

# Supporting Information

## *Part 1: Synthesis Section*

Modular synthesis of unsymmetrical [1]benzothieno[3,2-b][1]benzothiophene (BTBT)  
molecular semiconductors for organic transistors

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## 1. General synthesis procedures for BTBT derivatives

### General Experimental

All solvents and reagents were purchased from commercial sources and used as supplied.  $^1\text{H}$  NMR spectra were recorded on NMR spectrometers at 400 MHz and 500 MHz and  $^{13}\text{C}$  NMR at 101 MHz and 126 MHz, using the residual solvent peak of  $\text{CDCl}_3$  ( $^1\text{H}$ :  $\delta = 7.26$ ;  $^{13}\text{C}$ :  $\delta = 77.0$ ).  $^1\text{H}$  NMR chemical shifts ( $\delta_{\text{H}}$ ) and  $^{13}\text{C}$  NMR chemical shifts ( $\delta_{\text{C}}$ ) are quoted in parts per million (ppm) and coupling constants ( $J$ ) are quoted in Hertz (Hz). Abbreviations for NMR data are s (singlet), d (doublet), t (triplet), m (multiplet). Infrared (IR) spectra were recorded on a FTIR spectrometer and mass spectra were obtained using positive or negative electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI) techniques. Column chromatography was carried out using silica gel 60 Å, 240-400 mesh. Thin layer chromatography (TLC) was performed on aluminum sheets pre-coated with silica gel, 0.20 mm (Merck TLC Silica gel 60 F<sub>254</sub>). Melting points were measured on solids as obtained after recrystallization from EtOAc. Benzothiophene *S*-oxides were prepared as previously reported.<sup>1</sup> The following compounds were prepared and characterized as previously reported: **3aa**, **3eb** and **3eb'**.<sup>1</sup>

### General Procedure A: C-H Arylation of 3-Methoxybenzo[*b*]thiophene *S*-oxides

Under a nitrogen atmosphere, 3-methoxybenzo[*b*]thiophene-*S*-oxides **1** (1.0 equiv) and phenols **2** (1.5 equiv) were dissolved in THF (0.1 M) in an oven-dried tube flushed with N<sub>2</sub>. TFAA (1.5 equiv) was then added at -40 °C. After 15 min at -40 °C, the mixture was warmed to room temperature and stirred overnight. After removal of THF *in vacuo*, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (0.1 M). BF<sub>3</sub>·OEt<sub>2</sub> (0.20 equiv) was then added at room temperature, and the mixture was stirred at the same temperature for 30 min. The reaction was quenched with H<sub>2</sub>O, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The combined organic layers were dried over MgSO<sub>4</sub> and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with *n*-hexane and Et<sub>2</sub>O to obtain the 2-aryl benzothiophene products of cross-coupling **3**.

### General Procedure B: Synthesis of *S*-thiocarbamates

Under a nitrogen atmosphere, NaH (3.0 equiv) was added to a solution of the 2-aryl benzothiophene products of cross-coupling **3** in DMF (0.1 M) at room temperature. After 15 min at the same temperature, dimethylthiocarbamoyl chloride (2.0 equiv) was added to the reaction mixture. After the consumption of **3** (average reaction time = 16 h), the reaction was quenched with saturated aqueous NH<sub>4</sub>Cl and the aqueous layer was extracted with Et<sub>2</sub>O three times. The combined organic layers were dried over MgSO<sub>4</sub> and concentrated *in vacuo*. The *O*-thiocarbamate product was used in the next step without further purification.

The *O*-thiocarbamate was dissolved in Ph<sub>2</sub>O (0.1 M) and the solution heated at reflux. After completion of the reaction (average reaction time = 1 h), the crude product was purified by column chromatography on silica gel eluting with *n*-hexane in Et<sub>2</sub>O to obtain the *S*-thiocarbamate **5**.

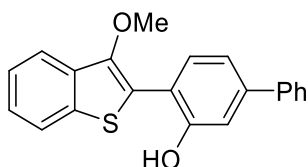
### General Procedure C: Hydrolysis and Cyclization to give BTBTs

KOMe (2.0 equiv) was added to a solution of *S*-thiocarbamate **5** in methanol/toluene (1:1 ratio, 0.05 M) in a 10 mL microwave vial. The vial was capped and heated to 120 °C. After the consumption of **5** (average reaction time = 1 h), the reaction mixture was cooled to room temperature. TsOH·H<sub>2</sub>O (8.0 equiv) was added to the crude mixture and then the solution was heated at 120 °C. After the completion of the reaction (average reaction time = 1 h), the reaction mixture was cooled to room temperature. Water was added to the reaction mixture, and then the aqueous layer was extracted with Et<sub>2</sub>O three times. The combined organic layers were dried over MgSO<sub>4</sub> and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with *n*-hexane in Et<sub>2</sub>O or recrystallized to afford BTBT **4**.

## 2. Experimental details for the synthesis of BTBT derivatives

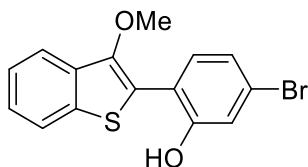
Compounds **3aa**, **3eb** and **3eb'** have previously been synthesized and reported by our group.<sup>1</sup>

### 4-(3-Methoxybenzo[*b*]thiophen-2-yl)-[1,1'-biphenyl]-3-ol (**3ab**)



**1a** (72 mg, 0.40 mmol), TFAA (83  $\mu$ L, 0.60 mmol), THF (4.0 mL), 3-phenylphenol (**2b**; 113 mg, 0.60 mmol),  $\text{BF}_3 \cdot \text{OEt}_2$  (10  $\mu$ L, 0.08 mmol),  $\text{CH}_2\text{Cl}_2$  (4.0 mL), gave **3ab** as a white solid (61 mg, 0.18 mmol, 46%); **M.p.**: 127-129 °C; **IR** (ATR): 3272, 1348, 1060, 759  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.15 (1H, s, OH), 7.83-7.76 (2H, m, ArH), 7.71-7.64 (2H, m, ArH), 7.57 (1H, d,  $J = 8.1$  Hz, ArH), 7.51-7.44 (3H, m, ArH), 7.44-7.35 (3H, m, ArH), 7.27 (1H, dd,  $J = 8.1, 1.7$  Hz, ArH), 3.94 (3H, s,  $\text{OCH}_3$ );  **$^{13}\text{C-NMR}$**  (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : 154.4 (ArC(OH)), 144.6 (ArC), 143.4 (ArC), 140.1 (ArC), 137.1 (ArC), 133.4 (ArC), 131.0 (ArCH), 128.8 (ArCH), 127.7 (ArCH), 127.0 (ArCH), 125.8 (ArC), 125.3 (ArCH), 124.6 (ArCH), 122.8 (ArCH), 120.6 (ArCH), 119.6 (ArCH), 118.1 (ArC), 116.9 (ArCH), 62.4 ( $\text{OCH}_3$ ); **HRMS** (APCI): Calcd. for  $\text{C}_{21}\text{H}_{17}\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 333.0944; found: 333.0940.

### 5-Bromo-2-(3-methoxybenzo[*b*]thiophen-2-yl)phenol (**3ac**)

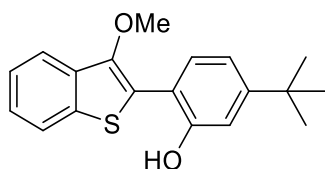


**1a** (72 mg, 0.40 mmol), TFAA (83  $\mu$ L, 0.60 mmol), THF (4.0 mL), 3-bromophenol (**2c**; 104 mg, 0.60 mmol),  $\text{BF}_3 \cdot \text{OEt}_2$  (10  $\mu$ L, 0.08 mmol),  $\text{CH}_2\text{Cl}_2$  (4.0 mL), gave **3ac** as a colorless oil (109 mg,

<sup>1</sup> Z. He, H. J. Shriver, J. A. Fernández-Salas, A. Abengózar, J. Neufeld, K. Yang, A. P. Pulis and D. J. Procter, *Angew. Chem. Int. Ed.* 2018, **57**, 5759–5764.

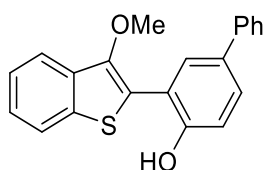
0.33 mmol; 81%); **IR** (ATR): 3245, 1478, 1349, 800  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$**  (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.13 (1H, s, OH), 7.80-7.69 (2H, m, ArH), 7.45-7.34 (2H, m, ArH), 7.32 (1H, d,  $J = 8.4$  Hz, ArH), 7.26 (1H, s, ArH), 7.11 (1H, d,  $J = 8.4$  Hz, ArH), 3.87 (3H, s,  $\text{OCH}_3$ );  **$^{13}\text{C-NMR}$**  (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : 154.8 (ArC(OH)), 144.8 (ArC), 137.0 (ArC), 133.2 (ArC), 131.5 (ArCH), 125.5 (ArCH), 124.8 (ArC), 124.7 (ArCH), 124.0 (ArCH), 123.8 (ArC), 122.8 (ArCH), 121.7 (ArCH), 120.7 (ArCH), 118.3 (ArC), 62.4 ( $\text{OCH}_3$ ); **HRMS** (ESI): Calcd. for  $\text{C}_{15}\text{H}_{10}\text{O}_2\text{BrS}$   $[\text{M-H}]^-$ : 332.9590; found: 332.9586.

### 5-(*tert*-Butyl)-2-(3-methoxybenzo[*b*]thiophen-2-yl)phenol (**3ad**)



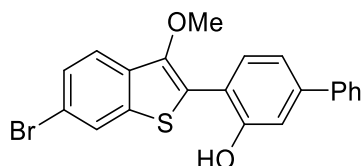
**1a** (72 mg, 0.40 mmol), TFAA (83  $\mu\text{L}$ , 0.60 mmol), THF (4.0 mL), 3-*tert*-butylphenol (**2d**; 90 mg, 0.60 mmol),  $\text{BF}_3 \cdot \text{OEt}_2$  (10  $\mu\text{L}$ , 0.08 mmol),  $\text{CH}_2\text{Cl}_2$  (4.0 mL), gave **3ad** as a colorless oil (84 mg, 0.27 mmol; 67%); **IR** (ATR): 3293, 1347, 1069, 809  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$**  (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.00 (1H, s, OH), 7.77 (1H, d,  $J = 8.0$  Hz, ArH), 7.75 (1H, d,  $J = 8.0$  Hz, ArH), 7.46-7.34 (3H, m, ArH), 7.12 (1H, d,  $J = 2.0$  Hz, ArH), 7.04 (1H, dd,  $J = 8.0, 2.0$  Hz, ArH), 3.90 (3H, s,  $\text{OCH}_3$ ), 1.36 (9H, s,  $(\text{CH}_3)_3$ );  **$^{13}\text{C-NMR}$**  (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : 154.2 (ArC(OH)), 153.7 (ArC), 144.2 (ArC), 136.9 (ArC), 133.5 (ArC), 130.1 (ArCH), 126.2 (ArC), 125.0 (ArCH), 124.5 (ArCH), 122.7 (ArCH), 120.5 (ArCH), 118.1 (ArCH), 116.1 (ArC), 115.5 (ArCH), 62.3 ( $\text{OCH}_3$ ), 34.7 ( $\text{C}(\text{CH}_3)_3$ ), 31.1 ( $\text{C}(\text{CH}_3)_3$ ); **HRMS** (APCI): Calcd. for  $\text{C}_{19}\text{H}_{20}\text{BrO}_2\text{S}$   $[\text{M}]^+$ : 391.0362; found: 391.0354.

### 3-(3-Methoxybenzo[*b*]thiophen-2-yl)-[1,1'-biphenyl]-4-ol (**3ae**)



**1a** (72 mg, 0.40 mmol), TFAA (83  $\mu$ L, 0.60 mmol), THF (4.0 mL), 4-phenylphenol (**3e**; 102 mg, 0.60 mmol),  $\text{BF}_3 \cdot \text{OEt}_2$  (10  $\mu$ L, 0.08 mmol),  $\text{CH}_2\text{Cl}_2$  (4.0 mL), gave **3ae** as a colorless amorphous solid (98 mg, 0.29 mmol, 74%); **IR** (ATR): 3327, 1347, 1260, 1092, 762  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.04 (1H, s, OH), 7.84-7.77 (2H, m, ArH), 7.75 (1H, s, ArH), 7.67-7.61 (2H, m, ArH), 7.59 (1H, dd,  $J = 8.6, 2.0$  Hz, ArH), 7.51-7.39 (4H, m, ArH), 7.36 (1H, t,  $J = 7.3$  Hz, ArH), 7.19 (1H, d,  $J = 8.6$  Hz, ArH), 3.94 (3H, s,  $\text{OCH}_3$ );  **$^{13}\text{C-NMR}$**  (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : 153.7 (ArC(OH)), 144.9 (ArC), 140.3 (ArC), 137.1 (ArC), 134.0 (ArC), 133.4 (ArC), 129.2 (ArCH), 129.1 (ArCH), 128.8 (ArCH), 126.9 (ArCH), 126.8 (ArCH), 125.6 (ArC), 125.3 (ArCH), 124.6 (ArCH), 122.8 (ArCH), 120.7 (ArCH), 119.4 (ArC), 118.9 (ArCH), 62.4 ( $\text{OCH}_3$ ); **HRMS** (APCI): Calcd. for  $\text{C}_{21}\text{H}_{17}\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 333.0930; found: 333.0932.

#### 4-(6-Bromo-3-methoxybenzo[*b*]thiophen-2-yl)-[1,1'-biphenyl]-3-ol (**3bb**)

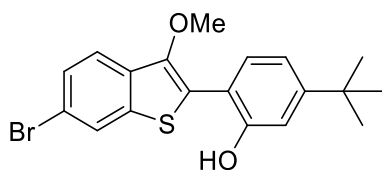


**1b** (78 mg, 0.30 mmol), TFAA (63  $\mu$ L, 0.45 mmol), THF (3.0 mL), 3-phenylphenol (**2b**; 68 mg, 0.45 mmol),  $\text{BF}_3 \cdot \text{OEt}_2$  (7  $\mu$ L, 0.06 mmol),  $\text{CH}_2\text{Cl}_2$  (3.0 mL), gave **3bb** as a white solid (76 mg, 0.18 mmol, 61%); **M.p.**: 135-136  $^\circ\text{C}$ ; **IR** (ATR): 3280, 1258, 1015, 790  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.96 (1H, s, OH), 7.93 (1H, d,  $J = 1.5$  Hz, ArH), 7.68-7.64 (2H, m, ArH), 7.62 (1H, d,  $J = 8.6$  Hz, ArH), 7.56-7.51 (2H, m, ArH), 7.51-7.43 (2H, m, ArH), 7.38 (1H, t,  $J = 8.6$  Hz, ArH), 7.35 (1H, d,  $J = 1.5$  Hz, ArH), 7.26 (1H, dd,  $J = 8.6, 1.5$  Hz, ArH), 3.91 (3H, s,  $\text{OCH}_3$ );  **$^{13}\text{C-NMR}$**  (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : 154.3 (ArC), 144.4 (ArC), 143.6 (ArC), 139.9 (ArC), 138.4 (ArC), 132.3



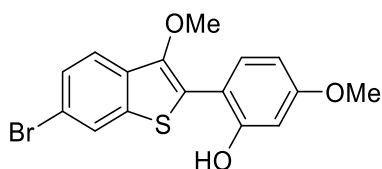
(ArC), 130.9 (ArCH), 128.8 (ArCH), 128.1 (ArCH), 127.8 (ArCH), 127.0 (ArCH), 126.2 (ArC), 125.3 (ArCH), 121.7 (ArCH), 119.7 (ArCH), 119.2 (ArC), 117.6 (ArC), 116.9 (ArCH), 62.5 (OCH<sub>3</sub>); **HRMS** (ESI): Calcd. for C<sub>21</sub>H<sub>14</sub>BrO<sub>2</sub>S [M-H]<sup>-</sup>: 408.9903; found: 408.9903.

### 2-(6-Bromo-3-methoxybenzo[b]thiophen-2-yl)-5-(tert-butyl)phenol (**3bd**)



**1b** (0.11 g, 0.42 mmol), TFAA (88  $\mu$ L, 0.63 mmol), THF (4.2 mL), 3-*tert*-butylphenol (**2d**; 95 mg, 0.63 mmol), BF<sub>3</sub>·OEt<sub>2</sub> (10  $\mu$ L, 0.08 mmol), CH<sub>2</sub>Cl<sub>2</sub> (4.2 mL), gave **3bd** as a white solid (133 mg, 0.34 mmol, 81%); **M.p.**: 120-121 °C; **IR** (ATR): 3288, 1067, 1020, 791 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.91 (1H, s, OH), 7.83 (1H, s, ArH), 7.59 (1H, d, *J* = 8.4 Hz, ArH), 7.51 (1H, d, *J* = 8.4 Hz, ArH), 7.39 (1H, d, *J* = 8.4 Hz, ArH), 7.12 (1H, s, ArH), 7.03 (1H, d, *J* = 8.4 Hz, ArH), 3.87 (3H, s, OCH<sub>3</sub>), 1.35 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>); **<sup>13</sup>C-NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$ : 154.6 (ArC), 153.7 (ArC), 143.9 (ArC), 138.2 (ArC), 132.3 (ArC), 130.0 (ArCH), 128.0 (ArCH), 126.6 (ArC), 125.2 (ArCH), 121.6 (ArCH), 118.9 (ArC), 118.2 (ArCH), 115.6 (ArC), 115.5 (ArCH), 62.4 (OCH<sub>3</sub>), 34.7 (C(CH<sub>3</sub>)<sub>3</sub>), 31.1 (C(CH<sub>3</sub>)<sub>3</sub>); **HRMS** (ESI): Calcd. for C<sub>19</sub>H<sub>18</sub>BrO<sub>2</sub>S [M-H]<sup>-</sup>: 389.0216; found: 389.0216.

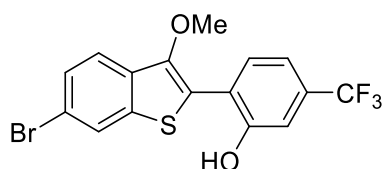
### 2-(6-Bromo-3-methoxybenzo[b]thiophen-2-yl)-5-methoxyphenol (**3bf**)



**1b** (0.10 g, 0.39 mmol), TFAA (82  $\mu$ L, 0.59 mmol), THF (3.9 mL), 3-methoxyphenol (**2f**; 64  $\mu$ L, 0.59 mmol), BF<sub>3</sub>·OEt<sub>2</sub> (10  $\mu$ L, 0.08 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3.9 mL), gave **3bf** as a white solid (115 mg,

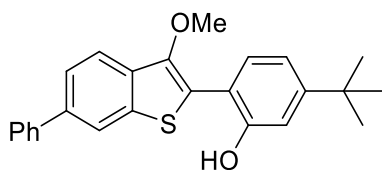
0.31, 82%); **M.p.**: 100-101 °C; IR (ATR): 3276, 1617, 1070, 795 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>) δ: 7.96 (1H, s, OH), 7.90 (1H, d, *J* = 1.5 Hz, ArH), 7.58 (1H, d, *J* = 8.3 Hz, ArH), 7.51 (1H, dd, *J* = 8.6, 1.5 Hz, ArH), 7.36 (1H, d, *J* = 8.8 Hz, ArH), 6.63 (1H, d, *J* = 2.4 Hz, ArH), 6.59 (1H, dd, *J* = 8.6, 2.7 Hz, ArH), 3.85 (3H, s, OCH<sub>3</sub>), 3.84 (3H, s, OCH<sub>3</sub>); **<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>) δ: 161.9 (ArC), 155.3 (ArC), 143.3 (ArC), 137.9 (ArC), 132.3 (ArC), 131.2 (ArCH), 127.9 (ArCH), 126.4 (ArC), 125.1 (ArCH), 121.4 (ArCH), 118.7 (ArC), 111.2 (ArC), 108.0 (ArCH), 102.9 (ArCH), 62.1 (OCH<sub>3</sub>), 55.4 (OCH<sub>3</sub>); **HRMS** (APCI): Calcd. for C<sub>16</sub>H<sub>14</sub>BrO<sub>3</sub>S [M+H]<sup>+</sup>: 364.9842; found: 364.9837.

### 2-(6-Bromo-3-methoxybenzo[*b*]thiophen-2-yl)-5-(trifluoromethyl)phenol (**3bg**)



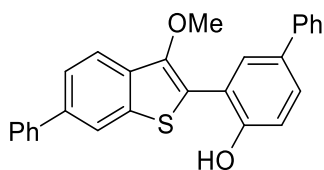
**1b** (0.10 g, 0.39 mmol), TFAA (82 μL, 0.58 mmol), THF (3.9 mL), 3-(trifluoromethyl)phenol (**2g**; 70 μL, 0.58 mmol), BF<sub>3</sub>·OEt<sub>2</sub> (10 μL, 0.08 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3.9 mL), gave **3bg** as a white solid (128 mg, 0.32, 82%); **M.p.**: 98-100 °C; IR (ATR): 3245, 1334, 1115, 1065, 811 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>) δ: 8.09 (1H, s, OH), 7.93 (1H, d, *J* = 1.5 Hz, ArH), 7.63 (1H, d, *J* = 8.5 Hz, ArH), 7.60-7.49 (2H, m, ArH), 7.36 (1H, s, ArH), 7.25 (1H, dd, *J* = 8.5, 1.5 Hz, ArH), 3.89 (3H, s, OCH<sub>3</sub>); **<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>) δ: 154.2 (ArC), 145.3 (ArC), 138.6 (ArC), 132.4 (q, *J* = 32.9 Hz, ArCCF<sub>3</sub>), 131.9 (ArC), 131.0 (ArCH), 128.4 (ArCH), 125.4 (ArCH), 124.7 (ArC), 123.7 (q, *J* = 270.8 Hz, CCF<sub>3</sub>), 122.1 (ArC), 122.0 (ArCH), 119.8 (ArC), 117.4 (q, *J* = 3.7 Hz, ArCH), 115.8 (q, *J* = 3.7 Hz, ArCH), 62.7 (OCH<sub>3</sub>); **HRMS** (APCI): Calcd. for C<sub>16</sub>H<sub>11</sub>BrF<sub>3</sub>O<sub>2</sub>S [M+H]<sup>+</sup>: 402.9610; found: 402.9613.

### 5-(*tert*-Butyl)-2-(3-methoxy-6-phenylbenzo[*b*]thiophen-2-yl)phenol (**3cd**)



**1c** (77 mg, 0.30 mmol), TFAA (63  $\mu$ L, 0.45 mmol), THF (3.0 mL), 3-*tert*-butylphenol (68 mg, 0.45 mmol),  $\text{BF}_3 \cdot \text{OEt}_2$  (7  $\mu$ L, 0.06 mmol),  $\text{CH}_2\text{Cl}_2$  (3.0 mL), gave **3cd** as a white solid (105 mg, 0.27 mmol, 90%); **M.p.**: 119-120  $^\circ\text{C}$ ; **IR** (ATR): 3279, 1352, 1060, 764  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.07 (1H, s, OH), 7.98 (1H, d,  $J = 1.0$  Hz, ArH), 7.81 (1H, d,  $J = 8.0$  Hz, ArH), 7.73-7.62 (3H, m, ArH), 7.54-7.46 (2H, m, ArH), 7.45 (1H, d,  $J = 8.0$  Hz, ArH), 7.39 (1H, t,  $J = 8.0$  Hz, ArH), 7.15 (1H, d,  $J = 2.0$  Hz, ArH), 7.06 (1H, dd,  $J = 8.0, 2.0$  Hz, ArH), 3.93 (3H, s,  $\text{OCH}_3$ ), 1.37 (9H, s,  $\text{C}(\text{CH}_3)_3$ );  **$^{13}\text{C-NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 154.3 (ArC), 153.7 (ArC), 144.0 (ArC), 140.8 (ArC), 138.4 (ArC), 137.6 (ArC), 132.6 (ArC), 130.1 (ArCH), 128.9 (ArCH), 127.4 (ArCH), 127.3 (ArCH), 126.6 (ArC), 124.2 (ArCH), 121.1 (ArCH), 120.7 (ArCH), 118.1 (ArCH), 116.1 (ArC), 115.5 (ArCH), 62.4 ( $\text{OCH}_3$ ), 34.7( $\text{C}(\text{CH}_3)_3$ ), 31.1( $\text{C}(\text{CH}_3)_3$ ); **HRMS** (APCI): Calcd. for  $\text{C}_{25}\text{H}_{23}\text{O}_2\text{S}$   $[\text{M-H}]^-$ : 387.1424; found: 387.1429.

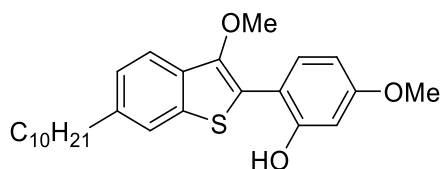
### 3-(3-Methoxy-6-phenylbenzo[*b*]thiophen-2-yl)-[1,1'-biphenyl]-4-ol (**3ce**)



**1c** (71 mg, 0.28 mmol), TFAA (58  $\mu$ L, 0.42 mmol), THF (2.8 mL), 4-phenylphenol (**3e**; 73 mg, 0.42 mmol),  $\text{BF}_3 \cdot \text{OEt}_2$  (7  $\mu$ L, 0.06 mmol),  $\text{CH}_2\text{Cl}_2$  (2.8 mL), gave **3ce** as a white powder (87 mg, 0.21 mmol, 77%); **M.p.**: 196-198  $^\circ\text{C}$ ; **IR** (ATR): 3232, 1257, 1011, 787  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.04 (1H, s, OH), 8.00 (1H, d,  $J = 1.0$  Hz, ArH), 7.84 (1H, d,  $J = 8.3$  Hz, ArH), 7.73 (1H, d,  $J = 2.2$  Hz, ArH), 7.71-7.65 (3H, m, ArH), 7.64-7.60 (2H, m, ArH), 7.58 (1H, dd,  $J = 8.3,$

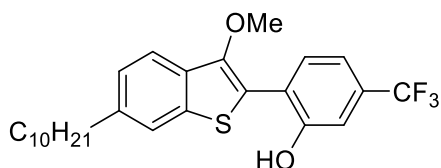
2.2 Hz, *ArH*), 7.53-7.43 (4H, m, *ArH*), 7.39 (1H, t,  $J = 7.3$  Hz, *ArH*), 7.35 (1H, t,  $J = 7.3$  Hz, *ArH*), 7.18 (1H, d,  $J = 8.3$  Hz, *ArH*), 3.96 (3H, s,  $\text{OCH}_3$ );  $^{13}\text{C-NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 153.6 (*ArC*), 144.7 (*ArC*), 140.7 (*ArC*), 140.3 (*ArC*), 138.7 (*ArC*), 137.8 (*ArC*), 134.0 (*ArC*), 132.5 (*ArC*), 129.19 (*ArCH*), 129.16 (*ArCH*), 128.9 (*ArCH*), 128.8 (*ArCH*), 127.5 (*ArCH*), 127.4 (*ArCH*), 127.0 (*ArCH*), 126.8 (*ArCH*), 126.0 (*ArC*), 124.4 (*ArCH*), 121.1 (*ArCH*), 120.9 (*ArCH*), 119.4 (*ArC*), 118.9 (*ArCH*), 62.5 ( $\text{OCH}_3$ ); **HRMS** (ESI): Calcd. for  $\text{C}_{27}\text{H}_{21}\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 409.1257; found: 409.1255.

### 2-(6-Decyl-3-methoxybenzo[*b*]thiophen-2-yl)-5-methoxyphenol (**3ef**)



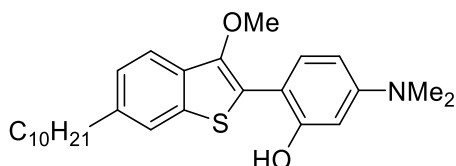
**1e** (94 mg, 0.29 mmol), TFAA (61  $\mu\text{L}$ , 0.44 mmol), THF (2.9 mL), 3-methoxyphenol (**2f**; 48  $\mu\text{L}$ , 0.44 mmol),  $\text{BF}_3 \cdot \text{OEt}_2$  (7  $\mu\text{L}$ , 0.06 mmol),  $\text{CH}_2\text{Cl}_2$  (2.9 mL), gave **3ef** as a colorless oil (91 mg, 0.21 mmol, 73%); **IR** (ATR): 3231, 1346, 1326, 1090  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.11 (1H, s, *OH*), 7.64 (1H, d,  $J = 8.1$  Hz, *ArH*), 7.56 (1H, s, *ArH*), 7.39 (1H, d,  $J = 8.6$  Hz, *ArH*), 7.24 (1H, d,  $J = 8.1$  Hz, *ArH*), 6.64 (1H, d,  $J = 2.4$  Hz, *ArH*), 6.59 (1H, dd,  $J = 8.6, 2.4$  Hz, *ArH*), 3.87 (3H, s,  $\text{OCH}_3$ ), 3.84 (3H, s,  $\text{OCH}_3$ ), 2.73 (2H, t,  $J = 7.0$  Hz, *ArCH}\_2*), 1.68 (2H, m,  $\text{CH}_2$ ), 1.45-1.16 (14H, m,  $\text{CH}_2$ ), 0.90 (3H, t,  $J = 7.0$  Hz,  $\text{CH}_3$ );  $^{13}\text{C-NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : 161.6 (*ArC(OH)*), 155.3 (*ArC*), 143.6 (*ArC*), 140.3 (*ArC*), 137.0 (*ArC*), 131.5 (*ArC*), 131.2 (*ArCH*), 125.6 (*ArCH*), 124.6 (*ArC*), 122.0 (*ArCH*), 120.1 (*ArCH*), 111.9 (*ArC*), 107.8 (*ArCH*), 102.9 (*ArCH*), 62.0 ( $\text{OCH}_3$ ), 55.4 ( $\text{OCH}_3$ ), 36.1 ( $\text{CH}_2$ ), 31.9 ( $\text{CH}_2$ ), 31.7 ( $\text{CH}_2$ ), 29.6 ( $\text{CH}_2$ ), 29.6 ( $\text{CH}_2$ ), 29.5 ( $\text{CH}_2$ ), 29.3 ( $\text{CH}_2$ ), 29.3 ( $\text{CH}_2$ ), 22.7 ( $\text{CH}_2$ ), 14.1 ( $\text{CH}_3$ ); **HRMS** (APCI): Calcd. for  $\text{C}_{26}\text{H}_{35}\text{O}_3\text{S}$   $[\text{M}+\text{H}]^+$ : 427.2301; found: 427.2300.

**2-(6-Decyl-3-methoxybenzo[*b*]thiophen-2-yl)-5-(trifluoromethyl)phenol (3eg)**



**1e** (69 mg, 0.22 mmol), TFAA (45  $\mu$ L, 0.32 mmol), THF (2.0 mL), 3-(trifluoromethyl)phenol (**2g**; 39  $\mu$ L, 0.32 mmol),  $\text{BF}_3 \cdot \text{OEt}_2$  (5  $\mu$ L, 0.04 mmol),  $\text{CH}_2\text{Cl}_2$  (2.0 mL), gave **3eg** as a colorless oil (75 mg, 0.16 mmol, 75%); **IR** (ATR): 3252, 1332, 1125, 800  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$**  (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.27 (1H, s, OH), 7.68 (1H, d,  $J = 8.0$  Hz, ArH), 7.59 (1H, s, ArH), 7.57 (1H, d,  $J = 8.0$  Hz, ArH), 7.34 (1H, s, ArH), 7.27 (1H, d,  $J = 8.0$  Hz, ArH), 7.23 (1H, d,  $J = 8.0$  Hz, ArH), 3.91 (3H, s,  $\text{OCH}_3$ ), 2.74 (2H, t,  $J = 7.5$  Hz,  $\text{ArCH}_2$ ), 1.68 (2H, m,  $\text{CH}_2$ ), 1.45-1.14 (14H, m,  $\text{CH}_2$ ), 0.88 (3H, t,  $J = 7.5$  Hz,  $\text{CH}_3$ );  **$^{13}\text{C-NMR}$**  (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : 154.2 (ArC(OH)), 145.5 (ArC), 141.3 (ArC), 137.7 (ArC), 131.9 (q,  $J = 32.1$  Hz,  $\text{ArCCF}_3$ ), 131.1 (ArC), 131.0 (ArCH), 126.0 (ArCH), 123.8 (q,  $J = 271.3$  Hz,  $\text{CF}_3$ ), 123.2 (ArC), 122.8, (ArC) 122.1 (ArCH), 120.6 (ArCH), 117.2 (q,  $J = 3.6$  Hz, ArCH), 115.7 (q,  $J = 3.6$  Hz, ArCH), 62.6 ( $\text{OCH}_3$ ), 36.1 ( $\text{CH}_2$ ), 31.9 ( $\text{CH}_2$ ), 31.6 ( $\text{CH}_2$ ), 29.6 ( $\text{CH}_2$ ), 29.6 ( $\text{CH}_2$ ), 29.5 ( $\text{CH}_2$ ), 29.3 ( $\text{CH}_2$ ), 29.3 ( $\text{CH}_2$ ), 22.7 ( $\text{CH}_2$ ), 14.1 ( $\text{CH}_3$ ); **HRMS** (APCI): Calcd. for  $\text{C}_{26}\text{H}_{32}\text{F}_3\text{O}_2\text{S}$  [ $\text{M}+\text{H}$ ] $^+$ : 465.2070; found: 465.2073.

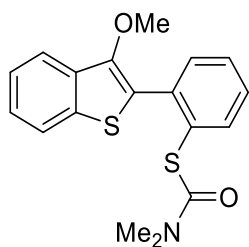
**2-(6-Decyl-3-methoxybenzo[*b*]thiophen-2-yl)-5-(dimethylamino)phenol (3eh)**



**1e** (0.10 g, 0.33 mmol), TFAA (68  $\mu$ L, 0.49 mmol), THF (3.3 mL), 3-(dimethylamino)phenol (**2h**; 67 mg, 0.49 mmol),  $\text{BF}_3 \cdot \text{OEt}_2$  (8  $\mu$ L, 0.07 mmol),  $\text{CH}_2\text{Cl}_2$  (3.3 mL), gave **3eh** as a white solid (72 mg, 0.16 mmol, 50%); **M.p.**: 78-79  $^\circ\text{C}$ ; **IR** (ATR): 3284, 1258, 1015  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.13 (1H, s, OH), 7.60 (1H, d,  $J = 8.5$  Hz, ArH), 7.54 (1H, s, ArH), 7.33 (1H, d,  $J = 8.5$

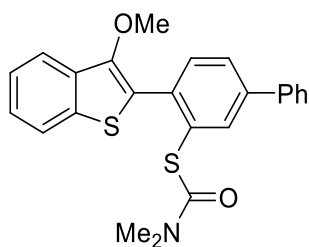
Hz, ArH), 7.21 (1H, d,  $J = 8.5$  Hz, ArH), 6.42-6.38 (1H, m, ArH), 6.41 (1H, s, ArH), 3.86 (3H, s, OCH<sub>3</sub>), 3.00 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>), 2.72 (2H, t,  $J = 7.5$  Hz, ArCH<sub>2</sub>), 1.74-1.60 (2H, m, CH<sub>2</sub>), 1.41-1.16 (14H, m, CH<sub>2</sub>), 0.89 (3H, t,  $J = 7.5$  Hz, CH<sub>3</sub>); <sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$ : 155.0 (ArC(OH)), 152.3 (ArC), 142.7 (ArC), 139.8 (ArC), 136.6 (ArC), 131.7 (ArC), 131.1 (ArCH), 125.9 (ArC), 125.5 (ArCH), 121.9 (ArCH), 119.8 (ArCH), 107.5 (ArC), 105.6 (ArCH), 100.9 (ArCH), 61.8 (OCH<sub>3</sub>), 40.3 (N(CH<sub>3</sub>)<sub>2</sub>), 36.1 (CH<sub>2</sub>), 31.9 (CH<sub>2</sub>), 31.7 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 22.7 (CH<sub>2</sub>), 14.1 (CH<sub>3</sub>); HRMS (APCI): Calcd. for C<sub>27</sub>H<sub>38</sub>NO<sub>2</sub>S [M+H]<sup>+</sup>: 440.2618; found: 440.2607.

**S-(2-(3-Methoxybenzo[b]thiophen-2-yl)phenyl) dimethylcarbamothioate (5aa)**



**3aa** (57 mg, 0.20 mmol), NaH (24 mg, 0.60 mmol), dimethylthiocarbamoyl chloride (43 mg, 0.40 mmol), DMF (2.0 mL), Ph<sub>2</sub>O (4.0 mL), gave **5aa** as a colorless oil (61 mg, 0.18 mmol, 89%); **IR** (ATR): 1262, 1088, 1017, 800, 734 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>) δ: 7.80 (1H, d, *J* = 7.8 Hz, ArH), 7.74 (1H, d, *J* = 7.8 Hz, ArH), 7.68 (1H, dd, *J* = 5.8, 3.5 Hz, ArH), 7.60 (1H, dd, *J* = 5.8, 3.5 Hz, ArH), 7.48-7.42 (2H, m, ArH), 7.42-7.33 (2H, m, ArH), 3.67 (3H, s, OCH<sub>3</sub>), 2.96 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>); **<sup>13</sup>C-NMR** (126 MHz, CDCl<sub>3</sub>) δ: (1 × ArCH missing), 166.3 (CO), 147.6 (ArC), 137.7 (ArCH), 137.5 (ArC), 137.0 (ArC), 133.6 (ArC), 132.3 (ArCH), 130.3 (ArC), 129.0 (ArCH), 124.9 (ArCH), 123.9 (ArCH), 122.3 (ArCH), 121.3 (ArC), 121.2 (ArCH), 60.9 (OCH<sub>3</sub>), 37.0 (N(CH<sub>3</sub>)<sub>2</sub>); **HRMS** (APCI): Calcd. for C<sub>18</sub>H<sub>18</sub>NO<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 344.0773; found: 344.0772.

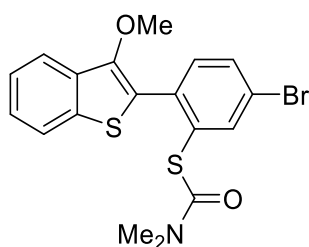
**S-(4-(3-Methoxybenzo[b]thiophen-2-yl)-[1,1'-biphenyl]-3-yl) dimethylcarbamothioate (5ab)**



**3ab** (53 mg, 0.16 mmol), NaH (60%, 19 mg, 0.48 mmol), dimethylthiocarbamoyl chloride (34 mg, 0.32 mmol), DMF (1.6 mL), Ph<sub>2</sub>O (1.6 mL), gave **5ab** as a white solid (49 mg, 0.12 mmol, 73%); **M.p.**: 106-108 °C; **IR** (ATR): 1664, 1349, 1095, 1061 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>) δ: 7.92 (1H, s, ArH), 7.81 (1H, d, *J* = 7.6 Hz, ArH), 7.75 (1H, d, *J* = 7.6 Hz, ArH), 7.70-7.63 (4H,

m, ArH), 7.49-7.43 (2H, m, ArH), 7.43-7.33 (3H, m, ArH), 3.73 (3H, s, OCH<sub>3</sub>), 2.98 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>) δ: 166.1 (CO), 147.8 (ArC), 141.9 (ArC), 139.7 (ArC), 137.0 (ArC), 136.3 (ArCH), 136.2 (ArC), 133.6 (ArC), 132.6 (ArCH), 130.6 (ArC), 128.8 (ArCH), 127.73 (ArCH), 127.65 (ArCH), 127.3 (ArCH), 124.9 (ArCH), 123.9 (ArCH), 122.4 (ArCH), 121.3 (ArC), 121.2 (ArCH), 61.0 (OCH<sub>3</sub>), 37.0 (N(CH<sub>3</sub>)<sub>2</sub>); **HRMS** (APCI): Calcd. for C<sub>24</sub>H<sub>22</sub>NO<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 420.1086; found: 420.1085.

**S-(5-Bromo-2-(3-methoxybenzo[*b*]thiophen-2-yl)phenyl) dimethylcarbamothioate (5ac)**

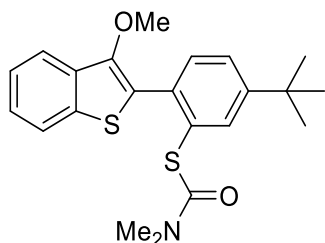


**3ac** (72 mg, 0.21 mmol), NaH (60%, 25 mg, 0.63 mmol), dimethylthiocarbamoyl chloride (45 mg, 0.42 mmol), DMF (2.1 mL), Ph<sub>2</sub>O (2.1 mL), gave **5ac** as a white amorphous solid (75 mg, 0.18 mmol, 83%); **IR** (ATR): 1667, 1348, 1093 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>) δ: 7.85 (1H, d, *J* = 2.0 Hz, ArH), 7.80 (1H, d, *J* = 8.0 Hz, ArH), 7.74 (1H, d, *J* = 8.0 Hz, ArH), 7.57 (1H, dd, *J* = 8.0, 2.0 Hz, ArH), 7.47 (1H, d, *J* = 8.0 Hz, ArH), 7.44-7.30 (2H, m, ArH), 3.68 (3H, s, OCH<sub>3</sub>), 2.96 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>); **<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>) δ: 165.4 (CO), 147.9 (ArC), 139.9 (ArCH), 137.0 (ArC), 136.3 (ArC), 133.4 (ArC), 133.3 (ArCH), 132.14 (ArC), 132.11 (ArCH), 125.1 (ArCH), 124.0 (ArCH), 122.41 (ArC), 122.35 (ArCH), 121.3 (ArCH), 120.3 (ArC), 61.0 (OCH<sub>3</sub>), 37.0 (N(CH<sub>3</sub>)<sub>2</sub>); **HRMS** (APCI): Calcd. for C<sub>18</sub>H<sub>17</sub>NO<sub>2</sub>BrS<sub>2</sub> [M+H]<sup>+</sup>: 421.9879; found: 421.9871.



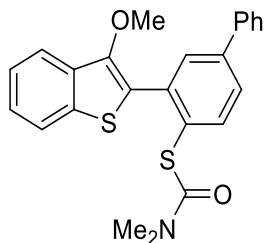
***S*-5-(*tert*-Butyl)-2-(3-methoxybenzo[*b*]thiophen-2-yl)phenyl) dimethylcarbamothioate**

**(5ad)**



**3ad** (71 mg, 0.23 mmol), NaH (60%, 27 mg, 0.68 mmol), dimethylthiocarbamoyl chloride (49 mg, 0.45 mmol), DMF (2.3 mL), Ph<sub>2</sub>O (2.3 mL), gave **5ad** as a white solid (65 mg, 0.16 mmol, 71%); **M.p.**: 165-166 °C; **IR** (ATR): 1672, 1258, 1090, 1015, 792 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>) δ: 7.70 (1H, d, *J* = 8.0 Hz, *ArH*), 7.64 (1H, d, *J* = 8.0 Hz, *ArH*), 7.59 (1H, s, *ArH*), 7.45 (1H, d, *J* = 8.0 Hz, *ArH*), 7.38 (1H, d, *J* = 8.0 Hz, *ArH*), 7.29 (1H, t, *J* = 7.0 Hz, *ArH*), 7.26 (1H, t, *J* = 7.0 Hz, *ArH*), 3.60 (3H, s, OCH<sub>3</sub>), 2.87 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>), 1.30 (9H, s, (CH<sub>3</sub>)<sub>3</sub>); **<sup>13</sup>C-NMR** (126 MHz, CDCl<sub>3</sub>) δ: 166.3 (CO), 152.0 (ArC), 147.5 (ArC), 136.9 (ArC), 134.8 (ArCH), 134.4 (ArC), 133.6 (ArC), 131.9 (ArCH), 129.4 (ArC), 126.3 (ArCH), 124.7 (ArCH), 123.8 (ArCH), 122.3 (ArCH), 121.6 (ArC), 121.1 (ArCH), 60.9 (OCH<sub>3</sub>), 37.0 (N(CH<sub>3</sub>)<sub>2</sub>), 34.7 (C(CH<sub>3</sub>)<sub>3</sub>), 31.2 (C(CH<sub>3</sub>)<sub>3</sub>); **HRMS** (APCI): Calcd. for C<sub>22</sub>H<sub>26</sub>NO<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 400.1399; found: 400.1391.

