

# Sequential cycloaddition and ring expansion reaction of arynes and methylenebenzothiopheneones: synthesis of benzo-fused eight-membered ring *via* sulfonium ylides

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## Supporting Information

### Table of Contents

<b>1</b>	<b>General Information</b>	S2
<b>2</b>	<b>General Procedure</b>	S2
<b>3</b>	<b>Characterization Data</b>	S8
	Spectroscopic Data of All Compounds	S8
<b>4</b>	<b>Control Experiments and Mechanistic Study</b>	S25
<b>5</b>	<b>Further Application of the Products</b>	S27
<b>6</b>	<b><sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of All Compounds</b>	S28

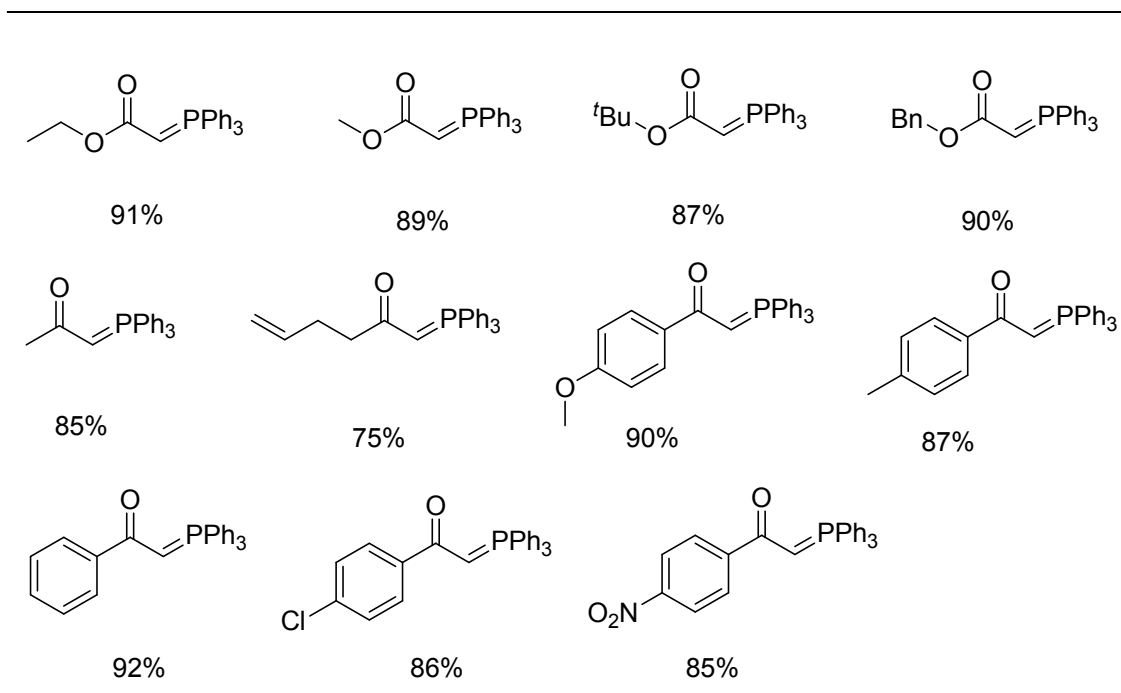
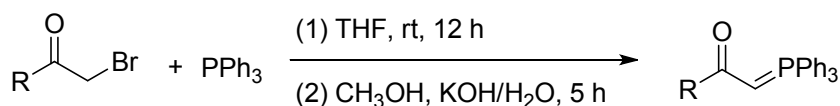
## 1 General Information

The NMR spectra were recorded on Bruker AC-500 spectrometer (500 MHz for  $^1\text{H}$  NMR and 125 MHz for  $^{13}\text{C}$  NMR) with  $\text{CDCl}_3$  as the solvent and TMS as internal reference.  $^1\text{H}$  NMR spectral data were reported as follows: chemical shift ( $\delta$ , ppm), multiplicity, integration, and coupling constant (Hz).  $^{13}\text{C}$  NMR spectral data were reported in terms of the chemical shift. The following abbreviations were used to indicate multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet. Low-resolution mass spectra were obtained with an Agilent spectrometer in API-ESI mode and are reported as  $m/z$  values. High-resolution mass spectra (HRMS) were recorded with a Waters Micromass GCT instrument. Melting points were obtained on a X-4 digital melting point apparatus without correction. Chemical yields referred to pure isolated product. Purification of products was accomplished by column chromatography packed with silica gel. Unless otherwise stated, all reagents were commercially purchased and used without further purification. Aryne precursors were prepared following published procedures.<sup>1-4</sup>

## 2 General Procedure

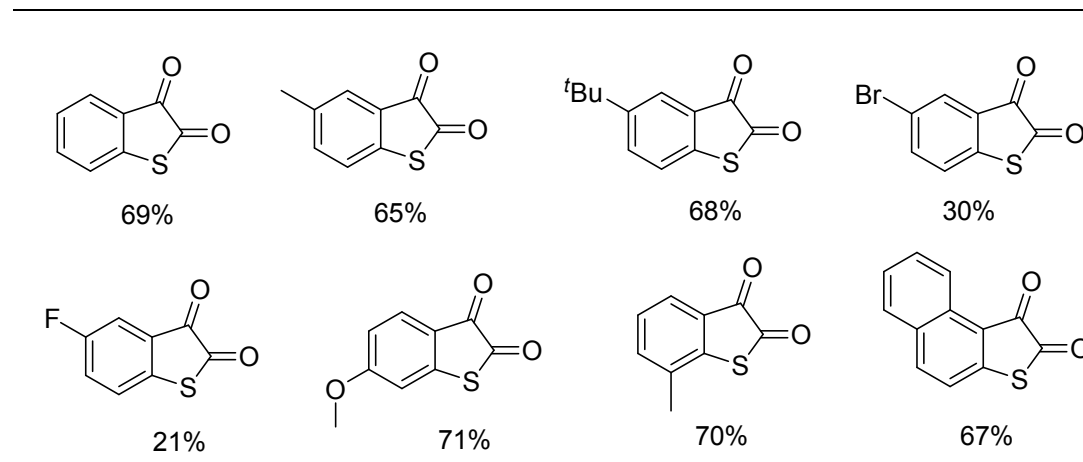
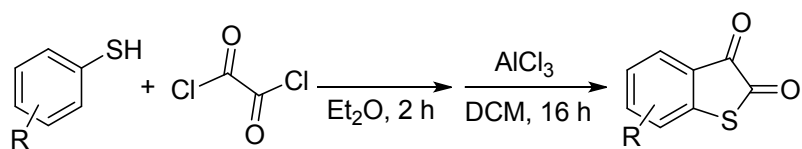
### 2.1 Wittig reagent (ylide) formation from the corresponding bromides<sup>5</sup>

Triphenyl phosphine (1.00 g, 3.81 mmol) was dissolved in THF (10 mL). To this mixture was added  $\alpha$ -bromoketones or  $\alpha$ -bromoacetates (3.81 mmol), respectively, The mixture was stirred at room temperature overnight. The resulting white precipitate was collected by filtration, washed with *n*-hexane (5 $\times$ 5 mL) and dried under reduced pressure. The dried white solid was dissolved in MeOH (20 mL). To this solution was added KOH (2.14 g, 38.1 mmol) dissolved in  $\text{H}_2\text{O}$  (20 mL) in a dropwise fashion. The mixture was allowed to stir at room temperature for 2 hours. The MeOH was removed under reduced pressure and the crude reaction mixture extracted with  $\text{Et}_2\text{O}$  (3 $\times$ 10 mL). The combined organic layers were washed with water (3 $\times$ 10 mL) and dried over magnesium sulphate. The solvent was removed under reduced pressure to afford the ylide, which was purified by re-crystallisation from hot ethanol.



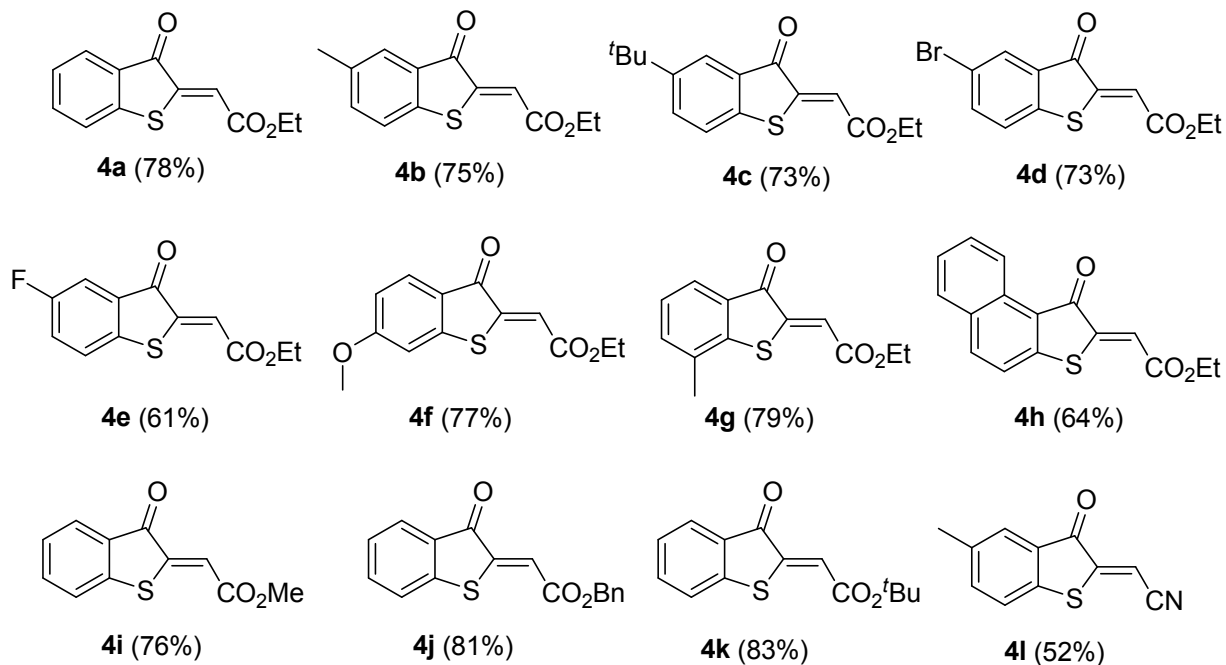
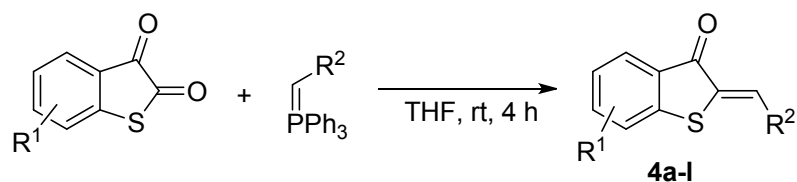
## 2.2 General procedure for the synthesis of benzo[*b*]thiophene-2,3-diones<sup>6,7</sup>

Following the reported procedure, to the mixture of thiophenol (50 mmol, 1equiv) in diethylether (100 mL) in a two neck flask equipped with a stirring bar under N<sub>2</sub>, was added dropwise oxalyl chloride (55 mmol, 4.7 mL; 1.1 equiv) at 0°C. The reaction mixture was stirred at room temperature for 2 hours. After the volatiles were removed *in vacuo*, the residue was dissolved in dichloromethane (100 mL). Then, AlCl<sub>3</sub> (175 mmol, 23.4 g; 3.5 equiv) was added dropwise at 0°C to the mixture. The resulting mixture was stirred for 16 hours at room temperature. Then, ice and 1M HCl was added until the mixture turned to be clear. After 1 hour, the phases were separated and the aqueous phase was extracted with dichloromethane (3×25 mL). The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated to afford an orange solid. The crude solid was purified by re-crystallisation from *n*-hexane to afford the benzo[*b*]thiophene-2,3-diones as an orange crystal.

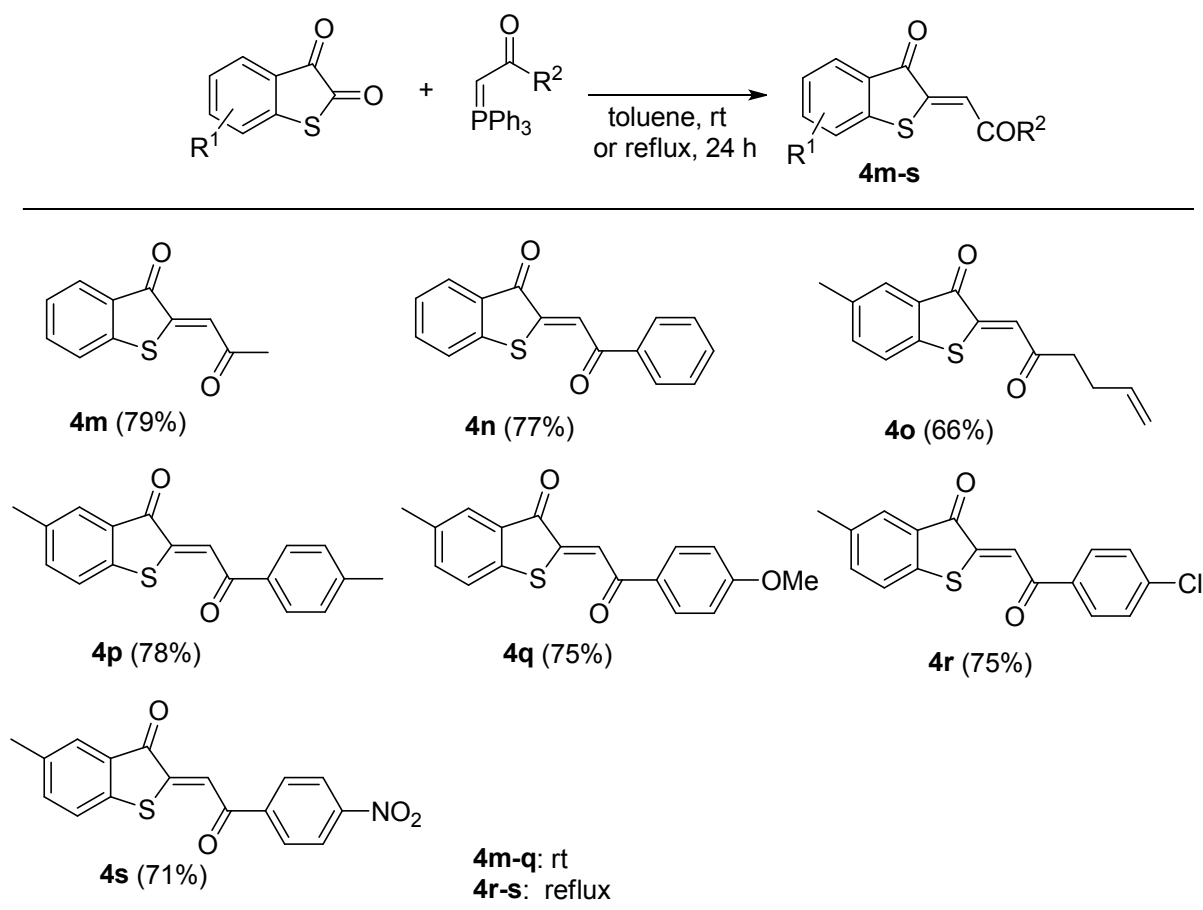


### 2.3 General procedure for the synthesis of 2-methylenebenzothienone-3-ones **4a-s** <sup>8</sup>

To a THF (20 mL) solution of benzo[*b*]thiophene-2,3-diones (5.0 mmol) was slowly added Wittig reagent (ylide) (5.1 mmol) in THF, and the mixture was stirred at room temperature for 4h. After the reaction complete (monitored by TLC), the solvent was removed under reduce pressure, and the residue was purified by column chromatography (ethyl acetate: petroleum ether = 1:10) to afford the pure product **4a-l**.



To a toluene (20 mL) solution of benzo[*b*]thiophene-2,3-diones (5.0 mmol) was added Wittig reagent (ylide) (5.1 mmol), and the mixture was stirred at room temperature or reflux temperature for 24h. After the reaction complete (monitored by TLC), the solvent was removed under reduce pressure, and the residue was purified by column chromatography (ethyl acetate: petroleum ether = 1:10) to afford the pure product **4m-s**.



## 2.4 General procedure for the preparation of dibenzo[*b,g*]thiocin-5-ones **5a-s**

TfOH (4.5 mmol) was added by means of a syringe to a stirred solution of  $\text{PhI}(\text{OAc})_2$  (2.3 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) at  $0^\circ\text{C}$  under  $\text{N}_2$ . The mixture was stirred under  $\text{N}_2$  at  $0^\circ\text{C}$  for 0.5h and at room temperature for 1.5 h. The clear yellow solution was cooled again to  $0^\circ\text{C}$ , followed by addition into the cold solution of the benzobis(oxadisilole) **1** (0.508 mg, 1.5 mmol) at  $0^\circ\text{C}$ . The mixture was stirred at  $0^\circ\text{C}$  for 0.5h and at room temperature for 3h. The clear yellow solution was washed with water (20 mL) and was extracted by  $\text{CH}_2\text{Cl}_2$  three times. The combined organic extracts were concentrated under reduced pressure to give a pale yellow solid **2**. The solution of **2** in  $\text{CH}_2\text{Cl}_2$  (10 mL) was dropwise added into the solution of **4a-s** (1.0 mmol) and CsF (3.0 mmol), trapping benzyne with 2-methylenebenzothiophene-3-ones **4a-s**. The mixture stirred reflux until **4a-s** was disappeared (monitored by TLC). The crude product was purified by column chromatography on silica gel using a gradient of eluant (ethyl acetate: petroleum ether = 1:30) as the eluent to afford products **5a-s**.

## 2.5 General procedure for the preparation of benzo[*b*]naphtho[2,3-*g*]thiocin-5-ones

### 9a-e

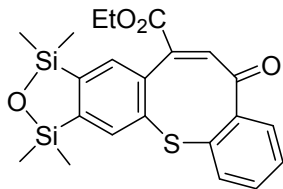
TfOH (4.5 mmol) was added by means of a syringe to a stirred solution of PhI(OAc)<sub>2</sub> (2.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) at 0 °C under N<sub>2</sub>. The mixture was stirred under N<sub>2</sub> at 0 °C for 0.5h and at room temperature for 1.5h. The clear yellow solution was cooled again to 0 °C, followed by addition into the cold solution of the 2,3-naphthoxadisilole **6** (0.388 mg, 1.5 mmol in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>) at 0 °C. The mixture was stirred at 0 °C for 0.5h and at room temperature for 3h. The clear yellow solution was washed with water (20 mL) and was extracted by CH<sub>2</sub>Cl<sub>2</sub> three times. The combined organic extracts were concentrated under reduced pressure to give a pale yellow solid **7**. The solution of **7** in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was dropwise added into the solution of **4** (1.0 mmol) and CsF (3.0 mmol), trapping naphthyne with 2-methylenebenzothiophene-3-ones **4**. The mixture stirred reflux until **4** was disappeared (monitored by TLC). The crude product was purified by column chromatography on silica gel using a gradient of eluant (ethyl acetate: petroleum ether = 1:20) as the eluent to afford products **9a-e**.

## References:

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8. Meng, X. T.; Jia, J. L.; Yu, A. M.; Ma, S. S.; Zhang, Y. Q.; Li, K. *Org. Lett.* **2017**, *19*, 6084.

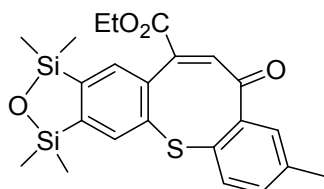
### 3 Characterization Data

#### 7-Ethoxycarbonyl-9,10-oxadisilole-5*H*-dibenzo[*b,g*]thiocine-5-one (5a)



Yield: 87%; yellow solid; m.p. 134-135 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.28 (s, 3H, SiMe), 0.32 (s, 3H, SiMe), 0.33 (s, 3H, SiMe), 0.37 (s, 3H, SiMe), 1.33 (t, *J* = 7.0 Hz, 3H, Me), 4.29-4.35 (m, 2H, OCH<sub>2</sub>), 7.31-7.34 (m, 1H, Ar-*H*), 7.44-7.47 (m, 2H, Ar-*H*), 7.67 (s, 1H, Ar-*H*), 7.69 (dd, *J* = 8.0, 1.0 Hz, 1H, Ar-*H*), 7.77 (dd, *J* = 7.5, 1.5 Hz, 1H, Ar-*H*), 7.85 (d, *J* = 0.5 Hz, 1H, =CH) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 0.76, 0.84, 0.9, 14.1, 61.7, 127.4, 131.4, 131.9, 132.1, 132.7, 133.3, 136.1, 136.4, 138.6, 139.4, 140.6, 141.0, 150.1, 150.4, 165.1, 196.0 ppm. MS (ESI) *m/z* (%): 441 (100, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. for: C<sub>22</sub>H<sub>24</sub>O<sub>4</sub>SSi<sub>2</sub> [M+H]<sup>+</sup>: 441.1007; Found: 441.1005.

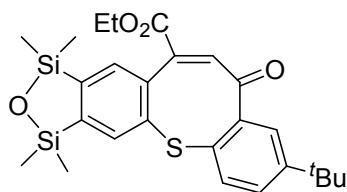
#### 3-Methyl-7-ethoxycarbonyl-9,10-oxadisilole-5*H*-dibenzo[*b,g*]thiocine-5-one (5b)



Yield: 84%; yellow solid; m.p. 182-183 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.27 (s, 3H, SiMe), 0.31 (s, 3H, SiMe), 0.33 (s, 3H, SiMe), 0.36 (s, 3H, SiMe), 1.33 (t, *J* = 7.0 Hz, 3H, Me), 2.32 (s, 3H, Me), 4.28-4.35 (m, 2H, OCH<sub>2</sub>), 7.27 (d, *J* = 1.5 Hz, 1H, Ar-*H*), 7.45 (s, 1H, Ar-*H*), 7.57 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.61 (s, 1H, Ar-*H*), 7.66 (s, 1H, Ar-*H*), 7.84 (s, 1H, =CH) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 0.7, 0.8, 0.9, 14.1, 20.7, 61.7, 131.9, 132.0, 132.1, 133.7, 133.9, 135.9, 136.2, 137.6, 137.8, 138.4, 139.4, 140.5, 150.0, 150.2, 165.2, 196.0 ppm. MS (ESI) *m/z* (%): 455 (100, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. for: C<sub>23</sub>H<sub>26</sub>O<sub>4</sub>SSi<sub>2</sub> [M+H]<sup>+</sup>: 455.1163; Found: 455.1162.

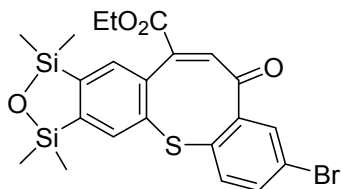


### 3-Tert-butyl-7-ethoxycarbonyl-9,10-oxadisilole-5H-dibenzo[*b,g*]thiocine-5-one (5c)



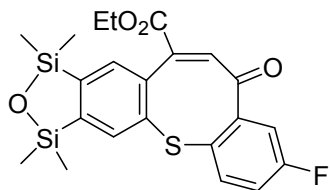
Yield: 87 %; yellow solid; m.p. 175-176 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.29 (s, 3H, SiMe), 0.32 (s, 3H, SiMe), 0.34 (s, 3H, SiMe), 0.37 (s, 3H, SiMe), 1.30-1.38 (m, 12H, Me), 4.28-4.36 (m, 2H,  $\text{OCH}_2$ ), 7.46 (s, 1H, Ar-*H*), 7.50 (dd,  $J = 8.0, 1.5$  Hz, 1H, Ar-*H*), 7.61 (d,  $J = 8.0$  Hz, 1H, Ar-*H*), 7.68 (s, 1H, Ar-*H*), 7.80 (d,  $J = 2.0$  Hz, 1H, Ar-*H*), 7.85 (s, 1H, =CH) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.7, 0.8, 0.9, 14.1, 31.0, 34.6, 61.6, 128.2, 130.2, 131.8, 132.0, 133.5, 135.8, 135.9, 137.8, 138.5, 139.5, 140.7, 149.9, 150.2, 150.8, 165.1, 196.5 ppm. MS (ESI)  $m/z$  (%): 497 (100,  $[\text{M}+\text{H}]^+$ ); HRMS (ESI): Calcd. for:  $\text{C}_{26}\text{H}_{32}\text{O}_4\text{SSi}_2$   $[\text{M}+\text{H}]^+$ : 497.1663; Found: 497.1630.

### 3-Bromo-7-ethoxycarbonyl-9,10-oxadisilole-5H-dibenzo[*b,g*]thiocine-5-one (5d)



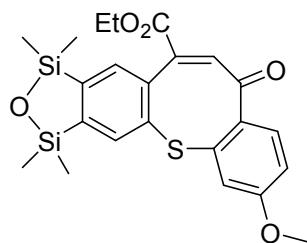
Yield: 79 %; yellow solid; m.p. 186-187 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.29 (s, 3H, SiMe), 0.32 (s, 3H, SiMe), 0.34 (s, 3H, SiMe), 0.36 (s, 3H, SiMe), 1.34 (t,  $J = 7.0$  Hz, 3H, Me), 4.29-4.36 (m, 2H,  $\text{OCH}_2$ ), 7.40 (s, 1H, Ar-*H*), 7.57 (d,  $J = 2.0$  Hz, 2H, Ar-*H*), 7.65 (s, 1H, Ar-*H*), 7.81 (s, 1H, =CH), 7.90-7.91 (m, 1H, Ar-*H*) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.8, 0.88, 0.92, 1.0, 14.2, 61.9, 121.6, 132.2, 133.1, 133.6, 134.1, 135.5, 136.6, 137.8, 138.5, 138.7, 140.1, 140.5, 150.4, 150.8, 165.0, 194.5 ppm. MS (ESI)  $m/z$  (%): 519 (90,  $[\text{M}+\text{H}]^+$ ); HRMS (ESI): Calcd. for:  $\text{C}_{22}\text{H}_{23}\text{O}_4\text{BrSSi}_2$   $[\text{M}+\text{H}]^+$ : 519.0112; Found: 519.0114.

### 3-Fluoro-7-ethoxycarbonyl-9,10-oxadisilole-5*H*-dibenzo[*b,g*]thiocine-5-one (5e)



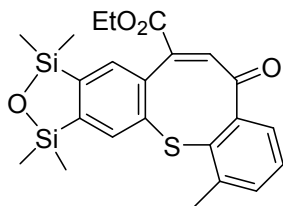
Yield: 75%; yellow solid; m.p. 185-186 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.29 (s, 3H, SiMe), 0.32 (s, 3H, SiMe), 0.34 (s, 3H, SiMe), 0.36 (s, 3H, SiMe), 1.34 (t, 3H, *J* = 7.0 Hz, Me), 4.29-4.36 (m, 2H, OCH<sub>2</sub>), 7.17-7.21 (m, 1H, Ar-*H*), 7.44 (s, 1H, Ar-*H*), 7.53 (dd, *J* = 9.0, 3.0 Hz, 2H, Ar-*H*), 7.65 (s, 1H, Ar-*H*), 7.69 (dd, *J* = 8.5, 5.0 Hz, 1H, Ar-*H*), 7.83 (s, 1H, =CH) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 0.8, 0.87, 0.91, 14.1, 61.9, 118.1 (d, *J*<sub>2</sub> = 23.4 Hz), 120.2 (d, *J*<sub>2</sub> = 21.8 Hz), 132.2, 133.7, 134.3 (d, *J*<sub>3</sub> = 7.1 Hz), 136.3 (d, *J*<sub>4</sub> = 3.4 Hz), 136.5, 138.2 (d, *J*<sub>3</sub> = 6.3 Hz), 138.4, 138.6, 140.3, 150.3, 150.6, 162.0 (d, *J*<sub>1</sub> = 248.4 Hz), 165.1, 194.4 ppm. <sup>19</sup>F-NMR (470 MHz, CDCl<sub>3</sub>): δ -62.63 (s, CF<sub>3</sub>) ppm. MS (ESI) *m/z* (%): 459 (100, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. for: C<sub>22</sub>H<sub>23</sub>O<sub>4</sub>FSSi<sub>2</sub> [M+H]<sup>+</sup>: 459.0912; Found: 459.0915.

### 2-Methoxy-7-ethoxycarbonyl-9,10-oxadisilole-5*H*-dibenzo[*b,g*]thiocine-5-one (5f)



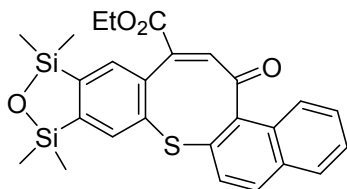
Yield: 82%; yellow solid; m.p. 161-162 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.28 (s, 3H, SiMe), 0.31 (s, 3H, SiMe), 0.33 (s, 3H, SiMe), 0.36 (s, 3H, SiMe), 1.33 (t, *J* = 7.0 Hz, 3H, Me), 3.89 (s, 3H, OMe), 4.27-4.37 (m, 2H, OCH<sub>2</sub>), 6.84 (dd, *J* = 9.0, 2.5 Hz, 1H, Ar-*H*), 7.20 (d, *J* = 2.5 Hz, 1H, Ar-*H*), 7.45 (s, 1H, Ar-*H*), 7.66 (s, 1H, Ar-*H*), 7.83 (d, *J* = 9.0 Hz, 1H, Ar-*H*), 7.84 (s 1H, =CH) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 0.7, 0.8, 0.87, 0.91, 14.1, 55.7, 61.7, 113.7, 117.9, 129.7, 132.2, 133.6, 133.7, 135.0, 138.4, 139.8, 140.5, 143.4, 149.9, 150.3, 162.8, 165.3, 194.1 ppm. MS (ESI) *m/z* (%): 471 (100, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. for: C<sub>23</sub>H<sub>26</sub>O<sub>5</sub>SSi<sub>2</sub> [M+H]<sup>+</sup>: 471.1112; Found: 471.113.

### 1-Methyl-7-ethoxycarbonyl-9,10-oxadisilole-5*H*-dibenzo[*b,g*]thiocine-5-one (5g)



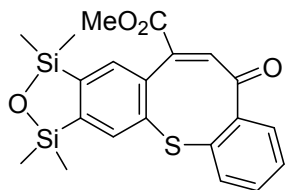
Yield: 84%; yellow solid; m.p. 173-174 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.29 (s, 3H, SiMe), 0.34 (s, 6H, SiMe<sub>2</sub>), 0.37(s, 3H, SiMe), 1.33 (t, *J* = 7.0 Hz, 3H, Me), 2.63 (s, 3H, Me), 4.30-4.35 (m, 2H, OCH<sub>2</sub>), 7.18 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 7.37 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.42 (s, 1H, Ar-*H*), 7.56 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.70 (s, 1H, Ar-*H*), 7.78 (s, 1H, =CH) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 0.7, 14.1, 21.4, 61.6, 126.3, 129.1, 131.8, 133.1, 134.1, 136.2, 136.9, 138.3, 139.0, 139.9, 140.8, 141.5, 150.0, 150.5, 164.9, 196.7 ppm. MS (ESI) *m/z* (%): 455 (100, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. for: C<sub>23</sub>H<sub>26</sub>O<sub>4</sub>SSi<sub>2</sub> [M+H]<sup>+</sup>: 455.1163; Found: 455.1161.

