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Supporting Information

Lewis acid promoted construction of chromen-4-one and isoflavone scaffolds *via* regio- and chemoselective domino Friedel-Crafts acylation/Allan-Robinson reaction

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Experimentals

1. General Remarks

^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Chemical shift (δ) values are given in parts per million (ppm) with reference to tetramethylsilane (TMS) as the internal standard. Coupling constant (J) values are given in Hertz (Hz). High resolution mass spectra were recorded by ESI method. Organic solvents were dried by standard methods prior to be used. Commercially obtained reagents were used after further purification when needed. All these reactions were monitored by TLC with silica gel coated plates. Column chromatography was carried out whenever needed, using silica gel of 100/200 mesh. Mixture of hexane/ethyl acetate in appropriate proportion (determined by TLC analysis) was used as eluent.

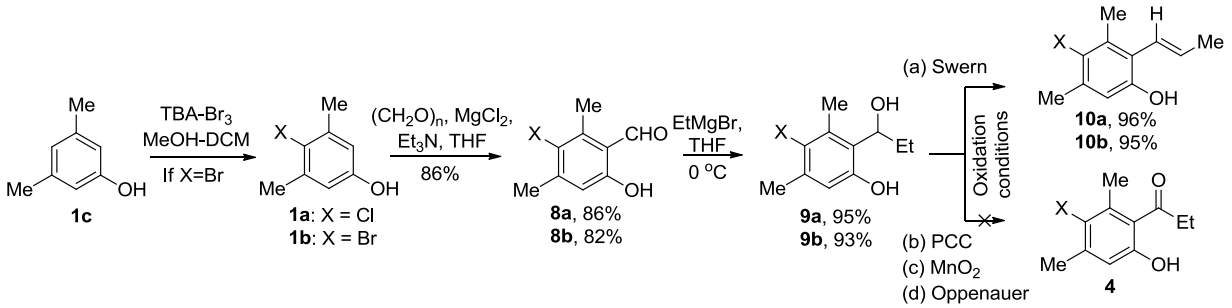
2. General reaction procedures

2. a. Preparation of **1b**:[1] 5 mmol of 3,5-dimethylphenol (**1c**) was dissolved in DCM (30 mL)-MeOH (20 mL) solvent system. 5 mmol of tetrabutylammonium tribromide was added portionwise with continuous stirring at rt., stirring was continued for another 30 minute until the orange color masked. Solvents were evaporated; water was added to the reaction mixture and extracted by ether (50×4). Crude obtained was directly used for the next step. Yield of **1b** so formed, was 89%. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.57 (s, 2H), 4.76 (s, 1H), 2.34 (s, 6H).

2. b. Procedure of $SnCl_4$ mediated O–acylation of substituted phenols **1** towards synthesis of **3**:
A mixture of 1 mmol of **1**, excess of **2** (10 mmol), and 2.5 mmol of $SnCl_4$ was heated at 100 °C under argon atmosphere for the stipulated period of time mentioned in Table 2 of the main manuscript (Completion of the reaction was monitored *via* TLC analysis). As in some cases boiling point of the initial substrate **2** was less than 100 °C, cold circulatory bath fitted with condenser was used to minimize the evaporation of the concerned substrate. After completion of the reaction, the residue obtained was dissolved in ethyl acetate (100 mL) and washed with 4% aqueous HCl (100 mL×2) followed by water, dilute $NaHCO_3$, and brine. Ethyl acetate was evaporated and crude was purified by column chromatography whenever needed using mixture of EtOAc and hexane in appropriate proportion as eluent.

2. c. $TiCl_4$ mediated synthesis of **5** via domino Friedel-Crafts/Allan Robinson reaction:
A mixture of 1 mmol of **1**, excess of **2** (10 mmol) and 2.5 mmol of $TiCl_4$ was heated at 100 °C under argon atmosphere for the stipulated period of time mentioned in Table 3 of the main manuscript (Completion of the reaction was monitored *via* TLC analysis). As in some cases boiling point of the initial substrate **2** was less than 100 °C, cold circulatory bath fitted with condenser was used to minimize the evaporation of the concerned substrate. After completion of the reaction, the residue obtained was dissolved in ethyl acetate (100 mL) and washed with 4% aqueous HCl (100 mL×2) followed by water, dilute $NaHCO_3$, and brine. Ethyl acetate was evaporated and crude thus obtained was purified by column chromatography whenever needed, using mixture of EtOAc and hexane in appropriate proportion as eluent.

Scheme 1. Attempted strategy for the synthesis of **4**.



2. d. Formylation of substituted phenol **1** towards synthesis of **8**[2]:

Parafomaldehyde (7 mmol) was added to a mixture of **1** (1 mmol), anhydrous $MgCl_2$ (1.5 mmol) and Et_3N (4 mmol) in dry THF (10 ml), and the mixture was heated to reflux for 24 h. Reaction was cooled to room temperature, solvent was evaporated. 50 mL of 5% aqueous HCl was poured to it and extracted with EtOAc (3×20). Combined organic layer was washed with water followed by brine. Solvent was evaporated in vacuo and subjected to column chromatography using mixture of EtOAc and hexane in appropriate proportion as eluent. Yield of **8a** is 86% and **8b** is 82%.

2. e. Procedure of Grignard addition to aldehyde **8** to synthesize alcohol **9**:

4 mmol of freshly prepared EtMgBr (1.5 M in THF) was added to the THF solution of **8** (1 mmol) at 0 °C. After 1 h the reaction was quenched with saturated NH_4Cl. Extracted with EtOAc (3×20 mL). Combined organic layer was washed with water followed by brine. Solvent was evaporated in vacuum that provided NMR pure alcohol **9**. Yield of **9a** and **9b** is 95% and 93% respectively.

2.f. Oxidation of alcohol **9:**

2.f.1. Oxidation of alcohol **9** by PCC:[3] 1 mmol of **9a** was dissolved in 10 mL of dry DCM followed by addition of 100 mg celite, 2-3 beads of activated 4 Å molecular sieves and 1.3 mmol of PCC. The reaction mixture was stirred at room temperature for 6 h. Work-up of the reaction did not provide even trace of the desired product **4**.

2.f.2. Oxidation by MnO_2:[4]

Procedure 1: MnO_2, DCM, room temperature:[4a] solution of **9** (1 mmol) in 10 mL of dry DCM was treated with 20 mmol of freshly prepared MnO_2. Unfortunately, even after stirring for 24 h at room temperature **9a** remained unconsumed.

Procedure 2: MnO_2, hexane, reflux:[4b] solution of **9** (1 mmol) in 10 mL of dry cyclohexane was treated with 20 mmol of freshly prepared MnO_2. Unfortunately, even after refluxing for 24 h at room temperature **9a** remained unconsumed.

2.f.3. Swern oxidation of alcohol **9**:[5]

Procedure 1:[5a] DMSO (2.8 mmol) was slowly added to the oxalyl chloride solution (1.4 mmol/2 mL of DCM) at -78 °C under argon, stirred for 15 min, 3 mL solution of **9** (1 mmol) in DCM+dioxane (2+1 mL) was added followed by 4 mmol of Et_3N, warmed to room temperature and stirred for 1 h, quenched with 1 N HCl. Extracted with EtOAc (3×20 mL). Combined organic layer was washed with water followed by brine. Solvent was evaporated in vacuum that provided NMR pure product **10** in quantitative yield;

Procedure 2:[5b] DMSO (5 mmol) was slowly added to the cyanuric chloride solution (1.2 mmol/10 mL of THF) at -30 °C under argon, stirred for 30 min, solution of **9** (1 mmol) in THF (4 mL) was added followed by 4 mmol of Et_3N and stirred for

15 min, warmed to room temperature and stirred for 1 h, solvent evaporated ether added and quenched with 1 N HCl; that provided **10** instead of the desired product **4**.

2.f.4. Different Oppenauer oxidation conditions:[6]

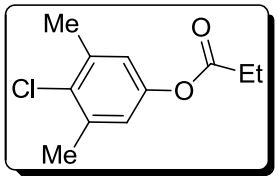
Procedure 1: $Al(O^iPr)_3$, cyclohexanone, toluene, room temperature:[6a]

Procedure 2: $Al(O^iPr)_3$, 3-nitrobenzaldehide, toluene, room temperature:[6b]

Procedure 3: KO^tBu, benzophenone, toluene, room temperature:[6c]

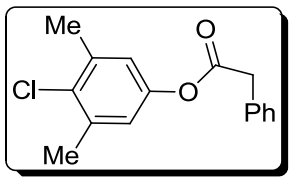
3. Characterization data of the synthesized molecules:

4-Chloro-3,5-dimethylphenylpropionate (**3ab**):



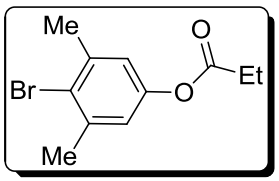
^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.81 (s, 2H), 2.59 (q, J = 7.5 Hz, 2H), 2.35 (s, 6H), 1.27 (t, J = 7.5 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 172.9, 148.3, 137.3, 131.5, 121.3, 27.6, 20.7, 8.9; HRMS (ESI-TOF) of $C_{13}H_{11}ClO_2$ (m/z) = 235.0504 [M+Na$^+$] (calculated = 235.0502).

4-Chloro-3,5-dimethylphenyl-2-phenylacetate (**3ag**):



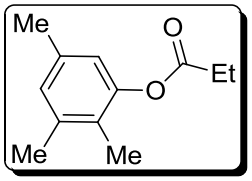
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.25-7.19 (m, 5H), 6.67 (s, 2H), 3.70 (s, 2H), 2.21 (s, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 169.8, 148.2, 137.3, 133.2, 131.6, 129.1, 128.6, 127.2, 121.1, 41.2, 20.6; HRMS (ESI-TOF) of $C_{16}H_{15}ClO_2$ (m/z) = 275.0838 [M+H$^+$] (calculated = 275.0839).

4-Bromo-3,5-dimethylphenylpropionate (**3bb**):



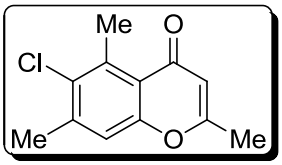
^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.81 (s, 2H), 2.593 (q, J = 7.5 Hz, 2H), 2.38 (s, 6H), 1.27 (t, J = 7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 172.8, 149.0, 139.3, 123.9, 121.1, 27.6, 23.8, 8.9;

2,3,5-Trimethylphenylpropionate (**3eb**):



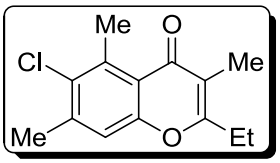
^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.83 (s, 1H), 6.65 (s, 1H), 2.62 (q, J = 7.5 Hz, 2H), 2.25-2.23 (m, 6H), 2.00 (s, 3H), 1.29 (t, J = 7.5 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 172.8, 148.9, 137.9, 135.7, 128.2, 125.2, 119.7, 27.5, 20.6, 19.8, 11.8, 9.1; HRMS (ESI-TOF) of $C_{12}H_{16}O_2$ (m/z) = 193.1228 [M+H$^+$] (calculated = 193.1229).

6-Chloro-2,5,7-trimethyl-4*H*-chromen-4-one (**5aa**)[7]:



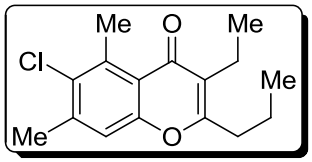
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.15 (s, 1H), 6.06 (s, 1H), 2.96 (s, 3H), 2.47 (s, 3H), 2.30 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 179.6, 163.9, 142.0, 138.0, 137.2, 132.3, 117.2, 111.8, 111.7, 21.8, 19.8, 18.0.

6-Chloro-2-ethyl-3,5,7-trimethyl-4*H*-chromen-4-one (**5ab**):



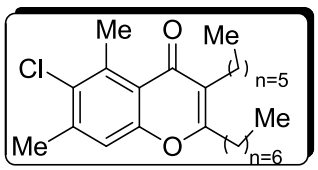
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.12 (s, 1H), 2.97 (s, 3H), 2.70 (q, J = 7.65 Hz, 2H), 2.44 (s, 3H), 2.00 (s, 3H), 1.30 (t, J = 7.65 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 179.4, 163.8, 155.2, 141.4, 137.8, 131.7, 119.8, 117.0, 116.6, 25.2, 21.7, 18.0, 11.2, 9.7; CCDC 932483; HRMS (ESI-TOF) of $C_{14}H_{15}ClO_2$ (m/z) = 251.0838 [M+H$^+$] (calculated m/z = 251.0839).

6-Chloro-3-ethyl-5,7-dimethyl-2-propyl-4*H*-chromen-4-one (**5ac**):



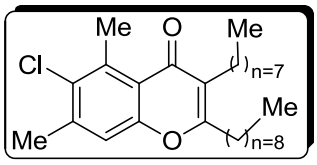
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.11 (s, 1H), 2.98 (s, 3H), 2.64-2.45 (m, 5H), 1.80-1.72 (m, 2H), 1.29-1.25 (m, 2H), 1.13 (t, J = 7.5 Hz, 3H), 1.04 (t, J = 7.5 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 178.9, 162.9, 155.2, 141.3, 137.8, 131.7, 123.3, 121.3, 120.3, 117.0, 33.2, 21.7, 20.7, 18.0, 13.8, 13.7; HRMS (ESI-TOF) of $C_{16}H_{19}ClO_2$ (m/z) = 279.1152 [M+H$^+$] (calculated = 279.1154).

6-Chloro-2-heptyl-3-hexyl-5,7-dimethyl-4*H*-chromen-4-one (**5ad**):



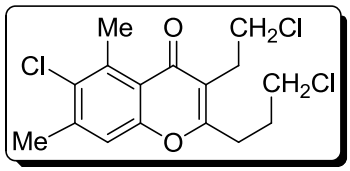
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.07 (s, 1H), 2.94 (s, 3H), 2.61 (t, J = 7.5 Hz, 2H), 2.41 (broad, 5H), 1.73-1.63 (m, 2H), 1.27-1.22 (broad, 15H), 0.86 (broad, 7H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 179.0, 163.3, 155.2, 141.3, 137.8, 131.7, 121.9, 120.2, 116.9, 31.6, 31.4, 29.5, 29.3, 29.2, 28.9, 28.8, 27.3, 24.8, 22.6, 22.5, 21.7, 18.1, 18.0, 14.0; HRMS (ESI-TOF) of $C_{24}H_{35}ClO_2$ (m/z) = 391.2401 [M+H$^+$] (calculated 391.2398).

6-Chloro-5,7-dimethyl-2-nonyl-3-octyl-4*H*-chromen-4-one (**5ae**):



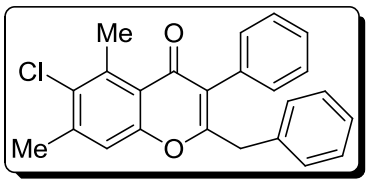
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.11 (s, 1H), 2.98 (s, 3H), 2.64 (t, J = 7.5 Hz, 2H), 2.45 (broad, 5H), 1.71-1.66 (m, 2H), 1.27 (broad, 23H), 0.87-0.85 (broad, 7H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 179.0, 163.3, 155.2, 141.3, 137.9, 131.7, 122.0, 120.3, 117.0, 31.8, 31.4, 29.9, 29.4, 29.3, 27.3, 24.8, 22.6, 21.7, 18.1, 14.0; HRMS (ESI-TOF) of $C_{28}H_{43}ClO_2$ (m/z) = 447.3033 [M+H$^+$] (calculated 447.3024).

6-Chloro-3-(2-chloroethyl)-2-(3-chloropropyl)-5,7-dimethyl-4*H*-chromen-4-one (**5af**):



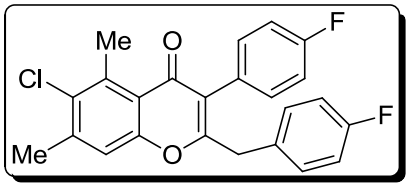
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.15 (s, 1H), 3.79 (t, J = 6.3 Hz, 2H), 3.65 (t, J = 6.3 Hz, 2H), 3.00-2.90 (m, 7H), 2.47 (s, 3H), 2.62-2.21 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 178.6, 163.4, 155.2, 142.1, 138.0, 132.3, 119.9, 118.4, 117.0, 43.9, 43.3, 29.8, 28.9, 28.6, 21.8, 18.0; HRMS (ESI-TOF) of $C_{16}H_{17}Cl_3O_2$ (m/z) = 389.0810 [M+Na$^+$] (calculated 389.0816).

2-Benzyl-6-chloro-5,7-dimethyl-3-phenyl-4*H*-chromen-4-one (**5ag**):



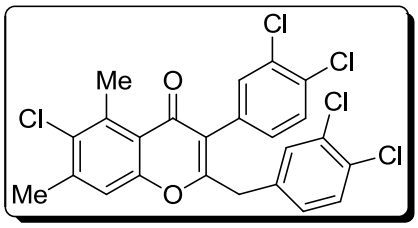
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.46-7.14 (m, 11H), 3.82 (s, 2H), 2.94 (s, 3H), 2.47 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 178.7, 161.7, 155.2, 142.1, 138.4, 135.9, 133.1, 132.3, 131.0, 130.6, 128.6, 127.0, 124.9, 120.8, 117.3, 38.6, 21.8, 18.2; HRMS (ESI-TOF) of $C_{24}H_{19}ClO_2$ (m/z) = 375.1153 [M+H$^+$] (calculated 375.1152).

6-Chloro-2-(4-fluorobenzyl)-3-(4-fluorophenyl)-5,7-dimethyl-4*H*-chromen-4-one (**5ah**):



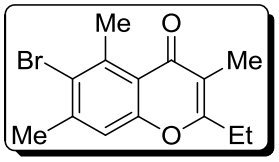
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.24-6.93 (m, 9H), 3.78 (s, 2H), 2.92 (s, 3H), 2.47 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 178.3, 164.1, 163.5, 161.8, 160.8, 160.2, 155.2, 142.4, 138.4, 132.5, 132.3, 132.2, 131.5, 130.1, 130.0, 128.7, 123.8, 120.5, 117.2, 115.7, 115.4, 37.4, 21.8, 18.0; HRMS (ESI-TOF) of $C_{14}H_{17}ClF_2O_2$ (m/z) = 411.0964 [M+H$^+$] (calculated 411.0958).

6-Chloro-2-(3,4-dichlorobenzyl)-3-(3,4-dichlorophenyl)-5,7-dimethyl-4*H*-chromen-4-one (**5ai**):



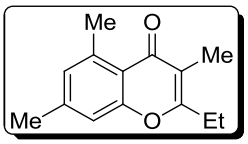
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.53 (d, J = 8.4 Hz, 1H), 7.35-7.32 (m, 2H), 7.25-7.18 (m, 2H), 7.09 (d, J = 8.1 Hz, 1H), 6.97 (d, J = 8.4 Hz, 1H), 3.77 (s, 2H), 2.92 (s, 3H), 2.49 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 177.7, 166.8, 160.9, 155.1, 142.9, 138.6, 135.5, 133.1, 132.9, 132.8, 132.8, 132.6, 132.5, 132.4, 130.7, 130.5, 129.9, 127.9, 123.1, 117.2, 117.2, 37.4, 21.9, 18.1; HRMS (ESI-TOF) of $C_{24}H_{15}Cl_5O_2$ (m/z) = 534.9376 [M+Na$^+$] (calculated 534.9383).

6-Bromo-2-ethyl-3,5,7-trimethyl-4*H*-chromen-4-one (**5bb**):



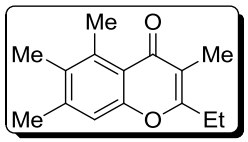
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.17 (s, 1H), 3.05 (s, 3H), 2.71 (q, J = 7.5 Hz), 2.51 (s, 3H), 2.01 (s, 3H), 1.26-1.25 (m, 3H); HRMS (ESI-TOF) of $C_{14}H_{15}BrO_2$ (m/z) = 294.0237 [M$^+$] (calculated 294.0255).

2-Ethyl-3,5,7-trimethyl-4*H*-chromen-4-one (**5cb**):



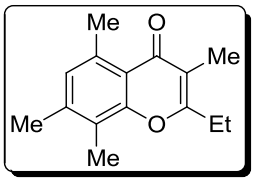
^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.98 (s, 1H), 6.84 (s, 1H), 2.81 (s, 3H), 2.68 (q, J = 7.5 Hz, 2H), 2.35 (s, 3H), 1.99 (s, 3H), 1.29 (t, J = 7.5 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 179.9, 163.8, 157.3, 142.5, 140.1, 128.2, 118.5, 116.2, 115.3, 25.1, 22.5, 21.2, 11.1, 9.3; HRMS (ESI-TOF) of $C_{14}H_{16}O_2$ (m/z) = 239.1046 [M+Na$^+$] (calculated 239.1043).

2-Ethyl-3,5,6,7-tetramethyl-4*H*-chromen-4-one (**5db**):



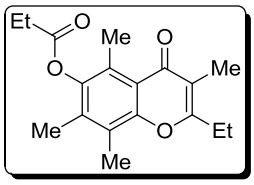
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.01 (s, 1H), 2.84 (s, 3H), 2.68 (q, J = 7.5 Hz, 2H), 2.34 (s, 3H), 2.21 (s, 3H), 2.00 (s, 3H), 1.29 (t, J = 7.5 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 180.4, 163.3, 155.3, 141.9, 137.9, 132.1, 118.9, 116.3, 115.7, 25.2, 21.5, 17.1, 15.1, 11.2, 9.7; HRMS (ESI-TOF) of $C_{15}H_{18}O_2$ (m/z) = 253.1193 [M+Na$^+$] (calculated 253.1199).

2-Ethyl-3,5,7,8-tetramethyl-4*H*-chromen-4-one (**5eb**):



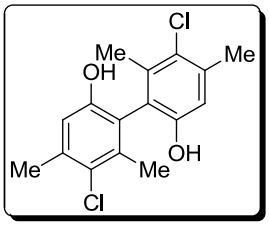
^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.86 (s, 1H), 2.78-2.68 (m, 5H), 2.32-2.29 (m, 6H), 2.00 (s, 3H), 1.33 (t, J = 7.5 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 180.6, 163.6, 155.3, 140.8, 136.8, 128.7, 122.3 118.8, 115.9, 25.2, 22.5, 20.0, 11.3, 9.4; HRMS (ESI-TOF) of $C_{15}H_{18}O_2$ (m/z) = 231.1381 [M+H$^+$] (calculated 231.1385).

2-Ethyl-3,5,7,8-tetramethyl-4-oxo-4*H*-chromen-6-yl propionate (**5fb**):



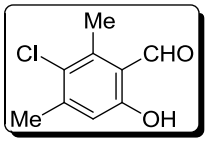
^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.73-2.64 (m, 7H), 2.35 (s, 3H), 2.16 (s, 3H), 2.00 (s, 3H), 1.35-1.25 (m, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 180.5, 172.4, 163.7, 153.1, 144.2, 134.4, 128.2, 123.8, 119.1, 116.0, 27.3, 25.2, 13.8, 13.6, 11.8, 11.2, 9.5, 9.2; HRMS (ESI-TOF) of $C_{18}H_{22}O_2$ (m/z) = 325.1410 [M+Na$^+$] (calculated 325.1410).

