Supporting Information

Visible-Light-Promoted Dithioacetalization of Aldehydes with Thiols under aerobic and photocatalyst-free conditions

Zhimin Xing[a], Mingyang Yang[a], Haiyu Sun[a], Zemin Wang[a], Peng Chen [a], Lin Liu[a], Xiaolei Wang*[a], Xingang Xie*[a] and Xuegong She[a,b]

[a] State Key Laboratory of Applied Organic Chemistry, Department of Chemistry, Lanzhou University, Lanzhou, 730000, People's Republic of China.
[b] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin, 30071, China.

Table of Contents

1. General information

Solvents were purified and dried by standard methods prior to use. All commercially available reagents were used without further purification unless otherwise noted. Column chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using silica gel GF254 plates with UV light to visualize the course of reaction. Melting points were determined with a digital Koffer apparatus and were uncorrected. ^{1}H and ^{13}C NMR data were recorded on a 400 MHz spectrometer using $CDCl_3$ as solvent at room temperature. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. MS were measured on a HP-5988 spectrometer by direct inlet at 70 eV and High-resolution mass spectra (HRMS) were obtained on a FT-ICR spectrometer. UV-Vis spectra and EPR spectra were recorded on UV-2600, Bruker X-band A300 respectively. The 6 W blue LEDs we used in the experiments were ordinary household bulbs which are commercially available in the luminaire shops or supermarkets and its wavelength was between 460-480 nm according to our private communication with the suppliers.

2. General procedure for dithioacetalization of aldehydes

A 10 mL a clear pyrex glass tube and was stirred with a Teflon-coated magnetic stir bar. Thiols (0.55 mmol, 1.1 eq) was added to the solution of aldehyde derivatives (0.5 mmol, 1 eq) and in MeCN (1.5 ml). Under visible-light generated from 6 W blue LEDs, the reaction mixture was stirred under air at room temperature for 24 h. After completion of the reaction, the solvent was removed under reduced pressure by rotary evaporator. Then, the residue was purified by silica gel column chromatography to give the desired product.

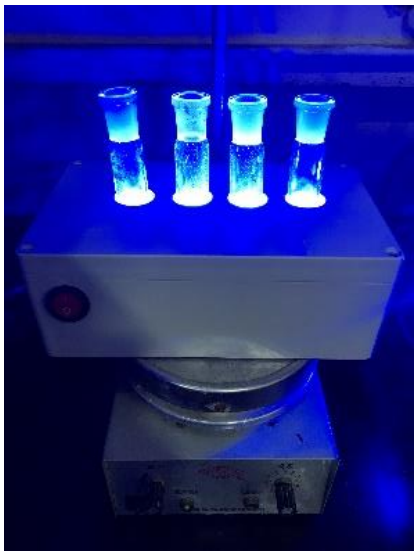


Figure s1. General procedure for dithioacetalization of aldehydes

3. X-ray crystal structure

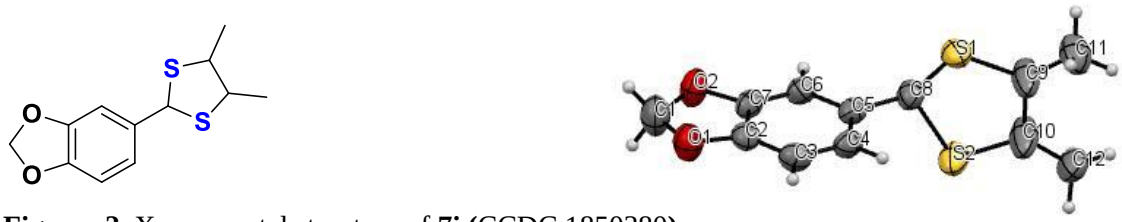
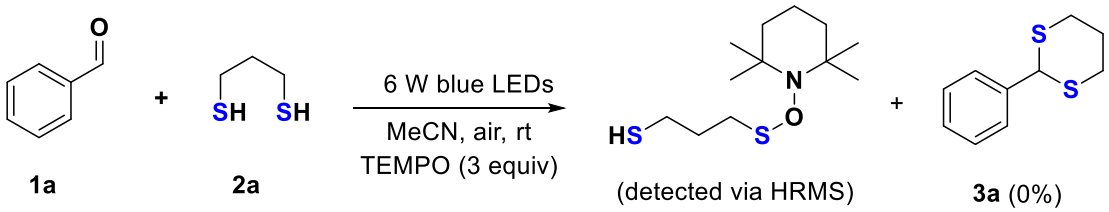


Figure s2. X-ray crystal structure of **7i (**CCDC 1850380**)**

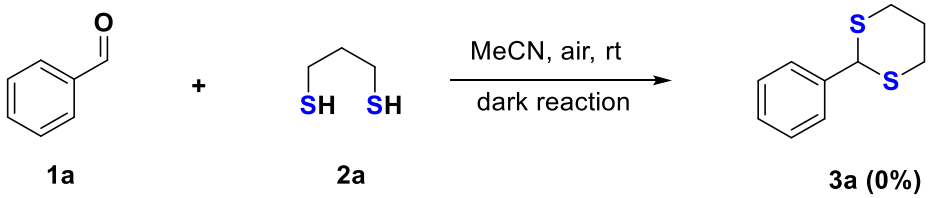
4. Preliminary mechanistic studies

4.1 TEMPO trapping experiment



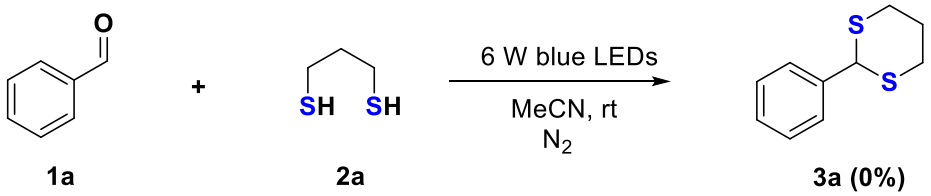
A 10 mL a clear pyrex glass tube and was stirred with a Teflon-coated magnetic stir bar. Thiols (0.55 mmol, 1.1 eq) and TEMPO (1.5 mmol, 3 eq) were added to the solution of benzaldehyde (0.5 mmol, 1 eq) and in MeCN (1.5 ml). Under visible-light generated from 6 W blue LEDs, the reaction mixture was stirred under air at room temperature for 24 h. In order to ensure whether the putative sulfur radical was trapped by TEMPO, HRMS analysis was performed from the crude reaction mixture. The mass spectrum clearly shows a peak corresponding to a coupled product between the TEMPO radical and the expected sulfur radical (HRMS (ESI): Calculated for $C_{12}H_{25}NOS_2$ $[M + Na]^+$: 286.1270, Found: 286.1269).

4.2 The model reaction was carried out in the absence of light irradiation



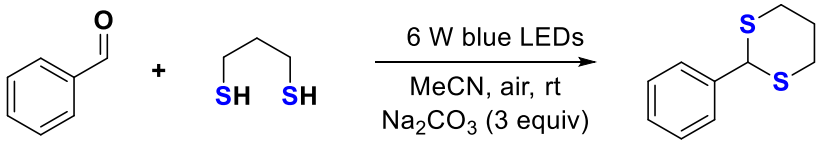
A 10 mL a clear pyrex glass tube and was stirred with a Teflon-coated magnetic stir bar. Thiols (0.55 mmol, 1.1 eq) was added to the solution of benzaldehyde (0.5 mmol, 1 eq) and in MeCN (1.5 ml). The reaction mixture was stirred under air without light irradiation at room temperature for 24 h. After completion of the reaction, the solution was concentrated in vacuum, no desired product **3a** was detected.

4.3 The model reaction was carried out under N_2



A 10 mL a clear pyrex glass tube and was stirred with a Teflon-coated magnetic stir bar. Thiols (0.55 mmol, 1.1 eq) was added to the solution of benzaldehyde (0.5 mmol, 1 eq) and in MeCN (1.5 ml). The reaction mixture was stirred under N_2 under the irradiation of 6 W blue LEDs at room temperature for 24 h. After completion of the reaction, the solution was concentrated in vacuum, no desired product **3a** was detected.

4.4 The addition of Na_2CO_3 in the model reaction system



1a **2a** **3a (0%)**

A 10 mL a clear pyrex glass tube and was stirred with a Teflon-coated magnetic stir bar. Thiols (0.55 mmol, 1.1 eq) and Na_2CO_3 (1.5 mmol, 3 eq) were added to the solution of benzaldehyde (0.5 mmol, 1 eq) and in MeCN (1.5 ml). Under visible-light generated from 6 W blue LEDs, the reaction mixture was stirred under air at room temperature for 24 h. After completion of the reaction, the solution was concentrated in vacuum, no desired product **3a** was detected.

5. Procedure for scale-up experiments

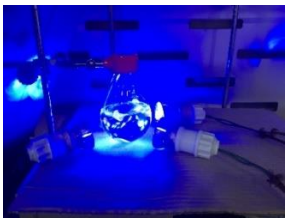


Figure s3. (At the beginning) (b)

Figure s4. (At the end) (b)

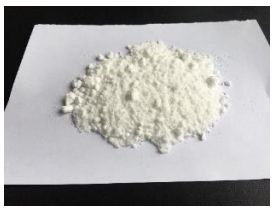
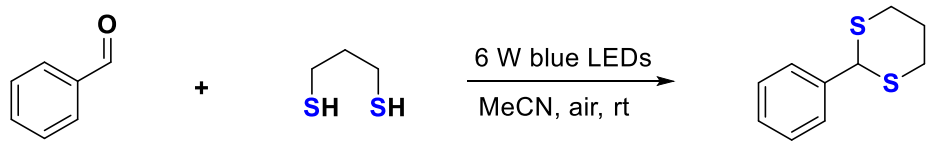


Figure s5. 2-phenyl-1,3-dithiane

Figure s6. (neat, At the beginning) (c)

Figure s7. (neat, At the end) (c)

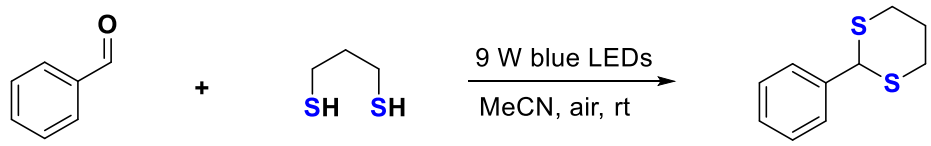
(a)



1a (1.00 g, 9.4 mmol) **2a** (1.09 g, 10.0 mmol) **3a** (1.75 g, 94%)

A 50 mL a flame-dried flask and was stirred with a Teflon-coated magnetic stir bar. Thiols (10.0 mmol, 1.1 eq) was added to the solution of benzaldehyde (9.4 mmol, 1 eq) and in MeCN (30.0 ml). Under visible-light generated from 6 W blue LEDs, the reaction mixture was stirred under air at room temperature for 24 h. After completion of the reaction, the solvent was removed under reduced pressure by rotary evaporator. Then, the residue was purified by silica gel column chromatography to give the desired product.

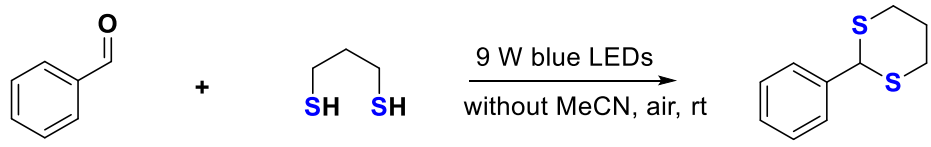
(b)



1a (6.47 g, 61.0 mmol) **2a** (6.93 g, 64.0 mmol) **3a** (11.02 g, 92%)

A 250 mL a flame-dried flask and was stirred with a Teflon-coated magnetic stir bar. Thiols (64.0 mmol, 1.05 eq) was added to the solution of benzaldehyde (61.0 mmol, 1 eq) and in MeCN (180.0 ml). Under visible-light generated from 9 W blue LEDs, the reaction mixture was stirred under air at room temperature for 24 h. After completion of the reaction, the solvent was removed under reduced pressure by rotary evaporator. Then, the residue was purified by silica gel column chromatography or recrystallization from ethanol to give the desired product.

(c)



1a (6.47 g, 61.0 mmol) **2a** (6.93 g, 64.0 mmol) **3a** (10.42 g, 87%)

A 100 mL a flame-dried flask and was stirred with a Teflon-coated magnetic stir bar. Thiols (64.0 mmol, 1.05 eq) was added to benzaldehyde (61.0 mmol, 1 eq). Under visible-light generated from 9 W blue LEDs, the reaction mixture was stirred under air at room temperature for 24 h. After completion of the reaction, the solvent was removed under reduced pressure by rotary evaporator. Then, the residue was purified by silica gel column chromatography to give the desired product.

6. UV-Vis experiments

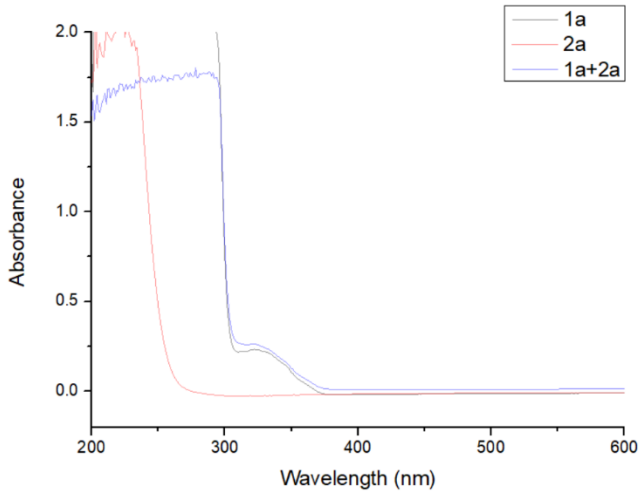
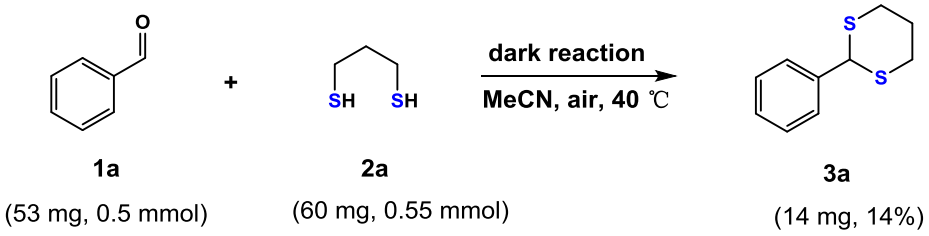


Figure S8. UV-Vis absorption spectra of substrates.

Although the results indicated that electron-donor acceptor (EDA) complex was not formed, our control experiment without LED lights irradiation (Table 1, entry 7) indicated that light irradiation was essential. Meanwhile, we found that the temperature of the reaction system was maintained between 25−30 °C during the course of LED lights irradiation. And we also performed the reaction without LED lights irradiation (in the dark) at 40 °C and the yield of the corresponding condensation product **3a** decreased to 14% (Scheme S1). The above two experiments indicated that LED light irradiation promoted this reaction by accelerating the generation of the sulphur radical under our standard conditions.



Scheme S1. Control heat experiment.

7. EPR experiments

b) EPR spectra of **1a** and **2a**, without irradiation

1a (0.5 mmol) and **2a** (0.55 mmol) in MeCN (1.5 mL) under air without irradiation at room temperature for few minutes, and then few of this solution was taken out by a capillary tube and sealed up, then analyzed by EPR at room temperature (Figure s9).

c) EPR spectra of **1a** and **2a**, with irradiation, 10 min

1a (0.5 mmol) and **2a** (0.55 mmol) under air in MeCN (1.5 mL) with blue LEDs irradiation at room temperature for 10 min, and then few of this solution was taken out by a capillary tube and sealed up, then analyzed by EPR at room temperature (Figure s9).

d) EPR spectra of **1a** and **2a**, with irradiation, 2h

1a (0.5 mmol) and **2a** (0.55 mmol) under air in MeCN (1.5 mL) with blue LEDs irradiation at room temperature for 2 h, and then few of this solution was taken out by a capillary tube and sealed up, then analyzed by EPR at room temperature (Figure s9).

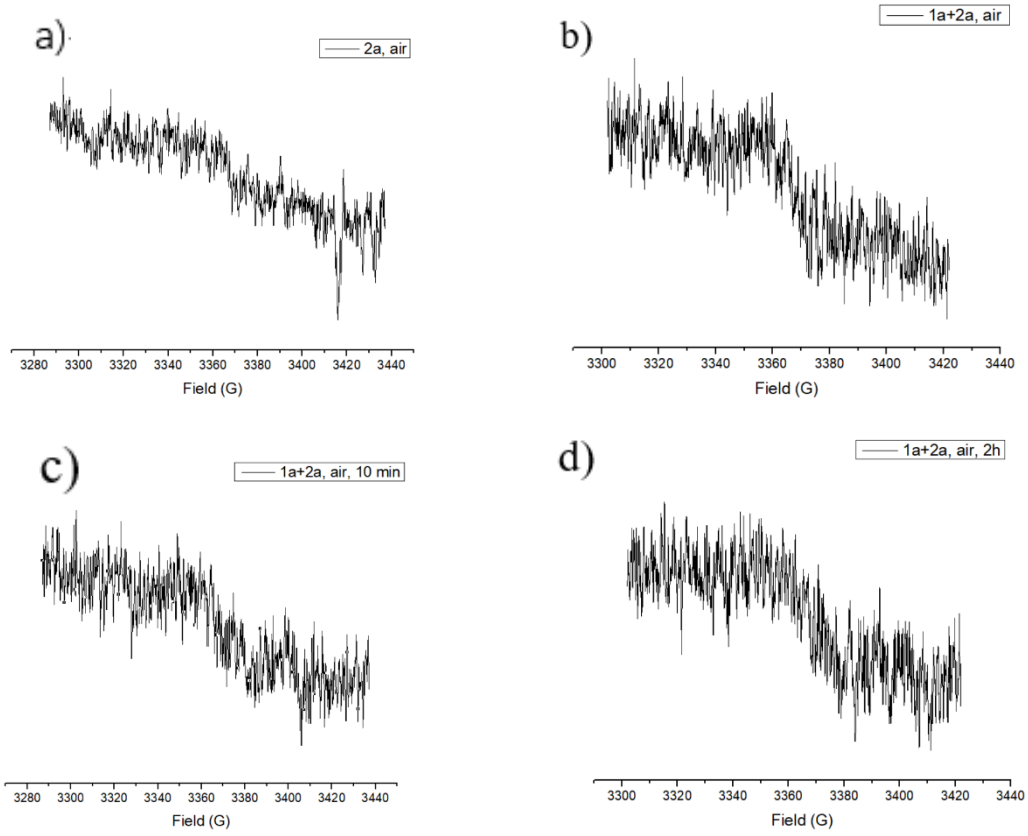


Figure S9. a) EPR spectra of a solution of **2a** (0.5 mmol) in MeCN (1.5 mL) under air without irradiation at room temperature. b) EPR spectra of a solution of **1a** (0.5 mmol) and **2a** (0.55 mmol) in MeCN (1.5 mL) under air without irradiation at room temperature. c) EPR spectra of a solution of **1a** (0.5 mmol) and **2a** (0.55 mmol) under air in MeCN (1.5 mL) with

blue LEDs irradiation at room temperature for 10 min. d) EPR spectra of a solution of **1a** (0.5 mmol) and **2a** (0.55 mmol) in MeCN (1.5 mL) under air with blue LEDs irradiation at room temperature for 2 h.

a) EPR spectra of **1a**, **2a** and DMPO, with irradiation

1a (0.2 mmol), **2a** (0.22 mmol) and DMPO (0.22 mmol) under air in MeCN (0.6 mL) with blue LEDs irradiation at room temperature for 10 min, and then few of this solution was taken out by a capillary tube and sealed up, then analyzed by EPR at room temperature (Figure 1).

b) EPR spectra of **2a** and DMPO, with irradiation

2a (0.22 mmol) and DMPO (0.22 mmol) under air in MeCN (0.6 mL) with blue LEDs irradiation at room temperature for 10 min, and then few of this solution was taken out by a capillary tube and sealed up, then analyzed by EPR at room temperature (Figure 1).

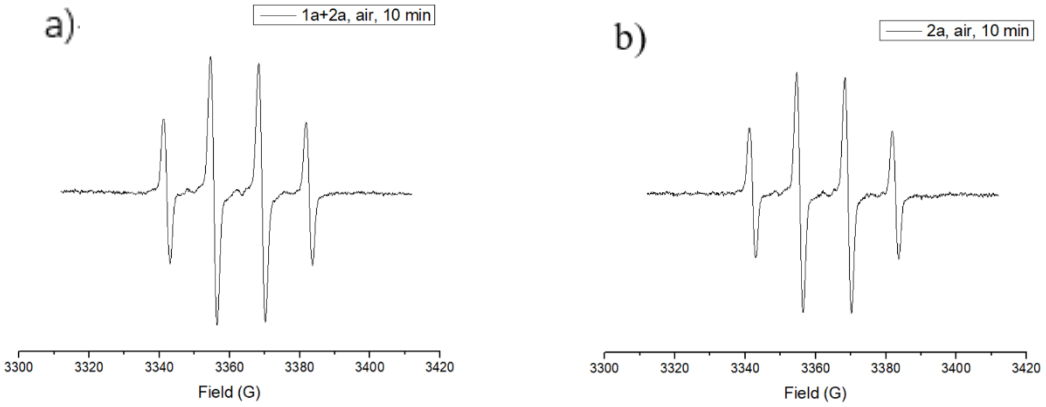
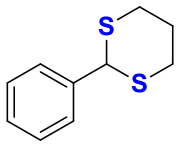


Figure 1. a) EPR spectra of mixture of **1a** (0.2 mmol), **2a** (0.22 mmol) and DMPO (0.22 mmol) under air in MeCN (0.6 mL) with blue LEDs irradiation at room temperature for 10 min. b) EPR spectra of a solution of **2a** (0.2 mmol) and DMPO (0.22 mmol) in MeCN (0.6 mL) under air with blue LEDs irradiation at room temperature for 10 min.

8. Characterization data

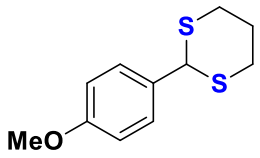
2-phenyl-1,3-dithiane (3a) [1]



3a

Afforded **3a** in 98% yield as a white solid; mp 72-74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 2H), 7.38 – 7.27 (m, 3H), 5.17 (s, 1H), 3.14 – 3.00 (m, 2H), 2.97 – 2.85 (m, 2H), 2.24 – 2.11 (m, 1H), 2.01 – 1.85 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 128.7, 128.4, 127.7, 51.4, 32.1, 25.0; MS (EI, 70 ev) m/z: 196, 153, 135, 121, 105, 91.

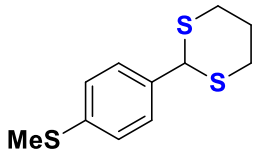
2-(4-methoxyphenyl)-1,3-dithiane (3b) [1]



3b

Afforded **3b** in 94% yield as a white solid; mp 118-120 ℃ (lit.[1] 115.5-116.5 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 5.14 (s, 1H), 3.79 (s, 3H), 3.10 – 2.98 (m, 2H), 2.94 – 2.85 (m, 2H), 2.22 – 2.09 (m, 1H), 2.00 – 1.82 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 131.2, 128.9, 114.0, 55.2, 50.7, 32.2, 25.0; MS (EI, 70 ev) m/z: 226, 152, 121, 108.

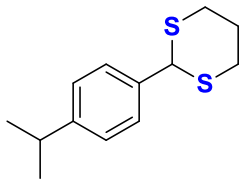
2-(4-(methylthio)phenyl)-1,3-dithiane (3c) [1]



3c

Afforded **3c** in 95% yield as a white solid; mp 90-92 ℃ (lit.[1] 93-94 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 5.13 (s, 1H), 3.12 – 2.98 (m, 2H), 2.94 – 2.84 (m, 2H), 2.46 (s, 3H), 2.22 – 2.08 (m, 1H), 1.98 – 1.82 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 135.6, 128.1, 126.4, 50.8, 32.0, 24.9, 15.5; MS (EI, 70 ev) m/z: 242, 168, 137, 124, 109.

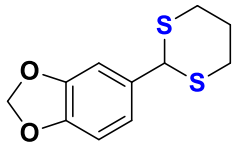
2-(4-isopropylphenyl)-1,3-dithiane (3d) [1]



3d

Afforded **3d** in 95% yield as a white solid; mp 57-58 ℃ (lit.[1] 58-60.4 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 5.15 (s, 1H), 3.13 – 2.98 (m, 2H), 2.95 – 2.82 (m, 3H), 2.25 – 2.10 (m, 1H), 2.02 – 1.83 (m, 1H), 1.23 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 136.4, 127.6, 126.8, 51.2, 33.8, 32.2, 25.1, 23.9; MS (EI, 70 ev) m/z: 238, 164, 149, 131, 105, 91.

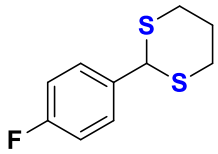
5-(1,3-dithian-2-yl)benzo[d][1,3]dioxole (3e) [2]



3e

Afforded **3e** in 92% yield as a white solid; mp 87-89 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 – 6.91 (m, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.95 (s, 2H), 5.09 (s, 1H), 3.12 – 2.96 (m, 2H), 2.94 – 2.81 (m, 2H), 2.21 – 2.04 (m, 1H), 2.02 – 1.80 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 147.6, 132.9, 121.2, 108.3, 101.2, 51.1, 32.1, 25.0; MS (EI, 70 ev) m/z: 240, 166, 135, 122, 107.

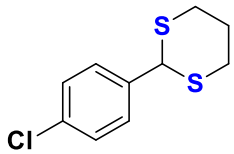
2-(4-fluorophenyl)-1,3-dithiane (3f) [1]



3f

Afforded **3f** in 93% yield as a white solid; mp 105-106 ℃ (lit.[1] 105.1-106.8 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.35 (m, 2H), 7.09 – 6.91 (m, 2H), 5.14 (s, 1H), 3.13 – 2.98 (m, 2H), 2.96 – 2.83 (m, 2H), 2.26 – 2.09 (m, 1H), 2.01 – 1.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, *J* = 245.8 Hz), 134.9 (d, *J* = 3.2 Hz), 129.4 (d, J = 8.3 Hz), 115.6 (d, *J* = 21.5 Hz), 50.4, 32.0, 24.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.2 (s); MS (EI, 70 ev) m/z: 214, 149, 139, 105, 95.

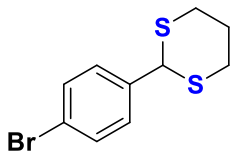
2-(4-chlorophenyl)-1,3-dithiane (3g) [2]



3g

Afforded **3g** in 94% yield as a white solid; mp 88-90 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 5.13 (s, 1H), 3.12 – 3.00 (m, 2H), 2.97 – 2.85 (m, 2H), 2.25 – 2.12 (m, 1H), 2.00 – 1.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 134.1, 129.1, 128.9, 50.5, 32.0, 24.9; MS (EI, 70 ev) m/z: 230, 156, 105.

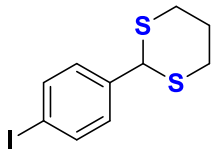
2-(4-bromophenyl)-1,3-dithiane (3h) [2]



3h

Afforded **3h** in 98% yield as a white solid; mp 94-96 °C (lit.[2] 93-94 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.5 Hz, 2H) 7.35 (d, J = 8.4 Hz, 2H), 5.12 (s, 1H), 3.12 – 2.99 (m, 2H), 2.96 – 2.85 (m, 2H), 2.25 – 2.11 (m, 1H), 2.01 – 1.83 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 131.8, 129.5, 122.3, 50.6, 31.9, 24.9; MS (EI, 70 ev) m/z: 276, 274, 202, 130, 120, 105.

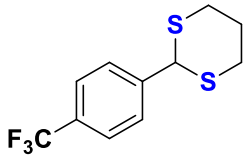
2-(4-iodophenyl)-1,3-dithiane (3i) [3]



3i

Afforded **3i** in 65% yield as a white solid; mp 122-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 5.10 (s, 1H), 3.10 – 2.98 (m, 2H), 2.95 – 2.84 (m, 2H), 2.22 – 2.10 (m, 1H), 1.99 – 1.82 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 137.8, 129.6, 94.0, 50.6, 31.9, 24.9; MS (EI, 70 ev) m/z: 322, 248, 130, 120, 105.

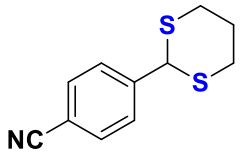
2-(4-(trifluoromethyl)phenyl)-1,3-dithiane (3j) [4]



3j

Afforded **3j** in 91% yield as a white solid; mp 107-109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 4H), 5.20 (s, 1H), 3.14 – 3.02 (m, 2H), 2.99 – 2.88 (m, 2H), 2.26 – 2.12 (m, 1H), 2.03 – 1.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 130.5 (q, J = 32.2 Hz), 128.2, 125.7 (q, J = 3.0 Hz), 123.9 (q, J = 270.4 Hz), 50.7, 31.9, 24.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6 (s); MS (EI, 70 ev) m/z: 264, 190, 189, 159, 145, 127, 105.

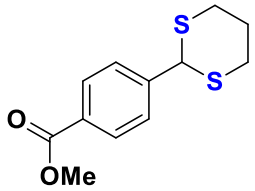
4-(1,3-dithian-2-yl)benzonitrile (3k) [2]



3k

Afforded **3k** in 74% yield as a white solid; mp 115-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.8 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 5.18 (s, 1H), 3.13 – 3.01 (m, 2H), 2.98 – 2.88 (m, 2H), 2.26 – 2.14 (m, 1H), 2.02 – 1.85 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 132.5, 128.7, 118.5, 112.1, 50.7, 31.7, 24.8; MS (EI, 70 ev) m/z: 221, 178, 156, 146, 130, 105.

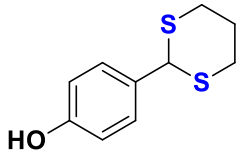
methyl 4-(1,3-dithian-2-yl)benzoate (3l) [2]



3l

Afforded **3l** in 92% yield as a white solid; mp 138-140 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 5.20 (s, 1H), 3.90 (s, 3H), 3.12 – 3.00 (m, 2H), 2.97 – 2.87 (m, 2H), 2.23 – 2.13 (m, 1H), 2.04 – 1.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 143.9, 130.1, 130.0, 127.9, 52.1, 51.0, 31.9, 25.0; MS (EI, 70 ev) m/z: 254, 180, 157, 149, 121, 105.

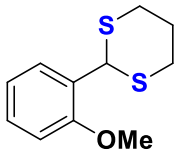
4-(1,3-dithian-2-yl)phenol (3i) [2]



3m

Afforded **3m** in 90% yield as a white solid; mp 158-159 ℃ (lit.[2] 116-118 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 5.12 (s, 1H), 5.09 (s, 1H), 3.14 – 2.98 (m, 2H), 2.95 – 2.82 (m, 2H), 2.24 – 2.10(m, 1H), 2.00– 1.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 131.3, 129.1, 115.5, 50.7, 32.1, 25.0; MS (EI, 70 ev) m/z: 212, 138, 107.

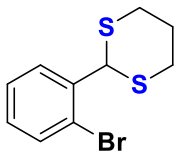
2-(2-methoxyphenyl)-1,3-dithiane (3n) [2]



3n

Afforded **3n** in 92% yield as a white solid; mp 128-129 ℃ (lit.[2] 127-129 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.29 – 7.18 (m, 1H), 6.99 – 6.91 (m, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 5.70 (s, 1H), 3.84 (s, 3H), 3.16 – 3.01 (m, 2H), 2.94 – 2.80 (m, 2H), 2.18 – 2.06 (m, 1H), 2.00 – 1.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 129.2, 129.0, 127.1, 120.8, 110.6, 55.6, 43.5, 32.2, 25.2; MS (EI, 70 ev) m/z: 226, 152, 119, 107, 91.

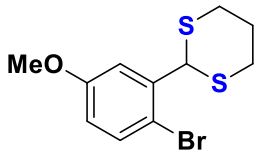
2-(2-bromophenyl)-1,3-dithiane (3o) [5]



3o

Afforded **3o** in 91% yield as a white solid; mp 97-99 ℃ (lit.[5] 98.3 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.55 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.32 (td, *J* = 7.6, 1.1 Hz, 1H), 7.14 (td, *J* = 7.9, 1.7 Hz, 1H), 5.60 (s, 1H), 3.19 – 3.05 (m, 2H), 2.98 – 2.82 (m, 2H), 2.27 – 2.11 (m, 1H), 2.04 – 1.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 132.9, 129.7, 128.1, 123.0, 50.7, 32.3, 25.1; MS (EI, 70 ev) m/z: 276, 224, 202, 200, 121, 105.

