

# Supporting Information

## **Ru(II) Catalyzed Synthesis of Hydroxylated Arenes with Ester as An Effective Directing Group**

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## Materials and Methods

All commercial materials (Alfa Aesar, Aladdin, J&K Chemical LTD.) were used without further purification. All solvents were analytical grade. The potassium persulfate were ground to powder. All esters were purchased or prepared from carboxylic acid with ethyl iodide <sup>[1]</sup> or benzoyl chloride with alcohol <sup>[2]</sup>. The ethyl 2-deuteriobenzoate was prepared from 2-deuteriobenzoic acid which was prepared by Daugilis's procedure <sup>[3]</sup>. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker AVANCE<sup>III</sup> 400 MHz spectrometer in CDCl<sub>3</sub> using TMS or solvent peak as a standard. All <sup>13</sup>C NMR spectra were recorded with complete proton decoupling. Low-resolution mass spectral analyses were performed with an Agilent 6340 or Waters AQUITY UPLC<sup>TM</sup>/MS. All reactions were carried out in sealed tube with Teflon cap. Analytical TLC was performed on Yantai Chemical Industry Research Institute silica gel 60 F254 plates and flash column chromatography was performed on Qingdao Haiyang Chemical Co. Ltd silica gel 60 (200-300mesh). The rotavapor was BUCHI's Rotavapor R-3.

### General procedure for the hydroxylation of all esters:

The [RuCl<sub>2</sub>(p-cymene)]<sub>2</sub>, oxidant and ester(1.0eq) were added to a sealed tube. Following that, trifluoroacetic acid (TFA) and trifluoroacetic anhydride (TFAH) were added. Then the reaction mixture was heated and stirred until its completion monitored by TLC. Add water to quench the reaction, extract with dichloromethane two times and wash with saturated ammonium chloride solution. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally the residue was purified by silica gel column chromatography to give corresponding products.

### The procedure for competition study:

Following the general procedure, [RuCl<sub>2</sub>(p-cymene)]<sub>2</sub> (5 mol%, 0.005mol), selectfluor (143 mg, 0.4 mmol), ethyl 4-methylbenzoate (16 mg, 0.1 mmol) and ethyl 4-fluorobenzoate (17 mg, 0.1mmol) were used with TFA: TFAH=0.6 ml:0.4 ml as solvent. The reaction mixture was stirred at 80 °C in the sealed tube for 3 h. After concentration, calculate the ratio of (3) to (6) by NMR. Finally, the ratio of (3) to (6) is 6.8.

### The procedure for preliminary mechanistic study (intramolecular):

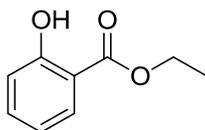
Following the general procedure, ethyl 2-deuteriobenzoate (30 mg, 0.2 mmol), selectfluor (143 mg, 0.4 mmol) and [RuCl<sub>2</sub>(p-cymene)]<sub>2</sub> (2.5 mol%, 0.005 mmol) were used with TFA: TFAH=0.6 ml:0.4 ml as solvent. The reaction mixture was stirred at 85 °C in the sealed tube for 1 h. After concentration, calculate the ratio of (40) to (2) by NMR. Finally, the ratio of (40) to (2) is 2.3.

### The procedure for preliminary mechanistic study (intermolecular):

Following the general procedure, [RuCl<sub>2</sub>(p-cymene)]<sub>2</sub> (5 mol%, 0.005mol), selectfluor (143 mg, 0.4 mmol), ethyl benzoate (15 mg, 0.1 mmol) and ethyl benzoate-d<sub>5</sub> (16 mg, 0.1mmol) were used with TFA: TFAH=0.6 ml:0.4 ml as solvent. The reaction mixture was stirred at 85 °C in the sealed tube for 2.5 h. After concentration, calculate the ratio of (2) to (42) by NMR. Finally, the ratio of (2) to (42) is 4.0.

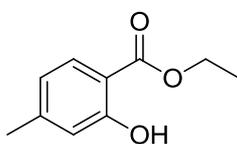
## References:

- [1] Sato, T; Otera, J; Nozaki, H. *J. Org. Chem.* **1992**, *57*, 2166.
- [2] Fatemeh, T.; Mohammad, A. A.; Leily, S. *Tetrahedron Lett.* **2005**, *46*, 7841.
- [3] Chiong, H. A.; Pham, Q. N.; Daugilis, O. *J. Am. Chem. Soc.* **2007**, *129*, 9879.



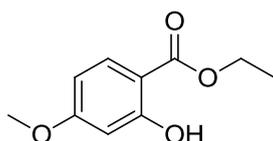
### ethyl 2-hydroxybenzoate ( 2 )

Following the general procedure, ethyl benzoate (30 mg, 0.2 mmol), selectfluor (143 mg, 0.4 mmol) and  $[\text{RuCl}_2(\text{p-cymene})]_2$  (2.5 mol%, 0.005 mmol) were used with TFA: TFAH=0.6 ml:0.4 ml as solvent. The reaction mixture was stirred at 85 °C in the sealed tube for 7.5 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **2** (24 mg, colorless oil) was isolated in 73% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 10.84 (s, 1H), 7.85 (dd,  $J = 1.68$  Hz,  $J = 8.00$  Hz, 1H), 7.42 - 7.47 (m, 1H), 6.98 (dd,  $J = 0.72$  Hz,  $J = 8.40$  Hz, 1H), 6.85 - 6.89 (m, 1H), 4.41 (q,  $J = 7.16$ , 2H), 1.42 (t,  $J = 7.16$  Hz, 3H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 170.3, 161.8, 135.7, 130.0, 119.2, 117.7, 112.8, 61.5, 14.32; LRMS (ESI) calcd for  $\text{C}_9\text{H}_{10}\text{O}_3$   $[\text{M}+\text{H}]^+$ : 167.06, found 166.71



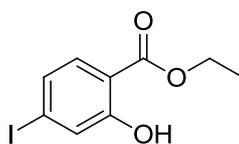
### ethyl 2-hydroxy-4-methylbenzoate ( 3 )

Following the general procedure, ethyl 4-methylbenzoate (328 mg, 2 mmol), potassium persulfate (570 mg, 2.1 mmol) and  $[\text{RuCl}_2(\text{p-cymene})]_2$  (2.5 mol%, 0.05 mmol) were used with TFA: TFAH=3 ml:2 ml as solvent. The reaction mixture was stirred at 80 °C in the sealed tube for 11 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: EtOAc = 100:1). Finally, compound **3** (219 mg, colorless oil) was isolated in 61% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 10.79 (s, 1H), 7.72 (d,  $J = 8.12$  Hz, 1H), 6.78 (s, 1H), 6.68 (dd,  $J=0.80$  Hz,  $J=8.08$  Hz, 1H), 4.39 (q,  $J=7.12$  Hz, 2H), 2.34 (s, 3H), 1.40 (t,  $J = 7.12$  Hz, 3H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 170.4, 161.8, 147.0, 129.8, 120.5, 117.8, 110.2, 61.3, 22.0, 14.2; LRMS (ESI) calcd for  $\text{C}_{10}\text{H}_{12}\text{O}_3$   $[\text{M}+\text{H}]^+$ : 181.08, found 181.17



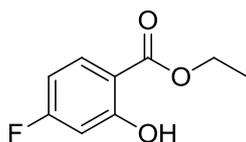
### ethyl 2-hydroxy-4-methoxybenzoate ( 4 )

Following the general procedure, ethyl 4-methoxybenzoate (54 mg, 0.3 mmol), potassium persulfate (90 mg, 0.33 mmol) and  $[\text{RuCl}_2(\text{p-cymene})]_2$  (2.5 mol%, 0.0075 mmol) were used with TFA: TFAH=1.4 ml:0.6 ml as solvent. The reaction mixture was stirred at 78 °C in the sealed tube for 10 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **4** (35 mg, colorless oil) was isolated in 60% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 11.07 (s, 1H), 7.74 (d,  $J = 8.44$  Hz, 1H), 6.43 (d,  $J = 8.44$  Hz, 1H), 6.41 (s, 1H), 4.36 (q,  $J = 7.12$  Hz, 2H), 3.81 (s, 3H), 1.39 (t,  $J = 7.12$  Hz, 3H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 170.1, 165.5, 163.8, 131.2, 107.4, 105.7, 100.7, 61.0, 55.4, 14.2; LRMS (ESI) calcd for  $\text{C}_{10}\text{H}_{12}\text{O}_4$   $[\text{M}+\text{H}]^+$ : 197.07, found 196.53



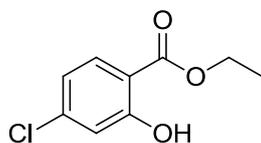
### ethyl 2-hydroxy-4-iodobenzoate ( 5 )

Following the general procedure, ethyl 4-iodobenzoate (55 mg, 0.2 mmol), iodic acid (39 mg, 0.22 mmol) and  $[\text{RuCl}_2(\text{p-cymene})]_2$  (2.5 mol%, 0.005 mmol) were used with TFA: TFAH=1.2 ml:0.8 ml as solvent. The reaction mixture was stirred at 105 °C in the sealed tube for 11 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **5** (41 mg, colorless oil) was isolated in 71% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 10.85 (s, 1H), 7.52 (d,  $J = 8.40$  Hz, 1H), 7.40 (d,  $J = 1.60$  Hz, 1H), 7.23 (dd,  $J = 1.64$  Hz,  $J = 8.40$  Hz, 1H), 4.40 (q,  $J = 7.12$  Hz, 2H), 1.41 (t,  $J = 7.12$  Hz, 3H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 170.0, 161.7, 130.8, 128.7, 127.1, 112.3, 102.7, 61.9, 14.3; LRMS (ESI) calcd for  $\text{C}_9\text{H}_9\text{IO}_3$   $[\text{M}+\text{H}]^+$ : 292.96, found 292.51



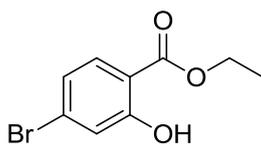
#### ethyl 4-fluoro-2-hydroxybenzoate (6)

Following the general procedure, ethyl 4-fluorobenzoate (34 mg, 0.2 mmol), selectfluor (143 mg, 0.4 mmol) and  $[\text{RuCl}_2(\text{p-cymene})]_2$  (2.5 mol%, 0.005 mmol) were used with TFA: TFAH=1.2 ml:0.8 ml as solvent. The reaction mixture was stirred at 110 °C in the sealed tube for 14 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **6** (26 mg, colorless oil) was isolated in 71% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 11.09 (s, 1H), 7.85 (dd,  $J = 6.68$  Hz,  $J = 8.76$  Hz, 1H), 6.66 (dd,  $J = 2.36$  Hz,  $J = 10.28$  Hz, 1H), 6.59 (m, 1H), 4.40 (q,  $J = 7.12$  Hz, 2H), 1.41 (t,  $J = 7.12$  Hz, 3H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 169.6, 167.2 (d,  $J_{\text{C-F}} = 252.95$  Hz), 163.77 (d,  $J_{\text{C-F}} = 14.10$  Hz), 132.1 (d,  $J_{\text{C-F}} = 11.36$  Hz), 109.3 (d,  $J_{\text{C-F}} = 2.35$  Hz), 107.2 (d,  $J_{\text{C-F}} = 22.50$  Hz), 104.3 (d,  $J_{\text{C-F}} = 24.10$  Hz), 61.5, 14.2; LRMS (ESI) calcd for  $\text{C}_9\text{H}_9\text{FO}_3$   $[\text{M}+\text{H}]^+$ : 185.05, found 184.91



#### ethyl 4-chloro-2-hydroxybenzoate (7)

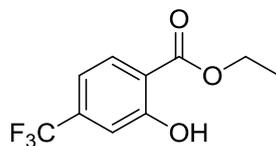
Following the general procedure, ethyl 4-chlorobenzoate (37 mg, 0.2 mmol), selectfluor (143 mg, 0.4 mmol) and  $[\text{RuCl}_2(\text{p-cymene})]_2$  (2.5 mol%, 0.005 mmol) were used with TFA: TFAH=0.6 ml:0.4 ml as solvent. The reaction mixture was stirred at 113 °C in the sealed tube for 10.5 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **7** (31 mg, colorless oil) was isolated in 77% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 10.94 (s, 1H), 7.77 (d,  $J = 8.56$  Hz, 1H), 7.00 (d,  $J = 2.00$  Hz, 1H), 6.86 (dd,  $J = 2.00$  Hz,  $J = 8.56$  Hz, 1H), 4.64 (q,  $J = 7.12$  Hz, 2H), 1.42 (t,  $J = 7.12$  Hz, 3H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 169.8, 162.4, 141.5, 131.0, 120.0, 117.9, 111.4, 61.8, 14.3; LRMS (ESI) calcd for  $\text{C}_9\text{H}_9\text{ClO}_3$   $[\text{M}-\text{H}]^-$ : 199.02, found 198.82



#### ethyl 4-bromo-2-hydroxybenzoate (8)

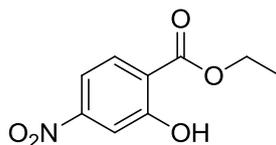
Following the general procedure, ethyl 4-bromobenzoate (46 mg, 0.2 mmol), selectfluor (143 mg, 0.4 mmol) and  $[\text{RuCl}_2(\text{p-cymene})]_2$  (5 mol%, 0.01 mmol) were used with TFA: TFAH=0.6 ml:0.4 ml as solvent. The reaction mixture was stirred at 110 °C in the sealed tube for 5.5 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: EtOAc = 100:1). Finally, compound **8** (41 mg,

colorless oil) was isolated in 84% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 10.95 (s, 1H), 7.72 (d, *J* = 8.52 Hz, 1H), 7.20 (d, *J* = 1.88 Hz, 1H), 7.04 (dd, *J* = 1.88 Hz, *J* = 8.52 Hz, 1H), 4.43 (q, *J* = 7.12 Hz, 2H), 1.44 (t, *J* = 7.12 Hz, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 169.8, 162.1, 130.9, 129.8, 122.6, 120.8, 111.6, 61.7, 14.2; LRMS (ESI) calcd for C<sub>9</sub>H<sub>9</sub>BrO<sub>3</sub> [M+H]<sup>+</sup>: 244.97, found 245.47



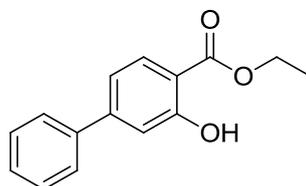
#### ethyl 2-hydroxy-4-(trifluoromethyl)benzoate ( 9 )

Following the general procedure, ethyl 4-(trifluoromethyl)benzoate (44 mg, 0.2 mmol), iodic acid (39 mg, 0.22 mmol) and [RuCl<sub>2</sub>(p-cymene)]<sub>2</sub> (2.5 mol%, 0.005 mmol) were used with TFA: TFAH=1.2 ml:0.8 ml as solvent. The reaction mixture was stirred at 108 °C in the sealed tube for 11 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene = 100:20). Finally, compound **9** (35 mg, colorless oil) was isolated in 74% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 10.96 (s, 1H), 7.95 (d, *J* = 8.28 Hz, 1H), 7.23 (s, 1H), 7.10 (d, *J* = 8.34 Hz, 1H), 4.44 (q, *J* = 7.16 Hz, 2H), 1.43 (t, *J* = 7.16 Hz, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 169.3, 161.6, 136.8 (q, *J*<sub>C-F</sub> = 32.56 Hz), 130.7, 129.9, 123.2 (q, *J*<sub>C-F</sub> = 271.28 Hz), 115.4 (q, *J*<sub>C-F</sub> = 3.61 Hz), 115.0 (q, *J*<sub>C-F</sub> = 3.92 Hz), 62.0, 14.1; LRMS (ESI) calcd for C<sub>10</sub>H<sub>9</sub>F<sub>3</sub>O<sub>3</sub> [M-H]<sup>-</sup>: 233.05, found 232.69



#### ethyl 2-hydroxy-4-nitrobenzoate ( 10 )

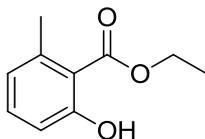
Following the general procedure, ethyl 4-nitrobenzoate (312 mg, 1.6 mmol), iodic acid (282 mg, 1.6 mmol) and [RuCl<sub>2</sub>(p-cymene)]<sub>2</sub> (5 mol%, 0.08 mmol) were used with TFA: TFAH=3 ml:1 ml as solvent. The reaction mixture was stirred at 110 °C in the sealed tube for 16 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: EtOAc = 100:1). Finally, compound **10** (257 mg, yellow solid) was isolated in 76% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 11.09 (s, 1H), 8.05 (d, *J* = 8.44 Hz, 1H), 7.83 (d, *J* = 2.00 Hz, 1H), 7.71 (dd, *J* = 2.00 Hz, *J* = 8.44 Hz, 1H), 4.49 (q, *J* = 7.16 Hz, 2H), 1.47 (t, *J* = 7.16 Hz, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 169.0, 162.2, 152.2, 131.3, 117.6, 113.6, 113.1, 62.7, 14.2; LRMS (ESI) calcd for C<sub>9</sub>H<sub>9</sub>NO<sub>5</sub> [M+H]<sup>+</sup>: 212.05, found 212.36



#### ethyl 3-hydroxy-[1,1'-biphenyl]-4-carboxylate ( 11 )

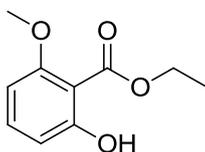
Following the general procedure, ethyl [1, 1'-biphenyl]-4-carboxylate (46 mg, 0.2 mmol), Potassium persulfate (60 mg, 0.22 mmol) and [RuCl<sub>2</sub>(p-cymene)]<sub>2</sub> (2.5 mol%, 0.005 mmol) were used with TFA: TFAH=1.2 ml:0.8 ml as solvent. The reaction mixture was stirred at 110 °C in the sealed tube for 9 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene = 100:20). Finally, compound **11** (30 mg, white solid) was isolated in 61% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 10.91 (s, 1H), 7.91 (d, *J* = 8.24 Hz, 1H), 7.63 – 7.61 (m, 2H), 7.48 – 7.44 (m, 2H), 7.42 – 7.39 (m, 1H), 7.22 (d, *J* = 1.72 Hz, 1H), 7.13 (dd, *J* = 1.76 Hz, *J* = 8.40 Hz, 1H), 4.43 (q, *J* = 7.12 Hz, 2H), 1.44 (t, *J* = 7.12 Hz, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ

(ppm) 170.1, 161.8, 148.4, 139.7, 130.3, 128.9, 128.4, 127.2, 118.1, 115.7, 111.4, 61.4, 14.2; LRMS (ESI) calcd for  $C_{15}H_{14}O_3$   $[M+H]^+$ : 243.09, found 243.01



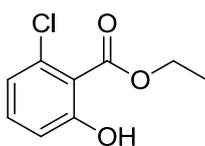
### ethyl 2-hydroxy-6-methylbenzoate ( 12 )

Following the general procedure, ethyl 2-methylbenzoate (49 mg, 0.3 mmol), potassium persulfate (60 mg, 0.33 mmol) and  $[RuCl_2(p\text{-cymene})]_2$  (2.5 mol%, 0.0075 mmol) were used with TFA: TFAH=1.4 ml:0.6 ml as solvent. The reaction mixture was stirred at 80 °C in the sealed tube for 11 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **12** (36 mg, colorless oil) was isolated in 66% yield.  $^1H$ -NMR (400 MHz,  $CDCl_3$ )  $\delta$  (ppm) 11.37 (s, 1H), 7.27 (t,  $J = 7.90$  Hz, 1H), 6.84 (d,  $J = 8.28$  Hz, 1H), 6.71 (d,  $J = 7.44$  Hz, 1H), 4.43 (q,  $J = 7.12$  Hz, 2H), 2.55 (s, 3H), 1.43 (t,  $J = 7.12$  Hz, 3H);  $^{13}C$ -NMR (100 MHz,  $CDCl_3$ )  $\delta$  (ppm) 171.8, 162.9, 141.4, 134.1, 122.9, 115.6, 112.4, 61.6, 24.1, 14.2; LRMS (ESI) calcd for  $C_{10}H_{12}O_3$   $[M+H]^+$ : 181.08, found 181.06



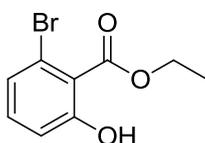
### ethyl 2-hydroxy-6-methoxybenzoate ( 13 )

Following the general procedure, ethyl 2-methoxybenzoate (36 mg, 0.2 mmol), potassium persulfate (60 mg, 0.22 mmol) and  $[RuCl_2(p\text{-cymene})]_2$  (2.5 mol%, 0.005 mmol) were used with TFA: TFAH=1.2 ml:0.8 ml as solvent. The reaction mixture was stirred at 80 °C in the sealed tube for 10 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **13** (33 mg, colorless oil) was isolated in 83% yield.  $^1H$ -NMR (400 MHz,  $CDCl_3$ )  $\delta$  (ppm) 11.50 (s, 1H), 7.32 (t,  $J = 8.36$  Hz, 1H), 6.59 (dd,  $J = 0.48$  Hz,  $J = 8.36$  Hz, 1H), 6.41 (d,  $J = 8.36$  Hz, 1H), 4.42 (q,  $J = 7.12$  Hz, 2H), 3.85 (s, 3H), 1.41 (t,  $J = 7.12$  Hz, 3H);  $^{13}C$ -NMR (100 MHz,  $CDCl_3$ )  $\delta$  (ppm) 171.1, 163.5, 161.0, 135.0, 110.1, 103.5, 102.4, 61.5, 56.1, 14.2; LRMS (ESI) calcd for  $C_{10}H_{12}O_4$   $[M+H]^+$ : 197.07, found 196.78



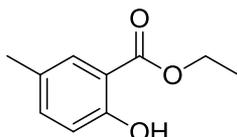
### ethyl 2-chloro-6-hydroxybenzoate ( 14 )

Following the general procedure, ethyl 2-chlorobenzoate (37 mg, 0.2 mmol), selectfluor (143 mg, 0.4 mmol) and  $[RuCl_2(p\text{-cymene})]_2$  (2.5 mol%, 0.005 mmol) were used with TFA: TFAH=0.6 ml:0.4ml as solvent. The reaction mixture was stirred at 105 °C in the sealed tube for 10.5 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene = 100:20). Finally, compound **14** (30 mg, colorless oil) was isolated in 75% yield.  $^1H$ -NMR (400 MHz,  $CDCl_3$ )  $\delta$  (ppm) 11.15 (s, 1H), 7.27 (t,  $J = 8.40$  Hz, 1H), 6.96 (dd,  $J = 1.20$  Hz,  $J = 8.00$  Hz, 1H), 6.90 (dd,  $J = 1.20$  Hz,  $J = 8.44$  Hz, 1H), 4.47 (q,  $J = 7.12$  Hz, 2H), 1.45 (t,  $J = 7.12$  Hz, 3H);  $^{13}C$ -NMR (100 MHz,  $CDCl_3$ )  $\delta$  (ppm) 169.6, 163.1, 134.9, 134.1, 122.7, 116.6, 112.3, 62.4, 14.1; LRMS (ESI) calcd for  $C_9H_9ClO_3$   $[M-H]^-$ : 199.02, found 199.05



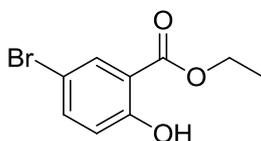
### ethyl 2-bromo-6-hydroxybenzoate ( 15 )

Following the general procedure, ethyl 2-bromobenzoate (46 mg, 0.2 mmol), selectfluor (143 mg, 0.4 mmol) and  $[\text{RuCl}_2(\text{p-cymene})]_2$  (2.5 mol%, 0.005 mmol) were used with TFA: TFAH=0.6 ml:0.4 ml as solvent. The reaction mixture was stirred at 110 °C in the sealed tube for 9 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **15** (42 mg, colorless oil) was isolated in 86% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 11.00 (s, 1H), 7.20 (m, 2H), 6.95 (dd,  $J = 2.80$  Hz,  $J = 6.76$  Hz, 1H), 4.48 (q,  $J = 7.16$  Hz, 2H), 1.48 (t,  $J = 7.16$  Hz, 3H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 169.4, 162.9, 134.4, 126.4, 122.6, 117.2, 114.0, 62.4, 14.1; LRMS (ESI) calcd for  $\text{C}_9\text{H}_9\text{BrO}_3$   $[\text{M}+\text{H}]^+$ : 244.97, found 244.77



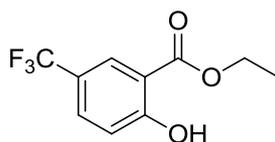
### ethyl 2-hydroxy-5-methylbenzoate ( 16 )

Following the general procedure, ethyl 3-methylbenzoate (50 mg, 0.3 mmol), Potassium persulfate (90 mg, 0.33mmol) and  $[\text{RuCl}_2(\text{p-cymene})]_2$  (2.5 mol%, 0.0075 mmol) were used with TFA: TFAH=1.4ml:0.6ml as solvent. The reaction mixture was stirred at 78 °C in the sealed tube for 10 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **16** (40 mg, colorless oil) was isolated in 73% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 10.63 (s, 1H), 7.63 (s, 1H), 7.26 (dd,  $J = 2.72$  Hz,  $J = 8.44$  Hz, 1H), 6.88 (d,  $J = 8.44$  Hz, 1H), 4.40 (q,  $J = 7.12$  Hz, 2H), 2.29 (s, 3H), 1.42 (t,  $J = 7.12$  Hz, 3H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 170.2, 159.6, 136.5, 129.6, 128.2, 117.3, 112.2, 62.3, 20.4, 14.2; LRMS (ESI) calcd for  $\text{C}_{10}\text{H}_{12}\text{O}_3$   $[\text{M}+\text{H}]^+$ : 181.1, found 181.2



### ethyl 5-bromo-2-hydroxybenzoate ( 17 )

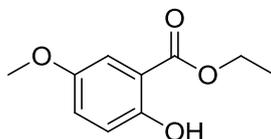
Following the general procedure, ethyl 3-bromobenzoate (46 mg, 0.2 mmol), selectfluor (143 mg, 0.4 mmol) and  $[\text{RuCl}_2(\text{p-cymene})]_2$  (2.5 mol%, 0.005 mmol) were used with TFA: TFAH=1.2 ml:0.8 ml as solvent. The reaction mixture was stirred at 105 °C in the sealed tube for 10 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **17** (41 mg, white solid) was isolated in 84% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 10.78 (s, 1H), 7.94 (s, 1H), 7.51 (dd,  $J = 1.60$  Hz,  $J = 8.84$  Hz, 1H), 6.86 (d,  $J = 8.88$  Hz, 1H), 4.40 (q,  $J = 7.12$  Hz, 2H), 1.41 (t,  $J = 7.12$  Hz, 3H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 169.1, 160.7, 138.3, 132.2, 119.5, 114.1, 110.7, 61.9, 14.2; LRMS (ESI) calcd for  $\text{C}_9\text{H}_9\text{BrO}_3$   $[\text{M}-\text{H}]^-$ : 242.97, found 243.41



### ethyl 2-hydroxy-5-(trifluoromethyl)benzoate ( 18 )

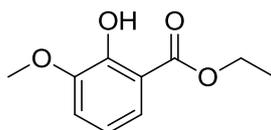
Following the general procedure, ethyl 3-(trifluoromethyl)benzoate (44 mg, 0.2 mmol), iodic acid (53 mg, 0.3 mmol) and  $[\text{RuCl}_2(\text{p-cymene})]_2$  (2.5 mol%, 0.005 mmol) were used with TFA: TFAH=1.2 ml:0.8 ml as solvent. The reaction mixture was stirred at 110 °C in the sealed tube for 10 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene = 100:20). Finally, compound **18** (36

mg, white solid) was isolated in 77% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 11.19 (s, 1H), 8.13 (d,  $J = 1.76$  Hz, 1H), 7.67 (dd,  $J = 2.28$  Hz,  $J = 8.80$  Hz, 1H), 7.07 (d,  $J = 8.76$  Hz, 1H), 4.46 (q,  $J = 7.16$  Hz, 2H), 1.42 (t,  $J = 7.16$  Hz, 3H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 169.5, 164.2, 132.2 (q,  $J_{\text{C-F}} = 3.49$  Hz), 127.8 (q,  $J_{\text{C-F}} = 3.81$  Hz), 124.0 (q,  $J_{\text{C-F}} = 269.66$  Hz), 121.7 (q,  $J_{\text{C-F}} = 32.97$  Hz), 118.5, 112.6, 62.3, 14.3; LRMS (ESI) calcd for  $\text{C}_{10}\text{H}_9\text{F}_3\text{O}_3$   $[\text{M-H}]^-$ : 233.05, found 232.80



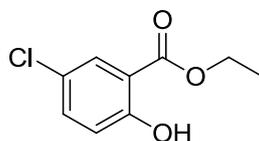
#### ethyl 2-hydroxy-5-methoxybenzoate ( 19a )

Following the general procedure, ethyl 3-methoxybenzoate (36 mg, 0.2 mmol), potassium persulfate (60 mg, 0.22mmol) and  $[\text{RuCl}_2(\text{p-cymene})]_2$  (2.5 mol%, 0.005 mmol) were used with TFA: TFAH=1.4 ml:0.6 ml as solvent. The reaction mixture was stirred at 80 °C in the sealed tube for 9.5 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **19a** (22 mg, colorless oil) was isolated in 55% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 10.46 (s, 1H), 7.30 (d,  $J = 3.20$  Hz, 1H), 7.07 (dd,  $J = 3.12$  Hz,  $J = 9.04$  Hz, 1H), 6.91 (d,  $J = 9.04$  Hz, 1H), 4.41 (q,  $J = 7.12$  Hz, 2H), 3.79 (s, 3H), 1.42 (t,  $J = 7.12$  Hz, 3H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 169.9, 156.1, 151.9, 123.7, 118.4, 112.1, 112.0, 61.5, 55.9, 14.2; LRMS (ESI) calcd for  $\text{C}_{10}\text{H}_{12}\text{O}_4$   $[\text{M+H}]^+$ : 197.07, found 196.97



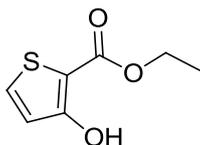
#### ethyl 2-hydroxy-3-methoxybenzoate ( 19b )

Following the general procedure, ethyl 3-methoxybenzoate (36 mg, 0.2 mmol), potassium persulfate (60 mg, 0.22 mmol) and  $[\text{RuCl}_2(\text{p-cymene})]_2$  (2.5 mol%, 0.005 mmol) were used with TFA: TFAH=1.4 ml:0.6 ml as solvent. The reaction mixture was stirred at 80 °C in the sealed tube for 9.5 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **19b** (5 mg, colorless oil) was isolated in 17% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 11.10 (s, 1H), 7.45 (dd,  $J = 1.48$  Hz,  $J = 8.16$  Hz, 1H), 7.05 (dd,  $J = 0.84$  Hz,  $J = 7.12$  Hz, 1H), 6.83 (t,  $J = 8.04$  Hz, 1H), 4.42 (q,  $J = 7.16$  Hz, 2H), 3.91 (s, 3H), 1.42 (t,  $J = 7.16$  Hz, 3H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 170.5, 152.1, 148.5, 121.0, 118.4, 116.4, 112.8, 61.5, 56.2, 14.2; LRMS (ESI) calcd for  $\text{C}_{10}\text{H}_{12}\text{O}_4$   $[\text{M+H}]^+$ : 197.07, found 196.97



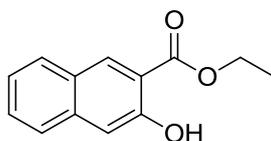
#### ethyl 5-chloro-2-hydroxybenzoate ( 20 )

Following the general procedure, ethyl 3-chlorobenzoate (39 mg, 0.2 mmol), selectfluor (143 mg, 0.4 mmol) and  $[\text{RuCl}_2(\text{p-cymene})]_2$  (2.5 mol%, 0.005 mmol) were used with TFA: TFAH=0.6 ml:0.4 ml as solvent. The reaction mixture was stirred at 105 °C in the sealed tube for 10 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **20** (23 mg, colorless oil) was isolated in 53% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 10.75 (s, 1H), 7.79 (d,  $J = 2.64$  Hz, 1H), 7.37 (dd,  $J = 2.64$  Hz,  $J = 8.88$  Hz, 1H), 6.91 (d,  $J = 8.88$  Hz, 1H), 4.41 (q,  $J = 7.12$  Hz, 2H), 1.42 (t,  $J = 7.12$  Hz, 3H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 169.2, 160.2, 135.5, 129.1, 123.8, 119.1, 113.5, 61.9, 14.1; LRMS (ESI) calcd for  $\text{C}_9\text{H}_9\text{ClO}_3$   $[\text{M-H}]^-$ : 199.02, found 199.38



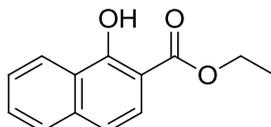
### ethyl 3-hydroxythiophene-2-carboxylate ( 21 )

Following the general procedure, ethyl thiophene-2-carboxylate (31 mg, 0.2 mmol), potassium persulfate (60 mg, 0.22mmol) and  $[\text{RuCl}_2(\text{p-cymene})]_2$  (2.5 mol%, 0.005 mmol) were used with TFA: TFAH=1.2 ml:0.8 ml as solvent. The reaction mixture was stirred at 75 °C in the sealed tube for 5.5 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **21** (14 mg, colorless oil) was isolated in 41% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 9.65 (s, 1H), 7.36 (d,  $J = 5.40$  Hz, 1H), 6.74 (d,  $J = 5.40$  Hz, 1H), 4.36 (q,  $J = 7.12$  Hz, 2H), 1.38 (t,  $J = 7.12$  Hz, 3H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 131.3, 119.2, 61.1, 14.3; LRMS (ESI) calcd for  $\text{C}_7\text{H}_8\text{O}_3\text{S} [\text{M-H}]^-$ : 171.02, found 171.48



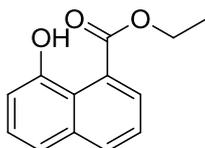
### ethyl 3-hydroxy-2-naphthoate ( 22a )

Following the general procedure, ethyl 2-naphthoate (60 mg, 0.3 mmol), potassium persulfate (90 mg, 0.33 mmol) and  $[\text{RuCl}_2(\text{p-cymene})]_2$  (2.5 mol%, 0.0075 mmol) were used with TFA: TFAH=1.4 ml:0.6 ml as solvent. The reaction mixture was stirred at 100 °C in the sealed tube for 11 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **22a** (36 mg, white solid) was isolated in 55% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 10.53 (s, 1H), 8.49 (s, 1H), 7.80 (d,  $J = 8.28$  Hz, 1H), 7.78 (d,  $J = 8.32$  Hz, 1H), 7.51 - 7.47 (m, 1H), 7.34 - 7.26 (m, 2H), 4.49 (q,  $J = 7.12$  Hz, 2H), 1.48 (t,  $J = 7.12$  Hz, 3H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 169.9, 156.4, 137.9, 132.3, 129.2, 129.0, 127.0, 126.3, 123.9, 114.5, 111.6, 61.8, 14.3; LRMS (ESI) calcd for  $\text{C}_{13}\text{H}_{12}\text{O}_3 [\text{M+H}]^+$ : 217.08, found 216.95



### ethyl 1-hydroxy-2-naphthoate ( 22b )

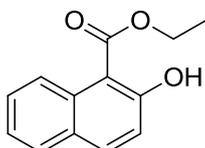
Following the general procedure, ethyl 2-naphthoate (60 mg, 0.3 mmol), potassium persulfate (90 mg, 0.33 mmol) and  $[\text{RuCl}_2(\text{p-cymene})]_2$  (2.5 mol%, 0.0075 mmol) were used with TFA: TFAH=1.4 ml:0.6 ml as solvent. The reaction mixture was stirred at 100 °C in the sealed tube for 11 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **22b** (5 mg, colorless oil) was isolated in 7% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 12.10 (s, 1H), 8.44 (d,  $J = 8.32$  Hz, 1H), 7.83 - 7.78 (m, 2H), 7.65 - 7.61 (m, 1H), 7.57 - 7.53 (m, 1H), 7.31 - 7.28 (m, 1H), 4.48 (q,  $J = 7.12$  Hz, 2H), 1.48 (t,  $J = 7.16$  Hz, 3H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 171.1, 161.0, 137.2, 129.3, 127.5, 125.7, 124.8, 124.3, 123.9, 118.5, 105.8, 61.4, 14.3; LRMS (ESI) calcd for  $\text{C}_{13}\text{H}_{12}\text{O}_3 [\text{M+H}]^+$ : 217.08, found 216.91



### ethyl 8-hydroxy-1-naphthoate ( 23a )

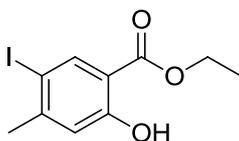
Following the general procedure, ethyl 1-naphthoate (60 mg, 0.3 mmol), potassium persulfate (90 mg, 0.33 mmol)

and  $[\text{RuCl}_2(\text{p-cymene})]_2$  (2.5 mol%, 0.0075 mmol) were used with TFA: TFAH=1.4 ml:0.6 ml as solvent. The reaction mixture was stirred at 70 °C in the sealed tube for 11 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **23a** (29 mg, green oil) was isolated in 44% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 10.63 (s, 1H), 8.27 (d,  $J = 7.24$  Hz, 1H), 8.04 (d,  $J = 8.08$  Hz, 1H), 7.46 - 7.40 (m, 3H), 7.16 (dd,  $J = 3.00$  Hz,  $J = 5.60$  Hz, 1H), 4.52 (q,  $J = 7.12$  Hz, 3H), 1.48 (t,  $J = 7.12$  Hz, 3H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 172.3, 153.2, 136.1, 135.7, 132.1, 127.6, 125.4, 123.8, 122.1, 121.1, 115.5, 62.9, 14.0; LRMS (ESI) calcd for  $\text{C}_{13}\text{H}_{12}\text{O}_3$   $[\text{M-H}]^-$ : 215.07, found 214.76



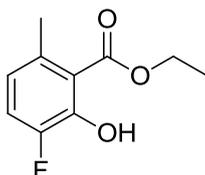
#### ethyl 2-hydroxy-1-naphthoate ( **23b** )

Following the general procedure, ethyl 1-naphthoate (60 mg, 0.3 mmol), potassium persulfate (90 mg, 0.33 mmol) and  $[\text{RuCl}_2(\text{p-cymene})]_2$  (2.5 mol%, 0.0075 mmol) were used with TFA: TFAH=1.4ml:0.6ml as solvent. The reaction mixture was stirred at 70 °C in the sealed tube for 11 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **23b** (7 mg, colorless oil) was isolated in 11% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 12.35 (s, 1H), 8.80 (d,  $J = 8.80$  Hz, 1H), 7.89 (d,  $J = 9.00$  Hz, 1H), 7.56 (d,  $J = 7.92$  Hz, 1H), 7.55 (dd,  $J = 1.52$  Hz,  $J = 8.72$  Hz, 1H), 7.37 (dd,  $J = 0.68$  Hz,  $J = 7.76$  Hz, 1H), 7.17 (d,  $J = 9.00$  Hz, 1H), 4.59 (q,  $J = 7.16$  Hz, 2H), 1.55 (t,  $J = 7.12$  Hz, 3H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 172.3, 164.3, 136.7, 131.8, 129.0, 128.6, 128.3, 125.2, 123.5, 119.3, 104.7, 61.9, 14.3; LRMS (ESI) calcd for  $\text{C}_{13}\text{H}_{12}\text{O}_3$   $[\text{M-H}]^-$ : 215.07, found 214.84



#### ethyl 2-hydroxy-5-iodo-4-methylbenzoate ( **24** )

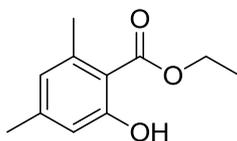
Following the general procedure, ethyl 3-iodo-4-methylbenzoate (44 mg, 0.15mmol), iodic acid (30 mg, 0.165 mmol) and  $[\text{RuCl}_2(\text{p-cymene})]_2$  (3.3 mol%, 0.005 mmol) were used with TFA: TFAH=0.6 ml:0.4 ml as solvent. The reaction mixture was stirred at 90 °C in the sealed tube for 20 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **24** (42 mg, colorless oil) was isolated in 92% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 10.68 (s, 1H), 8.21 (s, 1H), 6.90 (s, 1H), 4.40 (q,  $J = 7.12$  Hz, 2H), 2.40 (s, 3H), 1.42 (t,  $J = 7.12$ , 3H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 168.9, 161.5, 149.4, 139.5, 118.8, 112.5, 87.4, 61.7, 28.6, 14.2; LRMS (ESI) calcd for  $\text{C}_{10}\text{H}_{11}\text{IO}_3$   $[\text{M+H}]^+$ : 306.98, found 306.97



#### ethyl 3-fluoro-2-hydroxy-6-methylbenzoate ( **25** )

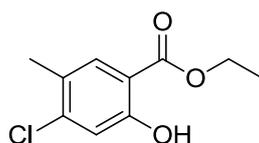
Following the general procedure, ethyl 5-fluoro-2-methylbenzoate (36 mg, 0.2 mmol), iodic acid (18 mg, 0.1 mmol), potassium persulfate (27 mg, 0.1 mmol) and  $[\text{RuCl}_2(\text{p-cymene})]_2$  (5 mol%, 0.01 mmol) were used with TFA: TFAH=0.6 ml:0.4 ml as solvent. The reaction mixture was stirred at 100 °C in the sealed tube for 9 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: EtOAc

