Electronic Supplementary Material (ESI) for Green Chemistry.


# Supporting Information

## Synthesis of 2-Subsituted Pyrimidines and Benzoxazoles via a Visible-Light-Driven Organocatalytic Aerobic Oxidation: Enhancement of Reaction Rate and Selectivity by a Base

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# 1. General Information:

**1.1 Solvents and Reagents:** Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted. Solvents were dried using standard methods and distilled before use. $PhCF_3$ was dried over 4 Å molecular sieves and stored over under argon. All reactions were carried out in glassware opened to the air unless specified.

**1.2 NMR and Mass Spectrometry & Chromatography:** $^{1}H$ and $^{13}C$ NMR spectra were recorded on Bruker AM-400 MHz instruments in $CDCl_3$ with TMS as internal standard. The chemical shifts (δ) are reported in ppm and coupling constants ( J ) in Hz. Chemical shifts are reported in parts per million (δ) relative to $CDCl_3$ (7.27 ppm) for $^{1}H$ NMR data and $CDCl_3$ (77.0 ppm) for $^{13}C$ NMR data. Multiplicities are indicated, s (singlet), brs (broad singlet), d (doublet) , t (triplet), q (quartet), dd (double doublets), m (multiplet). Mass spectra were obtained on Bruker ESQ6K4 and TRACE DSQ. High resolution mass spectra and were performed on Bruker Daltonics APEXII 47e Specifications. Column chromatography was performed with silica gel (200-300 meshes). Thin layer chromatography (TLC) was visualized using UV light.

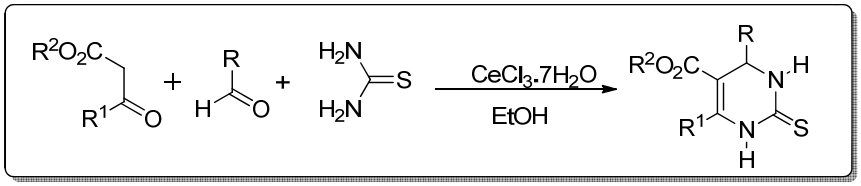
**1.3 Electrochemistry:** Electrochemical investigation was studied on a Princeton Applied Research Potentionstat-gravanostat model 283. Voltammograms were obtained using a standard three electrode cell under argon at room temperature with a glassy carbon working electrode and a platinum wire auxiliary electrode. A $Ag/AgNO_3$ (0.01 mmol.L-1) reference electrode was used and the supporting electrolyte solution was 0.1 M n-$Et_4NBF_4$, and potentials are reported relative to the $Fc/Fc^{+}$couple as 0.00 V. Between each scan the glassy carbon electrode was removed and polished using a 0.05 μm polycrystalline diamond suspension and rinsed with both acetone and deionized water to remove any adsorbed material.

**1.4 Electron spin resonance:** ESR spectra were recorded at room temperature using a Bruker ESP-300E spectrometer at 9.8 GHz, X-band with 100 Hz field modulation. TBA-eosinY, DHPMs **1a** and 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) or 2,2,6,6-tetramethylpiperidine (TEMP) in air-saturated methanol/water (10:1 v/v) was stirred in the dark , then the solution was injected into the quartz capillary. The samples were illuminated directly in the cavity of the ESR spectrometer with a Nd: YAG laser (532 nm, 5-6 ns pulse width, 10 Hz repetition frequency, 10 mJ pulse energy) for 10 s before measurement.

**1.5 Lash Flash photolysis :** The transient absorption spectroscopy was recorded on Edinburgh LP 920 at room temperature. A mixture of methanol/water (10:1 v/v) solution was degassed with nitrogen for 30 min before measurement. Excitation was provided using Nd:YAG laser (4th harmonic or OPO) at 532 nm and the detector was a xenon lamp on the Edinburgh LP 920 apparatus.

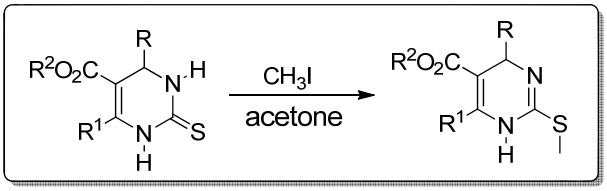
# 2. Preparation of starting materials.

## 2.1 General procedure for the preparation precursor of compounds 1a-1u with the Biginelli three-component-coupling reaction. [1]



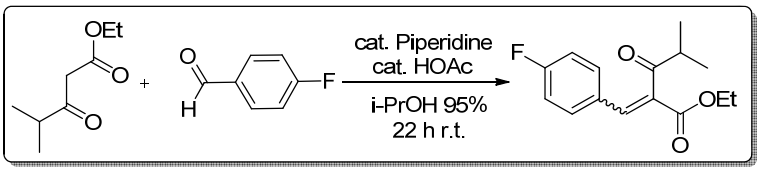

A round bottom flask was charged with ethanol (10 mL), appropriate aldehyde (20 mmol, 1.0 equiv), ethyl acetoacetate (20 mmol, 1.0 equiv), and urea (30 mmol, 1.5 equiv). To the mixture was added $CeCl_3 \cdot 7H_2O$ (1.863 g, 5 mmol, 0.1 equiv) and the batch was heated under reflux. The reaction was finished within 2-3 h (monitored by TLC until the conversion of aldehyde was completed). The mixture was cooled to room temperature and poured onto crushed ice (60 g) in the beaker. The product was stirred for 10min and then isolated by filtration. The wet cake was washed twice with cold water and once with ethanol (10 mL). Then the cake was recrystallized with ethanol (60 mL) and dried under reduced pressure at 40 ℃ overnight. Dihydropyrimidinone was obtained as a white solid.

## 2.2: General procedure for the preparation of compounds 1a-1u with methylation reaction.[2]



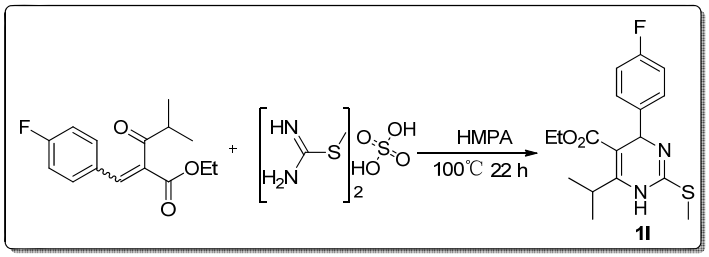

A flame-dried round-bottomed flask charged with a suitable magnetic stir bar, potassium carbonate (1.0 g, 7.25 mmol) and methyl iodide (220 uL, 3.5 mmol) was added into the suspension of 4-substituted-3,4-dihydropyrimidin-2(1*H*)-thione (3 mmol) in acetone (15 mL) under $N_2$ atmosphere. The reaction was stirred for overnight at room temperature (the reaction flask was wrapped in aluminium foil) and was diluted with EtOAc. The reaction system was filtered and the filtrate was washed with water and brine, dried with $MgSO_4$ and the solvent removed *in vacuo*. The crude residue was purified by flash chromatography ($CH_2C1_2$/acetone = 20:1) to afford the desired 4-substituted-1,4-dihydropyrimidine .

### 2.3: General procedure for the preparation precursor of compounds 1l. [3]



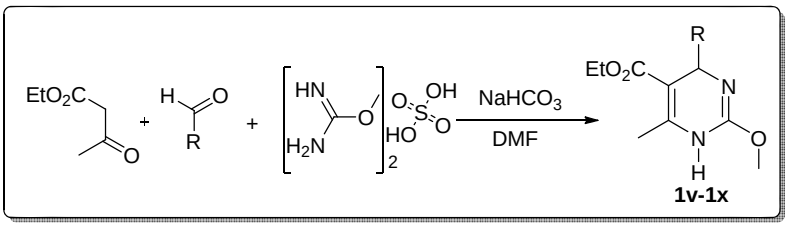

In a 10 mL round bottomed flask equipped with a magnetic stirrer was placed with ethyl isobutyrylacetate (2.11 g, 13.34 mmol), 4-fluorobenzaldehyde (1.613 g, 13.30 mmol), isopropanol (1.0 ml), pyperidine (72 μL) and glacious acetic acid (42 μL). The reaction mixture was stirred at room temperature under nitrogen for 22 h. The solvent was removed under reduced pressure. The residue was dissolved with methylene chloride (5 mL) and washed with sat. $NaHCO_3$ (3×10 mL) and dried over anhydrous $MgSO_4$. Removal of $MgSO_4$ and solvent afforded ethyl 2-(4-fluorobenzylidene)-4-methyl-3-oxopentanoate (3.19 g) in 95% yield as a mixture of cis/trans-isomers which was used in the subsequent step without further purification.

## 2.4: General procedure for the preparation compounds 1l. [4]




The mixture of a solution of 4.468 g of compound ethyl 2-(4-fluorobenzylidene)-4-methyl -3-oxopentanoate in 6.5 mL of HMPA and 2.824 g of S-methylisothiourea hydrogen sulfate was stirred at 100 ℃ for 22 h. The reaction mixture was extracted with $Et_2O$, and washed successively with sat. $NaHCO_3$ and water. The organic layer was dried, and the solvent was distilled away. The obtained residue was purified by flash chromatography(PE→PE/EtOAc = 100:1) to yield the corresponding **1l** as a pale yellow oil.

### 2.5: General procedure for the one-pot preparation of compounds 1v-1x. [5]

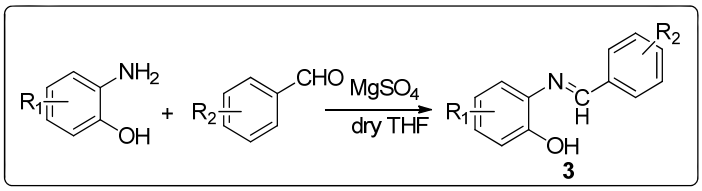



A round bottom flask was charged with a mixture of O-methylisourea hydrogensulfate (1.48 g, 12 mmol), ethyl 3-oxobutanoate (1.30 g, 1.28 mL, 11.0 mmol), the appropriate aldehyde (10

mmol), $NaHCO_3$ (3.36g, 40 mmol) and DMF (20 mL) was heated at 70 ℃ for 3-4 h. After cooling, the mixture was diluted with brine (30 mL) and extracted with ether (2 × 20 mL). The combined organic layers were washed with water (2 × 10 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The residue was chromatographed on alumina with $CH_2C1_2$/ acetone (20:1) to yield the following dihydropyrimidines.

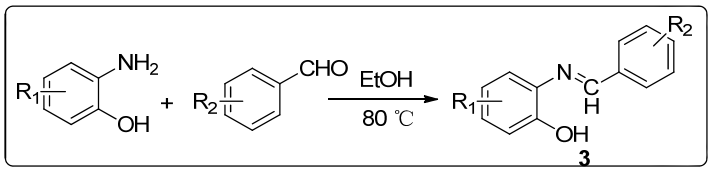
## 2.6: General procedure for the synthesis of phenolic imines:

**General Method A:** According to a procedure described by *Overman et al.*[6]



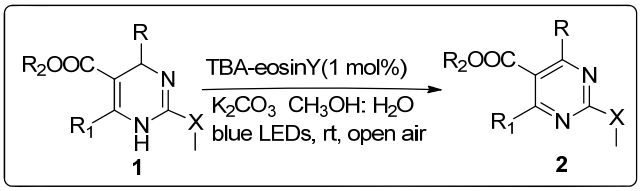

Benzaldehyde (0.76 g, 7.1 mmol) was added dropwise to a stirred slurry of 2-aminophenol (0.78 g, 7.1 mmol), anhydrous $MgSO_4$ (2.5 g), and THF (5 mL) at 0 ˚C, and the reaction was allowed to warm to rt. After 8 h, the reaction mixture was filtered and the filtrate and concentrated to give 1.43 g (100 %) of the crude imine, which was further purified by recrystallized with Toluene.

**General Method B:** According to a procedure described by *Cheon et al.*[7]




To a 150 mL round bottom flask was added o-Aminophenol (10 mmol; 1.0 equiv) and aldehyde (10 mmol; 1.0 equiv) were dissolved in absolute EtOH (80 mL). Then, the reaction mixture was stirred at 80℃ for 3-5 h under argon atmosphere. When the starting materials was consumed completely (monitored by TLC), the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The crude product was recrystallized with EtOH. The solid was collected by filtration and washed with cooled EtOH to give the corresponding imine.

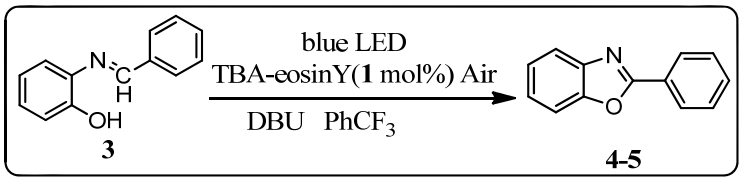
## 3. General procedure for Photoredox Synthesis of 2-Substituted Pyrimidines.




Under air atmosphere , a 15 mL reaction tube equipped with a magnetic stir bar , dihydropyrimidines **1** (0.10 mmol) , TBA-eosinY (0.1 mmol%) and $K_2CO_3$ (0.20 mmol) was added , then MeOH (5.0 mL) and $H_2O$ (0.5 mL) were added. The solution mixture was stirred in open air with a

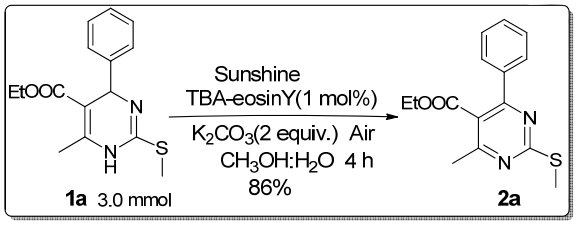
3 W 450 nm blue LEDs irradiated and monitored by TLC. On the completion of the reaction, the reaction mixture was concentrated *in vacuo*. The residue was dissolved with bits of methylene chloride, The crude residue was purified by flash chromatography to yield the corresponding 2-substituted pyrimidines **2**.

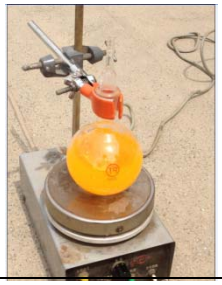
## 4. General procedure for Photoredox Synthesis of 2-Substituted Benzoxazoles.




In a dried 10 mL reaction tube equipped with a magnetic stir bar， imine **3** (0.10 mmol) and TBA-eosinY (0.001 mmol) dissolved in dry $PhCF_3$ (3.0 mL) were added, then DBU (0.20 mmol) was added to the reaction system. Then the solution mixture was stirred at room temperature in an open flask with a 3 W 450 nm blue LEDs irradiated and monitored by TLC. On the completion of the reaction, the reaction mixture was quenched with $H_2O$, and extracted with $Et_2O$. The organic layer was collected, dried over $Na_2SO_4$, and the solvent removed *in vacuo*. The crude residue was purified by flash chromatography to yield the corresponding 2-substituted benzoxazole as white solid.

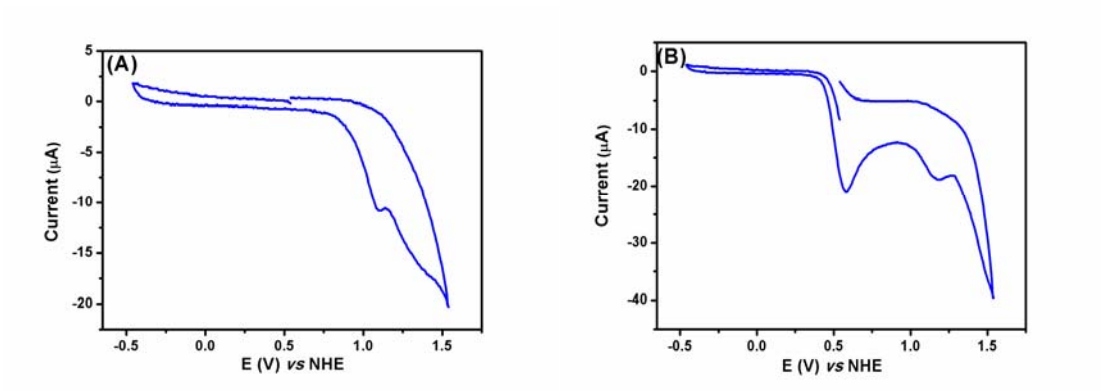
## 5. Gram scale dehydrogenative oxidation reaction under ambient sunlight



Under air atmosphere, a 250 mL round flask equipped with a magnetic stir bar，dihydropyrimidines **1a** (3. 0 mmol) , TBA-eosinY (0.1 mmol%) and $K_2CO_3$ (6.0 mmol) was added, then MeOH (150 mL) and $H_2O$ (15 mL) were added. The solution mixture was stirred in open air with sunshine irradiated and monitored by TLC. On the completion of the reaction, the reaction mixture was quenched with $H_2O$, and extracted with $Et_2O$. The organic layer was collected, dried over $Na_2SO_4$, and the solvent removed *in vacuo*. The crude residue was purified by flash chromatography to afford the desired product **2a**.

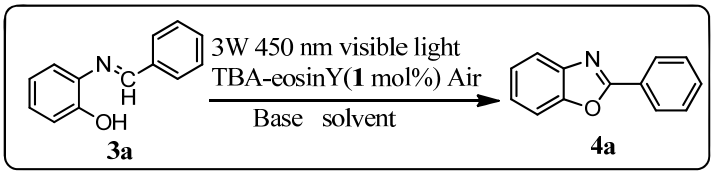
# 6 The electrochemistry of DHPMs 1a.




Cyclic voltammogram of **1a** (1.0 mmol.$L^{-1}$) with 0.1 mol.$L^{-1}$ *n*-$Et_4NBF_4$ in a mixture of methanol and water (10:1 v/v) in the absence (A) and presence (B) of $K_2CO_3$ (2.0 mmol.$L^{-1}$).

## 7 Optimization of photocatalytic aerobic preparation of 2-phenylbenzoxazole.

**Variations to standard aromatization Reaction conditions for synthesis of 2-Arylbenzoxazole.**[a]

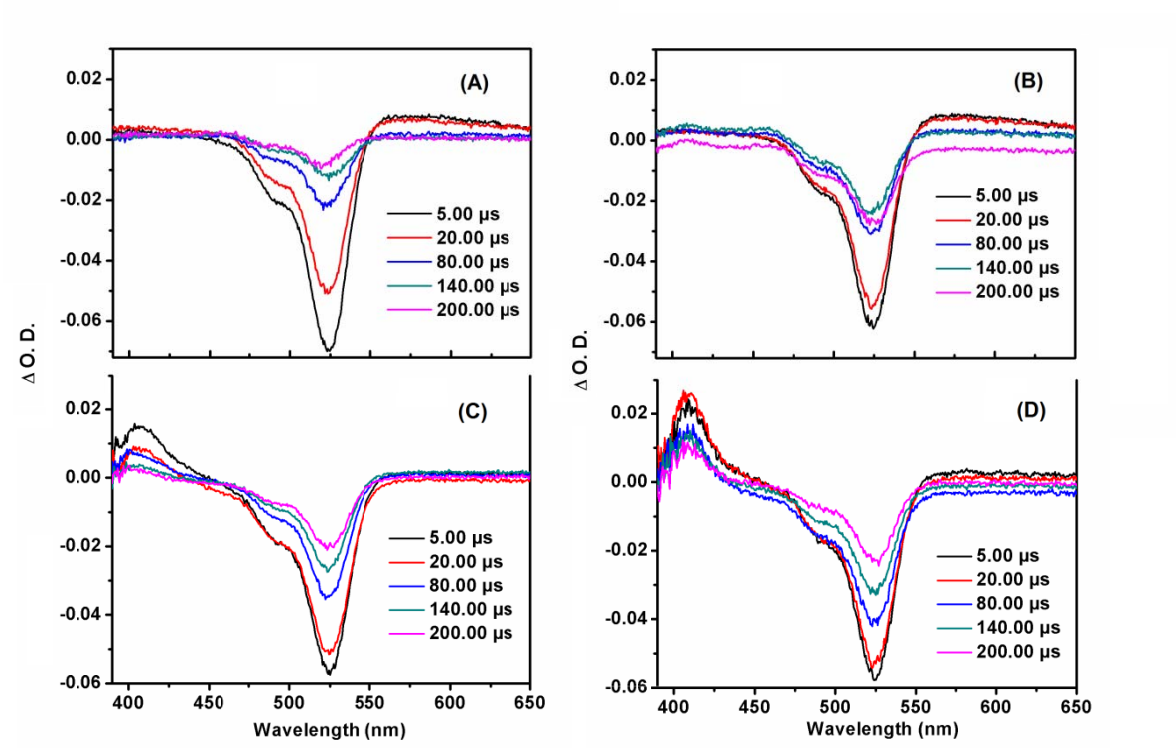



| Entry | Solvent | Base | $H_2O$[b] | t (h)[c] | Yield (%)[d] |
|---|---|---|---|---|---|
| 1 | MeOH | $K_2CO_3$ | + | 2 | 55 |
| 2 | MeOH | $K_2CO_3$ | - | 3 | 62 |
| 3 | MeOH | DBU | - | 3 | 80 |
| 4 | $CH_3CN$ | $K_2CO_3$ | - | 3 | 71 |
| 5 | $CH_3CN$ | 2,6-Lutidine | - | 3 | 75 |
| 6 | $CH_3CN$ | DBU | - | 3 | 79 |
| 7 | $CH_2Cl_2$ | DBU | - | 3 | 81 |
| 8 | $PhCH_3$ | DBU | - | 3 | 83 |
| 9 | $PhCF_3$ | $K_2CO_3$ | - | 3 | 66 |
| **10**[e] | **$PhCF_3$** | **DBU** | - | **3** | **90** |
| 11[f] | $PhCF_3$ | DBU | - | 3 | 77 |

| | | | | | |
|---|---|---|---|---|---|
| 12 | $PhCF_3$ | - | - | 10 | 57 |

[a] Reaction conditions: **3a** (0.1 mmol), TBA-eosinY (1 mol %). Base (0.2 mmol), Sovlent 3 mL, Air, 3 W 450 nm LED visible-light irradiation.
[b] "+" implys 0.5 mL of water was added to the system.
[c] The time when **1a** was no longer consumed (monitored by TLC).
[d] Isolated yield (average of two parallel experiments).
[e] DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene.
[f] An Eosin Y Disodium Salt was used instead of TBA-eosinY.

## 8. Study The Role of DBU by Transient Absorption Difference Spectra.



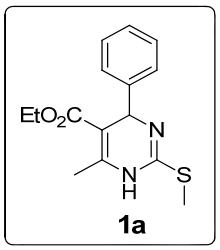

Transient absorption difference spectra of TBA-eosin Y ($1.0\times10^{-5}$mol.L$^{-1}$) with 532 nm light in anaerobic methanol. Figure A: In the absence of additives. Figure B: In presence of DBU ($2.0\times10^{-3}$ mol.L$^{-1}$). Figure C: In presence of **3a** ($1.0\times10^{-3}$ mol.L$^{-1}$). Figure D: In presence of **3a** ($1.0\times10^{-3}$ mol.L$^{-1}$) and DBU ($2.0\times10^{-3}$ mol.L$^{-1}$).

The mechanism studies of the dehydrogenation of phenolic imines **3a** was also studied by transient absorption difference spectra. When an anaerobic methanol solution containing TBA-eosin Y ($1.0\times10^{-5}$mol.L$^{-1}$) and DBU ($2.0\times10^{-3}$mol.L$^{-1}$) was excited by a 532 nm laser pulse, the transient

absorption difference spectra between 390 nm and 450 nm is transparent (Figure B). On the contrary, a typical absorption of TBA-eosin Y radical anion at 406 nm was clearly observed upon flash-photolysis of an anaerobic solution containing TBA-eosin Y ($1.0\times10^{-5}$mol.L$^{-1}$) and DBU ($2.0\times10^{-3}$mol.L$^{-1}$) and **3a** ($1.0\times10^{-3}$mol.L$^{-1}$) (Figure D). Combining the spectra of TBA-eosin Y (Figure A) and the spectra of TBA-eosin Y with **3a** (Figure C), it is clear that the organic base DBU is only used to dissociate the phenol to its anion, just as the role of inorganic base $K_2CO_3$for the dehydrogenation of DHPMs **1a**.

## 9. Characterization Data of the 2-Substituted dihydropyrimidines.

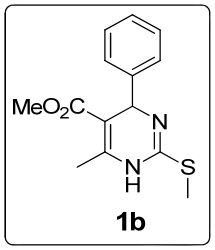
**Ethyl 6-methyl-2-(methylthio)-4-phenyl-1,4-dihydropyrimidine-5-carboxylate (1a):**



**1a**

White solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.35-7.22 (m, 5H), 6.35 (brs, 1H), 5.66 (brs, 1H), 4.14-4.08 (q, *J* = 7.2 Hz, 2H), 2.46 (s, 3H), 2.37 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 166.7, 144.6, 128.3, 127.3, 126.9, 59.8, 14.2, 13.5 ppm.

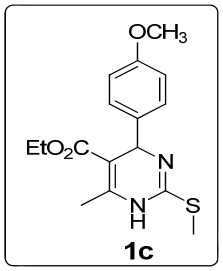
**Methyl 6-methyl-2-(methylthio)-4-phenyl-1,4-dihydropyrimidine-5-carboxylate (1b):**



**1b**

White solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.32-7.20 (m, 5H), 6.44 (s, 1H ), 5.62 (s, 1H), 3.63 (s, 3H), 2.42 (s, 3H), 2.32 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 167.3, 144.5, 128.4, 126.8, 51.0, 13.5 ppm.

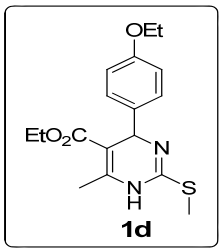
**Ethyl 4-(4-methoxyphenyl)-6-methyl-2-(methylthio)-1,4-dihydropyrimidine-5-carboxylate (1c):**



**1c**

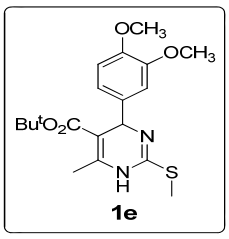
White solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.26-7.18 (m, 2H), 6.85-6.80 (m, 2H), 6.39 (s, 1H), 5.62 (s, 1H), 4.13-4.06 (m, 2H), 3.77 (s, 3H), 2.42 (s, 3H), 2.33 (s, 3H), 1.20 (t, 3H, *J* = 7.2 Hz) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 166.8, 158.8, 137.3, 128.0, 114.1, 113.6, 60.4, 59.7, 55.2, 14.2, 13.5 ppm.

**Ethyl 4-(4-ethoxyphenyl)-6-methyl-2-(methylthio)-1,4-dihydropyrimidine-5-carboxylate (1d):**



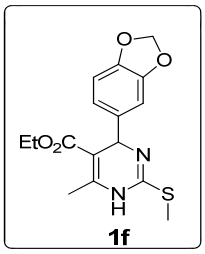

Pale yellow solid. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.26-7.07 (m, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.62 (s, 1H), 5.56 (s, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.99 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 2.35 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 166.7, 158.2, 136.8, 128.0, 114.2, 63.3, 59.8, 14.8, 14.2, 13.6 ppm.

**Tert-butyl 4-(3,4-dimethoxyphenyl)-6-methyl-2-(methylthio)-1,4-dihydropyrimidine-5-carb-oxylate (1e):**



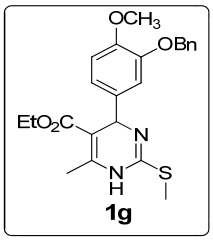

White solid. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 6.91 (s, 1H), 6.81 (dd, *J* = 2.0, 6.4 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.57 (brs, 1H), 5.56 (brs, 1H), 3.82 (s, 6H), 2.43 (s, 3H), 2.30 (s, 3H), 1.37 (s, 9H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 165.9, 148.5, 148.0, 137.2, 118.6, 110.7, 110.3, 80.1, 55.7, 28.14, 28.09, 13.6 ppm.

**Ethyl 4-(benzo[d][1,3]dioxol-5-yl)-6-methyl-2-(methylthio)-1,4-dihydropyrimidine-5-carbo-xylate (1f):**



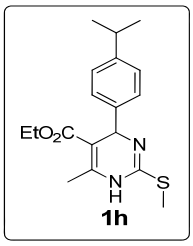

White solid. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 6.82 (d, *J* = 1.2 Hz, 1H), 6.77 (dd, *J* = 1.6, 6.4 Hz,1H), 6.70 (d, *J* = 8.0 Hz, 1H), 5.90 (s, 2H), 5.53 (s, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 2.42 (s,3H), 2.32 (s,3H), 1.20 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 166.7, 147.6, 146.7, 138.7, 120.1, 107.9, 107.5, 102.3, 100.9, 59.8, 57.6, 19.8, 14.2, 13.5 ppm.

**Ethyl 4-(3-(benzyloxy)-4-methoxyphenyl)-6-methyl-2-(methylthio)-1,4-dihydropyrimidine-5-carbxylate (1g):**



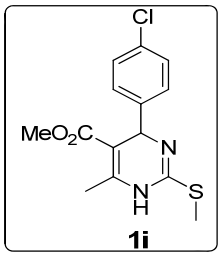

White solid. **$^{1}$H NMR (400 MHz, $CDCl_3$):** 7.41 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.27 (d, *J* = 14.4 Hz, 1H), 6.90 (d, *J* = 1.2 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 5.52 (s, 1H), 5.11 (s, 2H), 4.09-4.01 (m, 2H), 3.82 (s, 3H), 2.34 (s, 3H), 2.25 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H) ppm.**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 166.7, 148.6, 147.7, 137.4, 137.0, 128.3, 127.6, 127.2, 119.3, 112.9, 111.2, 59.6, 57.5, 55.8, 53.3, 14.1, 13.4 ppm.

**Ethyl 4-(4-isopropylphenyl)-6-methyl-2-(methylthio)-1,4-dihydropyrimidine-5-carboxylate (1h):**



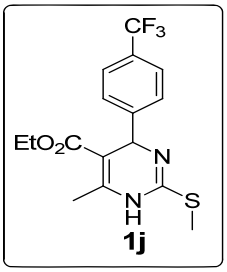

White solid. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.26-7.23 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.26 (brs, 1H), 5.61 (brs, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 2.90-2.83 (m, 1H), 2.44 (s, 3H), 2.33 (s, 3H), 1.23-1.19 (m, 9H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 166.9, 142.1, 126.7, 126.4, 59.8, 33.7, 23.9, 14.2, 13.5 ppm.

**Methyl 4-(4-chlorophenyl)-6-methyl-2-(methylthio)-1,4-dihydropyrimidine-5-carboxylate (1i):**



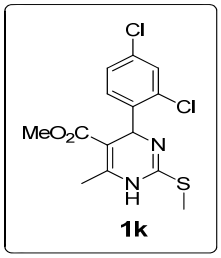

White solid. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ **$^{1}$H NMR ($CDCl_3$, 400 MHz):** δ 7.26 (s, 4H), 6.64 (brs, 1H), 5.61 (brs, 1H), 3.65 (s, 3H), 2.42 (s, 3H), 2.34 (s, 3H) ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 167.0, 142.9, 132.9, 128.5, 128.3, 51.2, 13.6 ppm.

**Ethyl 6-methyl-2-(methylthio)-4-(4-(trifluoromethyl)phenyl)-1,4-dihydropyrimidine-5-carboxylate (1j):**



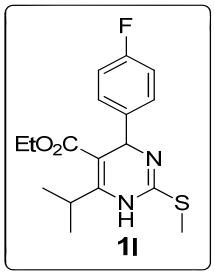

Yellow solid. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 6.36 (brs, 1H), 5.75 (brs, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 2.35 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 166.5, 127.2, 125.3, 60.0, 14.2, 13.5 ppm.

**Methyl 4-(2,4-dichlorophenyl)-6-methyl-2-(methylthio)-1,4-dihydropyrimidine-5-carboxylate (1k):**




White solid. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.39 (s, 1H), 7.18 (d, *J* = 1.2 Hz, 2H), 6.12 (brs, 1H), 5.94 (brs, 1H), 3.59 (s, 3H), 2.44 (s, 3H), 2.38 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 166.8, 129.9, 129.8, 129.5, 129.3, 127.4, 51.1, 14.0, 13.4 ppm.

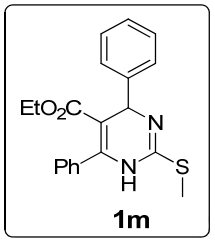
**Ethyl 4-(4-fluorophenyl)-6-isopropyl-2-(methylthio)-1,4-dihydropyrimidine-5-carboxylate (1l):**



**1l**

Yellow oil. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.26 (t, *J* = 6.0 Hz, 2H), 6.96 (t, *J* = 8.8 Hz, 2H), 6.43 (brs, 1H), 5.58 (brs, 1H), 4.08 (q, *J* = 7.2 Hz, 3H), 2.44 (s, 3H), 1.20-1.12 (m, 9H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 166.4, 163.2, 160.8, 140.6, 128.4, 128.3, 115.2, 115.0, 59.8, 53.4, 19.9, 14.1, 13.5 ppm.

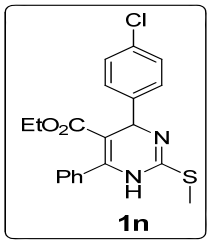
**Ethyl 2-(methylthio)-4,6-diphenyl-1,4-dihydropyrimidine-5-carboxylate (1m):**



**1m**

White solid. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.46-7.25 (m, 10H), 6.40 (brs, 1H), 5.73 (brs, 1H), 3.87 (q, *J* = 7.2 Hz, 2H), 2.47 (s, 3H), 0.86 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 166.3, 144.1, 129.1, 128.9, 128.5, 128.3, 128.0, 127.7, 127.6, 126.9, 59.9, 13.8, 13.6 ppm.

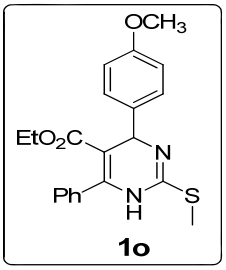
**Ethyl 4-(4-chlorophenyl)-2-(methylthio)-6-phenyl-1,4-dihydropyrimidine-5-carboxylate (1n):**



**1n**

Pale yellow Solid. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.41-7.31 (m, 9H), 6.51 (brs, 1H), 5.76 (brs, 1H), 3.89 (q, *J* = 7.2 Hz, 2H), 2.50 (s, 3H), 0.87 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 165.9, 129.5, 129.3, 129.0, 128.7, 128.3, 128.2, 127.8, 60.1, 13.9, 13.6 ppm.

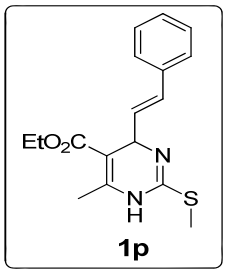
**Ethyl 4-(4-methoxyphenyl)-2-(methylthio)-6-phenyl-1,4-dihydropyrimidine-5-carboxylate (1o):**



**1o**

Yellow solid. **$^{1}$H NMR (400 MHz, $CDCl_3$): $^{1}$H NMR ($CDCl_3$, 400 MHz):** δ 7.39-7.37 (m, 7H), 6.89-6.87 (m, 2H), 5.67 (brs, 1H), 3.88 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 2.49 (s, 3H), 0.88 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 171.1, 159.0, 157.4, 133.7, 131.2, 130.7, 130.1, 129.6, 128.7, 128.6, 124.5, 119.8, 116.9, 114.4, 113.2, 88.2, 55.2, 52.7, 51.6 ppm.

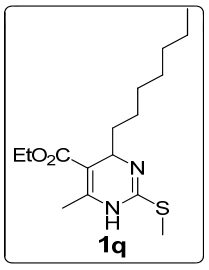
**(E)-ethyl 6-methyl-2-(methylthio)-4-styryl-1,4-dihydropyrimidine-5-carboxylate (1p):**



**1p**

Pale yellow Solid. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.34 (d, *J* = 7.2 Hz, 2H), 7.29-7.25 (m, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.40 (d, *J* = 15.6 Hz, 1H), 6.17 (dd, *J* = 6.4 Hz, 9.2 Hz, 1H), 5.25 (s, 1H), 4.23-4.11 (m, 2H), 2.46 (s, 1H), 2.30 (s, 1H), 1.26 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 166.6, 136.9, 129.1, 128.9, 128.4, 127.3, 126.4, 59.8, 14.3, 13.6 ppm.

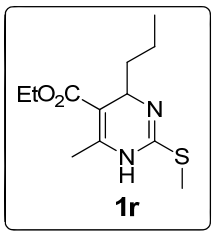
**Ethyl 4-heptyl-6-methyl-2-(methylthio)-1,4-dihydropyrimidine-5-carboxylate (1q):**



**1q**

Pale yellow oil. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 6.25 (brs, 1H), 4.50 (brs, 1H), 4.19-4.10 (m, 2H), 2.43 (s, 3H), 2.27 (s, 3H), 1.48-1.23 (m, 15H), 4.23-4.12 (m, 0.85 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 167.0, 59.6, 36.3, 31.8, 29.4, 29.2, 26.8, 24.5, 22.6, 14.3, 14.0, 13.6 ppm.

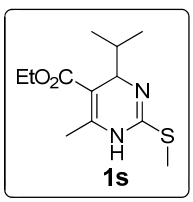
**Ethyl 6-methyl-2-(methylthio)-4-propyl-1,4-dihydropyrimidine-5-carboxylate (1r):**



**1r**

Pale yellow oil. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 6.44 (brs, 1H), 4.56 (brs, 1H), 4.21-4.13 (m, 2H), 2.48 (s, 3H), 2.30 (s, 3H), 1.54-1.26 (m, 7H), 0.91 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 166.9, 59.7, 53.6, 38.6, 20.1, 17.7, 14.3, 14.0, 13.7 ppm.

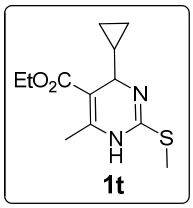
**Ethyl 4-isopropyl-6-methyl-2-(methylthio)-1,4-dihydropyrimidine-5-carboxylate (1s):**



**1s**

White solid. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 6.06 (brs, 1H), 4.41 (s, 1H), 4.21-4.10 (m, 2H), 2.48-2.46 (m, 3H), 2.30-2.28 (m, 3H), 1.80-1.76 (m, 1H), 1.29-1.25 (m, 3H), 0.90 (d, *J* = 5.6 Hz, 3H), 0.86-0.84 (m, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 167.5, 59.6, 34.9, 18.3, 16.9, 14.3, 13.64, 13.56 ppm.

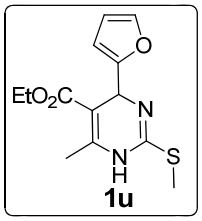
**Ethyl 4-cyclopropyl-6-methyl-2-(methylthio)-1,4-dihydropyrimidine-5-carboxylate (1t):**



**1t**

White solid. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 6.72 (brs, 1H), 4.19-4.09 (m, 2H), 4.04 (d, *J* = 7.6 Hz, 1H), 2.44 (s, 3H), 2.29 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.23-0.95 (m, 1H), 0.42-0.40 (m, 1H), 0.39-0.33 (m, 2H), 0.33-0.29 (m, 1H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 167.2, 102.6, 59.6, 56.3, 20.3, 17.0, 14.3, 13.6, 1.9, 1.7 ppm.

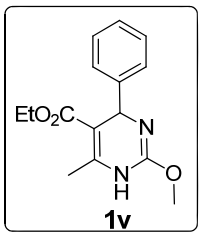
**Ethyl 4-(furan-2-yl)-6-methyl-2-(methylthio)-1,4-dihydropyrimidine-5-carboxylate (1u):**



**1u**

Yellow solid. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.31 (t, *J* = 0.8 Hz, 1H), 6.52 (brs, 1H), 6.26 (dd, *J* = 2.0, 1.2 Hz, 1H), 6.09 (d, *J* = 2.8 Hz,1H), 5.77 (s, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 2.34 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 166.4, 141.7, 110.0, 105.5, 59.8, 14.2, 13.6 ppm.

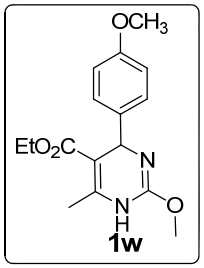
**Ethyl 2-methoxy-6-methyl-4-phenyl-1,4-dihydropyrimidine-5-carboxylate (1v):**



**1v**

White solid. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.33-7.21 (m, 5H), 6.11 (brs, 1H), 5.53 (s, 1H), 4.05 (q, *J* = 7.2 Hz, 2H), 3.77 (s, 3H), 2.35 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 166.7, 128.4, 126.9, 59.6, 54.0, 14.1 ppm.

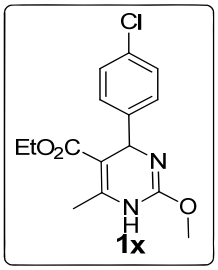
**Ethyl 2-methoxy-4-(4-methoxyphenyl)-6-methyl-1,4-dihydropyrimidine-5-carboxylate (1w):**



**1w**

Pale yellow oil. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.24-7.21 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 5.46 (s, 1H), 4.05 (q, *J* = 7.2 Hz, 2H), 3.76-3.74 (m, 6H), 2.33 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR (100 MHz, $CDCl_3$):** 166.8, 158.6, 137.9, 127.9, 113.5, 59.5, 55.1, 53.8, 53.4, 14.1.

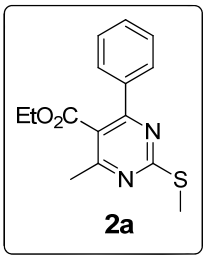
**Ethyl 4-(4-chlorophenyl)-2-methoxy-6-methyl-1,4-dihydropyrimidine-5-carboxylate (1x):**




Yellow solid. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.25 (s, 4H), 5.51 (brs, 1H), 4.06 (q, *J* = 7.2 Hz, 2H), 3.76 (s, 3H), 2.34 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H,). **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 166.5, 143.9, 132.9, 128.4, 128.3, 59.8, 54.1, 14.2 ppm.

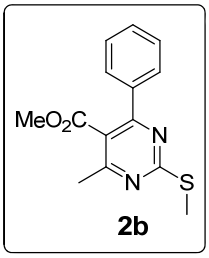
## 10. Characterization Data of the 2-Substituted Pyrimidines.

**Ethyl 4-methyl-2-(methylthio)-6-phenylpyrimidine-5-carboxylate (2a):**



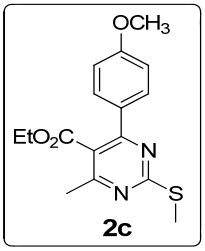

White oil. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.65-7.63 (m, 2H), 7.48-7.42 (m, 3H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.62 (s, 3H), 2.57 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 172.4, 168.0, 165.4, 163.5, 137.7, 130.0, 128.4, 128.2, 120.9, 61.6, 22.5, 14.1, 13.5 ppm. **HRMS (ESI):** calcd for $C_{15}H_{17}N_2O_2S$ $[M+H]^+$ *m/z* 289.1005; found 289.1007.

**Methyl 4-methyl-2-(methylthio)-6-phenylpyrimidine-5-carboxylate (2b):**



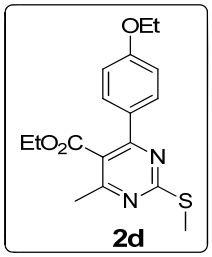

White oil. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.66-7.64 (m, 2H), 7.46 (d, *J* = 7.2 Hz, 3H), 3.69 (s, 3H), 2.63 (s, 3H), 2.57 (s, 3H).**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 172.6, 168.7, 165.5, 163.4, 137.6, 130.2, 128.5, 128.2, 120.6, 52.4, 22.6, 14.1 ppm. **HRMS (ESI):** calcd for $C_{14}H_{15}N_2O_2S$ $[M+H]^+$ *m/z* 275.0849; found 275.0857.

**Ethyl 4-(4-methoxyphenyl)-6-methyl-2-(methylthio)pyrimidine-5-carboxylate (2c):**



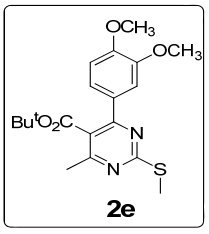

White oil. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.66 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 2.62 (s, 3H), 2.54 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H) ppm.**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 172.2, 168.5, 165.1, 162.7, 161.4, 130.04, 129.97, 120.4, 113.9, 61.7, 55.4, 22.5, 14.1, 13.8 ppm. **HRMS (ESI):** calcd for $C_{16}H_{19}N_2O_3S$ $[M+H]^+$ *m/z* 319.1111; found 319.1117.

**Ethyl 4-(4-ethoxyphenyl)-6-methyl-2-(methylthio)pyrimidine-5-carboxylate (2d):**



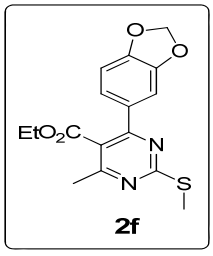

White oil. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.65 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 4.09 (q, *J* = 7.2 Hz, 2H), 2.62 (s, 3H), 2.55 (s, 3H), 1.45 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 172.0, 168.5, 165.0, 162.8, 160.9, 130.1, 129.6, 120.3, 114.4, 63.6, 61.8, 22.7, 22.4, 14.7, 14.2, 13.8 ppm. **HRMS (ESI):** calcd for $C_{17}H_{21}N_2O_3S$ $[M+H]^+$ *m/z* 333.1273; found 333.1271

**Tert-butyl 4-(3,4-dimethoxyphenyl)-6-methyl-2-(methylthio)pyrimidine-5-carboxylate (2e):**



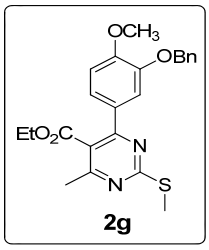

White solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.31-7.26 (m, 2H), 6.91 (d, *J* = 8.0 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 2.60 (s, 3H), 2.54 (s, 3H), 1.40 (s, 9H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 171.6, 167.5, 164.7, 162.4, 150.8, 148.9, 130.4, 122.2, 121.8, 111.7, 110.6, 82.8, 56.0, 27.8 ppm. **HRMS (ESI):** calcd for $C_{19}H_{25}N_2O_4S$ $[M+H]^+$ *m/z* 377.1530; found 377.1534.

**Ethyl 4-(benzo[d][1,3]dioxol-5-yl)-6-methyl-2-(methylthio)pyrimidine-5-carboxylate (2f):**



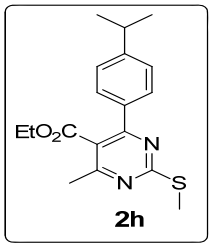

White oil. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.22 (s, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.02 (s, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.60 (s, 3H), 2.53 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 172.1, 168.3, 165.2, 162.4, 149.4, 147.9, 131.5, 123.0, 120.5, 108.8, 108.2, 101.5, 61.7, 22.5, 14.1, 13.8 ppm. **HRMS (ESI):** calcd for $C_{16}H_{17}N_2O_4S$ $[M+H]^+$ *m/z* 333.0904; found 333.0908.

**Ethyl 4-(3-(benzyloxy)-4-methoxyphenyl)-6-methyl-2-(methylthio)pyrimidine-5-carboxylate (2g):**



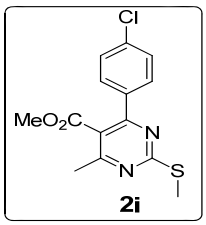

White solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.47 (d, *J* = 7.2 Hz, 2H), 7.40-7.24 (m, 5H), 6.93 (d, *J* = 8.4 Hz, 1H), 5.20 (s, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.94 (s, 3H), 2.53 (s, 6H), 1.12 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 172.0, 168.5, 165.0, 162.5, 151.5, 148.0, 136.7, 130.0, 128.6, 127.9, 127.2, 122.0, 120.4, 113.7, 111.0, 70.8, 61.7, 56.0, 22.4, 14.1, 13.8 ppm. **HRMS (ESI):** calcd for $C_{23}H_{25}N_2O_4S$ $[M+H]^+$ *m/z* 425.1530; found 425.1525.

**Ethyl 4-(4-isopropylphenyl)-6-methyl-2-(methylthio)pyrimidine-5-carboxylate (2h) :**



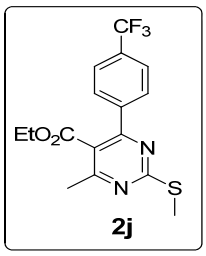

White oil. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.01-2.90 (m, 1H), 2.61 (s, 3H), 2.56 (s, 3H), 1.28 (s, 3H), 1.26 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H) ppm.**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 172.3, 168.2, 165.2, 163.5, 151.3, 135.1, 128.3, 126.5, 120.7, 61.6, 34.0, 26.8, 23.8, 22.5, 14.1, 13.5 ppm. **HRMS (ESI):** calcd for $C_{18}H_{23}N_2O_2S$ $[M+H]^+$ *m/z* 331.1475; found 331.1475.

**Methyl 4-(4-chlorophenyl)-6-methyl-2-(methylthio)pyrimidine-5-carboxylate (2i) :**



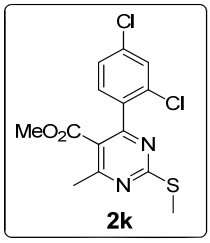

White oil. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4, 2H), 3.72 (s, 3H), 2.62 (s, 3H), 2.56 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 172.8, 168.5, 165.7, 162.2, 136.6, 136.0, 129.6, 128.8, 120.4, 52.6, 22.7, 14.18, 14.16 ppm. **HRMS (ESI):** calcd for $C_{14}H_{14}ClN_2O_2S$ $[M+H]^+$ *m/z* 309.0459; found 309.0461.

**Ethyl 4-methyl-2-(methylthio)-6-(4-(trifluoromethyl)phenyl)pyrimidine-5-carboxylate (2j):**



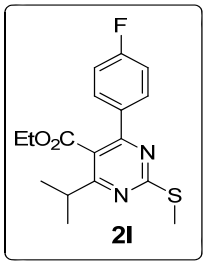

White oil. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.76-7.70 (m, 4H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.61 (s, 3H), 2.59 (s, 3H), 1.05 (t, *J* = 7.2 Hz, 3H) ppm.**$^{13}$C NMR (100 MHz , $CDCl_3$):** δ 172.9, 167.6, 166.0, 162.3, 141.2, 132.0, 131.7, 128.7, 128.6, 125.4, 125.3, 122.4, 120.9, 61.9, 22.7, 14.2, 13.5 ppm. **HRMS (ESI):** calcd for $C_{16}H_{16}F_3N_2O_2S$ $[M+H]^+$ *m/z* 357.0879; found 357.0881.

**Methyl 4-(2,4-dichlorophenyl)-6-methyl-2-(methylthio)pyrimidine-5-carboxylate (2k)**:



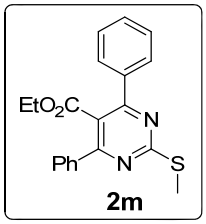

White solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.46 (d, *J* = 1.6 Hz, 1H), 7.36-7.27 (m, 2H), 3.65 (s, 3H), 2.67 (s, 3H), 2.59 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 173.4, 166.9， 166.7， 162.8， 136.0， 135.6， 132.9， 130.9， 129.4，127.1， 121.0， 52.3， 23.7, 14.2 ppm. **HRMS (ESI):** calcd for $C_{14}H_{13}C_{l2}N_2O_2S$ $[M+H]^+$ *m/z* 343.0069; found 343.0071.

**Ethyl 4-(4-fluorophenyl)-6-isopropyl-2-(methylthio)pyrimidine-5-carboxylate (2l):**



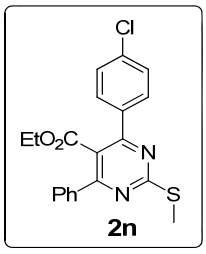

White oil. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.67-7.64 (m, 2H), 7.15-7.11 (m, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.21-3.15 (m, 1H), 2.62 (s, 3H), 1.32 (d, *J* = 6.4 Hz, 6H), 1.10 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 173.1, 172.6, 168.2, 165.1, 162.5 (d, *J* = 300.0 Hz), 133.9 (d, *J* = 3.0 Hz), 130.4 (d, *J* = 8.0 Hz), 120.2, 115.5 (d, *J* = 21.0 Hz), 61.8, 33.2, 21.6, 14.2, 13.7 ppm. **HRMS (ESI):** calcd for $C_{17}H_{20}FN_2O_2S$ $[M+H]^+$ *m/z* 335.1224; found 335.1230.

**Ethyl 2-(methylthio)-4,6-diphenylpyrimidine-5-carboxylate (2m):**



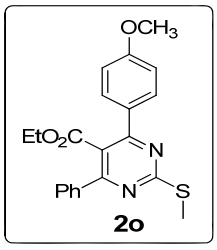

White solid. **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.72-7.69 (m, 4H), 7.50-7.44 (m, 6H), 4.05 (q, *J* = 7.2 Hz, 2H), 2.67 (s, 3H), 0.95 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 172.7, 168.1, 164.3, 137.4, 130.1, 128.43, 128.37, 120.8, 61.8, 14.3, 13.4 ppm. **HRMS (ESI):** calcd for $C_{20}H_{19}N_2O_2S$ $[M+H]^+$ *m/z* 351.1162; found 351.1166.

**Ethyl 4-(4-chlorophenyl)-2-(methylthio)-6-phenylpyrimidine-5-carboxylate (2n):**



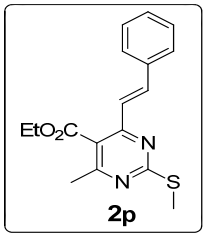

White solid. **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.70-7.64 (m, 4H), 7.50-7.44 (m, 5H), 4.06 (q, *J* = 7.2 Hz, 2H), 2.66 (s, 3H), 0.97 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 172.9, 167.9, 164.5, 163.0, 137.3, 136.4, 135.8, 130.2, 129.8, 128.7, 128.5, 128.3, 120.6, 61.9, 14.3, 13.4 ppm. **HRMS (ESI):** calcd for $C_{20}H_{18}ClN_2O_2S$ $[M+H]^+$ *m/z* 385.0772; found 385.0770.

**Ethyl 4-(4-methoxyphenyl)-2-(methylthio)-6-phenylpyrimidine-5-carboxylate (2o):**



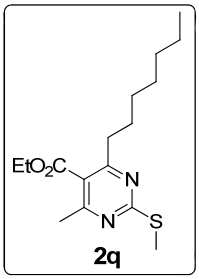

White solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.71-7.66 (m, 4H), 7.48-7.46 (m, 3H), 6.98 (dd, *J* = 2.0, 6.8 Hz, 2H), 4.07 (q, *J* = 7.2 Hz, 2H), 3.87 (s, 3H), 2.66 (s, 3H), 0.98 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 172.4, 168.5, 164.3, 163.5, 161.3, 137.5, 130.1, 129.9, 129.6, 128.4, 128.3, 120.3, 113.9, 61.8, 55.4, 14.3, 13.5 ppm. **HRMS (ESI):** calcd for $C_{21}H_{21}N_2O_3S$ $[M+H]^+$ *m/z* 381.1267; found 381.1271.

**(E)-ethyl 4-methyl-2-(methylthio)-6-styrylpyrimidine-5-carboxylate (2p):**



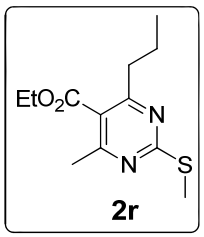

White oil. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 8.10 (d, *J* = 15.6 Hz, 1H), 7.58 (d, *J* = 6.8 Hz, 2H), 7.42-7.36 (m, 3H), 7.20 (d, *J* = 15.2 Hz, 1H), 4.48 (q, *J* = 7.2 Hz, 2H), 2.65 (s, 3H), 2.53 (s, 3H), 1.45 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 172.0, 167.4, 165.7, 159.0, 139.2, 135.7, 129.5, 128.8, 127.9, 122.3, 119.9, 61.8, 23.2, 14.3, 14.1 ppm. **HRMS (ESI):** calcd for $C_{17}H_{19}N_2O_2S$ $[M+H]^+$ *m/z* 315.1162; found 315.1160.

**Ethyl 4-heptyl-6-methyl-2-(methylthio)pyrimidine-5-carboxylate (2q):**



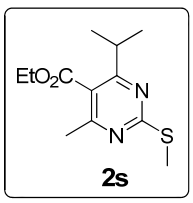

White oil. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 4.38 (q, *J* = 7.2 Hz, 2H), 2.70 (t, *J* = 8.0 Hz, 2H), 2.55 (s, 3H), 2.46 (s, 3H), 1.72-1.64 (m, 2H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.31-1.25 (m, 8H), 0.86 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 172.0, 168.1, 167.6, 164.5, 121.5, 61.6, 35.8, 31.6, 29.4, 29.0, 28.7, 22.8, 22.6, 14.1, 14.01, 13.99 ppm. **HRMS (ESI):** calcd for $C_{16}H_{27}N_2O_2S$ $[M+H]^+$ *m/z* 311.1787; found 311.1786.

**Ethyl 4-methyl-2-(methylthio)-6-propylpyrimidine-5-carboxylate (2r):**



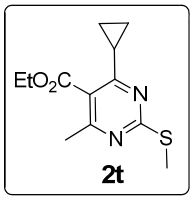

White oil. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 4.39 (q, *J* = 7.2 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.56 (s, 3H), 2.47 (s, 3H), 1.79-1.69 (m, 2H), 1.39 (t, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 7.6 Hz, 3H) ppm.**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 172.1, 167.9, 167.7, 164.6, 121.7, 61.6, 37.7, 22.9, 22.0, 14.1, 14.03, 13.95 ppm. **HRMS (ESI):** calcd for $C_{12}H_{19}N_2O_2S$ $[M+H]^+$ *m/z* 255.1162; found 255.1165.

**Ethyl 4-isopropyl-6-methyl-2-(methylthio)pyrimidine-5-carboxylate (2s):**



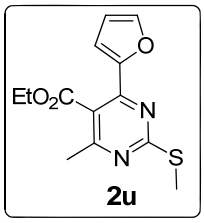

White oil. **$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 4.40 (q, *J* = 7.2 Hz, 2H), 3.11-3.01 (m, 1H), 2.57 (s, 3H), 2.45 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.25 (s, 3H), 1.25 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 172.1, 172.0, 167.9, 164.2, 121.1, 61.7, 33.4, 22.6, 21.6, 14.1, 14.0 ppm. **HRMS (ESI):** calcd for $C_{12}H_{19}N_2O_2S$ $[M+H]^+$ *m/z* 255.1162; found 255.1169.

**Ethyl 4-cyclopropyl-6-methyl-2-(methylthio)pyrimidine-5-carboxylate (2t):**



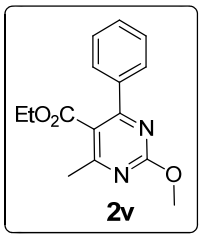

White oil. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 4.42 (q, *J* = 7.2 Hz, 2H), 2.49 (s, 3H), 2.46 (s, 3H), 2.13-2.08 (m, 1H), 1.40 (t, *J* = 7.6 Hz, 3H), 1.28-1.24 (m, 2H), 1.06-1.04 (m, 2H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 172.0, 169.0, 167.9, 163.7, 121.2, 61.7, 22.8, 14.5, 14.2, 13.9, 11.8 ppm. **HRMS (ESI):** calcd for $C_{12}H_{17}N_2O_2S$ $[M+H]^+$ *m/z* 253.1005; found 253.1004.

**Ethyl 4-(furan-2-yl)-6-methyl-2-(methylthio)pyrimidine-5-carboxylate (2u):**



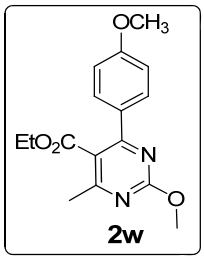

White oil. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.55 (s, 1H), 7.33 (d, *J* = 3.2 Hz, 1H), 6.57 (q, *J* = 1.6 Hz, 2H), 4.44 (q, *J* = 7.2 Hz, 2H), 2.61 (s, 3H), 2.49 (s, 3H), 1.37 (t, *J* = 7.6 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 171.9, 167.8, 164.9, 150.94, 150.85, 145.4, 117.5, 114.6, 112.4, 61.9, 29.7, 22.7, 22.2, 14.1 ppm. **HRMS (ESI):** calcd for $C_{13}H_{15}N_2O_3S$ $[M+H]^+$ *m/z* 279.0798; found 279.0796.

**Ethyl 2-methoxy-4-methyl-6-phenylpyrimidine-5-carboxylate (2v):**



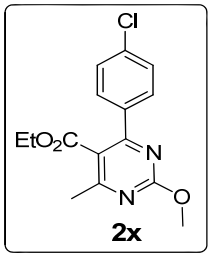

White oil. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.65 (dd, *J* = 1.6, 6.0 Hz, 2H), 7.47-7.42 (m, 3H), 4.15 (q, *J* = 7.2 Hz, 2H), 4.08 (s, 3H), 2.58 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 168.7, 168.3, 166.4, 164.5, 137.8, 130.1, 128.4, 128.2, 119.8, 61.6, 55.0, 22.8, 13.6 ppm. **HRMS (ESI):** calcd for $C_{15}H_{17}N_2O_3$ $[M+H]^+$ *m/z* 273.1234; found 273.1238.

**Ethyl 2-methoxy-4-(4-methoxyphenyl)-6-methylpyrimidine-5-carboxylate (2w):**




White oil. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.66-7.62 (m, 2H), 6.95-6.91 (m, 2H), 4 .19 (q, *J* = 7.2 Hz, 2H), 4.04 (s, 3H), 3.83 (s, 3H), 2.53 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** 168.6, 168.2, 165.4, 164.3, 161.2, 129.9, 119.2, 113.7, 61.5, 55.2, 54.8, 22.6, 13.7 ppm. **HRMS (ESI):** calcd for $C_{16}H_{19}N_2O_4$ $[M+H]^+$ *m/z* 303.1339; found 303.1340.

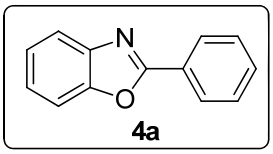
**Ethyl 4-(4-chlorophenyl)-2-methoxy-6-methylpyrimidine-5-carboxylate (2x):**



**2x**

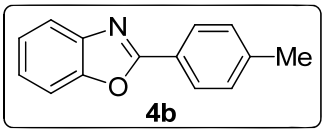
White oil. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.65 (dd, *J* = 2.0, 4.8 Hz, 2H), 7.42 (dd, *J* = 1.6, 5.2 Hz, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 4.08 (s, 3H), 2.58 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 168.9, 168.1, 165.2, 164.4, 136.4, 136.1, 129.7, 128.7, 119.7, 61.8, 55.1, 22.8, 13.7 ppm. **HRMS (ESI):** calcd for $C_{15}H_{16}ClN_2O_3$ $[M+H]^+$ *m/z* 307.0844; found 307.0851.

# 11. Characterization Data of the 2-Substituted Benzoxazoles.



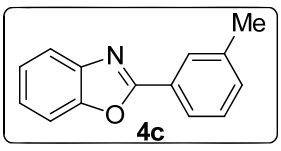
**4a**

**2-phenylbenzo[d]oxazole (4a):** The general procedure was followed using (E)-2-(benzylideneamino)phenol (19.7 mg, 0.10 mmol). Purification by column chromatography (PE→PE/EtOAc = 40:1) yielded **4a** (17.6 mg, 90%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.29-8.27 (m, 2H), 7.82-7.78 (m, 1H), 7.62-7.58 (m, 1H), 7.56-7.53 (m, 3H), 7.39-7.35 (m, 2H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 163.0, 150.7, 142.0, 131.5, 128.9, 127.6, 127.1, 125.1, 124.6, 120.0, 110.6 ppm. **MS (ESI):** calculated for $[C_{13}H_{10}NO]^+$: 196.08, found 196.03.



**4b**

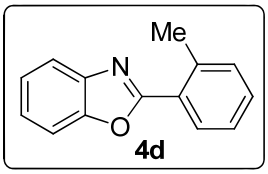
**2-(p-tolyl)benzo[d]oxazole(4b):** The general procedure was followed using (E)-2-((4-methylbenzylidene)amino)phenol (21.1 mg, 0.10 mmol). Purification by column chromatography (PE→PE/EtOAc = 40:1) yielded **4b** (14.8 mg, 71%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.16 (d, *J* = 8.4 Hz, 2H), 7.78-7.76 (m, 1H), 7.59-7.57 (m, 1H), 7.36-7.33 (m, 4H), 2.45 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 163.3, 150.7, 142.1, 129.6, 127.6, 124.9, 124.5, 124.3, 119.8, 110.5, 21.7 ppm. **MS (EI):** calculated for $[M^+] = [C_{14}H_{11}NO]^+$ : 209.08, found m/z (%) m/z (%) 209.9 (14.6), 208.9 ($M^+$, 100.0), 207.9 (26.3), 206.8 (3.3), 180.9 (3.5), 179.9 (6.2), 148.8 (32.3), 104.0 (3.1), 90.9 (8.4), 89.9 (3.9), 62.9 (5.1).



**4c**

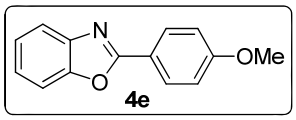
**2-(m-tolyl)benzo[d]oxazole (4c):** The general procedure was followed using (E)-2-((3-methylbenzylidene)amino)phenol (21.5 mg, 0.10 mmol). Purification by column chromatography (PE→PE/EtOAc

= 40:1) yielded **4c** (16.8 mg, 80%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.11 (s, 1H), 8.06 (d, *J* = 7.6 Hz, 1H), 7.81-7.78 (m, 1H), 7.60-7.56 (m, 1H), 7.44-7.40 (m, 1H), 7.38-7.35 (m, 3H), 2.46 (s, 3H) ppm.**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 163.2, 150.7, 142.0, 138.7 ,132.3， 128.8， 128.1， 126.9， 125.0，124.7，124.5，119.9， 110.5，21.3 ppm. **MS (EI):** calculated for $[M^+] = [C_{14}H_{11}NO]^+$ : 209.08, found m/z (%) 208.9 ($M^+$, 100.0), 179.8 (9.3), 104.4 (4.0), 90.9 (8.5), 62.9 (6.3).



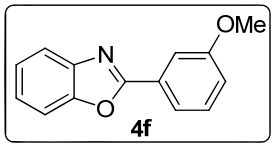
**4d**

**2-(o-tolyl)benzo[d]oxazole (4d):** The general procedure was followed using (E)-2-((2-methylbenz ylidene)amino)phenol (21.0 mg, 0.10 mmol). Purification by column chromatography (PE→PE/EtOAc = 40:1) yielded **4d** (16.1 mg, 80%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.20 (d, *J* = 2.0 Hz, 1H), 8.18-7.80 (m, 1H), 7.63-7.59 (m, 1H), 7.45-7.41 (m, 1H), 7.40-7.35 (m, 4H), 2.83 (s, 3H) ppm.**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 163.4, 150.3, 142.1, 138.8, 131.8, 130.9, 129.9, 126.2, 126.1, 125.0, 124.3, 120.1, 110.5, 22.2 ppm. **MS (ESI):** calculated for $[C_{14}H_{12}NO]^+$: 210.09, found 210.15.



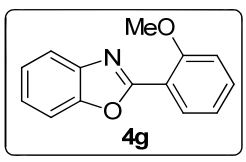
**4e**

**2-(4-methoxyphenyl)benzo[d]oxazole (4e):** The general procedure was followed using (E)-2-((4-methoxybenzylidene)amino)phenol (22.7 mg, 0.10 mmol). Purification by column chromatography (PE→PE/EtOAc = 20:1) yielded **4e** (21.6 mg, 96%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.21 (d, *J* = 8.8 Hz, 2H), 7.76-7.73 (m, 1H), 7.57-7.55 (m, 1H), 7.36-7.30 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 163.1, 162.3, 150.6, 142.2, 129.3, 124.6, 124.4, 119.7, 119.6, 114.3, 110.3, 55.4 ppm. **MS (ESI):** calculated for $[C_{14}H_{12}NO_2]^+$: 226.09, found 226.14.



**4f**

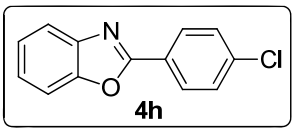
**2-(3-methoxyphenyl)benzo[d]oxazole (4f):** The general procedure was followed using (E)-2-((3-methoxybenzylidene)amino)phenol (23.0 mg, 0.10 mmol). Purification by column chromatograp- hy (PE→PE/EtOAc = 20:1) yielded **4f** (19.7 mg, 87%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.81-7.79 (m, 2H), 7.62-7.59 (m, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.40-7.35 (m, 2H), 7.12-7.09 (m, 2H), 3.94 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 162.9, 159.9, 150.7, 142.0, 130.0, 128.3, 125.2, 124.6, 120.1, 120.0, 118.4, 111.8, 110.6, 55.5 ppm. **MS (EI):** calculated for $[M^+] = [C_{14}H_{11}NO_2]^+$ : 225.08, found m/z (%) 225.9 (13.9), 224.9 ($M^+$, 100.0), 223.9 (48.8), 195.9 (10.9), 194.9 (20.3), 193.8 (4.4), 181.8 (5.5), 166.8 (5.7), 126.9 (3.1), 112.4 (4.9), 91.9 (3.0), 76.9 (2.8) , 63.9(4.6), 62.8 (5.3) , 43.8 (3.0).



**4g**

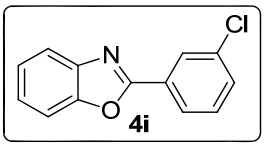
**2-(2-methoxyphenyl)benzo[d]oxazole (4g):** The general procedure was followed using (E)-2-((2-methoxybenzylidene)amino)phenol (22.6 mg, 0.10 mmol). Purification by column chromatograp- hy

(PE→PE/EtOAc = 20:1) yielded **4g** (18.5 mg, 83%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.15 (dd, *J* = 1.6, 6.0 Hz, 1H), 7.84-7.81 (m, 1H), 7.60-7.58 (m, 1H), 7.52-7.48 (m, 2H), 7.35-7.07 (m, 2H), 4.02 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 161.5, 158.4, 150.3, 142.1, 132.7, 131.2, 124.9, 124.2, 120.7, 120.2, 116.1, 112.0, 110.4, 56.2 ppm. **MS (ESI):** calculated for $[C_{14}H_{12}NO_2]^+$: 226.09, found 226.03.



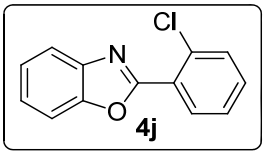
**4h**

**2-(4-chlorophenyl)benzo[d]oxazole (4h):** The general procedure was followed using (E)-2-((4-chlorobenzylidene)amino)phenol (23.2 mg, 0.10 mmol). Purification by column chromatography (PE→PE/EtOAc = 40:1) yielded **4h** (21.6 mg, 94%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.20 (d, *J* = 8.4 Hz, 2H), 7.79-7.76 (m, 1H), 7.60-7.58 (m, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.40-7.36 (m, 2H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 162.1, 150.8, 142.1, 137.8, 129.3, 128.9, 125.7, 125.4, 124.8, 120.2, 110 ppm. **MS (EI):** calculated for $[M^+] = [C_{13}H_8ClNO]^+$ : 229.03, found m/z (%) 230.9 (31.9), 229.9 (14.6), 228.8 ($M^+$, 100.0), 202.9 (3.4), 200.8 (10.1), 165.9 (6.0), 138.9 (2.1), 100.3 (3.6), 91.9 (3.7), 63.9 (5.5) , 62.9 (6.5).



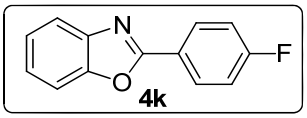
**4i**

**2-(3-chlorophenyl)benzo[d]oxazole (4i):** The general procedure was followed using (E)-2-((3-chlorobenzylidene)amino)phenol (23.0 mg, 0.10 mmol). Purification by column chromatography (PE→PE/EtOAc = 40:1) yielded **4i** (21.3 mg, 93%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.26 (d, *J* = 2.0 Hz, 1H), 8.16-8.13 (m, 1H), 7.81-7.77 (m, 1H), 7.62-7.57 (m, 1H), 7.52-7.50 (d, *J* = 8.4 Hz, 2H), 7.40-7.36 (m, 2H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 161.6, 150.7, 141.9, 135.0, 131.5, 130.2, 128.8, 127.6, 125.6, 125.5, 124.8, 120.2, 110.7 ppm. **MS (ESI):** calculated for $[C_{13}H_9ClNO]^+$: 230.04, found 229.99.



**4j**

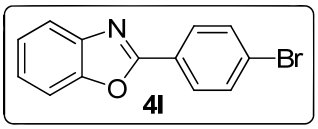
**2-(2-chlorophenyl)benzo[d]oxazole (4j):** The general procedure was followed using (E)-2-((2-chlorobenzylidene)amino)phenol (23.0 mg, 0.10 mmol). Purification by column chromatography (PE→PE/EtOAc = 40:1) yielded **4j** (20.4 mg, 89%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.11-8.09 (dd, *J* = 8.0 Hz, 1H), 7.86-7.81 (m, 1H), 7.57-7.54 (m, 1H), 7.51-7.48 (m, 1H), 7.37-7.31 (m, 4H) ppm.**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 160.6, 150.3, 141.5, 133.2, 131.6, 131.5, 131.1, 126.6, 125.9, 125.3, 124.4, 120.2, 110.5 ppm. **MS (EI):** calculated for $[M^+] = [C_{13}H_8ClNO]^+$ : 229.03, found m/z (%) 230.8 (33.0), 229.9 (16.6), 228.7 ($M^+$, 100.0), 202.8 (5.8), 200.7 (19.2), 193.9 (2.0), 165.9 (8.4),138.9 (2.6), 114.3 (2.2), 101.8 (2.5), 100.3 (6.5), 91.8 (6.9), 82.4 (3.9), 63.9 (8.5) , 62.9 (10.5).



**4k**

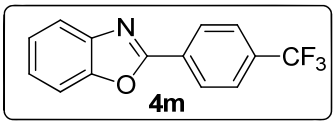
**2-(4-fluorophenyl)benzo[d]oxazole (4k) :** The general procedure was followed using (E)-2-((4-

fluorobenzylidene)amino)phenol (21.5 mg, 0.10 mmol). Purification by column chromatography (PE→PE/EtOAc = 40:1) yielded **4k** (16.0 mg, 75%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.30-8.25 (m, 2H), 7.80-7.76 (m, 1H), 7.60-7.57 (m, 1H), 7.39-7.35 (m, 2H), 7.25-7.20 (m, 2H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 166.1, 163.5, 162.1, 150.7, 142.0, 129.9 (d, *J* = 9.0 Hz), 125.1, 124.7, 123.5 (d, *J* = 3.0 Hz), 120.0, 116.2 (d, *J* = 22.0 Hz), 110.6 ppm. **MS (ESI):** calcd for $[C_{13}H_9FNO]^+$: 214.07; found 214.10.



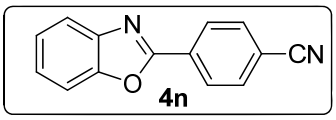
**4l**

**2-(4-bromophenyl)benzo[d]oxazole (4l):** The general procedure was followed using (E)-2-((4-bromobenzylidene)amino)phenol (27.5 mg, 0.10 mmol). Purification by column chromatography (PE→PE/EtOAc = 40:1) yielded **4l** (23.0 mg, 84%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.12 (d, *J* = 7.2 Hz, 2H), 7.80-7.75 (m, 1H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.60-7.56 (m, 1H), 7.39-7.35 (m, 2H). ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 162.1, 150.7, 142.0, 132.2, 129.0, 128.9, 126.2, 126.1, 125.4, 125.1, 124.7, 120.1, 120.0, 110.6 ppm. **MS (ESI):** calculated for $[C_{13}H_9BrNO]^+$: 273.99, found 274.07.



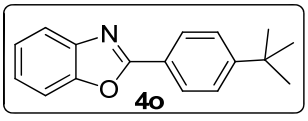
**4m**

**2-(4-(trifluoromethyl)phenyl)benzo[d]oxazole (4m):** The general procedure was followed using (E)-2-((4-(trifluoromethyl)benzylidene)amino)phenol (26.5 mg, 0.10 mmol). Purification by column chromatography (PE→PE/EtOAc = 20:1) yielded **4m** (21.6 mg, 82%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.39 (d, *J* = 8.0 Hz, 2H), 7.84-7.79 (m, 3H), 7.64-7.60 (m, 1H), 7.44-7.38 (m, 2H) ppm.**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 161.5, 150.8, 141.9, 133.1, 132.8, 130.4, 127.8, 126.0, 125.9, 125.9, 125.8, 125.1, 124.9, 122.4, 120.4, 110.8 ppm. **MS (EI):** calculated for $[M^+] = [C_{13}H_8BrNO]^+$ : 263.06 , found m/z (%) 263.9 (14.4), 262.8 ($M^+$, 100.0), 243.9 (6.3), 234.7 (19.2), 144.8 (3.4), 131.4 (3.8), 117.4 (3.1), 92.1 (7.1), 63.9 (7.7) , 62.9 (7.6).



**4n**

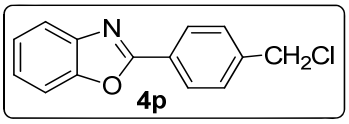
**4-(benzo[d]oxazol-2-yl)benzonitrile (4n):** The general procedure was followed using (E)-4-(((2-hydroxyphenyl)imino)methyl)benzonitrile (22.2 mg, 0.10 mmol). Purification by column chromatography (PE→PE/EtOAc = 30:1) yielded **4n** (17.4 mg, 79%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.38 (d, *J* = 8.8 Hz, 2H), 7.85-7.82 (m, 3H), 7.65-7.62 (m, 1H), 7.46-7.40 (m, 2H). ppm.**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 160.9, 150.9, 141.8, 132.7, 131.1, 127.9, 126.2, 125.1, 120.6, 118.2, 114.7, 110.9 ppm. **MS (EI):** calculated for $[M^+] = [C_{14}H_8N_2O]^+$ : 220.06, found m/z (%) 220.9 (14.9), 219.8 ($M^+$, 100.0), 209.9 (4.2), 191.9 (10.2), 146.9 (2.4), 96.0 (3.2), 91.8 (2.6), 63.9 (5.6), 62.9 (6.2) , 43.8 (6.9).



**4o**

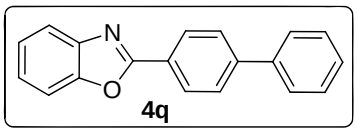
**2-(4-(tert-butyl)phenyl)benzo[d]oxazole (4o):** The general procedure was followed using (E)-2

-((4-(tert-butyl)benzylidene)amino)phenol (25.3 mg, 0.10 mmol). Purification by column chromate-eraphy (PE→PE/EtOAc = 40:1) yielded **4o** (23.6 mg, 94%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.80-7.77 (m, 1H), 7.60-7.55 (m, 3H), 7.37-7.34 (m, 2H), 1.39 (s, 9H) ppm.**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 163.2, 155.1, 150.7, 142.2, 127.4, 125.9, 124.8, 124.4, 124.3, 119.8, 110.5, 35.0, 31.1 ppm. **MS (EI):** calculated for $[M^+] = [C_{17}H_{17}NO]^+$ : 251.13, found m/z (%) 252.0 (6.9), 250.8 ($M^+$, 44.0), 237.0 (16.8), 235.9 (100.0), 233.9 (2.9), 219.9 (3.6), 207.9 (14.3), 206.9 (2.6),195.9 (3.1), 104.2 (6.3) , 103.5 (6.8).



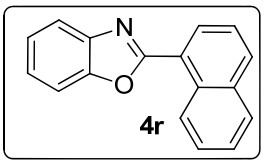
**4p**

**2-(4-(chloromethyl)phenyl)benzo[d]oxazole (4p):** The general procedure was followed using (E)-2-((4-(chloromethyl)benzylidene)amino)phenol (24.6 mg, 0.10 mmol). Purification by column chromateraphy (PE→PE/EtOAc = 40:1) yielded **4p** (22.6 mg, 93%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.27 (d, *J* = 8.4 Hz, 2H), 7.81-7.78 (m, 1H), 7.62-7.56 (m, 3H), 7.39-7.37 (m, 2H), 4.66 (s, 2H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 162.4, 150.8, 142.0, 140.8, 129.1, 128.0, 127.1, 125.3, 124.7, 110.6, 45.5 ppm. **MS (ESI):** calculated for $[C_{14}H_{11}ClNO]^+$: 244.05, found 244.00.



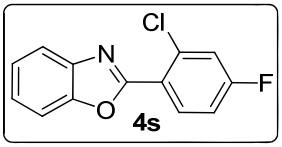
**4q**

**2-([1,1'-biphenyl]-4-yl)benzo[d]oxazole (4q):** The general procedure was followed using (E)-2-(([1,1'-biphenyl]-4-ylmethylene)amino)phenol (27.3 mg, 0.10 mmol). Purification by column chromat eraphy (PE→PE/EtOAc = 40:1) yielded **4q** (23.6 mg, 87%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.35 (d, *J* = 8.4 Hz, 2H), 7.82-7.77 (m, 3H), 7.70-7.68 (m, 2H), 7.63-7.61 (m, 1H), 7.52-7.50 (m, 2H), 7.48-7.37 (m, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 162.9, 150.8, 144.2, 142.2, 140.0, 128.9, 128.1, 127.6, 127.2, 125.9, 125.1, 124.6, 120.0, 110.6 ppm. **MS (EI):** calculated for $[M^+] = [C_{19}H_{13}NO]^+$ : 271.10, found m/z (%) 271.9 (18.5), 270.9 ($M^+$, 100.0), 269.6 (6.8), 242.9 (4.7), 240.9 (3.4), 178.9 (1.8), 177.9 (1.6), 152.9 (2.5), 151.9 (9.0), 150.9 (3.8), 135.7 (6.0), 135.1 (5.2), 63.9 (2.6), 62.9 (2.9).

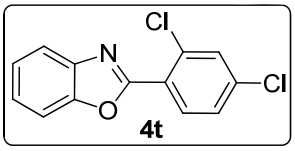


**4r**

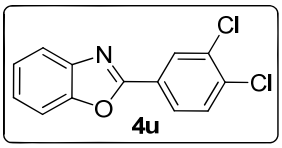
**2-(naphthalen-1-yl)benzo[d]oxazole (4r):** The general procedure was followed using (E)-2-((naphthalen-1-ylmethylene)amino)phenol (24.7 mg, 0.10 mmol). Purification by column chroma-teraphy (PE→PE/EtOAc = 40:1) yielded **4r** (21.3 mg, 87%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 9.51 (d, *J* = 8.4 Hz, 1H), 8.47-8.44 (m, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.97-7.91 (m, 2H), 7.76-7.72 (m, 1H), 7.68-7.60 (m, 3H), 7.45-7.41 (m, 2H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 162.7, 150.1, 142.2, 133.9, 132.3, 130.6, 129.3, 128.6, 127.9, 126.4, 126.2, 125.2, 124.9, 124.4, 123.5, 120.2, 110.5 ppm. **MS (EI):** calculated for $[M^+] = [C_{17}H_{11}NO]^+$ : 245.08, found m/z (%) 245.9 (13.0), 244.9 ($M^+$, 79.0), 243.8 (100.0), 216.9 (2.1), 215.9 (9.7), 214.9 (3.3), 213.9 (2.3), 188.9 (2.7), 152.9 (4.7), 126.9 (6.0), 125.9 (3.6), 108.4 (2.9), 63.9 (2.3), 62.9 (3.3).



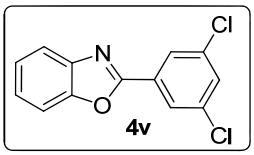

**2-(2-chloro-4-fluorophenyl)benzo[d]oxazole (4s):** The general procedure was followed using (E)-2-((2-chloro-4-fluorobenzylidene)amino)phenol (25.0 mg, 0.10 mmol). Purification by column chromat eraphy (PE→PE/EtOAc = 30:1) yielded **4s** (19.5 mg, 79%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.18 (dd, *J* = 2.8, 6.0 Hz, 1H), 7.86-7.84 (m, 1H), 7.63-7.61 (m, 1H), 7.43-7.33 (s, 2H), 7.32-7.17 (m, 1H), 7.16-7.13 (m, 1H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 164.9, 162.4, 160.1, 150.5, 141.6, 134.9, 134.9, 133.4, 133.3, 125.6, 124.7, 122.7, 122.7, 120.4, 118.9, 118.7, 114.7, 114.5, 110.7 **MS (ESI):** calculated for $[C_{13}H_8ClFNO]^+$: 248.03, found 247.98.




