromatography (30 % $CHCl_3$ in hexanes) gave **2n** (66.9 mg, 75%) as a yellow solid; m.p 50.2-52.6 °C, $\delta_H$ (400 MHz, $CDCl_3$) 0.87 (3 H, t, *J* 6.8 Hz, $CH_2CH_3$), 1.14 - 1.42 (7 H, m, $CH_2$), 1.47 - 1.62 (1 H, m, $CH_2$), 1.65 - 1.75 (2 H, m, $CH_2$), 3.17 (1 H, dd, *J* 13.7, 6.1 Hz, $ArCH_2CHCl$), 3.26 (1 H, dd, *J* 13.7, 8.2 Hz, $ArCH_2CHCl$), 3.78 (3 H, s, $OCH_3$), 3.87 (3 H, s, $OCH_3$), 4.21 (1 H, m, $CH_2CHClCH_2$), 6.57 (1 H, d, *J* 2.2 Hz, aryl H), 6.66 (1 H, d, *J* 2.2 Hz, aryl H), 7.13 (2 H, d, *J* 8.9 Hz, aryl H), 8.06 (2 H, d, *J* 8.9 Hz, aryl H); $\delta_C$ (100 MHz, $CDCl_3$) 14.0 ($CH_3$), 22.6 ($CH_2$), 26.6 ($CH_2$), 28.7 ($CH_2$), 31.6 ($CH_2$), 36.5 ($ArCH_2CHCl$), 38.0 ($CH_2$), 55.5 ($OCH_3$), 55.7 ($OCH_3$), 63.1 (CHCl), 100.6 (aryl C-H), 111.3 (aryl C-H), 123.9 (aryl C), 124.0 (aryl C-H), 126.2 (aryl C-H), 131.6 (aryl C), 145.1 (aryl C), 148.6 (aryl C), 159.5 (aryl C), 159.8 (aryl C); $\nu_{max}$ (thin film/$cm^{-1}$) 1044 (m), 1086 (m), 1144 (m), 1198 (m), 1298 (w), 1334 (s), 1460 (w), 1513 (m), 1595 (m), 2855 (w), 2929 (w); MS ($ES^+$) *m/z* 438.2 (M+H); HRMS $C_{22}H_{29}NO_4ClS$ (M+H) Expected 438.1506, Found 438.1500.

### *(2-(2-Chlorooctyl)-3,5-dimethoxyphenyl)(4-(trifluoromethyl)phenyl)sulfide* ***2o***



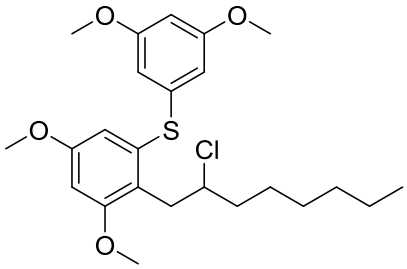

As described in general procedure C, **1f** (63.8 mg, 0.2 mmol), octene (160 μL, 1 mmol) and $FeCl_3$ (131 mg, 0.8 mmol), after purification by column chromatography (30 % $CHCl_3$ in hexanes) gave **2o** (69.8 mg, 75%) as a colourless oil; $\delta_H$ (400 MHz, $CDCl_3$) 0.88 (3 H, t, *J* 6.9 Hz, $CH_2CH_3$), 1.16 - 1.42 (7 H, m, $CH_2$), 1.50 - 1.63 (1 H, m, $CH_2$), 1.63 - 1.78 (2 H, m, $CH_2$), 3.20 (1 H, dd, *J* 13.6, 6.5 Hz, $ArCH_2CHCl$), 3.30 (1 H, dd, *J* 13.6, 8.0 Hz, $ArCH_2CHCl$), 3.75 (3 H, s, $OCH_3$), 3.86 (3 H, s, $OCH_3$), 4.23 (1 H, m, $CH_2CHClCH_2$), 6.52 (1 H, d, *J* 2.5 Hz, aryl H), 6.61 (1 H, d, *J* 2.5 Hz, aryl H), 7.18 (2 H, d, *J* 8.3 Hz, aryl H), 7.47 (2 H, d, *J* 8.3 Hz, aryl H); $\delta_C$ (100 MHz, $CDCl_3$) 14.1 ($CH_3$), 22.6 ($CH_2$), 26.7 ($CH_2$), 28.8 ($CH_2$), 31.7 ($CH_2$), 36.4 ($ArCH_2CHCl$), 37.9 ($CH_2$), 55.5 ($OCH_3$), 55.7 ($OCH_3$), 63.3 (CHCl), 99.9 (aryl C-H), 110.8 (aryl C-H), 123.3 (aryl C), 124.3 (q, *J* 271.4 Hz, $CF_3$), 125.7 (q, *J* 3.7 Hz, aryl C-H), 127.3 (aryl C-H), 128.3 (q, *J* 32.3 Hz, aryl C), 133.3 (aryl C), 143.3 (aryl C), 159.4 (aryl C), 159.6 (aryl C); $\nu_{max}$ (thin film/$cm^{-1}$) 1013 (m), 1047 (m), 1063 (m), 1123 (m), 1163 (m), 1324 (s), 1461 (w), 1570 (m), 1598 (m), 2857 (w), 2931 (w); MS ($ES^+$) *m/z* 461.5 (M+H); HRMS $C_{23}H_{28}O_2F_3S$ (M-Cl) Expected 425.1757, Found 425.1755.

*(2-(2-Chlorooctyl)-3,5-dimethoxyphenyl)(3-methoxyphenyl)sulfide* ***2p***



As described in general procedure C, **1g** (56.1 mg, 0.2 mmol), octene (160 µL, 1 mmol) and $FeCl_3$ (131 mg, 0.8 mmol), after purification by column chromatography (30 % $CHCl_3$ in hexanes) gave **2p** (52.7 mg, 60%) as a colourless oil; $\delta_H$ (500 MHz, $CDCl_3$) 0.90 (3 H, t, *J* 7.1 Hz, C*H*$_3$), 1.20 - 1.44 (7 H, m, C*H*$_2$), 1.56-1.66 (1 H, m, C*H*$_2$), 1.70 - 1.78 (2 H, m, C*H*$_2$), 3.26 (1 H, dd, *J* 13.9, 6.9 Hz, ArC*H*$_2$CHCl), 3.35 (1 H, dd, *J* 13.6, 7.3 Hz, ArC*H*$_2$CHCl), 3.71 (3 H, s, OC*H*$_3$), 3.77 (3 H, s, OC*H*$_3$), 3.84 (3 H, m, OC*H*$_3$), 4.30 (1 H, m, C*H*Cl), 6.44 (1 H, d, *J* 2.5 Hz, aryl H), 6.52 (1 H, d, *J* 2.5 Hz, aryl H), 6.76 (1 H, ddd, *J* 8.0, 2.5, 0.9 Hz, aryl H), 6.80 (1 H, dd, *J* 3.5, 2.5 Hz, aryl H), 6.82 - 6.85 (1 H, m, aryl H), 7.20 (1 H, t, *J* 8.0 Hz, aryl H); $\delta_C$ (125 MHz, $CDCl_3$) 14.1 (*C*H$_3$), 22.6 (*C*H$_2$), 26.7 (*C*H$_2$), 28.8 (*C*H$_2$), 31.8 (*C*H$_2$), 36.3 (Ar*C*H$_2$CHCl), 37.8 (*C*H$_2$), 55.26 (O*C*H$_3$), 55.4 (O*C*H$_3$), 55.6 (O*C*H$_3$), 63.4 (*C*HCl), 98.6 (aryl *C*-H), 109.4 (aryl *C*-H), 112.2 (aryl *C*-H), 115.0 (aryl *C*-H), 121.7 (aryl C), 122.0 (aryl *C*-H), 129.9 (aryl *C*-H), 136.0 (aryl C), 138.0 (aryl C), 159.2 (aryl C), 159.4 (aryl C), 160.1 (aryl C); $\nu_{max}$ (thin film/cm$^{-1}$) 1045 (s), 1144 (m), 1199 (m), 1247 (m), 1462 (m), 1476 (m), 1572 (s), 1585 (s), 2856 (w), 2930 (m), 3000 (w); MS (ES$^+$) *m/z* 422.9 (M+H); HRMS $C_{23}H_{31}O_3S$ (M-Cl) Expected 387.1994, Found 387.1992.

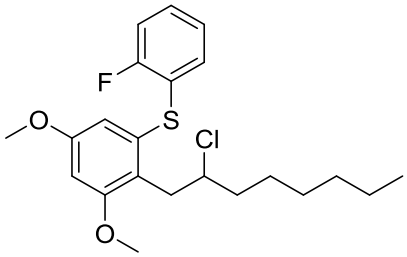
*(2-(2-Chlorooctyl)-3,5-dimethoxyphenyl)(3,5-dimethoxyphenyl)sulfide* ***2q***



As described in general procedure C, **1h** (62.2 mg, 0.2 mmol), octene (160 µL, 1 mmol) and $FeCl_3$ (131 mg, 0.8 mmol), after purification by column chromatography (50 % $CHCl_3$ in hexanes) gave **2q** (43.0 mg, 47%) as a white solid; m.p 62.1-64.3 °C, $\delta_H$ (400 MHz, $CDCl_3$) 0.88 (3 H, t, *J* 6.9 Hz, $CH_2CH_3$), 1.16 - 1.41 (7 H, m, C*H*$_2$), 1.51-1.64 (1 H, m, C*H*$_2$), 1.65 - 1.76 (2 H, m, C*H*$_2$), 3.21 (1 H, dd, *J* 13.8, 7.0 Hz, ArC*H*$_2$CHCl), 3.31 (1 H, dd, *J* 13.8, 7.5 Hz, ArC*H*$_2$CHCl), 3.72 (3 H, s, OC*H*$_3$), 3.74 (6 H, s, OC*H*$_3$), 3.83 (3 H, s, OC*H*$_3$), 4.25 (1 H, m, $CH_2CHClCH_2$), 6.27 - 6.31 (1 H, m, aryl H), 6.35 (2 H, d, *J* 2.0 Hz, aryl H), 6.43 (1 H, d, *J* 2.3 Hz, aryl H), 6.55 (1 H, d, *J* 2.3 Hz, aryl H); $\delta_C$ (100

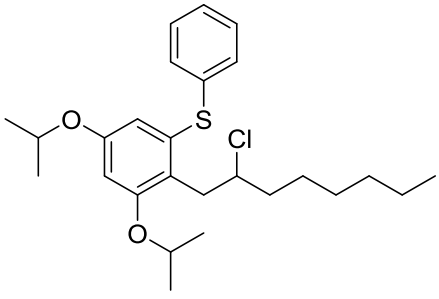
MHz, $CDCl_3$) 14.2 (*C*$H_3$), 22.7 (*C*$H_2$), 26.7 (*C*$H_2$), 28.8 (*C*$H_2$), 31.2 (*C*$H_2$), 36.3 (Ar*C*$H_2$CHCl), 37.8 (*C*$H_2$), 55.4 (O*C*$H_3$), 55.4 (O*C*$H_3$), 55.6 (O*C*$H_3$), 63.5 (*C*HCl), 98.6 (aryl *C*-H), 98.9 (aryl *C*-H), 107.0 (aryl *C*-H), 109.7 (aryl *C*-H), 122.0 (aryl C), 135.3 (aryl C), 139.0 (aryl C), 159.1 (aryl C), 159.3 (aryl C), 161.0 (aryl C); $\nu_{max}$ (thin film/$cm^{-1}$) 1044 (s), 1154 (s), 1202 (s), 1279 (m), 1417 (m), 1454 (m), 1570 (s), 1585 (s), 2856 (w), 2930 (m); MS ($ES^+$) *m/z* 453.4 (M+H); HRMS $C_{24}H_{34}O_4ClS$ (M+H) Expected 453.1866, Found 453.1873.

### *(2-(2-Chlorooctyl)-3,5-dimethoxyphenyl)(2-fluorophenyl)sulfide* ***2r***




As described in general procedure C, **1j** (53.7 mg, 0.2 mmol), octene (160 μL, 1 mmol) and $FeCl_3$ (131 mg, 0.8 mmol), after purification by column chromatography (30 % $CHCl_3$ in hexanes) gave **2r** (53.5 mg, 64%) as a colourless oil; $\delta_H$ (500 MHz, $CDCl_3$) 0.89 (3 H, t, *J* 6.9 Hz, C*H*$_3$), 1.19 - 1.44 (7 H, m, C*H*$_2$), 1.55-1.64 (1 H, m, C*H*$_2$), 1.68 - 1.80 (2 H, m, C*H*$_2$), 3.25 (1 H, dd, *J* 13.9, 6.9 Hz, ArC*H*$_2$CHCl), 3.35 (1 H, dd, *J* 13.9, 7.6 Hz, ArC*H*$_2$CHCl), 3.69 (3 H, m, OC*H*$_3$), 3.83 (3 H, s, OC*H*$_3$), 4.29 (1 H, m, $CH_2$C*H*Cl$CH_2$), 6.39 (1 H, d, *J* 2.5 Hz, aryl H), 6.42 (1 H, d, *J* 2.5 Hz, aryl H), 7.03 - 7.15 (3 H, m, aryl H), 7.21 - 7.26 (1 H, m, aryl H); $\delta_C$ (125 MHz, $CDCl_3$) 14.1 (*C*$H_3$), 22.6 (*C*$H_2$), 26.7 (*C*$H_2$), 28.9 (*C*$H_2$), 31.7 (*C*$H_2$), 36.3 (Ar*C*$H_2$CHCl), 37.7 (*C*$H_2$), 55.3 (O*C*$H_3$), 55.6 (O*C*$H_3$), 63.2 (*C*HCl), 98.4 (aryl *C*-H), 108.6 (aryl *C*-H), 115.8 (d, *J* 21.8 Hz, aryl *C*-H), 121.4 (aryl C), 123.4 (d, *J* 17.3 Hz, aryl C), 124.7 (d, *J* 3.6 Hz, aryl *C*-H), 128.8 (d, *J* 7.3 Hz, aryl *C*-H), 132.4 (aryl *C*-H), 135.2 (aryl C), 159.2 (aryl C), 159.4 (aryl C), 160.7 (d, *J* 246.1 Hz, *C*-F); $\nu_{max}$ (thin film/$cm^{-1}$) 1047 (s), 1145 (s), 1221 (m), 1297 (w), 1472 (s), 1572 (s), 1597 (s), 2857 (w), 2930 (m); MS ($ES^+$) *m/z* 411.3 (M+H); HRMS $C_{22}H_{29}O_2ClFS$ (M+H) Expected 411.1555, Found 411.1557.

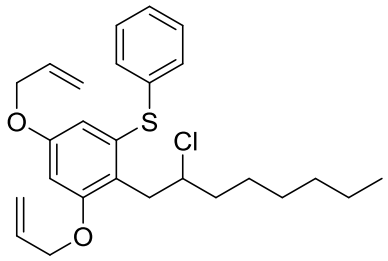
### *(2-(2-Chlorooctyl)-3,5-diisopropoxyphenyl)(phenyl)sulfide* ***2s***




As described in general procedure C, **1k** (61.4 mg, 0.2 mmol), octene (160 μL, 1 mmol) and $FeCl_3$ (131 mg, 0.8 mmol), after purification by column chromatography (30 % $CHCl_3$ in hexanes) gave **2s**

(59.5 mg, 65%) as a colourless oil; $\delta_H$ (400 MHz, $CDCl_3$) 0.89 (3 H, t, *J* 6.8 Hz, C*H*$_3$), 1.20 - 1.33 (12 H, m, OCH(C*H*$_3$)$_2$), 1.33 - 1.41 (7 H, m, C*H*$_2$), 1.50 - 1.65 (1 H, m, C*H*$_2$), 1.68-1.77 (2 H, q, *J* 7.4 Hz, C*H*$_2$), 3.23 (1 H, dd, *J* 13.6, 7.3 Hz, ArC*H*$_2$CHCl), 3.30 (1 H, dd, *J* 13.6, 7.3 Hz, ArC*H*$_2$CHCl), 4.23 - 4.40 (2 H, m, C*H*Cl + OC*H*(CH$_3$)$_2$), 4.53 (1 H, spt, *J* 6.0 Hz, OC*H*(CH$_3$)$_2$), 6.36 (2 H, s, aryl H), 7.17 - 7.32 (5 H, m, aryl H); $\delta_C$ (100 MHz, $CDCl_3$) 14.2 (*C*H$_3$), 21.9 (OCH(C*H*$_3$)$_2$), 22.0 (OCH(C*H*$_3$)$_2$), 22.1 (OCH(C*H*$_3$)$_2$), 22.7 (*C*H$_2$), 26.8 (*C*H$_2$), 28.8 (*C*H$_2$), 31.8 (*C*H$_2$), 36.6 (Ar*C*H$_2$CHCl), 37.8 (*C*H$_2$), 63.6 (*C*HCl), 69.8 (O*C*H(CH$_3$)$_2$), 69.9 (O*C*H(CH$_3$)$_2$), 101.3 (aryl *C*-H), 110.1 (aryl *C*-H), 121.6 (aryl C), 126.5 (aryl *C*-H), 129.1 (aryl *C*-H), 130.1 (aryl *C*-H), 136.6 (aryl C), 136.7 (aryl C), 157.3 (aryl C), 157.4 (aryl C); $\nu_{max}$ (thin film/cm$^{-1}$) 1037 (m), 1113 (s), 1135 (s), 1179 (m), 1273 (w), 1373 (w), 1384 (w), 1464 (m), 1566 (s), 1593 (w), 2857 (w), 2929 (m), 2975 (m); MS (ES$^+$) *m/z* 449.3 (M+H); HRMS $C_{26}H_{38}O_2ClS$ (M+H) Expected 449.2281, Found 449.2293.

### *(3,5-bis(Allyloxy)-2-(2-chlorooctyl)phenyl)(phenyl)sulfide* ***2t***



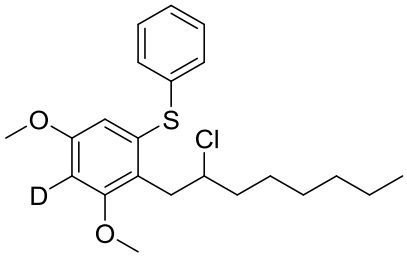

As described in general procedure C, **1k** (59.6 mg, 0.2 mmol), octene (160 μL, 1.0 mmol) and $FeCl_3$ (130 mg, 0.8 mmol), after purification by column chromatography (30% $CHCl_3$ in hexanes) gave **2t** (46.7 mg, 50%) as a colourless oil; $\delta_H$ (400 MHz, $CDCl_3$) 0.88 (3 H, t, *J* 6.8 Hz, C*H*$_3$), 1.20 - 1.42 (7 H, m, C*H*$_2$), 1.53 - 1.65 (1 H, m, C*H*$_2$), 1.70 - 1.78 (2 H, m, C*H*$_2$), 3.26 (1 H, dd, *J* 13.6, 7.2 Hz, ArC*H*$_2$CHCl), 3.36 (1 H, dd, *J* 13.6, 7.2 Hz, ArC*H*$_2$CHCl), 4.30 (1 H, m, C*H*Cl), 4.37 (2 H, dt, *J* 5.4, 1.3 Hz, OC*H*$_2$), 4.53 (2 H, dt, *J* 5.0, 1.5 Hz, OC*H*$_2$), 5.23 (1 H, dq, *J* 10.5, 1.3 Hz, CH=C*H*$_2$), 5.29 (1 H, dq, *J* 6.7, 1.5 Hz, CH=C*H*$_2$), 5.32 (1 H, q, *J* 1.3 Hz, CH=C*H*$_2$), 5.45 (1 H, dq, *J* 17.3, 1.5 Hz, CH=C*H*$_2$), 5.95 (1 H, ddt, *J* 17.2, 10.7, 5.5 Hz, C*H*=CH$_2$), 6.06 (1 H, ddt, *J* 17.2, 10.4, 5.1 Hz, C*H*=CH$_2$), 6.42 (1 H, d, *J* 2.4 Hz, aryl H), 6.43 (1 H, d, *J* 2.4 Hz, aryl H), 7.19 - 7.33 (5 H, m, aryl H); $\delta_C$ (125 MHz, $CDCl_3$) 14.1 (*C*H$_3$), 22.6 (*C*H$_2$), 26.7 (*C*H$_2$), 28.7 (*C*H$_2$), 31.7 (*C*H$_2$), 36.4 (Ar*C*H$_2$CHCl), 37.8 (*C*H$_2$), 63.3 (*C*HCl), 68.9 (O*C*H$_2$), 69.0 (O*C*H$_2$), 99.9 (*C*H=CH$_2$), 109.7 (*C*H=CH$_2$), 117.3 (CH=*C*H$_2$), 118.0 (CH=*C*H$_2$), 121.4 (aryl *C*), 126.7 (aryl *C*-H), 129.1 (aryl *C*-H), 130.3 (aryl *C*-H), 132.8 (aryl *C*-H), 132.9 (aryl *C*-H), 136.2 (aryl C), 136.8 (aryl C), 158.0 (aryl C), 158.1 (aryl C); $\nu_{max}$ (thin film/cm$^{-1}$); 924 (s), 1023 (s), 1044 (s), 1140 (w), 1172 (s), 1274 (w), 1416 (w), 1455 (w), 1569 (s), 1595 (s), 2856 (w), 2926 (w), 2953 (w), 3060 (w), 3074 (w); MS (ES$^+$) *m/z* 455 (M+H$^+$); HRMS $C_{26}H_{33}O_2S$ (M−Cl) Expected 409.2201 Found 409.2193.

## Manipulation of Products

*General Procedure D*

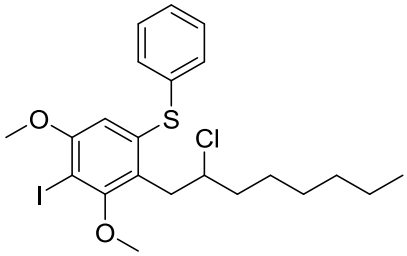
A solution of *n*-butyllithium (1.6 M in hexanes, 1.2 equiv.) was added to a solution of **2a** (0.1 M) precooled to -78 $^0$C. The mixture was warmed to room temperature, quenched and left to stir for 10 min. $NH_4Cl$ (2 mL) and EtOAc (2 mL) were then added. The organic layer was then washed twice more with $NH_4Cl$ (2 ml). The aqueous layer was extracted with EtOAc (2 × 2 mL). The combined organic extracts were dried with $Na_2SO_4$, filtered and solvent removed *in vacuo*.

*(2-(2-Chlorooctyl)-3,5-dimethoxyphenyl-4-d)(phenyl)sulfide* ***3a***




As described in general procedure D, the reaction of **2a** (50 mg, 0.13 mmol) was quenched with MeOD (48 μL) and, after purification by column chromatography (30 % $CHCl_3$ in hexanes), gave **3a** (51 mg, 100%) as a colourless oil; $\delta_H$ (400 MHz, $CDCl_3$) 0.88 (3 H, t, *J* 6.9 Hz, C*H*$_3$), 1.16 - 1.44 (7 H, m, C*H*$_2$), 1.53 - 1.65 (1 H, m, C*H*$_2$), 1.66 - 1.77 (2 H, m, C*H*$_2$), 3.23 (1 H, dd, *J* 13.8, 7.0 Hz, ArC*H*$_2$CHCl), 3.33 (1 H, dd, *J* 13.8, 7.5 Hz, ArC*H*$_2$CHCl), 3.68 (3 H, s, OC*H*$_3$), 3.83 (3 H, s, OC*H*$_3$), 4.23 - 4.32 (1 H, m, ArCH$_2$C*H*Cl), 6.44 (1 H, s, aryl H), 7.17 - 7.33 (5 H, m, aryl H); $\delta_C$ (100 MHz, $CDCl_3$) 14.1 (*C*H$_3$), 22.7 (*C*H$_2$), 26.7 (*C*H$_2$), 28.8 (*C*H$_2$), 31.8 (*C*H$_2$), 36.3 (Ar*C*H$_2$CHCl), 37.7 (*C*H$_2$), 55.3 (O*C*H$_3$), 55.6 (O*C*H$_3$), 63.4 (*C*HCl), 98.0 (t, *J* 24.2 Hz, aryl *C*-D), 108.8 (aryl *C*-H), 121.3 (aryl C), 126.6 (aryl *C*-H), 129.2 (aryl *C*-H), 130.0 (aryl *C*-H), 136.4 (aryl C), 136.5 (aryl C), 159.0 (aryl C), 159.2 (aryl C); $\nu_{max}$ (thin film/cm$^{-1}$) 1046 (s), 1094 (s), 1146 (m), 1199 (s), 1295 (m), 1387 (m), 1458 (m), 1565 (s), 1587 (s), 2856 (w), 2929 (m); MS (ES$^+$) *m/z* 394.3 (M+H); HRMS $C_{22}H_{29}DO_2ClS$ (M+H) Expected 394.1718, Found 394.1703.

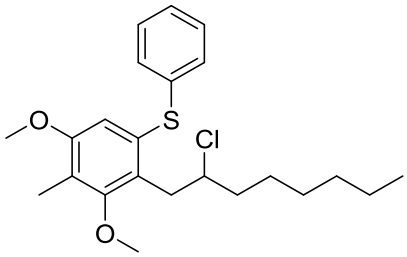
*(2-(2-Chlorooctyl)-4-iodo-3,5-dimethoxyphenyl)(phenyl)sulfide* ***3b***




As described in general procedure D, the reaction of **2a** (50 mg, 0.13 mmol) was quenched with $I_2$ (1.17 mL, 1.17 M in THF) and, after purification by column chromatography (30 % $CHCl_3$ in

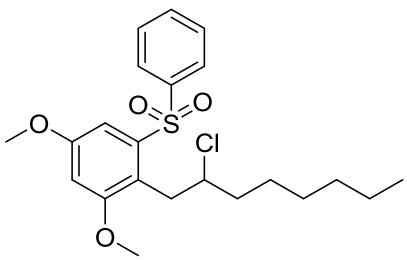
hexanes), gave **3b** (64 mg, 95%) as a yellow oil; $\delta_H$ (500 MHz, $CDCl_3$) 0.88 (3 H, t, *J* 6.9, C*H*$_3$), 1.19 - 1.43 (7 H, m, C*H*$_2$), 1.53 - 1.63 (1 H, m, C*H*$_2$), 1.67 - 1.80 (2 H, m, C*H*$_2$), 3.24 (1 H, dd, *J* 13.9, 6.6 Hz, ArC*H*$_2$CHCl), 3.36 (1 H, dd, *J* 14.0, 7.7 Hz, ArC*H*$_2$CHCl), 3.68 (3 H, s, OC*H*$_3$), 3.85 (3 H, s, OC*H*$_3$), 4.31 - 4.39 (1 H, m, $CH_2$C*H*ClCH$_2$), 6.51 (1 H, s, aryl H), 7.24 - 7.36 (5 H, m, aryl H); $\delta_C$ (125 MHz, $CDCl_3$) 14.1 (*C*H$_3$), 22.6 (C*H*$_2$), 26.7 (*C*H$_2$), 28.7 (C*H*$_2$), 31.7 (C*H*$_2$), 37.7 (*C*H$_2$), 37.9 (Ar*C*H$_2$CHCl), 56.5 (O*C*H$_3$), 61.1 (O*C*H$_3$), 62.9 (*C*HCl), 83.5 (aryl C), 110.9 (aryl *C*-H), 126.4 (aryl C), 127.3 (aryl *C*-H), 129.4 (aryl *C*-H), 130.7 (aryl *C*-H), 135.4, (aryl C), 138.0 (aryl C), 158.2 (aryl C), 160.3 (aryl C); $\nu_{max}$ (thin film/cm$^{-1}$) 1018 (w), 1086 (s), 1136 (m), 1198 (w), 1372 (m), 1456 (m), 1567 (m), 2855 (w), 2930 (m); MS (ES$^+$) *m/z* 541.2 (M+Na); HRMS $C_{22}H_{29}O_2ClIS$ (M+H) Expected 519.0616, Found 519.0610.

### *(2-(2-Chlorooctyl)-3,5-dimethoxy-4-methylphenyl)(phenyl)sulfide* ***3c***



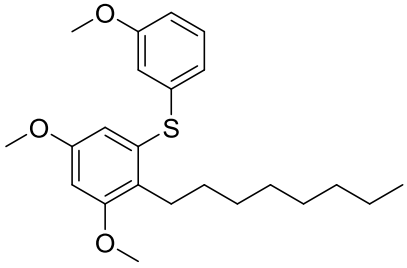

As described in general procedure D, the reaction of **2a** (50 mg, 0.13 mmol) was quenched with MeI (73 μL) and, after purification by column chromatography (30 % $CHCl_3$ in hexanes), gave **3c** (46.1 mg, 87%) as a colourless oil; $\delta_H$ (500 MHz, $CDCl_3$) 0.88 (3 H, t, *J* 6.9 Hz, C*H*$_3$) 1.18 - 1.41 (7 H, m, C*H*$_2$), 1.51-1.63 (1 H, m, C*H*$_2$), 1.66 - 1.78 (2 H, m, C*H*$_2$), 2.19 (3 H, s, ArC*H*$_3$), 3.19 (1 H, dd, *J* 13.7, 6.8 Hz, ArC*H*$_2$CHCl), 3.31 (1 H, dd, *J* 13.9, 7.6 Hz, ArC*H*$_2$CHCl), 3.70 (3 H, s, OC*H*$_3$), 3.75 (3 H, s, OC*H*$_3$), 4.28 - 4.36 (1 H, m, C*H*Cl), 6.70 (1 H, s, aryl H), 7.15 - 7.21 (3 H, m, aryl H), 7.24 - 7.29 (2 H, m, aryl H); $\delta_C$ (125 MHz, $CDCl_3$) 9.6 (Ar*C*H$_3$), 14.1 (*C*H$_3$), 22.6 (*C*H$_2$), 26.7 (*C*H$_2$), 28.7 (*C*H$_2$), 31.7 (*C*H$_2$), 37.1 (Ar*C*H$_2$CHCl), 37.8 (*C*H$_2$), 55.6 (O*C*H$_3$), 60.1 (O*C*H$_3$), 63.6 (*C*HCl), 112.2 (aryl *C*-H), 120.5 (aryl C), 126.0 (aryl *C*-H), 126.6 (aryl C), 128.6 (aryl *C*-H), 129.0 (aryl *C*-H), 131.6 (aryl C), 137.4 (aryl C), 157.6 (aryl C), 158.5 (aryl C); $\nu_{max}$ (thin film/cm$^{-1}$) 1024 (m), 1120 (s), 1192 (w), 1268 (w), 1388(w), 1438 (m), 1464 (m), 1583 (m), 2856 (w), 2929 (m); MS (ES$^+$) *m/z* 407.4 (M+H); HRMS $C_{23}H_{31}O_2S$ (M-Cl) Expected 371.2045, Found 371.2039.

### *2-(2-Chlorooctyl)-1,5-dimethoxy-3-(phenylsulfonyl)benzene* ***3d***



*m*-CPBA (≤77%) (67.3 mg, 0.39 mmol) was added to a solution of **2a** (50 mg, 0.13 mmol) in $CH_2Cl_2$ (1 mL). The mixture was stirred under reflux for 18 hr and then quenched with aqueous $NaHCO_3$ (2 mL). The aqueous layer was washed with $CH_2Cl_2$ (3 × 2 mL) and the combined organic extracts were dried with $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude product was purified by column chromatography (20% EtOAc in hexanes) to give **3d** (52.6 mg, 95%) as a colourless oil; $\delta_H$ (500 MHz, $CDCl_3$) 0.87 (3 H, t, *J* 7.1 Hz, C*H*$_3$), 1.11 - 1.36 (7 H, m, C*H*$_2$), 1.45 - 1.58 (3 H, m, C*H*$_2$), 3.21 (1 H, dd, *J* 13.6, 7.3 Hz, ArC*H*$_2$CHCl), 3.28 (1 H, dd, *J* 13.6, 7.6 Hz, ArC*H*$_2$CHCl), 3.80 (3 H, s, OC*H*$_3$), 3.89 (3 H, s, OC*H*$_3$), 4.25 - 4.34 (1 H, m, $CH_2$C*H*ClCH$_2$), 6.67 (1 H, d, *J* 2.5 Hz, aryl H), 7.40 (1 H, d, *J* 2.5 Hz, aryl H), 7.50 (2 H, t, *J* 7.3 Hz, aryl H), 7.58 (1 H, t, *J* 7.3 Hz, aryl H), 7.86 (2 H, d, *J* 7.3 Hz, aryl H); $\delta_C$ (125 MHz, $CDCl_3$) 14.1 (*C*H$_3$), 22.6 (*C*H$_2$), 26.8 (*C*H$_2$), 28.7 (*C*H$_2$), 31.7 (*C*H$_2$), 34.5 (Ar*C*H$_2$CHCl), 37.4 (*C*H$_2$), 55.8 (O*C*H$_3$), 55.9 (O*C*H$_3$), 63.0 (*C*HCl), 103.4 (aryl *C*-H), 105.5 (aryl *C*-H), 119.6 (aryl C), 127.4 (aryl *C*-H), 129.2 (aryl *C*-H), 133.2 (aryl *C*-H), 141.1 (aryl C), 141.9 (aryl C), 159.1 (aryl C), 160.1 (aryl C); $\nu_{max}$ (thin film/cm$^{-1}$) 1041 (m), 1057 (w), 1154 (s), 1204 (m), 1305 (s), 1461 (m), 1600 (m), 2856 (w), 2930 (m); MS (ES$^+$) *m/z* 389.3 (M+Na); HRMS $C_{22}H_{29}O_4SClNa$ (M+Na) Expected 447.1385, Found 447.1373.

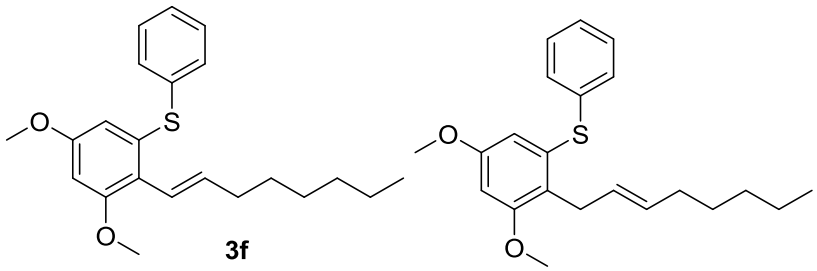
### *(3,5-Dimethoxy-2-octylphenyl)(3-methoxyphenyl)sulfide* ***3e***




AIBN (1.6 mg, 0.01 mmol) and $Bu_3SnH$ (65 μL, 0.24 mmol) were added to a solution of **2p** (50 mg, 0.13 mmol) in benzene (1 mL). The solution was stirred under reflux for 18 h, then cooled to room temperature and solvent removed *in vacuo*. The crude product mixture was then passed through a plug of 10% $K_2CO_3$/silica using hexane, then EtOAc as eluents. The solvent was then removed *in vacuo* and the resultant crude product purified by column chromatography (30% $CHCl_3$ in hexanes) to give **3e** (27.9 mg, 86% brsm) as a colourless oil; $\delta_H$ (400 MHz, $CDCl_3$) 0.83 - 0.92 (3 H, t, *J* 7 Hz, $CH_3$), 1.18 - 1.38 (10 H, m, C*H*$_2$), 1.39 - 1.51 (2 H, m, ArCH$_2$C*H*$_2$), 2.69 - 2.78 (2 H, m, ArC*H*$_2$CH$_2$), 3.70 (3 H, s, OC*H*$_3$), 3.76 (3 H, s, OC*H*$_3$), 3.81 (3 H, s, OC*H*$_3$), 6.41 (1 H, d, *J* 2.5 Hz, aryl H), 6.46 (1 H, d, *J* 2.5 Hz, aryl H), 6.71 - 6.76 (1 H, m, aryl H), 6.79 (1 H, t, *J* 2.0 Hz, aryl H), 6.82 (1 H, d, *J* 7.8 Hz, aryl H), 7.18 (1 H, t, *J* 8.0 Hz, aryl H); $\delta_C$ (100 MHz, $CDCl_3$) 14.1 (*C*H$_3$), 22.7 (C*H*$_2$), 27.3 (Ar*C*H$_2$CH$_2$), 29.3 (C*H*$_2$), 29.4 (C*H*$_2$), 29.8 (C*H*$_2$), 29.9 (C*H*$_2$), 31.9 (C*H*$_2$), 55.2 (O*C*H$_3$), 55.2 (O*C*H$_3$), 55.6 (O*C*H$_3$), 98.6 (aryl *C*-H), 108.8 (aryl *C*-H), 112.0 (aryl *C*-H), 114.9 (aryl *C*-H), 121.9 (aryl *C*-H), 126.4 (aryl C), 129.8 (aryl *C*-H), 134.4 (aryl C), 138.2 (aryl C), 158.4 (aryl C). 158.8 (aryl C), 159.9 (aryl C); $\nu_{max}$ (thin film/cm$^{-1}$) 1047 (s), 1147 (s), 1195 (w), 1230 (w), 1245 (w), 1282 (w), 1462 (m),

1476 (m), 1570 (s), 1590 (s), 2853 (w), 2925 (m), 2954 (m), 2999 (w); MS ($ES^+$) *m/z* 389.3 (M+H); HRMS $C_{23}H_{33}O_3S$ (M+H) Expected 389.2162, Found 389.2150.

