

**Highly efficient borylation Suzuki coupling process for  
4-bromo-2-ketothiazoles: Straightfoward access to  
Micrococcinate and Saramycetate esters.**

**SUPPORTING INFORMATION**

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## Table of contents

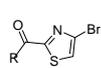
<i>General Informations</i>	S3
<i>Experimental Section</i>	S3
<b>Synthesis of 2-keto-4-bromothiazoles 4a-b</b>	S3
<b>General procedure for the evaluation of 4-bromo-2-ketothiazoles 4a-b in palladium-catalyzed BSC methodology</b>	S3
<b>General procedure for the borylation Suzuki coupling reactions</b>	S4
Synthesis of 1-(4-(pyridin-2-yl)thiazol-2-yl)ethanone <b>9a</b>	S4
Synthesis of 1-(4-(pyridin-2-yl)thiazol-2-yl)propan-1-one <b>9b</b>	S4
Synthesis of 1-(4-(6-methoxypyridin-2-yl)thiazol-2-yl)ethanone <b>14</b>	S4
Synthesis of 1-(4-(5-chloropyridin-2-yl)thiazol-2-yl)propan-1-one <b>15</b>	S5
Synthesis of 1-(4-(quinolin-2-yl)thiazol-2-yl)ethanone <b>16a</b>	S5
Synthesis of 1-(4-(quinolin-2-yl)thiazol-2-yl)propan-1-one <b>16b</b>	S5
Synthesis of <i>tert</i> -butyl sulfomycinamate thio-analog <b>1</b>	S5
Synthesis of 1-(4-(pyridin-3-yl)thiazol-2-yl)ethanone <b>17a</b>	S6
Synthesis of 1-(4-(pyridin-3-yl)thiazol-2-yl)propan-1-one <b>17b</b>	S6
Synthesis of 1-(4-(6-chloropyridin-3-yl)thiazol-2-yl)ethanone <b>18</b>	S6
Synthesis of 1-(4-(quinolin-3-yl)thiazol-2-yl)ethanone <b>19</b>	S6
Synthesis of 1-(4-(pyrazin-2-yl)thiazol-2-yl)ethanone <b>20</b>	S7
Synthesis of saramycetic acid	S7
Synthesis of (E)-1-(4-(3,4-dimethoxystyryl)thiazol-2-yl)ethanone <b>22a</b>	S7
Synthesis of (E)-1-(4-(3,4-dimethoxystyryl)thiazol-2-yl)propan-1-one <b>22b</b>	S8
<b>Synthesis of ethyl-<i>tert</i>-butyl micrococcinate 13</b>	S8
Synthesis of ethyl-5-bromopicolinate <b>6b</b>	S8
Synthesis of <i>tert</i> -butyl 2-(6-(ethoxycarbonyl)pyridin-3-yl)thiazole-4-carboxylate <b>10</b>	S8
Synthesis of <i>tert</i> -butyl 2-(2-chloro-6-(ethoxycarbonyl)pyridin-3-yl)thiazole-4-carboxylate <b>5b</b>	S9
Synthesis of ethyl 2-(2-bromoacetyl)thiazole-4-carboxylate <b>12</b>	S9
Synthesis of chlorodiazolylpyridine <b>11</b>	S10
Synthesis of ethyl- <i>tert</i> -butyl micrococcinate <b>13</b>	S11
<i>GC and GC-MS probes for the formation of boronate esters 8a-b</i>	S12
<i><sup>1</sup>H &amp; <sup>13</sup>C NMR spectra</i>	S14

## General Informations

THF and dioxane were distilled from benzophenone/Na, toluene was distilled from calcium hydride. Melting points are uncorrected. Column chromatography was performed using silica gel (mesh size 60-80  $\mu\text{m}$ ).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded at 300 MHz. Chemical shifts ( $\delta$ ) are given as ppm relative to the residual solvent peak. Microanalyses were carried out at the analytical laboratory of our Department (IRCOF). Commercially available starting materials were used without further purification.

## Experimental Section

### Synthesis of 1-(4-bromothiazol-2-yl)ethan-1-one (4a) and 1-(4-bromothiazol-2-yl)propan-1-one (4b) :

 The ketothiazoles **4a-b** were prepared according the Cossy's procedure.<sup>1</sup> To a solution of 2,4-dibromothiazole (1.2 g, 4.94 mmol) in THF (10 ml) was added dropwise *n*-butyllithium (2.17 ml, 5.43 mmol) at -78 °C under N<sub>2</sub>. After stirring 30 min, 1-morpholinoethan-1-one (1.2 ml, 10.37 mmol) (1-morpholinopropan-1-one (1.4 ml, 10.37 mmol)) was slowly added and the resulted mixture was stirred 1 h 30. Et<sub>2</sub>O (120 ml) and a satd. aq. sol. NH<sub>4</sub>Cl (10 ml) were then added and the separated organic phase was washed with a satd. aq. sol. NaHCO<sub>3</sub> (80 ml), brine (80 ml), and dried (MgSO<sub>4</sub>). After evaporation under vacuo, the crude product was purified by flash column chromatography on silica gel (Et<sub>2</sub>O-PE 4:96) to afford **4a** (all analyses are in accordance to those previously described) and **4b** (Rf = 0.21) (848 mg, 78%) as a white solid (mp = 46-47 °C).  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  = 1.19 (t, 3H, *J* = 7.3 Hz), 3.12 (q, 2H, *J* = 7.3 Hz), 7.55 (s, 1H);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  = 7.8, 31.8, 124.8, 126.8, 166.8, 193.3; IR (KBr)  $\nu$  1690, 2938, 2979, 3089 cm<sup>-1</sup>; Anal. Calcd for C<sub>6</sub>H<sub>6</sub>BrNOS (220.1) : C, 32.74; H, 2.75; N, 6.36; S, 14.57. Found : C, 32.70; H, 2.77; N, 6.31; S, 14.61.

### General procedure for the evaluation of 4-bromo-2-ketothiazoles 4a-b in palladium-catalyzed BSC methodology :

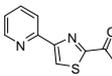
The borylation Suzuki coupling (BSC) reactions were carried out in a sealed tube at 110 °C under N<sub>2</sub>. 2-keto-4-bromothiazole **4a-b** (0.25 mmol) was allowed to react with bispinacolatodiboron (64 mg, 0.25 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (2 mol %), *n*-eicosane (12 mg, 20 mol %, internal standard), potassium acetate (49 mg, 0.50 mmol) and ligand (16 mol %, Table 1) in dioxane (0.85 ml). After complete completion of starting material to borylated thiazoles **8a-b** checked by GC analysis (see sections S9 and S10), a solution of 2-chloropyridine (20  $\mu\text{l}$ , 0.21 mmol) in dioxane (0.21 ml) and an aq. sol. K<sub>3</sub>PO<sub>4</sub> (0.21 ml, 5M) were added and the resulted mixture was stirred 12 h at 110 °C. EtOAc (50 ml) and drying MgSO<sub>4</sub> were added. After filtration through Celite<sup>®</sup> and concentration under vacuo, the crude product was analysed by GC.

<sup>1</sup> Gebauer, J. ; Arseniyadis, S. ; Cossy, J. *Org. Lett.* **2007**, 9, 3425-3427.

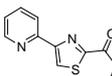
## General borylation Suzuki coupling (BSC) procedure for 4a-b :

The borylation Suzuki coupling (BSC) reactions were carried out in a 10 ml round bottom flask fitted with a condenser at 110 °C under N<sub>2</sub>. 2-keto-4-bromothiazole **4a-b** (1.0 mmol) was allowed to react with bispinacolatodiboron (254 mg, 1.0 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (2 mol %), potassium acetate (198 mg, 2.0 mmol) and ligand (16 mol %, Table 1) in dioxane (3.4 ml). After complete completion of starting material to borylated thiazoles **8a-b** checked by GC analysis (see sections S9 and S10), a solution of heteroarylhalide (0.84 mmol) in dioxane (0.85 ml) and an aq. sol. K<sub>3</sub>PO<sub>4</sub> (0.85 ml, 5M) were added and the resulted mixture was stirred 12 h at 110 °C. EtOAc (100 ml) and drying MgSO<sub>4</sub> were added. After filtration through Celite<sup>®</sup> and concentration under vacuo, the crude product was purified by flash column chromatography on silica gel using a mixture of EtOAc and petroleum ether as eluent to give the products **9a-b**, **14**, **15**, **16a**, **16b**, **1**, **17a**, **17b**, **18**, **19**, **20**, **21**, **22a**, **22b**.

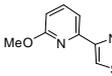
### Synthesis of 1-(4-(pyridin-2-yl)thiazol-2-yl)ethanone (**9a**) :

 According to the general above procedure from **4a** (206 mg, 1.0 mmol) using 2-bromopyridine (80 µl, 0.84 mmol) as electrophile and Pd<sub>2</sub>(dba)<sub>3</sub> / P[biphen-2-yl]Cy<sub>2</sub> (2:16 mol %) as catalyst. Standard workup followed by flash chromatography (EtOAc-PE 2:8, R<sub>f</sub> = 0.2) afforded **9a** (134 mg, 78%) as a white solid (mp = 126-127 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ = 2.78 (s, 3H), 7.29 (ddd, 1H, *J* = 1.5 Hz, *J* = 2.6 Hz, *J* = 4.8 Hz), 7.81 (td, 1H, *J* = 1.5 Hz, *J* = 7.8 Hz), 8.20 (d, 1H, *J* = 7.8 Hz), 8.41 (s, 1H), 8.63 (ddd, 1H, *J* = 1.5 Hz, *J* = 2.6 Hz, *J* = 4.8 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ = 26.2, 121.3, 123.5, 124.2, 137.3, 149.7, 151.9, 157.3, 167.0, 191.9 ; IR (KBr) ν 1681, 2358, 3083 cm<sup>-1</sup> ; Anal. Calcd for C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>OS (204.2) : C, 58.80; H, 3.95; N, 13.72.; S, 15.70. Found : C, 58.73; H, 3.97; N, 13.76; S, 15.66.

### Synthesis of 1-(4-(pyridin-2-yl)thiazol-2-yl)propan-1-one (**9b**) :

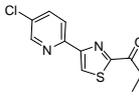
 According to the general procedure from **4b** (220 mg, 1.0 mmol) using 2-bromopyridine (80 µl, 0.84 mmol) as electrophile and Pd<sub>2</sub>(dba)<sub>3</sub> / P[biphen-2-yl]Cy<sub>2</sub> (2:16 mol %) as catalyst. Standard workup followed by flash chromatography (EtOAc-PE 1:9, R<sub>f</sub> = 0.13) afforded **9b** (114 mg, 62%) as a white solid (mp = 110-111 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ = 1.28 (t, 3H, *J* = 7.3 Hz), 3.27 (q, 2H, *J* = 7.3 Hz), 7.28 (ddd, 1H, *J* = 1.5 Hz, *J* = 2.7 Hz, *J* = 4.8 Hz), 7.81 (td, 1H, *J* = 1.5 Hz, *J* = 7.6 Hz), 8.19 (d, 1H, *J* = 7.6 Hz), 8.39 (s, 1H), 8.63 (ddd, 1H, *J* = 1.5 Hz, *J* = 2.7 Hz, *J* = 4.8 Hz) ; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ = 8.1, 32.0, 121.3, 123.5, 123.8, 137.3, 149.7, 152.0, 157.2, 166.8, 194.8 ; IR (KBr) ν 1603, 2936, 2976, 3123 cm<sup>-1</sup>; Anal. Calcd for C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>OS (218.3) : C, 60.53; H, 4.62; N, 12.83; S, 14.69. Found : C, 60.49; H, 4.65; N, 12.87; S, 14.71.

### Synthesis of 1-(4-(6-methoxypyridin-2-yl)thiazol-2-yl)ethanone (**14**) :

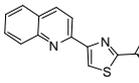
 According to the general above procedure from **4a** (206 mg, 1.0 mmol) using 2-bromo-6-methoxypyridine (103 µl, 0.84 mmol) as electrophile and Pd<sub>2</sub>(dba)<sub>3</sub> / P[biphen-2-yl]Cy<sub>2</sub> (2:16 mol %) as catalyst. Standard workup followed by flash chromatography (EtOAc-PE 1:9, R<sub>f</sub> = 0.21) afforded **14** (148 mg, 75%) as a white solid (mp = 118-119 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ = 2.79 (s, 3H), 4.02 (s, 3H), 6.75 (d, 1H, *J* = 8.1 Hz), 7.69 (dd, 1H, *J* = 8.1 Hz, *J* = 7.2 Hz), 7.80 (d, 1H, *J* = 7.2 Hz), 8.38 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ = 26.1, 53.4, 111.0, 113.9, 123.9, 139.6, 149.3, 157.4, 163.9,

166.9, 192.0 ; IR (KBr)  $\nu$  1687, 2925, 3124  $\text{cm}^{-1}$  ; Anal. Calcd for  $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_2\text{S}$  (234.3) : C, 56.39; H, 4.30; N, 11.96.; S, 13.69. Found : C, 56.44; H, 4.32; N, 11.92; S, 13.66.

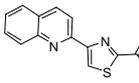
#### Synthesis of 1-(4-(5-chloropyridin-2-yl)thiazol-2-yl)propan-1-one (**15**) :

 According to the general above procedure from **4b** (221 mg, 1.0 mmol) using 2-5-dichloropyridine (124 mg, 0.84 mmol) as electrophile and  $\text{Pd}_2(\text{dba})_3$  / P[biphen-2-yl]Cy<sub>2</sub> (2:16 mol %) as catalyst. Standard workup followed by flash chromatography (Et<sub>2</sub>O-PE 5:5, R<sub>f</sub> = 0.20) afforded **15** (202 mg, 95%) as a white solid (mp = 101-102 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  = 1.29 (t, 3H, *J* = 7.3 Hz), 3.26 (q, 2H, *J* = 7.3 Hz), 7.78 (dd, 1H, *J* = 8.4 Hz, *J* = 2.4 Hz), 8.15 (d, 1H, *J* = 8.4 Hz), 8.38 (s, 1H), 8.63 (d, 1H, *J* = 2.4 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  = 8.1, 32.0, 122.0, 124.1, 131.7, 136.9, 148.6, 150.2, 156.1, 167.0, 194.7 ; IR (KBr)  $\nu$  1689, 2937, 2977, 3116  $\text{cm}^{-1}$  ; Anal. Calcd for  $\text{C}_{11}\text{H}_9\text{N}_2\text{ClOS}$  (252.7) : C, 52.28; H, 3.59; N, 11.08.; S, 12.69. Found : C, 52.34; H, 3.61; N, 11.13; S, 12.65.

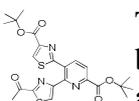
#### Synthesis of 1-(4-(quinolin-2-yl)thiazol-2-yl)ethanone (**16a**) :

 According to the general above procedure from **4a** (206 mg, 1.0 mmol) using 2-chloroquinoline (137 mg, 0.84 mmol) as electrophile and  $\text{Pd}_2(\text{dba})_3$  / XPhos (2:16 mol %) as catalyst. Standard workup followed by flash chromatography (Et<sub>2</sub>O-PE 1:9, R<sub>f</sub> = 0.26) afforded **16a** (213 mg, 100%) as a white solid (mp = 155-156 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  = 2.84 (s, 3H), 7.56 (td, 1H, *J* = 8.1 Hz, *J* = 1.4 Hz), 7.75 (td, 1H, *J* = 8.1 Hz, *J* = 1.4 Hz), 7.86 (d, 1H, *J* = 8.1 Hz), 8.12 (d, 1H, *J* = 8.6 Hz), 8.29 (d, 1H, *J* = 8.6 Hz), 8.37 (d, 1H, *J* = 8.6 Hz), 8.67 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  = 26.1, 119.4, 125.4, 126.8, 127.8, 128.0, 129.5, 130.0, 137.2, 148.1, 151.7, 157.7, 166.9, 191.8 ; IR (KBr)  $\nu$  1682, 2854, 2927, 3112  $\text{cm}^{-1}$  ; Anal. Calcd for  $\text{C}_{14}\text{H}_{10}\text{N}_2\text{OS}$  (254.3) : C, 66.12; H, 3.96; N, 11.02.; S, 12.61. Found : C, 66.09; H, 4.00; N, 11.06; S, 12.62.

#### Synthesis of 1-(4-(quinolin-2-yl)thiazol-2-yl)propan-1-one (**16b**) :

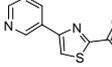
 According to the general above procedure from **4b** (221 mg, 1.0 mmol) using 2-chloroquinoline (137 mg, 0.84 mmol) as electrophile and  $\text{Pd}_2(\text{dba})_3$  / P[biphen-2-yl]Cy<sub>2</sub> (2:16 mol %) as catalyst. Standard workup followed by flash chromatography (CH<sub>2</sub>Cl<sub>2</sub>-PE 1:9, R<sub>f</sub> = 0.15) afforded **16b** (178 mg, 79%) as a white solid (mp = 136-137 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  = 1.32 (t, 3H, *J* = 7.3 Hz), 3.41 (q, 2H, *J* = 7.3 Hz), 7.56 (td, 1H, *J* = 8.1 Hz, *J* = 1.4 Hz), 7.75 (td, 1H, *J* = 8.1 Hz, *J* = 1.4 Hz), 7.85 (d, 1H, *J* = 8.1 Hz), 8.13 (d, 1H, *J* = 8.6 Hz), 8.28 (d, 1H, *J* = 8.6 Hz), 8.37 (d, 1H, *J* = 8.6 Hz), 8.63 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  = 8.1, 32.1, 119.5, 125.0, 126.8, 127.8, 128.1, 129.6, 130.0, 137.2, 148.2, 151.9, 157.5, 166.8, 194.8 ; IR (KBr)  $\nu$  1686, 2926, 3115  $\text{cm}^{-1}$  ; Anal. Calcd for  $\text{C}_{15}\text{H}_{12}\text{N}_2\text{OS}$  (268.3) : C, 67.14; H, 4.51; N, 10.44.; S, 11.35. Found : C, 67.12; H, 4.52; N, 10.50; S, 11.38.

#### Synthesis of *tert*-butyl sulfomycinamate thio-analog **1** :

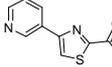
 The 2-acetyl-4-bromothiazole **4a** (30 mg, 0.15 mmol) was allowed to react with bispinacolatodiboron (37 mg, 0.15 mmol),  $\text{Pd}_2(\text{dba})_3$  (2 mg, 2 mol %), potassium acetate (28 mg, 0.29 mmol) and P[biphen-2-yl]Cy<sub>2</sub> (7 mg, 16 mol %) in dioxane (0.4 ml) at 110 °C in a sealed tube under N<sub>2</sub>. After 30 min, a solution of 6-chlorothiazolylpicolinate **5a** (48 mg, 0.12 mmol) in dioxane (0.12 ml) and an aq. sol. K<sub>3</sub>PO<sub>4</sub>

(0.12 ml, 5 M) were consecutively added. The resulted mixture was then stirred 12 h at 110 °C. EtOAc (20 ml) and dried MgSO<sub>4</sub> were added. After filtration through Celite® and concentration under vacuo, the crude product was purified by flash column chromatography on silica gel (EtOAc-EP 8:2, R<sub>f</sub> = 0.1) to afford **1** (52 mg, 87%) as a white solid. All analyses were in accordance with those previously reported.<sup>2</sup>

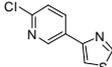
#### Synthesis of 1-(4-(pyridin-3-yl)thiazol-2-yl)ethanone (**17a**) :

 According to the general above procedure from **4a** (206 mg, 1.0 mmol) using 3-chloropyridine (80 µl, 0.84 mmol) as electrophile and Pd<sub>2</sub>(dba)<sub>3</sub> / XPhos (2:16 mol %) as catalyst. Standard workup followed by flash chromatography (EtOAc-PE 3:7, R<sub>f</sub> = 0.15) afforded **17a** (140 mg, 81%) as a white solid (mp = 103-104 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ = 2.79 (s, 3H), 7.42 (dd, 1H, *J* = 7.8 Hz, *J* = 4.2 Hz), 7.91 (s, 1H), 8.25 (dd, 1H, *J* = 8.0 Hz, *J* = 1.8 Hz), 8.63 (d, 1H, *J* = 4.2 Hz), 9.17 (d, 1H, *J* = 1.8 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ = 26.2, 121.2, 123.9, 129.7, 133.9, 147.8, 149.8, 154.4, 167.6, 191.8 ; IR (KBr) ν 1686, 2856, 2924, 3104 cm<sup>-1</sup>; Anal. Calcd for C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>OS (204.2) : C, 58.80; H, 3.95; N, 13.72; S, 15.70. Found : C, 58.81; H, 3.97; N, 13.71; S, 15.73.

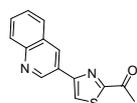
#### Synthesis of 1-(4-(pyridin-3-yl)thiazol-2-yl)propan-1-one (**17b**) :

 According to the general procedure from **4b** (220 mg, 1.0 mmol) using 3-chloropyridine (80 µl, 0.84 mmol) as electrophile and Pd<sub>2</sub>(dba)<sub>3</sub> / XPhos (2:16 mol %) as catalyst. Standard workup followed by flash chromatography (EtOAc-PE 5:5, R<sub>f</sub> = 0.28) afforded **17b** (121 mg, 66%) as a white solid (mp = 99-100 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ = 1.29 (t, 3H, *J* = 7.3 Hz), 3.29 (q, 2H, *J* = 7.3 Hz), 7.41 (dd, 1H, *J* = 7.8 Hz, *J* = 4.5 Hz), 7.89 (s, 1H), 8.25 (dd, 1H, *J* = 7.8 Hz, *J* = 2.0 Hz), 8.63 (d, 1H, *J* = 4.5 Hz), 9.18 (d, 1H, *J* = 2.0 Hz) ; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ = 8.0, 32.1, 120.8, 123.9, 133.9, 147.8, 149.8, 154.3, 167.4, 194.7 ; IR (KBr) ν 1683, 2854, 2926 cm<sup>-1</sup>; Anal. Calcd for C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>OS (218.3) : C, 60.53; H, 4.62; N, 12.83; S, 14.69. Found : C, 60.48; H, 4.60; N, 12.85; S, 14.73.

#### Synthesis of 1-(4-(6-chloropyridin-3-yl)thiazol-2-yl)ethanone (**18**) :

 According to the general above procedure from **4a** (206 mg, 1.0 mmol) using 2-chloro-5-iodopyridine (201 mg, 0.84 mmol) as electrophile and Pd<sub>2</sub>(dba)<sub>3</sub> / P[biphen-2-yl]Cy<sub>2</sub> (2:16 mol %) as catalyst. Standard workup followed by flash chromatography (EtOAc-PE 1:9, R<sub>f</sub> = 0.17) afforded **18** (140 mg, 70%) as a white solid (mp = 126-127 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ = 2.79 (s, 3H), 7.44 (d, 1H, *J* = 8.3 Hz), 7.90 (s, 1H), 8.22 (dd, 1H, *J* = 8.3 Hz, *J* = 2.4 Hz), 8.94 (d, 1H, *J* = 2.4 Hz) ; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ = 26.2, 121.5, 124.6, 128.7, 136.6, 147.6, 151.5, 153.2, 167.8, 191.7 ; IR (KBr) ν 1688, 1729, 2928, 2961, 3088 cm<sup>-1</sup>; Anal. Calcd for C<sub>10</sub>H<sub>7</sub>ClN<sub>2</sub>OS (204.2) : C, 50.32; H, 2.96; N, 11.74; S, 13.43. Found : C, 50.37; H, 2.98; N, 11.75; S, 13.39.

#### Synthesis of 1-(4-(quinolin-3-yl)thiazol-2-yl)ethanone (**19**) :

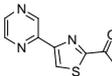


According to the general above procedure from **4a** (206 mg, 1.0 mmol) using 3-bromoquinoline (115 µl, 0.84 mmol) as electrophile and Pd<sub>2</sub>(dba)<sub>3</sub> / P[biphen-2-yl]Cy<sub>2</sub> (2:16 mol %) as catalyst. Standard workup followed by flash chromatography (Et<sub>2</sub>O-PE 2:8, R<sub>f</sub> = 0.20) afforded **19** (171 mg, 80%) as

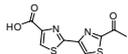
<sup>2</sup> Martin, T.; Verrier, C.; Hoarau, C.; Marsais, F. *Org. Lett.* **2008**, *10*, 2909-2912.

a white solid (mp = 140-141 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ = 2.84 (s, 3H), 7.61 (td, 1H, *J* = 7.1 Hz, *J* = 1.4 Hz), 7.76 (td, 1H, *J* = 7.1 Hz, *J* = 1.4 Hz), 7.94 (d, 1H, *J* = 8.3 Hz), 8.04 (s, 1H), 8.15 (d, 1H, *J* = 8.3 Hz), 8.73 (d, 1H, *J* = 2.0 Hz), 9.46 (d, 1H, *J* = 2.0 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ = 26.2, 121.4, 126.7, 127.4, 127.9, 128.4, 129.5, 130.1, 133.1, 148.1, 148.8, 154.5, 167.6, 191.8; IR (KBr) ν 1686, 2854, 2922, 3064 cm<sup>-1</sup>; Anal. Calcd for C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>OS (254.3) : C, 66.12; H, 3.96; N, 11.02.; S, 12.61. Found : C, 66.14; H, 4.01; N, 11.00; S, 12.58.