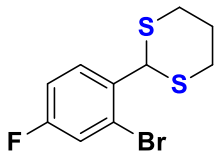
2-(2-bromo-5-methoxyphenyl)-1,3-dithiane (3p) [6]



3p

Afforded **3p** in 85% yield as a white solid; mp 70-72 ℃ (lit.[6] 67-70 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.8 Hz, 1H), 7.22 (d, *J* = 3.0 Hz, 1H), 6.71 (dd, *J* = 8.8, 3.0 Hz, 1H), 5.54 (s, 1H), 3.79 (s, 3H), 3.21 – 3.02 (m, 2H), 2.99 – 2.84 (m, 2H), 2.25 – 2.11 (m, 1H), 2.03 – 1.80 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 139.0, 133.3, 116.1, 114.8, 113.1, 55.5, 50.8, 32.2, 25.0; MS (EI, 70 ev) m/z: 306, 304, 232, 230, 225, 191, 151, 108.

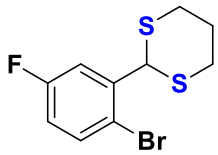
2-(2-bromo-4-fluorophenyl)-1,3-dithiane (3q)



3q

Afforded **3q** in 77% yield as a white solid; mp 111-113 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.62 (m, 1H), 7.30 (dd, *J* = 8.2, 2.6 Hz, 1H), 7.11 – 7.01 (m, 1H), 5.55 (s, 1H), 3.21 – 3.06 (m, 2H), 2.99 – 2.87 (m, 2H), 2.27 – 2.13 (m, 1H), 2.03 – 1.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7 (d, *J* = 250.6 Hz), 134.3 (d, *J* = 3.5 Hz), 130.8 (d, *J* = 8.6 Hz), 123.1 (d, *J* = 9.6 Hz), 120.0 (d, *J* = 24.5 Hz), 115.3 (d, *J* = 21.0 Hz), 49.7, 32.2, 24.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.0 (s); MS (EI, 70 ev) m/z: 294, 292, 220, 218, 213, 139, 105; HRMS (ESI): m/z calculated for $C_{10}H_{10}BrFS_2$ $[M + H]^+$: 294.9444, found: 294.9448.

2-(2-bromo-5-fluorophenyl)-1,3-dithiane (3r)

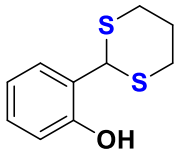


3r

Afforded **3r** in 63% yield as a white solid; mp 79-80 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 -7.38 (m, 2H), 6.98 – 6.83 (m, 1H), 5.53 (s, 1H), 3.13 (t, *J* = 13.1 Hz, 2H), 2.93 (d, *J* = 14.2 Hz, 2H), 2.19 (d, *J* = 13.9 Hz, 1H), 1.94 (q, *J* = 12.8 Hz, 1H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 162.1 (d, *J* = 246.3 Hz), 140.1 (d, *J* = 7.7 Hz), 134.0 (d, *J* = 7.9 Hz), 117.1 (d, *J* = 1.9 Hz), 117.0 (d, *J* = 3.3 Hz), 116.9 (d, *J* = 3.8 Hz), 50.3, 32.1, 24.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.1 (s); MS (EI, 70 ev) m/z: 294, 292, 220, 218, 213, 139, 105; HRMS (ESI): m/z calculated for $C_{10}H_{10}BrFS_2$ $[M + H]^+$: 294.9444, found: 294.9443.

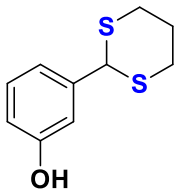
2-(1,3-dithian-2-yl)phenol (3s) [7]



3s

Afforded **3s** in 93% yield as a white solid; mp 135-138 ℃ (lit.[7] 131-133 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.24 – 7.17 (m, 1H), 6.94 – 6.82 (m, 2H), 6.39 (s, 1H), 5.41 (s, 1H), 3.15 – 3.01 (m, 2H), 2.98 – 2.87 (m, 2H), 2.25 – 2.14 (m, 1H), 2.01 – 1.85 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 130.1, 129.1, 123.5, 120.8, 117.3, 47.3, 31.6, 24.8; MS (EI, 70 ev) m/z: 212, 147, 138, 105.

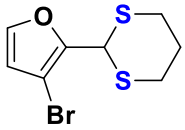
3-(1,3-dithian-2-yl)phenol (3t) [8]



3t

Afforded **3t** in 92% yield as a white solid; mp 124-126 ℃ (lit.[8a] 126 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.9 Hz, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 6.96 (s, 1H), 6.77 (dd, *J* = 8.1, 2.2 Hz, 1H), 5.33 (s, 1H), 5.12 (s, 1H), 3.13 – 2.99 (m, 2H), 2.97 – 2.86 (m, 2H), 2.24 – 2.10 (m, 1H), 2.04 – 1.76 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 140.5, 130.0, 120.1, 115.6, 114.7, 51.1, 32.0, 25.0; MS (EI, 70 ev) m/z: 212, 147, 138, 105.

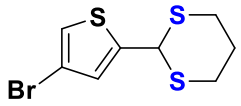
3-bromo-2-(1,3-dithian-2-yl)furan (3u)



3u

Afforded **3u** in 76% yield as a white solid; mp 81-82 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 6.42 (s, 1H), 5.33 (s, 1H), 3.18 – 2.92 (m, 4H), 2.24 – 1.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 142.8, 113.8, 96.9, 39.3, 30.4, 25.0; MS (EI, 70 ev) m/z: 266, 264, 192, 190, 185, 143, 119, 106; HRMS (ESI): Calculated for $C_8H_9BrS_3$ $[M + H]^+$: 266.9330, Found: 266.9334.

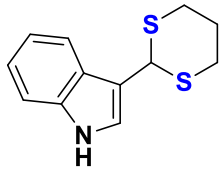
2-(4-bromothiophen-2-yl)-1,3-dithiane (3v)



3v

Afforded **3v** in 94% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 1.3 Hz, 1H), 7.11 (s, 1H), 5.25 (s, 1H), 3.06 – 2.83 (m, 4H), 2.20 – 2.08 (m, 1H), 2.06 – 1.90 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 129.1, 123.3, 109.1, 43.5, 29.8, 24.9; MS (EI, 70 ev) m/z: 282, 280, 217, 215, 208, 175, 154, 136, 122, 105; HRMS (ESI): m/z calculated for $C_8H_9BrOS_2$ $[M + H]^+$: 282.9102, found: 282.9110.

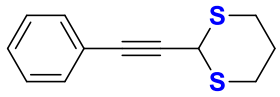
3-(1,3-dithian-2-yl)-1H-indole (3w) [9, 8b]



3w

Afforded **3w** in 64% yield as a yellow solid; mp 128-129 ℃ (lit.[9] 124-126 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.42 – 7.28 (m, 2H), 7.24 – 7.11 (m, 2H), 5.59 (s, 1H), 3.22 – 3.07 (m, 2H), 3.00 – 2.86 (m, 2H), 2.28 – 2.14 (m, 1H), 2.10 – 1.89 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 125.5, 122.8, 122.5, 119.8, 119.6, 114.3, 111.3, 42.7, 32.2, 25.4; MS (EI, 70 ev) m/z: 235, 161, 130, 102.

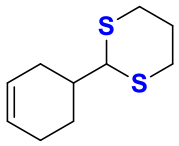
2-phenylethynyl-1,3-dithiane (5a) [10]



5a

Afforded **5a** in 34% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 2H), 7.38 – 7.29 (m, 3H), 4.80 (s, 1H), 3.41 – 3.24 (m, 2H), 2.89 – 2.78 (m, 2H), 2.19 – 2.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.8, 128.5, 128.2, 122.3, 85.9, 85.2, 33.3, 27.8, 25.8; MS (EI, 70 ev) m/z: 220, 192, 173, 145, 114, 102.

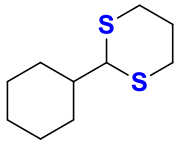
2-(3-Cyclohexenyl)-1,3-dithiane (5b) [2]



5b

Afforded **5b** in 81% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 – 5.61 (m, 2H), 4.11 (d, *J* = 5.8 Hz, 1H), 2.97 – 2.81 (m, 4H), 2.31 – 1.94 (m, 7H), 1.93 – 1.79 (m, 1H), 1.58 – 1.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.8, 125.8, 54.2, 38.8, 30.7, 30.7, 28.9, 26.4, 26.3, 25.3; MS (EI, 70 ev) m/z: 200, 119, 106, 91.

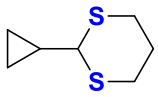
2-Cyclohexyl-1,3-dithiane (5c) [2]



5c

Afforded **5c** in 94% yield as a white solid; mp 52-54 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.05 (d, *J* = 5.3 Hz, 1H), 2.96 – 2.82 (m, 4H), 2.18 – 2.06 (m, 1H), 1.97 – 1.57 (m, 7H), 1.33 – 1.07 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 43.0, 30.9, 30.3, 26.4, 26.2, 26.1; MS (EI, 70 ev) m/z: 202, 119, 106.

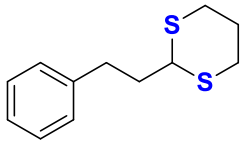
2-Cyclopropyl-1,3-dithiane (5d) [11]



5d

Afforded **5d** in 84% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 (d, *J* = 9.9 Hz, 1H), 2.92 – 2.76 (m, 4H), 2.19 – 2.05 (m, 1H), 1.95 – 1.76 (m, 1H), 1.13 – 0.96 (m, 1H), 0.75 – 0.62 (m, 2H), 0.51 – 0.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.2, 30.6, 25.8, 15.8, 5.7; MS (EI, 70 ev) m/z: 160, 119, 106, 85.

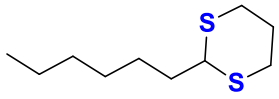
2-(2-Phenylethyl)-1,3-dithiane (5e) [2]



5e

Afforded **5e** in 94% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.24 – 7.16 (m, 3H), 3.99 (t, *J* = 7.0 Hz, 1H), 2.87 – 2.79 (m, 6H), 2.16 – 2.03 (m, 3H), 1.95 – 1.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 128.4, 128.3, 126.0, 46.4, 36.8, 32.4, 30.1, 25.9; MS (EI, 70 ev) m/z: 224, 133, 119, 106, 91.

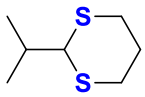
2-hexyl-1,3-dithiane (5f) [12]



5f

Afforded **5f** in 94% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.05 (t, *J* = 6.9 Hz, 1H), 2.97 – 2.73 (m, 4H), 2.21 – 2.05 (m, 1H), 1.96 – 1.80 (m, 1H), 1.79 – 1.68 (m, 2H), 1.58 – 1.44 (m, 2H), 1.37 – 1.21 (m, 6H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.6, 35.4, 31.5, 30.4, 28.8, 26.5, 26.0, 22.5, 14.0; MS (EI, 70 ev) m/z: 204, 119, 106.

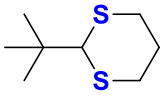
2-isopropyl-1,3-dithiane (5g) [8b]



5g

Afforded **5g** in 67% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.04 (d, *J* = 5.1 Hz, 1H), 2.96 – 2.79 (m, 4H), 2.21 – 1.95 (m, 2H), 1.94 – 1.75 (m, 1H), 1.10 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.2, 33.5, 30.7, 26.2, 19.9; MS (EI, 70 ev) m/z: 162, 147, 119, 106.

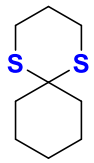
2-(tert-butyl)-1,3-dithiane (5d) [8b]



5h

Afforded **5h** in 63% yield as a white solid; mp 35-37 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.00 (s, 1H), 2.93 – 2.83 (m, 4H), 2.15 – 2.01 (m, 1H), 1.91 – 1.74 (m, 1H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 61.9, 61.9, 35.7, 31.2, 27.8, 25.9; MS (EI, 70 ev) m/z: 176, 119, 106.

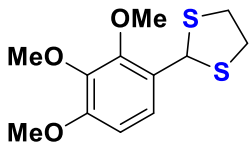
1,5-Dithia-spiro[5.5]undecane (5i) [2]



5i

Afforded **5i** in 89% yield as a white solid; mp 36-38 ℃ (lit.[2] 39-41 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.88 – 2.75 (m, 4H), 2.05 – 1.91 (m, 6H), 1.71 – 1.58 (m, 4H), 1.55 – 1.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.3, 37.8, 26.1, 25.8, 25.8, 21.9; MS (EI, 70 ev) m/z: 188, 155, 145, 114, 81.

2-(2,3,4-trimethoxyphenyl)-1,3-dithiolane (7a) [13]

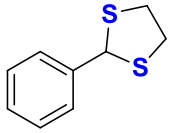


7a

Afforded **7a** in 82% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.8 Hz, 1H), 6.67 (d, *J* = 8.8 Hz, 1H), 6.00 (s, 1H), 3.95 (s, 3H), 3.85 (d, *J* = 4.4 Hz, 6H), 3.51 – 3.41 (m, 2H), 3.38 – 3.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 151.4, 141.7,

126.3, 122.8, 107.3, 61.4, 60.7, 56.0, 49.2, 39.7; MS (EI, 70 ev) m/z: 272, 257, 244, 213, 179, 167, 151, 121, 107.

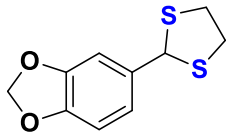
2-Phenyl-1,3-dithiolane (7b) [13]



7b

Afforded **7b** in 84% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.3 Hz, 2H), 7.36 – 7.20 (m, 3H), 5.63 (s, 1H), 3.54 – 3.42 (m, 2H), 3.40 – 3.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 128.4, 127.9, 127.9, 56.2, 40.2; MS (EI, 70 ev) m/z: 182, 153, 135, 121, 105.

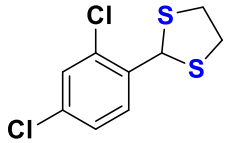
5-(1,3-dithiolan-2-yl)benzo[d][1,3]dioxole (7c) [13]



7c

Afforded **7c** in 62% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 1.8 Hz, 1H), 6.93 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 5.94 (s, 2H), 5.60 (s, 1H), 3.54 – 3.43 (m, 2H), 3.38 – 3.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 147.4, 133.9, 121.3, 108.3, 107.7, 101.2, 56.4, 40.2; MS (EI, 70 ev) m/z: 226, 197, 165, 135, 121, 107.

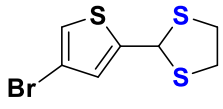
2-(2,4-dichlorophenyl)-1,3-dithiolane (7d) [14]



7d

Afforded **7d** in 94% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.5 Hz, 1H), 7.35 (d, *J* = 2.1 Hz, 1H), 7.27 – 7.20 (m, 1H), 6.00 (s, 1H), 3.40 – 3.31 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 133.8, 133.8, 130.1, 129.1, 127.3, 51.6, 39.7; MS (EI, 70 ev) m/z: 252, 250, 224, 222, 189, 187, 154, 146, 119, 111, 93.

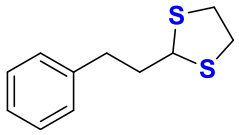
2-(4-bromothiophen-2-yl)-1,3-dithiolane (7e)



7e

Afforded **7e** in 76% yield as a white solid; mp 48-50 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 1.4 Hz, 1H), 6.98 (d, *J* = 0.5 Hz, 1H), 5.81 (s, 1H), 3.51 – 3.28 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 128.0, 122.8, 109.0, 50.1, 39.8; MS (EI, 70 ev) m/z: 268, 266, 240, 238, 207, 159, 141, 127, 95; HRMS (ESI): m/z calculated for $C_7H_7BrS_3$ $[M + H]^+$: 268.8946, found: 268.8950.

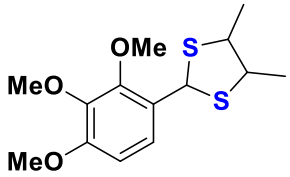
2-Phenyethyl-1,3-dithiolane (28a) [15]



7f

Afforded **7f** in 87% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.23 – 7.17 (m, 3H), 4.44 (t, *J* = 7.1 Hz, 1H), 3.34 – 3.13 (m, 4H), 2.84 – 2.72 (m, 2H), 2.20 – 2.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 128.5, 128.4, 126.0, 52.8, 41.1, 38.4, 35.2; MS (EI, 70 ev) m/z: 210, 117, 105, 91.

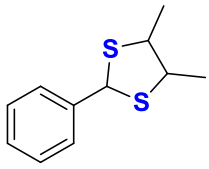
4,5-dimethyl-2-(2,3,4-trimethoxyphenyl)-1,3-dithiolane (7g)



7g

Afforded **7g** in 84% overall yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.44 (m, 1H), 6.77 – 6.62 (m, 1H), 6.10 – 5.94 (m, 1H), 4.14 – 3.91 (m, 3H), 3.85 (s, 6H), 3.61 – 3.33 (m, 2H), 1.50 – 1.35 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 153.0, 153.0, 151.6, 151.4, 151.1, 141.6, 127.8, 126.4, 124.5, 123.6, 123.1, 122.7, 107.6, 107.3, 107.1, 61.6, 61.5, 61.3, 60.7, 57.3, 55.9, 55.8, 53.6, 48.2, 46.9, 45.8, 18.1, 17.7, 17.0, 16.0; MS (EI, 70 ev) m/z: 300, 244, 213, 179, 151, 107.

4,5-dimethyl-2-phenyl-1,3-dithiolane (7h)

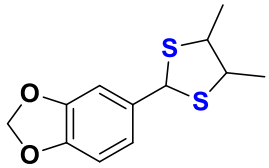


7h

Afforded **7h** in 87% overall yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.48 (m, 2H), 7.35 – 7.19 (m, 3H), 5.72 – 5.58 (m, 1H), 4.07 – 3.41 (m, 2H), 1.66 – 1.17 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 140.4, 138.7, 128.4, 128.3, 128.0, 127.9,

127.7, 57.6, 56.6, 55.8, 54.4, 53.9, 53.2, 18.5, 18.2, 17.0, 16.0; MS (EI, 70 ev) m/z: 210, 153, 145, 121, 105.

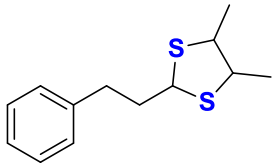
5-(4,5-dimethyl-1,3-dithiolan-2-yl)benzo[d][1,3]dioxole (7i)



7i

Afforded **7i** in 79% overall yield as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.07 (m, 1H), 6.99 – 6.84 (m, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 5.94 (s, 2H), 5.70 – 5.54 (m, 1H), 4.07 – 3.39 (m, 2H), 1.68 – 1.16 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 147.4, 134.1, 121.7, 121.4, 108.5, 107.7, 101.2, 66.8, 58.3, 57.6, 56.6, 53.9, 53.3, 18.5, 18.2, 17.0; MS (EI, 70 ev) m/z: 254, 198, 165, 135, 121, 107; HRMS (ESI): m/z calculated for $C_8H_9BrOS_2$ $[M + H]^+$: 255.0511, found: 250.0511.

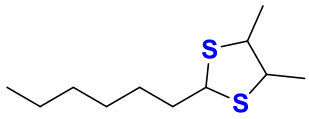
4,5-dimethyl-2-phenethyl-1,3-dithiolane (7j)



7j

Afforded **7j** in 90% overall yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.06 (m, 5H), 4.51 – 4.29 (m, 1H), 3.80 – 3.22 (m, 2H), 2.82 – 2.64 (m, 2H), 2.24 – 2.00 (m, 2H), 1.53 – 1.14 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 140.8, 140.7, 128.4, 128.4, 128.3, 128.3, 125.9, 125.9, 125.8, 56.2, 54.2, 52.5, 52.1, 52.0, 50.7, 49.5, 41.9, 41.4, 40.3, 35.4, 35.0, 34.8, 18.3, 17.6, 16.8, 16.0; MS (EI, 70 ev) m/z: 238, 133, 117, 105, 91.

2-hexyl-4,5-dimethyl-1,3-dithiolane (7k)



7k

Afforded **7k** in 69% overall yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.58 – 4.33 (m, 1H), 3.84 – 3.20 (m, 2H), 1.92 – 1.74 (m, 2H), 1.51 – 1.19 (m, 14H), 0.88 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 56.1, 54.3, 53.1, 52.3, 52.1, 51.6, 50.5, 40.3, 39.7, 38.6, 31.6, 31.6, 31.6, 29.5, 29.1, 28.9, 28.8, 28.8, 22.5, 18.4, 17.8, 16.9, 16.0, 14.0; MS (EI, 70 ev) m/z: 218, 133, 97.

7. References

1 B. Karimi and M. Vafaeezadeh, *RSC Adv*., 2013, **3**, 23207.

2 K. Inamoto, T. Yamada, S.-i. Kato, S. Kikkawa and Y. Kondo, *Tetrahedron*, 2013, **69**, 9192.

3 S. C. Tang, J. S. Lan, W. B. Du and L. X. Tian, CN 105085471, 2015.

4 L, Liu, G. h. Wang, J. Jiao and P. f. Li, *Org. Lett.*, 2017, **19**, 6132.

5 V. H. G. Rohde, P. Pommerening, H. F. T. Klare and M. Oestreich, *Organometallics*, 2014, **33**, 3618.

6 R. S. Paley, J. M. Liu, B. R. Lichtenstein, V. L. Knoedler, T. T. Sanan, D. J. Adams, J. Fernández, and P. R. Rablen, *Org. Lett*., 2003, **5**, 309.

7 B. Roy, D. Sengupta and B. Basu, *Tetrahedron Letters*., 2014, **55**, 6596.

8 (a) J. P. Fernandez, Y. Robbe,; J. P. Chapat, G. Caruana, M. Fatome and H. Sentenac-Roumanou, *Eur. J. Med. Chem*., 1984, **19**, 461; (b) J. S. Lan, W. B. Du, L. X. Tian, C. G. Zhao, X. G. She and S. C. Tang, *Org. Lett*., 2014, **16**, 4396.

9 P. Stütz and P. A. Stadler, *Helv. Chim. Acta*, 1972, **55**, 75.

10 C.-T. Chen, Y.-D. Lin and C.-Y. Liu, *Tetrahedron*, 2009, **65**, 10470.

11 J. Claydena, D. W. Watsona and M. Chambers, *Tetrahedron*, 2005, **61**, 3195.

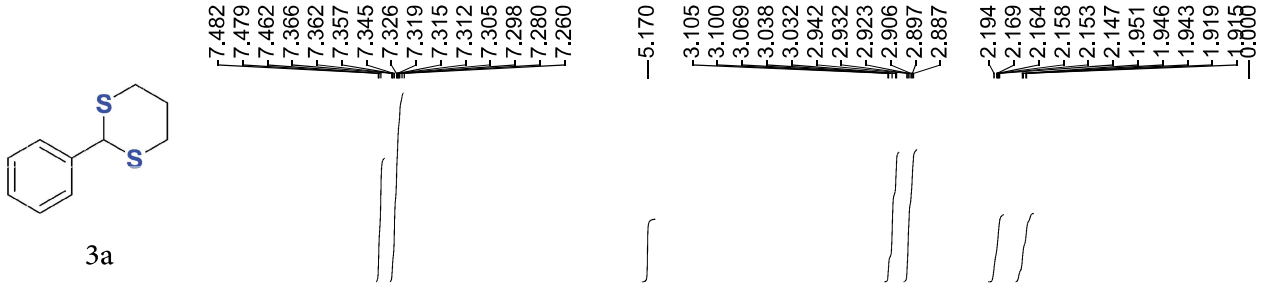
12 C.-J. Yu, R. Li and P. M. Gu, *Tetrahedron Letters*., 2016, **57**, 3568.

13 H. R. Shaterian, K. Azizi and N. Fahimi, *J. Sulfur. Chem*., 2011, **32**, 85.

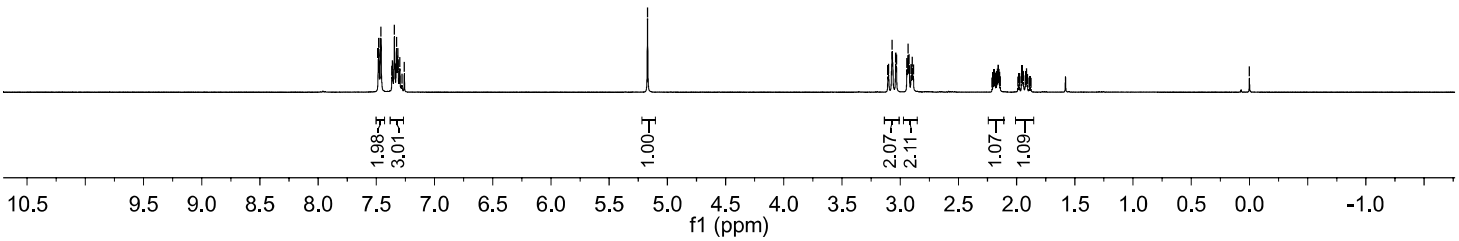
14. S. A. Pourmousavi and M. Hadavandkhani, *J. Sulfur. Chem*., 2009, **30**, 37.

15. N. Sakai, T. Miyazaki, T. Sakamoto, T. Yatsuda, T. Moriya, R. Ikeda, and T. Konakahara, *Org. Lett*., 2012, **14**, 4366.

8. ^{1}H, ^{13}C, ^{19}F NMR spectra

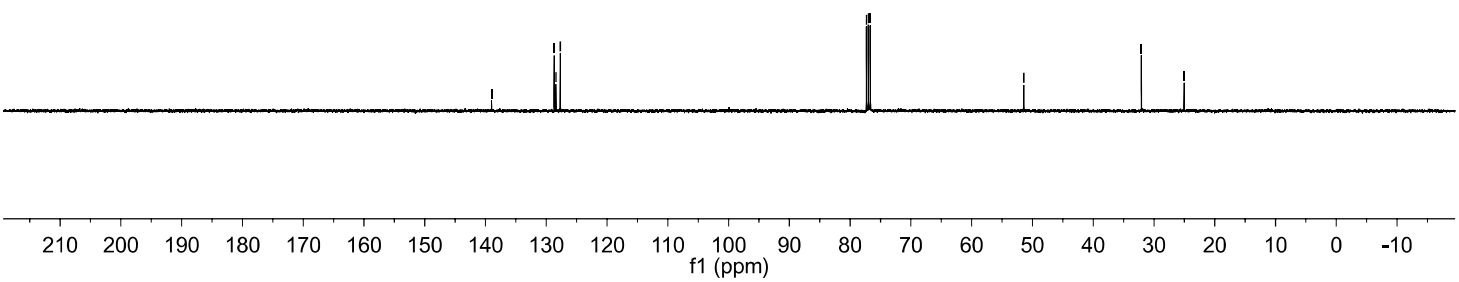

7.482
7.479
7.462
7.366
7.362
7.357
7.345
7.326
7.319
7.315
7.312
7.305
7.298
7.280
7.260
5.170
3.105
3.100
3.069
3.038
3.032
2.942
2.932
2.923
2.906
2.897
2.887
2.194
2.169
2.164
2.158
2.153
2.147
1.951
1.946
1.943
1.919
1.915
0.000

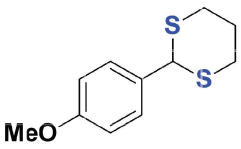
3a


1.98
3.01
1.00
2.07
2.11
1.07
1.09
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

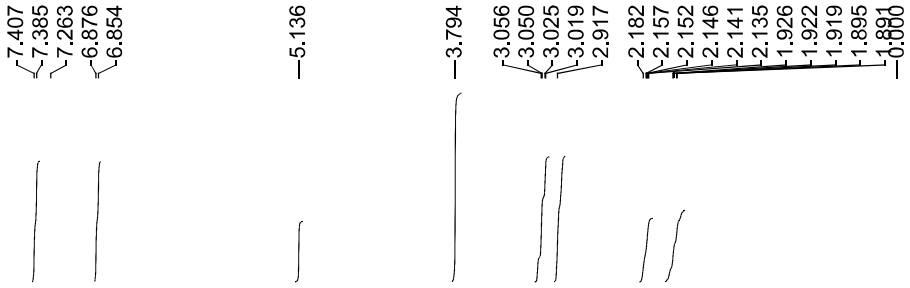

139.004
128.703
128.415
127.691
77.317
77.000
76.682
51.424
32.076
25.040

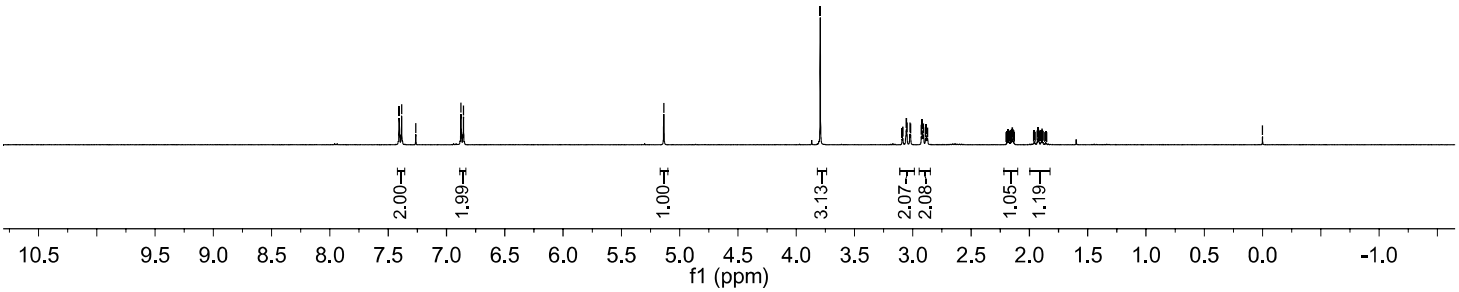
3a

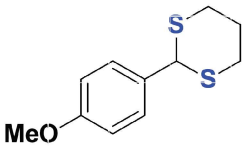

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


S
S
MeO

3b

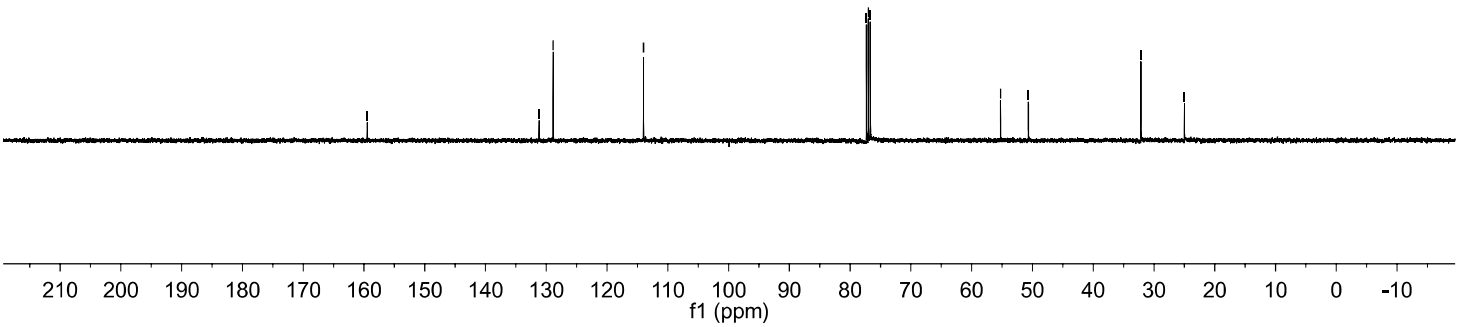

7.407
7.385
7.263
6.876
6.854
5.136
3.794
3.056
3.050
3.025
3.019
2.917
2.182
2.157
2.152
2.146
2.141
2.135
1.926
1.922
1.919
1.895
1.891
0.000

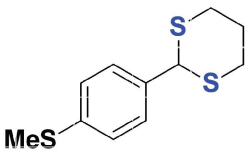

2.00
1.99
1.00
3.13
2.07
2.08
1.05
1.19
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)