**2-(2,4-dichlorophenyl)benzo[d]oxazole (4t):** The general procedure was followed using (E)-2-((2,4-dichlorobenzylidene)amino)phenol (26.6 mg, 0.10 mmol). Purification by column chromat eraphy (PE→PE/EtOAc = 40:1) yielded **4t** (18.9 mg, 71%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.87-7.85 (m, 1H), 7.64-7.61 (m, 2H), 7.44-7.40 (m, 3H) ppm.**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 160.1, 150.5, 141.6, 137.6, 134.3, 132.5, 131.3, 127.5, 125.8, 124.8, 124.8, 120.6, 110.8 ppm. **MS (ESI):** calculated for $[C_{13}H_8Cl_2NO]^+$: 264.00, found 263.98.

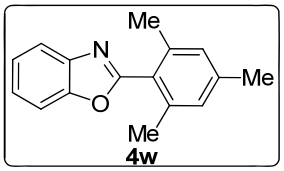



**2-(2,4-dichlorophenyl)benzo[d]oxazole (4u):** The general procedure was followed using (E)-2-((3,4-dichlorobenzylidene)amino)phenol (27.0 mg, 0.10 mmol). Purification by column chromat eraphy (PE→PE/EtOAc = 40:1) yielded **4u** (24.5 mg, 92%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.33 (d, *J* = 2.0 Hz, 1H), 8.07-8.04 (m, 1H), 7.78-7.76 (m, 1H), 7.59-7.57 (m, 2H), 7.39-7.37 (m, 2H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 160.8, 150.7, 141.8, 135.8, 133.4, 131.0, 129.2, 126.9, 126.4, 125.7, 124.9, 120.2, 110.7 ppm. **MS (EI):** calculated for $[M^+]$ = $[C_{13}H_7Cl_2NO]^+$ : 262.99, found m/z (%) 266.8 (10.3), 265.9 (9.1), 264.8 (62.3), 263.9 (14.9), 262.8 ($M^+$, 100.0), 236.8 (8.0), 235.9 (2.1), 234.8 (13.3), 227.8 (2.7), 199.8 (6.9), 132.3 (2.5), 131.3 (3.9), 117.3 (3.5), 91.9 (5.0), 63.9 (8.3), 62.9 (9.5).



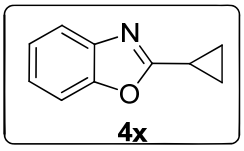

**(E)-2-((3,5-dichlorobenzylidene)amino)phenol (4v):** The general procedure was followed using (E)-2-((3,4-dichlorobenzylidene)amino)phenol (26.8 mg, 0.10 mmol). Purification by column chromat eraphy (PE→PE/EtOAc = 40:1) yielded **4v** (22.2 mg, 84%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.12 (d, *J* = 1.6 Hz, 2H), 7.79-7.75 (m, 1H), 7.59-7.57 (m, 1H), 7.49-7.48 (m, 1H), 7.41-7.36 (m, 2H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 160.3, 150.7, 141.7, 135.7, 131.2, 129.8, 125.9, 125.7, 125.0, 120.4, 110.8 ppm. **MS (EI):** calculated for $[M^+]$ = $[C_{13}H_7C_{12}NO]^+$ : 262.99, found m/z (%) 266.

8 (9.8), 265.9 (8.5), 264.8 (59.9), 263.9 (15.0), 262.8 ($M^+$, 100.0), 236.8 (9.1), 235.8 (2.2), 234.8 (14.0), 227.8 (3.0), 199.8 (5.6) , 163.8 (2.9) 144.8 (2.0), 132.3 (3.2), 131.3 (4.6) ,.117.3 (3.0), 91.8 (5.1) , 63.9 (8.6), 62.8 (9.7), 43.8 (3.3).



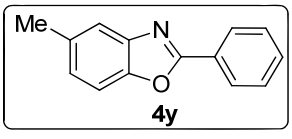
**4w**

**(E)-2-((3,5-dichlorobenzylidene)amino)phenol (4w):** The general procedure was followed using (E)-2-((2,4,6-trimethylbenzylidene)amino)phenol (24.0 mg, 0.10 mmol). Purification by column chromateraphy (PE→PE/EtOAc = 30:1) yielded **4w** (15.9 mg, 67%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.85-7.83 (m, 1H), 7.61-7.59 (m, 1H), 7.42-7.39 (m, 2H), 6.99 (m, 2H), 2.37 (m, 3H), 2.30 (s, 6H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 163.3, 150.6, 141.5, 140.3, 138.4, 128.6, 124.9, 124.2, 120.1, 110.6, 21.3, 20.3 ppm. **MS (EI):** calculated for $[M^+] = [C_{16}H_{15}NO]^+$ : 237.12, found m/z (%) 238.0 (16.5), 236.9 ($M^+$, 100.0), 235.9 (27.8), 221.9 (12.1), 220.9 (5.2), 219.9 (5.0), 207.9 (9.3), 206.9 (4.4), 146.9 (2.4) , 129.9 (3.1), 118.8 (7.0), 114.9 (2.6), 90.9 (3.0).



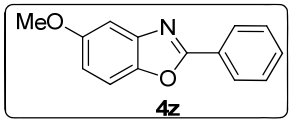
**4x**

**2-cyclopropylbenzo[d]oxazole (4x):** The general procedure was followed using (E)-2-((cyclopropylmethylene)amino)phenol (16.1 mg, 0.10 mmol). Purification by column chromat eraphy (PE→PE/EtOAc = 60:1) yielded **4x** (9.7mg, 61%) as a pale oil. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.61-7.59 (m, 1H), 7.43-7.41 (m, 1H), 7.29-7.22 (m, 2H), 2.24-2.17 (m, 1H), 1.29-1.25 (m, 2H), 1.19-1.14 (m, 2H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 168.6, 150.4, 141.5, 124.0, 123.9, 118.9, 110.0, 9.15 ppm. **MS (EI):** calculated for $[M^+]$ = [ C10H9NO]$^+$ : 159.07, found m/z (%) 159.9 (9.3), 158.9 ($M^+$, 100.0), 157.8 (82.4), 148.8 (8.5), 143.8 (8.7), 133.9 (5.0), 132.8 (59.4) , 131.8 (3.5), 130.9 (5.6), 129.9 (14.62) , 96.9 (4.7), 90.9 (6.3), 85.0 (6.3), 82.9 (6.0), 76.8 (6.4),71.0 (7.5), 63.9 (8.1), 62.8 (11.4),56.9 (9.9), 44.9 (7.8), 43.8 (61.2), 62.8 (11.4), 42.9 (10.8).



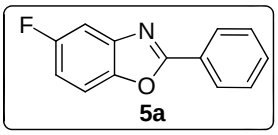
**4y**

**5-methyl-2-phenylbenzo[d]oxazole (4y):** The general procedure was followed using (E)-2-(benzylideneamino)-4-methylphenol (21.1 mg, 0.10 mmol). Purification by column chromat eraphy (PE→PE/EtOAc = 40:1) yielded **4y** (18.8 mg, 90%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.26-8.23(m, 2H), 7.56-7.50 (m, 4H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 2.48 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 163.1, 148.9, 142.2, 134.4, 131.4, 128.8, 127.5, 127.3, 126.2, 119.9, 109.9, 21.5 ppm. **MS (EI):** calculated for $[M^+] = [C_{14}H_{11}NO]^+$ : 209.08, found m/z (%) 209.9 (14.4), 208.9 ($M^+$, 100.0), 207.8 (35.5), 179.9 (4.7), 105.9 (5.9), 104.8 (8.5), 104.0 (2.6) , 77.9(13.3), 76.9 (11.0), 51.9 (3.5), 50.9 (5.0).



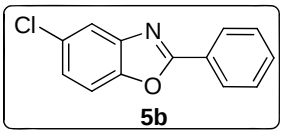
**4z**

**5-methoxy-2-phenylbenzo[d]oxazole (4z):** The general procedure was followed using (E)-2-(benzylideneamino)-4-methoxyphenol (22.7 mg, 0.10 mmol). Purification by column chromat eraphy (PE→PE/EtOAc = 20:1) yielded **4z** (20.9 mg, 93%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.24-8.22 (m, 2H), 7.54-7.50 (m, 3H), 7.46 (d, *J* = 9.2 Hz, 1H), 7.26 (d, *J* = 2.0 Hz, 1H), 6.96-6.93 (m, 1H), 3.87 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 163.8, 157.3, 145.4, 142.9, 131.4, 128.9, 127.4, 127.2, 113.7, 110.7, 102.8, 55.9 ppm. **MS (EI):** calculated for $[M^+] = [C_{14}H_{11}NO_2]^+$ : 225.08, found m/z (%) 225.9 (14.4), 224.9 ($M^+$, 100.0), 210.9 (7.5), 209.8 (53.9), 181.9 (2.8), 106.8 (10.8), 78.8 (10.9) , 52.9 (4.1), 50.9 (4.4), 43.8 (2.8).



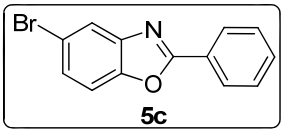
**5a**

**5-fluoro-2-phenylbenzo[d]oxazole (5a):** The general procedure was followed using (E)-2-(benzylideneamino)-4-fluorophenol (21.5 mg, 0.10 mmol). Purification by column chromat eraphy (PE→PE/EtOAc = 30:1) yielded **5a** (20.5 mg, 96%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.23 (d, *J* = 7.6 Hz, 2H), 7.58-7.50 (m, 3H), 7.47-7.45 (m, 1H), 7.11-7.07 (m, 1H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 164.7, 161.3, 158.9, 147.1, 142.9 (d, *J* = 13.0 Hz), 131.8, 128.9, 127.6, 126.8, 112.7 (d, *J* = 26.0 Hz), 110.8 (d, *J* = 22.0 Hz), 106.4 (d, *J* = 26.0 Hz) ppm. **MS (ESI):** calculated for $[C_{13}H_8ClFNO]^+$: 214.07, found 214.02.



**5b**

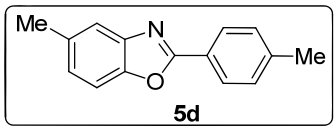
**5-chloro-2-phenylbenzo[d]oxazole (5b):** The general procedure was followed using (E)-2-(benzylideneamino)-4-chlorophenol (23.2 mg, 0.10 mmol). Purification by column chromat eraphy (PE→PE/EtOAc = 40:1) yielded **5b** (21.4 mg, 93%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.23 (d, *J* = 8.0 Hz, 2H), 7.75 (t, *J* = 0.8 Hz, 1H), 7.58-7.48 (m, 4H), 7.33-7.31 (m, 1H). **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 164.3, 149.3, 143.2, 131.9, 130.0, 128.9, 127.7, 126.6, 125.3, 119.9, 111.2. ppm. **MS (ESI):** calculated for $[C_{13}H_9ClNO]^+$: 230.04, found 229.99.



**5c**

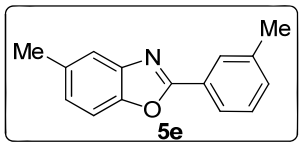
**5-bromo-2-phenylbenzo[d]oxazole (5c):** The general procedure was followed using (E)-2-(benzylideneamino)-4-bromophenol (27.6 mg, 0.10 mmol). Purification by column chromat eraphy (PE→PE/EtOAc = 40:1) yielded **5c** (21.7 mg, 79%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.26-8.24 (m, 2H), 7.92 (s, 1H), 7.60-7.52 (m, 3H), 7.48 (s, 2H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 164.2, 149.8, 143.8, 132.0, 129.0, 128.1, 127.8, 126.7, 123.0, 117.3, 111.8. ppm. **MS (EI):** calculated for $[M^+] = [\ C_{13}H_8BrNO\ ]^+$ : 272.98, found m/z (%) 275.8 (12.4), 274.8 (95.3), 273.8 (16.1), 272.8 ($M^+$, 100.0), 271.5 (3.6), 246.7 (10.7), 244.8 (10.1), 193.8 (4.9), 143.7 (3.9), 141.8 (4.4), 137.5

(5.6) , 123.3 (3.7), 90.9 (6.2), 76.9 (7.5), 62.9 (17.5), 61.9 (4.6) , 43.8 (12.7).



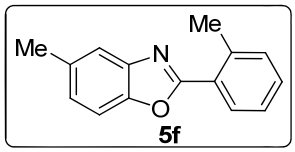
**5d**

**5-methyl-2-(p-tolyl)benzo[d]oxazoled (5d):** The general procedure was followed using (E)-4-methyl-2-((4-methylbenzylidene)amino)phenol (22.5 mg, 0.10 mmol). Purification by column chromateraphy (PE→PE/EtOAc = 40:1) yielded **5d** (20.1 mg, 90%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.14 (d, *J* = 8.0 Hz, 2H), 7.55 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 1H), 2.49 (s, 3H), 2.44 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 163.3, 148.9, 142.3, 141.9, 134.2, 129.6, 127.5, 125.9, 124.5, 119.7, 109.8, 21.6, 21.5 ppm. **HRMS (ESI):** calcd for $C_{15}H_{14}NO$ $[M+H]^+$ *m/z* 224.1070; found 224.1072.



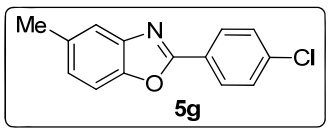
**5e**

**5-methyl-2-(m-tolyl)benzo[d]oxazole (5e):** The general procedure was followed using (E)-4-methyl-2-((3-methylbenzylidene)amino)phenol (22.8 mg, 0.10 mmol). Purification by column chromateraphy (PE→PE/EtOAc = 40:1) yielded **5e** (19.1 mg, 85%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.10 (s, 1H), 8.05 (d, *J* = 7.6 Hz, 1H), 7.57 (s, 1H), 7.47-7.40 (m, 2H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.18-7.16 (m, 1H), 2.50 (s, 3H), 2.47 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 163.3, 148.9, 142.2, 138.7, 134.4, 132.3, 128.8, 128.1, 127.1, 126.2, 124.7, 119.8, 109.9, 21.5, 21.3 ppm. **HRMS (ESI):** calcd for $C_{15}H_{14}NO$ $[M+H]^+$ *m/z* 224.1070; found 224.1070.



**5f**

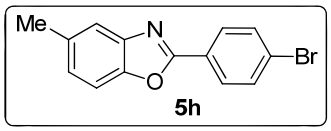
**5-methyl-2-(o-tolyl)benzo[d]oxazole (5f):** The general procedure was followed using (E)-4-methyl-2-((2-methylbenzylidene)amino)phenol (22.2 mg, 0.10 mmol). Purification by column chromateraphy (PE→PE/EtOAc = 40:1) yielded **5f** (18.6 mg, 84%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.19-8.16 (m, 1H), 7.61 (s, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.44 (d, *J* = 1.6 Hz, 1H), 7.42-7.33 (m, 2H), 7.18 (dd, *J* = 1.2, 7.2 Hz, 1H), 2.82 (s, 3H), 2.51 (s, 3H). **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 163.5, 148.5, 138.7, 134.1, 131.7, 130.7, 129.9, 126.4, 126.1, 126.0, 120.0, 109.8, 22.2, 21.5 ppm. **HRMS (ESI):** calcd for C15H14NO $[M+H]^+$ *m/z* 224.1070; found 224.1069.



**5g**

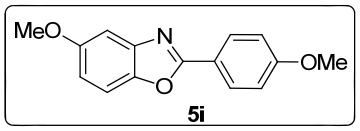
**2-(4-chlorophenyl)-5-methylbenzo[d]oxazole (5g):** The general procedure was followed using (E)-2-((4-chlorobenzylidene)amino)-4-methylphenol (24.6 mg, 0.10 mmol). Purification by column chromateraphy (PE→PE/EtOAc = 30:1) yielded **5g** (22.2 mg, 91%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.56 (s, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 2.50 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 162.1, 149.0, 142.1, 137.6, 134.6, 129.2, 128.8, 126.5, 125.7, 119.3, 110.0, 21.5 ppm. **HRMS (ESI):** calcd for $C_{14}H_{11}ClNO$

$[M+H]^+$ *m/z* 244.0529; found 244.0528.



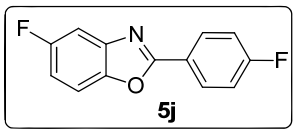
**5h**

**2-(4-bromophenyl)-5-methylbenzo[d]oxazole (5h):** The general procedure was followed using (E)-2-((4-bromobenzylidene)amino)-4-methylphenol (29.0 mg, 0.10 mmol). Purification by column chromateraphy (PE→PE/EtOAc = 30:1) yielded **5h** (25.0 mg, 87%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.11 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.56 (s, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.19-7.17 (m, 1H), 2.50 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 162.2, 149.0, 142.2, 134.6, 132.2, 128.9, 126.5, 126.2, 126.0, 120.0, 110.0, 21.5 ppm. **HRMS (ESI):** calcd for $C_{14}H_{11}BrNO$ $[M+H]^+$ *m/z* 288.0024; found 288.0030.



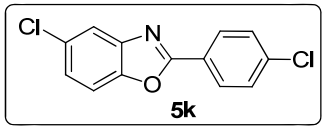
**5i**

**2-(4-bromophenyl)-5-methylbenzo[d]oxazole (5i):** The general procedure was followed using (E)-4-methoxy-2-((4-methoxybenzylidene)amino)phenol (25.8 mg, 0.10 mmol). Purification by column chromateraphy (PE→PE/EtOAc = 20:1) yielded **5i** (23.2 mg, 91%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.17 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 1H), 7.27-7.24 (m, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.93-6.90 (m, 1H), 3.89 (s, 3H), 3.87 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 163.9, 162.2, 157.2, 145.3, 143.0, 129.2, 119.7, 114.3, 112.9, 110.5, 55.9, 55.4 ppm. **HRMS (ESI):** calcd for $C_{15}H_{14}NO_3$ $[M+H]^+$ *m/z* 256.0968; found 256.0967.



**5j**

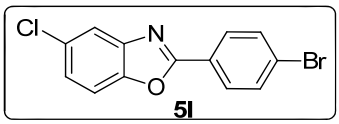
**5-fluoro-2-(4-fluorophenyl)benzo[d]oxazole (5j):** The general procedure was followed using (E)-4-fluoro-2-((4-fluorobenzylidene)amino)phenol (23.3 mg, 0.10 mmol). Purification by column chromateraphy (PE→PE/EtOAc = 40:1) yielded **5j** (20.8 mg, 90%) as a white solid. **$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.26-8.22 (m, 2H), 7.52-7.49 (m, 1H), 7.45-7.42 (m, 1H), 7.26-7.11 (m, 3H), 7.11-7.06 (m, 1H) **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 166.2, 163.8 (d, *J* = 16.0 Hz), 161.4, 159.0, 147.1, 142.9 (d, *J* = 13.0 Hz), 130.0 (d, *J* = 9.0 Hz), 123.2, 116.3 (d, *J* = 22.0 Hz), 112.7 (d, *J* = 26.0 Hz), 110.9 (d, *J* = 10.0 Hz), 106.4 (d, *J* = 25.0 Hz). **HRMS (ESI):** calcd for $C_{13}H_8F_2NO$ $[M+H]^+$ *m/z* 232.0568; found 232.0571.



**5k**

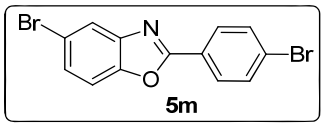
**5-chloro-2-(4-chlorophenyl)benzo[d]oxazole (5k):** The general procedure was followed using (E)-4-chloro-2-((4-chlorobenzylidene)amino)phenol (26.6 mg, 0.10 mmol). Purification by column chromateraphy (PE→PE/EtOAc = 40:1) yielded **5k** (23.5 mg, 89%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.20-8.16 (m, 2H), 7.75 (d, *J* = 1.6 Hz, 1H), 7.54-7.50 (m, 3H), 7.36-7.33 (m, 1H) **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 163.3, 149.3, 143.1, 138.2, 130.2, 129.3, 128.9, 125.6, 125.1, 120.0, 111.3

ppm. **HRMS (ESI):** calcd for $C_{13}H_8C_{12}NO$ $[M+H]^+$ *m/z* 263.9977; found 263.9989.



**5l**

**2-(4-bromophenyl)-5-chlorobenzo[d]oxazole (5l):** The general procedure was followed using (E)-2-((4-bromobenzylidene)amino)-4-chlorophenol (31.1 mg, 0.10 mmol). Purification by column chromateraphy (PE→PE/EtOAc = 30:1) yielded **5l** (26.2 mg, 85%) as a white solid. **$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.12-8.08 (m, 2H), 7.75 (d, *J* = 2.0 Hz, 1H), 7.69-7.67 (m, 2H), 7.50 (d, *J* = 8.8, 1H), 7.36-7.33 (m, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 163.4, 149.3, 143.1, 132.3, 130.2, 129.1, 126.7, 125.7, 125.6, 120.0, 111.4 ppm. **HRMS (ESI):** calcd for $C_{13}H_8BrClNO$ $[M+H]^+$ *m/z* 307.9472; found 307.9475.



**5m**

**5-bromo-2-(4-bromophenyl)benzo[d]oxazole (5m):** The general procedure was followed using (E)-4-bromo-2-((4-bromobenzylidene)amino)phenol (35.5 mg, 0.10 mmol). Purification by column chromateraphy (PE→PE/EtOAc = 40:1) yielded **5l** (28.8 mg, 81%) as a white solid. **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.91 (s, 1H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.51-7.46 (m, 2H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$):** 163.3, 149.7, 145.3, 143.6, 132.3, 129.1, 128.4, 126.8, 125.5, 123.1, 117.5, 111.9 ppm. **HRMS (ESI):** calcd for $C_{13}H_8Br_2NO$ $[M+H]^+$ *m/z* 351.8968; found 351.8972.

# 12. REFERENCES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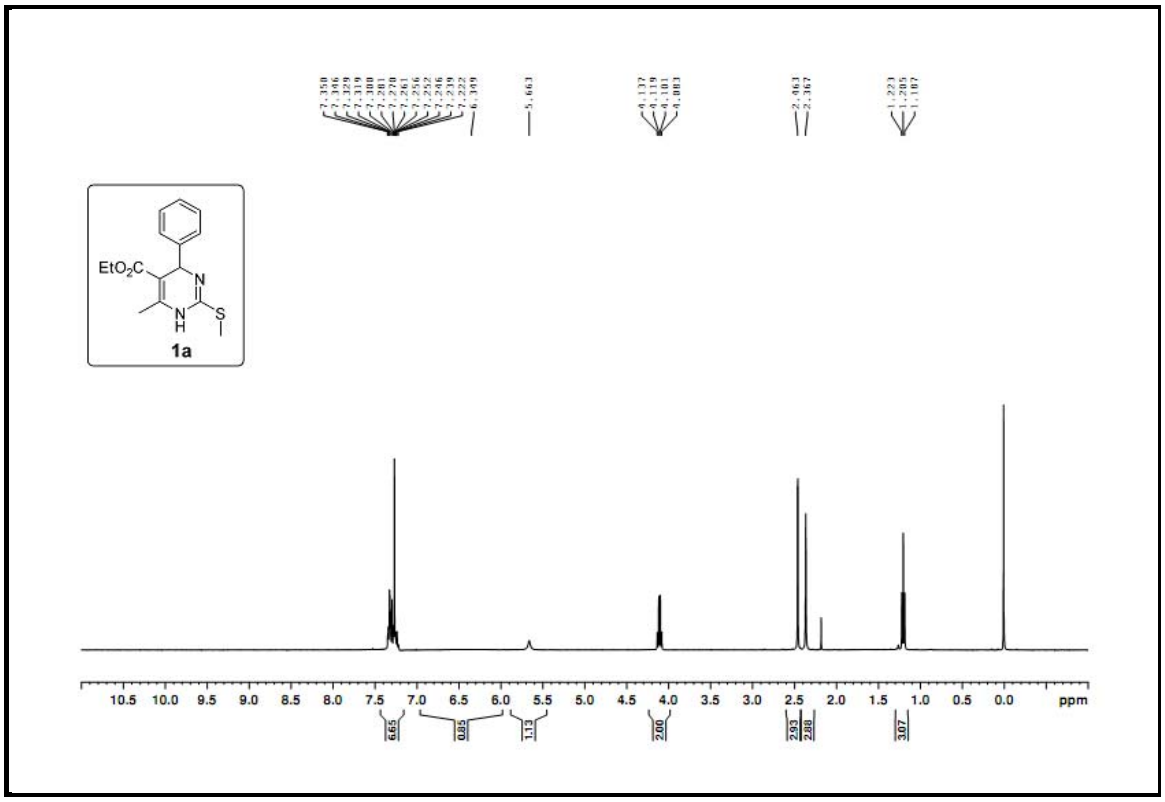
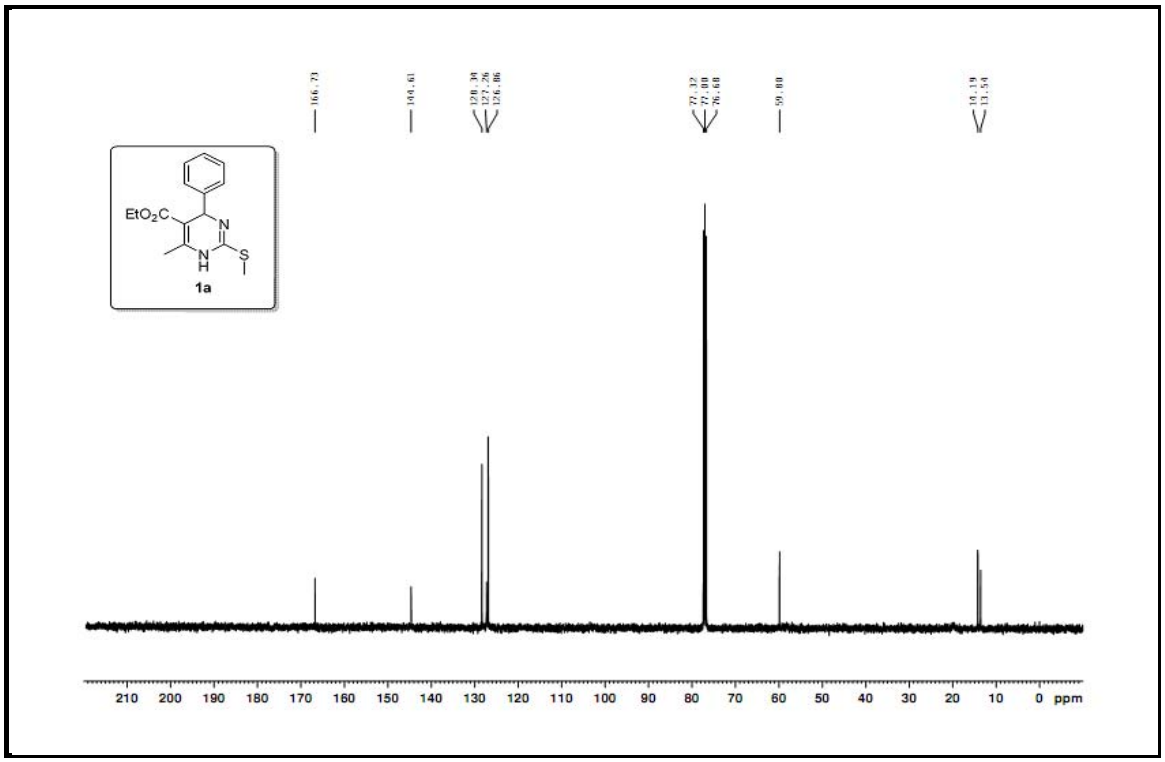
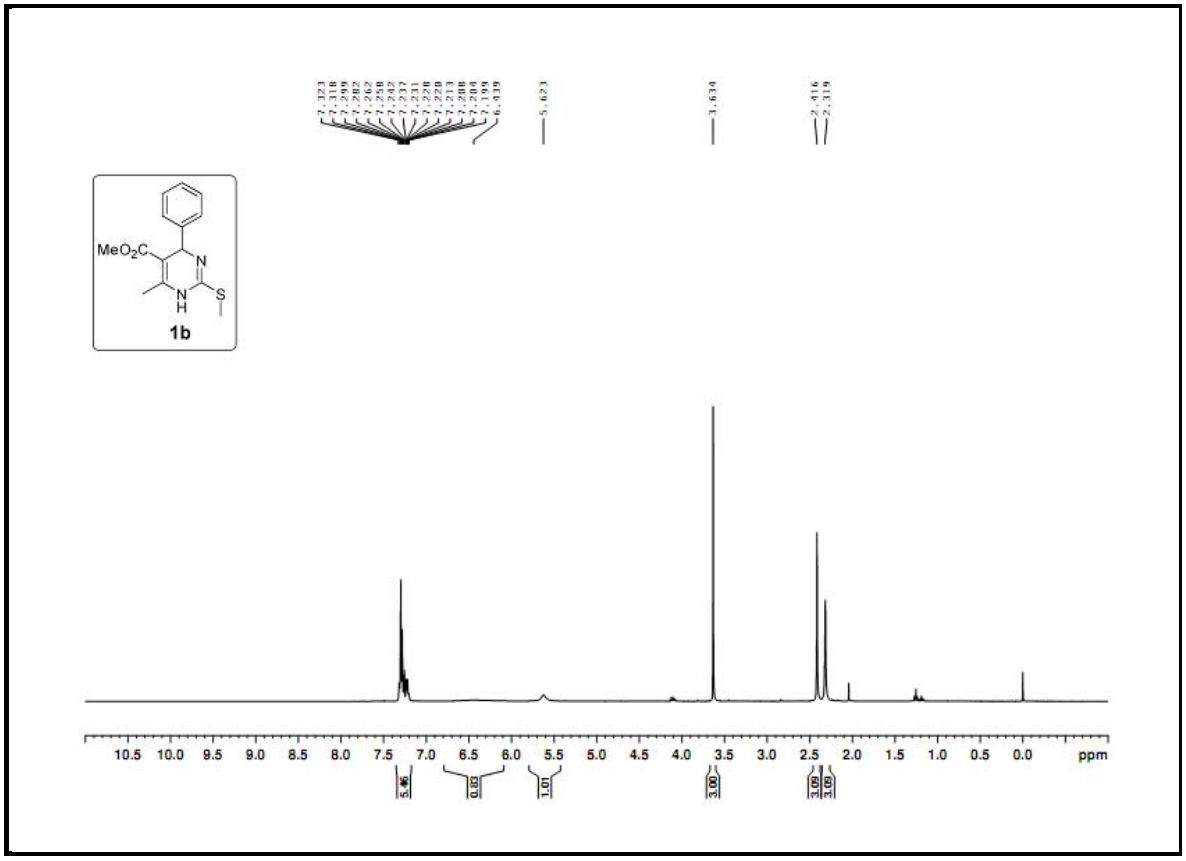
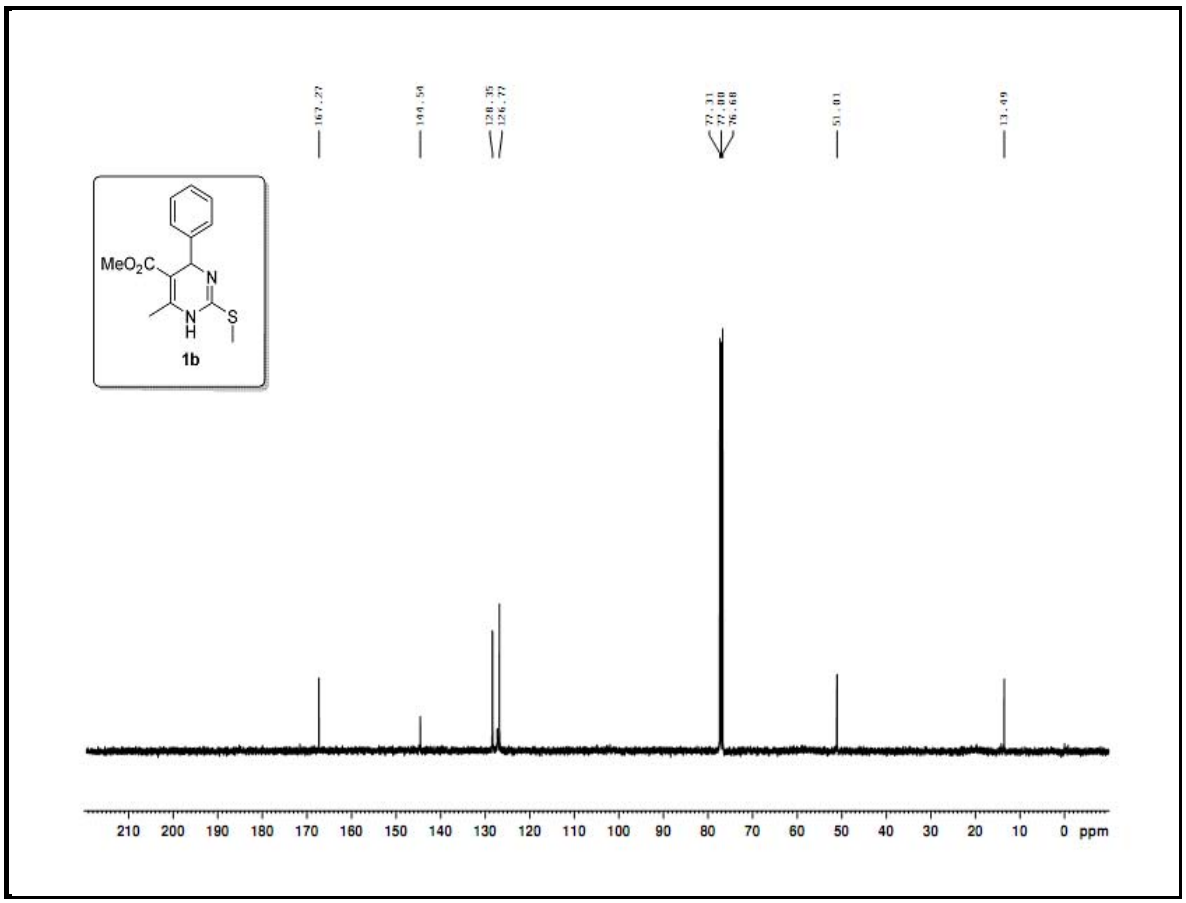
# 13. NMR SPECTRA

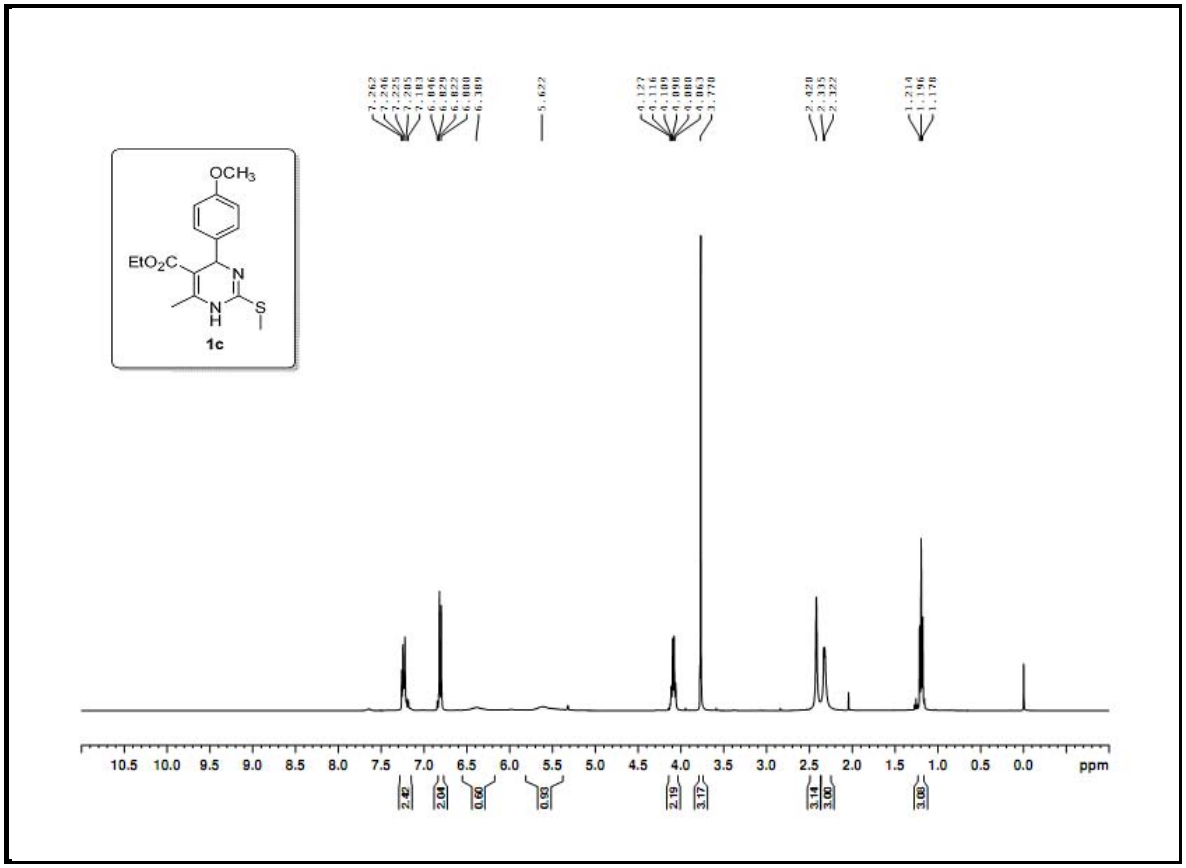
## 13.1 NMR Spectra Of 2-Substituted Dihydropyrimidines 1a-1x.

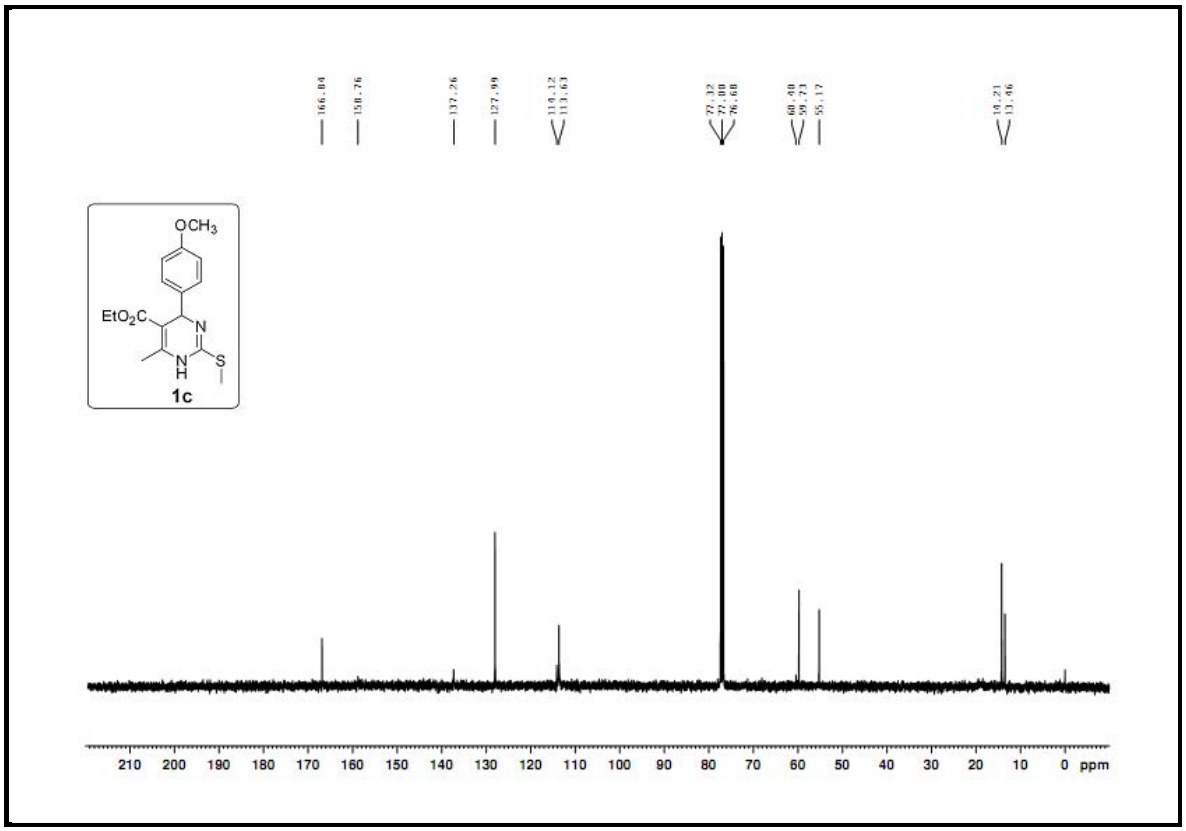


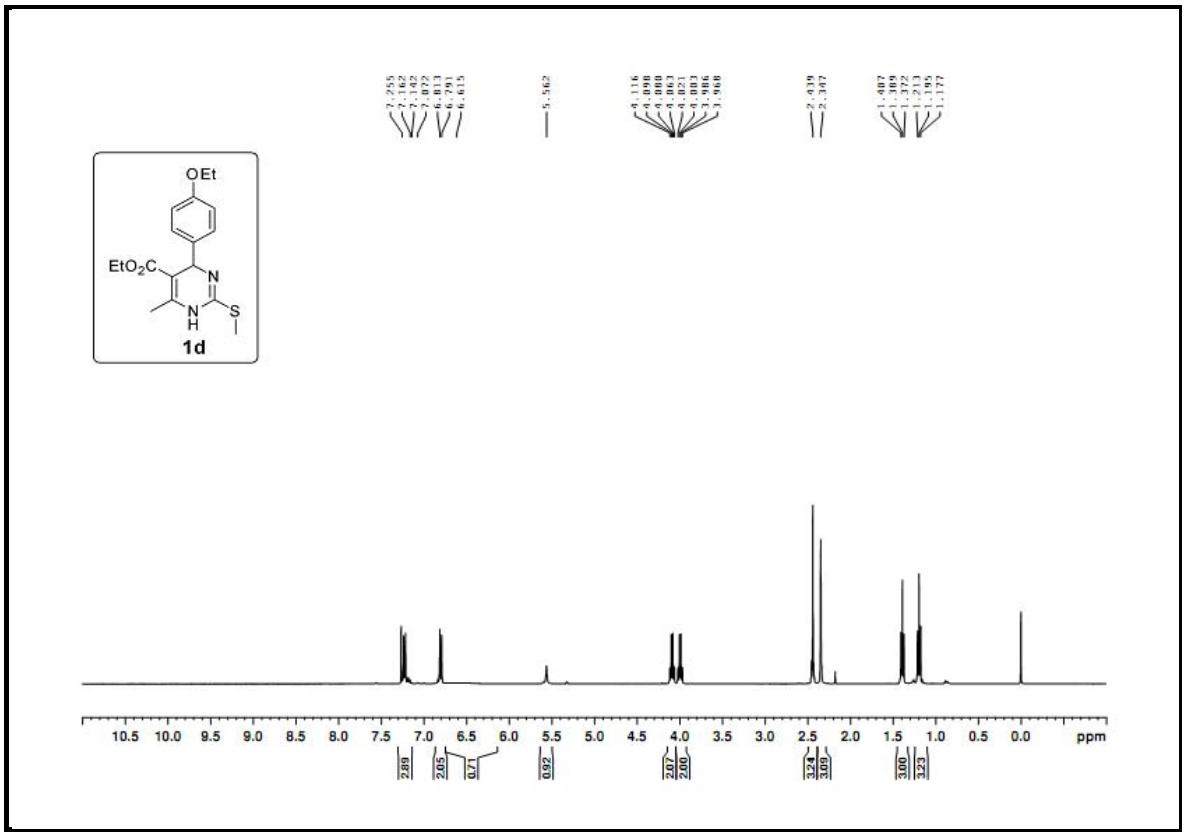



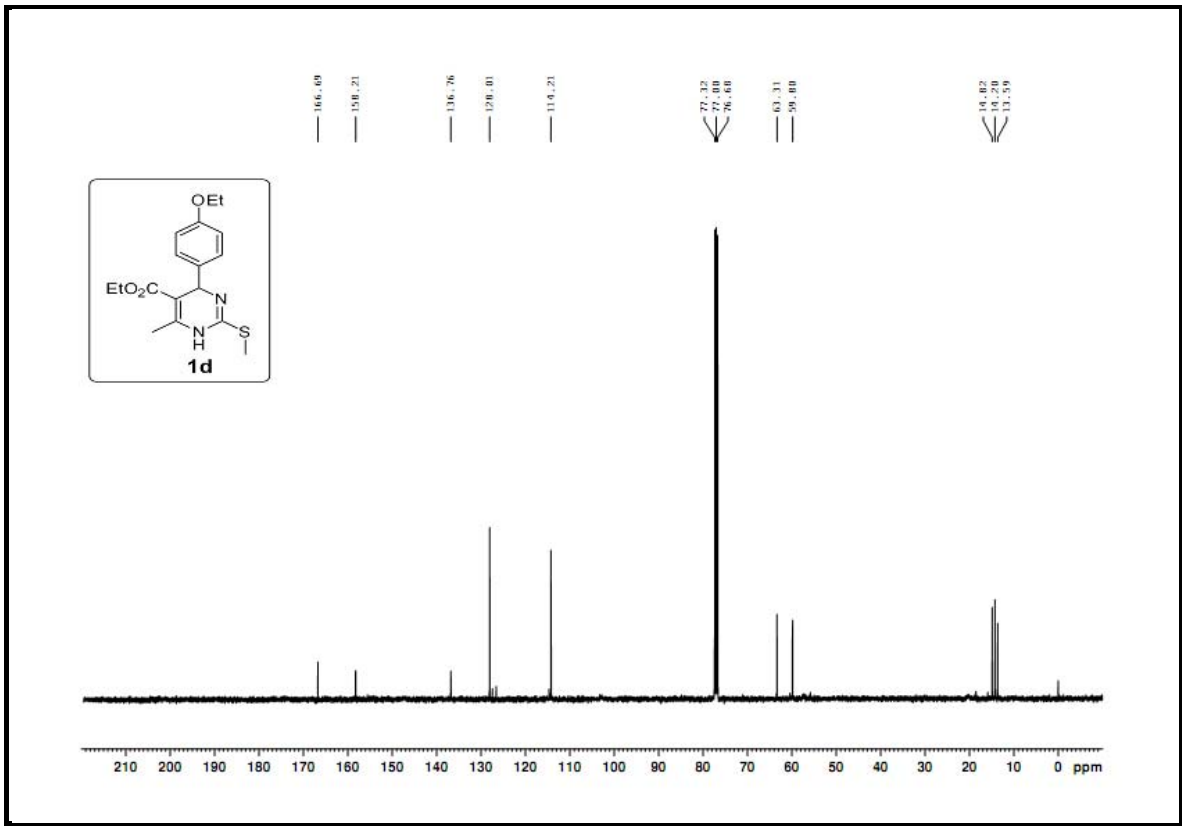

7.323
7.318
7.299
7.282
7.262
7.258
7.242
7.237
7.231
7.228
7.228
7.213
7.208
7.204
7.199
6.439
5.623
3.634
2.416
2.319
MeO2C
N
N
H
S
1b
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
5.96
0.88
1.00
3.00
1.08
3.09

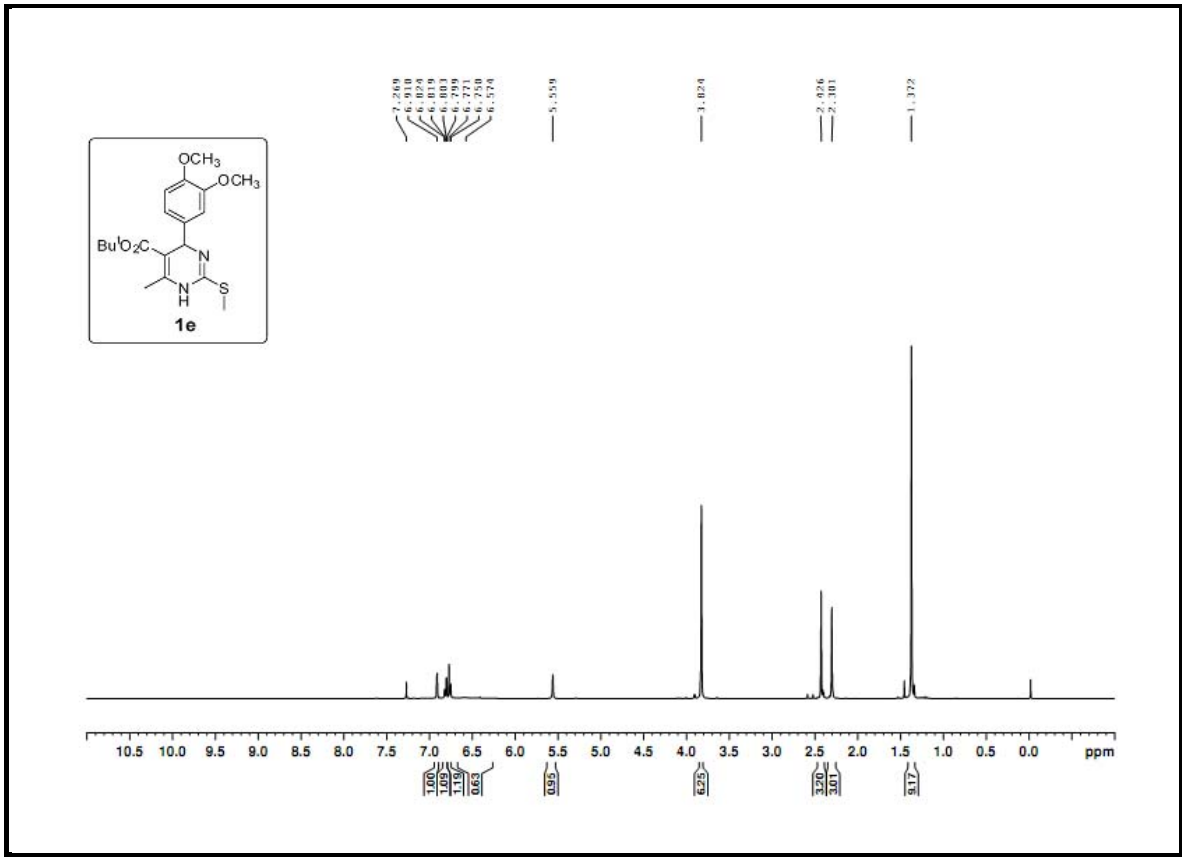

167.27
144.59
128.35
126.77
77.31
77.00
76.68
51.01
13.49
MeO2C
N
N
H
S
1b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

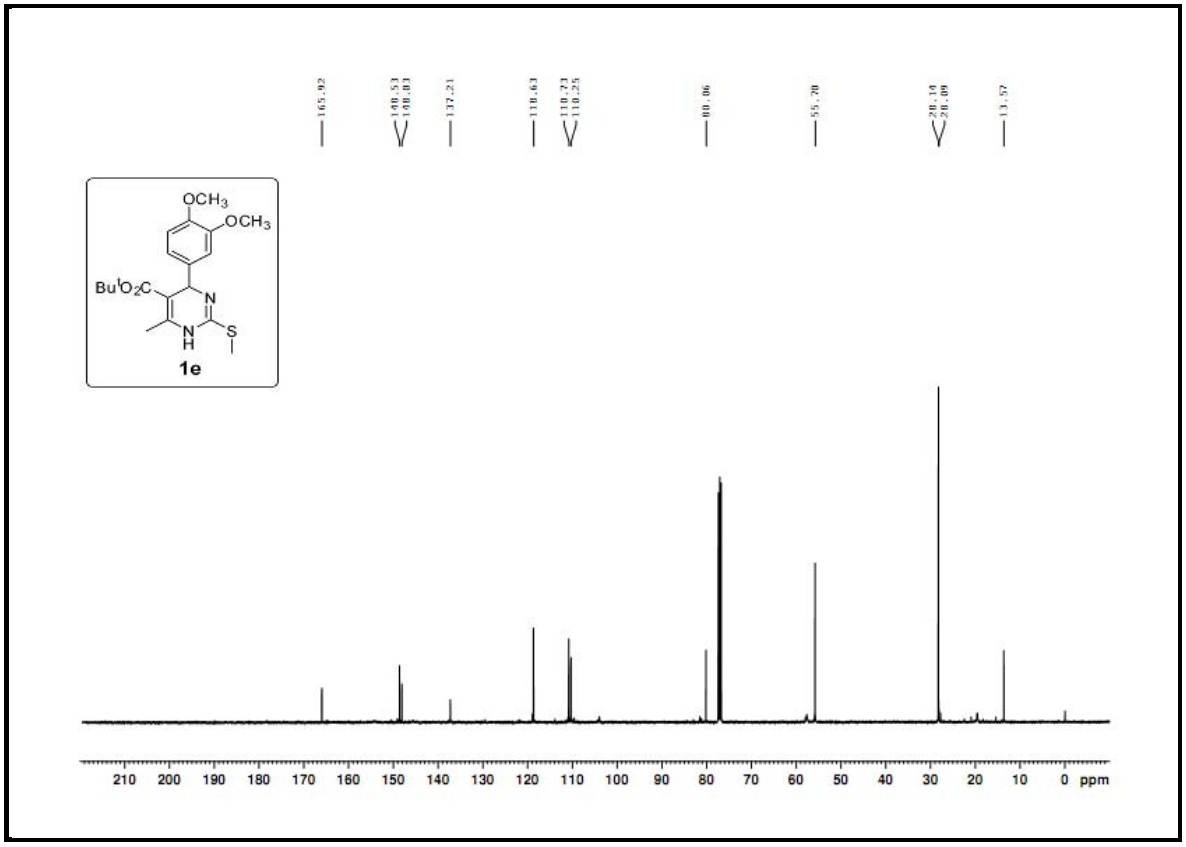

OCH3
EtO2C
N
N
H
S
1c
7.262
7.256
7.225
7.205
7.183
6.846
6.829
6.822
6.808
6.389
5.622
4.127
4.116
4.108
4.098
4.088
4.063
3.770
2.428
2.335
2.322
1.214
1.196
1.178
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.42
2.04
0.60
0.93
2.19
3.17
3.14
3.00
3.08

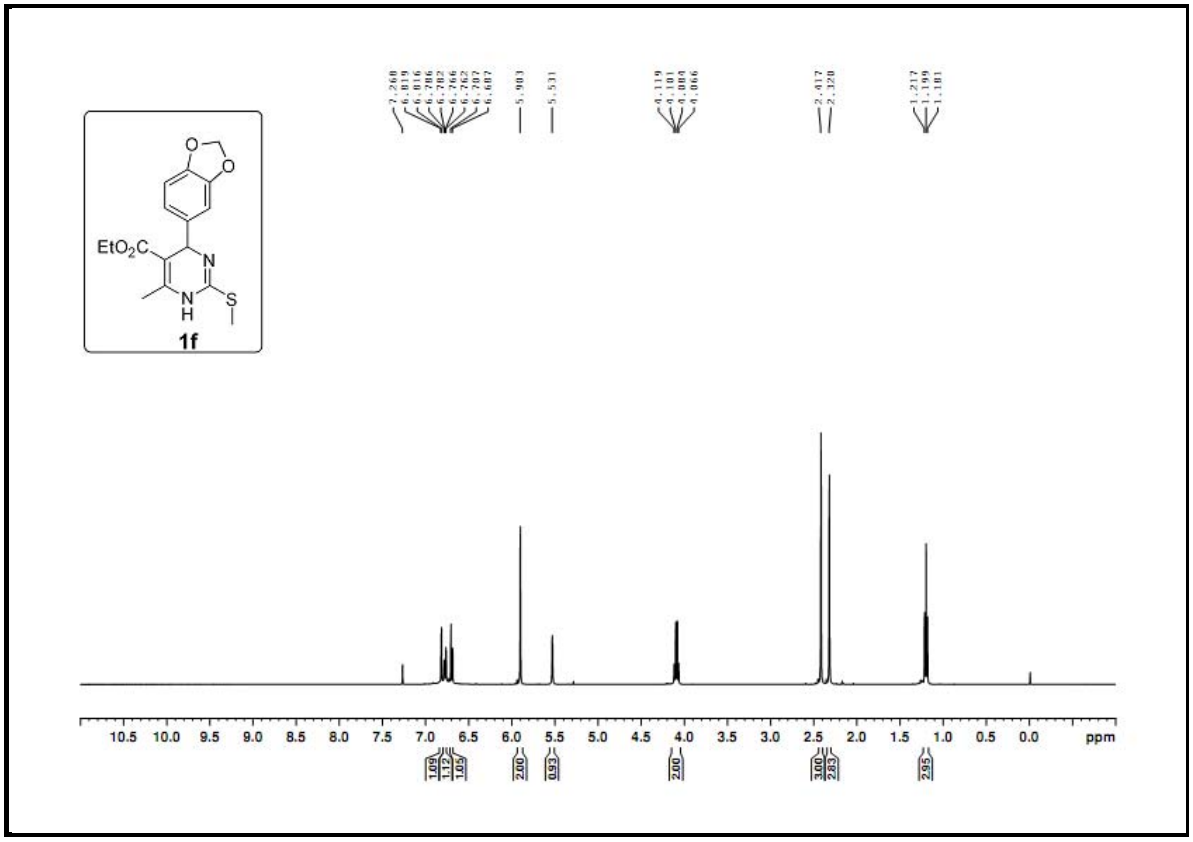

OCH3
EtO2C
N
N
H
S
1c
166.84
158.76
137.26
127.99
114.12
113.63
77.32
77.00
76.68
60.48
55.73
55.17
15.21
13.46
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

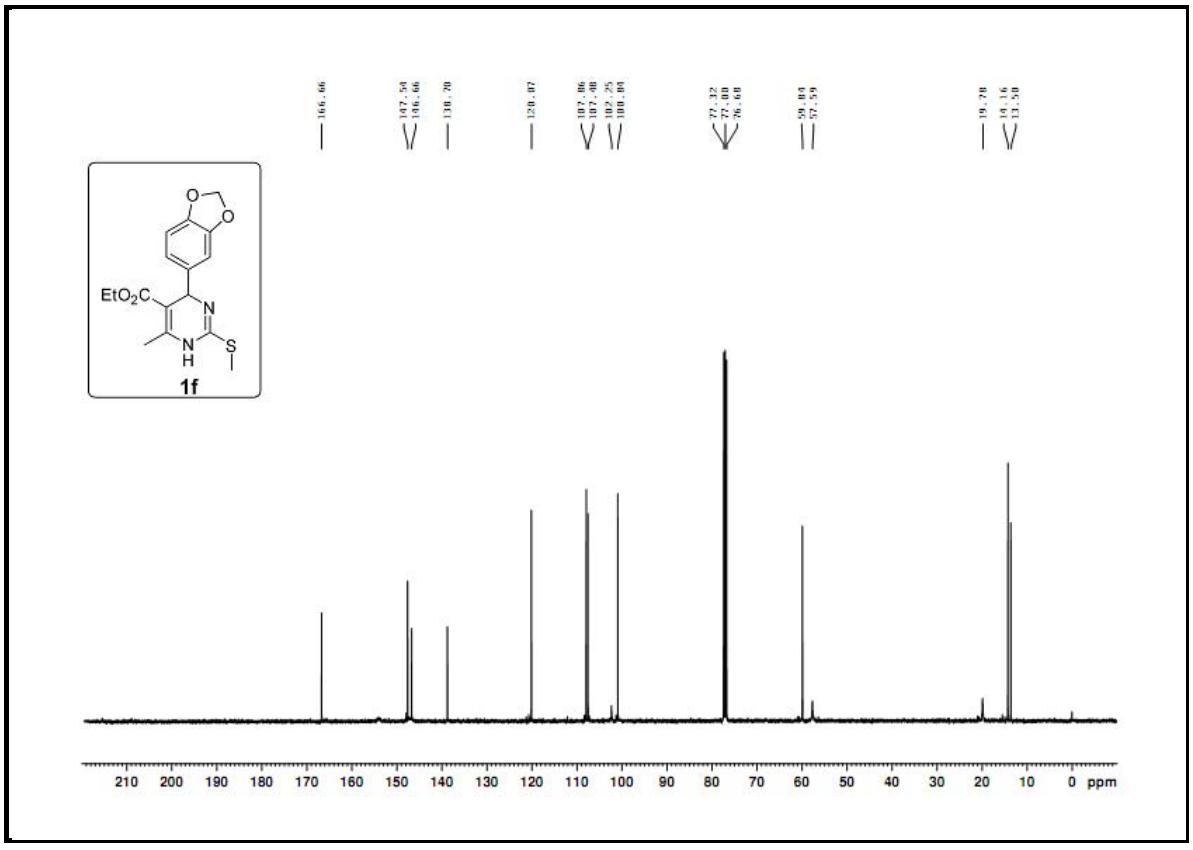

OEt
EtO2C
N
N
H
S
1d
ppm

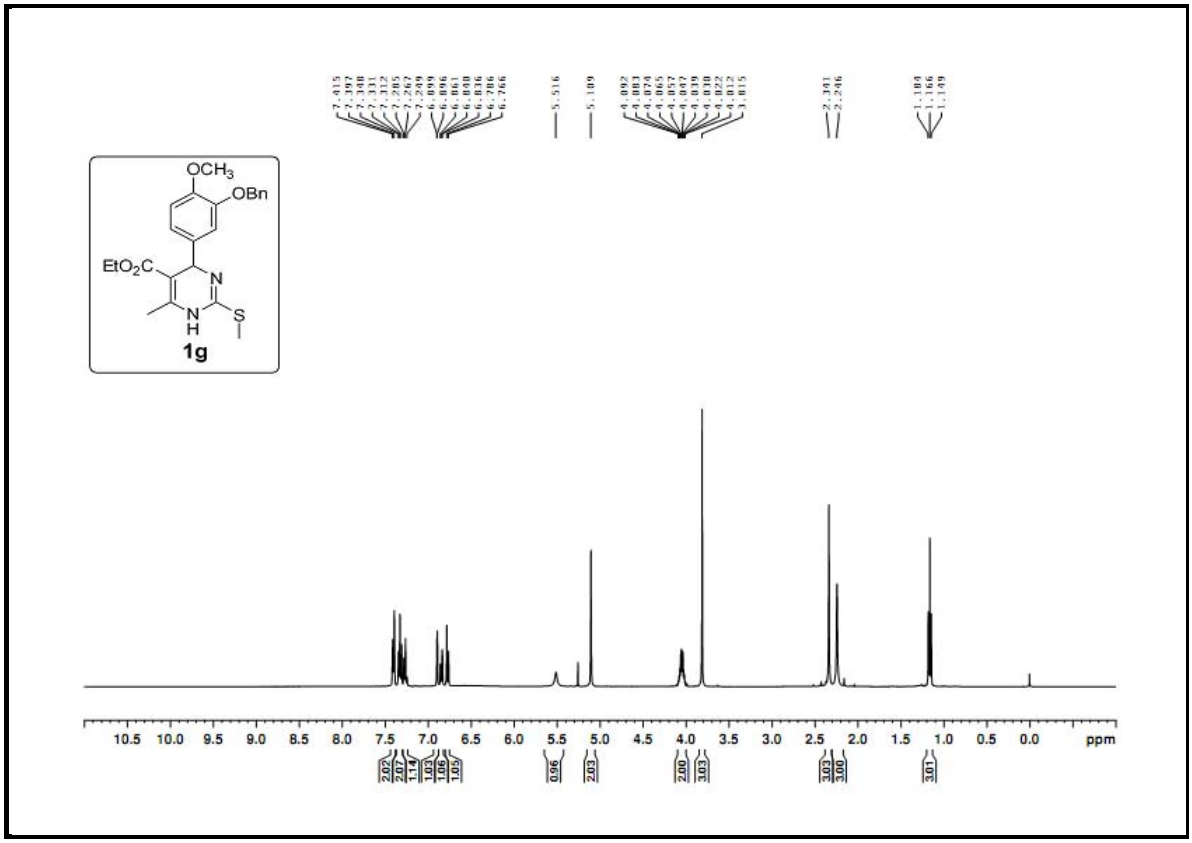

OEt
EtO2C
N
N
H
S
1d
ppm

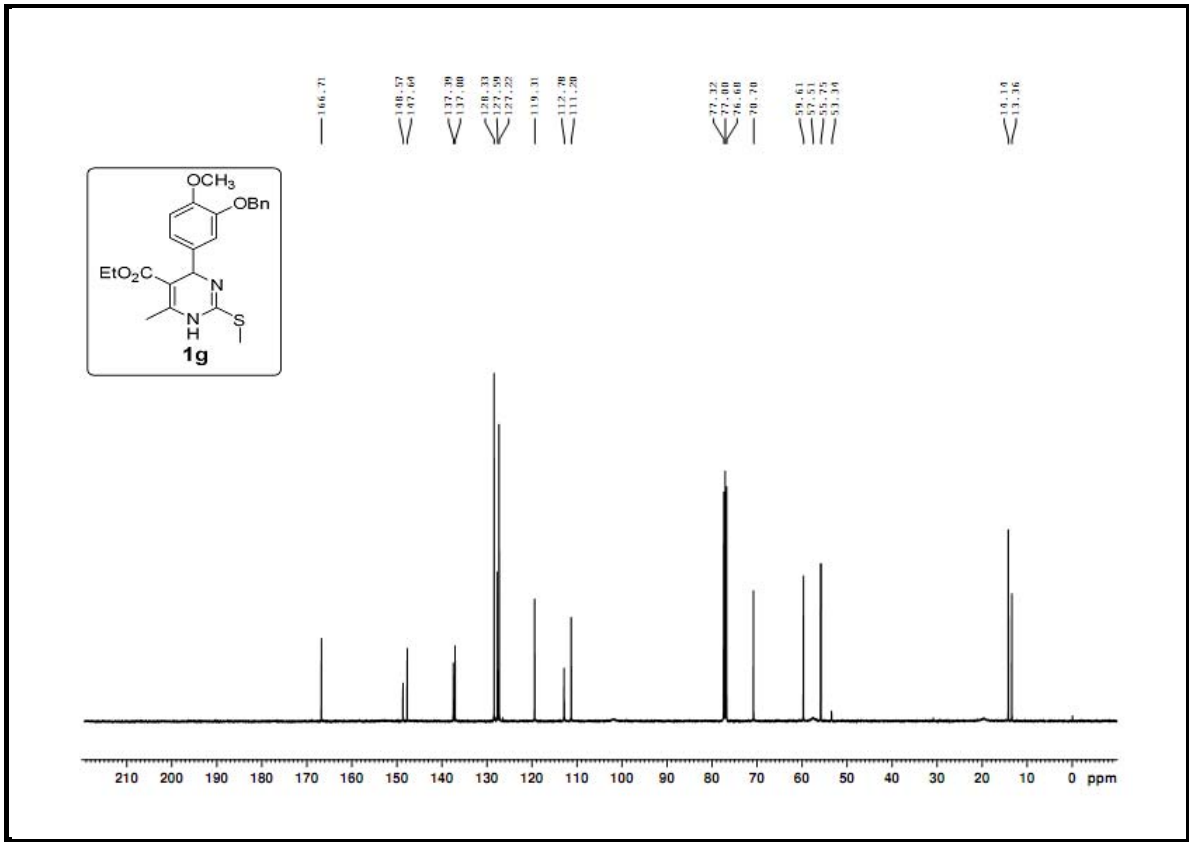

OCH3
OCH3
Bu^tO2C
N
N
H
S
1e
7.269
6.910
6.824
6.819
6.803
6.799
6.771
6.750
6.574
5.559
3.824
2.426
2.381
1.372
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.09
1.19
0.63
0.95
6.25
3.20
3.01
9.17

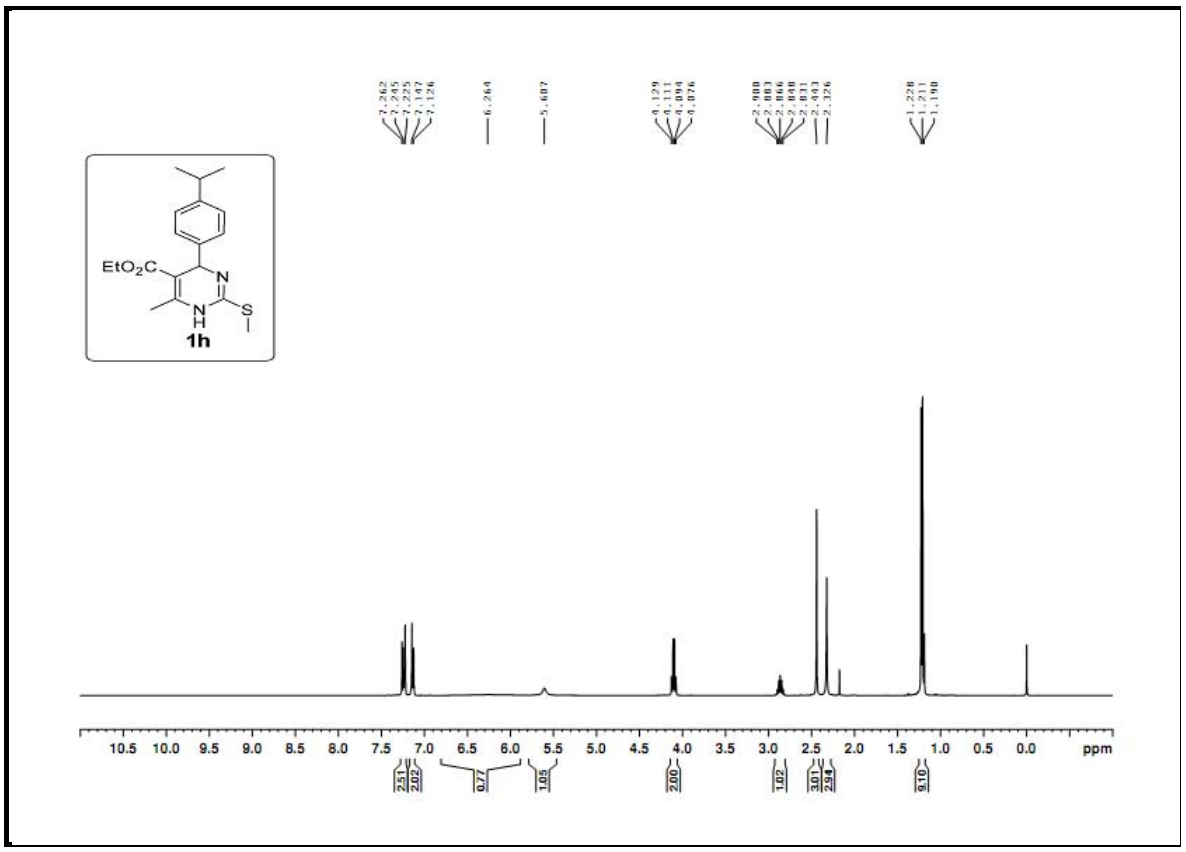

OCH3
OCH3
Bu^tO2C
N
N
H
S
1e
165.92
150.53
150.03
137.21
118.63
110.73
110.25
80.06
55.70
28.10
28.09
13.57
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

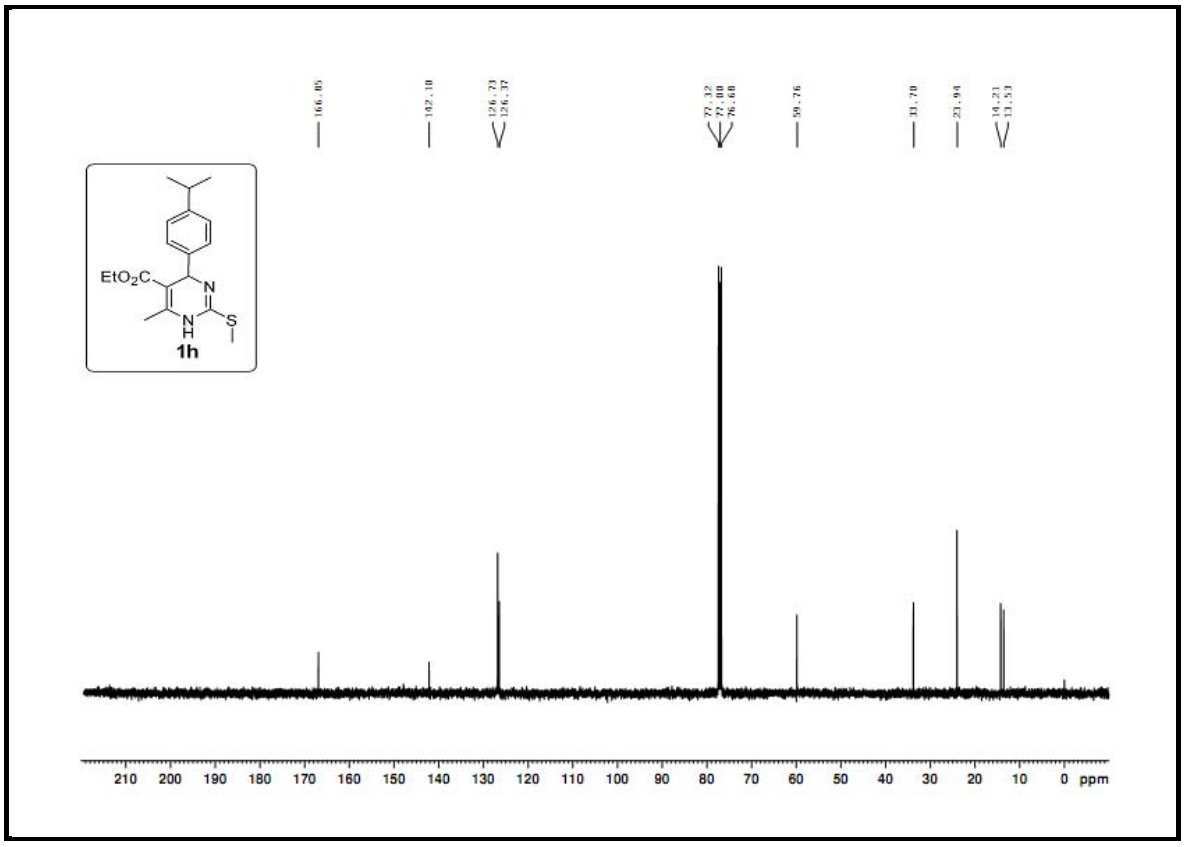

1f
7.268
6.819
6.816
6.706
6.702
6.766
6.762
6.707
6.687
5.903
5.531
4.119
4.101
4.084
4.066
2.417
2.320
1.217
1.199
1.181
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.09
1.12
1.05
2.00
0.93
2.00
3.00
2.93
2.95

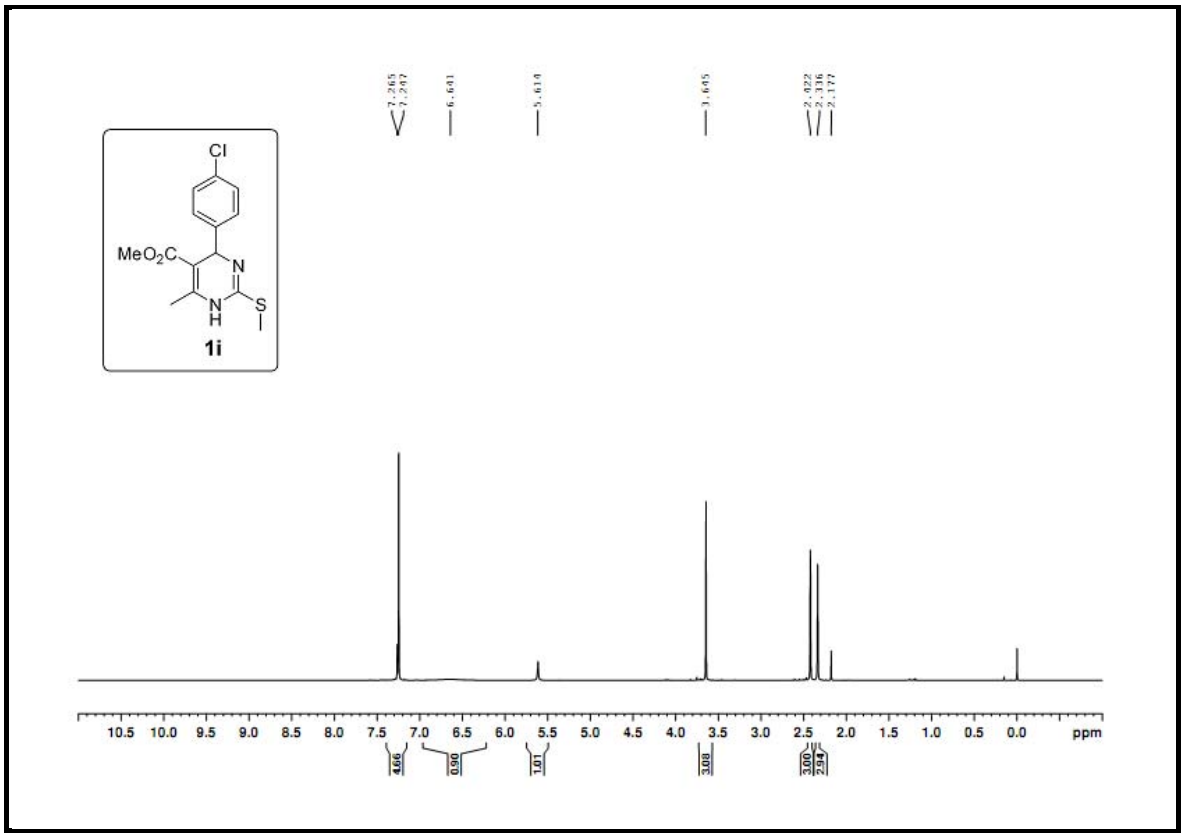

1f
166.66
147.58
146.66
138.70
120.87
107.86
107.08
102.25
100.80
77.32
77.00
76.68
59.84
57.59
19.78
14.16
13.58
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

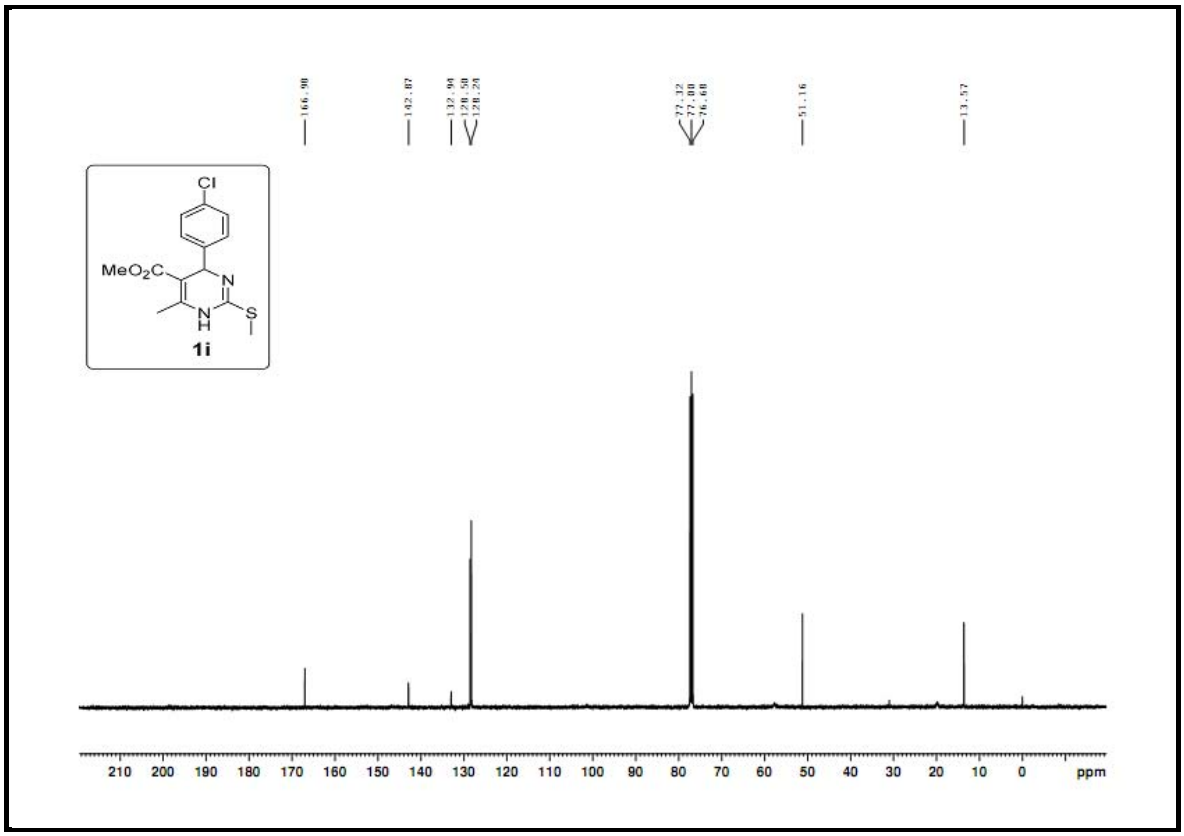

OCH3
OBn
EtO2C
N
N
H
S
1g
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

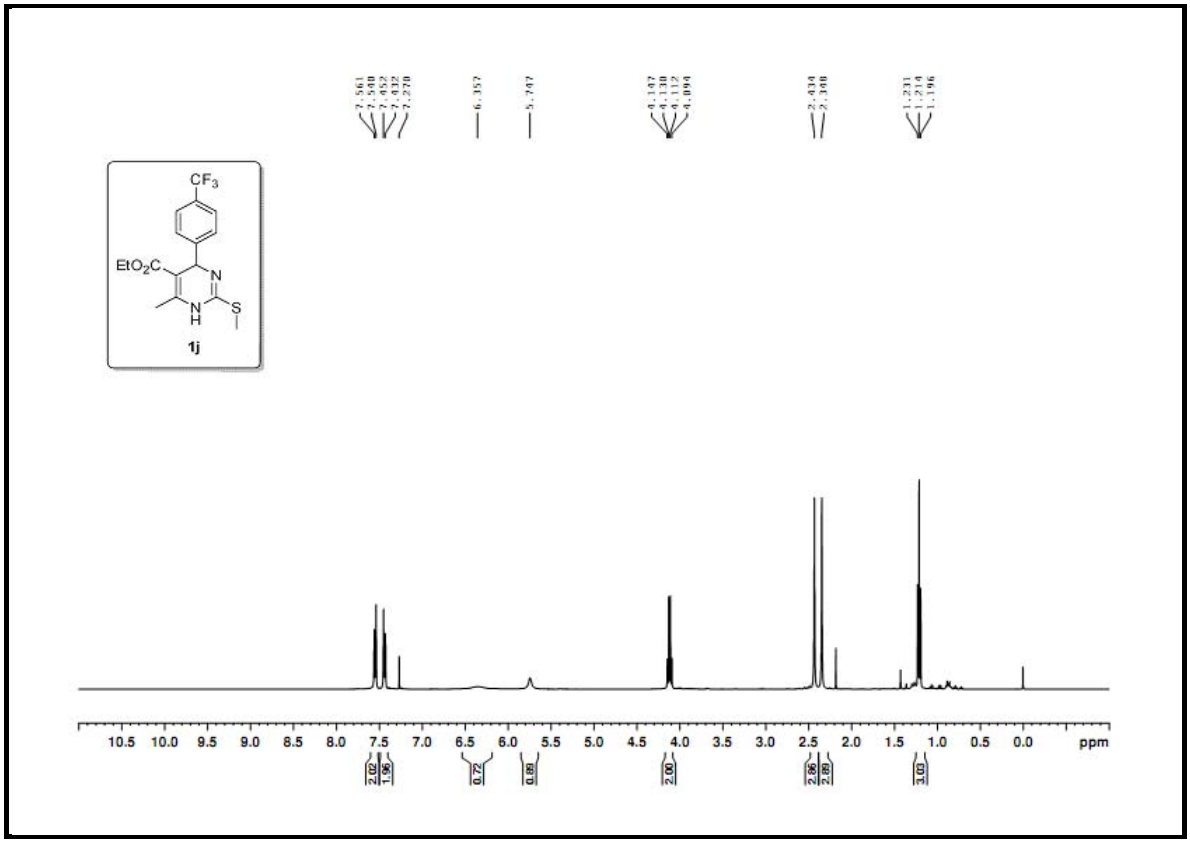

OCH3
OBn
EtO2C
N
N
H
S
1g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

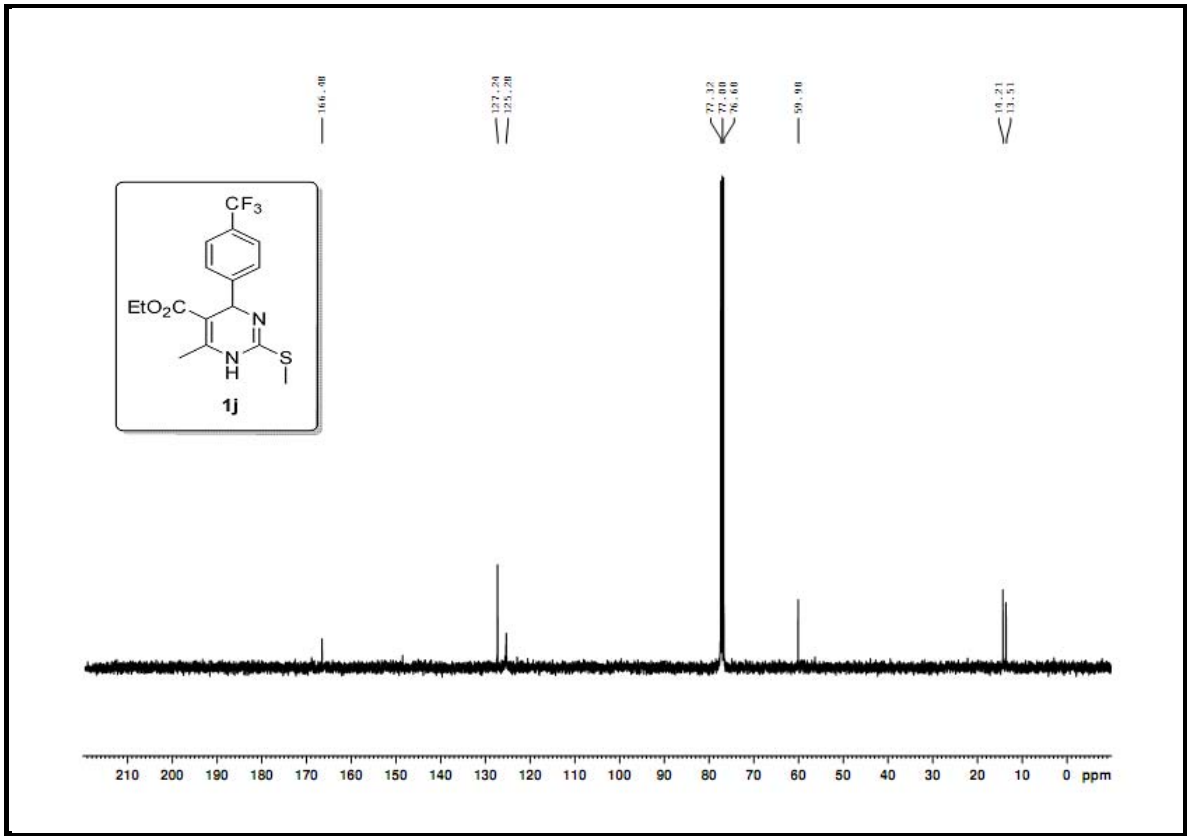

7.262
7.245
7.225
7.147
7.126
6.264
5.607
4.129
4.111
4.094
4.076
2.900
2.883
2.866
2.848
2.831
2.443
2.326
1.228
1.211
1.190
EtO2C
N
N
H
S
1h
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.51
2.02
0.77
1.05
2.00
1.02
3.01
2.94
9.10