### 2,3-Oxadisilole-14-ethoxycarbonyl-12*H*-benzo[*b*]naphtho[1,2-*g*]thiocin-12-one (5h)



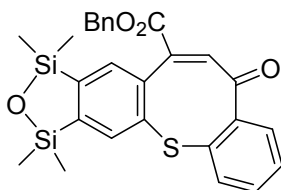
Yield: 82%; yellow solid; m.p. 166-167 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.32 (s, 6 H, SiMe<sub>2</sub>), 0.39 (s, 6 H, SiMe<sub>2</sub>), 1.34 (t, *J* = 7.0 Hz, 3H, Me), 4.35 (d, *J* = 6.5 Hz, 2H, OCH<sub>2</sub>), 7.46-7.50 (m, 1H, Ar-*H*), 7.51-7.55 (m, 1H, Ar-*H*), 7.62 (d, *J* = 8.5 Hz, 1H, Ar-*H*), 7.76 (s, 1H, Ar-*H*), 7.82 (dd, *J* = 8.5, 1.5 Hz, 1H, Ar-*H*), 7.86(d, *J* = 8.5 Hz, 1H, Ar-*H*), 7.89 (s, 1H, =CH), 8.08 (d, *J* = 9.0 Hz, 1H, Ar-*H*) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 0.8, 0.9, 61.7, 123.7, 126.3, 127.4, 128.3, 128.4, 130.6, 130.9, 131.4, 131.7, 131.9, 132.3, 137.1, 139.0, 140.5, 140.6, 142.0, 150.5, 150.9, 164.9, 198.1 ppm. MS (ESI) *m/z* (%): 491 (100, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. for: C<sub>26</sub>H<sub>26</sub>O<sub>4</sub>SSi<sub>2</sub> [M+H]<sup>+</sup>: 491.1163; Found: 491.1162.

### 7-Methoxycarbonyl-9,10-oxadisilole-5*H*-dibenzo[*b,g*]thiocine-5-one (5i)



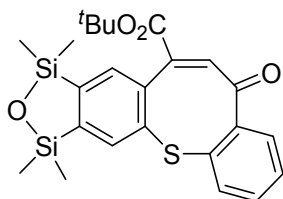
Yield: 88%; yellow solid; m.p. 138-139 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.27 (s, 3H, SiMe), 0.32 (s, 3H, SiMe), 0.33 (s, 3H, SiMe), 0.38 (s, 3H, SiMe), 3.85 (s, 3H, Me), 7.30-7.33 (m, 1H, Ar-*H*), 7.42-7.46 (m, 2H, Ar-*H*), 7.67-7.69 (m, 2H, Ar-*H*), 7.76 (dd, *J* = 8.0, 1.5 Hz, 1H, Ar-*H*), 7.85 (s, 1H, =CH) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 0.76, 0.78, 0.9, 52.7, 127.4, 131.4, 131.9, 131.9, 132.7, 133.3, 135.8, 136.3, 138.6, 139.6, 140.5, 140.9, 150.2, 150.5, 165.6, 195.8 ppm. MS (ESI) *m/z* (%): 427 (100, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. for: C<sub>21</sub>H<sub>22</sub>O<sub>4</sub>SSi<sub>2</sub> [M+H]<sup>+</sup>: 428.0850; Found: 427.0850.

### 7-Benzoxycarbonyl-9,10-oxadisilole-5*H*-dibenzo[*b,g*]thiocine-5-one (5j)



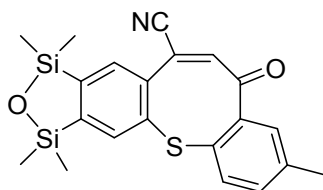
Yield: 92 %; yellow solid; m.p. 172-173 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.30 (s, 3H, SiMe), 0.34 (s, 3H, SiMe), 0.356 (s, 3H, SiMe), 0.364 (s, 3H, SiMe), 5.23 (d, *J* = 12.0 Hz, 1H, OCH<sub>2</sub>), 5.41 (d, *J* = 12.0 Hz, 1H, OCH<sub>2</sub>), 7.31-7.38 (m, 6H, Ar-*H*), 7.46 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 7.51 (s, 1H, Ar-*H*), 7.69-7.70 (m, 2H, Ar-*H*), 7.78 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.88 (s, 1H, =CH) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 0.68, 0.72, 0.8, 67.2, 127.3, 127.9, 128.2, 128.4, 131.3, 131.8, 131.9, 132.6, 133.3, 135.3, 135.7, 136.2, 138.5, 139.9, 140.4, 140.8, 150.0, 150.4, 164.8, 195.7 ppm. MS (ESI) *m/z* (%): 503 (100, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. for: C<sub>27</sub>H<sub>26</sub>O<sub>4</sub>SSi<sub>2</sub> [M+H]<sup>+</sup>: 503.1163; Found: 503.1160.

### 7-Tert-butoxycarbonyl-9,10-oxadisilole-5*H*-dibenzo[*b,g*]thiocine-5-one (5k)



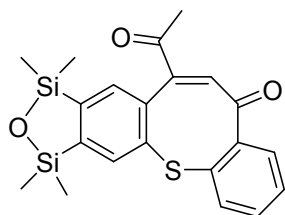
Yield: 91%; yellow solid; m.p. 201-202 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.27 (s, 3H, SiMe), 0.32 (s, 6H, SiMe<sub>2</sub>), 0.36 (s, 3H, SiMe), 1.52 (s, 9H, Bu), 7.30 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 7.36 (s, 1H, Ar-*H*), 7.43 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 7.67 (d, *J* = 9.0 Hz, 1H, Ar-*H*), 7.75 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.84 (s, 1H, =CH) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 0.67, 0.74, 0.8, 27.9, 82.0, 127.2, 131.3, 131.8, 132.2, 132.5, 133.2, 136.3, 137.3, 138.4, 138.6, 140.9, 141.0, 149.6, 150.1, 163.9, 196.2 ppm. MS (ESI) *m/z* (%): 469 (10, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. for: C<sub>24</sub>H<sub>28</sub>O<sub>4</sub>SSi<sub>2</sub> [M+H]<sup>+</sup>: 469.1320; Found: 469.1321.

### 3-Methyl-7-cyano-9,10-oxadisilole-5*H*-dibenzo[*b,g*]thiocine-5-one (5l)



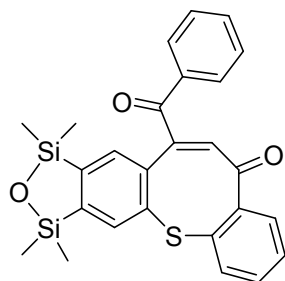
Yield: 80%; yellow solid; m.p. 179-180 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.33 (s, 6H, SiMe<sub>2</sub>), 0.36 (s, 6H, SiMe<sub>2</sub>), 2.34 (s, 3H, Me), 7.19 (s, 1H, Ar-*H*), 7.31-7.33(m, 1H, Ar-*H*), 7.62 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.65 (d, *J* = 2.0 Hz, 1H, Ar-*H*), 7.76 (s, 1 H, Ar-*H*), 7.91 (d, *J* = 0.5 Hz, 1H, =CH) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 0.75, 0.77, 20.8, 117.6, 118.3, 130.7, 132.3, 133.3, 134.5, 134.8, 136.3, 136.8, 138.2, 138.6, 138.8, 143.9, 151.6, 152.4, 192.3 ppm. MS (ESI) *m/z* (%): 407 (100, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. For: C<sub>26</sub>H<sub>24</sub>O<sub>3</sub>SSi<sub>2</sub> [M+H]<sup>+</sup>: 407.0826; Found: 407.0822.

### 7-Acetyl-9,10-oxadisilole-5*H*-dibenzo[*b,g*]thiocine-5-one (5m)



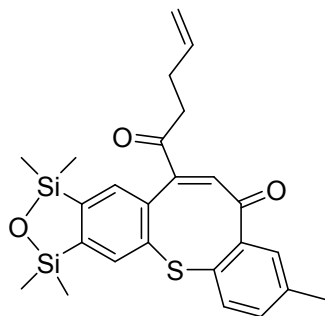
Yield: 90%; yellow solid; m.p. 166-167 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.27 (s, 3H, SiMe), 0.30 (s, 3H, SiMe), 0.33 (s, 3H, SiMe), 0.37 (s, 3H, SiMe), 2.49 (s, 3H, Me), 7.21 (s, 1H, Ar-*H*), 7.30-7.33 (m, 1H, Ar-*H*), 7.43-7.46 (m, 1H, Ar-*H*), 7.53 (s, 1H, Ar-*H*), 7.67 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.75 (dd, *J* = 7.5, 1.0 Hz, 1H, Ar-*H*), 7.85 (s, 1H, =CH) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 0.7, 0.8, 0.9, 26.7, 127.4, 131.5, 131.8, 131.9, 132.7, 133.3, 136.3, 138.1, 138.6, 140.8, 140.9, 143.3, 150.1, 150.6, 195.8, 196.7 ppm. MS (ESI) *m/z* (%): 411 (100, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. For: C<sub>21</sub>H<sub>22</sub>O<sub>3</sub>SSi<sub>2</sub> [M+H]<sup>+</sup>: 411.0901; Found: 411.0901.

### 7-Benzoyl-9,10-oxadisilole-5*H*-dibenzo[*b,g*]thiocine-5-one (5n)



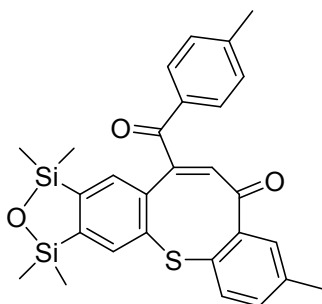
Yield: 93%; yellow solid; m.p. 184-185 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.31 (s, 12H, SiMe), 0.35 (s, 6H, SiMe), 6.87 (s, 1H, Ar-*H*), 7.33 (t, *J* = 7.5 Hz, 3H, Ar-*H*), 7.46-7.49 (m, 3H, Ar-*H*), 7.57 (t, *J* = 7.5 Hz, 2H, Ar-*H*), 7.75 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.79 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.87 (s, 1H, Ar-*H*), 7.93 (s, 1H, =CH), 8.08 (d, *J* = 7.5 Hz, 2H, Ar-*H*) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 0.7, 0.8, 127.5, 128.4, 130.0, 131.5, 131.6, 132.3, 132.7, 132.9, 133.5, 136.6, 136.8, 138.5, 138.6, 140.5, 140.9, 142.2, 150.2, 150.7, 194.6, 195.2 ppm. MS (ESI) *m/z* (%): 473 (100, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. For: C<sub>26</sub>H<sub>24</sub>O<sub>3</sub>SSi<sub>2</sub> [M+H]<sup>+</sup>: 473.1057; Found: 473.1059.

### 3-7-(4-pentenyl-1-carbonyl)-9,10-oxadisilole-5H-dibenzo[b,g]thiocine-5-one (5o)



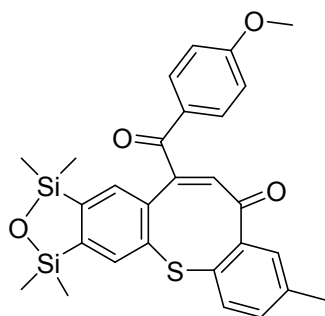
Yield: 413mg, 89%; yellow solid; m.p. 175-176 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.27 (s, 3H, SiMe), 0.31 (s, 3H, SiMe), 0.34 (s, 3H, SiMe), 0.38 (s, 3H, SiMe), 2.32 (s, 3H, Me), 2.46 (d, *J* = 7.0 Hz, 2H, CH<sub>2</sub>), 2.86-2.92 (m, 2 H), 4.98-5.08 (m, 2H, CH<sub>2</sub>), 5.83-5.87 (m, 1H, CH), 7.21 (s, 1H, Ar-*H*), 7.27 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.54-7.60 (m, 3H, Ar-*H*), 7.85 (s, 1H, =CH) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 0.7, 0.8, 0.9, 20.6, 27.9, 38.0, 115.4, 131.7, 131.8, 132.0, 133.6, 133.9, 136.2, 136.7, 137.1, 137.5, 137.6, 138.4, 140.8, 142.8, 150.0, 150.4, 196.0, 198.2 ppm. MS (ESI) *m/z* (%): 465 (100, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. For: C<sub>25</sub>H<sub>28</sub>O<sub>3</sub>SSi<sub>2</sub> [M+H]<sup>+</sup>: 465.1370; Found: 465.1369.

### 3-Methyl-7-(*P*-methylbenzoyl)-9,10-oxadisilole-5H-dibenzo[b,g]thiocine-5-one (5p)



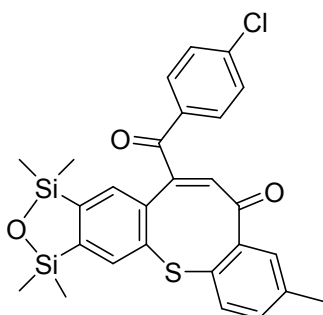
Yield: 85%; yellow solid; m.p. 207-208 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.31 (s, 6H, SiMe<sub>2</sub>), 0.34 (s, 6H, SiMe<sub>2</sub>), 2.33 (s, 3H, Me), 2.41 (s, 3H, Me), 6.83 (s, 1H, Ar-*H*), 7.27-7.30 (m, 3H, Ar-*H*), 7.64 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.86 (s, 1H, Ar-*H*), 7.90 (s, 1H, =CH), 8.0 (d, *J* = 8.0 Hz, 2H, Ar-*H*) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 0.8, 0.9, 20.7, 21.6, 129.2, 130.4, 131.6, 132.0, 132.6, 133.8, 134.0, 134.1, 136.9, 137.3, 137.8, 137.9, 138.4, 140.9, 142.4, 143.9, 150.1, 150.5, 194.5, 195.4 ppm. MS (ESI) *m/z* (%): 501 (100, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. For: C<sub>26</sub>H<sub>24</sub>O<sub>3</sub>SSi<sub>2</sub> [M+H]<sup>+</sup>: 501.1357; Found: 501.1363.

### 3-Methyl-7-(*P*-methoxybenzoyl)-9,10-oxadisilole-5*H*-dibenzo[*b,g*]thiocine-5-one (5q)



Yield: 83%; yellow solid; m.p. 201-202 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.33 (s, 12H, SiMe), 2.34 (s, 3H, Me), 3.86 (s, 3H, OMe), 6.78 (s, 1H, Ar-*H*), 6.96 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.29 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.64 (s, 2H, Ar-*H*), 7.88 (s, 1H, Ar-*H*), 7.89 (s, 1H, =CH), 8.12 (d, *J* = 8.0 Hz, 2H, Ar-*H*) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 0.8, 0.9, 20.7, 55.4, 113.8, 129.2, 131.5, 132.0, 132.66, 132.72, 133.7, 134.2, 136.6, 137.1, 137.2, 137.9, 138.4, 141.0, 142.6, 150.1, 150.6, 163.7, 193.5, 195.4 ppm. MS (ESI) *m/z* (%): 517 (100, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. For: C<sub>28</sub>H<sub>28</sub>O<sub>4</sub>SSi<sub>2</sub> [M+H]<sup>+</sup>: 517.1320; Found: 517.1321.

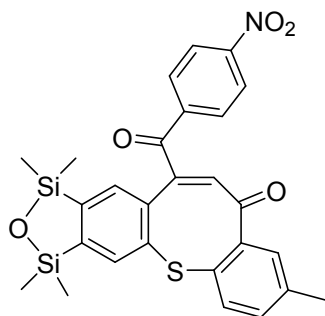
### 3-Methyl-7-(*P*-chlorobenzoyl)-9,10-oxadisilole-5*H*-dibenzo[*b,g*]thiocine-5-one (5r)



Yield: 77%; yellow solid; m.p. 193-194 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.31 (s, 12H, SiMe), 2.30 (s, 3H, Me), 6.80 (s, 1H, Ar-*H*), 7.42 (d, *J* = 7.0 Hz, 3H, Ar-*H*), 7.60 (s, 2H, Ar-*H*), 7.80 (s, 1H, Ar-*H*), 7.87 (s, 1H, =CH), 7.99 (d, *J* = 7.0 Hz, 2H, Ar-*H*) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 0.8, 20.8, 128.9, 131.6, 132.1, 132.6, 133.9, 134.1, 135.0, 136.8, 137.3, 138.1, 138.4, 138.5, 139.6, 140.5, 142.1, 150.4, 150.8, 193.6, 195.1 ppm. MS (ESI) *m/z* (%): 521 (90, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. For: C<sub>26</sub>H<sub>24</sub>O<sub>3</sub>SSi<sub>2</sub> [M+H]<sup>+</sup>: 521.0824; Found: 521.0818.

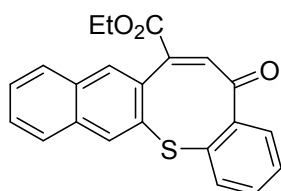


### 3-Methyl-7-(*P*-nitrobenzoyl)-9,10-oxadisilole-5*H*-dibenzo[*b,g*]thiocine-5-one (5s)



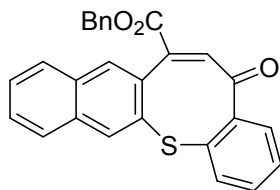
Yield: 82%; yellow solid; m.p. 204-203 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.29 (s, 6H, SiMe), 0.34 (s, 6H, SiMe), 2.33 (s, 3H, Me), 6.88 (s, 1H, Ar-*H*), 7.32 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.64 (t, *J* = 8.0 Hz, 2H, Ar-*H*), 7.80 (s, 1H, Ar-*H*), 7.92 (s, 1H, =CH), 8.18 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 8.31 (d, *J* = 8.5 Hz, 2H, Ar-*H*) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 0.7, 0.8, 20.7, 123.7, 130.8, 131.6, 132.1, 132.6, 133.9, 134.1, 136.4, 137.2, 138.1, 138.6, 139.9, 140.1, 141.6, 141.9, 150.0, 150.9, 193.1, 194.6 ppm. MS (ESI) *m/z* (%): 532 (100, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. For: C<sub>26</sub>H<sub>24</sub>O<sub>3</sub>SSi<sub>2</sub> [M+H]<sup>+</sup>: 532.1051; Found: 532.1056

### 7-Ethoxycarbonyl-5*H*-benzo[*b*]naphtho[2,3-*g*]thiocin-5-one (9a)



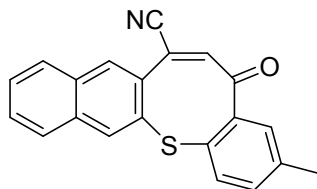
Yield: 78%; yellow solid; m.p. 166-167 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.35 (t, *J* = 7.0 Hz, 3H, Me), 4.33-4.38 (m, 2H, OCH<sub>2</sub>), 7.30-7.33 (m, 1H, Ar-*H*), 7.45-7.50 (m, 2H, Ar-*H*), 7.51-7.54 (m, 1H, Ar-*H*), 7.55 (s, 1H, Ar-*H*), 7.71-7.75 (m, 3H, Ar-*H*), 7.84 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.98 (s, 1H, Ar-*H*), 8.28 (s, 1H, =CH) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 14.2, 61.9, 127.2, 127.4, 127.7, 127.9, 128.2, 129.4, 130.3, 131.5, 131.8, 132.7, 133.3, 133.5, 135.9, 136.1, 136.5, 136.9, 140.2, 141.2, 165.3, 196.2 ppm. MS (ESI) *m/z* (%): 361 (100, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. For: C<sub>22</sub>H<sub>16</sub>O<sub>3</sub>S [M+H]<sup>+</sup>: 361.0893; Found: 361.0893.

### 7-Benzoxycarbonyl-5H-benzo[*b*]naphtho[2,3-*g*]thiocin-5-one (9b)



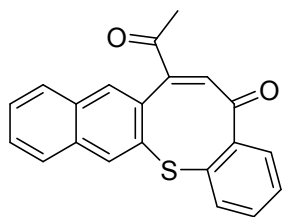
Yield: 79%; yellow solid; m.p. 191-192 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 5.34 (d, *J* = 12 Hz, 2H, OCH<sub>2</sub>), 7.31-7.33 (m, 1H, Ar-*H*), 7.34-7.41 (m, 5H, Ar-*H*), 7.45-7.50 (m, 2H, Ar-*H*), 7.51-7.53 (m, 1H, Ar-*H*), 7.59 (s, 1H, Ar-*H*), 7.71-7.75 (m, 3H, Ar-*H*), 7.83 (d, *J* = 8.5 Hz, 1H, Ar-*H*), 7.99 (s, 1H, Ar-*H*), 8.29 (s, 1H, =CH) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 67.4, 127.2, 127.4, 127.7, 127.9, 128.1, 128.2, 128.3, 128.6, 129.5, 130.3, 131.4, 131.8, 132.8, 133.3, 133.4, 135.5, 135.7, 135.8, 136.4, 136.9, 140.6, 141.1, 165.1, 196.1 ppm. MS (ESI) *m/z* (%): 423 (65, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. For: C<sub>27</sub>H<sub>18</sub>O<sub>3</sub>S [M+H]<sup>+</sup>: 423.1049; Found: 423.1052.

### 3-Methyl-7-Cyano-5H-benzo[*b*]naphtho[2,3-*g*]thiocin-5-one (9c)



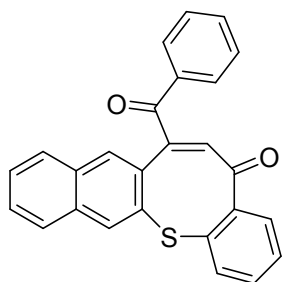
Yield: 79%; yellow solid; m.p. 196-197 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 2.31 (s, 3H, Me), 7.30 (d, *J* = 2.0 Hz, 2H, Ar-*H*), 7.54-7.58 (m, 3H, Ar-*H*), 7.65 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.85 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.86 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 8.11 (s, 1H, Ar-*H*), 8.32 (s, 1H, =CH) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 20.8, 118.1, 118.4, 127.7, 128.2, 128.3, 128.4, 129.2, 131.2, 132.2, 133.2, 133.4, 133.7, 133.9, 134.5, 136.0, 136.9, 137.3, 138.8, 144.4, 192.4 ppm. MS (ESI) *m/z* (%): 328 (100, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. For: C<sub>21</sub>H<sub>13</sub>NOS [M+H]<sup>+</sup>: 327.0791; Found: 328.0788.

### 7-Acetyl-5*H*-benzo[*b*]naphtho[2,3-*g*]thiocin-5-one (9d)



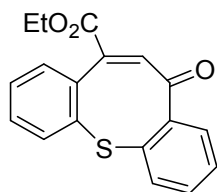
Yield: 77%; yellow solid; m.p. 200-201 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 2.54 (s, 3H, Me), 7.31-7.34 (m, 2H, Ar-*H*), 7.46-7.50 (m, 2H, Ar-*H*), 7.52-7.55 (m, 1H, Ar-*H*), 7.71-7.75 (m, 3H, Ar-*H*), 7.83-7.85 (m, 2H, Ar-*H*), 8.28 (s, 1H, =CH) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 26.9, 127.2, 127.5, 127.7, 128.0, 128.2, 129.2, 130.3, 131.5, 131.8, 132.8, 133.3, 133.5, 136.0, 136.5, 137.0, 138.8, 141.1, 143.3, 196.1, 196.8 ppm. MS (ESI) m/z (%): 331 (100, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. For: C<sub>21</sub>H<sub>14</sub>O<sub>2</sub>S [M+H]<sup>+</sup>: 331.0787; Found: 331.0786.

### 7-Benzoyl-5*H*-benzo[*b*]naphtho[2,3-*g*]thiocin-5-one (9e)



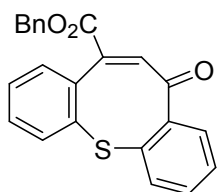
Yield: 83%; yellow solid; m.p. 204-205 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 6.99 (s, 1H, Ar-*H*), 7.31-7.34 (m, 1H, Ar-*H*), 7.45-7.52 (m, 5H, Ar-*H*), 7.56-7.59 (m, 1H, Ar-*H*), 7.73-7.76 (m, 2H, Ar-*H*), 7.79 (dd, *J*= 8.0, 1.0 Hz, 1H, Ar-*H*), 7.83 (d, *J*= 8.0 Hz, 1H, Ar-*H*), 8.10-8.12 (m, 2H, Ar-*H*), 8.16 (s, 1H, Ar-*H*), 8.31 (s, 1H, =CH) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 127.4, 127.7, 127.9, 128.0, 128.4, 128.7, 129.4, 130.3, 130.7, 131.7, 132.5, 132.9, 133.1, 133.4, 133.6, 136.0, 136.7, 137.0, 137.4, 139.1, 140.6, 142.7, 194.8, 195.5 ppm. MS (ESI) m/z (%): 393 (100, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. For: C<sub>26</sub>H<sub>16</sub>O<sub>2</sub>S [M+H]<sup>+</sup>: 393.0944; Found: 393.0942.

### 7-Ethoxycarbonyl-5*H*-dibenzo[*b,g*]thiocine-5-one (11a)



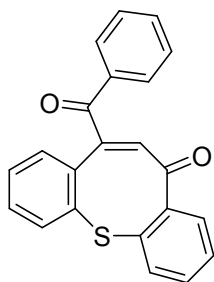
Yield: 270mg, 87%; yellow solid; m.p. 135-136 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.32 (t, *J* = 7.5 Hz, 3H, Me), 4.28-4.34 (m, 2H, CH<sub>2</sub>), 7.24-7.27 (m, 1H, Ar-*H*), 7.29-7.32 (m, 1H, Ar-*H*), 7.38-7.45 (s, 3H, Ar-*H*), 7.50 (dd, *J* = 7.5, 1.5Hz, 1H, Ar-*H*), 7.66-7.68 (m, 2H, Ar-*H*), 7.75(dd, *J* = 8.0, 1.5Hz, 1 H, Ar-*H*)ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 14.1, 61.7, 127.4, 129.5, 129.7, 130.1131.4, 131.9, 132.5, 132.6, 135.8, 136.3, 136.4, 139.5, 140.7, 140.8, 165.0, 195.7 ppm. MS (ESI) *m/z* (%): 311 (95, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. For: C<sub>18</sub>H<sub>14</sub>O<sub>3</sub>S [M+H]<sup>+</sup>: 311.0736; Found: 311.0731.

### 7-Benzoxycarbonyl-5*H*-dibenzo[*b,g*]thiocine-5-one (11b)



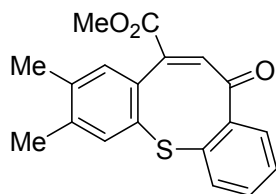
Yield: 272mg, 73%; yellow solid; m.p. 177-178 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 5.33 (q, *J* = 12 Hz, 2H, CH<sub>2</sub>), 7.25-7.28 (m, 1H, Ar-*H*), 7.29-7.32 (m, 1H, Ar-*H*), 7.34-7.45 (m, 7H, Ar-*H*), 7.52 (s, 1H, =CH), 7.55 (dd, *J* = 7.5, 1.5Hz 1H, Ar-*H*), 7.68-7.71 (m, 2H, Ar-*H*), 7.78(dd, *J* = 7.5, 1.5Hz, 1H, Ar-*H*)ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 67.2, 127.3, 127.9, 128.2, 128.4, 129.4, 129.6, 129.9, 131.3, 131.8, 132.4, 132.6, 135.3, 135.4, 136.2, 139.8, 140.5, 140.6, 164.7, 195.4ppm. MS (ESI) *m/z* (%):373 (100, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. For: C<sub>23</sub>H<sub>16</sub>O<sub>3</sub>S [M+H]<sup>+</sup>: 373.0893; Found: 373.0888.

### 7-Benzoyl-5*H*-dibenzo[*b,g*]thiocine-5-one (11c)



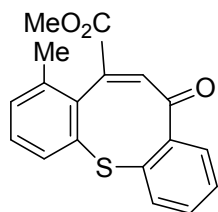
Yield: 274mg, 80%; yellow solid; m.p. 188-189 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 6.86 (s, 1H, =CH), 7.24-7.28 (m, 1H, Ar-*H*), 7.29-7.33 (m, 1H, Ar-*H*), 7.37-7.40 (m, 1H, Ar-*H*), 7.43-7.47 (m, 3H, Ar-*H*), 7.53-7.60 (m, 1H, Ar-*H*), 7.65 (dd, *J* = 7.5, 1.5 Hz, 1H, Ar-*H*), 7.72 (m, 2H, Ar-*H*), 7.76 (dd, *J* = 7.5, 1.5 Hz, 1H, Ar-*H*), 8.02-8.04 (m, 2H, Ar-*H*) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 127.6, 128.4, 129.5, 129.6, 130.0, 131.6, 132.3, 132.7, 132.8, 132.9, 136.3, 136.6, 137.0, 138.6, 140.3, 140.8, 142.2, 194.4, 195.0 ppm. MS (ESI) *m/z* (%): 343 (100, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. For: C<sub>22</sub>H<sub>14</sub>O<sub>2</sub>S [M+H]<sup>+</sup>: 343.0787; Found: 343.0781.

### 7-Methoxycarbonyl-9,10-dimethyl-5*H*-dibenzo[*b,g*]thiocine-5-one (11d)



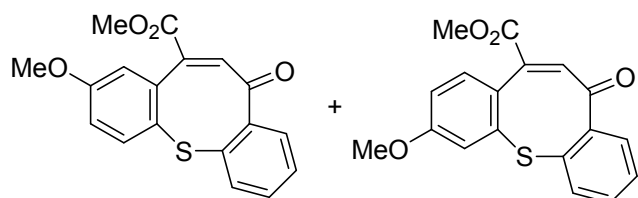
Yield: 165 mg, 51% yield, yellow solid: m.p. 152-154°C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 2.17 (s, 3H, Me), 2.25 (s, 3H, Me), 3.85 (s, 3H, Me), 7.24 (s, 1H, Ar-*H*), 7.30 (td, *J* = 7.5, 1.5 Hz, 1H, Ar-*H*), 7.38 (s, 1H, Ar-*H*), 7.42-7.45 (m, 2H, Ar-*H*), 7.65 (dd, *J* = 7.5, 1.0 Hz, 1 H, Ar-*H*), 7.74 (dd, *J* = 7.5, 1.5 Hz, 1 H, Ar-*H*) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 196.4, 166.0, 141.7, 139.7, 139.5, 138.8, 138.3, 137.3, 136.6, 135.9, 132.7, 131.9, 131.6, 130.6, 129.6, 127.4, 52.9, 19.9, 19.5 ppm. MS (ESI) *m/z* (%): 325 (80, [M+H]<sup>+</sup>); HRMS (ESI): calcd. for C<sub>19</sub>H<sub>17</sub>O<sub>3</sub>S [M+H]<sup>+</sup> 325.0898, Found: 325.0892.

