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Graphical Abstract

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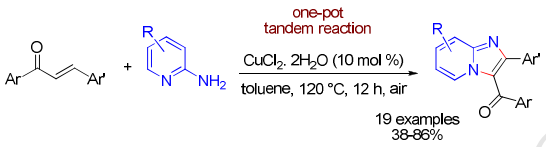

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Synthesis of 3-Aroylimidazo[1,2-*a*]pyridines *via* $CuCl_2$ Catalyzed Tandem Dual Carbon-nitrogen Bonding

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ABSTRACT

A novel tandem approach has been demonstrated for the direct synthesis of bioactive 3-aroylimidazo[1,2-*a*]pyridines from chalcones and 2-aminopyridines. The reported tandem reaction is atom-economical and expected to proceed *via* 1,4-Michael addition followed by copper catalyzed oxidative C−N bonding. Catalytic amount of copper was found to be crucial for the success of tandem reaction and it altered the reaction pathway to furnish entirely new products. This protocol proved to be convenient as reaction proceeds smoothly without the necessity of any ligand in the presence of air as oxidant.

1. Introduction

Imidazo[1,2-*a*]pyridines are the privileged structural motifs with endowed applications in multidisciplinary fields such as material science, organometallics, predominantly in medicinal chemistry.[1-6] These scaffolds are the key structures in many natural products and in commercially available drugs such as zolpidem, alpidem, necopidem, and saripidem (Figure 1). Furthermore, analogues of imidazo[1,2-*a*]pyridines were also studied against broad spectrum of biological targets.[7-12] Because of their diverse applications, synthesis and functionalization of imidazo[1,2-*a*]pyridines is the subject of current interest in many laboratories.[13-29]

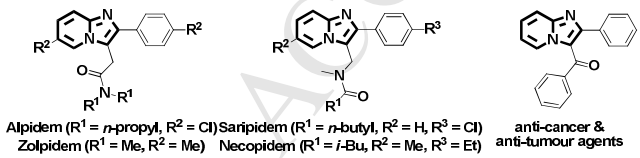
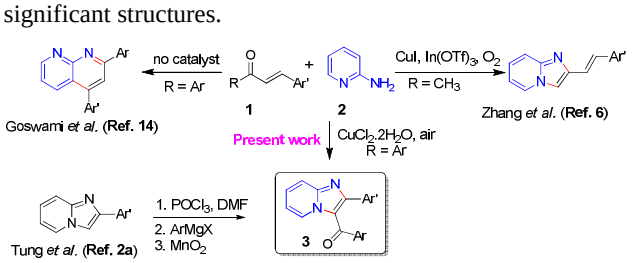


Fig. 1 Bio-active imidazo[1,2-a]pyridine derivatives.

The biological activities of imidazo[1,2-*a*]pyridines has proved to be greatly dependent on substituents at the C-2 and C-3 positions. For example, 3-aroylimidazo[1,2-*a*]pyridines have been studied as anticancer and antitumor agents.[7,30] Direct functionalization of imidazo[1,2-*a*]pyridines with aroyl chloride *via* Friedel-Crafts acylation was unsuccessful so 3-aroylimidazo[1,2-*a*]pyridines were synthesized in three steps; a) formylation of imidazo[1,2-*a*]pyridines, b) Grignard reaction of 3-formylimidazo[1,2-*a*]pyridines and c) oxidation (Scheme 1).[7] The Ila group has reported an efficient synthesis of 2-methylthio/alkoxy/amino-3-acyl-imidazo[1,2-*a*]pyridines by copper catalyzed ring closure.[31] Recently, Zhang *et al.* reported an excellent method for the synthesis of 2-alkenylimidazo[1,2-*a*]pyridines *via* copper catalyzed aerobic oxidative cyclization of methyl vinyl ketones (**1**, R = CH_3) and 2-aminopyridines (**2**) (Scheme 1).[32] In spite of the efforts, reports for the synthesis of 3-aroylimidazo[1,2-*a*]pyridines (**3**)[33,7,34] under ligand/additive-free aerobic conditions are rare.[35] Thus, there is an intrinsic need to develop a straightforward method for the synthesis of these biologically significant structures.



Scheme 1 Reactions of chalcones with 2-aminopyridines and synthesis of 3-aroylimidazo[1,2-*a*]pyridines.

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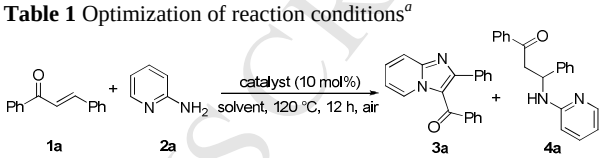
Transition metal catalyzed cross coupling reactions are of utmost importance and an ever growing part of the arsenal of useful synthetic tools available in modern organic chemistry.[36-38] Highly abundant and inexpensive copper salts have been employed to a great extent as effective catalysts for these sequential bond forming step-economy reactions.[39] The recent developments in copper catalyzed C−C and C−heteroatom bond forming reactions[40] have attracted the attention of the synthetic community to revisit the classical routes for revitalization as well as to construct the novel libraries for biological screenings. With the multiple reactive sites, chalcones have been proven to be important organic scaffolds. Particularly, copper catalyzed oxidative cyclizations of chalcones delivered a variety of heterocycles with high regioselectivities.[41,42] In the pursuit of our ongoing interest for the synthesis and functionalization of imidazo[1,2-*a*]pyridines,[43,44,13,45-47] herein we wish to disclose our recent findings for the synthesis of 3-aroylimidazo[1,2-*a*]pyridines (**3**) *via* copper catalyzed tandem reaction between chalcones (1-aryl-3-arylprop-2-en-1-one) (**1**) and 2-aminopyridines (**2**) (Scheme 1). The reported novel tandem approach is practical and expected to proceed *via* initial 1,4-Michael addition followed by copper catalyzed oxidative C−N bond formation to provide medicinally important 2-aryl-3-aroylimidazo[1,2-*a*]pyridines in one step.

2. Results and discussion

We envisioned that the reaction between chalcones and 2-aminopyridines in the presence of a copper catalyst could lead to the formation of 2-aryl-3-aroylimidazo[1,2-*a*]pyridines by oxidative cyclization, which could be a potential alternative for the synthesis of these motifs, as Friedel-Crafts aroylations of imidazo[1,2-*a*]pyridines were unsuccessful.[7] We were astonished to notice that Goswami and co-workers have already reported the reaction between these precursors, which resulted in exclusive formation of 1,8-naphthyridines *via* ring closure condensation followed by spontaneous aromatization with microwave assistance (Scheme 1).[48] Despite this report, a model reaction has been conducted using 1,3-diphenylprop-2-en-1-one (**1a**) and 2-aminopyridine (**2a**) in presence of catalytic amount of copper iodide in toluene at 120 °C for 12 h (Table 1). To our delight, expected 2-phenyl-3-benzoylimidazo[1,2-*a*]pyridine (**3a**) was isolated in 14% yield. Interestingly, neither the Michael adduct (**4a**) nor the 1,8-naphthyridine derivative were detected in the reaction under these conditions. The structure of **3a** was elucidated by IR and NMR spectroscopic data. In the IR spectrum of **3a**, a strong peak appeared at 1597 cm^{-1} for C=O (stretching) and in the ^1H NMR spectrum a characteristic doublet appeared at δ 9.55 for the C-5 proton and the carbonyl carbon appeared at δ 187.36 along with all other expected carbons in the ^{13}C NMR spectrum. The HRMS of **3a** displayed a peak at 299.1184 for $[M+H]^+$, further confirming the structure of the product.

With these results in hand, we further undertook the optimization of reaction condition by varying catalysts in conjunction with different solvents for the tandem reaction (Table 1). After screening a set of different copper catalysts for the synthesis of **3a**, $CuCl_2.2H_2O$ was found to give the highest yield (81%) of tandem product **3a** (Table 1, entry 7). Among other copper salts screened, $CuBr_2$, $Cu(OTf)_2$, $Cu(OAc)_2$ and CuOTf resulted in moderate to good yields of **3a**, whereas only Michael adduct (**4a**) was obtained in the case of CuO (entries 2-6). CuBr and $CuSO_4$ produced only traces of **3a** with major amount being unreacted substrates (entries 8-9). With an ambiguity, some Lewis as well as Bronsted acids were screened for the tandem cyclization. It was realized that $Sc(OTf)_3$, TFA, and AcOH were completely ineffective for this transformation while in case of $BF_3.Et_2O$, traces of **3a** was observed (Table 1, entries 10-13). These results indicated that the copper catalyst was crucial for the success of the tandem cyclization. With $CuCl_2.2H_2O$ as the optimum catalyst, we further focussed on finding the effect of solvent for the tandem process. Excitingly, toluene was proved to be an ideal choice among the solvents investigated, while other solvents were proved to be less effective for the tandem cyclization (Table 1, entries 14-18). Subsequently, effect of catalyst loading was also investigated. With increasing $CuCl_2.2H_2O$ loading from 10 mol % to 30 mol % there was slight improvement in the yield of 3**a** (Table 1, entries 20-21). However, decreasing $CuCl_2.2H_2O$ loading from 10 mol % to 5 mol % resulted in reduction of the yield of 3**a** to 50% (Table 1, entry 22). It should be noted that the same reaction under microwave irradiation resulted Michael adduct (**4a**) as a major product (Table 1, entry 23).