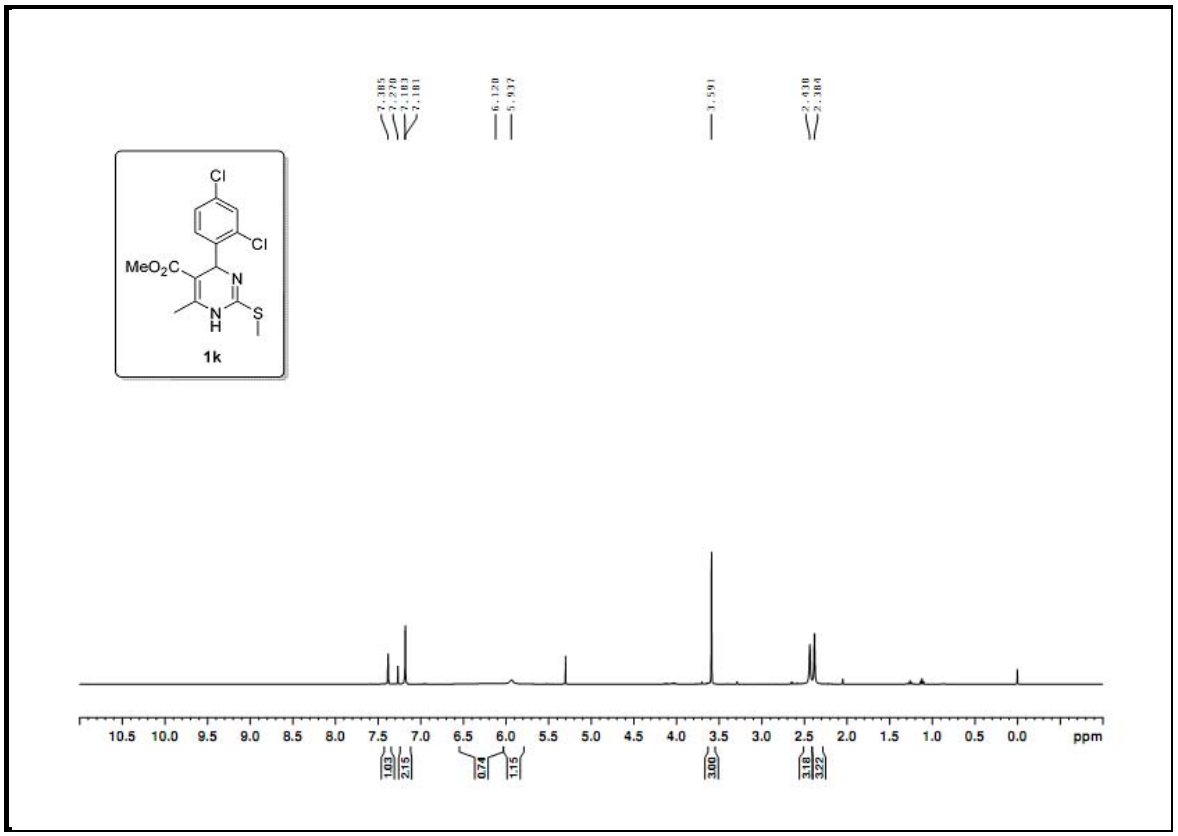

166.85
152.10
126.73
126.37
77.32
77.00
76.68
59.76
31.70
23.94
14.21
13.53
EtO2C
N
N
H
S
1h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

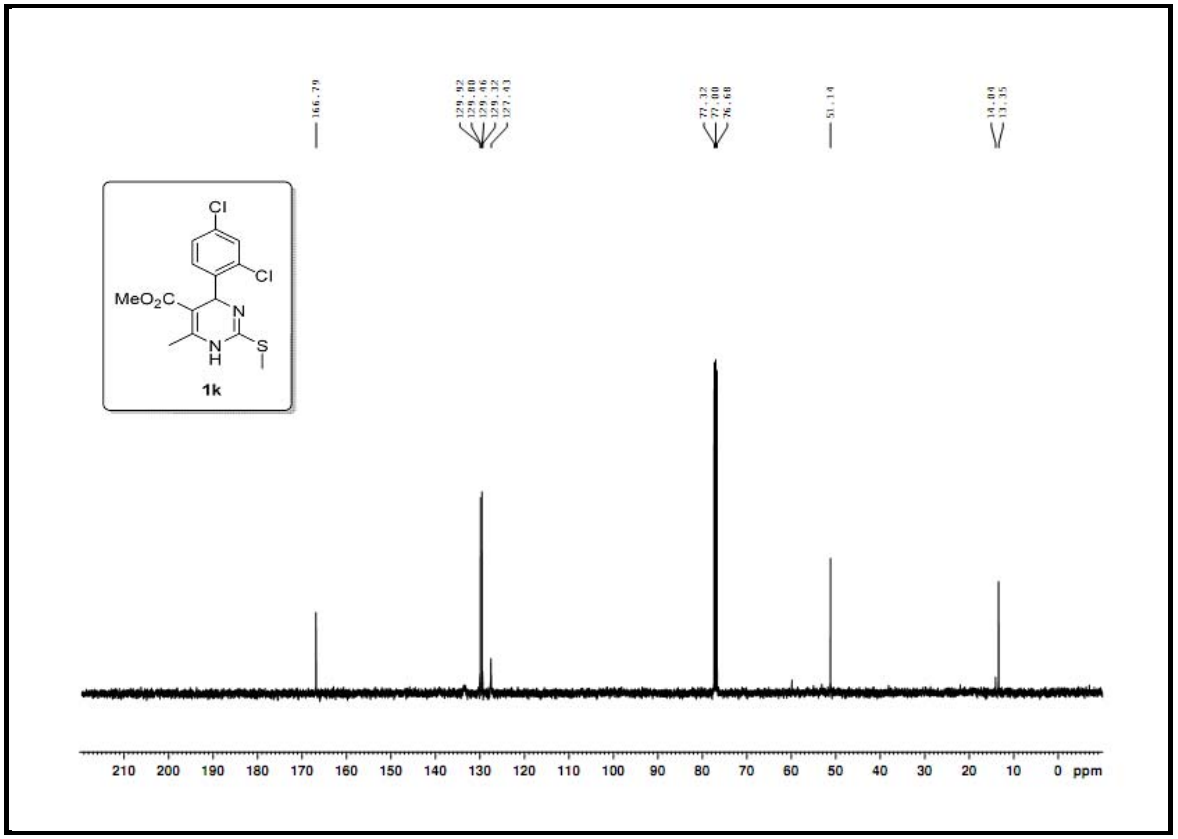

7.265
7.247
6.641
5.614
3.645
2.422
2.336
2.177
Cl
MeO2C
N
N
H
S
1i
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.66
0.90
1.01
3.08
3.00
2.94

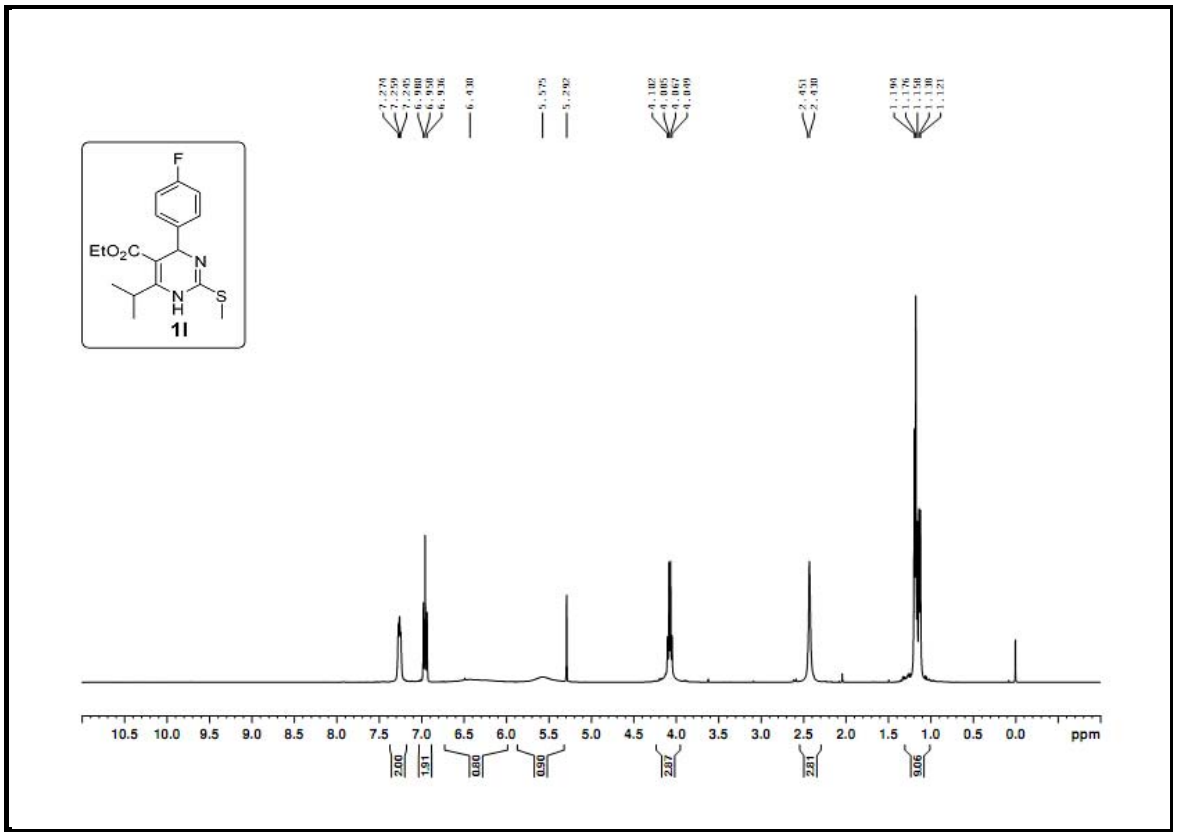

166.98
142.87
132.98
129.58
128.25
77.32
77.00
76.68
51.16
13.57
Cl
MeO2C
N
N
H
S
1i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

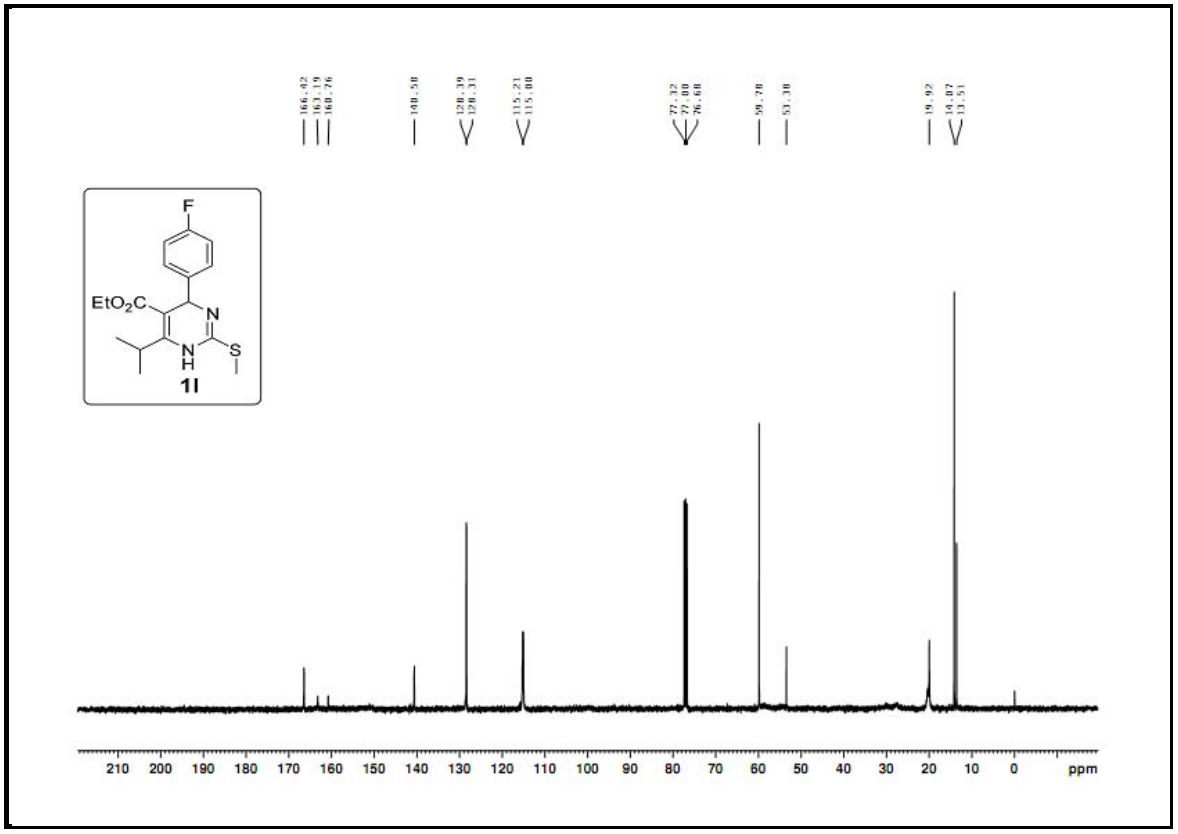

7.561
7.540
7.432
7.270
6.357
5.747
4.147
4.130
4.112
4.094
2.434
2.348
1.231
1.214
1.196
CF3
EtO2C
N
N
H
S
1j
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.02
1.96
0.72
0.89
2.00
2.96
2.89
3.03

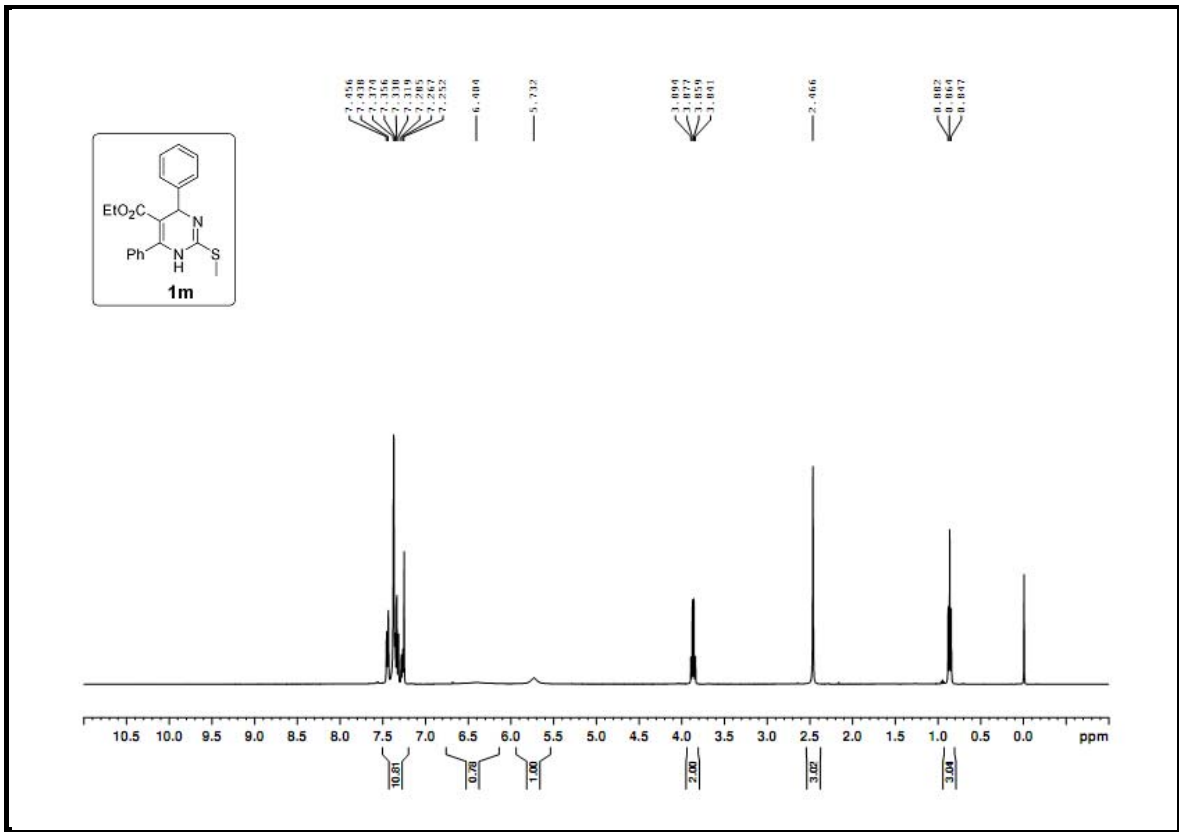

166.88
127.24
125.28
77.32
77.00
76.68
59.90
18.21
13.51
CF3
EtO2C
N
N
H
S
1j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

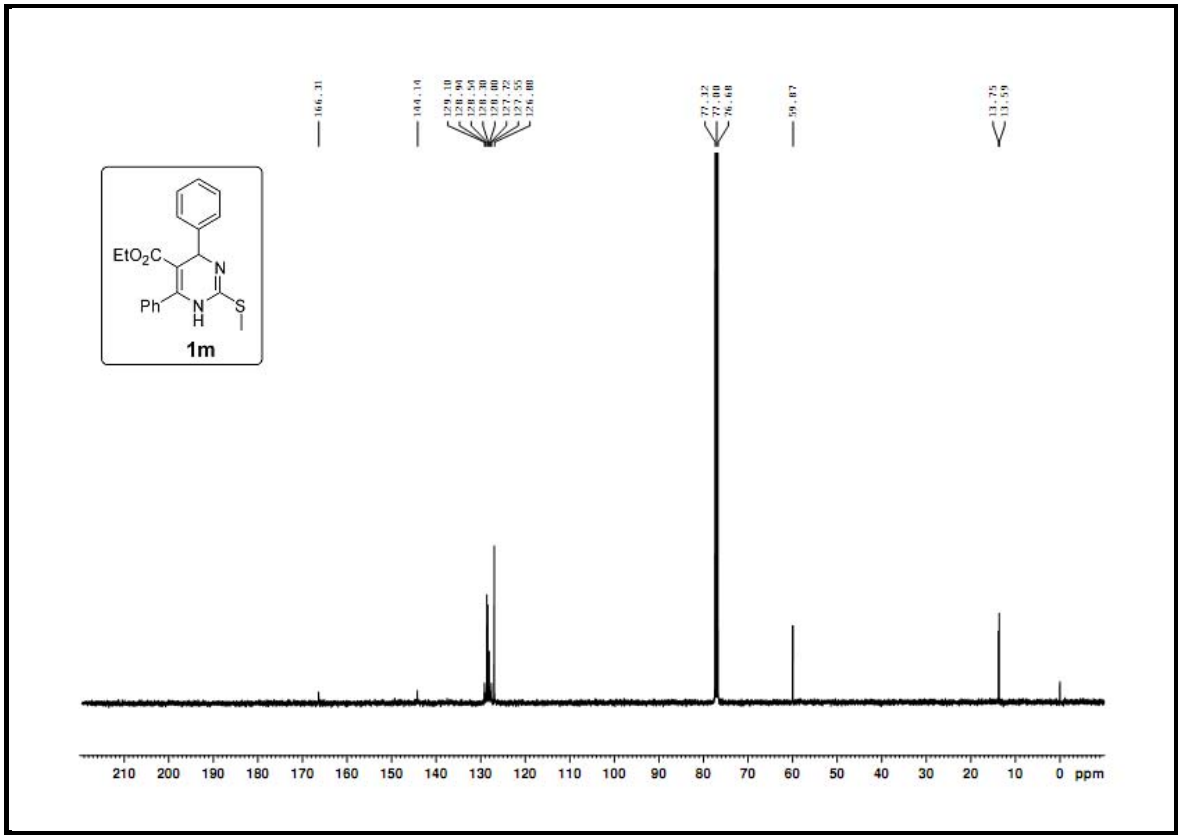

7.385
7.270
7.183
7.181
6.120
5.937
3.591
2.430
2.384
Cl
Cl
MeO2C
N
N
H
S
1k
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.03
2.15
0.74
1.15
3.00
3.18
3.22

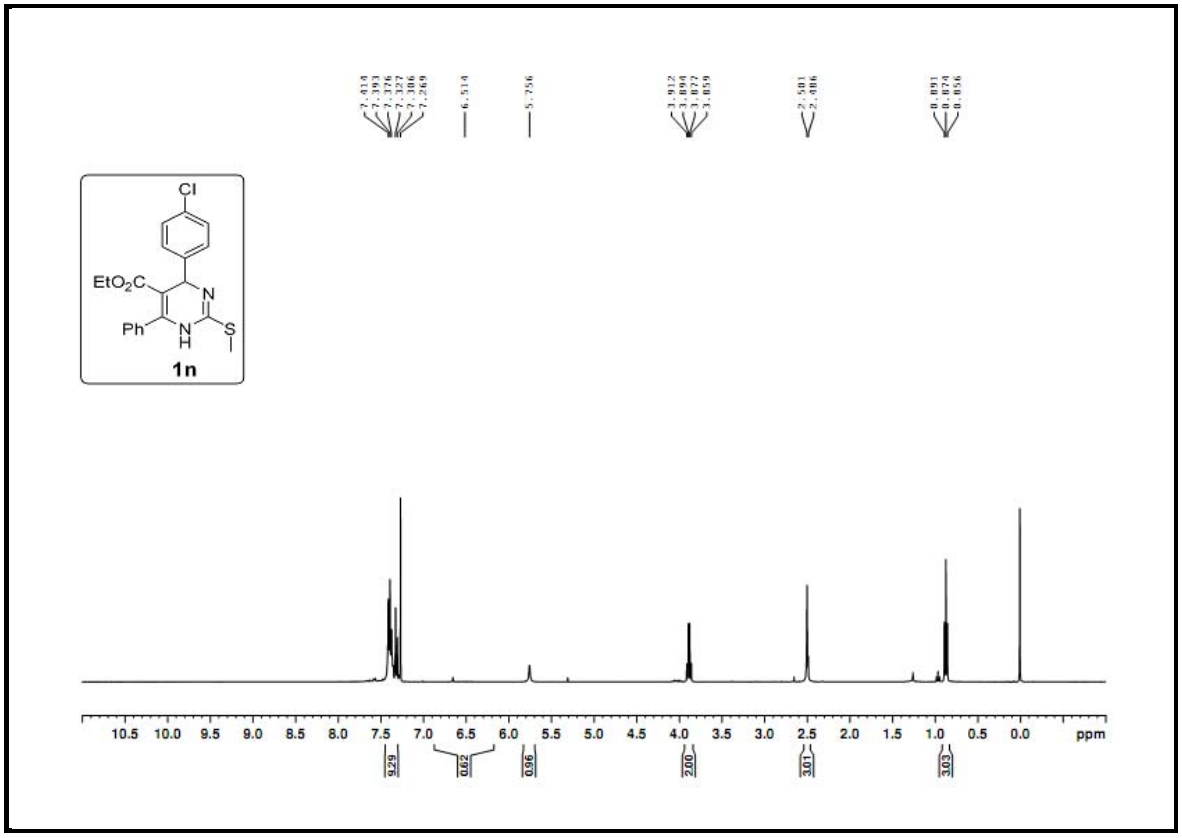

166.79
129.92
129.80
129.46
129.32
127.43
77.32
77.00
76.68
51.14
14.04
13.35
Cl
Cl
MeO2C
N
N
H
S
1k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

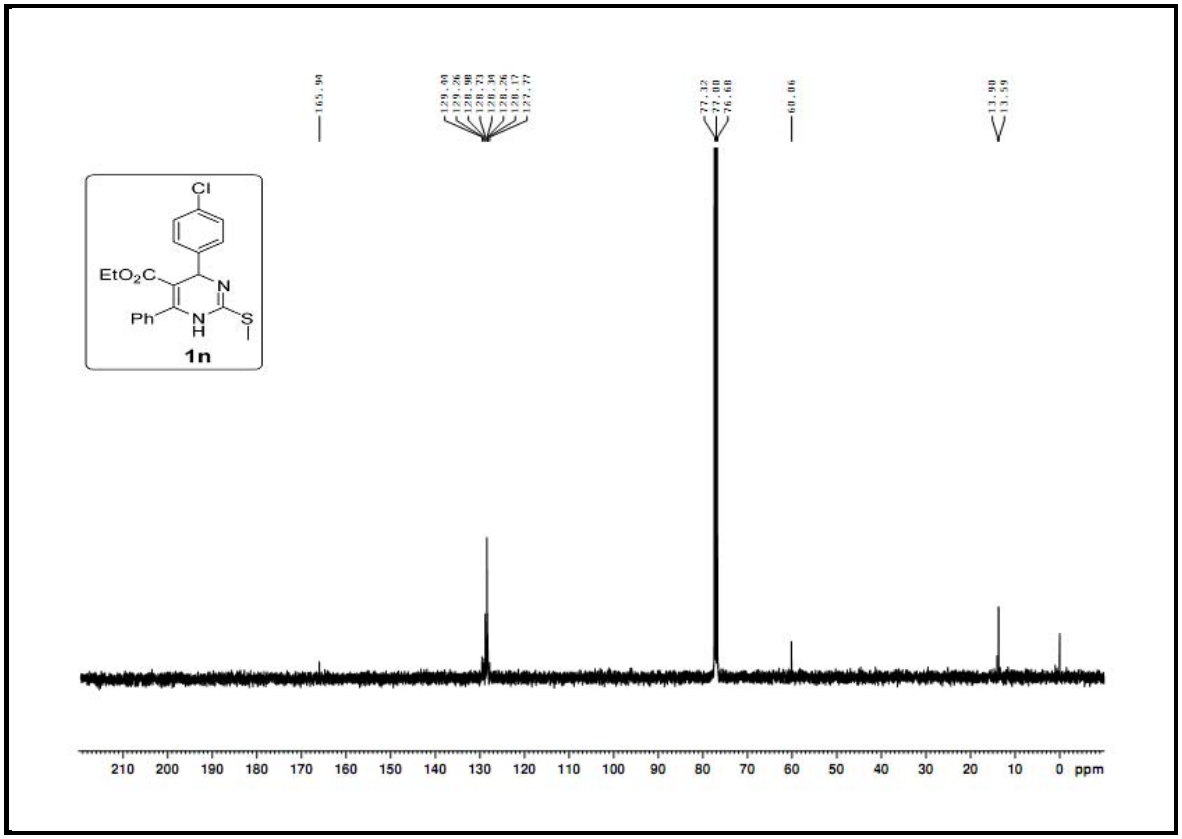

F
EtO2C
N
N
H
S
1l
7.270
7.259
7.245
6.980
6.950
6.936
6.430
5.575
5.292
4.102
4.085
4.067
4.049
2.451
2.430
1.190
1.176
1.158
1.138
1.121
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
1.91
0.80
0.90
2.87
2.81
9.06

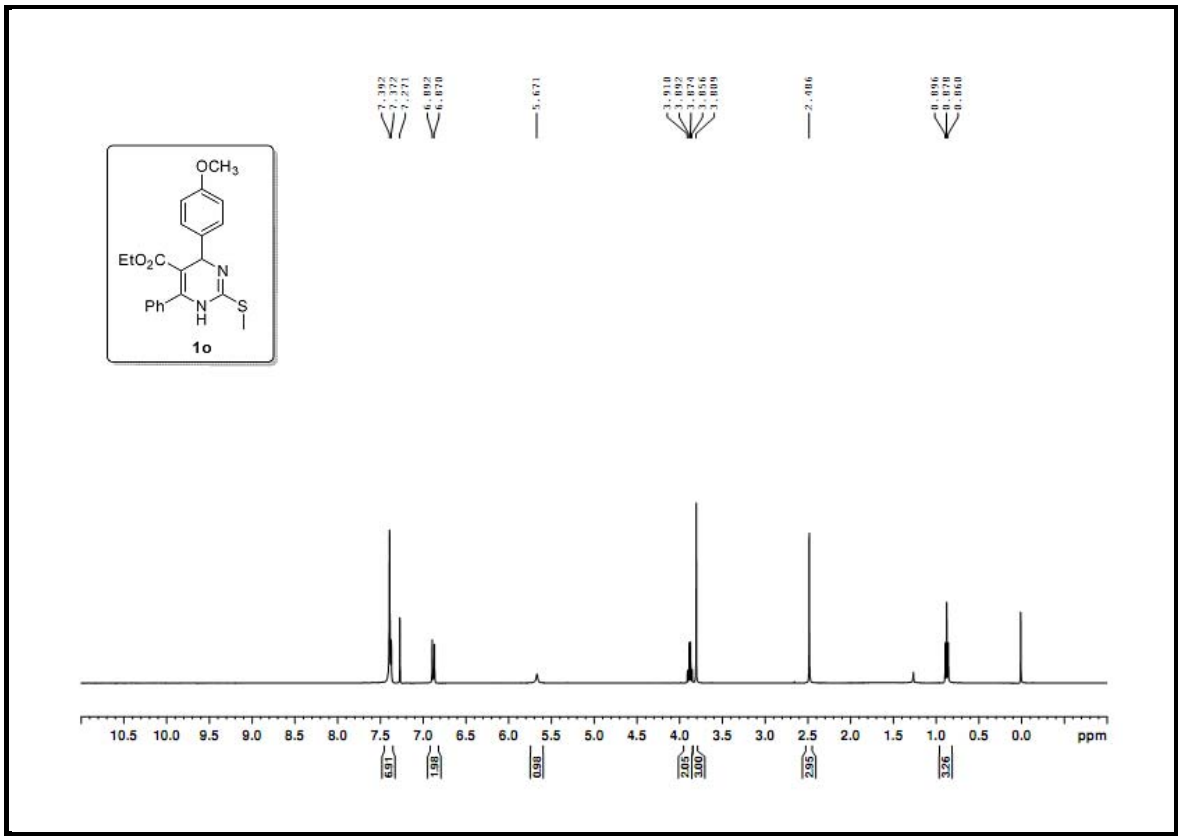

F
EtO2C
N
N
H
S
1l
166.42
163.19
160.76
140.58
128.39
128.31
115.21
115.00
77.32
77.00
76.68
59.78
53.38
19.92
14.07
13.51
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

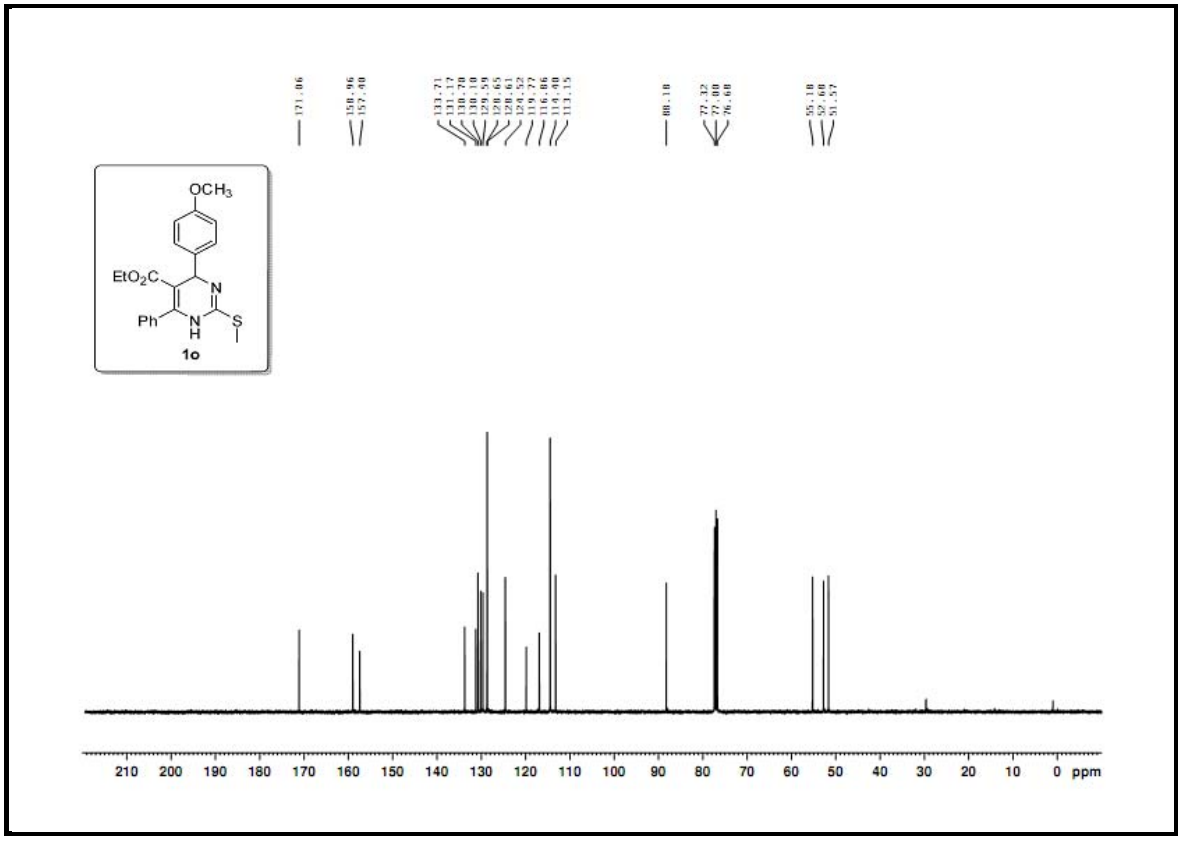

7.456
7.438
7.374
7.356
7.338
7.319
7.285
7.267
7.252
6.004
5.732
3.894
3.877
3.859
3.841
2.466
0.882
0.864
0.847
EtO2C
Ph
N
H
S
1m
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
10.81
0.78
1.00
2.00
3.07
3.04

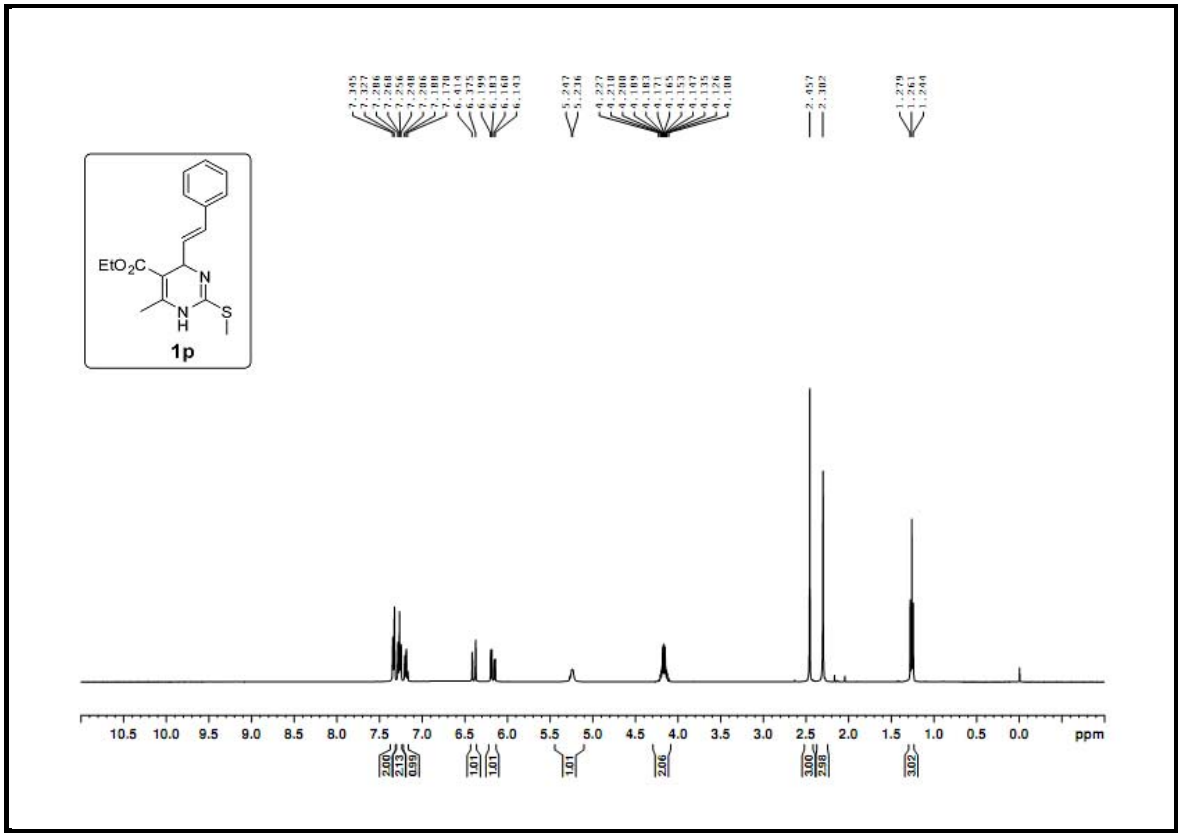

166.31
144.14
129.10
128.96
128.56
128.38
128.08
127.72
127.55
126.88
77.32
77.00
76.68
59.87
13.75
13.59
EtO2C
Ph
N
H
S
1m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

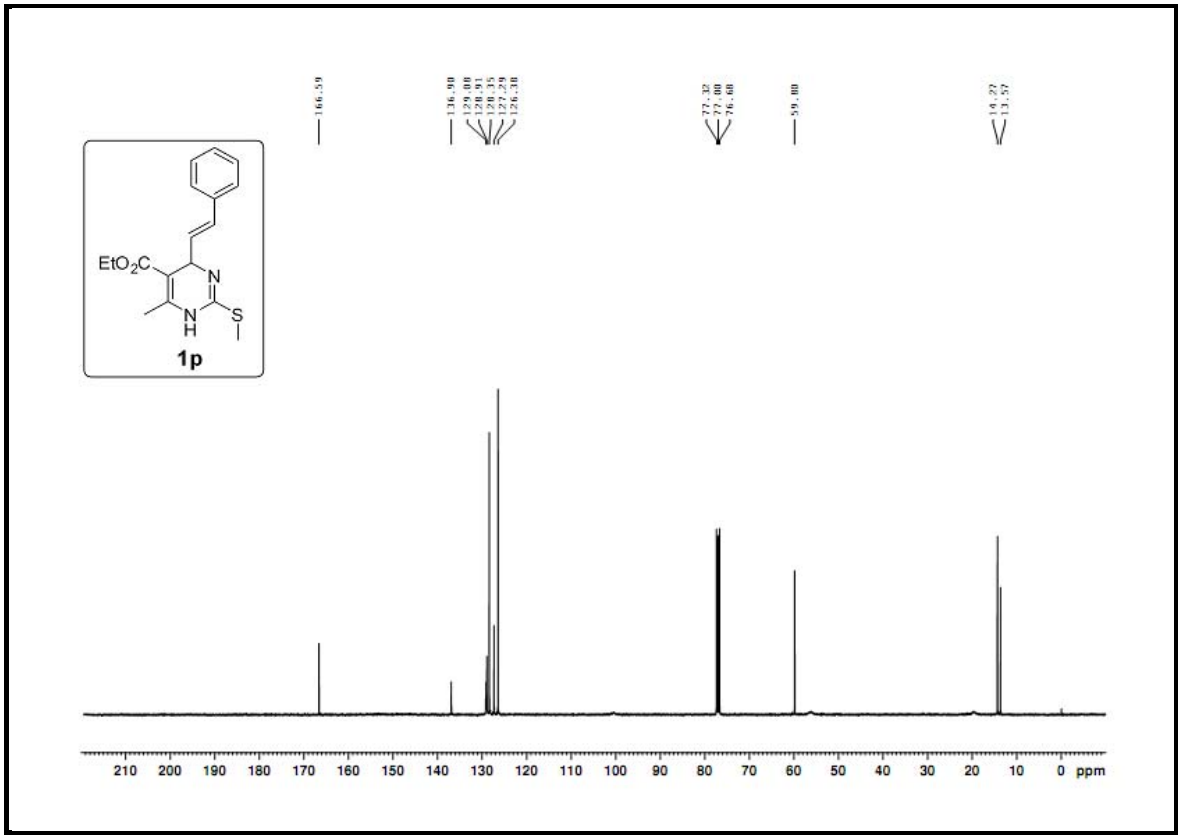

7.414
7.393
7.376
7.327
7.306
7.269
6.514
5.756
3.912
3.894
3.877
3.859
2.501
2.486
0.891
0.874
0.856
Cl
EtO2C
N
Ph
N
H
S
1n
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
9.29
0.62
0.96
2.00
3.01
3.03

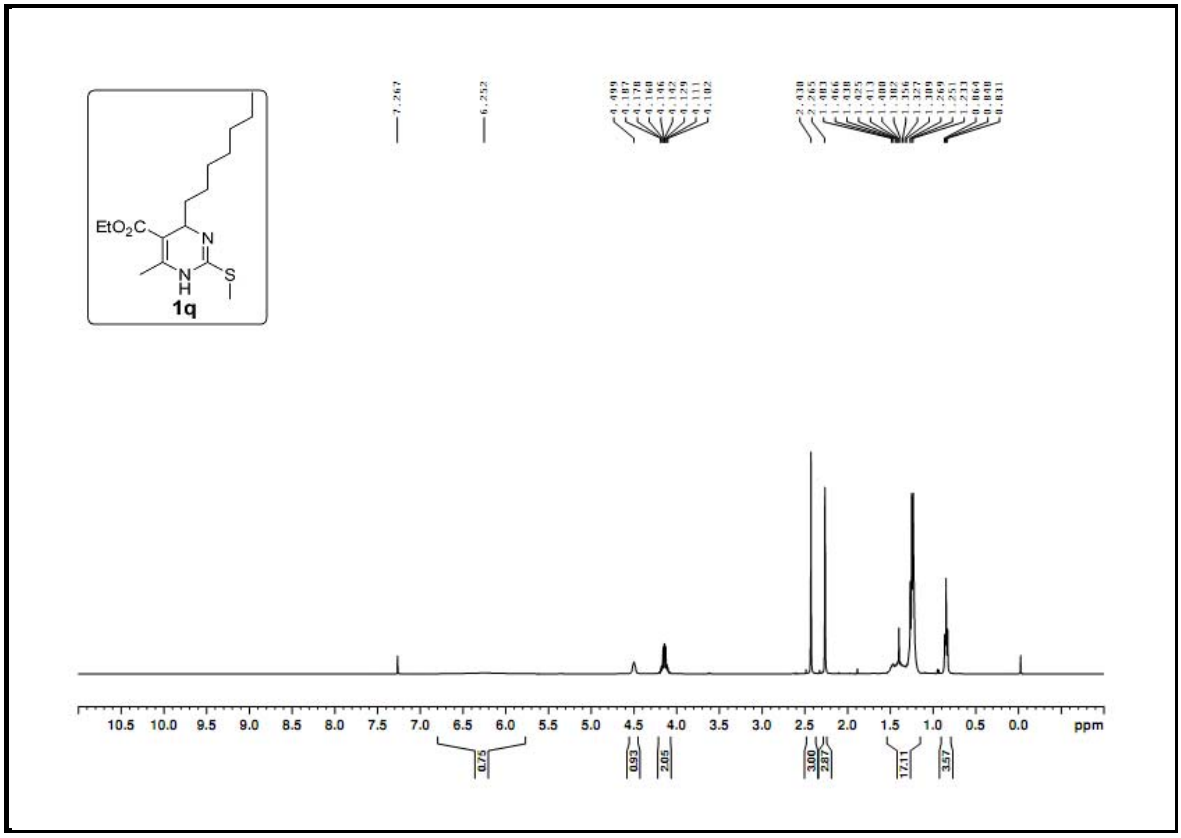

165.99
129.90
129.26
128.88
128.73
128.34
128.26
128.17
127.77
77.32
77.00
76.68
60.86
13.90
13.59
Cl
EtO2C
N
Ph
N
H
S
1n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

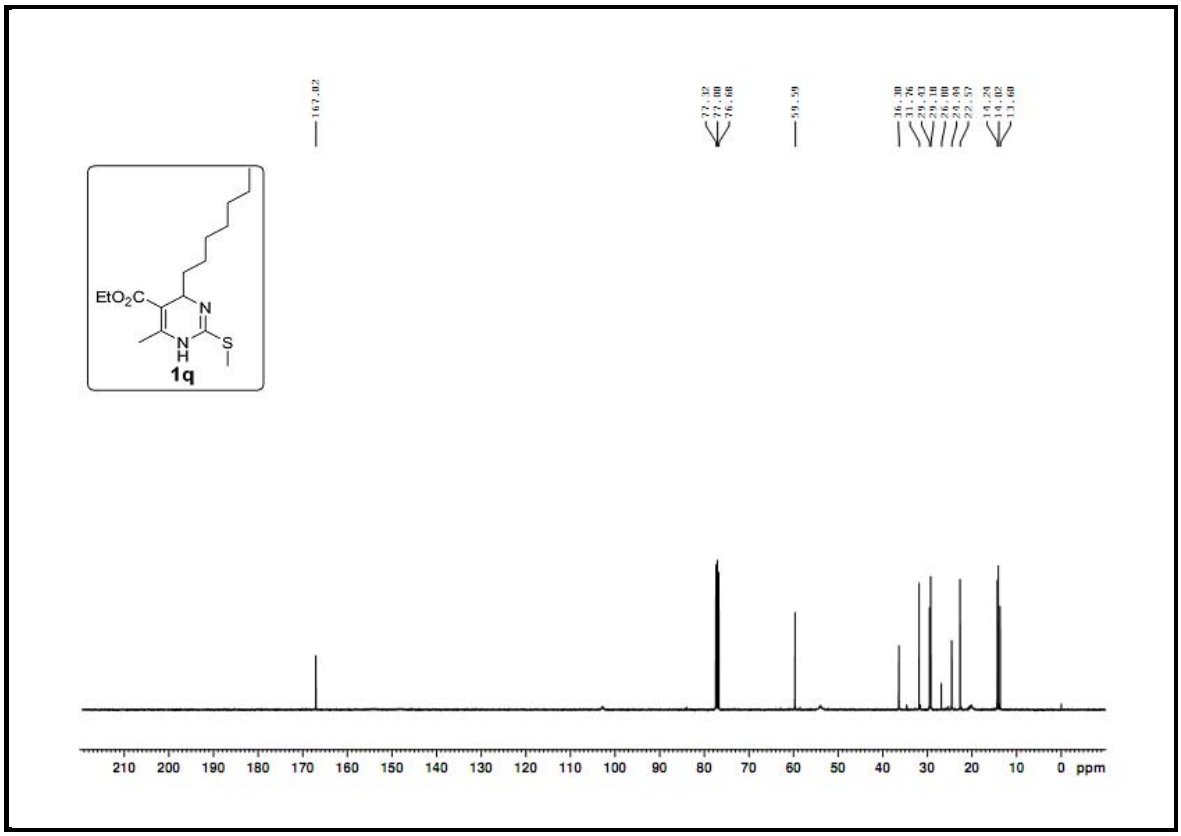

7.392
7.372
7.271
6.892
6.870
5.671
3.910
3.892
3.873
3.856
3.809
2.486
0.896
0.878
0.860
OCH3
EtO2C
N
Ph
N
H
S
1o
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
6.91
1.98
0.98
2.05
3.00
2.95
3.26

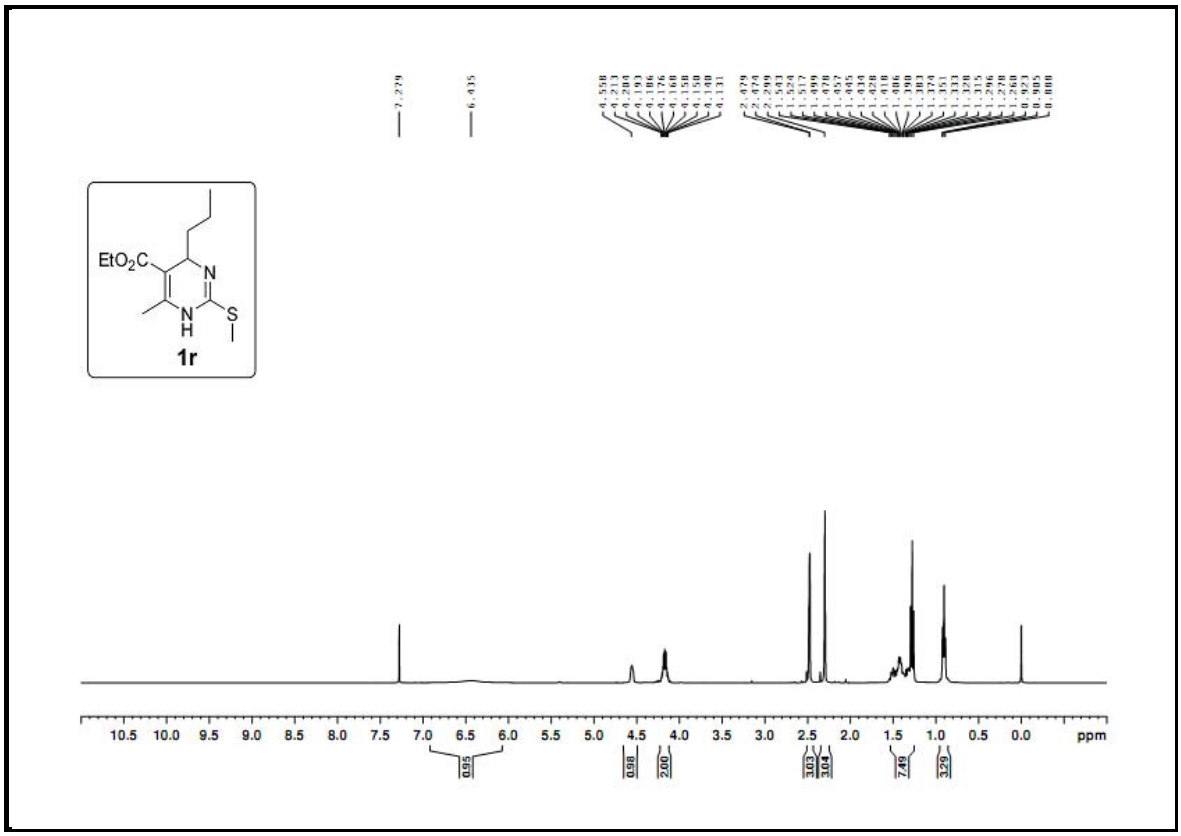

171.06
158.96
157.40
133.71
131.17
130.70
130.10
129.59
128.65
128.61
124.52
119.77
116.86
114.48
113.15
88.18
77.32
77.08
76.68
55.18
52.68
51.57
OCH3
EtO2C
N
Ph
N
H
S
1o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

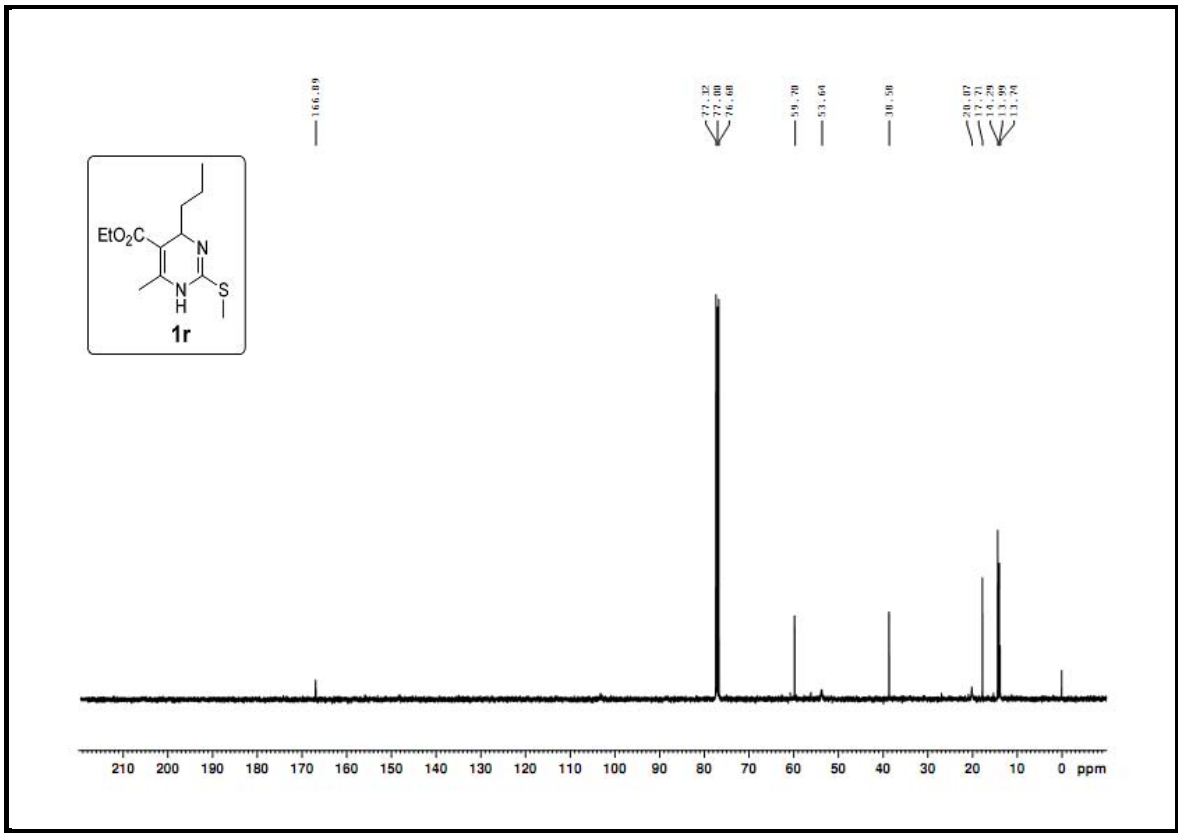

1p
ppm

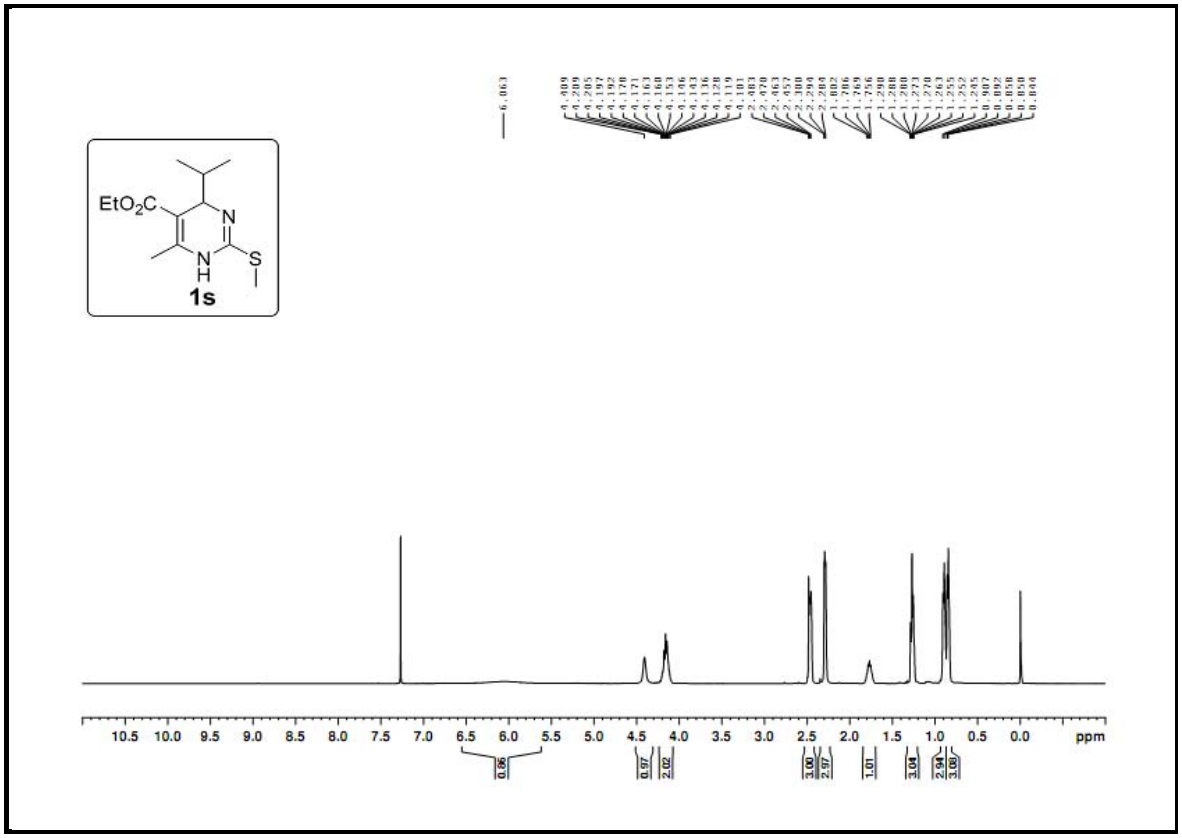

1p
ppm

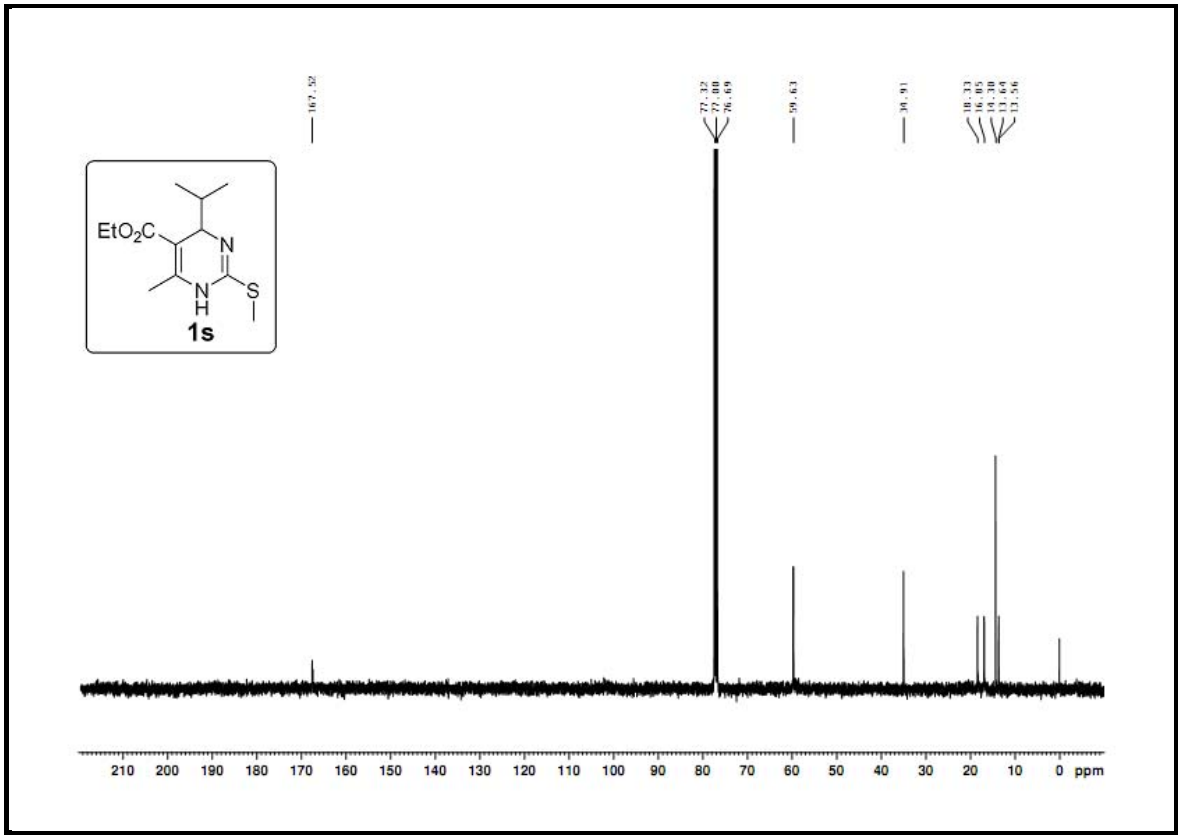

EtO2C
N
N
H
S
1q
7.267
6.252
6.499
6.187
6.178
6.168
6.156
6.146
6.142
6.129
6.111
6.102
2.438
2.265
1.883
1.466
1.438
1.425
1.413
1.400
1.382
1.356
1.327
1.309
1.269
1.251
1.233
0.864
0.848
0.831
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.75
0.93
2.65
3.00
2.87
17.11
3.57

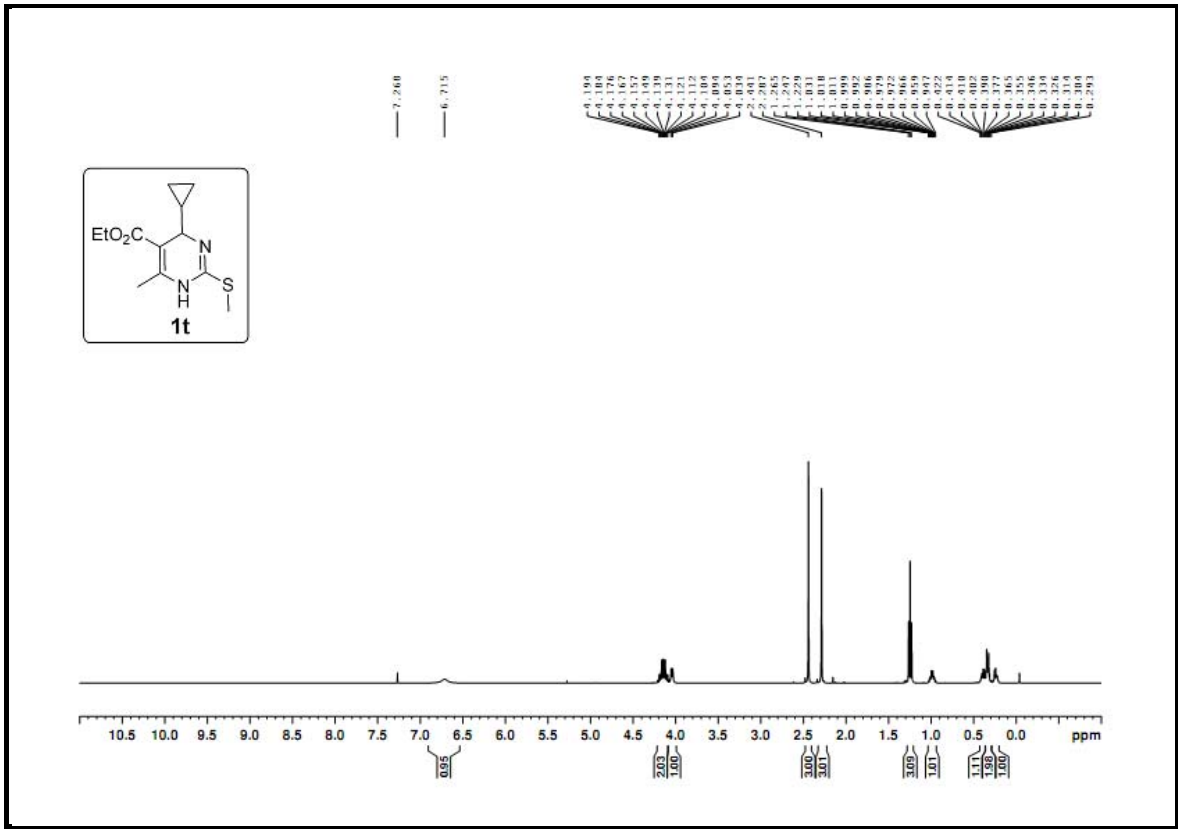

EtO2C
N
N
H
S
1q
167.82
77.32
77.00
76.68
59.59
36.30
31.76
29.93
29.18
29.08
26.04
22.57
14.28
14.02
13.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

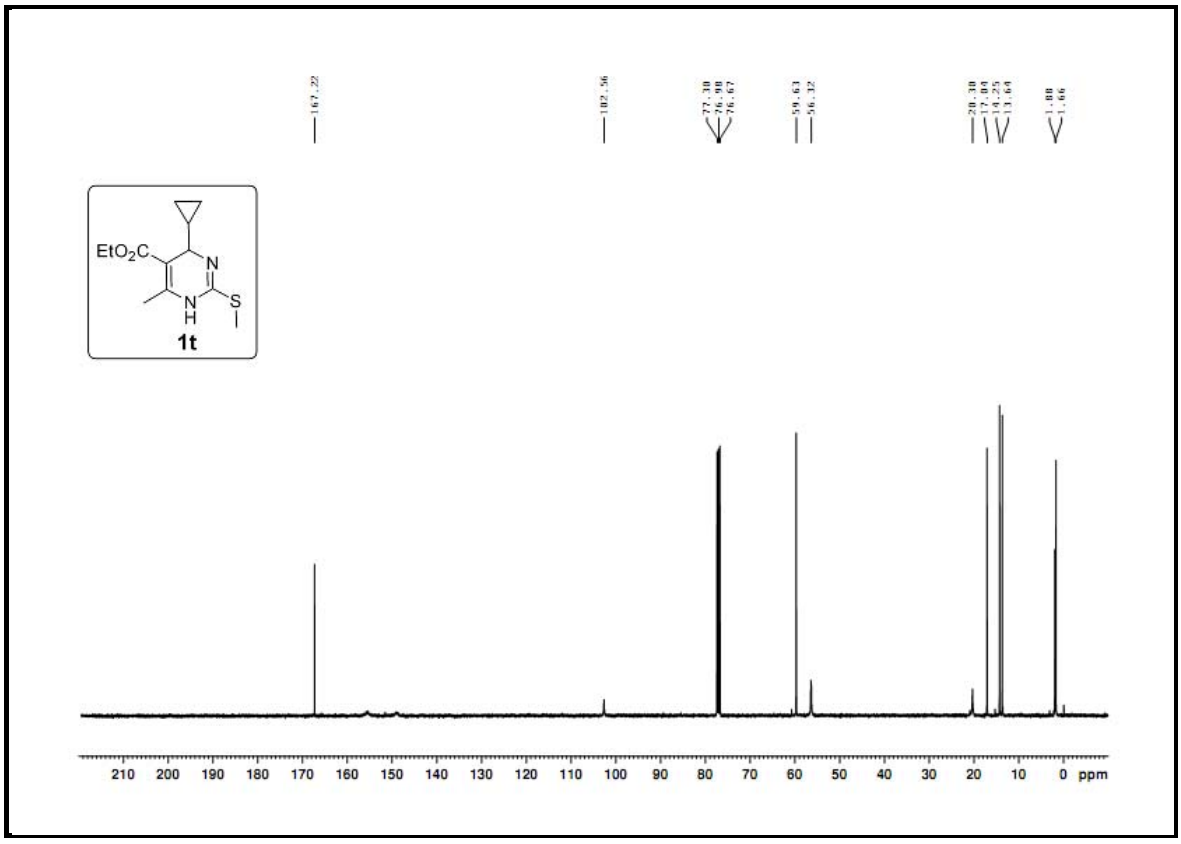

7.279
6.435
4.558
4.213
4.204
4.193
4.186
4.176
4.168
4.158
4.150
4.140
4.131
2.479
2.474
2.299
2.293
1.529
1.522
1.499
1.478
1.457
1.445
1.438
1.428
1.418
1.406
1.390
1.383
1.374
1.351
1.333
1.328
1.315
1.296
1.278
1.268
0.923
0.905
0.888
EtO2C
N
N
H
S
1r
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.95
0.98
2.00
3.03
3.04
7.49
3.29

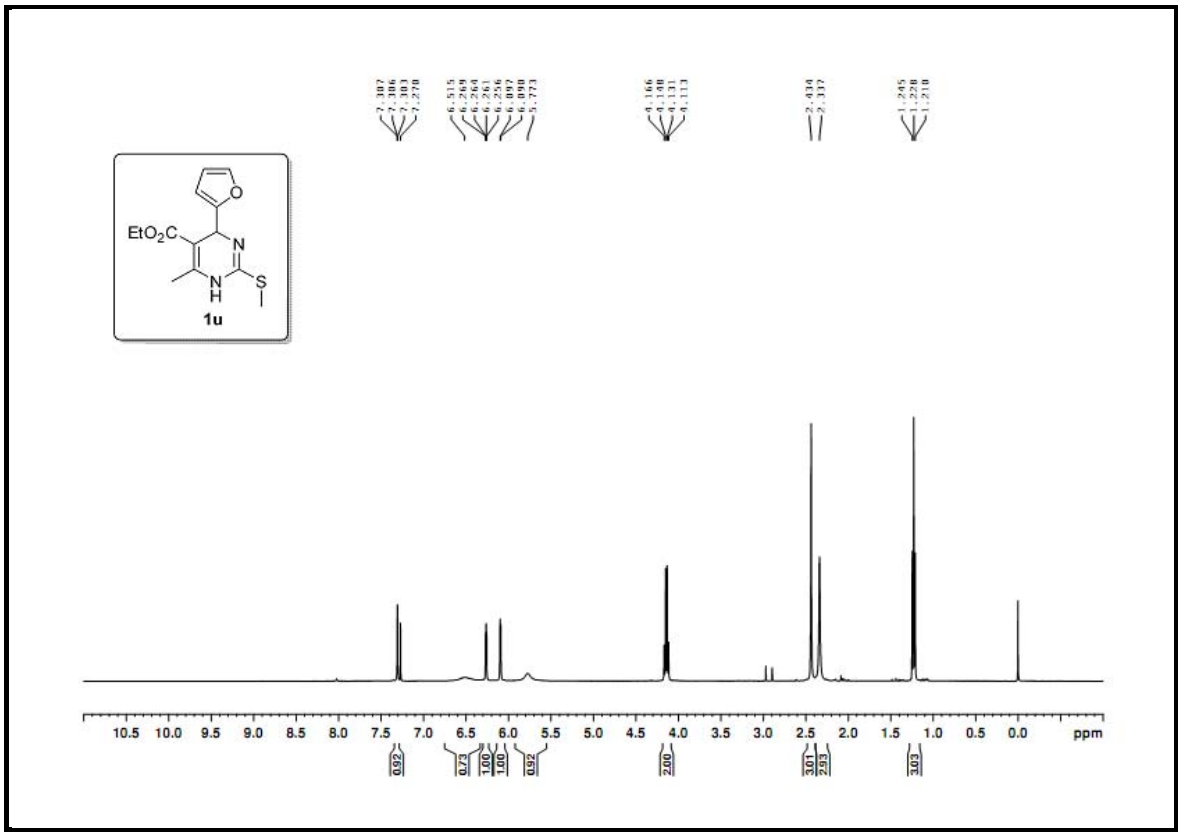

166.89
77.32
77.00
76.68
59.70
53.64
38.50
20.87
17.71
14.29
13.99
13.74
EtO2C
N
N
H
S
1r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

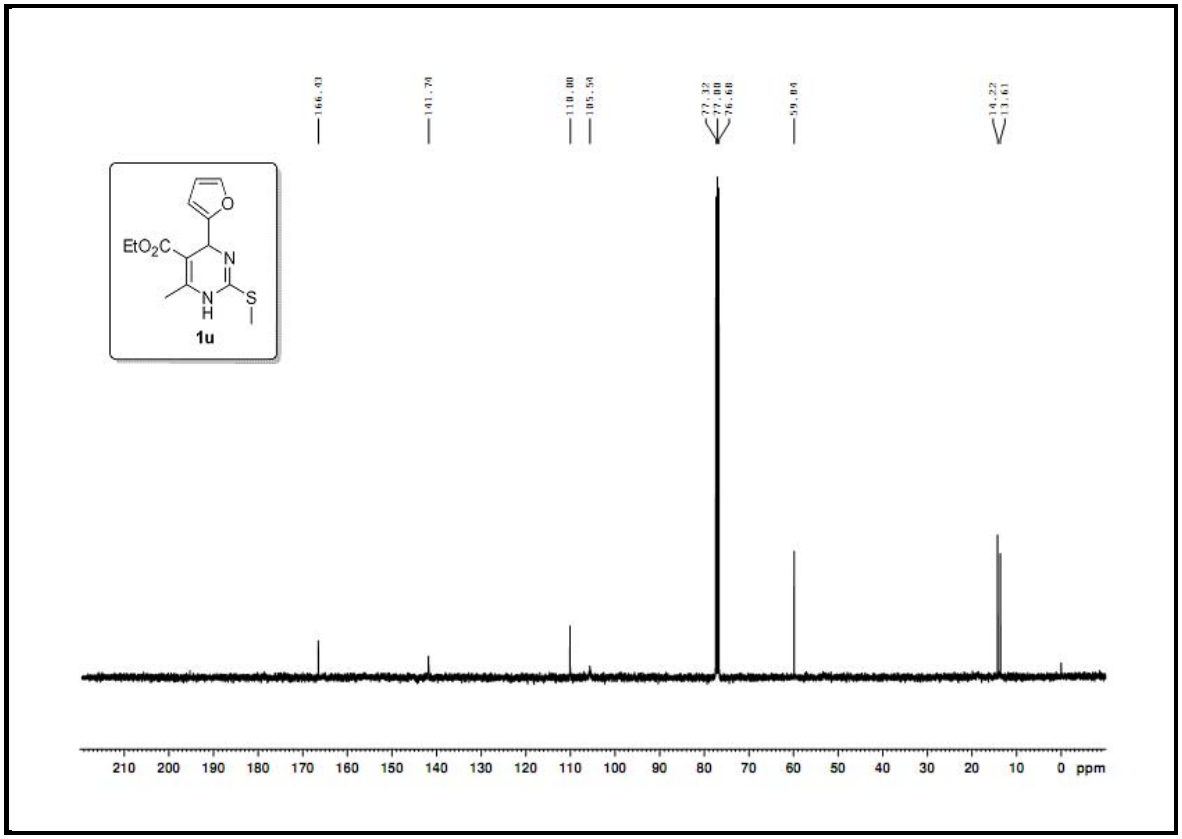

EtO2C
N
N
H
S
1s
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

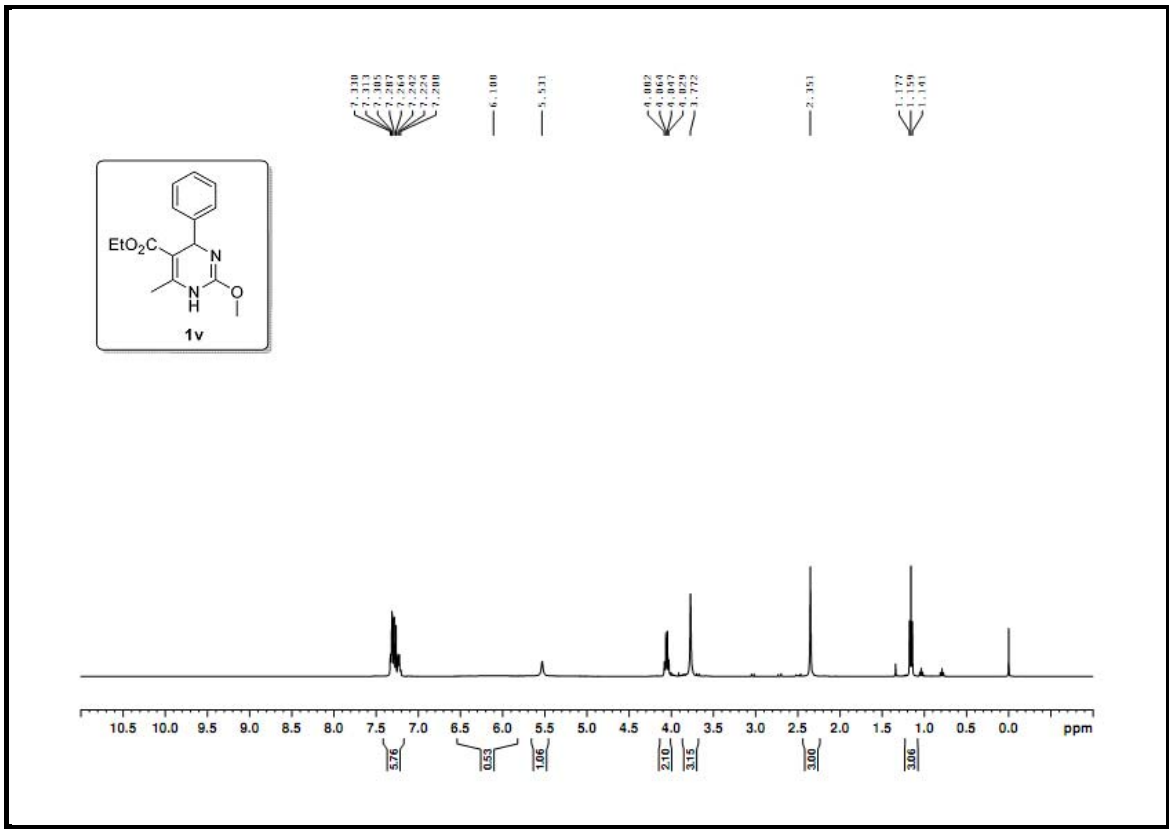

EtO2C
N
N
H
S
1s
167.52
77.32
77.00
76.69
59.63
34.91
18.33
16.05
14.30
13.64
13.56
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

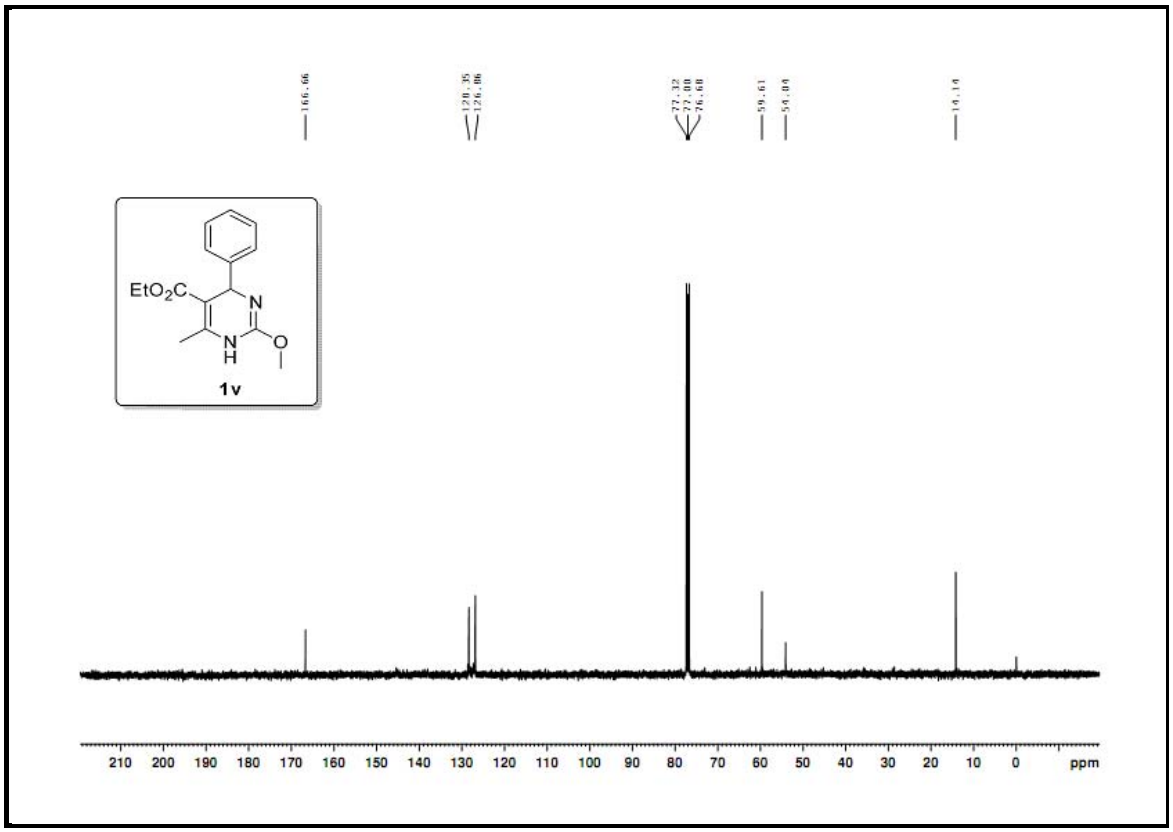

7.268
6.715
EtO2C
N
N
H
S
1t
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.95
2.03
1.00
3.00
3.01
3.09
1.01
1.19
1.98
1.00

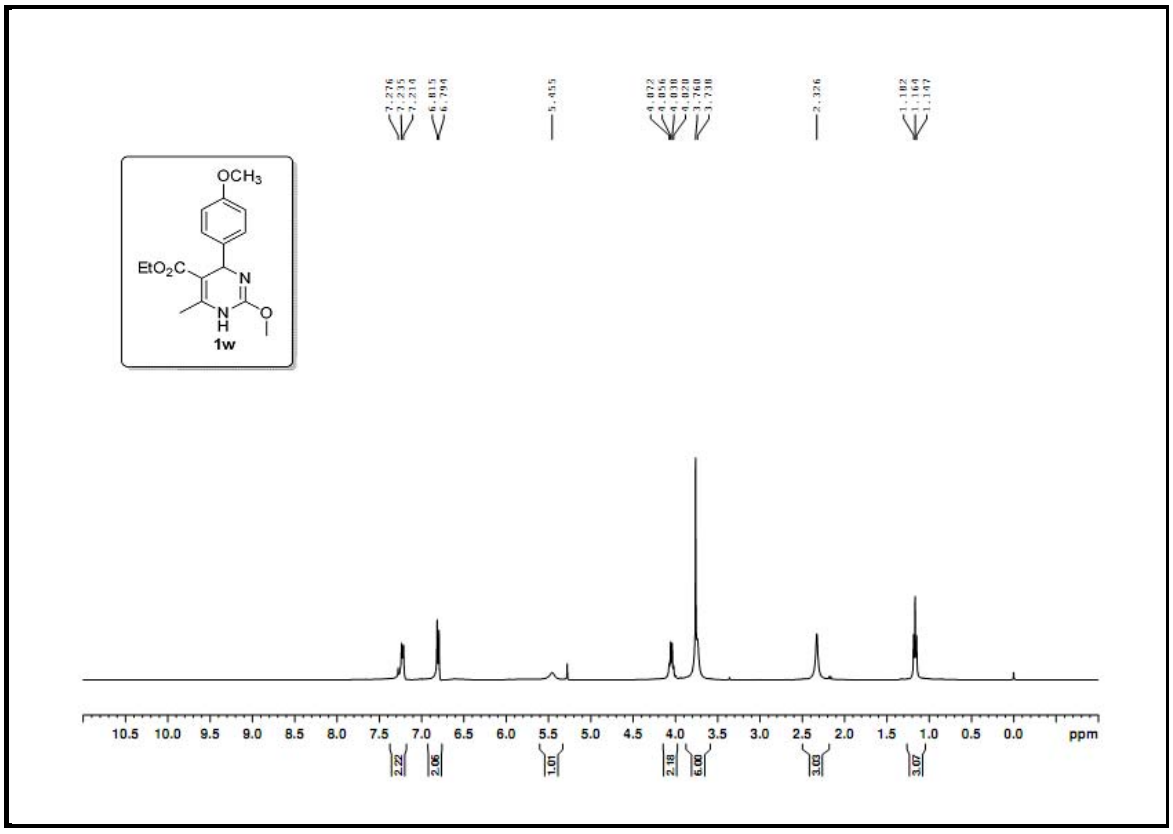

167.22
102.56
77.30
77.00
76.67
59.63
56.32
28.38
17.10
14.25
13.64
1.88
1.66
EtO2C
N
N
H
S
1t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

