

# CHEMISTRY

## A **European** Journal

### Supporting Information

#### **Sulfoxide-Directed Metal-Free *ortho*-Propargylation of Aromatics and Heteroaromatics**

Andrew J. Eberhart, Harry J. Shrives, Estela Álvarez, Amandine Carrër, Yuntong Zhang, and David J. Procter\*<sup>[a]</sup>

chem\_201406424\_sm\_miscellaneous\_information.pdf

## Supporting Information

### Contents

General Experimental .....	S2
General Procedure A Oxidation of Sulfides .....	S3
General Procedure B Preparation of 1,3- <i>bis</i> propargyl silanes.....	S7
General Procedure C Preparation of Propargyl Silanes .....	S10
Propargylation of Heterocycles .....	S12
General Procedure D: Propargylation of Aryl Sulfoxides .....	S20
Iterative, selective <i>ortho</i> -propargylation of 4-methoxyphenylmethyl sulfide .....	S25
Iodine Mediated Cyclization .....	S26
1-(3-Methylbenzo[b]thiophen-2-yl)propan-1-one <b>7c</b> .....	S26
<sup>1</sup> H and <sup>13</sup> C NMR.....	S28

## General Experimental

All experiments were performed under an atmosphere of nitrogen, using anhydrous solvents, unless stated otherwise. THF was distilled from sodium/benzophenone and CH<sub>2</sub>Cl<sub>2</sub> was distilled from CaH<sub>2</sub>. All other solvents and reagents were purchased from commercial sources and used as supplied.

<sup>1</sup>H NMR spectra were recorded on a 300, 400 or 500 MHz spectrometer. <sup>13</sup>C NMR spectra were recorded on a 75, 100 or 125 MHz spectrometer. All chemical shift values are reported in ppm, with coupling constants in Hz. Mass spectra were obtained using positive or negative electrospray (ES), electron ionization (EI), chemical ionization (CI) or gas chromatography-mass spectrometry methodology. Infra-red spectra were recorded as evaporated films or neat using FT/IR spectrometers.

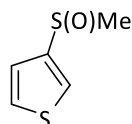
Melting points were measured on solids as obtained after chromatography. Column chromatography was carried out using 35 – 70 μ, 60Å silica gel. Routine TLC analysis was carried out on silica gel 60 F254 coated aluminium sheets of 0.2 mm thickness. Plates were viewed using a 254 nm ultraviolet lamp and developed by dipping in aqueous potassium permanganate solution.

Details for the preparation of all compounds (and associated characterization data) in table 2, compounds **2b-g**, **3al-p** and **3as** can be found in: A. J. Eberhart; D.J. Procter, *Angew. Chem. Int. Ed.*, **2013**, *52*, 4008.

For the preparation of compound **1ai** please see: A. J. Eberhart; J. E. Imbriglio, J. E.; D. J. Procter, *Org. Lett.*, **2011**, *13*, 5882-5885

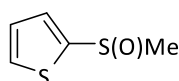
## General Procedure A Oxidation of Sulfides

### 3-(Methylsulfinyl)thiophene **1ab**<sup>1</sup>



To a solution of 3-(methylthio)thiophene (1.07 g, 8.25 mmol) in dichloromethane (8.25 mL, 1 M) at 0 °C, was added dropwise a solution of *m*-CPBA (1.99 g, 8.25 mmol) in dichloromethane. The resulting mixture was stirred at 0 °C for 1 hour before warming to room temperature after which it was stirred for a further 1 hour. The reaction was quenched with sat. NaHCO<sub>3</sub> solution (10 mL) and the layers separated. The aqueous layer was washed with dichloromethane (3 x 5 mL) and the combined organic layers dried with MgSO<sub>4</sub> and the solvent removed *in vacuo*. The resulting crude mixture was purified by column chromatography eluting with chloroform: ethyl acetate (95:5) to give **1ab** as a clear oil (1.17 g, 7.65 mmol 92 %);  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>) 7.74 (1 H, dd,  $J = 2.9, 1.2$  Hz, ArC-*H*), 7.48 (1 H, dd,  $J = 5.1, 3.0$  Hz, ArC-*H*), 7.25 (1 H, dd,  $J = 5.3, 1.3$  Hz, ArC-*H*), 2.78 (3 H, s, S-CH<sub>3</sub>);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>) 144.6 (ArC), 128.5 (ArC-*H*), 125.4 (ArC-*H*), 122.6 (ArC-*H*), 42.8 (S-CH<sub>3</sub>);  $m/z$  (GCMS) 146.0; (measured 145.9856, C<sub>5</sub>H<sub>6</sub>O<sub>1</sub>S<sub>2</sub> requires 145.9855).

### 2-(Methylsulfinyl)thiophene **1ac**<sup>1</sup>

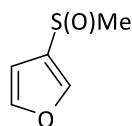


As described in General procedure **A**, to a solution of 2-(methylthio)thiophene (0.60 g, 4.60 mmol) in dichloromethane (5 mL, 1 M) at 0 °C, was added dropwise a solution of *m*-CPBA (0.79 g, 4.60 mmol) in dichloromethane. The resulting crude mixture was purified by column chromatography eluting with chloroform: ethyl acetate (95:5) to give **1ac** as a clear oil (0.37 g, 2.46 mmol 58 %);  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>) 7.62 (1 H, dd,  $J = 5.0, 1.2$  Hz, ArC-*H*), 7.45 (1 H, dd,  $J = 3.7, 1.2$  Hz, ArC-*H*), 7.09 (1 H, dd,  $J = 5.0, 3.7$  Hz, ArC-*H*), 2.89 (3 H, s, S-CH<sub>3</sub>);  $\delta_{\text{C}}$  (75 MHz,

<sup>1</sup>H. L. Hollan; C. D. Turner; P. R. Andreana; D. Nguyen *Can. J. Chem.*, **1999**, *77*, 463

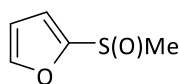
CDCl<sub>3</sub>) 147.55 (ArC), 131.15 (ArC-H), 129.62 (ArC-H), 127.72 (ArC-H), 44.73 (S-CH<sub>3</sub>); *m/z* (GCMS) 146.0; (measured 145.9855, C<sub>5</sub>H<sub>6</sub>O<sub>1</sub>S<sub>2</sub> requires 145.9855)

### 3-(Methylsulfinyl)furan **1ad**<sup>1</sup>



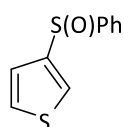
As described in General procedure **A**, to a solution of 3-(methylthio)thiophene (0.09 g, 0.78 mmol) in dichloromethane (1 mL, 1 M) at 0 °C, was added dropwise a solution of *m*-CPBA (0.13 g, 0.78 mmol) in dichloromethane. The resulting crude mixture was purified by column chromatography eluting with chloroform: ethyl acetate (95:5) to give **1ad** as a clear oil (0.06 g, 0.53 mmol 67 %);  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>) 7.75 (1 H, dd, *J* = 1.4, 0.9 Hz, ArC-H), 7.50 (1 H, t, *J* = 1.8 Hz, ArC-H), 6.67 (1 H, dd, *J* = 2.0, 0.8 Hz, ArC-H), 2.76 (3 H, s, S-CH<sub>3</sub>); *m/z* (GCMS) 130.0; (measured 130.0078, C<sub>5</sub>H<sub>6</sub>O<sub>1</sub>S<sub>2</sub> requires 130.0083).

### 2-(methylsulfinyl)furan **1ae**<sup>1</sup>



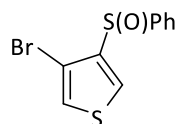
As described in General procedure **A**, to a solution of 2-(methylthio)thiophene (0.30 g, 2.63 mmol) in dichloromethane (2.6 mL, 1 M) at 0 °C, was added dropwise a solution of *m*-CPBA (0.43 g, 2.63 mmol) in dichloromethane. The resulting crude mixture was purified by column chromatography eluting with chloroform: ethyl acetate (95:5) to give **3ae** as a clear oil (0.26 g, 2.02 mmol 77 %);  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>) 7.59 - 7.67 (1 H, m, ArC-H), 6.92 (1 H, d, *J* = 3.4 Hz, ArC-H), 6.47 - 6.54 (1 H, m, ArC-H), 2.94 (3 H, s, S-CH<sub>3</sub>);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>) 152.8 (ArC), 146.7 (ArC-H), 115.2 (ArC-H), 111.4 (ArC-H), 38.6 (S-CH<sub>3</sub>); *m/z* (GCMS) 130.0; (measured 130.0079, C<sub>5</sub>H<sub>6</sub>O<sub>1</sub>S<sub>2</sub> requires 130.0083).

### 3-(Phenylsulfinyl)thiophene **1af**



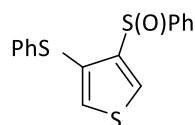
As described in General procedure **A**, to a solution of 3-(phenylthio)thiophene (0.60 g, 3.12 mmol) in dichloromethane (3 mL, 1 M) at 0 °C, was added dropwise a solution of *m*-CPBA (0.53 g, 3.12 mmol) in dichloromethane. The resulting crude mixture was purified by flash column chromatography eluting with chloroform: ethyl acetate (95:5) to give **1af** as a clear oil (0.37 g, 1.87 mmol 60 %);  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$  3110, 3078, 1474, 1444, 1412, 1304, 1196, 1095, 1080, 1036, 999, 988, 971, 894, 803, 745, 684, 625;  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ) 7.07 (1H, dd, *J* 5.1, 1.2 Hz, HetAr-*H*), 7.39 (1H, dd, *J* 5.1, 3.0 Hz, HetAr-*H*), 7.45 – 7.55 (3H, m, Ar-*H*), 7.61 – 7.69 (2H, m, Ar-*H*), 7.79 (1H, dd, *J* 3.0, 1.2 Hz, HetAr-*H*);  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ) 124.1 (ArCH), 124.6 (2 × ArCH), 127.2 (ArCH), 128.3 (ArCH), 129.2 (2 × ArCH), 131.0 (ArCH), 144.6 (ArC), 144.7 (ArC); *m/z* (GCMS) 208.0; (measured 208.0006,  $\text{C}_{10}\text{H}_8\text{O}_1\text{S}_2$  requires 208.0011).

### 3-Bromo-4-(phenylsulfinyl)thiophene **1ag**



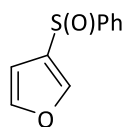
As described in General procedure **A**, to a solution of 4-bromo-3-(phenylthio)thiophene (0.27 g, 1.02 mmol) in dichloromethane (1 mL, 1 M) at 0 °C, was added dropwise a solution of *m*-CPBA (0.17 g, 1.02 mmol) in dichloromethane. The resulting crude mixture was purified by flash column chromatography eluting with chloroform: ethyl acetate (95:5) to give **1ag** as a clear oil (0.20 g, 0.75 mmol 74 %);  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$  3064, 1580, 1474, 1442, 1399, 1330, 1157, 1099, 1079, 1038, 997, 924, 844, 800, 747, 684, 626, 547;  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 7.36 (1H, d, *J* 3.5 Hz, HetAr-*H*), 7.47 – 7.53 (3H, m, Ar-*H*), 7.74 – 7.79 (2H, m, Ar-*H*), 7.86 (1H, d, *J* 3.5 Hz, HetAr-*H*);  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 107.2 (ArC), 125.7 (ArCH), 125.9 (ArCH), 127.9 (2 × ArCH), 129.2 (2 × ArCH), 131.6 (ArCH), 143.3 (ArC), 143.5 (ArC); *m/z* (GCMS) 287.9; (measured 285.9919,  $\text{C}_{10}\text{H}_7\text{O}_1\text{Br}_1\text{S}_2$  requires 285.9116).

### 3-(Phenylsulfinyl)-4-(phenylthio)thiophene **1ah**



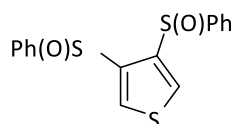
As described in General procedure **A**, to a solution of 3,4-bis(phenylthio)thiophene (0.40 g, 1.36 mmol) in dichloromethane (1.3 mL, 1 M) at 0 °C, was added dropwise a solution of *m*-CPBA (0.23 g, 1.36 mmol) in dichloromethane. The resulting crude mixture was purified by flash column chromatography eluting with chloroform: ethyl acetate (95:5) to give **1ah** as a clear oil (0.10 g, 0.34 mmol 25 %);  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$  3064, 2033, 1477, 1438, 1110, 1078, 1037, 857, 837, 749, 735;  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 7.00 – 7.05 (2H, m, Ar-*H*), 7.13 – 7.22 (3H, m, Ar-*H*), 7.34 – 7.43 (3H, m, Ar-*H*), 7.47 (1H, d, *J* 3.4 Hz, HetAr-*H*), 7.65 – 7.70 (2H, m, Ar-*H*), 7.99 (1H, d, *J* 3.4 Hz, HetAr-*H*);  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 125.6 (2 × ArCH), 126.3 (ArC), 126.4 (ArCH), 127.9 (ArCH), 127.9 (2 × ArCH), 129.0 (2 × ArCH), 129.0 (2 × ArCH), 131.2 (ArCH), 132.9 (CH), 135.5 (C), 143.9 (C), 146.4 (C); *m/z* (GCMS) 316.0; (measured 316.0039,  $\text{C}_{16}\text{H}_{12}\text{O}_1\text{S}_3$  requires 316.0045).

### 3-(Phenylsulfinyl)furan **1aj**



As described in General procedure **A**, to a solution of 3-(phenylthio)furan (0.41 g, 2.36 mmol) in dichloromethane (2.36 mL, 1 M) at 0 °C, was added dropwise a solution of *m*-CPBA (0.57 g, 2.36 mmol) in dichloromethane. The resulting crude mixture was purified by flash column chromatography eluting with chloroform: ethyl acetate (95:5) to give **1aj** as a clear oil (0.34 g, 1.77 mmol 75 %);  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$  3180, 1580, 1498, 1443, 1201, 1133, 1084, 1021, 934, 852, 746, 687, 597;  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ) 6.40 (1H, dd, *J* 2.0, 0.8 Hz, HetAr-*H*), 7.42 – 7.47 (1H, m, HetAr-*H*), 7.48 – 7.56 (3H, m, Ar-*H*), 7.63 – 7.71 (2H, m, Ar-*H*), 7.81 (1H, dd, *J* 1.5, 0.8 Hz, HetAr-*H*);  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ) 107.3 (ArCH), 124.4 (2 × ArCH), 124.4 (ArC), 129.1 (2 × ArCH), 130.9 (ArCH), 143.7 (ArC), 144.1 (ArCH), 144.9 (ArCH); *m/z* (GCMS) 192.0; (measured 192.0233,  $\text{C}_{10}\text{H}_8\text{O}_2\text{S}_1$  requires 192.0240).

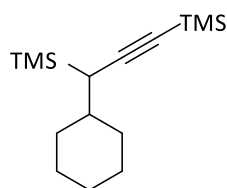
### 3,4-bis(Phenylsulfinyl)thiophene **1ak**



As described in General procedure **A**, to a solution of 3,4-*bis*(phenylthio)thiophene (0.40 g, 1.36 mmol) in dichloromethane (1.3 mL, 1 M) at 0 °C, was added dropwise a solution of *m*-CPBA (0.23 g, 1.36 mmol) in dichloromethane. The resulting crude mixture was purified by flash column chromatography eluting with hexane: ethyl acetate (3:1) to give **1ak** as a mixture of diastereo-isomers and a clear oil (0.15 g, 0.45 mmol 33 %);  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$  3054, 2133, 1428, 1438, 1210, 1028, 1012, 849, 837, 779, 730;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.36 – 7.52 (6H, m, Ar-*H*), 7.57 – 7.70 (4H, m, Ar-*H*), 7.81 (1H, s, Ar-*H*), 7.85 (1H, s, Ar-*H*);  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 125.2 (2 × ArCH), 125.4 (2 × ArCH), 129.1 (2 × ArCH), 129.3 (2 × ArCH), 129.3 (ArCH), 130.0 (ArCH), 131.3 (ArCH), 131.6 (ArCH), 142.6 (ArC), 143.2 (ArC), 143.3 (ArC), 143.7 (ArC);  $m/z$  (GCMS) 332.0; (measured 331.9981,  $\text{C}_{16}\text{H}_{12}\text{O}_2\text{S}_3$  requires 331.9994).

### General Procedure B Preparation of 1,3-*bis* propargyl silanes

#### (1,3-*bis*(Trimethylsilyl))-3-cyclohexyl-prop-1-yne **2l**<sup>2</sup>



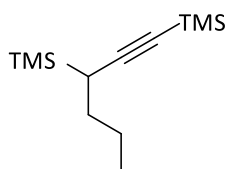
To a solution of 3-cyclohexyl-1-propyne (5 mmol, 0.89 ml) in THF (1 M, 5 ml) under nitrogen at -78 °C was added *n*-butyllithium (1.6 M in hexanes, 5.25 mmol, 3.28 ml). The mixture was stirred at -78 °C for 30 min before chlorotrimethylsilane (5.5 mmol, 0.69 ml) was added. The resultant white slurry was warmed to room temperature where it was maintained for 1 hour, after which it was cooled to -40 °C and treated with *t*-butyllithium (1.7 M in pentane, 5.5 mmol, 3.23 ml). The yellow solution formed was then stirred at -40 °C for 2 hours before addition of chlorotrimethylsilane (6 mmol, 0.76 ml). The reaction mixture was then allowed to warm to room temperature and was stirred for a further 1 hour before quenching the reaction with water (15 ml). The layers were separated and the organic layer extracted with diethyl ether (3 × 10 ml). The solution was then dried with  $\text{MgSO}_4$  and the solvent

<sup>2</sup> S. Rajagopalan; G. Zweifel, *Synthesis*, **1984**, 2, 111-112



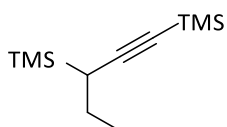
removed *in vacuo*. The crude product was purified using column chromatography on silica gel using 100% hexane as the eluent to give **2k** as a clear oil (0.153 g, 3.2 mmol, 64%);  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$  2926, 2852, 2147, 1889, 1656, 1449, 1247, 1053, 834, 757, 731, 693, 643;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 0.11 (9H, s,  $\text{Si}(\text{CH}_3)_3$ ), 0.14 (9H, s,  $\text{Si}(\text{CH}_3)_3$ ), 1.09-1.49 (7H, m, cyclohexyl 7 x CH), 1.55-1.64 (2H, m, cyclohexyl 2 x CH), 1.67 (1H, d,  $J = 4.5$ , Si-CH), 1.71-1.74 (2H, m, cyclohexyl 2 x CH);  $\delta_{\text{C}}$  (125 MHz) -1.8 ( $\text{Si}(\text{CH}_3)_3$ ), 0.4 ( $\text{Si}(\text{CH}_3)_3$ ), 26.0 (cyclohexyl- $\text{CH}_2$ ), 26.5 (cyclohexyl- $\text{CH}_2$ ), 26.6 (cyclohexyl- $\text{CH}_2$ ), 29.2 (cyclohexyl- $\text{CH}_2$ ), 31.0 (cyclohexyl- $\text{CH}_2$ ), 34.1 (cyclohexyl-CH), 37.7 (Si-CH), 86.2 (CCSi), 108.5 (CCSi);  $m/z$  (GCMS) 266.1.

### (1,3-bis(trimethylsilyl))-pent-1-yne **2h**<sup>2</sup>



As described in general procedure **B**, to 1-hexyne (0.814 g, 10 mmol) was added *n*-BuLi (3.28 ml, 5.25 mmol), chlorotrimethylsilane (0.69 ml, 5.5 mmol), *t*-BuLi (3.23 ml, 5.5 mmol) and chlorotrimethylsilane (0.76 ml, 6.0 mmol). Purification by flash column chromatography using *n*-hexane as eluent gave **2h** (2.10 g, 9.29 mmol, 93 %) as a clear oil.  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$  2957, 2155, 1465, 1247, 1138, 1053, 962, 832, 757, 695, 636, 617;  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 0.08 (9H, s,  $\text{Si}(\text{CH}_3)_3$ ), 0.13 (9H, s,  $\text{Si}(\text{CH}_3)_3$ ), 0.92 (3H, t,  $J = 7.0$  Hz,  $\text{CH}_3$ ), 1.32 – 1.45 (3H, m), 1.62 – 1.71 (2H, m);  $\delta_{\text{C}}$  (125 MHz) -3.6 ( $\text{Si}(\text{CH}_3)_3$ ), 0.0 ( $\text{Si}(\text{CH}_3)_3$ ), 13.4 ( $\text{CH}_3$ ), 20.8 ( $\text{CH}_2$ ), 22.3 ( $\text{CH}_2$ ), 30.8 (CH), 84.0 (CC-Si), 109.7 (CC-Si);  $m/z$  (GCMS), 226.2.

### (1,3-bis(trimethylsilyl))-pent-1-yne **2i**<sup>3</sup>

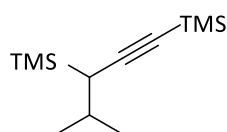


As described in general procedure **B**, to pent-1-yne (0.98 ml, 10 mmol) was added *n*-BuLi (6.56 ml, 10.5 mmol), chlorotrimethylsilane (1.38 ml, 11 mmol), *t*-BuLi (6.46 ml, 11 mmol) and chlorotrimethylsilane (1.52 ml, 12 mmol). Purification by flash column chromatography

<sup>3</sup> T. P. Lockhart; P. B. Comita; R. G. Bergman, *J. Am. Chem. Soc.*, **1981**, 103, 14, 4082-4090

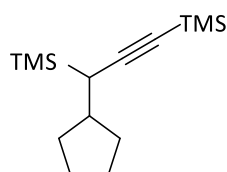
using *n*-hexane as eluent gave **2i** (0.53 g, 35 %) as a clear oil that gradually turned to clear pink on exposure to air.  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$  2958, 2151, 1406, 1248, 1146, 1067, 1027, 984, 896, 833, 757, 696, 658, 636;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 0.08 (9H, s,  $\text{Si}(\text{CH}_3)_3$ ), 0.14 (9H, s,  $\text{Si}(\text{CH}_3)_3$ ), 1.07 (3H, t,  $J = 7.2$ ,  $\text{CH}_3$ ), 1.35-1.55 (2H, m,  $\text{CH}_2$ ), 1.58-1.61 (1H, m, CH);  $\delta_{\text{C}}$  (125 MHz) -3.5 ( $\text{Si}(\text{CH}_3)_3$ ), 0.0 ( $\text{Si}(\text{CH}_3)_3$ ), 13.9 ( $\text{CH}_3$ ), 22.0 (CH), 23.1 ( $\text{CH}_2$ ), 84.3 (CC-Si), 109.6 (CC-Si);  $m/z$  (GCMS), 212.2.

### (1,3-bis(Trimethylsilyl))-4-methyl-pent-1-yne **2j**



As described in general procedure **B**, to 4-methyl-1-pentyne (0.59 ml, 5 mmol) was added *n*-BuLi (3.28 ml, 5.25 mmol), chlorotrimethylsilane (0.69 ml, 5.5 mmol), *t*-BuLi (3.23 ml, 5.5 mmol) and chlorotrimethylsilane (0.76 ml, 6.0 mmol). Purification by flash column chromatography using *n*-hexane as eluent gave **2j** (0.63 g, 2.84 mmol, 57 %) as a clear oil.  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$  2972, 2359, 2342, 1159, 1104, 950, 627, 595, 555, 538;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 0.11 (9H, s,  $\text{Si}(\text{CH}_3)_3$ ), 0.14 (9H, s,  $\text{Si}(\text{CH}_3)_3$ ), 0.98 (3H, d,  $J = 6.7$ ,  $\text{CH}_3$ ), 1.04 (3H, d,  $J = 6.6$ ,  $\text{CH}_3$ ), 1.69 (1H, d,  $J = 4.3$ ,  $\text{CH-Si}(\text{CH}_3)_3$ ), 1.86 (1H, m,  $\text{CH}(\text{CH}_3)_2$ );  $\delta_{\text{C}}$  (125 MHz) 0.0 ( $\text{Si}(\text{CH}_3)_3$ ), 2.4 ( $\text{Si}(\text{CH}_3)_3$ ), 22.4 ( $\text{CH-Si}(\text{CH}_3)_3$ ), 26.0 ( $\text{CH}_3$ ), 29.9 ( $\text{CH}_3$ ), 31.9 ( $\text{CH}(\text{CH}_3)_2$ ), 88.5 (CC-Si), 110.0 (CC-Si);  $m/z$  (GMCS), 226.1; (measured 226.1569  $\text{C}_{12}\text{H}_{26}\text{Si}_2$  requires 226.1573).

### (1,3-bis(Trimethylsilyl))-3-cyclopropyl-prop-1-yne **2k**

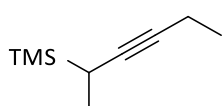


As described in general procedure **B**, to 3-cyclopentyl-1-propyne (0.65 ml, 5.0 mmol) was added *n*-BuLi (3.28 ml, 5.25 mmol), chlorotrimethylsilane (0.69 ml, 5.5 mmol), *t*-BuLi (3.23 ml, 5.5 mmol) and chlorotrimethylsilane (0.76 ml, 6.0 mmol). Purification by flash column chromatography using *n*-hexane as eluent gave **2k** (0.88 g, 4.92 mmol, 98 %) as a clear oil that gradually turned to clear pink on exposure to air.  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$  2954, 2151, 1247, 833, 757, 694, 644, 627;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 0.10 (9H, s,  $\text{Si}(\text{CH}_3)_3$ ), 0.14 (9H, s,  $\text{Si}(\text{CH}_3)_3$ ),

1.38-1.54 (4H, m, cyclopentyl 2 x CH<sub>2</sub>), 1.61-1.75 (4H, m, cyclopentyl 2 x CH<sub>2</sub>), 1.82 (1H, d, J = 5.5, CH-Si), 1.89-1.97 (1H, m, cyclopentyl CH);  $\delta_c$  (125 MHz) -1.9 (Si(CH<sub>3</sub>)<sub>3</sub>), 0.7 (Si(CH<sub>3</sub>)<sub>3</sub>), 25.7 (cyclopentyl CH<sub>2</sub>), 25.8 (cyclopentyl CH<sub>2</sub>), 30.9 (cyclopentyl CH<sub>2</sub>), 33.7 (cyclopentyl CH<sub>2</sub>), 39.6 (cyclopentyl CH), 85.5 (CCSi), 109.1 (CCSi);  $m/z$  (GCMS) 252.3; 25; (measured 252.1725 C<sub>14</sub>H<sub>28</sub>Si<sub>2</sub> requires 252.1729).

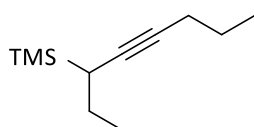
## General Procedure C Preparation of Propargyl Silanes

### 2-Trimethylsilyl-hex-3-yne 2m



To a solution of 4-octyne (0.56 ml, 5 mmol) in THF (1 M) under nitrogen at -40 °C was added *t*-BuLi (1.7 M in pentane, 3.23 ml, 5 mmol). The mixture was stirred at -40 °C for 2 hours before the addition of chlorotrimethylsilane (0.75 ml, 10 mmol). The reaction was then allowed to warm to room temperature and stirred for an additional hour before the addition of water 15 ml. The resultant layers were separated and the aqueous phase extracted with diethyl ether (3 x 15 ml) and the organic phases combined, dried with MgSO<sub>4</sub>, and the solvent removed *in vacuo*. The crude mixture was purified by flash column chromatography on silica gel using 100% hexane as the eluent to give **2m** as a clear oil (0.18 g, 1.2 mmol, 24 %);  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 2958, 1715, 1680, 1461, 1319, 1247, 1057, 1000, 970, 835, 753, 692, 642, 582;  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 0.06 (9H, s, Si(CH<sub>3</sub>)<sub>3</sub>), 1.10-1.14 (6H, m, 2 x CH<sub>3</sub>), 1.58-1.64 (1H, m, CH), 2.17 (2H, qd, J = 7.5, 2.6, CH<sub>2</sub>);  $\delta_c$  (125 MHz) -3.9 (Si(CH<sub>3</sub>)<sub>3</sub>), 12.3 (CH<sub>3</sub>), 12.5 (CH<sub>3</sub>), 14.4 (CH<sub>2</sub>), 14.7 (CH-Si), 80.7 (CC), 82.4 (CC);  $m/z$  (GCMS) 154.1; (measured 154.1172 C<sub>9</sub>H<sub>18</sub>Si<sub>1</sub> requires 154.1177).

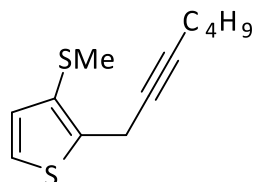
### 3-Trimethylsilyl-oct-4-yne 2n



As described in general procedure **C**, to 4-octyne (1.46 ml, 10 mmol) was added *t*-BuLi (6.46 ml, 5 mmol) and chlorotrimethylsilane (1.5 mL, 10 mmol). Purification by flash column chromatography using *n*-hexane as eluent gave **2n** (1.16 g, 6.4 mmol, 64 % yield) as a clear oil;  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$  2959, 2932, 2871, 1714, 1461, 1377, 1338, 1247, 1159, 1046, 836, 757, 692, 613, 572;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 0.07 (9H, s,  $\text{Si}(\text{CH}_3)_3$ ), 0.98 (3H, t,  $J = 7.4$ ,  $\text{CH}_3$ ), 1.07 (3H, t,  $J = 7.2$ ,  $\text{CH}_3$ ), 1.29-1.40 (1H, m,  $\text{CH}$ ), 1.47-1.54 (4H, m, 2 x  $\text{CH}_2$ ), 2.16 (2H, td,  $J = 6.9, 2.5$ ,  $\text{CH}_2$ );  $\delta_{\text{C}}$  (100 MHz) -3.1 ( $\text{Si}(\text{CH}_3)_3$ ), 13.5 ( $\text{CH}_3$ ), 14.4 ( $\text{CH}_3$ ), 21.0 ( $\text{CH}_2$ ), 21.9 ( $\text{CH}_2$ ), 22.8 ( $\text{CH}_2$ ), 22.9 ( $\text{CH-Si}$ ), 80.7 (CC), 81.7 (CC);  $m/z$  (GCMS) 182.2; (measured 182.1487  $\text{C}_{11}\text{H}_{22}\text{Si}_1$  requires 182.1490).

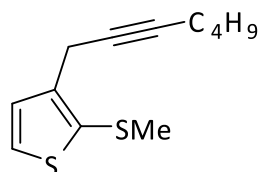
## Propargylation of Heterocycles

### 2-(Hept-2-ynyl)-3-(phenylthio)thiophene **3ab**



To an oven dried tube flushed with  $N_2$ , was added 3-(methylsulfinyl)thiophene (0.080 g, 0.54 mmol) and hept-2-yn-1-yltrimethylsilane (0.13 g, 0.81 mmol) in MeCN (3.3 mL). Trifluoroacetic anhydride was then added (0.19 mL, 1.35 mmol) at  $-40\text{ }^\circ\text{C}$  and the reaction was allowed to warm to room temperature over 18 hours. The solution was quenched with aqueous saturated  $\text{NaHCO}_3$  (6 mL) and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layer was dried ( $\text{MgSO}_4$ ) and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with 100% *n*-hexane to yield **3ab** as a colourless oil (0.10 g, 0.45 mmol, 84 %).  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$  2955, 2927, 2870, 1508, 1464, 1431, 1377, 1346, 1315, 1294, 1198, 1153, 1077, 969, 875, 853, 778, 704, 636, 572;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 0.92 (3H, t,  $J$  7.2 Hz,  $\text{CH}_3$ ), 1.38 – 1.55 (4H, m,  $\text{CH}_2\text{CH}_2$ ), 2.21 (2H, tt,  $J$  7.0, 2.4 Hz,  $\text{CCH}_2$ ), 2.38 (3H, s, S- $\text{CH}_3$ ), 3.77 (2H, t,  $J$  2.4 Hz, HetAr- $\text{CH}_2\text{C}$ ), 6.99 (1H, d,  $J$  5.3 Hz, HetAr- $H$ ), 7.17 (1H, d,  $J$  5.3 Hz, HetAr- $H$ );  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 13.6 ( $\text{CH}_3$ ), 18.4 ( $\text{CH}_2$ ), 18.9 ( $\text{CH}_3$ ), 18.9 ( $\text{CH}_2$ ), 21.9 ( $\text{CH}_2$ ), 30.8 ( $\text{CH}_2$ ), 76.9 (C), 82.4 (C), 122.9 (ArCH), 128.7 (ArC), 129.9 (ArCH), 139.7 (ArC);  $m/z$  (GCMS) 224.0; (measured 224.0689,  $\text{C}_{12}\text{H}_{16}\text{S}_2$  requires 224.0693).

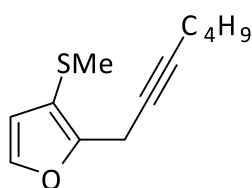
### 3-(Hept-2-yn-1-yl)-2-(methylthio)thiophene **3ac**



To an oven dried tube flushed with  $N_2$ , was added 2-(methylsulfinyl)thiophene (14.5 mg, 0.09 mmol) and hept-2-yn-1-yltrimethylsilane (25 mg, 0.13 mmol) in MeCN (3 mL). Trifluoroacetic anhydride was then added (0.03 mL, 0.25 mmol) at  $-40\text{ }^\circ\text{C}$  and the reaction

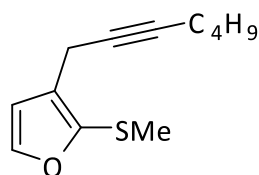
was allowed to warm to room temperature over 18 hours. The solution was quenched with aqueous saturated NaHCO<sub>3</sub> (6 mL) and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layer was dried (MgSO<sub>4</sub>) and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with 100% *n*-hexane to yield **3ac** as a colourless oil (0.06 g, 0.07 mmol, 74 %).  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 2955, 2922, 2858, 1728, 1523, 1464, 1420, 1377, 1312, 1216, 1093, 1020, 969, 877, 848, 831, 689, 651, 579;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 0.91 (3H, t, *J* 7.2 Hz, CH<sub>3</sub>), 1.33 – 1.55 (4H, m, CH<sub>2</sub>CH<sub>2</sub>), 2.19 (2H, tt, *J* 7.0, 2.4 Hz, CCH<sub>2</sub>), 2.39 (3H, s, S-CH<sub>3</sub>), 3.60 (2H, t, *J* 2.4 Hz, HetAr-CH<sub>2</sub>C), 7.12 (1H, d, *J* 5.4 Hz, HetAr-H), 7.28 (1H, d, *J* 5.4 Hz, HetAr-H);  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 13.6 (CH<sub>3</sub>), 18.5 (CH<sub>2</sub>), 19.0 (CH<sub>2</sub>), 21.9 (CH<sub>3</sub>), 21.9 (CH<sub>2</sub>), 31.0 (CH<sub>2</sub>), 77.4 (C), 81.5 (C), 127.1 (ArCH), 129.0 (ArCH), 130.6 (ArC), 141.4 (ArC); *m/z* (GCMS) 209.0 (M-CH<sub>3</sub>); (measured 225.0780, C<sub>12</sub>H<sub>17</sub>S<sub>2</sub> requires 225.0772).