Table 1 Optimization of reaction conditions[a]



Entry	Catalyst	Solvent	Yield (%)[b]
1	CuI	toluene	14
2	$CuBr_2$	toluene	60
3	$Cu(OTf)_2$	toluene	76
4	$Cu(OAc)_2$	toluene	67
5	CuO	toluene	45[c]
6	CuOTf	toluene	34
7	$CuCl_2.2H_2O$	toluene	81
8	CuBr	toluene	traces
9	$CuSO_4$	toluene	traces
10	$Sc(OTf)_3$	toluene	NR[d]
11	CF_3CO_2H	toluene	NR[d]
12	CH_3CO_2H	toluene	NR[d]
13	$BF_3.Et_2O$	toluene	traces
14	$CuCl_2.2H_2O$	benzene	15
15	$CuCl_2.2H_2O$	DMF	14
16	$CuCl_2.2H_2O$	THF	44
17	$CuCl_2.2H_2O$	1,4-dioxane	32
18	$CuCl_2.2H_2O$	MeCN	40
19	$CuCl_2.2H_2O$	toluene	60
20	$CuCl_2.2H_2O$	toluene	82[e]
21	$CuCl_2.2H_2O$	toluene	87[f]
22	$CuCl_2.2H_2O$	toluene	50[g]
23	$CuCl_2.2H_2O$	toluene	54[c,h]

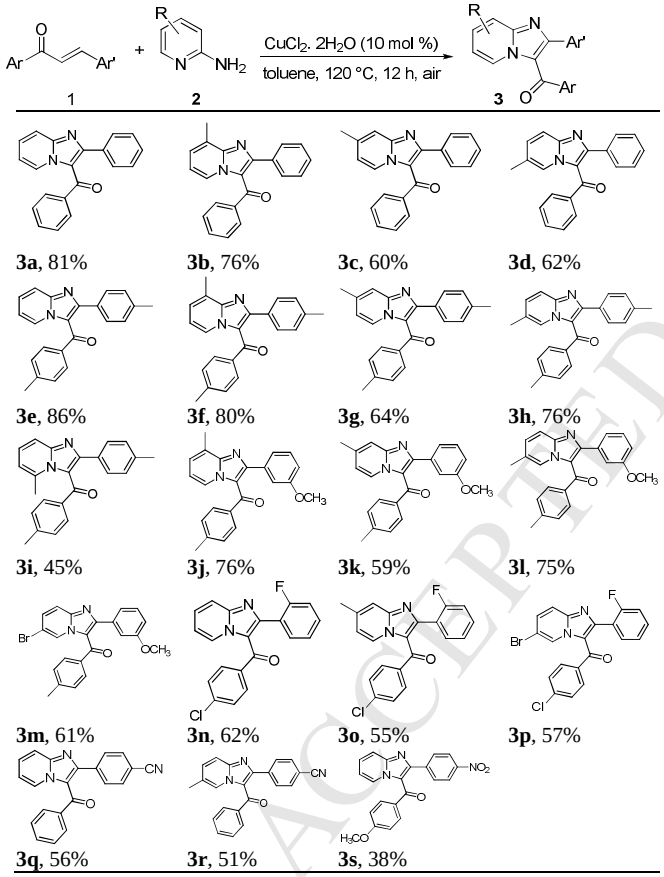
[a] Reagents and conditions: **1a** (1.0 mmol), **2a** (1.2 mmol), catalyst (10 mol %), solvent (5 mL), 120 °C, 12 h, ambient air.
[b] Isolated yields.
[c] Yield corresponds to **4a** (1,4-Michael adduct, 1,3-diphenyl-3-(pyridin-2-ylamino)propan-1-one.
[d] No reaction.
[e] 20 mol % of catalyst was used.
[f] 30 mol % of catalyst was used.
[g] 5 mol % of catalyst was used. [h]MW (120 °C, 30 min, 250 psi, 300 W).

The standardized condition is inherently modular and allowed assimilation of substituents at any site of imidazo[1,2-*a*]pyridines (Table 2). Initially, a wide variety of 2-aminopyridines (**2**) with substitutions at various positions were reacted with **1a** under the optimized reaction conditions, and moderate to high yields of tandem oxidative cyclization products were obtained. A labile bromo substituent at the C-5 position was well tolerated under the reaction conditions to afford the tandem products in good

yields (Table 2, **3m** and **3p**). Lower yields of 3-aroylimidazo[1,2-*a*]pyridines were observed for 2-amino-6-methylpyridine; this may be due to the steric congestion (Table 2, **3i**). Unfortunately, desired product was not observed when 2-amino-5-nitropyridine was reacted with **1a**.

With regard to substitutions of aryl rings on chalcones, a range of diverse groups could be employed, which demonstrates the high level of flexibility of the present approach. For example, chalcone derivatives bearing substituents like methyl, methoxy, fluoro, chloro, bromo, nitro and cyano at *ortho*, *meta* and *para* positions on aryl rings (Ar and Ar') were well tolerated to afford the desired products in good yields (Table 2, entries **3e-s**). Generally, chalcones bearing electron donating substituents on the Ar and/or Ar' rings afforded higher yields of tandem products **3** as compared with the chalcones bearing electron withdrawing groups. The electron withdrawing substituents such as nitro and cyano on Ar' of chalcones greatly influenced the yields of tandem products (Table 2, entries **3q-s**). It was also observed that the chalcones with *ortho*-substituted aryl rings (Ar') produced lower yields of tandem product (Table 2, entries **3n-p**). Structures of all the synthesized 3-aroylimidazo[1,2-*a*]pyridines (**3**) were confirmed by IR and NMR spectroscopy and HRMS data.

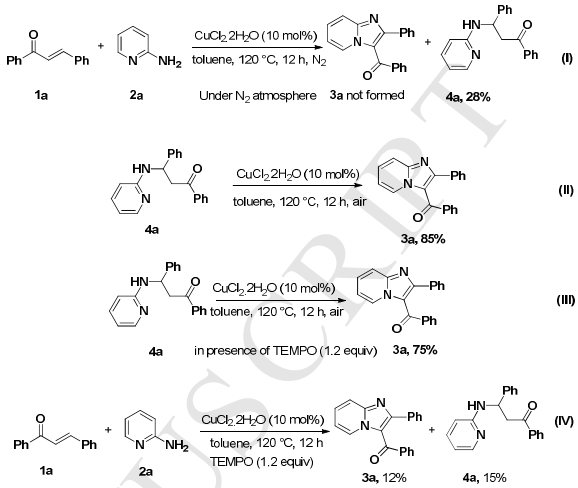
Table 2 Synthesis of 3-aroylimidazo[1,2-*a*]pyridines **3**[a,b]



[a] Reagents and conditions: **1** (1.0 mmol), **2** (1.2 mmol), $CuCl_2.2H_2O$ (10 mol %), toluene (5 mL), 120 °C, 12 h, ambient air.

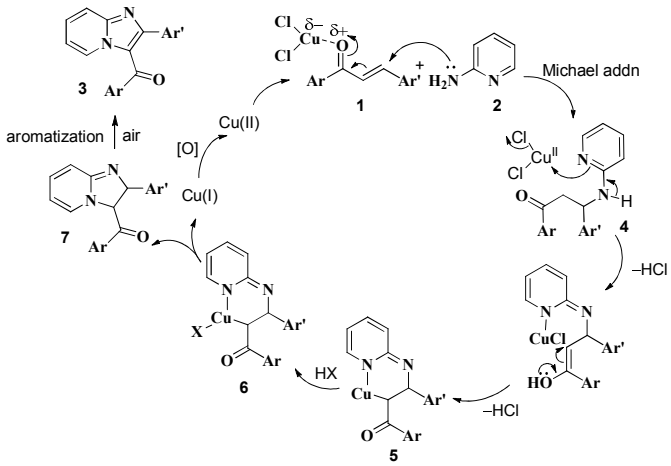
[b] Isolated yields.

Some control experiments have been performed to explore the mechanism for the proposed tandem reaction (Scheme 2). When the chalcone (**1a**) was reacted with **2a** in the presence of nitrogen atmosphere, moderate yield of Michael adduct (**4a**) was obtained without formation of the cyclized product (**3a**) clarifies the crucial role of aerobic conditions for the success of tandem reaction (Scheme 2, eq **I**). When Michael adduct (**4a**) was subjected to the optimized reaction conditions, quantitative conversion was observed (isolated yield 85%, Scheme 2, eq **II**). This observation suggests that the key intermediate in the reported tandem process is **4a**. When radical scavenger TEMPO (1.2 equiv) was used in the oxidative cyclization of the Michael adduct (**4a**), there was minimal reduction in yields were observed, which confirms that the oxidative cyclization proceeds through a non-radical mechanism pathway (Scheme 2, eq **III**). Surprisingly, only traces of product (**3a**) were observed, together with low yields of the Michael adduct, when TEMPO was used in the standard reaction (Scheme 2, eq **IV**).



Scheme 2 Control experiments

Based on the results obtained and recent literature,[8] the plausible mechanism for the formation of 3-aroylimidazo[1,2-*a*]pyridines (**3**) is shown in Scheme 3. It is believed that initially $CuCl_2$ assists in the Michael addition of 2-aminopyridine to give the Michael adduct, 1,3-diaryl-3-(pyridin-2-ylamino)propan-1-one (**4**). Concurrent binding of pyridinium nitrogen followed by the enolic carbon to the copper salt provides intermediate **5**. Oxidation of **5** to **6** followed by reductive elimination produces intermediate **7**, which on rapid oxidative aromatization under aerobic conditions leads to the tandem product, 3-aroylimidazo[1,2-*a*]pyridines (**3**). Regeneration of Cu(II) from Cu(I) under aerobic oxygen completes the catalytic cycle.[15]



Scheme 3 Plausible mechanism for the formation of **3** by copper catalyzed tandem reaction between **1** and **2**.

3. Conclusion

In summary, we have demonstrated a straightforward, atom-economical, high yielding one-pot procedure for the synthesis of bioactive 3-aroylimidazo[1,2-*a*]pyridines from chalcones and 2-aminopyridines *via* unprecedented $CuCl_2$ catalyzed tandem aza-Michael addition and oxidative C−N coupling. The catalytic amount of copper catalyst was found to be crucial for the success

of tandem reaction, which altered the synthetic pathway of the reaction to give the aforementioned tandem products, whereas entirely dissimilar products were reported in the earlier methods with the same precursors, but in the absence of a copper catalyst. The method allows regioseletive introduction of an aryl ring at the C-2 position and an aroyl group at the C-3 position in single step. Dual C−N bond formation in presence of an economically attractive copper salt, ligand and additive free conditions, and ubiquitous air as an oxidant are the salient features of this protocol.

4. Experimental section

General: Melting points were determined in open capillary tubes on an EZ-Melt Automated melting point apparatus and are uncorrected. Reactions were monitored by using thin layer chromatography (TLC) on 0.2 mm silica gel F254 plates (Merck). The chemical structures of final products were determined by nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) using Bruker AV NMR 300 MHz, Bruker AV 400 MHz and Varian 500 MHz spectrometers. ^{13}C NMR spectra are fully decoupled. Chemical shifts were reported in parts per million (ppm) using deuterated solvent peak or tetramethylsilane (internal) as the standard. The HRMS data were recorded in ESI mode using Agilent Q-TOF Mass spectrometer, and IR spectra were obtained an using ABB Bomen MB 3000 FTIR instrument. The α,β-unsaturated ketones (chalcones) **1** were prepared by the treatment of an appropriate acetophenone with benzaldehydes in the presence of sodium hydroxide as reported in literature.[14] All other chemicals were obtained from the commercial suppliers and used without further purification.