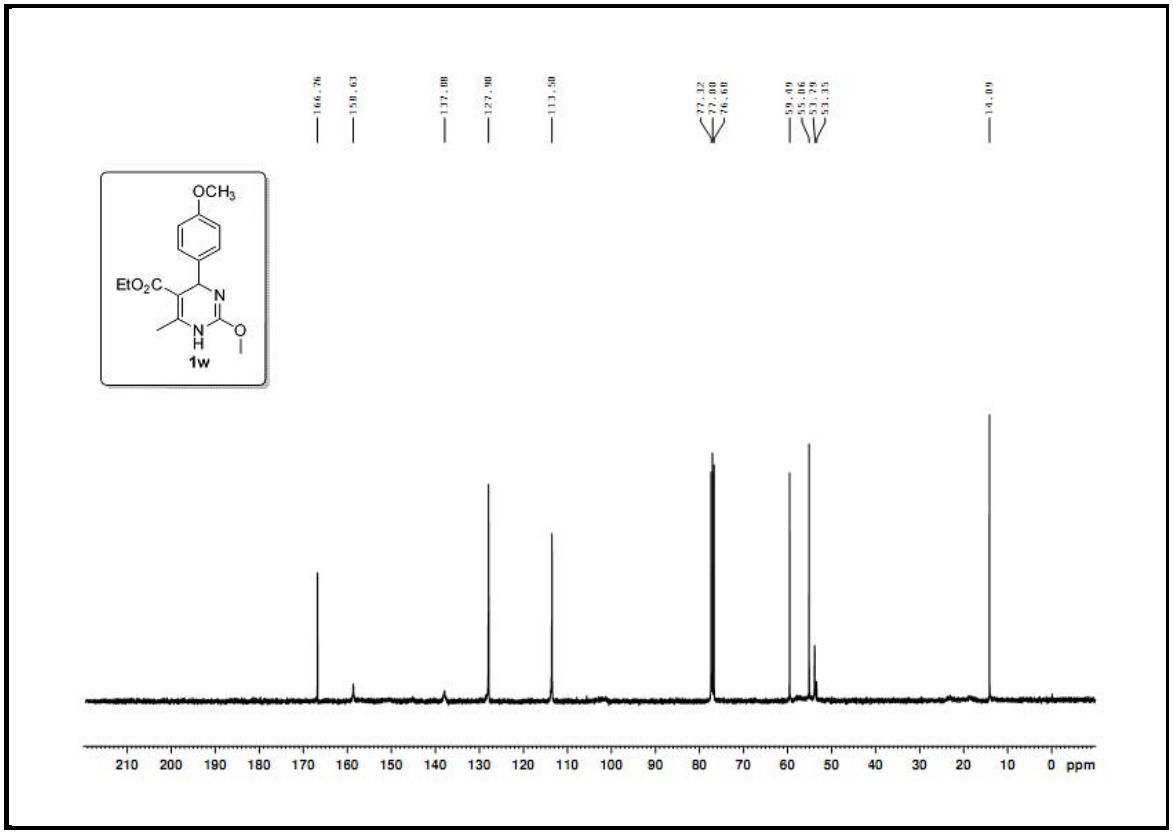

7.307
7.286
7.283
7.270
6.515
6.269
6.264
6.261
6.256
6.097
6.090
5.773
4.166
4.148
4.131
4.113
2.434
2.317
1.245
1.228
1.210
EtO2C
N
S
N
H
1u
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.92
0.73
1.00
1.00
0.92
2.00
3.01
2.93
3.03

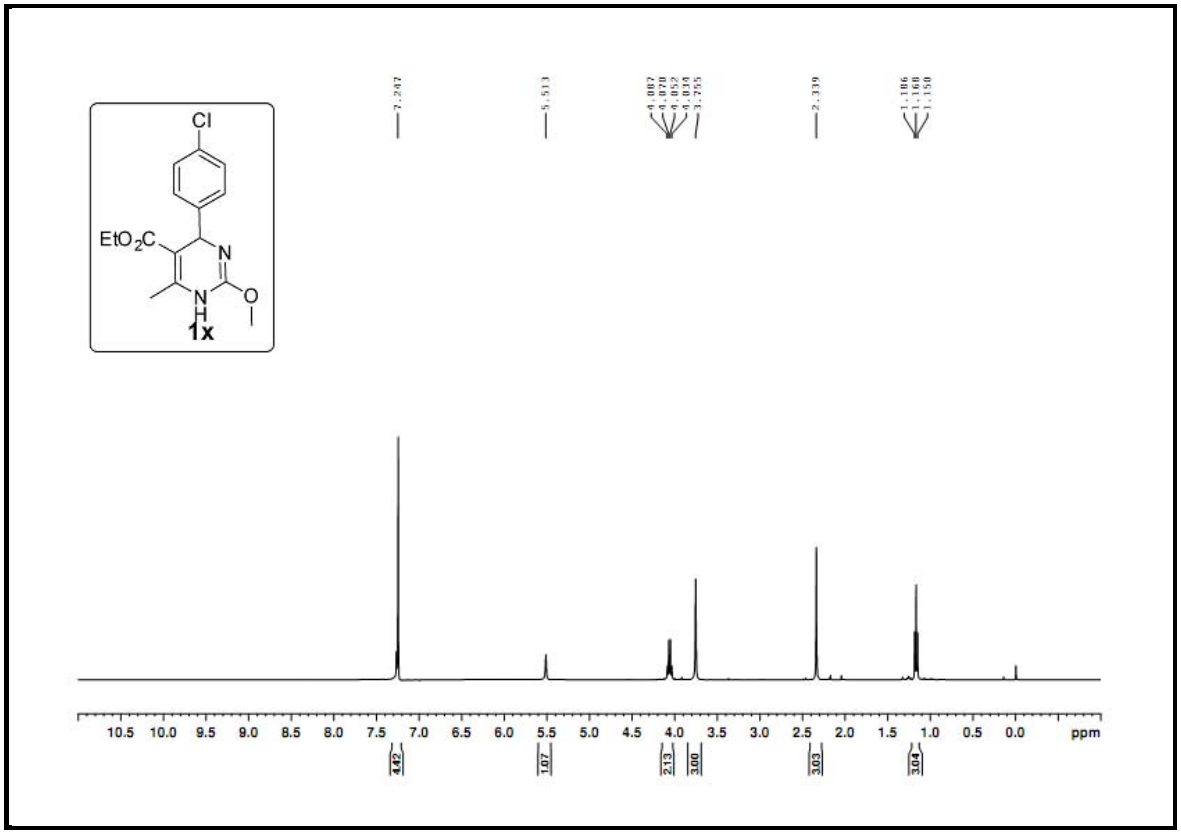

166.43
141.79
118.80
105.59
77.32
77.00
76.68
59.84
14.22
13.61
EtO2C
N
S
N
H
1u
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

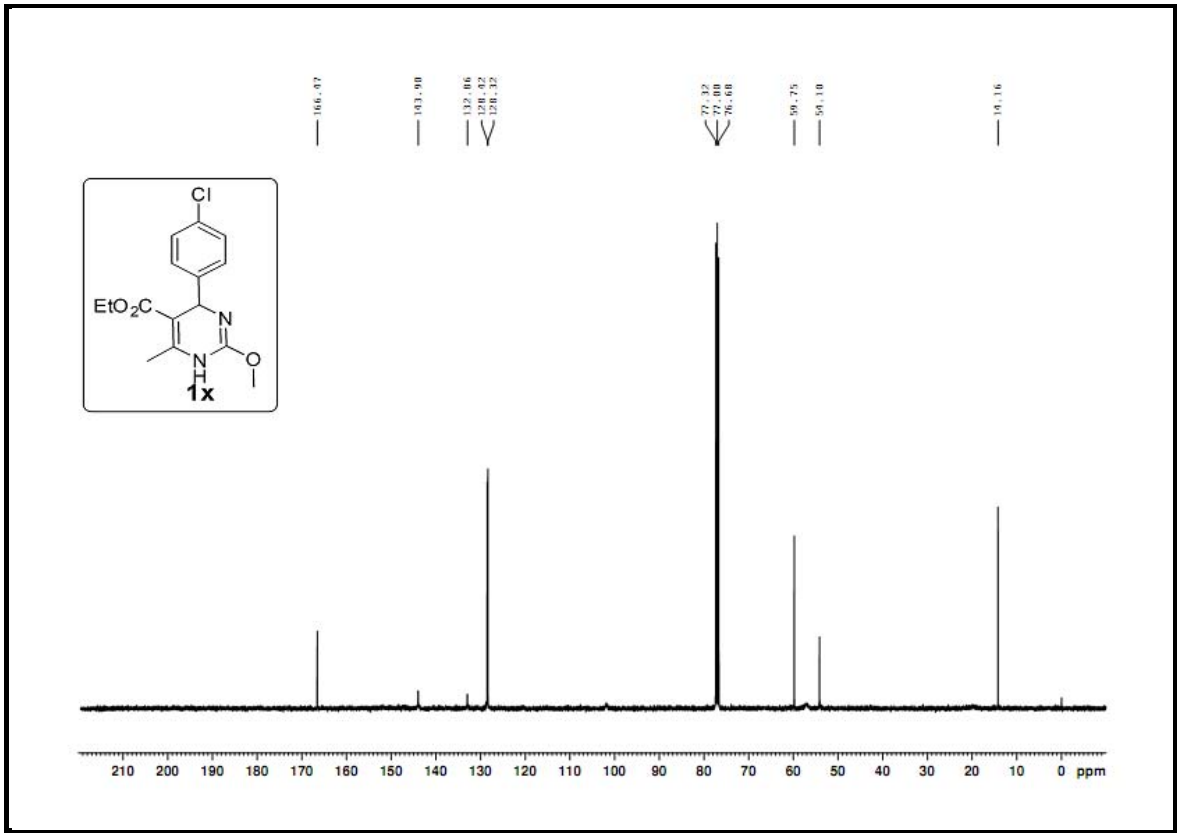

7.330
7.313
7.305
7.287
7.264
7.252
7.229
7.208
6.108
5.531
4.082
4.064
4.047
4.029
1.772
2.351
1.172
1.159
1.141
EtO2C
N
N
H
O
1v
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
5.76
0.53
1.06
2.10
3.15
3.00
3.06


166.66
120.35
126.86
77.32
77.00
76.68
59.61
54.04
14.14
EtO2C
N
N
H
O
1v
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

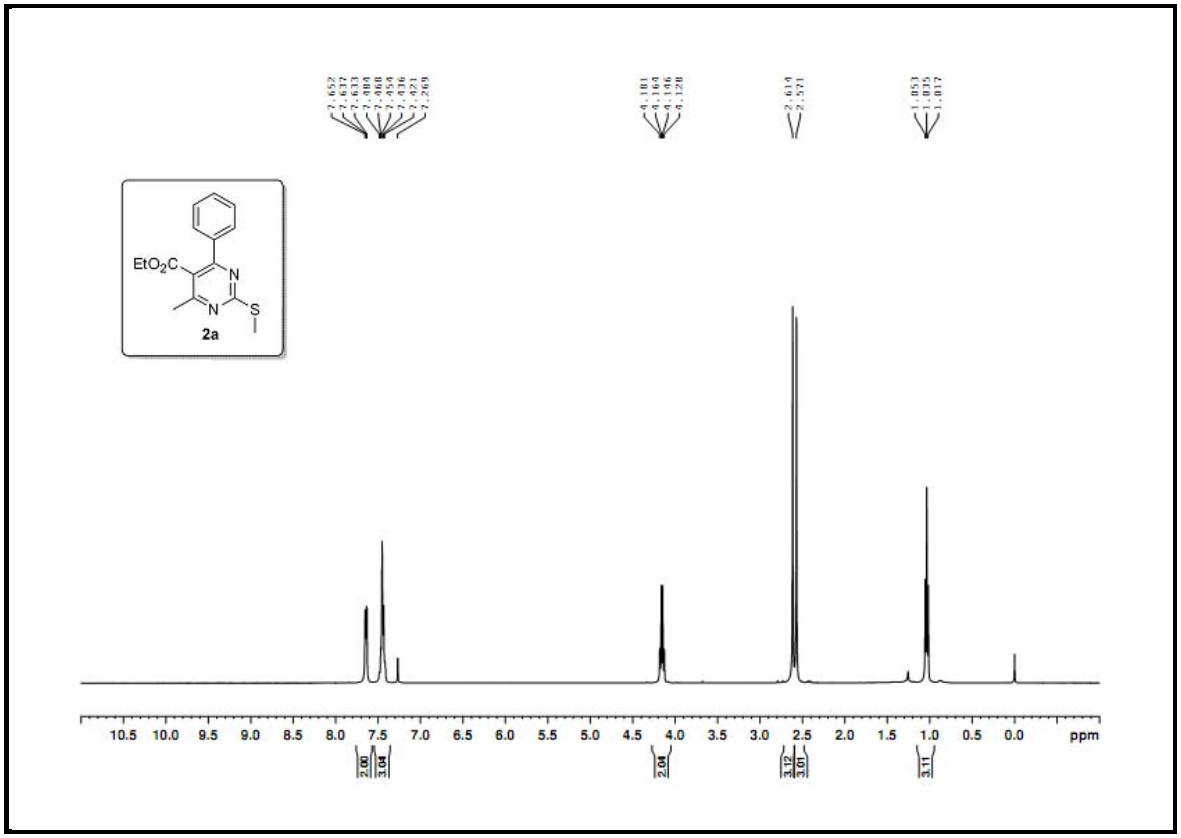

7.276
7.235
7.214
6.815
6.794
5.455
4.872
4.856
4.838
4.820
3.760
3.738
2.326
1.182
1.164
1.147
OCH3
EtO2C
N
N
H
O
1w
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.22
2.06
1.00
2.18
6.00
3.00
3.07

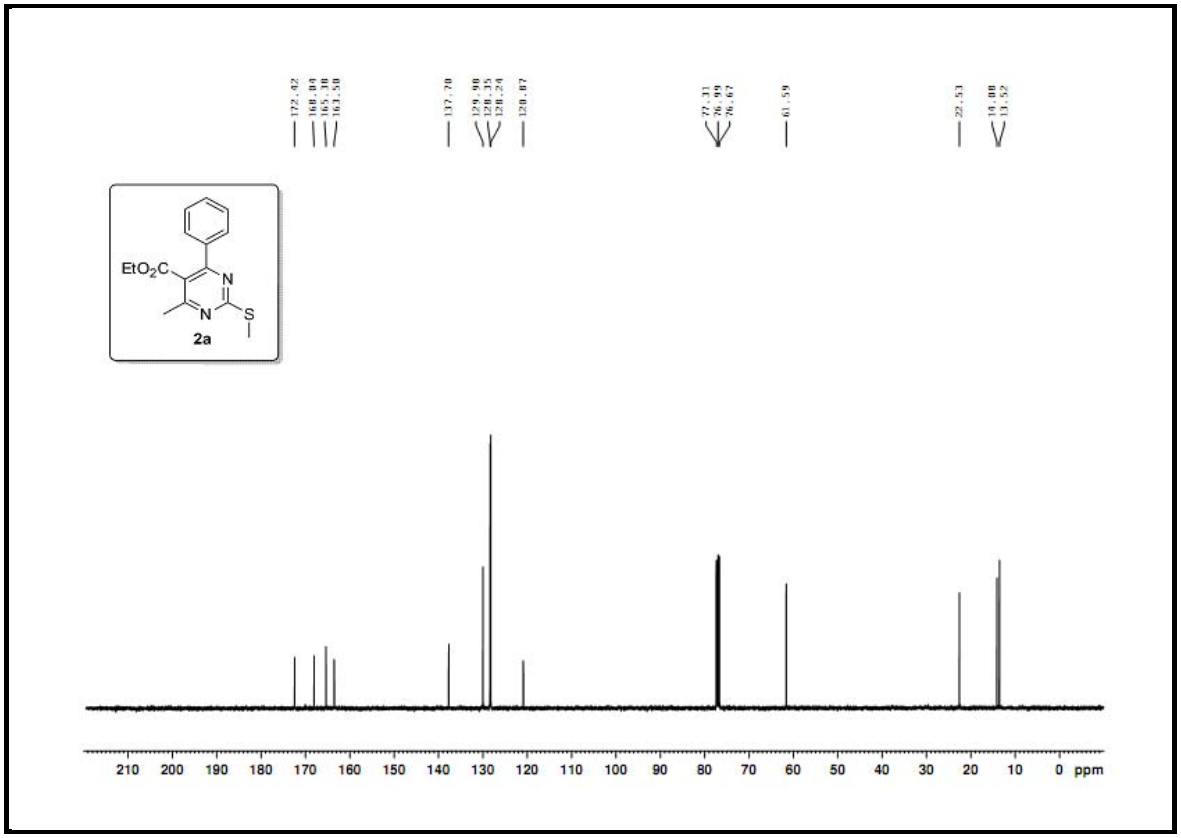

166.76
158.63
137.88
127.90
113.50
77.32
77.00
76.68
59.09
55.06
53.79
53.35
14.09
OCH3
EtO2C
N
N
H
O
1w
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

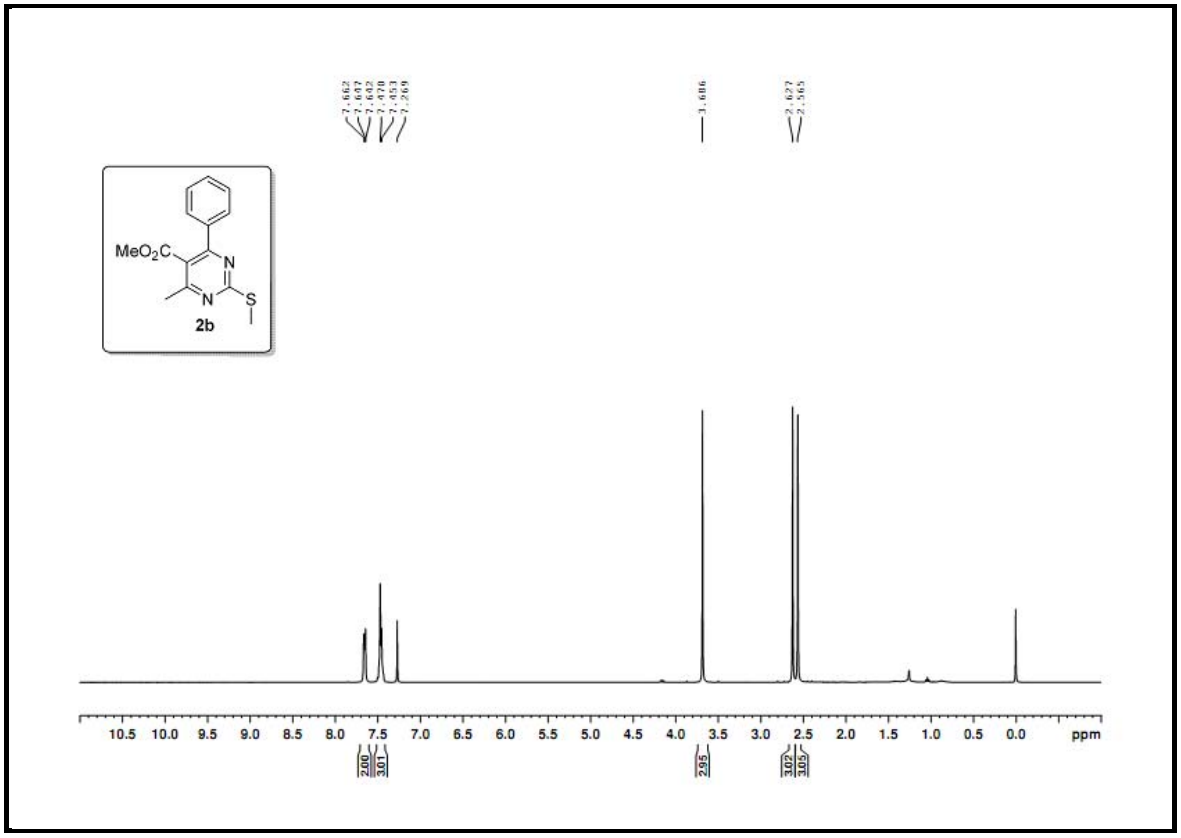

Cl
EtO2C
N
N
H
O
1x
7.247
5.513
4.082
4.070
4.052
4.035
3.755
2.339
1.186
1.168
1.150
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.42
1.07
2.13
3.00
3.03
3.04

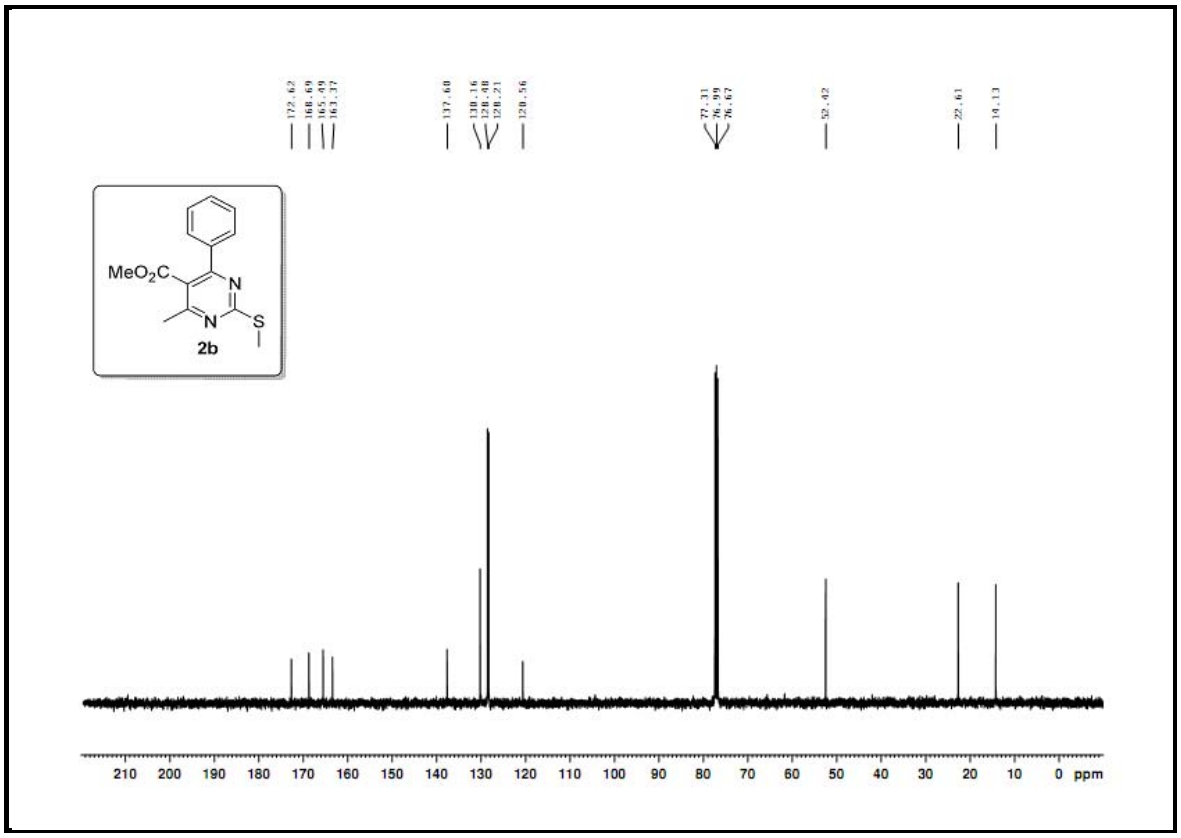

Cl
EtO2C
N
N
H
O
1x
166.47
143.90
132.86
128.62
128.32
77.32
77.00
76.68
59.75
50.10
14.16
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

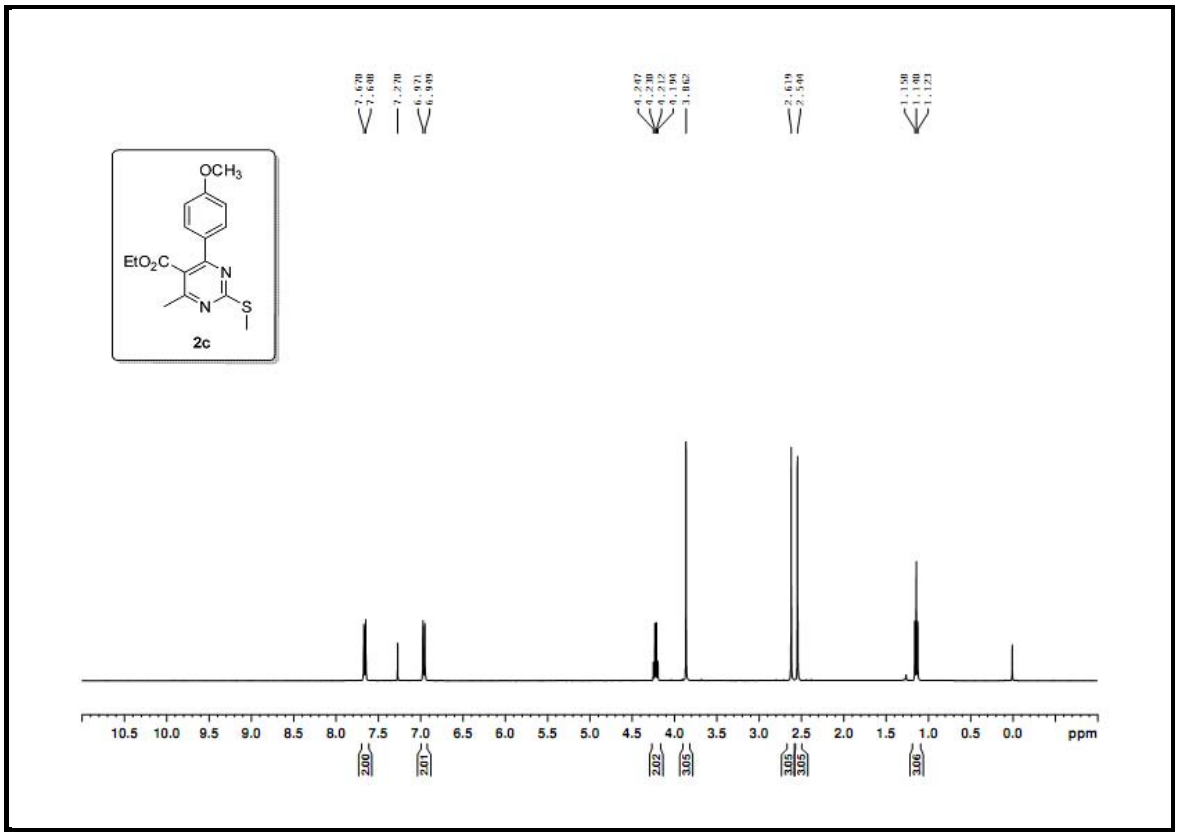
## 13.2 NMR Spectra Of 2-Substituted Pyrimidines 2a-2x.

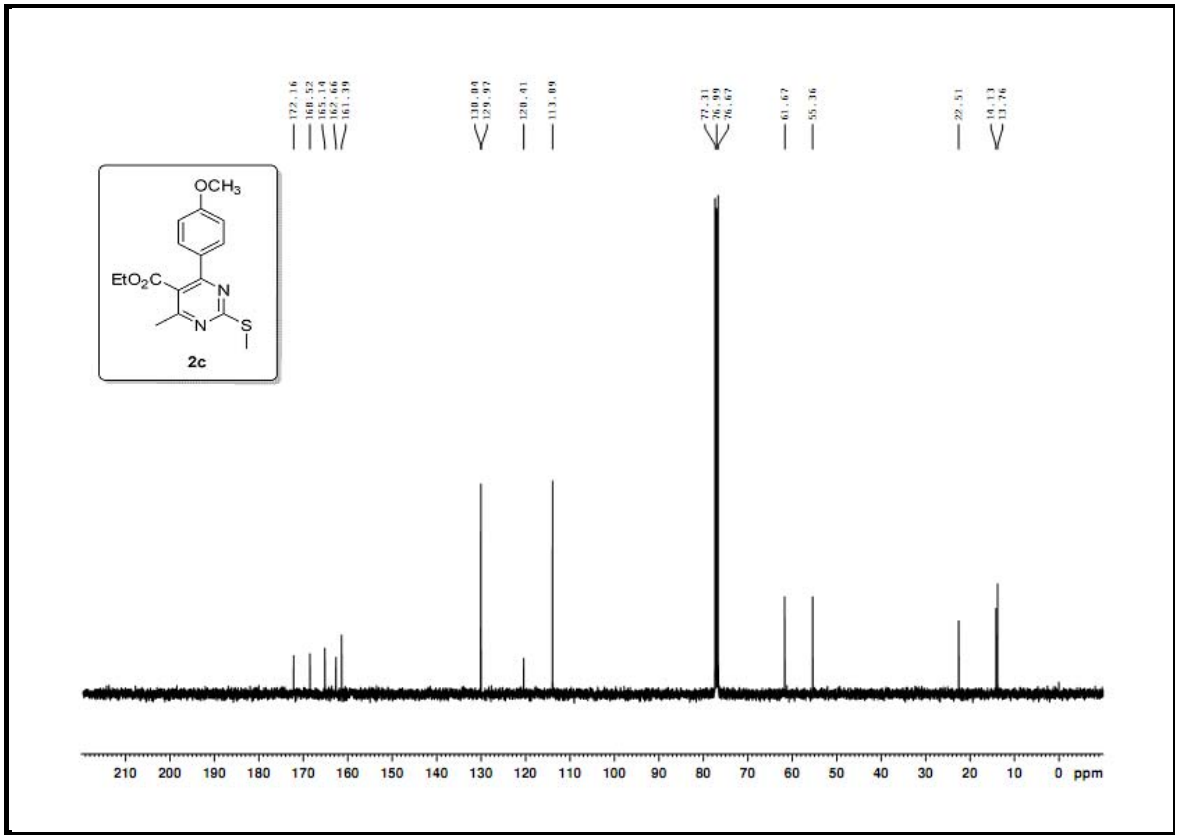


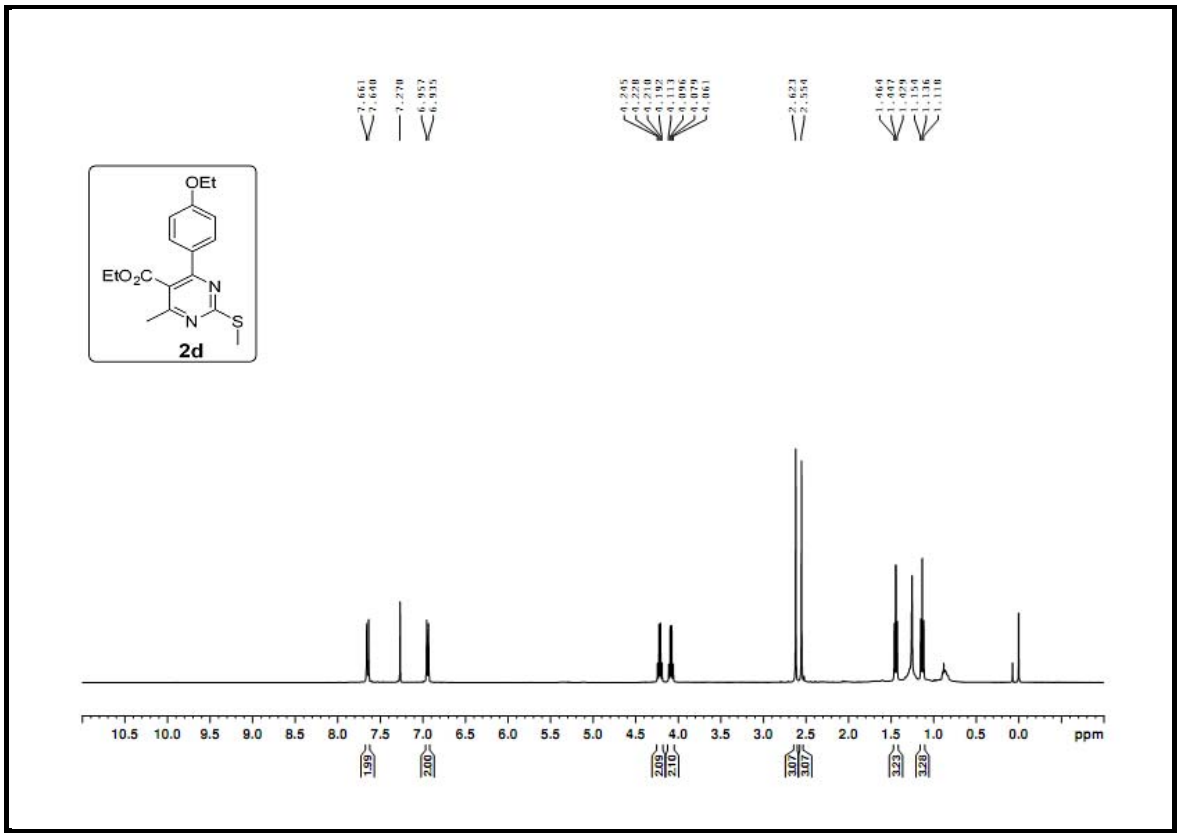



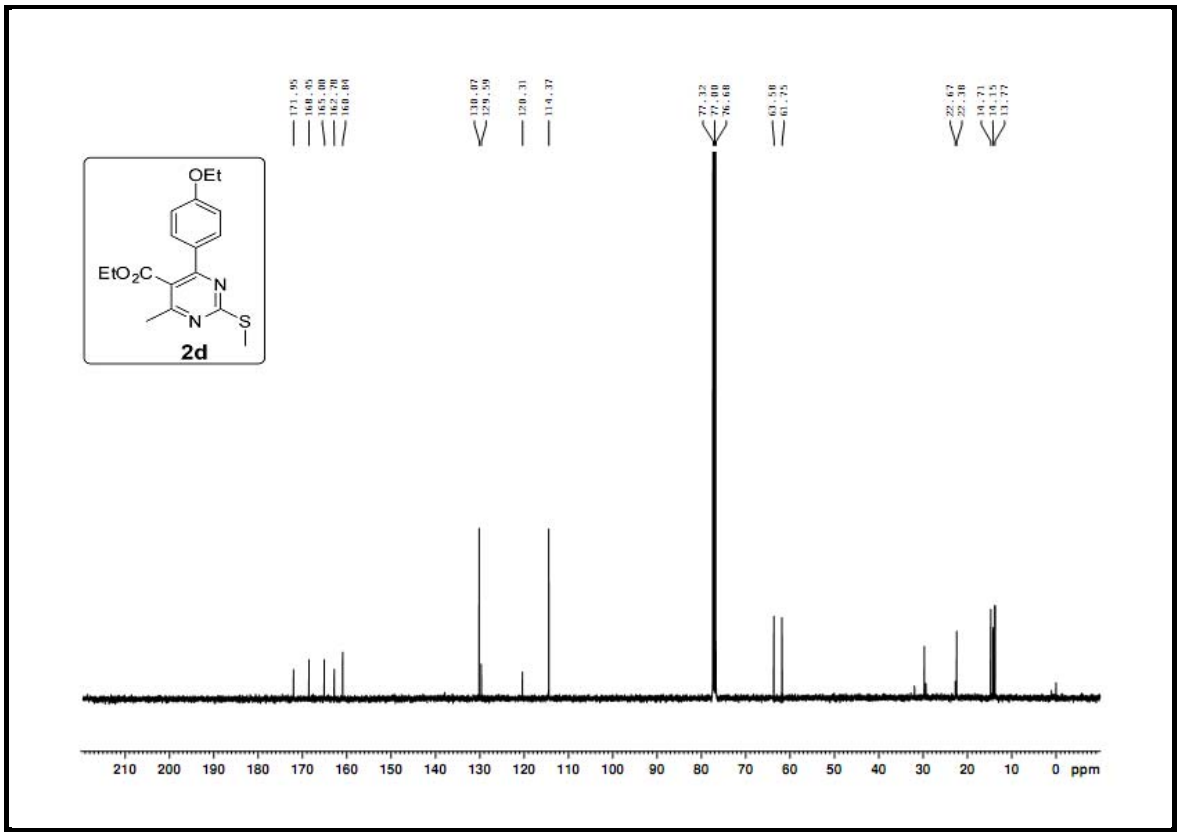

7.662
7.647
7.628
7.470
7.453
7.269
3.686
2.627
2.565
MeO2C
N
N
S
2b
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
3.01
2.95
3.02
3.05

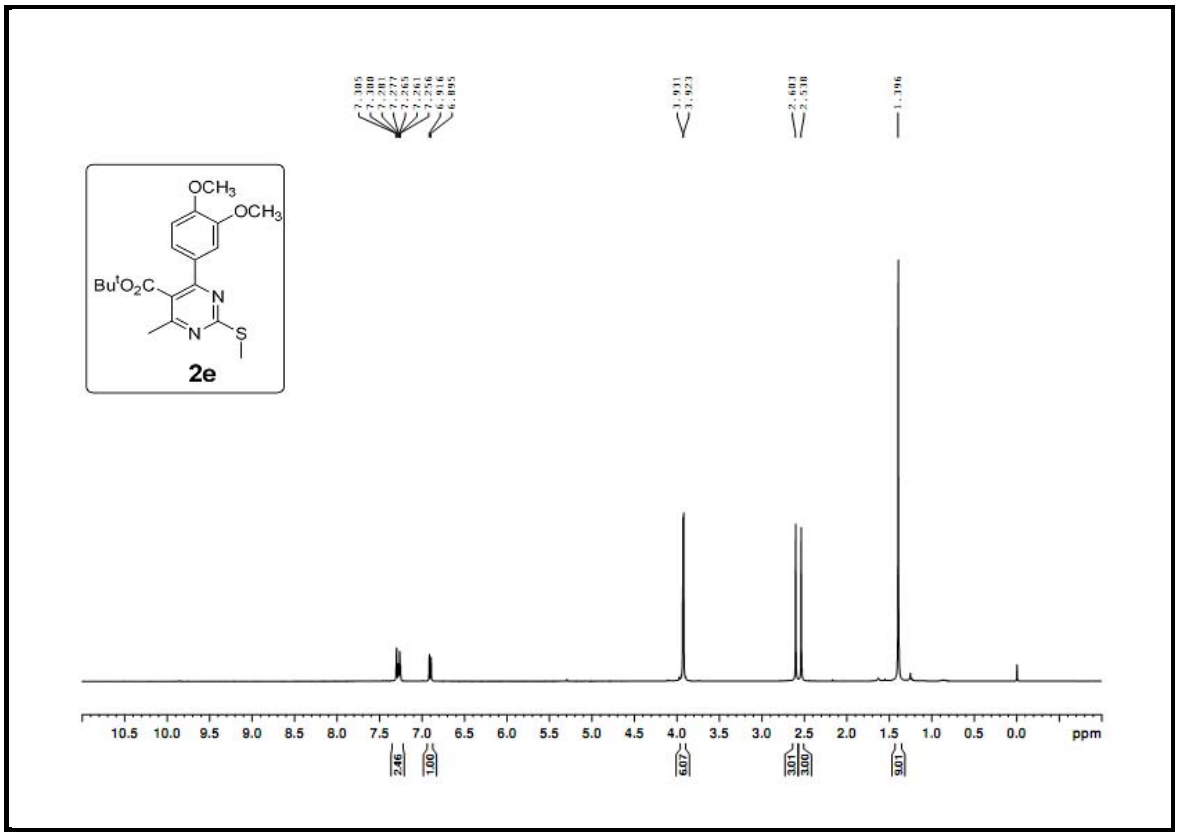

172.62
168.69
165.49
163.37
137.68
130.16
128.48
128.21
128.56
77.31
76.99
76.67
52.42
22.61
14.13
MeO2C
N
N
S
2b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

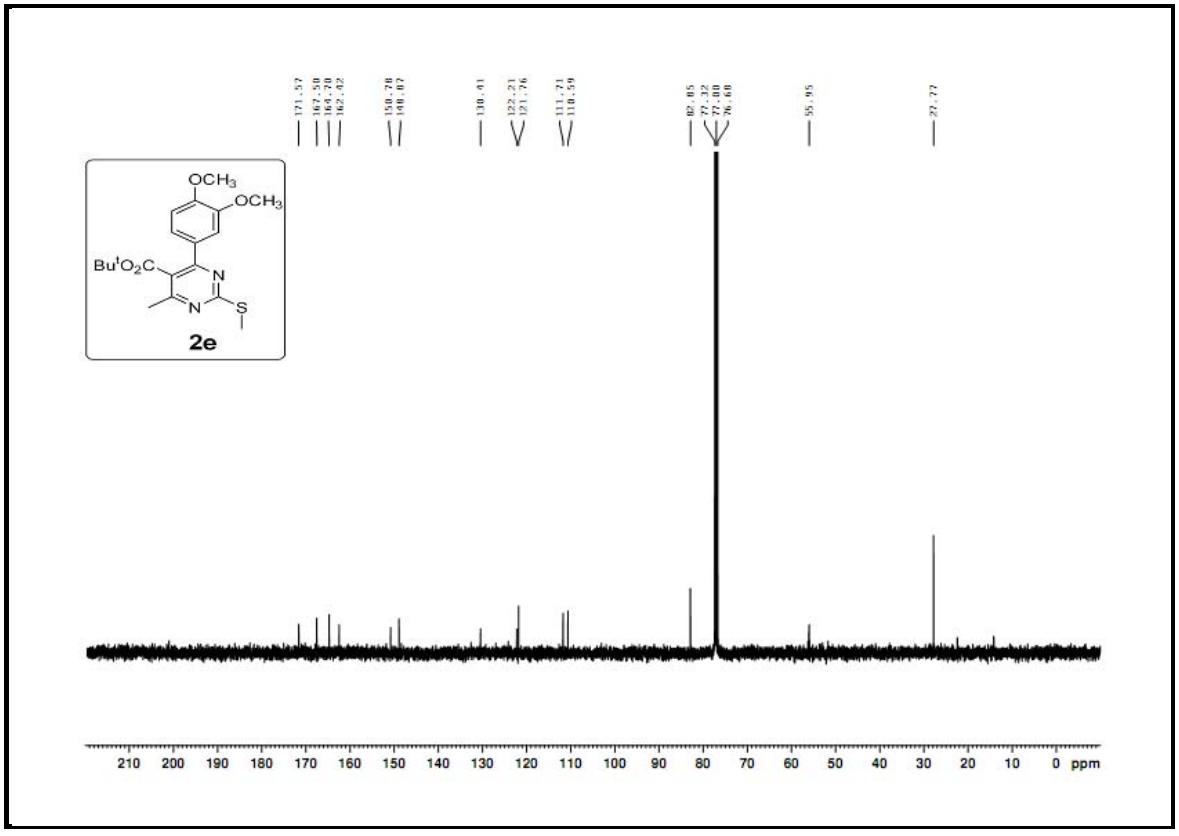

7.679
7.648
7.278
6.971
6.949
4.207
4.188
4.172
4.153
3.862
2.619
2.594
1.158
1.140
1.123
OCH3
EtO2C
N
N
S
2c
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
2.01
2.02
3.05
3.05
3.05
3.06

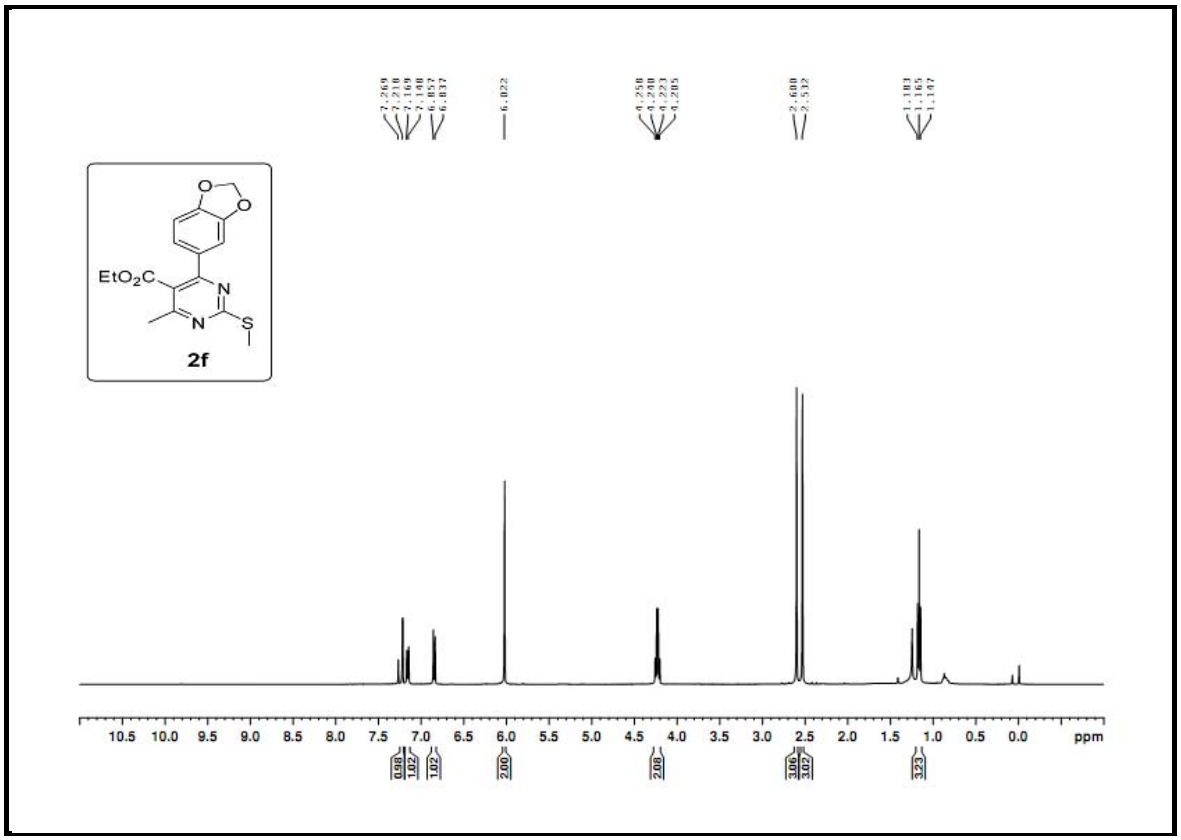

172.16
168.52
165.14
162.66
161.39
130.04
129.97
128.41
113.89
77.31
76.99
76.67
61.67
55.36
22.51
14.13
13.76
OCH3
EtO2C
N
N
S
2c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

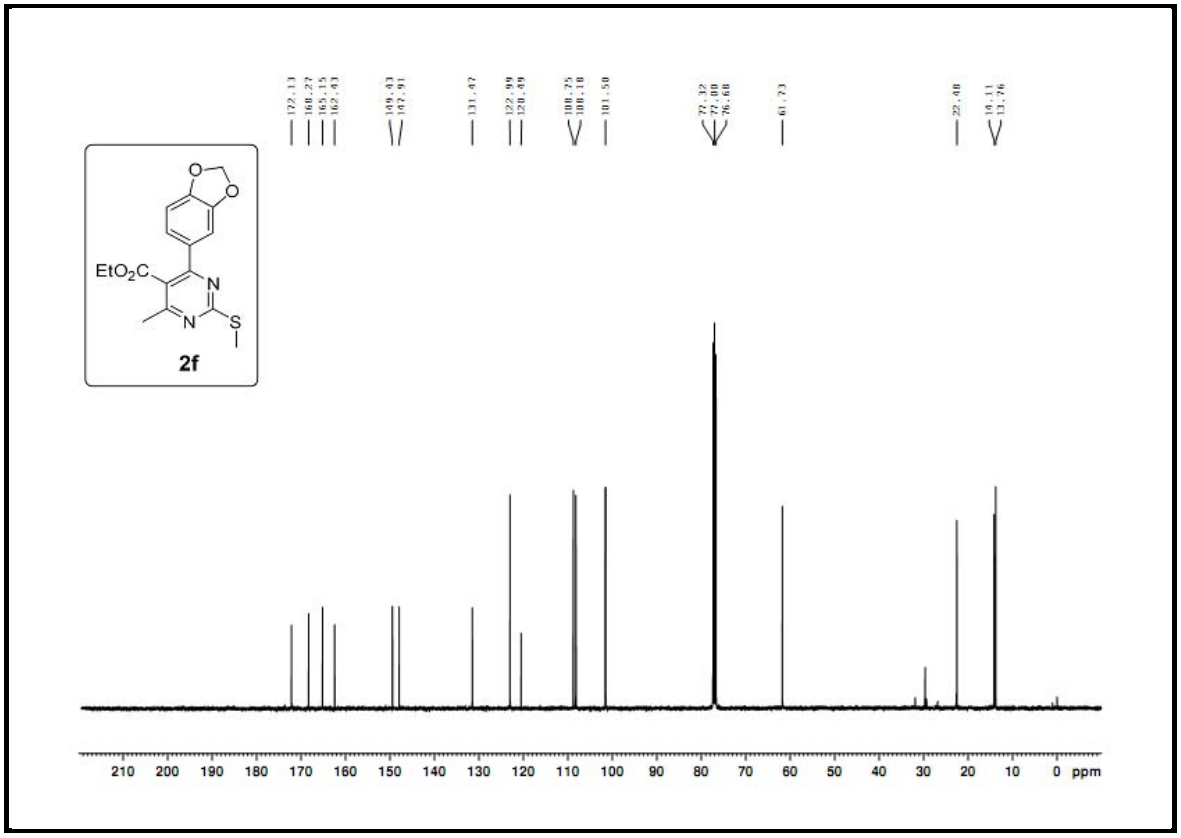

OEt
EtO2C
N
N
S
2d
7.661
7.640
7.270
6.952
6.935
4.295
4.278
4.210
4.192
4.113
4.096
4.079
4.061
2.623
2.554
1.464
1.447
1.429
1.412
1.136
1.118
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
199
200
209
210
307
307
323
328

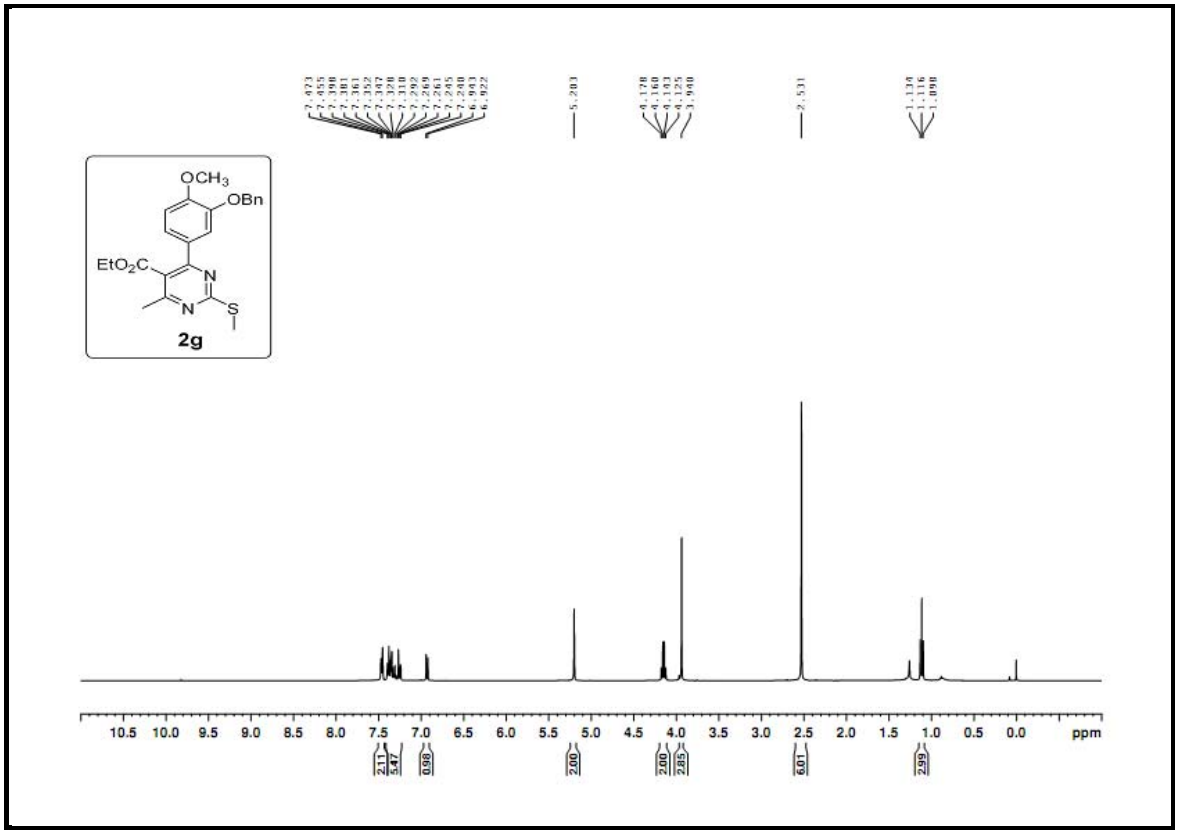

OEt
EtO2C
N
N
S
2d
171.95
168.45
165.00
162.78
160.80
130.07
129.59
128.31
114.37
77.32
77.00
76.68
63.58
61.75
22.67
22.38
14.71
14.15
13.77
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

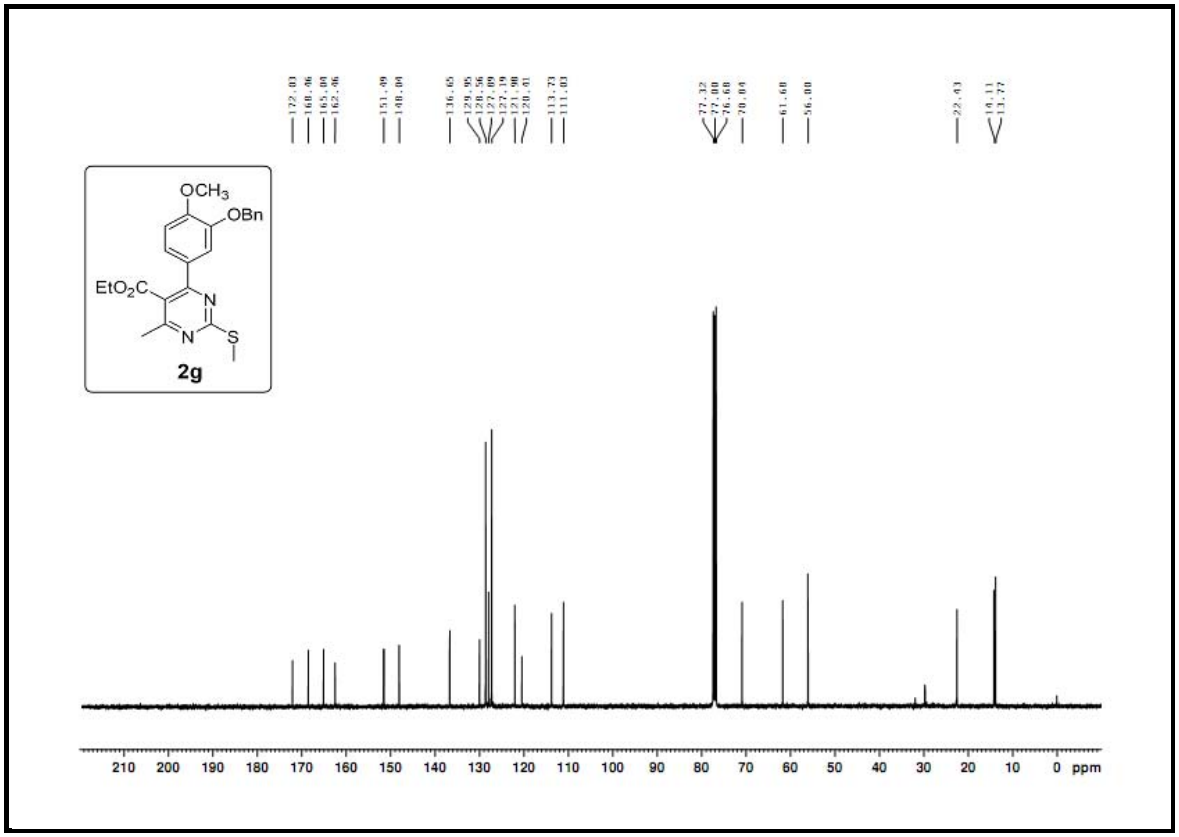

OCH3
OCH3
Bu^tO2C
N
N
S
2e
7.305
7.300
7.281
7.277
7.265
7.261
7.256
6.916
6.895
1.931
1.923
2.603
2.530
1.396
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.46
1.00
6.07
3.01
3.00
9.01

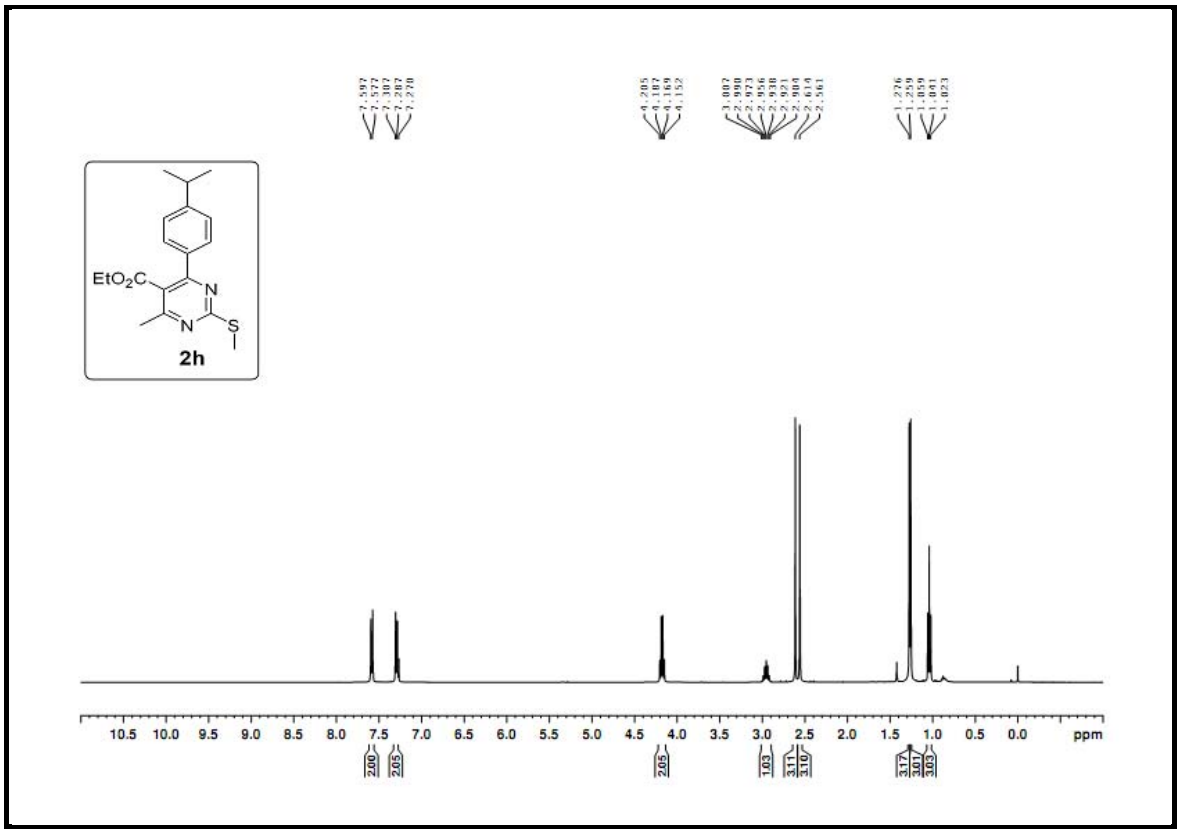

OCH3
OCH3
Bu^tO2C
N
N
S
2e
171.57
167.50
165.70
162.02
150.78
140.87
130.41
122.21
121.76
111.71
110.59
82.85
77.32
77.00
76.68
55.95
27.77
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

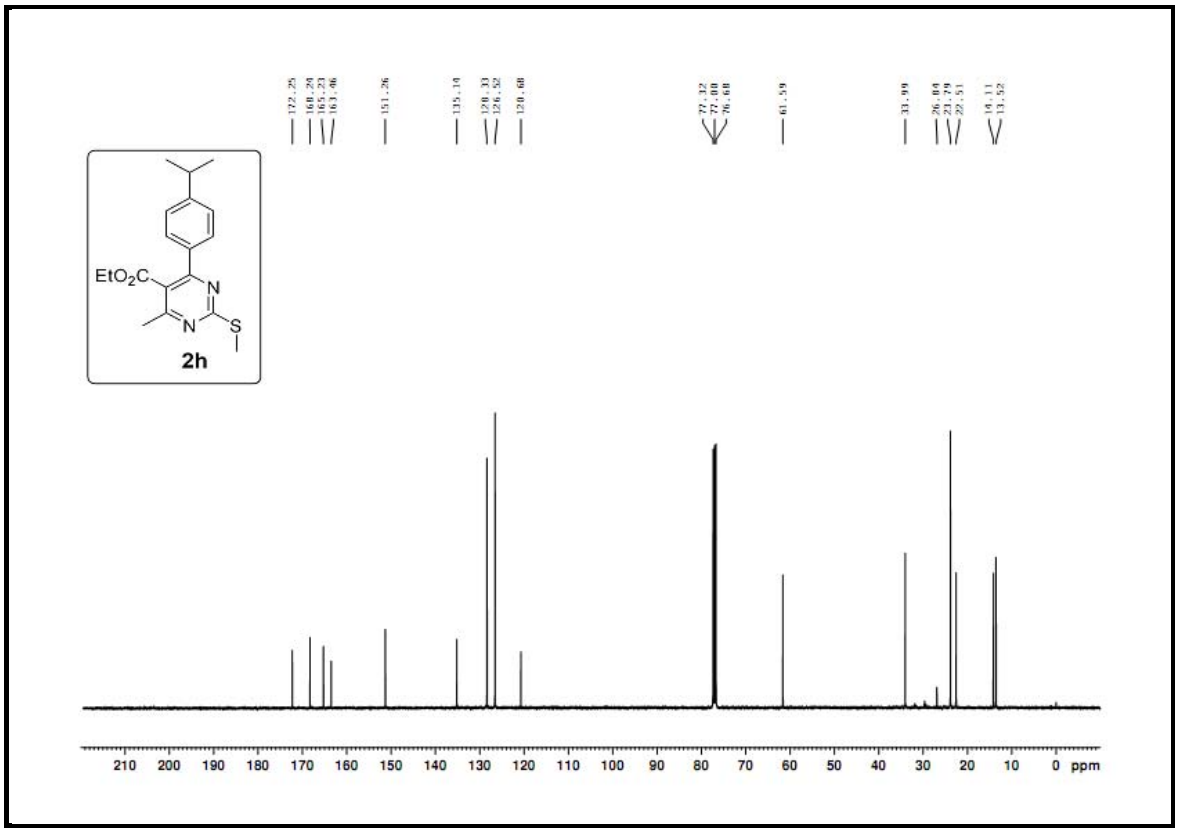

7.269
7.210
7.169
7.100
6.857
6.837
6.022
4.258
4.240
4.223
4.205
2.600
2.532
1.183
1.165
1.147
EtO2C
N
N
S
2f
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.98
1.02
1.02
2.00
2.08
3.06
3.02
3.23

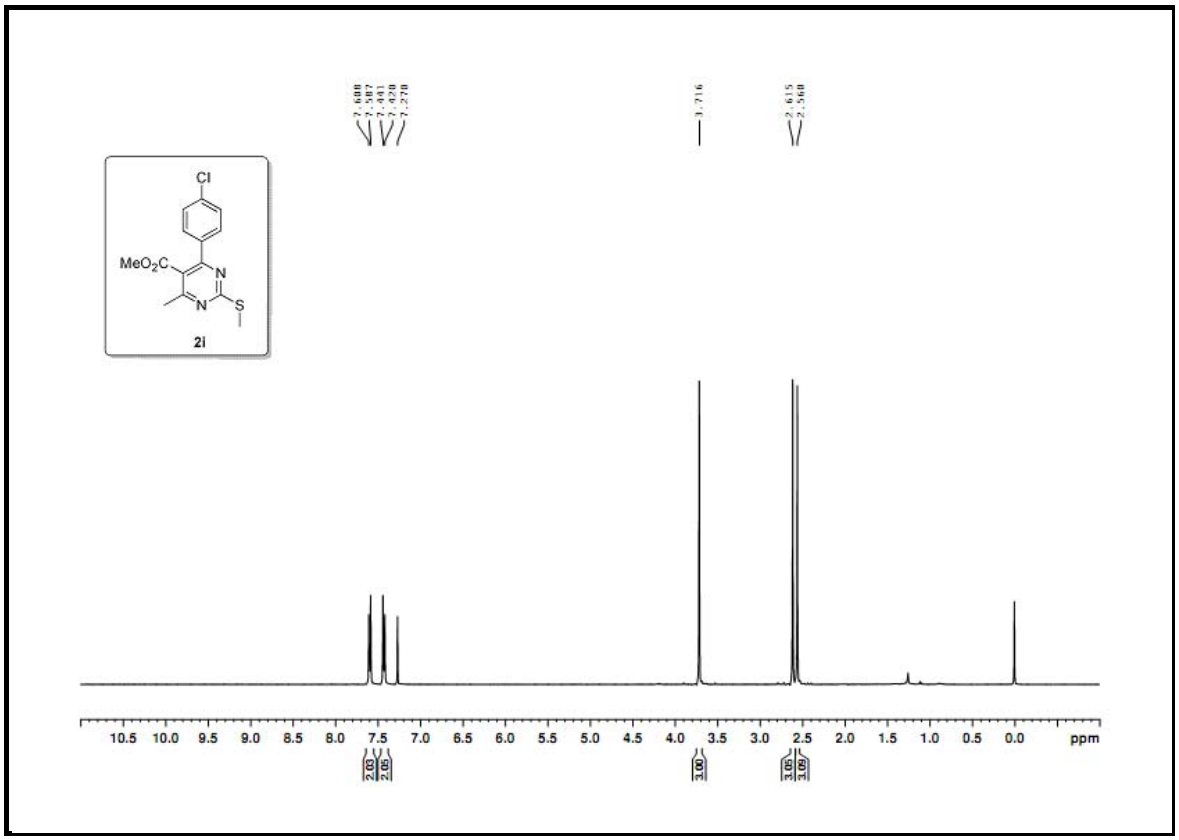

172.13
168.27
165.15
162.43
149.43
147.91
131.47
122.99
120.89
101.75
101.18
101.50
77.32
77.00
76.68
61.73
22.48
15.11
13.76
EtO2C
N
N
S
2f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

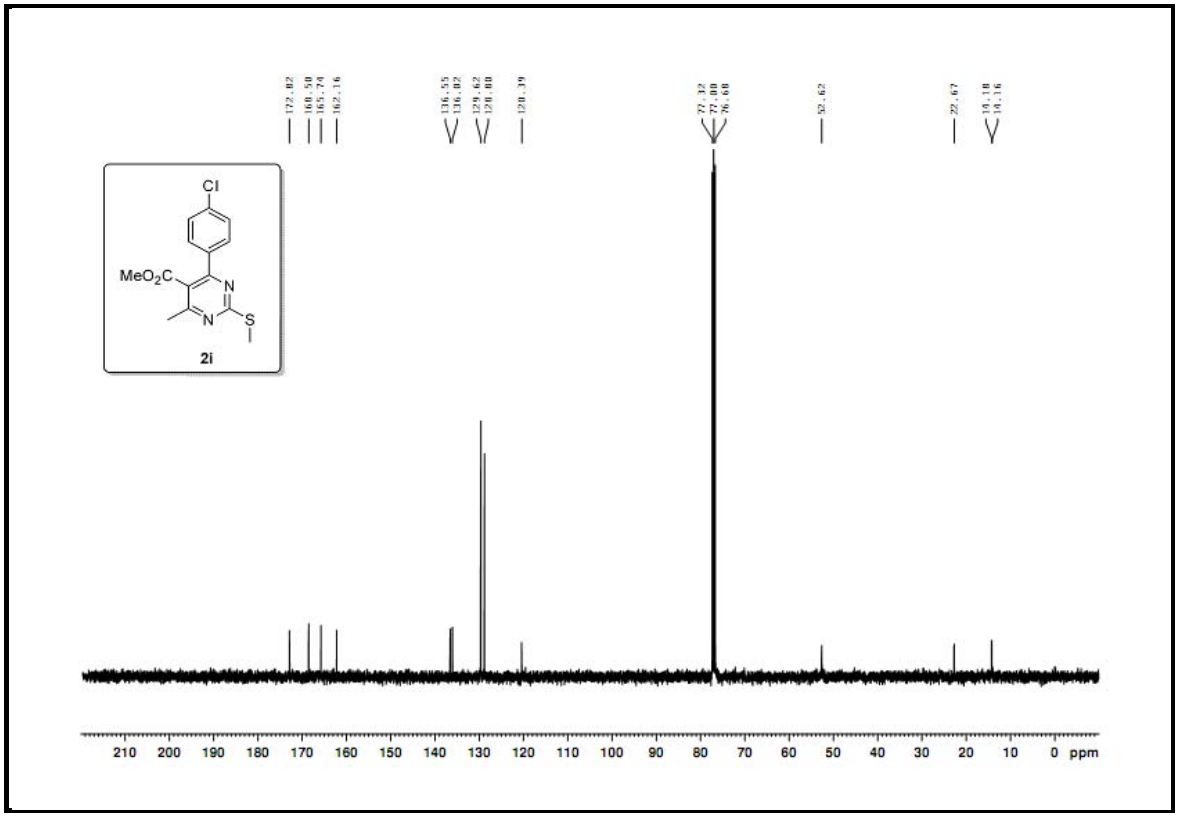

OCH3
OBn
EtO2C
N
N
S
2g
ppm

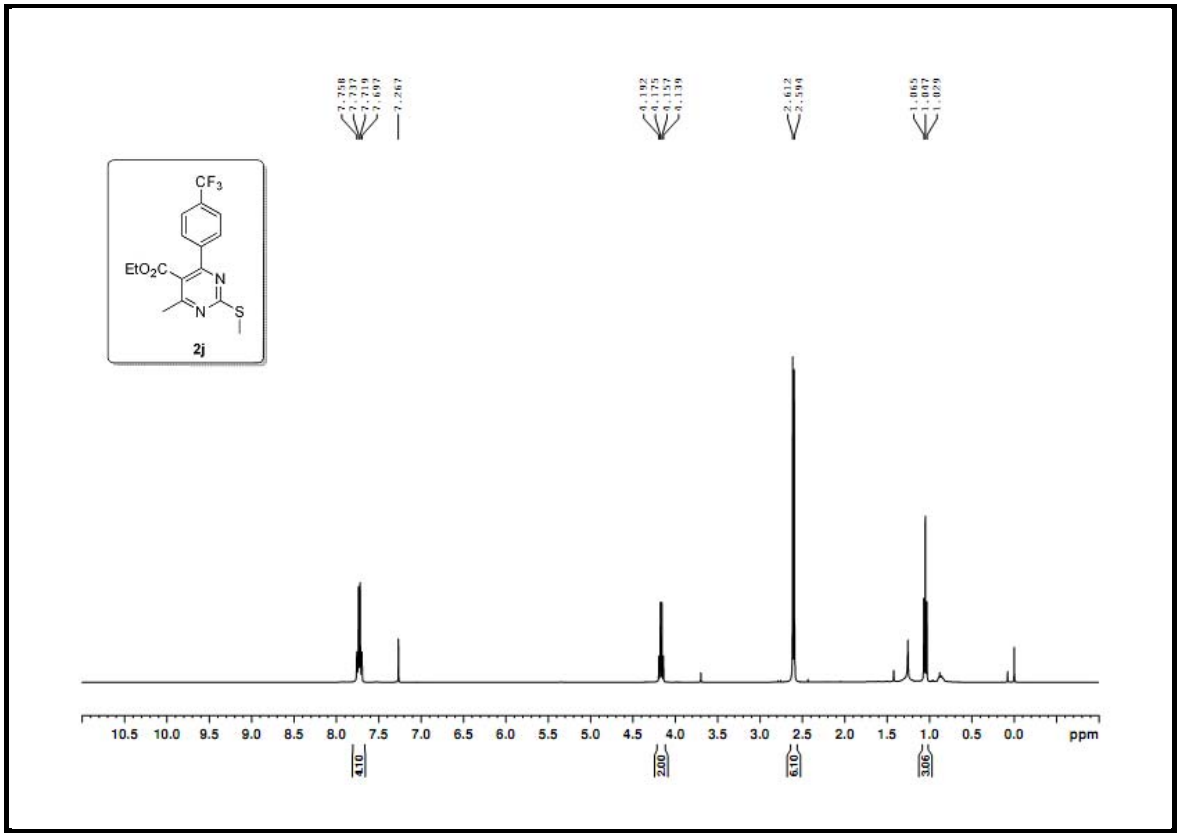

OCH3
OBn
EtO2C
N
N
S
2g
ppm

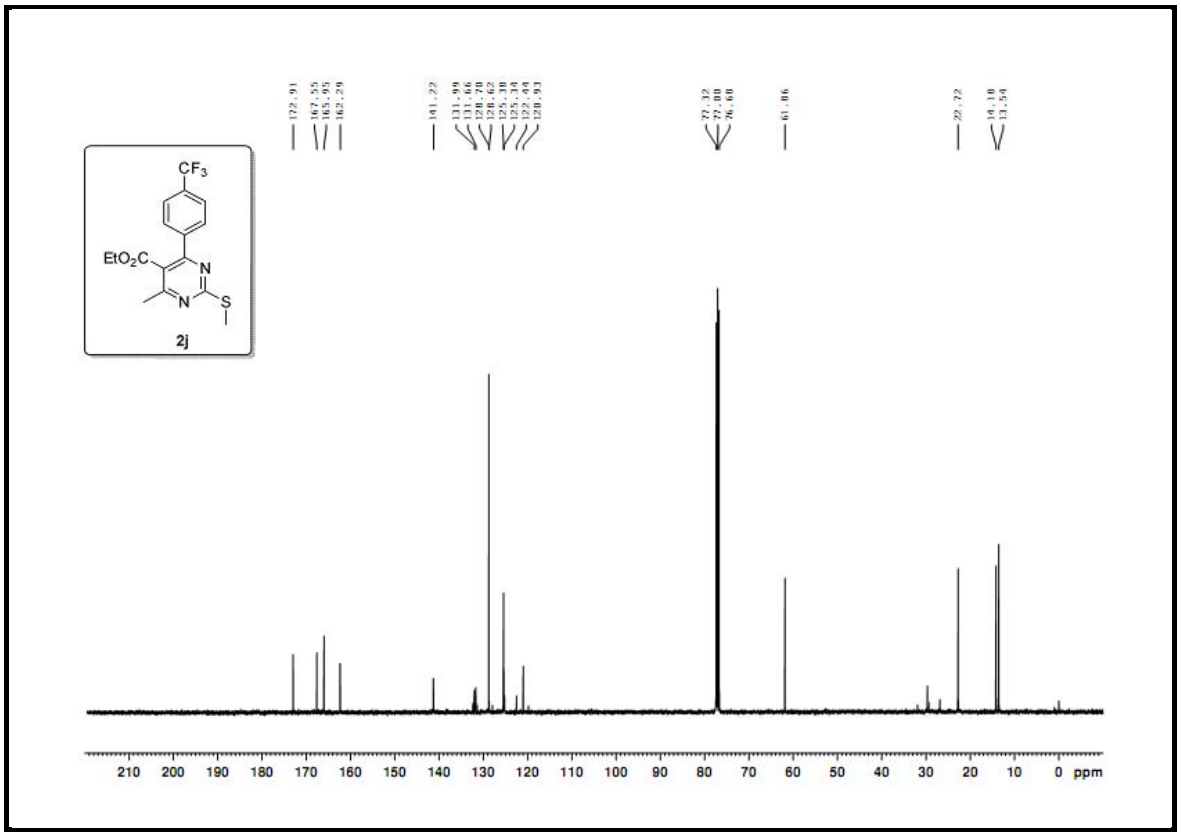

2h
ppm

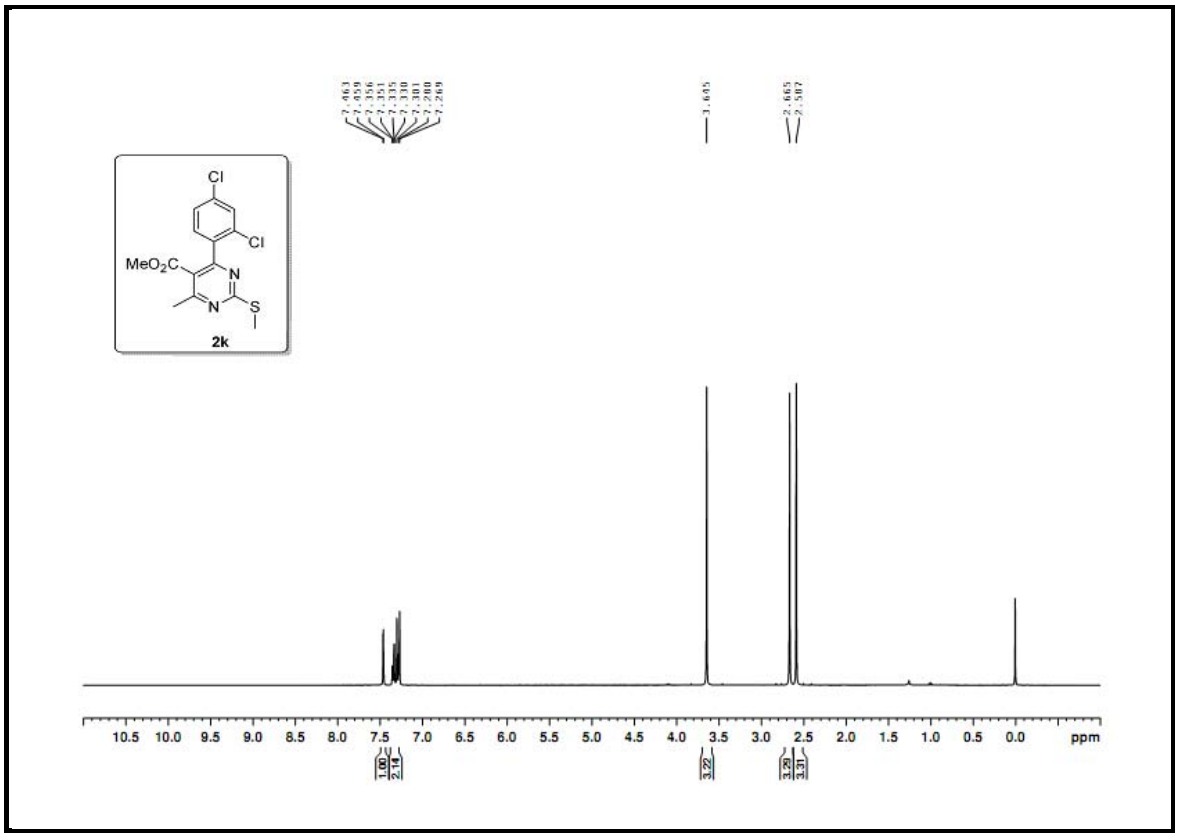

2h
ppm

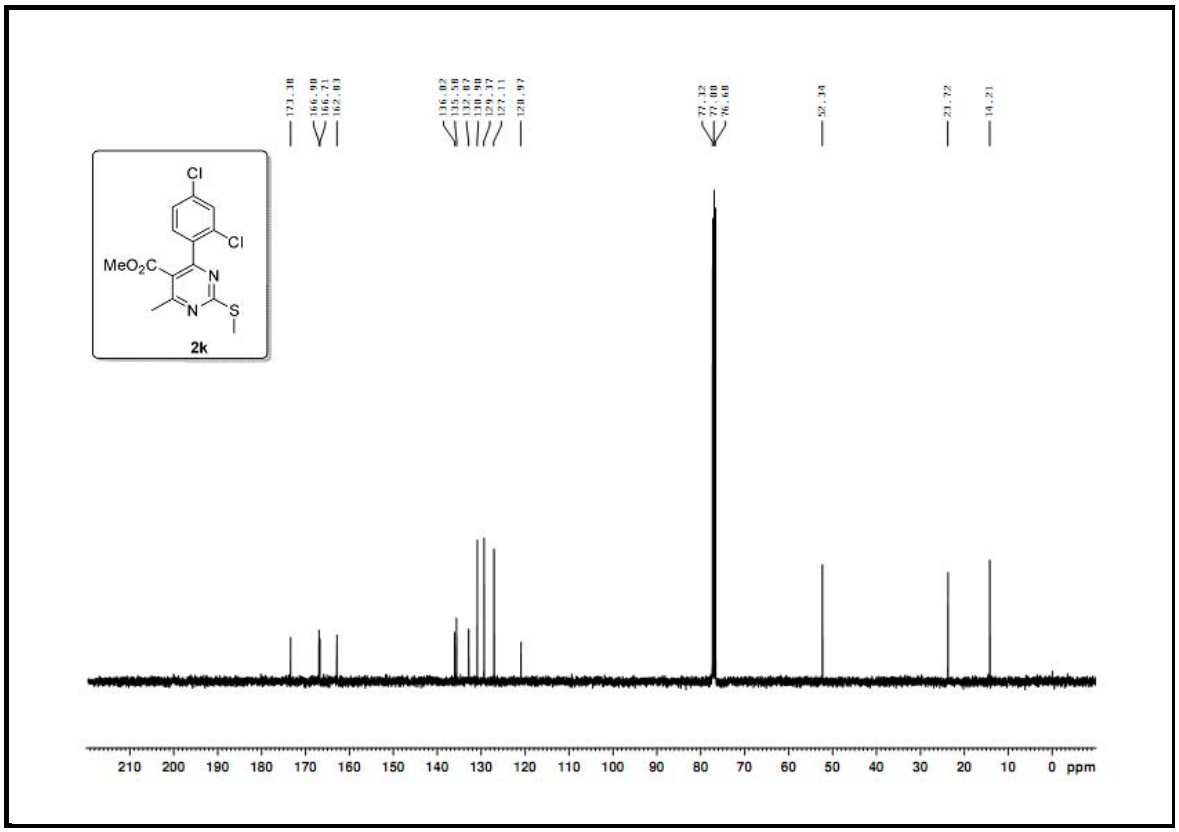

7.688
7.667
7.441
7.420
7.270
3.716
2.615
2.568
Cl
MeO2C
N
N
S
2i
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
2.06
3.00
3.06
3.06

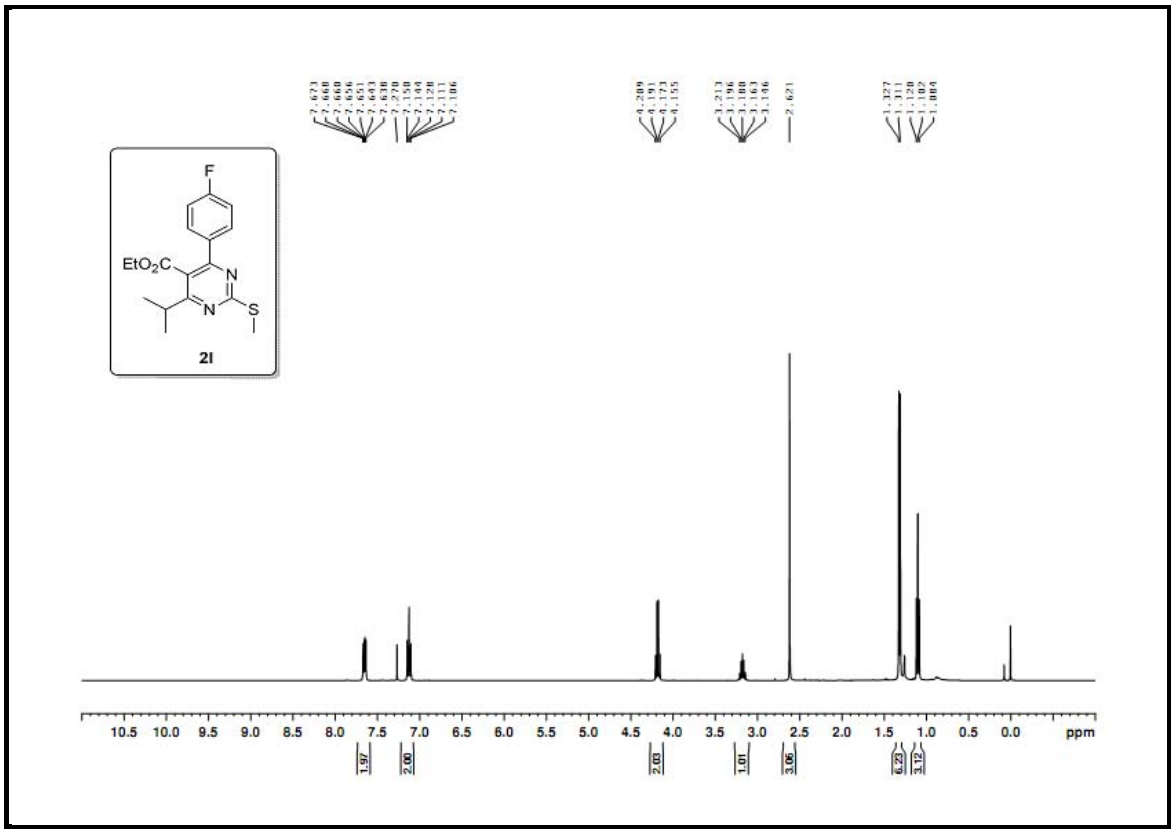

172.82
160.50
165.74
162.16
136.55
136.02
129.62
128.80
128.39
77.32
77.00
76.68
52.62
22.67
18.18
14.16
Cl
MeO2C
N
N
S
2i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