= 100:1). Finally, compound **25** (32 mg, colorless oil) was isolated in 81% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 11.39 (s, 1H), 7.09 (dd, *J* = 8.76 Hz, *J* = 10.08 Hz, 1H), 6.61 (dd, *J* = 4.84 Hz, *J* = 8.28 Hz, 1H), 4.44 (q, *J* = 7.16 Hz, 2H), 2.50 (s, 3H), 1.43 (t, *J* = 7.16 Hz, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 169.6, 165.6 (*J*<sub>C-F</sub> = 252.41 Hz), 161.7 (d, *J*<sub>C-F</sub> = 13.9 Hz), 132.4 (d, *J*<sub>C-F</sub> = 8.36 Hz), 116.3 (d, *J*<sub>C-F</sub> = 18.35 Hz), 108.8 (d, *J*<sub>C-F</sub> = 2.53 Hz), 103.9 (d, *J*<sub>C-F</sub> = 25.33 Hz), 61.4, 14.2, 13.71 (d, *J*<sub>C-F</sub> = 3.34 Hz); LRMS (ESI) calcd for C<sub>10</sub>H<sub>11</sub>FO<sub>3</sub> [M-H]<sup>-</sup>: 197.07, found 196.91



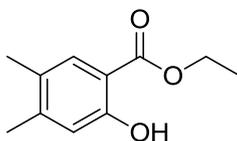
#### ethyl 2-hydroxy-4,6-dimethylbenzoate ( **26** )

Following the general procedure, ethyl 2,4-dimethylbenzoate (54 mg, 0.3mmol), iodic acid (26 mg, 0.15 mmol), potassium persulfate (49 mg, 0.18 mmol) and [RuCl<sub>2</sub>(p-cymene)]<sub>2</sub> (2.5 mol%, 0.0075 mmol) were used with TFA: TFAH=0.6 ml:0.4 ml as solvent. The reaction mixture was stirred at 79 °C in the sealed tube for 7.5 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **26** (36 mg, colorless oil) was isolated in 66% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 11.43 (s, 1H), 6.65 (s, 1H), 6.52 (s, 1H), 4.40 (q, *J* = 7.12 Hz, 2H), 2.50 (s, 3H), 2.26 (s, 3H), 1.41 (t, *J* = 7.12 Hz, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 171.7, 163.0, 145.1, 141.0, 124.2, 115.7, 109.6, 61.3, 24.0, 21.4, 14.1; LRMS (ESI) calcd for C<sub>11</sub>H<sub>14</sub>O<sub>3</sub> [M-H]<sup>-</sup>: 193.09, found 192.90



#### ethyl 4-chloro-2-hydroxy-5-methylbenzoate ( **27** )

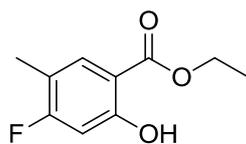
Following the general procedure, ethyl 4-chloro-3-methylbenzoate (40 mg, 0.2 mmol), selectfluor (143 mg, 0.4 mmol) and [RuCl<sub>2</sub>(p-cymene)]<sub>2</sub> (2.5 mol%, 0.005 mmol) were used with TFA: TFAH=0.6 ml:0.4 ml as solvent. The reaction mixture was stirred at 85 °C in the sealed tube for 10.5 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **27** (32 mg, colorless oil) was isolated in 78% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 10.68 (s, 1H), 7.68 (s, 1H), 7.01 (s, 1H), 4.40 (q, *J* = 7.16 Hz, 2H), 2.30 (s, 3H), 1.42 (t, *J* = 7.16 Hz, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 169.7, 160.0, 141.5, 131.1, 126.8, 117.9, 111.2, 61.6, 19.1, 14.2; LRMS (ESI) calcd for C<sub>10</sub>H<sub>11</sub>ClO<sub>3</sub> [M-H]<sup>-</sup>: 213.04, found 212.81



#### ethyl 2-hydroxy-4,5-dimethylbenzoate ( **28** )

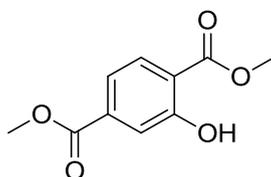
Following the general procedure, ethyl 3,4-dimethylbenzoate (35 mg, 0.2 mmol), potassium persulfate (57 mg, 0.21 mmol) and [RuCl<sub>2</sub>(p-cymene)]<sub>2</sub> (5 mol%, 0.01 mmol) were used with TFA: TFAH=0.6 ml:0.4 ml as solvent. The reaction mixture was stirred at 85 °C in the sealed tube for 6 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: EtOAc = 100:1). Finally, compound **28** (27 mg, colorless oil) was isolated in 70% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 10.59 (s, 1H), 7.56 (s, 1H), 6.77 (s, 1H), 4.38 (q, *J* = 7.12 Hz, 2H), 2.24 (s, 3H), 2.19 (s, 3H), 1.41 (t, *J* = 7.12 Hz, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 170.2, 159.8, 145.7, 129.8, 127.4, 118.2, 110.0, 61.1, 20.4, 18.8, 14.3; LRMS (ESI) calcd for C<sub>11</sub>H<sub>14</sub>O<sub>3</sub>

[M-H]<sup>-</sup>: 193.09, found 192.97



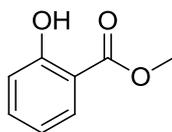
#### ethyl 4-fluoro-2-hydroxy-5-methylbenzoate ( 29 )

Following the general procedure, ethyl 4-fluoro-3-methylbenzoate (37 mg, 0.2mmol), Potassium persulfate (60 mg, 0.22 mmol) and [RuCl<sub>2</sub>(p-cymene)]<sub>2</sub> (2.5 mol%, 0.005 mmol) were used with TFA: TFAH=1.4 ml:0.6 ml as solvent. The reaction mixture was stirred at 90 °C in the sealed tube for 11 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **29** (21 mg, colorless oil) was isolated in 52% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 10.83 (d, *J* = 1.64 Hz, 1H), 7.65 (d, *J* = 8.76 Hz, 1H), 6.60 (d, *J* = 10.92 Hz, 1H), 4.37 (q, *J* = 7.16 Hz, 2H), 2.18 (d, *J* = 1.16 Hz, 3H), 1.39 (t, *J* = 7.12 Hz, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 171.2 (d, *J* = 3.52 Hz) 150.1 (d, *J* = 241.26 Hz), 151.2, 136.1 (d, *J* = 4.04 Hz), 121.4 (d, *J* = 6.33 Hz), 119.8 (d, *J* = 16.75 Hz), 114.1 (d, *J* = 2.42 Hz), 62.0, 23.6, 14.1; LRMS (ESI) calcd for C<sub>10</sub>H<sub>11</sub>FO<sub>3</sub> [M-H]<sup>-</sup>: 197.07, found 196.98



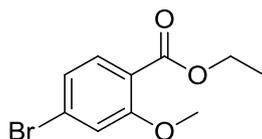
#### dimethyl 2-hydroxyterephthalate ( 30 )

Following the general procedure, dimethyl terephthalate (39 mg, 0.2 mmol), selectfluor (143 mg, 0.4 mmol) and [RuCl<sub>2</sub>(p-cymene)]<sub>2</sub> (2.5 mol%, 0.005 mmol) were used with TFA: TFAH=0.6 ml:0.4 ml as solvent. The reaction mixture was stirred at 113 °C in the sealed tube for 9.5 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **30** (39 mg, light green solid) was isolated in 93% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 10.76 (s, 1H), 7.92 (d, *J* = 8.28 Hz, 1H), 7.65 (d, *J* = 1.52 Hz, 1H), 7.55 (dd, *J* = 1.52 Hz, *J* = 8.28 Hz, 1H), 4.00 (s, 3H), 3.95 (s, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 170.0, 166.0, 161.3, 136.5, 130.0, 119.7, 119.0, 115.7, 52.6, 52.5; LRMS (ESI) calcd for C<sub>10</sub>H<sub>10</sub>O<sub>5</sub> [M+H]<sup>+</sup>: 211.1, found 211.2



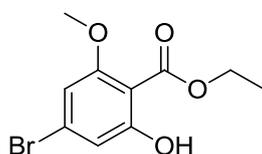
#### methyl 2-hydroxybenzoate ( 31 )

Following the general procedure, methyl benzoate (45 mg, 0.3mmol), Potassium persulfate (90 mg, 0.33 mmol) and [RuCl<sub>2</sub>(p-cymene)]<sub>2</sub> (2.5mol%, 0.0075mmol) were used with TFA: TFAH=1.9 ml:0.1 ml as solvent. The reaction mixture was stirred at 85 °C in the sealed tube for 10 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **31** (29 mg, colorless oil) was isolated in 60% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 10.75 (s, 1H), 7.83 (dd, *J* = 1.56 Hz, *J* = 7.96 Hz, 1H), 7.47 - 7.42 (m, 1H), 6.97 (d, *J* = 8.36 Hz, 1H), 6.87 (t, *J* = 7.52 Hz, 1H), 3.94 (s, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 170.6, 161.6, 135.7, 130.0, 119.2, 117.6, 112.4, 52.3 ; LRMS (ESI) calcd for C<sub>8</sub>H<sub>8</sub>O<sub>3</sub> [M-H]<sup>-</sup>: 151.05, found 150.89



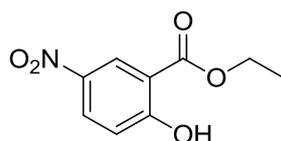
#### ethyl 4-bromo-2-methoxybenzoate ( 33 )

Ethyl 4-bromo-2-hydroxybenzoate (8) (147 mg, 0.6 mmol) was dissolved with 2 ml DMF in a round-bottom flask, following that, potassium carbonate (166 mg, 1.2 mmol) and methyl iodide (341 mg, 2.4 mmol) were added. The mixture was stirred at room temperature for 2 h. After that, add DCM, wash with water three times and saturated brine one time. Remove the solvent under reduced pressure, the residue was purified by silica gel column chromatography (Petroleum ether: EtOAc = 100:5). Finally, compound **33** (152mg, colorless oil) was isolated in 98% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.67 (d, *J* = 8.68 Hz, 1H), 7.13 - 7.11 (m, 2 H), 4.34 (q, *J* = 7.12 Hz, 2H), 3.90 (s, 3H), 1.37 (q, *J* = 7.16 Hz, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 165.6, 159.9, 132.9, 127.6, 123.5, 119.4, 115.8, 61.1, 56.4, 14.4; LRMS (ESI) calcd for C<sub>10</sub>H<sub>11</sub>BrO<sub>3</sub> [M+H]<sup>+</sup>:258.99, found 258.89



#### ethyl 4-bromo-2-hydroxy-6-methoxybenzoate ( 34 )

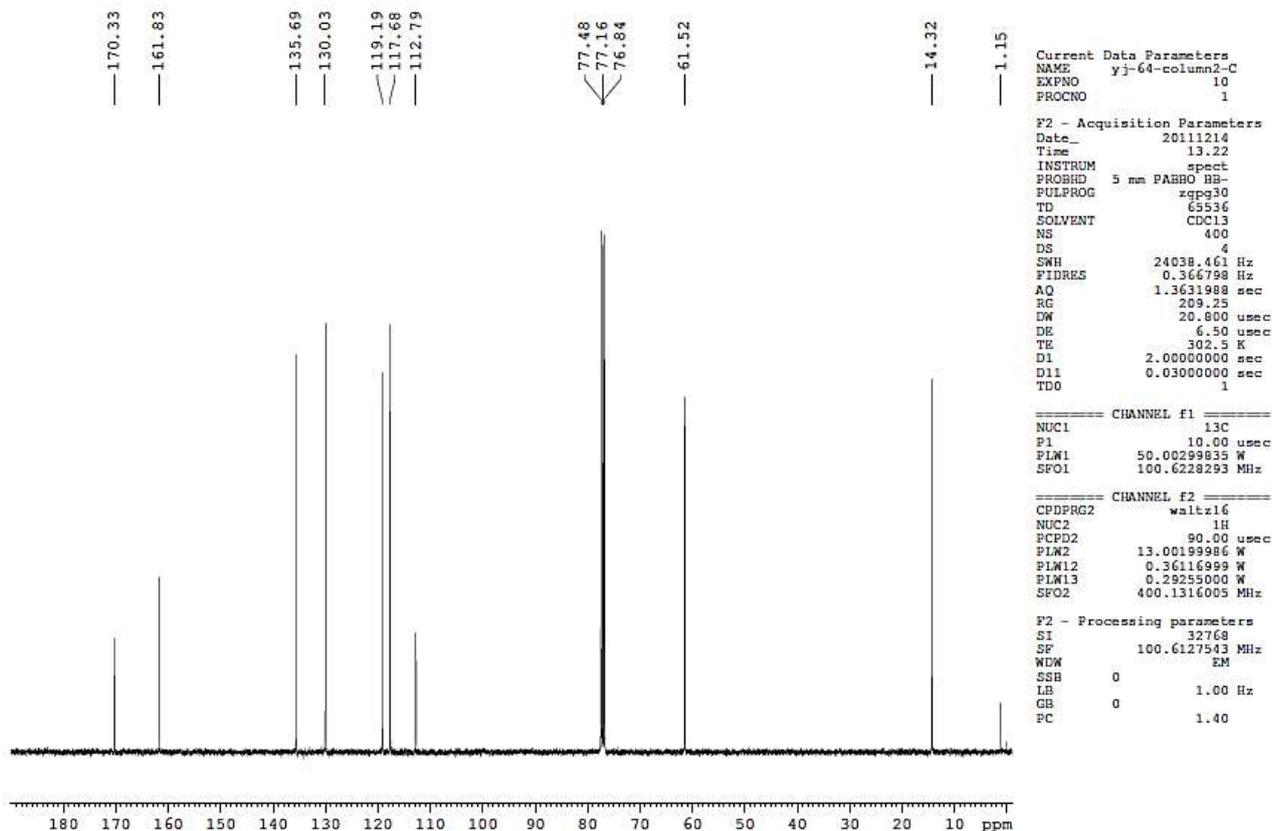
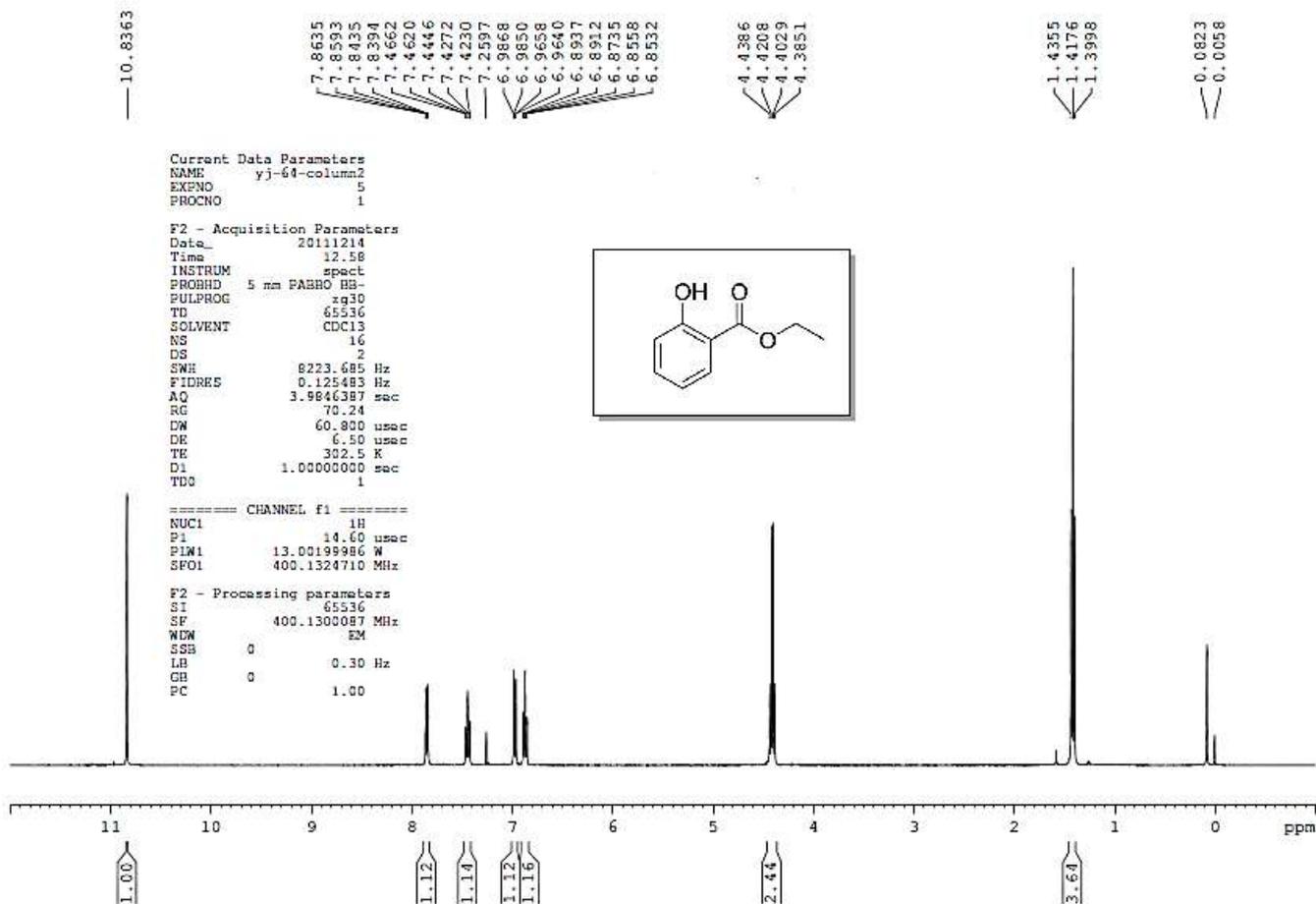
Following the general procedure, ethyl 4-bromo-2-methoxybenzoate (33) (52 mg, 0.2 mmol), Potassium persulfate (55mg, 0.2 mmol) and [RuCl<sub>2</sub>(p-cymene)]<sub>2</sub> (2.5 mol%, 0.005 mmol) were used with TFA: TFAH=0.6 ml:0.4 ml as solvent. The reaction mixture was stirred at 80°C in the sealed tube for 11 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene: EtOAc = 100:20:0.3). Finally, compound **34** (37 mg, white solid) was isolated in 71% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 11.71 (s, 1H), 6.78 (d, *J* = 1.56 Hz, 1H), 6.55 (d, *J* = 1.44 Hz, 1H), 4.41 (d, *J* = 7.16 Hz, 2H), 3.84 (s, 3H), 1.40 (t, *J* = 7.12 Hz, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 170.9, 164.1, 161.3, 129.5, 113.7, 106.6, 102.5, 61.9, 56.5, 14.3; LRMS (ESI) calcd for C<sub>10</sub>H<sub>11</sub>BrO<sub>4</sub> [M+H]<sup>+</sup>:274.98, found 274.91



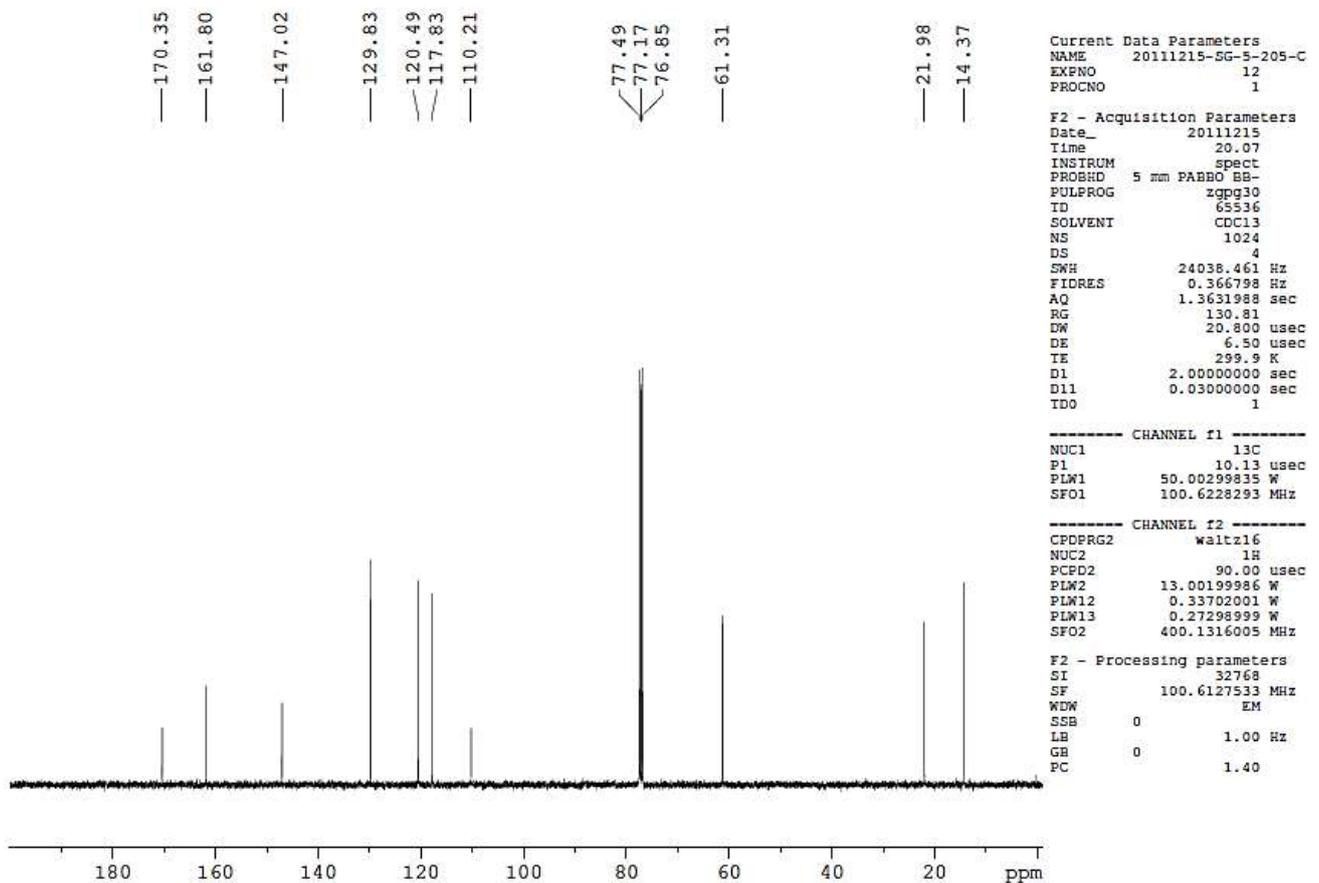
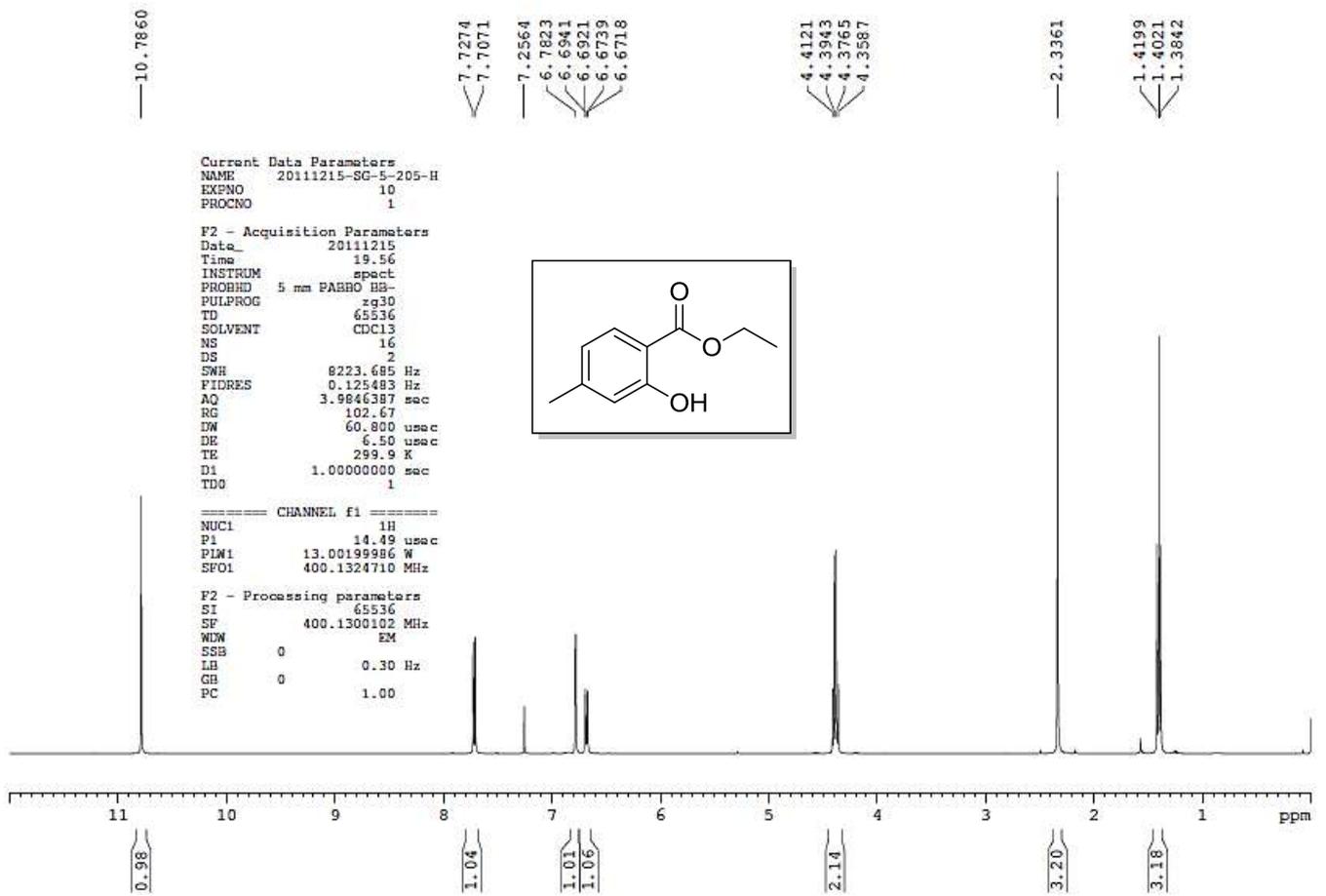
#### ethyl 2-hydroxy-5-nitrobenzoate ( 36 )

Following the general procedure, ethyl 3-nitrobenzoate (39 mg, 0.2 mmol), iodic acid (63 mg, 0.36 mmol) and [RuCl<sub>2</sub>(p-cymene)]<sub>2</sub> (5 mol%, 0.01 mmol) were used with TFA: TFAH=1.5 ml:0.5 ml as solvent. The reaction mixture was stirred at 120°C in the sealed tube for 8 h. After completion of the reaction, the residue was purified by silica gel column chromatography (Petroleum ether: toluene= 100:20). Finally, compound **36** (30mg, yellow solid) was isolated in 72% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 11.54 (s, 1H), 8.78 (d, *J* = 2.84 Hz, 1H), 8.32 (dd, *J* = 2.84 Hz, *J* = 9.20 Hz, 1H), 7.07 (d, *J* = 9.20 Hz, 1H), 4.49 (q, *J* = 7.16 Hz, 2H), 1.47 (t, *J* = 7.16 Hz, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 168.9, 166.3, 139.9, 130.4, 126.6, 118.5, 112.3, 62.6, 14.1; LRMS (ESI) calcd for C<sub>9</sub>H<sub>9</sub>NO<sub>5</sub> [M+H]<sup>+</sup>: 212.05, found 211.69

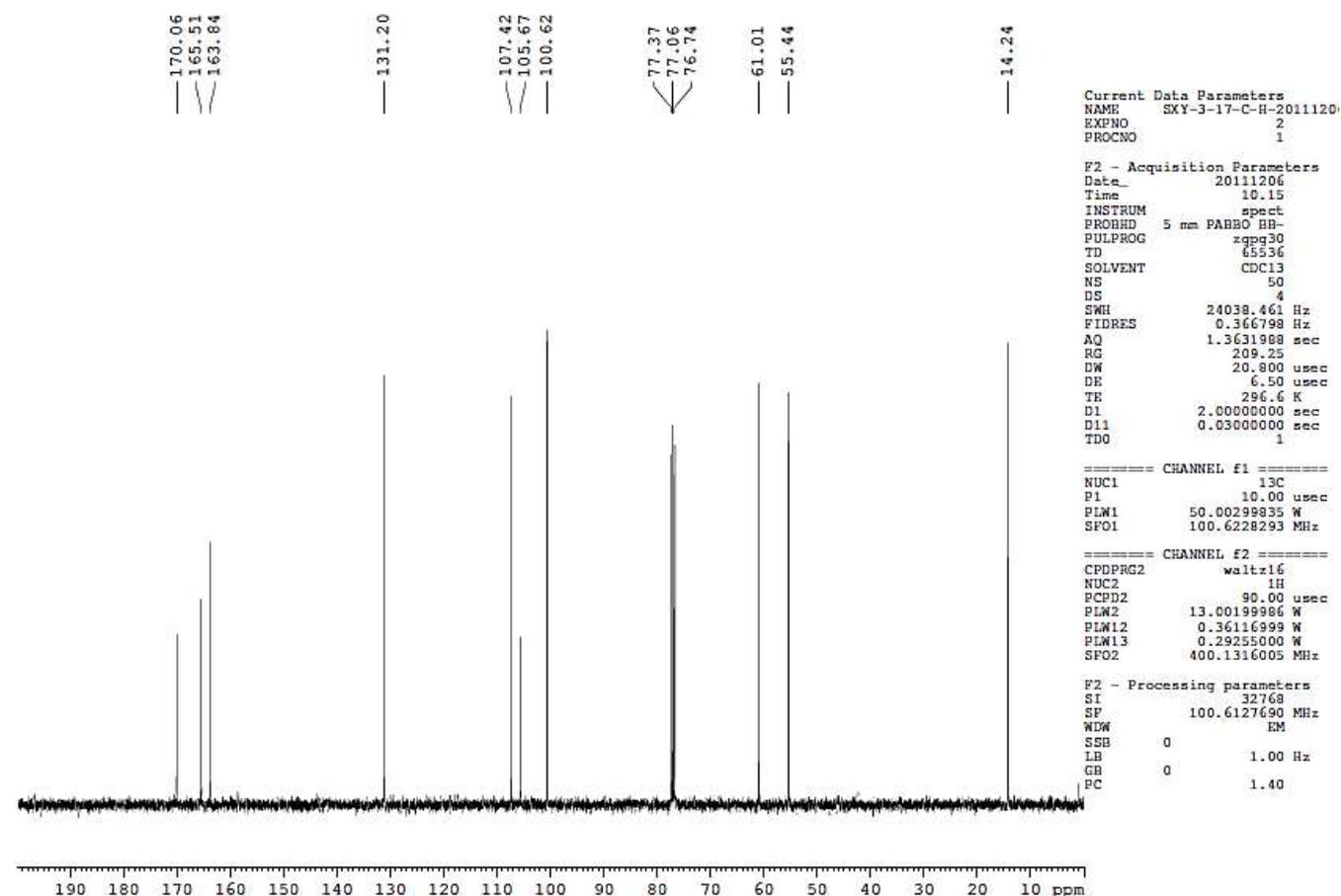
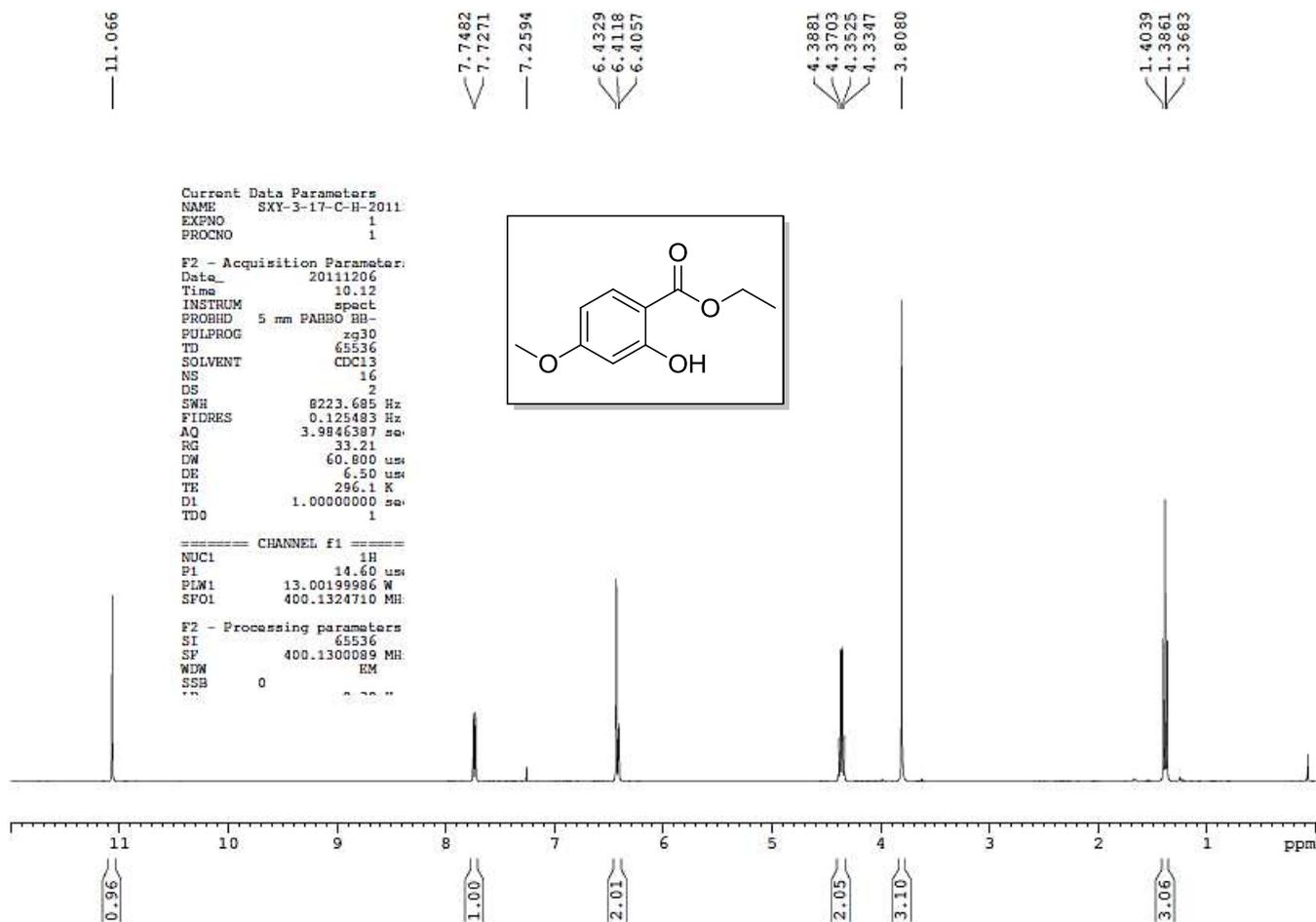
The spectrum of product (2)



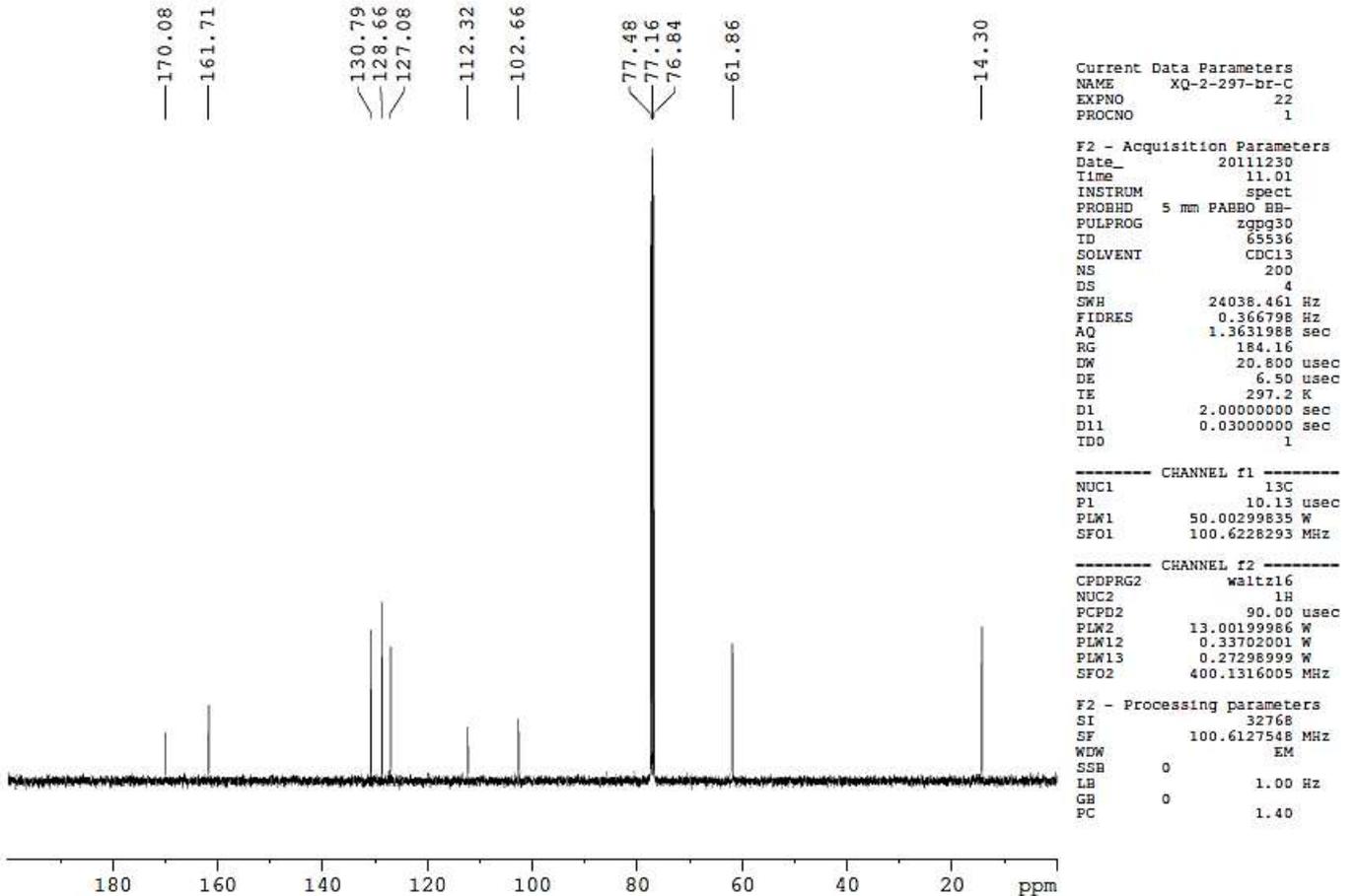
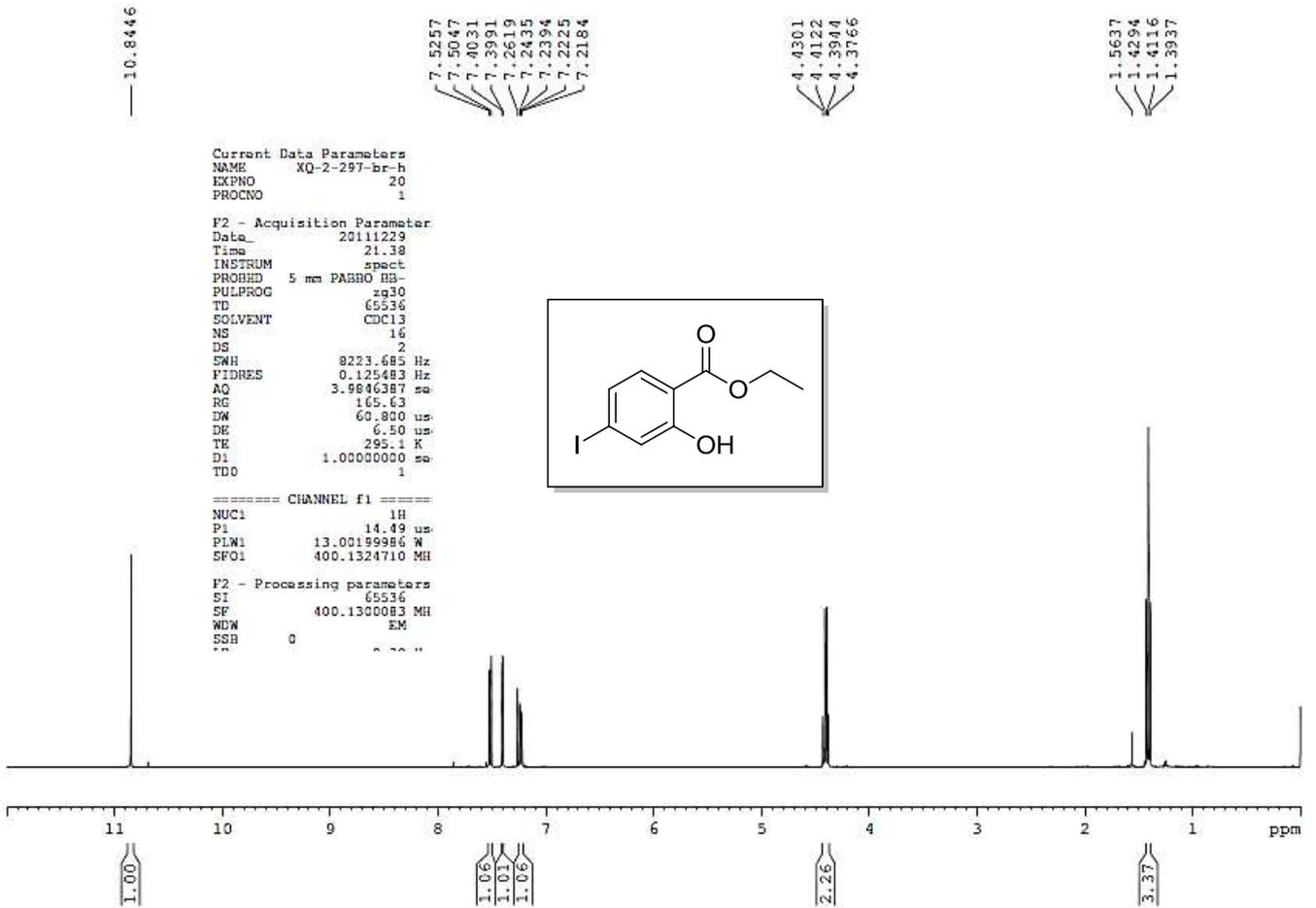
The spectrum of product (3)



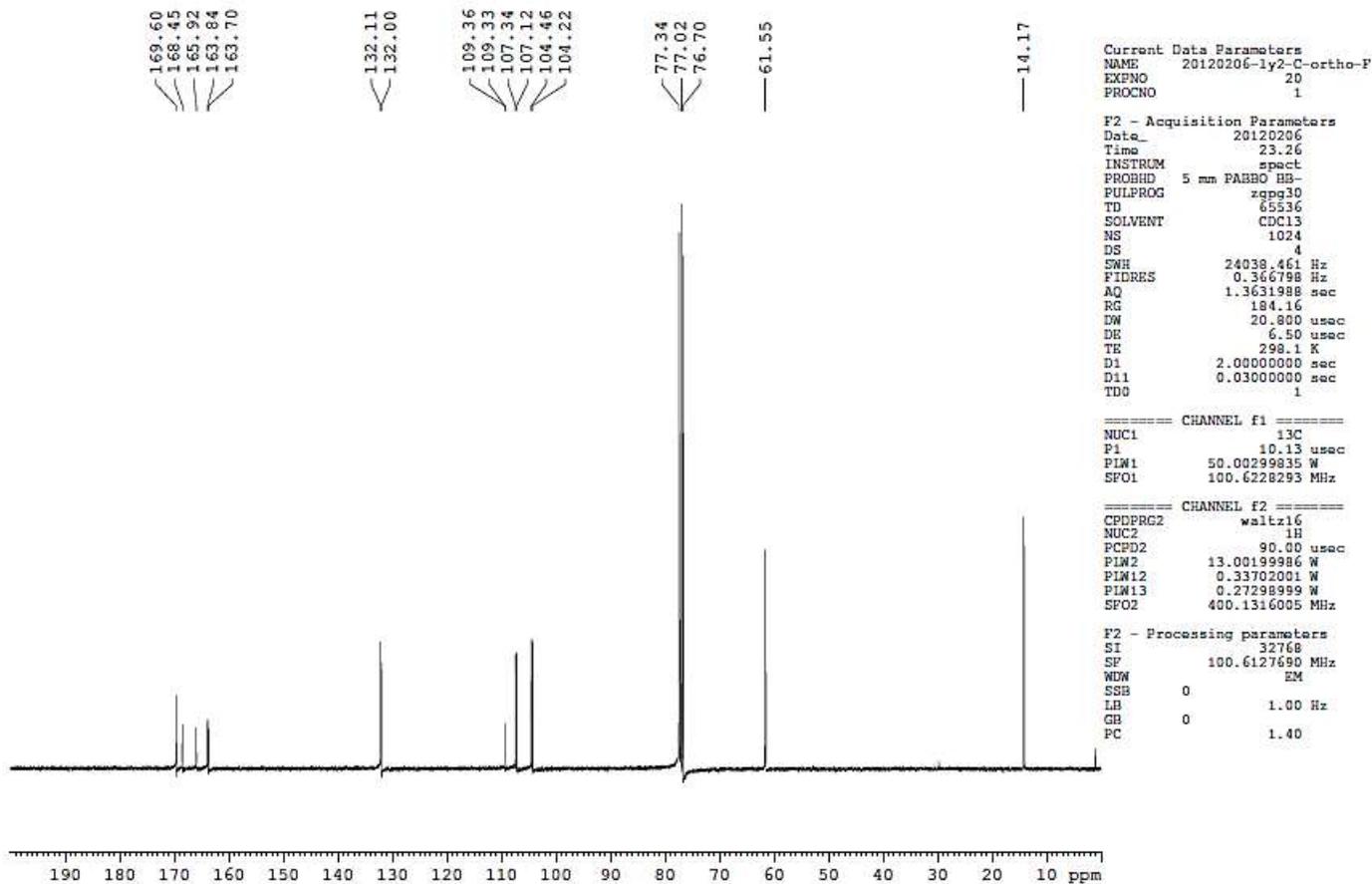
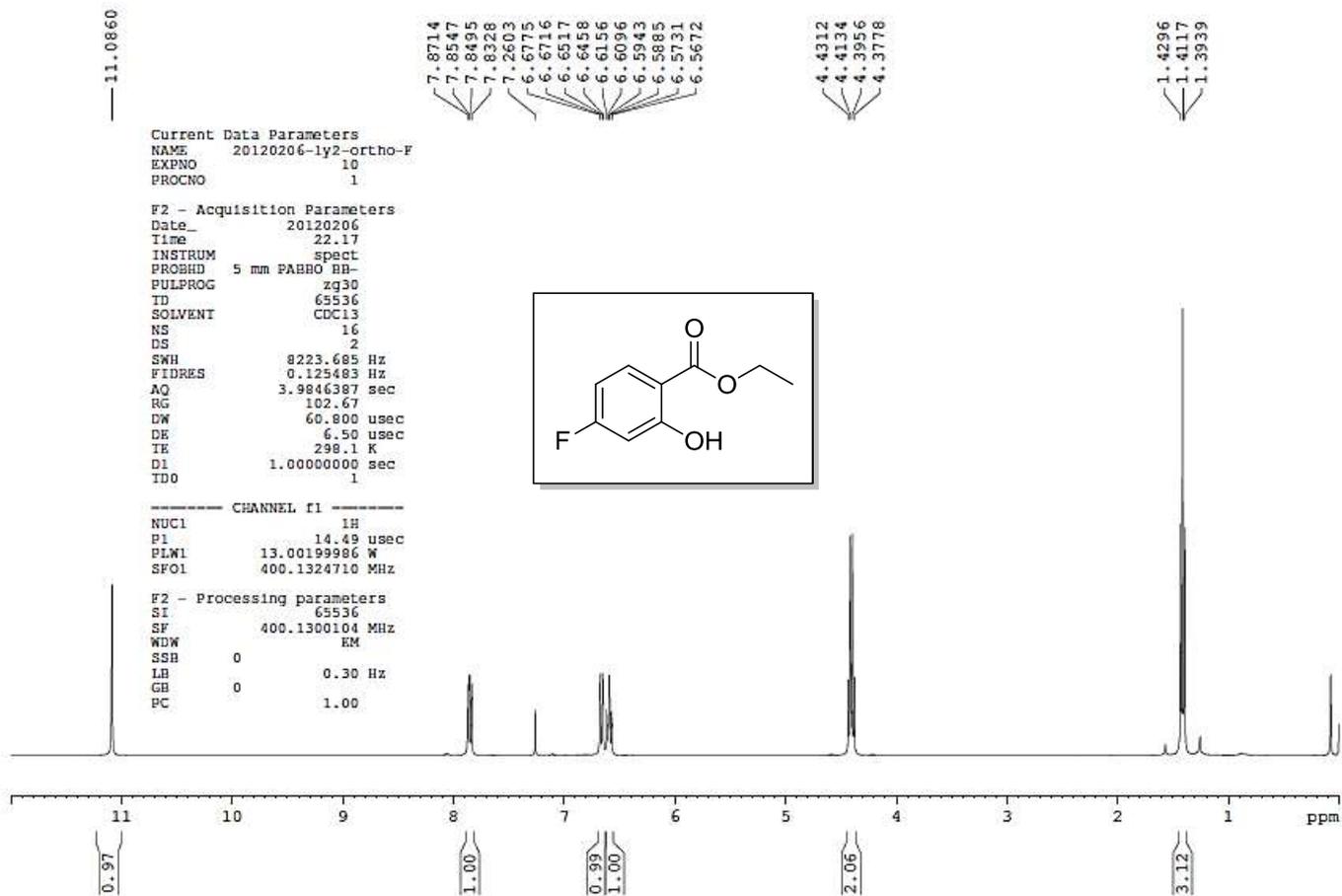
The spectrum of product (4)



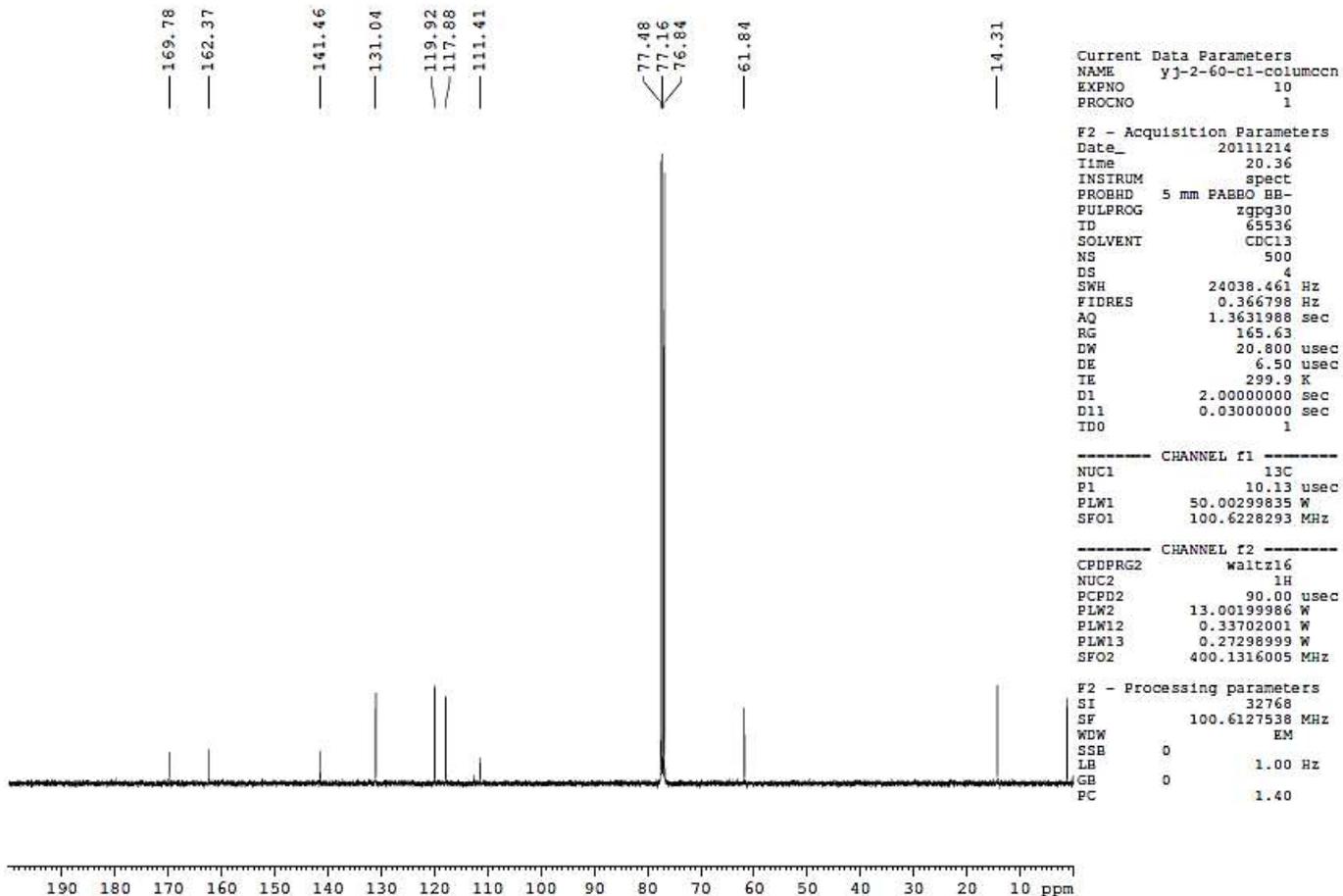
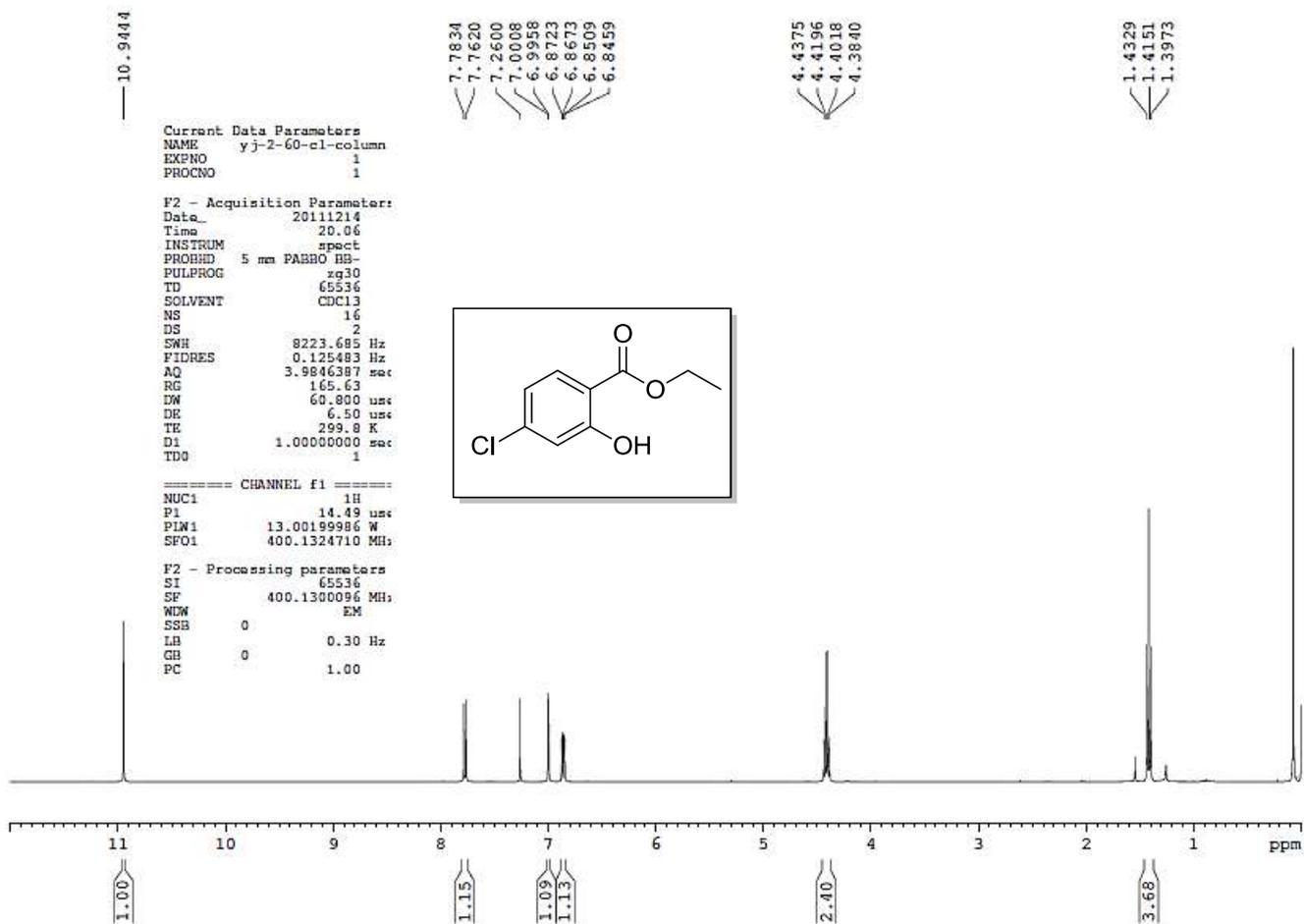
The spectrum of product (5)



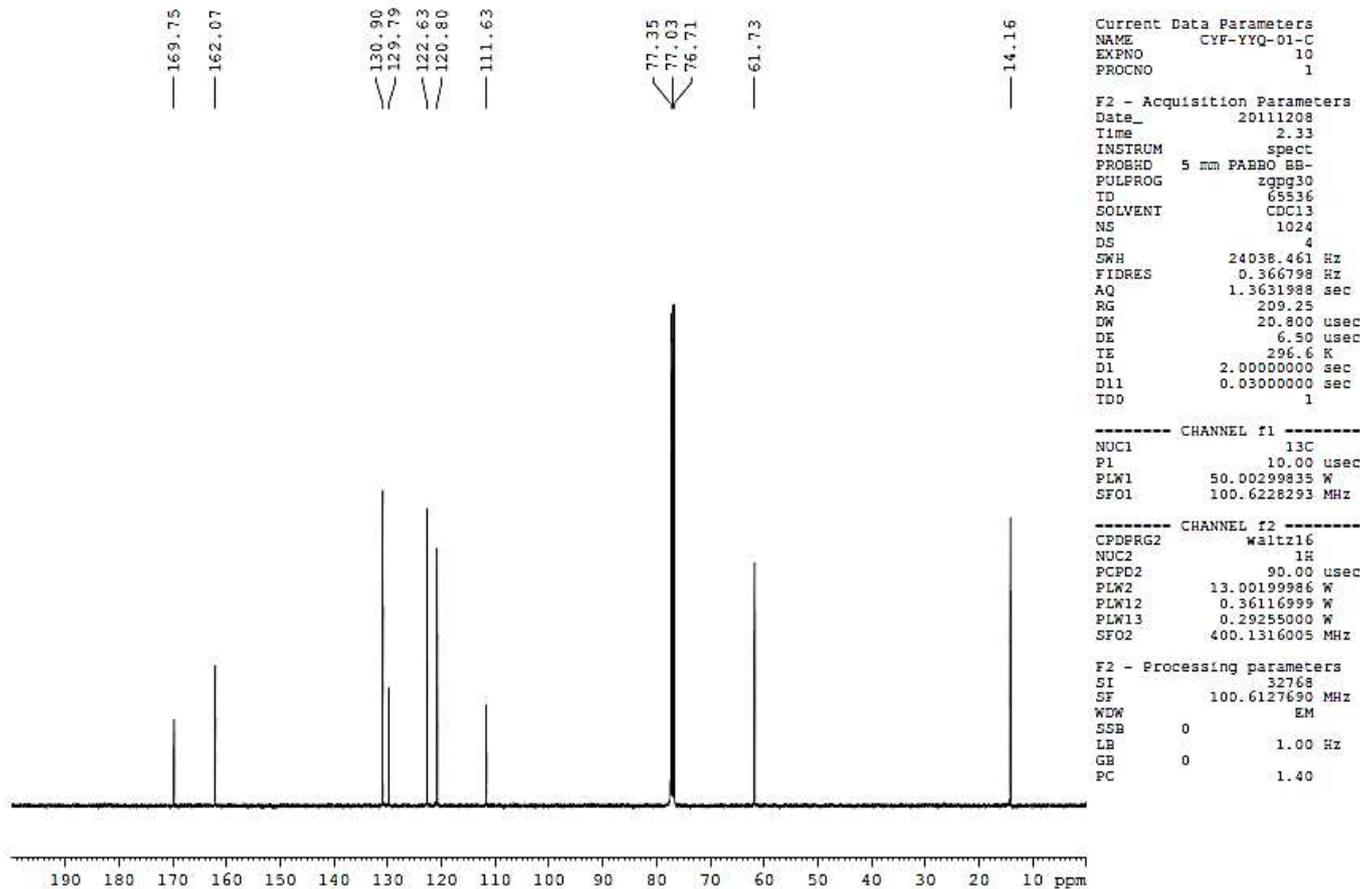
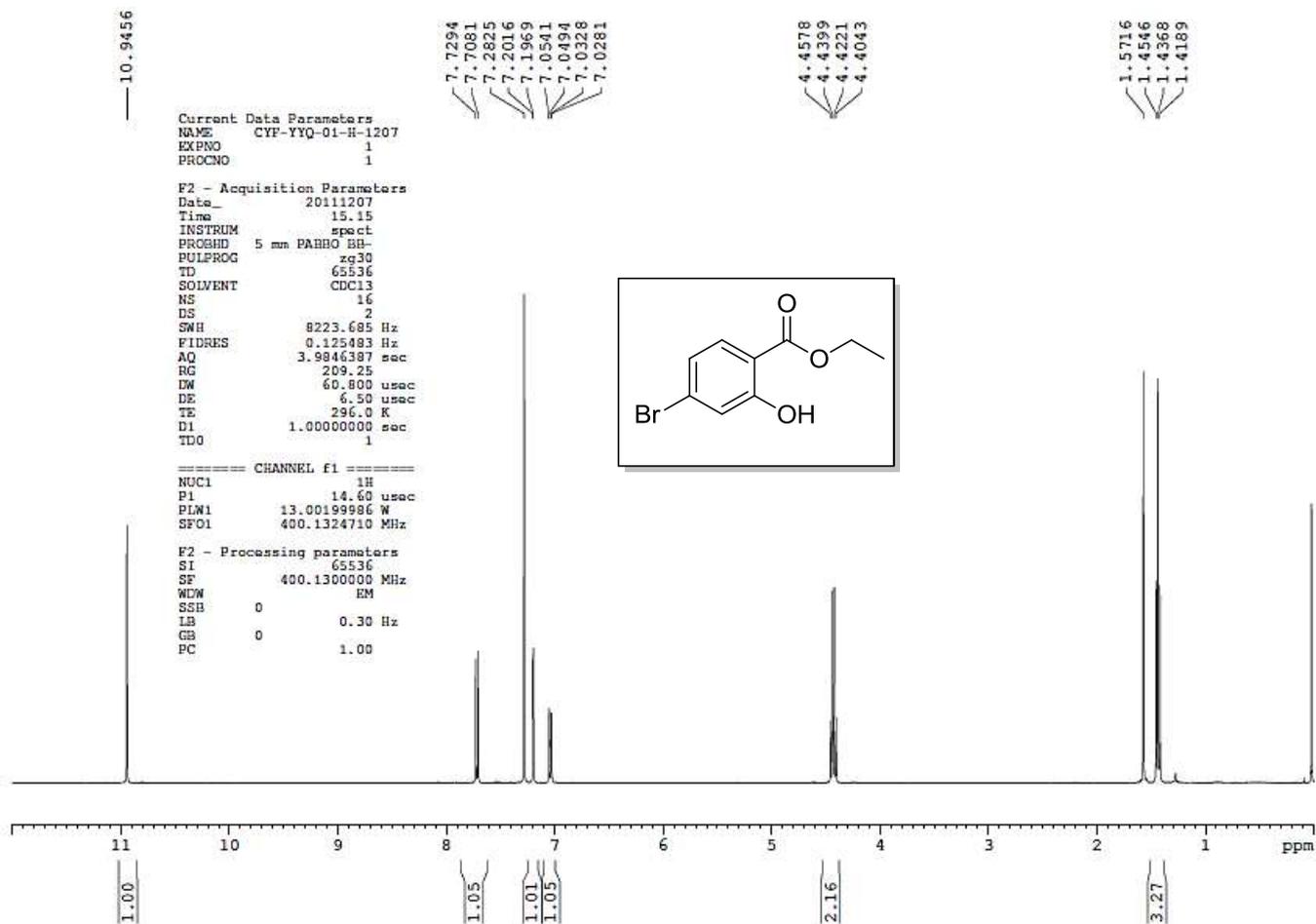
The spectrum of product (6)



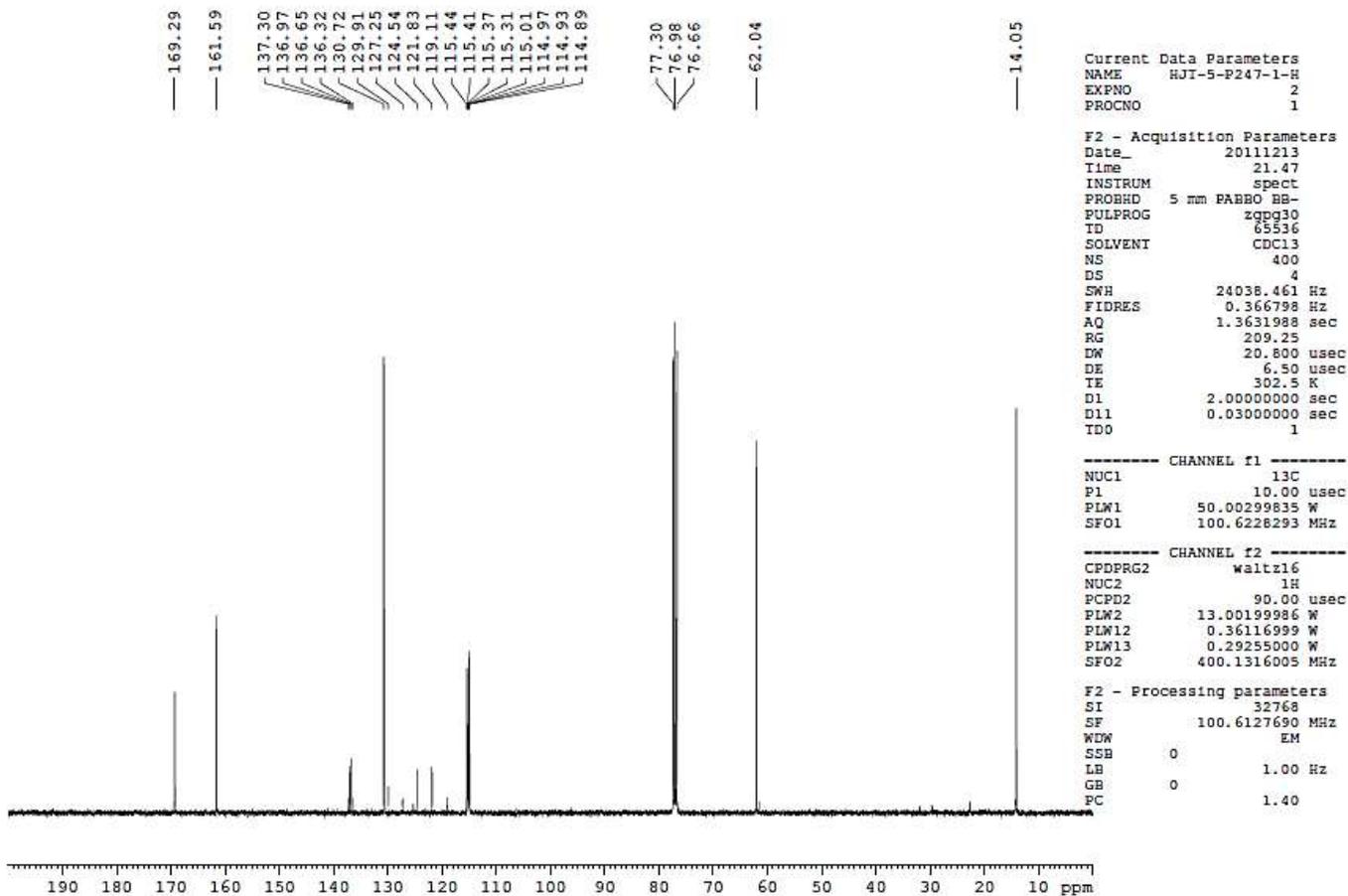
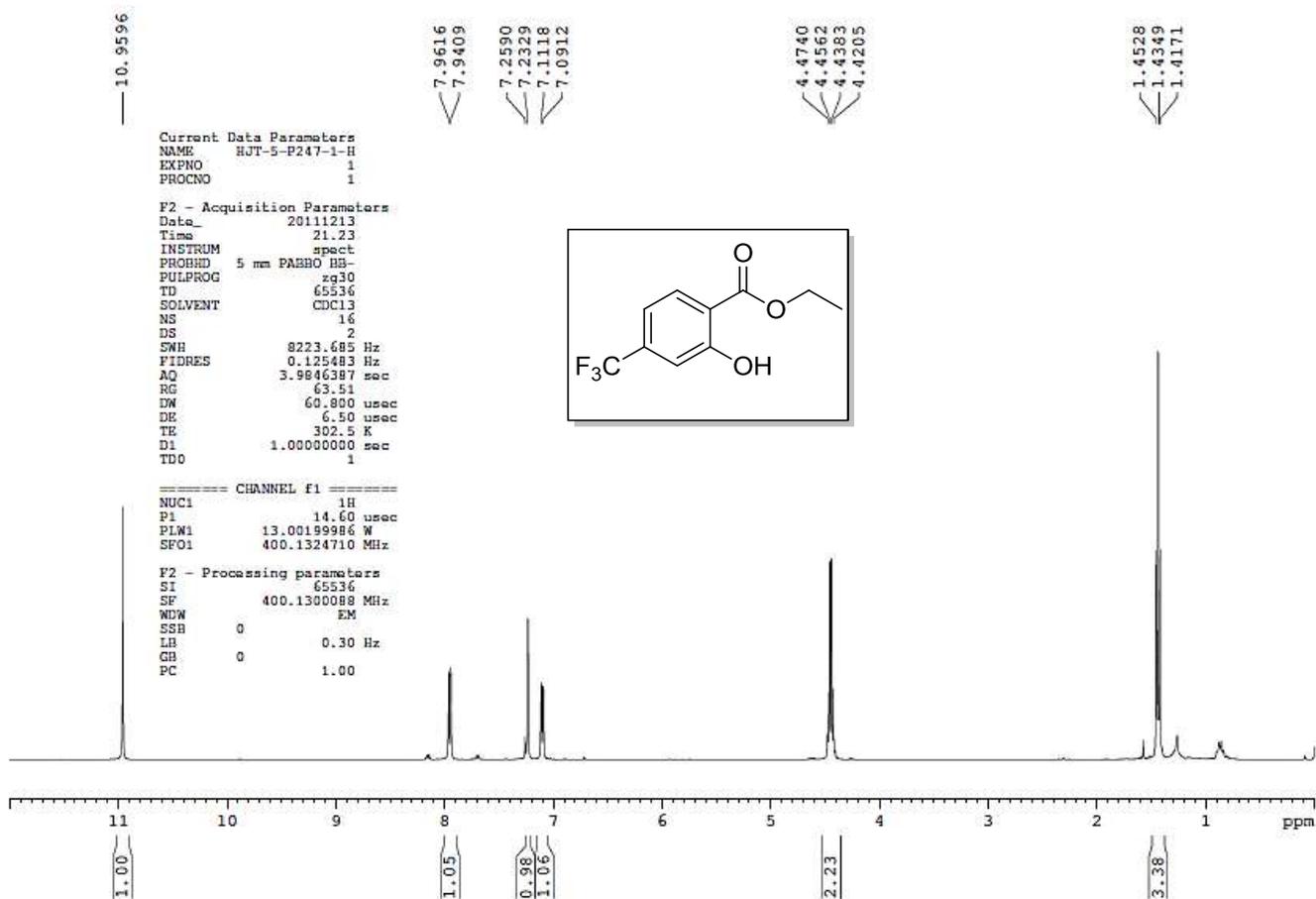
The spectrum of product (7)



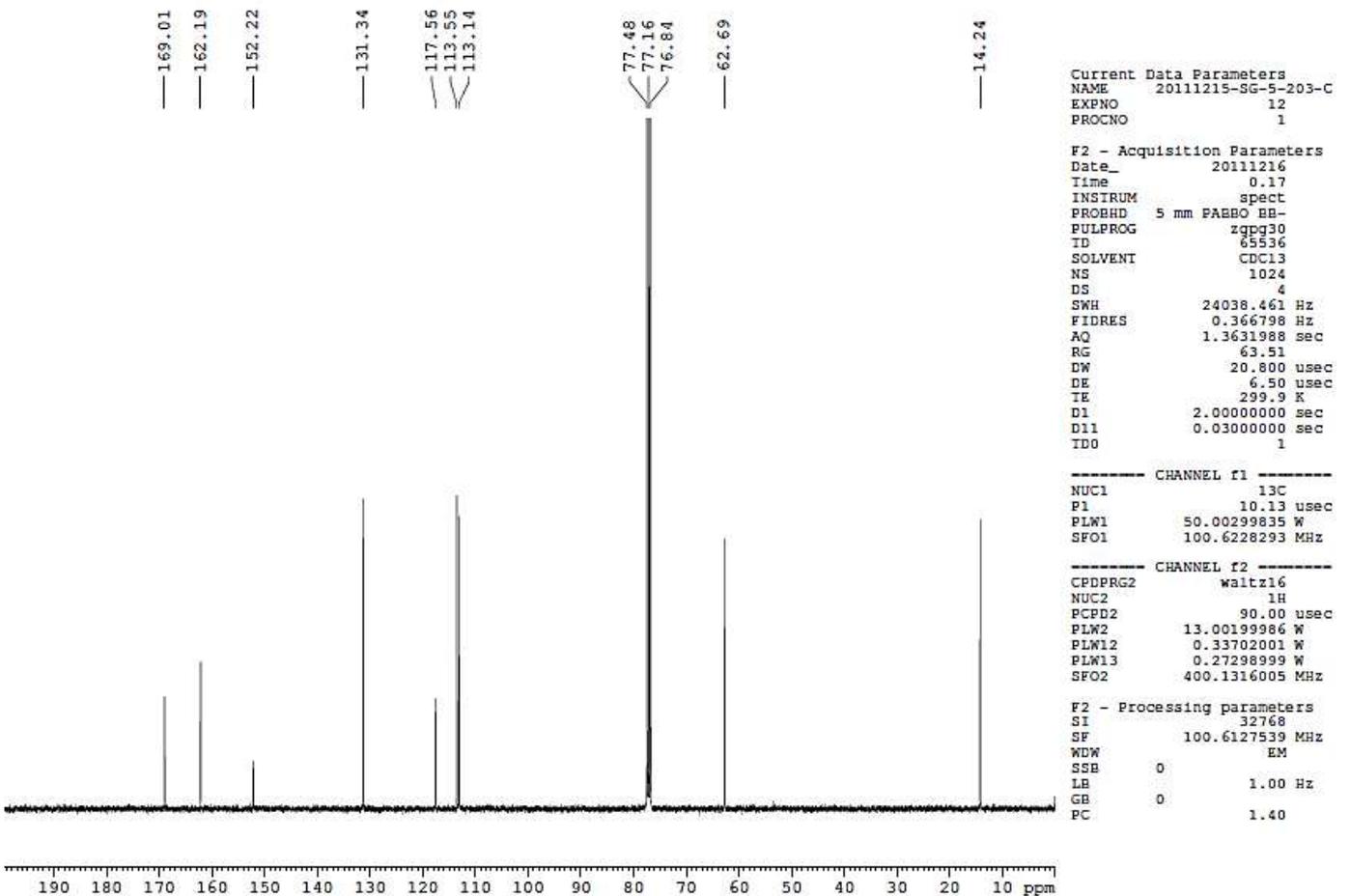
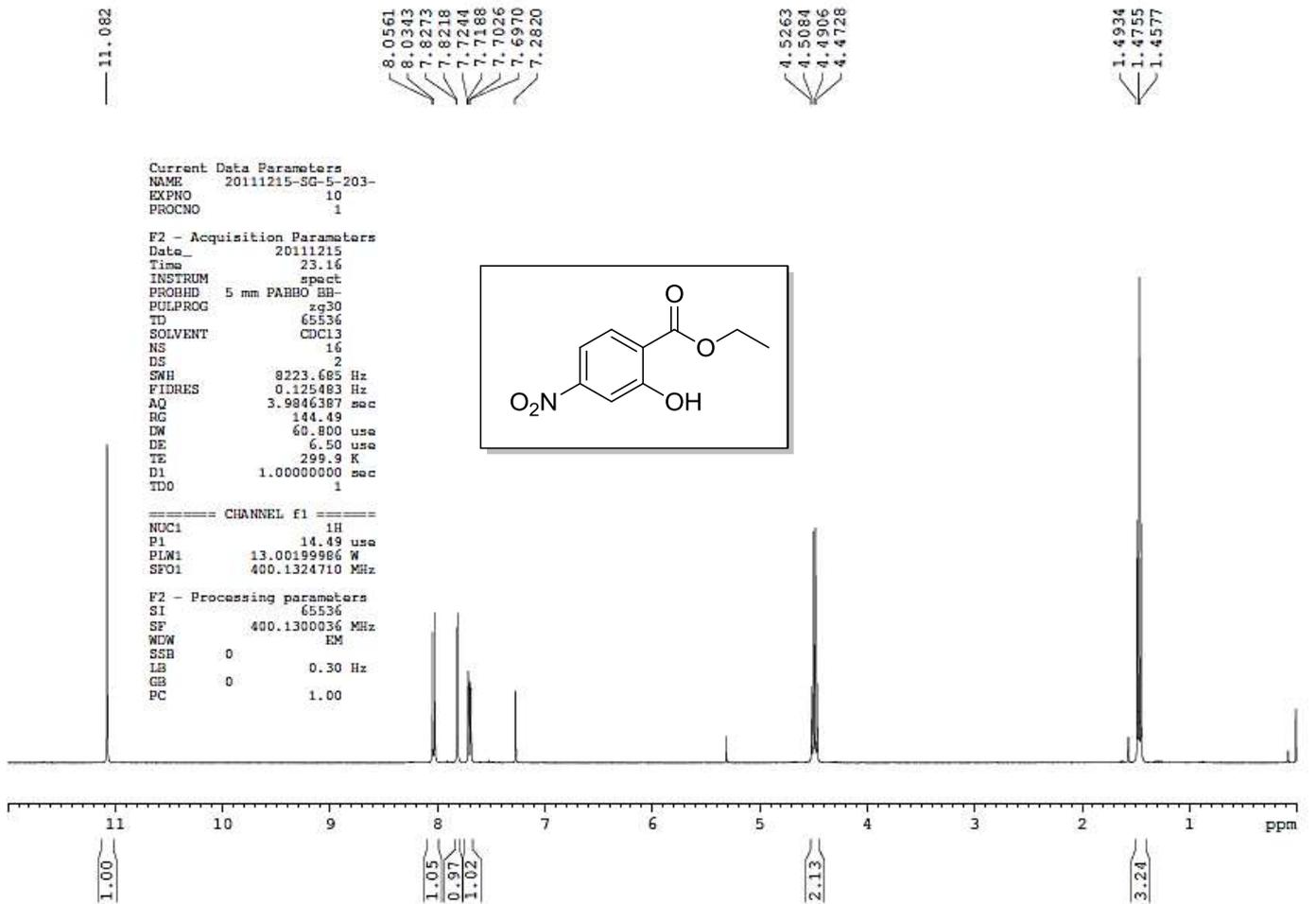
The spectrum of product (8)



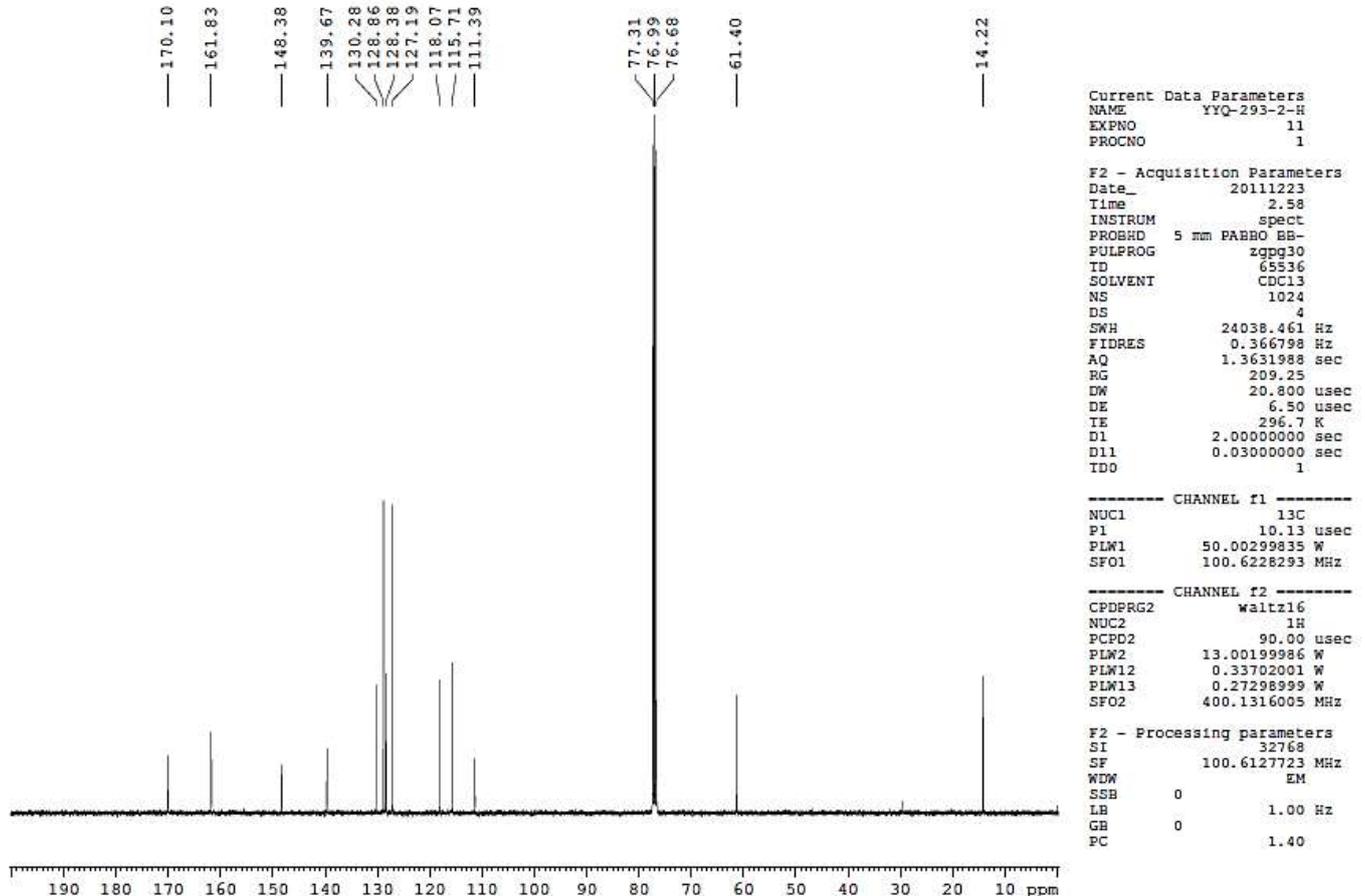
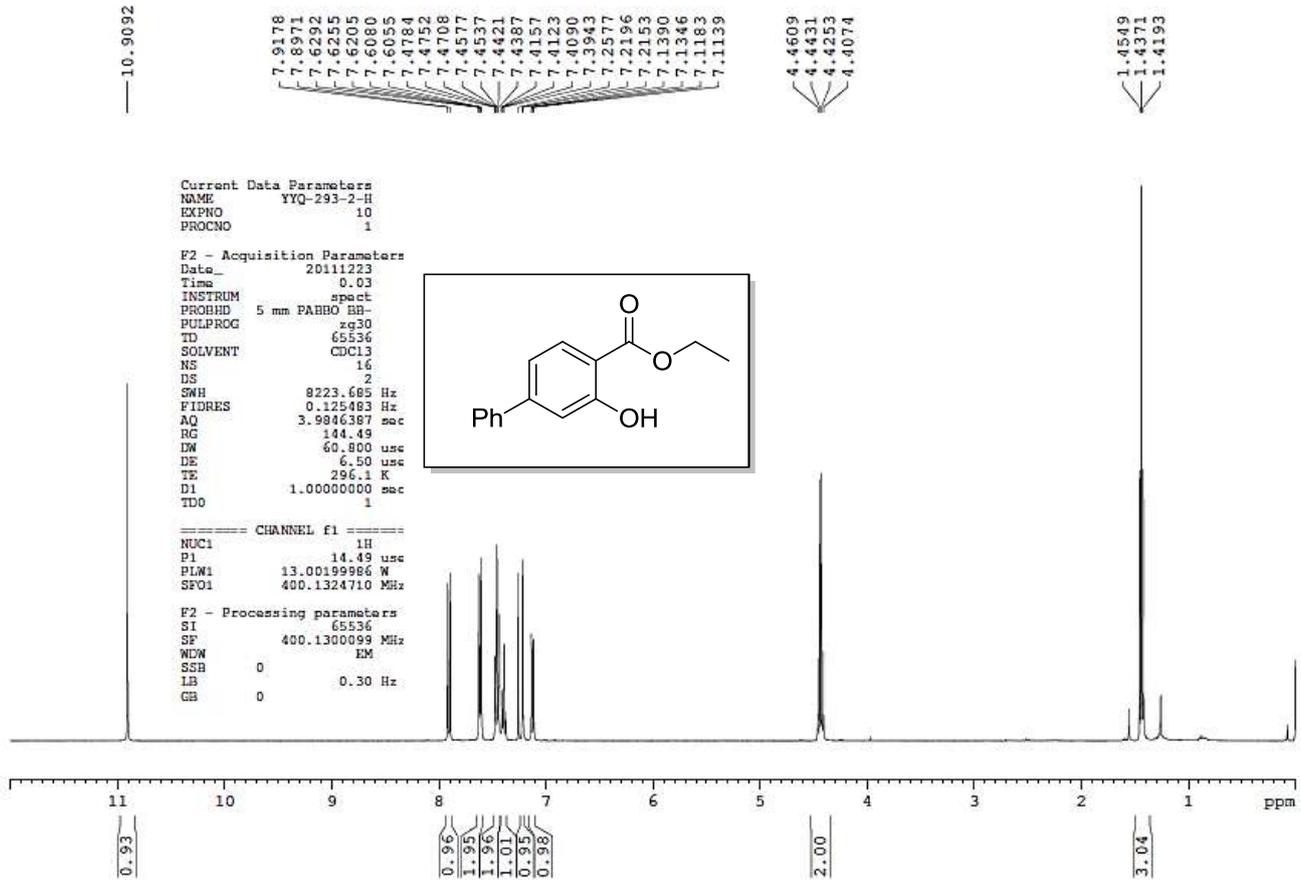
The spectrum of product (9)



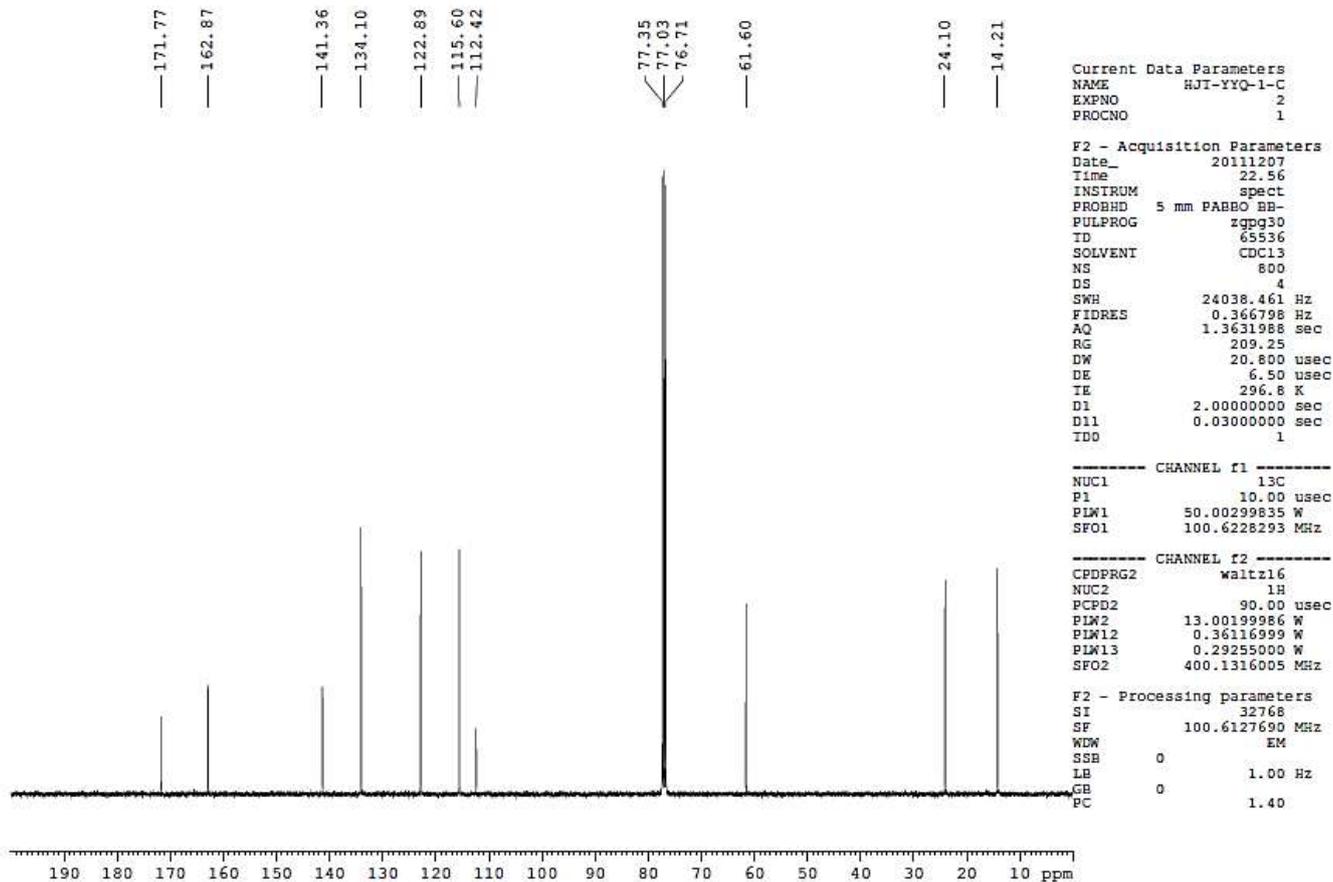
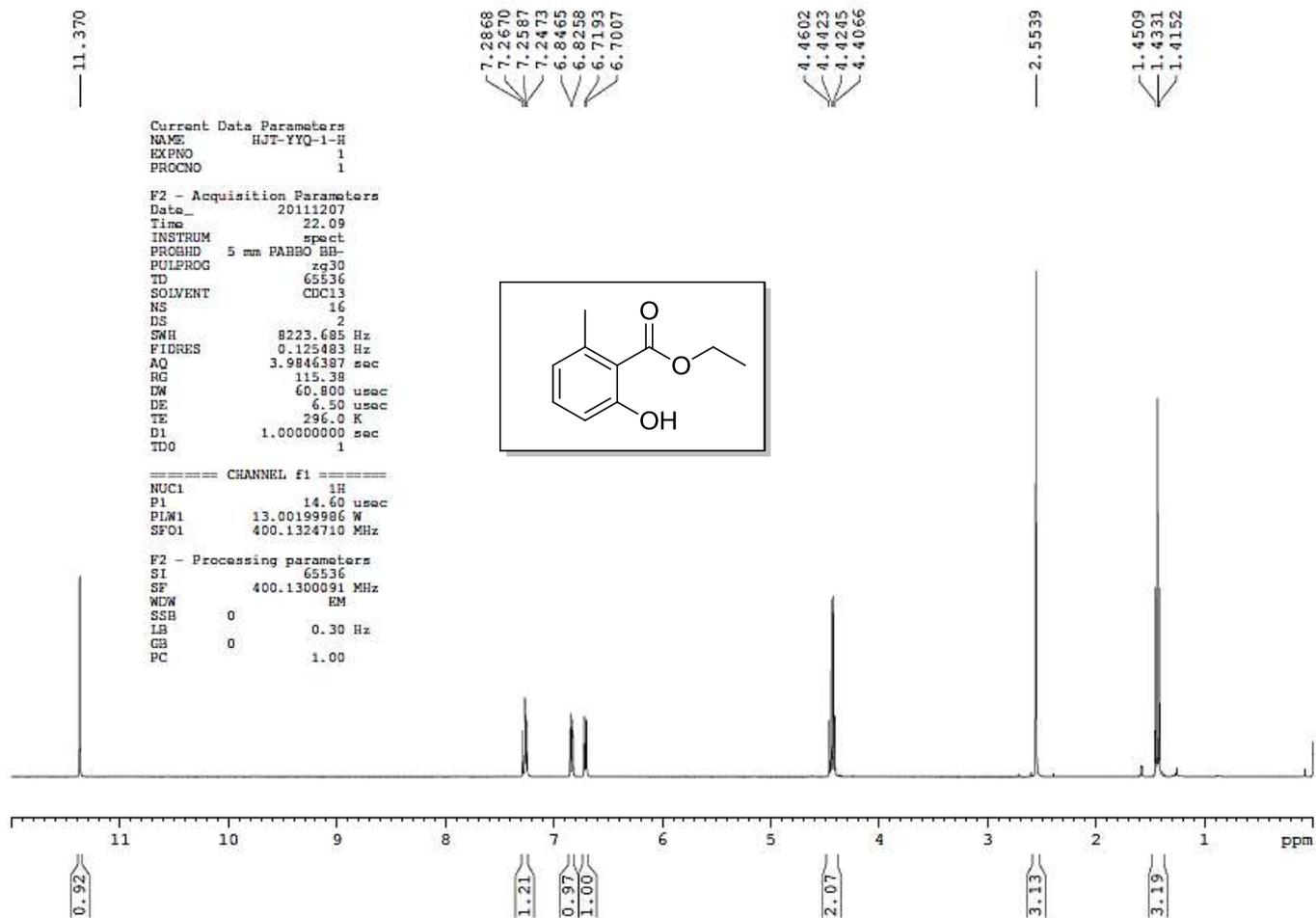
The spectrum of product (10)



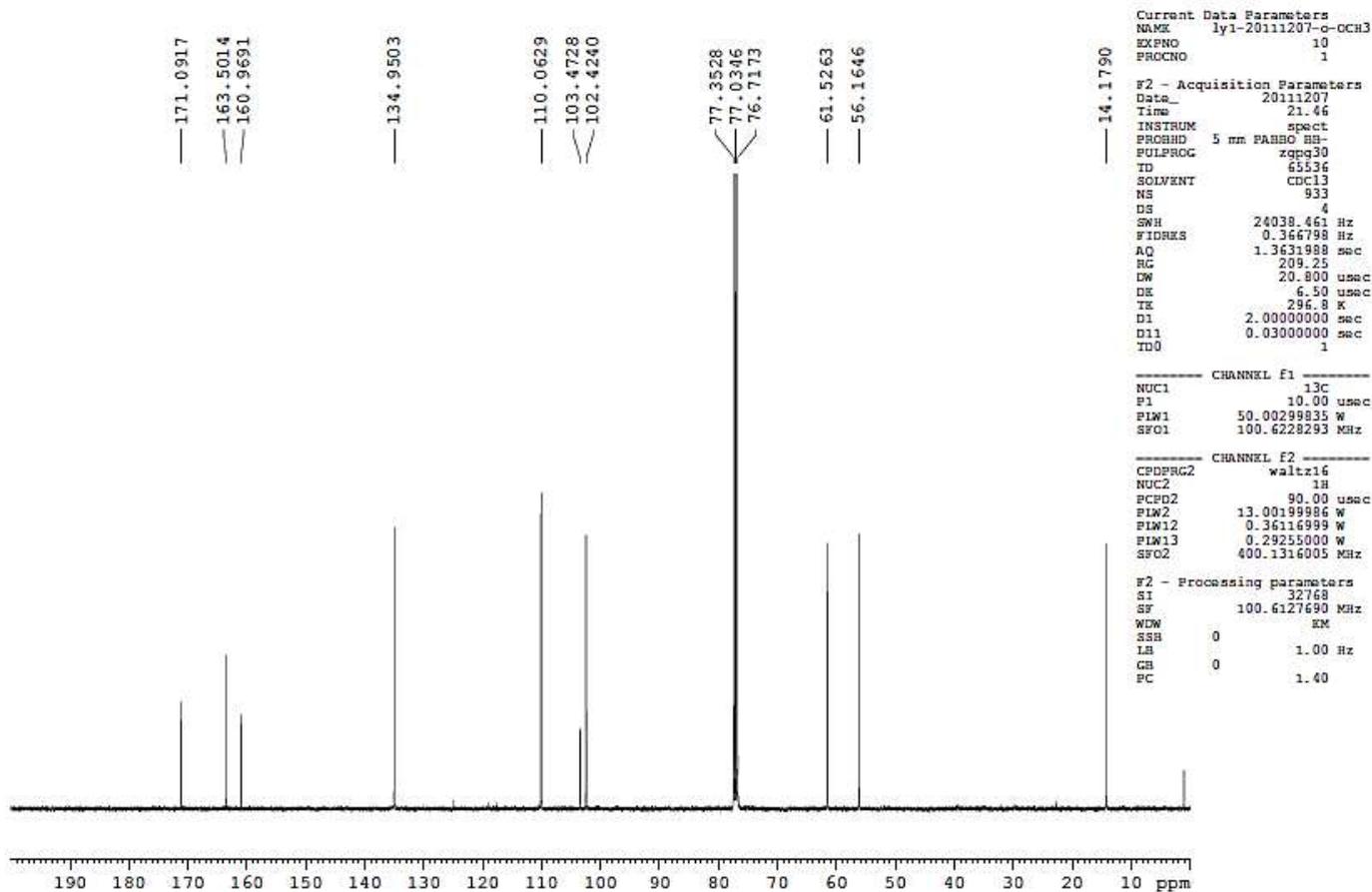
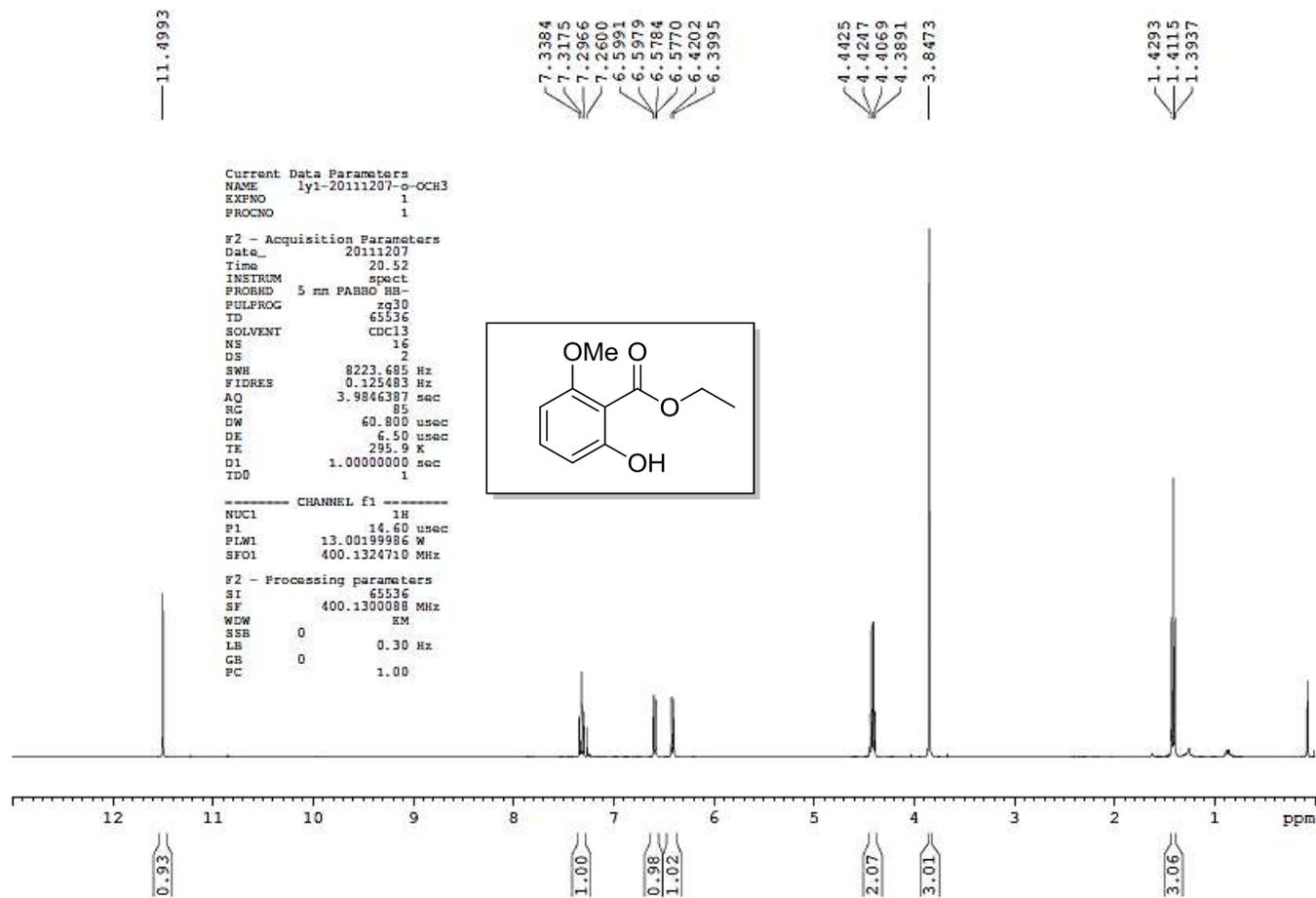
The spectrum of product (11)



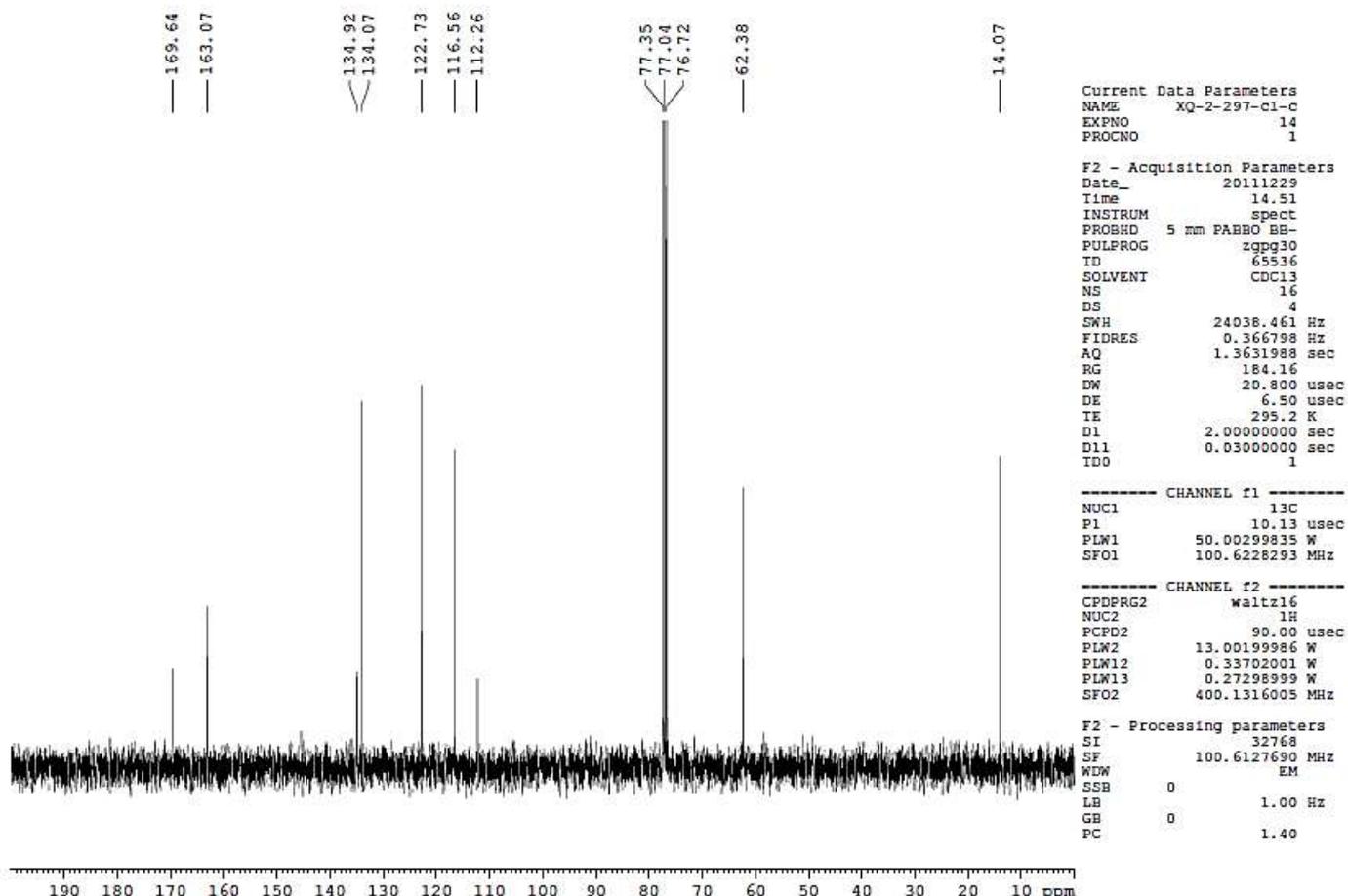
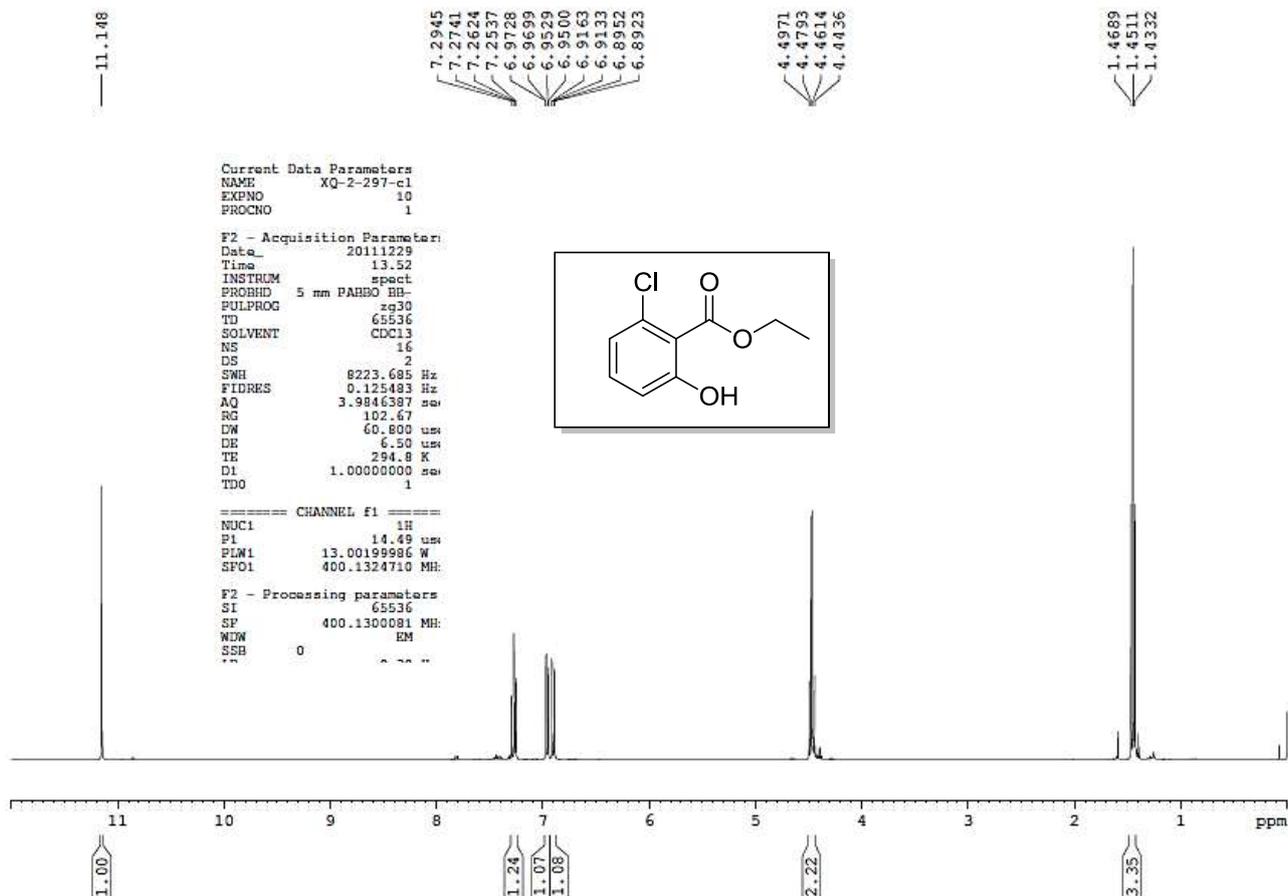
The spectrum of product (12)



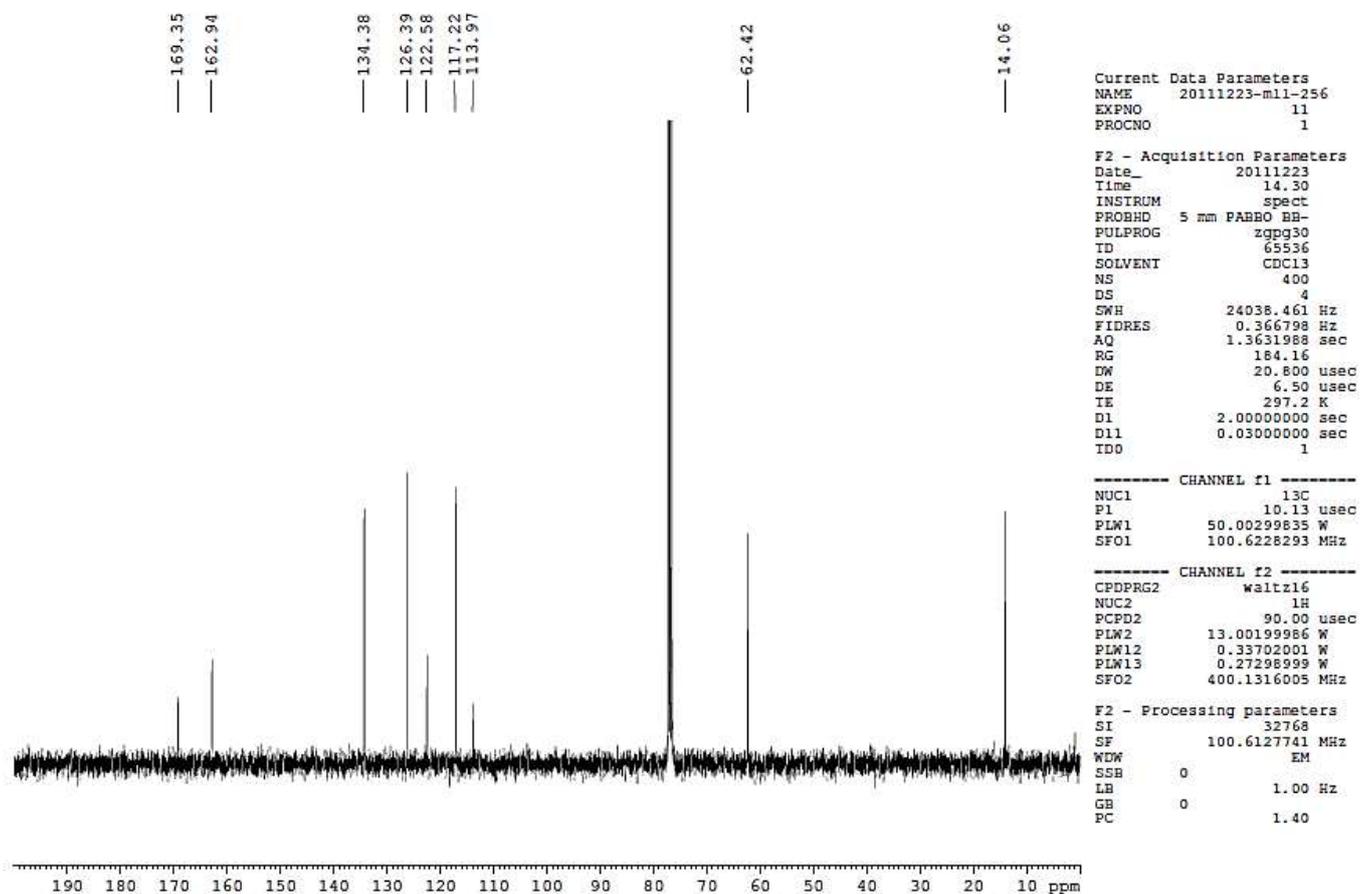
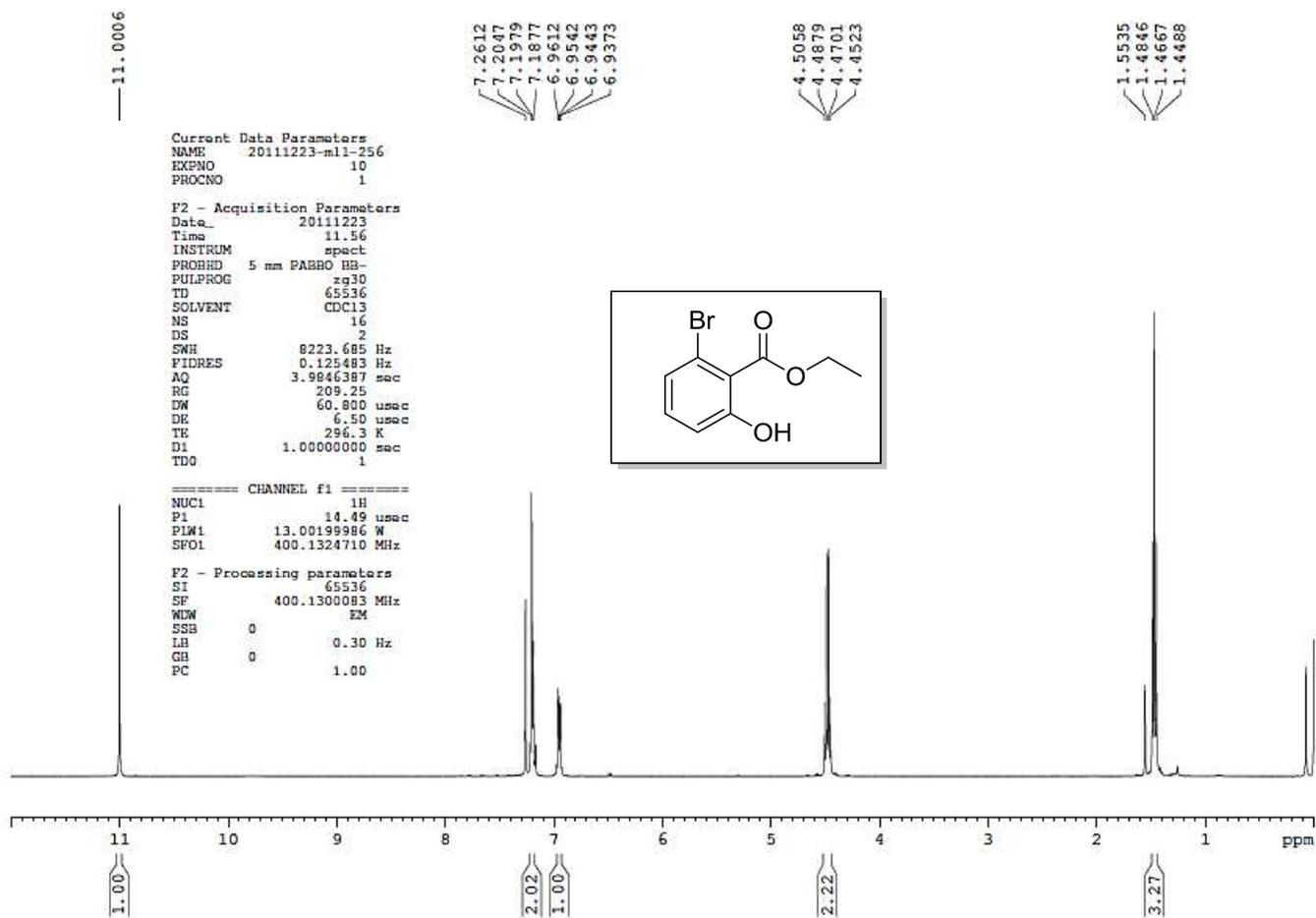
The spectrum of product (13)



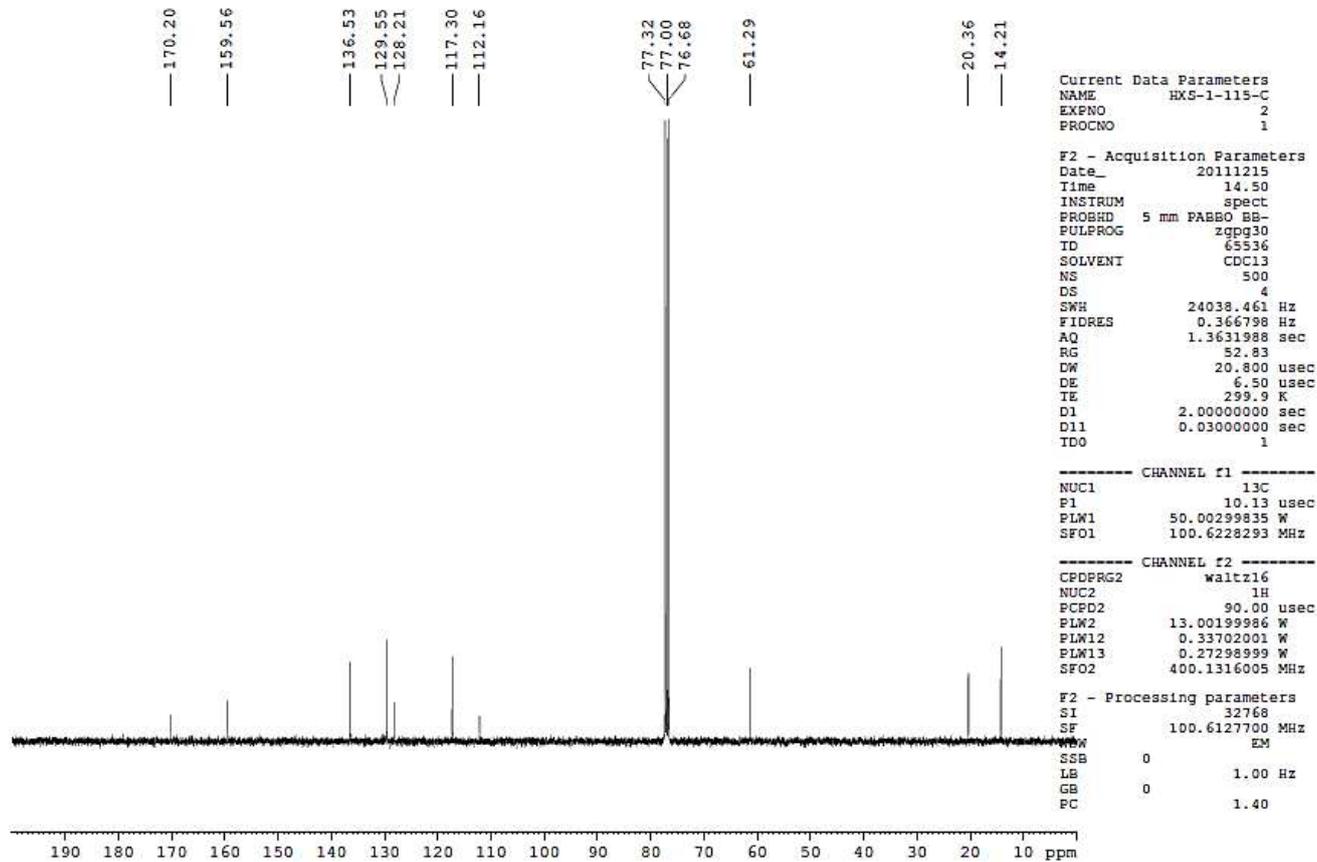
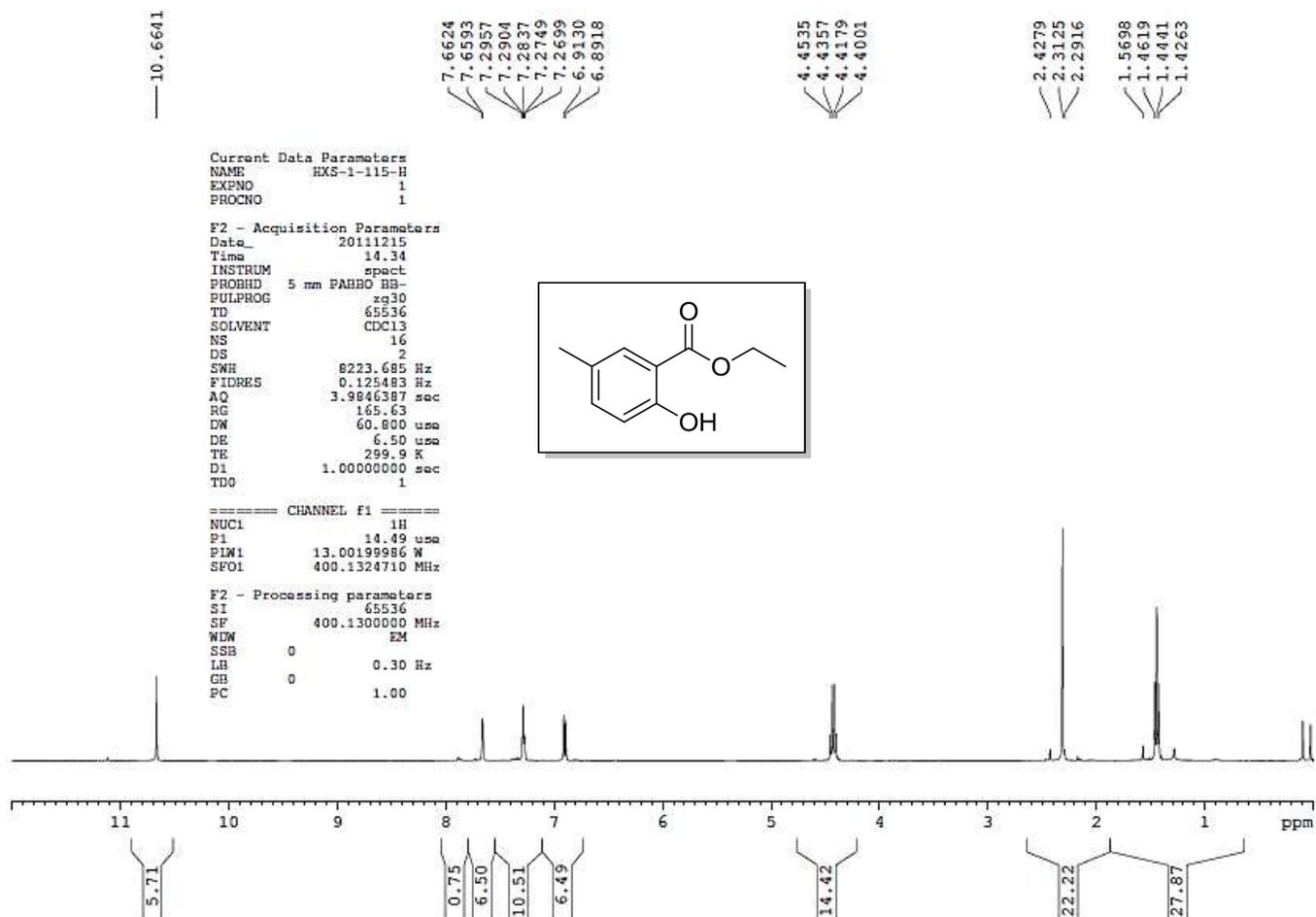
The spectrum of product (14)



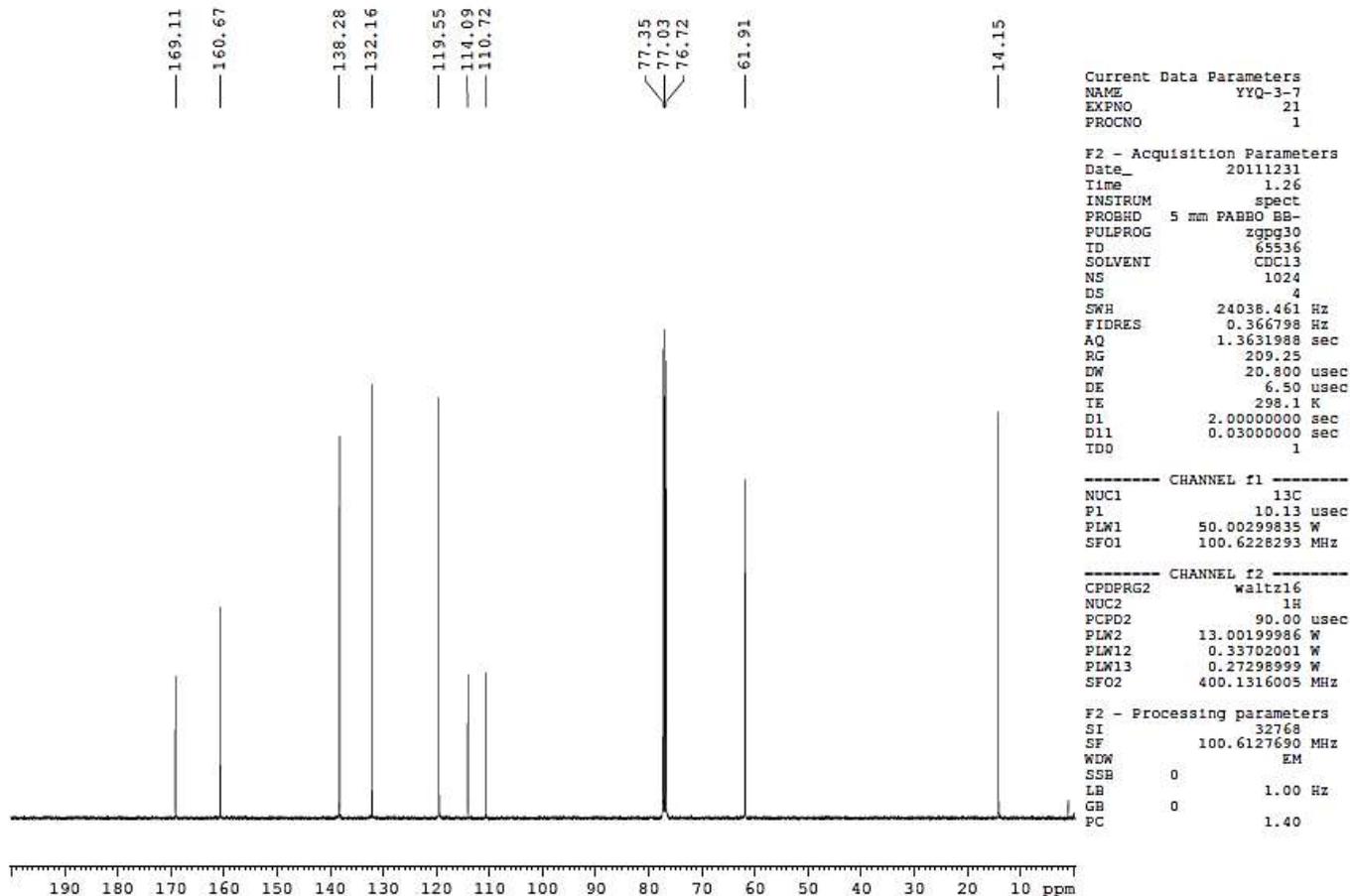
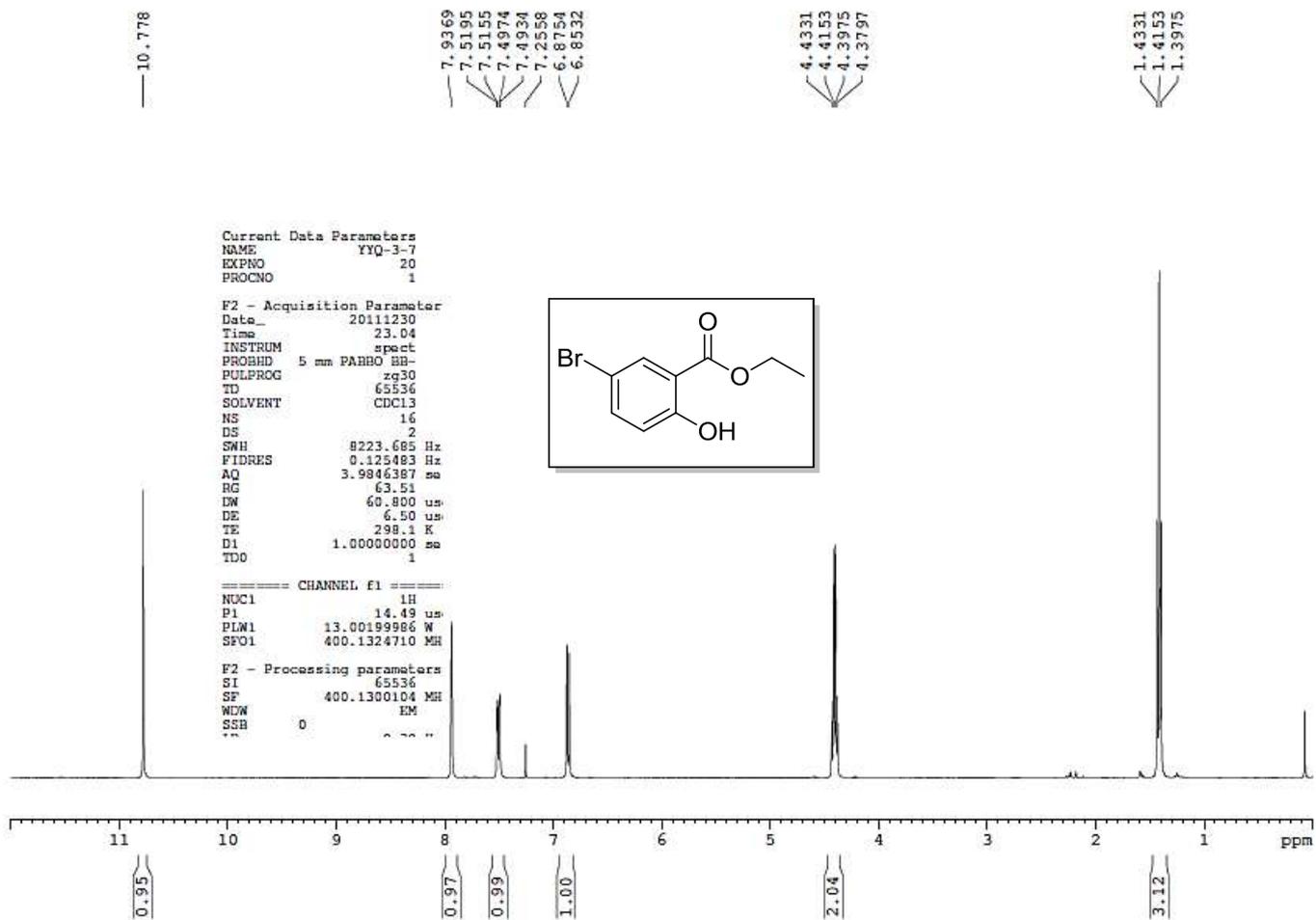
The spectrum of product (15)



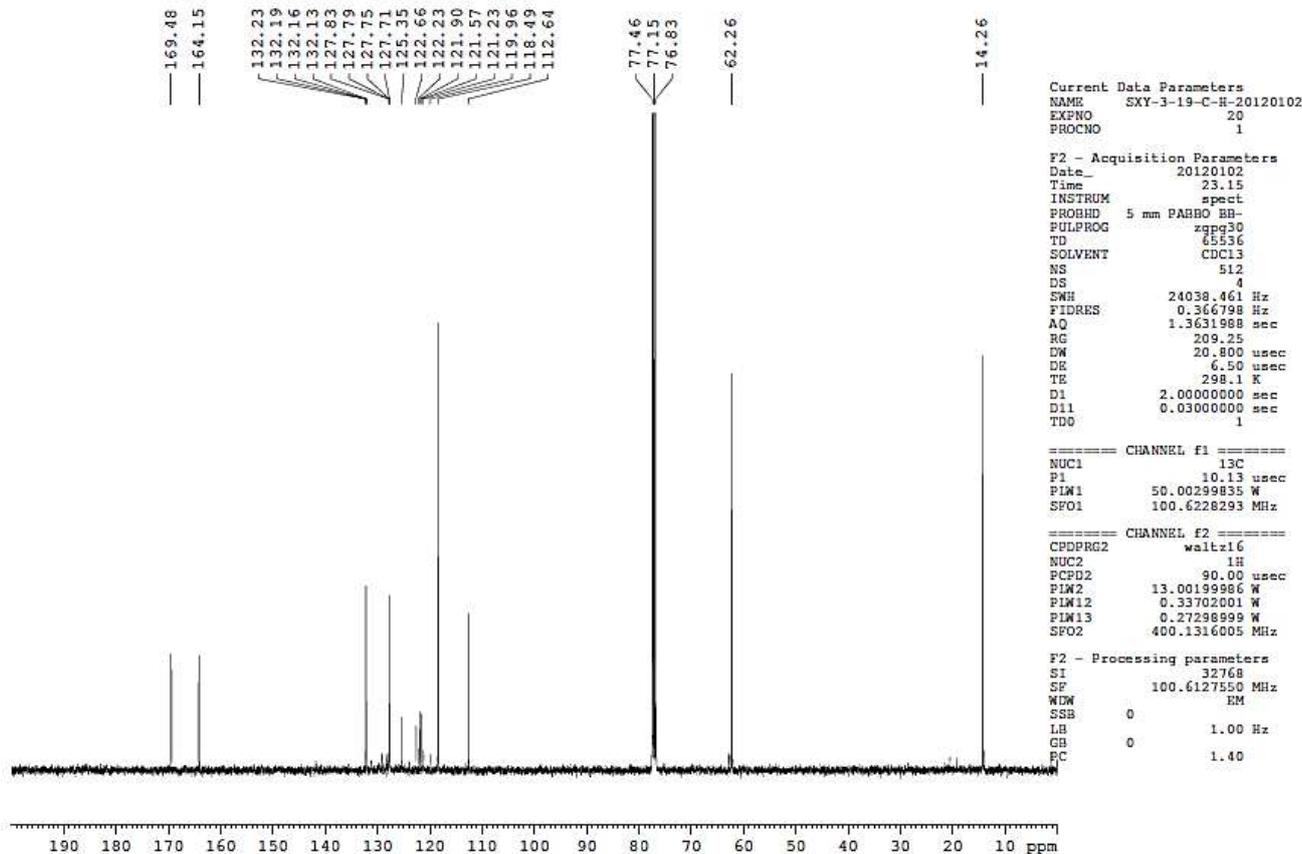
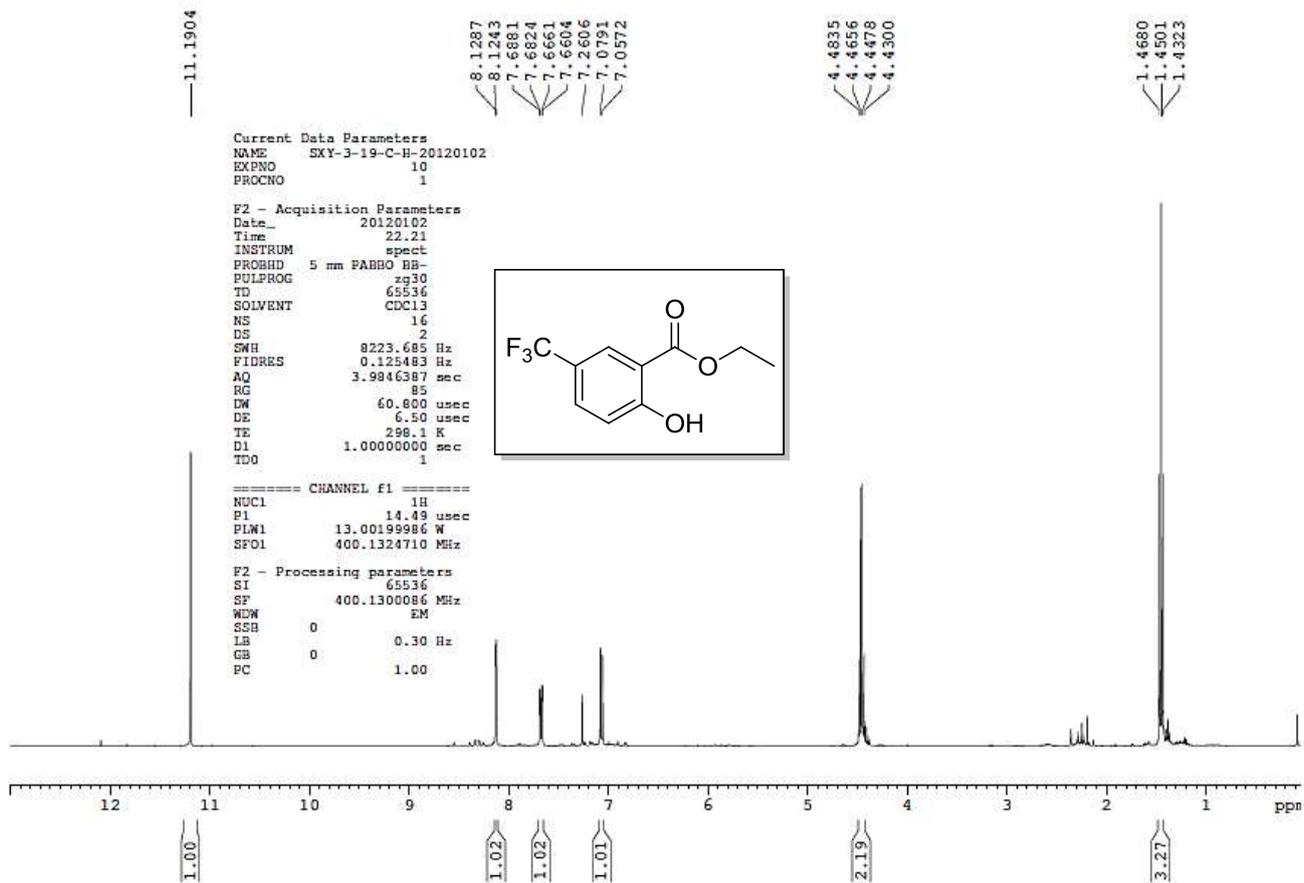
The spectrum of product (16)



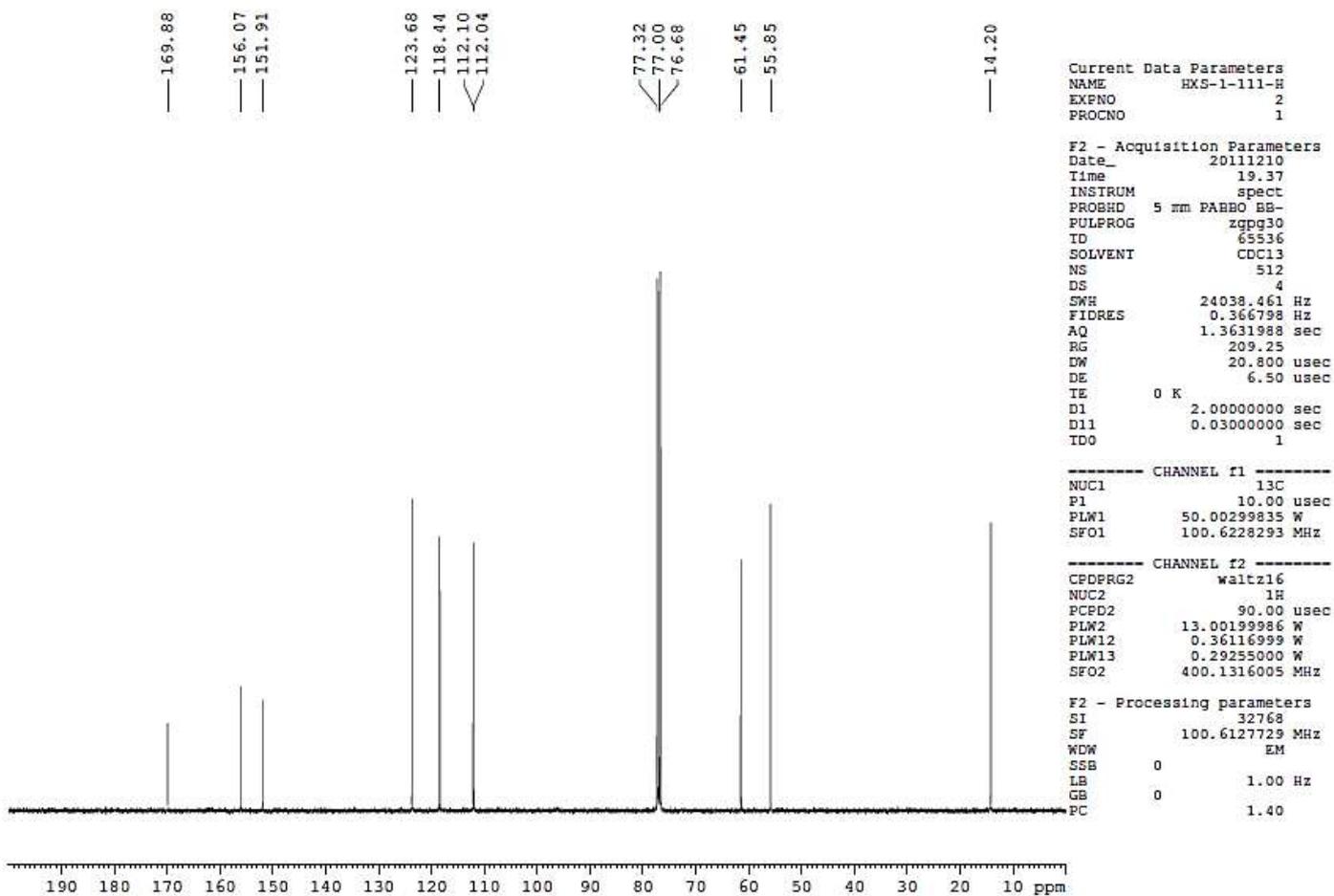
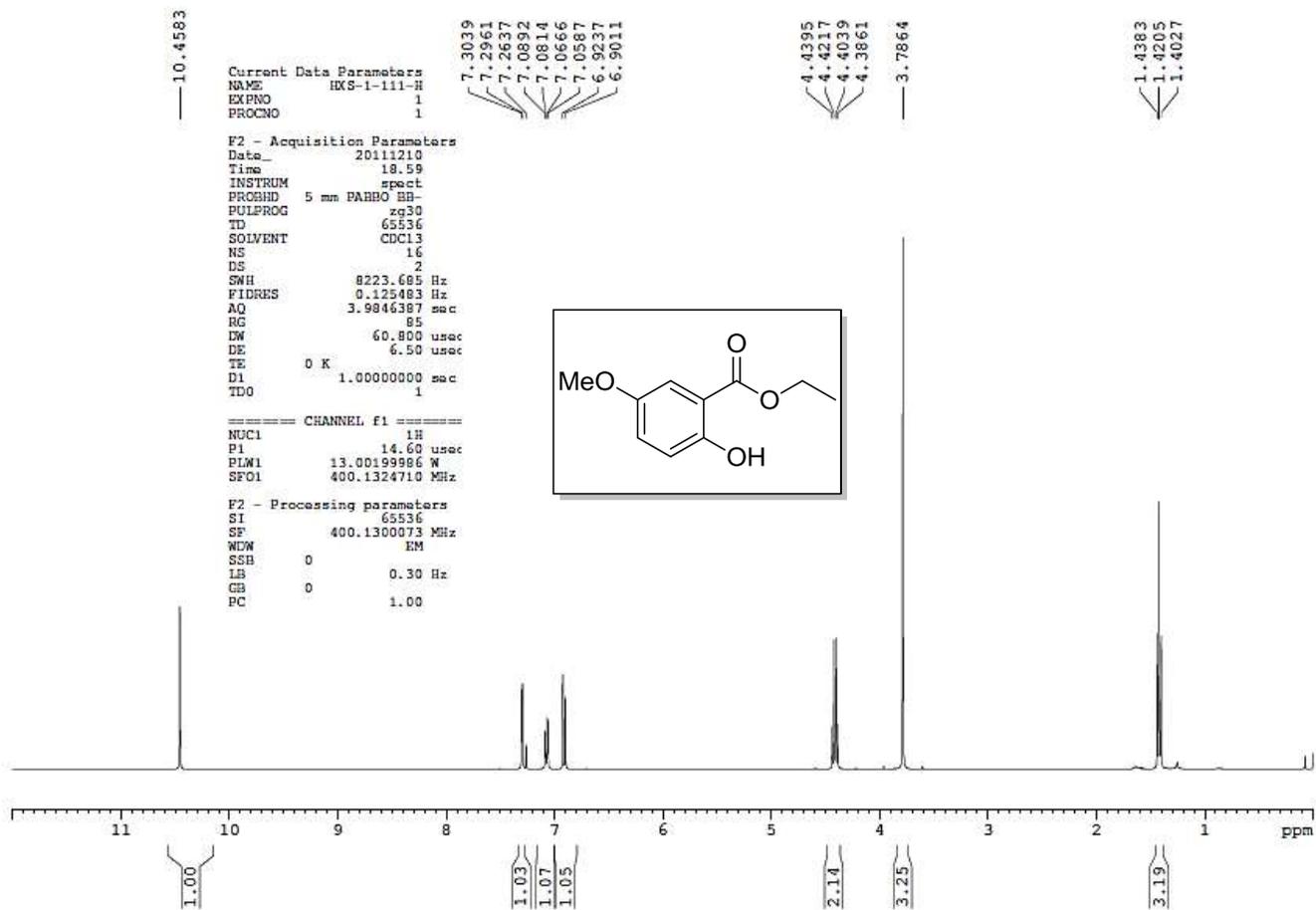
The spectrum of product (17)



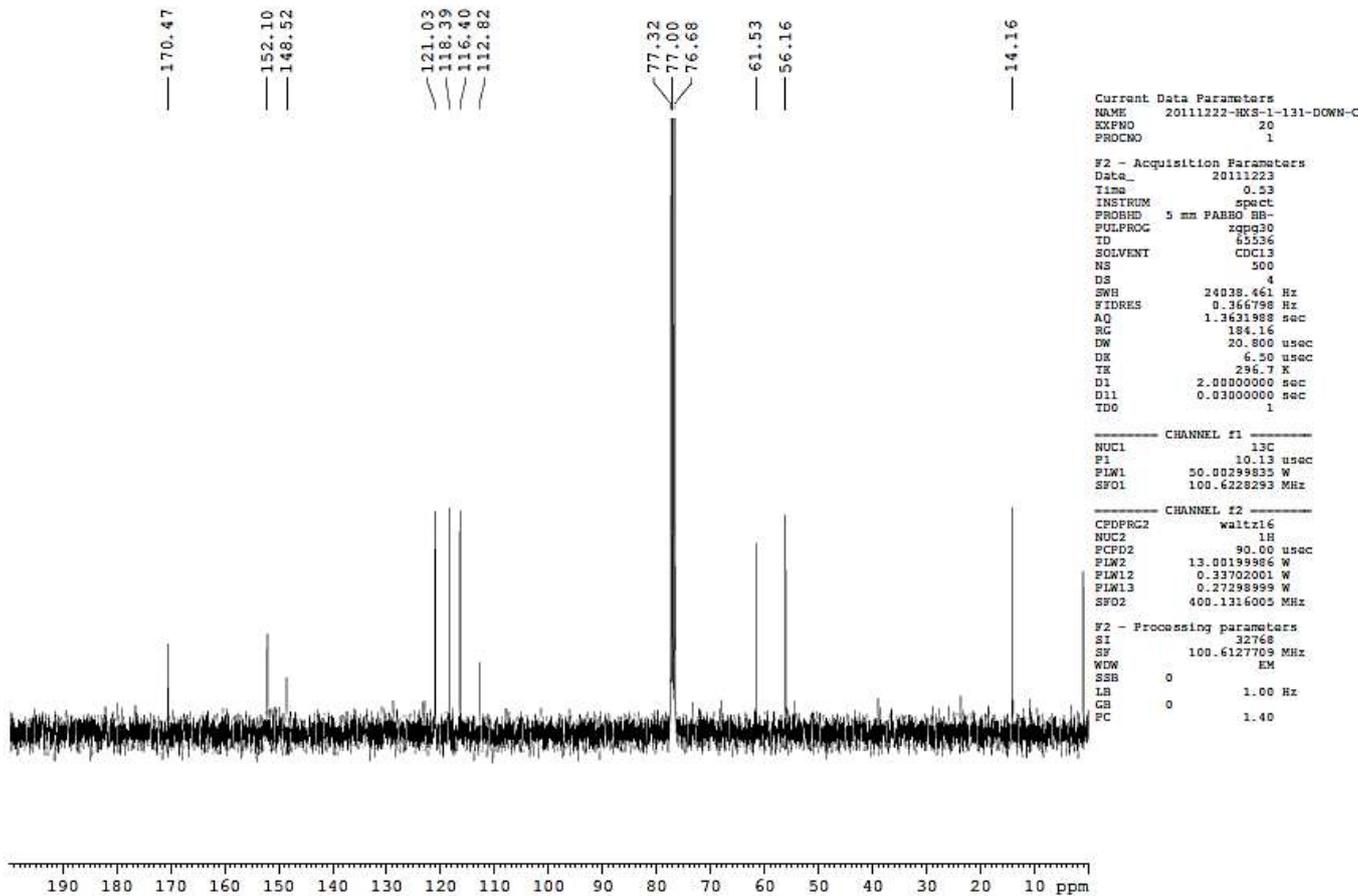
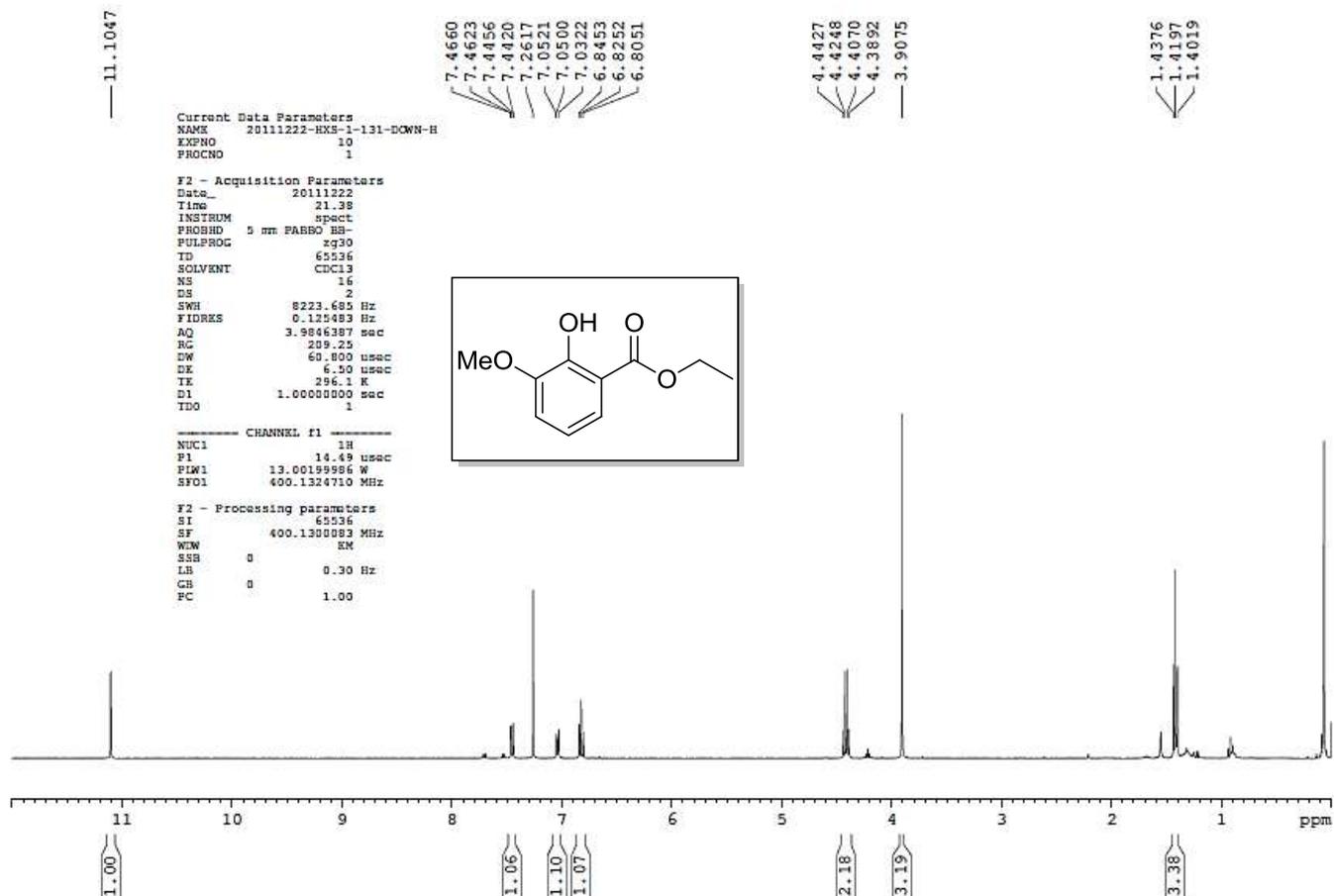
The spectrum of product (18)



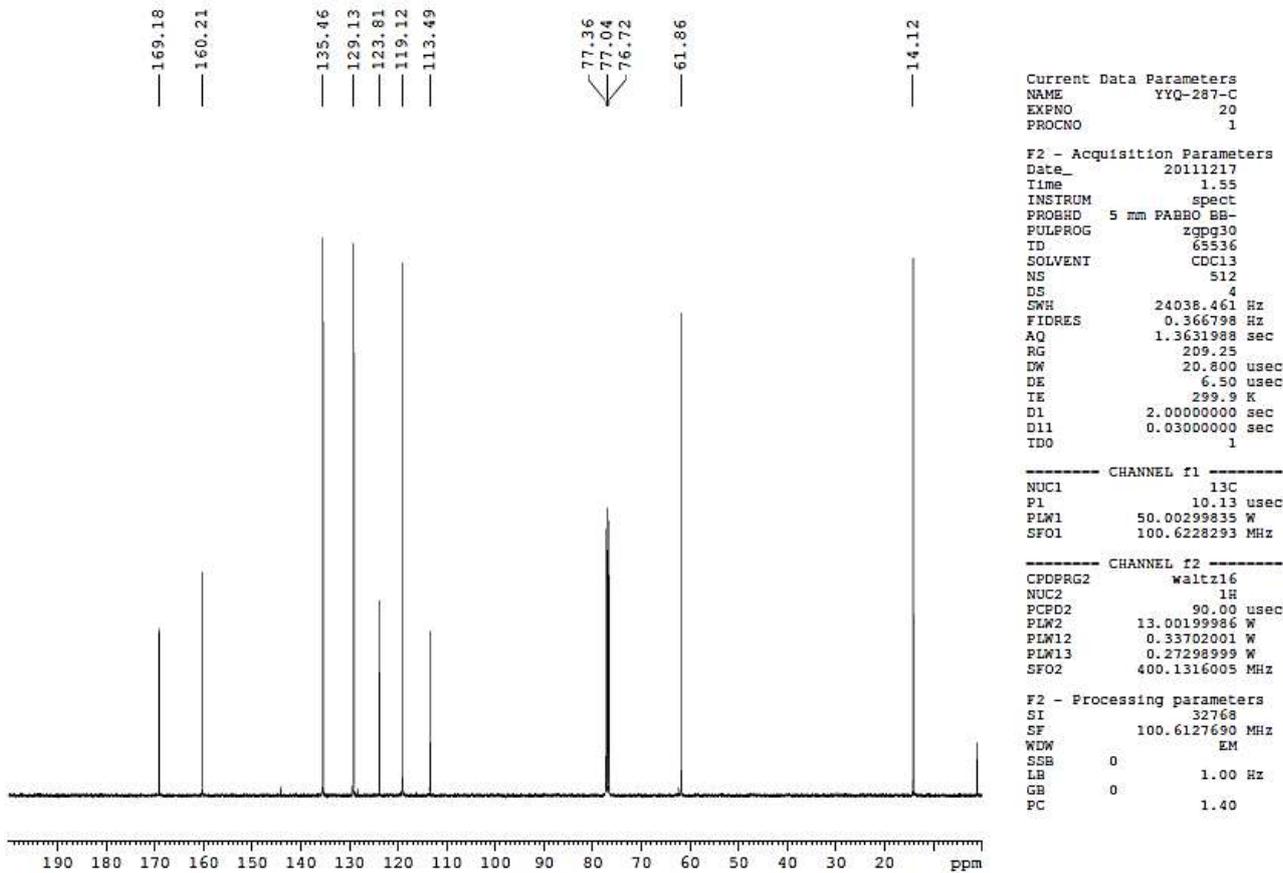
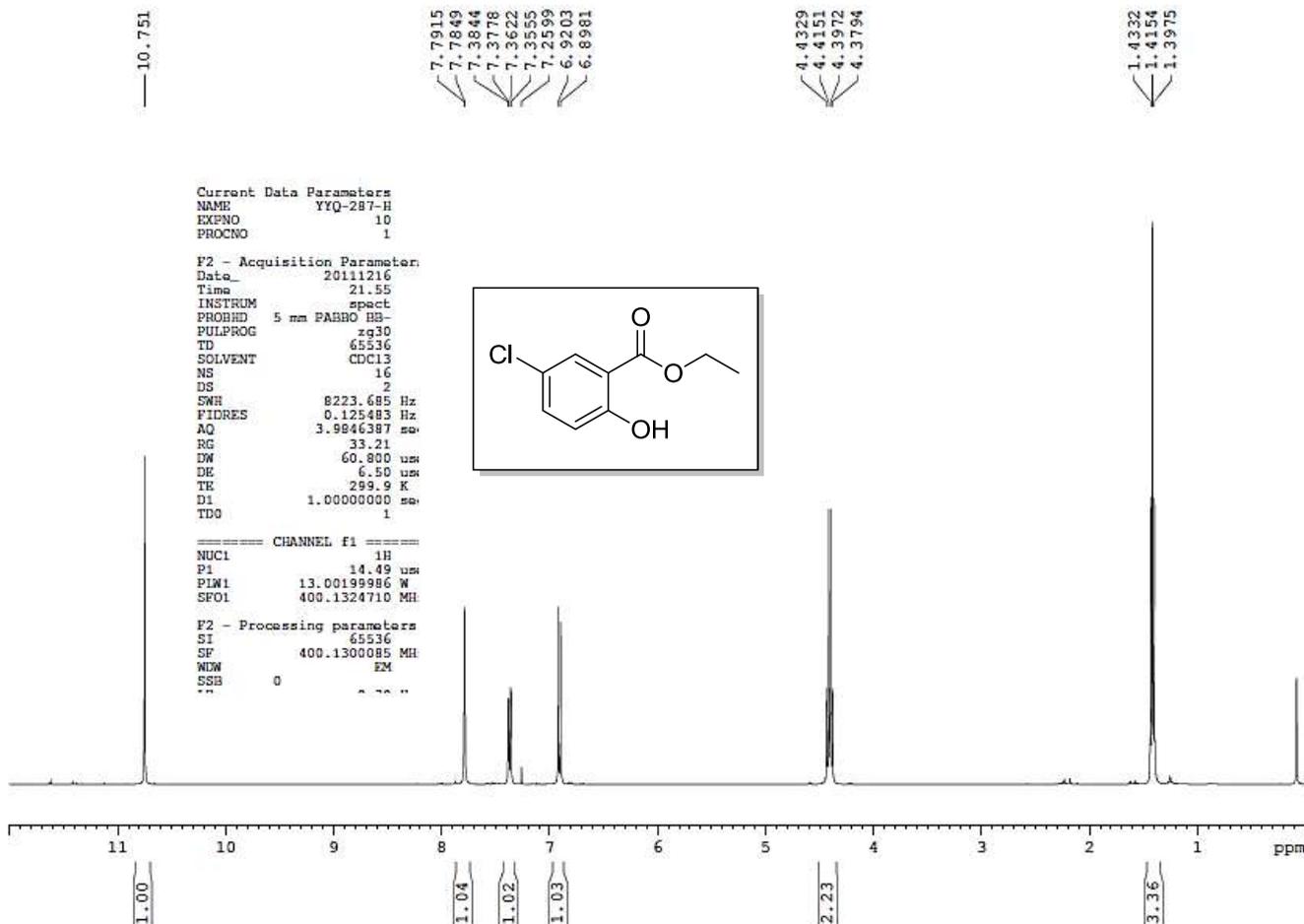
The spectrum of product (19a)



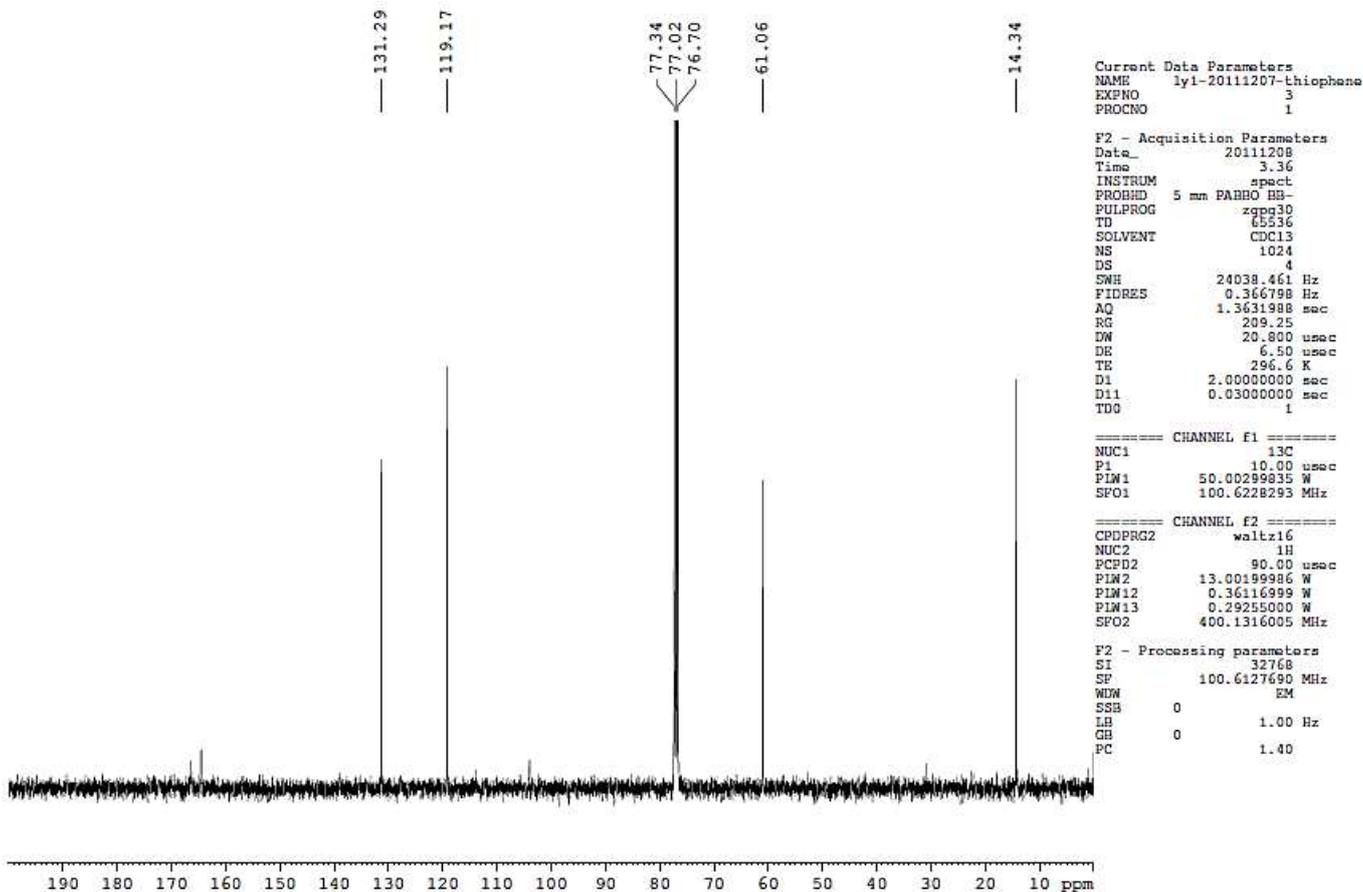
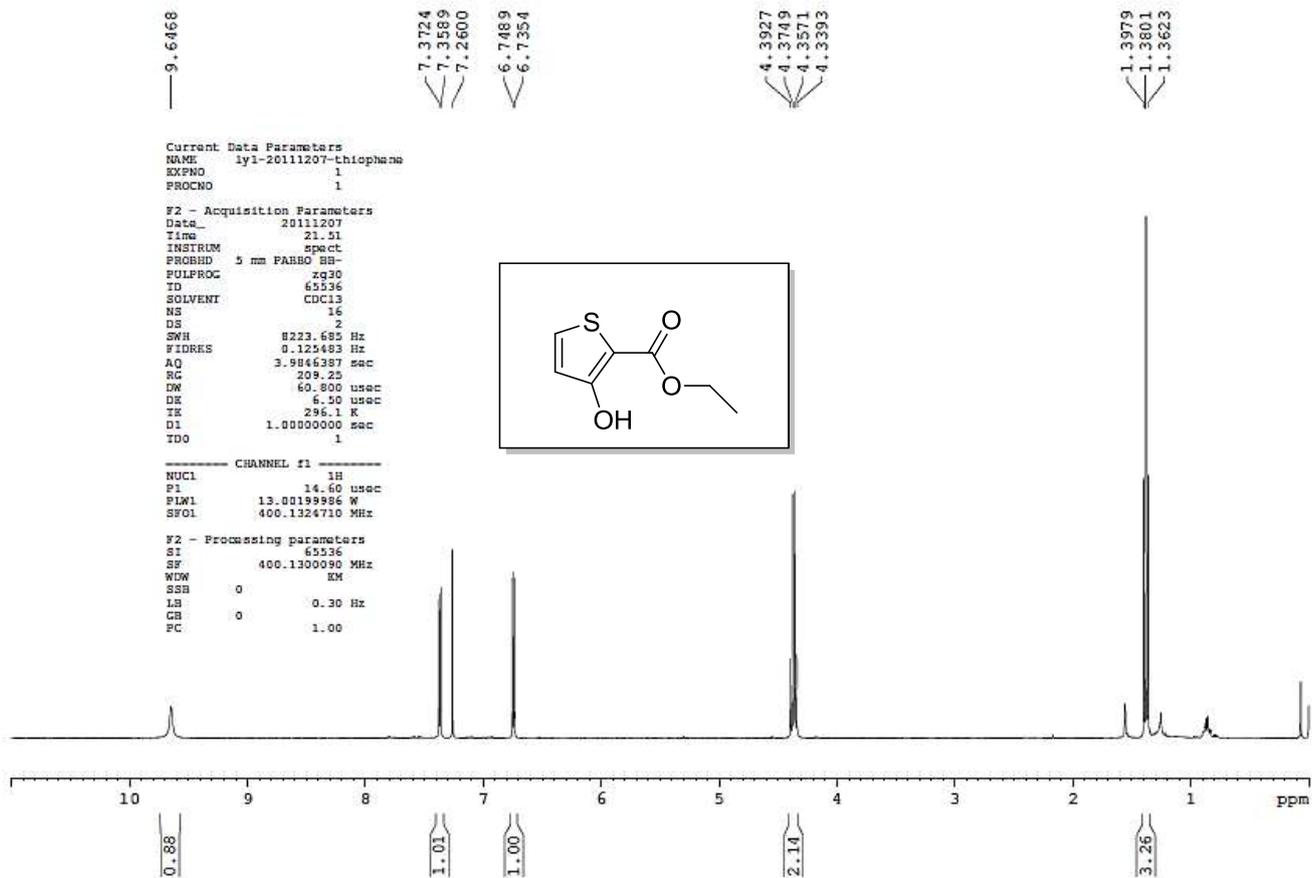
The spectrum of product (19b)



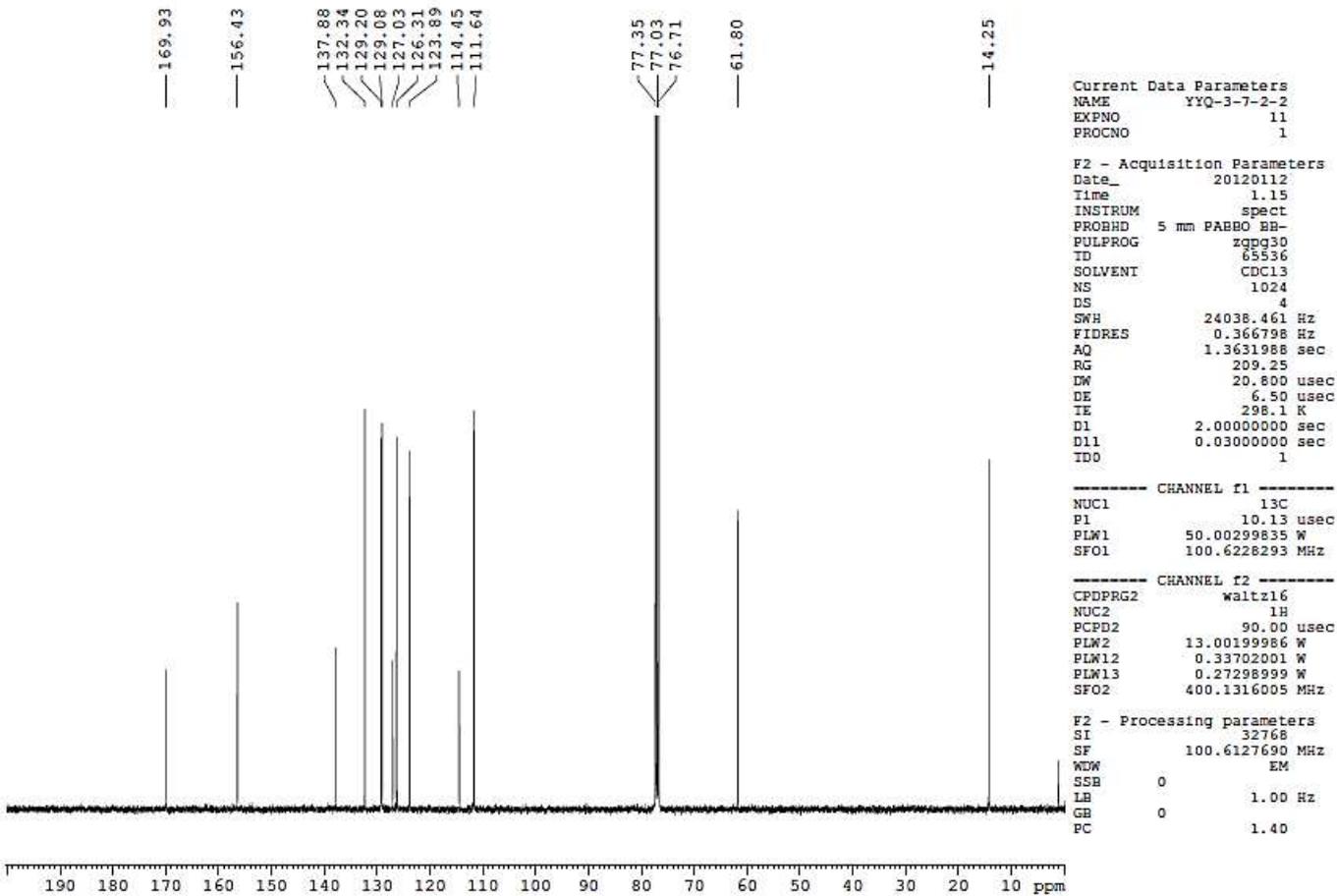
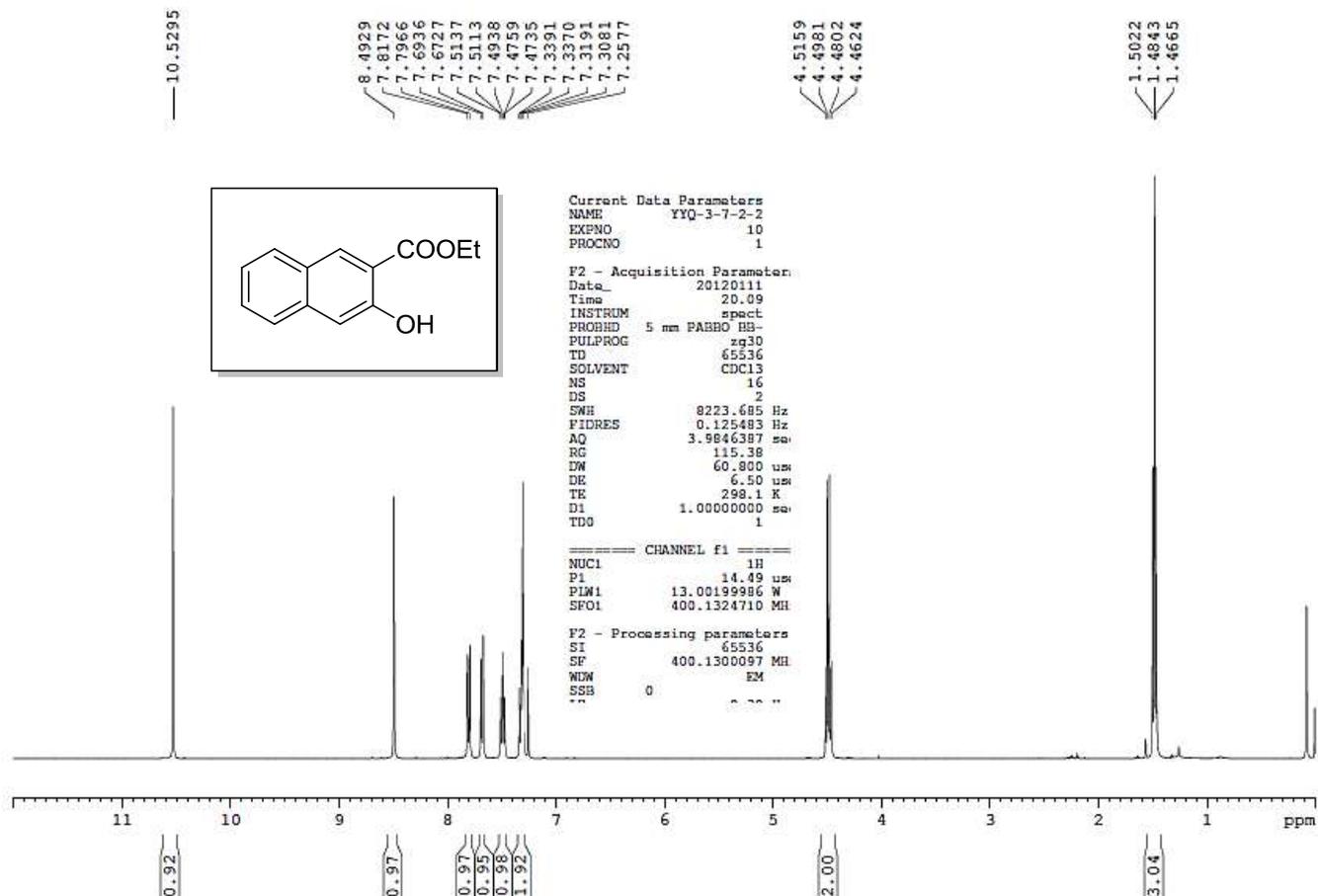
The spectrum of product (20)



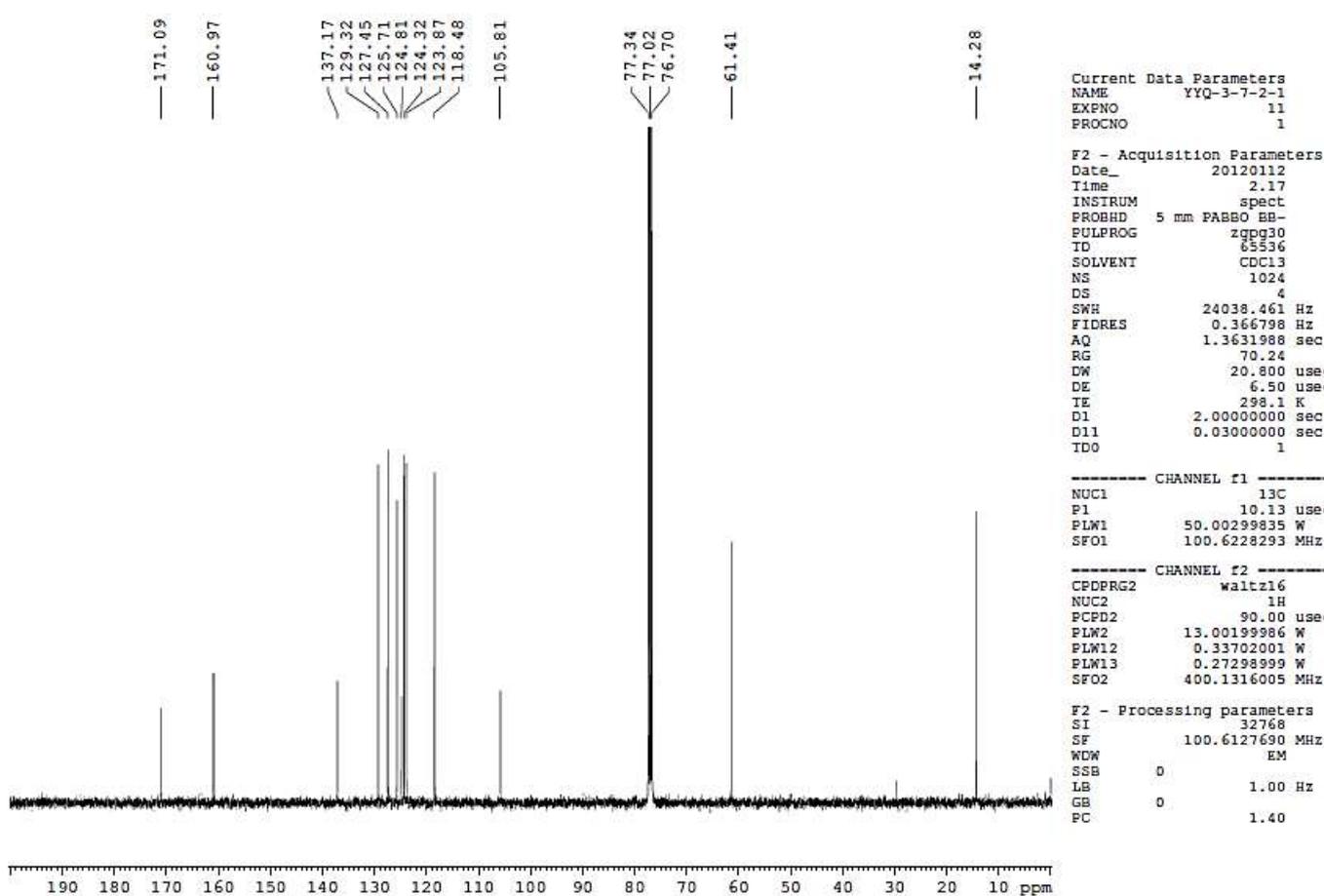
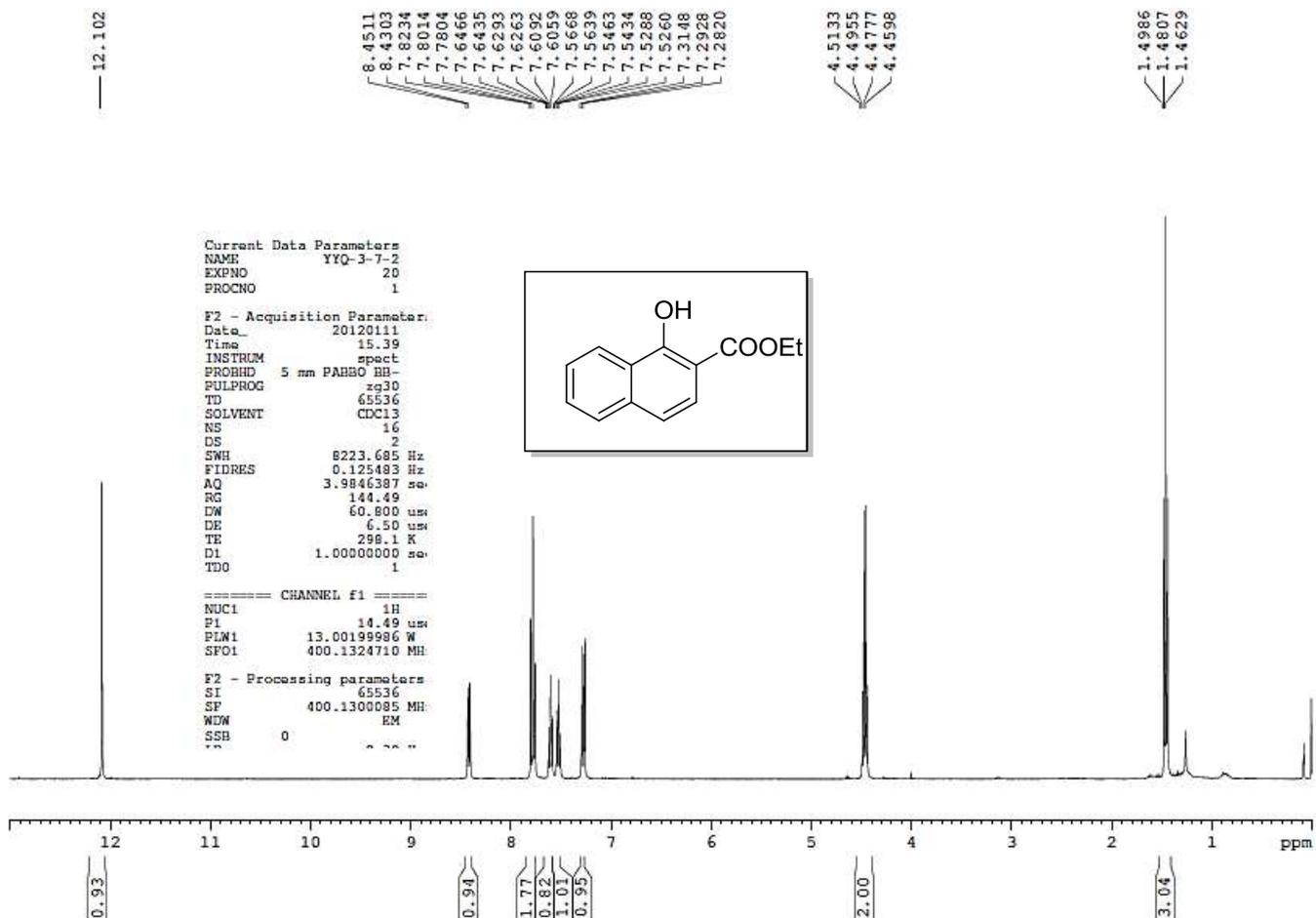
The spectrum of product (21)



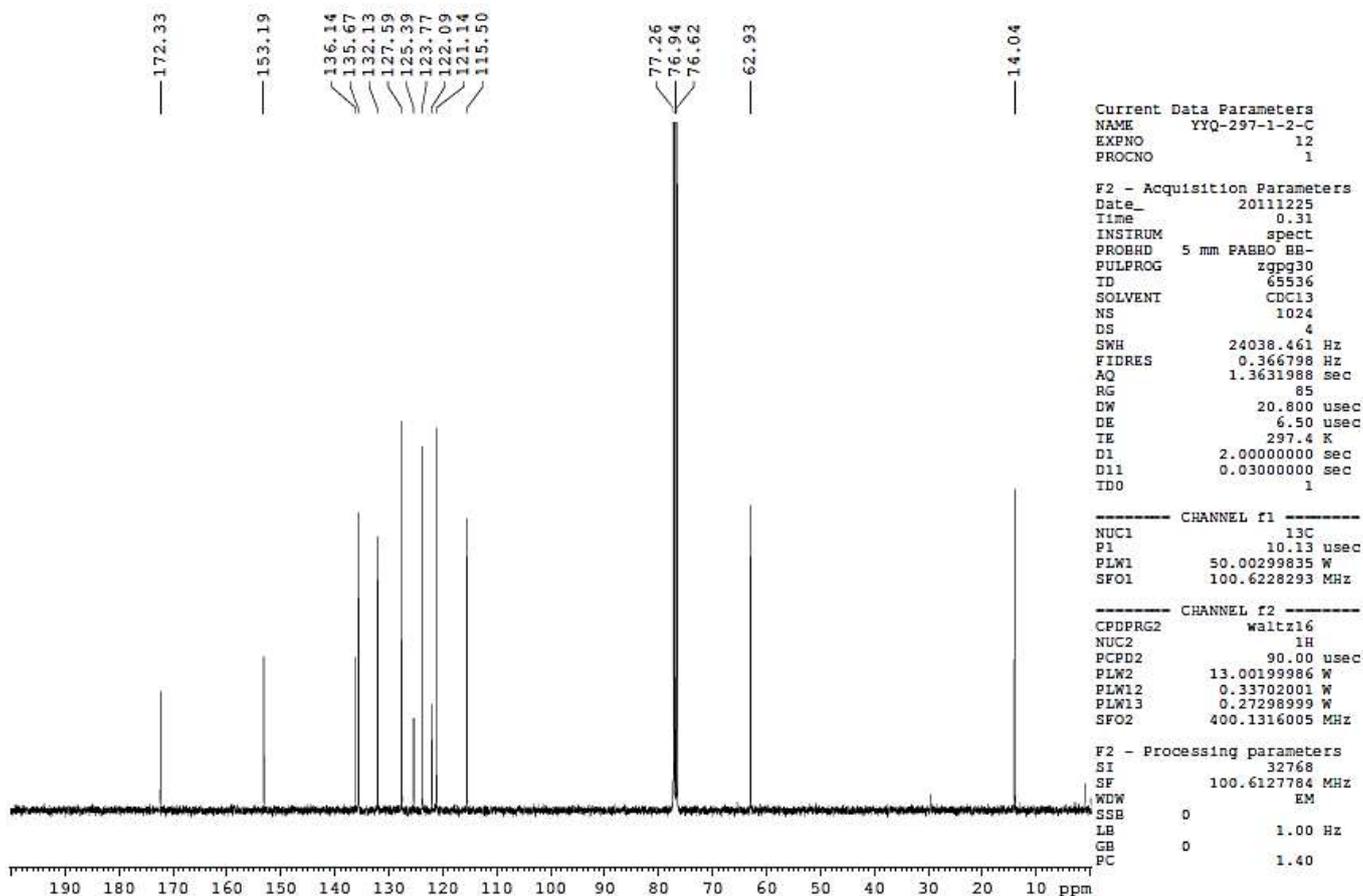
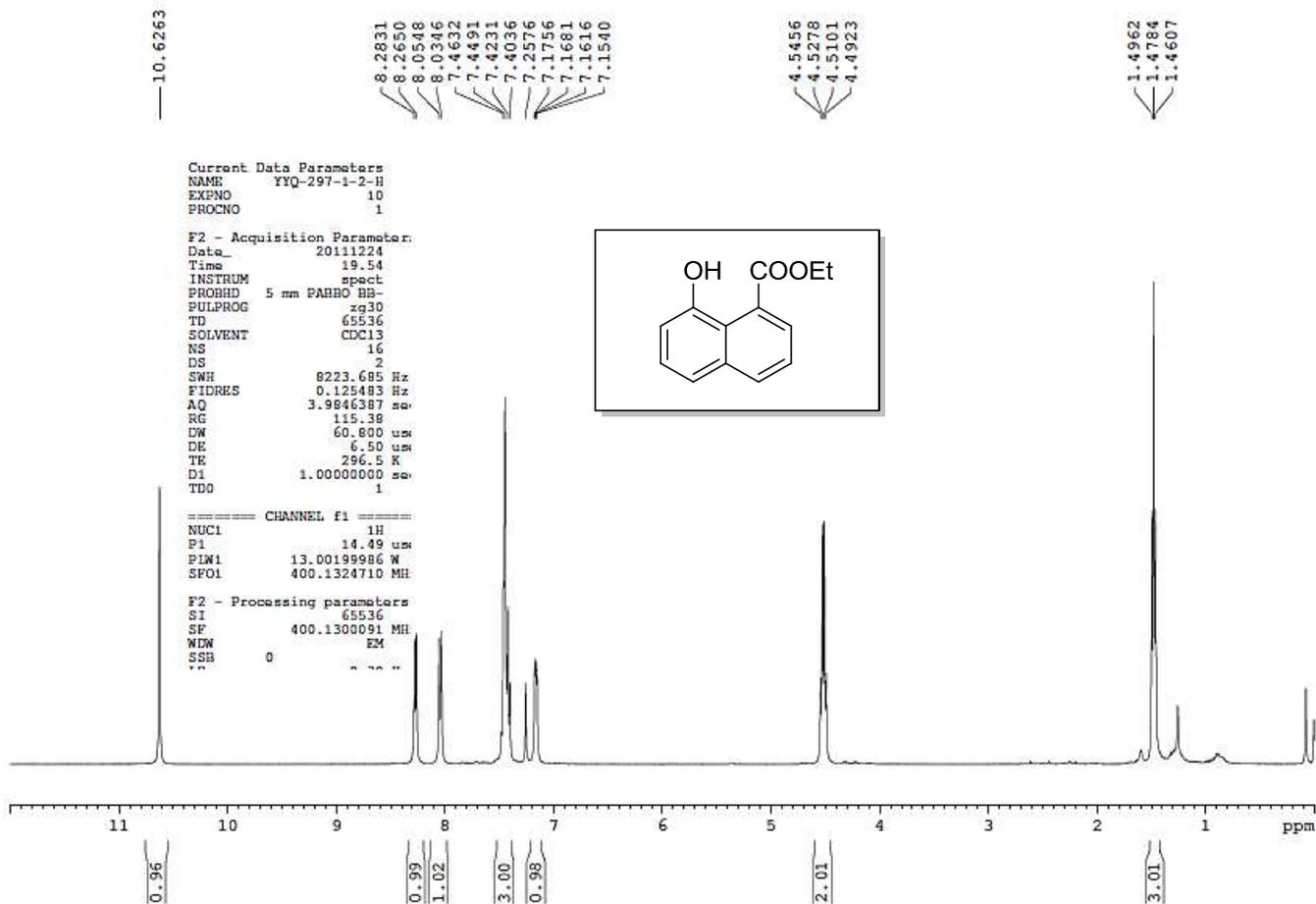
The spectrum of product (22a)



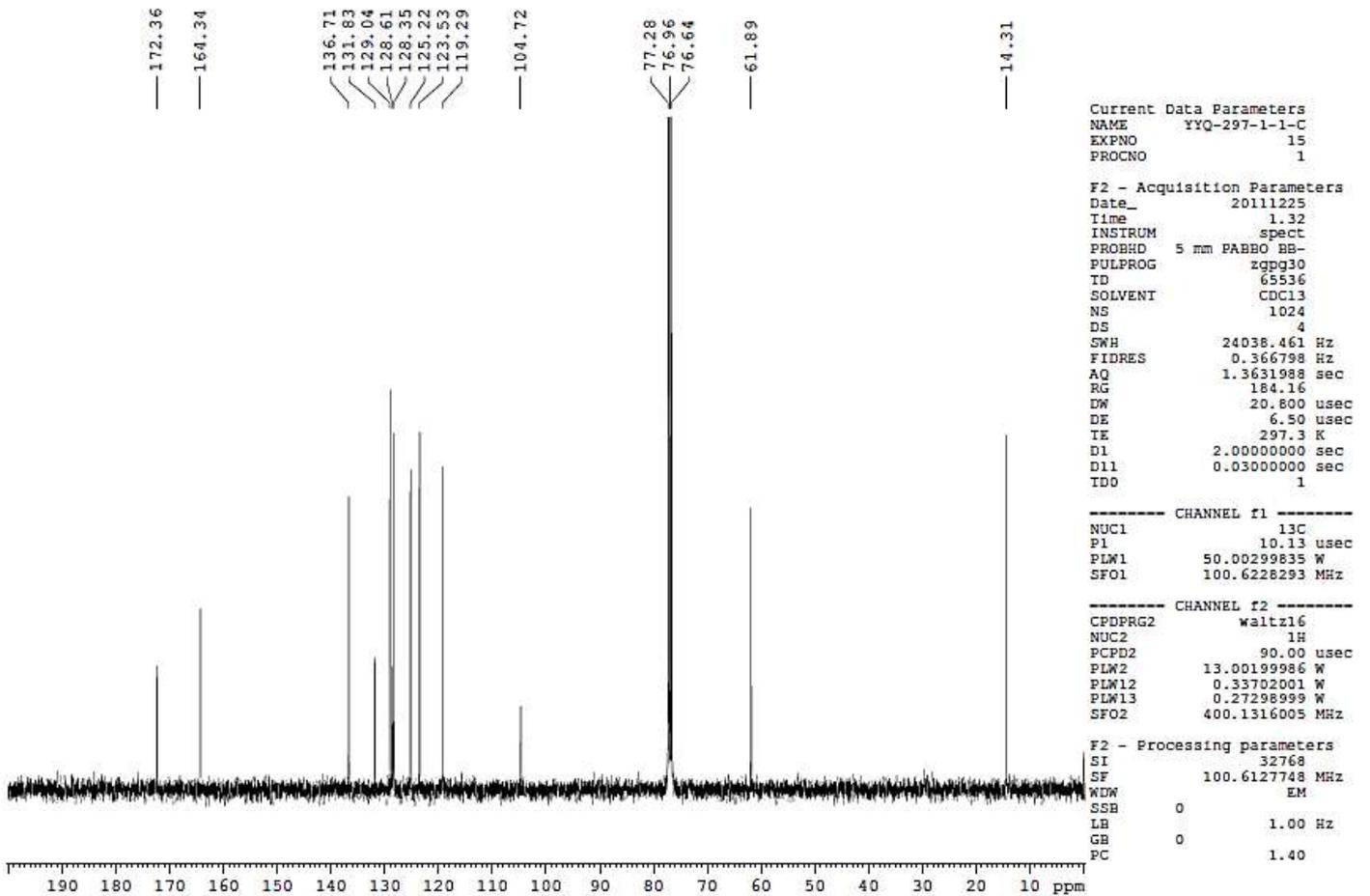
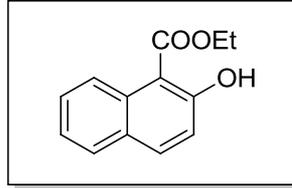
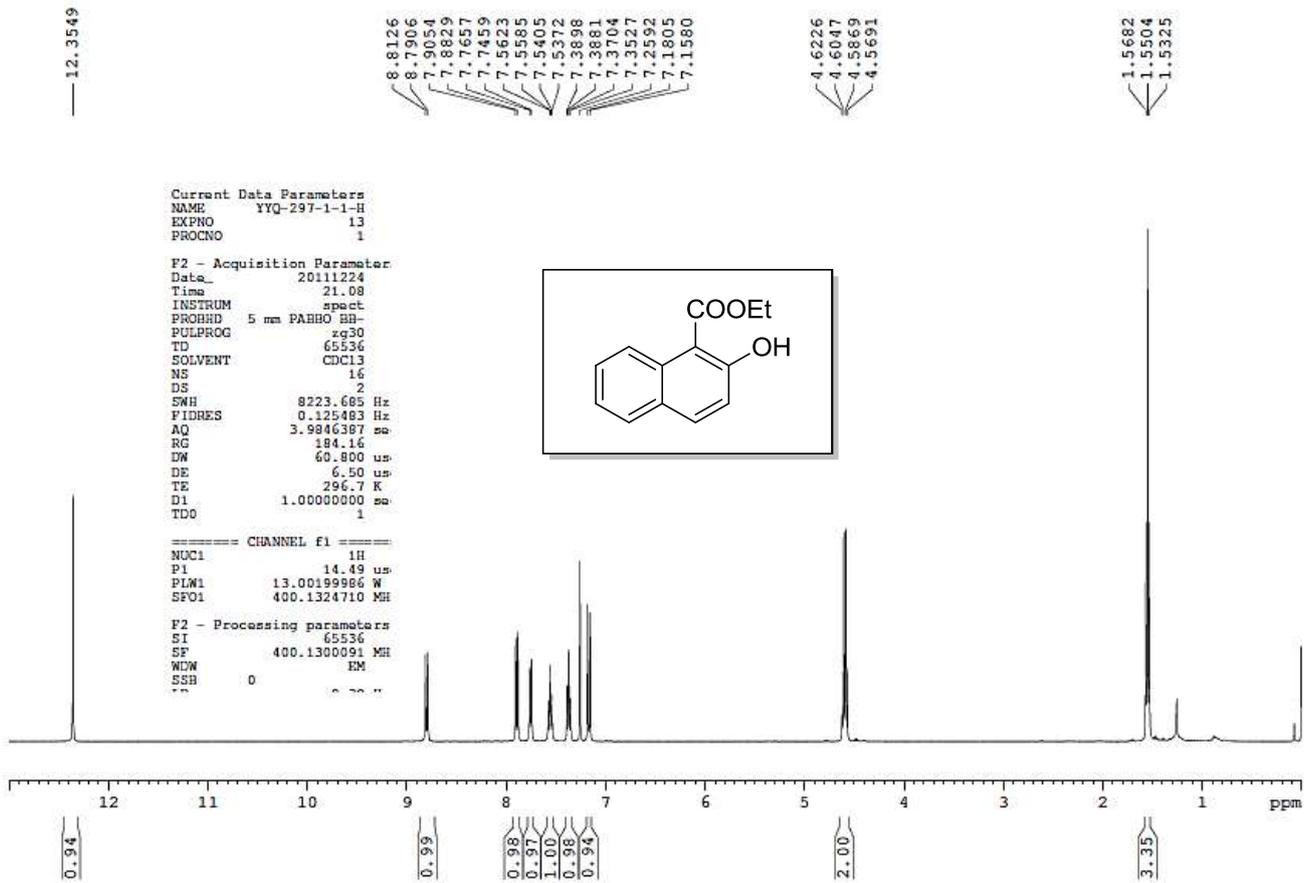
The spectrum of product (22b)



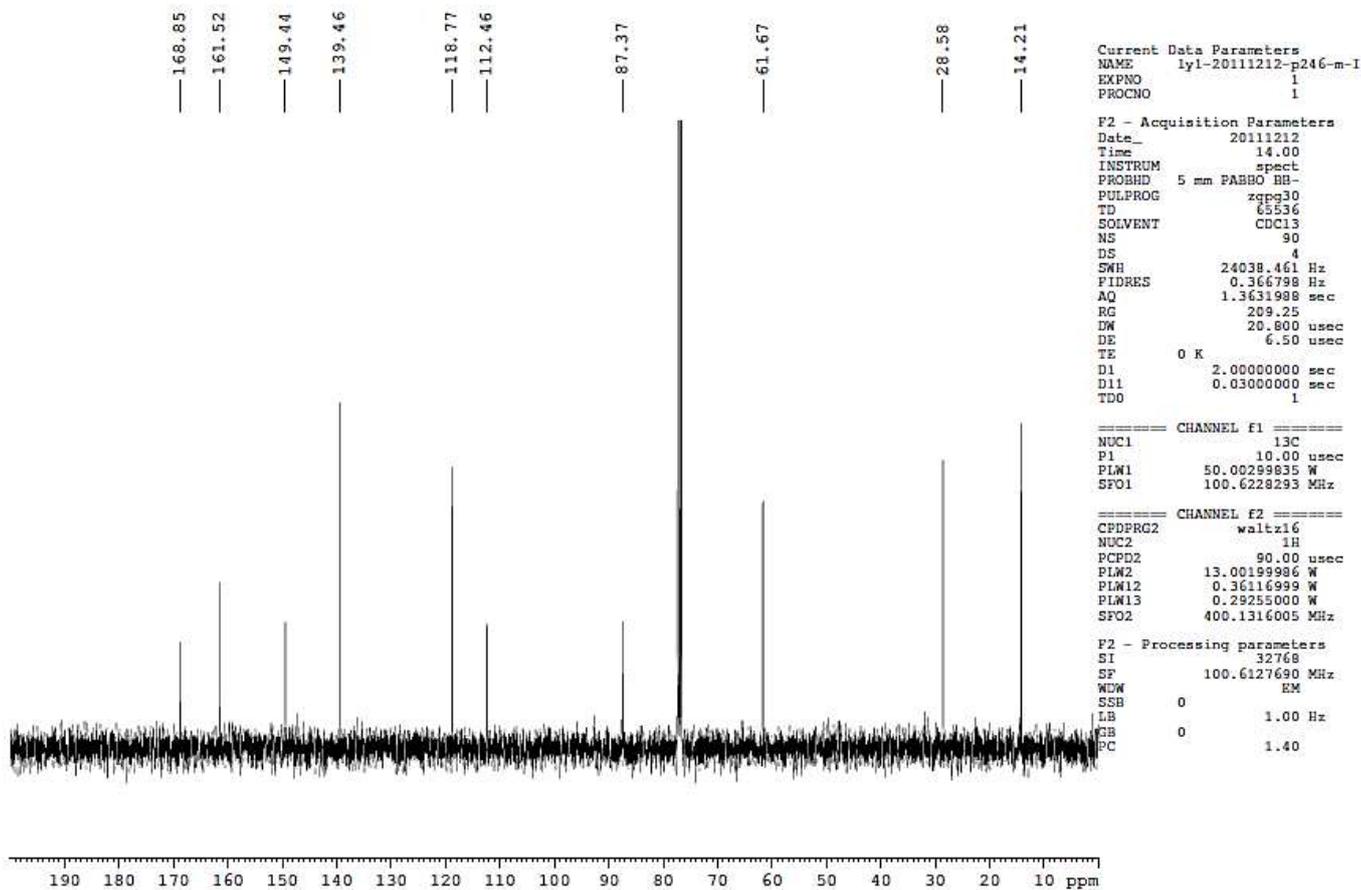
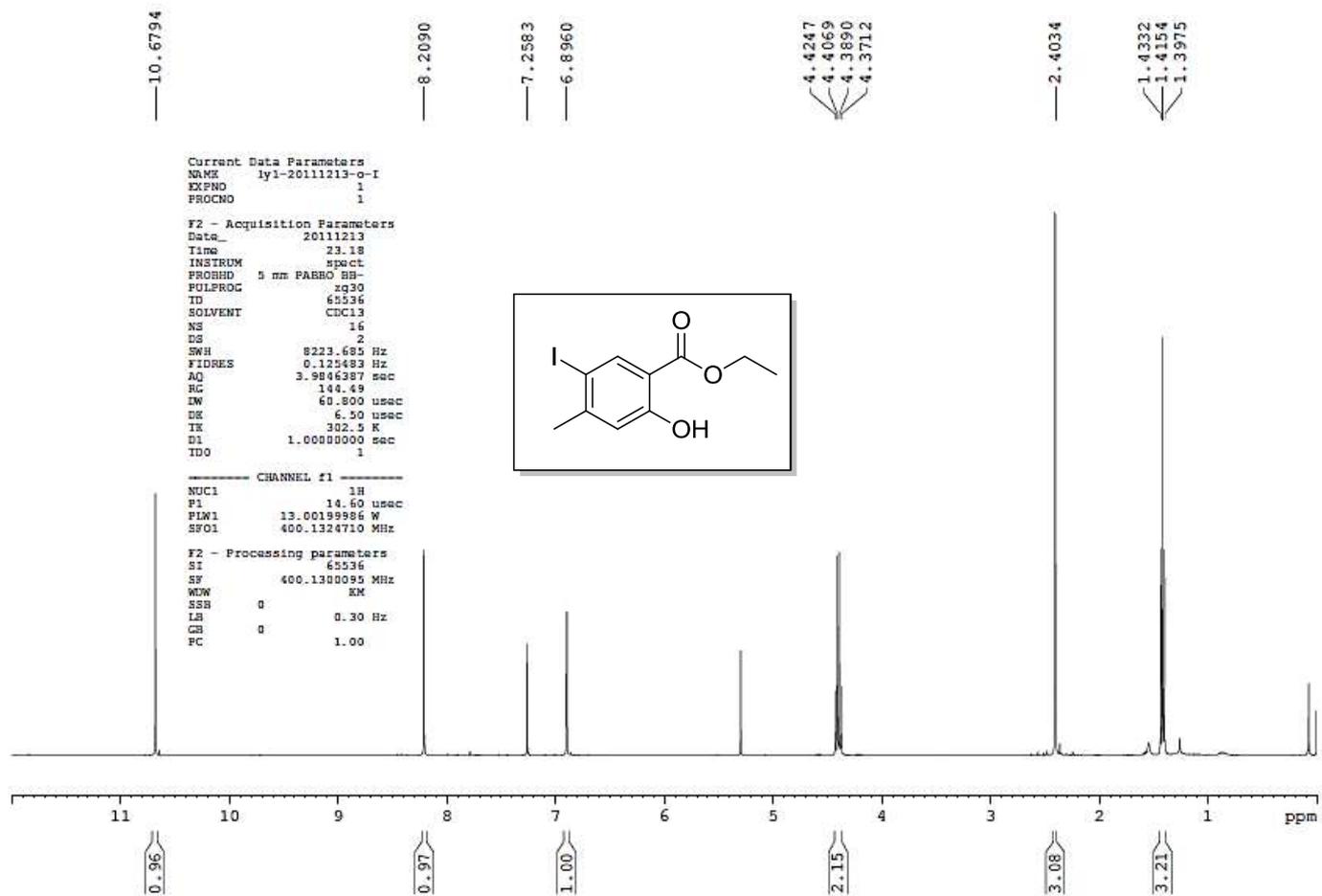
The spectrum of product (23a)



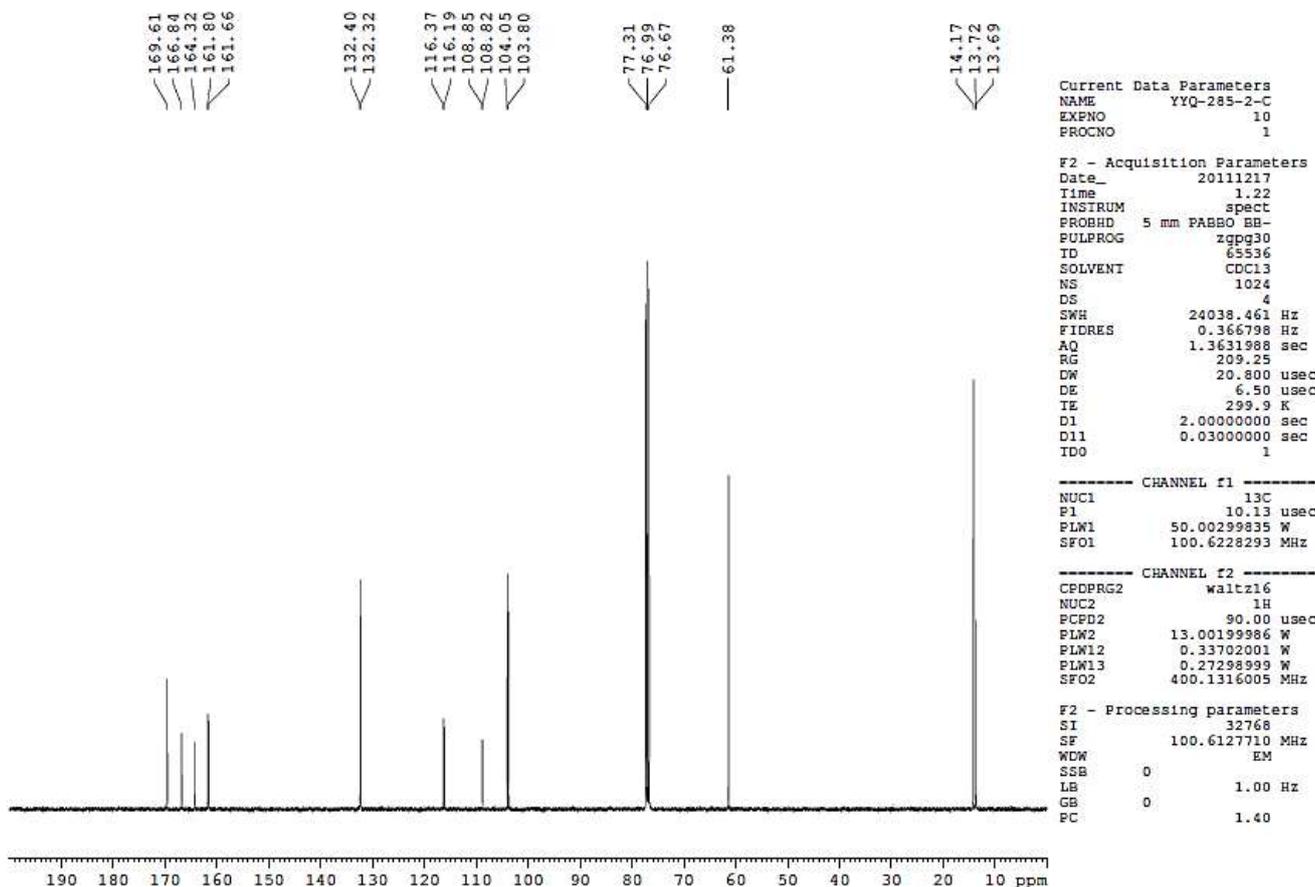
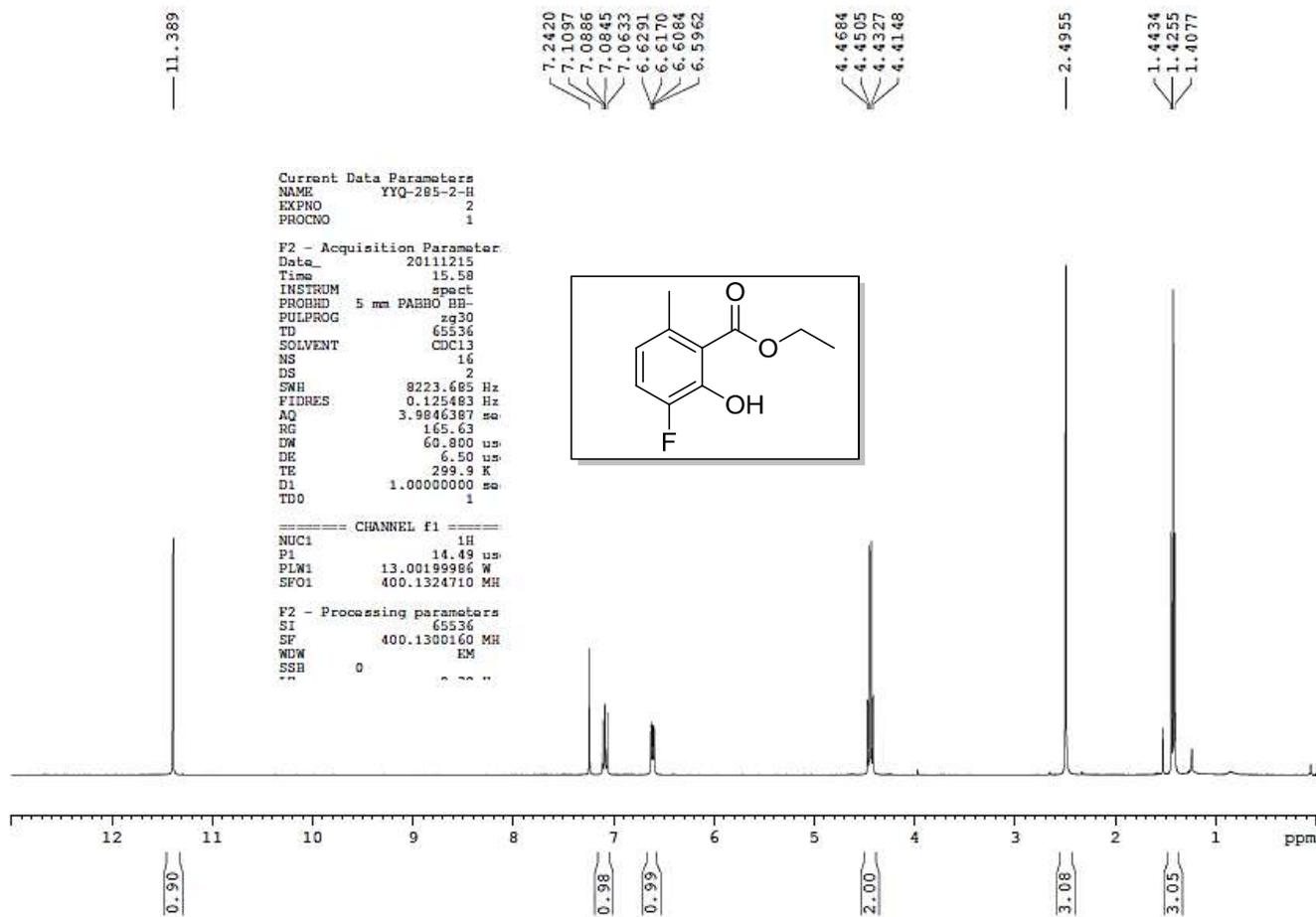
The spectrum of product (23b)



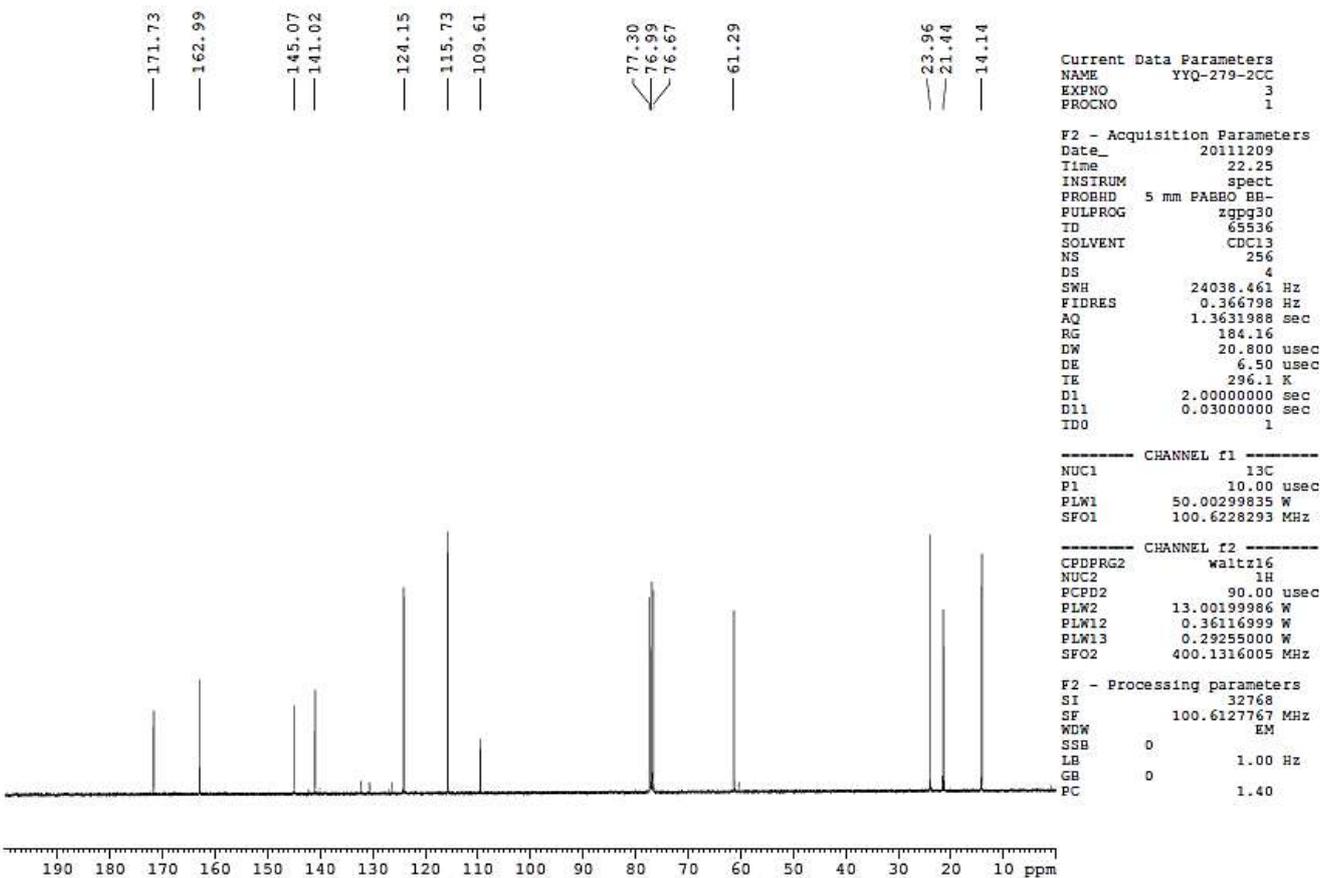
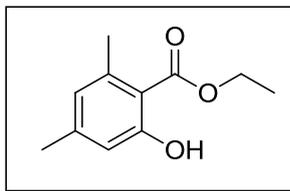
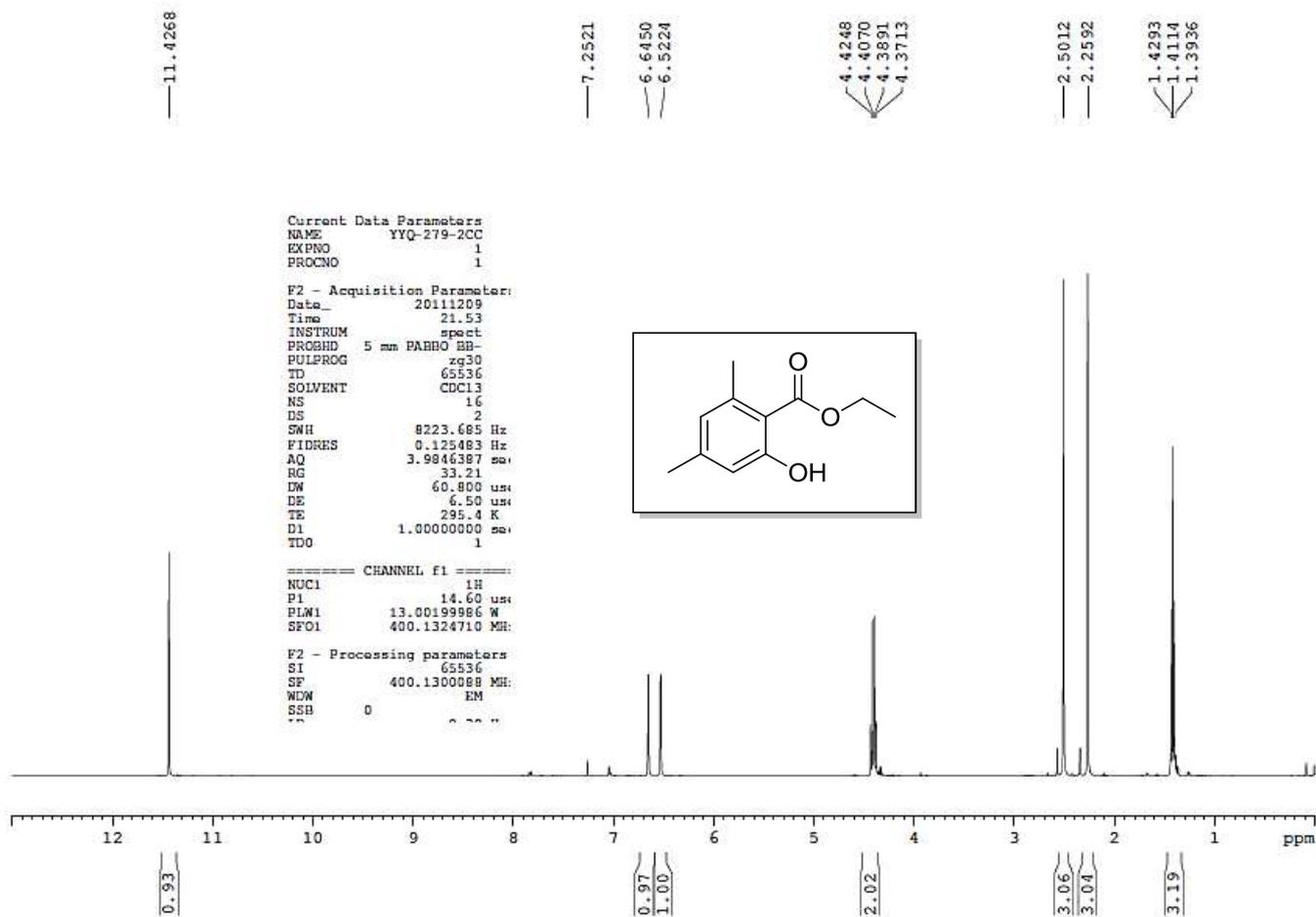
The spectrum of product (24)



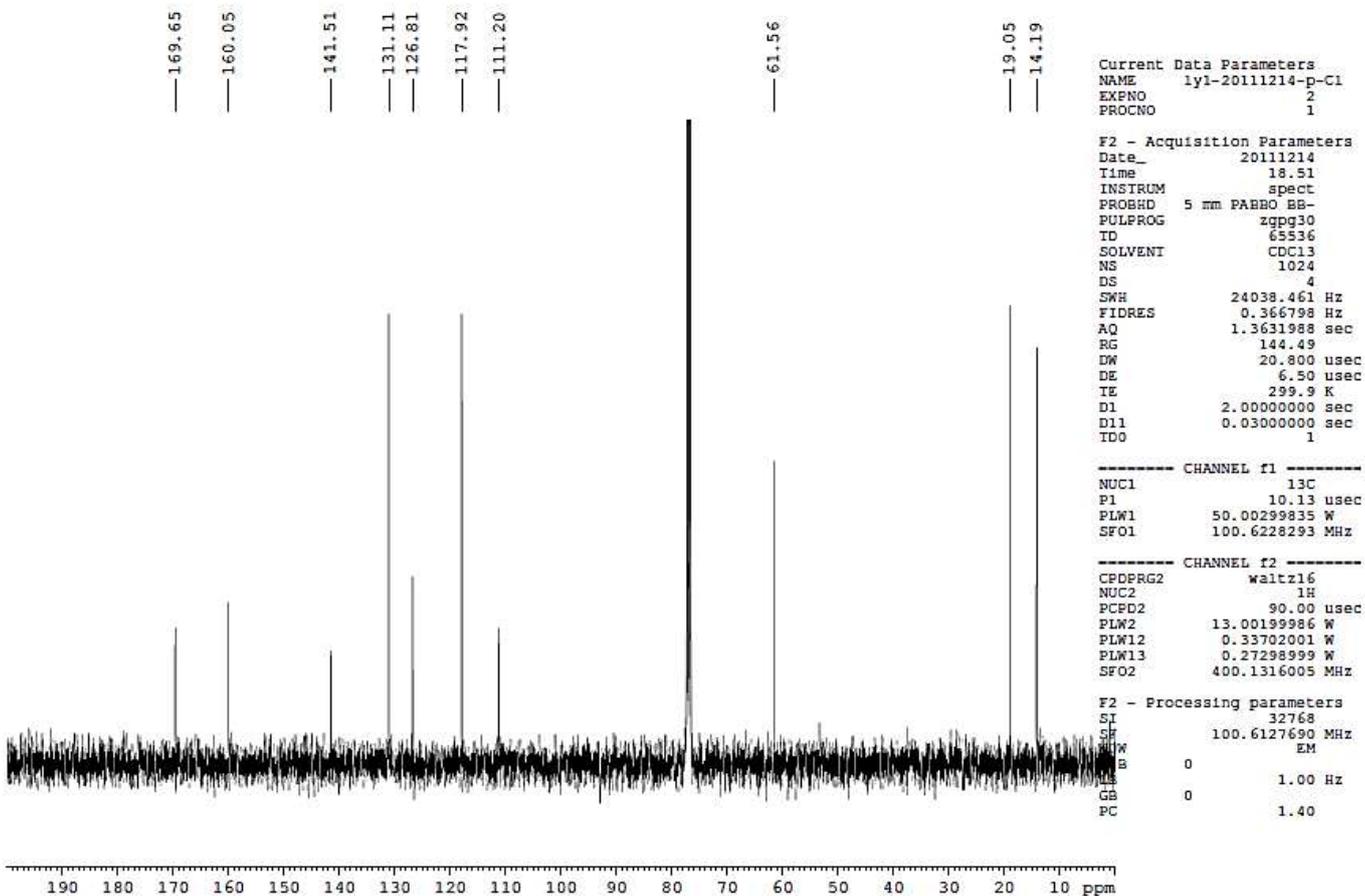
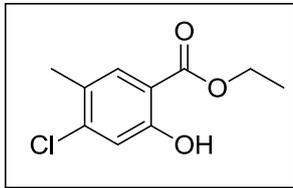
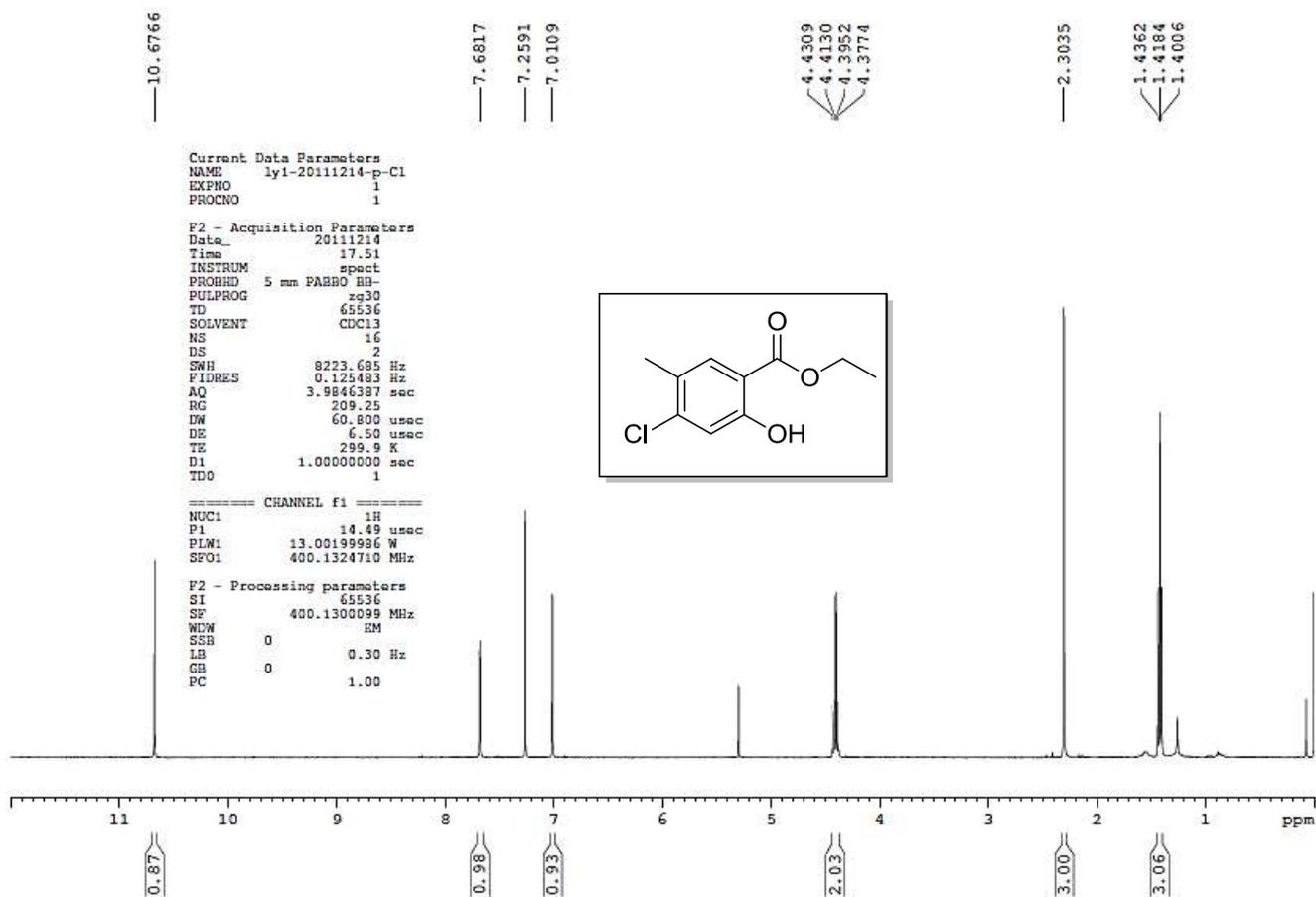
The spectrum of product (25)



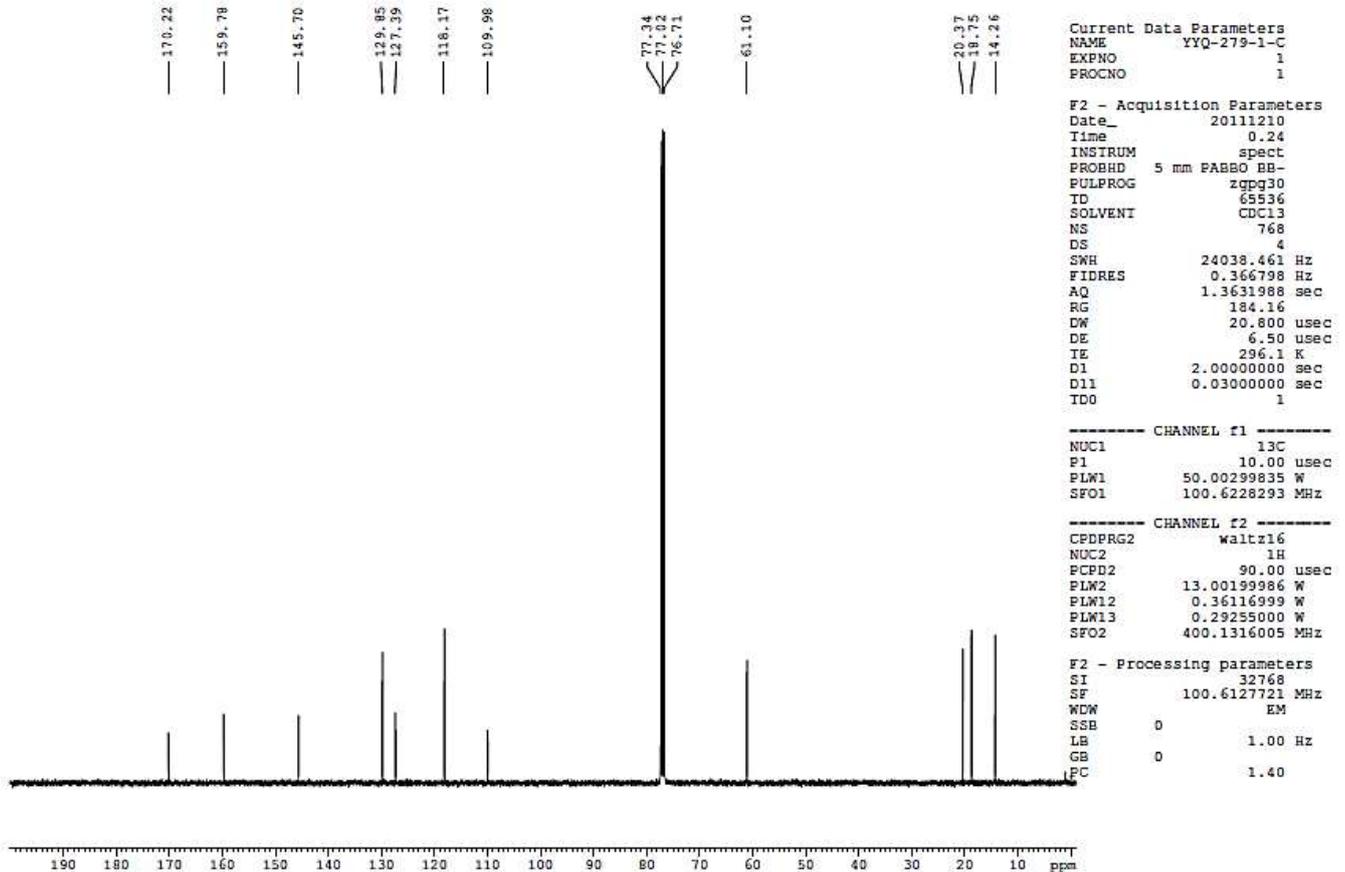
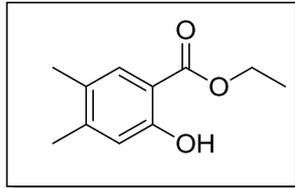
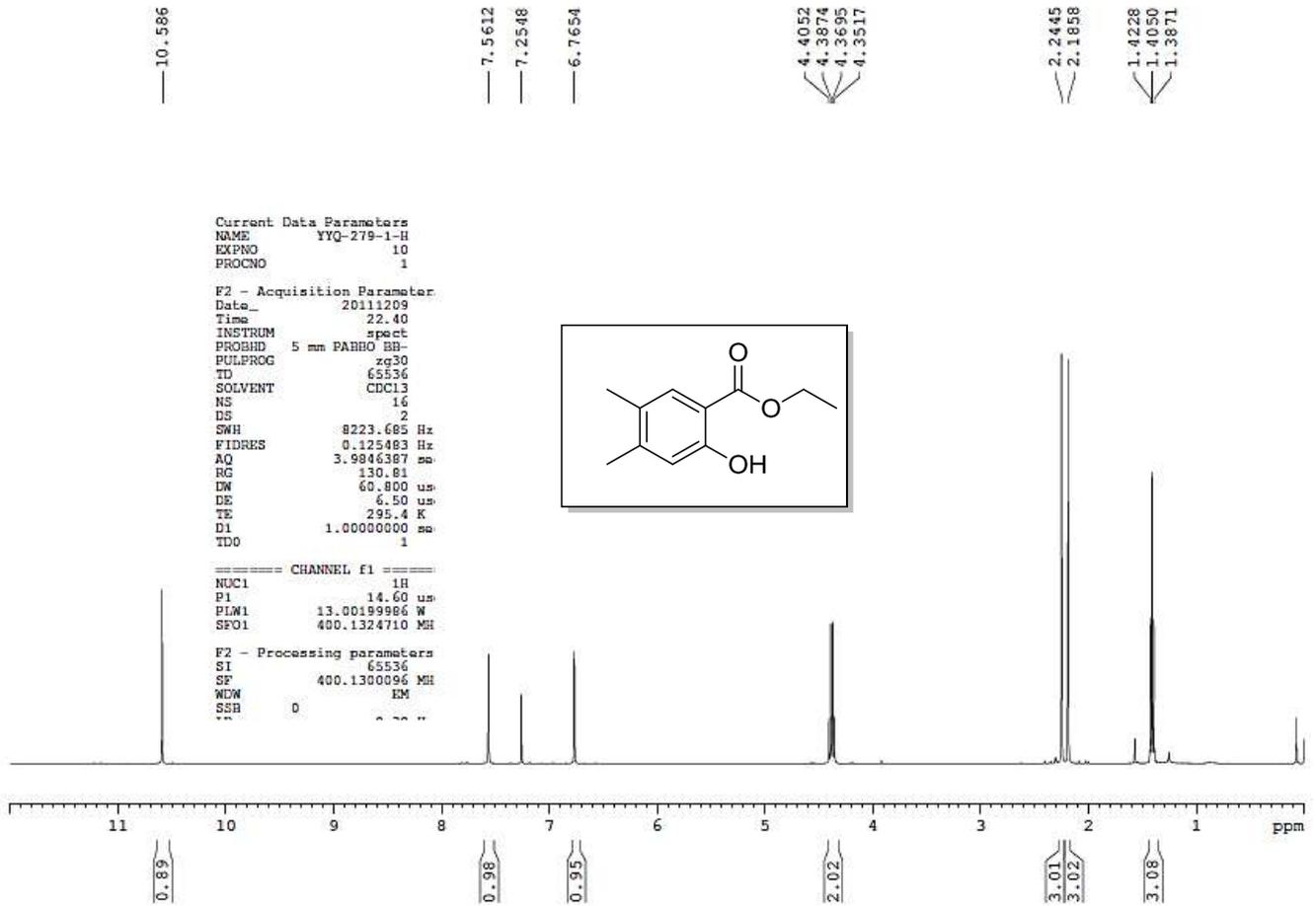
The spectrum of product (26)



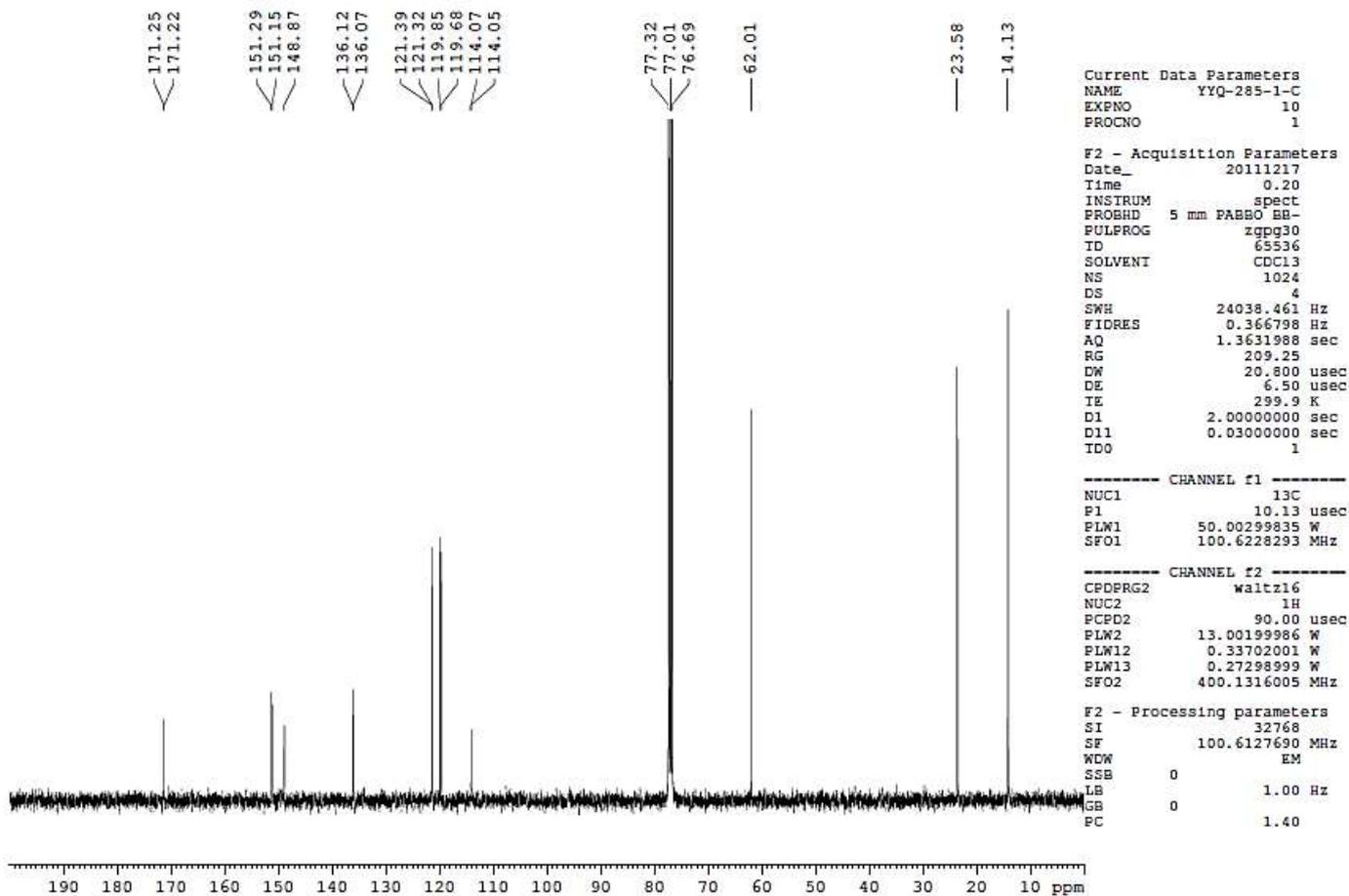
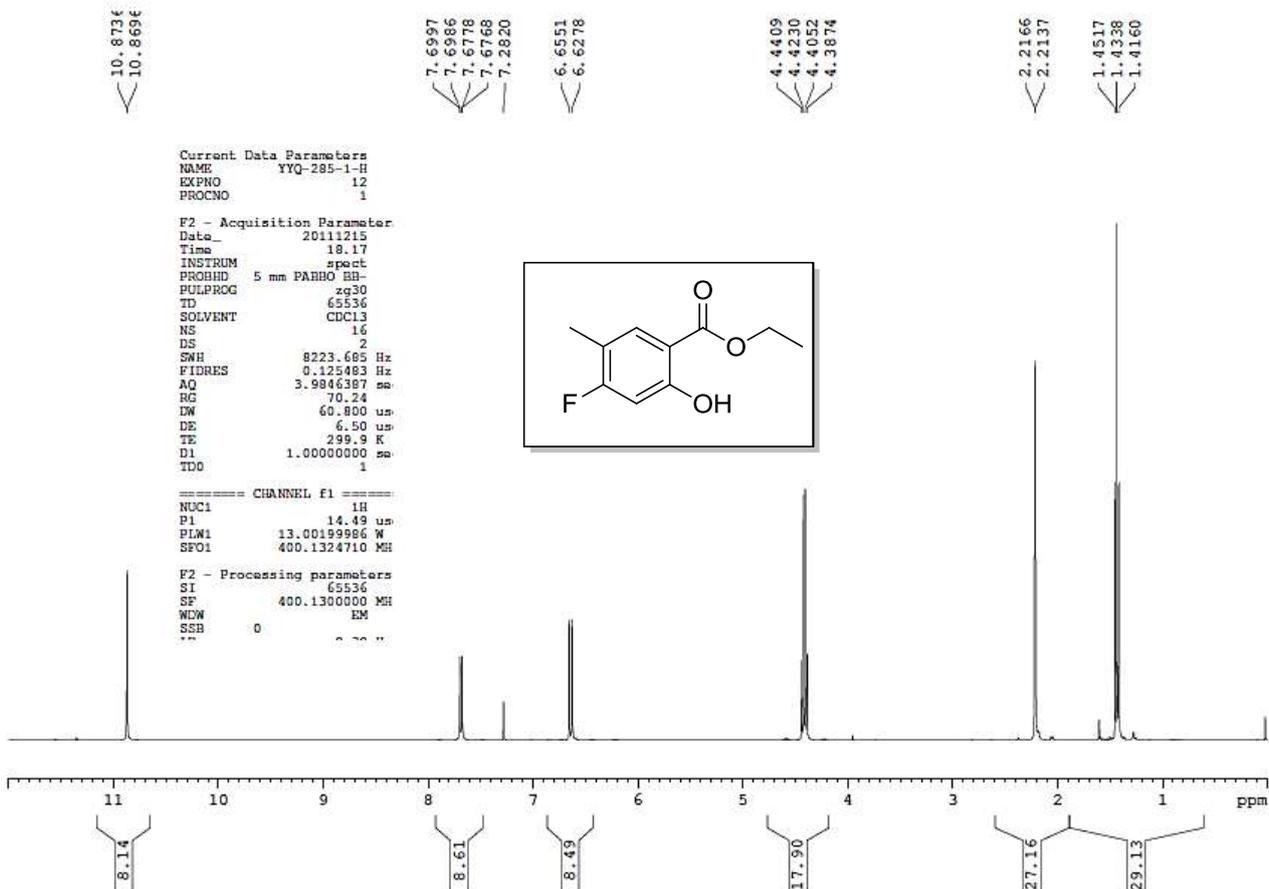
The spectrum of product (27)



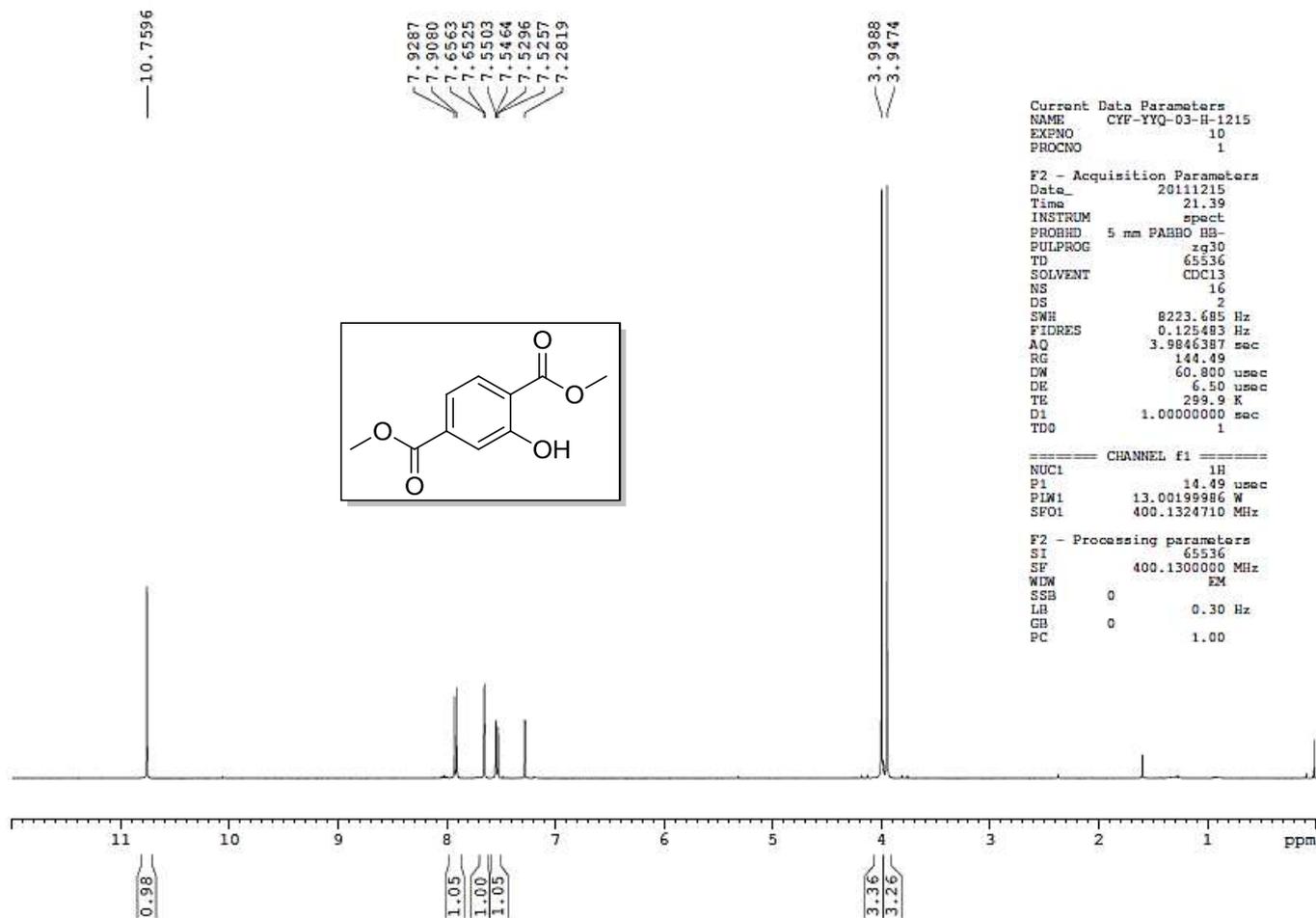
The spectrum of product (28)



The spectrum of product (29)



The spectrum of product (30)



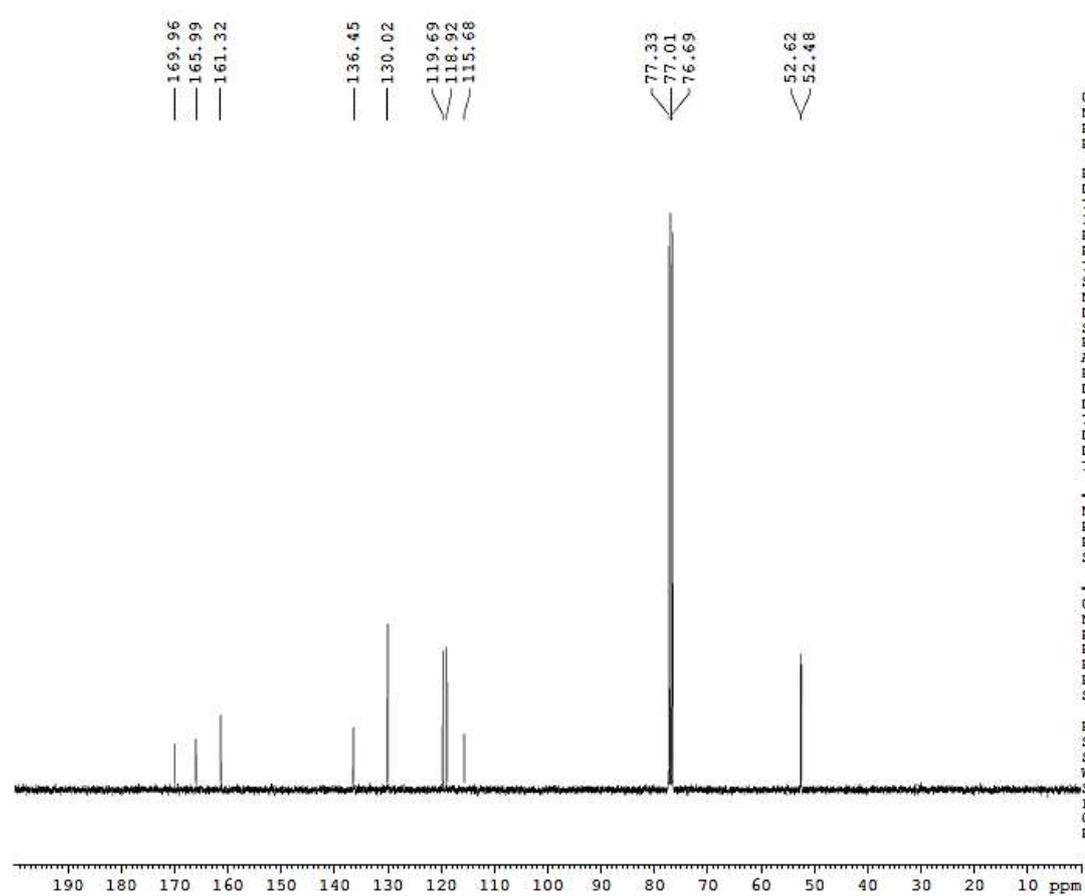
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Current Data Parameters
NAME      CYF-YYQ-03-H-1215
EXPNO    10
PROCNO    1

F2 - Acquisition Parameters
Date_    20111215
Time     21.39
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zg30
TD       65536
SOLVENT  CDCl3
NS       16
DS       2
SWH      8223.685 Hz
FIDRES   0.125483 Hz
AQ       3.9846387 sec
RG       144.49
DW       60.800 usec
DE       6.50 usec
TE       299.9 K
D1       1.00000000 sec
TD0      1

===== CHANNEL f1 =====
NUC1     1H
P1       14.49 usec
PLW1     13.00199986 W
SFO1     400.1324710 MHz

F2 - Processing parameters
SI       65536
SF       400.1300000 MHz
WDW      EM
SSB      0
LB       0.30 Hz
GB       0
PC       1.00
    
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```

Current Data Parameters
NAME      CYF-YYQ-03-C-1215
EXPNO    11
PROCNO    1

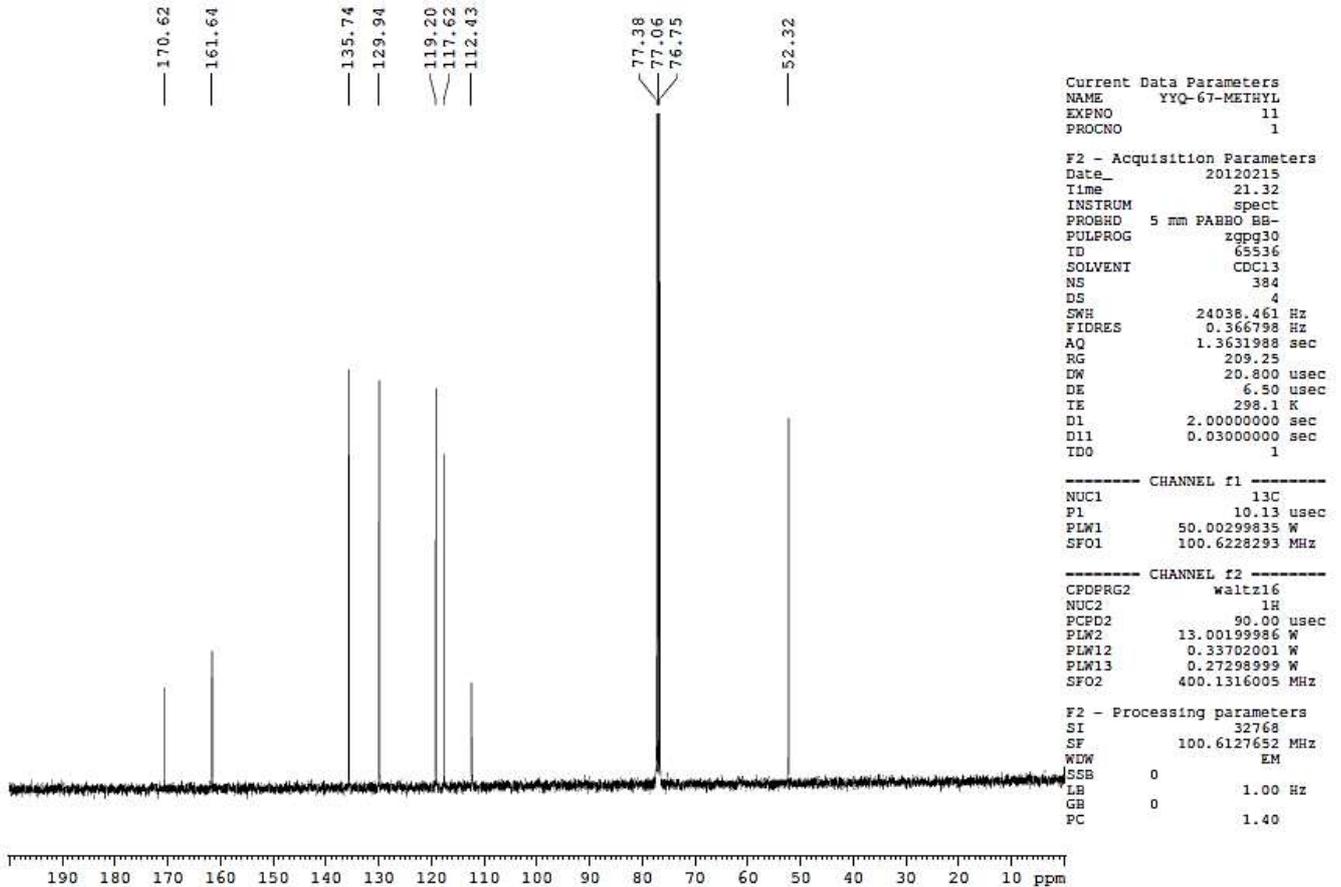
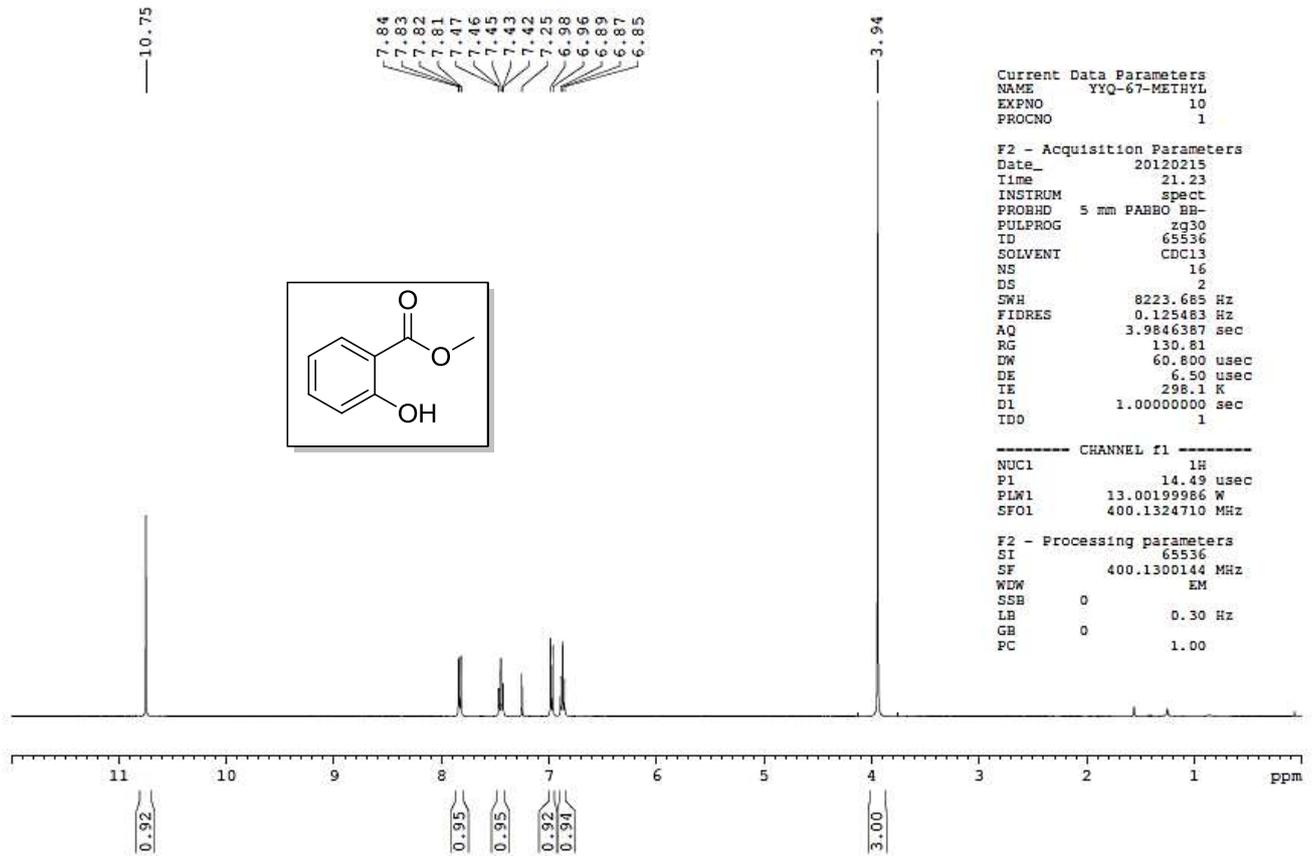
F2 - Acquisition Parameters
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Time     21.55
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zgpg30
TD       65536
SOLVENT  CDCl3
NS       256
DS       4
SWH      24038.461 Hz
FIDRES   0.366798 Hz
AQ       1.3631988 sec
RG       165.63
DW       20.800 usec
DE       6.50 usec
TE       299.9 K
D1       2.00000000 sec
D11      0.03000000 sec
TD0      1

===== CHANNEL f1 =====
NUC1     13C
P1       10.13 usec
PLW1     50.00299835 W
SFO1     100.6228293 MHz

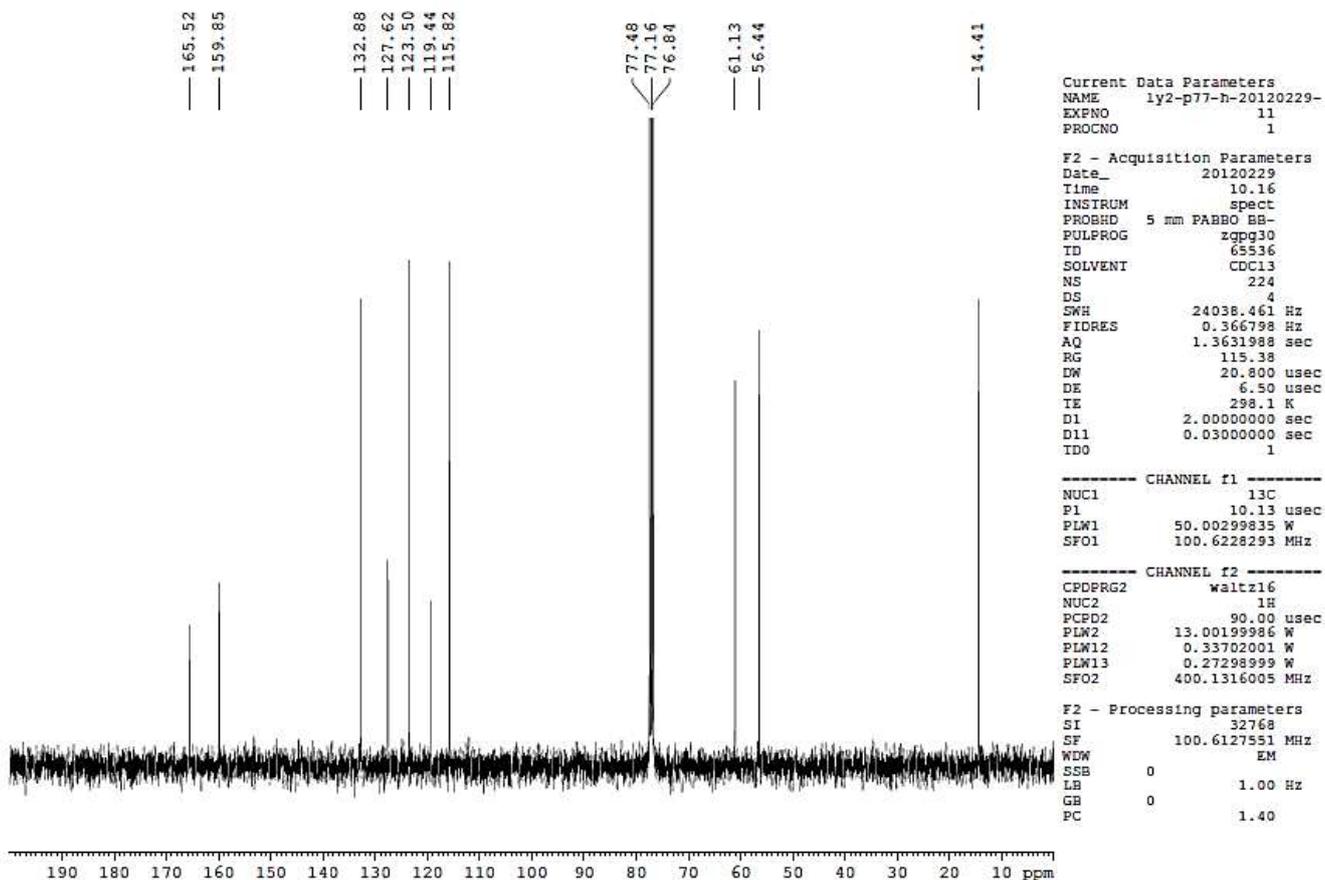
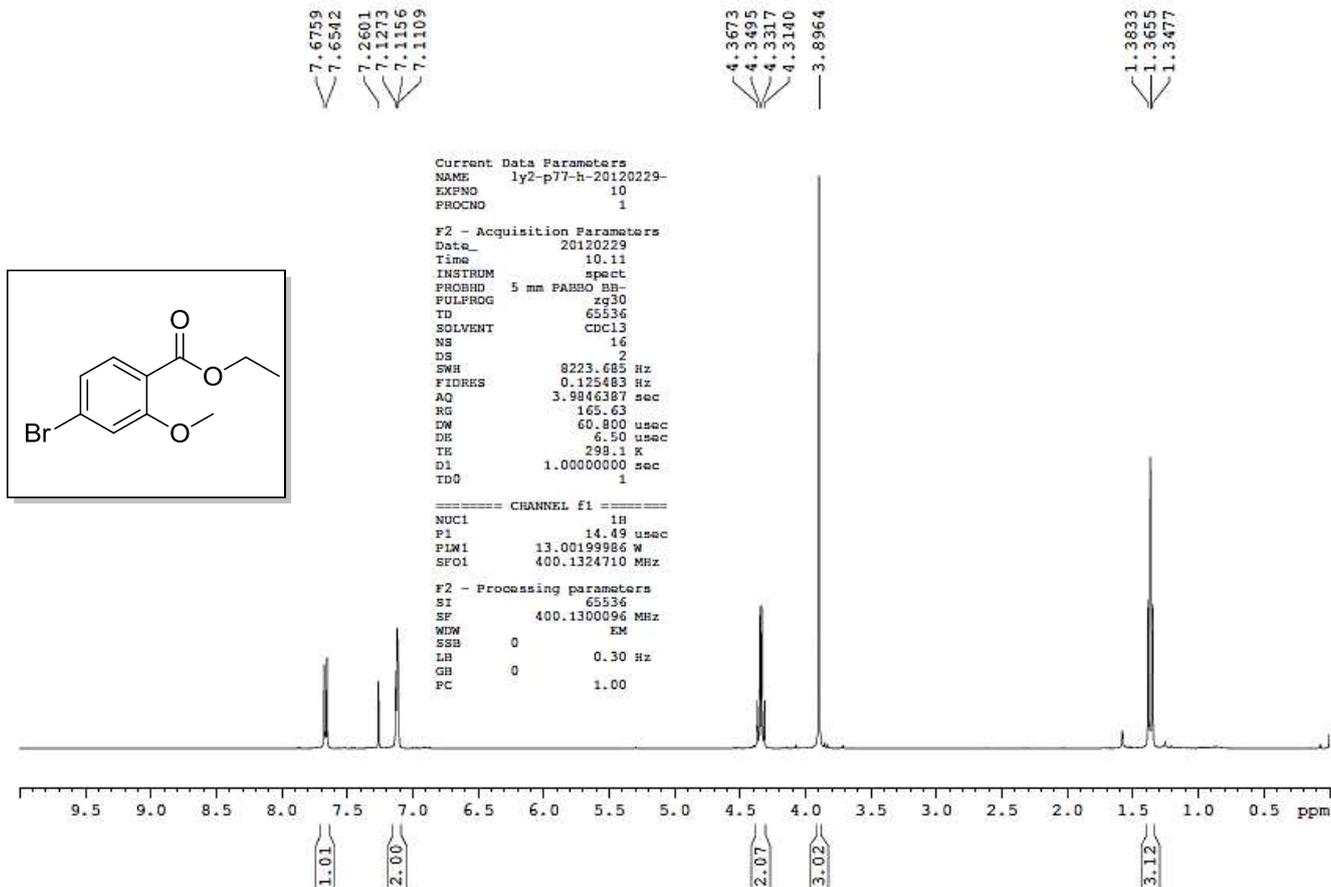
===== CHANNEL f2 =====
CPDPRG2  waltz16
NUC2     1H
PCPD2    90.00 usec
PLW2     13.00199986 W
PLW12    0.33702001 W
PLW13    0.27298999 W
SFO2     400.1316005 MHz

F2 - Processing parameters
SI       32768
SF       100.6127690 MHz
WDW      EM
SSB      0
LB       1.00 Hz
GB       0
PC       1.40
    
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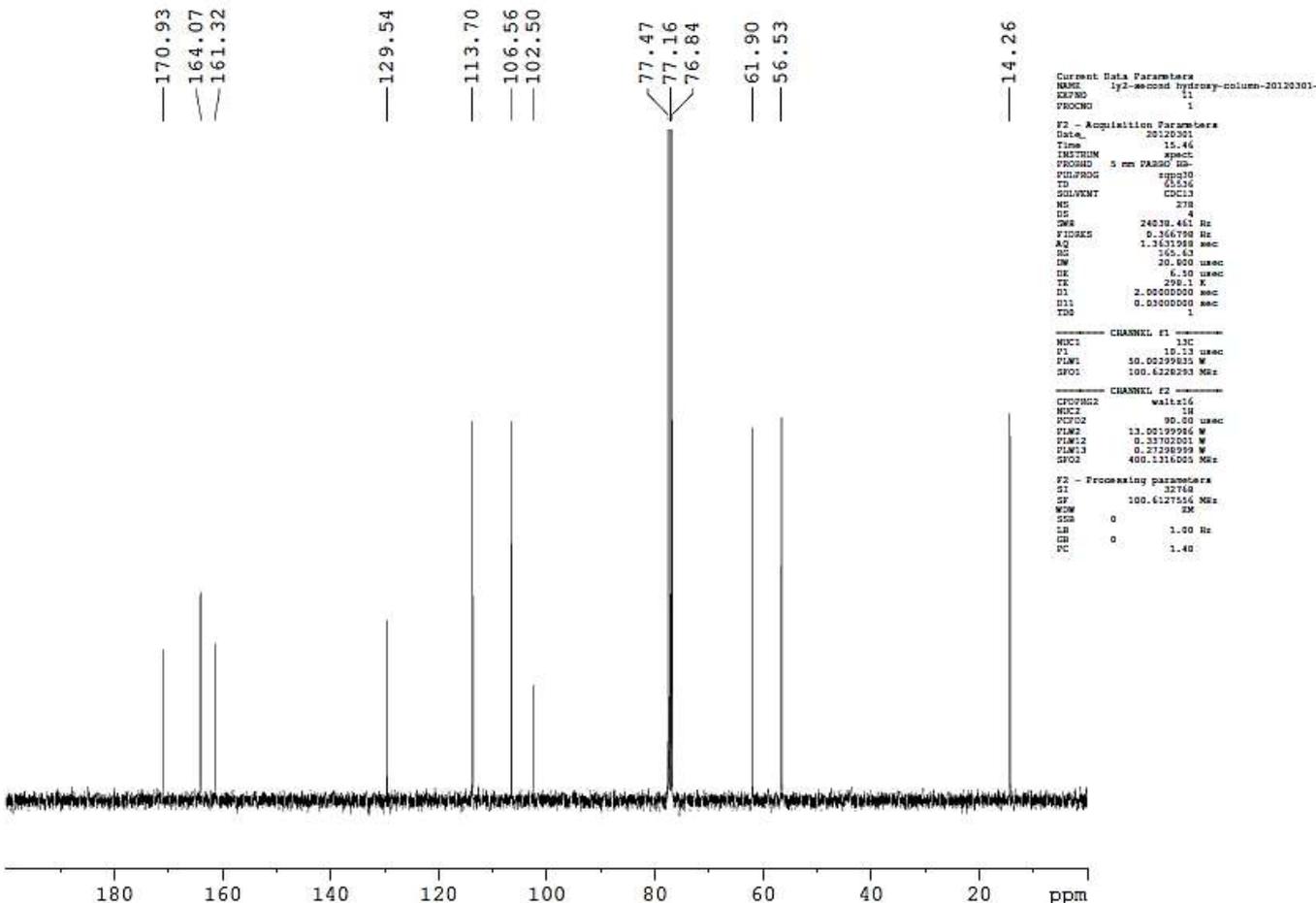
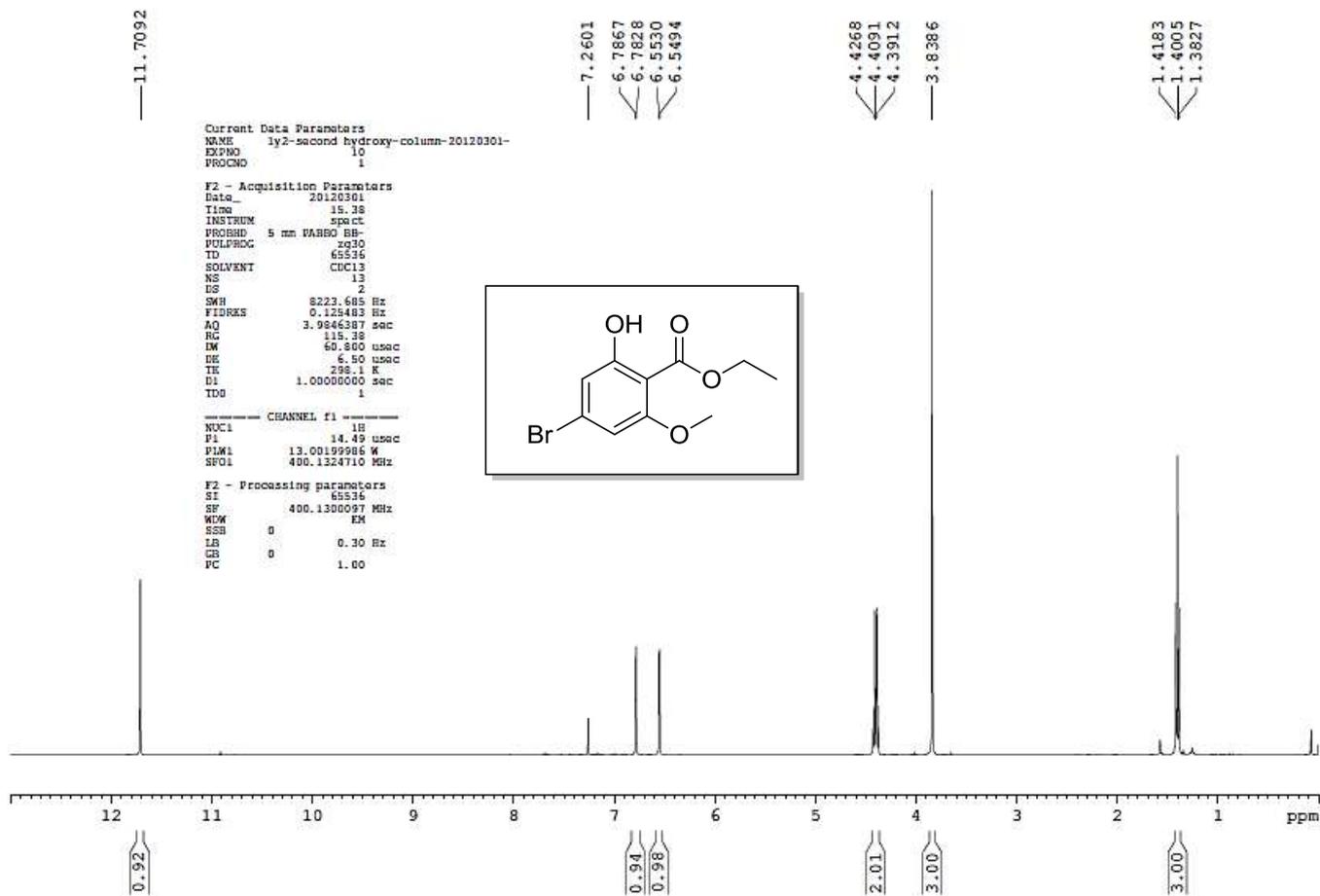
The spectrum of product (31)



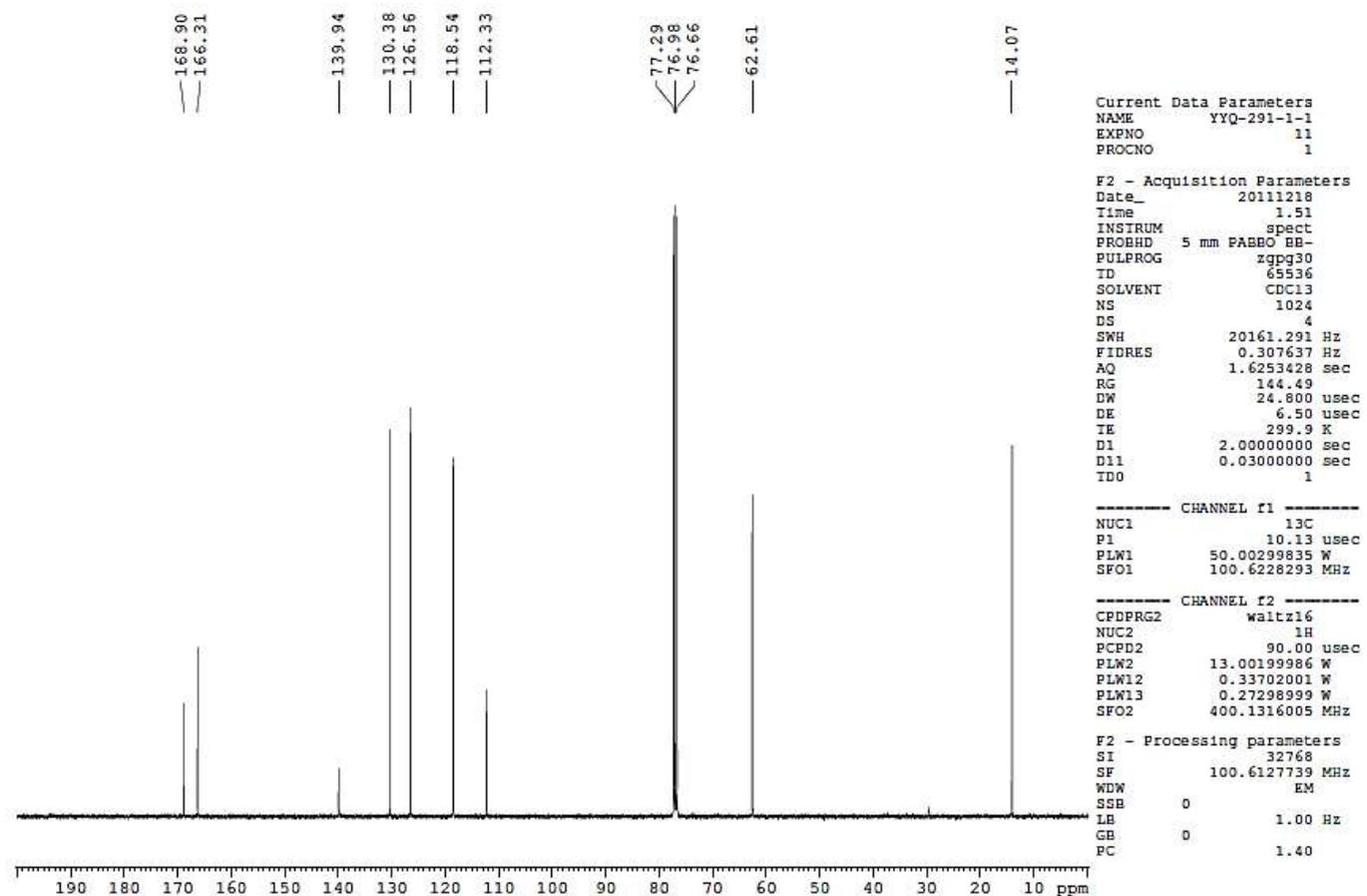
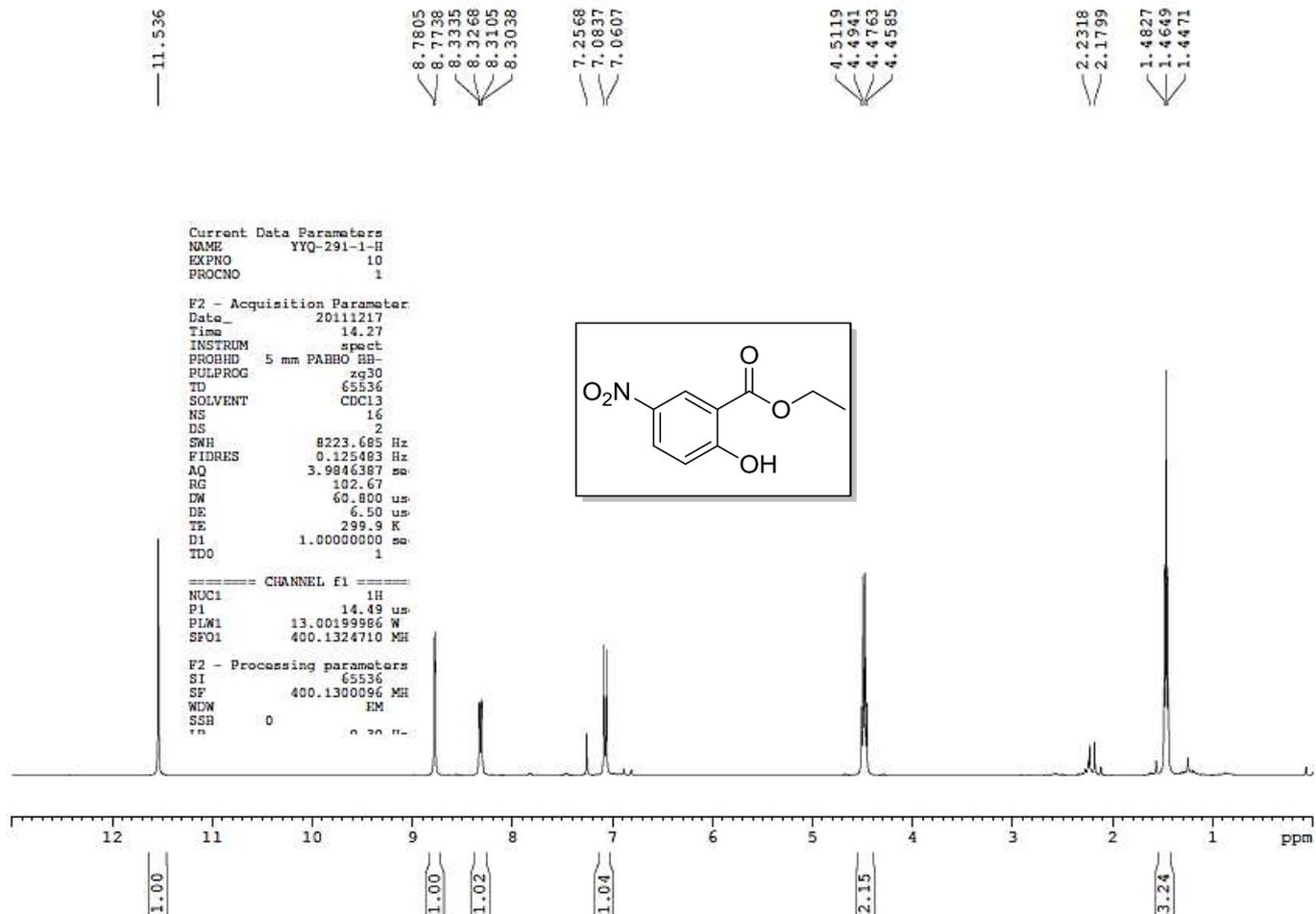
The spectrum of product (33)



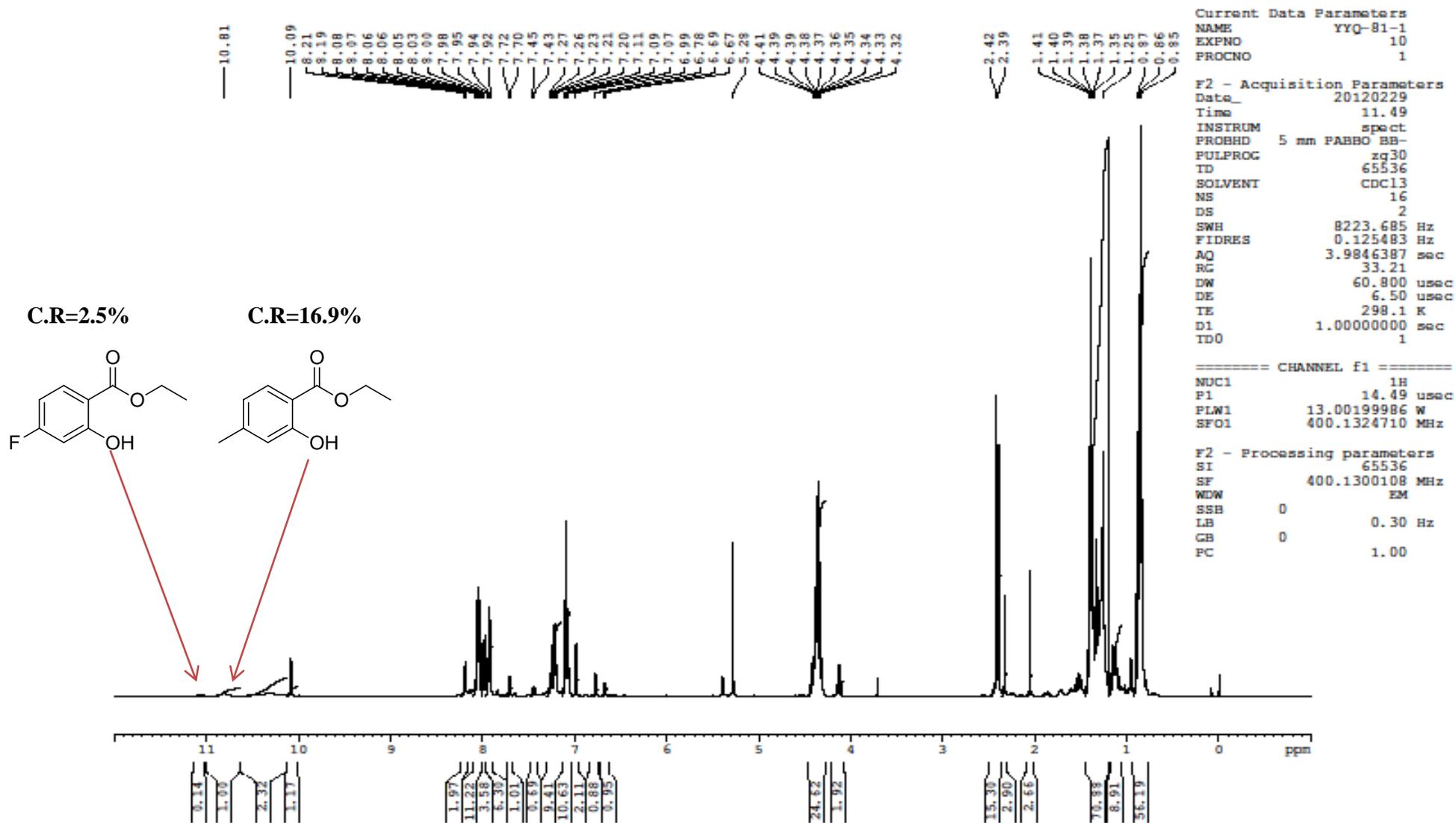
The spectrum of product (34)



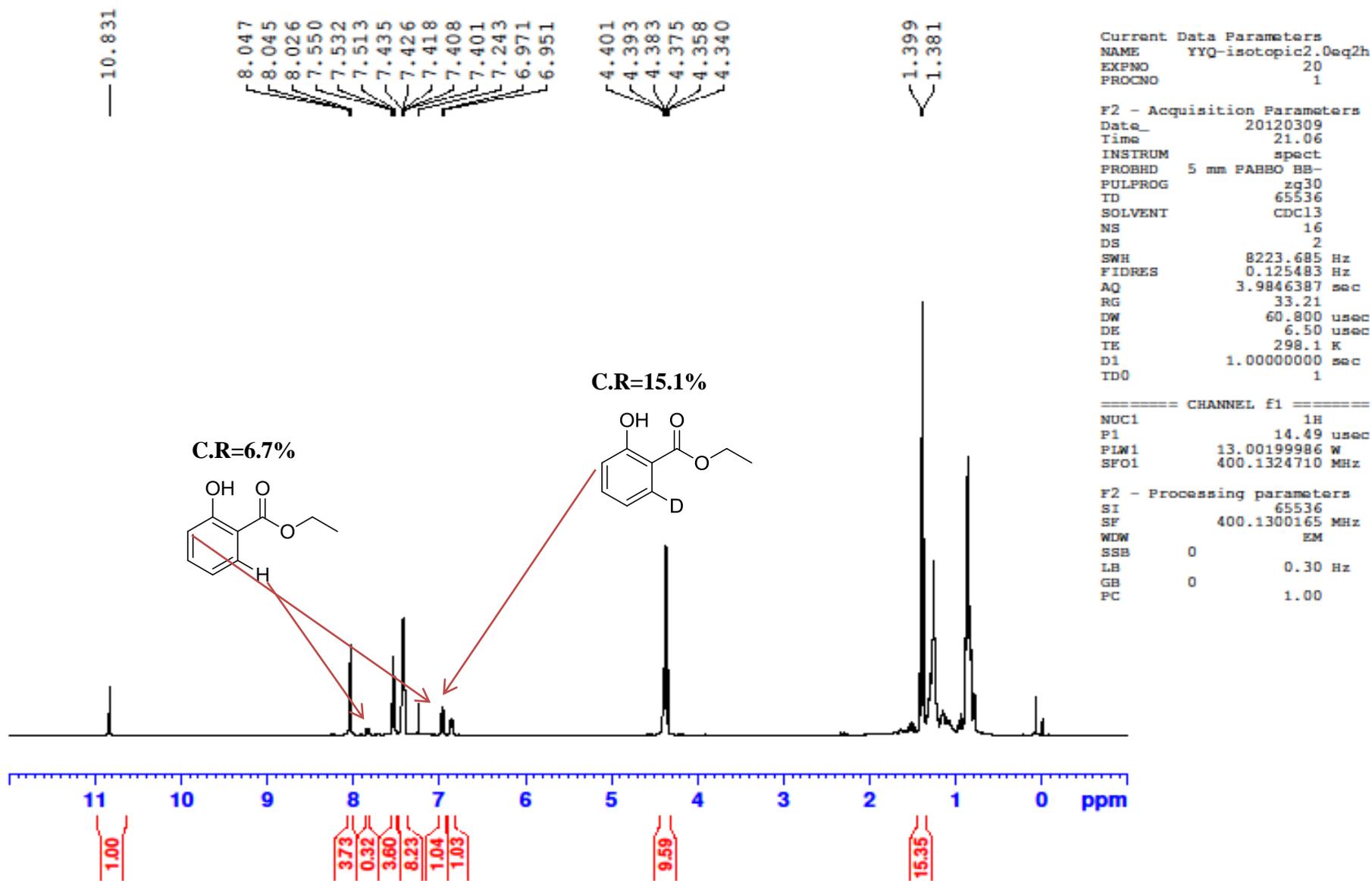
The spectrum of product (36)



# The NMR of competition study



The NMR of preliminary mechanistic study (intramolecular)



The NMR of preliminary mechanistic study (intermolecular)