*Procedure for synthesis of 3-aroylimidazo[1,2-a]pyridine (**3a**)* A clean oven dried 10 ml RB flask was charged with chalcone (**1a**) (200 mg, 0.961 mmol), 2-aminopyridine (**2a**) (108 mg, 1.15 mmol), $CuCl_2.2H_2O$ (16 mg, 0.096 mmol) and toluene (5.0 ml). The resulting solution was stirred at 120 °C for 12 h under ambient air. On completion, the reaction mass was evaporated to dryness. The crude residue was purified by column chromatography (EtOAc: Hexanes, 2: 3) to obtain phenyl(2-phenylimidazo[1,2-*a*]pyridin-3-yl)methanone (**3a**) in 81% yield (232 mg).

*Phenyl(2-phenylimidazo[1,2-a]pyridin-3-yl)methanone (**3a**):* Yield 81%; Colourless solid; mp 124-127 °C; R_f = 0.63 (30% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.55 (d, *J* = 7.0 Hz, 1H, C-5 ArH), 7.81 (d, *J* = 8.9 Hz, 1H, ArH), 7.57 – 7.45 (m, 3H, ArH), 7.32 (dd, *J* = 7.8, 1.4 Hz, 2H, ArH), 7.29 – 7.21 (m, 1H, ArH), 7.17 – 7.02 (m, 6H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.4 (C=O), 155.0, 147.4, 138.7, 134.0, 131.7, 130.2, 129.6, 129.2, 128.3, 128.2, 127.7, 120.0, 117.5, 114.6; IR (KBr) *v*: 3070, 1597 ($C=O_{str}$), 1388, 1326, 1218 cm^{-1}; HRMS calcd for $C_{20}H_{15}N_2O$ 299.1179 found 299.1184 $[M+H]^+$.

*(8-Methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)(phenyl) methanone (**3b**):* Yield 76%; Colourless solid; mp 139-141 °C; R_f = 0.86 (20% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (d, *J* = 4.9 Hz, 1H, C-5 ArH), 7.53 (d, *J* = 6.5 Hz, 2H, ArH), 7.40 – 7.32 (m, 3H, ArH), 7.31 – 7.24 (m, 1H, ArH), 7.17 – 7.07 (m, 5H, ArH), 7.06 – 7.03 (m, 1H, ArH), 2.77 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5 (C=O), 154.6, 147.7, 138.9, 134.3, 131.6, 130.3, 129.6, 128.1, 127.8, 127.7, 127.5, 126.0, 120.5, 114.6, 17.2; IR (KBr) *v*: 3063, 1606 ($C=O_{str}$), 1466, 1388, 1250, 910, 702 cm^{-1}; HRMS calcd for $C_{21}H_{17}N_2O$ 313.1335 found 313.1333 $[M+H]^+$.

*(7-Methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)(phenyl) methanone (**3c**):* Yield 60%; Off-white solid; mp 140-142 °C; R_f = 0.71 (25% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (d, *J* = 3.0 Hz, 1H, C-5 ArH), 7.59 (s, 1H, ArH), 7.52 (d, *J* = 6.2 Hz, 2H, ArH), 7.34 (t, *J* = 11.5 Hz, 2H, ArH), 7.28 (d, *J* = 8.5 Hz, 1H, ArH), 7.18 – 7.06 (m, 5H, ArH), 6.97 (d, *J* = 0.9 Hz, 1H, ArH), 2.54 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.1 (C=O), 155.4, 147.9, 140.9, 138.8, 134.2, 131.6, 130.2, 129.5, 128.2, 127.8, 127.7, 127.5, 117.1, 116.1, 21.6; IR (KBr) *v*: 3060, 1605 ($C=O_{str}$), 1466, 1396, 918, 694 cm^{-1}; HRMS calcd for $C_{21}H_{17}N_2O$ 313.1335 found 313.1335 $[M+H]^+$.

*(6-Methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)(phenyl) methanone (**3d**):* Yield 62%; Colorless solid; mp 156-158 °C; R_f = 0.66 (30% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 1H, C-5 ArH), 7.73 (d, *J* = 8.9 Hz, 1H, ArH), 7.53 (d, *J* = 7.2 Hz, 2H, ArH), 7.40 (d, *J* = 8.9 Hz, 1H, ArH), 7.33 (d, *J* = 6.7 Hz, 2H, ArH), 7.31 – 7.24 (m, 1H, ArH), 7.17 – 7.06 (m 5H, ArH), 2.47 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3 (C=O), 154.9, 146.4, 138.8, 134.2, 132.1, 131.7, 130.2, 129.6, 128.1, 127.7, 127.7, 126.2, 124.6, 119.9, 116.7, 18.5; IR (KBr) *v*: 3063, 1605 ($C=O_{str}$), 1466, 1389, 903, 733 cm^{-1}; HRMS calcd for $C_{21}H_{17}N_2O$ 313.1335 found 313.1339 $[M+H]^+$.

*p-Tolyl(2-p-tolylimidazo[1,2-a]pyridin-3-yl)methanone (**3e**):* Yield 86%; Colorless solid; mp 111-114 °C; R_f = 0.67 (30% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (d, *J* = 6.4 Hz, 1H, C-5 ArH), 7.80 (d, *J* = 8.7 Hz, 1H, ArH), 7.52 (d, *J* = 7.3 Hz, 1H, ArH), 7.46 (d, *J* = 7.4 Hz, 2H, ArH), 7.29 – 7.22 (m, 2H, ArH), 7.07 (t, *J* = 6.3 Hz, 1H, ArH), 6.93 – 6.85 (m, 4H, ArH), 2.28 (s, 6H, CH_3, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3 (C=O), 154.5, 147.3, 142.5, 138.1, 136.0, 131.1, 130.1, 129.8, 128.8, 128.4, 128.1, 120.0, 117.3, 114.3, 21.5, 21.2; IR (KBr) *v*: 3063, 1605 ($C=O_{str}$), 1504, 1412, 1381, 903, 818 cm^{-1}; HRMS calcd for $C_{22}H_{19}N_2O$ 327.1492 found 327.1500 $[M+H]^+$.

*(8-Methyl-2-p-tolylimidazo[1,2-a]pyridin-3-yl)(p-tolyl)meth-anone (**3f**):* Yield 80%; Colourless solid; mp 127-129 °C; R_f = 0.70 (25% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34 (d, *J* = 5.5 Hz, 1H, C-5 ArH), 7.45 (d, *J* = 7.2 Hz, 2H, ArH), 7.34 – 7.20 (m, 3H, ArH), 7.00 – 6.96 (m, 1H, ArH), 6.93 – 6.85 (m, 4H, ArH), 2.75 (s, 3H, CH_3), 2.27 (s, 6H, CH_3, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.4 (C=O), 154.1, 147.5, 142.3, 137.9, 136.1, 131.5, 130.2, 129.8, 128.4, 128.4, 127.7, 127.3, 125.8, 120.4, 114.3, 21.5, 21.2, 17.1; IR (KBr) *v*: 3060, 1605 ($C=O_{str}$), 1381, 910, 733 cm^{-1}; HRMS calcd for $C_{23}H_{21}N_2O$ 341.1648 found 341.1659 $[M+H]^+$.

*(7-Methyl-2-p-tolylimidazo[1,2-a]pyridin-3-yl)(p-tolyl)meth-anone (**3g**):* Yield 64%; Pale yellow solid; mp 190-192 °C; R_f = 0.68 (25% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (d, *J* = 6.9 Hz, 1H, C-5 ArH), 7.56 (s, 1H, ArH), 7.43 (d, *J* = 7.4 Hz, 2H, ArH), 7.24 (d, *J* = 7.3 Hz, 2H, ArH), 6.92 – 6.83 (m, 5H, ArH), 2.52 (s, 3H, CH_3), 2.27 (s, 6H, CH_3, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.0 (C=O), 154.9, 147.8, 142.2, 140.4, 138.0, 136.2, 131.3, 130.1, 129.7, 128.4, 127.4, 119.7, 116.8, 116.0, 21.6, 21.4, 21.2; IR (KBr) *v*: 3024, 1597 ($C=O_{str}$), 1474, 1227, 926, 703 cm^{-1}; HRMS calcd for $C_{23}H_{21}N_2O$ 341.1648 found 341.1647 $[M+H]^+$.

*(6-Methyl-2-p-tolylimidazo[1,2-a]pyridin-3-yl)(p-tolyl)meth-anone (**3h**):* Yield 76%; Colourless solid; mp 149-151 °C; R_f = 0.60 (30% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H, C-5 ArH), 7.70 (d, *J* = 8.9 Hz, 1H, ArH), 7.45 (d, *J* = 7.4 Hz, 2H, ArH), 7.36 (d, *J* = 8.9 Hz, 1H, ArH), 7.24 (d, *J* = 7.3 Hz, 2H, ArH), 6.92 – 6.85 (m, 4H, ArH), 2.44 (s, 3H, CH_3), 2.27 (s, 6H, CH_3, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.2 (C=O), 154.4, 146.3, 142.3, 137.9, 136.1, 131.7, 131.3, 130.1, 129.8, 128.4, 126.0, 124.2, 119.8, 116.6, 21.5, 21.2, 18.5; IR (KBr) *v*:

3063, 1605 (C=O_{str}), 1504, 1412, 1381, 903, 818 cm^{-1}; HRMS calcd for $C_{23}H_{21}N_2O$ 341.1648 found 341.1657 $[M+H]^+$.

*(5-Methyl-2-p-tolylimidazo[1,2-a]pyridin-3-yl)(p-tolyl) methanone (**3i**):* Yield 45%; Colorless solid; mp 134-136 °C; R_f = 0.69 (25% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.68 (m, 3H, ArH), 7.47 (d, *J* = 3.6 Hz, 2H, ArH), 7.39 – 7.25 (m, 1H, ArH), 7.09 – 6.90 (m, 4H, ArH), 6.75 (s, 1H, ArH), 2.43 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.29 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5 (C=O), 149.0, 147.5, 144.4, 137.9, 137.5, 136.0, 130.7, 130.5, 129.3, 129.0, 128.8, 127.0, 120.1, 115.2, 114.5, 22.1, 21.7, 21.2; IR (KBr) *v*: 3063, 1651, 1597 (C=O_{str}), 1474, 1381, 1234, 926, 733 cm^{-1}; HRMS calcd for $C_{23}H_{21}N_2O$ 341.1648 found 341.1652 $[M+H]^+$.