*(E)-(3,5-Dimethoxy-2-(oct-1-en-1-yl)phenyl)(phenyl)sulfide* ***3f*** *and (E)-(3,5-dimethoxy-2-(oct-2-en-1-yl)phenyl)(phenyl)sulfide*

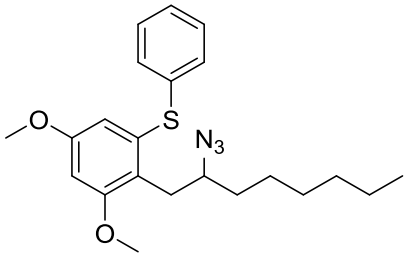



**3f**

A solution of NaOEt in EtOH (21 wt%, 100 μL, 0.26 mmol) was added to a solution of **2a** (50 mg, 0.13 mmol) in EtOH (1.2 mL). The solution was stirred under reflux for 18 h, then cooled to room temperature and quenched with $H_2O$ (2 mL) and diluted with EtOAc (5 mL). The organic phase was washed with $H_2O$ (3 × 2 mL), dried over $MgSO_4$, filtered and solvent removed *in vacuo*. The crude mixture was purified by column chromatography (10% EtOAc in hexanes) to give **3f** (24.6 mg, 53 %) and (E)-(3,5-dimethoxy-2-(oct-2-en-1-yl)phenyl)(phenyl)sulfide (15.3 mg, 33%) as colourless oils; For **3f**, $\delta_H$ (500 MHz, $CDCl_3$) 0.89 (3 H, t, *J* 6.6 Hz, C$H_3$), 1.23 - 1.37 (6 H, m, C$H_2$), 1.37 - 1.45 (2 H, m, C$H_2$), 2.19 (2 H, qd, *J* 6.9, 1.3 Hz, CH=CHC$H_2$CH$_2$), 3.66 (3 H, s, OC$H_3$), 3.83 (3 H, s, OC$H_3$), 6.27 (1 H, dt, *J* 16.1, 6.9 Hz, ArCH=C*H*CH$_2$), 6.35 (1 H, d, *J* 2.5 Hz, aryl H), 6.39 (1 H, d, *J* 2.5 Hz, aryl H), 6.53 (1 H, dt, *J* 16.1, 1.3 Hz, ArC*H*=CHCH$_2$), 7.21 - 7.33 (5 H, m, aryl H); $\delta_C$ (125 MHz, $CDCl_3$) 14.2 (*C*H$_3$), 22.7 (*C*H$_2$), 28.9 (*C*H$_2$), 29.4 (*C*H$_2$), 31.8 (*C*H$_2$), 34.1 (CH=CH*C*H$_2$CH$_2$), 55.3 (O*C*H$_3$), 55.6 (O*C*H$_3$), 98.0 (aryl *C*-H), 107.8 (aryl *C*-H), 121.0 (aryl C), 122.7 (ArCH=*C*HCH$_2$), 126.9 (aryl *C*-H), 129.1 (aryl *C*-H), 131.1 (aryl *C*-H), 135.7 (aryl C), 136.1 (aryl C), 136.6 (Ar*C*H=CHCH$_2$), 158.6 (aryl C), 158.7 (aryl C); $\nu_{max}$ (thin film/cm$^{-1}$) 1046 (s), 1153 (s), 1200 (m), 1210 (m), 1298 (m), 1407 (w), 1434 (w), 1459 (m), 1563 (s), 1593 (s), 2854 (w), 2925 (m), 2954 (w), 3000 (w); MS ($ES^+$) *m/z* 357.3 (M+H); HRMS $C_{22}H_{29}O_2S$ (M+H) Expected 357.1883, Found 357.1887; For (E)-(3,5-dimethoxy-2-(oct-2-en-1-yl)phenyl)(phenyl)sulfide, $\delta_H$ (400 MHz, $CDCl_3$) 0.82 - 0.92 (3 H, t, *J* 7 Hz, C$H_3$), 1.16 - 1.36 (6 H, m, C$H_2$), 1.91 (2 H, q, *J* 6.6 Hz, CHCHC$H_2$CH$_2$), 3.49 (2 H, d, *J* 5.8 Hz, ArC$H_2$CHCH), 3.68 (3 H, s, OC$H_3$), 3.82 (3 H, s, OC$H_3$), 5.30 - 5.50 (2 H, m, ArCH$_2$C*H*C*H*CH$_2$), 6.42 (2 H, q, *J* 2.1 Hz, aryl H), 7.16 - 7.31 (5 H, m, aryl H); $\delta_C$ (100 MHz, $CDCl_3$) 14.1 (C$H_3$), 22.5 (C$H_2$), 29.1 (C$H_2$), 30.2 (Ar*C*H$_2$CHCH), 31.4 (C$H_2$), 32.5 (CHCH*C*H$_2$), 55.3 (O*C*H$_3$), 55.7 (O*C*H$_3$), 98.4 (aryl *C*-H), 108.6 (aryl *C*-H), 123.8 (aryl *C*), 126.4 (aryl *C*-H), 127.3 (CH$_2$CH=*C*HCH$_2$), 129.0 (aryl *C*-H), 130.1 (aryl *C*-H), 131.2 (CH$_2$*C*H=CHCH$_2$), 135.5 (aryl *C*), 136.6 (aryl *C*), 158.7 (aryl *C*), 158.8 (aryl *C*); $\nu_{max}$ (thin film/cm$^{-1}$) 1050 (s), 1144 (s), 1166 (w), 1205 (m) 1274 (w), 1296 (w), 1409 (w), 1437 (w), 1460 (m), 1477 (m), 1572 (s), 1596 (s), 2854 (w), 2925

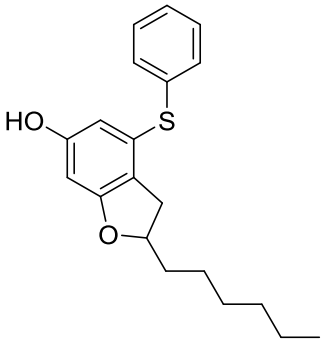
(m), 2955 (w); MS ($ES^+$) *m/z* 357.3 (M+H); HRMS $C_{22}H_{29}O_2S$ (M+H) Expected 357.1883, Found 357.1886.

### *(2-(2-Azidooctyl)-3,5-dimethoxyphenyl)(phenyl)sulfide* ***3g***




$NaN_3$ (42.3 mg, 0.65 mmol) was added to a solution of **2a** (50 mg, 0.13 mmol) in DMF (1.3 mL) and heated to 80 °C for 18 h. The mixture was cooled to room temperature and diluted with EtOAc (5 mL). An aqueous solution of LiCl (10% wt) (5 mL) was added and the organic phase was extracted with aqueous LiCl (3 × 5 mL). The organic extracts were dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude was purified by column chromatography (10 % EtOAc in hexanes) to give **3g** (22.9 mg, 44 %) as a colourless oil; $\delta_H$ (500 MHz, $CDCl_3$) 0.89 (t, *J* 6.9 Hz, 3 H, C*H*$_3$), 1.21 - 1.38 (m, 7 H, C*H*$_2$), 1.44 - 1.60 (m, 3 H, C*H*$_2$), 2.98 (dd, *J* 13.6, 6 Hz, 1 H, ArC*H*$_2$CH($N_3$)), 3.09 (dd, *J* 13.6, 8.2 Hz, 1 H, ArC*H*$_2$CH($N_3$)), 3.50 - 3.58 (m, 1 H, ArCH$_2$C*H*($N_3$)CH$_2$), 3.69 (s, 3 H, OC*H*$_3$), 3.84 (s, 3 H, OC*H*$_3$), 6.42 (d, *J* 2.5 Hz, 1 H, aryl H), 6.43 (d, *J* 2.5 Hz, 1 H, aryl H), 7.19 - 7.32 (m, 5 H, aryl H); $\delta_C$ (125 MHz, $CDCl_3$) 14.1 (*C*H$_3$), 22.6 (*C*H$_2$), 26.2 (*C*H$_2$), 29.0 (*C*H$_2$), 31.7 (*C*H$_2$), 32.3 (Ar*C*H$_2$CH($N_3$)), 34.2 (*C*H$_2$), 55.3 (O*C*H$_3$), 55.6 (O*C*H$_3$), 62.9 (*C*H($N_3$)), 98.2 (aryl *C*-H), 108.8 (aryl *C*-H), 121.0 (aryl C), 126.6 (aryl *C*-H), 129.1 (aryl *C*-H), 130.0 (aryl *C*-H), 136.2 (aryl C), 136.3 (aryl C), 159.1 (aryl C), 159.3 (aryl C); $\nu_{max}$ (thin film/$cm^{-1}$) 1048 (s), 1146 (s), 1197 (m), 1276 (w), 1460 (m), 1571 (s), 1597 (s), 2100 (s), 2856 (w), 2929 (m); MS ($ES^+$) *m/z* 400.2 (M+H); HRMS $C_{22}H_{30}O_2N_3S$ (M+H) Expected 400.2053, Found 400.2056.

### *2-Hexyl-4-(phenylsulfanyl)-2,3-dihydrobenzofuran-6-ol* ***3h***

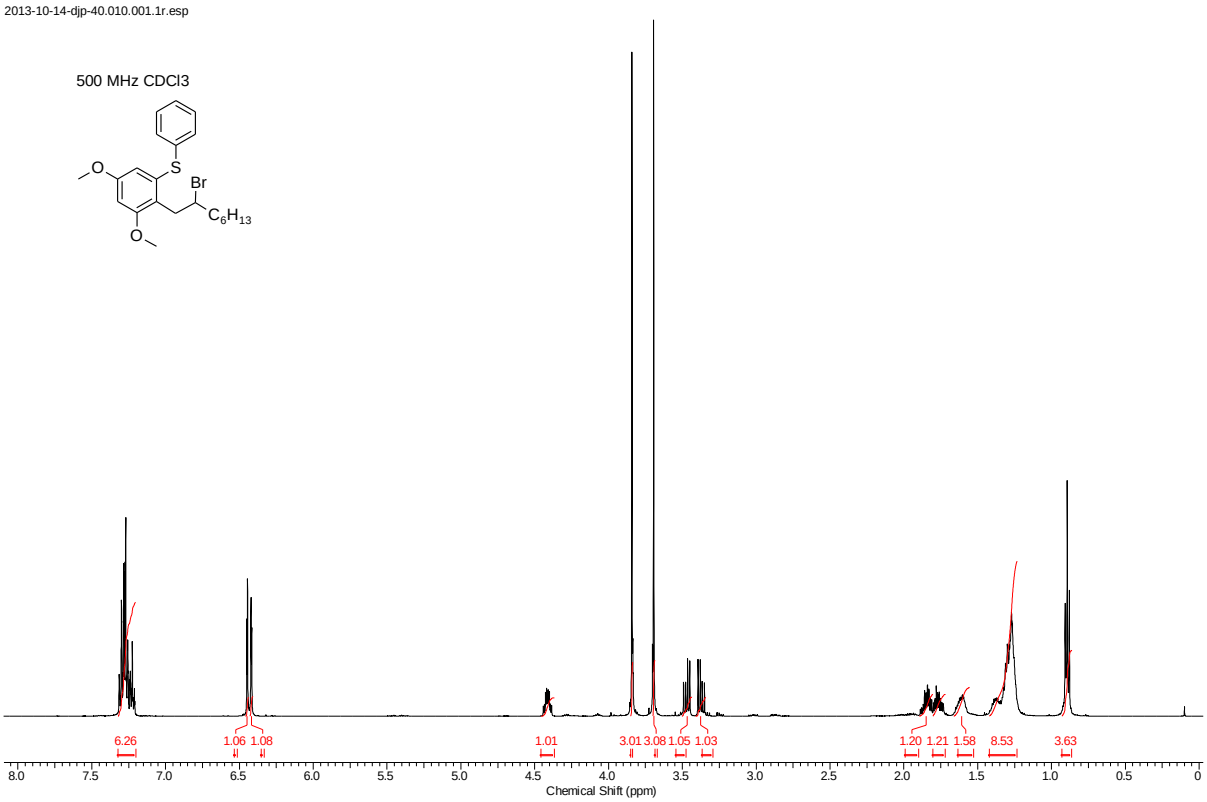


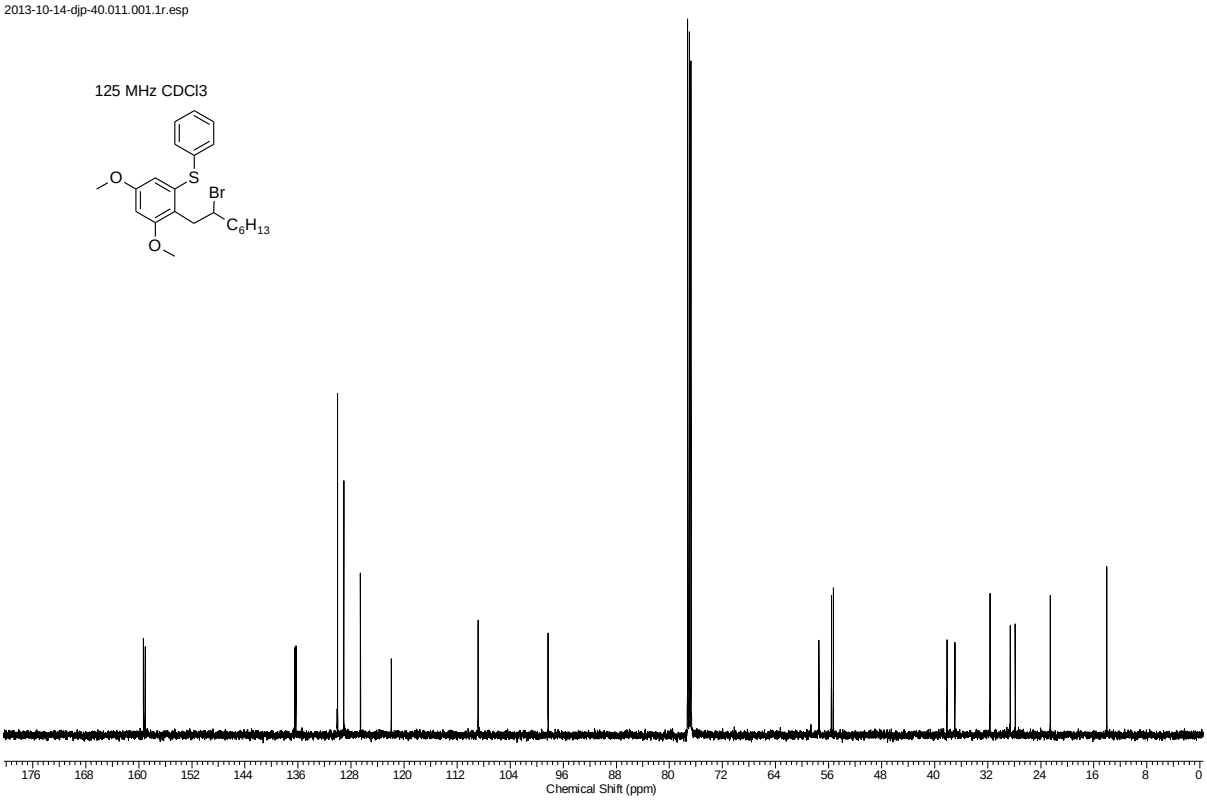

Tetrakis(triphenylphosphine)palladium(0) (25.3 mg, 0.02 mmol) was added to a solution of **2t** (85.6 mg, 0.20 mmol) in methanol (2 mL) under $N_2$. After 5 minutes of stirring, potassium carbonate (170.8 mg, 1.20 mmol) was added and the resulting mixture was stirred for 4 h. The mixture was then

concentrated *in vacuo*, before treating with 1M HCl (2 mL), extracting with $CH_2Cl_2$ (3 × 2 mL), washing with brine (3 × 2 mL), drying over $MgSO_4$ and concentrating *in vacuo*. The crude product was purified by column chromatography (20% EtOAc in hexanes) to give **3h** (33.4 mg, 53%) as a yellow oil; $\delta_H$ (500 MHz, $CDCl_3$) 0.89 (3 H, t, *J* 6.5 Hz, C*H*$_3$), 1.23 - 1.37 (7 H, m, C*H*$_2$), 1.41 - 1.49 (1 H, m, C*H*$_2$), 1.59 - 1.68 (1 H, m, C*H*$_2$), 1.74 - 1.84 (1 H, m, C*H*$_2$), 2.64 (1 H, dd, *J* 15.5, 7.6 Hz, ArC*H*$_2$CH(O)), 3.08 (1 H, dd, *J* 15.5, 8.9 Hz, ArC*H*$_2$CH(O)), 4.66 (1 H, s, O*H*) 4.74 - 4.83 (1 H, m, C*H*(O)), 6.14 (1 H, s, aryl H), 6.19 (1 H, s, aryl H), 7.24 - 7.38 (5 H, m, aryl H); $\delta_C$ (125 MHz, $CDCl_3$) 14.1 (*C*H$_3$), 22.6 (*C*H$_2$), 25.2 (*C*H$_2$), 29.1 (*C*H$_2$), 31.7 (*C*H$_2$), 34.3 (Ar*C*H$_2$CH(O)), 36.1 (*C*H$_2$), 84.6 (CH$_2$*C*H(O)), 96.4 (aryl *C*-H), 108.5 (aryl *C*-H), 120.4 (aryl C), 127.2 (aryl *C*-H), 129.2 (aryl *C*-H), 131.2 (aryl *C*-H), 132.3 (aryl C) 133.9 (aryl C) 156.2 (aryl C) 161.0 (aryl C); $\nu_{max}$ (thin film/cm$^{-1}$) 994 (w), 1025 (s), 1113 (w), 1174 (w), 1262 (s), 1377 (s), 1439 (w), 1478 (w), 1585 (s), 1609 (s), 2853 (w), 2923 (w), 3367 (w, br); MS (ES$^-$) *m/z* 327 (M−H); HRMS $C_{20}H_{23}O_2S$ (M−H) Expected 327.1419 Found 327.1419.

# Spectra

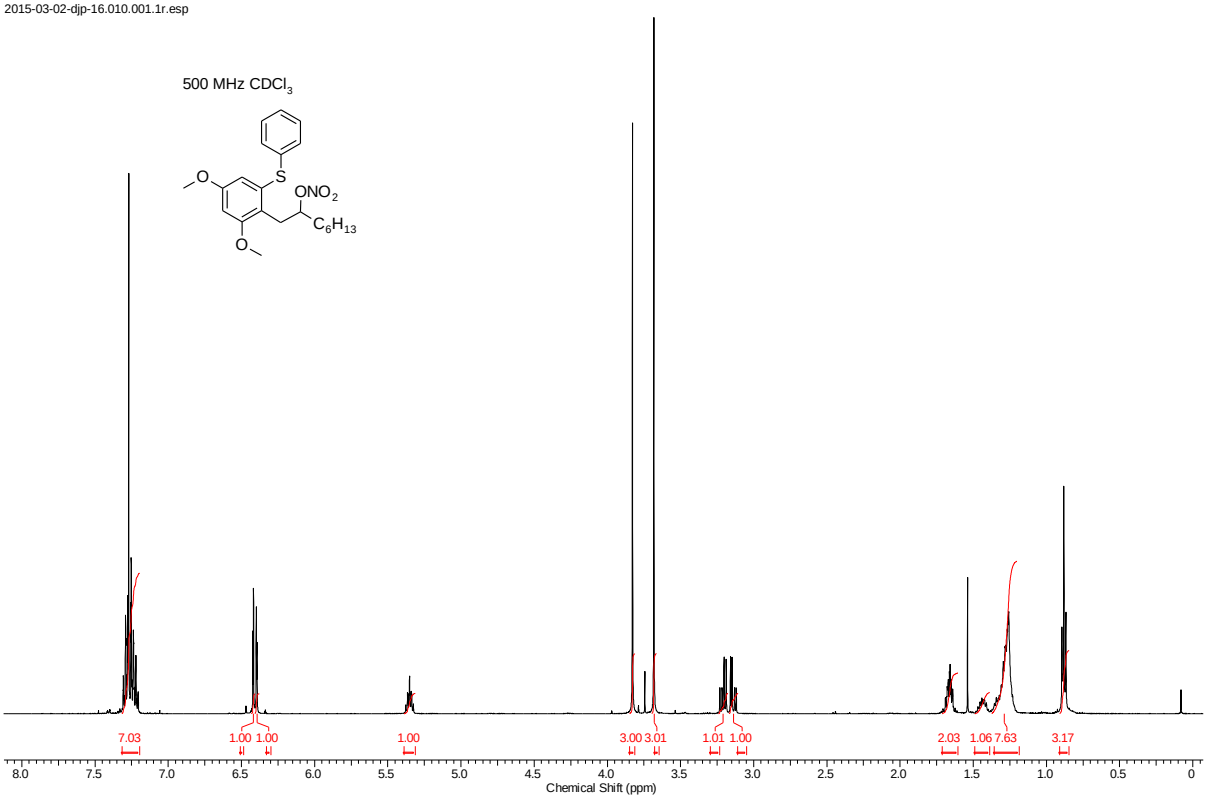
*(2-(2-Bromooctyl)-3,5-dimethoxyphenyl)(phenyl)sulfide*