### 7-Methoxycarbonyl-8-methyl-5H-dibenzo[b,g]thiocine-5-one (11e)



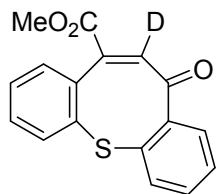
Yield: 54% yield, yellow solid: m.p. 148-150°C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 2.45 (s, 3H, Me), 3.86 (s, 3H, Me), 7.21 (dd, *J* = 7.5, 1.0 Hz, 1H, *Ar-H*), 7.27 (t, *J* = 7.5 Hz, 1H, *Ar-H*), 7.31-7.33 (m, 1H, *Ar-H*), 7.35 (dd, *J* = 7.5, 1.0 Hz 1H, *Ar-H*), 7.40 (s, 1H, *Ar-H*), 7.46 (td, *J* = 7.5, 1.5 Hz, 1H, *Ar-H*) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 21.9, 52.7, 127.1, 127.6, 129.4, 131.1, 131.7, 132.2, 132.6, 132.9, 136.8, 137.3, 139.3, 139.8, 141.152, 143.8, 165.8, 195.7 ppm. MS (ESI) *m/z* (%): 311 (95, [M+H]<sup>+</sup>); HRMS (ESI): calcd. for C<sub>18</sub>H<sub>14</sub>O<sub>3</sub>S [M+H]<sup>+</sup> 311.0664, Found: 311.0661.

### 7-Methoxycarbonyl-9-methoxy-5H-dibenzo[b,g]thiocine-5-one (11f) and 7-Methoxycarbonyl-10-methoxy-5H-dibenzo[b,g]thiocine-5-one (11f')



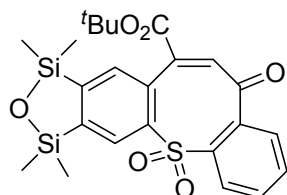
Yield: (1:1.2) 56% yield, yellow solid: m.p. 160-161°C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 3.75 (s, 3H, Me), 3.80 (s, 3.7H, Me), 3.85 (s, 3H, Me), 3.86 (s, 3.7H, Me), 6.80 (dd, *J* = 8.5, 2.5 Hz, 1.2H, *Ar-H*), 6.96 (dd, *J* = 8.5, 2.5 Hz, 1H, *Ar-H*), 6.98 (d, *J* = 3.0 Hz, 1.2H, *Ar-H*), 7.20 (d, *J* = 2.5 Hz, 1H, *Ar-H*), 7.29-7.35 (m, 2.3 H, *Ar-H*), 7.40-7.47 (m, 5.5 H, *Ar-H*), 7.57 (d, *J* = 8.5 Hz, 1.2H, *Ar-H*), 7.63 (dd, *J* = 8.0, 1.0 Hz, 1.2H, *Ar-H*), 7.67 (dd, *J* = 8.0, 1.0 Hz, 1H, *Ar-H*), 7.73 (dd, *J* = 8.0, 1.0 Hz, 1.2H, *Ar-H*), 7.77 (dd, *J* = 8.0, 1.5 Hz, 1H, *Ar-H*) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 52.68, 52.7, 55.4, 55.5, 114.3, 115.9, 116.8, 120.6, 123.8, 127.2, 127.6, 130.6, 131.4, 131.45, 131.5, 132.0, 132.5, 132.7, 132.9, 133.7, 135.3, 135.7, 136.2, 136.5, 137.6, 139.4, 139.9, 140.6, 141.9, 142.2, 159.9, 160.6, 165.5, 165.9, 195.8, 196.0 ppm. MS (ESI) *m/z* (%): 327 (90, [M+H]<sup>+</sup>); HRMS (ESI): calcd. for C<sub>18</sub>H<sub>14</sub>O<sub>4</sub>S [M+H]<sup>+</sup> 327.0613, Found: 327.0608.

### 7-Methoxycarbonyl--5*H*-dibenzo[*b,g*]thiocine-5-one ([D]-11g)



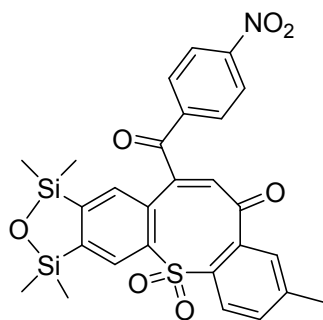
Yield: 226 mg, 76% yield, yellow solid; m.p. 146-147°C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 3.84 (s, 3H, Me), 7.26 (td, *J* = 8.0, 1.5 Hz, 1H, Ar-H), 7.31 (td, *J* = 7.5, 1.0 Hz, 1H, Ar-H), 7.38-7.42 (m, 1.33H), 7.43-7.45 (m, 1H, Ar-H), 7.50 (dd, *J* = 7.5, 1.0 Hz, 1H, Ar-H), 7.66-7.69 (m, 2H, Ar-H), 7.75-7.77 (m, 1H, Ar-H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 195.7, 165.7, 140.9, 140.8, 140.7, 139.9, 139.6 (t, *J* = 25 Hz), 136.49, 136.47, 136.4, 135.7, 135.6, 132.8, 132.69, 132.66, 132.1, 132.0, 131.6, 130.1, 129.82, 129.81, 129.7, 127.6, 52.8 ppm. MS (ESI) *m/z* (%): 298 (70, [M+H]<sup>+</sup>); HRMS (ESI): calcd. for C<sub>17</sub>H<sub>12</sub>DO<sub>3</sub>S [M+H]<sup>+</sup> 298.0643, Found: 298.0641.

### 7-Tert-butoxycarbonyl-9,10-oxadisilole-5*H*-dibenzo[*b,g*]thiocine-5-one-12,12-dioxide (12a)



Yield: 84%; white solid; m.p. 207-209 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.23 (s, 3H, SiMe), 0.28 (s, 3H, SiMe<sub>2</sub>), 0.32 (s, 3H, SiMe), 0.34 (s, 3H, SiMe), 1.50 (s, 9H, Bu), 7.30 (td, *J* = 7.5, 1.0 Hz, 1H, Ar-H), 7.60-7.61 (m, 2H, Ar-H), 7.81 (td, *J* = 7.5, 1.0 Hz, 1H, Ar-H), 7.88 (s, 1H, Ar-H), 7.37 (dd, *J* = 7.5, 1.0 Hz, 1H, Ar-H), 8.28 (dd, *J* = 8.0, 1.0 Hz, 1H, Ar-H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 0.66, 0.74, 0.8, 0.9, 27.9, 83.2, 122.2, 123.8, 129.9, 129.9, 131.5, 132.6, 133.0, 133.1, 134.7, 140.6, 145.7, 149.3, 150.41, 150.44, 163.4, 190.3 ppm. MS (ESI) *m/z* (%): 501 (100, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. for: C<sub>24</sub>H<sub>28</sub>O<sub>6</sub>SSi<sub>2</sub> [M+H]<sup>+</sup>: 501.1145; Found: 501.1139.

**3-Methyl-7-(*P*-nitrobenzoyl)-9,10-oxadisilole-5*H*-dibenzo[*b,g*]thiocine-5-one-12,12-dioxide (12b)**

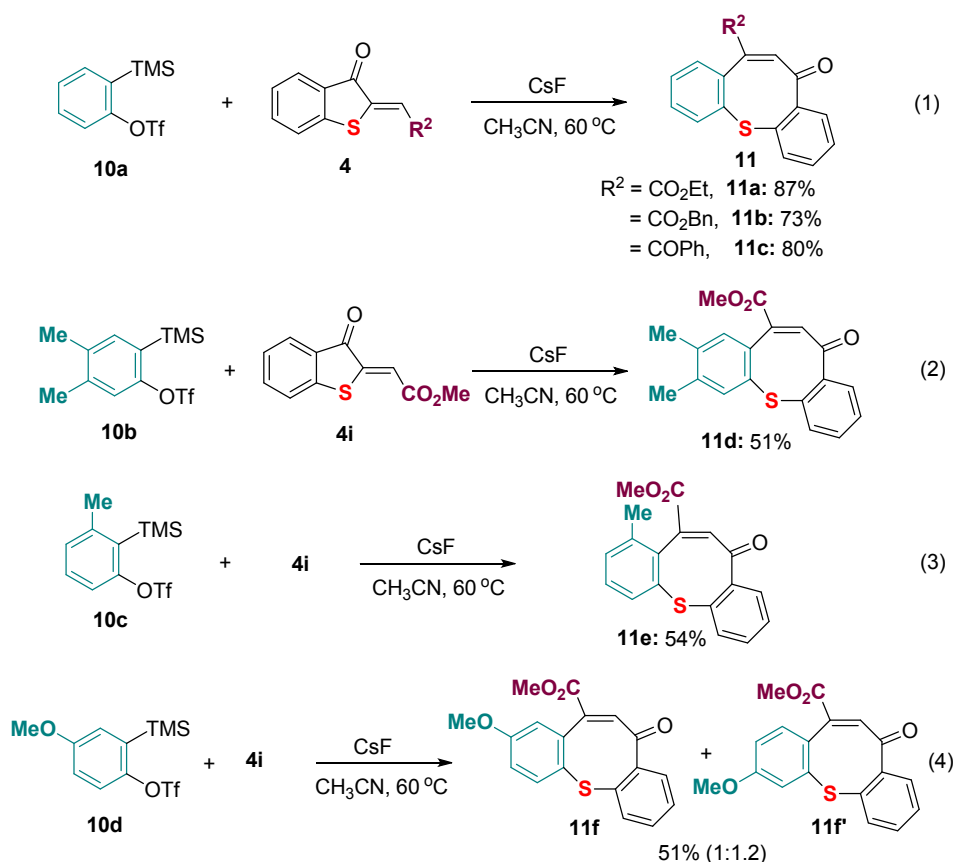


Yield: 79%; white solid; m.p. 211-212 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.27 (s, 3H, SiMe), 0.30 (s, 3H, SiMe), 0.33 (s, 3H, SiMe), 0.34 (s, 3H, SiMe), 2.41 (s, 3H, Me), 7.06 (s, 1H, Ar-*H*), 7.66 (dd, *J* = 8.0, 1.0 Hz, 1H, Ar-*H*), 7.75 (s, 1H, Ar-*H*), 7.89 (d, *J* = 1.0 Hz, 1H, Ar-*H*), 7.99 (d, *J* = 1.0 Hz, 1H, Ar-*H*), 8.14-8.16 (m, 2H, Ar-*H*), 8.20 (d, *J* = 8.5 Hz, 1H, Ar-*H*), 8.35-8.37 (m, 2H, Ar-*H*) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 0.7, 0.8, 20.9, 122.2, 123.9, 124.0, 129.0, 131.0, 131.7, 132.3, 132.5, 135.9, 137.4, 140.4, 140.7, 140.74, 146.12, 141.15, 150.4, 151.5, 151.7, 188.8, 192.6 ppm. MS (ESI) *m/z* (%): 564 (100, [M+H]<sup>+</sup>); HRMS (ESI): Calcd. For: C<sub>27</sub>H<sub>25</sub>O<sub>7</sub>SSi<sub>2</sub> [M+H]<sup>+</sup>: 564.0890; Found: 564.0884.



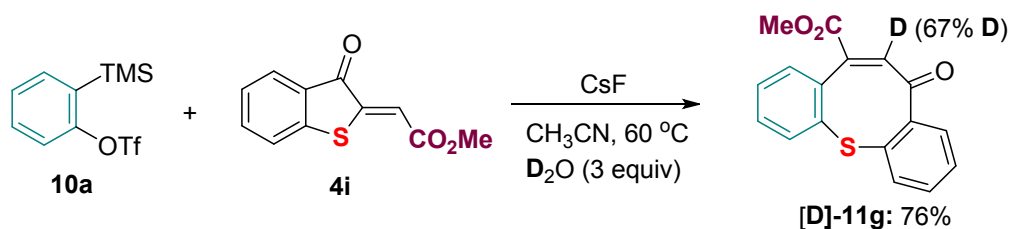
## 4 Control Experiments and Mechanistic Study

### a) Reactions with benzyne precursor ortho-(trimethylsilyl)aryl triflate

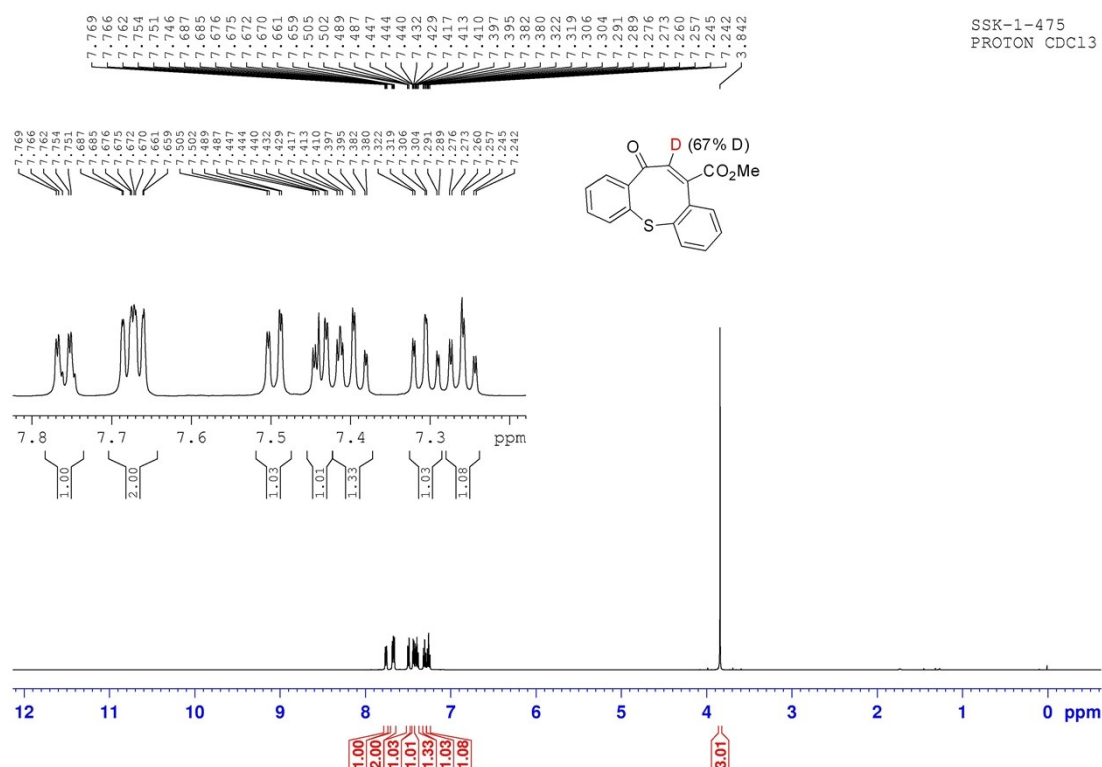


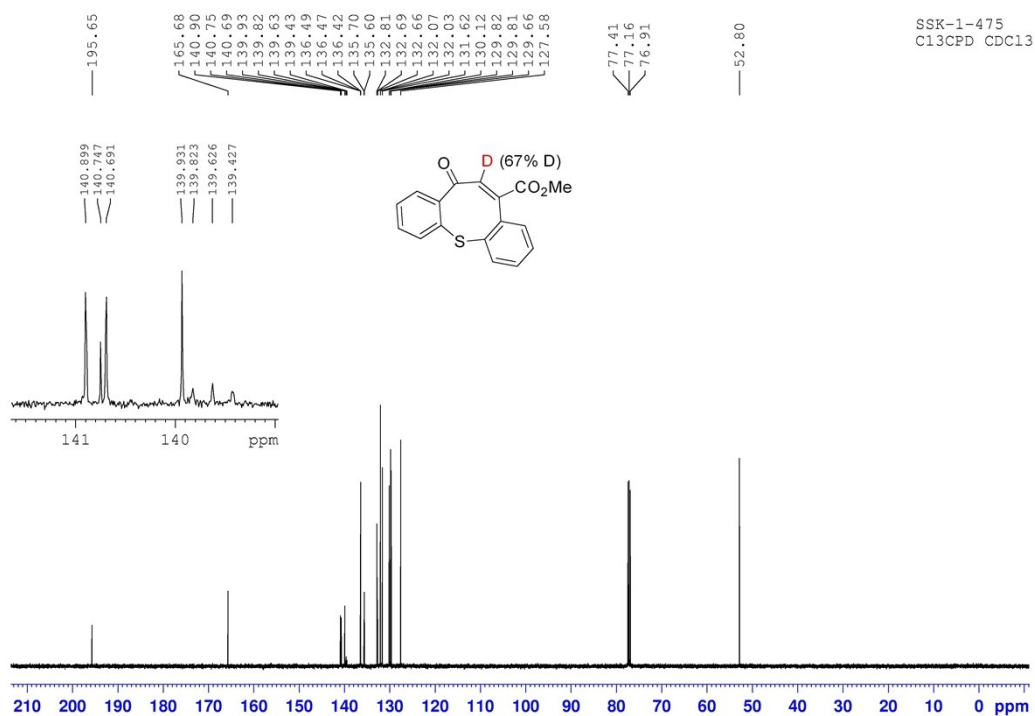
To a two neck flask containing 2-methylenebenzothiophene-3-ones **4** (1.0 mmol), CsF (3.0 mol) in was added MeCN (10 mL) and the reaction mixture was stirred for 5 minutes at room temperature, followed by the addition of benzyne precursor (ortho-(trimethylsilyl)aryl triflate) **10** (1.5 mmol) at the same temperature. The two neck flask was then placed in a preheated (60°C) oil bath. The progress of the reaction was monitored by TLC. After completion of the reaction, MeCN was evaporated on a rotary evaporator. The crude products obtained were purified by flash silica gel column chromatography using a gradient of ethyl acetate : petroleum ether to afford the corresponding products **11a-e**.

## b) Reaction with D<sub>2</sub>O under the optimal conditions

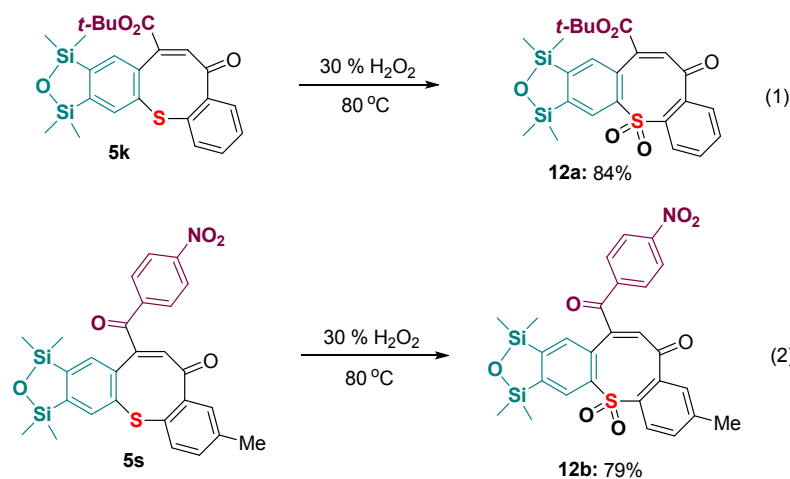


To a two neck flask containing 2-methylenebenzothiophene-3-ones **4i** (1.0 mmol), CsF (3.0 mol ) in was added MeCN (10 mL) and the reaction mixture was stirred for 5 minutes at room temperature, followed by the addition of benzyne precursor (ortho-(trimethylsilyl)aryl triflate) **10a** (1.5 mmol) and D<sub>2</sub>O (3 equiv) at the same temperature. The two neck flask was then placed in a preheated (60°C) oil bath. The progress of the reaction was monitored by TLC. After completion of the reaction, MeCN was evaporated on a rotary evaporator. The crude products obtained were purified by flash silica gel column chromatography using a gradient of ethyl acetate : petroleum ether to afford the corresponding products **[D]-11g**.





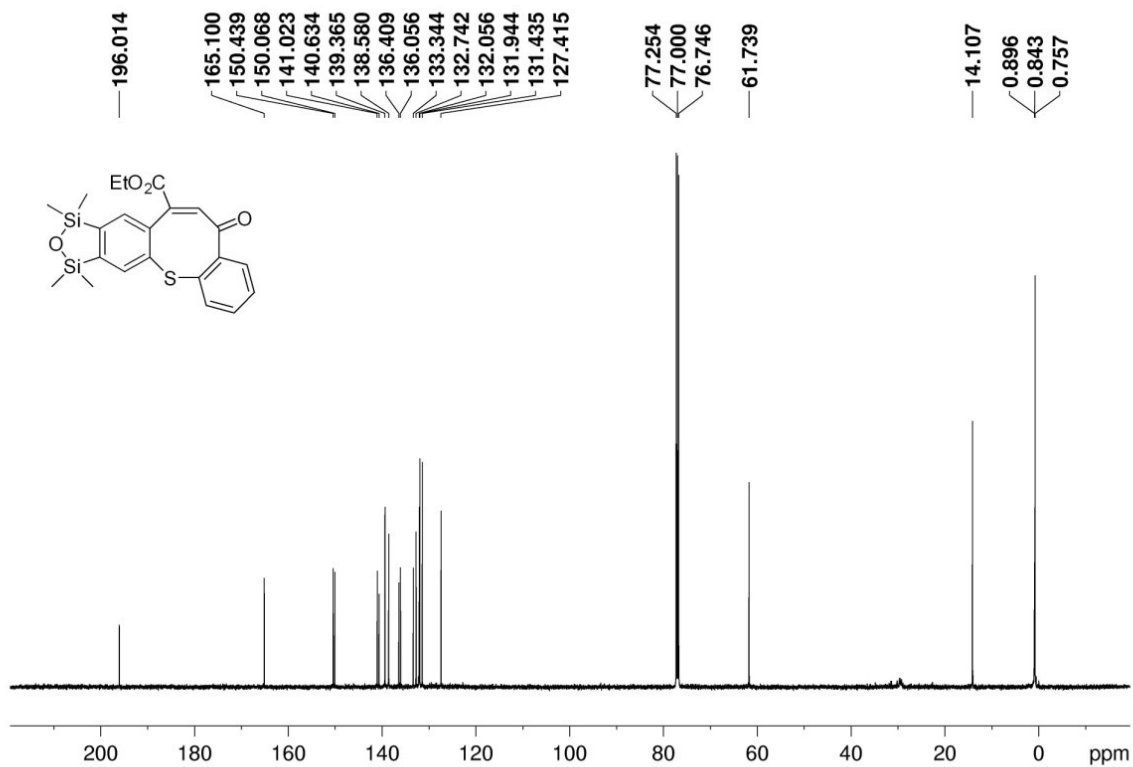
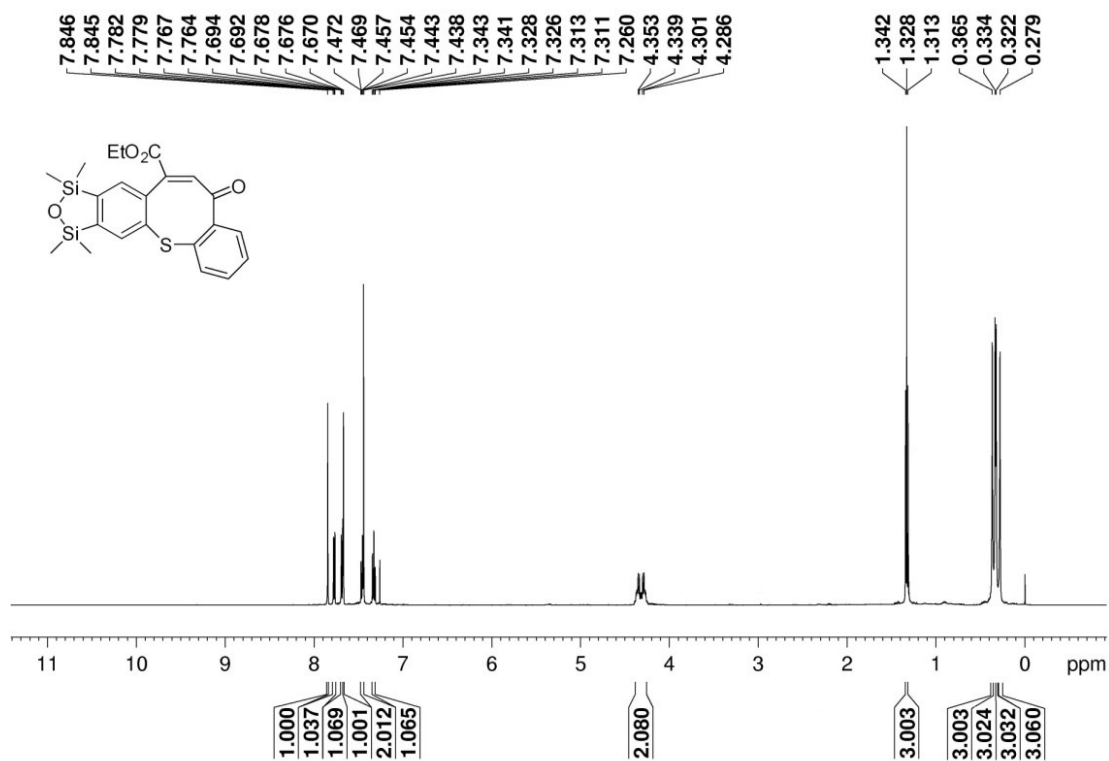
## 5 Further Application of the Products



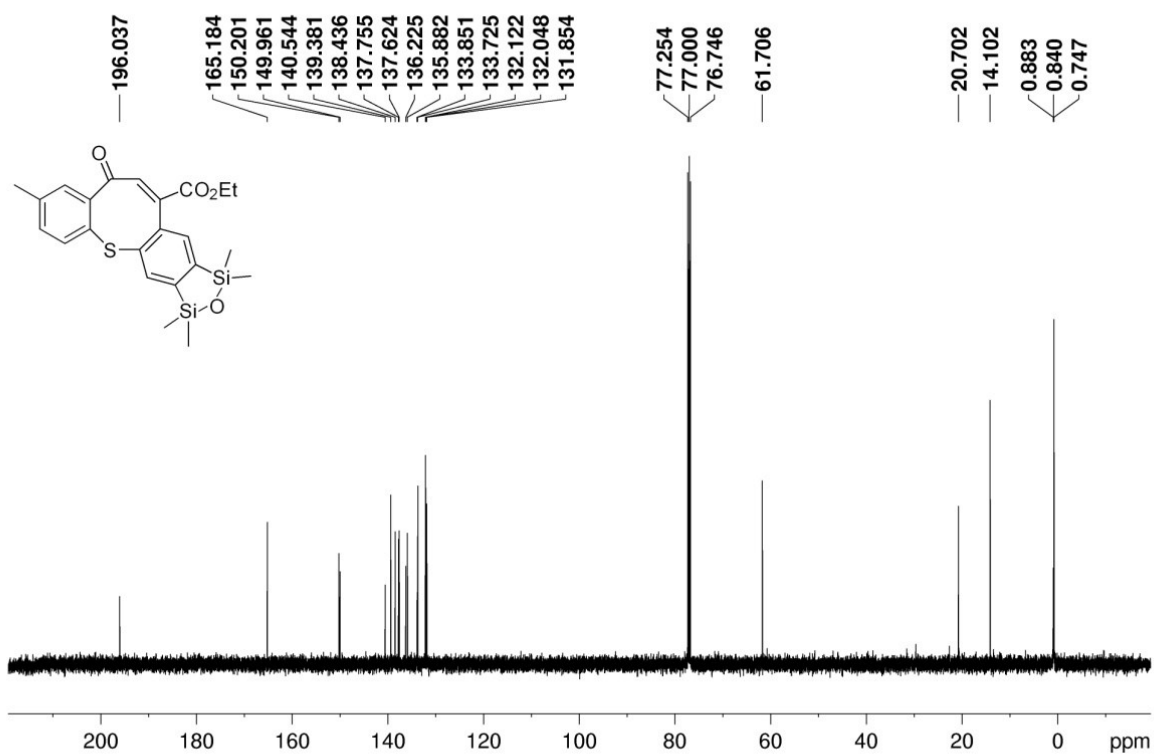
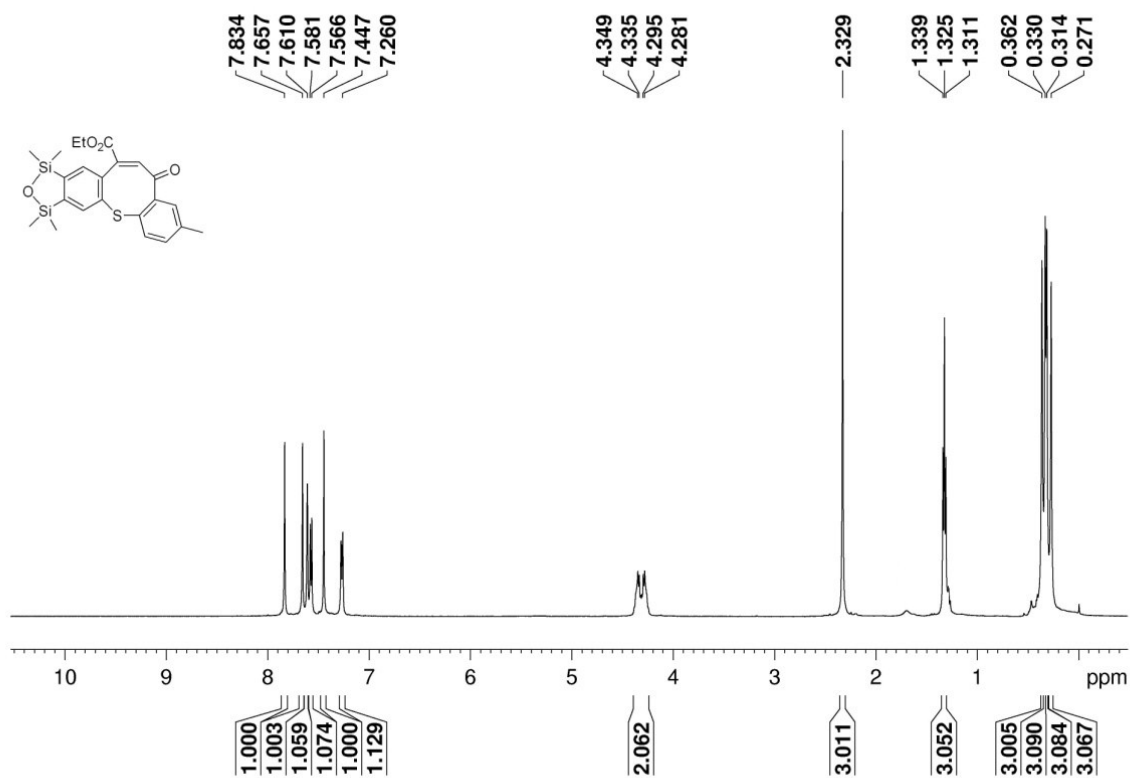
To a stirring solution of **5** (0.3 mmol,) in AcOH ( 5 mL) at 80 °C was slowly added H<sub>2</sub>O<sub>2</sub> (1.3 ml, 30% wt in H<sub>2</sub>O). The reaction mixture was refluxed for 0.5 h and was then left to cool to room temperature which resulted in the precipitation of pure product which was collected by filtration and washed with water. Further product can be precipitated by addition of more H<sub>2</sub>O to the filtrate. The product was dried at 70°C overnight to obtain pure product **12** as a white solid .