5,5'-dichloro-4,4',6,6'-tetramethyl-[1,1'-biphenyl]-2,2'-diol (**6a**)[8]:



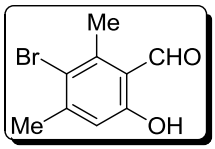
^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.82 (s, 2H), 4.59 (s, 2H), 2.40 (s, 6H), 2.04 (s, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 151.7, 138.7, 136.6, 127.1, 118.6, 115.6, 21.0, 17.7.

3-Chloro-6-hydroxy-2,4-dimethylbenzaldehyde (**8a**)[9]:



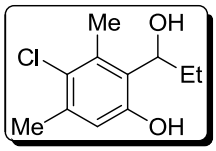
^{1}H-NMR (300 MHz, $CDCl_3$) δ 11.98 (s, 1H), 10.28 (s, 1H), 6.78 (s, 1H), 2.64 (s, 3H), 2.38 (s, 3H).

3-Bromo-6-hydroxy-2,4-dimethylbenzaldehyde (**8b**):



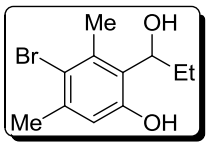
^{1}H-NMR (300 MHz, $CDCl_3$) δ 12.03 (s, 1H), 10.30 (s, 1H), 6.77 (s, 1H), 2.69 (s, 3H), 2.42 (s, 3H).

4-Chloro-2-(1-hydroxypropyl)-3,5-dimethylphenol (**9a**):



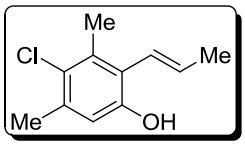
^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.61 (s, 1H), 6.61 (s, 1H), 5.07 (br, 1H), 2.82 (s, 1H), 2.29 (s, 3H), 2.25 (s, 3H), 1.95-1.64 (m, 2H), 1.03 (t, J = 7.5 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 154.2, 136.4, 132.4, 125.9, 124.4, 117.4, 117.3, 74.8, 29.1, 20.9, 16.3, 10.3.

4-Bromo-2-(1-hydroxypropyl)-3,5-dimethylphenol (**9b**):



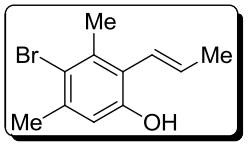
^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.69 (s, 1H), 6.63 (s, 1H), 5.08 (broad, 1H), 2.93 (s, 1H), 2.32 (s, 1H), 2.30 (s, 1H), 1.91-1.69 (m, 2H), 1.03 (t, J = 7.35 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 154.8, 138.4, 134.2, 124.5, 118.6, 117.5, 117.4, 75.2, 29.1, 24.2, 19.6, 10.3.

4-Chloro-3,5-dimethyl-2-(prop-1-en-1-yl)phenol (**10a**):



^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.94 (s, 1H), 6.28-6.23 (m, 1H), 5.96-5.84 (m, 1H), 5.39 (s, 1H), 2.33 (s, 1H), 2.27 (s, 1H), 1.96 (d, J = 6 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 150.7, 135.8, 134.6, 133.1, 126.0, 125.4, 123.0, 114.8, 20.8, 18.7, 17.8; HRMS (ESI-TOF) of $C_{11}H_{13}ClO$ = 197.0572 [M+H$^+$] (calculated 197.0728).

4- Bromo -3,5-dimethyl-2-(prop-1-en-1-yl)phenol (**10b**):



^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.71 (s, 1H), 6.29-6.23 (m, 1H), 5.92-5.85 (m, 1H), 5.43 (s, 1H), 2.34 (s, 3H), 2.32 (s, 3H), 1.96 (d, J = 6 Hz, 2H);); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 151.3, 137.8, 136.4, 133.3, 125.6, 123.1, 118.3, 114.8, 23.9, 21.0, 18.8.

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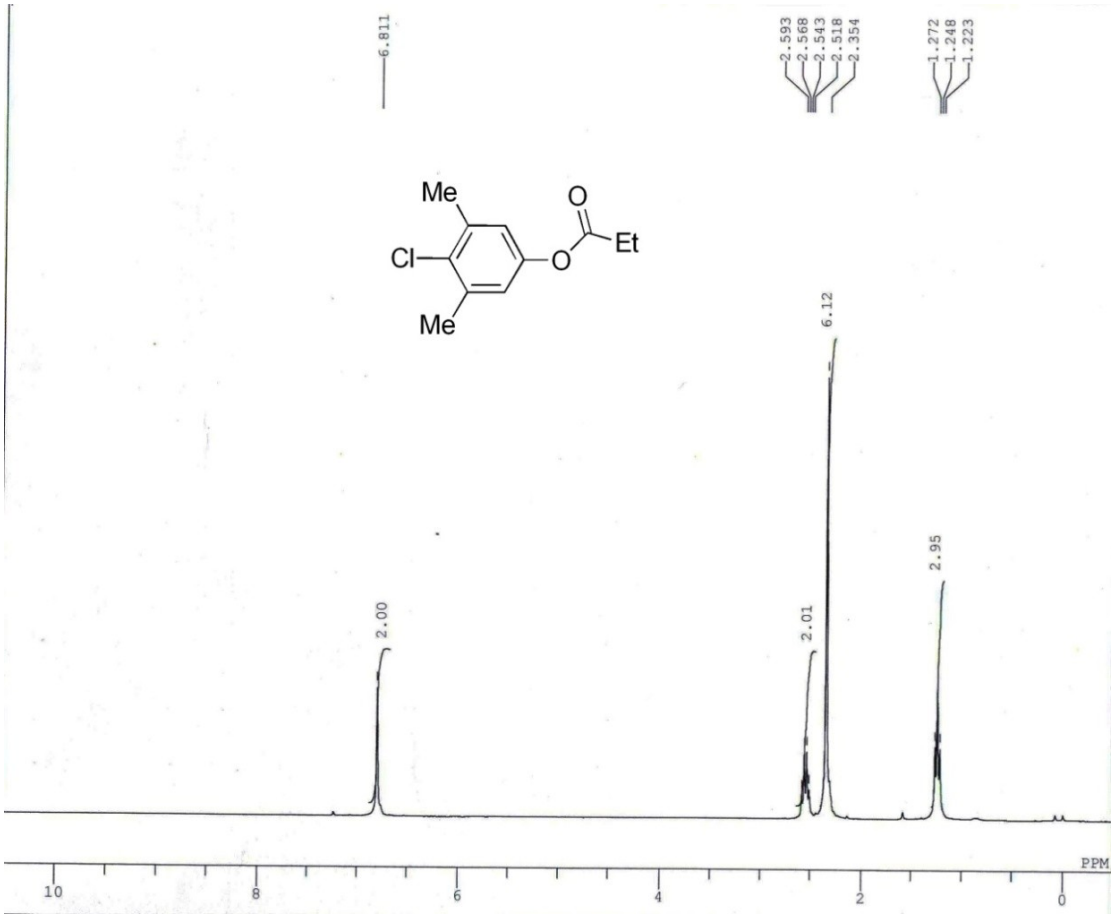
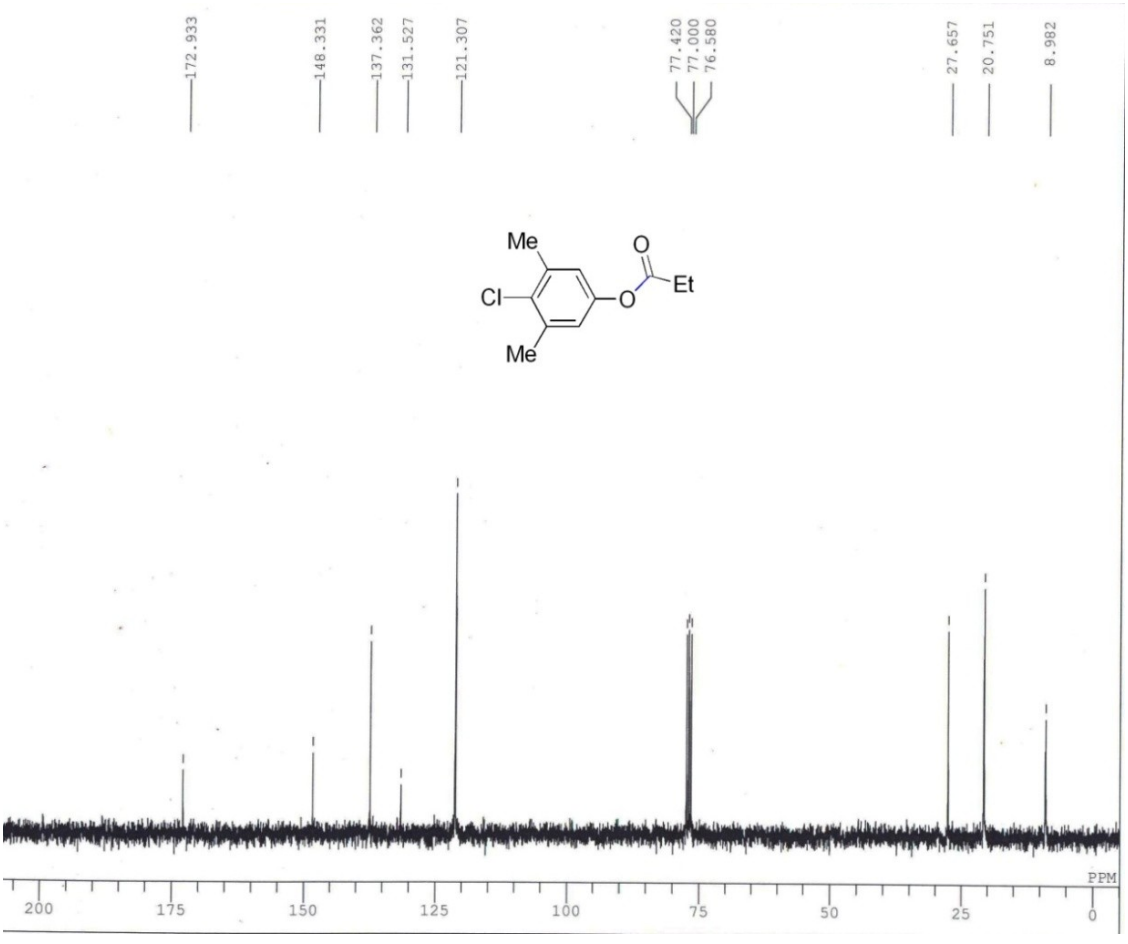
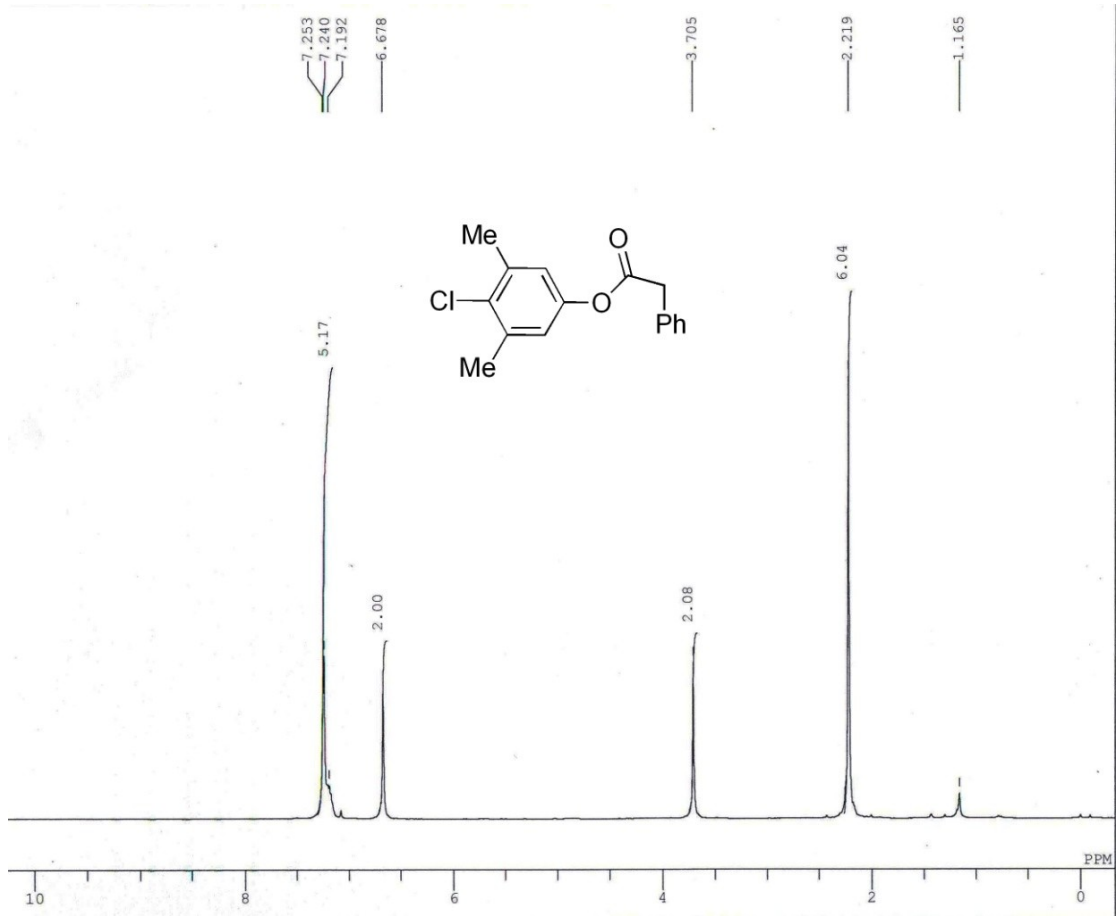
(9) CAS Registry Number: 81322-67-0.