S
S
MeO

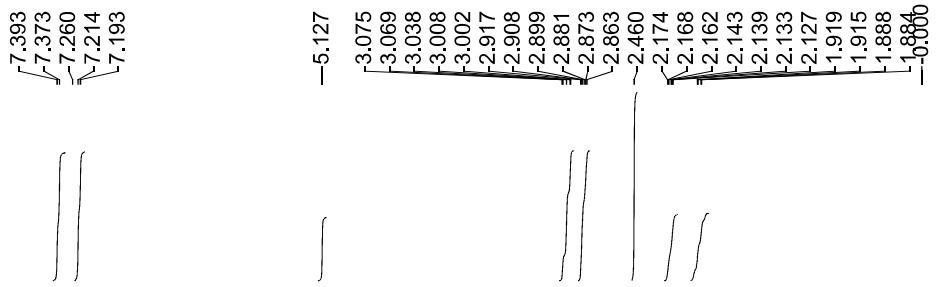
3b

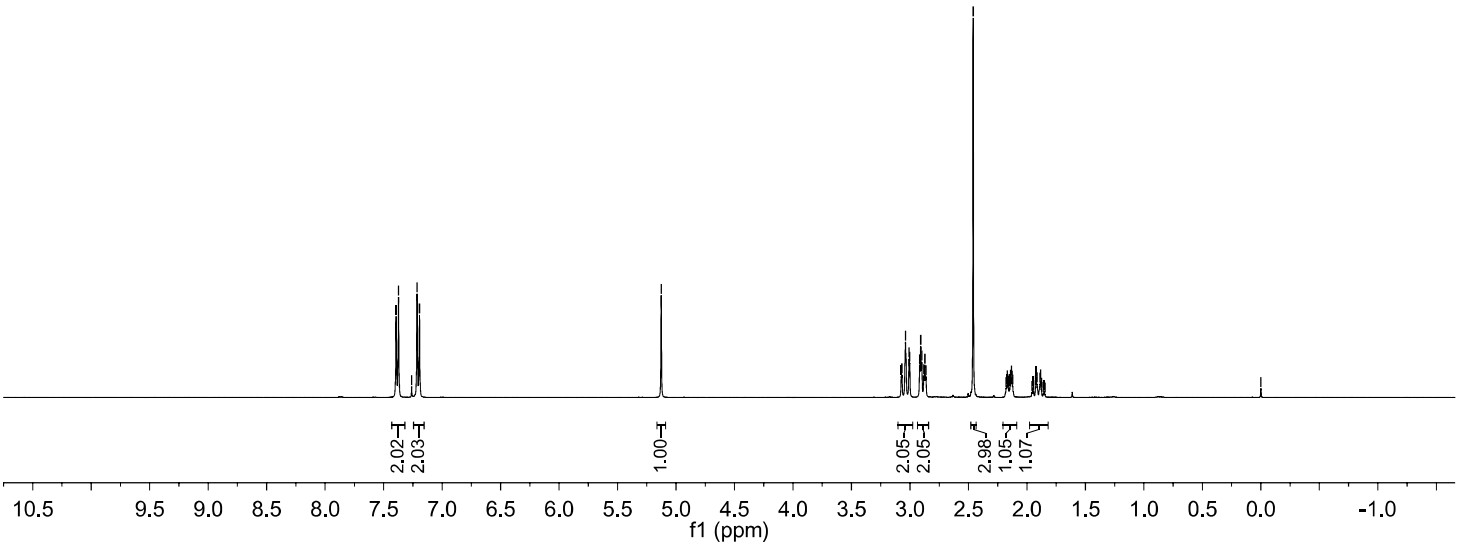

159.457
131.184
128.866
114.002
77.317
77.000
76.683
55.249
50.666
32.163
24.994

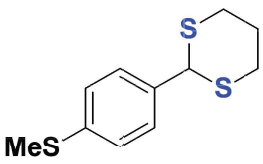

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


S
S
MeS

3c

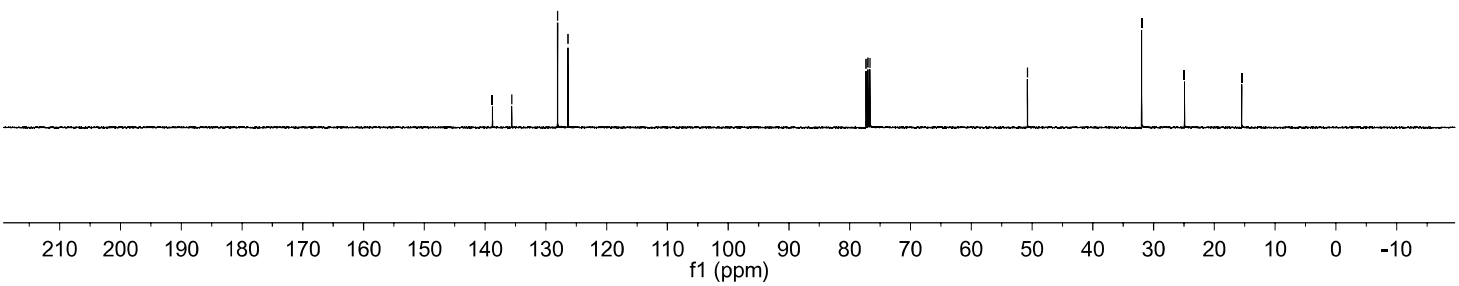

7.393
7.373
7.260
7.214
7.193
5.127
3.075
3.069
3.038
3.008
3.002
2.917
2.908
2.899
2.881
2.873
2.863
2.460
2.174
2.168
2.162
2.143
2.139
2.133
2.127
1.919
1.915
1.888
1.884
0.000

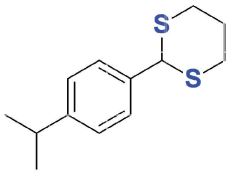

2.02
2.03
1.00
2.05
2.05
2.98
1.05
1.07
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)


S
S
MeS

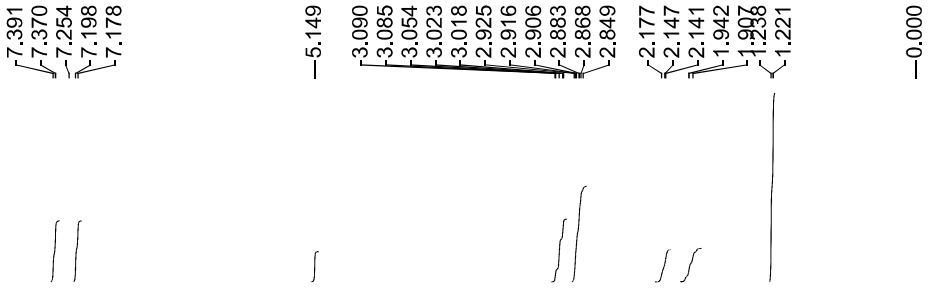
3c

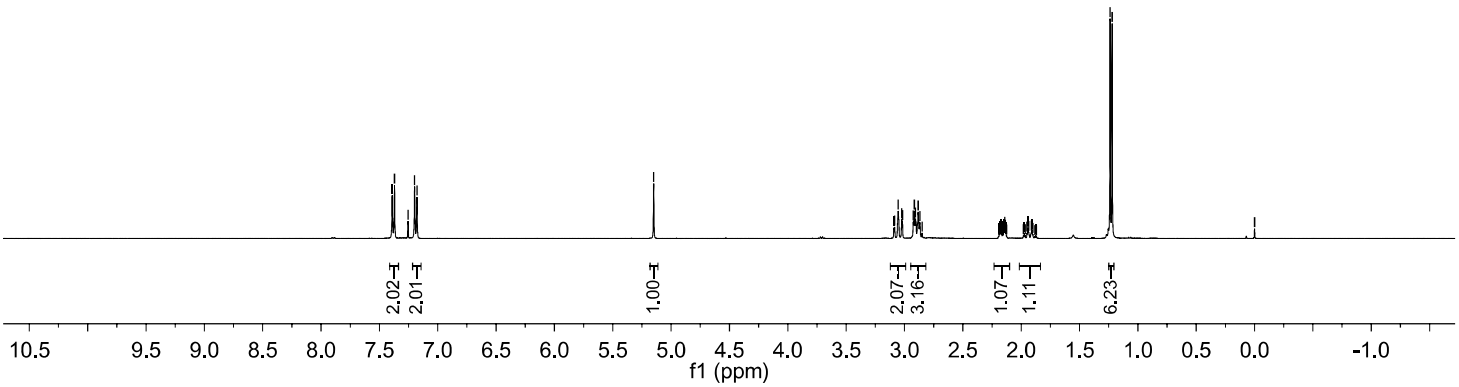

138.787
135.618
128.073
126.365
77.317
77.000
76.682
50.763
31.978
24.911
15.517

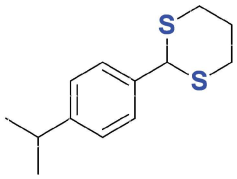

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



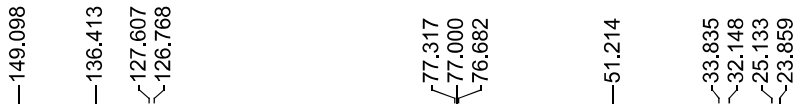
3d

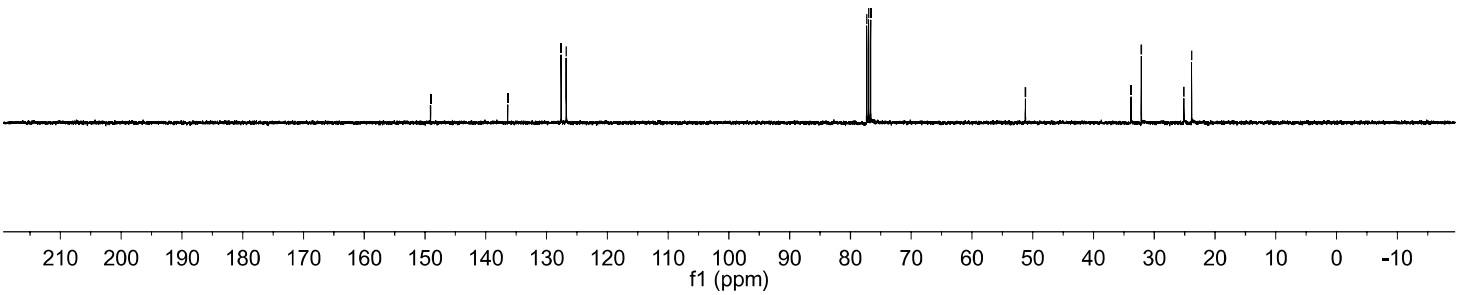

7.391
7.370
7.254
7.198
7.178
5.149
3.090
3.085
3.054
3.023
3.018
2.925
2.916
2.906
2.883
2.868
2.849
2.177
2.147
2.141
1.942
1.907
1.238
1.221
0.000

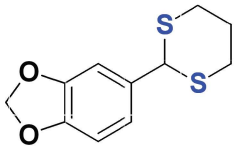

2.02
2.01
1.00
2.07
3.16
1.07
1.11
6.23
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)



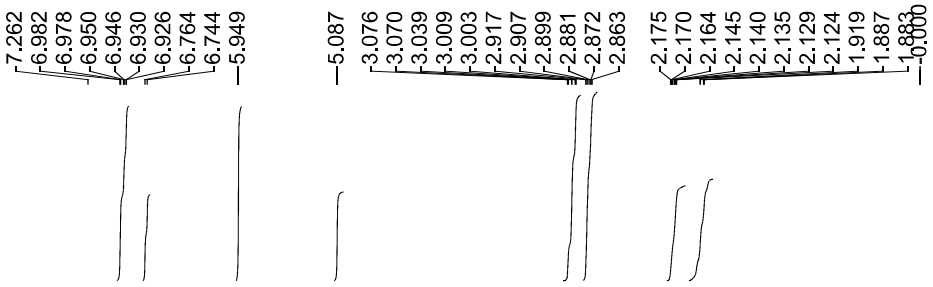
3d

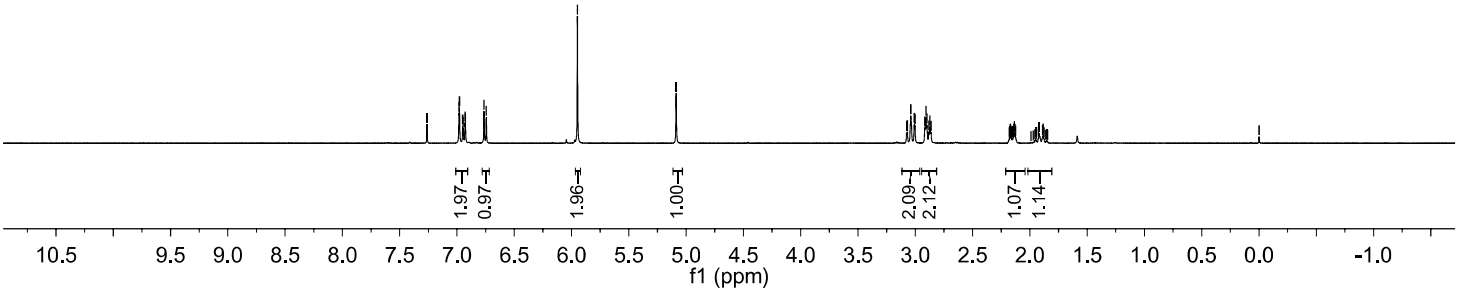

149.098
136.413
127.607
126.768
77.317
77.000
76.682
51.214
33.835
32.148
25.133
23.859

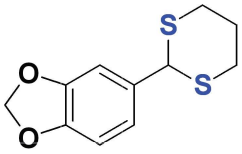

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



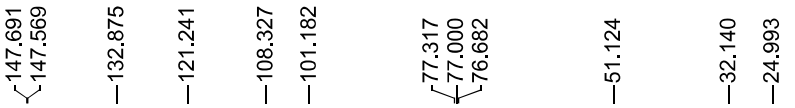
3e

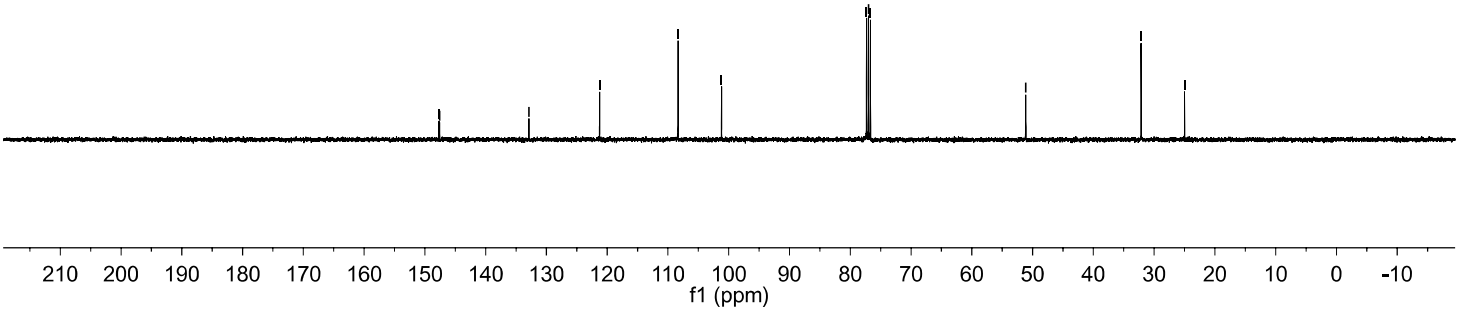

7.262
6.982
6.978
6.950
6.946
6.930
6.926
6.764
6.744
5.949
5.087
3.076
3.070
3.039
3.009
3.003
2.917
2.907
2.899
2.881
2.872
2.863
2.175
2.170
2.164
2.145
2.140
2.135
2.129
2.124
1.919
1.887
1.883
0.000

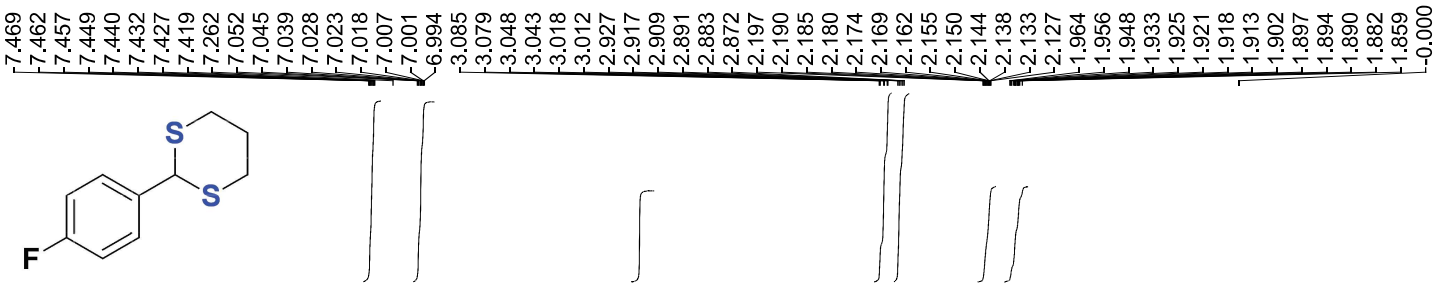

1.97
0.97
1.96
1.00
2.09
2.12
1.07
1.14
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)



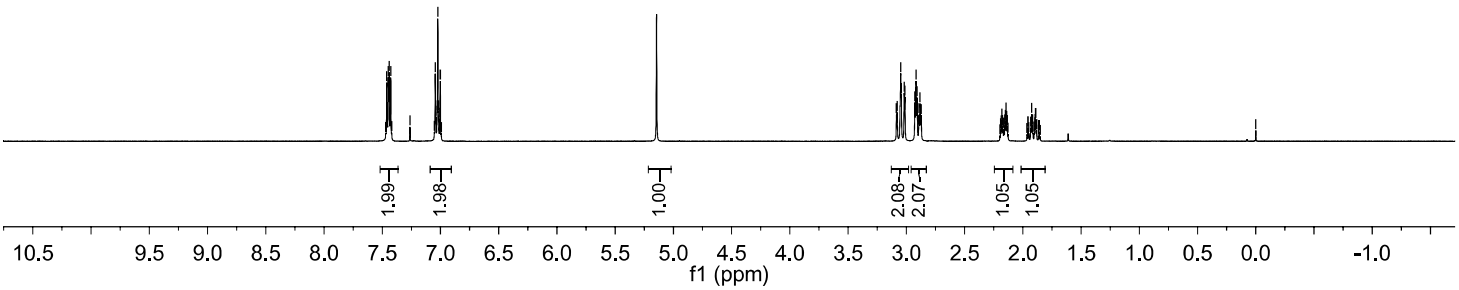
3e

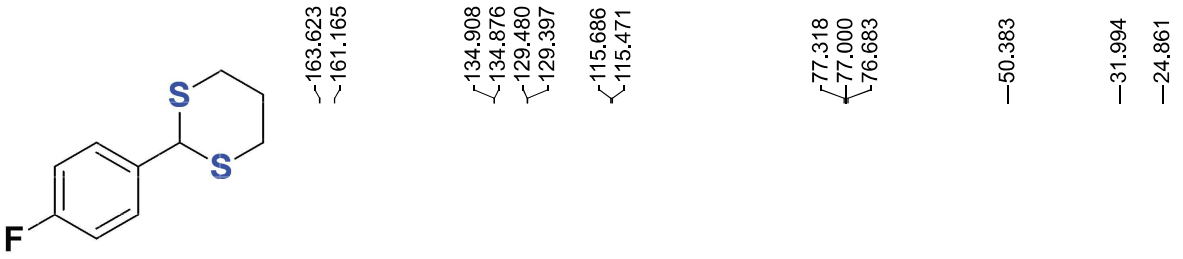

147.691
147.569
132.875
121.241
108.327
101.182
77.317
77.000
76.682
51.124
32.140
24.993


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

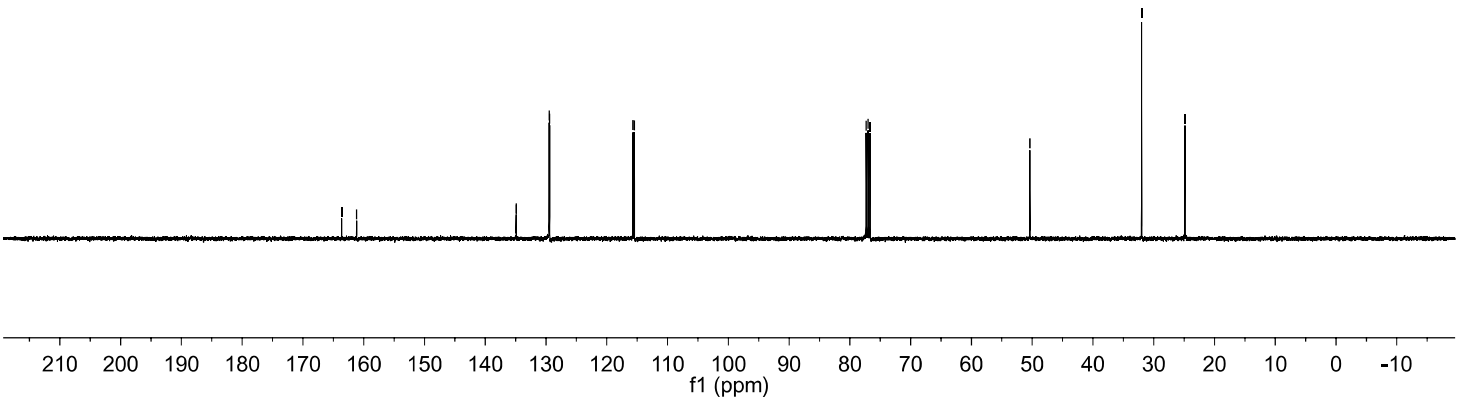

7.469
7.462
7.457
7.449
7.440
7.432
7.427
7.419
7.262
7.052
7.045
7.039
7.028
7.023
7.018
7.007
7.001
6.994
3.085
3.079
3.048
3.043
3.018
3.012
2.927
2.917
2.909
2.891
2.883
2.872
2.197
2.190
2.185
2.180
2.174
2.169
2.162
2.155
2.150
2.144
2.138
2.133
2.127
1.964
1.956
1.948
1.933
1.925
1.921
1.918
1.913
1.902
1.897
1.894
1.890
1.882
1.859
0.000
S
S
F

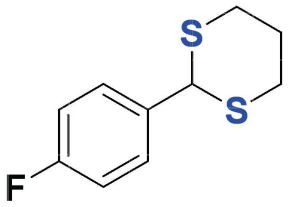
3f


1.99
1.98
1.00
2.08
2.07
1.05
1.05
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)


163.623
161.165
134.908
134.876
129.480
129.397
115.686
115.471
77.318
77.000
76.683
50.383
31.994
24.861
S
S
F

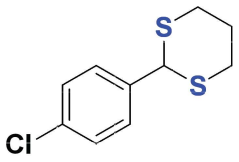
3f


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

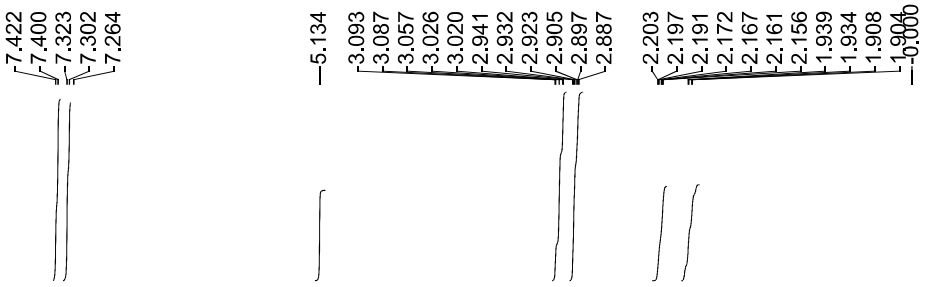

S
S
F

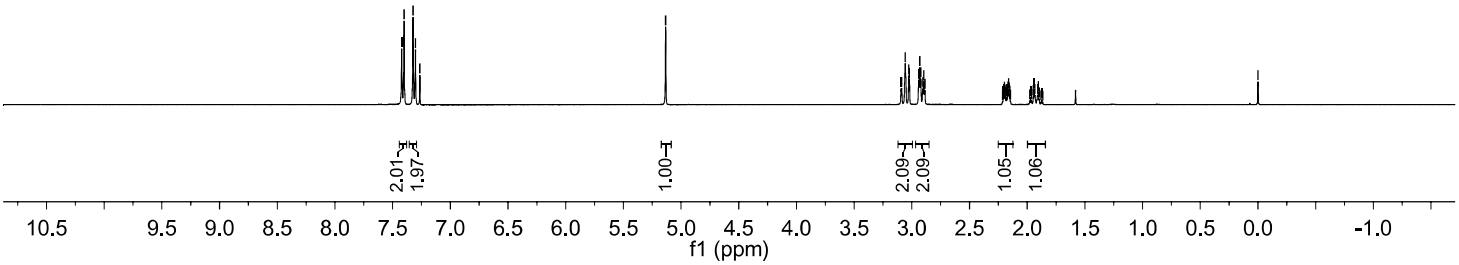
3f

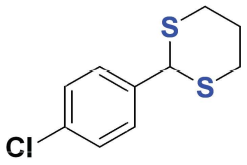
-113.172
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)


S
S
Cl

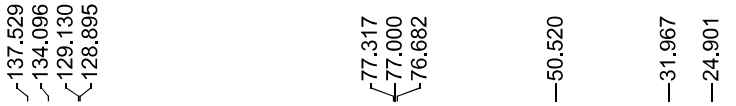
3g

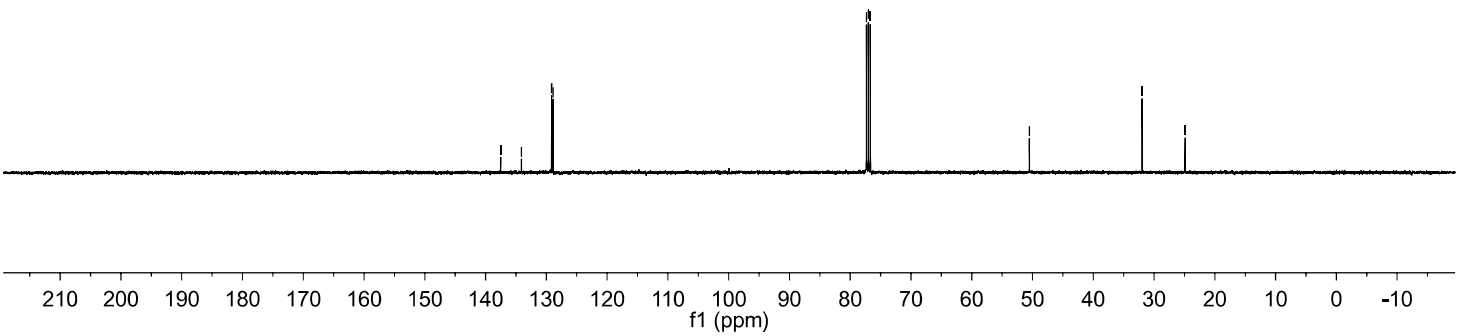

7.422
7.400
7.323
7.302
7.264
5.134
3.093
3.087
3.057
3.026
3.020
2.941
2.932
2.923
2.905
2.897
2.887
2.203
2.197
2.191
2.172
2.167
2.161
2.156
1.939
1.934
1.908
1.904
0.000

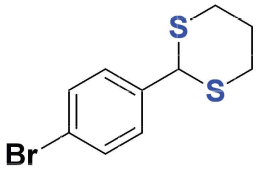

2.01
1.97
1.00
2.09
2.09
1.05
1.06
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)


S
S
Cl

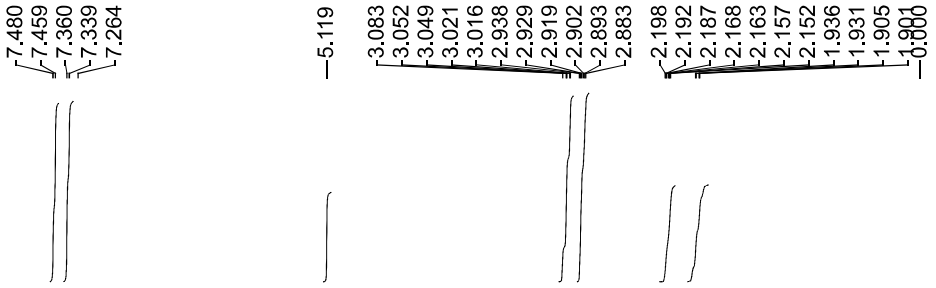
3g

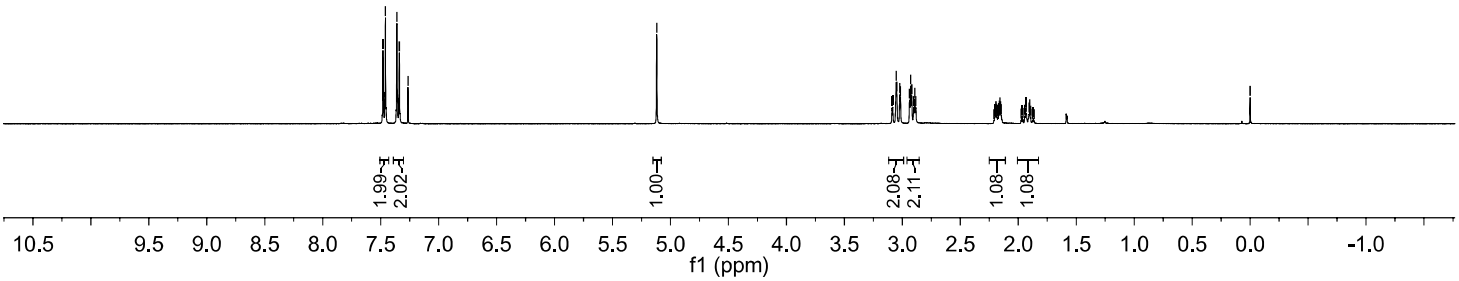

137.529
134.096
129.130
128.895
77.317
77.000
76.682
50.520
31.967
24.901

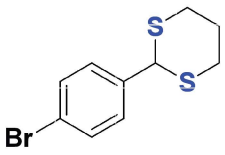

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


S
S
Br

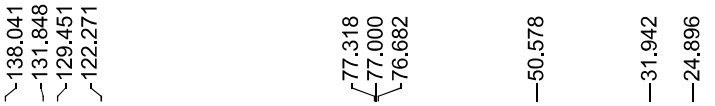
3h

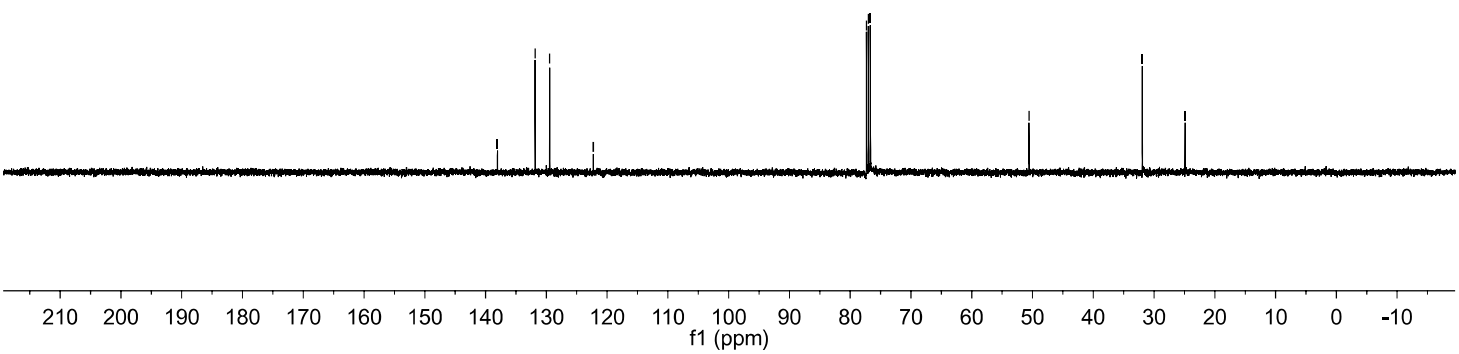

7.480
7.459
7.360
7.339
7.264
5.119
3.083
3.052
3.049
3.021
3.016
2.938
2.929
2.919
2.902
2.893
2.883
2.198
2.192
2.187
2.168
2.163
2.157
2.152
1.936
1.931
1.905
1.901
0.000

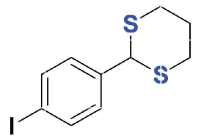

1.99
2.02
1.00
2.08
2.11
1.08
1.08
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)


S
S
Br

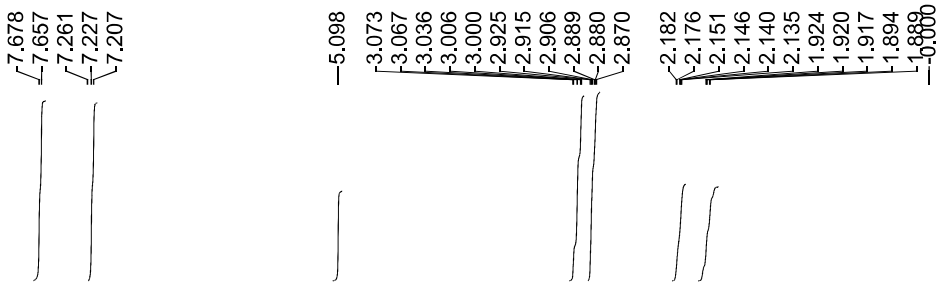
3h

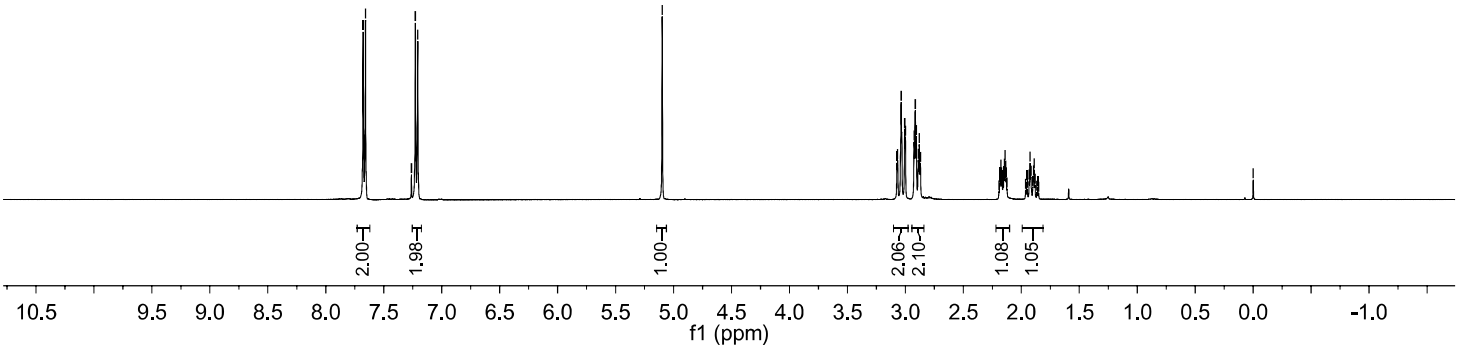

138.041
131.848
129.451
122.271
77.318
77.000
76.682
50.578
31.942
24.896

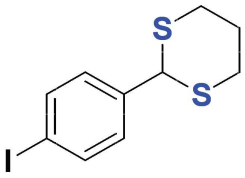

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



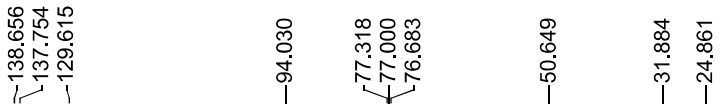
3i

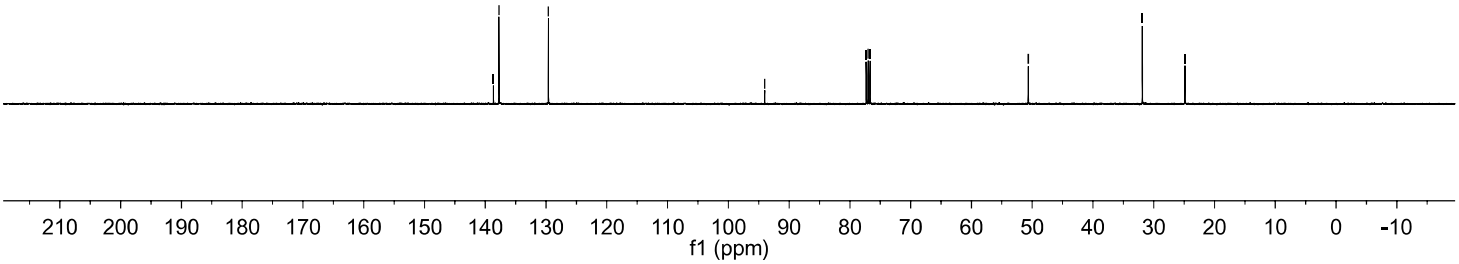

7.678
7.657
7.261
7.227
7.207
5.098
3.073
3.067
3.036
3.006
3.000
2.925
2.915
2.906
2.889
2.880
2.870
2.182
2.176
2.151
2.146
2.140
2.135
1.924
1.920
1.917
1.894
1.889
0.000