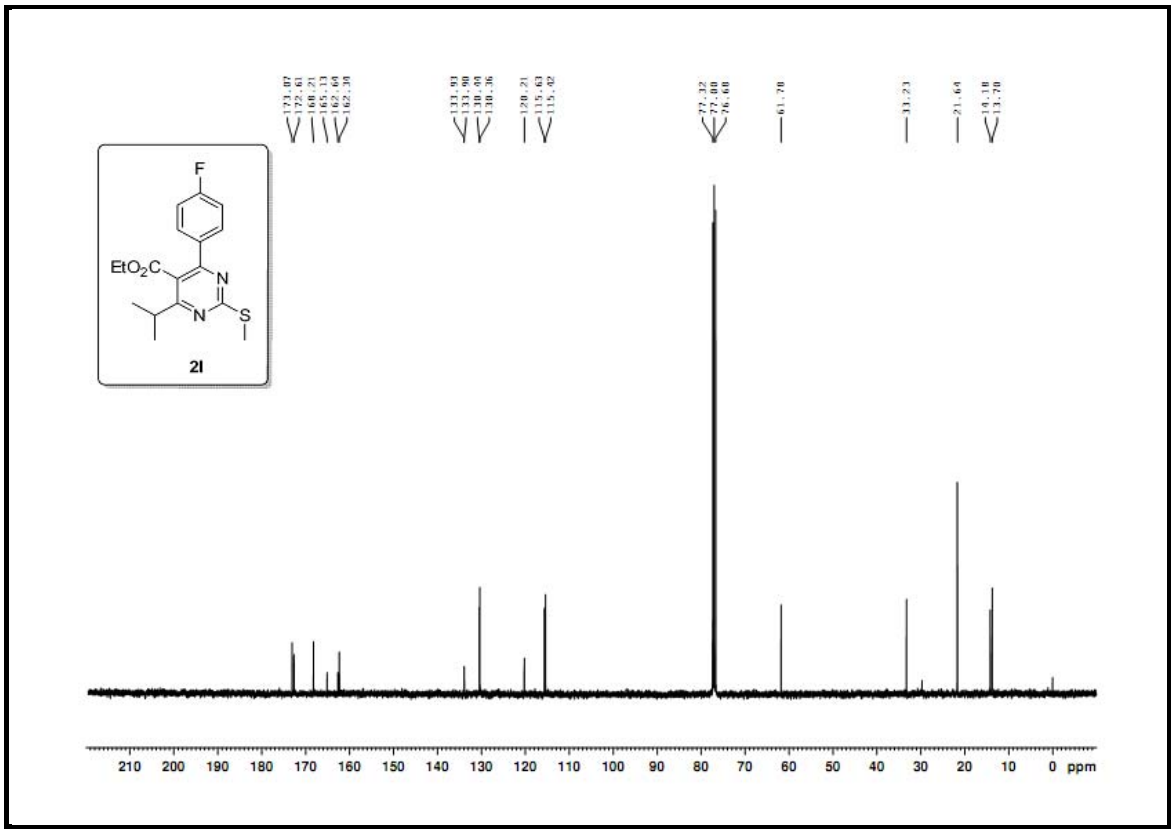

7.758
7.737
7.719
7.697
7.267
4.192
4.175
4.157
4.139
2.612
2.594
1.065
1.047
1.029
CF3
EtO2C
N
N
S
2j
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.10
2.00
6.10
3.06

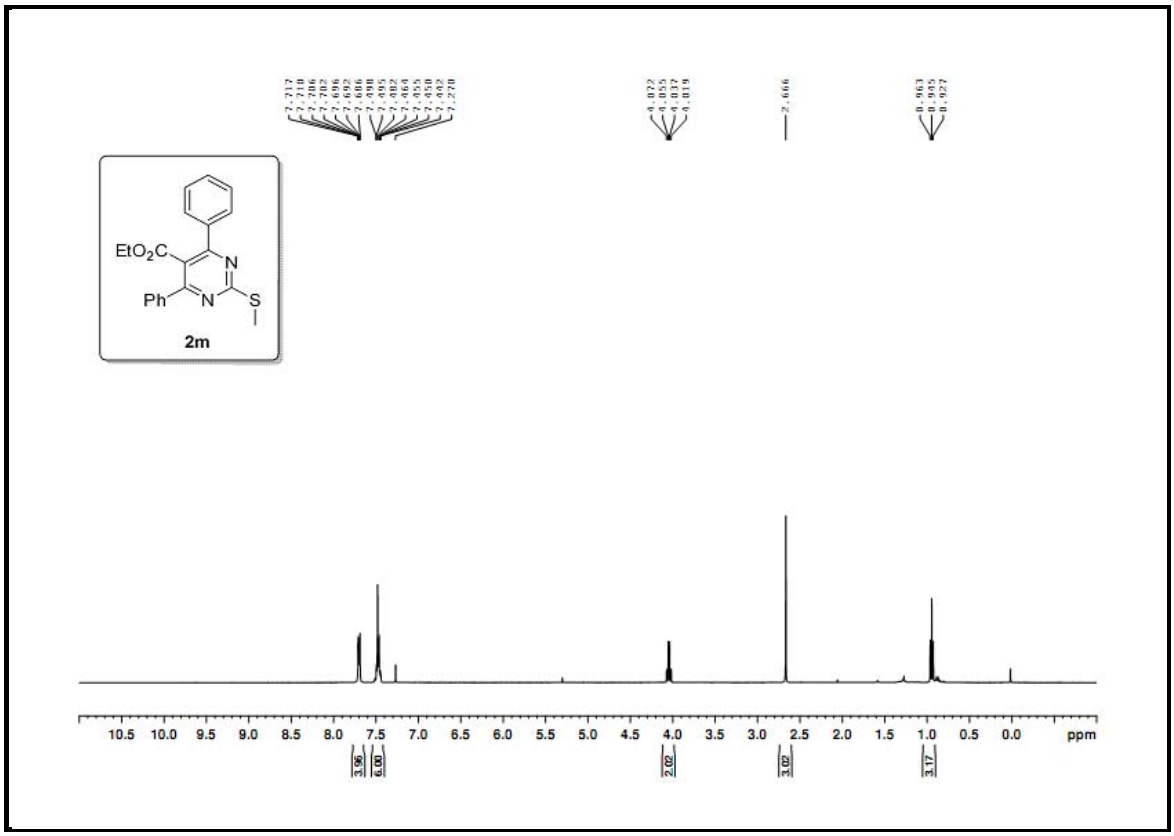

172.91
167.55
165.95
162.29
141.22
131.99
131.66
128.78
128.62
125.38
125.34
122.44
120.93
77.32
77.00
76.68
61.86
22.72
14.18
13.54
CF3
EtO2C
N
N
S
2j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

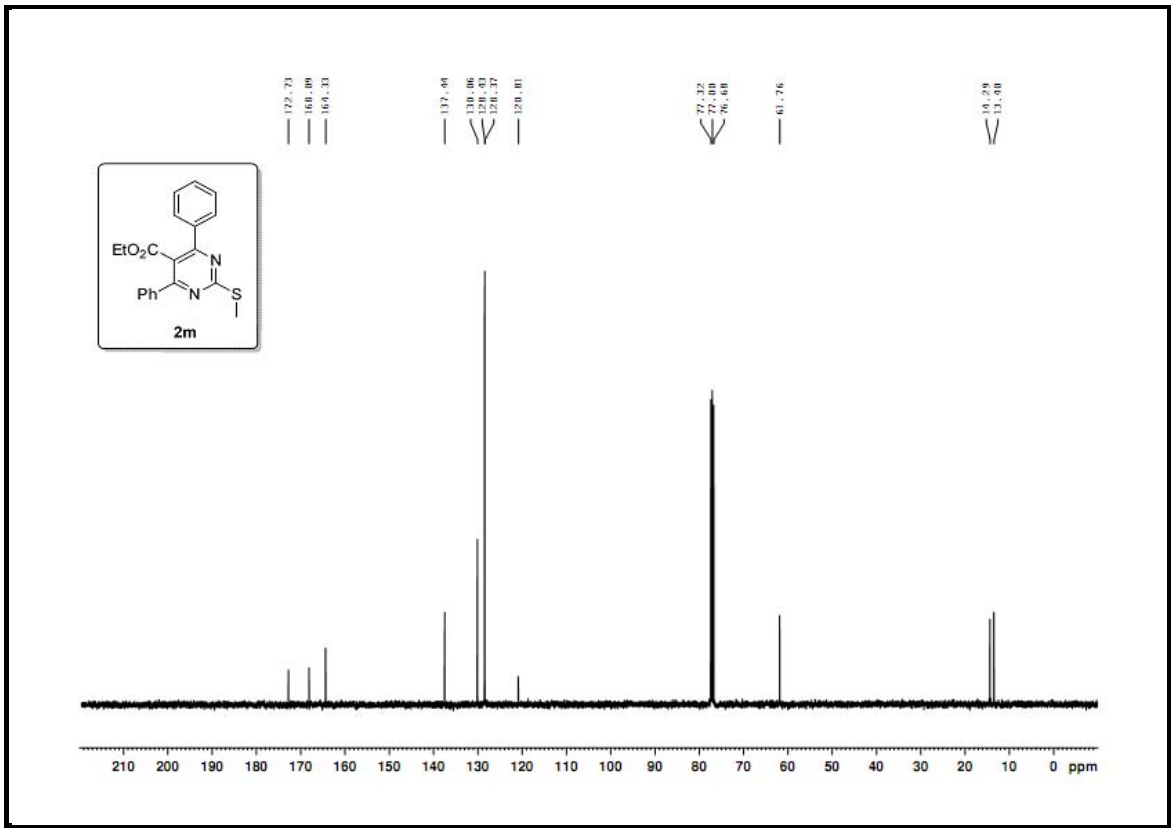

7.463
7.459
7.356
7.351
7.335
7.330
7.301
7.298
7.269
3.645
2.665
2.587
Cl
Cl
MeO2C
N
N
S
2k
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
2.14
3.22
3.28
3.31

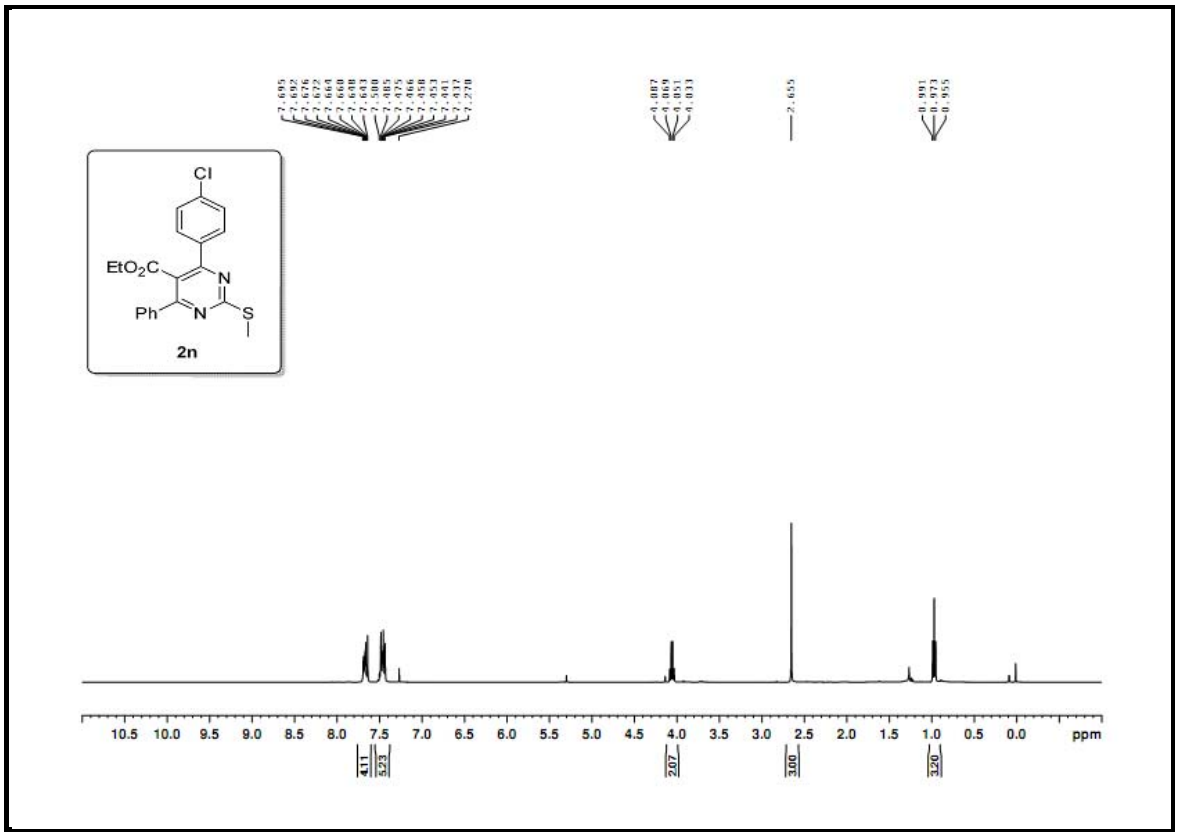

173.38
166.90
166.71
162.83
136.82
135.58
132.57
130.90
129.37
127.11
120.97
77.32
77.00
76.68
52.34
23.72
14.21
Cl
Cl
MeO2C
N
N
S
2k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

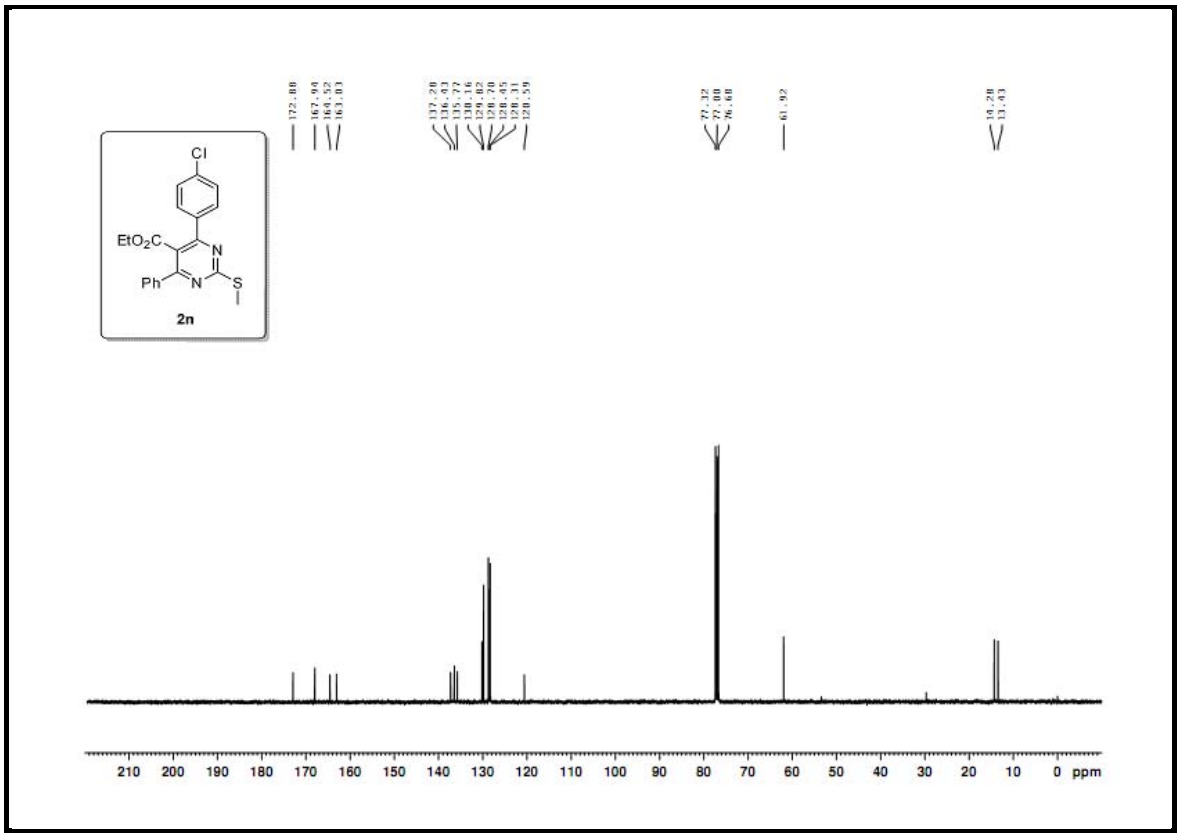

2l
ppm

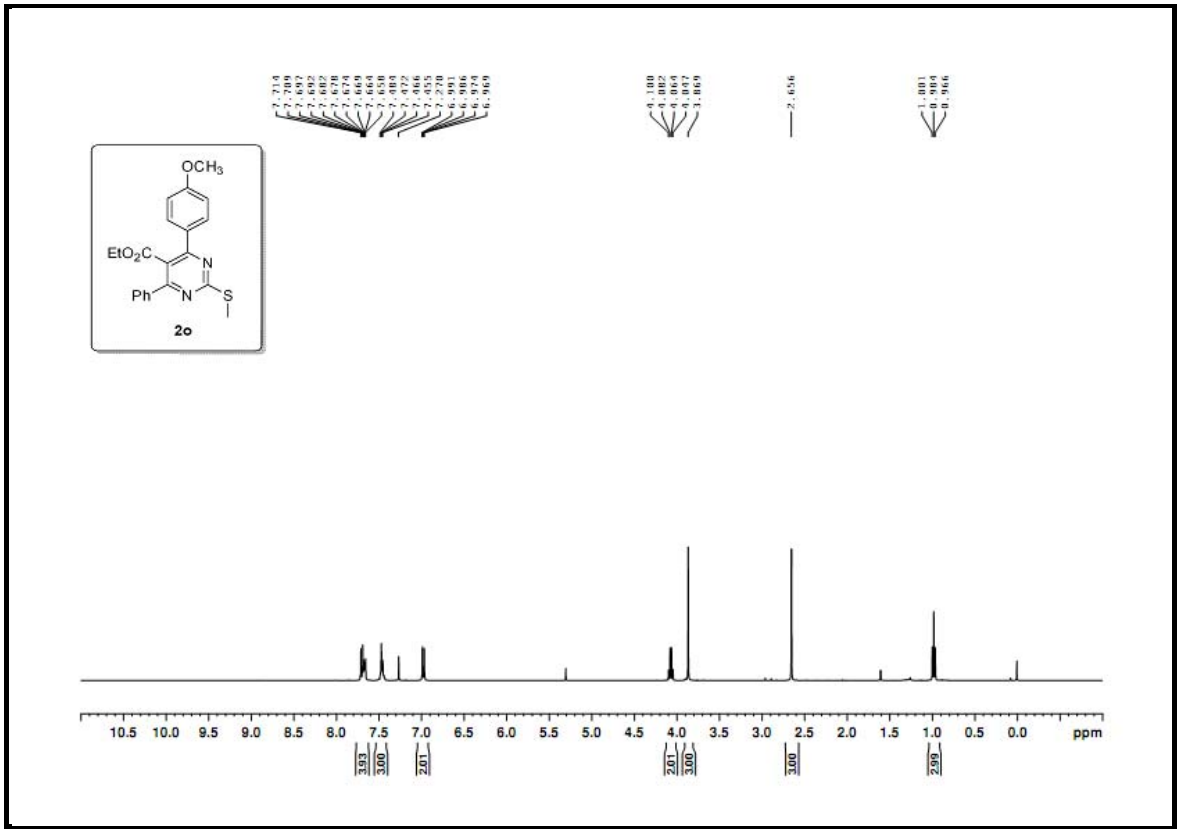

2l
ppm

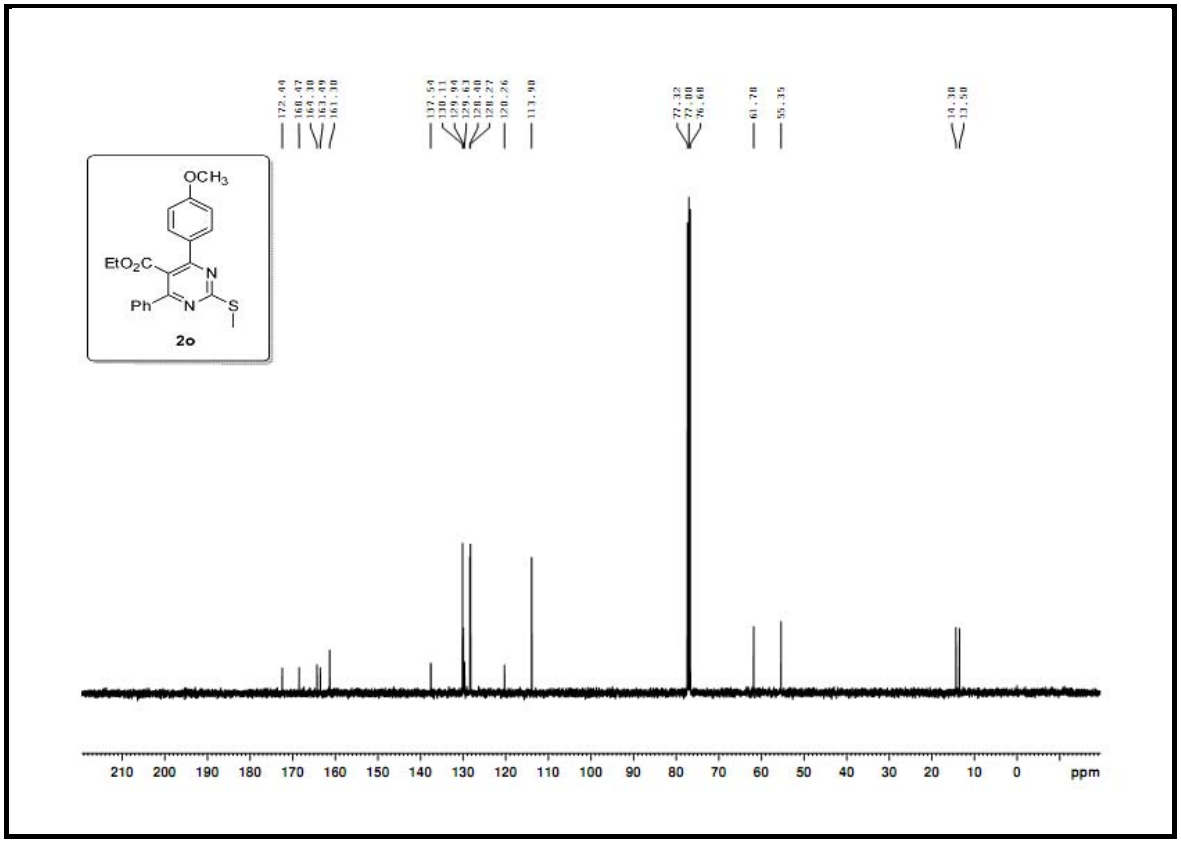

7.717
7.710
7.706
7.702
7.696
7.692
7.686
7.680
7.495
7.482
7.464
7.455
7.450
7.432
7.270
4.022
4.005
4.037
4.019
2.666
0.963
0.945
0.927
EtO2C
N
Ph
N
S
2m
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
3.96
6.00
2.02
3.02
3.17

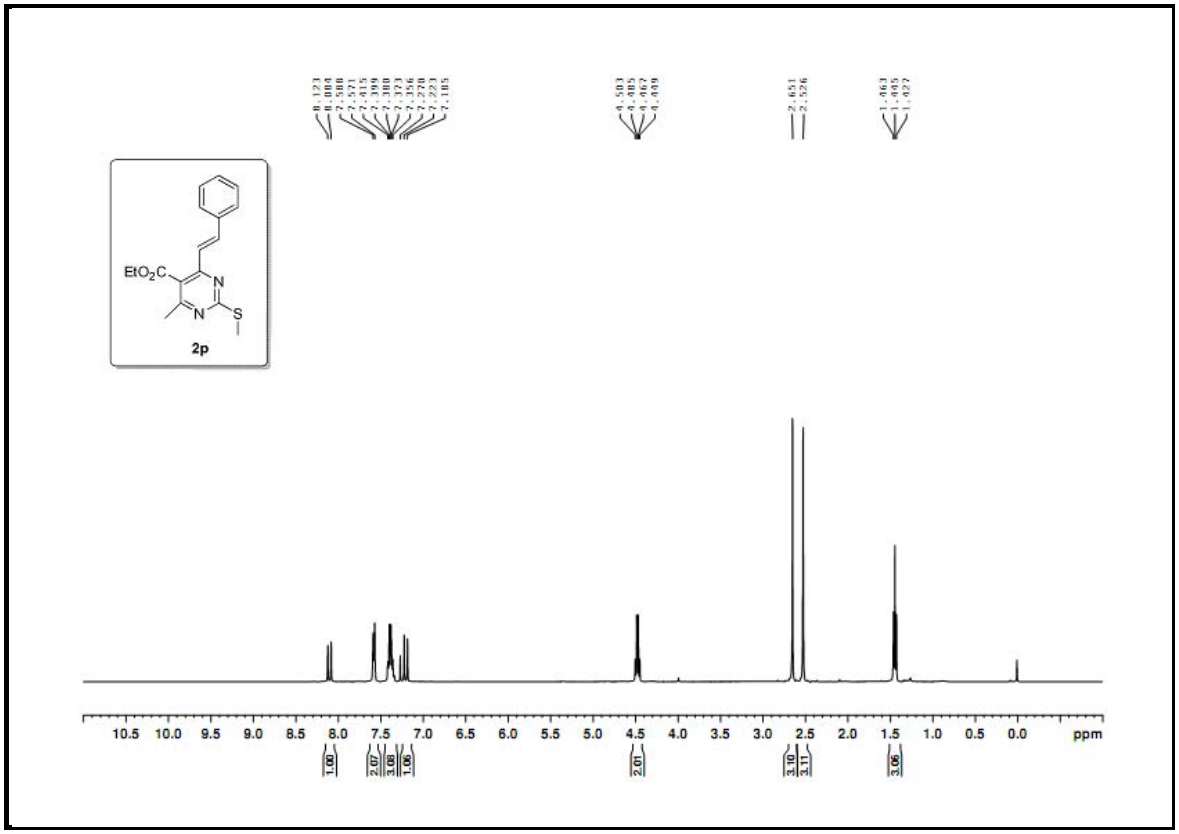

172.73
168.09
164.33
137.66
130.06
129.03
128.37
120.81
77.32
77.00
76.68
61.76
15.29
13.98
EtO2C
N
Ph
N
S
2m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

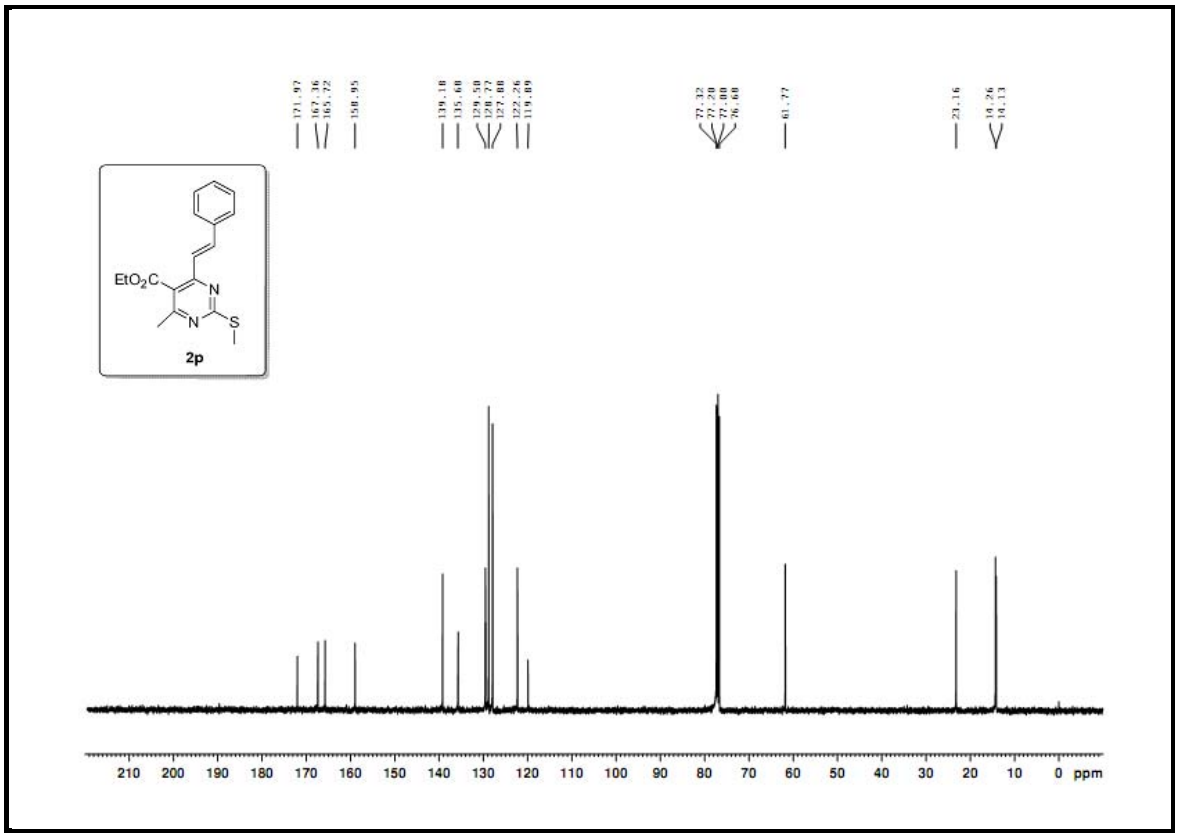

Cl
EtO2C
N
Ph
N
S
2n
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

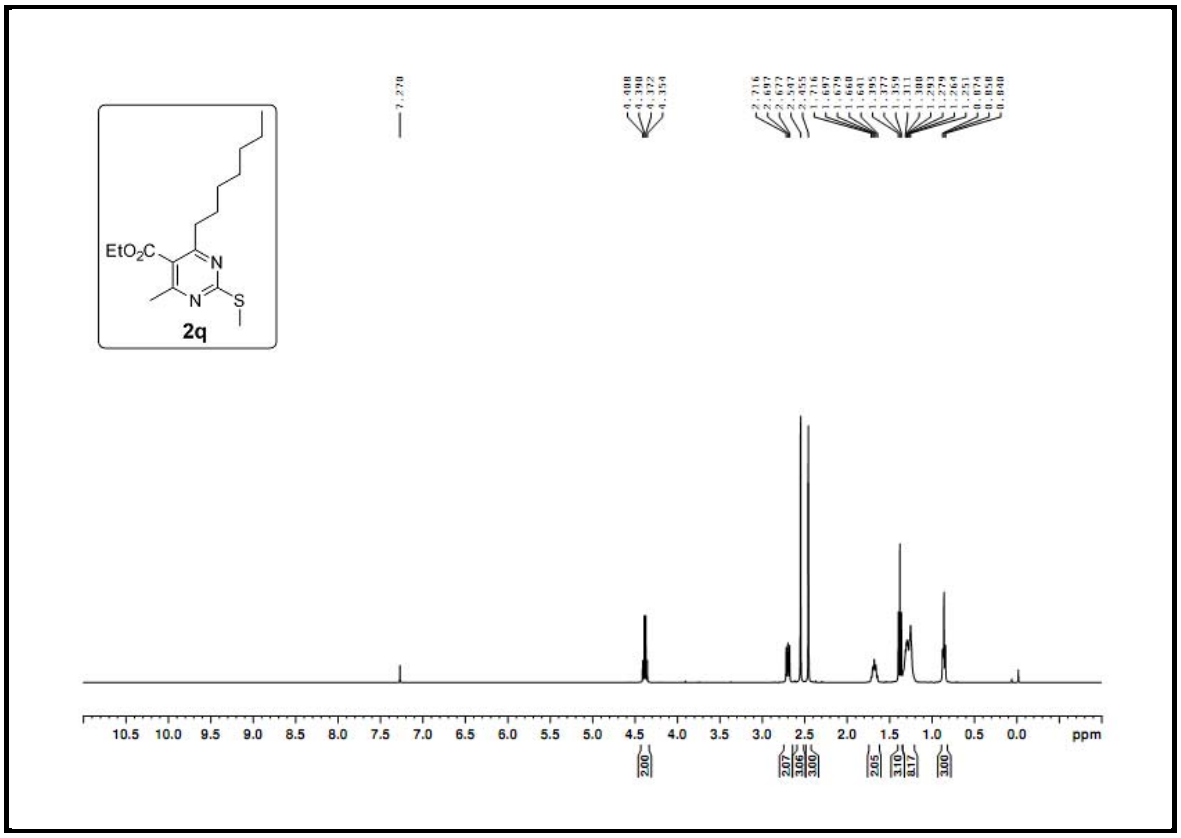

Cl
EtO2C
N
Ph
N
S
2n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

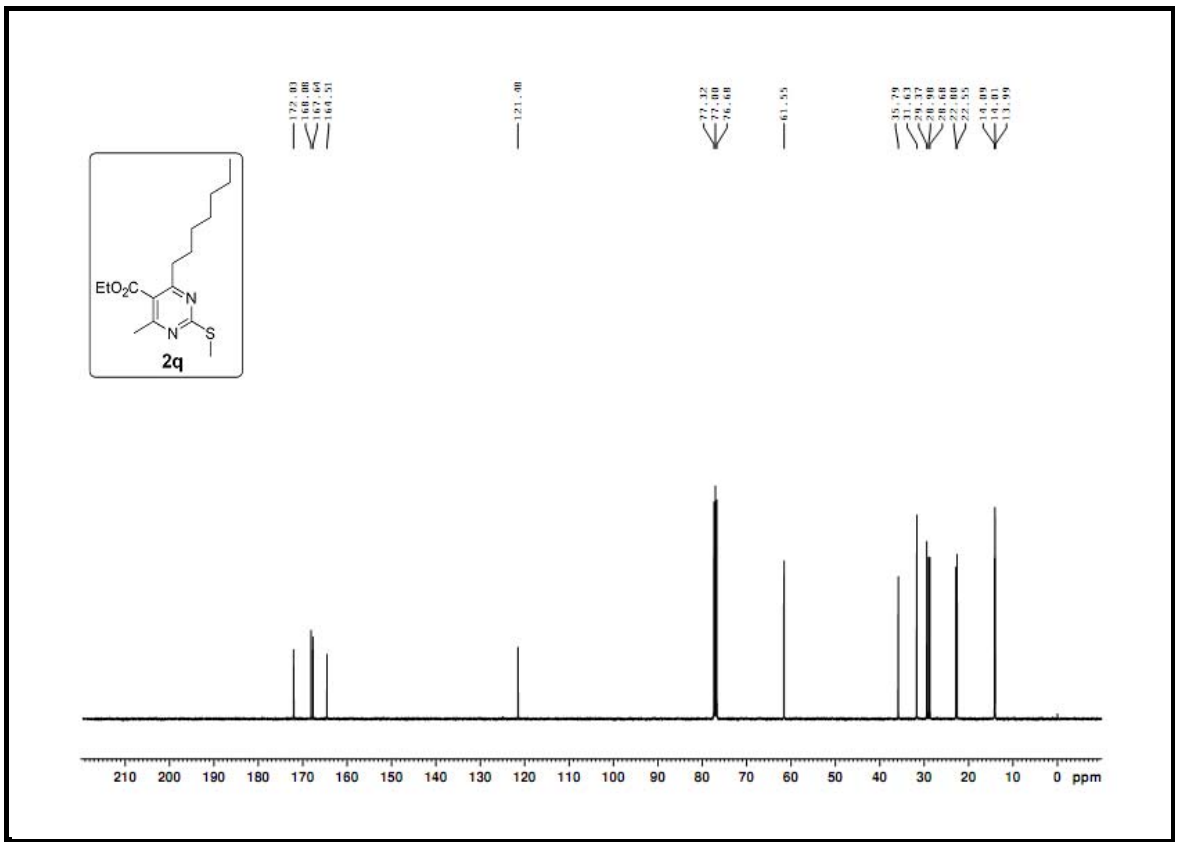

OCH3
EtO2C
N
Ph
N
S
2o
ppm

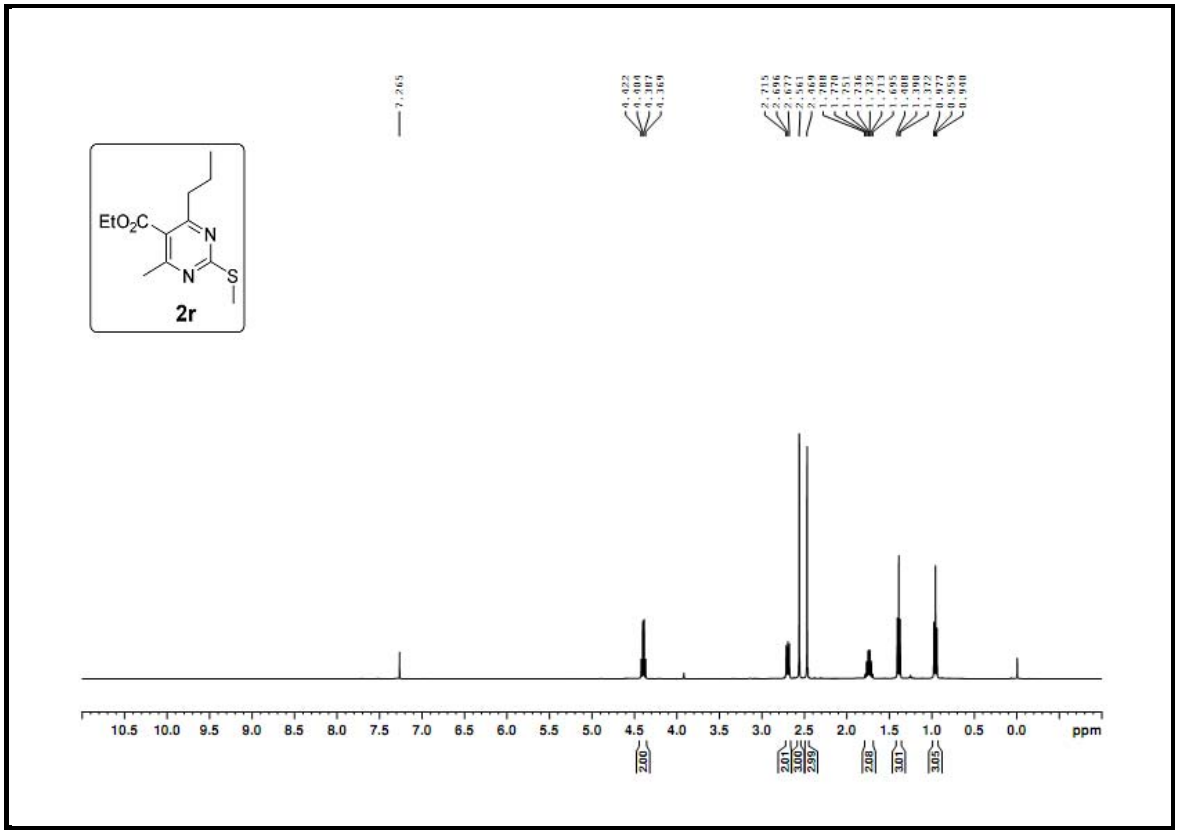

OCH3
EtO2C
N
Ph
N
S
2o
ppm

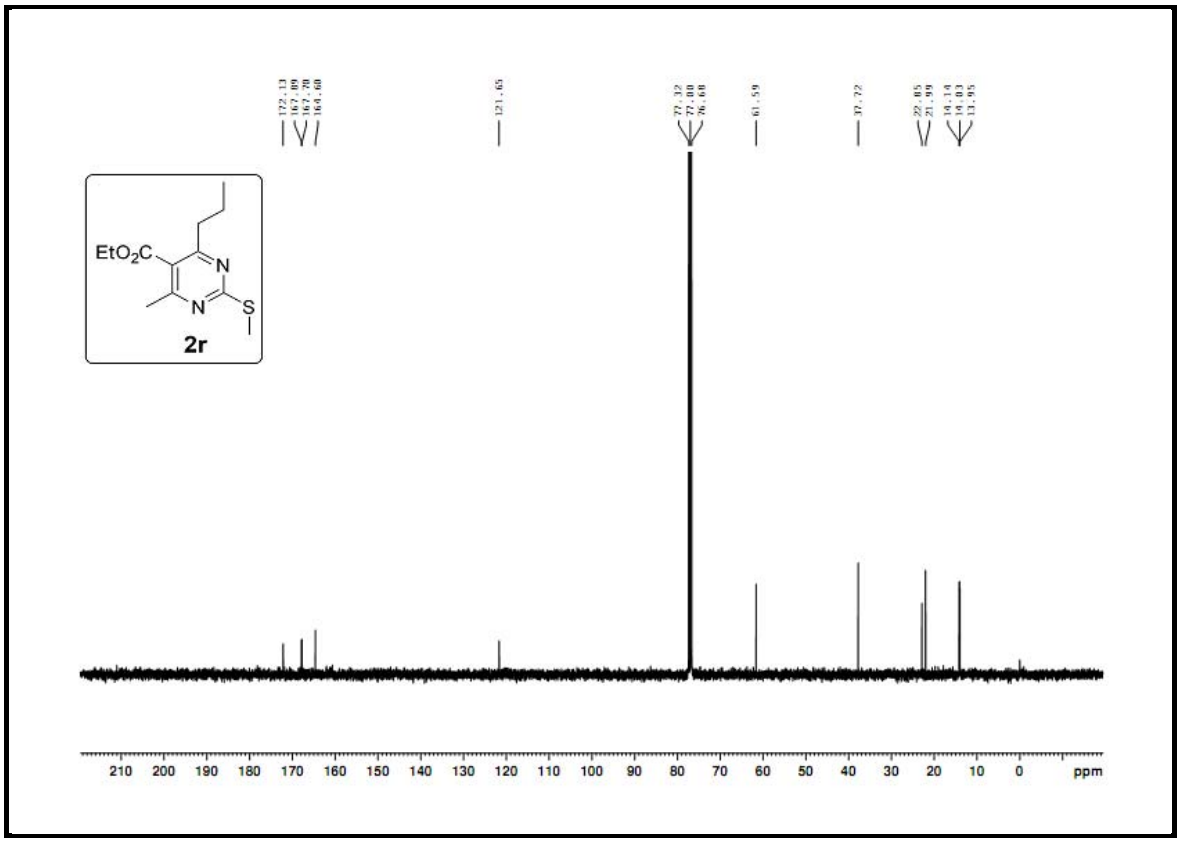

8.173
8.088
8.080
8.068
8.058
7.571
7.415
7.399
7.380
7.373
7.356
7.276
7.223
7.185
4.503
4.485
4.467
4.449
2.651
2.526
1.463
1.445
1.427
EtO2C
N
N
S
2p
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
2.07
3.08
1.00
2.07
3.10
3.17
3.06

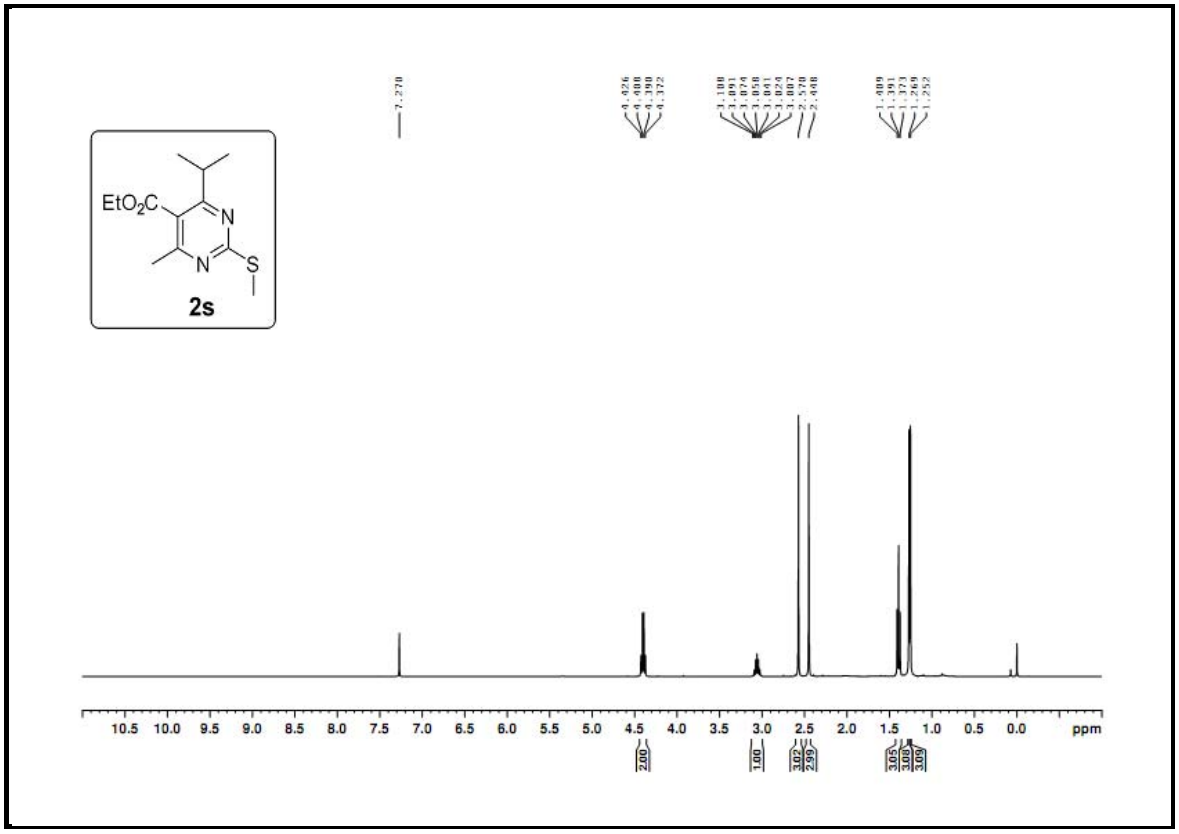

171.97
167.36
163.72
158.95
139.18
135.68
129.50
128.77
127.88
122.26
119.89
77.32
77.20
77.08
76.68
61.77
23.16
14.26
14.13
EtO2C
N
N
S
2p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

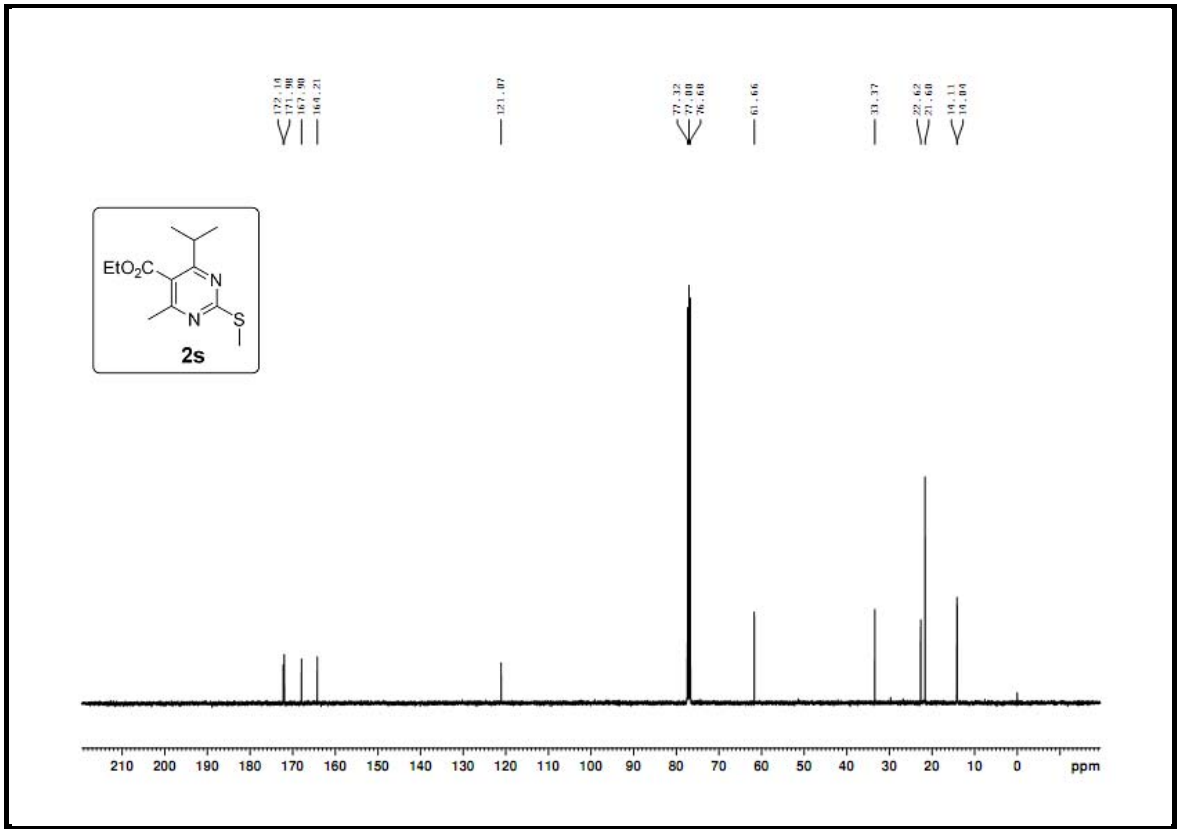

EtO2C
N
N
S
2q
7.270
4.408
4.390
4.372
4.354
2.716
2.697
2.677
2.657
2.635
1.716
1.697
1.679
1.660
1.641
1.622
1.375
1.359
1.311
1.300
1.279
1.264
1.251
0.874
0.858
0.840
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
2.07
3.06
3.00
2.05
3.10
8.17
3.00

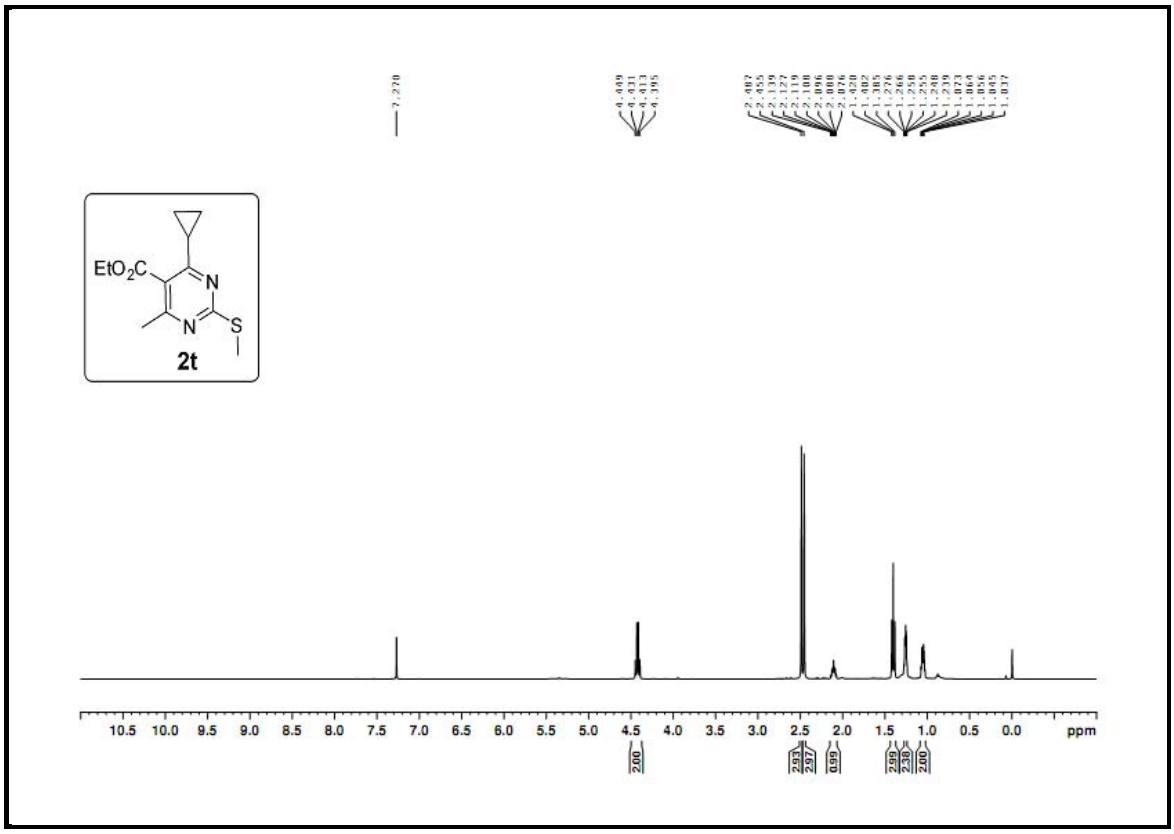

EtO2C
N
N
S
2q
172.03
168.88
167.65
164.51
121.08
77.32
77.00
76.68
61.55
35.79
31.63
29.37
28.80
28.68
22.80
22.55
14.09
14.01
13.99
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

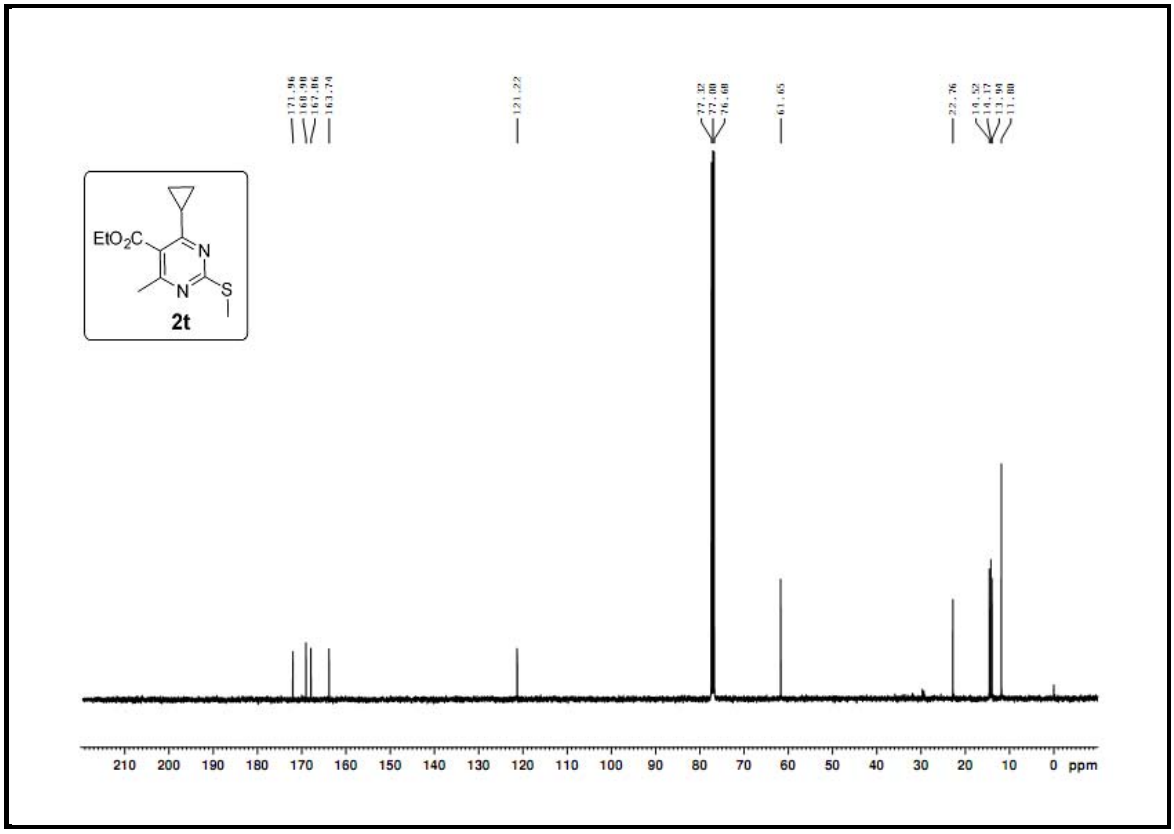

7.265
4.422
4.404
4.387
4.369
2.715
2.696
2.677
2.561
2.069
1.788
1.770
1.751
1.736
1.713
1.695
1.388
1.372
0.977
0.959
0.940
EtO2C
N
N
S
2r
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
200
201
300
299
208
301
305

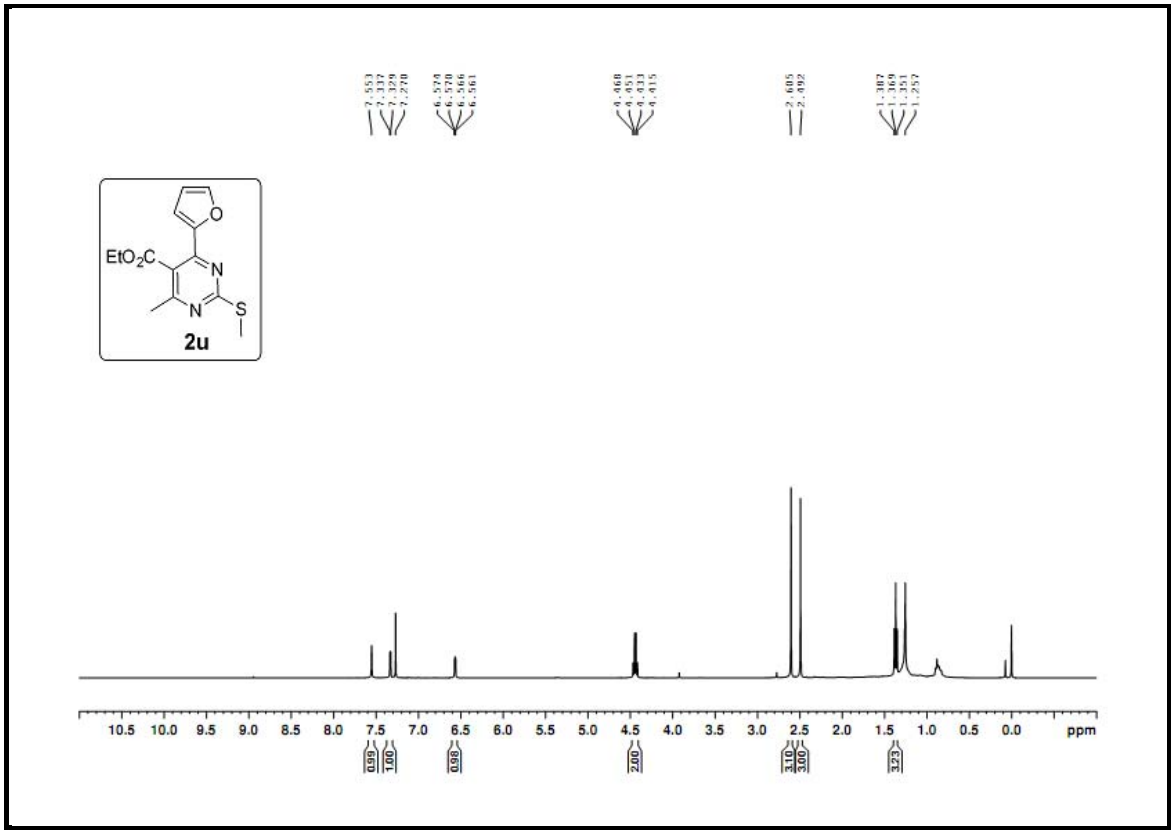

172.13
167.89
167.70
164.68
121.65
77.32
77.00
76.68
61.59
37.72
22.85
21.99
14.14
14.03
13.95
EtO2C
N
N
S
2r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

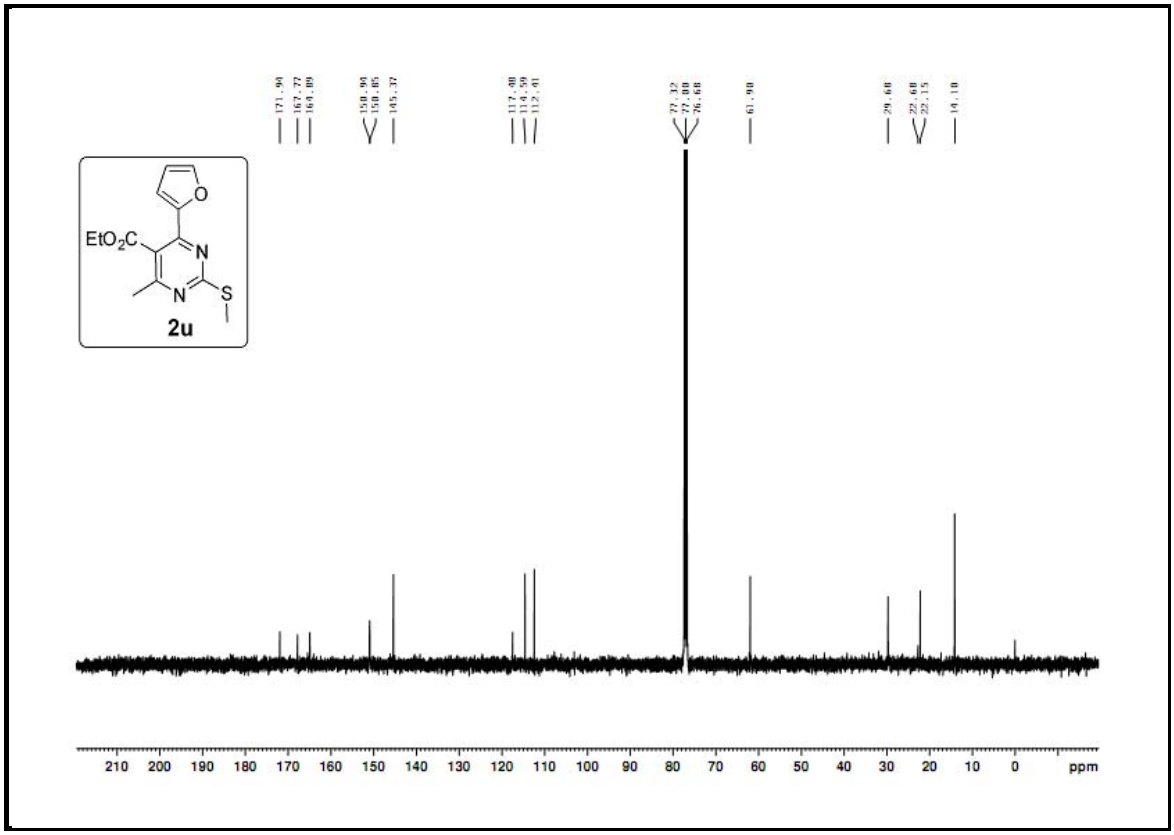

7.270
4.426
4.408
4.390
4.372
3.108
3.091
3.074
3.058
3.041
3.024
3.007
2.990
2.530
2.448
1.409
1.391
1.373
1.356
1.252
EtO2C
N
N
S
2s
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
1.00
3.02
2.99
3.05
3.08
3.09

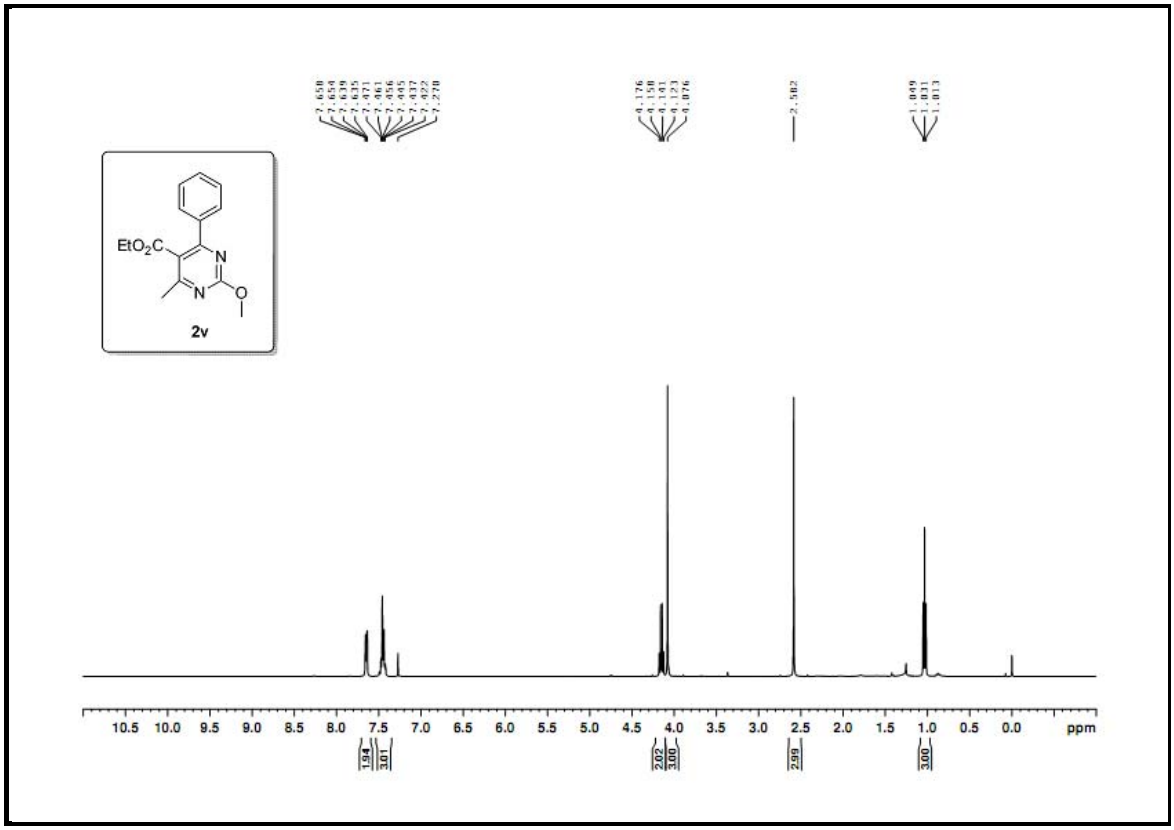

172.16
171.98
167.90
164.21
121.07
77.32
77.00
76.68
61.66
33.37
22.62
21.60
14.11
13.84
EtO2C
N
N
S
2s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

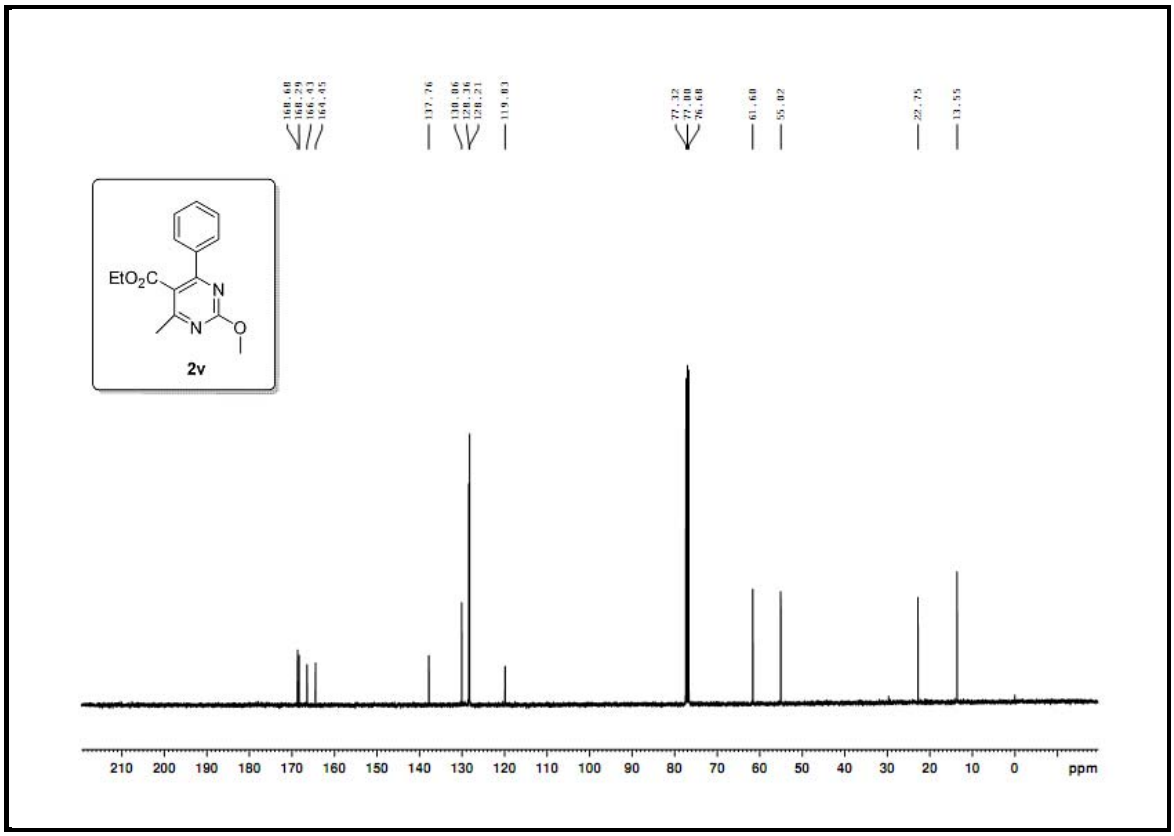

7.270
4.409
4.431
4.413
4.395
2.482
2.455
2.139
2.127
2.119
2.100
2.086
2.080
2.076
1.420
1.402
1.385
1.276
1.266
1.258
1.255
1.248
1.239
1.073
1.063
1.056
1.045
1.037
EtO2C
N
N
S
2t
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
2.93
2.97
0.99
2.89
2.38
2.00

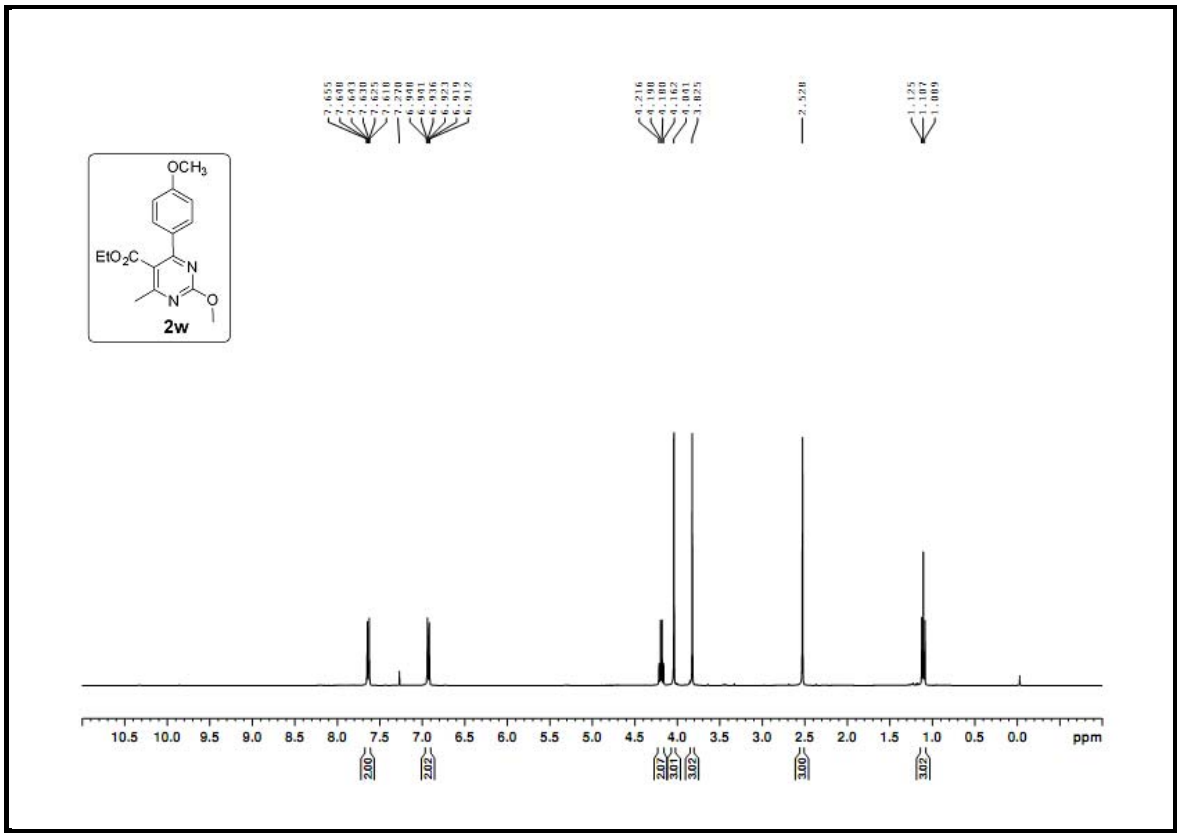

171.96
169.98
167.86
163.74
121.22
77.32
77.00
76.68
61.65
22.76
14.52
14.17
13.98
11.88
EtO2C
N
N
S
2t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

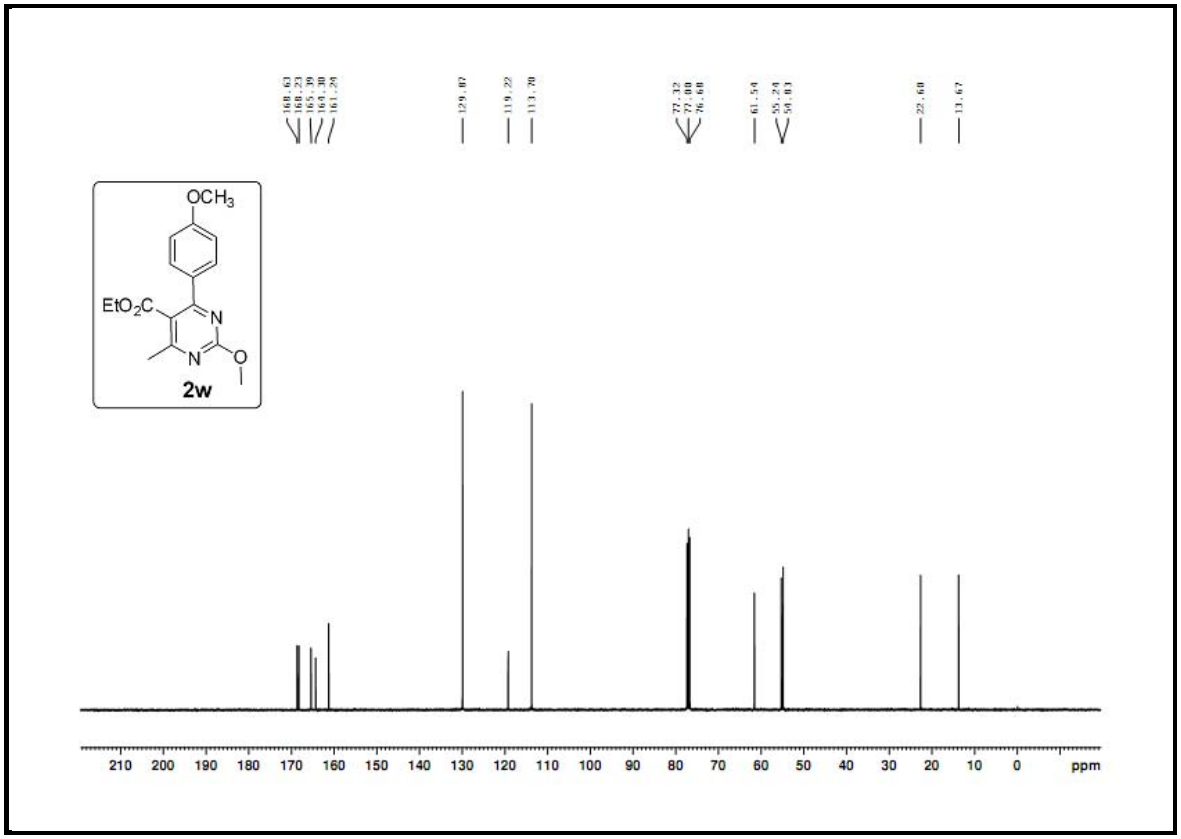

2u
ppm

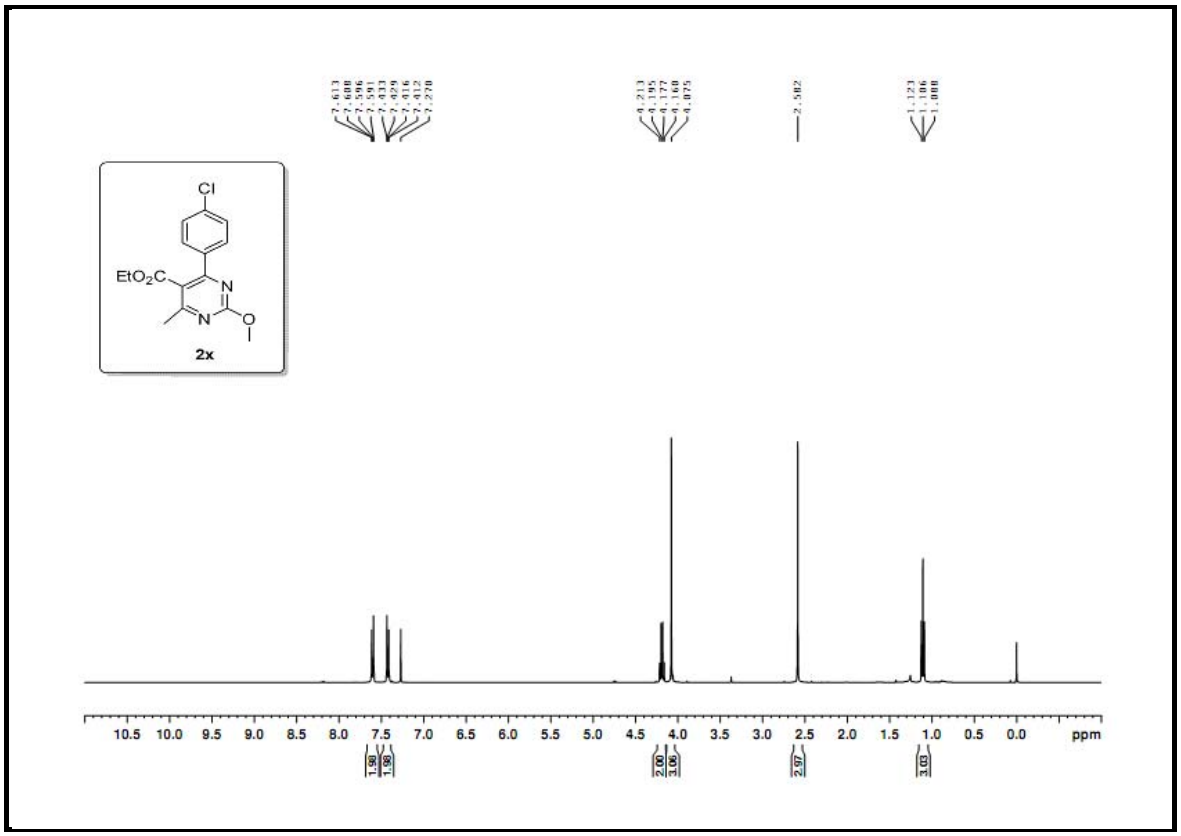

2u
ppm

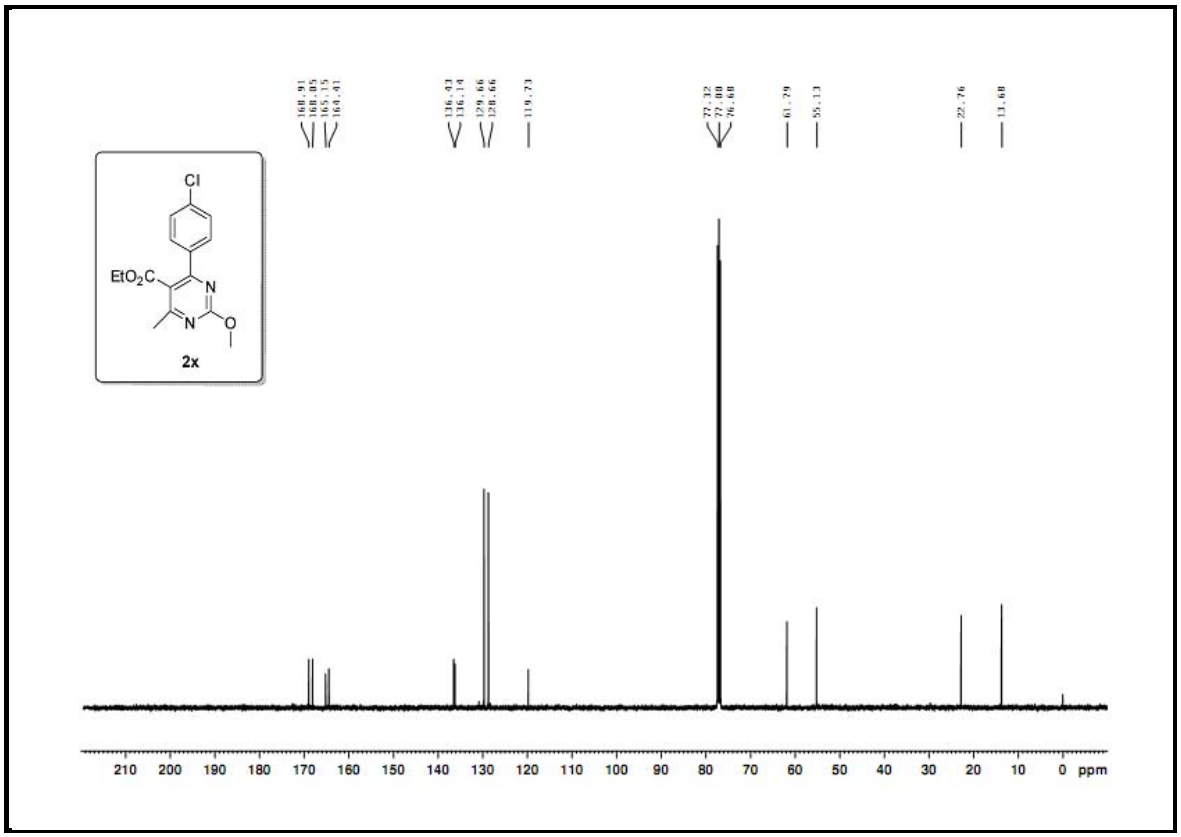

7.658
7.654
7.639
7.635
7.471
7.461
7.456
7.445
7.437
7.422
7.278
4.176
4.158
4.141
4.123
4.076
2.582
1.849
1.831
1.813
EtO2C
N
N
O
2v
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.94
3.01
2.02
3.00
2.99
3.00


168.68
168.29
166.43
164.45
137.76
130.86
129.16
128.21
119.83
77.32
77.00
76.68
61.60
55.82
22.75
13.55
EtO2C
N
N
O
2v
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