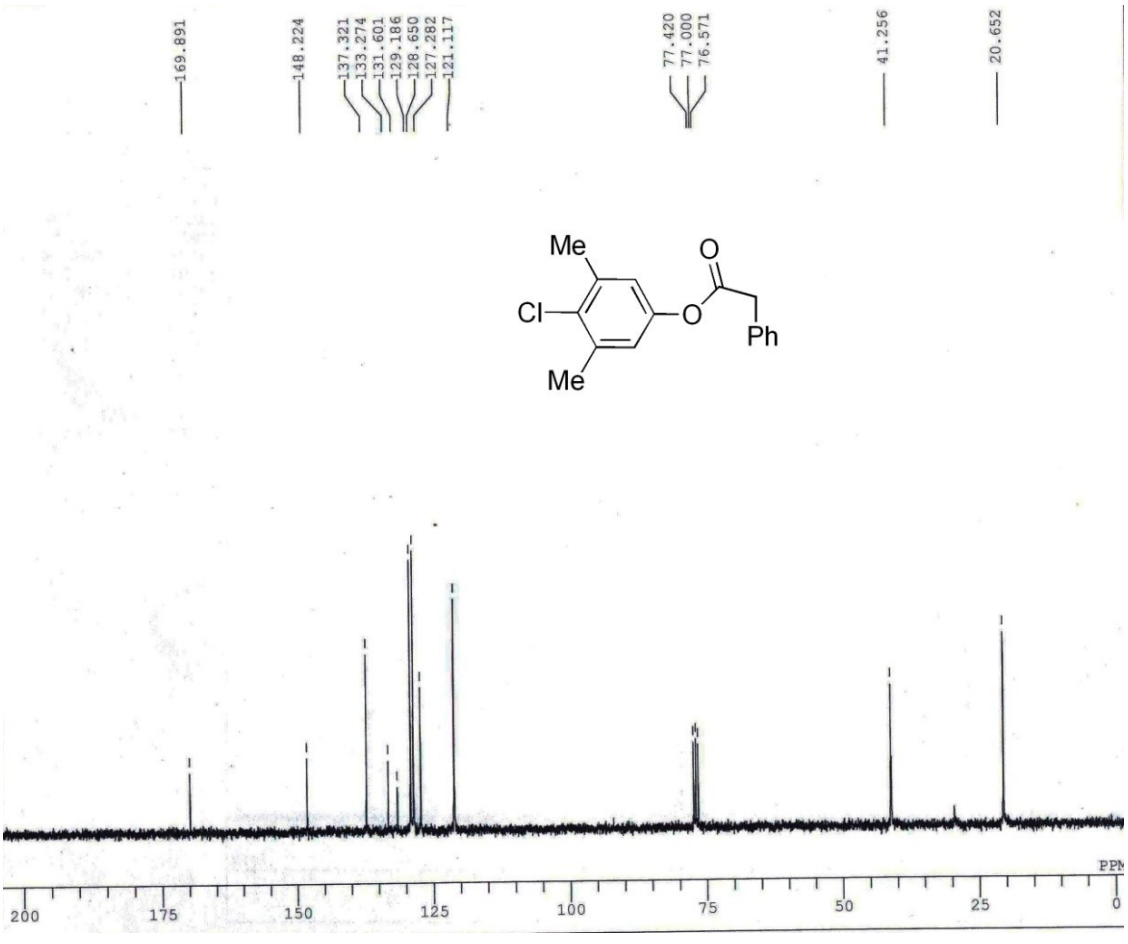
^{1}H and ^{13}C-NMR of **3ab**



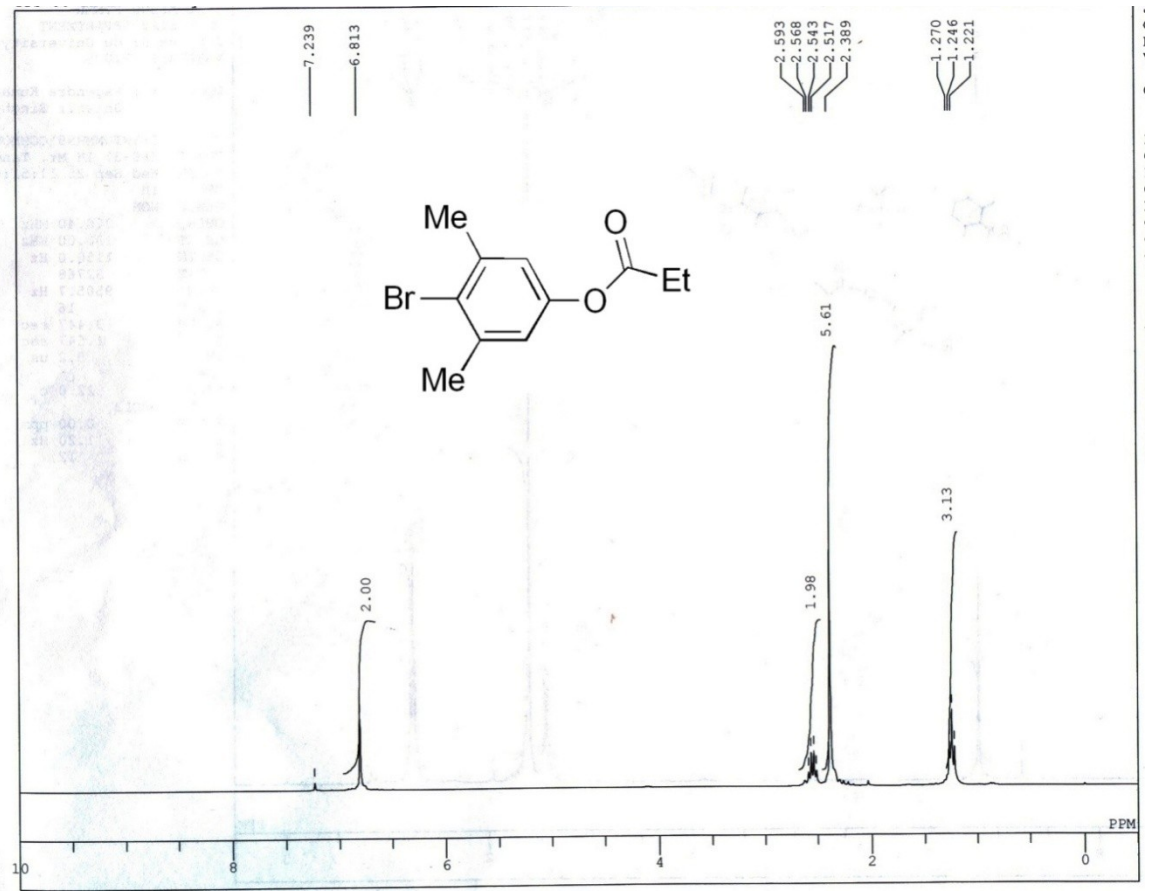


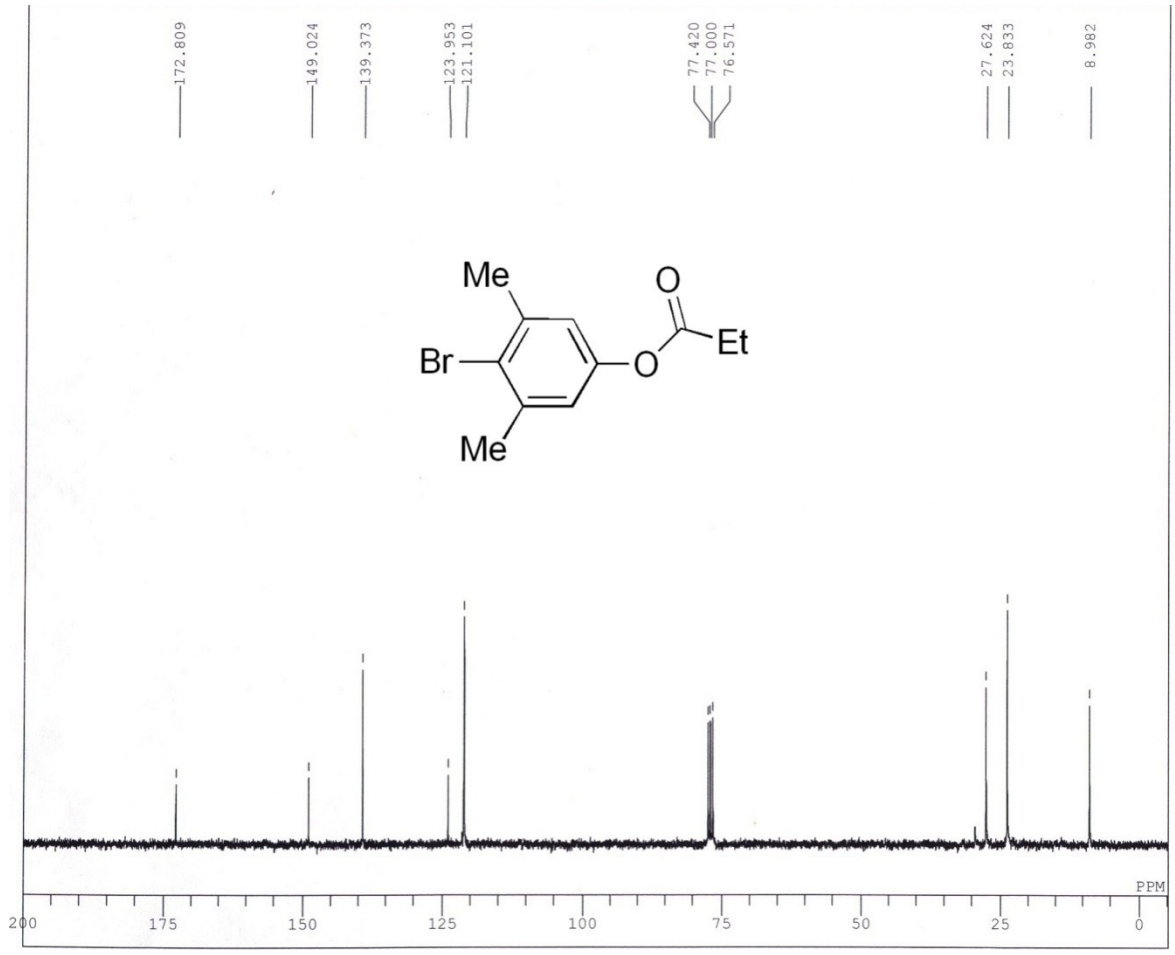
^{1}H and ^{13}C-NMR of **3ag**



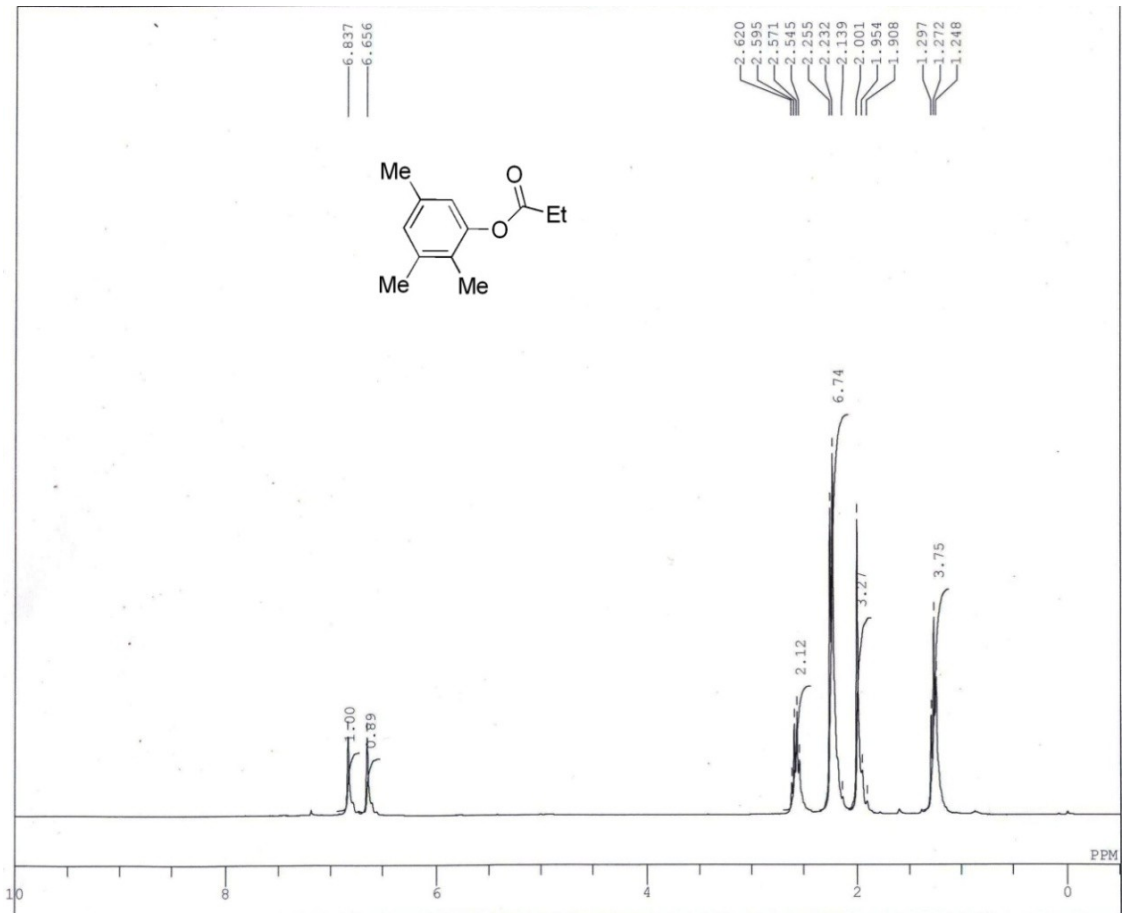


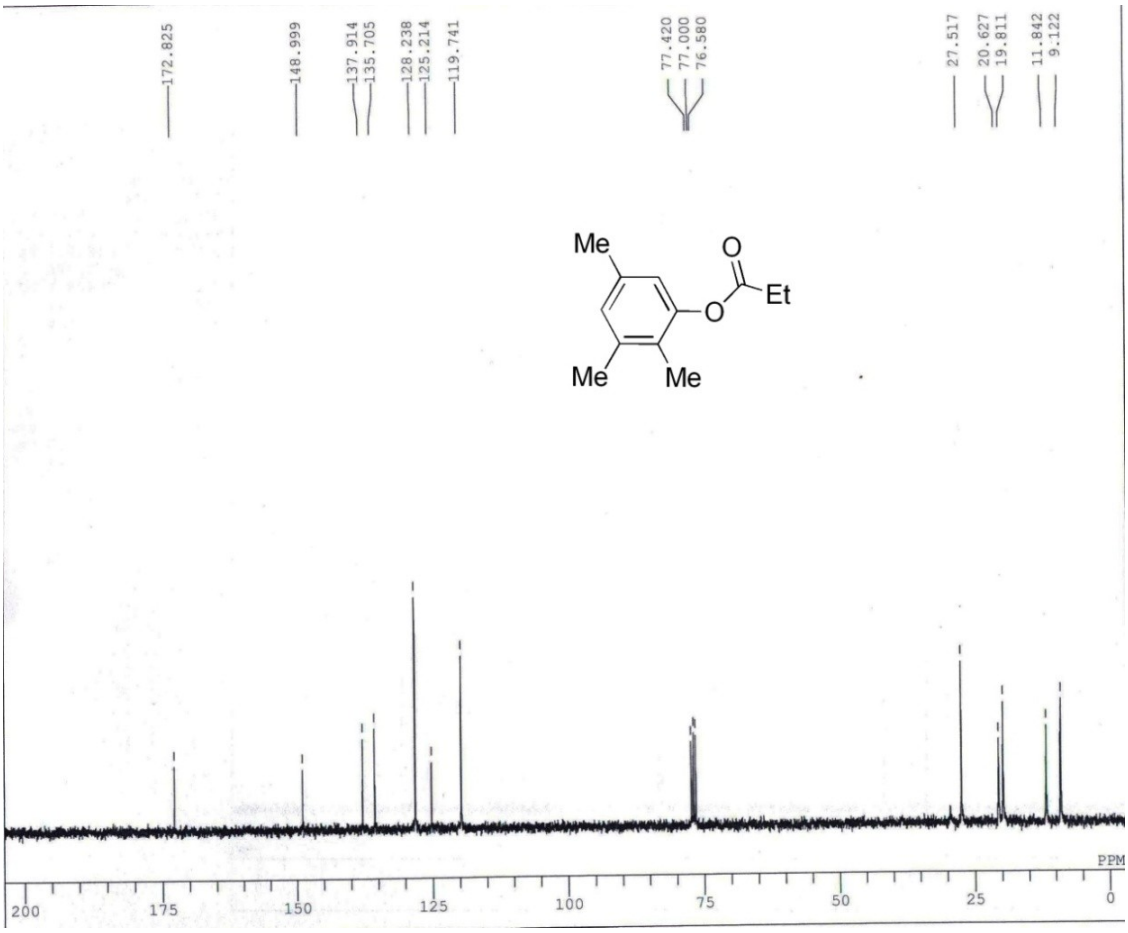
^{1}H and ^{13}C-NMR of **3bb**



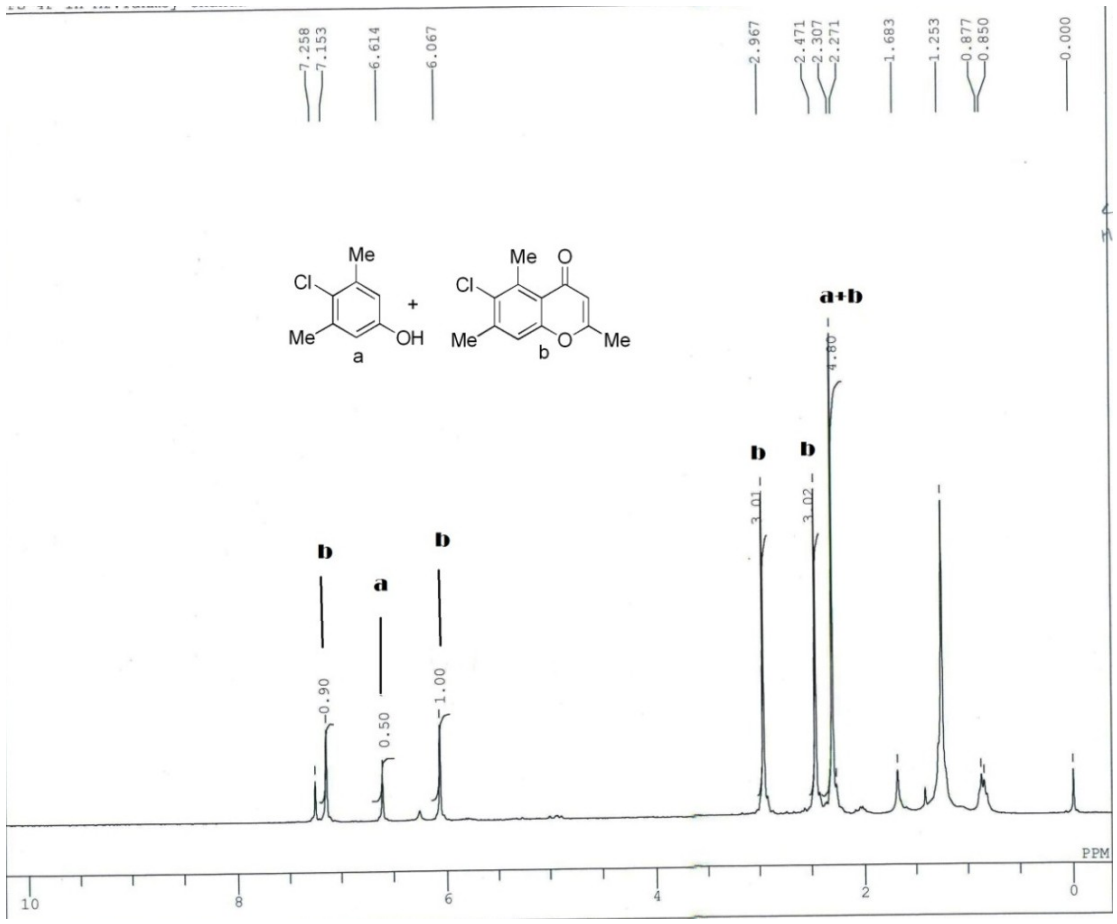


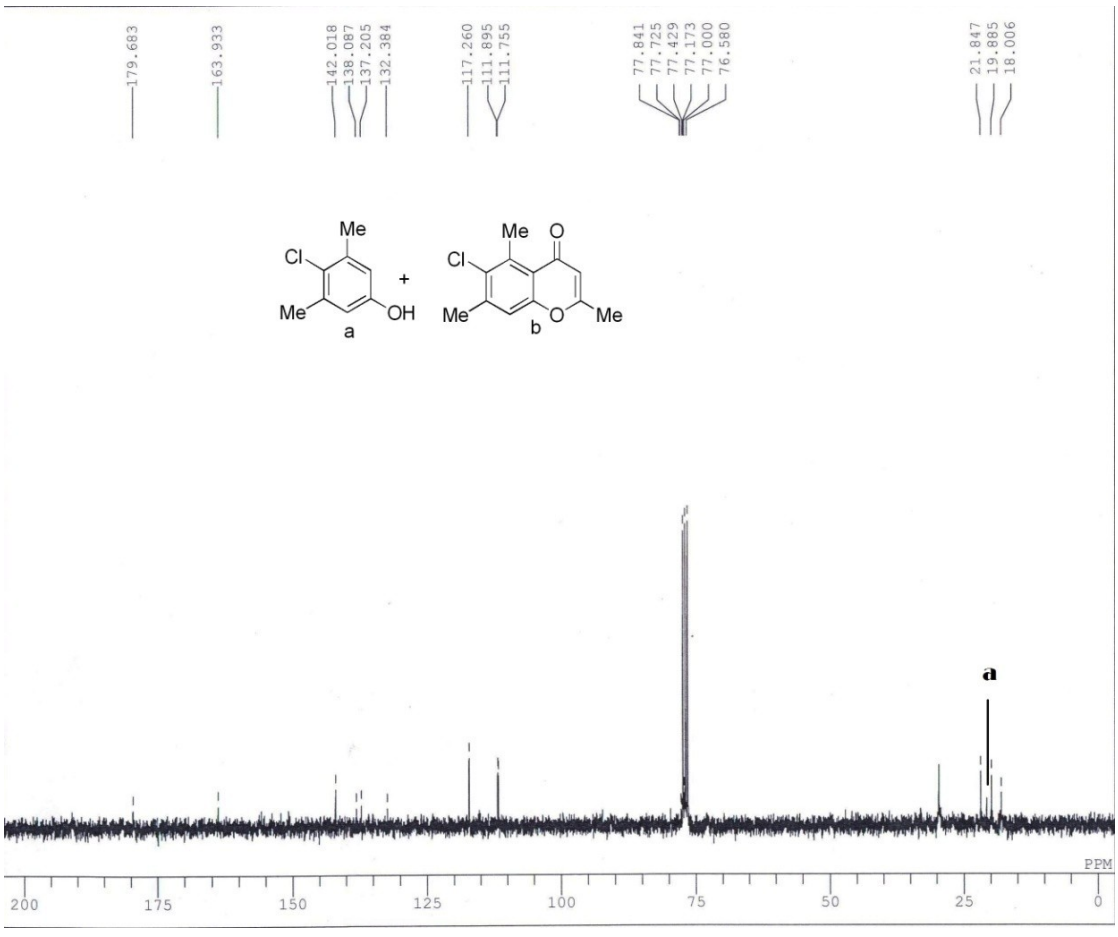
^{1}H and ^{13}C-NMR of **3eb**



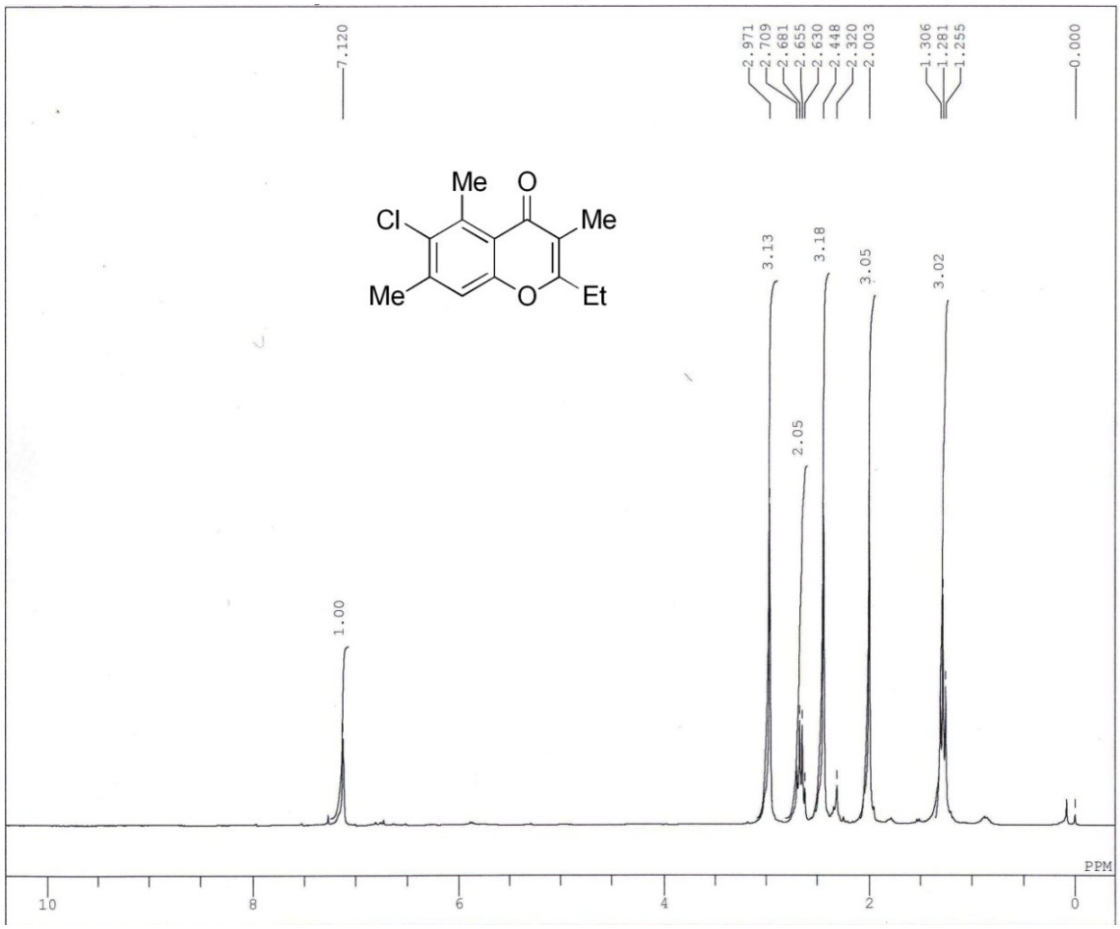


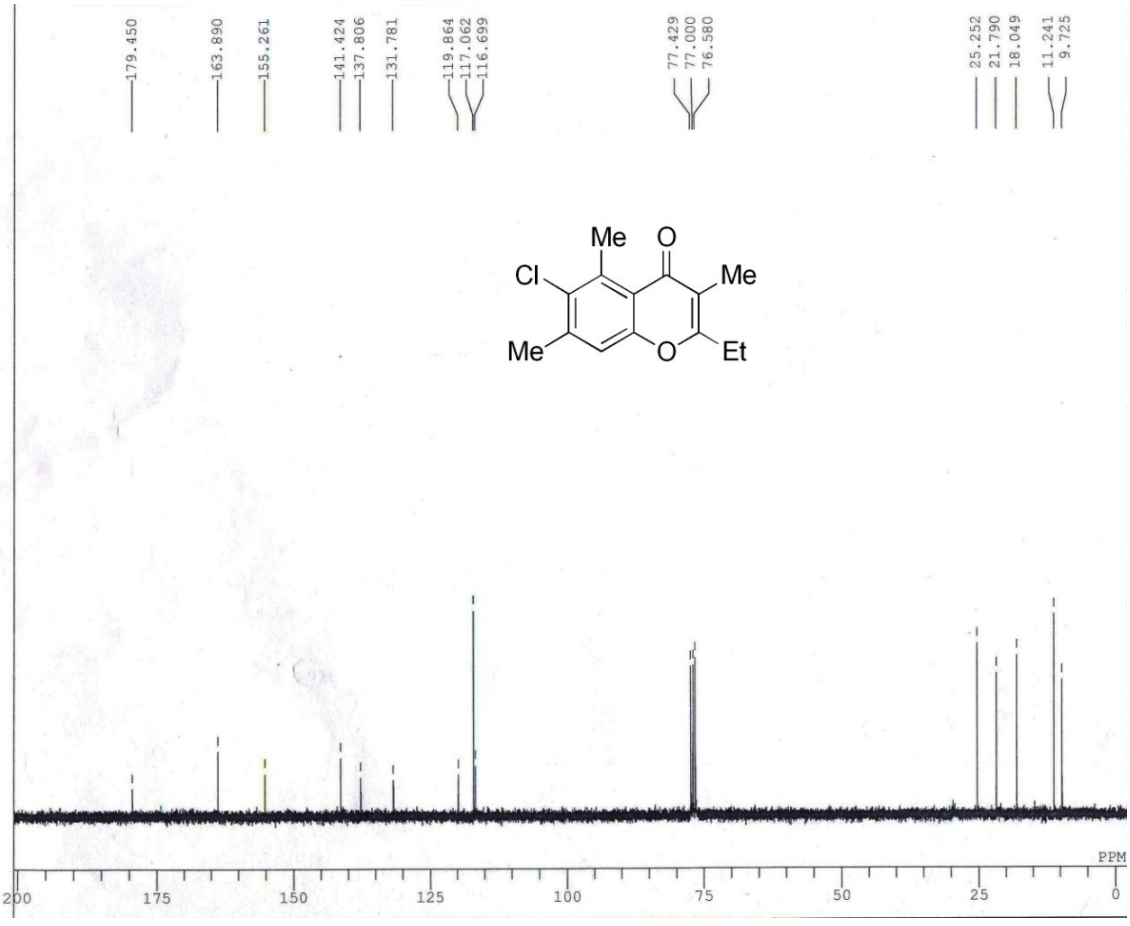
^{1}H and ^{13}C-NMR of the inseparable mixture of **5aa** and **1a** (2:1)