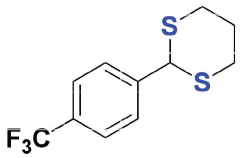

2.00
1.98
1.00
2.06
2.10
1.08
1.05
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)



3i

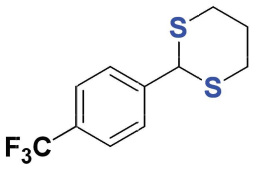

138.656
137.754
129.615
94.030
77.318
77.000
76.683
50.649
31.884
24.861


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


S
S
F3C

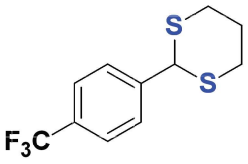
3j

7.604
7.265
5.205
3.114
3.108
3.083
3.077
3.071
3.047
3.041
2.965
2.955
2.947
2.921
2.219
2.195
2.189
2.183
2.178
2.172
1.968
1.963
1.960
1.937
1.932
0.000
4.08
1.00
2.10
2.12
1.06
1.06
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)


S
S
F3C

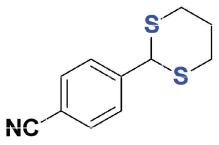
3j

142.869
130.934
130.612
130.289
129.948
128.234
125.771
125.734
125.696
125.659
125.208
122.504
77.317
77.000
76.682
50.727
31.878
24.875
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

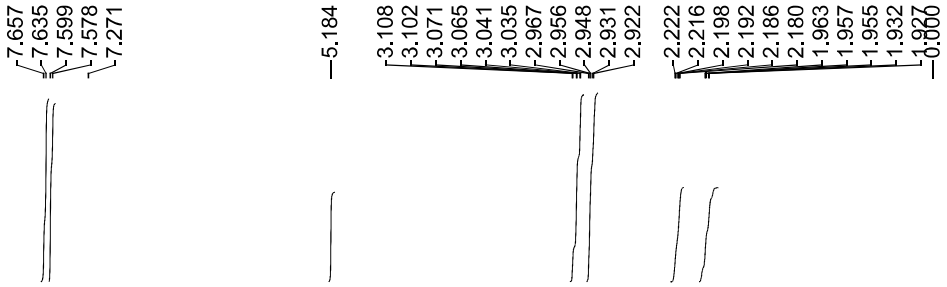

S
S
F3C

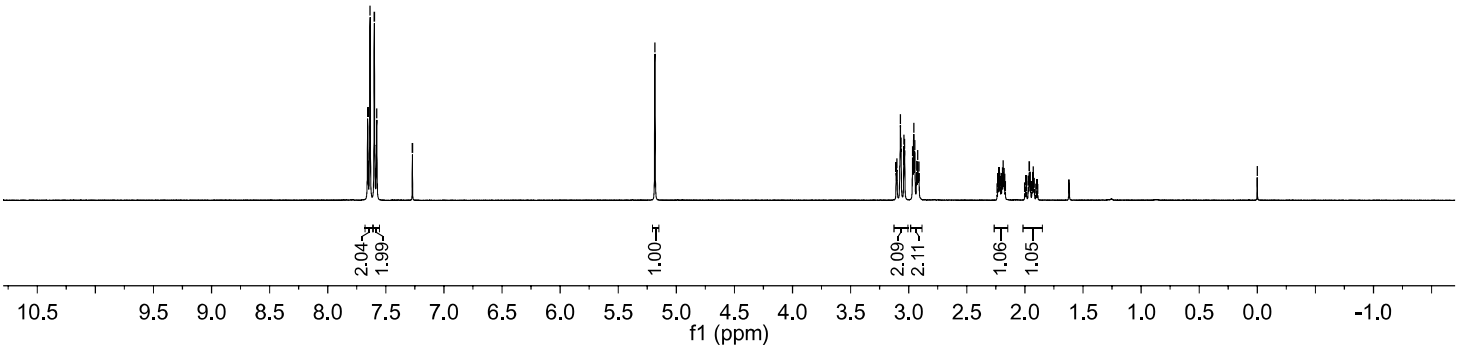
3j

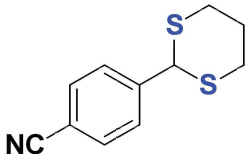
-62.608
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)



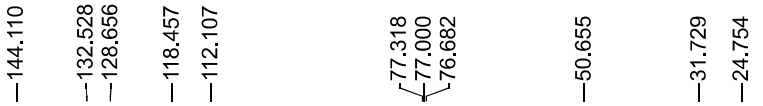
3k

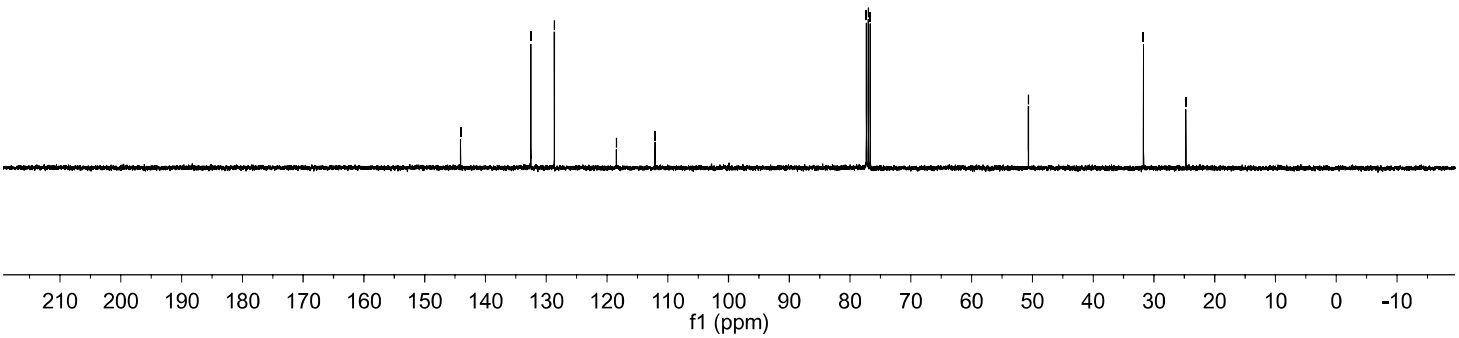

7.657
7.635
7.599
7.578
7.271
5.184
3.108
3.102
3.071
3.065
3.041
3.035
2.967
2.956
2.948
2.931
2.922
2.222
2.216
2.198
2.192
2.186
2.180
1.963
1.957
1.955
1.932
1.927
0.000

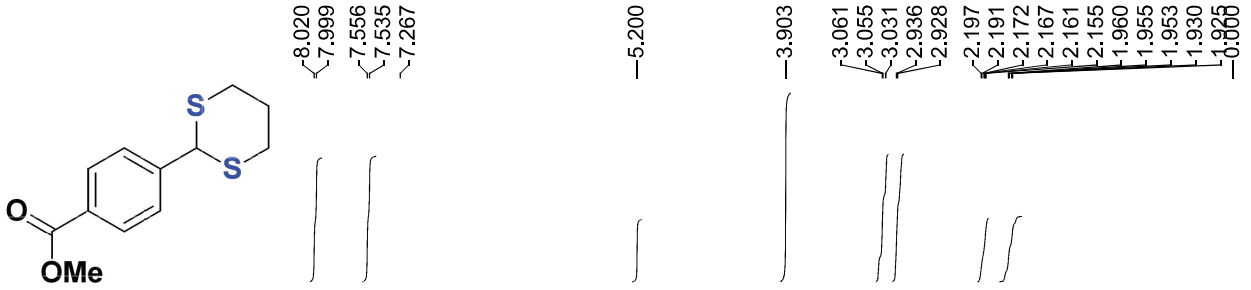

2.04
1.99
1.00
2.09
2.11
1.06
1.05
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)



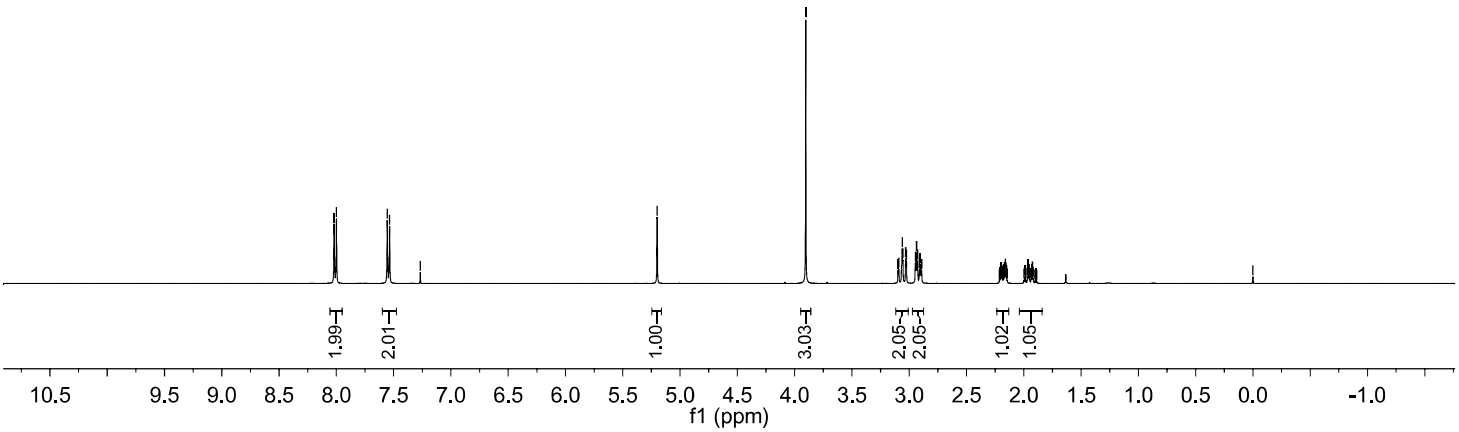
3k

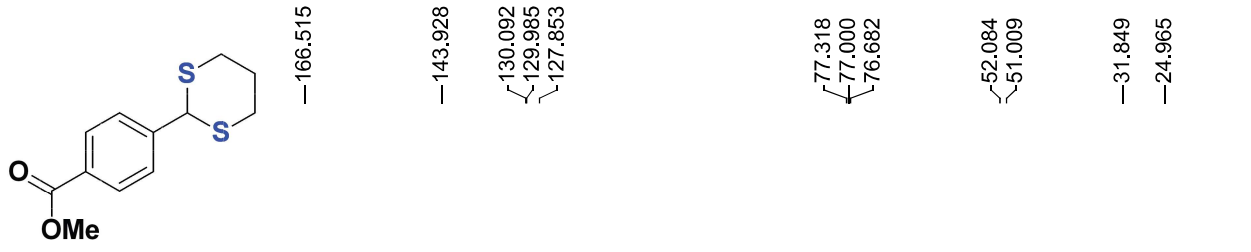

144.110
132.528
128.656
118.457
112.107
77.318
77.000
76.682
50.655
31.729
24.754


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

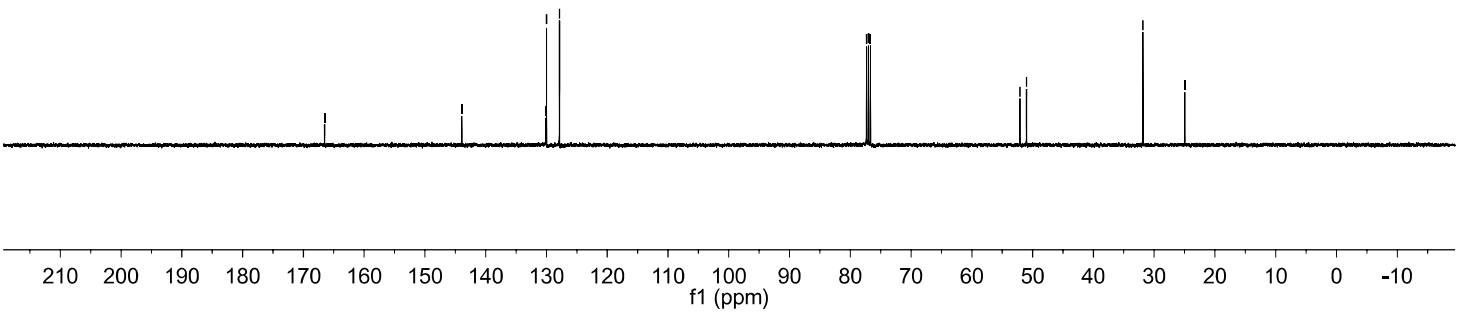

8.020
7.999
7.556
7.535
7.267
5.200
3.903
3.061
3.055
3.031
2.936
2.928
2.197
2.191
2.172
2.167
2.161
2.155
1.960
1.955
1.953
1.930
1.925
0.000
S
S
O
OMe

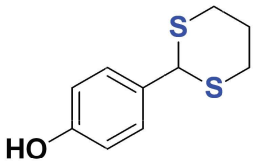
3l


1.99
2.01
1.00
3.03
2.05
2.05
1.02
1.05
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

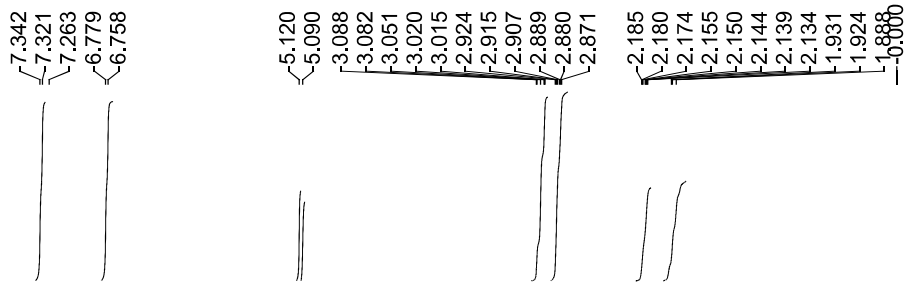

166.515
143.928
130.092
129.985
127.853
77.318
77.000
76.682
52.084
51.009
31.849
24.965
S
S
O
OMe

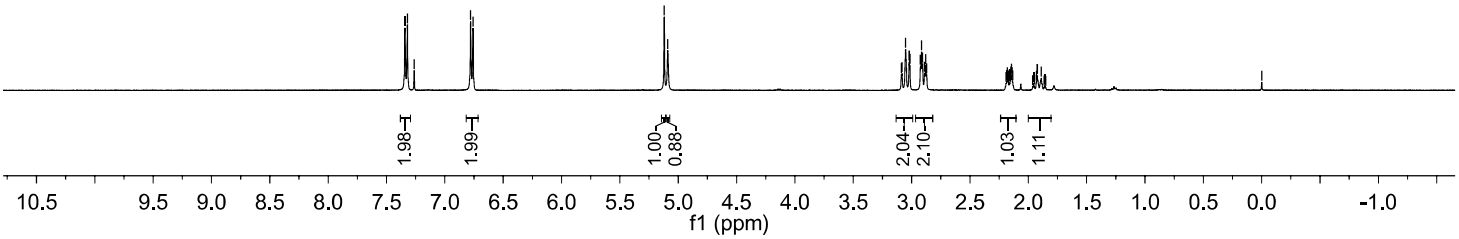
3l

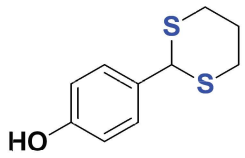

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


S
S
HO

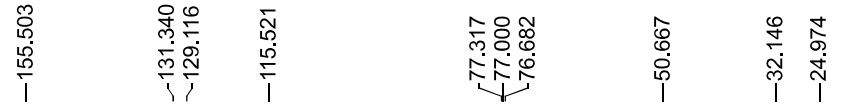
3m

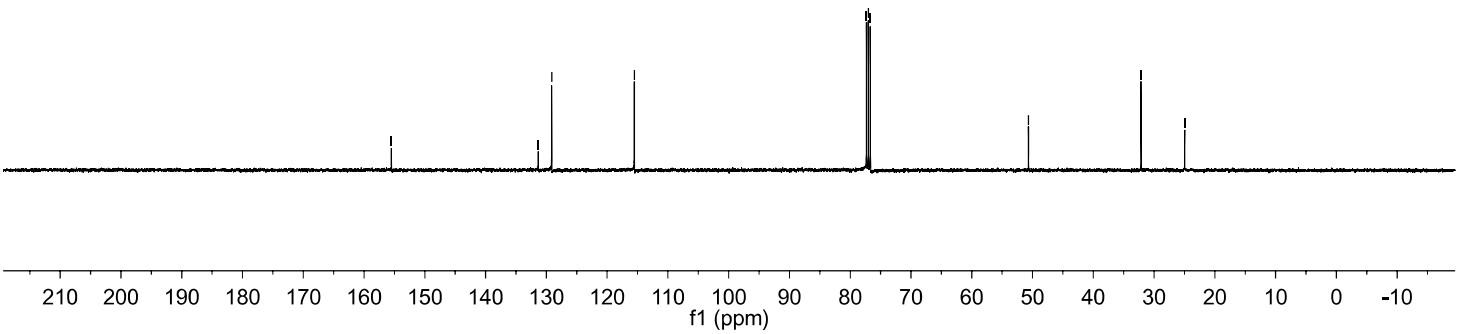

7.342
7.321
7.263
6.779
6.758
5.120
5.090
3.088
3.082
3.051
3.020
3.015
2.924
2.915
2.907
2.889
2.880
2.871
2.185
2.180
2.174
2.155
2.150
2.144
2.139
2.134
1.931
1.924
1.888
0.000

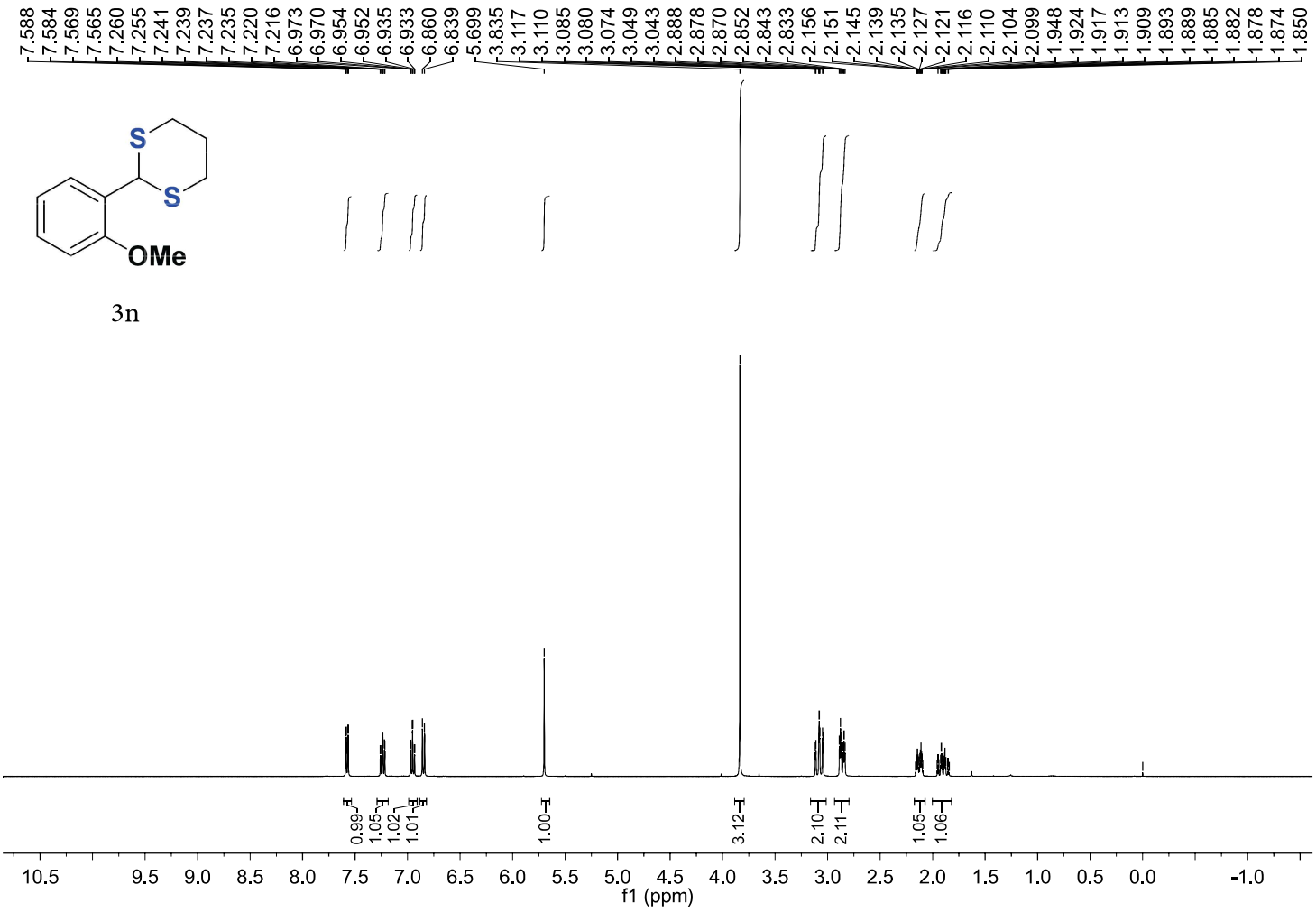

1.98
1.99
1.00
0.88
2.04
2.10
1.03
1.11
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)


S
S
HO

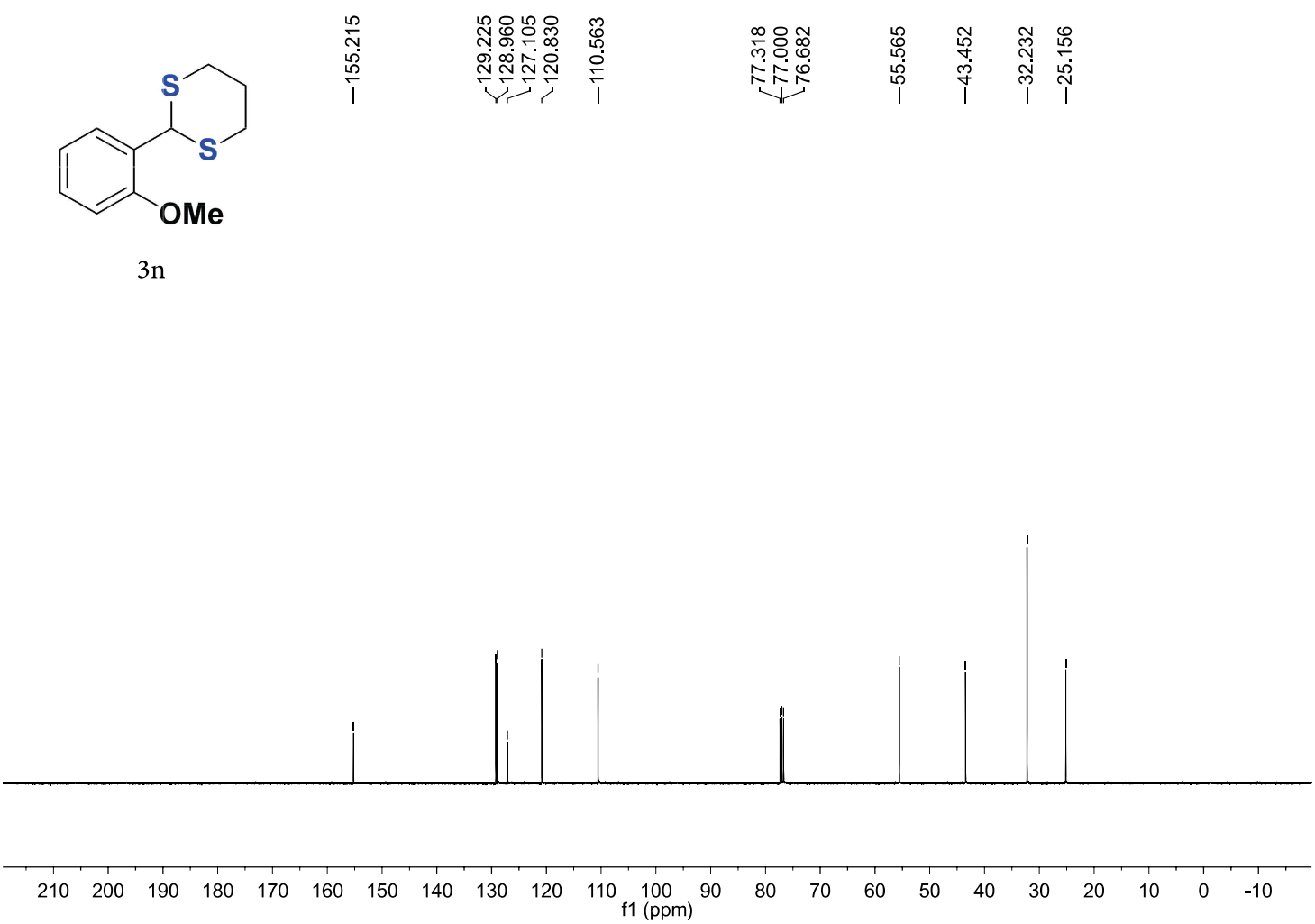
3m


155.503
131.340
129.116
115.521
77.317
77.000
76.682
50.667
32.146
24.974

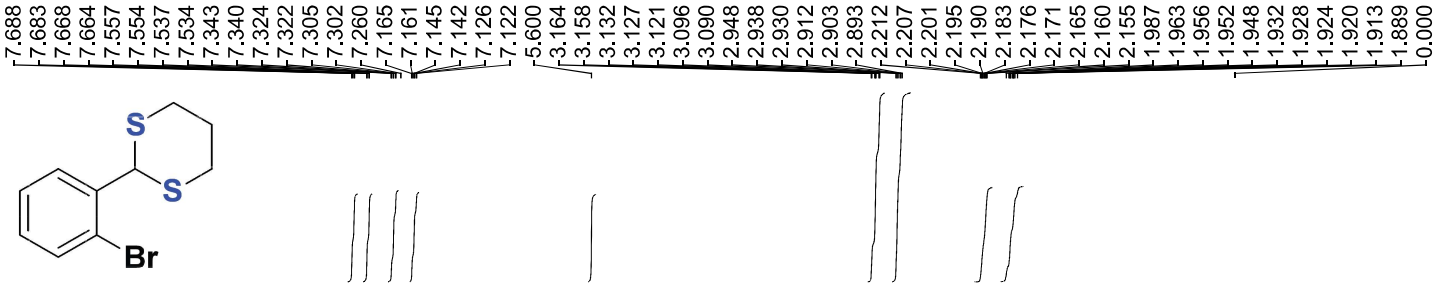

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.588
7.584
7.569
7.565
7.260
7.255
7.241
7.239
7.237
7.235
7.220
7.216
6.973
6.970
6.954
6.952
6.935
6.933
6.860
6.839
5.699
3.835
3.117
3.110
3.085
3.080
3.074
3.049
3.043
2.888
2.878
2.870
2.852
2.843
2.833
2.156
2.151
2.145
2.139
2.135
2.127
2.121
2.116
2.110
2.104
2.099
1.948
1.924
1.917
1.913
1.909
1.893
1.889
1.885
1.882
1.878
1.874
1.850
S
S
OMe
0.99
1.05
1.02
1.01
1.00
3.12
2.10
2.11
1.05
1.06
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

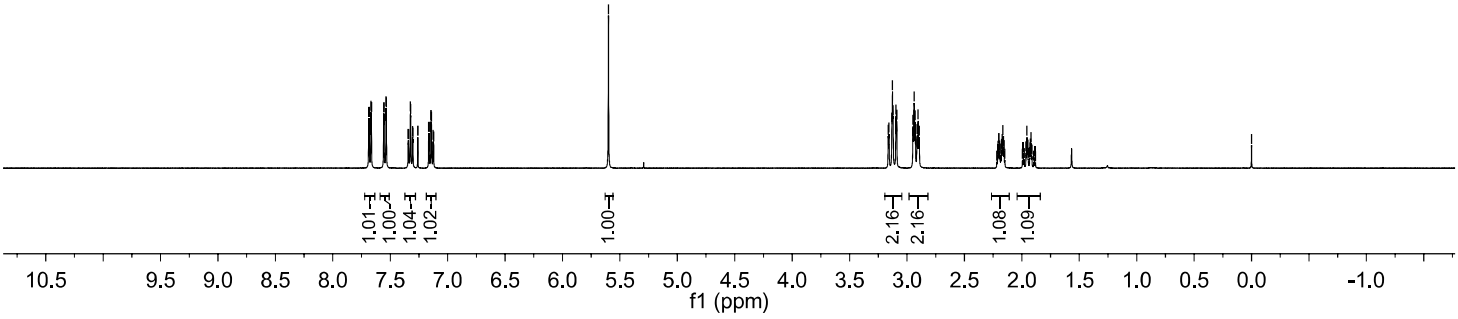
3n

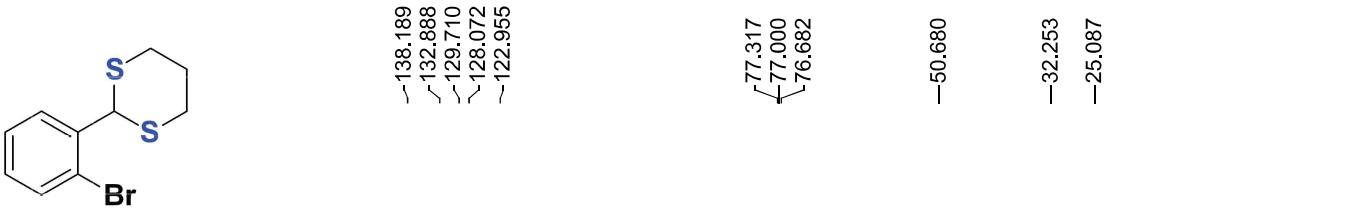

155.215
129.225
128.960
127.105
120.830
110.563
77.318
77.000
76.682
55.565
43.452
32.232
25.156
S
S
OMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3n

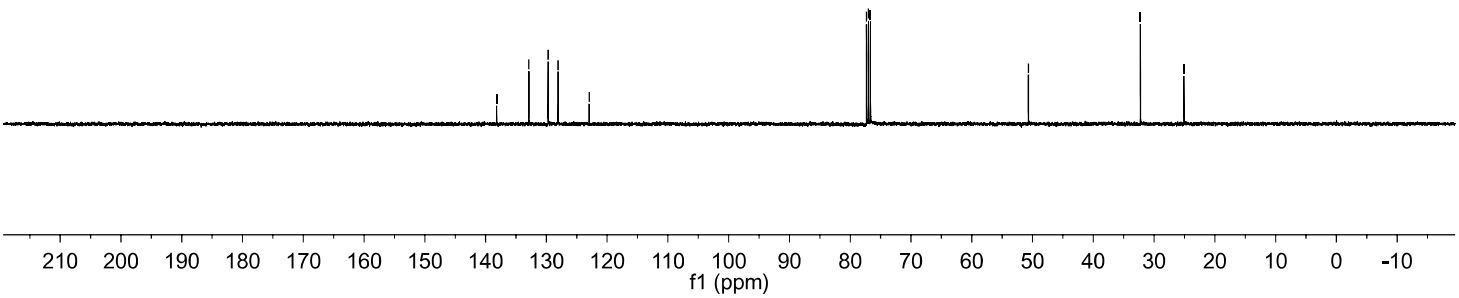

7.688
7.683
7.668
7.664
7.557
7.554
7.537
7.534
7.343
7.340
7.324
7.322
7.305
7.302
7.260
7.165
7.161
7.145
7.142
7.126
7.122
5.600
3.164
3.158
3.132
3.127
3.121
3.096
3.090
2.948
2.938
2.930
2.912
2.903
2.893
2.212
2.207
2.201
2.195
2.190
2.183
2.176
2.171
2.165
2.160
2.155
1.987
1.963
1.956
1.952
1.948
1.932
1.928
1.924
1.920
1.913
1.889
0.000
S
S
Br