### 2-(Hept-2-yn-1-yl)-3-(methylthio)furan **3ad**



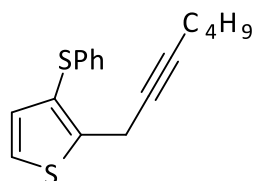
To an oven dried tube flushed with N<sub>2</sub>, was added 3-(methylsulfinyl)furan (0.057 g, 0.43 mmol) and hept-2-yn-1-yltrimethylsilane (0.11 g, 0.64 mmol) in MeCN (3 mL). Trifluoroacetic anhydride was then added (0.15 mL, 1.0 mmol) at -40 °C and the reaction was allowed to warm to room temperature over 18 hours. The solution was quenched with aqueous saturated NaHCO<sub>3</sub> (6 mL) and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layer was dried (MgSO<sub>4</sub>) and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with 100% *n*-hexane to yield **3ad** as a Colourless oil (0.077 g, 0.35 mmol, 82 %).  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 2956, 2928, 2871, 1771, 1582, 1465, 1378, 1248, 1193, 1054, 1006, 971, 988, 880, 728;  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>) 0.90 (3H, t, *J* 7.3 Hz, CH<sub>3</sub>), 1.34 – 1.44 (2H, m, CH<sub>2</sub>CH<sub>2</sub>), 1.44 – 1.52 (2H, m, CH<sub>2</sub>CH<sub>2</sub>), 2.17 (2H, tt, *J* 7.1, 2.4 Hz, CCH<sub>2</sub>), 2.30 (3H, s, S-CH<sub>3</sub>), 3.65 (2H, t, *J* 2.4 Hz, HetAr-CH<sub>2</sub>C), 6.39 (1H, d, *J* 1.9 Hz, HetAr-H), 7.34 (1H, d, *J* 1.9 Hz, HetAr-H);  $\delta_{\text{C}}$  (125 MHz, CDCl<sub>3</sub>) 13.6 (CH<sub>3</sub>), 16.7 (CH<sub>2</sub>), 18.4 (CH<sub>2</sub>), 19.3 (CH<sub>3</sub>), 21.9 (CH<sub>2</sub>), 30.9 (CH<sub>2</sub>), 74.4 (C), 81.5 (C), 113.0 (ArC), 114.0 (ArCH), 141.4 (ArCH), 151.4 (ArC); *m/z* (GCMS) 208.0; (measured 208.0906 C<sub>12</sub>H<sub>16</sub>O<sub>1</sub>S<sub>1</sub> requires 208.0916).

### 3-(Hept-2-yn-1-yl)-2-(methylthio)furan **3ae**



To an oven dried tube flushed with  $N_2$ , was added 2-(methylsulfinyl)furan (0.059 g, 0.45 mmol) and hept-2-yn-1-yltrimethylsilane (0.11 g, 0.67 mmol) in MeCN (3 mL). Trifluoroacetic anhydride was then added (0.16 mL, 1.12 mmol) at  $-40\text{ }^\circ\text{C}$  and the reaction was allowed to warm to room temperature over 18 hours. The solution was quenched with aqueous saturated  $\text{NaHCO}_3$  (6 mL) and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layer was dried ( $\text{MgSO}_4$ ) and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with 100% *n*-hexane to yield **3ae** as a colourless oil (0.082 g, 0.41 mmol, 92 %).  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$  2933, 1685, 1574, 1467, 1425, 1390, 1321, 1250, 1196, 1144, 1064, 996, 900, 884, 859, 755, 649;  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ) 0.91 (3H, t,  $J$  7.2 Hz,  $\text{CH}_3$ ), 1.31 – 1.56 (4H, m  $\text{CH}_2\text{CH}_2$ ), 2.18 (2H, tt,  $J$  6.9, 2.4 Hz,  $\text{CCH}_2$ ), 2.33 (3H, s, S- $\text{CH}_3$ ), 3.40 (2H, t,  $J$  2.4 Hz, HetAr- $\text{CH}_2\text{C}$ ), 6.48 (1H, d,  $J$  2.0 Hz, HetAr- $H$ ), 7.44 (1H, d,  $J$  2.0 Hz, HetAr- $H$ );  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ) 13.6 ( $\text{CH}_3$ ), 16.0 ( $\text{CH}_2$ ), 18.4 ( $\text{CH}_2$ ), 18.9 ( $\text{CH}_3$ ), 21.9 ( $\text{CH}_2$ ), 31.0 ( $\text{CH}_2$ ), 77.1 (C), 81.0 (C), 112.4 (ArCH), 126.4 (ArC), 142.9 (ArC), 144.4 (ArCH);  $m/z$  (GCMS) 208.0; (measured 208.0910  $\text{C}_{12}\text{H}_{16}\text{O}_1\text{S}_1$  requires 208.0916).

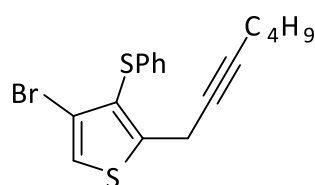
### 2-(Hept-2-yn-1-yl)-3-(phenylthio)thiophene **3af**



To an oven dried-tube flushed with  $N_2$ , was added 3-(phenylsulfinyl)thiophene (0.087 g, 0.41 mmol) and hept-2-yn-1-yltrimethylsilane (0.10 g, 0.62 mmol) in MeCN (3 mL). Trifluoroacetic anhydride was then added (0.14 mL, 1.0 mmol) at room temperature and the reaction was stirred for 2 hours. The solution was quenched with aqueous saturated  $\text{NaHCO}_3$  (6 mL) and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layer was

dried ( $\text{MgSO}_4$ ) and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with 100% *n*-hexane to yield **3af** as a colourless oil (0.11 g, 0.38 mmol, 93 %).  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$  3072, 2955, 2929, 2870, 1661, 1581, 1521, 1439, 1398, 1297, 1218, 1135, 1080, 1023, 998, 832, 737, 688;  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ) 0.92 (3H, t,  $J$  7.2 Hz,  $\text{CH}_3$ ), 1.33 – 1.54 (4H, m,  $\text{CH}_2\text{CH}_2$ ), 2.19 (2H, tt,  $J$  6.8, 2.4 Hz,  $\text{CCH}_2$ ), 3.77 (2H, t,  $J$  2.4 Hz, HetAr- $\text{CH}_2\text{C}$ ), 6.99 (1H, d,  $J$  5.2 Hz, HetAr- $H$ ), 7.03 – 7.16 (3H, m, Ar- $H$ ), 7.24 (1H, d,  $J$  5.2 Hz, HetAr- $H$ ), 7.17 – 7.26 (2H, m, Ar- $H$ );  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ) 13.6 ( $\text{CH}_3$ ), 18.4 ( $\text{CH}_2$ ), 19.2 ( $\text{CH}_2$ ), 21.9 ( $\text{CH}_2$ ), 30.8 ( $\text{CH}_2$ ), 77.2 (C), 82.8 (C), 123.3 (ArCH), 123.9 (ArC), 125.5 (ArCH), 127.0 (2  $\times$  ArCH), 128.9 (2  $\times$  ArCH), 132.6 (ArCH), 137.5 (ArC), 145.3 (ArC);  $m/z$  (GCMS) 209.0 (M- $\text{C}_6\text{H}_5$ ); (measured 286.0833,  $\text{C}_{17}\text{H}_{18}\text{S}_2$  requires 286.0844).

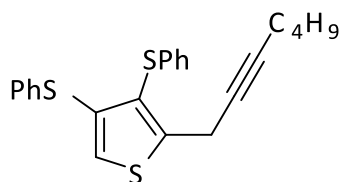
#### 4-Bromo-2-(hept-2-yn-1-yl)-3-(phenylthio)thiophene **3ag**



To an oven-dried tube flushed with  $\text{N}_2$ , was added 3-bromo-4-(phenylsulfinyl)thiophene (0.080 g, 0.27 mmol) and hept-2-yn-1-yltrimethylsilane (0.070 g, 0.41 mmol) in MeCN (3 mL). Trifluoroacetic anhydride (0.097 mL, 0.67 mmol) was then added at room temperature and the reaction was stirred for 2 hours. The solution was quenched with aqueous saturated  $\text{NaHCO}_3$  (6 mL) and the aqueous layer was extracted with EtOAc (3  $\times$  5 mL). The combined organic layer was dried ( $\text{MgSO}_4$ ) and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with 100% *n*-hexane to yield **3ag** as a colourless oil (0.083 g, 0.23 mmol, 86 %).  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$  2955, 2928, 2869, 1724, 1581, 1477, 1439, 1377, 1317, 1081, 1024, 906, 734, 687, 630;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 0.92 (3H, t,  $J$  7.2 Hz,  $\text{CH}_3$ ), 1.36 – 1.55 (4H, m,  $\text{CH}_2\text{CH}_2$ ), 2.18 (2H, tt,  $J$  = 6.8, 2.4 Hz,  $\text{CCH}_2$ ), 3.82 (2H, t,  $J$  = 2.4 Hz, HetAr- $\text{CH}_2\text{C}$ ), 7.00 – 7.08 (2H, m, Ar- $H$ ), 7.10 – 7.17 (1H, m, Ar- $H$ ), 7.18 – 7.25 (2H, m, Ar- $H$ ), 7.31 (1H, s, HetAr- $H$ );  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 13.6 ( $\text{CH}_3$ ), 18.3 ( $\text{CH}_2$ ), 20.8 ( $\text{CH}_2$ ), 21.9 ( $\text{CH}_2$ ), 30.7 ( $\text{CH}_2$ ), 75.6 (C), 83.8 (C), 117.4 (ArC), 121.0 (ArCH), 124.9 (ArC), 125.6 (ArCH), 126.5 (2  $\times$  ArCH), 128.9 (2  $\times$  ArCH), 136.2 (ArC), 148.1 (ArC);  $m/z$  (GCMS) 364.0; (measured 363.9943  $\text{C}_{17}\text{H}_{17}\text{Br}_1\text{S}_1$  requires 363.9950).

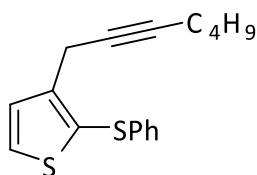


### 2-(Hept-2-yn-1-yl)-3,4-bis(phenylthio)thiophene **3ah**



To an oven-dried tube flushed with  $N_2$ , was added 3-(phenylsulfinyl)-4-(phenylthio)thiophene (0.080 g, 0.25 mmol) and hept-2-yn-1-yltrimethylsilane (0.063 g, 0.37 mmol) in MeCN (3 mL). Trifluoroacetic anhydride (0.088 mL, 0.92 mmol) was then added at room temperature and the reaction was stirred for 2 hours. The solution was quenched with aqueous saturated  $NaHCO_3$  (6 mL) and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layer was dried ( $MgSO_4$ ) and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with 100% *n*-hexane to yield **3ah** as a colourless oil (0.071 g, 0.27 mmol, 75 %).  $\nu_{max}$  (neat)/ $cm^{-1}$  3057, 2955, 2928, 2869, 1666, 1581, 1476, 1377, 1308, 1081, 1023, 998, 948, 907, 853, 734, 687;  $\delta_H$  (500 MHz,  $CDCl_3$ ) 0.89 (3H, t,  $J$  7.2 Hz,  $CH_3$ ), 1.35 – 1.43 (2H, m,  $CH_2CH_2$ ), 1.43 – 1.50 (2H, m,  $CH_2CH_2$ ), 2.16 (2H, tt,  $J$  7.0, 2.4 Hz,  $CCH_2$ ), 3.75 (2H, t,  $J$  2.4 Hz, HetAr- $CH_2C$ ), 6.94 – 7.00 (2H, m, Ar- $H$ ), 7.04 – 7.08 (1H, m, Ar- $H$ ), 7.09 (1H, s, HetAr- $H$ ), 7.12 – 7.18 (3H, m, Ar- $H$ ), 7.18 – 7.26 (4H, m, Ar- $H$ );  $\delta_C$  (125 MHz,  $CDCl_3$ ) 13.6 ( $CH_3$ ), 18.4 ( $CH_2$ ), 20.4 ( $CH_2$ ), 21.9 ( $CH_2$ ), 30.8 ( $CH_2$ ), 75.9 (C), 83.5 (C), 124.0 (ArCH), 125.4 (ArCH), 125.6 (ArC), 126.7 (2 x ArCH), 126.8 (ArCH), 128.8 (2 x ArCH), 129.0 (2 x ArCH), 130.4 (2 x ArCH), 135.4 (ArC), 135.9 (ArC), 136.6 (ArC), 148.8 (ArC);  $m/z$  (GCMS) 394.1; (measured 394.0875  $C_{23}H_{22}S_3$  requires 394.0878).

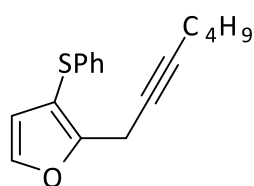
### 3-(Hept-2-yn-1-yl)-2-(phenylthio)thiophene **3ai**



To an oven dried tube flushed with  $N_2$ , was added 2-(phenylsulfinyl)thiophene (0.029 g, 0.14 mmol) and hept-2-yn-1-yltrimethylsilane (0.058 g, 0.35 mmol) in MeCN (3 mL). Trifluoroacetic anhydride (0.058 mL, 0.35 mmol) was then added at  $-78^\circ C$  and the reaction

was stirred for 2 hours. The solution was quenched with aqueous saturated NaHCO<sub>3</sub> (6 mL) and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layer was dried (MgSO<sub>4</sub>) and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with 100% *n*-hexane to yield **3ai** as a colourless oil (0.031 g, 0.11 mmol, 80 %).  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 2955, 2928, 2869, 1724, 1581, 1477, 1439, 1377, 1317, 1081, 1024, 906, 734, 687, 630;  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>) 0.91 (3H, t, *J* 7.2 Hz, CH<sub>3</sub>), 1.29 – 1.53 (4H, m, CH<sub>2</sub>CH<sub>2</sub>), 2.16 (2H, tt, *J* 6.9, 2.4 Hz, CCH<sub>2</sub>), 3.56 (2H, t, *J* 2.4 Hz, HetAr-CH<sub>2</sub>C), 7.02 – 7.18 (3H, m, Ar-H), 7.18 – 7.32 (2H, m, Ar-H), 7.27 (1H, d, *J* 5.4 Hz, HetAr-H), 7.45 (1H, d, *J* 5.4 Hz, HetAr-H);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>) 13.6 (CH<sub>3</sub>), 18.4 (CH<sub>2</sub>), 19.2 (CH<sub>2</sub>), 21.9 (CH<sub>2</sub>), 31.0 (CH<sub>2</sub>), 77.2 (C), 81.9 (C), 124.7 (ArC), 125.7 (ArCH), 126.5 (2 x ArCH), 129.0 (2 x ArCH), 129.4 (ArCH), 129.6 (ArCH), 138.0 (ArC), 144.8 (ArC); *m/z* (GCMS) 209.0 (M-C<sub>6</sub>H<sub>5</sub>); (measured 286.0834, C<sub>17</sub>H<sub>18</sub>S<sub>2</sub> requires 286.0844).

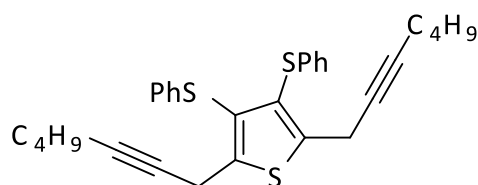
### 2-(Hept-2-yn-1-yl)-3-(phenylthio)furan **3aj**



To an oven dried tube flushed with N<sub>2</sub>, was added 3-(phenylsulfinyl)furan (0.030 g, 0.15 mmol) and hept-2-yn-1-yltrimethylsilane (0.039 g, 0.23 mmol) in MeCN (3 mL). Trifluoroacetic anhydride (0.054 mL, 0.39 mmol) was then added at -20 °C and the reaction allowed to warm to room temperature over 2 hours. The solution was quenched with aqueous saturated NaHCO<sub>3</sub> (6 mL) and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layer was dried (MgSO<sub>4</sub>) and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with 100% *n*-hexane to yield **3aj** as a colourless oil (0.081 g, 0.11 mmol, 74 %).  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 2956, 2930, 2870, 1582, 1511, 1477, 1412, 1305, 1249, 1195, 1123, 1084, 1024, 1008, 885, 736, 689, 652, 558;  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>) 0.89 (3H, t, *J* 7.1 Hz, CH<sub>3</sub>), 1.28 – 1.52 (4H, m, CH<sub>2</sub>CH<sub>2</sub>), 2.14 (2H, tt, *J* 6.9, 2.4 Hz, CCH<sub>2</sub>), 3.68 (2H, t, *J* 2.4 Hz, HetAr-CH<sub>2</sub>C), 6.40 (1H, d, *J* 1.9 Hz, HetAr-H), 7.08 – 7.18 (3H, m, Ar-H), 7.18 – 7.26 (2H, m, Ar-H), 7.45 (1H, d, *J* 1.9 Hz, HetAr-H);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>) 13.6 (CH<sub>3</sub>), 16.8 (CH<sub>2</sub>), 18.4 (CH<sub>2</sub>), 21.9 (CH<sub>2</sub>), 30.8 (CH<sub>2</sub>), 77.2 (C), 82.8 (C), 123.3

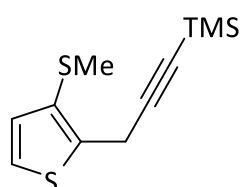
(ArCH), 123.9 (ArC), 125.5 (ArCH), 127.0 (2 × ArCH), 128.9 (2 × ArCH), 132.6 (ArCH), 137.5 (ArC), 145.3 (ArC);  $m/z$  (GCMS) 271.7; (measured 270.1080  $C_{17}H_{18}O_1S_3$  requires 270.1073).

### 2,5-Di(hept-2-yn-1-yl)-3,4-bis(phenylthio)thiophene **3ak**



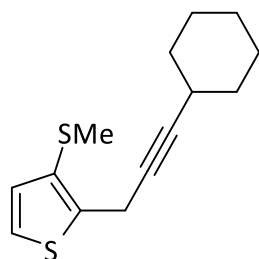
To an oven dried tube flushed with  $N_2$ , was added 3,4-bis(phenylsulfanyl)thiophene (0.058 g, 0.17 mmol) and hept-2-yn-1-yltrimethylsilane (0.088 g, 0.51 mmol) in MeCN (1.5 mL). Trifluoroacetic anhydride (0.098 mL, 0.85 mmol) was then added at room temperature and the reaction was stirred for 2 hours. The solution was quenched with aqueous saturated  $NaHCO_3$  (6 mL) and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layer was dried ( $MgSO_4$ ) and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with 100% *n*-hexane to yield **3ak** as a colourless oil (0.045 g, 0.10 mmol, 62 %).  $\nu_{max}$  (neat)/ $cm^{-1}$  2956, 2930, 2870, 1717, 1663, 1582, 1477, 1439, 1378, 1082, 1023, 737, 688, 603, 581;  $\delta_H$  (500 MHz,  $CD_3CN$ ) 0.90 (6H, t,  $J$  7.2 Hz, 2 ×  $CH_3$ ), 1.36 – 1.49 (8H, m, 2 ×  $CH_2CH_2$ ), 2.18 (4H, tt,  $J$  6.8, 2.4 Hz, 2 ×  $CCH_2$ ), 3.80 (4H, t,  $J$  2.4 Hz, 2 × HetAr- $CH_2C$ ), 6.93 – 6.97 (4H, m, Ar- $H$ ), 7.07 – 7.11 (2H, m, Ar- $H$ ), 7.15 – 7.20 (4H, m, Ar- $H$ );  $\delta_C$  (125 MHz,  $CD_3CN$ ) 13.9 (2 ×  $CH_3$ ), 18.9 (2 ×  $CH_2$ ), 20.7 (2 ×  $CH_2$ ), 22.7 (2 ×  $CH_2$ ), 31.6 (2 ×  $CH_2$ ), 77.1 (2 × C), 84.3 (2 × C), 126.6 (2 × ArCH), 127.5 (4 × ArCH), 128.8 (2 × ArC), 130.0 (4 × ArCH), 137.9 (2 × ArC), 146.9 (2 × ArC);  $m/z$  (GCMS) 488.1; (measured 488.1647  $C_{30}H_{32}S_3$  requires 488.1661).

### (3-(3-(Methylthio)thiophen-2-yl)prop-1-yn-1-yl)trimethylsilane **3aq**



To an oven-dried tube flushed with N<sub>2</sub>, was added 3-(methylsulfinyl)thiophene (0.032 g, 0.21 mmol) and 1,3-bis(trimethylsilyl)-prop-1-yne (0.060 g, 0.32 mmol) in MeCN (3 mL). Trifluoroacetic anhydride (0.077 mL, 0.52 mmol) was then added at -40 °C and the reaction was allowed to warm to room temperature over 18 hours. The solution was quenched with aqueous saturated NaHCO<sub>3</sub> (6 mL) and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layer was dried (MgSO<sub>4</sub>) and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with 100% *n*-hexane to yield **3aq** as a colourless oil (0.031 g, 0.13 mmol, 64 %).  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 2921, 1249, 1025, 842, 759;  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>) 0.19 (9H, s, Si(CH<sub>3</sub>)<sub>3</sub>), 2.38 (3H, s, S-CH<sub>3</sub>), 3.84 (2H, s, HetAr-CHC), 7.00 (1H, d, *J* 5.3 Hz, HetAr-H), 7.19 (1H, d, *J* 5.3 Hz, HetAr-H);  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 0.1 (3 x CH<sub>3</sub>), 19.0 (CH<sub>3</sub>), 20.0 (CH<sub>2</sub>), 86.7 (C), 103.3 (C), 123.2 (ArCH), 129.3 (ArC), 130.1 (ArCH), 138.3 (ArC); *m/z* (GCMS) 240.0; (measured 240.0447 C<sub>11</sub>H<sub>16</sub>S<sub>2</sub>Si<sub>1</sub> requires 240.0457).

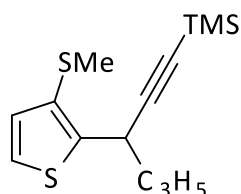
### 2-(3-Cyclohexylprop-2-yn-1-yl)-3-(methylthio)thiophene **3ar**



To an oven-dried tube flushed with N<sub>2</sub>, was added 3-(methylsulfinyl)thiophene (0.060 g, 0.41 mmol) and (3-cyclohexylprop-2-yn-1-yl)trimethylsilane (0.11 g, 0.61 mmol) in MeCN (3 mL). Trifluoroacetic anhydride (0.14 mL, 1.02 mmol) was then added at -40 °C and the reaction was allowed to warm to room temperature over 18 hours. The solution was quenched with aqueous saturated NaHCO<sub>3</sub> (6 mL) and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layer was dried (MgSO<sub>4</sub>) and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with 100% *n*-hexane to yield **3ar** as a colourless oil (0.071 g, 0.29 mmol, 71 %).  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 2925, 2851, 1709, 1651, 1499, 1332, 1291, 1205, 1157, 1027, 969, 888, 859, 769, 709, 642, 609;  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>) 1.13 – 1.28 (3H, m), 1.31 – 1.45 (3H, m), 1.58 – 1.66 (2H, m, CH<sub>2</sub>), 1.66 – 1.76 (2H, m, CH<sub>2</sub>), 2.24 – 2.35 (1H, m, CCH), 2.27 (3H, s, S-CH<sub>3</sub>), 3.68 (2H, d, *J* 2.2 Hz HetAr-CHC), 6.88 (1H, d, *J* 5.3 Hz, HetAr-H), 7.06 (1H, d, *J* 5.3 Hz, HetAr-H);  $\delta_{\text{C}}$  (125 MHz, CDCl<sub>3</sub>)

18.8 (CH<sub>3</sub>), 18.9 (CH<sub>2</sub>), 24.8 (CH<sub>2</sub>), 25.9 (2 × CH<sub>2</sub>), 29.0 (CH), 32.7 (2 × CH<sub>2</sub>), 76.9 (C), 86.7(C), 122.8 (ArCH), 128.6 (ArC), 129.9 (ArCH), 139.9 (ArC); *m/z* (GCMS) 235.1 (-CH<sub>3</sub>) ; (measured 235.0603 C<sub>13</sub>H<sub>15</sub>S<sub>2</sub> requires 235.0610).

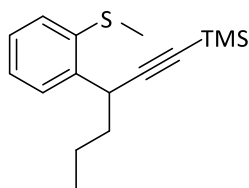
### **(3-(3-(Methylthio)thiophen-2-yl)hex-1-yn-1-yl)trimethylsilane 3at**



To an oven-dried tube flushed with N<sub>2</sub>, was added 3-(methylsulfinyl)thiophene (0.06 g, 0.41 mmol) and 1,3-bis(trimethylsilane)hex-1-yne (0.13 g, 0.61 mmol) in MeCN (3 mL). Trifluoroacetic anhydride (0.14 mL, 0.61 mmol) was then added at -40 °C and the reaction was allowed to warm to room temperature over 18 hours. The solution was quenched with aqueous saturated NaHCO<sub>3</sub> (6 mL) and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layer was dried (MgSO<sub>4</sub>) and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with 100% *n*-hexane to yield **3at** as a colourless oil (0.070 g, 0.26 mmol, 64 %).  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 2957, 2169, 1248, 1029, 953, 838, 759, 700, 666, 637;  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>) 0.18 (9H, s, Si(CH<sub>3</sub>)<sub>3</sub>), 0.95 (3H, t, *J* 7.4 Hz, CH<sub>3</sub>), 1.40 – 1.62 (2H, m, CH<sub>3</sub>CH<sub>2</sub>), 1.68 – 1.85 (2H, m, CHCH<sub>2</sub>), 2.39 (3H, s, S-CH<sub>3</sub>), 4.27 (1H, dd, *J* 8.4, 6.2 Hz, HetAr-CHC), 6.98 (1H, d, *J* 5.3 Hz, HetAr-H), 7.19 (1H, d, *J* 5.3 Hz, HetAr-H);  $\delta_{\text{C}}$  (125 MHz, CDCl<sub>3</sub>) 0.0 (3 × CH<sub>3</sub>), 13.7 (CH<sub>3</sub>), 19.2 (CH<sub>3</sub>), 20.4 (CH<sub>2</sub>), 32.3 (CH), 40.4 (CH<sub>2</sub>), 86.6 (C), 107.8 (C), 123.1 (ArCH), 128.5 (ArC), 129.7 (ArCH), 144.5 (ArC); *m/z* (GCMS) 282.1; (measured 282.0913 C<sub>14</sub>H<sub>22</sub>S<sub>2</sub>Si<sub>1</sub> requires 282.0927).

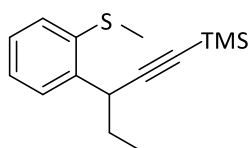
### **General Procedure D: Propargylation of Aryl Sulfoxides**

#### **Trimethyl(3(2-(methylsulfonyl)phenyl)hex-1-yn-1-yl)silane 3au**



To an oven dried tube flushed with N<sub>2</sub>, was added methyl phenyl sulfoxide (70.0 mg, 0.5 mmol) and 1,3-bis(trimethylsilyl)-1-hexyne (169 mg, 0.75 mol) in MeCN (3 mL). Triflic anhydride (12.6 μL, 0.75 mmol) and 2,6-lutidine (14.5 μL, 1.25 mmol) were then added sequentially at room temperature and the reaction mixture was heated for 18 hours at 60 °C. After cooling to room temperature, the solution was quenched with aqueous saturated NaHCO<sub>3</sub> (6 mL) and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layer was washed successively with aqueous HCl 1.0 M (5ml) and brine (5ml), dried (MgSO<sub>4</sub>) and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with 1% EtOAc in *n*-hexane to yield **3au** (0.072 g, 52 %) as a yellow oil;  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 2957, 2872, 2168, 1588, 1465, 1438, 1248, 1111, 1040, 957, 908, 868, 838, 756, 733, 697, 651, 567;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 0.21 (9H, s, Si(CH<sub>3</sub>)<sub>3</sub>), 0.97 (3H, t, J 7.3, CH<sub>3</sub>), 1.49-1.75 (4H, m, 2 x CH<sub>2</sub>), 2.48 (3H, s, SCH<sub>3</sub>), 4.24 (1H, dd, J 8.9, 5, CH-C), 7.18-7.25 (3H, m, Ar-H), 7.59-7.62 (1H, m, Ar-H);  $\delta_{\text{C}}$  (125 MHz) 0.1 (Si(CH<sub>3</sub>)<sub>3</sub>), 13.7 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 16.7 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 20.6 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 35.3 (CHCH<sub>2</sub>), 39.3 (SCH<sub>3</sub>), 86.7 (CC-Si), 108.5 (CC-Si), 125.6 (Ar-CH), 126.9 (Ar-CH), 127.2 (Ar-CH), 127.8 (Ar-CH), 135.9 (Ar-C), 140.9 (Ar-C); *m/z* (GCMS) 276.1; (measured: 276.1356, C<sub>16</sub>H<sub>24</sub>S<sub>1</sub>Si<sub>1</sub> requires 276.1368).

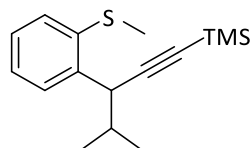
### Trimethyl(3-(2-methylsulfanyl)pent-1-yn-yl)silane **3av**



As described in general procedure **D**, methyl phenyl sulfoxide (323 mg, 2.3 mmol), 1,3-bis(trimethylsilyl)-1-pentyne (538 mg, 3.4 mmol), triflic anhydride (580 μL, 3.4 mmol), 2,6-lutidine (670 μL, 5.7 mmol) and MeCN (14 mL) were heated at 60 °C for 18 hours. Purification by column chromatography on silica gel eluting with 1% EtOAc in *n*-hexane gave **3av** (0.317 g, 52 %) as a yellow oil;  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 2961, 2168, 1464, 1438, 1248, 1038, 984, 838, 746, 697, 650;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 0.20 (9H, s, Si(CH<sub>3</sub>)<sub>3</sub>), 1.05 (3H, t, J = 7.3, CH<sub>3</sub>), 1.6 -

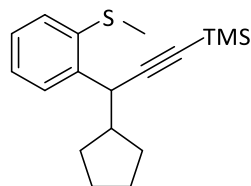
1.84 (2H, m, CH<sub>2</sub>), 2.47 (3H, s, S-CH<sub>3</sub>), 4.16 (1H, dd, J 8.7, 4.9, CH), 7.17-7.25 (3H, m, Ar-H), 7.59 (1H, m, Ar-H);  $\delta_c$  (125 MHz) 0.4 (Si(CH<sub>3</sub>)<sub>3</sub>), 12.0 (CH<sub>3</sub>), 17.0 (CH<sub>2</sub>), 30.5 (CH), 37.4 (SCH<sub>3</sub>), 87.3 (Si-CC), 108.6 (Si-CC), 125.8 (Ar-CH), 127.2 (Ar-CH), 127.5 (Ar-CH), 128.2 (Ar-CH), 136.3 (Ar-C), 140.8 (Ar-C);  $m/z$  (GCMS) 262.1; (measured 262.1200, C<sub>15</sub>H<sub>22</sub>S<sub>1</sub>Si<sub>1</sub> requires 262.1211).

### Trimethyl(4-methyl-3-(2-(methylsulfonyl)phenyl)pent-1-yn-1-yl)silane **3aw**



As described in general procedure **D**, methyl phenyl sulfoxide (70 mg, 0.5 mmol), 1,3-bis(trimethylsilyl)-4-methyl-1-pentyne (170 mg, 0.75 mmol), triflic anhydride (12.6  $\mu$ L, 0.75 mmol), 2,6-lutidine (14.5  $\mu$ L, 1.25 mmol) and MeCN (3 mL) were heated at 60 °C for 18 hours. Purification by column chromatography on silica gel eluting with 1% EtOAc in *n*-hexane gave **3aw** (0.084 g, 61 %) as a yellow oil;  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 2959, 2870, 2169, 1587, 1465, 1438, 1383, 1366, 1318, 1248, 1135, 1040, 1009, 908, 838, 744, 698, 678, 630, 615, 561;  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 0.21 (9H, s, Si(CH<sub>3</sub>)<sub>3</sub>), 0.90 (3H, d, J 6.7, CH<sub>3</sub>), 1.08 (3H, d, J 6.7, CH<sub>3</sub>), 1.96-2.04 (1H, m, CH(CH<sub>3</sub>)<sub>2</sub>), 2.47 (3H, s, SCH<sub>3</sub>), 4.16 (1H, d, J 4.8, CH-C), 7.17-7.27 (3H, m, Ar-H), 7.56 (1H, dd, J 7.4, 1.5, Ar-H);  $\delta_c$  (125 MHz) -0.1 (Si(CH<sub>3</sub>)<sub>3</sub>), 16.4 (CH<sub>3</sub>), 17.1 (CH<sub>3</sub>), 21.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 32.5 (CH), 42.2 (SCH<sub>3</sub>), 87.8 (CC-Si), 106.2 (CC-Si), 124.8 (Ar-CH), 126.5 (Ar-CH), 126.8 (Ar-CH), 128.4 (Ar-CH), 136.1 (Ar-C), 139.4 (Ar-C);  $m/z$  (GCMS) 276.1; (measured 276.1356, C<sub>16</sub>H<sub>24</sub>S<sub>1</sub>Si<sub>1</sub> requires 276.1368).