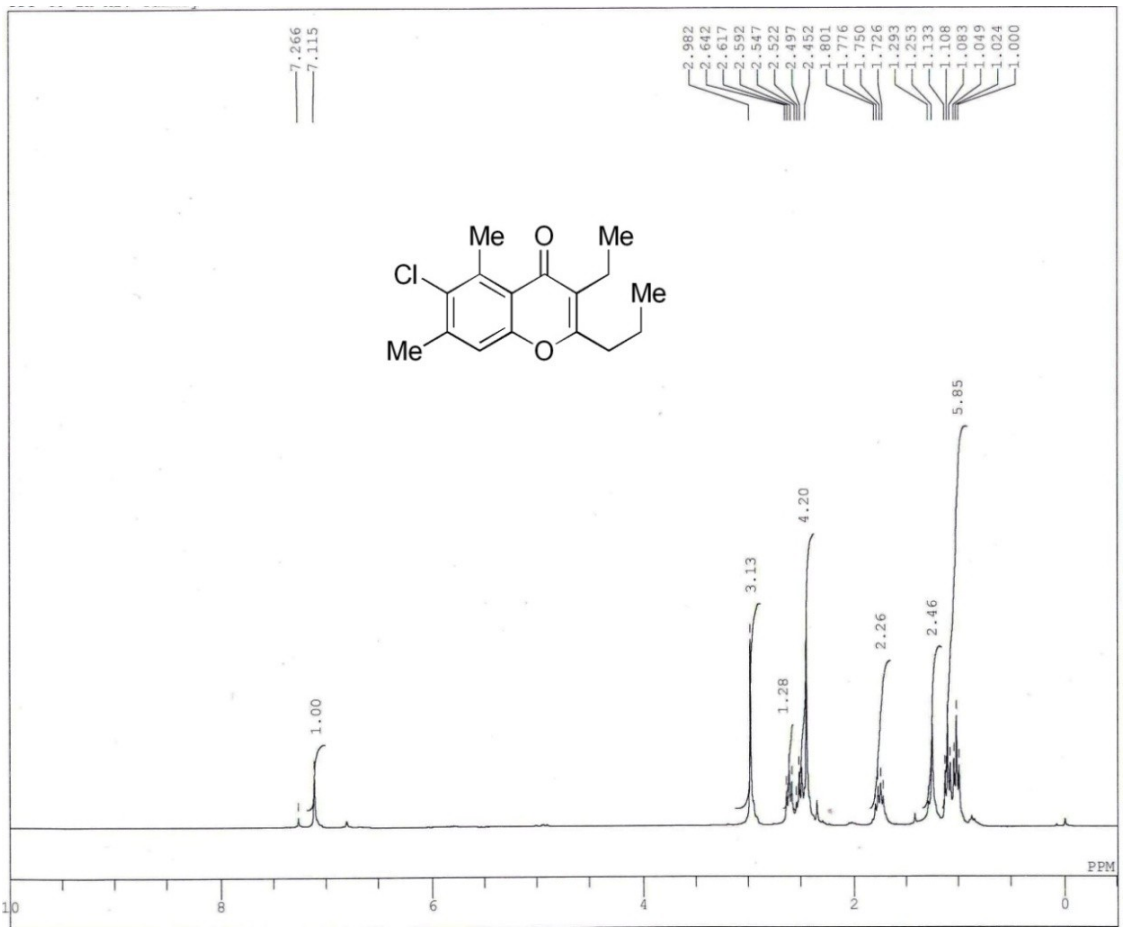


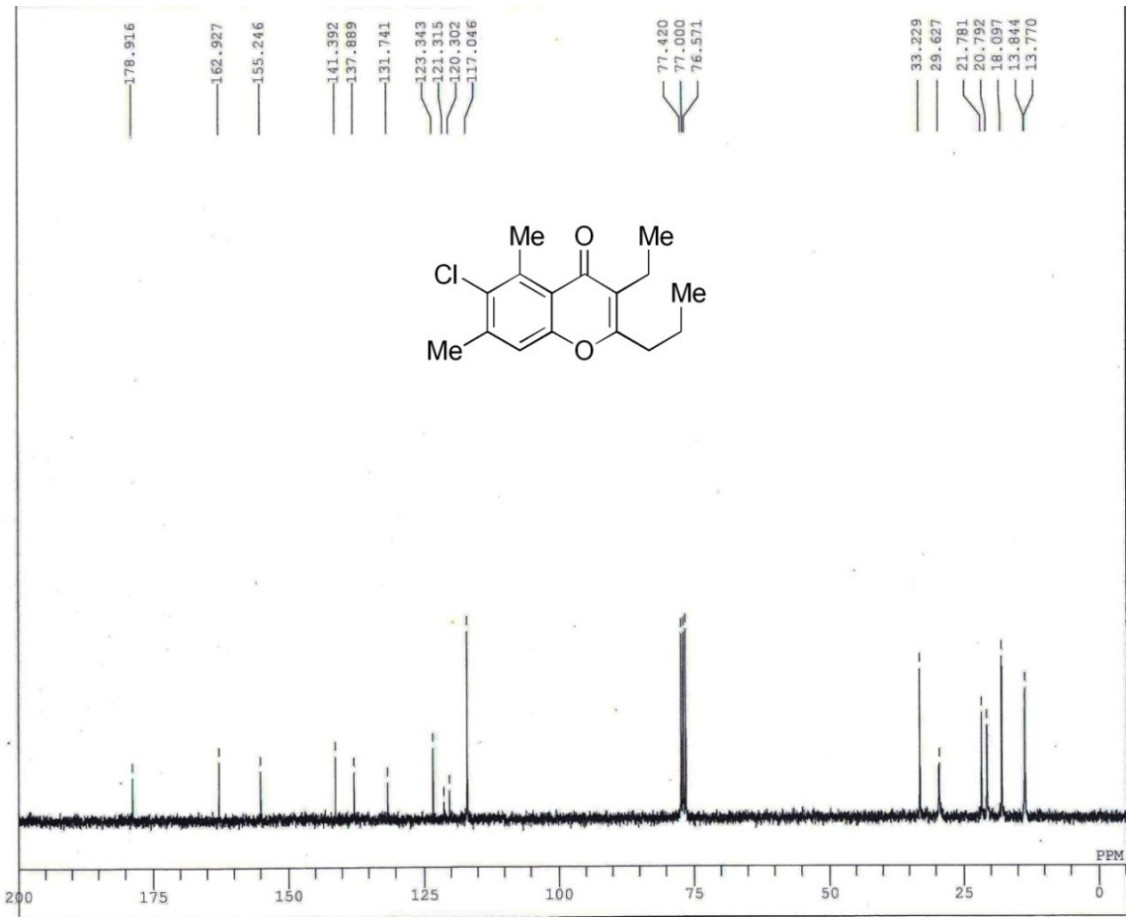
^{1}H and ^{13}C-NMR of **5ab**



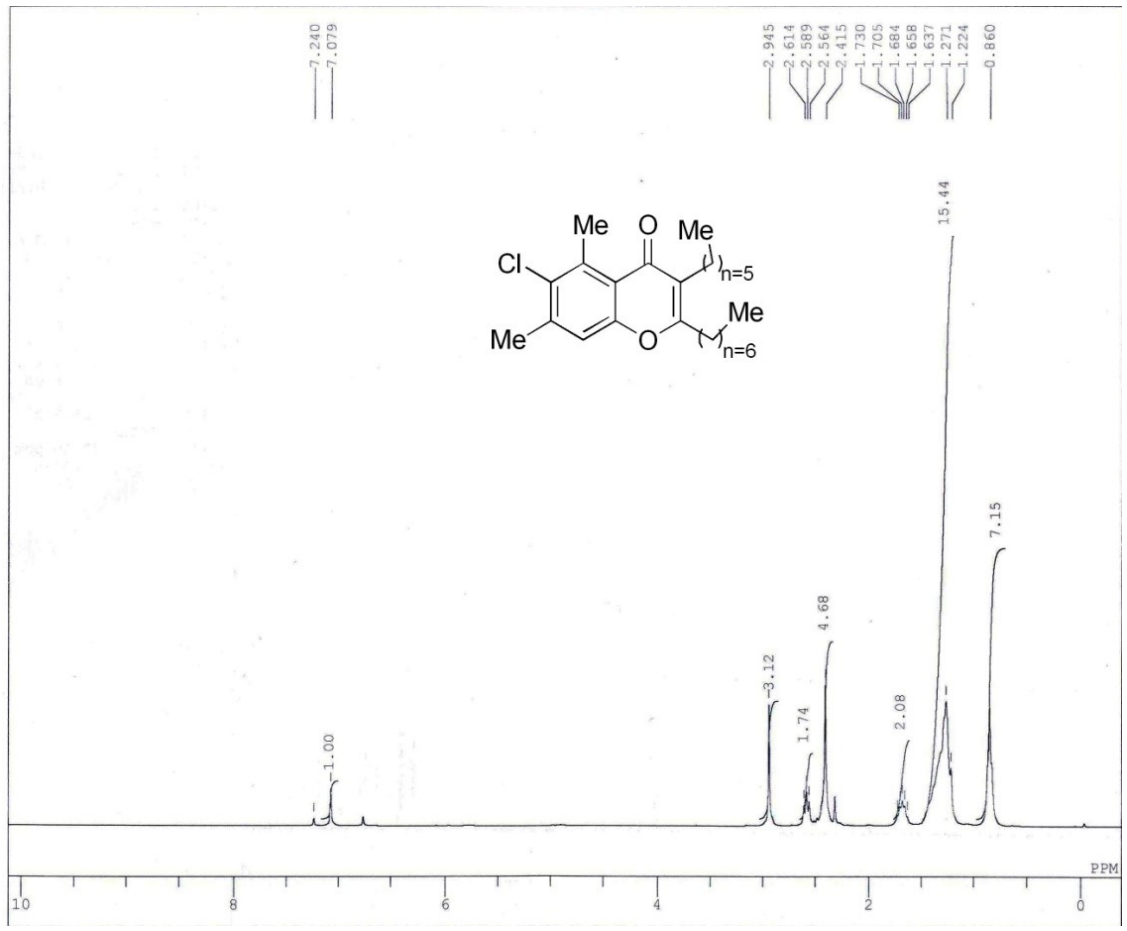


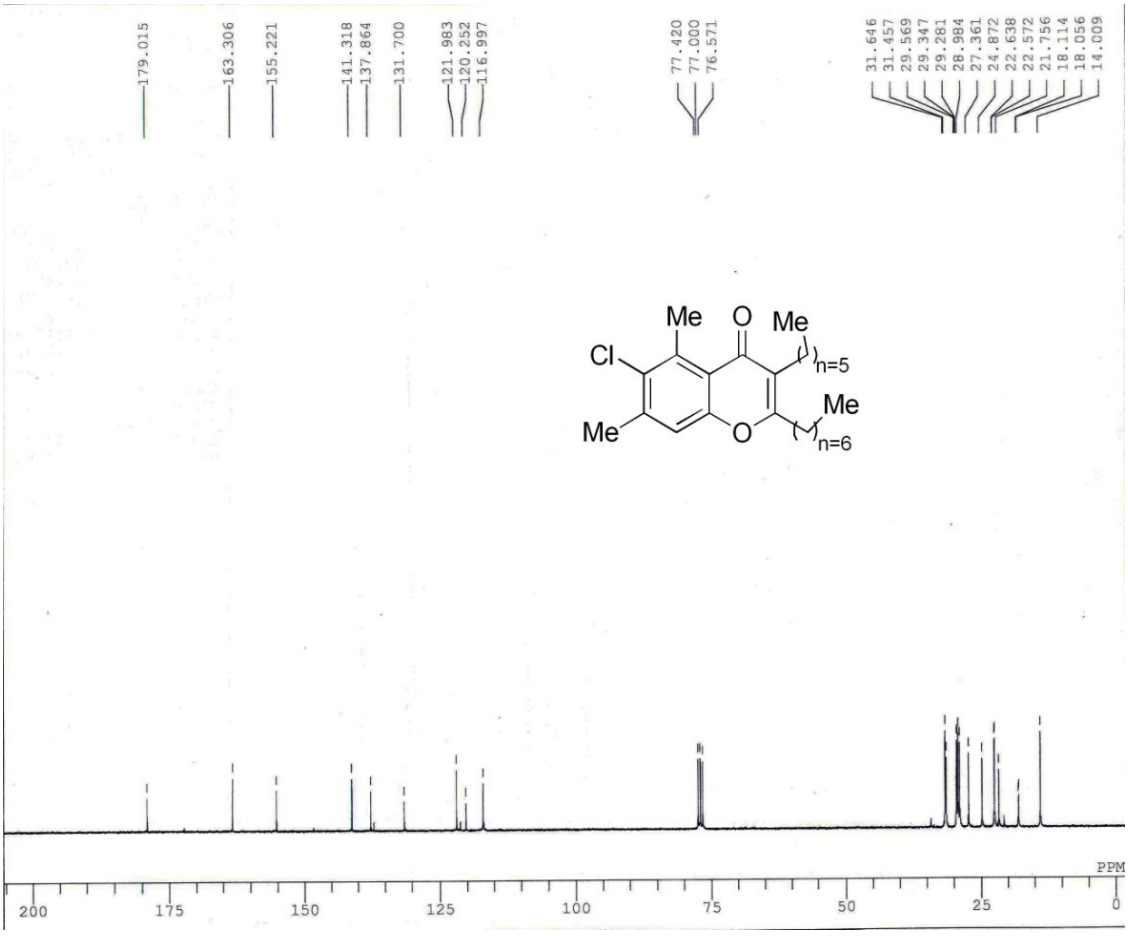
^{1}H and ^{13}C-NMR of **5ac**



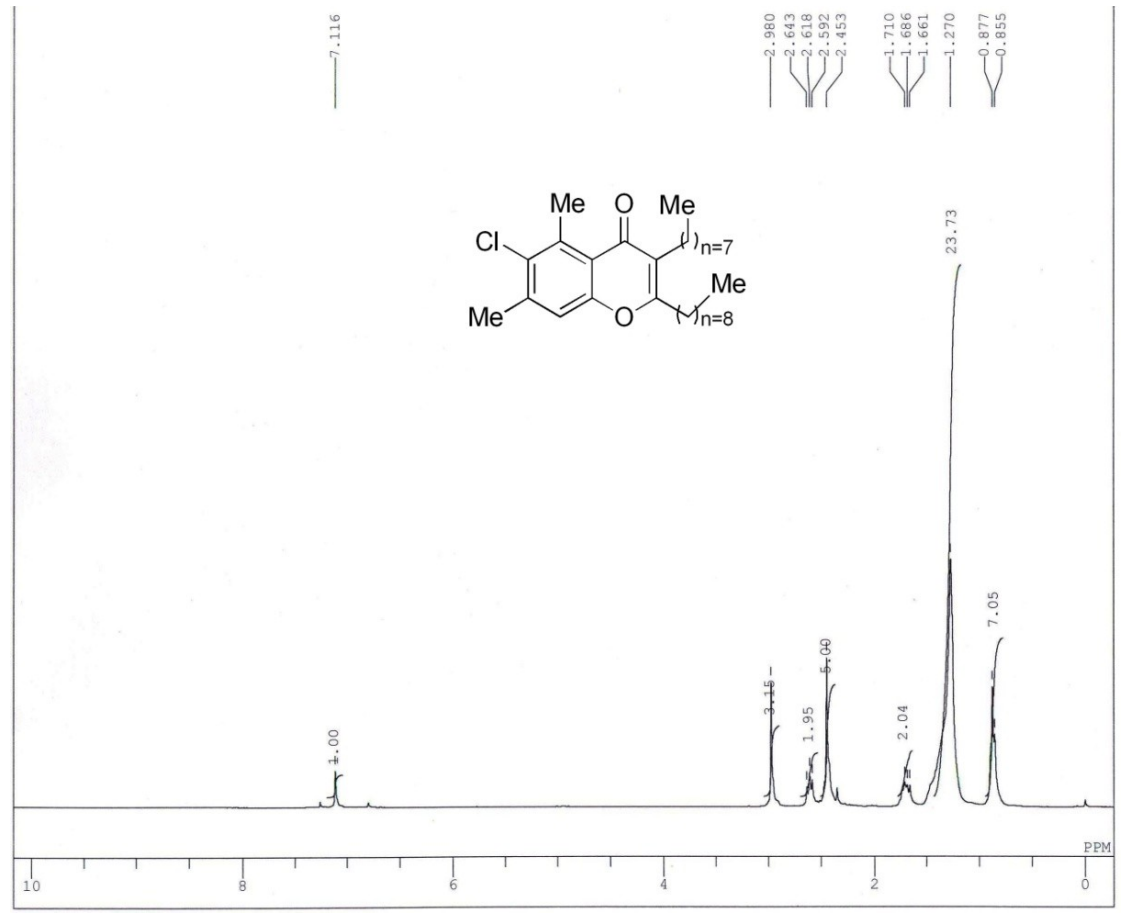


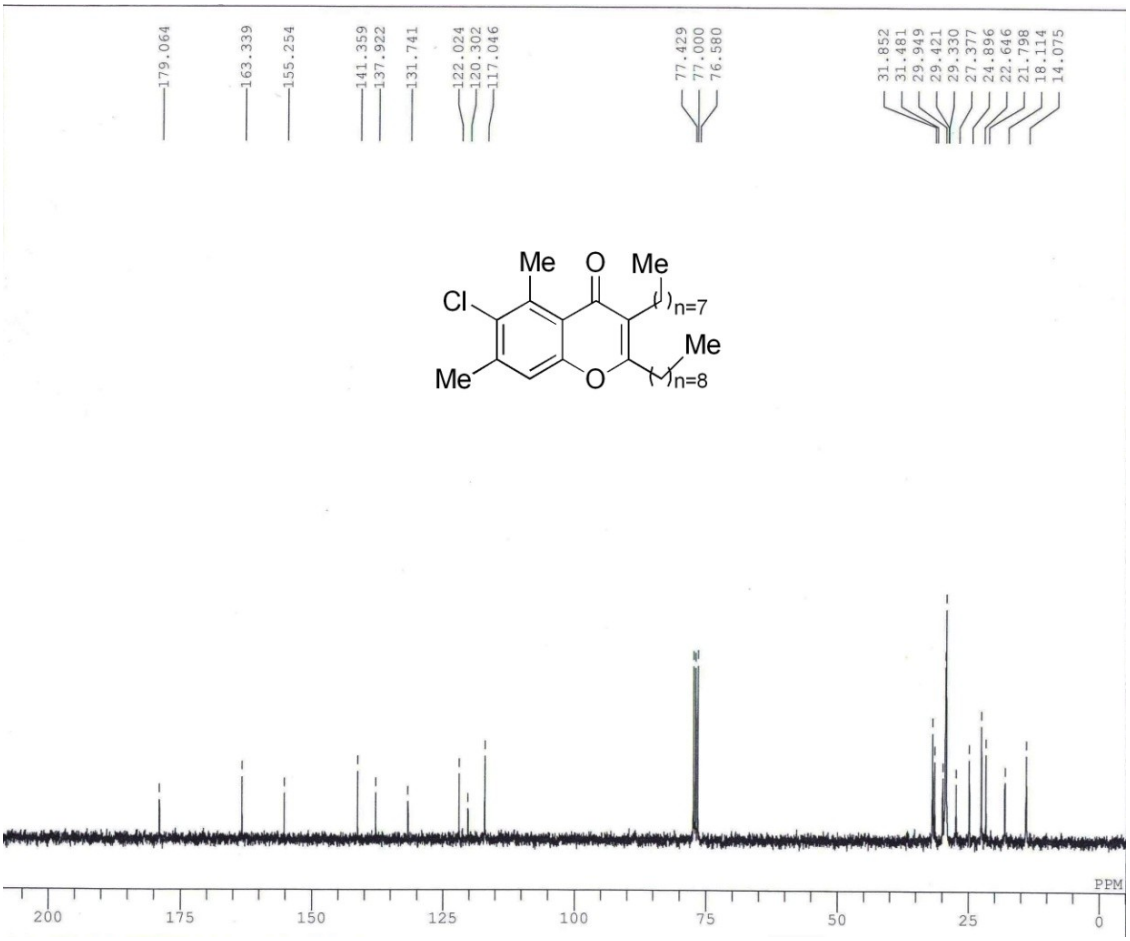
^{1}H and ^{13}C-NMR of **5ad**



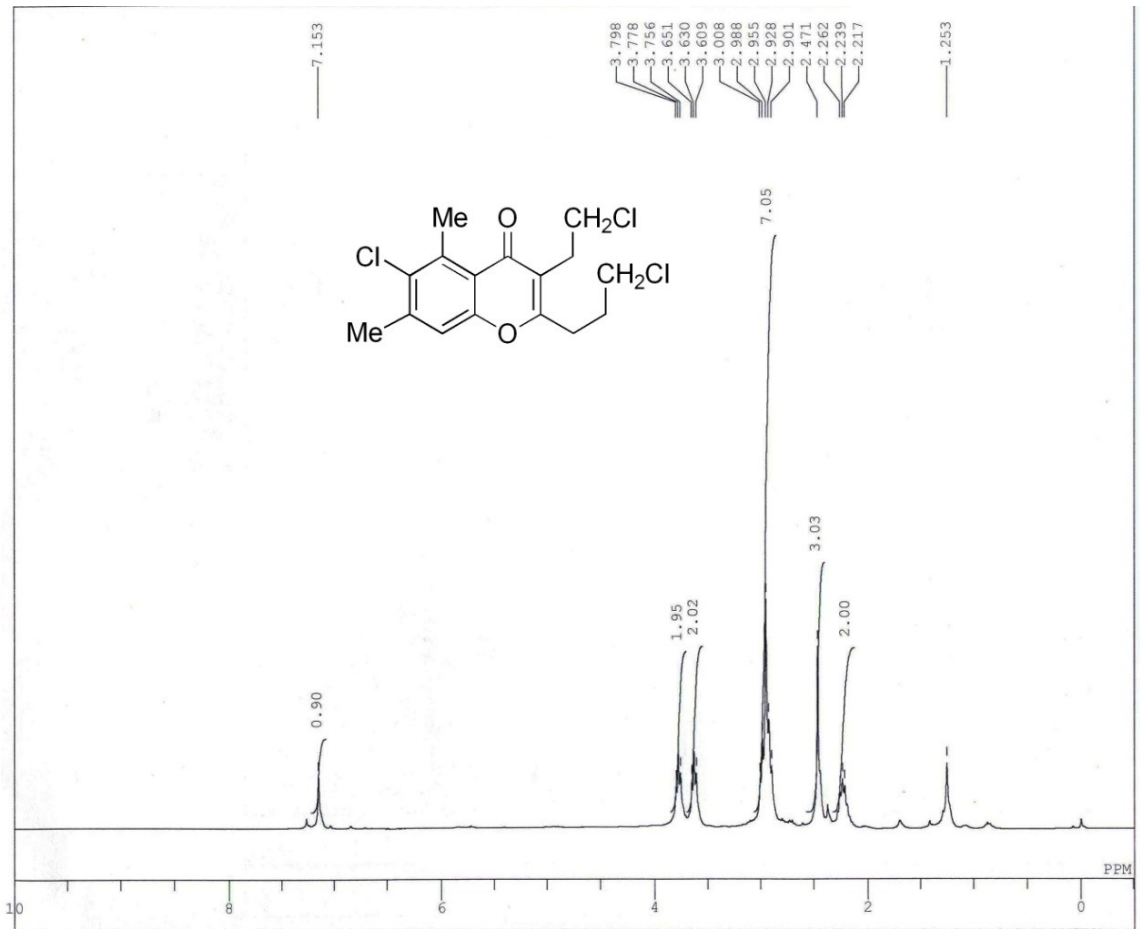


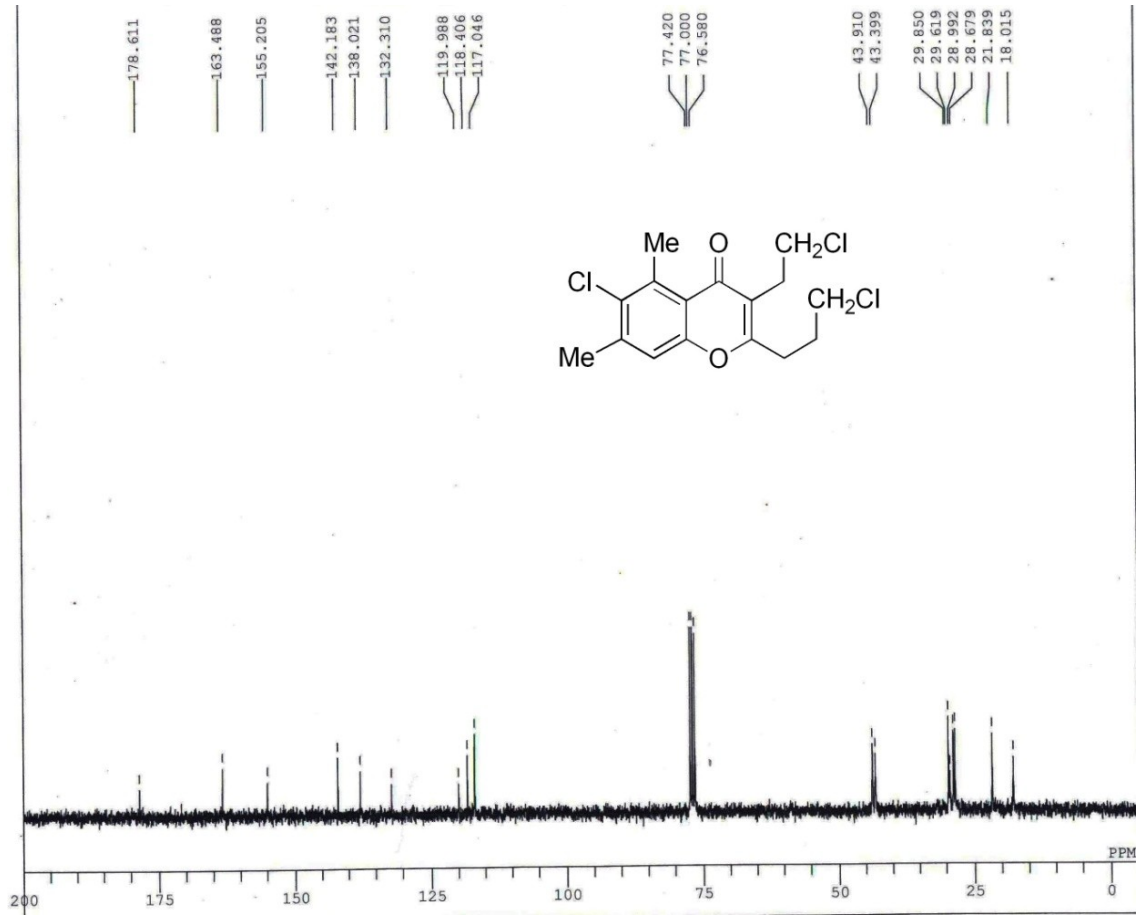
^{1}H and ^{13}C-NMR of **5ae**



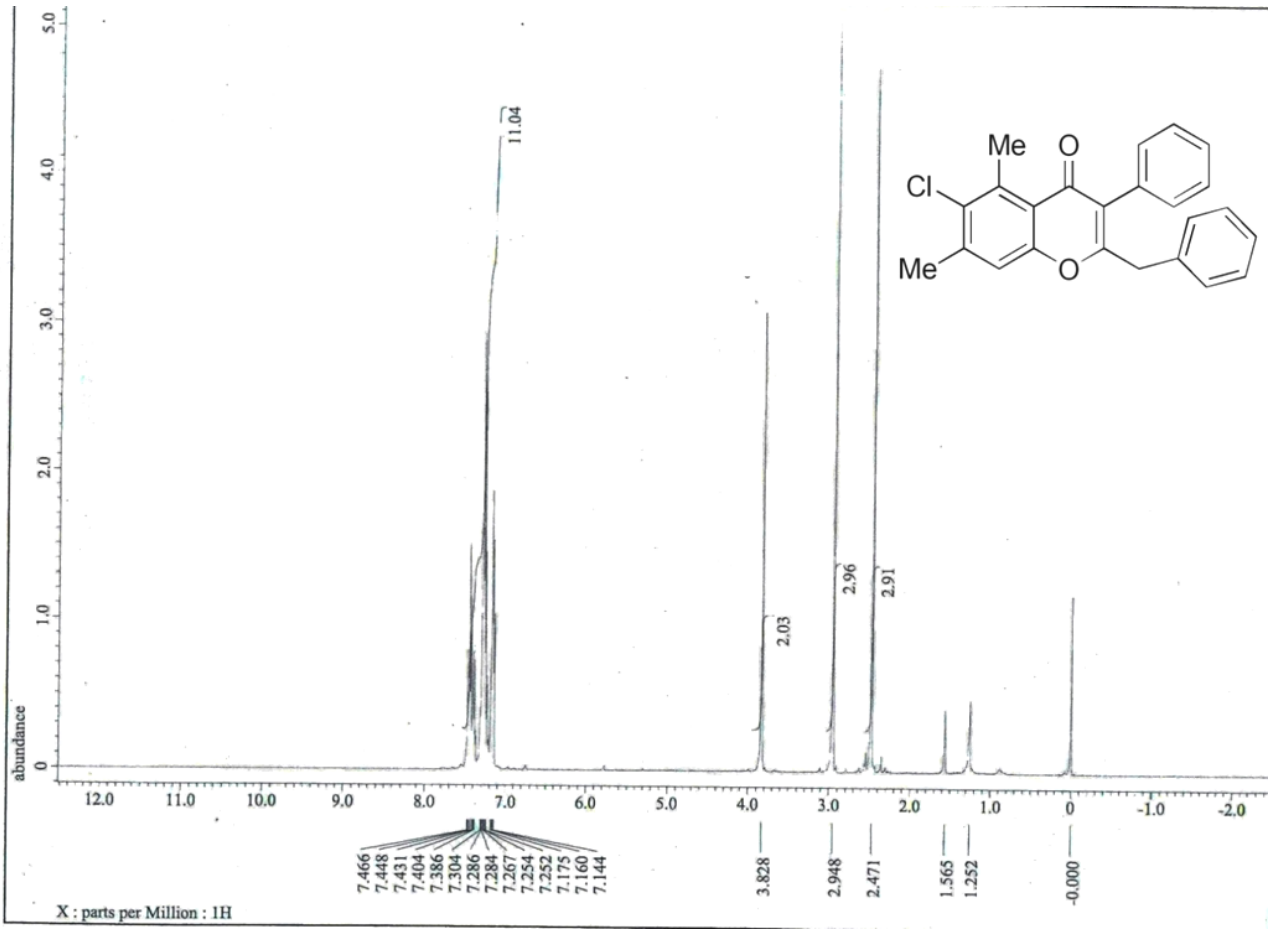


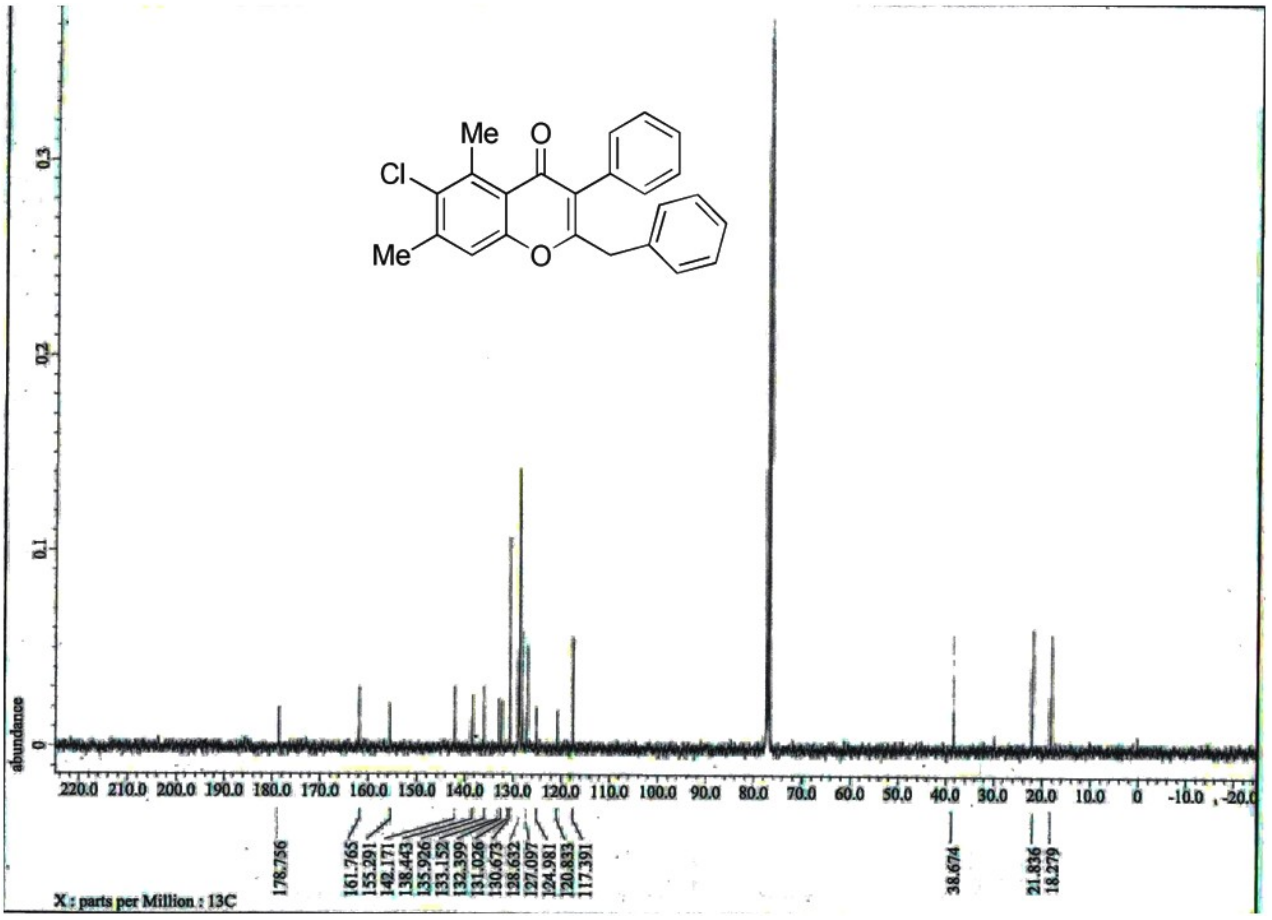
^{1}H and ^{13}C-NMR of **5af**



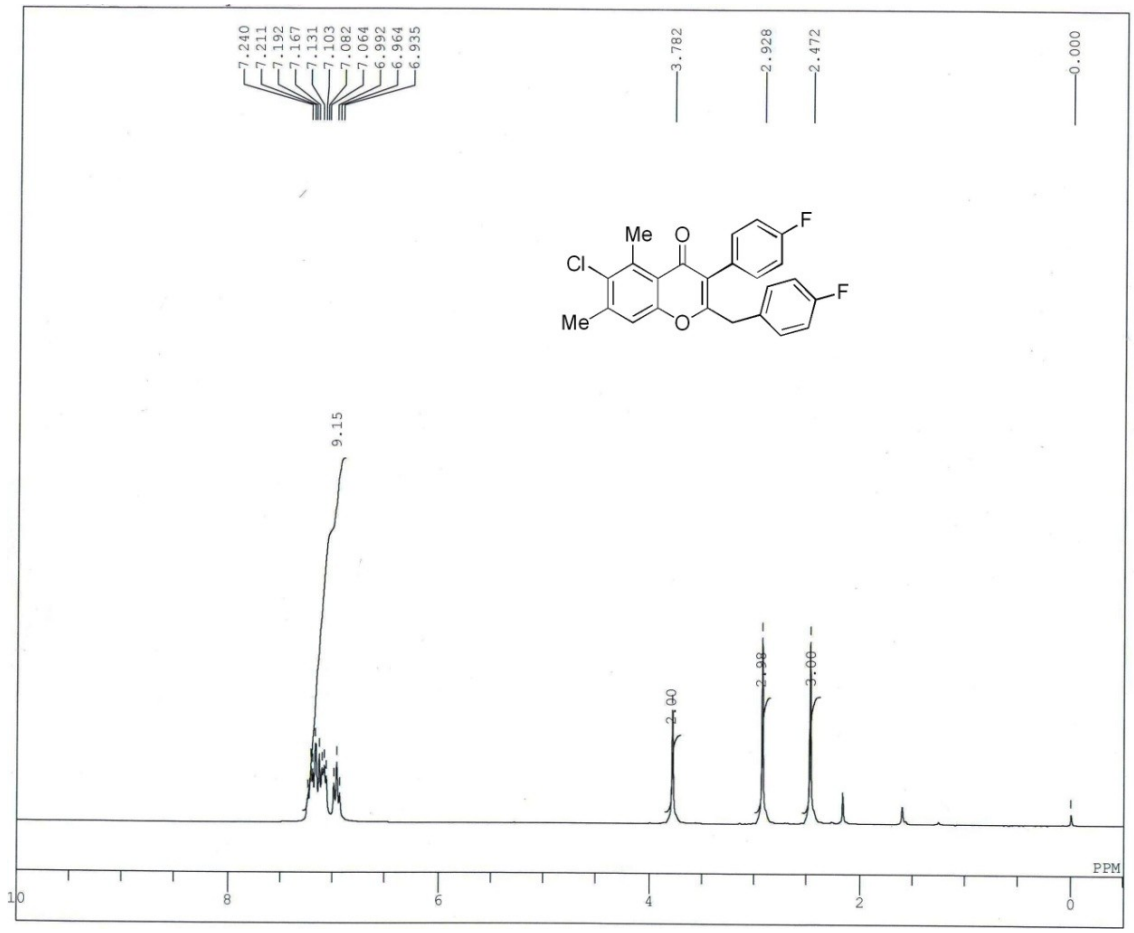


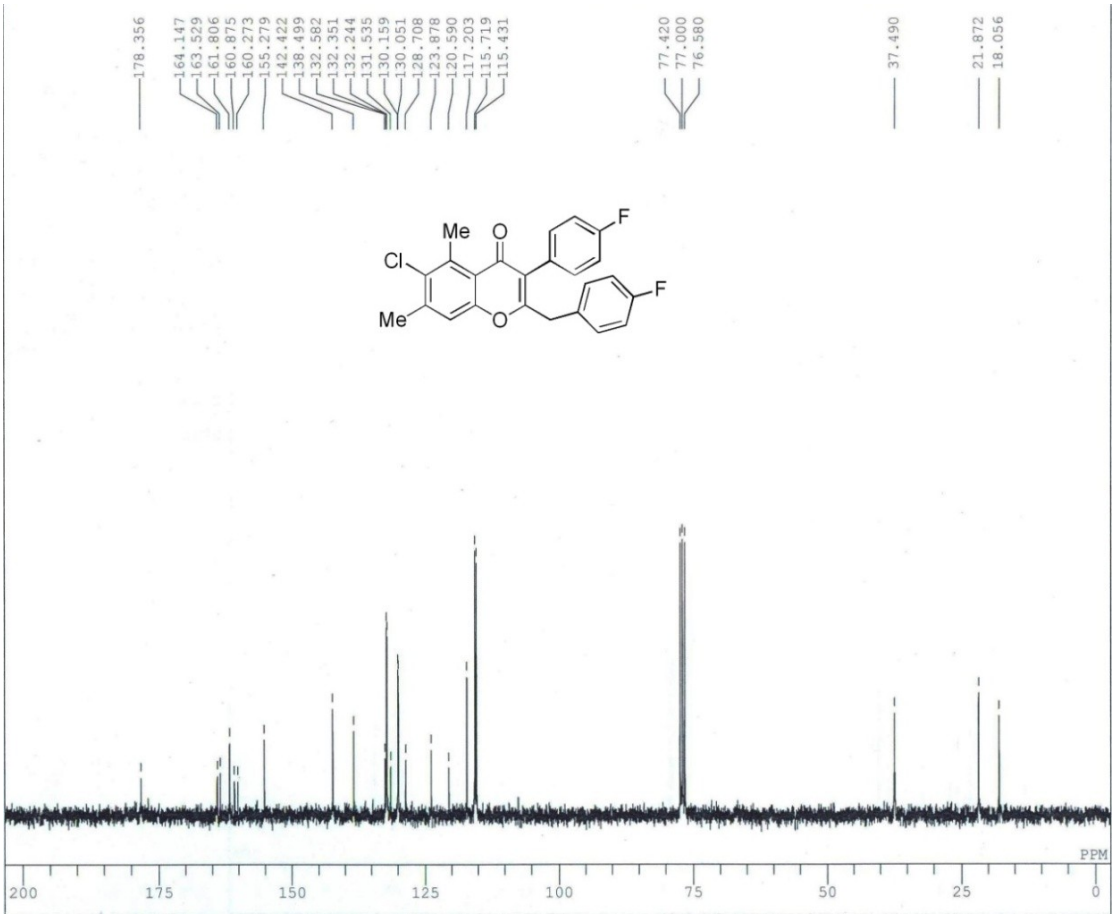
^{1}H and ^{13}C-NMR of **5ag**



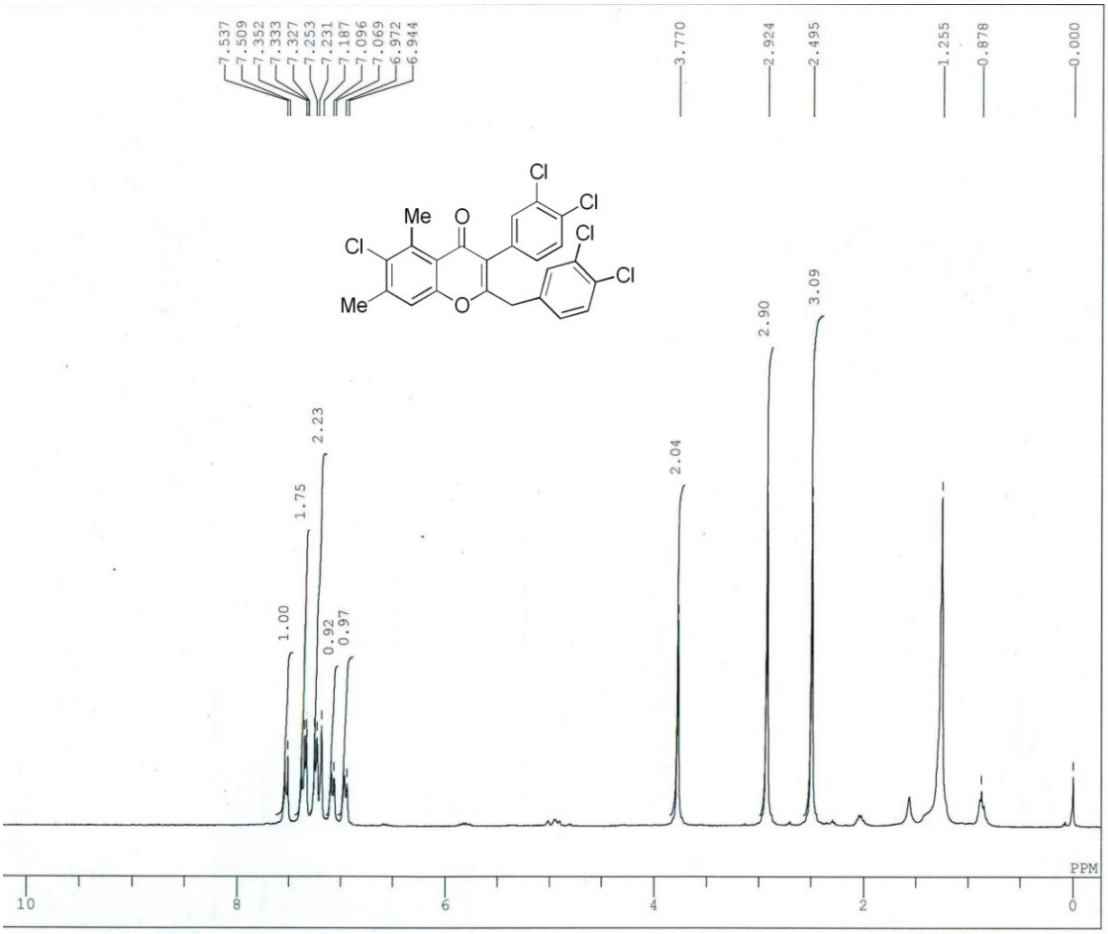


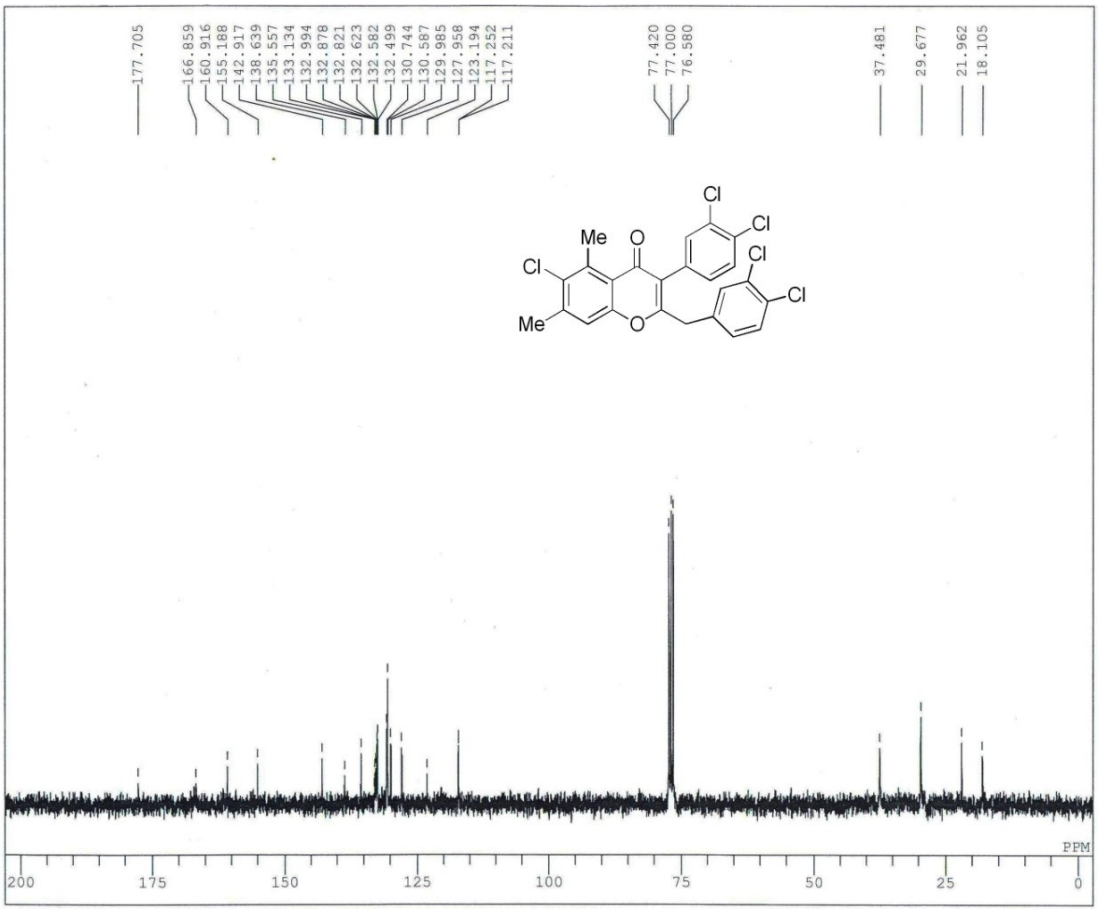
^{1}H and ^{13}C-NMR of **5ah**



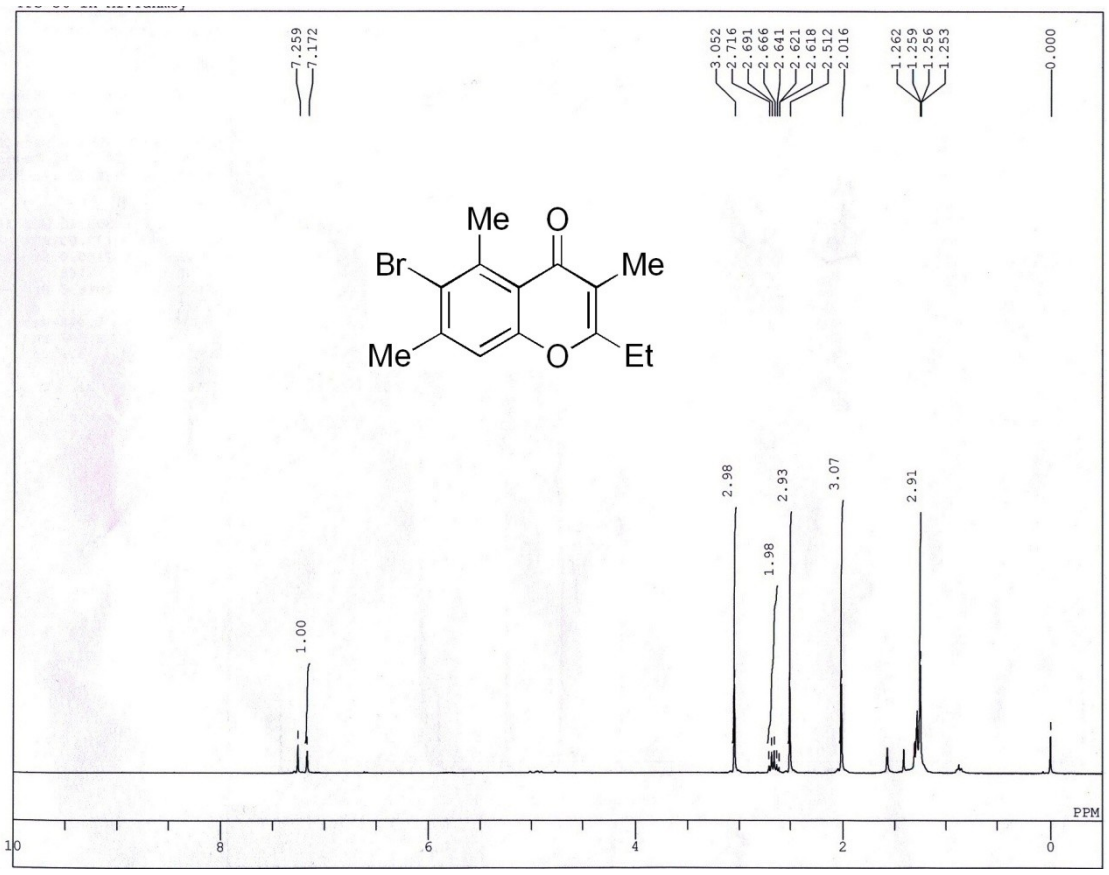