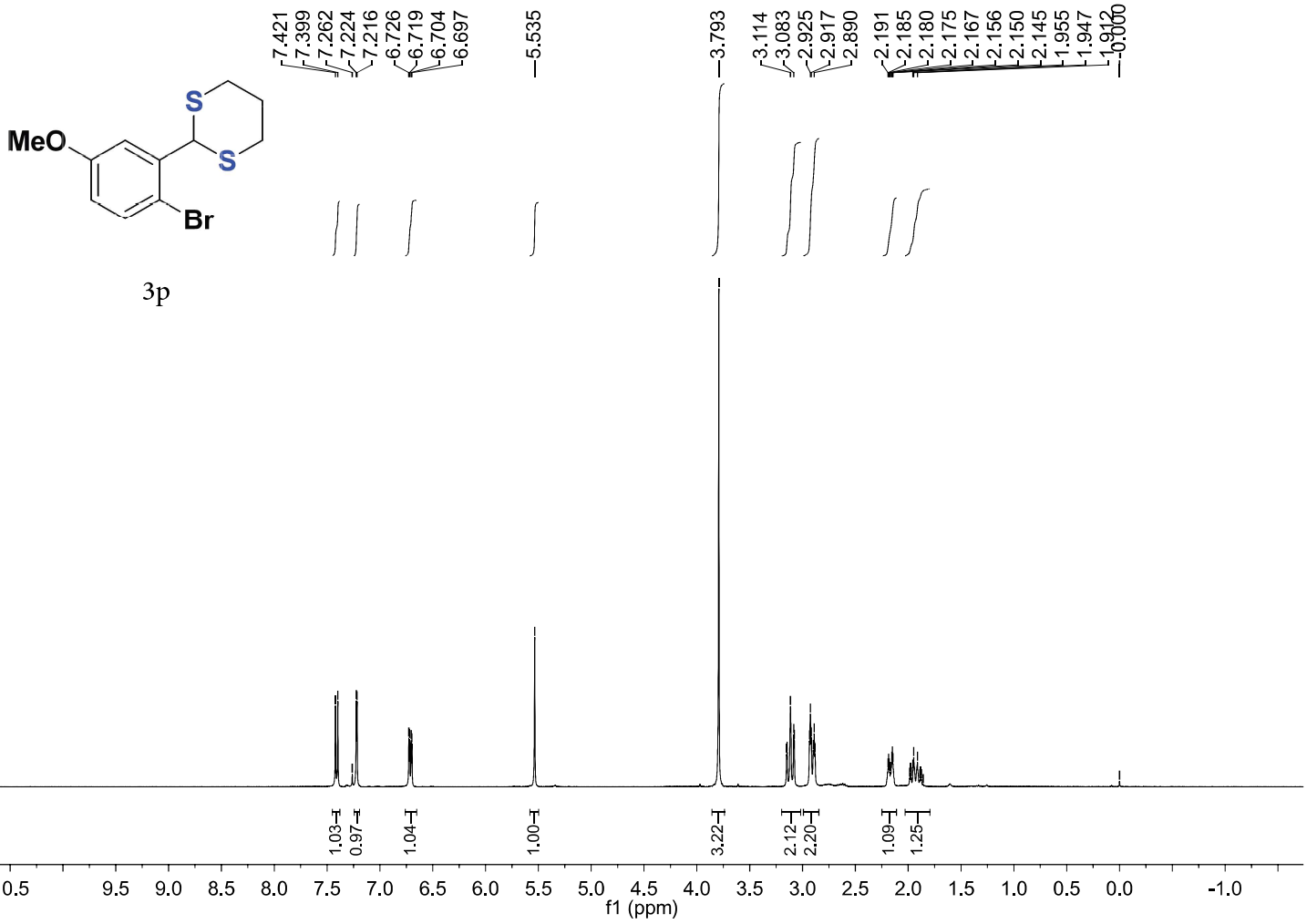
3o


1.01
1.00
1.04
1.02
1.00
2.16
2.16
1.08
1.09
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

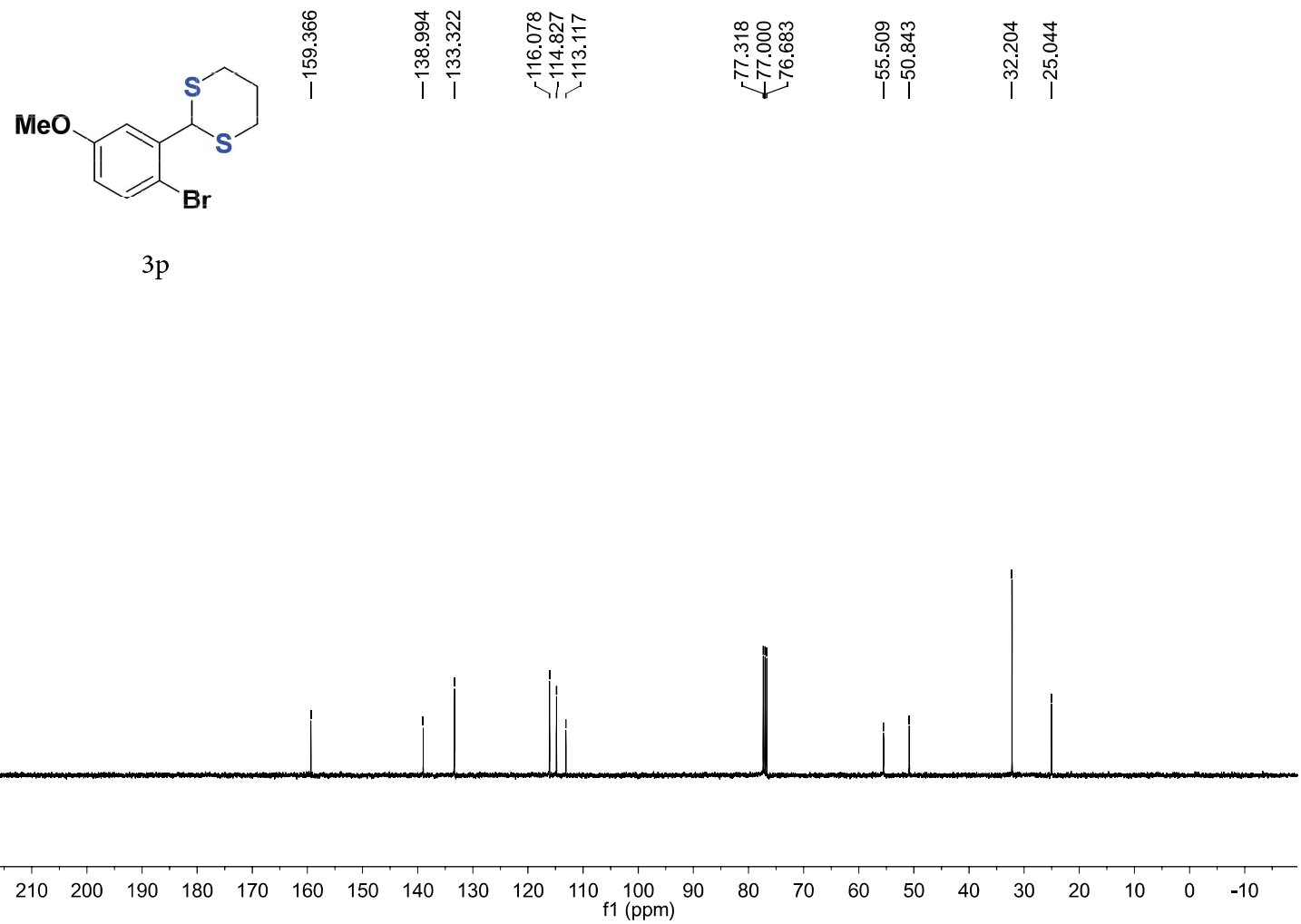

138.189
132.888
129.710
128.072
122.955
77.317
77.000
76.682
50.680
32.253
25.087
S
S
Br

3o

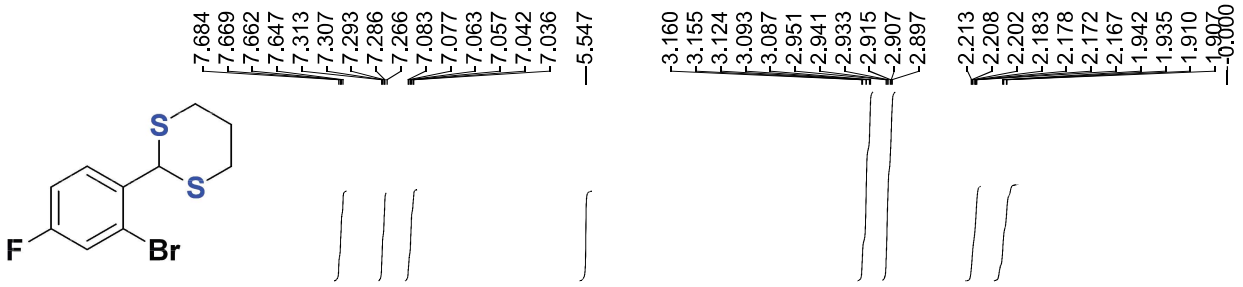

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.421
7.399
7.262
7.224
7.216
6.726
6.719
6.704
6.697
5.535
3.793
3.114
3.083
2.925
2.917
2.890
2.191
2.185
2.180
2.175
2.167
2.156
2.150
2.145
1.955
1.947
1.912
0.000
MeO
S
S
Br
1.03
0.97
1.04
1.00
3.22
2.12
2.20
1.09
1.25
f1 (ppm)

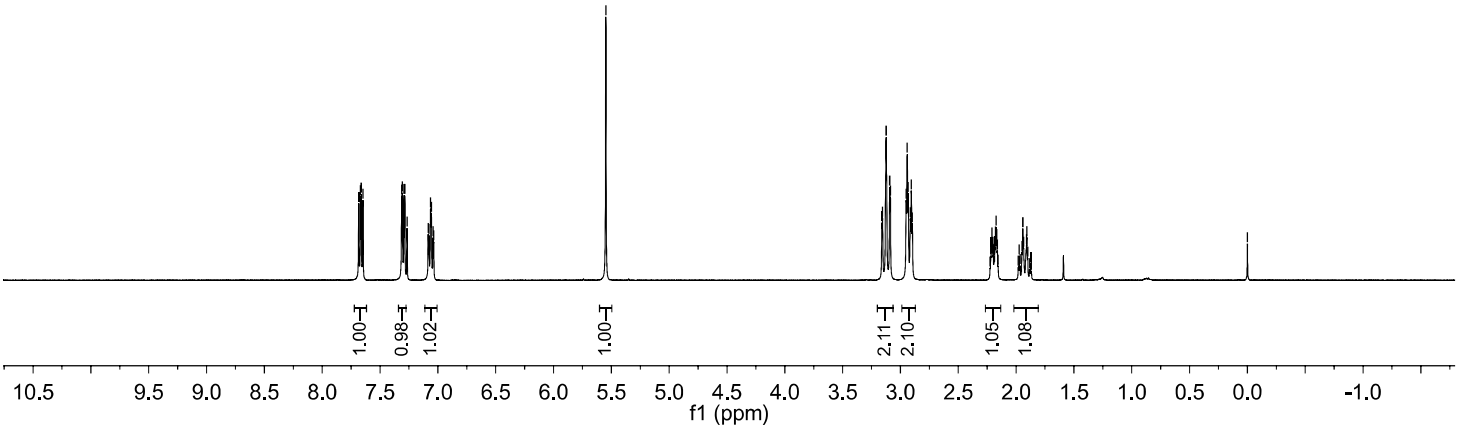
3p

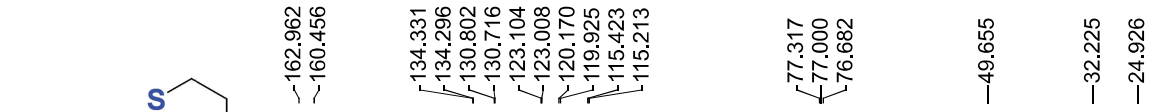

159.366
138.994
133.322
116.078
114.827
113.117
77.318
77.000
76.683
55.509
50.843
32.204
25.044
MeO
S
S
Br
f1 (ppm)

3p

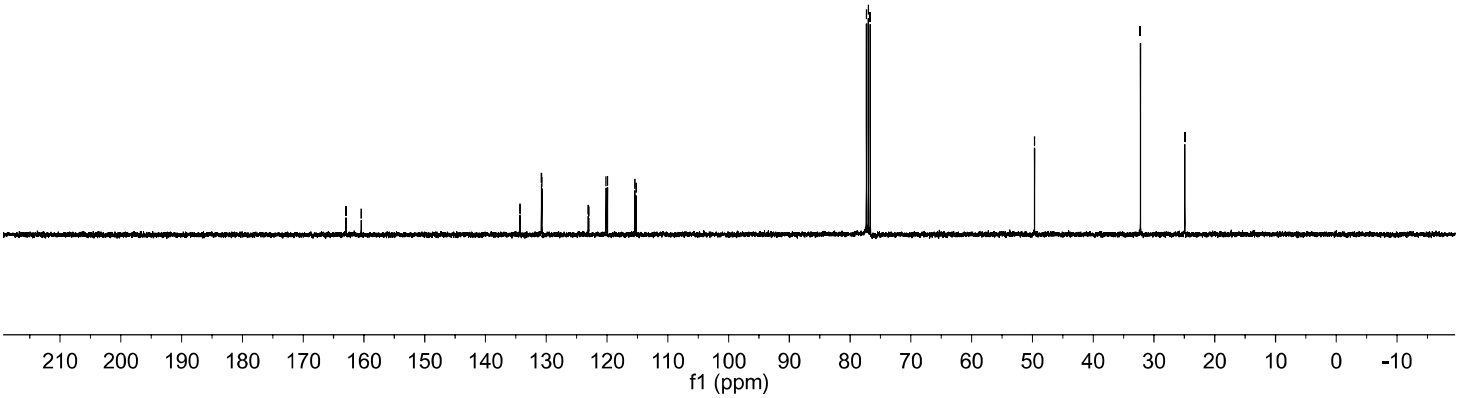

7.684
7.669
7.662
7.647
7.313
7.307
7.293
7.286
7.266
7.083
7.077
7.063
7.057
7.042
7.036
5.547
3.160
3.155
3.124
3.093
3.087
2.951
2.941
2.933
2.915
2.907
2.897
2.213
2.208
2.202
2.183
2.178
2.172
2.167
1.942
1.935
1.910
1.907
0.000
S
S
F
Br

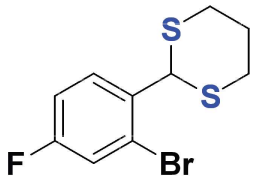
3q


1.00
0.98
1.02
1.00
2.11
2.10
1.05
1.08
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)


162.962
160.456
134.331
134.296
130.802
130.716
123.104
123.008
120.170
119.925
115.423
115.213
77.317
77.000
76.682
49.655
32.225
24.926
S
S
F
Br

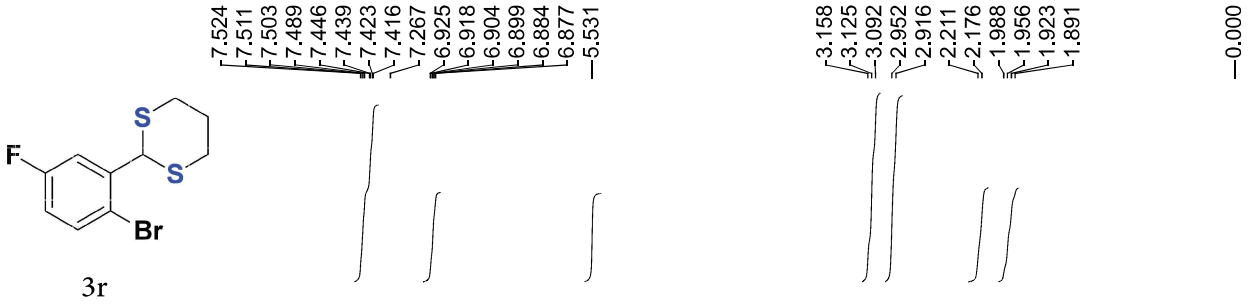
3q


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

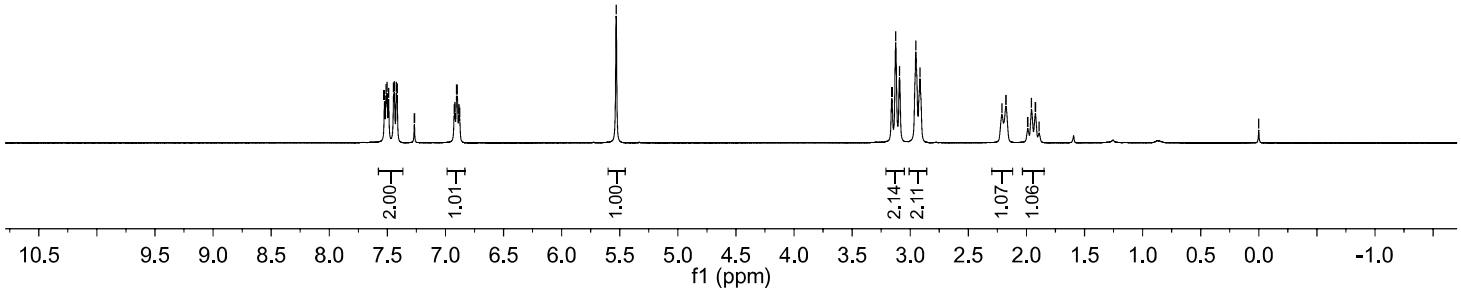

S
S
F
Br

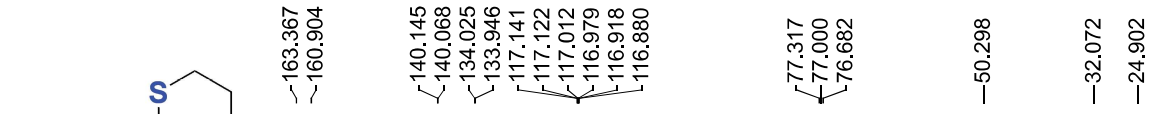
3q

-110.979
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

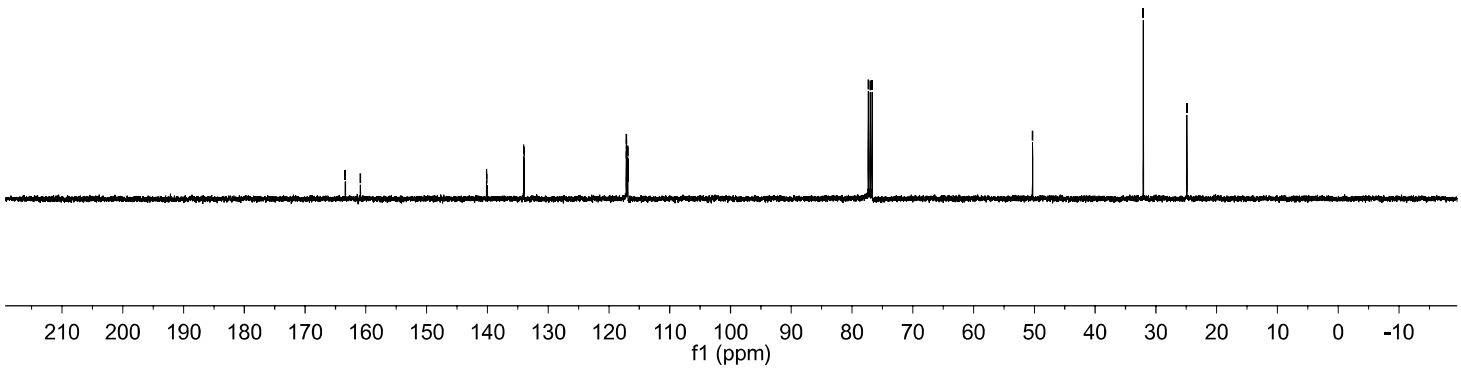

7.524
7.511
7.503
7.489
7.446
7.439
7.423
7.416
7.267
6.925
6.918
6.904
6.899
6.884
6.877
5.531
3.158
3.125
3.092
2.952
2.916
2.211
2.176
1.988
1.956
1.923
1.891
0.000
S
S
F
Br

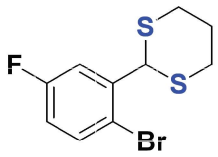
3r


2.00
1.01
1.00
2.14
2.11
1.07
1.06
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)


163.367
160.904
140.145
140.068
134.025
133.946
117.141
117.122
117.012
116.979
116.918
116.880
77.317
77.000
76.682
50.298
32.072
24.902
S
S
F
Br

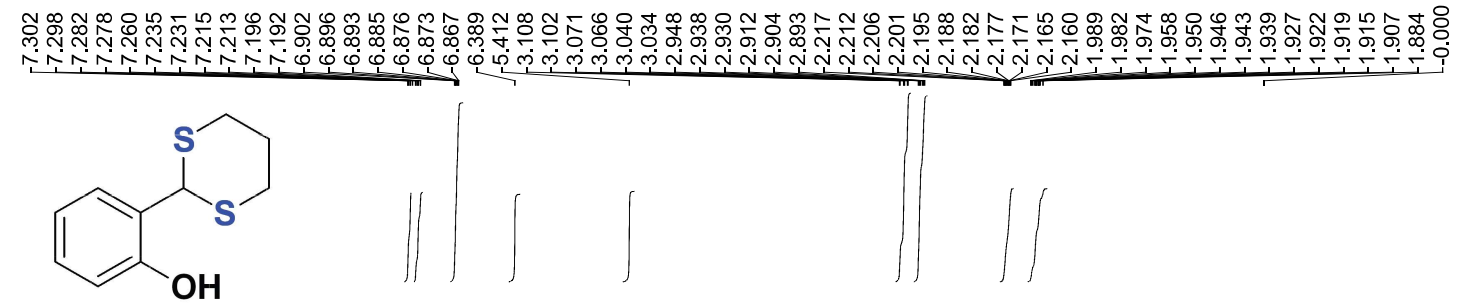
3r


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

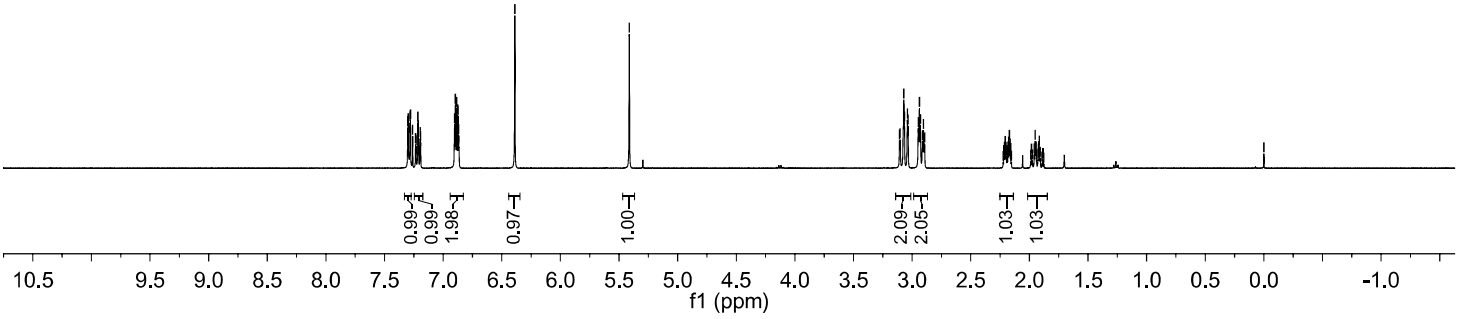

S
F
S
Br

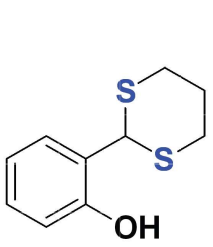
3r

-113.137
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)


7.302
7.298
7.282
7.278
7.260
7.235
7.231
7.215
7.213
7.196
7.192
6.902
6.896
6.893
6.885
6.876
6.873
6.867
6.389
5.412
3.108
3.102
3.071
3.066
3.040
3.034
2.948
2.938
2.930
2.912
2.904
2.893
2.217
2.212
2.206
2.201
2.195
2.188
2.182
2.177
2.171
2.165
2.160
1.989
1.982
1.974
1.958
1.950
1.946
1.943
1.939
1.927
1.922
1.919
1.915
1.907
1.884
0.000
S
S
OH

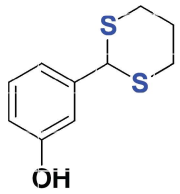
3s


0.99
0.99
1.98
0.97
1.00
2.09
2.05
1.03
1.03
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

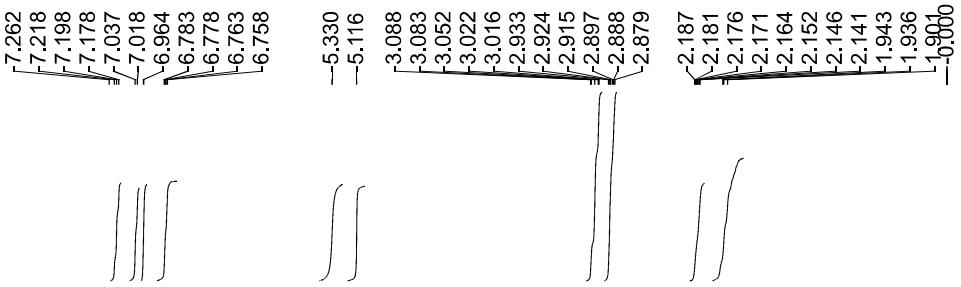

S
S
OH

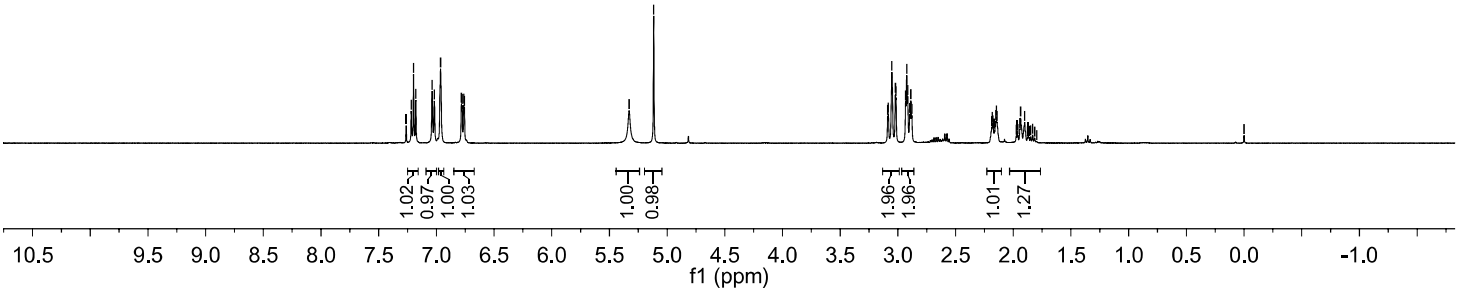
3s

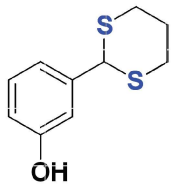
154.418
130.120
129.102
123.453
120.751
117.285
77.317
77.000
76.682
47.344
31.560
24.776
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


S
S
OH

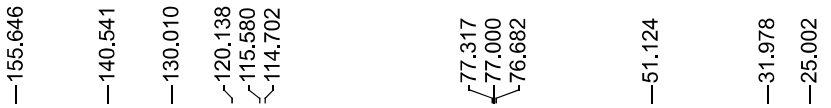
3t

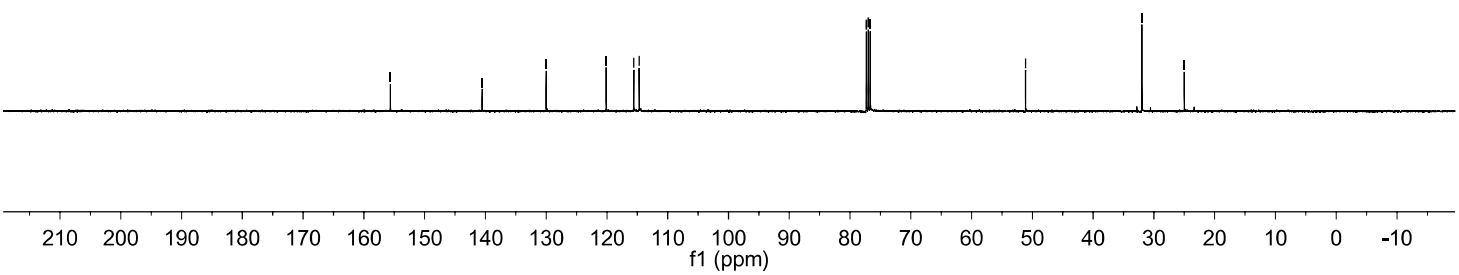

7.262
7.218
7.198
7.178
7.037
7.018
6.964
6.783
6.778
6.763
6.758
5.330
5.116
3.088
3.083
3.052
3.022
3.016
2.933
2.924
2.915
2.897
2.888
2.879
2.187
2.181
2.176
2.171
2.164
2.152
2.146
2.141
1.943
1.936
1.901
0.000

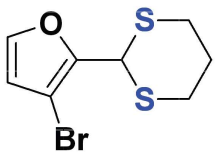

1.02
0.97
1.00
1.03
1.00
0.98
1.96
1.96
1.01
1.27
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)


S
S
OH

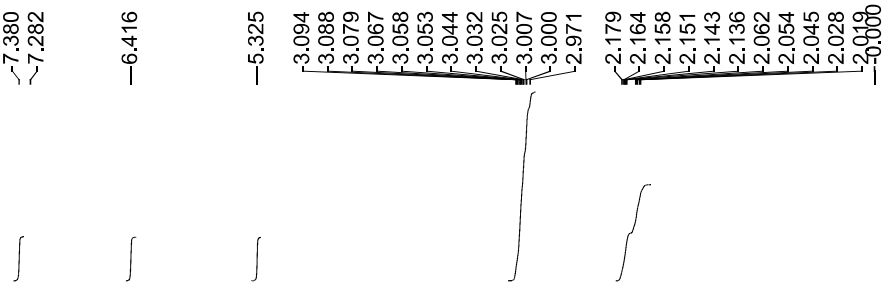
3t

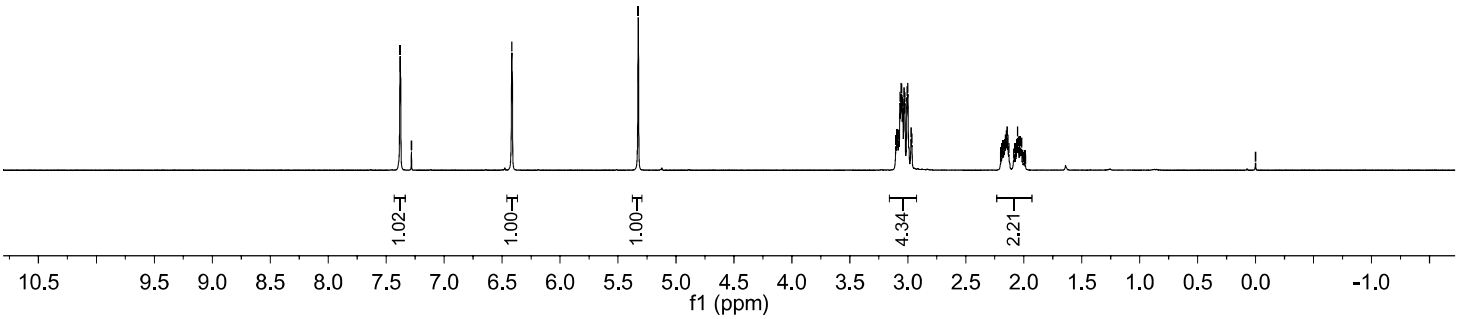

155.646
140.541
130.010
120.138
115.580
114.702
77.317
77.000
76.682
51.124
31.978
25.002