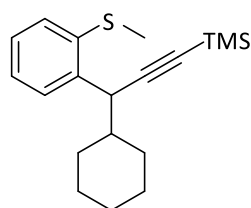
### (3-Cyclopentyl-3-(2-(methylsulfonyl)phenyl)prop-1-yn-1-yl)trimethylsilane **3ax**



As described in general procedure **D**, methyl phenyl sulfoxide (70 mg, 0.5 mmol), 1,3-bis(trimethylsilyl)-3-cyclopentyl-1-propyne (189 mg, 0.75 mmol), triflic anhydride (12.5  $\mu$ L, 0.75 mmol), 2,6-lutidine (14.5  $\mu$ L, 1.25 mmol) and MeCN (3 mL) were heated at 60 °C for 18

hours. Purification by column chromatography on silica gel eluting with 1% EtOAc in *n*-hexane gave **3ax** (0.087 g, 57 %) as a yellow oil;  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$  2954, 2865, 2168, 1587, 1465, 1438, 1247, 1042, 941, 838, 757, 697, 635;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 0.20 (9H, s,  $\text{Si}(\text{CH}_3)_3$ ), 1.46-1.70 (9H, m, cyclopentyl H), 2.47 (3H, s,  $\text{SCH}_3$ ), 4.30 (1H, d,  $J$  6.1, CH), 7.17-7.25 (3H, m, Ar-H), 7.58 (1H, dd,  $J$  7.4, 1.6, Ar-H);  $\delta_{\text{C}}$  (125 MHz) 0.5 ( $\text{Si}(\text{CH}_3)_3$ ), 17.1 (cyclopentyl- $\text{CH}_2$ ), 25.5 (cyclopentyl- $\text{CH}_2$ ), 25.7 (cyclopentyl- $\text{CH}_2$ ), 29.1 (cyclopentyl- $\text{CH}_2$ ), 31.1 (cyclopentyl-CH), 39.9 (CH), 45.5 ( $\text{SCH}_3$ ), 87.3 (CC-Si), 108.0 (CC-Si), 125.7 (Ar-CH), 127.1 (Ar-CH), 127.4 (Ar-CH), 128.6 (Ar-CH), 136.3 (Ar-C), 140.8 (Ar-C);  $m/z$  (GCMS) 287.1 ( $-\text{CH}_3$ ); (measured 287.1277,  $\text{C}_{17}\text{H}_{23}\text{S}_1\text{Si}_1$  requires 287.1284).

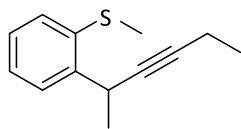
### (3-Cyclohexyl-3-(2-methylsulfonyl)phenyl)prop-1-yn-1-yl)trimethylsilane **3ay**



As described in general procedure **D**, methyl phenyl sulfoxide (70 mg, 0.5 mmol), 1,3-bis(trimethylsilyl)-3-cyclohexyl-1-propyne (199 mg, 0.75 mmol), triflic anhydride (12.6  $\mu\text{L}$ , 0.75 mmol), 2,6-lutidine (14.5  $\mu\text{L}$ , 1.25 mmol) and MeCN (3 mL) were heated at 60 °C for 18 hours. Purification by column chromatography on silica gel eluting with 1% EtOAc in *n*-hexane gave **3ay** (0.120g, 63%) as a yellow oil;  $\nu_{\max}$  (neat)/ $\text{cm}^{-1}$  2923, 2851, 2168, 1587, 1464, 1442, 1317, 1247, 1061, 1042, 996, 948, 878, 838, 752, 734, 699, 661, 639, 627, 584, 543;  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 0.20 (9H, s,  $\text{Si}(\text{CH}_3)_3$ ), 1.10-1.37 (5H, m, cyclohexyl), 1.58- 1.75 (6H, m, cyclohexyl), 2.47 (3H, s,  $\text{SCH}_3$ ), 4.13 (1H, d,  $J$  5.2, Ph-CHC), 7.16-7.27 (3H, m, Ar-H), 7.53 (1H, d,  $J$  7.5, Ar-H);  $\delta_{\text{C}}$  (125 MHz) 0.05 ( $(\text{CH}_3)_3\text{Si}$ ), 16.5 (cyclohexyl  $\text{CH}_2$ ), 25.9 (cyclohexyl  $\text{CH}_2$ ), 26.1 (cyclohexyl  $\text{CH}_2$ ), 26.2 (cyclohexyl  $\text{CH}_2$ ), 28.0 (cyclohexyl  $\text{CH}_2$ ), 31.4 (cyclohexyl CH), 41.6 (Ph-CH), 42.3 (S- $\text{CH}_3$ ), 87.4 (Si-CC-C), 107.1 (Si-CC-C), 124.8 (Ar-CH), 126.6 (Ar-CH), 126.8 (Ar-CH), 128.6 (Ar-CH), 136.25 (Ar-C), 139.2 (Ar-C);  $m/z$  (GCMS) 316.2; (measured 316.1680,  $\text{C}_{19}\text{H}_{28}\text{S}_1\text{Si}_1$  requires 316.1675).

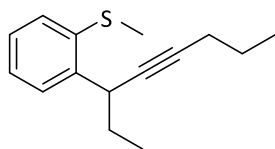
### (2-(Hex-3-yn-2-yl)phenyl)(methyl)sulfide **3az**





As described in general procedure **D**, methyl phenyl sulfoxide (70 mg, 0.5 mmol), 2-trimethylsilyl-3-hexyne (115 mg, 0.75 mmol), triflic anhydride (12.5  $\mu\text{L}$ , 0.75 mmol), 2,6-lutidine (14.5  $\mu\text{L}$ , 1.25 mmol) and MeCN (3 mL) were heated at 60  $^{\circ}\text{C}$  for 18 hours. Purification by column chromatography on silica gel eluting with 1% EtOAc in *n*-hexane gave **3az** (0.054 g, 53 %) as a yellow oil;  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$  3058, 2973, 2920, 1715, 1587, 1568, 1467, 1437, 1368, 1318, 1257, 1189, 1154, 1042, 967, 686, 608, 560;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 1.16 (3H, t, J 7.6,  $\text{CH}_3\text{CH}_2$ ), 1.43 (3H, d, J 7.1,  $\text{CH}_3\text{CH}$ ), 2.24 (2H, qd, J 7.5, 2.3,  $\text{CH}_3\text{CH}_2$ ), 2.48 (3H, s,  $\text{SCH}_3$ ), 4.23 (1H, qt, J 7.0, 2.2,  $\text{CH}_3\text{CH}$ ), 7.17-7.26 (3H, m, Ar-H), 7.62 (1H, m, Ar-H);  $\delta_{\text{C}}$  (125 MHz) 12.5 ( $\text{CH}_2\text{CH}_3$ ), 14.2 ( $\text{CHCH}_3$ ), 16.6 ( $\text{CH}_2\text{CH}_3$ ), 23.5 ( $\text{CHCH}_3$ ), 28.9 ( $\text{SCH}_3$ ), 82.2 ( $\text{CC-CH}_2\text{CH}_3$ ), 83.2 ( $\text{CC-CH}_2\text{CH}_3$ ), 125.7 (Ar-CH), 126.7 (Ar-CH), 127.14 (Ar-CH), 127.1 (Ar-CH), 135.6 (Ar-C), 142.6 (Ar-C);  $m/z$  (GCMS) 204.1; (measured 203.0891,  $\text{C}_{13}\text{H}_{25}\text{S}_1$  requires 203.0889).

#### Methyl(2-(oct-4-yn-3-yl)phenyl)sulfide **3ba**

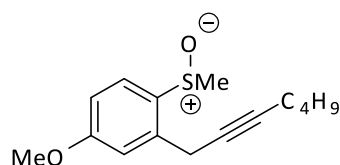


As described in general procedure **D**, methyl phenyl sulfoxide (70 mg, 0.5 mmol), 3-trimethylsilyl-4-octyne (136 mg, 0.75 mmol), triflic anhydride (12.5  $\mu\text{L}$ , 0.75 mmol), 2,6-lutidine (14.5  $\mu\text{L}$ , 1.25 mmol) and MeCN (3 mL) were heated at 60  $^{\circ}\text{C}$  for 18 hours. Purification by column chromatography on silica gel eluting with 1% EtOAc in *n*-hexane gave **3aaa** (0.046 g, 45 %) as a yellow oil;  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$  2961, 2929, 2870, 1587, 1438, 1377, 1338, 1276, 1061, 1042, 967, 906, 816, 692, 625;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 1.01-1.07 (6H, m, 2 x  $\text{CH}_3$ ), 1.53- 1.84 (4H, m, 2 x  $\text{CH}_2$ ), 2.23 (2H, td, J 7, 2.2,  $\text{CH}_2$ ), 2.47 (3H, s,  $\text{SCH}_3$ ), 4.10 (1H, m, Ph-CH), 7.17-7.26 (3H, m, Ar-H), 7.60 (1H, dd, J 7.5, 5.9, Ar-H);  $\delta_{\text{C}}$  (125 MHz) 11.5 ( $\text{CH}_3(\text{CH}_2)_2$ ), 13.2 ( $\text{CH}_3\text{CH}_2\text{CH}$ ), 16.3 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 20.5 ( $\text{CH}_3\text{CH}_2\text{CH}$ ), 22.2 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 30.1 ( $\text{CH}_3\text{CH}_2\text{CH}$ ), 35.8 (S- $\text{CH}_3$ ), 81.3 ( $\text{CH}_2\text{CC}$ ), 82.4 (CC-CH), 125.1 (Ar-CH), 126.3 (Ar-CH), 126.7

(Ar-CH), 127.5 (Ar-CH), 135.62 (Ar-C), 141.1 (Ar-C);  $m/z$  (GCMS) 232.1; (measured 232.1276,  $C_{15}H_{20}S_1$  requires 232.1280).

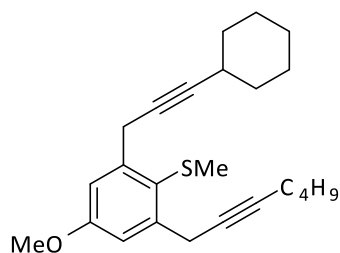
### Iterative, selective *ortho*-propargylation of 4-methoxyphenylmethyl sulphide

#### 2-(Hept-2-yn-1-yl)-4-methoxy-1-(methylsulfinyl)benzene 1aI



To a solution of (2-(hept-2-ynyl)-4-methoxyphenyl)(methyl)sulfide (0.186 g, 0.75 mmol) in  $CH_2Cl_2$  (10 mL) was added  $NaHCO_3$  (0.069 g, 0.825 mmol) followed by a solution of *m*-CPBA (0.188 g, 0.825 mmol) in  $CH_2Cl_2$  (5 mL) at 0 °C. The reaction mixture was then allowed to warm to room temperature for two hours before quenching with aqueous saturated  $NaHCO_3$  (10 mL). The aqueous layer was then extracted with  $CH_2Cl_2$  (3 x 10 mL) and the combined organic layers were washed with brine (20 mL), dried ( $MgSO_4$ ) and concentrated in vacuo. The crude product was purified by column chromatography on silica gel eluting with 10% EtOAc in  $CH_2Cl_2$  to yield the product (0.182 g, 92% yield) as a yellow oil;  $\nu_{max}$  (neat)/ $cm^{-1}$  2956, 2930, 1594, 1455, 1322, 1282, 1159, 1084, 732;  $\delta_H$  (400 MHz,  $CDCl_3$ ) 0.90 (3H, t,  $J$  7.2,  $CH_3$ ), 1.51 - 1.34 (4H, m,  $2 \times CH_2$ ), 2.17 (2H, tt,  $J$  2.4, 7.2,  $CCH_2$ ), 2.74 (3H, s,  $SCH_3$ ), 3.61 (2H, t,  $J$  2.4,  $Ph-CH_2C$ ), 3.85 (3H, s,  $OCH_3$ ), 7.02-6.99 (2H, m, Ar-H) 7.91 (1H, m, ArCH);  $\delta_C$  (100 MHz,  $CDCl_3$ ) 13.7 ( $CH_3$ ), 18.6 ( $CCH_2$ ), 22.1 ( $CH_2$ ), 22.2 ( $PhCH_2$ ), 31.0 ( $CH_2$ ), 43.4 ( $SCH_3$ ), 55.6 ( $OCH_3$ ), 76.4 (CC), 84.2 (CC), 114.0 (ArCH), 115.1 (ArCH), 125.7 (ArCH), 134.8 (ArC), 136.6 (ArC), 162.2 (ArC);  $m/z$  (ES+) (M + H), 265; (Found: M + H, 265.1259.  $C_{15}H_{21}O_2S$  requires M + H, 265.1257).

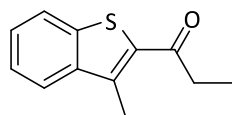
#### (2-(3-Cyclohexylprop-2-yn-1-yl)-6-(hept-2-yn-1-yl)-4-methoxyphenyl)(methyl)sulfane 3bb



An oven-dried microwave tube was flushed with N<sub>2</sub> before adding a solution containing 2-(hept-2-yn-1-yl)-4-methoxy-1-(methylsulfinyl)benzene (132 mg, 0.50 mmol) and (3-cyclohexylprop-2-ynyl)trimethylsilane (146 mg, 0.75 mol) in MeCN (2.5 mL). Triflic anhydride (125  $\mu$ L, 0.75 mmol) and 2,6-lutidine (145  $\mu$ L, 0.625 mmol) were added sequentially at room temperature and the reaction mixture was then heated in a microwave reactor for 15 min at 130 °C. After cooling to room temperature, the solution was quenched with aqueous saturated NaHCO<sub>3</sub> (10 mL) and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed successively with aqueous HCl 1.0 M (10 mL) and brine (10 mL), dried (MgSO<sub>4</sub>) and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with 5% CH<sub>2</sub>Cl<sub>2</sub> in hexane to yield the product (0.136 g, 74% yield) as a clear oil;  $\nu_{\text{max}}$  (neat)/cm<sup>-1</sup> 2928, 1594, 1452, 1322, 1283, 1159, 1084;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 0.91 (3H, t, *J* 7.2, CH<sub>3</sub>), 1.34 - 1.26 (3H, m, CH<sub>2</sub>), 1.53 - 1.40 (7H, m, CH<sub>2</sub>), 1.72-1.69 (2H, m, CH<sub>2</sub>), 1.83-1.80 (2H, m, CH<sub>2</sub>), 2.19 (3H, s, SCH<sub>3</sub>), 2.24-2.22 (2H, m, CCH<sub>2</sub>), 2.46-2.38 (1H, m, CH), 3.84 (3H, s, OCH<sub>3</sub>), 3.91-3.88 (4H, m, Ph-CH<sub>2</sub>C), 7.11 (1H, d, *J* 2.8, Ar-H), 7.15 (1H, d, *J* 2.8, Ar-H);  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 13.8 (CH<sub>3</sub>), 18.7 (CCH<sub>2</sub>), 19.5 (SCH<sub>3</sub>), 22.1 (CH<sub>2</sub>), 25.0 (PhCH<sub>2</sub> + CH<sub>2</sub>), 25.1 (CCH), 26.1 (PhCH<sub>2</sub>), 29.4 (CH<sub>2</sub>), 31.3 (CH<sub>2</sub>), 33.2 (CH<sub>2</sub>), 55.3 (OCH<sub>3</sub>), 78.0 (CC), 78.1 (CC), 83.3 (CC), 87.7 (CC), 113.2 (ArCH), 113.4 (ArCH), 124.7 (ArC), 144.1 (ArC), 144.2 (ArC), 160.1 (ArC); *m/z* (GCMS) 353.2 (C<sub>23</sub>H<sub>29</sub>O<sub>1</sub>S<sub>1</sub>); (measured 369.2253, C<sub>24</sub>H<sub>33</sub>O<sub>1</sub>S<sub>1</sub> requires 369.2252).

## Iodine Mediated Cyclisation

### 1-(3-methylbenzo[b]thiophen-2-yl)propan-1-one **7c**



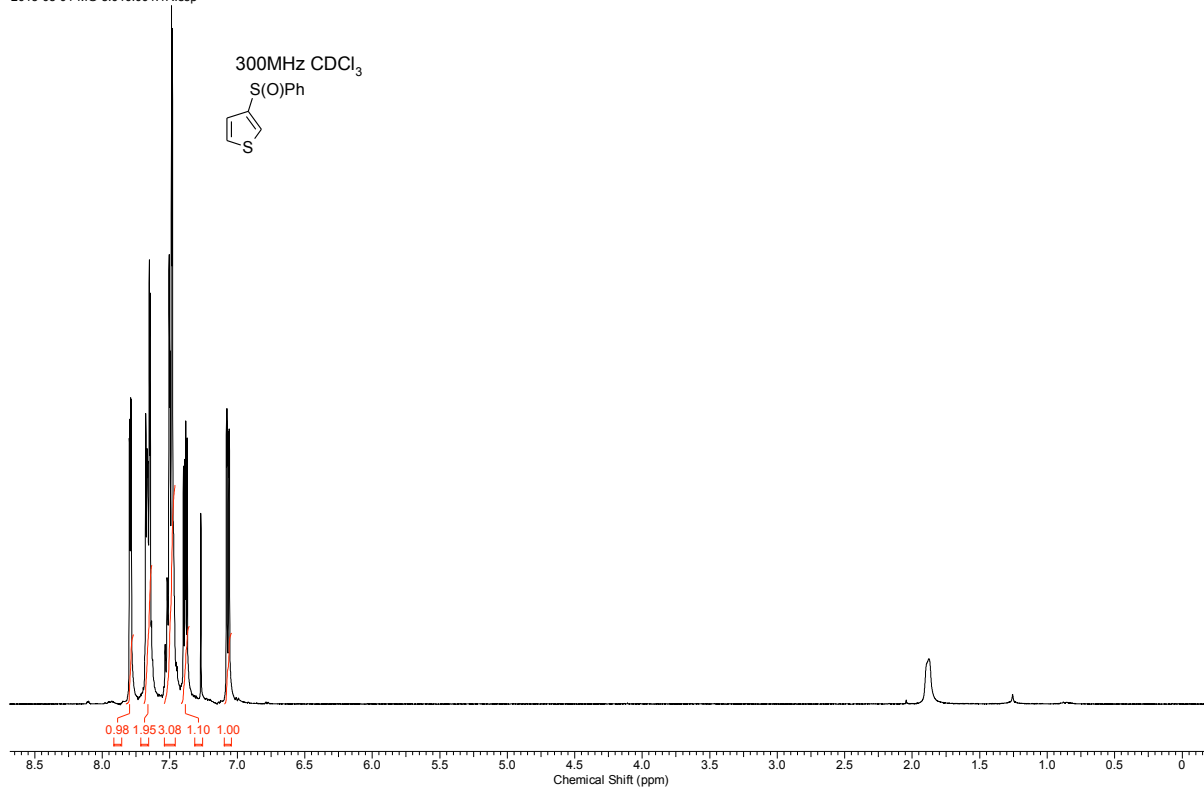
To an oven-dried tube was added (2-Hex-3-yn-2-yl)phenyl(methyl)sulfide **3az** (20.0 mg, 0.1 mmol), Iodine (17.7 mg, 0.07 mmol) and toluene (2 mL, 0.05 M). Oxygen was bubbled through the reaction for 15 minutes before the mixture was heated to 80 °C for 18 hours. After this period the reaction was allowed to stir for 48 hours at room temperature before it was quenched with sat. sodium thiosulphate solution (5 mL). The aqueous phase was

separated and extracted with Et<sub>2</sub>O (3 X 5 mL). The combined organic layers were then washed with brine (5 mL), dried using Na<sub>2</sub>SO<sub>4</sub> and filtered before the solvent was removed *in vacuo*. Purification by preparative thin layer chromatography eluting with hexane gave **7c** as a white solid (19.5 mg, 0.095 mmol, 95%); mp: 83-85 °C;  $\nu_{\max}$  (neat/cm<sup>-1</sup>); 3064, 2971, 2918, 2846, 1644, 1558, 1517, 1449, 1408, 1380, 1315, 1262, 1157, 1090, 1040, 977, 874, 814, 729;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 1.26 (3 H, t, *J*=7.19 Hz, CH<sub>3</sub>), 2.78 (3 H, s, CH<sub>3</sub>), 2.99 (2 H, q, *J*=7.31 Hz, CH<sub>2</sub>), 7.37 - 7.59 (2 H, m, ArCH), 7.76 - 7.97 (2 H, m, ArCH);  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 8.28 (CH<sub>3</sub>), 13.84 (CH<sub>3</sub>), 36.00 (CH<sub>2</sub>), (122.73 (ArCH), 124.08 (ArCH), 124.64 (ArCH), 127.38 (ArCH), 135.08 (ArC), 139.15 (ArC), 139.76 (ArC), 140.49 (ArC), 196.37 (CO); *m/z* (GCMS); 204.0; (measured 204.0597, C<sub>12</sub>H<sub>12</sub>O<sub>1</sub>S<sub>1</sub> requires 204.0603).

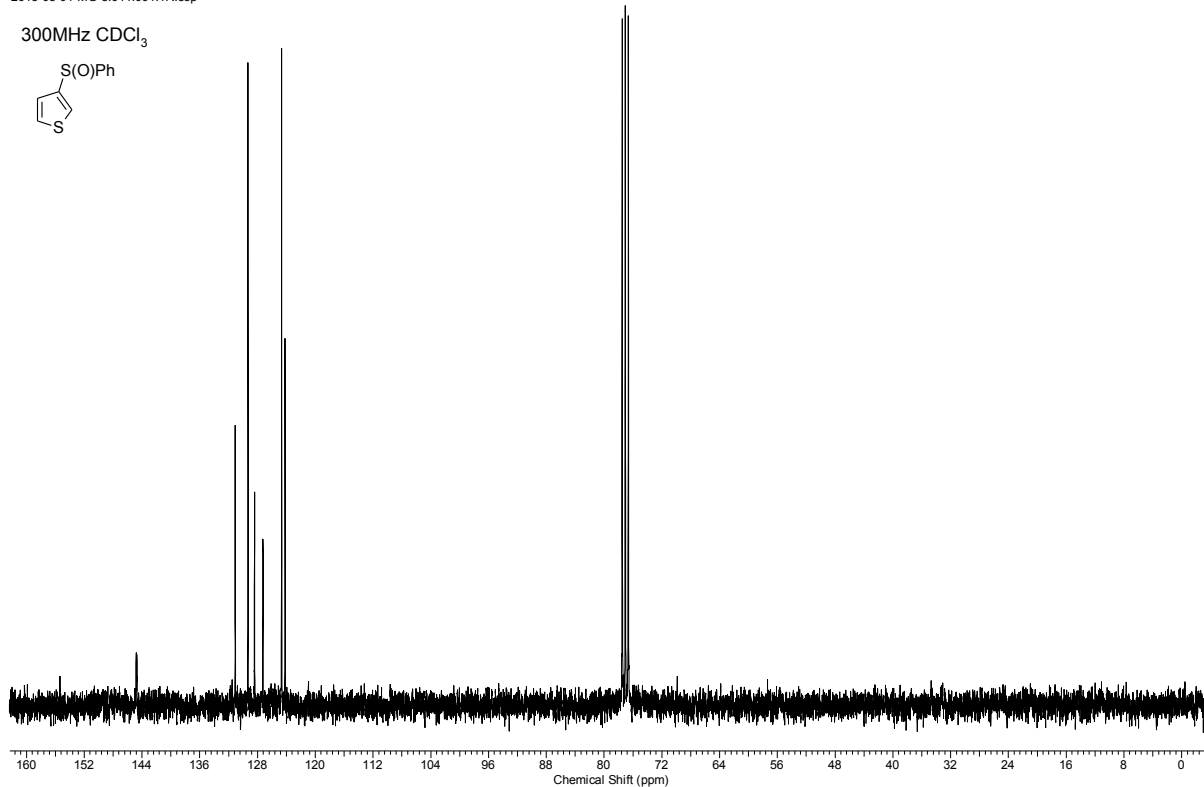
# $^1\text{H}$ and $^{13}\text{C}$ NMR

## 3-(Phenylsulfinyl)thiophene 1af

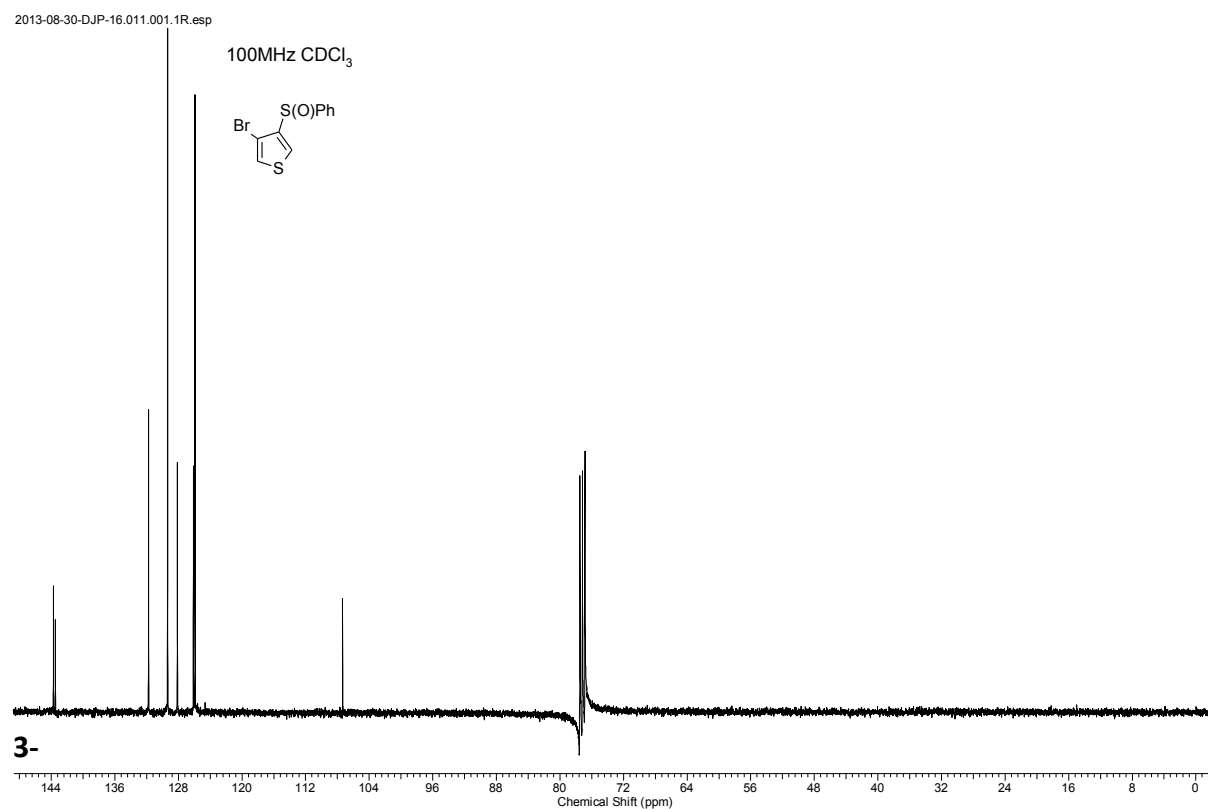
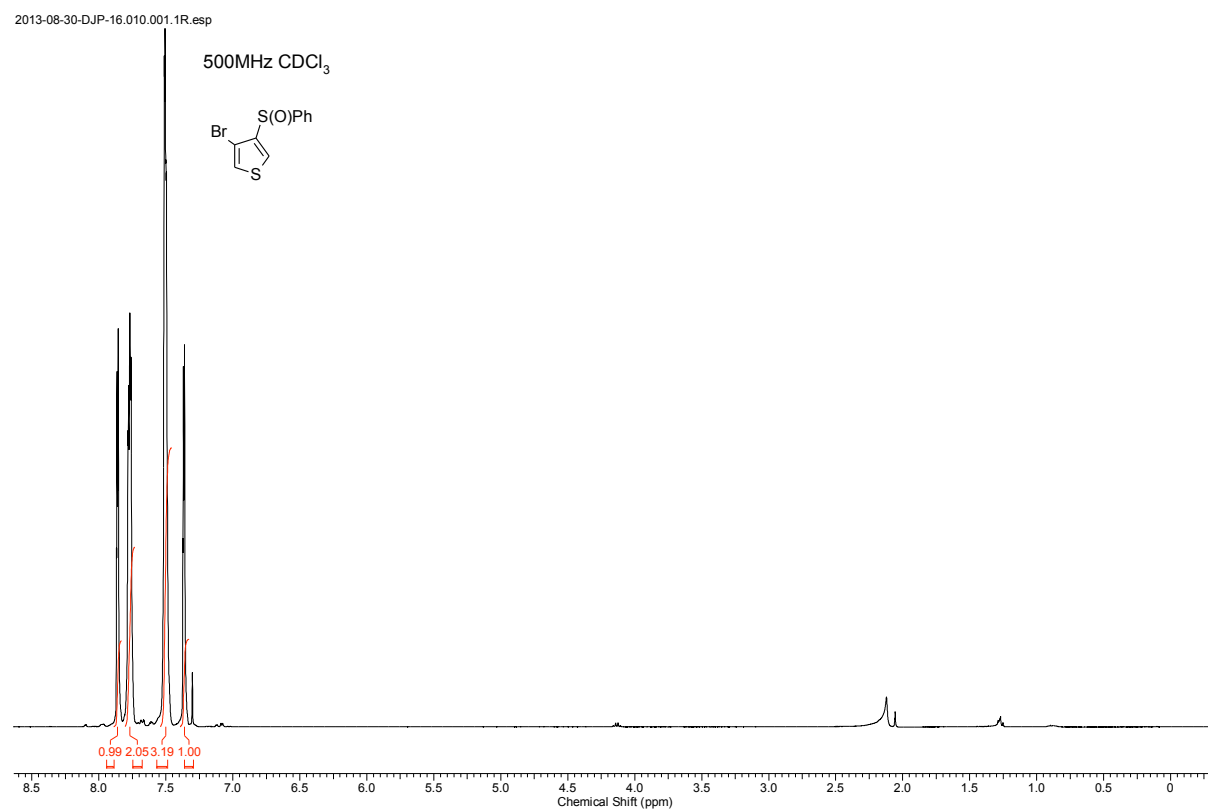
2013-08-01-MG-8.010.001.1R.esp