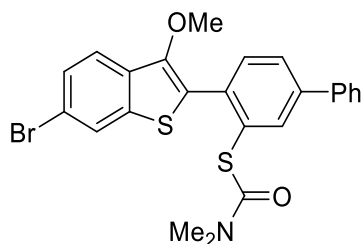
***S*-3-(3-Methoxybenzo[*b*]thiophen-2-yl)-[1,1'-biphenyl]-4-yl) dimethylcarbamothioate (5ae)**



**3ae** (76 mg, 0.23 mmol), NaH (60%, 28 mg, 0.69 mmol), dimethylthiocarbamoyl chloride (49 mg, 0.46 mmol), DMF (2.3 mL), Ph<sub>2</sub>O (2.0 mL), gave **5ae** as a colorless amorphous solid (96 mg, 0.23 mmol, quant.); **IR** (ATR): 1666, 1348, 1094, 762 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>) δ: 7.85

(1H, d,  $J = 3.0$  Hz, ArH), 7.81 (1H, d,  $J = 8.0$  Hz, ArH), 7.75 (1H, d,  $J = 8.0$  Hz, ArH), 7.74 (1H, d,  $J = 8.0$  Hz, ArH), 7.67 (1H, dd,  $J = 8.0, 3.0$  Hz, ArH), 7.66-7.61 (2H, m, ArH), 7.48-7.43 (2H, m, ArH), 7.43-7.34 (3H, m, ArH), 3.72 (3H, s, OCH<sub>3</sub>), 2.99 (6H, br s, N(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>) δ: 166.3 (CO), 147.7 (ArC), 141.9 (ArC), 139.7 (ArC), 138.1 (ArCH), 137.8 (ArC), 137.0 (ArC), 133.6 (ArC), 130.8 (ArCH), 129.1 (ArC), 128.9 (ArCH), 127.9 (ArCH), 127.6 (ArCH), 127.2 (ArCH), 124.9 (ArCH), 124.0 (ArCH), 122.4 (ArCH), 121.3 (ArCH), 121.2 (ArC), 61.0 (OCH<sub>3</sub>), 37.0 (N(CH<sub>3</sub>)<sub>2</sub>); HRMS (APCI): Calcd. for C<sub>24</sub>H<sub>22</sub>NO<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 420.1086; found: 420.1070.

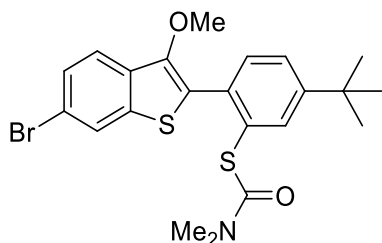
**S-(4-(6-Bromo-3-methoxybenzo[*b*]thiophen-2-yl)-[1,1'-biphenyl]-3-yl)  
dimethylcarbamothioate (**5bb**)**



**3bb** (70 mg, 0.17 mmol), NaH (60%, 20 mg, 0.51 mmol), dimethylthiocarbamoyl chloride (37 mg, 0.34 mmol), DMF (1.7 mL), Ph<sub>2</sub>O (1.7 mL), gave **5bb** as a colorless amorphous solid (55 mg, 0.11 mmol, 65%); IR (ATR): 1667, 1258, 1017, 791 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.91 (1H, s, ArH), 7.88 (1H, s, ArH), 7.72-7.60 (5H, m, ArH), 7.53-7.42 (3H, m, ArH), 7.38 (1H, d,  $J = 7.3$  Hz, ArH), 3.70 (3H, s, OCH<sub>3</sub>), 2.98 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>) δ: 165.9 (CO), 147.5 (ArC), 142.1 (ArC), 139.6 (ArC), 138.4 (ArC), 136.4 (ArCH), 135.7 (ArC), 132.52 (ArCH), 132.45 (ArC), 130.6 (ArC), 128.8 (ArCH), 127.8 (ArCH), 127.7 (ArCH), 127.4 (ArCH), 127.2 (ArCH), 124.8 (ArCH), 122.5 (ArCH), 121.3 (ArC), 118.8 (ArC), 61.0 (OCH<sub>3</sub>), 37.0 (N(CH<sub>3</sub>)<sub>2</sub>); HRMS (ESI): Calcd. for C<sub>24</sub>H<sub>20</sub>BrNO<sub>2</sub>S<sub>2</sub> [M+Na]<sup>+</sup>: 520.0011; found: 520.0002.

**S-(2-(6-Bromo-3-methoxybenzo[*b*]thiophen-2-yl)-5-(*tert*-butyl)phenyl)**

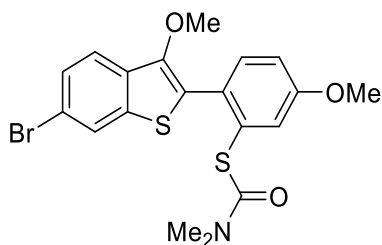
**dimethylcarbamothioate (5bd)**



**3bd** (0.13 g, 0.32 mmol), NaH (60%, 39 mg, 0.97 mmol), dimethylthiocarbamoyl chloride (70 mg, 0.65 mmol), DMF (3.2 mL), Ph<sub>2</sub>O (3.2 mL), gave **5bd** as an off-yellow amorphous solid (110 mg, 0.23 mmol, 71%); **IR** (ATR): 1667, 1347, 1080, 780 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>) δ: 7.86 (1H, s, ArH), 7.66 (1H, s, ArH), 7.63 (1H, d, *J* = 8.4 Hz, ArH), 7.52 (1H, d, *J* = 8.4 Hz, ArH), 7.49-7.42 (2H, m, ArH), 3.65 (3H, s, OCH<sub>3</sub>), 2.96 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>), 1.37 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>); **<sup>13</sup>C-NMR** (126 MHz, CDCl<sub>3</sub>) δ: 166.0 (CO), 152.3 (ArC), 147.1 (ArC), 138.2 (ArC), 134.8 (ArCH), 134.0 (ArC), 132.4 (ArC), 131.8 (ArCH), 129.4 (ArC), 127.2 (ArCH), 126.3 (ArCH), 124.7 (ArCH), 122.3 (ArCH), 121.6 (ArC), 118.5 (ArC), 60.8 (OCH<sub>3</sub>), 36.9 (N(CH<sub>3</sub>)<sub>2</sub>), 34.7 (C(CH<sub>3</sub>)<sub>3</sub>), 31.1 (C(CH<sub>3</sub>)<sub>3</sub>); **HRMS** (ESI): Calcd. for C<sub>22</sub>H<sub>25</sub>BrNO<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 478.0505; found: 478.0507.

**S-(2-(6-Bromo-3-methoxybenzo[*b*]thiophen-2-yl)-5-methoxyphenyl)**

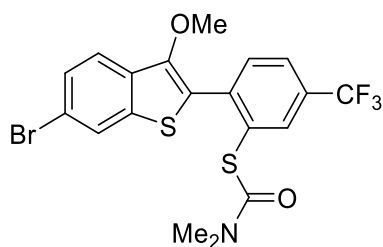
**dimethylcarbamothioate (5bf)**



**3bf** (0.11 g, 0.30 mmol), NaH (60%, 36 mg, 0.90 mmol), dimethylthiocarbamoyl chloride (65 mg, 0.60 mmol), DMF (3.0 mL), Ph<sub>2</sub>O (3.0 mL), gave **5bf** as a colorless amorphous solid (77 mg, 0.17 mmol, 57%); **IR** (ATR): 1670, 1257, 1036, 794 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>) δ: 7.84

(1H, s, ArH), 7.62 (1H, d,  $J = 8.6$  Hz, ArH), 7.49 (1H, d,  $J = 8.8$  Hz, ArH), 7.47 (1H, d,  $J = 8.8$  Hz, ArH), 7.22 (1H, d,  $J = 2.2$  Hz, ArH), 6.99 (1H, dd,  $J = 8.8, 2.2$  Hz, ArH), 3.86 (3H, s, OCH<sub>3</sub>), 3.64 (3H, s, OCH<sub>3</sub>), 2.96 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$ : 165.9 (CO), 159.8 (ArC), 147.2 (ArC), 138.3 (ArC), 133.0 (ArCH), 132.5 (ArCH), 131.3 (ArC), 129.0 (ArC), 127.3 (ArCH), 124.8 (ArC), 122.4 (ArCH), 122.2 (ArCH), 121.4 (ArC), 118.6 (ArC), 115.7 (ArCH), 60.8 (OCH<sub>3</sub>), 55.5 (OCH<sub>3</sub>), 37.1 (N(CH<sub>3</sub>)<sub>2</sub>); **HRMS** (APCI): Calcd. for C<sub>19</sub>H<sub>19</sub>BrNO<sub>3</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 451.9984; found: 451.9976.

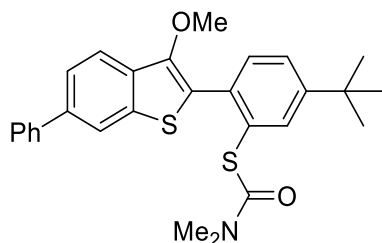
**S-(2-(6-Bromo-3-methoxybenzo[*b*]thiophen-2-yl)-5-(trifluoromethyl)phenyl)-*N,N*-dimethylcarbamothioate (5bg)**



**3bg** (0.12 g, 0.30 mmol), NaH (60%, 36 mg, 0.90 mmol), dimethylthiocarbamoyl chloride (64 mg, 0.60 mmol), DMF (3.0 mL), Ph<sub>2</sub>O (3.0 mL), gave **5bg** as yellow crystals (101 mg, 0.21 mmol, 69%); **M.p.**: 136-138 °C; **IR** (ATR): 1675, 1317, 1122, 1075 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.96 (1H, s, ArH), 7.88 (1H, s, ArH), 7.80-7.59 (3H, m, ArH), 7.50 (1H, dd,  $J = 8.6, 1.2$  Hz, ArH), 3.66 (3H, s, OCH<sub>3</sub>), 2.97 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ : 165.0 (CO), 148.0 (ArC), 140.7 (ArC), 138.4 (ArC), 134.5 (q,  $J = 3.9$  Hz, ArCH), 132.5 (ArCH), 132.1 (ArC), 131.5 (ArC), 131.1 (q,  $J = 32.0$  Hz, CCF<sub>3</sub>), 127.6 (ArCH), 125.7 (q,  $J = 3.6$  Hz, ArCH), 124.9 (ArCH), 123.5 (q,  $J = 273.2$  Hz, CCF<sub>3</sub>), 122.6 (ArCH), 120.2 (ArC), 119.2 (ArC), 61.2 (OCH<sub>3</sub>), 37.0 (N(CH<sub>3</sub>)<sub>2</sub>); **HRMS** (ESI): Calcd. for C<sub>19</sub>H<sub>15</sub>BrF<sub>3</sub>NO<sub>2</sub>S<sub>2</sub>Na [M+Na]<sup>+</sup>: 511.9572; found: 511.9560.

***S*-(5-(*tert*-Butyl)-2-(3-methoxy-6-phenylbenzo[*b*]thiophen-2-yl)phenyl)**

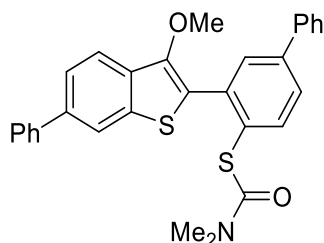
**dimethylcarbamothioate (5cd)**



**3cd** (0.10 g, 0.26 mmol), NaH (60%, 31 mg, 0.77 mmol), dimethylthiocarbamoyl chloride (55 mg, 0.51 mmol), DMF (2.6 mL), Ph<sub>2</sub>O (2.6 mL), gave **5cd** as a colorless amorphous solid (82 mg, 0.17 mmol, 67%); IR (ATR): 1660, 1258, 1016, 791 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.95 (1H, s, ArH), 7.85 (1H, d, *J* = 8.3 Hz, ArH), 7.73-7.60 (4H, m, ArH), 7.56 (1H, d, *J* = 8.1 Hz, ArH), 7.52-7.43 (3H, m, ArH), 7.37 (1H, t, *J* = 7.3 Hz, ArH), 3.71 (3H, s, OCH<sub>3</sub>), 2.98 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>), 1.39 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>) δ: 166.3 (CO), 152.1 (ArC), 147.4 (ArC), 141.1 (ArC), 138.1 (ArC), 137.6 (ArC), 134.9 (ArCH), 134.4 (ArC), 132.8 (ArC), 131.9 (ArCH), 129.4 (ArC), 128.8 (ArCH), 127.3 (ArCH), 127.2 (ArCH), 126.3 (ArCH), 123.5 (ArCH), 122.1 (ArC), 121.4 (ArCH), 120.7 (ArCH), 60.9 (OCH<sub>3</sub>), 37.0 (N(CH<sub>3</sub>)<sub>2</sub>), 34.8 (C(CH<sub>3</sub>)<sub>3</sub>), 31.2 (C(CH<sub>3</sub>)<sub>3</sub>); HRMS (APCI): Calcd. for C<sub>28</sub>H<sub>30</sub>NO<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 476.1712; found: 476.1713.

***S*-(3-(3-Methoxy-6-phenylbenzo[*b*]thiophen-2-yl)-[1,1'-biphenyl]-4-yl)**

**dimethylcarbamothioate (5ce)**

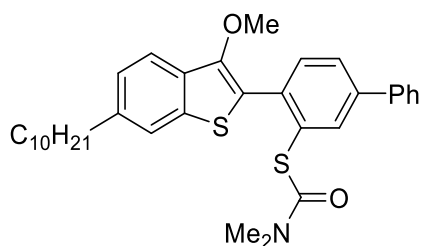


**3ce** (72 mg, 0.18 mmol), NaH (60%, 21 mg, 0.53 mmol), dimethylthiocarbamoyl chloride (38 mg, 0.35 mmol), DMF (1.8 mL), Ph<sub>2</sub>O (1.8 mL), gave **5ce** as an off-yellow amorphous solid (63 mg,

0.13 mmol, 72%); **IR** (ATR): 1711, 1359, 1008, 787  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.96 (1H, d,  $J = 1.0$  Hz, ArH), 7.87 (1H, d,  $J = 8.1$  Hz, ArH), 7.86 (1H, s, ArH), 7.75 (1H, d,  $J = 8.3$  Hz, ArH), 7.71-7.61 (6H, m, ArH), 7.52-7.42 (4H, m, ArH), 7.41-7.33 (2H, m, ArH), 3.74 (3H, s,  $\text{OCH}_3$ ), 3.00 (6H, s,  $\text{N}(\text{CH}_3)_2$ );  **$^{13}\text{C-NMR}$**  (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : 166.4 (CO), 147.7 (ArC), 142.0 (ArC), 141.1 (ArC), 139.8 (ArC), 138.4 (ArC), 138.1 (ArCH), 137.9 (ArC), 137.7 (ArC), 132.8 (ArC), 130.8 (ArCH), 129.1 (ArC), 128.92 (ArCH), 128.89 (ArCH), 127.9 (ArCH), 127.7 (ArCH), 127.4 (ArCH), 127.34 (ArCH), 127.26 (ArCH), 123.7 (ArCH), 121.7 (ArC), 121.5 (ArCH), 120.8 (ArCH), 61.1 ( $\text{OCH}_3$ ), 37.1 ( $\text{N}(\text{CH}_3)_2$ ); **HRMS** (ESI): Calcd. for  $\text{C}_{30}\text{H}_{25}\text{NO}_2\text{S}_2\text{Na}$   $[\text{M}+\text{Na}]^+$ : 518.1230; found: 518.1211.

**S-(4-(6-Decyl-3-methoxybenzo[*b*]thiophen-2-yl)-[1,1'-biphenyl]-3-yl)**

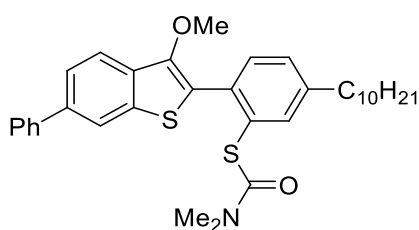
**dimethylcarbamothioate (5eb)**



**3eb** (91 mg, 0.19 mmol), NaH (60%, 23 mg, 0.57 mmol), dimethylthiocarbamoyl chloride (41 mg, 0.38 mmol), DMF (1.9 mL),  $\text{Ph}_2\text{O}$  (1.9 mL), gave **5eb** as a colorless amorphous solid (69 mg, 0.12 mmol, 64%); **IR** (ATR): 1668, 1466, 1351, 1094  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.92 (1H, s, ArH), 7.71 (1H, d,  $J = 8.0$  Hz, ArH), 7.70-7.64 (4H, m, ArH), 7.55 (1H, s, ArH), 7.50-7.42 (2H, m, ArH), 7.38 (1H, d,  $J = 8.0$  Hz, ArH), 7.23 (1H, dd,  $J = 8.0, 1.2$  Hz, ArH), 3.72 (3H, s,  $\text{OCH}_3$ ), 2.98 (6H, s,  $\text{N}(\text{CH}_3)_2$ ), 2.74 (2H, t,  $J = 7.7$  Hz,  $\text{ArCH}_2$ ), 1.81-1.62 (2H, m,  $\text{CH}_2$ ), 1.47-1.15 (14H, m,  $\text{CH}_2$ ), 0.89 (3H, t,  $J = 6.8$  Hz,  $\text{CH}_2\text{CH}_3$ );  **$^{13}\text{C-NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : (1  $\times$   $\text{CH}_2$  missing), 166.2 (CO), 147.7 (ArC), 141.7 (ArC), 140.2 (ArC), 139.7 (ArC), 137.3 (ArC), 136.33 (ArC), 136.28 (ArCH), 132.6 (ArCH), 131.6 (ArC), 130.5 (ArC), 128.8 (ArCH), 127.7 (ArCH),

127.6 (ArCH), 127.2 (ArCH), 125.1 (ArCH), 121.6 (ArCH), 120.9 (ArCH), 120.2 (ArC), 61.0 (OCH<sub>3</sub>), 37.0 (N(CH<sub>3</sub>)<sub>2</sub>), 36.1 (CH<sub>2</sub>), 31.9 (CH<sub>2</sub>), 31.8 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 22.7 (CH<sub>2</sub>), 14.1 (CH<sub>3</sub>); **HRMS** (APCI): Calcd. for C<sub>34</sub>H<sub>42</sub>NO<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 560.2651; found: 560.2640.

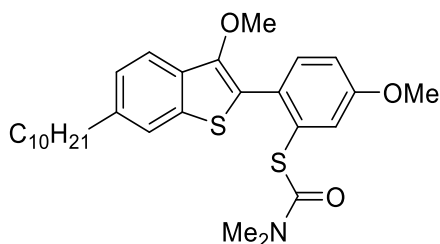
**S-(5-Decyl-2-(3-methoxy-6-phenylbenzo[b]thiophen-2-yl)phenyl) dimethylcarbamothioate (5eb')**



**3eb'** (142 mg, 0.30 mmol), NaH (60%, 36 mg, 0.90 mmol), dimethylthiocarbamoyl chloride (74 mg, 0.60 mmol), DMF (3.0 mL), Ph<sub>2</sub>O (3.0 mL), gave **5eb'** as a colorless solid (117 mg, 0.21 mmol, 70%); **IR** (ATR): 1671, 1464, 1353, 1062 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>) δ: 7.93 (1H, dd, *J* = 1.6, 0.6 Hz, ArH), 7.84 (1H, dd, *J* = 8.3, 0.6 Hz, ArH), 7.70-7.64 (2H, m, ArH), 7.62 (1H, dd, *J* = 8.3, 1.6 Hz, ArH), 7.52 (1H, d, *J* = 8.2 Hz, ArH), 7.50 (1H, d, *J* = 1.5 Hz, ArH), 7.49 – 7.44 (2H, m, ArH), 7.40-7.33 (1H, m, ArH), 7.27 (1H, dd, *J* = 8.0, 1.9 Hz, ArH), 3.69 (3H, s, OCH<sub>3</sub>), 2.97 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>), 2.67 (2H, t, *J* = 7.8 Hz, ArCH<sub>2</sub>), 1.68 (2H, tt, *J* = 7.8, 7.8 Hz, CH<sub>2</sub>), 1.46-1.20 (14H, m, CH<sub>2</sub>), 0.89 (3H, t, *J* = 6.9 Hz, CH<sub>2</sub>CH<sub>3</sub>); **<sup>13</sup>C-NMR** (126 MHz, CDCl<sub>3</sub>) δ: 166.4 (CO), 147.4 (ArC), 144.4 (ArC), 141.1 (ArC), 138.1 (ArC), 137.63 (ArCH), 137.60 (ArC), 134.6 (ArC), 132.8 (ArC), 132.1 (ArCH), 129.7 (ArC), 129.3 (ArCH), 128.8 (ArCH), 127.35 (ArCH), 127.26 (ArCH), 123.6 (ArCH), 122.0 (ArC), 121.4 (ArCH), 120.7 (ArCH), 60.9 (OCH<sub>3</sub>), 37.0 (N(CH<sub>3</sub>)<sub>2</sub>), 35.6 (CH<sub>2</sub>), 31.9 (CH<sub>2</sub>), 31.1 (CH<sub>2</sub>), 29.62 (CH<sub>2</sub>), 29.58 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 29.4 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 22.7 (CH<sub>2</sub>), 14.1 (CH<sub>3</sub>); **HRMS** (ESI): Calcd. for C<sub>34</sub>H<sub>41</sub>NO<sub>2</sub>S<sub>2</sub> [M+Na]<sup>+</sup>: 582.2471; found: 582.2445.

***S*-(2-(6-Decyl-3-methoxybenzo[*b*]thiophen-2-yl)-5-methoxyphenyl)**

**dimethylcarbamothioate (5ef)**

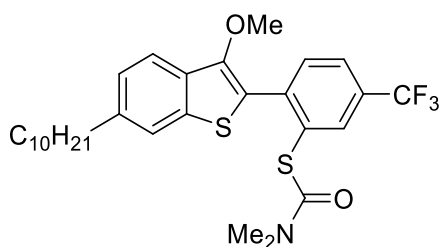


**3ef** (82 mg, 0.19 mmol), NaH (60%, 23 mg, 0.58 mmol), dimethylthiocarbonyl chloride (41 mg, 0.38 mmol), DMF (1.9 mL), Ph<sub>2</sub>O (1.9 mL), gave **5ef** as a colorless oil (74 mg, 0.14 mmol, 75%); **IR** (ATR): 1661, 1259, 1097, 1051, 1033 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>) δ: 7.68 (1H, d, *J* = 8.2 Hz, Ar*H*), 7.53 (1H, s, Ar*H*), 7.50 (1H, d, *J* = 8.2 Hz, Ar*H*), 7.23 (1H, d, *J* = 2.1 Hz, Ar*H*), 7.21 (1H, d, *J* = 8.2 Hz, Ar*H*), 6.99 (1H, dd, *J* = 8.2, 2.1 Hz, Ar*H*), 3.86 (3H, s, OCH<sub>3</sub>), 3.67 (3H, s, OCH<sub>3</sub>), 2.96 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>), 2.73 (2H, t, *J* = 7.6 Hz, ArCH<sub>2</sub>), 1.68 (2H, m, CH<sub>2</sub>), 1.50-1.15 (14H, m, CH<sub>2</sub>), 0.89 (3H, t, *J* = 6.7 Hz, CH<sub>3</sub>); **<sup>13</sup>C-NMR** (126 MHz, CDCl<sub>3</sub>) δ: (1 × CH<sub>2</sub> missing), 166.1 (CO), 159.5 (ArC), 147.4 (ArC), 139.9 (ArC), 137.1 (ArC), 133.0 (ArCH), 131.6 (ArC), 131.2 (ArC), 129.6 (ArC), 125.0 (ArCH), 122.0 (ArCH), 121.5 (ArCH), 120.8 (ArCH), 120.1 (ArC), 115.5 (ArCH), 60.7 (OCH<sub>3</sub>), 55.5 (OCH<sub>3</sub>), 37.0 (N(CH<sub>3</sub>)<sub>2</sub>), 36.1 (CH<sub>2</sub>), 31.9 (CH<sub>2</sub>), 31.8 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 22.6 (CH<sub>2</sub>), 14.1 (CH<sub>3</sub>); **HRMS** (APCI): Calcd. for C<sub>29</sub>H<sub>40</sub>NO<sub>3</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 514.2444; found: 514.2445.

***S*-(2-(6-Decyl-3-methoxybenzo[*b*]thiophen-2-yl)-5-(trifluoromethyl)phenyl)**

**dimethylcarbamothioate (5eg)**

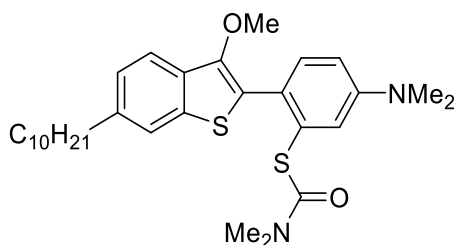




**3eg** (70 mg, 0.15 mmol), NaH (60%, 18 mg, 0.45 mmol), dimethylthiocarbamoyl chloride (32 mg, 0.30 mmol), DMF (1.5 mL), Ph<sub>2</sub>O (1.5 mL), gave **5eg** as a colorless oil (66 mg, 0.12 mmol, 79%); **IR** (ATR): 1673, 1321, 1258 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>) δ: 7.96 (1H, s, *ArH*), 7.76-7.69 (2H, m, *ArH*), 7.67 (1H, d, *J* = 8.1 Hz, *ArH*), 7.55 (1H, s, *ArH*), 7.24 (1H, d, *J* = 8.1 Hz, *ArH*), 3.68 (3H, s, OCH<sub>3</sub>), 2.98 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>), 2.73 (2H, t, *J* = 7.5 Hz, *ArCH*<sub>2</sub>), 1.68 (2H, m, *CH*<sub>2</sub>), 1.42-1.14 (14H, m, *CH*<sub>2</sub>), 0.89 (3H, t, *J* = 7.6 Hz, *CH*<sub>3</sub>); **<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>) δ: (1 × *CH*<sub>2</sub> missing), 165.3 (CO), 148.4 (*ArC*), 141.3 (*ArC*), 140.7 (*ArC*), 137.4 (*ArC*), 134.4 (q, *J* = 2.9 Hz, *ArCH*), 132.6 (*ArCH*), 131.5 (*ArC*), 131.3 (*ArC*), 130.7 (q, *J* = 33.1 Hz, CCF<sub>3</sub>), 125.6 (q, *J* = 3.6 Hz, *ArCH*), 125.3 (*ArCH*), 123.6 (q, *J* = 271.3 Hz, CF<sub>3</sub>), 121.7 (*ArCH*), 121.1 (*ArCH*), 119.2 (*ArC*), 61.1 (OCH<sub>3</sub>), 37.0 (N(CH<sub>3</sub>)<sub>2</sub>), 36.1 (*CH*<sub>2</sub>), 31.9 (*CH*<sub>2</sub>), 31.7 (*CH*<sub>2</sub>), 29.62 (*CH*<sub>2</sub>), 29.58 (*CH*<sub>2</sub>), 29.5 (*CH*<sub>2</sub>), 29.3 (*CH*<sub>2</sub>), 22.7 (*CH*<sub>2</sub>), 14.1 (*CH*<sub>3</sub>); **HRMS** (APCI): Calcd. for C<sub>29</sub>H<sub>37</sub>F<sub>3</sub>NO<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 522.2232; found: 522.2209.

**S-(2-(6-Decyl-3-methoxybenzo[*b*]thiophen-2-yl)-5-(dimethylamino)phenyl)**

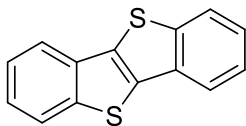
**dimethylcarbamothioate (5eh)**



**3eh** (45 mg, 0.10 mmol), NaH (60%, 12 mg, 0.31 mmol), dimethylthiocarbamoyl chloride (22 mg, 0.20 mmol), DMF (1.0 mL), Ph<sub>2</sub>O (1.0 mL), gave **5eh** as a colorless oil (15 mg, 0.028 mmol,

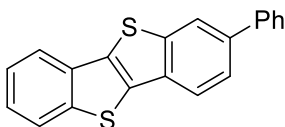
28%); **IR** (ATR): 1668, 1466, 1351, 1094  $\text{cm}^{-1}$ ;  **$^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.65 (1H, d,  $J = 8.5$  Hz, ArH), 7.50 (1H, s, ArH), 7.42 (1H, d,  $J = 8.5$  Hz, ArH), 7.18 (1H, d,  $J = 8.5$  Hz, ArH), 6.98 (1H, d,  $J = 2.0$  Hz, ArH), 6.77 (1H, dd,  $J = 8.5, 2.0$  Hz, ArH), 3.67 (3H, s,  $\text{OCH}_3$ ), 3.01 (6H, s,  $\text{N}(\text{CH}_3)_2$ ), 2.95 (6H, s,  $\text{N}(\text{CH}_3)_2$ ), 2.71 (2H, t,  $J = 7.7$  Hz,  $\text{ArCH}_2$ ), 1.75-1.60 (2H, m,  $\text{CH}_2$ ), 1.40-1.13 (14H, m,  $\text{CH}_2$ ), 0.88 (3H, t,  $J = 6.6$  Hz,  $\text{CH}_3$ );  **$^{13}\text{C-NMR}$**  (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : (1  $\times$  ArCH missing) 166.7 (CO), 150.4 (ArC), 147.1 (ArC), 139.6 (ArC), 137.0 (ArC), 132.8 (ArCH), 131.9 (ArC), 130.2 (ArC), 124.8 (ArCH), 124.5 (ArC), 121.5 (ArCH), 121.2 (ArC), 120.6 (ArCH), 113.0 (ArCH), 60.6 ( $\text{OCH}_3$ ), 40.3 ( $\text{N}(\text{CH}_3)_2$ ), 37.0 ( $\text{N}(\text{CH}_3)_2$ ), 36.1 ( $\text{CH}_2$ ), 31.9 ( $\text{CH}_2$ ), 31.8 ( $\text{CH}_2$ ), 29.62 ( $\text{CH}_2$ ), 29.59 ( $\text{CH}_2$ ), 29.5 ( $\text{CH}_2$ ), 29.34 ( $\text{CH}_2$ ), 29.33 ( $\text{CH}_2$ ), 22.7 ( $\text{CH}_2$ ), 14.1 ( $\text{CH}_3$ ); **HRMS** (APCI): Calcd. for  $\text{C}_{30}\text{H}_{43}\text{N}_2\text{O}_2\text{S}_2$   $[\text{M}+\text{H}]^+$ : 527.2760; found: 527.2757.

**[1]Benzothieno[3,2-*b*][1]benzothiophene (4aa)<sup>2</sup>**



**5aa** (18 mg, 0.052 mmol), KOMe (90%, 8 mg, 0.10 mmol), MeOH (1.0 mL), toluene (1.0 mL), TsOH·H<sub>2</sub>O (79 mg, 0.42 mmol, 8.0 equiv), gave **4aa** as a white solid (8 mg, 0.033 mmol, 70%); **M.p.**: 217-218 °C; **IR** (ATR): 1436, 1335, 739 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>) δ: 7.93 (2H, d, *J* = 7.8 Hz, *ArH*), 7.90 (2H, d, *J* = 7.8 Hz, *ArH*), 7.47 (2H, t, *J* = 7.8 Hz, *ArH*), 7.41 (2H, t, *J* = 7.8 Hz, *ArH*); **<sup>13</sup>C-NMR** (126 MHz, CDCl<sub>3</sub>) δ: 142.2 (*ArC*), 133.4 (*ArC*), 133.1 (*ArC*), 125.0 (*ArCH*), 124.9 (*ArCH*), 124.0 (*ArCH*), 121.6 (*ArCH*); **HRMS** (APCI): Calcd. for C<sub>14</sub>H<sub>9</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 241.0140; found: 241.0140.

**2-Phenyl[1]benzothieno[3,2-*b*][1]benzothiophene (4ab)<sup>3</sup>**



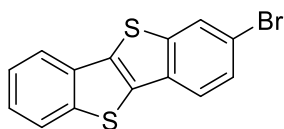
**5ab** (42 mg, 0.10 mmol), KOMe (90%, 16 mg, 0.20 mmol), MeOH (1.0 mL), toluene (1.0 mL), TsOH·H<sub>2</sub>O (0.15 g, 0.80 mmol, 8.0 equiv), gave **4ab** as a white solid (25 mg, 0.079 mmol, 77%); **M.p.**: 242 °C; **IR** (ATR): 1258, 1016, 790 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>) δ: 8.14 (1H, s, *ArH*), 7.99-7.92 (2H, m, *ArH*), 7.90 (1H, d, *J* = 7.8 Hz, *ArH*), 7.78-7.63 (3H, m, *ArH*), 7.55-7.45 (3H, m, *ArH*), 7.45-7.35 (2H, m, *ArH*); **<sup>13</sup>C-NMR** (126 MHz, CDCl<sub>3</sub>) δ: 143.1 (*ArC*), 142.3 (*ArC*), 140.7 (*ArC*), 138.4 (*ArC*), 133.7 (*ArC*), 133.2 (*ArC*), 133.1 (*ArC*), 132.2 (*ArC*), 128.9 (*ArCH*), 127.5 (*ArCH*), 127.3 (*ArCH*), 125.0 (*ArCH*), 124.9 (*ArCH*), 124.5 (*ArCH*), 124.1 (*ArCH*), 122.4 (*ArCH*), 121.8 (*ArCH*), 121.6 (*ArCH*); **HRMS** (APCI): Calcd. for C<sub>20</sub>H<sub>13</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 317.0453;

<sup>2</sup> T. Kitamura, K. Morita, H. Nakamori and J. Oyamada, *J. Org. Chem.* 2019, **84**, 4191–4199.

<sup>3</sup> A. Sanzone, S. Mattiello, G. M. Garavaglia, A. M. Calascibetta, C. Ceriani, M. Sassi and L. Beverina, *Green Chem.* 2019, **21**, 4400–4405.

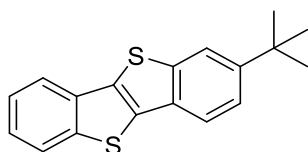
found: 317.0450.

**2-Bromo[1]benzothieno[3,2-*b*][1]benzothiophene (4ac)<sup>2</sup>**



**5ac** (75 mg, 0.18 mmol), KOMe (90%, 28 mg, 0.36 mmol), MeOH (1.8 mL), toluene (1.8 mL), TsOH·H<sub>2</sub>O (0.27 g, 1.4 mmol, 8.0 equiv), gave **4ac** as a white solid (35 mg, 0.11 mmol, 62%); **M.p.**: 214-216 °C; **IR** (ATR): 1258, 1085, 1029, 808 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>) δ: 8.05 (1H, s, ArH), 7.92 (1H, d, *J* = 7.8 Hz, ArH), 7.87 (1H, d, *J* = 7.8 Hz, ArH), 7.73 (1H, d, *J* = 8.6 Hz, ArH), 7.56 (1H, d, *J* = 8.6 Hz, ArH), 7.47 (1H, t, *J* = 7.8 Hz, ArH), 7.42 (1H, t, *J* = 7.8 Hz, ArH); **<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>) δ: 143.6 (ArC), 142.3 (ArC), 133.7 (ArC), 123.9 (ArC), 132.8 (ArC), 131.9 (ArC), 128.3 (ArCH), 126.5 (ArCH), 125.3 (ArCH), 125.0 (ArCH), 124.1 (ArCH), 122.5 (ArCH), 121.6 (ArCH), 118.5 (ArC); **HRMS** (APCI): Calcd. for C<sub>14</sub>H<sub>7</sub>BrS<sub>2</sub> [M]<sup>+</sup>: 317.9167; found: 317.9170.

**2-tert-Butyl[1]benzothieno[3,2-*b*][1]benzothiophene (4ad)<sup>4</sup>**

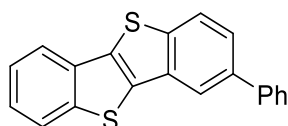


**5ad** (61 mg, 0.15 mmol), KOMe (90%, 24 mg, 0.31 mmol), MeOH (1.5 mL), toluene (1.5 mL), TsOH·H<sub>2</sub>O (0.23 g, 1.2 mmol, 8.0 equiv), gave **4ad** as a white solid (40 mg, 0.13 mmol, 88%); **M.p.**: 175-177 °C; **IR** (ATR): 1253, 816, 745 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>) δ: 7.95-7.89

<sup>4</sup> G. Schweicher, V. Lemaur, C. Niebel, C. Ruzié, Y. Diao, O. Goto, W. Lee, Y. Kim, J. Arlin, J. Karpinska, A. R. Kennedy, S. R. Parkin, Y. Olivier, S. C. B. Mannsfeld, J. Cornil, Y. H. Geerts and Z. Bao, *Adv. Mater.*, 2015, **27**, 3066–3072.

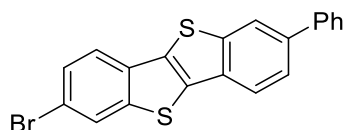
(2H, m, *ArH*), 7.88 (1H, d,  $J = 8.0$  Hz, *ArH*), 7.82 (1H, d,  $J = 8.0$  Hz, *ArH*), 7.52 (1H, d,  $J = 8.0$  Hz, *ArH*), 7.45 (1H, t,  $J = 8.0$  Hz, *ArH*), 7.39 (1H, t,  $J = 8.0$  Hz, *ArH*), 1.42 (9H, s,  $(\text{CH}_3)_3$ );  $^{13}\text{C}$ -NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : 148.6 (*ArC*), 142.6 (*ArC*), 142.1 (*ArC*), 133.3 (*ArC*), 133.2 (*ArC*), 132.8 (*ArC*), 130.7 (*ArC*), 124.8 (*ArCH*), 124.7 (*ArCH*), 124.0 (*ArCH*), 123.8 (*ArCH*), 121.4 (*ArCH*), 121.1 (*ArCH*), 120.3 (*ArCH*), 35.1 ( $\text{C}(\text{CH}_3)_3$ ), 31.5 ( $\text{C}(\text{CH}_3)_3$ ); HRMS (APCI): Calcd. for  $\text{C}_{18}\text{H}_{17}\text{S}_2$   $[\text{M}+\text{H}]^+$ : 297.0766; found: 297.0763.

### 3-Phenyl[1]benzothieno[3,2-*b*][1]benzothiophene (**4ae**)



**5ae** (60 mg, 0.14 mmol), KOMe (90%, 22 mg, 0.29 mmol), MeOH (1.4 mL), toluene (1.4 mL), TsOH·H<sub>2</sub>O (0.22 g, 1.1 mmol, 8.0 equiv), gave **4ae** as a white solid (33 mg, 0.10 mmol, 77%); **M.p.**: 168-170 °C; **IR** (ATR): 1437, 1260, 1016, 751  $\text{cm}^{-1}$ ;  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.08 (1H, d,  $J = 1.5$  Hz, *ArH*), 7.98 (1H, d,  $J = 8.3$  Hz, *ArH*), 7.94 (1H, d,  $J = 7.8$  Hz, *ArH*), 7.91 (1H, d,  $J = 7.8$  Hz, *ArH*), 7.76-7.68 (2H, m, *ArH*), 7.66 (1H, dd,  $J = 8.3, 1.7$  Hz, *ArH*), 7.55-7.45 (2H, m, *ArH*), 7.45 (1H, dd,  $J = 7.1, 1.2$  Hz, *ArH*), 7.45-7.36 (2H, m, *ArH*).  $^{13}\text{C}$ -NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : (1  $\times$  *ArCH* missing), 142.2 (*ArC*), 141.2 (*ArC*), 140.9 (*ArC*), 138.5 (*ArC*), 134.0 (*ArC*), 133.6 (*ArC*), 133.5 (*ArC*), 133.1 (*ArC*), 128.9 (*ArCH*), 127.4 (*ArCH*), 125.1 (*ArCH*), 124.9 (*ArCH*), 124.5 (*ArCH*), 124.2 (*ArCH*), 124.1 (*ArCH*), 121.6 (*ArCH*), 120.0 (*ArCH*); HRMS (APCI): Calcd. for  $\text{C}_{20}\text{H}_{13}\text{S}_2$   $[\text{M}+\text{H}]^+$ : 317.0453; found: 317.0450.

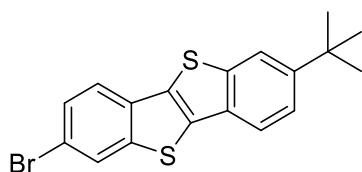
### 2-Bromo-7-phenyl[1]benzothieno[3,2-*b*][1]benzothiophene (**4bb**)



**5bb** (87 mg, 0.17 mmol), KOMe (90%, 27 mg, 0.35 mmol), MeOH (1.7 mL), toluene (1.7 mL),

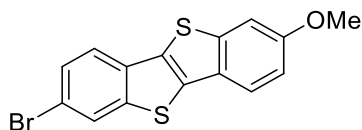
TsOH·H<sub>2</sub>O (0.24 g, 1.4 mmol, 8.0 equiv), gave **4bb** as a white solid (45 mg, 0.11 mmol, 65%); **M.p.**: 294-296 °C; **IR** (ATR): 810, 759, 690 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>) δ: 8.13 (1H, s, ArH), 8.07 (1H, s, ArH), 7.93 (1H, d, *J* = 8.3 Hz, ArH), 7.78-7.71 (2H, m, ArH), 7.71-7.66 (2H, m, ArH), 7.57 (1H, d, *J* = 8.3 Hz, ArH), 7.53-7.45 (2H, m, ArH), 7.41 (1H, d, *J* = 8.3 Hz, ArH); **<sup>13</sup>C-NMR** (126 MHz, CDCl<sub>3</sub>) δ: 143.7 (ArC), 153.1 (ArC), 140.6 (ArC), 138.7 (ArC), 133.6 (ArC), 133.2 (ArC), 131.94 (ArC), 131.90 (ArC), 129.0 (ArCH), 128.3 (ArCH), 127.6 (ArCH), 127.3 (ArCH), 126.5 (ArCH), 124.7 (ArCH), 122.5 (ArCH), 122.4 (ArCH), 121.8 (ArCH), 118.6 (ArC); **HRMS** (APCI): Calcd. for C<sub>20</sub>H<sub>12</sub>BrS<sub>2</sub> [M+H]<sup>+</sup>: 394.9558; found: 394.9546.

