

# Supporting Information

## Visible-Light-Induced Photocatalytic Four-Component fluoroalkylation–dithiocarbamylation via Difunctionalization of Styrenes

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|   |       |                |
|---|-------|----------------|
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| Compound <b>8h</b> <sup>1</sup> H, <sup>13</sup> C{ <sup>1</sup> H} NMR and <sup>19</sup> F NMR | ..... | <b>S96-S97</b> |
| Compound <b>9</b> <sup>1</sup> H, <sup>13</sup> C{ <sup>1</sup> H} NMR and <sup>19</sup> F NMR  | ..... | <b>S98-S99</b> |
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## General information

The light-promoted reactions were used in the blue LED, using a homemade photoreactor having blue LED strips with  $\lambda$  460-463 nm. 36W Blue LEDs were purchased from the market available commercial source (budget led). Borosilicate reaction tube was used as material of the irradiation vessel. Distance between light source and reaction tube was approximately 5 cm and no filter was used for the reaction. A fan was used to ensure reactions remained at or near room temperature when using LED.



Figure S1. The photo reaction setup and blue LED lamps

## Graphical supporting information for visible-light-induced photocatalytic four-component difluoroalkylation–dithiocarbamylation via difunctionalization of alkenes (0.2 mmol scale)

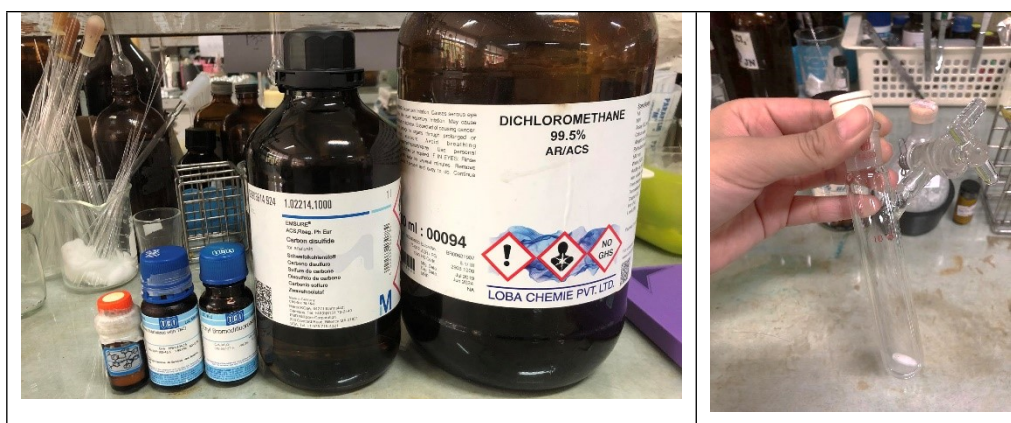
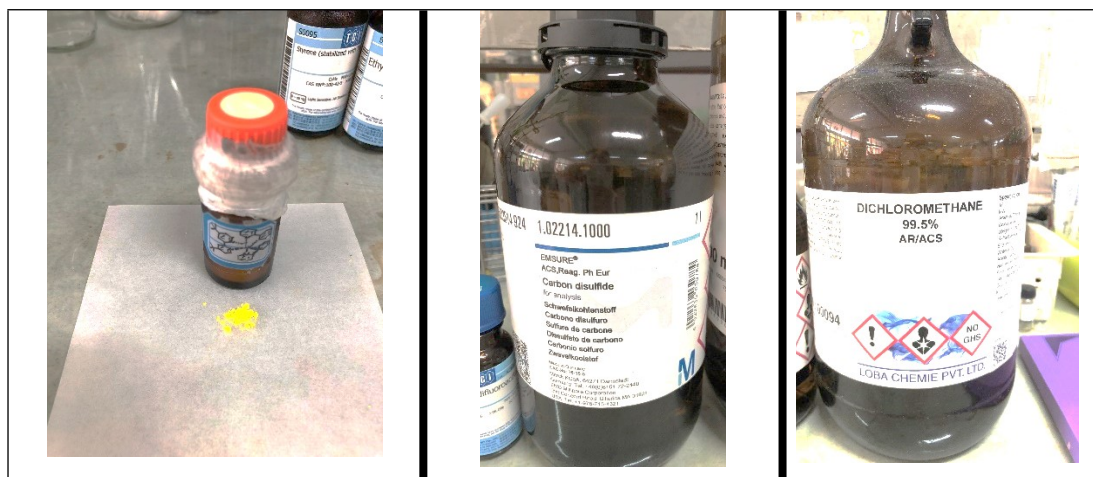
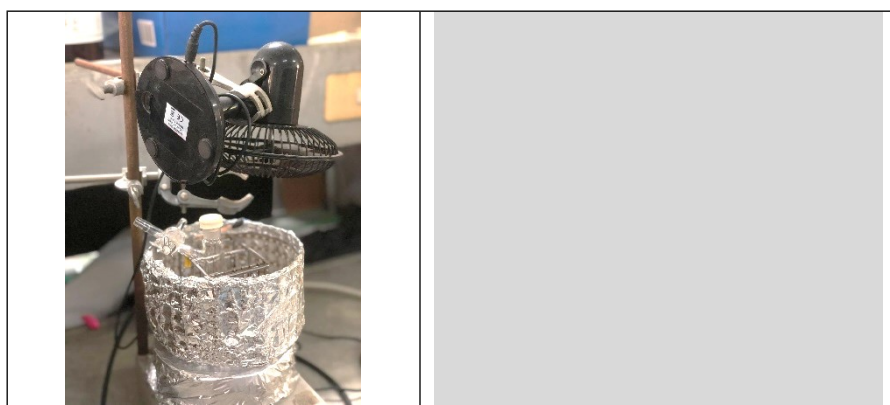


Figure S2. (Left) Starting materials for visible-light-induced photocatalytic four-component difluoroalkylation–dithiocarbamylation via difunctionalization reaction. (Right) 10.0 mL of Schlenk tube.





**Figure S3.** (Left) Photocatalyst  $[\text{Ir}(2',4'\text{-dF-5-CF}_3\text{-ppy})_2(4,4'\text{-dtbbpy})]\text{PF}_6$  (yellow solid) were weighed on the bench top. (Center) Carbondisulfide ( $\text{CS}_2$ ) (Right) Solvent (DCM) for visible-light-induced photocatalytic four-component difluoroalkylation–dithiocarbamylation via difunctionalization reaction.



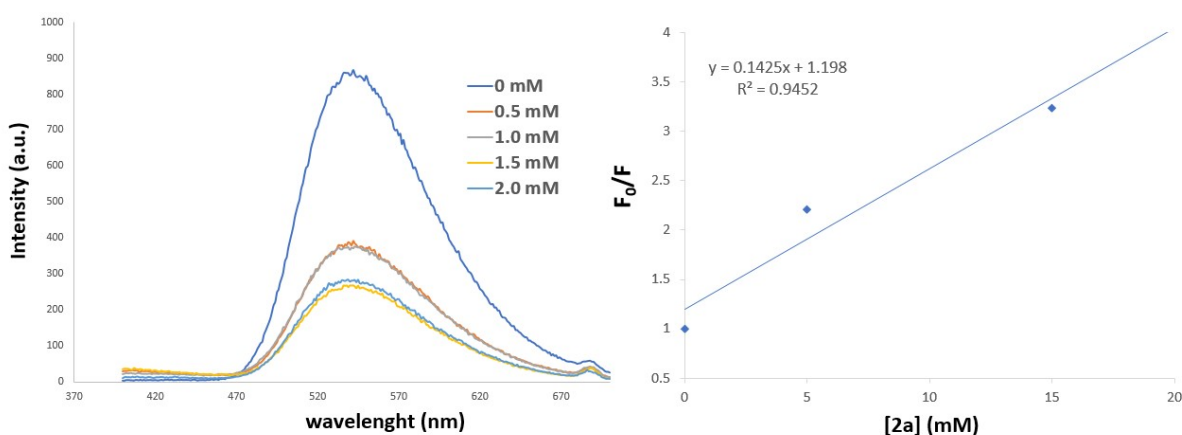
**Figure S4.** The tube was evacuated, refilled with  $\text{N}_2$  and the reaction stirred under blue LEDs at room temperature.

### Stern-Volmer fluorescence quenching studies

The fluorescence quenching experiment was conducted using a fluorescence spectrophotometer (Agilent Technologies). The excitation wavelength was 360 nm, and the emission intensity was collected at 524 nm. Samples were prepared by mixing  $[\text{Ir}(\text{ppy})_2(4,4'\text{-dtb-bpy})]\text{PF}_6$  ( $1.0 \times 10^{-4}$  M) with varying amounts of quencher **2a** ( $\text{BrF}_2\text{CO}_2\text{Et}$ ) in DCM (total volume = 5.0 mL) in a quartz fluorescence cuvette. For each quenching experiment, different volumes of the quencher's stock solution were titrated into a solution of  $[\text{Ir}(\text{ppy})_2(4,4'\text{-dtb-bpy})]\text{PF}_6$  (2.5 mL, maintaining a total volume of 5.0 mL). The emission intensity was then measured.

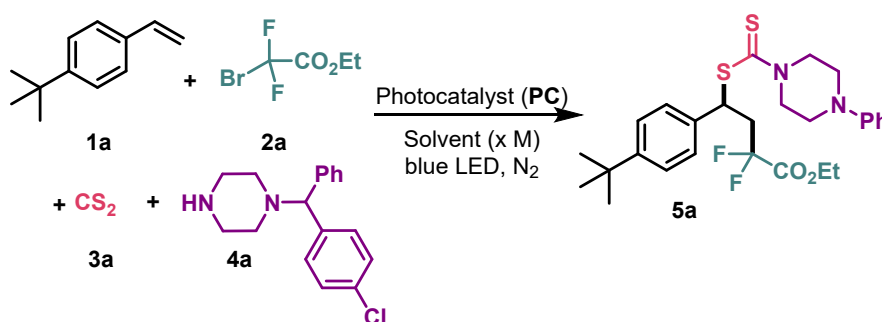
| Entry | $[\text{Ir}(\text{ppy})_2(4,4'\text{-dtb-bpy})]\text{PF}_6$ | Quencher <b>2a</b><br>( $\text{BrF}_2\text{CO}_2\text{Et}$ ) | DCM    | Total volume |
|-------|---|--|--------|--------------|
| 1     | 2.5 mL ( $5 \times 10^{-5}$ M)                              | 0 mL (0 mM)  | 2.5 mL | 5.0 mL       |
| 2     | 2.5 mL ( $5 \times 10^{-5}$ M)                              | 0.5 mL (5 mM)  | 2.0 mL | 5.0 mL       |
| 3     | 2.5 mL ( $5 \times 10^{-5}$ M)                              | 1.0 mL (10 mM)   | 1.5 mL | 5.0 mL       |
| 4     | 2.5 mL ( $5 \times 10^{-5}$ M)                              | 1.5 mL (15 mM)   | 1.0 mL | 5.0 mL       |
| 5     | 2.5 mL ( $5 \times 10^{-5}$ M)                              | 2.0 mL (20 mM)   | 0.5 mL | 5.0 mL       |

Inspired by the significant results, we sought to gain insights into the mechanism. We conducted Stern–Volmer fluorescence quenching experiments using  $[\text{Ir}(\text{ppy})_2(4,4'\text{-dtb-bpy})]\text{PF}_6$  in the presence of  $\text{BrF}_2\text{CO}_2\text{Et}$  (**2a**).  $F_0$  and  $F$  show the intensities of the emission in the absence and presence of the quencher at 524 nm. The results indicated that compound **2a** could effectively quench the excited state of the photosensitizer  $[\text{Ir}(\text{ppy})_2(4,4'\text{-dtb-bpy})]\text{PF}_6^*$ .



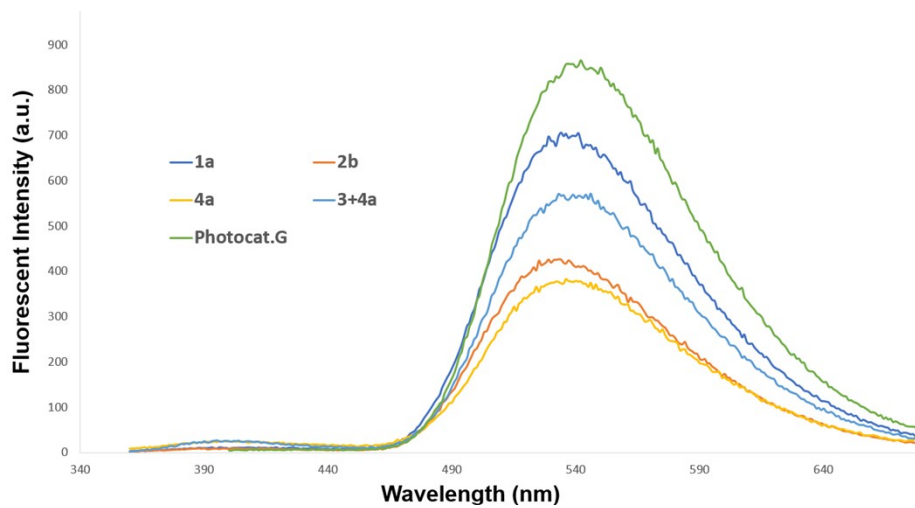
**Figure S5. Fluorescence quenching experiment**

Stern-Volmer fluorescence quenching experiments were run with a freshly prepared solution of  $[\text{Ir}(\text{ppy})_2(4,4'\text{-dtb-bpy})]\text{PF}_6$  ( $1.0 \times 10^{-4}$  M) in DCM. Samples were prepared by mixing  $[\text{Ir}(\text{ppy})_2(4,4'\text{-dtb-bpy})]\text{PF}_6$  ( $1.0 \times 10^{-4}$  M) with 5 mM of quenchers alkene (**1a**),  $\text{BrF}_2\text{CO}_2\text{Et}$  (**2a**),  $\text{CS}_2$  (**3a**) and piperazine derivative (**4a**) in DCM (total volume = 5.0 mL) in a quartz fluorescence cuvette. For each quenching experiment, different quenchers with 5 mM were titrated into a solution of  $[\text{Ir}(\text{ppy})_2(4,4'\text{-dtb-bpy})]\text{PF}_6$  (2.5 mL, maintaining a total volume of 5.0 mL). The emission intensity was then measured.



| Entry | Substrates           | Conc.         | Cat.G                          | DCM    | Total volume |
|-------|----------------------|---------------|--------------------------------|--------|--------------|
| 1     | -                    | -             | 2.5 mL ( $5 \times 10^{-5}$ M) | 2.5 mL | 5.0 mL       |
| 2     | Quencher <b>1a</b>   | 0.5 mL (5 mM) | 2.5 mL ( $5 \times 10^{-5}$ M) | 2.0 mL | 5.0 mL       |
| 3     | Quencher <b>2a</b>   | 0.5 mL (5 mM) | 2.5 mL ( $5 \times 10^{-5}$ M) | 2.0 mL | 5.0 mL       |
| 4     | Quencher <b>4a</b>   | 0.5 mL (5 mM) | 2.5 mL ( $5 \times 10^{-5}$ M) | 2.0 mL | 5.0 mL       |
| 5     | Quencher <b>3+4a</b> | 0.5 mL (5 mM) | 2.5 mL ( $5 \times 10^{-5}$ M) | 2.0 mL | 5.0 mL       |

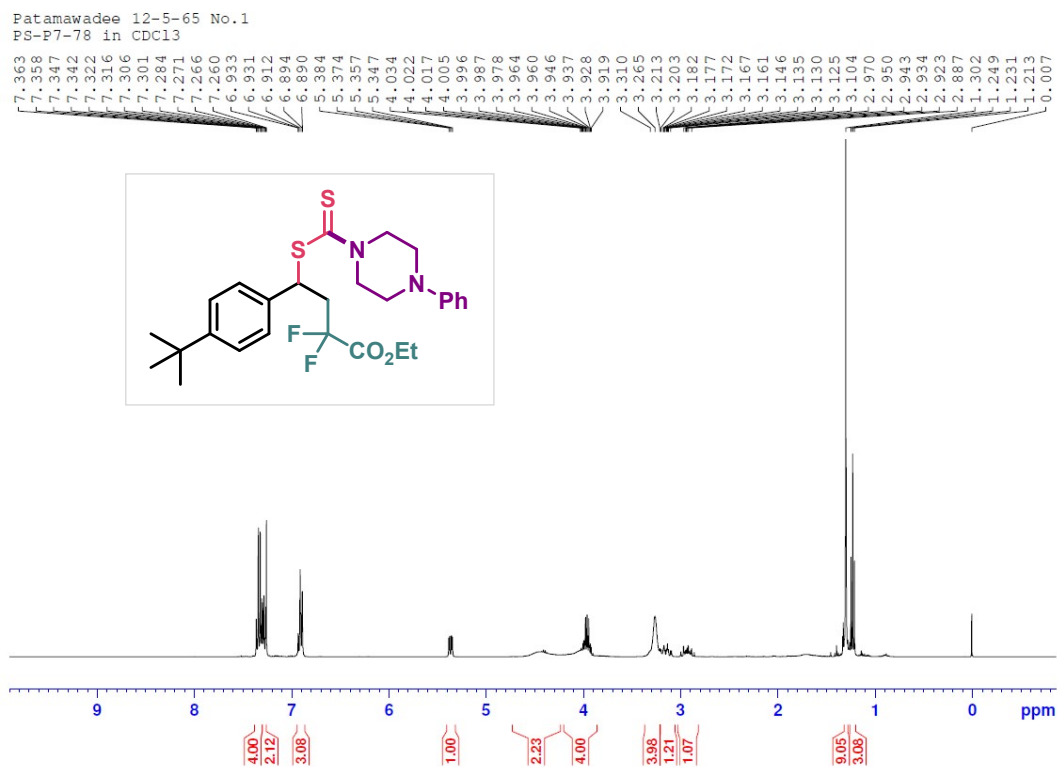
The fluorescence quenching studies illustrated in the provided graph (see SI; Stern-Volmer graph, **Figure S6**) show the interaction of the photoexcited  $[\text{Ir}(\text{ppy})_2(4,4'\text{-dtb-bpy})]\text{PF}_6^*$  with different substrates. The higher fluorescence intensity quenching observed with  $\text{BrF}_2\text{CO}_2\text{Et}$  (**2a**) and the piperazine derivative (**4a**) suggests a more efficient single electron transfer (SET) event compared to the other substrates (**1a** and **3a+4a**). Inspired by these important results, we sought to gain further insights into the mechanism. The formation of dithiocarbamate **3+4a** was readily achieved from the piperazine derivative (**4a**) and  $\text{CS}_2$  (**3a**), even in the absence of a base. Therefore, the interaction of the photoexcited  $[\text{Ir}(\text{ppy})_2(4,4'\text{-dtb-bpy})]\text{PF}_6$  in the presence of either piperazine derivative (**4a**) or  $\text{BrF}_2\text{CO}_2\text{Et}$  (**2a**) revealed that only compound **2a** could effectively quench the excited state of  $[\text{Ir}(\text{ppy})_2(4,4'\text{-dtb-bpy})]\text{PF}_6^*$ . Therefore, the result of fluorescence quenching experiments indicated that **2a** was a more efficient quencher of the excited state of  $[\text{Ir}(\text{ppy})_2(4,4'\text{-dtb-bpy})]\text{PF}_6^*$  than **4a**.



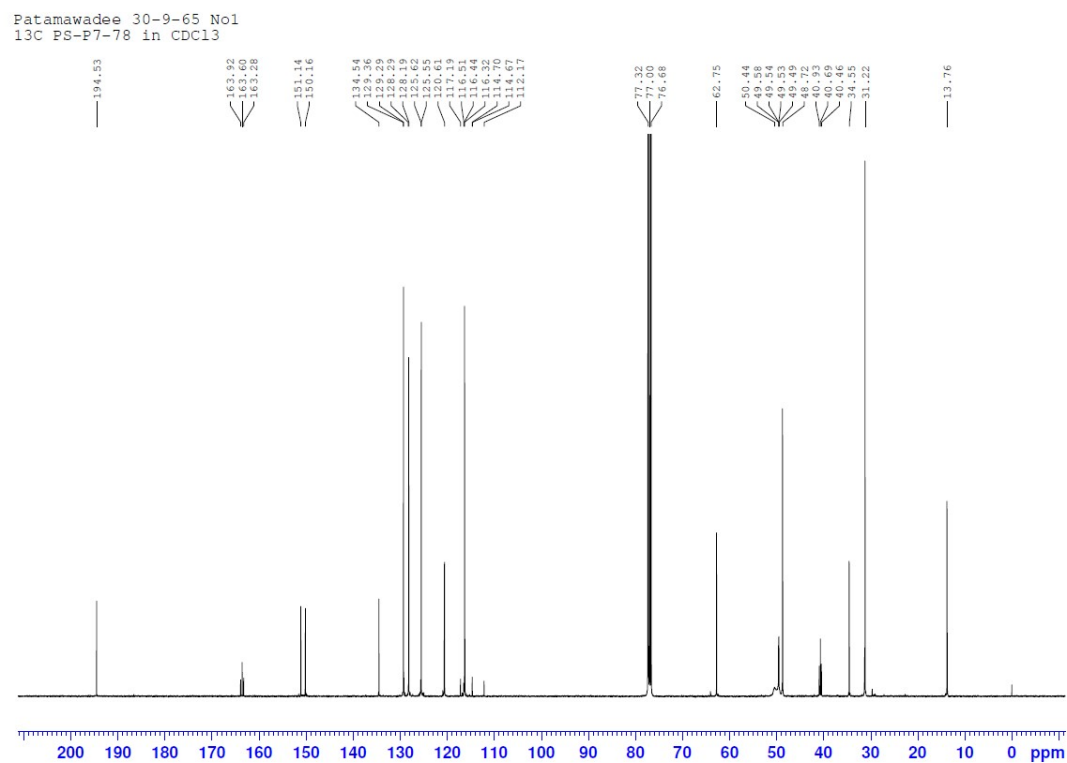
**Figure S6. Fluorescence quenching experiments.**

## Spectra for visible-light-induced photocatalytic four-component difluoroalkylation-dithiocarbamylation via difunctionalization reaction

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of ethyl 4-(4-(*tert*-butyl)phenyl)-2,2-difluoro-4-(4-phenylpiperazine-1-carbonylthio)butanoate (**5a**):

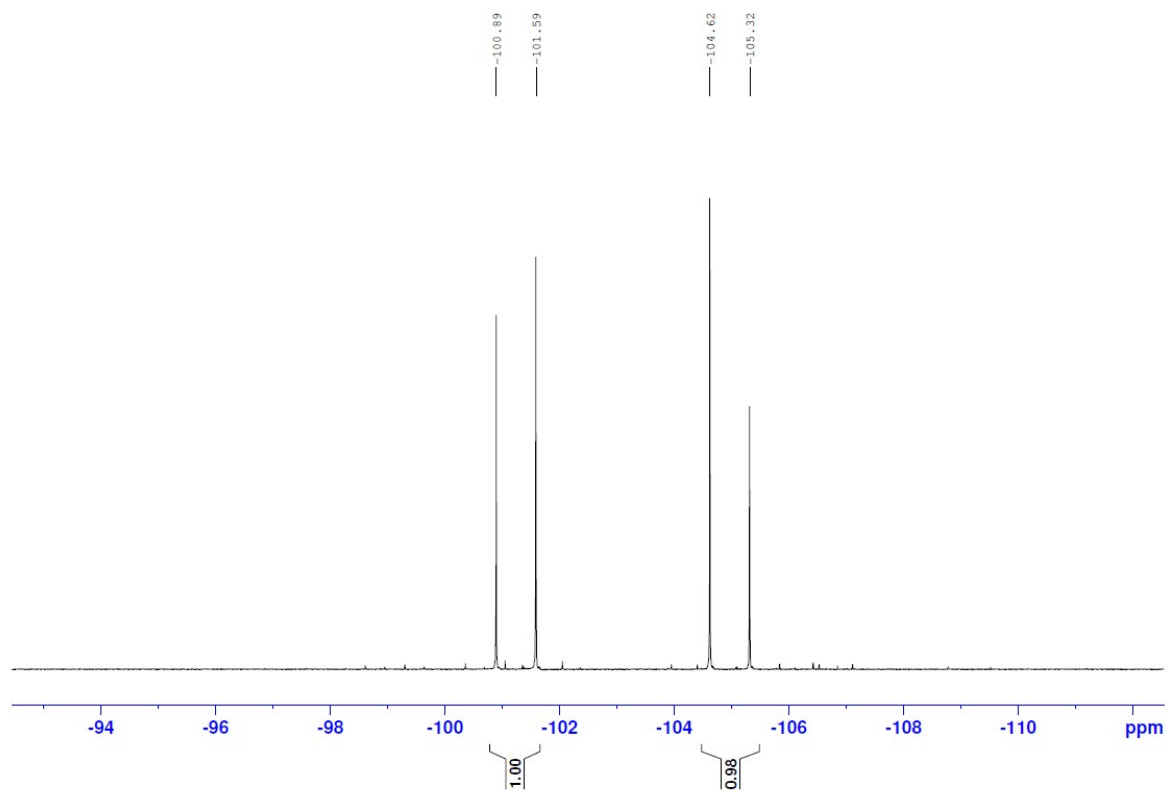


**5a**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )



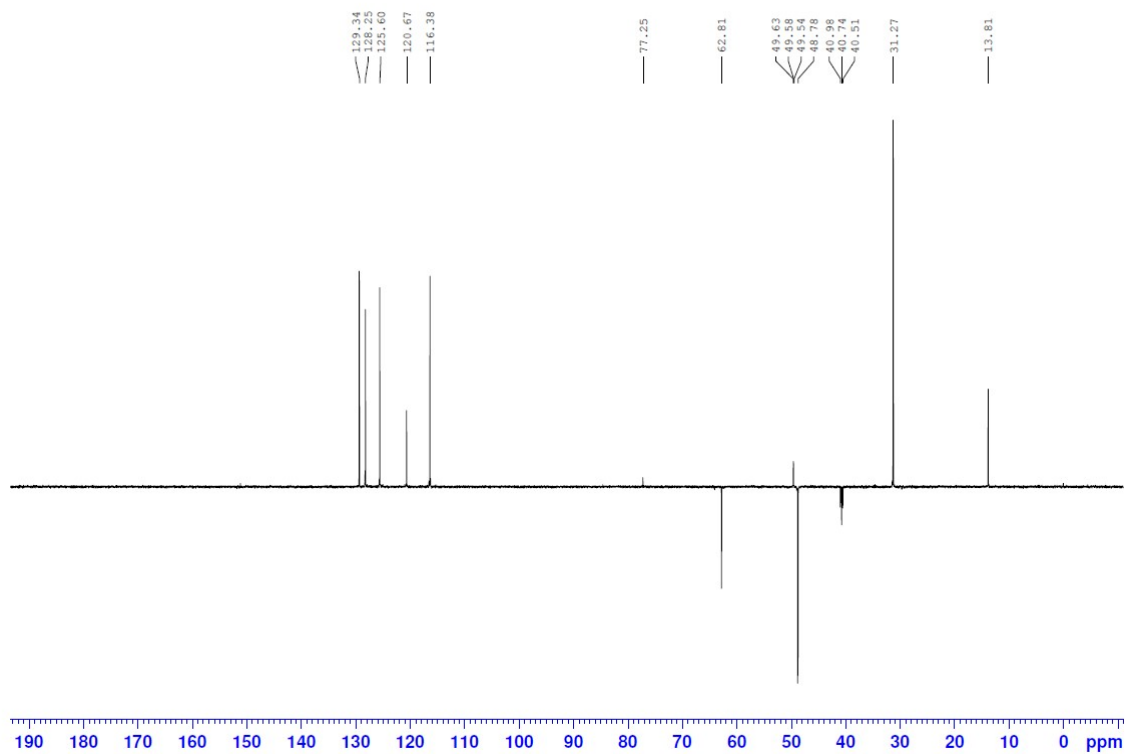
**5a**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 12-5-65 No.3  
 $^{19}\text{F}\{^1\text{H}\}$  PS-P7-78 in  $\text{CDCl}_3$



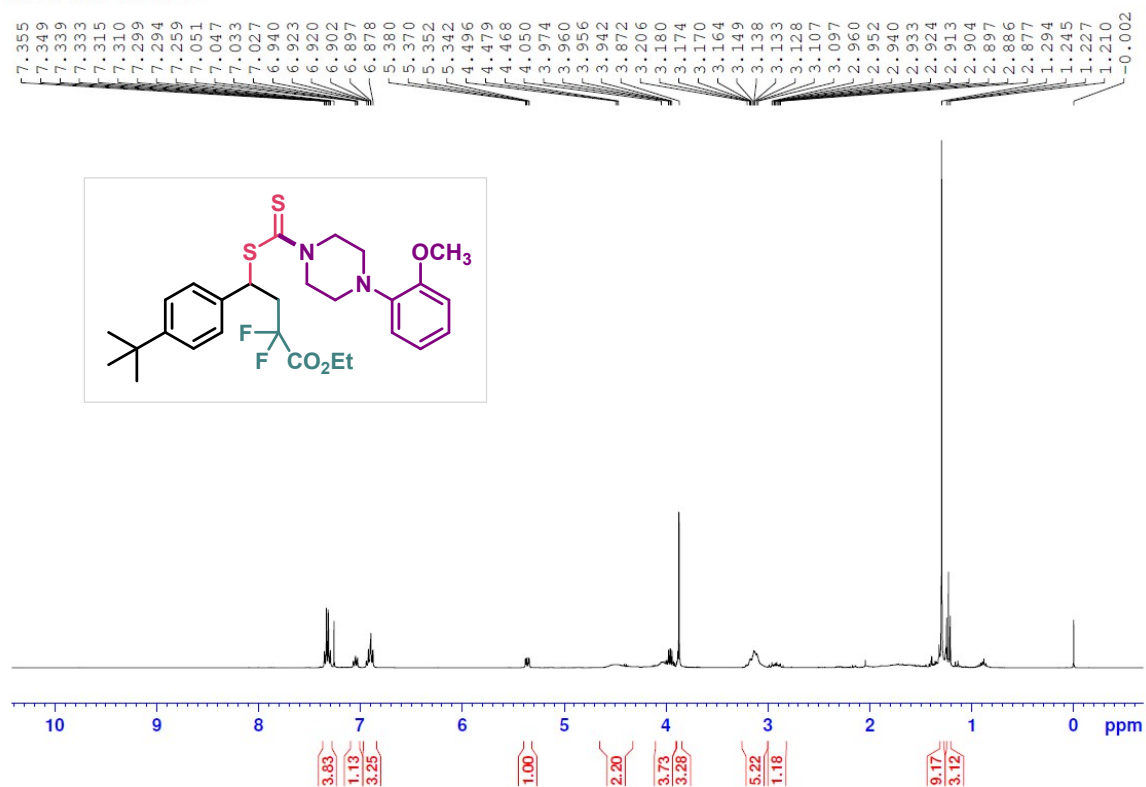
**5a** DEPT135 NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 12-5-65 No.2  
DEPT135 PS-P7-78 in  $\text{CDCl}_3$



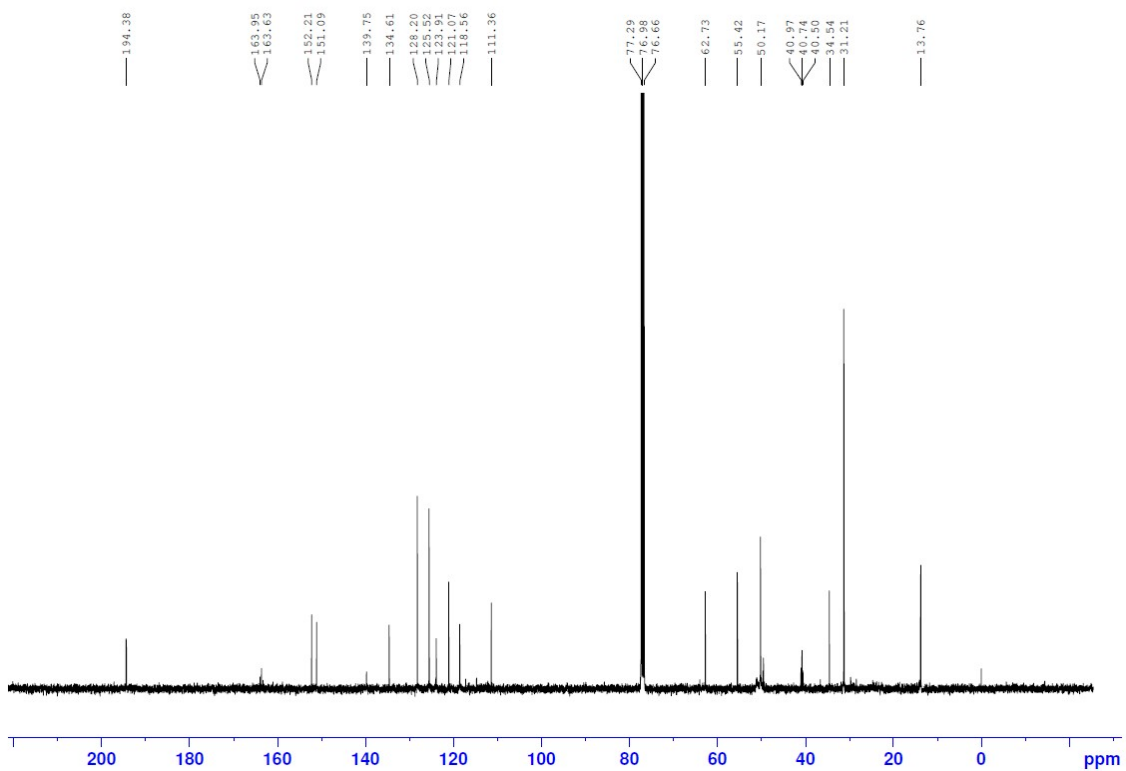
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of ethyl 4-(4-(*tert*-butyl)phenyl)-2,2-difluoro-4-((4-(2-methoxyphenyl)piperazine-1-carbonylthio)thio)butanoate (**5b**):

Patamawadee 13-6-65 No.1  
PS-P7-106 in  $\text{CDCl}_3$



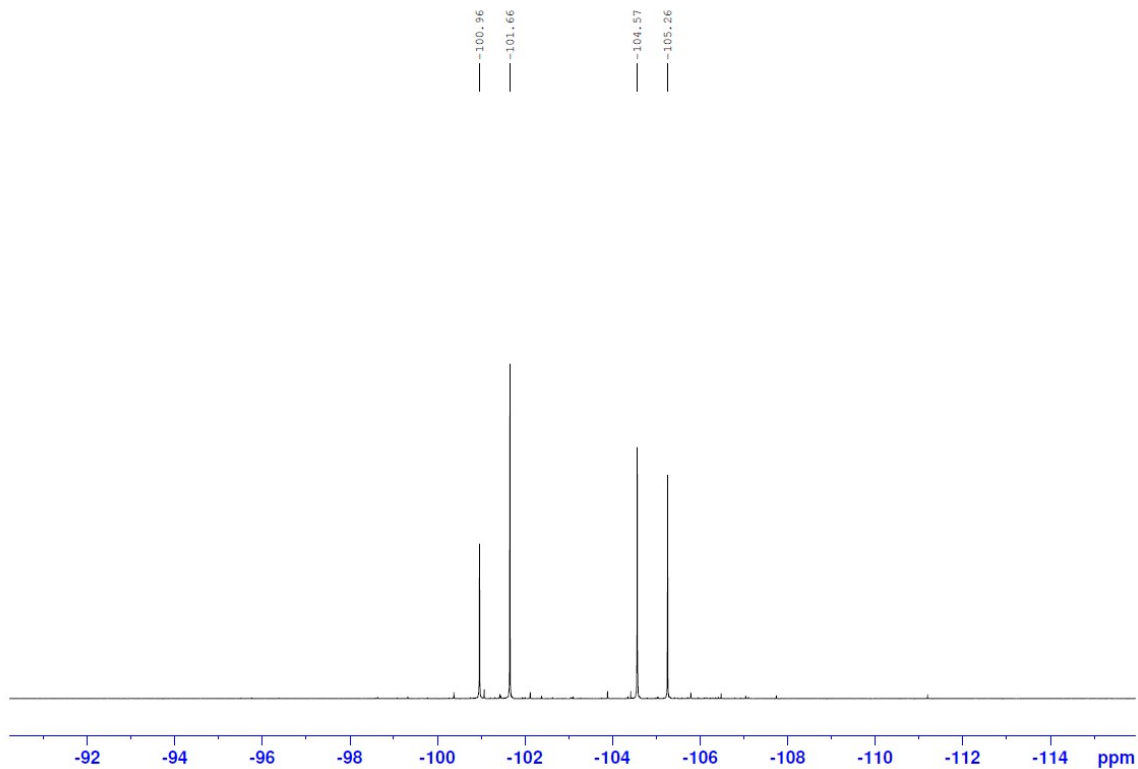
**5b**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 13-6-65 No.2  
 $^{13}\text{C}$  PS-P7-106 in  $\text{CDCl}_3$



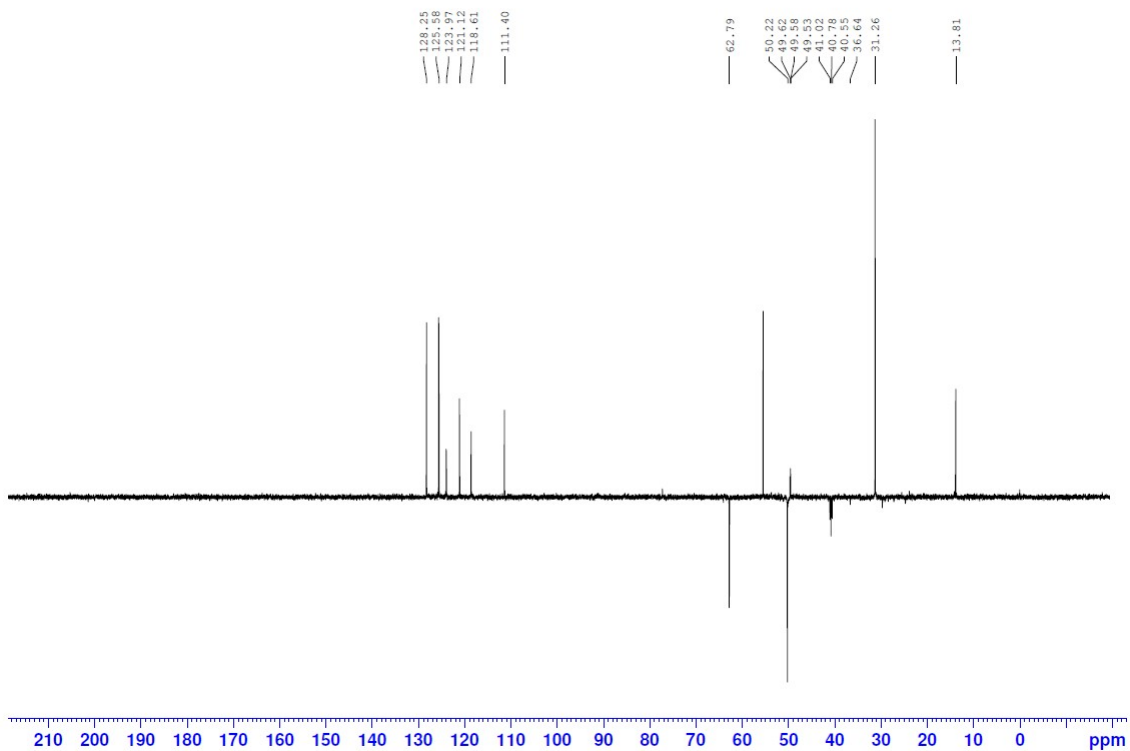
**5b**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 13-6-65 No.5  
 $^{19}\text{F}\{^1\text{H}\}$  PS-P7-106 in  $\text{CDCl}_3$



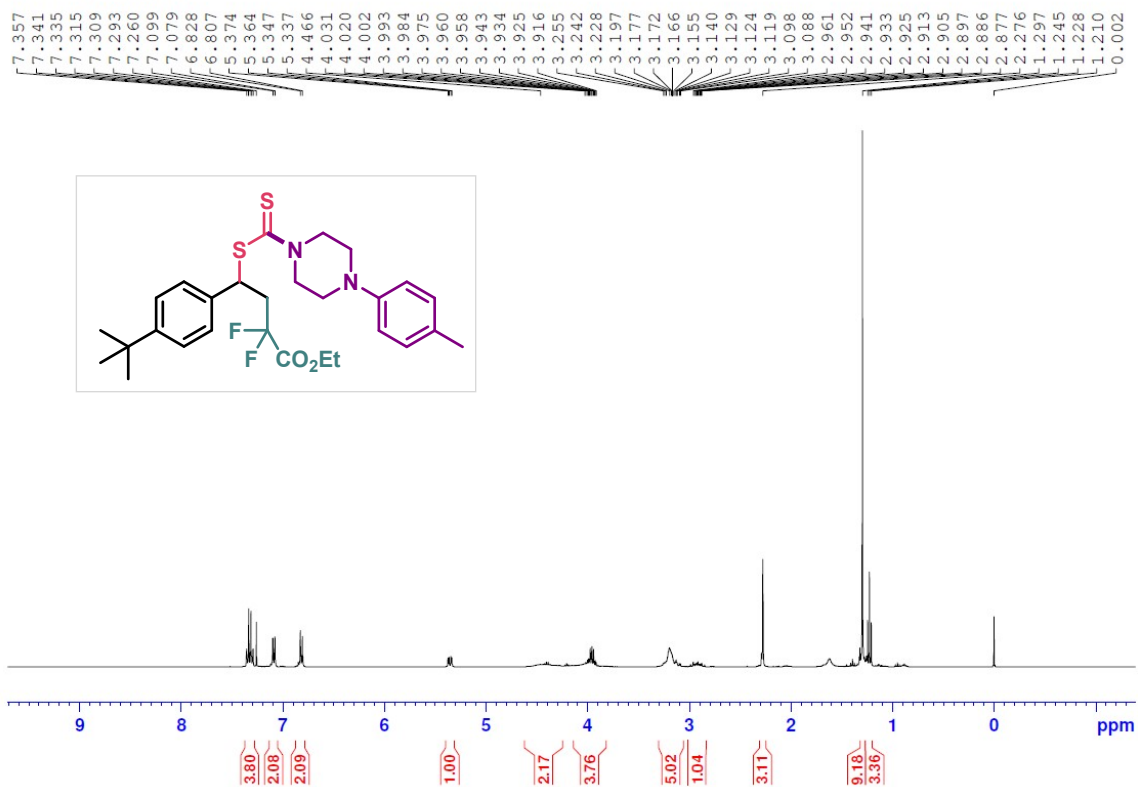
**5b** DEPT135 NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 13-6-65 No.3  
DEPT135 PS-P7-106 in  $\text{CDCl}_3$



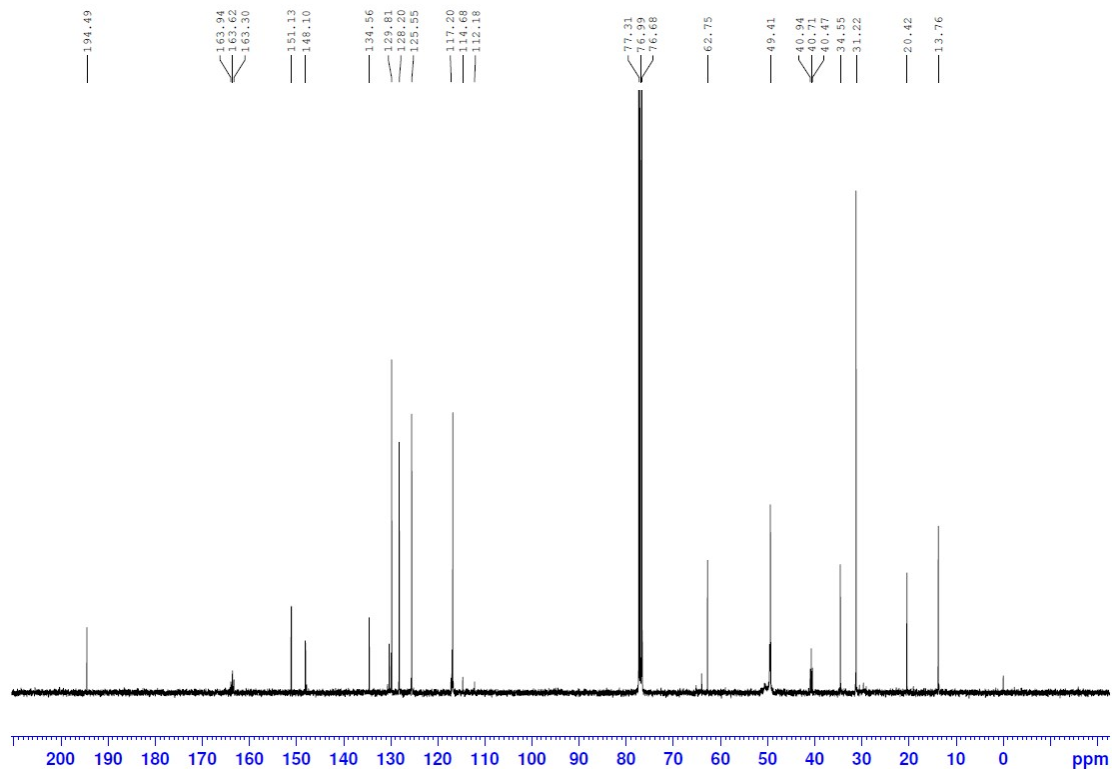
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of ethyl 4-(4-(*tert*-butyl)phenyl)-2,2-difluoro-4-((4-(*p*-tolyl)piperazine-1-carbonylthio)butanoate (**5c**):

Patamawadee 26-6-65 No.4  
PS-P7-119 in  $\text{CDCl}_3$



**5c**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

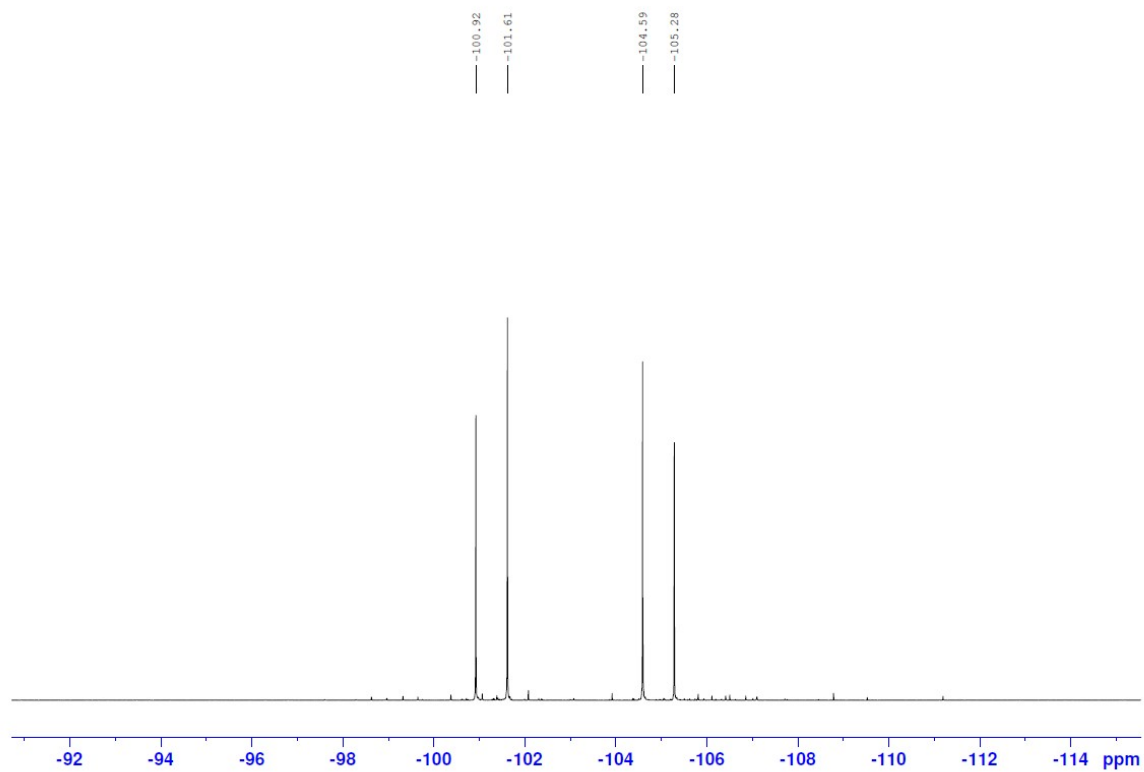
Patamawadee 21-6-65 No.5  
13C PS-P7-119 in  $\text{CDCl}_3$





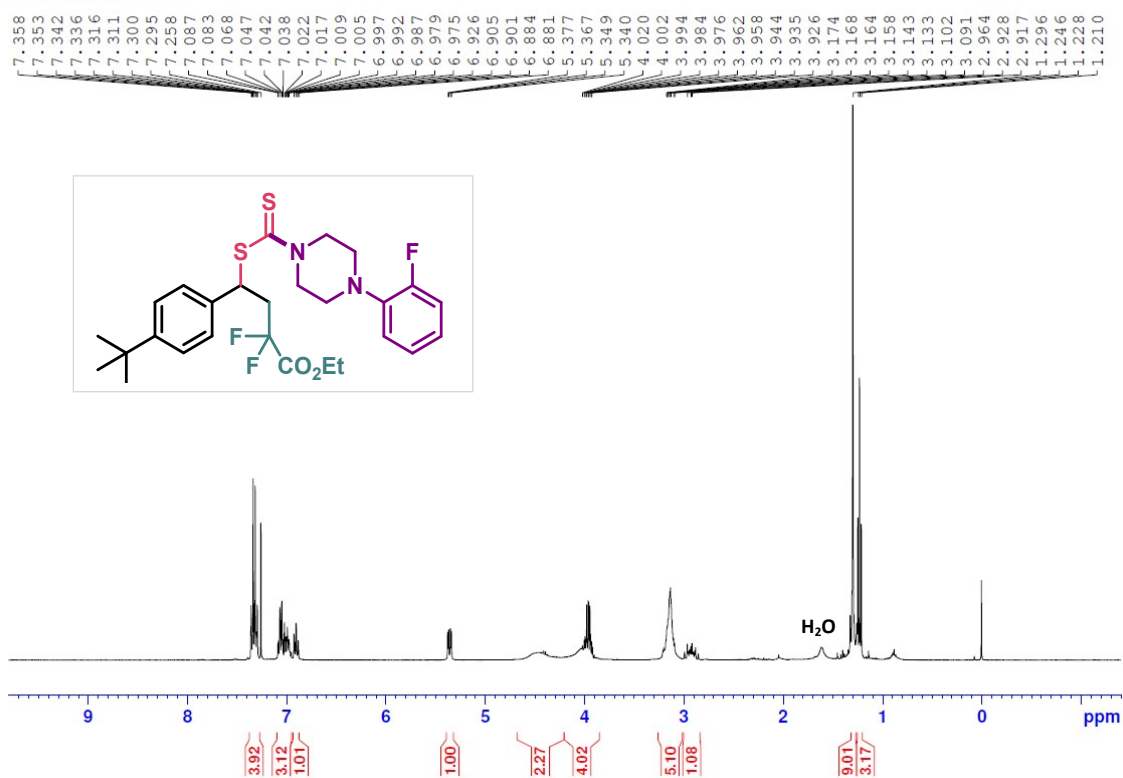
**5c**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 21-6-65 No.6  
 $^{19}\text{F}\{^1\text{H}\}$  PS-P7-119 in  $\text{CDCl}_3$