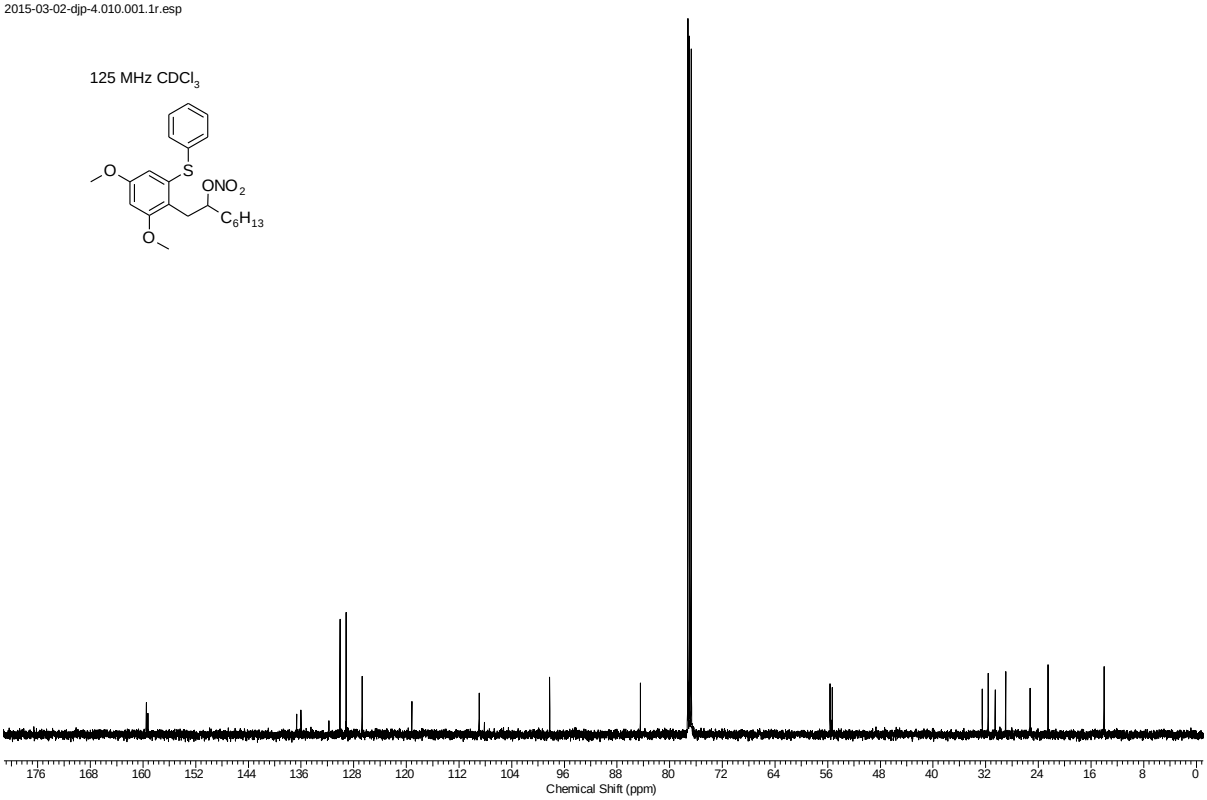



*1-(2,4-Dimethoxy-6-(phenylsulfanyl)phenyl)octan-2-yl nitrate*

2015-03-02-djp-16.010.001.1r.esp

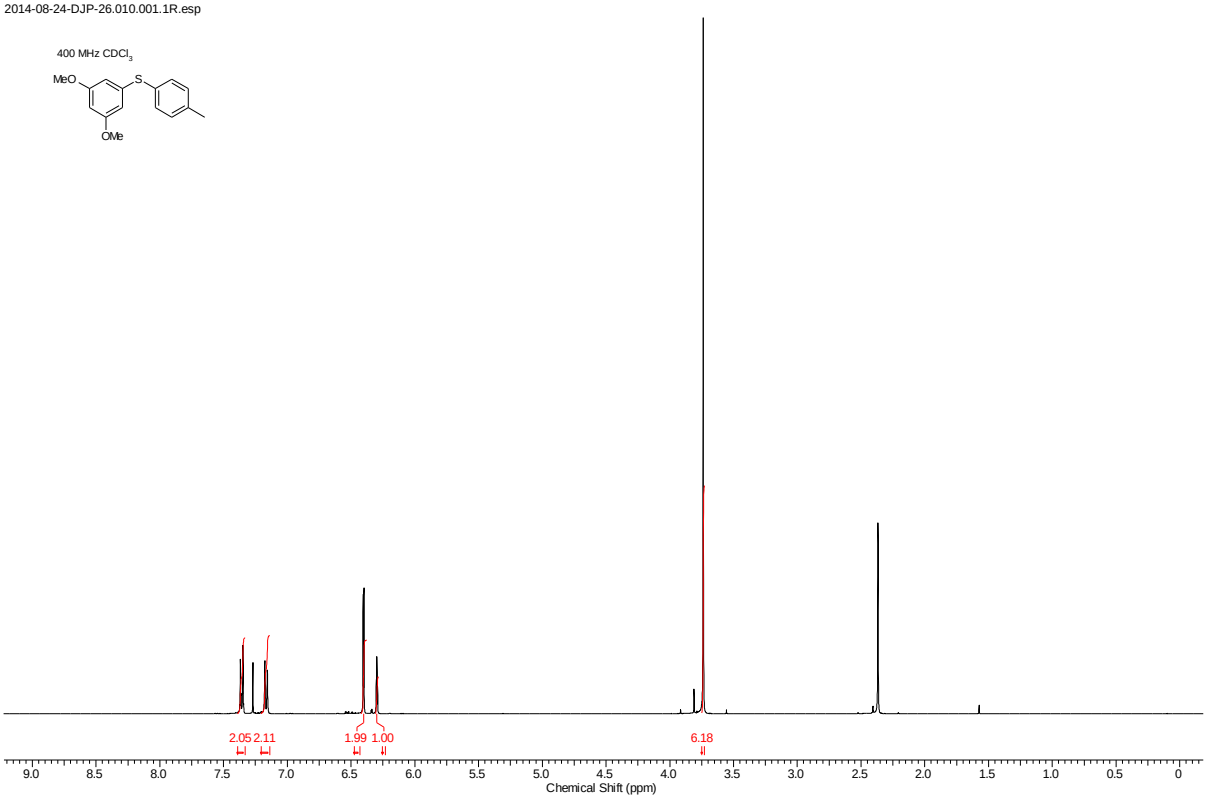



2015-03-02-djp-4.010.001.1r.esp

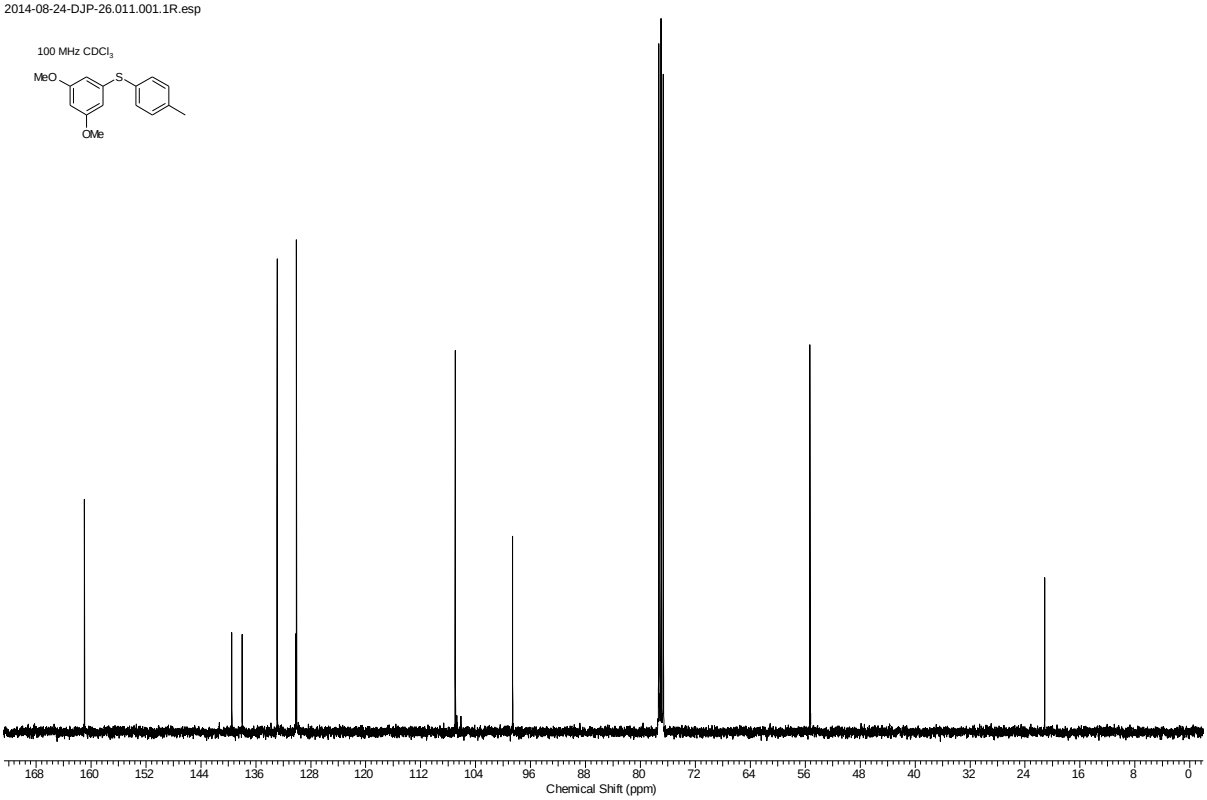


## *(3,5-Dimethoxyphenyl)(p-tolyl)sulfide* ***1b***

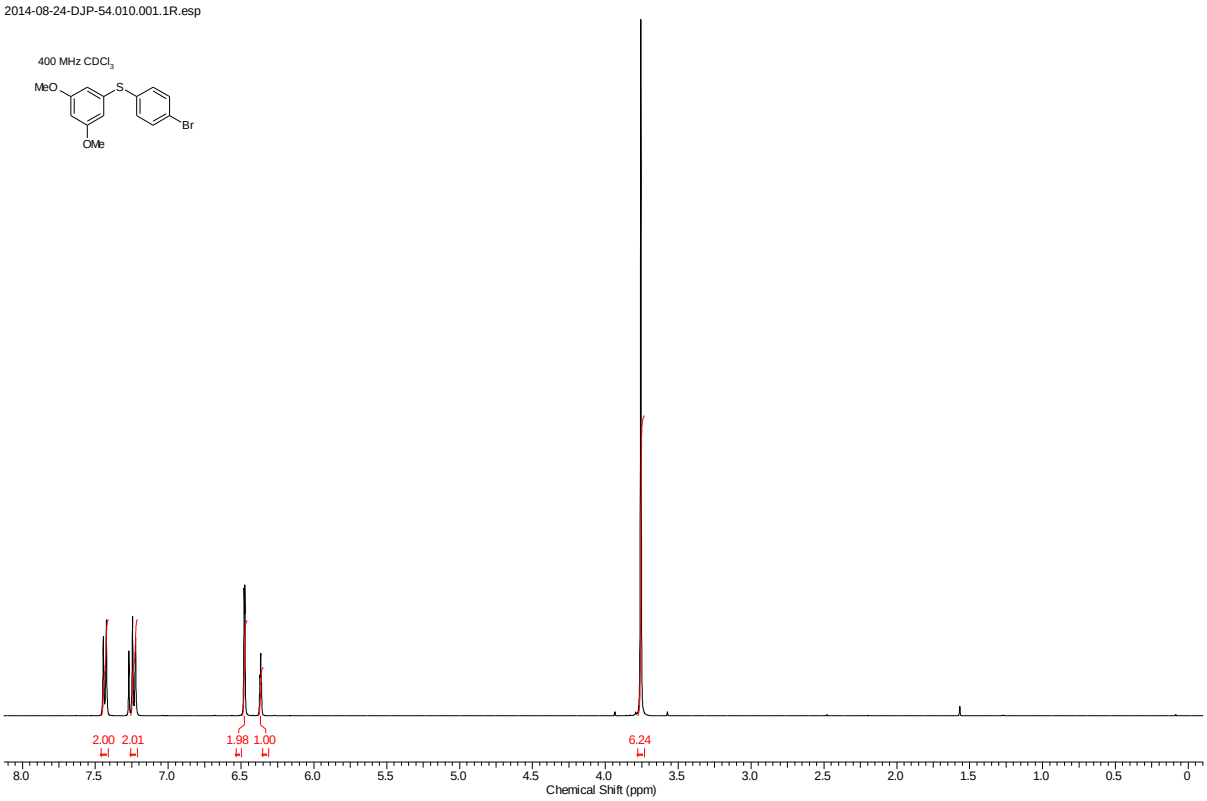
2014-08-24-DJP-26.010.001.1R.esp

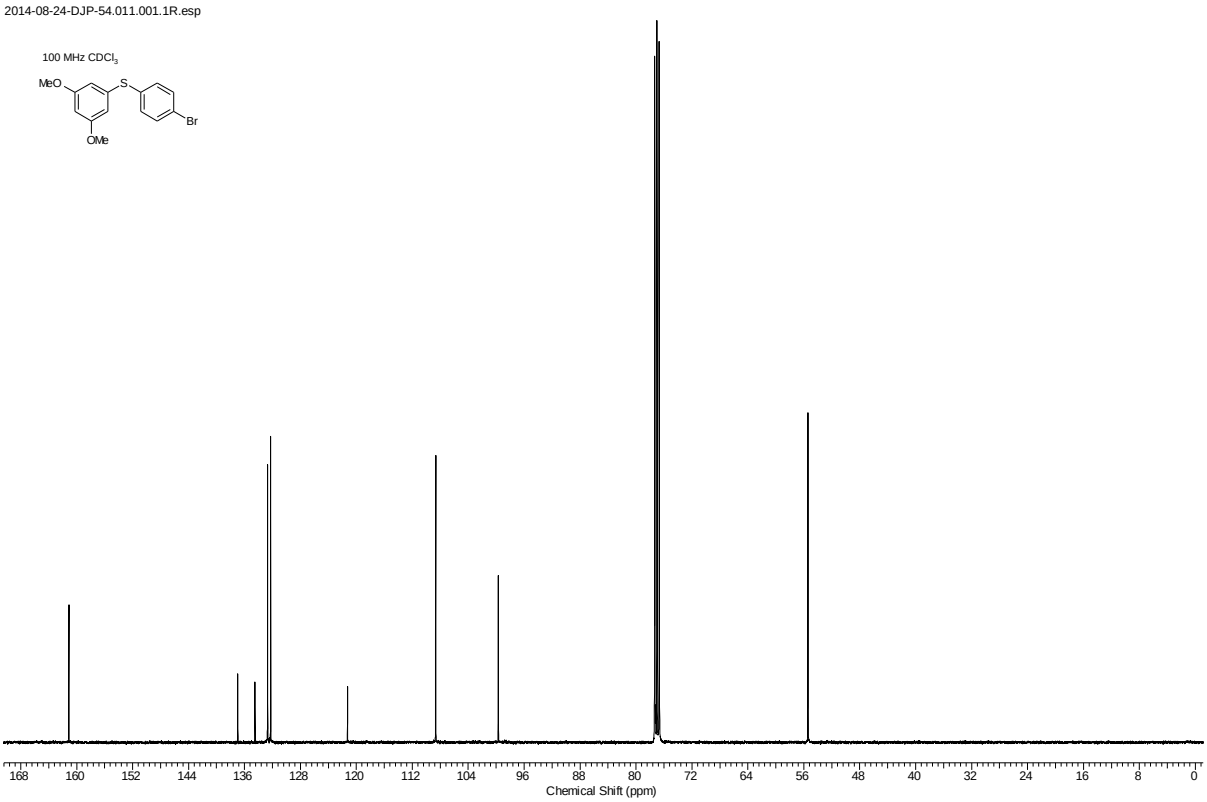



2014-08-24-DJP-26.011.001.1R.esp

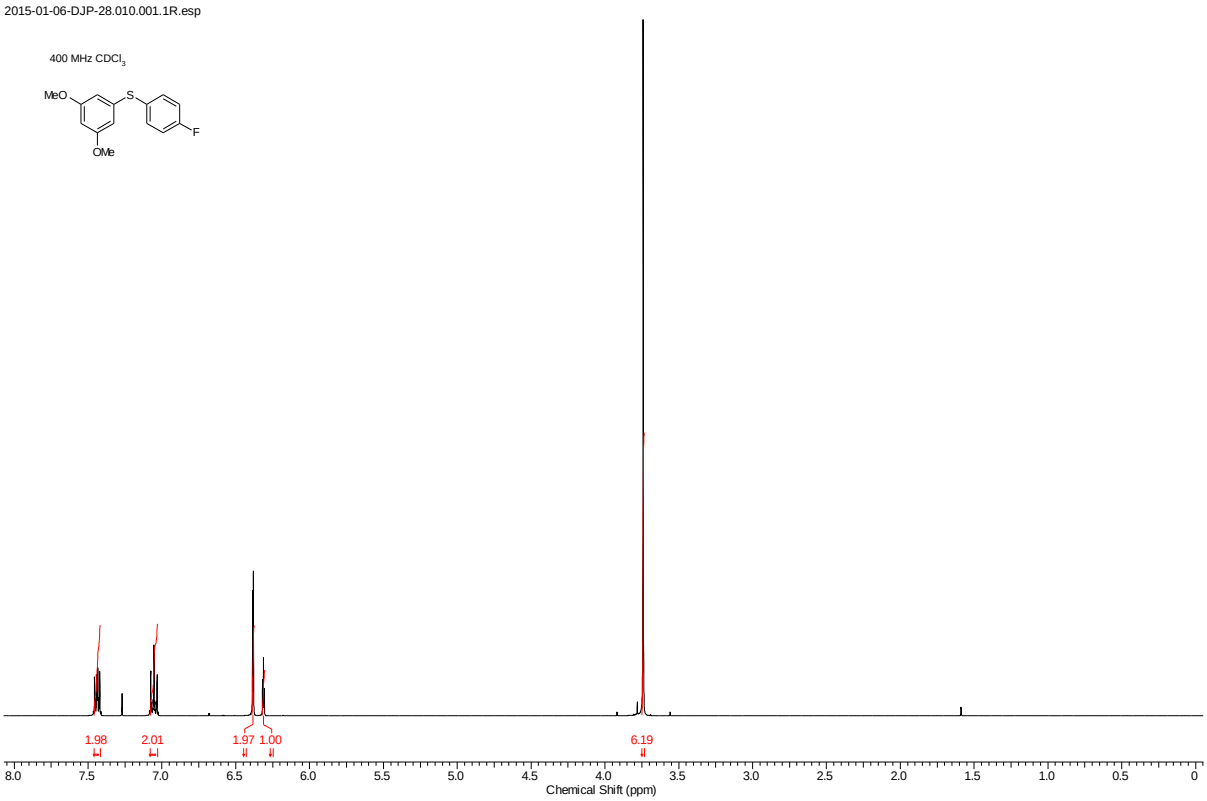


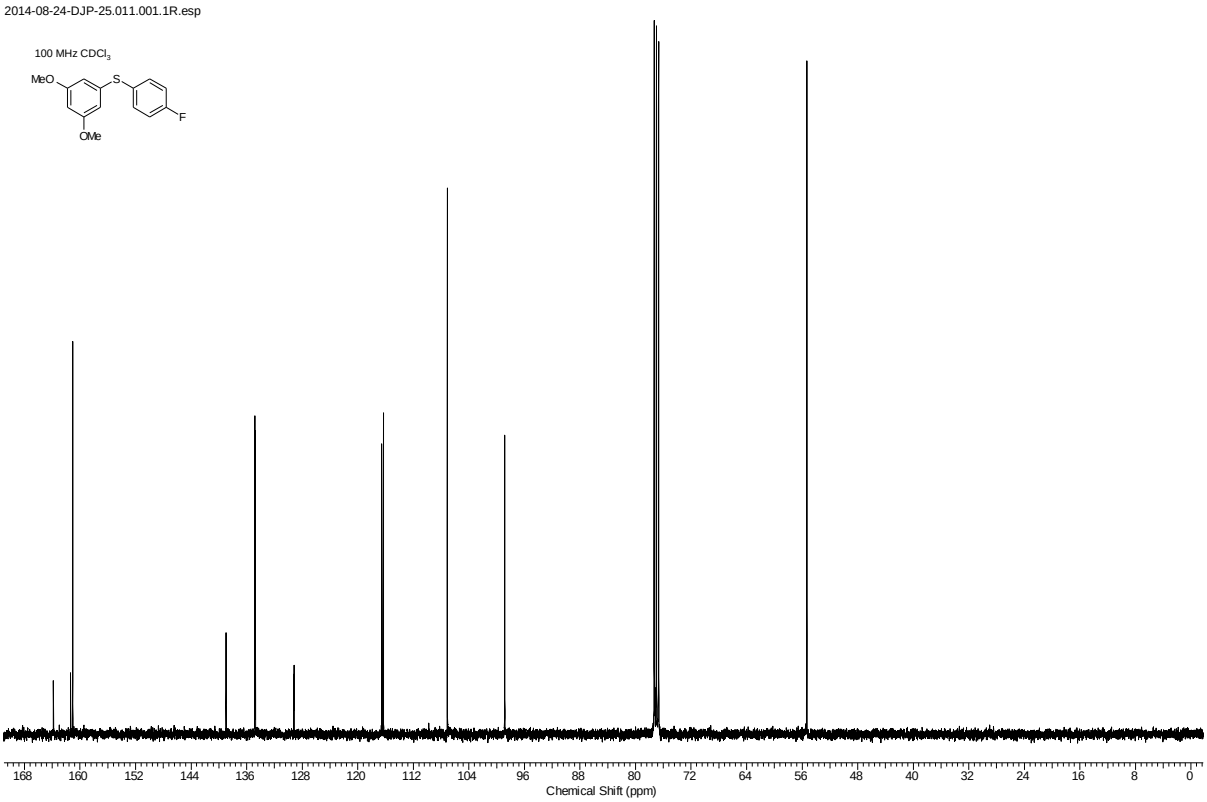
## *(4-Bromophenyl)(3,5-dimethoxyphenyl)sulfide* ***1c***



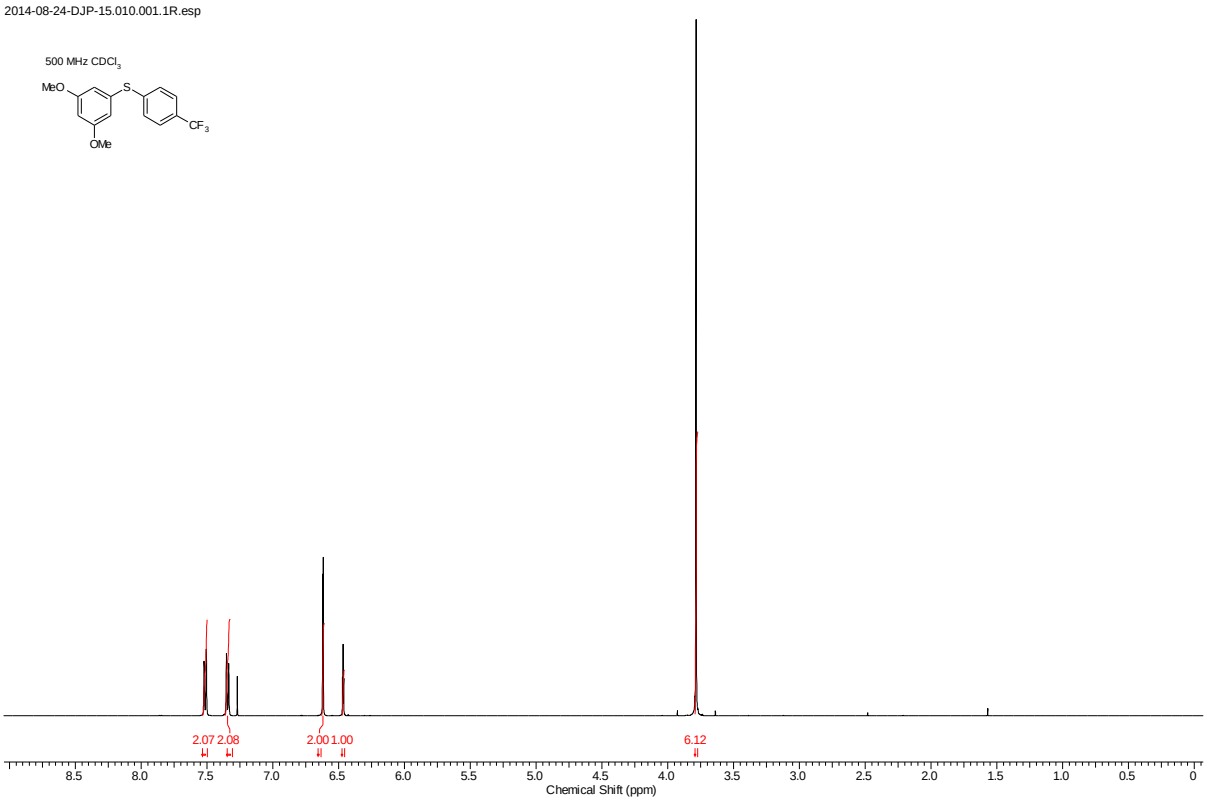



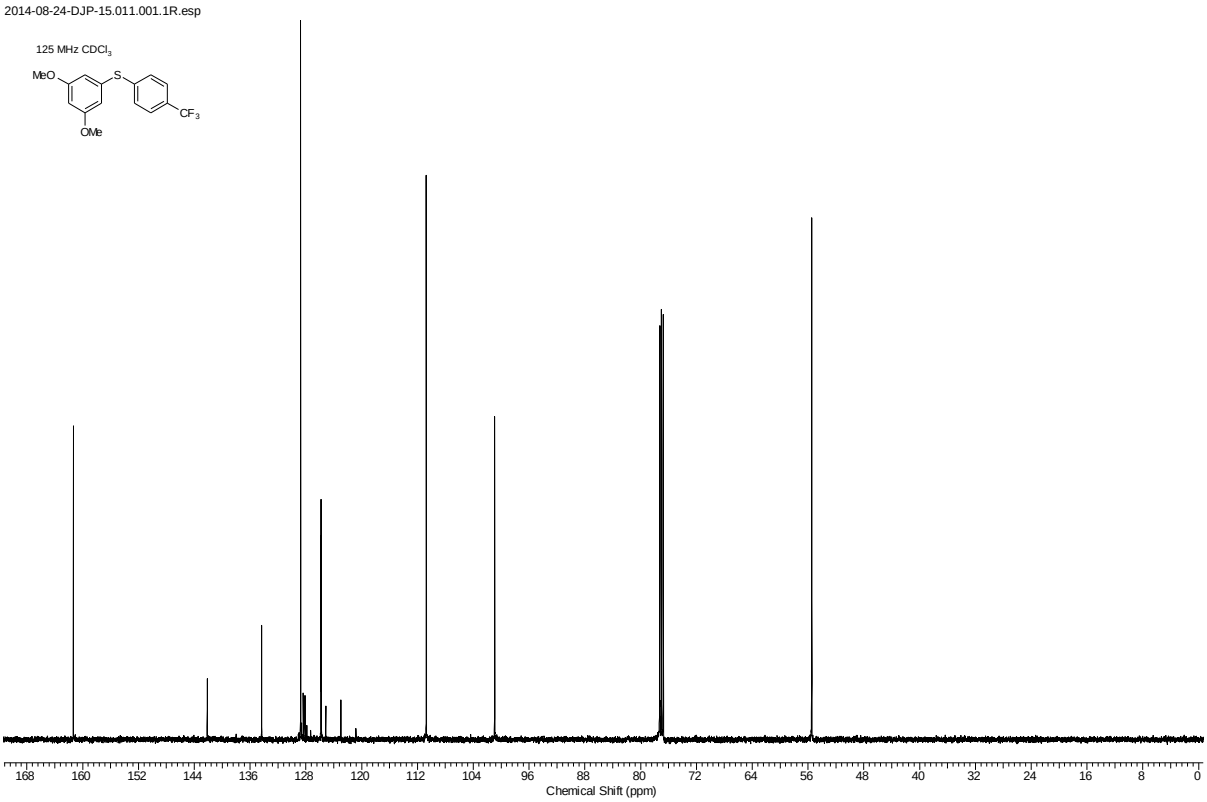
## *(3,5-Dimethoxyphenyl)(4-fluorophenyl)sulfide* ***1d***



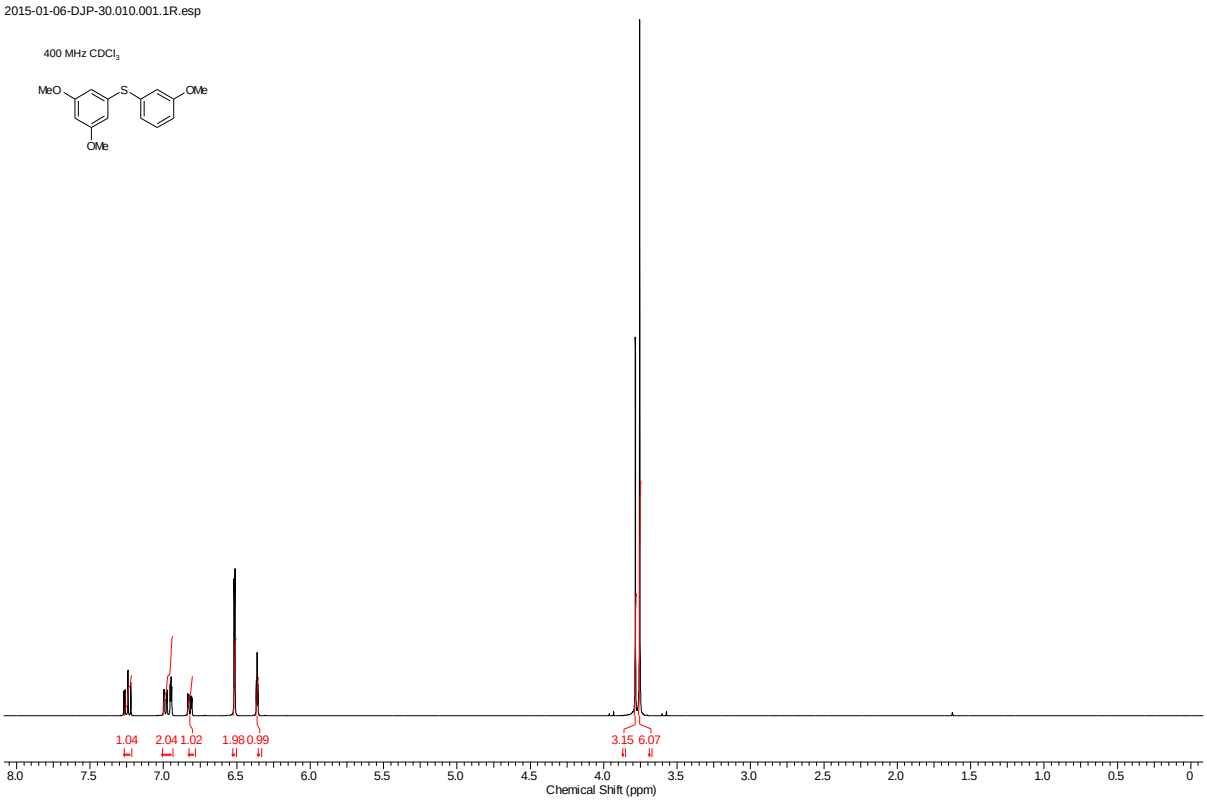



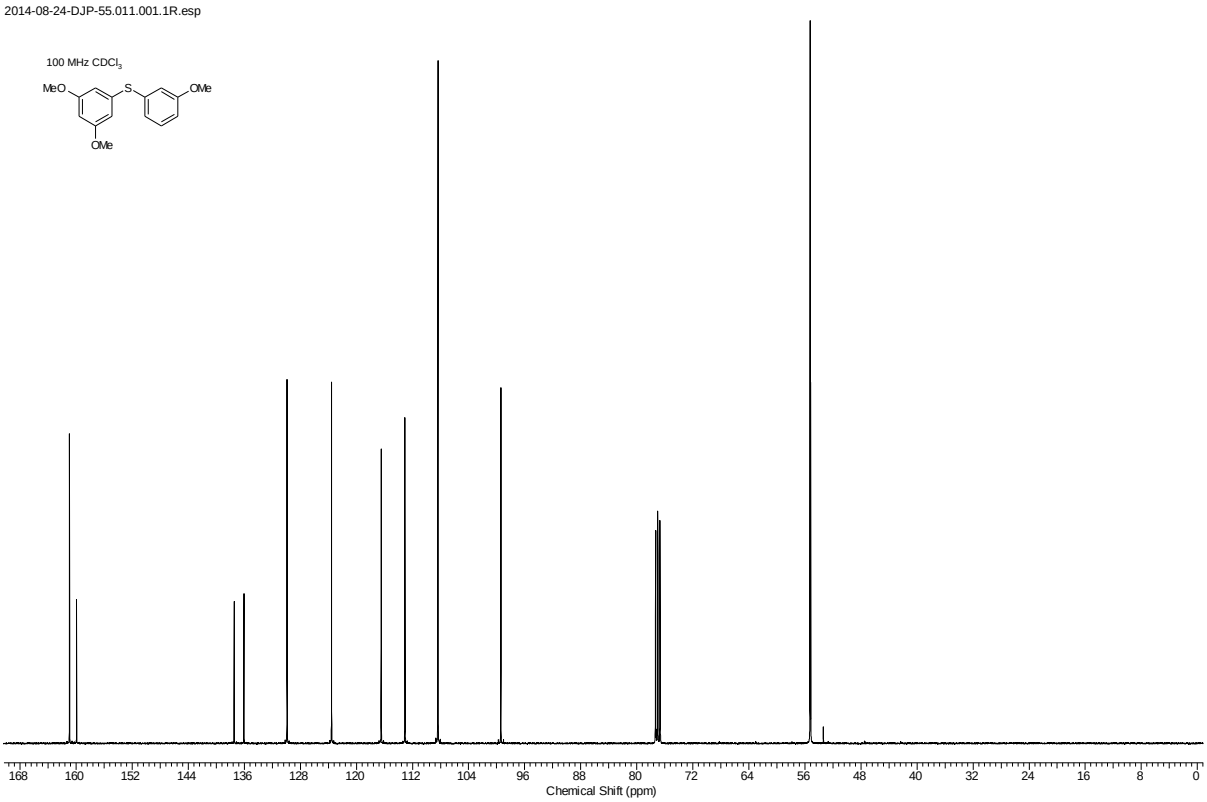
## *(3,5-Dimethoxyphenyl)(4-(trifluoromethyl)phenyl)sulfide* ***1f***



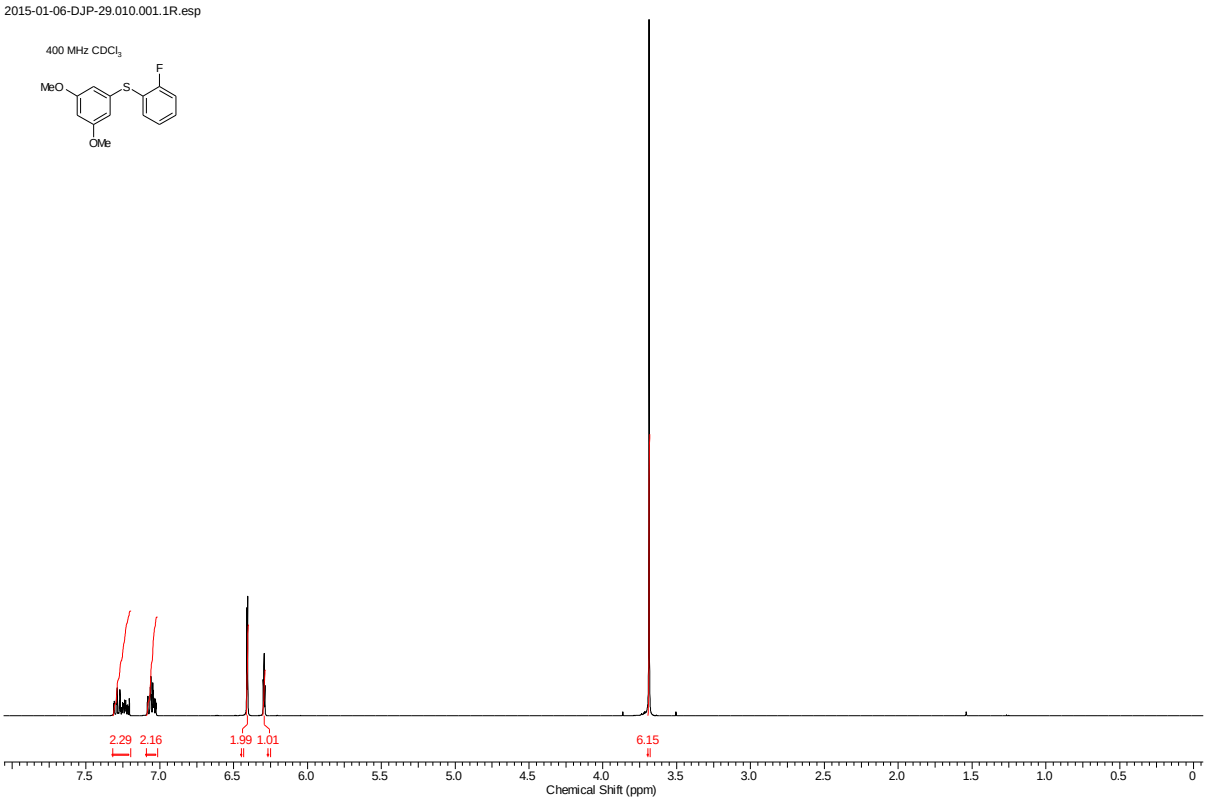



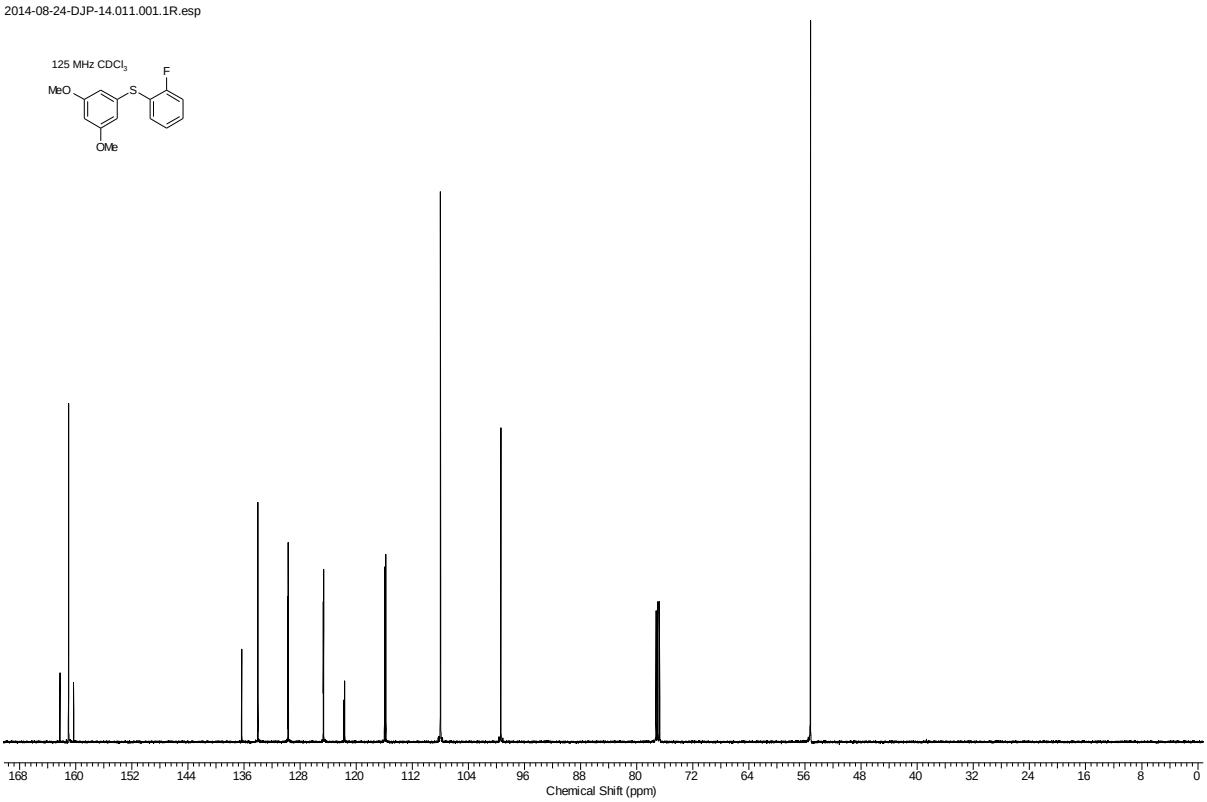
## *(3,5-Dimethoxyphenyl)(3-methoxyphenyl)sulfide* ***1g***



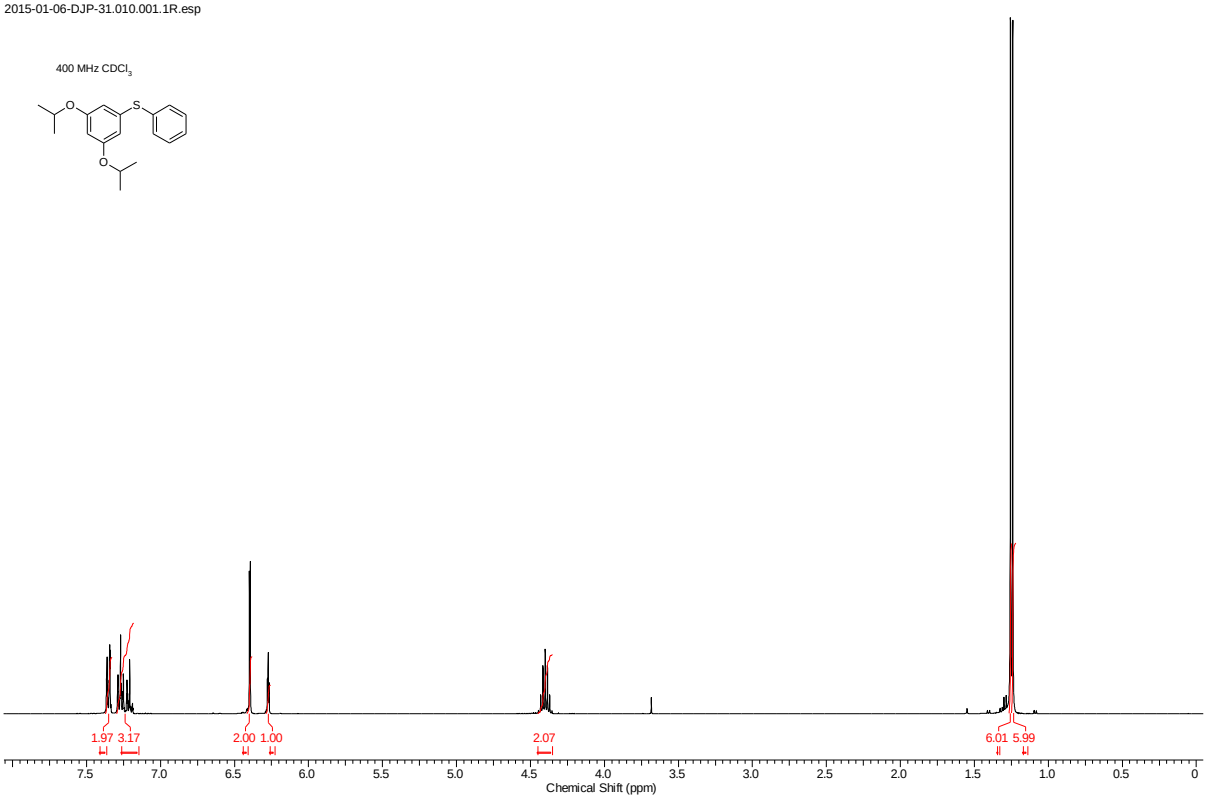
## *(3,5-Dimethoxyphenyl)(2-fluorophenyl)sulfide* ***1i***