#### 2-Bromo-7-*tert*-butyl[1]benzothieno[3,2-*b*][1]benzothiophene (**4bd**)



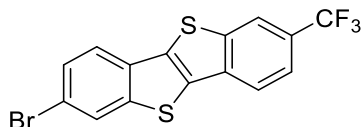
**5bd** (105 mg, 0.22 mmol), KOMe (90%, 34 mg, 0.44 mmol), MeOH (1.1 mL), toluene (1.1 mL), TsOH·H<sub>2</sub>O (0.33 g, 1.8 mmol, 8.0 equiv), gave **4bd** as a white solid (40 mg, 0.11 mmol, 49%); **M.p.**: 278-280 °C; **IR** (ATR): 1257, 1012, 787 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>) δ: 8.05 (1H, s, ArH), 7.91 (1H, s, ArH), 7.80 (1H, d, *J* = 8.4 Hz, ArH), 7.73 (1H, d, *J* = 8.4 Hz, ArH), 7.55 (1H, d, *J* = 8.4 Hz, ArH), 7.54 (1H, d, *J* = 8.4 Hz, ArH), 1.42 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>); **<sup>13</sup>C-NMR** (126 MHz, CDCl<sub>3</sub>) δ: 149.0 (ArC), 143.5 (ArC), 142.6 (ArC), 133.6 (ArC), 132.4 (ArC), 132.1 (ArC), 130.5 (ArC), 128.2 (ArCH), 126.5 (ArCH), 123.3 (ArCH), 122.4 (ArCH), 121.1 (ArCH), 120.3 (ArCH), 118.2 (ArC), 35.2 (C(CH<sub>3</sub>)<sub>3</sub>), 31.5 (C(CH<sub>3</sub>)<sub>3</sub>); **HRMS** (ESI): Calcd. for C<sub>18</sub>H<sub>16</sub>BrS<sub>2</sub> [M+H]<sup>+</sup>: 374.9871; found: 374.9872.

### 2-Bromo-7-methoxy[1]benzothieno[3,2-*b*][1]benzothiophene (**4bf**)



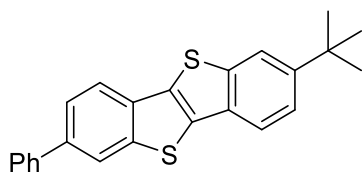
**5bf** (70 mg, 0.16 mmol), KOMe (90%, 24 mg, 0.31 mmol), MeOH (1.5 mL), toluene (1.5 mL), TsOH·H<sub>2</sub>O (0.19 g, 1.1 mmol, 7.0 equiv), gave **4bf** as a white solid (40 mg, 0.11 mmol, 74%); **M.p.**: 200-202 °C; **IR** (ATR): 1259, 1021, 795 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>) δ: 8.03 (1H, d, *J* = 2.0 Hz, *ArH*), 7.75 (1H, d, *J* = 8.6 Hz, *ArH*), 7.68 (1H, d, *J* = 8.6 Hz, *ArH*), 7.54 (1H, dd, *J* = 8.6, 2.0 Hz, *ArH*), 7.39 (1H, d, *J* = 2.0 Hz, *ArH*), 7.07 (1H, dd, *J* = 8.6, 2.0 Hz, *ArH*), 3.92 (3H, s, OCH<sub>3</sub>); **<sup>13</sup>C-NMR** (126 MHz, CDCl<sub>3</sub>) δ: 158.1 (ArC), 144.1 (ArC), 143.2 (ArC), 133.7 (ArC), 132.2 (ArC), 130.8 (ArC), 128.2 (ArCH), 126.8 (ArC), 126.4 (ArCH), 122.3 (ArCH), 122.1 (ArCH), 117.9 (ArC), 114.6 (ArCH), 107.0 (ArCH), 55.7 (OCH<sub>3</sub>); **HRMS** (APCI): Calcd. for C<sub>15</sub>H<sub>10</sub>BrOS<sub>2</sub> [M+H]<sup>+</sup>: 348.9351; found: 348.9344.

### 2-Bromo-7-trifluoromethyl[1]benzothieno[3,2-*b*][1]benzothiophene (**4bg**)



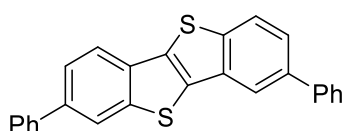
**5bg** (97 mg, 0.20 mmol), KOMe (90%, 31 mg, 0.40 mmol), MeOH (2.0 mL), toluene (2.0 mL), TsOH·H<sub>2</sub>O (0.26 g, 1.6 mmol, 8.0 equiv), gave **4bg** as a white solid (36 mg, 0.093 mmol, 47%); **M.p.**: 255-257 °C; **IR** (ATR): 1317, 1168, 1109, 806 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>) δ: 8.21 (1H, s, *ArH*), 8.09 (1H, d, *J* = 1.2 Hz, *ArH*), 7.97 (1H, d, *J* = 8.6 Hz, *ArH*), 7.79 (1H, d, *J* = 8.6 Hz, *ArH*), 7.70 (1H, d, *J* = 8.6 Hz, *ArH*), 7.60 (1H, dd, *J* = 8.6, 1.2 Hz, *ArH*); **<sup>13</sup>C-NMR** (126 MHz, CDCl<sub>3</sub>) δ: 144.1 (ArC), 142.1 (ArC), 135.6 (ArC), 135.2 (ArC), 133.1 (ArC), 131.5 (ArC), 128.6 (ArCH), 127.3 (q, *J* = 32.0 Hz, CCF<sub>3</sub>), 126.7 (ArCH), 124.2 (q, *J* = 272.8 Hz, CCF<sub>3</sub>), 123.0 (ArCH), 122.0 (q, *J* = 4.2 Hz, ArCH), 121.9 (ArC), 121.5 (q, *J* = 3.9 Hz, ArCH), 119.6 (ArCH); **HRMS** (APCI): Calcd. for C<sub>15</sub>H<sub>6</sub>BrF<sub>3</sub>S<sub>2</sub> [M]<sup>+</sup>: 385.9041; found: 385.9036.

### 2- *tert*-Butyl-7-phenyl[1]benzothieno[3,2-*b*][1]benzothiophene (**4cd**)



**5cd** (44 mg, 0.093 mmol), KOMe (90%, 14 mg, 0.19 mmol), MeOH (1.0 mL), toluene (1.0 mL), TsOH·H<sub>2</sub>O (0.11 g, 0.65 mmol; 7.0 equiv), gave **4cd** as a white solid (21 mg, 0.056 mmol, 61%); **M.p.**: 268-270 °C; **IR** (ATR): 818, 760, 690 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>) δ: 8.14 (1H, d, *J* = 1.5 Hz, *ArH*), 7.99-7.91 (2H, m, *ArH*), 7.85 (1H, d, *J* = 8.4 Hz, *ArH*), 7.75-7.66 (3H, m, *ArH*), 7.55 (1H, dd, *J* = 8.4, 1.5 Hz, *ArH*), 7.53-7.47 (2H, m, *ArH*), 7.40 (1H, t, *J* = 8.4 Hz, *ArH*), 1.45 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>); **<sup>13</sup>C-NMR** (126 MHz, CDCl<sub>3</sub>) δ: 148.7 (ArC), 142.9 (ArC), 142.6 (ArC), 140.8 (ArC), 138.1 (ArC), 133.5 (ArC), 132.6 (ArC), 132.3 (ArC), 130.8 (ArC), 128.9 (ArCH), 127.4 (ArCH), 127.3 (ArCH), 124.4 (ArCH), 123.1 (ArCH), 122.3 (ArCH), 121.6 (ArCH), 121.1 (ArCH), 120.3 (ArCH), 35.1 (C(CH<sub>3</sub>)<sub>3</sub>), 31.5 (C(CH<sub>3</sub>)<sub>3</sub>); **HRMS** (APCI): Calcd. for C<sub>24</sub>H<sub>21</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 373.1079; found: 373.1064.

### 2,8-Diphenyl[1]benzothieno[3,2-*b*][1]benzothiophene (**4ce**)

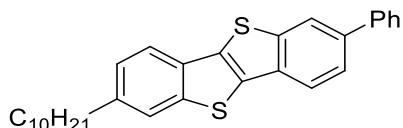


**5ce** (60 mg, 0.12 mmol), KOMe (90%, 19 mg, 0.24 mmol), MeOH (1.2 mL), toluene (1.2 mL), TsOH·H<sub>2</sub>O (0.18 g, 0.96 mmol, 8.0 equiv), gave **4ce** as a white solid (30 mg, 0.076 mmol, 63%); **M.p.**: 222-224 °C; **IR** (ATR): 1257, 1012, 787 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>) δ: 8.15 (1H, d, *J* = 1.5 Hz, *ArH*), 8.09 (1H, d, *J* = 1.5 Hz, *ArH*), 7.99 (1H, d, *J* = 8.4 Hz, *ArH*), 7.96 (1H, d, *J* = 8.4 Hz, *ArH*), 7.77-7.69 (5H, m, *ArH*), 7.66 (1H, dd, *J* = 8.4, 1.5 Hz, *ArH*), 7.54-7.45 (4H, m, *ArH*), 7.45-7.35 (2H, m, *ArH*); **<sup>13</sup>C-NMR** (126 MHz, CDCl<sub>3</sub>) δ: (2 × ArCH missing), 143.1 (ArC), 141.3 (ArC), 140.9 (ArC), 140.7 (ArC), 138.6 (ArC), 138.5 (ArC), 133.80 (ArC), 133.79 (ArC),



133.7 (ArC), 132.2 (ArC), 128.93 (ArCH), 128.91 (ArCH), 127.5 (ArCH), 127.4 (ArCH), 127.3 (ArCH), 124.6 (ArCH), 124.3 (ArCH), 122.4 (ArCH), 121.8 (ArCH), 120.0 (ArCH); **HRMS** (APCI): Calcd. for C<sub>26</sub>H<sub>17</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 393.0766; found: 393.0759.

**2-Decyl-7-phenyl[1]benzothieno[3,2-b][1]benzothiophene (4eb)**<sup>5</sup>

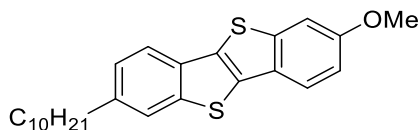


**5eb** (53 mg, 0.095 mmol), KOMe (90%, 15 mg, 0.19 mmol), MeOH (1.0 mL), toluene (1.0 mL), TsOH·H<sub>2</sub>O (0.11 g, 0.59 mmol, 6.0 equiv), gave **4eb** as a white solid (30 mg, 0.066 mmol, 69%); **IR** (ATR): 1258, 1014, 798 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>) δ: 8.12 (1H, d, *J* = 1.2 Hz, *ArH*), 7.92 (1H, d, *J* = 8.2 Hz, *ArH*), 7.80 (1H, d, *J* = 8.2 Hz, *ArH*), 7.73 (1H, s, *ArH*), 7.72-7.66 (3H, m, *ArH*), 7.45-7.54 (2H, m, *ArH*), 7.38 (1H, d, *J* = 7.8 Hz, *ArH*), 7.29 (1H, dd, *J* = 7.8, 1.2 Hz, *ArH*), 2.77 (2H, t, *J* = 7.8 Hz, *ArCH*<sub>2</sub>), 1.71 (2H, tt, *J* = 7.8, 7.8 Hz, *CH*<sub>2</sub>), 1.44-1.18 (14H, m, *CH*<sub>2</sub>), 0.88 (3H, t, *J* = 6.7 Hz, *CH*<sub>3</sub>); **<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>) δ: (1 × *ArC* missing) 142.9 (*ArC*), 142.6 (*ArC*), 140.8 (*ArC*), 140.5 (*ArC*), 138.1 (*ArC*), 133.7 (*ArC*), 132.3 (*ArC*), 131.0 (*ArC*), 128.9 (*ArCH*), 127.4 (*ArCH*), 127.3 (*ArCH*), 126.0 (*ArCH*), 124.4 (*ArCH*), 123.4 (*ArCH*), 122.3 (*ArCH*), 121.6 (*ArCH*), 121.2 (*ArCH*), 36.1 (*CH*<sub>2</sub>), 31.9 (*CH*<sub>2</sub>), 31.7 (*CH*<sub>2</sub>), 29.6 (*CH*<sub>2</sub>), 29.6 (*CH*<sub>2</sub>), 29.5 (*CH*<sub>2</sub>), 29.32 (*CH*<sub>2</sub>), 29.30 (*CH*<sub>2</sub>), 22.7 (*CH*<sub>2</sub>), 14.1 (*CH*<sub>3</sub>); **HRMS** (APCI): Calcd. for C<sub>30</sub>H<sub>33</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 457.2018; found: 457.2009.

From **5eb'**: **5eb'** (56 mg, 0.1 mmol), KOMe (90%, 16 mg, 0.2 mmol), MeOH (1.0 mL), toluene (1.0 mL), TsOH·H<sub>2</sub>O (0.15 g, 0.8 mmol, 8.0 equiv), gave **4eb** as a white solid (41 mg, 0.091 mmol, 91%).

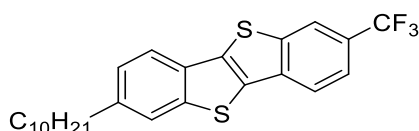
<sup>5</sup> H. Iino, T. Usui and J. Hanna, *Nat. Commun.* 2015, **6**, 6828.

### 2-Decyl-7-methoxy[1]benzothieno[3,2-*b*][1]benzothiophene (4ef)



**5ef** (68 mg, 0.13 mmol), KOMe (90%, 20 mg, 0.26 mmol), MeOH (1.3 mL), toluene (1.3 mL), TsOH·H<sub>2</sub>O (0.20 g, 1.1 mmol, 8.0 equiv), gave **4ef** as a white solid (41 mg, 0.10 mmol, 76%); **M.p.**: 138-140 °C; **IR** (ATR): 1259, 1030, 810, 789 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>) δ: 7.74 (1H, d, *J* = 4.0 Hz, Ar*H*), 7.72 (1H, d, *J* = 4.0 Hz, Ar*H*), 7.69 (1H, s, Ar*H*), 7.39 (1H, s, Ar*H*), 7.26 (1H, d, *J* = 8.0 Hz, Ar*H*), 7.06 (1H, d, *J* = 8.0 Hz, Ar*H*), 3.91 (3H, s, OCH<sub>3</sub>), 2.75 (2H, t, *J* = 7.7 Hz, ArCH<sub>2</sub>), 1.76-1.63 (2H, m, CH<sub>2</sub>), 1.47-1.19 (14H, m, CH<sub>2</sub>), 0.88 (3H, t, *J* = 6.7 Hz, CH<sub>3</sub>); **<sup>13</sup>C-NMR** (126 MHz, CDCl<sub>3</sub>) δ: 157.7 (ArCOCH<sub>3</sub>), 143.7 (ArC), 142.1 (ArC), 139.7 (ArC), 132.4 (ArC), 131.3 (ArC), 131.2 (ArC), 127.2 (ArC), 125.8 (ArCH), 123.3 (ArCH), 122.0 (ArCH), 120.8 (ArCH), 114.2 (ArCH), 107.0 (ArCH), 55.7 (OCH<sub>3</sub>), 36.1 (CH<sub>2</sub>), 31.9 (CH<sub>2</sub>), 31.7 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 22.7 (CH<sub>2</sub>), 14.1 (CH<sub>3</sub>); **HRMS** (APCI): Calcd. for C<sub>25</sub>H<sub>31</sub>OS<sub>2</sub> [M+H]<sup>+</sup>: 411.1811; found: 411.1807.

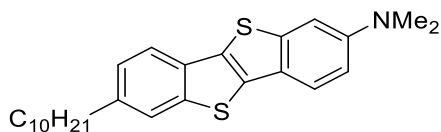
### 2-Decyl-7-trifluoromethyl[1]benzothieno[3,2-*b*][1]benzothiophene (4eg)



**5eg** (44 mg, 0.080 mmol), KOMe (90%, 12 mg, 0.16 mmol), MeOH (0.8 mL), toluene (0.8 mL), TsOH·H<sub>2</sub>O (0.12 g, 0.64 mmol, 8.0 equiv), gave **4eg** as a white solid (34 mg, 0.076 mmol, 96%); **M.p.**: 210-212; **IR** (ATR): 1319, 1119, 1084, 817 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>) δ: 8.18 (1H, s, Ar*H*), 7.93 (1H, d, *J* = 8.0 Hz, Ar*H*), 7.82 (1H, d, *J* = 8.0 Hz, Ar*H*), 7.74 (1H, s, Ar*H*), 7.67 (1H, d, *J* = 8.0 Hz, Ar*H*), 7.31 (1H, d, *J* = 8.0 Hz, Ar*H*), 2.77 (2H, t, *J* = 7.0 Hz, ArCH<sub>2</sub>), 1.70 (2H, m, CH<sub>2</sub>), 1.42-1.17 (14H, m, CH<sub>2</sub>), 0.88 (3H, t, *J* = 7.0 Hz, CH<sub>3</sub>); **<sup>13</sup>C-NMR** (126 MHz, CDCl<sub>3</sub>) δ: 143.0 (ArC), 141.8 (ArC), 141.4 (ArC), 136.0 (ArC), 135.6 (ArC), 131.9 (ArC), 130.6

(ArC), 126.6 (q,  $J = 33.0$  Hz,  $\text{CCF}_3$ ), 126.2 (ArCH), 124.4 (q,  $J = 270.2$  Hz,  $\text{CF}_3$ ), 123.4 (ArCH), 121.7 (q,  $J = 3.6$  Hz, ArCH), 121.6 (ArCH), 121.5 (ArCH), 121.1 ( $J = 4.2$  Hz, ArCH), 36.2 ( $\text{CH}_2$ ), 31.9 ( $\text{CH}_2$ ), 31.6 ( $\text{CH}_2$ ), 29.6 ( $\text{CH}_2$ ), 29.6 ( $\text{CH}_2$ ), 29.5 ( $\text{CH}_2$ ), 29.3 ( $\text{CH}_2$ ), 29.3 ( $\text{CH}_2$ ), 22.7 ( $\text{CH}_2$ ), 14.1 ( $\text{CH}_3$ ); **HRMS** (APCI): Calcd. for  $\text{C}_{25}\text{H}_{27}\text{F}_3\text{S}_2$   $[\text{M}]^+$ : 448.1501; found: 448.1498.

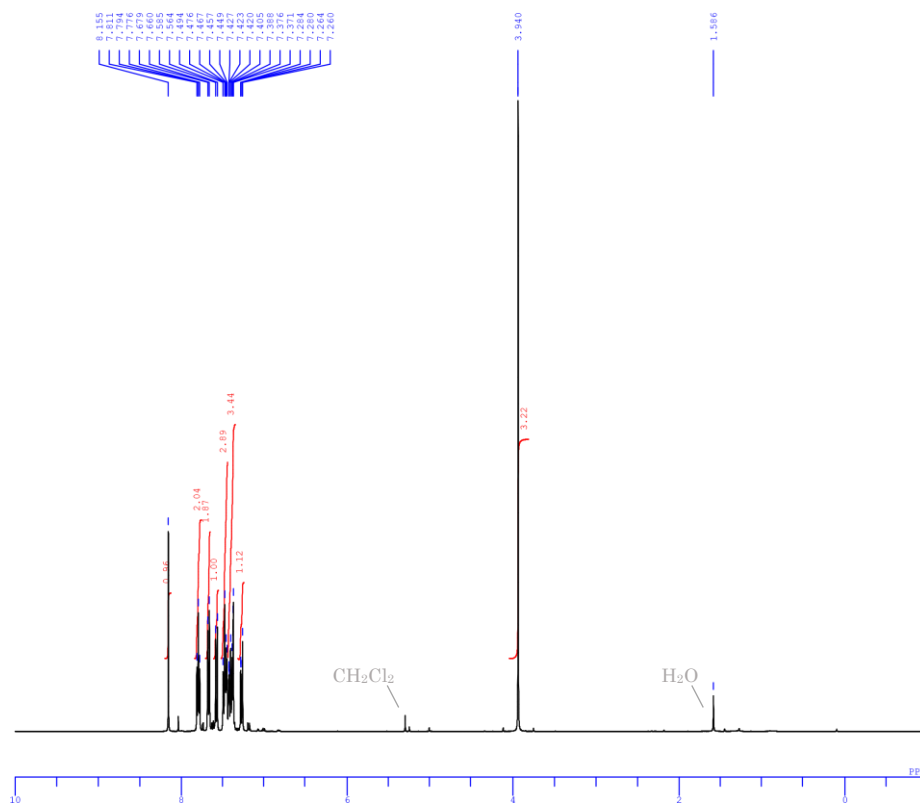
### 2-Decyl-7-dimethylamino[1]benzothieno[3,2-*b*][1]benzothiophene (4eh)



**5eh** (25 mg, 0.047 mmol), KOMe (90%, 7 mg, 0.095 mmol), MeOH (1.0 mL), toluene (1.0 mL), TsOH·H<sub>2</sub>O (72 mg, 0.38 mmol, 8.0 equiv), gave **4eh** as a white solid (5 mg, 0.012 mmol, 25%); **M.p.**: 120-122 °C; **IR** (ATR): 1258, 1082, 1017, 792  $\text{cm}^{-1}$ ; **<sup>1</sup>H-NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.68-7.55 (3H, m, ArH), 7.16 (1H, d,  $J = 8.5$  Hz, ArH), 7.10 (1H, s, ArH), 6.86 (1H, d,  $J = 8.5$  Hz, ArH), 3.05 (6H, s,  $\text{N}(\text{CH}_3)_2$ ), 2.73 (2H, t,  $J = 7.7$  Hz, ArCH<sub>2</sub>), 1.76-1.62 (2H, m, CH<sub>2</sub>), 1.41-1.14 (14H, m, CH<sub>2</sub>), 0.87 (3H, t,  $J = 6.5$  Hz, CH<sub>3</sub>); **<sup>13</sup>C-NMR** (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : 148.7 (ArC), 144.5 (ArC), 141.8 (ArC), 139.1 (ArC), 132.7 (ArC), 131.5 (ArC), 129.4 (ArC), 125.7 (ArCH), 124.0 (ArC), 123.2 (ArCH), 121.7 (ArCH), 120.4 (ArCH), 112.1 (ArCH), 106.1 (ArCH), 41.0 ( $\text{N}(\text{CH}_3)_2$ ), 36.1 (CH<sub>2</sub>), 31.9 (CH<sub>2</sub>), 31.8 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 22.7 (CH<sub>2</sub>), 14.1 (CH<sub>3</sub>); **HRMS** (APCI): Calcd. for  $\text{C}_{26}\text{H}_{34}\text{NS}_2$   $[\text{M}+\text{H}]^+$ : 424.2127; found: 424.2116.

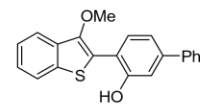
### 3. $^1\text{H}$ and $^{13}\text{C}$ NMR of BTBT derivatives

#### $^1\text{H}$ NMR of 3ab (400 MHz, $\text{CDCl}_3$ )

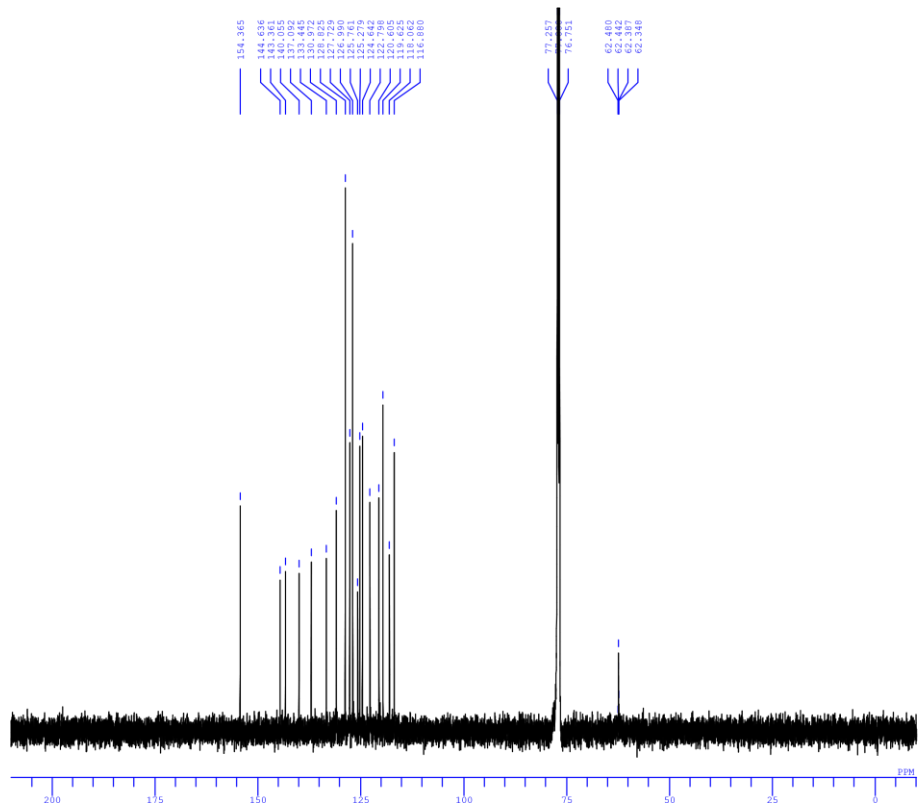


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PROBHD 5mm
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OBSETE 2.47 KHz
OBSETE 0.57 Hz
POINT 32768
FREQU 8012.02 Hz
SCANS 16
ACQTM 4.0894 sec
PD 1.0000 sec
FWD 10.00 usec
IRNUC 400.0 c
CTEMP 400.0 c
SLVNT CDCl3
EXREF 7.26 ppm
RF 0.30 Hz
RGAIN 287
    
```

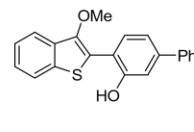


#### $^{13}\text{C}$ NMR of 3ab (126 MHz, $\text{CDCl}_3$ )

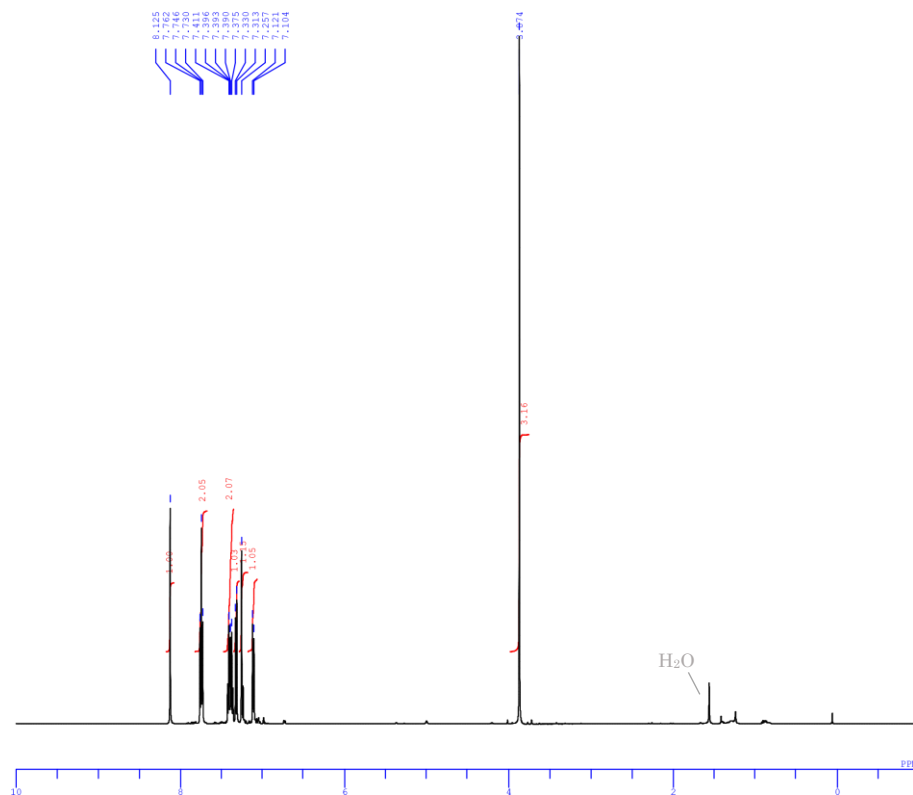


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DATEIM 2019-07-18 22:33:23
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PROBHD 5mm
PULPROG zgpg30
F1 125.76 MHz
OBSETE 7.33 KHz
OBSETE 9.88 Hz
POINT 32768
FREQU 32051.28 Hz
SCANS 2048
ACQTM 1.0224 sec
PD 2.0000 sec
FWD 8.00 usec
IRNUC 125.76 MHz
CTEMP 24.9 c
SLVNT CDCl3
EXREF 77.00 ppm
RF 1.00 Hz
RGAIN 184
    
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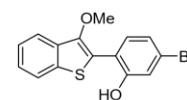


**<sup>1</sup>H NMR of 3ac (500 MHz, CDCl<sub>3</sub>)**

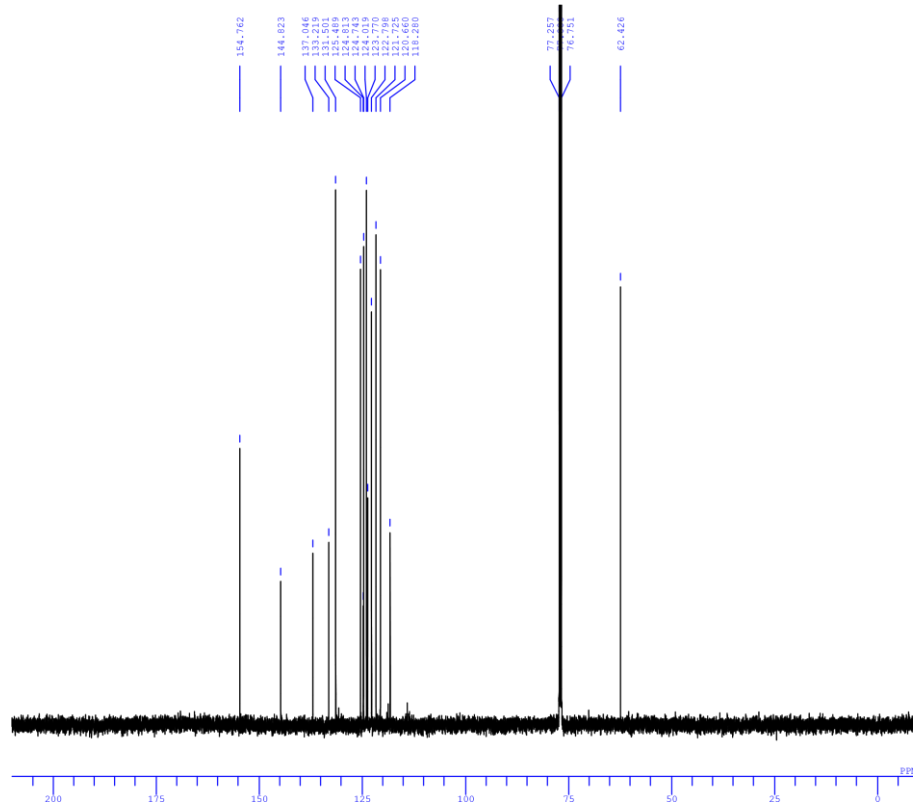


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ORSET 3.08 KHz
ORFIN 8.88 Hz
PCINT 65536
FREQU 10000.00 Hz
SCANS 16
ACQTM 3.2768 sec
PD 1.0000 sec
PWI 11.50 usec
IRNUC
CTEMP
SLVNT CDCl3 24.0 c
EXREF 7.26 ppm
RF 0.30 Hz
RGAIN 30
    
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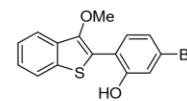


**<sup>13</sup>C NMR of 3ac (126 MHz, CDCl<sub>3</sub>)**

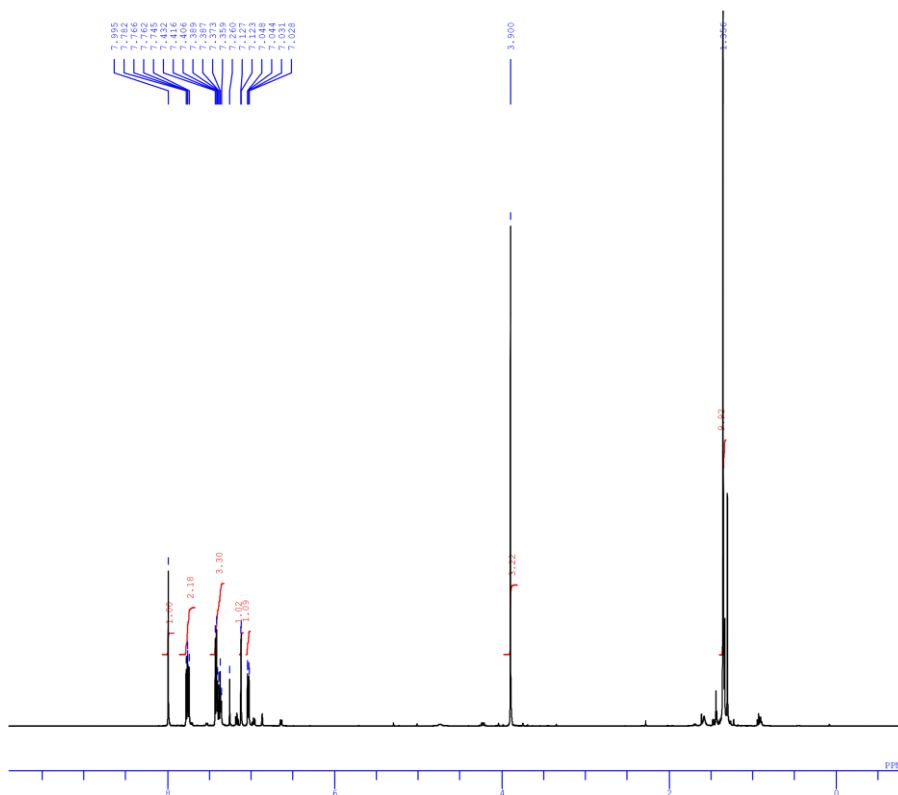


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EXMOD zgpg30
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ORSET 7.33 KHz
ORFIN 9.88 Hz
PCINT 32768
FREQU 32051.28 Hz
SCANS 32
ACQTM 1.0224 sec
PD 2.0000 sec
PWI 10.10 usec
IRNUC
CTEMP
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EXREF 77.00 ppm
RF 1.00 Hz
RGAIN 184
    
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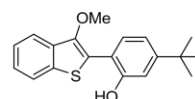


**<sup>1</sup>H NMR of 3ad (500 MHz, CDCl<sub>3</sub>)**

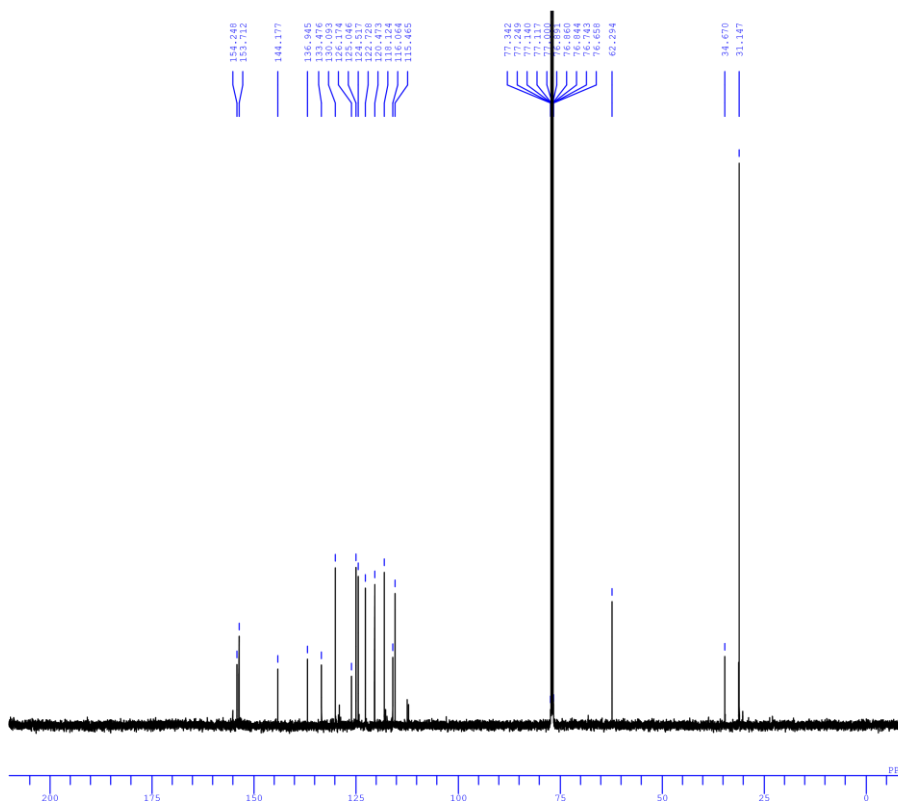


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OBSEF 3.08 KHz
OSFIN 5.89 Hz
POINT 65536
FREQU 10000.00 Hz
SCANS 16
AQTM 3.2768 sec
PD 1.0000 sec
PWI 11.50 usec
IRNUC
CTEMP 24.9 c
SLVNT CDCl3
EXREF 7.26 ppm
BF 0.30 Hz
RGAIN 30
    
```

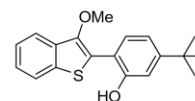


**<sup>13</sup>C NMR of 3ad (126 MHz, CDCl<sub>3</sub>)**

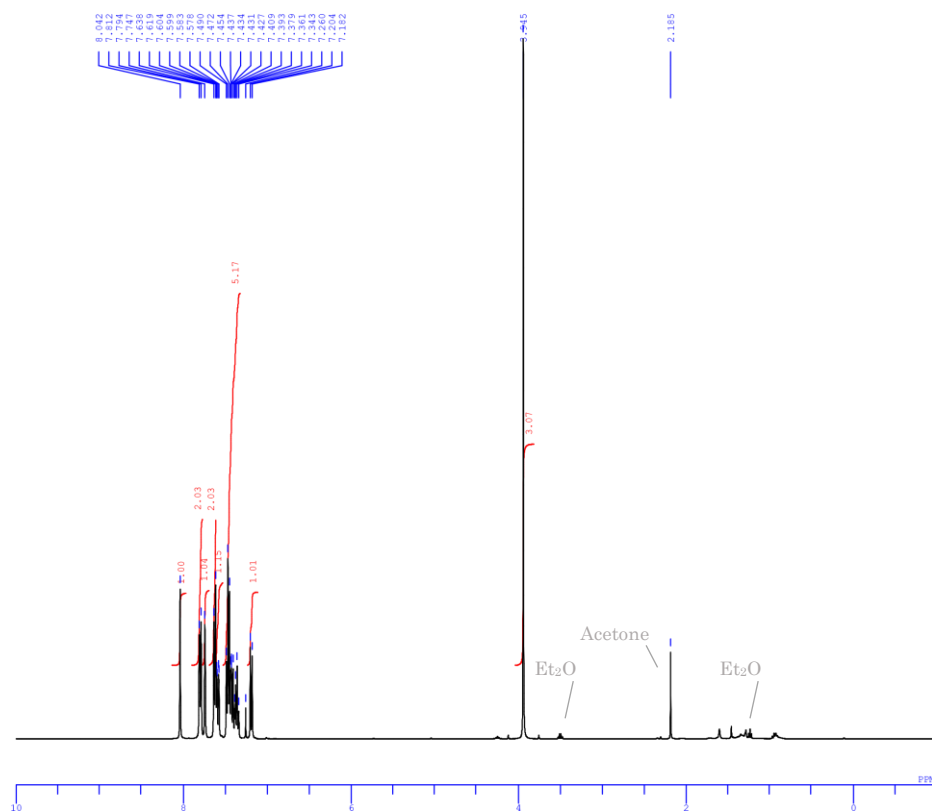


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EXMOD zgpg30
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OBSEF 7.33 KHz
OSFIN 9.88 Hz
POINT 32768
FREQU 32051.28 Hz
SCANS 32
AQTM 1.0224 sec
PD 2.0000 sec
PWI 10.10 usec
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CTEMP 24.9 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 184
    
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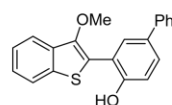


**<sup>1</sup>H NMR of 3ae (400 MHz, CDCl<sub>3</sub>)**

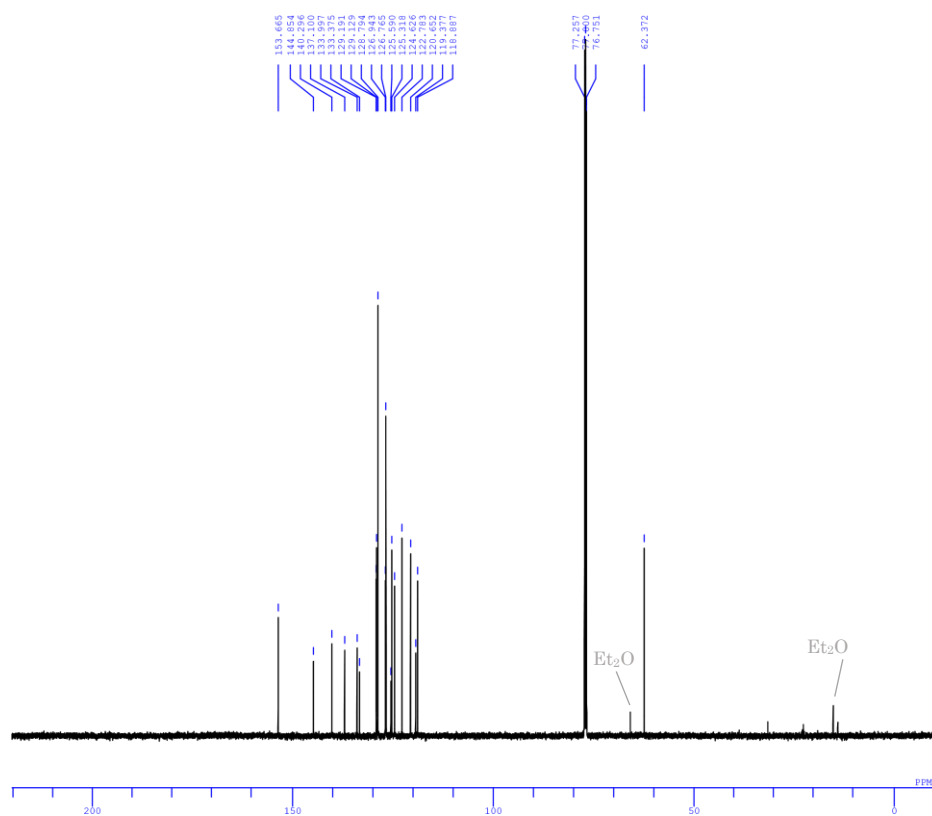


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OBSET 2.47 Hz
OBFIN 0.97 Hz
POINT 32768
FREQU 0012.62 Hz
SCANS 16
AQTM 4.0894 sec
PD 1.0000 sec
FW 15.00 usec
IRNUC
CTEMP 400.0 c
SLVNT CDCl3
EXREF 7.26 ppm
BF 0.30 Hz
RGAIN 144
    
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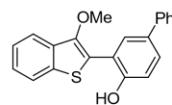