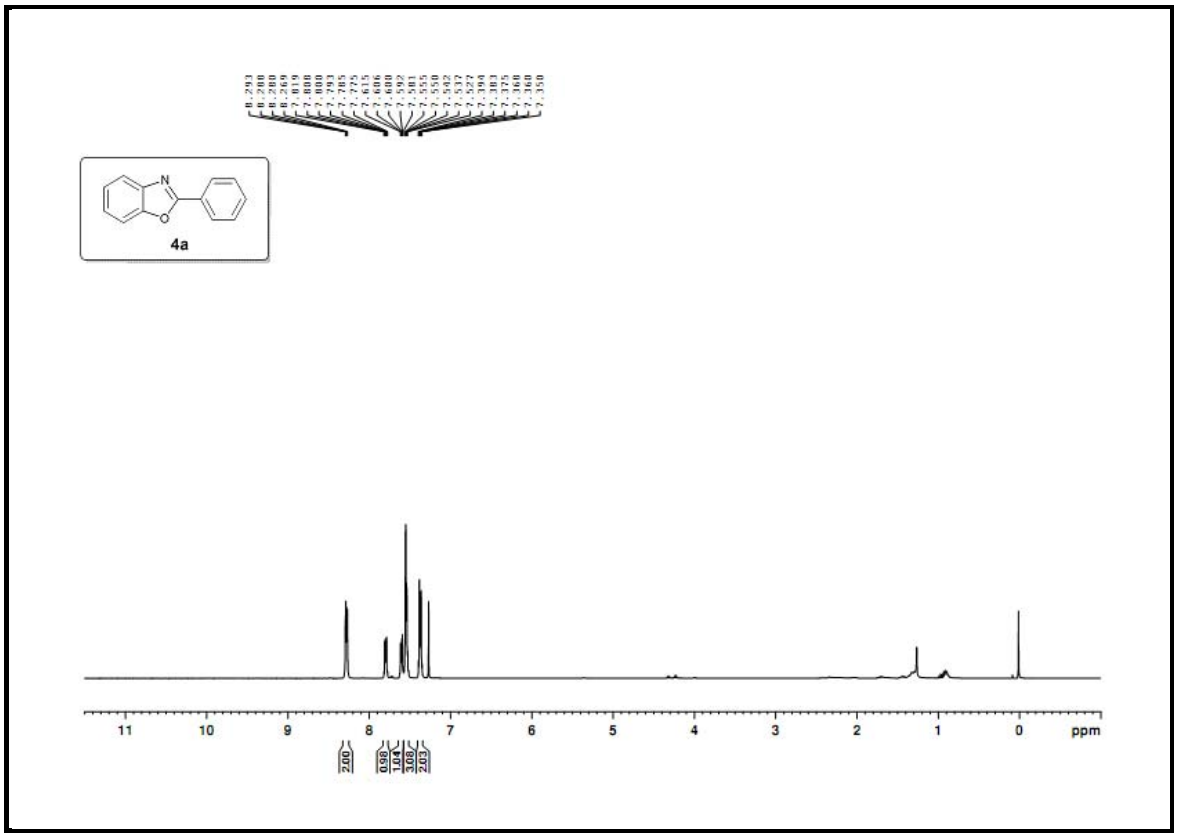

OCH3
EtO2C
N
N
O
2w
7.655
7.638
7.643
7.630
7.625
7.618
7.278
6.940
6.941
6.936
6.923
6.919
6.917
4.216
4.198
4.180
4.162
4.041
3.825
2.528
1.125
1.107
1.089
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
2.02
2.07
3.01
1.02
3.00
3.07

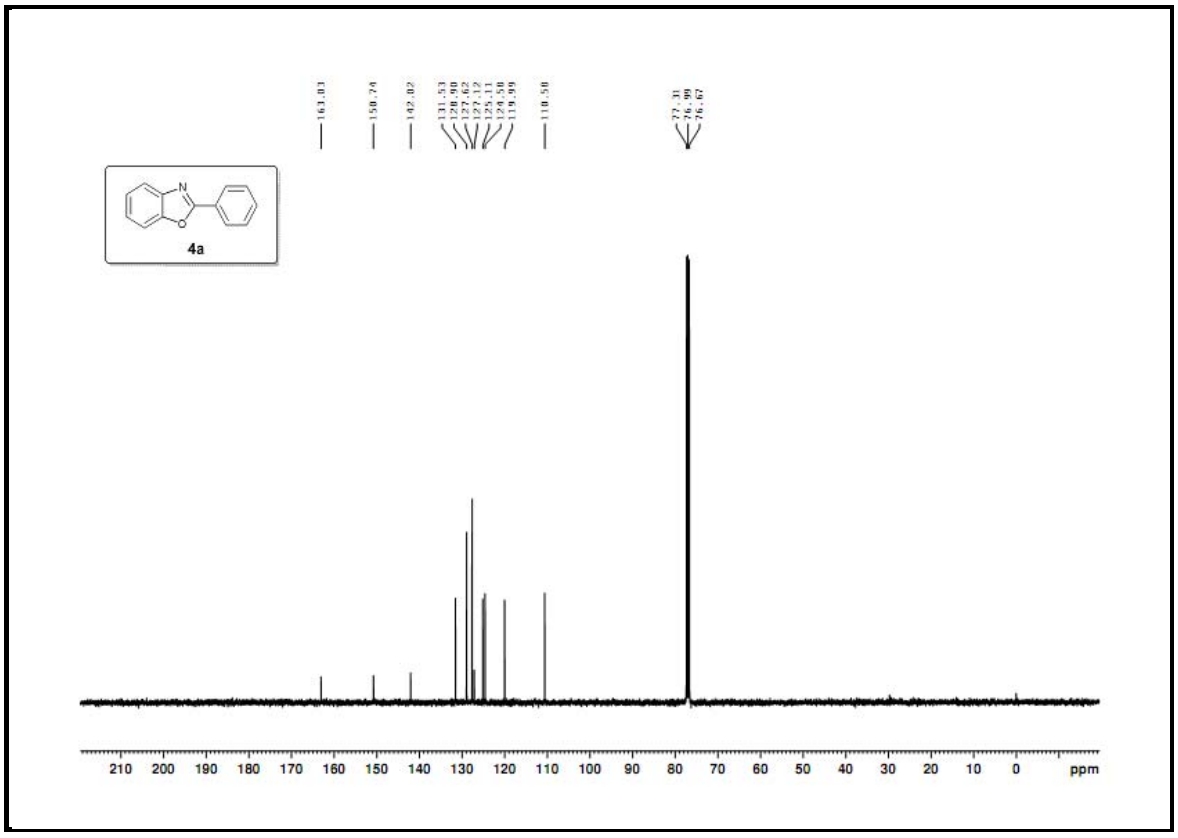

OCH3
EtO2C
N
N
O
2w
168.63
168.53
165.39
163.30
161.29
129.87
119.22
113.70
77.32
77.00
76.68
61.54
55.24
50.83
22.68
13.67
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

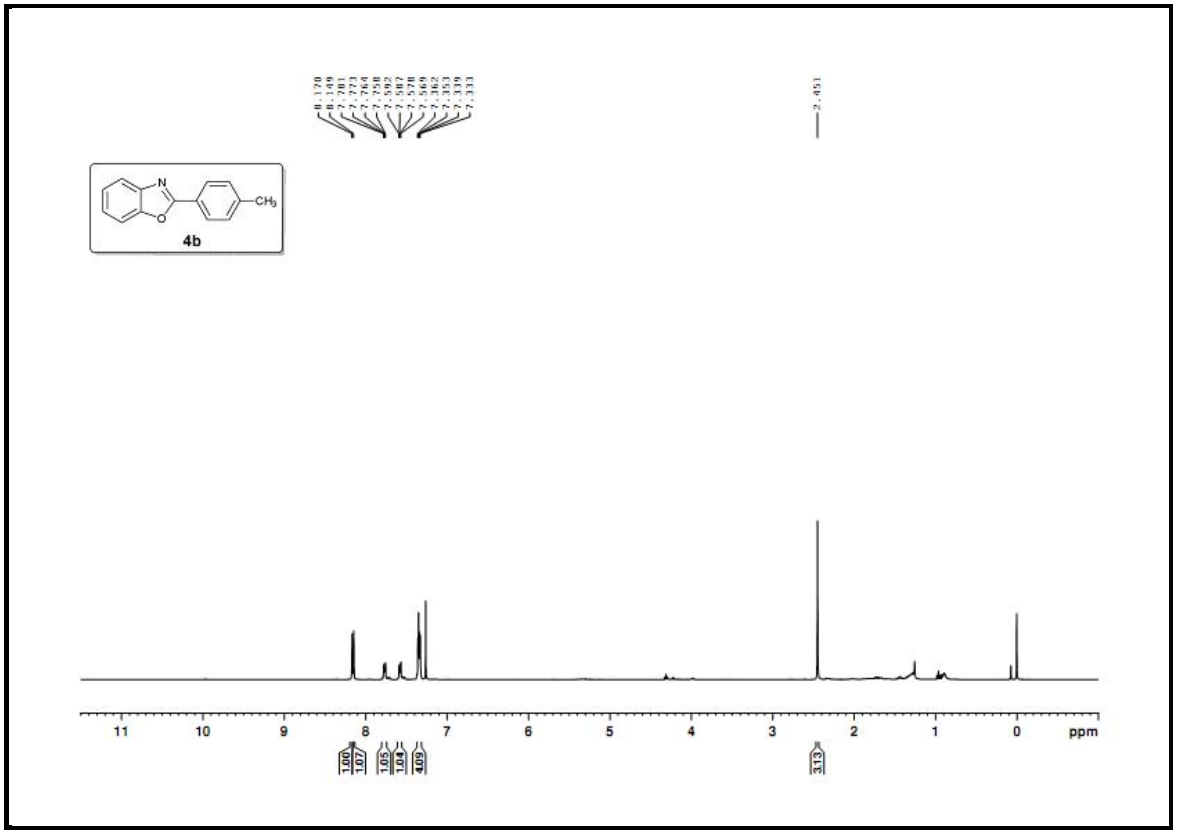

7.613
7.600
7.596
7.591
7.433
7.429
7.416
7.412
7.270
4.213
4.195
4.177
4.160
4.075
2.582
1.123
1.106
1.088
Cl
EtO2C
N
N
O
2x
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.98
1.98
2.00
3.06
2.97
3.03

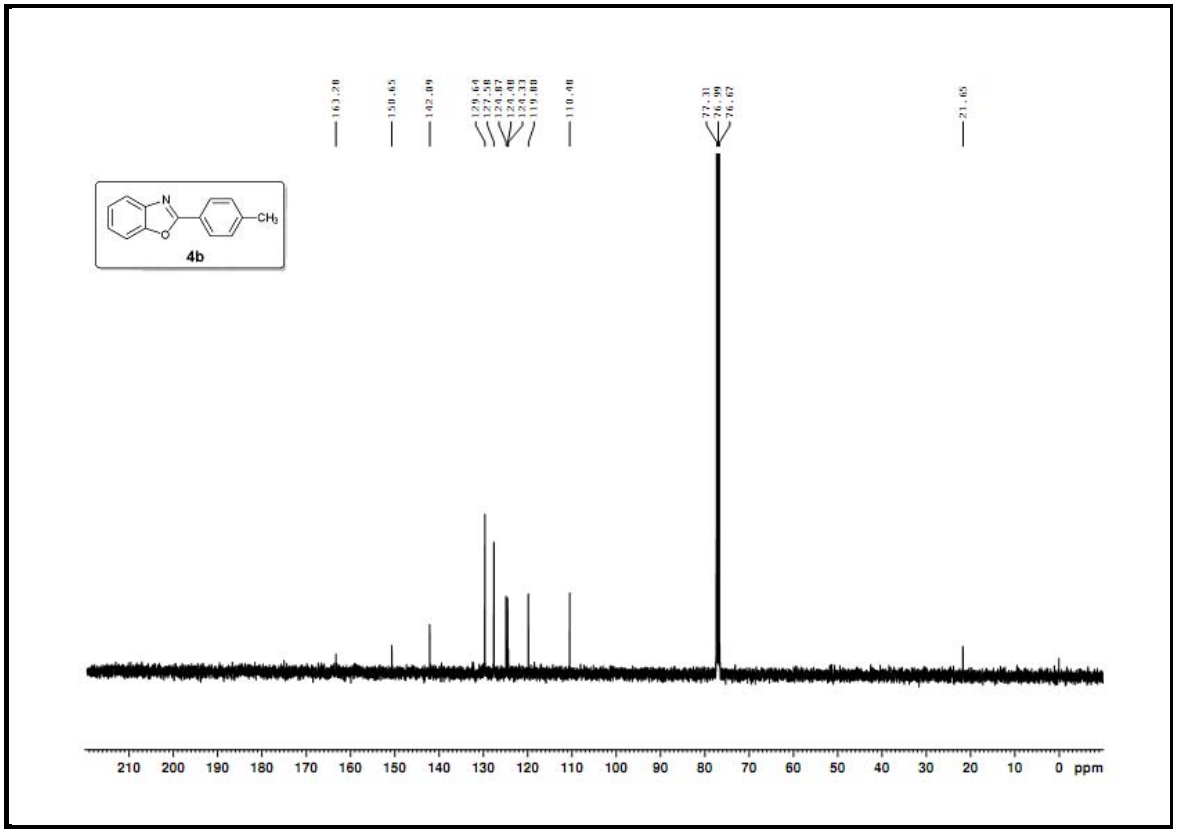

168.91
168.05
165.15
164.41
136.43
136.14
129.66
128.66
119.73
77.32
77.00
76.68
61.79
55.13
22.76
13.68
Cl
EtO2C
N
N
O
2x
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

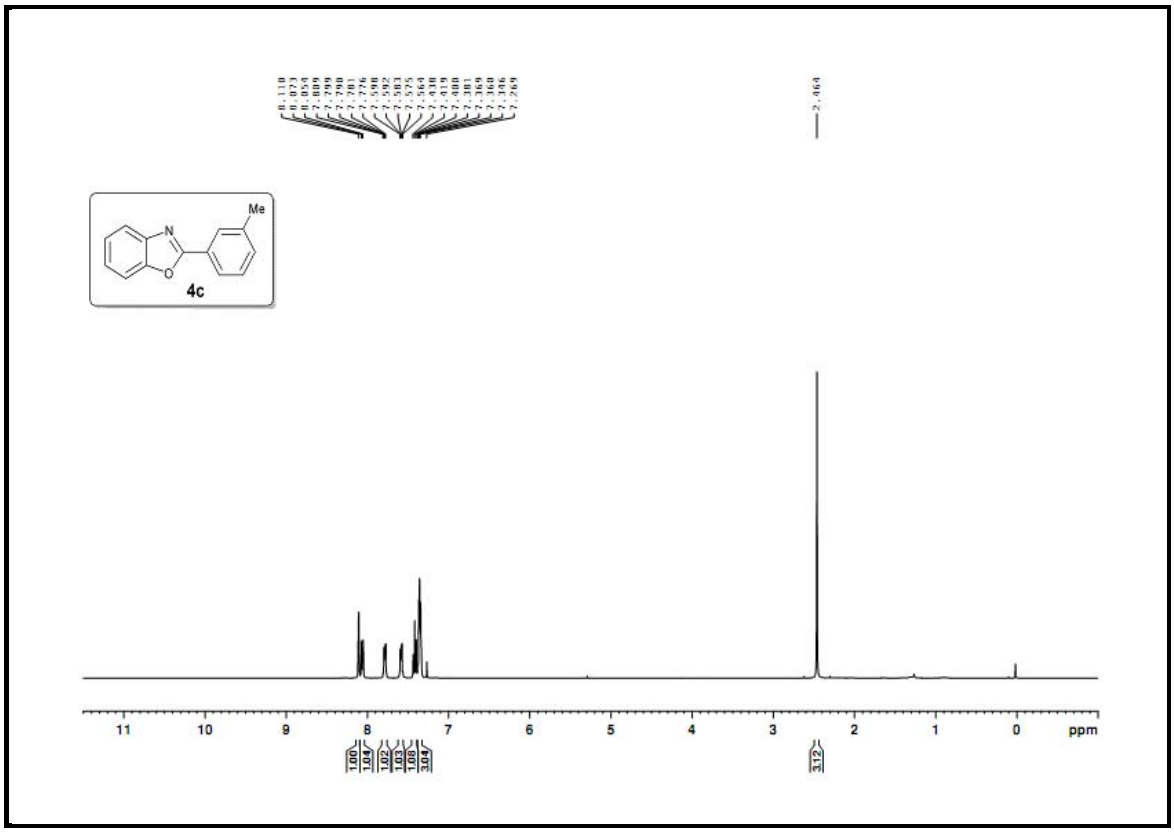
## 13.3 NMR Spectra Of 2-Substituted Benzoxazoles 4a-5m.

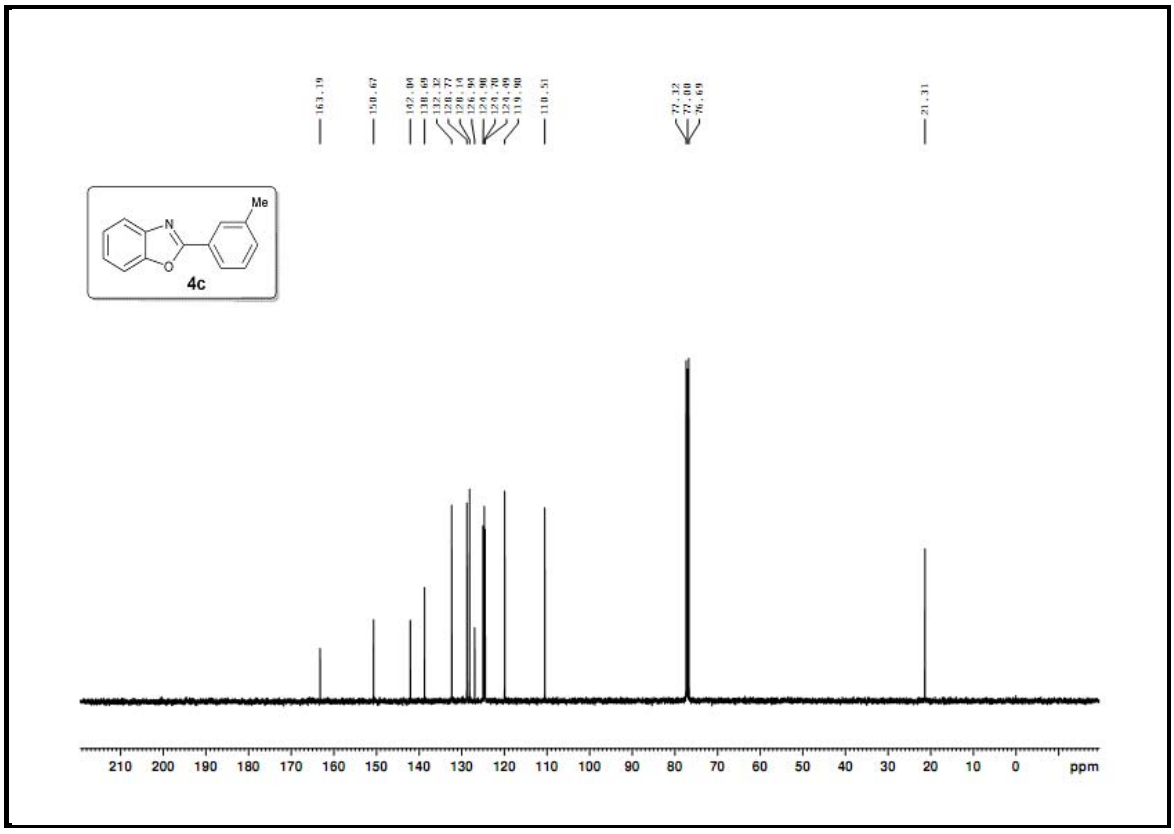


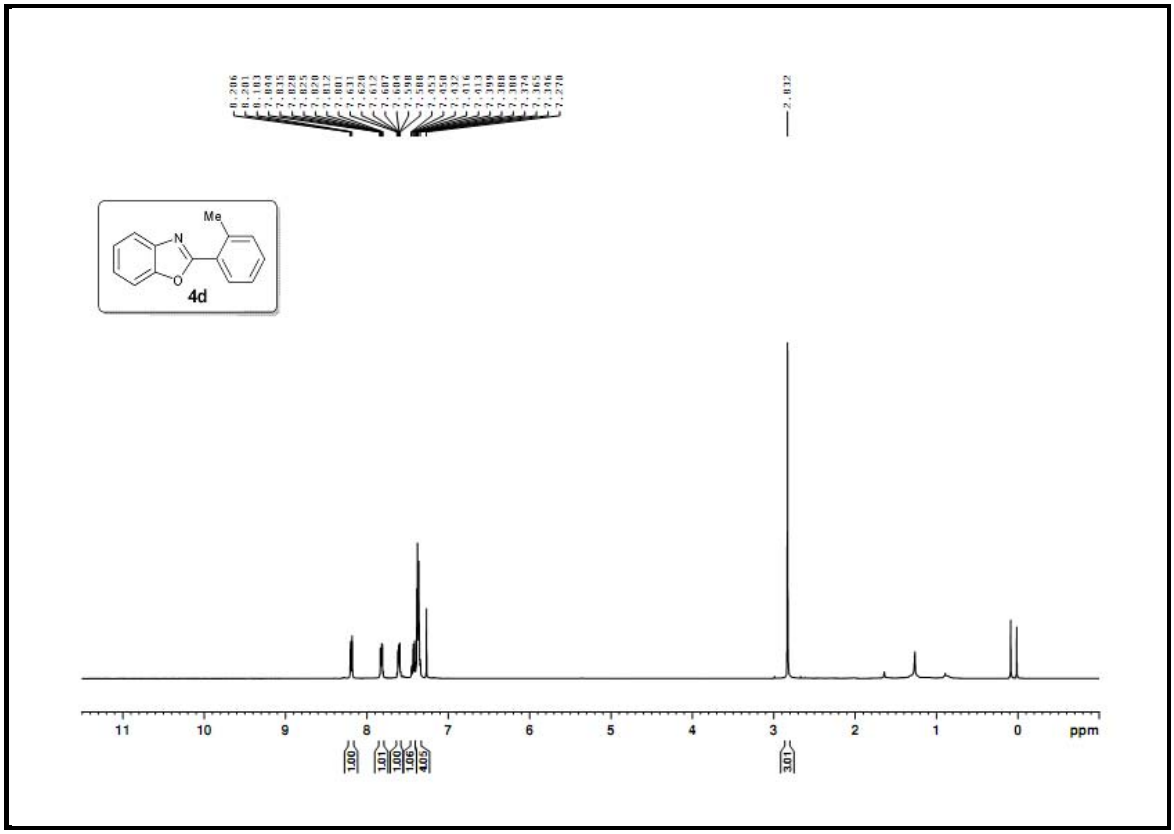



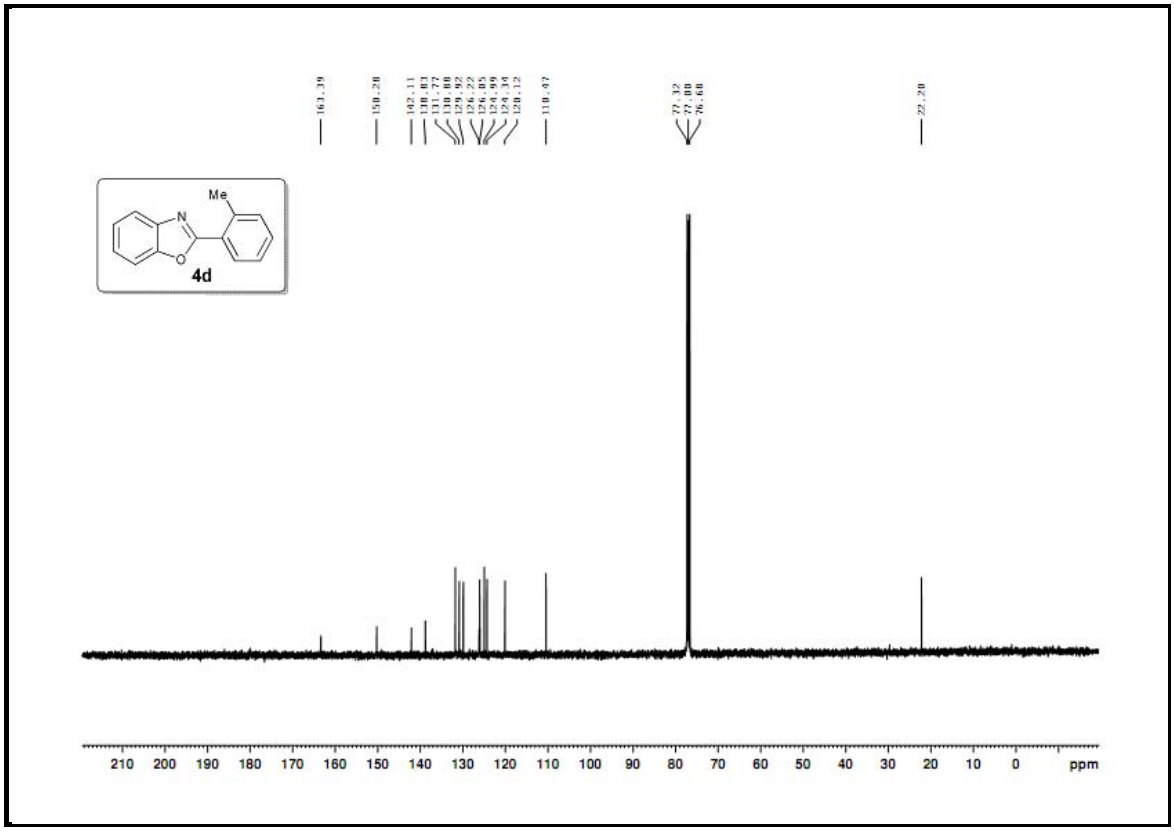

8.170
8.149
7.781
7.773
7.764
7.758
7.592
7.587
7.578
7.569
7.362
7.353
7.339
7.333
2.451
4b
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.07
1.05
1.04
4.09
3.13


163.28
150.65
142.89
129.64
127.58
124.87
124.38
120.33
119.80
110.48
77.31
76.99
76.67
21.65
4b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.110
8.073
8.054
7.809
7.799
7.748
7.781
7.776
7.598
7.592
7.583
7.575
7.564
7.438
7.419
7.400
7.381
7.369
7.360
7.336
7.269
2.464
Me
N
O
4c
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.04
1.02
1.08
1.08
3.04
3.12


163.19
150.67
142.09
138.69
132.32
128.77
126.14
124.98
124.78
124.09
119.90
110.51
77.32
77.00
76.69
21.31
Me
N
O
4c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Me
N
O
4d
2.832
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.00
1.06
4.05
3.01


163.39
150.28
142.11
138.83
131.77
130.88
129.92
126.22
125.85
124.95
124.34
120.12
110.97
77.32
77.00
76.68
22.20
Me
N
O
4d
210
200
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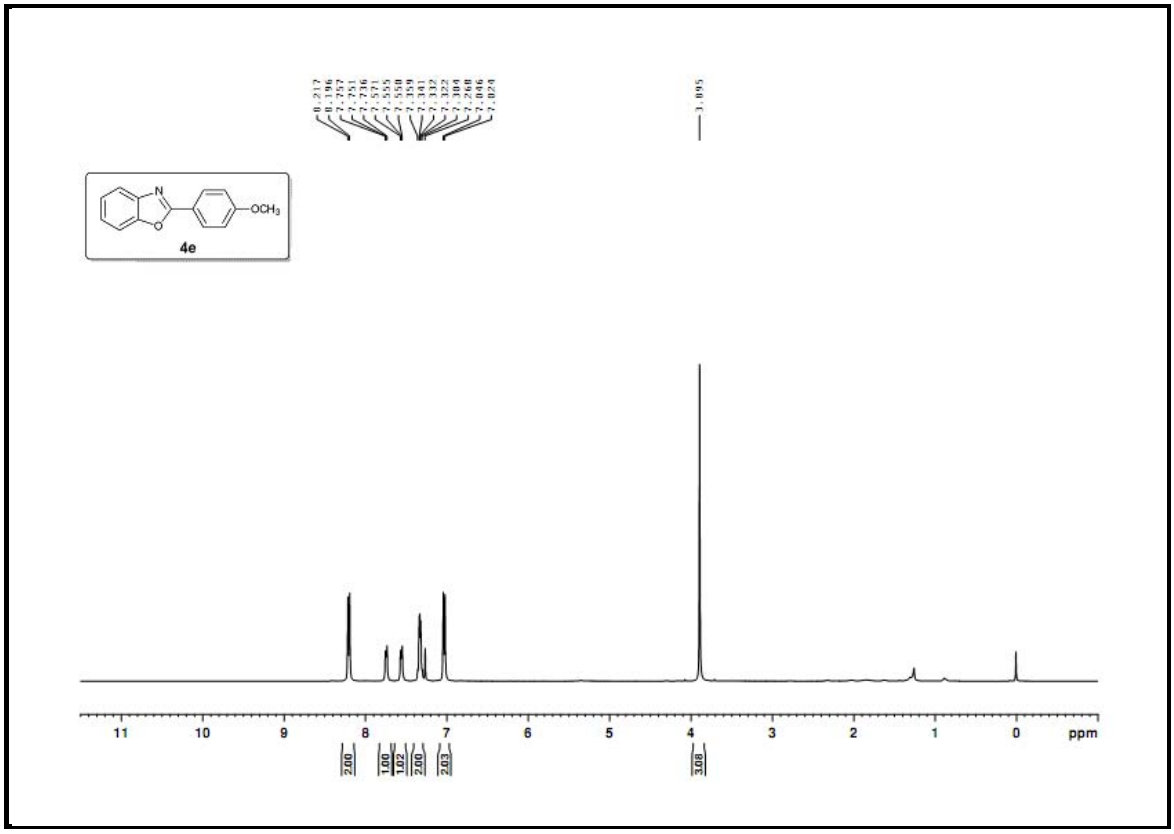
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7.304
7.248
7.046
7.029
3.895
OCH3
4e
11
10
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4
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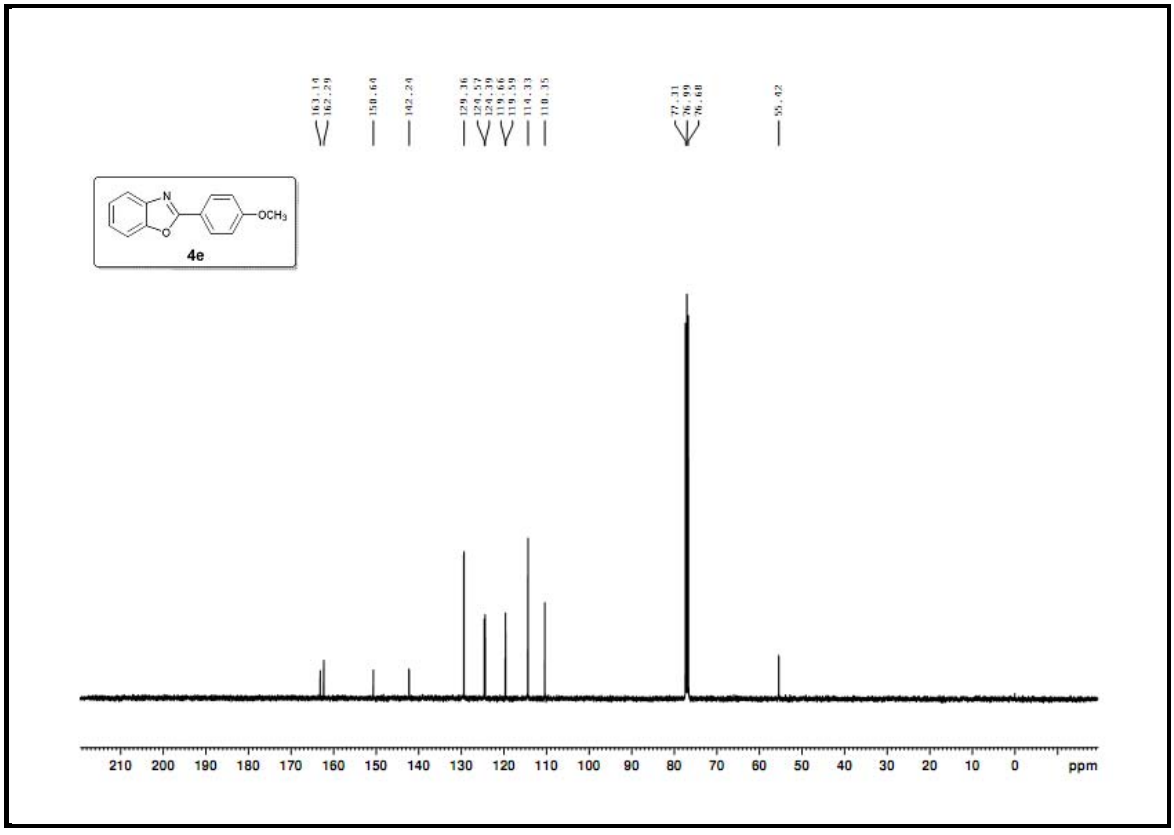
2.00
2.03
3.08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76.68
55.42
OCH3
4e
210
200
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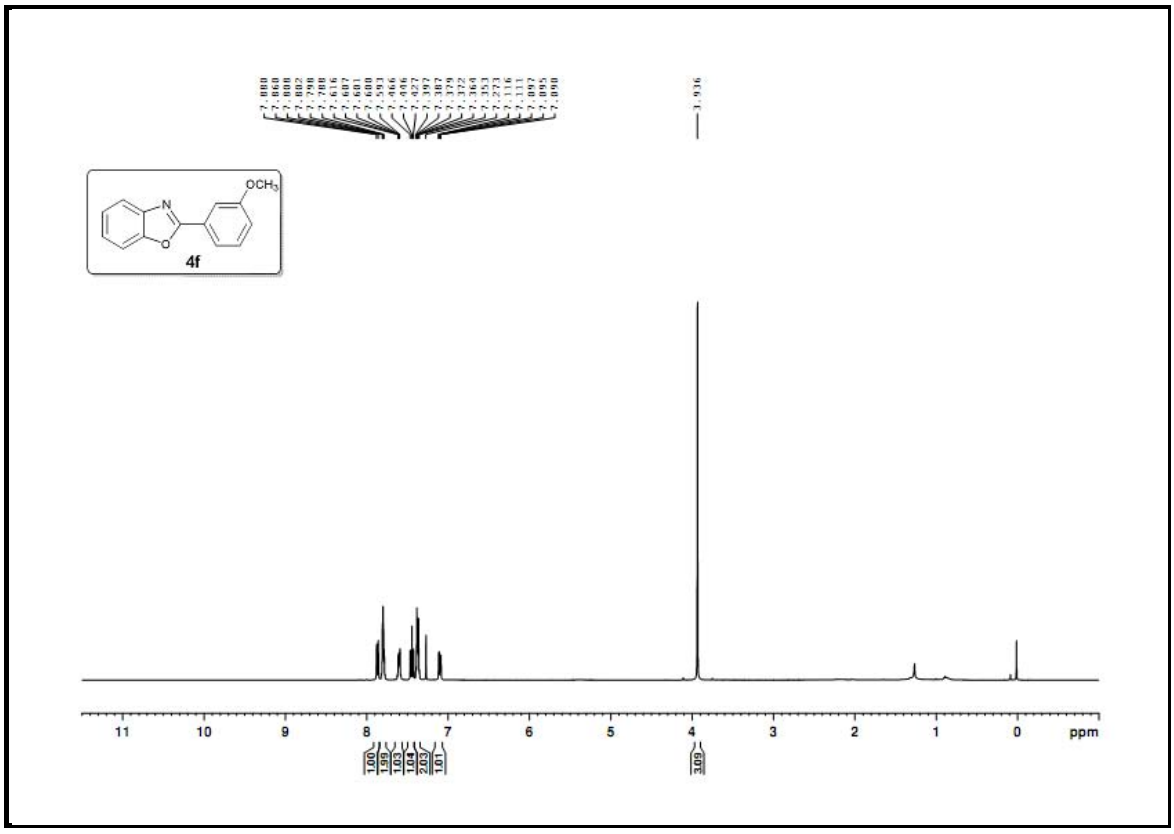
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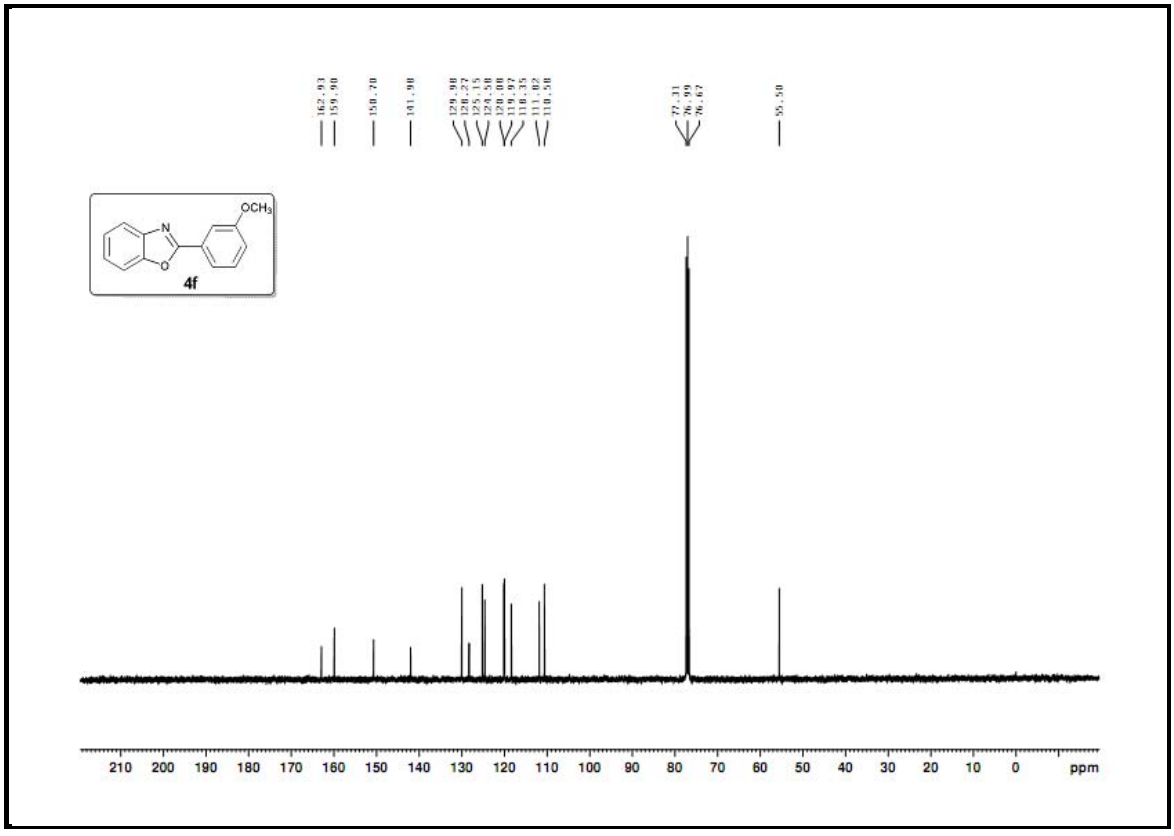
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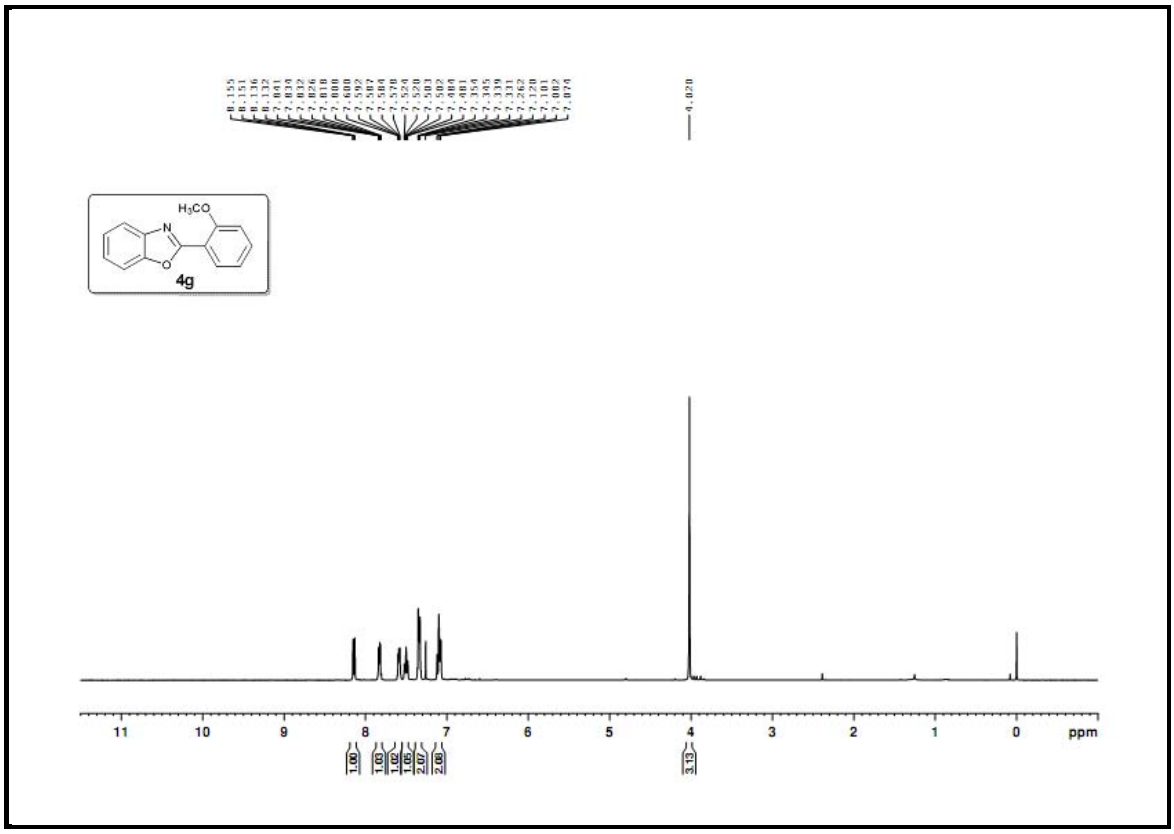
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8.136
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7.826
7.818
7.680
7.592
7.587
7.584
7.578
7.526
7.520
7.503
7.500
7.486
7.481
7.354
7.345
7.339
7.331
7.262
7.120
7.101
7.082
7.074
4.029
H3CO
N
O
4g
11
10
9
8
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1.06
1.05
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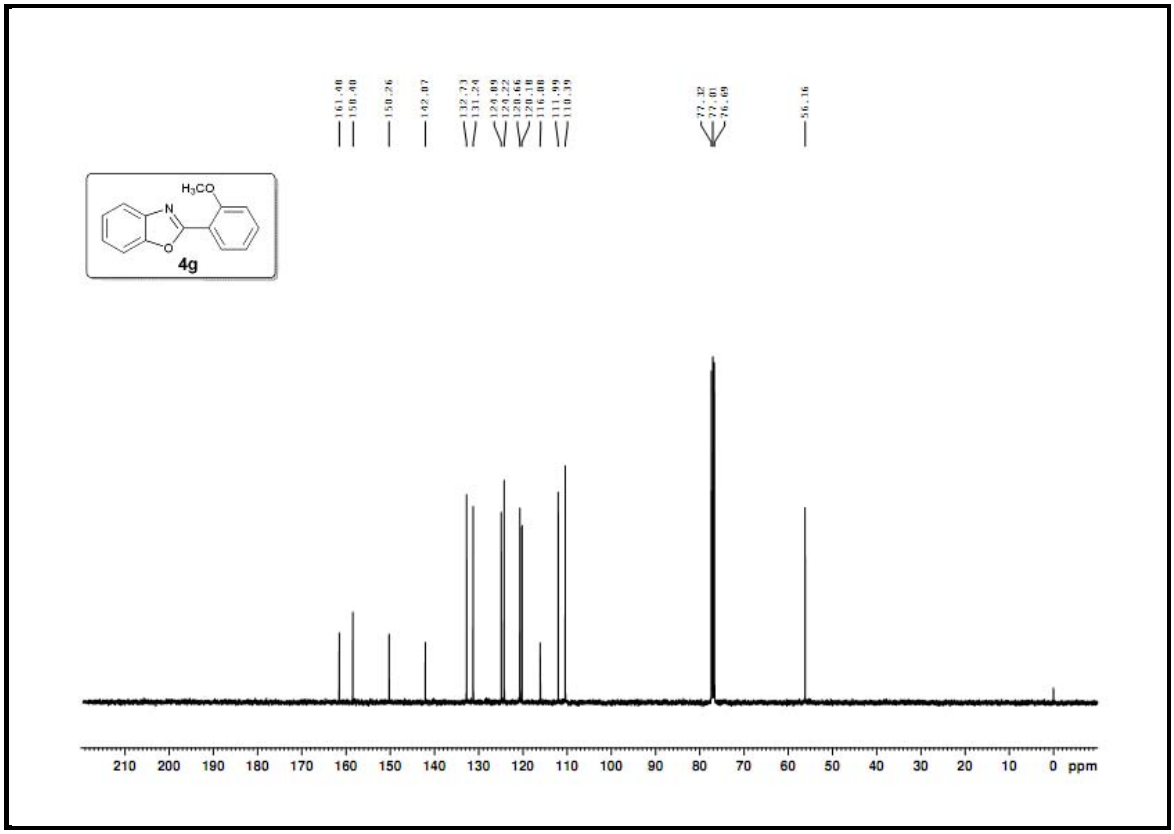
2.08
3.13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120.18
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111.99
110.39
77.32
77.01
76.69
56.16
H3CO
N
O
4g
210
200
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180
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150
140
130
120
110
100
90
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60
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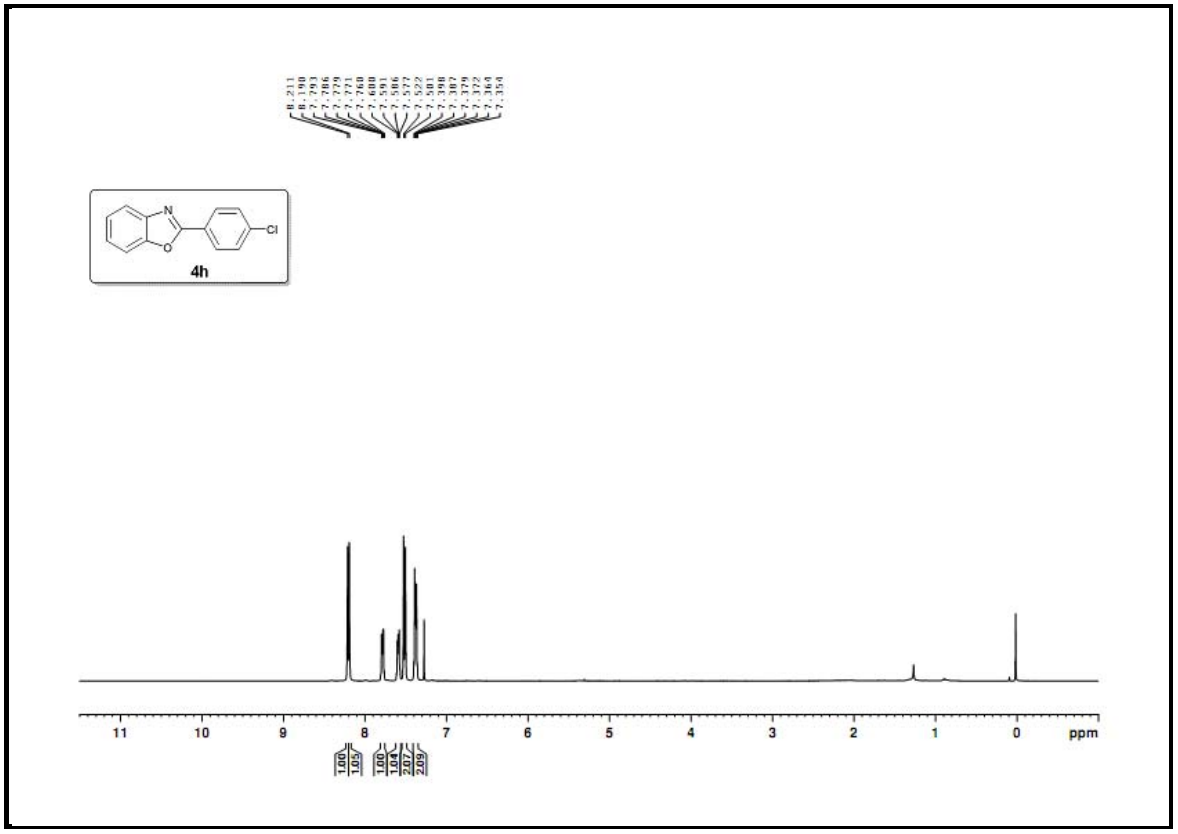
10
0
ppm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7.779
7.771
7.760
7.680
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7.586
7.577
7.522
7.501
7.398
7.397
7.379
7.372
7.364
7.354
N
O
Cl
4h
11
10
9
8
7
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4
3
2
1
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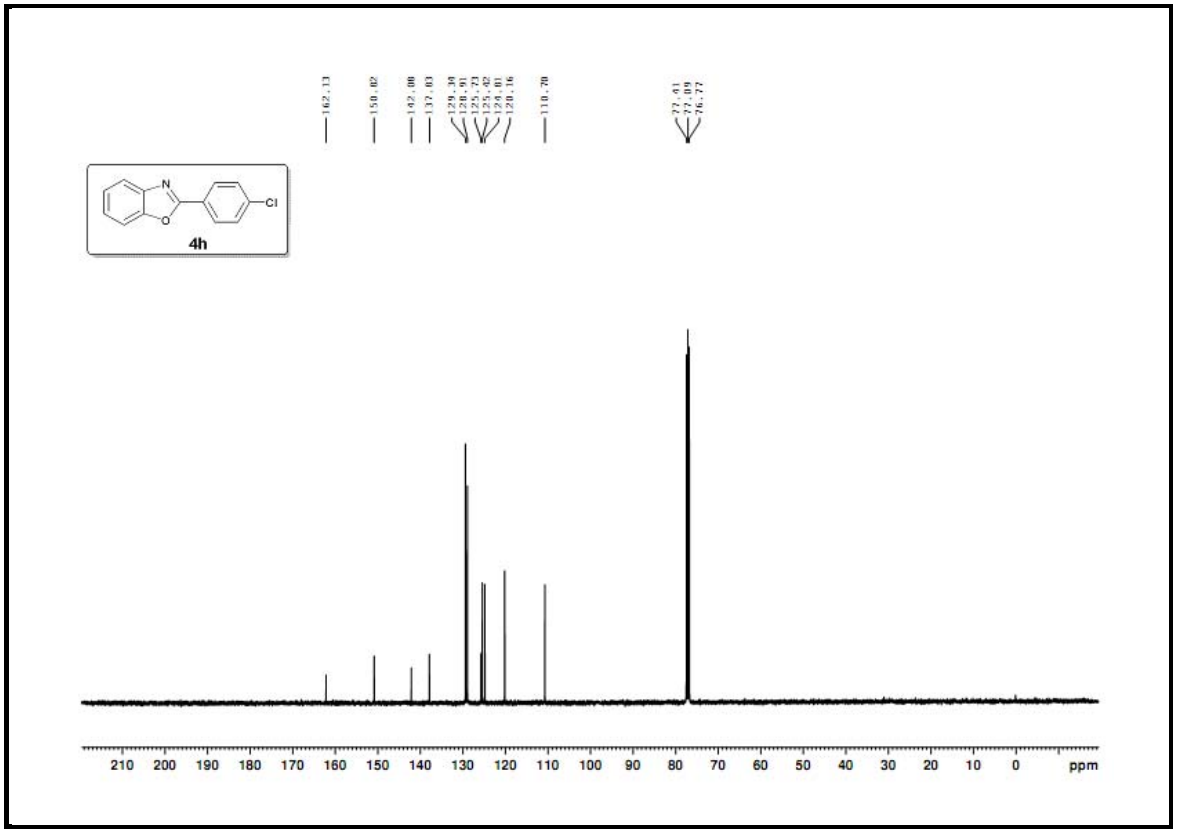
1.05
1.00
1.04
2.07
2.09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125.42
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120.16
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77.41
77.09
76.77
N
O
Cl
4h
210
200
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60
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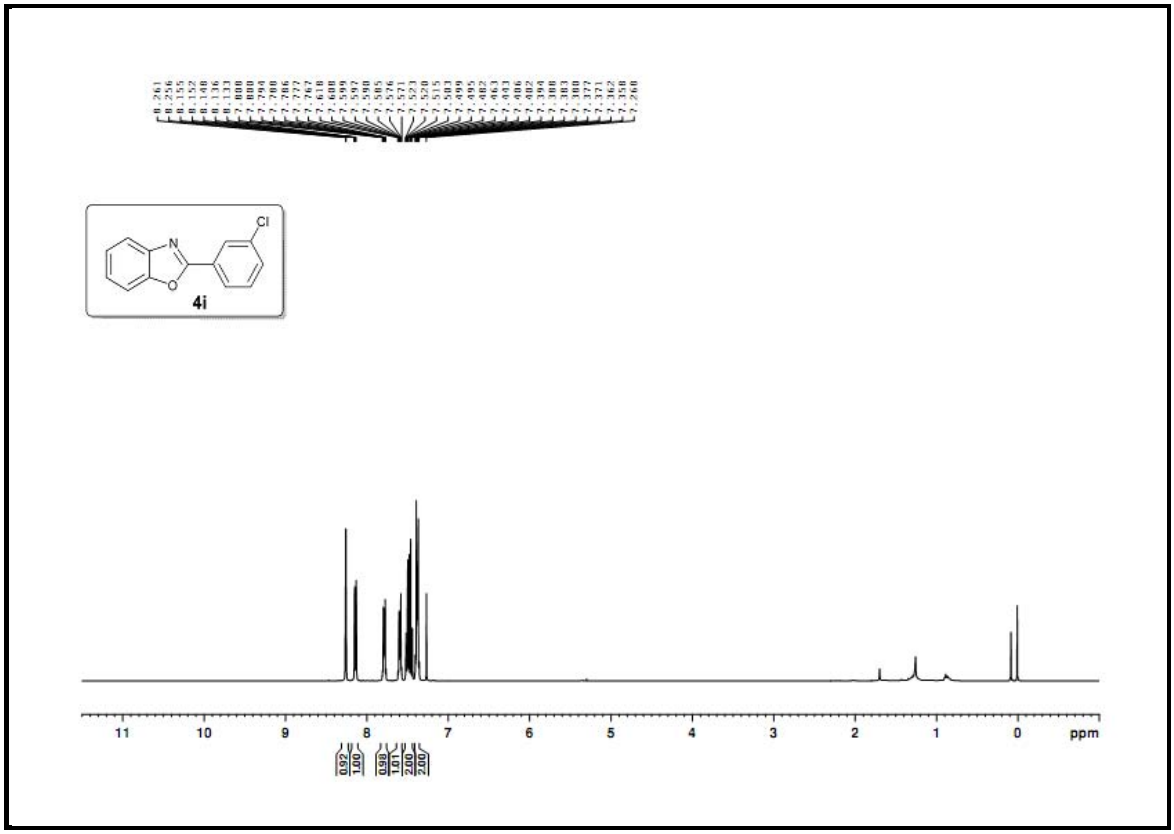
30
20
10
0
ppm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8.152
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8.136
8.133
7.888
7.794
7.788
7.786
7.772
7.767
7.618
7.608
7.599
7.594
7.590
7.585
7.576
7.571
7.523
7.520
7.515
7.503
7.499
7.495
7.482
7.464
7.443
7.406
7.402
7.394
7.388
7.385
7.380
7.377
7.371
7.362
7.358
7.288
Cl
N
O
4i
11
10
9
8
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4
3
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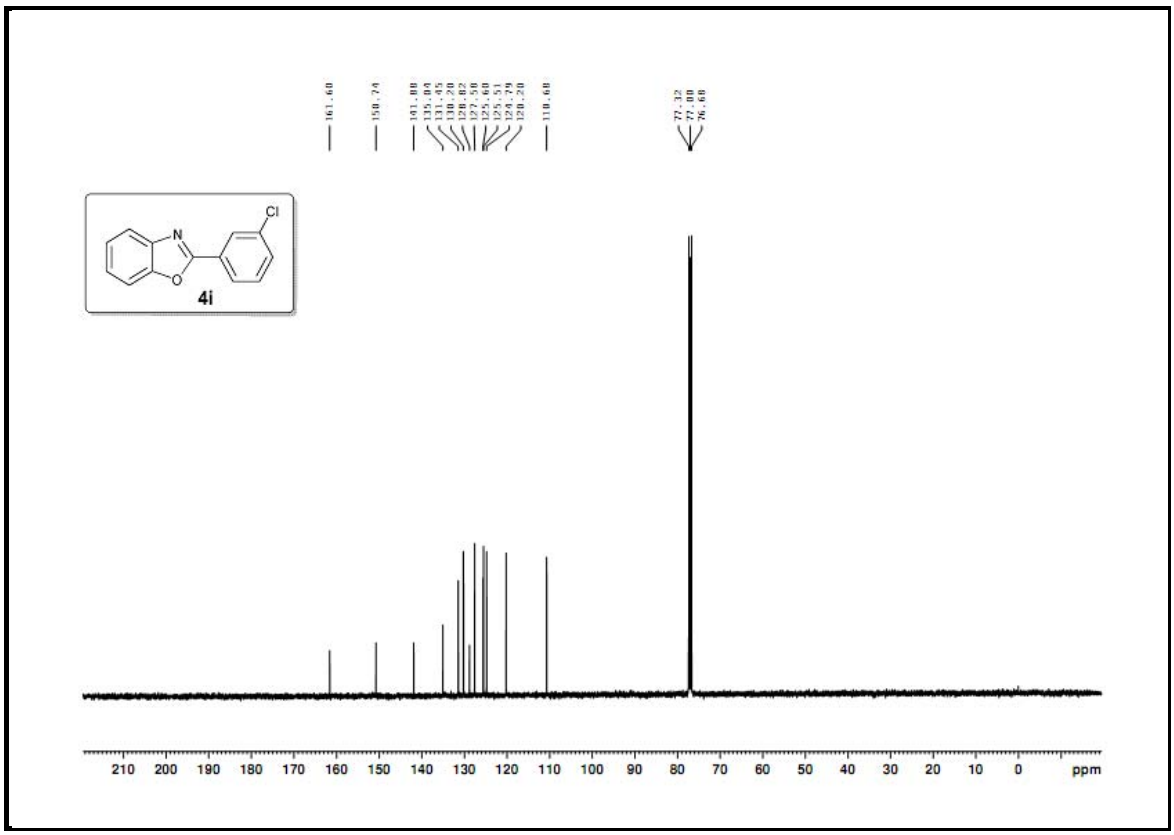
1.01
2.00
2.00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127.58
125.60
125.51
124.79
120.20
110.68
77.32
77.00
76.68
Cl
N
O
4i
210
200
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140
130
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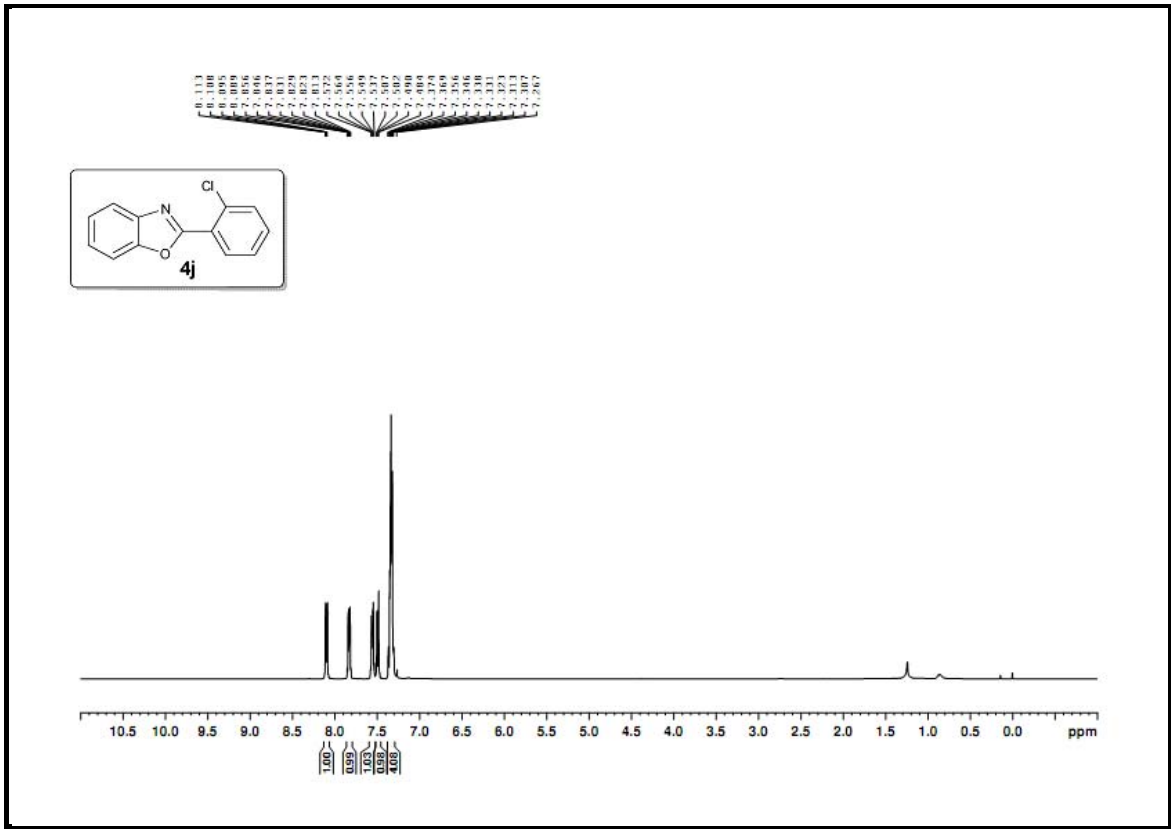
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8.095
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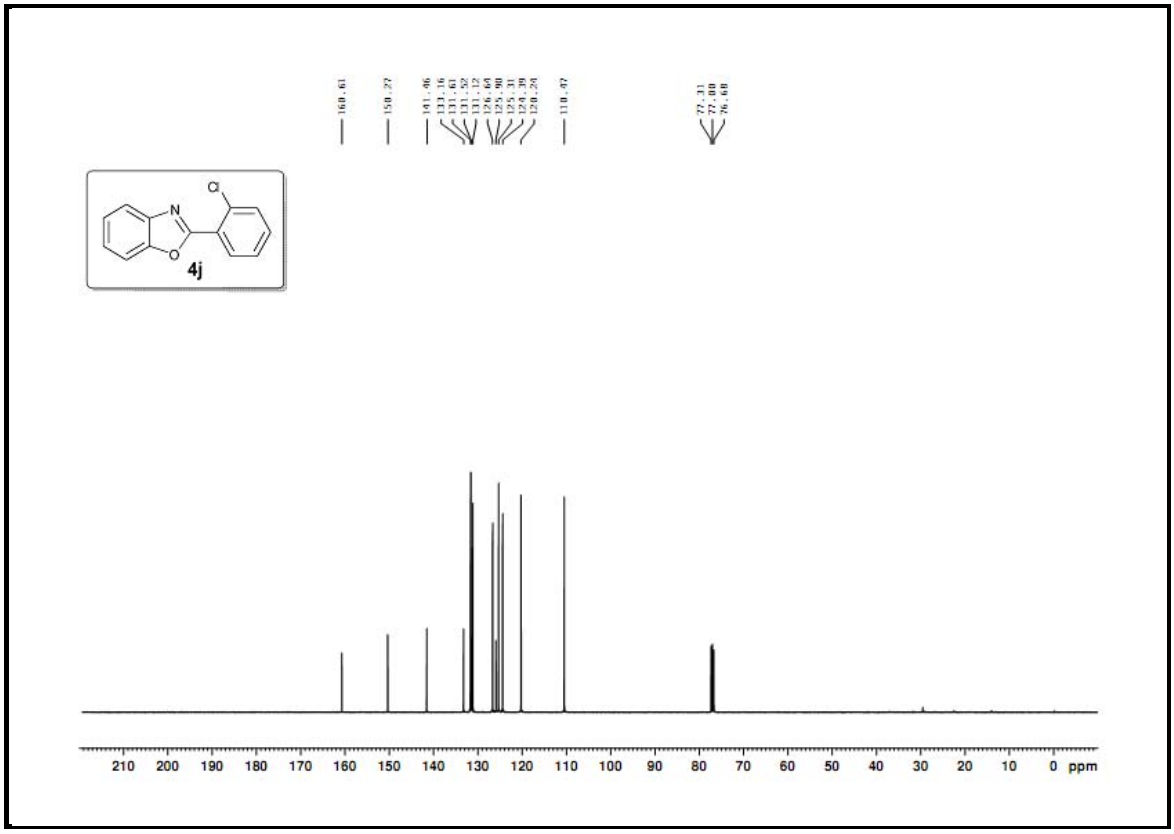
7.846
7.837
7.831
7.829
7.823
7.813
7.722
7.564
7.556
7.549
7.537
7.507
7.500
7.498
7.484
7.374
7.369
7.356
7.346
7.338
7.331
7.323
7.313
7.307
7.267
Cl
N
O
4j
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
0.99
1.03
0.98
4.08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131.16
131.03
131.52
131.12
126.65
125.90
125.31
123.38
120.29
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77.31
77.00
76.68
Cl
N
O
4j
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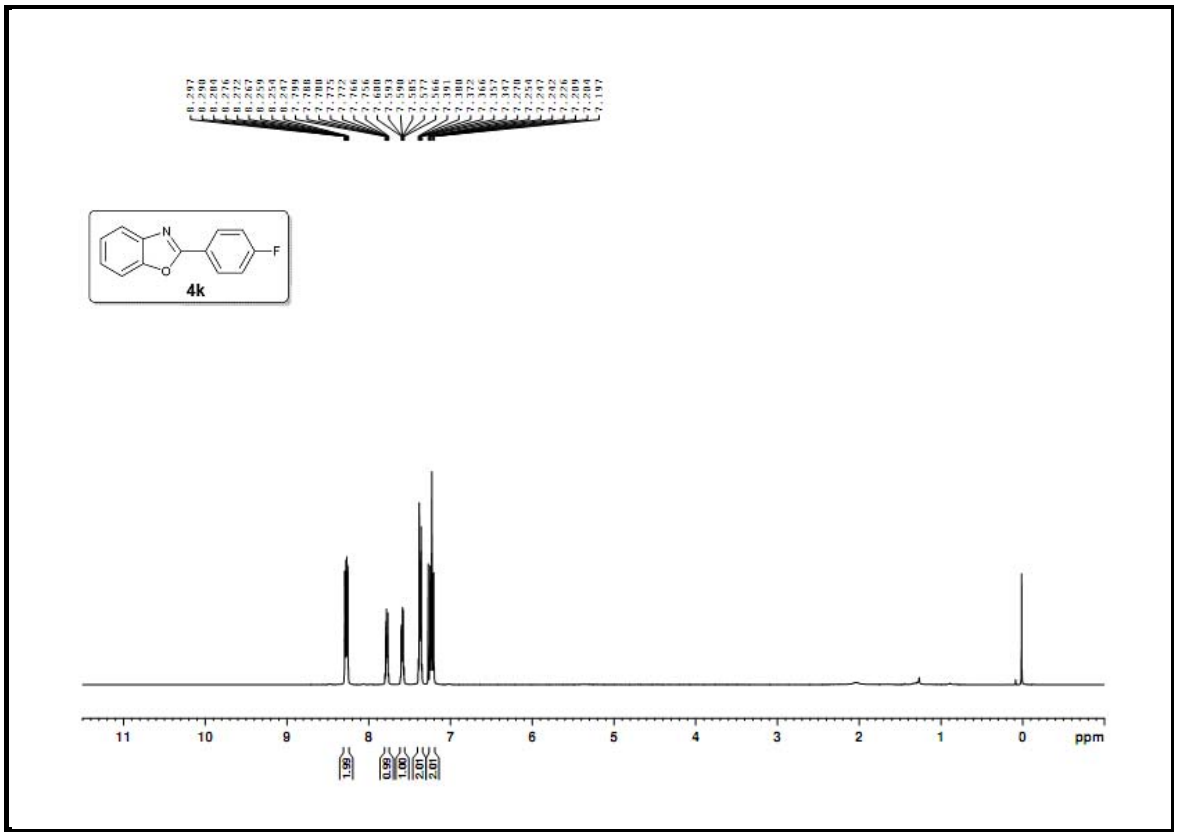
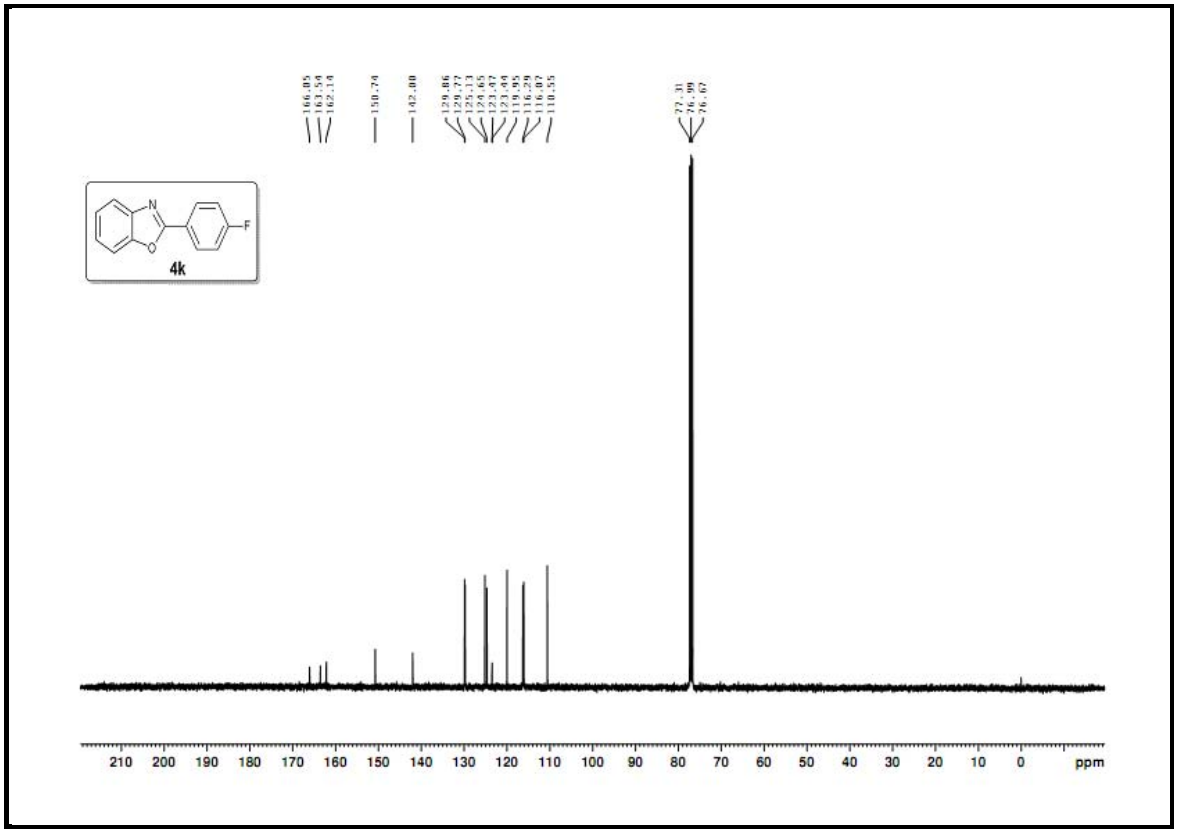