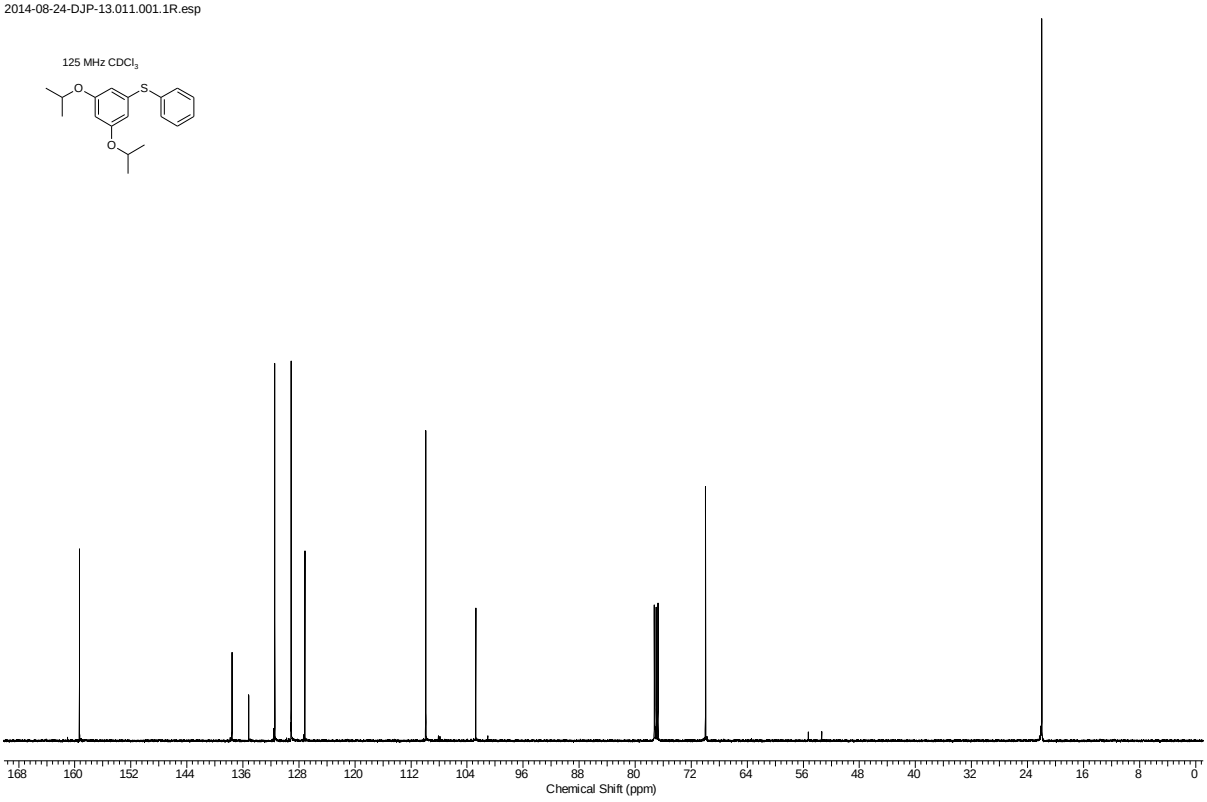



## *(3,5-Diisopropoxyphenyl)(phenyl)sulfide* ***1j***

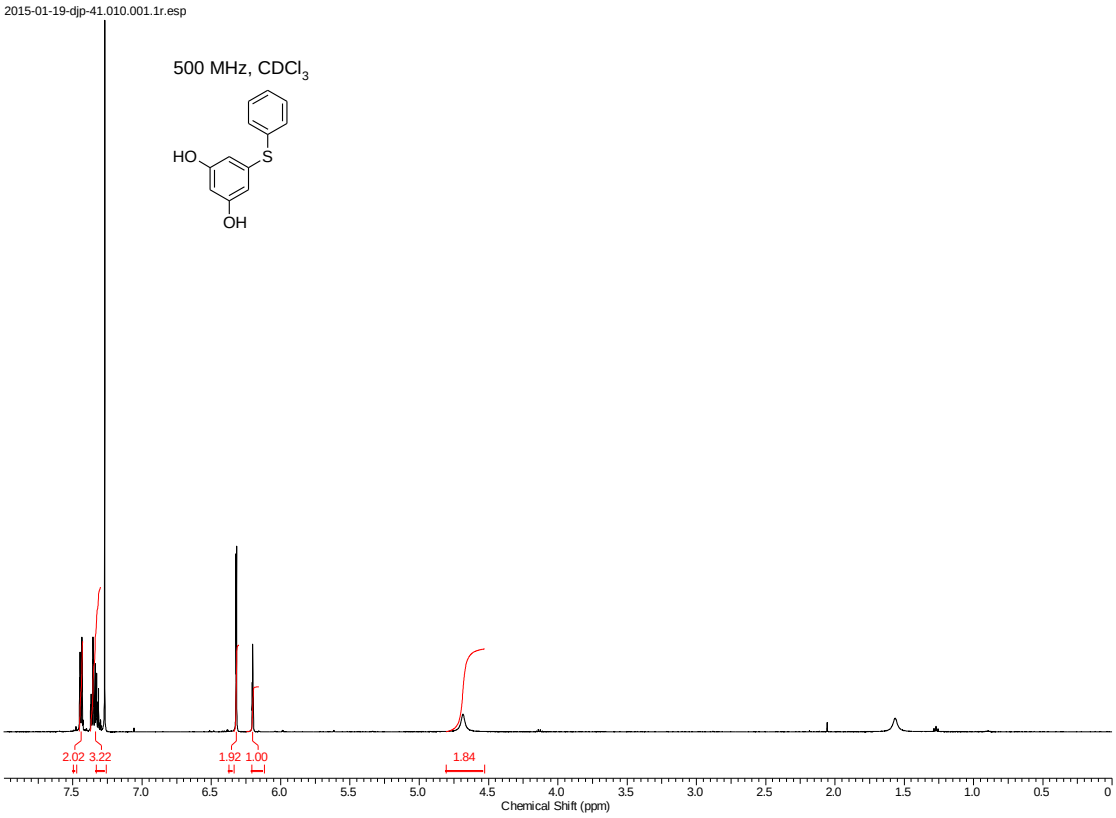
2015-01-06-DJP-31.010.001.1R.esp

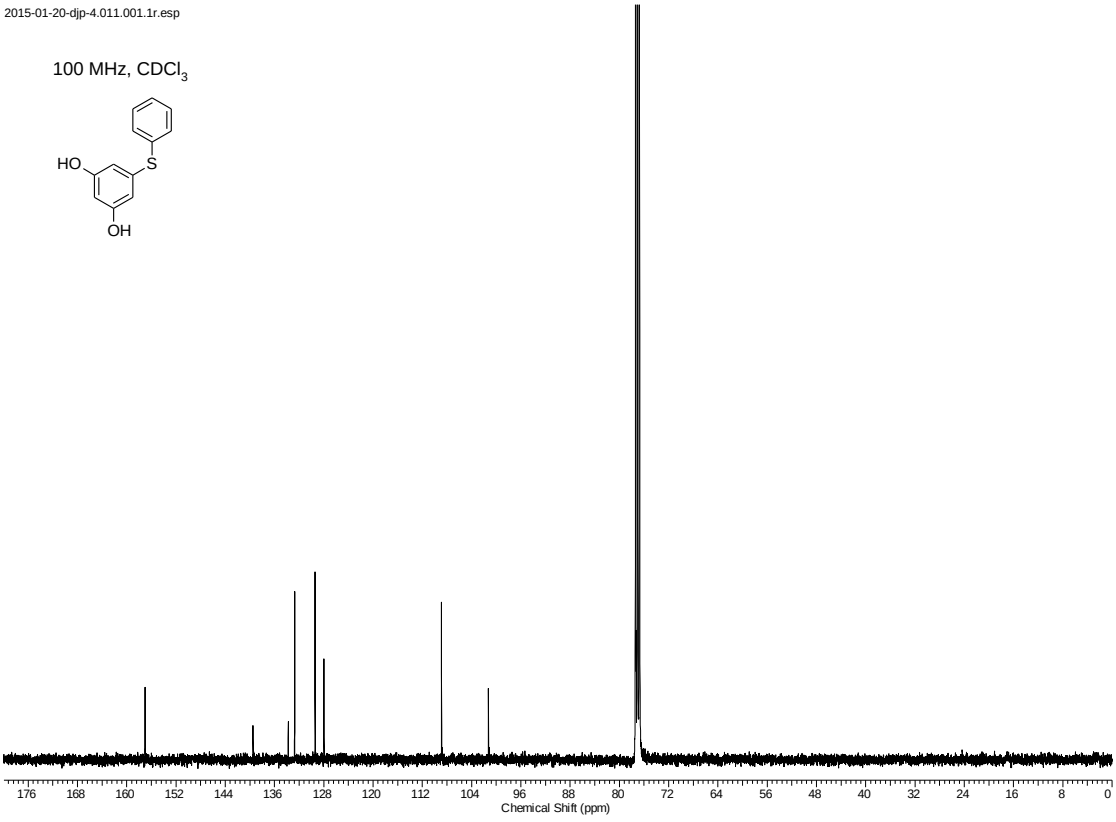



2014-08-24-DJP-13.011.001.1R.esp

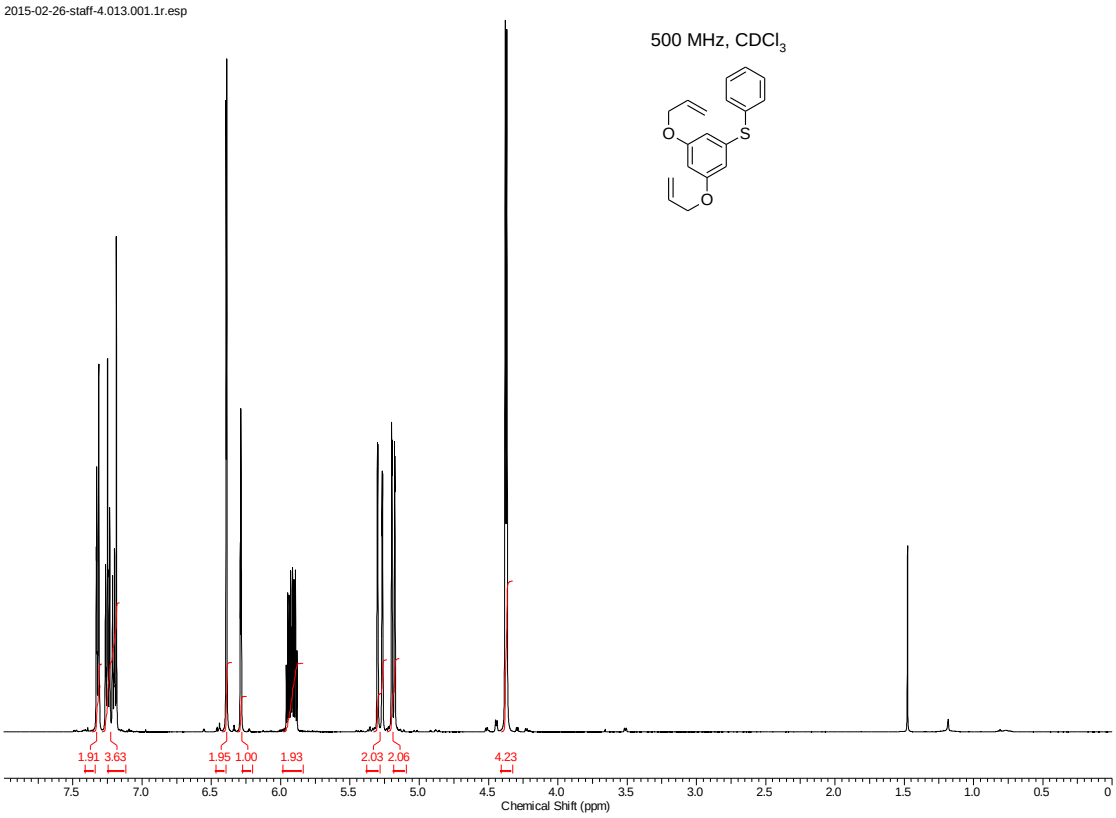


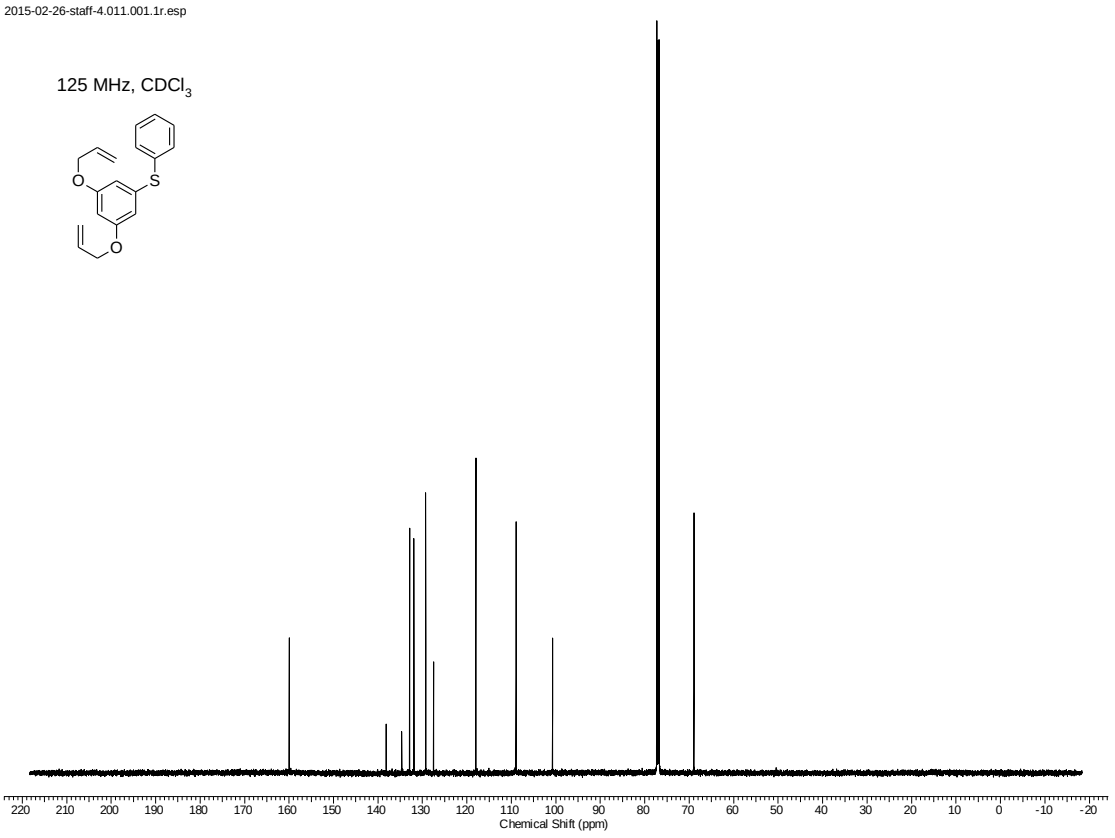
## *5-(Phenylsulfanyl)benzene-1,3-diol*



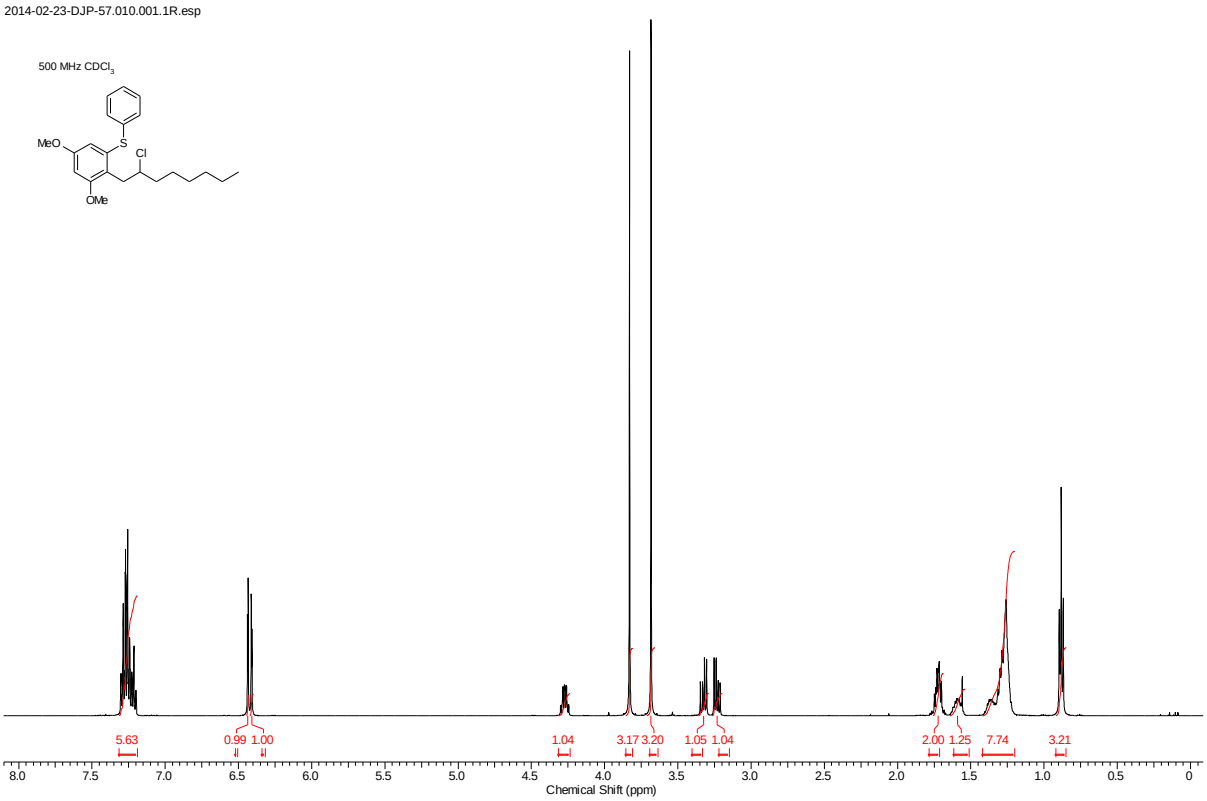



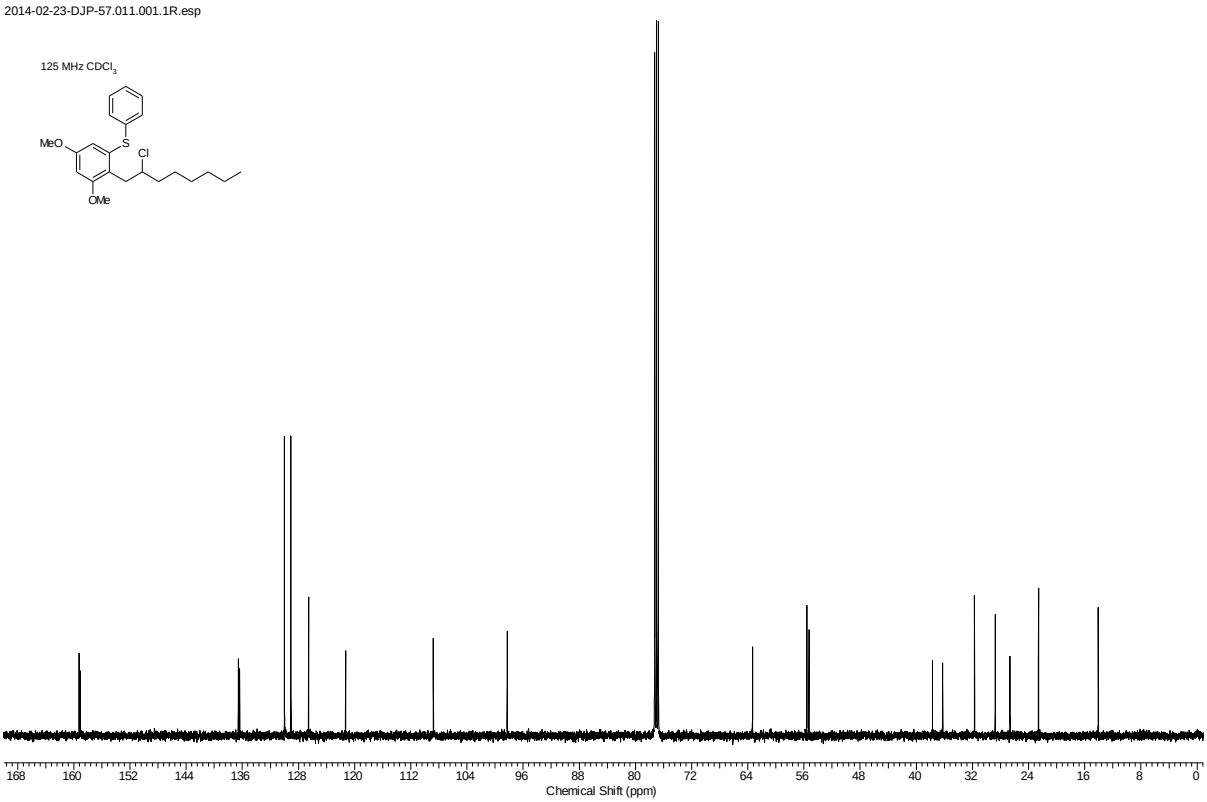
## *(3,5-bis(Allyloxy)phenyl)(phenyl)sulfide* ***1k***



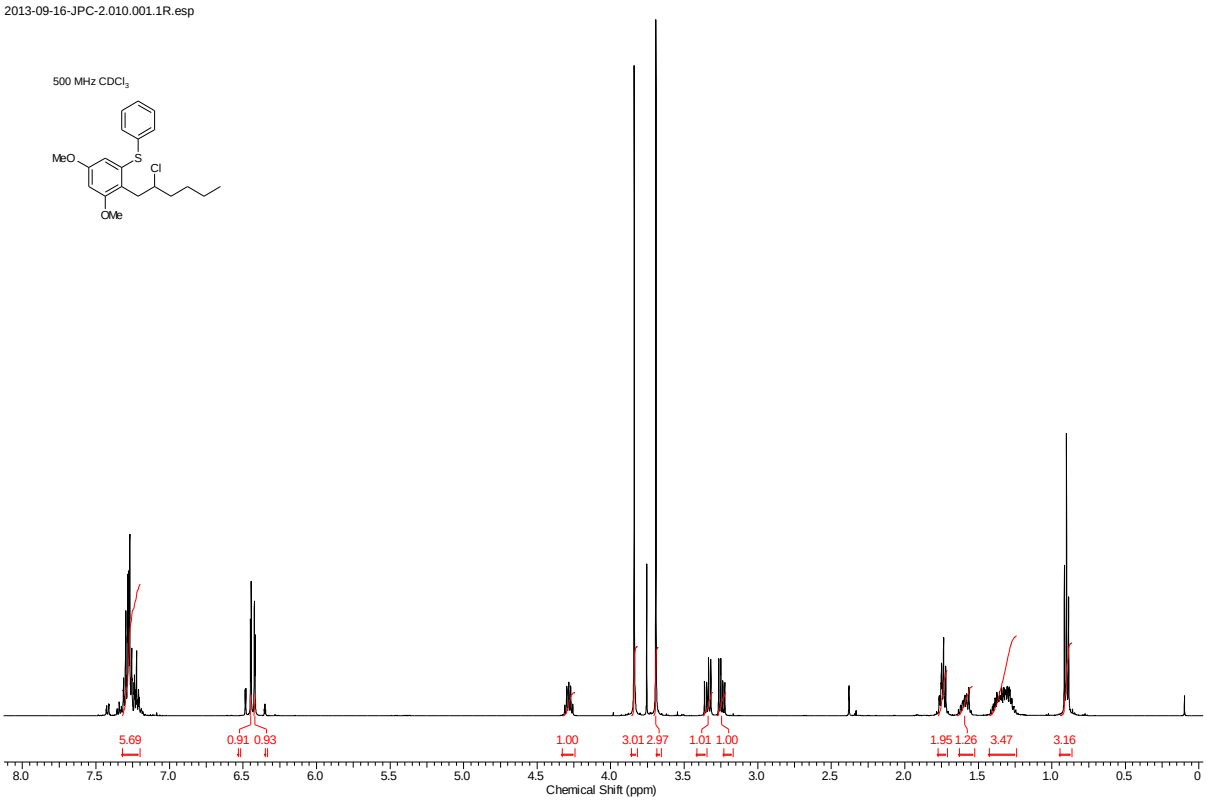



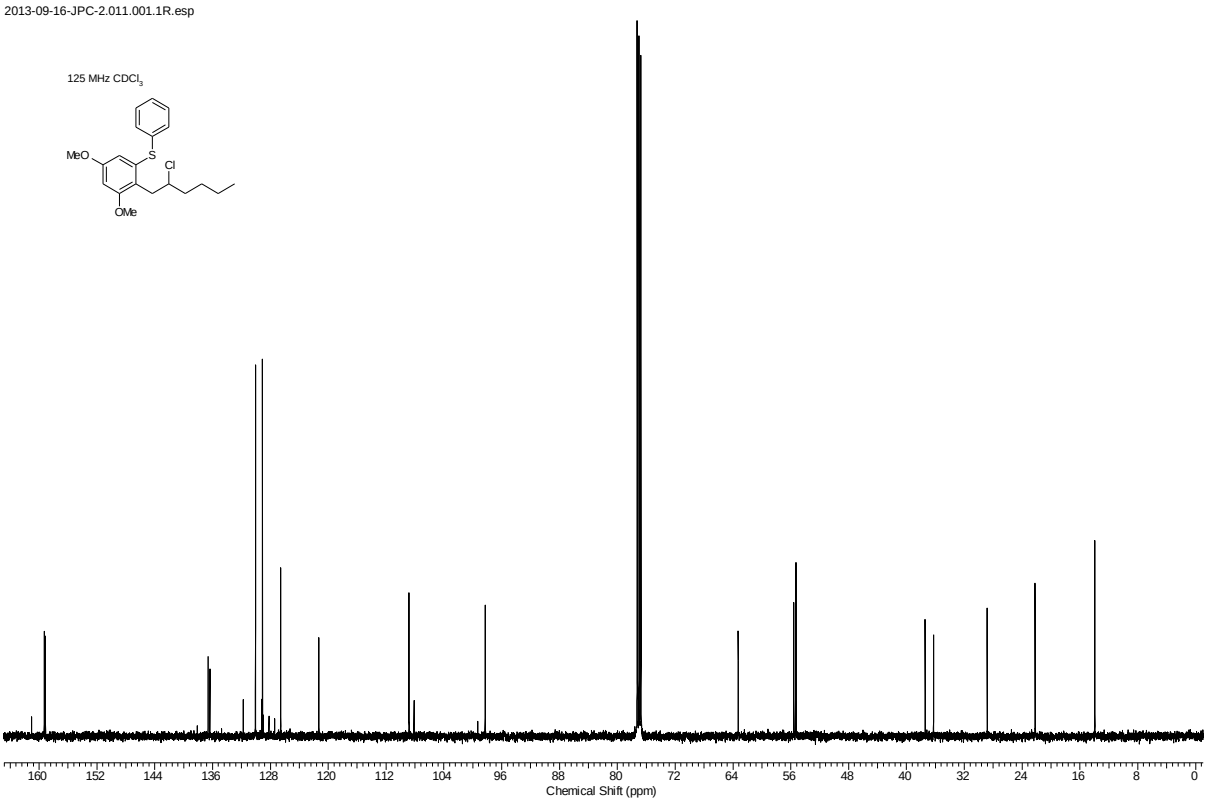
*(2-(2-Chlorooctyl)-3,5-dimethoxyphenyl)(phenyl)sulfide* ***2a***



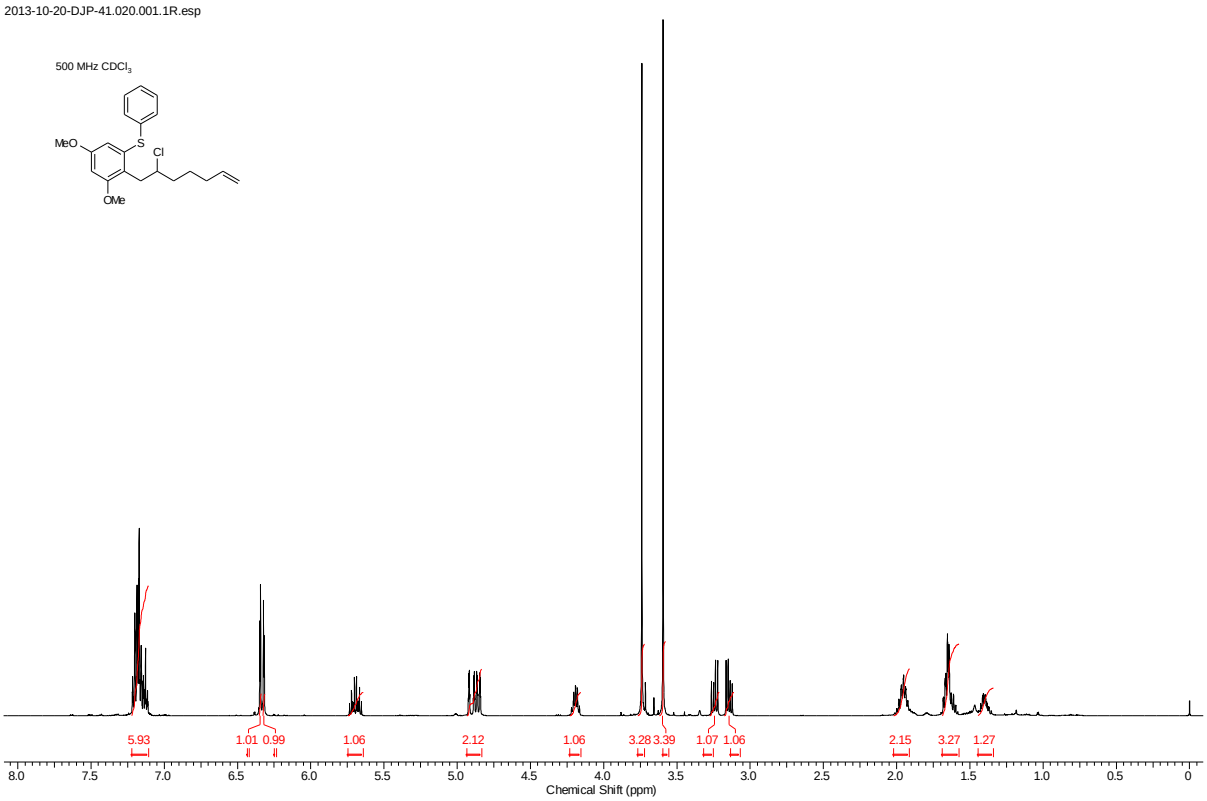



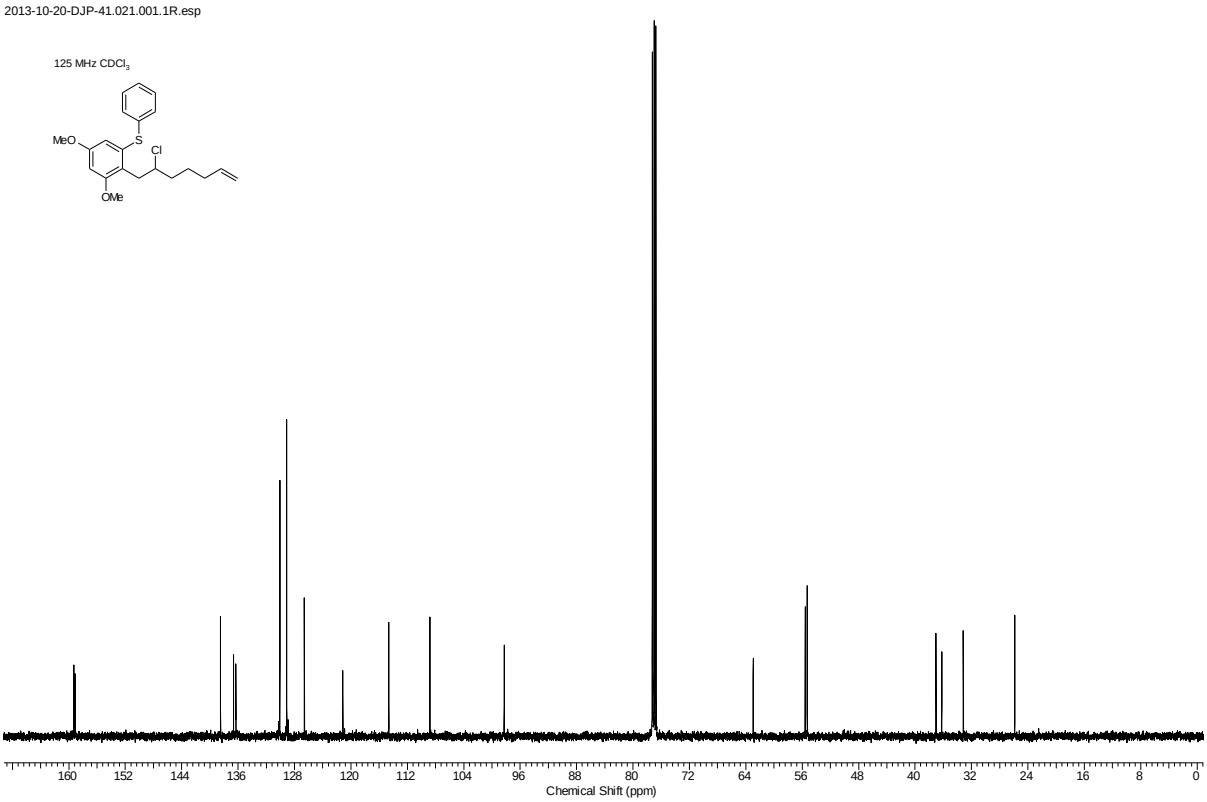
*(2-(2-Chlorohexyl)-3,5-dimethoxyphenyl)(phenyl)sulfide* ***2b***



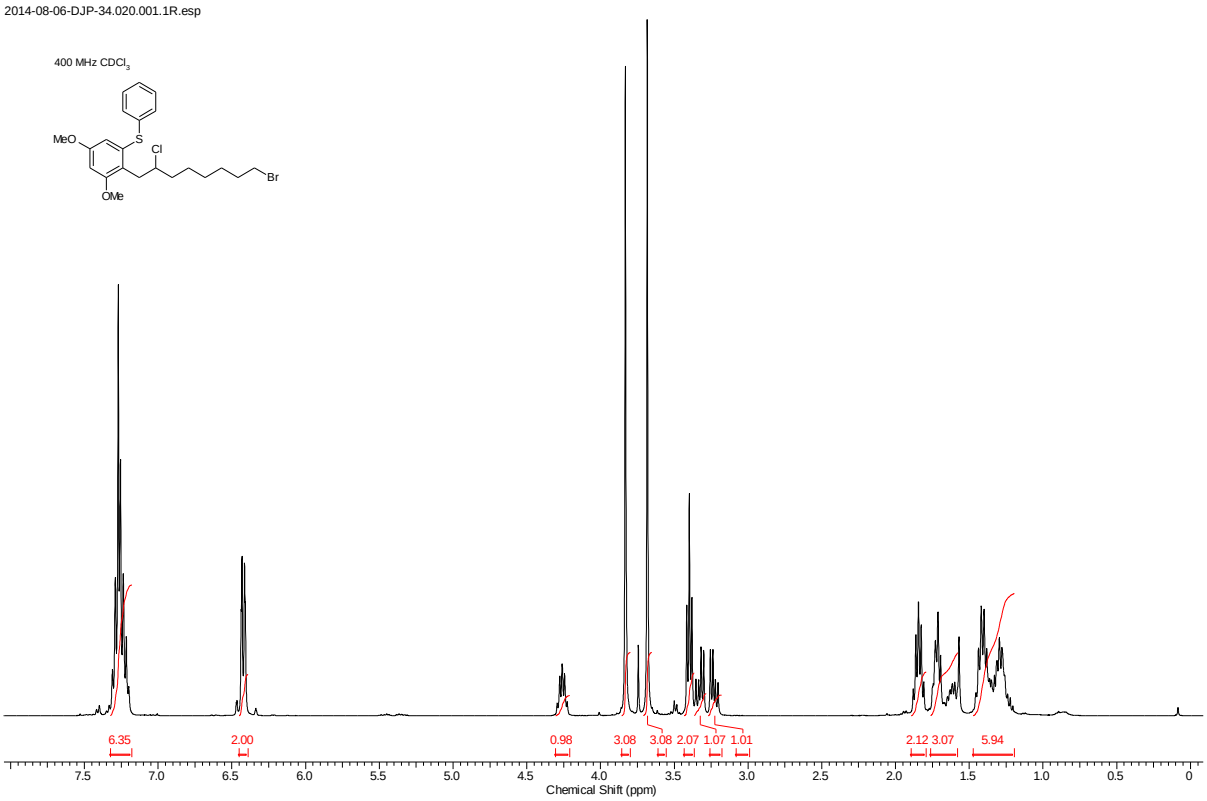



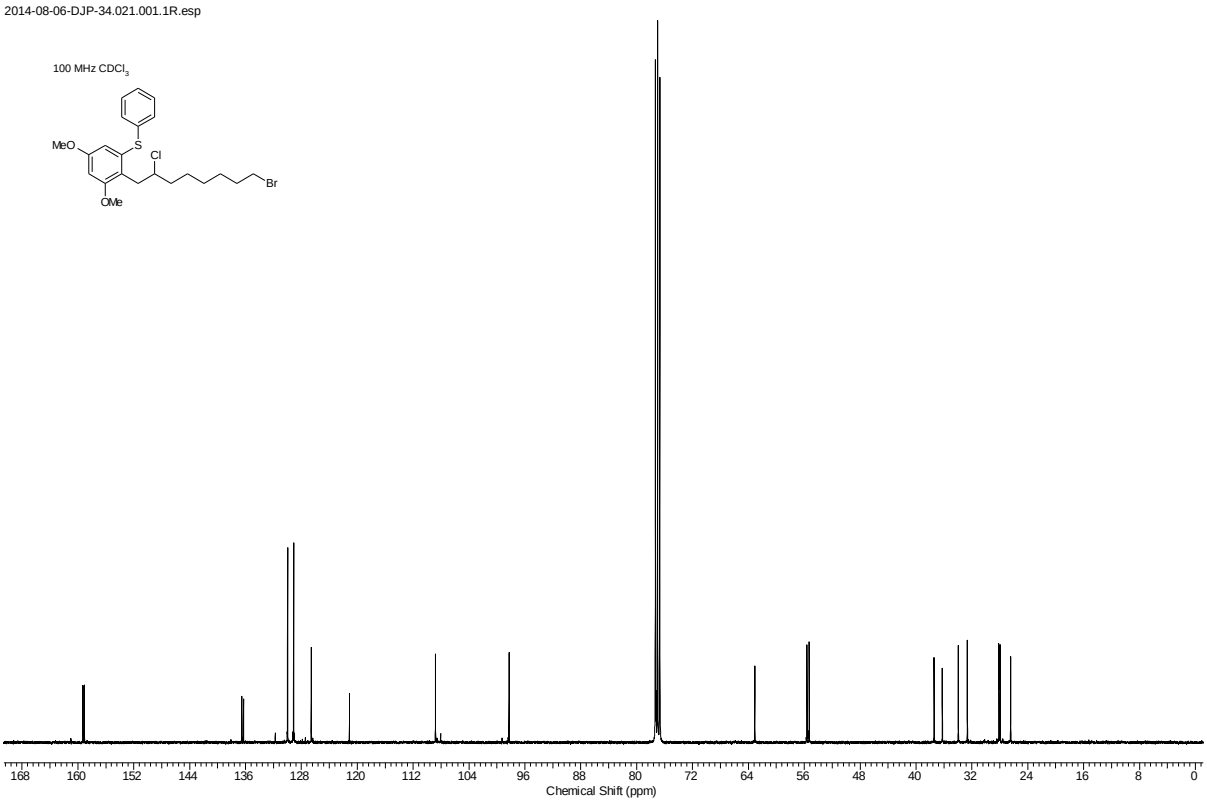
*(2-(2-Chlorohept-6-en-1-yl)-3,5-dimethoxyphenyl)(phenyl)sulfide* ***2c***



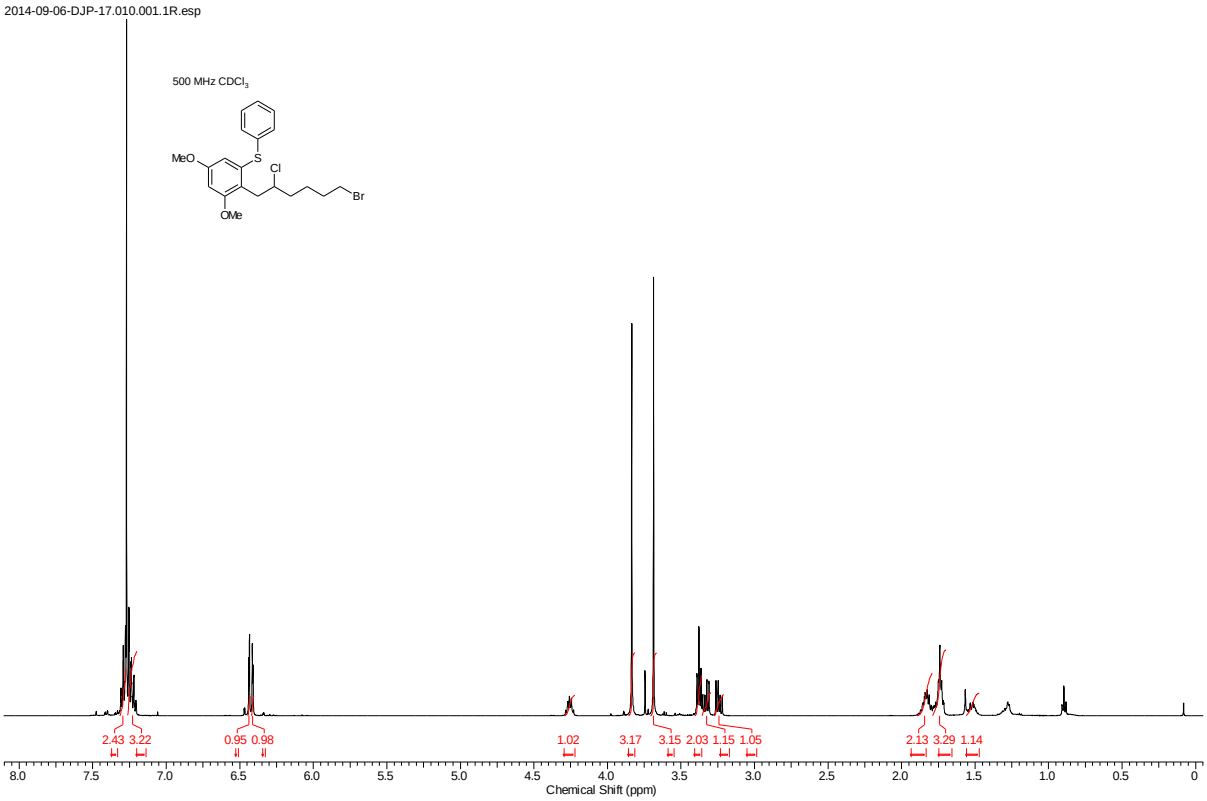



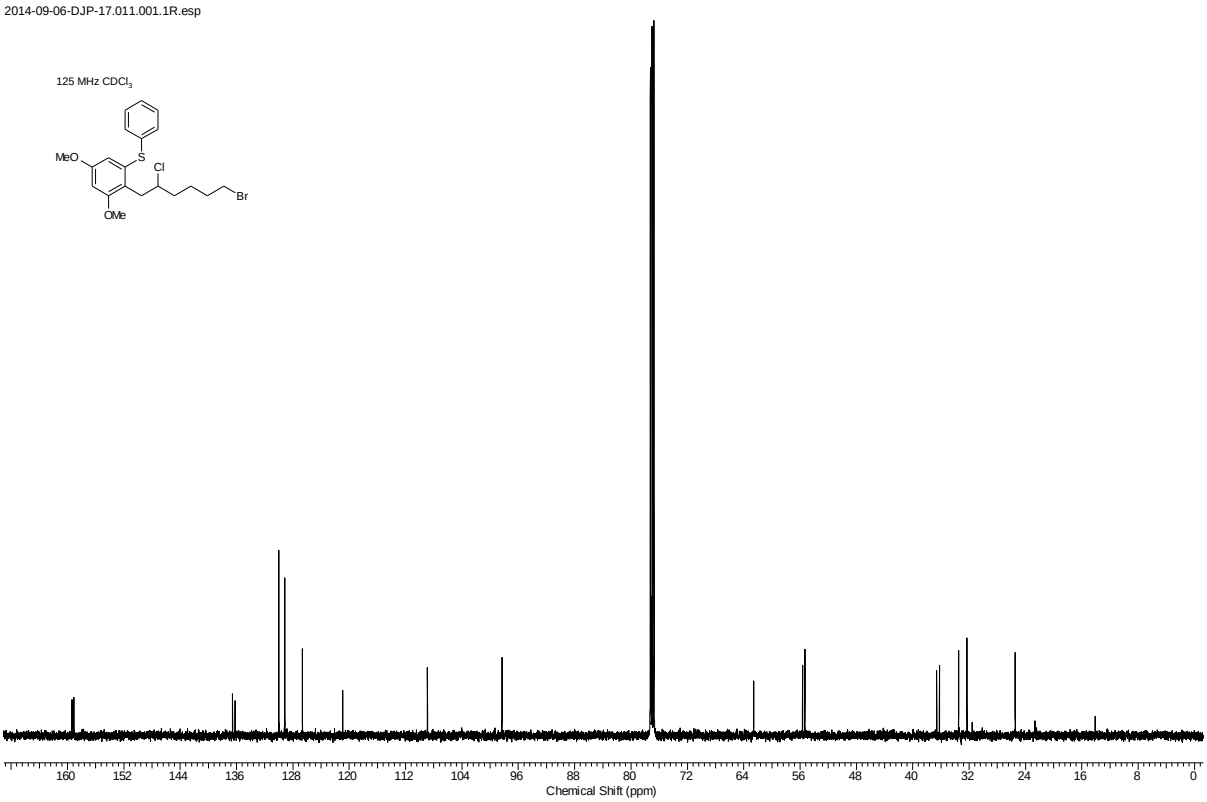
*(2-(8-Bromo-2-chlorooctyl)-3,5-dimethoxyphenyl)(phenyl)sulfide* ***2d***