**<sup>13</sup>C NMR of 3ae (126 MHz, CDCl<sub>3</sub>)**

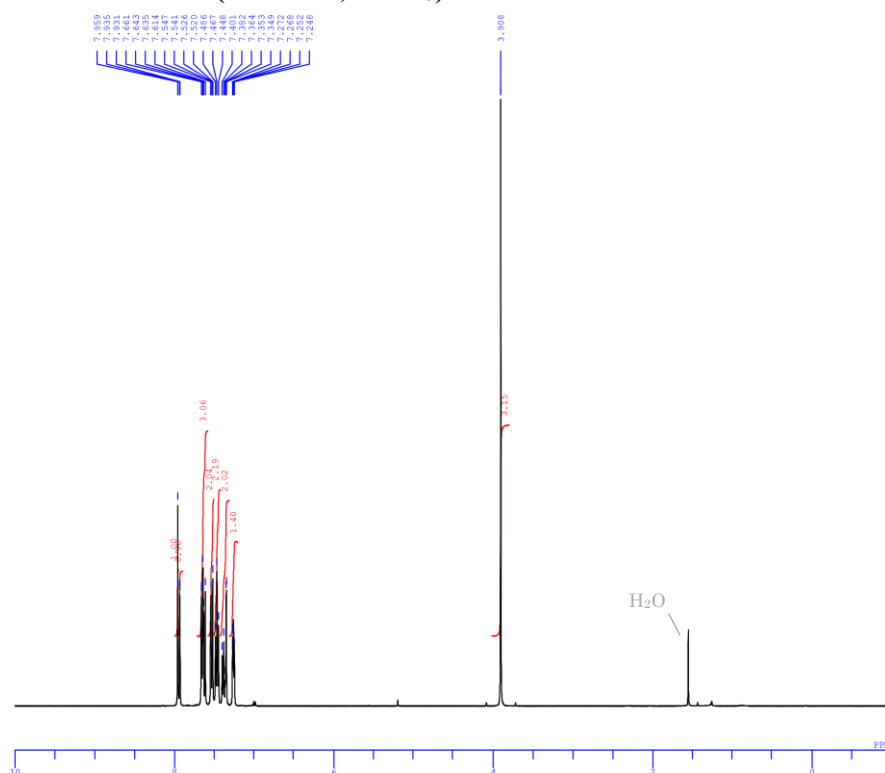


```

COMNT Ref DJP-MT01-104aC
DATIM 2019-01-28 14:07:32
OBMDC 13C
EXMOD zgpg30
OBFRQ 125.78 MHz
OBSET 7.33 Hz
OBFIN 9.88 Hz
POINT 32768
FREQU 32051.28 Hz
SCANS 32
AQTM 1.0224 sec
PD 2.0000 sec
FW 10.10 usec
IRNUC
CTEMP 24.8 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 184
    
```

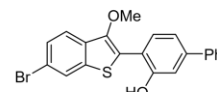


**<sup>1</sup>H NMR of 3bb (400 MHz, CDCl<sub>3</sub>)**

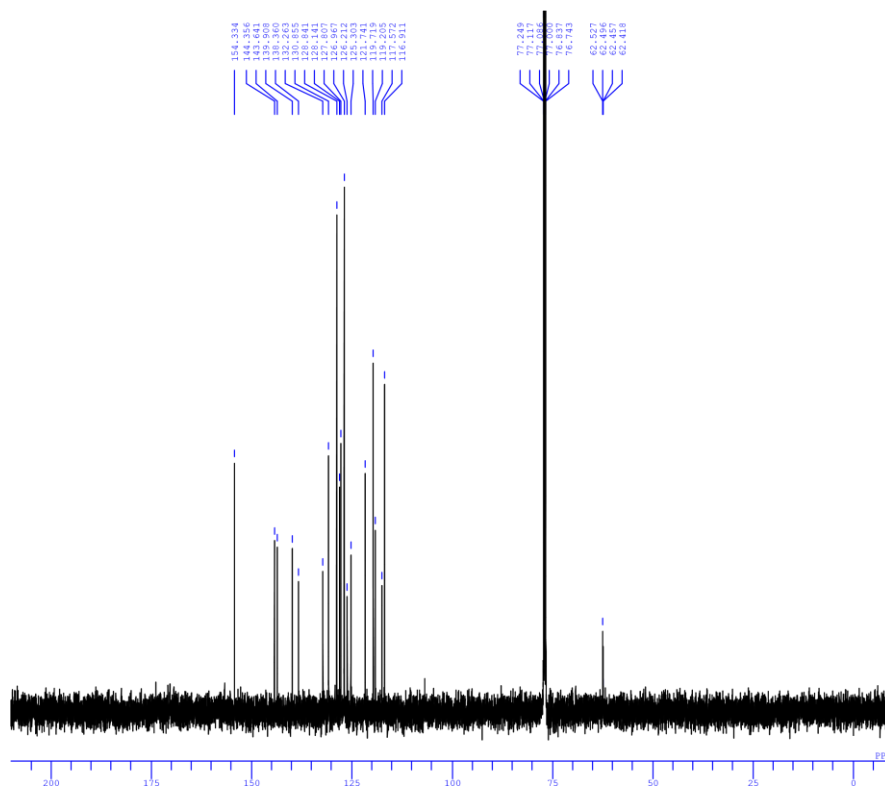


```

COMPT  Ref  DJ9-MT01-173aH
DATIM  2019-04-29 16:15:24
OBNDIC 1H
EXMOD  zg30
OBFREQ 400.13 MHz
OBSET  2.47 KHz
OBFIN  0.97 Hz
POINT  32768
FREQD  8012.82 Hz
SCANS  16
AQTM  4.0894 sec
PD  1.0000 sec
PWI  15.00 usec
IRNOC  CDCl3
CTEMP  22.2 c
SLVNT  CDCl3
EXREF  7.26 ppm
BF  0.30 Hz
RGAIN  362
    
```

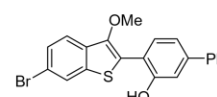


**<sup>13</sup>C NMR of 3bb (126 MHz, CDCl<sub>3</sub>)**



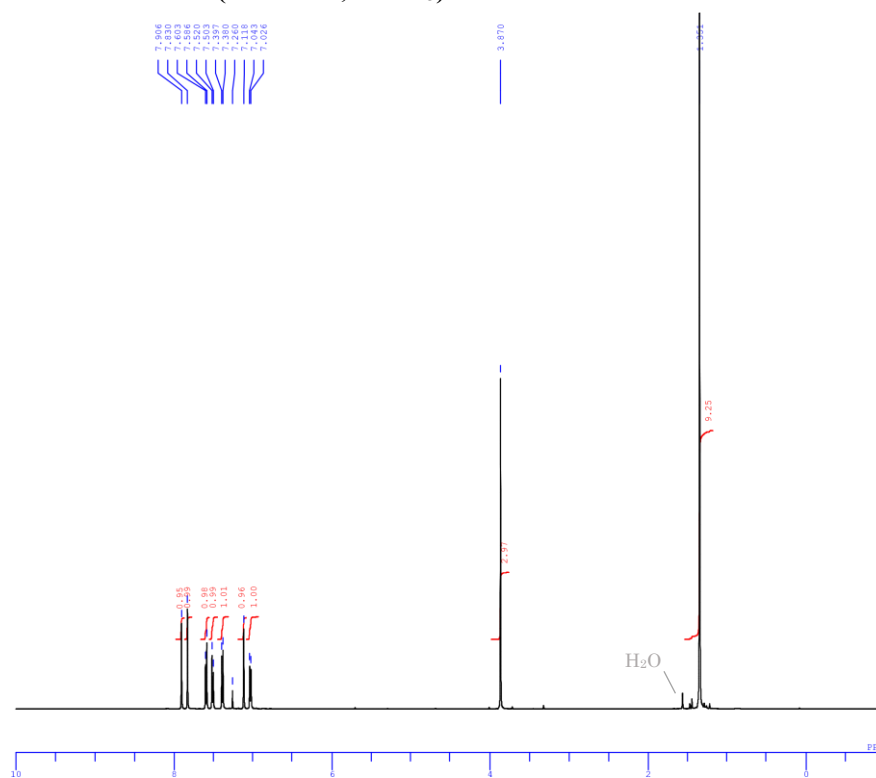
```

DFILE  Br-Ph-OH-C.a1s
COMPT  Ref  DJ9-MT01-173aC
DATIM  2019-04-30 14:10:14
OBNDIC 13C
EXMOD  zgpg30
OBFREQ 125.76 MHz
OBSET  7.33 KHz
OBFIN  9.68 Hz
POINT  32768
FREQD  32051.28 Hz
SCANS  32
AQTM  1.0224 sec
PD  2.0000 sec
PWI  8.00 usec
IRNOC  CDCl3
CTEMP  24.9 c
SLVNT  CDCl3
EXREF  77.00 ppm
BF  1.00 Hz
RGAIN  184
    
```



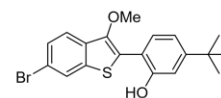


**<sup>1</sup>H NMR of 3bd (500 MHz, CDCl<sub>3</sub>)**

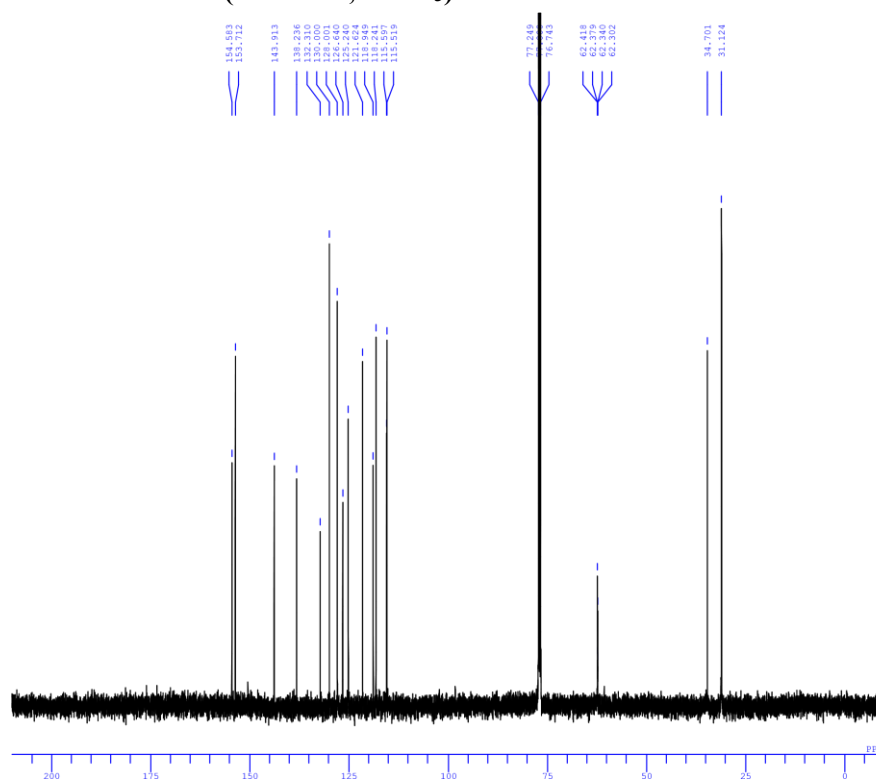


```

DFILE Br_tBu_OH_H.a1s
COMMT Ref DIF-MT01-152aH
DATIM 2019-04-01 09:35:24
ORNUC 1H
EXMOD zg30
OBFRQ 500.19 MHz
OBSET 3.00 Hz
OBFIN 8.88 Hz
POINT 65536
FREQU 10000.00 Hz
SCANS 16
ACQTM 3.2768 sec
PD 1.0000 sec
FWI 8.00 usec
FNUC
CTEMP 24.9 c
SUNT CDCl3
EXREF 7.26 ppm
BF 0.30 Hz
RGAIN 30
    
```

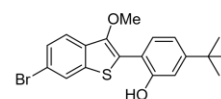


**<sup>13</sup>C NMR of 3bd (126 MHz, CDCl<sub>3</sub>)**

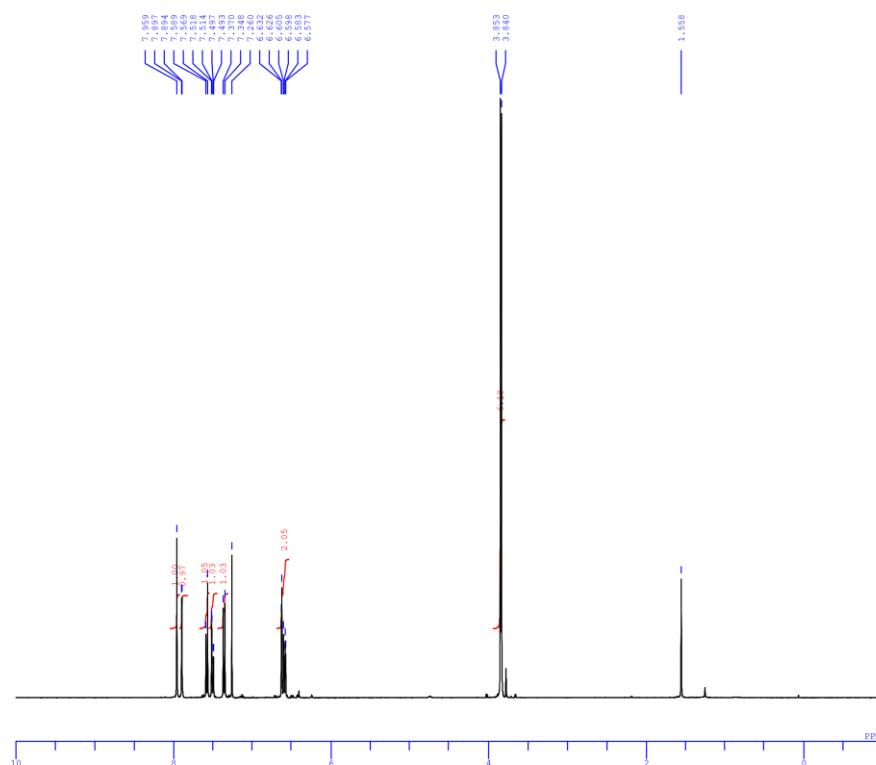


```

DFILE Br_tBu_OH_C.a1s
COMMT Ref DIF-MT01-153aC
DATIM 2019-04-01 09:38:21
ORNUC 13C
EXMOD zgpg30
OBFRQ 125.78 MHz
OBSET 7.33 Hz
OBFIN 9.88 Hz
POINT 27768
FREQU 32031.28 Hz
SCANS 32
ACQTM 1.0224 sec
PD 2.0000 sec
FWI 8.00 usec
FNUC
CTEMP 24.8 c
SUNT CDCl3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 184
    
```

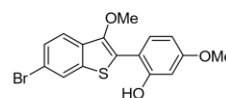


**<sup>1</sup>H NMR of 3bf (400 MHz, CDCl<sub>3</sub>)**

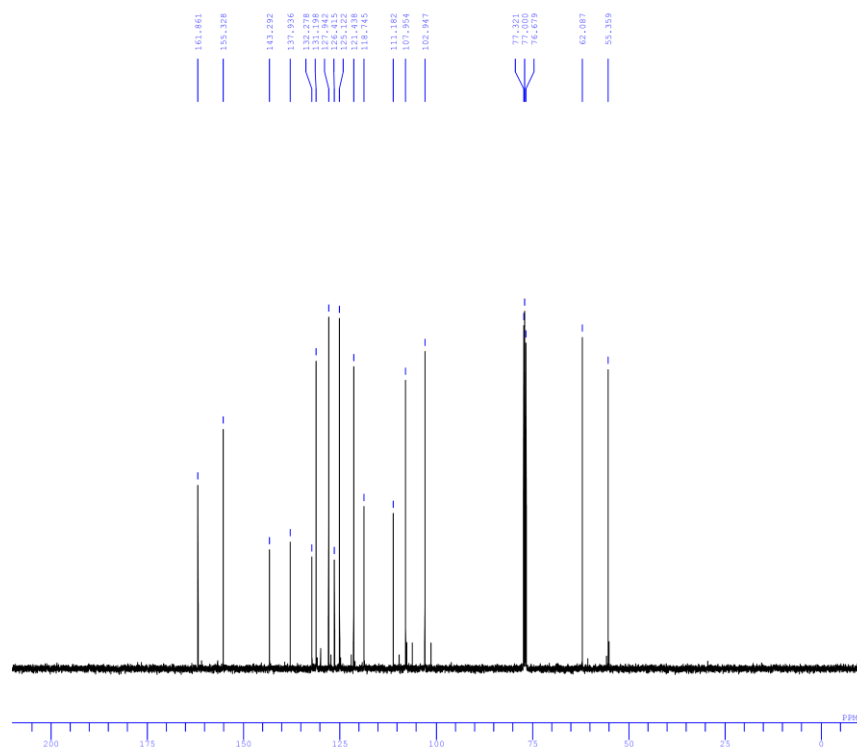


```

COMNT Ref DJP-MT01-174aH
DATIM 2019-05-15 11:14:55
GBNUC 1H
EXMOD zg30
OBFRQ 400.13 MHz
OBSET 2.47 Hz
OBFIN 0.97 Hz
FOINT 32768
FREQU 8012.02 Hz
SCANS 16
ACQTH 4.0984 sec
PD 1.0000 sec
PWI 15.00 usec
IRNUC
CTEMP 20.8 c
SLVNT CDCl3
EKREF 7.26 ppm
BF 0.30 Hz
RGAIN 456
  
```

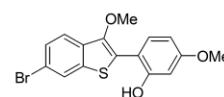


**<sup>13</sup>C NMR of 3bf (101 MHz, CDCl<sub>3</sub>)**

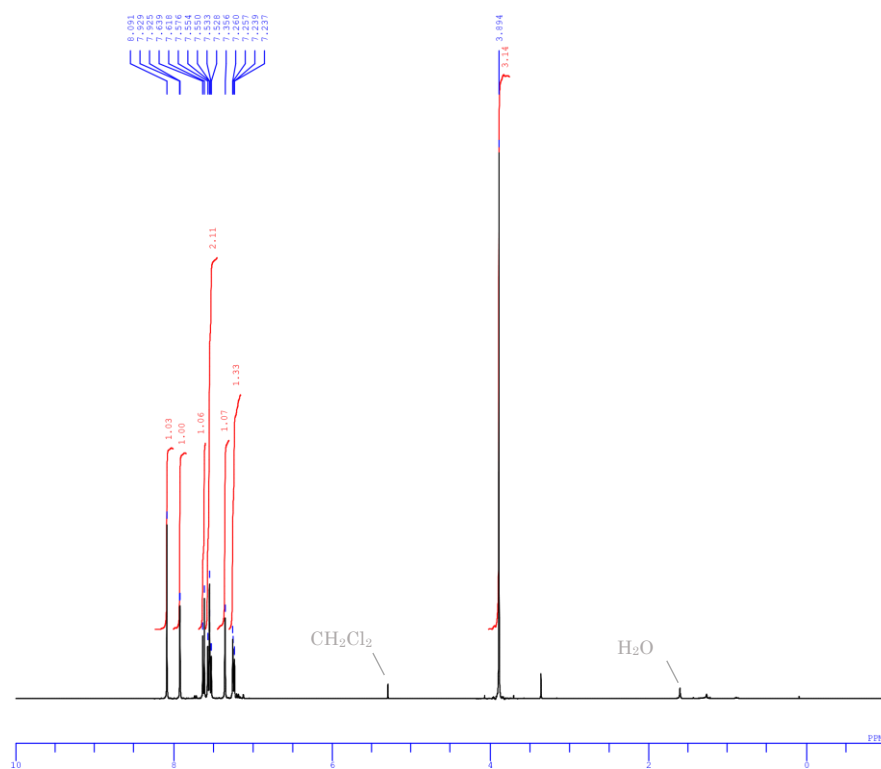


```

DFILE Br OMe OH C.ala
COMNT Ref DJP-MT01-174aC
DATIM 2019-05-14 22:33:49
GBNUC 13C
EXMOD zgpg30
OBFRQ 100.62 MHz
OBSET 2.82 KHz
OBFIN 9.80 Hz
FOINT 32768
FREQU 32051.28 Hz
SCANS 256
ACQTH 1.0224 sec
PD 2.0000 sec
PWI 10.00 usec
IRNUC
CTEMP 21.5 c
SLVNT CDCl3
EKREF 77.00 ppm
BF 1.00 Hz
RGAIN 2050
  
```

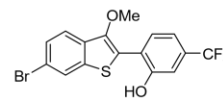


**<sup>1</sup>H NMR of 3bg (400 MHz, CDCl<sub>3</sub>)**

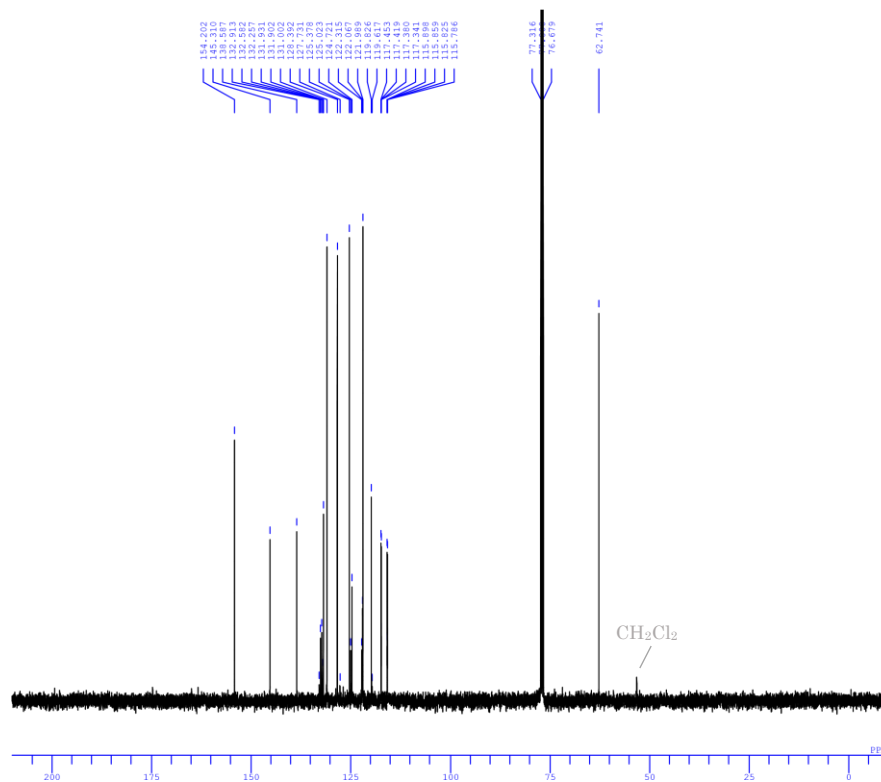


```

COMMENT Ref DJF-MT01-178aH
DATEIM 2019-04-29 14:47:06
ORNUC 1H
EXMOD zg30
ORFQ 400.07 MHz
ORSET 2.40 Hz
ORFIN 0.42 Hz
POINT 32768
FREQ 8223.68 Hz
SCANS 4
ACQTM 3.9846 sec
PD 1.0000 sec
PW 12.00 usec
IRNUC
CTEMP 24.8 c
SLVNT CDCl3
EXREF 7.26 ppm
RF 0.30 Hz
RGAIN 57
    
```

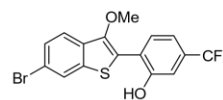


**<sup>13</sup>C NMR of 3bg (101 MHz, CDCl<sub>3</sub>)**

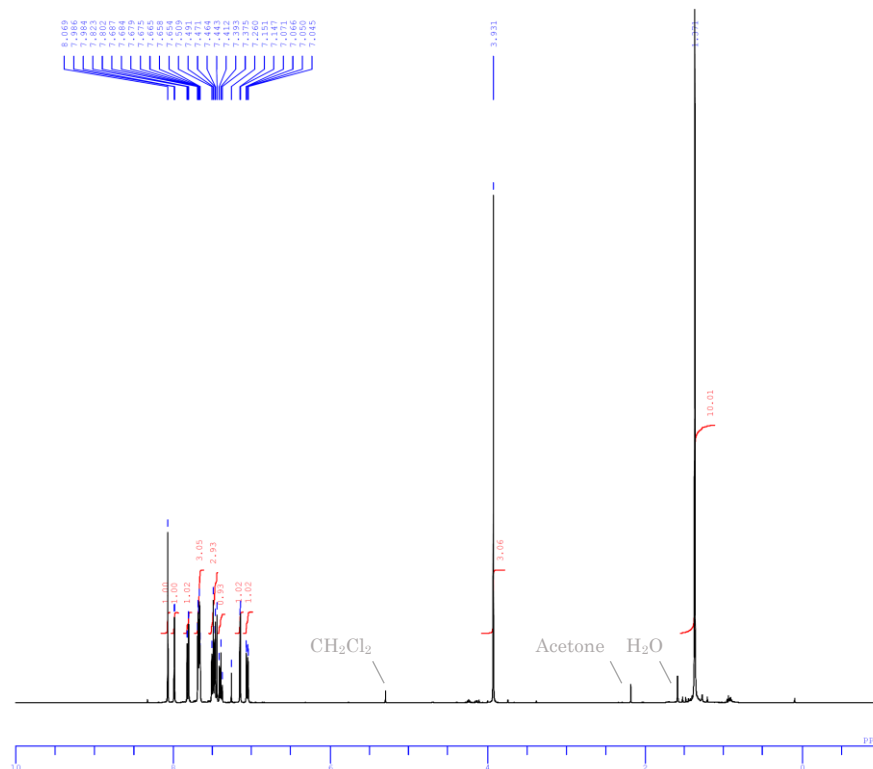


```

DFILE Br CF3 OH C.als
COMMENT Ref DJF-MT01-178aC
DATEIM 2019-04-29 14:49:01
ORNUC 13C
EXMOD zgpg30
ORFQ 100.60 MHz
ORSET 9.25 Hz
ORFIN 0.25 Hz
POINT 65536
FREQ 32051.28 Hz
SCANS 16
ACQTM 1.0224 sec
PD 2.0000 sec
PW 10.00 usec
IRNUC
CTEMP 24.9 c
SLVNT CDCl3
EXREF 77.00 ppm
RF 1.00 Hz
RGAIN 71
    
```

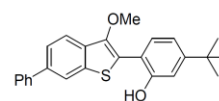


<sup>1</sup>H NMR of 3cd (400 MHz, CDCl<sub>3</sub>)

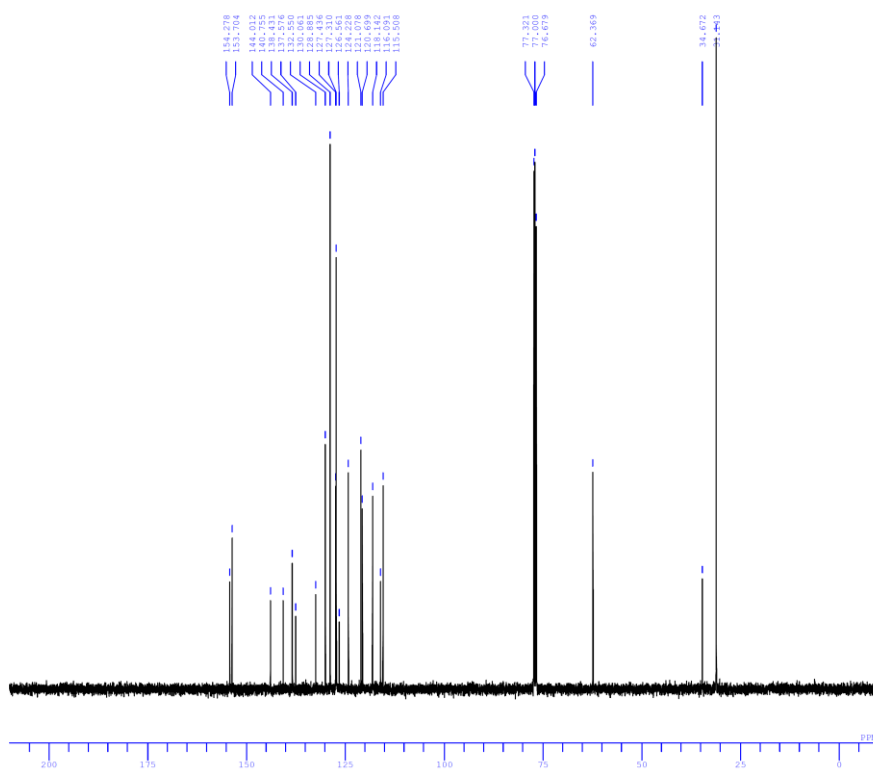


```

DFFILE Ph_tBu_OH_H_als
COMNT Ref DJF-MF01-167aH
DATIM 2019-04-16 18:48:32
CHNHC 1H
EXMOD zg30
GPFREQ 400.13 MHz
OBSET 2.47 KHz
GBFIN 0.97 Hz
POINT 32768
FREQU 8012.82 Hz
SCANS 16
ACQTM 4.0894 sec
PD 1.0000 sec
F1 15.00 usec
IRNHC 400.0 c
CTEMP CDCl3
SLVNT CDCl3
EKREF 7.26 ppm
BF 0.30 Hz
RGAIN 128
  
```

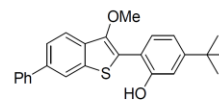


<sup>13</sup>C NMR of 3cd (101 MHz, CDCl<sub>3</sub>)

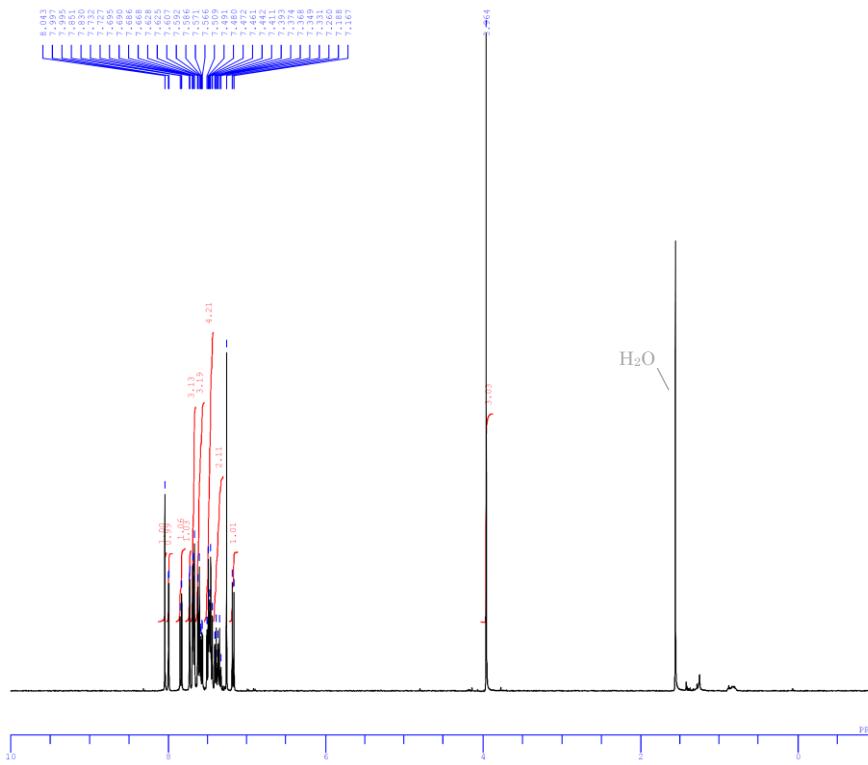


```

DFFILE Ph_tBu_OH_C_als
COMNT Ref DJF-MF01-167aC
DATIM 2019-04-17 20:42:53
CHNHC 13C
EXMOD zgpg30
GPFREQ 100.62 MHz
OBSET 2.82 KHz
GBFIN 9.40 Hz
POINT 32768
FREQU 32051.28 Hz
SCANS 256
ACQTM 1.0224 sec
PD 2.0000 sec
F1 10.00 usec
IRNHC 400.0 c
CTEMP CDCl3
SLVNT CDCl3
EKREF 77.00 ppm
BF 1.00 Hz
RGAIN 2050
  
```

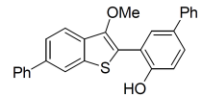


**$^1\text{H}$  NMR of 3ce (400 MHz,  $\text{CDCl}_3$ )**

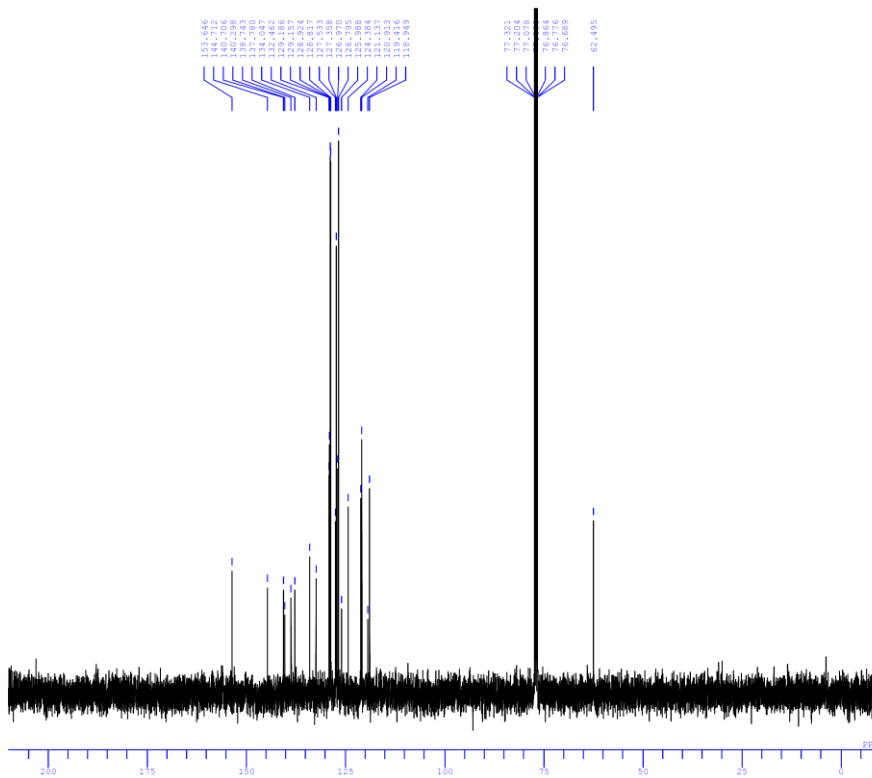


```

DIFILE Ph_4-Ph_OH_M.als
COMNT Ref DJF-MT01-168aH
DAYTM 2019-04-17 11:06:59
SOLUC 1H
EXMOD zg30
GBFQ 400.13 MHz
OBSET 2.47 KHz
GBFIN 0.97 Hz
POINT 32768
FREQD 8012.82 Hz
SCANS 16
ACQTM 4.0894 sec
FD 1.0000 sec
PWL 15.00 usec
FIDUC
CTEMP 400.0 c
SLVNT CDCl3
ENREF 7.26 ppm
RF 0.30 Hz
RGAIN 456
    
```

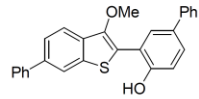


**$^{13}\text{C}$  NMR of 3ce (101 MHz,  $\text{CDCl}_3$ )**

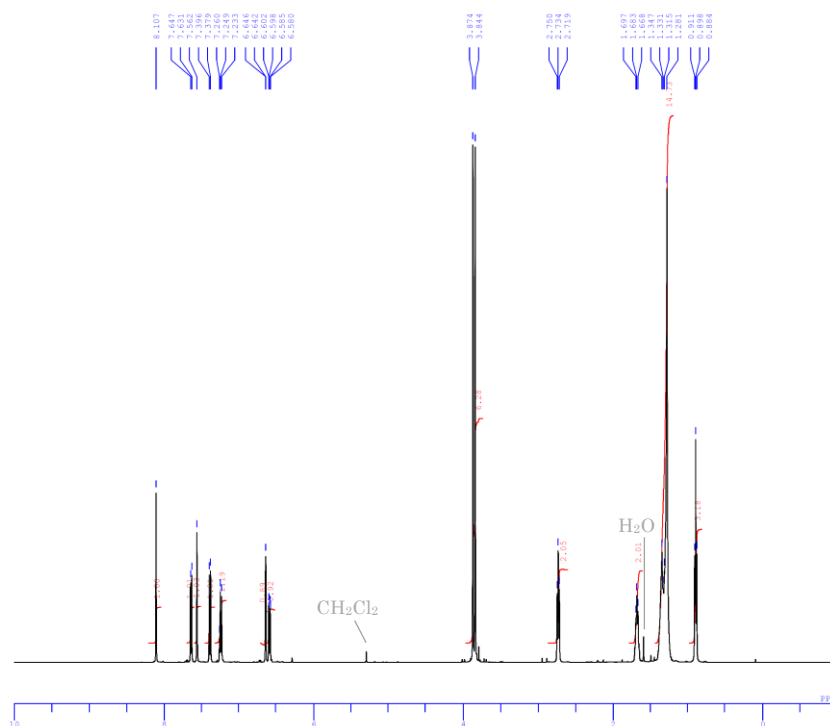


```

DIFILE Ph_4-Ph_OH_C.als
COMNT Ref DJF-MT01-168aC
DAYTM 2019-04-17 22:17:42
SOLUC 13C
EXMOD zgpg30
GBFQ 100.62 MHz
OBSET 2.82 KHz
GBFIN 9.80 Hz
POINT 32768
FREQD 32051.28 Hz
SCANS 256
ACQTM 1.0224 sec
FD 2.0000 sec
PWL 10.00 usec
FIDUC
CTEMP 400.0 c
SLVNT CDCl3
ENREF 77.00 ppm
RF 1.00 Hz
RGAIN 2050
    
```

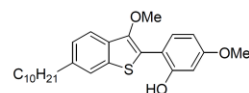


### <sup>1</sup>H NMR of 3ef (500 MHz, CDCl<sub>3</sub>)

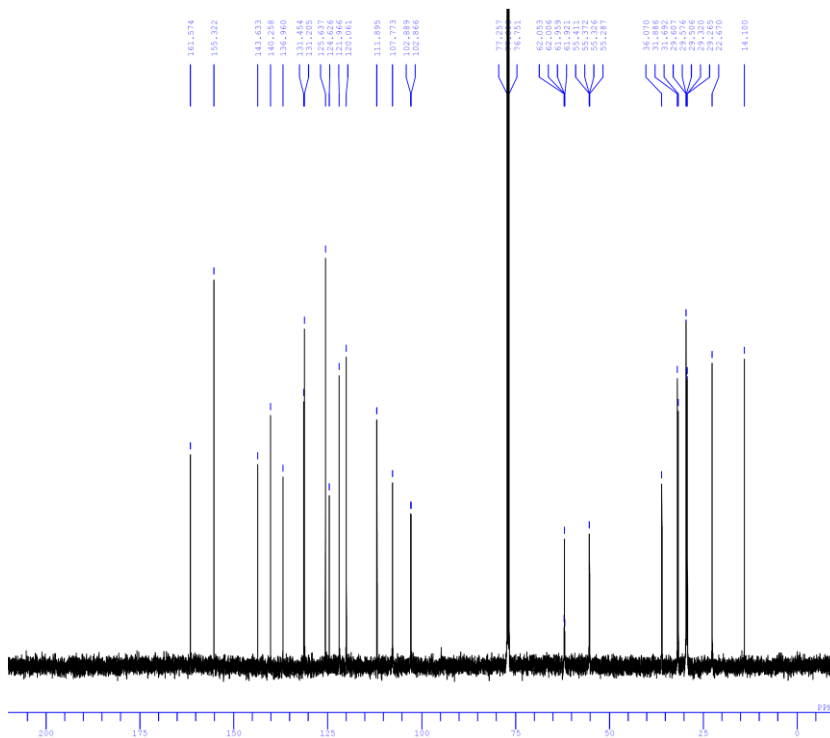


```

D1FILE C10_0Me_OH_H.e1s
D1NAME Ref D1F-MHUI-141aH
D1DATE 2019-02-28 16:33:54
D1NMUC 1H
EXPNO 320
PROCNO 1
PROCPS 500.139 MHz
SFOFF 1.000000
SFOFF1 24.9 c
SFOFF2 7.26 ppm
SFOFF3 0.30 Hz
RGAIN 30
  
```

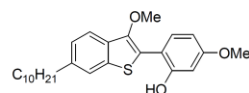


### <sup>13</sup>C NMR of 3ef (126 MHz, CDCl<sub>3</sub>)

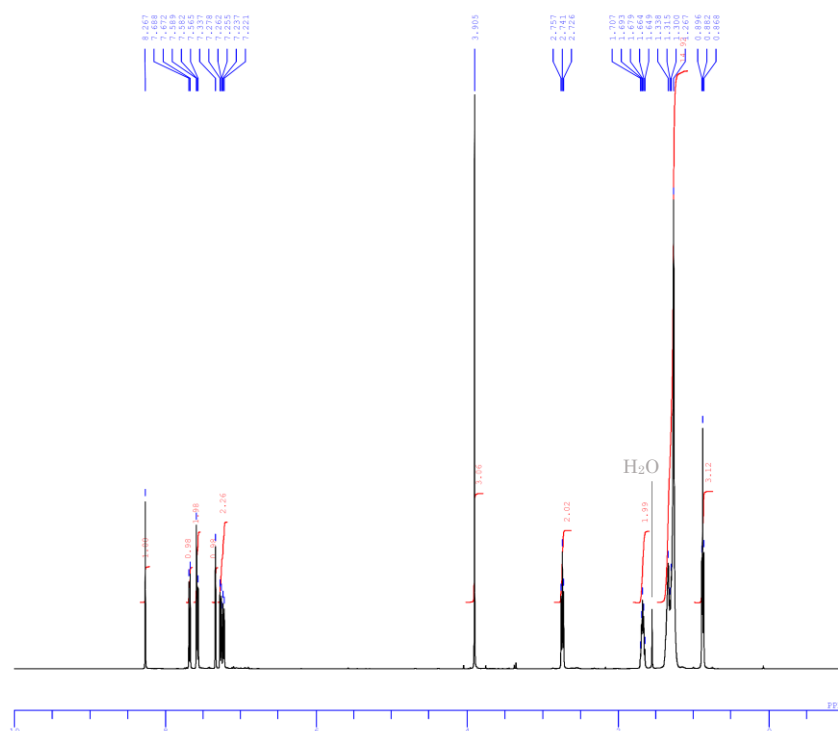


```

D1FILE C10_0Me_OH_C.e1s
D1NAME Ref D1F-MHUI-141aC
D1DATE 2019-02-28 16:42:19
D1NMUC 13C
EXPNO 320
PROCNO 1
PROCPS 125.76 MHz
SFOFF 1.0224 sec
SFOFF1 24.8 c
SFOFF2 77.00 ppm
SFOFF3 1.00 Hz
RGAIN 184
  