*(2-(3-Methoxyphenyl)-8-methylimidazo[1,2-a]pyridin-3-yl)(p-tolyl)methanone (**3j**):* Yield 76%; Red viscous liquid; R_f = 0.46 (50% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 9.36 (d, *J* = 6.6 Hz, 1H, C-5 ArH), 7.47 (d, *J* = 7.2 Hz, 2H, ArH), 7.31 (dd, *J* = 9.0, 4.1 Hz, 1H, ArH), 7.02 – 6.94 (m, 3H, ArH), 6.94 (d, *J* = 7.4 Hz, 2H, ArH), 6.89 (s, 1H, ArH), 6.72 (d, *J* = 7.5 Hz, 1H, ArH), 3.66 (s, 3H, OCH_3), 2.75 (s, 3H, CH_3), 2.28 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.2 (C=O), 159.0, 153.7, 147.5, 142.4, 136.2, 135.6, 129.7, 128.9, 128.4, 127.8, 127.5, 125.9, 123.0, 120.6, 115.0, 114.8, 114.5, 55.2, 21.5, 17.1; IR (CCl_4) *v*: 3055, 2955, 1606 (C=O_{str}), 1474, 1285, 803, 756 cm^{-1}; HRMS calcd for $C_{23}H_{21}N_2O_2$ 357.1598 found 357.1602 $[M+H]^+$.

*(2-(3-Methoxyphenyl)-7-methylimidazo[1,2-a]pyridin-3-yl)(p-tolyl)methanone (**3k**):* Yield 59%; Pale yellow sold; mp 110-112 °C; R_f = 0.41 (65% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 9.43 – 9.41 (m, 1H, C-5 ArH), 7.58 – 7.56 (m, 1H, ArH), 7.47 (d, *J* = 3.4 Hz, 2H, ArH), 7.11 – 6.92 (m, 5H, ArH), 6.87 (s, 1H, ArH), 6.75 (d, *J* = 0.4 Hz, 1H, ArH), 3.66 (s, 3H, OCH_3), 2.54 (s, 3H, CH_3), 2.29 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9 (C=O), 159.0, 154.5, 147.7, 142.4, 140.6, 136.2, 135.5, 129.7, 128.8, 128.4, 127.4, 122.9, 119.9, 117.0, 116.0, 115.0, 114.8, 55.2, 21.6, 21.5; IR (KBr) *v*: 3063, 2955, 1606 (C=O_{str}), 1455, 1281, 833, 746 cm^{-1}; HRMS calcd for $C_{23}H_{21}N_2O_2$ 357.1598 found 357.1598 $[M+H]^+$.

*(2-(3-Methoxyphenyl)-6-methylimidazo[1,2-a]pyridin-3-yl)(p-tolyl) methanone (**3l**):* Yield 75%; Off-white solid; mp 83-85 °C; R_f = 0.40 (60% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 9.32 (s, 1H, C-5 ArH), 7.73 (d, *J* = 8.4 Hz, 1H, ArH), 7.49 (d, *J* = 6.4 Hz, 2H, ArH), 7.39 (d, *J* = 8.2 Hz, 1H, ArH), 7.10 – 6.92 (m, 4H, ArH), 6.89 (s, 1H, ArH), 6.74 (d, *J* = 5.9 Hz, 1H, ArH), 3.66 (s, 3H, OCH_3), 2.46 (s, 3H, CH_3), 2.29 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.1 (C=O), 159.0, 154.0, 146.2, 142.5, 136.2, 135.4, 131.9, 129.7, 128.8, 128.5, 126.0, 124.4, 122.9, 119.9, 116.7, 115.0, 114.7, 55.2, 21.5, 18.5; IR (KBr) *v*: 3055, 2955, 1606 (C=O_{str}), 1474, 1281, 833, 756 cm^{-1}; HRMS calcd for $C_{23}H_{21}N_2O_2$ 357.1598 found 357.1597 $[M+H]^+$.

*(6-Bromo-2-(3-methoxyphenyl)imidazo[1,2-a]pyridin-3-yl)(p-tolyl)methanone (**3m**):* Yield 61%; Yellow liquid; R_f = 0.41 (60% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 9.65 (s, 1H, C-5 ArH), 7.71 (d, *J* = 9.2 Hz, 1H, ArH), 7.59 (d, *J* = 9.4 Hz, 1H, ArH), 7.48 (d, *J* = 7.4 Hz, 2H, ArH), 7.06 (t, *J* = 7.5 Hz, 1H, ArH), 6.97 – 6.89 (m, 3H, ArH), 6.88 (s, 1H, ArH), 6.75 (d, *J* = 7.9 Hz, 1H, ArH), 3.66 (s, 3H, OCH_3), 2.29 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.0 (C=O), 159.1, 154.0, 145.6, 143.1, 135.6, 134.8, 132.3, 129.7, 129.0, 128.6, 128.2, 122.9, 120.2, 118.0, 115.3, 114.7, 109.2, 55.2, 21.5; IR (CCl_4) *v*: 3060, 2955, 1606 (C=O_{str}), 1474, 1381, 910, 703 cm^{-1}; HRMS calcd for $C_{22}H_{18}BrN_2O_2$ 421.0546 found 421.0546 $[M+H]^+$ 423.0524 $[M+H+2]^+$.

*(4-Chlorophenyl)(2-(2-fluorophenyl)imidazo[1,2-a]pyridin-3-yl)methanone (**3n**):* Yield 62%; Off-white solid; mp 144-146 °C; R_f = 0.60 (40% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 9.57 (d, *J* = 6.6 Hz, 1H, C-5 ArH), 7.85 (d, *J* = 8.8 Hz, 1H, ArH), 7.61 – 7.49 (m, 2H, ArH), 7.47 (d, *J* = 8.0 Hz, 2H, ArH), 7.24 (d, *J* = 5.4 Hz, 1H, ArH), 7.19 – 7.05 (m, 4H, ArH), 6.72 (t, *J* = 9.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.8 (C=O), 159.1 (d, *J* = 248.7 Hz), 148.5, 147.7, 137.8, 136.9, 131.2 (d, *J* = 2.4 Hz), 131.0, 130.7 (d, *J* = 8.3 Hz), 129.3, 128.3, 127.7, 124.2 (d, *J* = 3.5 Hz), 122.8, 122.8 (d, *J* = 14.1 Hz), 117.7, 115.2 (d, *J* = 22.0 Hz), 114.98; IR (KBr) *v*: 3055, 2924, 1612 (C=O_{str}), 1481, 1227, 1080, 764 cm^{-1}; HRMS calcd for $C_{20}H_{13}ClFN_2O$ 351.0695 found 351.0698 $[M+H]^+$.

*(4-Chlorophenyl)(2-(2-fluorophenyl)-7-methylimidazo[1,2-a]pyridin-3-yl)methanone (**3o**):* Yield 55%; Off-white solid; mp 157-159 °C; R_f = 0.63 (30% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 9.45 (d, *J* = 7.1 Hz, 1H, C-5 ArH), 7.59 (s, 1H, ArH), 7.49 (td, *J* = 7.4, 1.7 Hz, 1H, ArH), 7.46 – 7.41 (m, 2H, ArH), 7.26 – 7.19 (m, 1H, ArH), 7.12 – 7.04 (m, 3H, ArH), 6.99 (dd, *J* = 7.1, 1.6 Hz, 1H, ArH), 6.74 – 6.65 (m, 1H, ArH), 2.54 (s, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 185.6 (C=O), 159.1 (d, *J* = 248.7 Hz), 148.8, 148.2, 141.1, 137.6, 137.0, 131.3 (d, *J* = 2.5 Hz), 130.8 (d, *J* = 8.3 Hz), 130.5, 127.6, 127.5, 124.1 (d, *J* = 3.4 Hz), 122.9 (d, *J* = 14.3 Hz), 120.6, 117.5, 116.2, 115.2 (d, *J* = 22.0 Hz), 21.6; IR(KBr) *v*: 3055, 2965, 1612 (C=O_{str}), 1481, 1227, 1076, 764 cm^{-1}; HRMS calcd for $C_{21}H_{15}ClFN_2O$ 365.0851 found 365.0851 $[M+H]^+$.

*(6-Bromo-2-(2-fluorophenyl)imidazo[1,2-a]pyridin-3-yl)(4-chloro phenyl)methanone (**3p**):* Yield 57%; Off-white solid; mp 172-175 °C; R_f = 0.80 (20% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H, C-5 ArH), 7.75 (d, *J* = 9.3 Hz, 1H, ArH), 7.64 (d, *J* = 9.4 Hz, 1H, ArH), 7.54 (t, *J* = 6.9 Hz, 1H, ArH), 7.46 (d, *J* = 7.4 Hz, 2H, ArH), 7.26 (d, *J* = 5.4 Hz, 1H, ArH), 7.15 – 7.06 (m, 3H, ArH), 6.73 (t, *J* = 9.1 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.7 (C=O), 159.1 (d, *J* = 249.1 Hz), 148.3, 146.07, 138.2, 136.4 (d, *J* = 1.9 Hz), 132.7, 131.2, 131.1, 130.5, 128.3, 127.8, 124.3 (d, *J* = 3.5 Hz), 122.3 (d, *J* = 14.0 Hz), 120.9, 118.1, 115.3 (d, *J* = 22.0 Hz), 109.87; IR (KBr) *v*: 3101, 3055, 2924, 1612 (C=O_{str}), 1481, 1389, 1227, 1080, 764 cm^{-1}; HRMS calcd for $C_{20}H_{12}BrClFN_2O$ 428.9800 found 428.9801 $[M+H]^+$ 430.9780 $[M+H+2]^+$.

*4-(3-Benzoylimidazo[1,2-a]pyridin-2-yl)benzonitrile (**3q**):* Yield 56%; Off-white solid; mp 173-175 °C; R_f = 0.43 (50% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 9.54 (d, *J* = 4.5 Hz, 1H, C-5 ArH), 7.84 (d, *J* = 8.5 Hz, 1H, ArH), 7.59 (d, *J* = 7.3 Hz, 1H, ArH), 7.50 (d, *J* = 6.5 Hz, 2H, ArH), 7.45 (d, *J* = 5.7 Hz, 2H, ArH), 7.39 (d, *J* = 7.9 Hz, 2H, ArH), 7.35 (d, *J* = 6.9 Hz, 1H, ArH), 7.18 – 7.12 (m, 3H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9 (C=O), 152.4, 147.5, 138.7, 138.4, 132.4, 131.4, 130.7, 129.7, 129.5, 128.3, 128.0, 120.4, 118.6, 117.7, 115.2, 111.7; IR (KBr) *v*: 3109, 3070, 2222 (C≡N_{str}), 1612 (C=O_{str}), 1474, 1227, 933, 702 cm^{-1}; HRMS calcd for $C_{21}H_{14}N_3O$ 324.1131 found 324.1131 $[M+H]^+$.