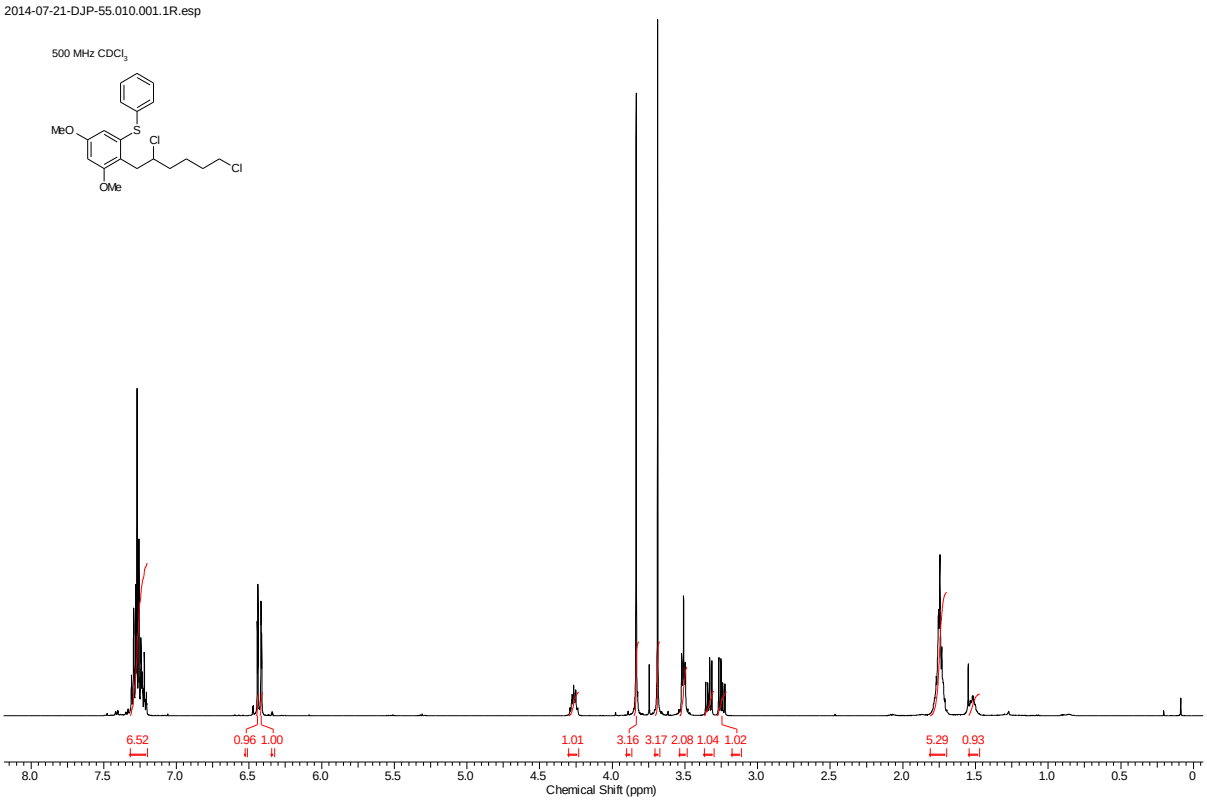



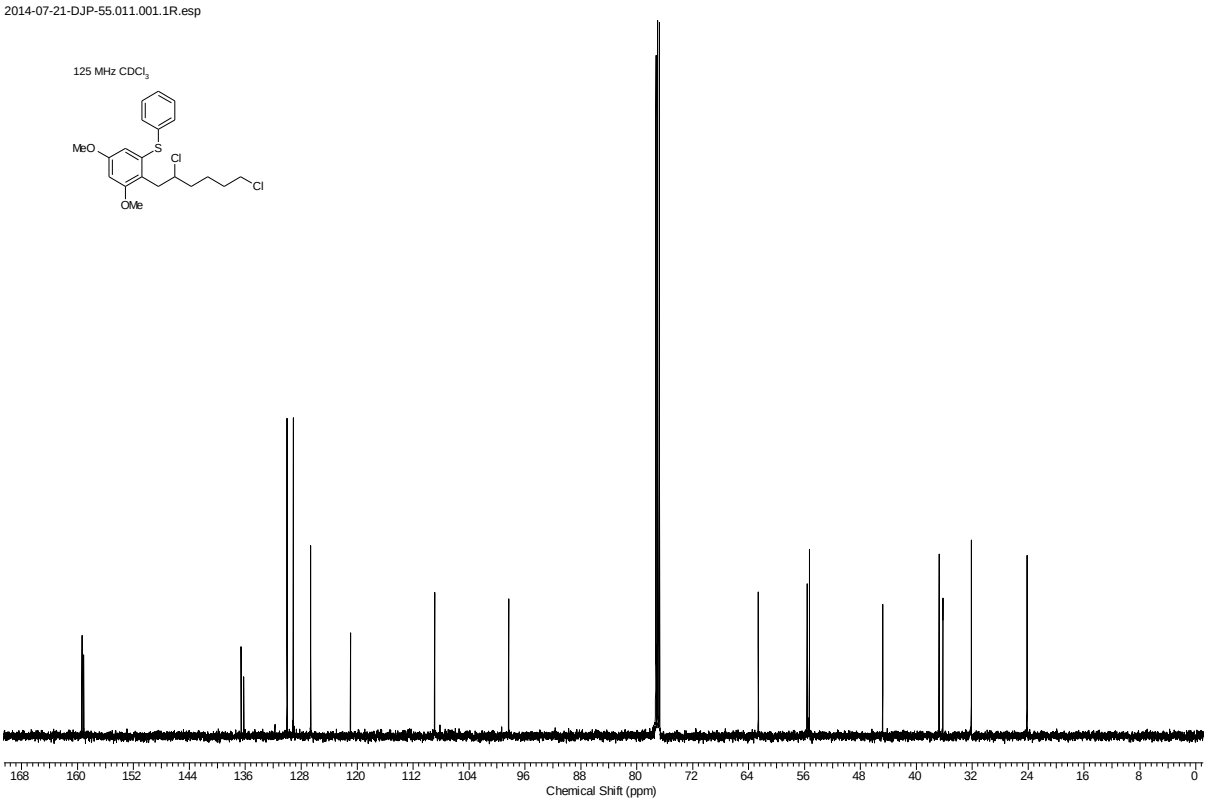
*(2-(6-Bromo-2-chlorohexyl)-3,5-dimethoxyphenyl)(phenyl)sulfide* ***2e***



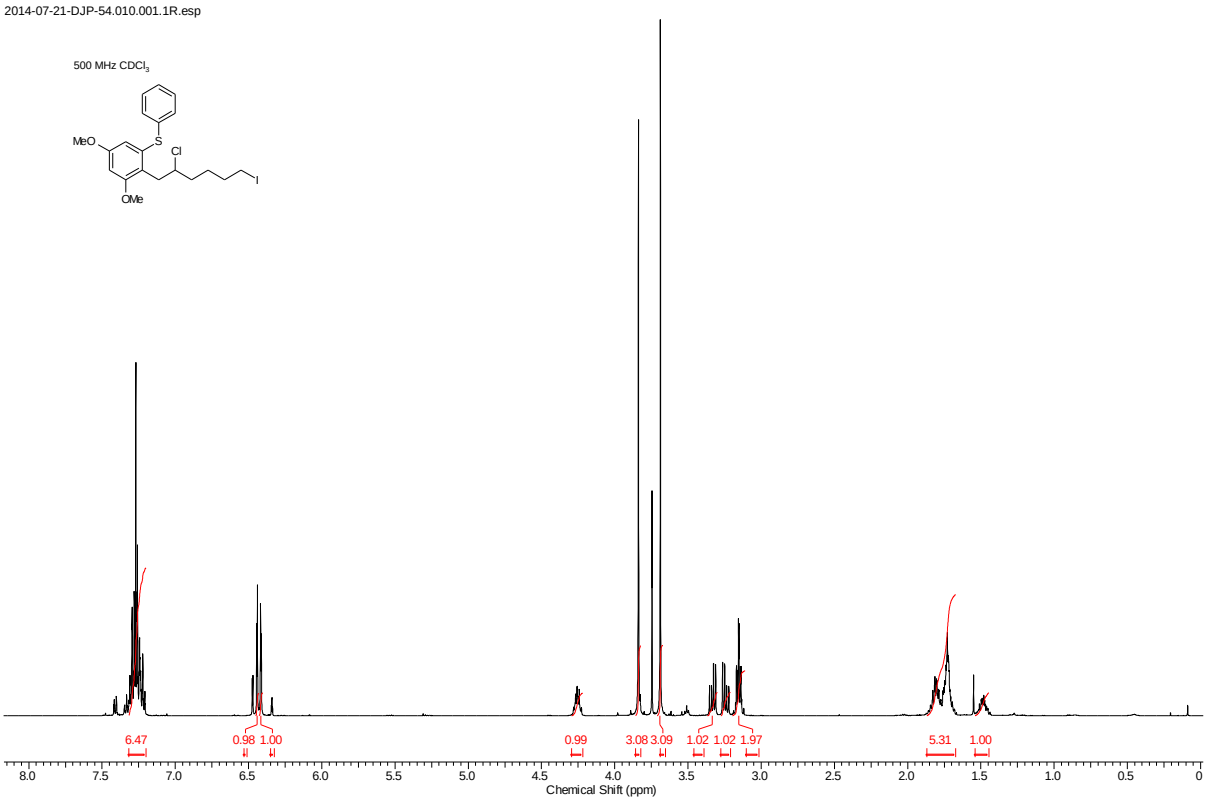



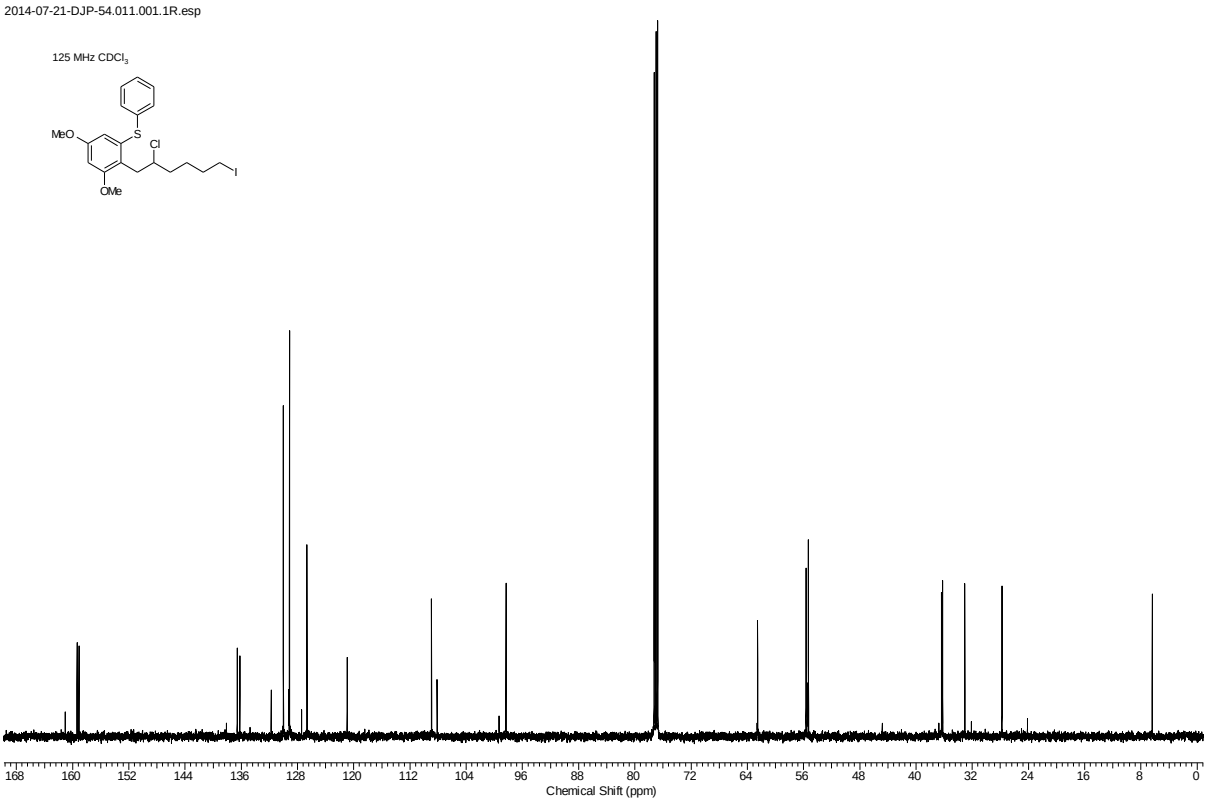
*(2-(2,6-Dichlorohexyl)-3,5-dimethoxyphenyl)(phenyl)sulfide* ***2f***



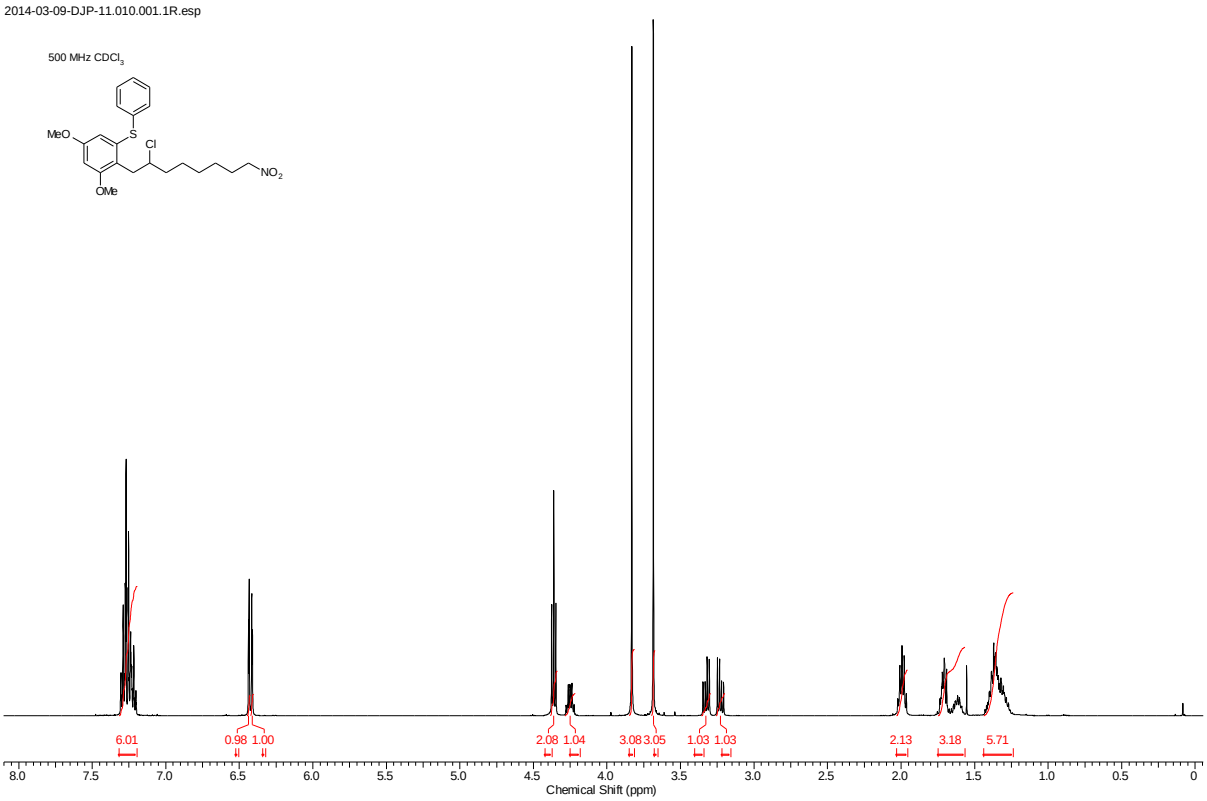



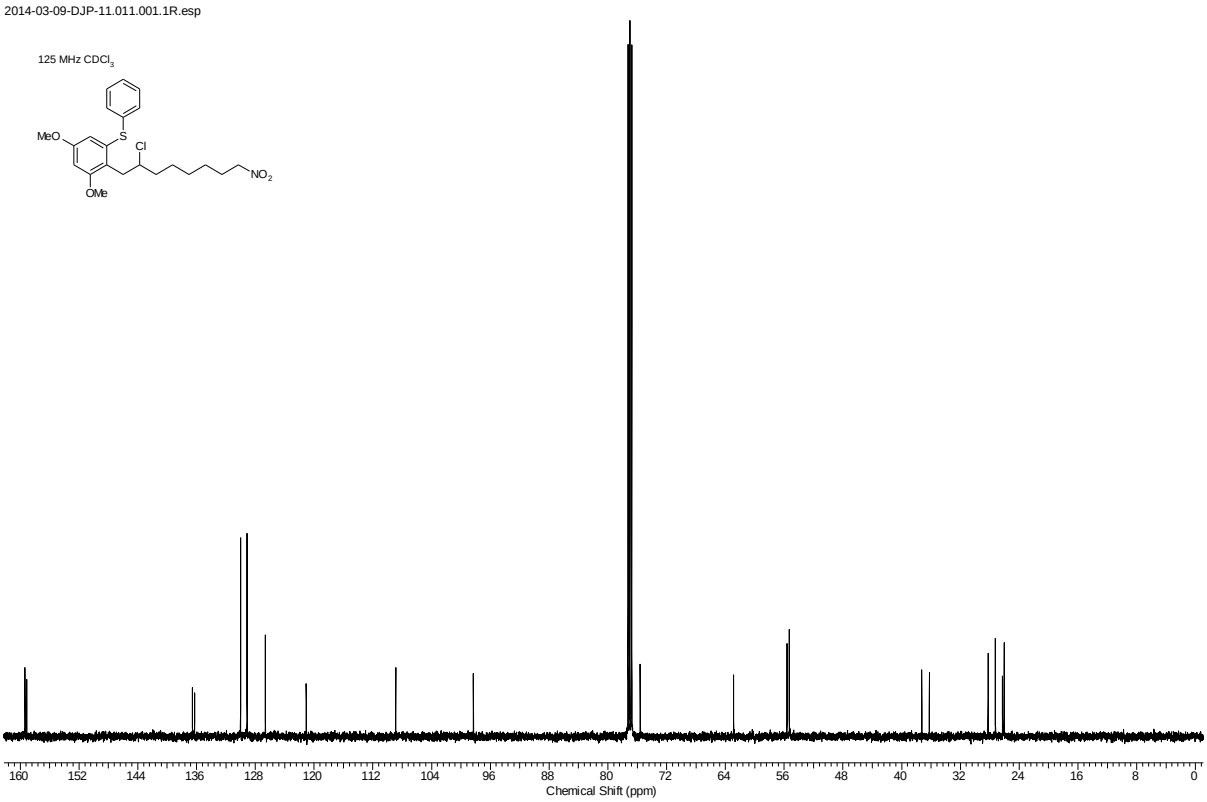
*(2-(2-Chloro-6-iodohexyl)-3,5-dimethoxyphenyl)(phenyl)sulfide* ***2g***



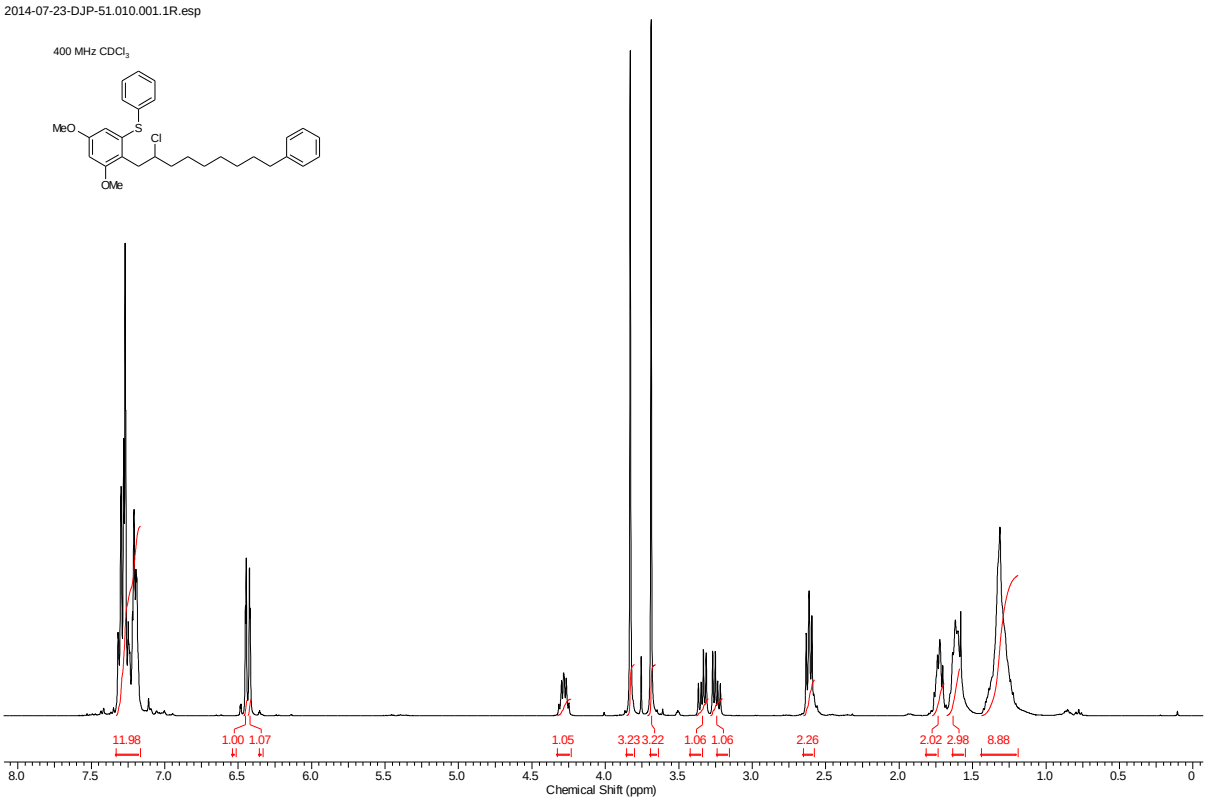



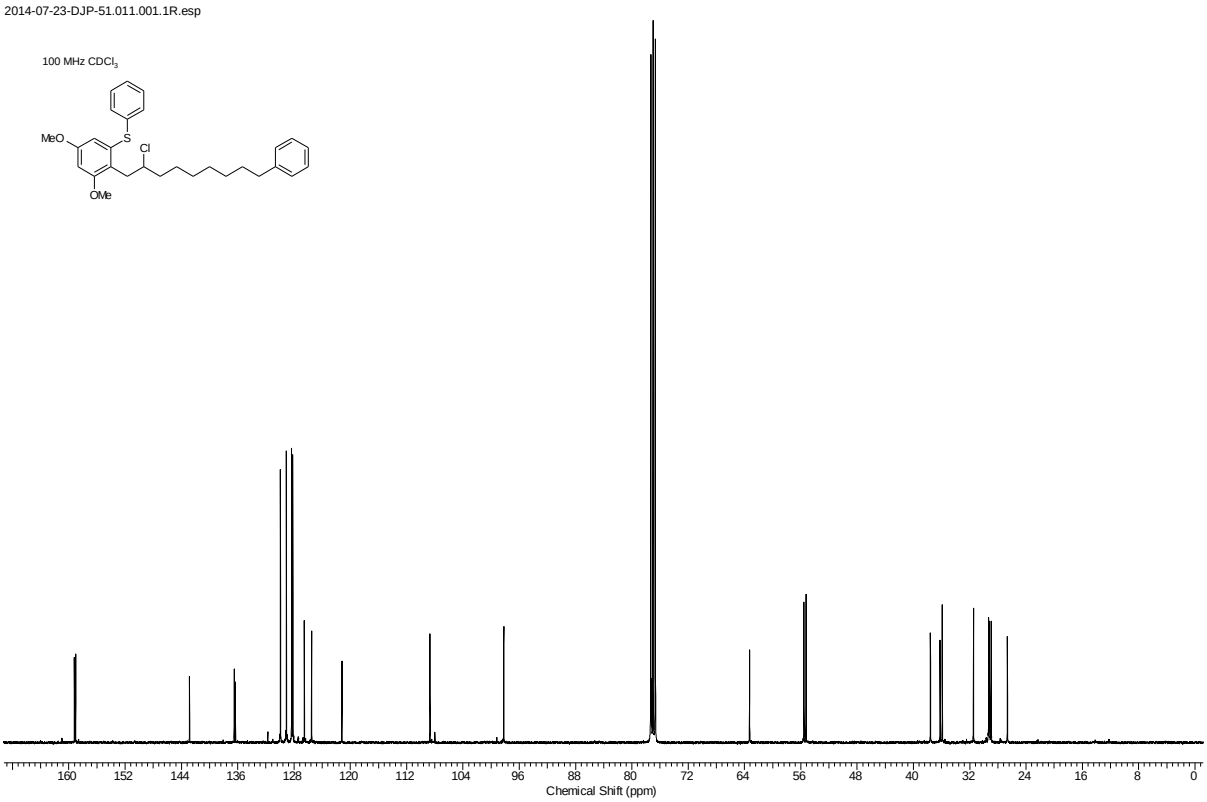
*(2-(2-Chloro-8-nitrooctyl)-3,5-dimethoxyphenyl)(phenyl)sulfide* ***2h***



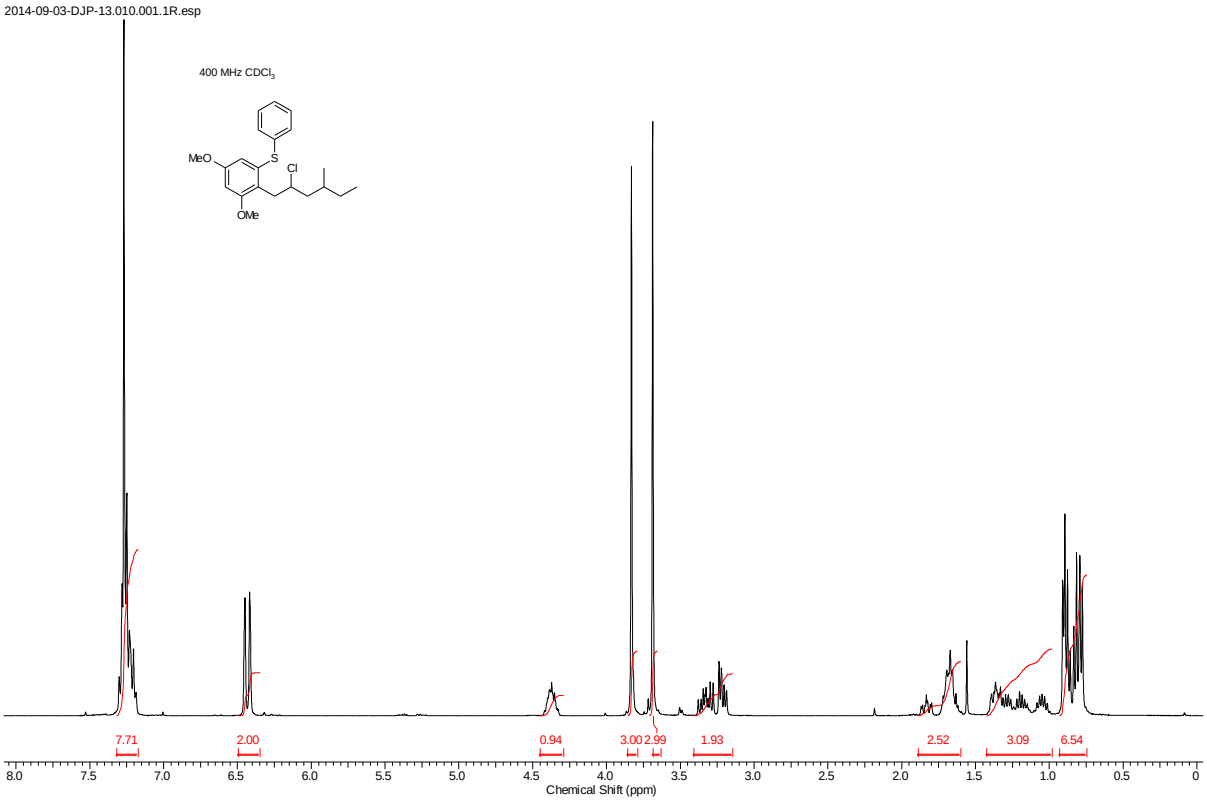



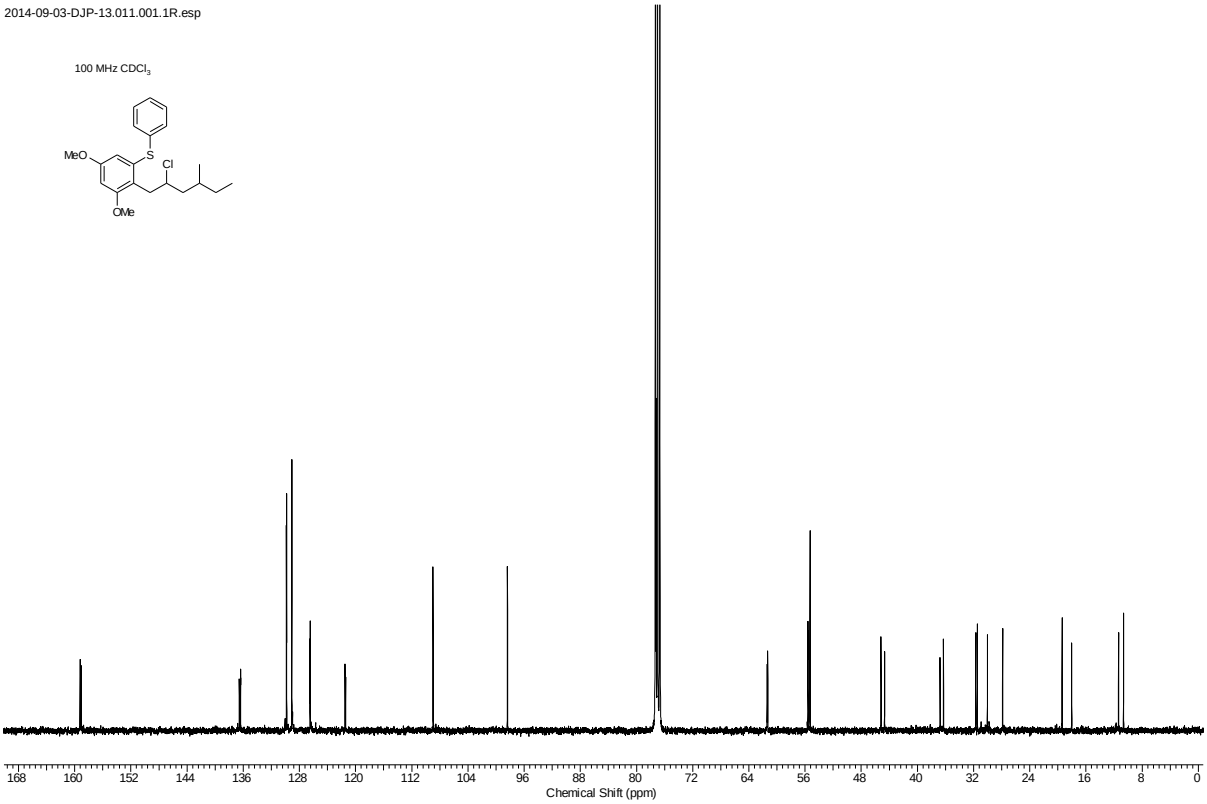
*(2-(2-Chloro-9-phenylnonyl)-3,5-dimethoxyphenyl)(phenyl)sulfide* ***2i***



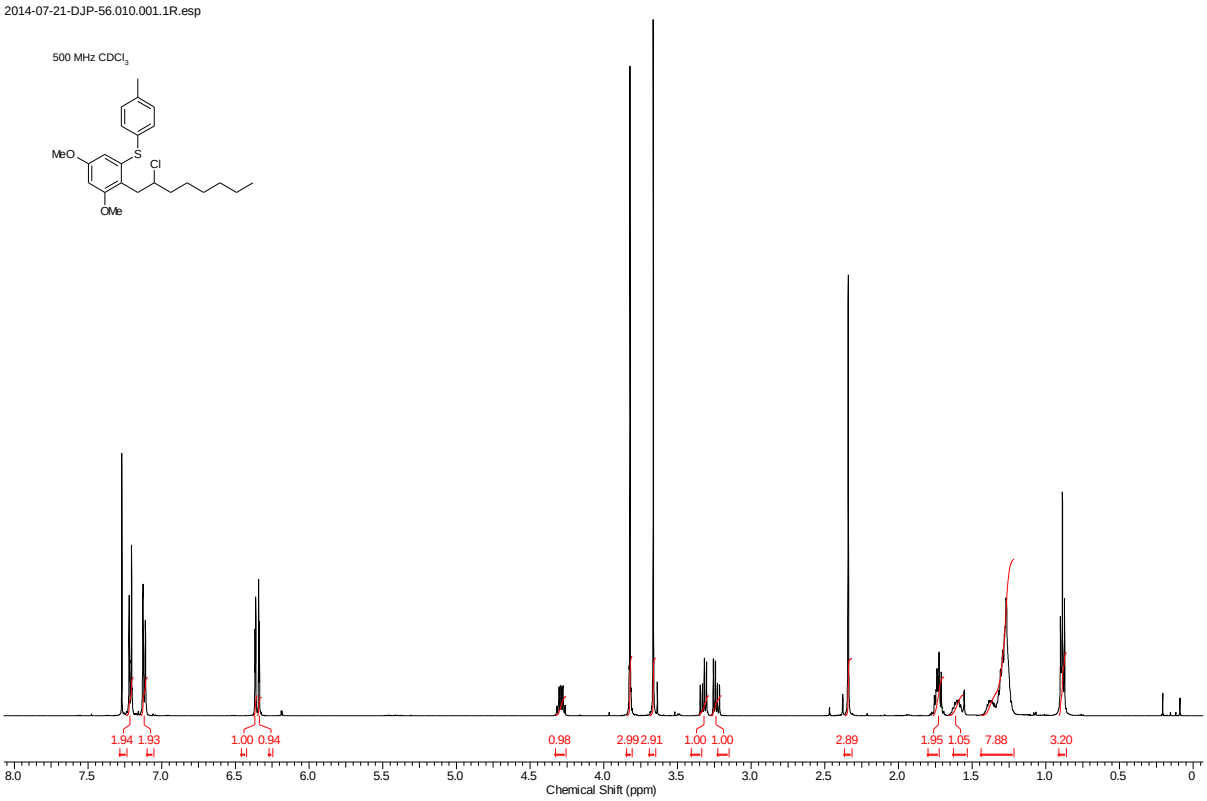



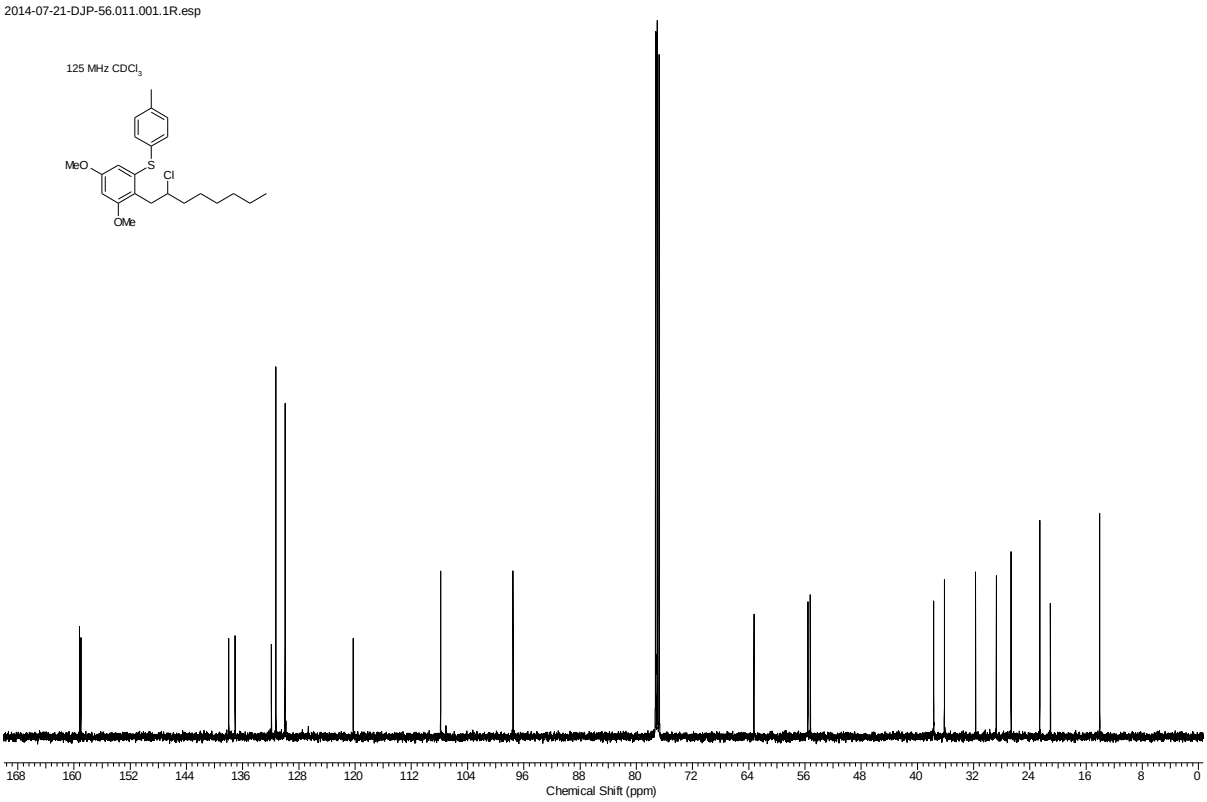
*(2-(2-Chloro-4-methylpentyl)-3,5-dimethoxyphenyl)(phenyl)sulfide* ***2j***