```

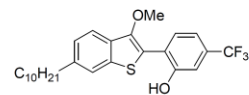


**<sup>1</sup>H NMR of 3eg (500 MHz, CDCl<sub>3</sub>)**

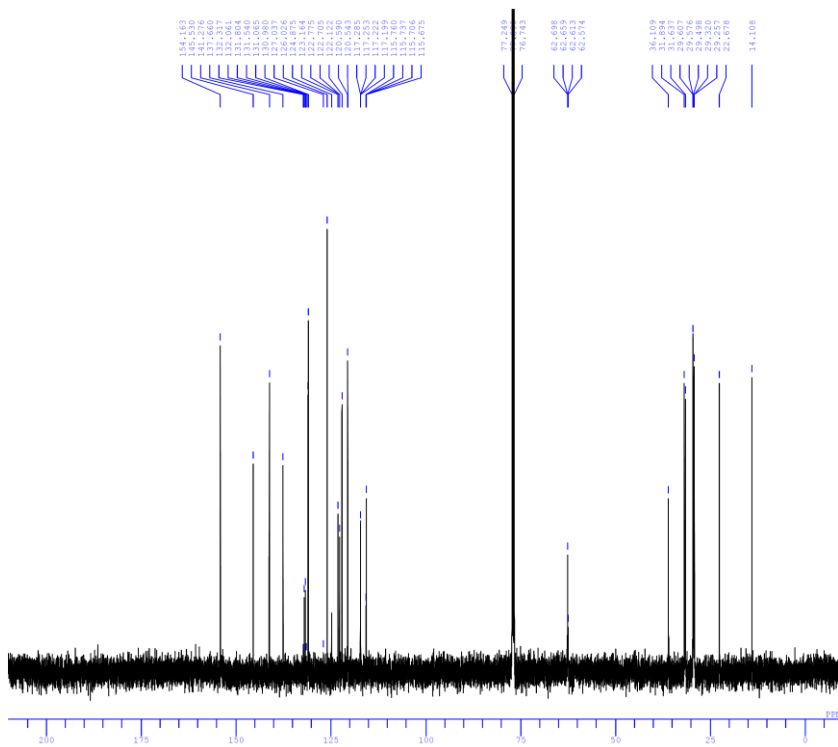


```

D1FILE C10-CP3 OH H.11s
C0MPT Ref:13P-MPTL-13s
DATM 2019-02-26 16:18:01
OBHDC 1H
EXMCO sgg30
OBFFQ 500.19 KHz
OBSET 3.08 KHz
OBFTN 8.88 Hz
FOINT 8536
FREQU 10000.00 Hz
SCANS 16
AQTM 3.2768 sec
PD 1.0000 sec
PWL 8.00 usec
IRFUC 24.9 c
CTEMP CDCl3
SLVNT CDCl3
ESREF 7.26 ppm
BF 0.30 Hz
RGAIN 30
    
```

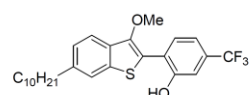


**<sup>13</sup>C NMR of 3eg (126 MHz, CDCl<sub>3</sub>)**



```

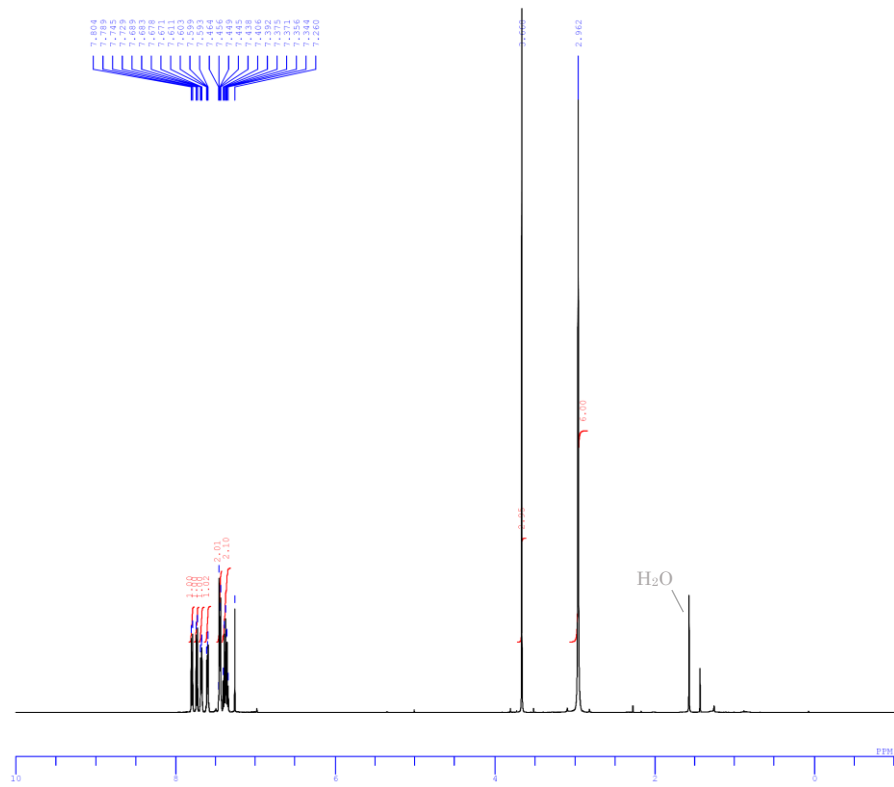
D1FILE C10-CP3 OH C.11s
C0MPT Ref:13P-MPTL-13s
DATM 2019-02-26 16:20:55
OBHDC 13C
EXMCO sgg30
OBFFQ 125.78 KHz
OBSET 7.33 KHz
OBFTN 9.88 Hz
FOINT 32768
FREQU 32051.28 Hz
SCANS 32
AQTM 1.0224 sec
PD 2.0000 sec
PWL 8.00 usec
IRFUC 24.9 c
CTEMP CDCl3
SLVNT CDCl3
ESREF 77.00 ppm
BF 1.00 Hz
RGAIN 184
    
```





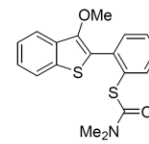


<sup>1</sup>H NMR of 5aa (500 MHz, CDCl<sub>3</sub>)

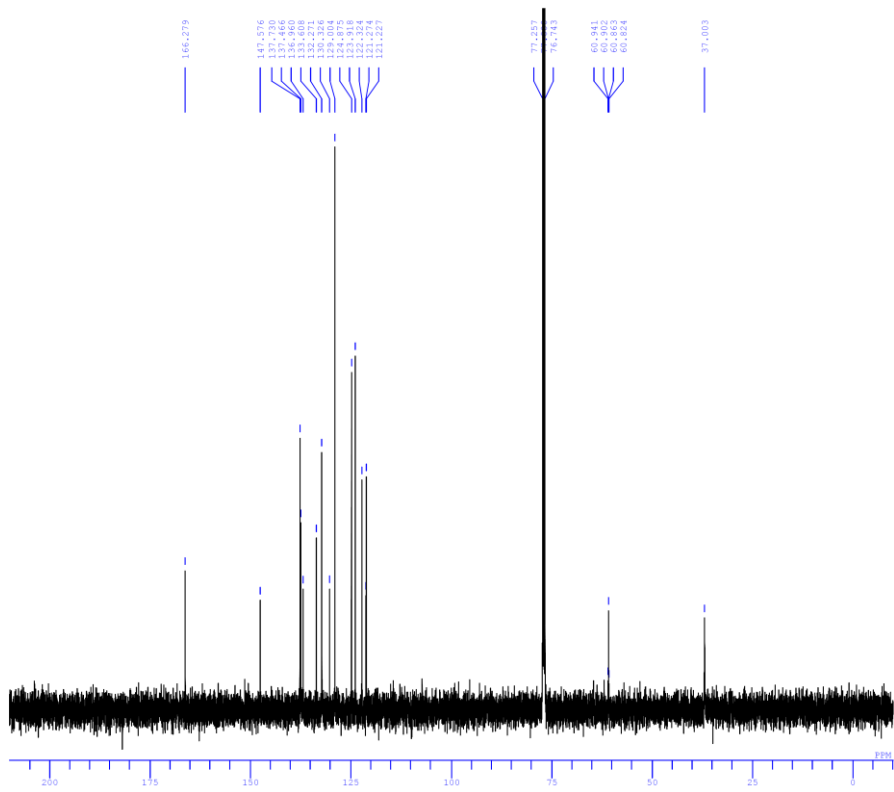


```

D1FILE H H S H.s1s
C0M0T Ref D1F-MT HHS H
D1TIM 2019-07-18 11:07:44
GBNUC 1H
EXNOO z930
OBFREQ 500.19 MHz
OBSET 3.08 MHz
OBFIN 8.88 Hz
POINT 65536
FREQ0 10000.00 Hz
SCANS 16
AQ0TH 3.2768 sec
PD 1.0000 sec
PFI 8.00 usec
IRNUC
CTEMP 24.9 c
SLVNT CDCl3
EXREF 7.26 ppm
BF 0.30 Hz
RGAIN 68
    
```

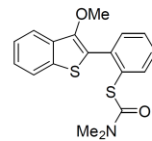


<sup>13</sup>C NMR of 5aa (126MHz, CDCl<sub>3</sub>)

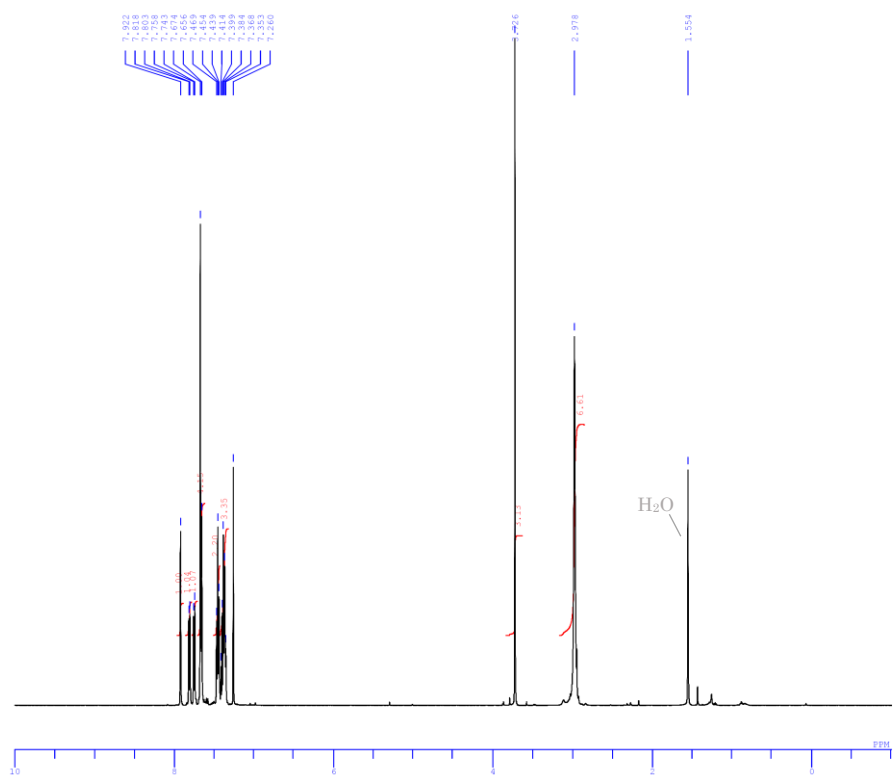


```

D1FILE H H S C.s1s
C0M0T Ref D1F-MT HHS C
D1TIM 2019-07-18 10:35:24
GBNUC 13C
EXNOO z9350
OBFREQ 125.78 MHz
OBSET 7.33 MHz
OBFIN 9.88 Hz
POINT 32768
FREQ0 32051.28 Hz
SCANS 32
AQ0TH 1.0224 sec
PD 2.0000 sec
PFI 8.00 usec
IRNUC
CTEMP 24.9 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 154
    
```

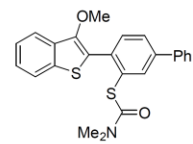


**<sup>1</sup>H NMR of 5ab (500 MHz, CDCl<sub>3</sub>)**

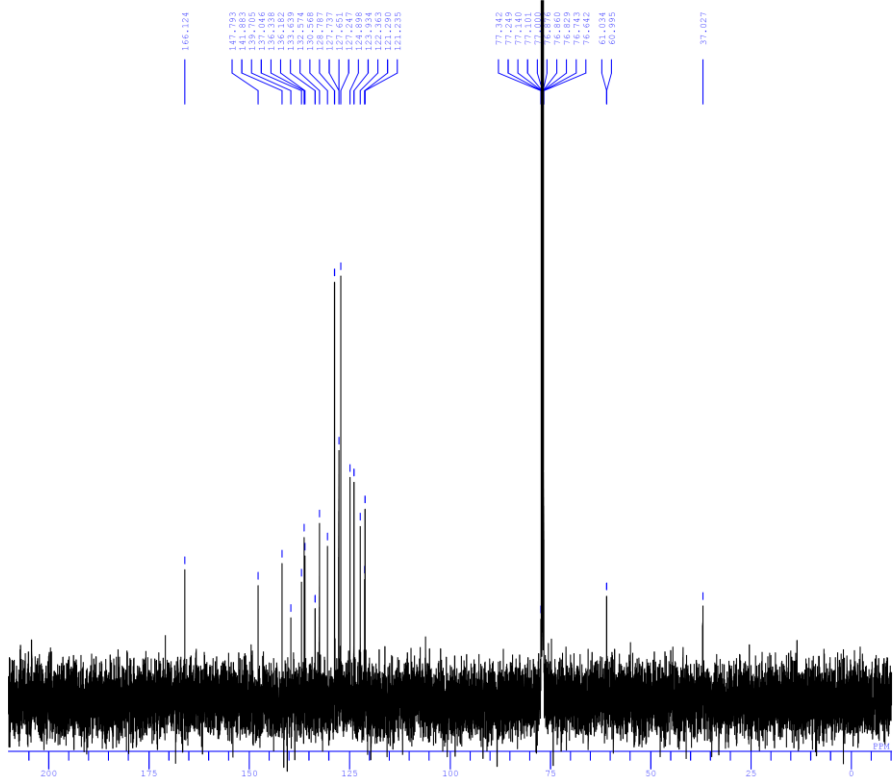


```

DFILE H Ph S H.als
COMMT Ref DJF-MT01-1374H
DATIM 2019-02-25 12:05:25
ORNTC 1H
EXMNO zq30
OBFYQ 500.19 MHz
OBSFT 3.08 Hz
OBFIN 8.88 Hz
POINT 65536
FREQU 10000.00 Hz
SCANS 16
ACQTM 3.2768 sec
ED 1.0000 sec
FVI 8.00 usec
TEMPC 24.8 c
SLVNT CDCl3
OBSFT 7.26 ppm
BF 0.30 Hz
RGAIN 75
    
```

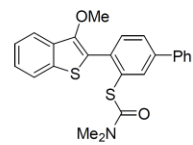


**<sup>13</sup>C NMR of 5ab (126 MHz, CDCl<sub>3</sub>)**

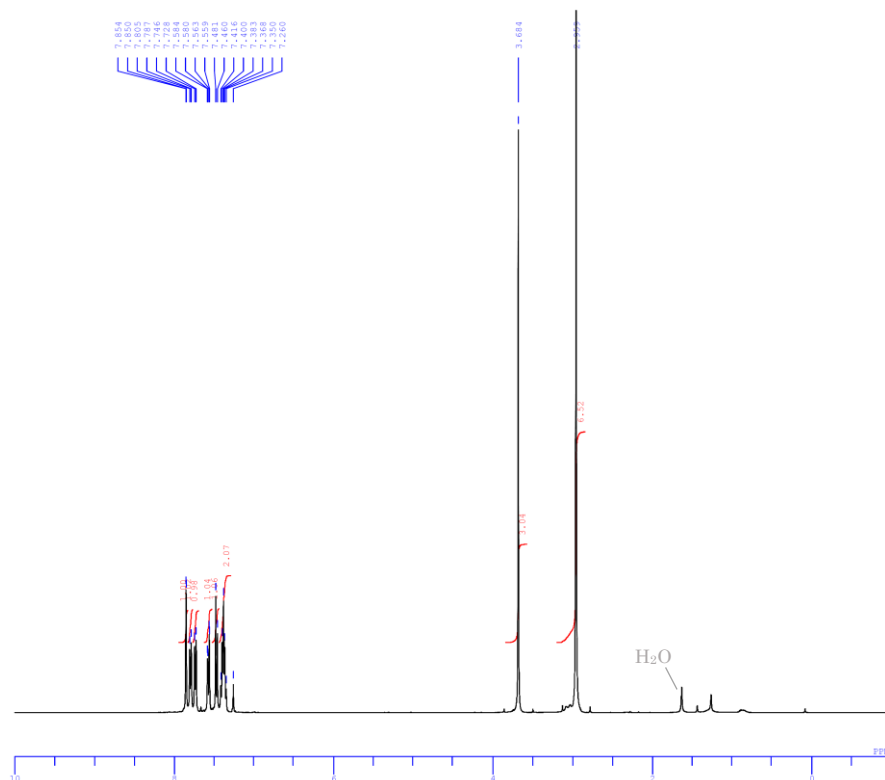


```

DFILE H Ph S C.als
COMMT Ref DJF-MT01-1374C
DATIM 2019-02-25 12:08:19
ORNTC 13C
EXMNO zq30
OBFYQ 125.78 MHz
OBSFT 7.33 Hz
OBFIN 9.88 Hz
POINT 32768
FREQU 32051.28 Hz
SCANS 32
ACQTM 1.0224 sec
ED 2.0000 sec
FVI 8.00 usec
TEMPC 24.8 c
SLVNT CDCl3
OBSFT 77.00 ppm
BF 1.00 Hz
RGAIN 194
    
```

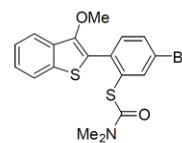


<sup>1</sup>H NMR of 5ac (400 MHz, CDCl<sub>3</sub>)

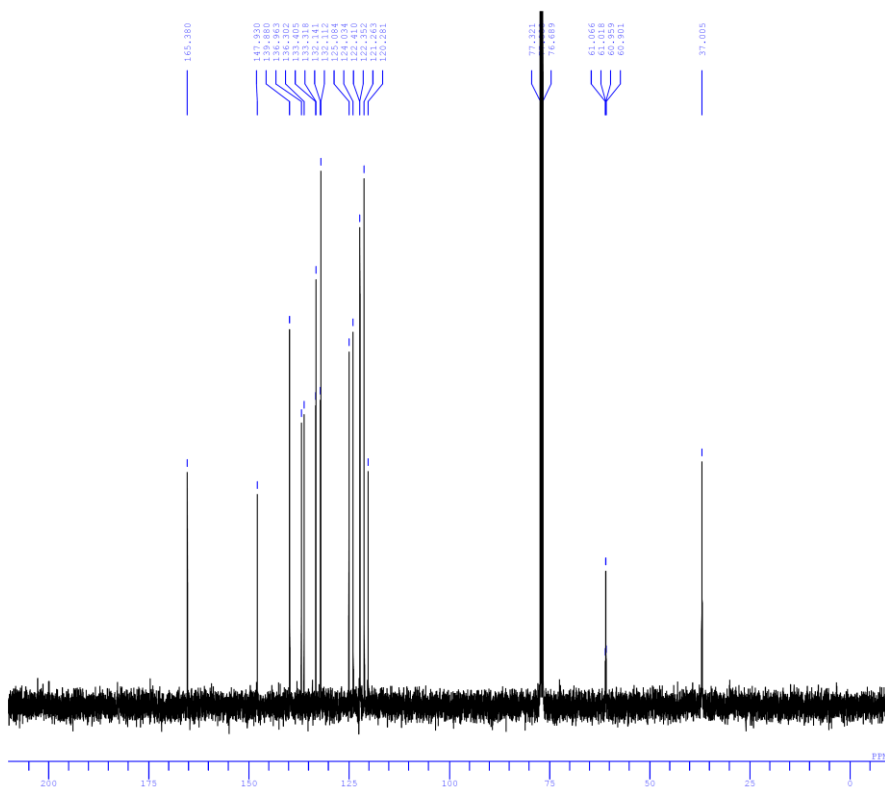


```

DFILE H.Br.S.H.als
COMMT Ref EJP-MT01-133aH
DATIM 2019-02-20 16:47:57
OBNUC 1H
EXNO 2930
OBFFQ 400.13 MHz
OBSET 2.47 Hz
OBFIN 0.37 Hz
POINT 32768
FREQU 8012.92 Hz
SCANS 16
AQTM 4.0894 sec
PD 1.0000 sec
PWI 10.00 usec
IRNUC
CTEMP 400.0 c
SLVWT CDCl3
EXREF 7.26 ppm
BF 0.30 Hz
RGAIN 228
    
```

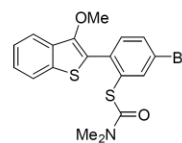


<sup>13</sup>C NMR of 5ac (101 MHz, CDCl<sub>3</sub>)

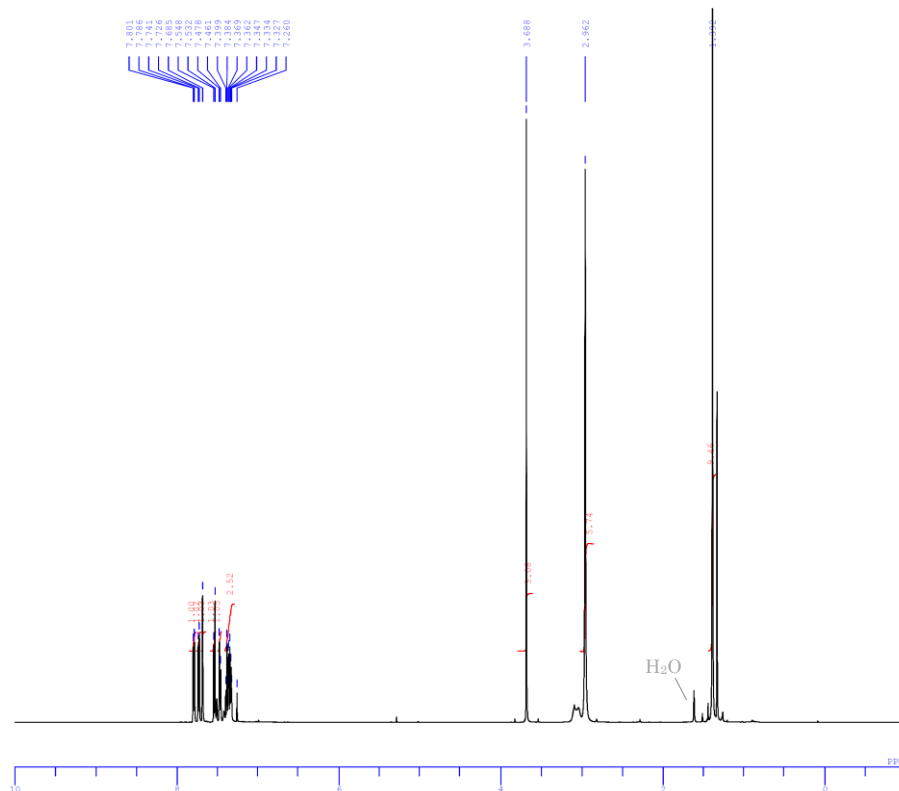


```

DFILE H.Br.S.C.als
COMMT Ref EJP-MT01-133aC
DATIM 2019-02-21 00:33:17
OBNUC 13C
EXNO 136
EXNO 2930
OBFFQ 100.62 MHz
OBSET 2.82 MHz
OBFIN 9.50 Hz
POINT 32768
FREQU 32051.28 Hz
SCANS 256
AQTM 1.0224 sec
PD 2.0000 sec
PWI 8.00 usec
IRNUC
CTEMP 400.0 c
SLVWT CDCl3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 2000
    
```

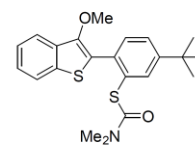


**<sup>1</sup>H NMR of 5ad (500 MHz, CDCl<sub>3</sub>)**

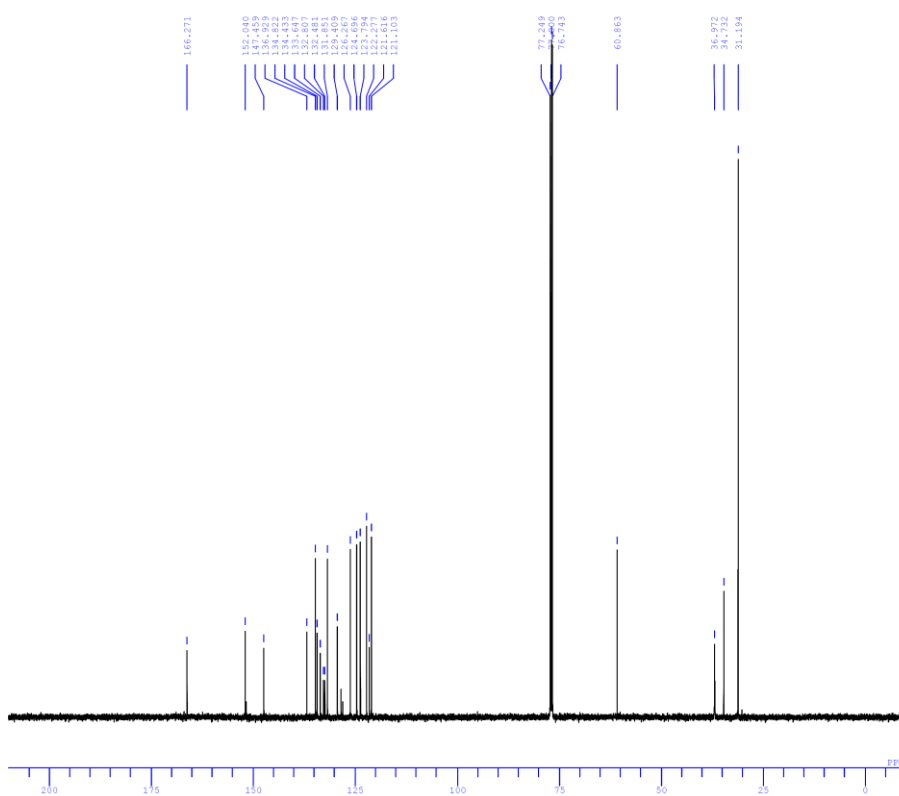


```

D1FILE H_1Bu_g_H_1a19
COMMT Ref D0F-MT01-123aH
DATIM 2019-02-12 14:51:41
DBNVC 1H
EXMOD zg30
OBPFG 500.19 MHz
OBSST 3.68 MHz
OBFIN 8.88 Hz
POINT 65536
FREQU 10000.00 Hz
SCANS 16
ACQTM 3.2768 sec
PD 1.0000 sec
PWI 11.50 usec
IRNUC
CTEMP 24.9 c
SLVNT CDCl3
EXREF 7.26 ppm
RF 0.30 Hz
RGAIN 30
  
```

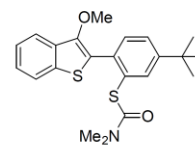


**<sup>13</sup>C NMR of 5ad (126 MHz, CDCl<sub>3</sub>)**

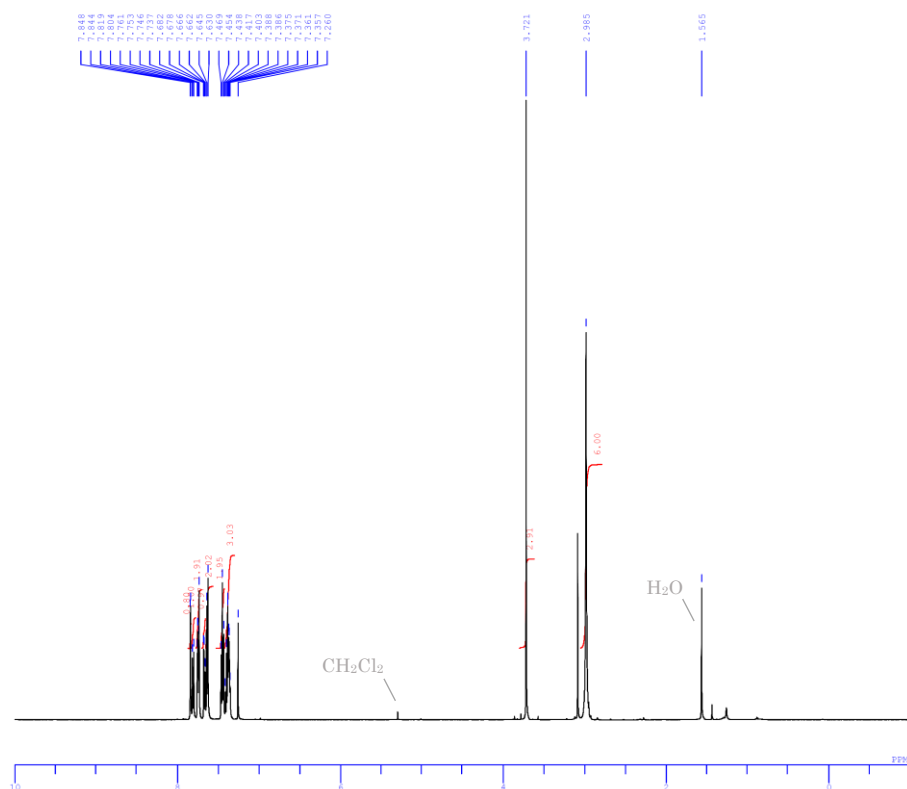


```

D1FILE H_1Bu_s_C_1a19
COMMT Ref D0F-MT01-123ac
DATIM 2019-02-12 14:54:37
DBNVC 13c
EXMOD zgpg30
OBPFG 125.76 MHz
OBSST 7.33 KHz
OBFIN 9.88 Hz
POINT 32768
FREQU 32051.28 Hz
SCANS 32
ACQTM 1.0254 sec
PD 2.0000 sec
PWI 10.10 usec
IRNUC
CTEMP 24.9 c
SLVNT CDCl3
EXREF 77.00 ppm
RF 1.00 Hz
RGAIN 164
  
```

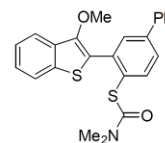


**<sup>1</sup>H NMR of 5ae (500 MHz, CDCl<sub>3</sub>)**

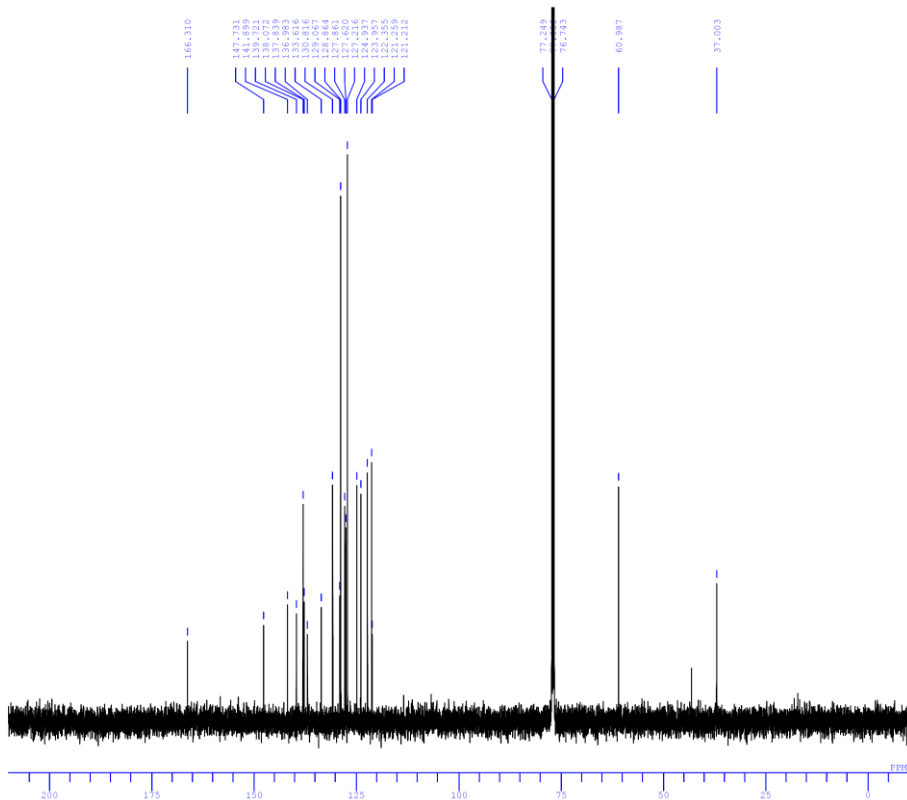


```

OFF1  H-4-Ph. s C. a1s
COM1  Hf. DJF-H701-108H
DATE1  2019-02-06 09:27:20
ORNUC  1H
EXMOD  zg30
OBPFC  500.19 MHz
OBSET  3.08 KHz
OBFIN  8.88 Hz
PQINH  65336
FREQU  10000.00 Hz
SCANS  16
ACQTM  3.2768 sec
PD  1.0000 sec
PWL  11.50 usec
IRNUC  CDCl3 24.8 c
CTEMP  24.8 c
EXREF  1.57 ppm
BF  0.30 Hz
RGAIN  47
    
```

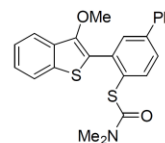


**<sup>13</sup>C NMR of 5ae (126 MHz, CDCl<sub>3</sub>)**

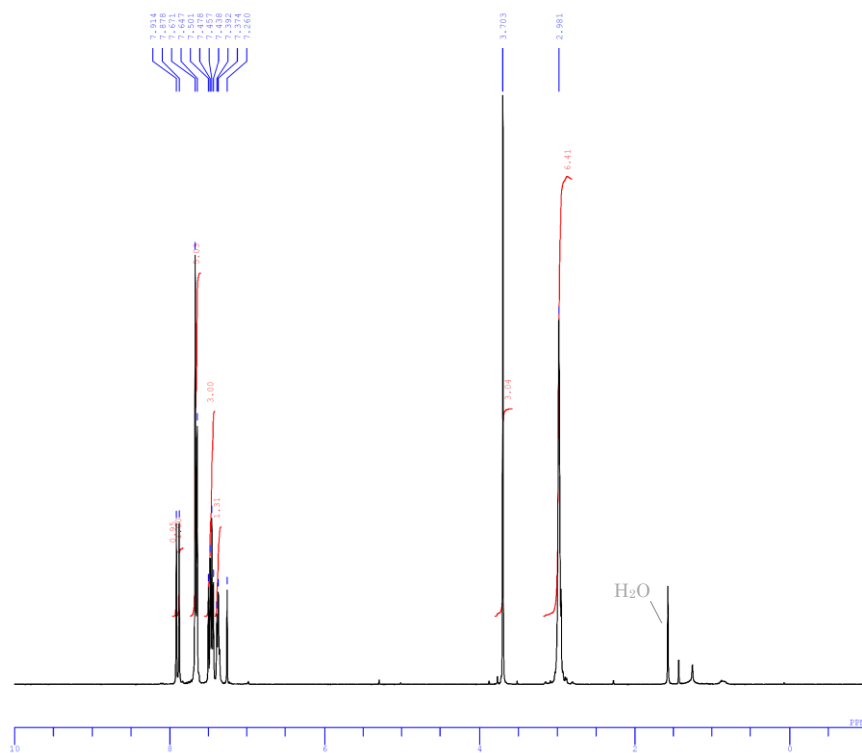


```

OFF1  H-4-Ph. s C. a1s
COM1  Hf. DJF-H701-108C
DATE1  2019-02-06 09:30:14
ORNUC  13C
EXMOD  zgpg30
OBPFC  125.78 MHz
OBSET  7.33 KHz
OBFIN  9.88 Hz
PQINH  32768
FREQU  32051.28 Hz
SCANS  32
ACQTM  1.0224 sec
PD  2.0000 sec
PWL  10.10 usec
IRNUC  CDCl3 24.8 c
CTEMP  24.8 c
EXREF  77.00 ppm
BF  1.00 Hz
RGAIN  184
    
```



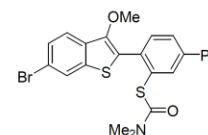
### $^1\text{H}$ NMR of **5bb** (400 MHz, $\text{CDCl}_3$ )



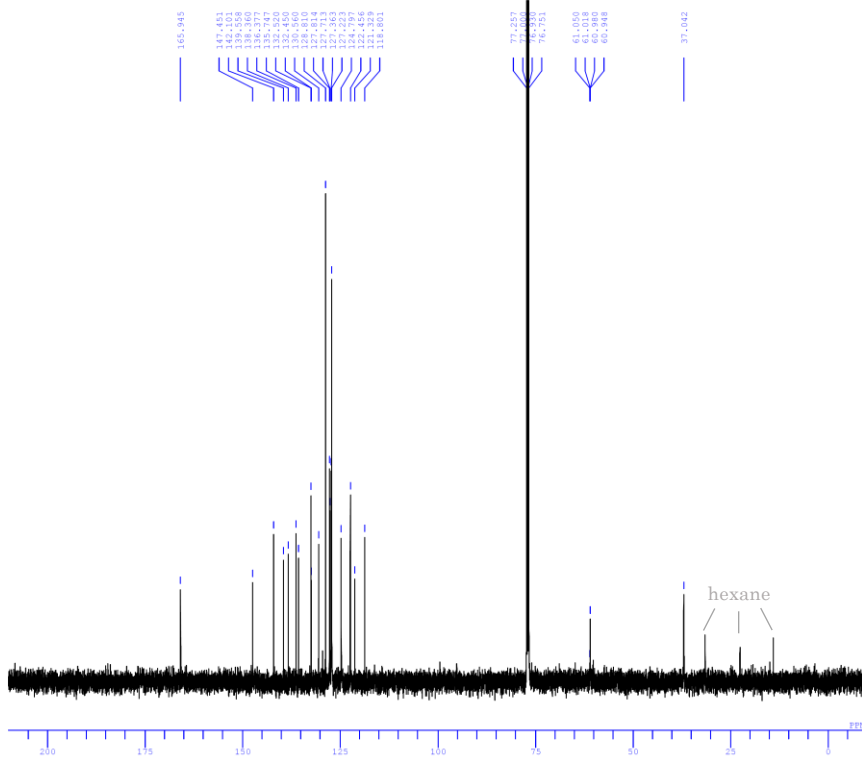
```

D1FILE Br_Ph_8.H.als
COMMT ReF D1P-M701-156aH
DATIM 2019-03-27 16:27:20
OHNO2 1H
EXMOD zg30
OBFRC 400.13 MHz
OBSET 2.47 Hz
OBTIN 0.97 Hz
POINT 32768
FREQO 8012.62 Hz
SCANS 16
ACQTM 4.0894 sec
PD 1.0000 sec
PWI 10.00 usec
INNOU
CTEMP 400.0 c
SINWT CDCl3
EKREF 7.26 ppm
BF 0.30 Hz
RGAIN 575

```



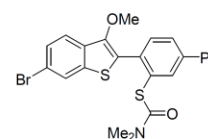
### $^{13}\text{C}$ NMR of **5bb** (126 MHz, $\text{CDCl}_3$ )



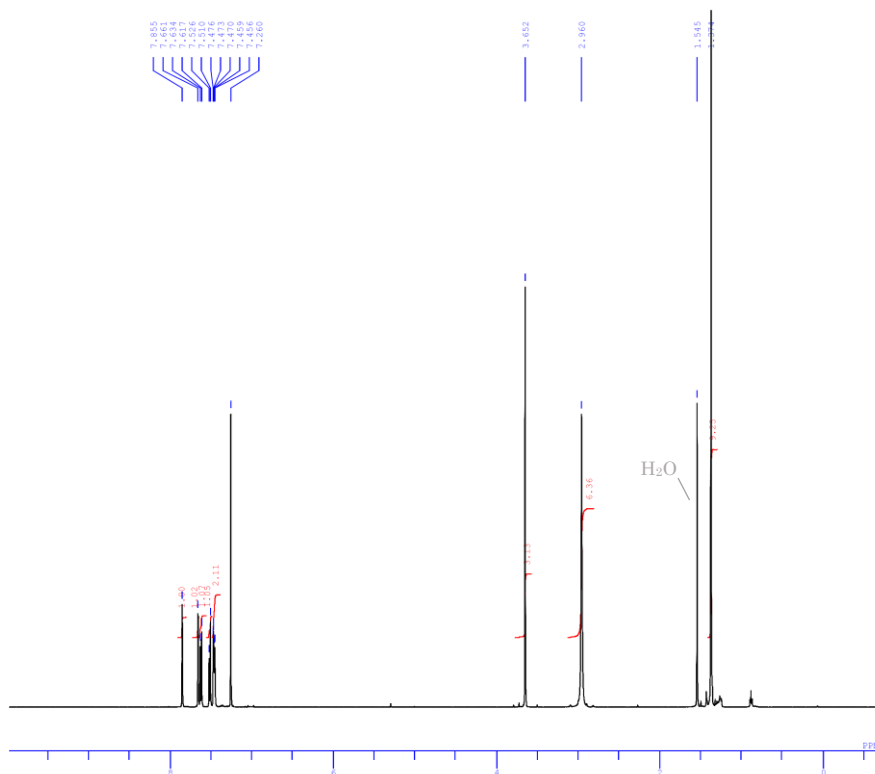
```

D1FILE Br_Ph_8.C.als
COMMT ReF D1P-M701-156aC
DATIM 2019-03-27 14:45:52
OHNO2 13C
EXMOD zgpg30
OBFRC 125.78 MHz
OBSET 7.33 Hz
OBTIN 9.88 Hz
POINT 32768
FREQO 3201.08 Hz
SCANS 32
ACQTM 1.0224 sec
PD 2.0000 sec
PWI 8.00 usec
INNOU
CTEMP 24.9 c
SINWT CDCl3
EKREF 77.00 ppm
BF 1.00 Hz
RGAIN 194

```

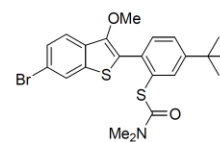


**<sup>1</sup>H NMR of 5bd (500 MHz, CDCl<sub>3</sub>)**

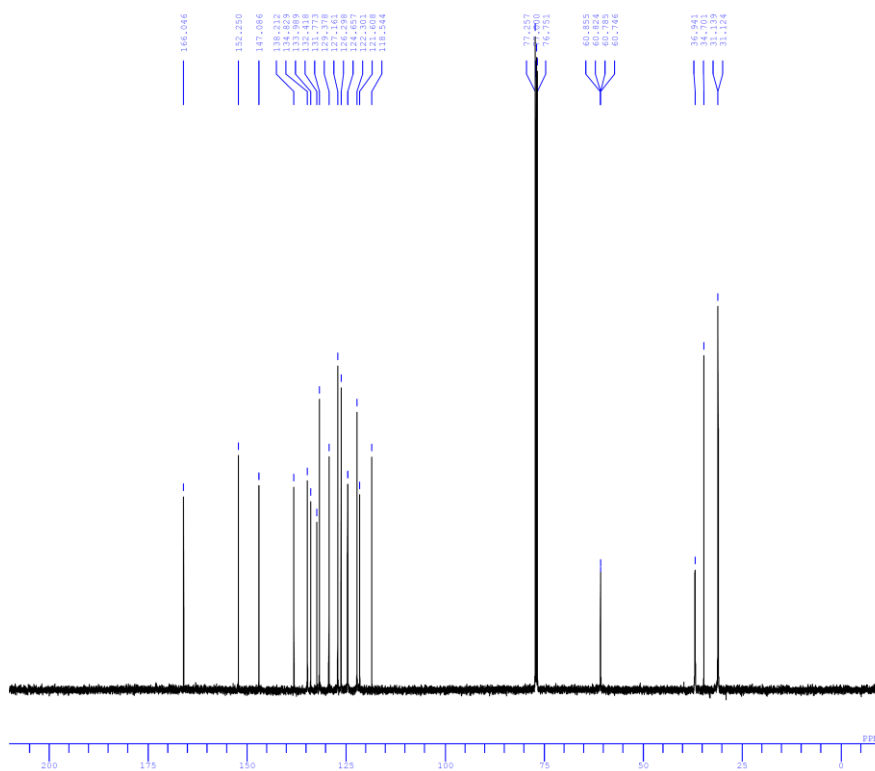


```

DFFILE Br tBu S H.als
CMNPT Ref DJF-RT01-162aH
DATIM 2019-04-02 15:47:10
OBNUC 1H
EXMOD zg30
SFFRQ 500.19 MHz
GBSET 3.08 kHz
GBFIN 5.55 Hz
POINT 65536
FREQU 10000.00 Hz
SCANS 16
AQTM 3.2768 sec
FD 1.0000 sec
PWL 8.00 usec
IRNUC
CTEMP 24.9 c
SLVNT CDCl3
XKREF 7.26 ppm
BF 0.30 Hz
RGAIN 84
    
```