2013-08-01-MG-8.011.001.1R.esp

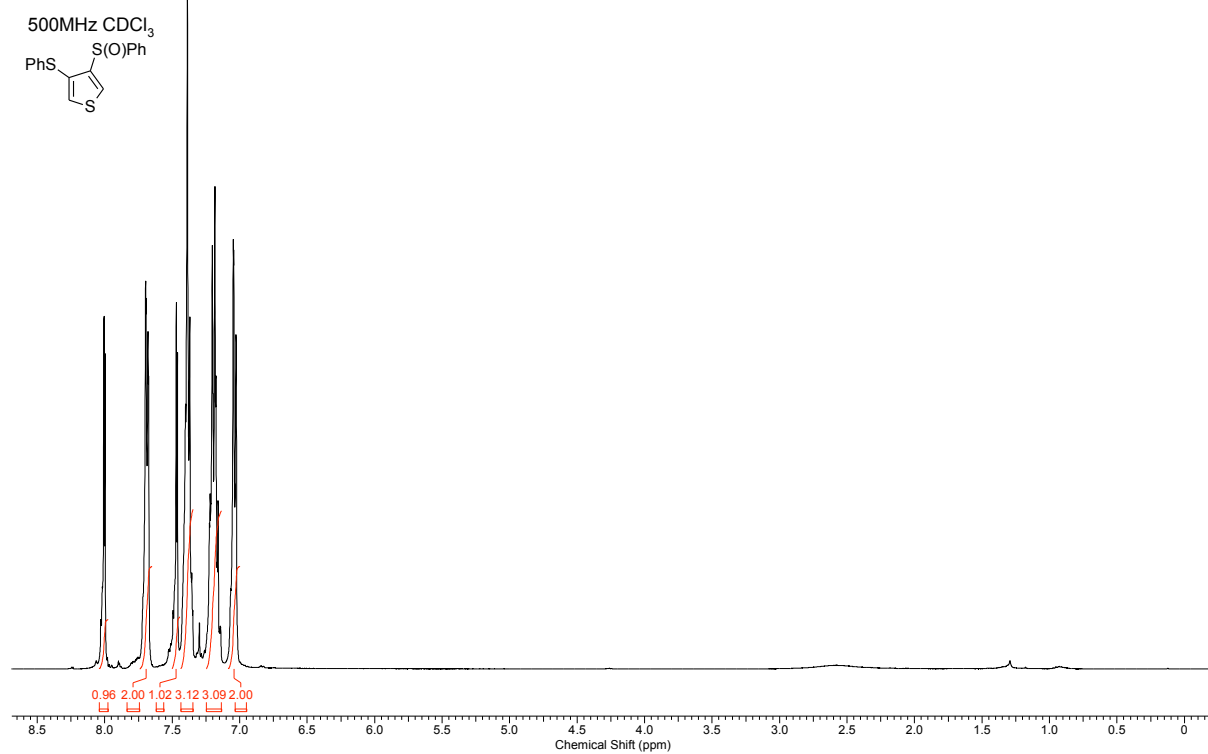


### 3-Bromo-4-(phenylsulfinyl)thiophene 1ag

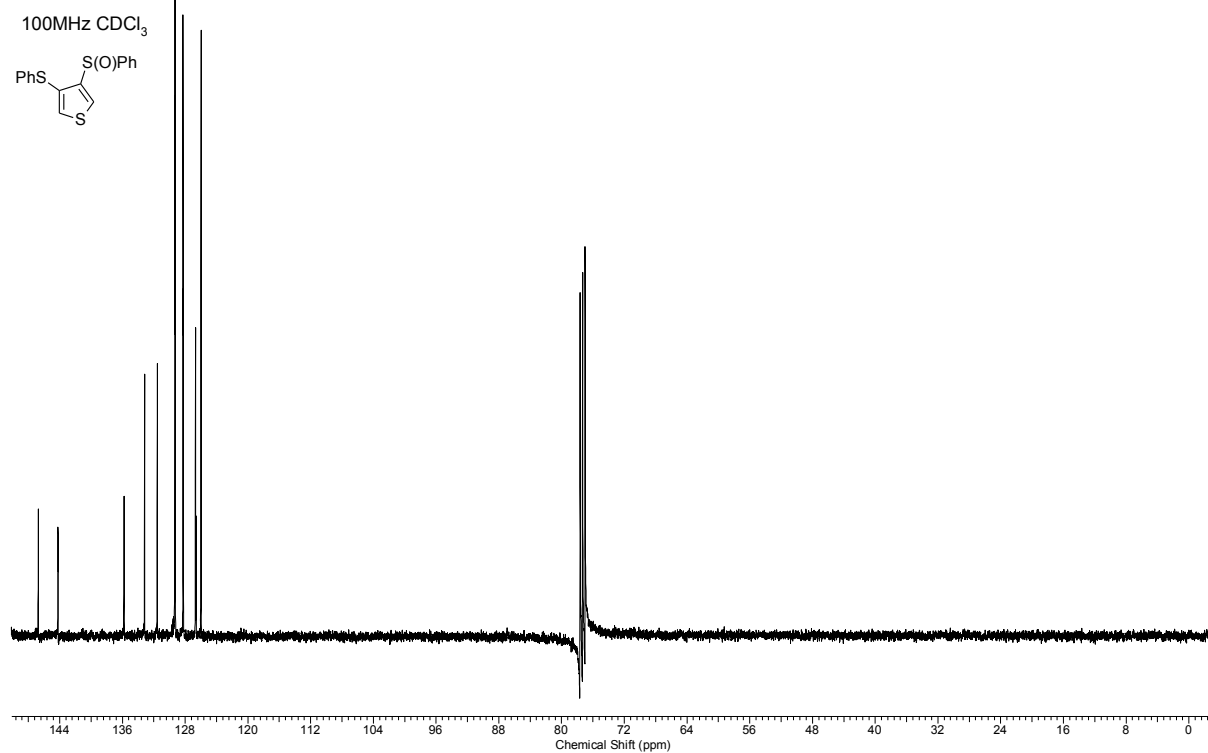


# (Phenylsulfinyl)-4-(phenylthio)thiophene 1ah

2013-09-02-DJP-60.010.001.1R.esp



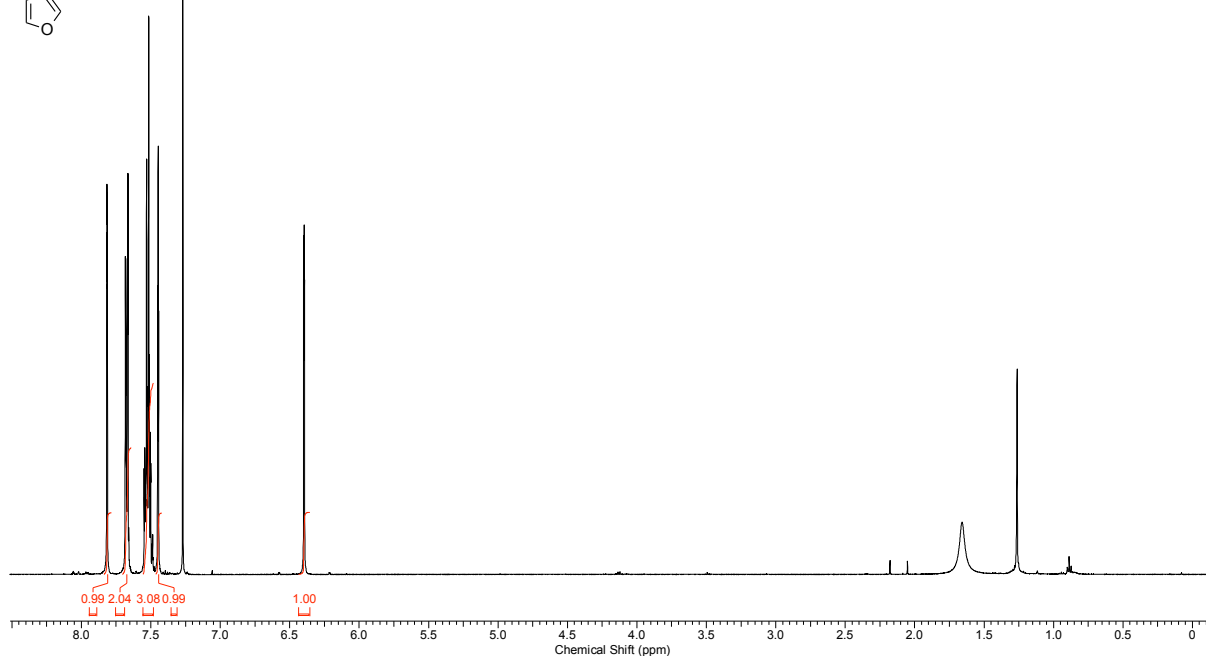
2013-09-02-DJP-60.011.001.1R.esp



### 3-(Phenylsulfinyl)furan 1aj

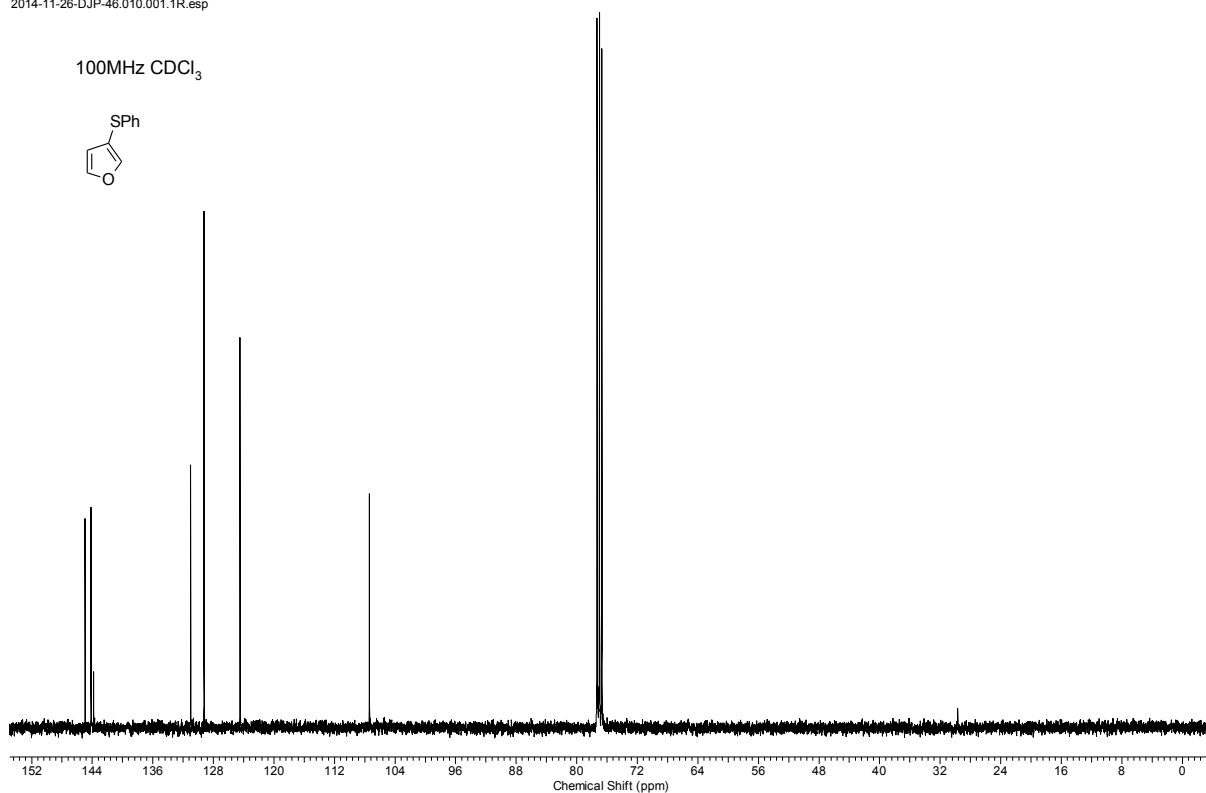
EAM-32-B-H-500.010.001.1R.esp

300MHz CDCl<sub>3</sub>



2014-11-26-DJP-46.010.001.1R.esp

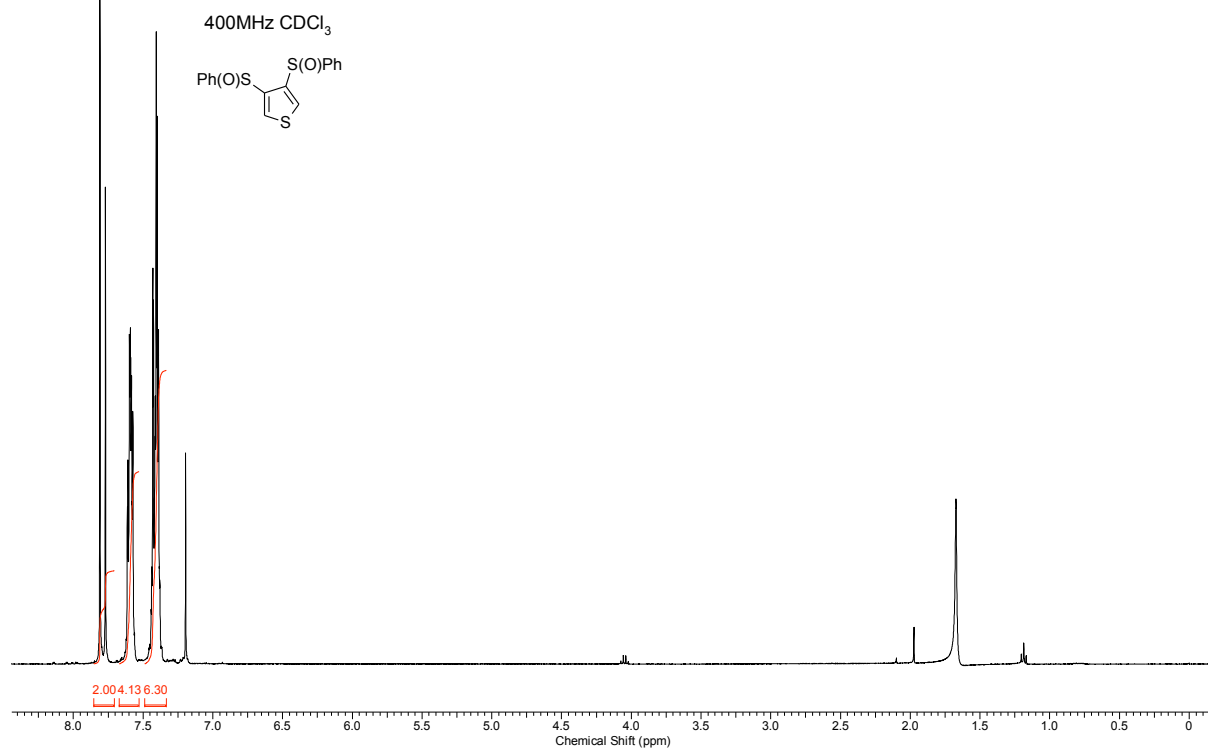
100MHz CDCl<sub>3</sub>



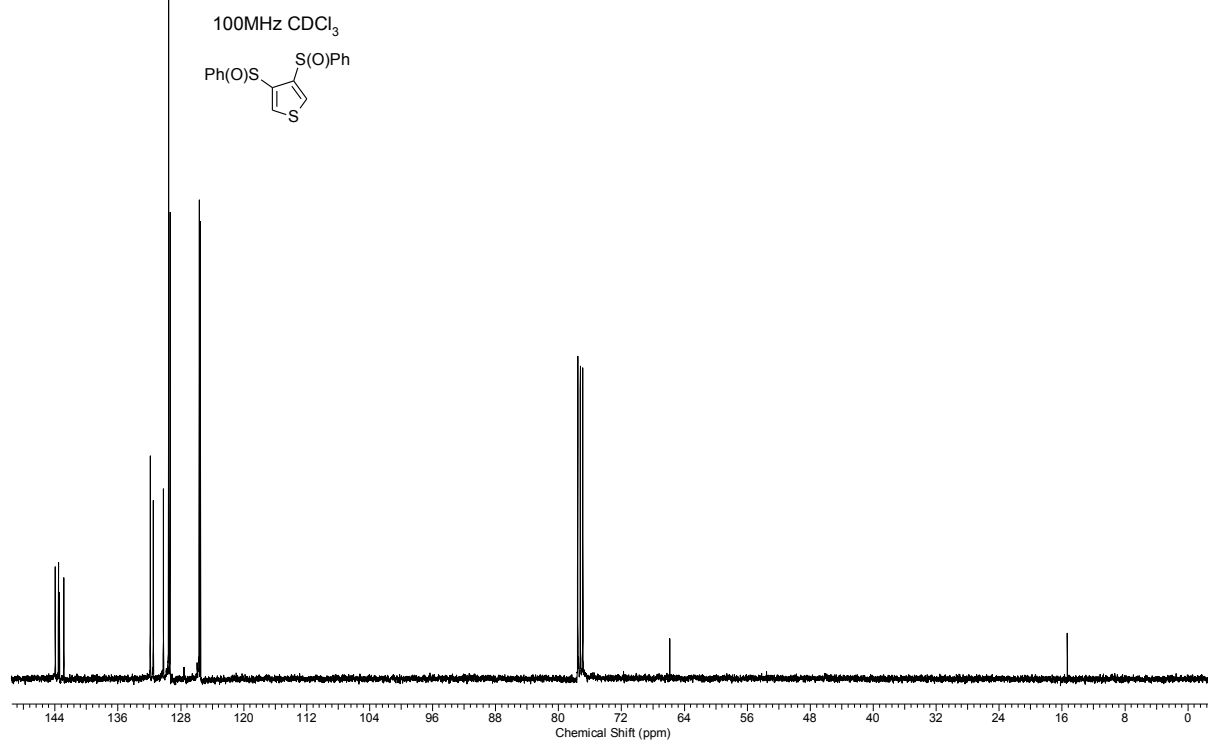


# 3,4-bis(phenylsulfinyl)thiophene 1ak

2013-09-02-DJP-59.010.001.1R.esp

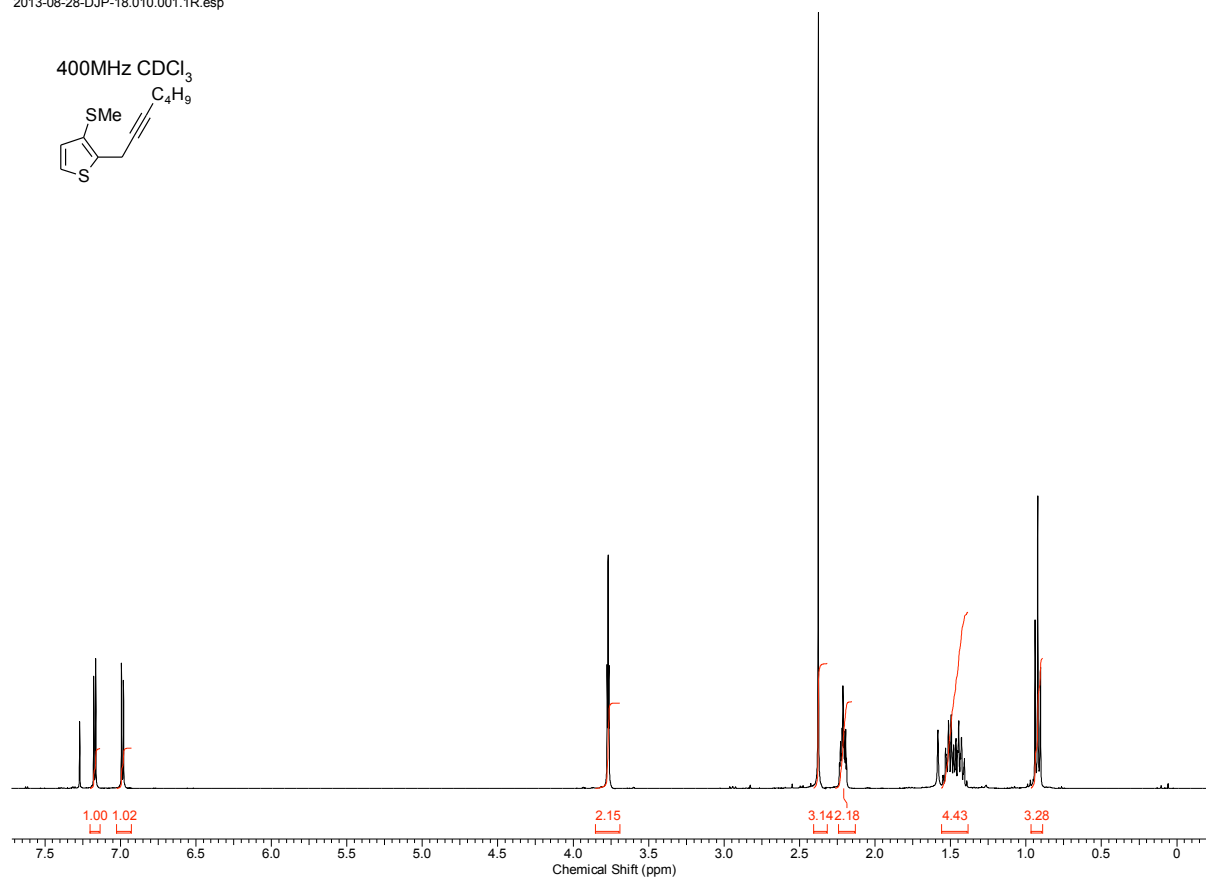


EAM-43-F2-F4.011.001.1R.esp

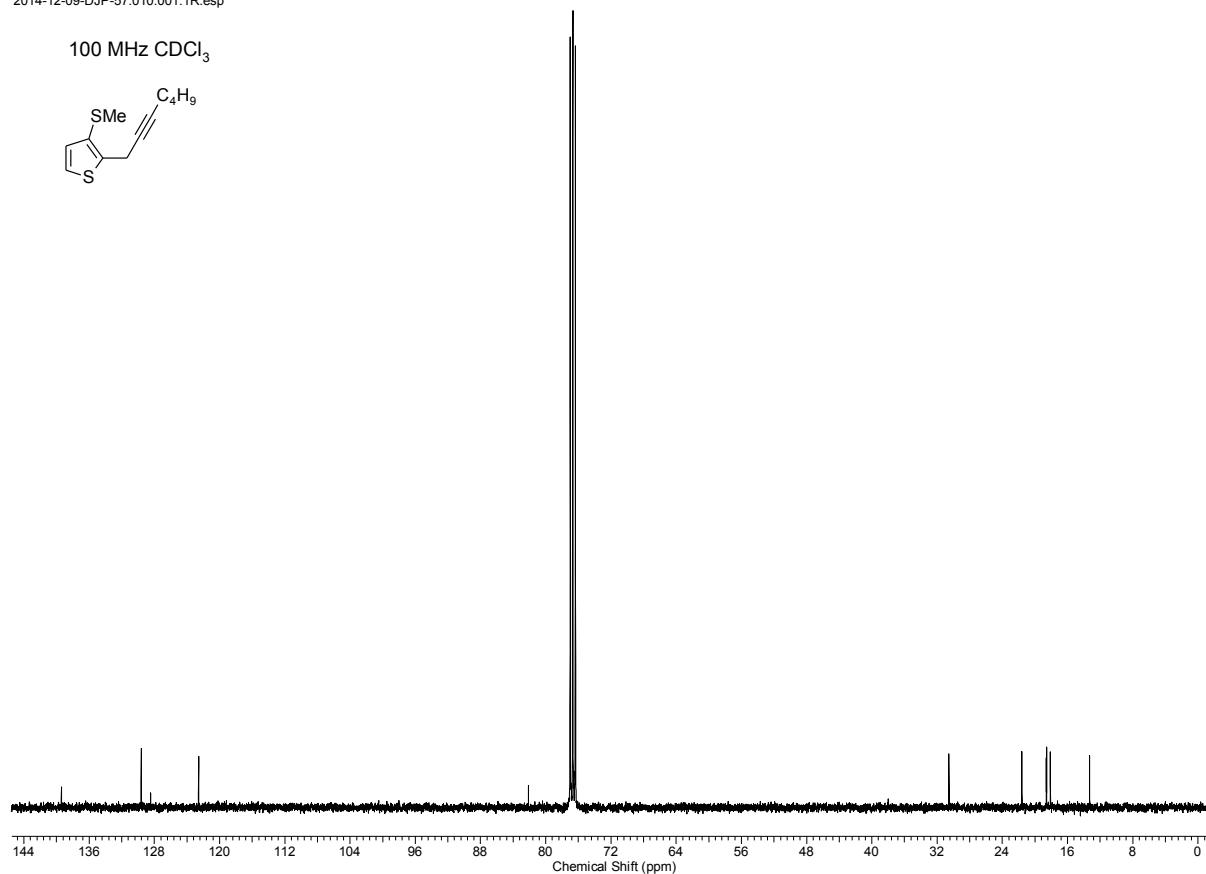


## 2-(Hept-2-yn-1-yl)-3-(methylsulfanyl)thiophene 3ab

2013-08-28-DJP-18.010.001.1R.esp



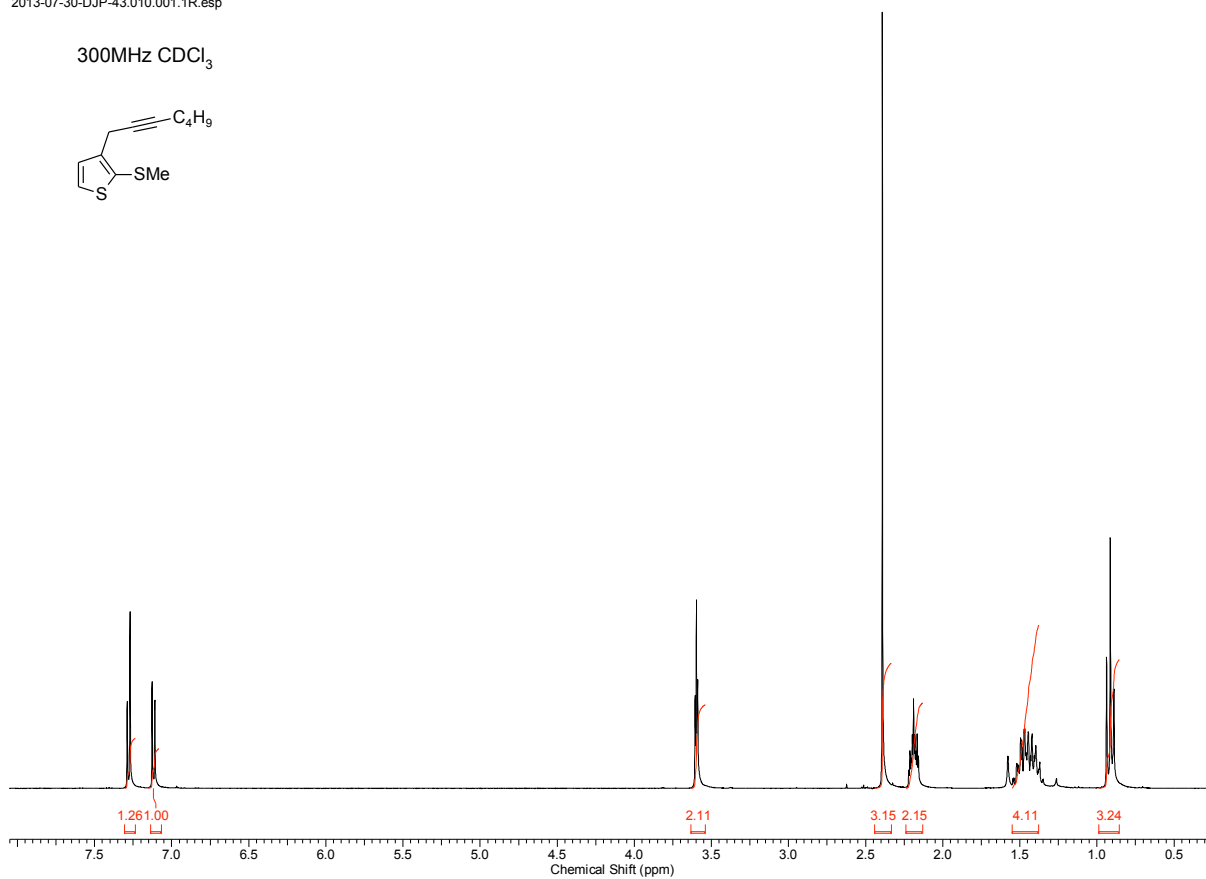
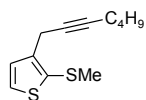
2014-12-09-DJP-57.010.001.1R.esp



### 3-(Hept-2-yn-1-yl)-2-(methylsulfanyl)thiophene 3ac

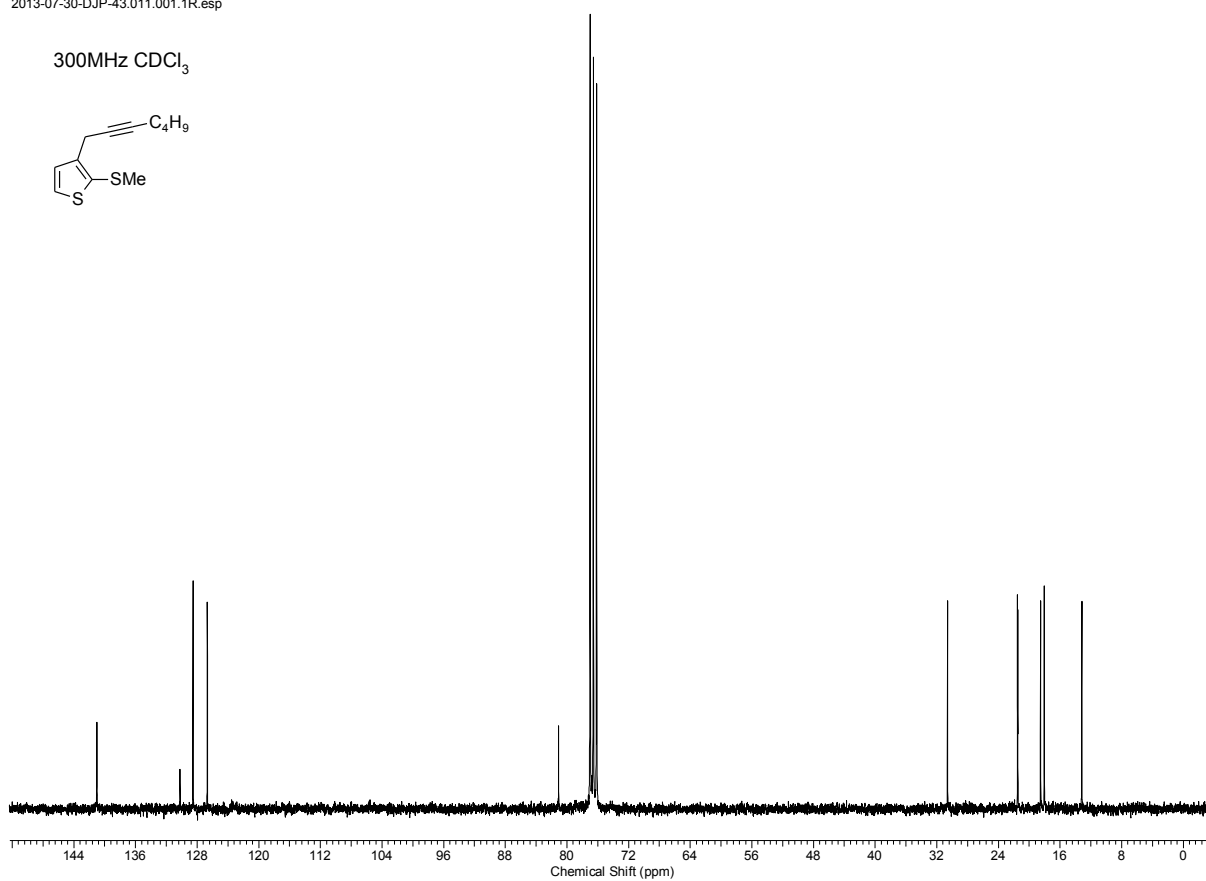
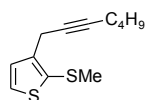
2013-07-30-DJP-43.010.001.1R.esp

300MHz CDCl<sub>3</sub>



2013-07-30-DJP-43.011.001.1R.esp

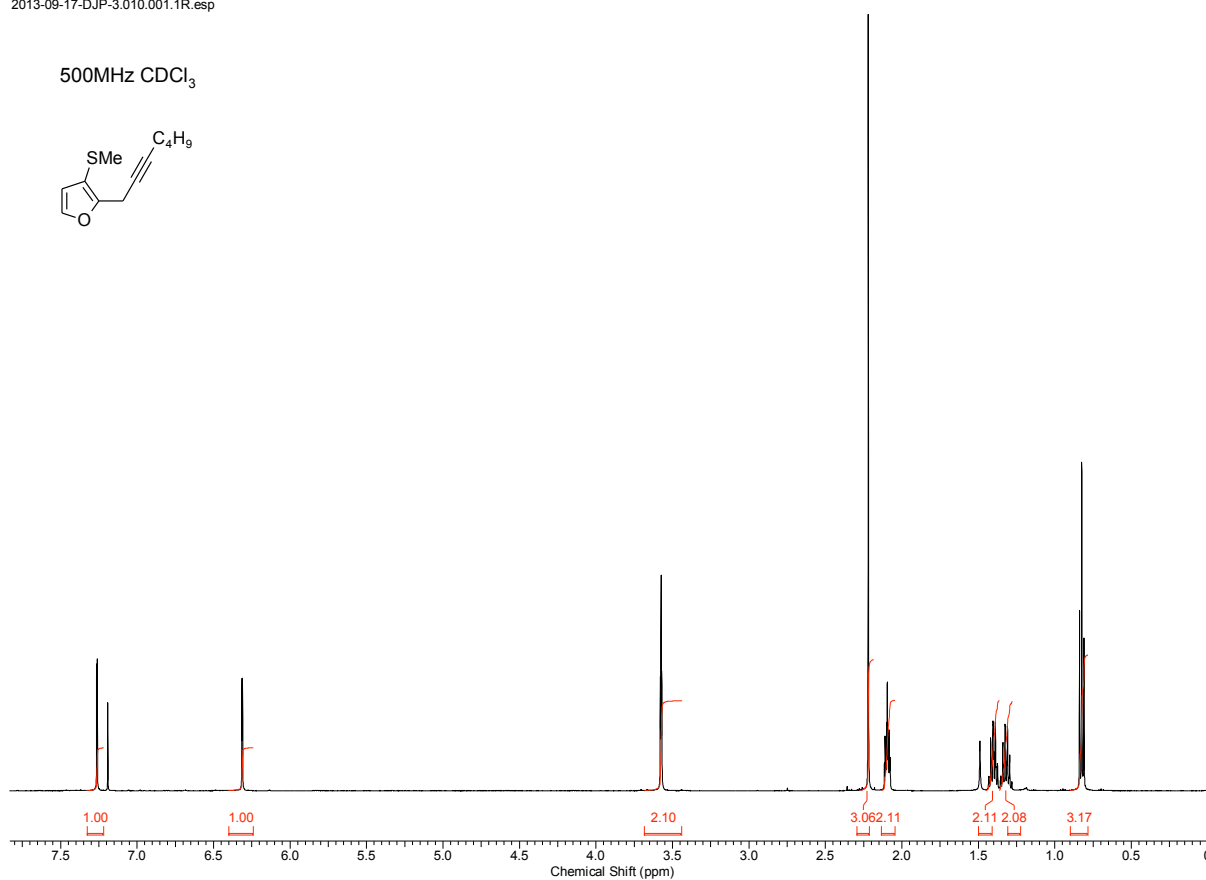
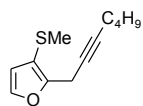
300MHz CDCl<sub>3</sub>