# 6 <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of All Compounds

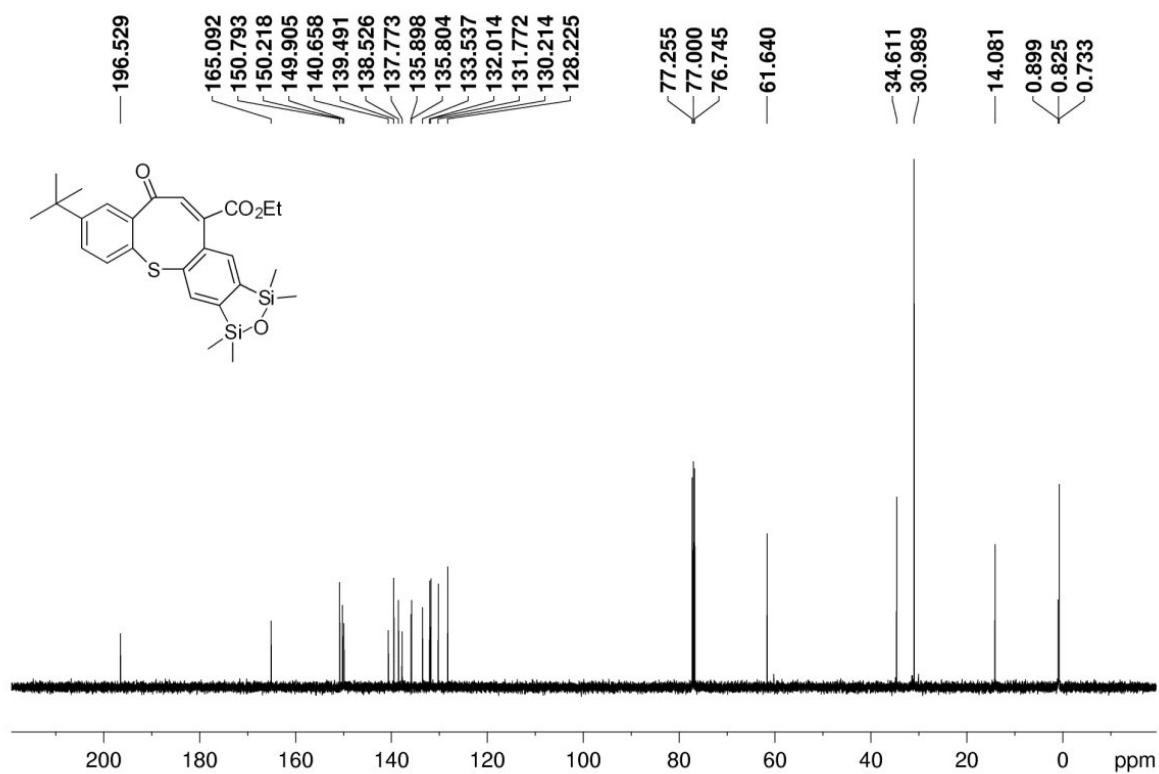
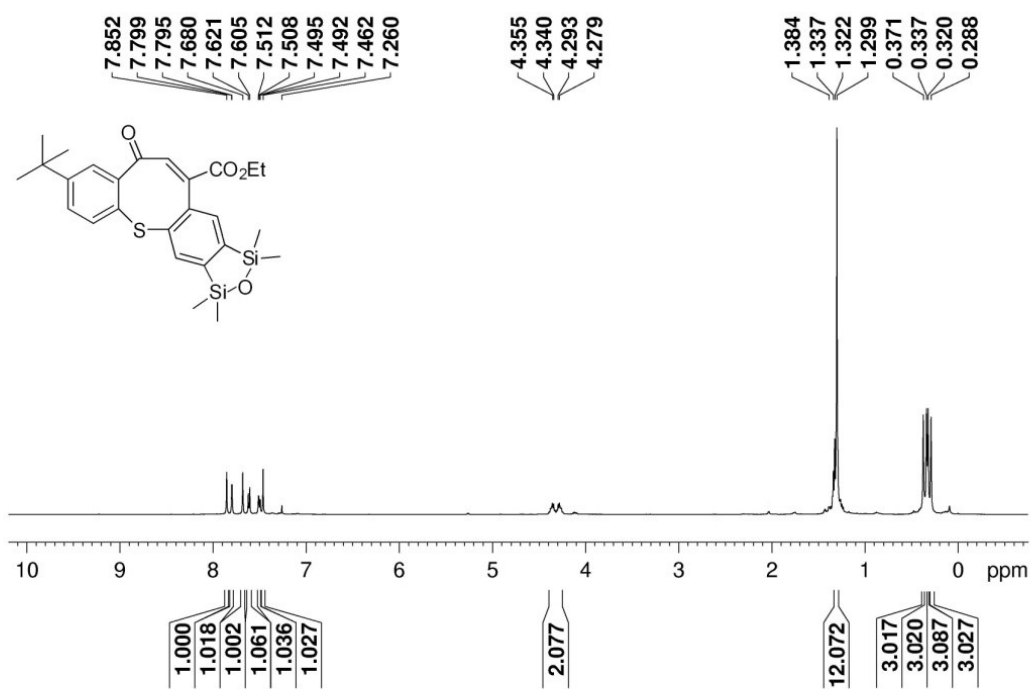
## Compound 5a



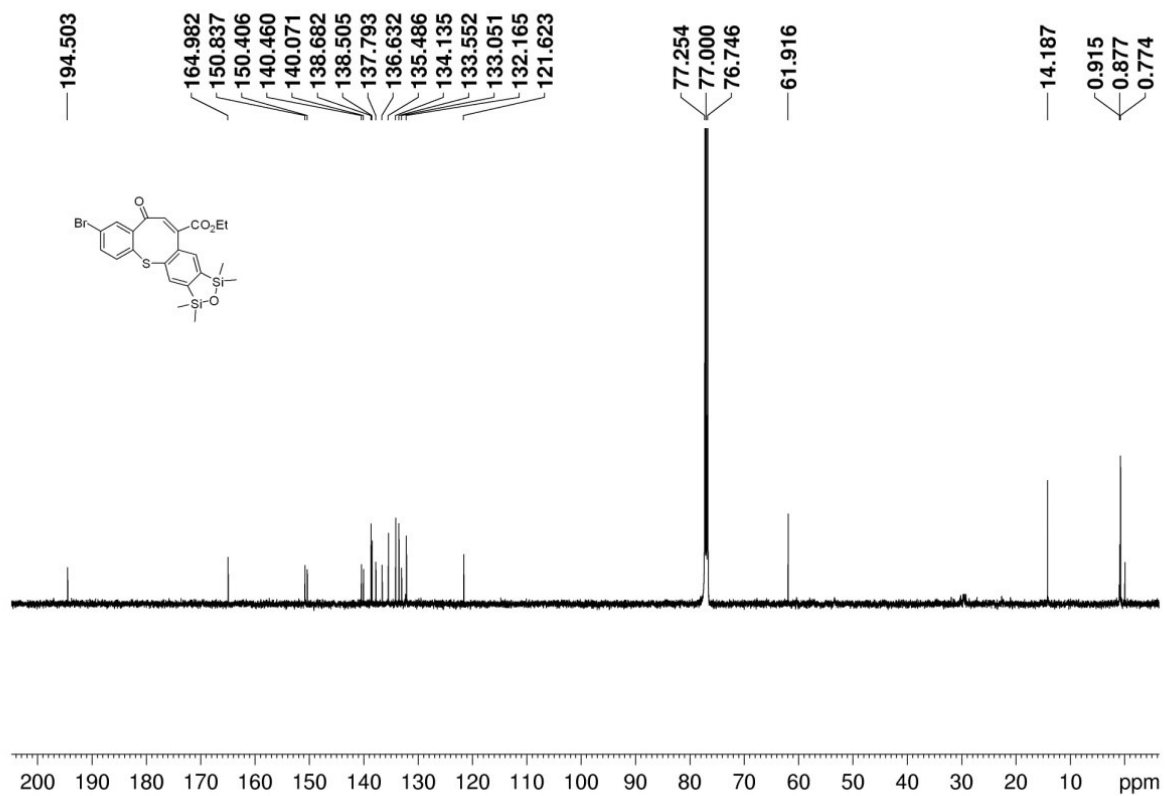
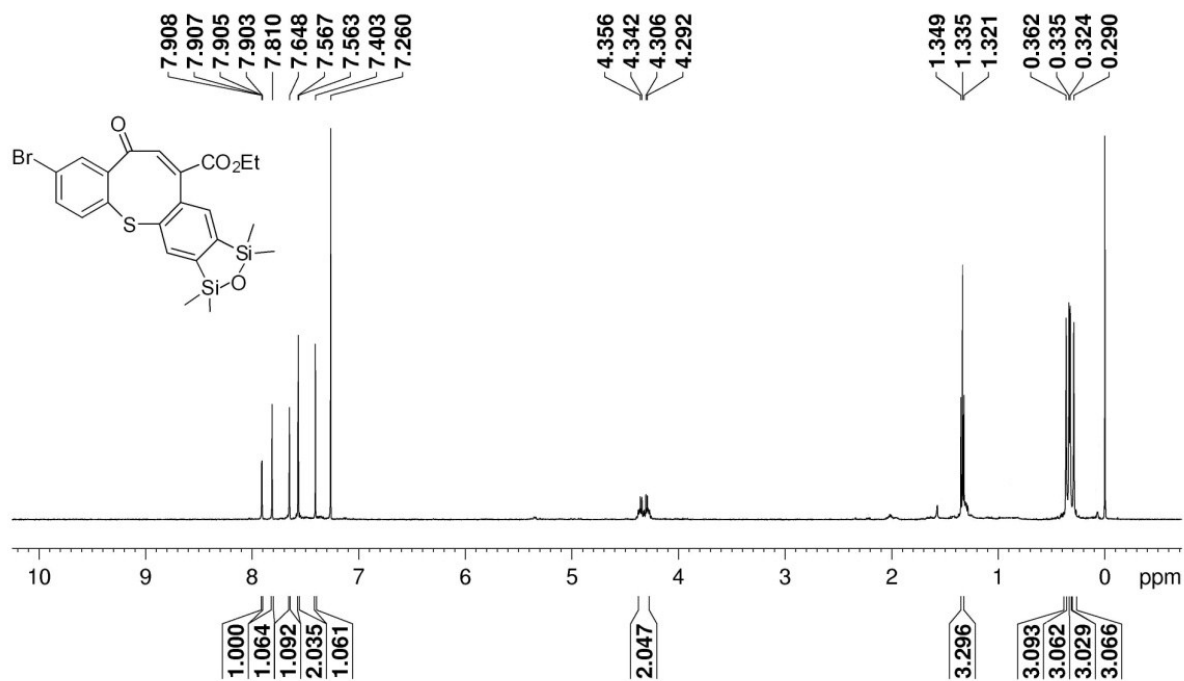
# Compound 5b



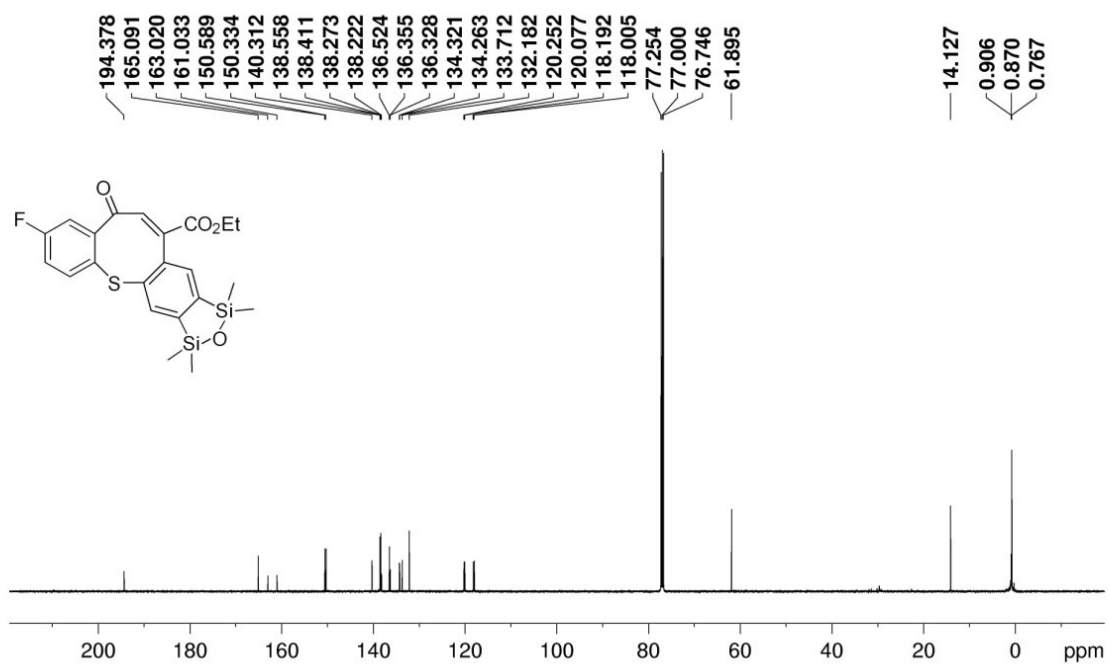
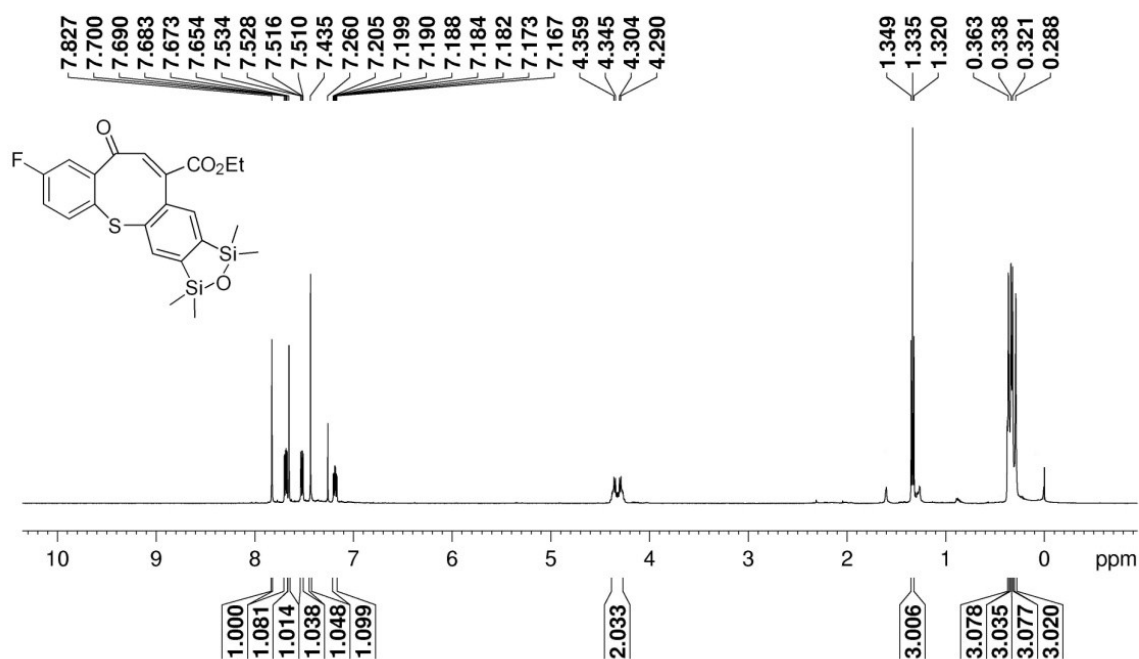
# Compound 5c



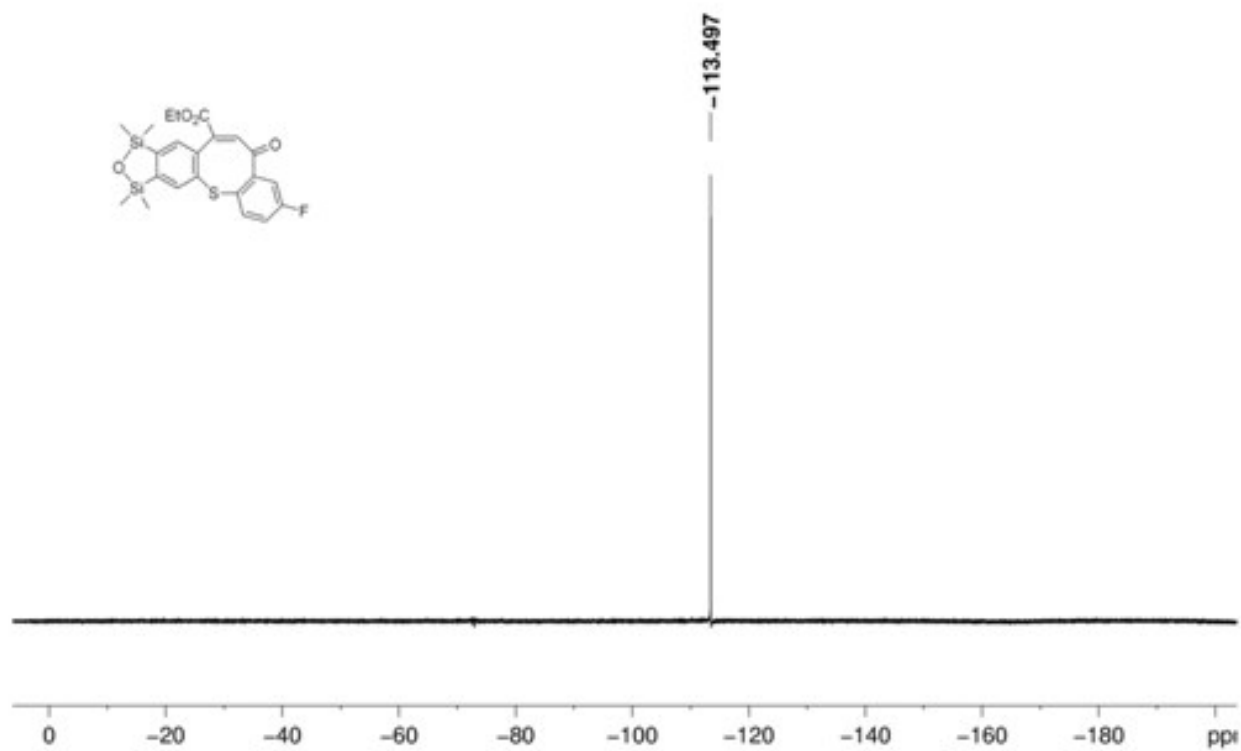
# Compound 5d



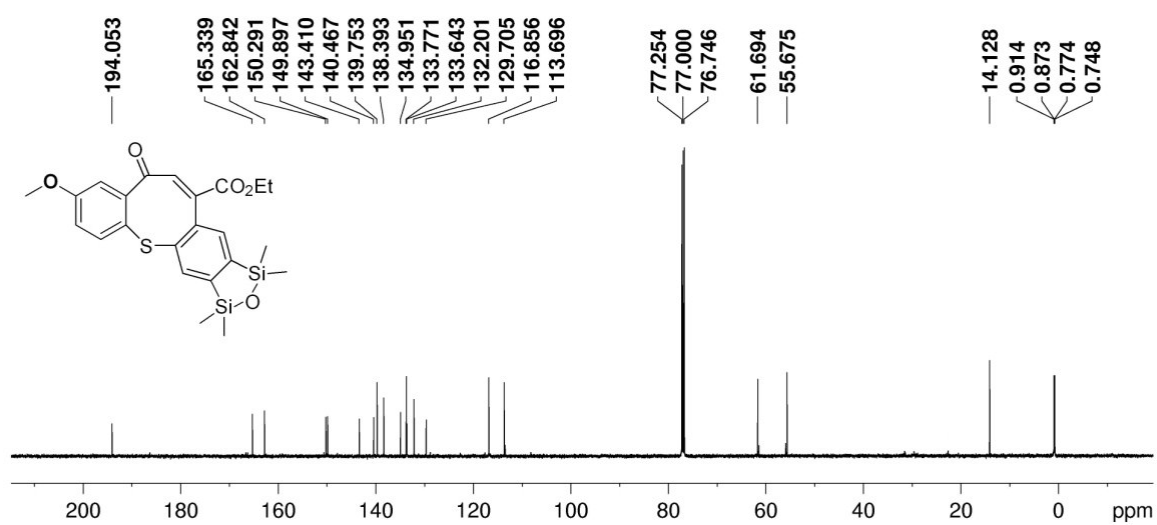
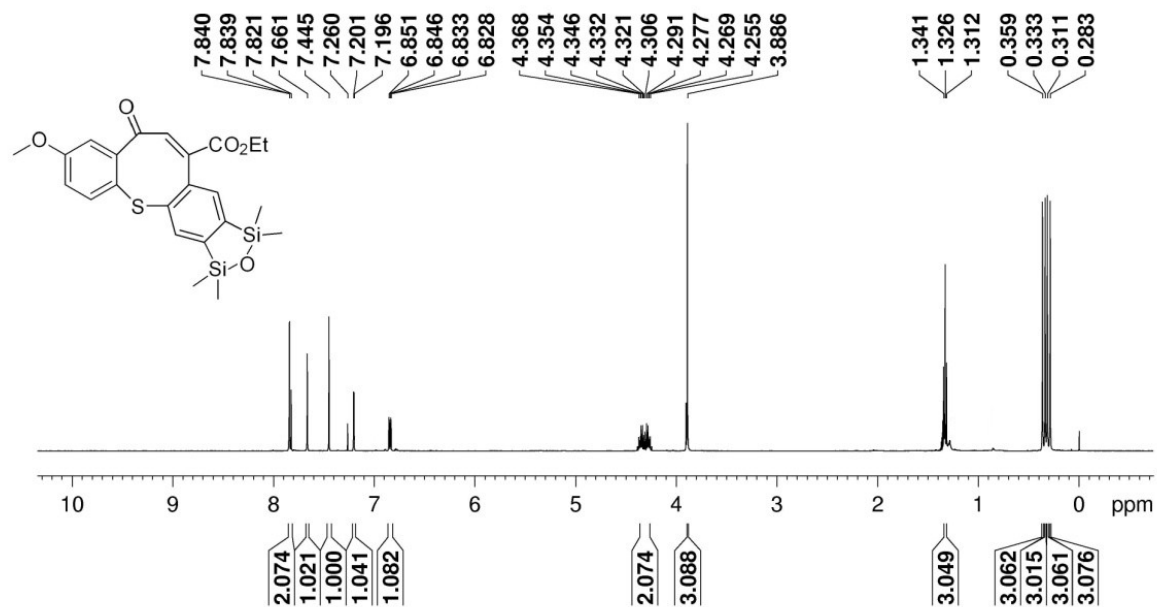
# Compound 5e



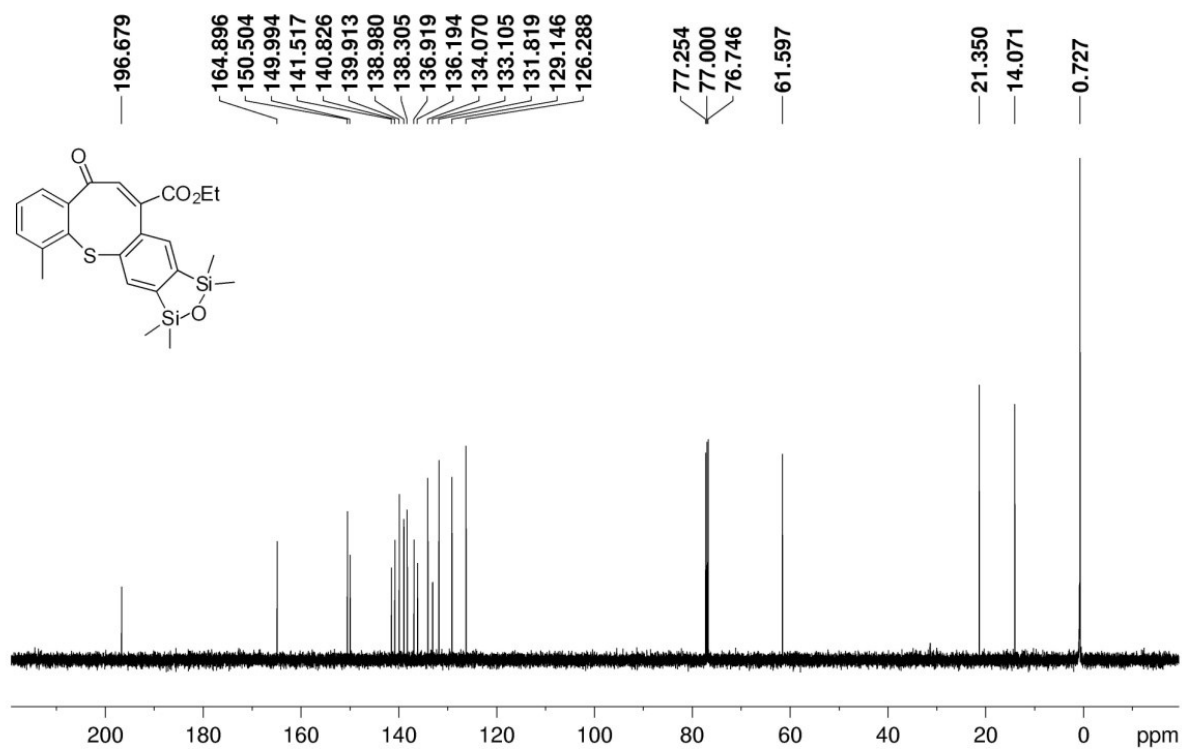
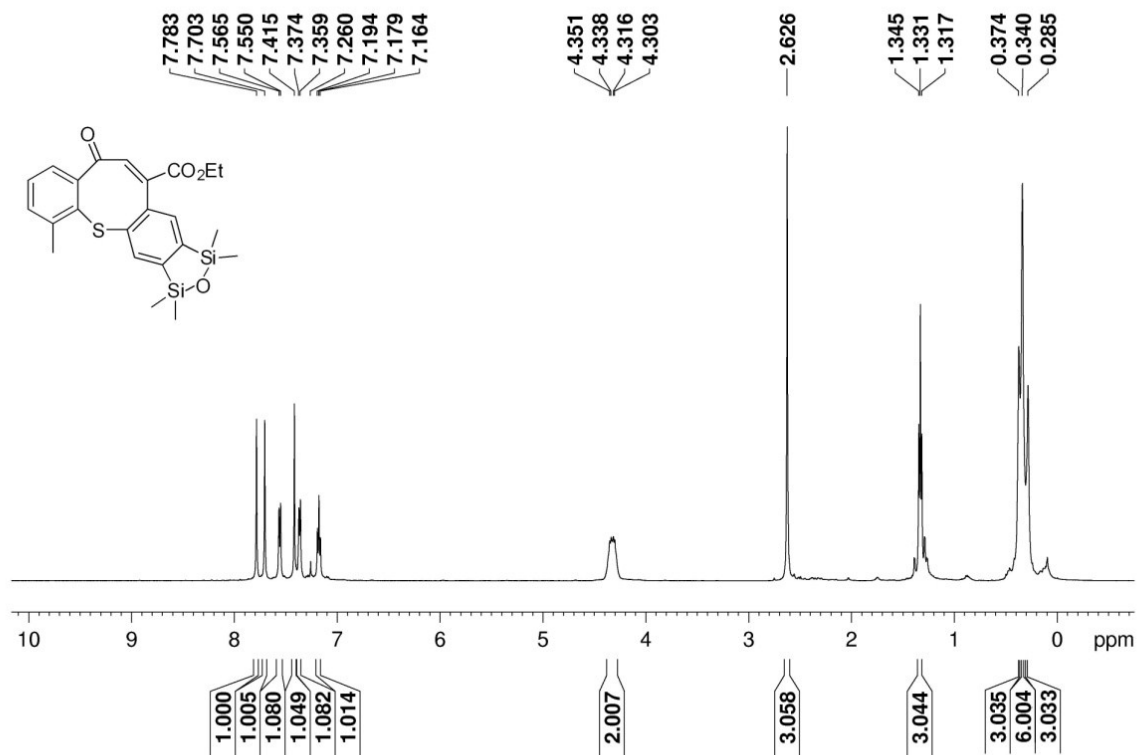




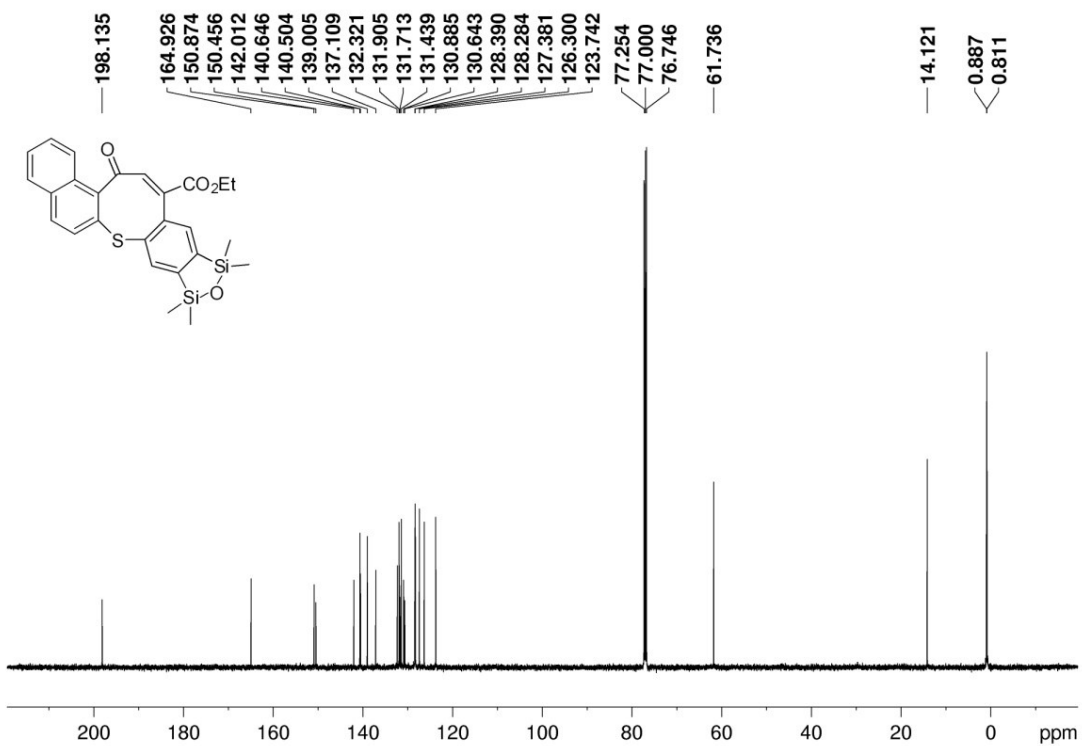
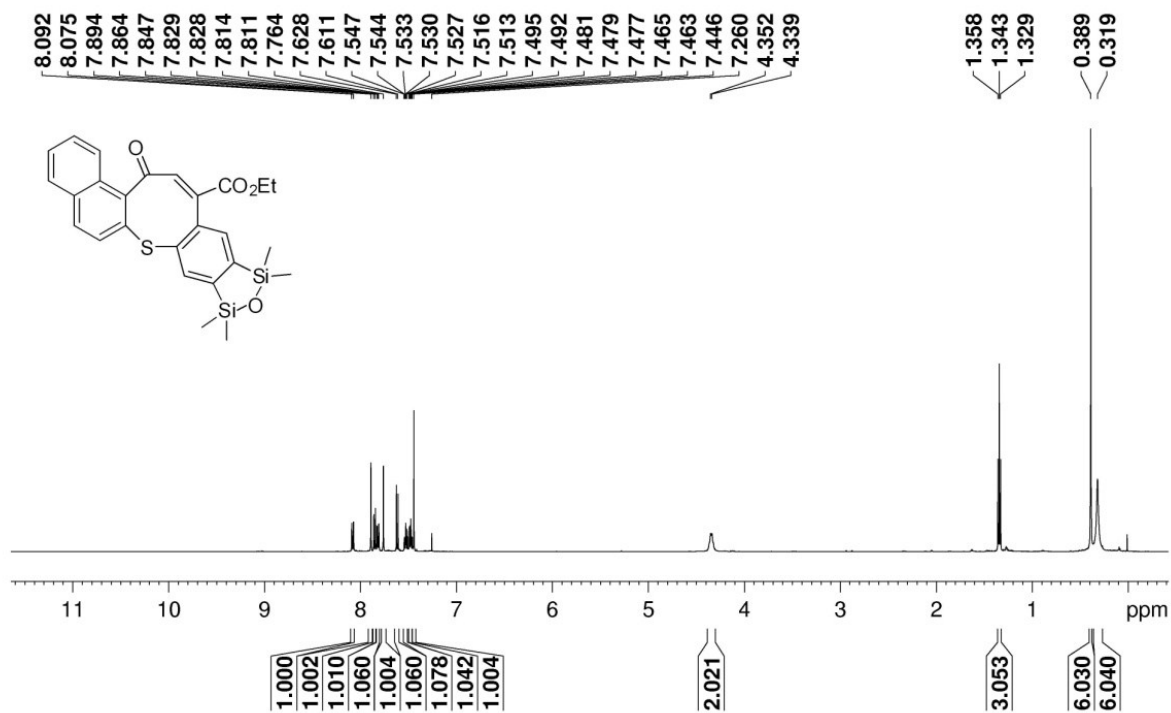
# Compound 5f