4k
11
10
9
8
7
6
5
4
3
2
1
0
ppm


4k
210
200
190
180
170
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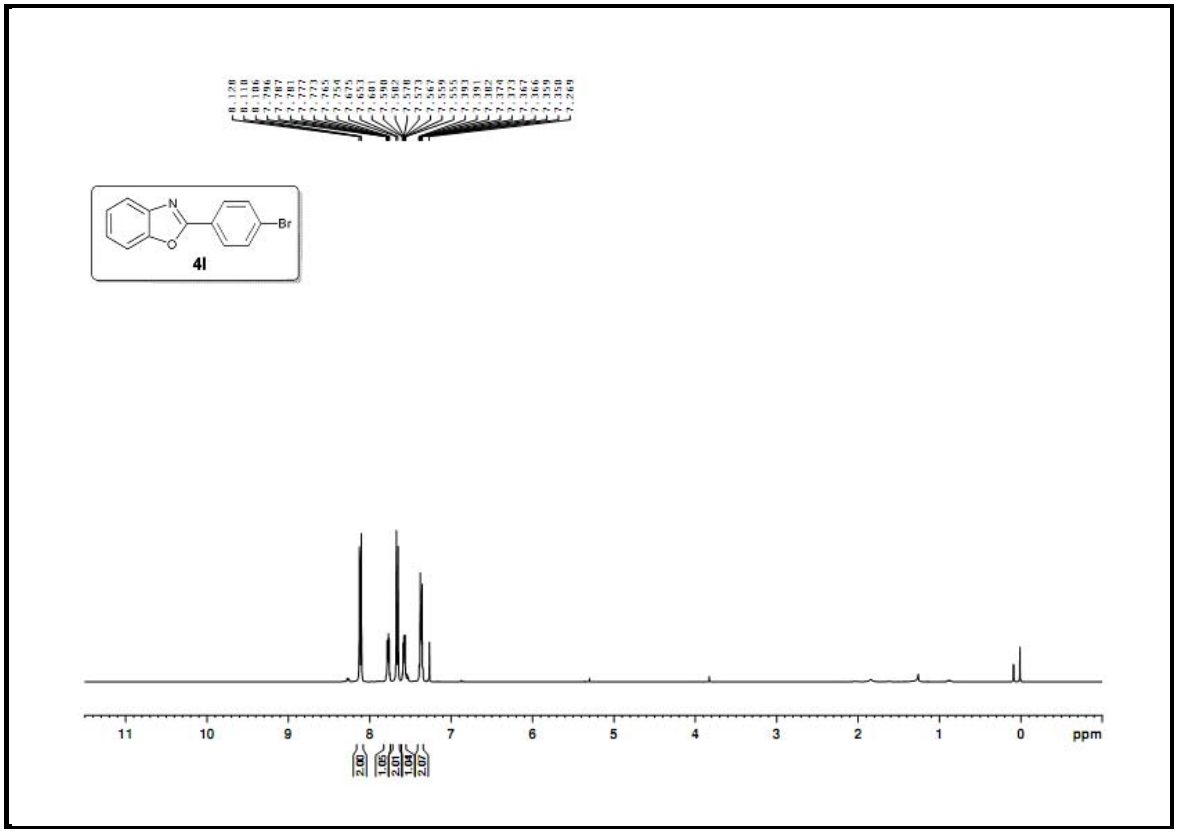
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.777
7.773
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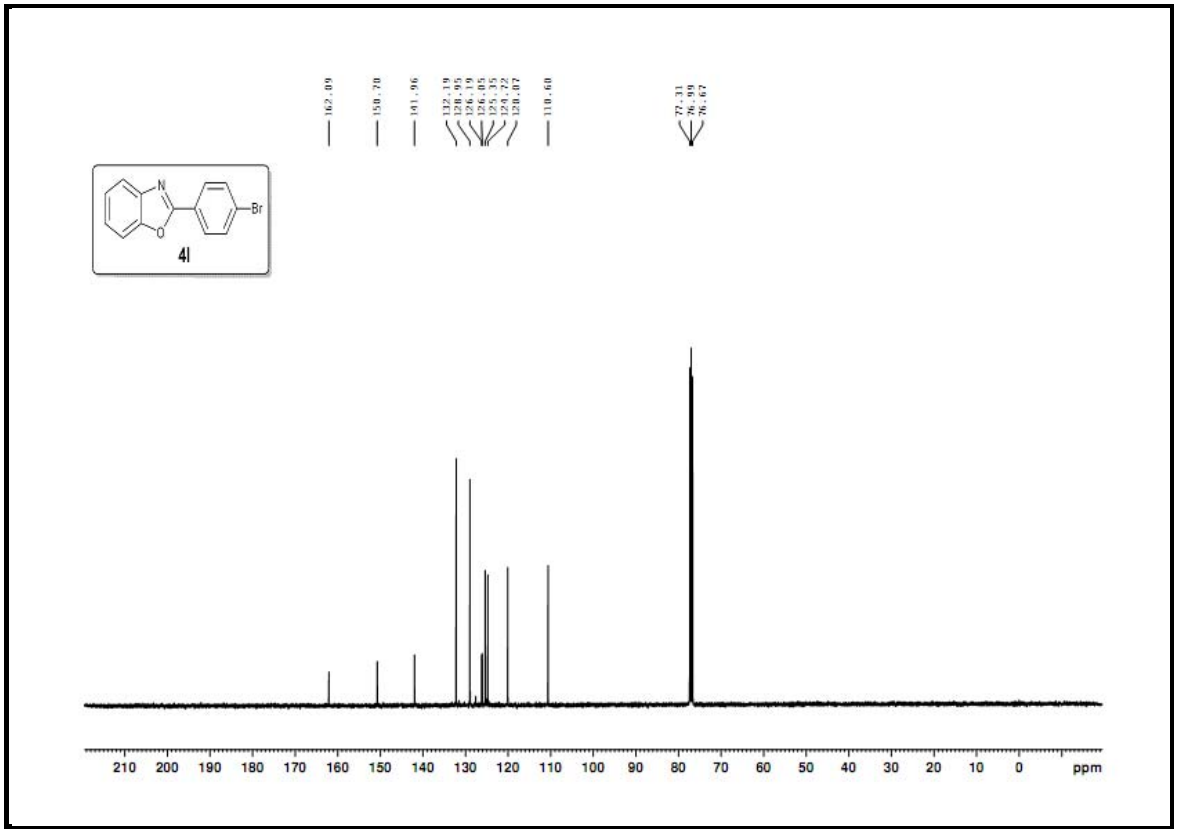
7.754
7.675
7.653
7.601
7.598
7.582
7.578
7.573
7.567
7.559
7.555
7.393
7.391
7.382
7.374
7.373
7.367
7.366
7.359
7.350
7.269
N
O
Br
4l
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.00
2.01
1.04
2.07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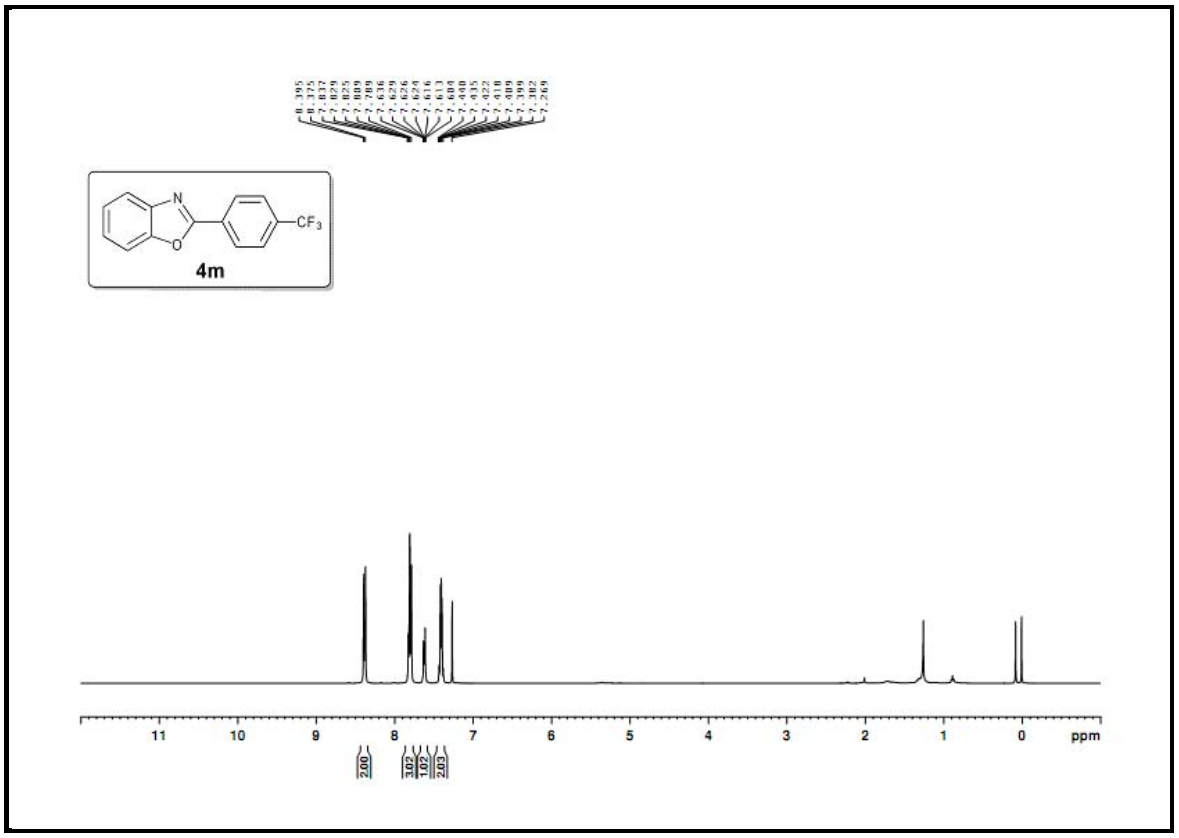
126.19
126.05
125.35
124.72
120.07
110.60
77.31
77.00
76.67
N
O
Br
4l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.629
7.626
7.624
7.616
7.611
7.603
7.448
7.435
7.422
7.418
7.409
7.399
7.382
7.269
N
O
CF3
4m
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10
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8
7
6
5
4
3
2
1
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ppm
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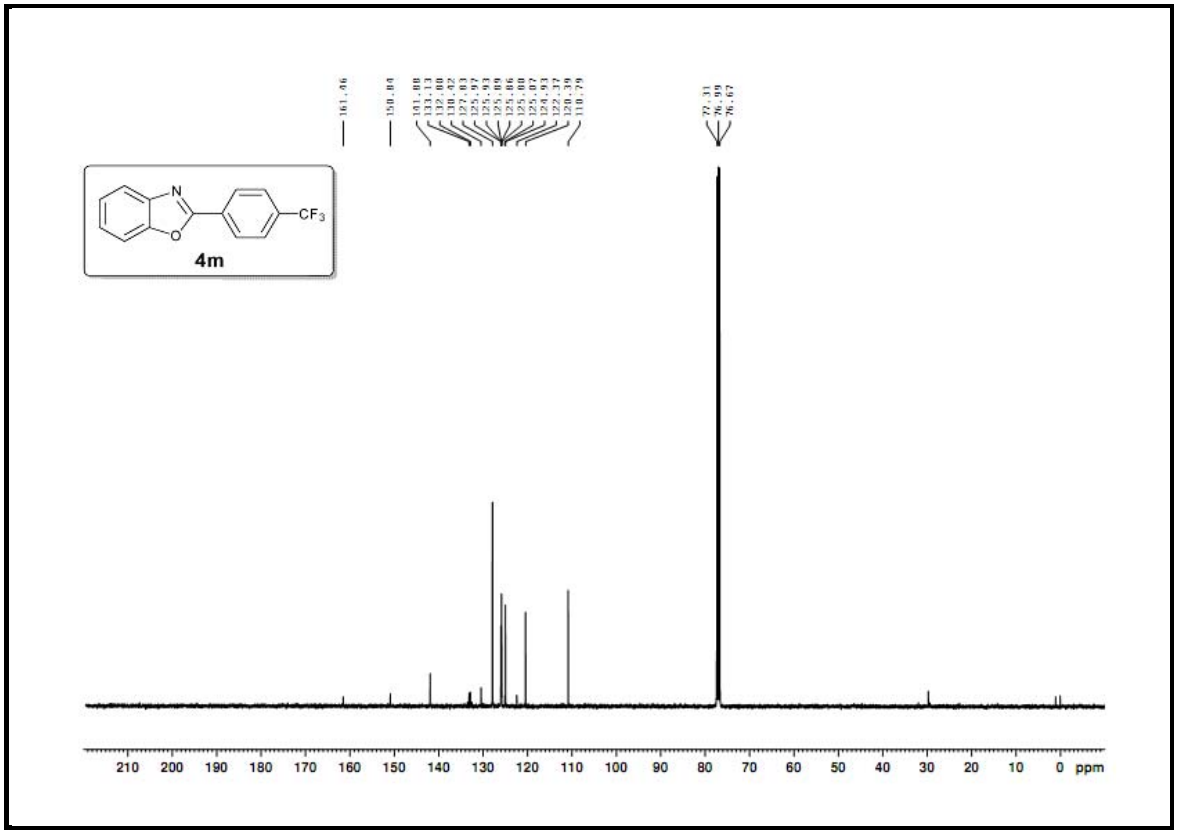
3.02
1.02
2.03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125.97
125.93
125.86
125.85
125.80
125.07
124.93
122.37
120.39
110.79
77.31
76.99
76.67
N
O
CF3
4m
210
200
190
180
170
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150
140
130
120
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100
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80
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60
50
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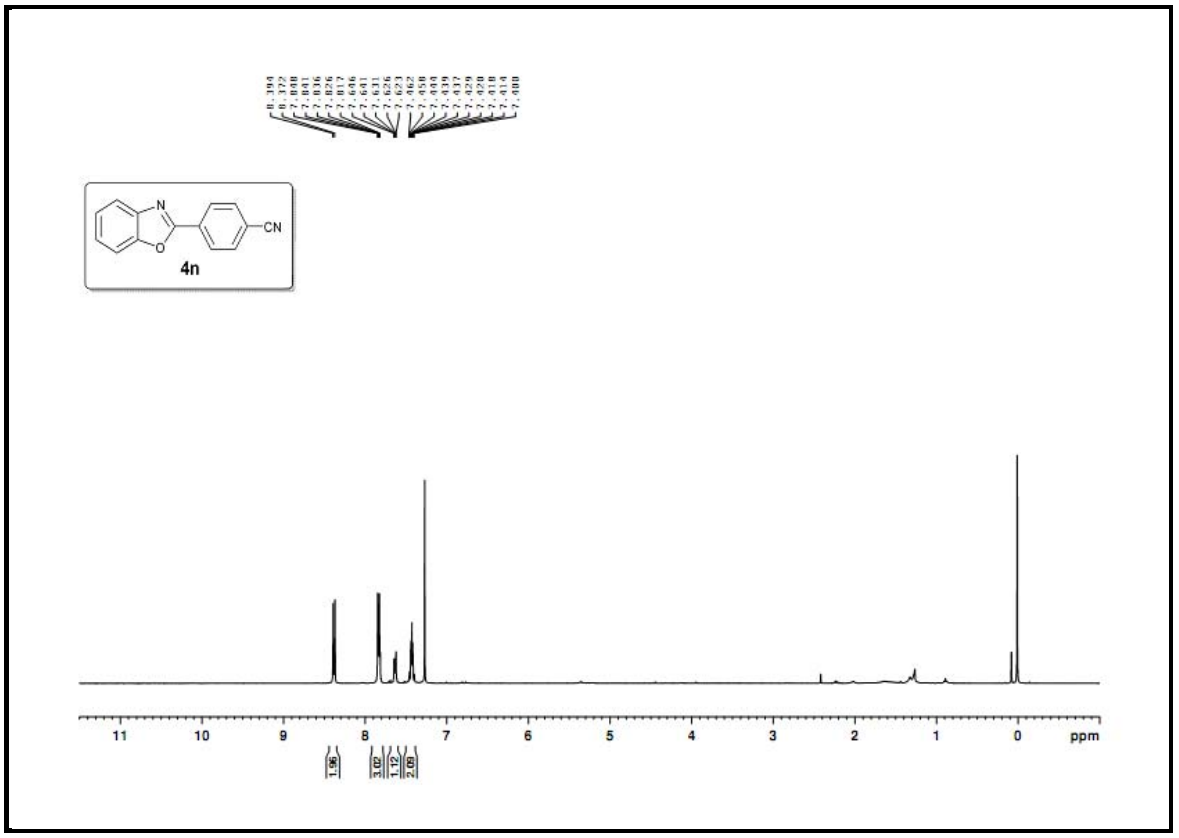
30
20
10
0
ppm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7.646
7.641
7.631
7.626
7.623
7.462
7.458
7.444
7.439
7.437
7.429
7.420
7.418
7.414
7.400
N
O
CN
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6
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ppm
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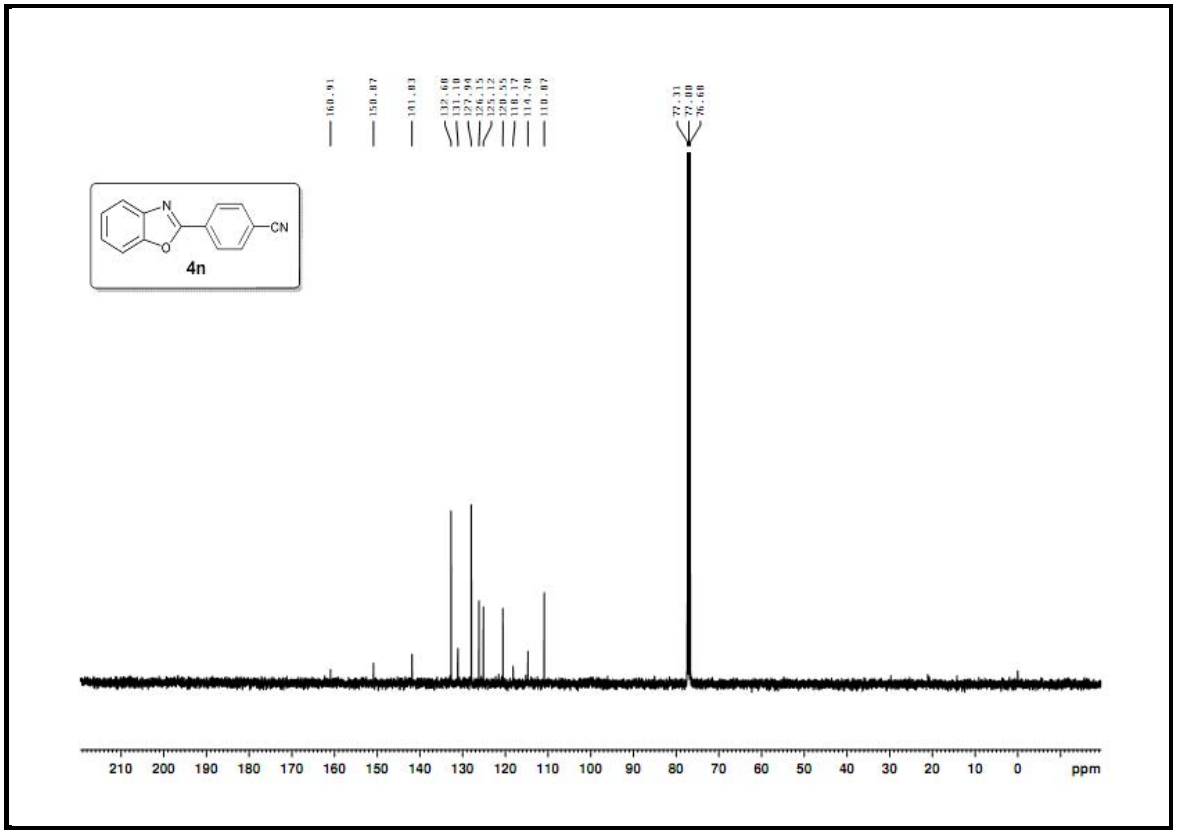
2.08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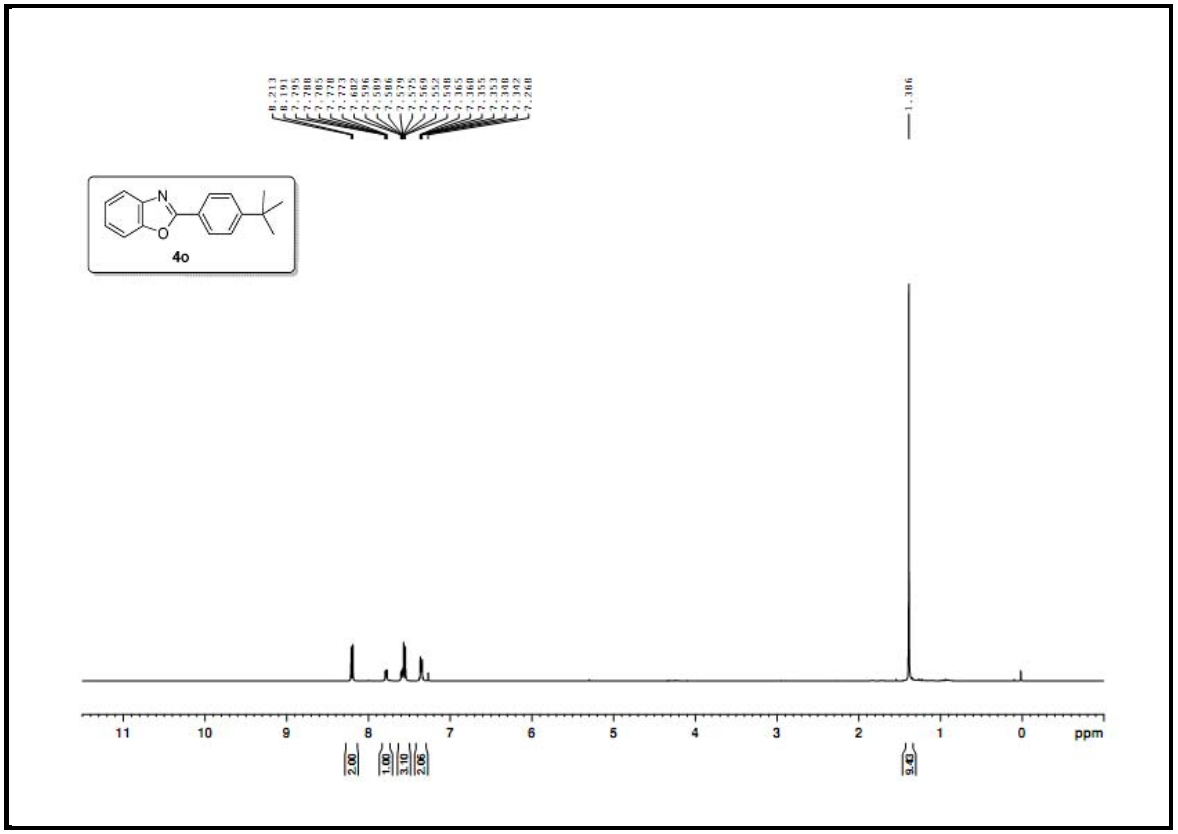
129.84
126.15
125.12
120.55
118.17
114.78
110.87
77.31
77.00
76.68
N
O
CN
4n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.770
7.723
7.602
7.596
7.589
7.586
7.579
7.575
7.569
7.552
7.548
7.365
7.360
7.355
7.353
7.348
7.342
7.268
1.386
4o
11
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6
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4
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2
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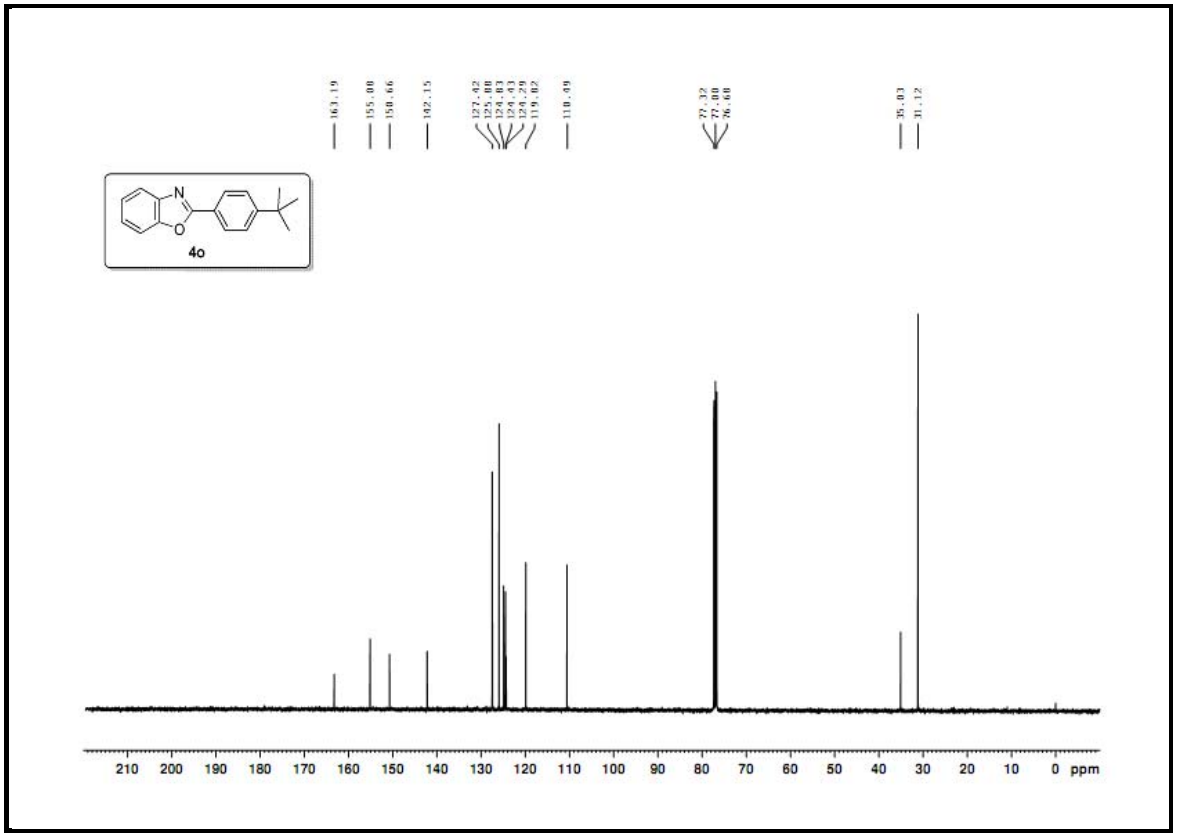
2.06
9.43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124.43
120.28
119.82
110.49
77.32
77.00
76.68
35.03
31.12
4o
210
200
190
180
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150
140
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100
90
80
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60
50
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20
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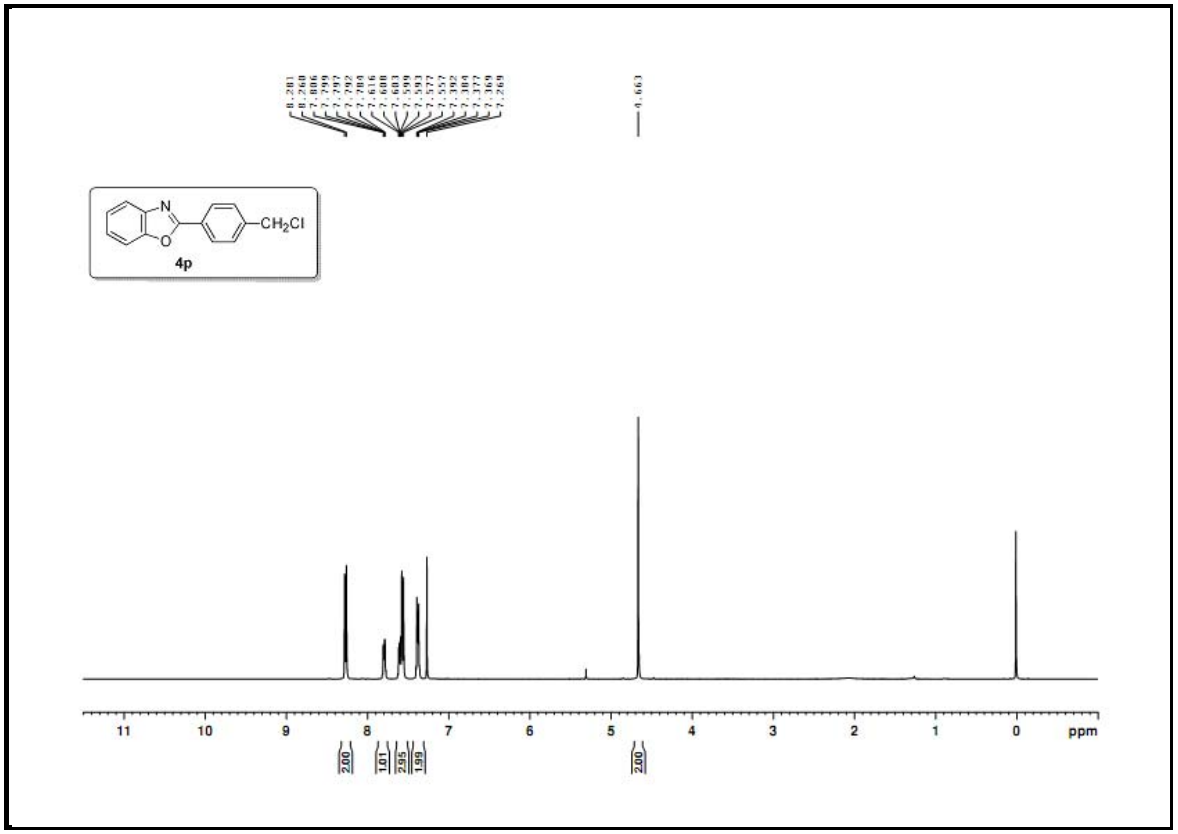
0
ppm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7.616
7.608
7.603
7.599
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7.577
7.557
7.539
7.388
7.377
7.369
7.269
4.663
N
O
CH2Cl
4p
11
10
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8
7
6
5
4
3
2
1
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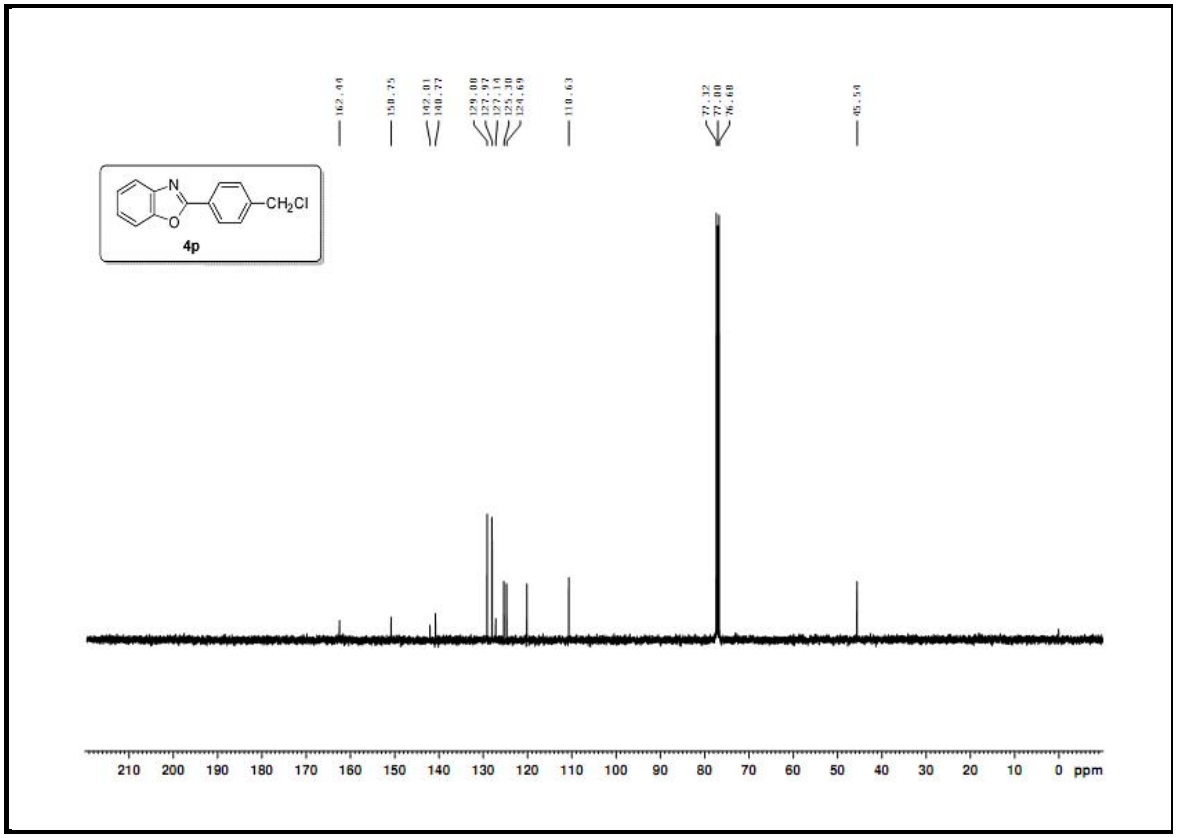
ppm
2.00
1.01
2.95
1.99
2.00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127.14
125.38
124.69
110.63
77.32
77.00
76.68
45.54
N
O
CH2Cl
4p
210
200
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180
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140
130
120
110
100
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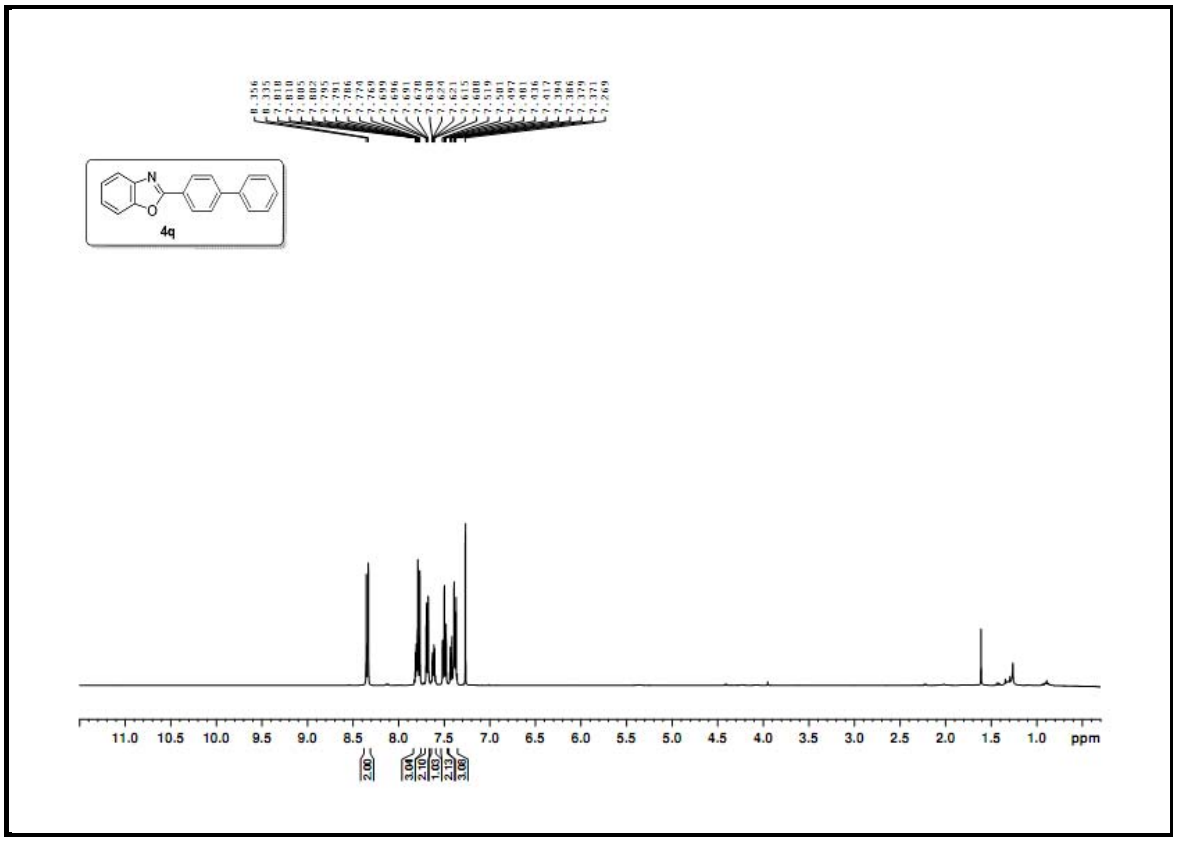
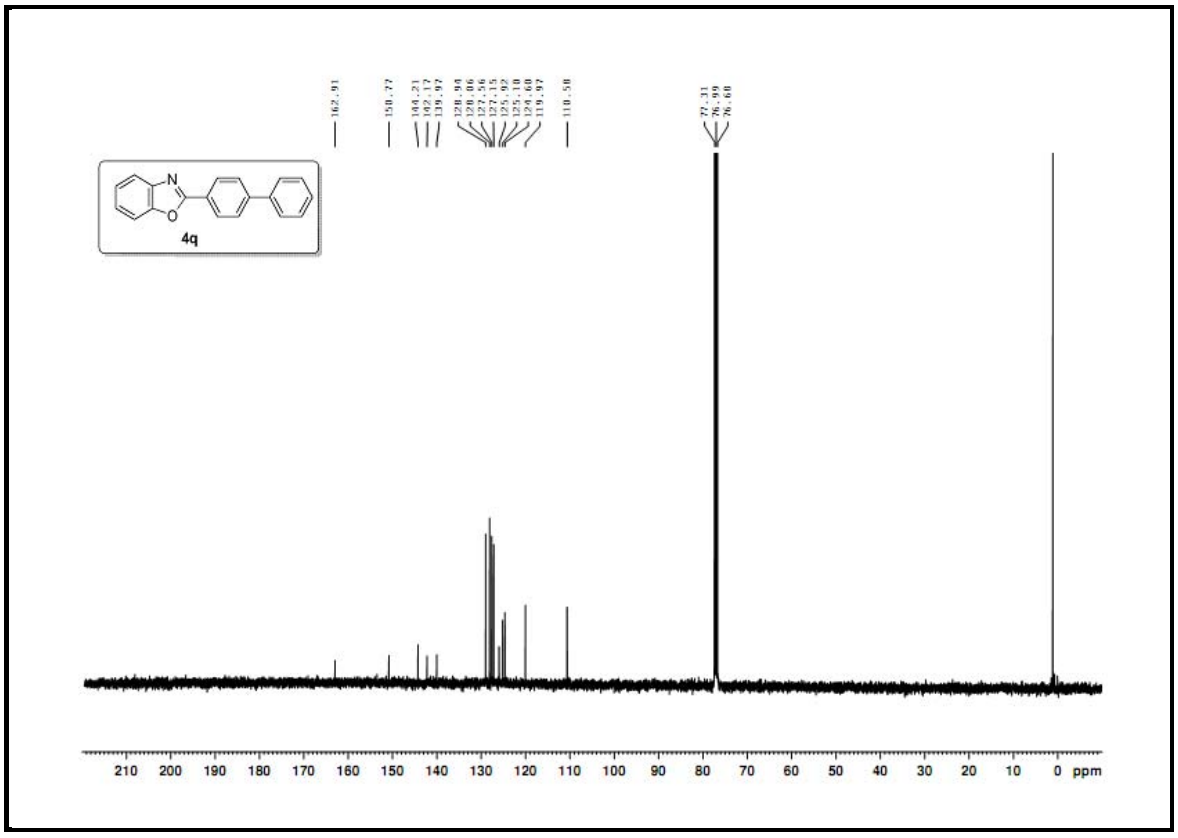
80
70
60
50
40
30
20
10
0
ppm


4q
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm


4q
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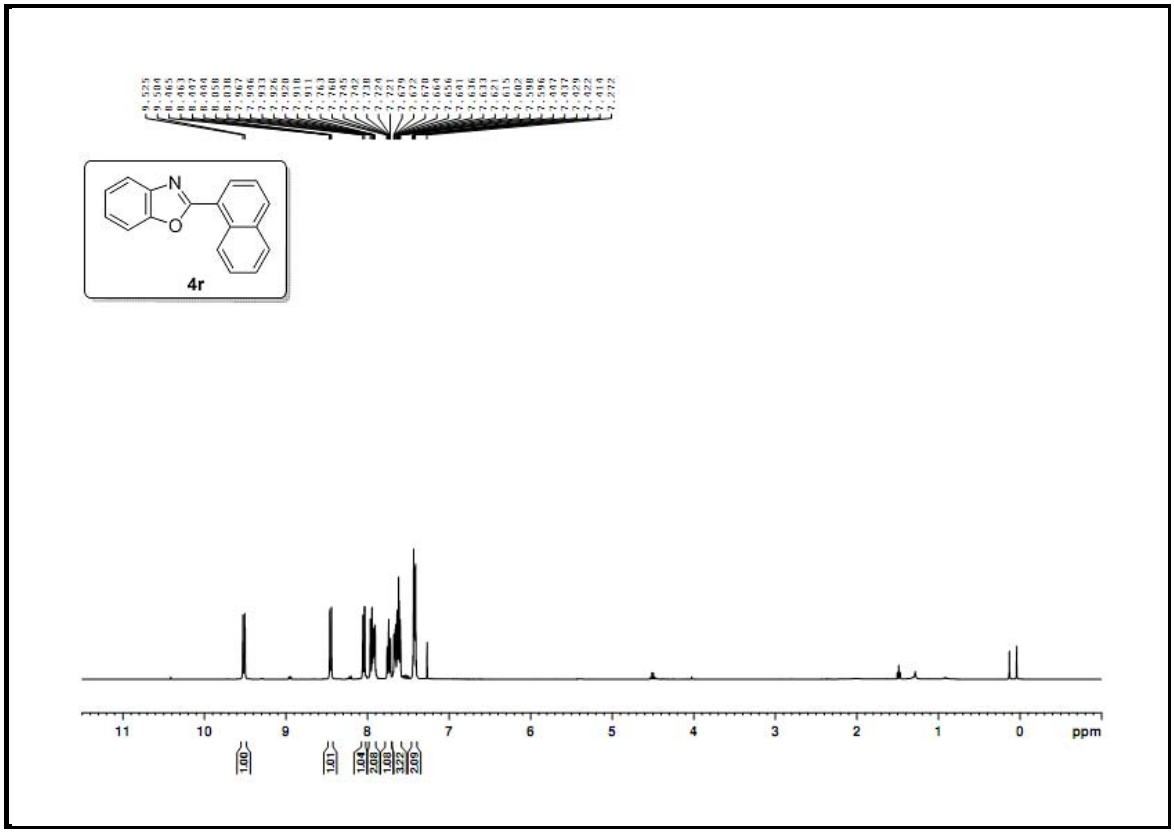
4r
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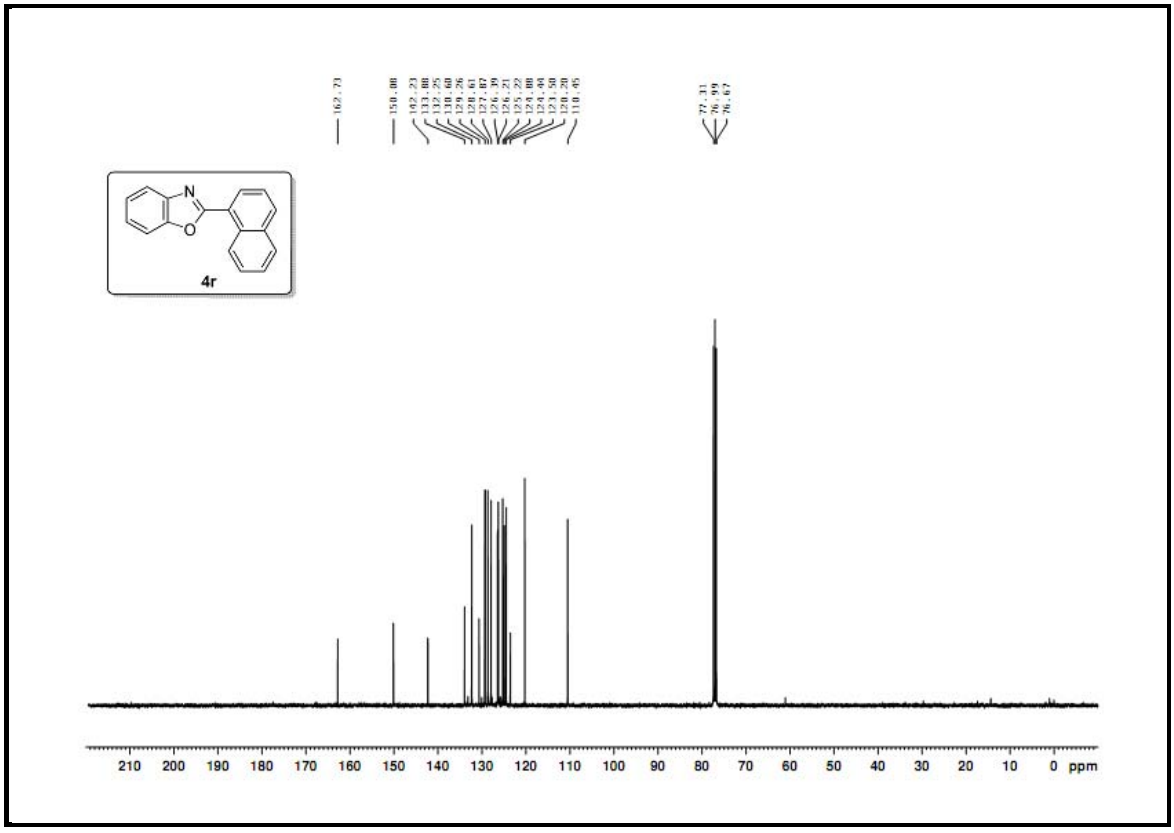
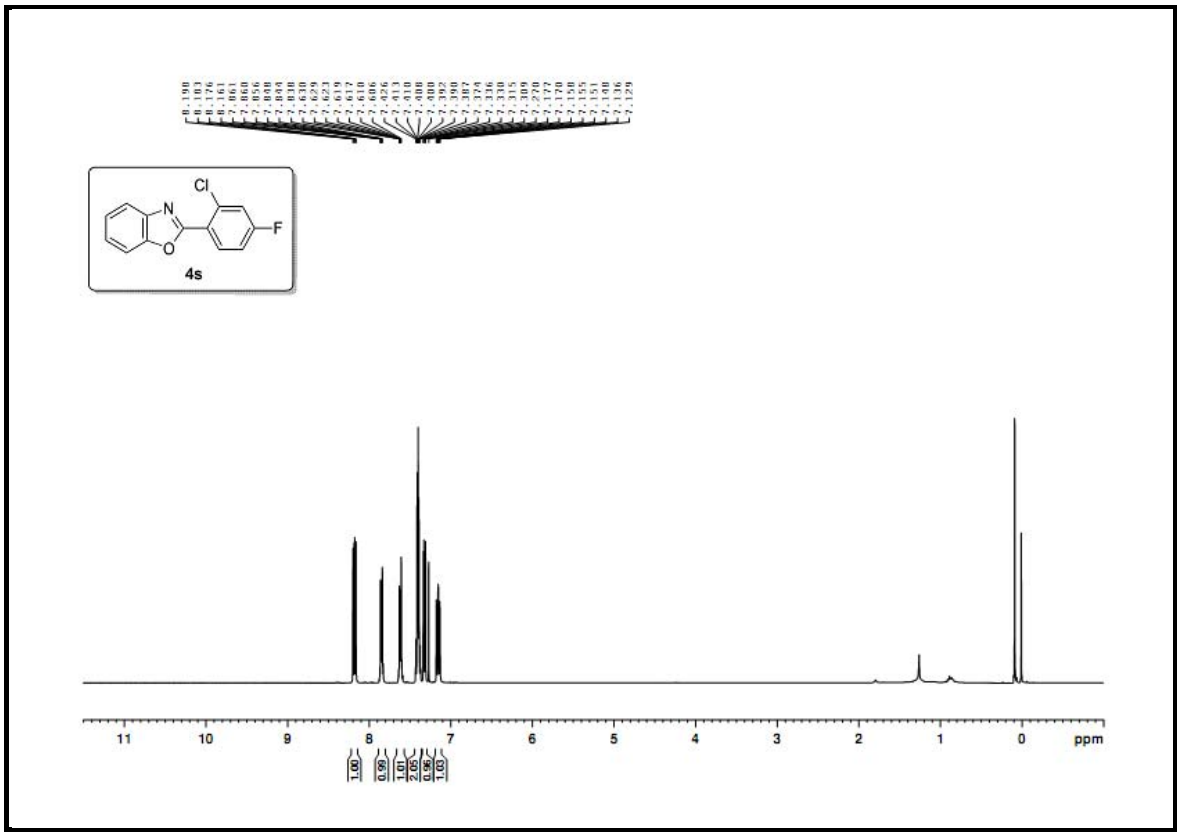
10
9
8
7
6
5
4
3
2
1
0
ppm


4r
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Cl
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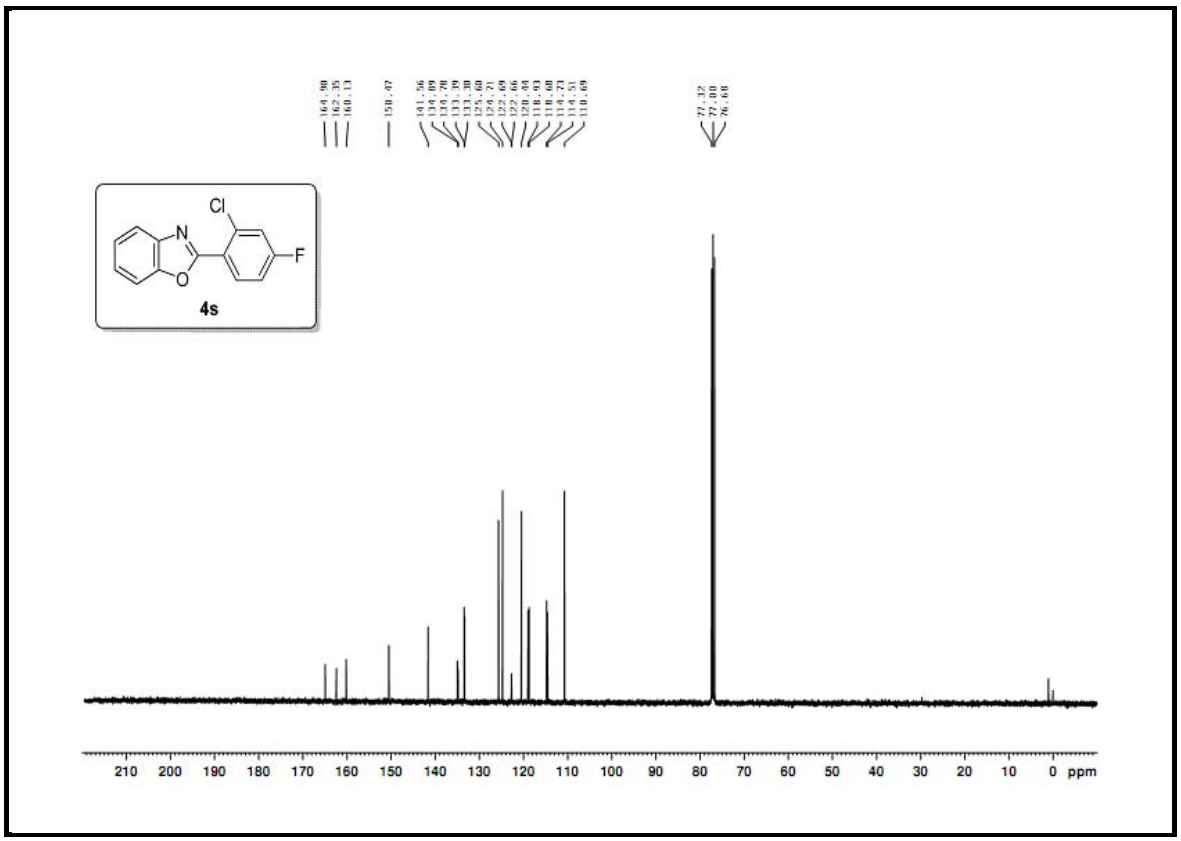
O
F
4s
11
10
9
8
7
6
5
4
3
2
1
0
ppm


Cl
N
O
F
4s
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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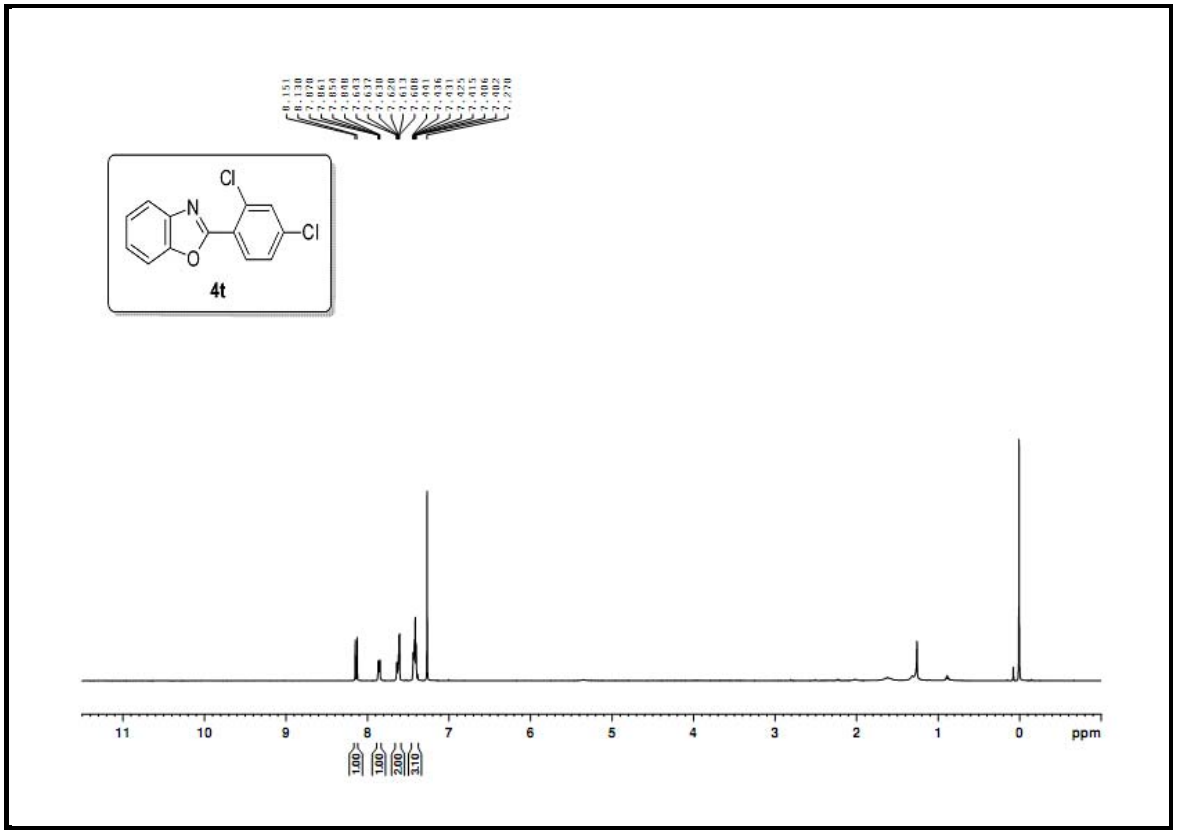
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8.130
7.870
7.861
7.854
7.848
7.643
7.632
7.630
7.620
7.613
7.608
7.601
7.436
7.431
7.425
7.415
7.406
7.402
7.270
Cl
N
O
Cl
4t
11
10
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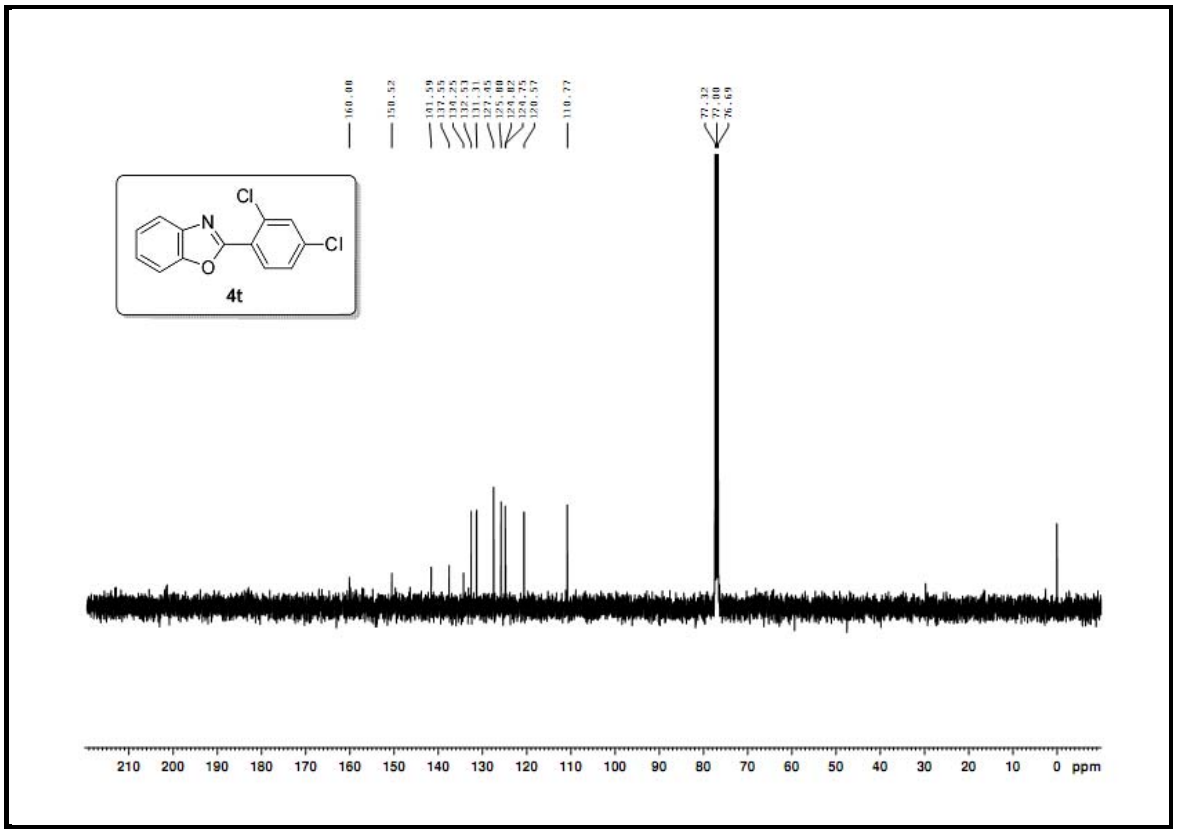
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
2.00
3.10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137.35
136.23
132.53
131.31
127.45
125.88
124.92
124.75
120.57
110.77
77.32
77.00
76.69
Cl
N
O
Cl
4t
210
200
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150
140
130
120
110
100
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80
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60
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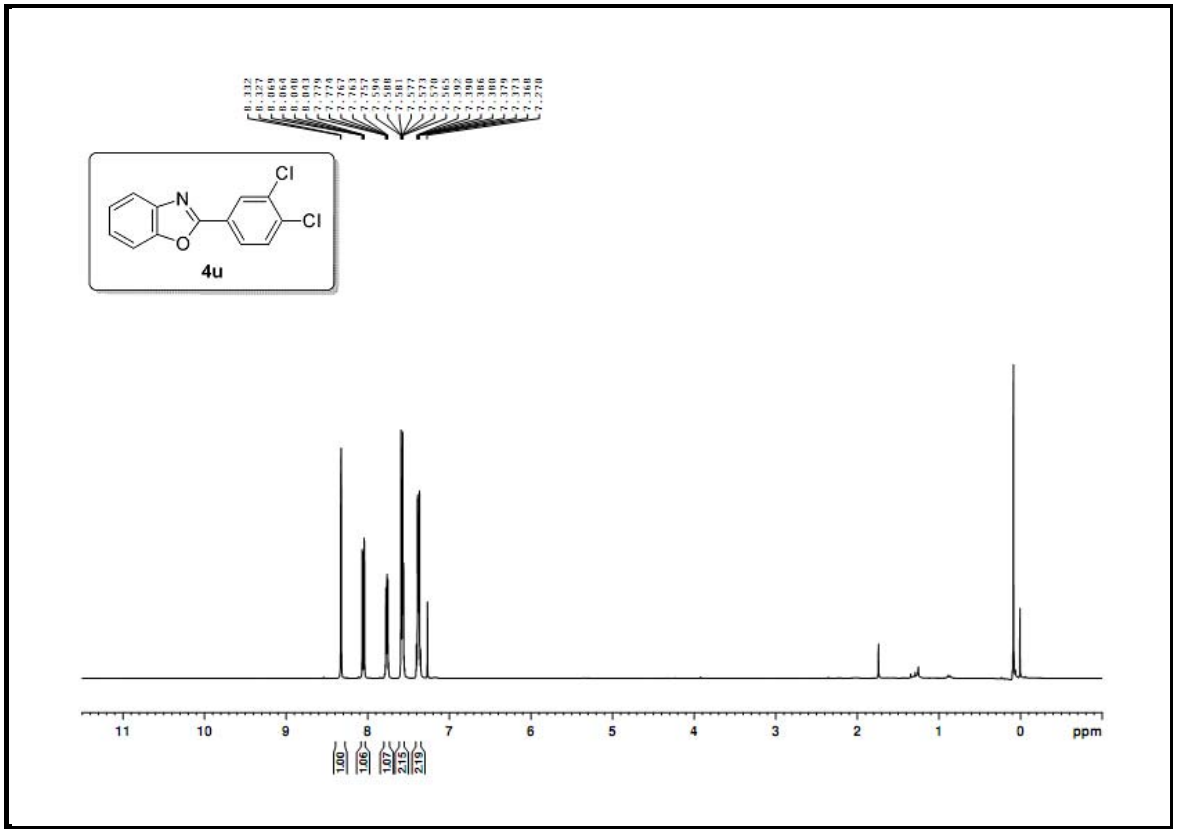
30
20
10
0
ppm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7.774
7.767
7.763
7.757
7.594
7.588
7.581
7.577
7.573
7.570
7.565
7.392
7.390
7.386
7.380
7.379
7.373
7.368
7.270
Cl
N
O
Cl
4u
11
10
9
8
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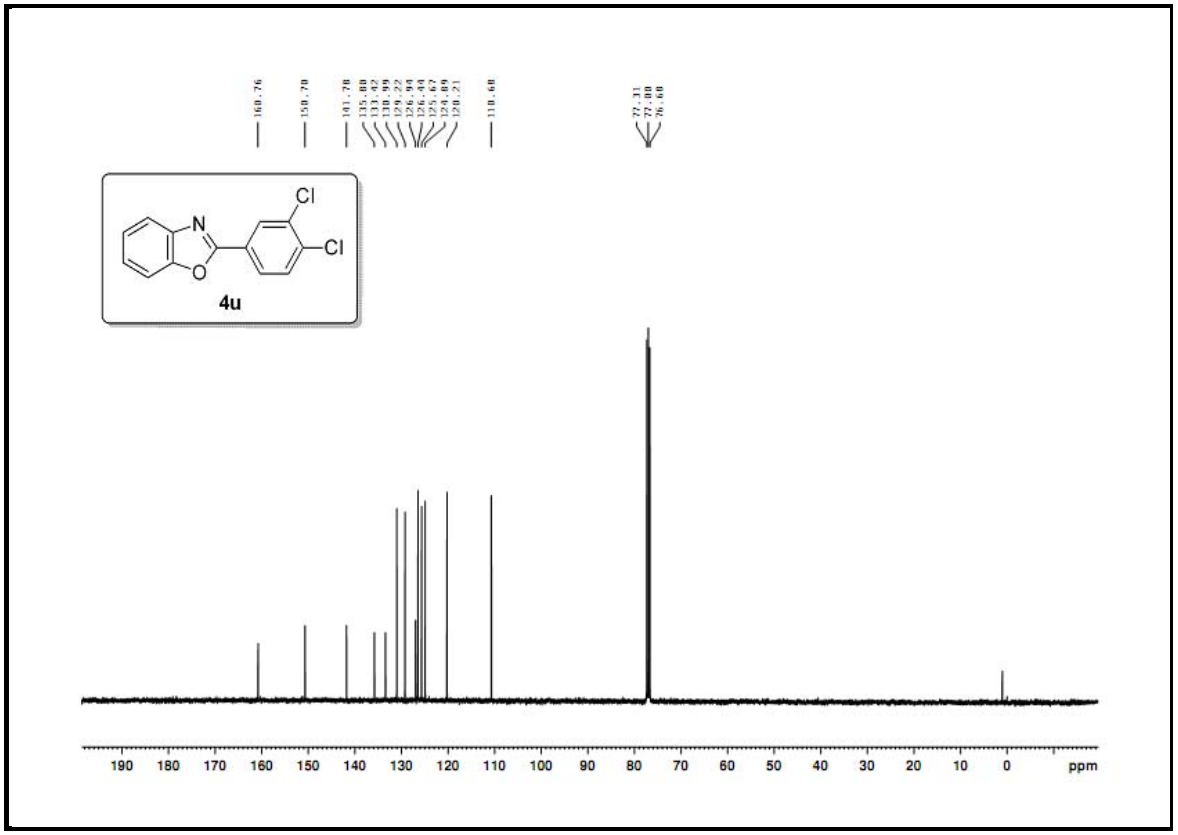
6
5
4
3
2
1
0
ppm
1.00
1.06
1.07
2.15
2.19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150.70
141.78
135.88
133.42
130.99
130.22
126.94
126.44
125.67
124.89
120.21
110.68
77.31
77.00
76.68
Cl
N
O
Cl
4u
190
180
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150
140
130
120
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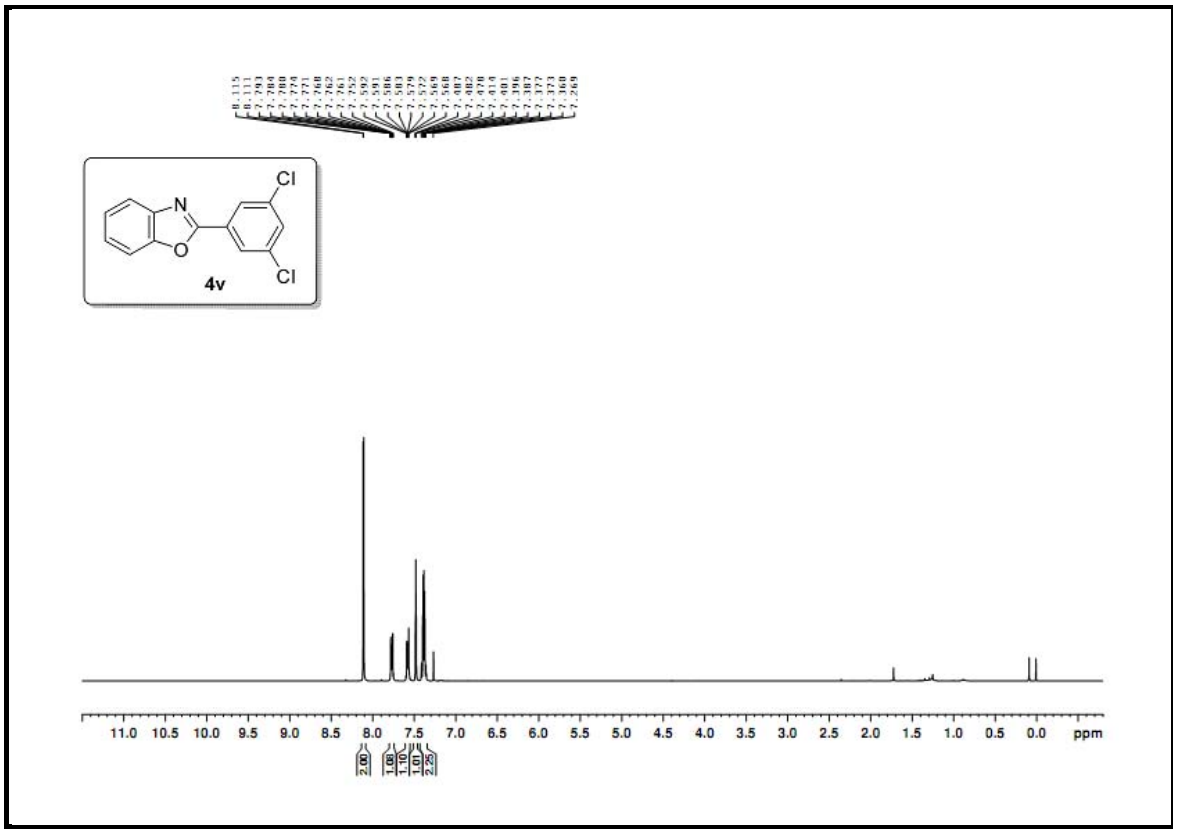
100
90
80
70
60
50
40
30
20
10
0
ppm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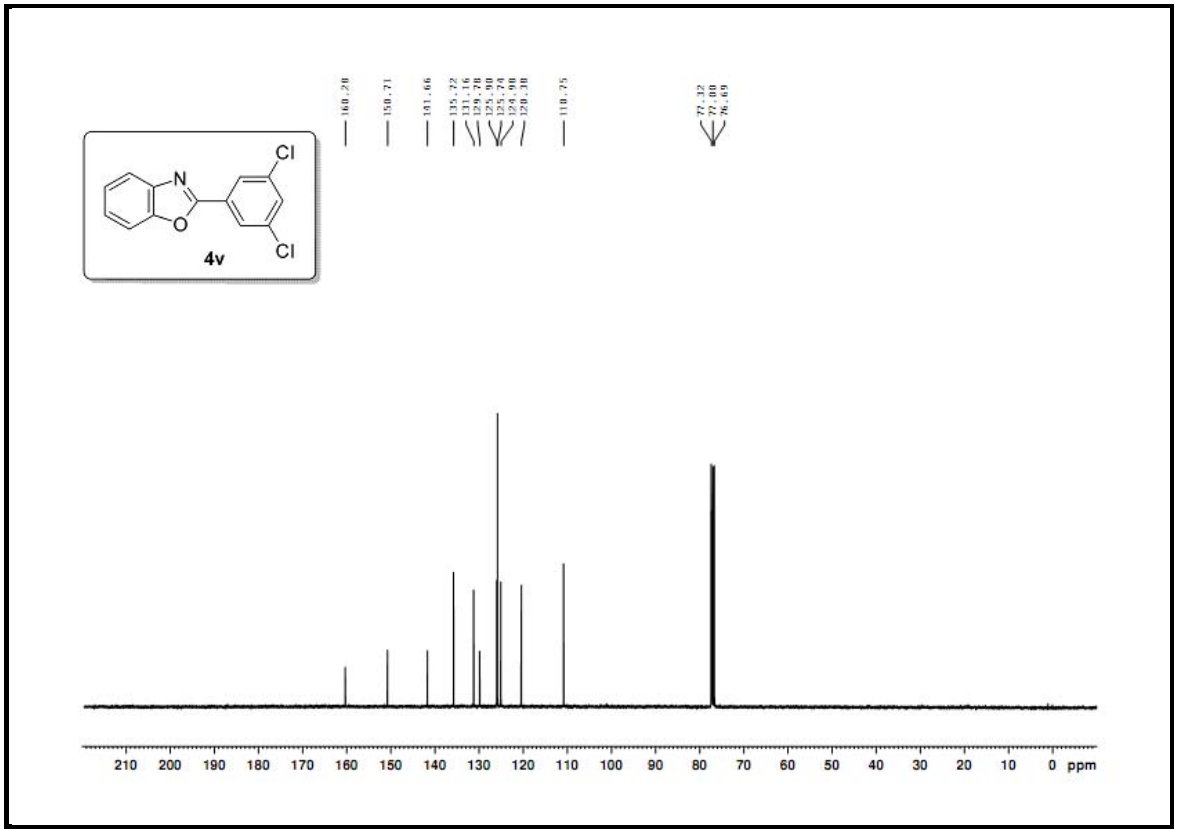
8.111
7.793
7.786
7.780
7.774
7.771
7.768
7.762
7.756
7.752
7.592
7.591
7.586
7.583
7.579
7.572
7.569
7.568
7.487
7.482
7.478
7.418
7.401
7.396
7.387
7.377
7.373
7.368
7.269
Cl
N
O
Cl
4v
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
1.08
1.10
1.00
2.29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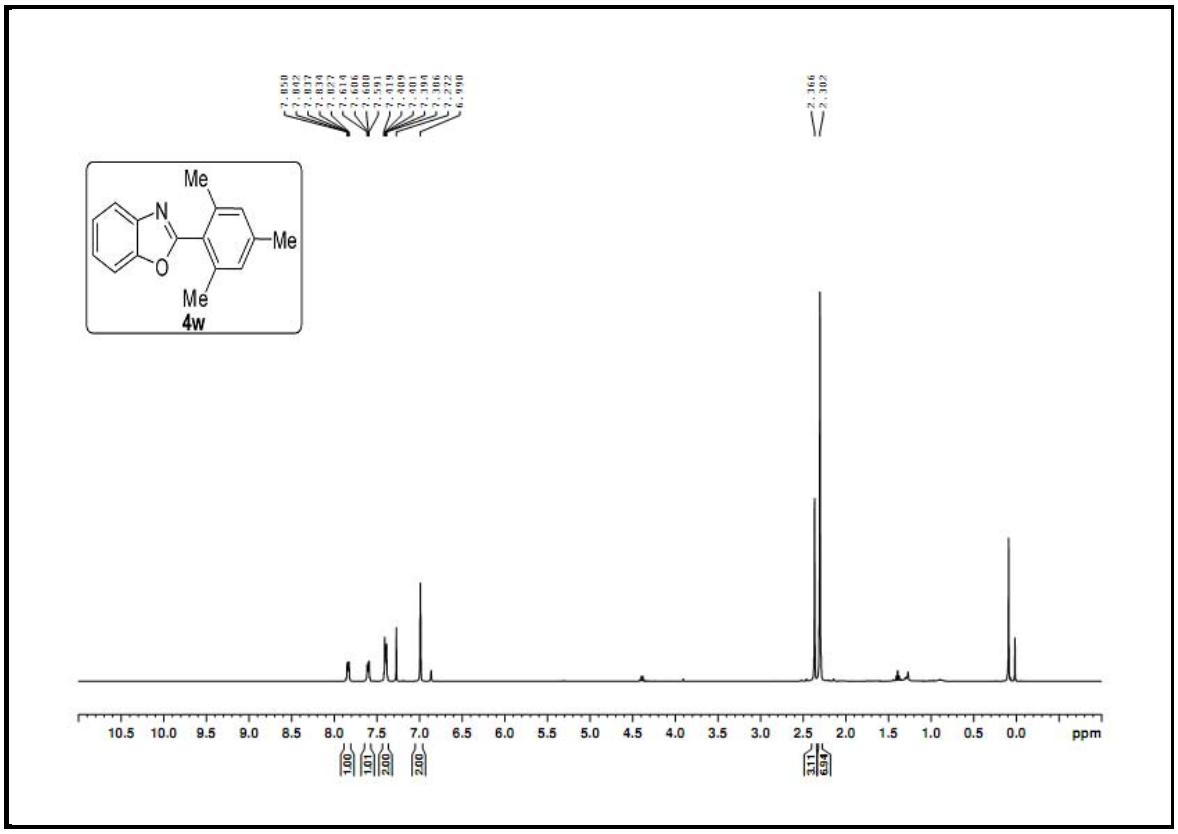
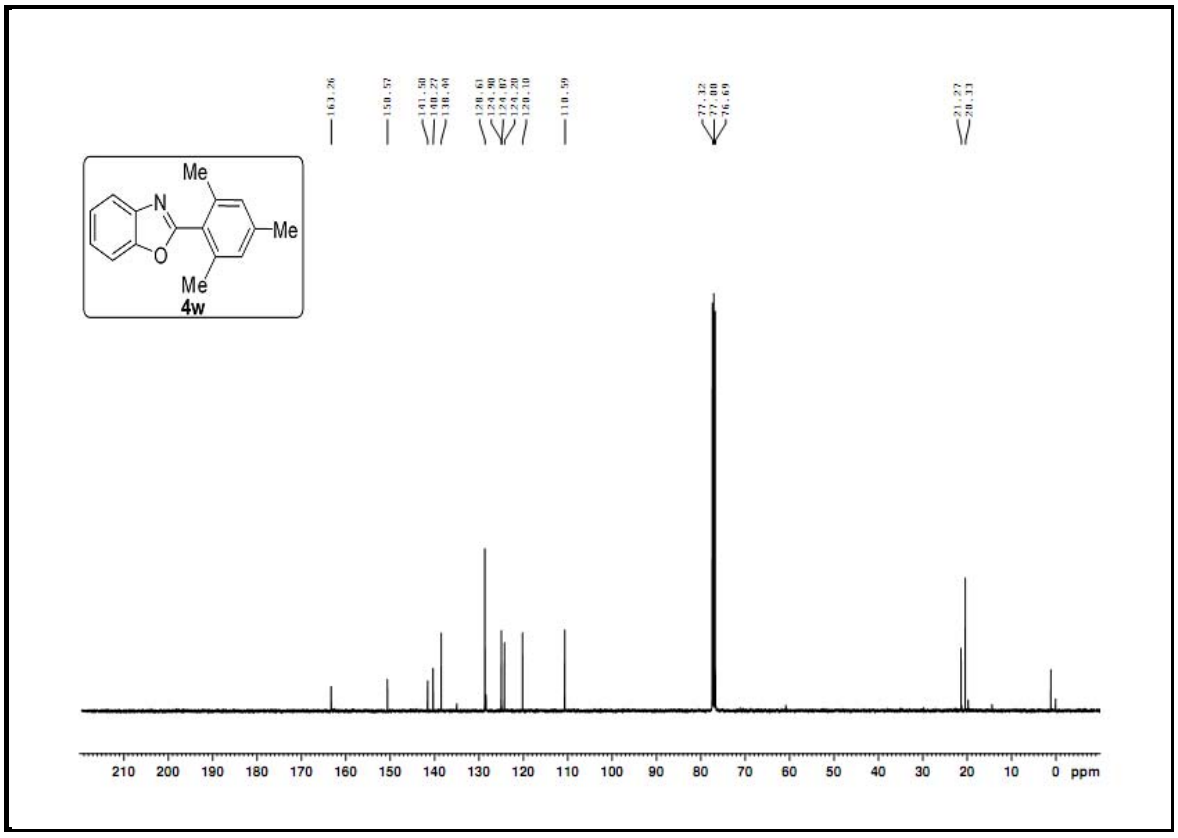
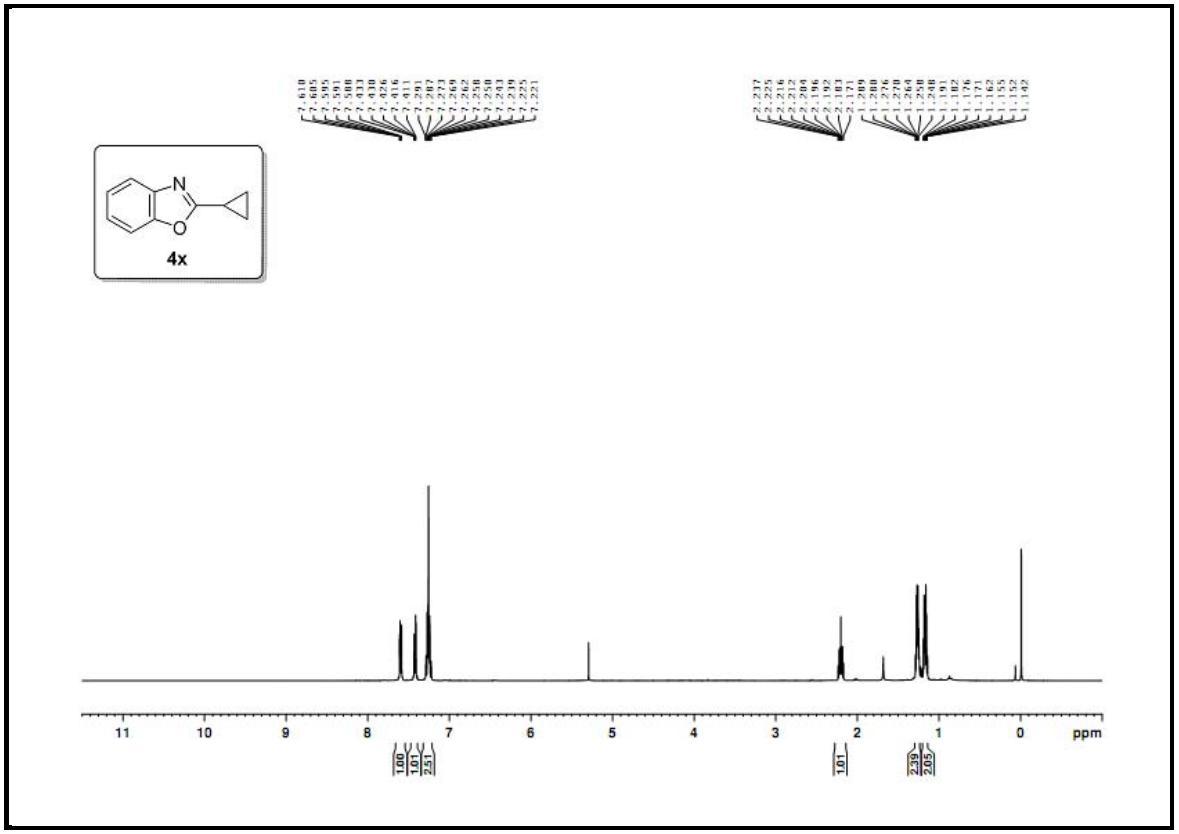
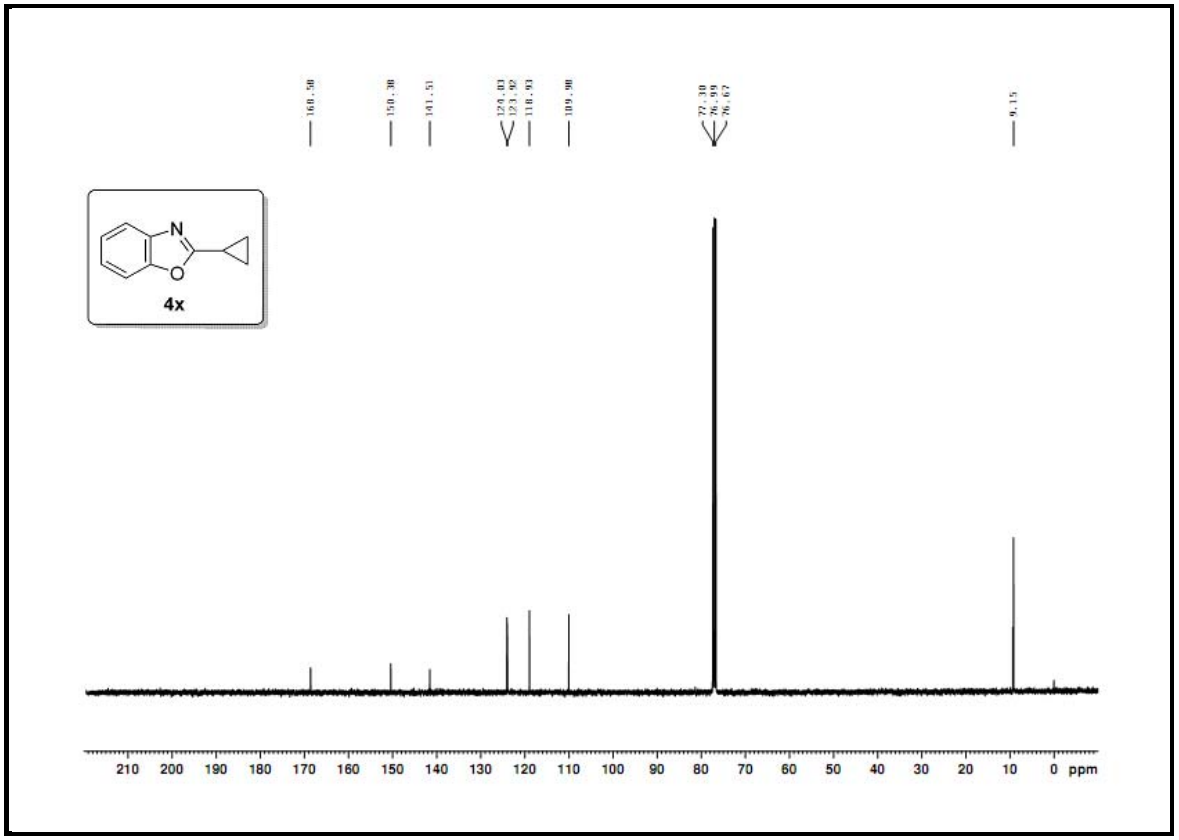
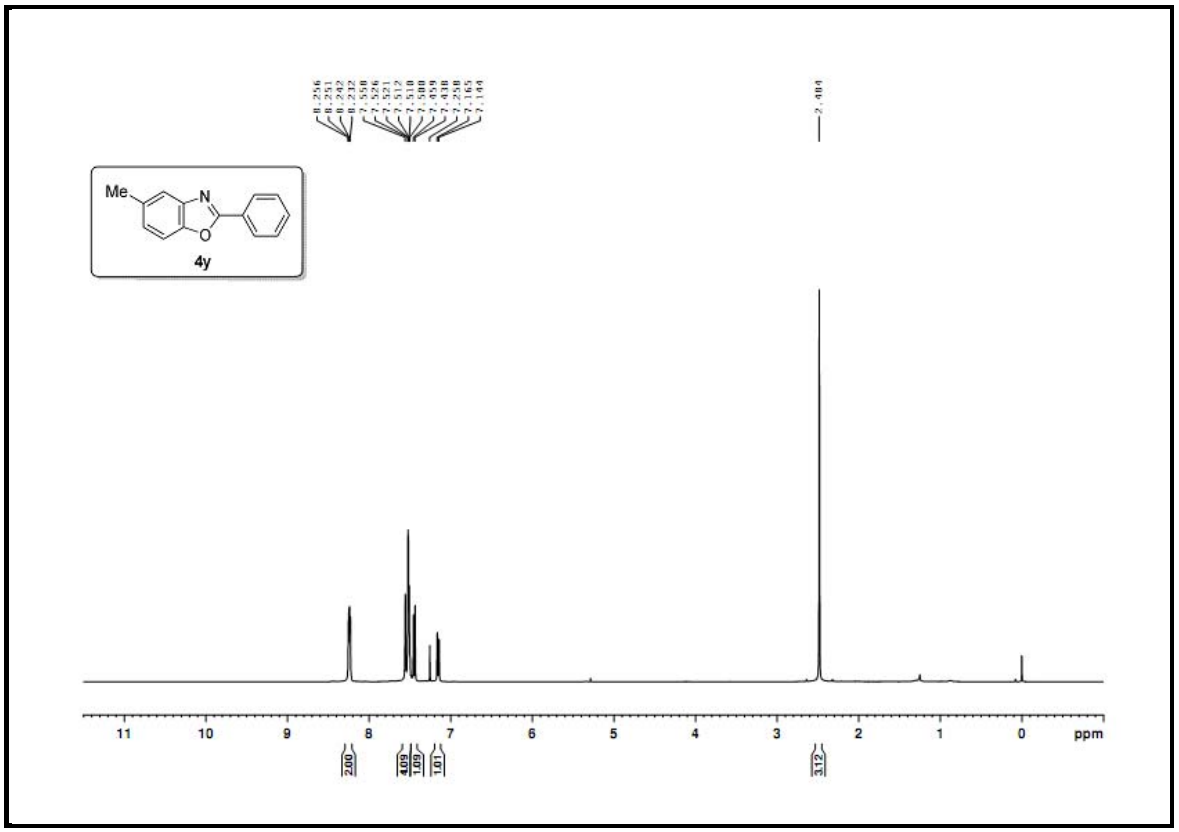
150.71
141.66
135.22
131.16
129.78
125.90
125.74
124.90
120.38
110.75
77.32
77.00
76.69
Cl
N
O
Cl
4v
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