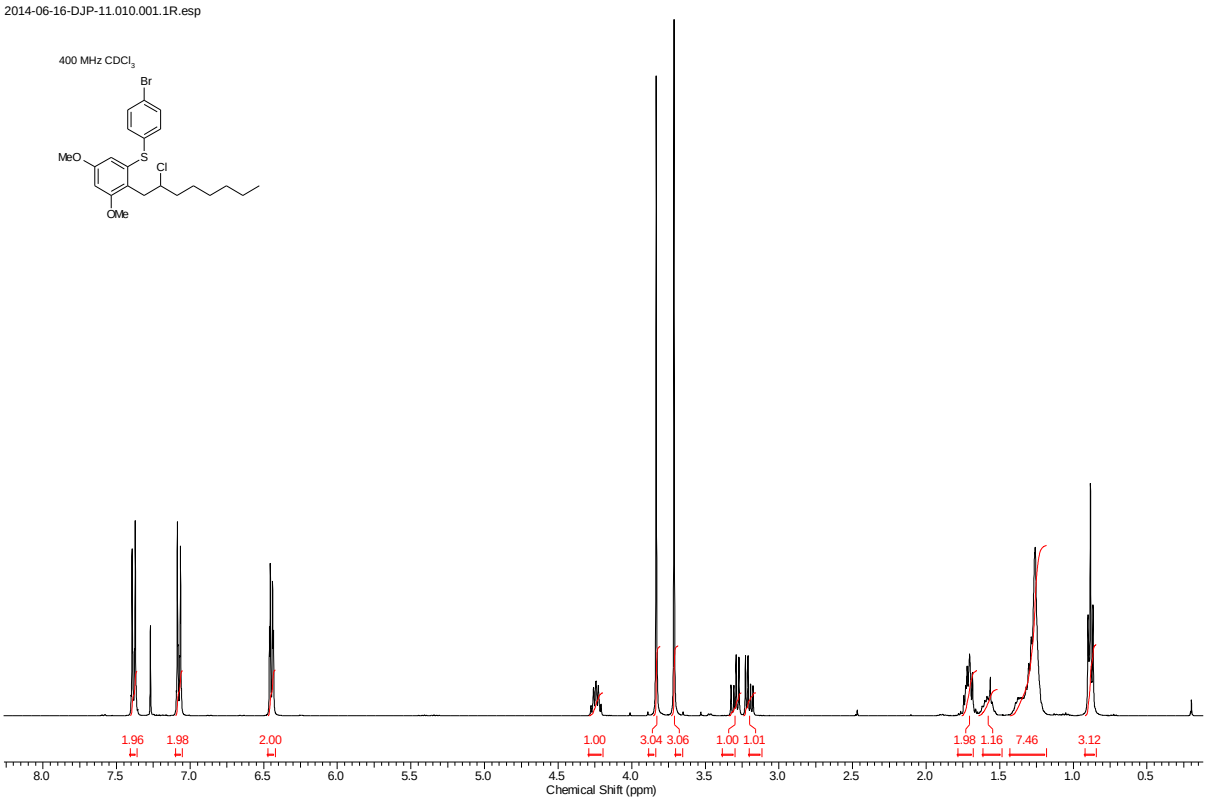



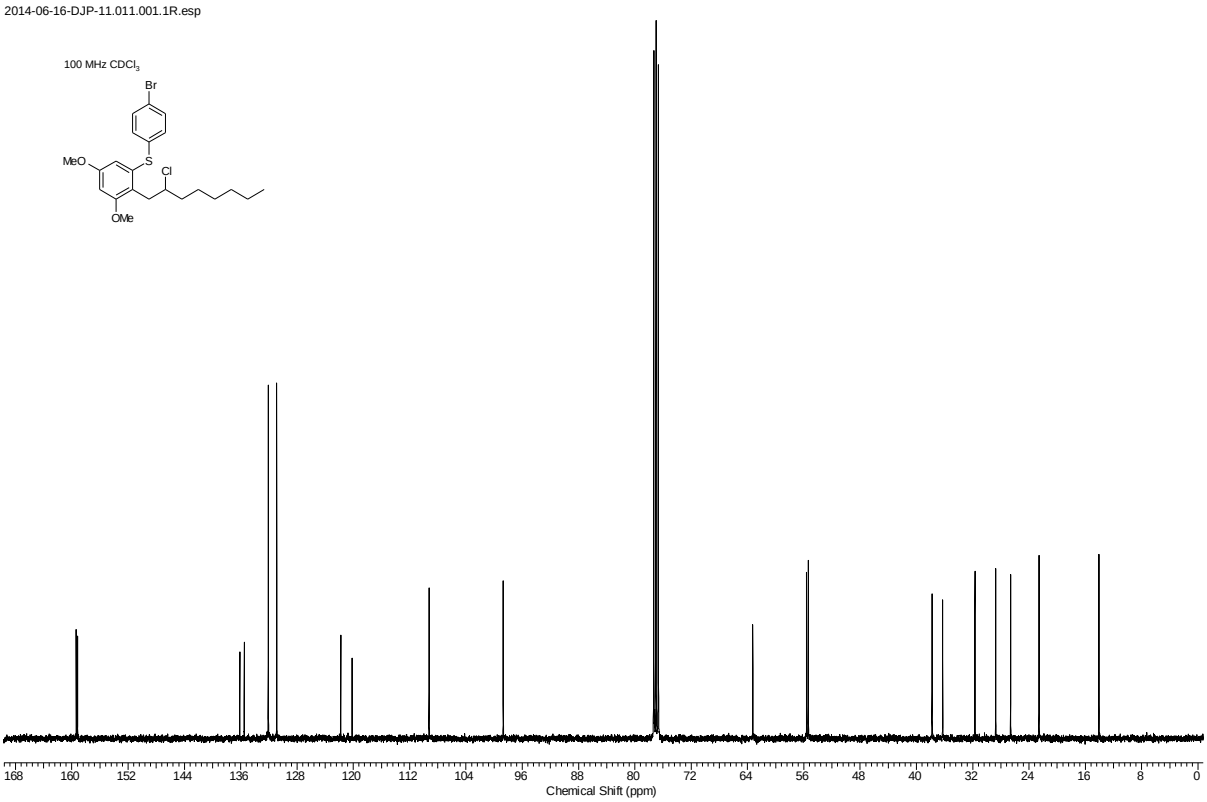
*(2-(2-Chlorooctyl)-3,5-dimethoxyphenyl)(p-tolyl)sulfide* ***2k***



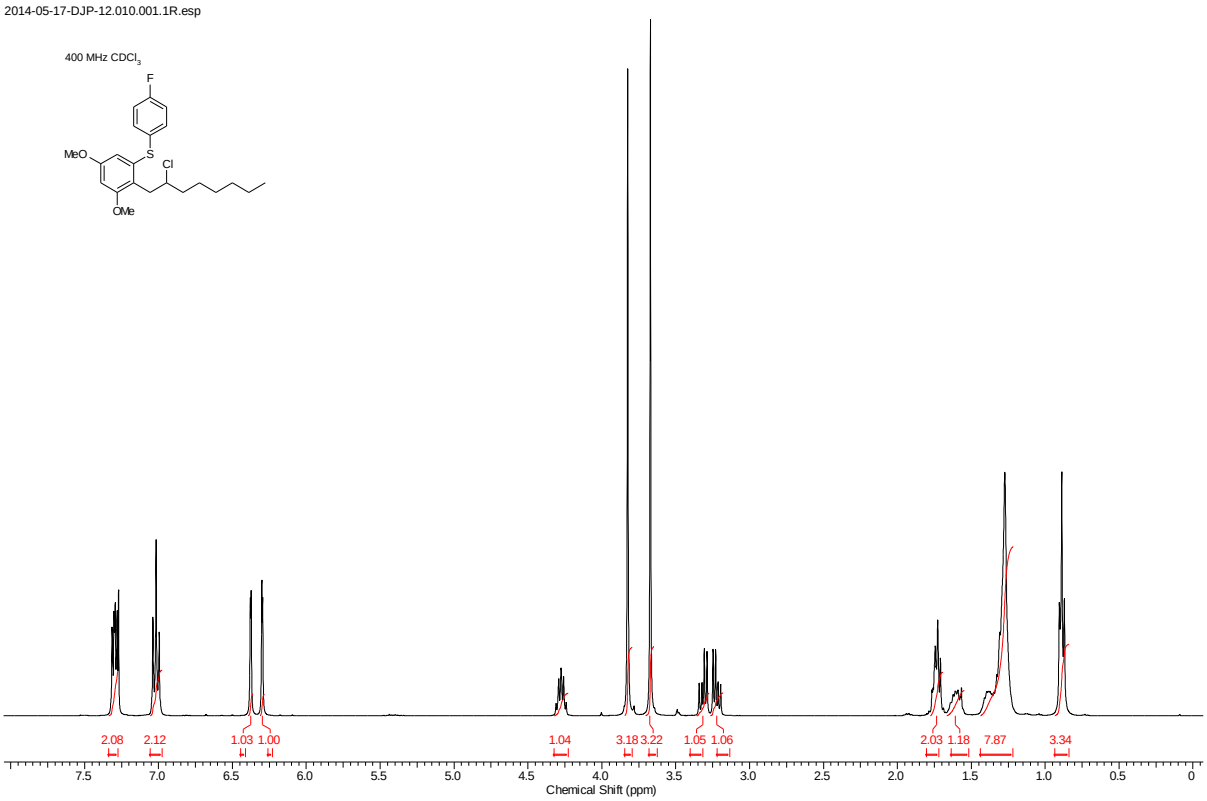



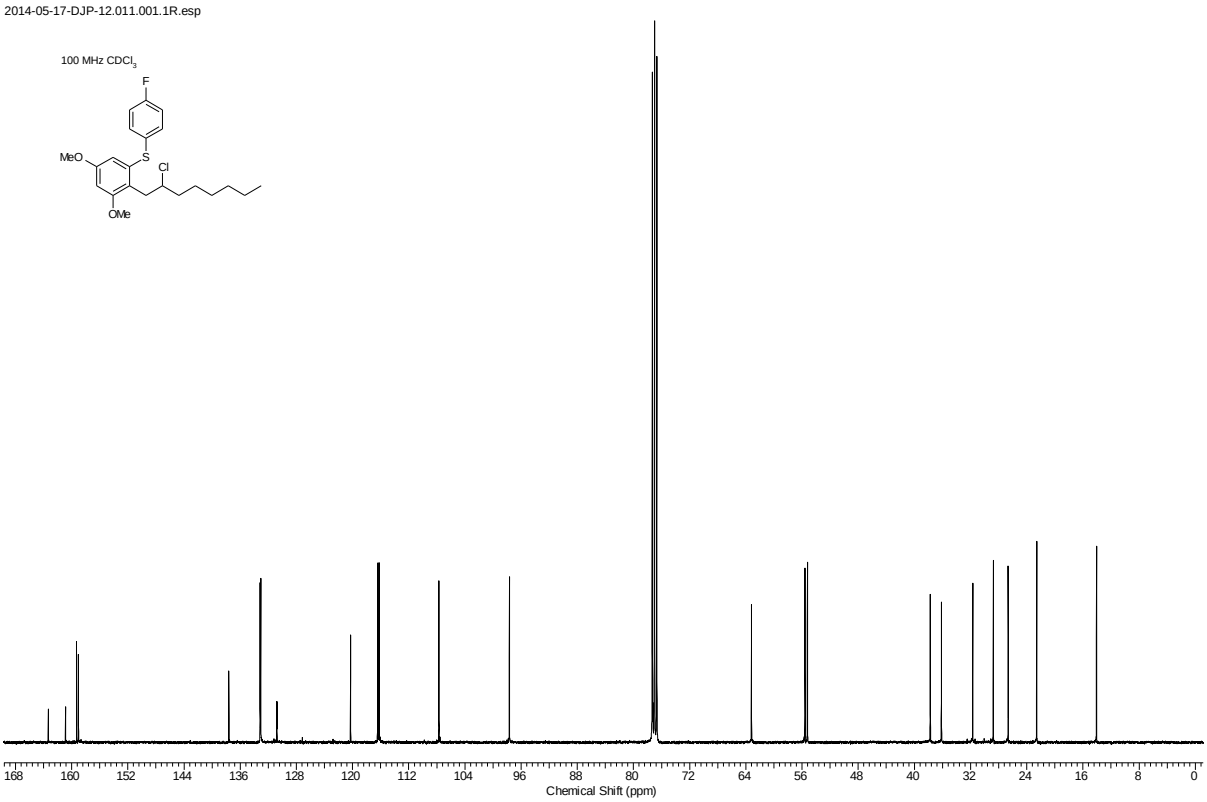
*(4-Bromophenyl)(2-(2-chlorooctyl)-3,5-dimethoxyphenyl)sulfide* ***2l***



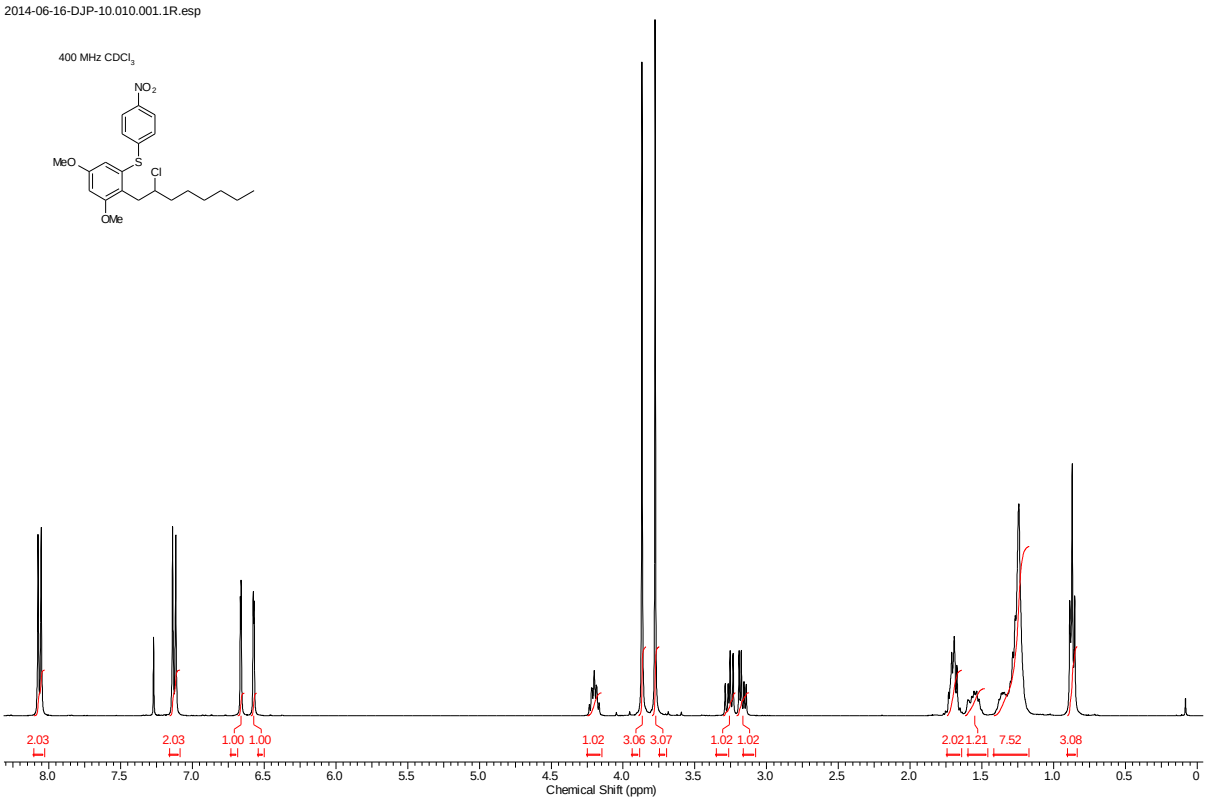



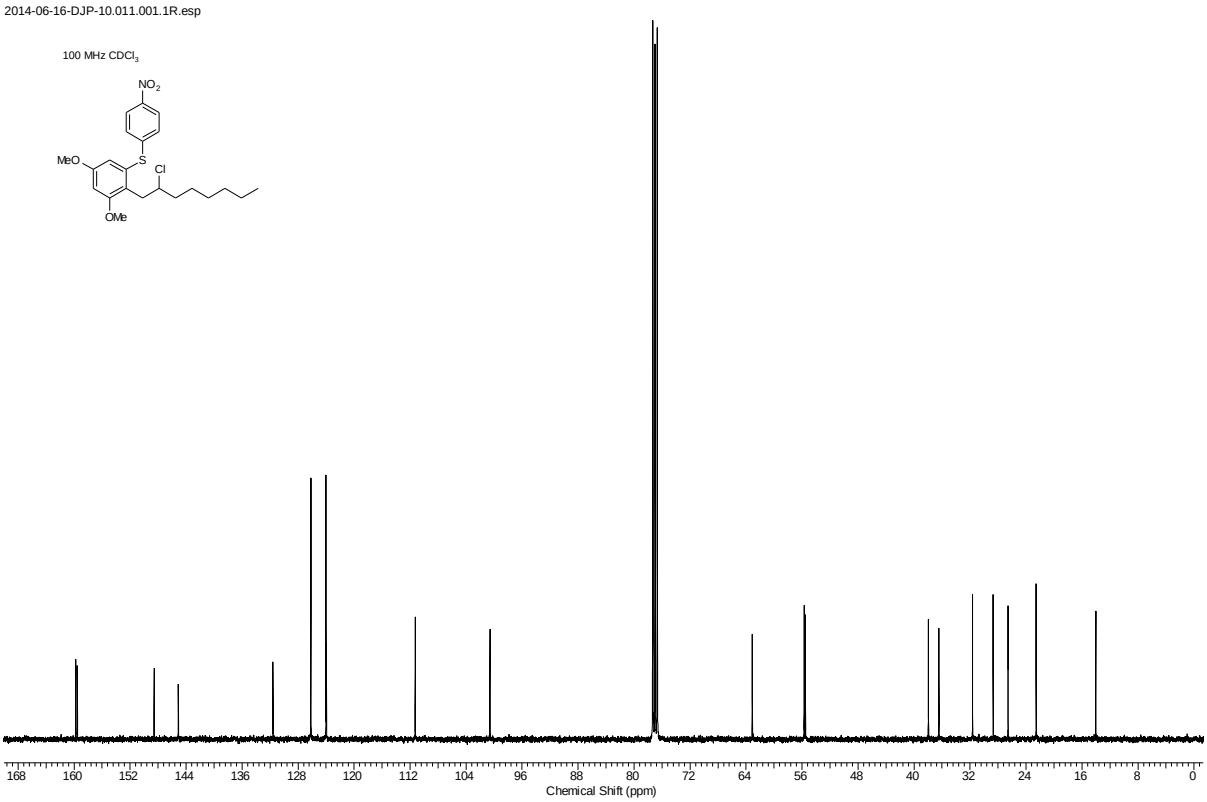
*(2-(2-Chlorooctyl)-3,5-dimethoxyphenyl)(4-fluorophenyl)sulfide* ***2m***



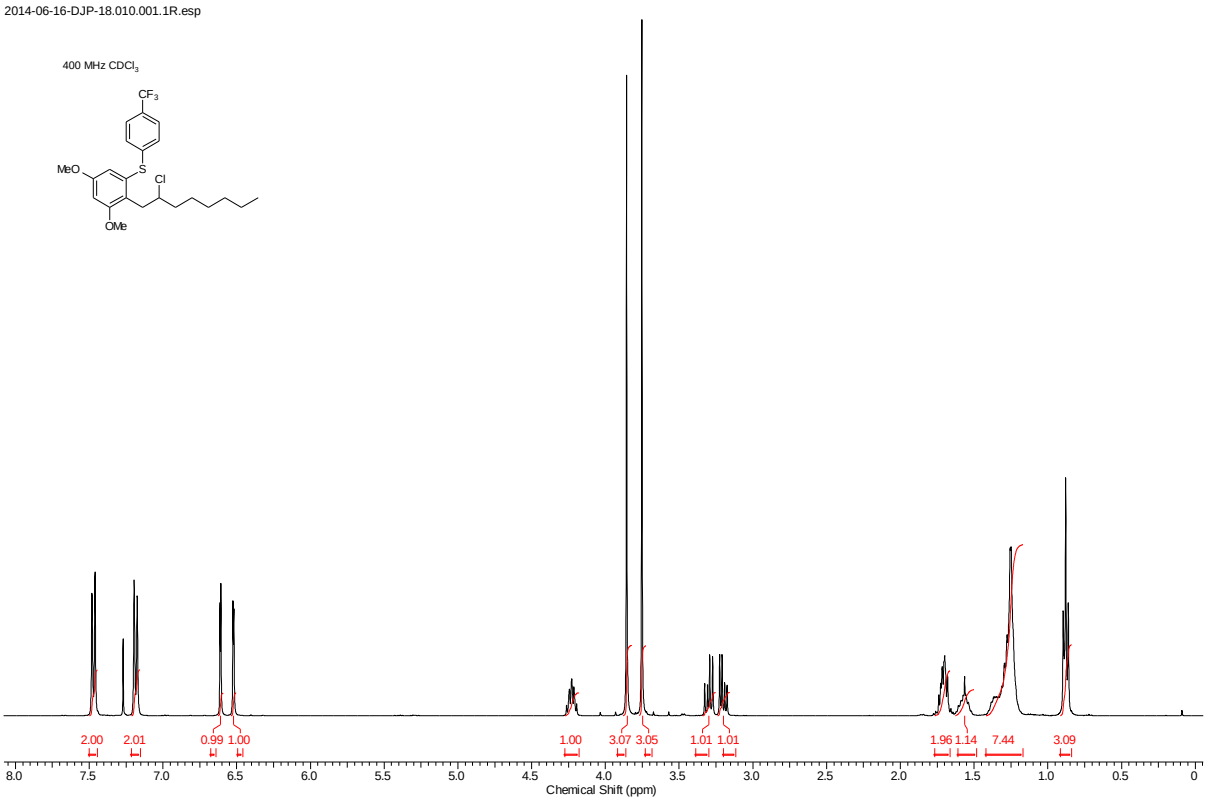



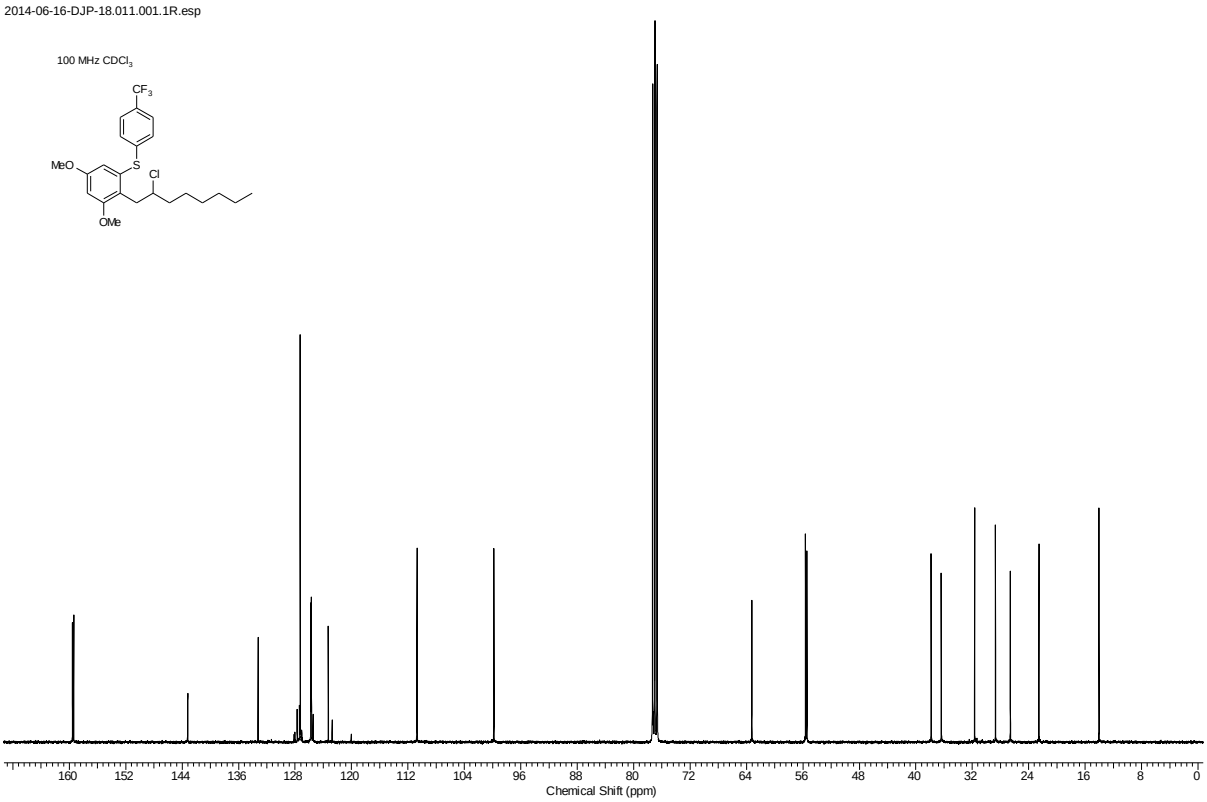
## *(2-(2-Chlorooctyl)-3,5-dimethoxyphenyl)(4-nitrophenyl)sulfide* ***2n***



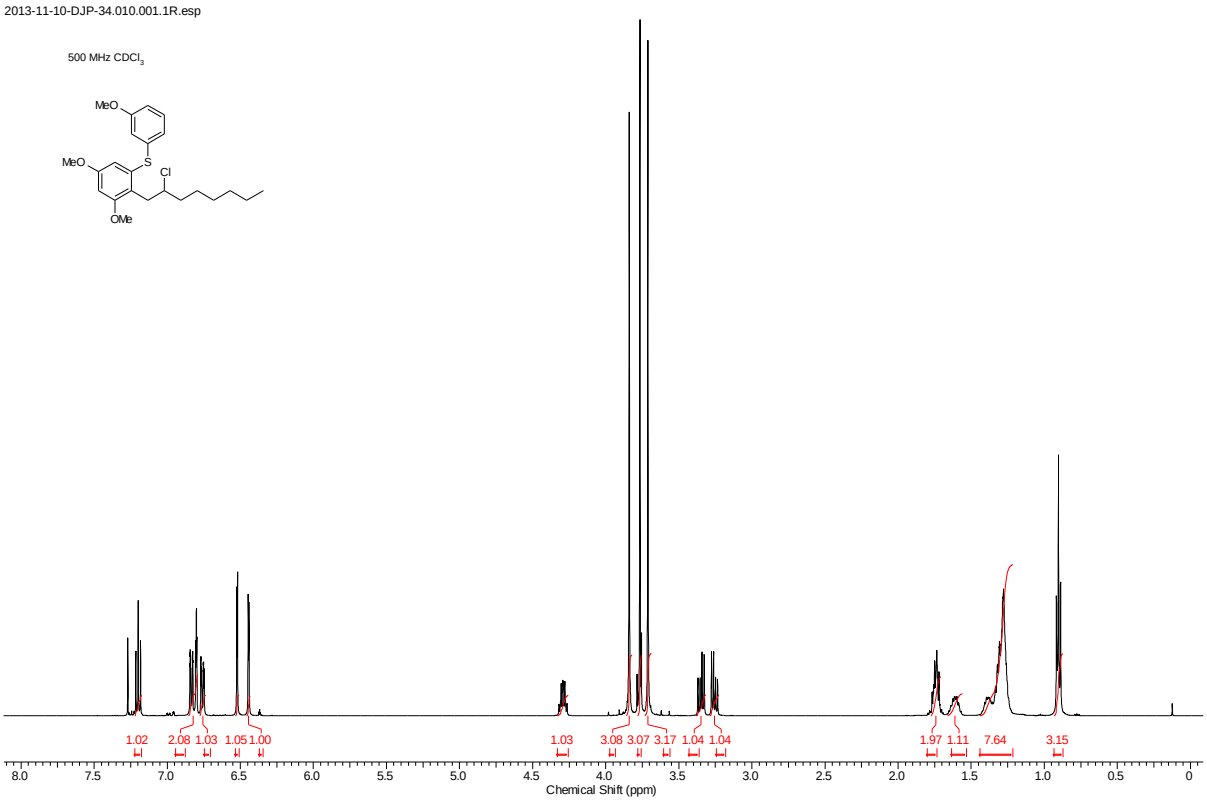



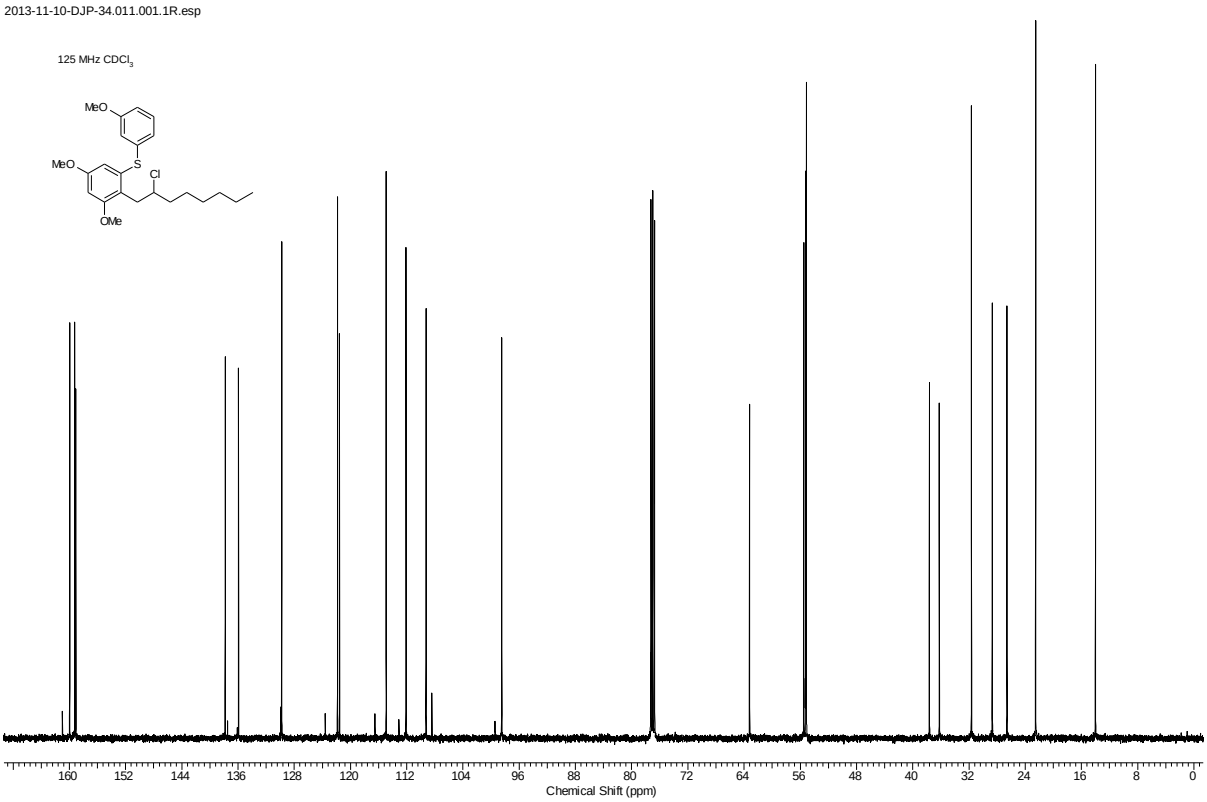
*(2-(2-Chlorooctyl)-3,5-dimethoxyphenyl)(4-(trifluoromethyl)phenyl)sulfide* ***2o***