^{1}H and ^{13}C-NMR of **5ai**

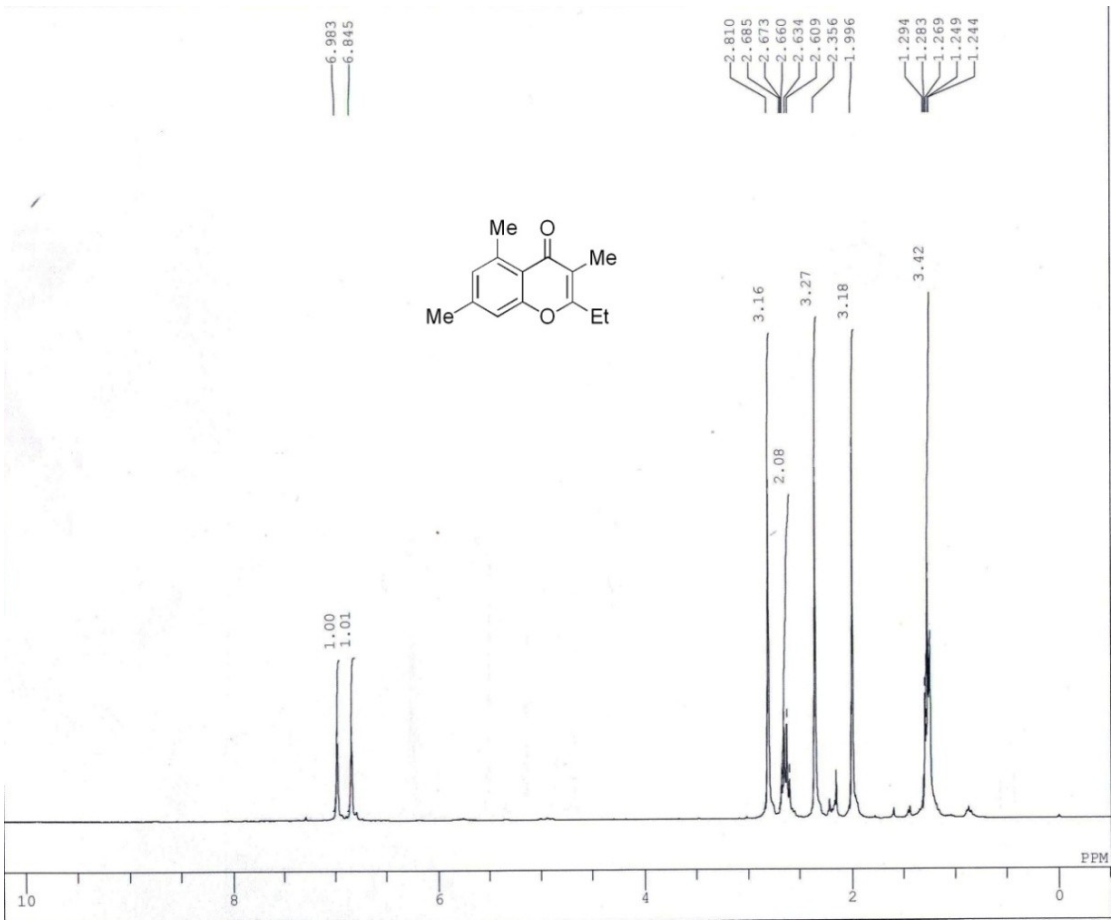


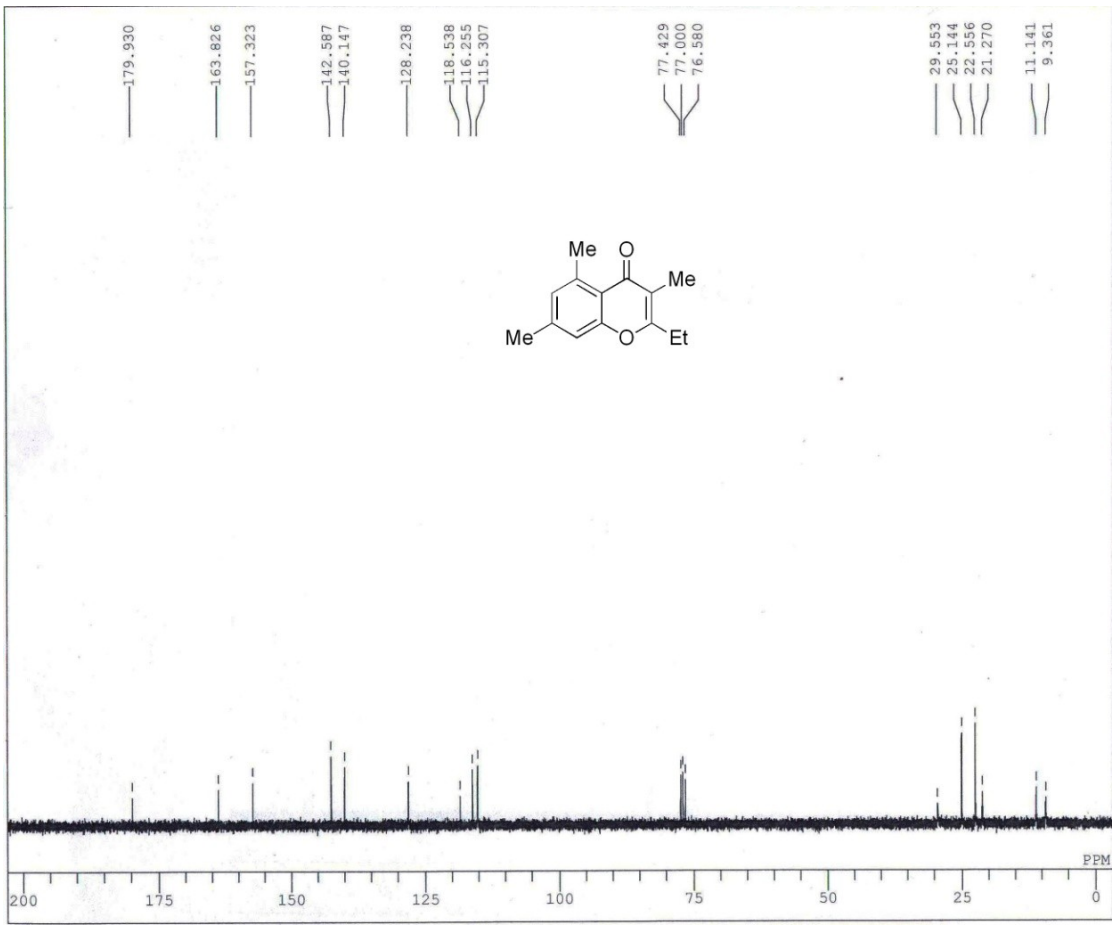


^{1}H and ^{13}C-NMR of **5bb**

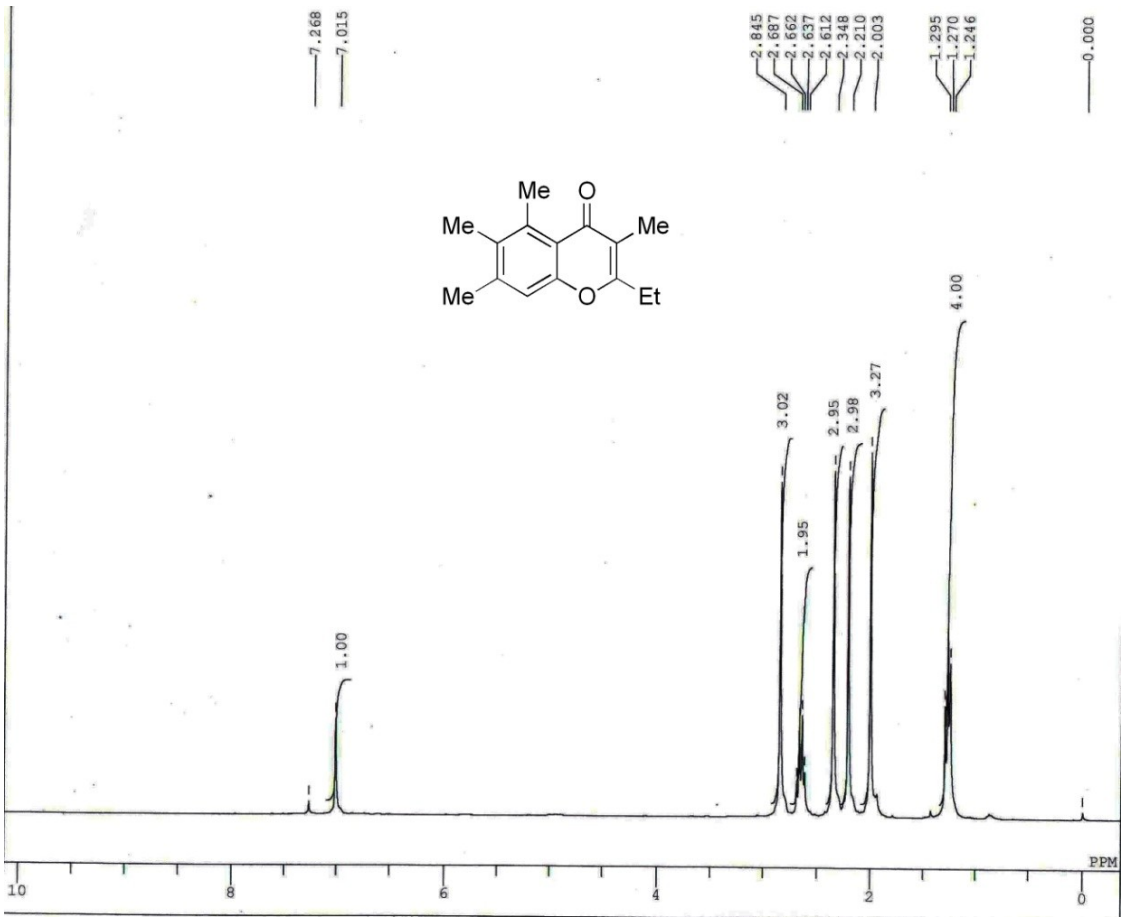


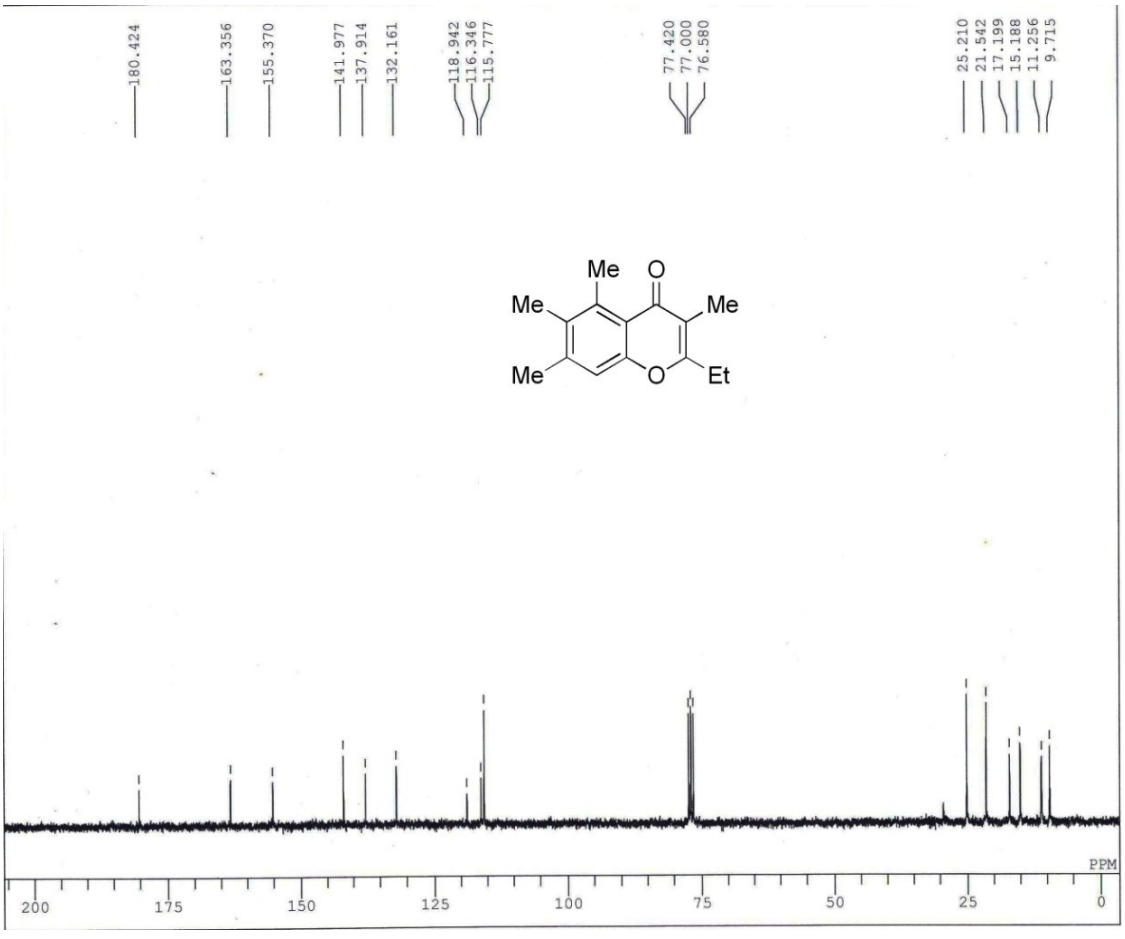
^{1}H and ^{13}C-NMR of **5cb**



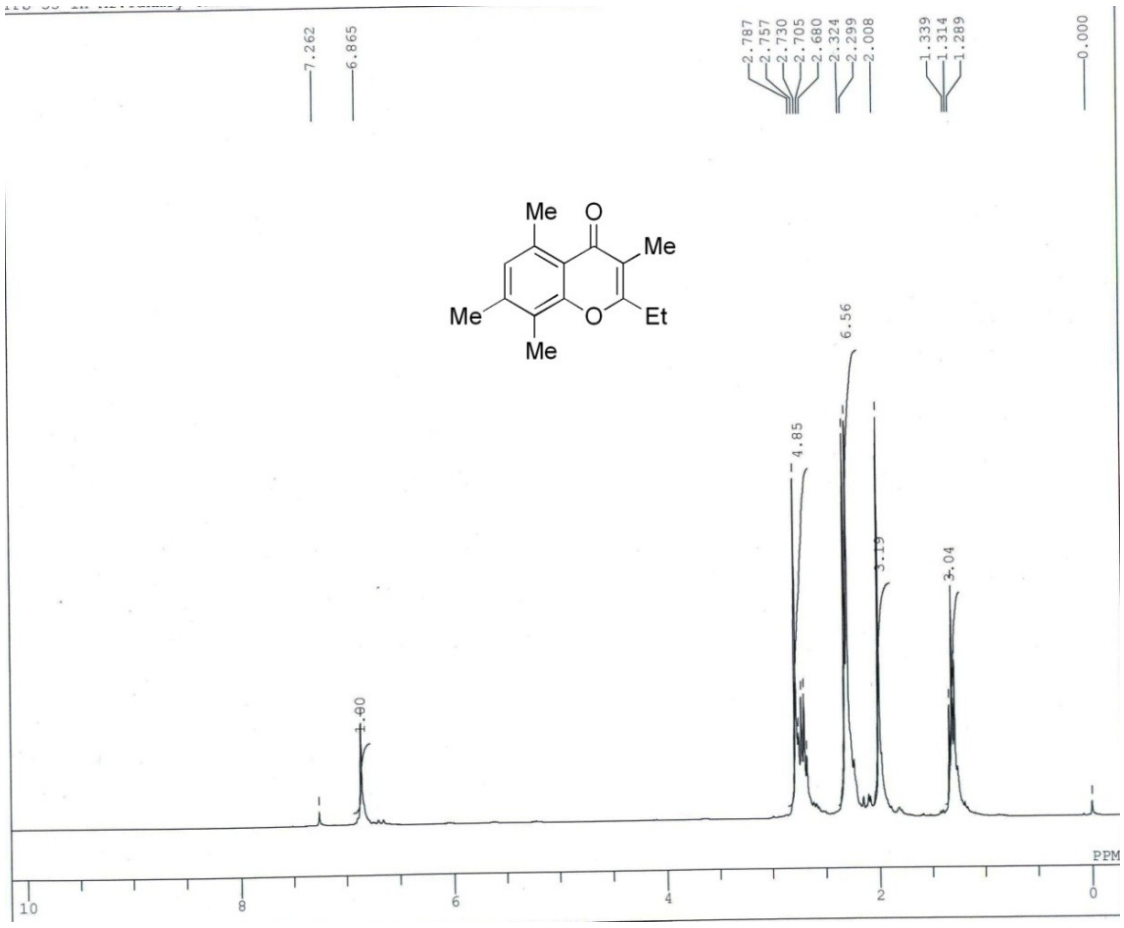


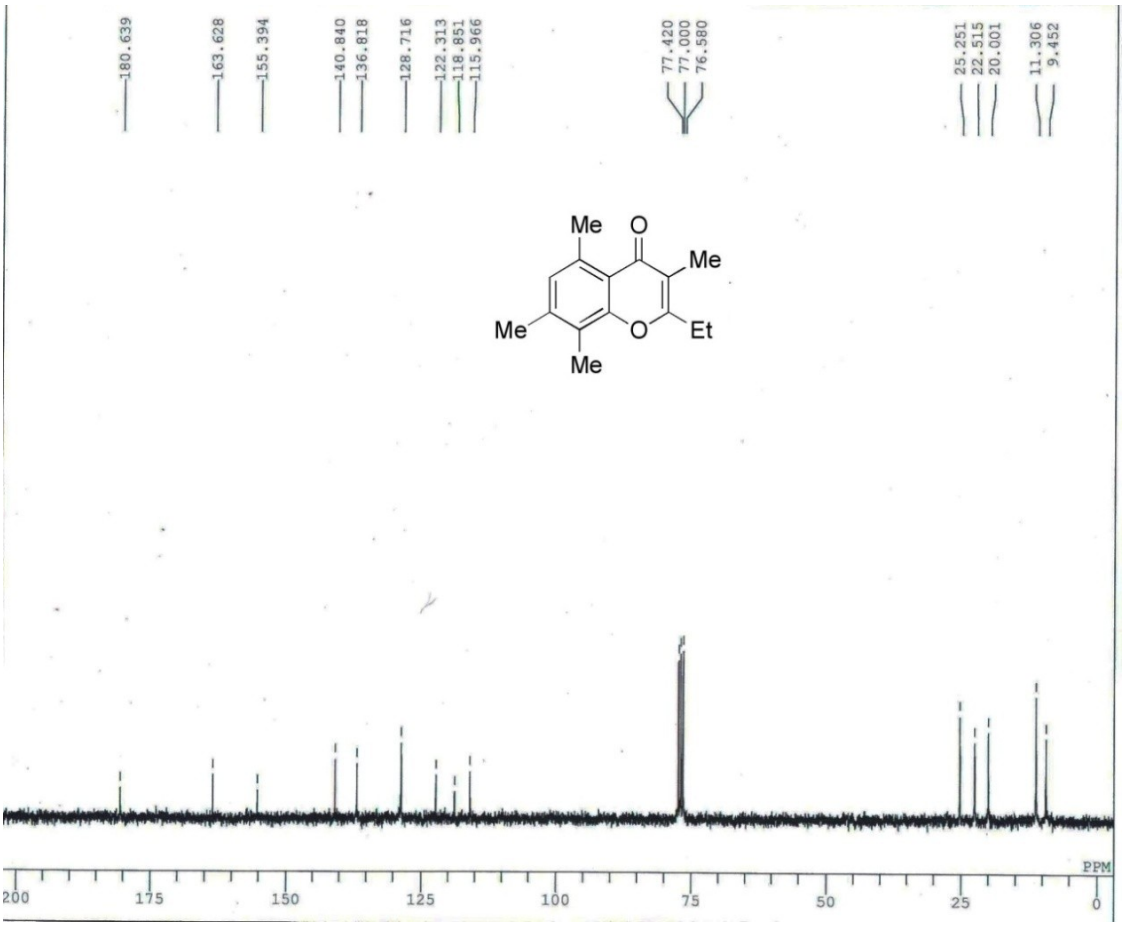
^{1}H and ^{13}C-NMR of **5db**



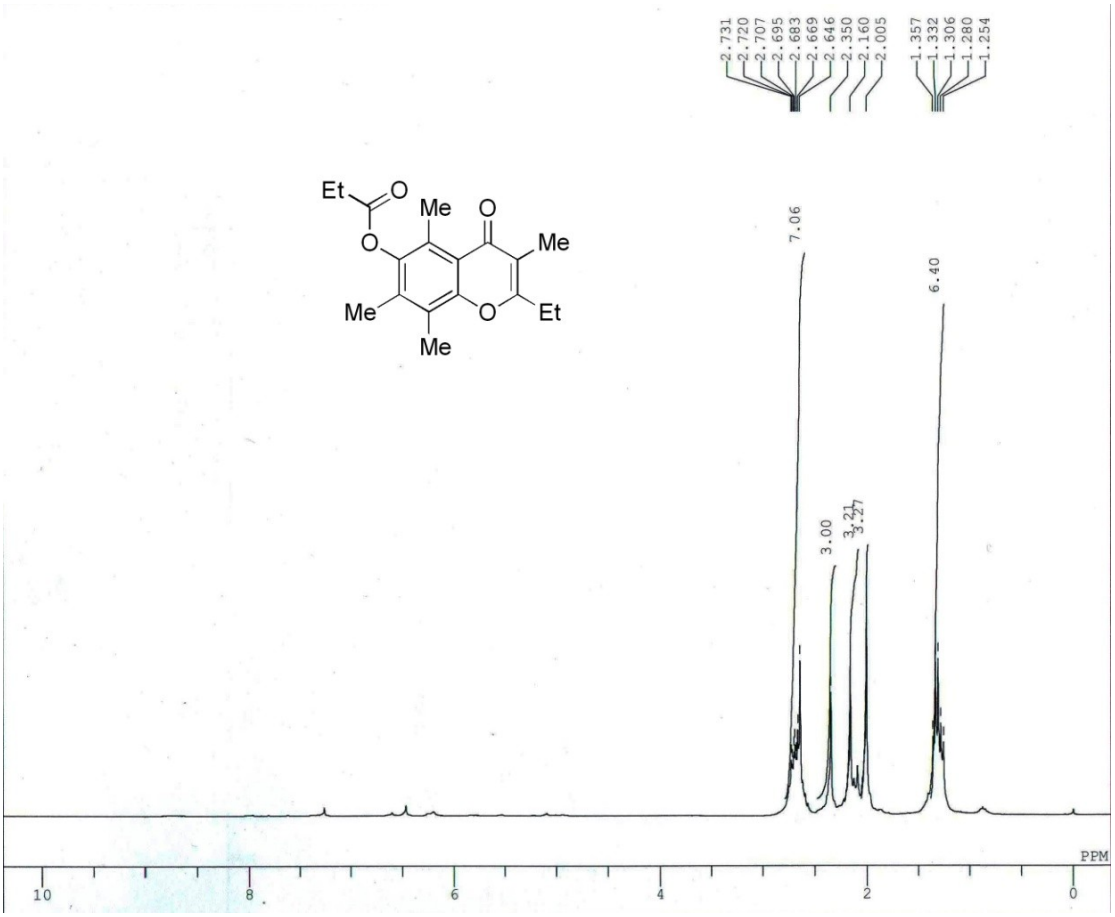