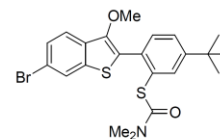


**<sup>13</sup>C NMR of 5bd (126 MHz, CDCl<sub>3</sub>)**

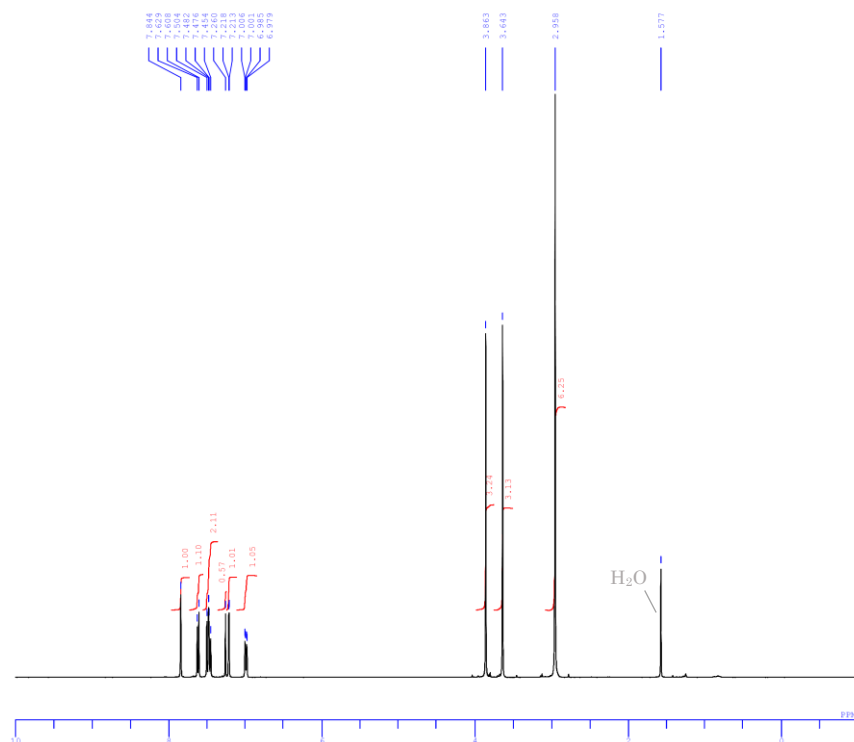


```

DFFILE Br tBu S C.als
CMNPT Ref DJF-RT01-162aC
DATIM 2019-04-03 08:36:23
OBNUC 13C
EXMOD zgpg30
SFFRQ 125.78 MHz
GBSET 7.33 kHz
GBFIN 9.88 Hz
POINT 32768
FREQU 32051.28 Hz
SCANS 32
AQTM 1.0224 sec
FD 2.0000 sec
PWL 8.00 usec
IRNUC
CTEMP 24.9 c
SLVNT CDCl3
XKREF 77.00 ppm
BF 1.00 Hz
RGAIN 164
    
```

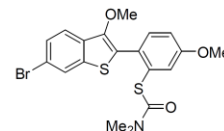


**<sup>1</sup>H NMR of 5bf (400 MHz, CDCl<sub>3</sub>)**

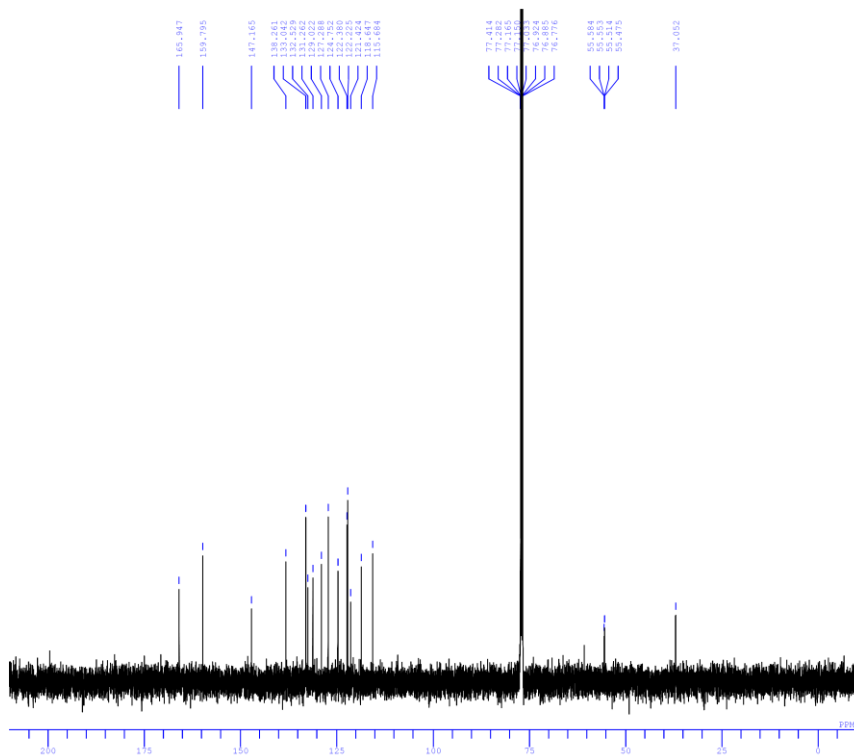


```

OFFILE Br-OMe 5 H.a1s
COMMENT Ref DJF-HT01-188aH
DATIM 2019-05-21 09:44:12
ORNUC 1H
EXMOD z930
ORFQ 400.13 MHz
ORSET 2.47 KHz
ORFIN 0.97 Hz
POINT 32768
FREQU 8012.82 Hz
SCANS 16
ACQTH 4.0894 sec
PD 1.0000 sec
PWL 15.00 usec
IRNUC
CTEMP 400.0 c
SLVNT CDCl3
EXPRT 7.26 ppm
BF 0.30 Hz
RGAIN 362
    
```

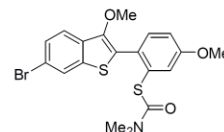


**<sup>13</sup>C NMR of 5bf (126 MHz, CDCl<sub>3</sub>)**



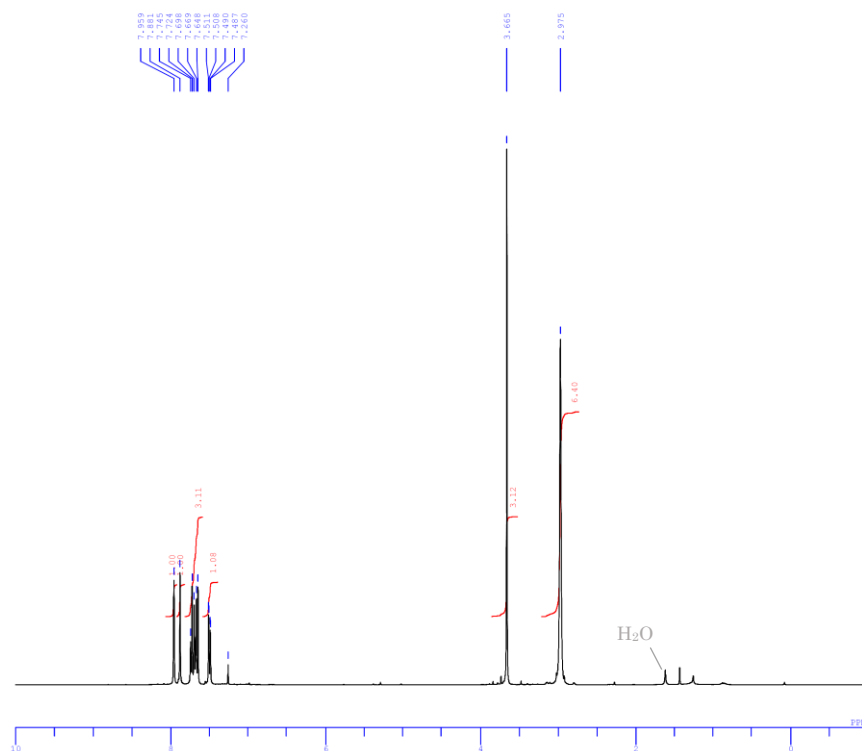
```

OFFILE Br-OMe 5 C.a1s
COMMENT Ref DJF-HT01-188aC
DATIM 2019-05-20 16:19:22
ORNUC 13C
EXMOD z9p930
ORFQ 125.78 MHz
ORSET 7.33 KHz
ORFIN 9.88 Hz
POINT 32768
FREQU 32051.28 Hz
SCANS 32
ACQTH 1.0224 sec
PD 2.0000 sec
PWL 8.00 usec
IRNUC
CTEMP 24.5 c
SLVNT CDCl3
EXPRT 242.42 ppm
BF 1.00 Hz
RGAIN 184
    
```

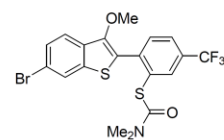




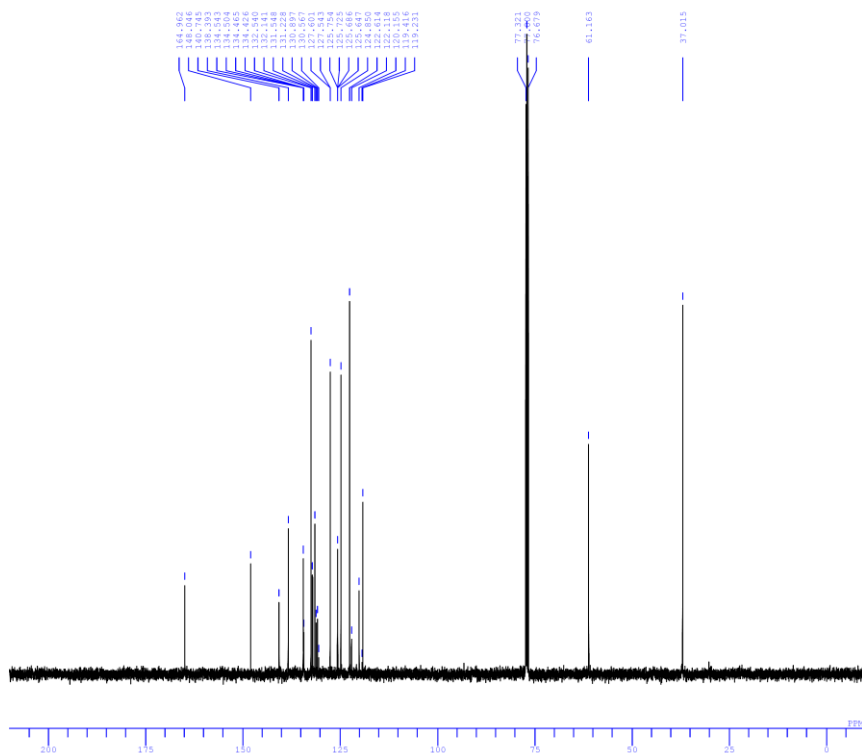
# <sup>1</sup>H NMR of 5bg (400 MHz, CDCl<sub>3</sub>)



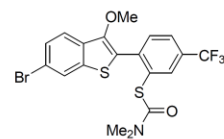
```
DFILE Br CF3 S H.a1s  
COMBT Ref DLF-RH01-181aH  
DATIM 2019-05-02 17:19:29  
ORHUC 1H  
EXMOD zg30  
ORFQ 400.13 MHz  
ORSET 2.47 Hz  
ORFIN 0.97 Hz  
POINT 32768  
FREQO 8012.82 Hz  
SCANS 16  
ACQTM 4.0894 sec  
FD 1.0000 sec  
PWI 15.00 usec  
FNUC  
CTEMP 20.0 c  
SLVNT CDCl3  
EXREF 7.26 ppm  
BF 0.30 Hz  
RGAIN 144
```



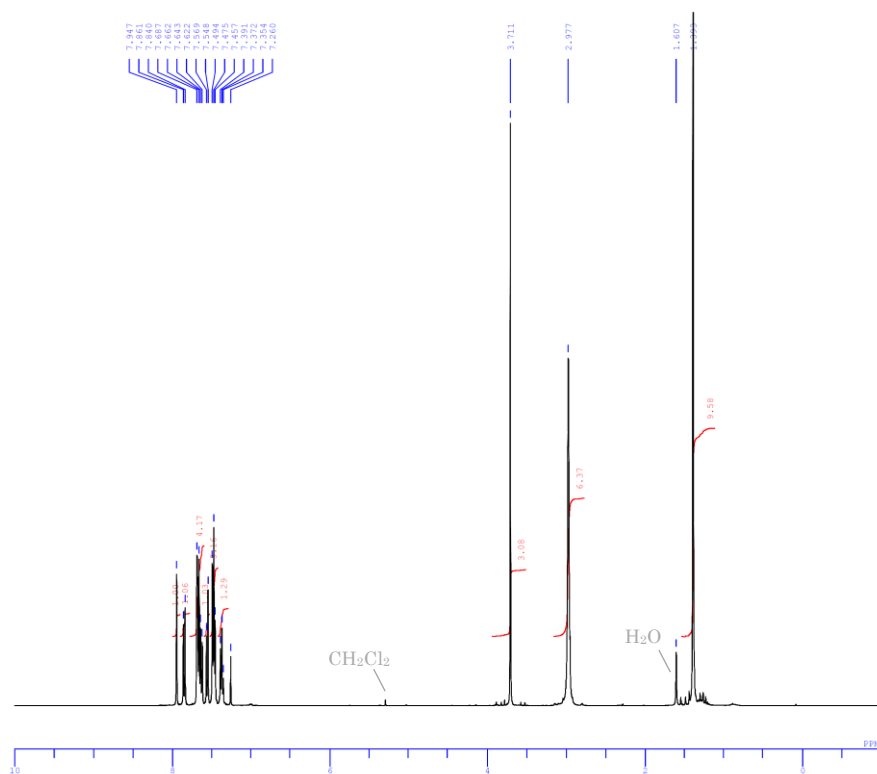
# <sup>13</sup>C NMR of 5bg (101 MHz, CDCl<sub>3</sub>)



```
DFILE Br CF3 S C.a1s  
COMBT Ref DLF-RH01-181aC  
DATIM 2019-05-03 01:30:29  
ORHUC 13C  
EXMOD #ppg90  
ORFQ 100.62 MHz  
ORSET 2.82 MHz  
ORFIN 9.80 Hz  
POINT 32768  
FREQO 32031.28 Hz  
SCANS 256  
ACQTM 1.0224 sec  
FD 2.0000 sec  
PWI 10.00 usec  
FNUC  
CTEMP 20.6 c  
SLVNT CDCl3  
EXREF 77.00 ppm  
BF 1.50 Hz  
RGAIN 2050
```

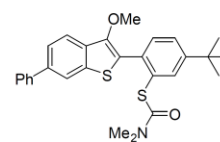


<sup>1</sup>H NMR of 5cd (400 MHz, CDCl<sub>3</sub>)

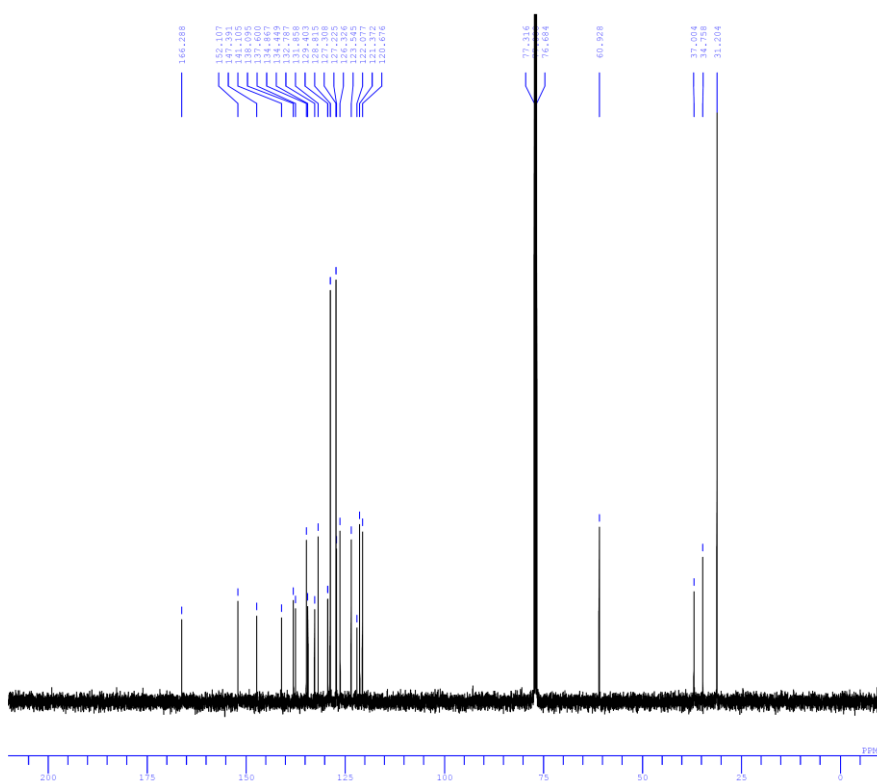


```

f1f11 Ph_tBu_S_H.als
c0m1t Ref DJF-H01-177aH
dAtIm 2019-04-25 11:06:40
oBnuC 1h
EXMOd zg30
OBSFQ 400.13 MHz
OBSSEt 2.47 kHz
OBSPI 0.97 Hz
POINt 32768
FREQU 8012.82 Hz
SCANS 16
ACQTM 4.0894 sec
FD 1.0000 sec
PWI 15.00 usec
IRNUC
CTEM 19.2 c
SLVNT CDCl3
EXREF 7.26 ppm
RF 0.30 Hz
RGAIN 161
    
```

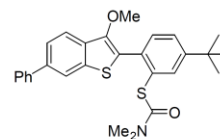


<sup>13</sup>C NMR of 5cd (101 MHz, CDCl<sub>3</sub>)

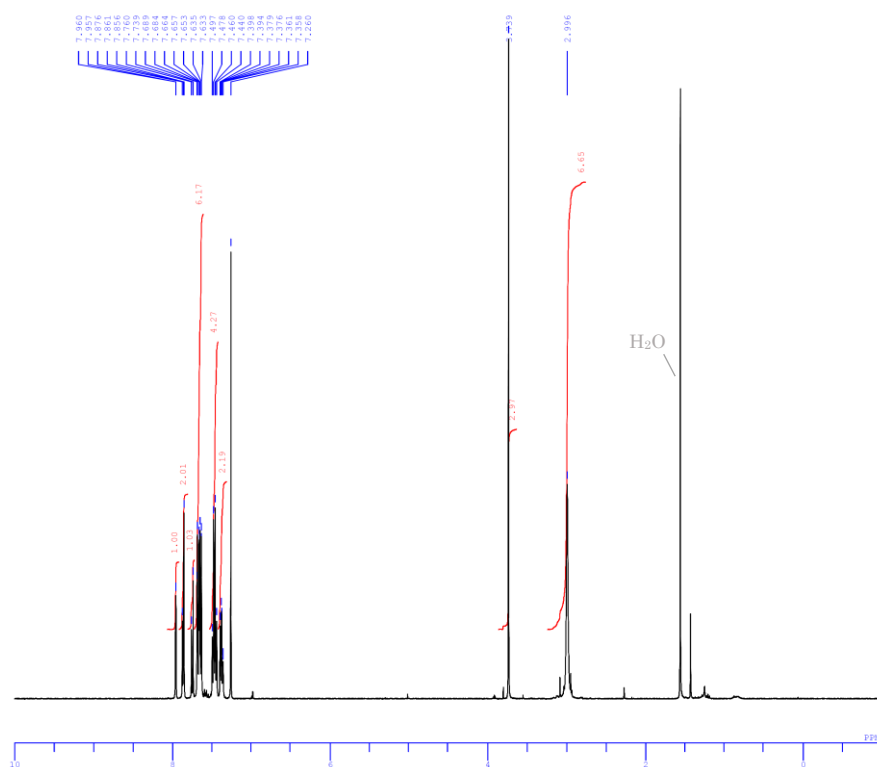


```

f1f11 Ph_tBu_S_C.als
c0m1t Ref DJF-H01-177ac
dAtIm 2019-04-29 14:42:43
oBnuC 13C
EXMOd zgpg30
OBSFQ 100.60 MHz
OBSSEt 9.25 kHz
OBSPI 0.25 Hz
POINt 65536
FREQU 32051.26 Hz
SCANS 16
ACQTM 1.0224 sec
FD 2.0000 sec
PWI 10.00 usec
IRNUC
CTEM 24.8 c
SLVNT CDCl3
EXREF 77.00 ppm
RF 1.00 Hz
RGAIN 71
    
```

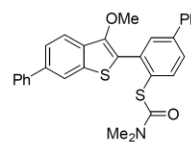


# <sup>1</sup>H NMR of 5ce (400 MHz, CDCl<sub>3</sub>)

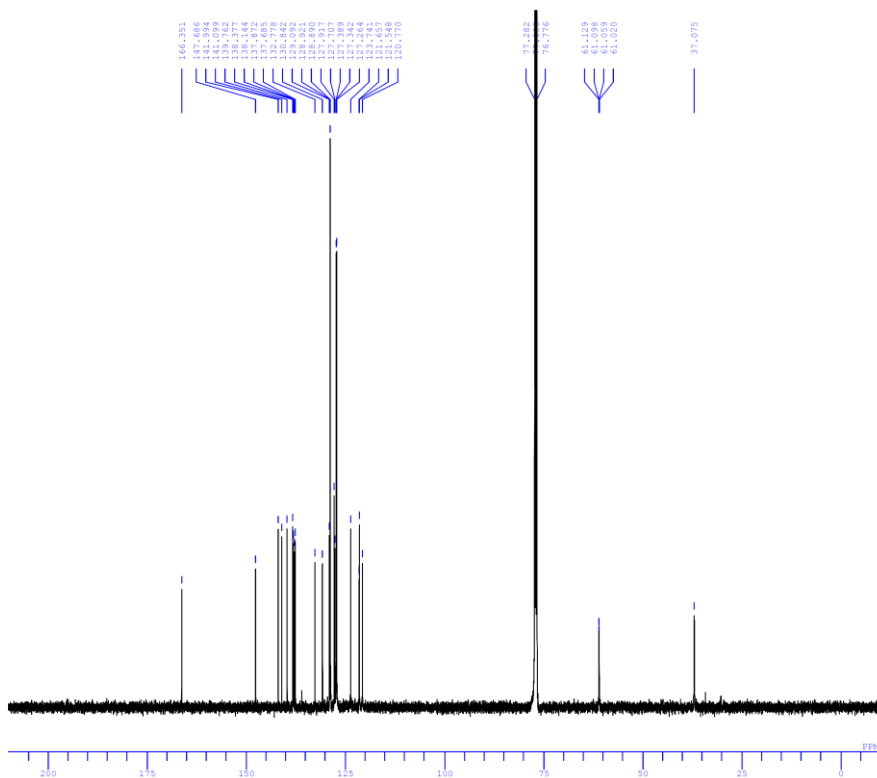


```

DFILE Ph_4-Ph_S_H.als
COMPT Ref.DJP-WF01-176aH
DATIM 2019-04-24 14:46:52
ORNUC 1H
EXMOD zg30
OBPQ 400.13 MHz
OBSET 2.47 MHz
OBFIN 0.97 Hz
POINT 32768
FREQ 8012.62 Hz
SCANS 16
ACQTH 4.0894 sec
FD 1.0000 sec
FID 15.00 usec
IRNUC CDCl3
CTEMP 19.4 c
SLVNF CDCl3
EXREF 7.26 ppm
BF 0.30 Hz
RGAIN 912
    
```

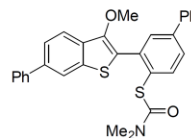


# <sup>13</sup>C NMR of 5ce (126 MHz, CDCl<sub>3</sub>)

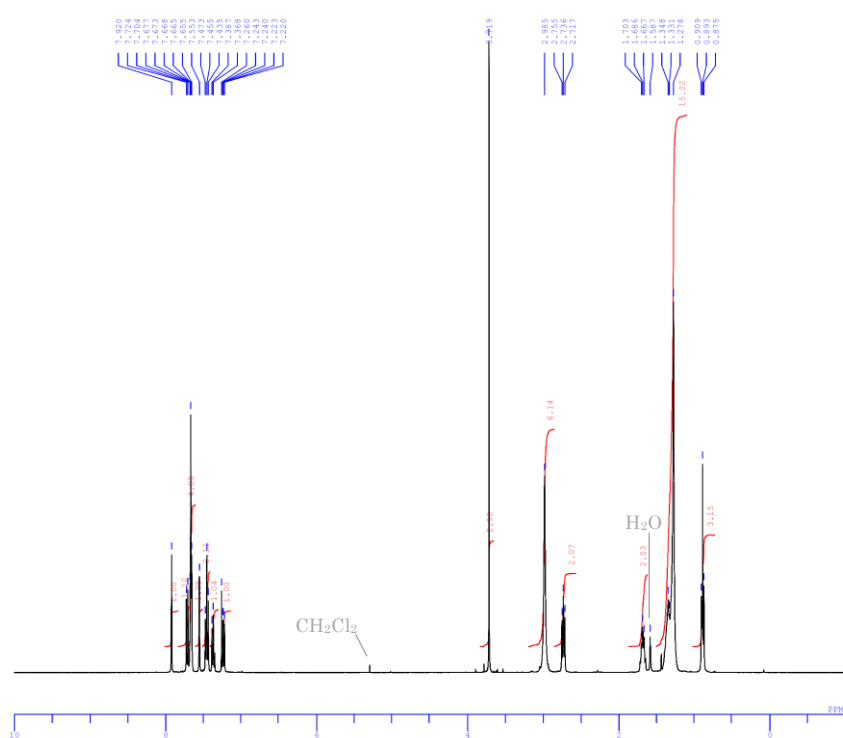


```

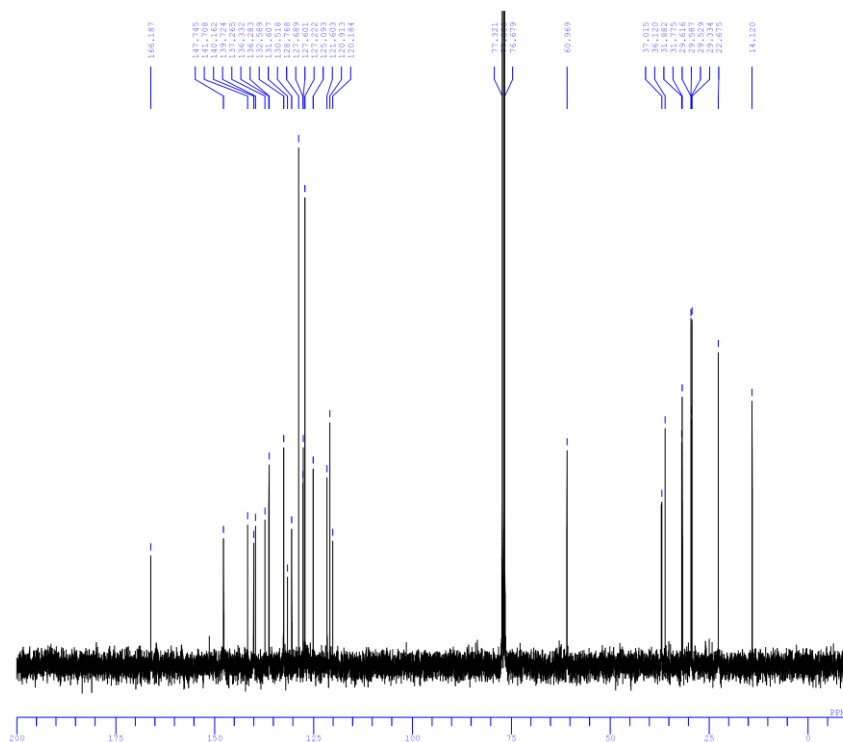
DFILE Ph_4-Ph_S_C.als
COMPT Ref.DJP-WF01-176aC2
DATIM 2019-04-24 20:55:47
ORNUC 13C
EXMOD zgpg30
OBPQ 125.78 MHz
OBSET 7.33 MHz
OBFIN 9.88 Hz
POINT 32768
FREQ 32051.28 Hz
SCANS 2048
ACQTH 1.0224 sec
FD 2.0000 sec
FID 8.00 usec
IRNUC CDCl3
CTEMP 24.8 c
SLVNF CDCl3
EXREF 242.42 ppm
BF 1.00 Hz
RGAIN 184
    
```



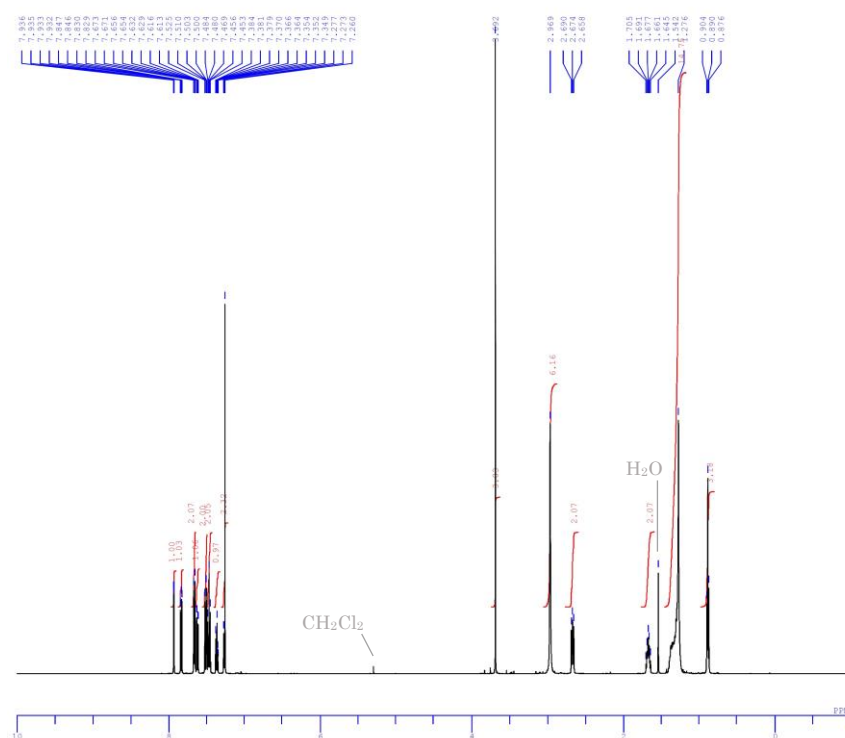
**<sup>1</sup>H NMR of 5eb (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR of 5eb (101 MHz, CDCl<sub>3</sub>)**

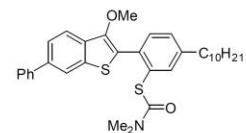


**<sup>1</sup>H NMR of 5eb' (500 MHz, CDCl<sub>3</sub>)**

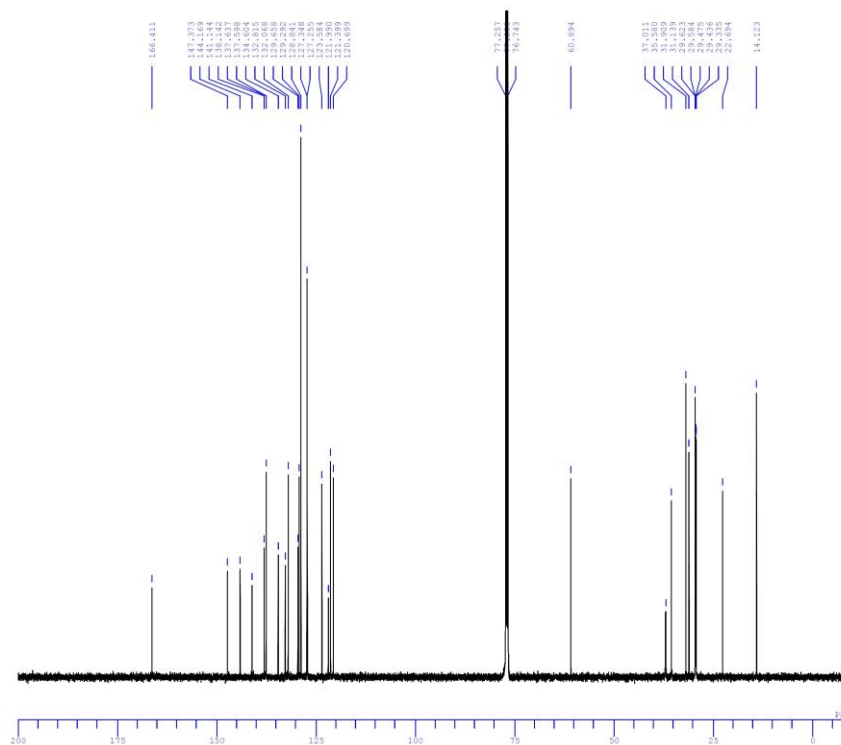


```

DFILE 5eb'H.a1s
COMBI Ref CP-01-007 Col (3)
DATEI 2020-07-01 16:52:46
GENUC 1H
EXNO0 zq30
OBPFRQ 500.19 MHz
OBSEET 3.08 Hz
OBFIN 8.98 Hz
POLIN 45536
FREQ0 10000.00 Hz
SCANS 76
ACQTM 3.2768 sec
PD 1.0000 sec
PUL 12.00 usec
INNUC CDCl3
CTEMP 24.9 c
SIVNT CDCl3
EXREF 7.26 ppm
RF 9.30 Hz
RGAIN 53
    
```

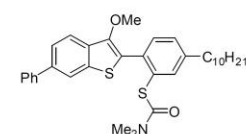


**<sup>13</sup>C NMR of 5eb' (126 MHz, CDCl<sub>3</sub>)**

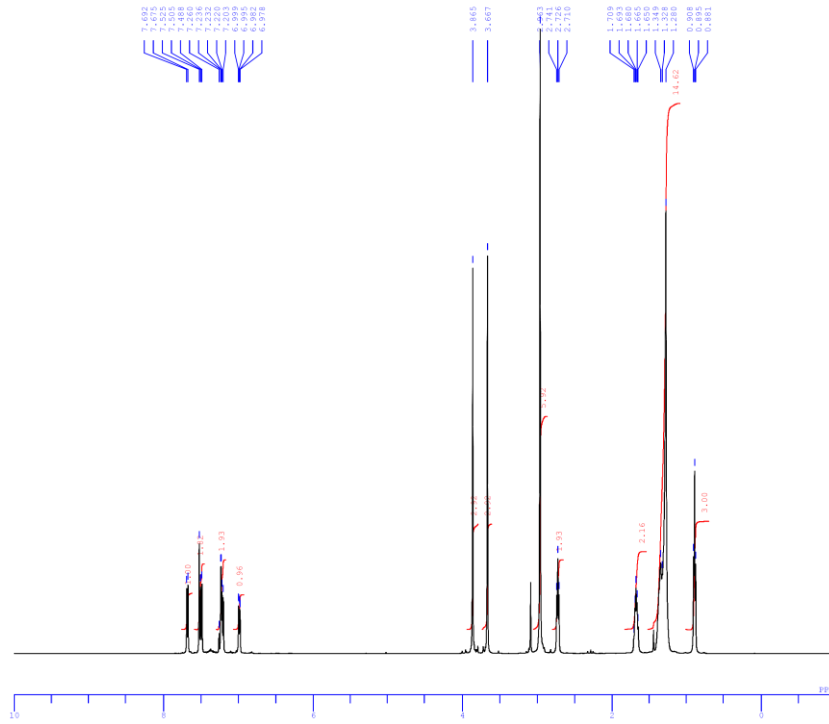


```

DFILE 5eb'C.a1s
COMBI Ref CP-01-007 Col (1)
DATEI 2020-07-03 02:15:01
GENUC 13C
EXNO0 zqg30
OBPFRQ 125.76 MHz
OBSEET 7.33 Hz
OBFIN 9.88 Hz
POLIN 32768
FREQ0 32051.28 Hz
SCANS 2048
ACQTM 3.0224 sec
PD 2.0000 sec
PUL 11.00 usec
INNUC CDCl3
CTEMP 24.9 c
SIVNT CDCl3
EXREF 77.00 ppm
RF 1.00 Hz
RGAIN 184
    
```

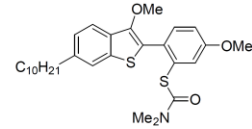


**<sup>1</sup>H NMR of 5ef (500 MHz, CDCl<sub>3</sub>)**

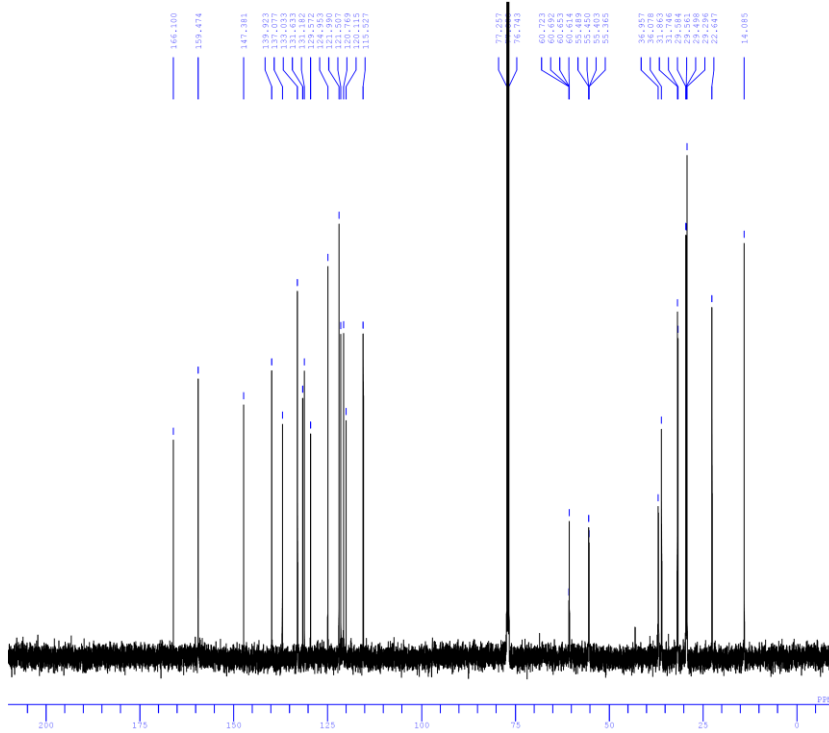


```

DFILE C10_0me_S_H.n1s
COMPT Ref'DJP-MT01-144a1
DATIM 2019-03-04 16:13:43
OSMUC 1H
EXPNO zgp30
PROBHD 500.19 MHz
SOLVENT 3.08 MHz
PULPROG zgpg30
F2 - 65536
POINT 10000.00 Hz
SCANS 16
ACQTIM 3.278 sec
PD 1.0000 sec
SFO 500.1363 MHz
IRNUC CDCl3
SLVNT 24.9 c
EXREF 7.26 ppm
RF 0.30 Hz
RGAIN 30
    
```

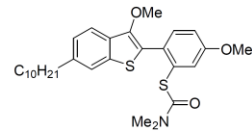


**<sup>13</sup>C NMR of 5ef (126 MHz, CDCl<sub>3</sub>)**

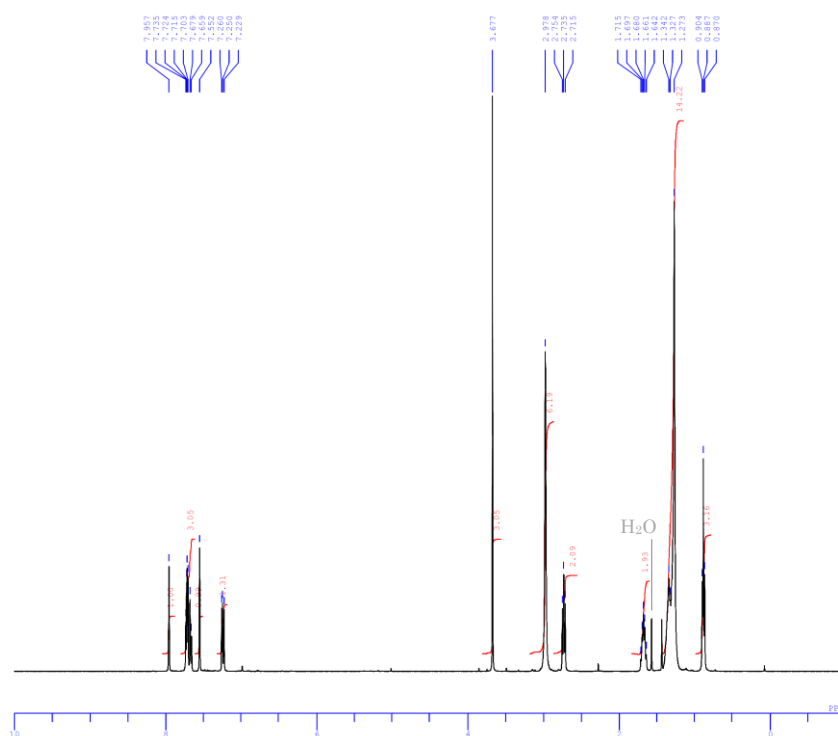


```

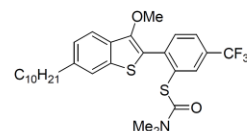
DFILE C10_0me_S_C.n1s
COMPT Ref'DJP-MT01-144a2
DATIM 2019-03-04 16:16:44
OSMUC 13C
EXPNO zgp30
PROBHD 125.78 MHz
SOLVENT 77.00 MHz
PULPROG zgpg30
F2 - 33768
POINT 32051.28 Hz
SCANS 32
ACQTIM 1.0224 sec
PD 2.0000 sec
SFO 125.7613 MHz
IRNUC CDCl3
SLVNT 24.9 c
EXREF 77.00 ppm
RF 1.00 Hz
RGAIN 184
    
```



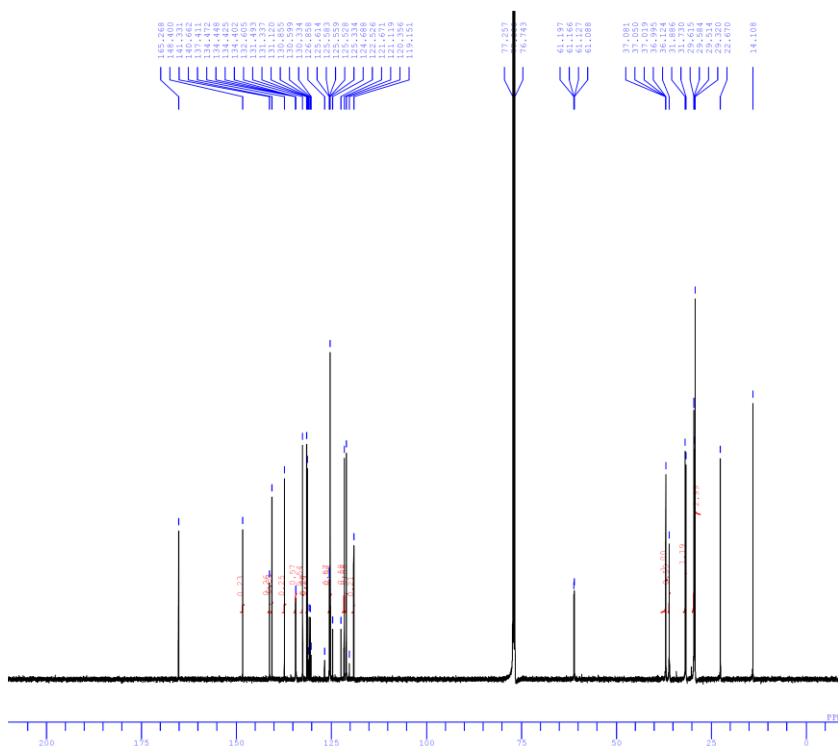
# <sup>1</sup>H NMR of 5eg (400 MHz, CDCl<sub>3</sub>)