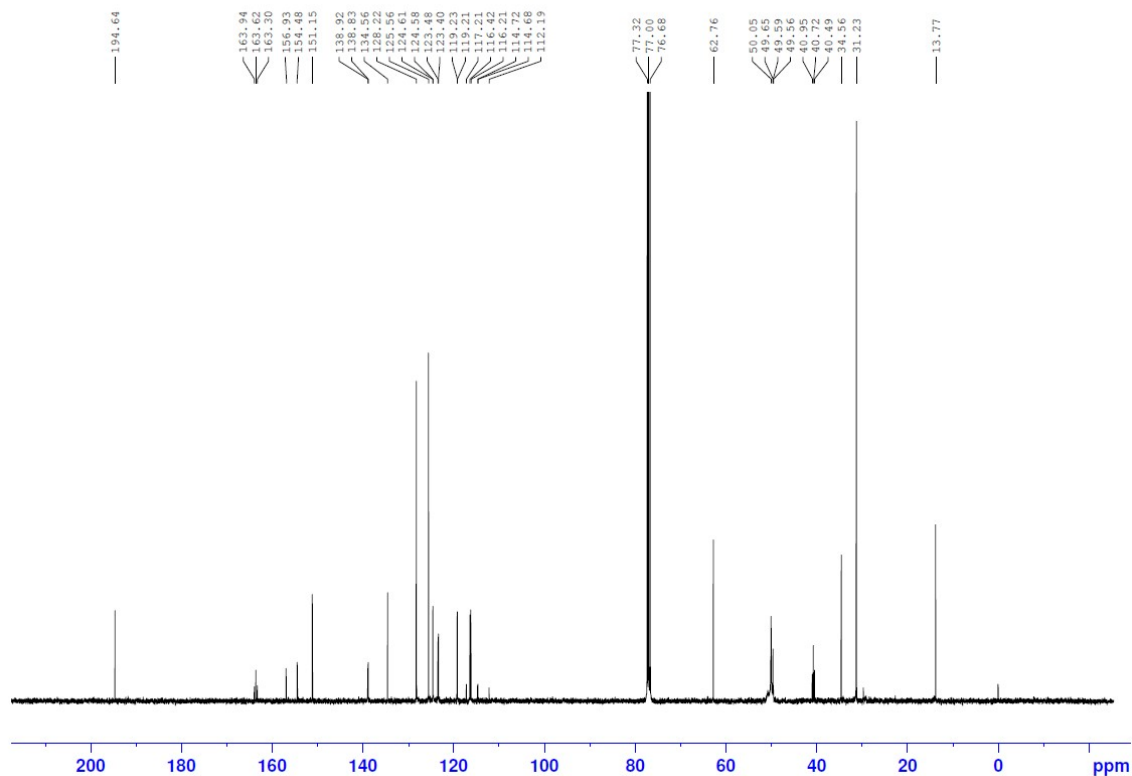
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of ethyl 4-(4-(*tert*-butyl)phenyl)-2,2-difluoro-4-((4-(2-fluorophenyl)piperazine-1-carbonylthio)butanoate) (**5d**):

Patamawadee 9-6-65 No.1  
PS-P7-107 in  $\text{CDCl}_3$



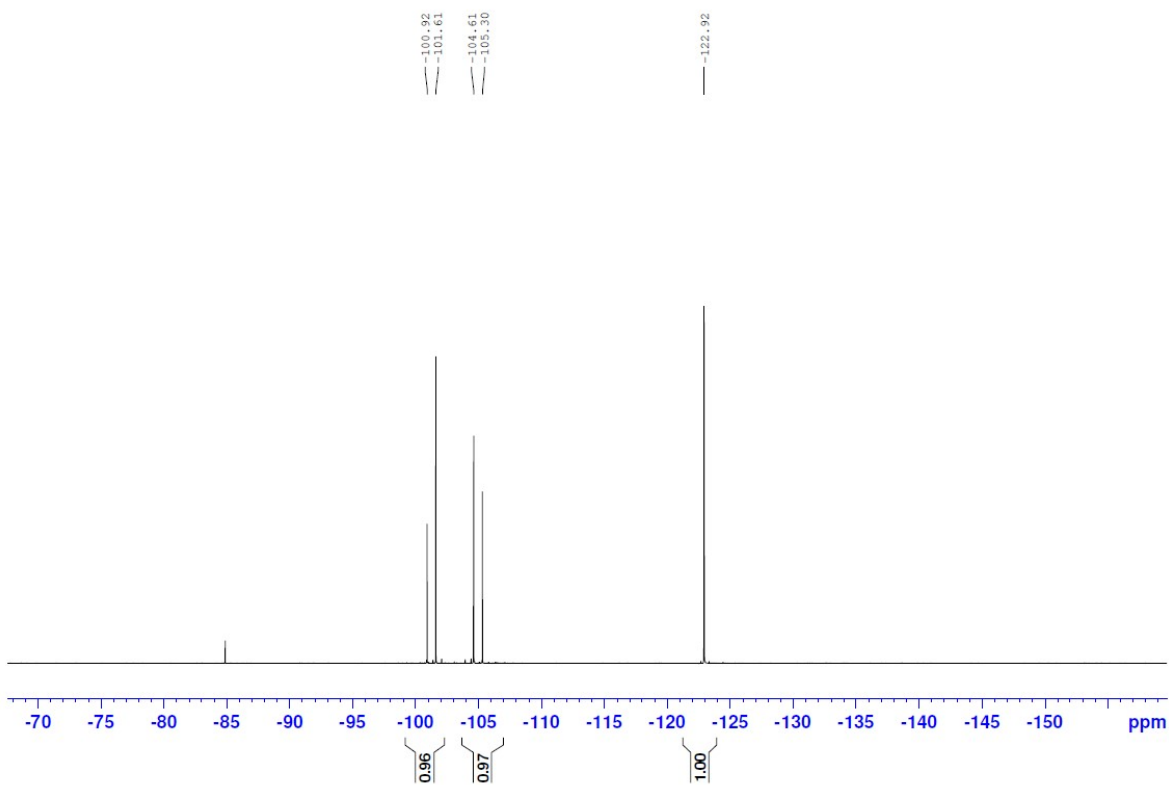
**5d**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 9-6-65 No.2  
 $^{13}\text{C}$  PS-P7-107 in  $\text{CDCl}_3$



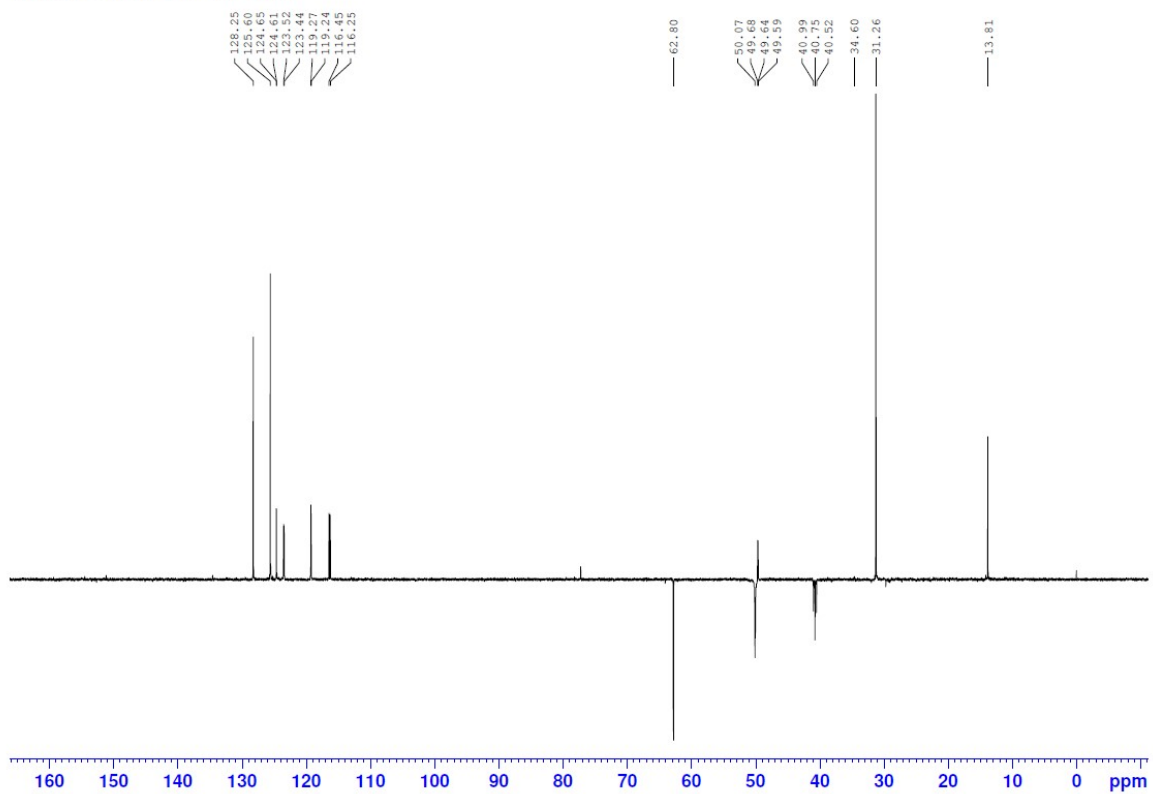
### 5d $^{19}\text{F}\{^1\text{H}\}$ NMR (400 MHz, $\text{CDCl}_3$ )

Patamawadee 9-6-65 No.5  
 $^{19}\text{F}\{^1\text{H}\}$  PS-P7-107 in  $\text{CDCl}_3$



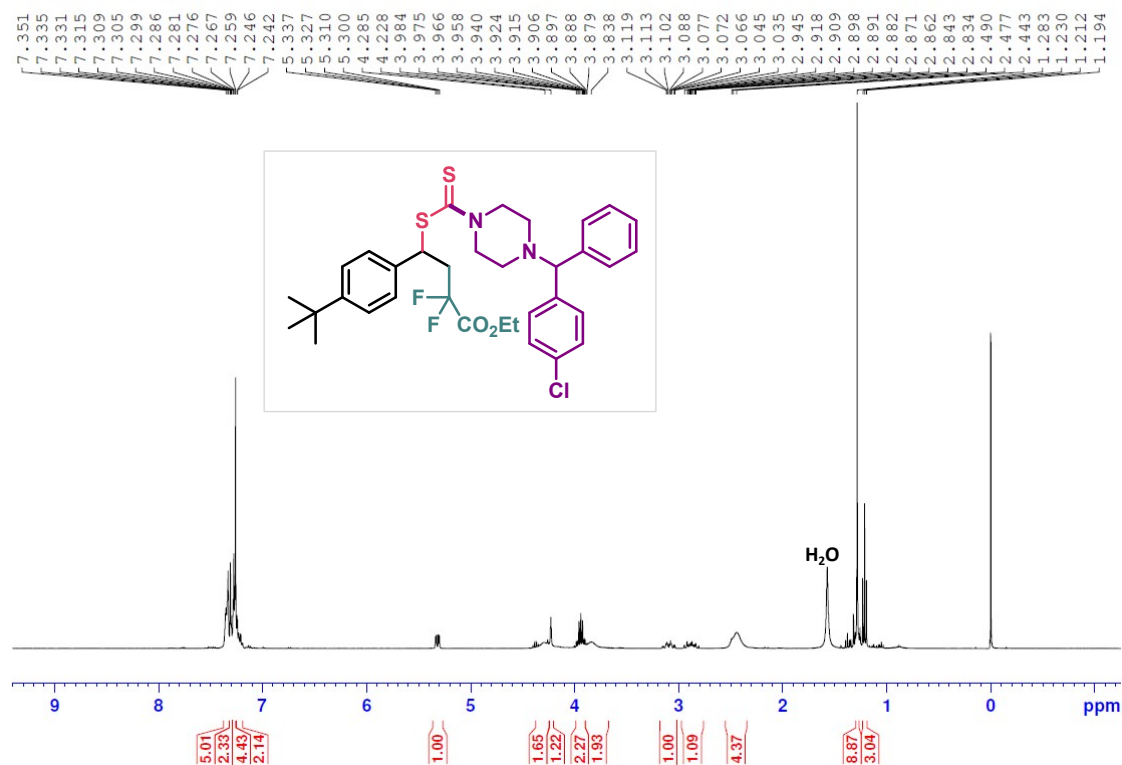
### 5d DEPT135 NMR (100 MHz, $\text{CDCl}_3$ )

Patamawadee 9-6-65 No.3  
DEPT135 PS-P7-107 in  $\text{CDCl}_3$



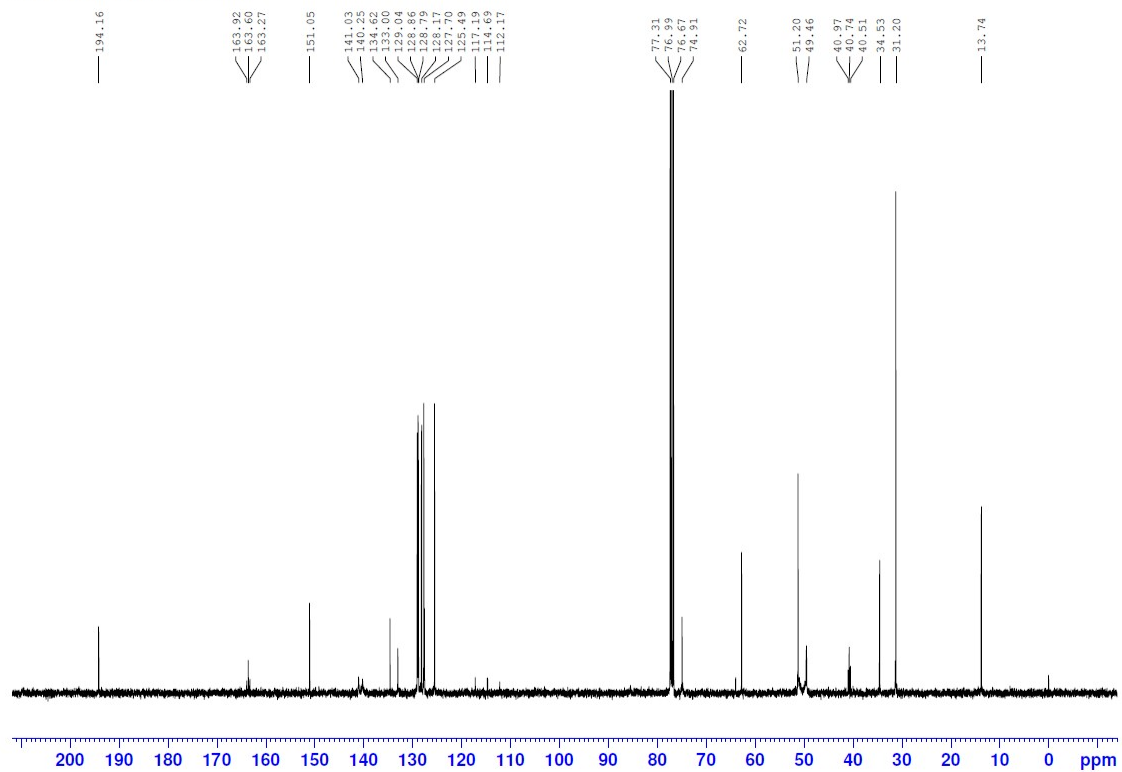
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of ethyl 4-(4-(*tert*-butyl)phenyl)-4-((4-(4-chlorophenyl)(phenyl)methyl)piperazine-1-carbonylthio)-2,2-difluorobutanoate (**5e**):

Patamawadee 15-6-65 No.5  
PS-P7-108 in CDCl<sub>3</sub>



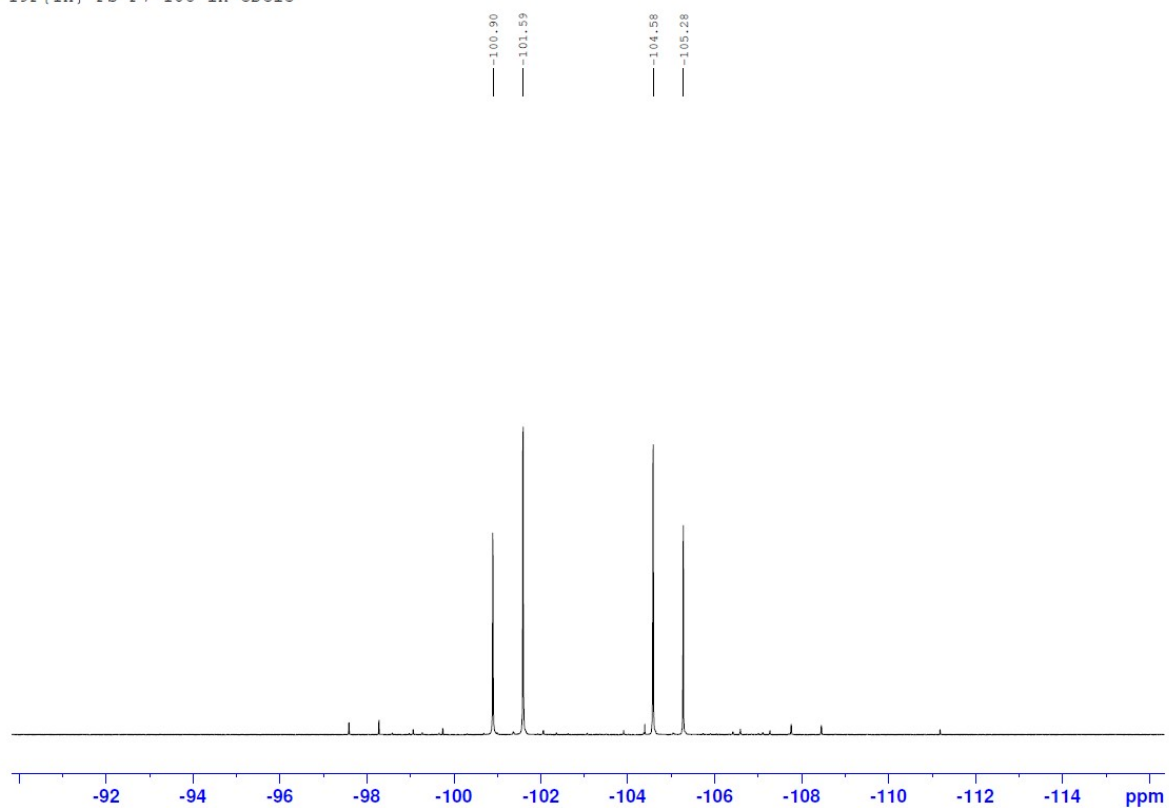
**5e** <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)

Patamawadee 16-6-65 No.5  
13C PS-P7-108 in CDCl<sub>3</sub>



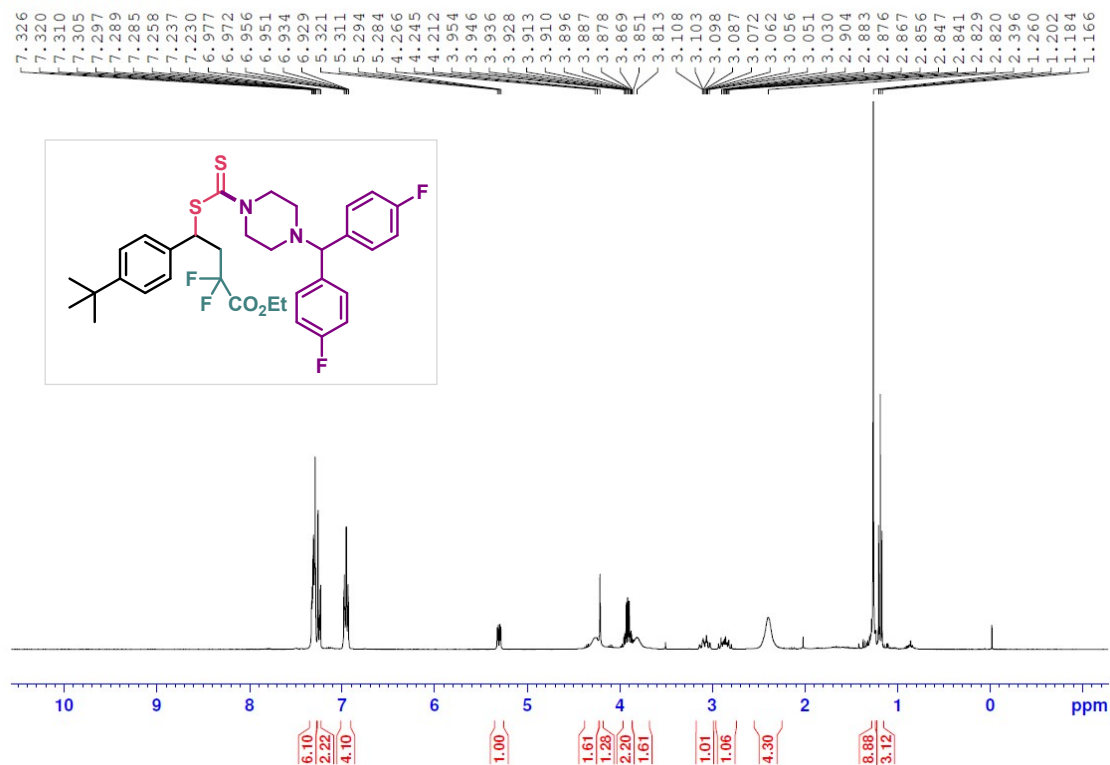
**5e**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 16-6-65 No.6  
 $^{19}\text{F}\{^1\text{H}\}$  PS-P7-108 in  $\text{CDCl}_3$



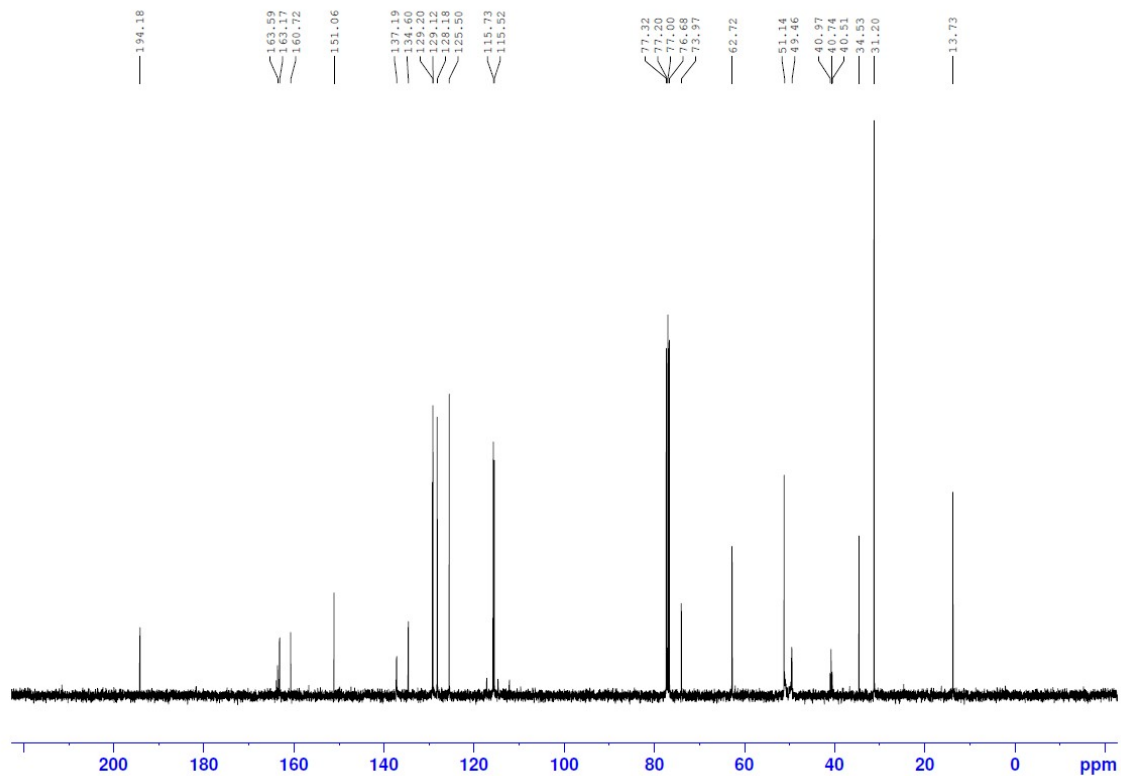
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of ethyl 4-((4-(bis(4-fluorophenyl)methyl)piperazine-1-carbonylthio)-4-(4-(tert-butyl)phenyl)-2,2-difluorobutanoate (**5f**):

Patamawadee 8-6-65 No.5  
PS-P7-105 in  $\text{CDCl}_3$



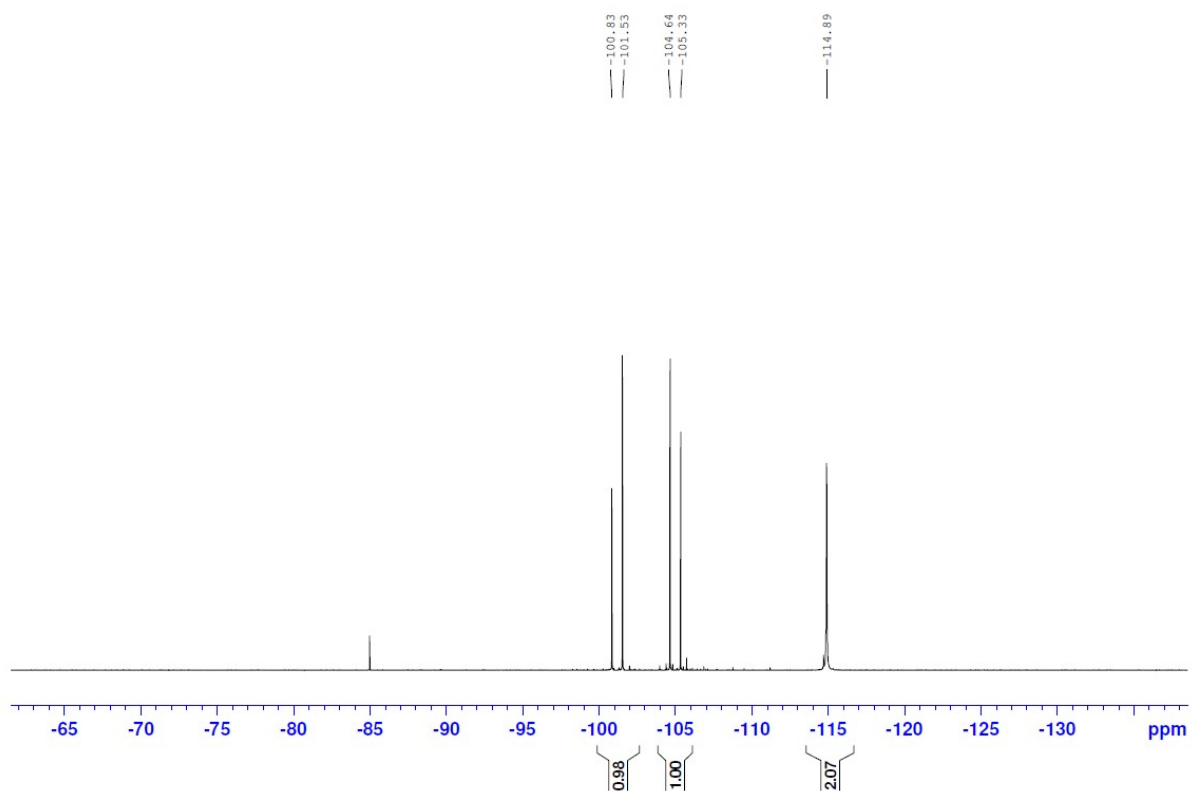
**5f**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 8-6-65 No.6  
13C PS-P7-105 in  $\text{CDCl}_3$



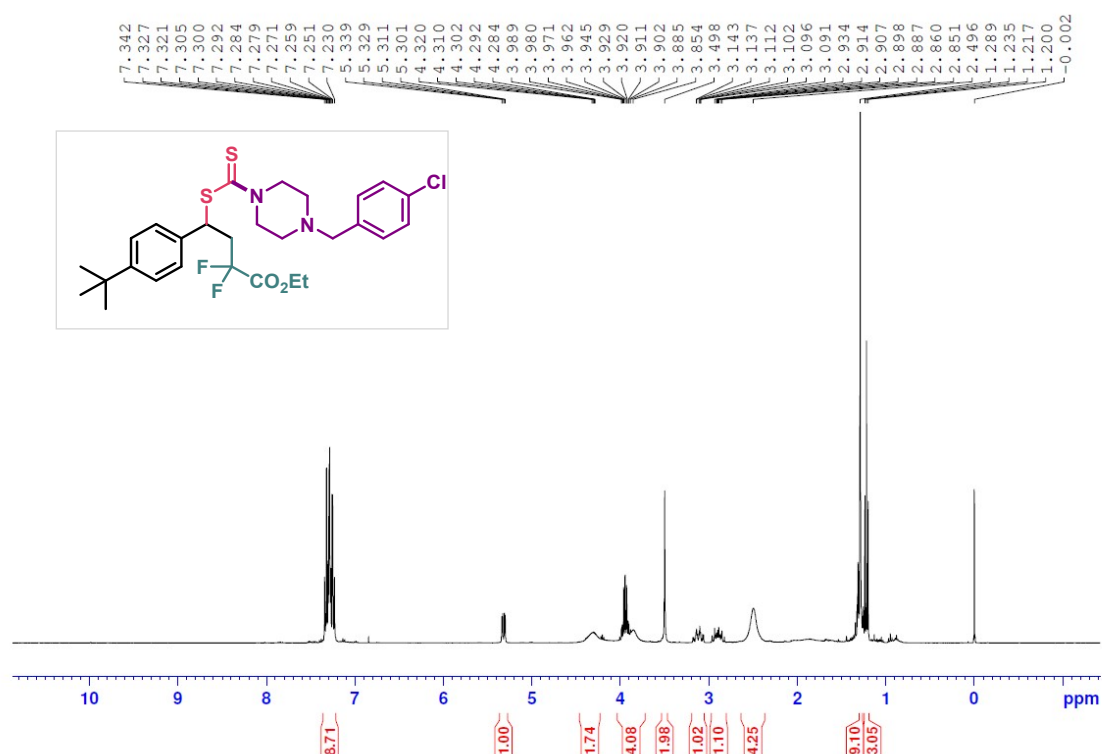
**5f**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 8-6-65 No.9  
 $^{19}\text{F}\{^1\text{H}\}$  PS-P7-105 in  $\text{CDCl}_3$



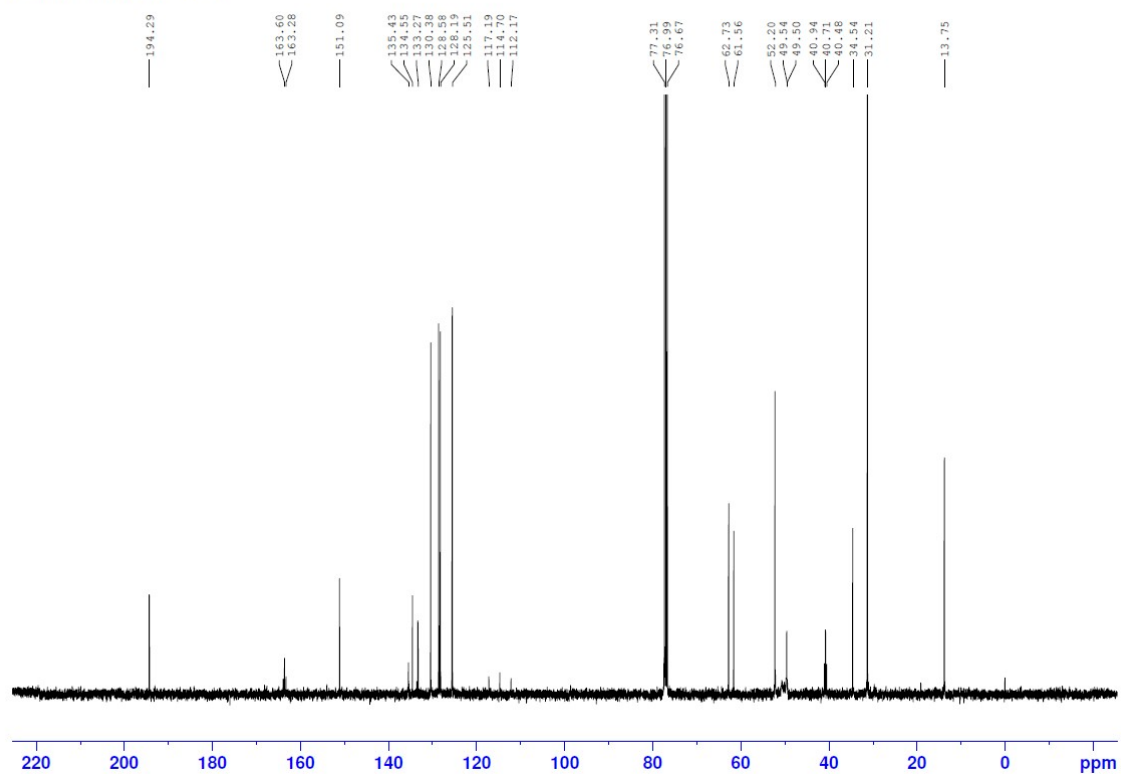
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of ethyl 4-(4-(*tert*-butyl)phenyl)-4-((4-(4-chlorobenzyl)piperazine-1-carbonylthio)-2,2-difluorobutanoate (**5g**):

Patamawadee 22-6-65 No.3  
PS-P7-115 in CDCl<sub>3</sub>



**5g** <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)

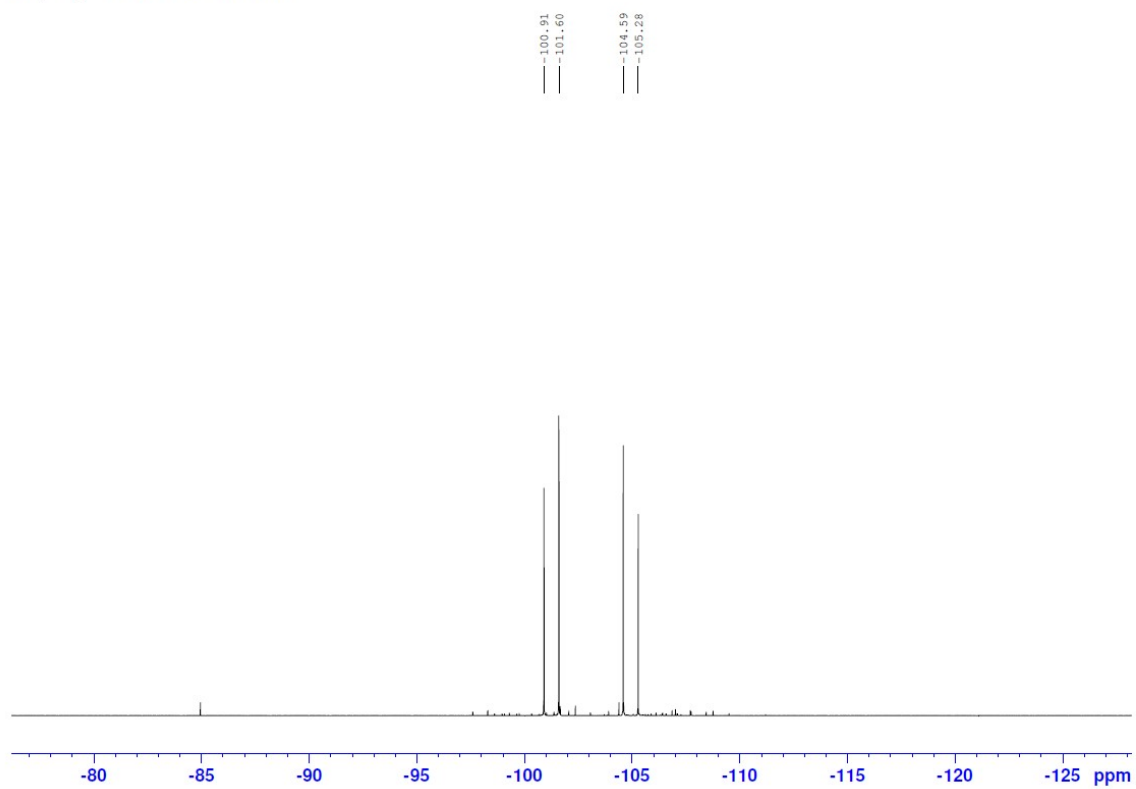
Patamawadee 23-6-65 No.3  
13C PS-P7-115 in CDCl<sub>3</sub>





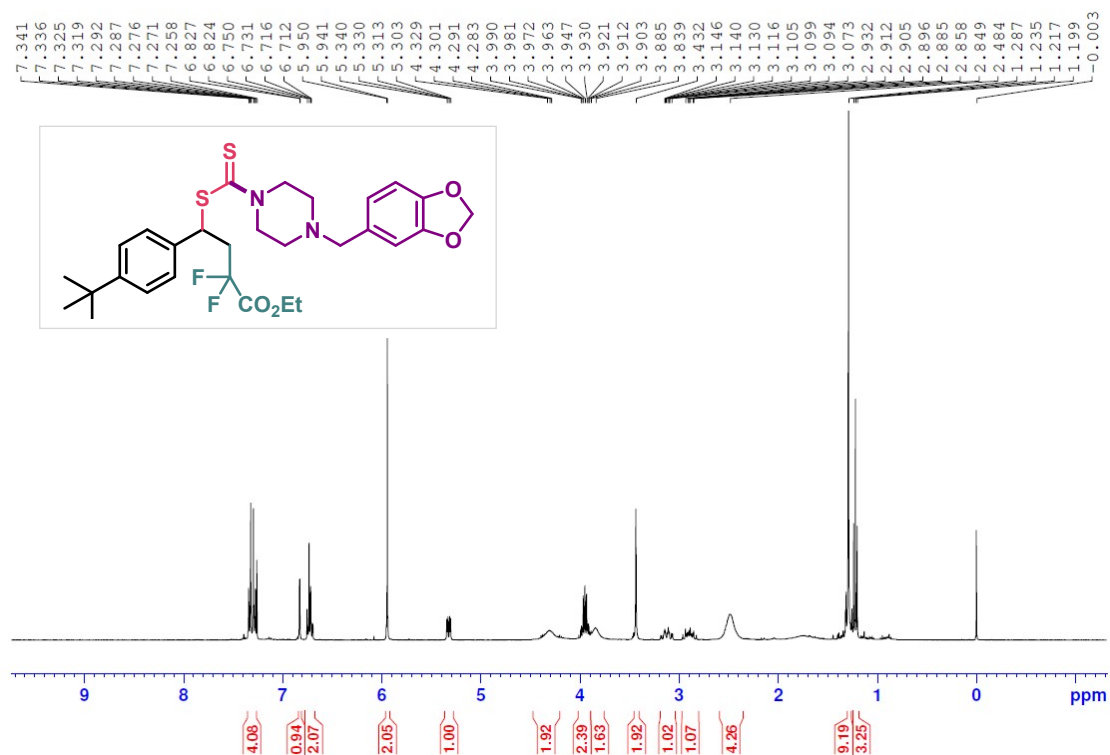
**5g**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 23-6-65 No.4  
 $^{19}\text{F}\{^1\text{H}\}$  PS-P7-115 in  $\text{CDCl}_3$



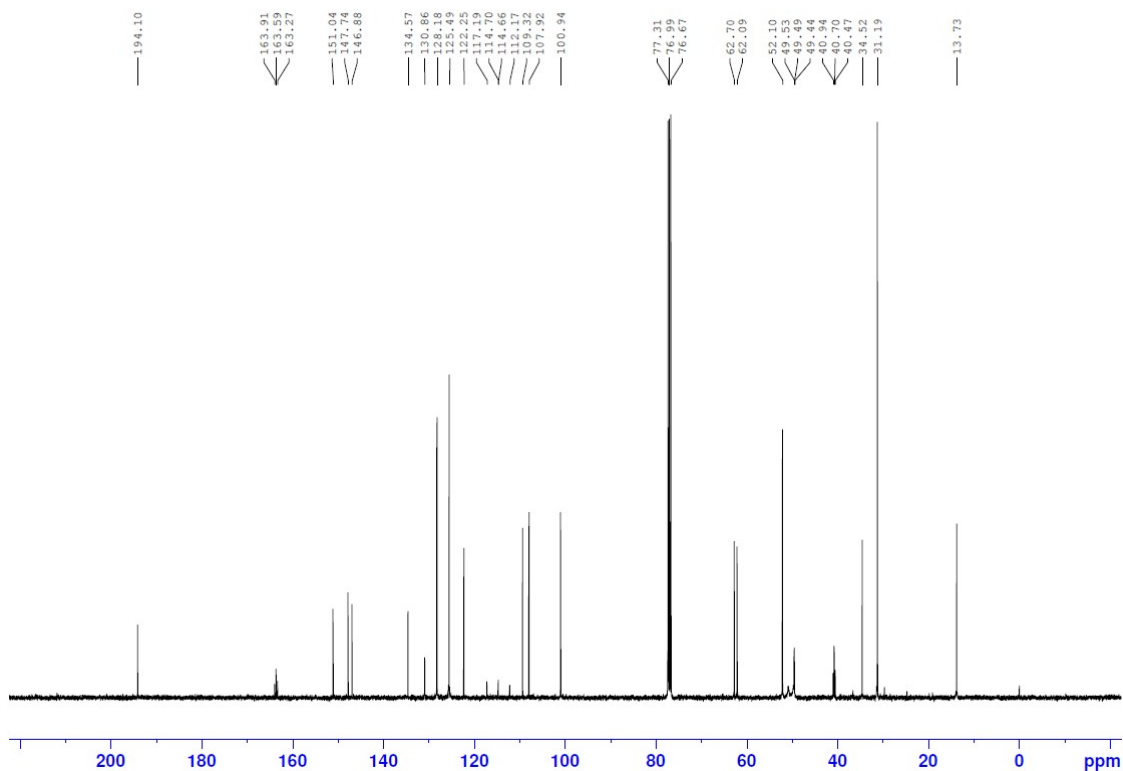
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of ethyl 4-((4-(benzo[d][1,3]dioxol-5-ylmethyl)piperazine-1-carbonothioyl)thio)-4-(4-(tert-butyl)phenyl)-2,2-difluorobutanoate (**5h**):

Patamawadee 15-6-65 No.4  
PS-P7-109 in CDCl<sub>3</sub>



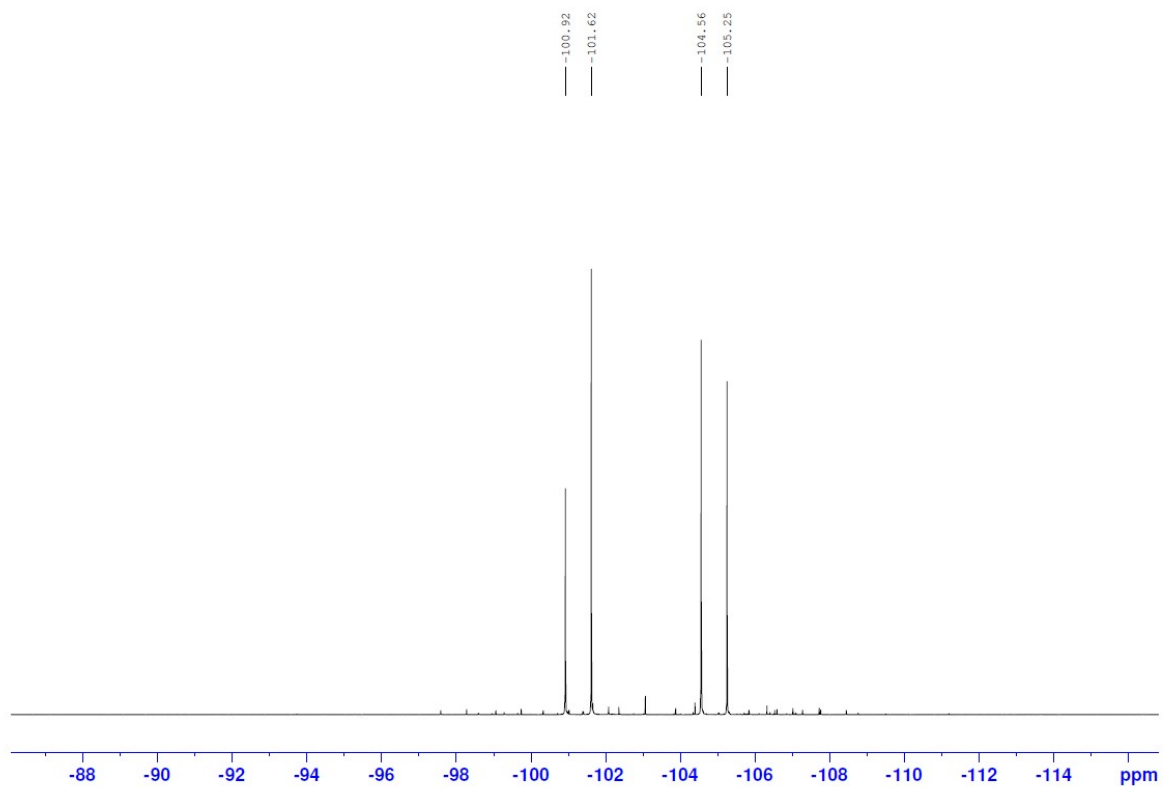
**5h** <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)

Patamawadee 16-6-65 No.1  
13C PS-P7-109 in CDCl<sub>3</sub>



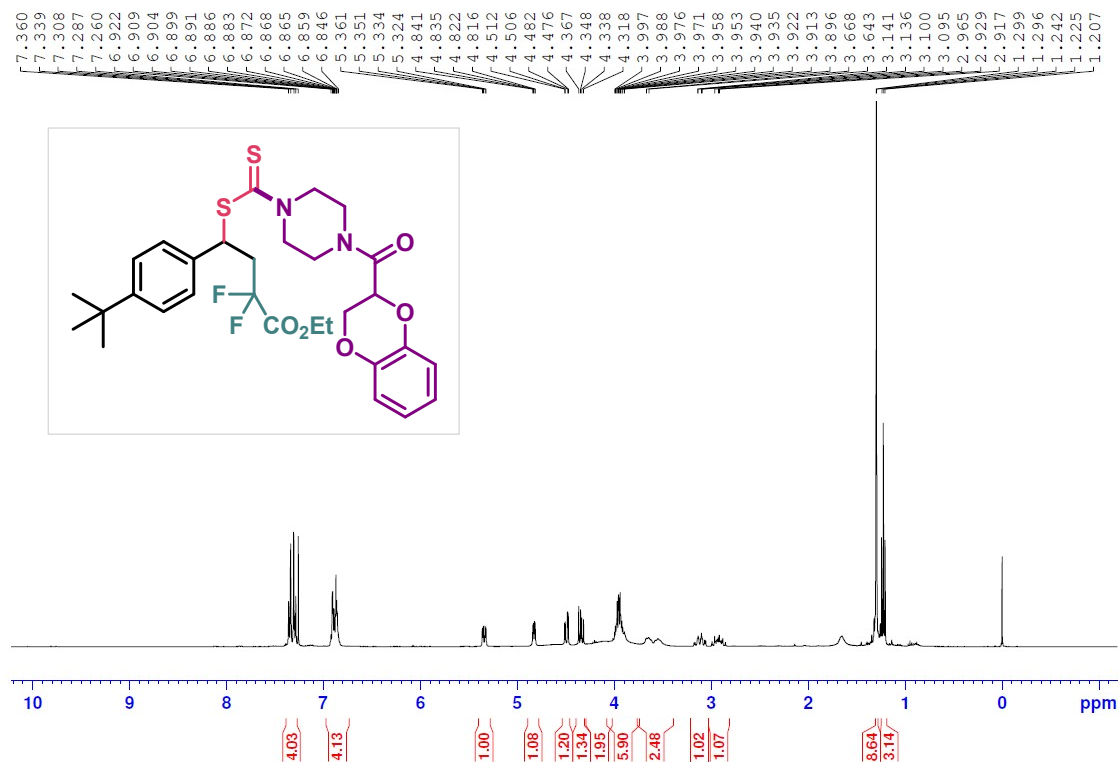
**5h**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 16-6-65 No.2  
19F{1H} PS-P7-109 in  $\text{CDCl}_3$



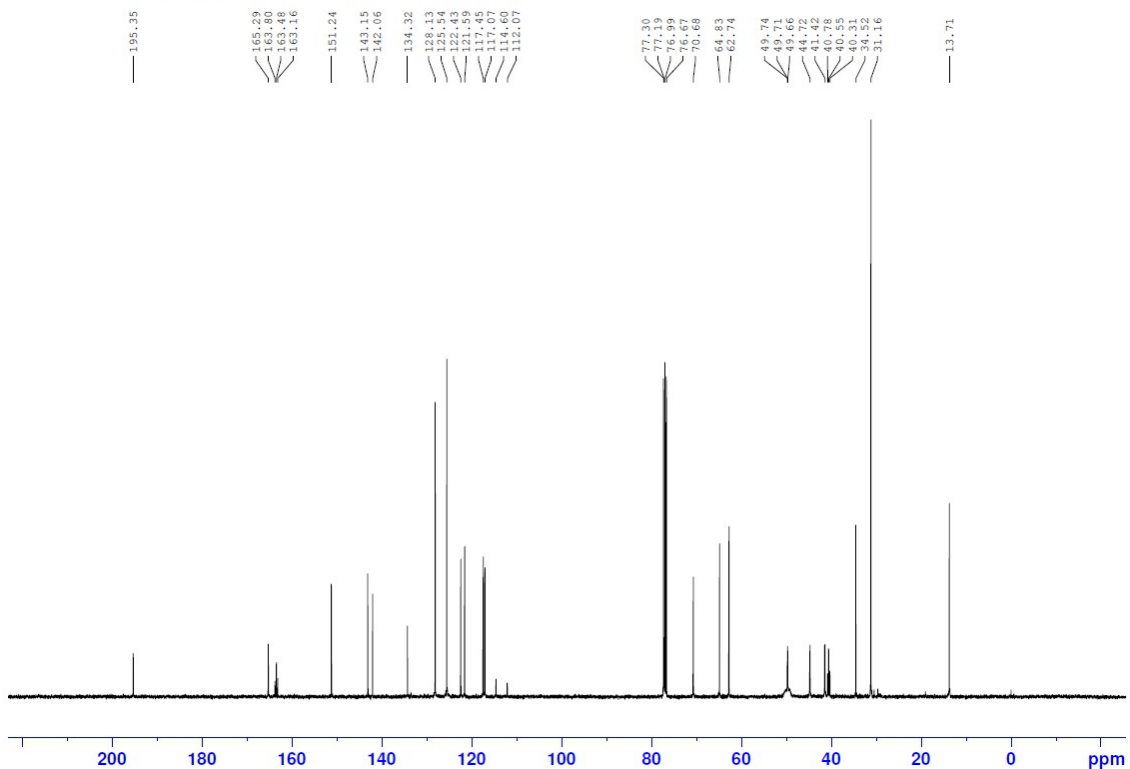
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of ethyl 4-(4-(*tert*-butyl)phenyl)-4-((4-(2,3-dihydrobenzo[*b*][1,4]dioxine-2-carbonyl)piperazine-1-carbonothioyl)thio)-2,2-difluorobutanoate (**5i**):

Patamawadee 22-6-65 No.7  
PS-P7-110 in CDCl<sub>3</sub>



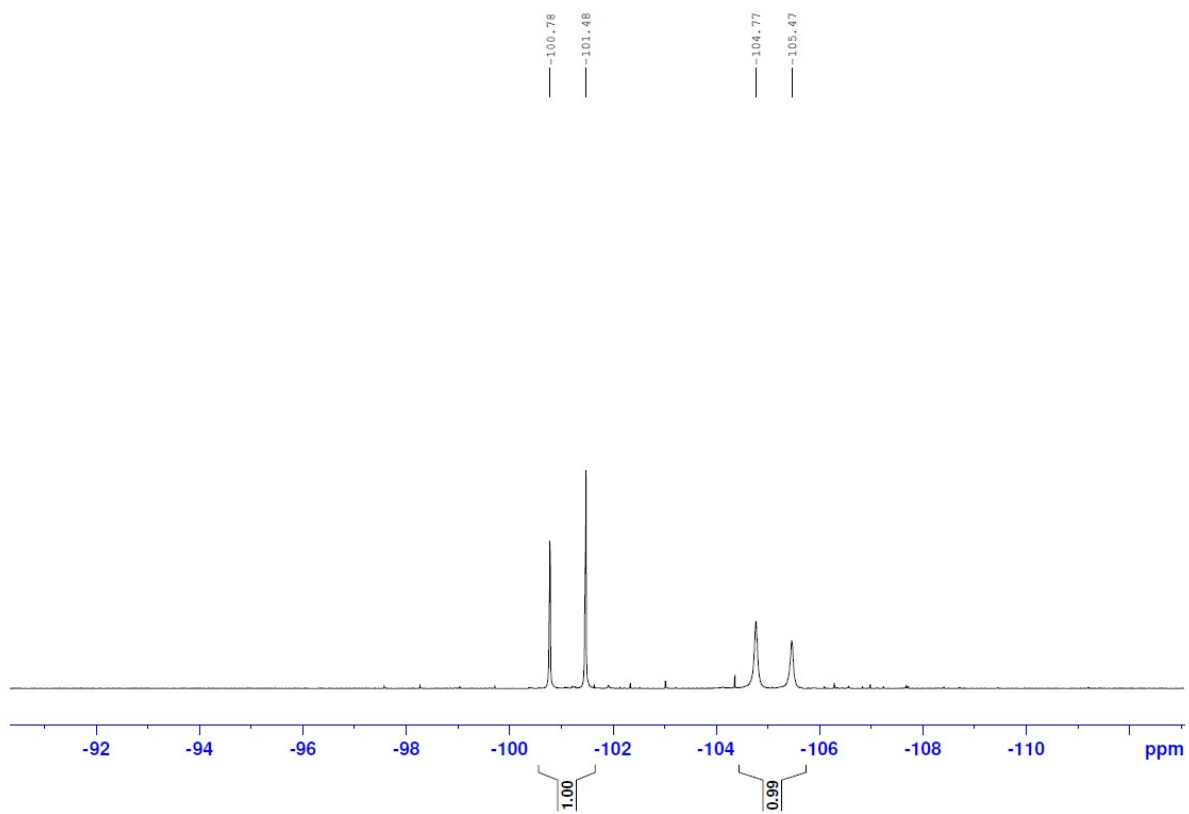
**5i** <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)

Patamawadee 23-6-65 No.1  
13C PS-P7-110 in CDCl<sub>3</sub>



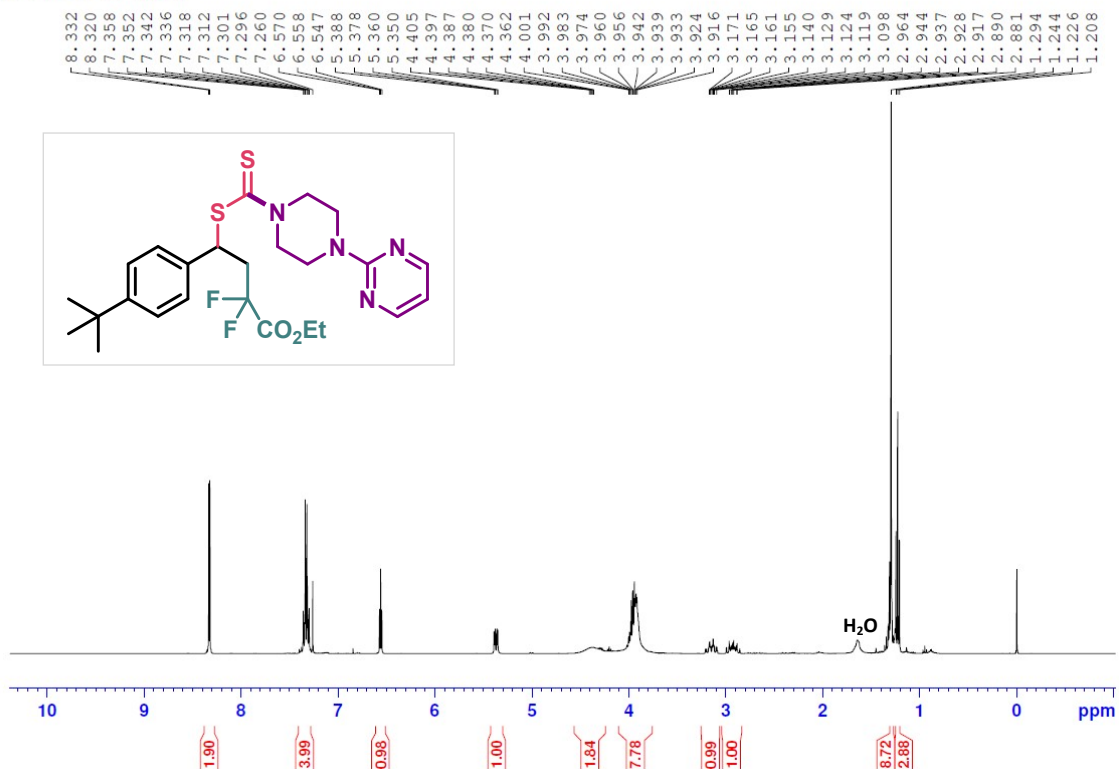
**5i**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 23-6-65 No.2  
 $^{19}\text{F}\{^1\text{H}\}$  PS-P7-110 in  $\text{CDCl}_3$



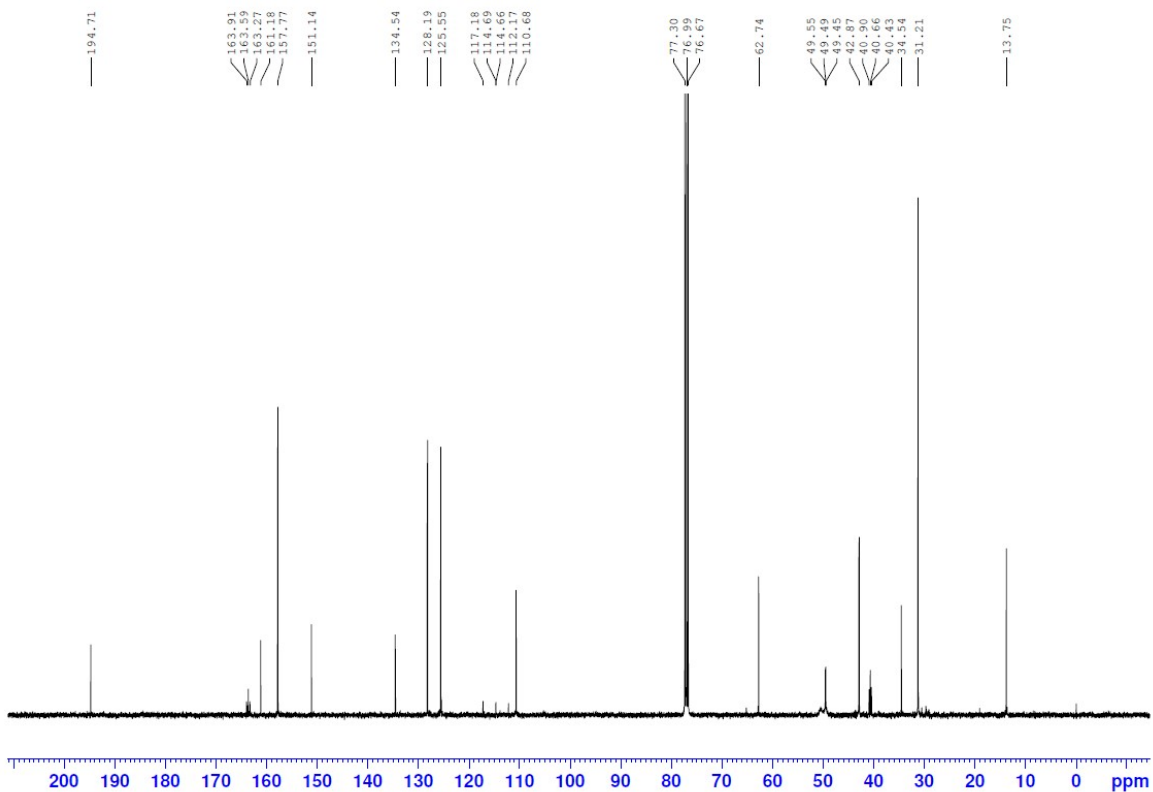
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of ethyl 4-(4-(*tert*-butyl)phenyl)-2,2-difluoro-4-((4-(pyrimidin-2-yl)piperazine-1-carbonylthio)butanoate (**5j**):

Patamawadee 22-6-65 No.1  
PS-P7-114 in  $\text{CDCl}_3$



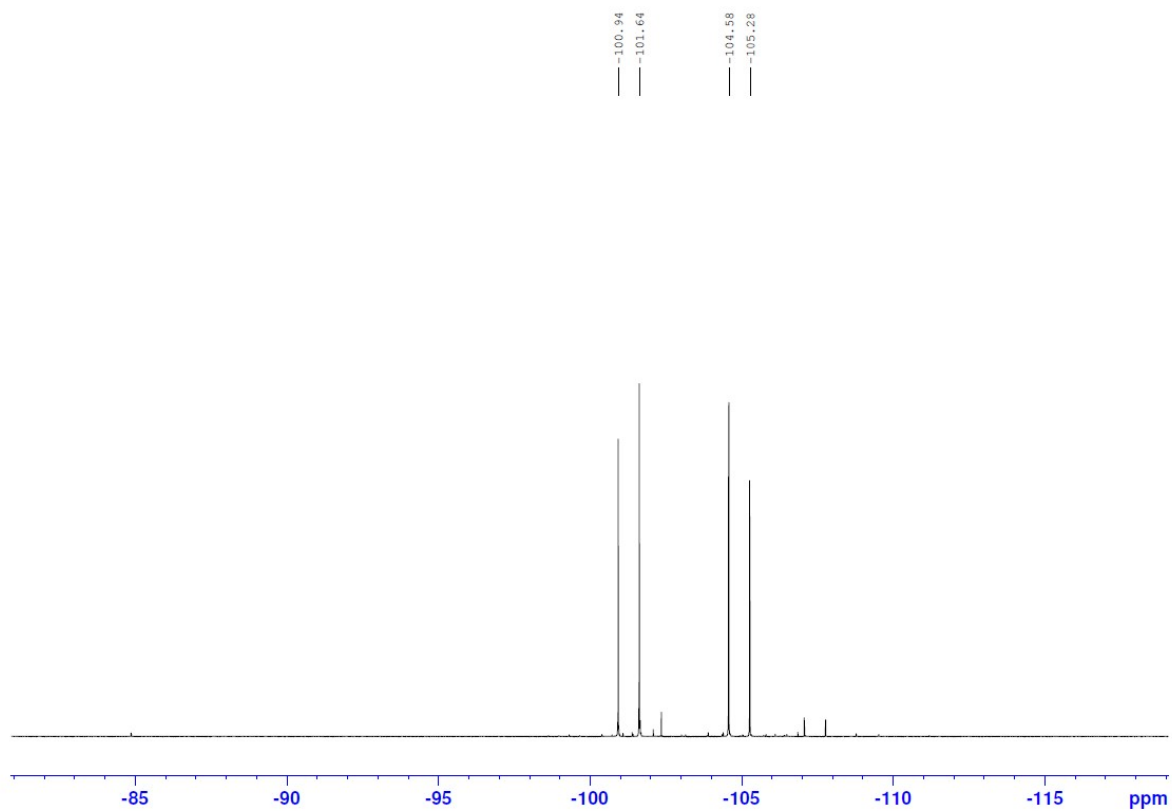
**5j**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 21-6-65 No.2  
 $^{13}\text{C}$  PS-P7-114 in  $\text{CDCl}_3$



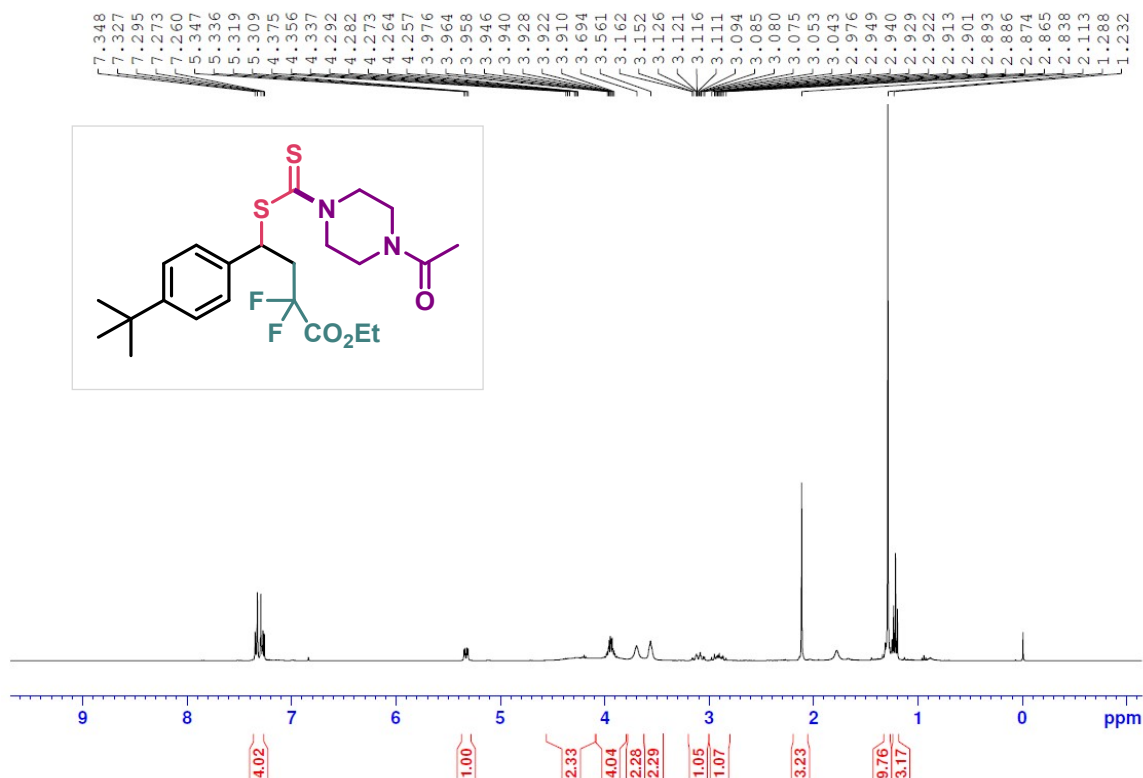
**5j**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 21-6-65 No.3  
 $^{19}\text{F}\{^1\text{H}\}$  PS-P7-114 in  $\text{CDCl}_3$



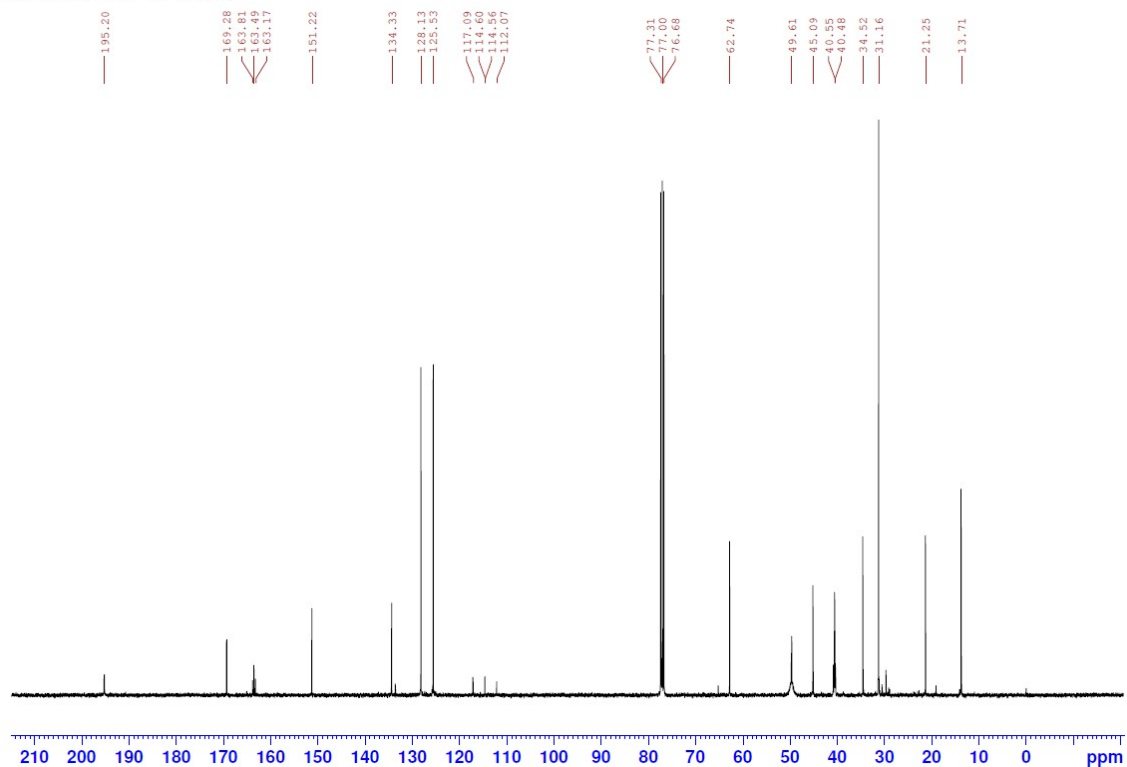
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of ethyl 4-(4-(*tert*-butyl)phenyl)-2,2-difluoro-4-((4-(pyrimidin-2-yl)piperazine-1-carbonylthio)butanoate) (5I):

Patamawadee 28-9-65 No.3  
PS-P7-224 in  $\text{CDCl}_3$



$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 29-9-65 No.2  
13C PS-P7-224 in  $\text{CDCl}_3$





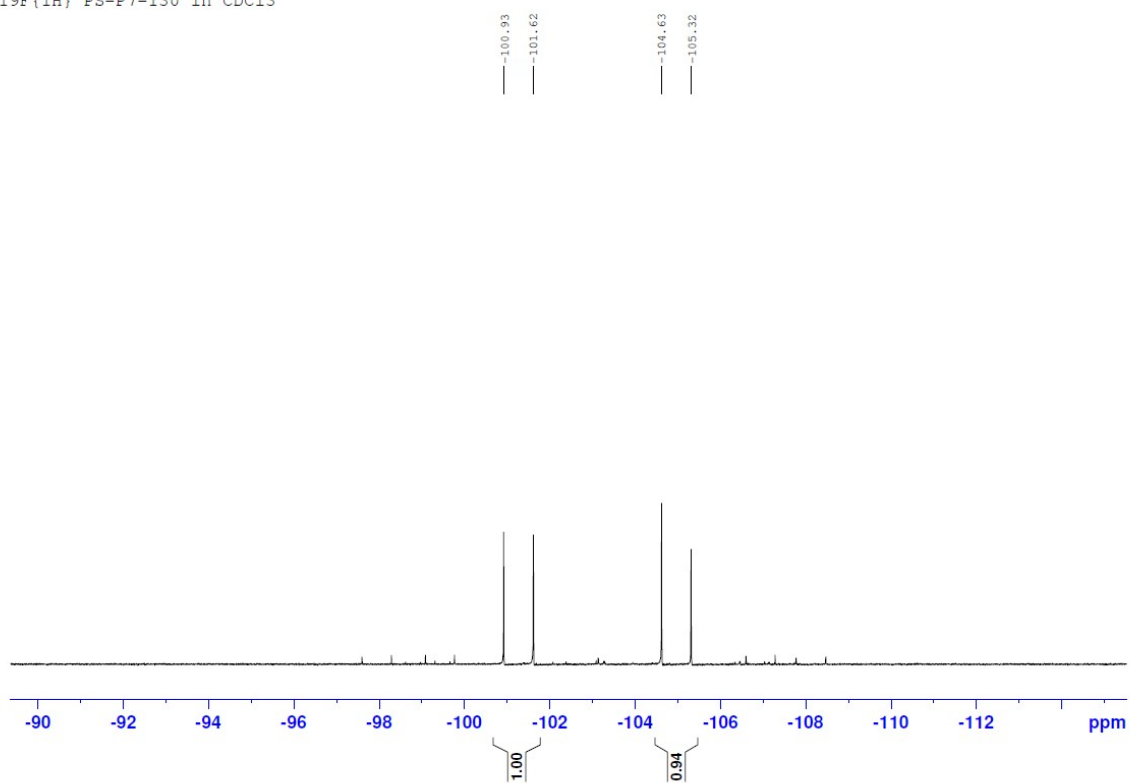
**5I**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )





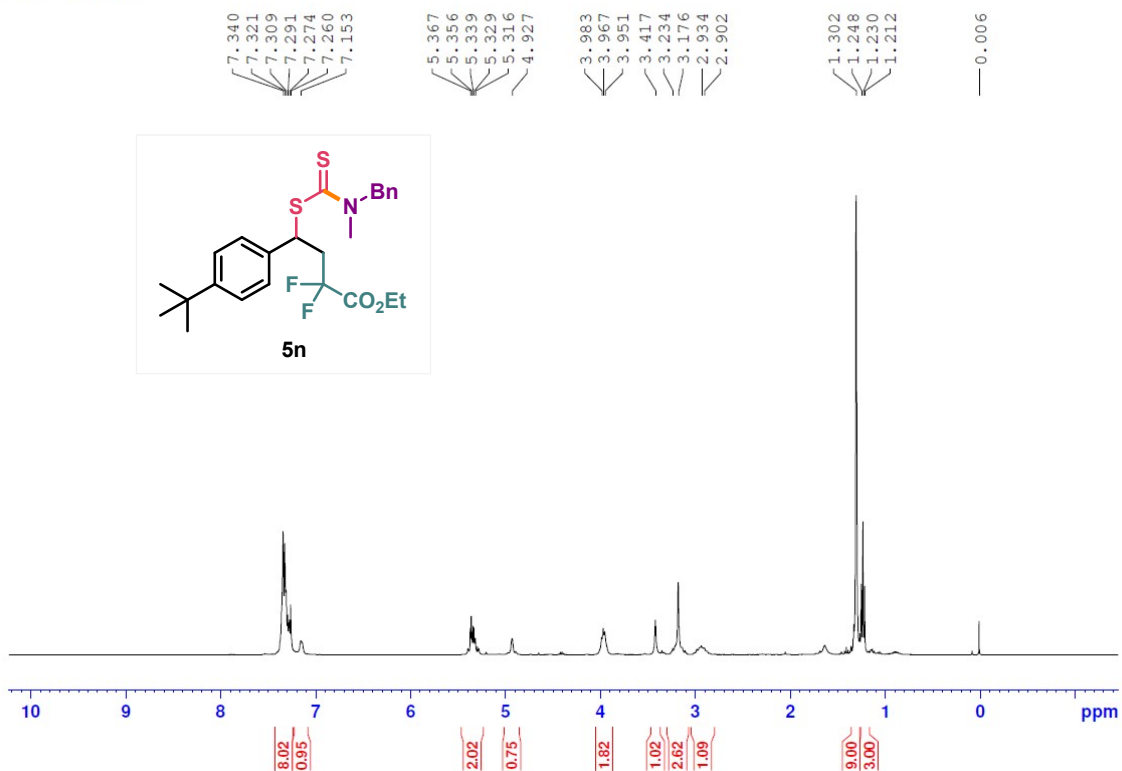
**5m**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 6-7-65 No.3  
 $^{19}\text{F}\{^1\text{H}\}$  PS-P7-130 in  $\text{CDCl}_3$



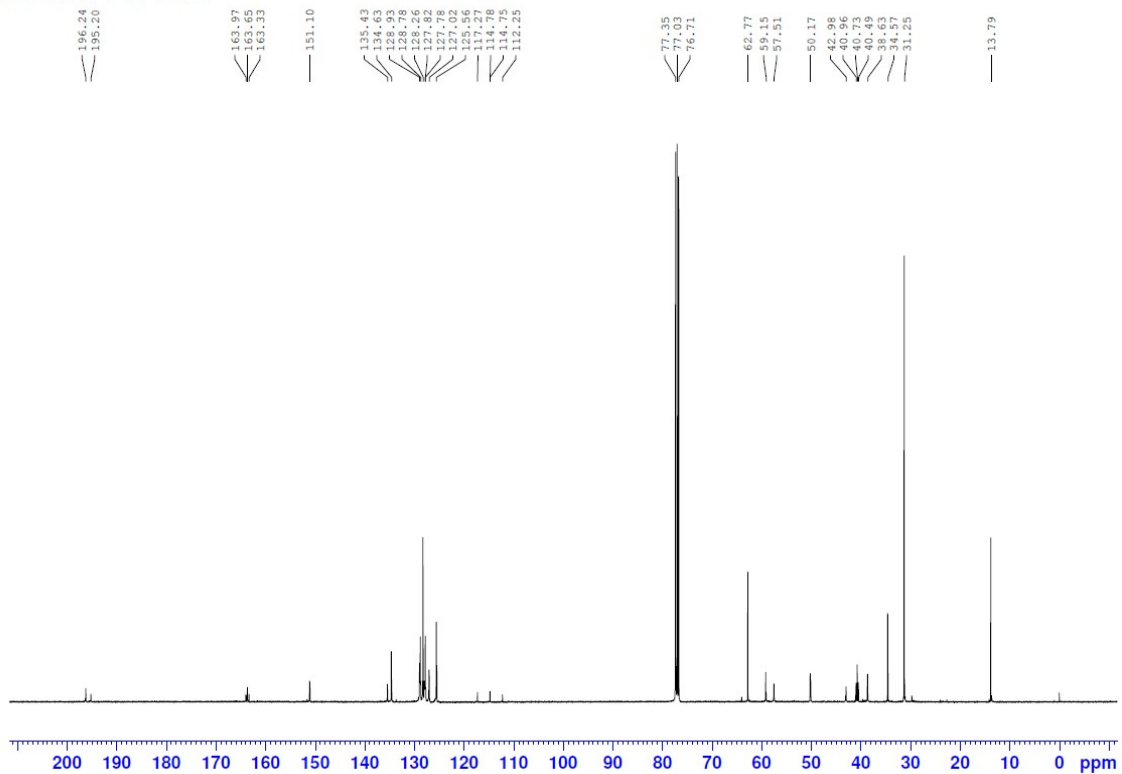
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of ethyl 4-((benzyl(methyl)carbamothioyl)thio)-4-(4-(tert-butyl)phenyl)-2,2-difluorobutanoate (**5n**):

Patamawadee 30-5-67 No.2  
PS-P8-7 in  $\text{CDCl}_3$



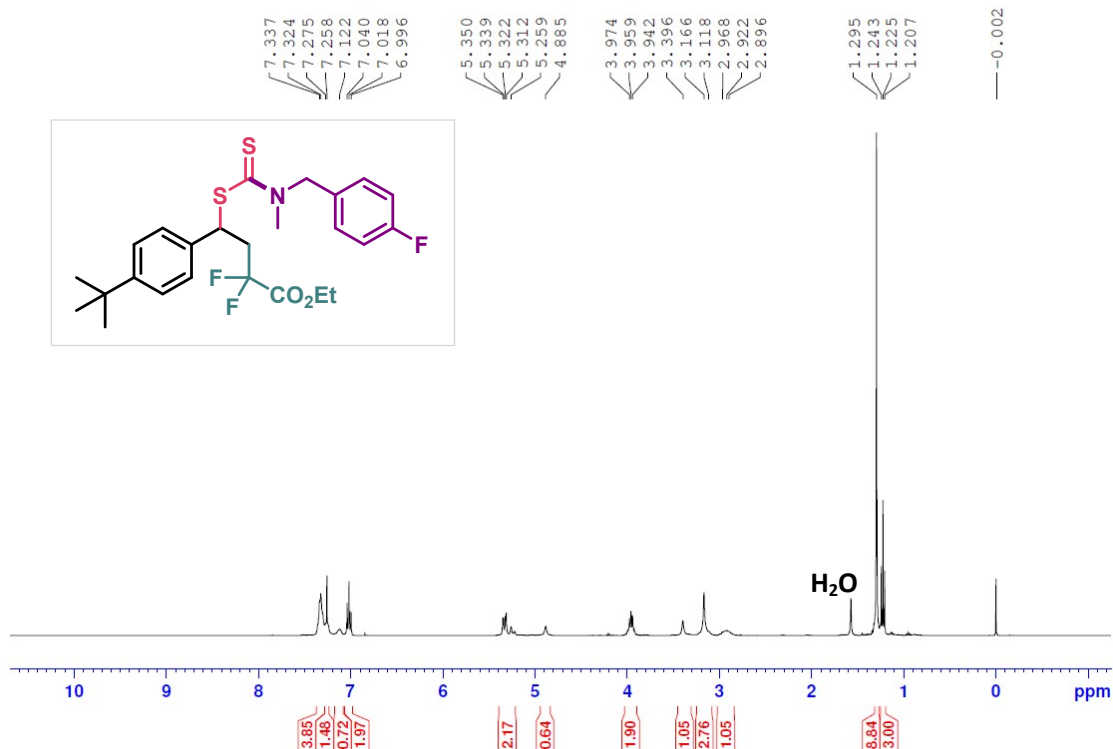
**5n**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 31-5-67 No.1  
 $^{13}\text{C}$  PS-P8-7 in  $\text{CDCl}_3$



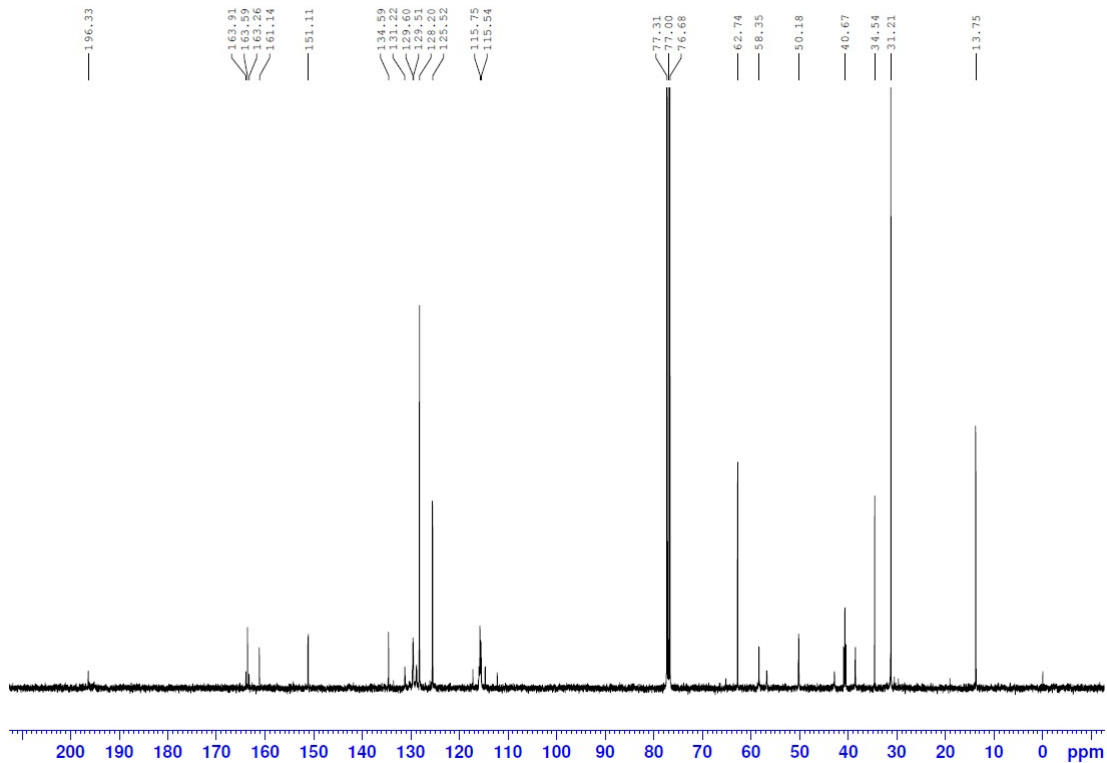
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of ethyl 4-(4-(*tert*-butyl)phenyl)-2,2-difluoro-4-(((4-fluorobenzyl)(methyl)carbamothioyl)thio)butanoate (**5o**):

Patamawadee 22-6-65 No.5  
PS-P7-117 in  $\text{CDCl}_3$



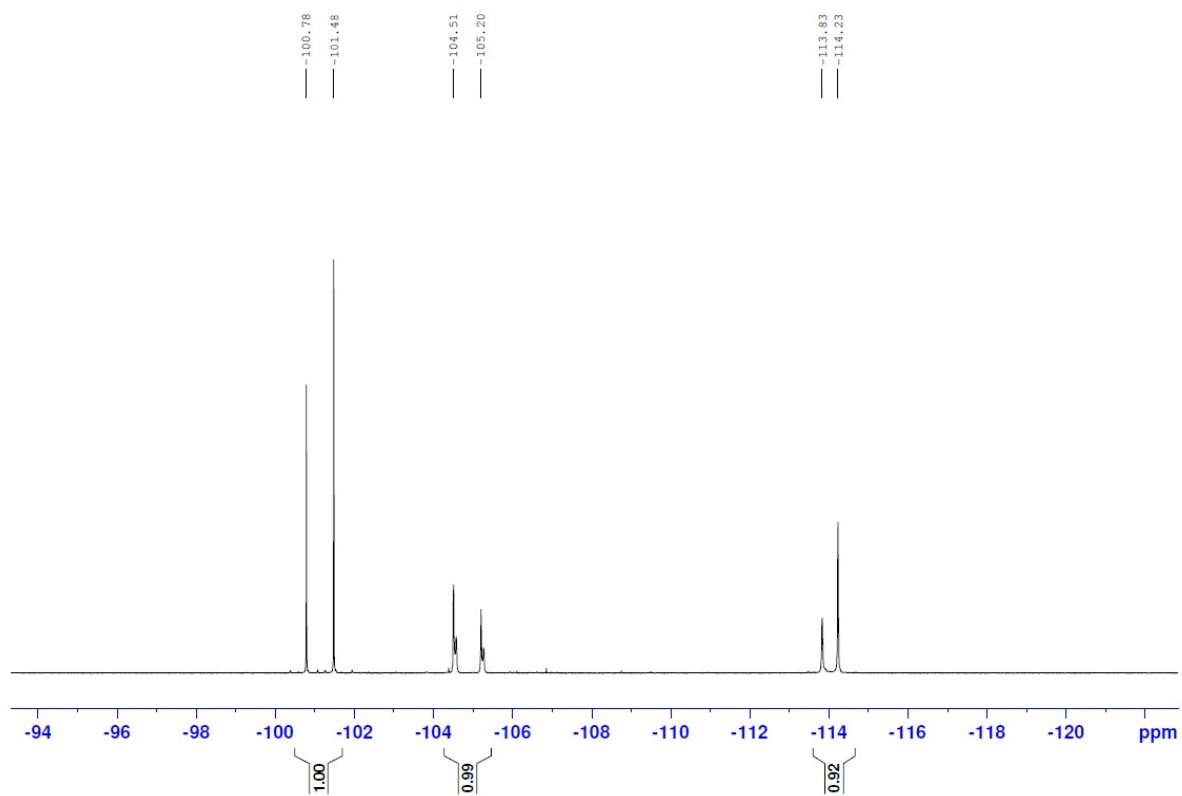
**5o**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 23-6-65 No.5  
 $^{13}\text{C}$  PS-P7-117 in  $\text{CDCl}_3$



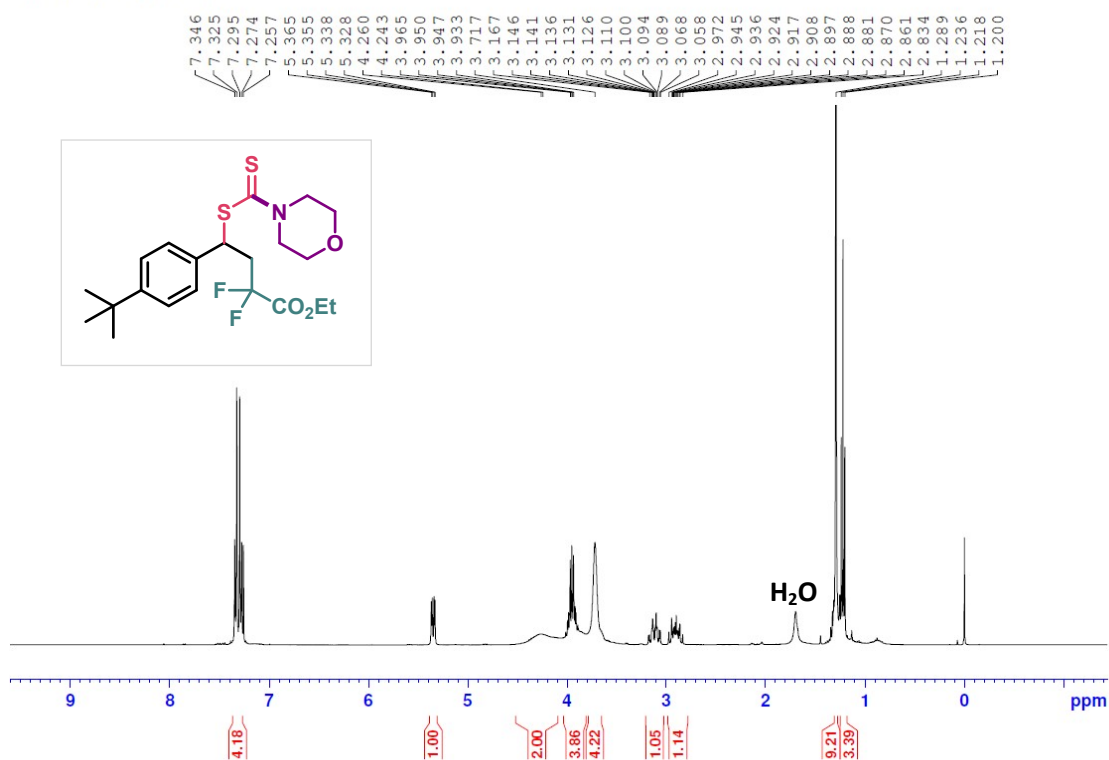
**5o**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 23-6-65 No.6  
 $^{19}\text{F}\{^1\text{H}\}$  PS-P7-117 in  $\text{CDCl}_3$



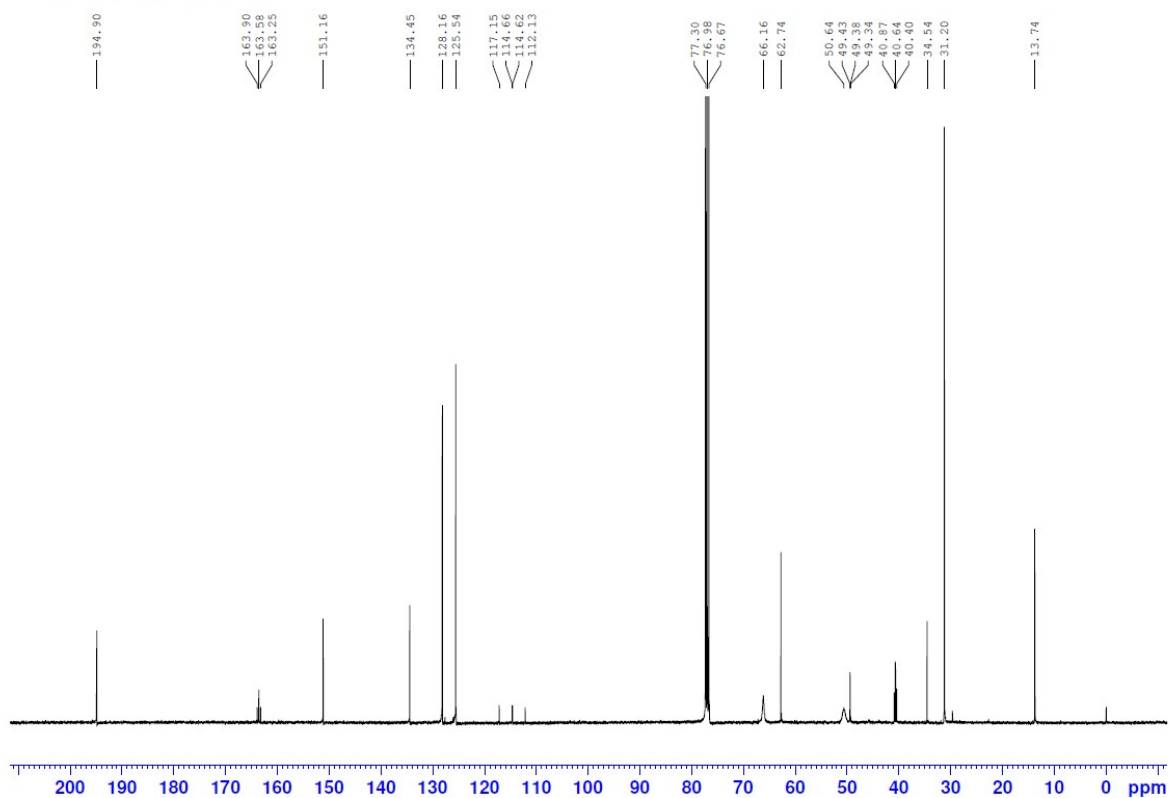
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of ethyl 4-(4-(*tert*-butyl)phenyl)-2,2-difluoro-4-((morpholine-4-carbonothioyl)thio)butanoate (**5p**):

Patamawadee 27-5-67 No.16  
PS-P7-131-1 in  $\text{CDCl}_3$



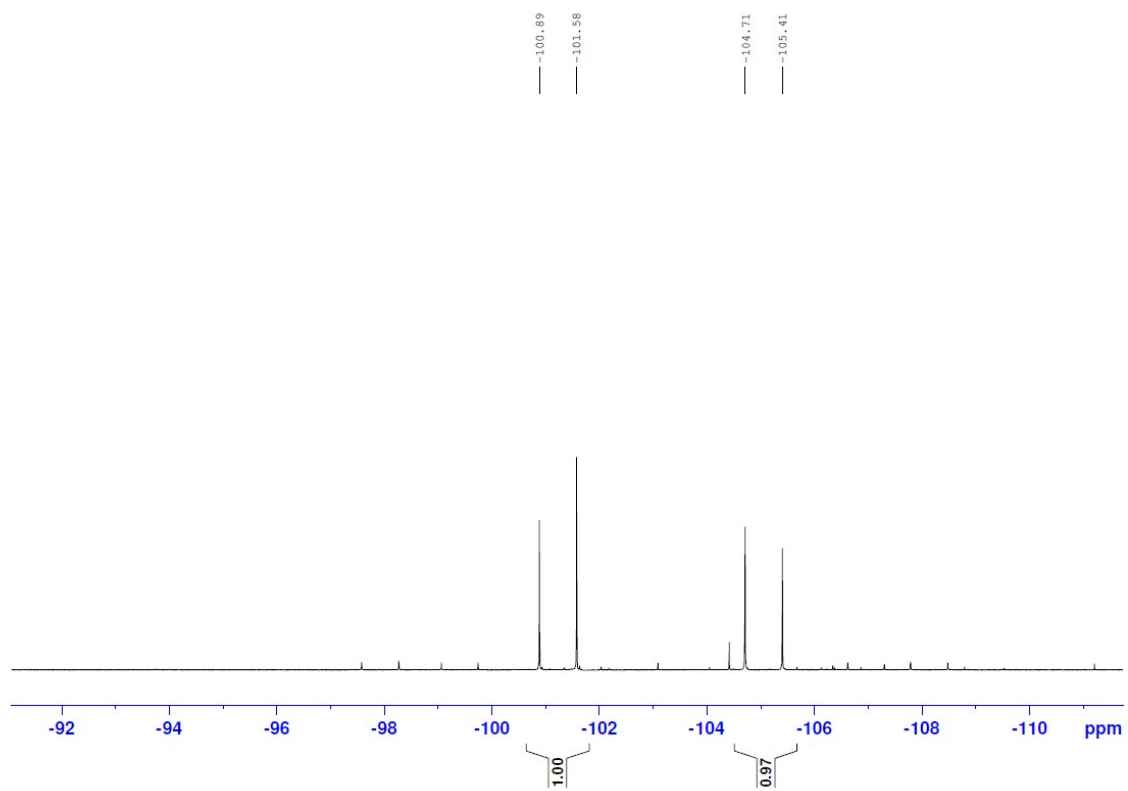
**5p**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 27-5-67 No.17  
 $^{13}\text{C}$  PS-P7-131-1 in  $\text{CDCl}_3$



**5p**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

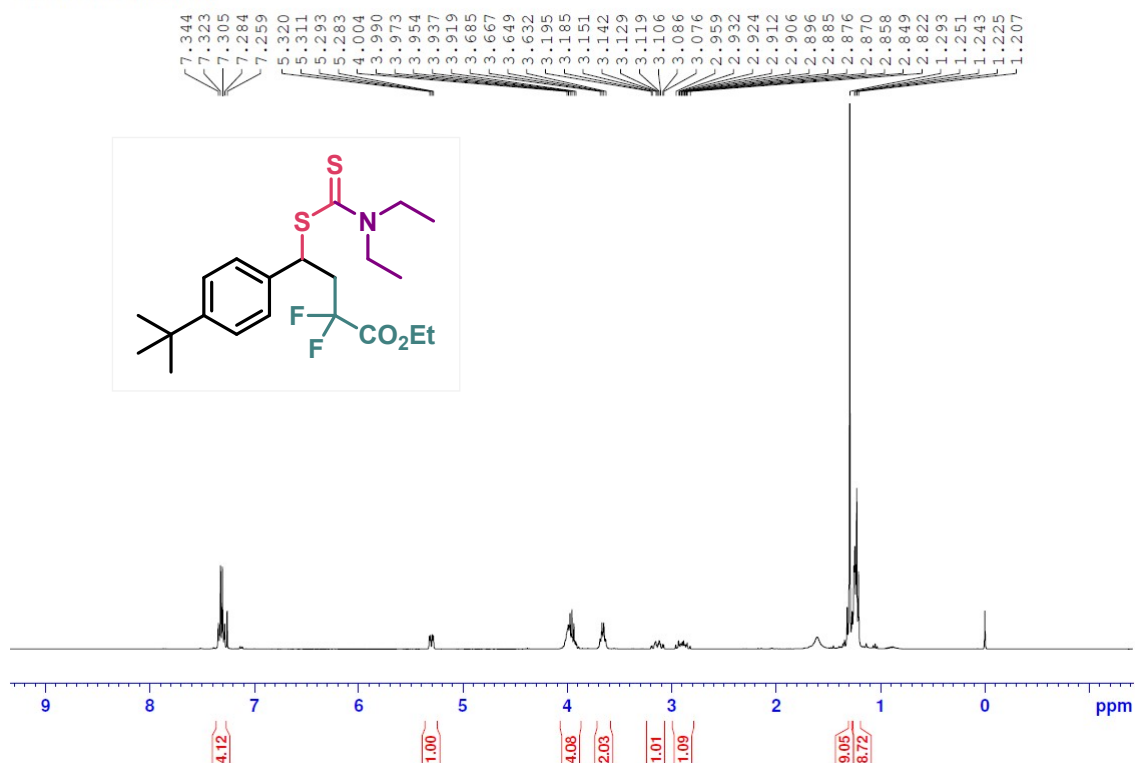
Patamawadee 29-6-65 No.3  
 $^{19}\text{F}\{^1\text{H}\}$  PS-P7-131 in  $\text{CDCl}_3$





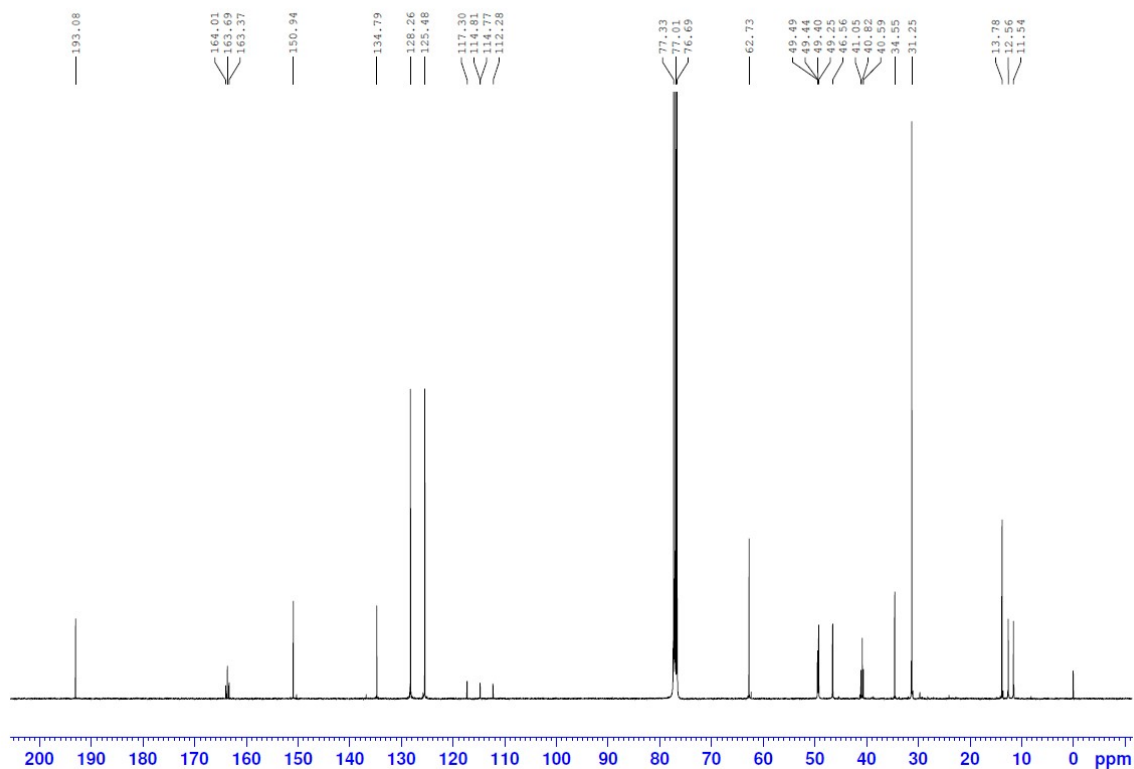
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of ethyl 4-(4-(*tert*-butyl)phenyl)-4-((diethylcarbamothioyl)thio)-2,2-difluorobutanoate (**5q**):

Patamawadee 14-6-67 No.1  
PS-P8-17-1 in  $\text{CDCl}_3$



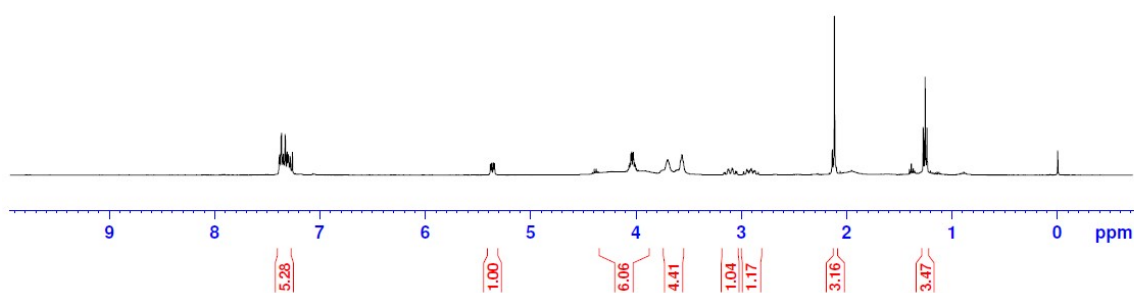
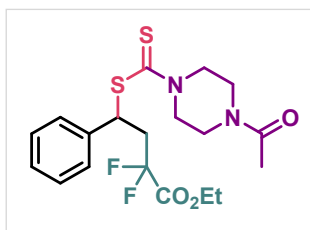
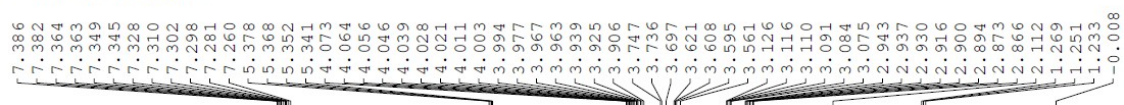
**5q**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 14-6-67 No.  
 $^{13}\text{C}$  PS-P8-17-1 in  $\text{CDCl}_3$



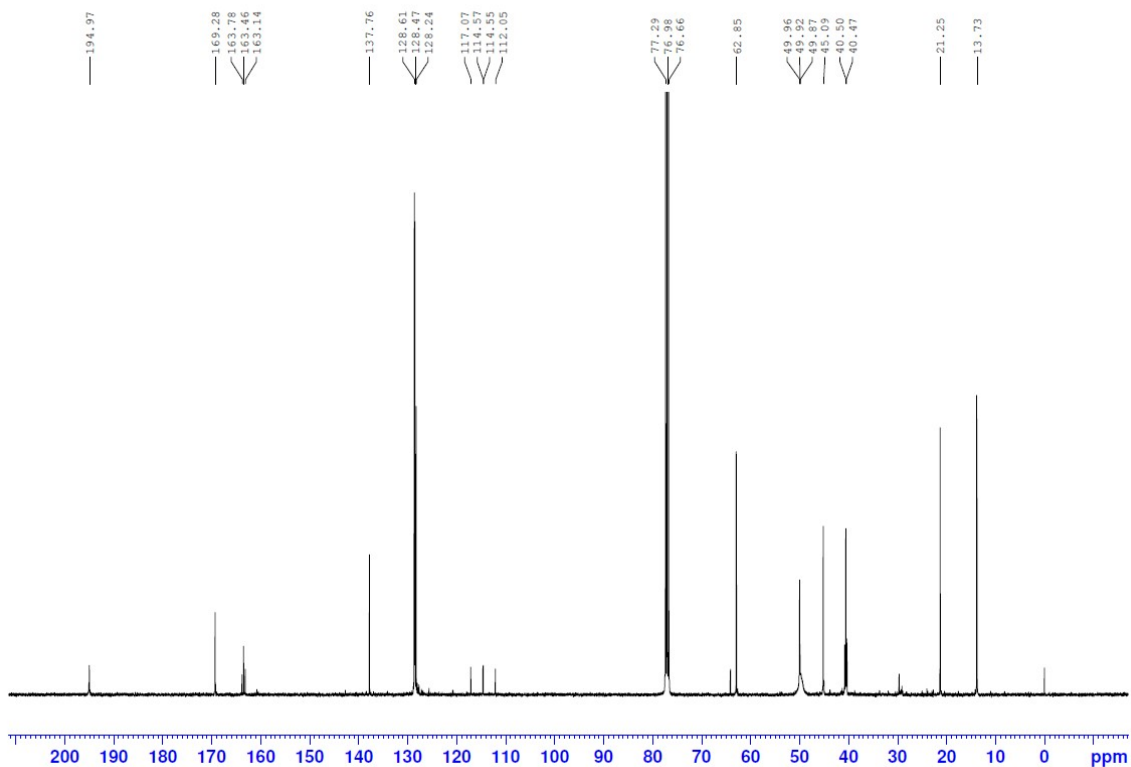
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of ethyl 4-((4-acetylpiperazine-1-carbonylthio)-2,2-difluoro-4-phenylbutanoate (**6a**):

Patamawadee 13-9-65 No.4  
PS-P7-201 in  $\text{CDCl}_3$



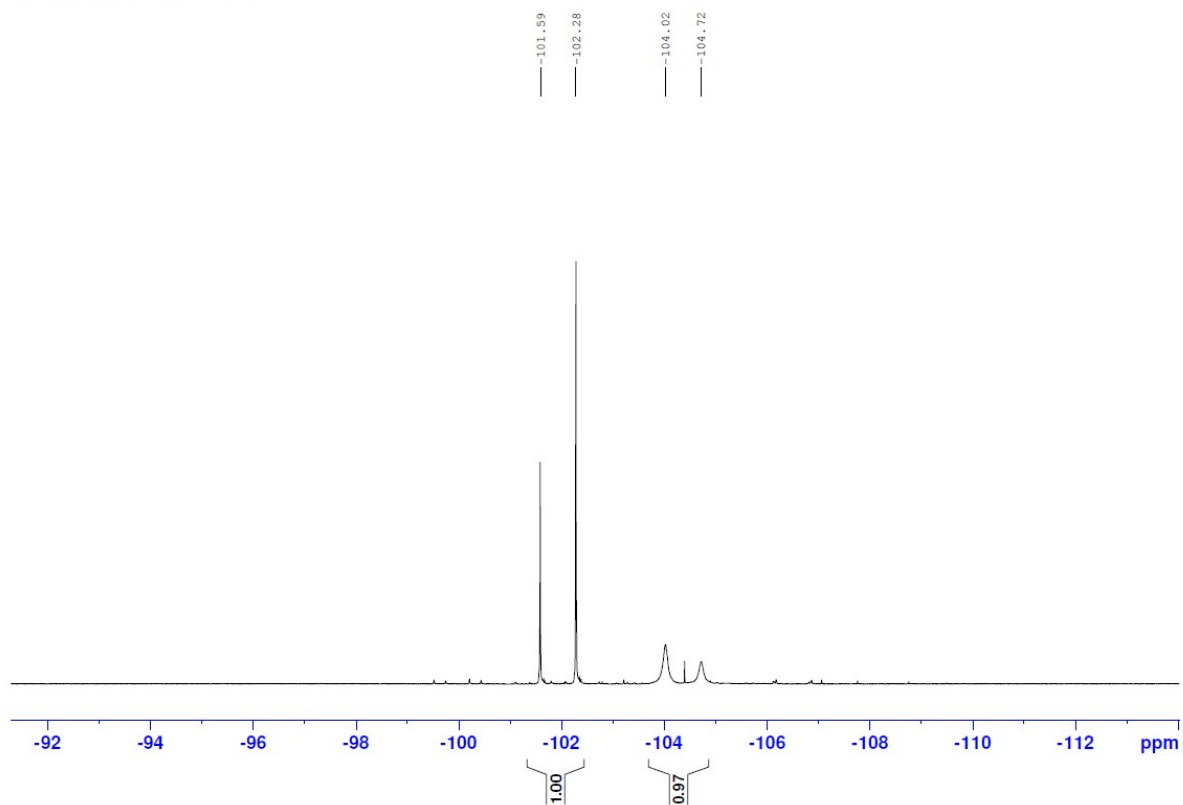
**6a**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 13-9-65 No.6  
13C PS-P7-201 in  $\text{CDCl}_3$



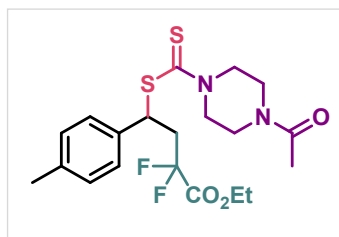
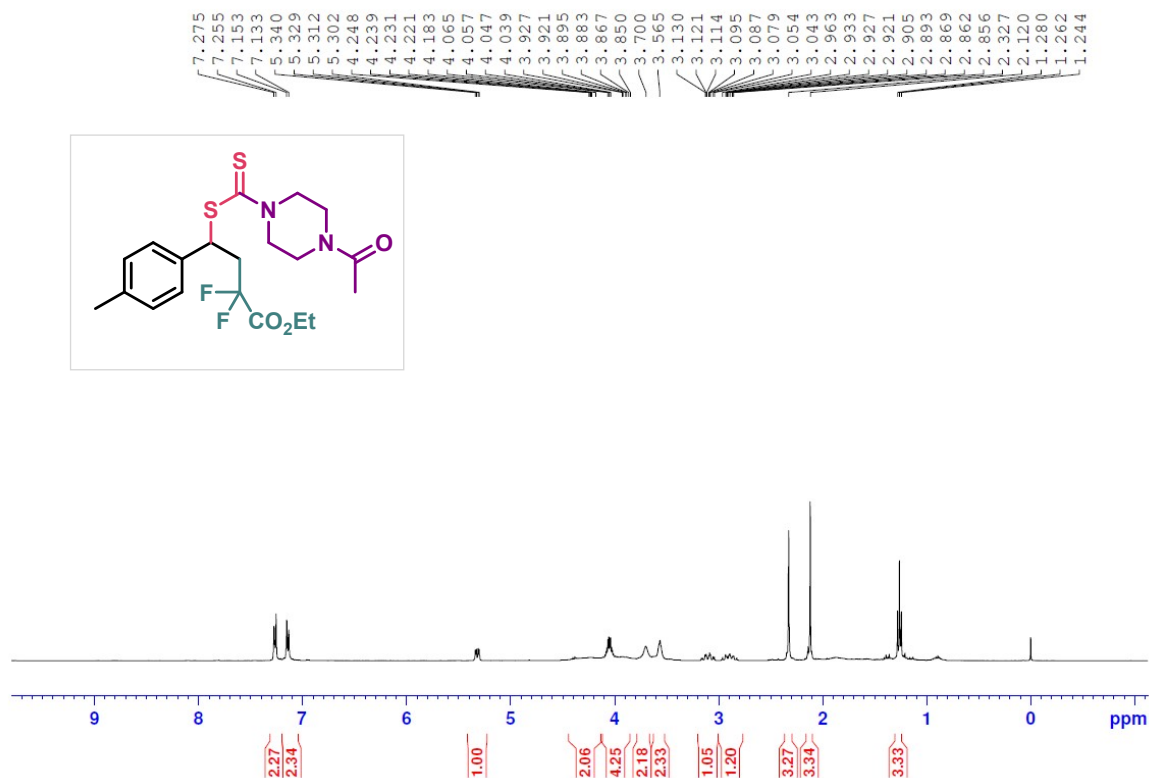
**6a**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 13-9-65 No.5  
19F PS-P7-201 in  $\text{CDCl}_3$



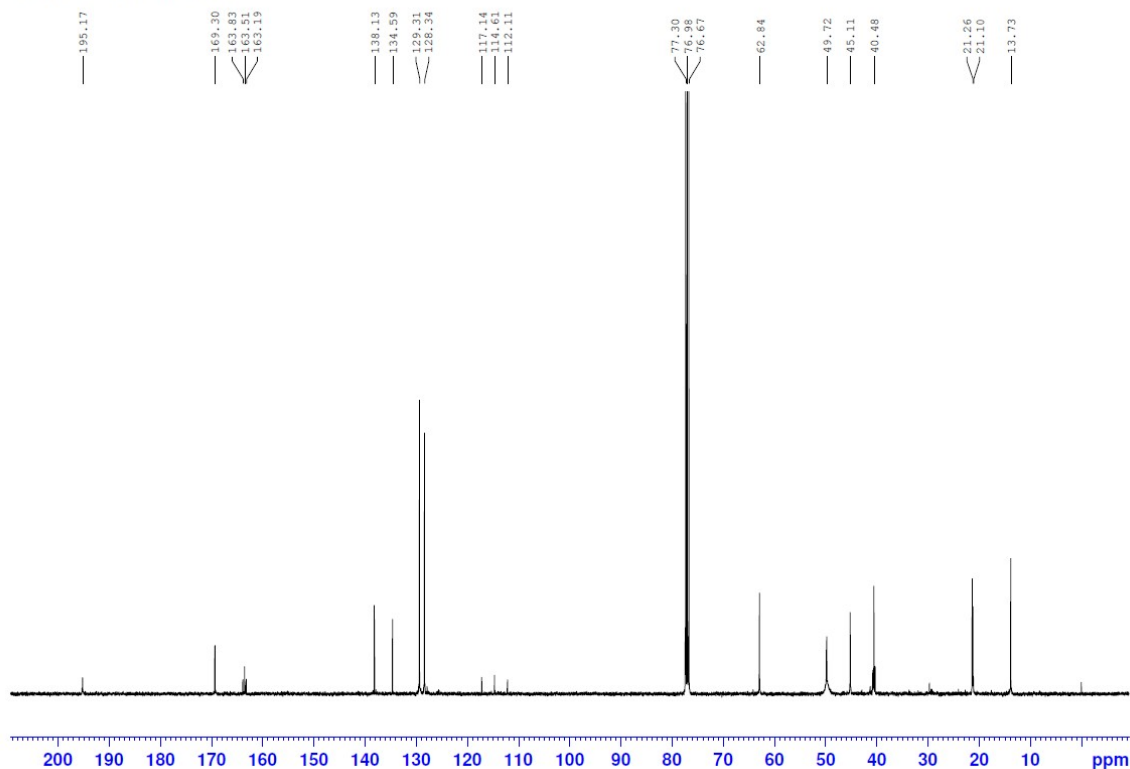
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of ethyl 4-((4-acetylpiperazine-1-carbonylthio)-2,2-difluoro-4-(p-tolyl)butanoate (**6b**):

Patamawadee 9-9-65 No.5  
PS-P7-202 in  $\text{CDCl}_3$



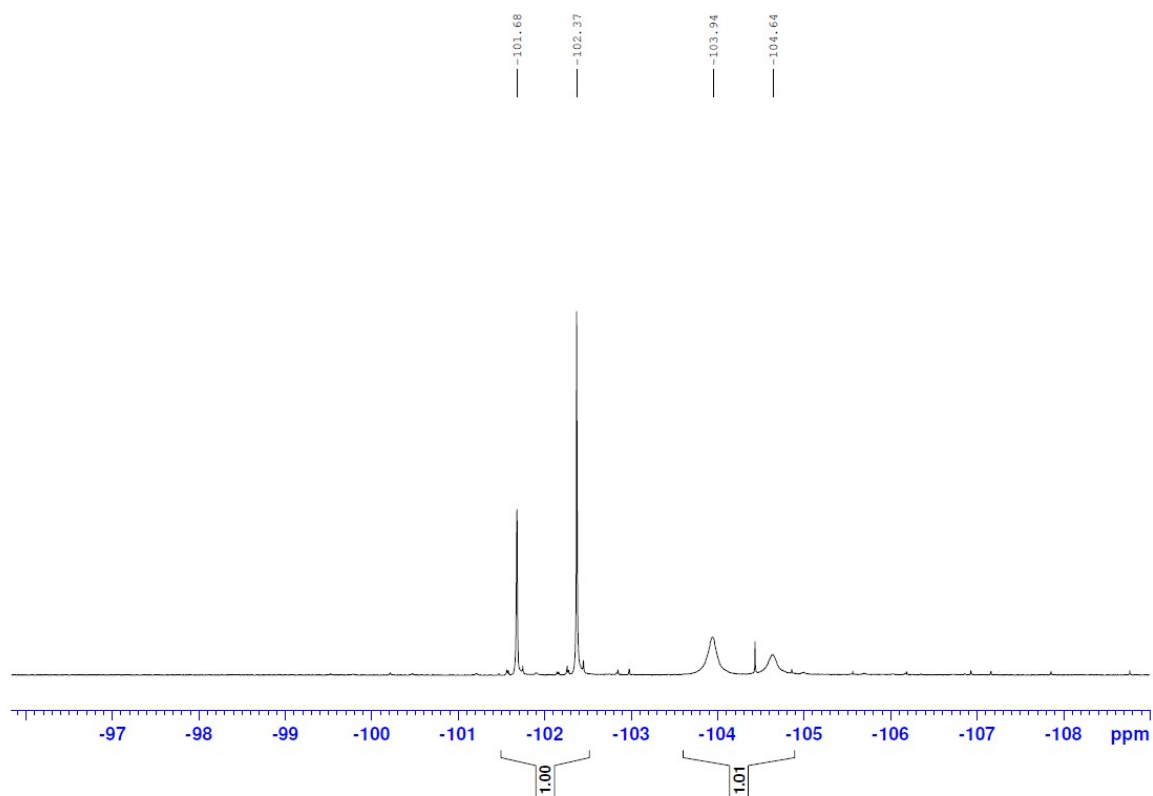
**6b**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 13-9-65 No.3  
13C PS-P7-202 in  $\text{CDCl}_3$



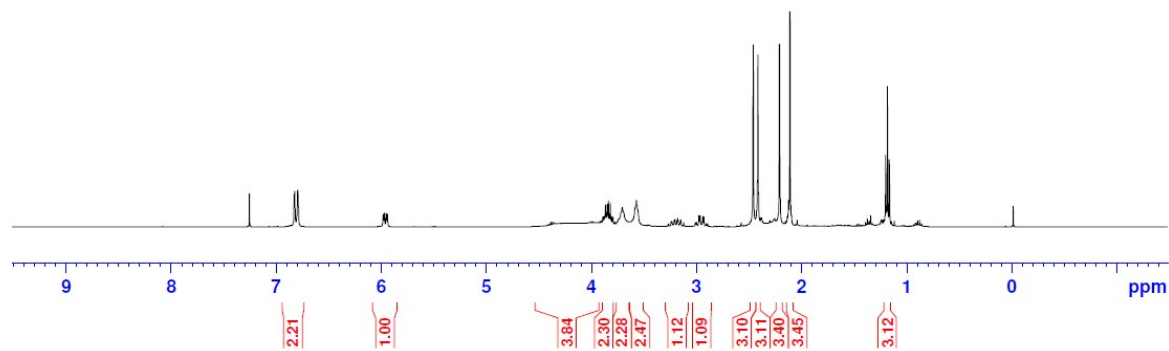
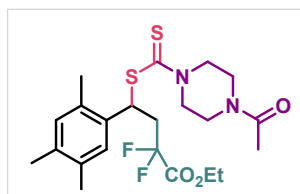
**6b**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 13-9-65 No.2  
19F PS-P7-202 in  $\text{CDCl}_3$



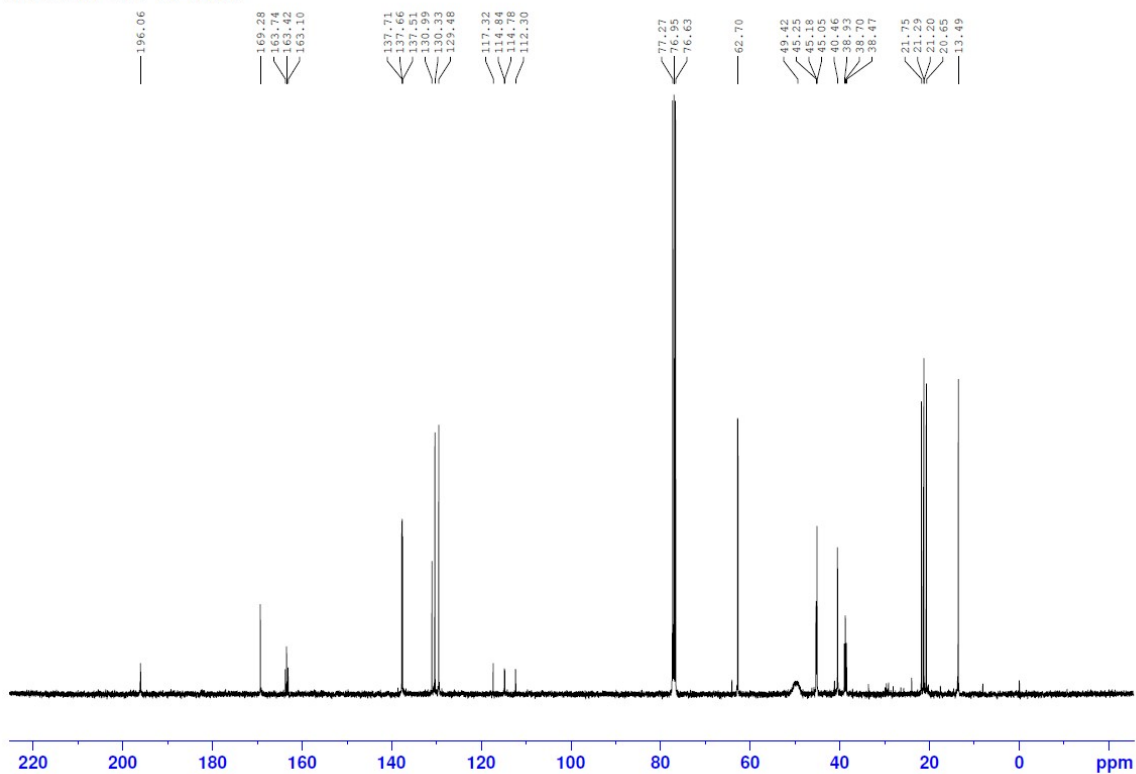
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of ethyl 4-((4-acetylpiperazine-1-carbonothioyl)thio)-2,2-difluoro-4-(2,4,5-trimethylphenyl)butanoate (**6c**):

Patamawadee 14-9-65 No.6  
PS-P7-199 in CDCl<sub>3</sub>



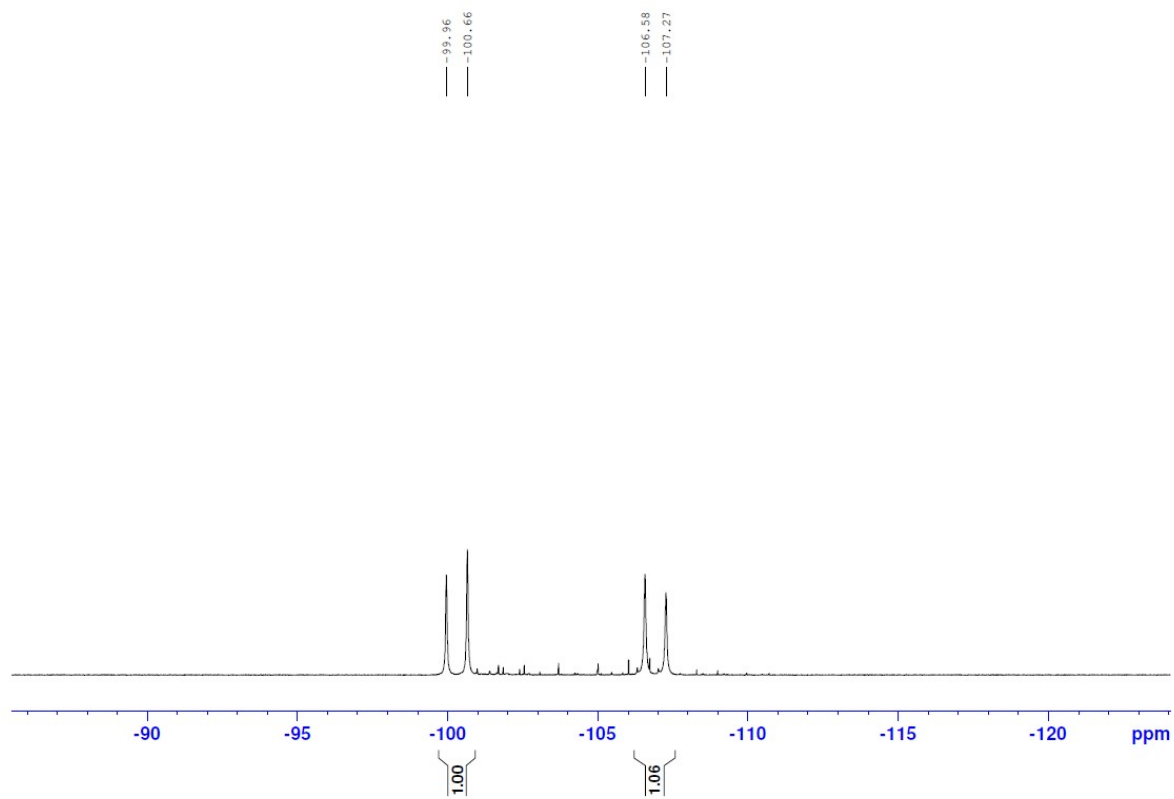
**6c** <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)

Patamawadee 14-9-65 No.8  
<sup>13</sup>C PS-P7-199 in CDCl<sub>3</sub>



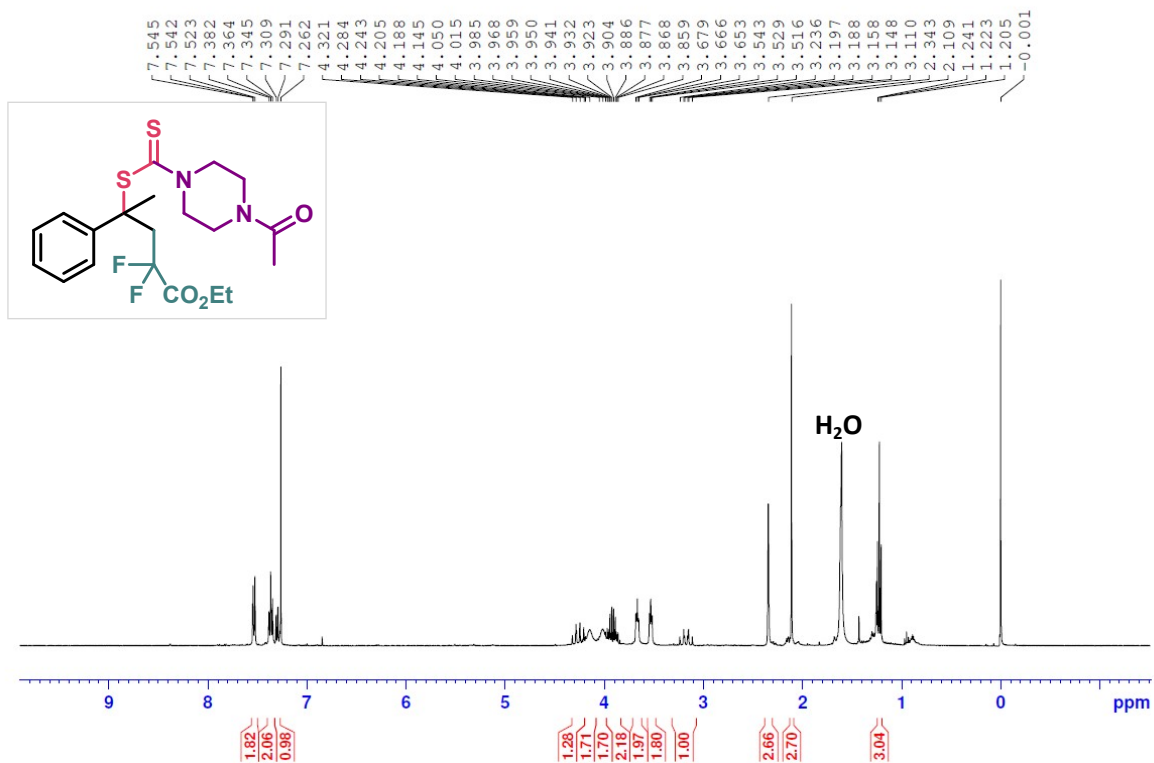
**6c**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 14-9-65 No.7  
19F PS-P7-199 in  $\text{CDCl}_3$



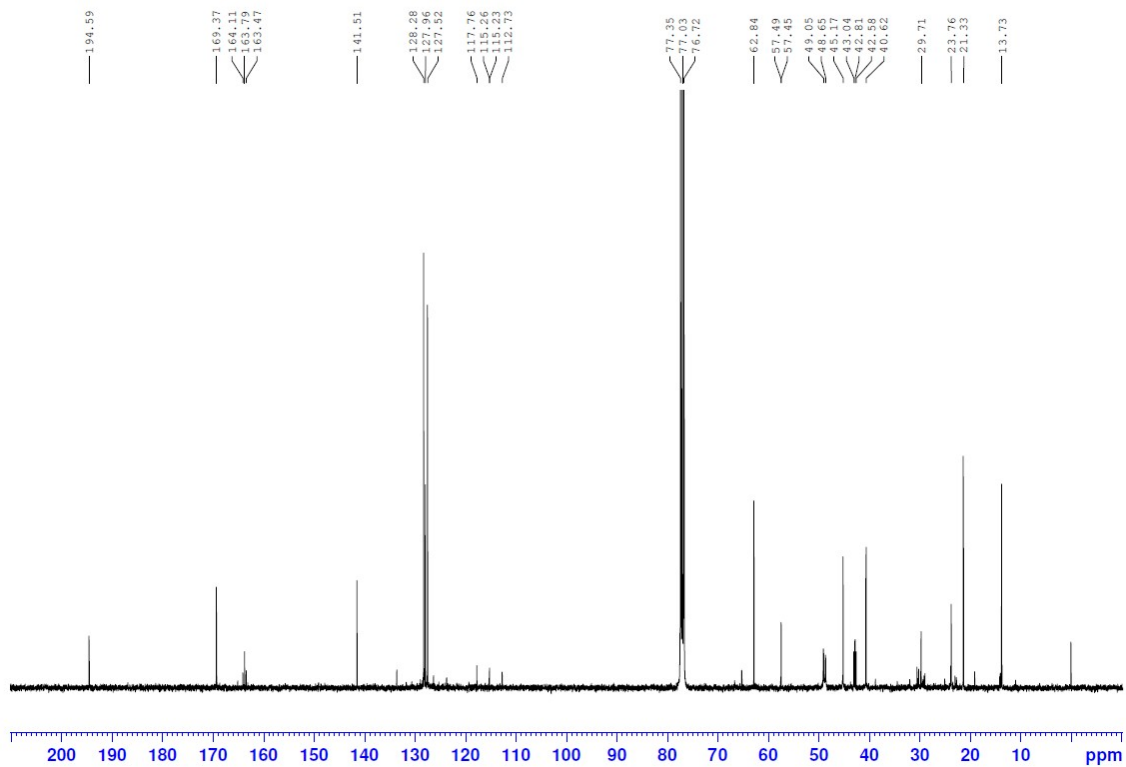
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of ethyl 4-((4-acetylpiperazine-1-carbonothioyl)thio)-2,2-difluoro-4-phenylpentanoate (**6d**):

Patamawadee 28-9-65 No.6  
PS-P7-223 in CDCl<sub>3</sub>



**6d** <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)

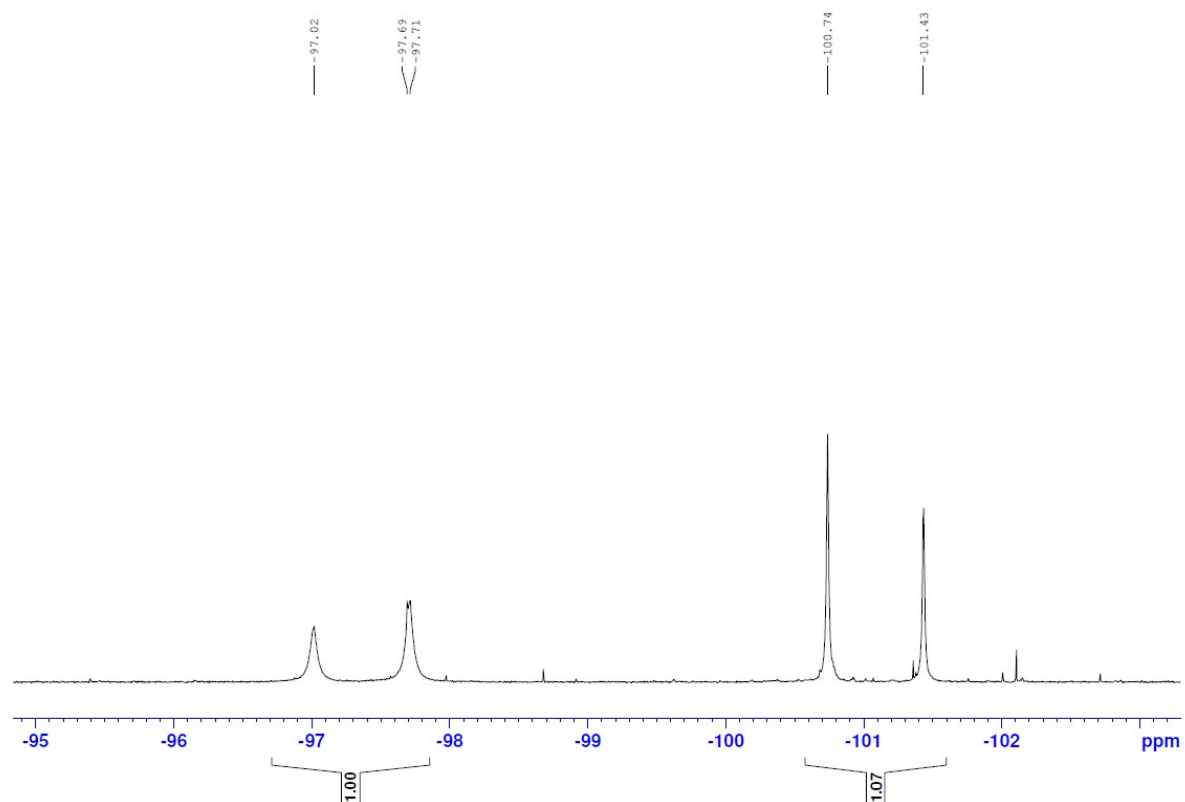
Patamawadee 29-9-65 No.6  
13C PS-P7-223 in CDCl<sub>3</sub>





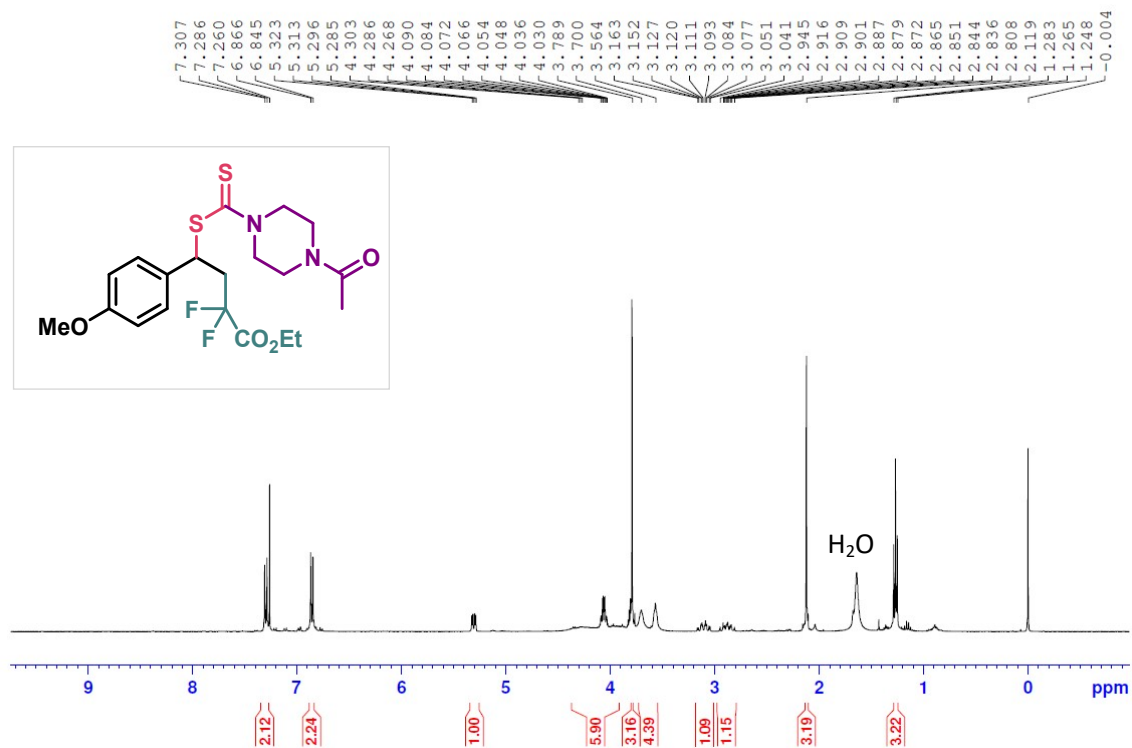
**6d**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 29-9-65 No.5  
 $^{19}\text{F}$  PS-P7-223 in  $\text{CDCl}_3$



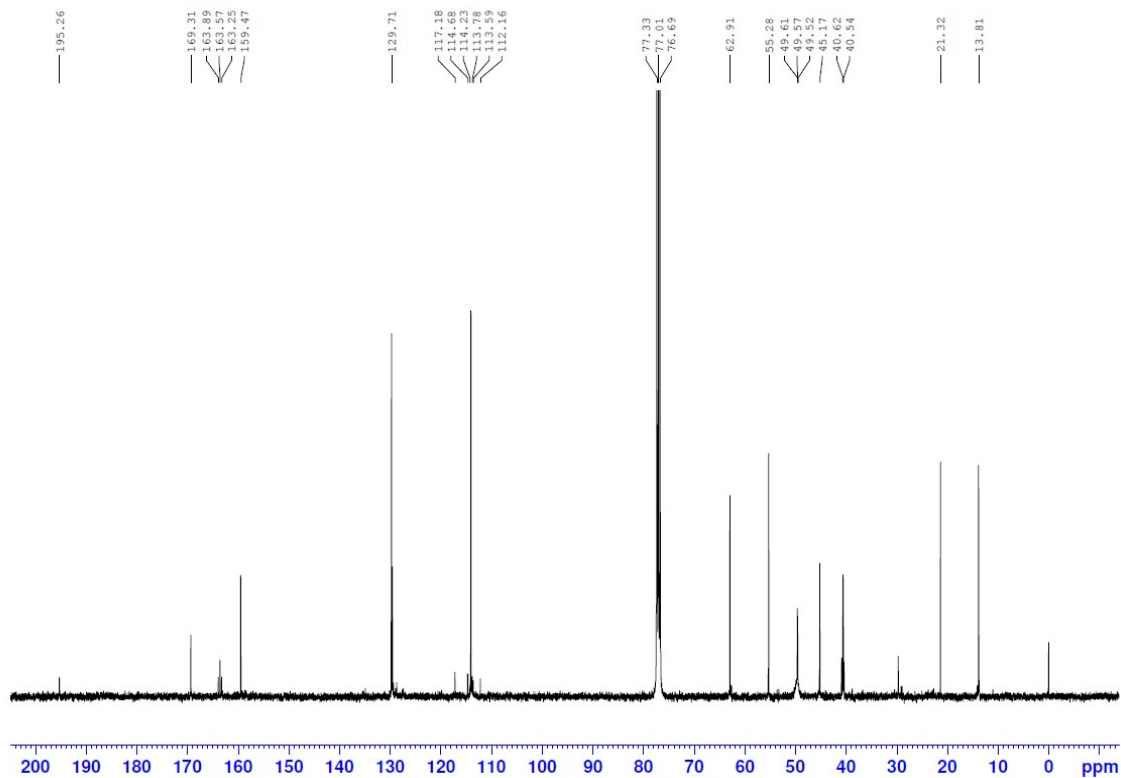
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of ethyl 4-((4-acetylpiperazine-1-carbonylthio)-2,2-difluoro-4-(4-methoxyphenyl)butanoate (**6e**):

Patamawadee 6-10-65 No.2  
PS-P7-230 in  $\text{CDCl}_3$



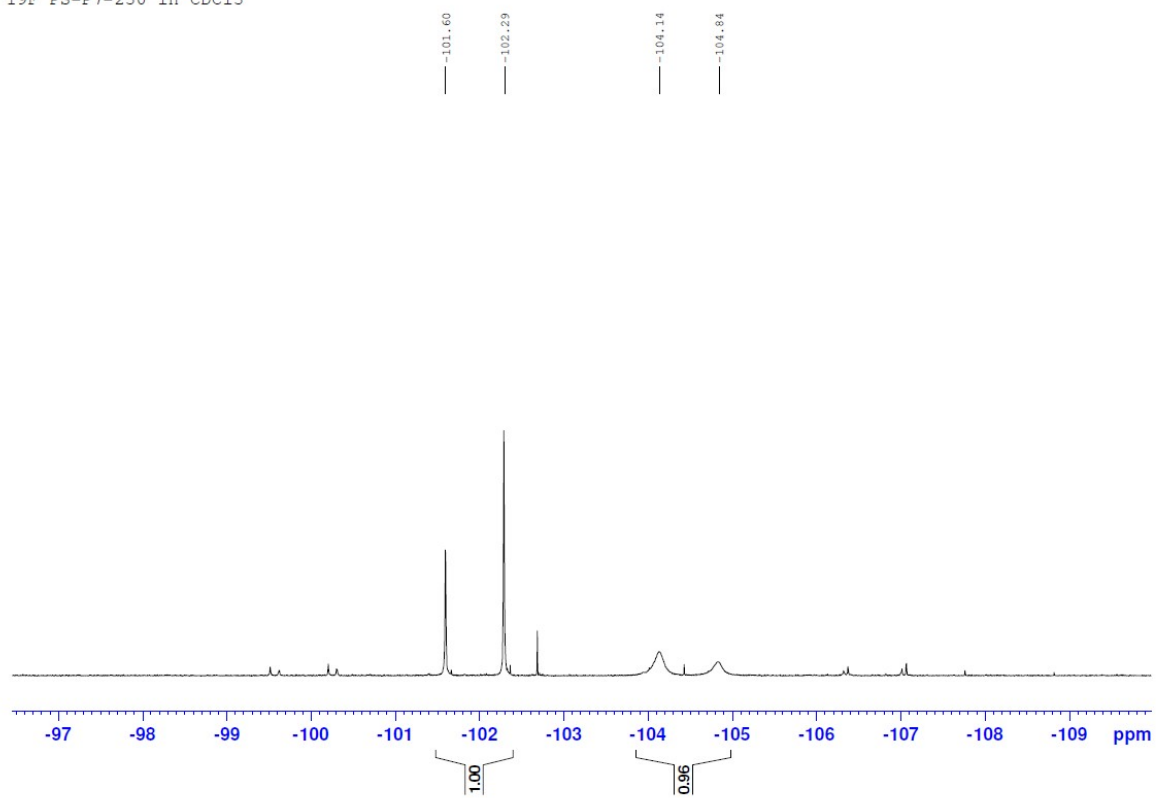
**6e**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 8-10-65 No.4  
 $^{13}\text{C}$  PS-P7-230 in  $\text{CDCl}_3$



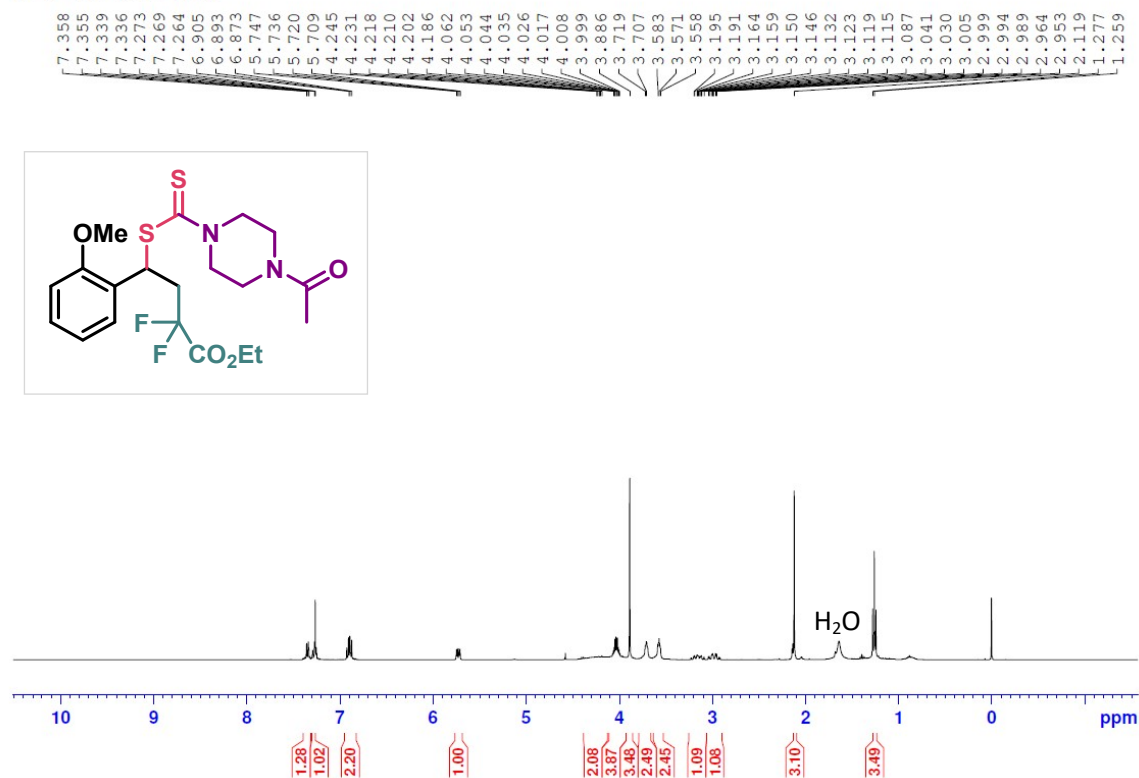
**6e**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 8-10-65 No.3  
 $^{19}\text{F}$  PS-P7-230 in  $\text{CDCl}_3$



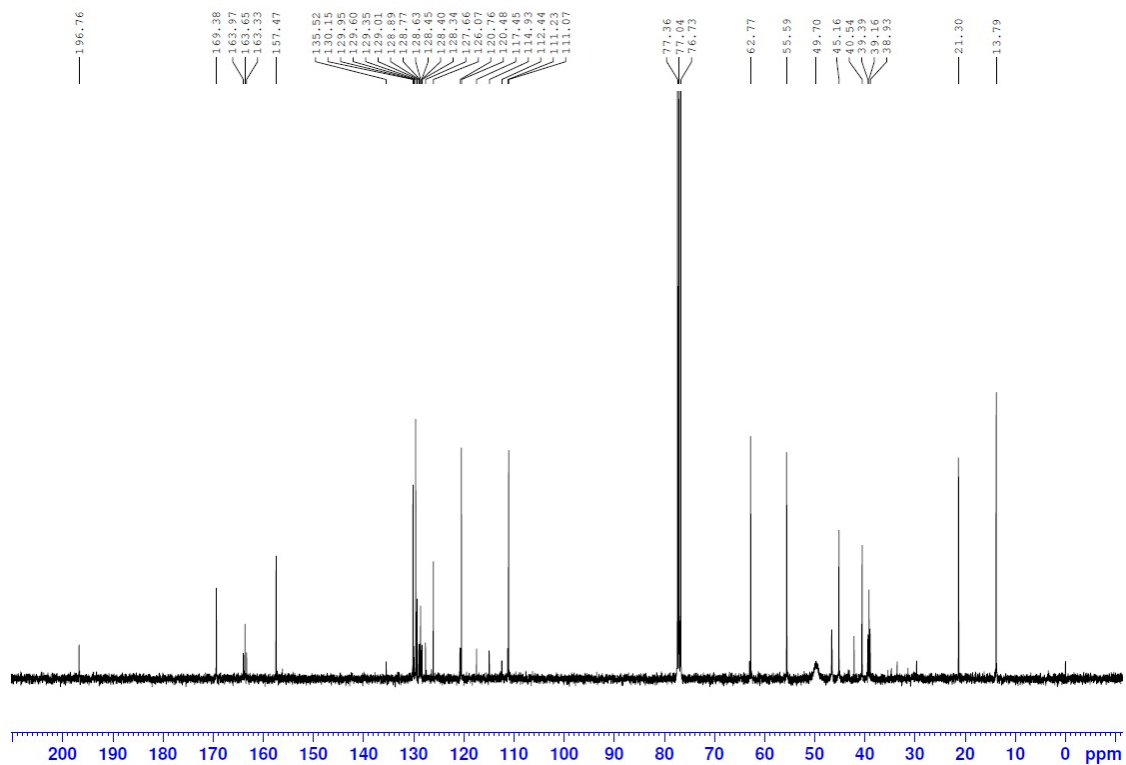
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of ethyl 4-((4-acetylpiperazine-1-carbonylthio)-2,2-difluoro-4-(2-methoxyphenyl)butanoate (**6f**):

Patamawadee 27-5-67 No.4  
PS-P7-233-1 in  $\text{CDCl}_3$



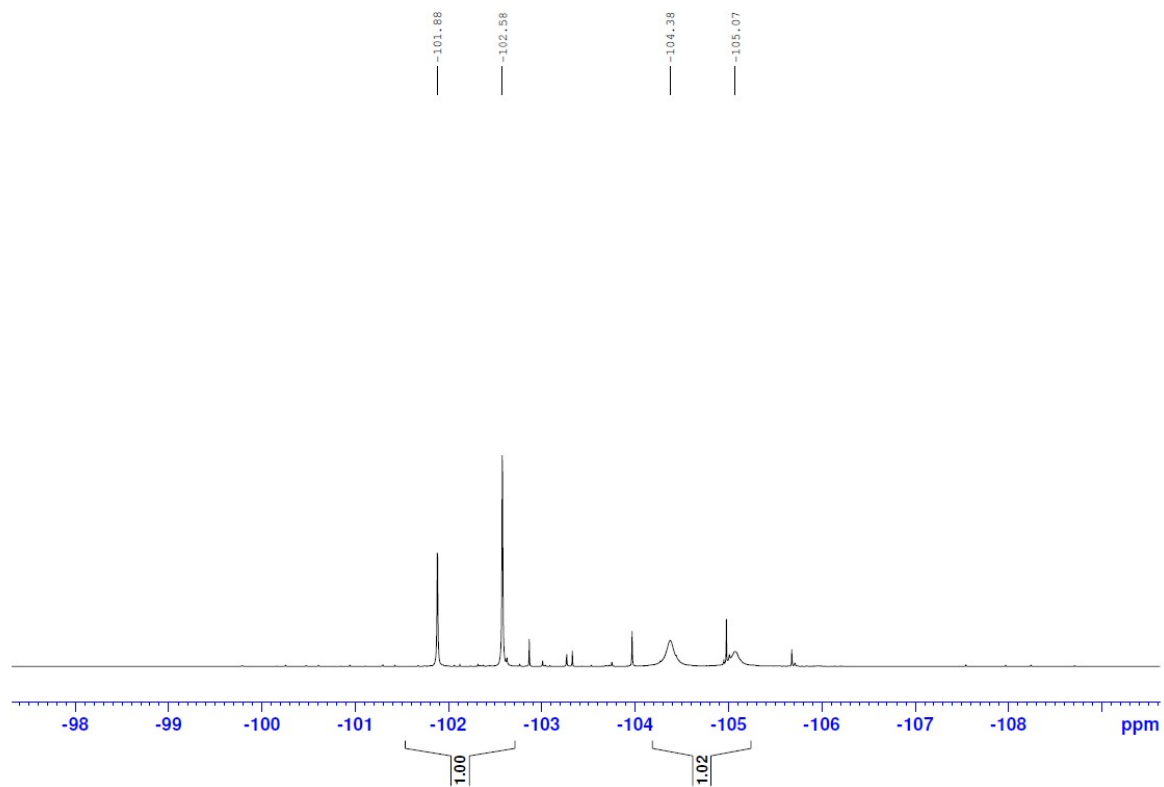
**6f**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 7-10-65 No.7  
 $^{13}\text{C}$  PS-P7-233-1 in  $\text{CDCl}_3$



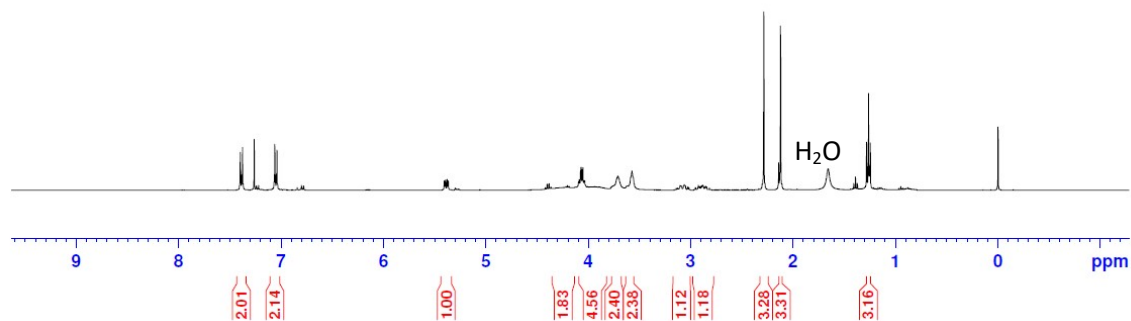
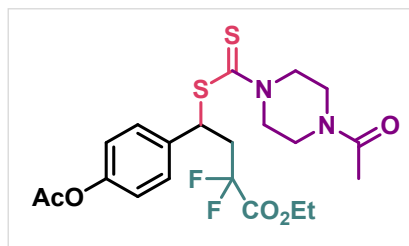
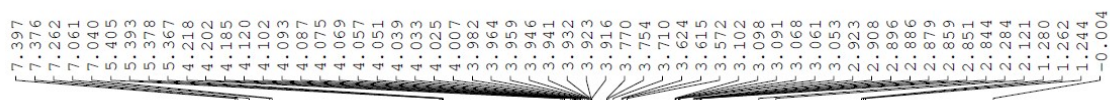
**6f**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 7-10-65 No.6  
 $^{19}\text{F}$  PS-P7-233-1 in  $\text{CDCl}_3$



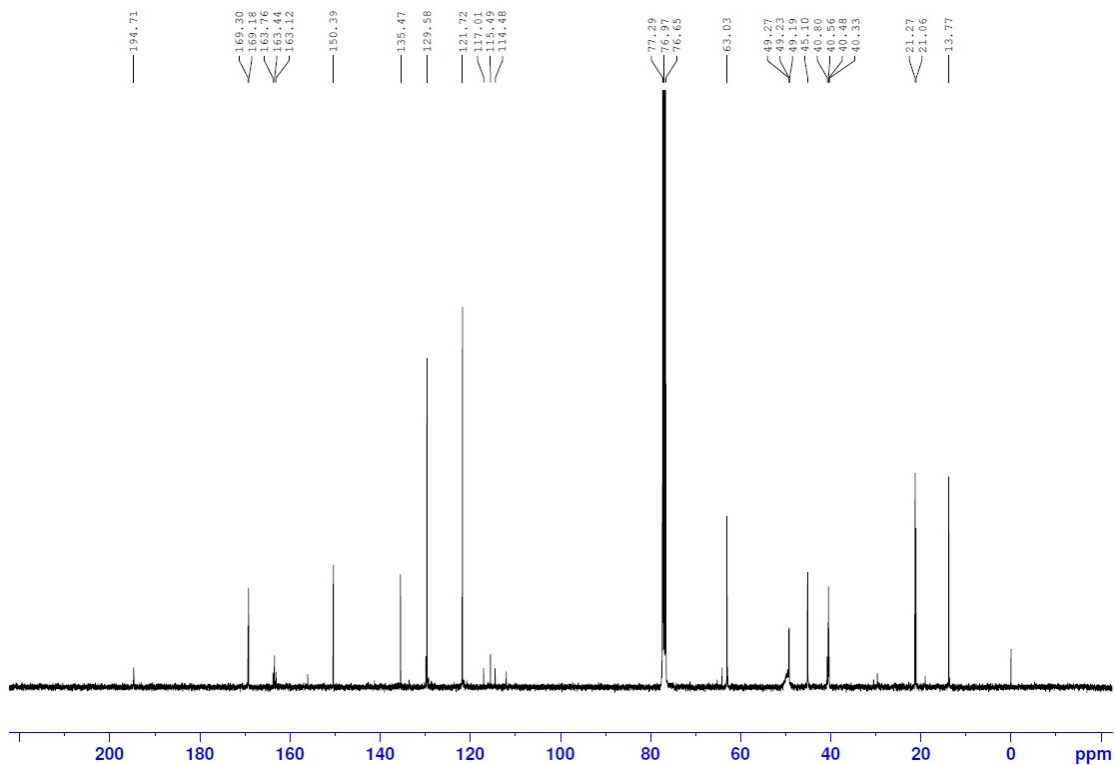
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of ethyl 4-(4-acetoxyphenyl)-4-((4-acetylpiperazine-1-carbonothioyl)thio)-2,2-difluorobutanoate (**6g**):