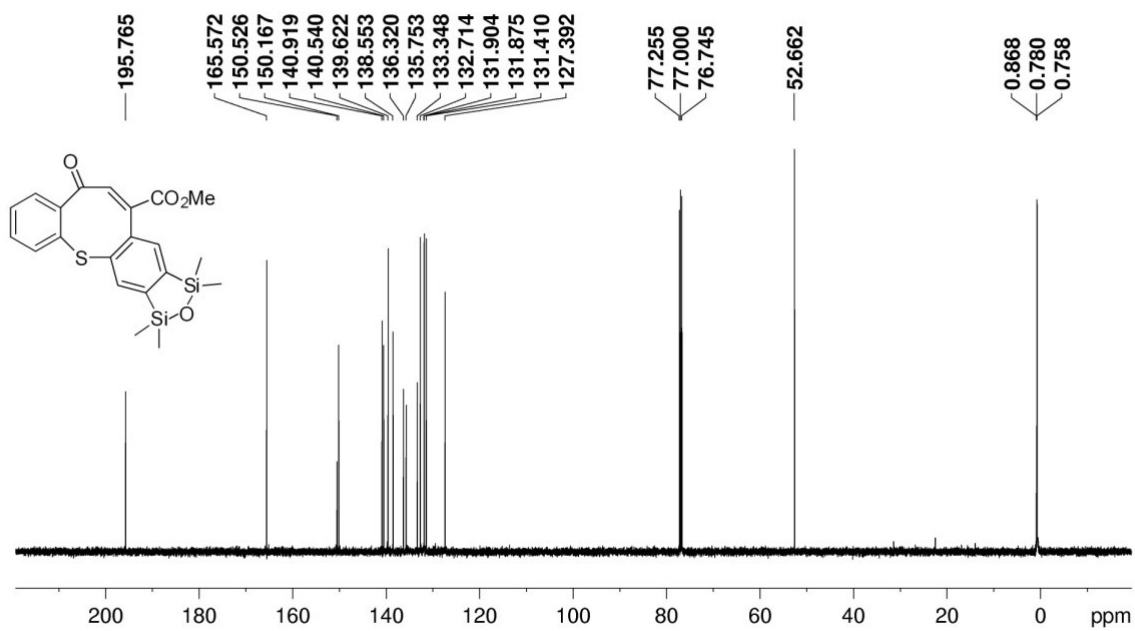
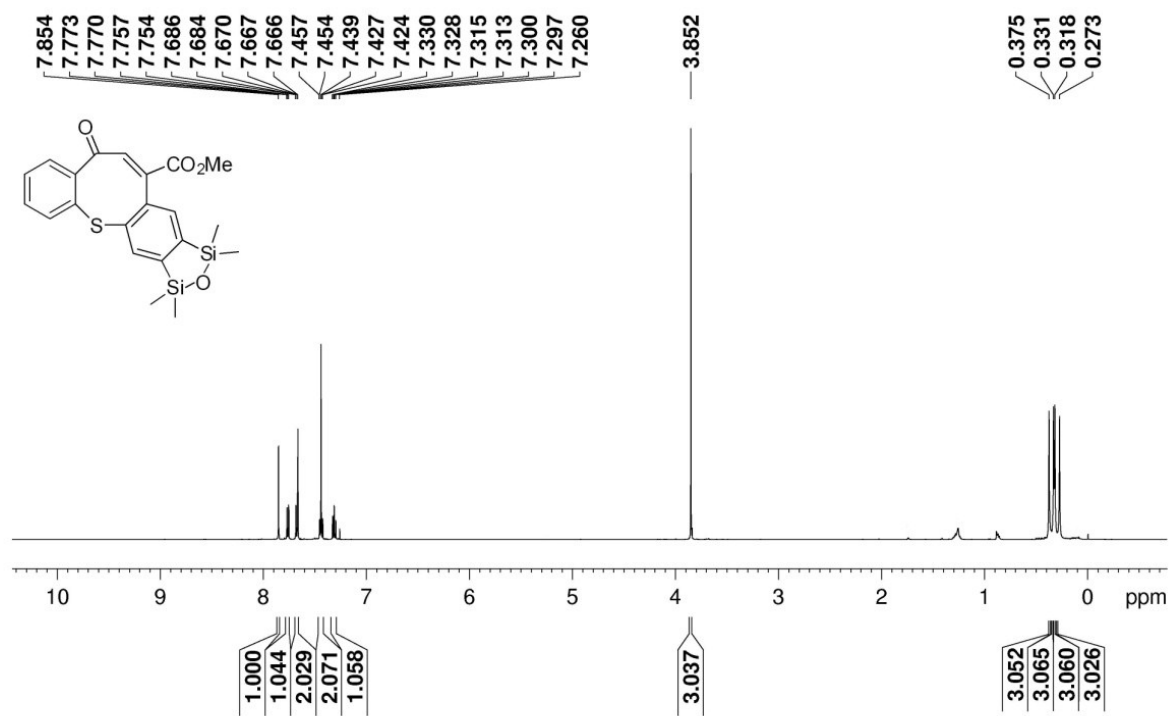
# Compound 5g



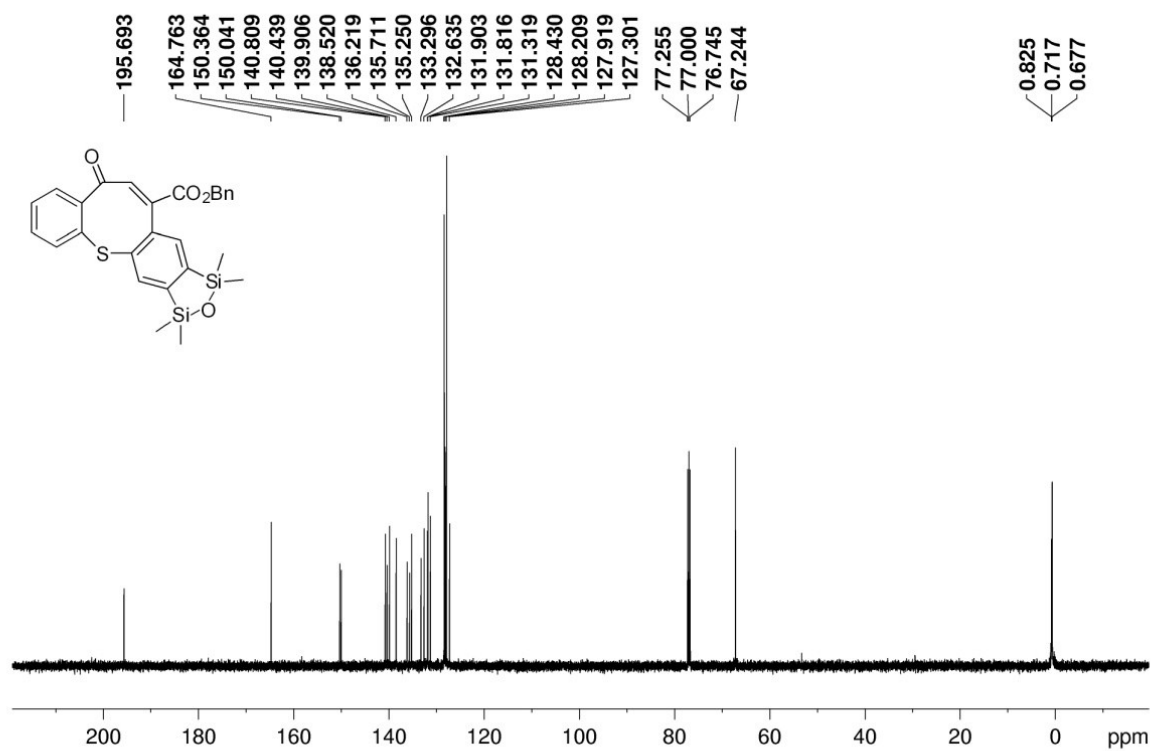
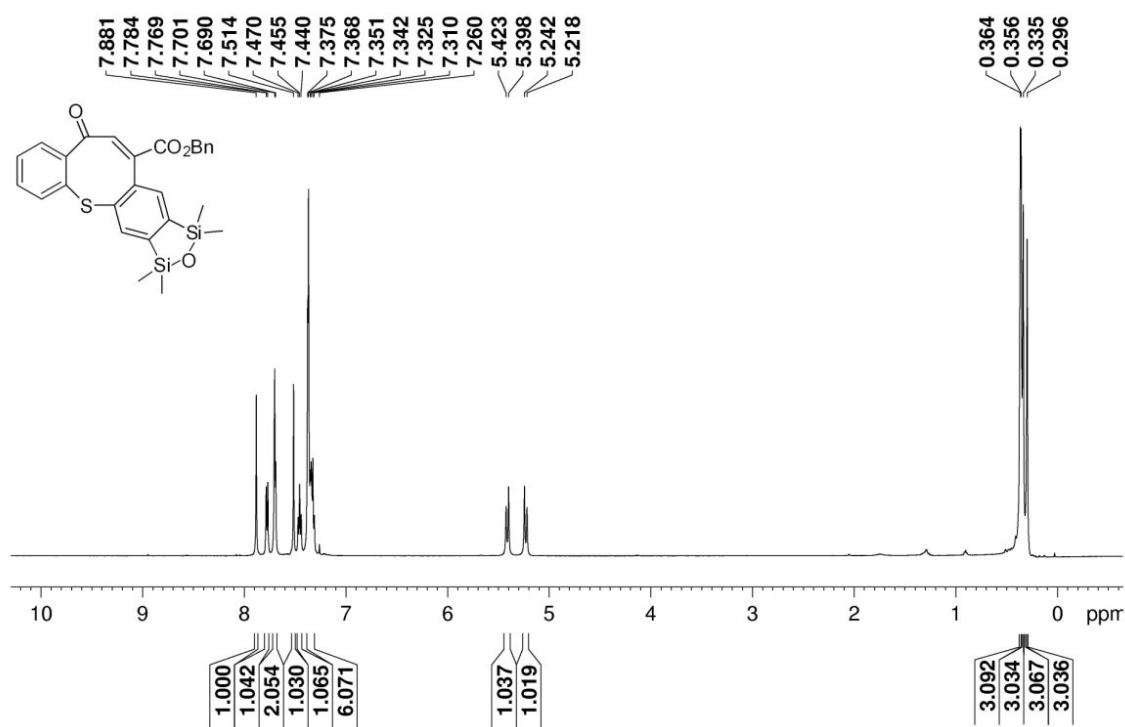
# Compound 5h



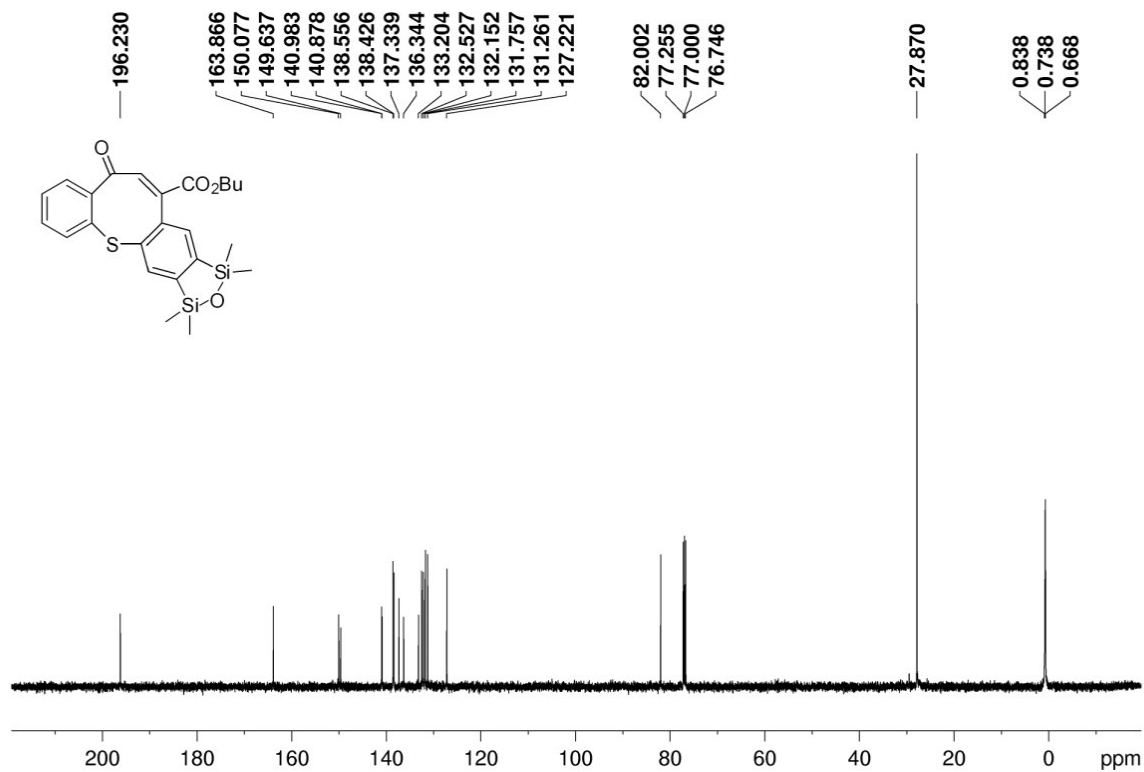
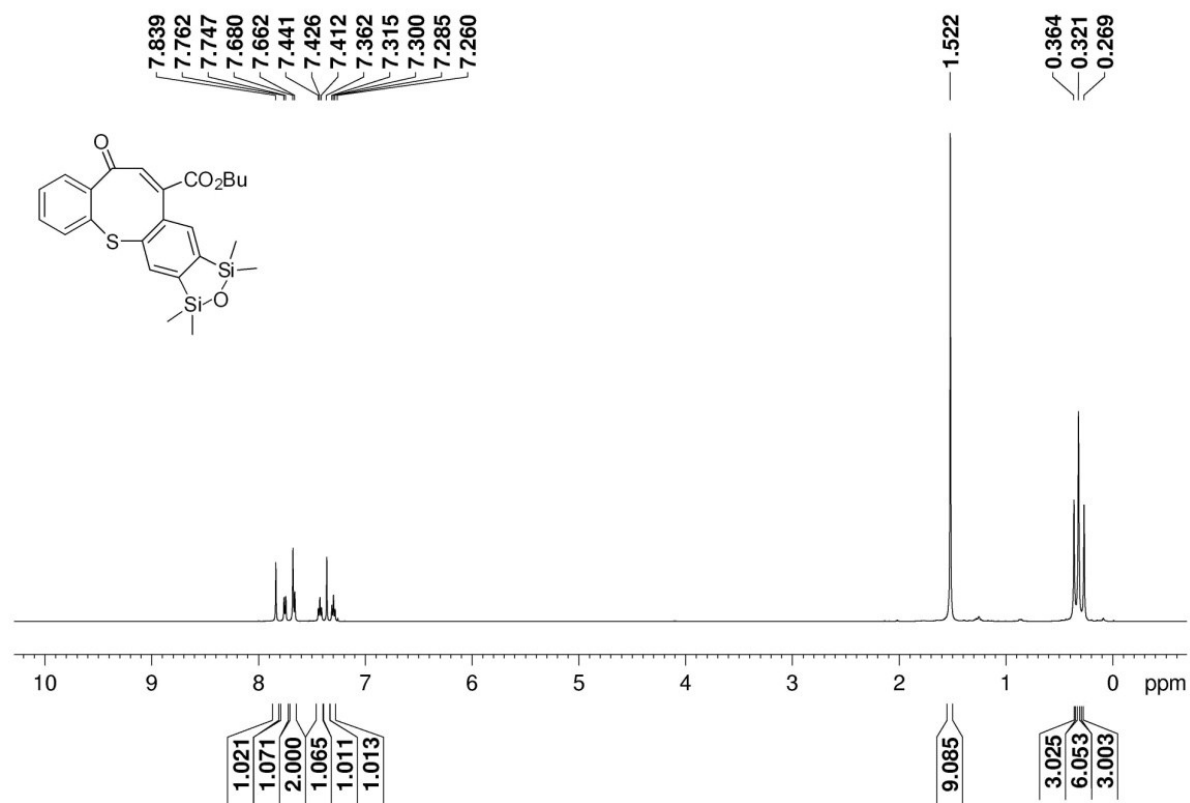
# Compound 5i



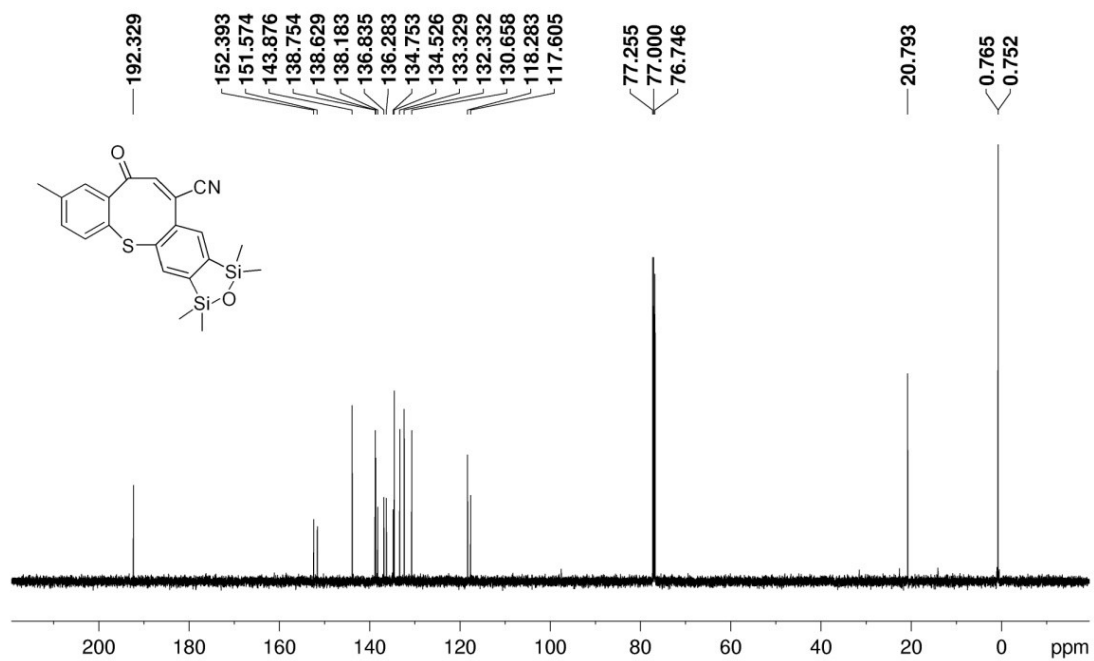
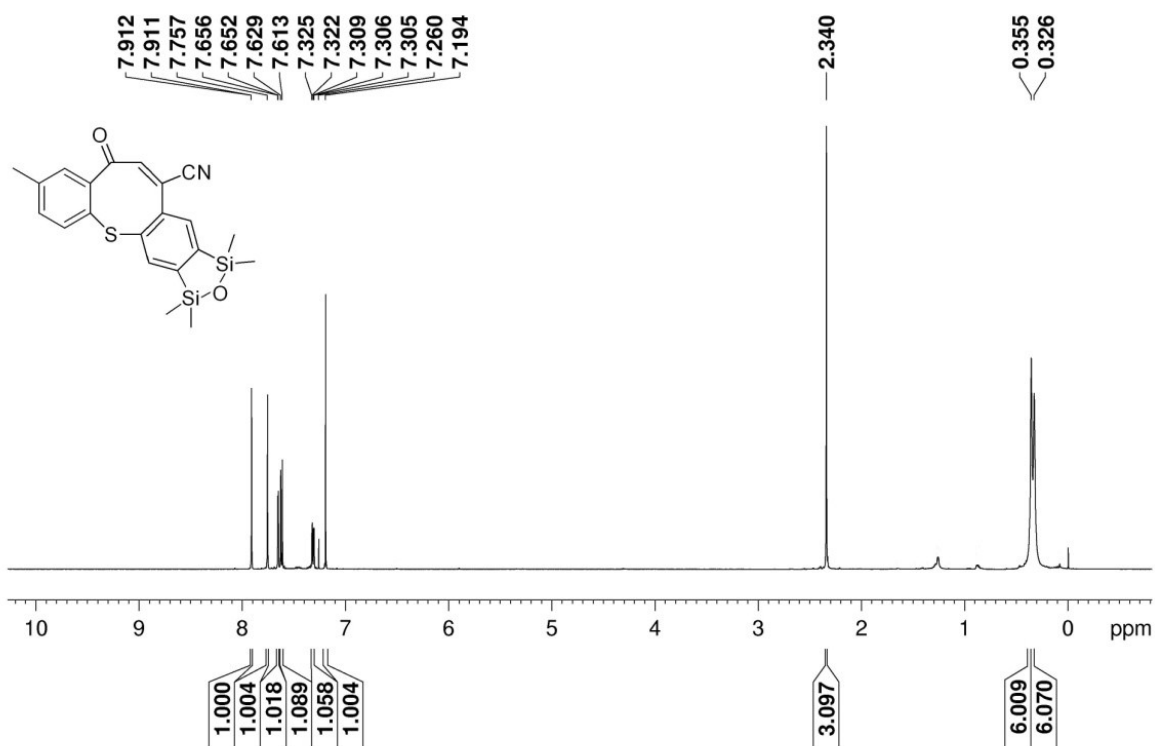
# Compound 5j



# Compound 5k

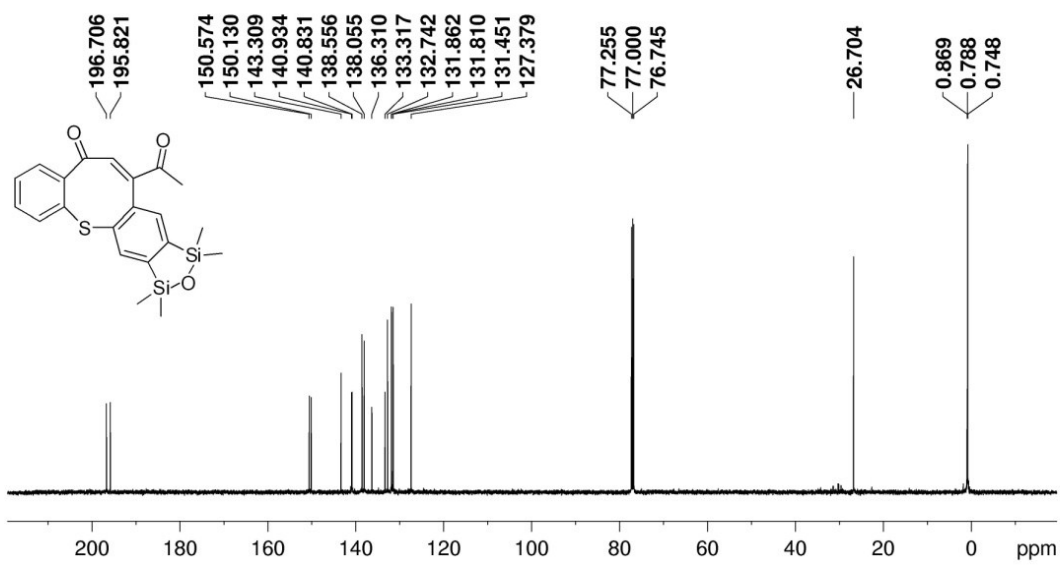
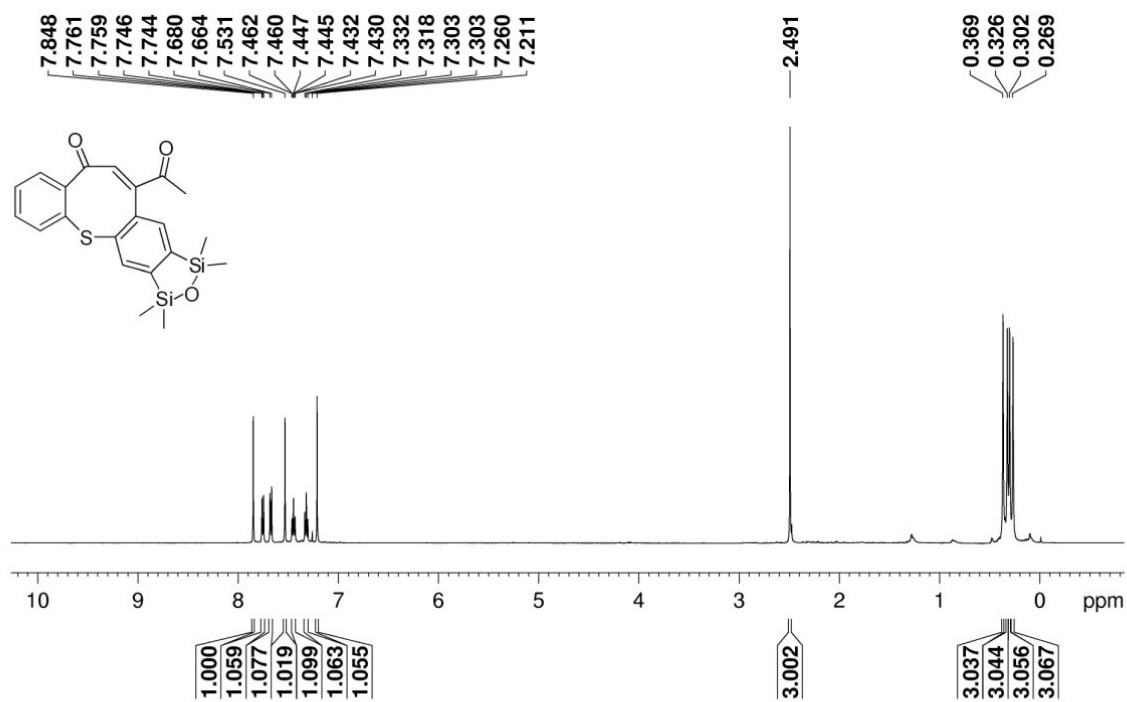


# Compound 5l

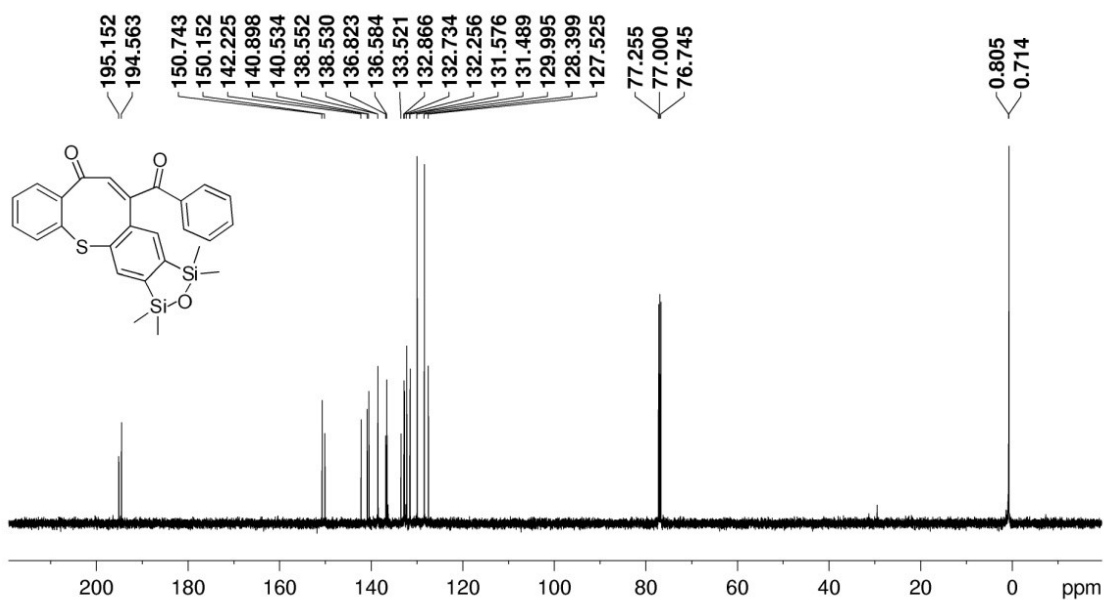
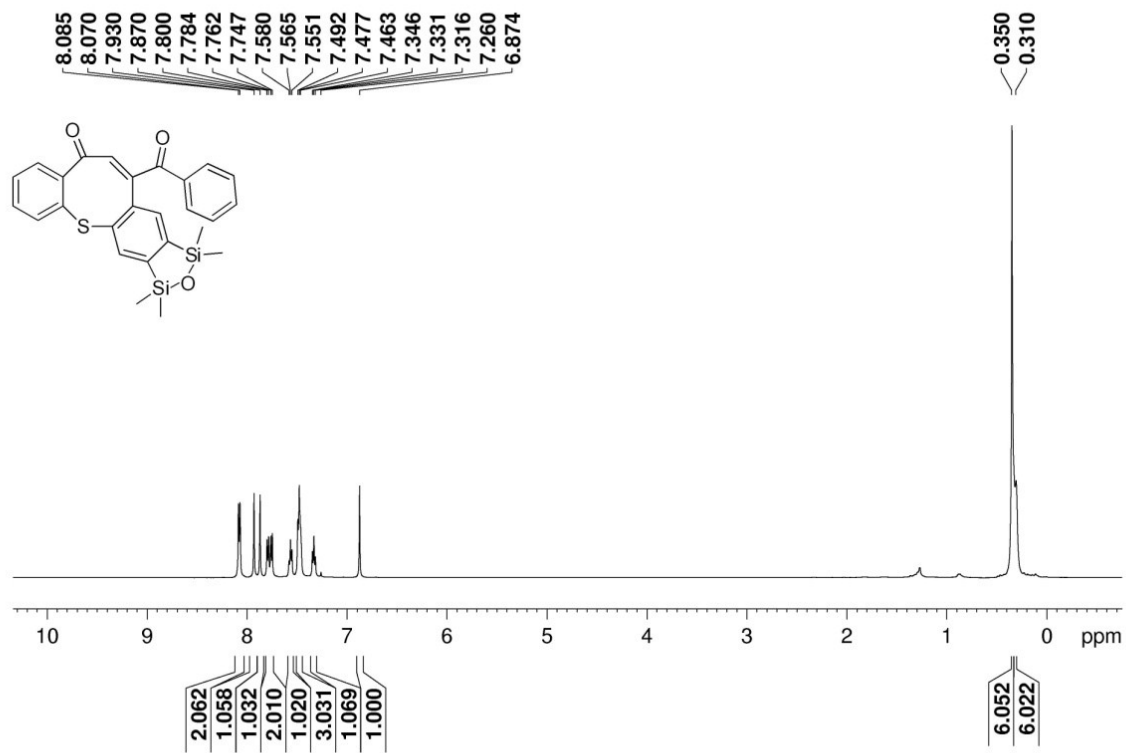