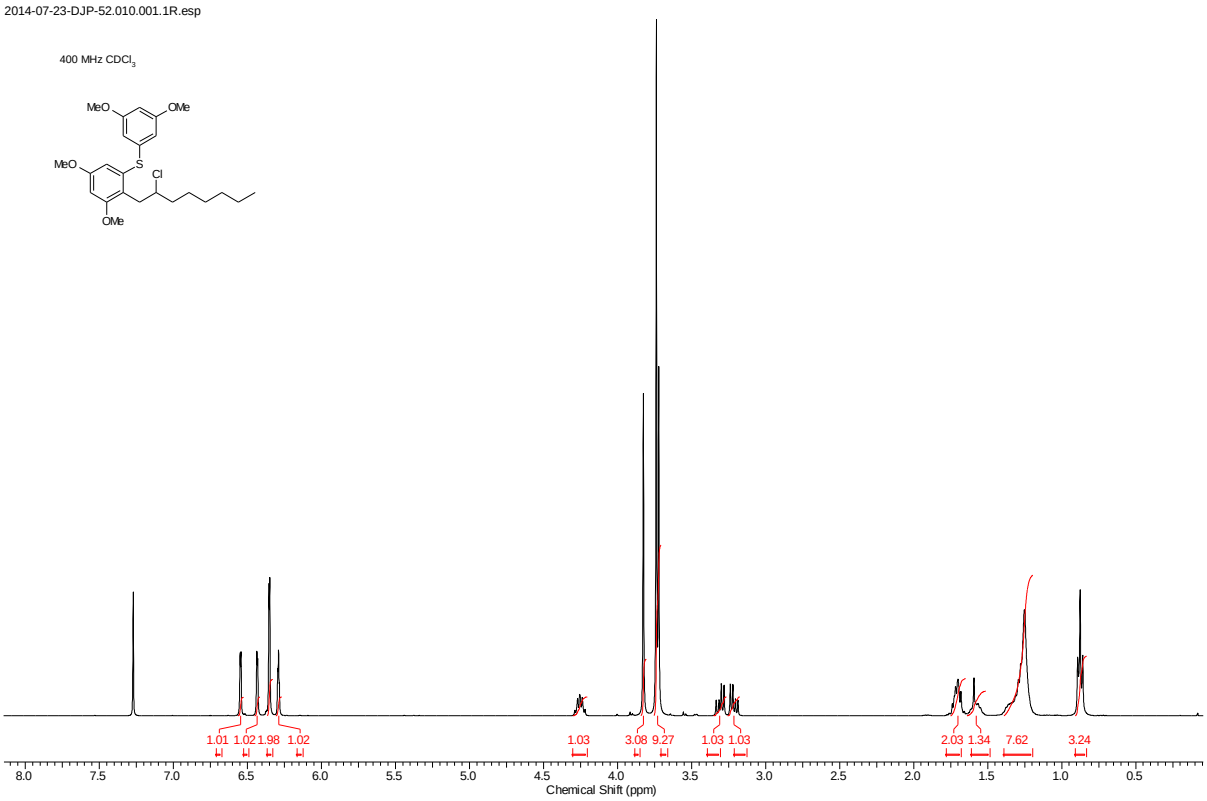



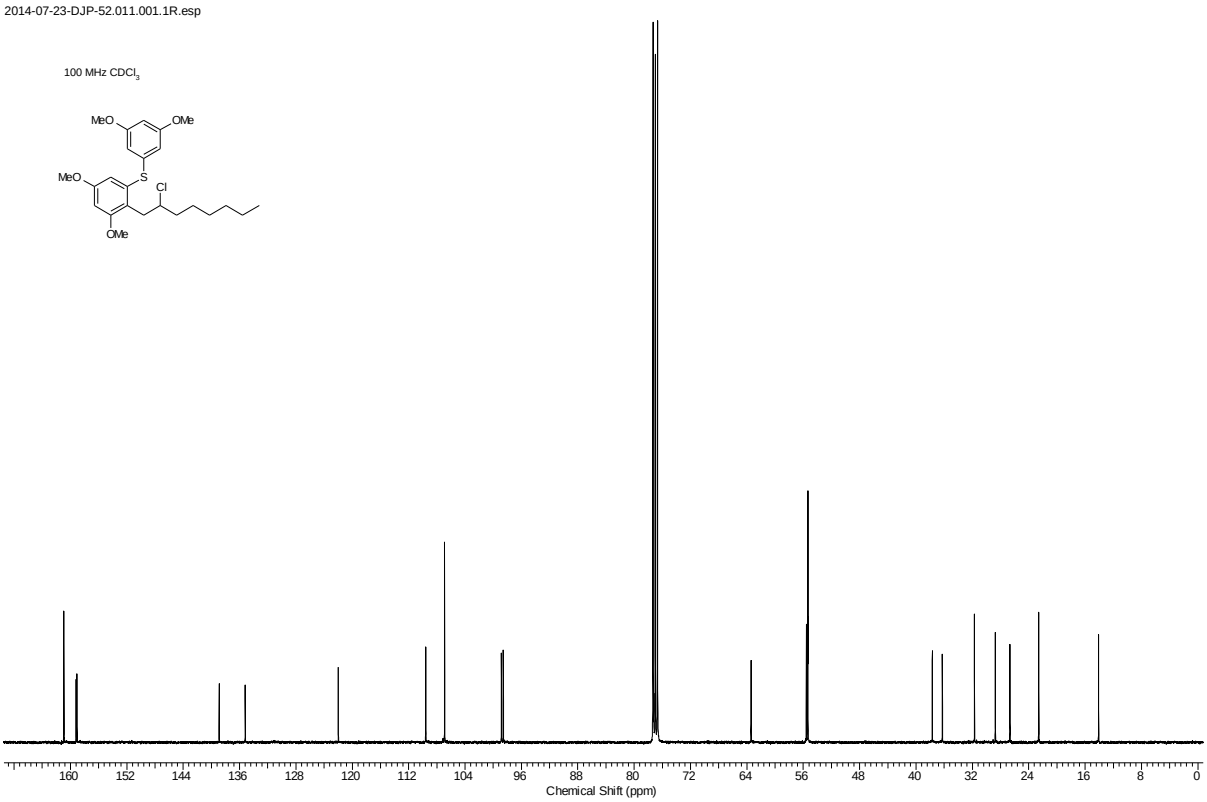
*(2-(2-Chlorooctyl)-3,5-dimethoxyphenyl)(3-methoxyphenyl)sulfide* ***2p***



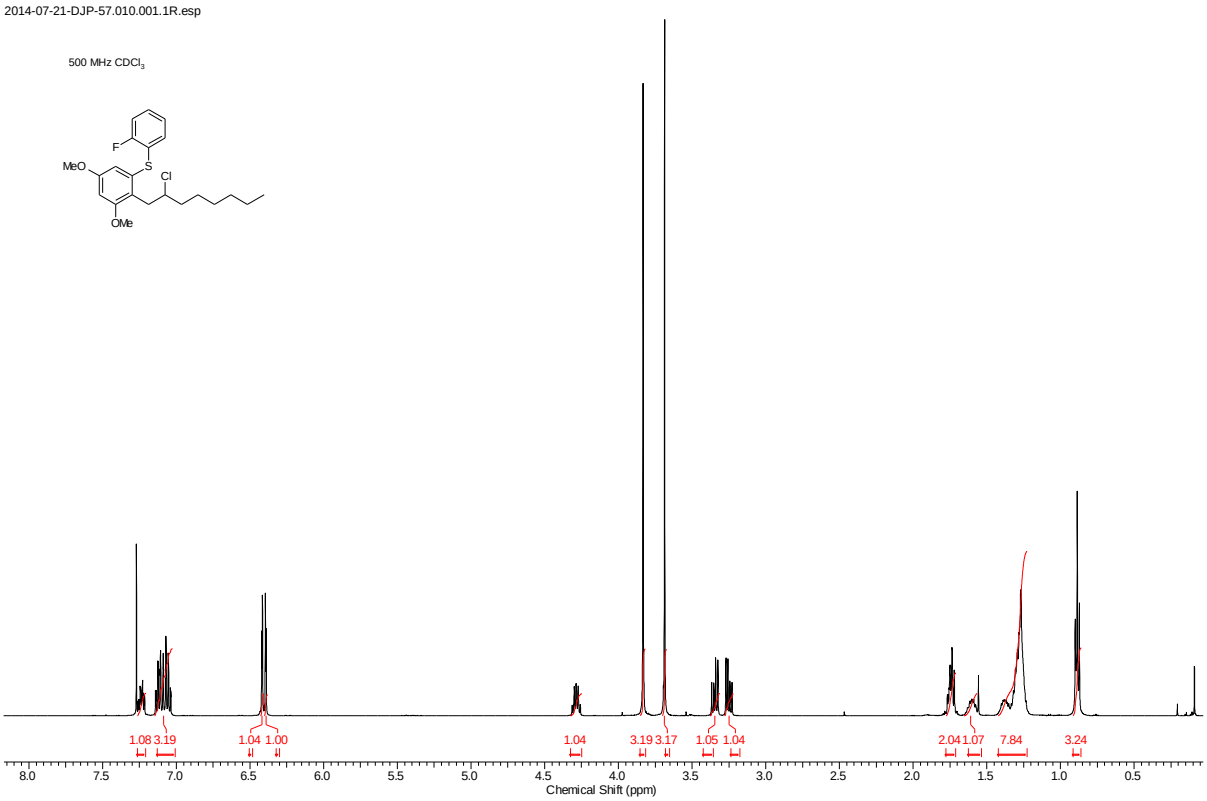



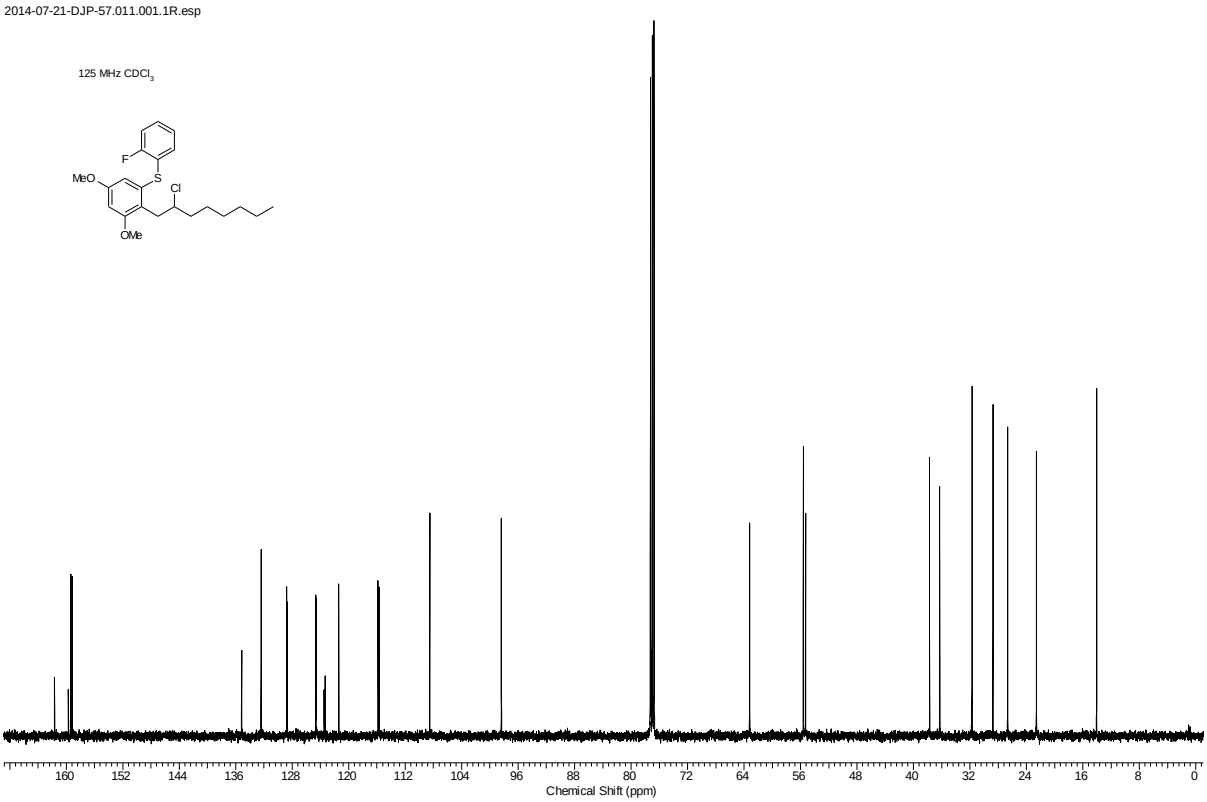
*(2-(2-Chlorooctyl)-3,5-dimethoxyphenyl)(3,5-dimethoxyphenyl)sulfide* ***2q***



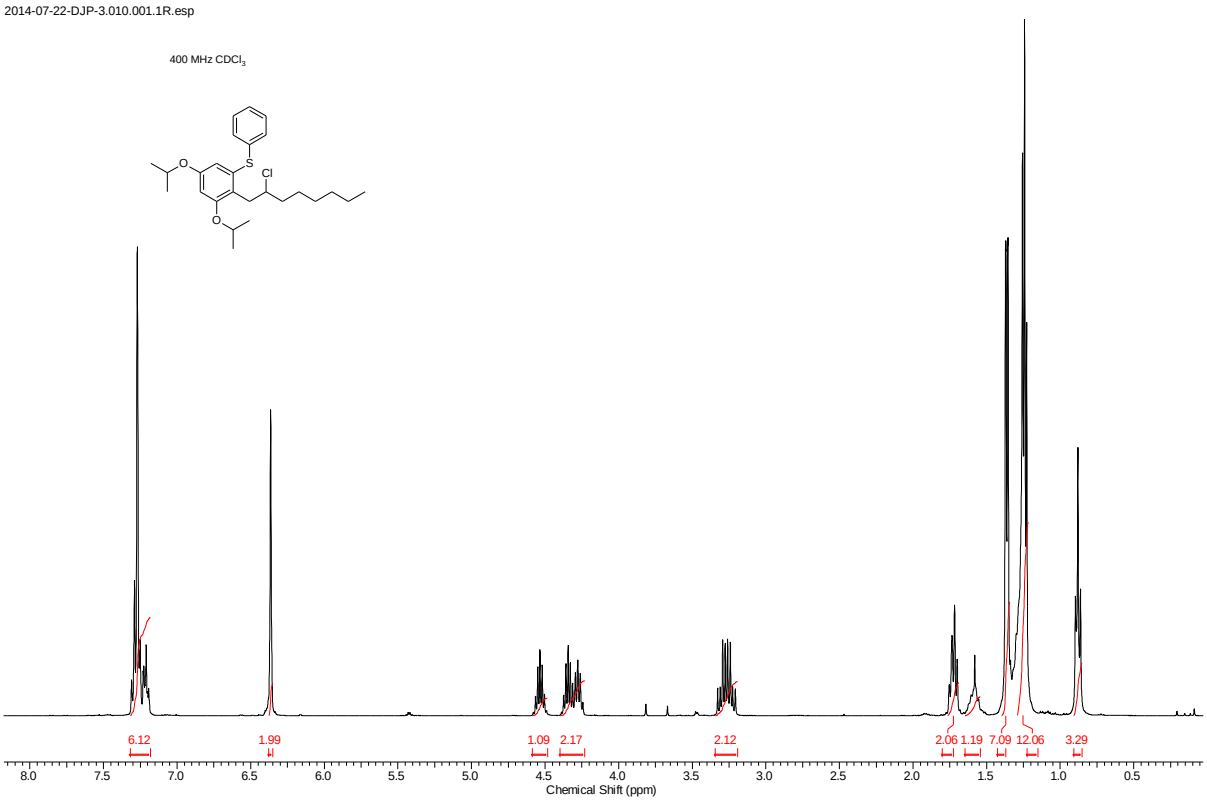



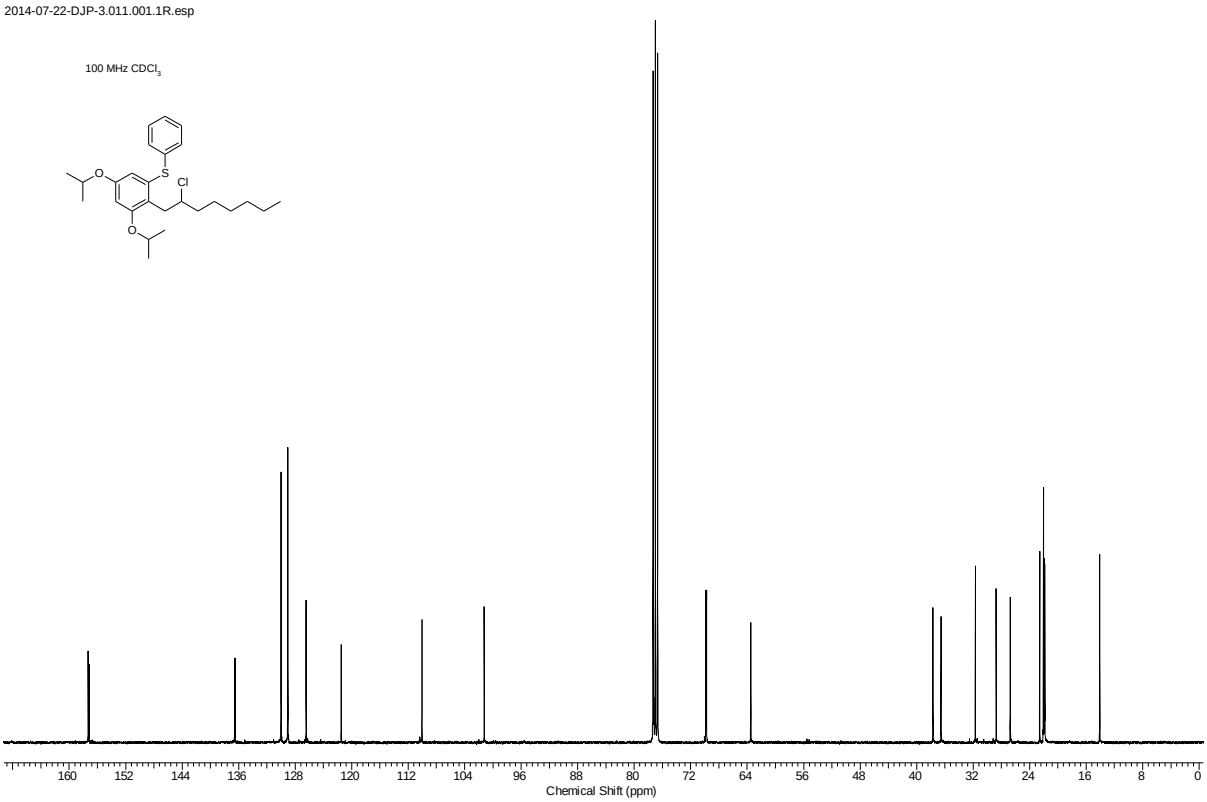
*(2-(2-Chlorooctyl)-3,5-dimethoxyphenyl)(2-fluorophenyl)sulfide* ***2r***



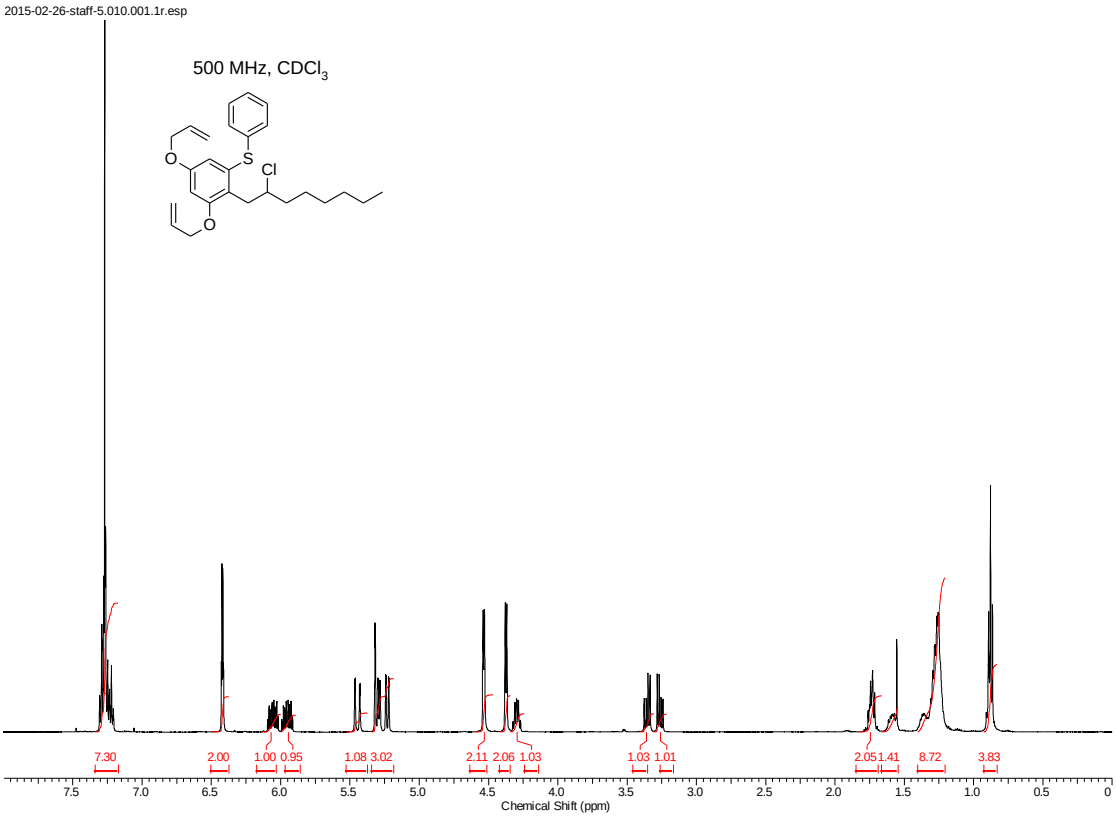



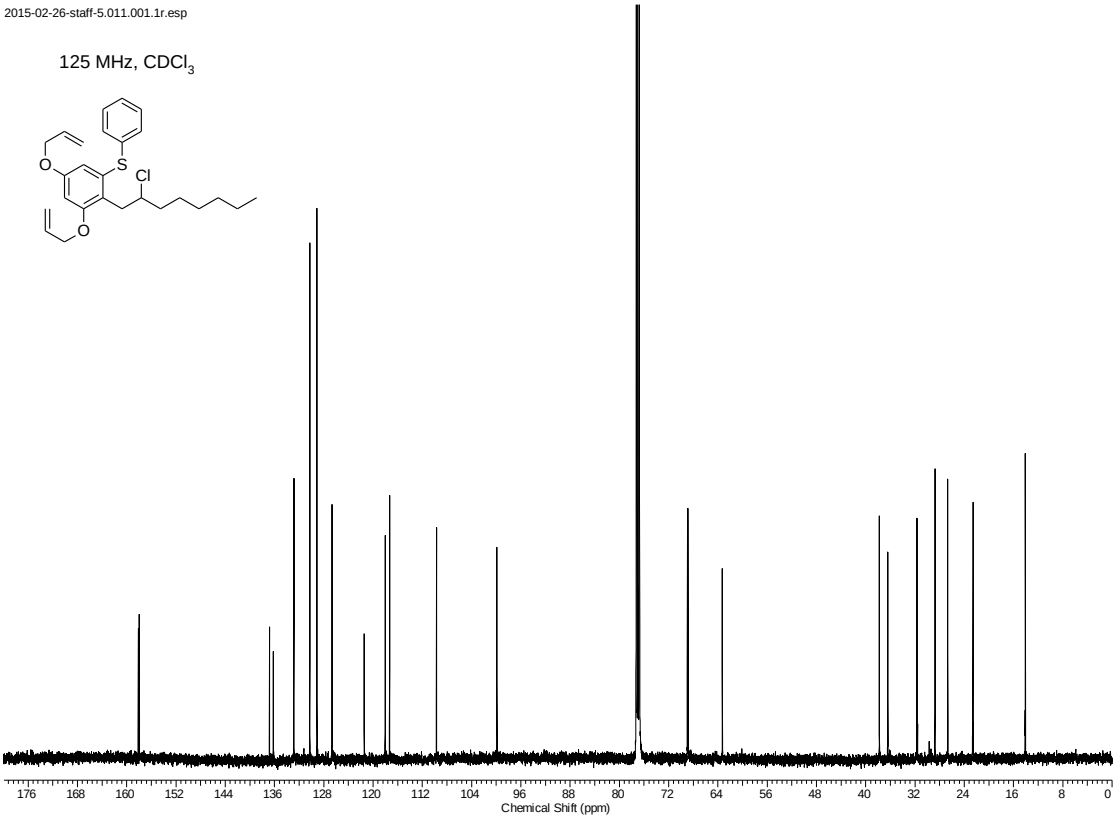
*(2-(2-Chlorooctyl)-3,5-diisopropoxyphenyl)(phenyl)sulfide* ***2s***



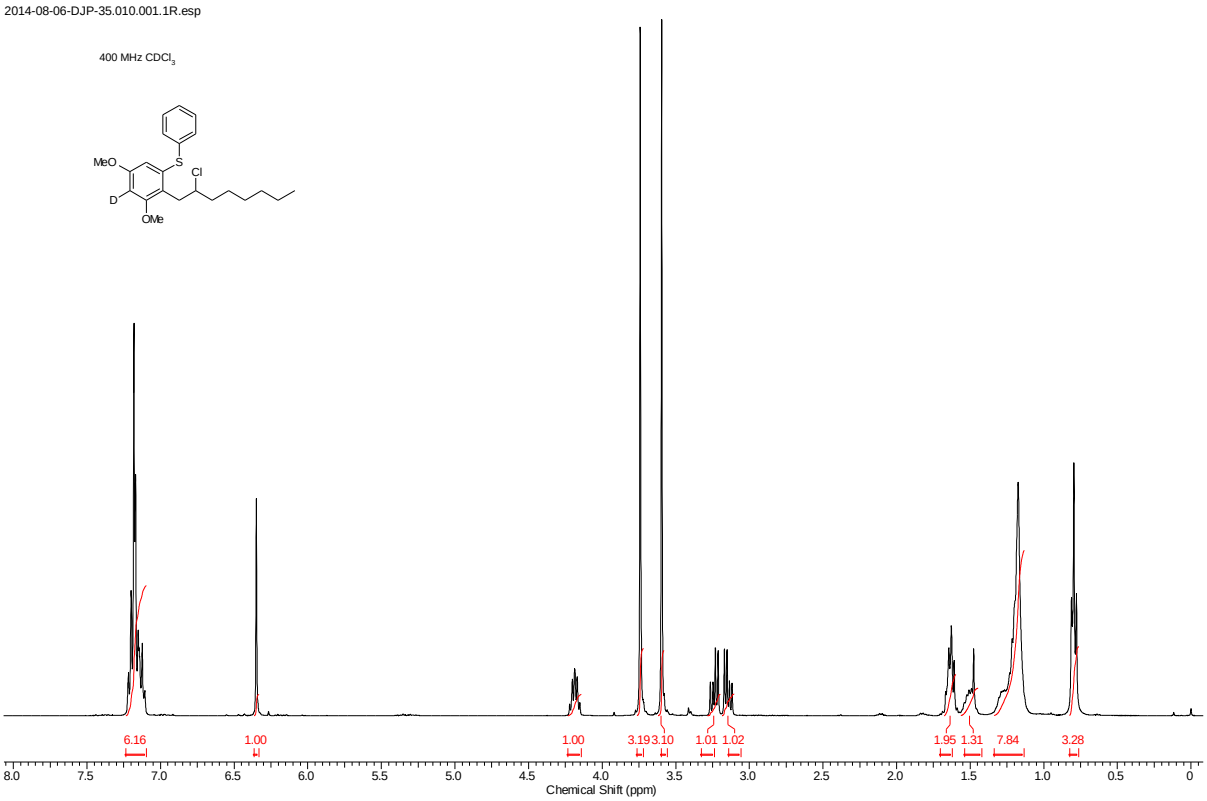



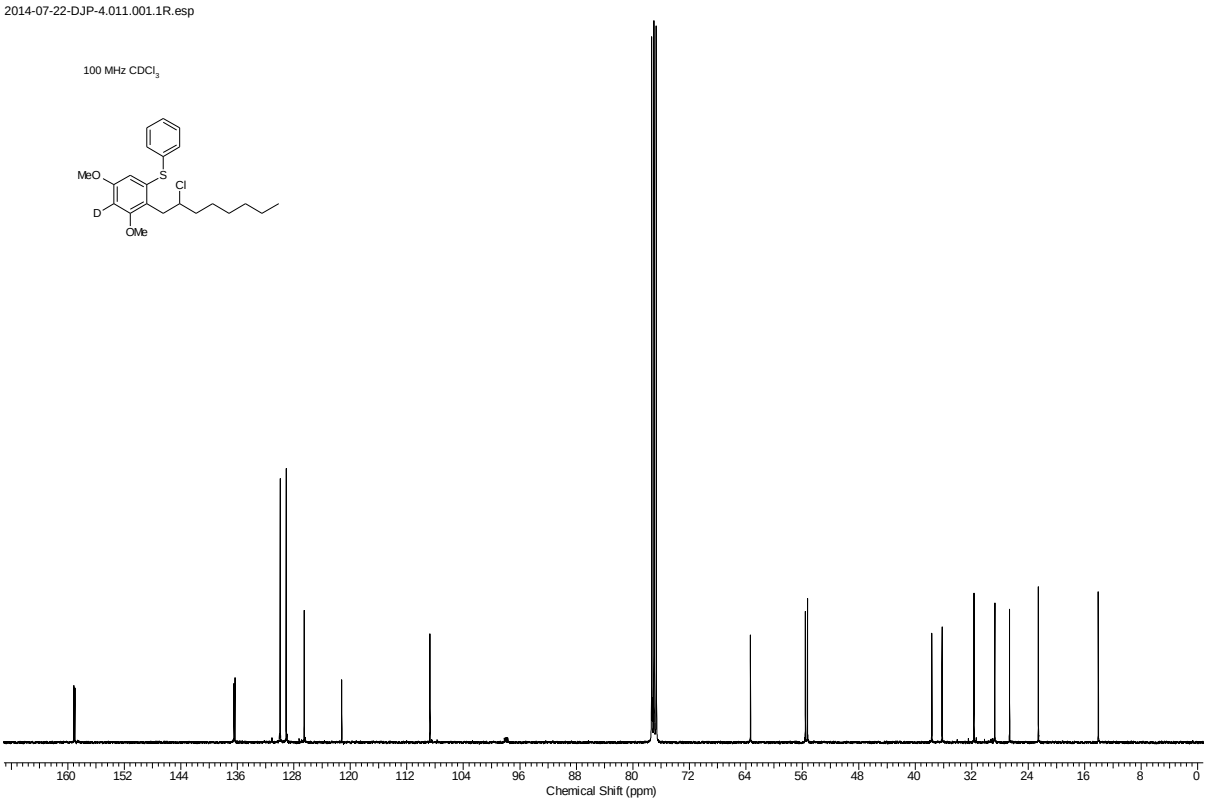
*(3,5-bis(Allyloxy)-2-(2-chlorooctyl)phenyl)(phenyl)sulfide* ***2t***



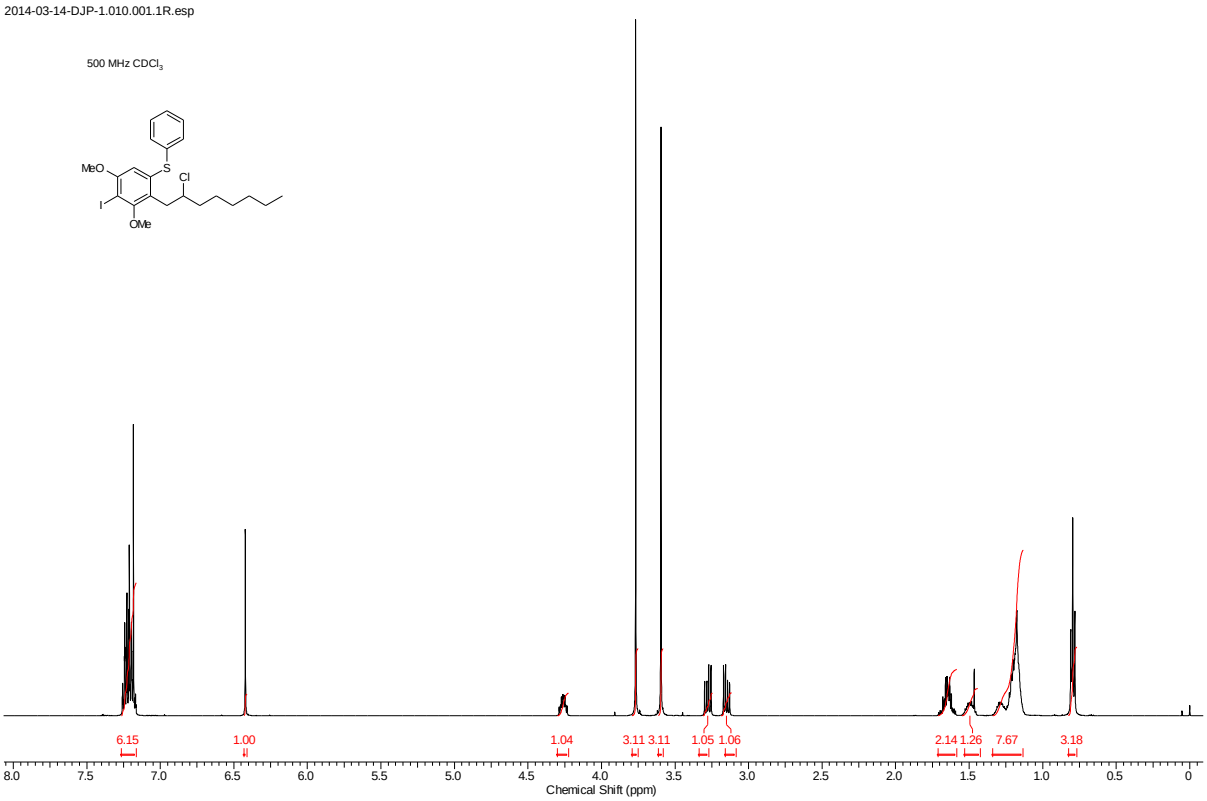



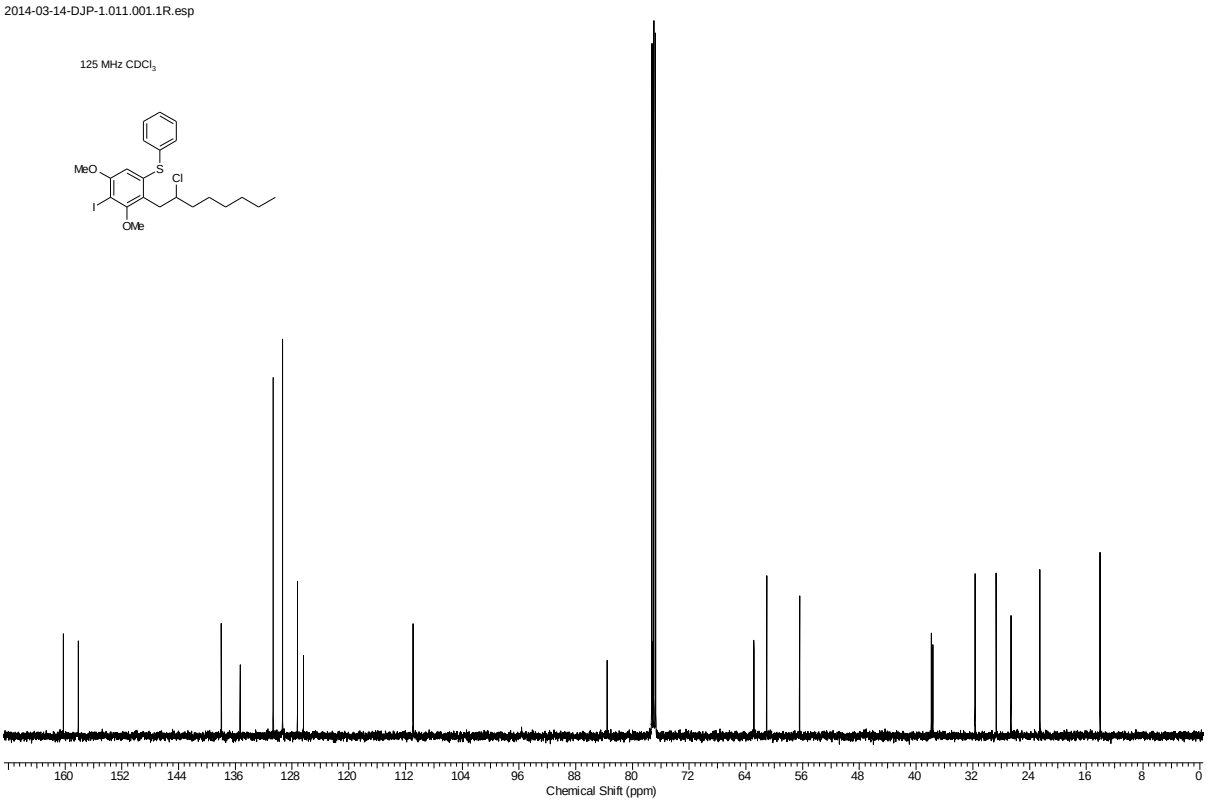
*(2-(2-Chlorooctyl)-3,5-dimethoxyphenyl-4-d)(phenyl)sulfide* ***3a***