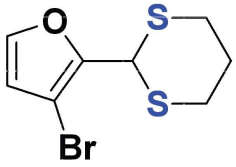

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
S
S
Br

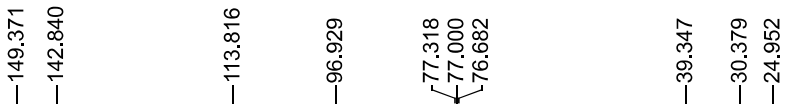
3u

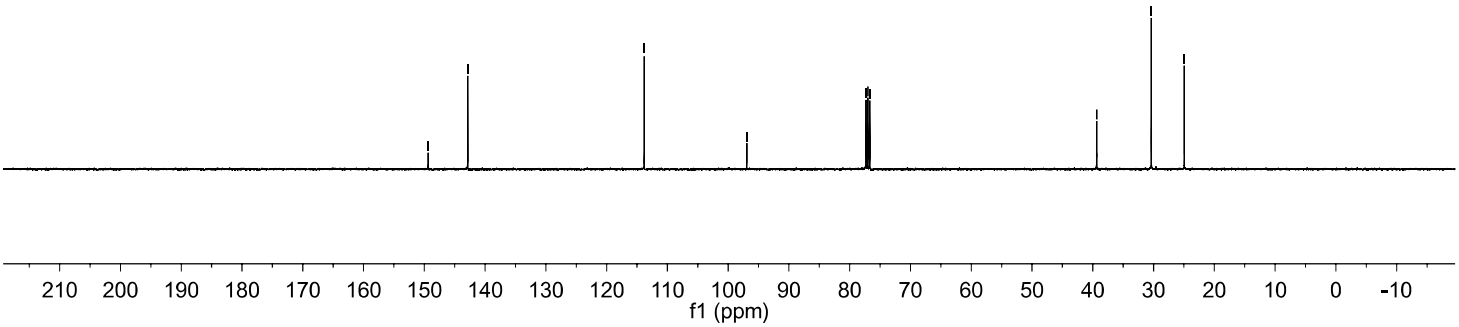

7.380
7.282
6.416
5.325
3.094
3.088
3.079
3.067
3.058
3.053
3.044
3.032
3.025
3.007
3.000
2.971
2.179
2.164
2.158
2.151
2.143
2.136
2.062
2.054
2.045
2.028
2.019
0.000

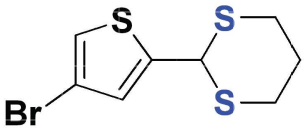

1.02
1.00
1.00
4.34
2.21
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)


O
S
S
Br

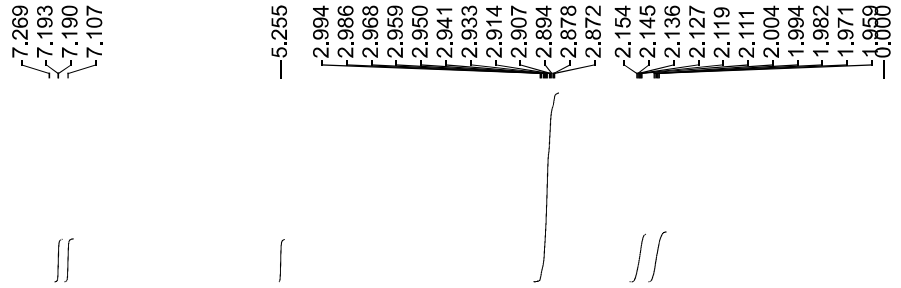
3u

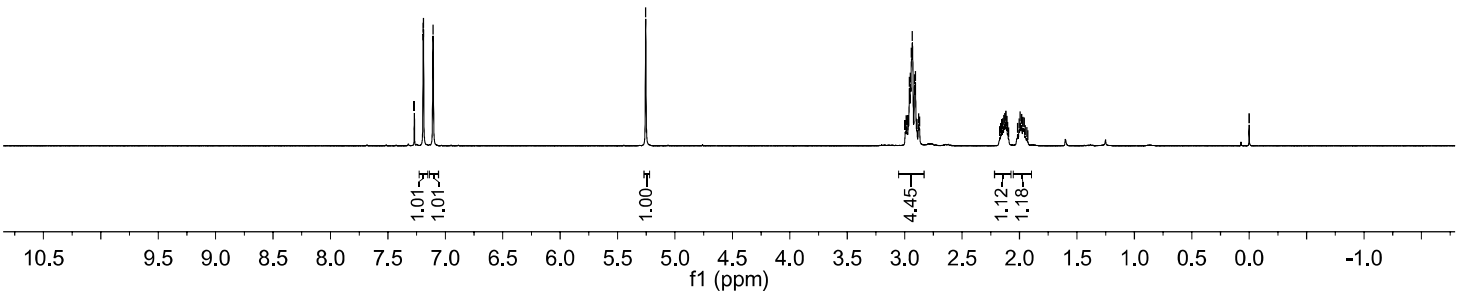

149.371
142.840
113.816
96.929
77.318
77.000
76.682
39.347
30.379
24.952

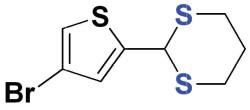

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


S
S
S
Br

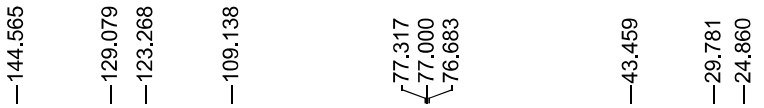
3v

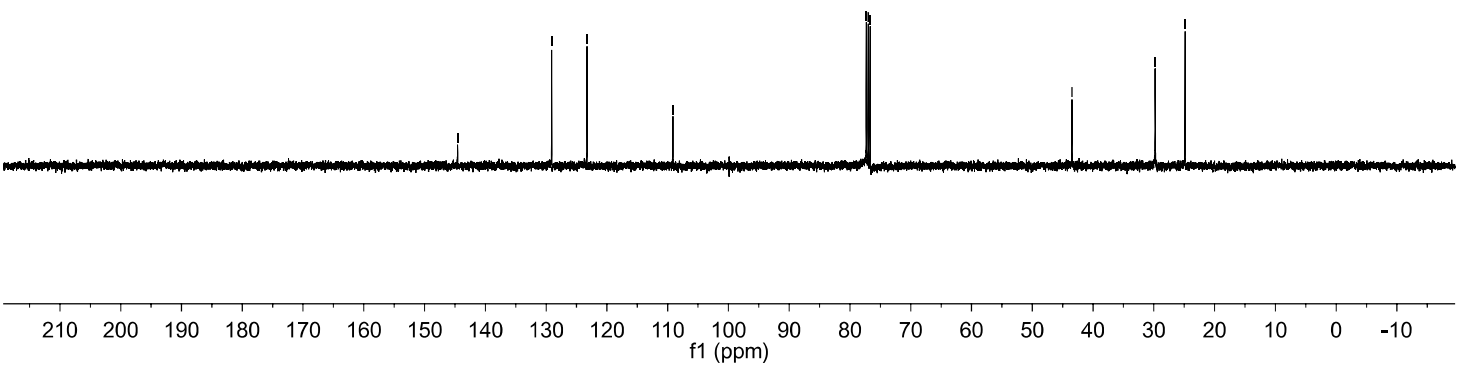

7.269
7.193
7.190
7.107
5.255
2.994
2.986
2.968
2.959
2.950
2.941
2.933
2.914
2.907
2.894
2.878
2.872
2.154
2.145
2.136
2.127
2.119
2.111
2.004
1.994
1.982
1.971
1.959
0.000

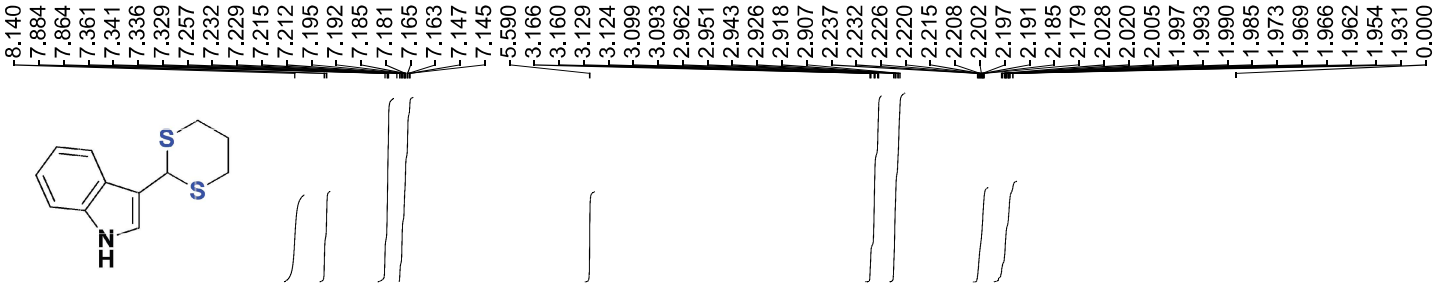

1.01
1.01
1.00
4.45
1.12
1.18
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)


S
S
S
Br

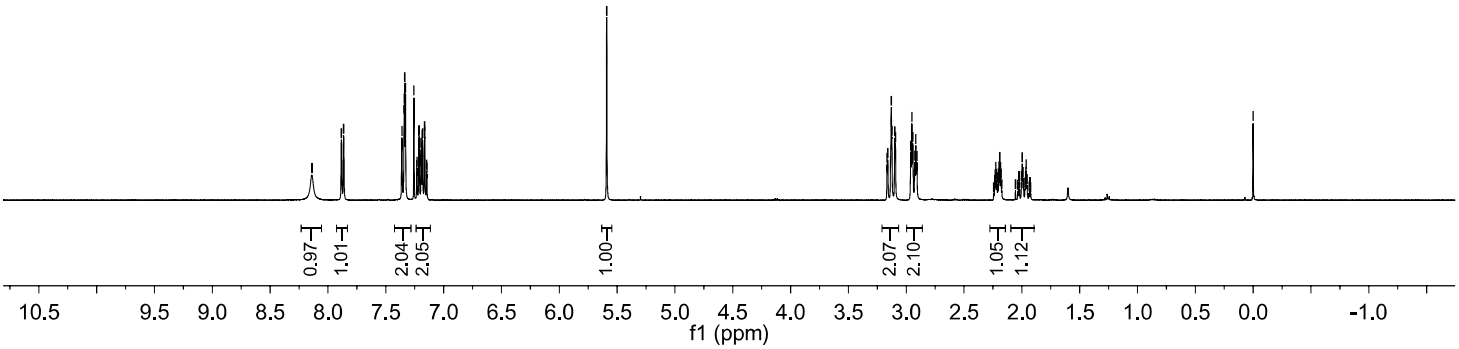
3v

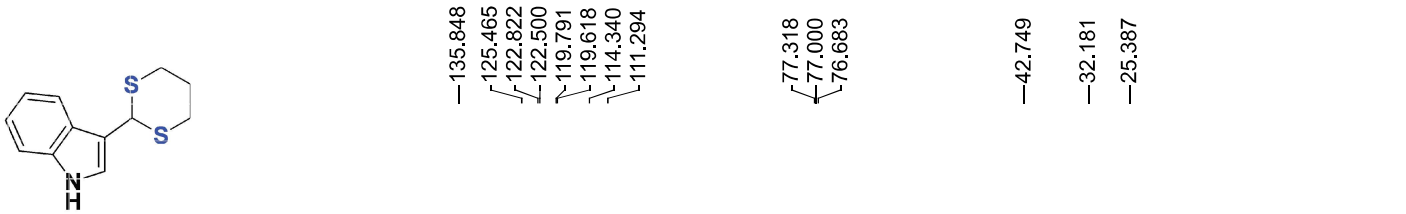

144.565
129.079
123.268
109.138
77.317
77.000
76.683
43.459
29.781
24.860


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

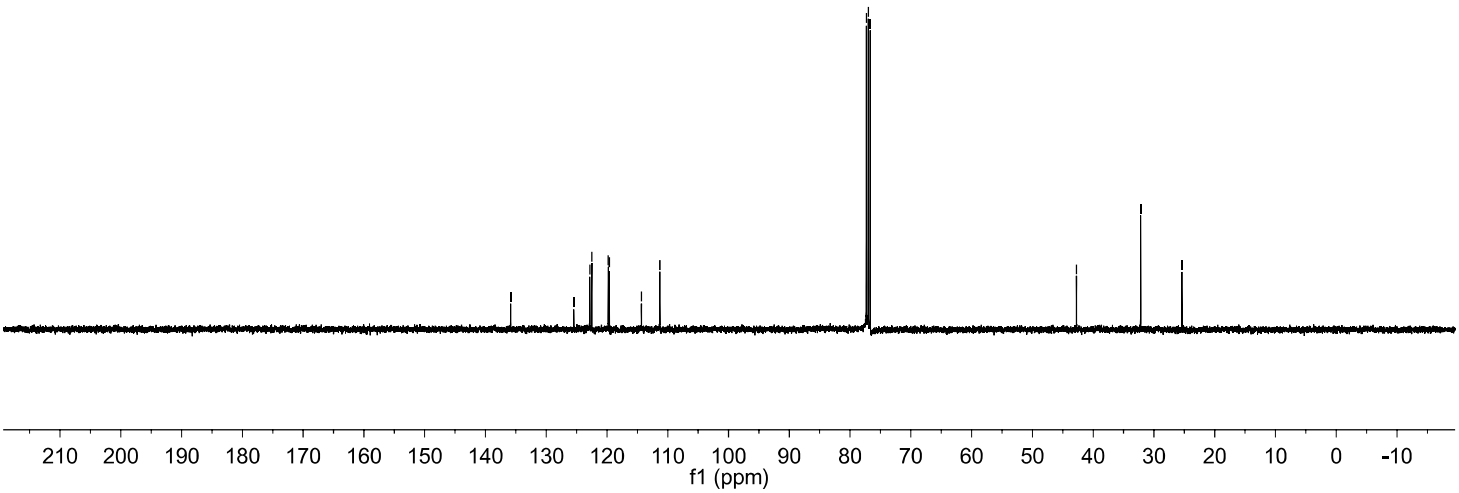

8.140
7.884
7.864
7.361
7.341
7.336
7.329
7.257
7.232
7.229
7.215
7.212
7.195
7.192
7.185
7.181
7.165
7.163
7.147
7.145
5.590
3.166
3.160
3.129
3.124
3.099
3.093
2.962
2.951
2.943
2.926
2.918
2.907
2.237
2.232
2.226
2.220
2.215
2.208
2.202
2.197
2.191
2.185
2.179
2.028
2.020
2.005
1.997
1.993
1.990
1.985
1.973
1.969
1.966
1.962
1.954
1.931
0.000
S
S
N
H

3w

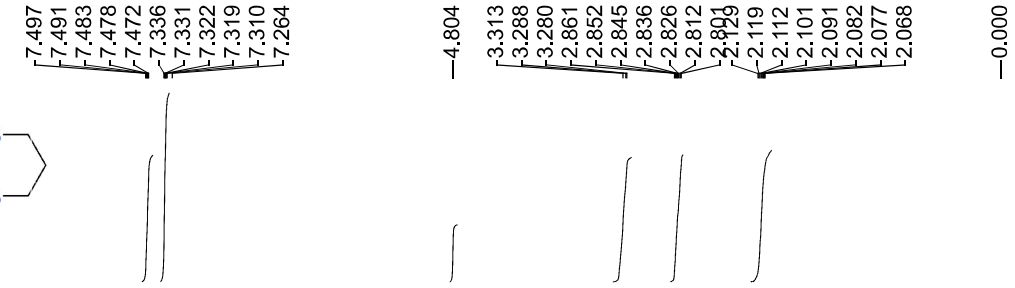

0.97
1.01
2.04
2.05
1.00
2.07
2.10
1.05
1.12
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

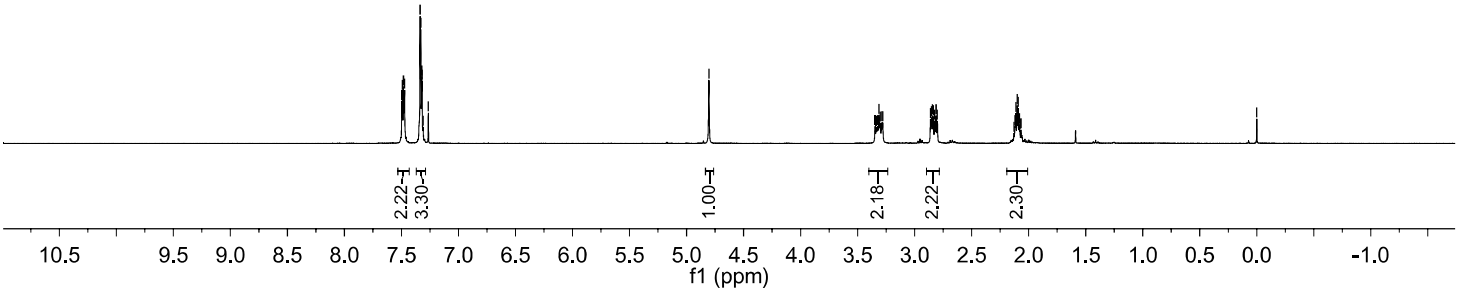

135.848
125.465
122.822
122.500
119.791
119.618
114.340
111.294
77.318
77.000
76.683
42.749
32.181
25.387
S
S
N
H

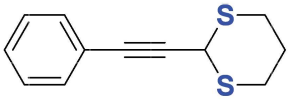
3w


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

5a

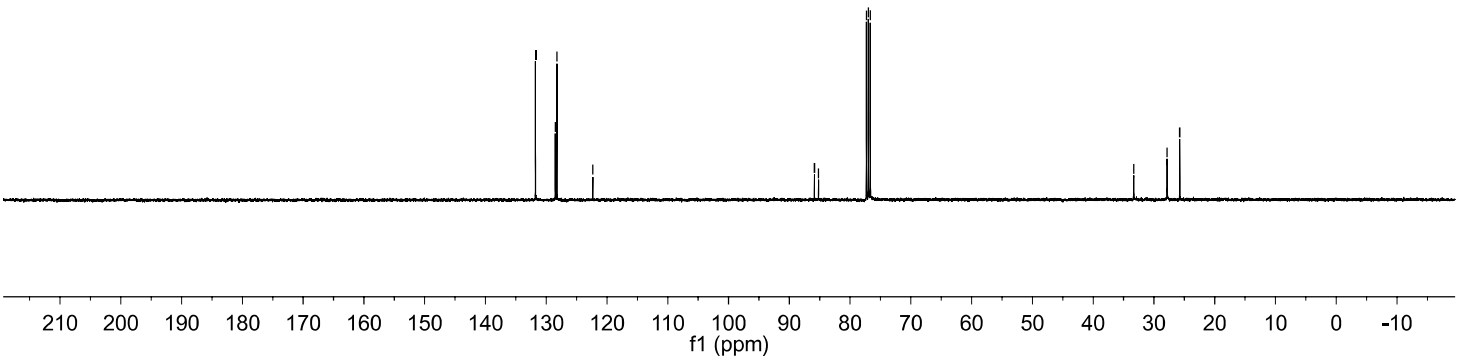

7.497
7.491
7.483
7.478
7.472
7.336
7.331
7.322
7.319
7.310
7.264
4.804
3.313
3.288
3.280
2.861
2.852
2.845
2.836
2.826
2.812
2.801
2.129
2.119
2.112
2.101
2.091
2.082
2.077
2.068
0.000

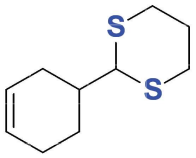

2.22
3.30
1.00
2.18
2.22
2.30
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)



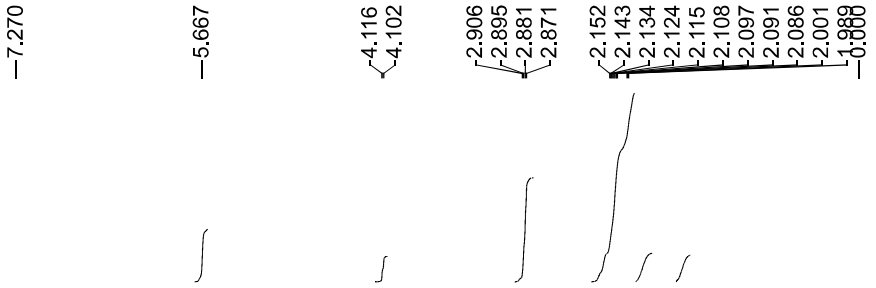
5a

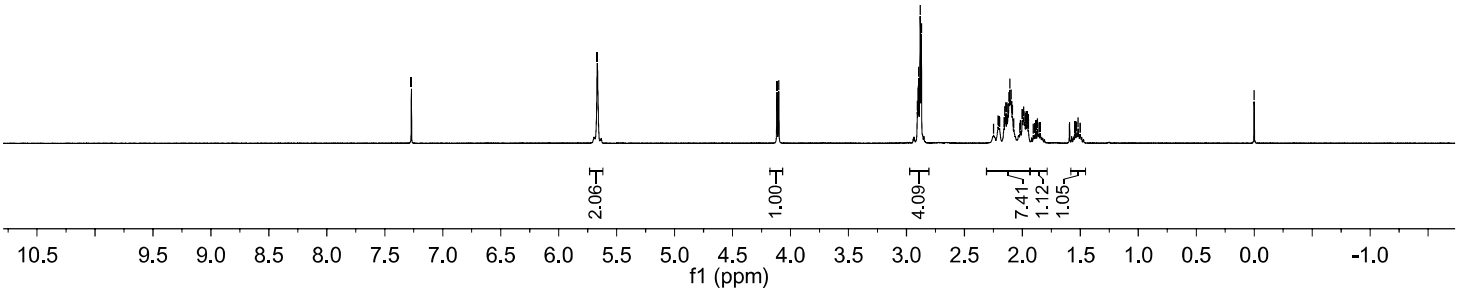

131.782
128.511
128.231
122.335
85.870
85.191
77.318
77.000
76.682
33.324
27.845
25.756

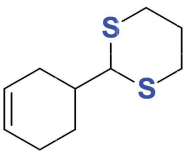

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



5b

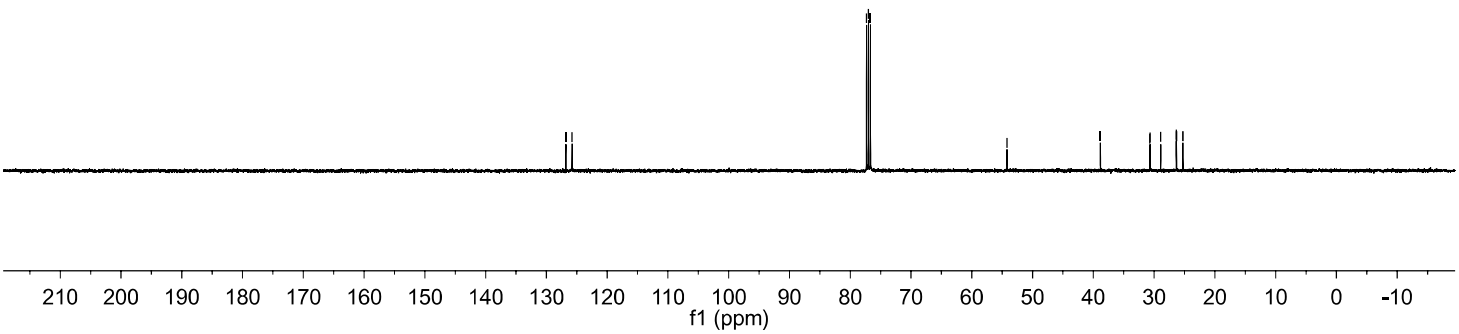

7.270
5.667
4.116
4.102
2.906
2.895
2.881
2.871
2.152
2.143
2.134
2.124
2.115
2.108
2.097
2.091
2.086
2.001
1.989
0.000

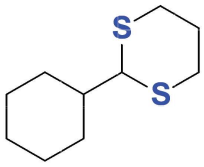

2.06
1.00
4.09
7.41
1.12
1.05
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)



5b

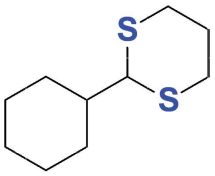

126.795
125.774
77.317
77.000
76.682
54.208
38.838
30.725
30.667
28.913
26.352
26.309
25.263


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



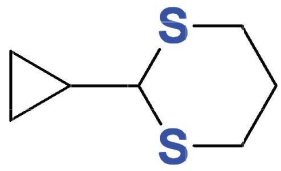
5c

7.281
4.057
4.044
2.896
2.889
2.880
2.869
2.862
2.834
1.897
1.886
1.881
1.768
1.754
1.665
1.276
1.247
1.226
1.220
0.000
1.00
4.14
1.06
7.65
5.41
f1 (ppm)



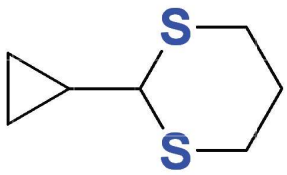
5c

77.318
77.000
76.682
55.306
43.021
30.899
30.344
26.364
26.165
26.094
f1 (ppm)



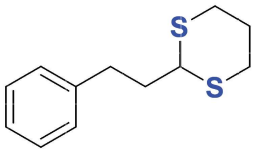
5d

7.280
3.411
3.386
2.839
2.822
2.814
2.128
2.092
1.871
1.859
0.694
0.691
0.674
0.475
0.462
0.450
0.000
1.00
4.21
1.05
1.08
0.98
2.05
2.05
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

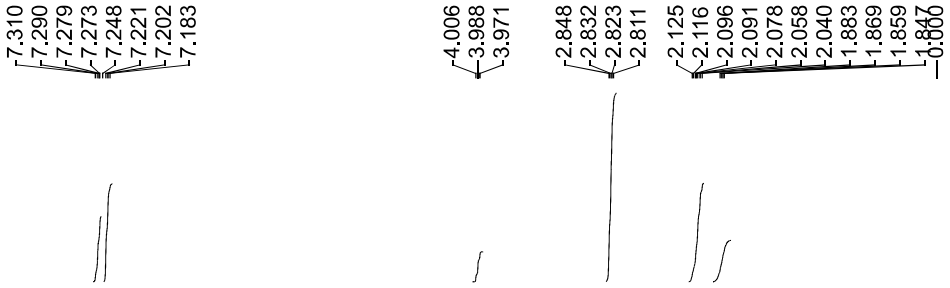


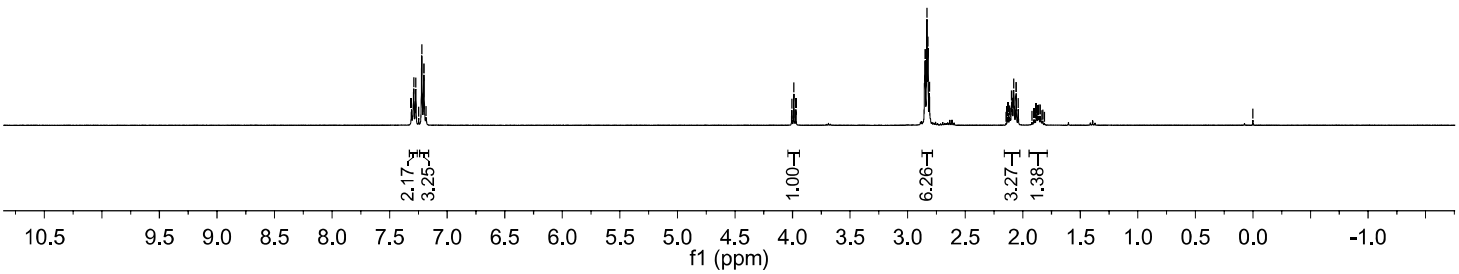
5d

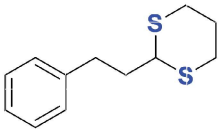
77.318
77.000
76.683
52.177
30.649
25.829
15.831
5.659
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



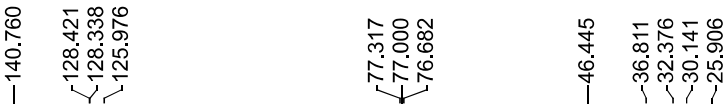
5e

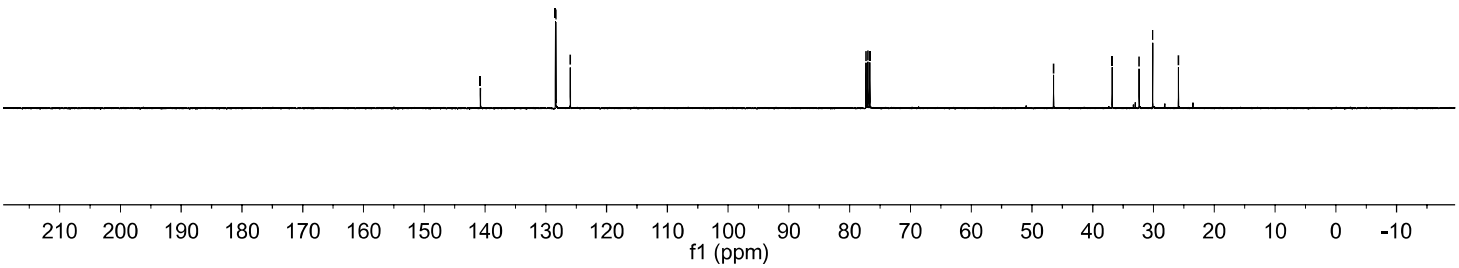

7.310
7.290
7.279
7.273
7.248
7.221
7.202
7.183
4.006
3.988
3.971
2.848
2.832
2.823
2.811
2.125
2.116
2.096
2.091
2.078
2.058
2.040
1.883
1.869
1.859
1.847
0.000

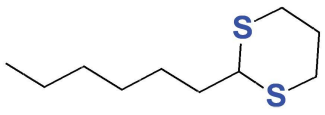

2.17
3.25
1.00
6.26
3.27
1.38
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)



5e

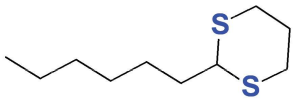

140.760
128.421
128.338
125.976
77.317
77.000
76.682
46.445
36.811
32.376
30.141
25.906


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



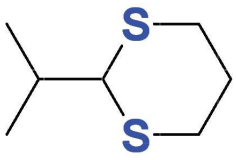
5f

7.291
4.064
4.047
4.030
2.882
2.854
2.846
2.835
2.825
1.751
1.731
1.713
1.498
1.479
1.325
1.307
1.285
0.896
0.880
0.863
0.000
1.00
4.04
1.01
1.03
2.00
2.03
6.08
3.05
f1 (ppm)



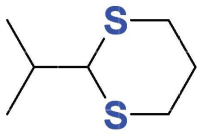
5f

77.318
77.000
76.683
47.584
35.381
31.474
30.413
28.803
26.484
25.991
22.456
13.965
f1 (ppm)



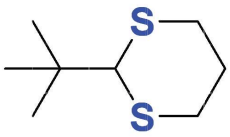
5g

7.292
4.050
4.037
2.894
2.888
2.880
2.869
2.860
2.846
2.126
2.091
2.083
2.047
2.030
1.108
1.092
0.000
1.00
4.13
2.07
1.06
6.24
f1 (ppm)



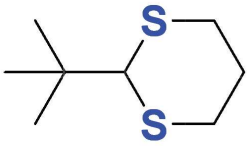
5g

77.318
77.000
76.683
56.244
33.477
30.729
26.210
19.886
f1 (ppm)



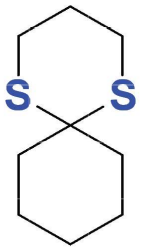
5h

7.293
3.998
2.904
2.897
2.894
2.884
2.876
2.095
2.069
2.060
1.819
1.785
1.117
0.000
1.00
4.11
1.05
1.04
9.38
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0
f1 (ppm)



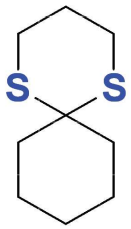
5h

77.318
77.000
76.682
61.892
61.876
35.680
31.210
27.835
25.933
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



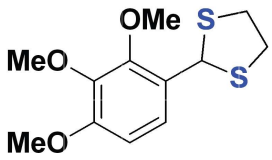
5i

7.286
2.827
2.813
2.798
2.005
1.990
1.984
1.976
1.962
1.641
1.626
1.612
1.597
1.472
1.459
0.000
4.00
5.77
3.96
2.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