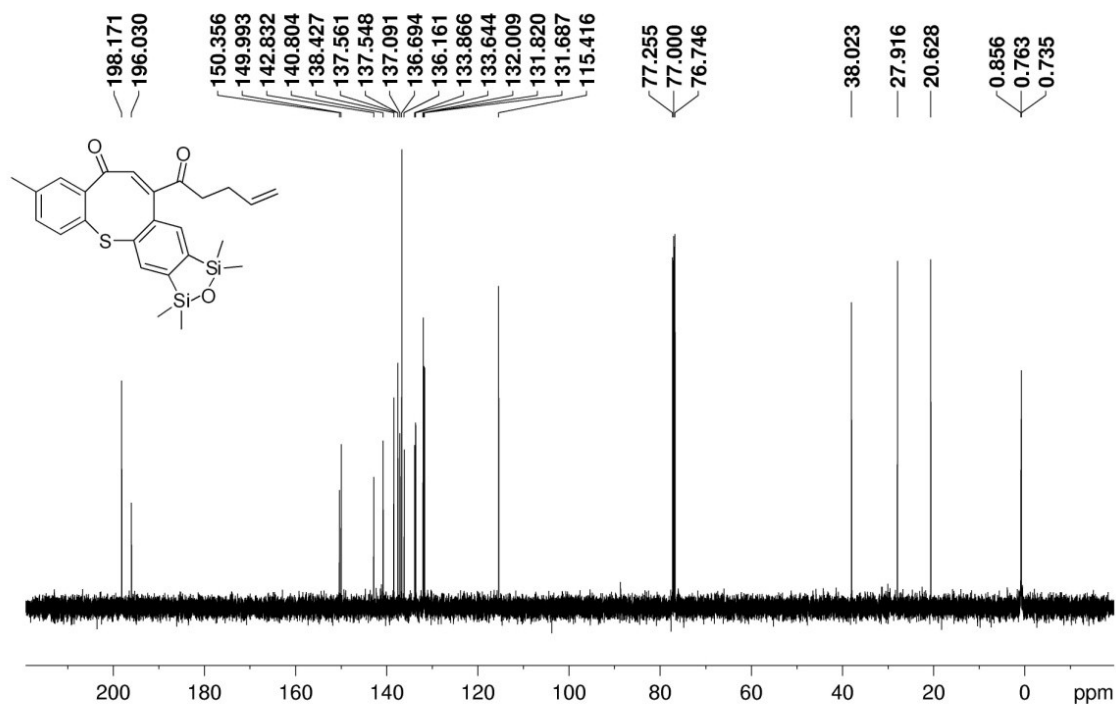
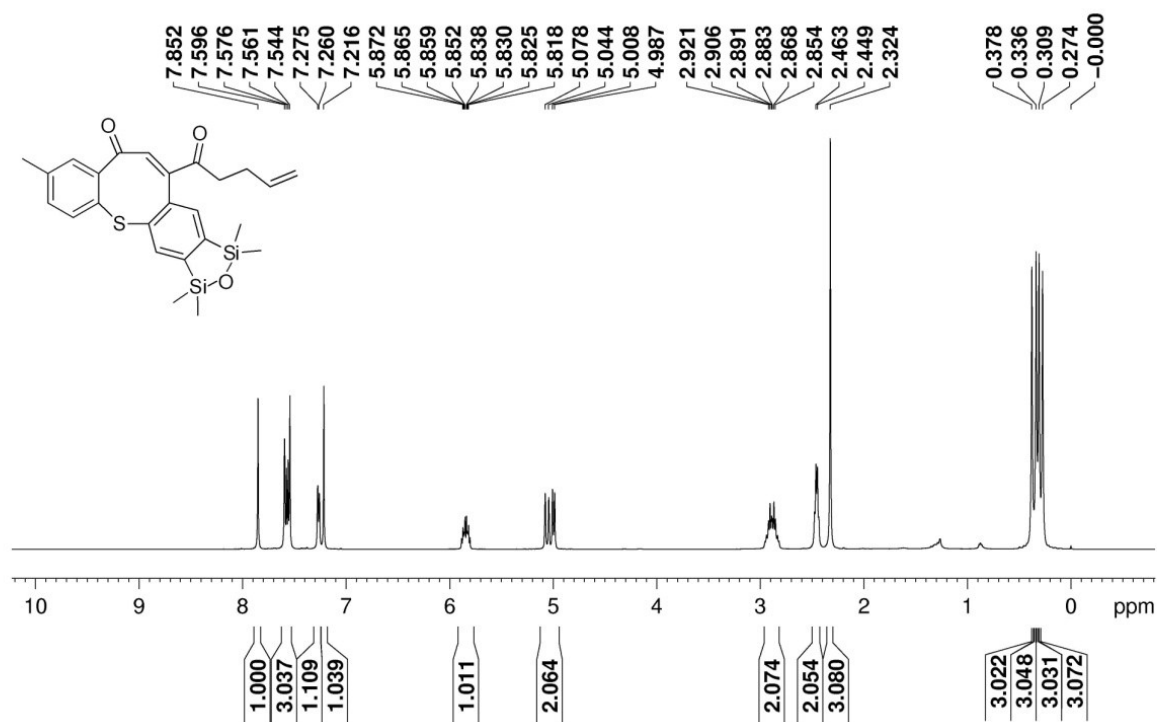
# Compound 5m



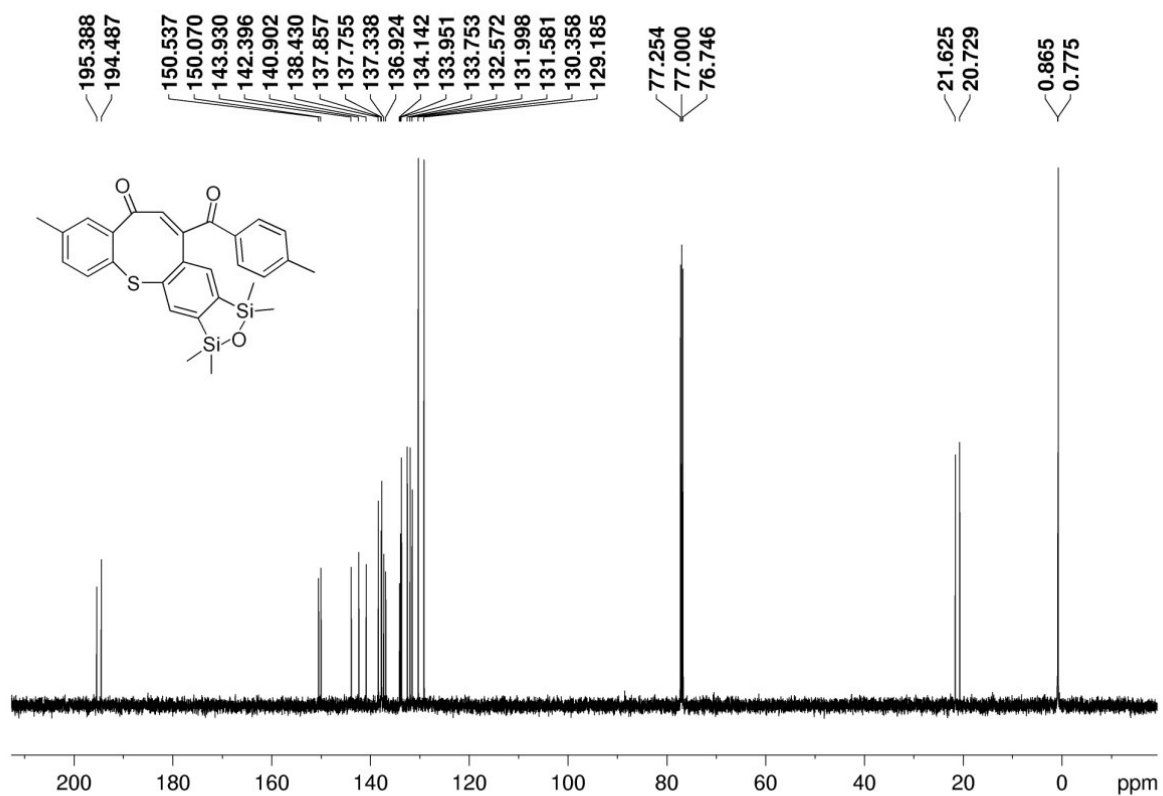
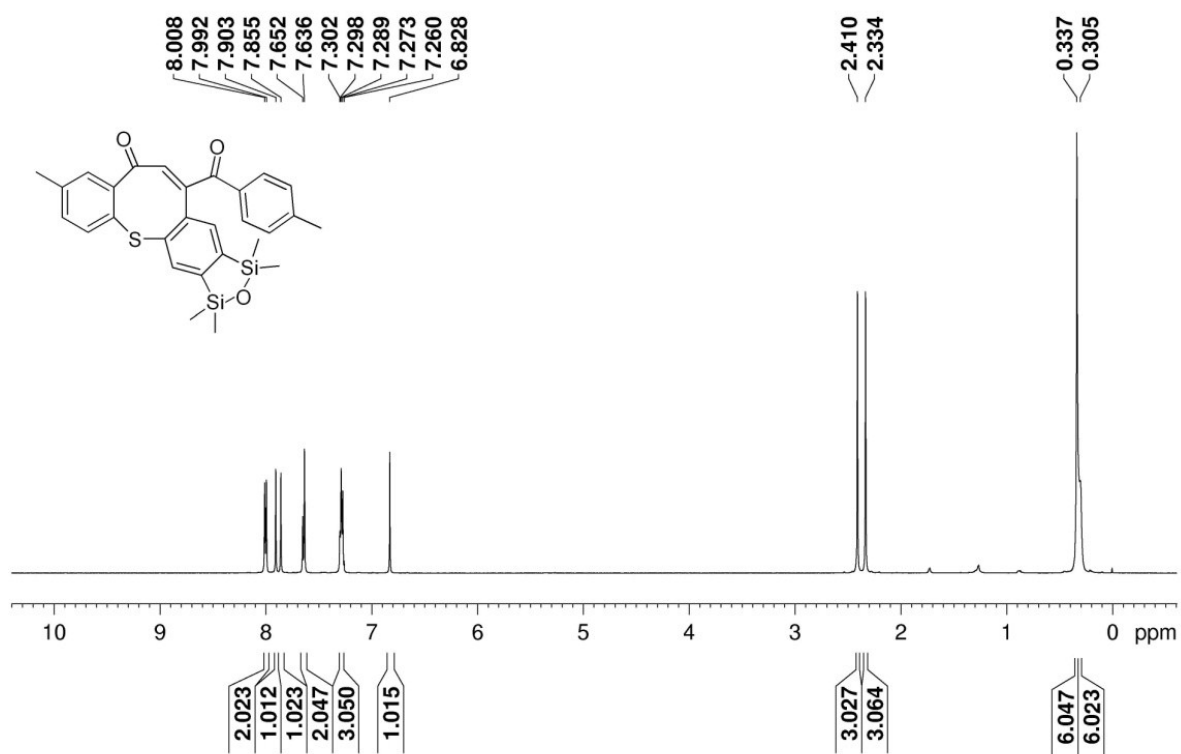
# Compound 5n



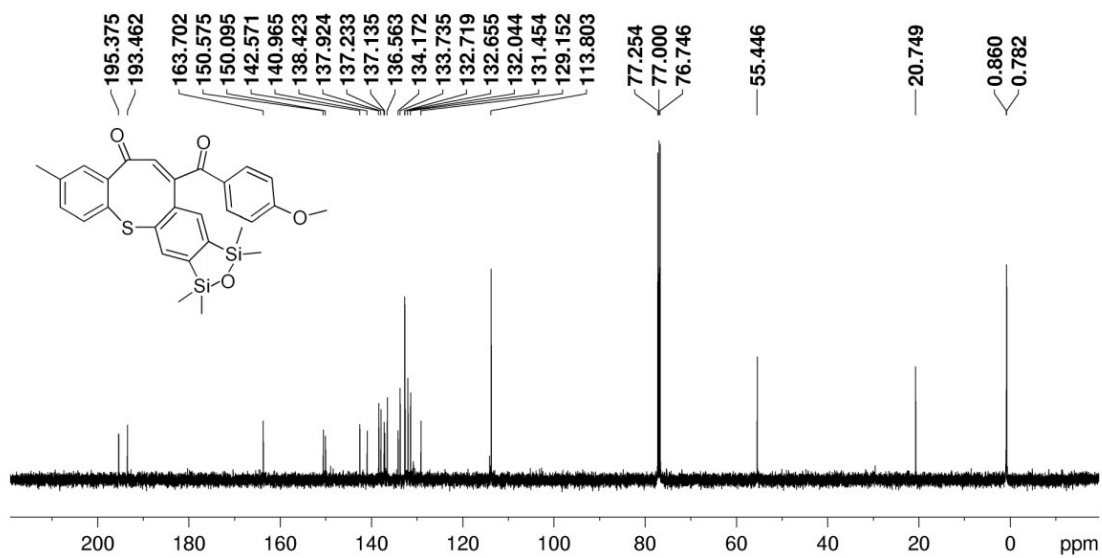
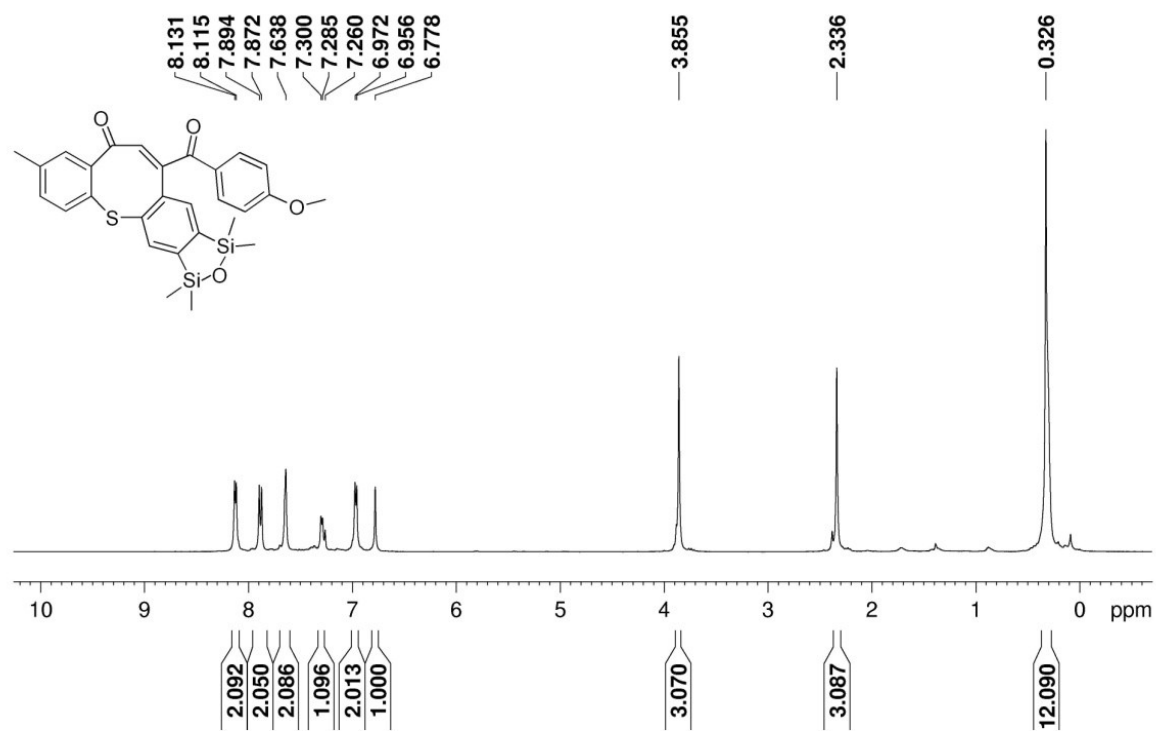
# Compound 5o



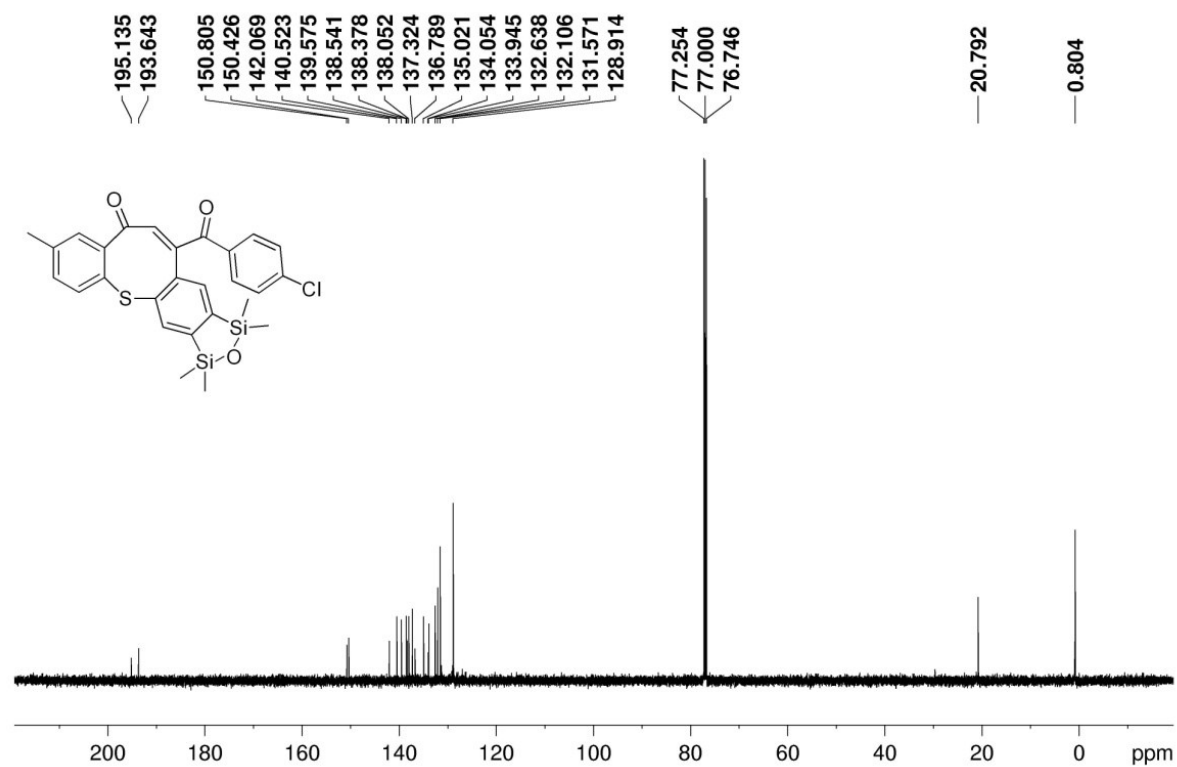
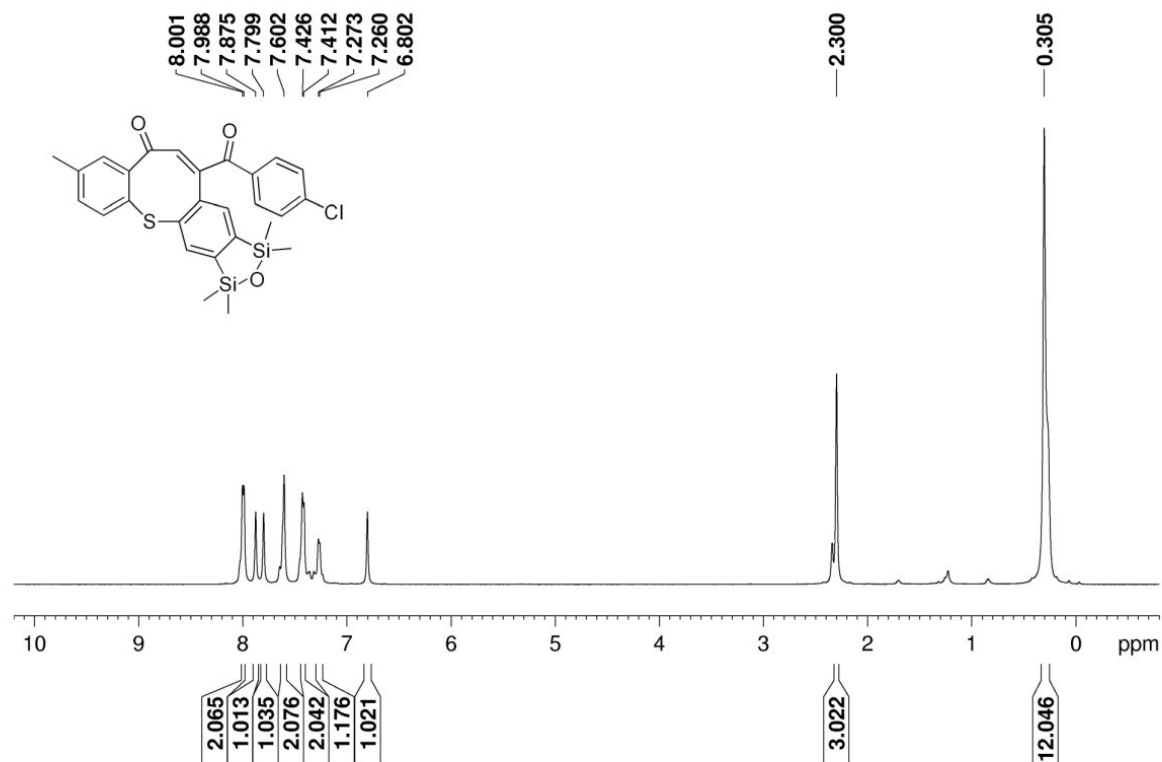
# Compound 5p



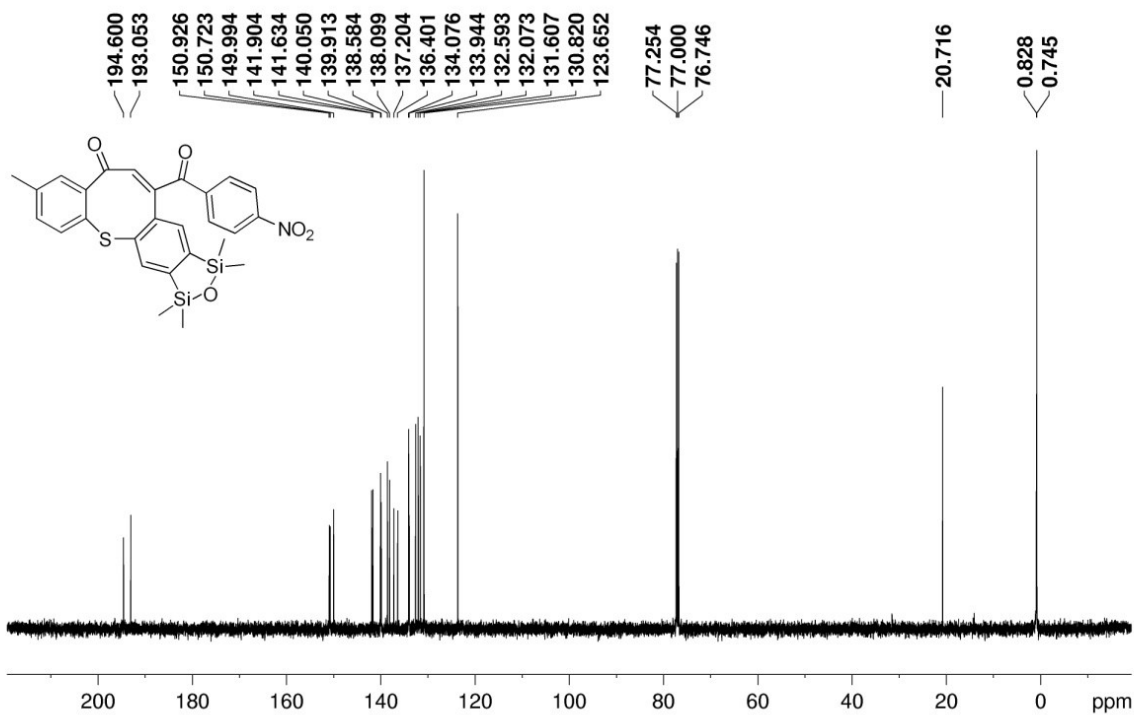
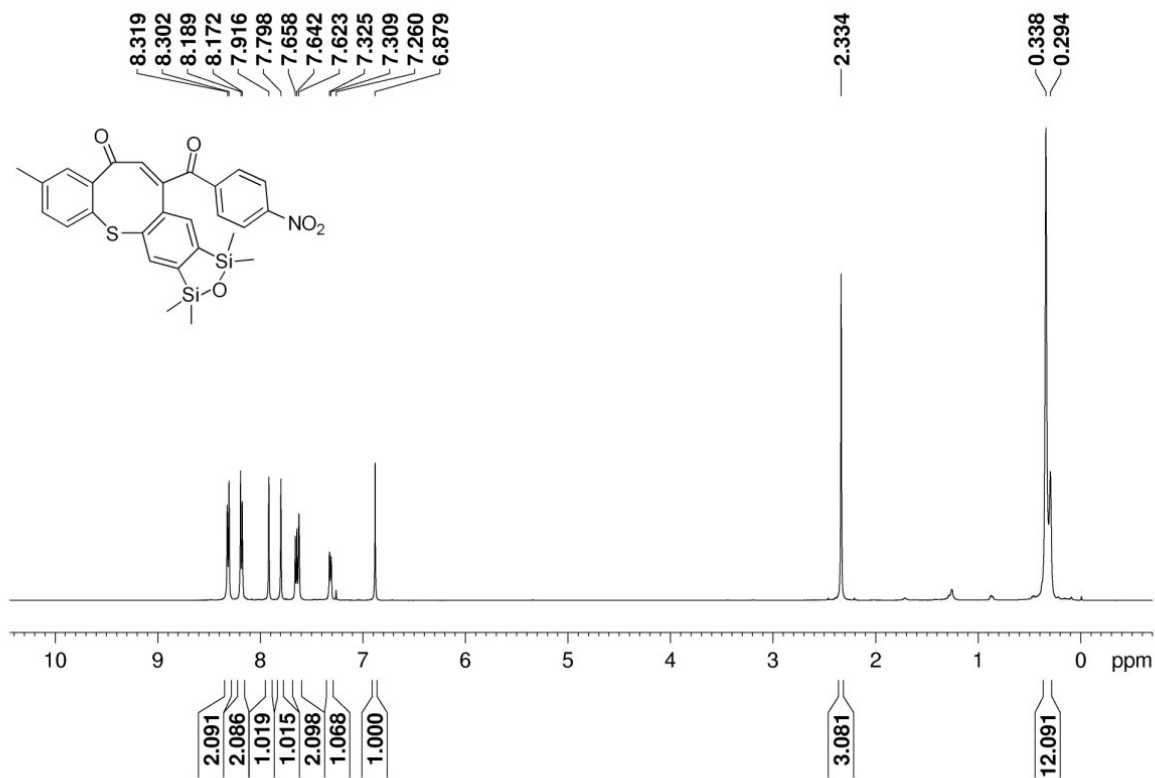
# Compound 5q



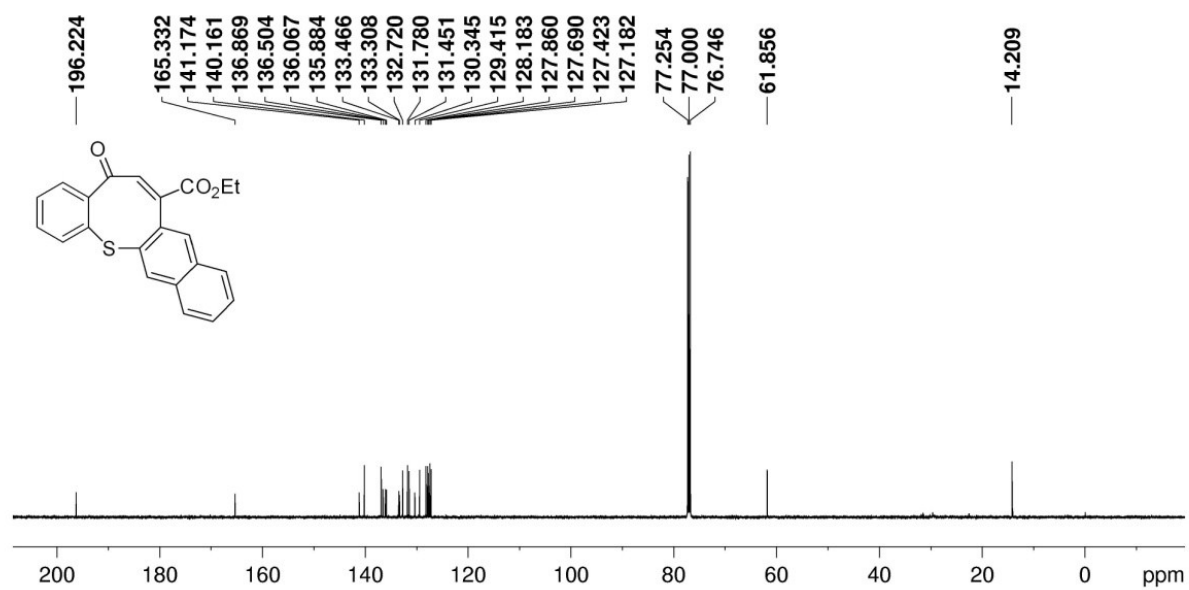
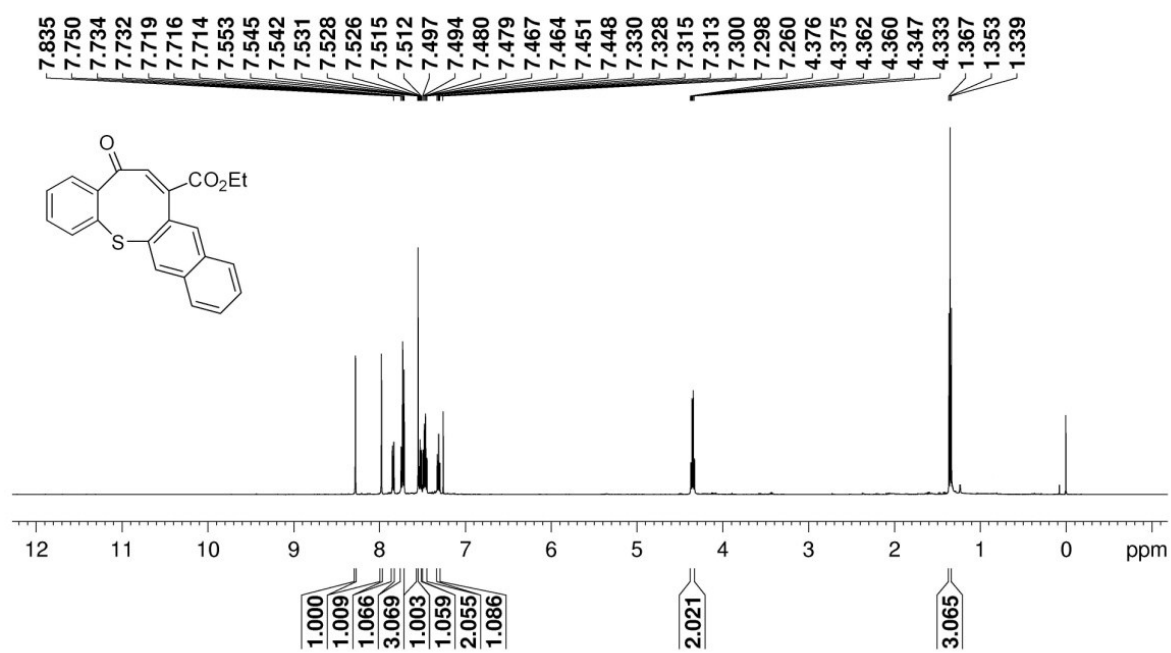
# Compound 5r