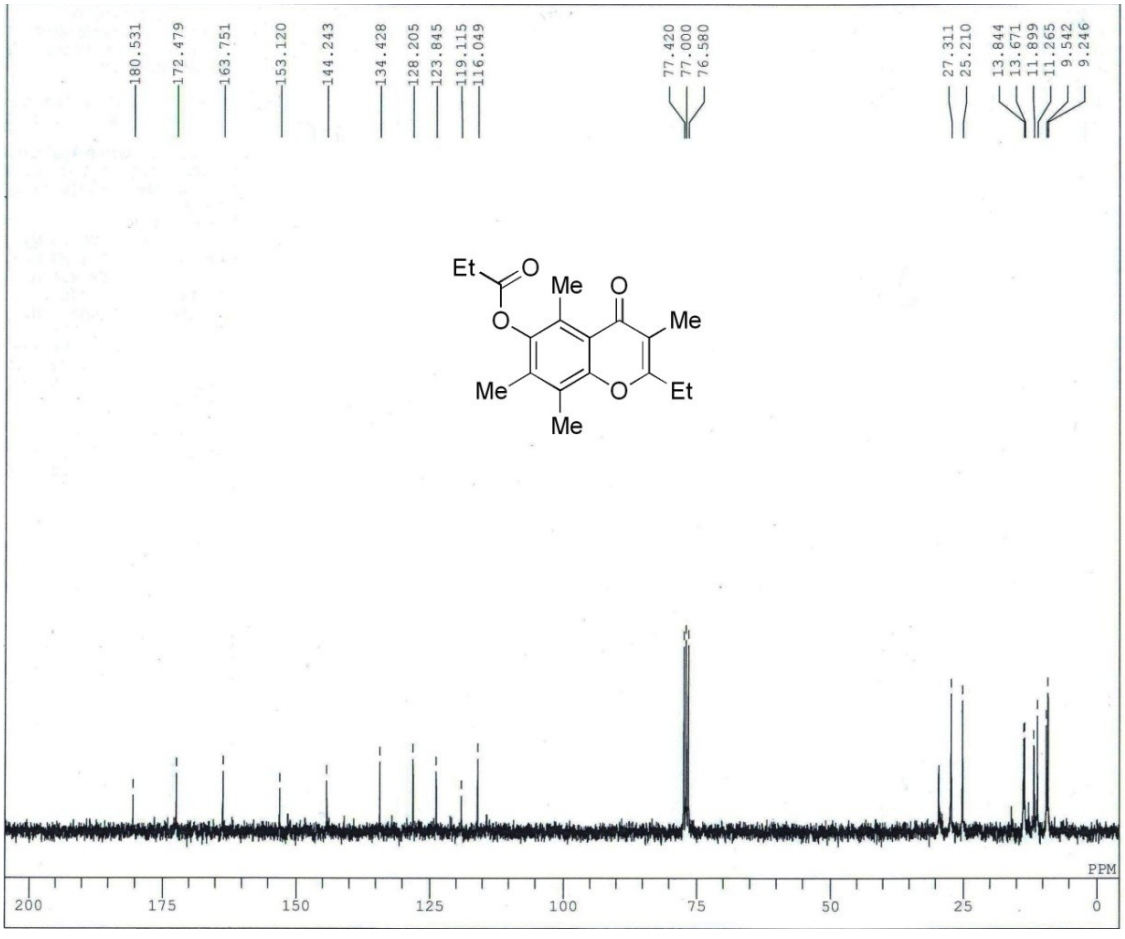
^{1}H and ^{13}C-NMR of **5eb**



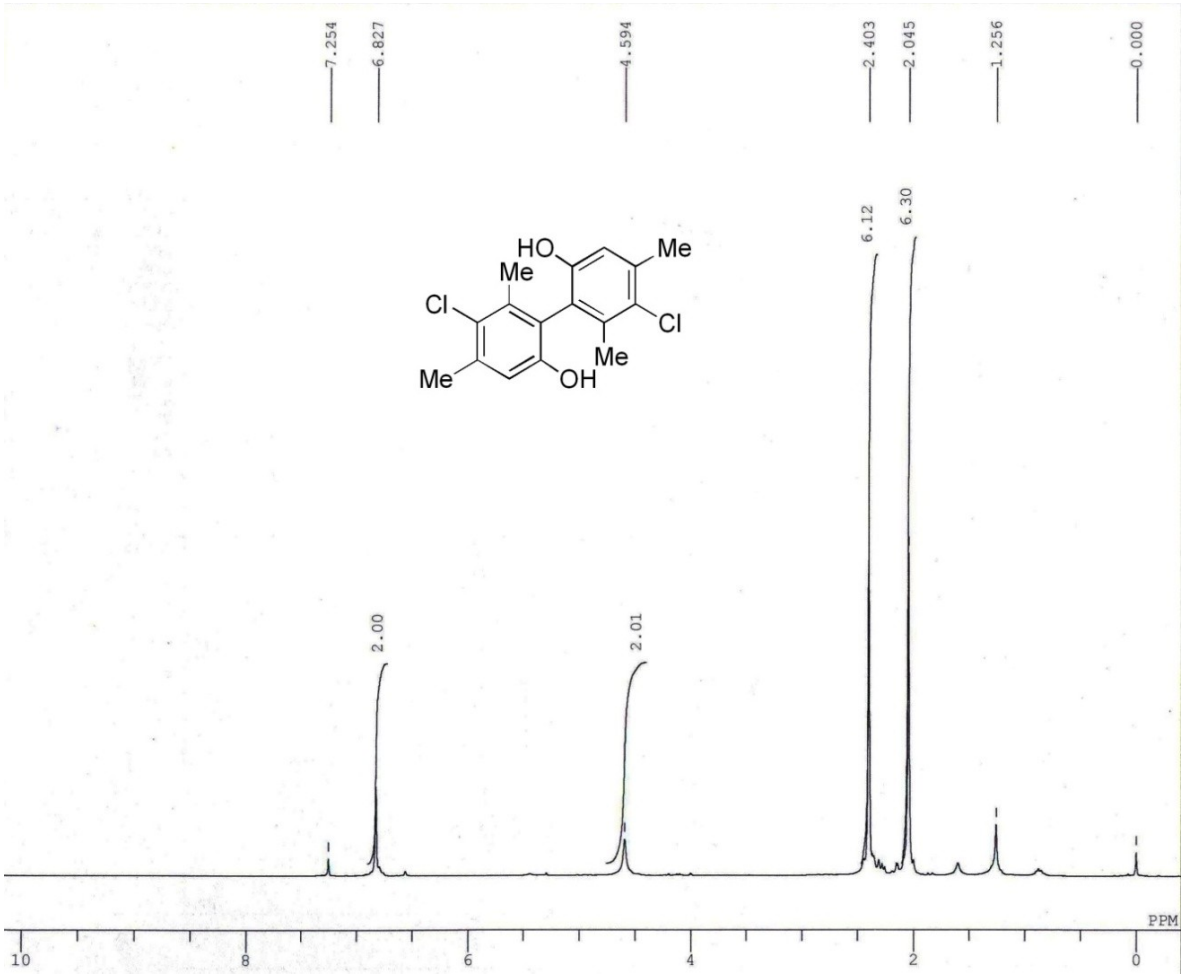


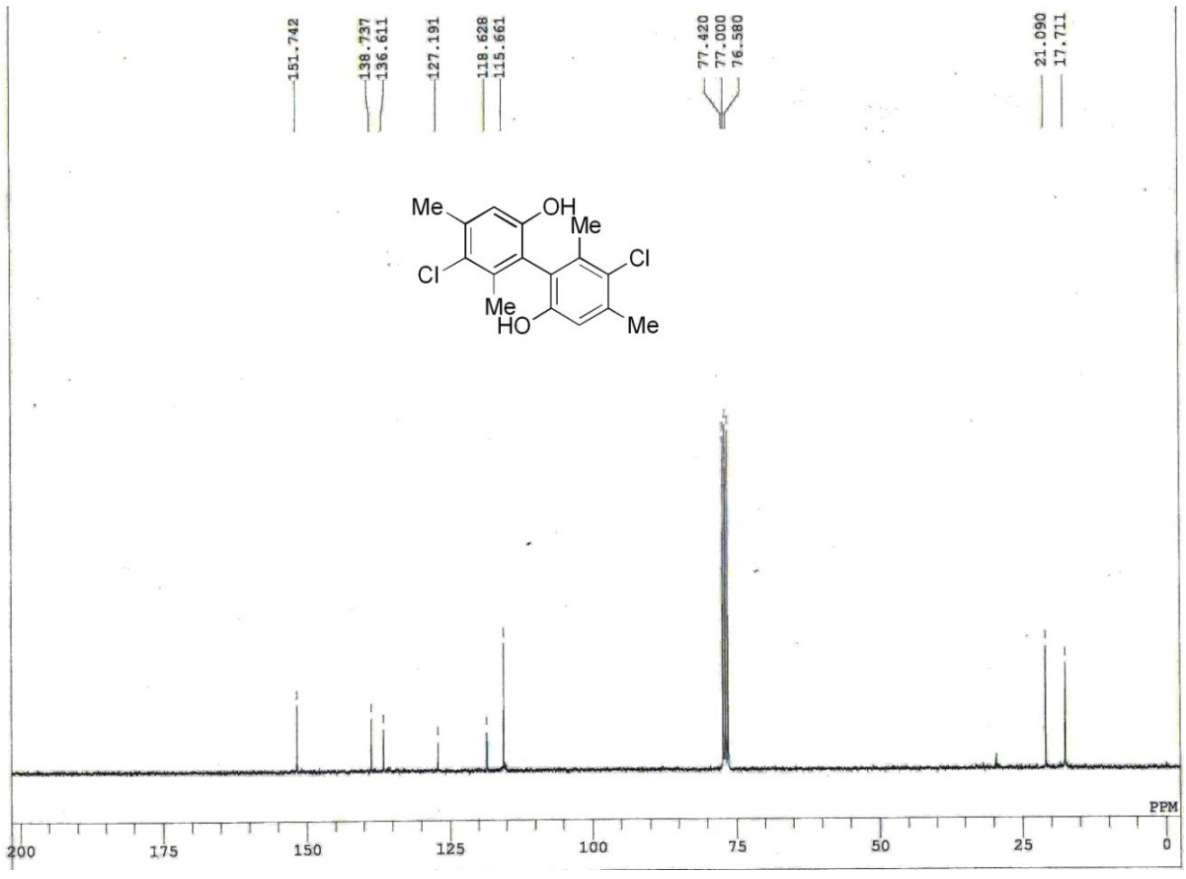
^{1}H and ^{13}C-NMR of **5fb**



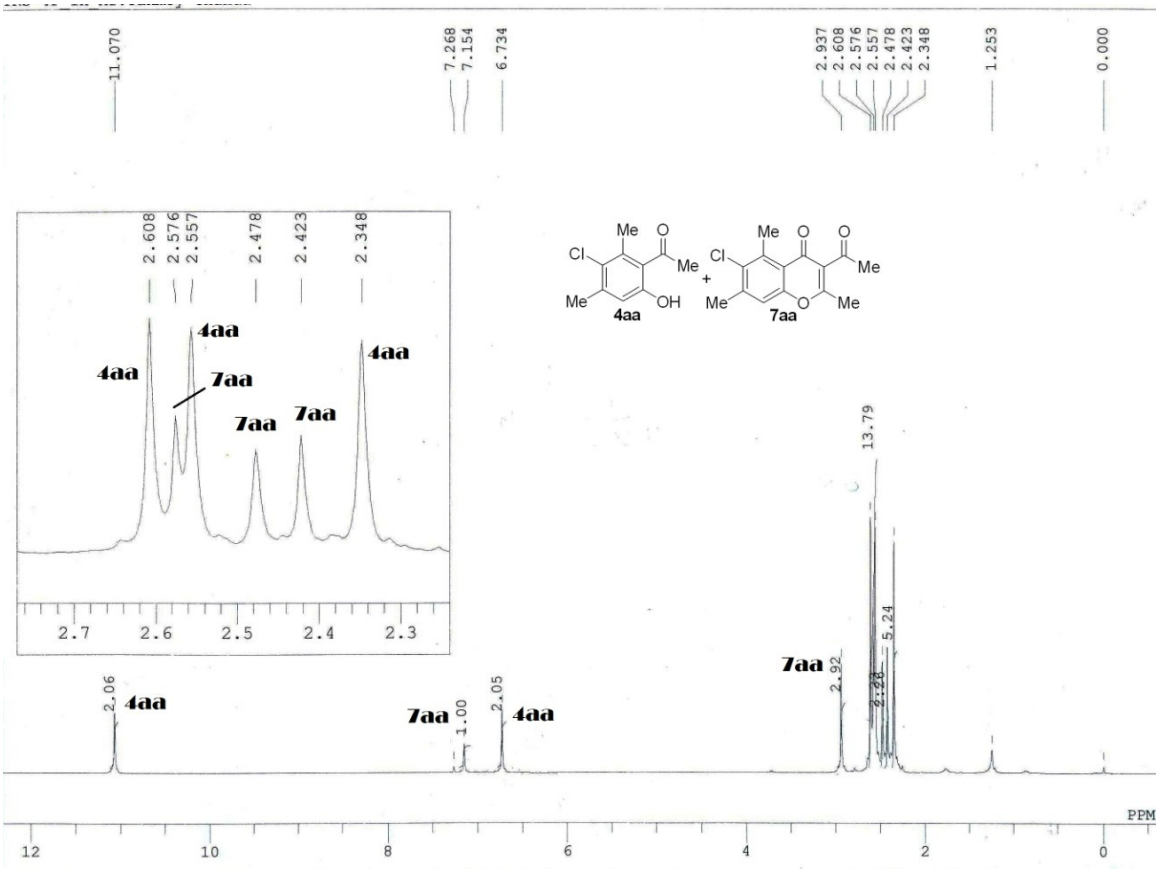


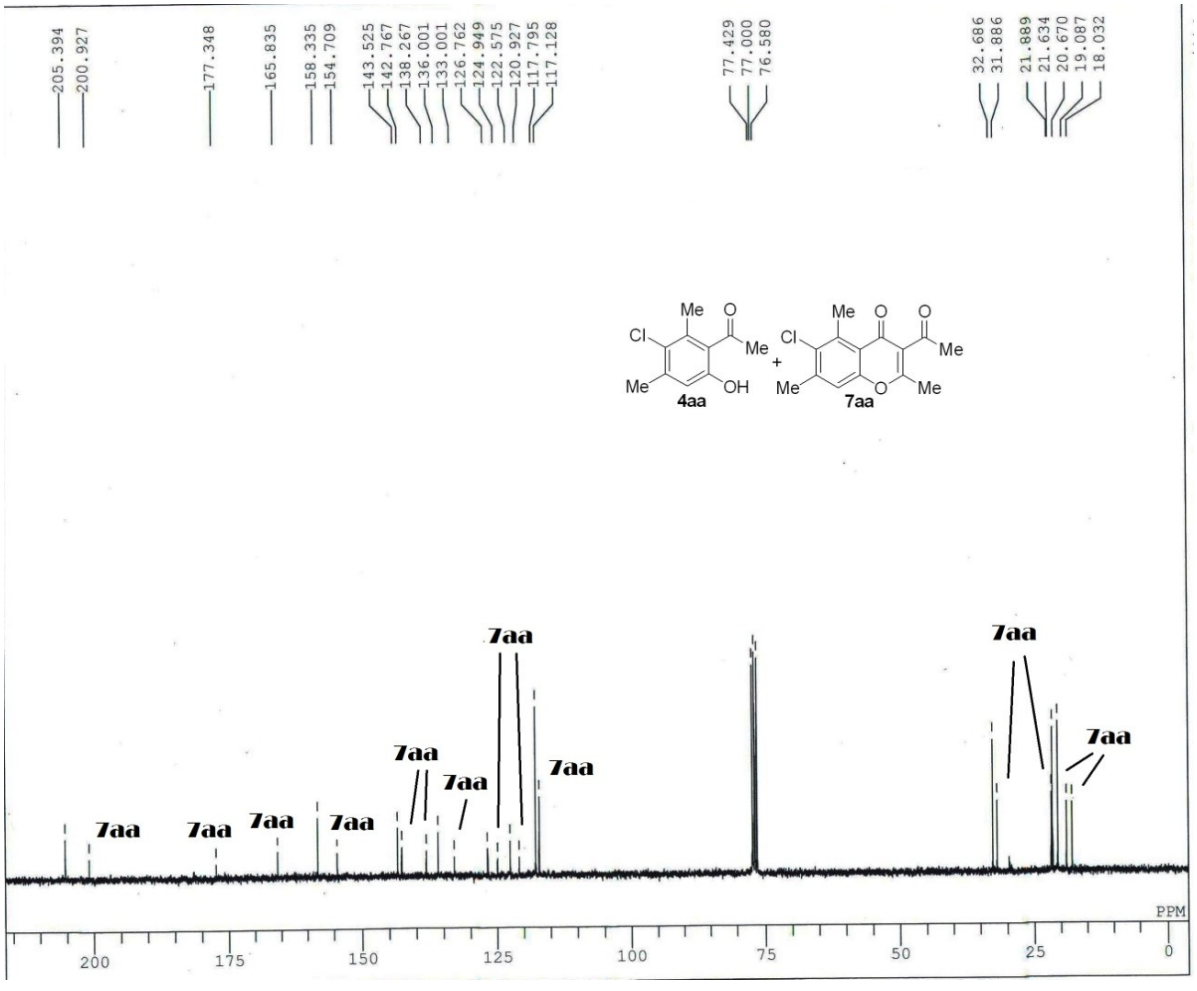
^{1}H and ^{13}C-NMR of **6a**



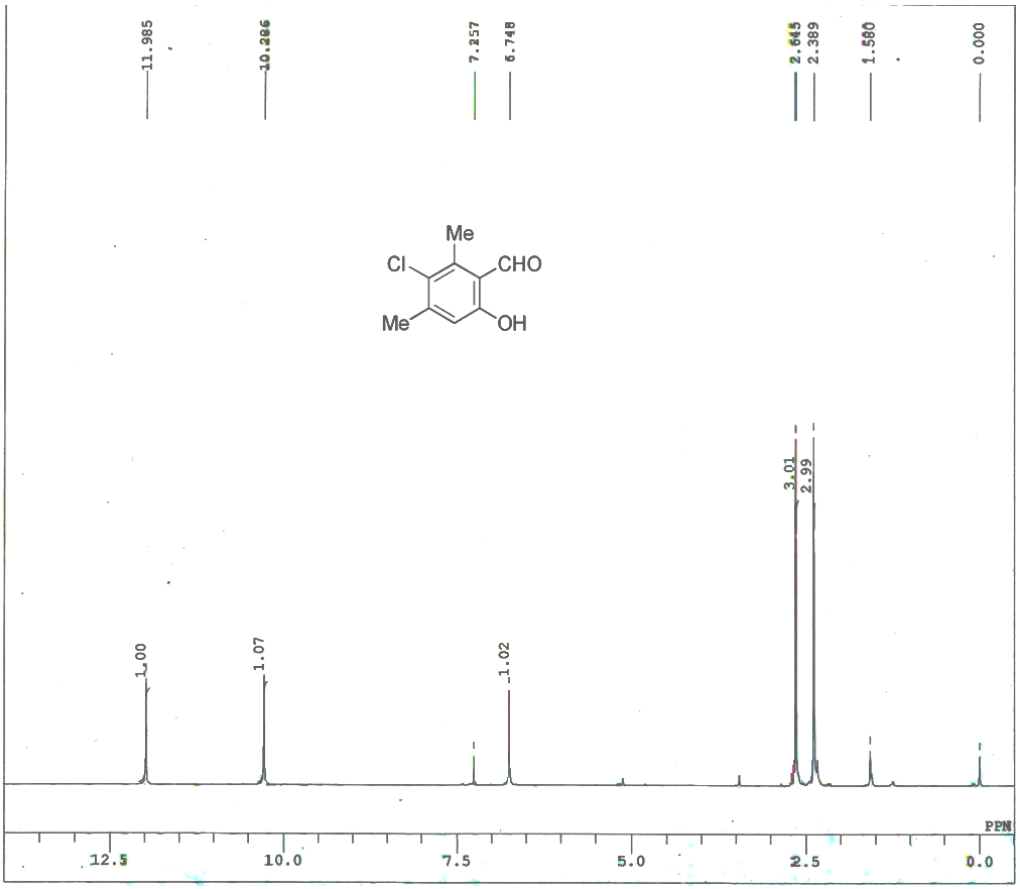


^{1}H and ^{13}C-NMR of the inseparable mixture of **4aa** and **7aa** (2:1)