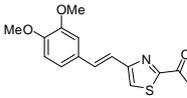
#### Synthesis of 1-(4-(pyrazin-2-yl)thiazol-2-yl)ethanone (**20**) :

 According to the general above procedure from **4a** (206 mg, 1.0 mmol) using 2-chloropyrazine (75 μl, 0.84 mmol) as electrophile and Pd<sub>2</sub>(dba)<sub>3</sub> / P[biphen-2-yl]Cy<sub>2</sub> (2:16 mol %) as catalyst. Standard workup followed by flash chromatography (EtOAc-PE 3:7, R<sub>f</sub> = 0.22) afforded **20** (110 mg, 64%) as a white solid (mp = 138-139 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ = 2.80 (s, 3H), 8.45 (s, 1H), 8.57 (s, 2H), 9.43 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ = 26.2, 125.8, 143.0, 144.2, 144.3, 147.4, 154.6, 167.7, 191.7; IR (KBr) ν 1686, 2856, 2926, 3078 cm<sup>-1</sup>; Anal. Calcd for C<sub>9</sub>H<sub>7</sub>N<sub>3</sub>OS (205.2) : C, 52.67; H, 3.44; N, 20.47; S, 15.62. Found : C, 52.69; H, 3.41; N, 20.51; S, 15.65

#### Synthesis of saramycetic acid :

 According to the general borylation Suzuki coupling procedure from **4a** (206 mg, 1.0 mmol) using ethyl 2-bromothiazole-4-carboxylate (198 mg, 0.84 mmol) as electrophile and Pd<sub>2</sub>(dba)<sub>3</sub> / P[biphen-2-yl]Cy<sub>2</sub> (2:16 mol %) as catalyst. Standard workup followed by flash chromatography (EtOAc-PE 2:8, R<sub>f</sub> = 0.13) afforded **21** (176 mg, 74%) as a white solid (mp = 169-170 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ = 1.44 (t, 3H, *J* = 7.1 Hz), 2.78 (s, 3H), 4.46 (q, 2H, *J* = 7.1 Hz), 8.23 (s, 1H), 8.46 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ = 14.5, 26.1, 61.8, 124.3, 128.4, 148.3, 150.3, 161.4, 162.5, 167.3, 191.3; IR (KBr) ν 1687, 1725, 2981, 3092, 3128 cm<sup>-1</sup>; Anal. Calcd for C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>S<sub>2</sub> (282.3) : C, 46.79; H, 3.57; N, 9.92; S, 22.71. Found : C, 46.82; H, 3.61; N, 9.93; S, 22.77. A solution of **21** (70 mg, 0.25 mmol) and LiOH·H<sub>2</sub>O (31 mg, 0.75 mmol) in MeOH/H<sub>2</sub>O (2.5 ml, 1:1) was stirred at room temperature for 3 hours. An aqueous solution of HCl (5%) was then added until pH = 3. The resulted mixture was extracted three times with EtOAc (20 ml) and the combined organic layers were dried (MgSO<sub>4</sub>) and concentrated in vacuo to afford pure saramycetic acid (64 mg, 100%) as a white solid (mp > 250 °C). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz) δ = 1.44 (t, 3H, *J* = 7.1 Hz), 2.78 (s, 3H), 4.46 (q, 2H, *J* = 7.1 Hz), 8.23 (s, 1H), 8.46 (s, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75 MHz) δ = 14.5, 26.1, 61.8, 124.3, 128.4, 148.3, 150.3, 161.4, 162.5, 167.3, 191.3; IR (KBr) ν 1687, 1725, 2981, 3092, 3128 cm<sup>-1</sup>; Anal. Calcd for C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>S<sub>2</sub> (282.3) : C, 46.79; H, 3.57; N, 9.92; S, 22.71. Found : C, 46.82; H, 3.61; N, 9.93; S, 22.77. These data were in reasonable agreement with the literature data.<sup>3</sup>

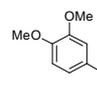
#### Synthesis of (E)-1-(4-(3,4-dimethoxystyryl)thiazol-2-yl)ethanone (**22a**) :

 According to the general above procedure from **4a** (206 mg, 1.0 mmol) using (E)-4-(2-bromovinyl)-1,2-dimethoxybenzene (204.12 mg, 0.84 mmol) as electrophile and Pd<sub>2</sub>(dba)<sub>3</sub> / XPhos (2:16 mol %) as catalyst. Standard workup followed by flash chromatography (EtOAc-PE 1:9, R<sub>f</sub> = 0.14) afforded **22a** (155 mg, 65%) as a pale yellow solid (mp = 90-91 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ = 2.78 (s, 3H), 3.91

<sup>3</sup> Glover, C.; Merritt, E.A.; Bagley, M.C. *Tetrahedron Lett.* **2007**, *48*, 7027-7030.

(s,3H), 3.95 (s, 3H), 6.88 (d, 1H,  $J = 7.8$  Hz), 7.01 (d, 1H,  $J = 16.3$  Hz), 7.09 (s, 1H), 7.10 (d, 1H,  $J = 7.8$  Hz), 7.45 (s, 1H), 7.47 (d, 1H,  $J = 16.3$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta = 26.2, 56.0, 56.1, 109.1, 111.3, 119.0, 120.6, 121.1, 129.7, 132.6, 149.3, 149.6, 156.6, 166.8, 192.0$ ; IR (KBr)  $\nu 1517, 1679, 2965, 3082\text{ cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{15}\text{H}_{15}\text{NO}_3\text{S}$  (289.3) : C, 62.26; H, 5.23; N, 4.84; S, 11.08. Found : C, 62.35; H, 5.28; N, 4.89; S, 11.01.

#### Synthesis of (E)-1-(4-(3,4-dimethoxystyryl)thiazol-2-yl)propan-1-one (**22b**) :



According to the general above procedure from **4b** (220 mg, 1.0 mmol) using (E)-4-(2-bromovinyl)-1,2-dimethoxybenzene (204.12 mg, 0.84 mmol) as electrophile and  $\text{Pd}_2(\text{dba})_3 / \text{P}[\text{biphen-2-yl}]\text{Cy}_2$  (2:16 mol %) as catalyst. Standard workup followed by flash chromatography (EtOAc-PE 2:8,  $R_f = 0.17$ ) afforded **22b** (173 mg, 68%) as a pale yellow solid (mp = 88-89 °C).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta = 1.28$  (t, 3H,  $J = 7.2$  Hz), 3.25 (q, 2H,  $J = 7.2$  Hz), 3.91 (s, 3H), 3.95 (s, 3H), 6.88 (d, 1H,  $J = 7.8$  Hz), 7.01 (d, 1H,  $J = 16.3$  Hz), 7.09 (s, 1H), 7.10 (d, 1H,  $J = 7.8$  Hz), 7.43 (s, 1H), 7.44 (d, 1H,  $J = 16.3$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta = 8.1, 32.1, 56.0, 56.1, 109.1, 111.4, 119.1, 120.5, 120.7, 129.7, 132.5, 149.3, 149.6, 156.4, 166.6, 194.9$ ; IR (KBr)  $\nu 1682, 2852, 2926\text{ cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{16}\text{H}_{17}\text{NO}_3\text{S}$  (303.4) : C, 63.34; H, 5.65; N, 4.62; S, 10.57. Found : C, 63.26; H, 5.58; N, 4.68; S, 11.02.

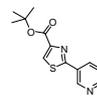
#### Synthesis of ethyl-*tert*-butyl microccinate :

##### Synthesis of ethyl-5-bromopicolinate (**6b**) :



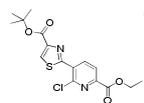
A solution of methyl-5-bromopicolinate (1.5 g, 6.94 mmol) and *p*-toluenesulfonic acid (132 mg, 0.69 mmol) in ethyl alcohol (70 ml) was refluxed 24 h. After concentration under vacuo,  $\text{Et}_2\text{O}$  was added (150 ml) and the separated organic layer was washed with aq. satd.  $\text{NaHCO}_3$  (40 ml), brine (40 ml) and concentrated under vacuo. The crude product was purified by flash column chromatography on silica gel (EtOAc-PE 9:1,  $R_f = 0.13$ ) to afford **6b** (1.42 g, 89%) as a white solid (mp = 63-64 °C).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta = 1.39$  (t, 3H,  $J = 7.1$  Hz), 4.43 (q, 2H,  $J = 7.1$  Hz), 7.93 (dd, 1H,  $J = 8.3$  Hz,  $J = 2.0$  Hz), 7.98 (d, 1H,  $J = 8.3$  Hz), 8.75 (d, 1H,  $J = 2.0$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta = 14.3, 62.3, 125.0, 126.3, 139.7, 146.6, 151.1, 164.6$ ; IR (KBr)  $\nu 1733, 2960, 2982, 3059\text{ cm}^{-1}$ ; Anal. Calcd for  $\text{C}_8\text{H}_8\text{BrNO}_2$  (230.1) : C, 41.77; H, 3.50; N, 6.09. Found : C, 41.83; H, 3.51; N, 6.14.

##### Synthesis of *tert*-butyl 2-(6-(ethoxycarbonyl)pyridin-3-yl)thiazole-4-carboxylate (**10**) :



The *tert*-butyl-4-thiazolecarboxylate **7** (300 mg, 1.62 mmol) was allowed to react with ethyl-5-bromopicolinate (746 mg, 3.24 mmol), palladium acetate (18 mg, 5 mol %), cesium carbonate (1.06 g, 3.24 mmol) and  $\text{P}[\text{biphen-2-yl}]\text{Cy}_2$  (57 mg, 10 mol %) in DMF (6 ml) at 110 °C for 18 h in a sealed tube under  $\text{N}_2$ . After filtration through Celite<sup>®</sup> washed with ethyl acetate, the resulted filtrate was concentrated under vacuo and the crude product was purified by flash column chromatography on silica gel (EtOAc-Cy 3:7,  $R_f = 0.2$ ) to afford **10** (401 mg, 74%) as a white solid (mp = 154-155 °C).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta = 1.45$  (t, 3H,  $J = 7.1$  Hz), 1.62 (s, 9H), 4.50 (q, 2H,  $J = 7.1$  Hz), 8.15 (s, 1H), 8.21 (d, 1H,  $J = 8.2$  Hz), 8.49 (dd, 1H,  $J = 8.2$  Hz,  $J = 1.8$  Hz), 9.28 (d, 1H,  $J = 1.8$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta = 14.4, 28.3, 62.4, 82.7, 125.4, 127.7, 131.6, 135.0, 147.9, 149.3, 150.3, 160.2, 163.8, 164.7$ ; IR (KBr)  $\nu 1709, 1726, 2931, 2978, 3133\text{ cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_4\text{S}$  (334.4) : C, 57.47; H, 5.43; N, 8.38; S, 9.59. Found : C, 57.53; H, 5.34; N, 8.33; S, 9.67.

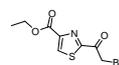
### Synthesis of *tert*-butyl 2-(2-chloro-6-(ethoxycarbonyl)pyridin-3-yl)thiazole-4-carboxylate (**5b**) :



The 5-(4-(*tert*-Butoxycarbonyl)thiazol-2-yl)-2-(ethoxycarbonyl)pyridine *N*-oxide was prepared according to the Caron's procedure.<sup>4</sup> TFAA (557  $\mu$ l, 4.00 mmol) was added dropwise to a cooled solution (0  $^{\circ}$ C) of **10** (638 mg, 1.91 mmol) and UHP (359 mg, 3.82 mmol) in CH<sub>3</sub>CN (4.75 ml). After 60 min stirring, an aq. sol. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (10 %, 5 ml) and water (25 ml) were added. The resulted mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layers were dried (MgSO<sub>4</sub>) and concentrated in vacuo to afford 5-(4-(*tert*-butoxycarbonyl)thiazol-2-yl)-2-(ethoxycarbonyl)pyridine *N*-oxide (668 mg, 100%) as a pure pale yellow solid (mp = 113-114  $^{\circ}$ C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  = 1.39 (t, 3H, *J* = 7.1 Hz), 1.59 (s, 9H), 4.45 (q, 2H, *J* = 7.1 Hz), 7.68 (d, 1H, *J* = 8.2 Hz), 7.86 (dd, 1H, *J* = 8.2 Hz, *J* = 1.5 Hz), 8.16 (s, 1H), 8.85 (d, 1H, *J* = 1.5 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  = 14.1, 28.2, 62.9, 82.9, 122.4, 127.2, 128.3, 133.4, 138.7, 142.1, 150.4, 159.9, 160.9, 161.2; IR (KBr)  $\nu$  1724, 1742, 2936, 2974, 3086 cm<sup>-1</sup>; Anal. Calcd for C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>O<sub>5</sub>S (350.4) : C, 54.85; H, 5.18; N, 7.99; S, 9.15. Found : C, 54.92; H, 5.11; N, 8.02; S, 9.16.

The subsequent  $\alpha$ -chlorination reaction was achieved according to the Fagnou's procedure.<sup>5</sup> A solution of POCl<sub>3</sub> (266  $\mu$ l, 2.85 mmol) in toluene (5.7 ml) and DMF (5.7 ml) was cooled at 0  $^{\circ}$ C. After 10 min a solution of the freshly prepared 5-(4-(*tert*-Butoxycarbonyl)thiazol-2-yl)-2-(ethoxycarbonyl)pyridine *N*-oxide (500 mg, 1.43 mmol) in DMF (2.9 ml) was slowly added. After 10 min stirring, the mixture was allowed to warm to room temperature. After 12 h stirring, solvents were removed under vacuo. The crude residue was cooled in an ice bath and a sat. aq. sol. NaHCO<sub>3</sub> was added. The solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layers were washed with brine, dried (MgSO<sub>4</sub>) and concentrated under vacuo. The crude product was purified by flash column chromatography on silica gel (EtOAc-PE 2:8, R<sub>f</sub> = 0.2) afforded **5b** (411 mg, 78%) as a white solid (mp = 129-130  $^{\circ}$ C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  = 1.46 (t, 3H, *J* = 7.1 Hz), 1.64 (s, 9H), 4.51 (q, 2H, *J* = 7.1 Hz), 8.17 (d, 1H, *J* = 8.1 Hz), 8.27 (s, 1H), 8.98 (d, 1H, *J* = 8.1 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  = 14.4, 28.3, 62.7, 82.7, 124.0, 129.1, 131.1, 140.7, 147.9, 148.4, 149.0, 160.3, 160.8, 163.6; IR (KBr)  $\nu$  1702, 1724, 2907, 2934, 2986, 3110 cm<sup>-1</sup>; Anal. Calcd for C<sub>16</sub>H<sub>17</sub>ClN<sub>2</sub>O<sub>4</sub>S (368.8) : C, 52.10; H, 4.65; N, 7.60; S, 8.69. Found : C, 52.04; H, 4.69; N, 7.49; S, 8.73.

### Synthesis of ethyl 2-(2-bromoacetyl)thiazole-4-carboxylate (**12**) :



To a solution of 2-bromothiazole-4-carboxylate **15** (500 mg, 2.17 mmol) in THF (42 ml) was added dropwise isopropylmagnesium chloride lithium chloride complex (1.95 ml, 1.3 M in THF) at -78  $^{\circ}$ C. After 30 min stirring, the *N*-acetylmorpholine (985  $\mu$ l, 8.47 mmol) was slowly added and the reaction mixture was then stirred for 1 h 30. Et<sub>2</sub>O (60 ml) was then added and the resulted solution was washed with a satd. aq. sol. NaHCO<sub>3</sub> (60 ml), brine (60 ml) and dried (MgSO<sub>4</sub>). After concentration under vacuo, the crude product was purified by flash column chromatography on silica gel (EtOAc-PE 8:2, R<sub>f</sub> = 0.2) to afford 2-acetylthiazole-4-carboxylate (307 mg, 71%) as a white solid (mp = 65-66  $^{\circ}$ C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  = 1.40 (t, 3H, *J* = 7.1 Hz), 2.75 (s, 3H), 4.42 (q, 2H, *J* = 7.1 Hz), 8.41 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  = 14.4, 26.2, 61.9, 133.5, 148.8, 160.1, 167.5, 191.7; IR (KBr)  $\nu$  1689, 1729, 2994, 3114 cm<sup>-1</sup>; Anal. Calcd for C<sub>8</sub>H<sub>9</sub>NO<sub>3</sub>S (199.2) : C, 48.23; H, 4.55; N, 7.03; S, 16.09. Found : C, 48.19; H, 4.52; N, 7.06; S, 16.12.

To a cooled solution (0  $^{\circ}$ C) of ethyl 2-acetylthiazole-4-carboxylate (100 mg, 0.50 mmol) and Et<sub>3</sub>N (222  $\mu$ l, 1.61 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 ml) was slowly added tert-

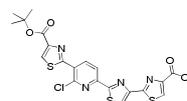
<sup>4</sup> Caron, S.; Do, N.M.; Sieser, J. *Tetrahedron Lett.* **2000**, *41*, 2299-2302.

<sup>5</sup> Leclerc, J.-P.; Fagnou, K. *Angew. Chem. Int. Ed.* **2006**, *45*, 7781-7786.

butyldimethylsilyltrifluoromethanesulfonate (254  $\mu$ l, 1.10 mmol). After 2 h 30 stirring at 0  $^{\circ}$ C, water (5 ml) was then added and the mixture was extracted three times with  $\text{CH}_2\text{Cl}_2$  (10 ml). The combined organic extracts were dried ( $\text{MgSO}_4$ ) and concentrated under vacuo. The crude product was purified by flash column chromatography on silica gel to afford ethyl 2-(1-(tert-butyldimethylsilyloxy)vinyl)thiazole-4-carboxylate (156 mg, 100%) as an oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  = 0.26 (s, 6H), 1.01 (s, 9H), 1.41 (t, 3H,  $J$  = 7.1 Hz), 4.42 (q, 2H,  $J$  = 7.1 Hz), 4.56 (d, 1H,  $J$  = 1.5 Hz), 5.65 (d, 1H,  $J$  = 1.5 Hz), 8.12 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  = -4.6, 14.5, 18.3, 25.8, 61.6, 93.5, 127.7, 148.0, 148.9, 161.7, 168.5; IR (KBr)  $\nu$  1720, 1737, 2859, 2931  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{14}\text{H}_{14}\text{ClN}_3\text{O}_2\text{S}_2$  (313.5): C, 53.64; H, 7.40; N, 4.47; S, 10.23. Found: C, 53.58; H, 7.48; N, 4.51; S, 10.29.

The *N*-bromosuccinimide (51 mg, 0.29 mmol) was then added to a cooled solution (0  $^{\circ}$ C) of ethyl 2-(1-(tert-butyldimethylsilyloxy)vinyl)thiazole-4-carboxylate (90 mg, 0.29 mmol) in THF (2.8 ml). After 1 h stirring at the same temperature, water (5 ml) was added and the resulted mixture was extracted three times with  $\text{Et}_2\text{O}$  (10 ml). The combined organic layers were dried ( $\text{MgSO}_4$ ), concentrated under vacuo and the crude product was purified by flash column chromatography on silica gel ( $\text{EtOAc-PE}$  2:8,  $R_f$  = 0.21) to afford **12** (57 mg, 70%) as a white solid (mp = 80-81  $^{\circ}$ C).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  = 1.43 (t, 3H,  $J$  = 7.1 Hz), 4.46 (q, 2H,  $J$  = 7.1 Hz), 4.81 (s, 2H), 8.50 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  = 14.4, 31.2, 62.2, 134.3, 149.2, 160.6, 164.1, 184.9; IR (KBr)  $\nu$  1703, 1728, 2947, 2991, 3128  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_8\text{H}_8\text{BrNO}_3\text{S}$  (278.1): C, 34.55; H, 2.90; N, 5.04; S, 11.53. Found: C, 34.61; H, 2.84; N, 5.06; S, 11.56.

#### Synthesis of chlorodiazolylpyridine (**11**):



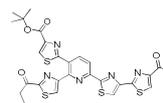
A solution of the ester **10** (430 mg, 1.17 mmol) in aq. sol.  $\text{NH}_3$  (10%, 26 ml) and THF (17 ml) was stirred for 12 h at room temperature. This solution was then extracted three times with ethyl acetate (25 ml) and the combined organic layers were washed with brine (25 ml), dried ( $\text{MgSO}_4$ ) and concentrated under vacuo to afford *tert*-butyl 2-(6-carbamoyl-2-chloropyridin-3-yl)thiazole-4-carboxylate (326 mg, 82%) as a white solid (mp = 198-199  $^{\circ}$ C).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  = 1.64 (s, 9H), 5.69 (bs, 1H), 7.64 (bs, 1H), 8.26 (d, 1H,  $J$  = 8.1 Hz), 8.26 (s, 1H), 8.99 (d, 1H,  $J$  = 8.1 Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  = 28.3, 82.7, 121.7, 129.0, 130.8, 141.3, 146.7, 149.0, 149.8, 160.3, 160.9, 164.8; IR (KBr)  $\nu$  1698, 1712, 3095, 3136, 3458  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{14}\text{H}_{14}\text{ClN}_3\text{O}_3\text{S}$  (339.8): C, 49.49; H, 4.15; N, 12.37; S, 9.44. Found: C, 49.54; H, 4.19; N, 12.45; S, 9.42.

A solution of the *tert*-butyl 2-(6-carbamoyl-2-chloropyridin-3-yl)thiazole-4-carboxylate (420 mg, 1.24 mmol) and Lawesson's reagent (300 mg, 0.74 mmol) in toluene (6.2 ml) was refluxed for 3 h. After cooling, this solution was extracted three times with  $\text{EtOAc}$  (25 ml) and the combined organic layers were washed with brine (25 ml), dried ( $\text{MgSO}_4$ ) and concentrated under vacuo. The crude product was purified by flash column chromatography on silica gel ( $\text{EtOAc-PE}$  2:8,  $R_f$  = 0.23) to afford the *tert*-butyl 2-(6-carbamothioyl-2-chloropyridin-3-yl)thiazole-4-carboxylate (335 mg, 76%) as an orange solid (mp = 160-161  $^{\circ}$ C).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  = 1.63 (s, 9H), 7.85 (bs, 1H), 8.26 (s, 1H), 8.69 (d, 1H,  $J$  = 8.2 Hz), 8.94 (d, 1H,  $J$  = 8.2 Hz), 9.19 (bs, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  = 28.3, 82.7, 124.2, 129.0, 130.4, 140.7, 145.8, 149.0, 150.3, 160.3, 160.9, 193.1; IR (KBr)  $\nu$  1707, 1729, 3090, 3378  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{14}\text{H}_{14}\text{ClN}_3\text{O}_2\text{S}_2$  (355.9): C, 47.25; H, 3.97; N, 11.81; S, 18.02. Found: C, 47.31; H, 4.00; N, 11.77; S, 17.99.

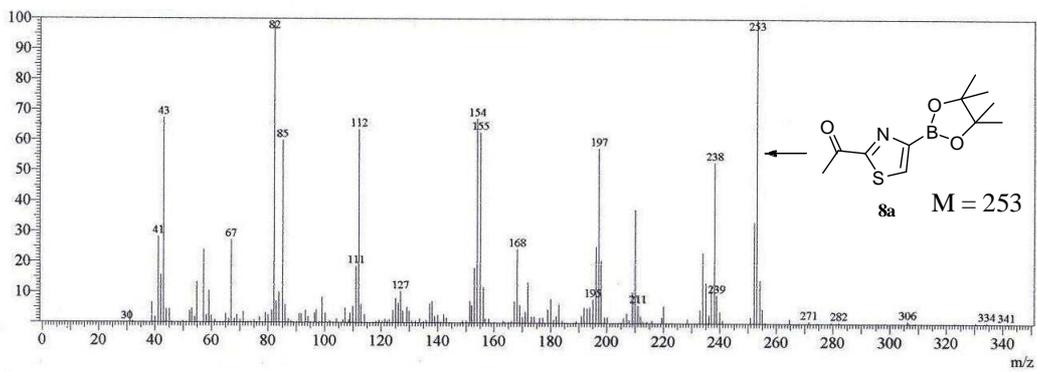
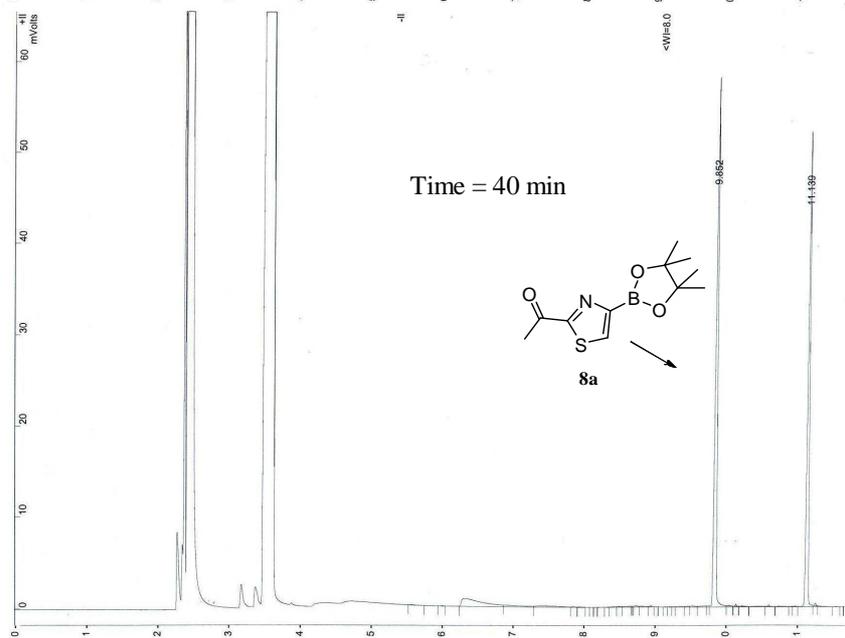
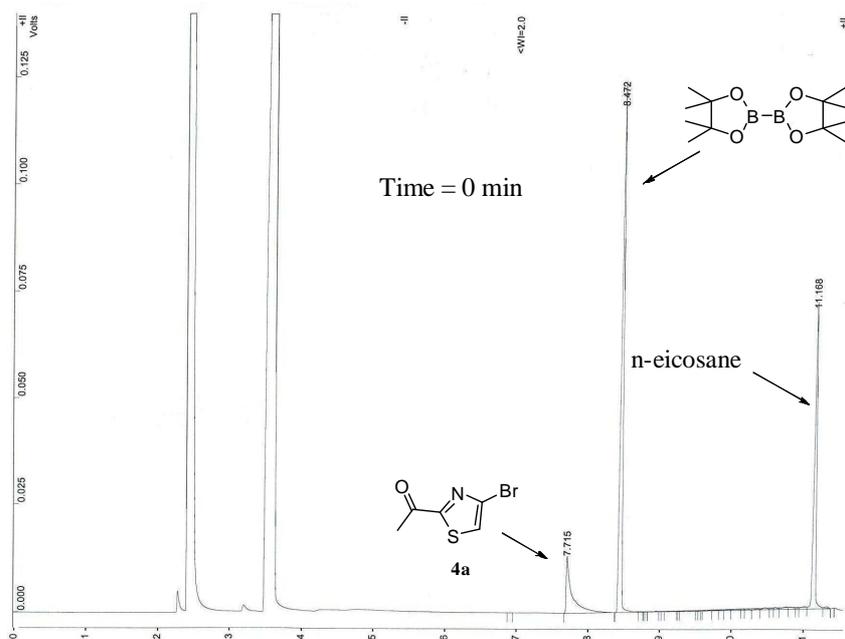
A solution of *tert*-butyl 2-(6-carbamothioyl-2-chloropyridin-3-yl)thiazole-4-carboxylate (186 mg, 0.52 mmol) and  $\alpha$ -bromoketone **12** (146 mg, 0.52 mmol) in  $\text{EtOH}$  (2.6 ml) and THF (2.6 ml) was refluxed for 4 h. After cooling, the solution was extracted three times with  $\text{EtOAc}$  (20 ml) and the combined organic layers were washed with brine (20 ml), dried ( $\text{MgSO}_4$ ) and