Patamawadee 21-9-65 No.1  
PS-P7-217 in  $\text{CDCl}_3$



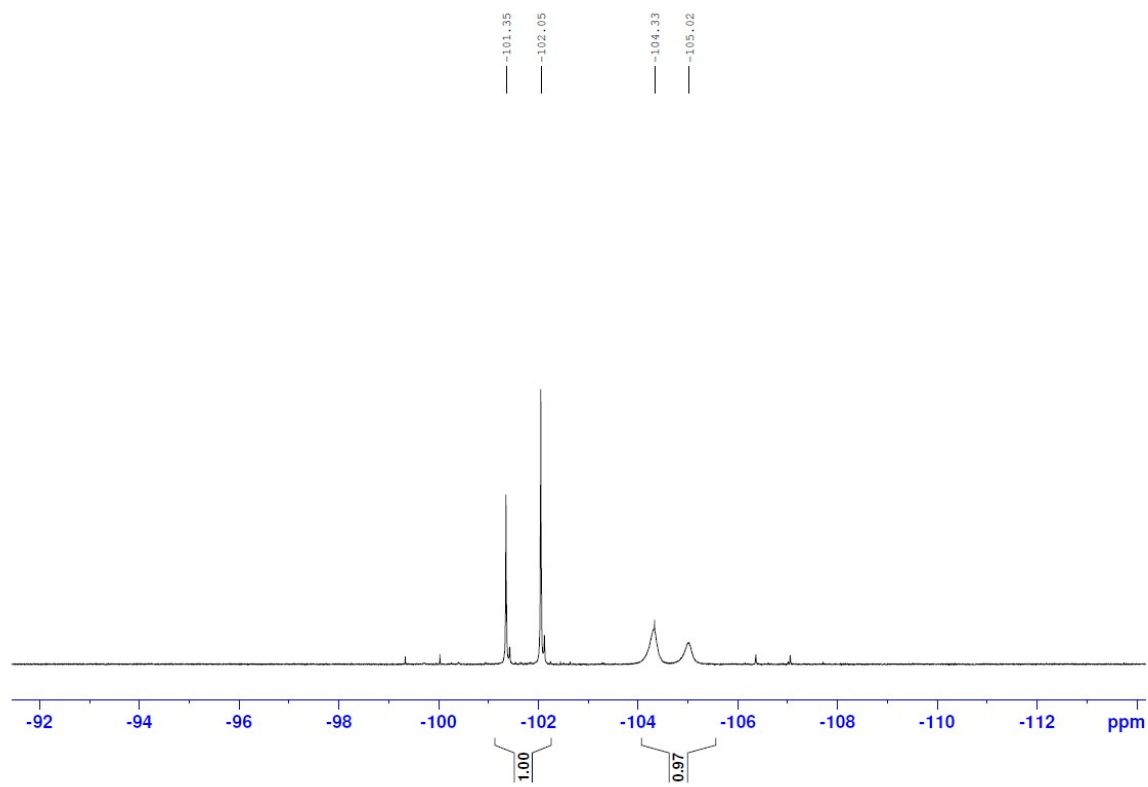
**6g**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 21-9-65 No.3  
 $^{13}\text{C}$  PS-P7-217 in  $\text{CDCl}_3$



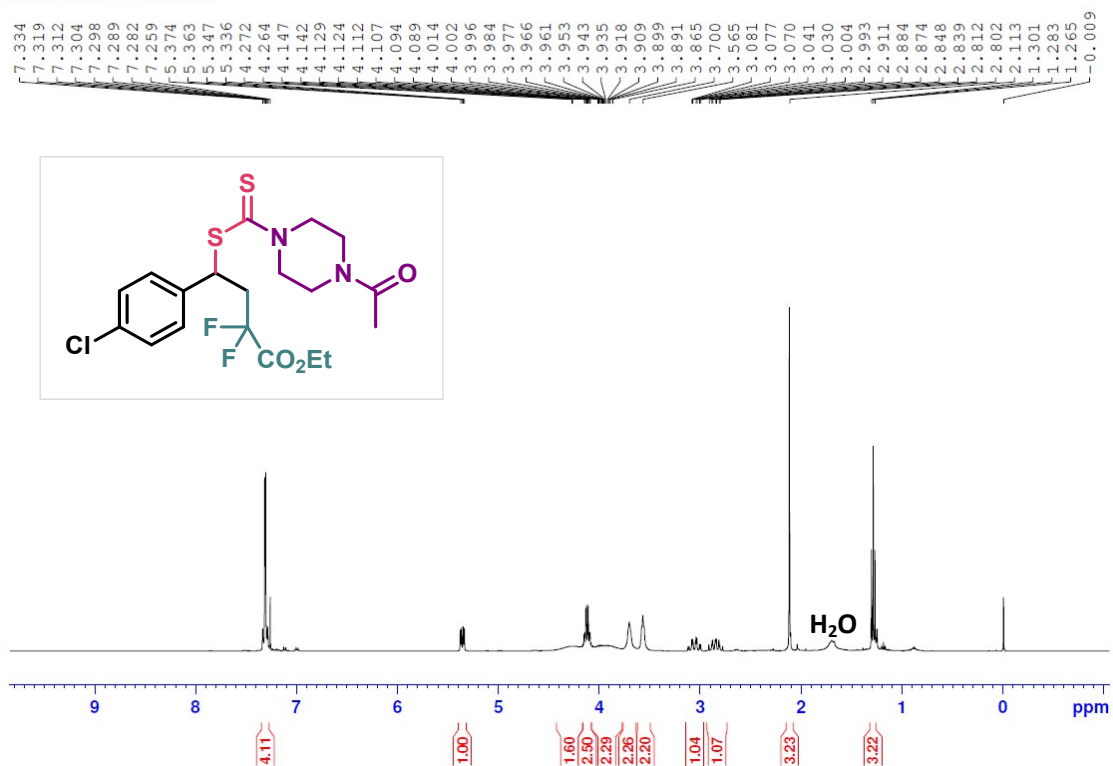
**6g**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 21-9-65 No.2  
 $^{19}\text{F}$  PS-P7-217 in  $\text{CDCl}_3$



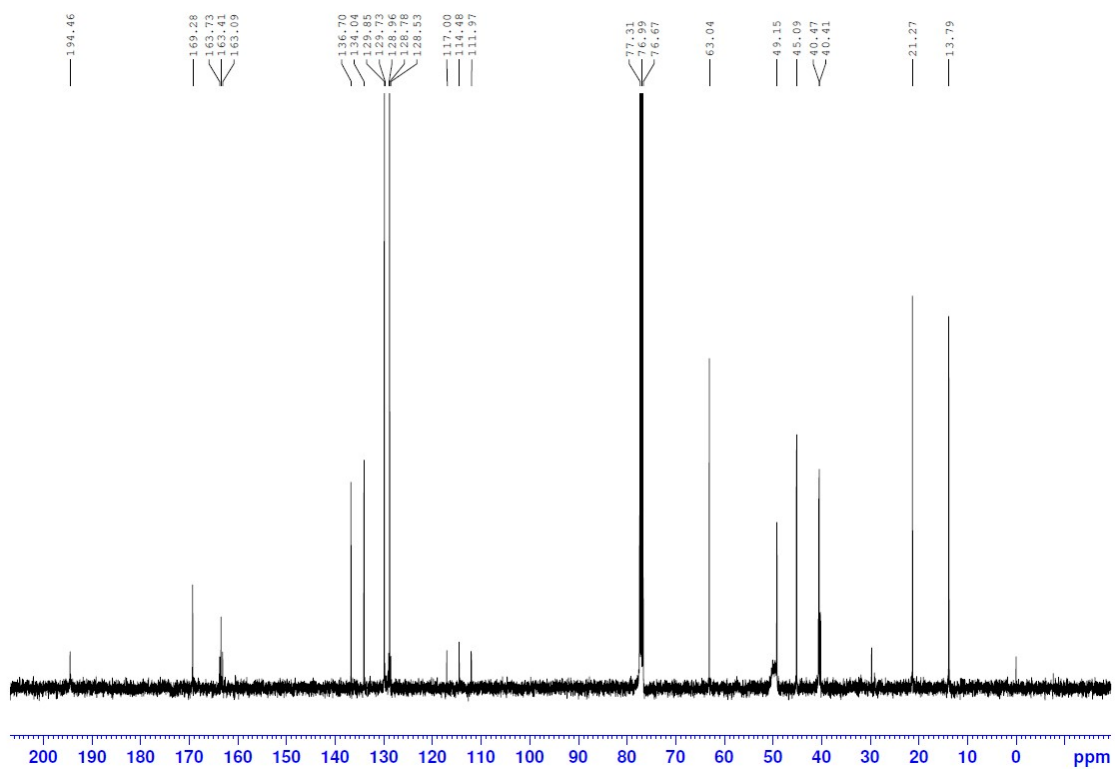
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of ethyl 4-((4-acetylpiperazine-1-carbonylthio)-4-(4-chlorophenyl)-2,2-difluorobutanoate (**6h**):

Patamawadee 6-10-65 No.7  
PS-P7-232-1 in  $\text{CDCl}_3$



**6h**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

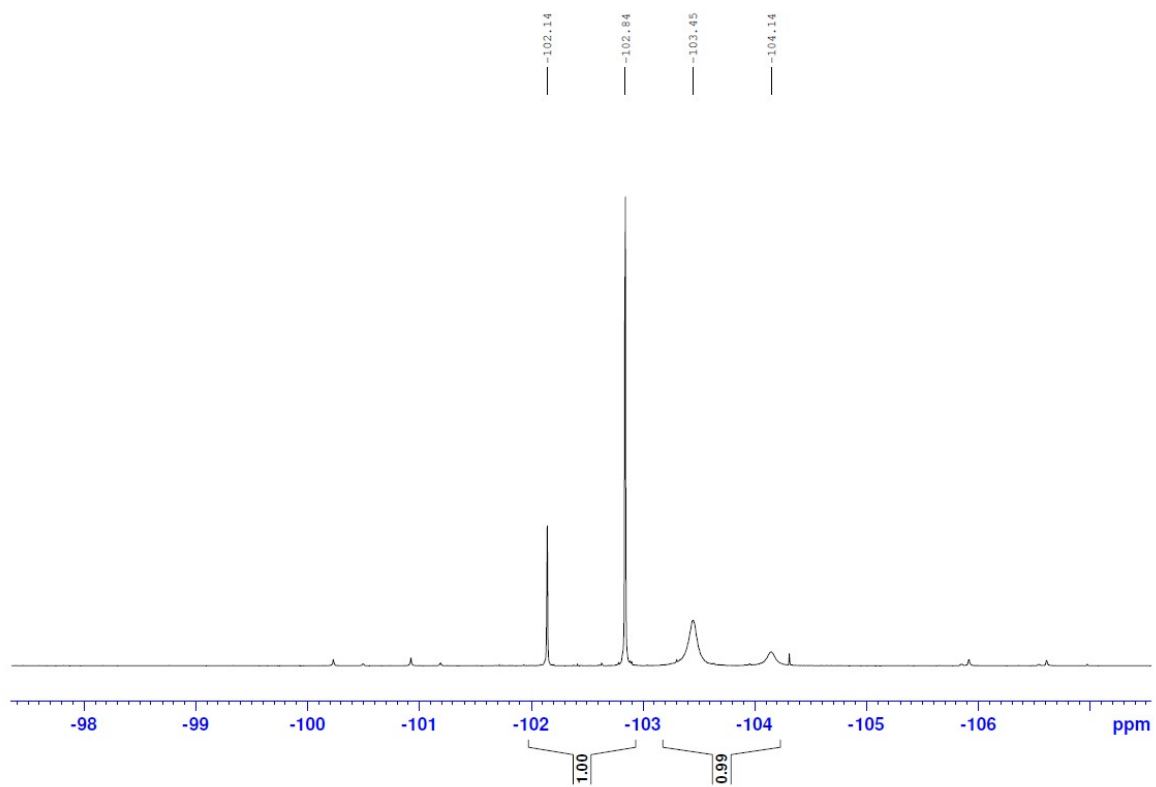
Patamawadee 7-10-65 No.15  
13C PS-P7-232-1 in  $\text{CDCl}_3$





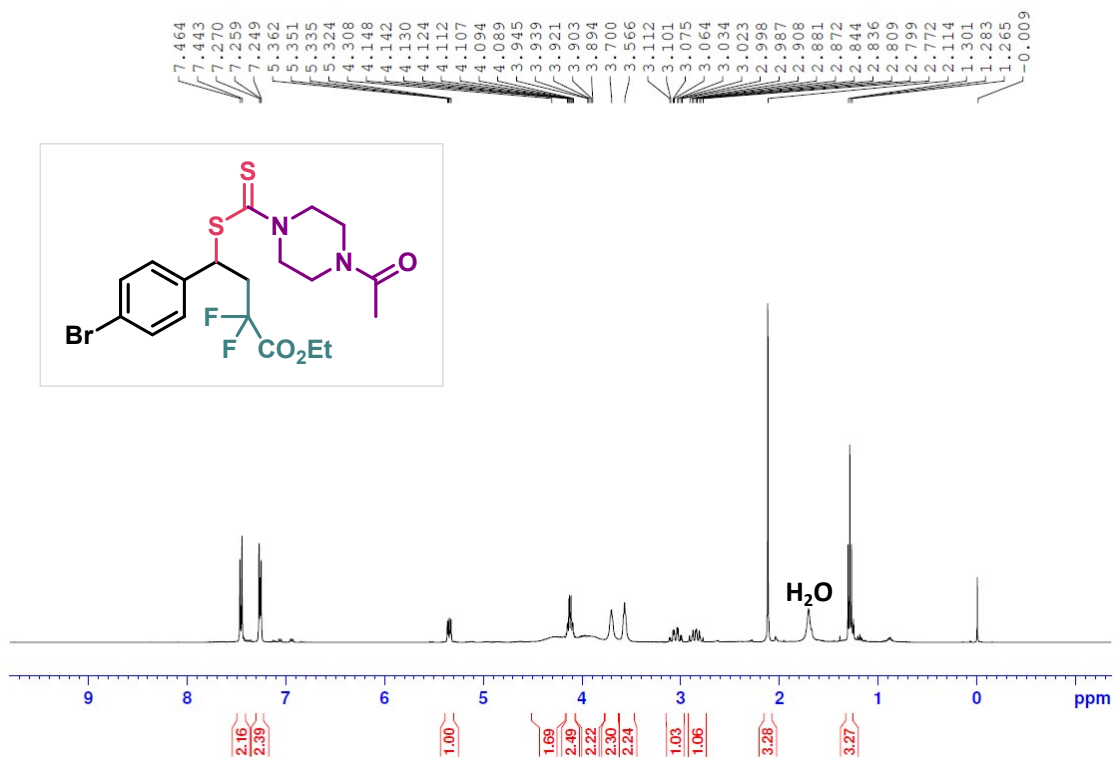
**6h**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 7-10-65 No.14  
19F PS-P7-232-1 in  $\text{CDCl}_3$



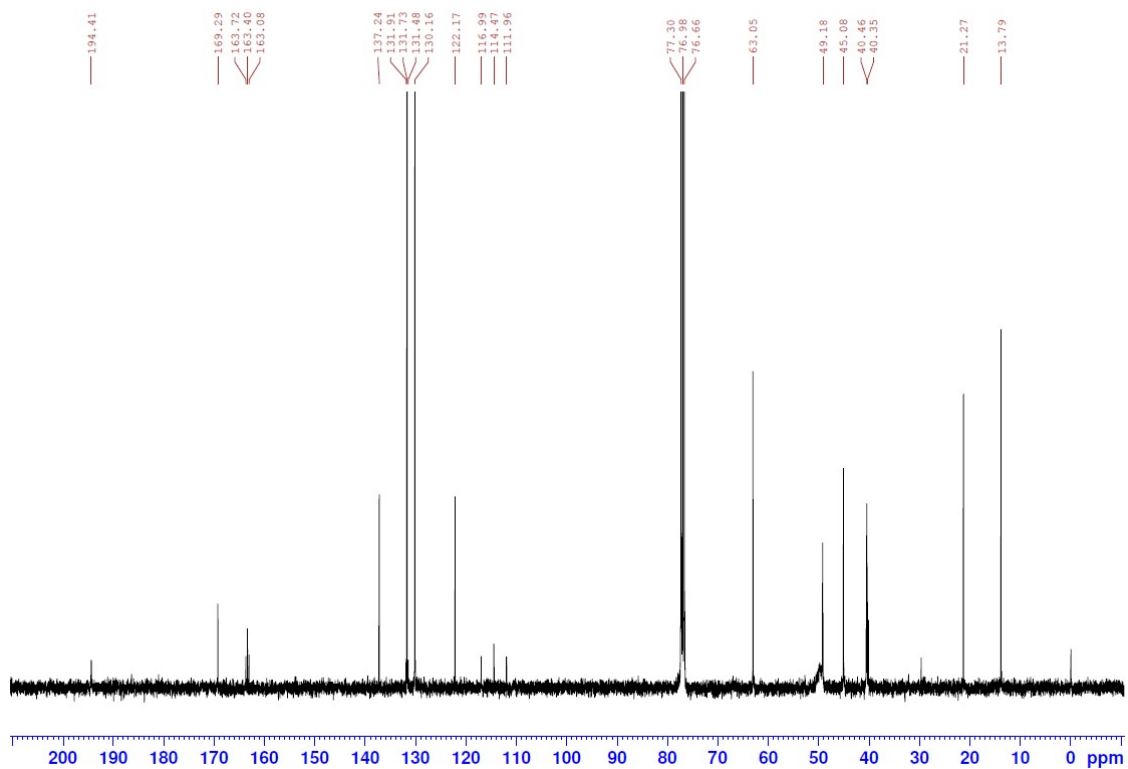
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of ethyl 4-((4-acetylpiperazine-1-carbonylthio)-4-(4-bromophenyl)-2,2-difluorobutanoate (**6i**):

Patamawadee 28-9-65 No.2  
PS-P7-228-1 in CDCl<sub>3</sub>



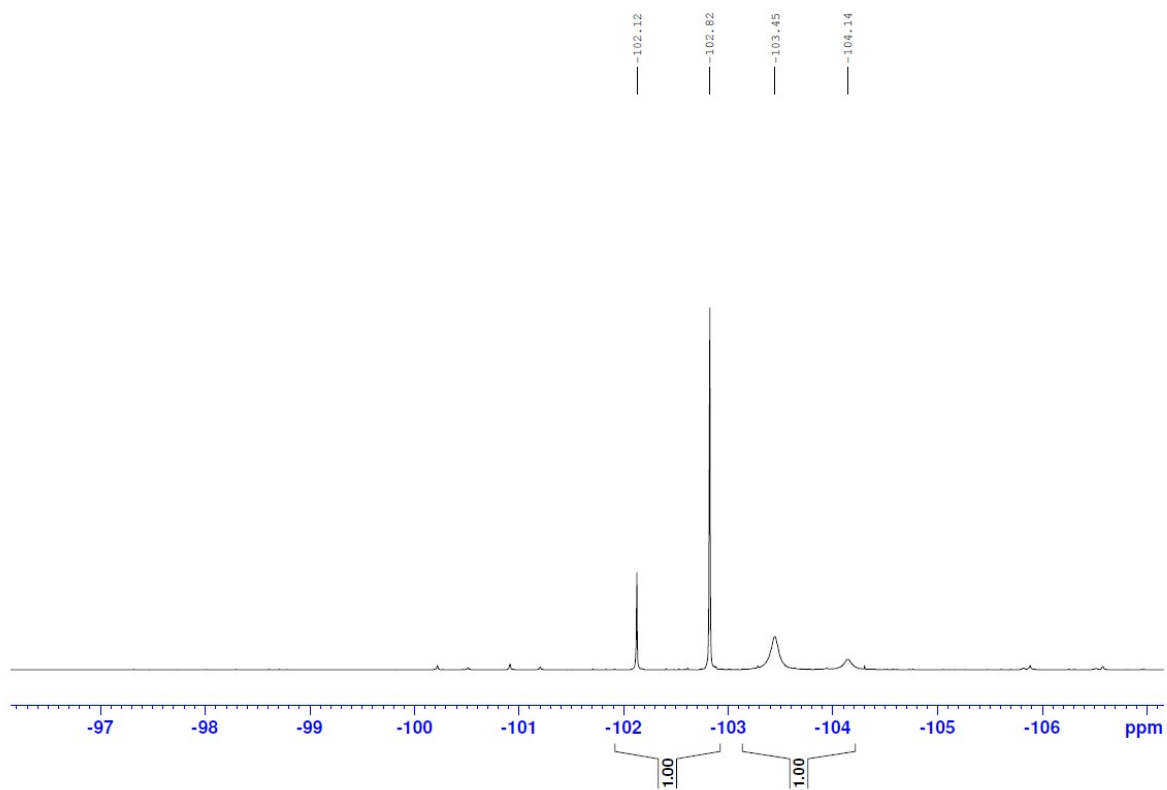
**6i** <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)

Patamawadee 29-9-65 No.4  
13C PS-P7-228-1 in CDCl<sub>3</sub>



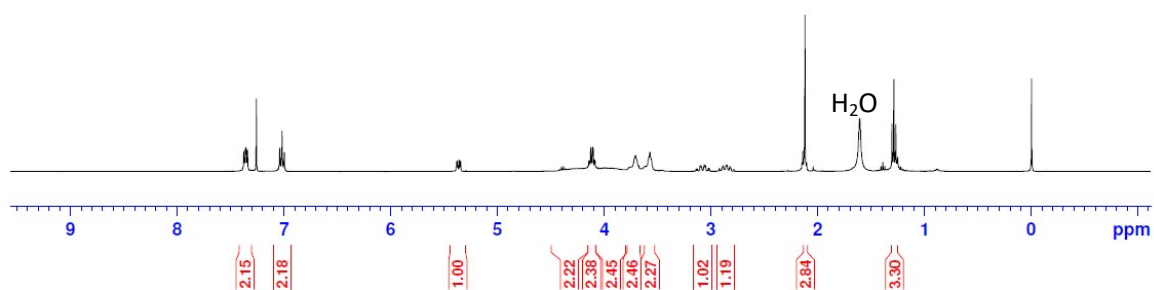
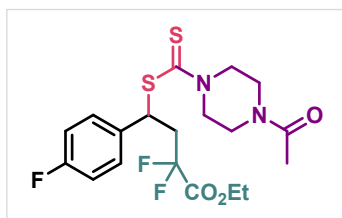
**6i**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 29-9-65 No.3  
19F PS-P7-228-1 in  $\text{CDCl}_3$



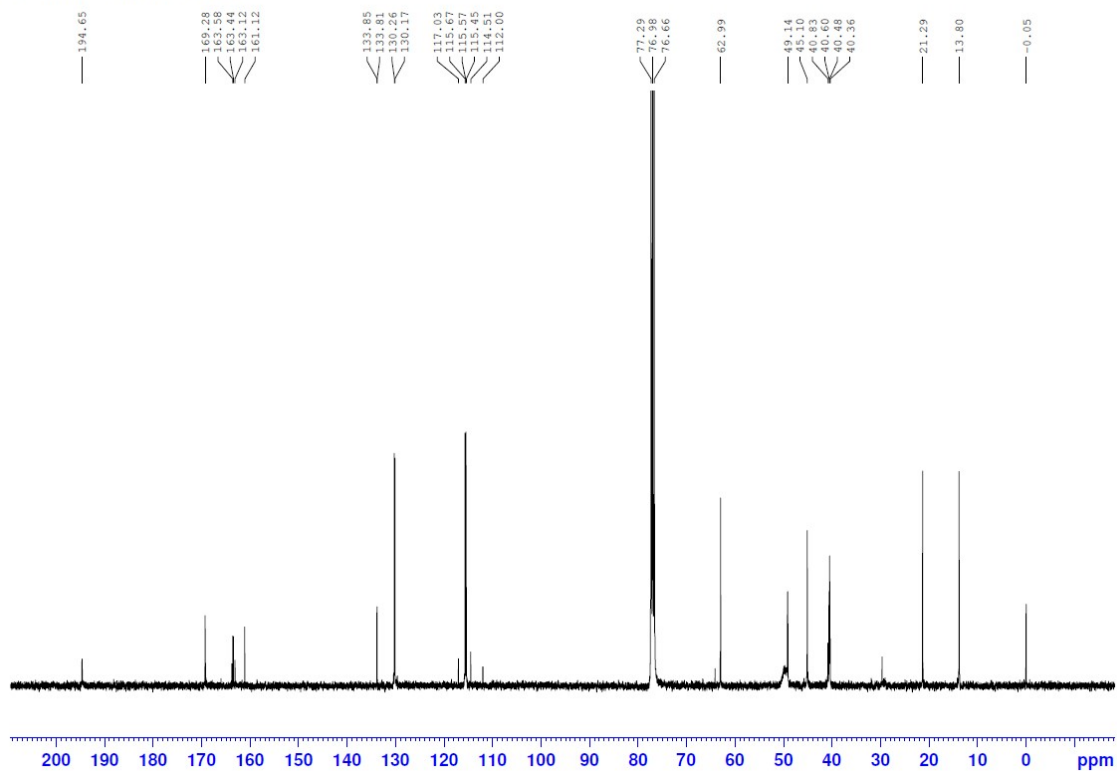
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of ethyl 4-((4-acetylpiperazine-1-carbonothioyl)thio)-2,2-difluoro-4-(4-fluorophenyl)butanoate (**6j**):

Patamawadee 14-9-65 No.4  
PS-P7-204 in CDCl<sub>3</sub>



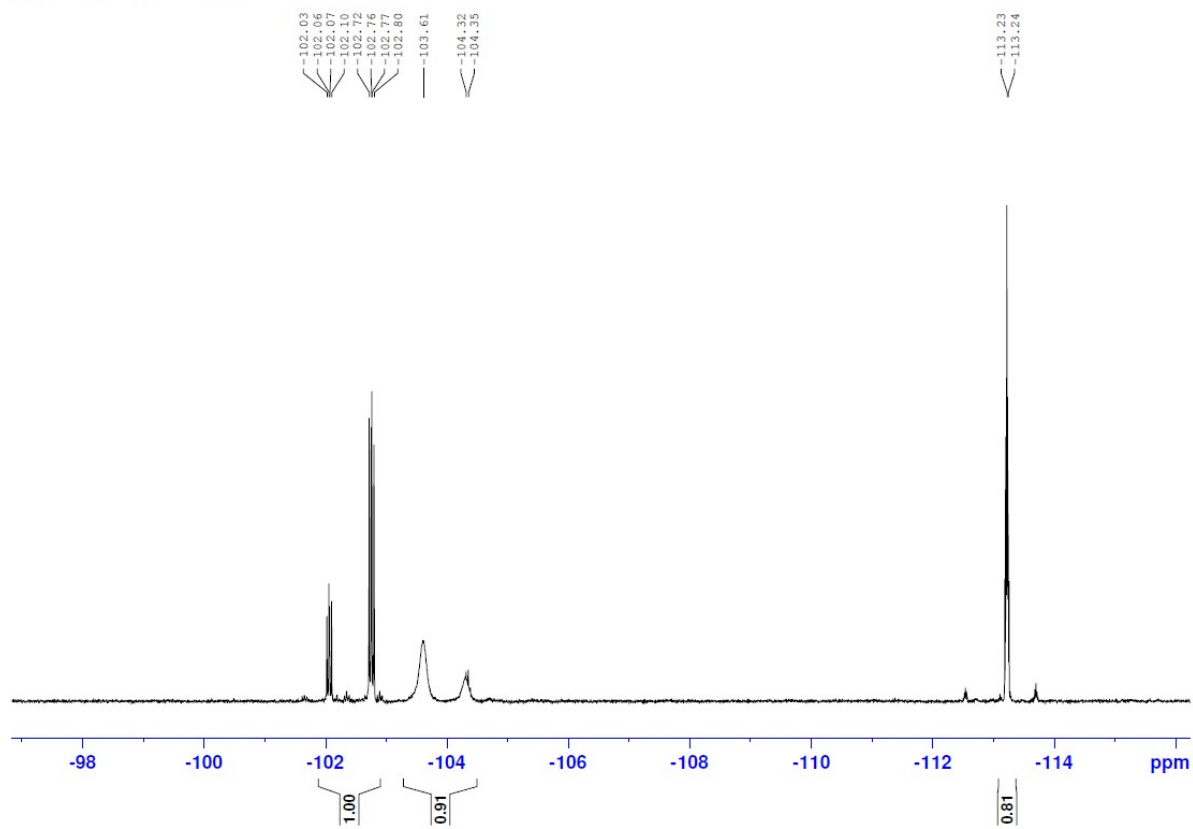
**6j** <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)

Patamawadee 16-9-65 No.3  
13C PS-P7-204 in CDCl<sub>3</sub>



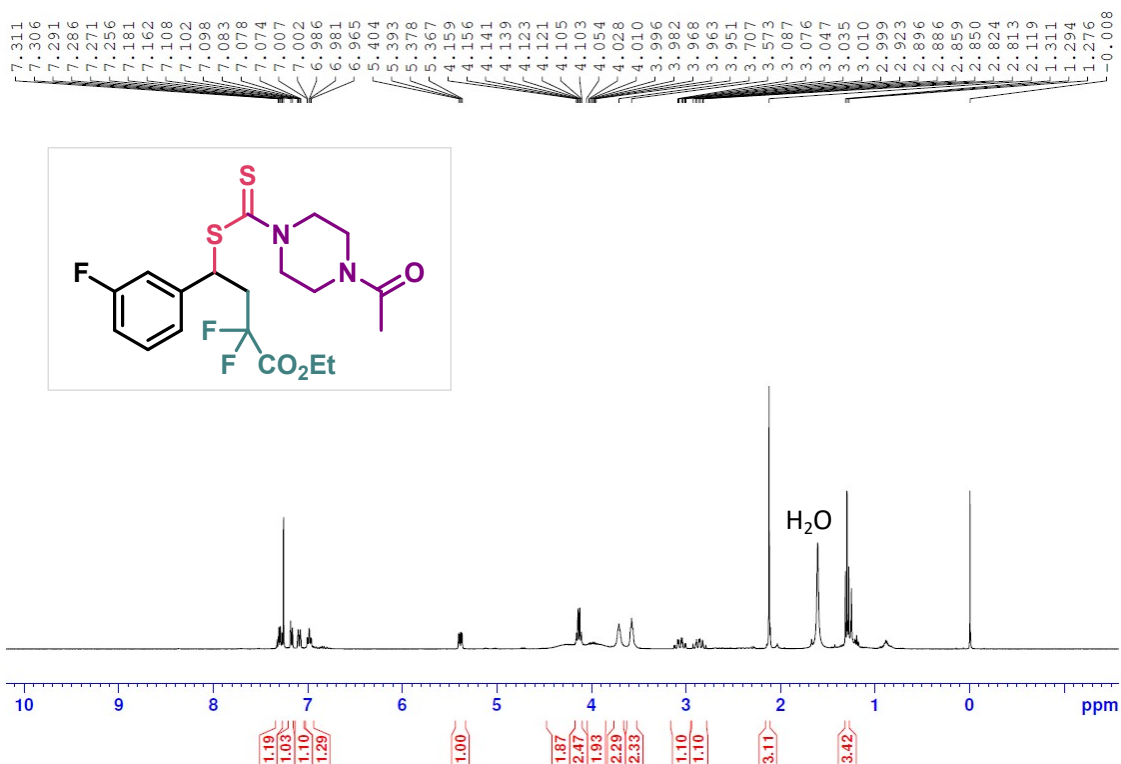
6j  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 29-11-66 No.8  
19F PS-P7-204 in  $\text{CDCl}_3$



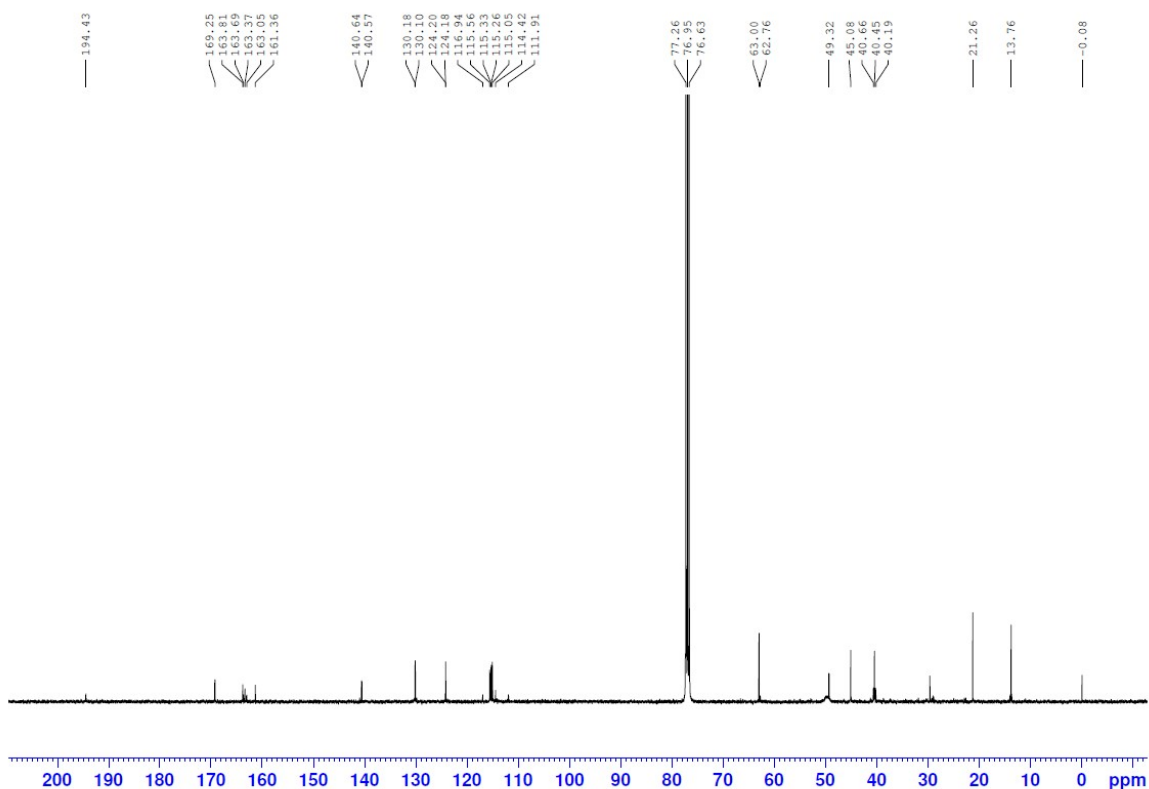
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of ethyl 4-((4-acetylpiperazine-1-carbonylthio)thio)-2,2-difluoro-4-(3-fluorophenyl)butanoate (**6k**):

Patamawadee 6-10-65 No.8  
PS-P7-231 in CDCl<sub>3</sub>



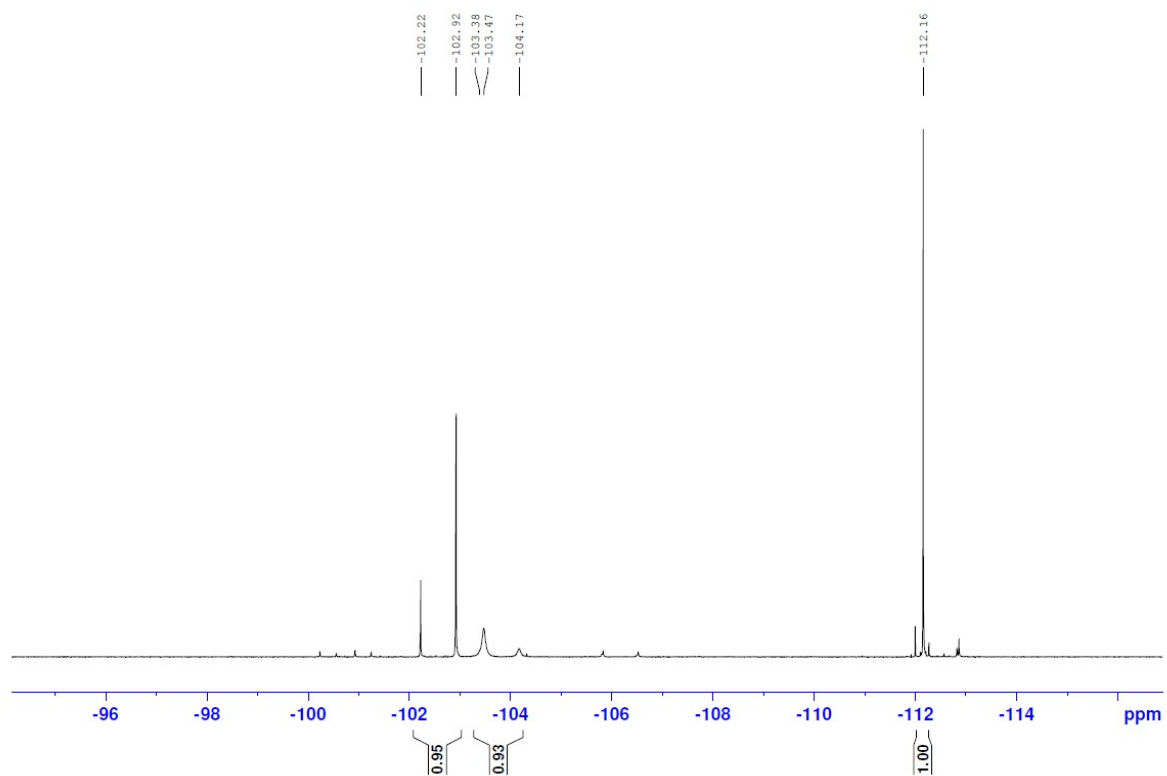
**6k** <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)

Patamawadee 8-10-65 No.2  
13C PS-P7-231 in CDCl<sub>3</sub>



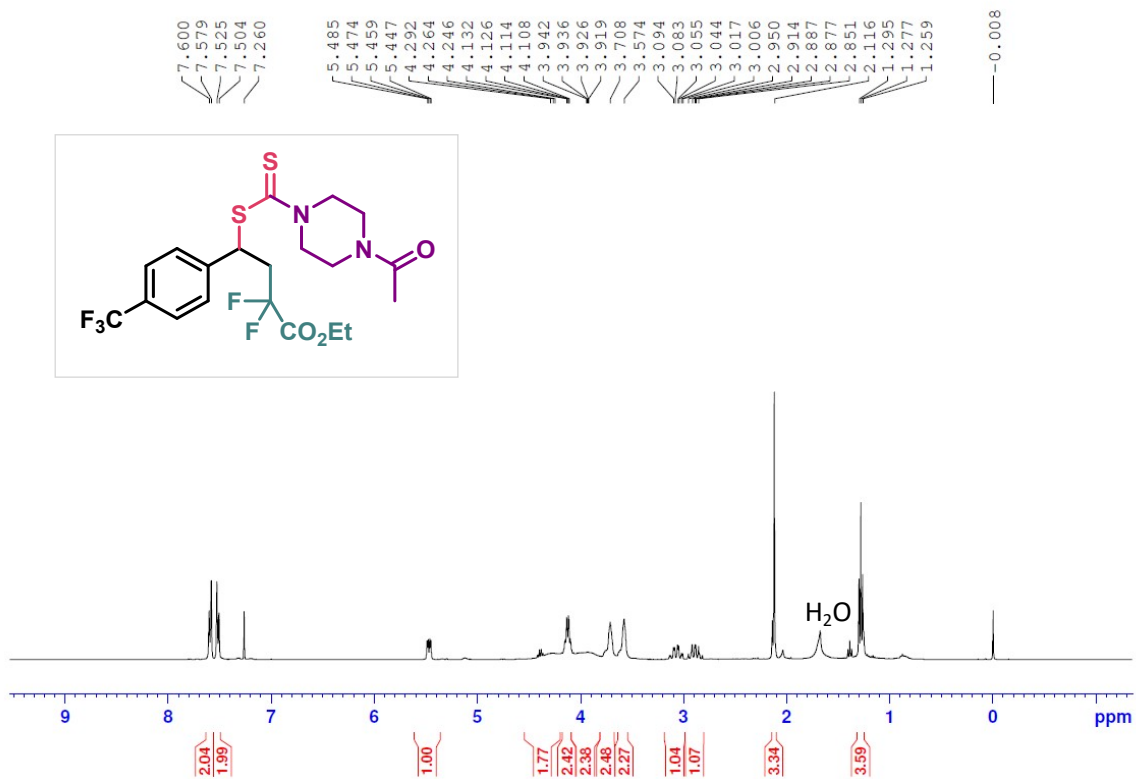
**6k**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 8-10-65 No.1  
19F PS-P7-231 in  $\text{CDCl}_3$



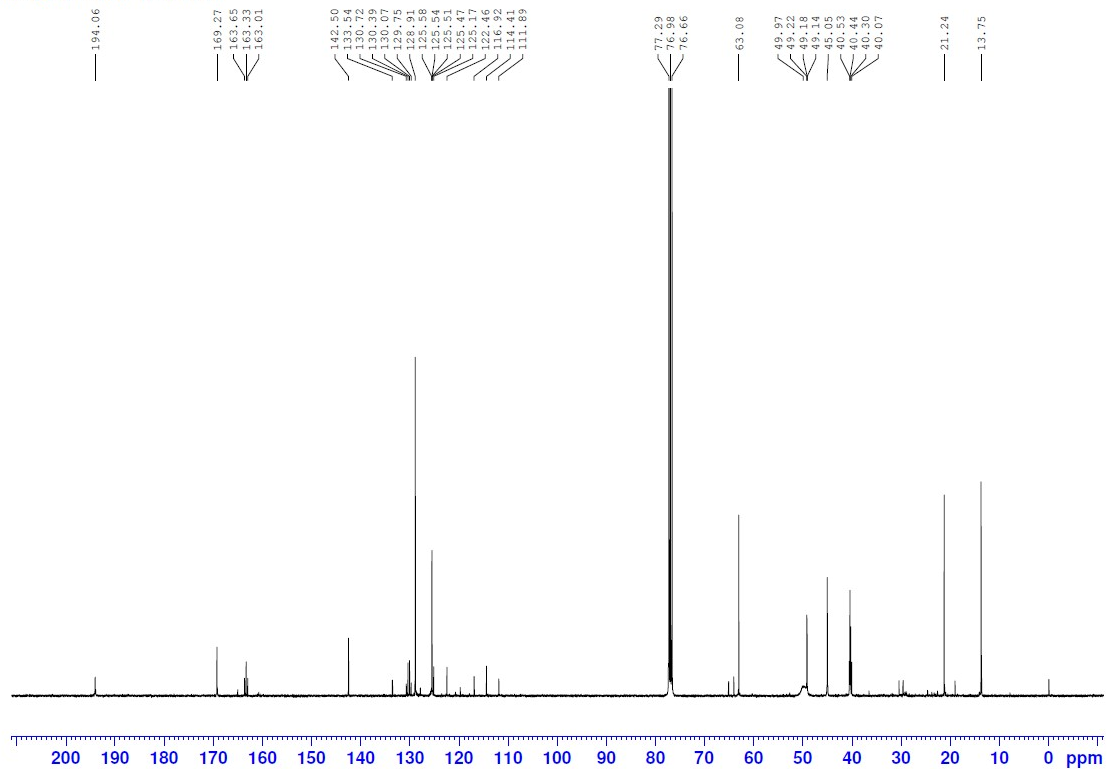
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of ethyl 4-((4-acetylpiperazine-1-carbonothioyl)thio)-2,2-difluoro-4-(4-(trifluoromethyl)phenyl)butanoate (**6I**):

Patamawadee 5-6-67 No.2  
PS-P7-205 in CDCl<sub>3</sub>



**6I** <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)

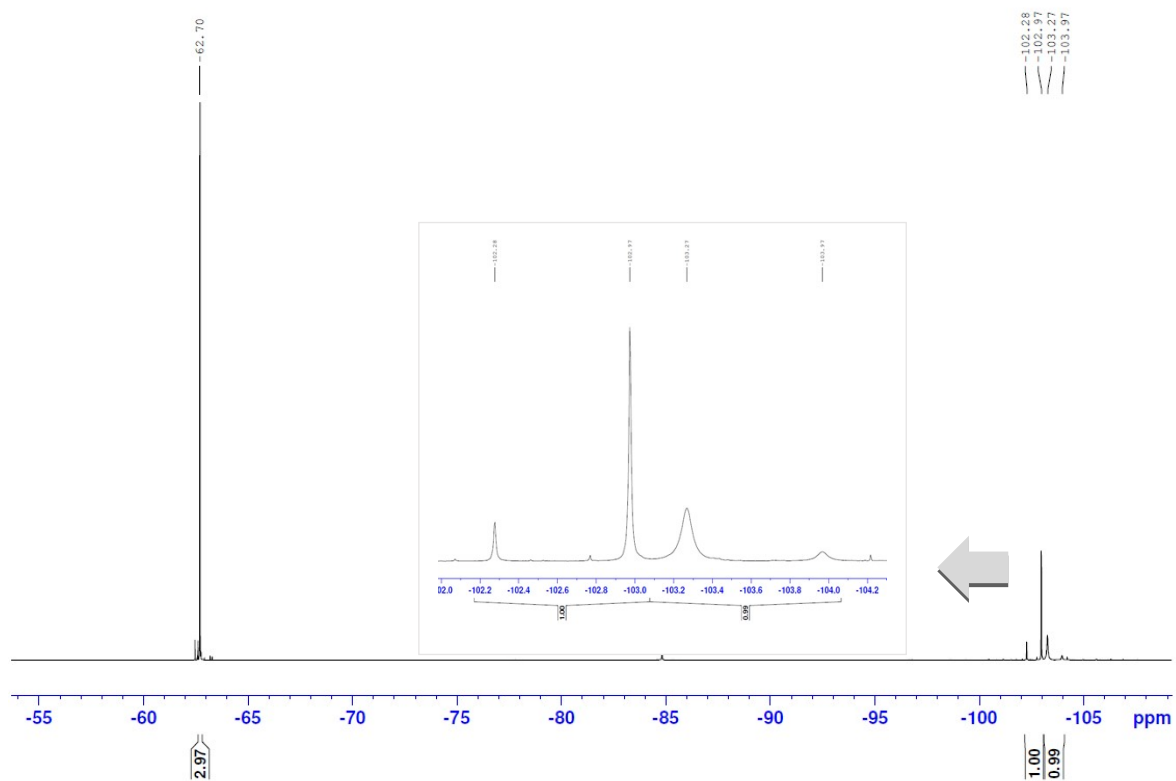
Patamawadee 19-9-65 No.6  
13C PS-P7-205 in CDCl<sub>3</sub>





6I  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

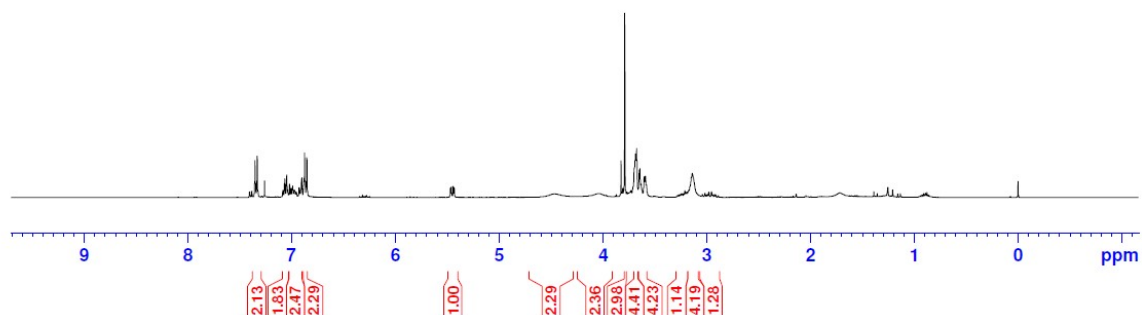
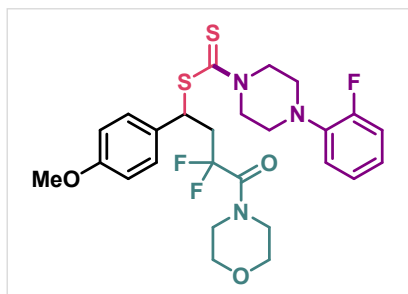
Patamawadee 19-9-65 No.5  
19F PS-P7-205 in  $\text{CDCl}_3$



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of 3,3-difluoro-1-(4-methoxyphenyl)-4-morpholino-4-oxobutyl 4-(2-fluorophenyl)piperazine-1-carbodithioate (**7a**):

Patamawadee 5-8-65 No.7  
PS-P7-159 in  $\text{CDCl}_3$

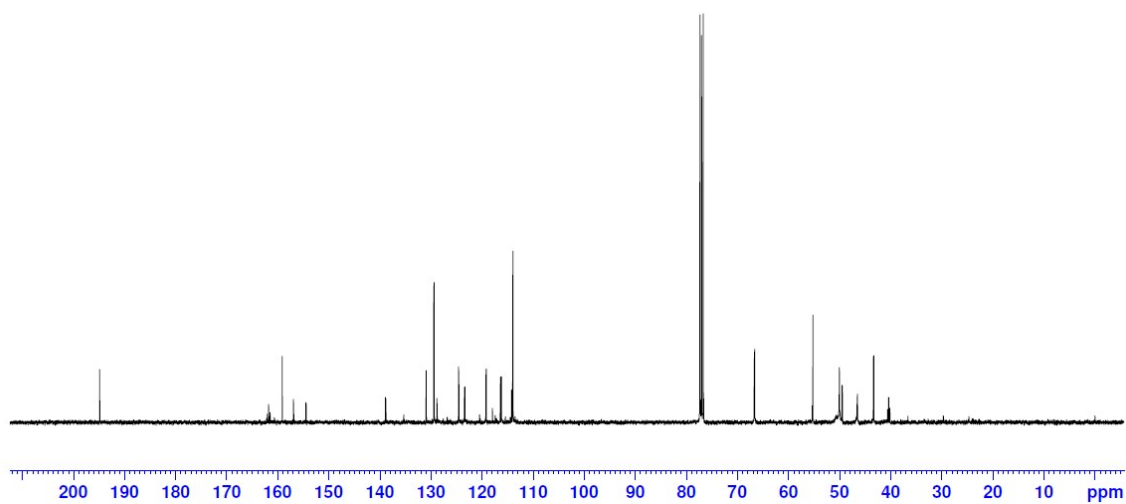
7.352  
7.330  
7.065  
7.045  
7.019  
6.988  
6.901  
6.874  
6.852  
5.468  
5.459  
5.442  
5.432  
4.466  
4.041  
3.788  
3.686  
3.672  
3.647  
3.641  
3.632  
3.601  
3.589  
3.240  
3.230  
3.217  
3.206  
3.199  
3.185  
3.171  
3.137  
3.014  
2.976  
2.951



**7a**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

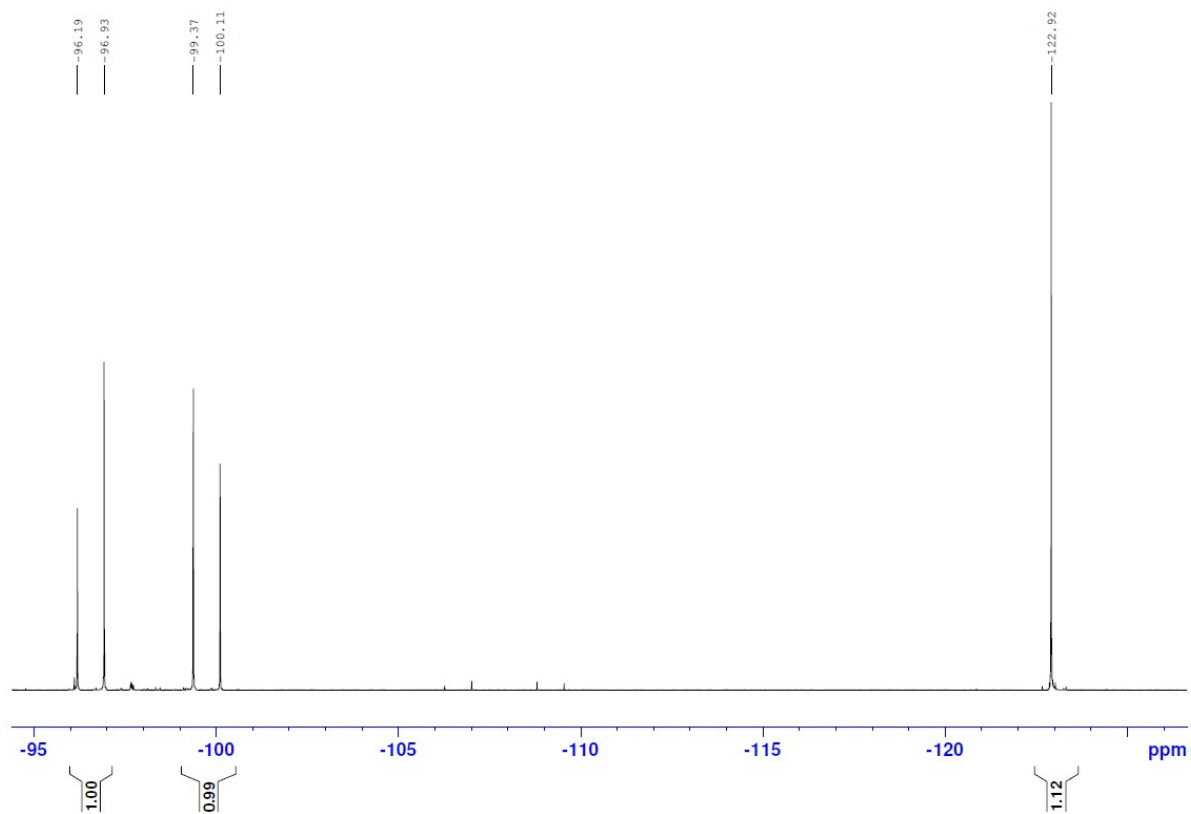
Patamawadee 5-8-65 No.9  
13C PS-P7-159 in  $\text{CDCl}_3$