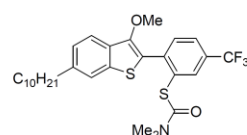
```
DFILE C10 CF3 8 H.ala
CMET Ref C10CF3M01-140aH
DATIM 2019-02-27 15:37:22
ORHNC 1H
EORND spg30
OBFFQ 400.13 MHz
OBSET 2.47 KHz
OBFIN 0.37 Hz
FOINT 32768
FREQO 8012.82 Hz
SCANS 18
AQTM 4.0894 sec
PD 1.0000 sec
PW 10.00 usec
IRNUC
CTEMP CDCl3 400.0 c
SLVNT CDCl3
ESREF 7.26 ppm
BF 6.39 Hz
RGAIN 256
```



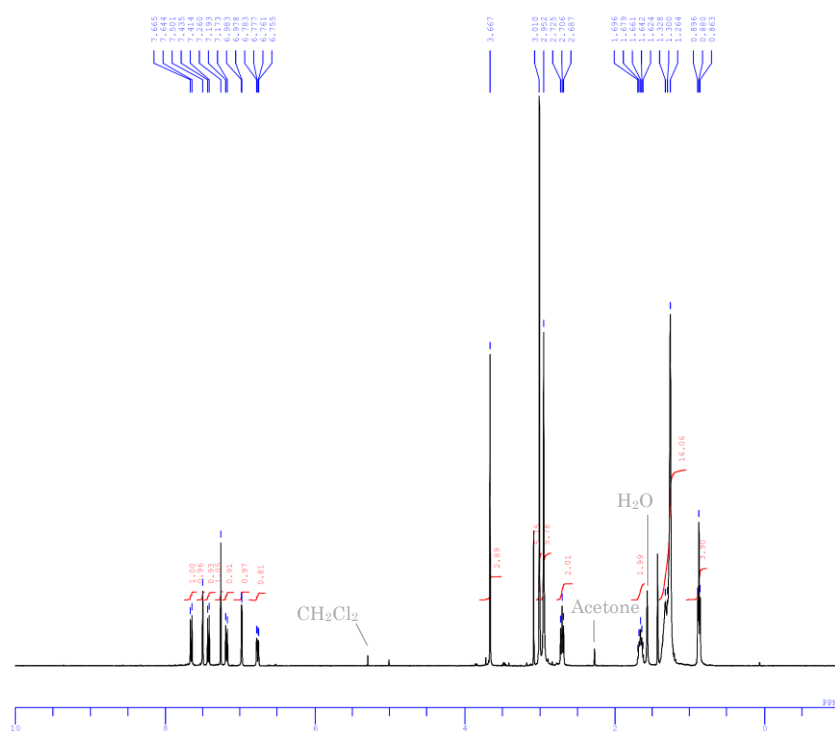
# <sup>13</sup>C NMR of 5eg (126 MHz, CDCl<sub>3</sub>)



```
DFILE C10 CF3 8 C.ala
CMET Ref C10CF3M01-140aC
DATIM 2019-07-20 06:33:32
ORHNC 13C
EORND spg30
OBFFQ 125.76 MHz
OBSET 7.33 KHz
OBFIN 9.88 Hz
FOINT 32768
FREQO 32051.28 Hz
SCANS 2048
AQTM 1.0224 sec
PD 2.0000 sec
PW 6.00 usec
IRNUC
CTEMP CDCl3 24.9 c
SLVNT CDCl3
ESREF 77.00 ppm
BF 1.00 Hz
RGAIN 184
```

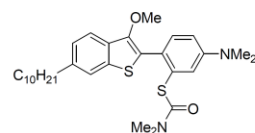


<sup>1</sup>H NMR of 5eh (400 MHz, CDCl<sub>3</sub>)

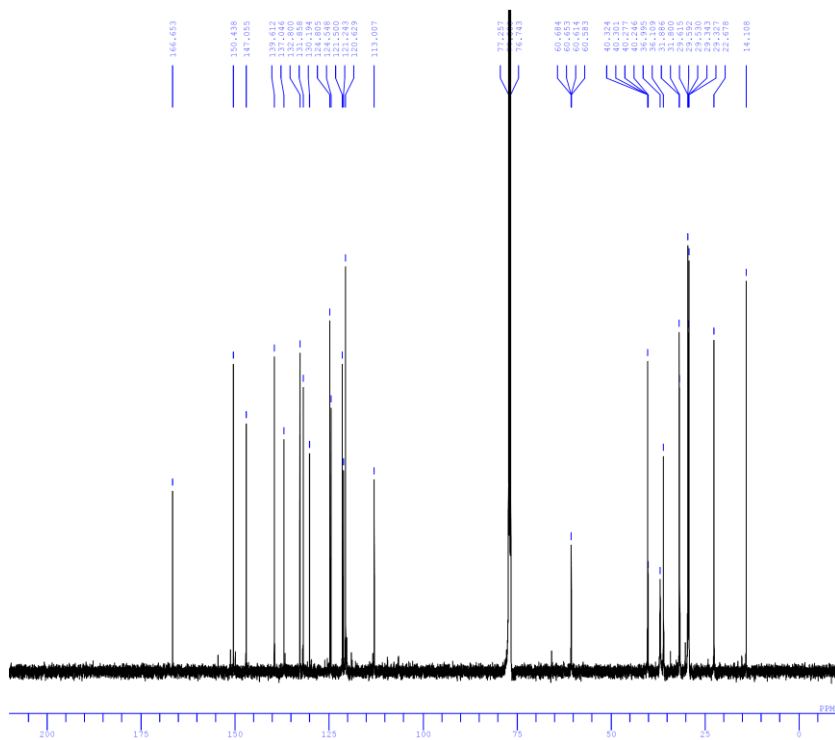


```

D1FILE C10_NMe2_8_H.als
COMPT Ref'DUP-RDU-150aH
DATIM 2019-07-18 16:49:12
SBRUC 1H
EXMOD zgpg30
OBFRQ 400.13 MHz
OBSET 2.47 MHz
OBFIN 0.97 Hz
POINT 32768
FREQO 8012.82 Hz
SCANS 16
ACQTH 4.0884 sec
PD 1.0000 sec
PWL 10.00 usec
IRNUC
CTEMP 400.0 c
SLUNT CDCl3
EXREF 7.26 ppm
RF 6.30 Hz
RGAIN 575
    
```

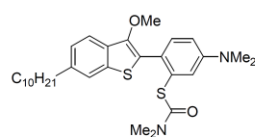


<sup>13</sup>C NMR of 5eh (126 MHz, CDCl<sub>3</sub>)



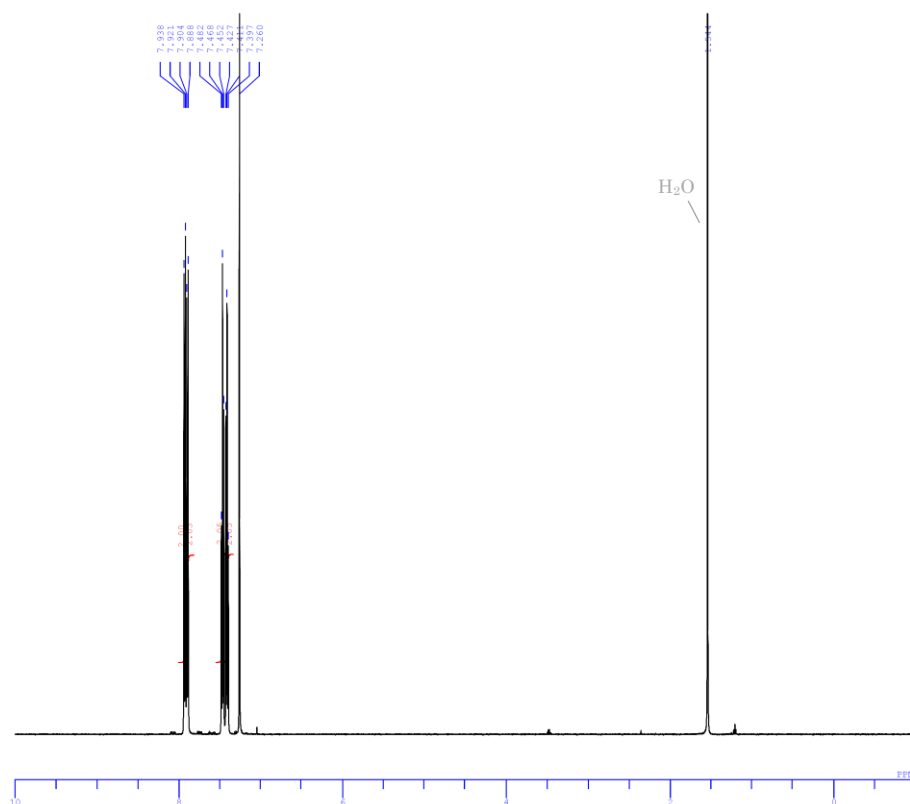
```

D1FILE C10_NMe2_8_C.als
COMPT Ref'DUP-RDU-C10NMe2202048
DATIM 2019-07-18 20:43:32
SBRUC 13C
EXMOD zgpg30
OBFRQ 125.76 MHz
OBSET 7.38 MHz
OBFIN 9.88 Hz
POINT 32768
FREQO 32051.28 Hz
SCANS 248
ACQTH 1.0224 sec
PD 2.0000 sec
PWL 8.00 usec
IRNUC
CTEMP 24.9 c
SLUNT CDCl3
EXREF 77.00 ppm
RF 1.00 Hz
RGAIN 184
    
```

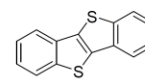




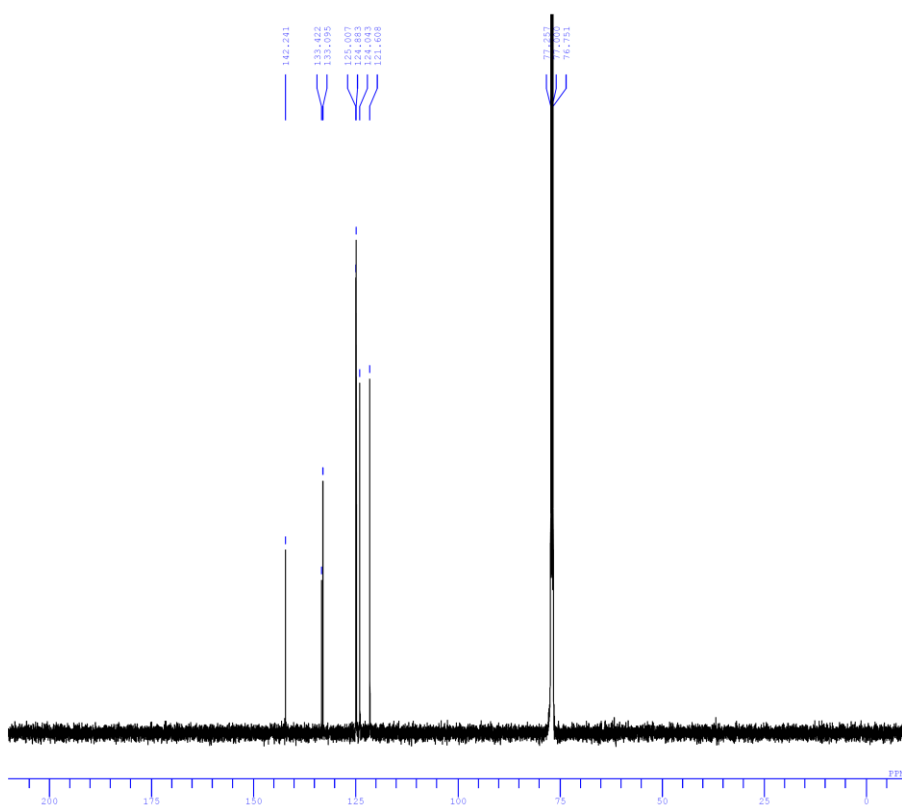
### <sup>1</sup>H NMR of 4aa (500 MHz, CDCl<sub>3</sub>)



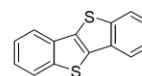
```
DFILE H BTBT H H.ala
COMPT Ref DDP-MT BTBT_H
DATIM 2019-08-09 15:34:34
ORNUC 1H
EXMOD zg30
OBFQ 500.19 MHz
OBSET 3.08 KHz
OBFIN 8.88 Hz
FOINP 63536
FREQU 10000.00 Hz
SCANS 16
AQCTM 3.2768 sec
PD 1.0000 sec
PWI 8.00 usec
IRNUC
CTEMP 24.8 c
SLOUT CDCl3
EXREF 7.26 ppm
RF 0.30 Hz
RGAIN 107
```



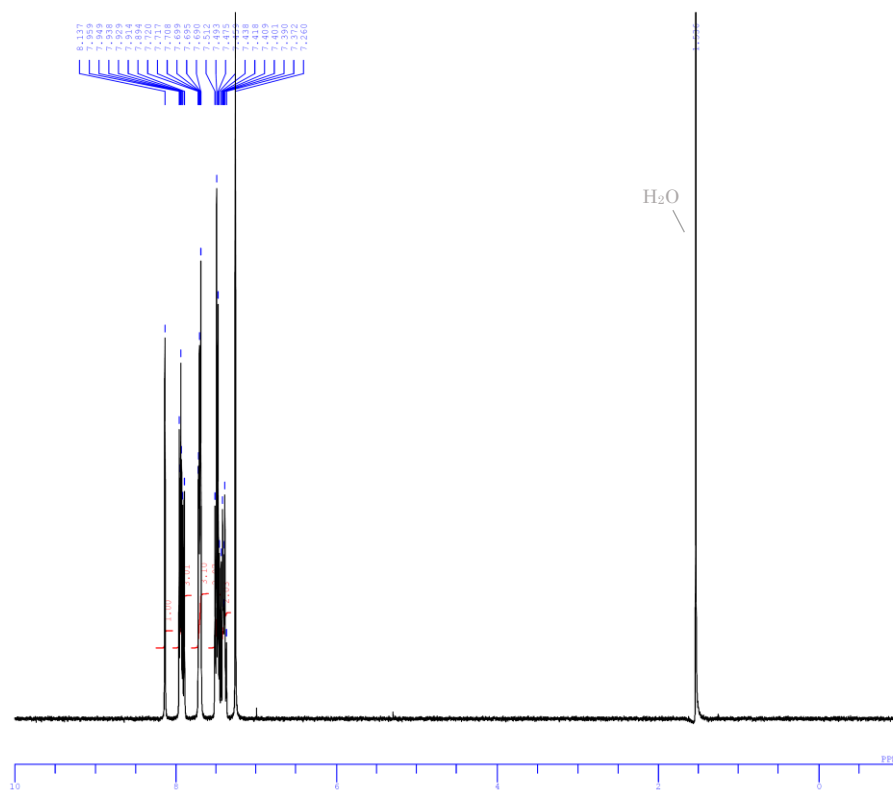
### <sup>13</sup>C NMR of 4aa (126 MHz, CDCl<sub>3</sub>)



```
DFILE H BTBT H C.ala
COMPT Ref DDP-MT BTBT_C
DATIM 2019-08-10 05:34:00
ORNUC 13C
EXMOD zgpg30
OBFQ 125.76 MHz
OBSET 7.33 KHz
OBFIN 9.88 Hz
FOINP 32768
FREQU 32051.28 Hz
SCANS 2048
AQCTM 1.0224 sec
PD 2.0000 sec
PWI 8.00 usec
IRNUC
CTEMP 24.9 c
SLOUT CDCl3
EXREF 77.00 ppm
RF 1.00 Hz
RGAIN 184
```

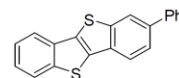


**<sup>1</sup>H NMR of 4ab (400 MHz, CDCl<sub>3</sub>)**

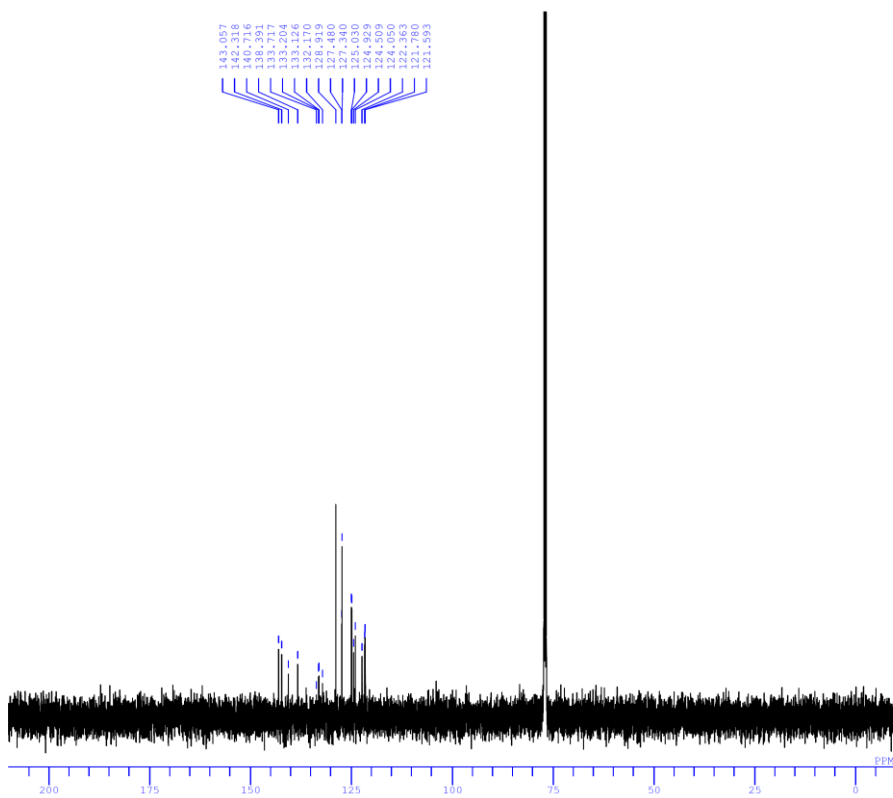


```

DFILE H_FR_BTBT_H.als
COMNT Ref DJT-MT01-138ab
DATIM 2019-07-17 11:53:44
OBNUC 1H
EXMOD zg30
GBFRC 400.13 MHz
GBSET 2.47 KHz
GBFIN 0.37 Hz
POINT 32768
FREQO 8012.82 Hz
SCANS 16
ACQTM 4.0894 sec
PD 1.0000 sec
PWL 15.00 usec
IRNUC
CTEMP 24.9 c
SLVNT CDCl3
EXREF 7.26 ppm
BF 0.30 Hz
RGAIN 649
    
```

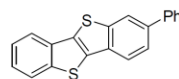


**<sup>13</sup>C NMR of 4ab (126 MHz, CDCl<sub>3</sub>)**

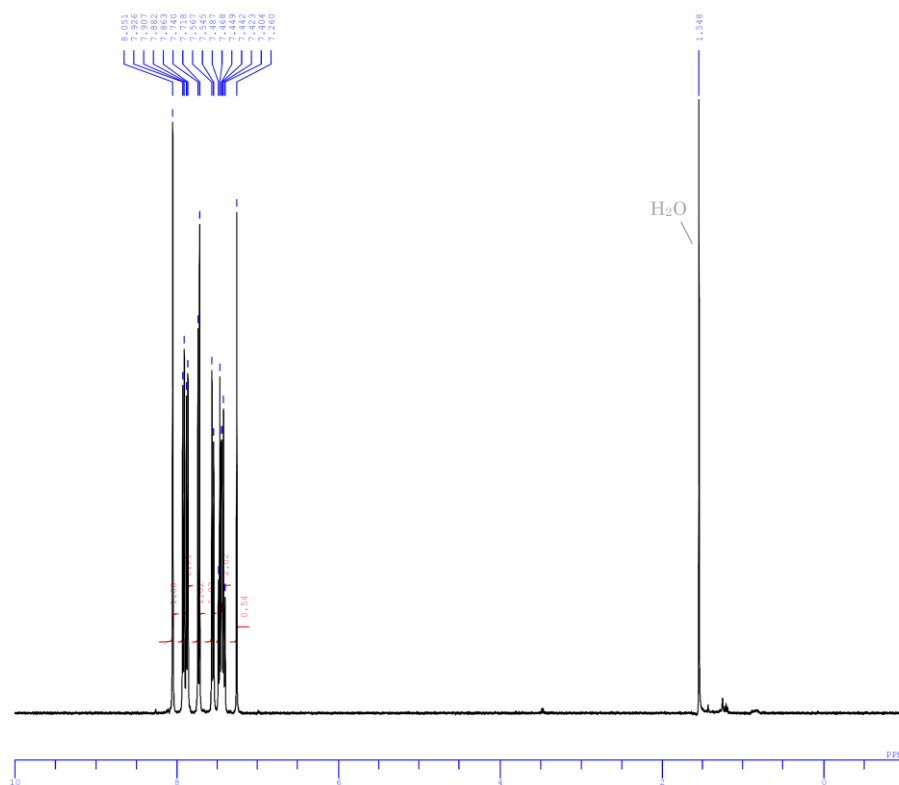


```

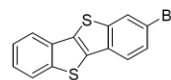
DFILE 1.a18
COMNT Ref DJT-MT01-138C
DATIM 2019-02-27 01:28:41
OBNUC 13C
EXMOD zgpg30
GBFRC 125.78 MHz
GBSET 7.33 KHz
GBFIN 9.88 Hz
POINT 32768
FREQO 32051.28 Hz
SCANS 32
ACQTM 1.0224 sec
PD 2.0000 sec
PWL 8.00 usec
IRNUC
CTEMP 24.8 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 184
    
```



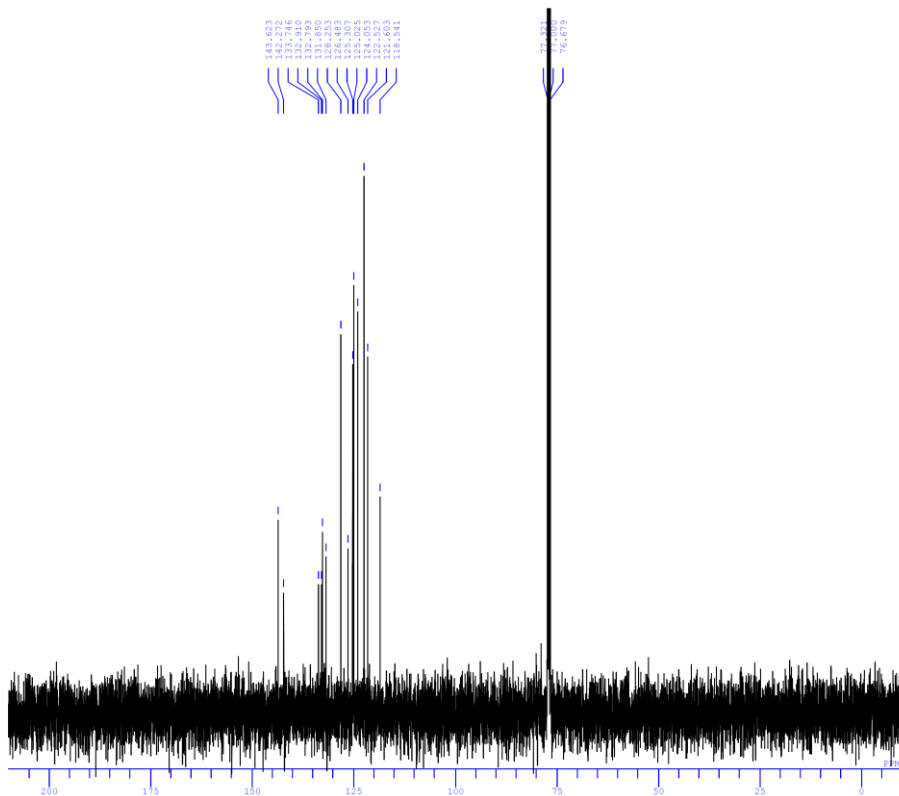
### $^1\text{H}$ NMR of 4ac (400 MHz, $\text{CDCl}_3$ )



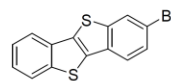
```
DNAME H Br BTBT H.als  
COMMT Ref DJJ-MF01-135aH  
DATEM 2019-03-06 16:10:21  
ORNUC 1H  
EXMOD zg30  
OBFRQ 400.13 MHz  
OBSST 2.47 Hz  
OBSFN 0.97 Hz  
POINT 32768  
FREQU 801.62 Hz  
SCANS 16  
AQUM 4.0894 sec  
PD 1.0000 sec  
PWI 10.00 usec  
IBNUC  
CTEMP 400.0 c  
SLVNT  $\text{CDCl}_3$   
EXREF 7.26 ppm  
BF 0.30 Hz  
RGAIN 1030
```



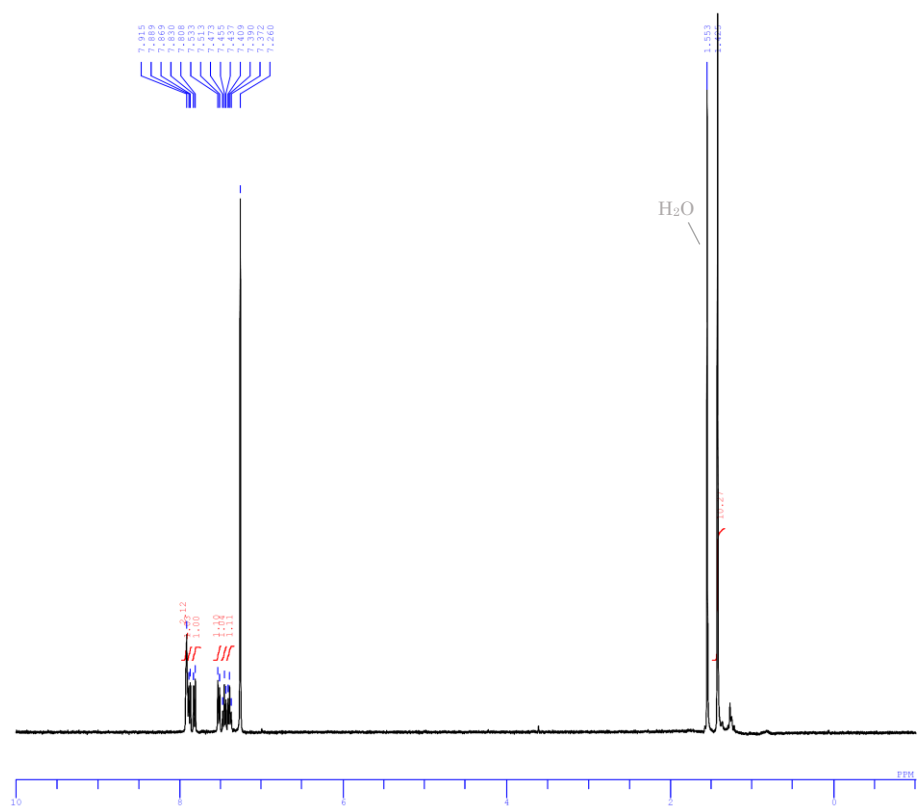
### $^{13}\text{C}$ NMR of 4ac (101 MHz, $\text{CDCl}_3$ )



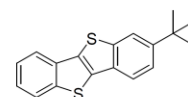
```
DNAME H Br BTBT C.als  
COMMT Ref DJJ-MF01-135aC  
DATEM 2019-03-05 23:45:18  
ORNUC  $^{13}\text{C}$   
EXMOD zgpg30  
OBFRQ 100.62 MHz  
OBSST 2.62 MHz  
OBSFN 9.80 Hz  
POINT 32768  
FREQU 32051.28 Hz  
SCANS 256  
AQUM 1.0224 sec  
PD 2.0000 sec  
PWI 8.00 usec  
IBNUC  
CTEMP 400.0 c  
SLVNT  $\text{CDCl}_3$   
EXREF 77.00 ppm  
BF 1.00 Hz  
RGAIN 2050
```



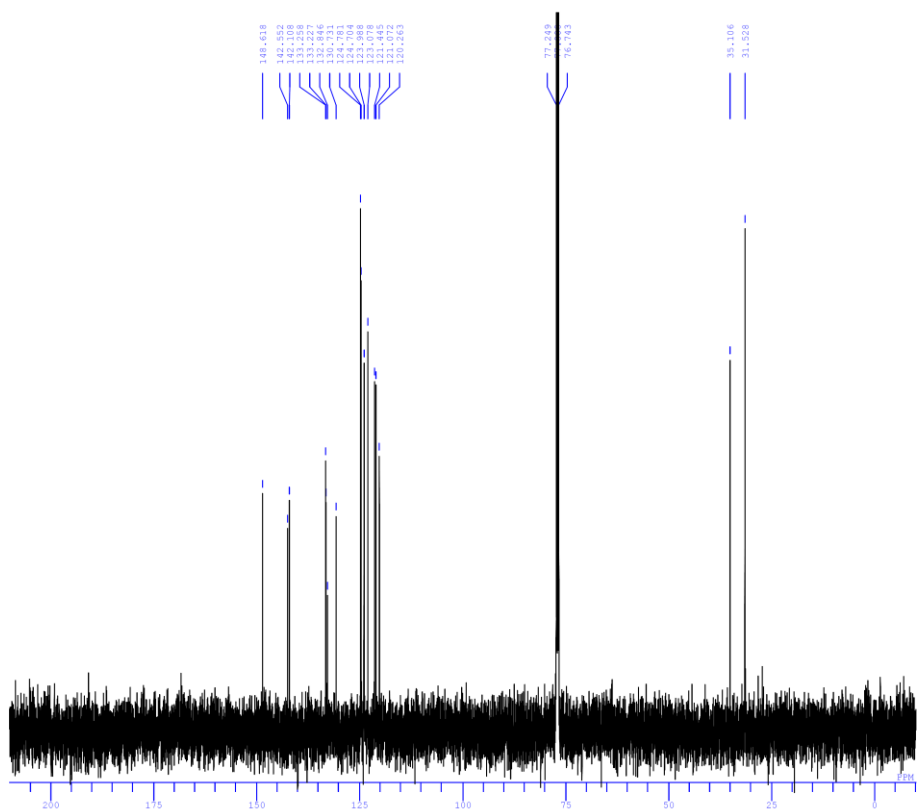
### <sup>1</sup>H NMR of 4ad (400 MHz, CDCl<sub>3</sub>)



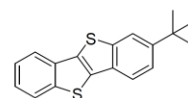
```
DFILE H_tBu_BTBT_H.ala
COMNT Ref D3P-MTU-125A
DATIN 2019-04-10 12:34:05
ORNUC 1H
EXMOD zg30
DEFRQ 400.13 MHz
ORSET 2.47 KHz
OBFIN 0.97 Hz
FOINT 32768
FREQU 8012.82 Hz
SCANS 16
ACQTH 4.0894 sec
PD 1.0000 sec
FW 15.00 usec
IRNUC
CTEMP
SLOWF CDCl3 400.0 c
EXREF 7.26 ppm
RF 0.30 Hz
RGAIN 812
```



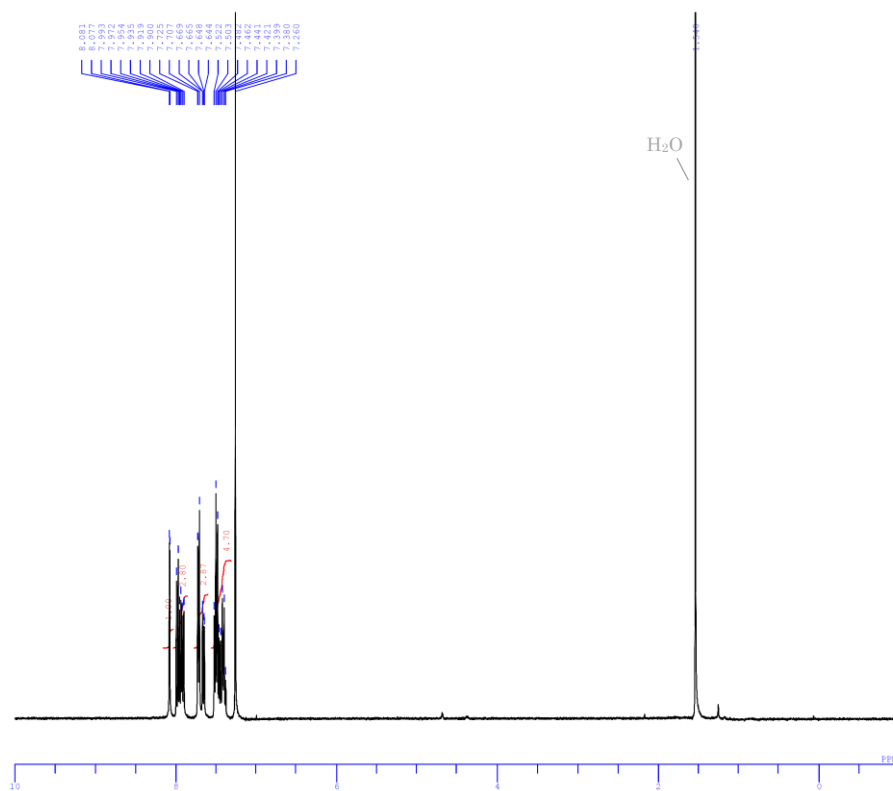
### <sup>13</sup>C NMR of 4ad (126 MHz, CDCl<sub>3</sub>)



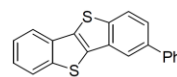
```
DFILE H_tBu_BTBT_C.ala
COMNT Ref D3P-MT H_BTBT_tBuc
DATIN 2019-07-15 16:33:01
ORNUC 13C
EXMOD zgpg30
DEFRQ 125.78 MHz
ORSET 7.33 KHz
OBFIN 2.88 Hz
FOINT 32768
FREQU 32051.28 Hz
SCANS 32
ACQTH 1.0224 sec
PD 2.0000 sec
FW 8.00 usec
IRNUC
CTEMP
SLOWF CDCl3 24.8 c
EXREF 77.00 ppm
RF 1.00 Hz
RGAIN 184
```



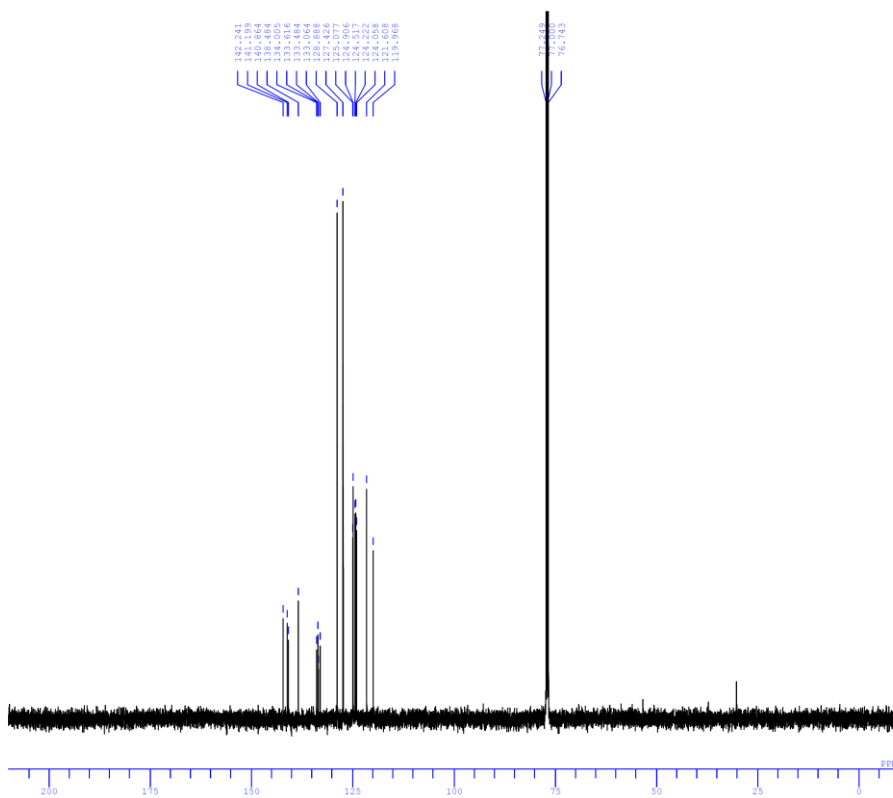
### <sup>1</sup>H NMR of 4ae (400 MHz, CDCl<sub>3</sub>)



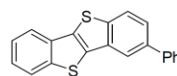
```
DFILE H_4-Ph_BTBT_E.sls  
CONV Ref DJF-MT01-119a8  
DATE 2019-07-16 11:15:38  
NUC1 1H  
EXMOD zg30  
OBFO 400.13 MHz  
OBET 2.47 Hz  
OBF 0.97 Hz  
POINT 32768  
FREQ 8012.82 Hz  
SCANS 16  
ACQ 4.0894 sec  
PD 1.0000 sec  
PUL 15.00 usec  
INUC  
CTEMP 24.9 c  
SOLV CDCl3  
EXREF 7.26 ppm  
BF 0.30 Hz  
RGAIN 912
```



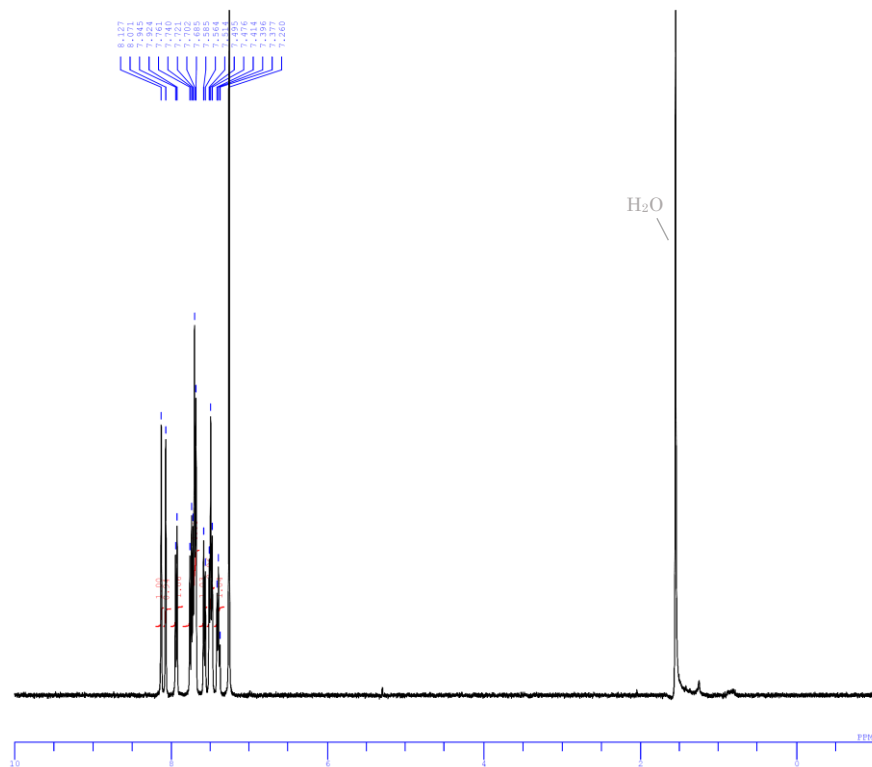
### <sup>13</sup>C NMR of 4ae (126 MHz, CDCl<sub>3</sub>)



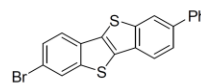
```
DFILE H_4-Ph_BTBT_C.sls  
CONV Ref DJF-MT01-119c  
DATE 2019-02-08 08:57:35  
NUC1 13C  
EXMOD zgpg30  
OBFO 125.76 MHz  
OBET 7.33 Hz  
OBF 9.88 Hz  
POINT 32768  
FREQ 32051.28 Hz  
SCANS 32  
ACQ 1.0024 sec  
PD 2.0000 sec  
PUL 10.10 usec  
INUC  
CTEMP 24.9 c  
SOLV CDCl3  
EXREF 77.00 ppm  
BF 1.00 Hz  
RGAIN 184
```



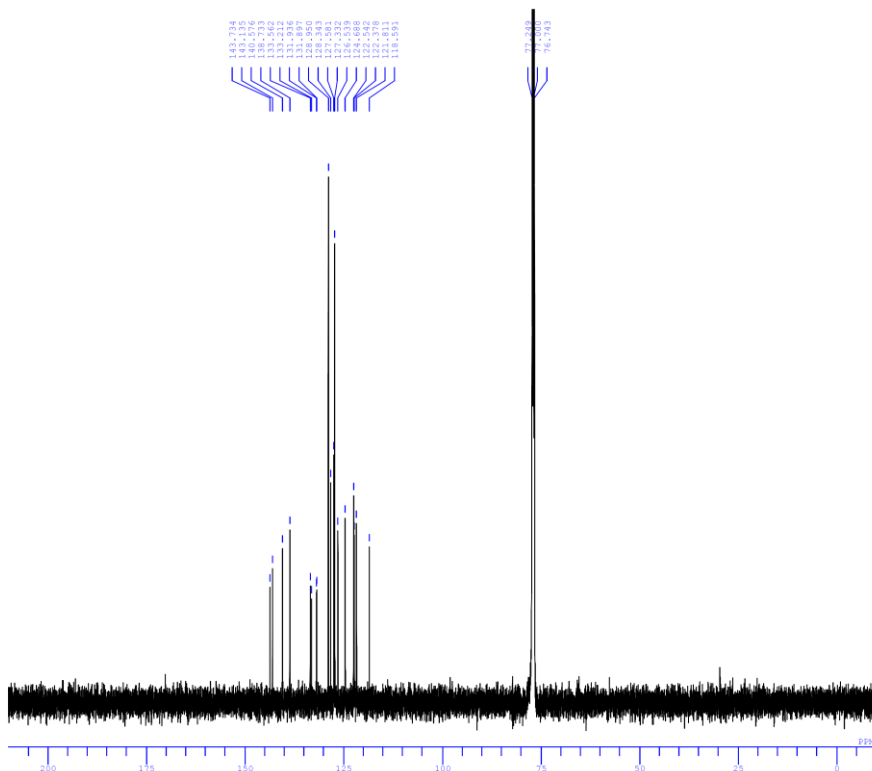
### <sup>1</sup>H NMR of 4bb (400 MHz, CDCl<sub>3</sub>)



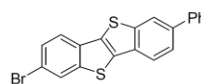
```
DFILE Br-Ph-BTBT-H.als
COMMENT Ref DJP=HT01-160ah
DATE_ 2019-04-10 11:48:55
OBNUC 1H
EPROG zg30
OBPFRQ 400.13 MHz
OBSETE 2.47 MHz
OBSFEN 6.97 Hz
POINT 32768
FREQU 8012.68 Hz
SCANS 16
AQTM 4.0884 sec
PD 1.0000 sec
PWL 15.00 usec
IRNUC
CTEMP 400.0 c
SLVNT CDCl3
EXREF 7.26 ppm
BF 0.30 Hz
RGAIN 912
```