# Compound 5s

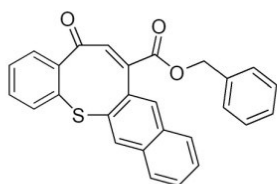
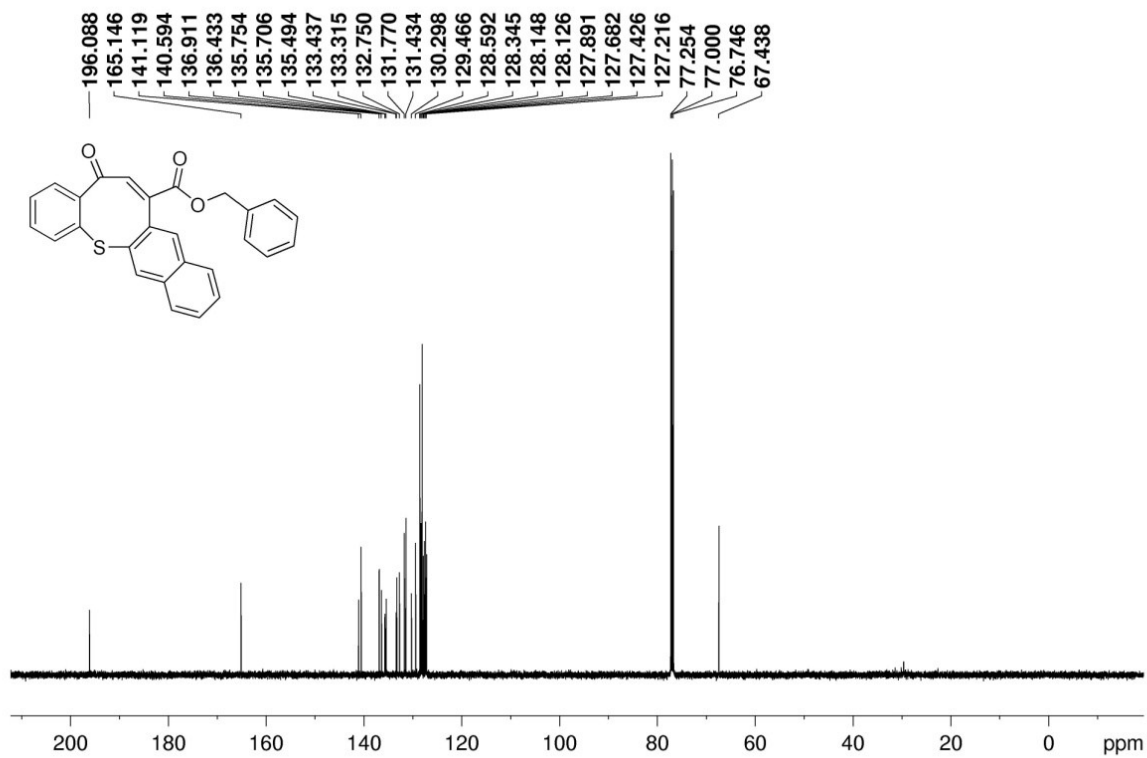
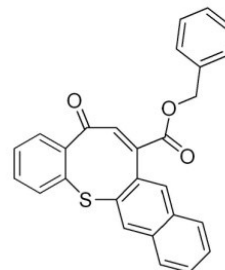
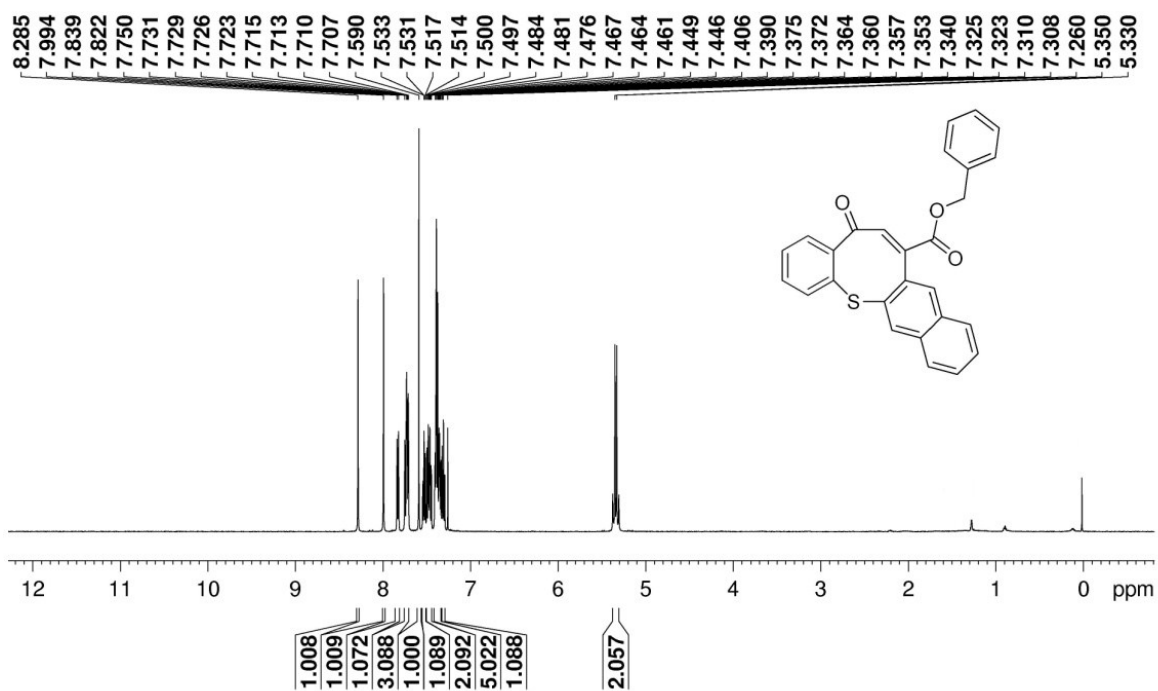


# Compound 9a

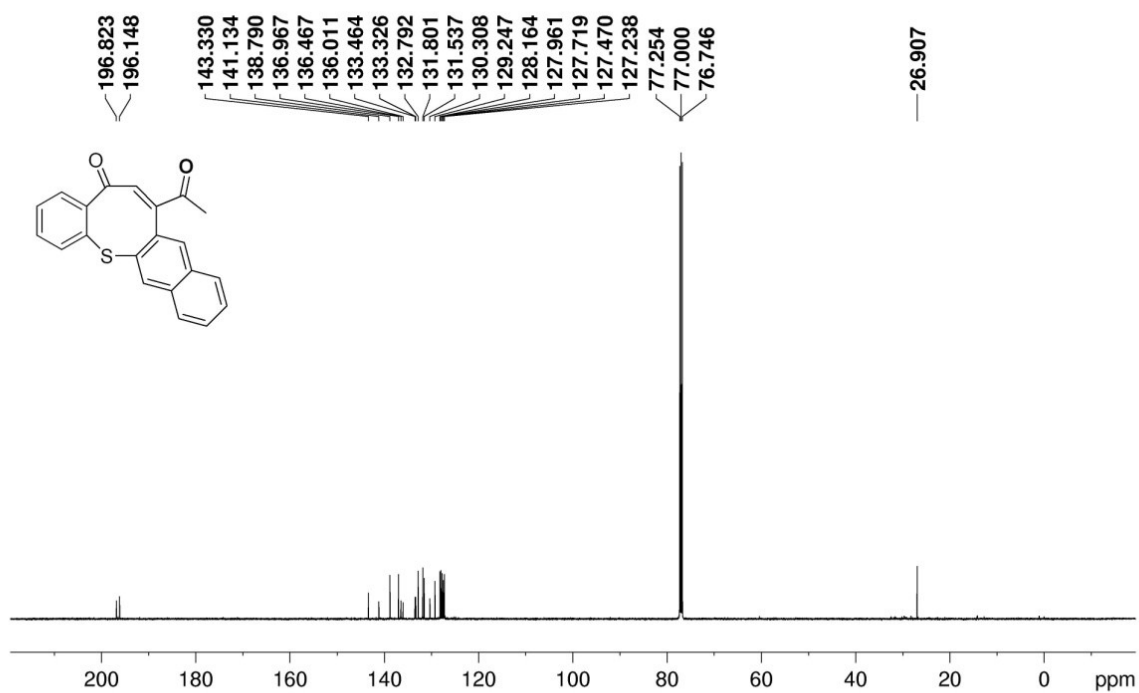
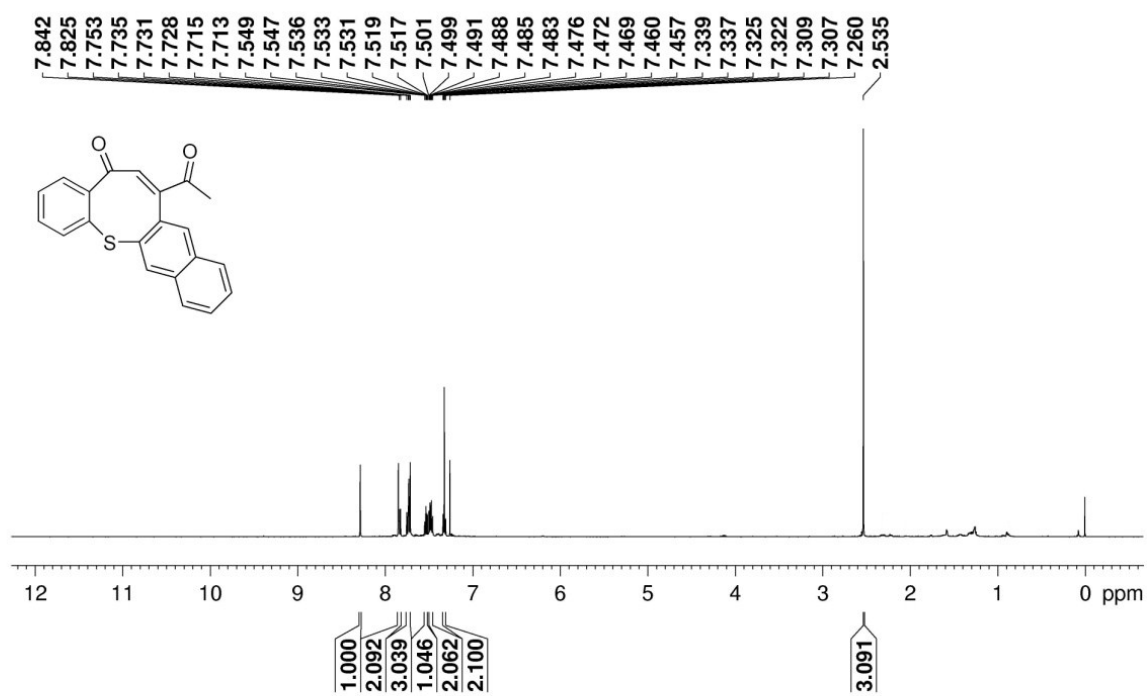




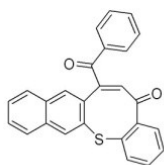
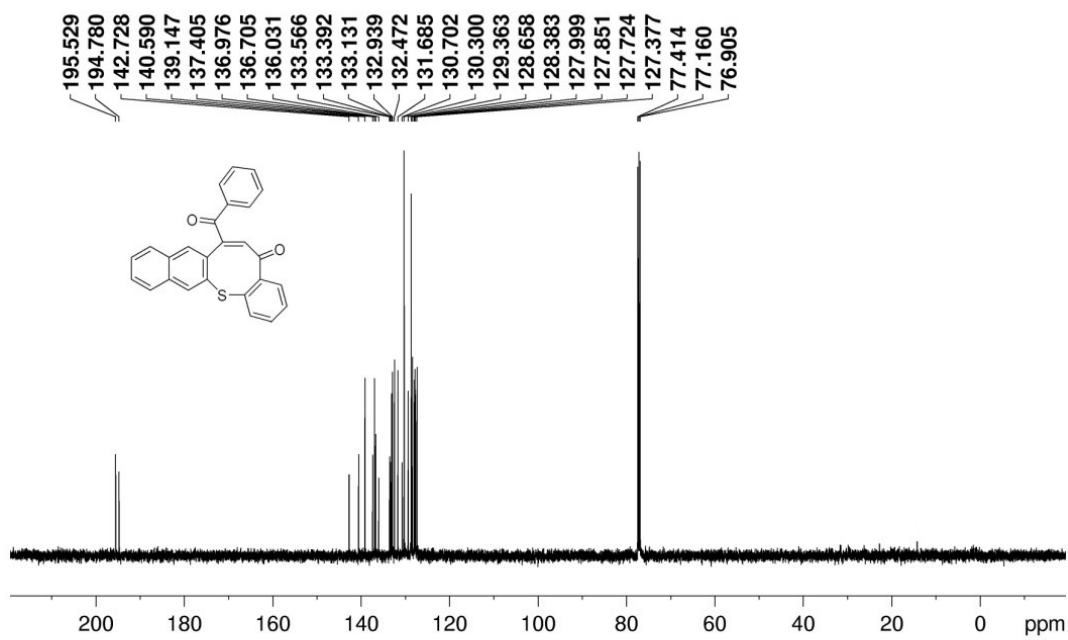
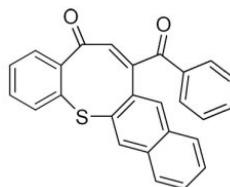
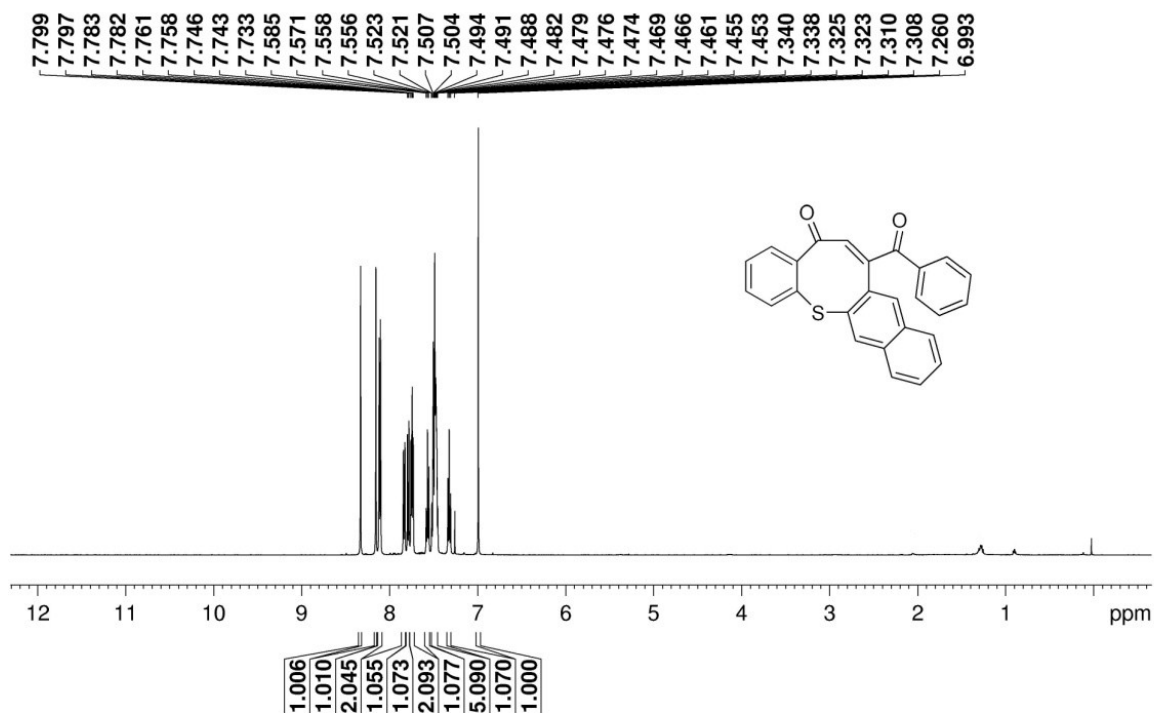
# Compound 9b



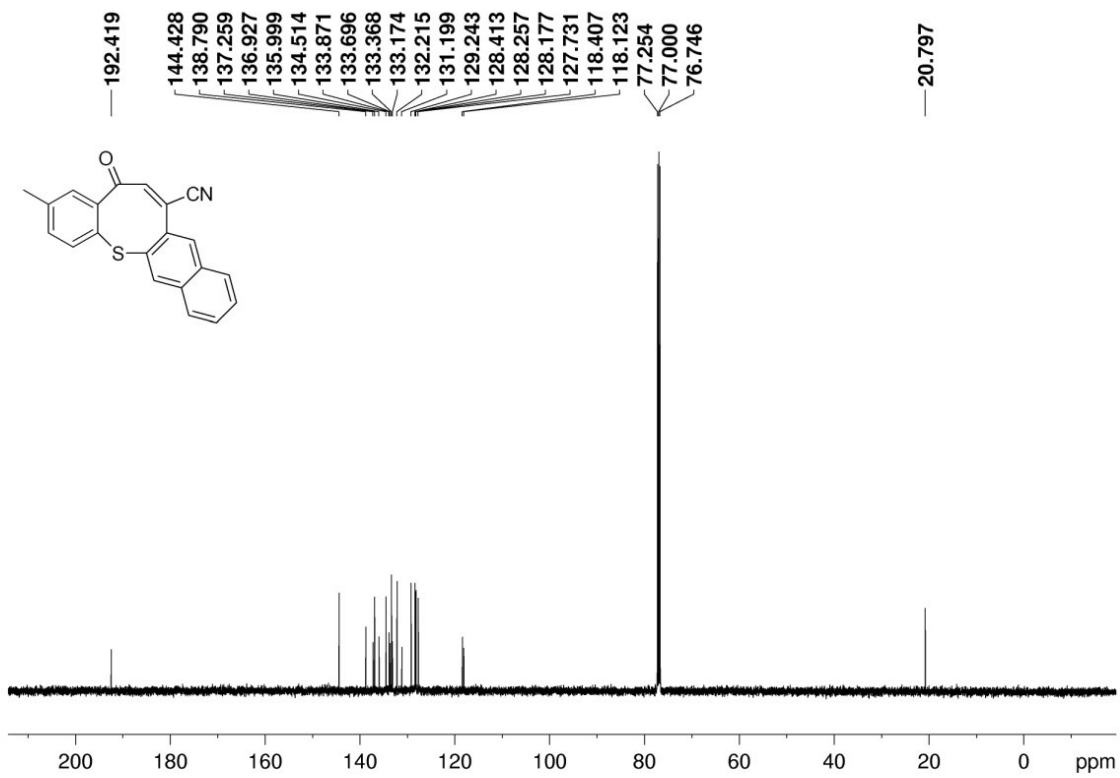
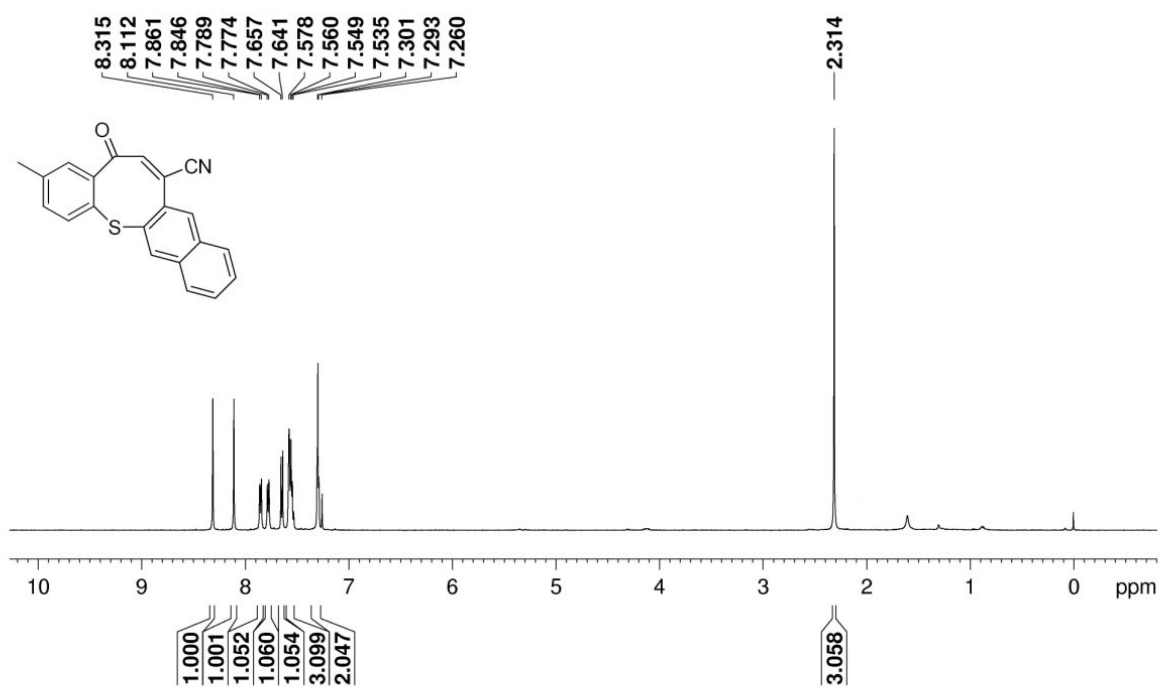
# Compound 9c



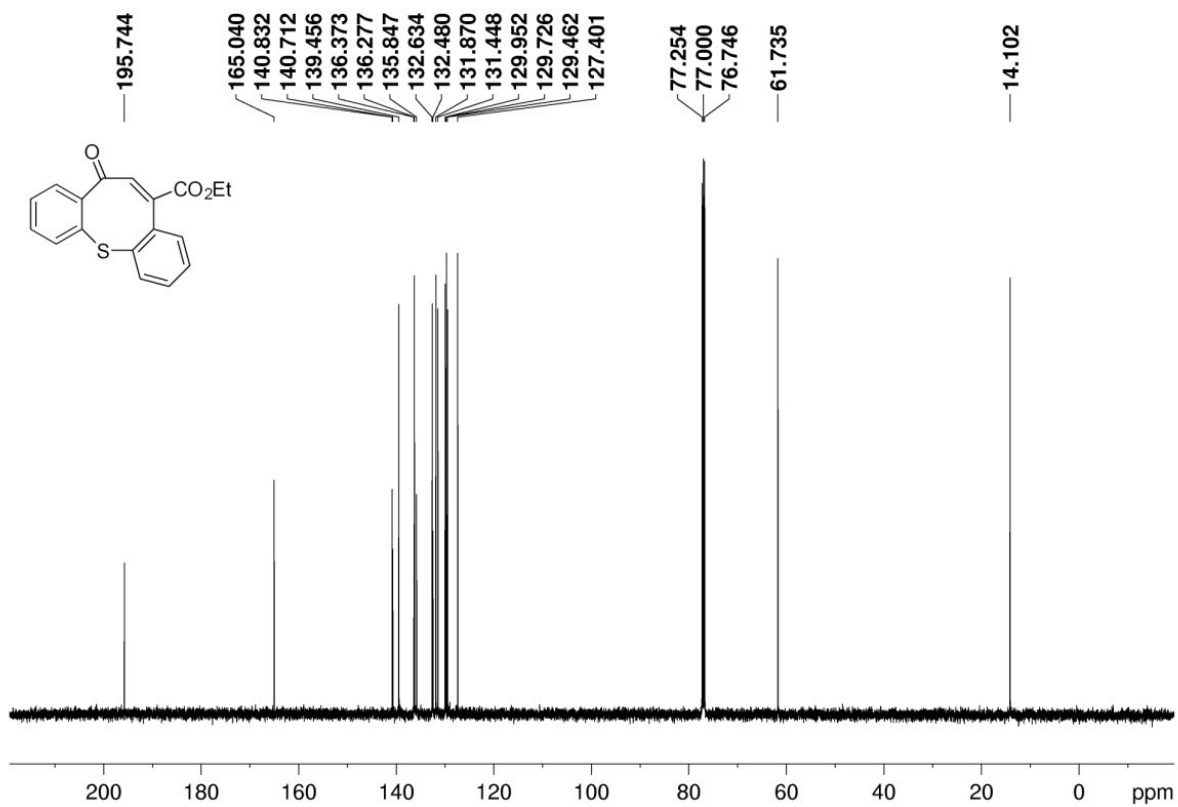
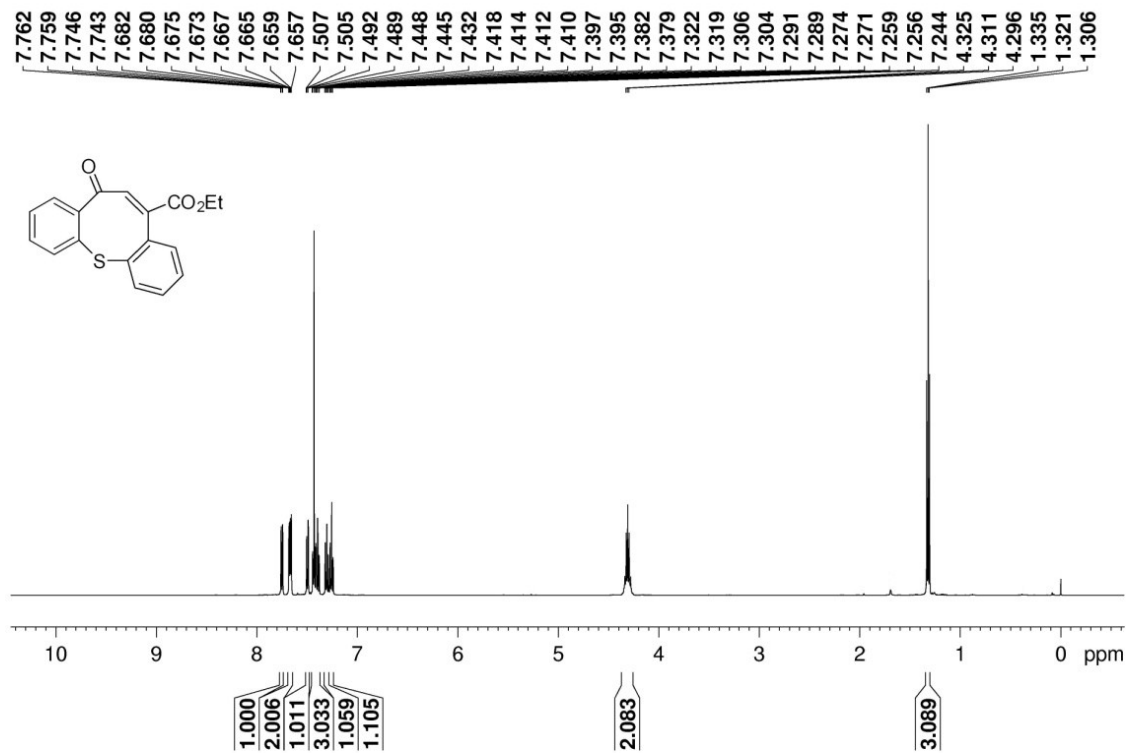
# Compound 9d