*4-(3-Benzoyl-6-methylimidazo[1,2-a]pyridin-2-yl)benzonitrile (**3r**):* Yield 51%; Pale yellow solid; mp 179-182 °C; R_f = 0.42 (50% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 9.36 (s, 1H, C-5 ArH), 7.73 – 7.71 (m, 1H, ArH), 7.50 – 7.32 (m, 8H, ArH), 7.15 (d, *J* = 5.0 Hz, 2H, ArH), 2.48 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.9 (C=O), 152.2, 146.5, 138.9, 138.6, 132.7, 132.3, 131.4, 130.6, 129.6, 128.0, 126.1, 120.2, 118.7, 116.9, 111.6, 18.6; IR (KBr) *v*: 3102, 3059, 2222 (C≡N_{str}), 1608 (C=O_{str}), 1478, 1232, 933, 699 cm^{-1}; HRMS calcd for $C_{22}H_{16}N_3O$ 338.1288 found 338.1292 $[M+H]^+$.

*(4-Methoxyphenyl)(2-(4-nitrophenyl)imidazo[1,2-a]pyridin-3-yl)methanone (**3s**):* Yield 38%; Pale yellow solid; mp 199-202 °C; R_f = 0.44 (65% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34 (s, 1H, C-5 ArH), 8.03 (d, *J* = 6.9 Hz, 2H, ArH), 7.83 (d, *J* = 8.7 Hz, 1H, ArH), 7.64 – 7.51 (m, 5H, ArH), 7.13 – 7.09 (m, 1H, ArH), 6.66 (d, *J* = 6.8 Hz, 2H, ArH), 3.76 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.6 (C=O), 163.4, 150.3, 147.3, 147.2, 140.7, 132.0, 130.9, 130.8, 129.2, 127.9, 123.0, 120.6, 117.7, 114.9, 113.5, 55.5; IR (KBr) *ν*: 3102, 1597 ($C=O_{str}$), 1512, 1342, 1227, 1026, 756 cm^{-1}; HRMS calcd for $C_{21}H_{16}N_3O_4$ 374.1135 found 374.1132 $[M+H]^+$.

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Supplementary Material

Supplementary data (Copies of the ^{1}H, ^{13}C NMR and HRMS data for compound **3a-s)** associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/.....

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zSupporting Information

Synthesis of 3-Aroylimidazo[1,2-*a*]pyridines *via* $CuCl_2$ Catalyzed Tandem Dual Carbon-nitrogen Bonding

Pinku Kaswan,[a] Kasiviswanadharaju Pericherla,[a] Rajnikant[b] and Anil Kumar*[a]

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[b]*Department of Physics, University of Jammu, Jammu Tawi, 180006, India*

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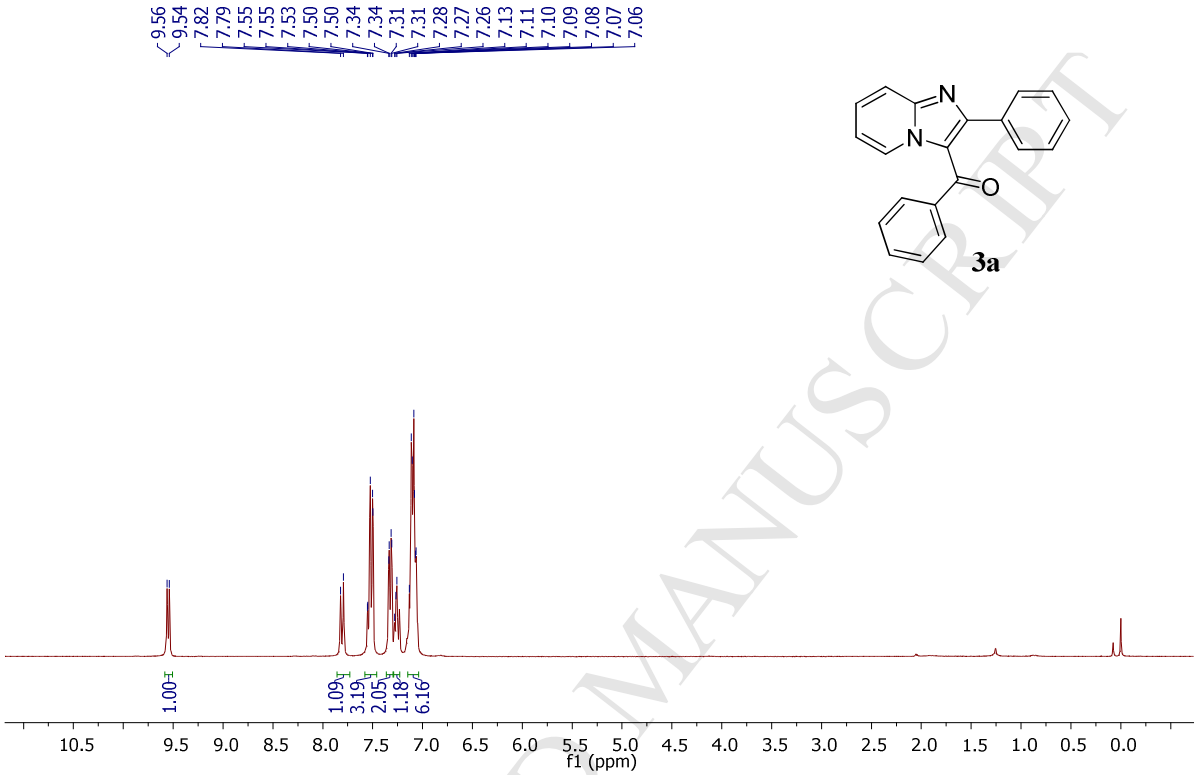
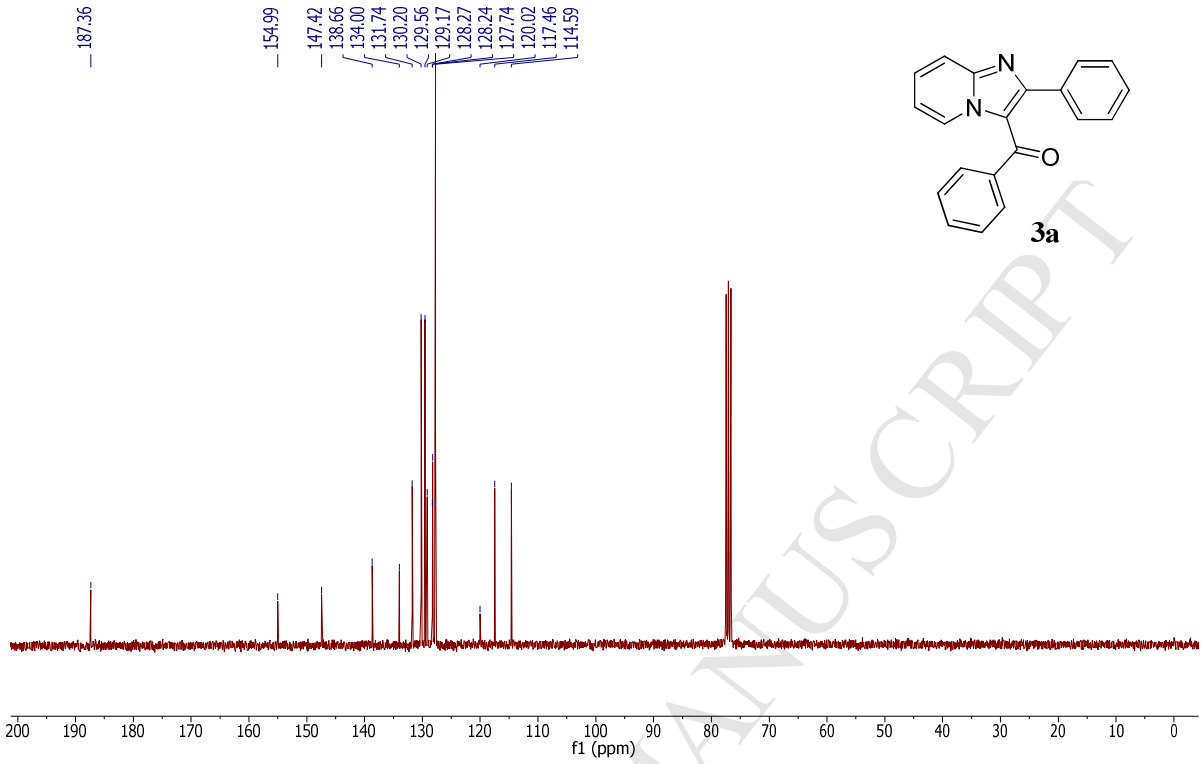
Content