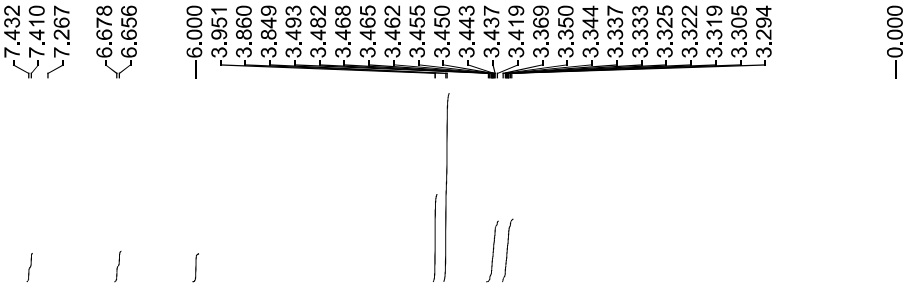


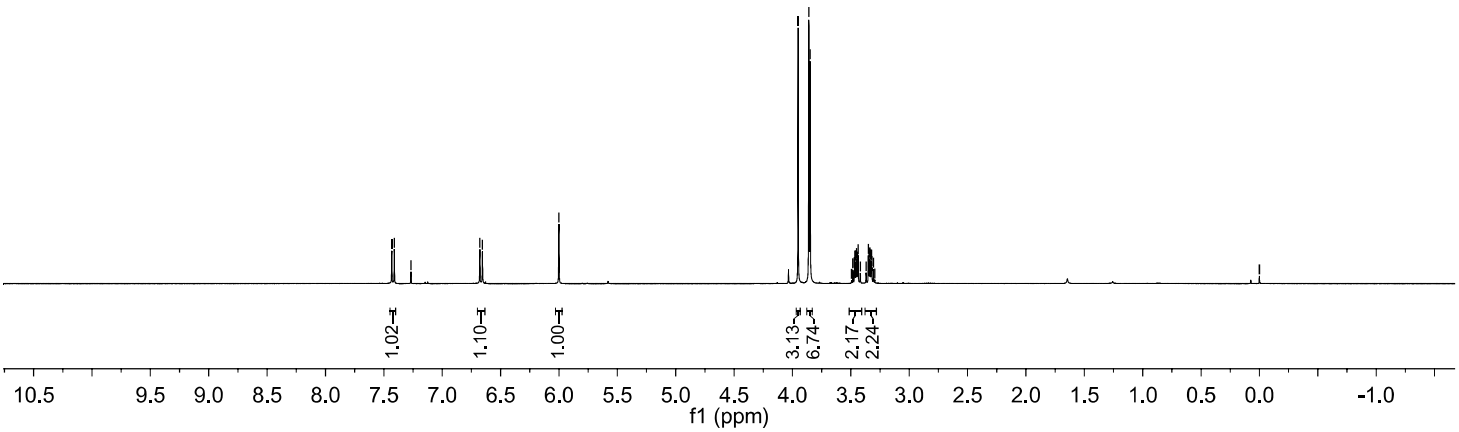
5i

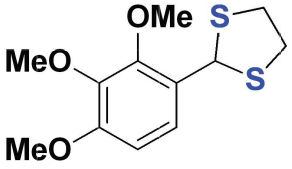
77.317
77.000
76.682
50.281
37.794
26.080
25.828
25.757
21.935
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OMe
S
MeO
S
MeO

7a

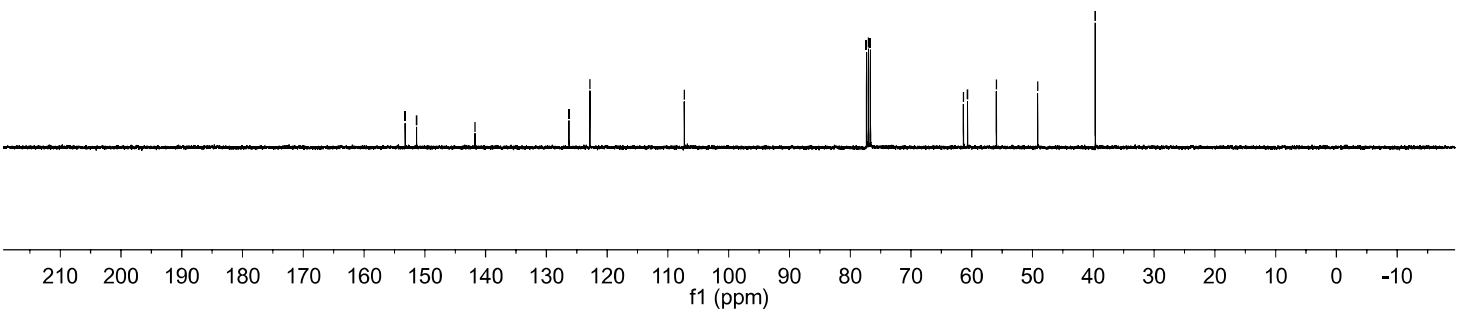

7.432
7.410
7.267
6.678
6.656
6.000
3.951
3.860
3.849
3.493
3.482
3.468
3.465
3.462
3.455
3.450
3.443
3.437
3.419
3.369
3.350
3.344
3.337
3.333
3.325
3.322
3.319
3.305
3.294
0.000

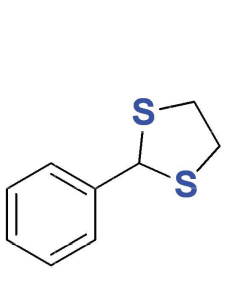

1.02
1.10
1.00
3.13
6.74
2.17
2.24
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)


OMe
S
MeO
S
MeO

7a

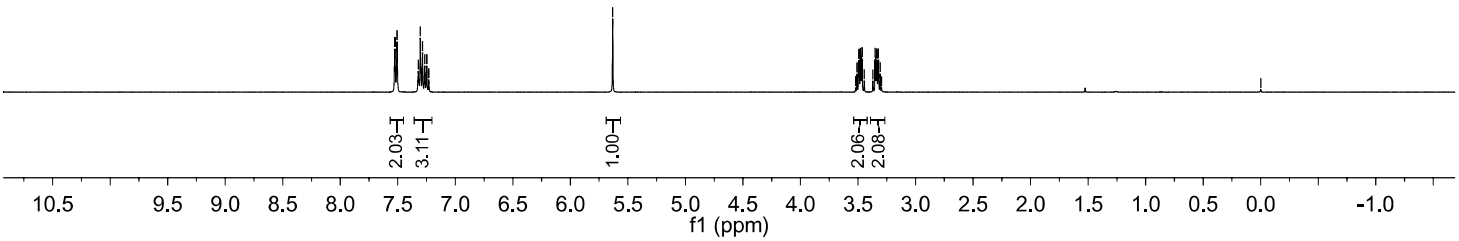

153.225
151.353
141.748
126.281
122.832
107.299
77.318
77.000
76.683
61.379
60.703
55.957
49.162
39.684

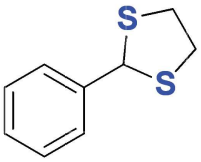

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



7.525
7.507
7.322
7.304
7.286
7.266
7.254
7.248
7.231
5.632
3.521
3.509
3.496
3.492
3.490
3.481
3.478
3.471
3.464
3.446
3.371
3.352
3.346
3.339
3.335
3.325
3.321
3.308
3.295
-0.000

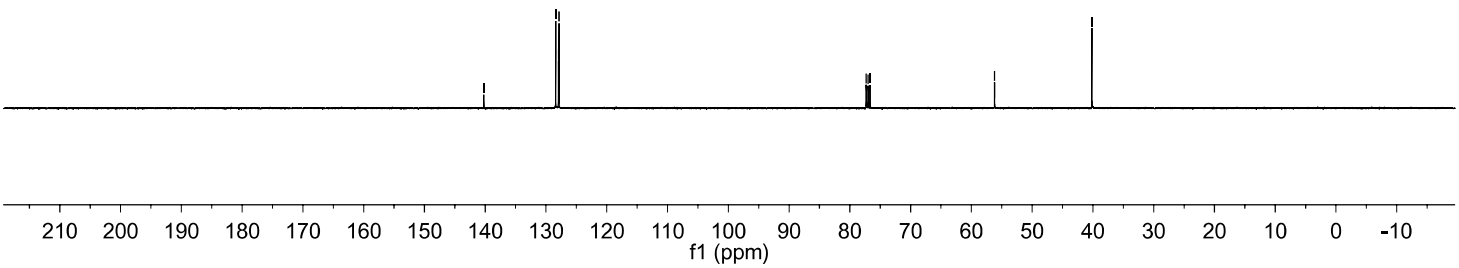
7b

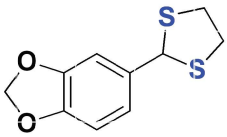




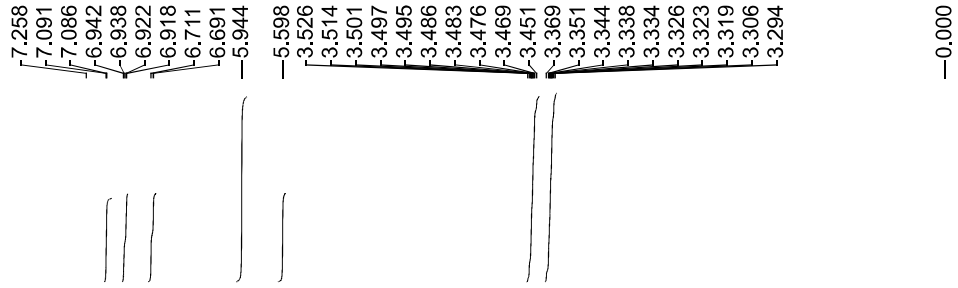
140.228
128.400
127.947
127.859
77.322
77.000
76.687
56.186
40.172

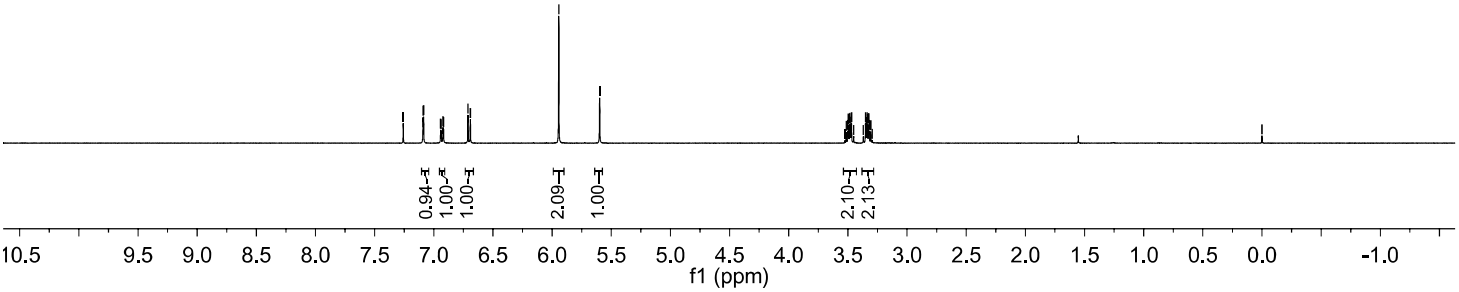
7b

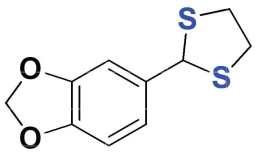




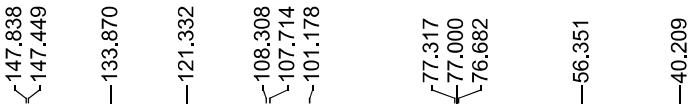
7c

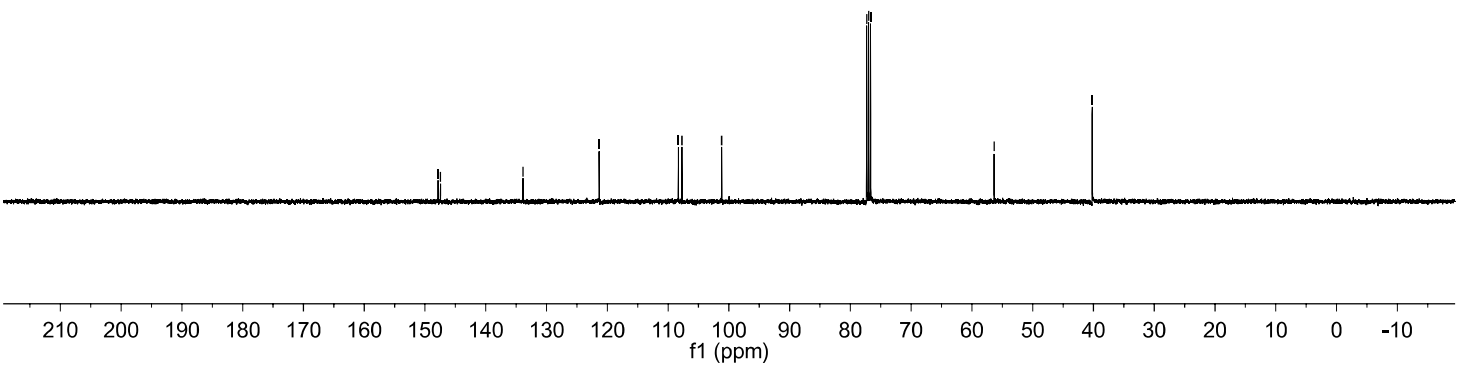

7.258
7.091
7.086
6.942
6.938
6.922
6.918
6.711
6.691
5.944
5.598
3.526
3.514
3.501
3.497
3.495
3.486
3.483
3.476
3.469
3.451
3.369
3.351
3.344
3.338
3.334
3.326
3.323
3.319
3.306
3.294
0.000

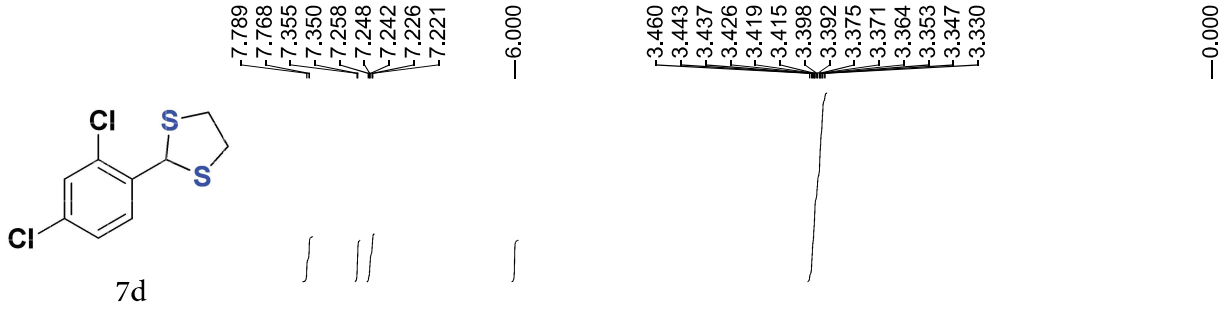

0.94
1.00
1.00
2.09
1.00
2.10
2.13
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)



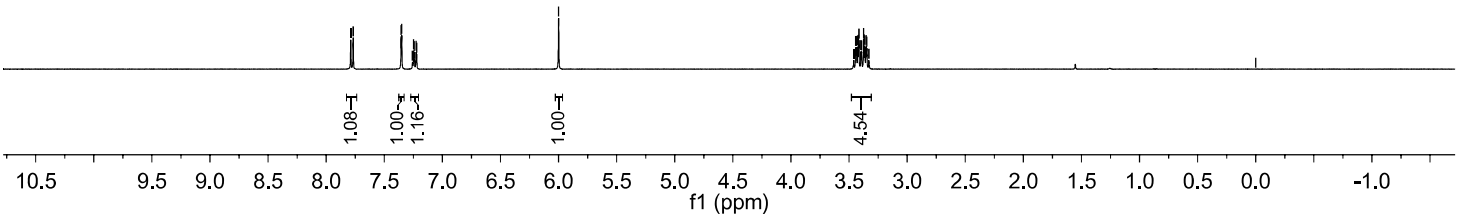
7c

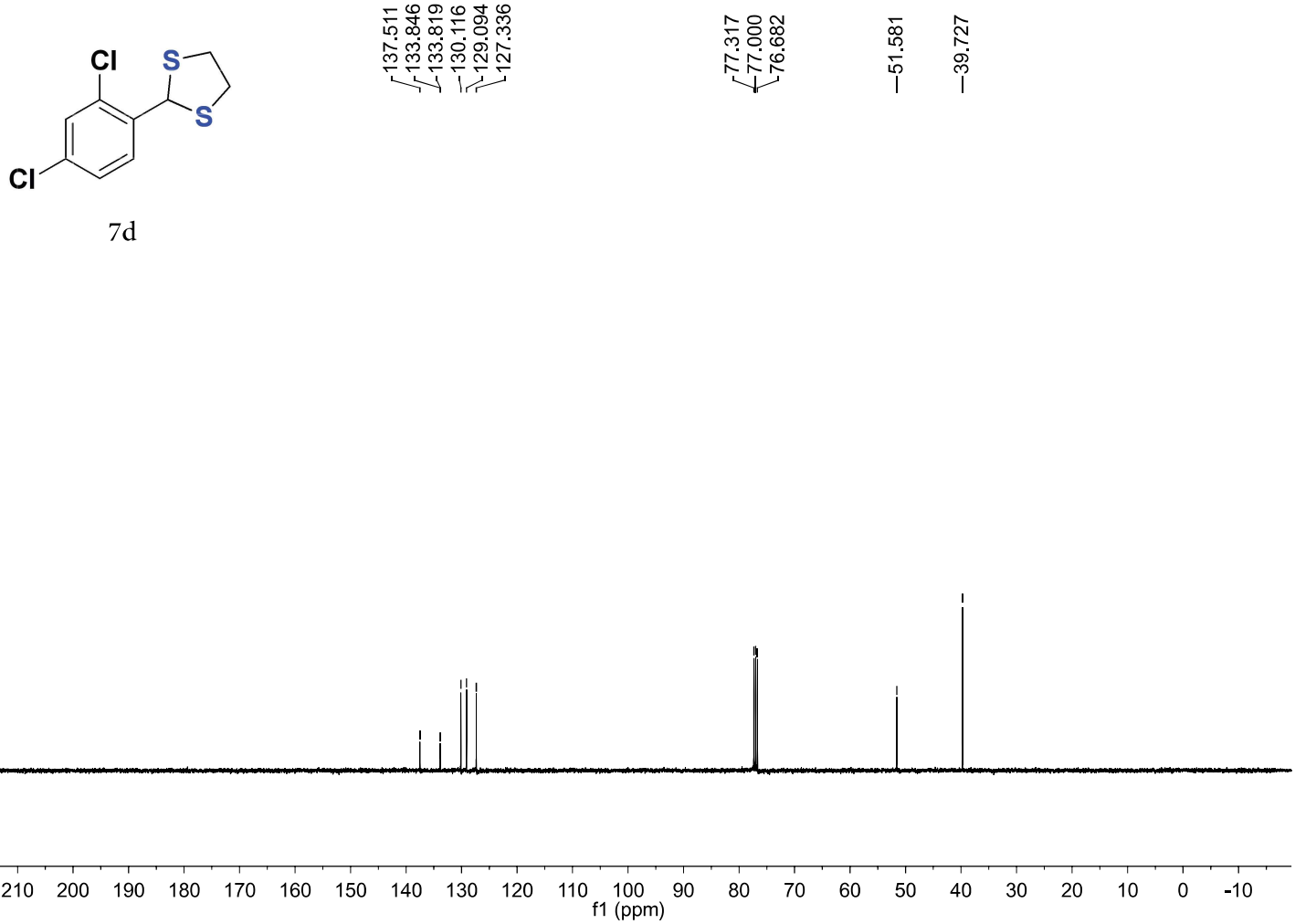

147.838
147.449
133.870
121.332
108.308
107.714
101.178
77.317
77.000
76.682
56.351
40.209


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

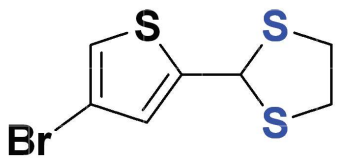

7.789
7.768
7.355
7.350
7.258
7.248
7.242
7.226
7.221
6.000
3.460
3.443
3.437
3.426
3.419
3.415
3.398
3.392
3.375
3.371
3.364
3.353
3.347
3.330
0.000
Cl
S
S
Cl

7d


1.08
1.00
1.16
1.00
4.54
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

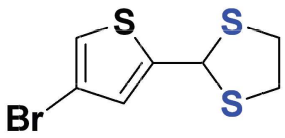

137.511
133.846
133.819
130.116
129.094
127.336
77.317
77.000
76.682
51.581
39.727
Cl
S
S
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

7d


S
S
S
Br

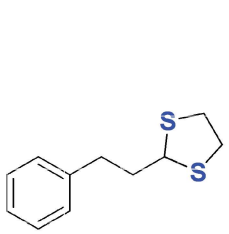
7e

7.259
7.123
7.119
6.985
6.984
5.808
3.480
3.471
3.454
3.450
3.444
3.438
3.431
3.426
3.408
3.378
3.360
3.355
3.348
3.342
3.336
3.332
3.315
3.306
0.000
0.99
1.02
1.00
4.42
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

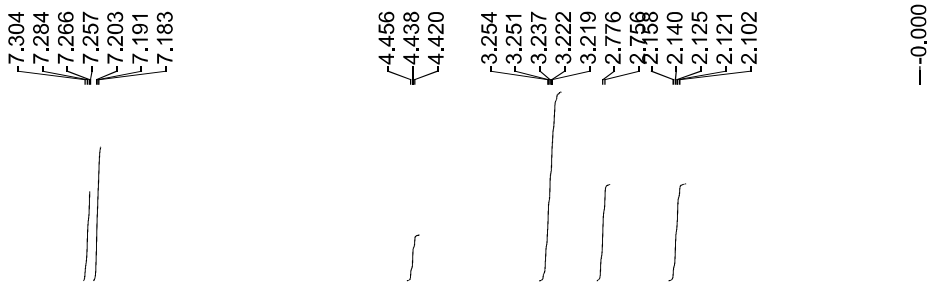

S
S
S
Br

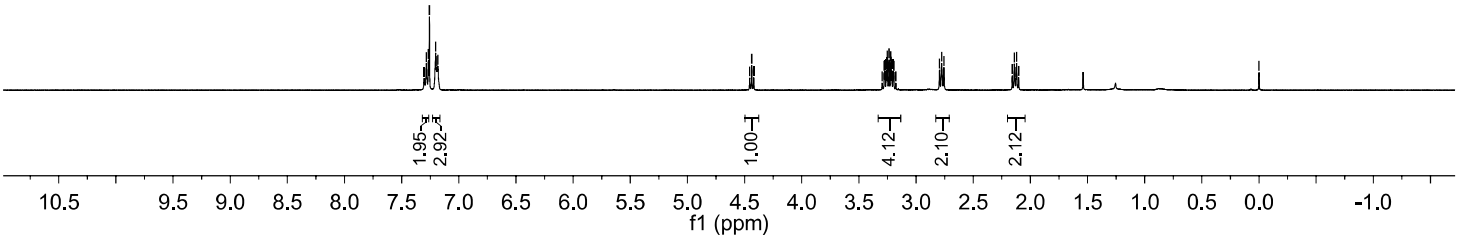
7e

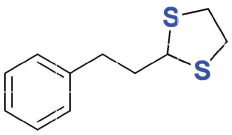
148.851
128.005
122.781
109.043
77.317
77.000
76.682
50.087
39.775
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



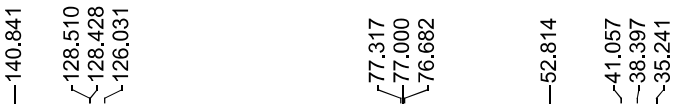
7f

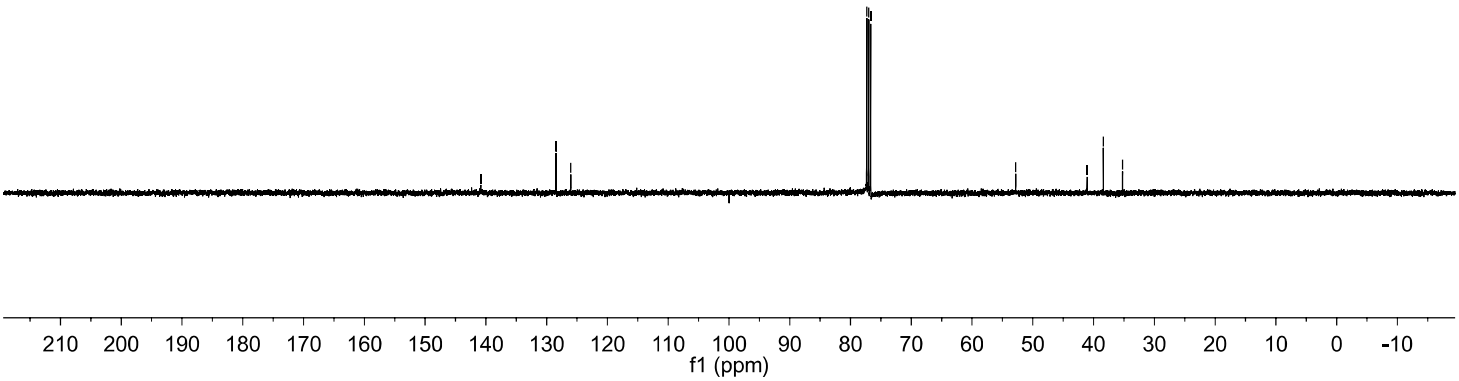

7.304
7.284
7.266
7.257
7.203
7.191
7.183
4.456
4.438
4.420
3.254
3.251
3.237
3.222
3.219
2.776
2.140
2.125
2.121
2.102
0.000

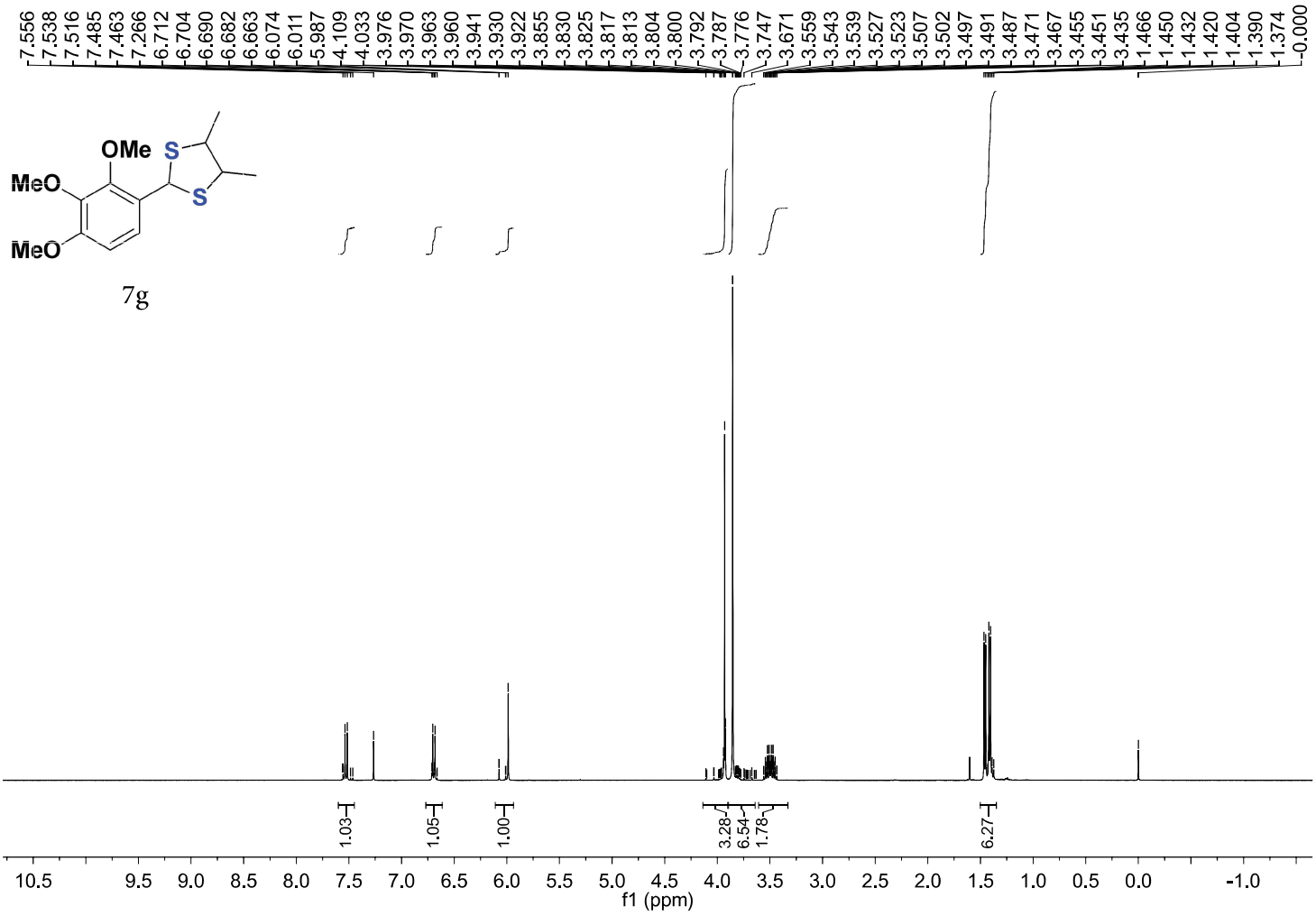

1.95
2.92
1.00
4.12
2.10
2.12
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)



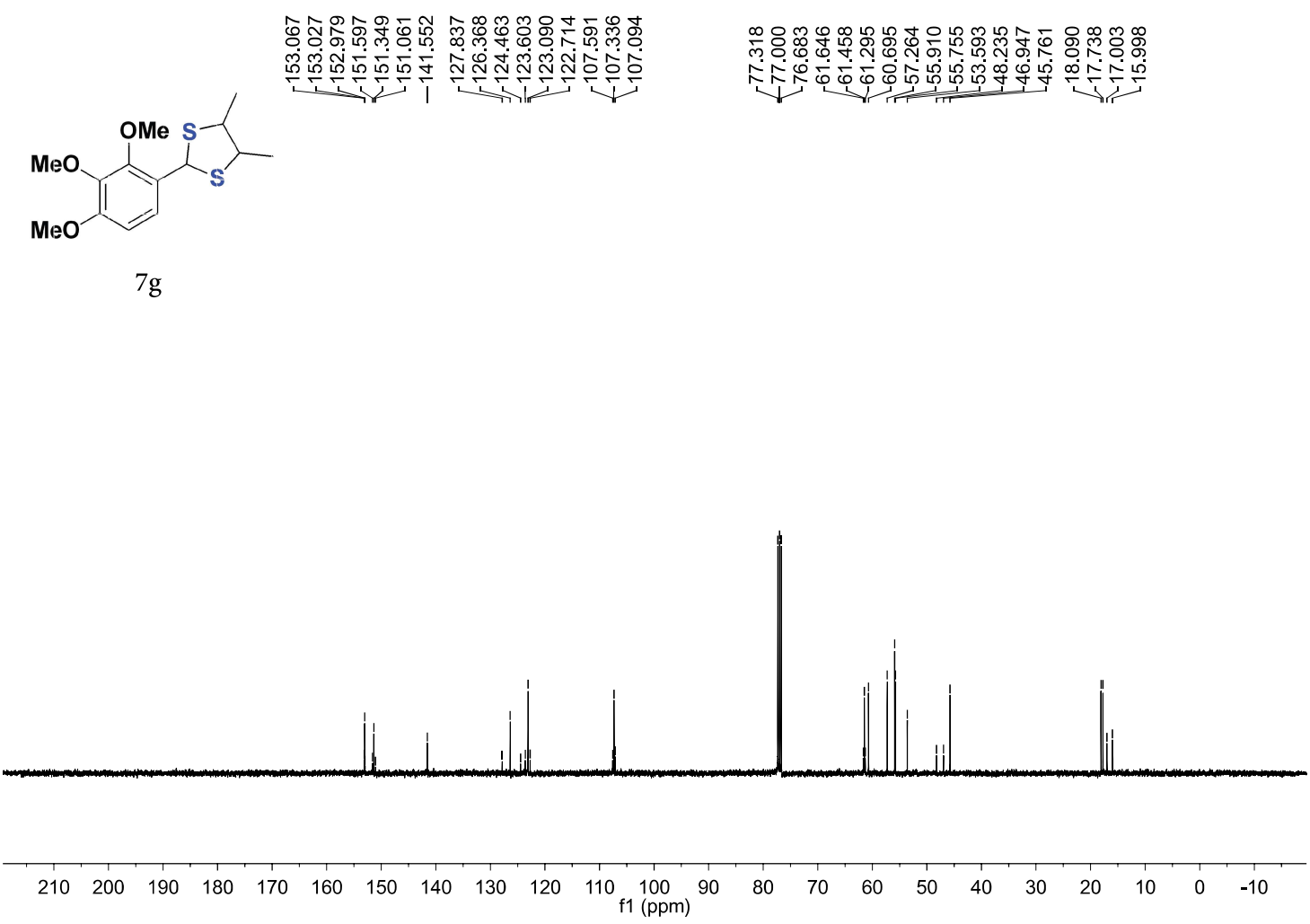
7f


140.841
128.510
128.428
126.031
77.317
77.000
76.682
52.814
41.057
38.397
35.241

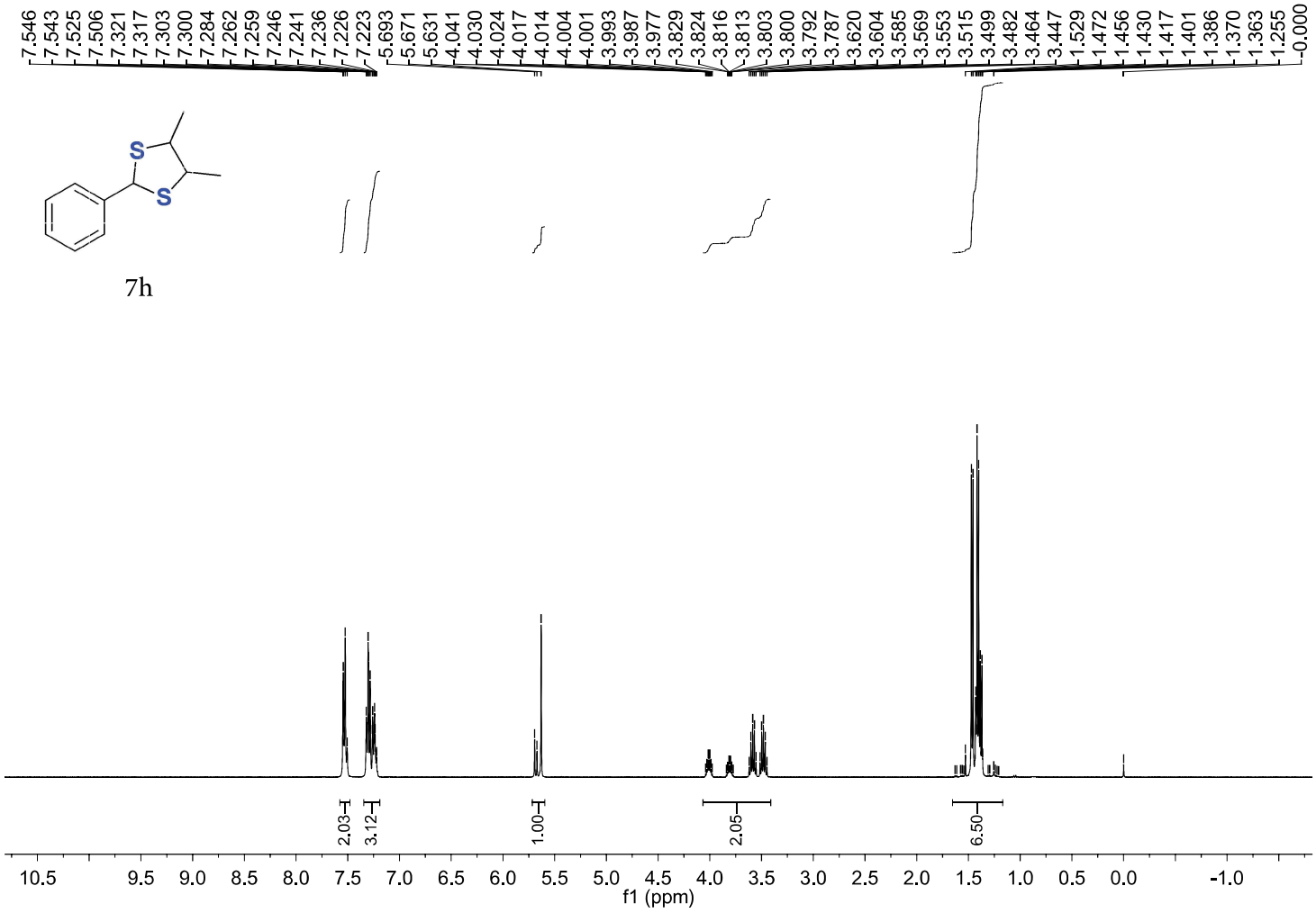

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.556
7.538
7.516
7.485
7.463
7.266
6.712
6.704
6.690
6.682
6.663
6.074
6.011
5.987
4.109
4.033
3.976
3.970
3.963
3.960
3.941
3.930
3.922
3.855
3.830
3.825
3.817
3.813
3.804
3.800
3.792
3.787
3.776
3.747
3.671
3.559
3.543
3.539
3.527
3.523
3.507
3.502
3.497
3.491
3.487
3.471
3.467
3.455
3.451
3.435
1.466
1.450
1.432
1.420
1.404
1.390
1.374
0.000
OMe
S
MeO
S
MeO
1.03
1.05
1.00
3.28
6.54
1.78
6.27
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