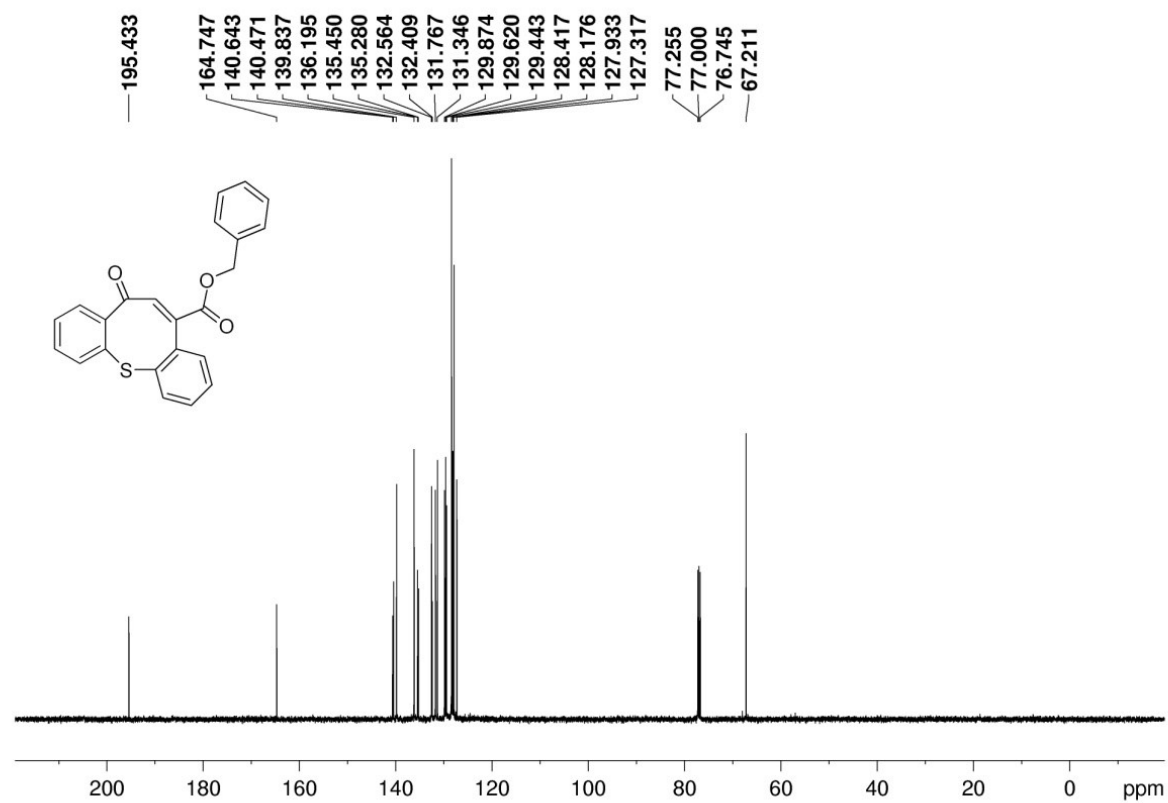
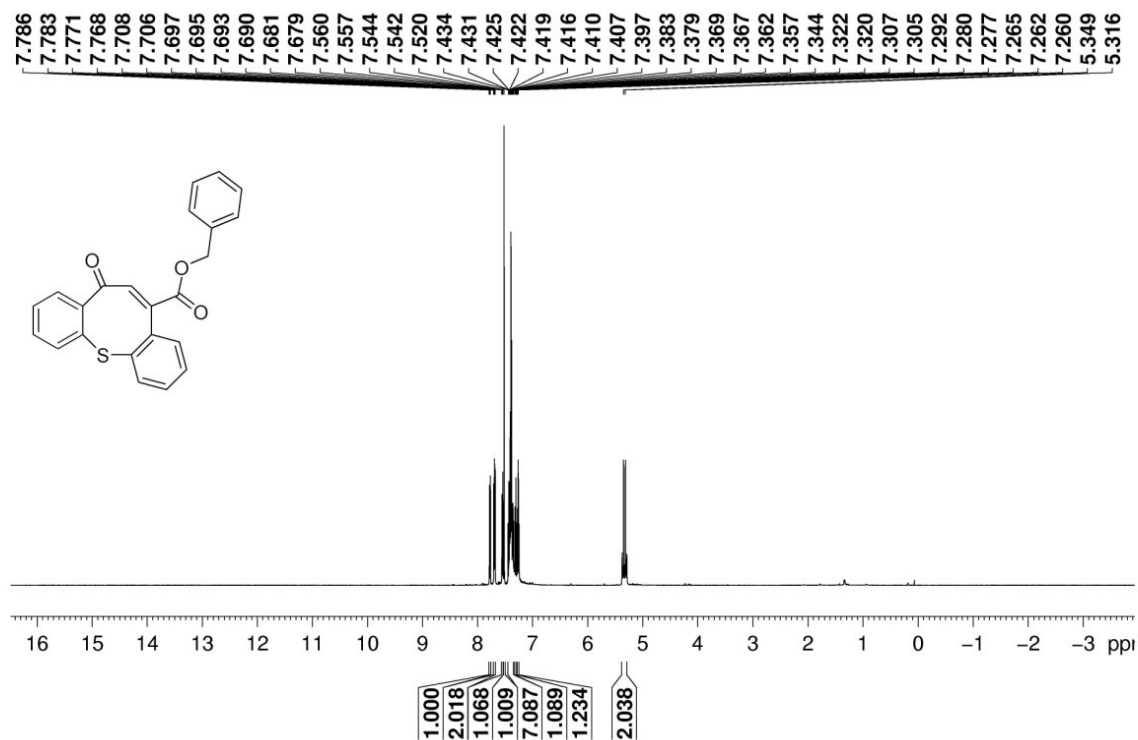
# Compound 9e



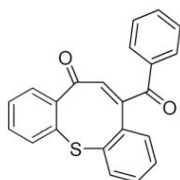
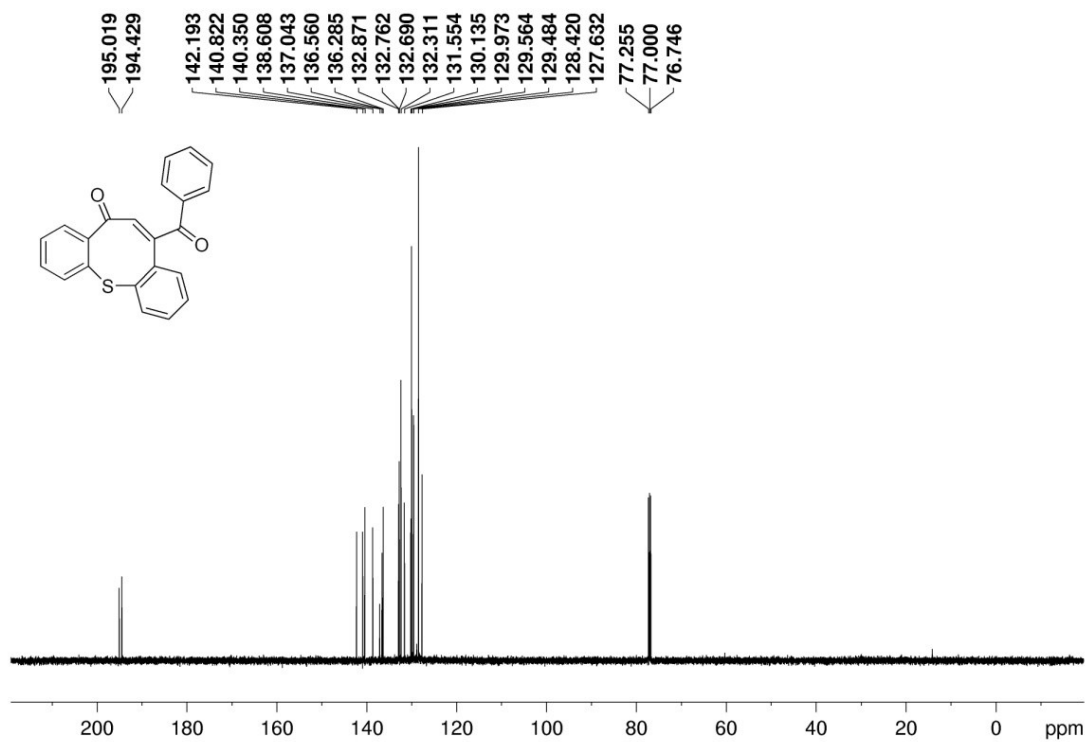
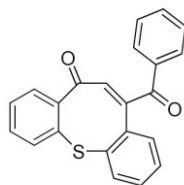
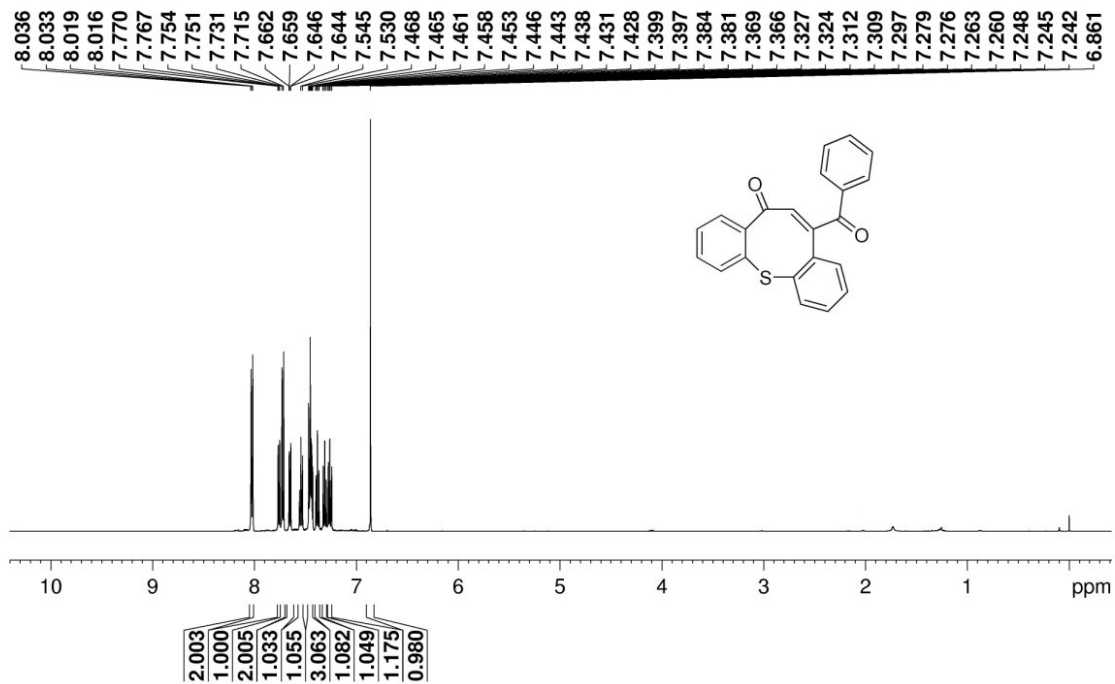
# Compound 11a



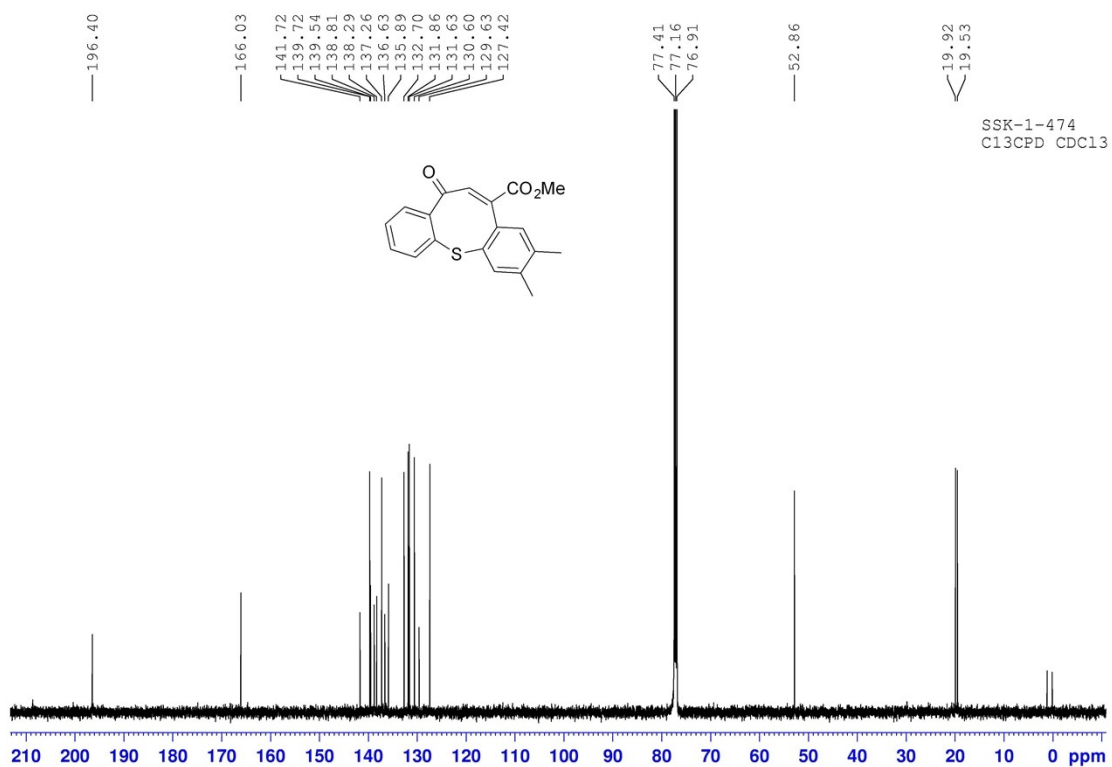
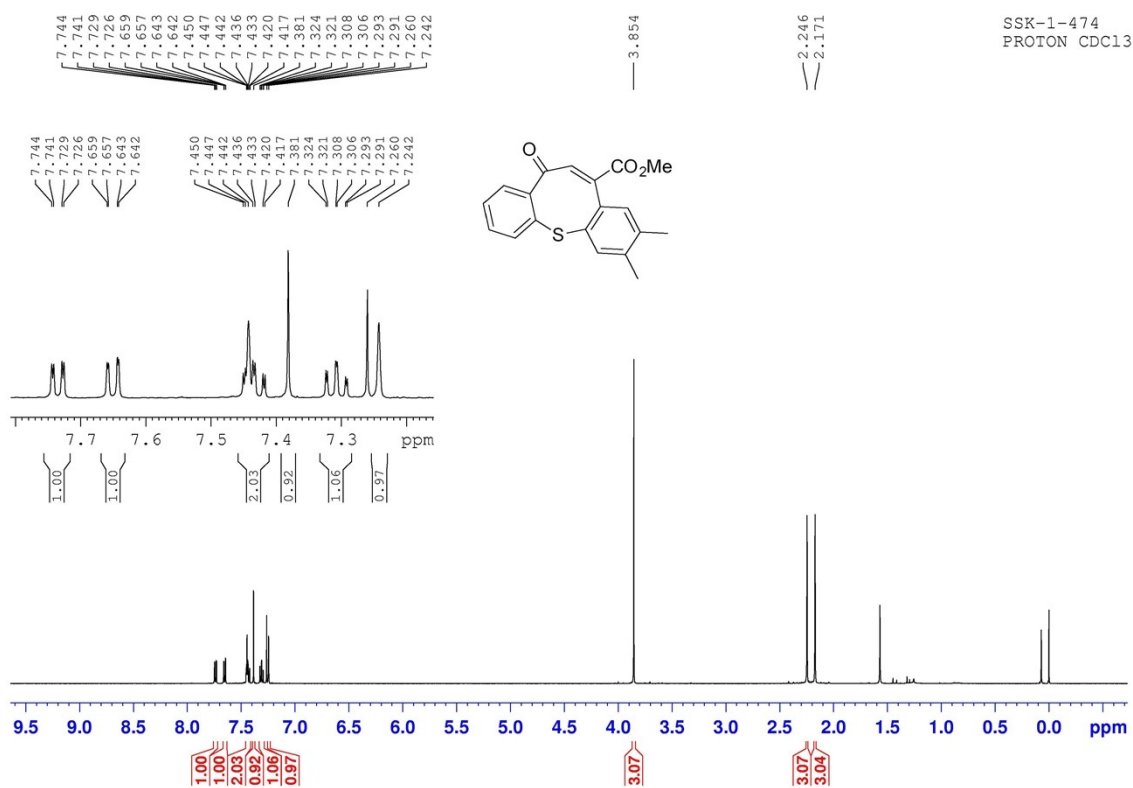
# Compound 11b



# Compound 11c

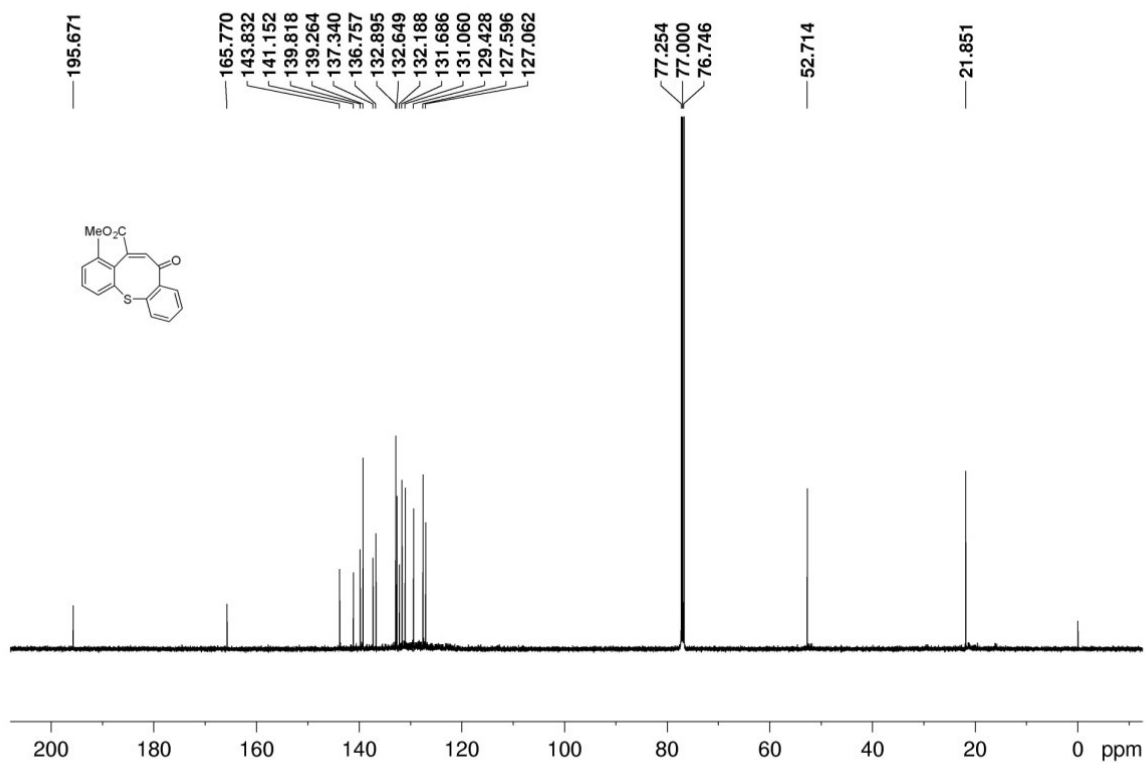
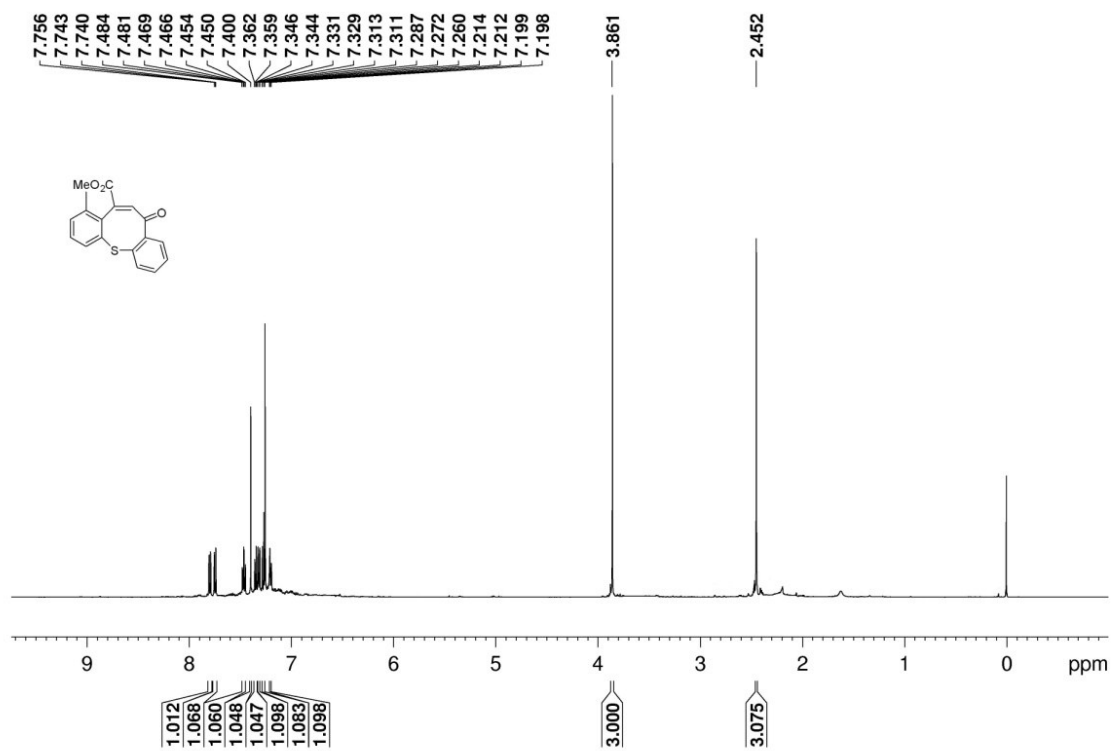


# Compound 11d

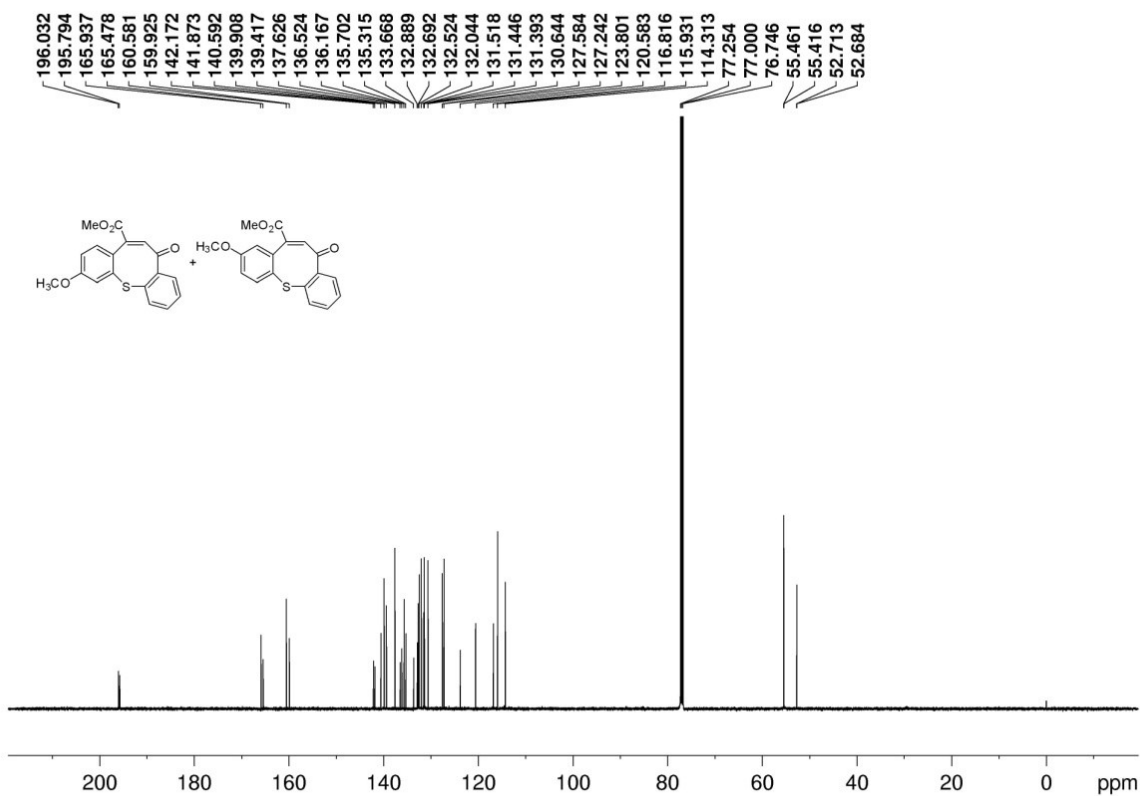
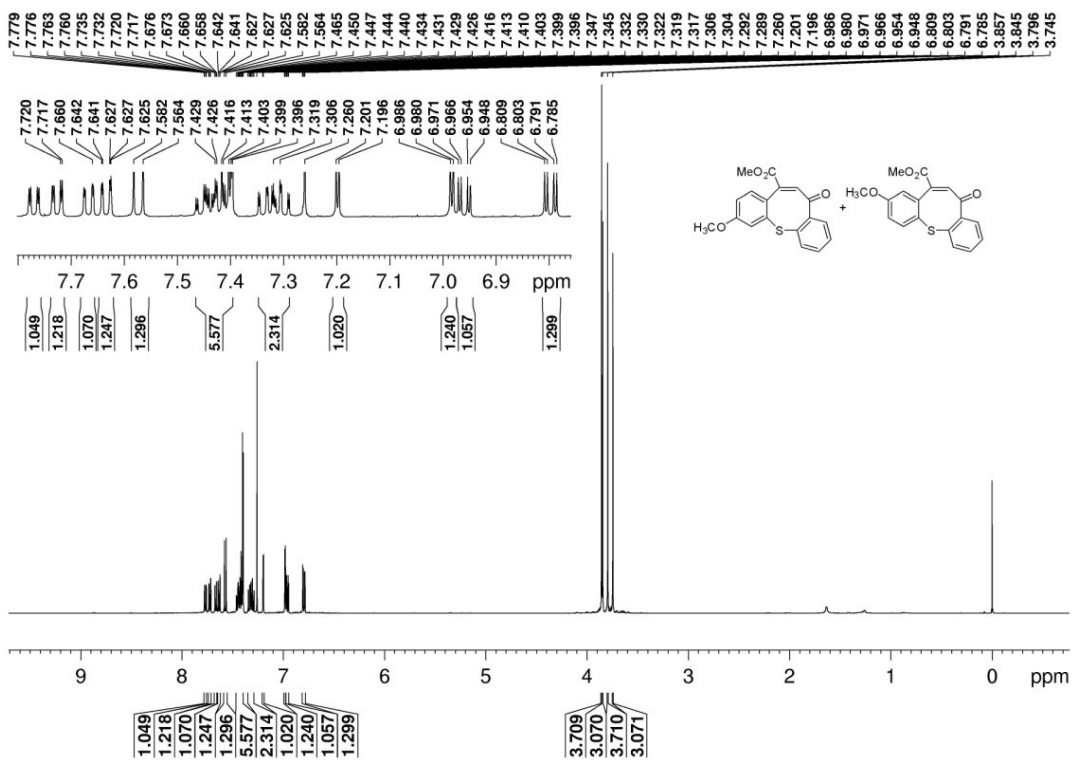




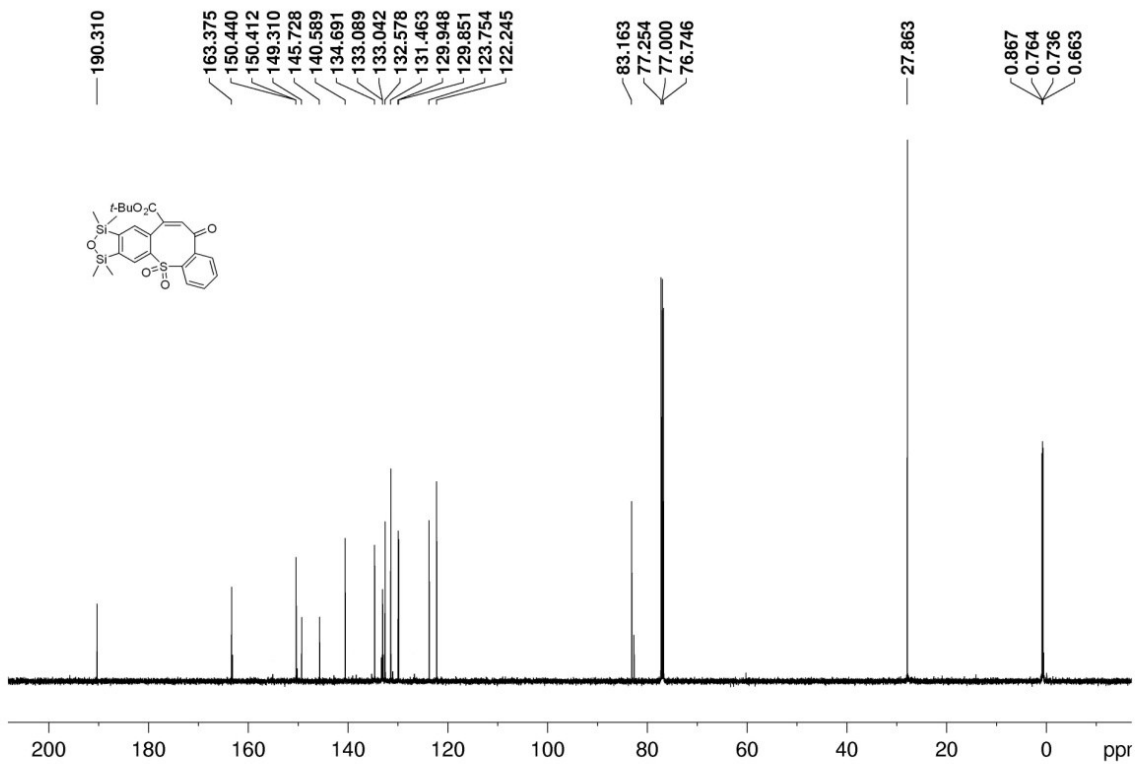
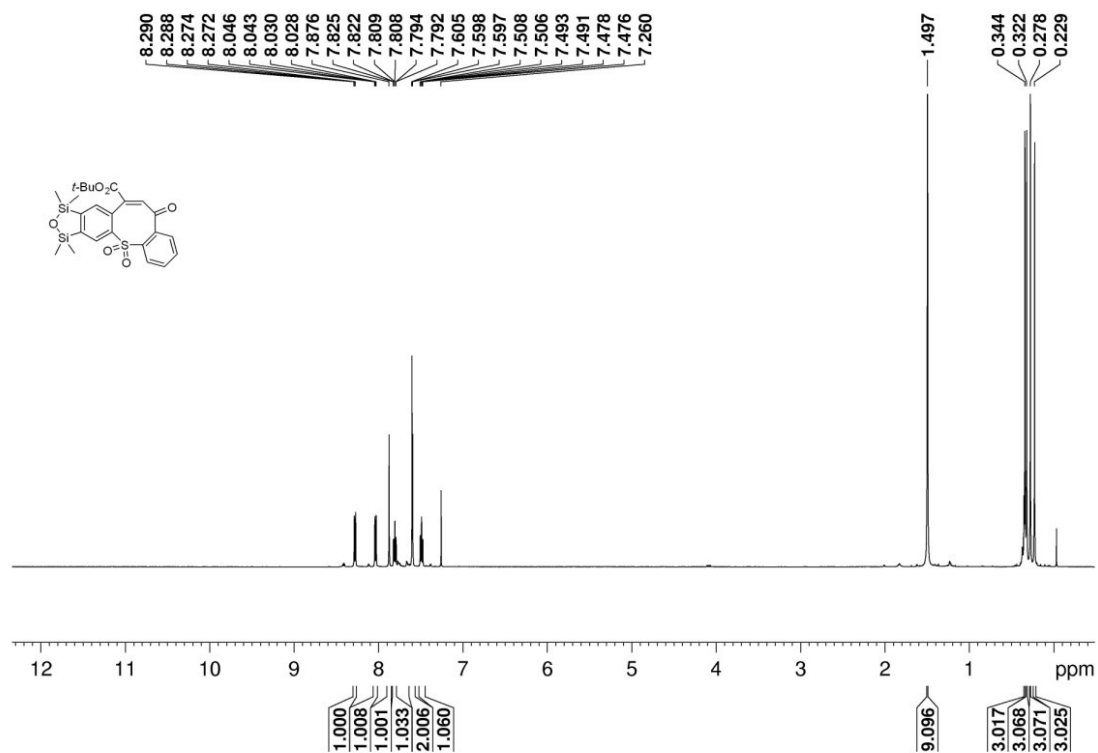
# Compound 11e



# Compound 11f



# Compound 12a



# Compound 12b