Copies of ^{1}H NMR, ^{13}C NMR and HRMS for **3a-s**

Copies of ^{1}H NMR , ^{13}C NMR and HRMS for 3a-s





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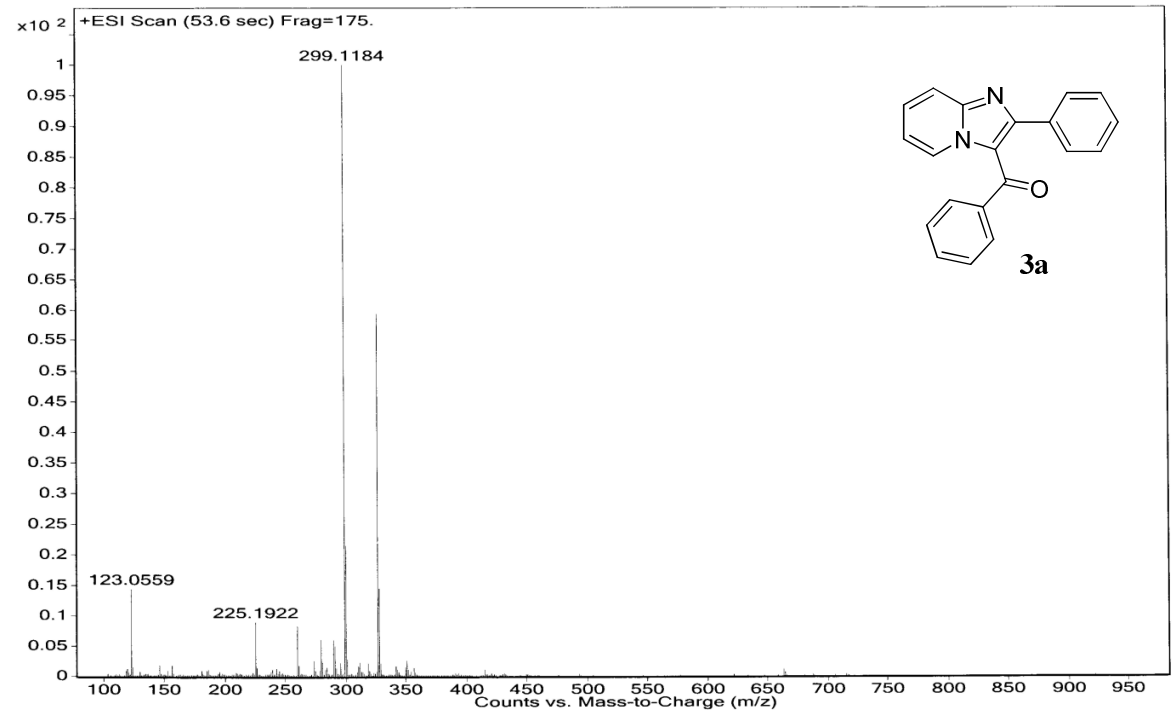