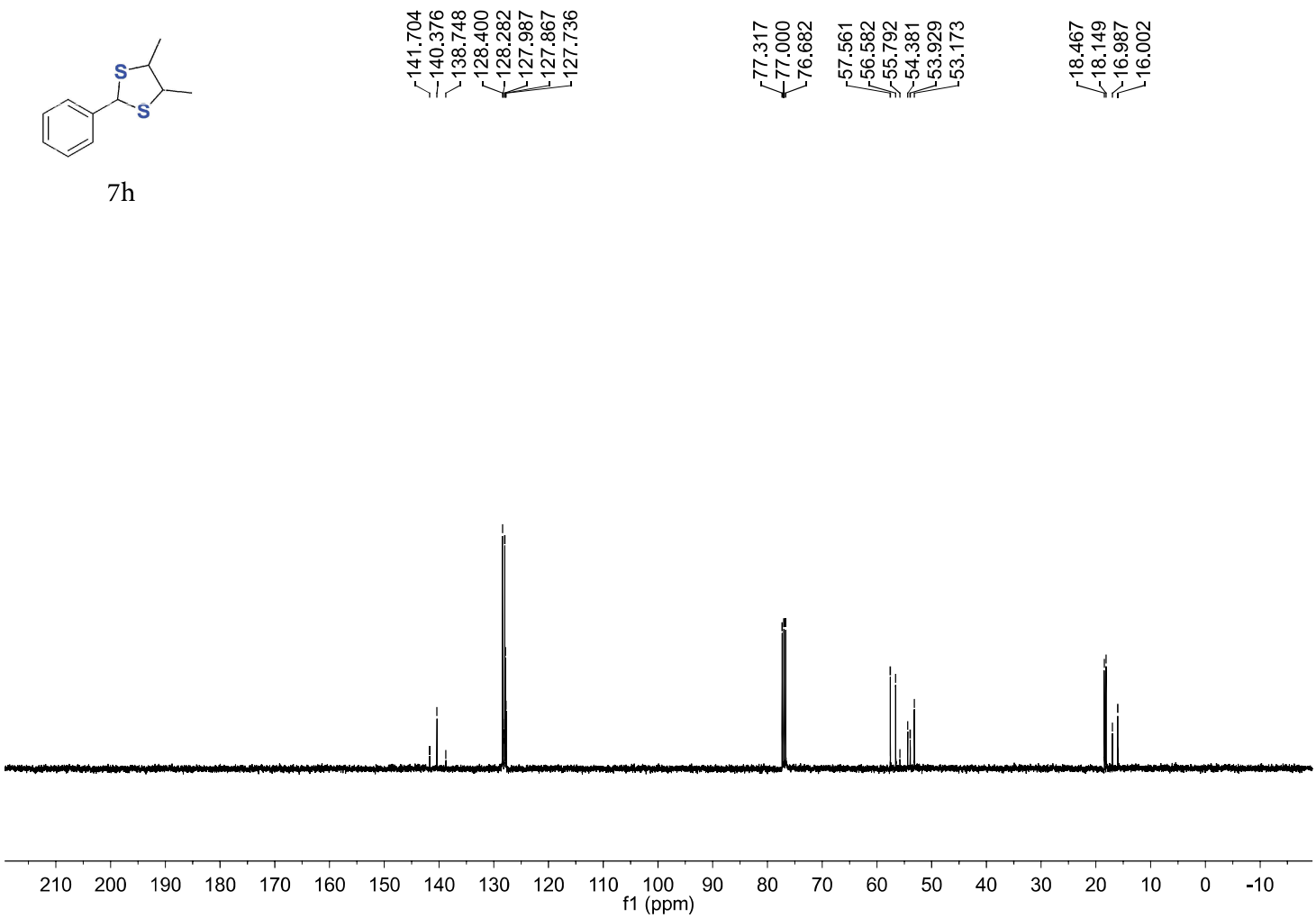
7g


153.067
153.027
152.979
151.597
151.349
151.061
141.552
127.837
126.368
124.463
123.603
123.090
122.714
107.591
107.336
107.094
77.318
77.000
76.683
61.646
61.458
61.295
60.695
57.264
55.910
55.755
53.593
48.235
46.947
45.761
18.090
17.738
17.003
15.998
OMe
S
MeO
S
MeO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

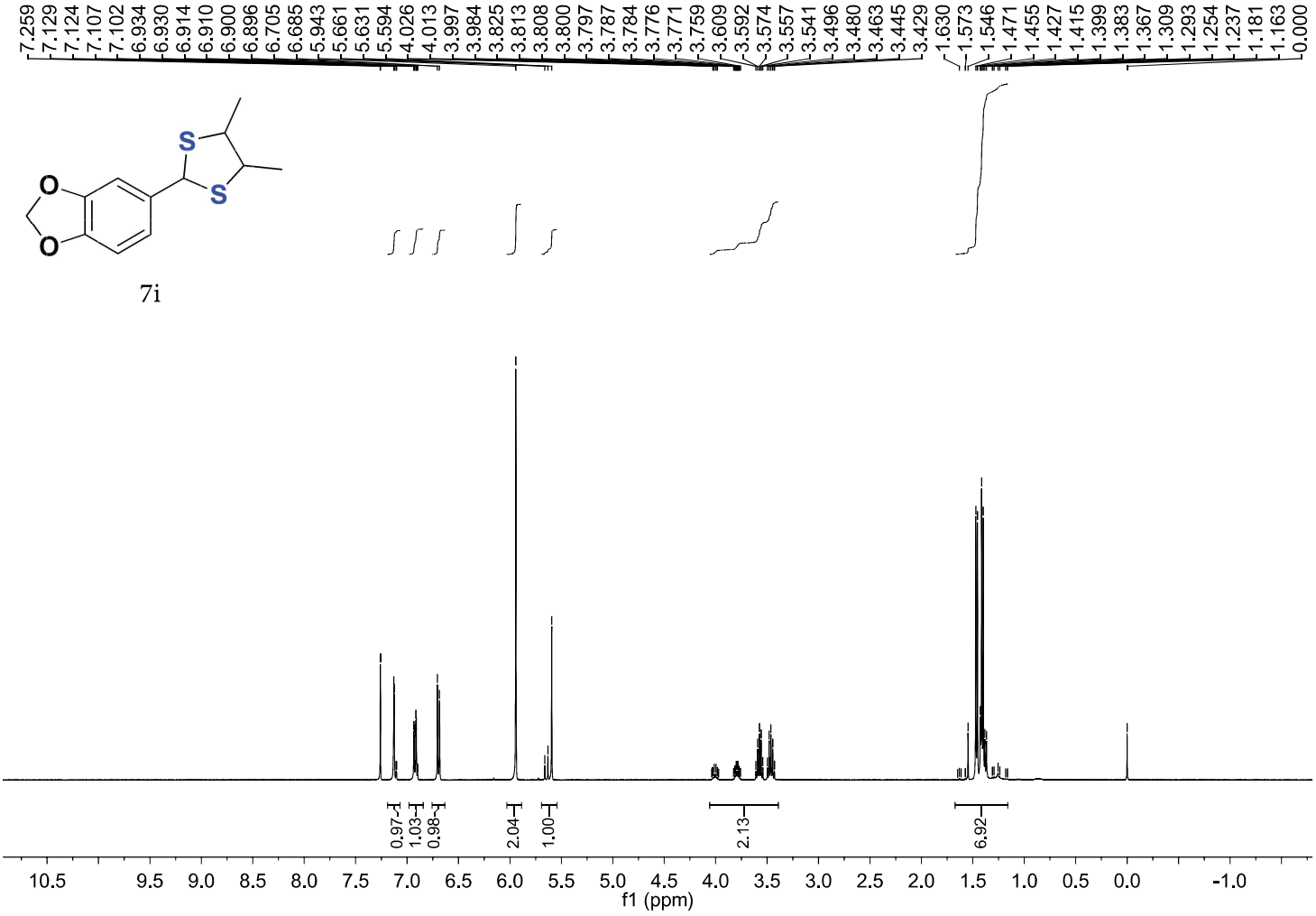
7g


7.546
7.543
7.525
7.506
7.321
7.317
7.303
7.300
7.284
7.262
7.259
7.246
7.241
7.236
7.226
7.223
5.693
5.671
5.631
4.041
4.030
4.024
4.017
4.014
4.004
4.001
3.993
3.987
3.977
3.829
3.824
3.816
3.813
3.803
3.800
3.792
3.787
3.620
3.604
3.585
3.569
3.553
3.515
3.499
3.482
3.464
3.447
1.529
1.472
1.456
1.430
1.417
1.401
1.386
1.370
1.363
1.255
0.000
S
S
2.03
3.12
1.00
2.05
6.50
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

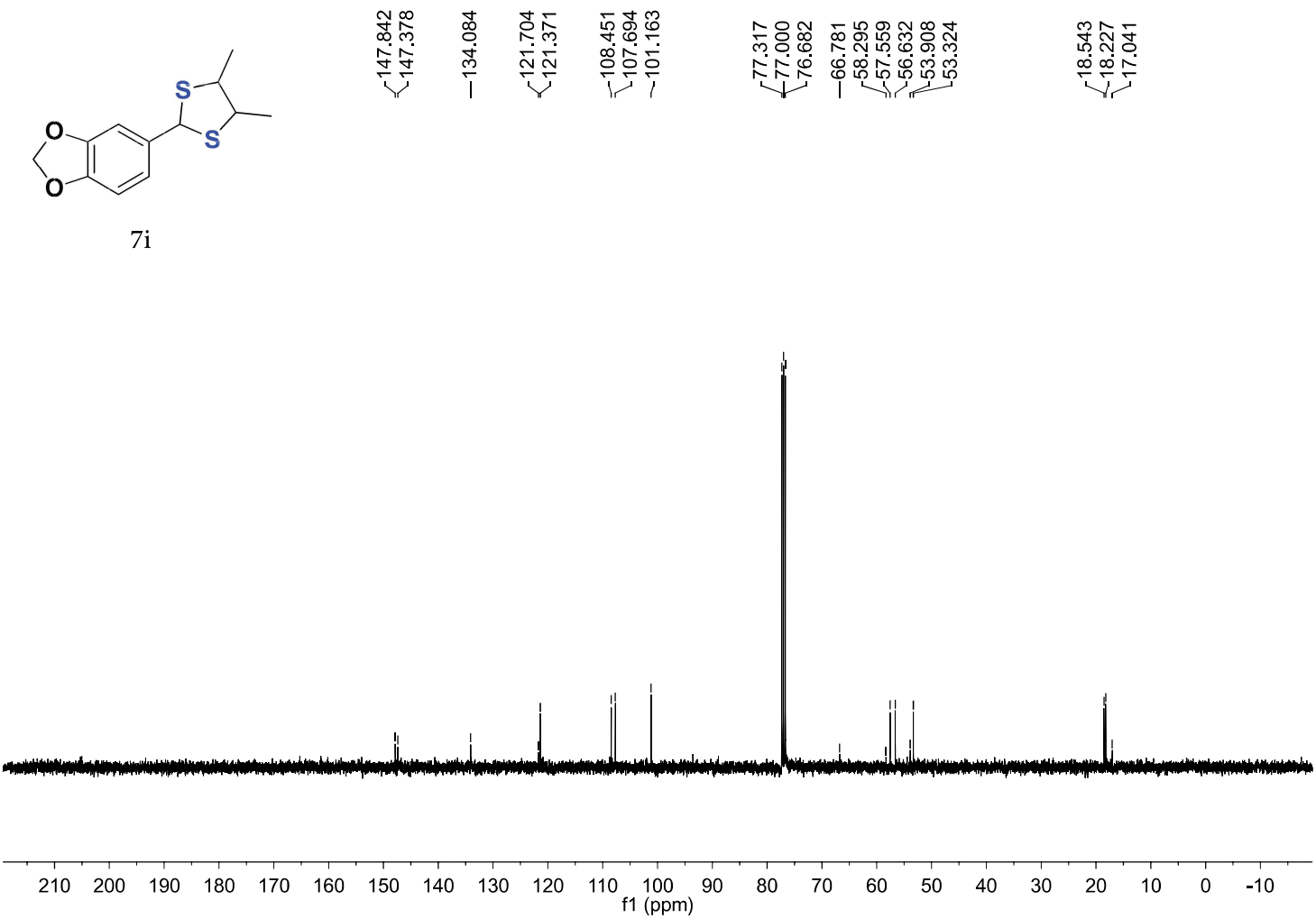
7h


141.704
140.376
138.748
128.400
128.282
127.987
127.867
127.736
77.317
77.000
76.682
57.561
56.582
55.792
54.381
53.929
53.173
18.467
18.149
16.987
16.002
S
S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

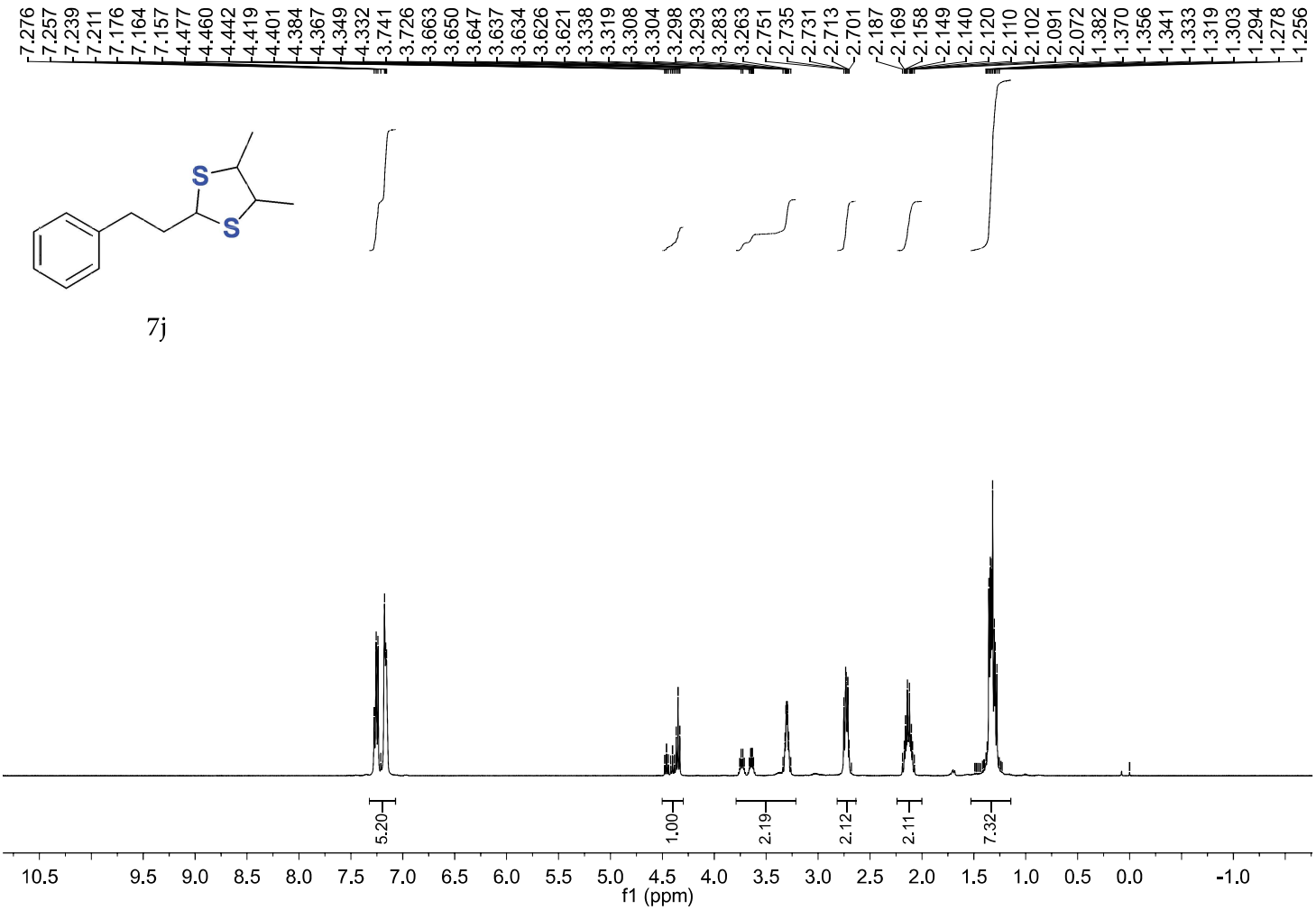
7h


7.259
7.129
7.124
7.107
7.102
6.934
6.930
6.914
6.910
6.900
6.896
6.705
6.685
5.943
5.661
5.631
5.594
4.026
4.013
3.997
3.984
3.825
3.813
3.808
3.800
3.797
3.787
3.784
3.776
3.771
3.759
3.609
3.592
3.574
3.557
3.541
3.496
3.480
3.463
3.445
3.429
1.630
1.573
1.546
1.471
1.455
1.427
1.415
1.399
1.383
1.367
1.309
1.293
1.254
1.237
1.181
1.163
0.000
S
S
O
O
0.97
1.03
0.98
2.04
1.00
2.13
6.92
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

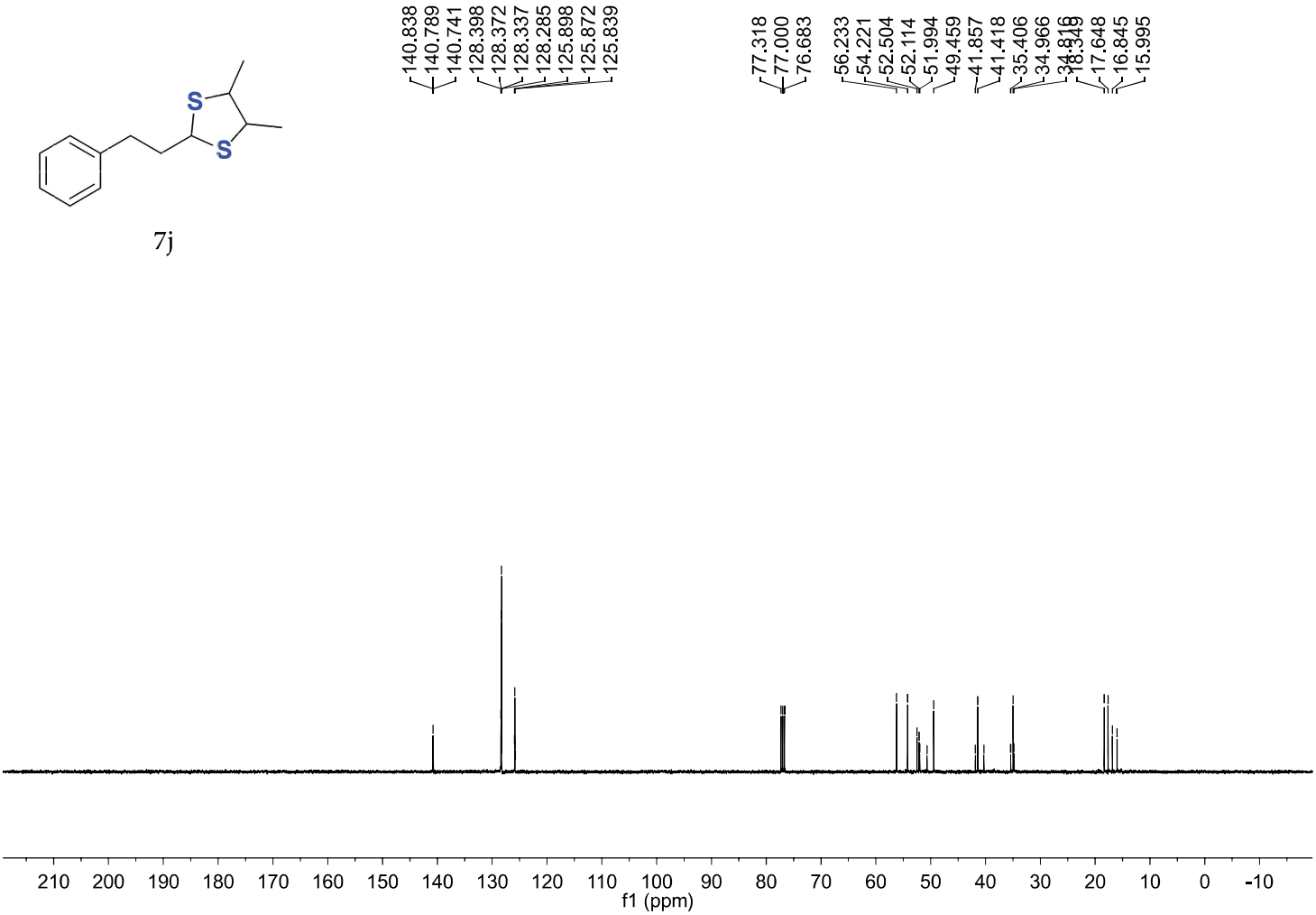
7i


147.842
147.378
134.084
121.704
121.371
108.451
107.694
101.163
77.317
77.000
76.682
66.781
58.295
57.559
56.632
53.908
53.324
18.543
18.227
17.041
S
S
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

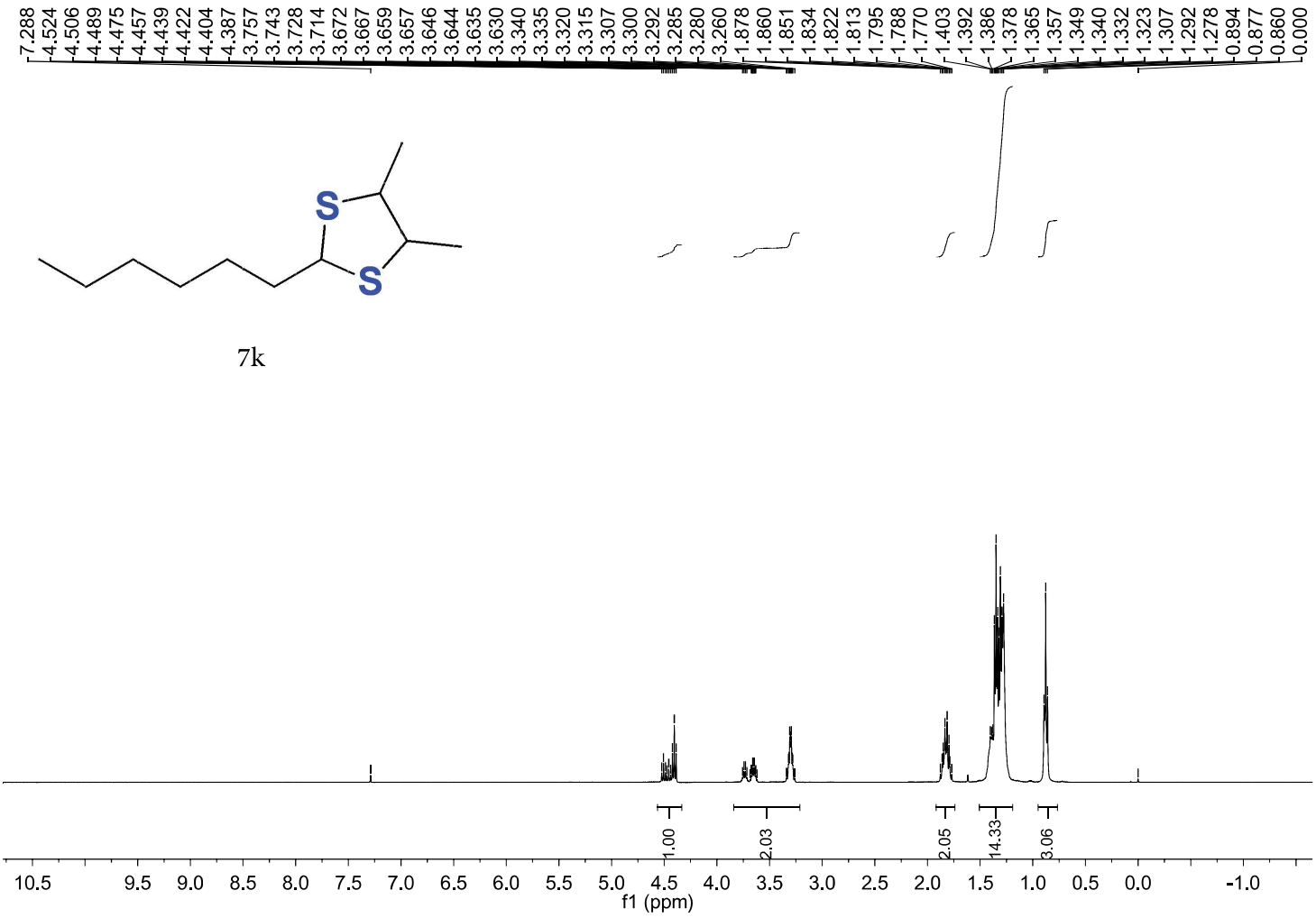
7i


7.276
7.257
7.239
7.211
7.176
7.164
7.157
4.477
4.460
4.442
4.419
4.401
4.384
4.367
4.349
4.332
3.741
3.726
3.663
3.650
3.647
3.637
3.634
3.626
3.621
3.338
3.319
3.308
3.304
3.298
3.293
3.283
3.263
2.751
2.735
2.731
2.713
2.701
2.187
2.169
2.158
2.149
2.140
2.120
2.110
2.102
2.091
2.072
1.382
1.370
1.356
1.341
1.333
1.319
1.303
1.294
1.278
1.256
S
S
5.20
1.00
2.19
2.12
2.11
7.32
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

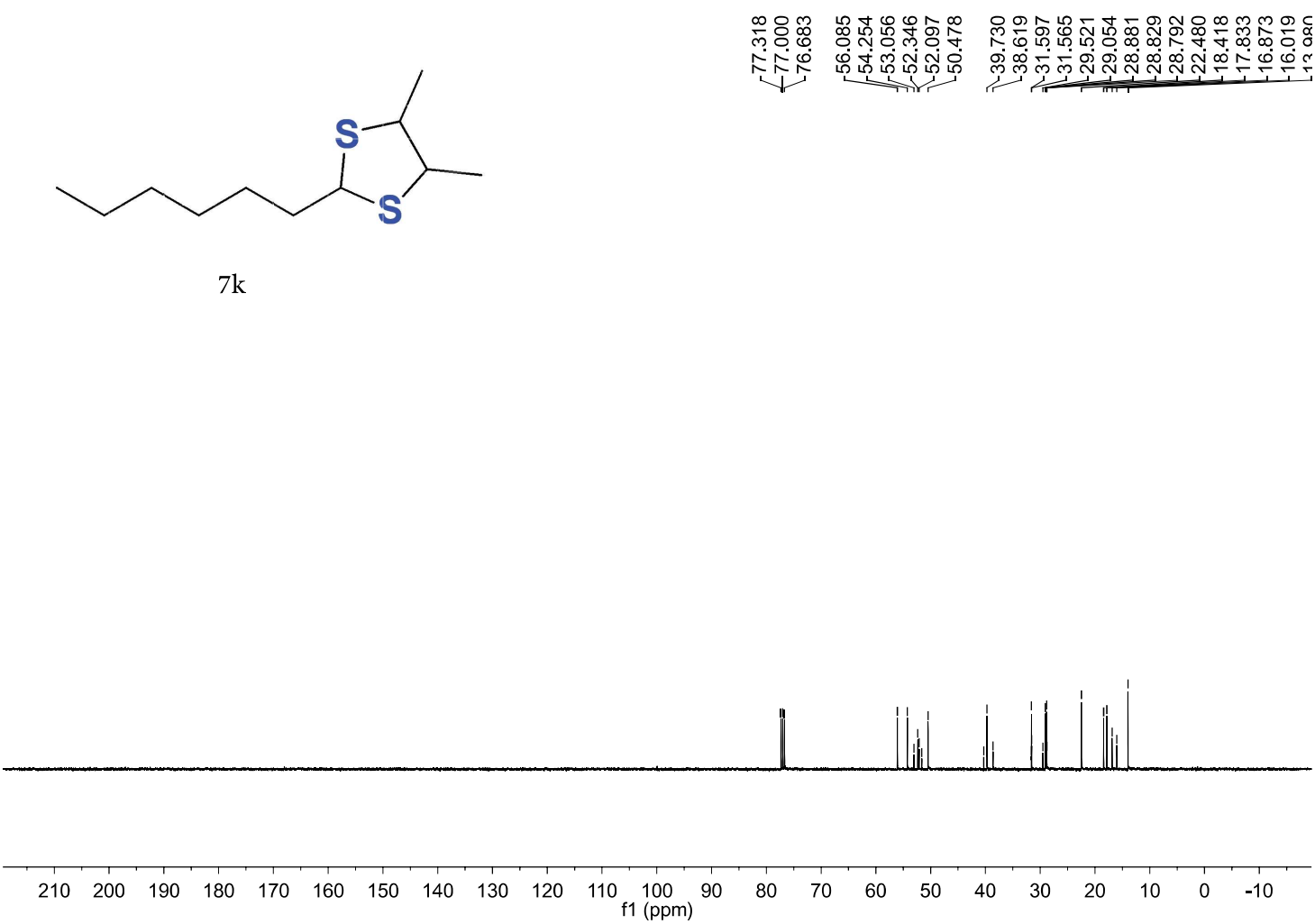
7j


140.838
140.789
140.741
128.398
128.372
128.337
128.285
125.898
125.872
125.839
77.318
77.000
76.683
56.233
54.221
52.504
52.114
51.994
49.459
41.857
41.418
35.406
34.966
34.816
34.349
17.648
16.845
15.995
S
S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

7j


7.288
4.524
4.506
4.489
4.475
4.457
4.439
4.422
4.404
4.387
3.757
3.743
3.728
3.714
3.672
3.667
3.659
3.657
3.646
3.644
3.635
3.630
3.340
3.335
3.320
3.315
3.307
3.300
3.292
3.285
3.280
3.260
1.878
1.860
1.851
1.834
1.822
1.813
1.795
1.788
1.770
1.403
1.392
1.386
1.378
1.365
1.357
1.349
1.340
1.332
1.323
1.307
1.292
1.278
0.894
0.877
0.860
0.000
S
S
1.00
2.03
2.05
14.33
3.06
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

7k


77.318
77.000
76.683
56.085
54.254
53.056
52.346
52.097
50.478
39.730
38.619
31.597
31.565
29.521
29.054
28.881
28.829
28.792
22.480
18.418
17.833
16.873
16.019
S
S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

7k