## 2-(Hept-2-yn-1-yl)-3-(methylsulfonyl)furan 3ad

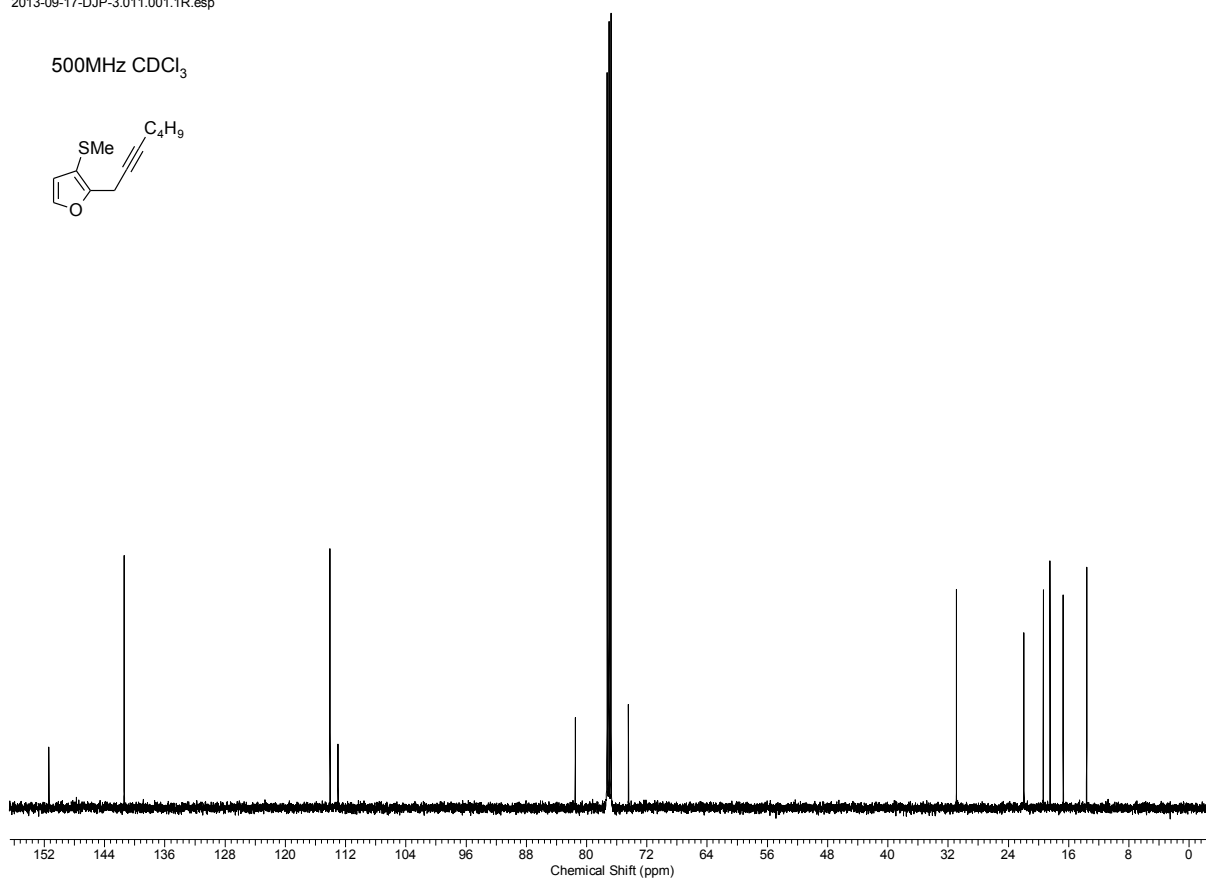
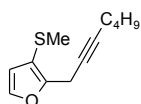
2013-09-17-DJP-3.010.001.1R.esp