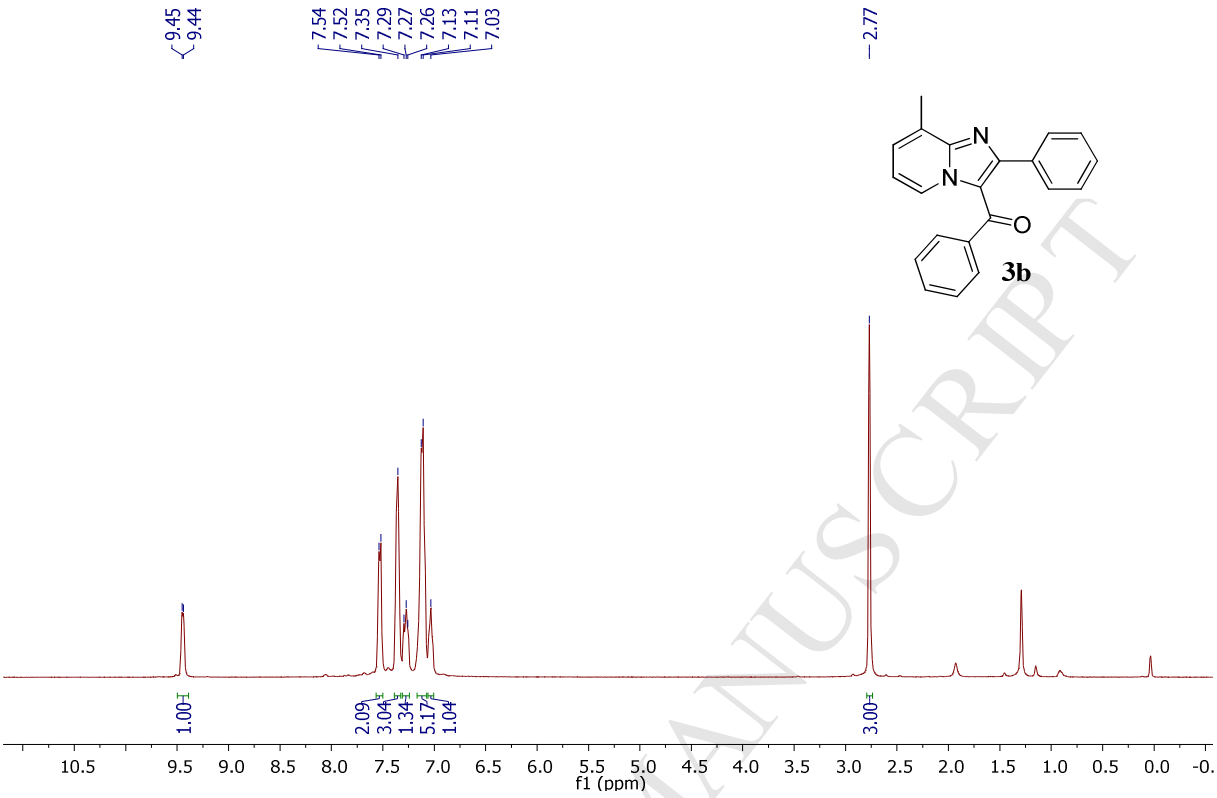

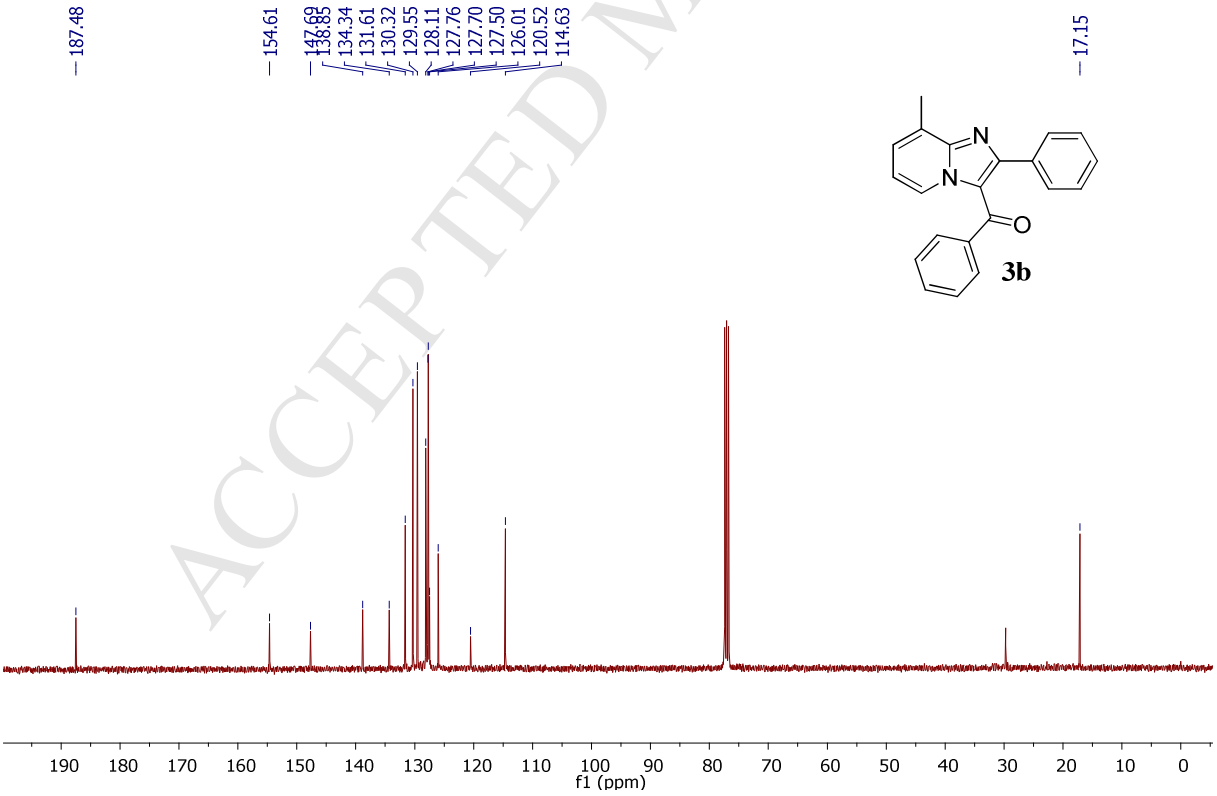

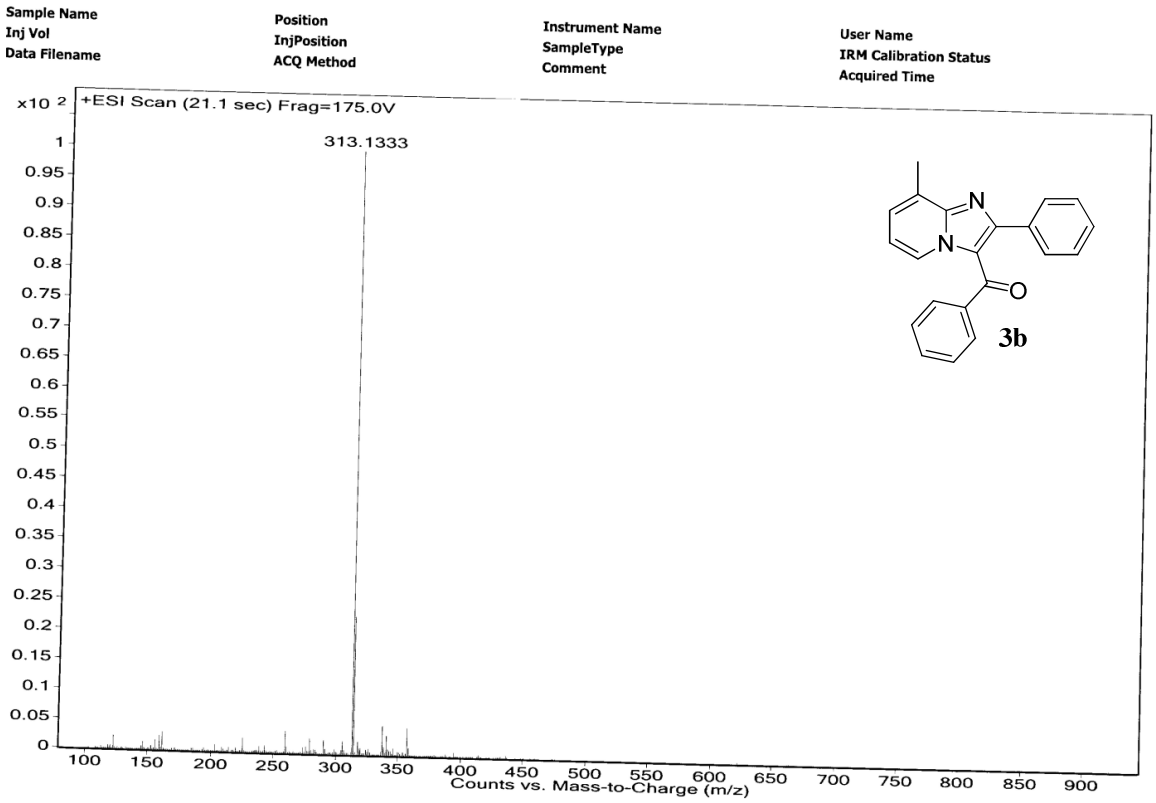

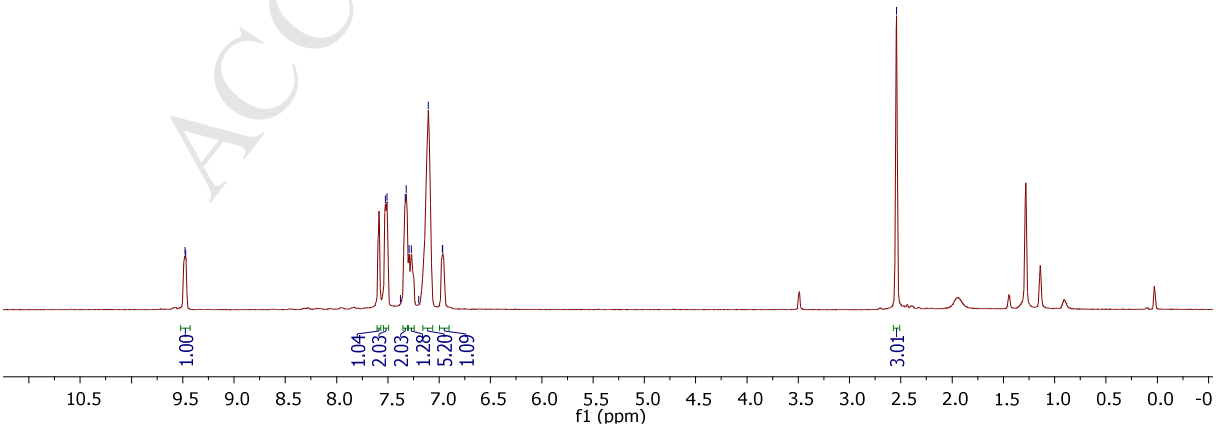

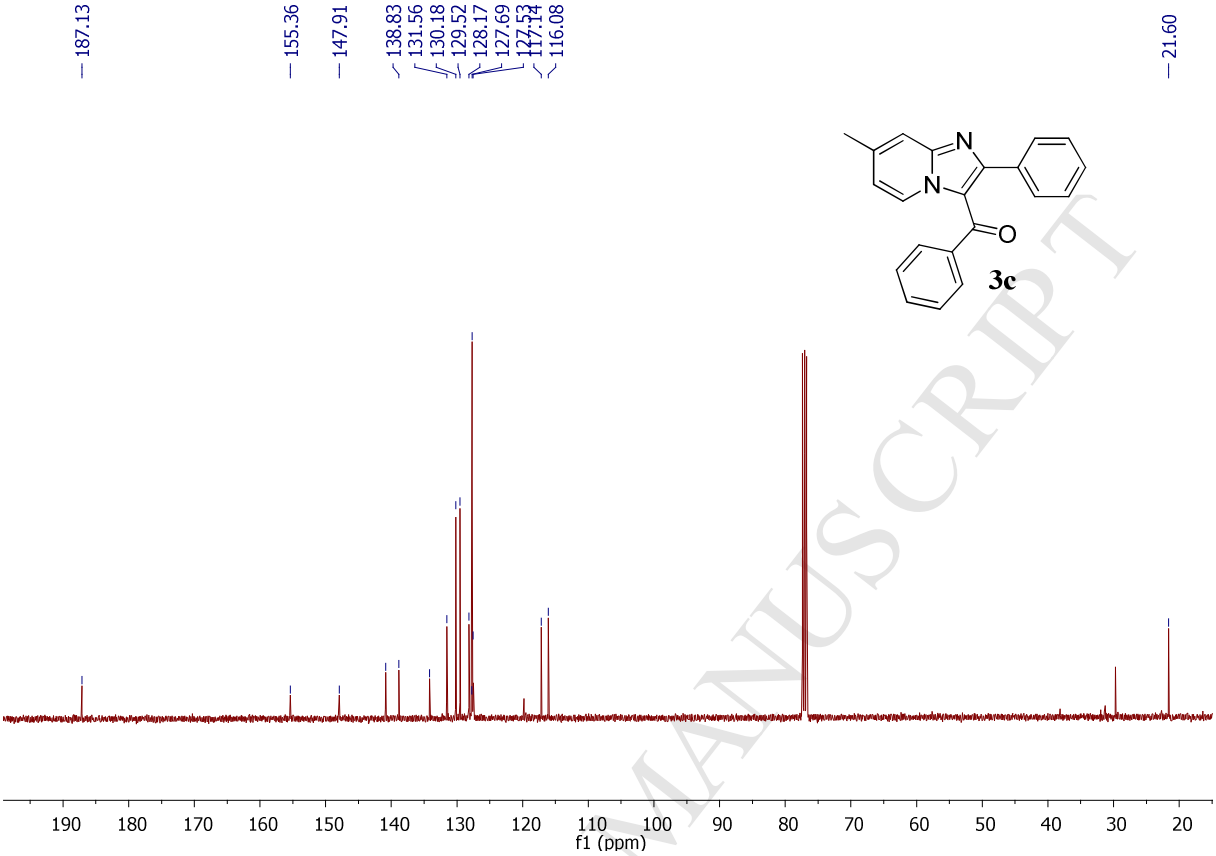
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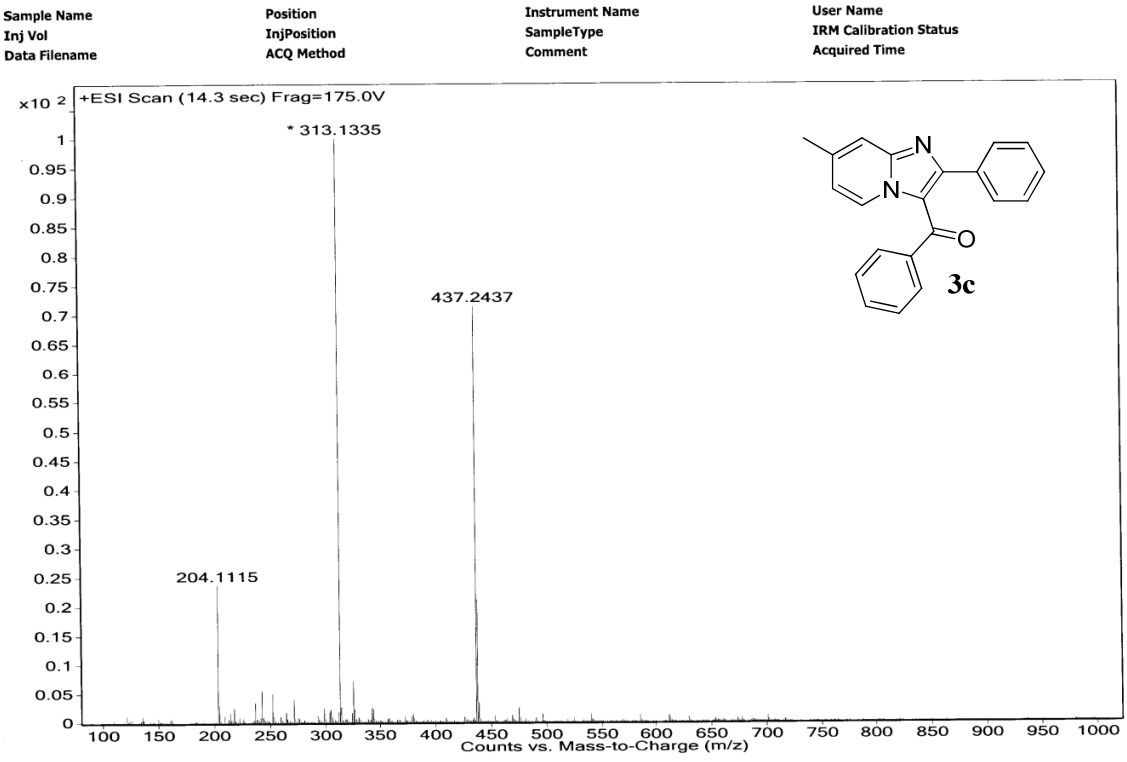
147.91
138.83
131.56
130.18
129.52
128.17
127.69
127.53
117.14
116.08
21.60
N
N
O
3c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)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Data Filename
Position
InjPosition
ACQ Method
Instrument Name
SampleType
Comment
User Name
IRM Calibration Status
Acquired Time
+ESI Scan (14.3 sec) Frag=175.0V
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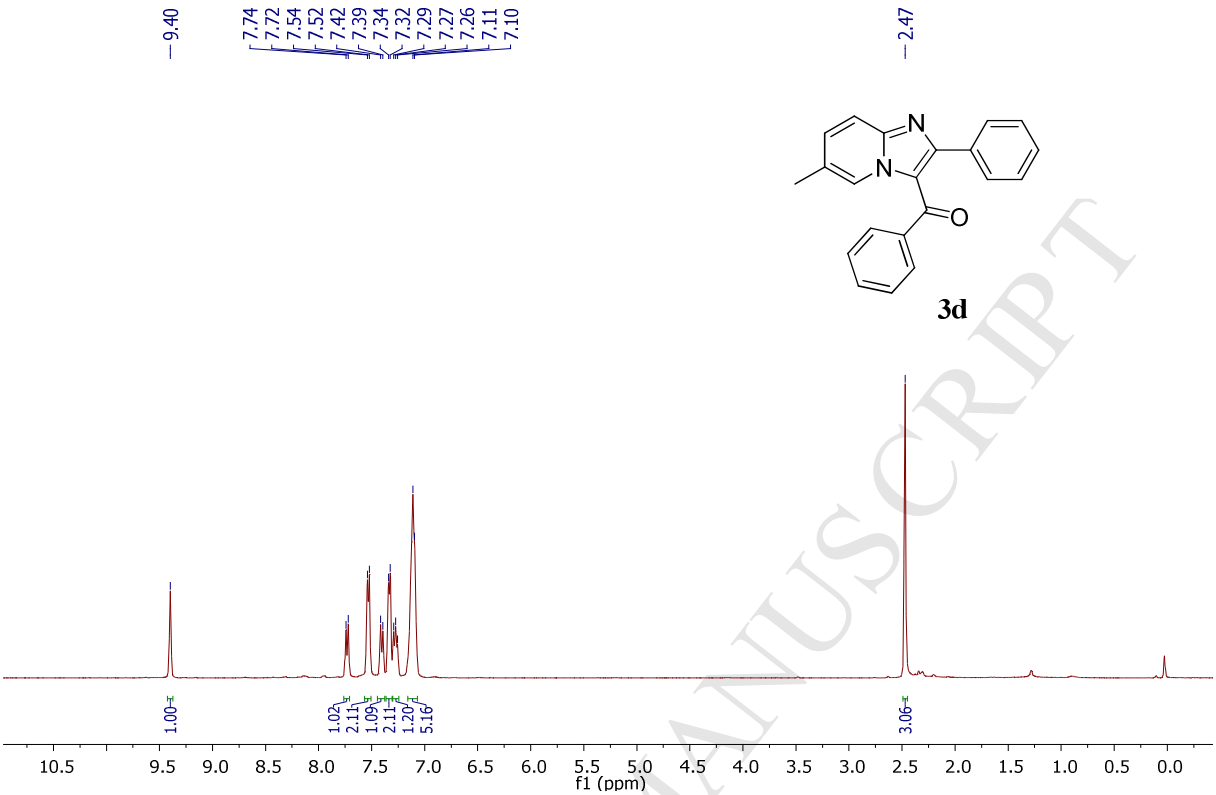
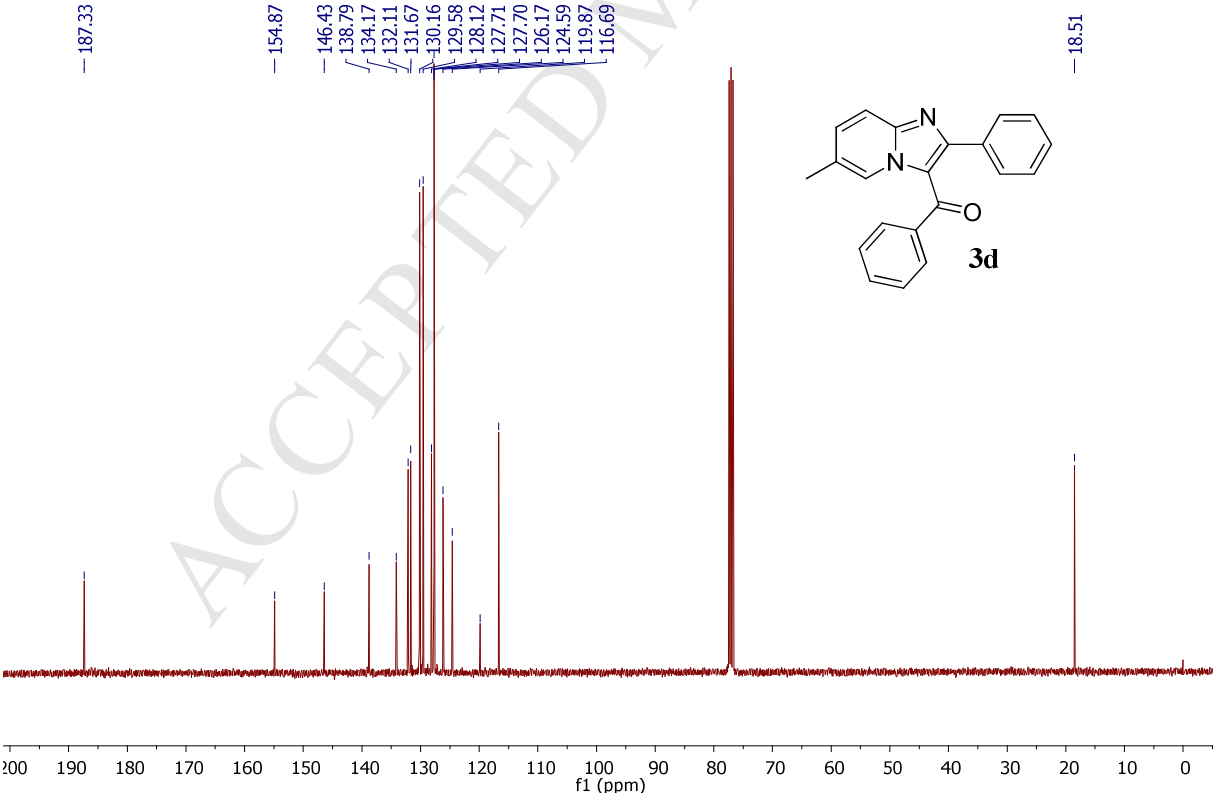
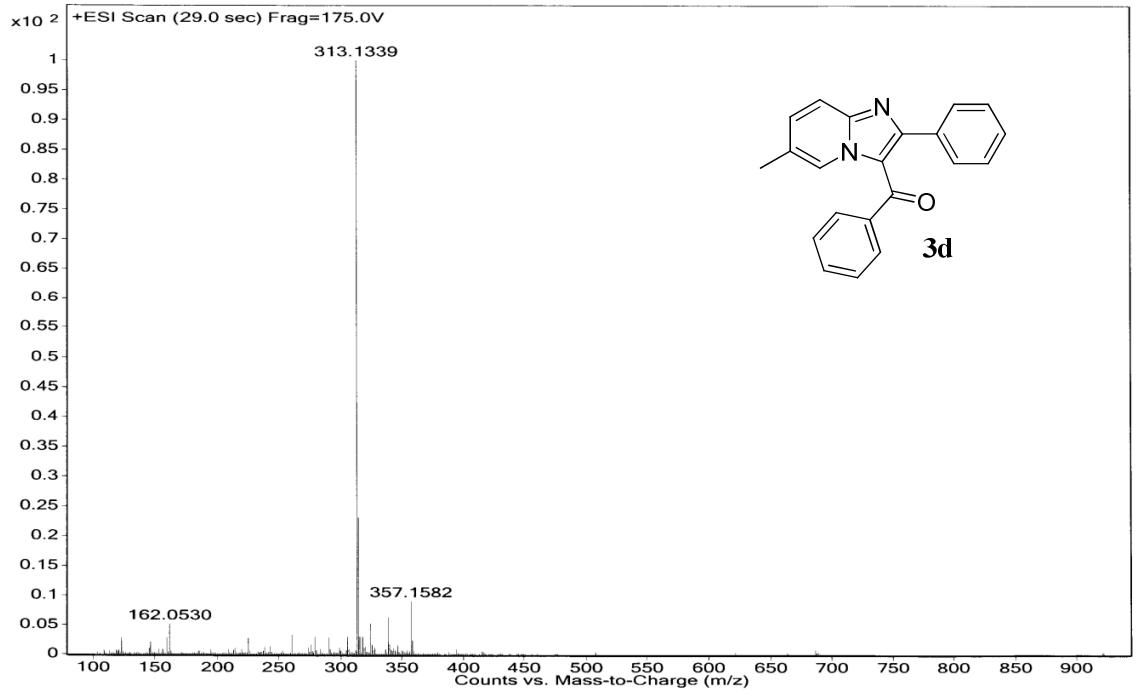
N
O
3c
Counts vs. Mass-to-Charge (m/z)