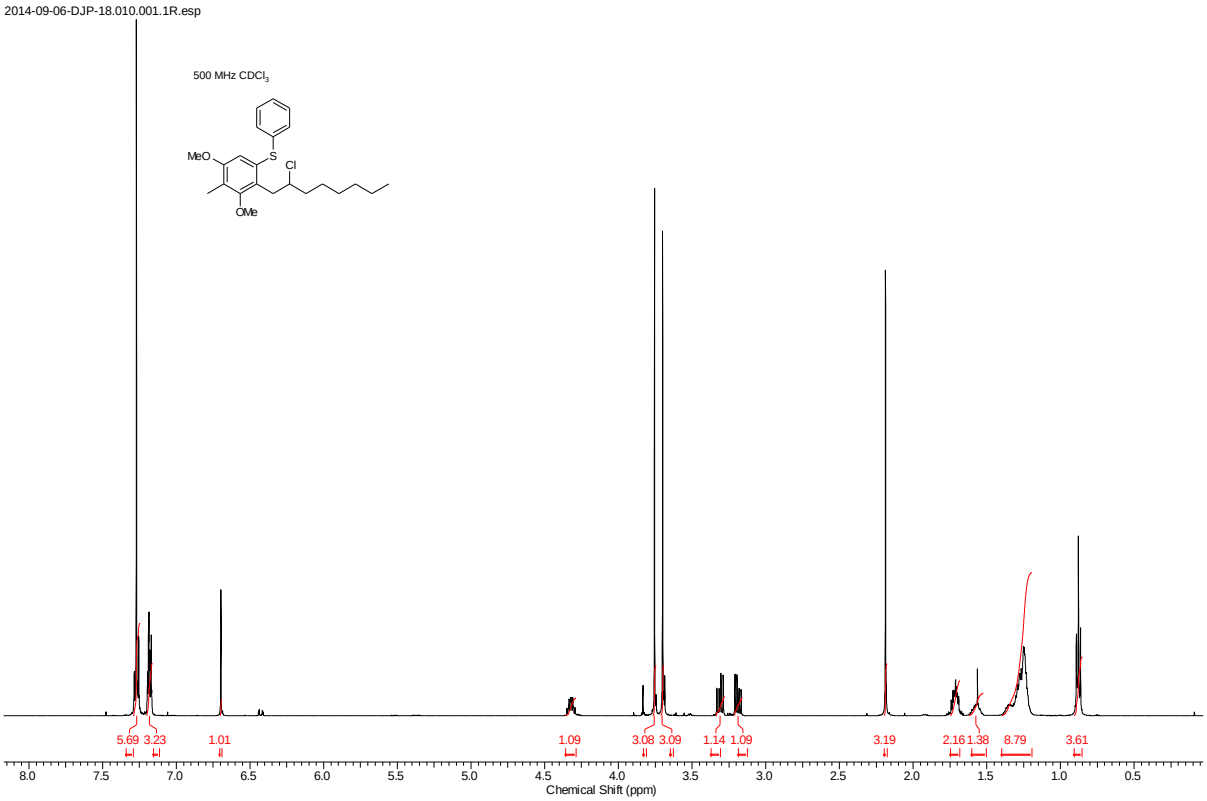



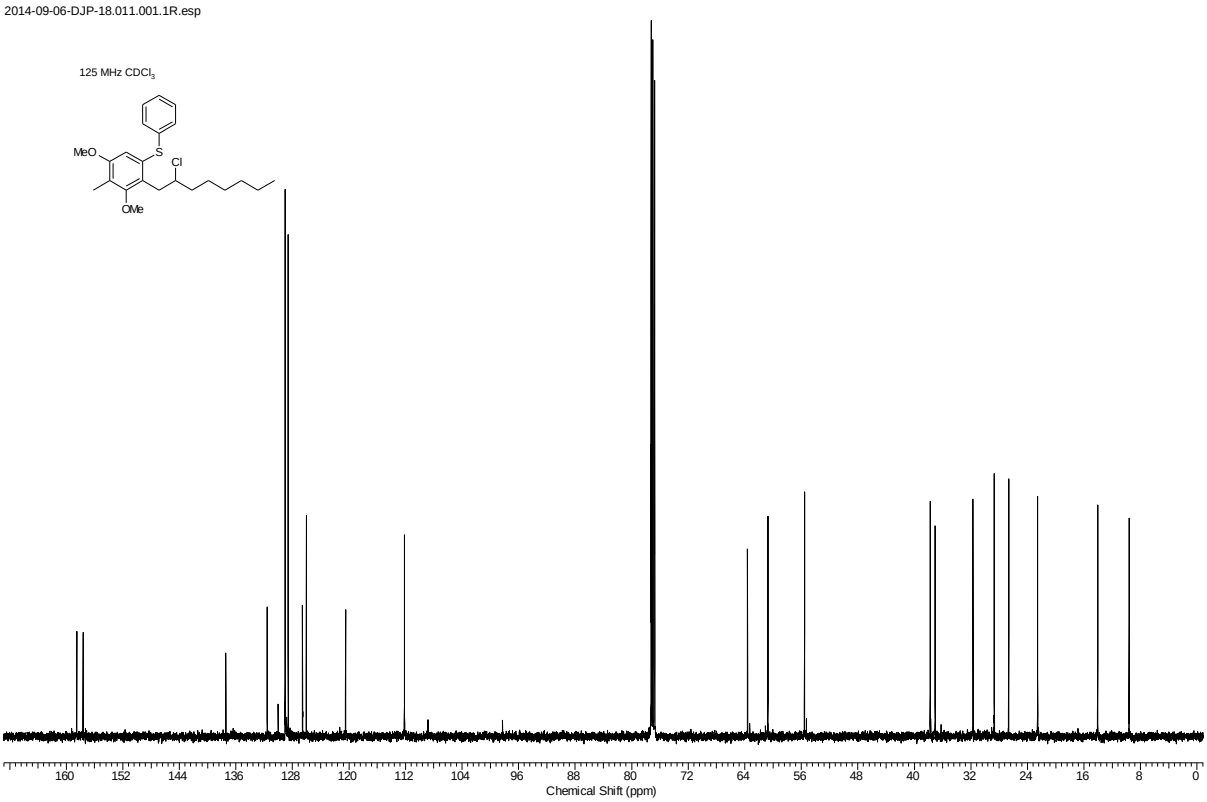
*(2-(2-Chlorooctyl)-4-iodo-3,5-dimethoxyphenyl)(phenyl)sulfide* ***3b***



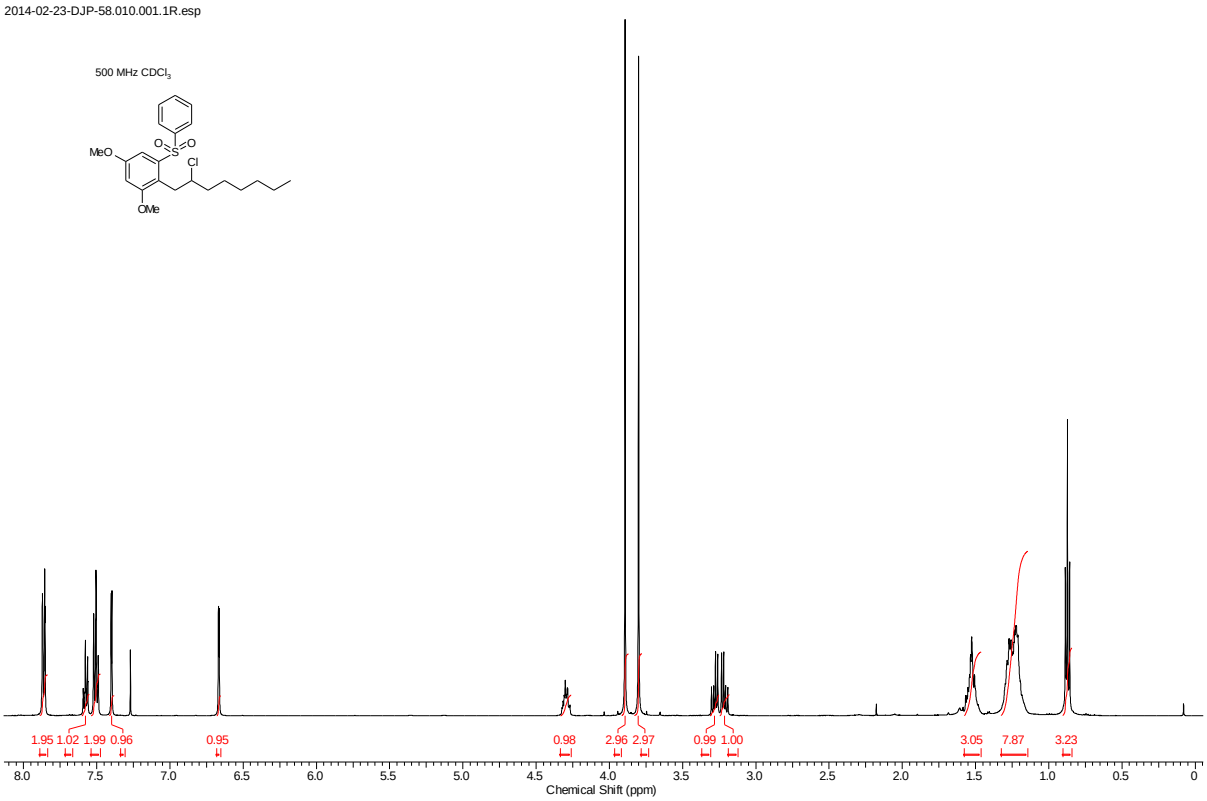



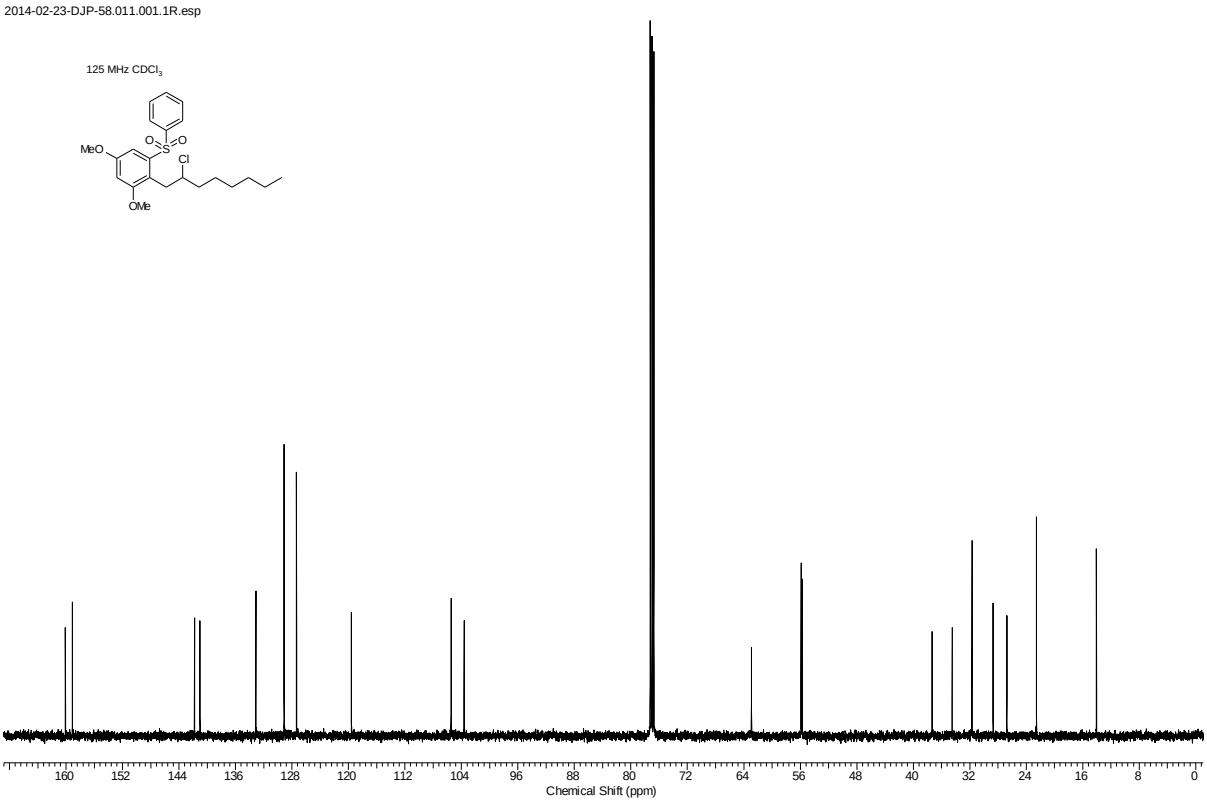
*(2-(2-Chlorooctyl)-3,5-dimethoxy-4-methylphenyl)(phenyl)sulfide* ***3c***



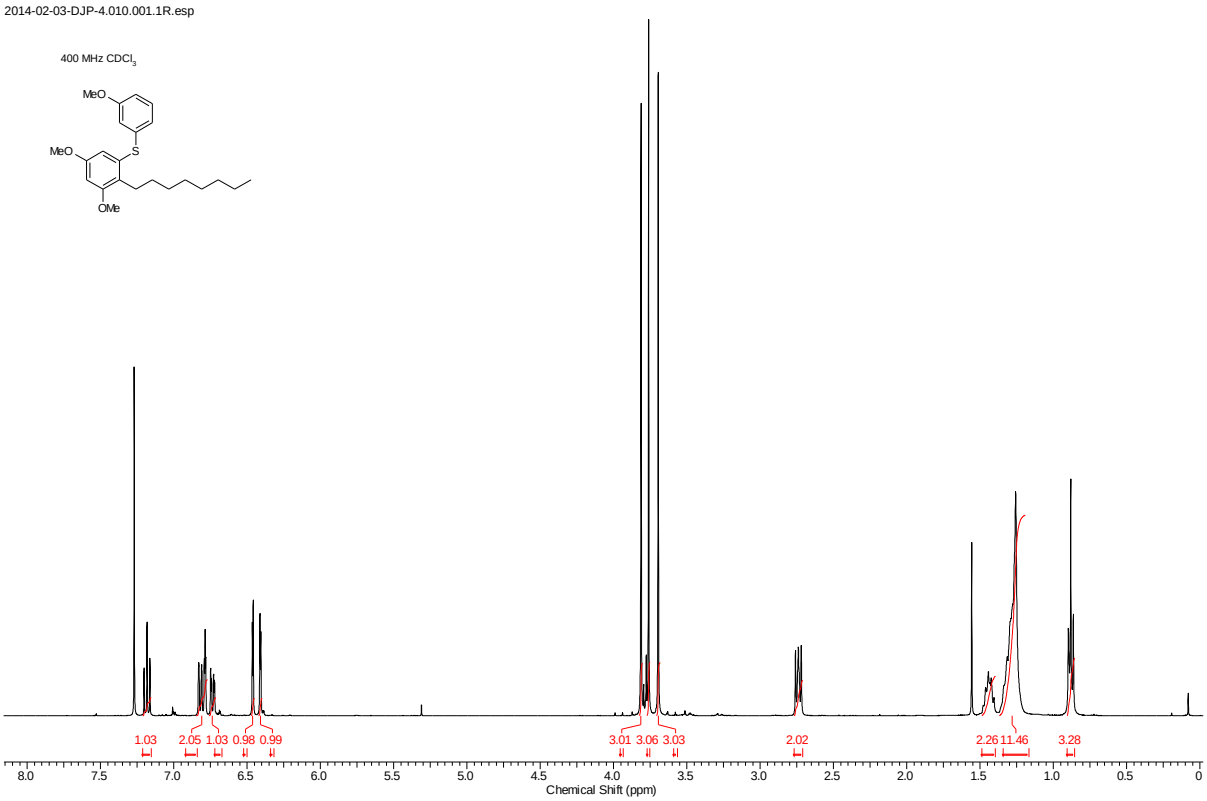



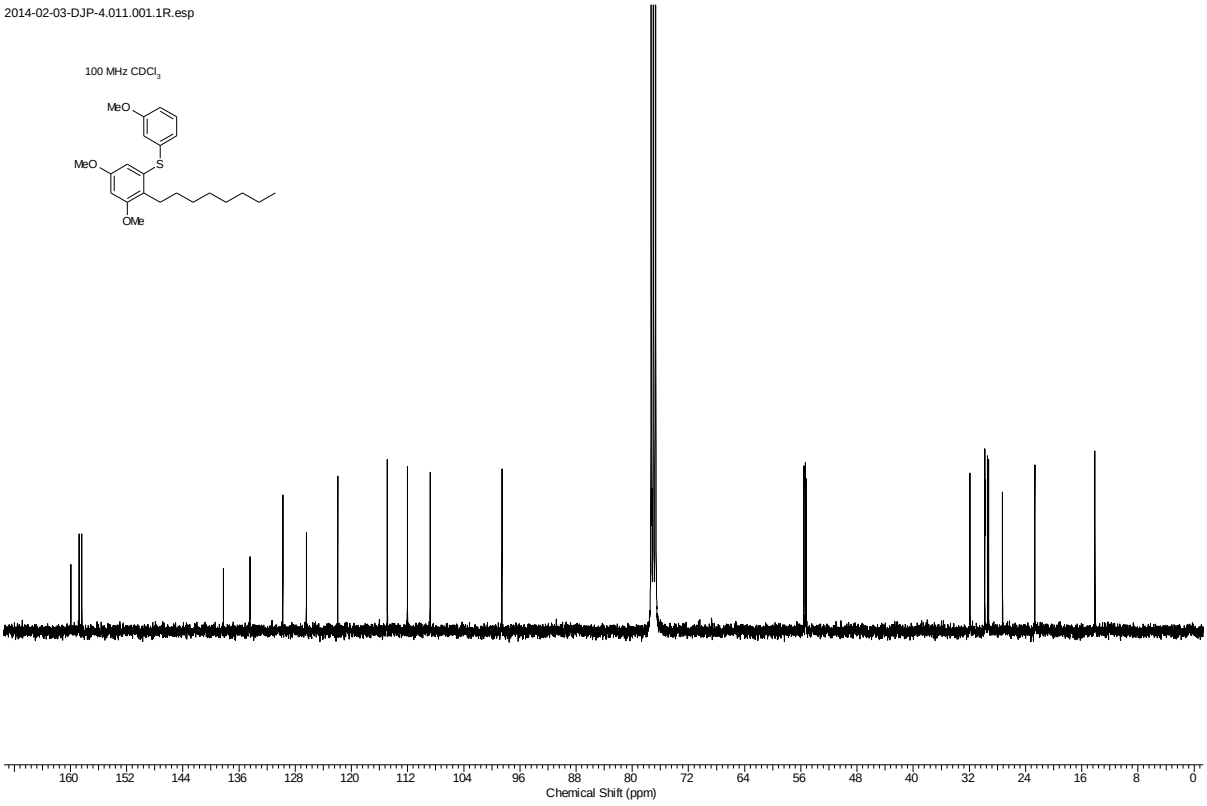
## *2-(2-Chlorooctyl)-1,5-dimethoxy-3-(phenylsulfonyl)benzene* ***3d***



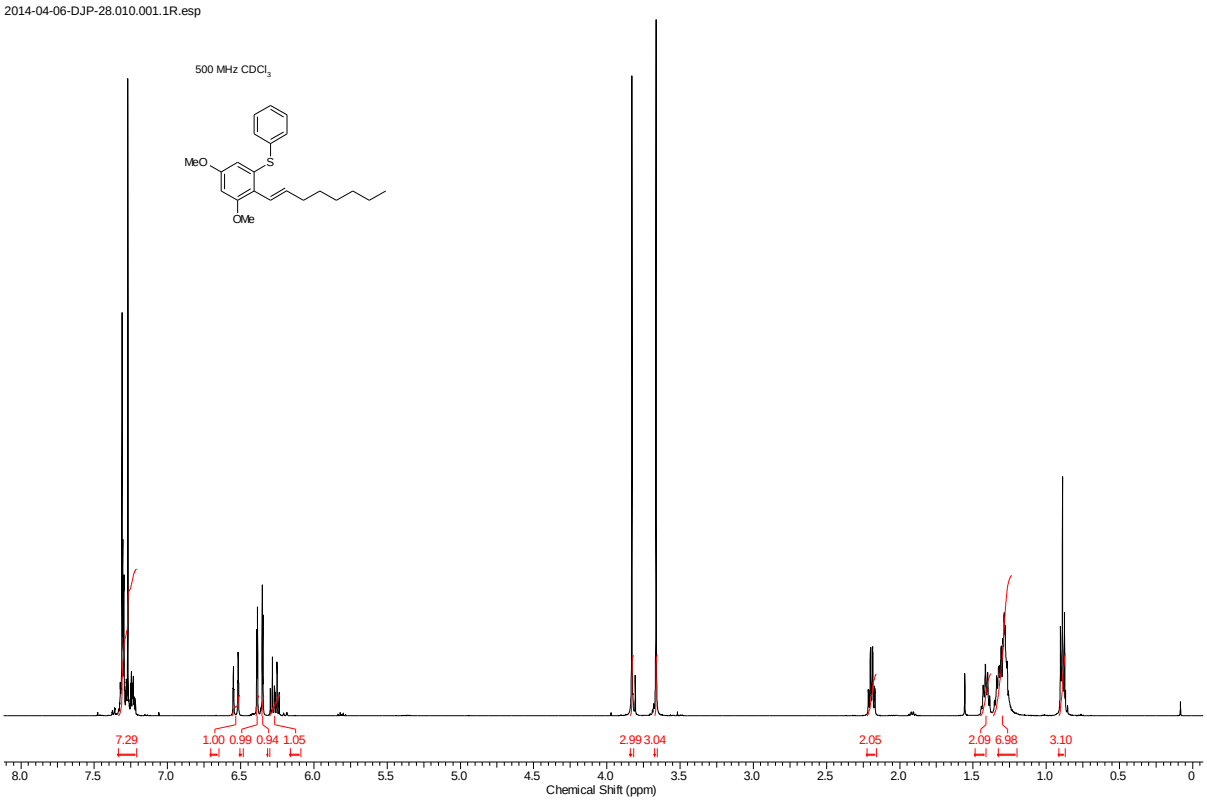



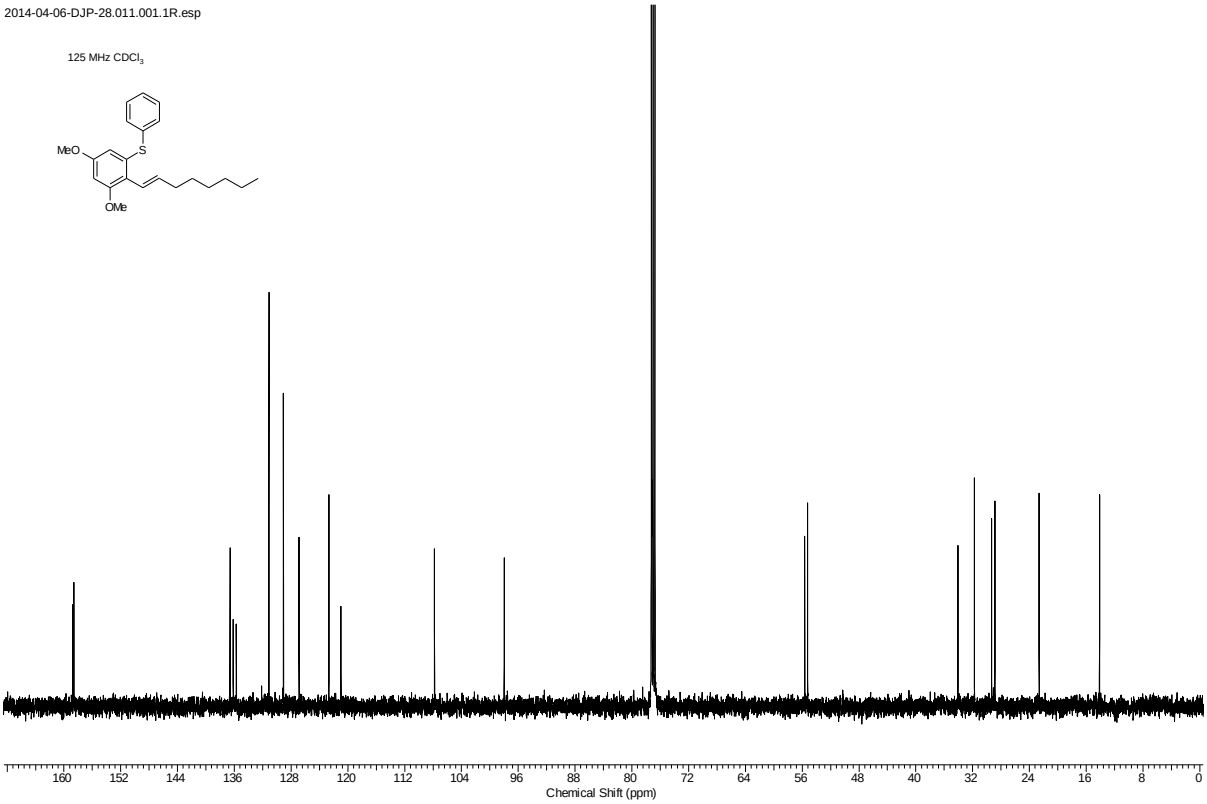
## *(3,5-Dimethoxy-2-octylphenyl)(3-methoxyphenyl)sulfide* ***3e***



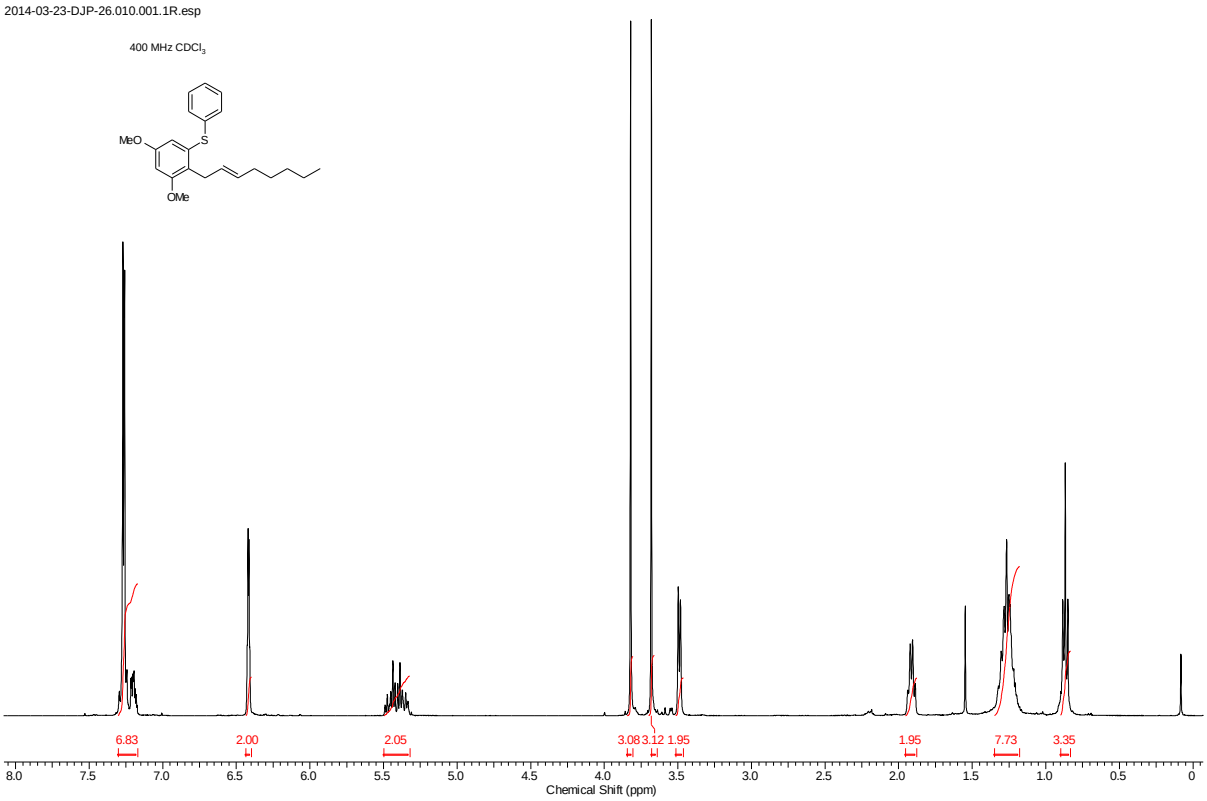



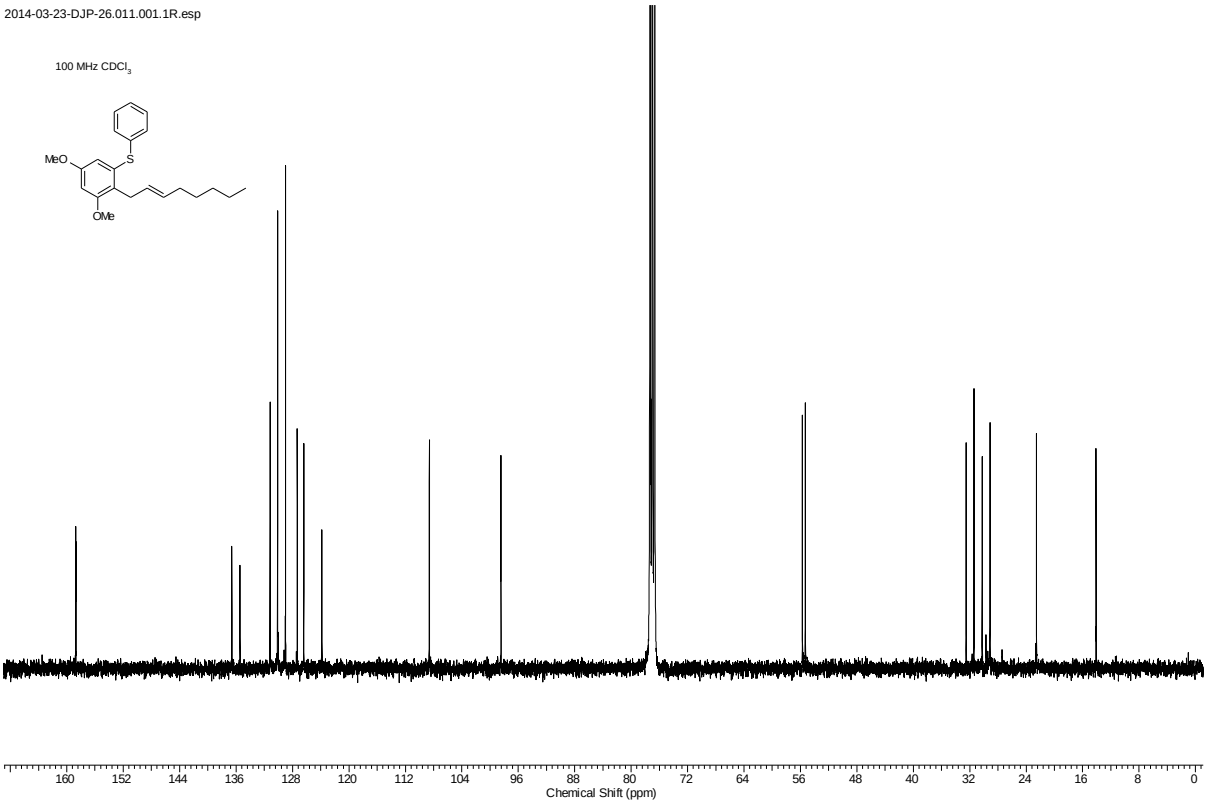
*(E)-(3,5-Dimethoxy-2-(oct-1-en-1-yl)phenyl)(phenyl)sulfide* ***3f***



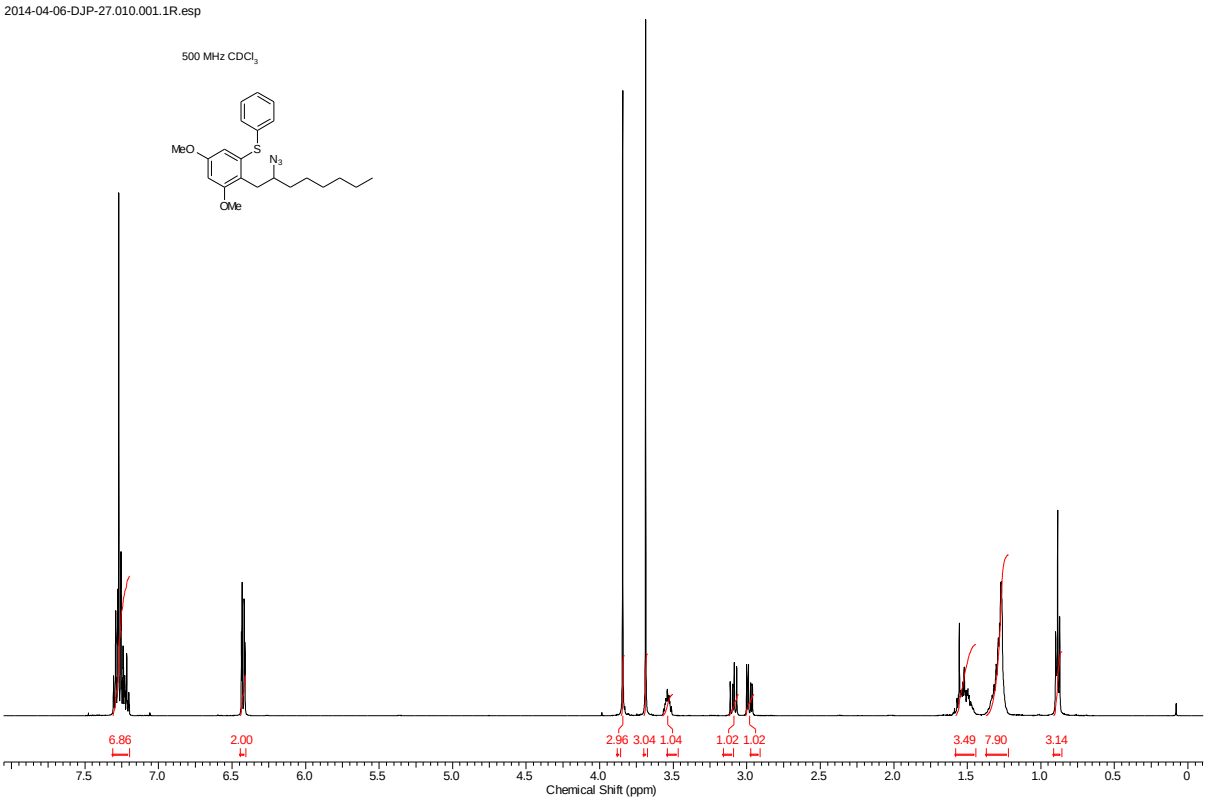



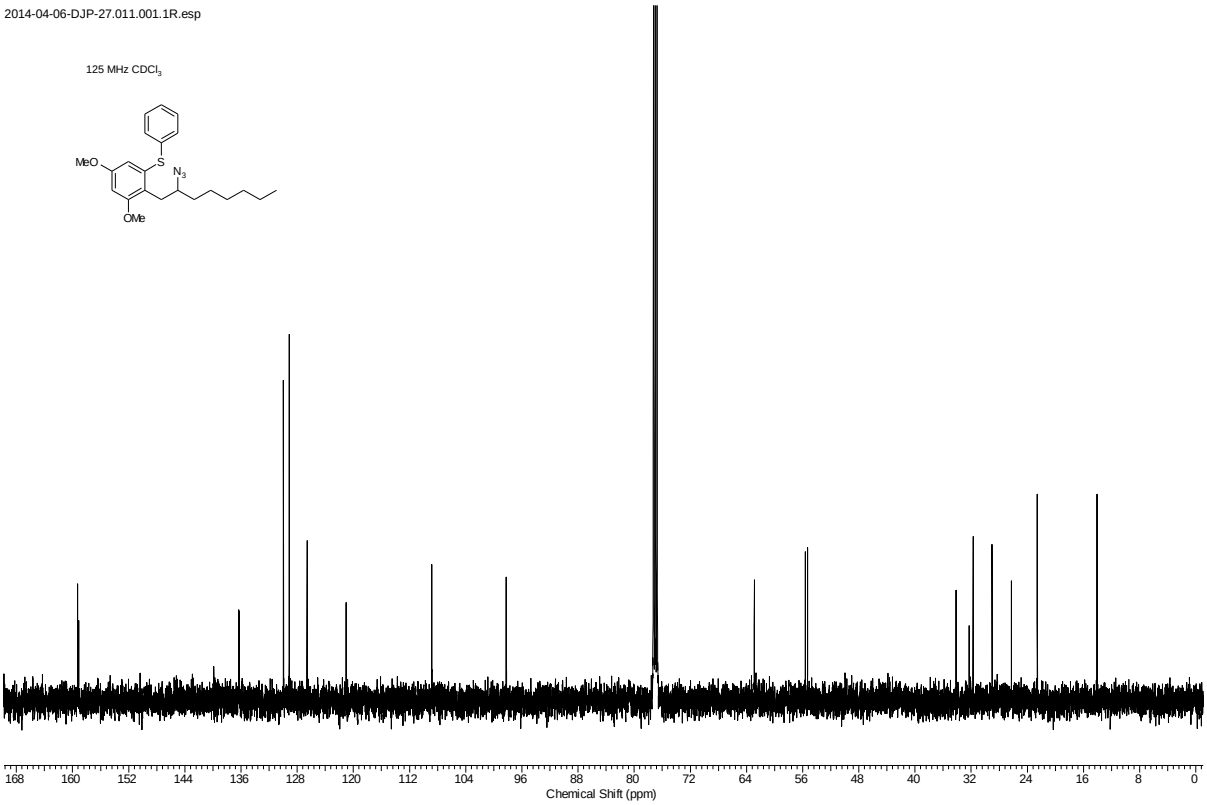
*(E)-(3,5-Dimethoxy-2-(oct-2-en-1-yl)phenyl)(phenyl)sulfide*



*(2-(2-Azidooctyl)-3,5-dimethoxyphenyl)(phenyl)sulfide* ***3g***



## *2-Hexyl-4-(phenylsulfanyl)-2,3-dihydrobenzofuran-6-ol* ***3h***