Me
N
O
Me
Me
4w
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm


Me
N
O
Me
Me
4w
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


4x
ppm


4x
ppm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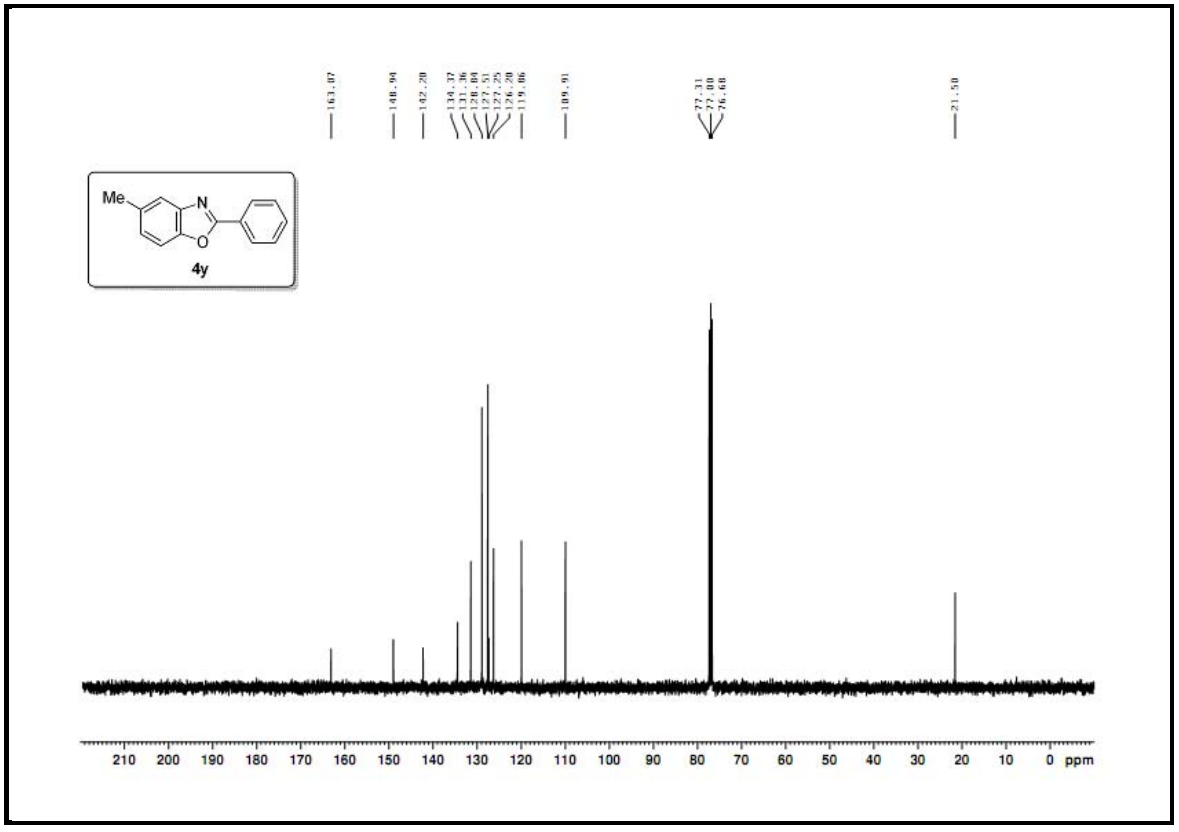
8.251
8.243
8.232
7.558
7.526
7.521
7.513
7.510
7.508
7.459
7.438
7.258
7.165
7.144
2.484
Me
N
O
4y
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
4.09
1.09
1.01
3.12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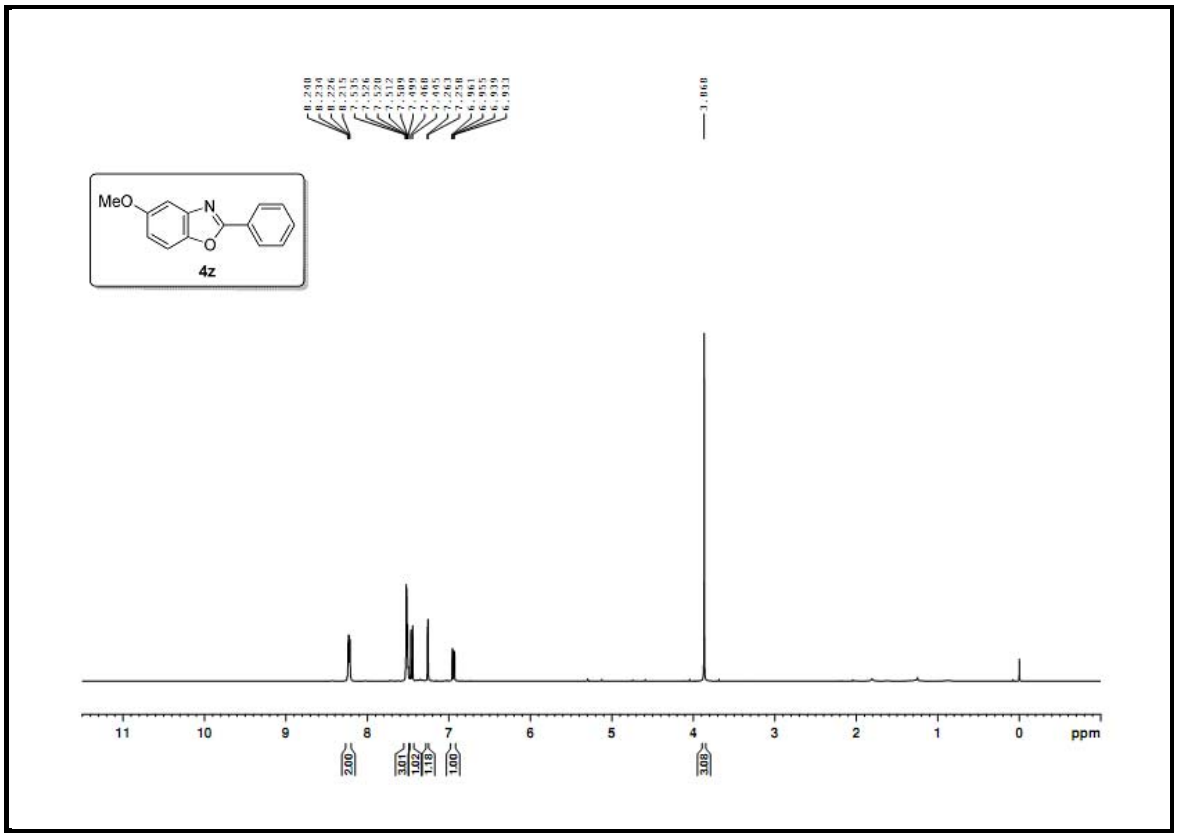
148.94
142.29
134.37
131.36
128.84
127.51
127.25
126.38
119.86
109.91
77.31
77.00
76.68
21.50
Me
N
O
4y
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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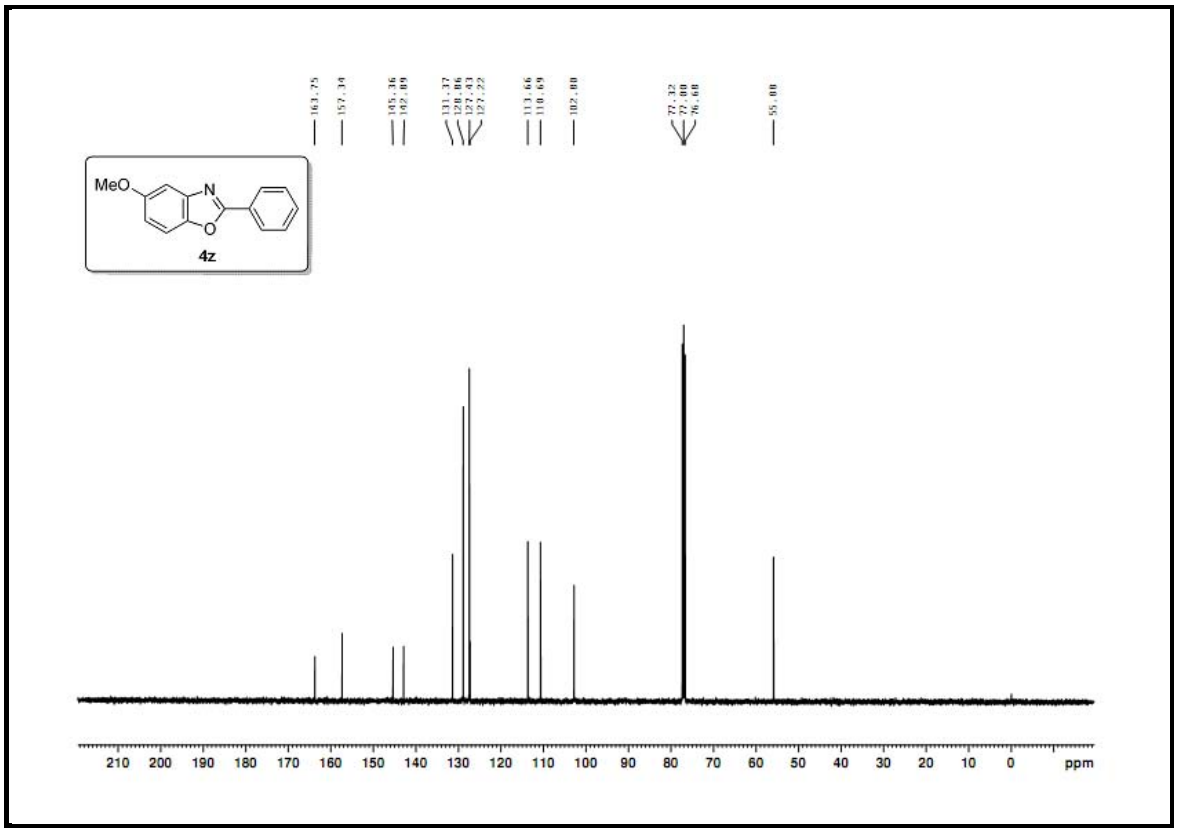
8.234
8.226
8.221
8.215
7.526
7.520
7.512
7.509
7.499
7.496
7.445
7.263
7.258
6.961
6.955
6.939
6.933
3.868
MeO
N
O
4z
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
3.01
1.02
1.18
1.00
3.08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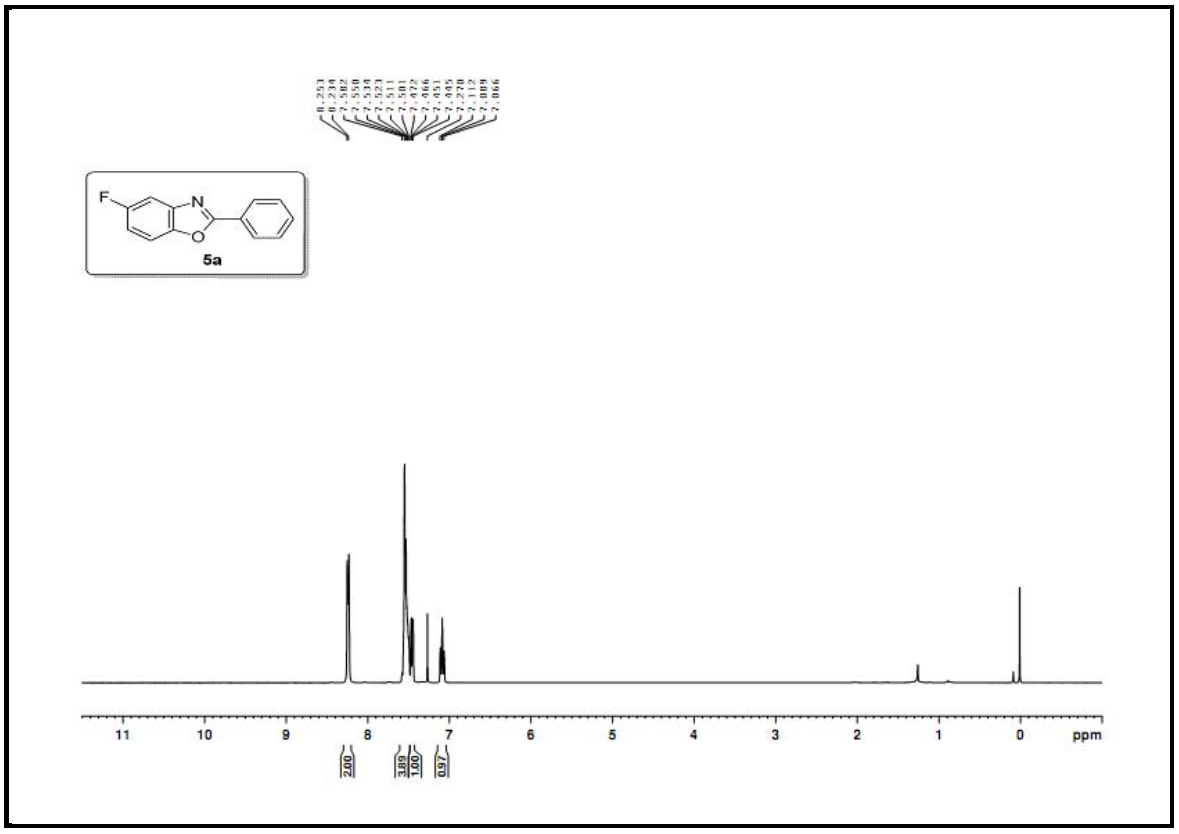
157.34
145.36
142.89
131.37
128.86
127.43
127.22
113.66
110.69
102.80
77.32
77.00
76.68
55.88
MeO
N
O
4z
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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8.234
7.582
7.558
7.538
7.523
7.511
7.501
7.472
7.466
7.451
7.445
7.270
7.112
7.089
7.066
F
N
O
5a
11
10
9
8
7
6
5
4
3
2
1
0
ppm
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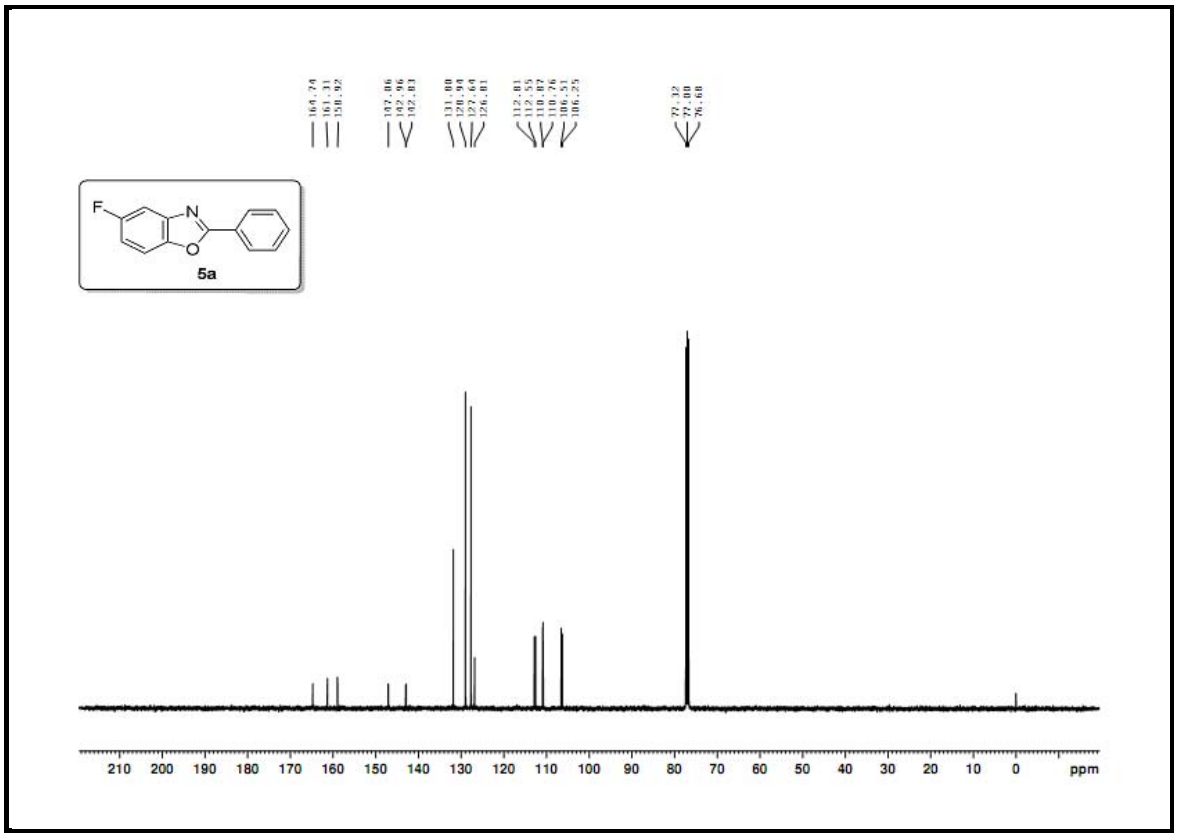
3.89
1.00
0.97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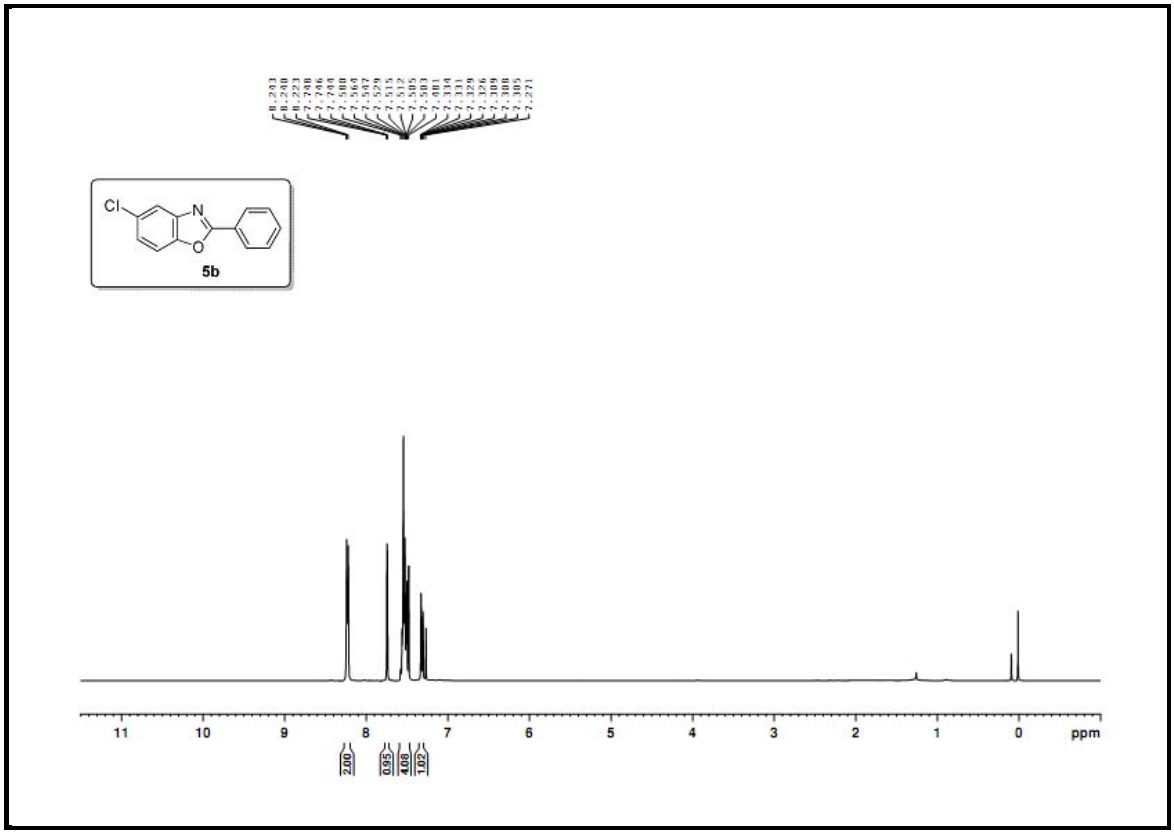
132.96
132.83
131.80
130.94
127.64
126.81
112.81
112.55
110.87
110.76
106.51
106.25
77.32
77.00
76.68
F
N
O
5a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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8.240
8.223
7.748
7.746
7.744
7.580
7.566
7.542
7.529
7.515
7.512
7.505
7.503
7.081
7.334
7.331
7.329
7.326
7.308
7.305
7.271
Cl
N
O
5b
11
10
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8
7
6
5
4
3
2
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0
ppm
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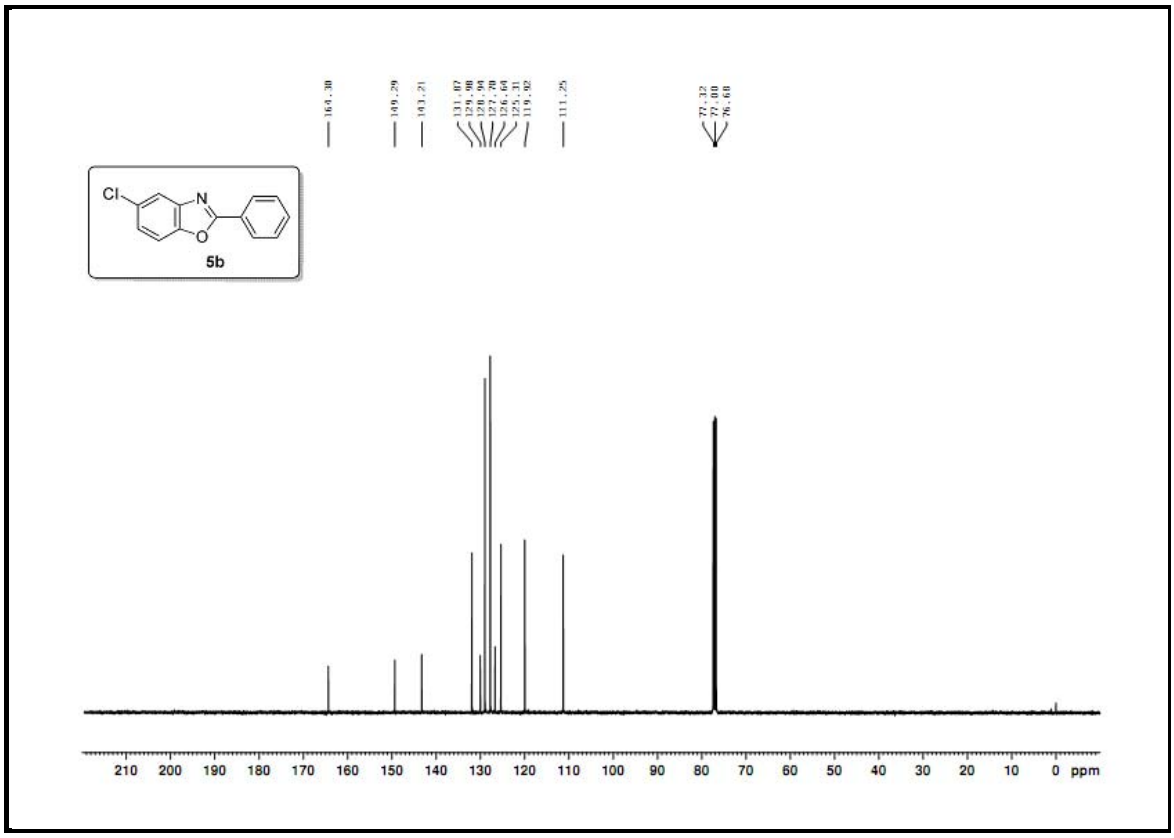
0.95
4.08
1.02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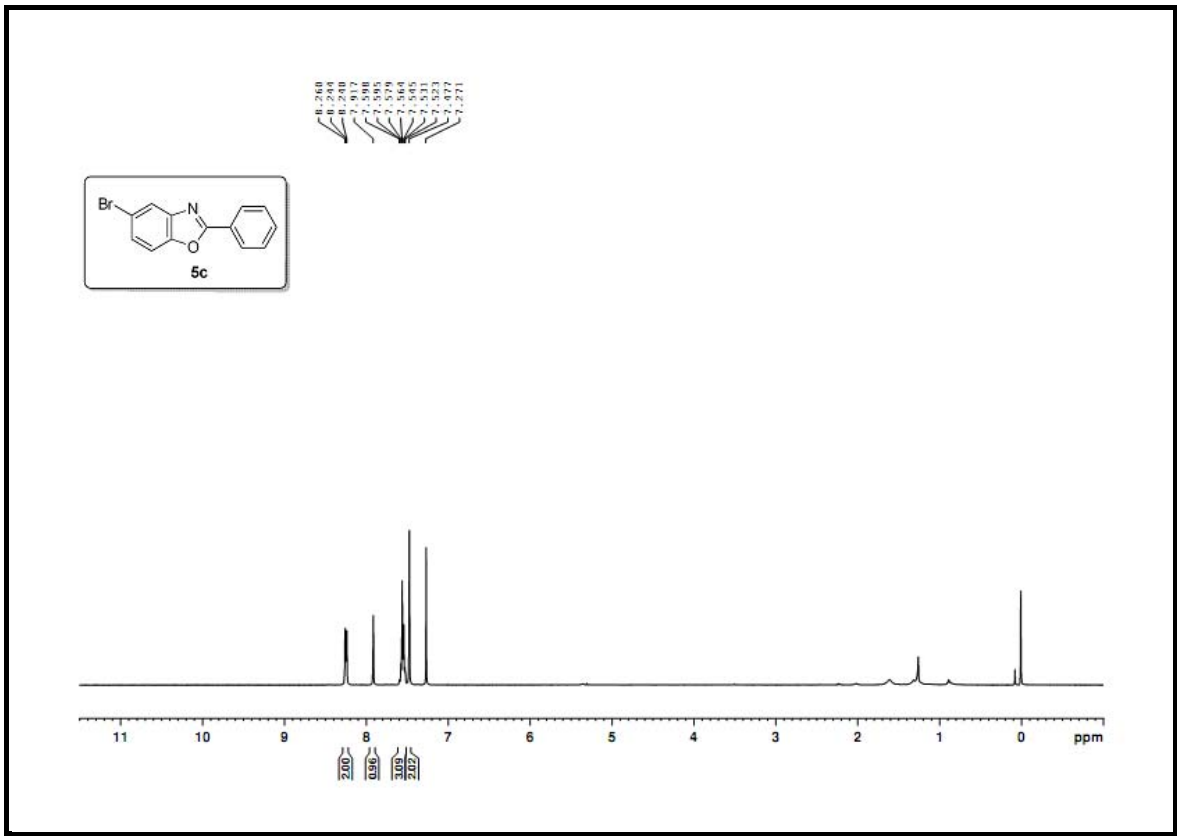
149.29
143.21
131.87
129.98
129.06
127.70
126.64
125.31
119.92
111.25
77.32
77.00
76.68
Cl
N
O
5b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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8.238
8.217
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7.595
7.579
7.564
7.545
7.531
7.523
7.477
7.271
Br
N
O
5c
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10
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8
7
6
5
4
3
2
1
0
ppm
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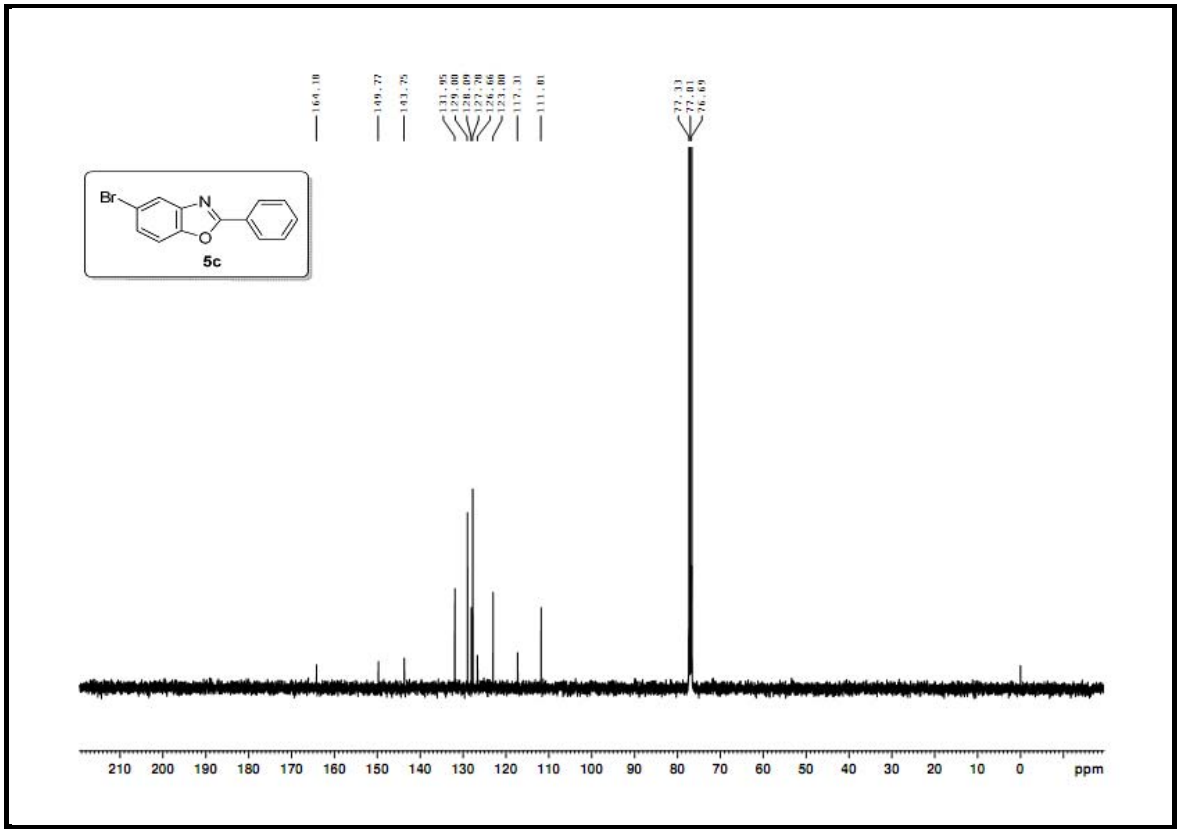
0.96
3.09
2.02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129.88
129.05
127.78
126.66
123.80
117.33
111.01
77.33
77.01
76.69
Br
N
O
5c
210
200
190
180
170
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150
140
130
120
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100
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80
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60
50
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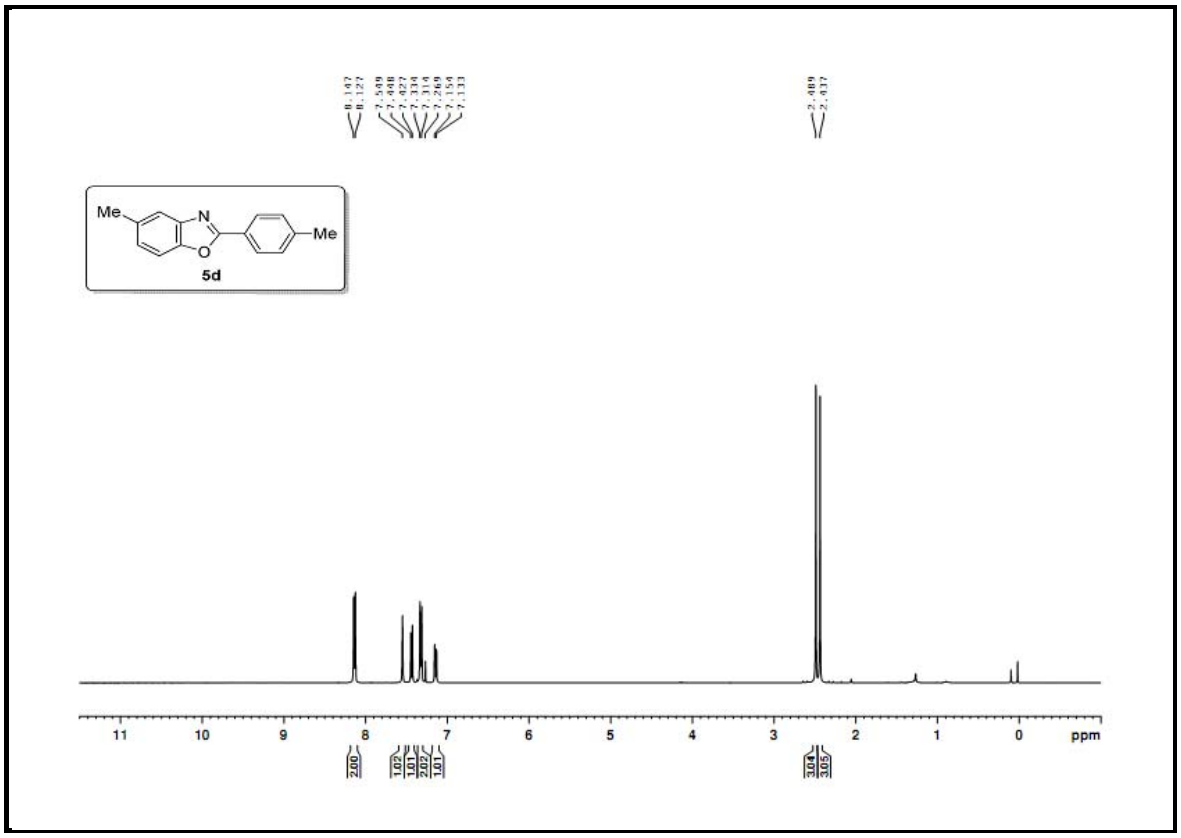
30
20
10
0
ppm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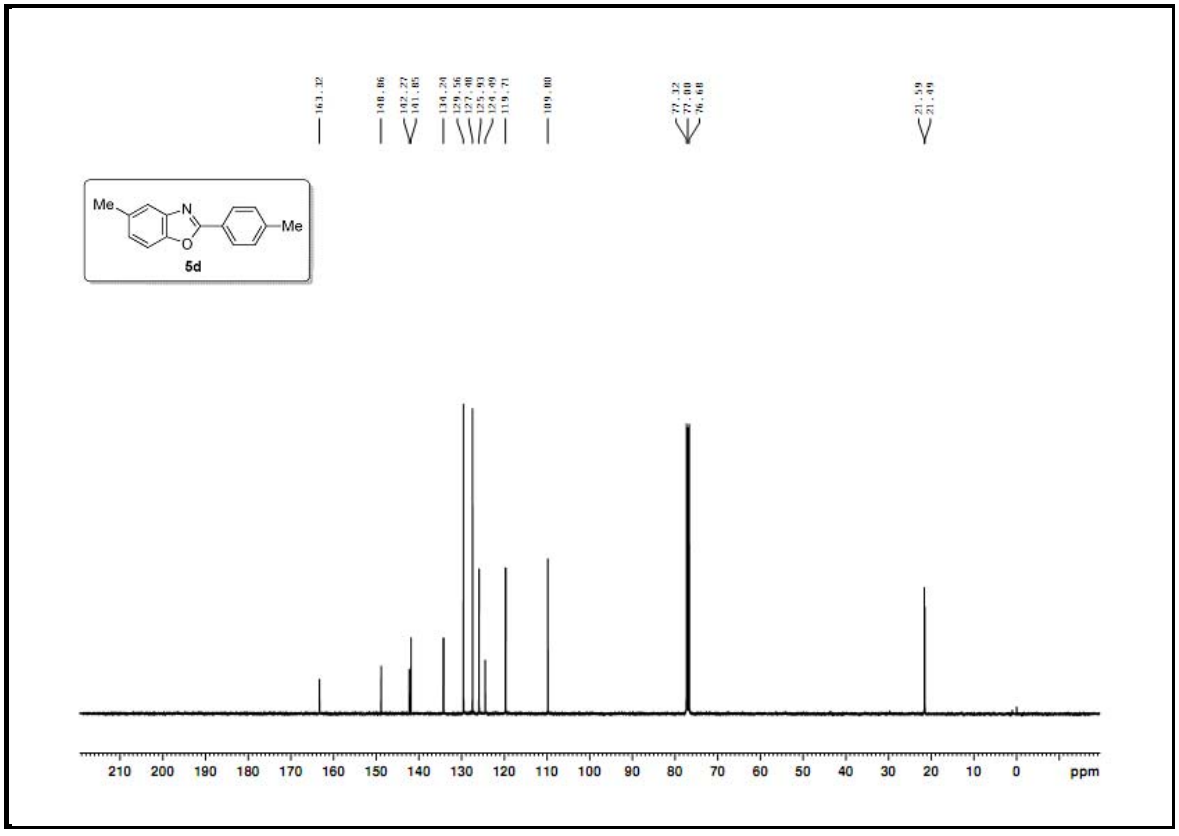
7.316
7.269
7.154
7.133
2.489
2.437
Me
N
O
Me
5d
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.07
1.01
2.02
1.01
3.04
3.05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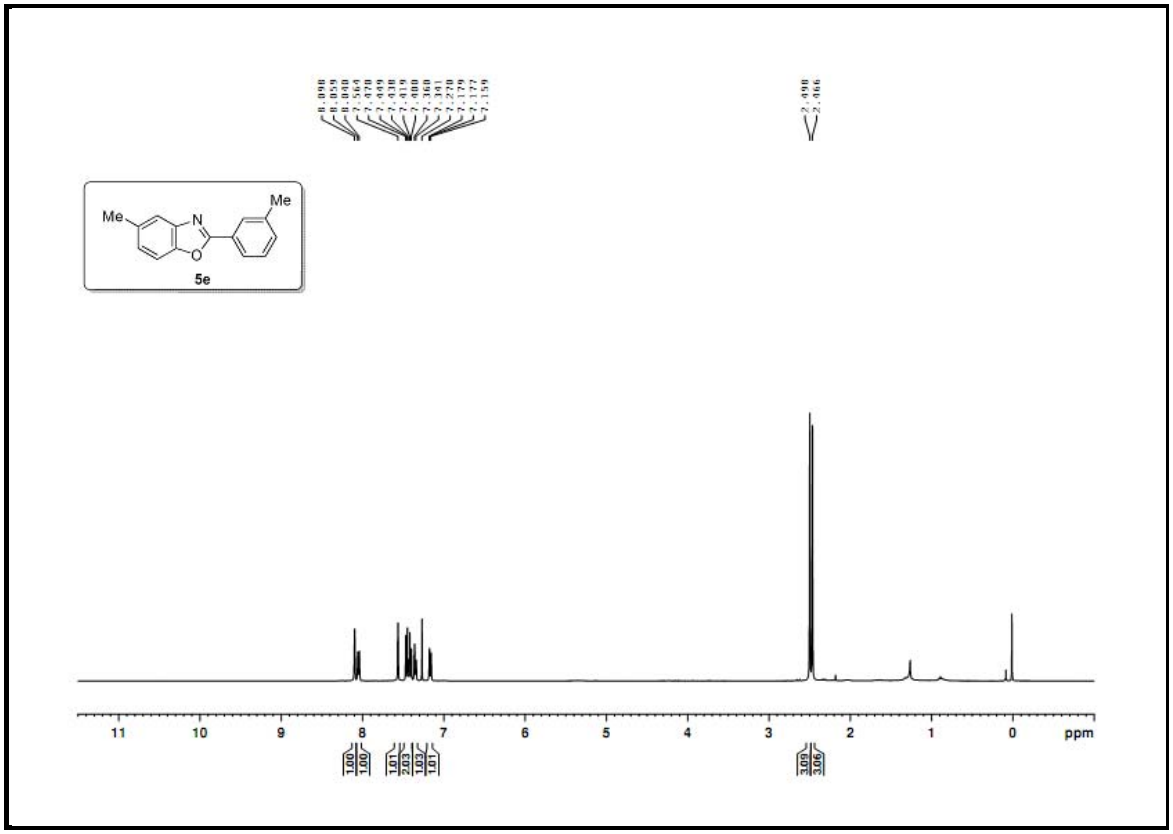
125.85
124.09
119.71
109.80
77.32
77.00
76.68
21.59
21.49
Me
N
O
Me
5d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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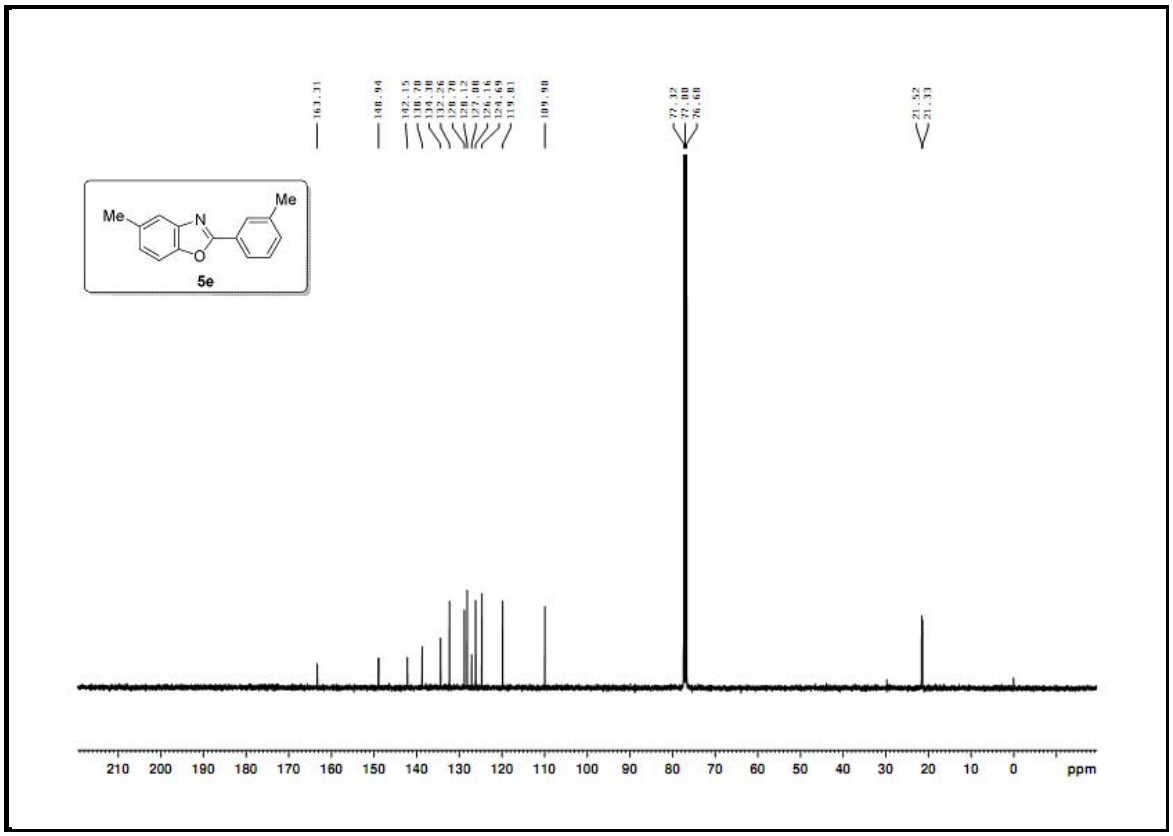
7.447
7.439
7.438
7.419
7.417
7.408
7.406
7.360
7.358
7.281
7.279
7.270
7.268
7.179
7.177
7.159
2.498
2.486
Me
Me
N
O
5e
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.01
2.03
1.02
1.01
3.00
3.06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130.78
130.38
127.26
126.78
126.12
125.08
124.16
124.69
119.81
109.98
77.32
77.00
76.68
21.52
21.33
Me
Me
N
O
5e
210
200
190
180
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140
130
120
110
100
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60
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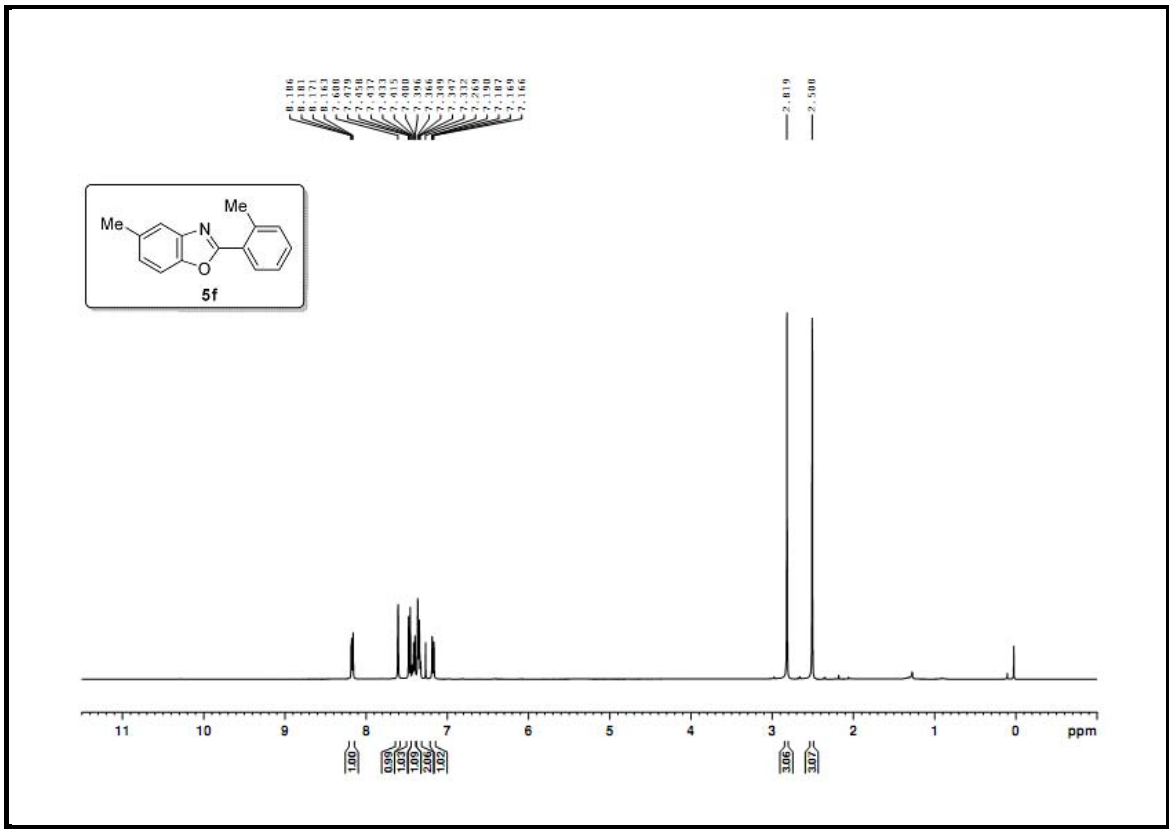
30
20
10
0
ppm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7.679
7.458
7.437
7.433
7.415
7.400
7.396
7.366
7.349
7.349
7.332
7.269
7.190
7.187
7.169
7.166
2.819
2.500
Me
Me
N
O
5f
11
10
9
8
7
6
5
4
3
2
1
0
ppm
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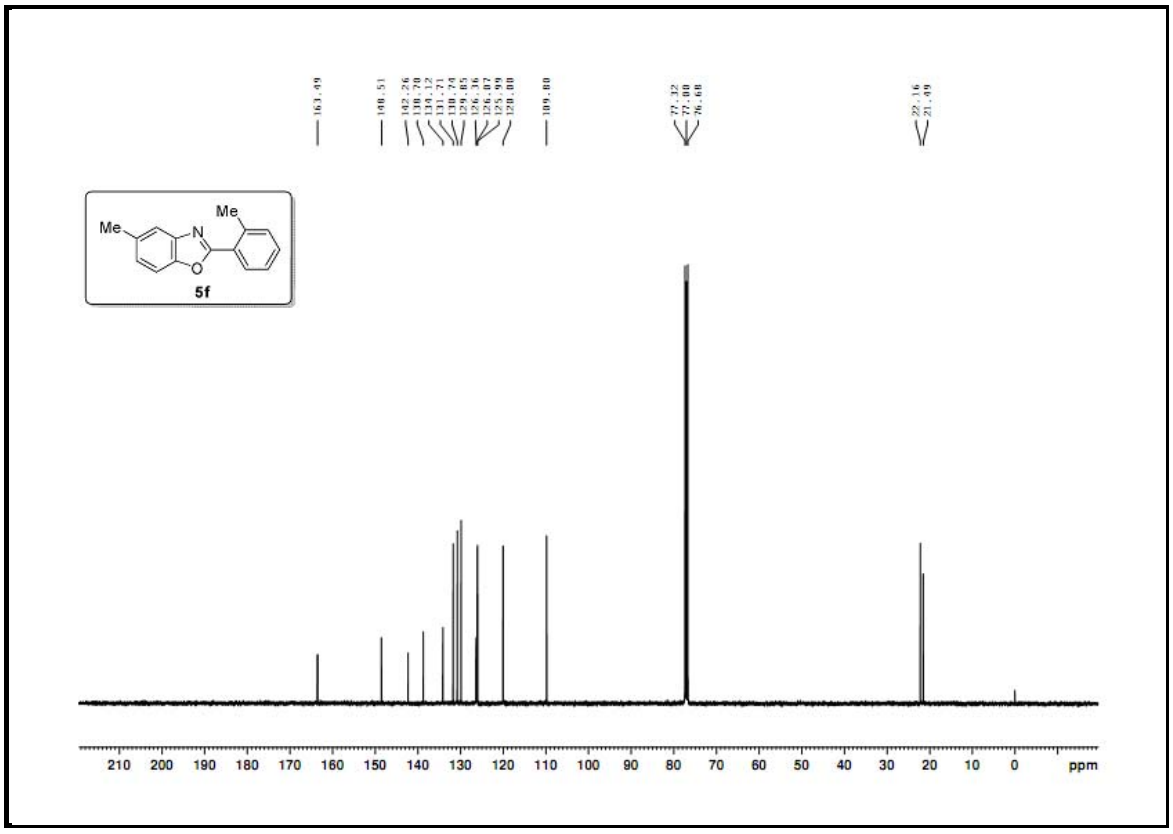
0.99
1.03
1.09
2.06
1.02
3.06
3.07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130.12
127.71
126.74
129.85
126.36
126.07
125.99
120.80
109.80
77.32
77.00
76.68
22.16
21.49
Me
Me
N
O
5f
210
200
190
180
170
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150
140
130
120
110
100
90
80
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60
50
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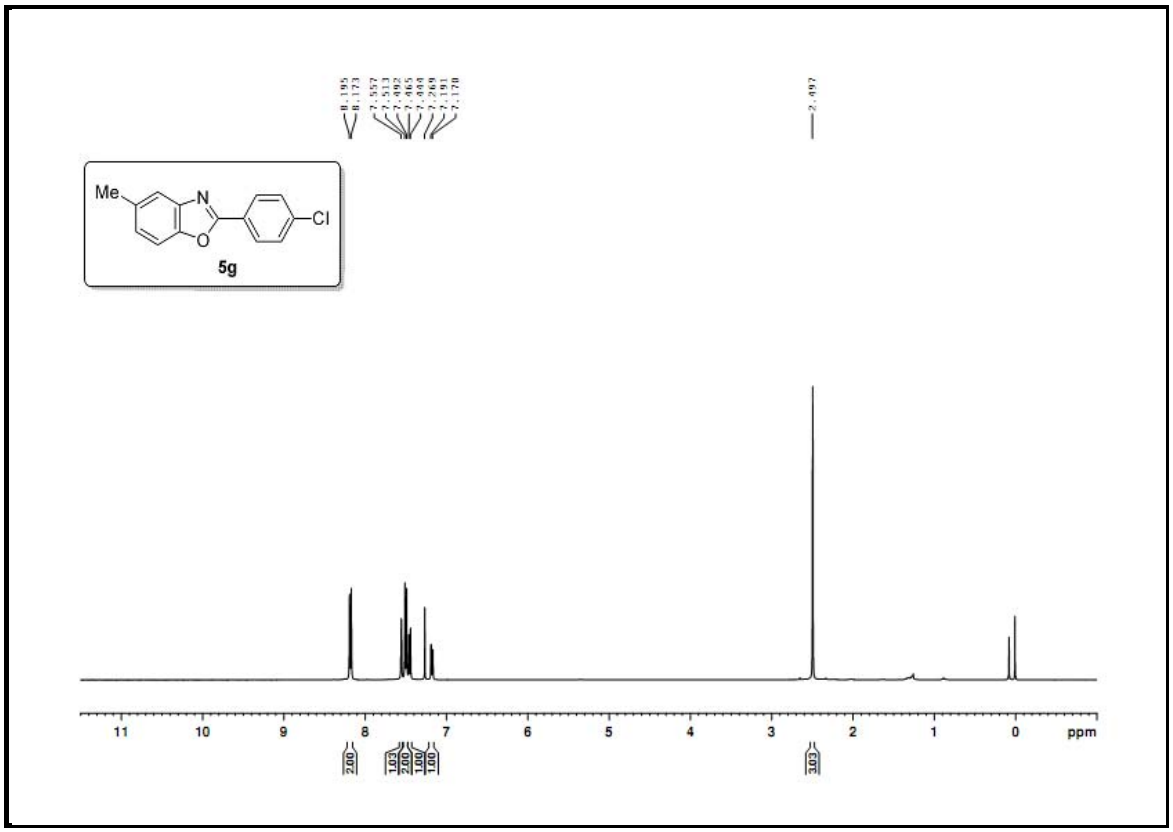
30
20
10
0
ppm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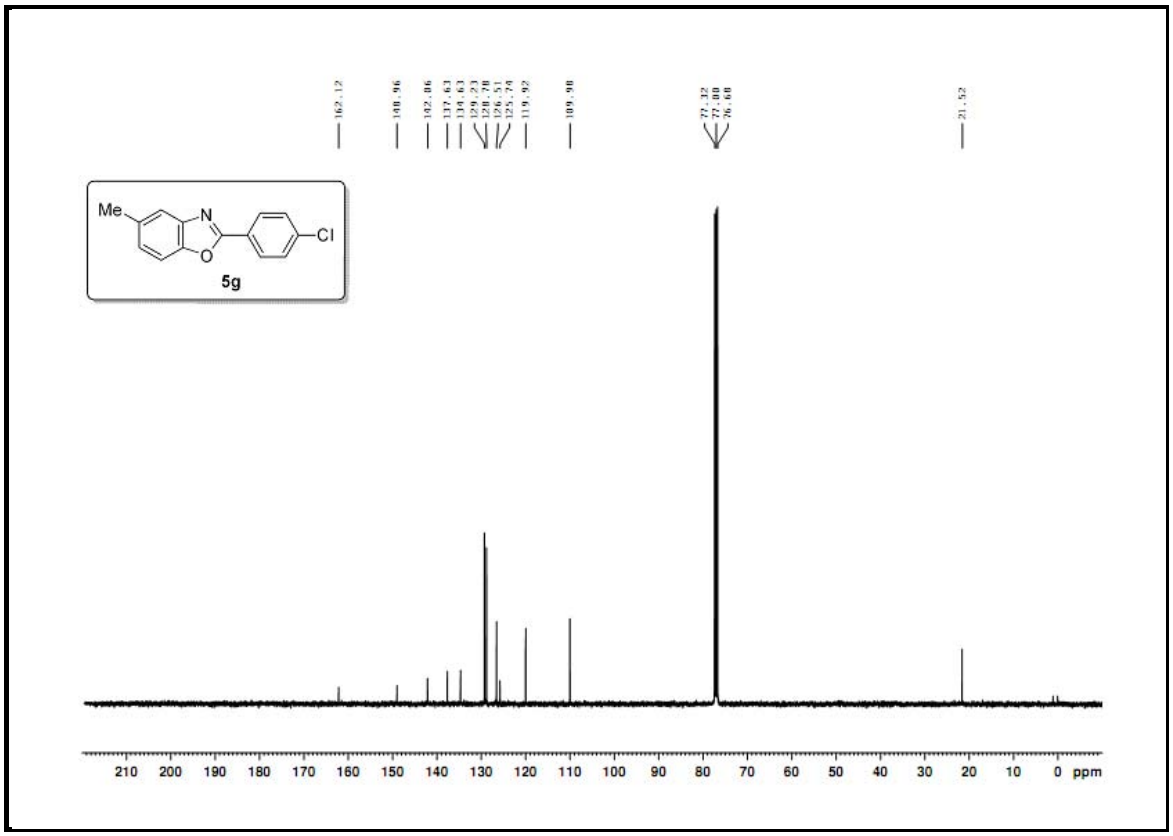
7.465
7.269
7.191
7.170
2.497
Me
N
O
Cl
5g
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.03
2.00
1.00
1.00
3.03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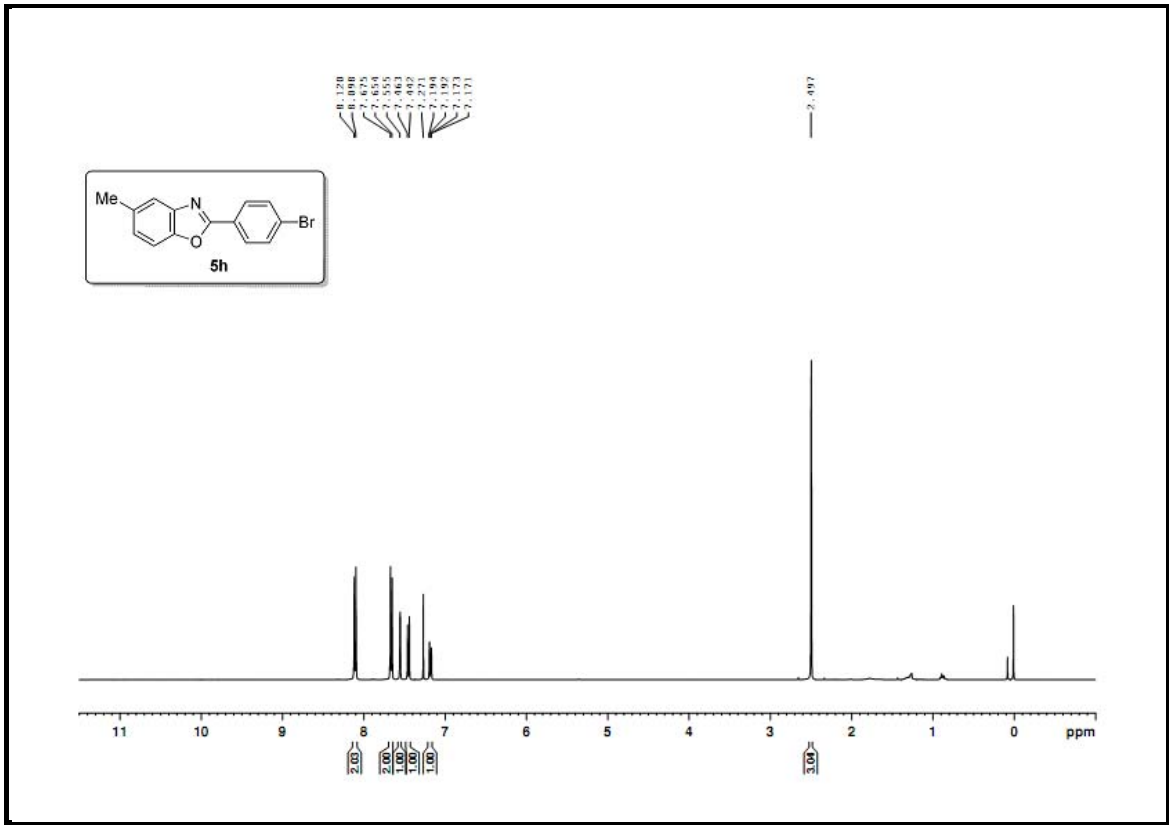
137.63
134.63
129.23
128.78
126.51
125.74
119.92
109.98
77.32
77.00
76.68
21.52
Me
N
O
Cl
5g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.483
7.463
7.271
7.194
7.192
7.173
7.171
2.497
Me
N
O
Br
5h
11
10
9
8
7
6
5
4
3
2
1
0
ppm
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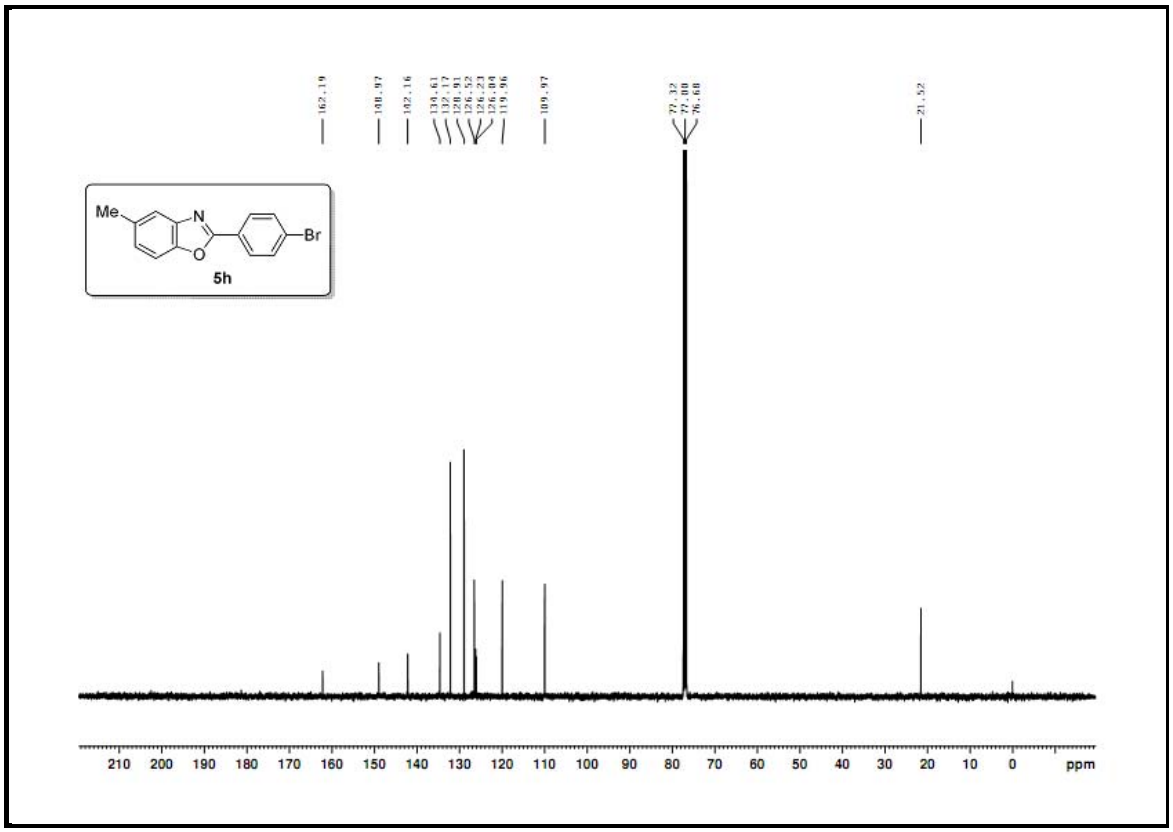
2.00
1.00
1.00
1.00
3.04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138.97
132.16
135.61
132.17
130.91
126.52
126.23
126.04
119.96
109.97
77.32
77.08
76.68
21.52
Me
N
O
Br
5h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
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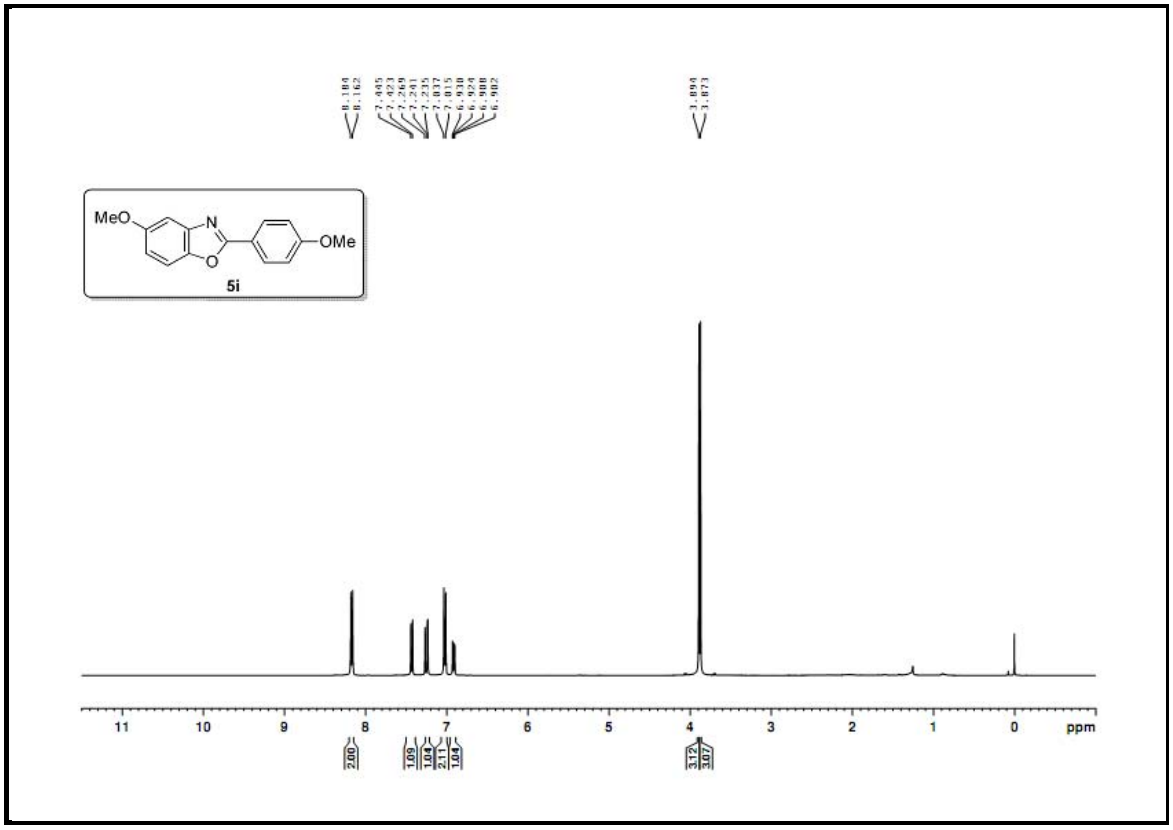
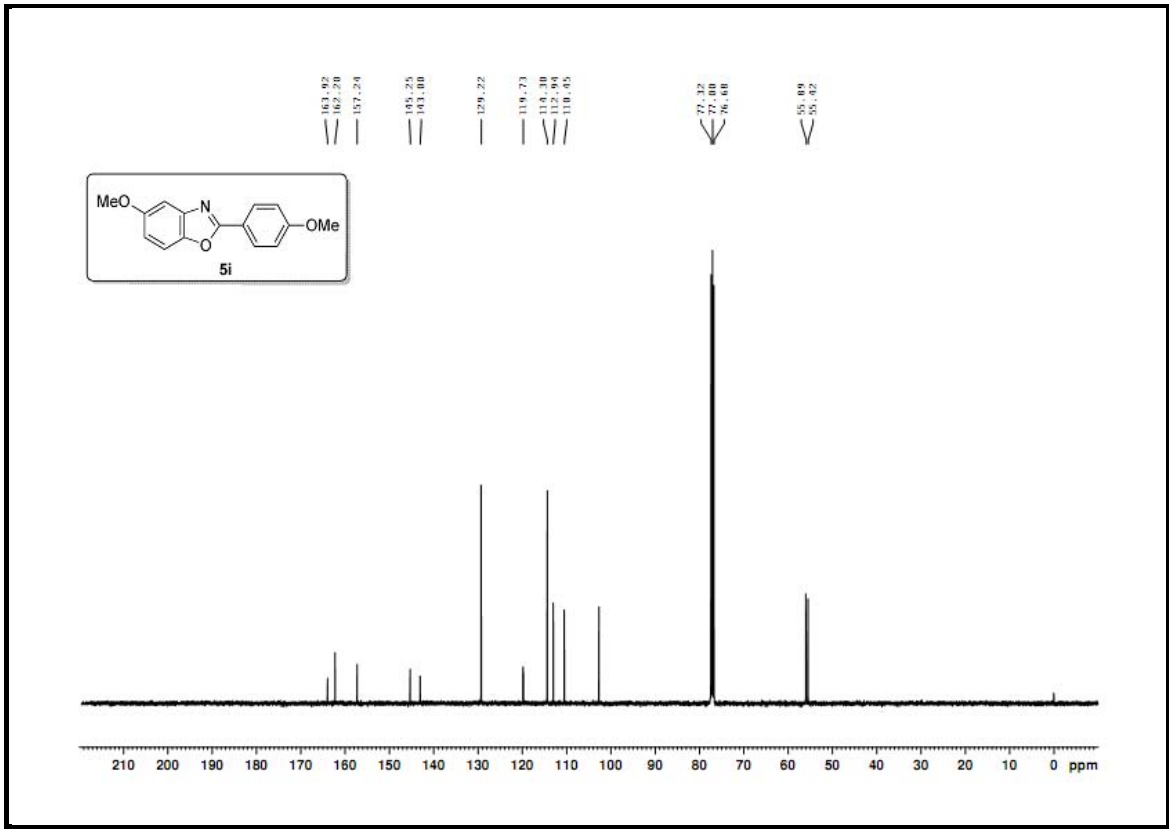
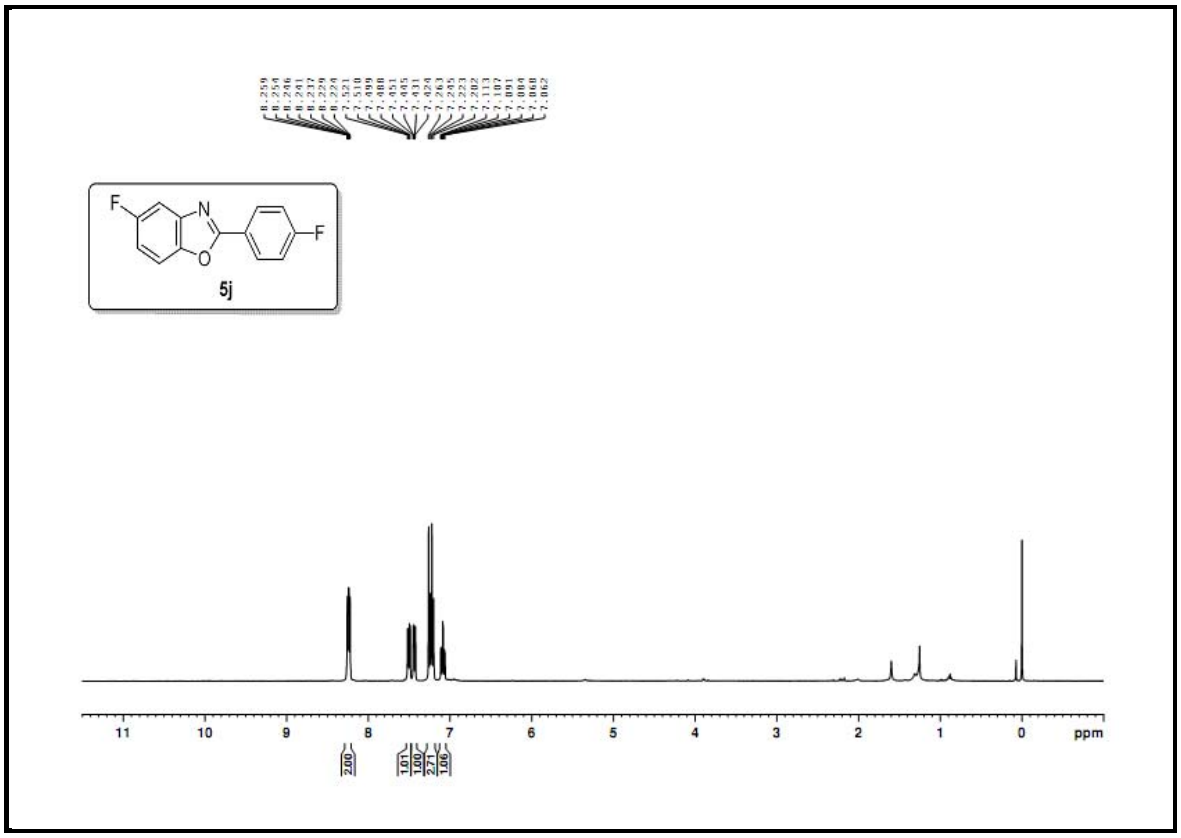
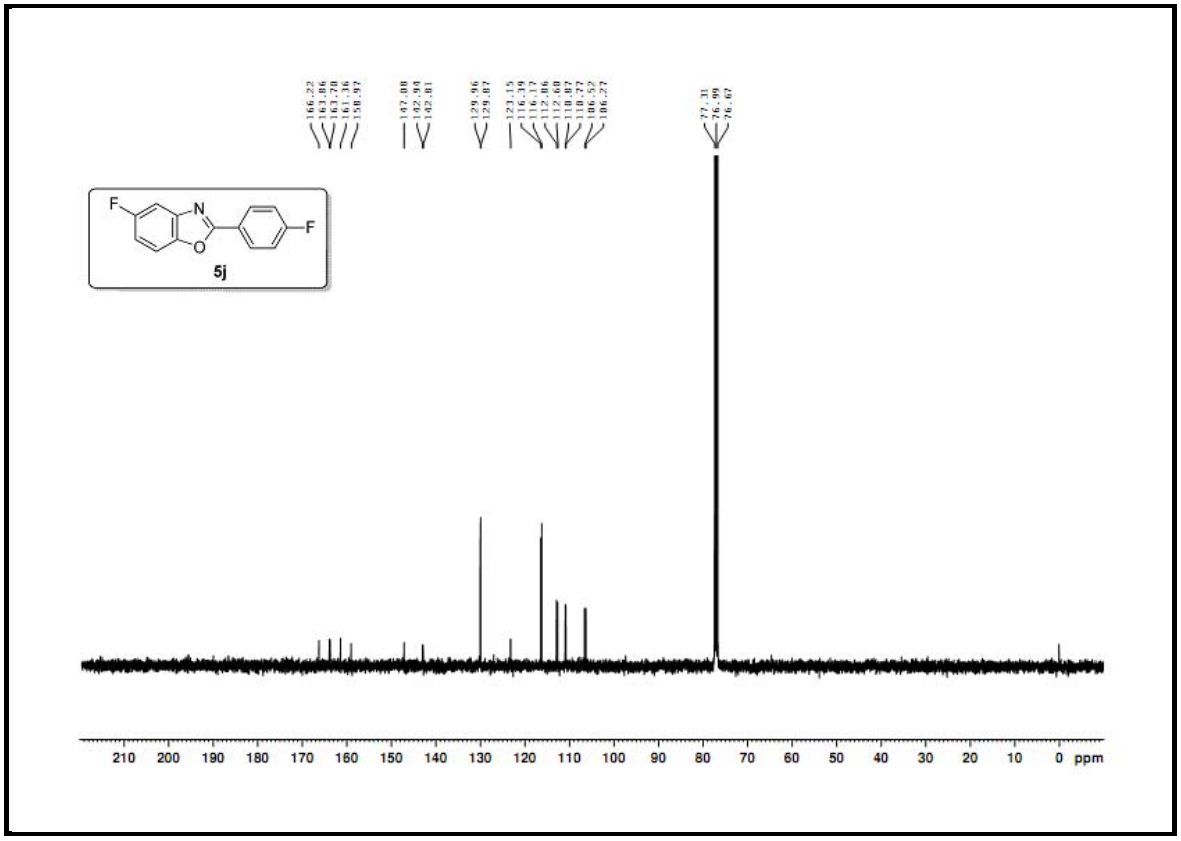
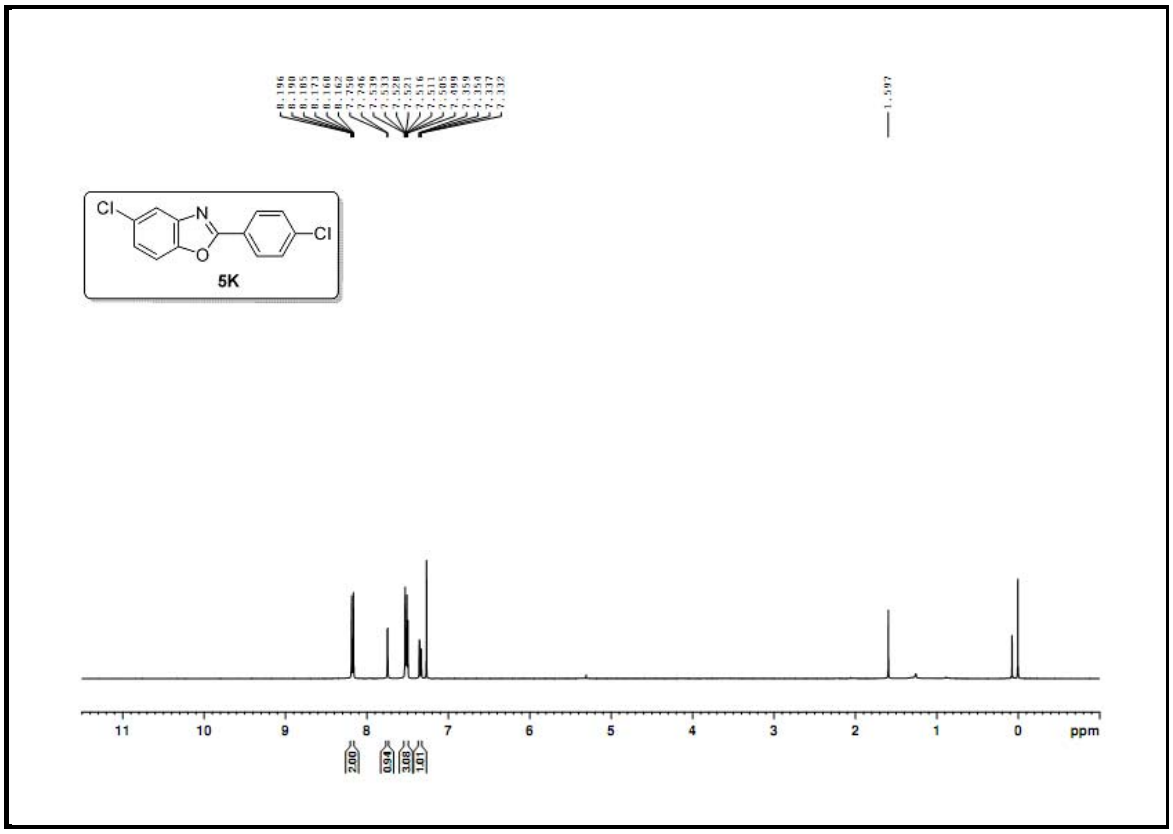
ppm

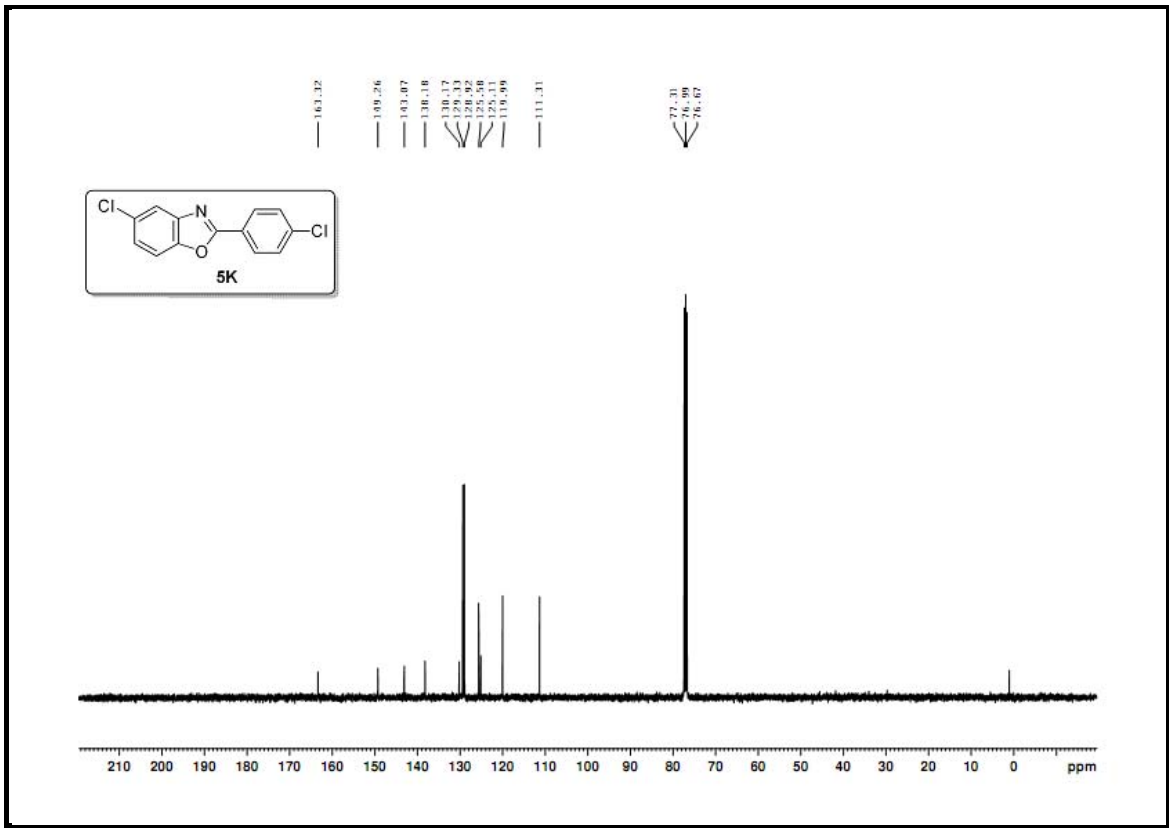

8.166
8.162
7.445
7.423
7.269
7.241
7.235
7.037
7.015
6.930
6.924
6.908
6.902
3.894
3.873
MeO
OMe
N
O
5i
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.09
1.04
2.11
1.04
3.12
3.07

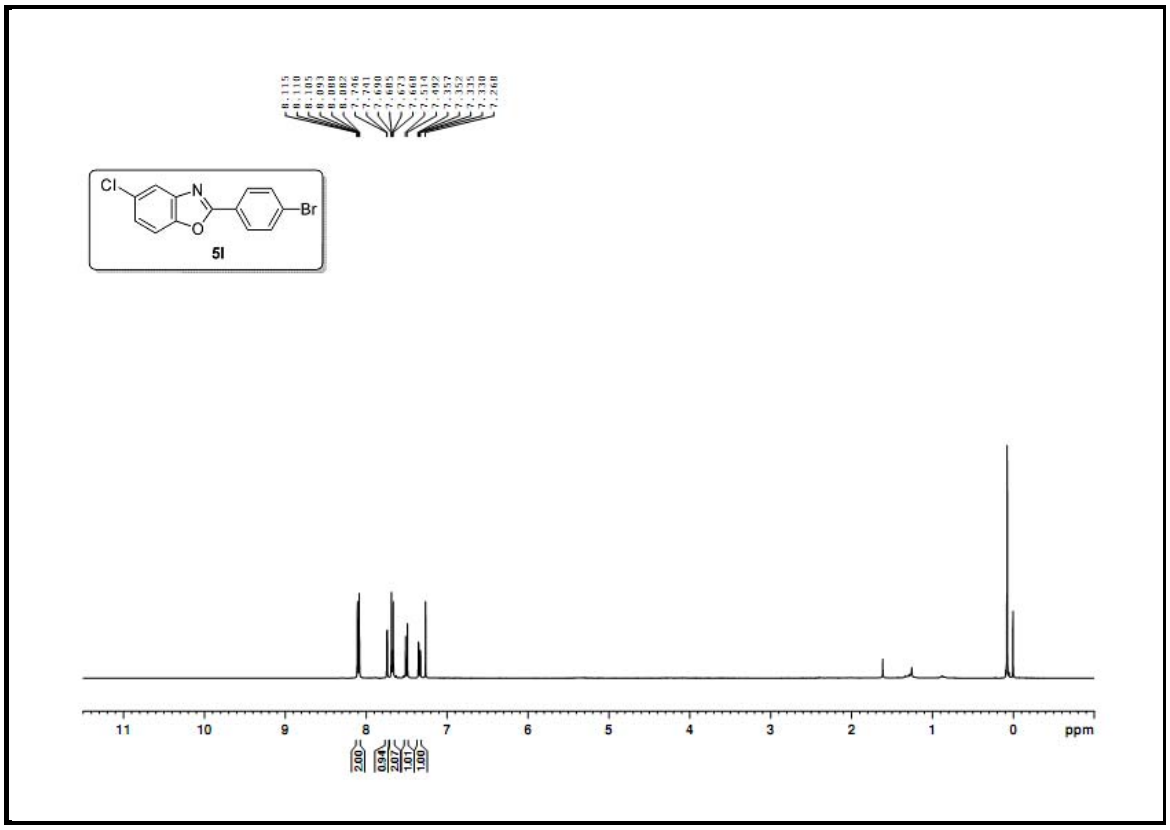

163.92
162.20
157.24
145.25
143.00
129.22
119.73
114.30
112.94
110.45
77.32
77.00
76.68
55.89
55.42
MeO
OMe
N
O
5i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

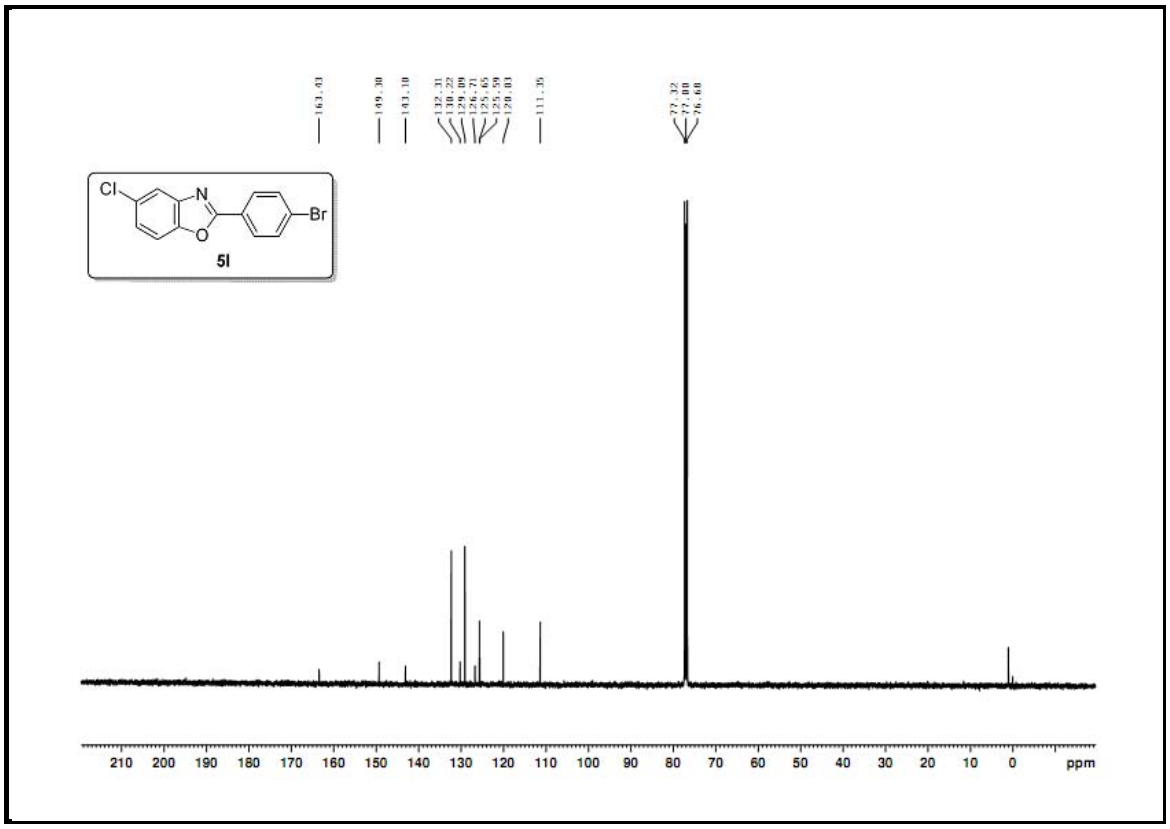

8.259
8.254
8.246
8.241
8.237
8.229
8.224
7.521
7.510
7.488
7.451
7.435
7.431
7.424
7.414
7.295
7.223
7.202
7.113
7.107
7.091
7.004
7.062
F
N
O
F
5j
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.01
1.00
2.71
1.06

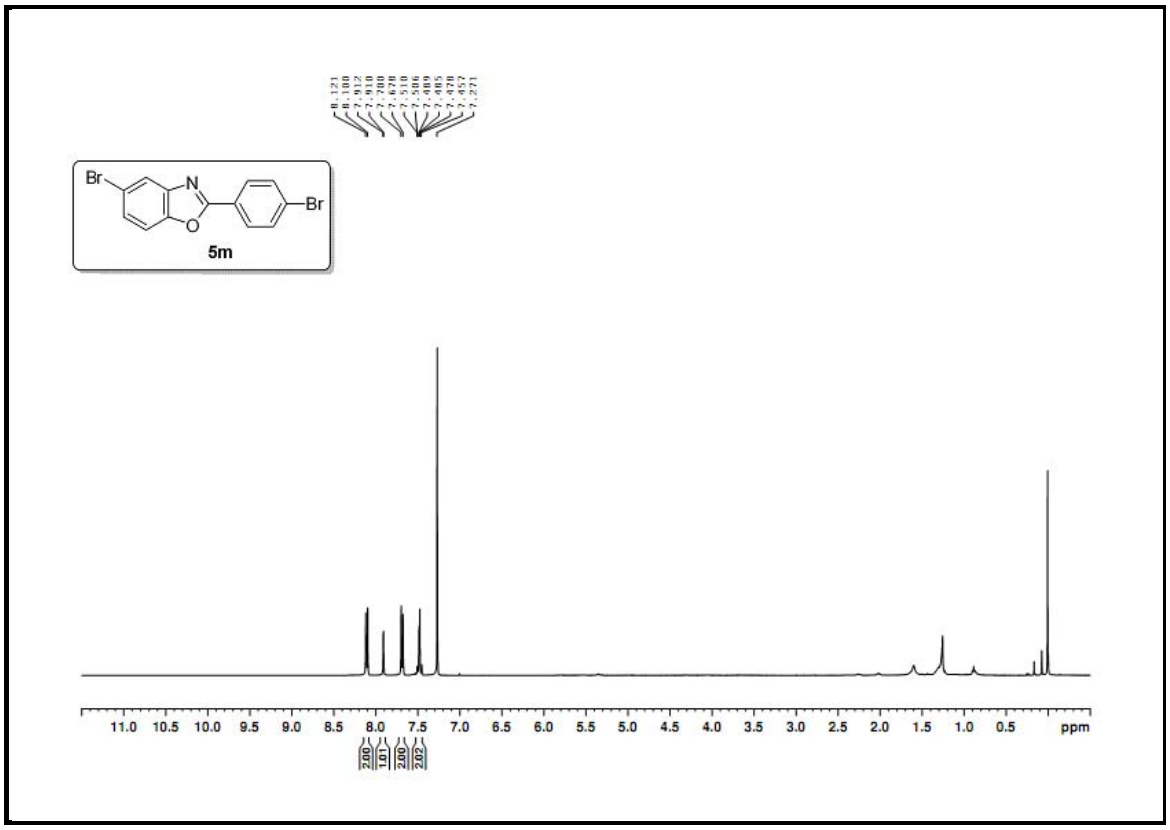

166.22
163.86
163.78
161.36
150.97
147.08
142.94
142.81
129.96
129.87
123.15
116.39
116.17
112.86
112.68
110.87
110.77
106.52
106.27
77.31
76.99
76.67
F
N
O
F
5j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

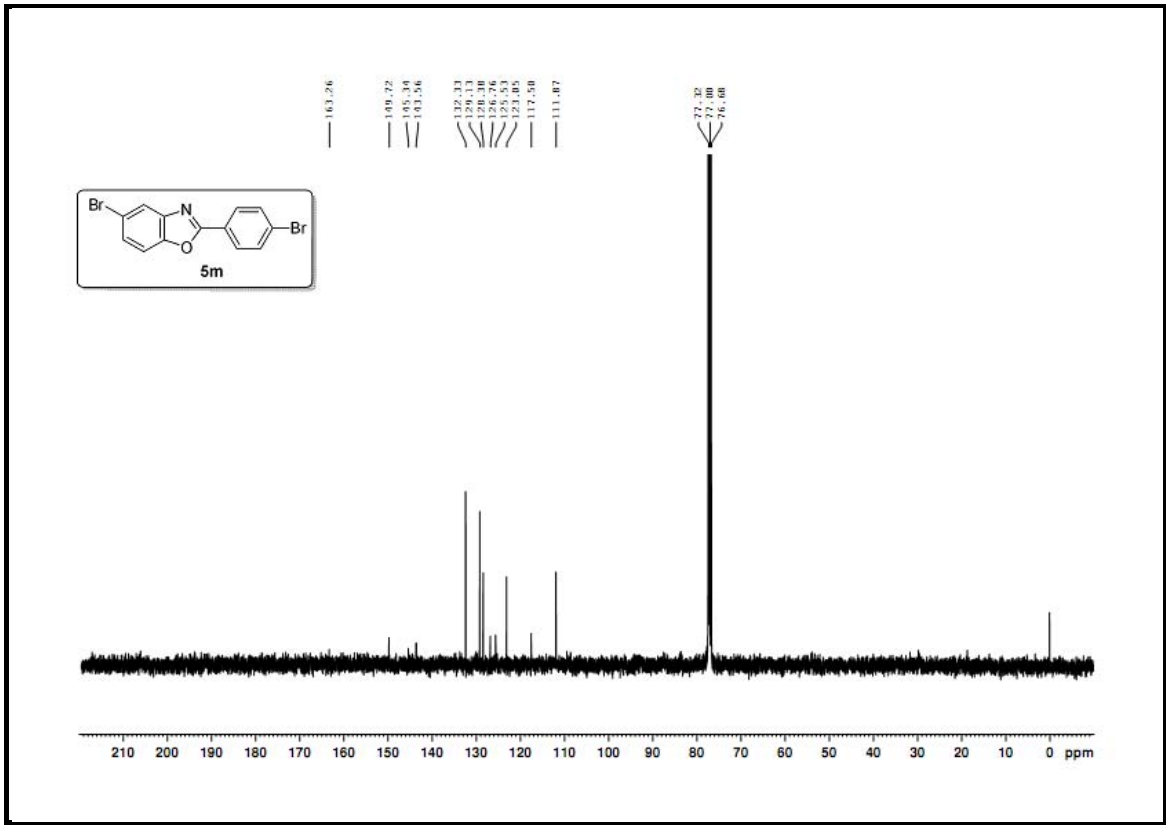

8.196
8.190
8.185
8.173
8.166
8.162
7.750
7.746
7.539
7.533
7.528
7.521
7.516
7.511
7.505
7.499
7.359
7.354
7.337
7.332
1.597
Cl
N
O
Cl
5K
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
0.94
3.08
1.01


163.32
159.26
143.07
138.18
130.17
129.33
129.02
126.58
125.11
119.99
111.31
77.31
76.99
76.67
Cl
N
O
Cl
5K
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.115
8.110
8.105
8.093
8.088
8.082
7.746
7.741
7.690
7.685
7.673
7.668
7.540
7.492
7.357
7.352
7.335
7.330
7.248
Cl
N
O
Br
5l
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
0.94
2.07
1.01
1.00


163.03
149.30
143.10
132.31
130.22
129.09
126.71
125.65
125.59
120.03
111.35
77.32
77.00
76.68
Cl
N
O
Br
5l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.121
8.100
7.912
7.910
7.700
7.678
7.510
7.506
7.489
7.485
7.478
7.457
7.271
Br
N
O
Br
5m
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
1.01
2.00
2.02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149.72
145.34
143.56
132.33
129.33
128.38
126.76
125.53
123.85
117.50
111.87
77.32
77.00
76.68
Br
N
O
Br
5m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm