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## Graphical Abstract

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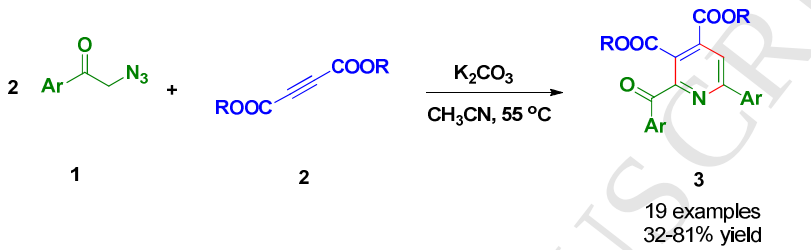

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# A New Strategy for Facile Synthesis of Tetrasubstituted Pyridine Derivatives

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ABSTRACT

A facile and efficient reaction of α-azidomethyl aryl ketones and dialkyl but-2-ynedioate offers a new strategy for the synthesis of tetrasubstituted pyridines in mild condition. This method tolerates a range of functionality and a possible mechanism is proposed.

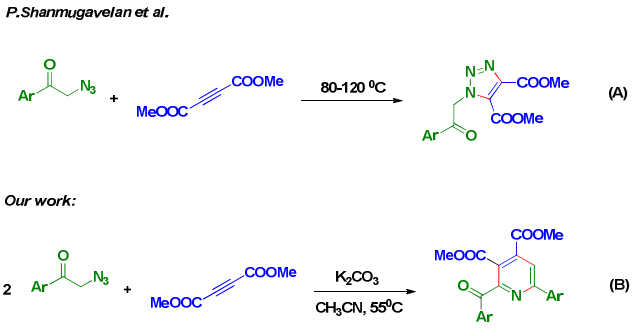


## 1. Introduction

Substituted pyridines are one of the most prevalent heterocycles in natural products, [1] pharmaceuticals, [2] and various kinds of functional materials. [3] Over the past decades, a variety of synthetic strategies have been developed to obtain substituted pyridines, including copper-catalyzed coupling of oxime acetates with aldehydes, [4] rhodium-catalyzed coupling of ketoximes and alkynes, [5] microwave-assisted condensation, [6] Bohlmann-Rahtz reaction, [7] condensation of ketoximines and alkenylboronic acids [8] and so on.[9] The existing methods require transition metal catalysts and harsh reaction conditions. Therefore, versatile and efficient methods for the construction of pyridine rings which are compatible with functional groups and utilize readily available starting materials remain highly desirable.

α-azidomethyl aryl ketones are a pivotal synthon for new scaffold construction. In the past decades, a plethora of reactions have been reported in the literature. [10] We have utilized the α-azidomethyl aryl ketones for the formation of substituted imidazole. [11] As part of an ongoing research program in α-azidomethyl aryl ketones, we were interested in developing a novel methodology from this simple synthon.

To the best of our knowledge, $Cu^{I}$-catalyzed synthesis of 1,2,3-triazoles from azides and alkynes, namely "Click Chemistry" , was widely reported in the literature.[12] However, due to the strong power of the "Click Chemistry", there are fewer studies on the reaction of azides and alkynes under other reacion conditions. P. Shanmugavelan et al. reported the formation of 1,2,3-triazoles from α-azidomethyl aryl ketones and alkynes in metal-free condtion. (**Scheme 1A**) [13] Here, we explored a different, efficient and novel reaction from α-azidomethyl aryl ketones and alkyne to afford tetrasubstituted pyridines under a relatively mild, metal-free reaction conditions. (**Scheme 1B**)




**Scheme 1** Reaction of α-azidomethyl aryl ketones with electron-deficient alkynes

## 2. Results and discussion

Initially, the reaction of α-2-azido-1-phenylethanone and dimethyl but-2-ynedioate was chosen as the model reaction. No reaction was observed without any base. (**Table 1, entry 10**) The transformation occurred when the reaction was performed in the presence of a variety of bases. (**Table 1**)

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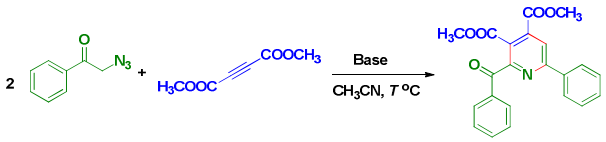
Screening of the base and solvent reveals that $K_2CO_3$ was the most efficient base and acetonitrile was superior to other protic and aprotic solvents, (**Table 1, entries 1 to 9**) but the yield was significantly reduced when the reaction was performed at 80 $^oC$ or at room temperature. (**Table 1, entries 11, 12**) When only 1.2 equiv. of dimethyl but-2-ynediote was used, the conversion of the reaction maintained. (**Table 1, entry 13**). And the yield was less reduced when only 1 equiv. of dimethyl but-2-ynediote was used. (**Table 1 entry 14)** On the basis of this initial study, the optimal reactivity was obtained in $CH_3CN$ at 55 $^0C$ when 1.2 eqiuv. of dimethyl but-2-ynedioate was employed in the presence of $K_2CO_3$. (90%; **Table 1, entry 13**)

**Table 1** Optimization of reaction conditions [a]

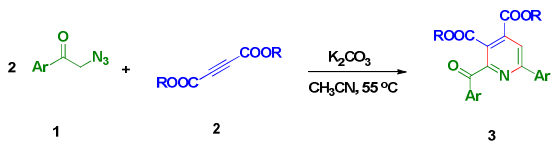



| Entry | Base | Solvent | T($^oC$) | Conversion[d] [%] |
|---|---|---|---|---|
| 1 | $K_2CO_3$ | $CH_3CN$ | 55 | 90 |
| 2 | $K_2CO_3$ | DMF | 55 | 13 |
| 3 | $K_2CO_3$ | EtOH | 55 | 16 |
| 4 | $K_2CO_3$ | Toluene | 55 | 10 |
| 5 | $K_2CO_3$ | THF | 55 | 64 |
| 6 | $Cs_2CO_3$ | $CH_3CN$ | 55 | 80 |
| 7 | EtONa | $CH_3CN$ | 55 | 17 |
| 8 | $Et_3N$ | $CH_3CN$ | 55 | 76 |
| 9 | DBU | $CH_3CN$ | 55 | 80 |
| 10 | / | $CH_3CN$ | 55 | N.R. |
| 11 | $K_2CO_3$ | $CH_3CN$ | r.t. | 61 |
| 12 | $K_2CO_3$ | $CH_3CN$ | 80 | 76 |
| **13**[b] | **$K_2CO_3$** | **$CH_3CN$** | **55** | **90** |
| 14[c] | $K_2CO_3$ | $CH_3CN$ | 55 | 85 |

[a] Reaction conditions: α-2-azido-1-phenylethanone (0.5 mmol, 1.0 equiv.), dimethyl but-2-ynedioate (0.6 mmol, 1.2 equiv.), base (1 mmol, 2 equiv.), 2 mL of solvent, 12 h, 55 $^oC$. [b] 0.3 mmol (1.2 equiv.). of dimethyl but-2-ynedioate was used. [c] 0.25 mmol (1 equiv.) of dimethyl but-2-ynedioate was used. [d] Determined by high-performance liquid chromatography, based on the starting α-2-azido-1-phenylethanone. The most successful entry is highlighted in bold.

With the optimized reaction conditions in hand, the scope of the reaction was studied using a set of α-azidomethyl aryl ketones **1**, internal alkynes **2**. As shown in **Table 2**, various substituted α-azidomethyl aryl ketones worked well with internal alkynes to provide the desired products. Good yields were obtained when **1** contained an electron-donating group and electron-withdrawing group on the aromatic ring (the isolated yield > 60%). But it gave lower yields when a strong electron-withdrawing group was present on the aromatic ring of **1.** (**Table 2, 3s**) Not surprisingly, heteroaromatic α-azidomethyl aryl ketones were also able to furnish the desired products in good efficiency. (**Table 2, 3i** and **3j**) The steric effect was also examined in this scope. As expected, the steric effect on the aromatic ring did influence the reaction efficiency with a slight reduction in the isolated yield. (**Table 2, 3k** compared to **3q** and **3l** compared **3r**)

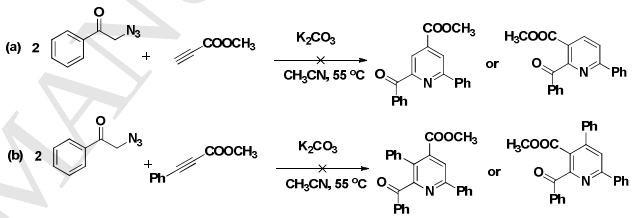
**Table 2** Scope of the reaction [a]




| Entry | Ar | R | Product | Yield [%][b] |
|---|---|---|---|---|
| 1 | $C_6H_5$ | $CH_3$ | 3a | 79 |
| 2 | $C_6H_5$ | $CH_3CH_2$ | 3b | 74 |
| 3 | 4-$CH_3$-$C_6H_4$ | $CH_3$ | 3c | 75 |
| 4 | 4-$CH_3$-$C_6H_4$ | $CH_3CH_2$ | 3d | 73 |
| 5 | 4-Br-$C_6H_4$ | $CH_3$ | 3e | 77 |
| 6 | 4-Br-$C_6H_4$ | $CH_3CH_2$ | 3f | 79 |
| 7 | 4-$OCH_3$-$C_6H_4$ | $CH_3$ | 3g | 75 |
| 8 | 4-$OCH_3$-$C_6H_4$ | $CH_3CH_2$ | 3h | 75 |
| 9 | 2-Thiophene | $CH_3$ | 3i | 72 |
| 10 | 2-Thiophene | $CH_3CH_2$ | 3j | 70 |
| 11 | 2-Cl-$C_6H_4$ | $CH_3$ | 3k | 65 |
| 12 | 2-Cl-$C_6H_4$ | $CH_3CH_2$ | 3l | 60 |
| 13 | 3-$OCH_3$-$C_6H_4$ | $CH_3$ | 3m | 77 |
| 14 | 3-$OCH_3$-$C_6H_4$ | $CH_3CH_2$ | 3n | 76 |
| 15 | 3,4-di$OCH_3$-$C_6H_3$ | $CH_3$ | 3o | 73 |
| 16 | 3,4-di$OCH_3$-$C_6H_3$ | $CH_3CH_2$ | 3p | 74 |
| 17 | 4-Cl-$C_6H_4$ | $CH_3$ | 3q | 81 |
| 18 | 4-Cl-$C_6H_4$ | $CH_3CH_2$ | 3r | 81 |
| 19 | 4-$NO_2$-$C_6H_4$ | $CH_3$ | 3s | 32 |

[a] Reaction conditions: α-azidomethyl aryl ketones (0.5 mmol, 1.0 equiv.), dialkyl but-2-ynedioate (0.6 mmol, 1.2 equiv.), $K_2CO_3$ (1 mmol, 2 equiv.), 2 mL of acetonitrile, 12 h, 55 $^oC$. [b] Isolated yield.

Methyl propiolate and methyl 3-phenylpropiolate were also used under the standard conditon in order to explore the scope of unsymmetrically substituted alkynes. To our disappointment, no desired product were observed. (**Scheme 2**)




**Scheme 2**. Attempted reaction of asymmetrical alkynes

The structures of the tetrasubstituted pyridines were characterized by $^1H$ NMR, $^{13}C$ NMR and HRMS. The structure of **3i** was further proved by X-ray crystal structural analysis as shown in **Fig. 1**.

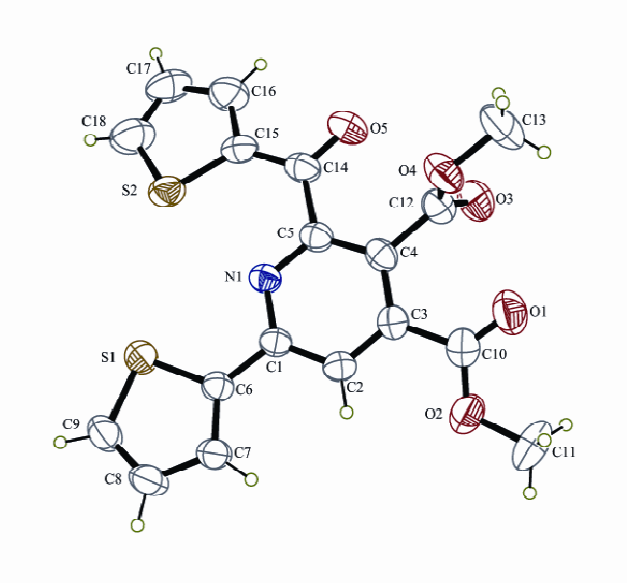
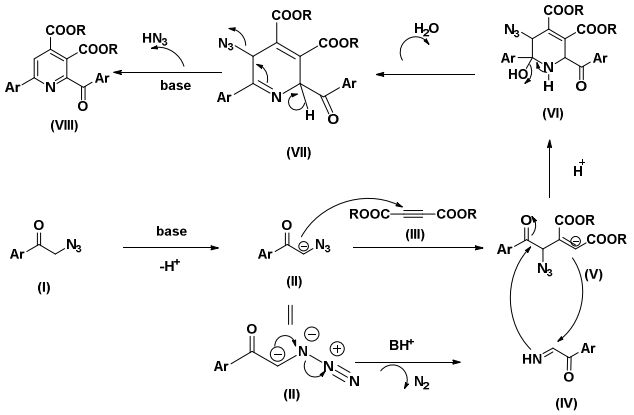



**Fig.1** X-Ray crystal structure of **3i**

On the basis of the results presented above, we proposed the following possible mechanism for this reaction, as shown in **Scheme 3**. In the presence of base, α-azidomethyl aryl ketone gave the intermediate (**II**), which would condense with internal alkynes (**III**) to afford the intermediate (**V**). Another equiv. of (**II**) affords the imine intermediate (**IV**) with a loss of nitrogen,[11] and cyclization of (**IV)** and (**V)** formed intermediate (**VI**). Subsequently, (**VI**) underwent a loss of $H_2O$ molecule to form the intermediate (**VII)**. Aromatization of the resulting (**VII)** by kicking off hydrogen azide assisted by a base gave the final product (**VIII**). [14]




**Scheme 3** The proposed mechanism

## 3. Conclusions

In summary, we have developed a mild reaction to prepare tetrasubstituted pyridines from α-azidomethyl aryl ketones with dialkyl but-2-ynedioate. Mild and metal-free reaction conditions and substituent variation are all notable aspects of this methodology. Although the scope of asymmetric alkyne reaction is still limited, these results will initiate further studies towards an optimization of this new method.

## 4. Experimental section

### 4.1 General

Purification of reaction products were carried out by chromatography using silica gel (200-300mesh). Melting points were recorded on a BÜCHI B-540 melting point apparatus. NMR spectra were in $CDCl_3$ or DMSO ($^1H$ at 500 MHz and $^{13}C$ at 125 MHz) and data are reported as follows: chemical shift, integration, multiplicity ( s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant(s) in Hz. HRMS data were obtained with using ESI ionization. Infrared spectra were recorded on FTIR spectrophotometer. Unless otherwise noted, all reagents were obtained commercially and used without further purification. The starting material α-azidomethyl aryl ketones were prepared according to literature methods.[1]

### 4.2 General procedure for the synthesis of 3

To a 10 ml flask, α-azido ketones (0.5 mmol, 1 equiv.), dimethyl but-2-ynedioate (0.6 mmol, 1.2 equiv.), $K_2CO_3$ (1 mmol, 2 equiv.) and 2 mL acetonitrile was added successively. The reaction mixture was stirred at 55 ℃ for 12 h. Acetonitrile was removed by rotary evaporation under reduced pressure. And then the residue was added 20 mL $H_2O$, extracted with 15 mL EtOAc twice. The organic layer was wished with 20 mL $H_2O$, 20 mL brine and dried with $Na_2SO_4$. And then EtOAc with removed under reduced pressure, the residue was purified by flash chromatography (Petroleum ether/EtOAc) on slica gel to afford **3a-3s**.

*4.2.1. dimethyl 2-benzoyl-6-phenylpyridine-3,4-dicarboxylate (3a):* white solid, Mp: 123-125 $^0$C. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.06 (dd, J = 6.7, 3.0 Hz, 2H), 8.01 (dd, J=6.7, 3.0 Hz 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.52 – 7.47 (m, 5H), 4.00 (s, 3H), 3.88 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 192.58, 166.74, 165.17, 157.73, 154.98, 139.54, 136.62, 135.50, 133.54, 130.87, 130.57, 129.06, 128.32, 127.28, 126.84, 120.45, 53.36, 53.06. IR (KBr) *v*: 2952, 1732, 1676, 1584, 1444, 1358 1261, 1100, 950, 804, 759, 691 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{22}H_{17}NO_5$ $[M+H]^+$: 376.1179. Found: 376.1182.

*4.2.2. diethyl 2-benzoyl-6-phenylpyridine-3,4-dicarboxylate (3b):* white solid. Mp: 87-89 $^0$C. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.07 (dd, J = 6.5, 3.3 Hz, 2H), 8.03 (dd, J = 8.3, 1.1 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.53 – 7.47 (m, 5H), 4.47 (q, J = 7.2 Hz, 2H), 4.34 (q, J = 7.2 Hz, 2H), 1.44 (t, J = 7.2 Hz, 3H), 1.26 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 192.70, 165.95, 165.05, 157.74, 155.49, 140.30, 136.75, 135.57, 133.52, 130.76, 130.49, 129.02, 128.33, 127.30, 126.44, 120.22, 62.64, 62.23, 14.04, 13.63. IR (KBr) *v*: 3065, 2985, 1729, 1673, 1577, 1454, 1371, 1259, 1171, 1110, 1018, 904, 860, 754, 691 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{24}H_{21}NO_5$ $[M+H]^+$: 404.1492. Found: 404.1496.

*4.2.3. dimethyl 2-(4-methylbenzoyl)-6-(p-tolyl)pyridine-3,4-dicar -boxylate (3c):* white solid. Mp: 169-171 $^0$C. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.98 (d, J = 8.2 Hz, 2H), 7.94 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 4.1 Hz, 2H), 7.29 (d, J = 4.2 Hz, 2H), 4.00 (s, 3H), 3.87 (s, 3H), 2.46 (s, 3H), 2.42 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 192.29, 166.82, 165.37, 157.71, 155.28, 144.52, 140.92, 139.49, 133.95, 132.99, 131.03, 129.76, 129.05, 127.19, 126.26, 119.86, 53.29, 52.98, 21.82, 21.38. IR (KBr) *v*: 2953, 1734, 1665, 1584, 1442, 1353, 1276, 1109, 1058, 950, 827, 770, 727 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{24}H_{21}NO_5$ $[M+H]^+$ : 404.1492. Found: 404.1489.

*4.2.4. diethyl 2-(4-methylbenzoyl)-6-(p-tolyl)pyridine-3,4-dica rboxylate (3d):* white solid. Mp: 146-148 $^0$C. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.98 (d, J = 8.2 Hz, 2H), 7.93 (d, J = 8.2 Hz, 2H), 7.30 - 7.27 (m, 4H), 4.46 (q, J = 7.2 Hz, 2H), 4.31 (q, J = 7.2 Hz, 2H), 2.46 (s, 3H), 2.42 (s, 3H), 1.43 (t, J = 7.2 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 192.41, 166.04, 165.24, 157.70, 155.74, 144.46, 140.82, 140.22, 134.07, 133.07, 130.93, 129.72, 129.05, 127.22, 125.89, 119.64, 62.56, 62.13, 21.82, 21.38, 14.04, 13.64. IR (KBr) *v*: 2983, 1729, 1666, 1579, 1370, 1260, 1177, 1108, 1020, 905, 826, 769, 724 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{26}H_{25}NO_5$ $[M+H]^+$ : 432.1805. Found: 432.1812.

*4.2.5. dimethyl 2-(4-bromobenzoyl)-6-(4-bromophenyl)pyridine-3,4-dicarboxylate (3e):* pale yellow solid. Mp: 185-187 $^0$C $^1$H NMR (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.93 (d, J = 8.6 Hz, 2H), 7.89 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 8.6 Hz, 2H), 7.64 (d, J = 8.6 Hz, 2H), 4.02 (s, 3H), 3.91 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 191.33, 166.51, 164.83, 156.58, 154.44, 139.75, 132.35, 131.71, 128.70, 125.49, 120.47, 53.45, 53.15. IR (KBr) *v*: 2950, 1735, 1672, 1582, 1488, 1441, 1405, 1353, 1273, 1110, 1067, 1009, 949, 906, 883, 773, 736, 687, 637 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{22}H_{15}Br_2NO_5$ $[M+H]^+$: 531.9390. Found: 531.9396.

*4.2.6. diethyl 2-(4-bromobenzoyl)-6-(4-bromophenyl)pyridine-3,4-dicarboxylate (3f):* pale yellow solid. Mp: 150-152 $^0$C. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.93 (d, J = 8.6 Hz, 2H), 7.88 (d, J = 8.6 Hz, 2H), 7.62 - 7.66 (m, 4H) 4.47 (q, J = 7.1 Hz, 2H), 4.35 (q, J = 7.2 Hz, 2H), 1.43 (t, J = 7.2 Hz, 3H), 1.28 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 191.45, 165.76, 164.69, 156.54, 154.88, 140.46, 135.44, 134.24, 132.30, 132.18, 131.72, 129.01, 128.73, 127.01, 125.40, 120.26, 62.78, 62.36, 14.03, 13.67. IR (KBr) *v*: 2983, 1728, 1672, 1581, 1402, 1262, 1177, 1107, 1009, 905, 836, 774 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{24}H_{19}Br_2NO_5$ $[M+H]^+$: 559.9703. Found: 559.9705.

*4.2.7. dimethyl 2-(4-methoxybenzoyl)-6-(4-methoxyphenyl)pyridi-ne-3,4-dicarboxylate (3g):* white solid. Mp: 125-127 $^0$C. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.05 - 8.02 (m, 4H), 7.00 - 6.97 (m, 4H), 4.00 (s, 3H), 3.91 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 191.25, 166.91, 165.48, 163.95, 161.68, 157.30, 155.52, 139.48, 133.31, 129.31, 128.80, 128.49, 125.68, 119.20, 114.39, 113.64, 55.53, 55.43, 53.27, 52.96. IR (KBr) *v*: 3103, 2954, 2839, 1734, 1655, 1595, 1512, 1433, 1357, 1259, 1173, 1110, 946, 835, 773, 719 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{24}H_{21}NO_7$ $[M+H]^+$: 436.1391. Found: 436.1391.

*4.2.8. diethyl 2-(4-methoxybenzoyl)-6-(4-methoxyphenyl)pyridine-3,4-dicarboxylate (3h):* colorless liquid. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.05 - 8.00 (m, 4H), 6.99 - 6.96 (m, 4H), 4.45 (q, J = 7.1 Hz, 2H), 4.30 (q, J = 7.2 Hz, 2H), 3.90 (s, 3H), 3.86 (s, 3H), 1.42 (t, J = 7.2 Hz, 3H), 1.24 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 191.40, 166.09, 165.34, 163.92, 161.64, 157.32, 155.99, 140.25, 133.16, 129.43, 128.81, 128.61, 125.27, 118.96, 114.36, 113.64, 62.50, 62.06, 55.50, 55.40, 14.03, 13.63. IR (KBr) *v*: 2892, 2838, 1728, 1661, 1596, 1512, 1461, 1425, 1372, 1258, 1173, 1107, 1027, 905, 840, 775 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{26}H_{25}NO_7$ $[M+H]^+$: 464.1704. Found: 464.1709.

*4.2.9. dimethyl 6-(thiophen-2-yl)-2-(thiophene-2-carbonyl)pyridi-ne-3,4-dicarboxylate (3i):* yellow solid. Mp: 143-145 $^0$C. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.30 - 8.29 (m, 2H), 7.84 – 7.82 (m, 2H), 7.56 (dd, J = 5.0, 1.0 Hz, 1H), 7.23 - 7.20 (m, 2H), 4.02 (s, 3H), 4.01 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 181.89, 167.30, 164.23, 152.85, 151.90, 142.20, 139.27, 138.39, 137.11, 136.96, 130.03, 128.58, 127.78, 127.74, 127.34, 120.55, 53.39, 53.10. IR (KBr) *v*: 3091, 2945, 1737, 1636, 1582, 1435, 1273, 1150, 1094, 745, 691 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{18}H_{13}NO_5S_2$ $[M+H]^+$: 388.0308. Found: 388.0310.

*4.2.10. diethyl 6-(thiophen-2-yl)-2-(thiophene-2-carbonyl)pyridin-e-3,4-dicarboxylate (3j):* yellow solid. Mp:117-119 $^0$C. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.25 (dd, J = 3.9, 1.2 Hz, 1H), 7.84 – 7.80 (m, 2H), 7.55 (dd, J = 5.0, 0.9 Hz, 1H), 7.27 – 7.19 (m, 2H), 4.49 – 4.44 (m, 4H), 1.43 (t, J = 7.1 Hz, 3H), 1.39 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 182.17, 166.58, 164.05, 152.69, 152.31, 142.31, 139.64, 139.07, 136.92, 136.71, 129.93, 128.54, 127.80, 127.63, 127.23, 120.34, 62.70, 62.16, 14.05, 13.82. IR (KBr) *v*: 3111, 2982, 1724, 1638, 1581, 1405, 1357, 1277, 1238, 1152, 1095, 1018, 851, 718 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{20}H_{17}NO_5S_2$ $[M+H]^+$: 416.0621. Found: 416.0621.

*4.2.11. dimethyl 2-(2-chlorobenzoyl)-6-(2-chlorophenyl)pyridine-3,4-dicarboxylate (3k):* colorless liquid. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.63 (dd, J = 7.6, 1.3 Hz, 1H), 7.51(dd, J = 7.5, 2.0Hz, 1H), 7.48 – 7.41 (m, 3H), 7.39 – 7.30 (m, 3H), 4.03 (s, 3H), 4.00 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 193.44, 167.04, 164.27, 157.39, 152.63, 137.42, 136.92, 136.72, 132.87, 132.45, 132.27, 131.69, 131.17, 130.66, 130.31, 130.02, 127.86, 127.22, 126.78, 126.69, 53.40, 53.28. IR (KBr) *v*: 3088, 2952, 1744, 1680, 1587, 1435, 1358, 1277, 1219, 1153, 1123, 1072, 951, 745, 705, 638 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{22}H_{15}C_{l2}NO_5$ $[M+H]^+$: 444.0400. Found: 444.0406.

*4.2.12. diethyl 2-(2-chlorobenzoyl)-6-(2-chlorophenyl)pyridine-3,4-dicarboxylate (3l):* colorless liquid. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.63 (dd, J =7.3, 2.1 Hz, 1H), 7.50 (dd, J = 7.3, 2.1 Hz, 1H), 7.46 – 7.40 (m, 3H), 7.27-7.36 (m, 3H), 4.43 – 4.52 (m 4H), 1.40 - 1.43 (m, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 193.43, 166.41, 163.97, 157.24, 152.91, 137.96, 136.99, 136.82, 132.86, 132.40, 132.27, 131.65, 131.17, 130.60, 130.29, 130.03, 127.94, 127.19, 126.66, 62.68, 62.37, 14.03, 13.82. IR (KBr) *v*: 2985, 1737, 1687, 1588, 1438, 1374, 1280, 1167, 1120, 755 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{24}H_{19}Cl_2NO_5$ $[M+H]^+$: 472.0713. Found: 472.0717.

*4.2.13. dimethyl 2-(3-methoxybenzoyl)-6-(3-methoxyphenyl)pyrid-ine-3,4-dicarboxylate (3m):* white solid. Mp: 92-94 $^0$C. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.64 – 7.62 (m, 3H), 7.56 (d, J = 7.7 Hz, 1H), 7.40 - 7.37 (m, 2H), 7.18 (dd, J=8, 2.5Hz, 1H), 7.02 (dd, J = 8, 2.5 Hz, 1H), 4.00 (s, 3H), 3.89 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 192.26, 166.67, 165.15, 160.23, 159.56, 157.47, 154.82, 139.53, 137.99, 136.77, 130.06, 129.22, 126.89, 124.03, 120.59, 120.31, 119.56, 116.46, 114.50, 112.53, 55.45, 55.35, 53.34, 53.04. IR (KBr) *v*: 2979, 1732, 1671, 1587, 1458, 1268, 1221, 1099, 1040, 862, 770, 726, 684 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{24}H_{21}NO_7$ $[M+H]^+$: 436.1391. Found: 436.1389.

*4.2.14. diethyl 2-(3-methoxybenzoyl)-6-(3-methoxyphenyl)pyridin-e-3,4-dicarboxylate (3n):* colorless liquid. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.64 - 7.61 (m, 3H), 7.54 (d, J = 7.7 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.17 (dd, J = 8.0, 2.5Hz, 1H), 7.01 (dd, J = 8.0, 2.5Hz, 1H), 4.46 (q, J = 7.1 Hz, 2H), 4.34 (q, J = 7.2 Hz, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 1.43 (t, J = 7.1 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 192.39, 165.91, 165.02, 160.21, 159.57, 157.47, 155.31, 140.26, 138.14, 136.84, 130.03, 129.25, 126.52, 123.98, 120.38, 120.30, 119.61, 116.33, 114.35, 112.62, 62.63, 62.23, 55.46, 55.36, 14.03, 13.66. IR (KBr) *v*: 3018, 2948, 2839, 1730, 1665, 1580, 1490, 1436, 1291, 1224, 1150, 1099, 1043, 955, 878, 768, 728, 668 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{26}H_{25}NO_9$ $[M+H]^+$ :464.1704. Found: 464.1707.

*4.2.15. dimethyl 2-(3,4-dimethoxybenzoyl)-6-(3,4-dimethoxyphen-yl)pyridine-3,4-dicarboxylate (3o):* white solid. Mp: 86-88 $^0$C . $^1$H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.72 (d, J = 1.9 Hz, 1H), 7.70 – 7.66 (m, 2H), 7.59 (dd, J = 8.4, 1.9 Hz, 1H), 6.97 (d, J = 8.8 Hz, 1H), 6.90 (d, J = 8.5 Hz, 1H), 4.00 (s, 3H), 3.97 (s, 3H), 3.96 (s, 3H), 3.95 (s, 3H), 3.92 (s, 3H), 3.87 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 191.19, 165.80, 165.54, 157.26, 155.41, 153.85, 151.37, 149.48, 148.94, 139.62, 129.52, 128.59, 126.85, 125.64, 120.36, 119.26, 112.06, 111.16, 110.06, 109.80, 56.12, 56.02, 53.29, 52.96. IR (KBr) *v*: 3003, 2951, 2838, 1733, 1657, 1587, 1515, 1457, 1423, 1346, 1269, 1153, 1021, 807, 768, 721 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{26}H_{25}NO_9$ $[M+H]^+$: 496.1602. Found: 496.1606.

*4.2.16. diethyl 2-(3,4-dimethoxybenzoyl)-6-(3,4-dimethoxypheny -l)pyridine-3,4-dicarboxylate (3p):* colorless liquid. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.71 (d, J = 1.9 Hz, 1H), 7.68 – 7.65 (m, 2H), 7.54 (dd, J = 8.4, 1.9 Hz, 1H), 6.96 (d, J = 8.2 Hz, 1H), 6.88 (d, J = 8.5 Hz, 1H), 4.45 (q, J = 7.1 Hz, 2H), 4.29 (q, J = 7.2 Hz, 2H), 3.95 (s, 3H), 3.94 (s, 3H), 3.94 (s, 3H), 3.91 (s, 3H), 1.41 (t, J = 7.2 Hz, 3H), 1.24 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 191.37, 166.01, 165.41, 157.28, 155.83, 153.80, 151.30, 149.44, 148.95, 140.34, 129.64, 128.68, 126.78, 125.25, 120.37, 119.07, 111.85, 111.13, 110.12, 109.82, 62.56, 62.10, 56.10, 56.03, 56.01, 14.02, 13.67. IR (KBr) *v*: 3083, 2974, 2840, 1729, 1662, 1591, 1518, 1460, 1425, 1378, 1343, 1268, 1175, 1146, 1106, 1017, 861, 768, 721 $cm^{-1}$. HRMS (ESI) m/z calcd for $C_{28}H_{29}NO_9$ $[M+H]^+$: 524.1915. Found: 524.1916.

*4.2.17. dimethyl 2-(4-chlorobenzoyl)-6-(4-chlorophenyl)pyridine -3,4-dicarboxylate (3q):* pale yellow solid. Mp:171-173 $^{0}$C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.00 – 7.96 (m, 4H), 7.49 – 7.46 (m, 4H), 4.02 (s, 3H), 3.91 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 191.15, 166.52, 164.85, 156.49, 154.48, 140.22, 139.72, 137.05, 134.87, 133.76, 132.21, 129.37, 128.73, 128.48, 127.29, 120.48, 53.45, 53.15. IR (KBr) *v*: 3092, 2951, 1735, 1672, 1585, 1492, 1441, 1411, 1410, 1354, 1270, 1169, 1104, 1013, 951, 836, 773 $cm^{-1}$. HRMS (ESI) m/z calcd for $C_{22}H_{15}C_{l2}NO_5$ $[M+H]^+$: 444.0400. Found: 444.0409.

*4.2.18. diethyl 2-(4-chlorobenzoyl)-6-(4-chlorophenyl)pyridine-3,4-dicarboxylate (3r):* pale yellow solid. Mp: 132-134 $^{0}$C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.00 – 7.95 (m, 4H), 7.51 – 7.45 (m, 4H), 4.47 (q, J = 7.2 Hz, 2H), 4.35 (q, J = 7.2 Hz, 2H), 1.44 (t, J = 7.1 Hz, 3H), 1.28 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 191.28, 165.77, 164.72, 156.47, 154.93, 140.45, 140.18, 136.96, 134.99, 133.83, 132.11, 129.33, 128.74, 128.51, 126.95, 120.26, 62.78, 62.35, 14.04, 13.67. IR (KBr) *v*: 3088, 2984, 1729, 1671, 1583, 1405, 1370, 1262, 1177, 1103, 1013, 838, 775 $cm^{-1}$. HRMS (ESI) m/z calcd for $C_{24}H_{19}Cl_2NO_5$ $[M+H]^+$: 472.0713. Found: 472.0719.

*4.2.19. dimethyl 2-(4-nitrobenzoyl)-6-(4-nitrophenyl)pyridine-3,4-dicarboxylate (3s):* yellow solid. Mp: 70-72 $^{0}$C . $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.38 – 8.34 (m, 4H), 8.20 – 8.16 (m, 4H), 4.05 (s, 3H), 3.96 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 190.48, 166.12, 164.17, 155.30, 153.56, 150.51, 149.15, 141.77, 140.13, 140.00, 131.68, 128.96, 128.10, 124.37, 123.52, 122.24, 53.70, 53.40. IR (KBr) *v*: 1730, 1636, 1596, 1514, 1397, 1342, 1109, 844, 738, 687 $cm^{-1}$. HRMS (ESI) m/z calcd for $C_{22}H_{15}N_3O_9$ $[M+H]^+$: 466.0881. Found: 466.0877.

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**Supplementary Material**

Copies of NMR spectra for all products and single-crystal X-ray diffraction analysis of 3i.

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# Supporting information

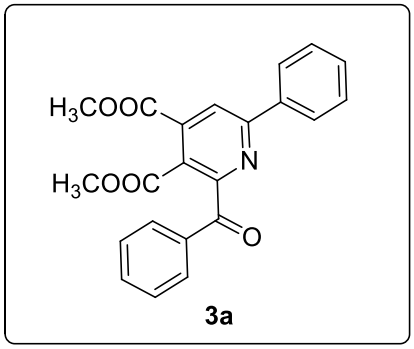
## General Information:

Purification of reaction products were carried out by chromatography using silica gel (200-300mesh). Melting points were recorded on a BÜCHI B-540 melting point apparatus. NMR spectra were in $CDCl_3$ or DMSO ($^1H$ at 500 MHz and $^{13}C$ at 125 MHz) and data are reported as follows: chemical shift, integration, multiplicity ( s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant(s) in Hz. Infrared spectra were recorded on FTIR spectrophotometer. HRMS data were obtained with using ESI ionization. Unless otherwise noted, all reagents were obtained commercially and used without further purification. The starting material α-azido ketones were prepared according to literature methods.[1]

## General Procedure for the Synthesis of 3a-3s

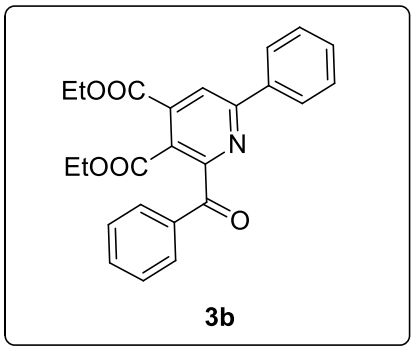
To a 10 ml flask, α-azido ketones (0.5 mmol, 1 equiv.), dimethyl but-2-ynedioate (0.6 mmol, 1.2 equiv.), $K_2CO_3$ (1 mmol, 2 equiv.) and 2 mL acetonitrile was added successively. The reaction mixture was stirred at 55 ℃ for 12 h. Acetonitrile was removed by rotary evaporation under reduced pressure. And then the residue was added 20 mL $H_2O$, extracted with 15 mL EtOAc twice. The organic layer was wished with 20 mL $H_2O$, 20 mL brine and dried with $Na_2SO_4$. And then EtOAc with removed under reduced pressure, the residue was purified by flash chromatography (Petroleum ether/EtOAc) on slica gel to afford **3a-3s**.

# Characterization Data:



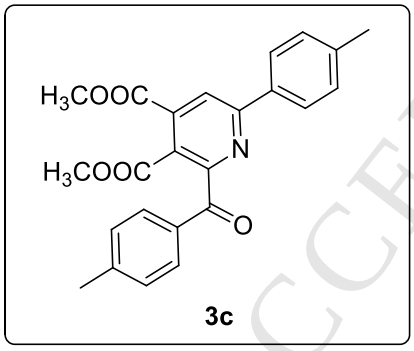

**3a**

**dimethyl 2-benzoyl-6-phenylpyridine-3,4-dicarboxylate (3a):** white solid, Mp: 123-125 $^{0}$C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.06 (dd, J = 6.7, 3.0 Hz, 2H), 8.01 (dd, J=6.7, 3.0 Hz 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.52 – 7.47 (m, 5H), 4.00 (s, 3H), 3.88 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 192.58, 166.74, 165.17, 157.73, 154.98, 139.54, 136.62, 135.50, 133.54, 130.87, 130.57, 129.06, 128.32, 127.28, 126.84, 120.45, 53.36, 53.06. IR (KBr) *v*: 2952, 1732, 1676, 1584, 1444, 1358 1261, 1100, 950, 804, 759, 691 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{22}H_{17}NO_5$ $[M+H]^+$ :376.1179. Found:376.1182.



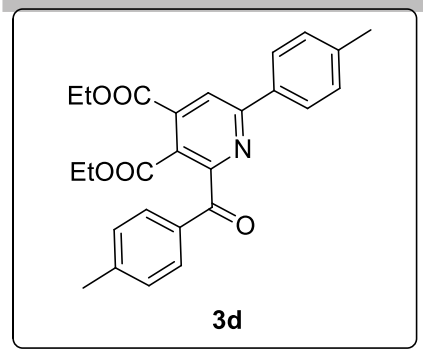

**3b**

**diethyl 2-benzoyl-6-phenylpyridine-3,4-dicarboxylate (3b):** white solid. Mp: 87-89 $^{0}$C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.07 (dd, J = 6.5, 3.3 Hz, 2H), 8.03 (dd, J = 8.3, 1.1 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.53 – 7.47 (m, 5H), 4.47 (q, J = 7.2 Hz, 2H), 4.34 (q, J = 7.2 Hz, 2H), 1.44 (t, J = 7.2 Hz, 3H), 1.26 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 192.70, 165.95, 165.05, 157.74, 155.49, 140.30, 136.75, 135.57, 133.52, 130.76, 130.49, 129.02, 128.33, 127.30, 126.44, 120.22, 62.64, 62.23, 14.04, 13.63. IR (KBr) *v*: 3065, 2985, 1729, 1673, 1577, 1454, 1371, 1259, 1171, 1110, 1018, 904, 860, 754, 691 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{24}H_{21}NO_5$ $[M+H]^+$ :404.1492. Found: 404.1496.



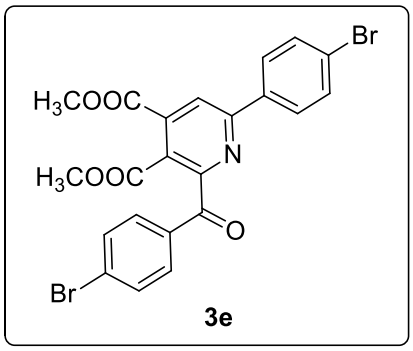

**3c**

**dimethyl 2-(4-methylbenzoyl)-6-(p-tolyl)pyridine-3,4-dicarboxylate (3c):** white solid. Mp: 169-171 $^{0}$C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.98 (d, J = 8.2 Hz, 2H), 7.94 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 4.1 Hz, 2H), 7.29 (d, J = 4.2 Hz, 2H), 4.00 (s, 3H), 3.87 (s, 3H), 2.46 (s, 3H), 2.42 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 192.29, 166.82, 165.37, 157.71, 155.28, 144.52, 140.92, 139.49, 133.95, 132.99, 131.03, 129.76, 129.05, 127.19, 126.26, 119.86, 53.29, 52.98, 21.82, 21.38. IR (KBr) *v*: 2953, 1734, 1665, 1584, 1442, 1353, 1276, 1109, 1058, 950, 827, 770, 727 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{24}H_{21}NO_5$ $[M+H]^+$ :404.1492. Found: 404.1489.



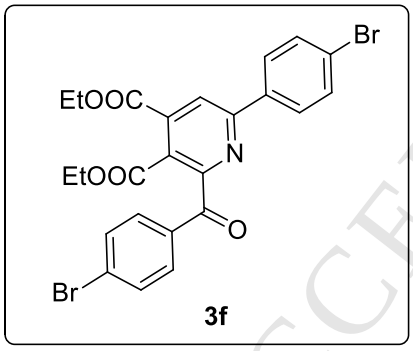

**3d**

**diethyl 2-(4-methylbenzoyl)-6-(p-tolyl)pyridine-3,4-dicarboxylate (3d):** white solid. Mp: 146-148 $^{0}$C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.98 (d, J = 8.2 Hz, 2H), 7.93 (d, J = 8.2 Hz, 2H), 7.30 - 7.27 (m, 4H), 4.46 (q, J = 7.2 Hz, 2H), 4.31 (q, J = 7.2 Hz, 2H), 2.46 (s, 3H), 2.42 (s, 3H), 1.43 (t, J = 7.2 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 192.41, 166.04, 165.24, 157.70, 155.74, 144.46, 140.82, 140.22, 134.07, 133.07, 130.93, 129.72, 129.05, 127.22, 125.89, 119.64, 62.56, 62.13, 21.82, 21.38, 14.04, 13.64. IR (KBr) *v*: 2983, 1729, 1666, 1579, 1370, 1260, 1177, 1108, 1020, 905, 826, 769, 724 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{26}H_{25}NO_5$ $[M+H]^+$ : 432.1805. Found: 432.1812.



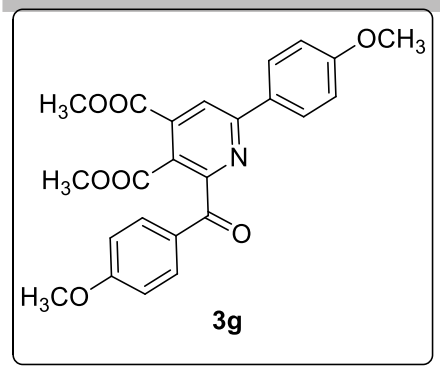

**3e**

**dimethyl 2-(4-bromobenzoyl)-6-(4-bromophenyl)pyridine-3,4-dicarboxylate (3e):** pale yellow solid. Mp: 185 - 187 $^{0}$C $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.93 (d, J = 8.6 Hz, 2H), 7.89 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 8.6 Hz, 2H), 7.64 (d, J = 8.6 Hz, 2H), 4.02 (s, 3H), 3.91 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 191.33, 166.51, 164.83, 156.58, 154.44, 139.75, 132.35, 131.71, 128.70, 125.49, 120.47, 53.45, 53.15. IR (KBr) *v*: 2950, 1735, 1672, 1582, 1488, 1441, 1405, 1353, 1273, 1110, 1067, 1009, 949, 906, 883, 773, 736, 687, 637 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{22}H_{15}Br_2NO_5$ $[M+H]^+$ : 531.9390. Found: 531.9396.



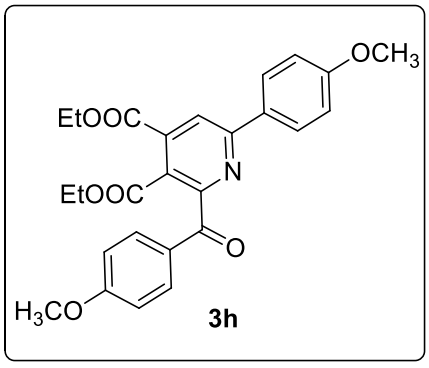

**3f**

**diethyl 2-(4-bromobenzoyl)-6-(4-bromophenyl)pyridine-3,4-dicarboxylate(3f):** pale yellow solid. Mp: 150-152 $^{0}$C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.93 (d, J = 8.6 Hz, 2H), 7.88 (d, J = 8.6 Hz, 2H), 7.62 - 7.66 (m, 4H) 4.47 (q, J = 7.1 Hz, 2H), 4.35 (q, J = 7.2 Hz, 2H), 1.43 (t, J = 7.2 Hz, 3H), 1.28 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 191.45, 165.76, 164.69, 156.54, 154.88, 140.46, 135.44, 134.24, 132.30, 132.18, 131.72, 129.01, 128.73, 127.01, 125.40, 120.26, 62.78, 62.36, 14.03, 13.67. IR (KBr) *v*: 2983, 1728, 1672, 1581, 1402, 1262, 1177, 1107, 1009, 905, 836, 774 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{24}H_{19}Br_2NO_5$ $[M+H]^+$ : 559.9703. Found:559.9705.



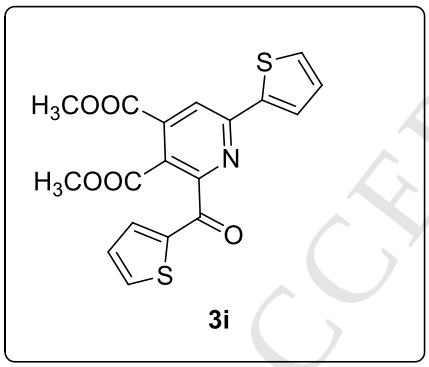

**3g**

**dimethyl 2-(4-methoxybenzoyl)-6-(4-methoxyphenyl)pyridine-3,4-dicarboxylate (3g):** white solid. Mp: 125-127 $^{0}$C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.05 - 8.02 (m, 4H), 7.00 - 6.97 (m, 4H), 4.00 (s, 3H), 3.91 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 191.25, 166.91, 165.48, 163.95, 161.68, 157.30, 155.52, 139.48, 133.31, 129.31, 128.80, 128.49, 125.68, 119.20, 114.39, 113.64, 55.53, 55.43, 53.27, 52.96. IR (KBr) *v*: 3103, 2954, 2839, 1734, 1655, 1595, 1512, 1433, 1357, 1259, 1173, 1110, 946, 835, 773, 719 $cm^{-1}$. HRMS (ESI) m/z calcd for $C_{24}H_{21}NO_7$ $[M+H]^+$ :436.1391. Found: 436.1391.



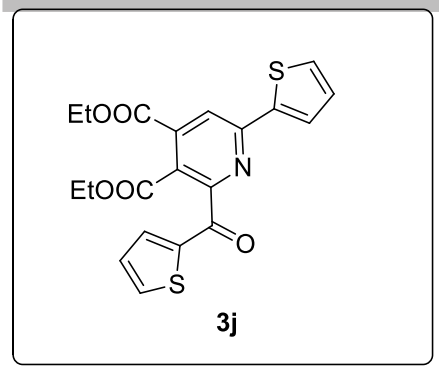

**3h**

**diethyl 2-(4-methoxybenzoyl)-6-(4-methoxyphenyl)pyridine-3,4-dicarboxylate(3h):** colorless liquid. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.05 - 8.00 (m, 4H), 6.99 - 6.96 (m, 4H), 4.45 (q, J = 7.1 Hz, 2H), 4.30 (q, J = 7.2 Hz, 2H), 3.90 (s, 3H), 3.86 (s, 3H), 1.42 (t, J = 7.2 Hz, 3H), 1.24 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 191.40, 166.09, 165.34, 163.92, 161.64, 157.32, 155.99, 140.25, 133.16, 129.43, 128.81, 128.61, 125.27, 118.96, 114.36, 113.64, 62.50, 62.06, 55.50, 55.40, 14.03, 13.63. IR (KBr) *v*: 2892, 2838, 1728, 1661, 1596, 1512, 1461, 1425, 1372, 1258, 1173, 1107, 1027, 905, 840, 775 $cm^{-1}$. HRMS (ESI) m/z calcd for $C_{26}H_{25}NO_7$ $[M+H]^+$ :464.1704. Found:464.1709.



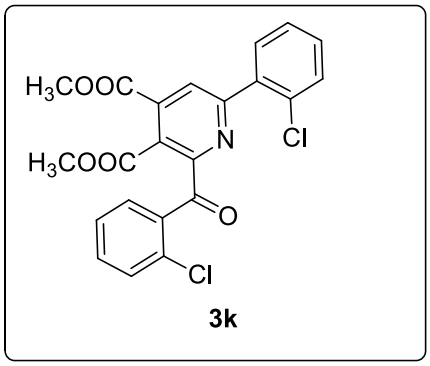

**3i**

**dimethyl 6-(thiophen-2-yl)-2-(thiophene-2-carbonyl)pyridine-3,4-dicarboxylate (3i):** yellow solid. Mp: 143-145 $^{0}$C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.30 - 8.29 (m, 2H), 7.84 – 7.82 (m, 2H), 7.56 (dd, J = 5.0, 1.0 Hz, 1H), 7.23 - 7.20 (m, 2H), 4.02 (s, 3H), 4.01 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 181.89, 167.30, 164.23, 152.85, 151.90, 142.20, 139.27, 138.39, 137.11, 136.96, 130.03, 128.58, 127.78, 127.74, 127.34, 120.55, 53.39, 53.10. IR (KBr) *v*: 3091, 2945, 1737, 1636, 1582, 1435, 1273, 1150, 1094, 745, 691 $cm^{-1}$. HRMS (ESI) m/z calcd for $C_{18}H_{13}NO_5S_2$ $[M+H]^+$ :388.0308. Found: 388.0310.



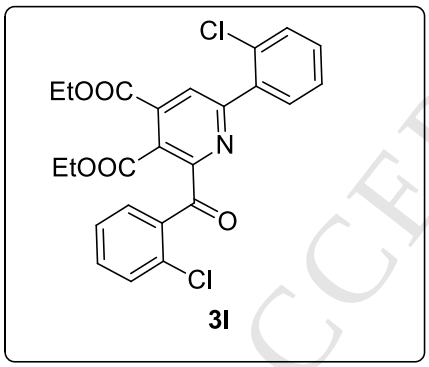

**3j**

**diethyl 6-(thiophen-2-yl)-2-(thiophene-2-carbonyl)pyridine-3,4-dicarboxylate (3j):** yellow solid. Mp:117-119 $^{0}$C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.25 (dd, J = 3.9, 1.2 Hz, 1H), 7.84 – 7.80 (m, 2H), 7.55 (dd, J = 5.0, 0.9 Hz, 1H), 7.27 – 7.19 (m, 2H), 4.49 – 4.44 (m, 4H), 1.43 (t, J = 7.1 Hz, 3H), 1.39 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 182.17, 166.58, 164.05, 152.69, 152.31, 142.31, 139.64, 139.07, 136.92, 136.71, 129.93, 128.54, 127.80, 127.63, 127.23, 120.34, 62.70, 62.16, 14.05, 13.82. IR (KBr) *v*: 3111, 2982, 1724, 1638, 1581, 1405, 1357, 1277, 1238, 1152, 1095, 1018, 851, 718 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{20}H_{17}NO_5S_2$ $[M+H]^+$ : 416.0621. Found: 416.0621.



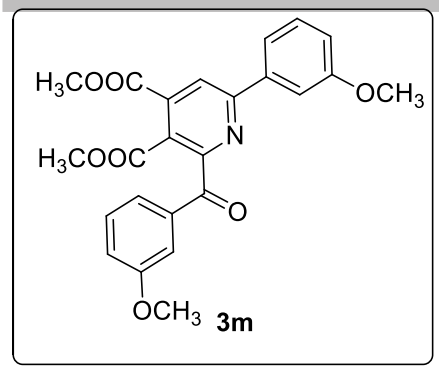

**3k**

**dimethyl 2-(2-chlorobenzoyl)-6-(2-chlorophenyl)pyridine-3,4-dicarboxylate (3k):** colorless liquid. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.63 (dd, J = 7.6, 1.3 Hz, 1H), 7.51(dd, J = 7.5, 2.0Hz, 1H), 7.48 – 7.41 (m, 3H), 7.39 – 7.30 (m, 3H), 4.03 (s, 3H), 4.00 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 193.44, 167.04, 164.27, 157.39, 152.63, 137.42, 136.92, 136.72, 132.87, 132.45, 132.27, 131.69, 131.17, 130.66, 130.31, 130.02, 127.86, 127.22, 126.78, 126.69, 53.40, 53.28. IR (KBr) *v*: 3088, 2952, 1744, 1680, 1587, 1435, 1358, 1277, 1219, 1153, 1123, 1072, 951, 745, 705, 638 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{22}H_{15}Cl_2NO_5$ $[M+H]^+$ : 444.0400. Found: 444.0406.

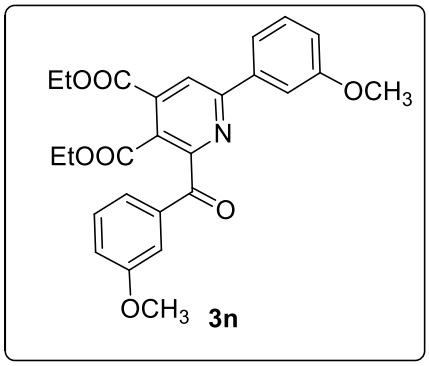



**3l**

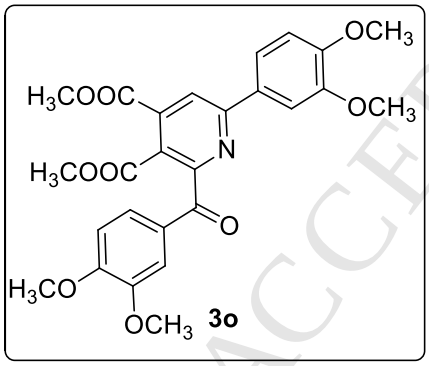
**diethyl 2-(2-chlorobenzoyl)-6-(2-chlorophenyl)pyridine-3,4-dicarboxylate (3l):** colorless liquid. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.63 (dd, J =7.3, 2.1 Hz, 1H), 7.50 (dd, J = 7.3, 2.1 Hz, 1H), 7.46 – 7.40 (m, 3H), 7.27-7.36 (m, 3H), 4.43 – 4.52 (m 4H), 1.40 - 1.43 (m, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 193.43, 166.41, 163.97, 157.24, 152.91, 137.96, 136.99, 136.82, 132.86, 132.40, 132.27, 131.65, 131.17, 130.60, 130.29, 130.03, 127.94, 127.19, 126.66, 62.68, 62.37, 14.03, 13.82. IR (KBr) *v*: 2985, 1737, 1687, 1588, 1438, 1374, 1280, 1167, 1120, 755 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{24}H_{19}Cl_2NO_5$ $[M+H]^+$ : 472.0713. Found : 472.0717.



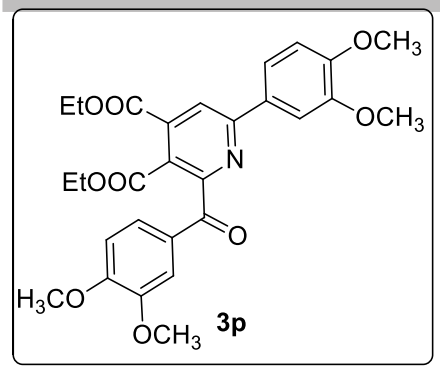

**dimethyl 2-(3-methoxybenzoyl)-6-(3-methoxyphenyl)pyridine-3,4-dicarboxylate (3m):** white solid. Mp: 92-94 $^{0}$C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.64 – 7.62 (m, 3H), 7.56 (d, J = 7.7 Hz, 1H), 7.40 - 7.37 (m, 2H), 7.18 (dd, J=8, 2.5Hz, 1H), 7.02 (dd, J = 8, 2.5 Hz, 1H), 4.00 (s, 3H), 3.89 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 192.26, 166.67, 165.15, 160.23, 159.56, 157.47, 154.82, 139.53, 137.99, 136.77, 130.06, 129.22, 126.89, 124.03, 120.59, 120.31, 119.56, 116.46, 114.50, 112.53, 55.45, 55.35, 53.34, 53.04. IR (KBr) *v*: 2979, 1732, 1671, 1587, 1458, 1268, 1221, 1099, 1040, 862, 770, 726, 684 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{24}H_{21}NO_7$ $[M+H]^+$ :436.1391. Found: 436.1389.



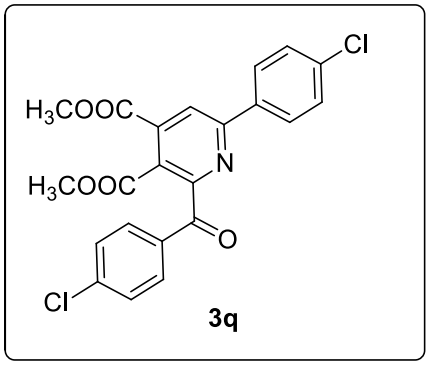

**diethyl 2-(3-methoxybenzoyl)-6-(3-methoxyphenyl)pyridine-3,4-dicarboxylate (3n):** colorless liquid. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.64 - 7.61 (m, 3H), 7.54 (d, J = 7.7 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.17 (dd, J = 8.0, 2.5Hz, 1H), 7.01 (dd, J = 8.0, 2.5Hz, 1H), 4.46 (q, J = 7.1 Hz, 2H), 4.34 (q, J = 7.2 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 192.39, 165.91, 165.02, 160.21, 159.57, 157.47, 155.31, 140.26, 138.14, 136.84, 130.03, 129.25, 126.52, 123.98, 120.38, 120.30, 119.61, 116.33, 114.35, 112.62, 62.63, 62.23, 55.46, 55.36, 14.03, 13.66. IR (KBr) *v*: 3018, 2948, 2839, 1730, 1665, 1580, 1490, 1436, 1291, 1224, 1150, 1099, 1043, 955, 878, 768, 728, 668 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{26}H_{25}NO_9$ $[M+H]^+$ :464.1704. Found: 464.1707.



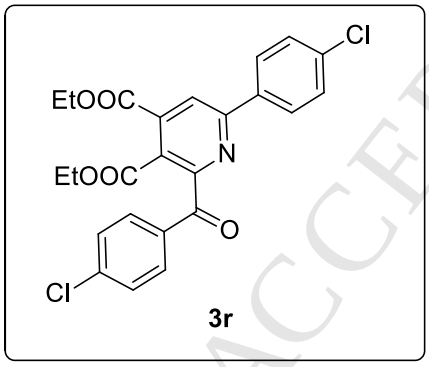

**dimethyl 2-(3,4-dimethoxybenzoyl)-6-(3,4-dimethoxyphenyl)pyridine-3,4-dicarboxylate (3o):** white solid. Mp: 86-88 $^{0}$C . $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.72 (d, J = 1.9 Hz, 1H), 7.70 – 7.66 (m, 2H), 7.59 (dd, J = 8.4, 1.9 Hz, 1H), 6.97 (d, J = 8.8 Hz, 1H), 6.90 (d, J = 8.5 Hz, 1H), 4.00 (s, 3H), 3.97 (s, 3H), 3.96 (s, 3H), 3.95 (s, 3H), 3.92 (s, 3H), 3.87 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 191.19, 165.80, 165.54, 157.26, 155.41, 153.85, 151.37, 149.48, 148.94, 139.62, 129.52, 128.59, 126.85, 125.64, 120.36, 119.26, 112.06, 111.16, 110.06, 109.80, 56.12, 56.02, 53.29, 52.96. IR (KBr) *v*: 3003, 2951, 2838, 1733, 1657, 1587, 1515, 1457, 1423, 1346, 1269, 1153, 1021, 807, 768, 721 cm$^{-1}$. HRMS (ESI) m/z calcd for $C_{26}H_{25}NO_9$ $[M+H]^+$ : 496.1602. Found: 496.1606.