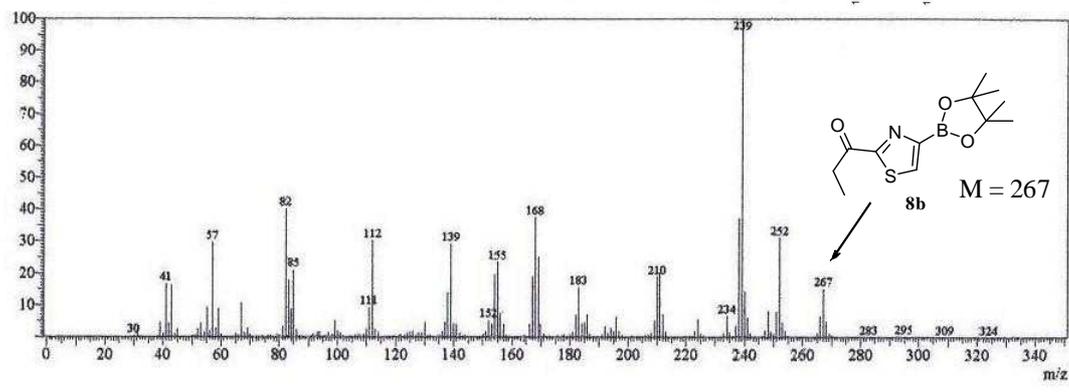
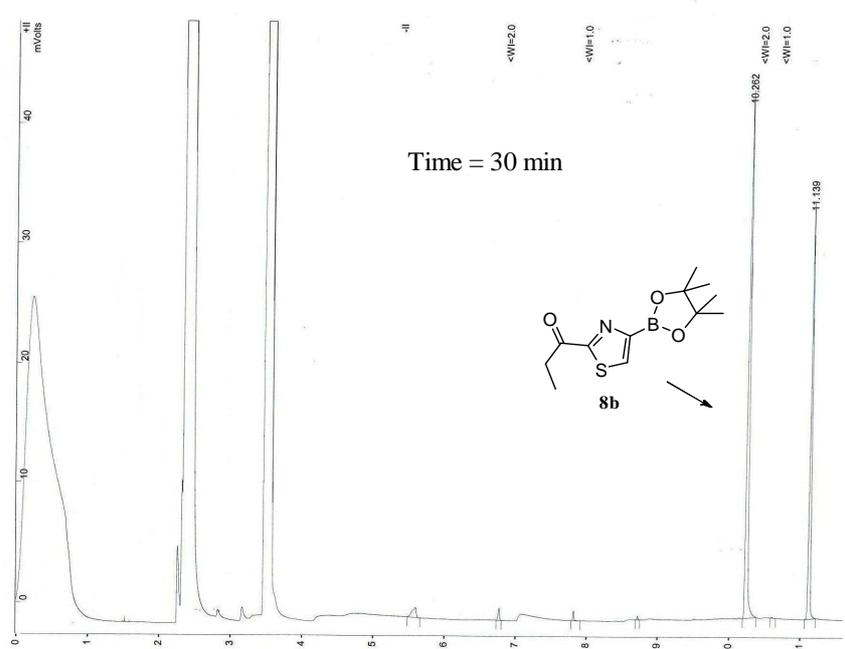
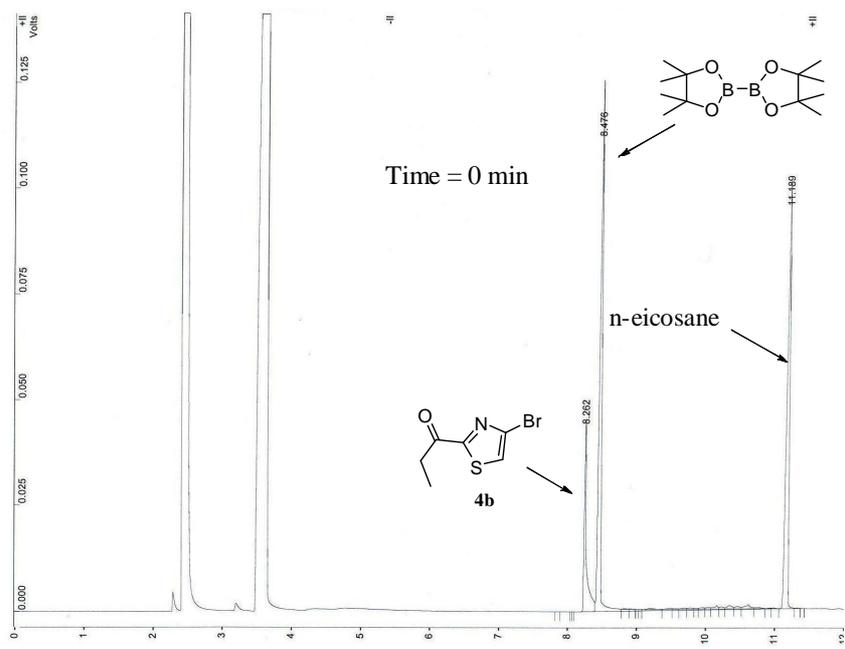
concentrated under vacuo. The crude product was purified by flash column chromatography on silica gel (EtOAc-PE 7:3, Rf = 0.2) to afford **11** (181 mg, 65%) as a white solid (mp = 182-183 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ = 1.44 (t, 3H, J = 7.1 Hz), 1.64 (s, 9H), 4.46 (q, 2H, J = 7.1 Hz), 8.23 (s, 1H), 8.24 (s, 1H), 8.30 (d, 1H, J = 8.2 Hz), 8.34 (s, 1H), 8.97 (d, 1H, J = 8.2 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ = 14.5, 28.3, 61.8, 82.6, 118.9, 121.3, 128.2, 128.7, 129.1, 140.9, 147.7, 148.1, 148.8, 150.1, 151.0, 160.4, 161.3, 161.5, 163.1, 166.9; IR (KBr) ν 1715, 2933, 2978, 3125 cm<sup>-1</sup>; Anal. Calcd for C<sub>22</sub>H<sub>19</sub>ClN<sub>4</sub>O<sub>4</sub>S<sub>3</sub> (535.1): C, 49.38; H, 3.58; N, 10.47; S, 17.98. Found: C, 49.43; H, 3.56; N, 10.42; S, 18.01.

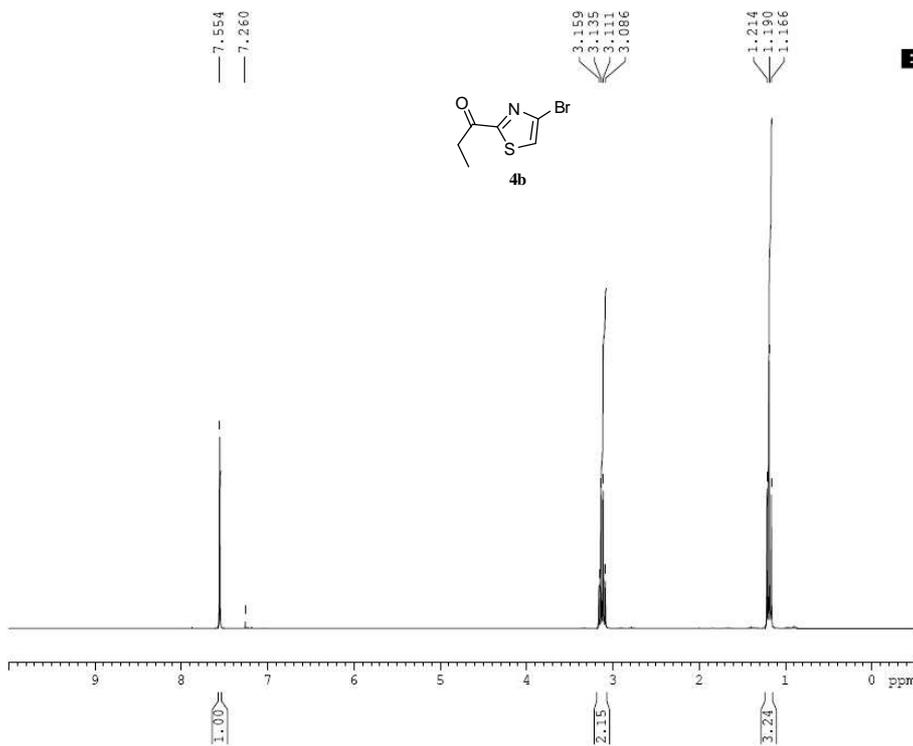
#### Synthesis of ethyl-*tert*-butyl micrococciate (**13**):



The 1-(4-bromothiazol-2-yl)propan-1-one **4b** (25 mg, 0.11 mmol) was allowed to react with bispinacolatodiboron (29 mg, 0.11 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (1 mg, 2 mol %), potassium acetate (19 mg, 0.19 mmol) and P[biphen-2-yl]Cy<sub>2</sub> (5 mg, 16 mol %) in dioxane (0.4 ml) at 110 °C in a sealed tube under N<sub>2</sub>. After 30 min, a solution of **11** (50 mg, 0.09 mmol) in dioxane (0.21 ml) and an aq. sol. K<sub>3</sub>PO<sub>4</sub> (0.21 ml, 5 M) were added. The resulted mixture was stirred at 110 °C for 12 h. EtOAc (20 ml) and dried MgSO<sub>4</sub> were then added. After filtration through Celite<sup>®</sup> and concentration under vacuo, the crude product was purified by flash column chromatography on silica gel (EtOAc-PE 7:3, Rf = 0.15) to afford **13** (52 mg, 87%) as a white solid (mp = 188-189 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ = 1.11 (t, 3H, J = 7.3 Hz), 1.44 (t, 3H, J = 7.1 Hz), 1.61 (s, 9H), 2.76 (q, 2H, J = 7.3 Hz), 4.46 (q, 2H, J = 7.1 Hz), 8.17 (s, 1H), 8.24 (s, 1H), 8.25 (d, 1H, J = 8.2 Hz), 8.32 (s, 1H), 8.35 (d, 1H, J = 8.2 Hz), 8.41 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ = 8.1, 14.5, 28.3, 31.8, 61.8, 82.5, 118.9, 120.7, 128.1, 128.2, 128.2, 129.0, 140.7, 148.2, 148.9, 150.1, 150.2, 151.1, 154.9, 160.5, 161.6, 163.3, 165.4, 165.9, 168.4, 194.6; IR (KBr) ν 1689, 1718, 1736, 2979, 3118 cm<sup>-1</sup>; Anal. Calcd for C<sub>28</sub>H<sub>25</sub>N<sub>5</sub>O<sub>5</sub>S<sub>4</sub> (639.8): C, 52.56; H, 3.94; N, 10.95; S, 20.05. Found: C, 52.62; H, 3.99; N, 10.90; S, 20.06.





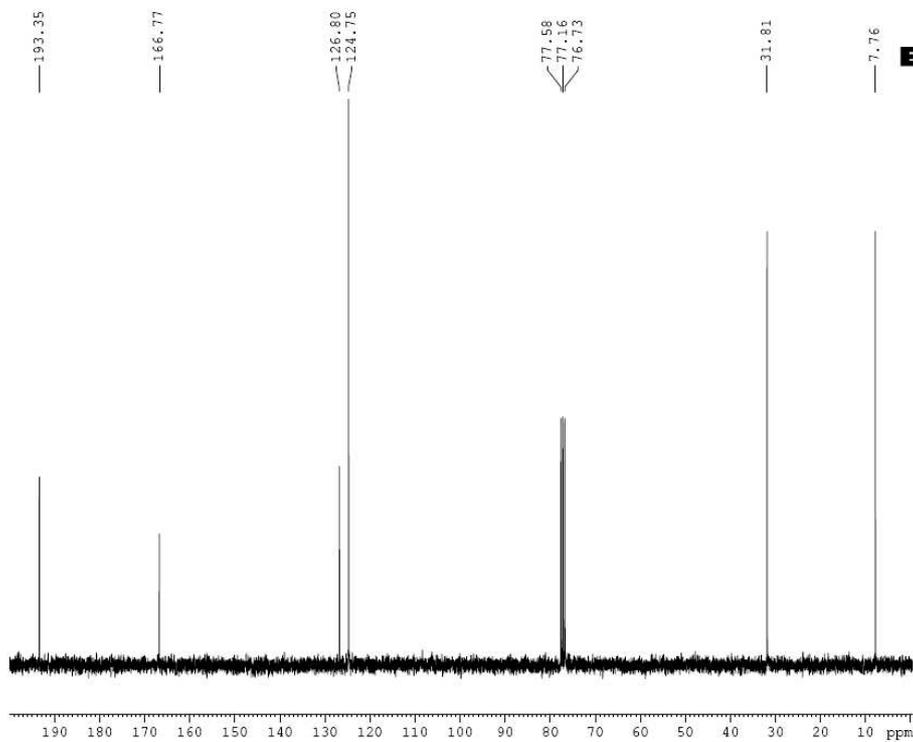


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DS            0
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FIDRES       0.184190 Hz
AQ           5.3084600 sec
RG           101.6
SQ           81.000 usec
DE           10.00 usec
TE           294.2 K
D1           1.00000000 sec
TD0          1

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SI           32768
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SSB          0
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PC           1.00

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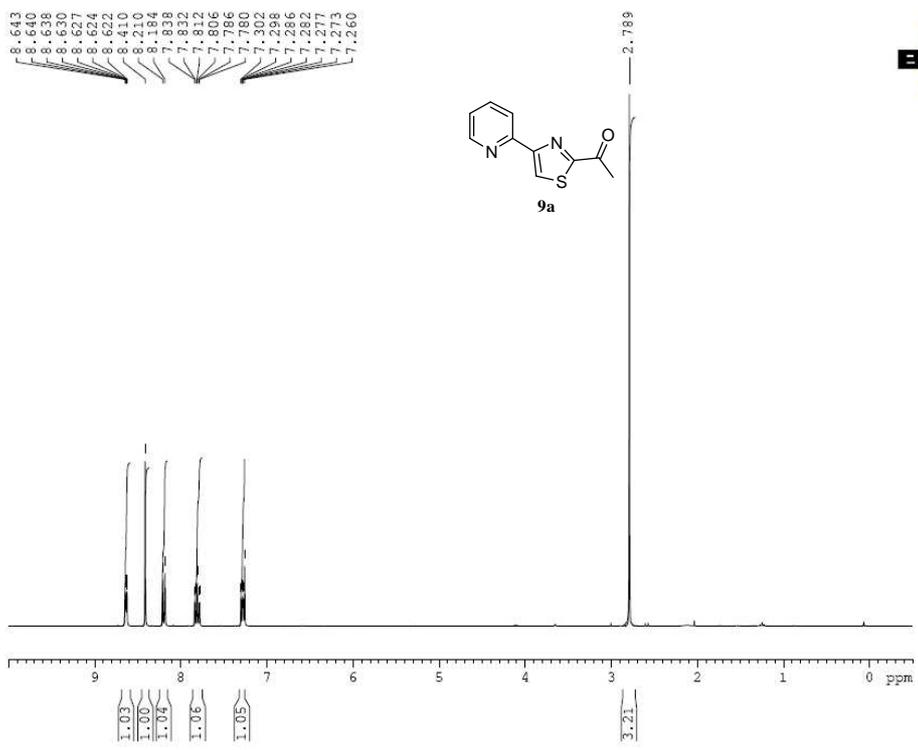
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PROCNO         1
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D11          0.03000000 sec
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TD0          1

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PCPD2        100.00 usec
PL2          -6.00 dB
PL12         11.00 dB
PL13         11.00 dB
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WDW          EM
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GB           0
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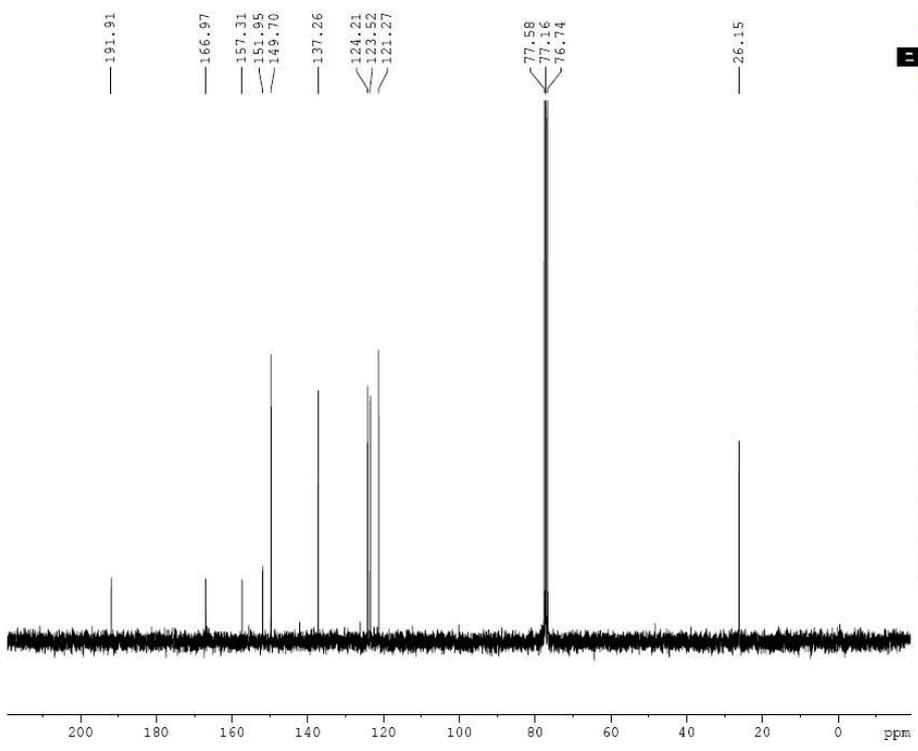
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SOLVENT       CDCl3
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SWH           6112.819 Hz
FIDRES       0.094190 Hz
AQ           0.3098660 sec
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TE           300.2 K
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TD0          1

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PL1           -6.00 dB
SFO1         300.131034 MHz
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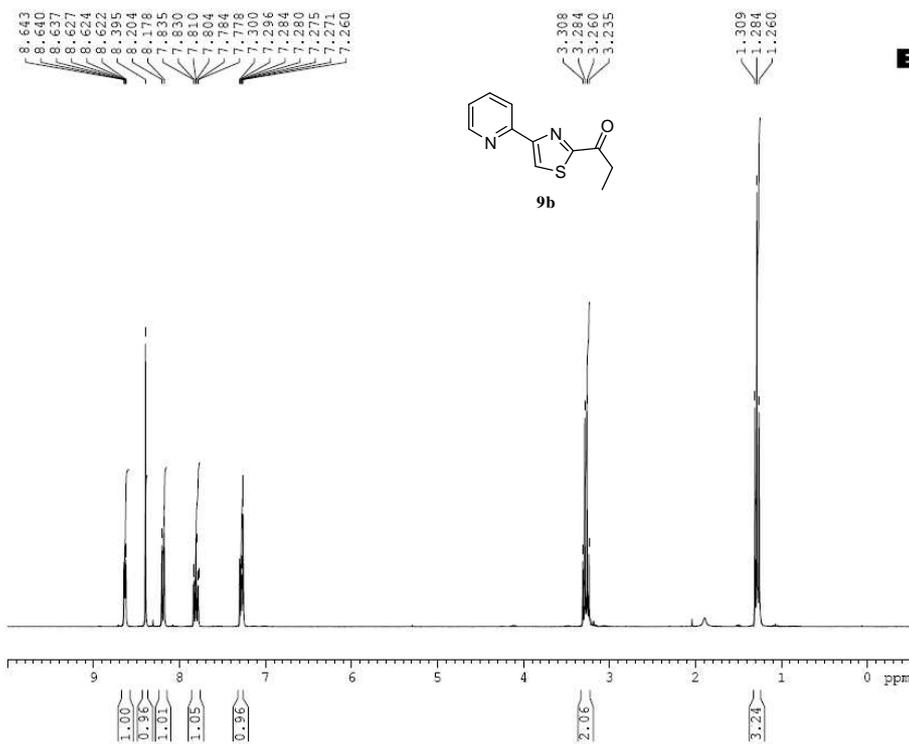


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SOLVENT       CDCl3
NS            4
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FIDRES       0.274439 Hz
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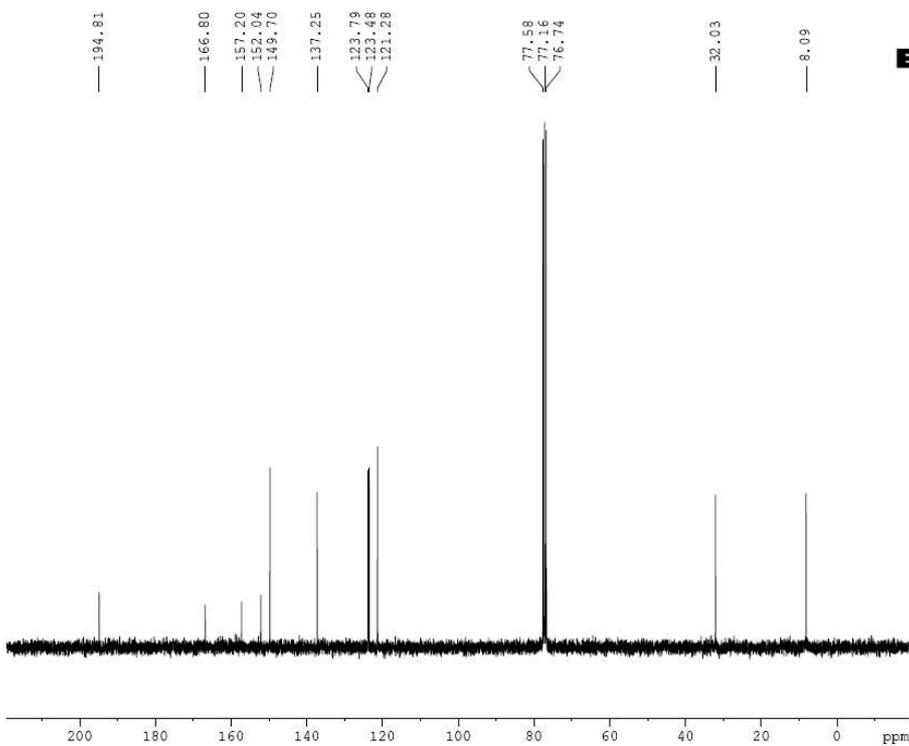
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SS            0
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GB            0
PC           1.40
  
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FIDRES        0.084390 Hz
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SSB           0
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TE            294.2 K
TE          1.00000000 sec
DELTA         1.89999999 sec
TD0           1

----- CHANNEL f1 -----
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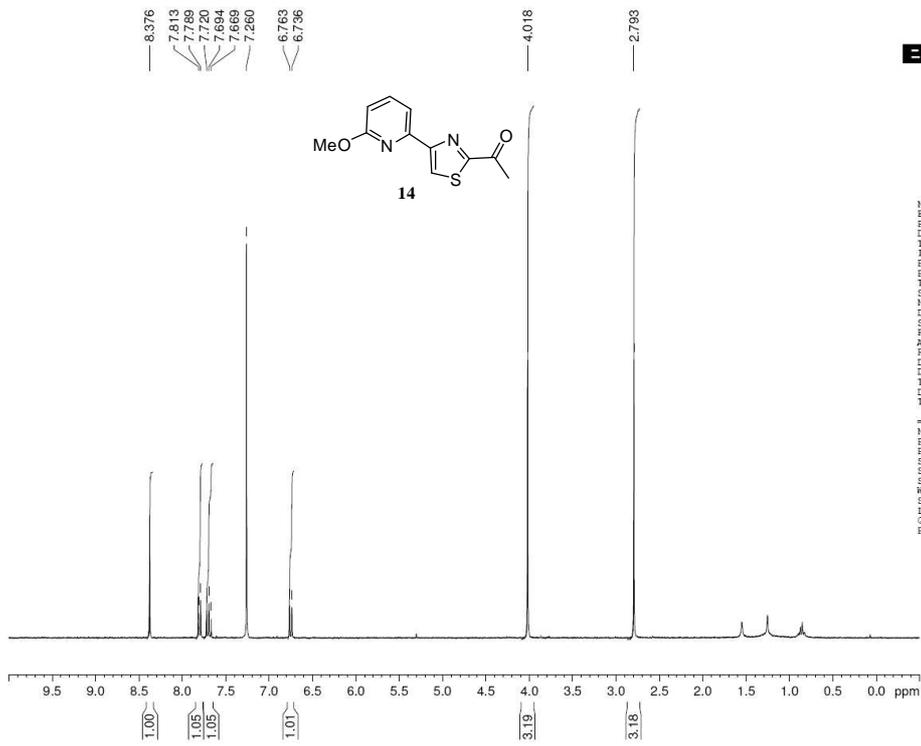


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NS            8
DS            4
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FIDRES        1.8219908 Hz
AQ            1.8219908 sec
RG            190.8
WDW           EM
SSB           0
DE            10.00 usec
TE            294.2 K
TE          2.00000000 sec
DELTA         1.89999999 sec
TD0           1

----- CHANNEL F1 -----
NUC1          13
P1            10.50 usec
PL1           0.00 dB
SFO1         75.4752653 MHz

----- CHANNEL F2 -----
PULPROG2      waltz16
NUC2          13
PCPD2         100.00 usec
PL2           -4.00 dB
PL12          11.00 dB
PL13          11.00 dB
SFO2         300.1312005 MHz
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WDW           EM
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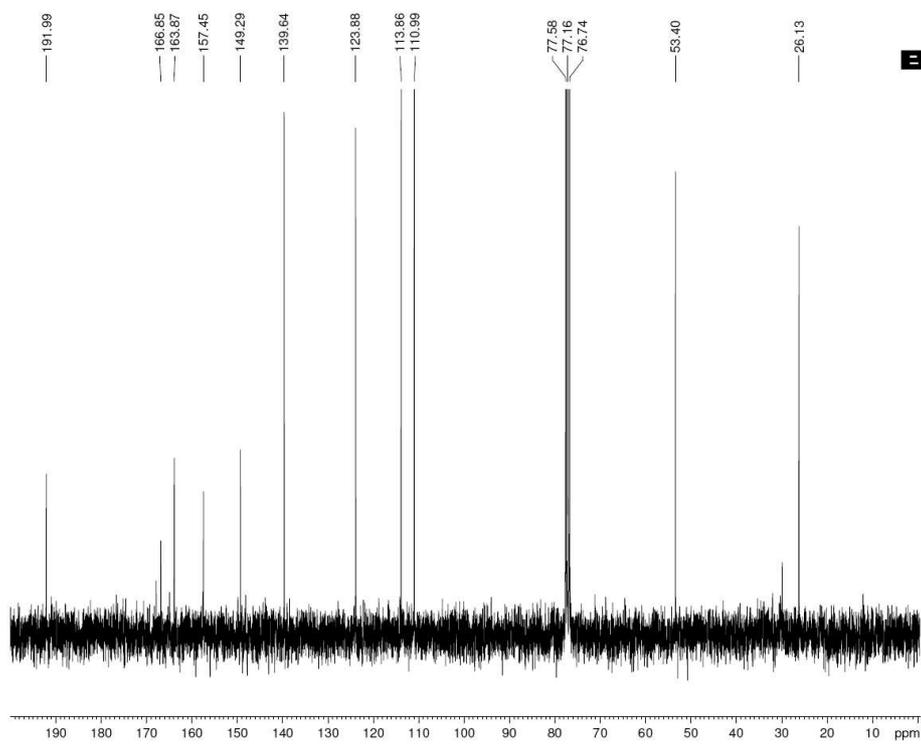