500MHz CDCl<sub>3</sub>



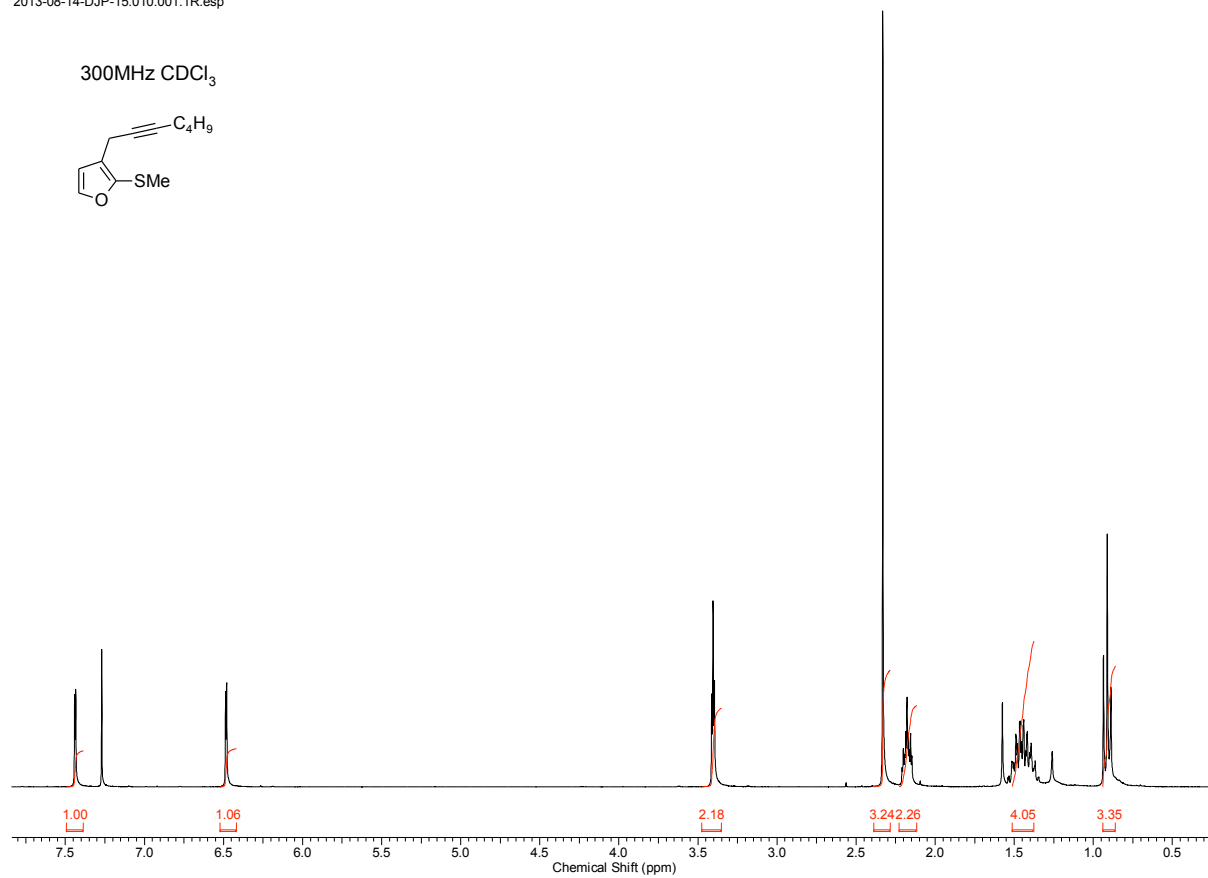
2013-09-17-DJP-3.011.001.1R.esp

500MHz CDCl<sub>3</sub>

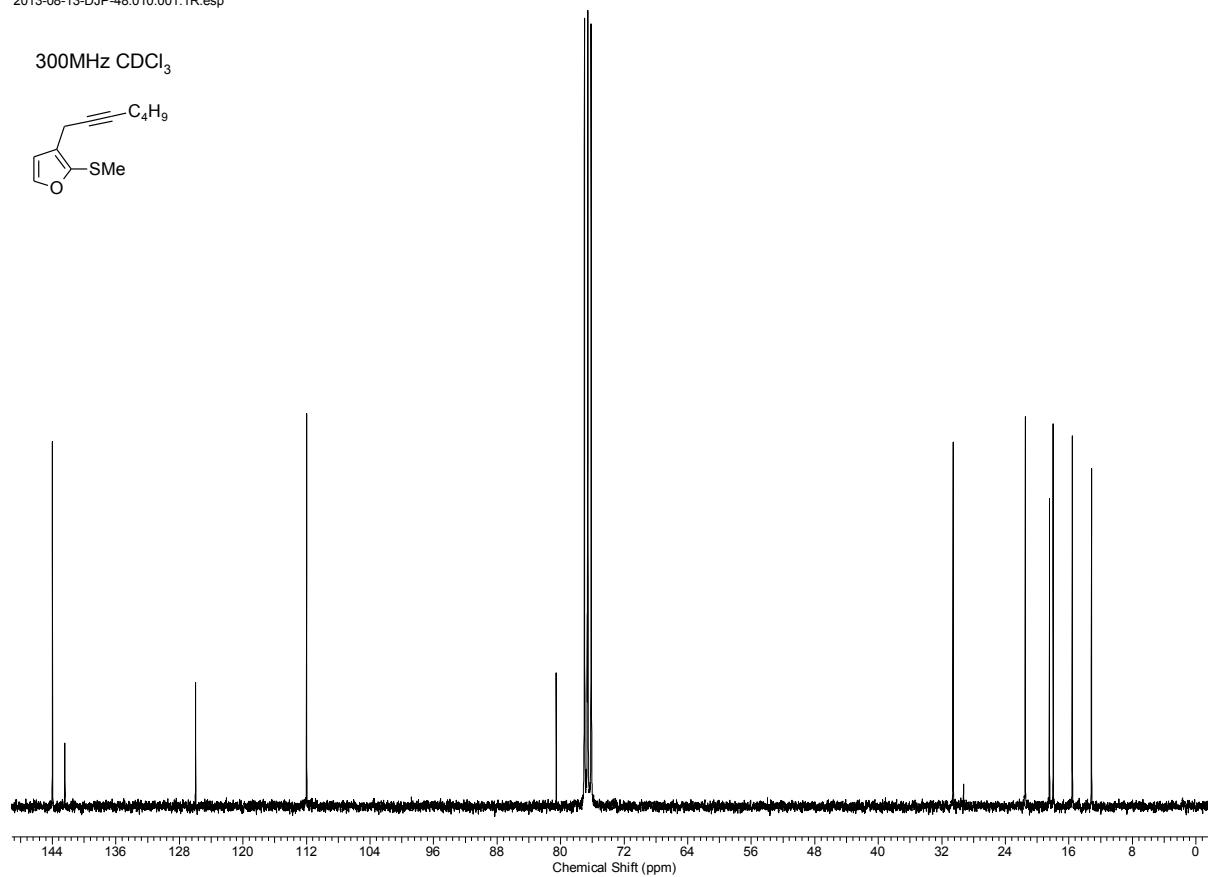


### 3-(Hept-2-yn-1-yl)-2-(methylsulfonyl)furan 3ae

2013-08-14-DJP-15.010.001.1R.esp

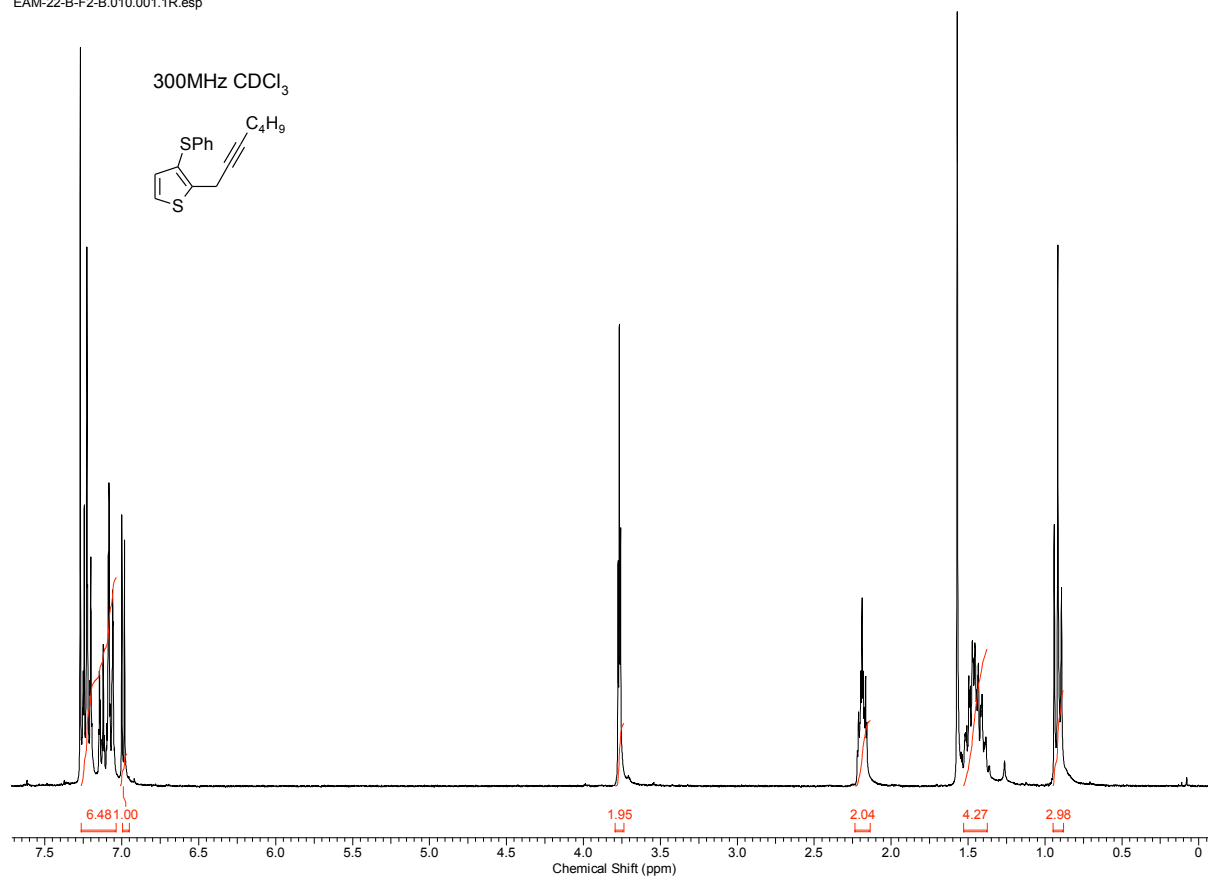


2013-08-13-DJP-48.010.001.1R.esp

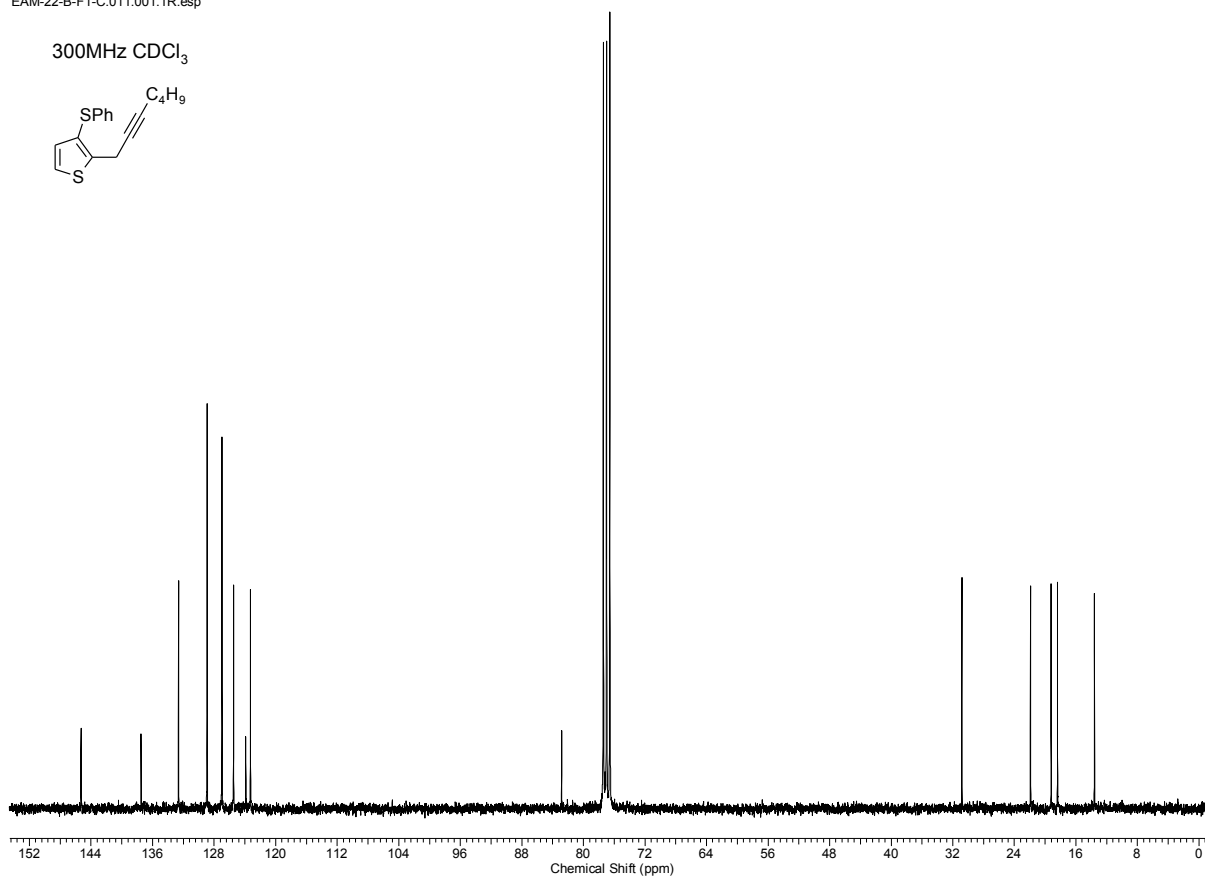


## 2-(Hept-2-yn-1-yl)-3-(phenylsulfanyl)thiophene 3af

EAM-22-B-F2-B.010.001.1R.esp

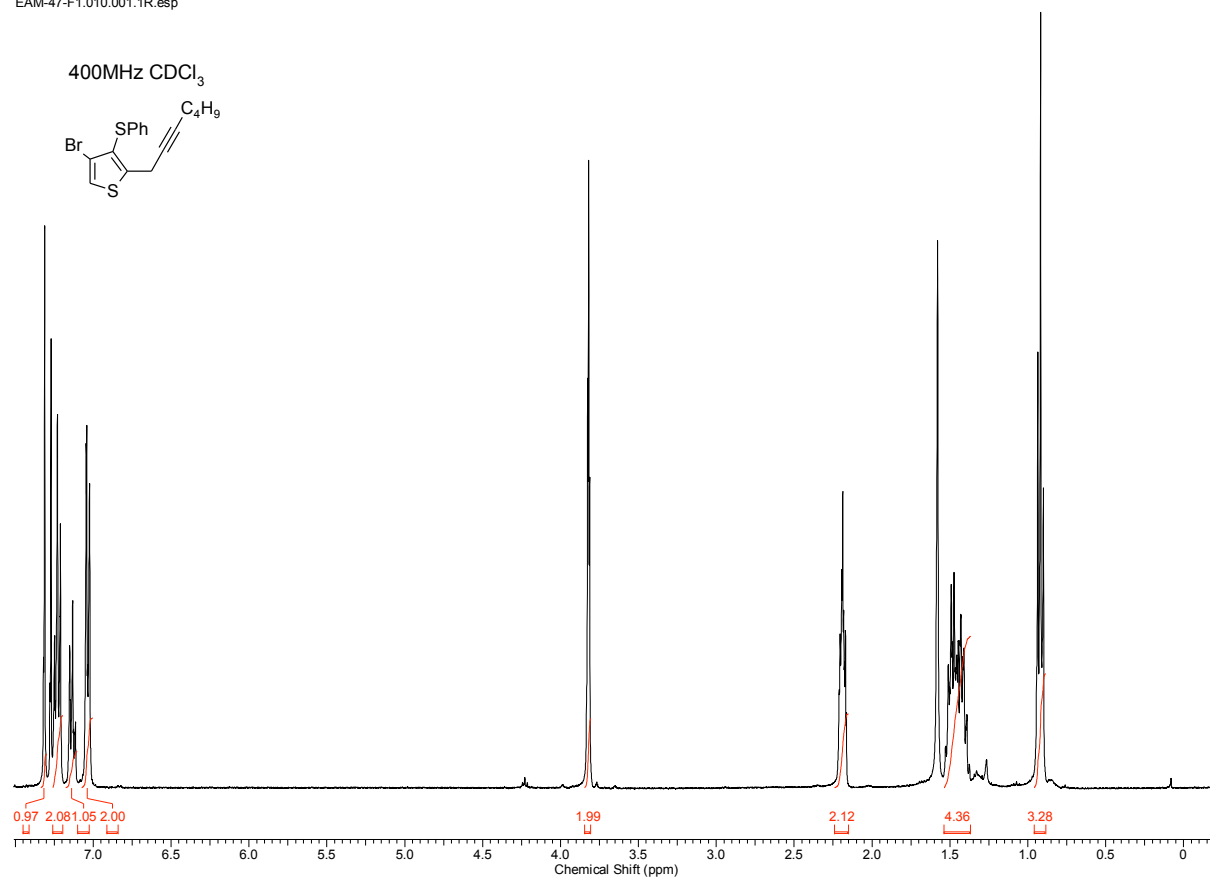


EAM-22-B-F1-C.011.001.1R.esp

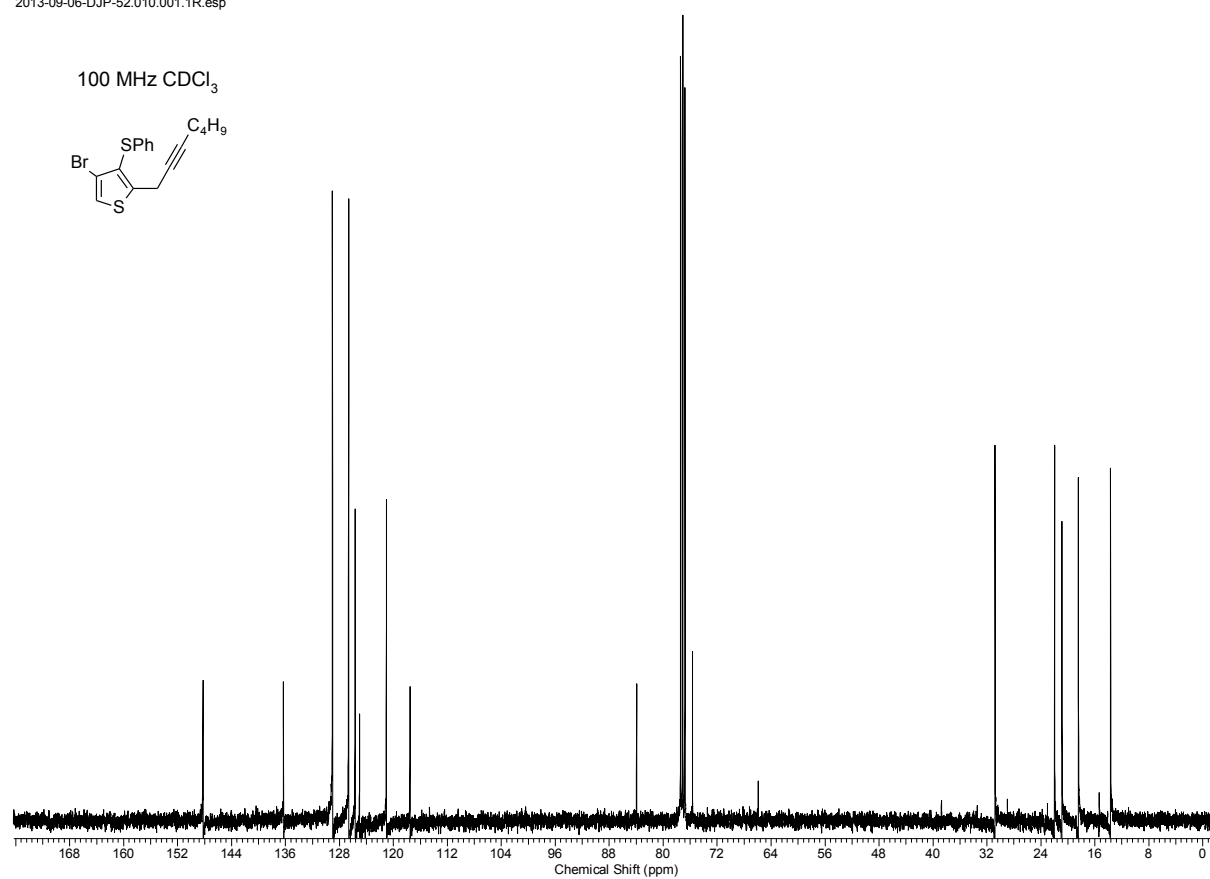


# 4-Bromo-2-(hept-2-yn-1-yl)-3-(phenylsulfanyl)thiophene 3ag

EAM-47-F1.010.001.1R.esp

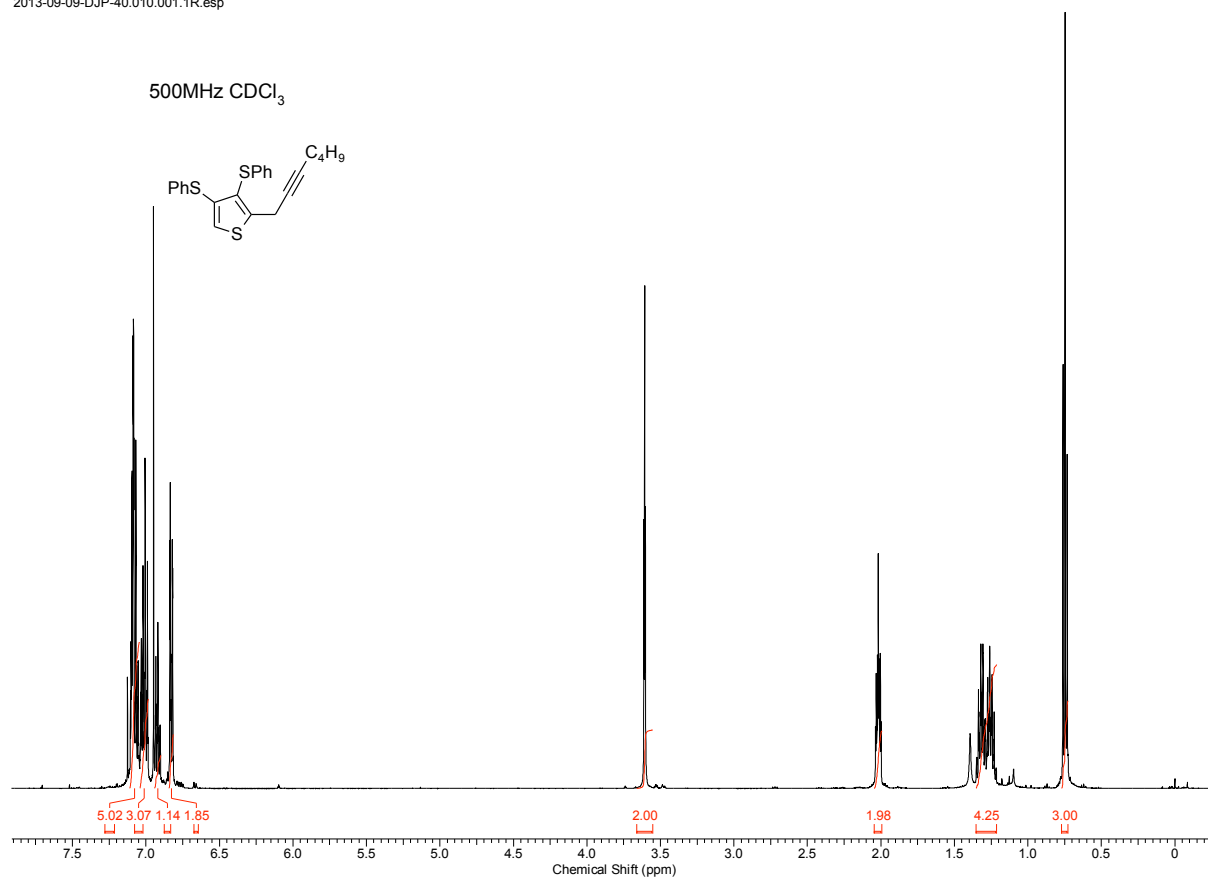


2013-09-06-DJP-52.010.001.1R.esp

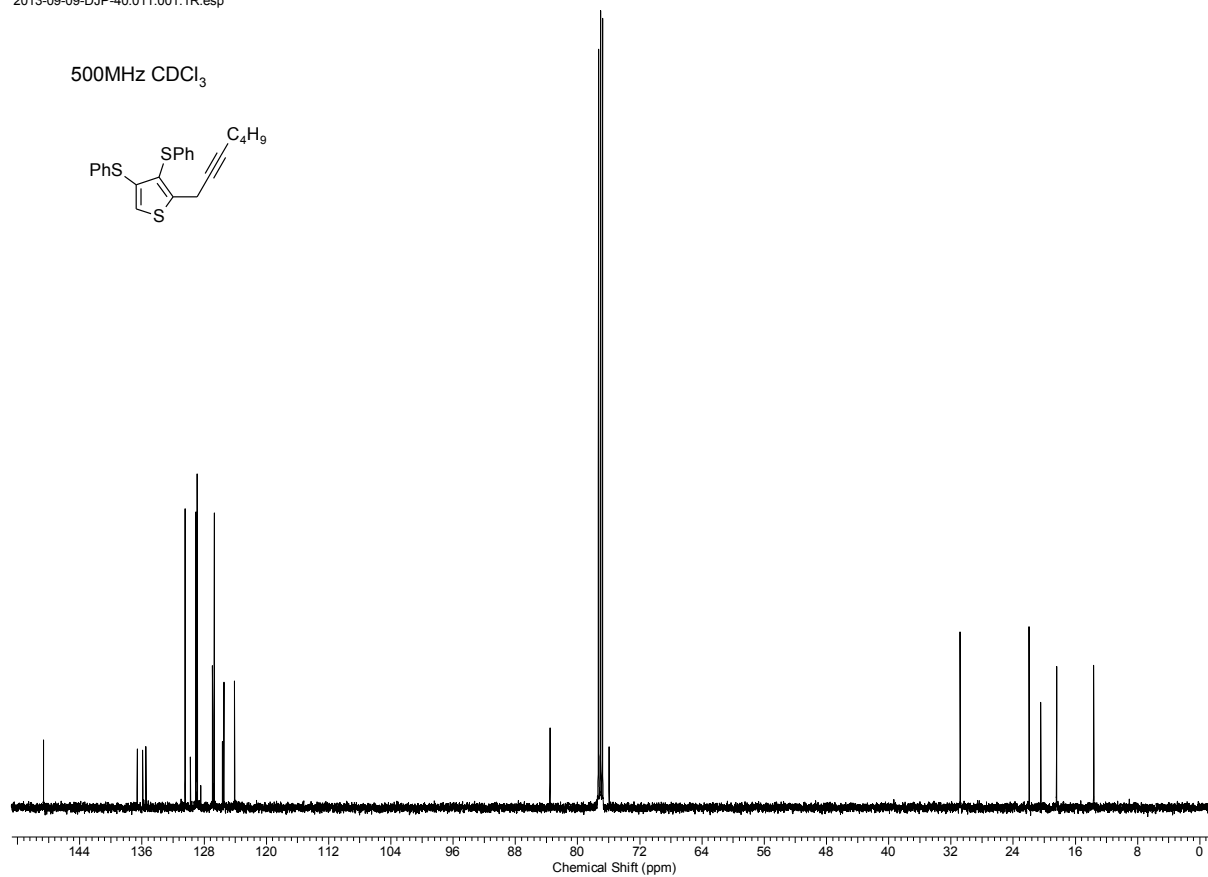


# 2-(Hept-2-yn-1-yl)-3,4-bis(phenylsulfanyl)thiophene 3ah

2013-09-09-DJP-40.010.001.1R.esp



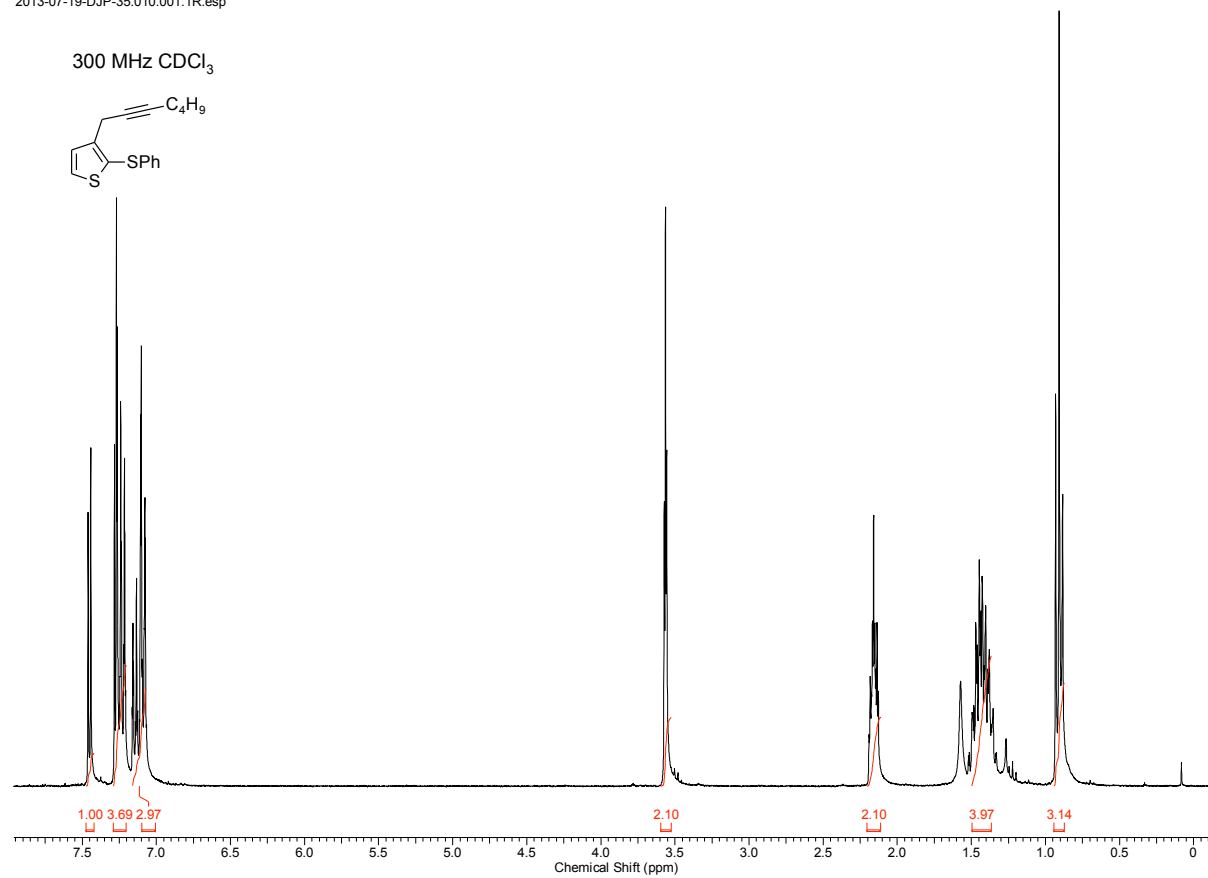
2013-09-09-DJP-40.011.001.1R.esp



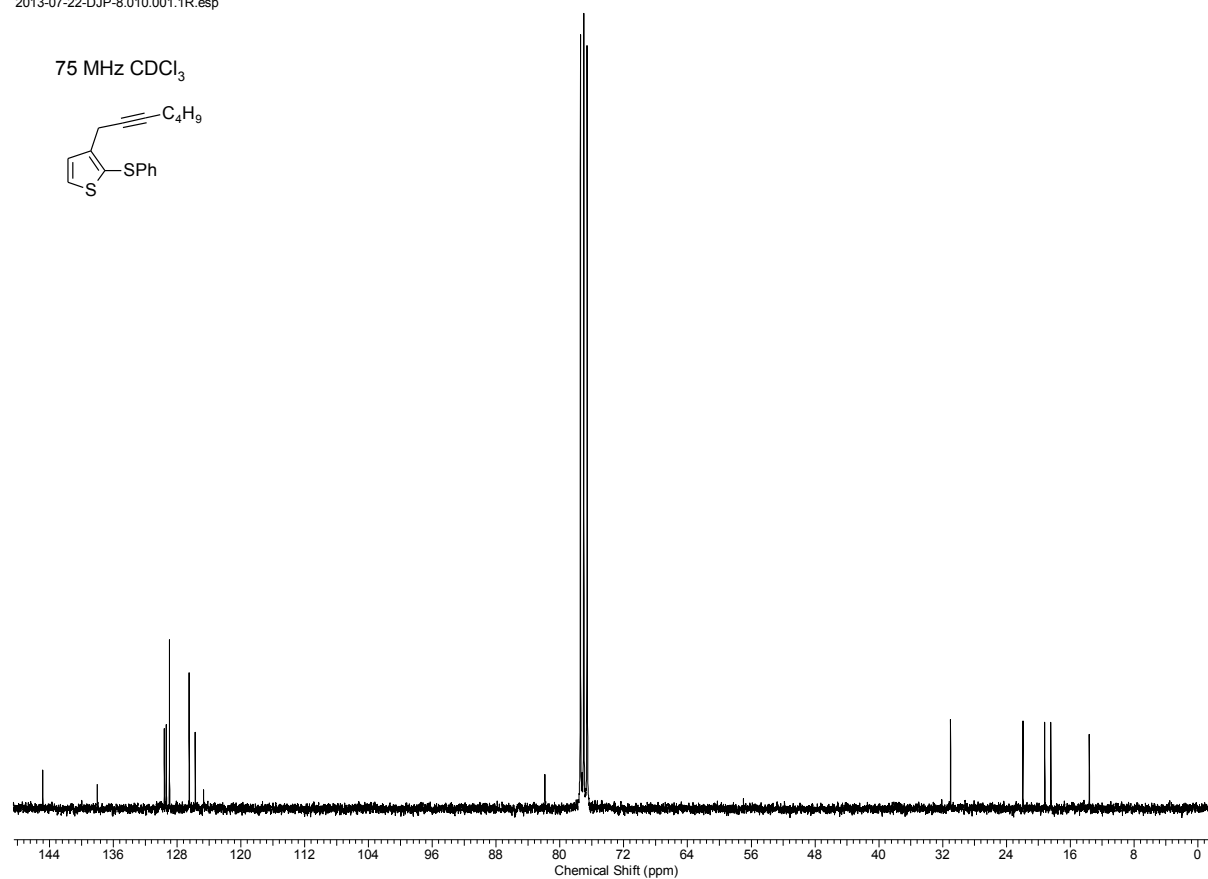


### 3-(Hept-2-yn-1-yl)-2-(phenylthio)thiophene 3ai

2013-07-19-DJP-35.010.001.1R.esp

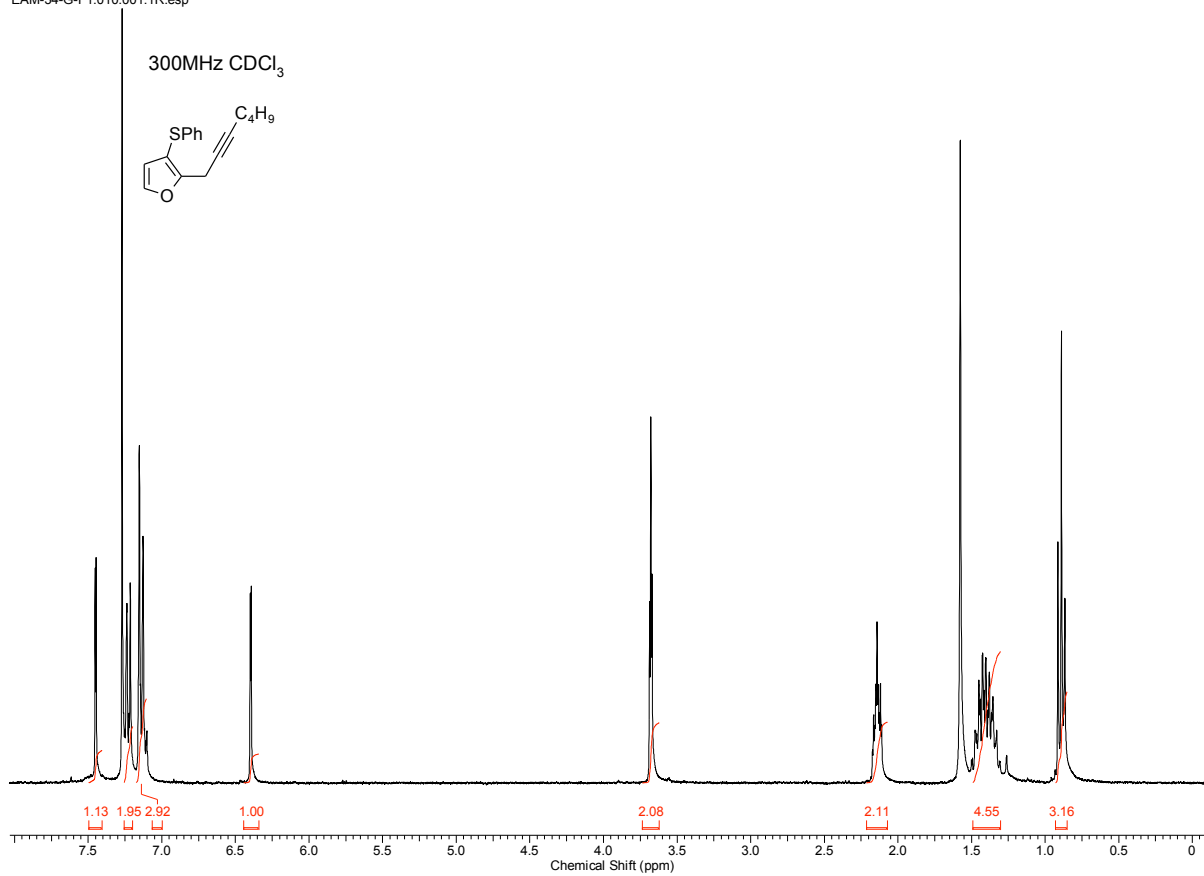


2013-07-22-DJP-8.010.001.1R.esp



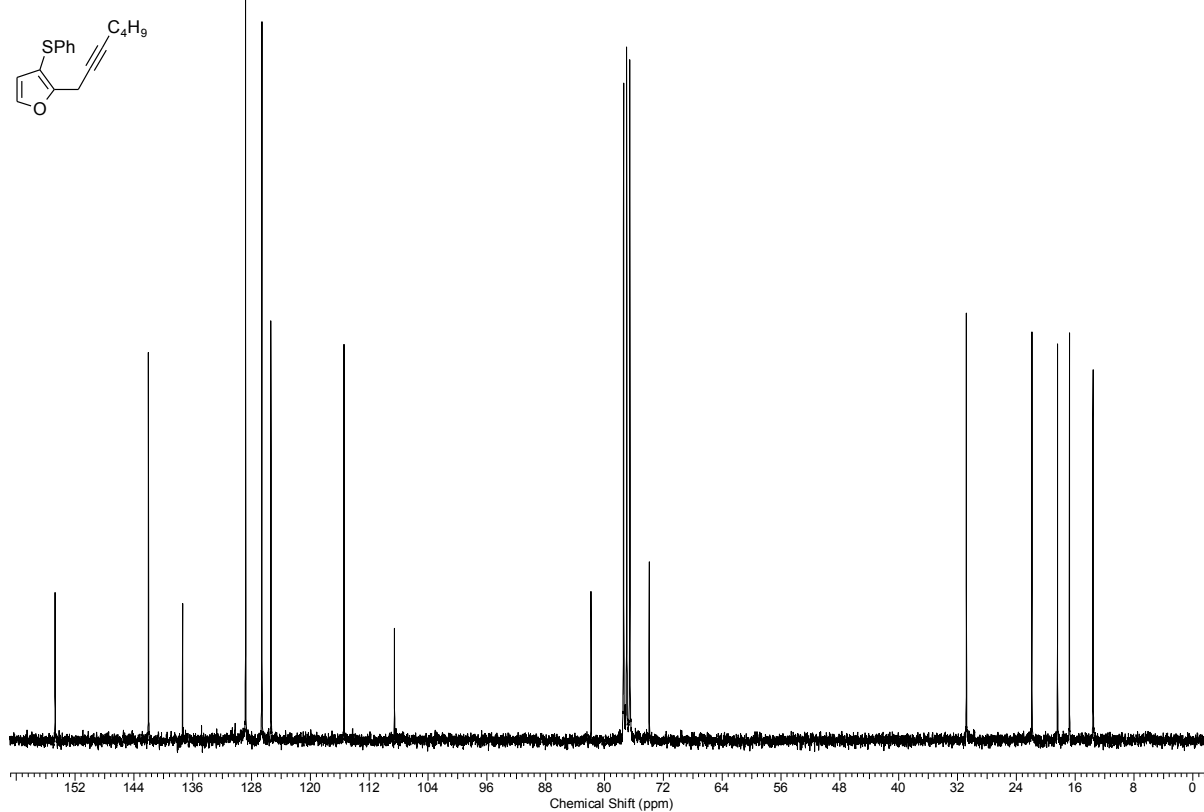
## 2-(Hept-2-yn-1-yl)-3-(phenylsulfanyl)furan 3aj

EAM-34-G-F1.010.001.1R.esp



2013-08-21-DJP-11.010.001.1R.esp

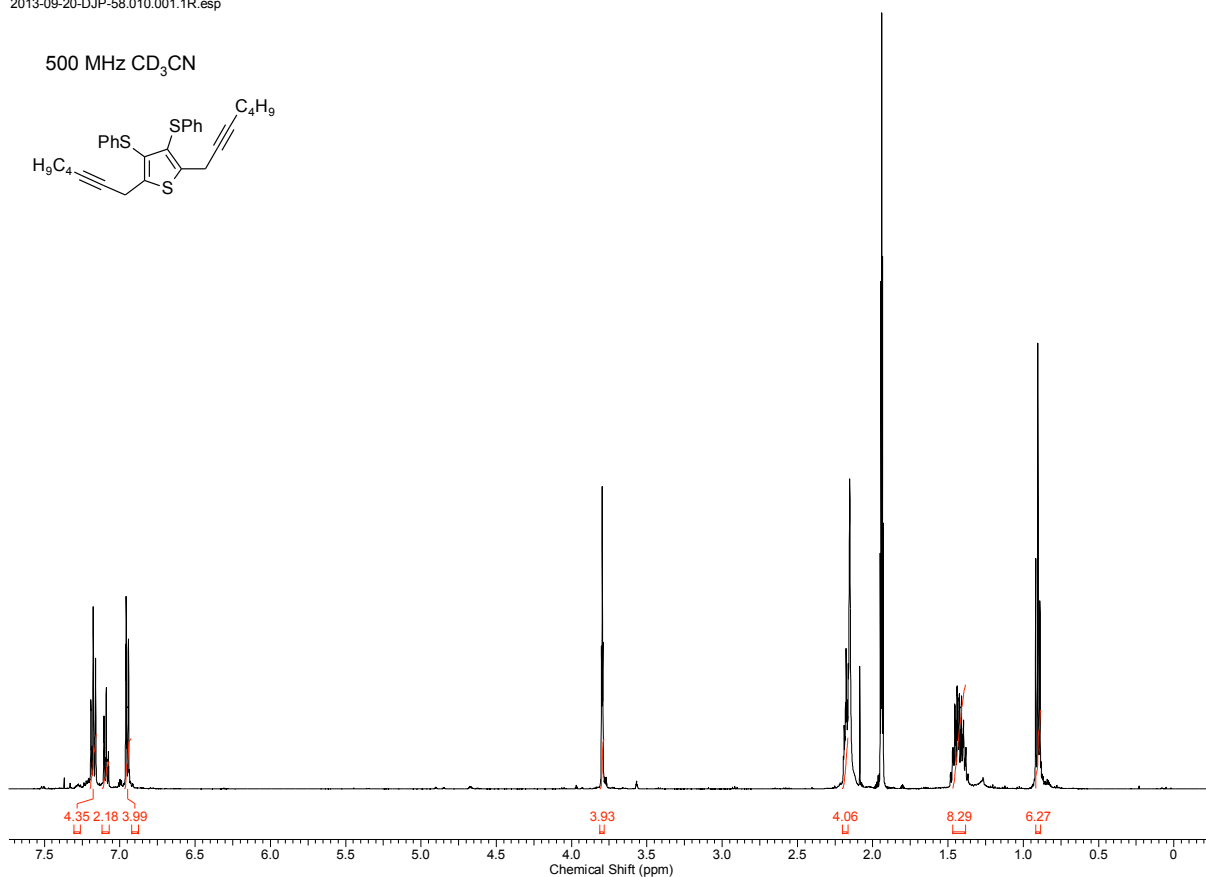
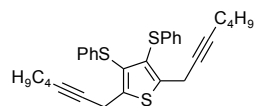
300MHz CDCl<sub>3</sub>



## 2,5-Di(hept-2-yn-1-yl)-3,4-bis(phenylthio)thiophene 3ak

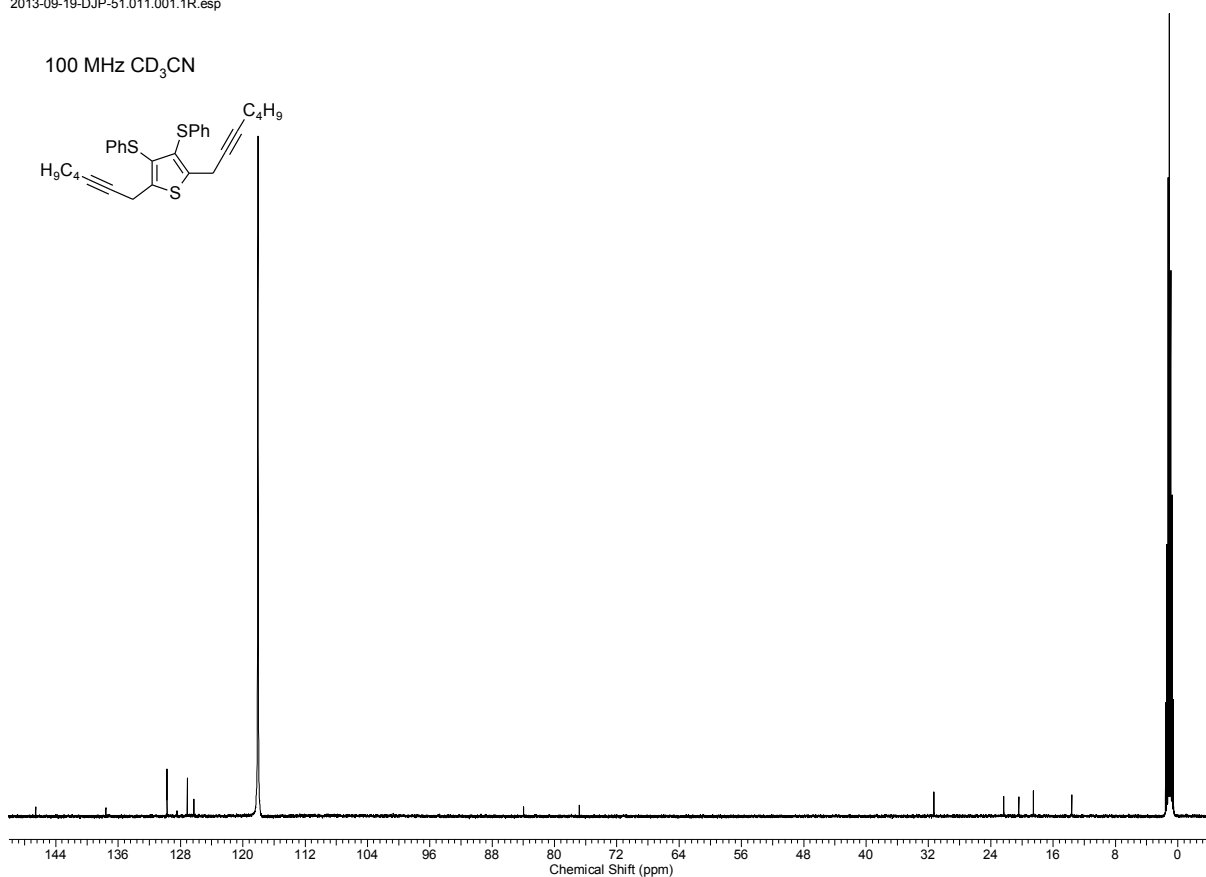
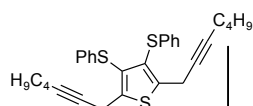
2013-09-20-DJP-58.010.001.1R.esp

500 MHz CD<sub>3</sub>CN



2013-09-19-DJP-51.011.001.1R.esp

100 MHz CD<sub>3</sub>CN

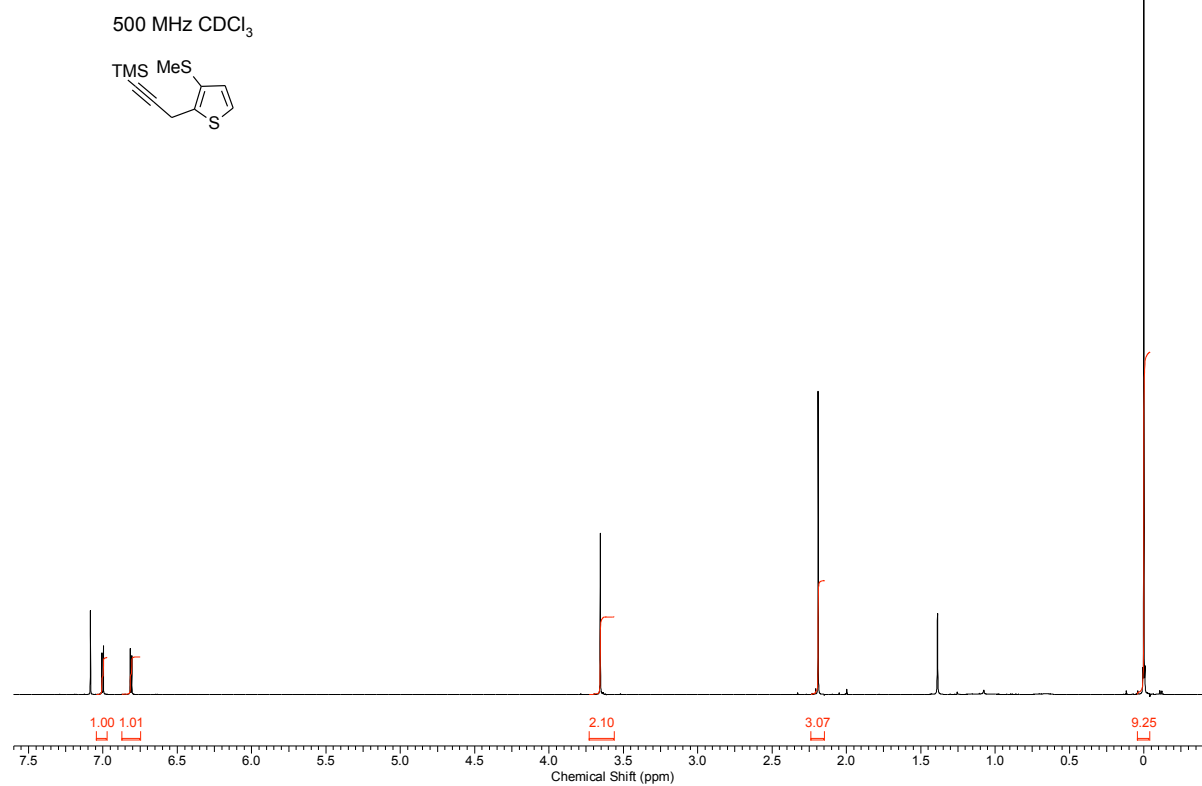


# Trimethyl(3-(3-(methylsulfanyl)thiophen-2-yl)prop-1-yn-1-yl)silane 3aq

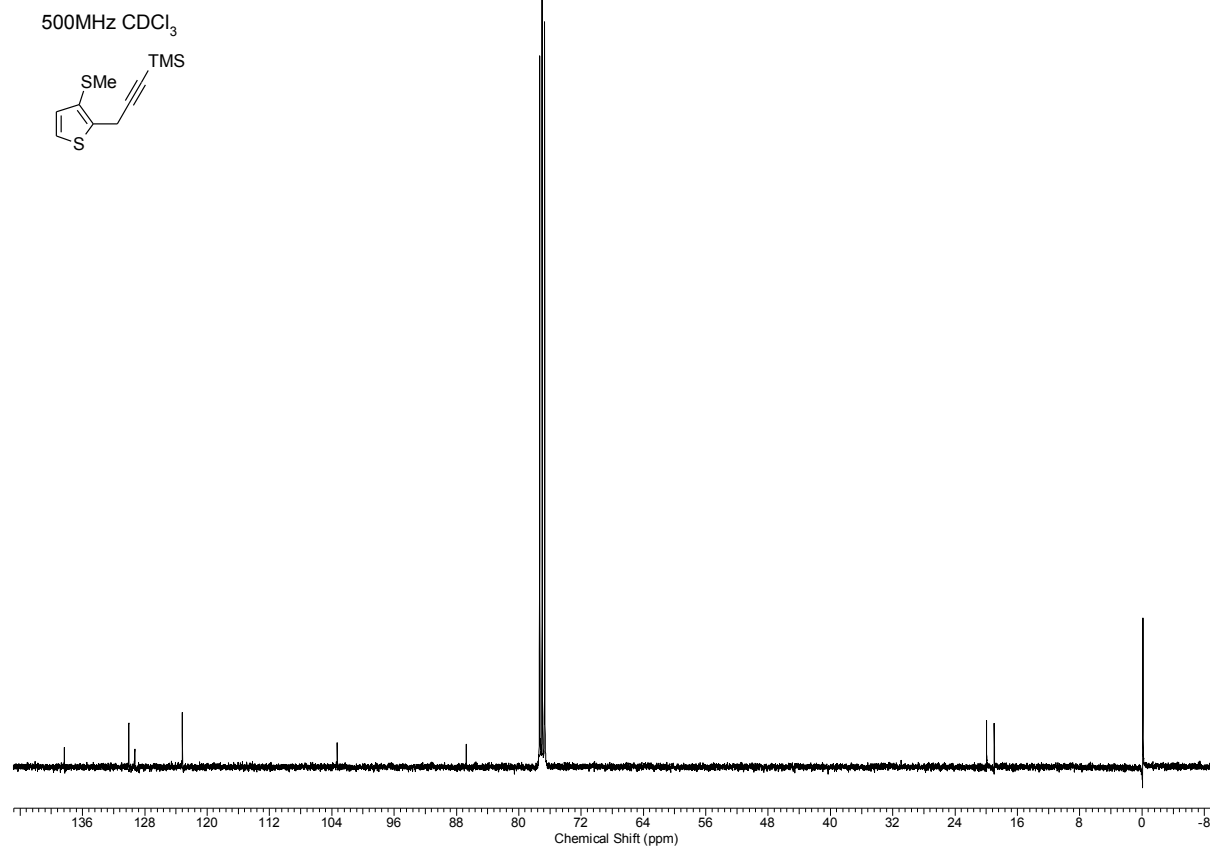
EAM-75.esp

VerticalScaleFactor = 1

24/11/2014 10:52:36



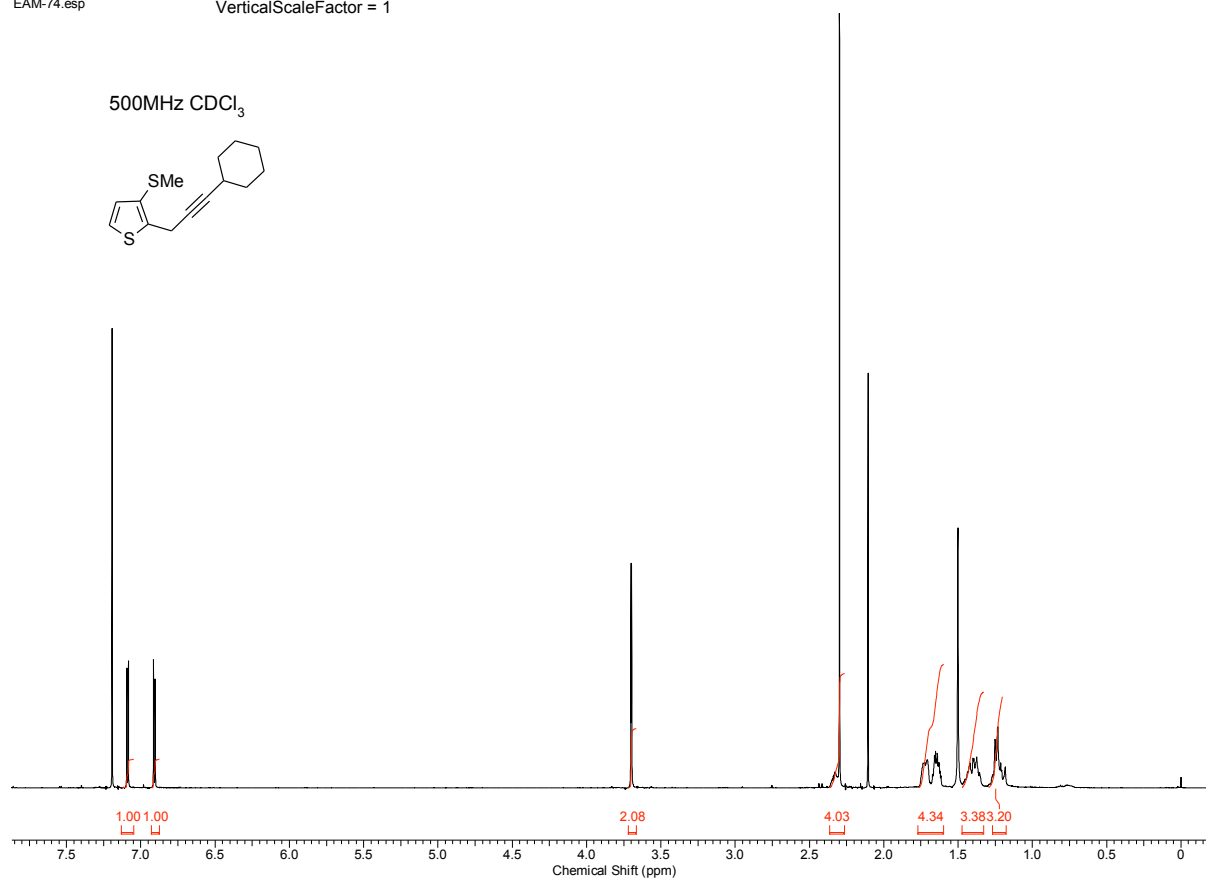
2013-09-27-DJP-44.010.001.1R.esp



# 2-(3-Cyclohexylprop-2-yn-1-yl)-3-(methylsulfanyl)thiophene 3ar

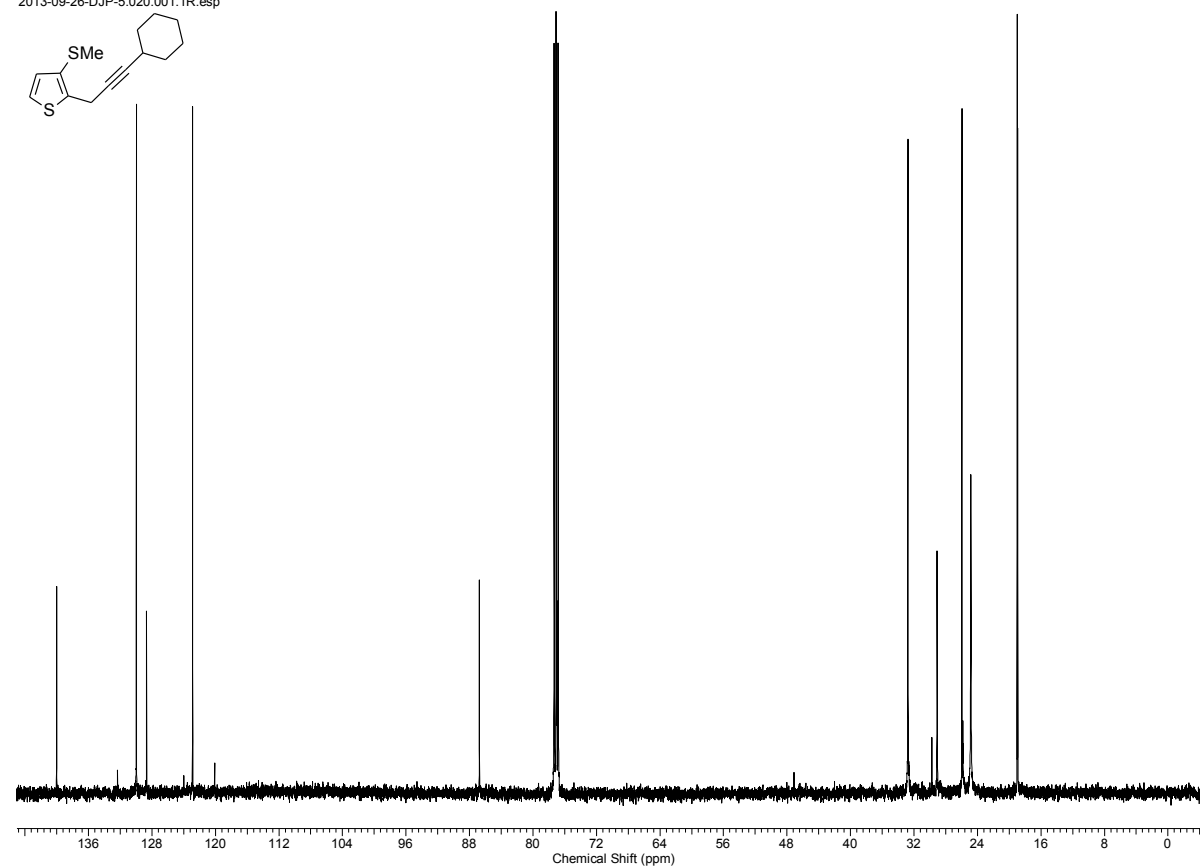
EAM-74.esp

VerticalScaleFactor = 1



500MHz CDCl<sub>3</sub>

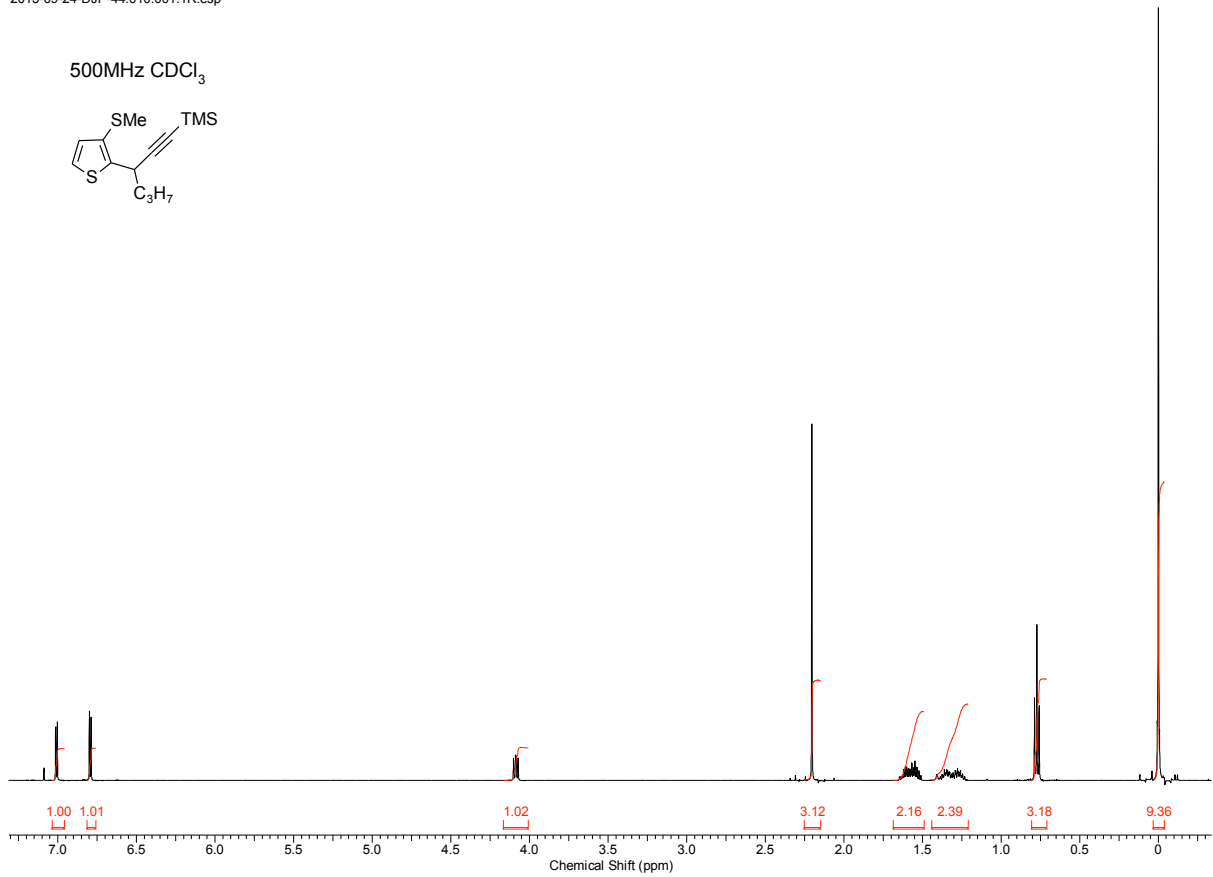
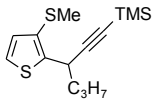
2013-09-26-DJP-5.020.001.1R.esp