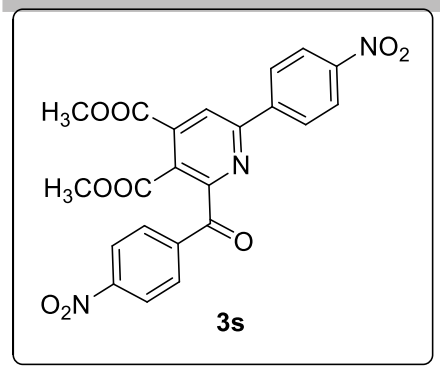

**diethyl 2-(3,4-dimethoxybenzoyl)-6-(3,4-dimethoxyphenyl)pyridine-3,4-dicarboxylate (3p):** colorless liquid. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.71 (d, J = 1.9 Hz, 1H), 7.68 – 7.65 (m, 2H), 7.54 (dd, J = 8.4, 1.9 Hz, 1H), 6.96 (d, J = 8.2 Hz, 1H), 6.88 (d, J = 8.5 Hz, 1H), 4.45 (q, J = 7.1 Hz, 2H), 4.29 (q, J = 7.2 Hz, 2H), 3.95 (s, 3H), 3.94 (s, 3H), 3.94 (s, 3H), 3.91 (s, 3H), 1.41 (t, J = 7.2 Hz, 3H), 1.24 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 191.37, 166.01, 165.41, 157.28, 155.83, 153.80, 151.30, 149.44, 148.95, 140.34, 129.64, 128.68, 126.78, 125.25, 120.37, 119.07, 111.85, 111.13, 110.12, 109.82, 62.56, 62.10, 56.10, 56.03, 56.01, 14.02, 13.67. IR (KBr) *v*: 3083, 2974, 2840, 1729, 1662, 1591, 1518, 1460, 1425, 1378, 1343, 1268, 1175, 1146, 1106, 1017, 861, 768, 721 $cm^{-1}$. HRMS (ESI) m/z calcd for $C_{28}H_{29}NO_9$ $[M+H]^+$ : 524.1915. Found: 524.1916.




**dimethyl 2-(4-chlorobenzoyl)-6-(4-chlorophenyl)pyridine-3,4-dicarboxylate (3q):** pale yellow solid. Mp:171-173 $^{0}$C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.00 – 7.96 (m, 4H), 7.49 – 7.46 (m, 4H), 4.02 (s, 3H), 3.91 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 191.15, 166.52, 164.85, 156.49, 154.48, 140.22, 139.72, 137.05, 134.87, 133.76, 132.21, 129.37, 128.73, 128.48, 127.29, 120.48, 53.45, 53.15. IR (KBr) *v*: 3092, 2951, 1735, 1672, 1585, 1492, 1441, 1411, 1410, 1354, 1270, 1169, 1104, 1013, 951, 836, 773 $cm^{-1}$. HRMS (ESI) m/z calcd for $C_{22}H_{15}C_{l2}NO_5$ $[M+H]^+$ : 444.0400. Found: 444.0409.



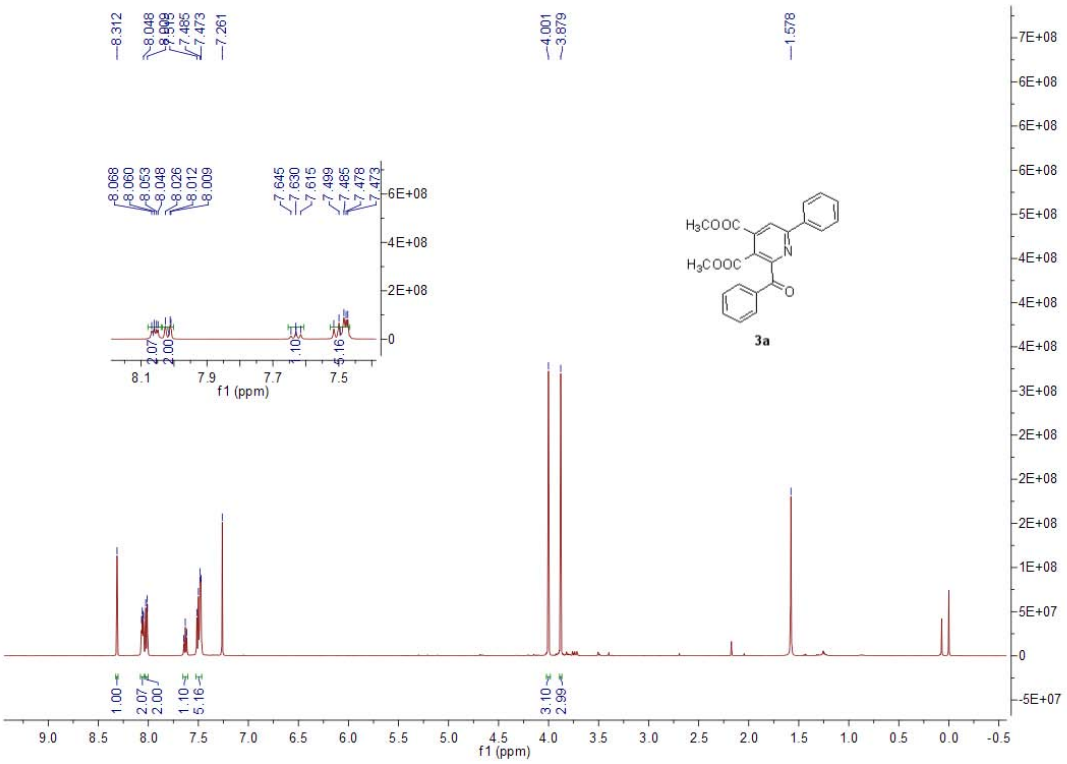

**diethyl 2-(4-chlorobenzoyl)-6-(4-chlorophenyl)pyridine-3,4-dicarboxylate (3r):** pale yellow solid. Mp: 132-134 $^{0}$C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.00 – 7.95 (m, 4H), 7.51 – 7.45 (m, 4H), 4.47 (q, J = 7.2 Hz, 2H), 4.35 (q, J = 7.2 Hz, 2H), 1.44 (t, J = 7.1 Hz, 3H), 1.28 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 191.28, 165.77, 164.72, 156.47, 154.93, 140.45, 140.18, 136.96, 134.99, 133.83, 132.11, 129.33, 128.74, 128.51, 126.95, 120.26, 62.78, 62.35, 14.04, 13.67. IR (KBr) *v*: 3088, 2984, 1729, 1671, 1583, 1405, 1370, 1262, 1177, 1103, 1013, 838, 775 $cm^{-1}$. HRMS (ESI) m/z calcd for $C_{24}H_{19}Cl_2NO_5$ $[M+H]^+$ :472.0713. Found: 472.0719.

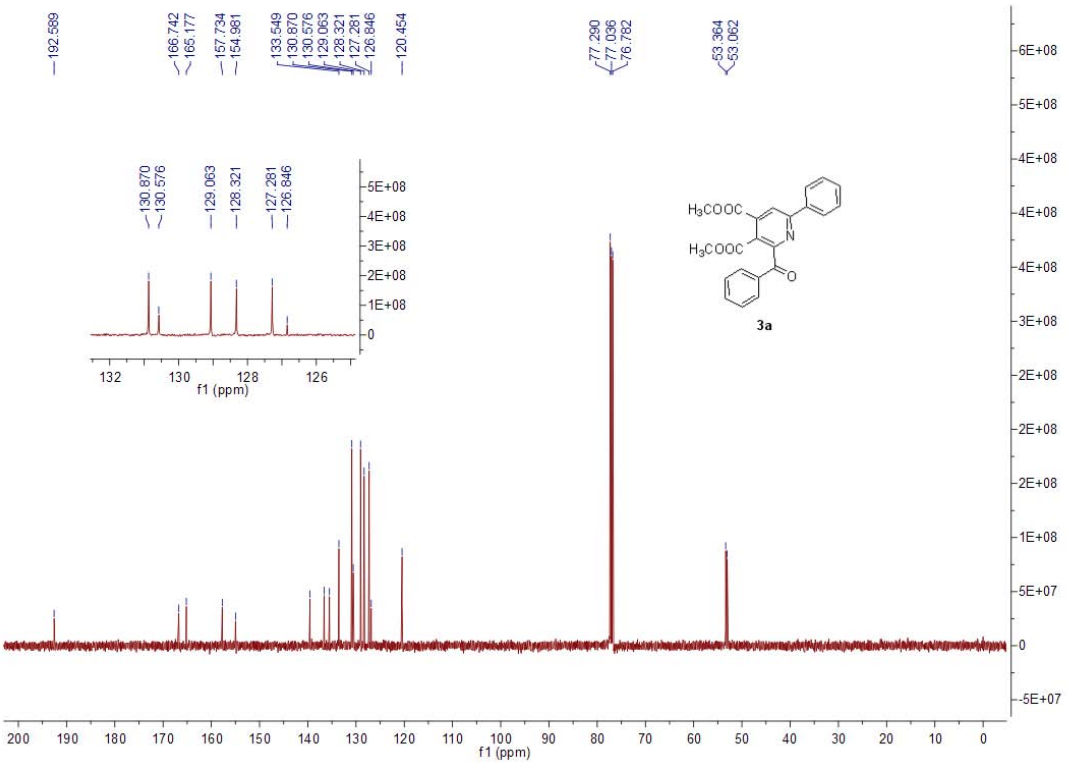


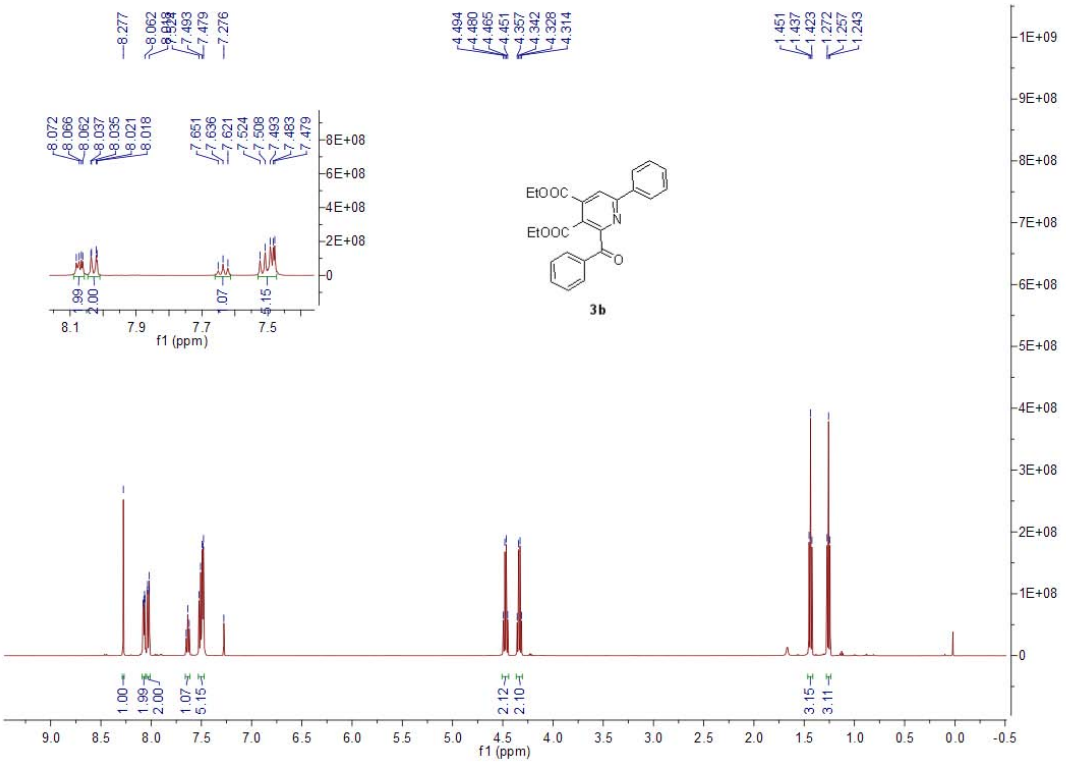

**3s**

**dimethyl 2-(4-nitrobenzoyl)-6-(4-nitrophenyl)pyridine-3,4-dicarboxylate (3s):** yellow solid. Mp: 70-72 $^{0}$C . $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.38 – 8.34 (m, 4H), 8.20 – 8.16 (m, 4H), 4.05 (s, 3H), 3.96 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 190.48, 166.12, 164.17, 155.30, 153.56, 150.51, 149.15, 141.77, 140.13, 140.00, 131.68, 128.96, 128.10, 124.37, 123.52, 122.24, 53.70, 53.40. IR (KBr) *v*: 1730, 1636, 1596, 1514, 1397, 1342, 1109, 844, 738, 687 $cm^{-1}$. HRMS (ESI) m/z calcd for $C_{22}H_{15}N_3O_9$ $[M+H]^+$ : 466.0881. Found: 466.0877.

**$^{1}$H NMR and $^{13}$C NMR spectra：**

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8.018
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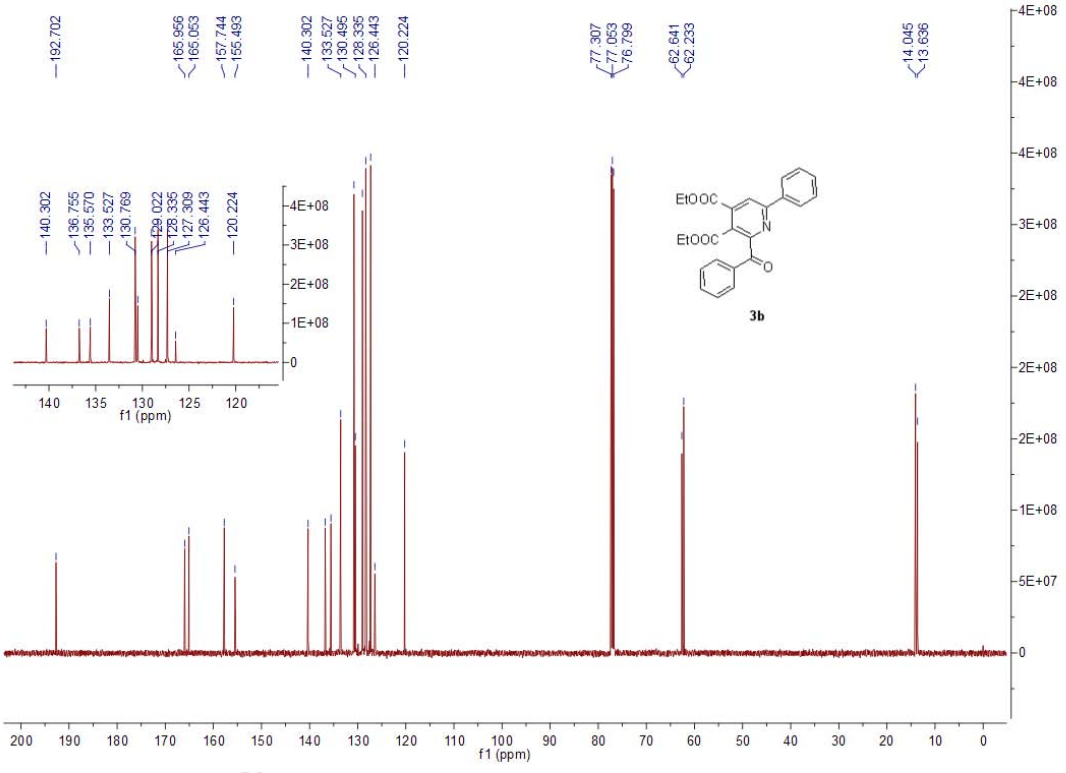
7.636
7.621
7.524
7.508
7.493
7.483
7.479
7.276
4.494
4.480
4.465
4.451
4.357
4.342
4.328
4.314
1.451
1.437
1.423
1.272
1.257
1.243
EtOOC
EtOOC
N
O
3b
f1 (ppm)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133.527
130.495
128.335
126.443
120.224
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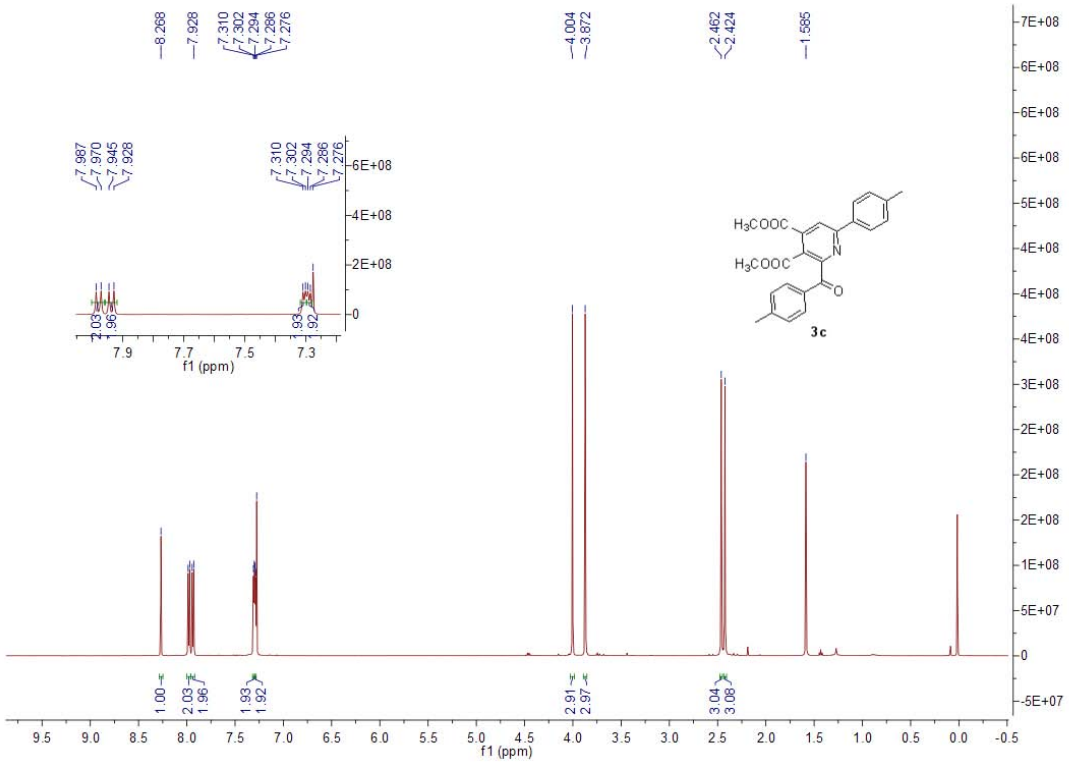
76.799
62.641
62.233
14.045
13.636
EtOOC
EtOOC
N
O
3b
f1 (ppm)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4.004
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2.462
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7.987
7.970
7.945
7.928
2.03
1.96
3.93
1.92
f1 (ppm)
H3COOC
H3COOC
O
N
3c
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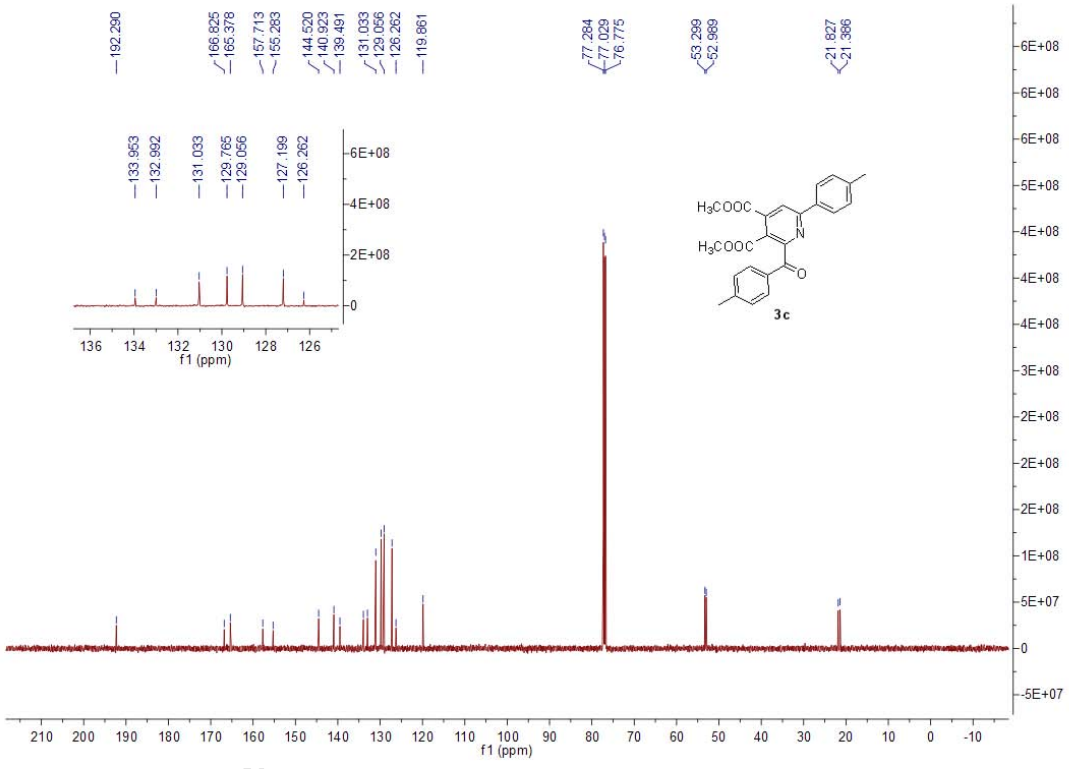
1.96
1.93
1.92
2.91
2.97
3.04
3.08
f1 (ppm)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129.056
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77.284
77.029
76.775
53.299
52.969
21.827
21.386
133.953
132.992
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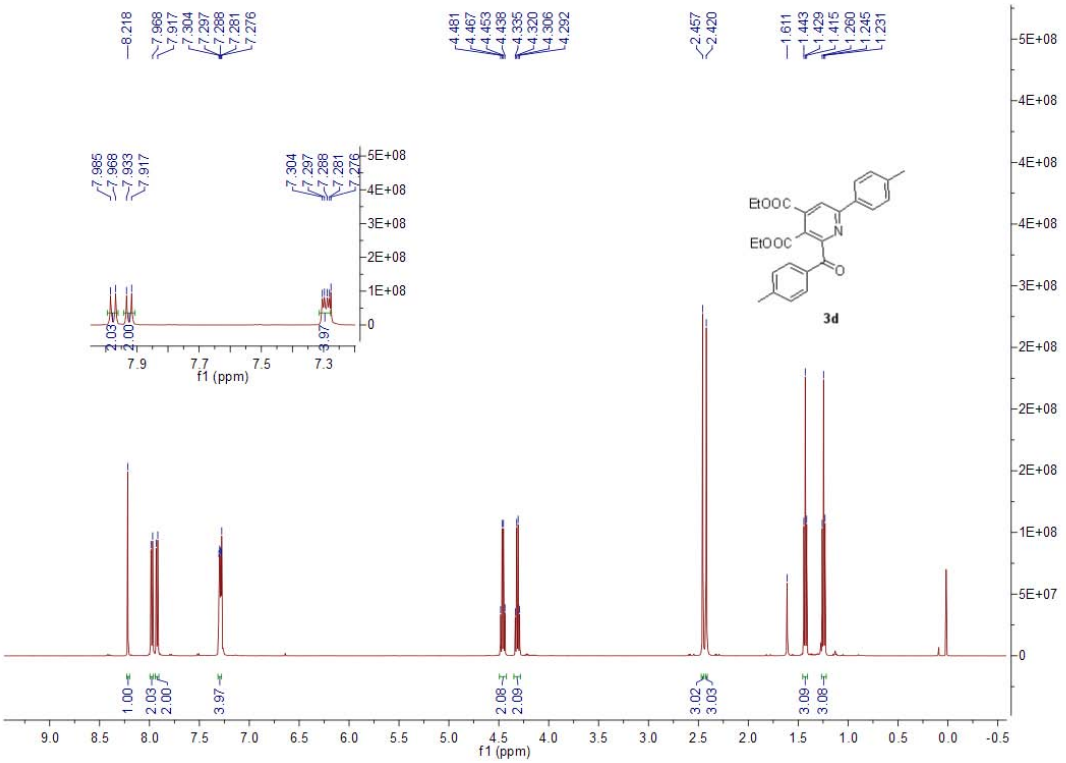
H3COOC
H3COOC
O
N
3c
f1 (ppm)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4.467
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4.438
4.335
4.320
4.306
4.292
2.457
2.420
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1.443
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1.415
1.260
1.245
1.231
EtOOC
EtOOC
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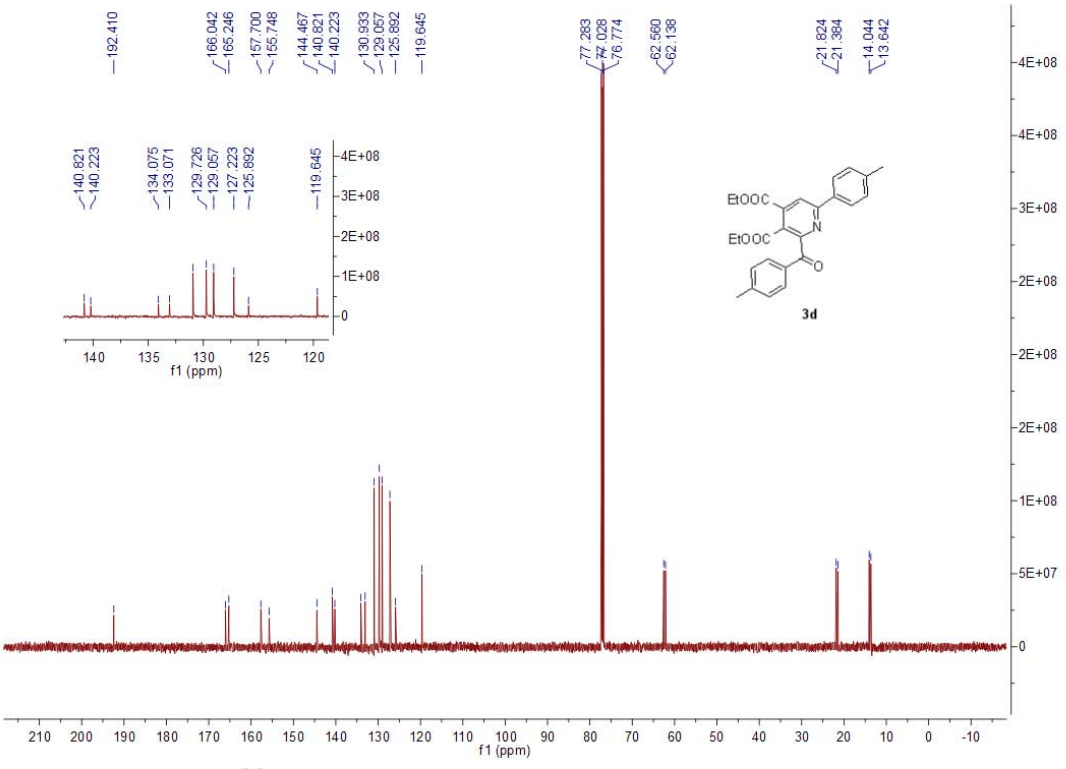
O
3d
f1 (ppm)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129.057
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119.645
77.283
77.028
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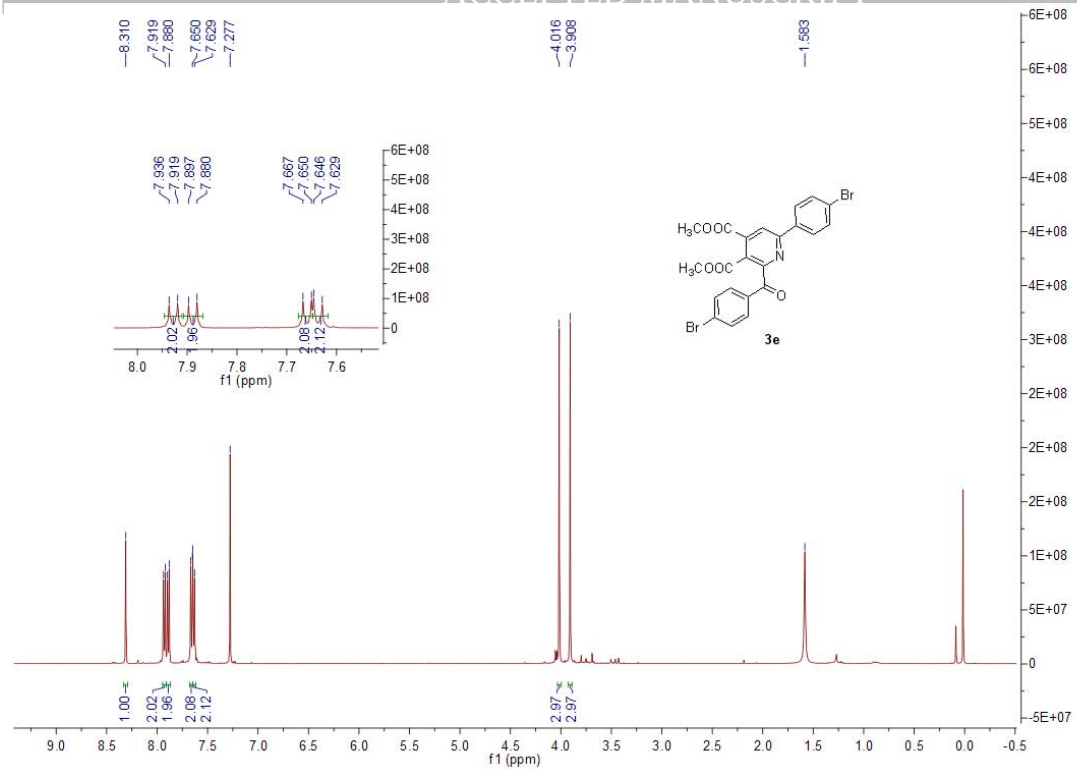
21.824
21.384
14.044
13.642
EtOOC
EtOOC
N
O
3d
f1 (ppm)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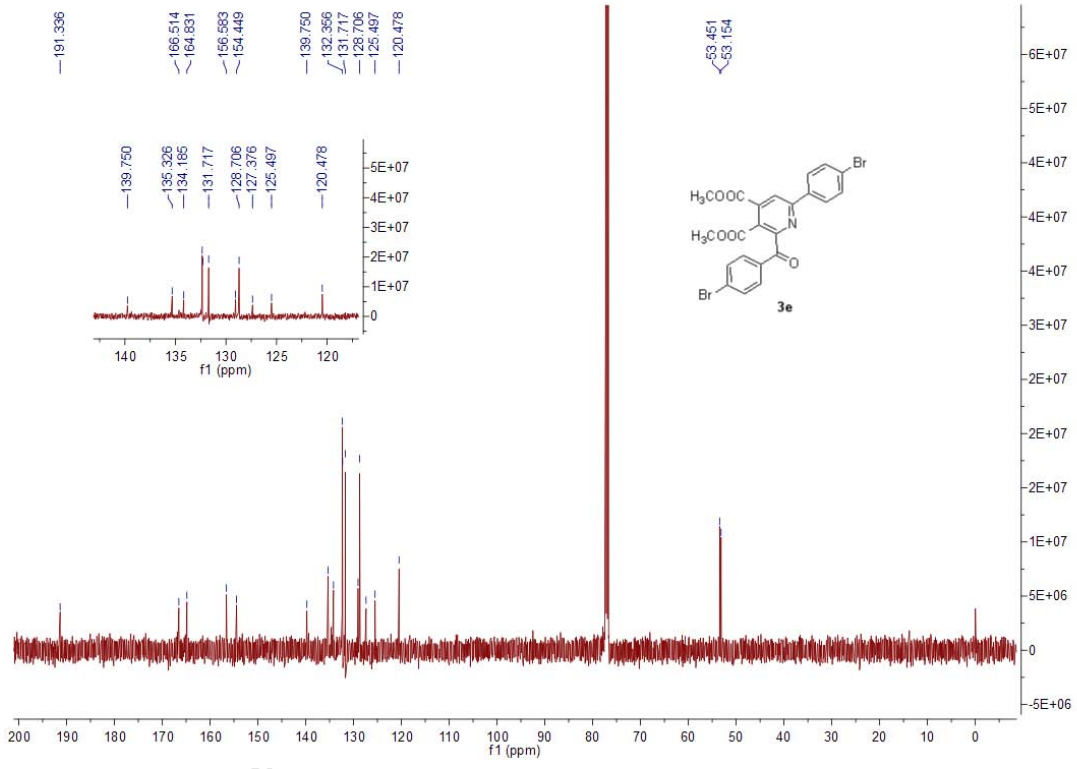
7.880
7.650
7.629
7.277
4.016
3.908
1.583
7.936
7.919
7.897
7.880
7.667
7.650
7.646
7.629
2.02
1.96
2.08
2.12
f1 (ppm)
1.00
2.02
1.96
2.08
2.12
2.97
2.97
f1 (ppm)
H3COOC
H3COOC
Br
Br
N
O
3e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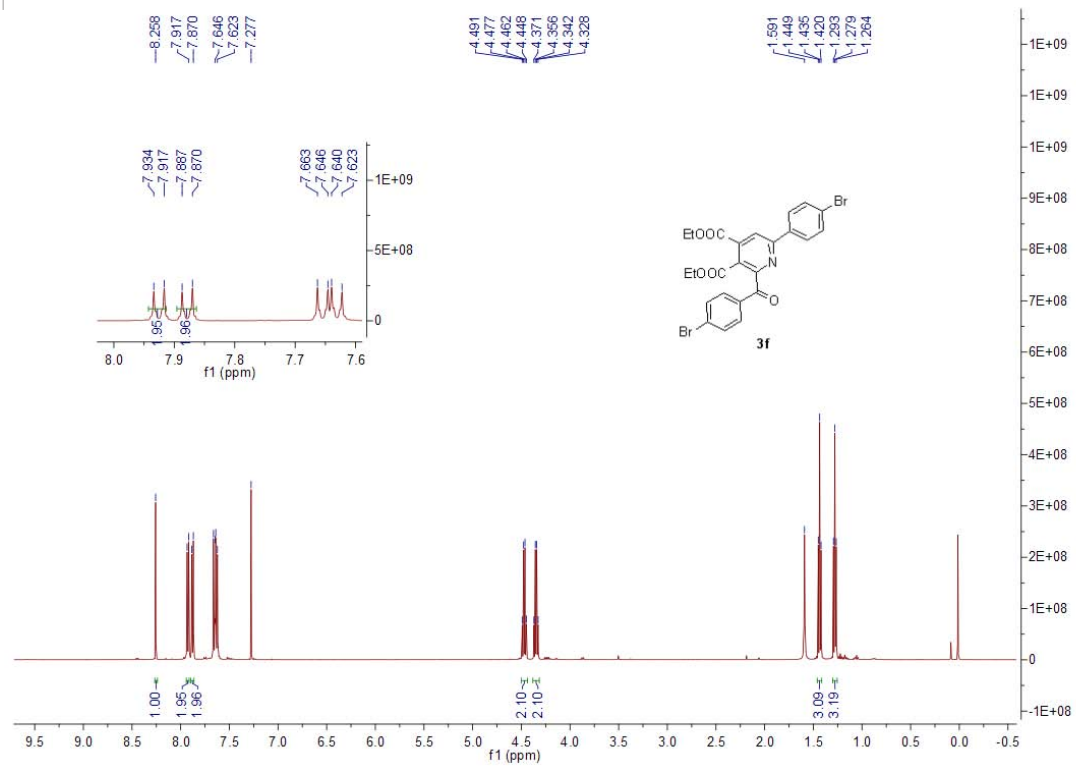
156.583
154.449
139.750
132.356
131.717
128.706
125.497
120.478
53.451
53.154
139.750
135.326
134.185
131.717
128.706
127.376
125.497
120.478
f1 (ppm)
H3COOC
H3COOC
Br
Br
N
O
3e
f1 (ppm)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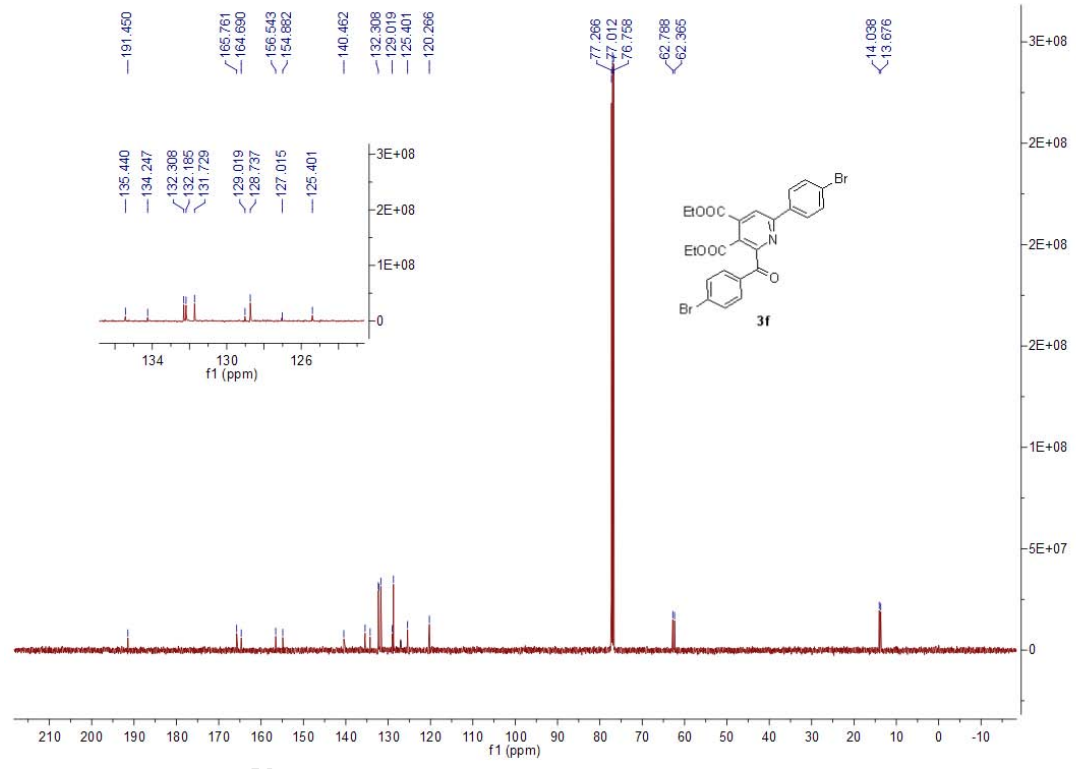
4.356
4.342
4.328
1.591
1.449
1.435
1.420
1.293
1.279
1.264
7.934
7.917
7.887
7.870
7.663
7.646
7.640
7.623
1.00
1.95
1.96
2.10
2.10
3.09
3.19
f1 (ppm)
EtOOC
EtOOC
Br
Br
3f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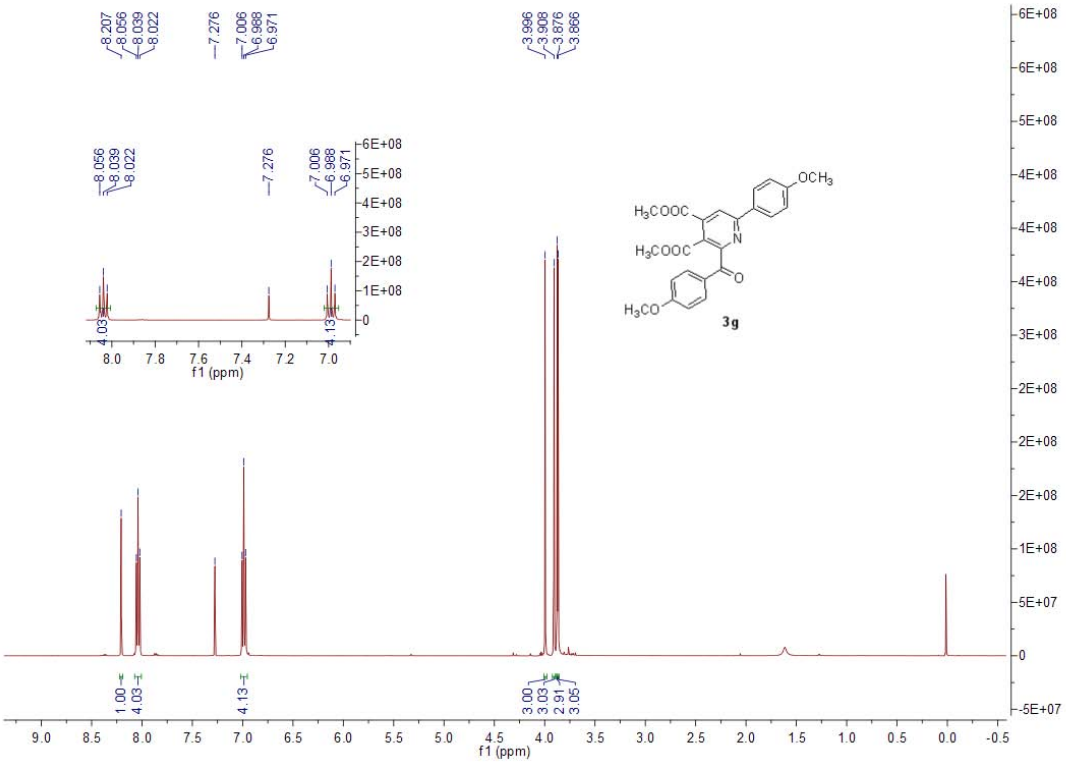
140.462
132.308
129.019
125.401
120.266
77.266
77.012
76.758
62.788
62.365
14.038
13.676
135.440
134.247
132.308
132.185
131.729
129.019
128.737
127.015
125.401
f1 (ppm)
EtOOC
EtOOC
Br
Br
3f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8.022
7.276
7.006
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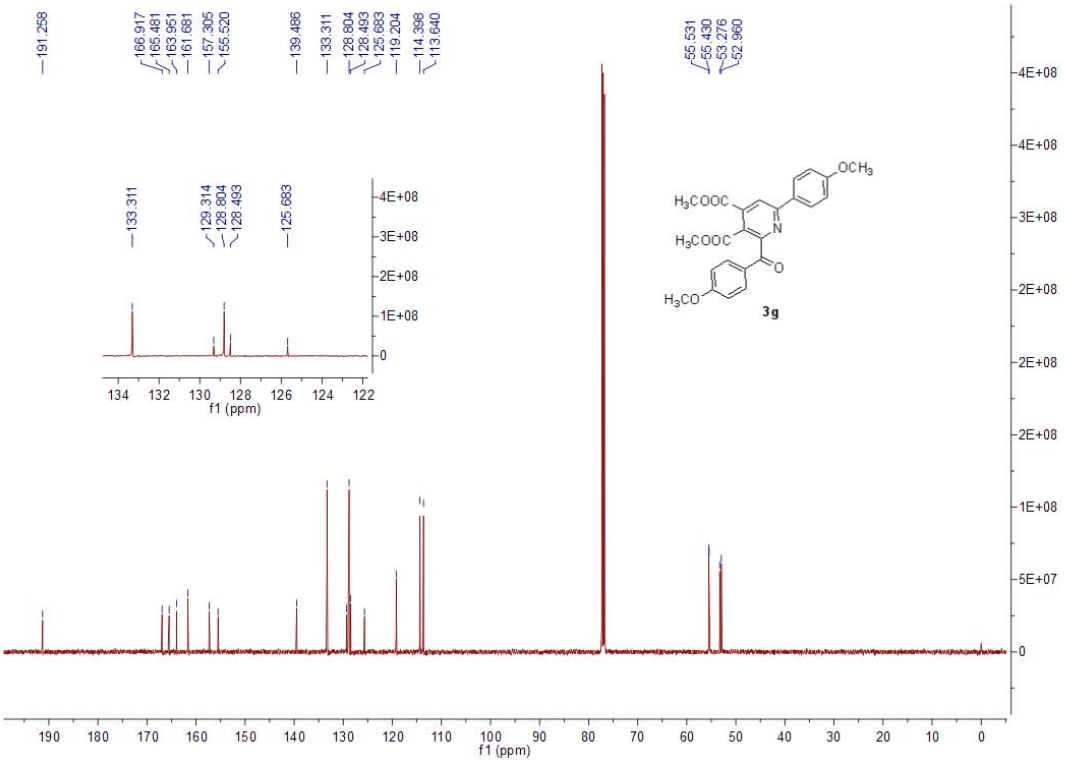
6.971
3.996
3.908
3.876
3.866
1.00
4.03
4.13
3.00
3.03
2.91
3.05
f1 (ppm)
3g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157.305
155.520
139.486
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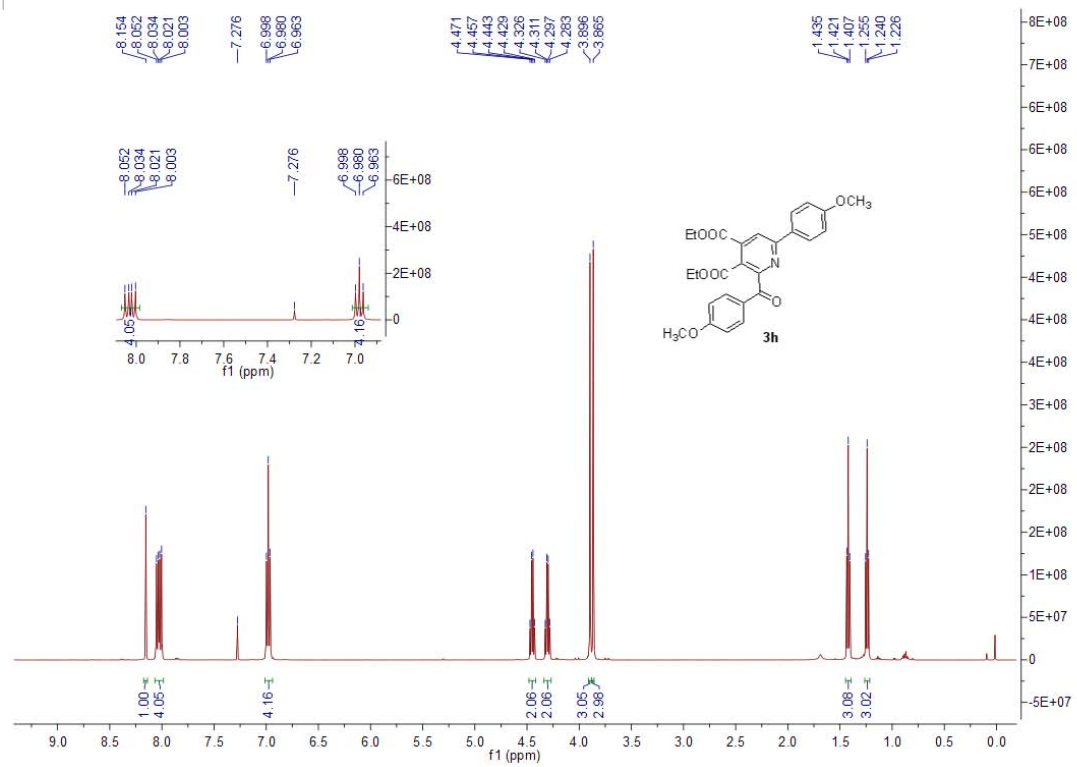
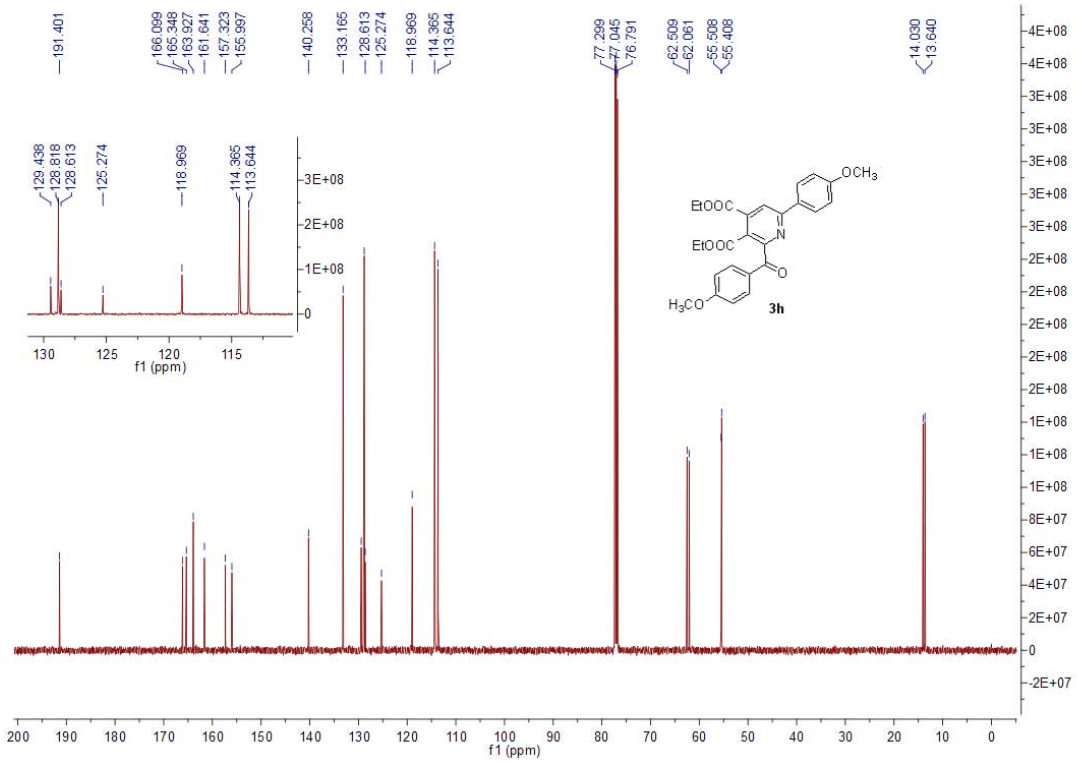
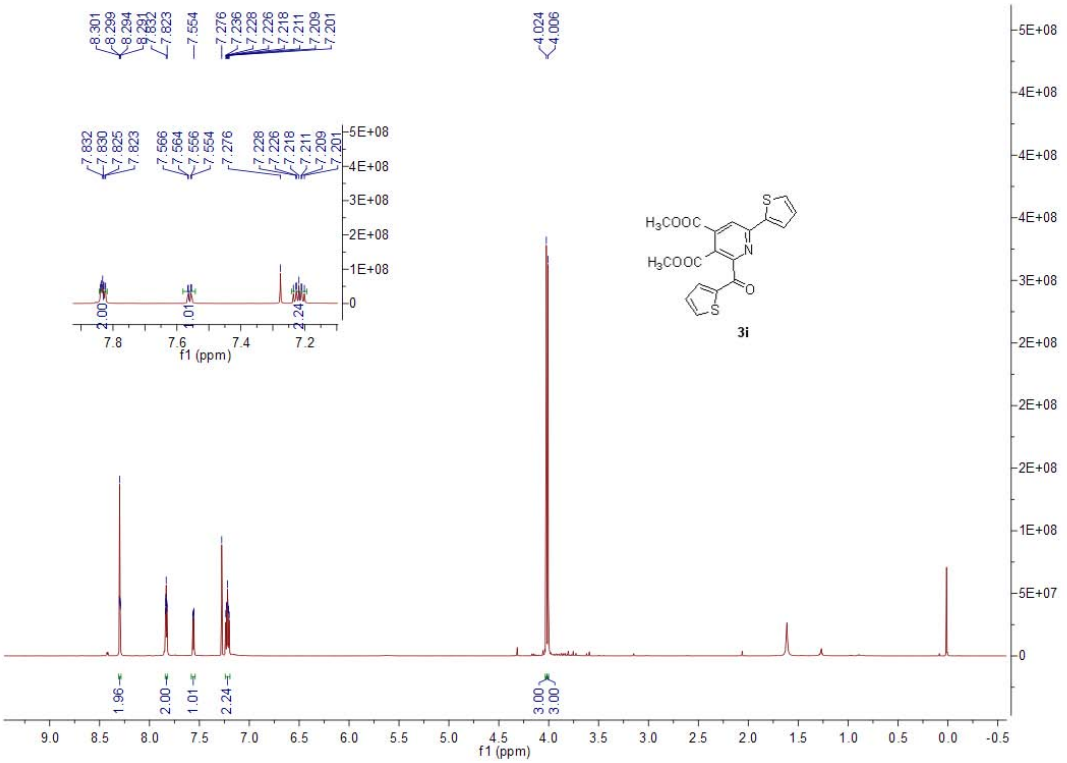
119.204
114.398
113.640
55.531
55.430
53.276
52.960
f1 (ppm)
3g

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7.276
7.236
7.228
7.226
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7.211
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7.201
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4.006
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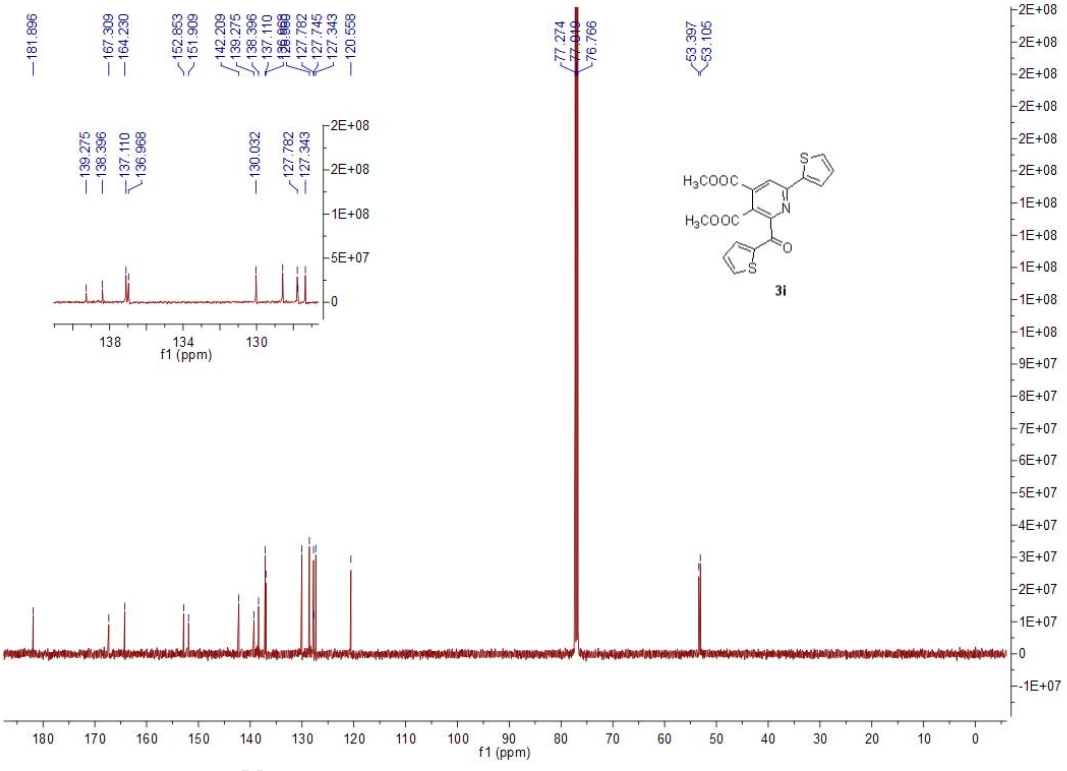
2.00
1.01
2.24
3.00
3.00
f1 (ppm)
3i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137.110
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120.558
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77.019
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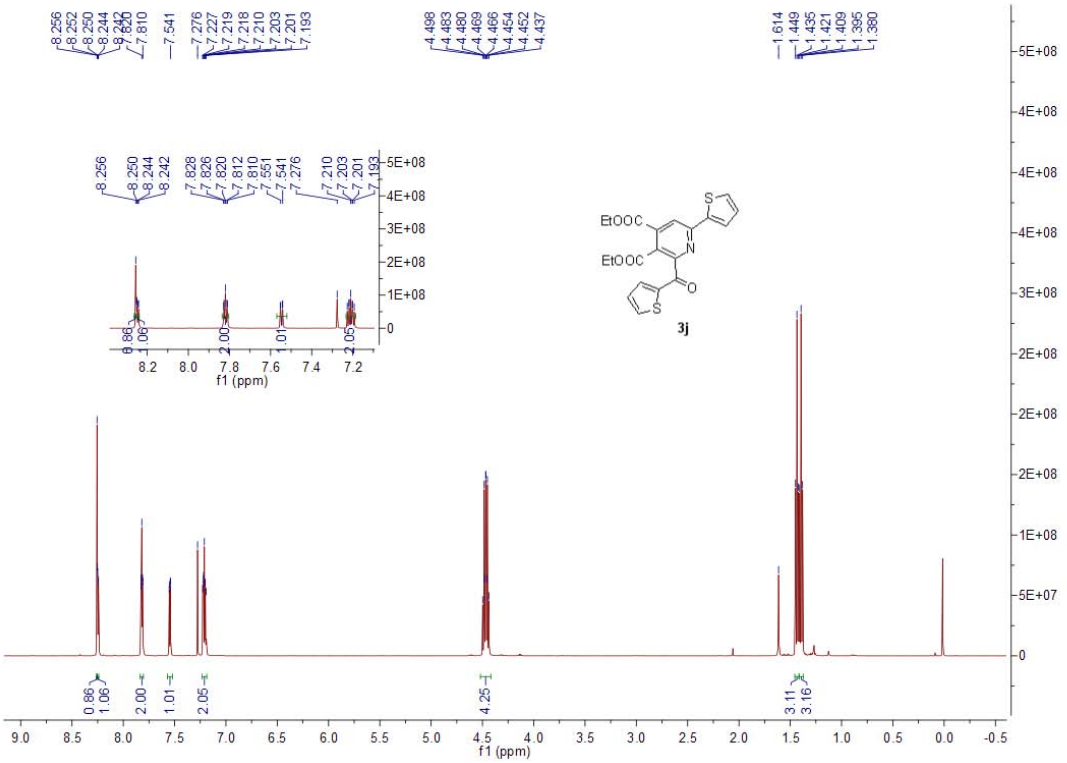
53.105
f1 (ppm)
3i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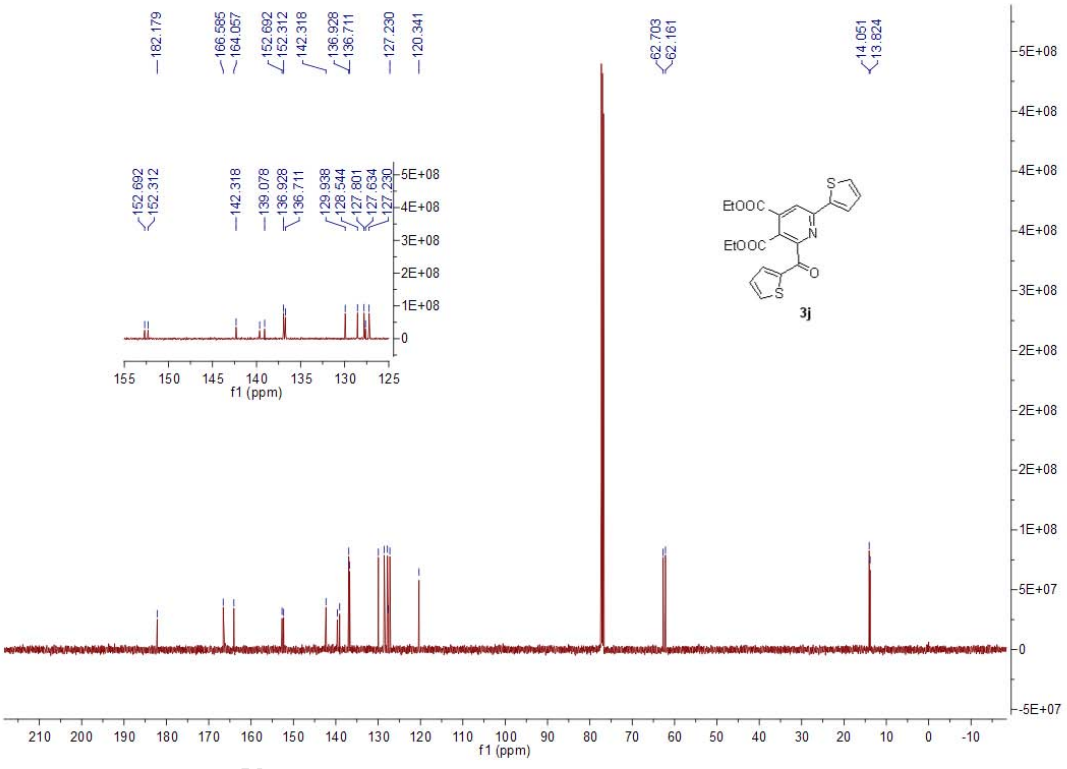
7.219
7.218
7.210
7.203
7.201
7.193
4.498
4.483
4.480
4.469
4.466
4.454
4.452
4.437
1.614
1.449
1.435
1.421
1.409
1.395
1.380
EtOOC
EtOOC
3j
0.86
1.06
2.00
1.01
2.05
4.25
3.11
3.16
f1 (ppm)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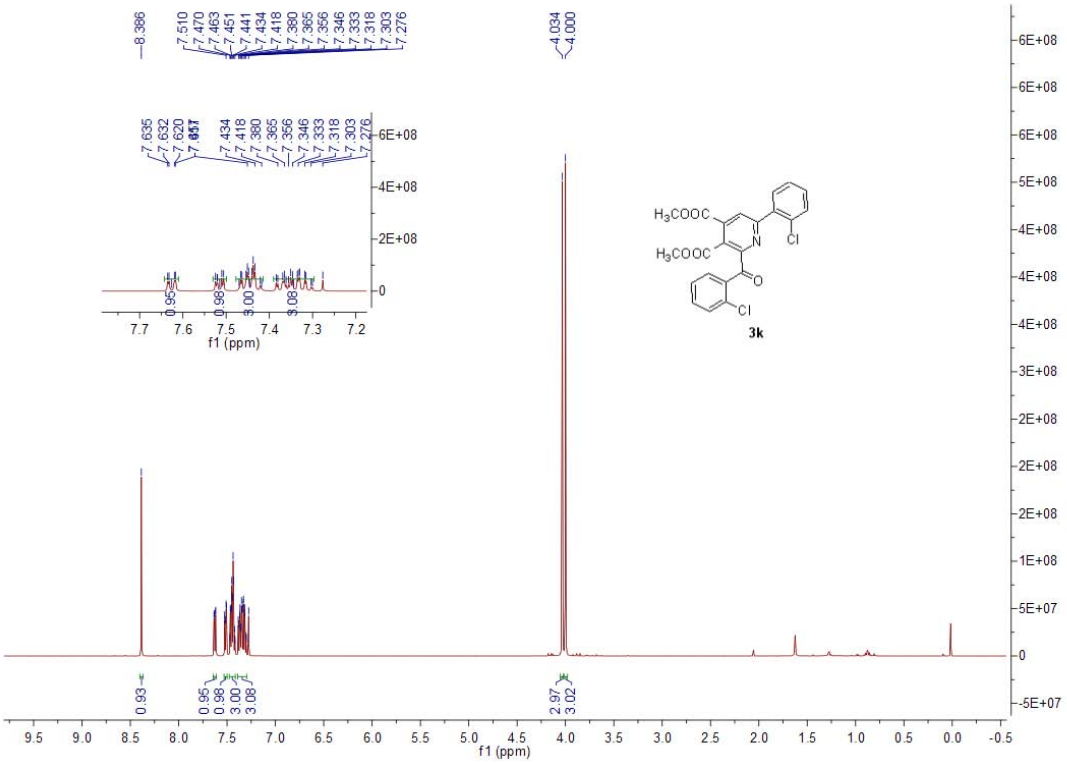
127.634
EtOOC
EtOOC
3j
f1 (ppm)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7.333
7.318
7.303
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0.93
0.95
0.98
3.00
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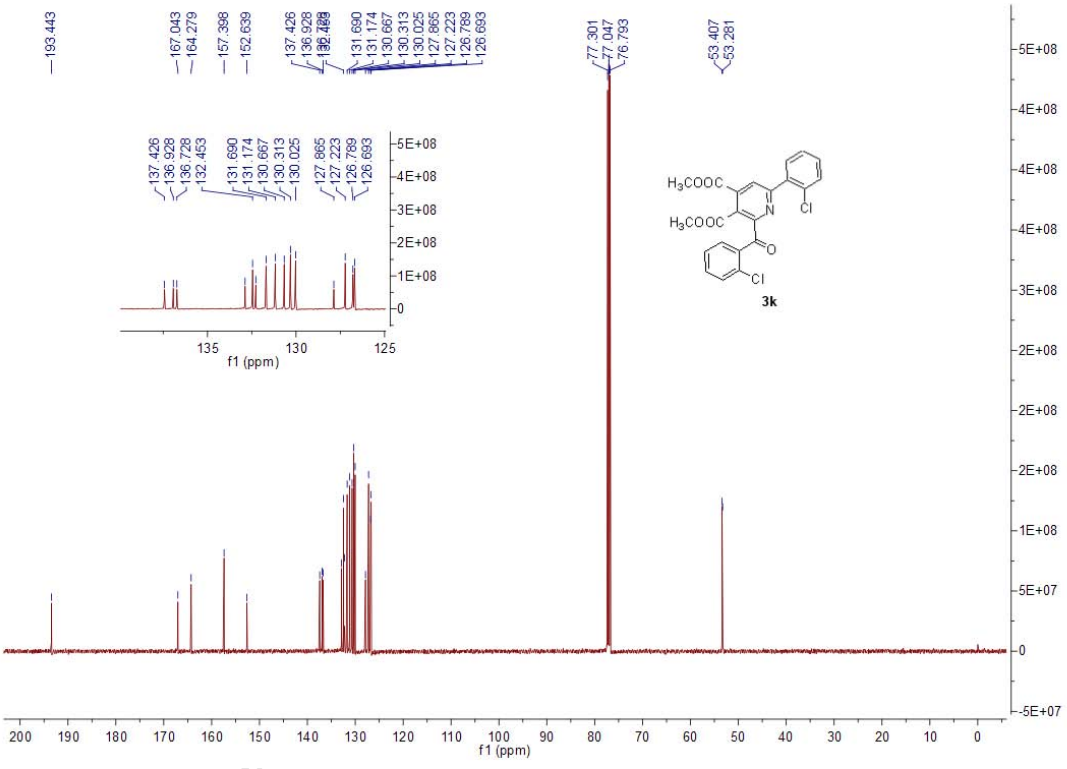
2.97
3.02
f1 (ppm)
3k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130.313
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126.789
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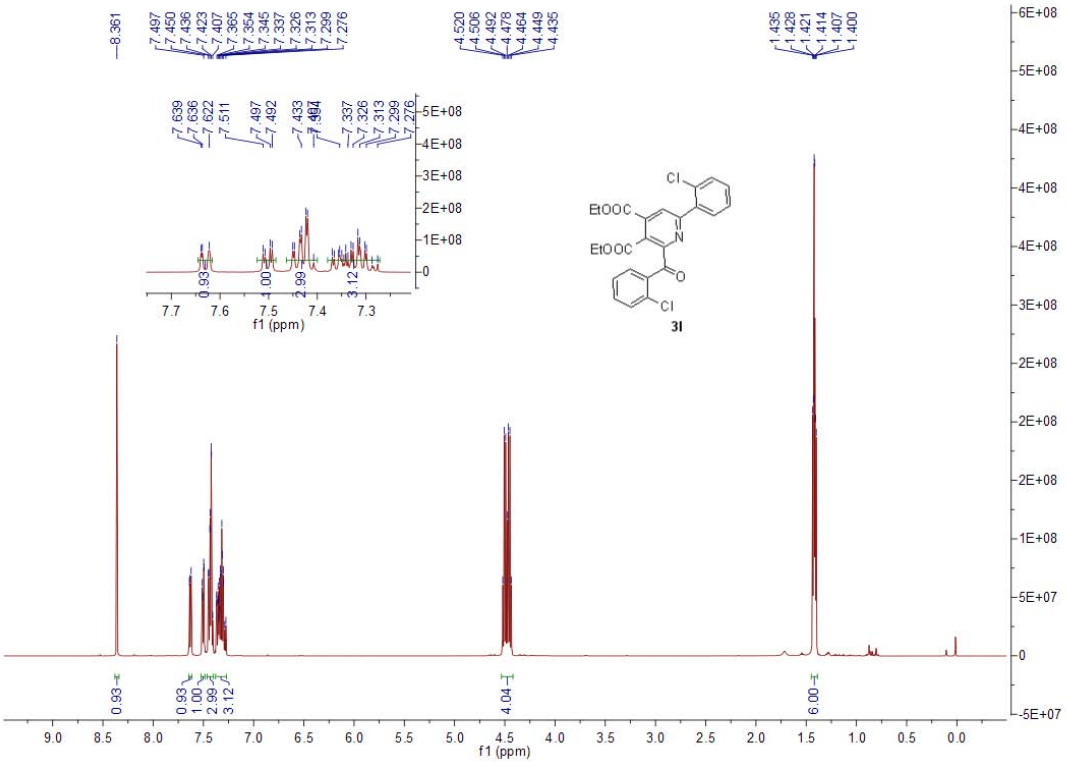
77.301
77.047
76.793
53.407
53.281
f1 (ppm)
3k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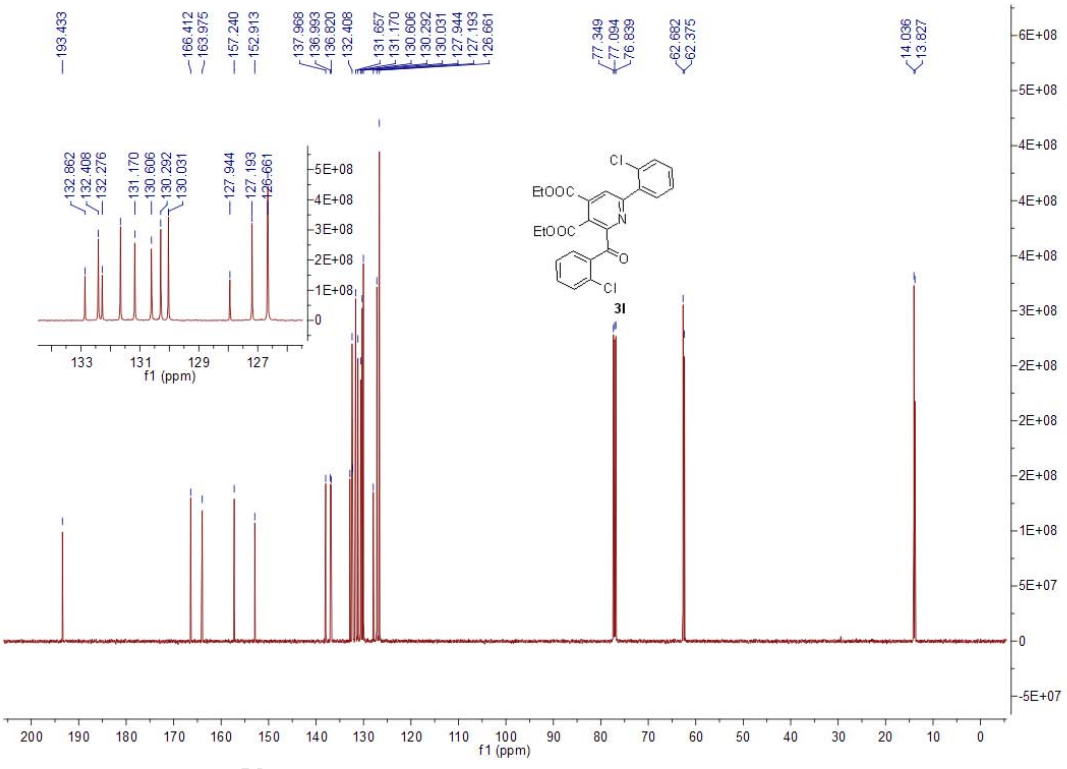
7.326
7.313
7.299
7.276
4.520
4.506
4.492
4.478
4.464
4.449
4.435
1.435
1.428
1.421
1.414
1.407
1.400
0.93
0.93
1.00
2.99
3.12
4.04
6.00
f1 (ppm)
EtOOC
EtOOC
Cl
Cl
N
O
3l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130.292
130.031
127.944
127.193
126.661
77.349
77.094
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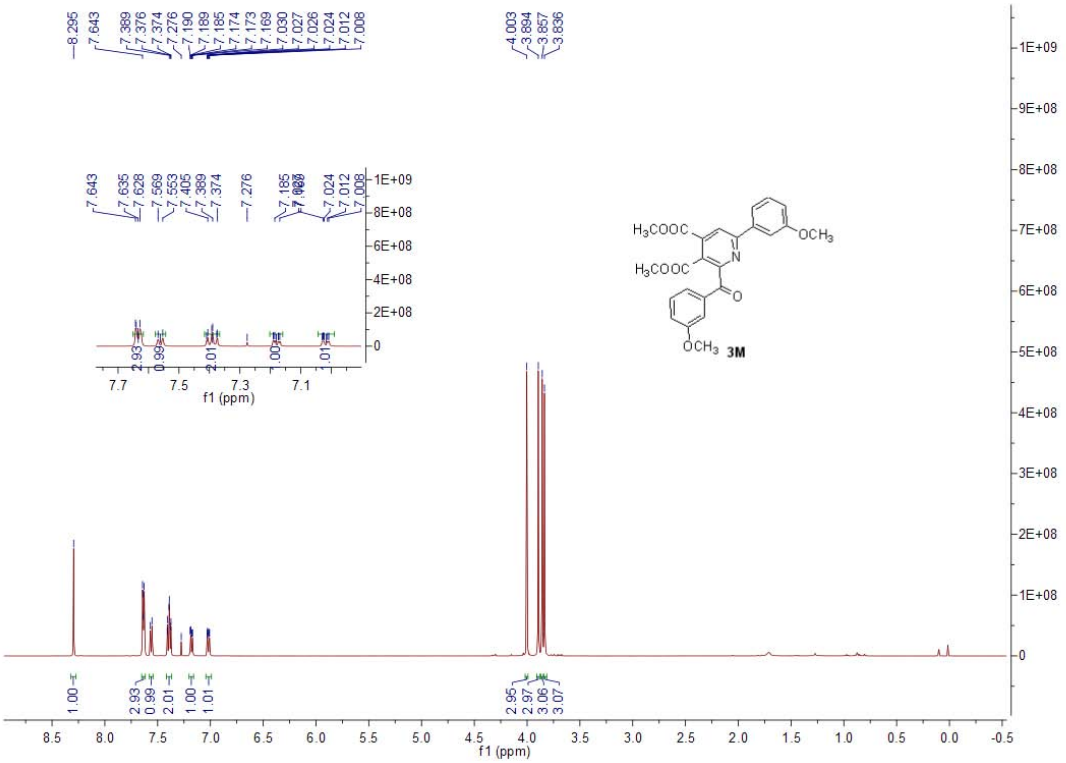
f1 (ppm)
EtOOC
EtOOC
Cl
Cl
N
O
3l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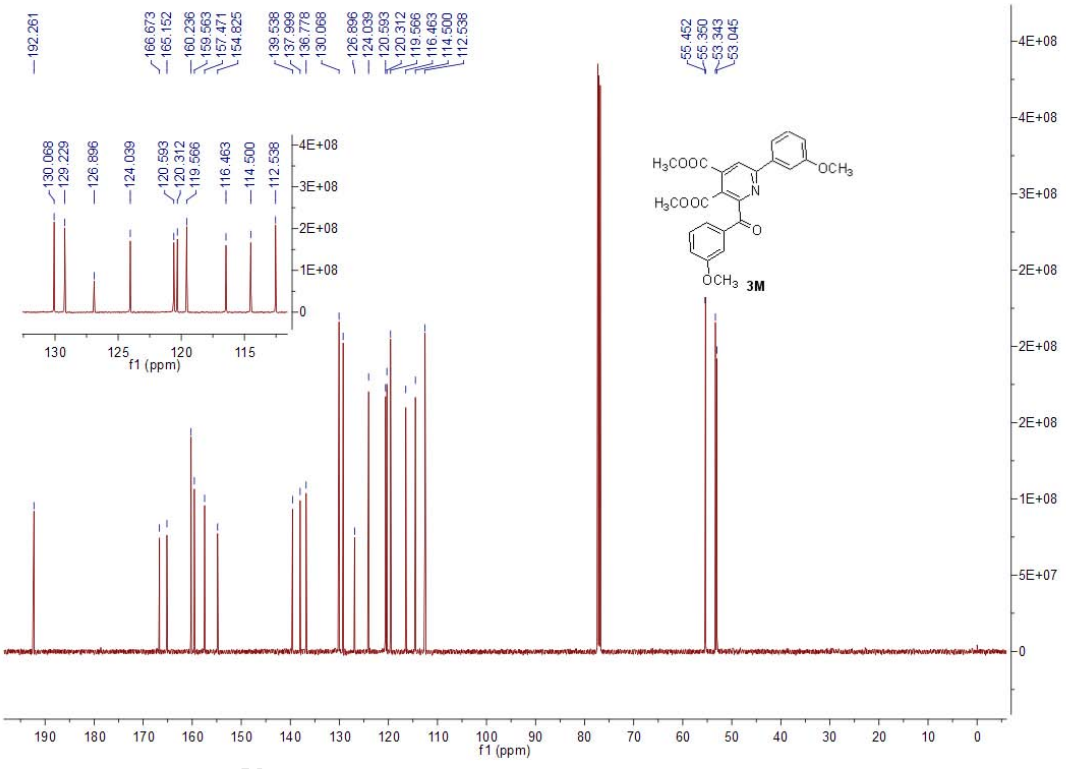
7.030
7.027
7.026
7.024
7.012
7.008
4.003
3.894
3.857
3.836
1.00
2.93
0.99
2.01
1.00
1.01
2.95
2.97
3.06
3.07
f1 (ppm)
H3COOC
OCH3
H3COOC
O
OCH3
3M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120.593
120.312
119.566
116.463
114.500
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53.343
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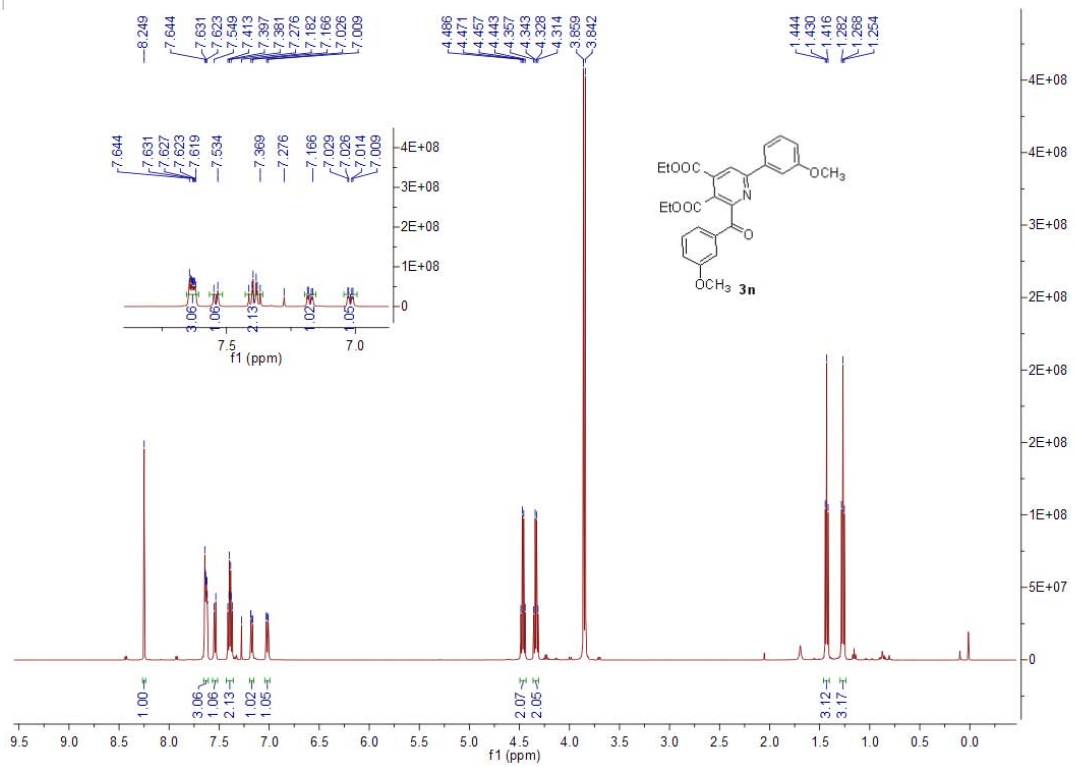
f1 (ppm)
H3COOC
OCH3
H3COOC
O
OCH3
3M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7.276
7.182
7.166
7.029
7.026
7.014
7.009
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4.471
4.457
4.443
4.357
4.343
4.328
4.314
3.859
3.842
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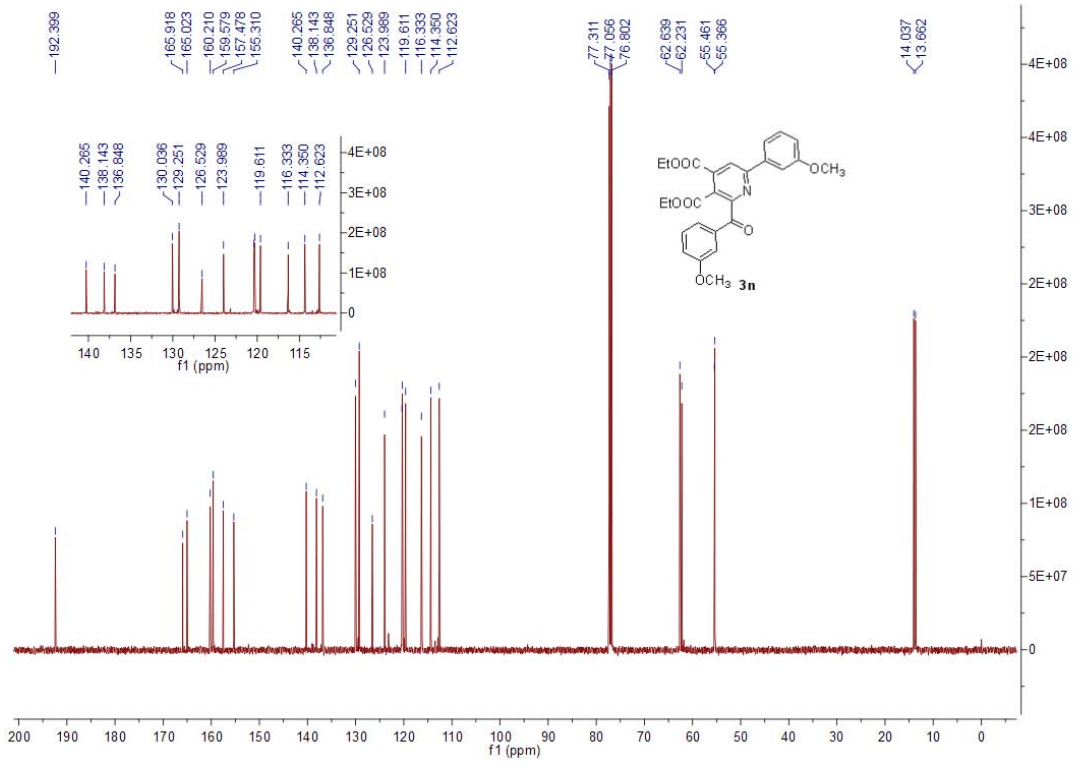
1.282
1.268
1.254
EtOOC
EtOOC
OCH3
OCH3
3n
f1 (ppm)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119.611
116.333
114.350
112.623
77.311
77.056
76.802
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55.366
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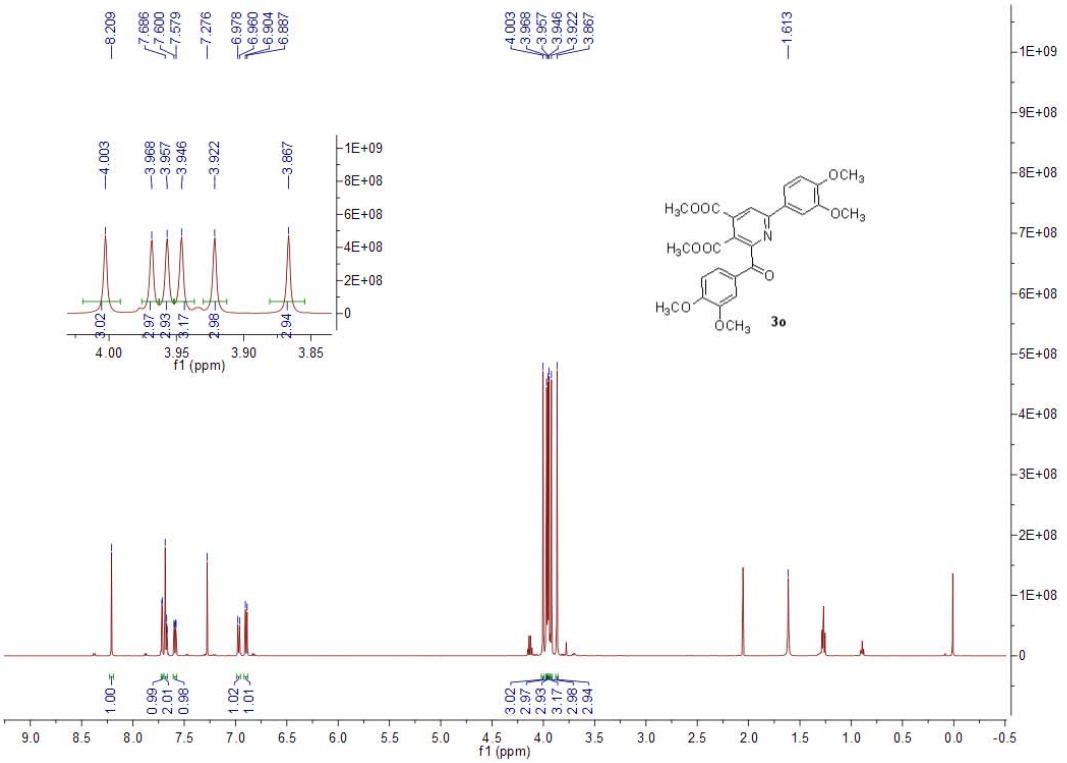
EtOOC
OCH3
OCH3
3n
f1 (ppm)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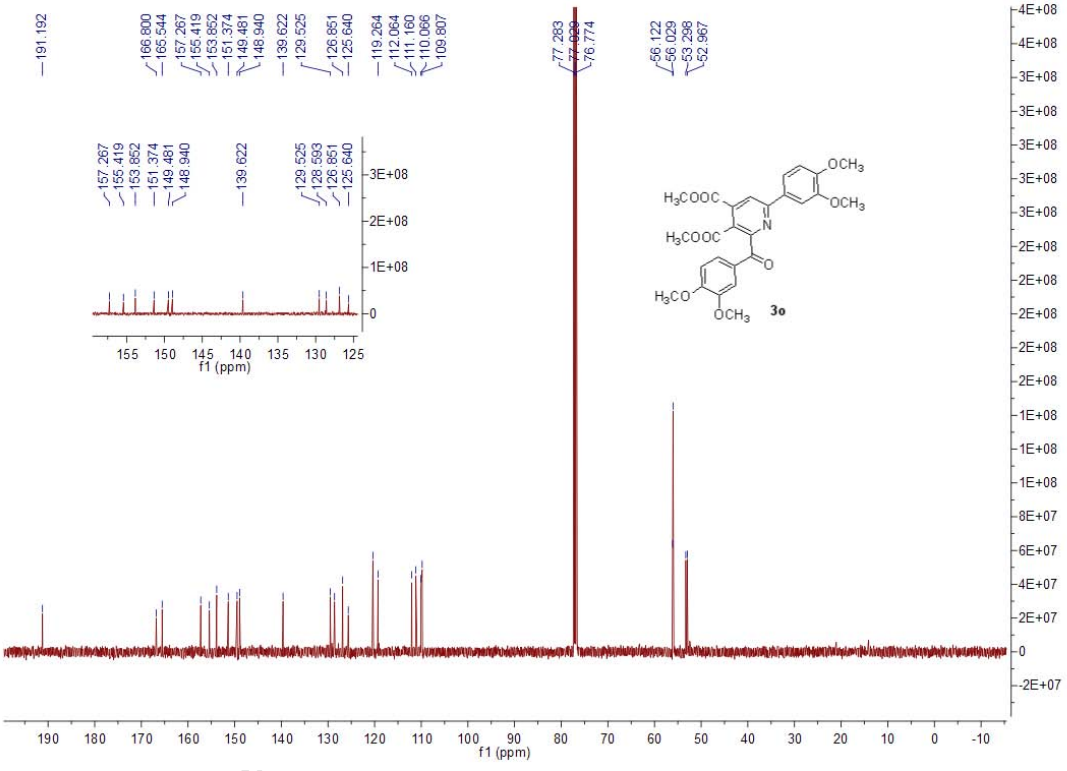
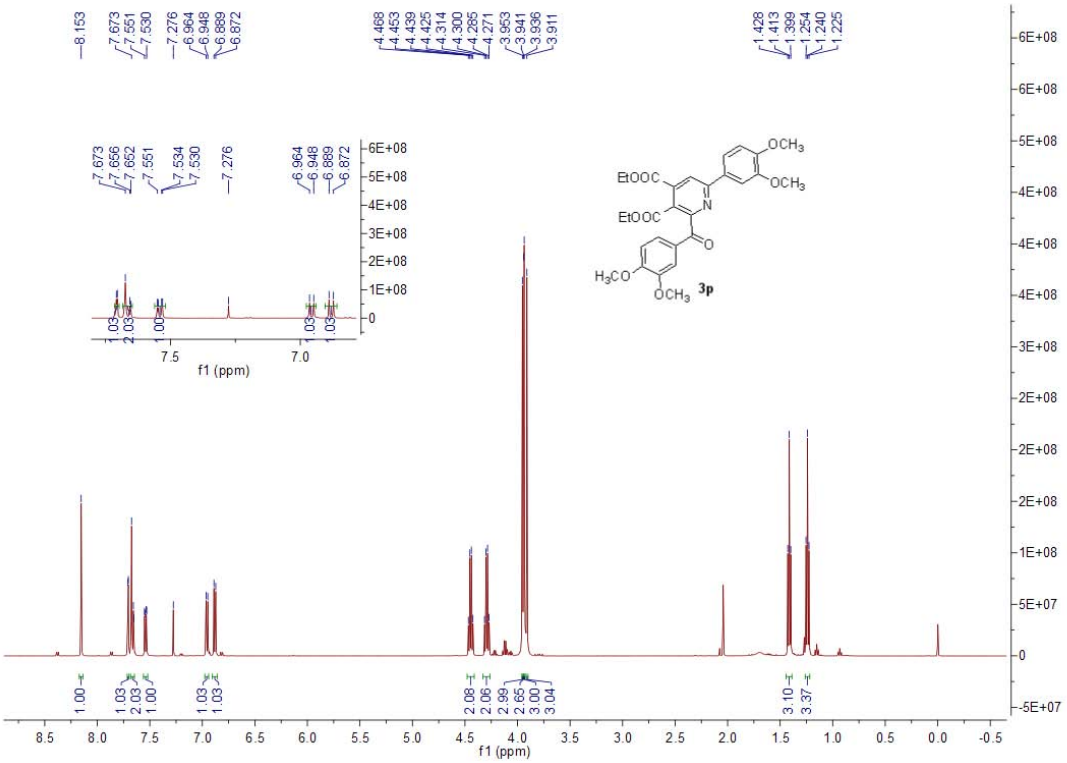
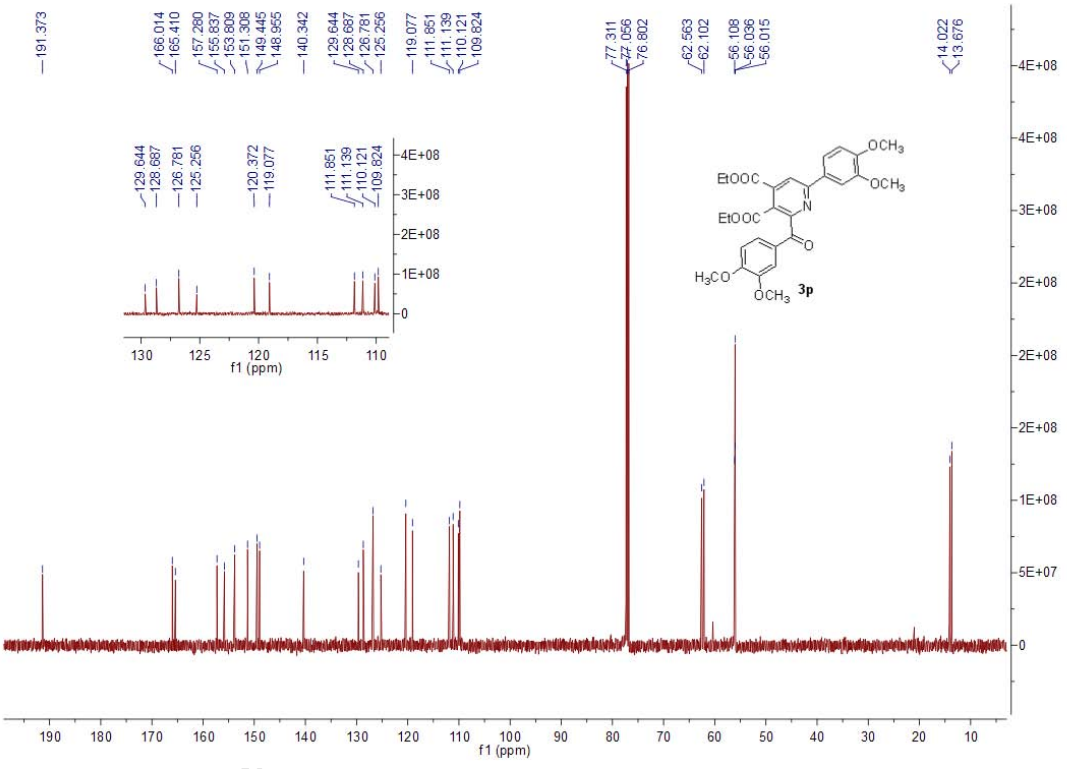
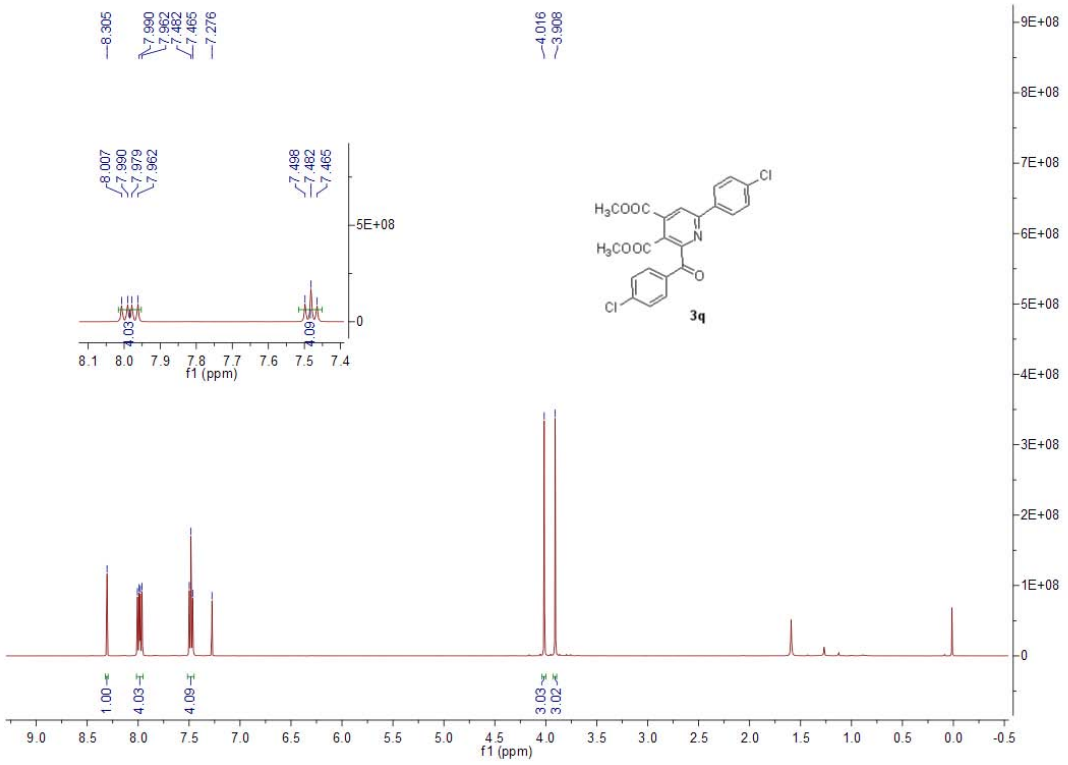
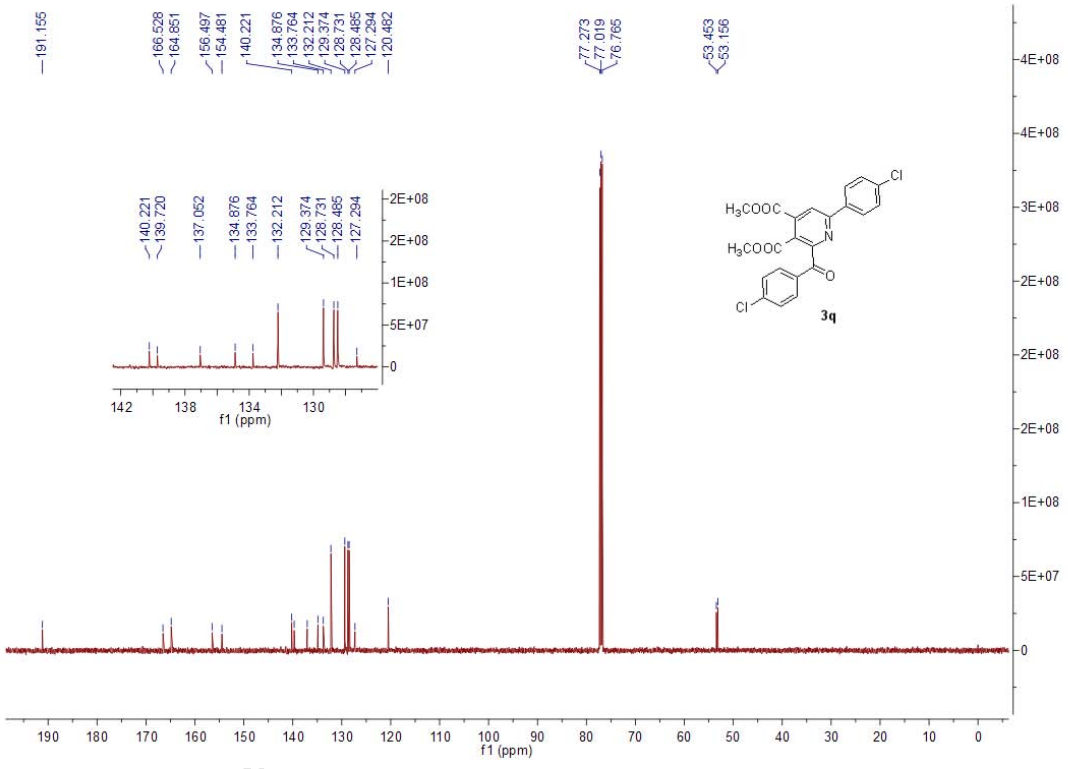
3.957
3.946
3.922
3.867
1.613
1.00
0.99
2.01
0.98
1.02
1.01
3.02
2.97
2.93
3.17
2.98
2.94
f1 (ppm)
3o

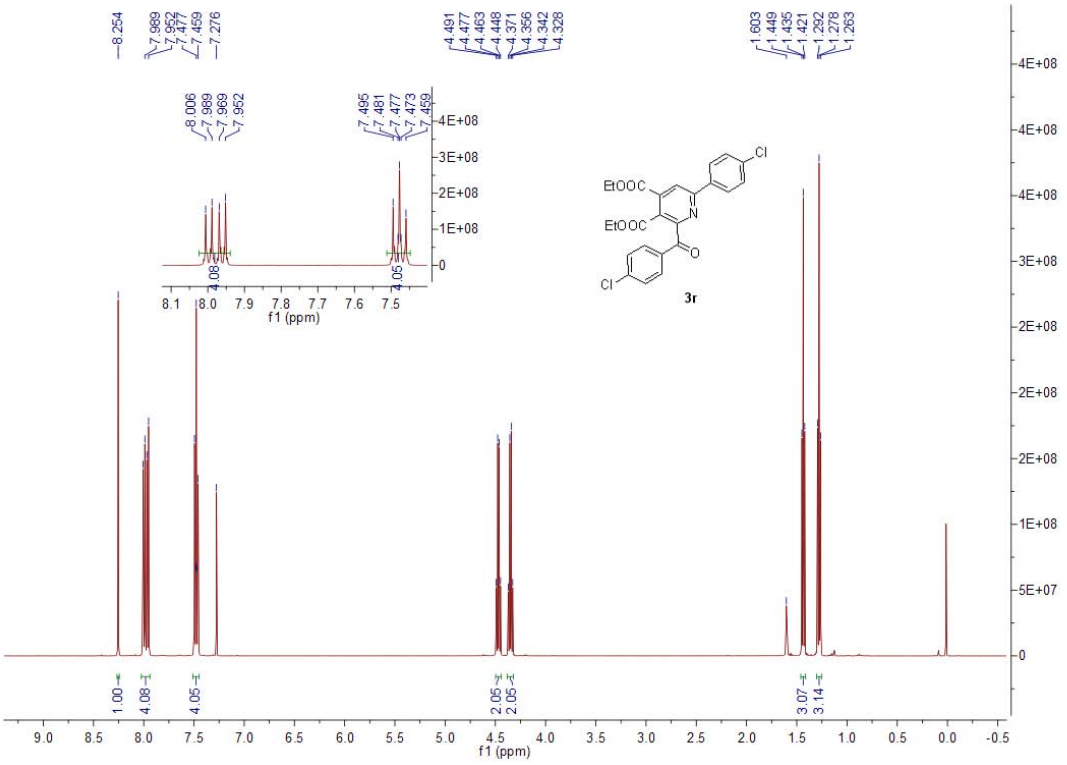

191.192
166.800
165.544
157.267
155.419
153.852
151.374
149.481
148.940
139.622
129.525
126.851
125.640
119.264
112.064
111.160
110.066
109.807
77.283
77.029
76.774
56.122
56.029
53.298
52.967
f1 (ppm)
3o

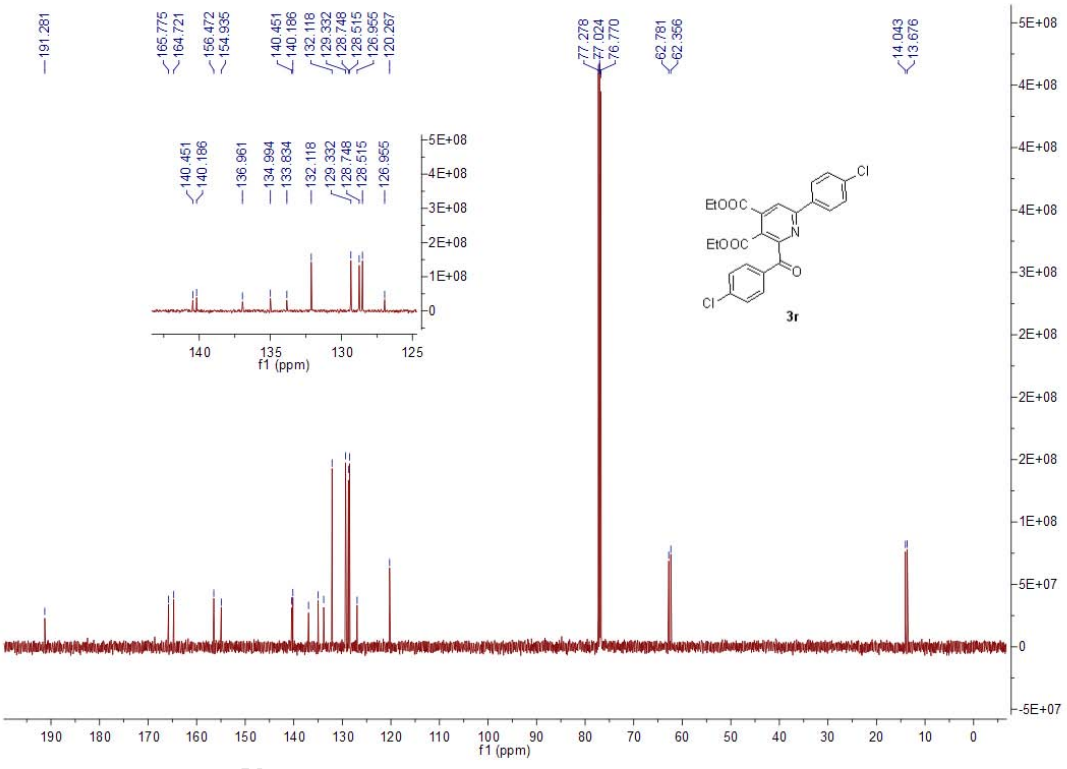


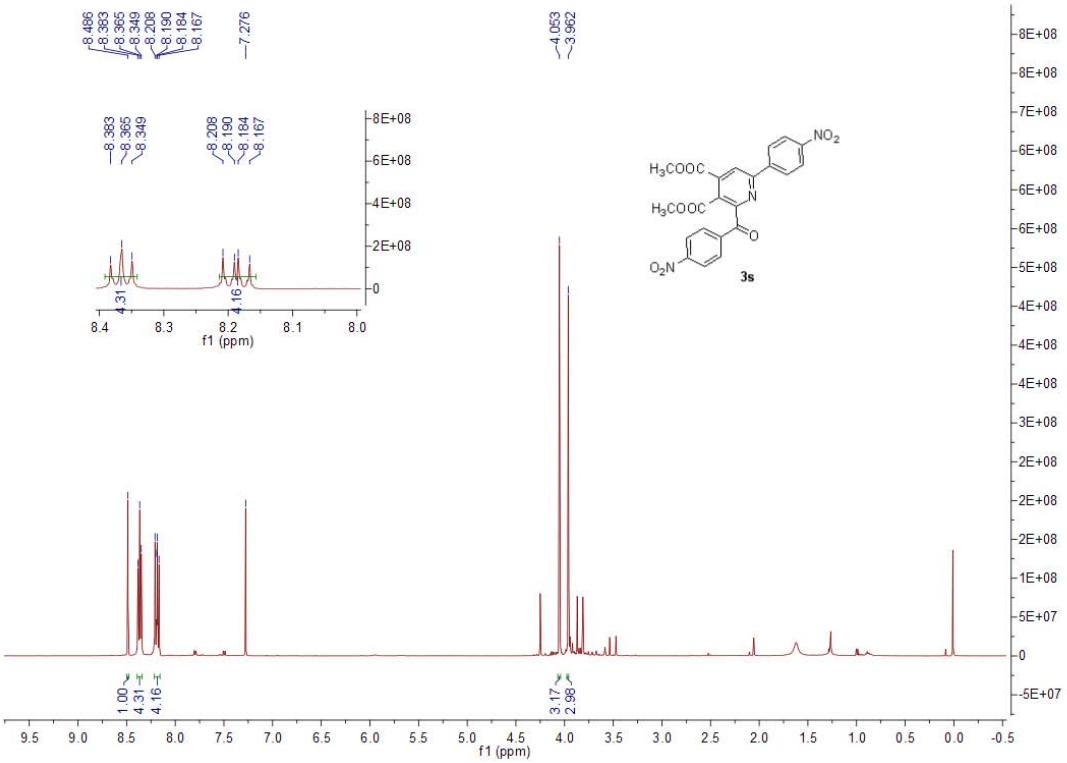



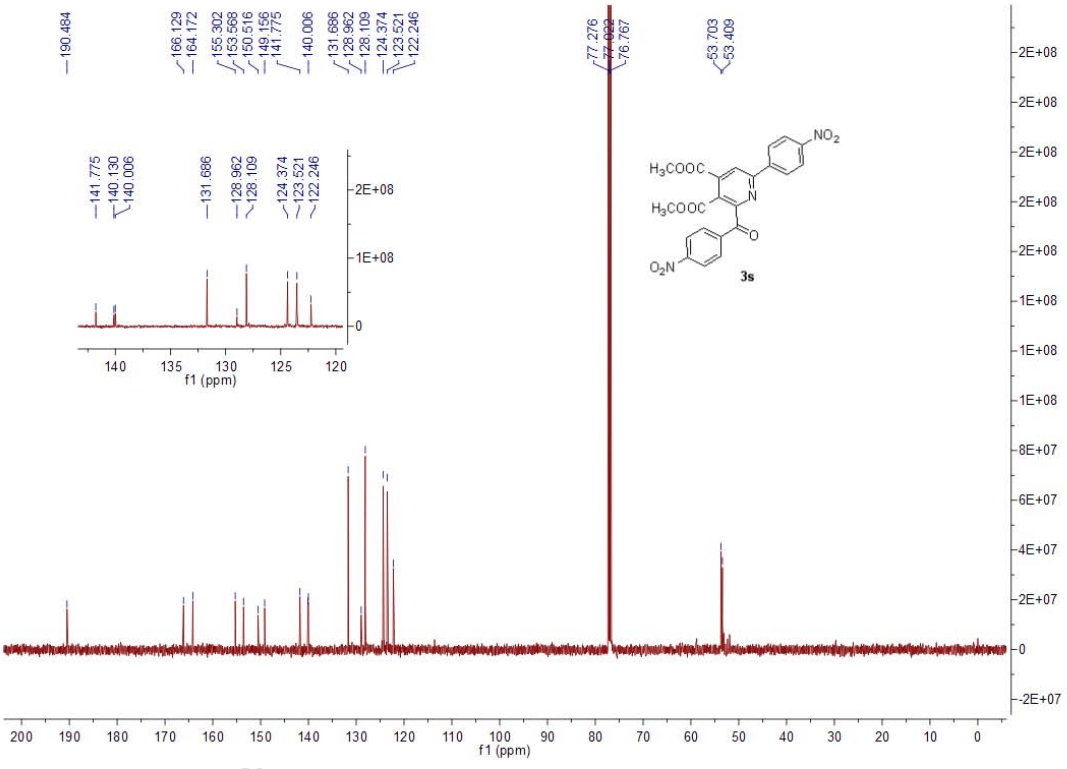

8.305
7.990
7.962
7.482
7.465
7.276
4.016
3.908
8.007
7.990
7.979
7.962
7.498
7.482
7.465
5E+08
0
4.03
4.09
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4
f1 (ppm)
H3COOC
H3COOC
N
O
Cl
Cl
3q
1.00
4.03
4.09
3.03
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0


191.155
166.528
164.851
156.497
154.481
140.221
134.876
133.764
132.212
129.374
128.731
128.485
127.294
120.462
77.273
77.019
76.765
53.453
53.156
140.221
139.720
137.052
134.876
133.764
132.212
129.374
128.731
128.485
127.294
2E+08
2E+08
1E+08
5E+07
0
142 138 134 130
f1 (ppm)
H3COOC
H3COOC
N
O
Cl
Cl
3q
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.254
7.989
7.952
7.477
7.459
7.276
4.491
4.477
4.463
4.448
4.371
4.356
4.342
4.328
1.603
1.449
1.435
1.421
1.292
1.278
1.263
8.006
7.989
7.969
7.952
7.495
7.481
7.477
7.473
7.459
4.08
4.05
f1 (ppm)
EtOOC
EtOOC
Cl
Cl
O
N
3r
1.00
4.08
4.05
2.05
2.05
3.07
3.14
f1 (ppm)

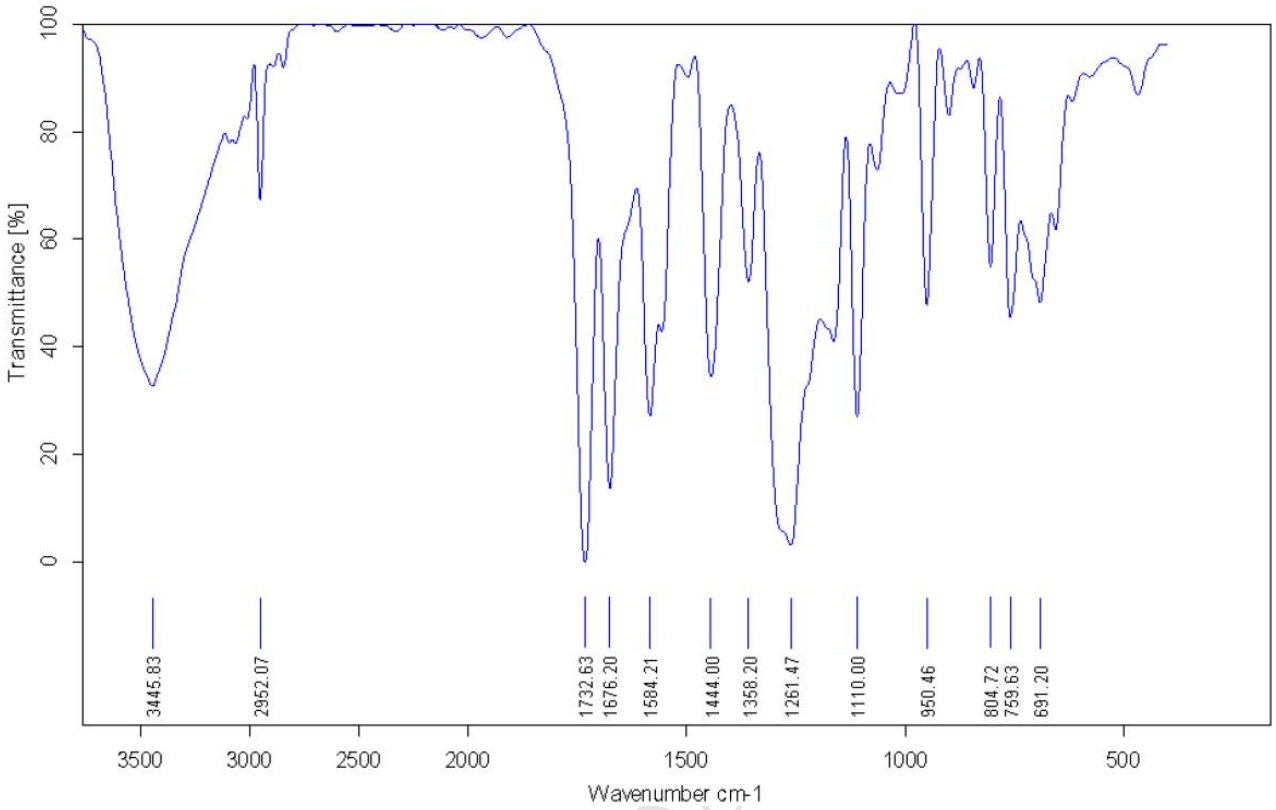

191.281
165.775
164.721
156.472
154.935
140.451
140.186
132.118
129.332
128.748
128.515
126.955
120.267
77.278
77.024
76.770
62.781
62.356
14.043
13.676
136.961
134.994
133.834
f1 (ppm)
EtOOC
EtOOC
Cl
Cl
O
N
3r
f1 (ppm)


8.486
8.383
8.365
8.349
8.208
8.190
8.184
8.167
7.276
4.053
3.962
1.00
4.31
4.16
3.17
2.98
f1 (ppm)
3s

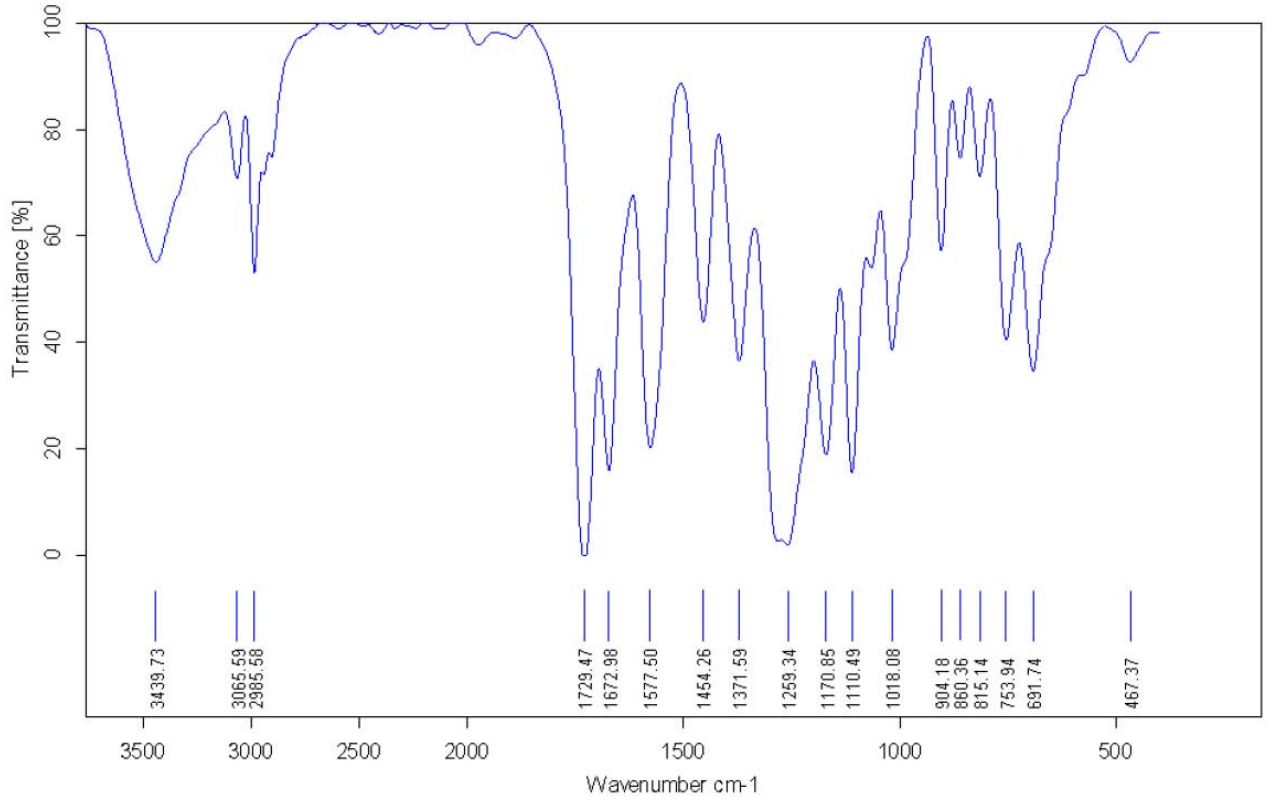

190.484
166.129
164.172
155.302
153.568
150.516
149.156
141.775
140.006
131.686
128.962
128.109
124.374
123.521
122.246
77.276
53.703
53.409
f1 (ppm)
3s

## IR spectra:

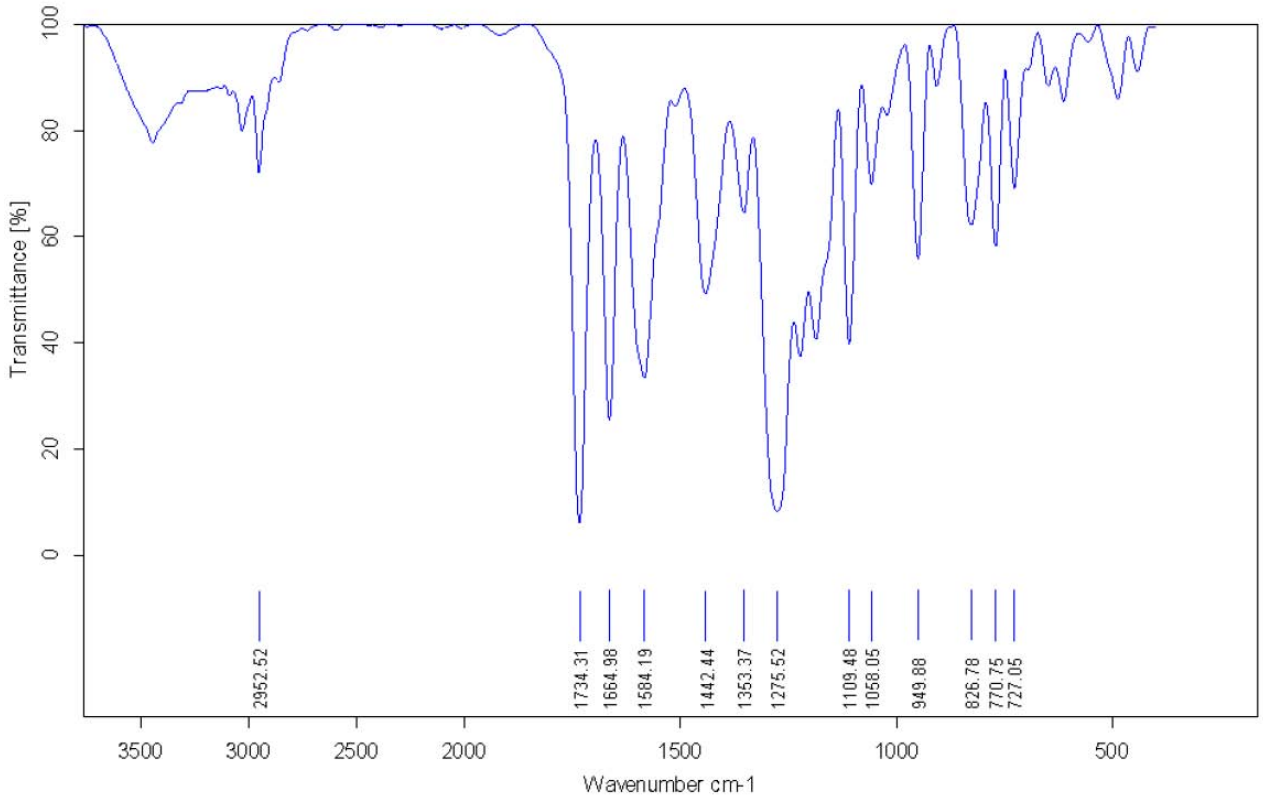
IR spectra of compound **3a**



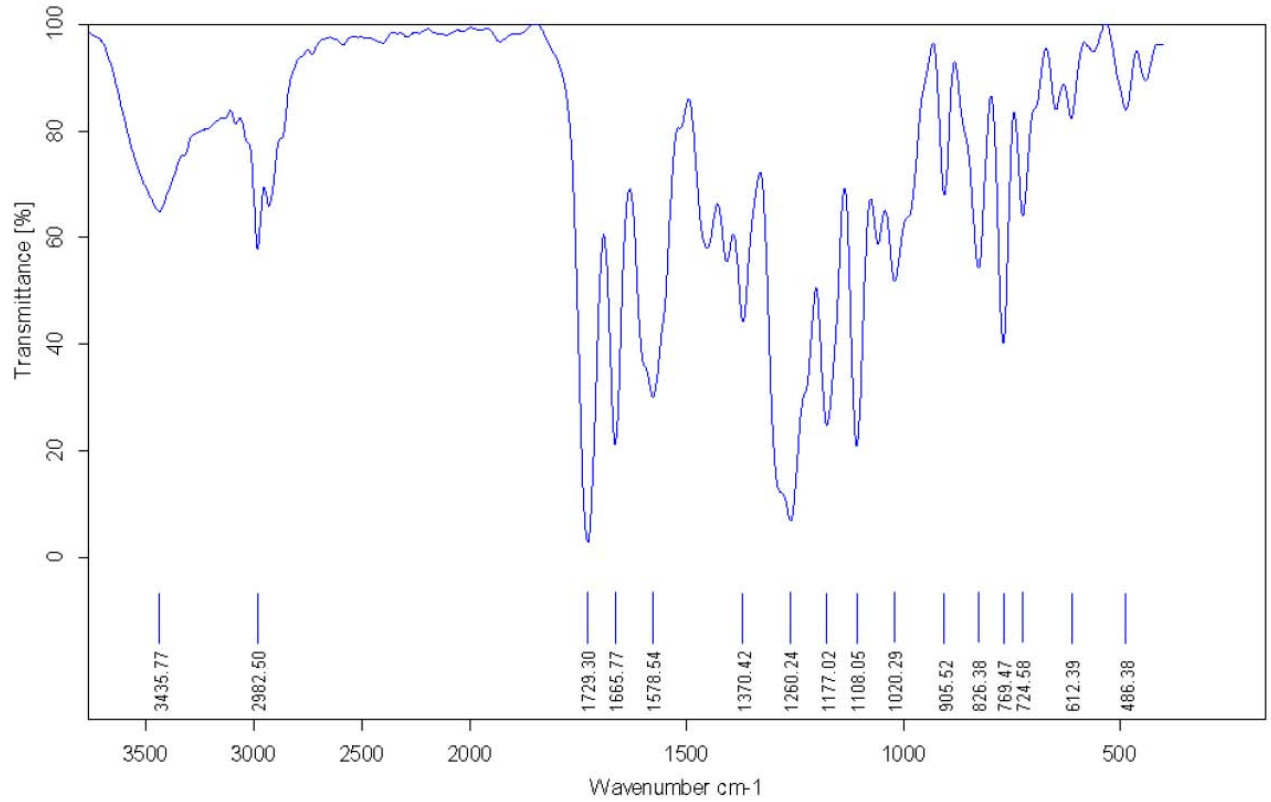

IR spectra of compound **3b**



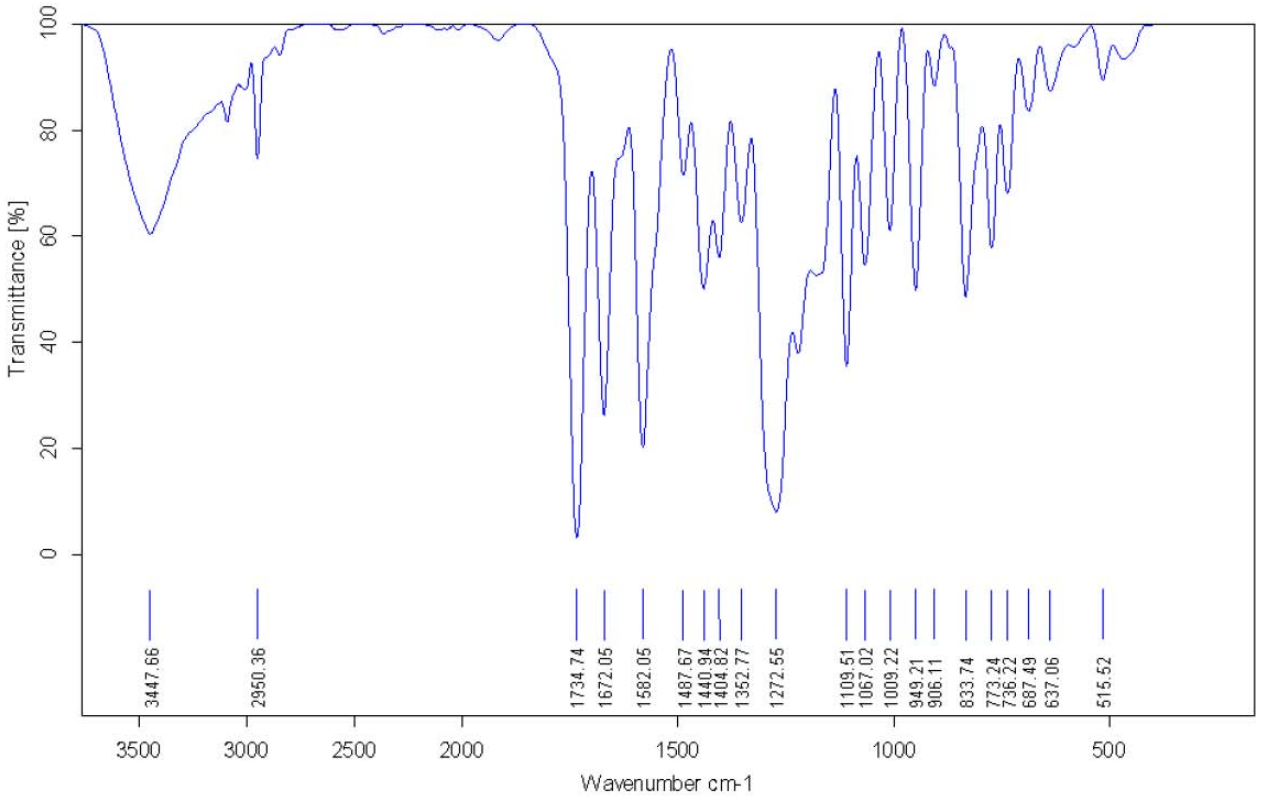
IR spectra of compound **3c**



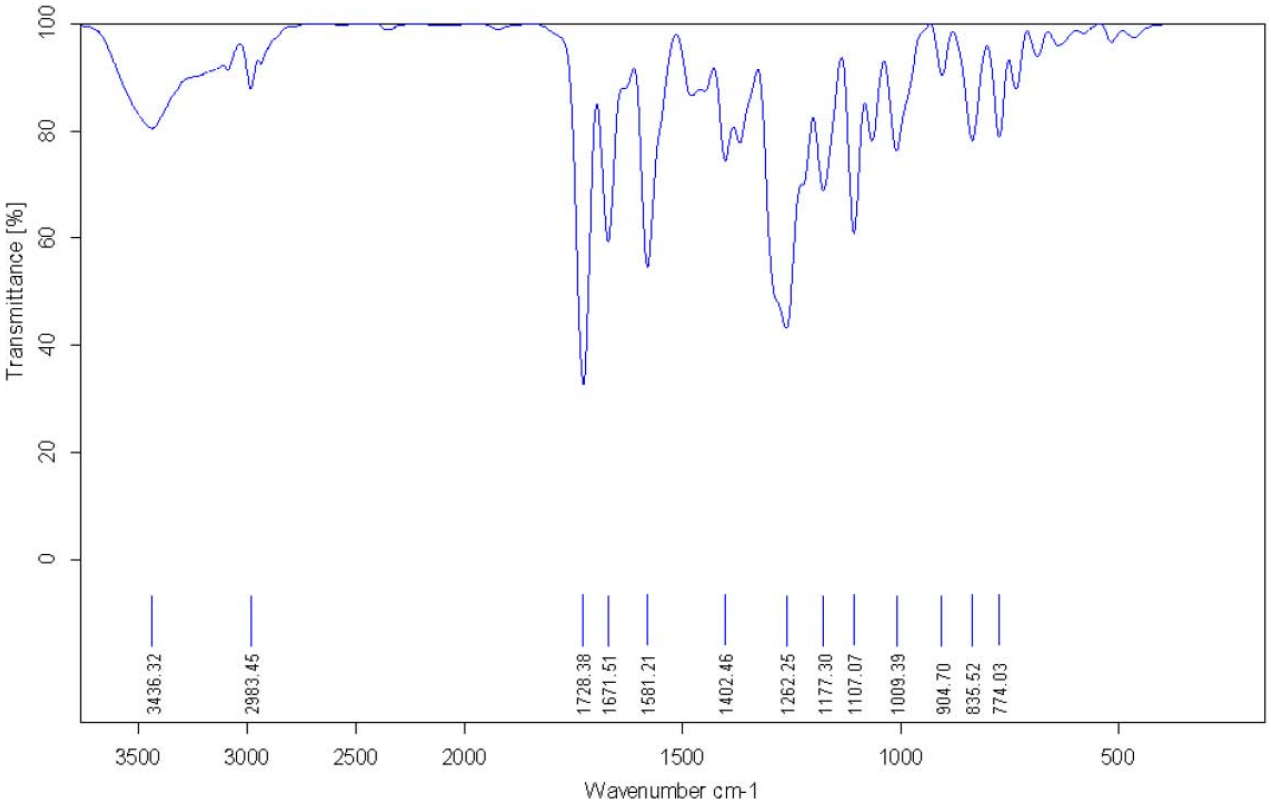

IR spectra of compound **3d**



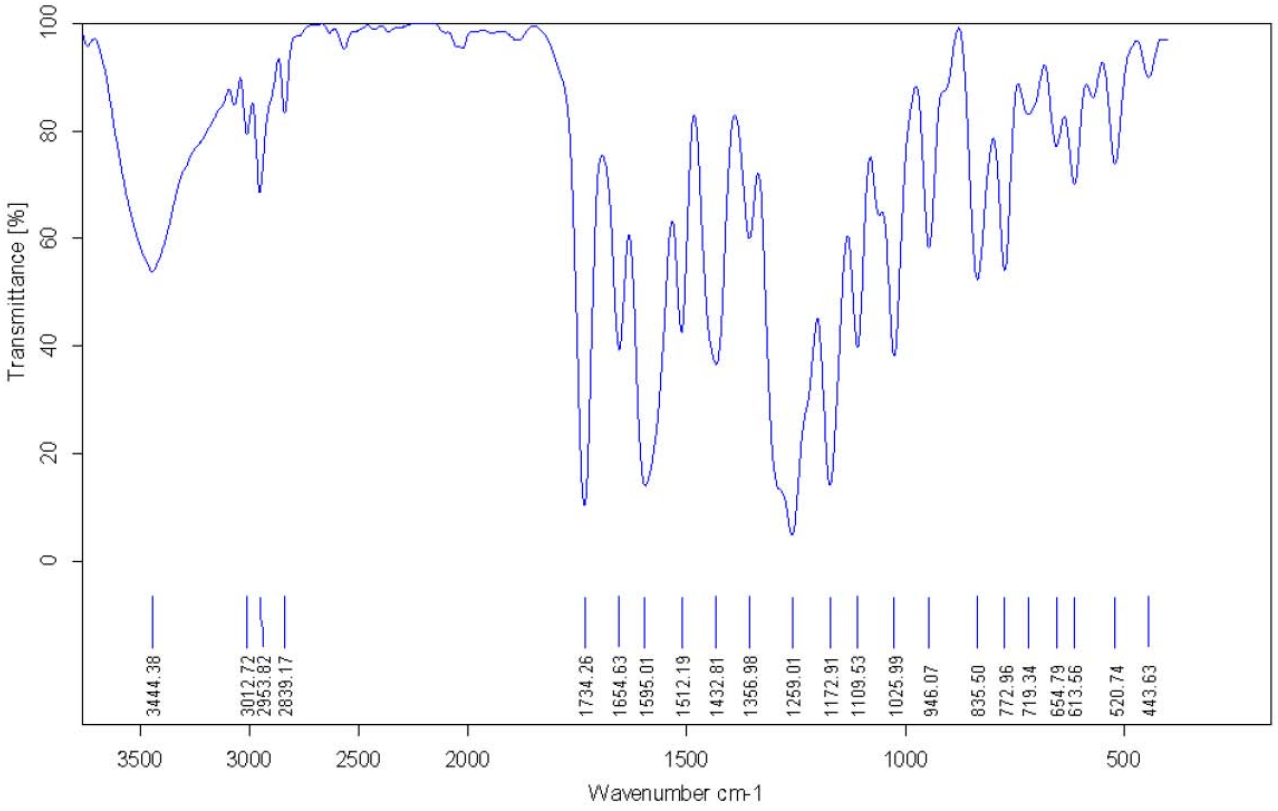
IR spectra of compound **3e**



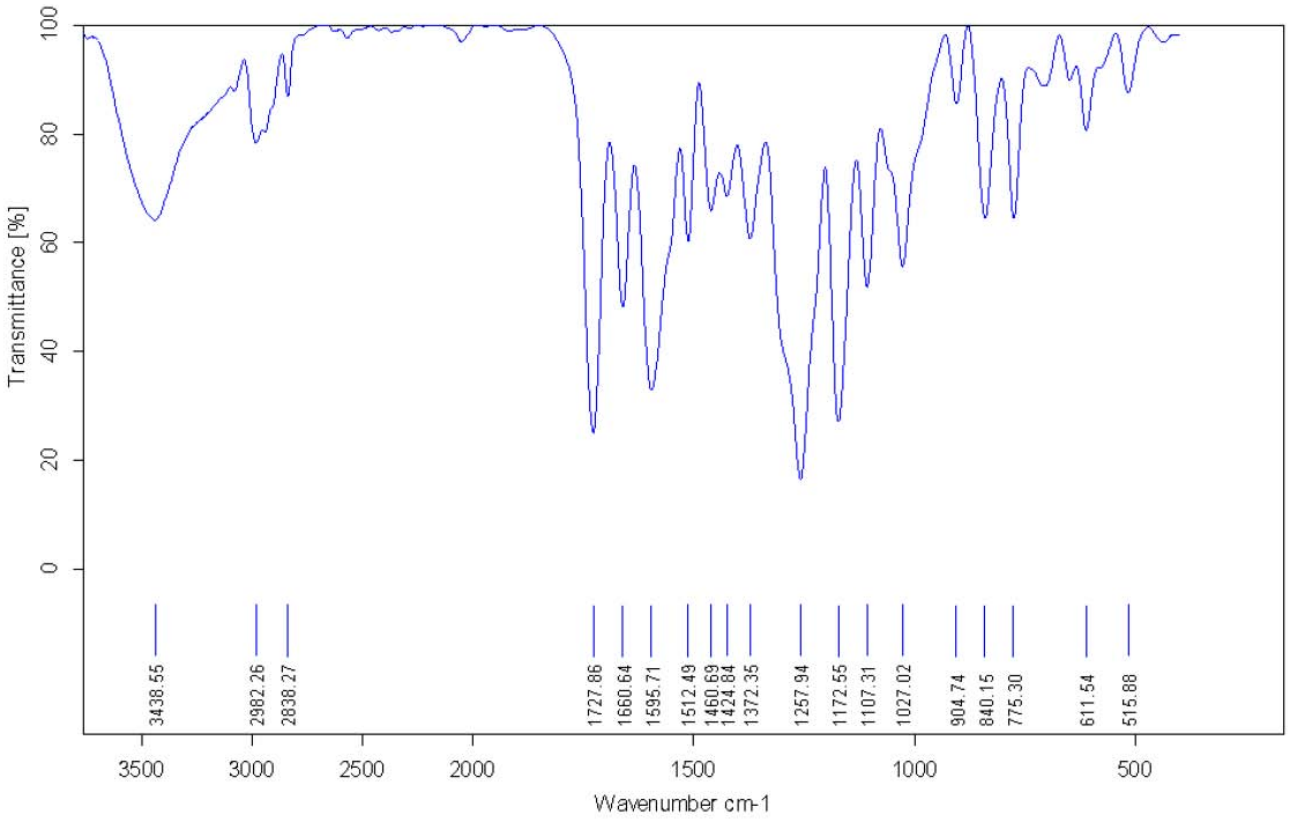

IR spectra of compound **3f**



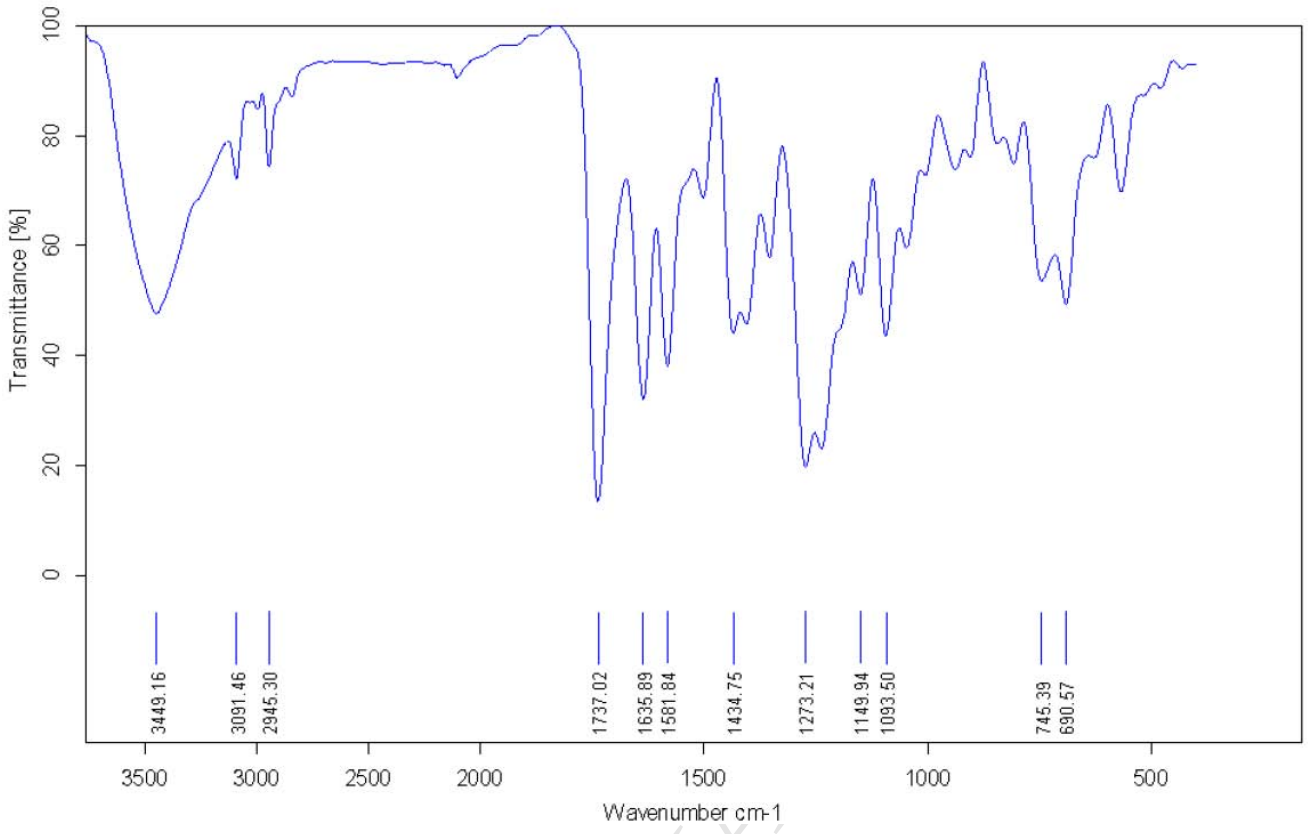
IR spectra of compound **3g**



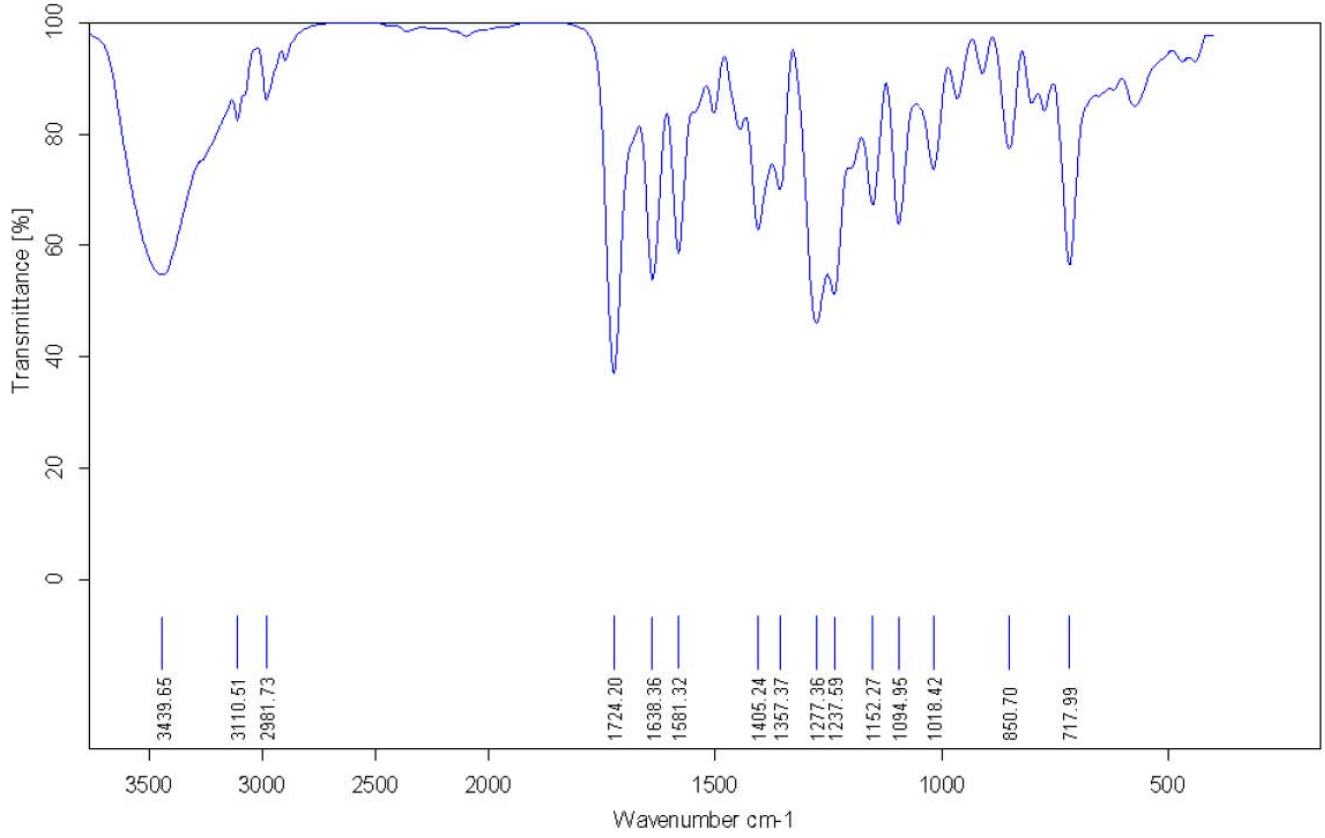

IR spectra of compound **3h**



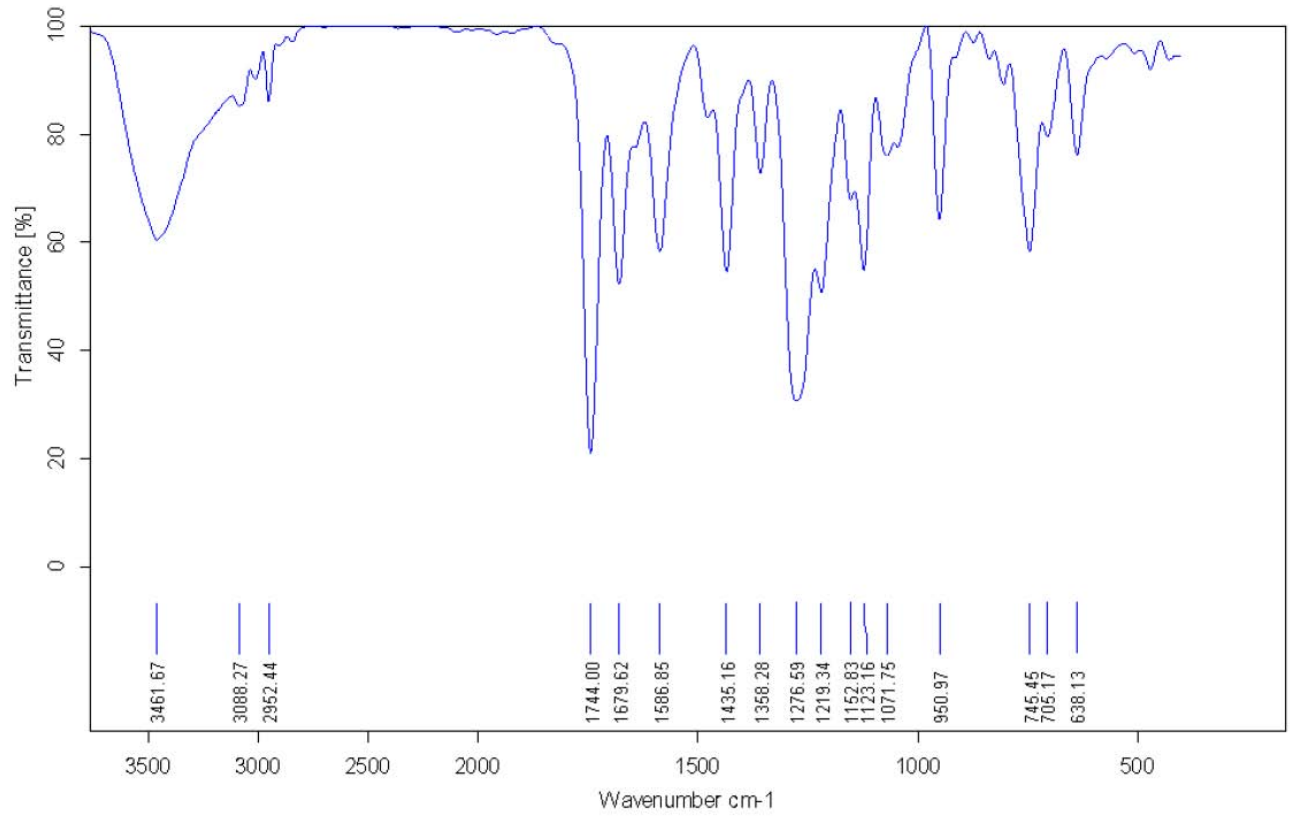
IR spectra of compound **3i**



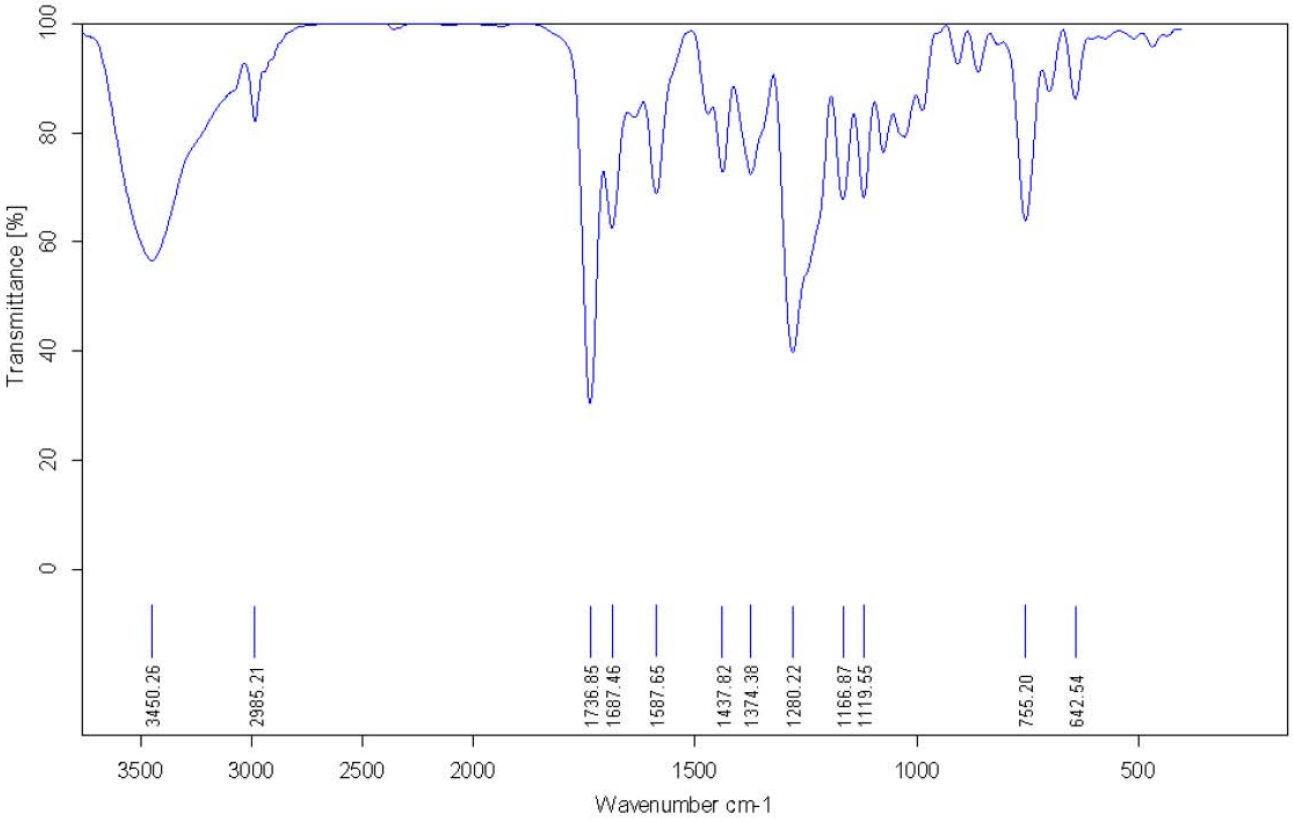

IR spectra of compound **3j**



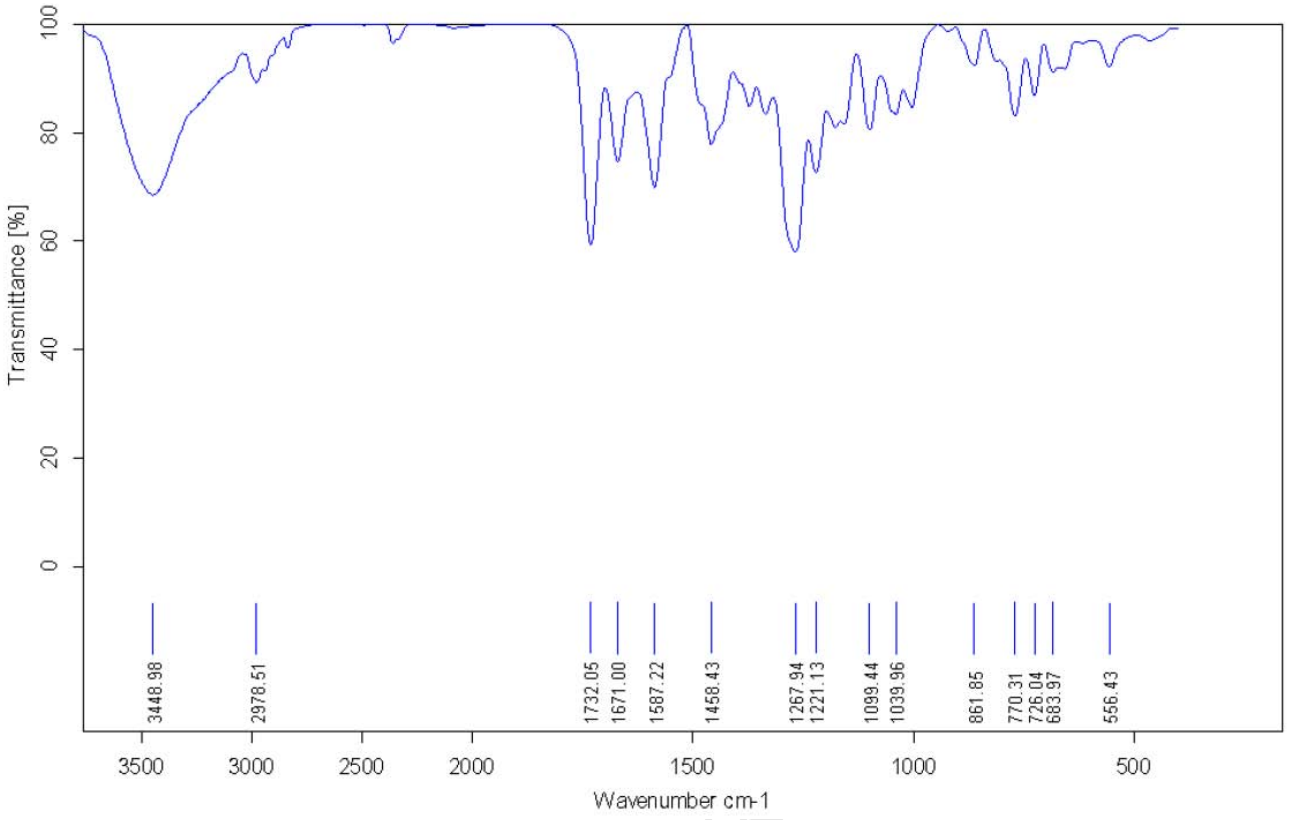
IR spectra of compound **3k**



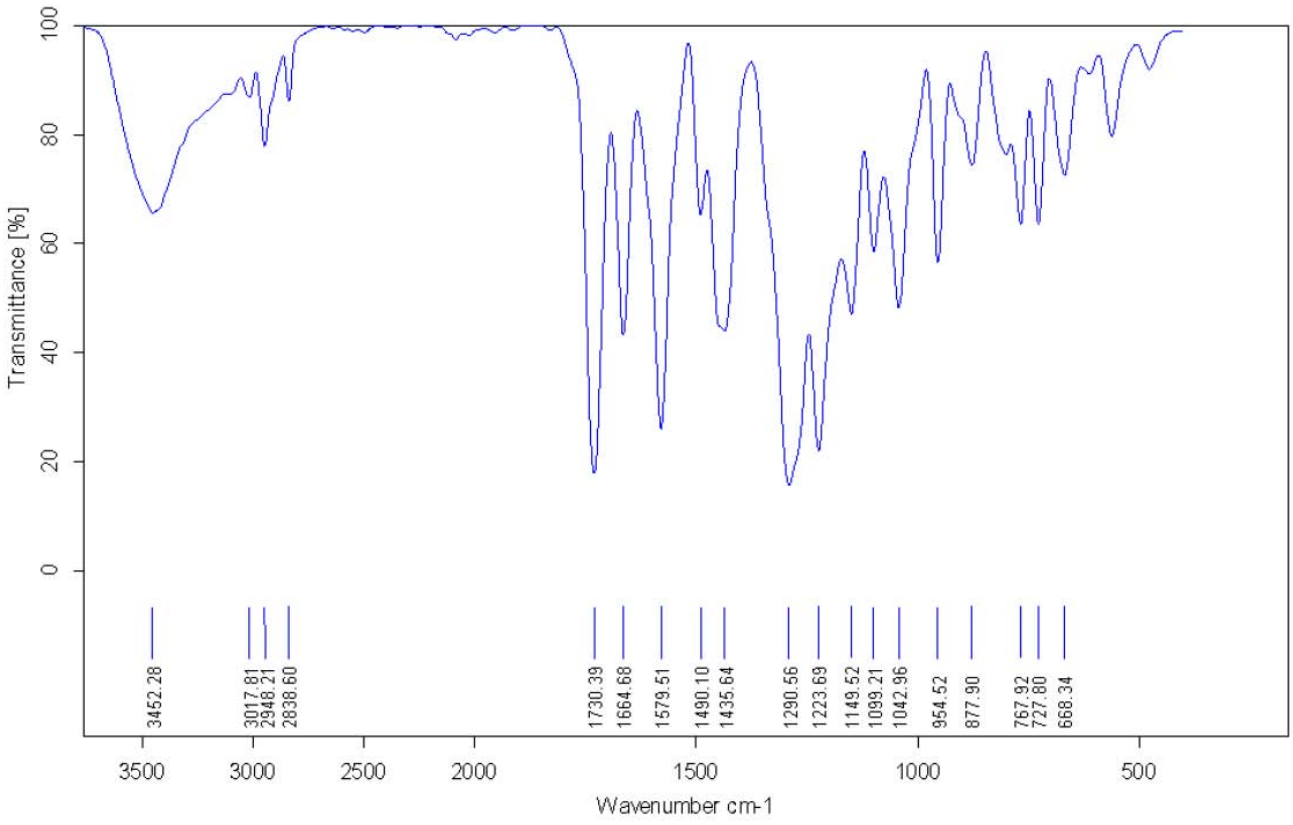

IR spectra of compound **3l**



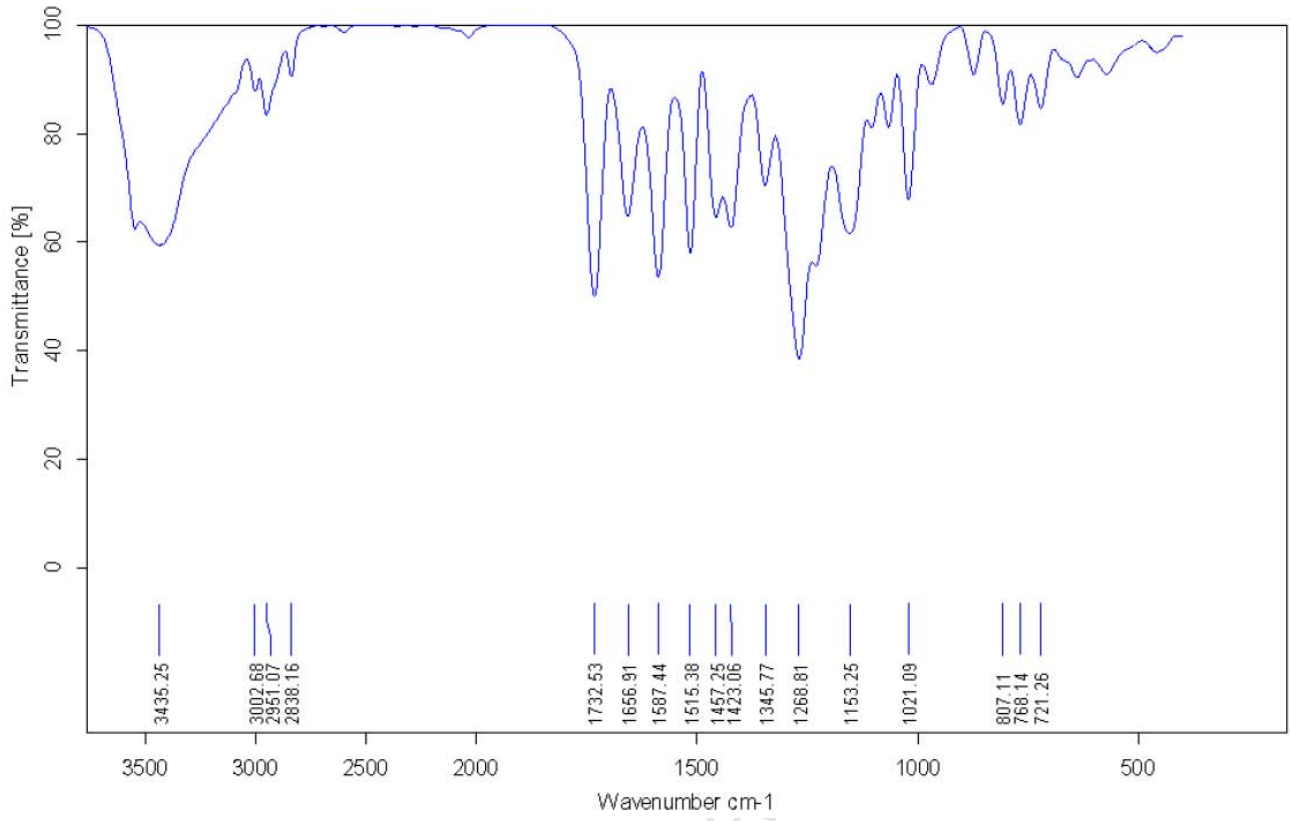
IR spectra of compound **3m**



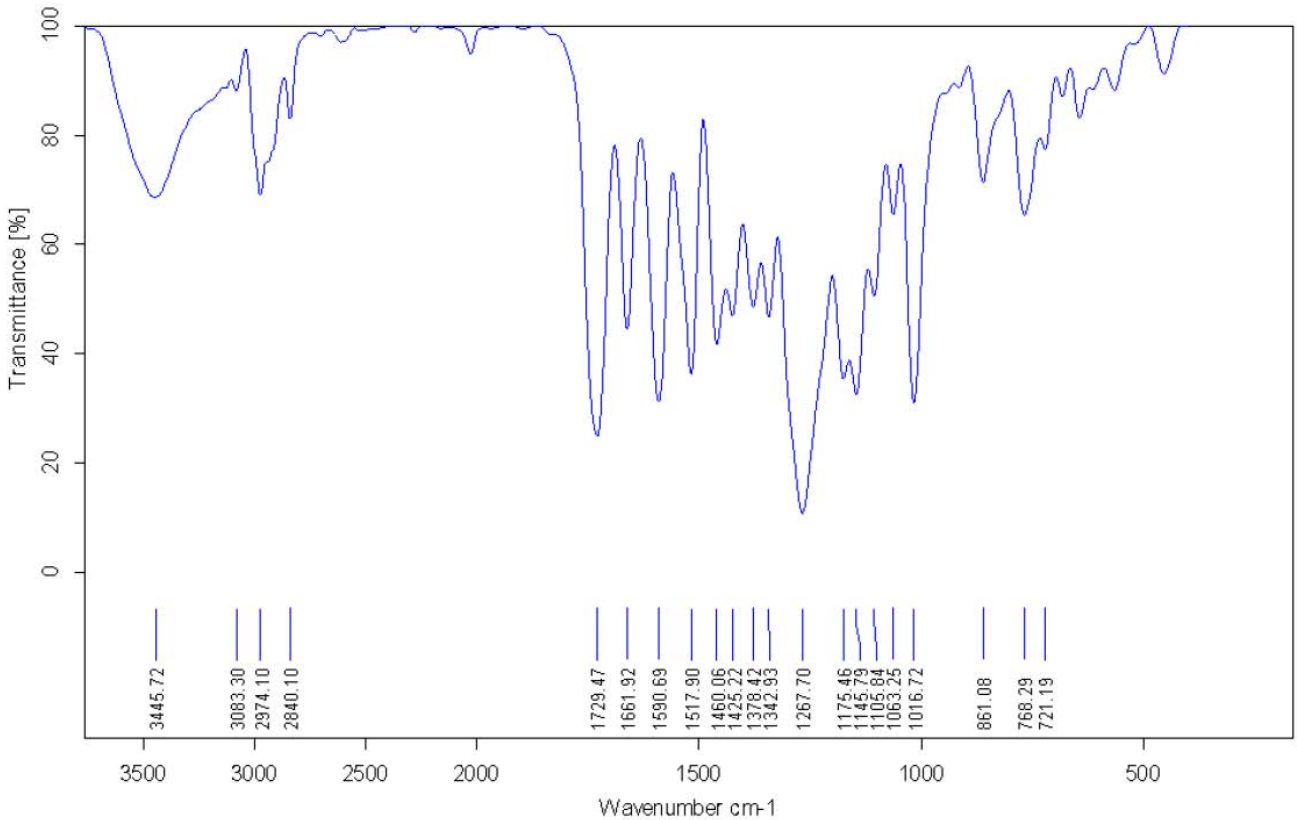

IR spectra of compound **3n**



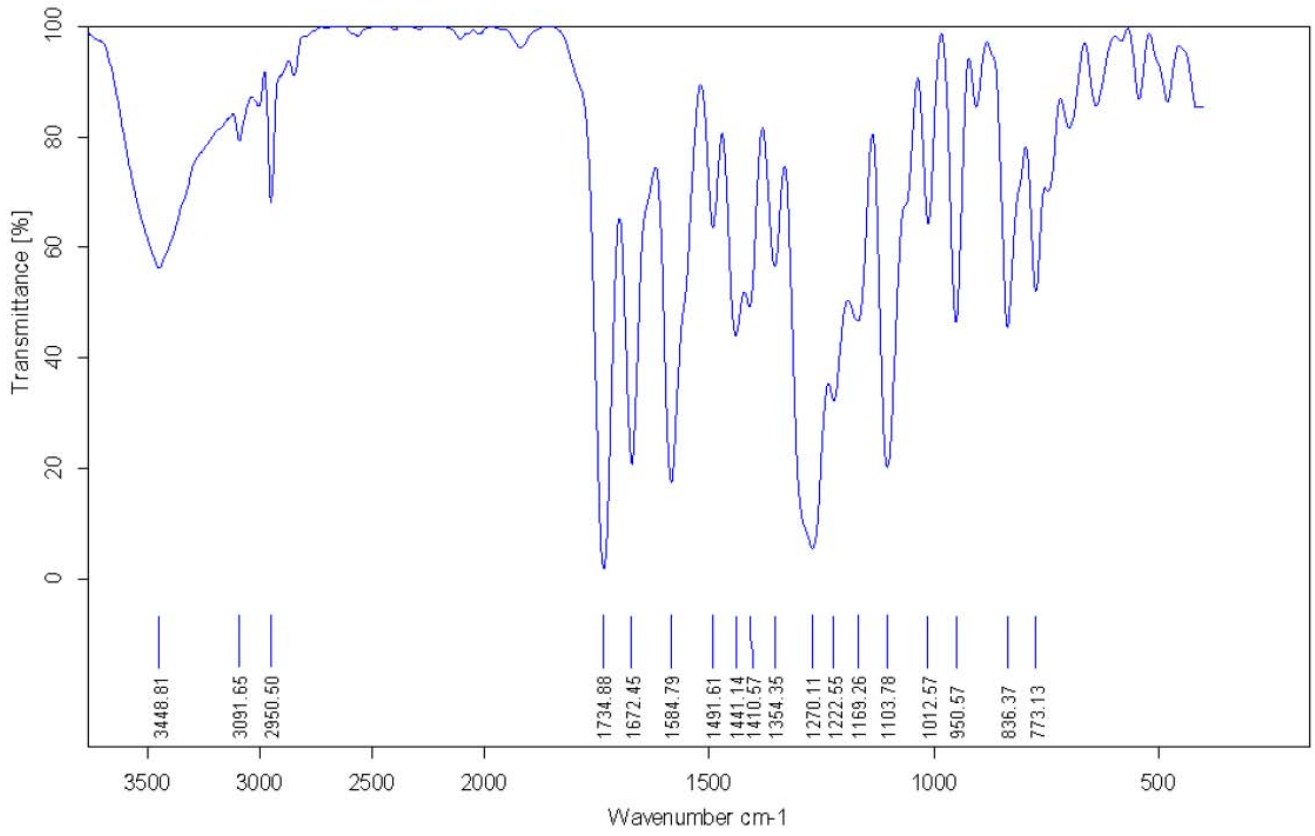
IR spectra of compound **3o**



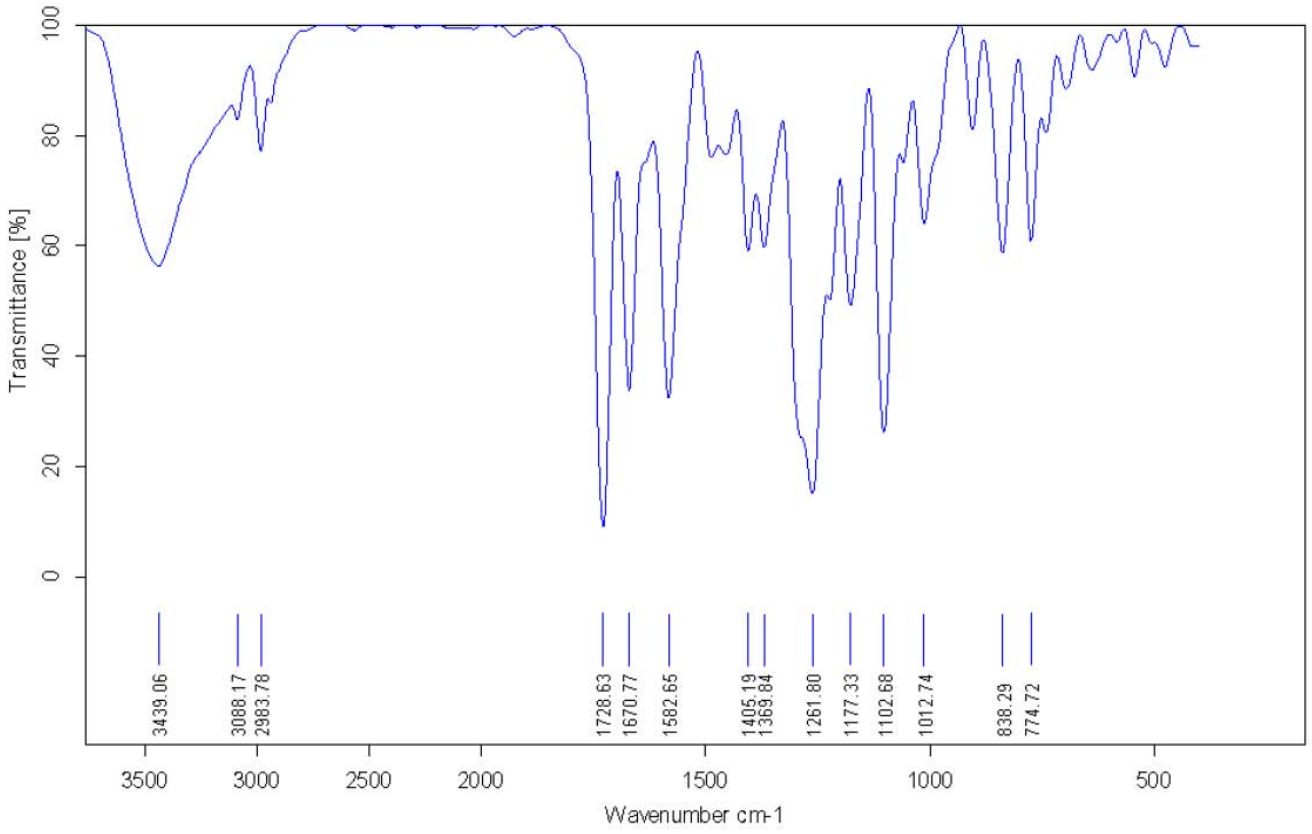

IR spectra of compound **3p**



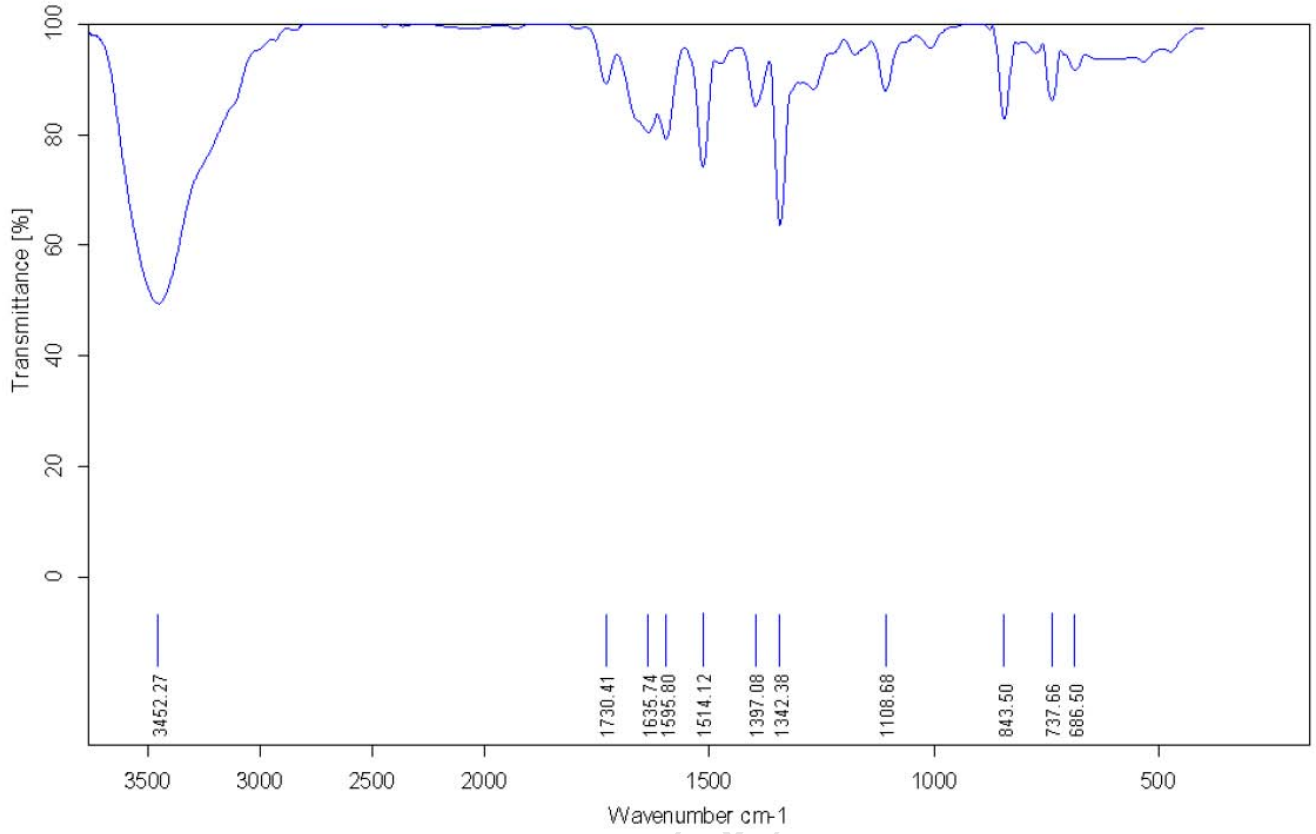
IR spectra of compound **3q**




IR spectra of compound **3r**



IR spectra of compound **3s**



## X-ray crystallography Data of 3i

Single crystals of compound **3i** were measured on a Rigaku RAXIS-RAPID single-crystal diffractometer. The recrystallization solvent of **3i** was methanol.

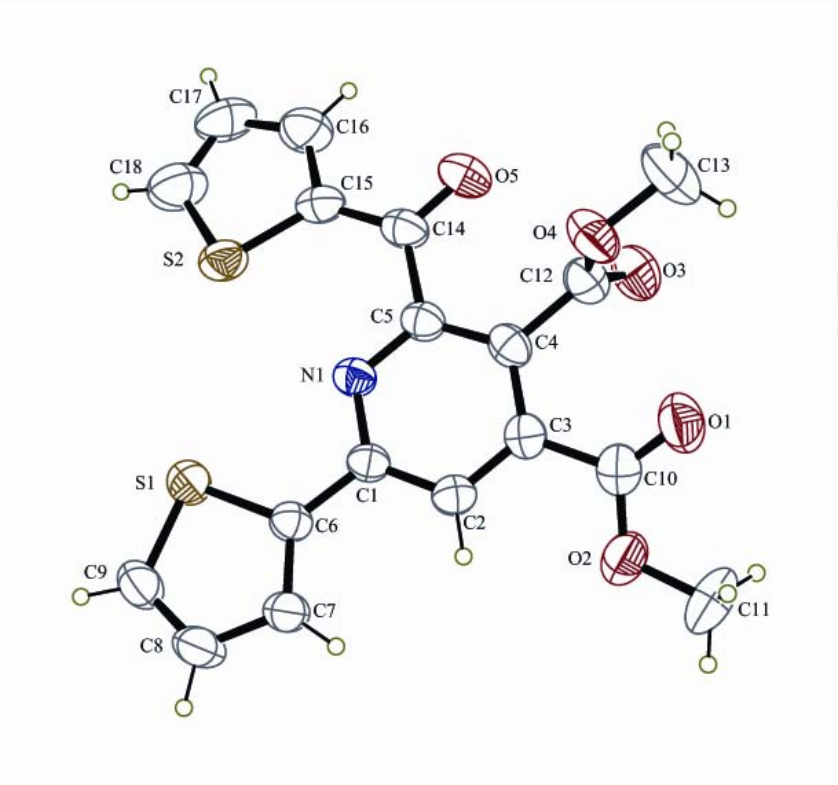



**Fig. S1** X-ray crystal structure of **3i**

**Table S1 X-ray crystallography data of 3i**

| | |
|---|---|
| Formula moiety | $C_{12}H_{13}NO_5S_2$ |
| Formula sum | $C_{12}H_{13}NO_5S_2$ |
| Formula weight | 387.41 |
| Temperature | 296(2)K |
| Crystal system | Monoclinic |
| Space group | C 2/c |
| Unit cell dimensions | a=25.3709(8) Å<br>b=11.4204(4) Å<br>C=13.8513(4) Å<br>alfa=90.00deg.<br>beta=119.1470 (10) deg.<br>Gamma=90.00 deg. |
| Volume | 3505.16 (19) $Å^3$ |
| Z | 4 |
| Calculated density | 1.468 $Mg/M^3$ |
| Absorption coefficient | 0.334 $mm^{-1}$ |
| F(000) | 1600 |
| Crystal size | 0.47×0.41×0.32 mm |
| Theta range for data collection | 3.0 to 27.4 deg. |
| Reflections collected/unique | 13487/3096 [R(int) = 0.0281] |
| Data/restraints/parameters | 3096/10/255 |
| Goodness-of-fit on F2 | 1.074 |
| Final R indices [I>2sigma(I)] | R1=0.0404, wR2=0.1025 |

| | |
|---|---|
| R indices (all data) | R1=0.0504, wR2=0.1159 |

## Reference:

(1) Myers, L. E.; Raines, T. R. *Angew. Chem, Int. Ed.* **2009**, *48*, 2359.