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SWH        6172.839 Hz
FIDRES     0.094190 Hz
AQ         5.3084660 sec
RG         1290.2
DM         81.000 usec
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TE         296.2 K
D1         1.0000000 sec
TD         1

===== CHANNEL f1 =====
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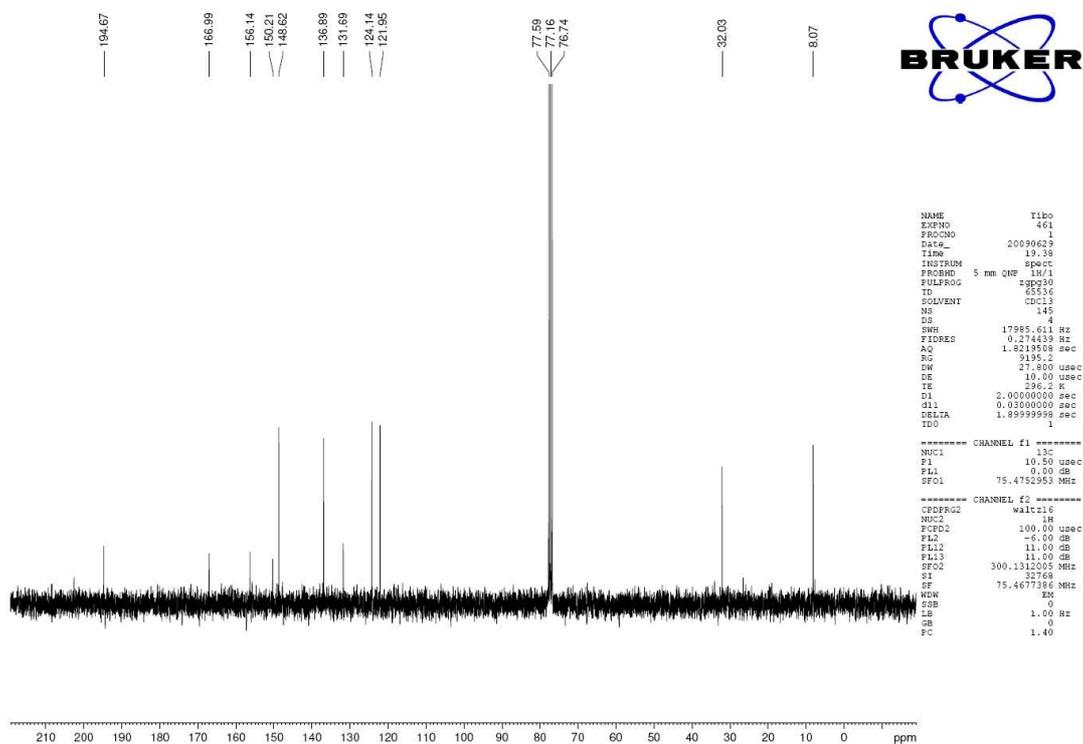
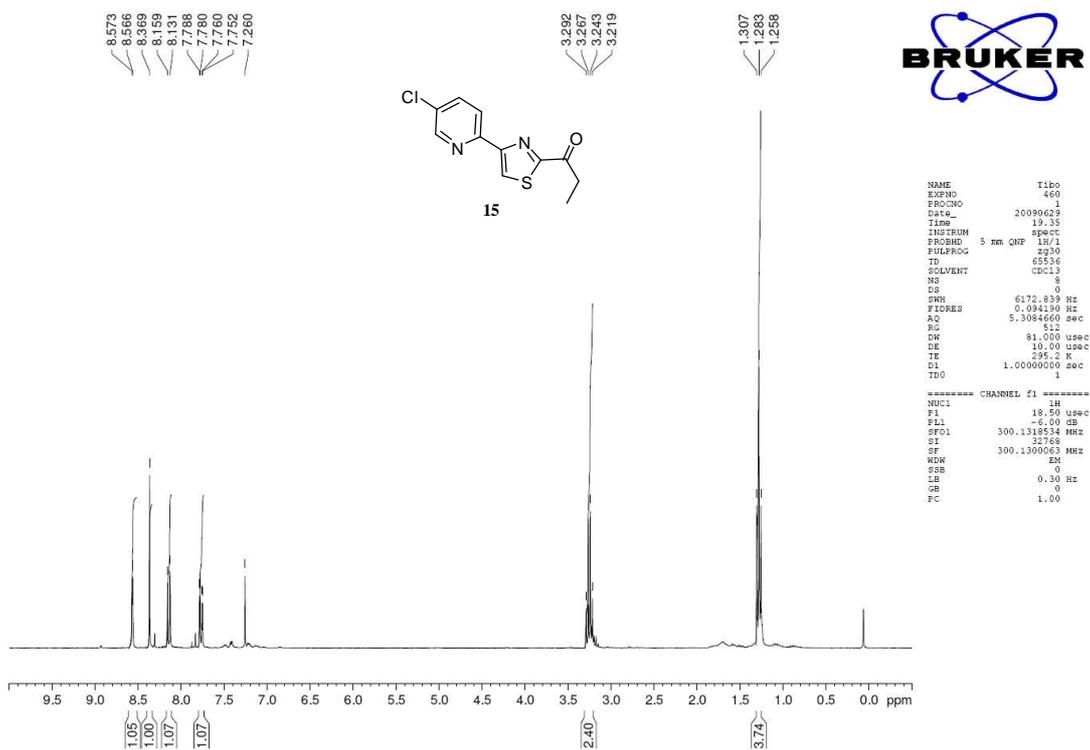
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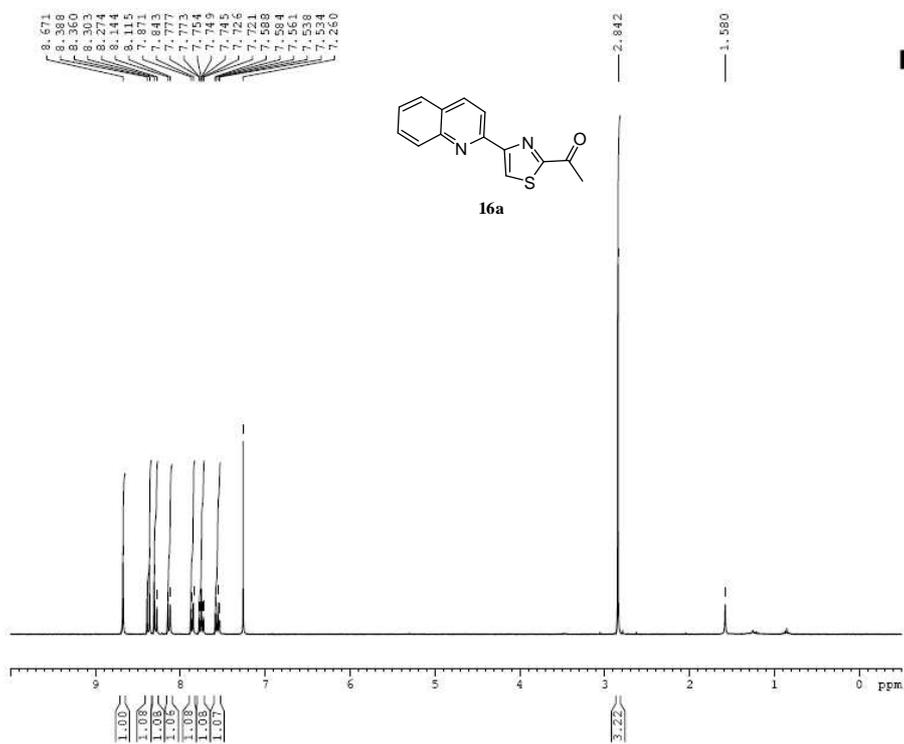
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RG         13004
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TE         296.2 K
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DELTA      1.8999998 sec
TD         1

===== CHANNEL f1 =====
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SFO1       75.4752813 MHz

===== CHANNEL f2 =====
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PL2        -6.00 dB
PL12       11.00 dB
PL13       11.00 dB
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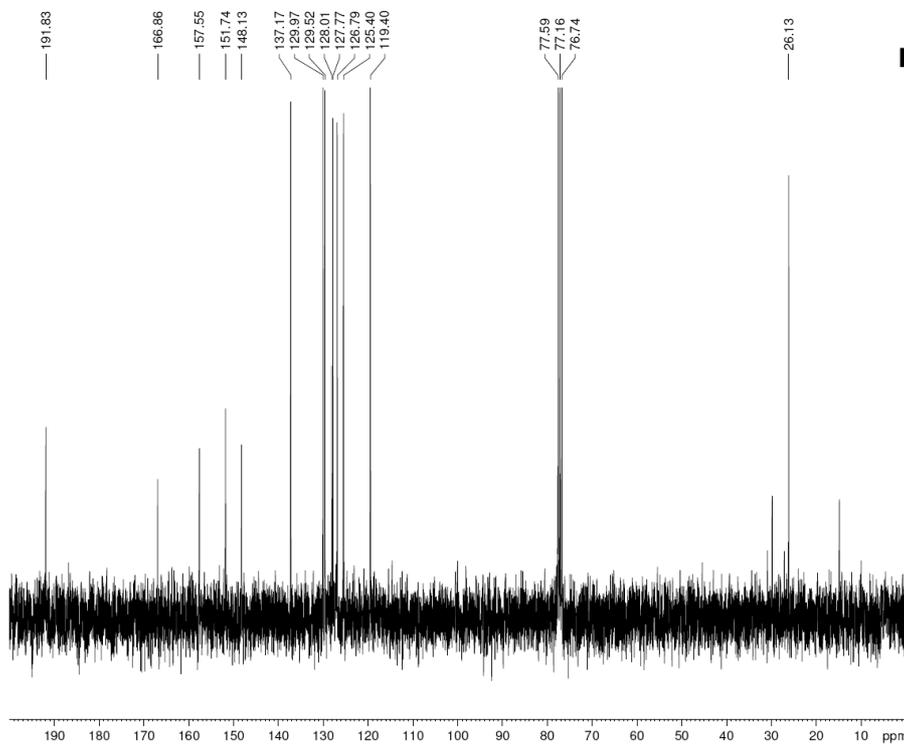
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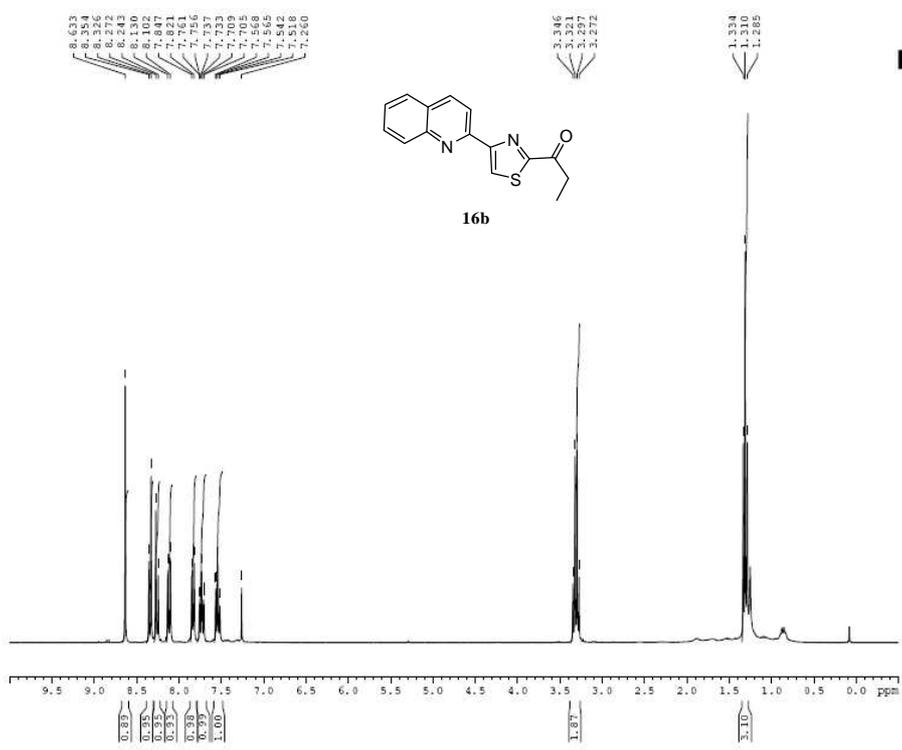
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FIDRES    0.004190 Hz
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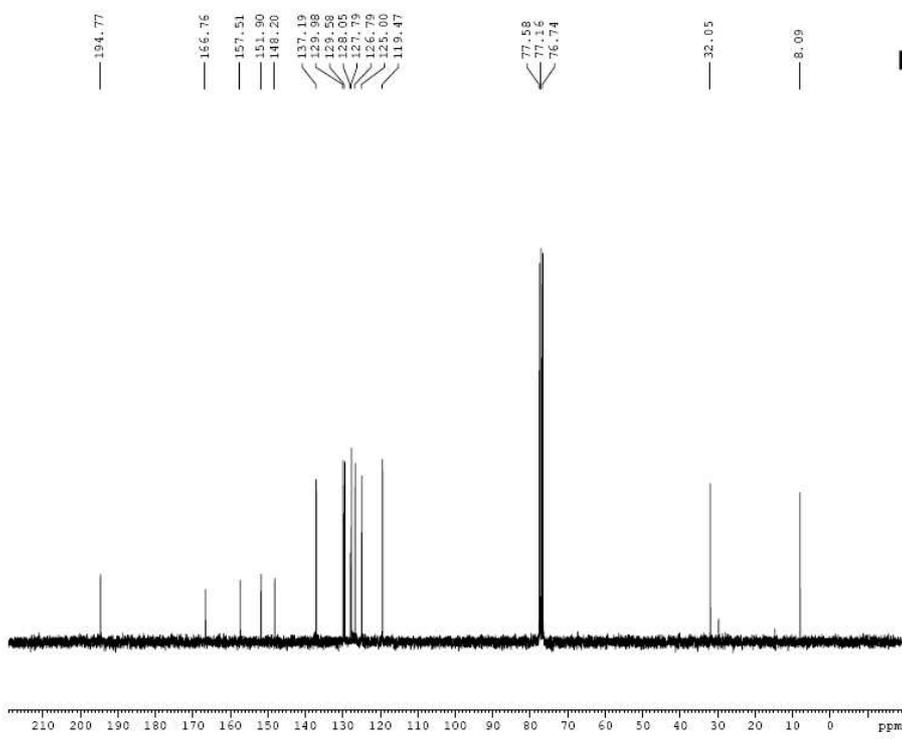
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DS        4
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RG        1024
SFO1      300.1318534 MHz
SF         300.1300162 MHz
SF2        300.1300162 MHz
SSB       EM
LB         1.00 Hz
GB         0
PC         1.40
  
```



```

NAME      CLAIRS L
EXPNO    1
PROCNO   1
Date_    20090616
Time     14.28
INSTRUM  spect
PROBHD   5 mm QNP 1H/1
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        8
DS        4
SWH       6172.839 Hz
FIDRES   0.094190 Hz
AQ        9.3984400 sec
RG        213.2
EW        61.990 usec
DE        15.00 usec
TE        296.2 K
D1        1.00000000 sec
TD0       1

----- CHANNEL f1 -----
NUC1      13C
P1        18.50 usec
PL1       -1.00 dB
SFO1     300.1300000 MHz
SI        32768
SF        300.1300000 MHz
WDW       EM
SS        0
LB        0.30 Hz
GB        1.00
PC
  
```

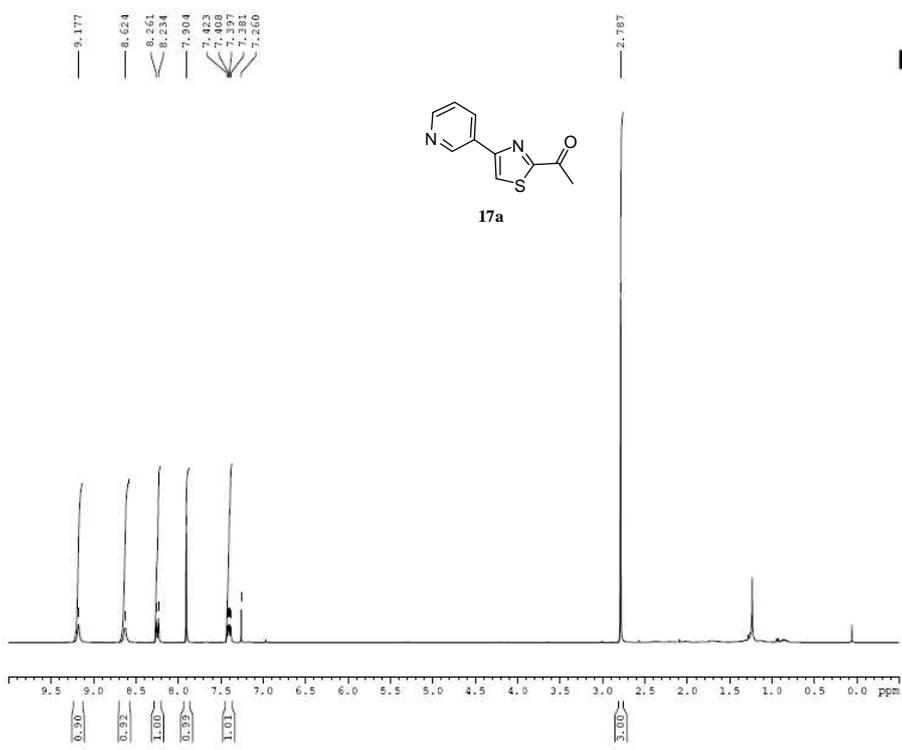


```

NAME      CLAIRS L
EXPNO    1
PROCNO   1
Date_    20090616
Time     14.46
INSTRUM  spect
PROBHD   5 mm QNP 1H/1
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        8
DS        4
SWH       17985.611 Hz
FIDRES   0.274209 Hz
AQ        1.6213508 sec
RG        379.246
EW        27.000 usec
DE        10.00 usec
TE        296.2 K
D1        2.00000000 sec
d11       0.03000000 sec
DELTA    1.89999998 sec
TD0       1

----- CHANNEL f1 -----
NUC1      13C
P1        10.50 usec
PL1       0.00 dB
SFO1     75.4752953 MHz

----- CHANNEL f2 -----
PULPROG2  waicmg16
NUC2       1H
PCPD02    100.00 usec
PL2       -4.00 dB
PL12      11.00 dB
PL13      11.00 dB
SFO2     300.1310000 MHz
SI        32768
SF        75.4752953 MHz
WDW       EM
SS        0
LB        1.00 Hz
GB        1.40
PC
  
```

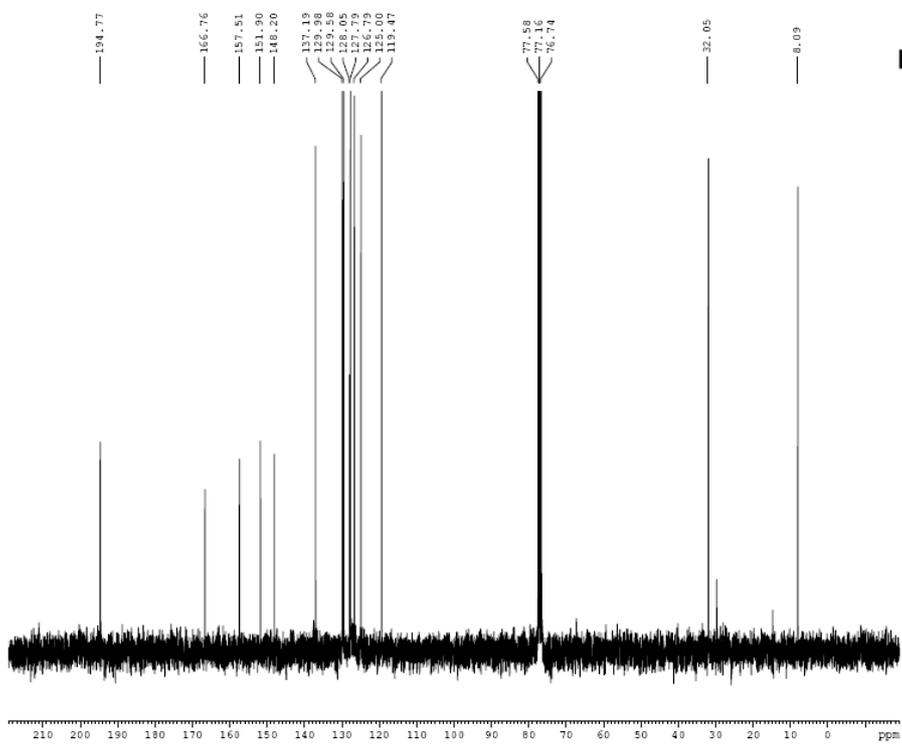


```

NAME      Claire L
EXPNO     1
PROCNO    1
Date_     20090615
Time      14.29
INSTRUM   spect
PROBHD    5 mm QNP 1H/1
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         8
DS         4
SWH        6172.838 Hz
FIDRES     0.094190 Hz
AQ         5.3094500 sec
RG         456.1
SQ         41.000 usec
DE         10.00 usec
TE         296.2 K
D1         1.00000000 sec
DELTA     1
  
```

```

----- CHANNEL f1 -----
NUC1       1H
P1         18.50 usec
PL1        -6.00 dB
SFO1       300.1319534 MHz
SI         32768
SF         300.1300063 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
  
```

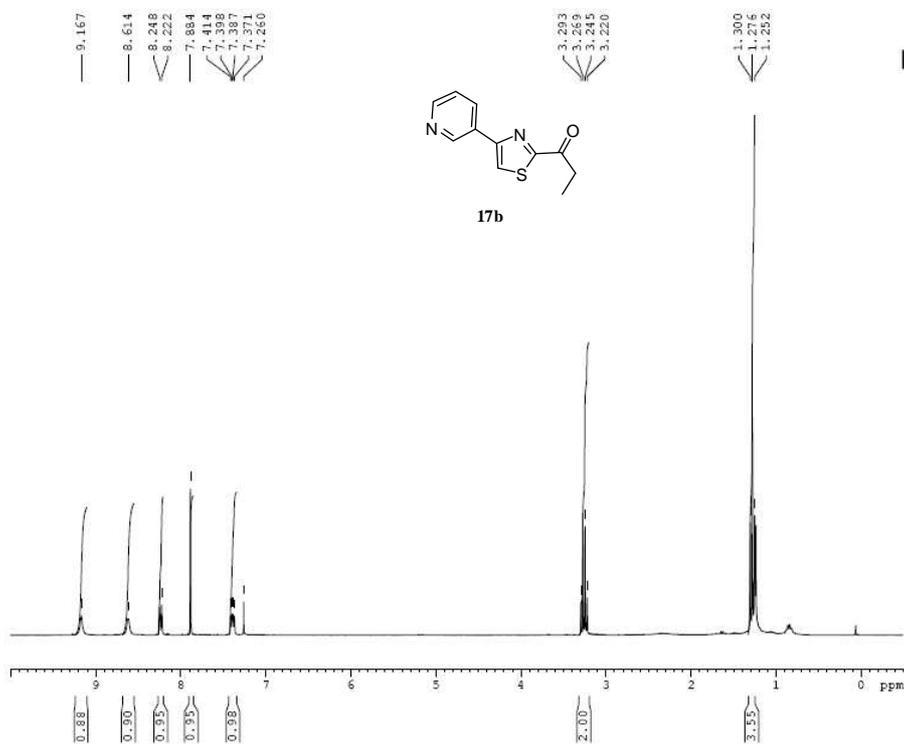


```

NAME      Claire L
EXPNO     241
PROCNO    1
Date_     20090616
Time      14.46
INSTRUM   spect
PROBHD    5 mm QNP 1H/1
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         8
DS         4
SWH        17985.411 Hz
FIDRES     0.274439 Hz
AQ         1.6219508 sec
RG         5792.6
SQ         27.800 usec
DE         10.00 usec
TE         296.2 K
D1         2.00000000 sec
d11        0.00000000 sec
DELTA     1.89999999 sec
TD0        1
  
```

```

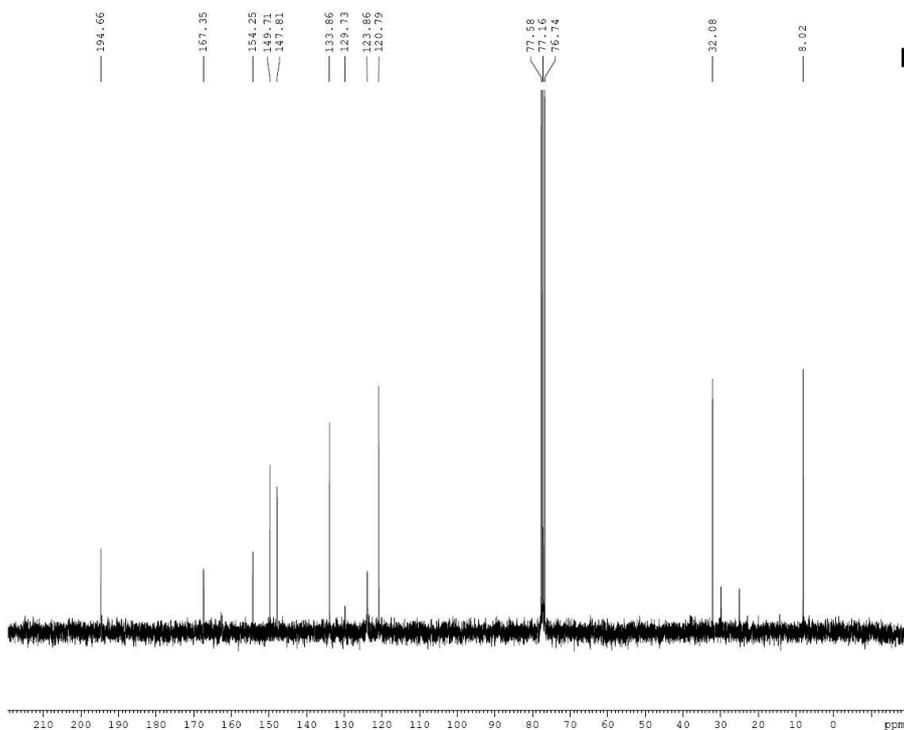
----- CHANNEL f1 -----
NUC1       13C
P1         10.50 usec
PL1        -6.00 dB
SFO1       75.4752833 MHz
----- CHANNEL f2 -----
PULPROG2  waltz16
NUC2       1H
PCPD2     100.00 usec
P22        -6.00 dB
P112       11.00 dB
P113       11.00 dB
SFO2       300.1312045 MHz
SI         32768
SF         75.4677489 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.00
  
```



```

NAME      Claire L
EXPNO     1
PROCNO    1
Date_     20090619
Time      14.24
INSTRUM   spect
PROBHD    5 mm QNP 1H/1
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         3
DS         3
SWH        6172.830 Hz
FIDRES     0.094190 Hz
AQ         0.3024460 sec
RG         323.2
DW         61.000 usec
DE         10.00 usec
TE         296.2 K
D1         1.90000000 sec
D11        1
TD0        1

===== CHANNEL f1 =====
NUC1       1H
P1         18.00 usec
PL1        -1.00 dB
SFO1       300.1314834 MHz
SI         32768
SF         300.1300000 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         1.00
PC         1.00
  
```

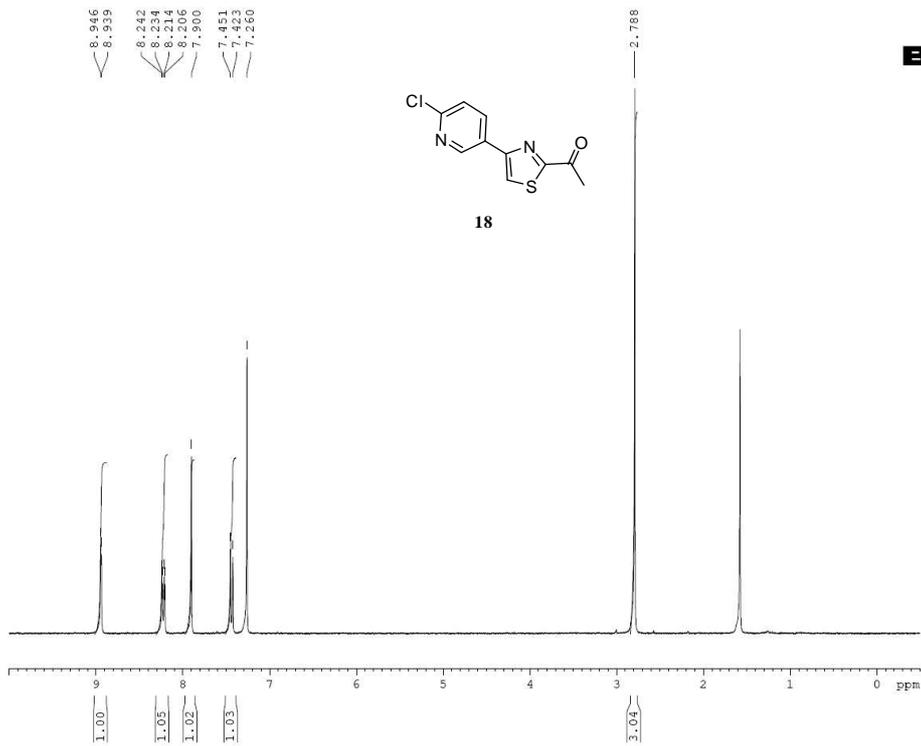


```

NAME      Claire L
EXPNO     261
PROCNO    1
Date_     20090623
Time      15.03
INSTRUM   spect
PROBHD    5 mm QNP 1H/1
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         184
DS         3
SWH        17995.611 Hz
FIDRES     0.274439 Hz
AQ         1.8219398 sec
RG         11583.2
DW         27.800 usec
DE         10.00 usec
TE         296.2 K
D1         2.00000000 sec
D11        0.03000000 sec
DELTA     1.83999999 sec
TD0        1

===== CHANNEL f1 =====
NUC1       13C
P1         10.00 usec
PL1        0.00 dB
SFO1       75.4752953 MHz

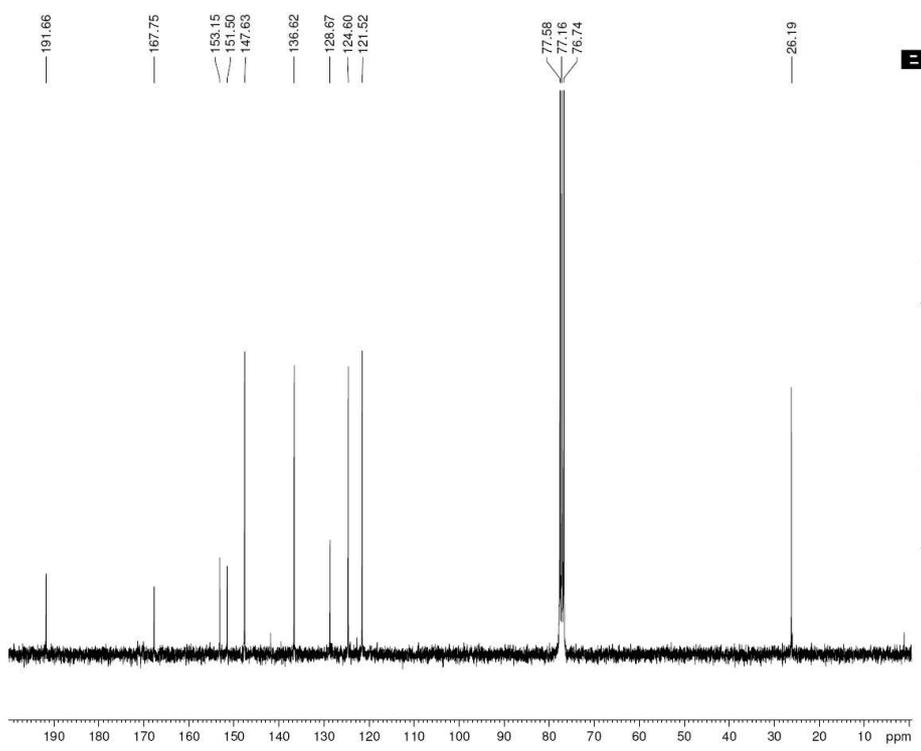
===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
P2         100.00 usec
PL2        -6.00 dB
PL12       11.00 dB
PL13       11.00 dB
SFO2       300.1312005 MHz
SI         32768
SF         75.4677408 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         1.40
PC         1.40
  
```



```

NAME      Tibo
EXPNO     470
PROCNO    1
Date_     20090701
Time      18:13
INSTRUM   spect
PROBHD    5 mm QNP
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         8
DS         4
SWH        6172.839 Hz
FIDRES     0.094199 Hz
AQ         5.3084660 sec
RG         3149.4
DW         11.000 usec
DE         10.00 usec
TE         298.2 K
D1         1.00000000 sec
TD0
===== CHANNEL f1 =====
NUC1       1H
P1         18.50 usec
PL1        -6.00 dB
SFO1       300.1318534 MHz
SI         32768
SF         300.1300059 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00

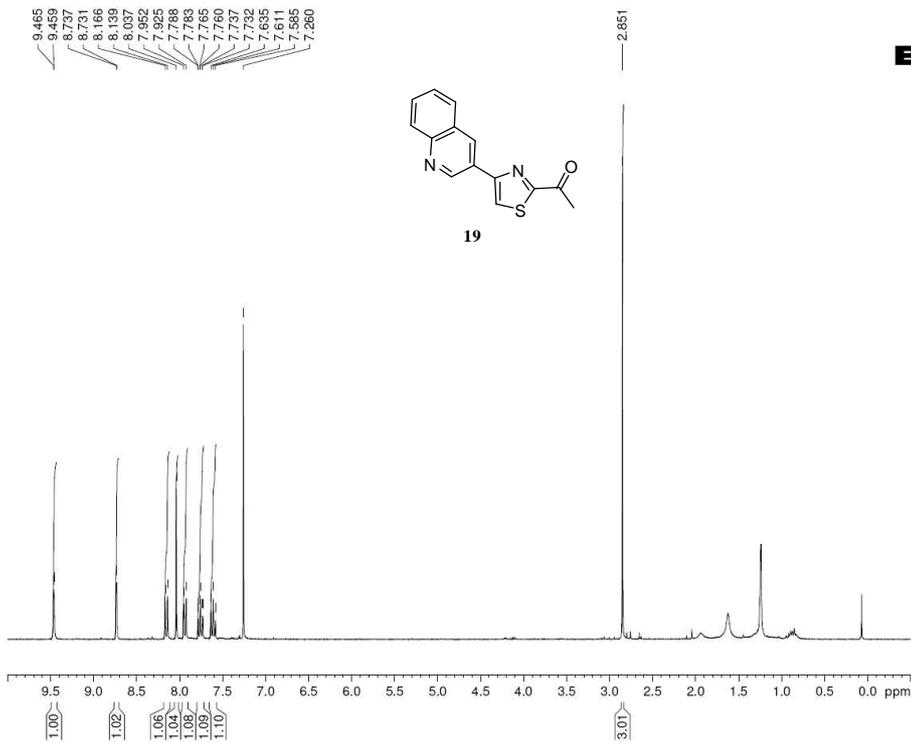
```



```

NAME      Tibo
EXPNO     120
PROCNO    1
Date_     20090713
Time      12:04
INSTRUM   spect
PROBHD    5 mm QNP 1H/1
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         1668
DS         4
SWH        17985.611 Hz
FIDRES     0.274439 Hz
AQ         1.8219508 sec
RG         3543.1
DW         27.800 usec
DE         10.00 usec
TE         298.2 K
D1         2.00000000 sec
d11        0.03000000 sec
DELTA     1.83999998 sec
TD0
===== CHANNEL f1 =====
NUC1       13C
P1         9.00 usec
PL1        0.00 dB
SFO1       75.4752853 MHz
===== CHANNEL f2 =====
CFPRG2    waltz16
NUC2       1H
P2         100.00 usec
PL2        -6.00 dB
PL12       20.00 dB
PL13       20.00 dB
SFO2       300.1312095 MHz
SI         32768
SF         75.4677397 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40

```



```

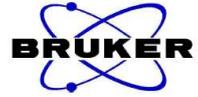
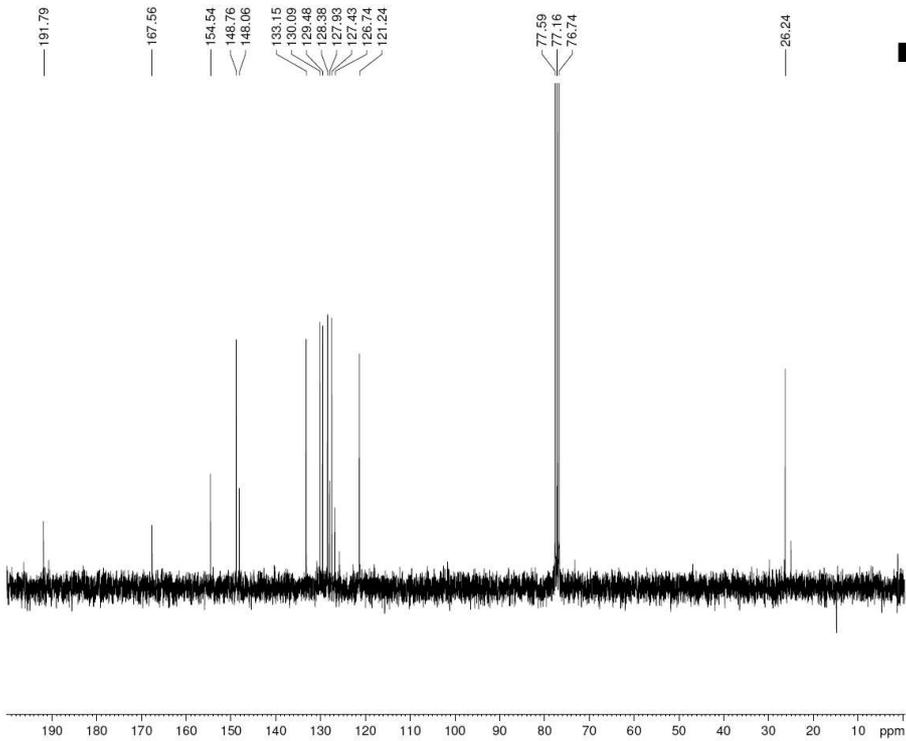
NAME      Claire L
EXPNO     1
PROCNO    1
Date_     20090625
Time      15.29
INSTRUM   spect
PROBHD    5 mm QNP 1H/1
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         8
DS         4
SWH        6172.839 Hz
FIDRES     0.094190 Hz
AQ         5.1084560 sec
RG         912.3
DW         81.000 usec
DE         10.000 usec
TE         296.2 K
D1         1.00000000 sec
TDO        1

```

```

===== CHANNEL f1 =====
NUC1       1H
P1         18.50 usec
PL1        -6.00 dB
SFO1       300.1310534 MHz
SI         32768
SF         300.1300063 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00

```



```

NAME      Tibo
EXPNO     40
PROCNO    1
Date_     20090630
Time      10.45
INSTRUM   spect
PROBHD    5 mm QNP 1H/1
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         96
DS         4
SWH        17985.611 Hz
FIDRES     0.274439 Hz
AQ         1.8213508 sec
RG         14596.5
DW         27.800 usec
DE         10.000 usec
TE         296.2 K
D1         2.00000000 sec
d11        0.03000000 sec
DELTA     1.89999998 sec
TDO        1

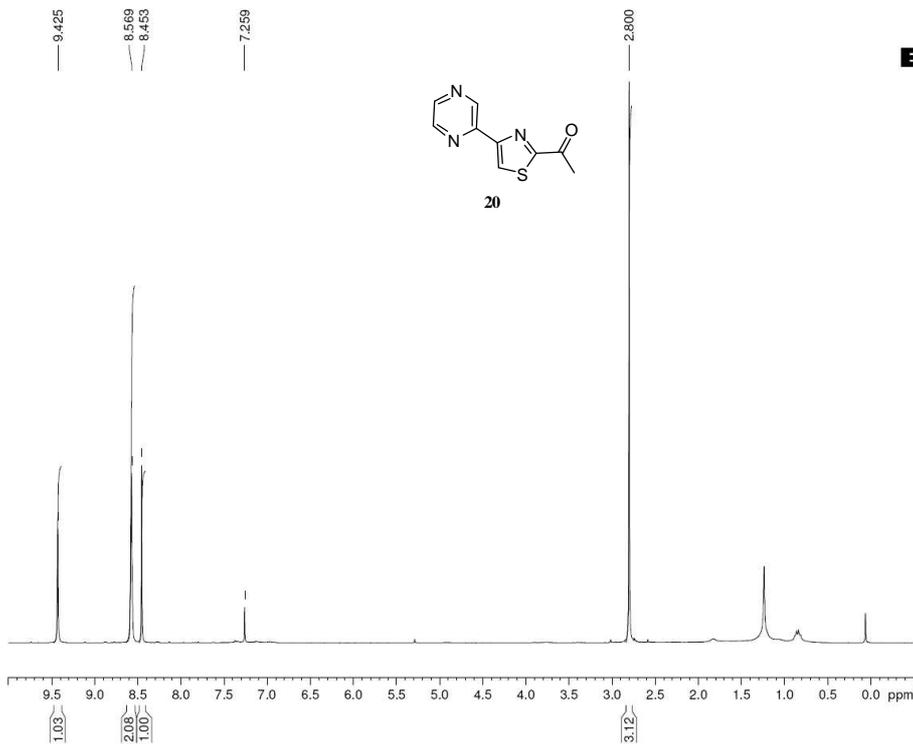
```

```

===== CHANNEL f1 =====
NUC1       13C
P1         10.50 usec
PL1        0.00 dB
SFO1       75.4752953 MHz

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
PCPD2     100.00 usec
PL2        -6.00 dB
PL12       11.00 dB
PL13       11.00 dB
SFO2       300.1312095 MHz
SI         32768
SF         75.4677408 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40

```

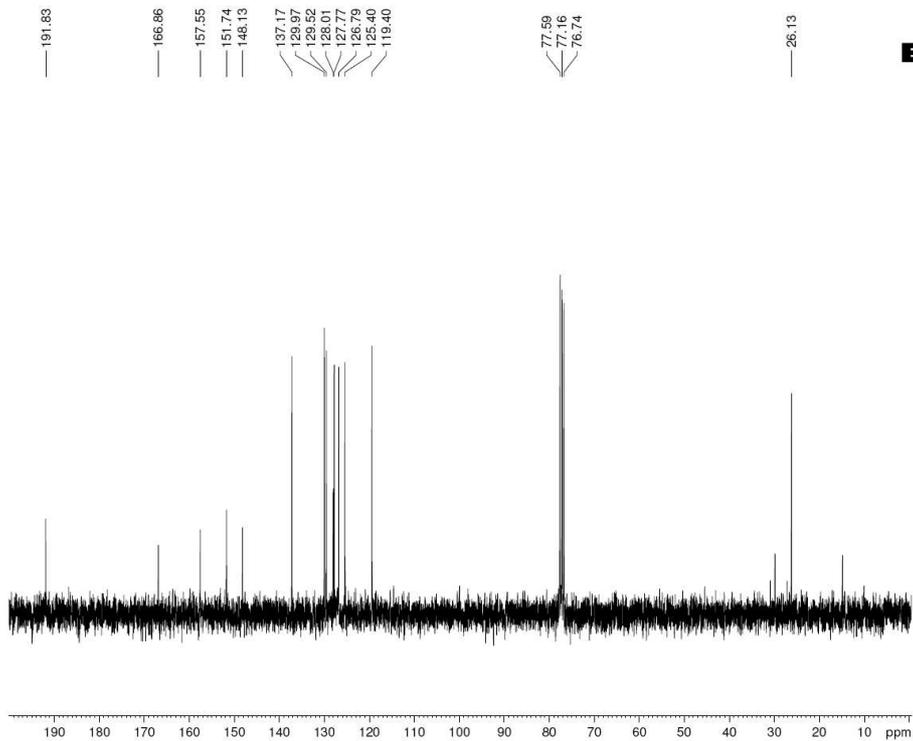


```

NAME          Tibo
EXPNO         410
PROCNO        1
Date_         20090623
Time          18.00
INSTRUM       spect
PROBHD        5 mm QNP 1H/1
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            6
DS            0
SWH           6172.839 Hz
FIDRES       0.09439 Hz
AQ           5.3084680 sec
RG           322
DW           81.000 usec
DE           10.00 usec
TE           295.2 K
D1           1.0000000 sec
TD0          1

===== CHANNEL f1 =====
NUC1          1H
P1            18.50 usec
PL1           -6.00 dB
SFO1         300.1318534 MHz
SI           32768
SF           300.1300065 MHz
WDW           EM
SSB           0
LB           0.30 Hz
GB           0
PC           1.00

```



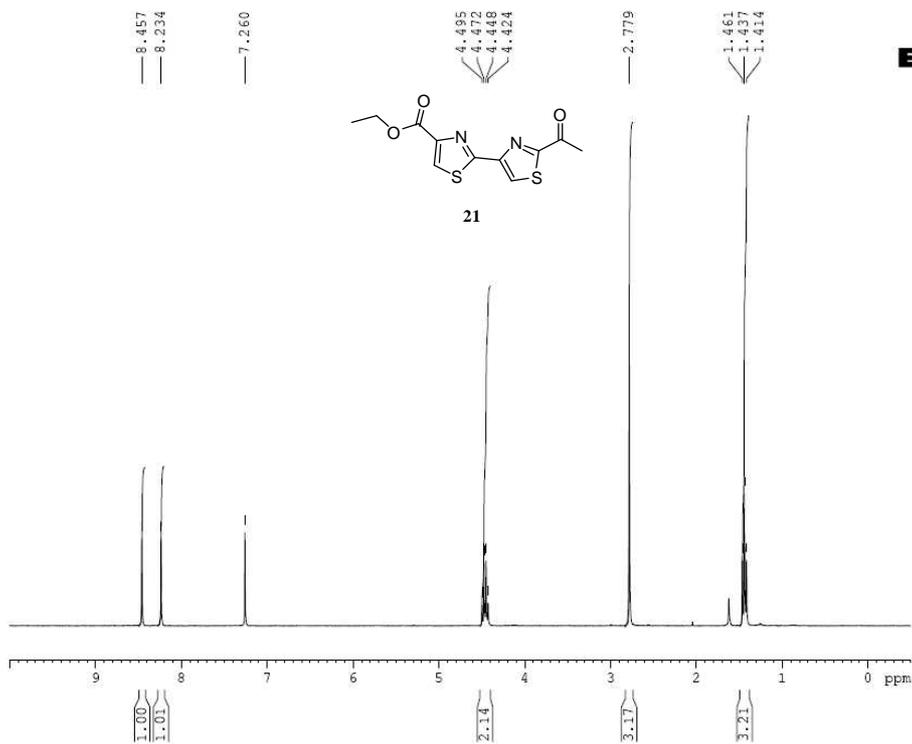
```

NAME          Tibo
EXPNO         411
PROCNO        1
Date_         20090630
Time          17.30
INSTRUM       spect
PROBHD        5 mm QNP 1H/1
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            23
DS            4
SWH           17985.611 Hz
FIDRES       0.274439 Hz
AQ           1.8219908 sec
RG           10321.3
DW           27.800 usec
DE           10.00 usec
TE           295.2 K
D1           2.0000000 sec
d11          0.0300000 sec
DELTA        1.8999999 sec
TD0          1

===== CHANNEL f1 =====
NUC1          13C
P1            10.50 usec
PL1           0.00 dB
SFO1         75.4752953 MHz

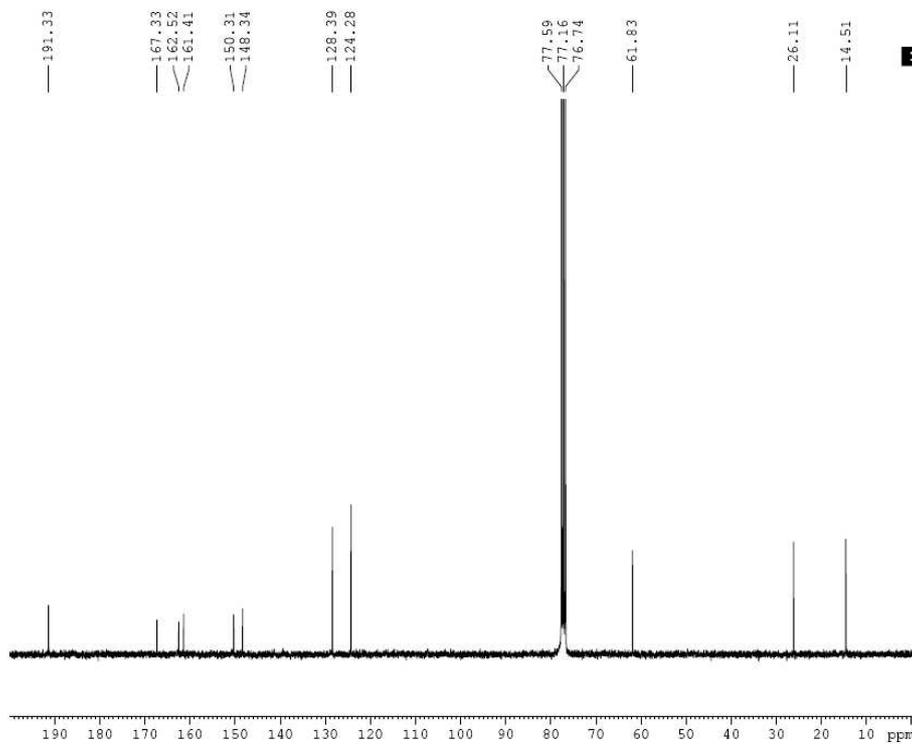
===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
F2P2         100.00 usec
PL2          -6.00 dB
PL12         11.00 dB
PL13         11.00 dB
SFO2         300.1312005 MHz
SI           32768
SF           75.4677430 MHz
WDW           EM
SSB           0
LB           1.00 Hz
GB           0
PC           1.40

```



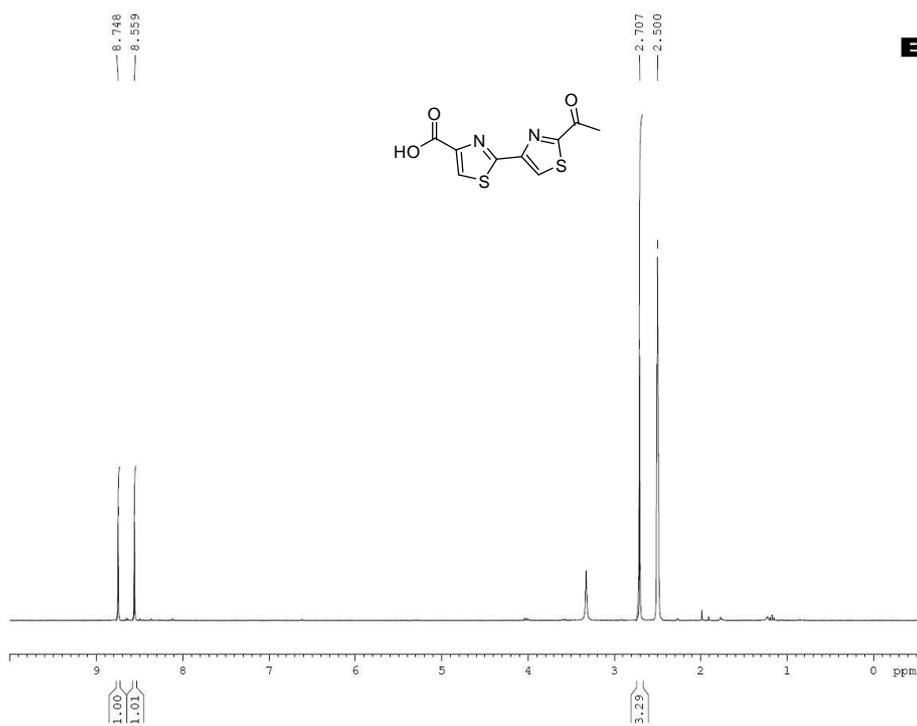
```

NAME           Tibo
EXPNO          1
PROCNO         1
Date_          20090406
Time           14.30
INSTRUM        spect
PROBHD         5 mm QNP
PULPROG        zgpg30
TD             65536
SOLVENT        CDCl3
NS             0
DS             0
SWH            6172.839 Hz
FIDRES         0.39439 Hz
AQ            5.3084660 sec
RG            327.9
WDW            EM
DE            81.000 usec
TE            300.2 K
DELTA          1.000 usec
DI            1.00000000 sec
DO            1
----- CHANNEL F1 -----
NUC1           1H
P1            19.00 usec
PL1           -2.00 dB
SFO1          300.1300534 MHz
SI            327.69
SF            300.1300062 MHz
WDW            EM
SSB            0
LB            0.30 Hz
GB            0
PC            1.00
  
```



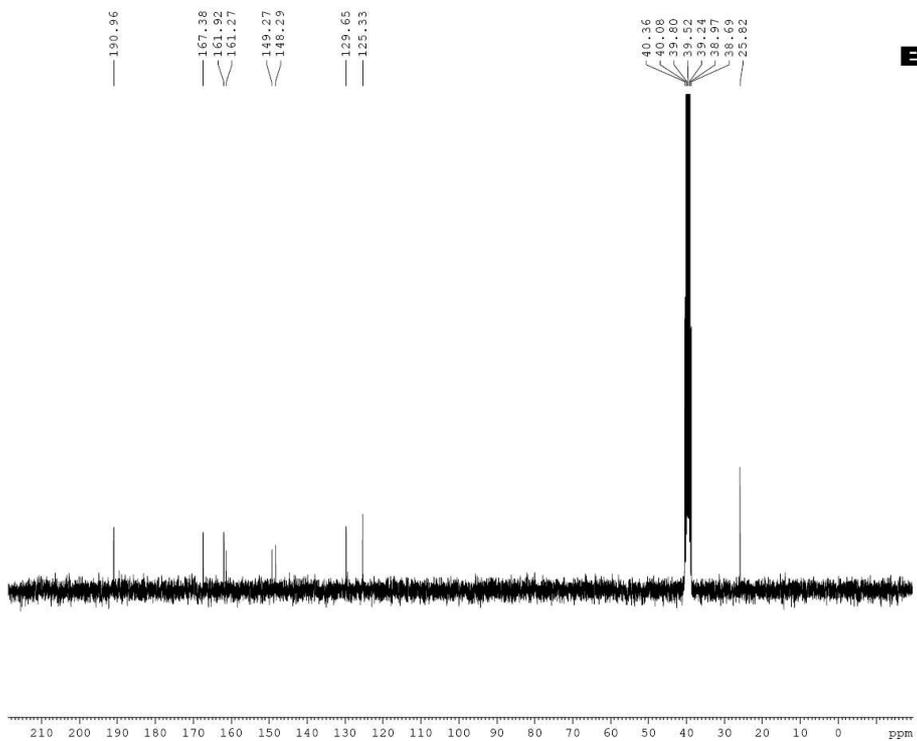
```

NAME           Tibo
EXPNO          1
PROCNO         1
Date_          20090406
Time           22.04
INSTRUM        spect
PROBHD         5 mm QNP
PULPROG        zgpg30
TD             65536
SOLVENT        CDCl3
NS             0
DS             0
SWH            17985.61 Hz
FIDRES         0.21439 Hz
AQ            1.8219509 sec
RG            14594.5
WDW            EM
DE            27.800 usec
TE            300.2 K
DELTA          2.00000000 sec
DI            0.02000000 sec
DO            1.89999999 sec
----- CHANNEL F1 -----
NUC1           13C
P1            10.50 usec
PL1           0.00 dB
SFO1          76.4752653 MHz
----- CHANNEL E2 -----
P1E2           waitz16
P2E2           100.00 usec
PL2E2         -4.00 dB
PL1E2         11.00 dB
PL1E3         11.00 dB
SFO2          300.1312005 MHz
SI            327.69
SF            76.4617380 MHz
WDW            EM
SSB            0
LB            1.00 Hz
GB            0
PC            1.40
  
```



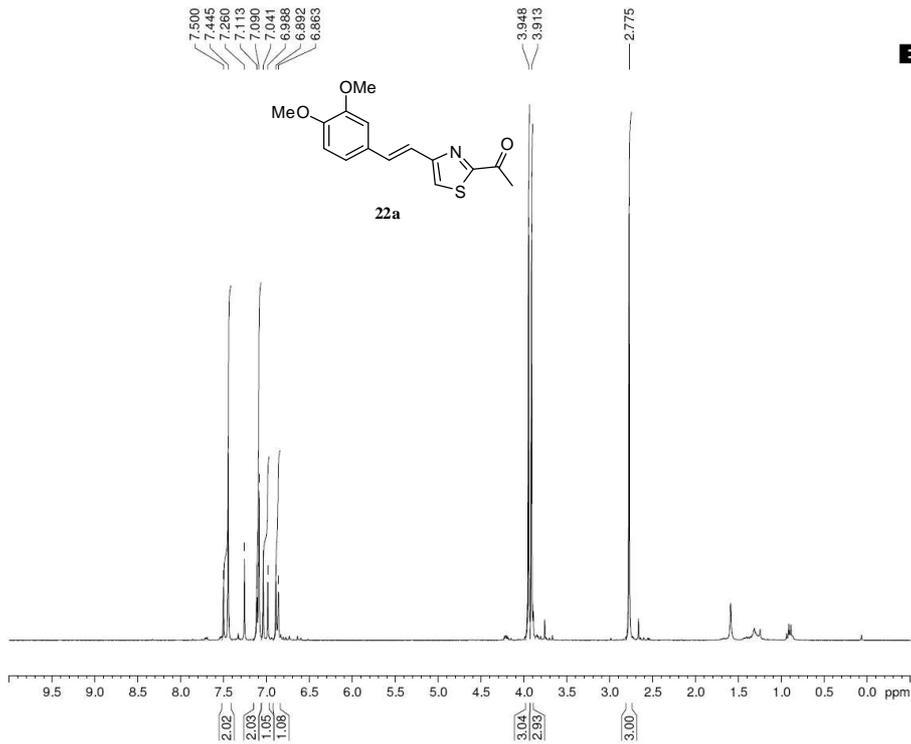
```

NAME          Tibo
EXPNO         211
PROCNO        1
Date_         20090629
Time          14.43
INSTRUM       spect
PROBHD        5 mm QNP 1H/1
PULPROG       zg30
TD            65536
SOLVENT       DMSO
NS            8
DS            0
SWH           6172.939 Hz
FIDRES       0.094190 Hz
AQ           5.3084660 sec
RG           912.7
DW           81.000 usec
DE           10.00 usec
TE           296.2 K
D1           1.00000000 sec
TD0          1
===== CHANNEL f1 =====
NUC1          1H
P1            18.50 usec
PL1           -6.00 dB
SFO1         300.1318514 MHz
SI           32768
SF           300.1300014 MHz
WDW           EM
SSB           0
GB           0.30 Hz
PC           1.00
  
```



```

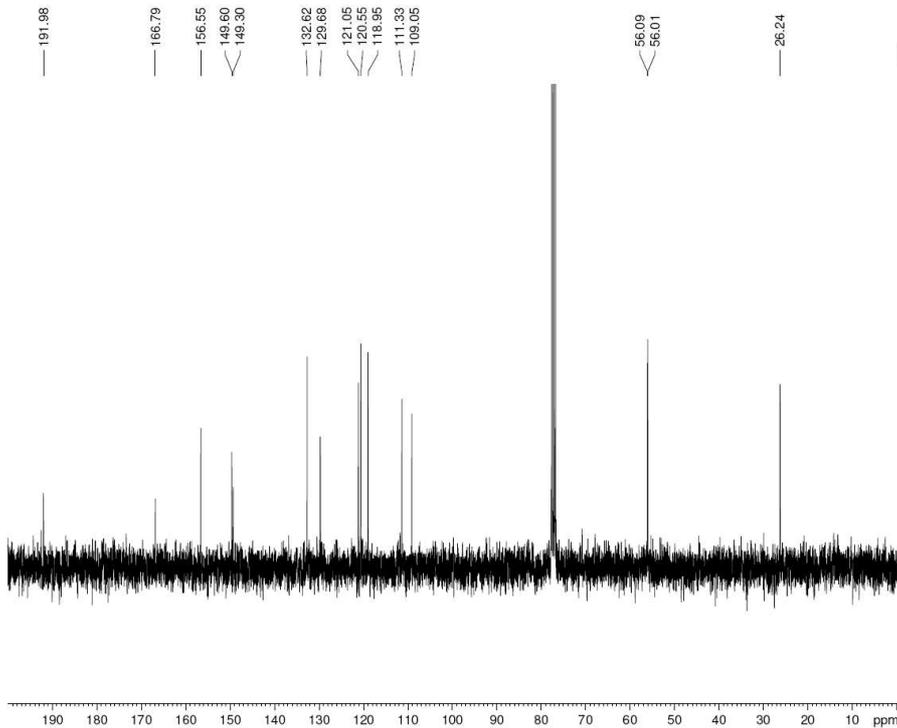
NAME          Tibo
EXPNO         210
PROCNO        1
Date_         20090629
Time          14.23
INSTRUM       spect
PROBHD        5 mm QNP 1H/1
PULPROG       zgpg30
TD            65536
SOLVENT       DMSO
NS            4
DS            4
SWH           17985.611 Hz
FIDRES       0.274439 Hz
AQ           1.8215008 sec
RG           3196.2
DW           27.800 usec
DE           10.00 usec
TE           296.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.83988998 sec
TD0          1
===== CHANNEL f1 =====
NUC1          13C
P1            10.50 usec
PL1           0.00 dB
SFO1         75.4752538 MHz
===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
DCPD2         100.00 usec
PL2           -4.00 dB
PL12          11.00 dB
PL13          11.00 dB
SFO2         300.1318505 MHz
SI           32768
SF           75.4677833 MHz
WDW           EM
SSB           0
GB           1.00 Hz
PC           1.40
  
```



```

NAME      Tibo
EXPNO    130
PROCNO   1
Date_    20090701
Time     11.47
INSTRUM  spect
PROBHD   5 mm QNP 1H/1
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        4
DS        0
SWH       6172.839 Hz
FIDRES   0.094190 Hz
AQ        5.3084660 sec
RG        512
DW        81.000 usec
DE        10.00 usec
TE        296.2 K
D1        1.00000000 sec
TD0       1

===== CHANNEL f1 =====
NUC1      1H
P1         18.50 usec
PL1        -6.00 dB
SFO1      300.1319534 MHz
SI         32768
SF         300.1300000 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
  
```

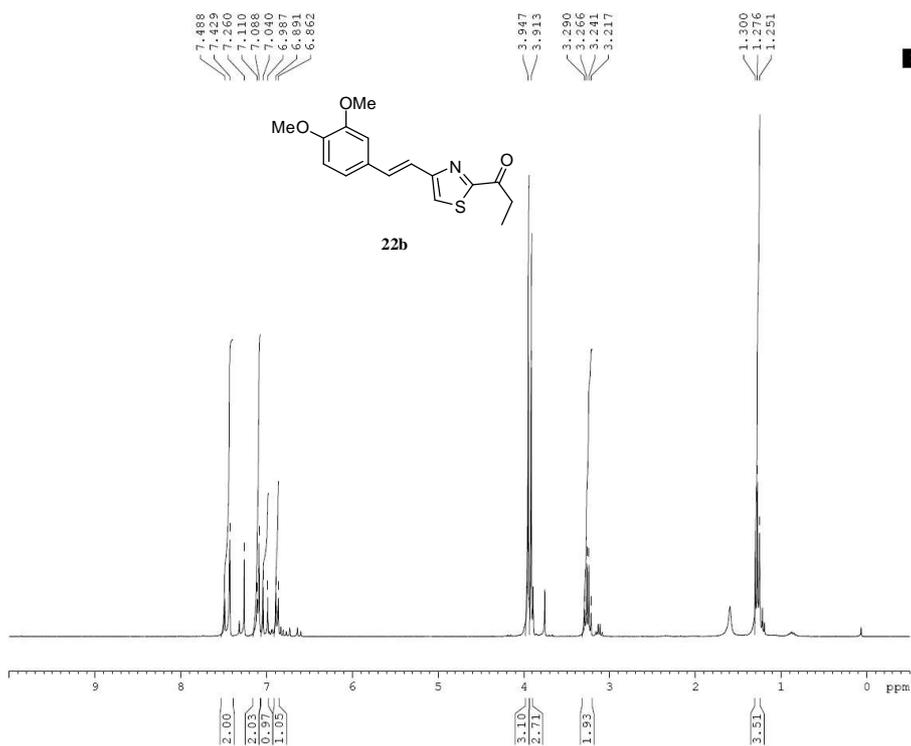


```

NAME      Tibo
EXPNO    131
PROCNO   1
Date_    20090701
Time     11.52
INSTRUM  spect
PROBHD   5 mm QNP 1H/1
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        4
DS        0
SWH       17985.611 Hz
FIDRES   0.274439 Hz
AQ        1.8219508 sec
RG        19384
DW        27.900 usec
DE        10.00 usec
TE        296.2 K
D1        2.00000000 sec
d11       0.03000000 sec
DELTA    1.89999998 sec
TD0       1

===== CHANNEL f1 =====
NUC1      13C
P1         10.50 usec
PL1        0.00 dB
SFO1      75.4752953 MHz

===== CHANNEL f2 =====
CDPRG2   waltz16
NUC2      1H
PCPD2    100.00 usec
PL2       -6.00 dB
PL12     11.00 dB
PL13     11.00 dB
SFO2     300.1312005 MHz
SI        32768
SF        75.4677391 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
  
```

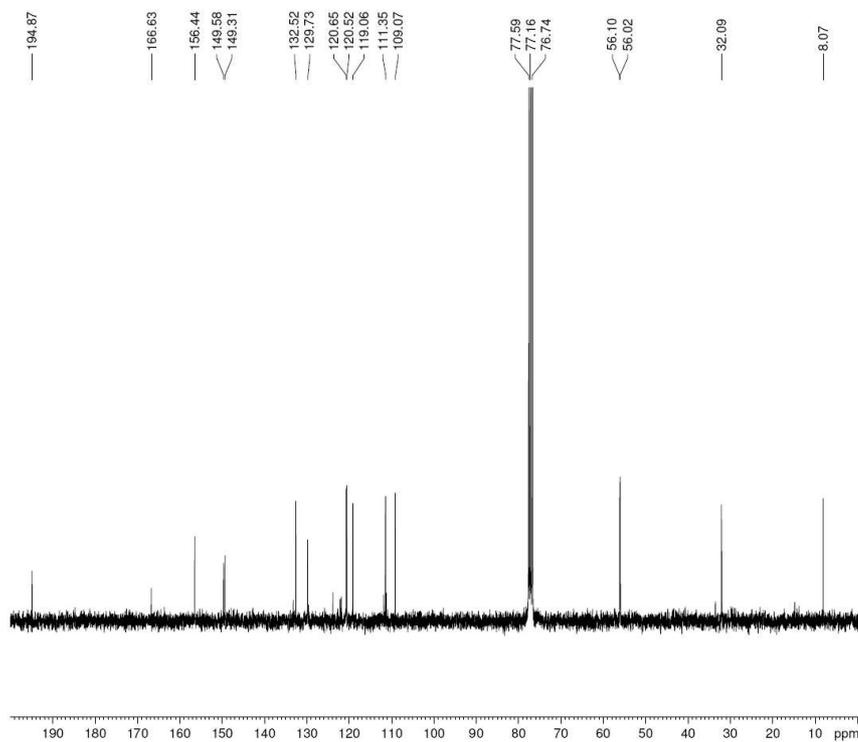


```

NAME      Tlbc
EXPNO     90
PROCNO    1
Date_     20090702
Time      12.46
INSTRUM   spect
PROBHD    5 mm QNP 1H/1
PULPROG   zgpg30
TD        65536
SOLVENT   CDCl3
NS        8
DS        4
SWH       6172.839 Hz
FIDRES    0.094190 Hz
AQ        5.3084600 sec
RG        574.7
DW        81.000 usec
DE        10.00 usec
TE        296.2 K
D1        1.00000000 sec
TD0       1

===== CHANNEL f1 =====
NUC1      1H
P1        18.50 usec
PL1       -6.00 dB
SFO1     300.1318334 MHz
SI        32768
SF        300.1300000 MHz
WDW       EM
SSB       0
LB        0.10 Hz
GB        0
PC        1.00

```



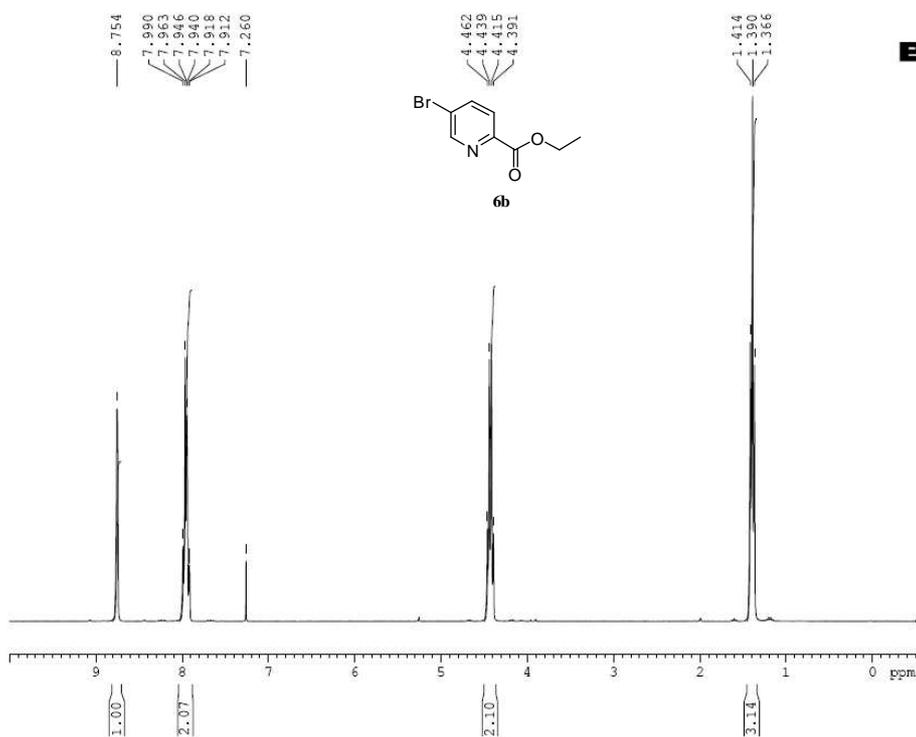
```

NAME      Tlbc
EXPNO     1
PROCNO    1
Date_     20090702
Time      13.55
INSTRUM   spect
PROBHD    5 mm QNP 1H/1
PULPROG   zgpg30
TD        65536
SOLVENT   CDCl3
NS        1024
DS        4
SWH       17985.611 Hz
FIDRES    0.274439 Hz
AQ        1.8219508 sec
RG        13004
DW        27.800 usec
DE        10.00 usec
TE        296.2 K
D1        2.00000000 sec
d11       0.03000000 sec
DELTA     1.89999998 sec
TD0       1

===== CHANNEL f1 =====
NUC1      13C
P1        10.50 usec
PL1       0.00 dB
SFO1     75.4752953 MHz

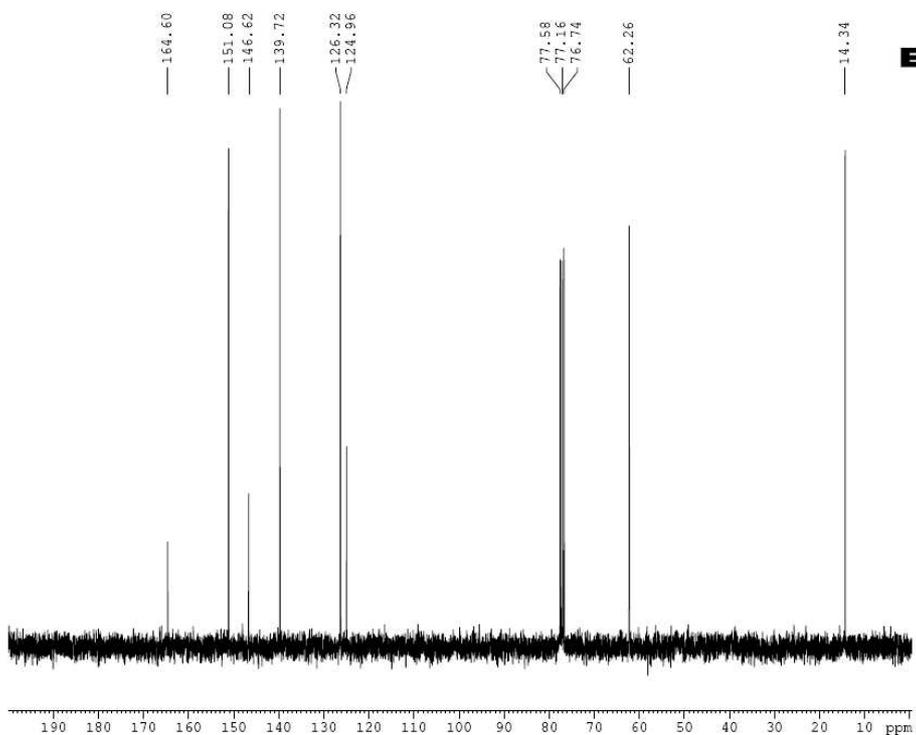
===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2      1H
PCPD2     100.00 usec
PL2       -6.00 dB
PL12     11.00 dB
PL13     11.00 dB
SFO2     300.1312000 MHz
SI        32768
SF        75.4677386 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.40

```



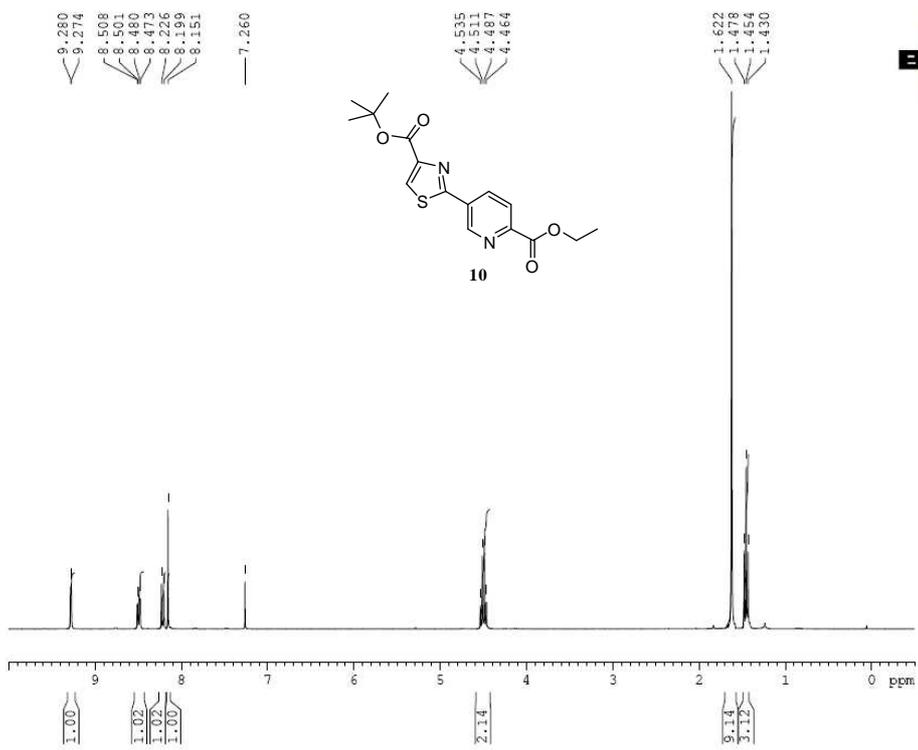
```

NAME          Tlbo
EXPNO         1
PROCNO        1
Date_         20090113
Time          19.32
INSTRUM       spect
PROBHD        5 mm QNP
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            8
DS            4
SWH           6172.939 Hz
FIDRES        0.394390 Hz
AQ            5.3084690 sec
RG            64.0
DE            81.000 usec
TE            300.2 K
DE            10.000 usec
TE            300.2 K
D1            1.00000000 sec
TD0           1
----- CHANNEL f1 -----
NUC1          1H
P1            19.50 usec
PL1           -1.00 dB
SFO1         300.1318134 MHz
SI            32769
SF           300.1300059 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
  
```



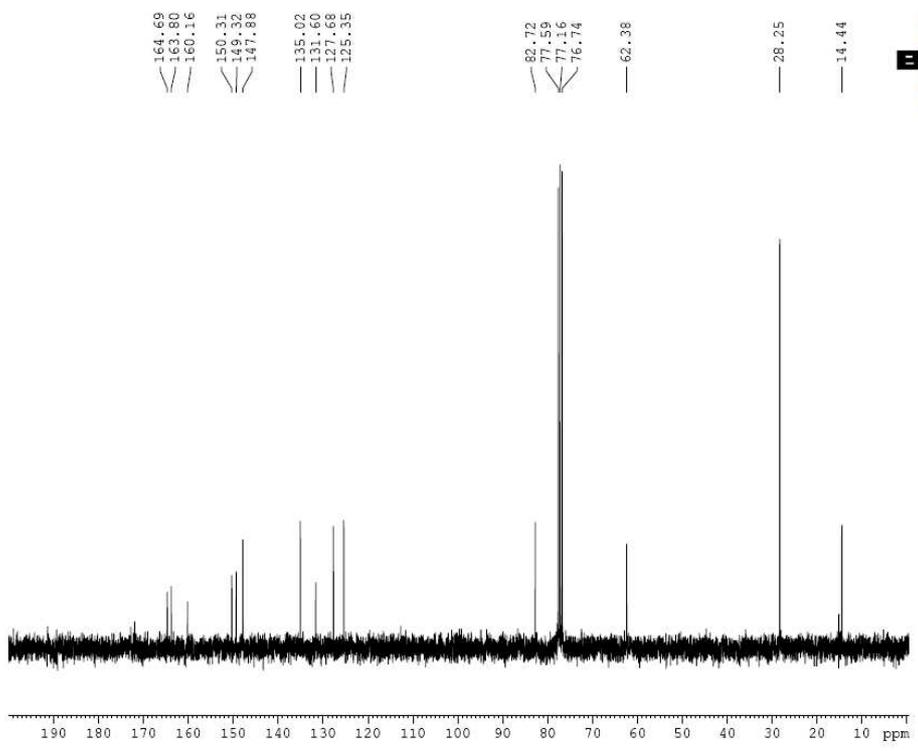
```

NAME          Tlbo
EXPNO         531
PROCNO        1
Date_         20090113
Time          19.36
INSTRUM       spect
PROBHD        5 mm QNP
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            56
DS            4
SWH           17985.611 Hz
FIDRES        0.374493 Hz
AQ            1.8219509 sec
RG            64.0
DE            27.802 usec
TE            300.2 K
DE            10.000 usec
TE            300.2 K
D1            2.00000000 sec
D11           0.33000000 sec
DELTA         1.89999999 sec
TD0           1
----- CHANNEL f1 -----
NUC1          13C
P1            10.00 usec
PL1           0.00 dB
SFO1         75.4752153 MHz
----- CHANNEL f2 -----
NAME2         waltz16
NUC2          1H
P2D2         100.00 usec
PL2           0.00 dB
PL12         11.00 dB
PL13         11.00 dB
SFO2         300.1312005 MHz
SI            32769
SF           75.4677447 MHz
WDW           EM
SSB           2
LB            1.00 Hz
GB            0
PC            1.40
  
```



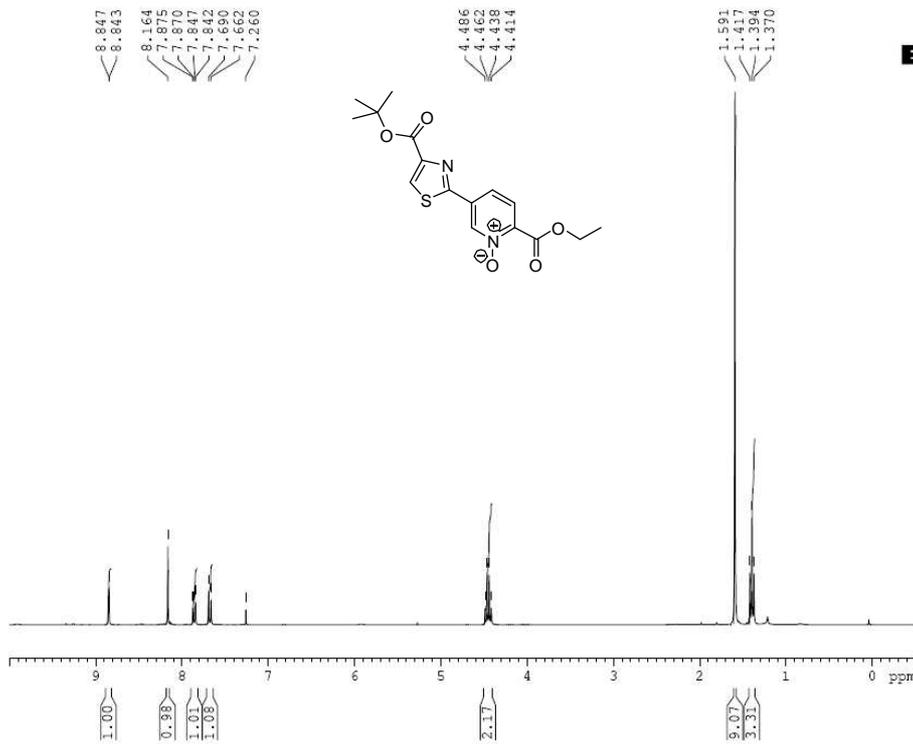
```

NAME          Tibo
EXPERNO       330
PROCNO        1
Date_         20090115
Time          14.55
INSTRUM       spect
PROCPRG       5 mm QNP 1H/1
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            8
DS            0
SWH           612.839 Hz
FIDRES       0.394590 Hz
AQ           5.3304400 sec
RG           297.4
SW          81.300 usec
DE           10.00 usec
TE           300.2 K
D1           1.00000000 sec
TD0          1
----- CHANNEL F1 -----
NUC1          1H
P1           19.50 usec
PL1          -6.00 dB
SFO1         300.1318534 MHz
SI           32768
SF           300.1300001 MHz
WDW          EM
SSB          0
LB           0.30 Hz
GB           0
PC           1.00
  
```



```

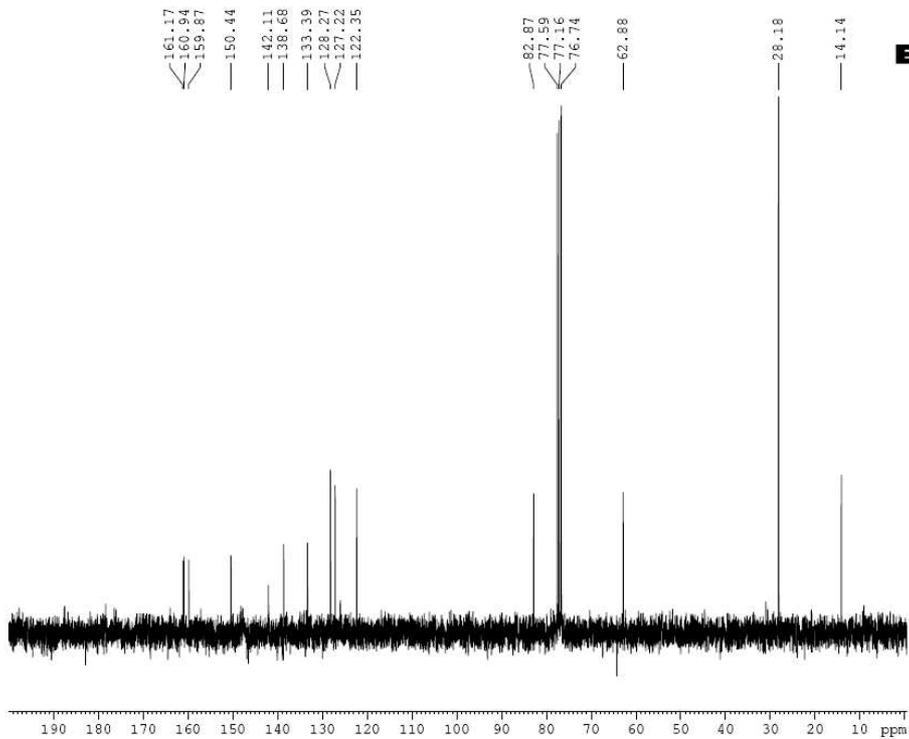
NAME          Tibo
EXPERNO       340
PROCNO        1
Date_         20090112
Time          17.55
INSTRUM       spect
PROCPRG       5 mm QNP 1H/1
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            48
DS            0
SWH           17985.611 Hz
FIDRES       0.274439 Hz
AQ           1.8219508 sec
RG           14596.5
SW          27.900 usec
DE           10.00 usec
TE           300.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.88999998 sec
TD0          1
----- CHANNEL F1 -----
NUC1          13C
P1           10.50 usec
PL1          0.00 dB
SFO1         75.47123073 MHz
----- CHANNEL F2 -----
CPDPRG2      waltz16
NUC2          1H
F1-CD2       100.00 usec
PL2          -6.00 dB
PL12         11.00 dB
PL13         11.00 dB
SFO2         300.1312095 MHz
SI           32768
SF           75.46774113 MHz
WDW          EM
SSB          0
LB           1.00 Hz
GB           0
PC           1.00
  
```



```

NAME           Tlbc
EXPNO          1
PROCNO         1
Data_         20090116
Time          15.24
INSTRUM       spect
PROBHD        5 mm QNP 1H/1
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            4
DS            4
SWH           6172.839 Hz
FIDRES        0.384105 Hz
AQ           5.308466 sec
RG            643.7
DE           81.302 usec
TE            294.2 K
DE            10.00 usec
TE            294.2 K
D1            1.00000000 sec
TD0           1
----- CHANNEL f1 -----
NUC1           1H
P1            18.50 usec
PL1           -6.00 dB
SFO1          300.1338534 MHz
SI            32768
SF            300.1300061 MHz
WDW           EM
SSB            0
LB            0.30 Hz
GB            0
PC            1.00

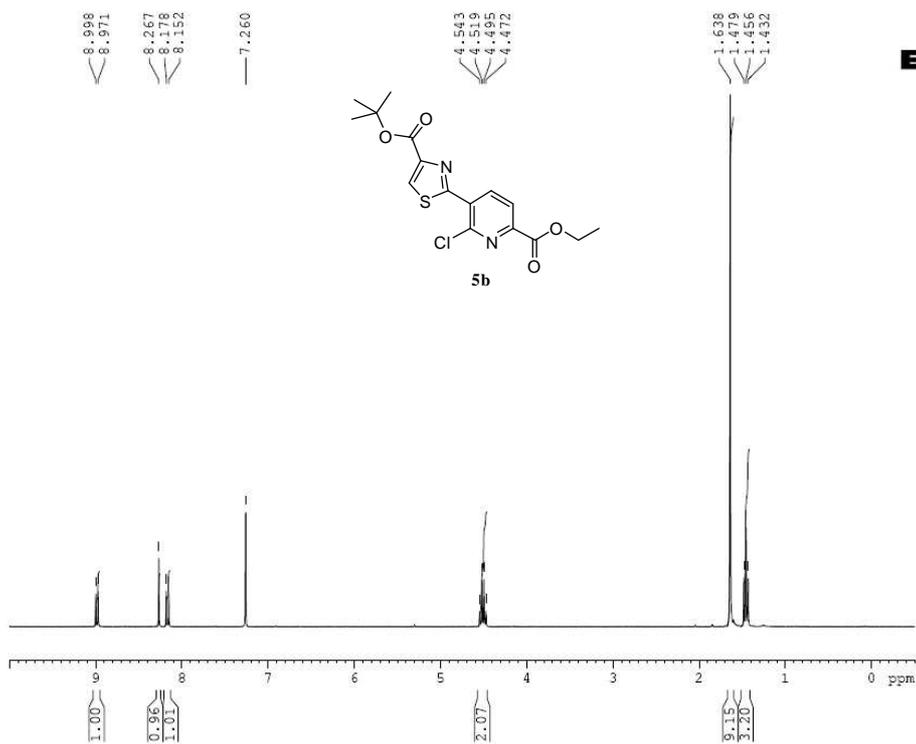
```



```

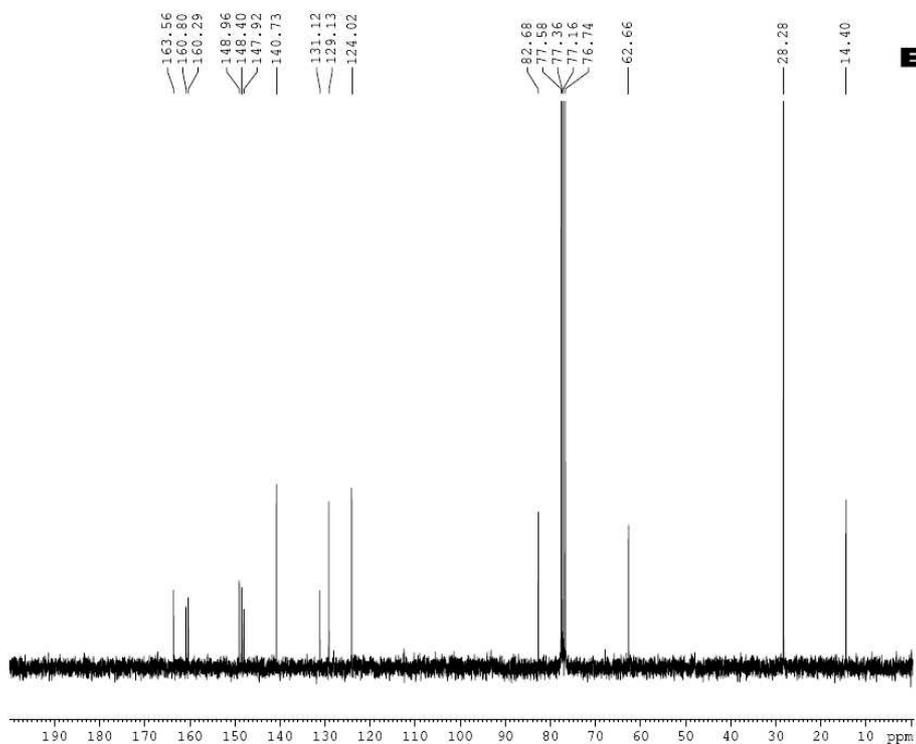
NAME           Tlbc
EXPNO          1
PROCNO         1
Data_         20090116
Time          15.27
INSTRUM       spect
PROBHD        5 mm QNP 1H/1
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            4
DS            4
SWH           17965.611 Hz
FIDRES        0.274439 Hz
AQ           1.6219568 sec
RG            6502
DE           27.800 usec
TE            294.2 K
DE            10.00 usec
TE            294.2 K
D1            2.00000000 sec
d11            0.03000000 sec
DELTA         1.89999996 sec
TD0           1
----- CHANNEL f1 -----
NUC1           13C
P1            10.50 usec
PL1            0.00 dB
SFO1          75.4751953 MHz
----- CHANNEL f2 -----
CEPRG         waltz16
NUC2           1H
P2            100.00 usec
PL2            0.00 dB
PL12           11.00 dB
PL13           11.00 dB
SFO2          300.1312005 MHz
SI            32768
SF            75.4677447 MHz
WDW           EM
SSB            0
LB            1.00 Hz
GB            0
PC            1.40

```



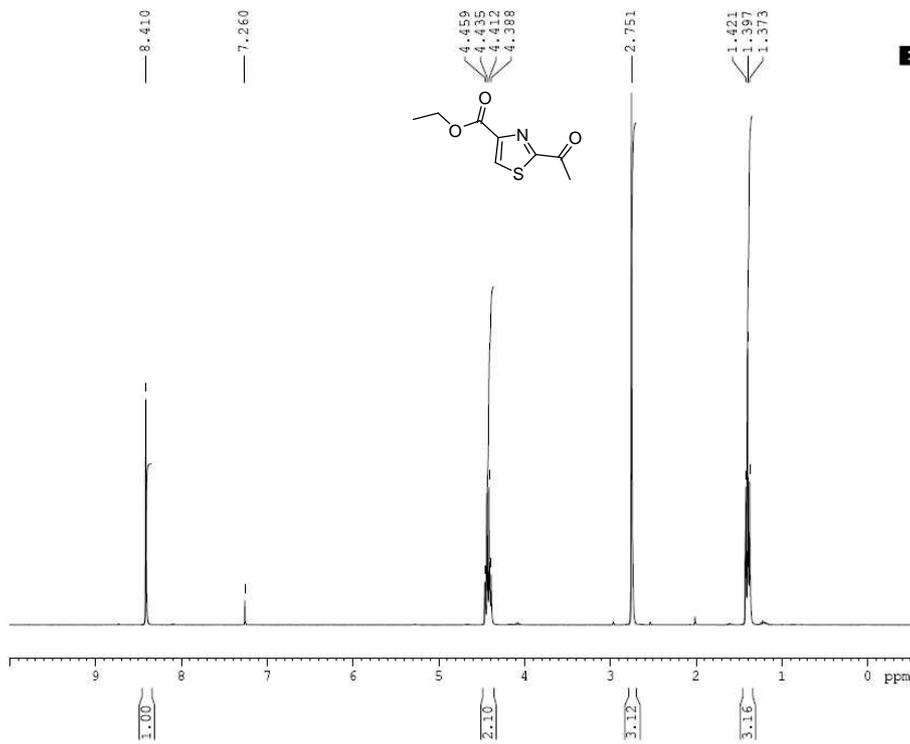
```

===== CHANNEL F1 =====
NUC1 1H
F1 400.146300 MHz
PC1 -6.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
  
```



```

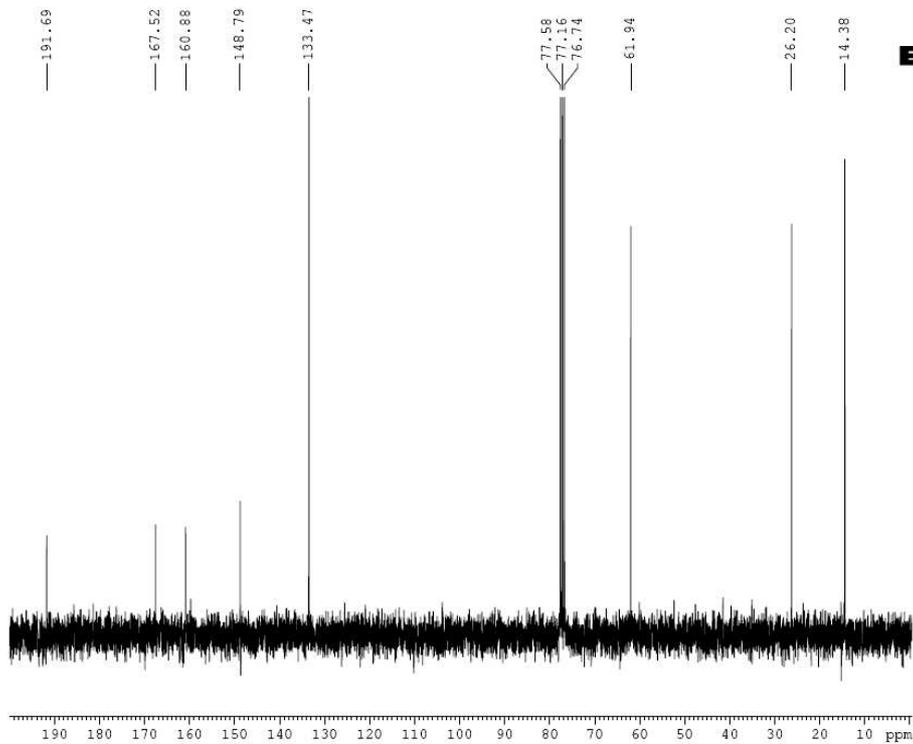
===== CHANNEL F1 =====
NUC1 13C
F1 101.625000 MHz
PC1 0.00 dB
SFO1 75.4752953 MHz
===== CHANNEL F2 =====
CPDPRG2 waltz16
NUC2 1H
PCPC2 100.000000 MHz
PL -6.00 dB
PL12 11.00 dB
PL13 11.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677468 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
  
```



```

NAME           Tabo
EXPNO          270
PROCNO        1
Date_         20090204
Time          15.45
INSTRUM       spect
PROBHD        5 mm QNP 1H/1
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            8
DS            4
SWH           6172.839 Hz
FIDRES       0.184490 Hz
AQ           5.3084690 sec
RG           161.3
SQ           81.000 usec
DE           10.00 usec
TE           293.2 K
D1           1.00000000 sec
TD0          1

===== CHANNEL f1 =====
NUC1          1H
P1           19.50 usec
PL1          -6.00 dB
SFO1         300.1318534 MHz
SI           32769
SF           300.1310039 MHz
WDW          EM
SSB          0
LB           0.30 Hz
GB           0
PC           1.00
  
```

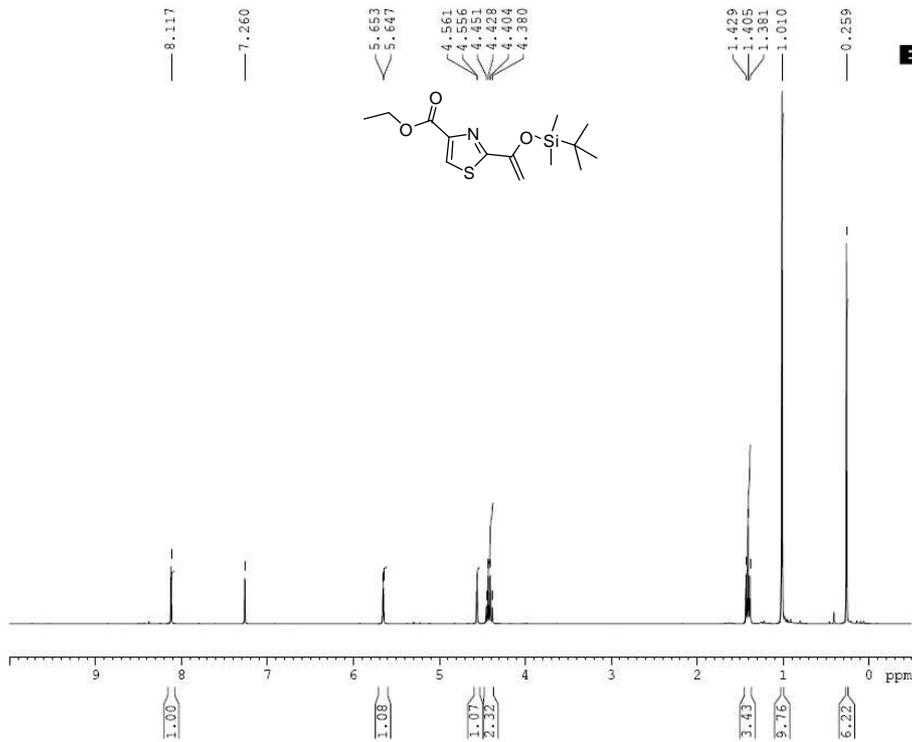


```

NAME           Tabo
EXPNO          271
PROCNO        1
Date_         20090204
Time          15.47
INSTRUM       spect
PROBHD        5 mm QNP 1H/1
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            8
DS            4
SWH           17995.511 Hz
FIDRES       0.274439 Hz
AQ           1.8219599 sec
RG           14596.5
SQ           21.800 usec
DE           10.00 usec
TE           293.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999999 sec
TD0          1

===== CHANNEL F1 =====
NUC1          13C
P1           10.50 usec
PL1          0.00 dB
SFO1         75.4752953 MHz

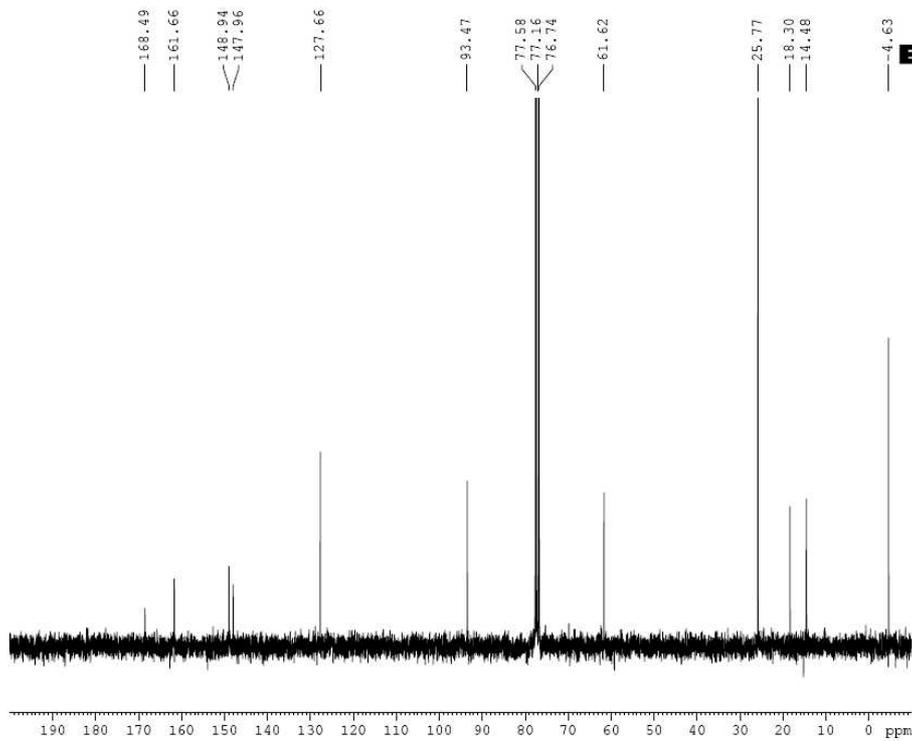
===== CHANNEL F2 =====
GRPRG2       waltz16
NUC2          1H
PCPD2        100.00 usec
PL2          -6.00 dB
PL12         11.00 dB
PL13         11.00 dB
SFO2         300.1310039 MHz
SI           32769
SF           75.4617430 MHz
WDW          EM
SSB          0
LB           1.00 Hz
GB           0
PC           1.40
  
```



```

NAME          Tibo
EXPRO         220
PROCNO        1
Date_         20090212
Time          15.44
INSTRUM       spect
PROBHD        5 mm QNP 1H/1
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            8
DS            4
SWH           6172.839 Hz
FIDRES        0.094190 Hz
AQ            5.1884860 sec
RG            512
SQ            61.000 usec
DE            10.00 usec
TE            298.2 K
D1            1.00000000 sec
DELTA         1
TD0           1

===== CHANNEL f1 =====
NUC1          13C
P1            16.50 usec
PL1          -1.00 dB
SFO1         100.1361934 MHz
SI           32768
SF           300.1360989 MHz
WFO          EM
SFO          0
LB            0.30 Hz
GB            0
PC            1.00
  
```

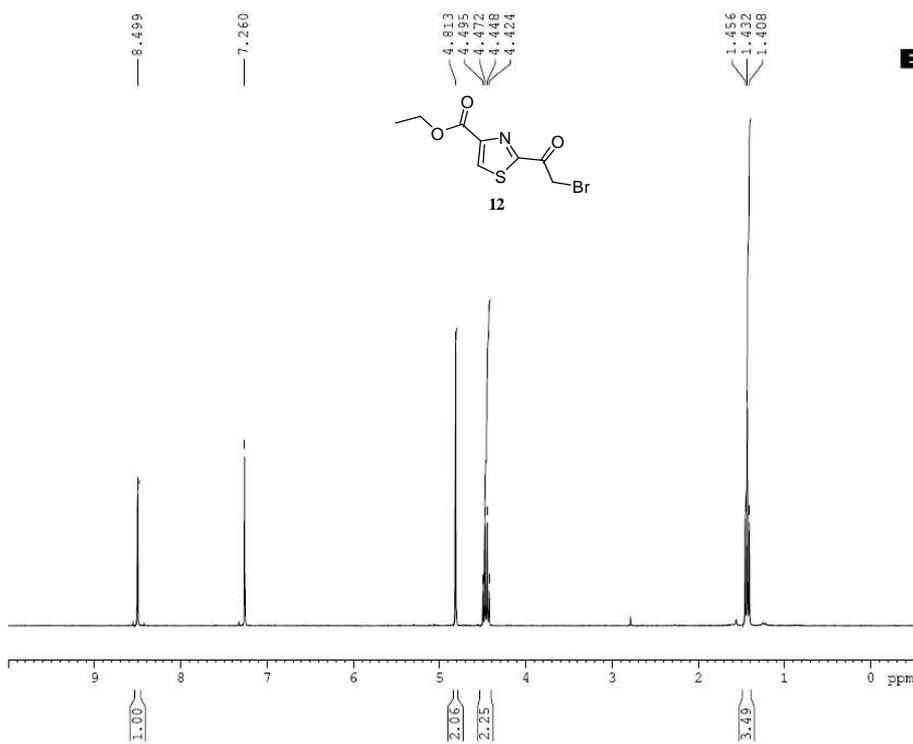


```

NAME          Tibo
EXPRO         380
PROCNO        1
Date_         20090212
Time          19.16
INSTRUM       spect
PROBHD        5 mm QNP 1H/1
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            8
DS            4
SWH           17395.611 Hz
FIDRES        0.216419 Hz
AQ            1.8219508 sec
RG            14384
SQ            21.800 usec
DE            10.00 usec
TE            298.2 K
D1            2.00000000 sec
DELTA         0.03000000 sec
NUC1          13C
SFO1         100.1361934 MHz
SI           32768
SF           300.1360989 MHz
WFO          EM
SFO          0
LB            1.00 Hz
GB            0
PC            1.00

===== CHANNEL F1 =====
NUC1          13C
P1            10.50 usec
PL1           0.00 dB
SFO1         75.4752953 MHz