# Trimethyl(3-(3-(methylsulfanyl)thiophen-2-yl)hex-1-yn-1-yl)silane 3at

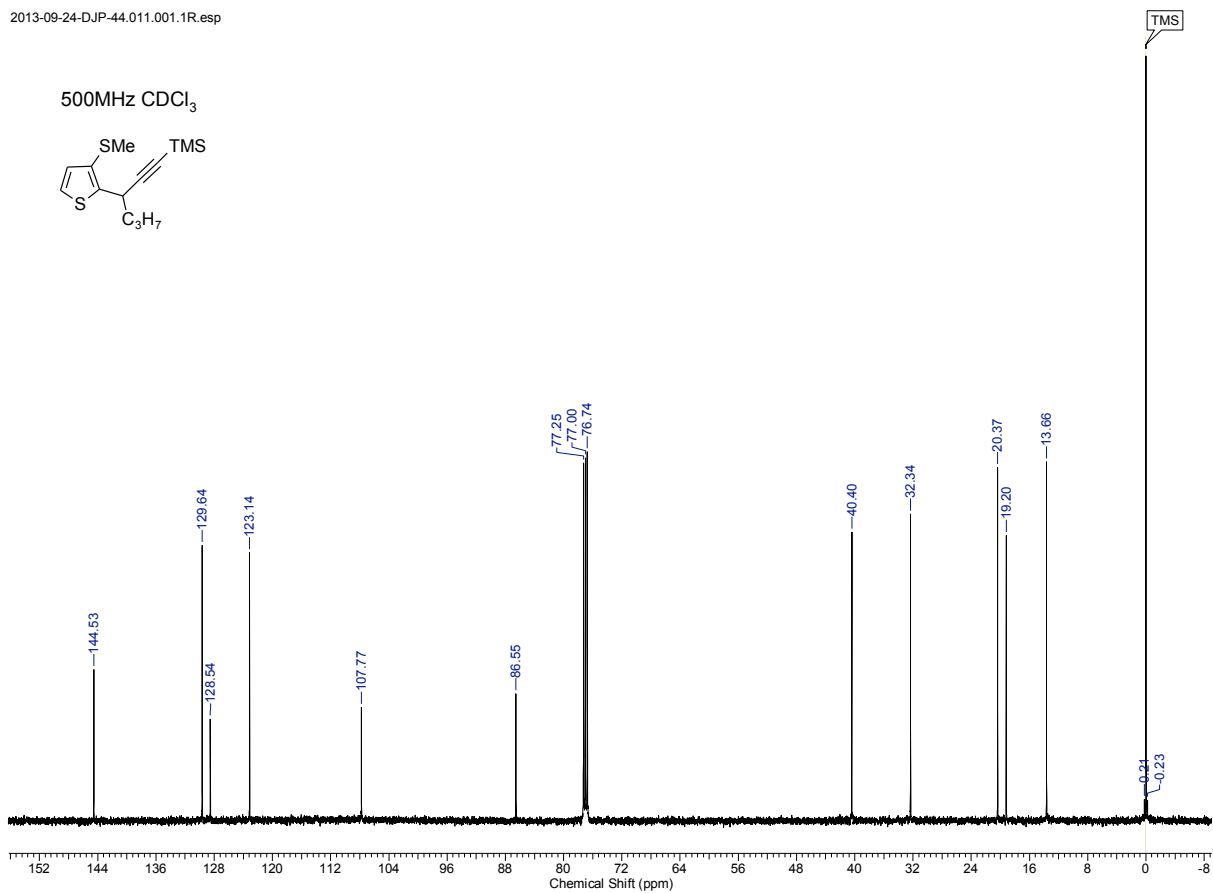
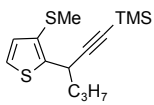
2013-09-24-DJP-44.010.001.1R.esp

500MHz CDCl<sub>3</sub>



2013-09-24-DJP-44.011.001.1R.esp

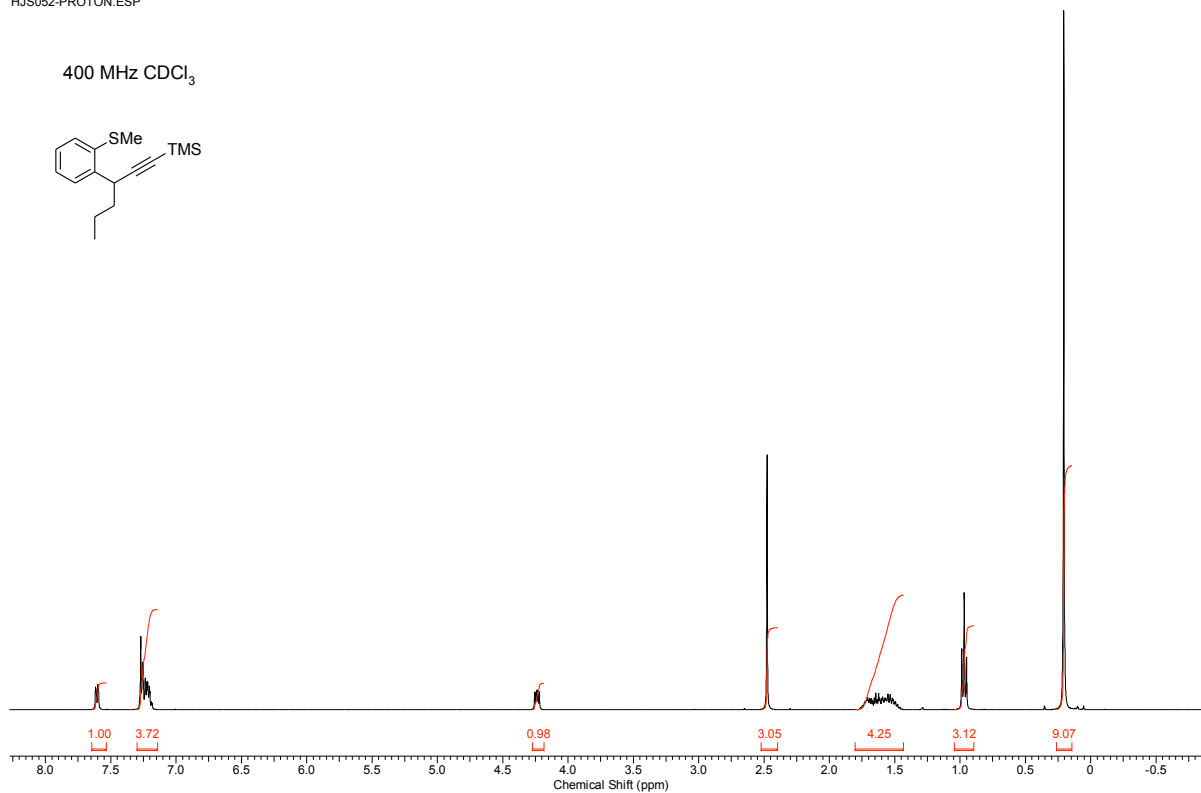
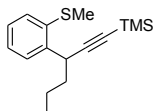
500MHz CDCl<sub>3</sub>



# Trimethyl(3(2-(methylsulfanyl)phenyl)hex-1-yn-1-yl)silane 3au

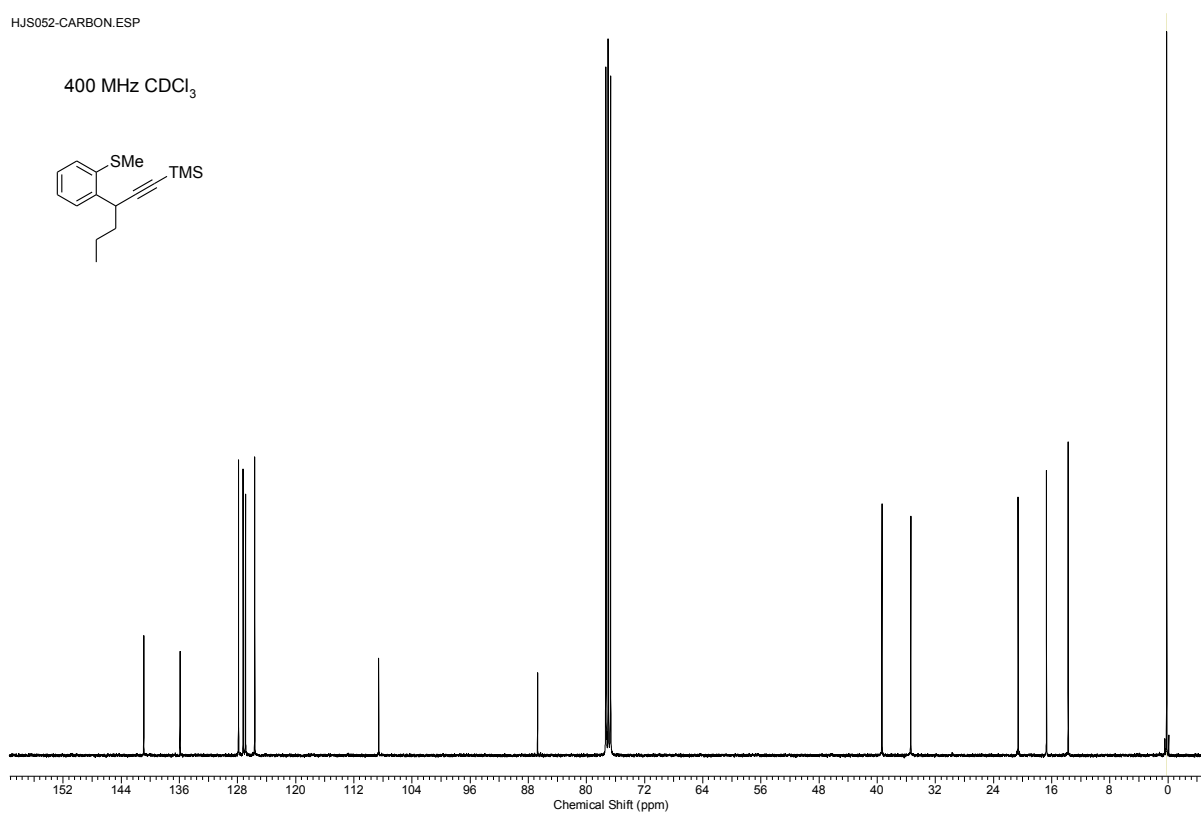
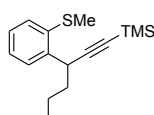
HJS052-PROTON.ESP

400 MHz CDCl<sub>3</sub>



HJS052-CARBON.ESP

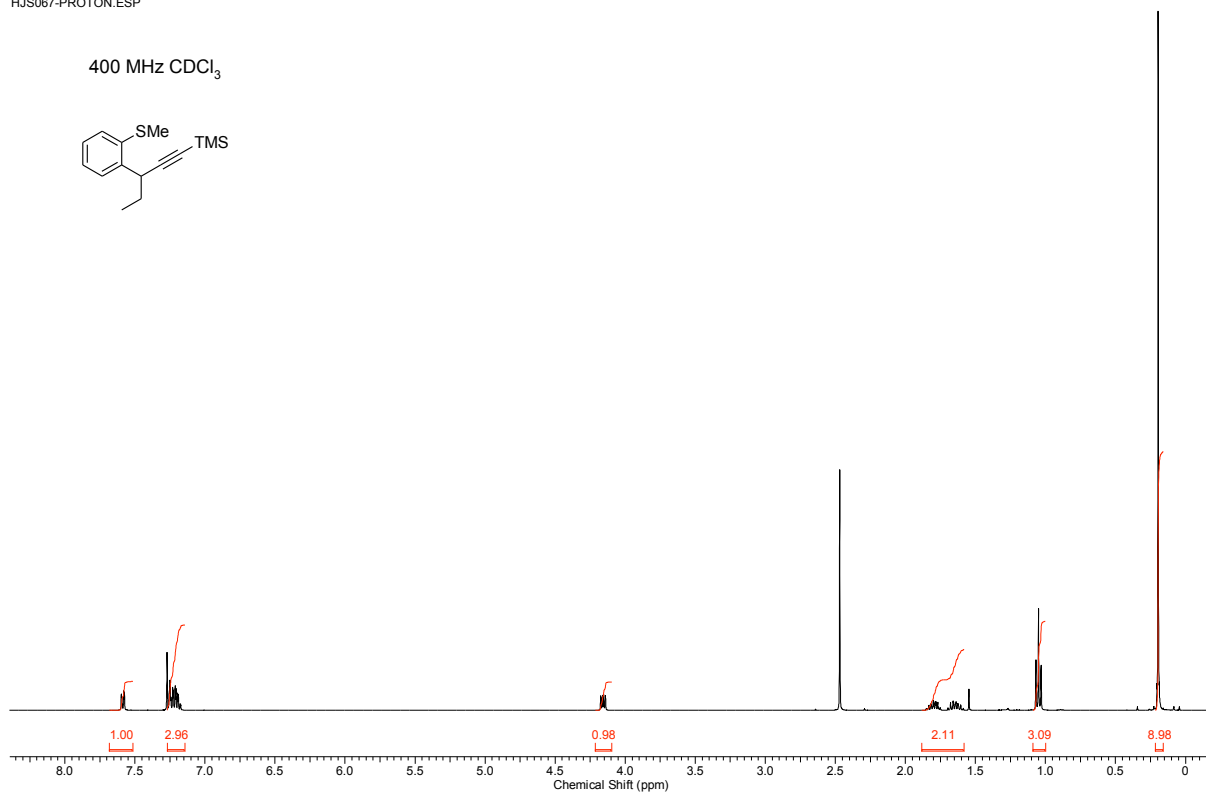
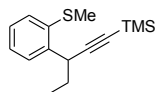
400 MHz CDCl<sub>3</sub>



# Trimethyl(3-(2-methylsulfonyl)pent-1-yn-yl)silane 3av

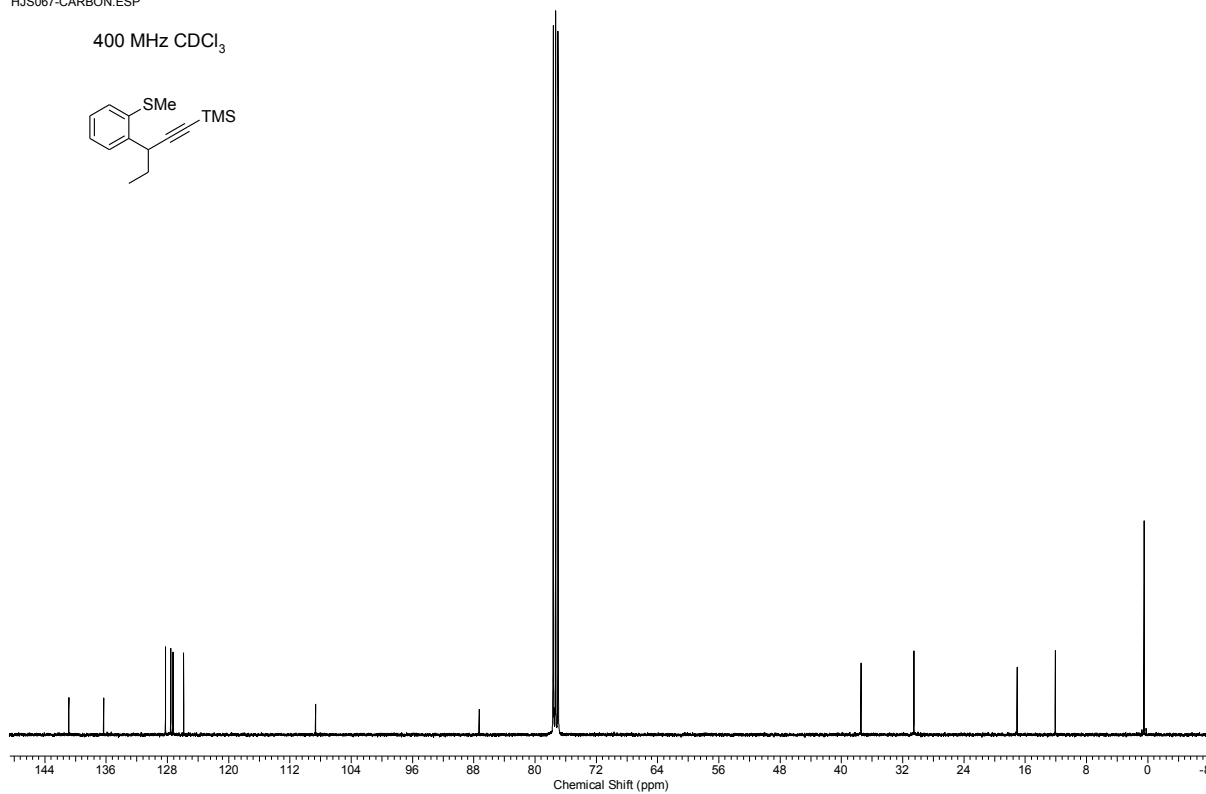
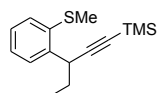
HJS067-PROTON.ESP

400 MHz CDCl<sub>3</sub>



HJS067-CARBON.ESP

400 MHz CDCl<sub>3</sub>

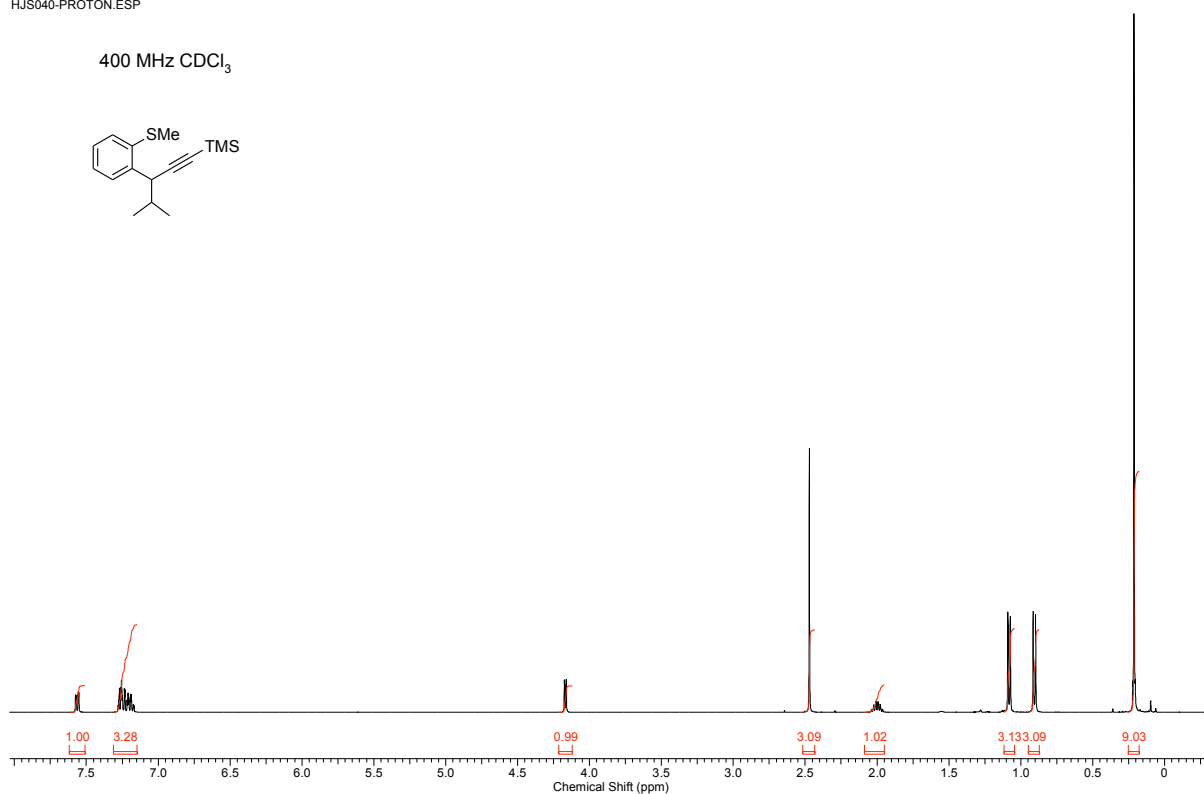
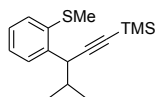




# Trimethyl(4-methyl-3-(2-(methylsulfanyl)phenyl)pent-1-yn-1-yl)silane 3aw

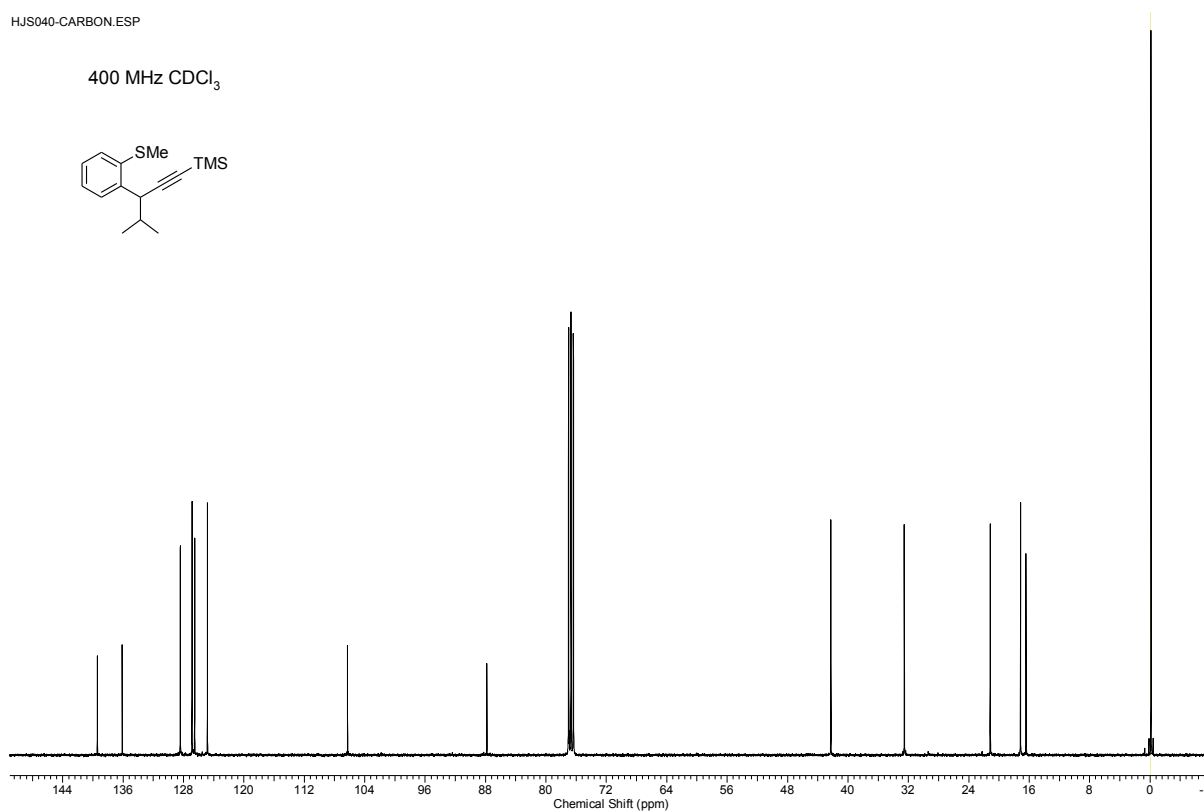
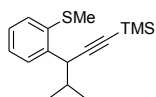
HJS040-PROTON.ESP

400 MHz CDCl<sub>3</sub>



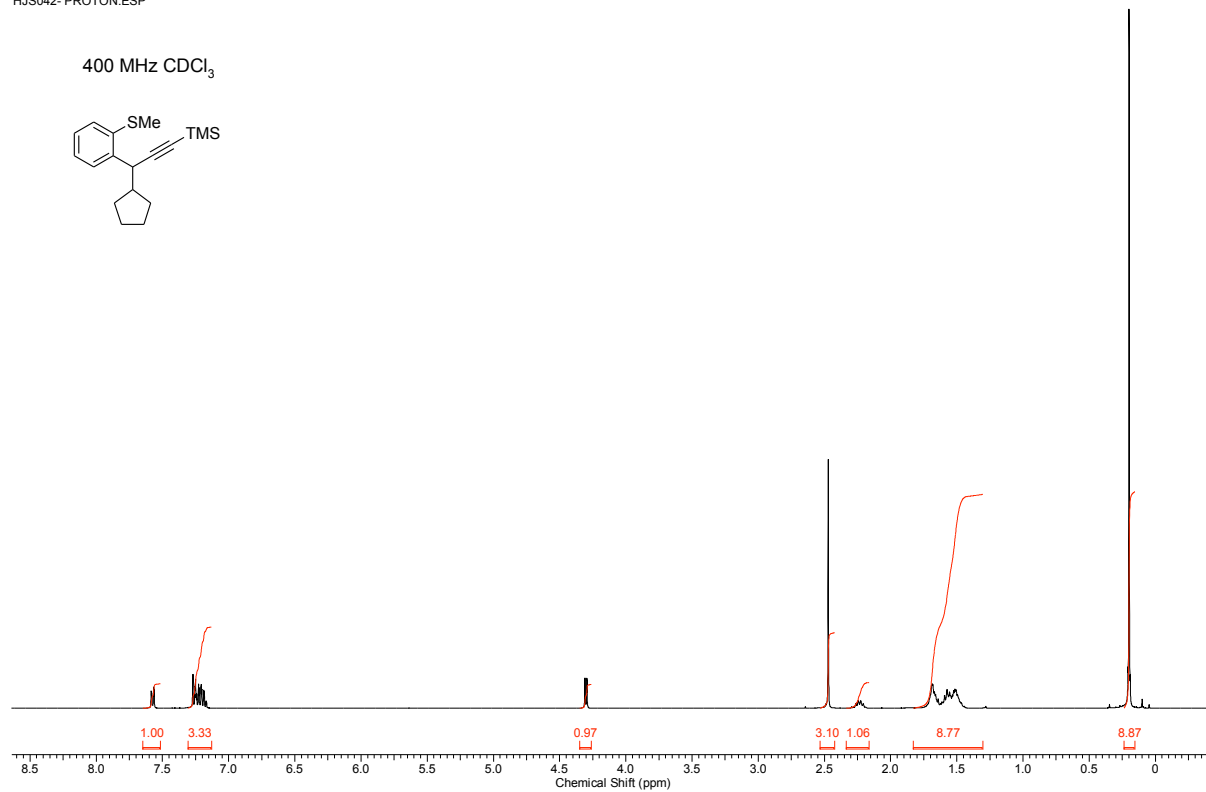
HJS040-CARBON.ESP

400 MHz CDCl<sub>3</sub>

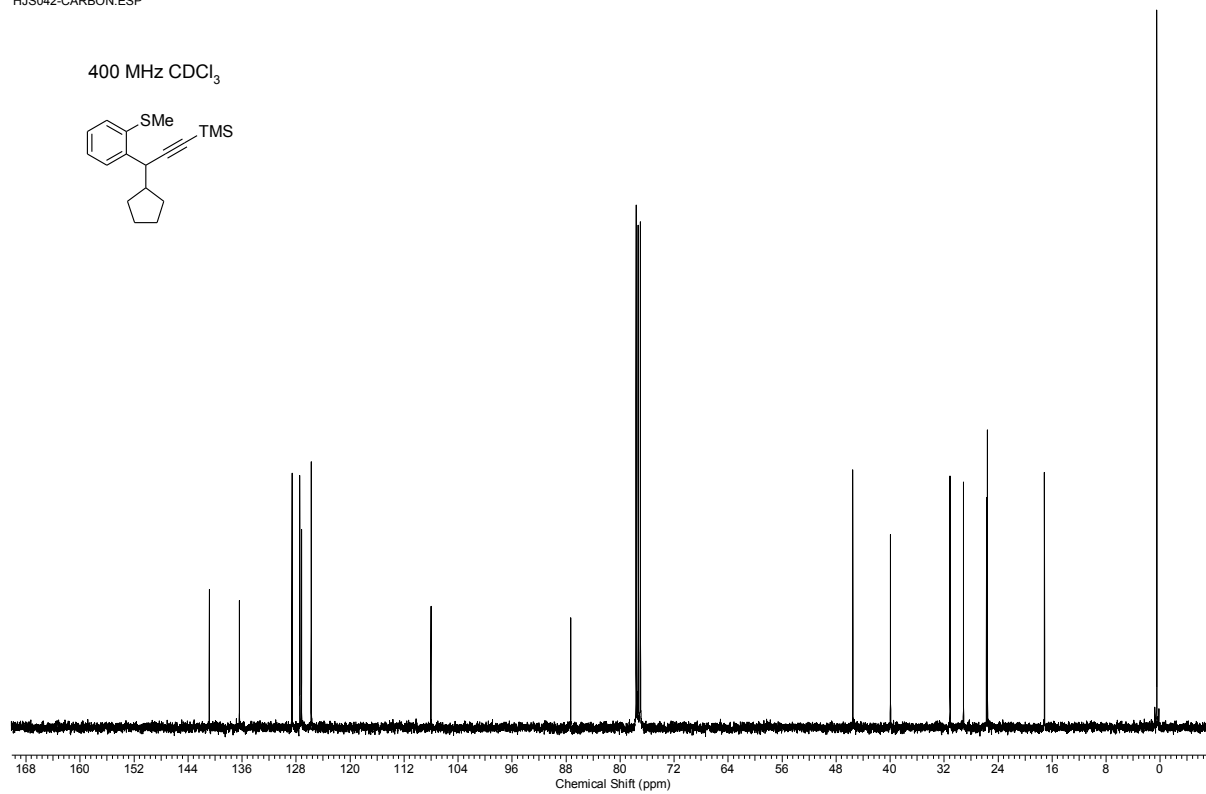


# (3-Cyclopentyl-3-(2-(methylsulfanyl)phenyl)prop-1-yn-1-yl)trimethylsilane 3ax

HJS042-PROTON.ESP



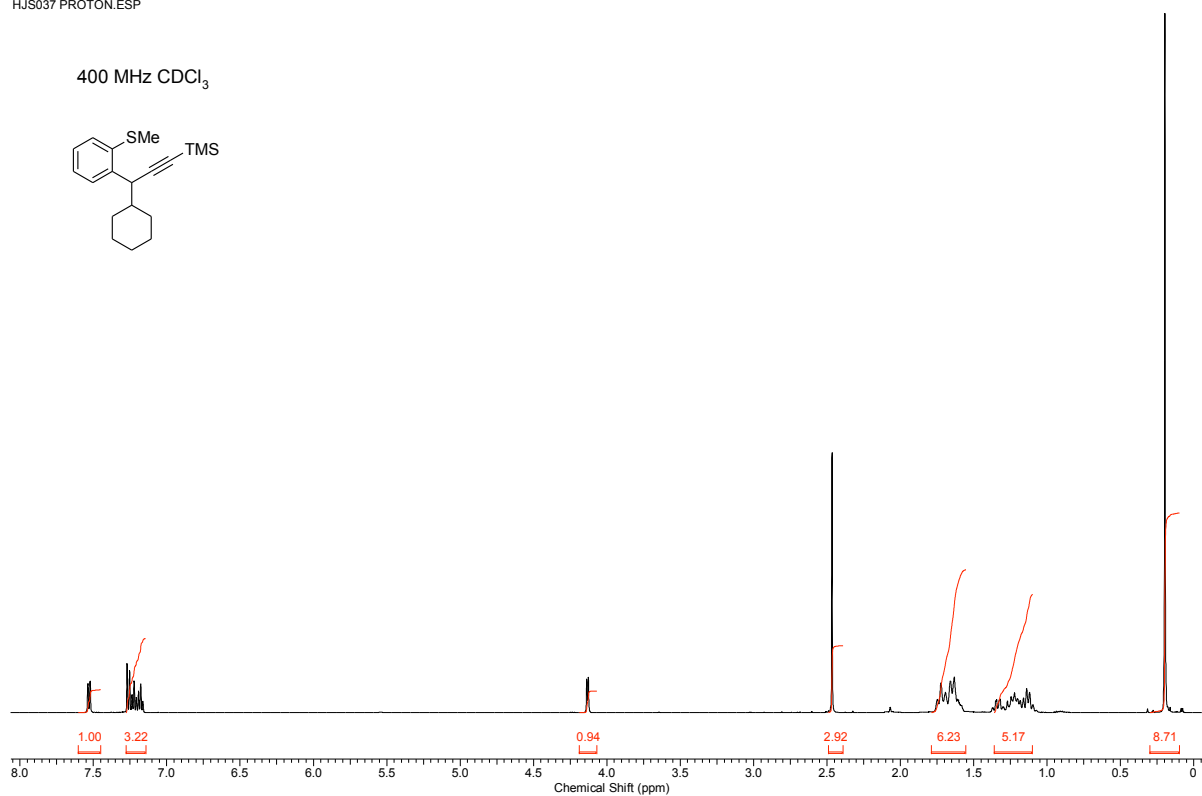
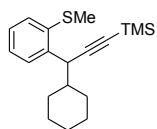
HJS042-CARBON.ESP



# (3-Cyclohexyl-3-(2-methylsulfanyl)phenyl)prop-1-yn-1-yl)trimethylsilane 3ay

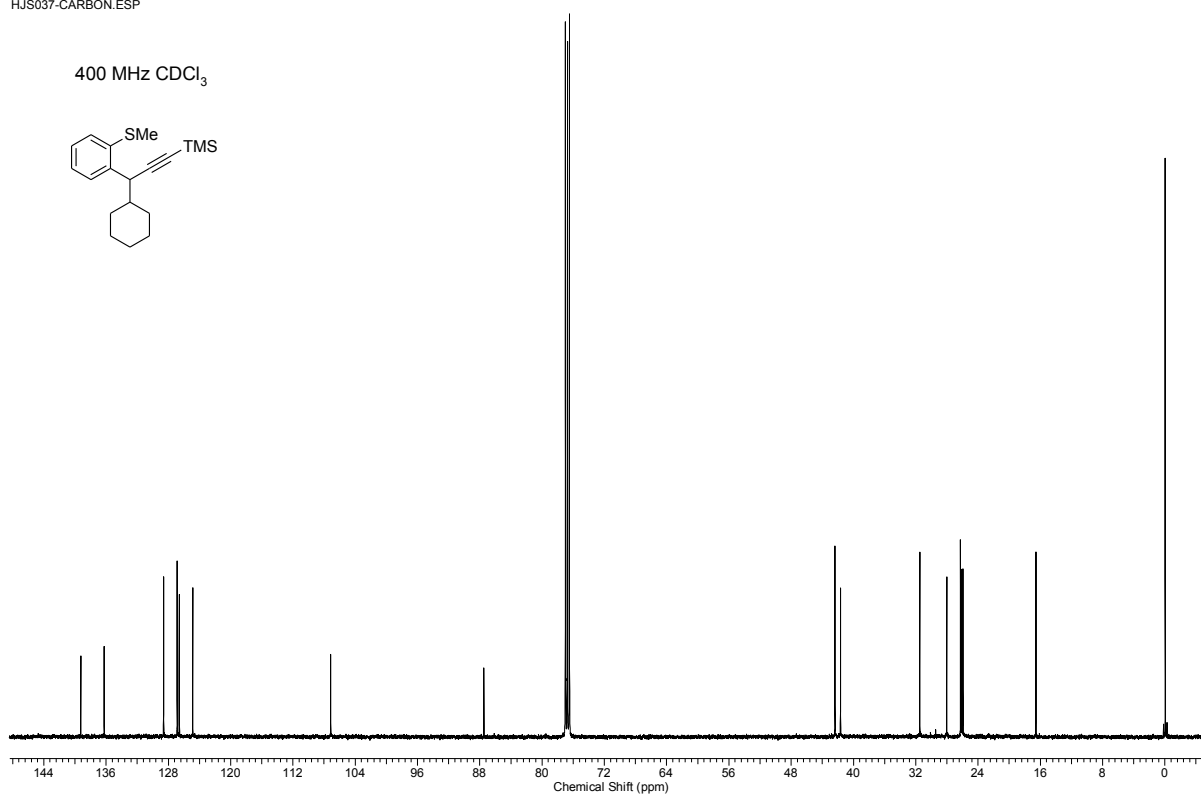
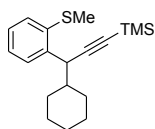
HJS037-PROTON.ESP

400 MHz CDCl<sub>3</sub>



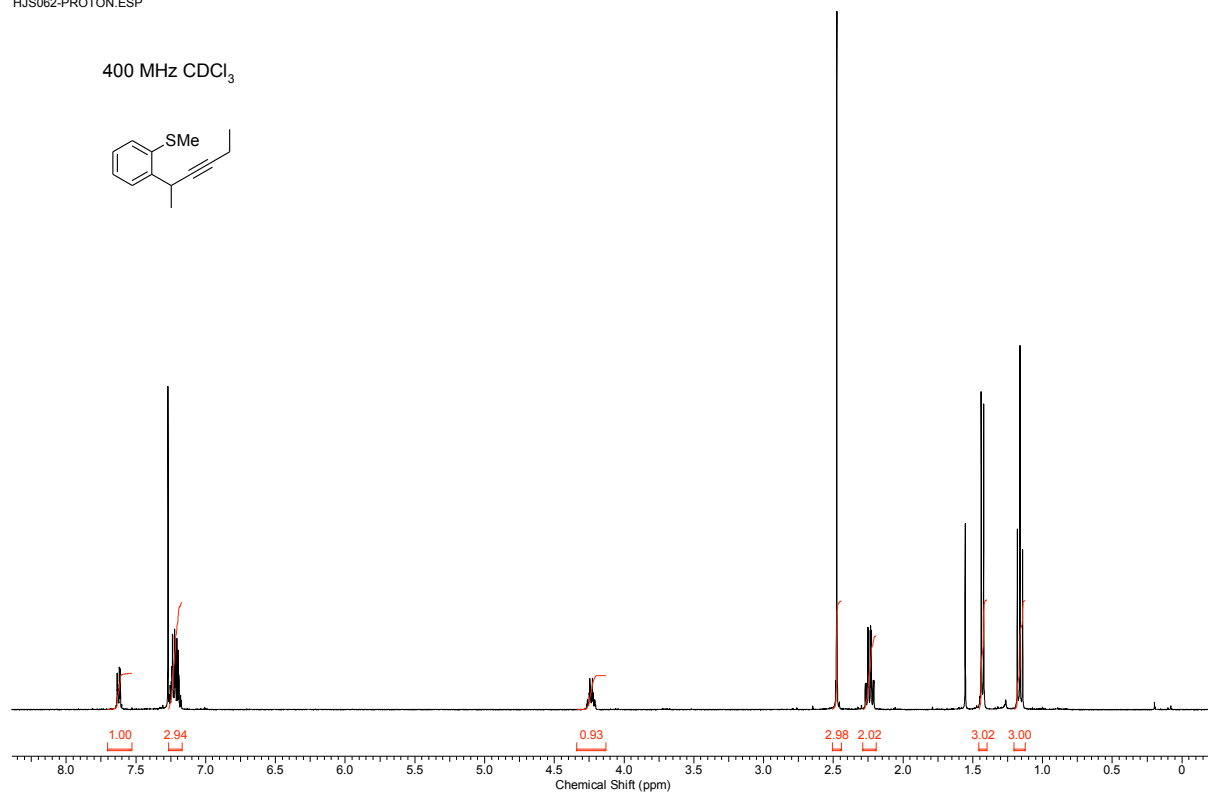
HJS037-CARBON.ESP

400 MHz CDCl<sub>3</sub>

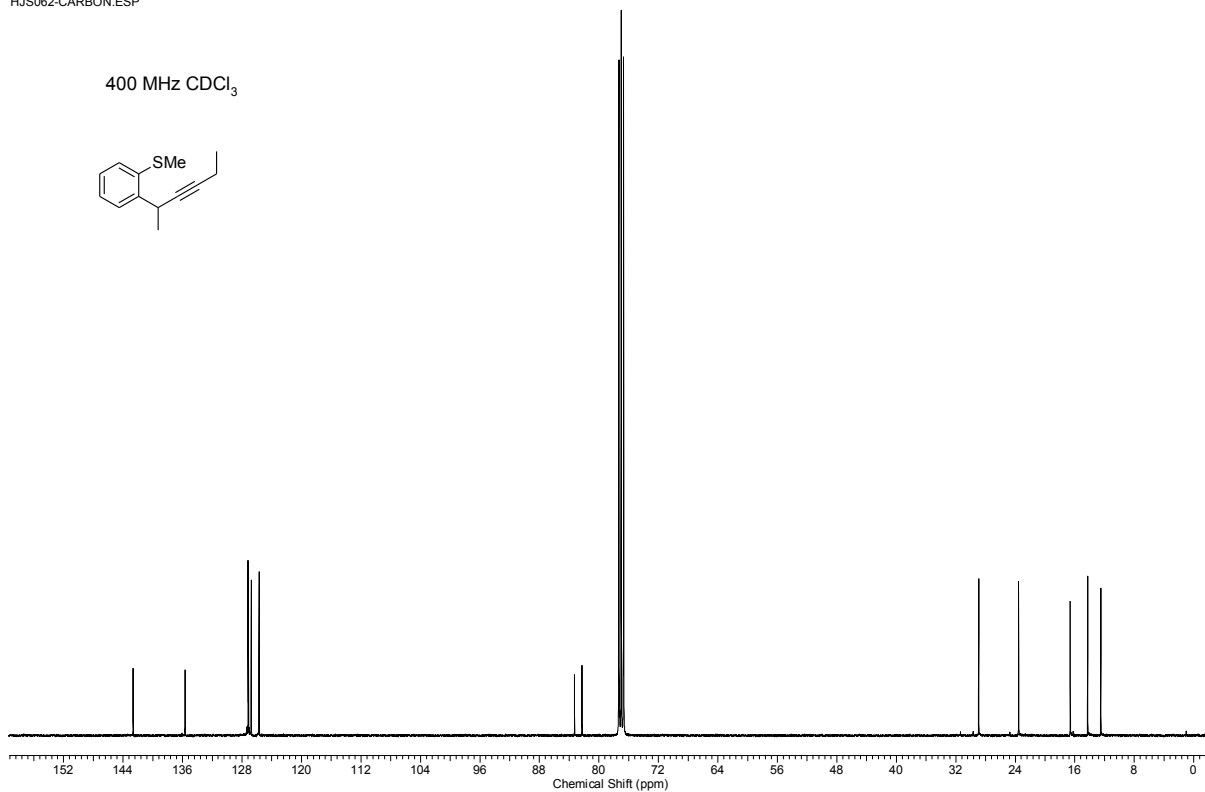


# (2-(Hex-3-yn-2-yl)phenyl)(methyl)sulfide 3az

HJS062-PROTON.ESP



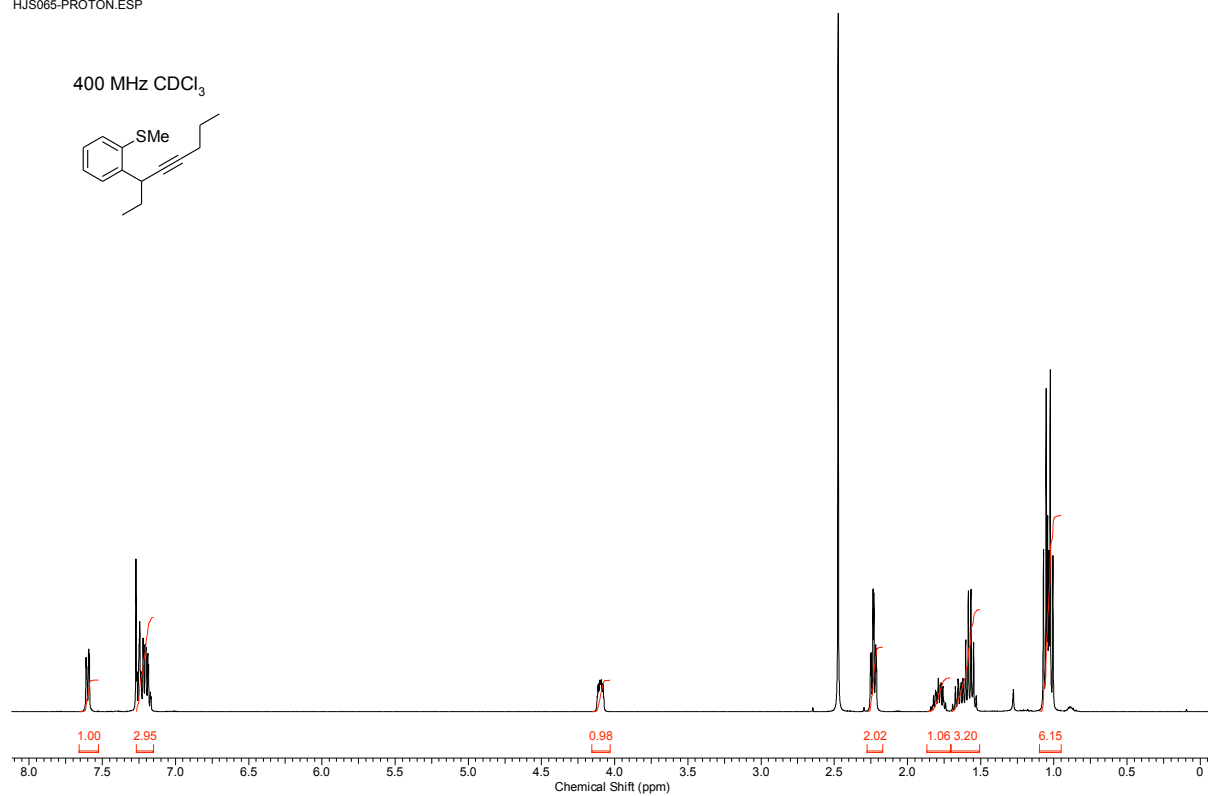
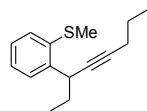
HJS062-CARBON.ESP



# Methyl(2-(oct-4-yn-3-yl)phenyl)sulfide 3ba

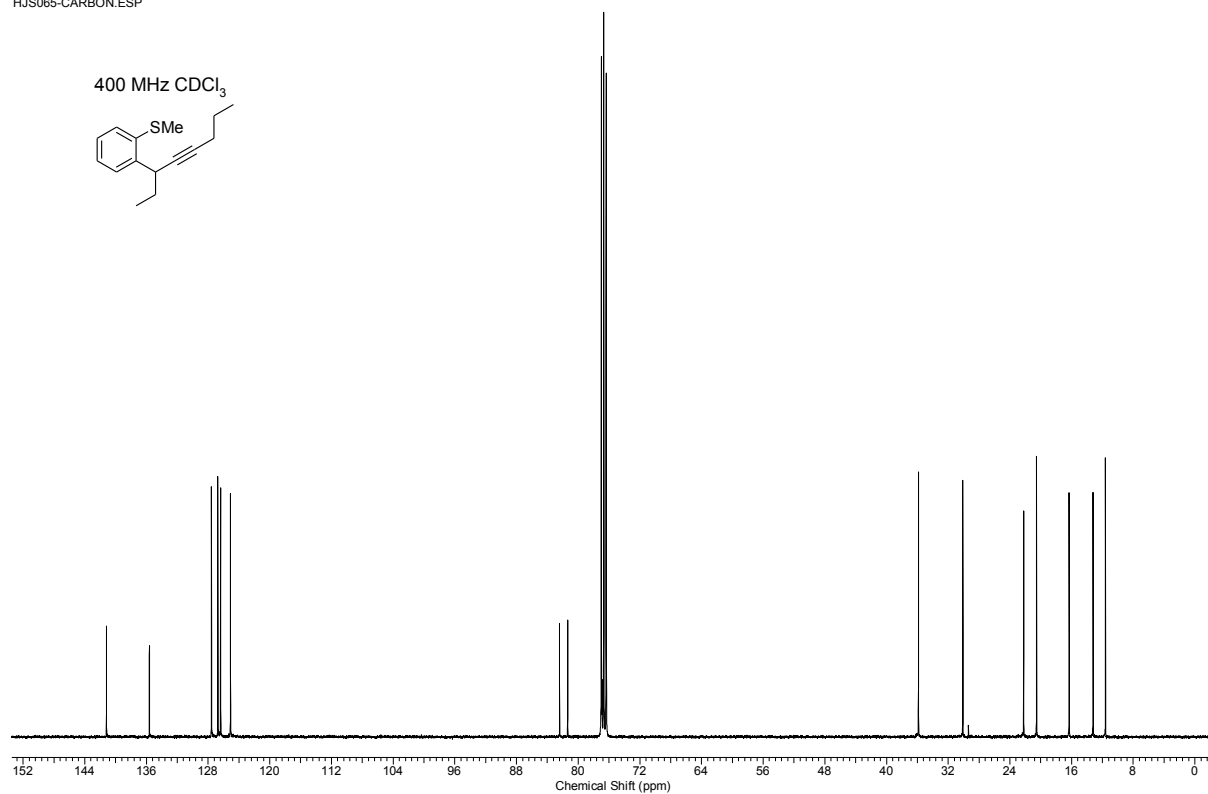
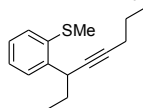
HJS065-PROTON.ESP

400 MHz CDCl<sub>3</sub>



HJS065-CARBON.ESP

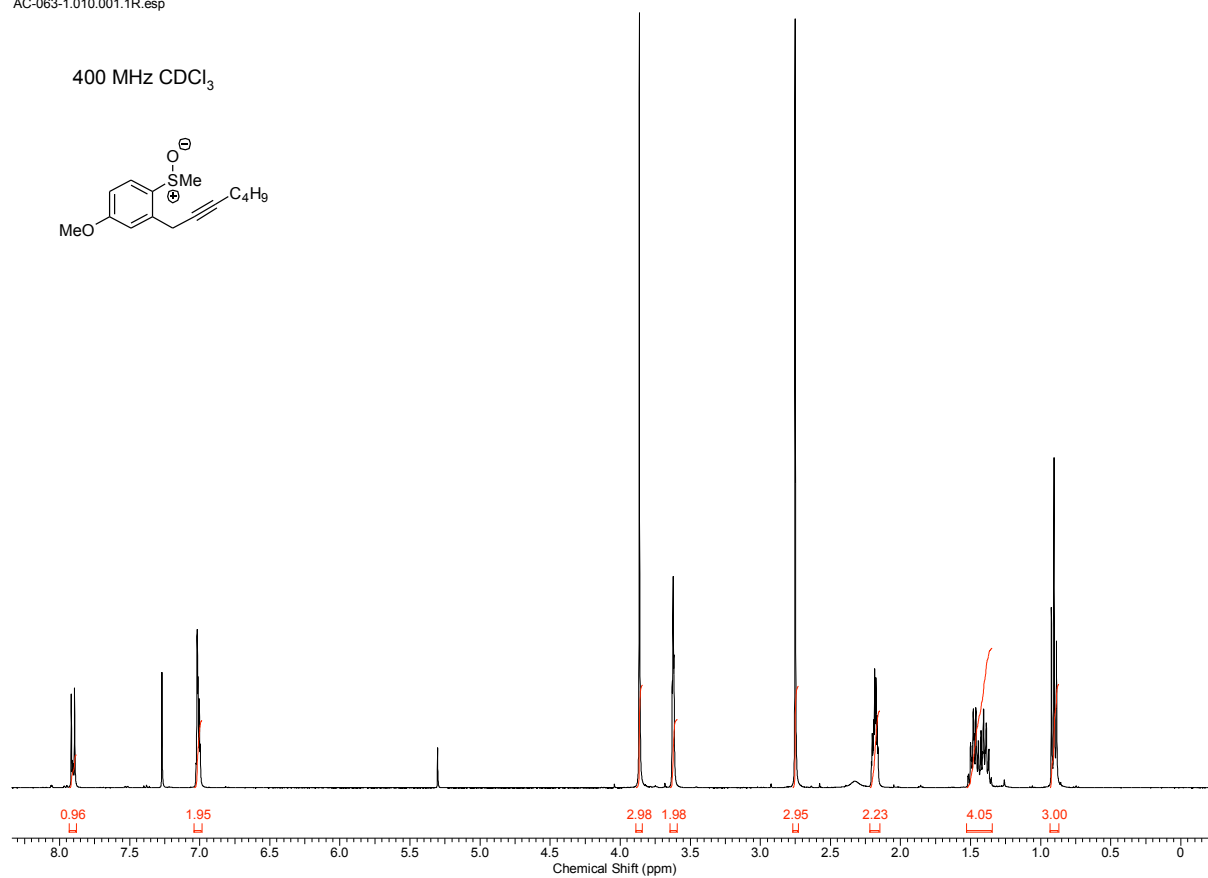
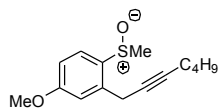
400 MHz CDCl<sub>3</sub>



# 2-(Hept-2-yn-1-yl)-4-methoxy-1-(methylsulfinyl)benzene 1a

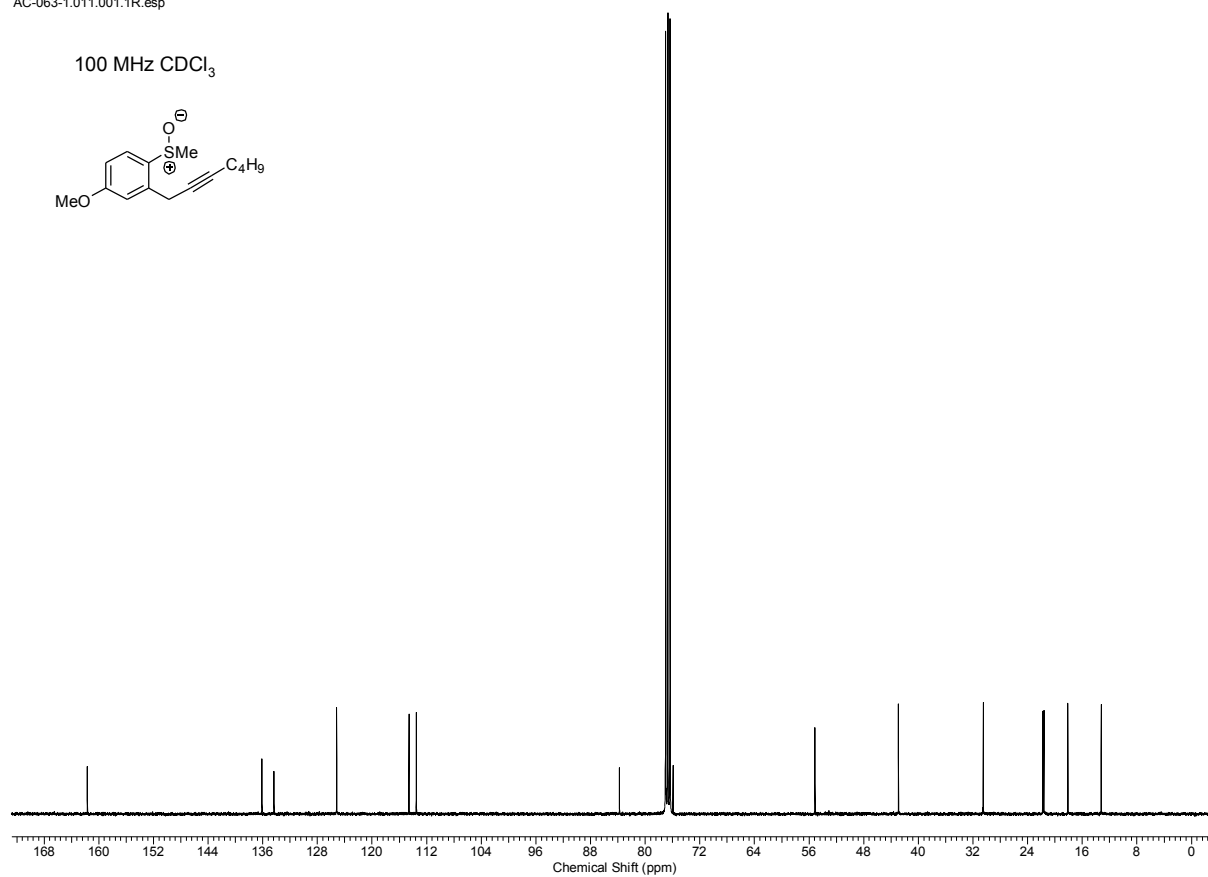
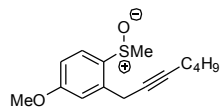
AC-063-1.010.001.1R.esp

400 MHz CDCl<sub>3</sub>



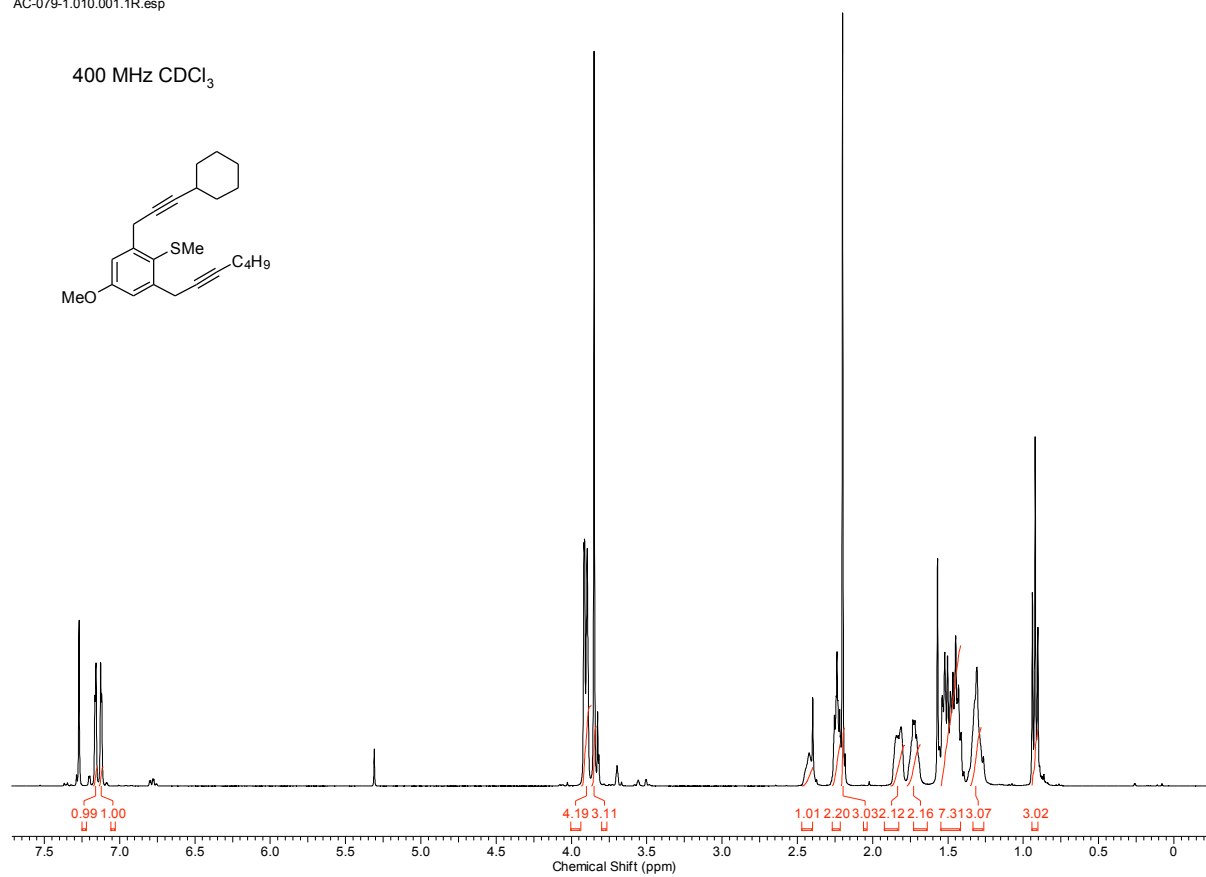
AC-063-1.011.001.1R.esp

100 MHz CDCl<sub>3</sub>

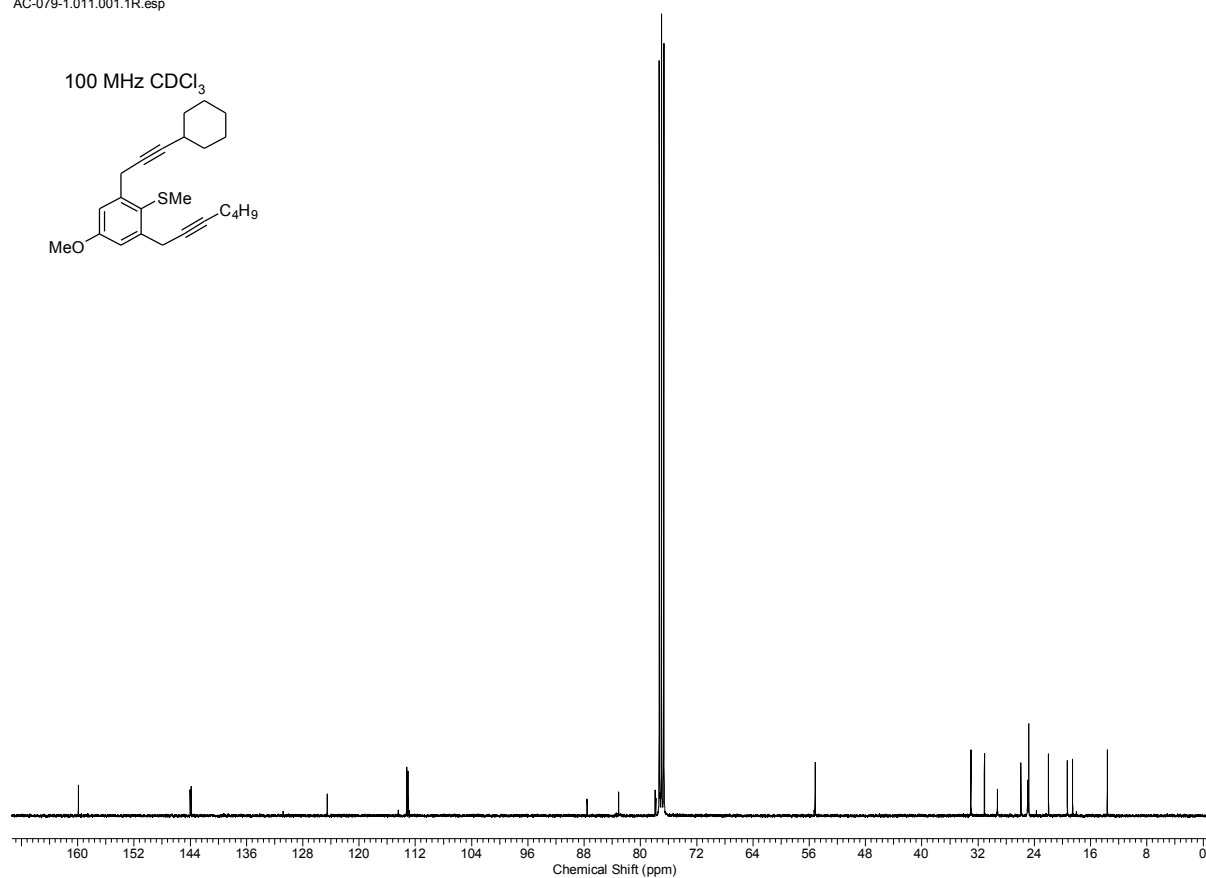


# (2-(3-Cyclohexylprop-2-yn-1-yl)-6-(hept-2-yn-1-yl)-4-methoxyphenyl)(methyl)sulfane 3ba

AC-079-1.010.001.1R.esp



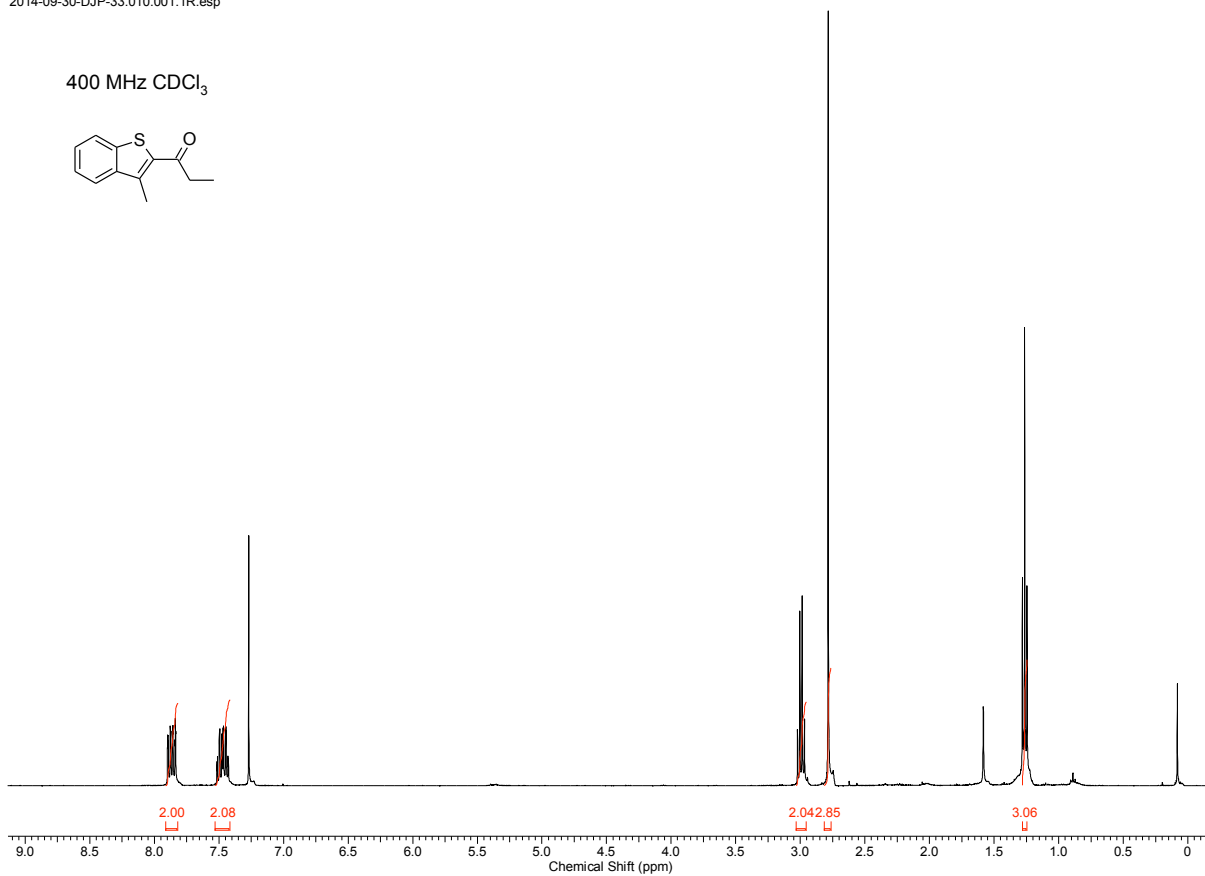
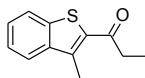
AC-079-1.011.001.1R.esp



# 1-(3-methylbenzo[b]thiophen-2-yl)propan-1-one 7c

2014-09-30-DJP-33.010.001.1R.esp

400 MHz CDCl<sub>3</sub>



2014-10-02-DJP-44.010.001.1R.esp

100 MHz CDCl<sub>3</sub>