194.91  
161.79  
159.16  
156.91  
154.47  
138.93  
136.64  
130.94  
129.43  
128.83  
124.60  
123.86  
123.44  
123.36  
119.22  
118.40  
116.20  
114.21  
113.97  
77.82  
77.80  
76.68  
66.68  
66.61  
55.32  
55.20  
49.48  
46.56  
46.49  
46.43  
43.33  
40.57  
40.36  
40.15



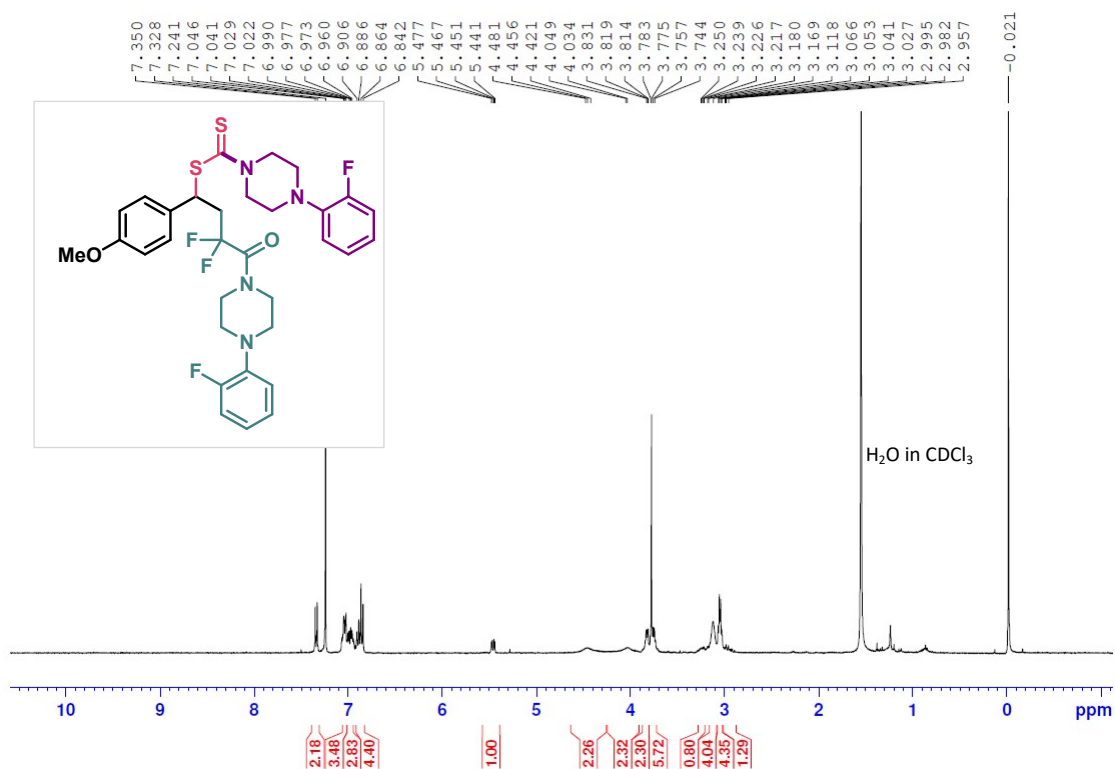
**7a**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 5-8-65 No.8  
19F{1H} PS-P7-159 in  $\text{CDCl}_3$



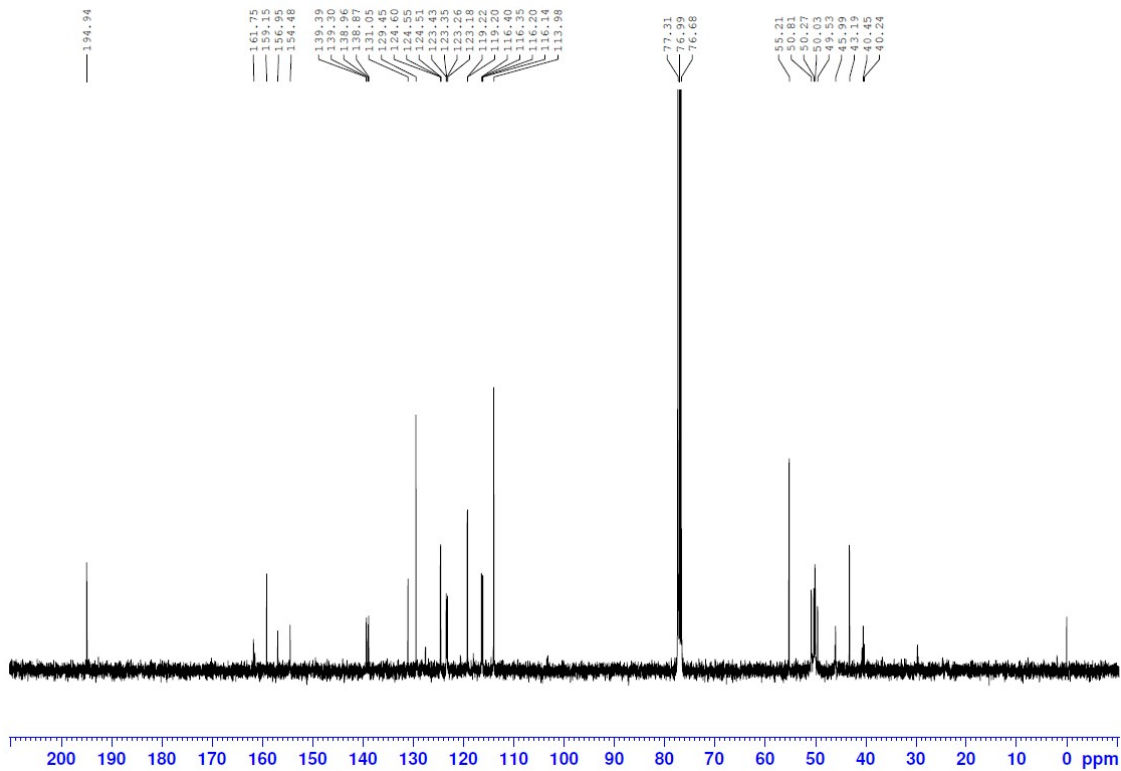
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of 3,3-difluoro-4-(4-(2-fluorophenyl)piperazin-1-yl)-1-(4-methoxyphenyl)-4-oxobutyl 4-(2-fluorophenyl)piperazine-1-carbodithioate (**7b**):

Patamawadee 17-8-65 No.2  
PS-P7-170 in  $\text{CDCl}_3$



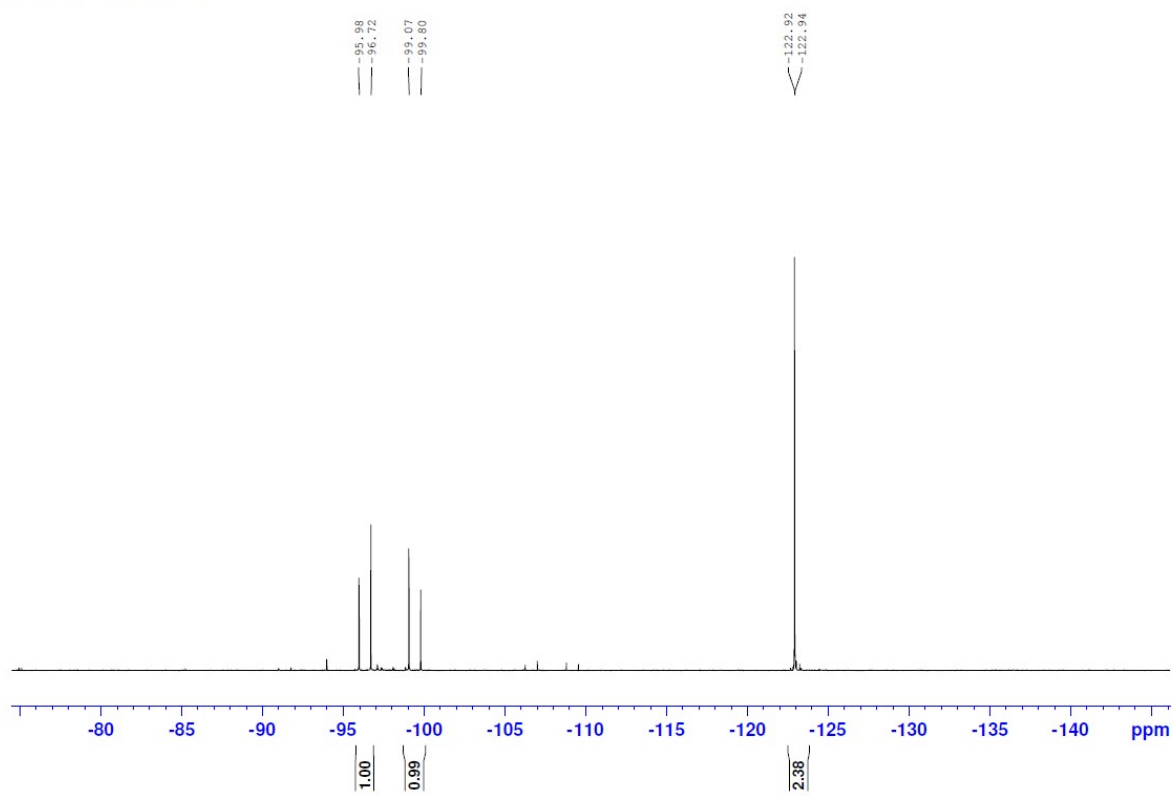
**7b**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 20-8-65 No.3  
 $^{13}\text{C}$  PS-P7-170 in  $\text{CDCl}_3$



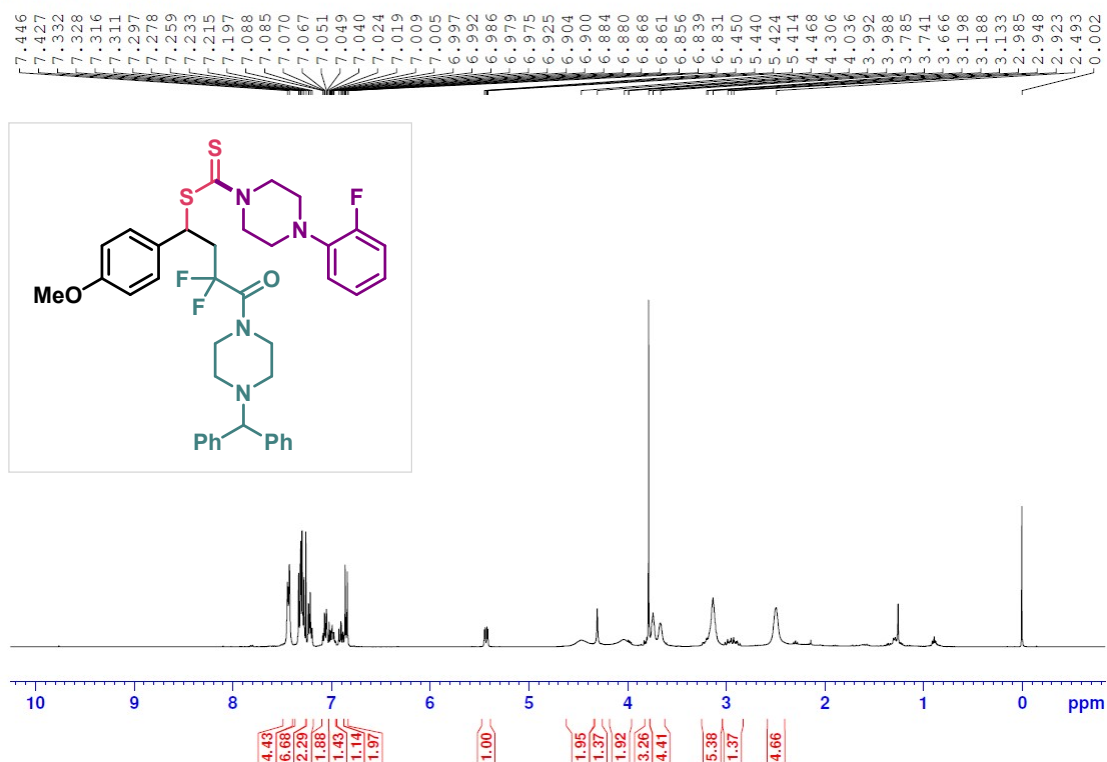
**7b**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 20-8-65 No.2  
19F PS-P7-170 in  $\text{CDCl}_3$



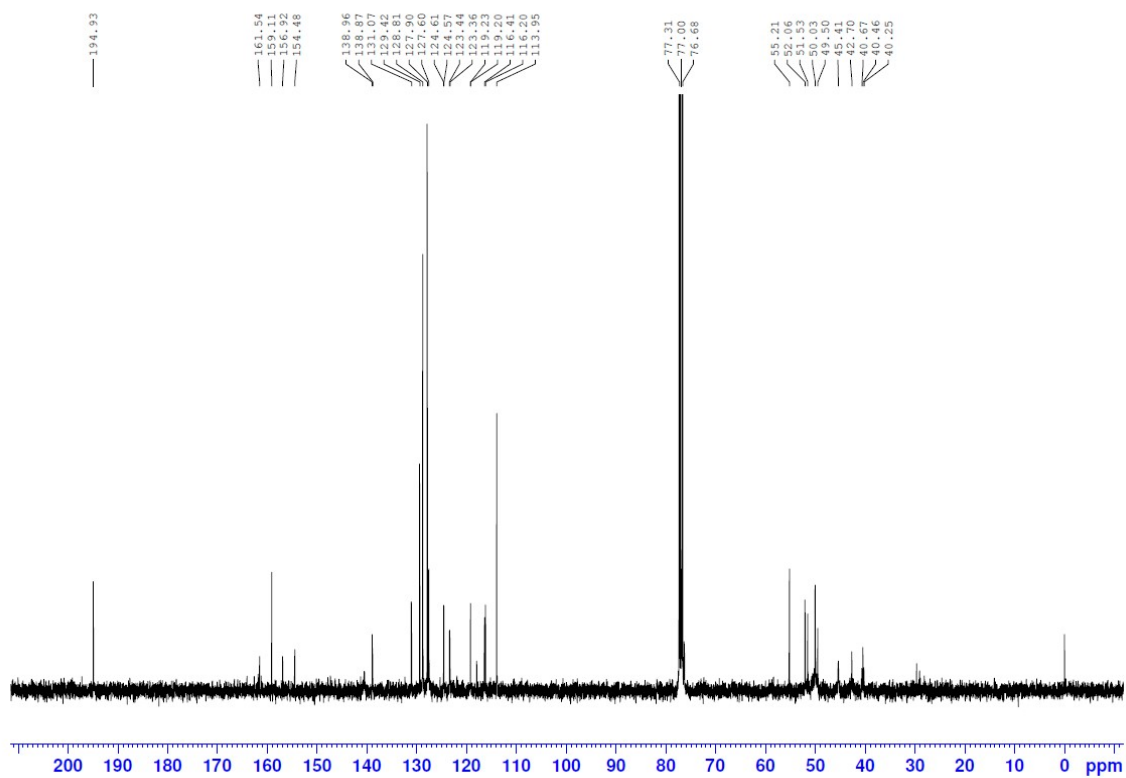
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 4-(4-benzhydrylpiperazin-1-yl)-3,3-difluoro-1-(4-methoxyphenyl)-4-oxobutyl 4-(2-fluorophenyl)piperazine-1-carbodithioate (**7c**):

Patamawadee 18-8-65 No.14  
PS-P7-160 in CDCl<sub>3</sub>



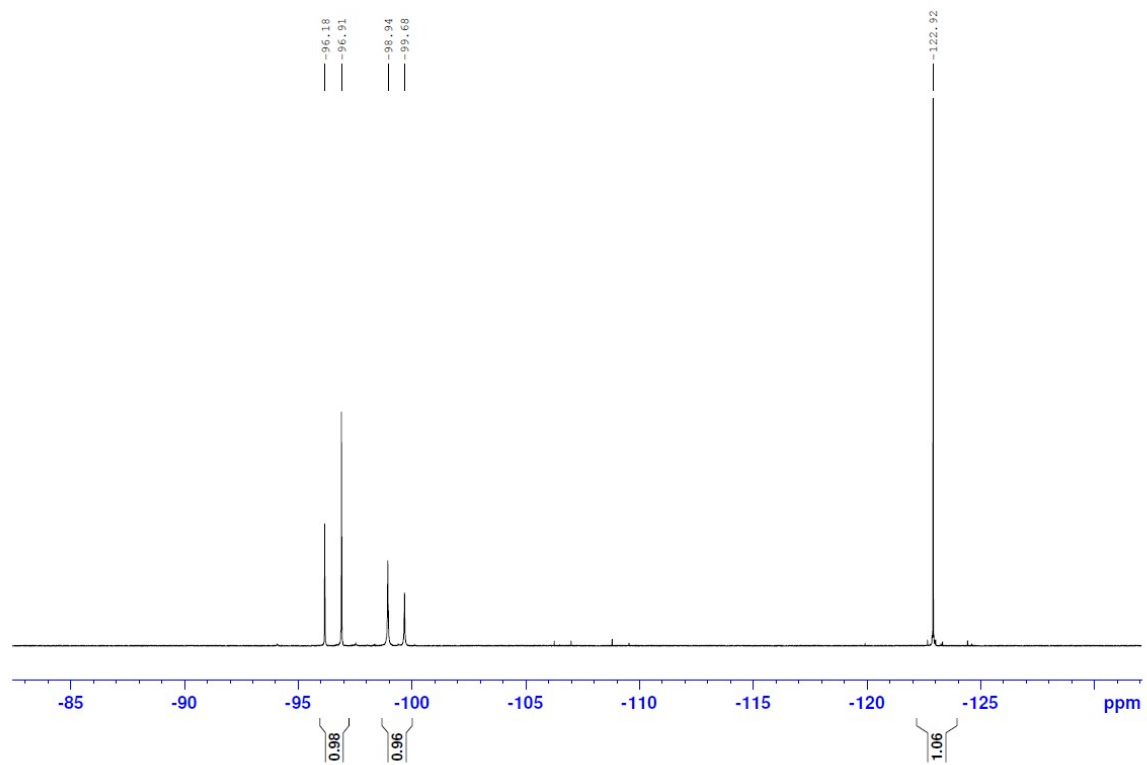
**7c** <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)

Patamawadee 18-8-65 No.16  
13C PS-P7-160 in CDCl<sub>3</sub>



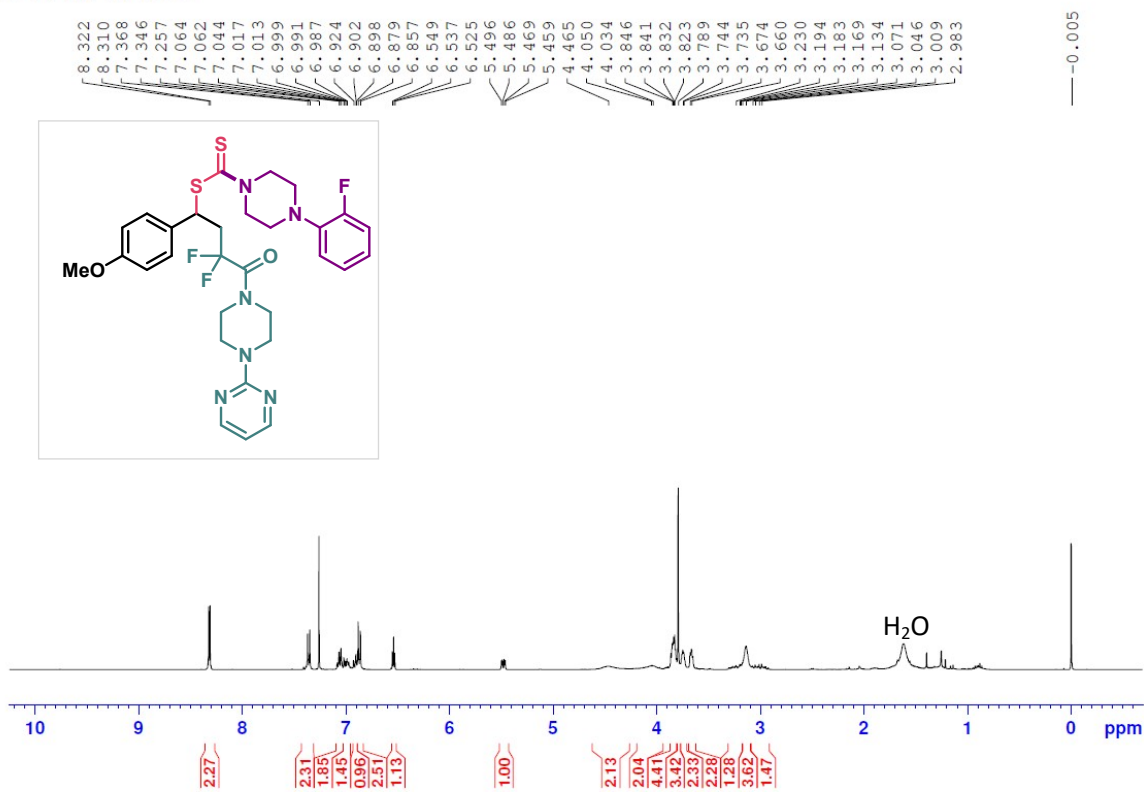
**7c**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 18-8-65 No.15  
 $^{19}\text{F}$  PS-P7-160 in  $\text{CDCl}_3$



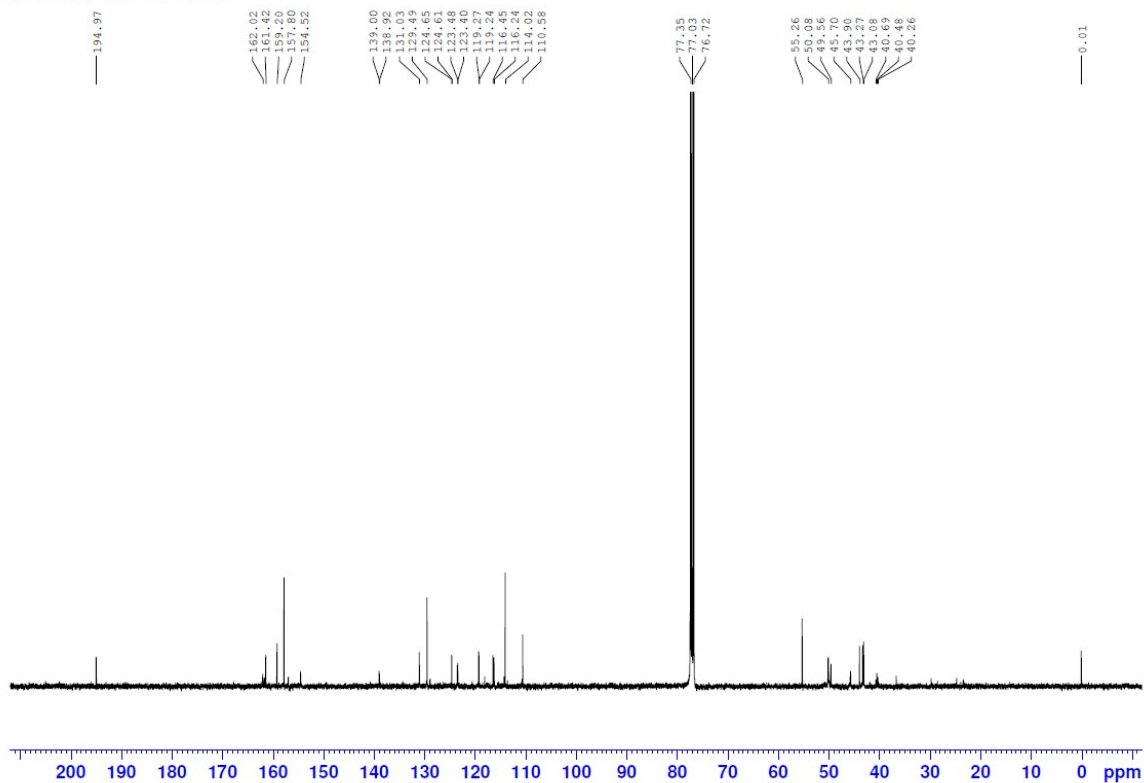
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of 3,3-difluoro-1-(4-methoxyphenyl)-4-oxo-4-(4-(pyrimidin-2-yl)piperazin-1-yl)butyl 4-(2-fluorophenyl)piperazine-1-carbodithioate (**7d**):

Patamawadee 30-5-67 No.6  
PS-P7-161 in  $\text{CDCl}_3$



**7d**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

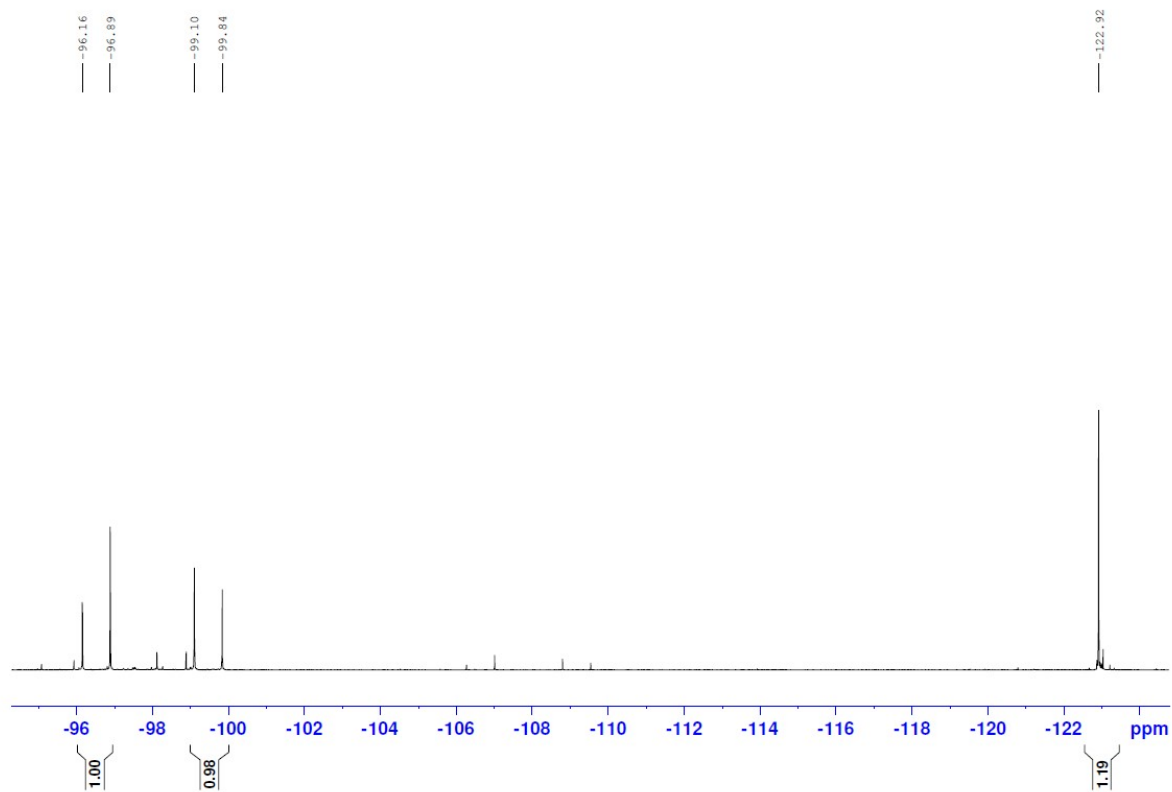
Patamawadee 30-5-67 No.13  
 $^{13}\text{C}$  PS-P7-161 in  $\text{CDCl}_3$





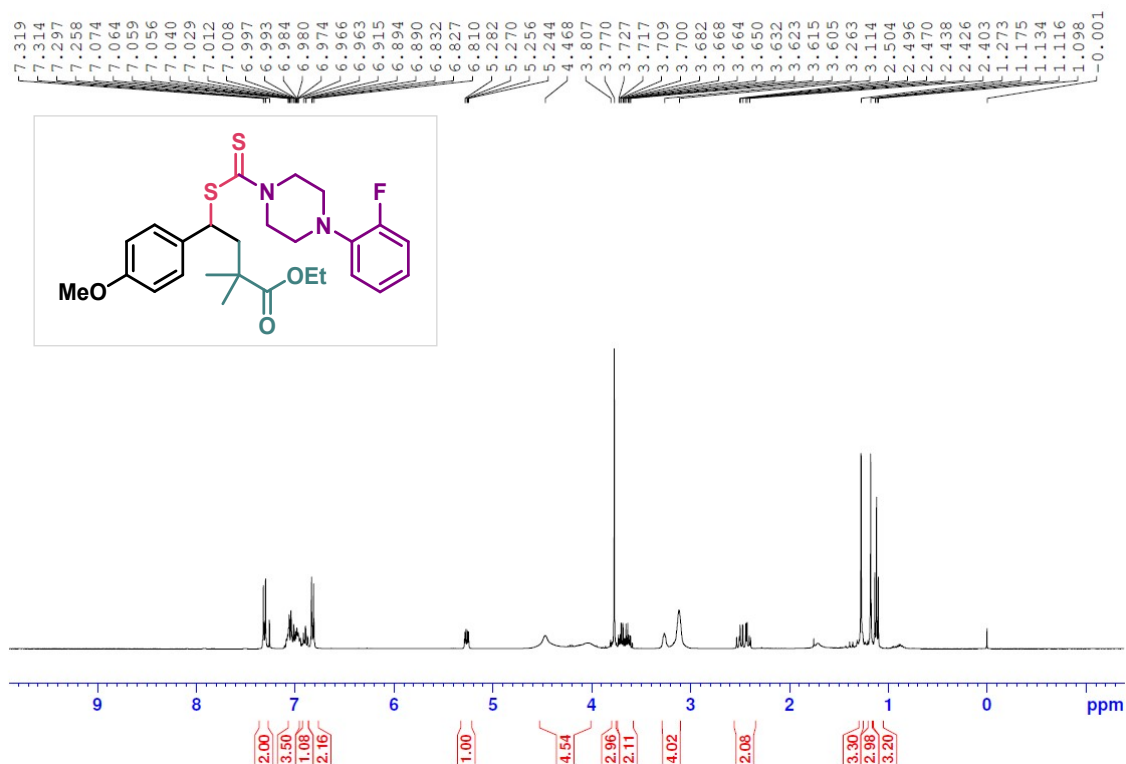
**7d**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 25-8-65 No.27  
 $^{19}\text{F}$  PS-P7-161 in  $\text{CDCl}_3$



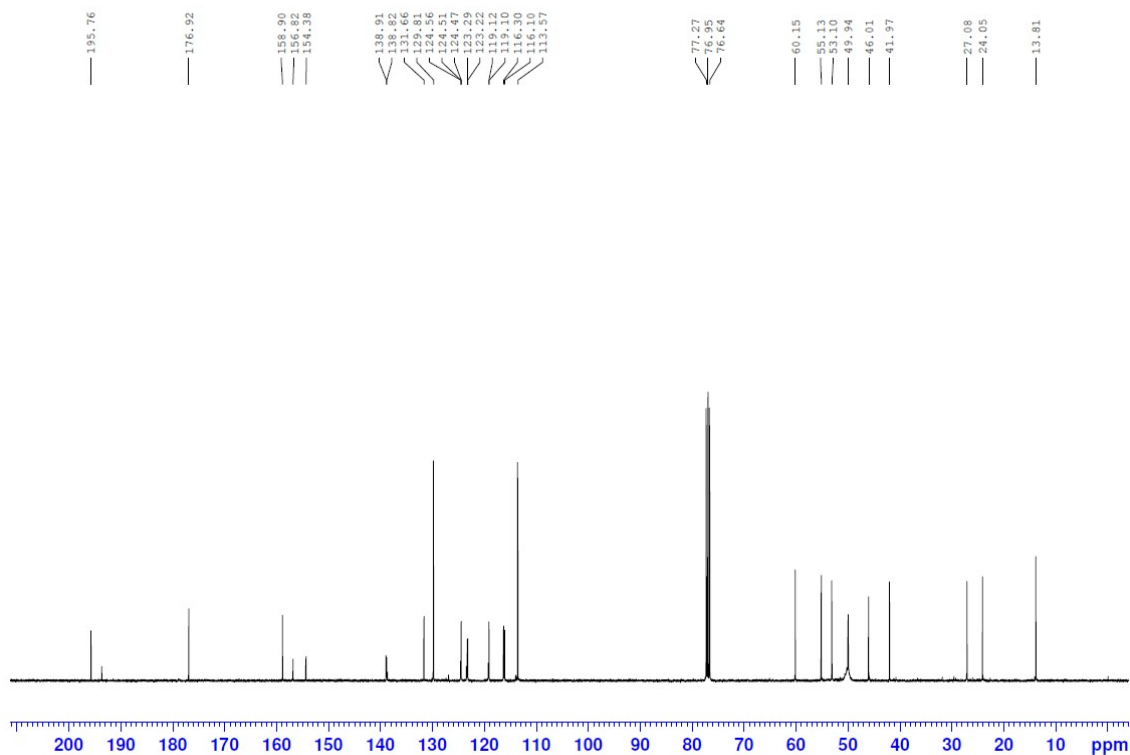
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of ethyl 4-((4-(2-fluorophenyl)piperazine-1-carbonylthio)-4-(4-methoxyphenyl)-2,2-dimethylbutanoate (**7e**):

Patamawadee 15-9-65 No.1  
PS-P7-209 in CDCl<sub>3</sub>



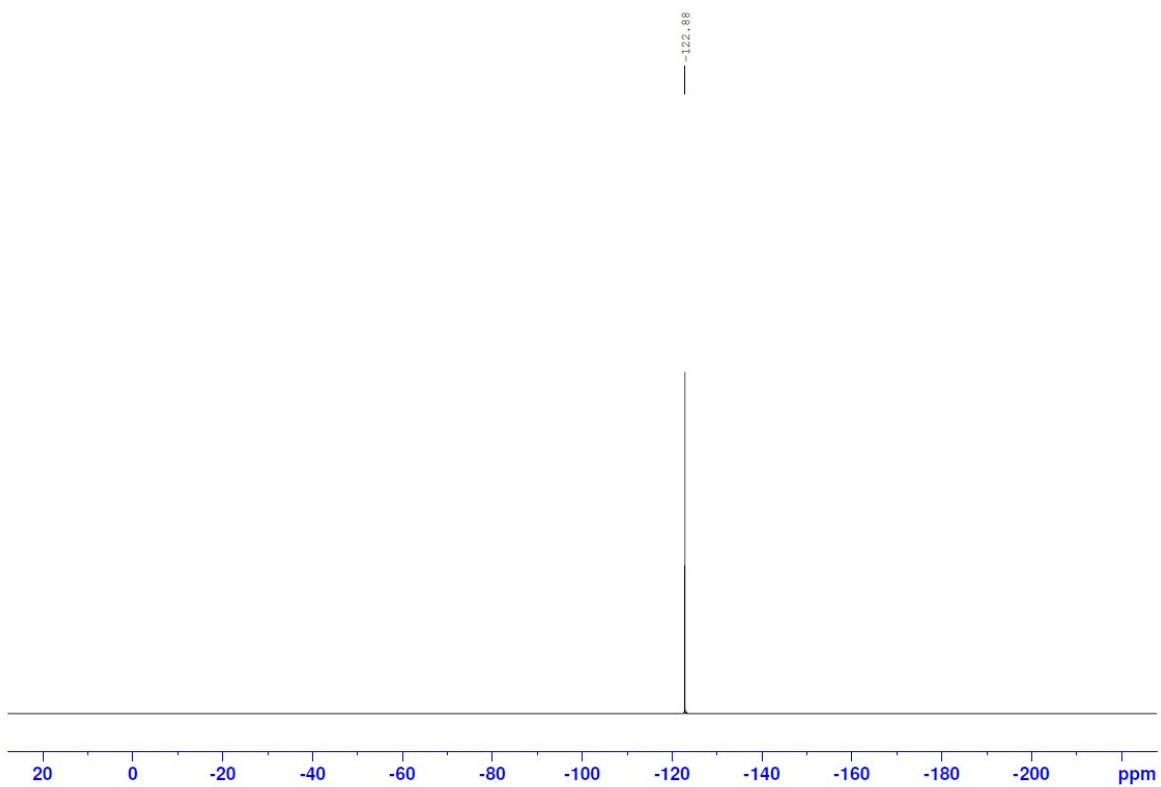
**7e** <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)

Patamawadee 15-9-65 No.3  
13C PS-P7-209 in CDCl<sub>3</sub>



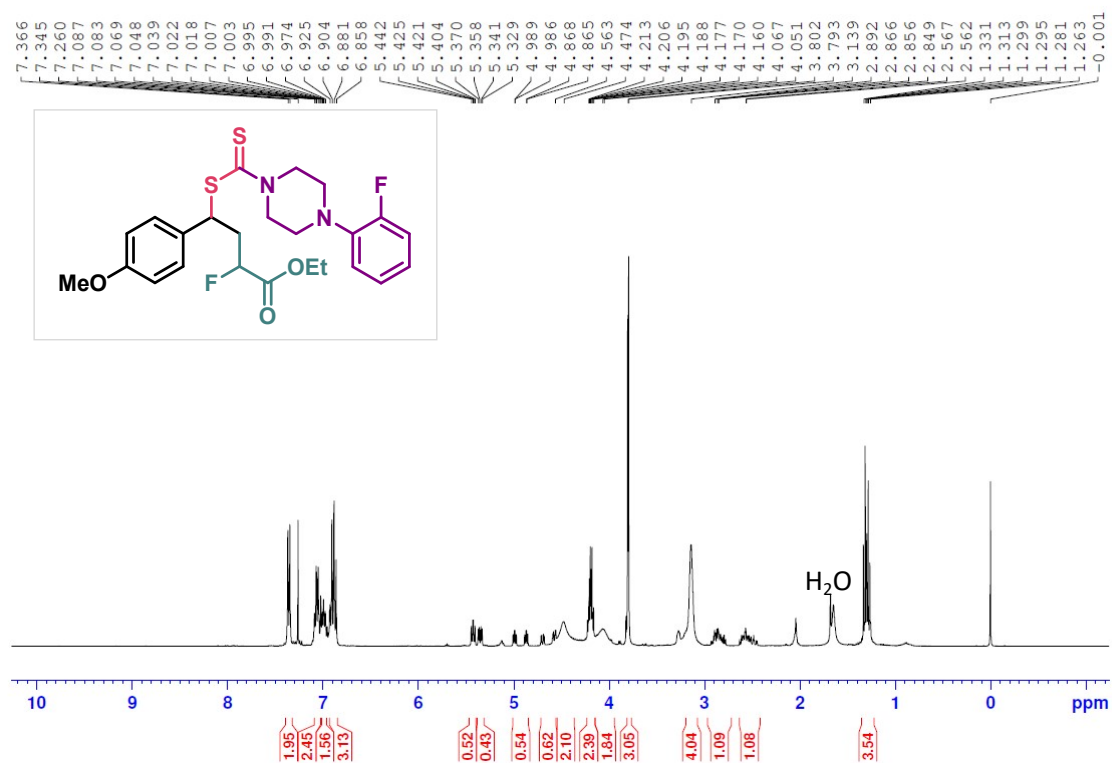
**7e**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 15-9-65 No.2  
19F PS-P7-209 in  $\text{CDCl}_3$



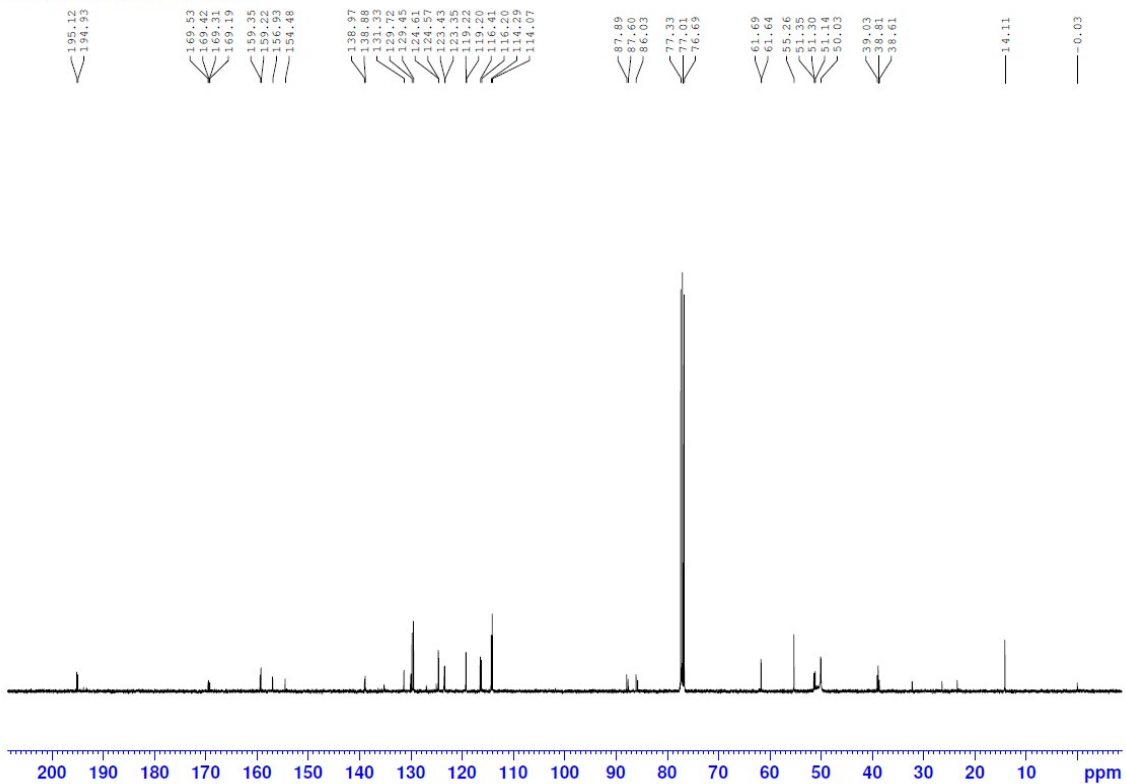
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of ethyl ethyl 2-fluoro-4-((4-(2-fluorophenyl)piperazine-1-carbonthioyl)thio)-4-(4-methoxyphenyl)butanoate (**7f**):

Patamawadee 8-12-65 No.1  
PS-P7-276-2 in CDCl<sub>3</sub>



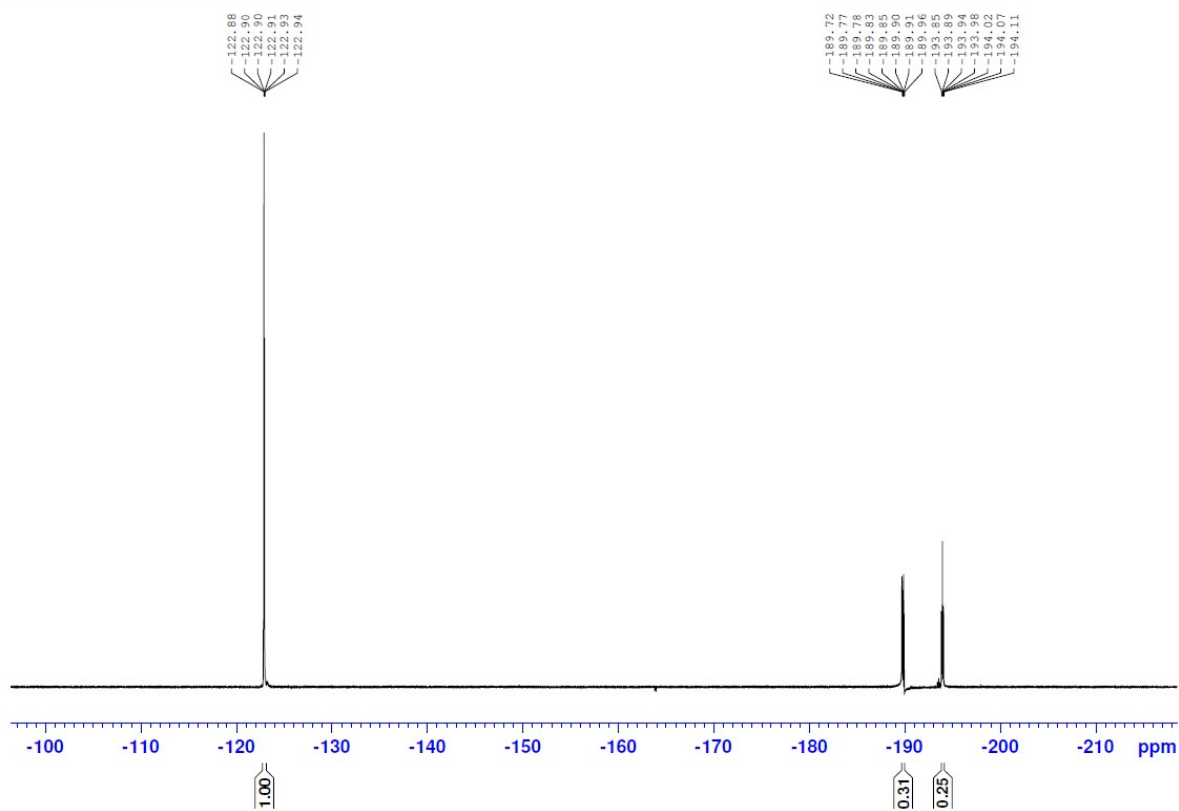
**7f** <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)

Patamawadee 10-12-65 No.3  
13C PS-P7-276-2 in CDCl<sub>3</sub>

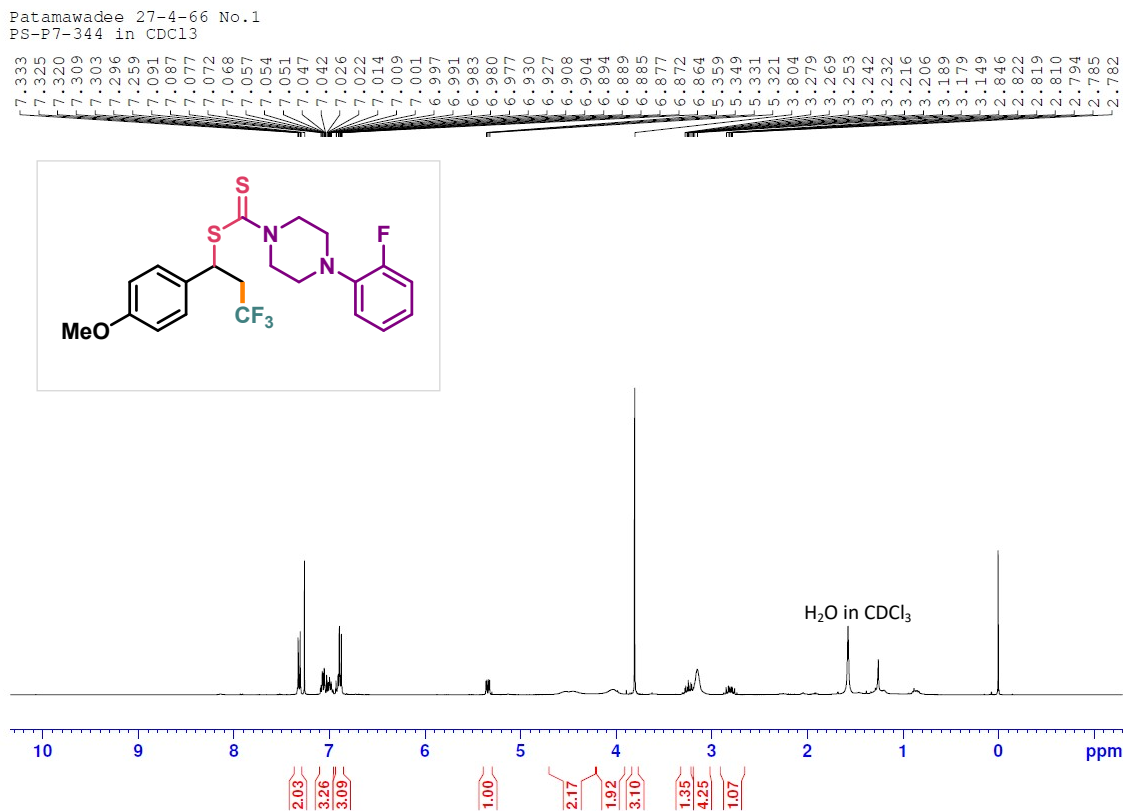


7f  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

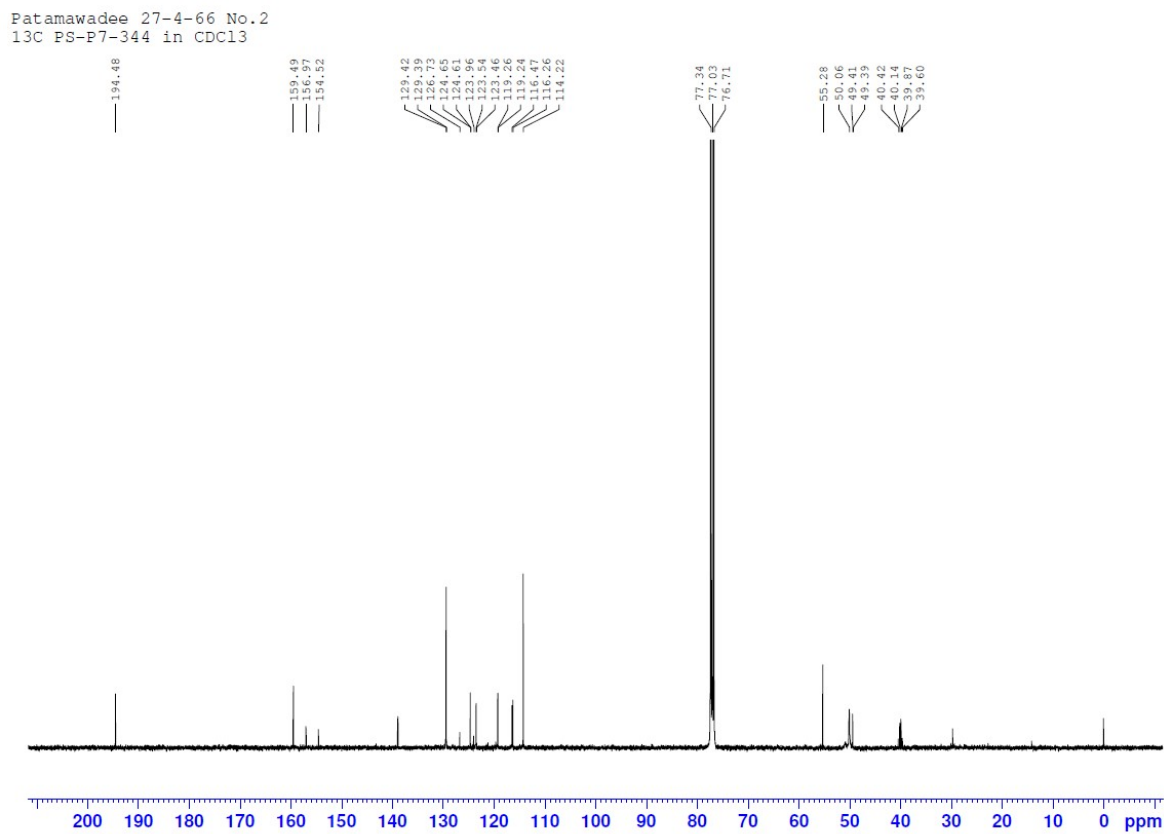
Patamawadee 20-9-66 No.5  
19F PS-P7-276-2 in  $\text{CDCl}_3$



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of 3,3,3-trifluoro-1-(4-methoxyphenyl)propyl 4-(2-fluorophenyl)piperazine-1-carbodithioate (**7g**):