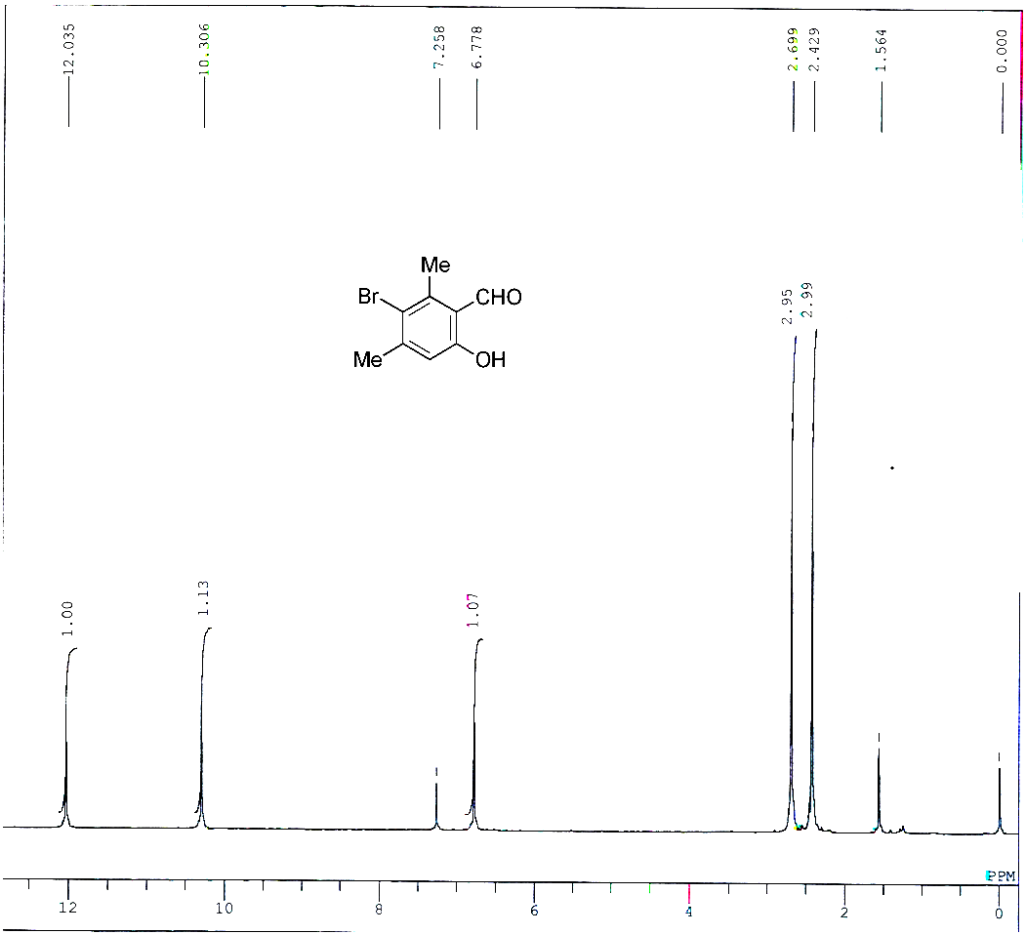




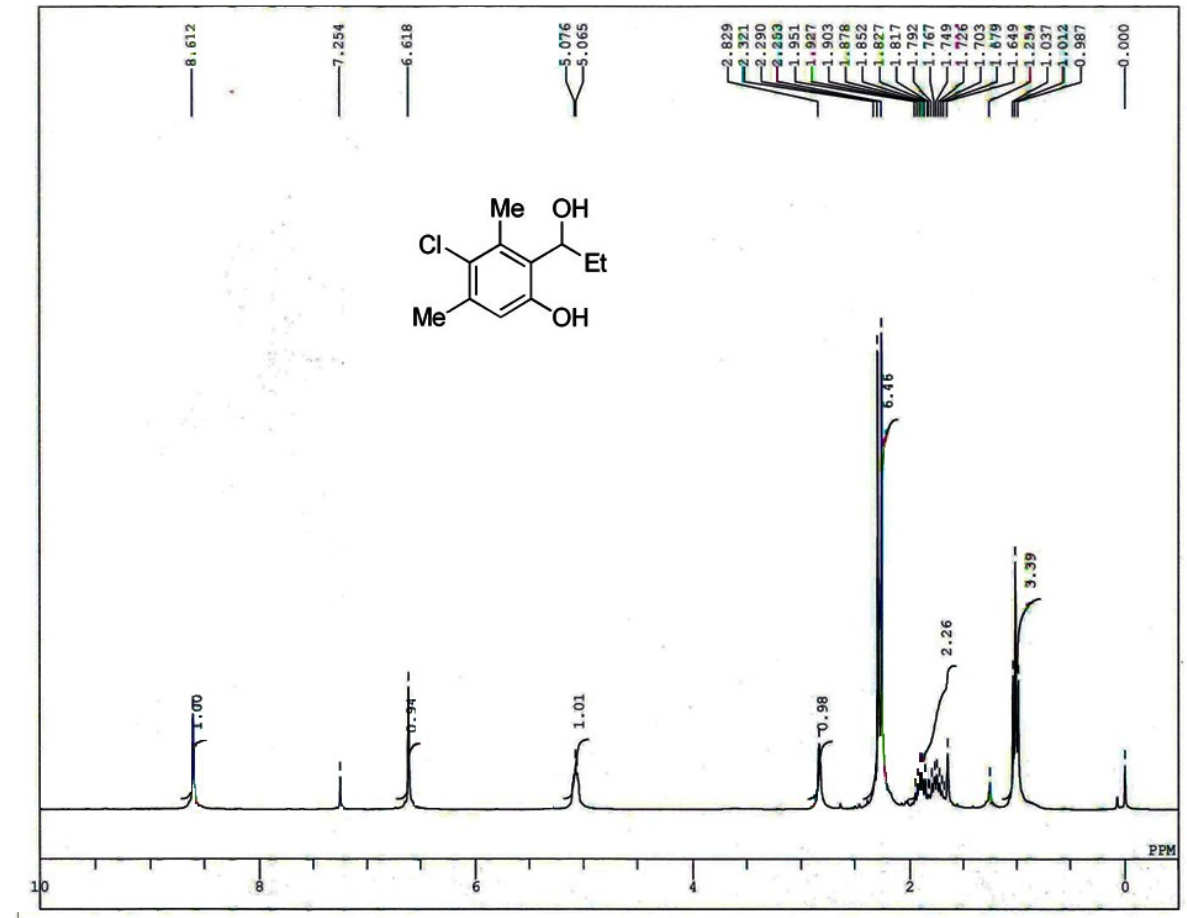
^{1}H-NMR of **8a**

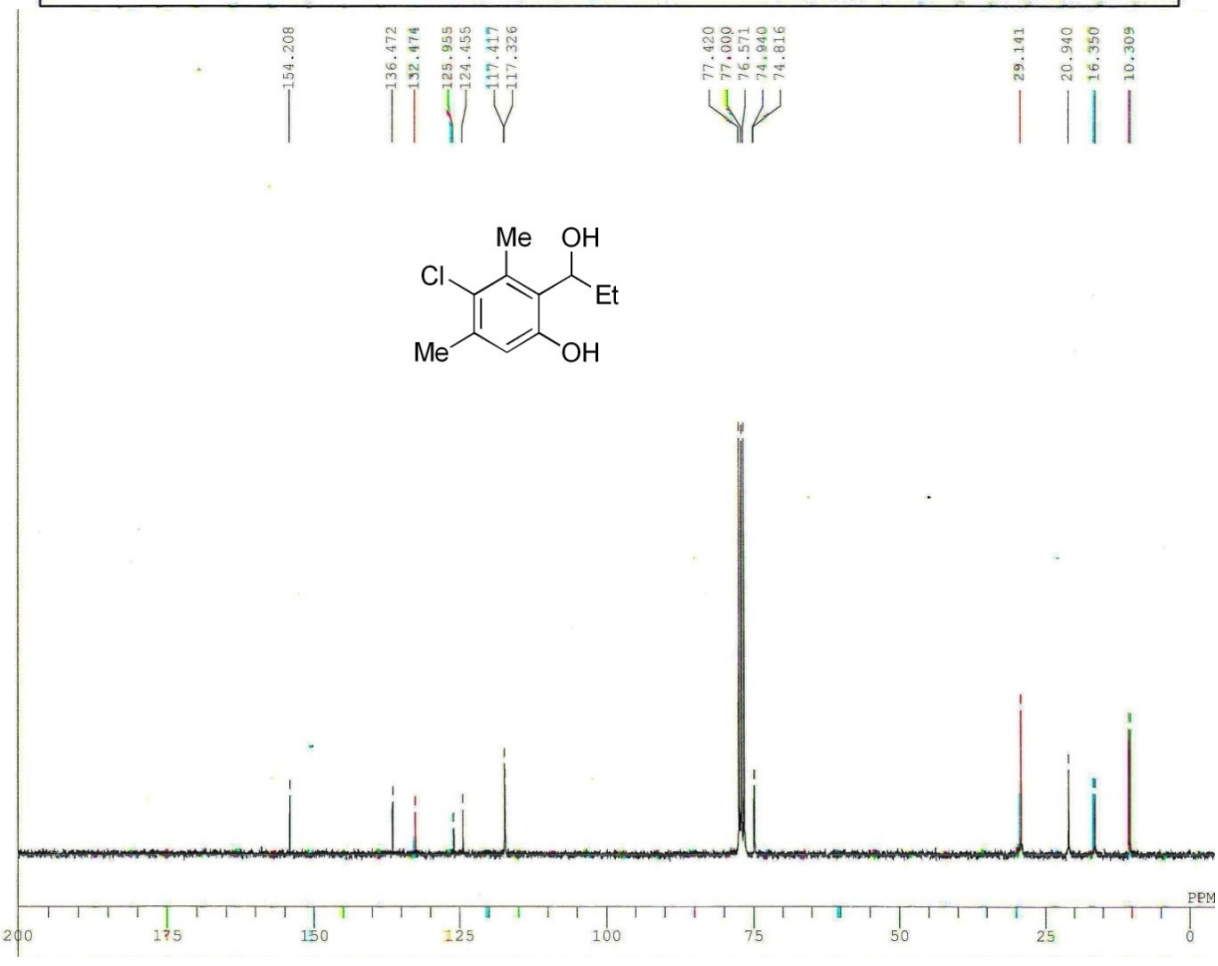


^{1}H-NMR of **8b**

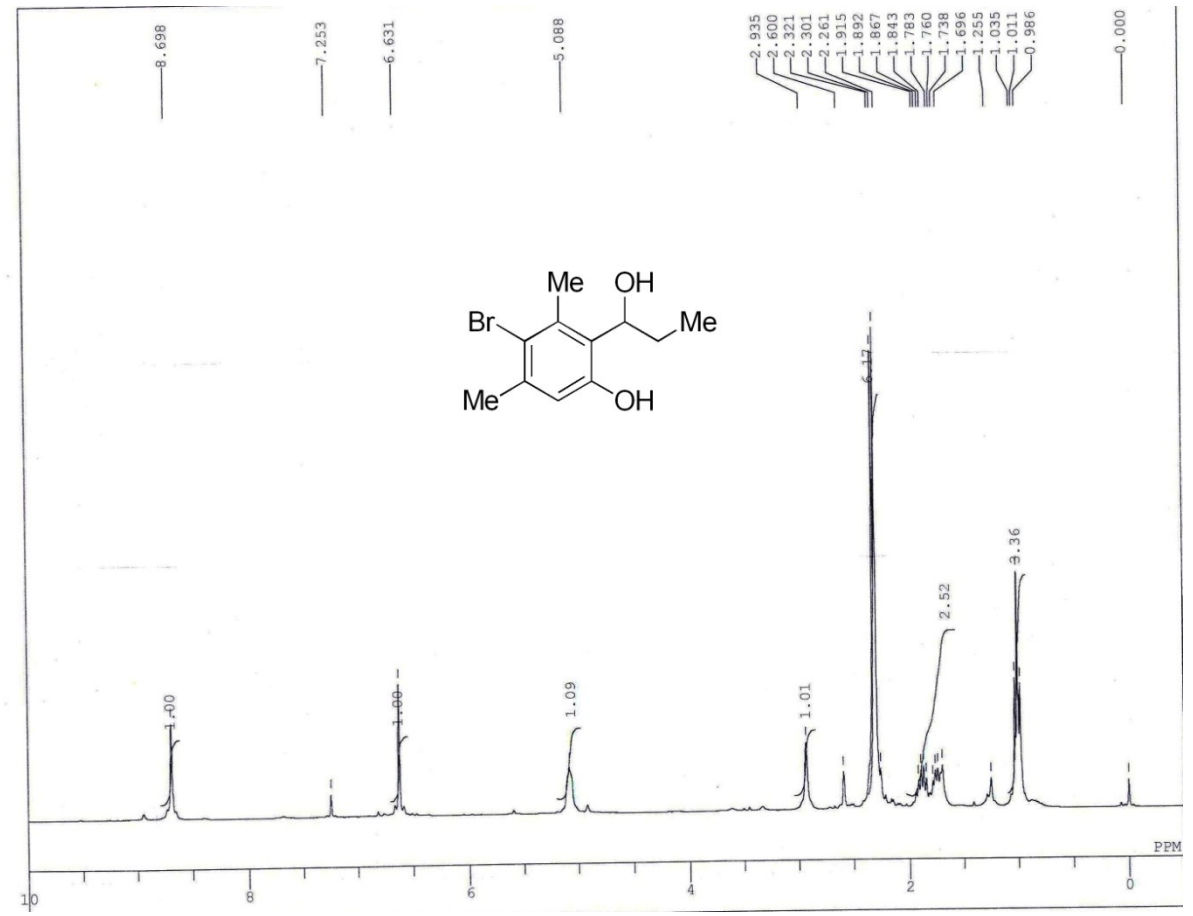


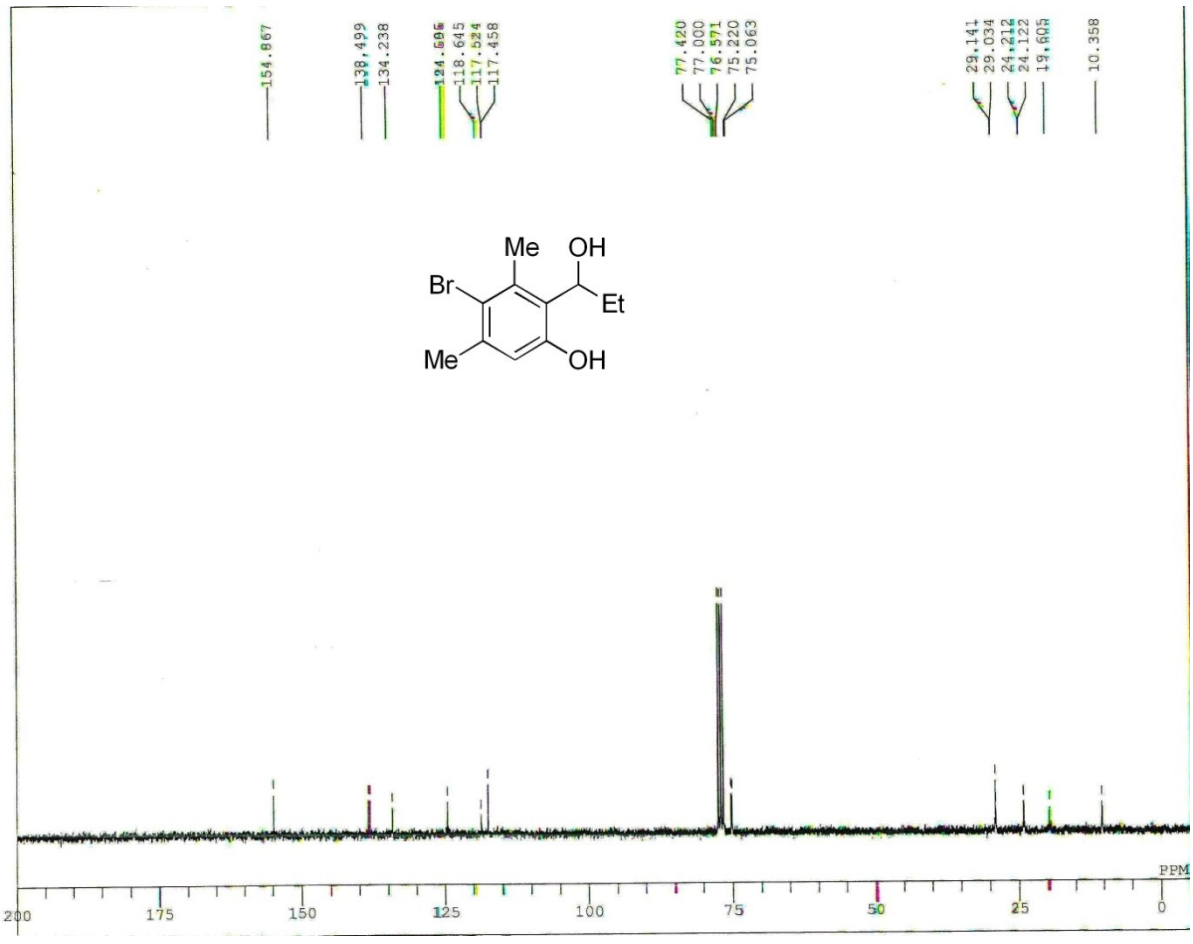
^{1}H and ^{13}C-NMR of **9a**



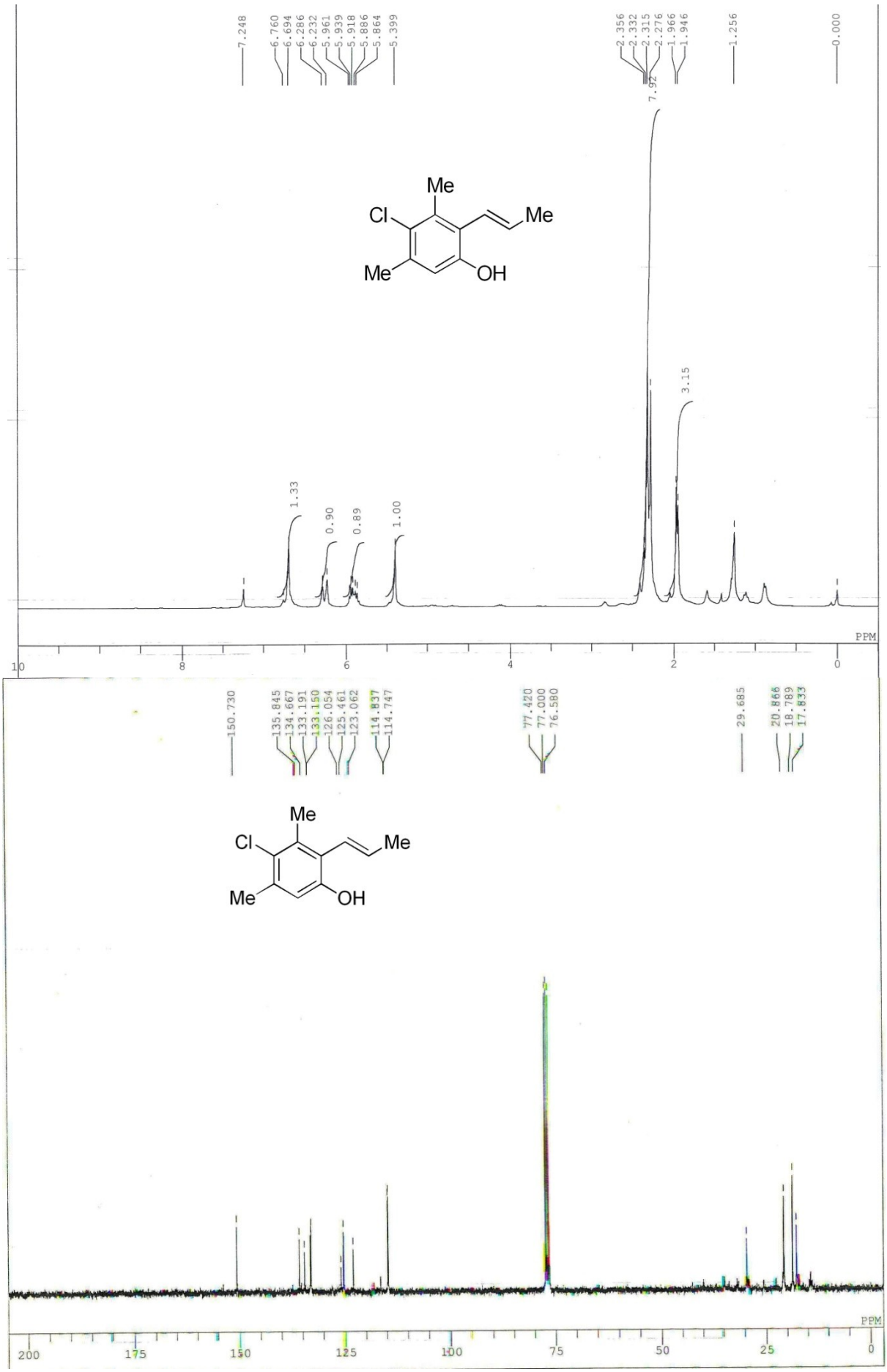


^{1}H and ^{13}C-NMR of **9b**





^{1}H and ^{13}C-NMR of **10a**



^{1}H and ^{13}C-NMR of **10b**