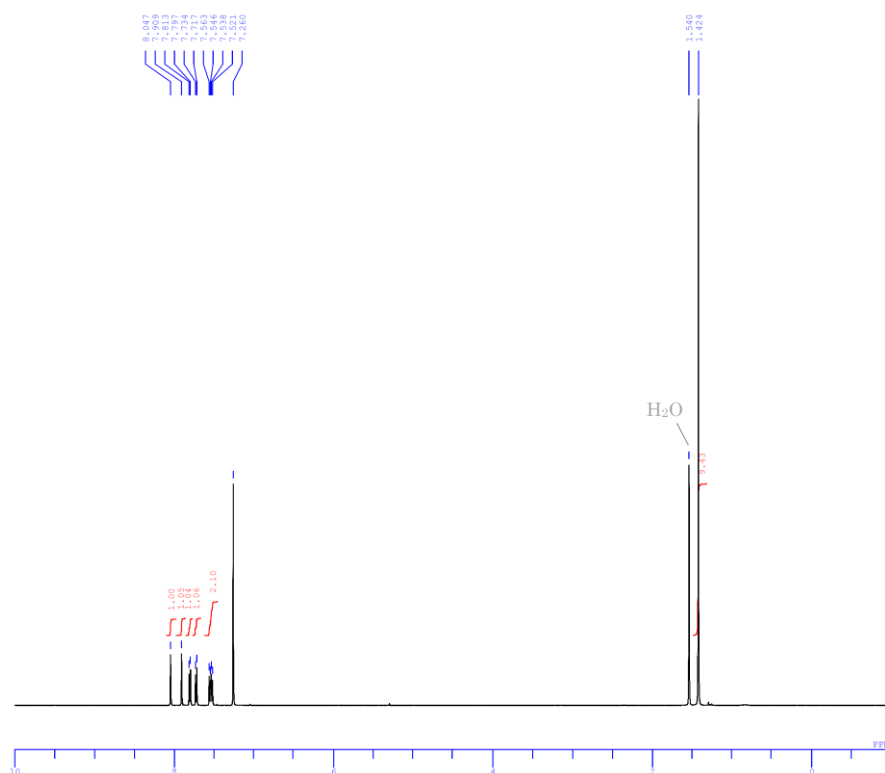
### <sup>13</sup>C NMR of 4bb (126 MHz, CDCl<sub>3</sub>)



```
DFILE Br-Ph-BTBT-C.als
COMMENT Ref DJP=HT01-195ac
DATE_ 2019-07-19 18:53:14
OBNUC 13C
EPROG zgpg30
OBPFRQ 125.78 MHz
OBSETE 7.33 MHz
OBSFEN 9.08 Hz
POINT 32768
FREQU 32051.28 Hz
SCANS 2048
AQTM 1.0224 sec
PD 2.0000 sec
PWL 8.00 usec
IRNUC
CTEMP 24.8 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 184
```

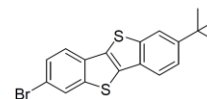


**<sup>1</sup>H NMR of 4bd (500 MHz, CDCl<sub>3</sub>)**

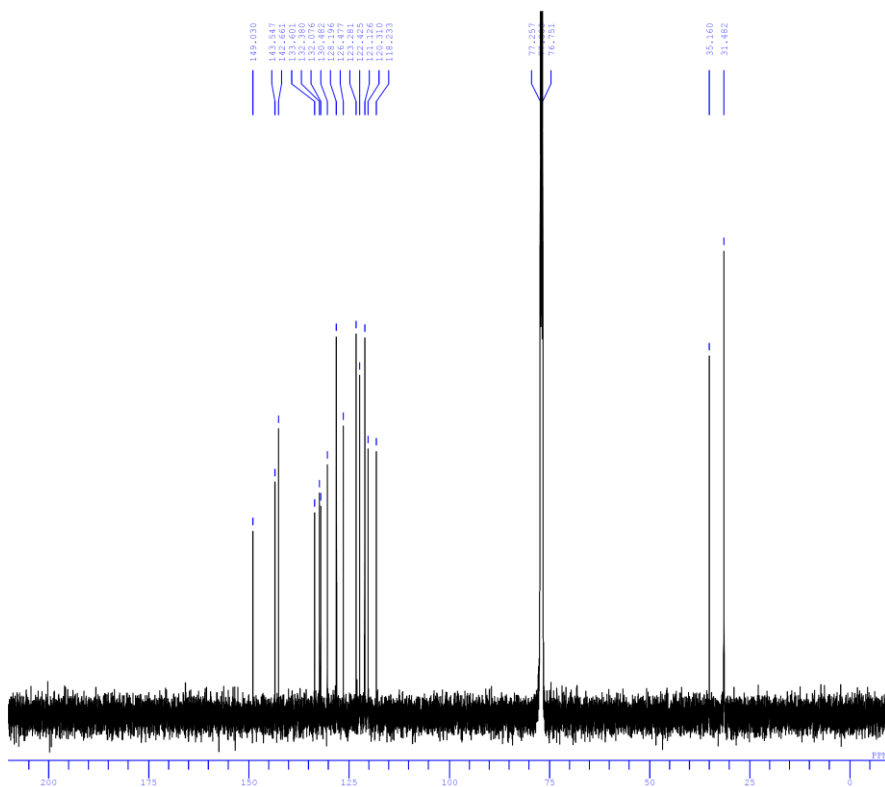


```

D:\FILE Br-tBu BTBT H.als
COMMT Ref DJF-MT01-1634H
DATIM 2018-04-04 14:06:03
OBNUC 1H
EXMD 2930
OBFFQ 500.19 MHz
OBSET 3.08 MHz
OBFIN 8.88 Hz
POINT 65536
FREQ 10000.00 Hz
SCANS 16
ACQTM 3.2768 sec
PD 1.0000 sec
PWL 8.00 usec
IRNUC
CTEMP 24.9 c
SLVMT CDCl3
EXREF 7.26 ppm
BF 0.30 Hz
RGAIN 84
    
```

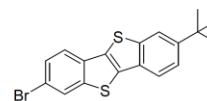


**<sup>13</sup>C NMR of 4bd (126 MHz, CDCl<sub>3</sub>)**

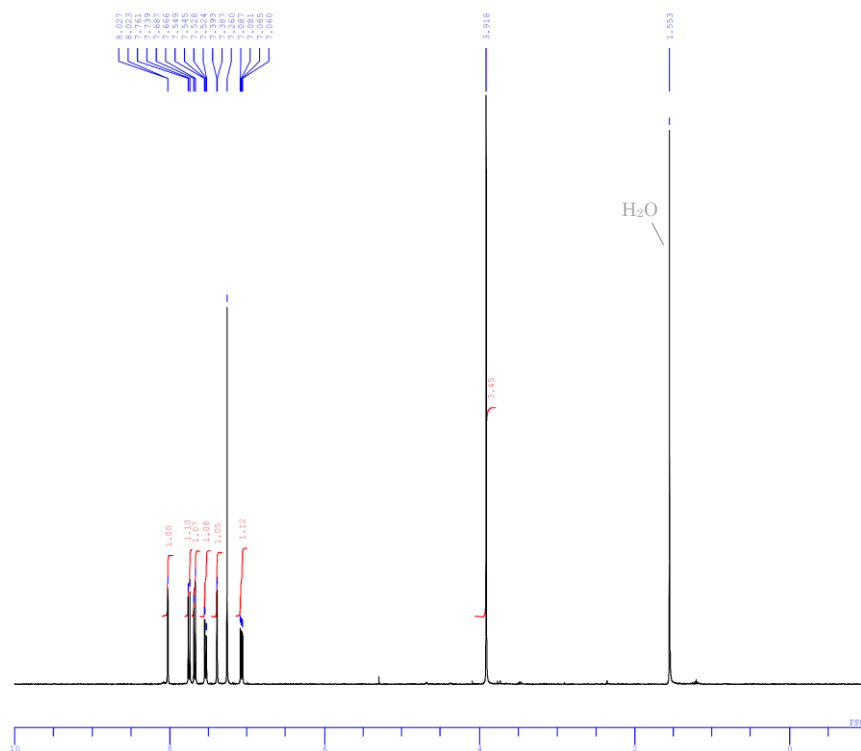


```

D:\FILE Br-tBu BTBT C.als
COMMT Ref DJF-MT01-1634C
DATIM 2019-07-17 00:18:23
OBNUC 13C
EXMD 2930
OBFFQ 125.78 MHz
OBSET 7.33 MHz
OBFIN 9.88 Hz
POINT 32768
FREQ 32051.28 Hz
SCANS 2048
ACQTM 1.0224 sec
PD 2.0000 sec
PWL 8.00 usec
IRNUC
CTEMP 24.8 c
SLVMT CDCl3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 184
    
```

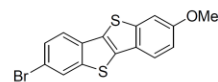


**<sup>1</sup>H NMR of 4bf (400 MHz, CDCl<sub>3</sub>)**

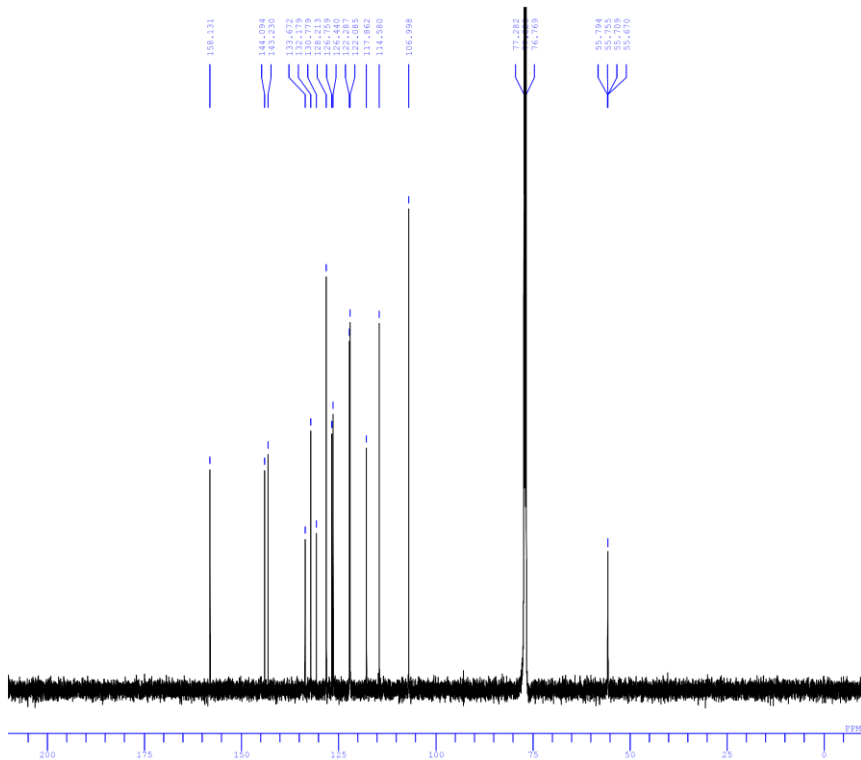


```

D:\FILE Br_OMe_BTBT_H.als
COMBT Ref DJF-MT01-196aH
DATIM 2019-06-19 09:10:37
CHNUC 1H
EXMOD zg30
PROBHD
P1 400.13 MHz
OBSET 2.47 kHz
ORFIM 0.97 Hz
POINT 32768
FREQO 8012.82 Hz
SCANS 16
AQTM 4.0894 sec
EP 1.0000 sec
PWI 15.00 usec
IRNUC
CTEMP 20.9 c
SLOWT CDCl3
EXREF 7.26 ppm
BF 0.30 Hz
RGAIN 645
    
```

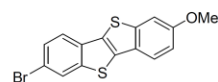


**<sup>13</sup>C NMR of 4bf (126 MHz, CDCl<sub>3</sub>)**



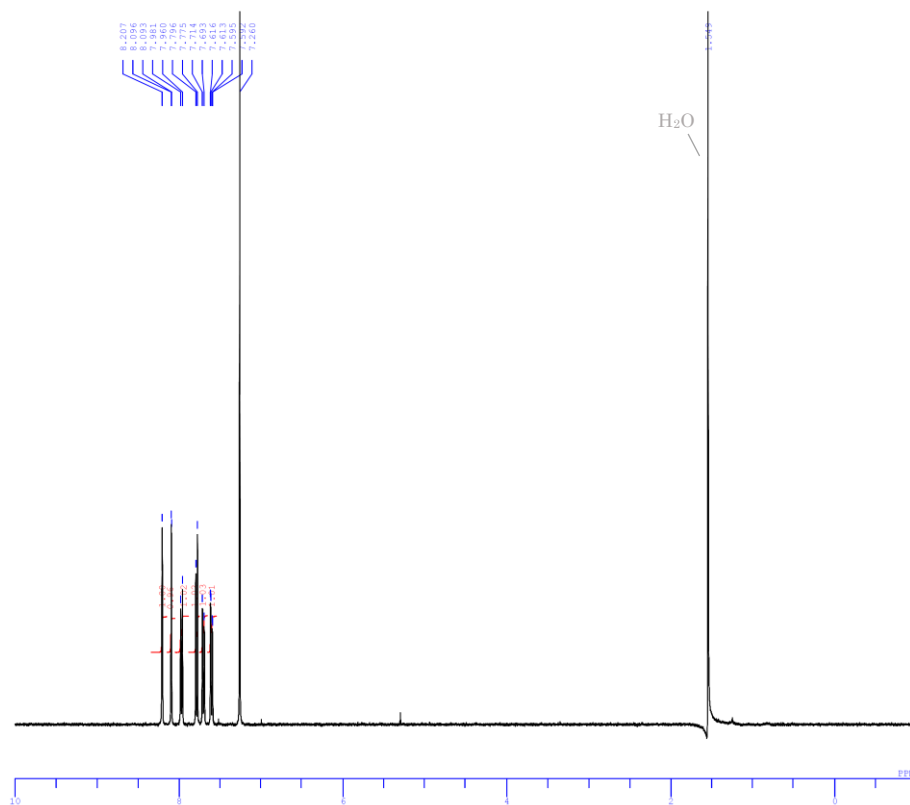
```

D:\FILE Br_OMe_BTBT_C.als
COMBT Ref DJF-MT01-196aC
DATIM 2019-06-26 03:46:12
CHNUC 13C
EXMOD zgpg30
PROBHD
P1 125.78 MHz
OBSET 7.33 kHz
ORFIM 8.68 Hz
POINT 32768
FREQO 32051.28 Hz
SCANS 2048
AQTM 1.0224 sec
EP 2.0000 sec
PWI 8.00 usec
IRNUC
CTEMP 24.9 c
SLOWT CDCl3
EXREF 242.42 ppm
BF 1.00 Hz
RGAIN 184
    
```



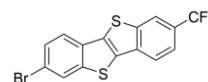


**<sup>1</sup>H NMR of 4b (400 MHz, CDCl<sub>3</sub>)**

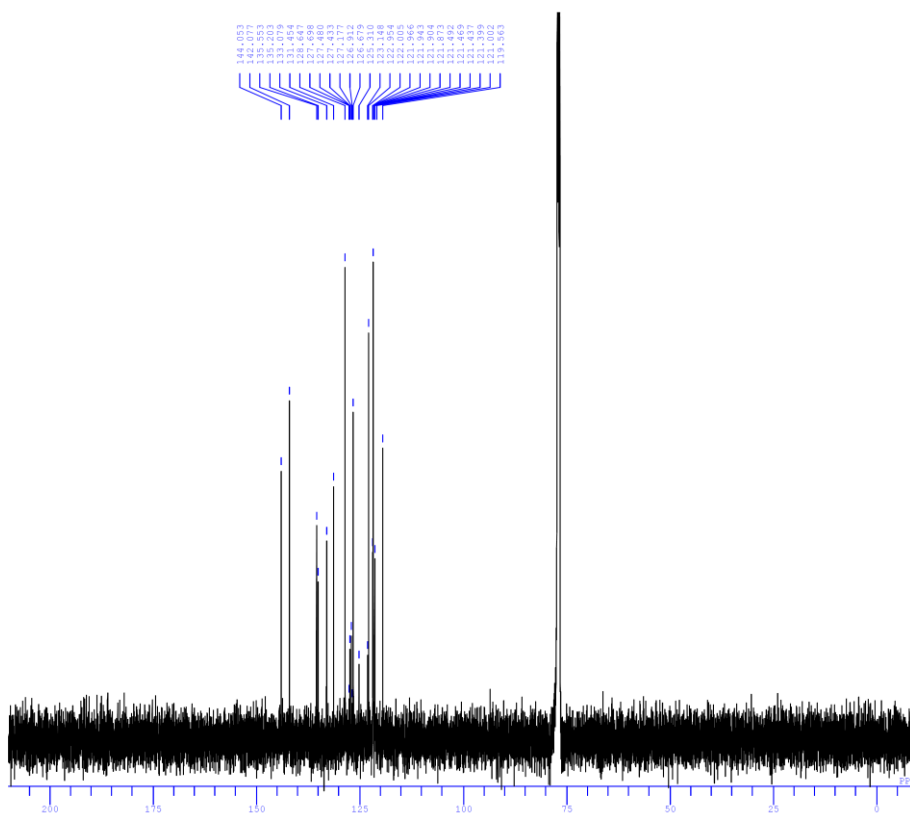


```

DFILE Br CF3 BTBT_H.als
COMMT Ref DJF-MT01-183aH
DATIM 2019-05-14 12:00:25
ORNUC 1H
EXMMD zg30
OBFRQ 400.13 MHz
OBSET 2.47 MHz
OBFIN 0.97 Hz
POINT 32768
FREQU 8012.82 Hz
SCANS 16
AQCTM 4.0894 sec
PD 1.0000 sec
PWI 15.00 usec
IRNUC
CTEMP 20.8 c
SIVNT CDCl3
EXREF 7.26 ppm
BF 0.30 Hz
RGAIN 1000
    
```

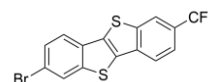


**<sup>13</sup>C NMR of 4b (126 MHz, CDCl<sub>3</sub>)**



```

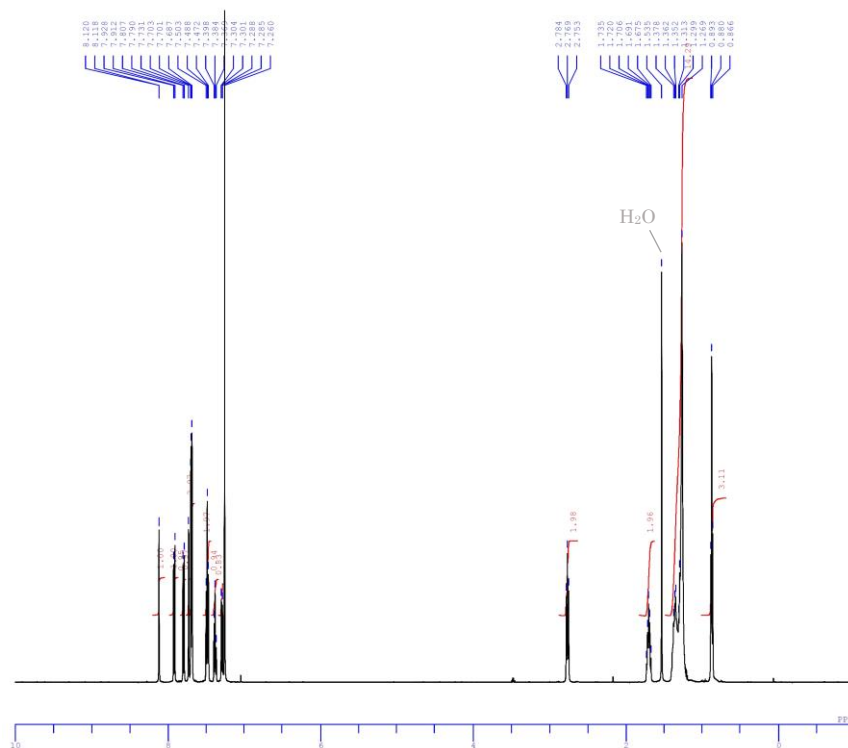
DFILE Br CF3 BTBT_C.als
COMMT Ref DJF-MT01-183aC
DATIM 2019-07-23 06:36:00
ORNUC 13C
EXMMD zgpg30
OBFRQ 125.78 MHz
OBSET 7.33 KHz
OBFIN 9.98 Hz
POINT 32768
FREQU 32051.28 Hz
SCANS 2048
AQCTM 1.0224 sec
PD 2.0000 sec
PWI 8.00 usec
IRNUC
CTEMP 24.8 c
SIVNT CDCl3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 194
    
```



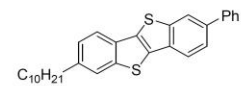




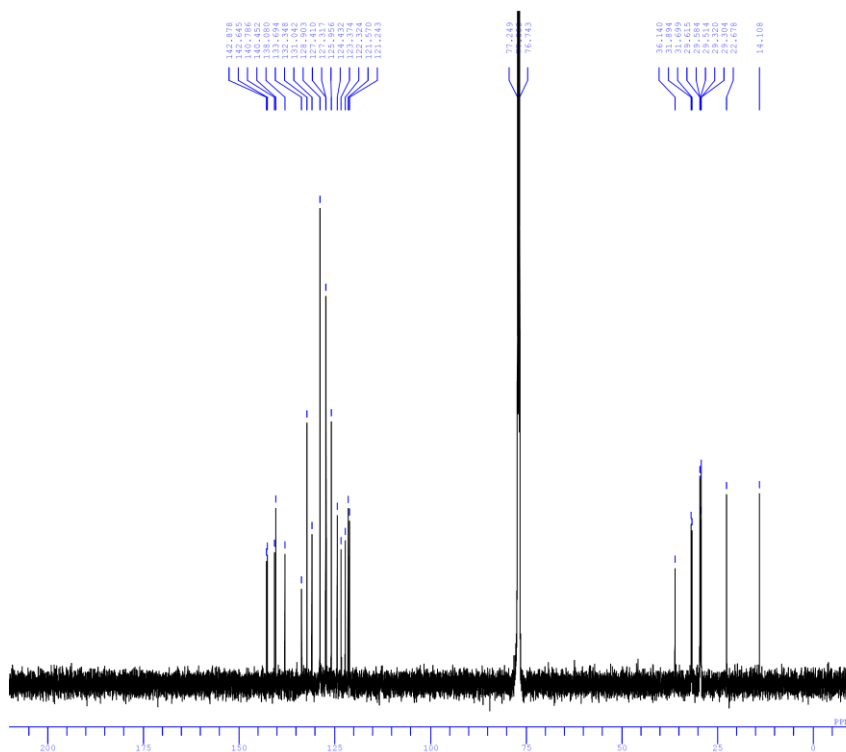
### $^1\text{H}$ NMR of 4eb (500 MHz, $\text{CDCl}_3$ )



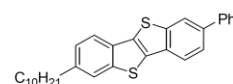
```
D1FILE 4ebH2.e1s  
COMPT Ref GP-01-099 Col 2 Dry  
DATIM 2020-07-08 20:21:19  
SNAME IN  
SUNIT 19  
EXMOD zgpg30  
OBPFO 500.13 MHz  
OBSET 3.05 Hz  
OBSIN 8.88 Hz  
POINT 42526  
FREQU 10000.00 Hz  
SCANS 16  
ACQTM 3.2768 sec  
PD 1.0000 sec  
PWL 12.00 usec  
IRFNC  
CTEMP 24.9 c  
SLVNT  $\text{CDCl}_3$   
EXREF 7.26 ppm  
BF 0.30 Hz  
RGAIN 75
```



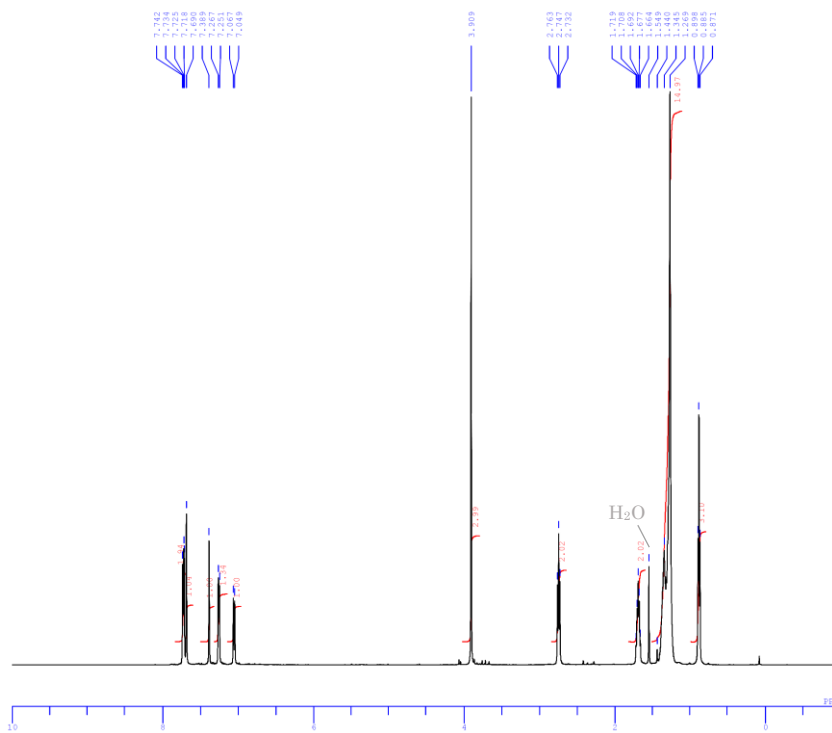
### $^{13}\text{C}$ NMR of 4eb (126 MHz, $\text{CDCl}_3$ )



```
D1FILE C10 Ph WTDF C.e1s  
COMPT Ref D1F-MT C10_BTBT_ph_c2048  
DATIM 2016-08-15 07:35:57  
SNAME 13C  
SUNIT 19  
EXMOD zgpg30  
OBPFO 125.78 MHz  
OBSET 7.33 MHz  
OBSIN 9.88 Hz  
POINT 32768  
FREQU 32051.28 Hz  
SCANS 2048  
ACQTM 1.0224 sec  
PD 2.0000 sec  
PWL 8.00 usec  
IRFNC  
CTEMP 24.9 c  
SLVNT  $\text{CDCl}_3$   
EXREF 77.00 ppm  
BF 1.00 Hz  
RGAIN 184
```

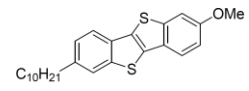


**<sup>1</sup>H NMR of 4ef (500 MHz, CDCl<sub>3</sub>)**

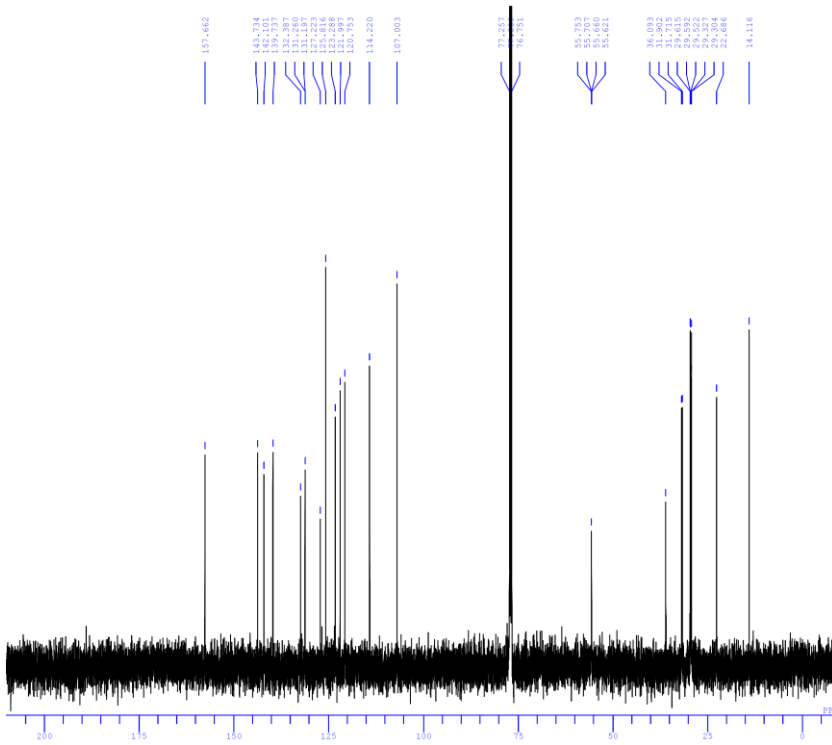


```

D1FILE C:\0_0me_BTBT_H_01.e
COMPT Ref:\03-06-17\01-14148
DATIM 2019-03-06 17:03:32
ORHDC 1H
EXMCD spg30
OBPFC 500.19 MHz
OSRET 3.08 KHz
OBFIN 8.88 Hz
POINT 6356
FREQU 10000.00 Hz
SCANS 16
ACQTM 3.2768 sec
PD 1.0000 sec
PWL 8.00 usec
IRHDC
CTEMP 24.8 c
SLVNT CDCl3
EXREF 7.26 ppm
BF 0.10 Hz
RGAIN 53
    
```

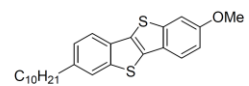


**<sup>13</sup>C NMR of 4ef (126 MHz, CDCl<sub>3</sub>)**

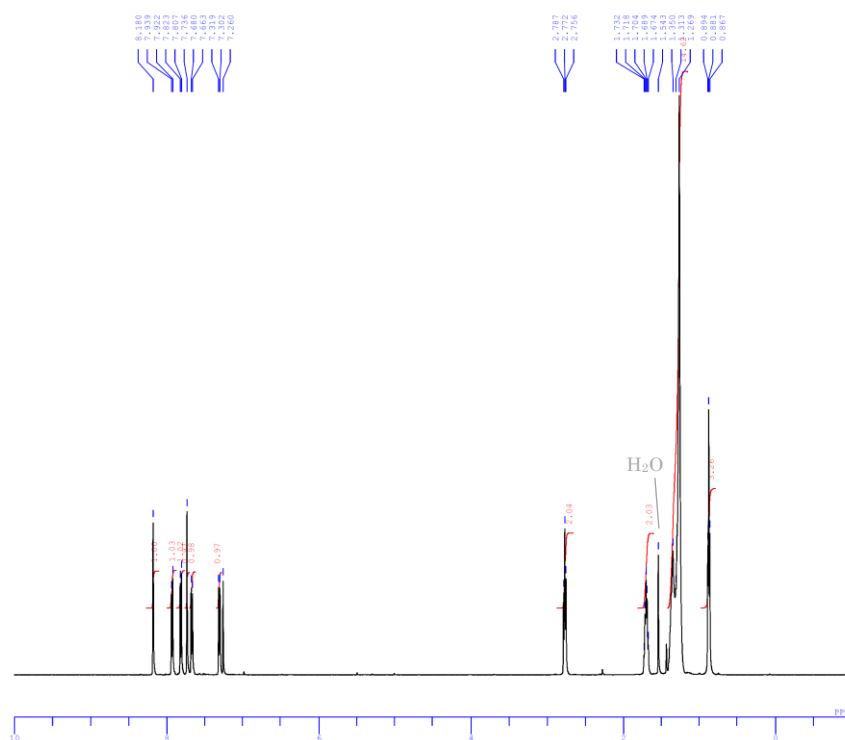


```

D1FILE C:\0_0me_BTBT_C_01.e
COMPT Ref:\03-06-17\06126
DATIM 2019-03-06 17:06:26
ORHDC 13C
EXMCD spg30
OBPFC 125.70 MHz
OSRET 7.33 KHz
OBFIN 9.88 Hz
POINT 32768
FREQU 32051.28 Hz
SCANS 32
ACQTM 1.0224 sec
PD 1.0000 sec
PWL 8.00 usec
IRHDC
CTEMP 24.9 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 184
    
```

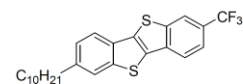


**<sup>1</sup>H NMR of 4eg (500 MHz, CDCl<sub>3</sub>)**

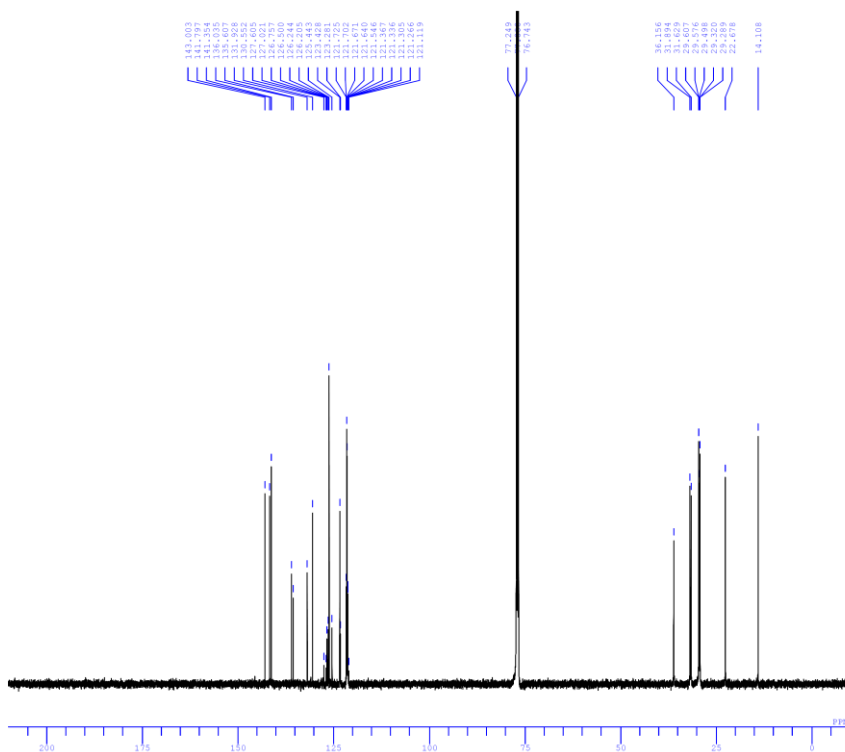


```

DFILE C10 CF3 BTWT N.s1s
COMPT Ref DFTM11-1424H
DATIM 2018-03-01 16:35:26
SOLUC 1H
EXMOD zg30
PROBHD 500.19 MHz
PULPROG zgpg30
OBFTFQ 3.08 MHz
OBFTET 3.08 MHz
OBFIN 8.98 Hz
POINT 65536
FREQU 10000.00 Hz
SCANS 16
ACQTM 3.2768 sec
PD 1.0000 sec
PE 8.00 usec
PWI 1.0000 sec
PVM 24.8 c
SOLVENT CDCl3
EXREF 7.26 ppm
BF 0.30 Hz
RGAIN 68
    
```

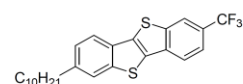


**<sup>13</sup>C NMR of 4eg (126 MHz, CDCl<sub>3</sub>)**

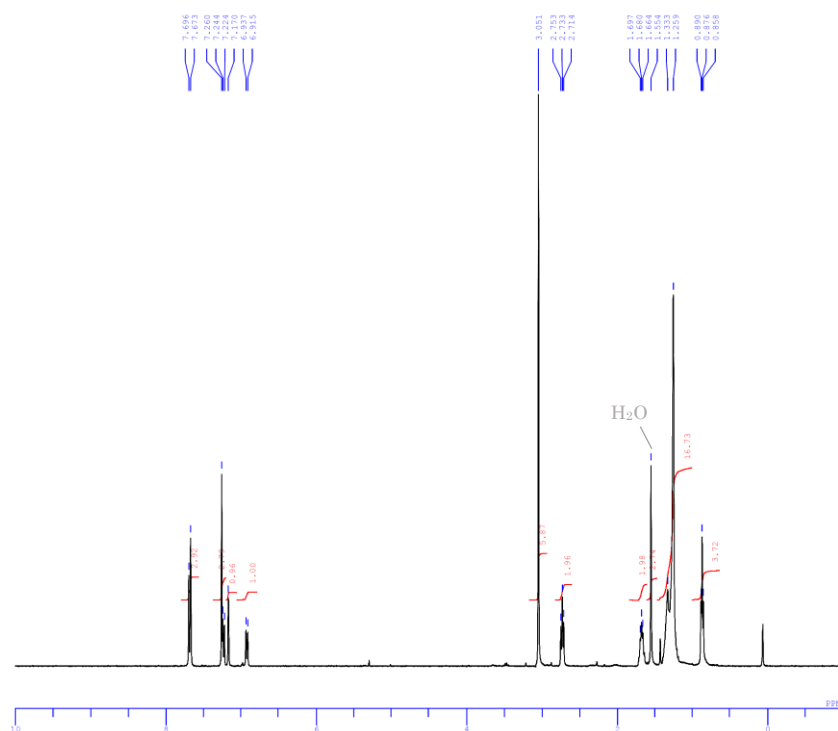


```

DFILE C10 CF3 BTWT C.s1s
COMPT Ref DFTM11-1424H
DATIM 2018-07-20 04:44:12
SOLUC 13C
EXMOD zgpg30
PROBHD 125.76 MHz
PULPROG zgpg30
OBFTFQ 7.33 MHz
OBFTET 7.33 MHz
OBFIN 32768 Hz
POINT 32768
FREQU 32051.28 Hz
SCANS 2048
ACQTM 1.0224 sec
PD 2.0000 sec
PE 8.00 usec
PWI 1.0000 sec
PVM 24.8 c
SOLVENT CDCl3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 104
    
```

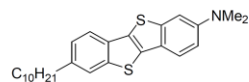


**<sup>1</sup>H NMR of 4eh (400 MHz, CDCl<sub>3</sub>)**

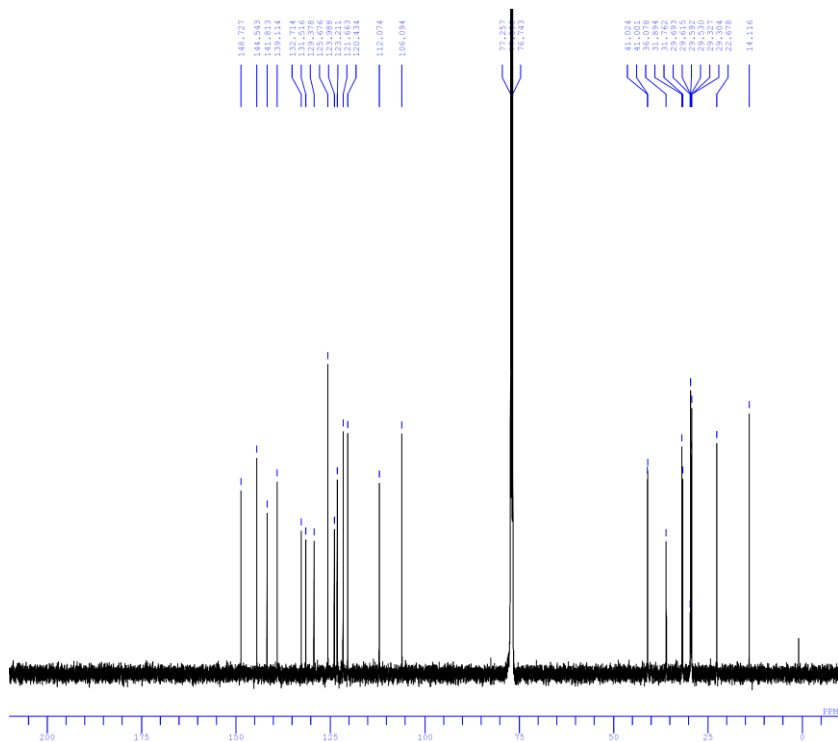


```

DFILE C10_NMe2_BTBT_H.e1a
CONNT HcF10P-H01-T5aH
DATIM 2019-04-01 09:29:50
ORNUC 1H
EXMOD zpp30
OBFRQ 400.13 MHz
OBSET 2.47 Hz
OFFIN 0.97 Hz
POINT 32760
FREQO 8012.82 Hz
SCANS 16
ACQTM 4.0594 sec
PD 1.0000 sec
PKI 15.00 usec
IRNUC
CTEMP 19.8 c
SIVNT CDCl3
EXREF 7.26 ppm
BF 0.10 Hz
RGAIN 575
    
```

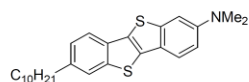


**<sup>13</sup>C NMR of 4eh (126 MHz, CDCl<sub>3</sub>)**



```

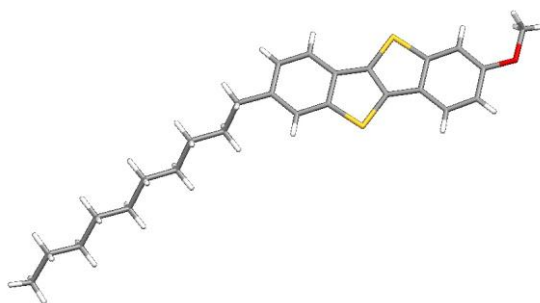
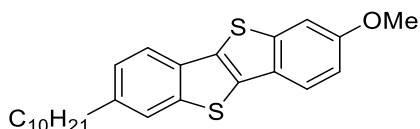
DFILE C10_NMe2_BTBT_C.e1a
CONNT HcF10P-H01-T5aC
DATIM 2019-06-05 20:32:48
ORNUC 13C
EXMOD zpp30
OBFRQ 125.76 MHz
OBSET 7.33 Hz
OFFIN 9.88 Hz
POINT 32760
FREQO 32051.28 Hz
SCANS 2048
ACQTM 1.0224 sec
PD 2.0000 sec
PKI 8.00 usec
IRNUC
CTEMP 24.9 c
SIVNT CDCl3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 184
    
```



#### 4. X-ray structure of 4ef

##### 2-Decyl-7-methoxy[1]benzothieno[3,2-*b*][1]benzothiophene

CCDC 2103832



Bond Precision	C–C = 0.0124 Å	Wavelength	0.71073
Cell	a = 7.6759(3)	b = 48.446(2)	c = 5.9459(3)
	alpha = 90	beta = 90	gamma = 90
Temperature	240 K		
	Calculated	Reported	
Volume	2211.08(17)	2211.08(17)	
Space group	P c a 21	P c a 21	
Hall group	P 2c -2ac	P 2c -2ac	
Moiety formula	C <sub>25</sub> H <sub>30</sub> O S <sub>2</sub>	C <sub>25</sub> H <sub>30</sub> O S <sub>2</sub>	
Sum formula	C <sub>25</sub> H <sub>30</sub> O S <sub>2</sub>	C <sub>25</sub> H <sub>30</sub> O S <sub>2</sub>	
Mr	410.61	410.61	
Dx, g cm <sup>-3</sup>	1.234	1.233	
Z	4	4	
Mu (mm <sup>-1</sup> )	0.254	0.254	
F000	880.0	880.0	
F000'	881.28		
k,k,lmax	10,69,8	10,63,7	
Nref	6746[ 3685]	5052	
Tmin,Tmax	0.929,0.970	0.499,1.000	
Tmin'	0.913		
Correction method= # Reported T Limits: Tmin=0.499 Tmax=1.000 AbsCorr = MULTI-SCAN			
Data completeness	1.37/0.75	Theta(max)	30.484
R(reflections)	0.0900( 4117)	wR2(reflections)	0.1988( 5052)
S	1.101	Npar	255