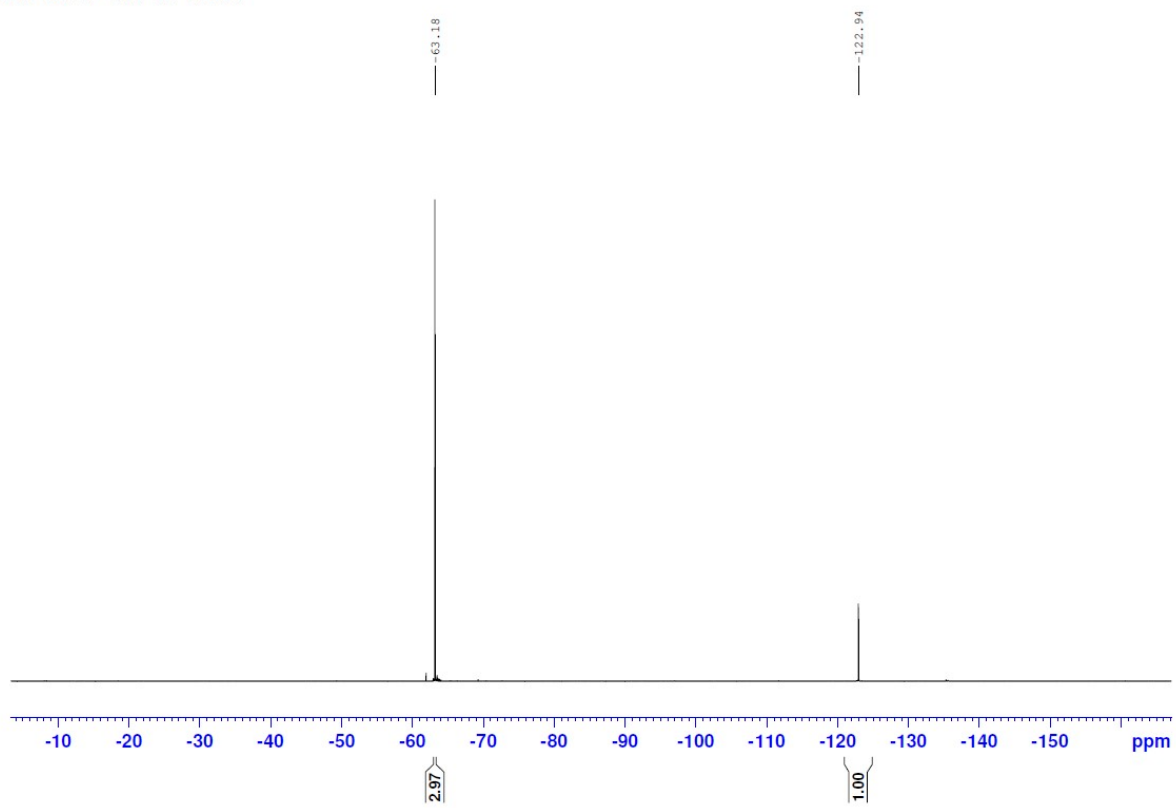


**7g**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )



**7g**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 20-9-66 No.3  
19F PS-P7-344 in  $\text{CDCl}_3$

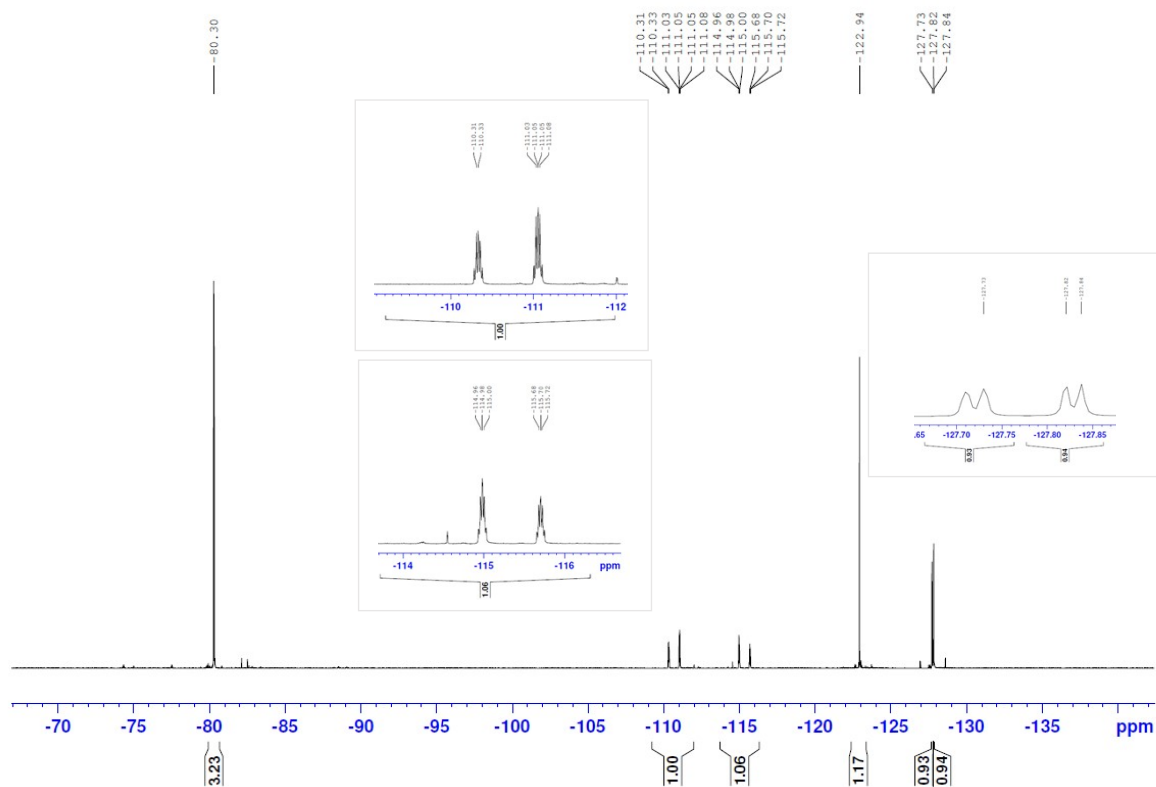






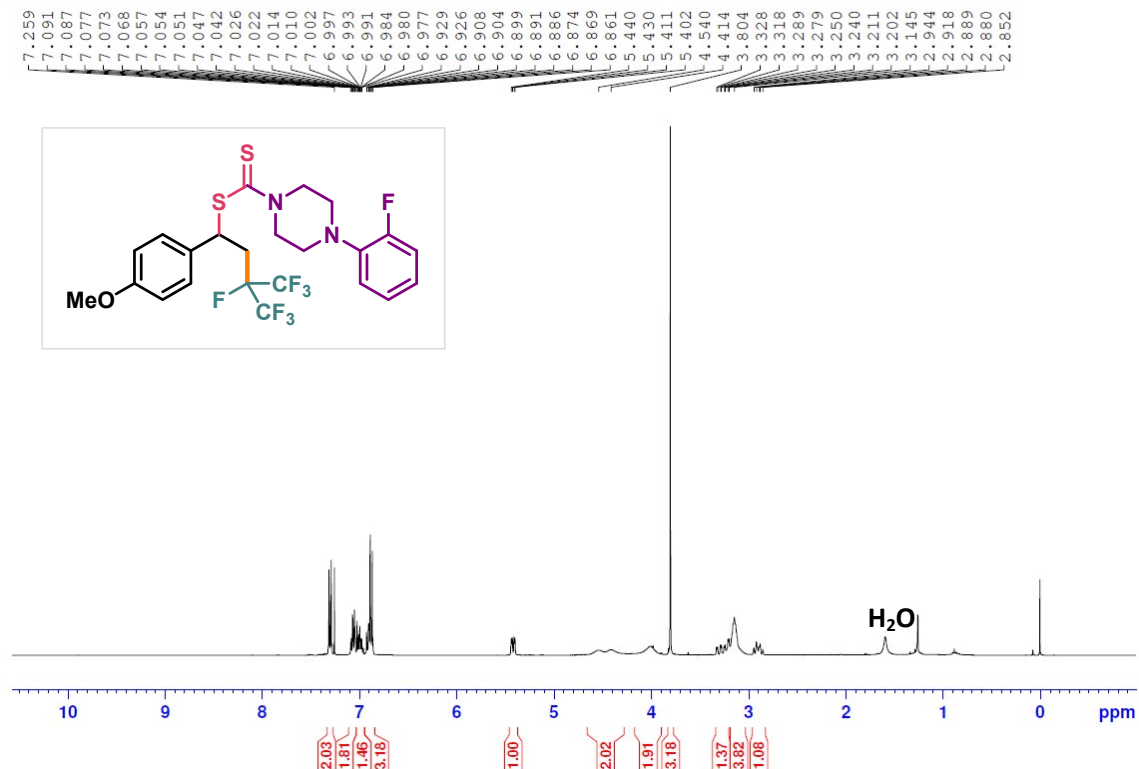
# 7h $^{19}\text{F}\{^1\text{H}\}$ NMR (400 MHz, $\text{CDCl}_3$ )

Patamawadee 24-2-66 No.7  
19F PS-P7-330 in  $\text{CDCl}_3$



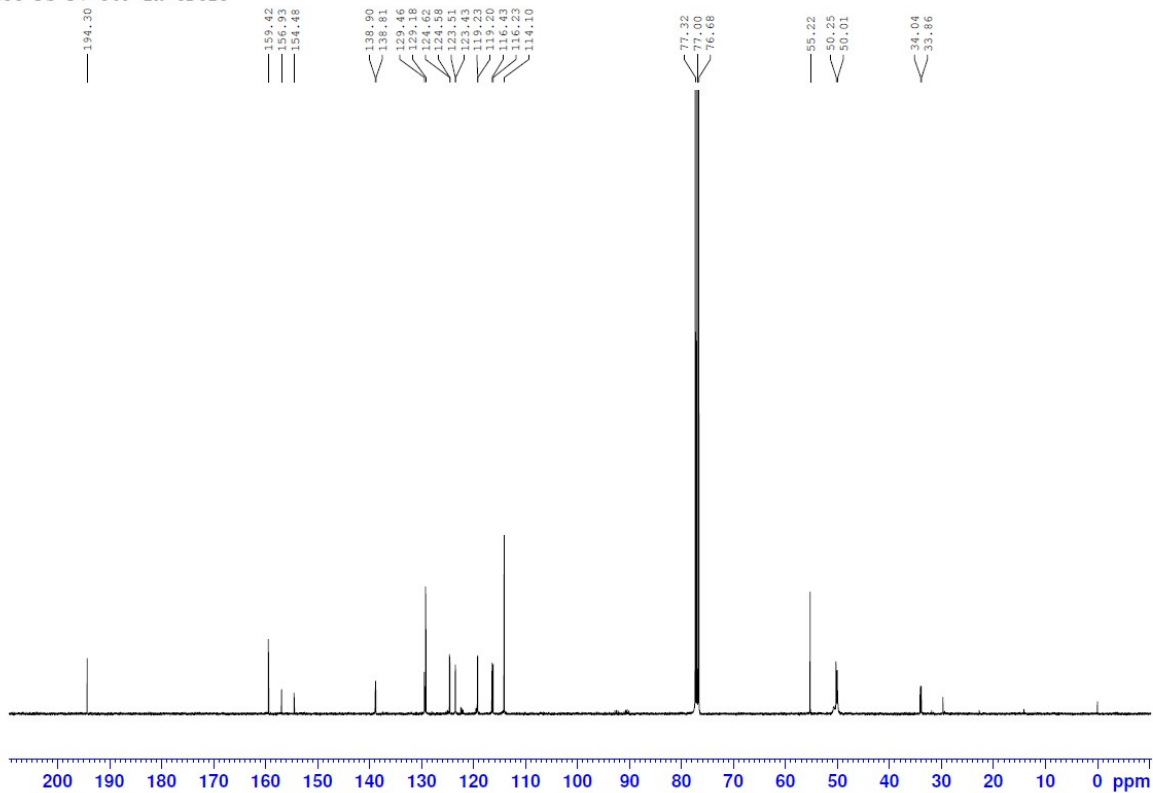
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of 3,4,4,4-tetrafluoro-1-(4-methoxyphenyl)-3-(trifluoromethyl)butyl 4-(2-fluorophenyl)piperazine-1-carbodithioate (**7i**):

Patamawadee 18-5-66 No.1  
PS-P7-369 in  $\text{CDCl}_3$



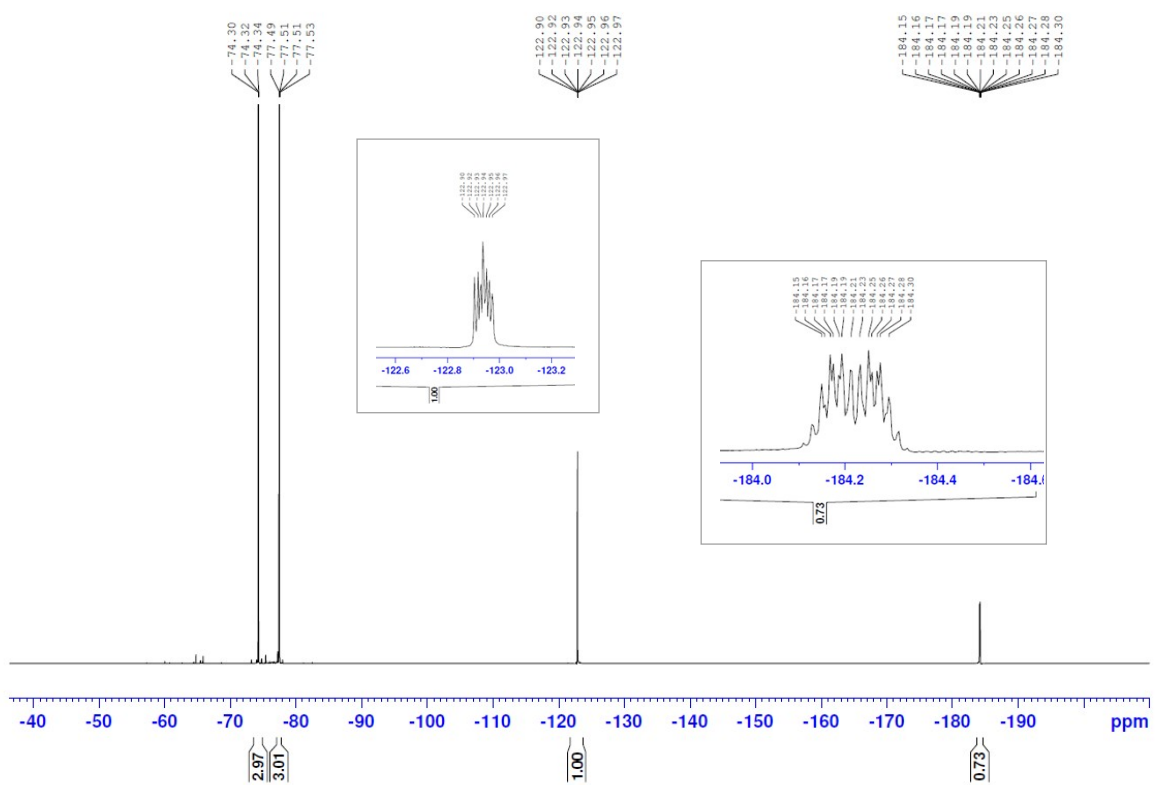
**7i**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 18-5-66 No.2  
13C PS-P7-369 in  $\text{CDCl}_3$



7i  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

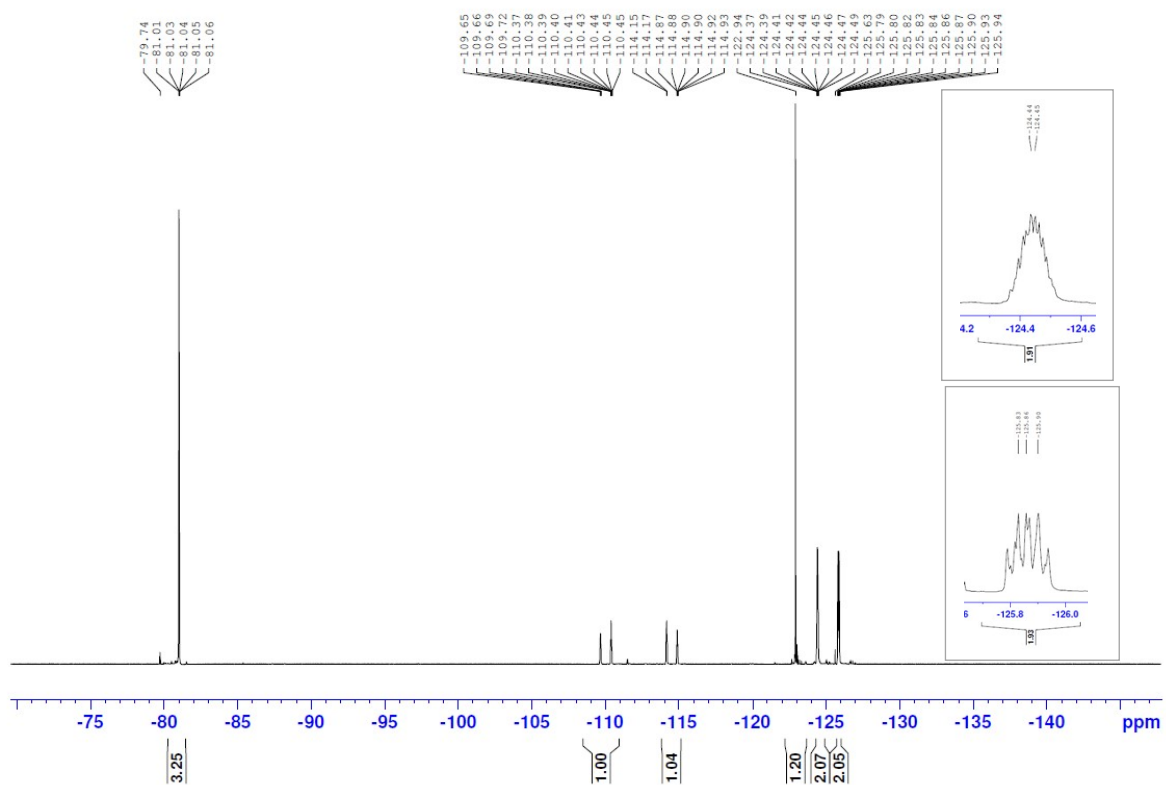
Patamawadee 20-9-66 No.2  
19F PS-P7-369 in  $\text{CDCl}_3$





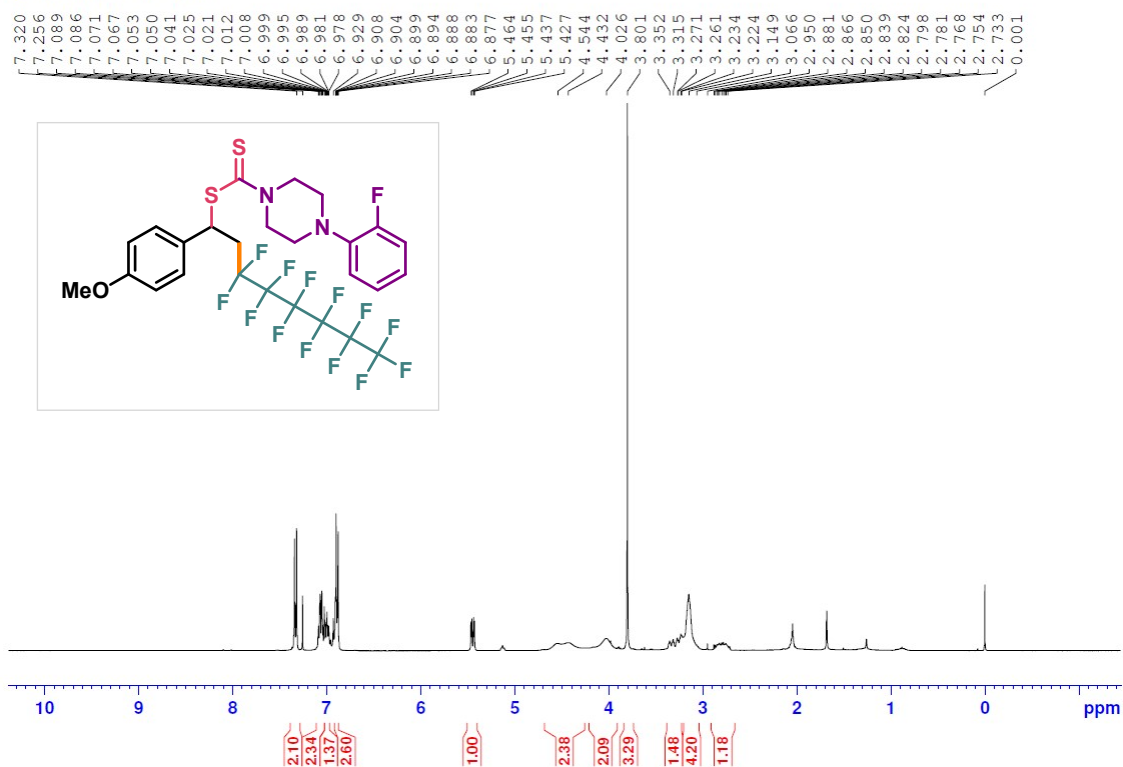
7j  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 6-2-66 No.2  
19F PS-P7-321 in  $\text{CDCl}_3$



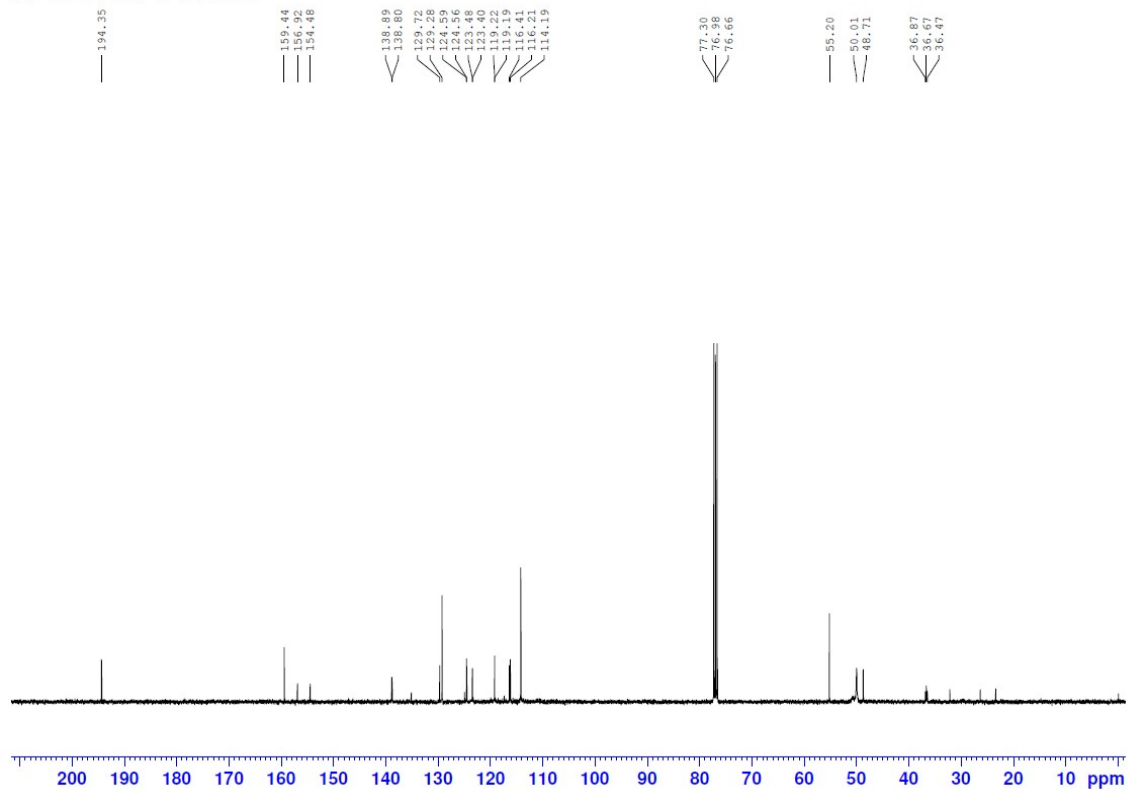
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-(4-methoxyphenyl)octyl 4-(2-fluorophenyl)piperazine-1-carbodithioate (**7k**):

Patamawadee 1-12-65 No.10  
PS-P7-275-1 in CDCl<sub>3</sub>



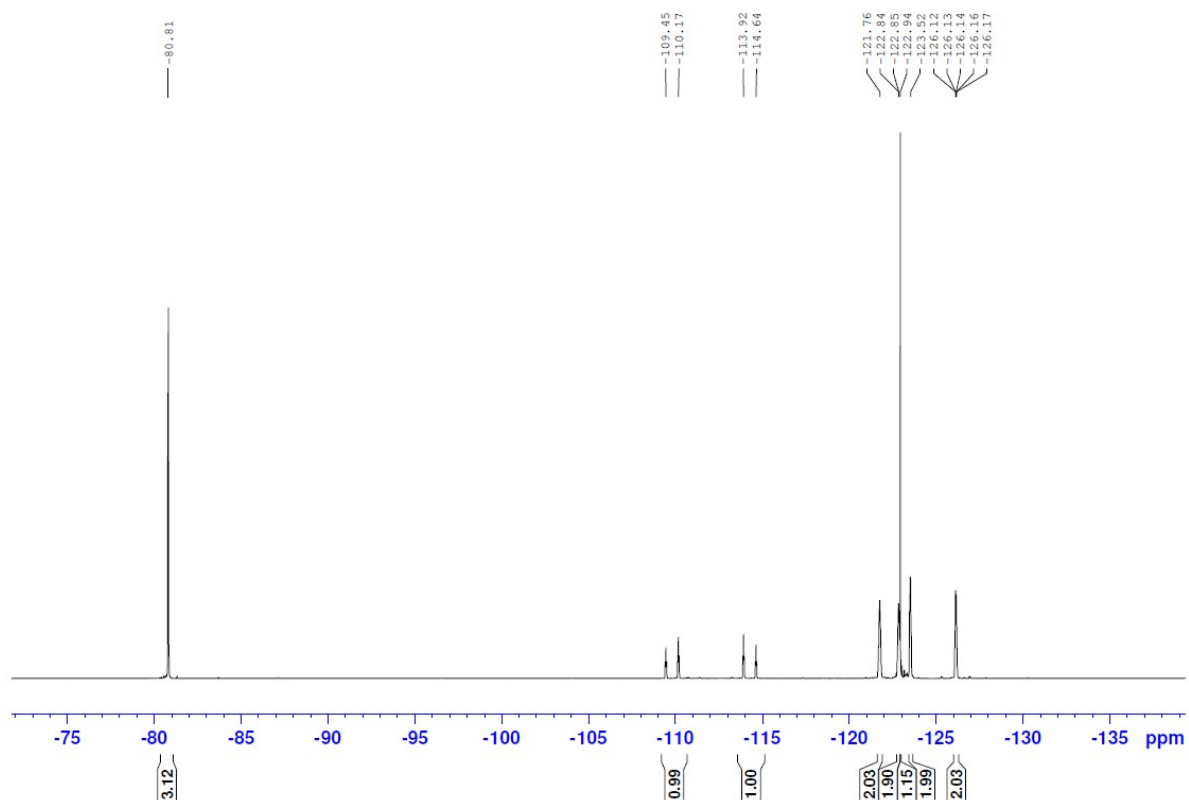
**7k** <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)

Patamawadee 1-12-65 No.11  
13C PS-P7-275-1 in CDCl<sub>3</sub>



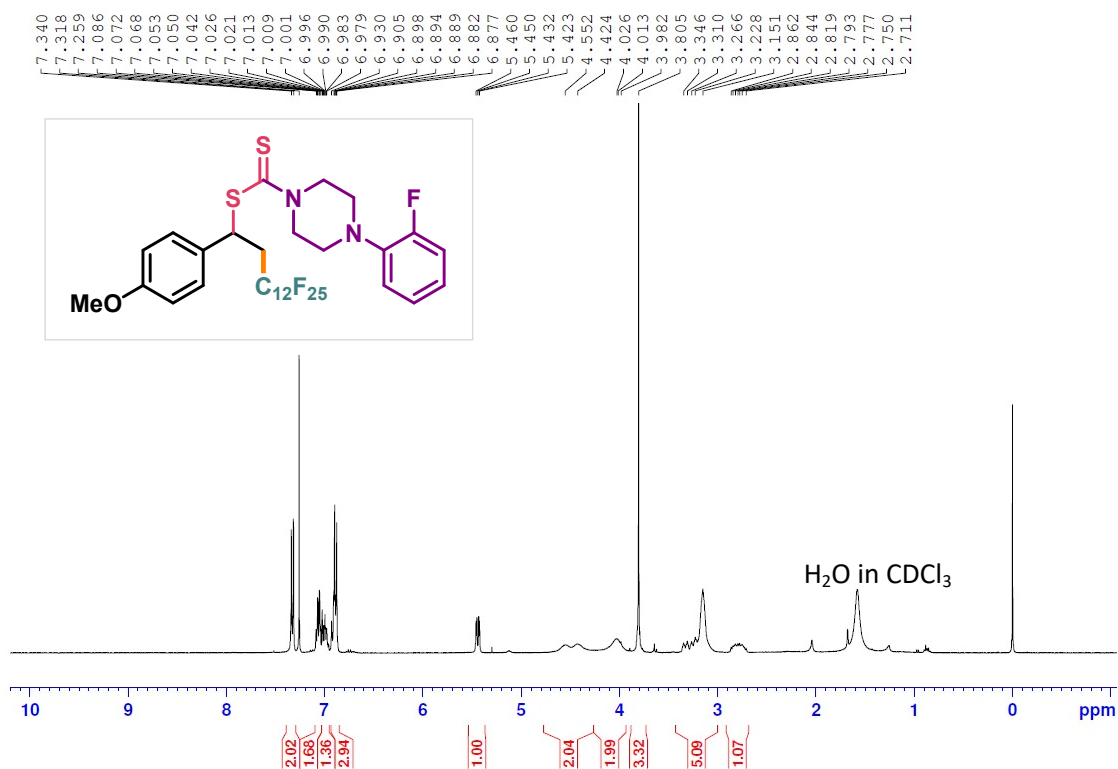
**7k**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 1-12-65 No.12  
19F PS-P7-275-1 in  $\text{CDCl}_3$



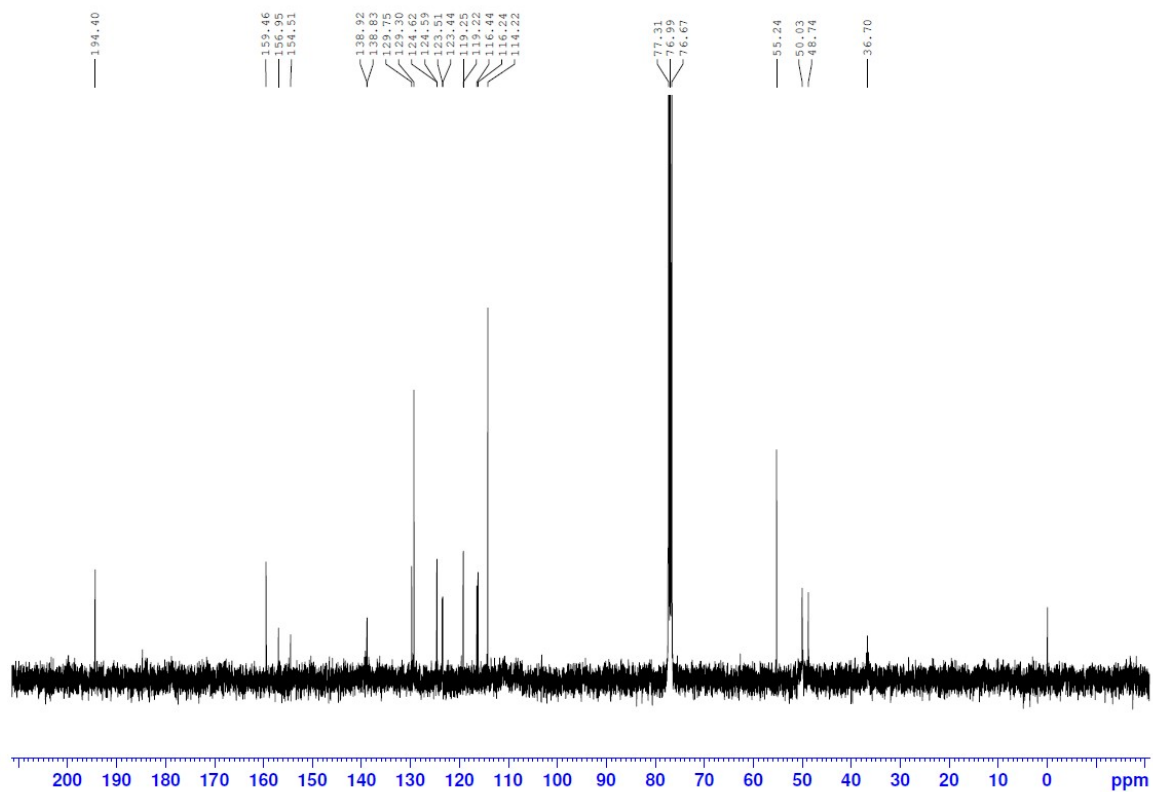
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-(4-methoxyphenyl)octyl 4-(2-fluorophenyl)piperazine-1-carbodithioate (**7m**):

Patamawadee 13-3-66 No.3  
PS-P7-338 in CDCl<sub>3</sub>



**7m** <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)

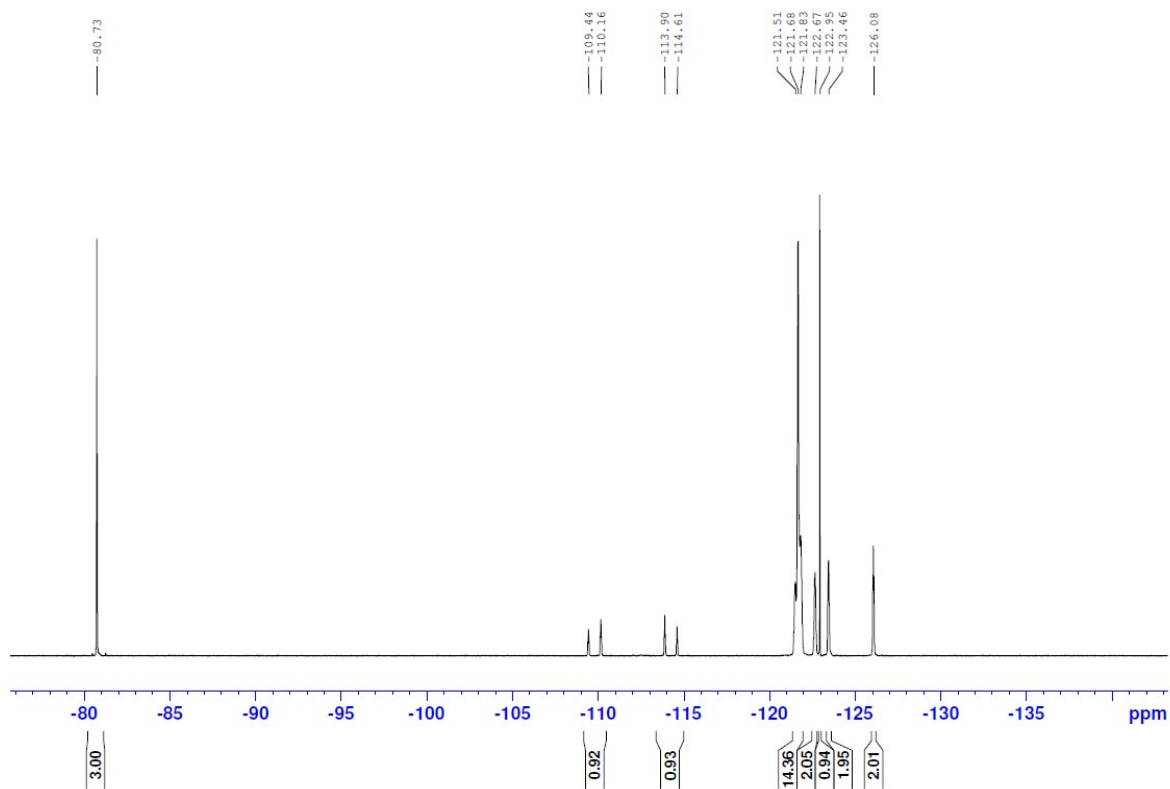
Patamawadee 13-3-66 No.5  
13C PS-P7-338 in CDCl<sub>3</sub>





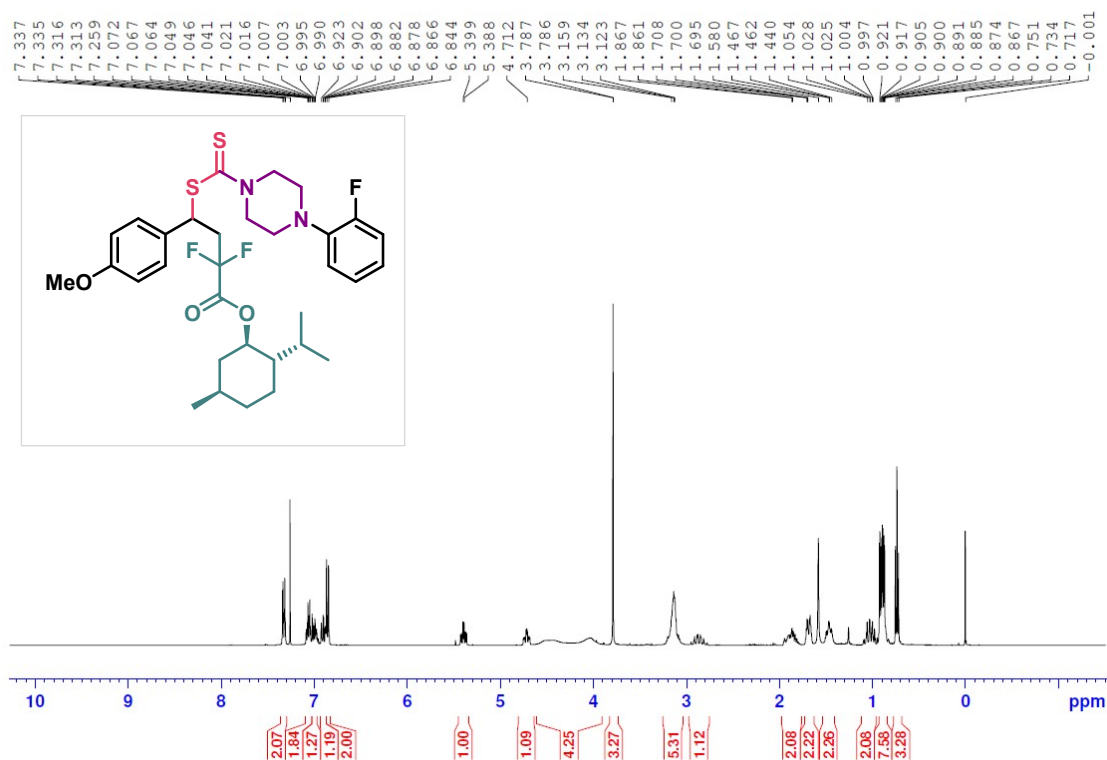
7m  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 13-3-66 No.4  
 $^{19}\text{F}$  PS-P7-338 in  $\text{CDCl}_3$



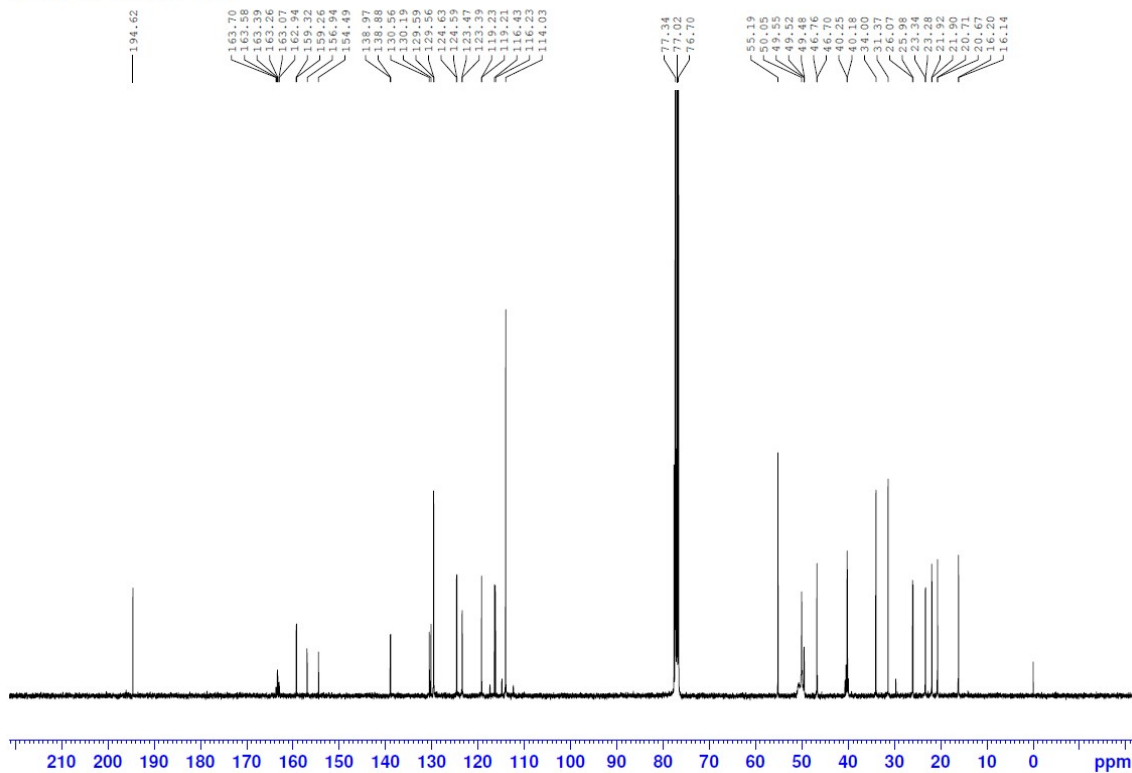
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of (1*R*,2*R*,5*R*)-2-isopropyl-5-methylcyclohexyl 2,2-difluoro-4-((4-(2-fluorophenyl)piperazine-1-carbonylthio)-4-(4-methoxyphenyl)butanoate (**8a**):

Patamawadee 18-5-66 No.5  
PS-P7-381 in  $\text{CDCl}_3$



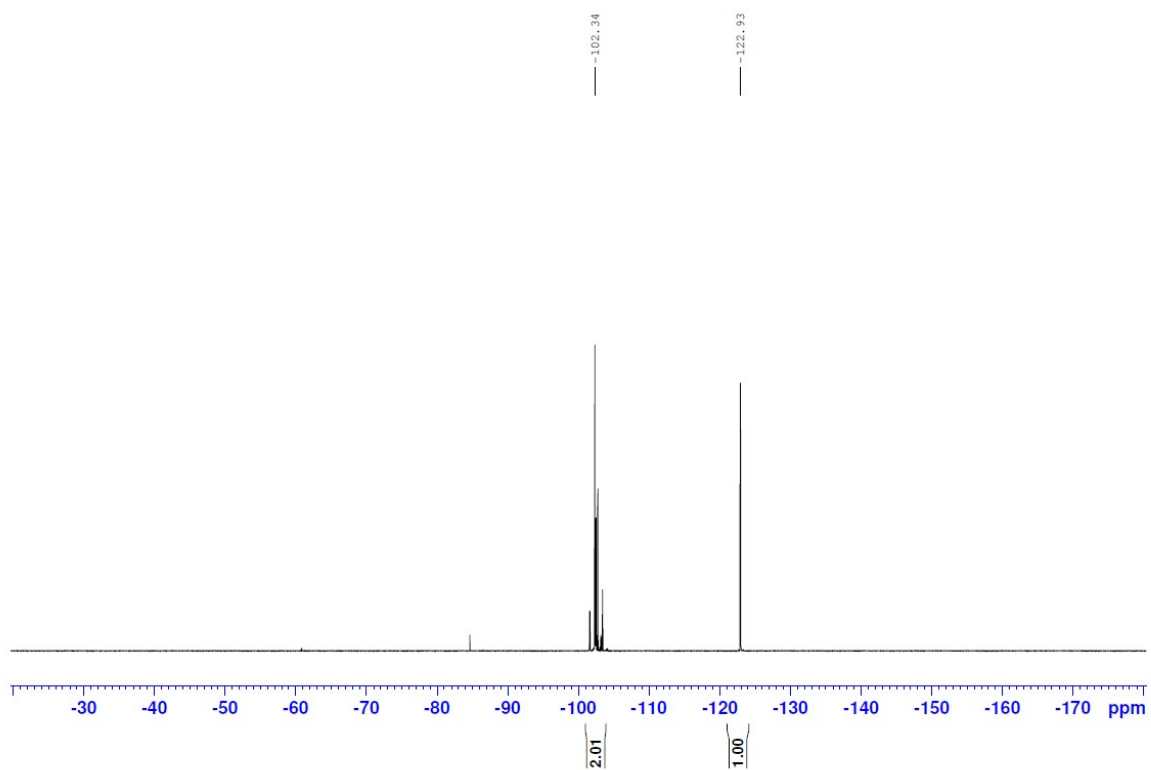
**8a**  $^{13}\text{C}$ { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 18-5-66 No.6  
13C PS-P7-381 in  $\text{CDCl}_3$



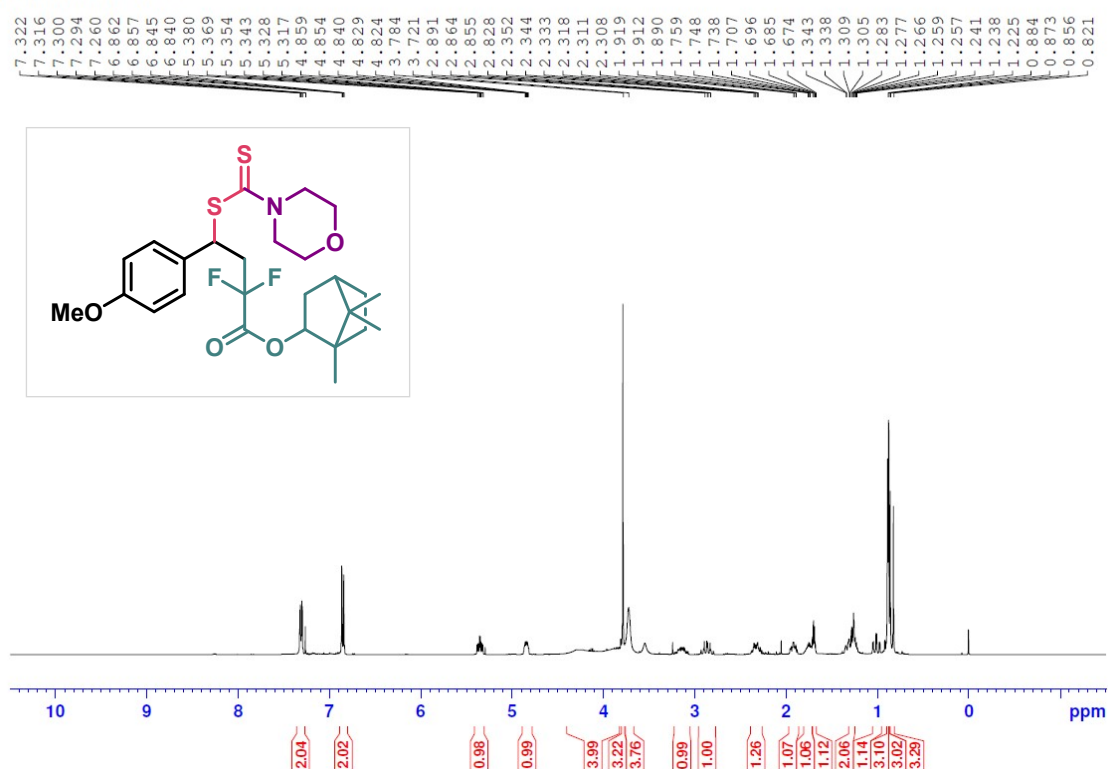
**8a**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 20-9-66 No.4  
 $^{19}\text{F}$  PS-P7-381 in  $\text{CDCl}_3$



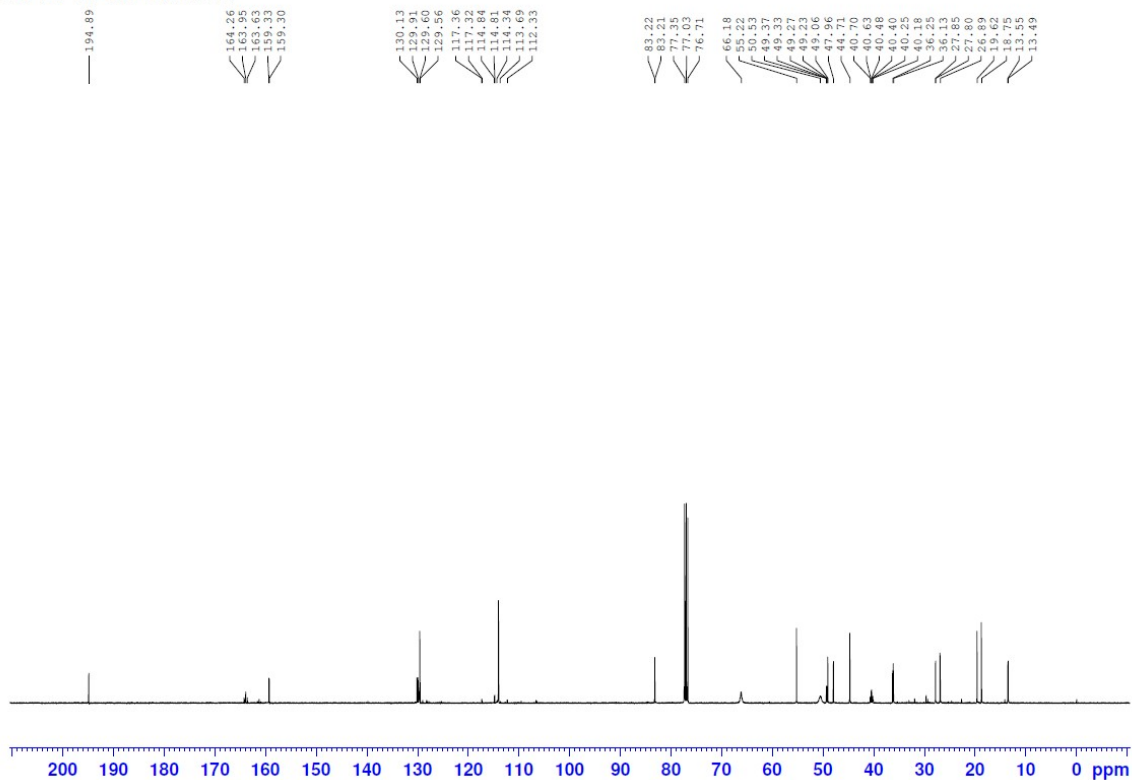
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of (1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2,2-difluoro-4-(4-methoxyphenyl)-4-((morpholine-4-carbonylthio)thio)butanoate (**8b**):

Patamawadee 21-6-66 No.1  
PS-P7-409 in  $\text{CDCl}_3$



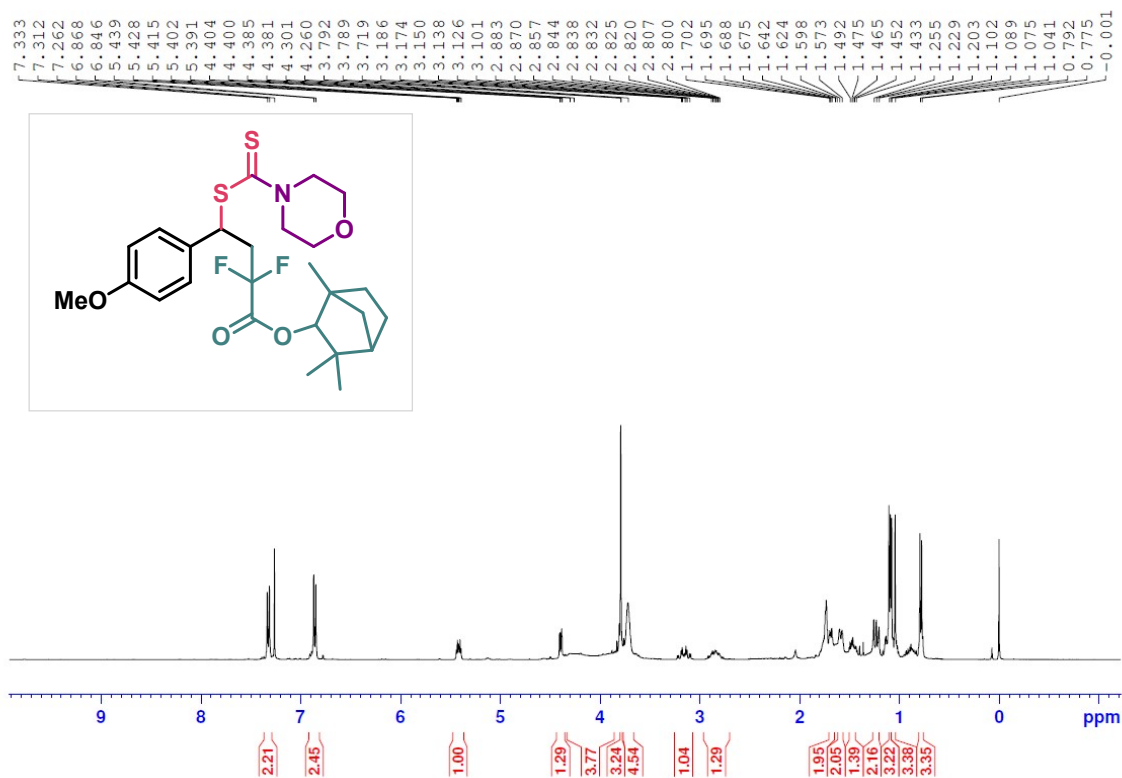
**8b**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 21-6-66 No.2  
13C PS-P7-409 in  $\text{CDCl}_3$