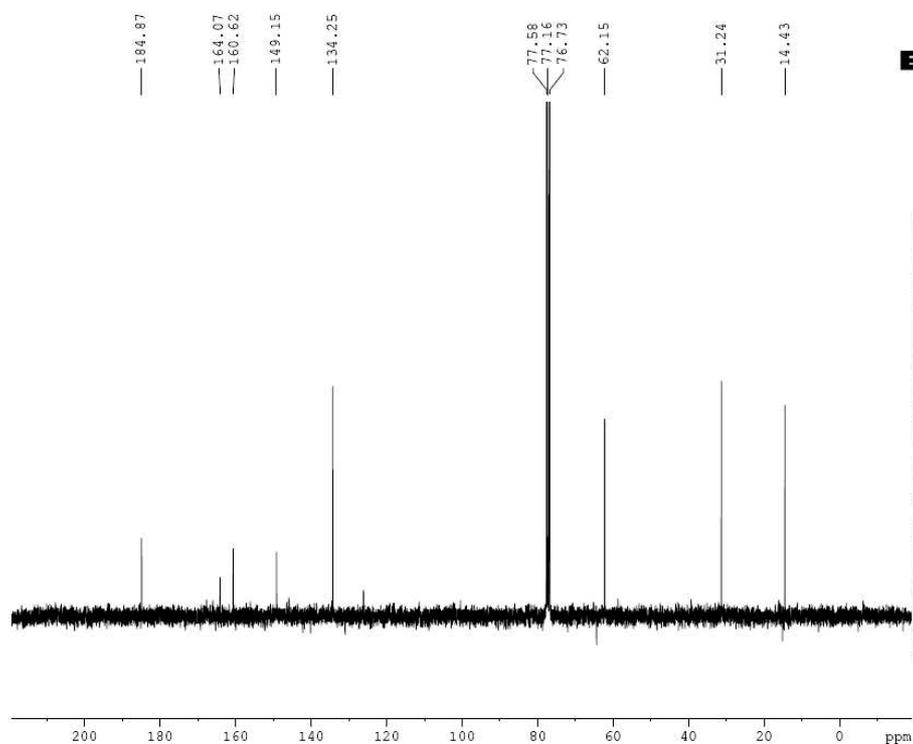
===== CHANNEL F2 =====
CPDPRG2       waltz16
NUC2          1H
P2            100.00 usec
PL2           -6.00 dB
SFO2         400.1464015 MHz
SI           32768
SF           300.1360989 MHz
WFO          EM
SFO          0
LB            1.00 Hz
GB            0
PC            1.00
  
```



```

NAME      Tibo
EXPERNO   300
PROCNO    1
Date_     20090302
Time      19.19
INSTRUM   spect
PROBHD    5 mm QNP 1H/1
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         8
DS         4
SWH        6172.839 Hz
FIDRES     0.094190 Hz
AQ         5.3084500 sec
RG         1024
DM         61.000 usec
DE         10.00 usec
TE         294.2 K
D1         1.00000000 sec
TD0        1
===== CHANNEL f1 =====
NUC1       13C
P1         19.50 usec
PL1        -6.00 dB
SFO1       300.1313338 MHz
SI         32769
SF          300.1300957 MHz
WCOM       EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00

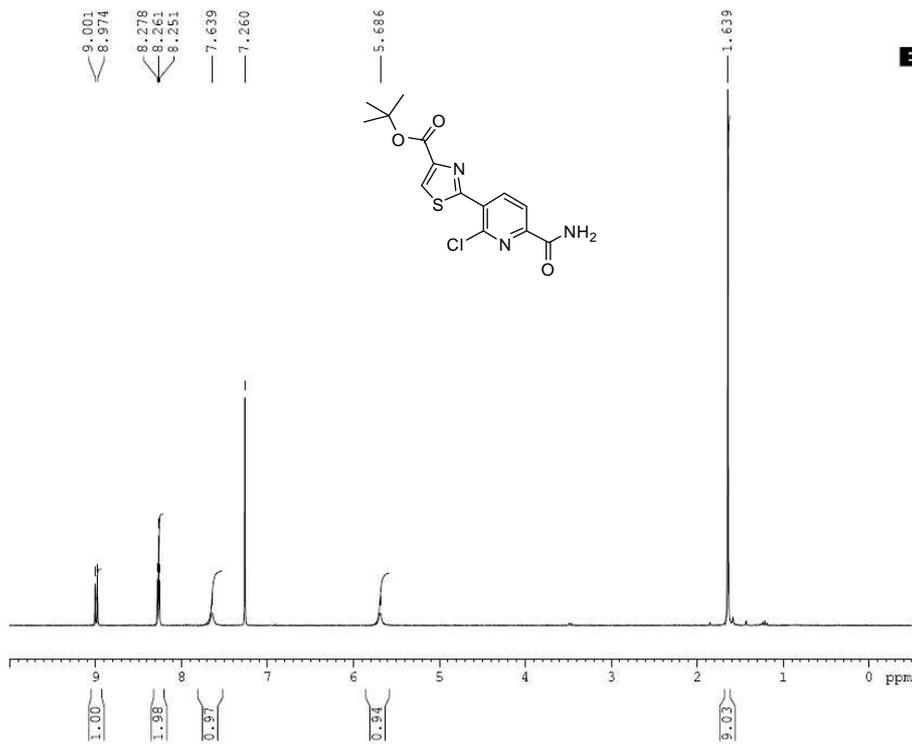
```



```

NAME      Tibo
EXPERNO   140
PROCNO    1
Date_     20090303
Time      12.09
INSTRUM   spect
PROBHD    5 mm QNP 1H/1
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         4
DS         4
SWH        17965.611 Hz
FIDRES     0.274439 Hz
AQ         1.8239508 sec
RG         7296.2
DM         27.600 usec
DE         10.00 usec
TE         294.2 K
D1         2.00000000 sec
d11        0.03000000 sec
DELTA      1.89999999 sec
TD0        1
===== CHANNEL f1 =====
NUC1       13C
P1         19.50 usec
PL1        0.00 dB
SFO1       75.4752953 MHz
===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
PCPD2     100.00 usec
PL2        -6.00 dB
PL12      11.00 dB
PL13      11.00 dB
SFO2       300.1312005 MHz
SI         32769
SF          75.4677402 MHz
WCOM       EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40

```



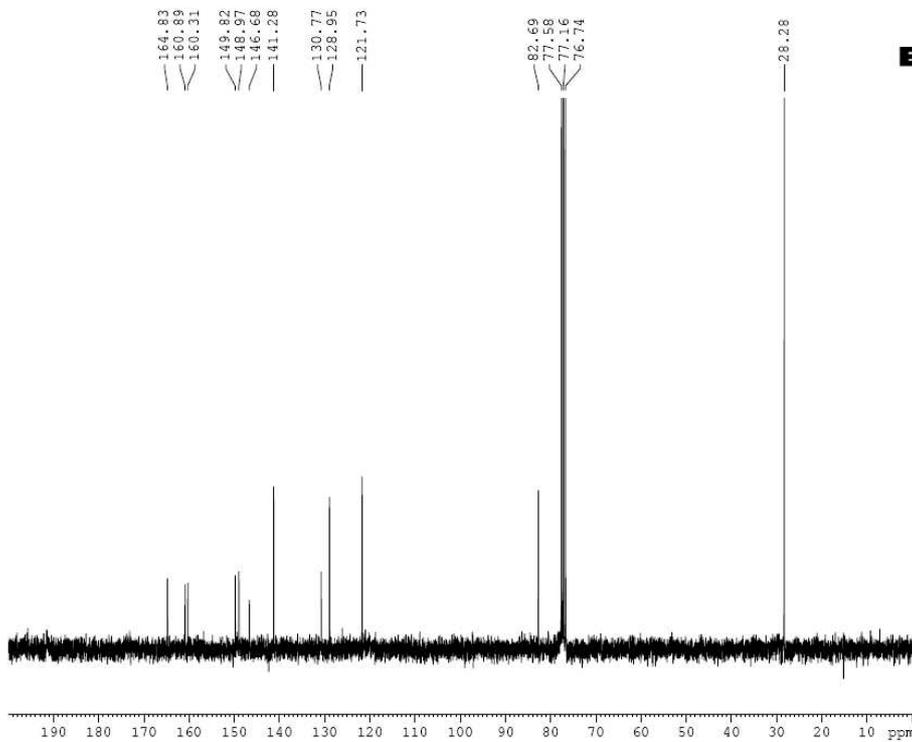
```

NAME      Tlbo
EXPNO     70
PROCNO    1
Date_     20090212
Time      10.21
INSTRUM   spect
PROBHD    5 mm QNP 1H/2
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         8
DS         8
SWH        6172.839 Hz
FIDRES     0.094190 Hz
AQ         0.308480 sec
RG         1024
DQ         81.000 usec
DE         10.00 usec
TE         293.2 K
DELTA     1.0000000 sec
TD0        1
  
```

---

```

----- CHANNEL f1 -----
NUC1      13C
P1         18.00 usec
PL1        -6.00 dB
SFO1      300.1318534 MHz
SI         32768
SF         300.1300059 MHz
WDW        EM
SSB         0
LB         0.30 Hz
GB         0
PC         1.00
  
```



```

NAME      Tlbo
EXPNO     1
PROCNO    1
Date_     20090204
Time      10.19
INSTRUM   spect
PROBHD    5 mm QNP 1H/1
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         10
DS         10
SWH        17969.611 Hz
FIDRES     0.274039 Hz
AQ         1.9219508 sec
RG         13024
DQ         21.800 usec
DE         10.00 usec
TE         293.2 K
DELTA     2.0000000 sec
delt1     0.0300000 sec
DELTA     1.8999999 sec
TD0        1
  
```

---

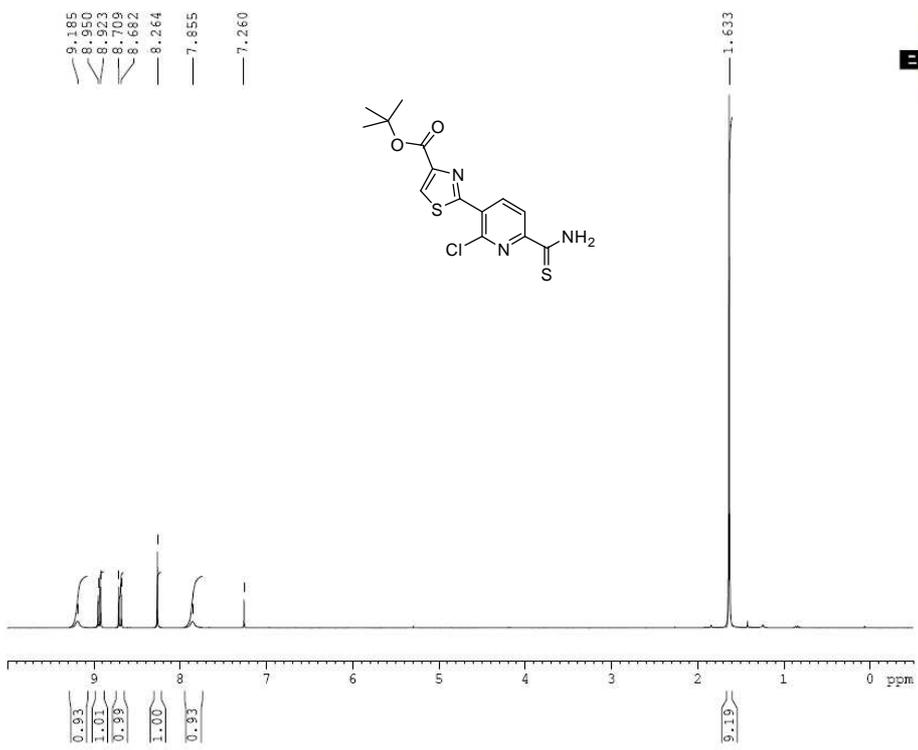
```

----- CHANNEL f1 -----
NUC1      13C
P1         10.00 usec
PL1         0.00 dB
SFO1      75.4752953 MHz
  
```

---

```

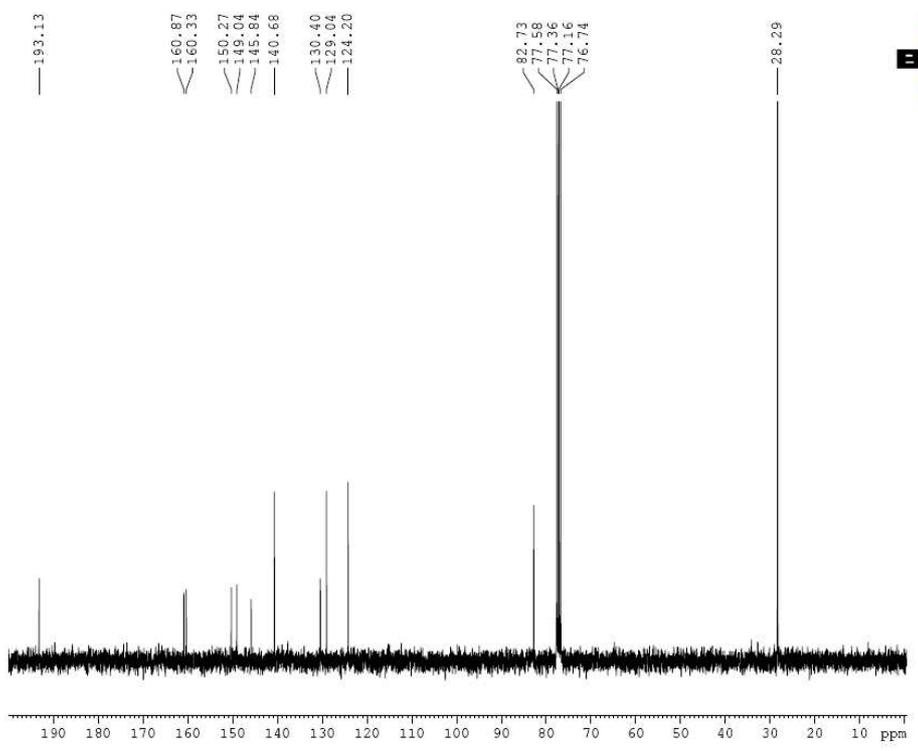
----- CHANNEL f2 -----
CFPRG2    waltz16
NUC2      1H
PCPRG2    100.00 usec
PL2        -6.00 dB
PL12       11.00 dB
PL13       11.00 dB
SFO2      300.1312005 MHz
SI         32768
SF         75.4677413 MHz
WDW        EM
SSB         0
LB         1.00 Hz
GB         0
PC         1.40
  
```



```

NAME           Tibo
EXPRO          430
PROCNO         1
Date_          20090311
Time           19.04
INSTRUM        spect
PROCNO         5 mm QNP 1H/2
PULPROG        zgpg30
TD             65536
SOLVENT        CDCl3
NS             8
DS             4
SWH            6172.839 Hz
FIDRES        0.094190 Hz
AQ            2.3084600 sec
RG            406.4
SQ            61.000 usec
DE            10.00 usec
TE            298.2 K
D1            1.00000000 sec
TD0           1
===== CHANNEL f1 =====
NUC1           1H
P1            16.50 usec
PL1           -2.00 dB
SFO1          300.1360534 MHz
SI            32768
SF            300.1360539 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00

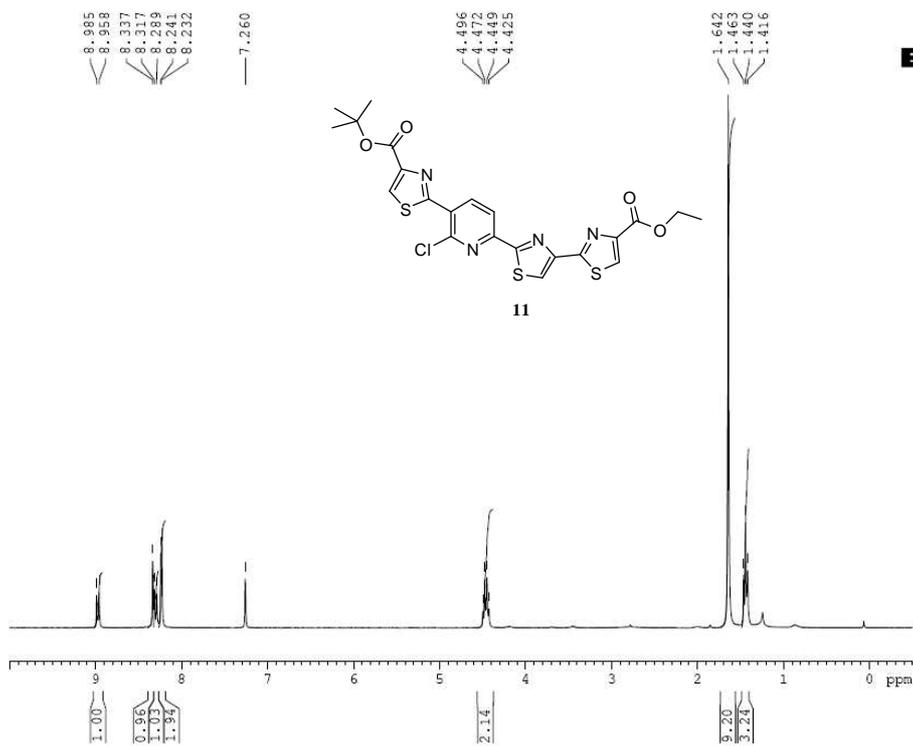
```



```

NAME           Tibo
EXPRO          431
PROCNO         1
Date_          20090311
Time           19.10
INSTRUM        spect
PROCNO         5 mm QNP 1H/2
PULPROG        zgpg30
TD             65536
SOLVENT        CDCl3
NS             4
DS             4
SWH            17995.411 Hz
FIDRES        0.274439 Hz
AQ            1.8215508 sec
RG            5160.6
SQ            27.100 usec
DE            10.00 usec
TE            298.2 K
D1            2.00000000 sec
d11           0.20000000 sec
DELTA         1.89999998 sec
TD0           1
===== CHANNEL f1 =====
NUC1           13C
P1            10.50 usec
PL1           0.00 dB
SFO1          75.4762983 MHz
===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2           1H
P2            100.00 usec
PL2           -2.00 dB
PL12          11.00 dB
PL13          11.00 dB
SFO2          300.1312005 MHz
SI            32768
SF            75.4677400 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40

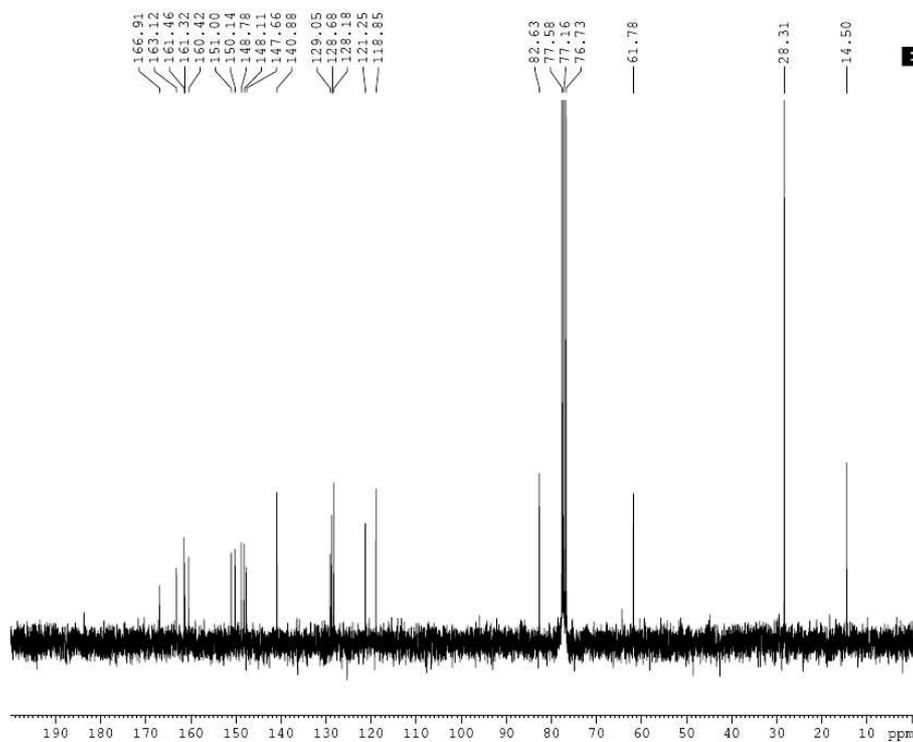
```



```

NAME           Tibo
EXPNO          380
PROCNO        1
Date_         20090305
Time          19.38
INSTRUM       spect
PROBHD        5 mm QNP 1H/1
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            8
DS            4
SWS          6172.839 Hz
FIDRES       0.0941950 Hz
AQ           2.3884866 sec
RG           512
SWH          81.000 usec
DE           10.00 usec
TE           294.2 K
D1           1.00000000 sec
TD0          1

===== CHANNEL f1 =====
NUC1          1H
P1            18.50 usec
PL1          -6.00 dB
SFO1         300.1362536 MHz
SI           32768
SF           300.1300960 MHz
WFO         EM
SSB          0
LB           0.30 Hz
GB           0
PC           1.00
  
```

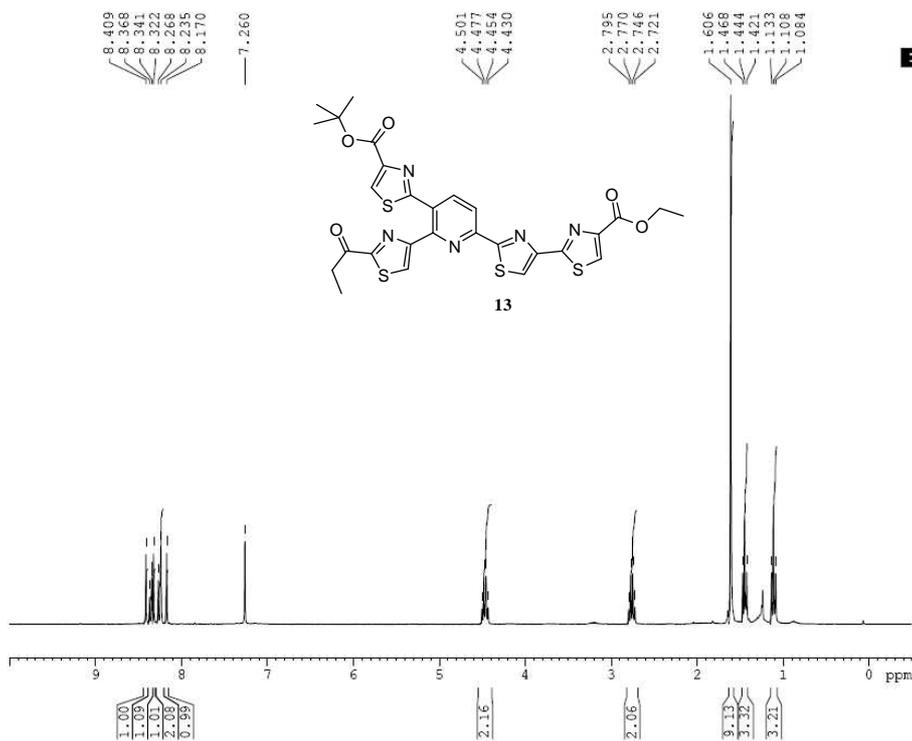


```

NAME           Tibo
EXPNO          10
PROCNO        1
Date_         20090306
Time          10.21
INSTRUM       spect
PROBHD        5 mm QNP 1H/1
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            427
DS            4
SWS          17965.811 Hz
FIDRES       0.274439 Hz
AQ           1.6219950 sec
RG           11595.2
SWH          27.800 usec
DE           10.00 usec
TE           294.2 K
D1           2.00000000 sec
d11          0.33000000 sec
DELTA        1.89999999 sec
TD0          1

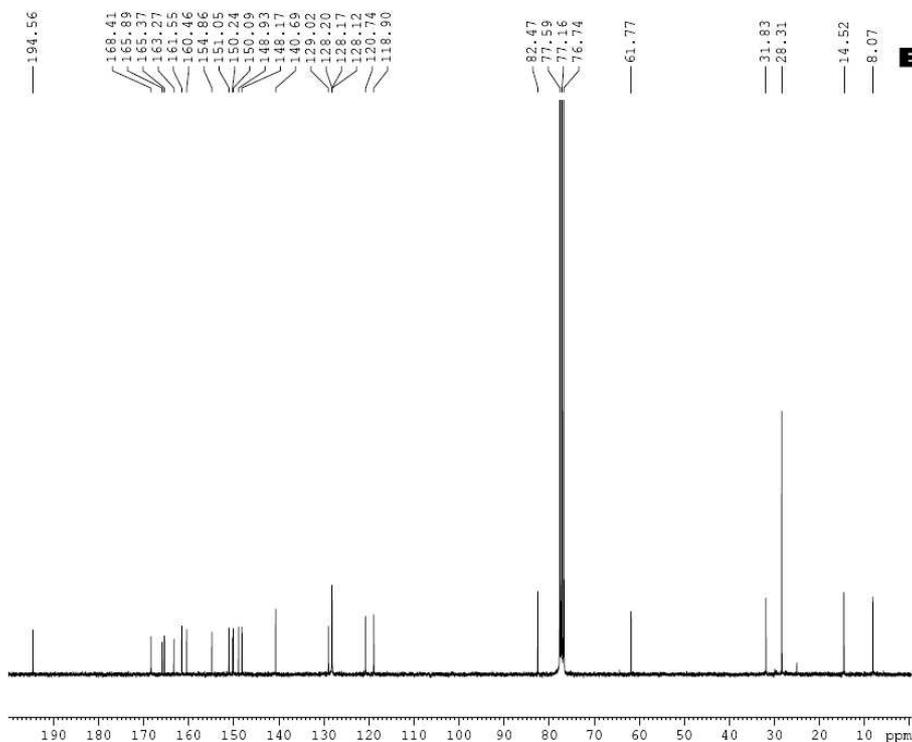
===== CHANNEL f1 =====
NUC1          13C
P1            10.00 usec
PL1           0.00 dB
SFO1         75.4752953 MHz

===== CHANNEL f2 =====
NAME2         waltz16
NUC2          1H
P2           100.00 usec
PL2          -6.00 dB
PL12         11.00 dB
PL13         11.00 dB
SFO2         300.132005 MHz
SI           32768
SF           75.4677401 MHz
WFO         EM
SSB          0
LB           1.00 Hz
GB           0
PC           1.00
  
```



```

NAME          Tibo
EXPNO         300
PROCNO        4
Date_         20090305
Time          17.02
INSTRUM       spect
PROBHD        5 mm QNP 1H/1
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            8
DS            4
SWH           6172.839 Hz
FIDRES        0.094190 Hz
AQ           0.3084802 sec
RG            574.7
DE           61.00 usec
TE           10.00 usec
DE           296.2 K
DI           1.00000000 sec
DQ            1
----- CHANNEL f1 -----
NUC1          13
P1            18.50 usec
PL1           -6.00 dB
SFO1          300.131934 MHz
SI            32768
SF            300.1300800 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
  
```



```

NAME          Tibo
EXPNO         300
PROCNO        4
Date_         20090308
Time          20.08
INSTRUM       spect
PROBHD        5 mm QNP 1H/1
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            8
DS            4
SWH           17985.611 Hz
FIDRES        0.274439 Hz
AQ           1.8239508 sec
RG            14596.5
DE           27.00 usec
TE           10.00 usec
DE           296.2 K
DI           2.00000000 sec
DQ            0.03000000 sec
DELTA         1.89999998 sec
TD0            1
----- CHANNEL f1 -----
NUC1          13
P1            10.50 usec
PL1           0.00 dB
SFO1          75.4752833 MHz
----- CHANNEL f2 -----
CPDPRG2       waltz16
NUC2          13
PCPD2         100.00 usec
PL2           -6.00 dB
PL12          11.00 dB
PL13          11.00 dB
SFO2          300.1310005 MHz
SI            32768
SF            75.4677397 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
  
```