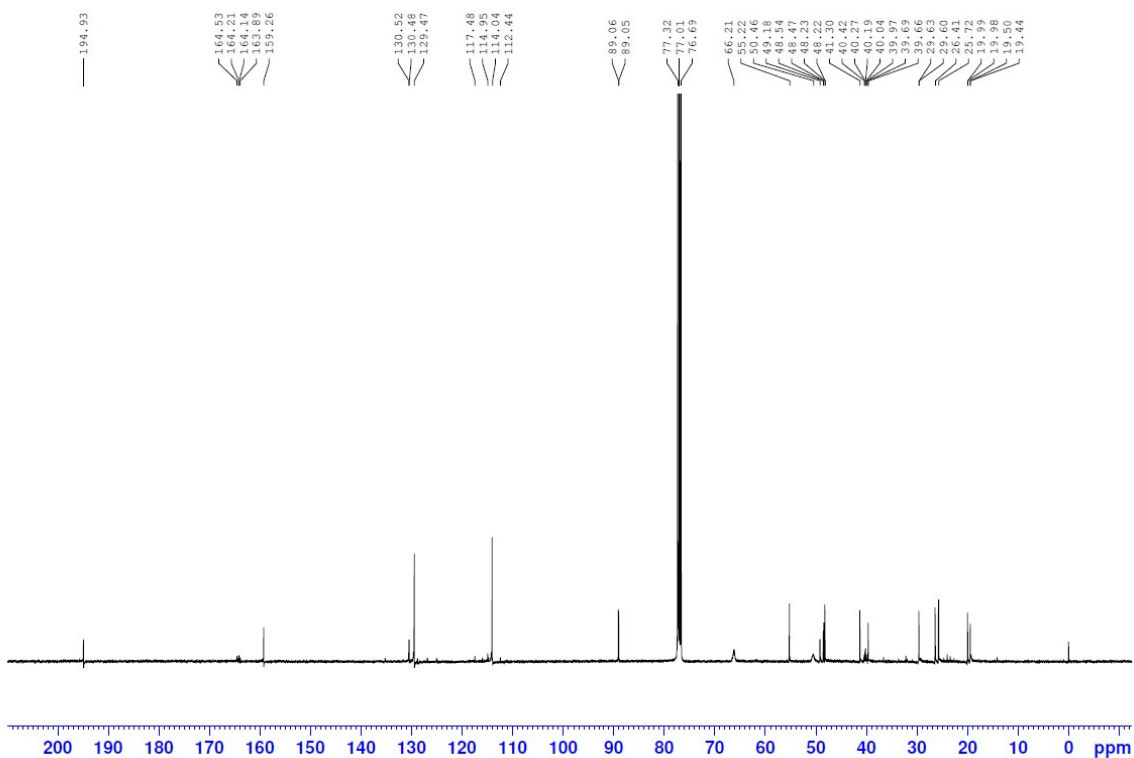
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of 1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 2,2-difluoro-4-(4-methoxyphenyl)-4-((morpholine-4-carbonothioyl)thio)butanoate (**8c**):

Patamawadee 10-6-67 No.1  
PS-P7-442 in  $\text{CDCl}_3$



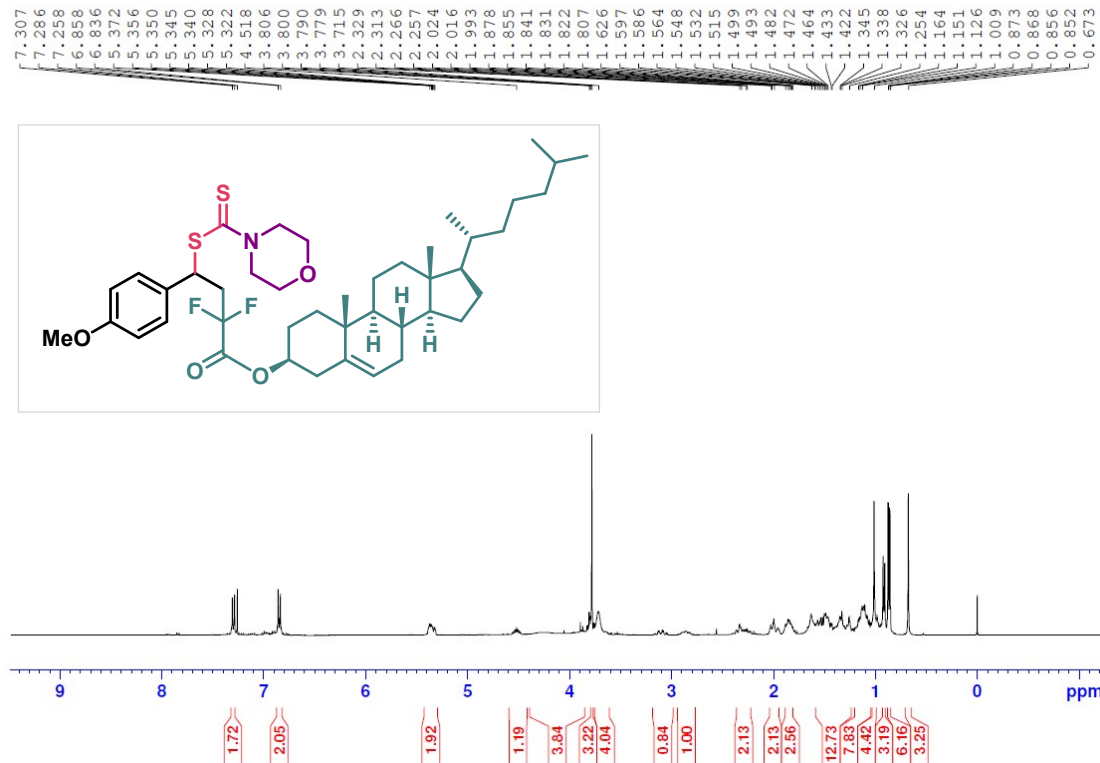
**8c**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 11-6-67 No.1  
 $^{13}\text{C}$  PS-P7-442 in  $\text{CDCl}_3$



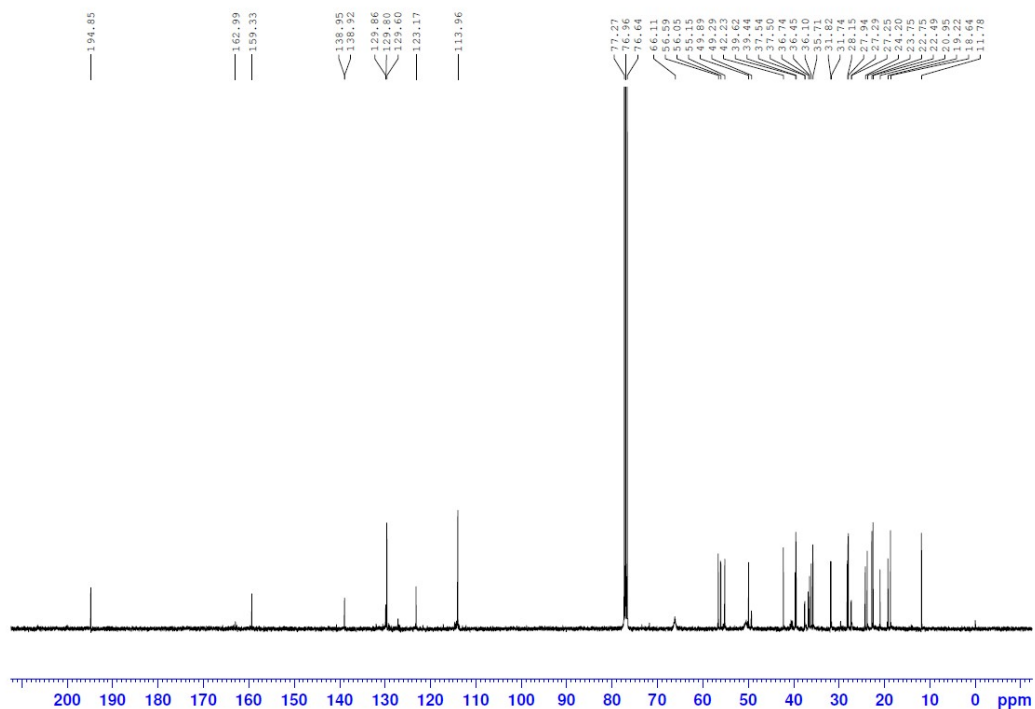
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of (3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 2,2-difluoro-4-(4-methoxyphenyl)-4-((morpholine-4-carbonothioyl)thio)butanoate (**8d**):

Patamawadee 4-7-66 No.6  
PS-P7-427-1 in  $\text{CDCl}_3$



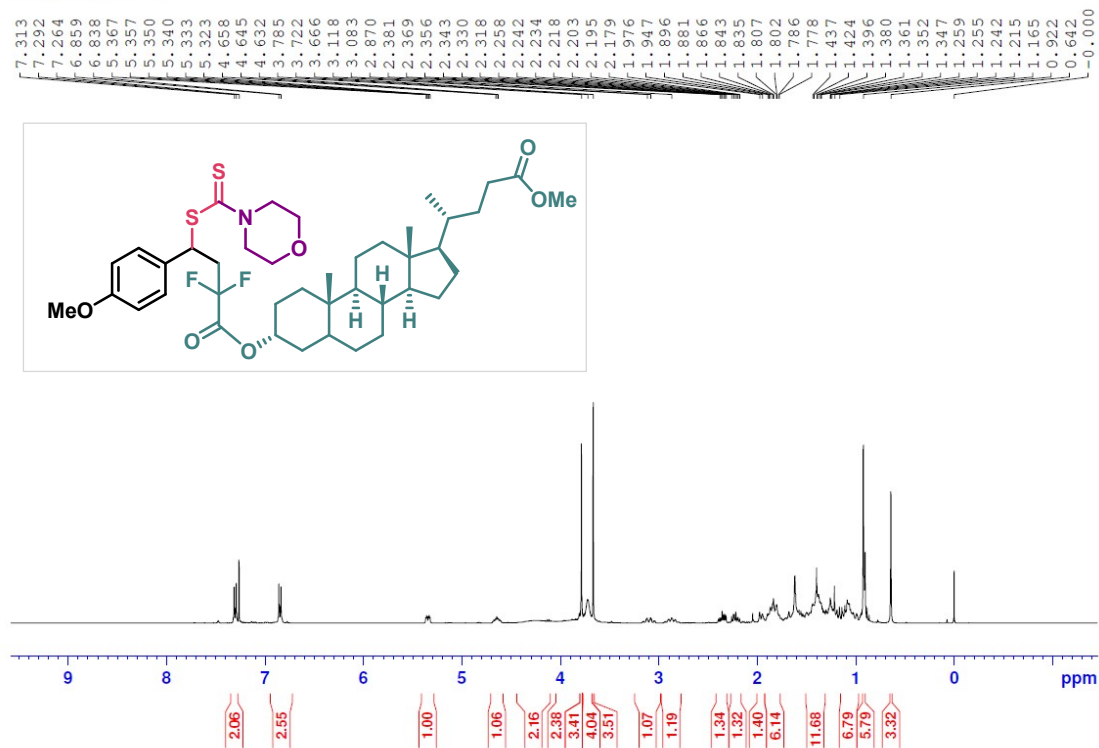
**8d**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 4-7-66 No.7  
13C PS-P7-427-1 in  $\text{CDCl}_3$



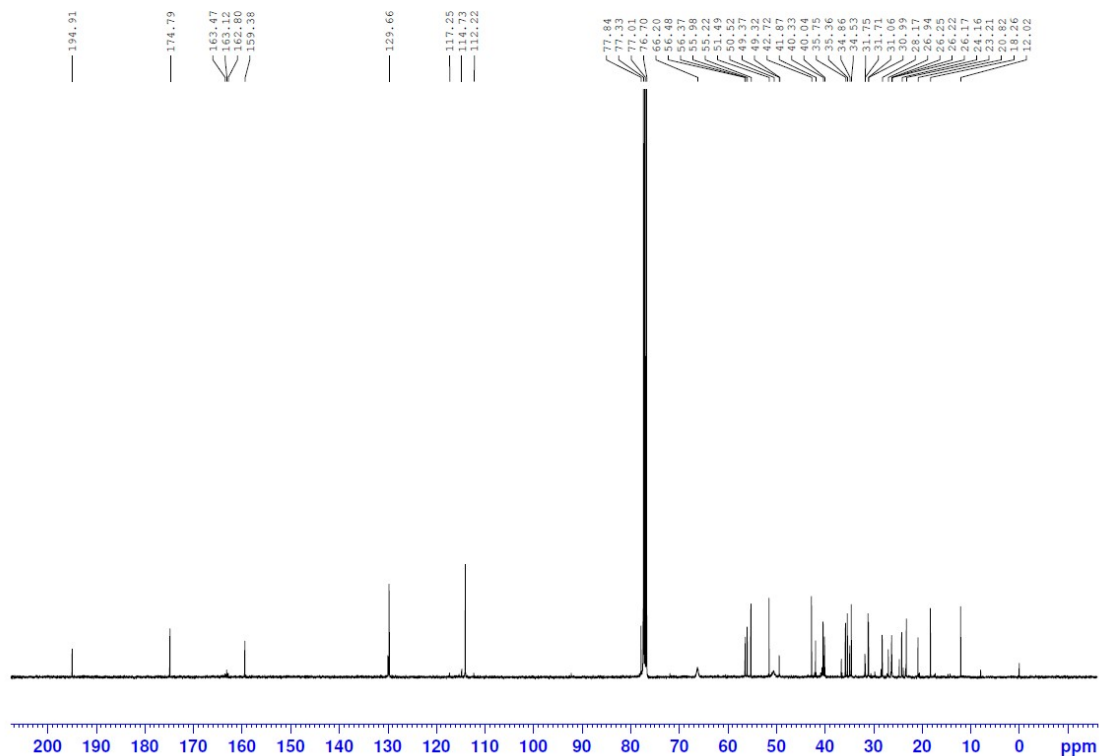
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of (methyl (4R)-4-((3R,8R,9S,10S,13R,14S,17R)-3-((2,2-difluoro-4-(4-methoxyphenyl)-4-((morpholine-4-carbonothioyl)thio)butanoyl)oxy)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (**8e**):

Patamawadee 30-5-67 No.5  
PS-P7-435 in  $\text{CDCl}_3$



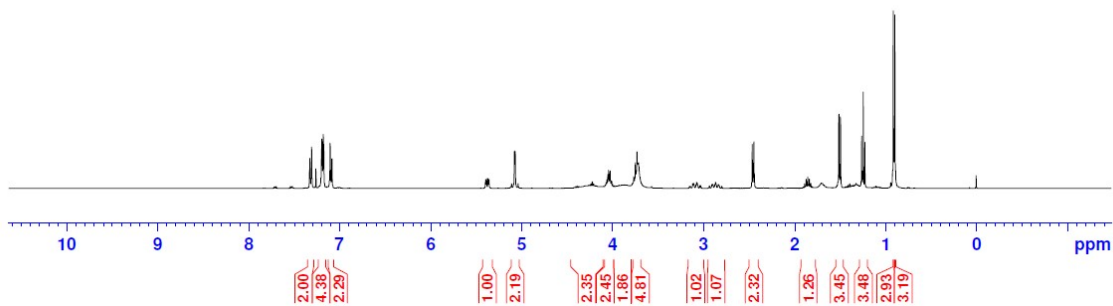
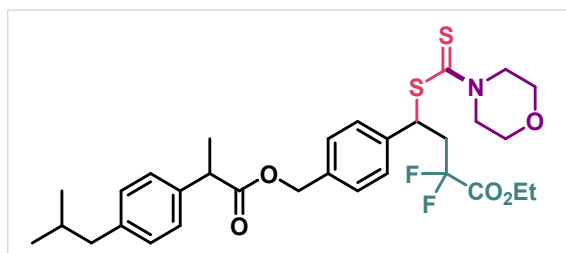
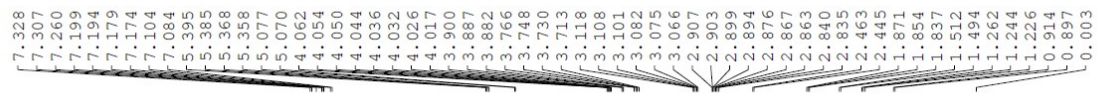
**8e**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 30-5-67 No.12  
 $^{13}\text{C}$  PS-P7-435 in  $\text{CDCl}_3$



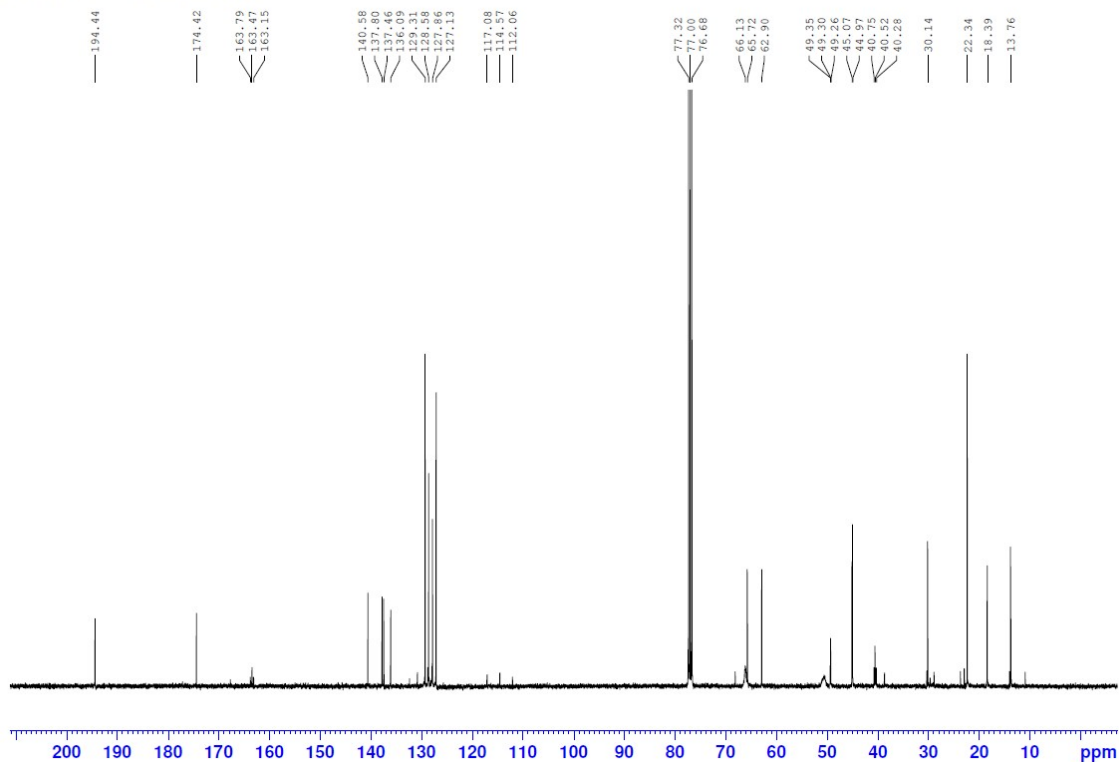
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of  
ethyl 2,2-difluoro-4-(4-(((2-(4-isobutylphenyl)propanoyl)oxy)methyl)phenyl)-4-((morpholine-4-carbonothioyl)thio)butanoate (**8f**):

Patamawadee 20-7-66 No.18  
PS-P7-447-1 in CDCl<sub>3</sub>



**8f** <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)

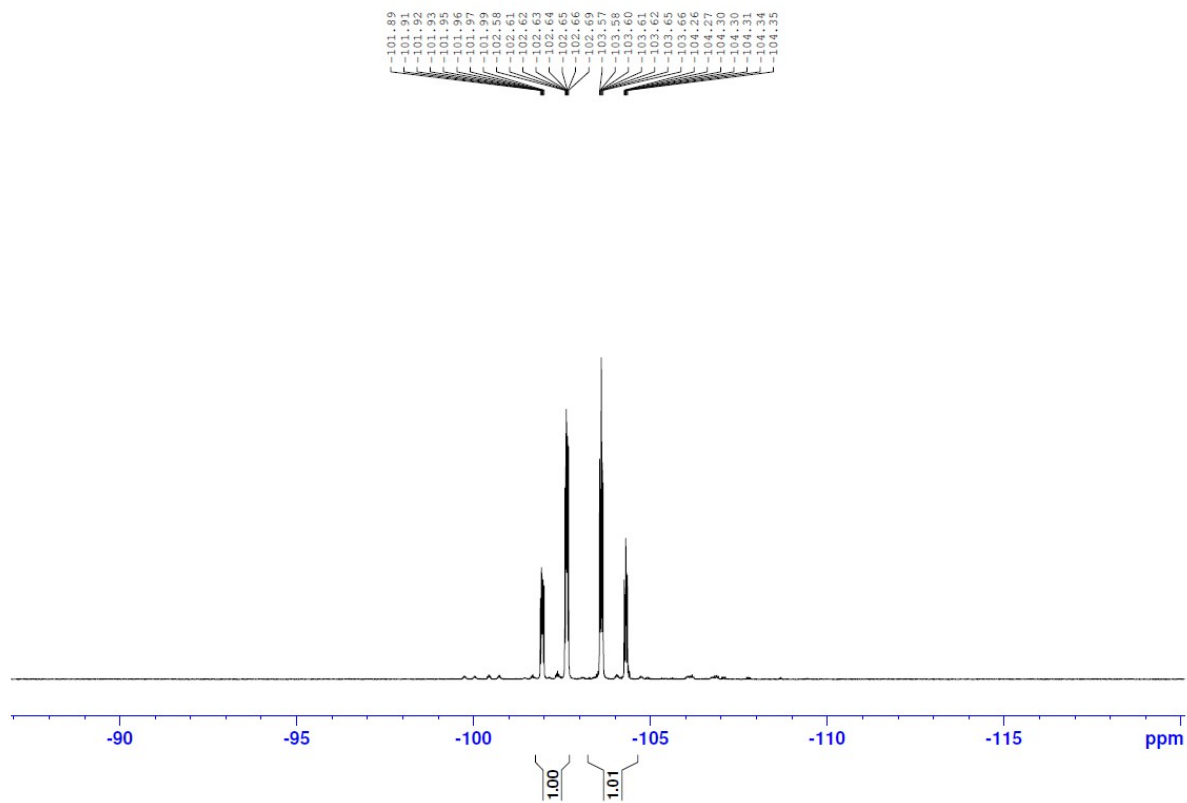
Patamawadee 20-7-66 No.19  
13C PS-P7-447-1 in CDCl<sub>3</sub>





**8f**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

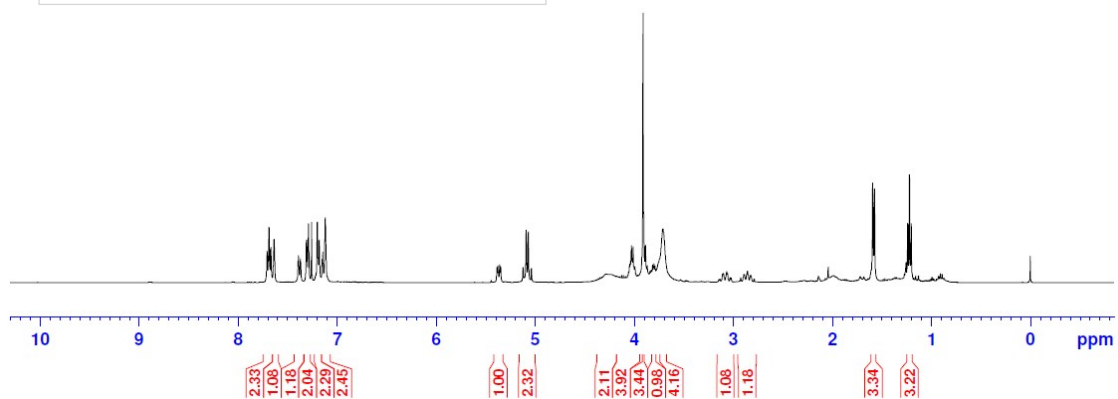
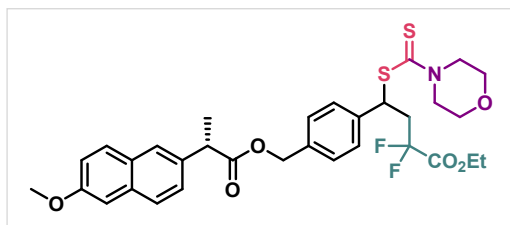
Patamawadee 29-11-66 No.2  
19F PS-P7-447 in  $\text{CDCl}_3$



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of ethyl 2,2-difluoro-4-(4-(((S)-2-(6-methoxynaphthalen-2-yl)propanoyl)oxy)methyl)phenyl)-4-((morpholine-4-carbonylthio)thio)butanoate (**8g**):

Patamawadee 27-5-67 No.14  
PS-P7-456 in  $\text{CDCl}_3$

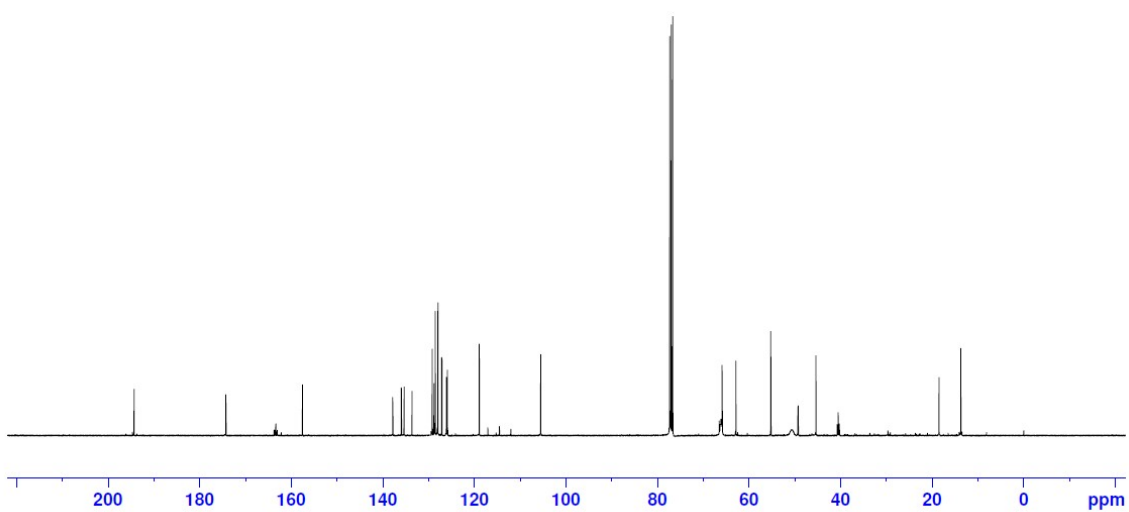
7.709  
7.690  
7.670  
7.639  
7.393  
7.372  
7.311  
7.292  
7.260  
7.201  
7.182  
7.152  
7.146  
7.121  
5.388  
5.378  
5.361  
5.351  
5.125  
5.093  
5.072  
5.040  
4.286  
4.048  
4.041  
4.030  
4.023  
3.913  
3.803  
3.791  
3.712  
3.110  
3.102  
3.068  
3.059  
2.895  
2.859  
2.827  
1.594  
1.576  
1.240  
1.223  
1.205



**8g**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

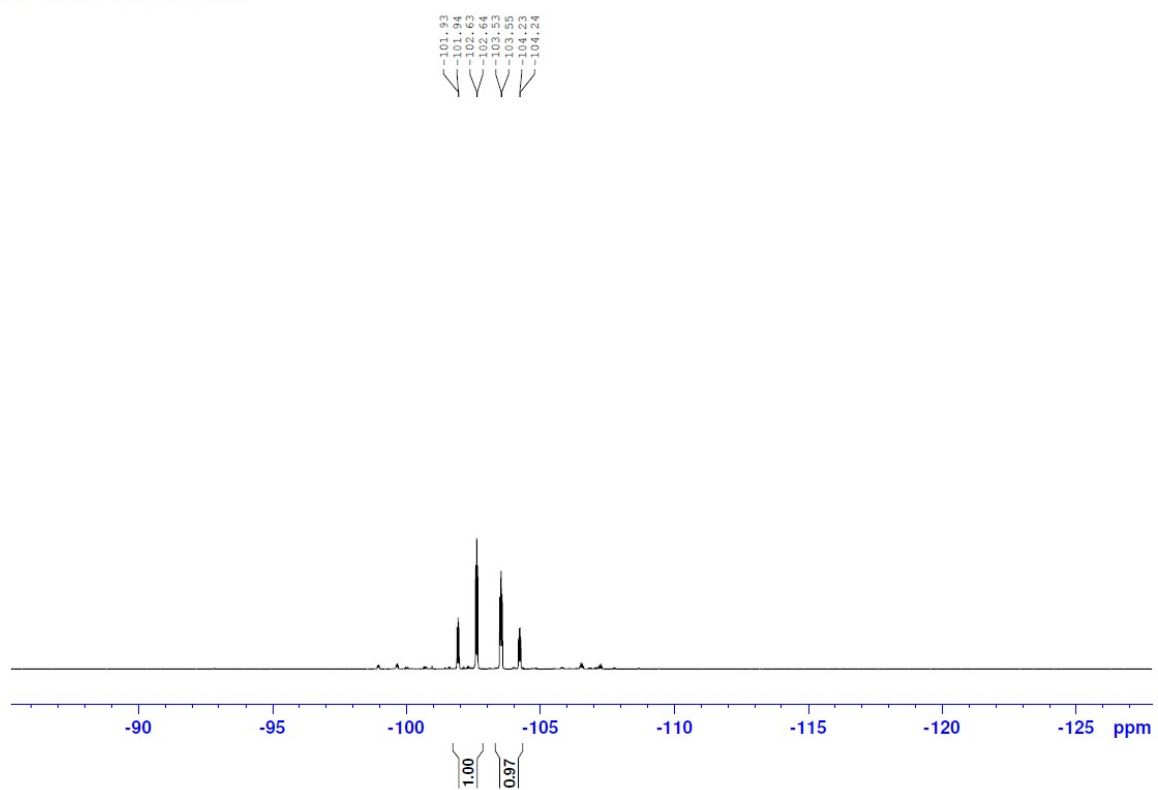
Patamawadee 27-5-67 No.15  
13C PS-P7-456 in  $\text{CDCl}_3$

194.35  
174.28  
163.72  
163.40  
163.08  
157.54  
137.81  
135.93  
135.23  
133.62  
132.47  
129.47  
129.17  
128.78  
128.70  
128.10  
127.95  
127.09  
126.10  
125.96  
125.96  
118.90  
117.03  
114.51  
112.03  
105.47  
77.27  
76.95  
76.63  
66.46  
66.28  
66.28  
62.83  
62.83  
55.20  
55.20  
49.23  
49.19  
45.32  
40.66  
40.66  
40.21  
18.43  
13.68



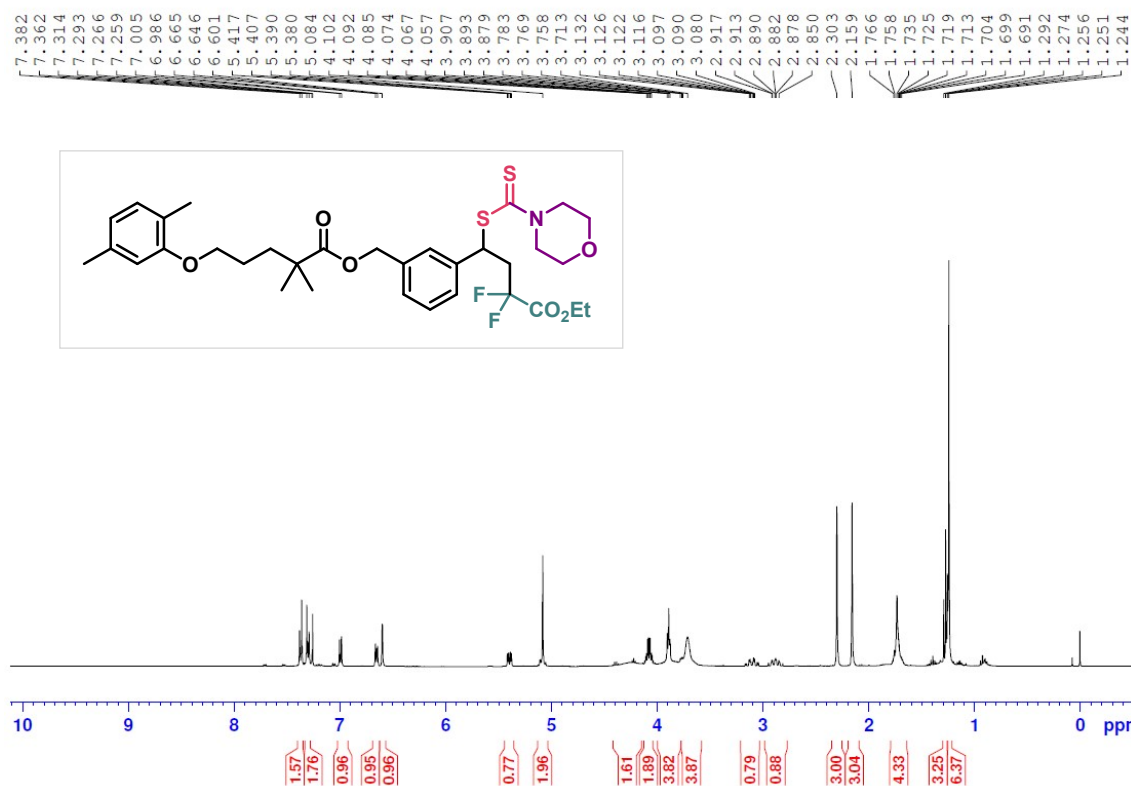
**8g**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 29-11-66 No.4  
19F PS-P7-456 in  $\text{CDCl}_3$



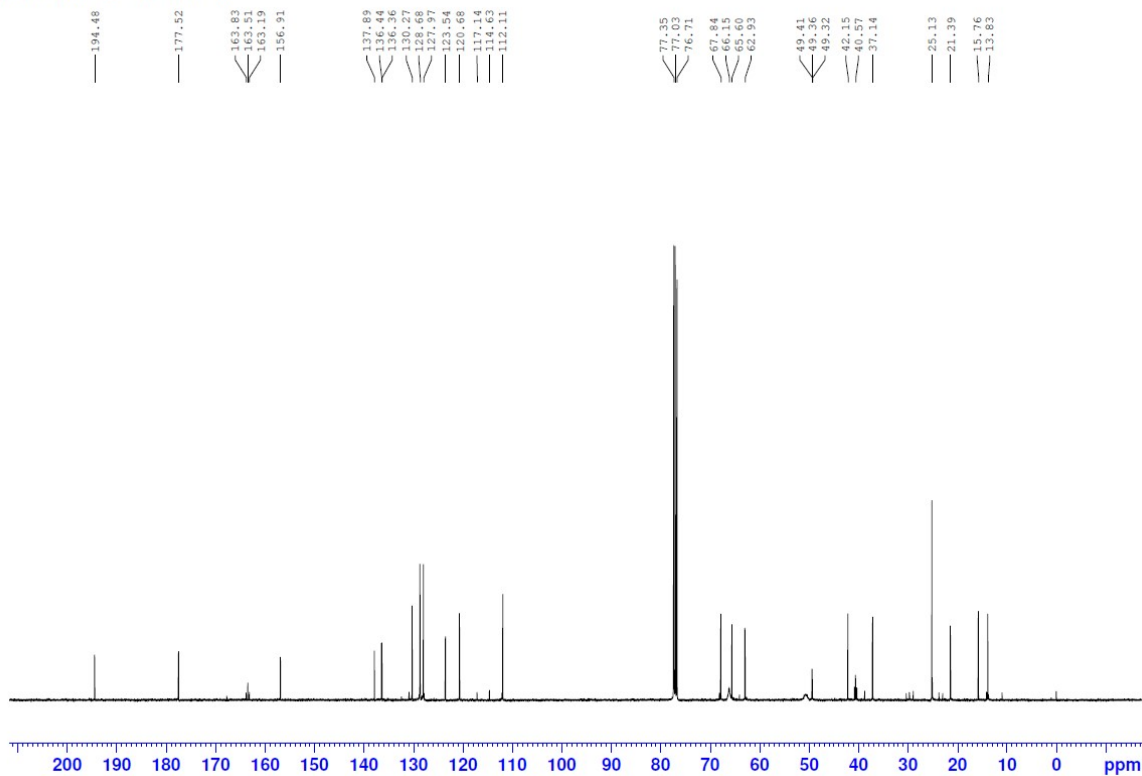
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 3-(4-ethoxy-3,3-difluoro-1-((morpholine-4-carbonylthio)-4-oxobutyl)benzyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (**8h**):

Patamawadee 14-9-66 No.3  
PS-P7-460-rel in CDCl<sub>3</sub>



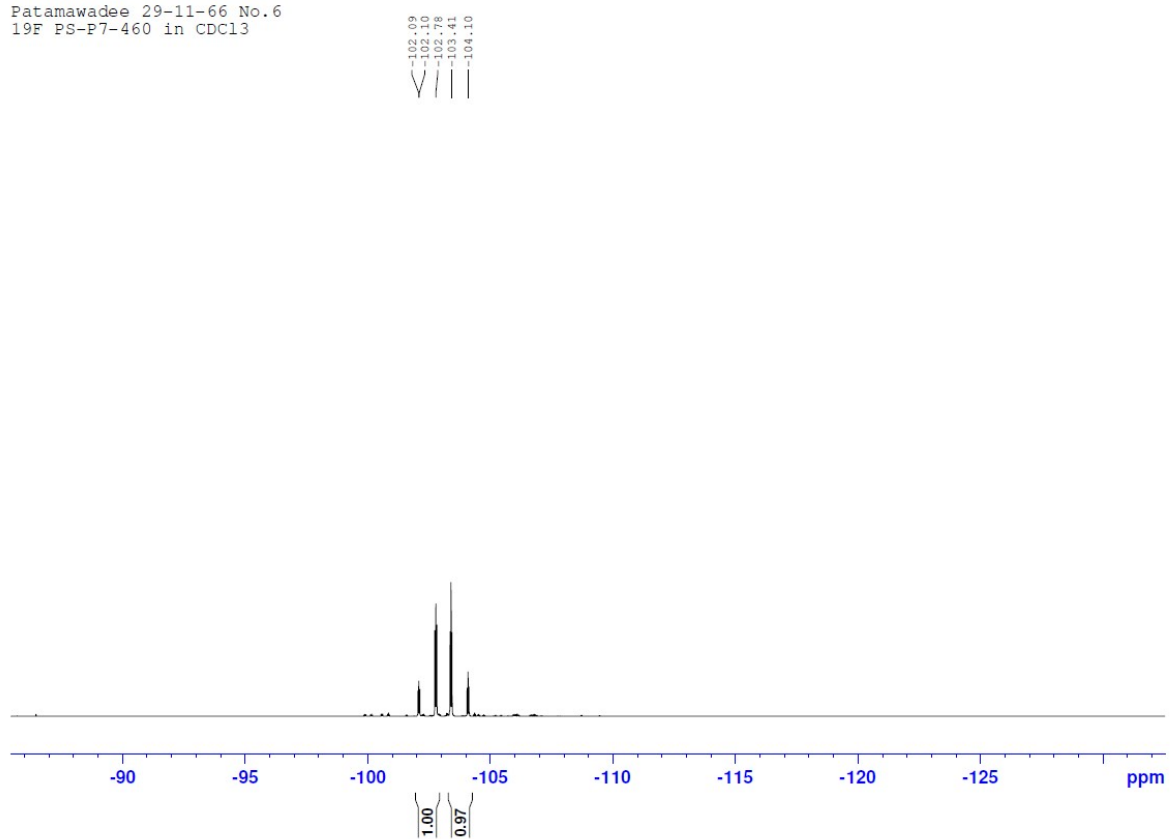
**8h** <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)

Patamawadee 15-9-66 No.4  
PS-P7-460-rel in CDCl<sub>3</sub>



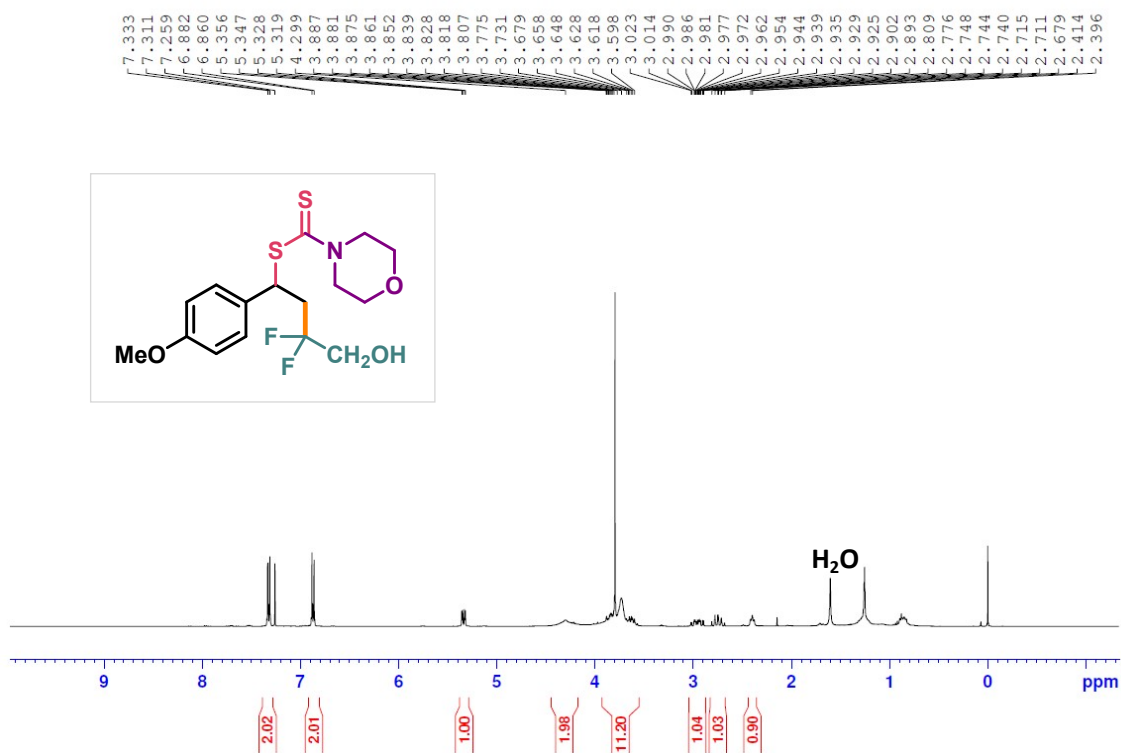
**8h**  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 29-11-66 No.6  
 $^{19}\text{F}$  PS-P7-460 in  $\text{CDCl}_3$



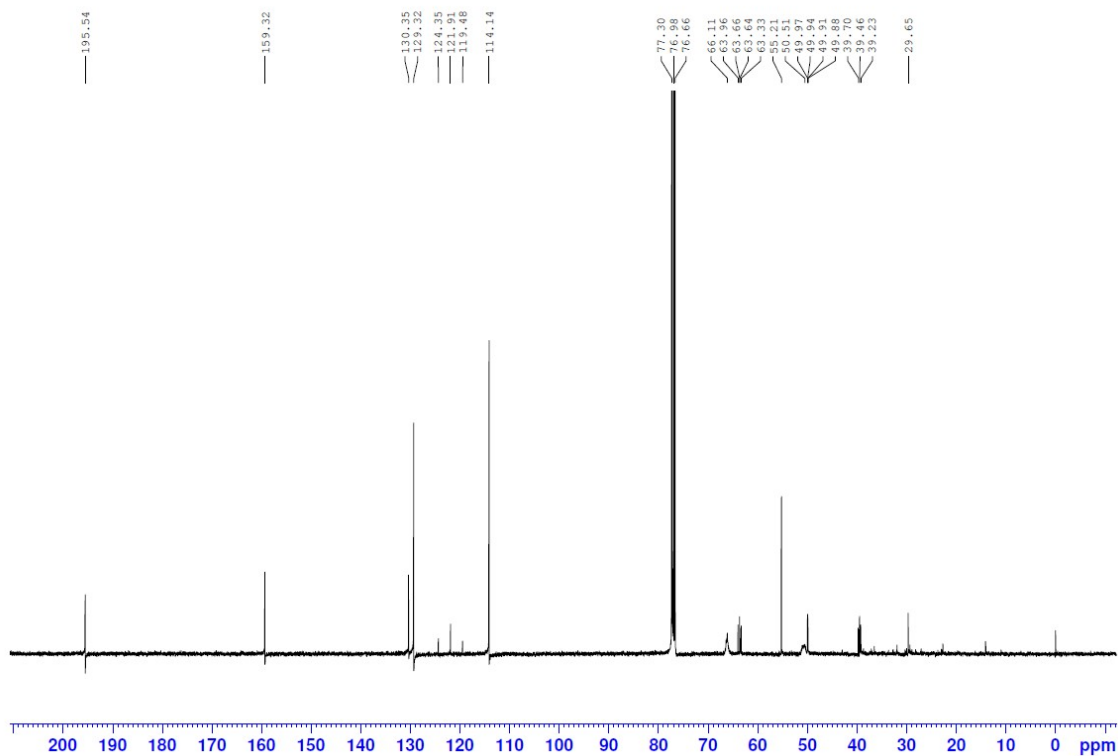
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of 3,3-difluoro-4-(4-methoxyphenyl)butyl morpholine-4-carbodithioate (**9**):

Patamawadee 27-9-66 No.1  
PS-P7-471 in  $\text{CDCl}_3$



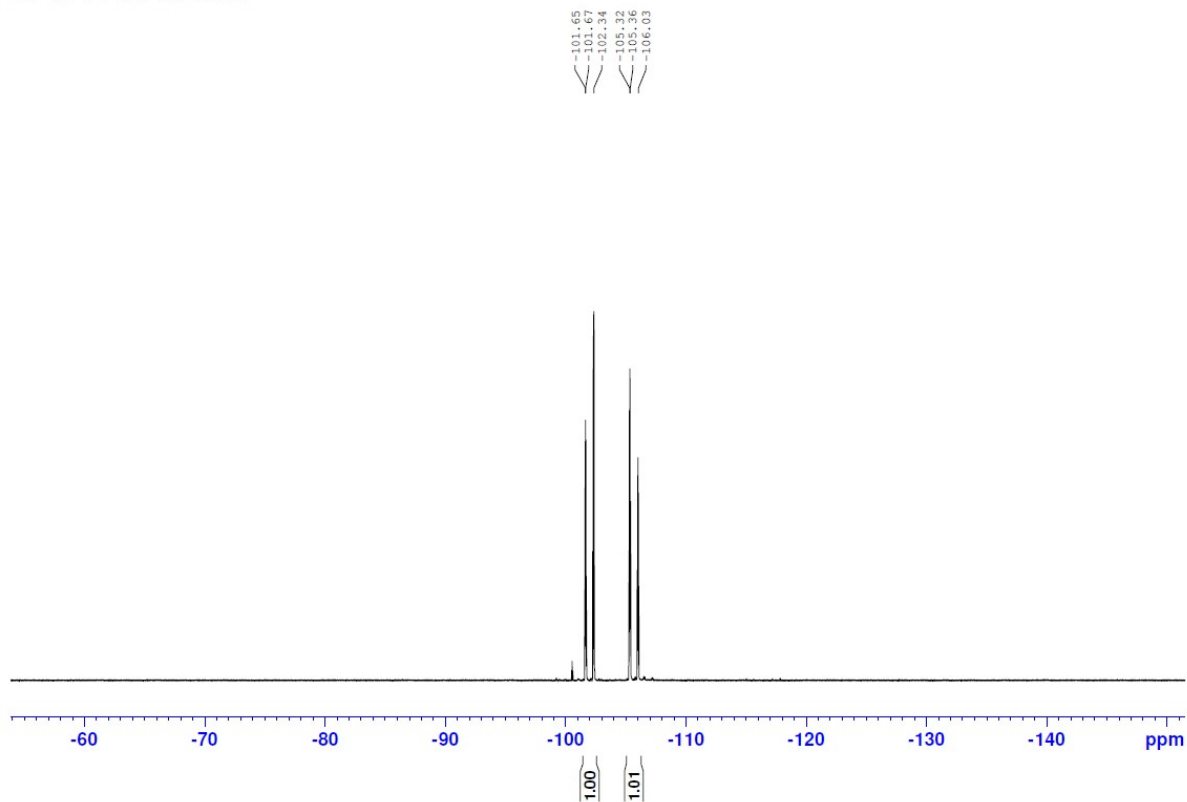
$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )

Patamawadee 28-9-66 No.1  
 $^{13}\text{C}$  PS-P7-471 in  $\text{CDCl}_3$



9  $^{19}\text{F}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CDCl}_3$ )

Patamawadee 29-11-66 No.5  
19F PS-P7-471 in  $\text{CDCl}_3$



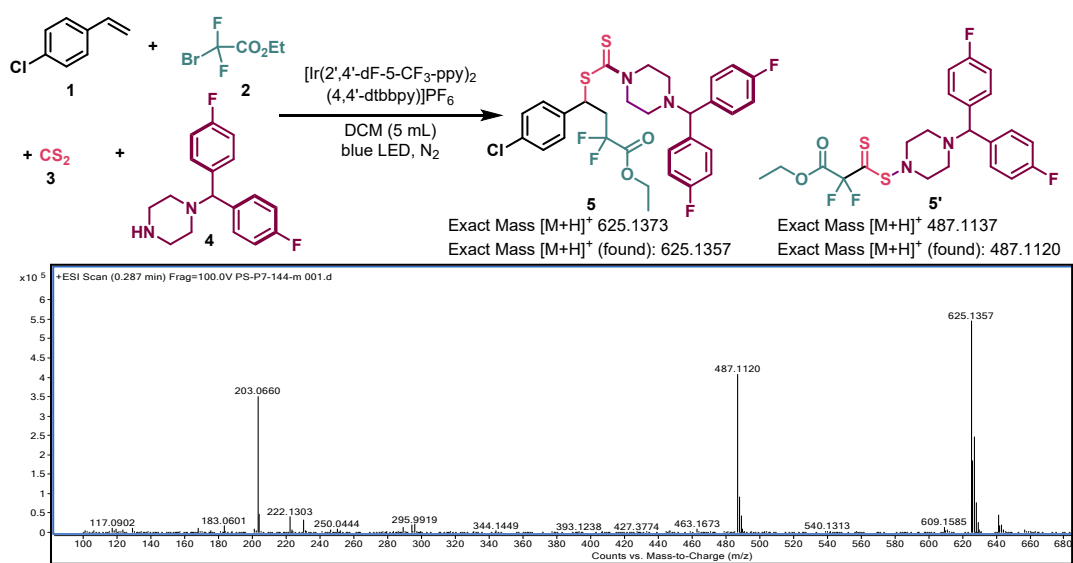
## Troubleshooting & FAQ

### Could I use other alkenes besides styrenes in this reaction?

Currently, our protocol is limited to styrenes. The other alkenes such as indene or vinylcyclohexane were found to be incompetent reaction partners for visible-light-induced photocatalytic four-component fluoroalkylation–dithiocarbamylation.

### Which by-products should I expect in this reaction?

The main by-product is three component coupling products originating from the difluorobromoacetate (**2a**), CS<sub>2</sub> (**3**) and amines (**4**) by fluoroalkylation–dithiocarbamylation reaction, as detected by HRMS.



### Is it necessary to wait for 24 hours for the visible-light-induced photocatalytic four-component fluoroalkylation–dithiocarbamylation reaction?

The reaction does not proceed to completion if less than 24 h and there is still starting material and show the same spot with three component product (by-product) and target product on TLC. We suggest the reaction needs to completion for easily to isolated.

### How important is the equivalent of reaction to the success of the visible-light-induced photocatalytic four-component fluoroalkylation–dithiocarbamylation reaction?

The equivalent amount of reactant is crucial for the success of the reaction. Our findings indicate that employing 3.0 equivalents of compounds **2**, **3**, and **4** was optimal for yielding the four-component coupling product **5** in high yield. Conversely, using 1.5 to 2.0 equivalents resulted in lower yields of product **5** compared to the 3.0 equivalent.

### How do I purify my product?

We use silica gel flash column chromatography.

### How do I remove three component product (by-product)?



We use silica gel flash column chromatography.

**Our research bears similarities to the study conducted by Wang's group in 2023. How can I effectively analyze and compare the differences and advantages between our research and the study conducted by Wang's group?**

Wang's group developed a visible-light induced four-component reaction of styrene with  $\text{BrCF}_2\text{CO}_2\text{Et}$  to furnish thiodifluoroesters in moderate to good yields.<sup>1</sup> This method has a limited substrate scope and relies on a stoichiometric amount of base. Our work allows the important expansion of the chemical space of this class of compounds that can be practically applied to target molecules containing drug and natural product skeletons under mild conditions and without the need for any special additives (Cu catalyst) or strong bases.

### References and notes

[1] Yang, S.-H.; Song, J.-C.; Yang, H.; Zhou, M.-Y.; Wei, Z.-H.; Gao, J.-H.; Dong, D.-Q.; Wang, Z.-L. *Chinese Chemical Letters* **2023**, 34.