Sample Name	**Position**	**Instrument Name**	**User Name**
Inj Vol	**InjPosition**	**SampleType**	**IRM Calibration Status**
Data Filename	**ACQ Method**	**Comment**	**Acquired Time**



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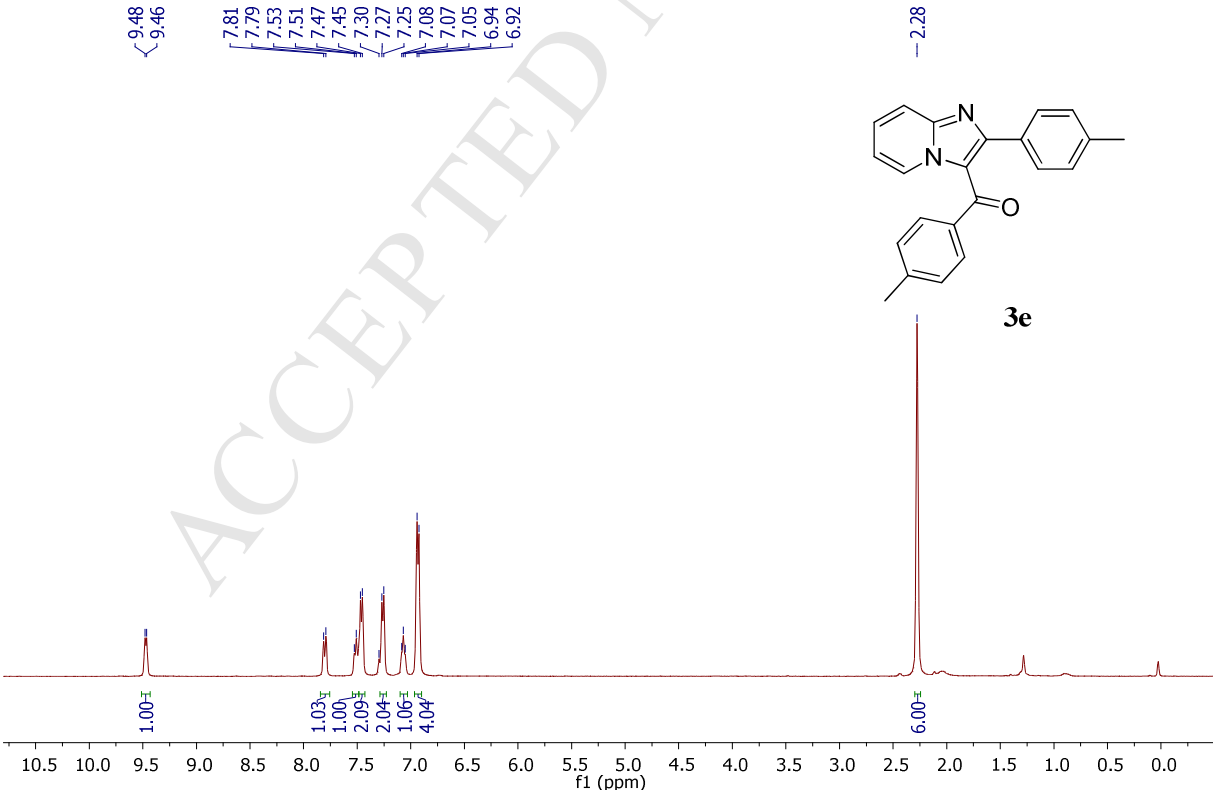

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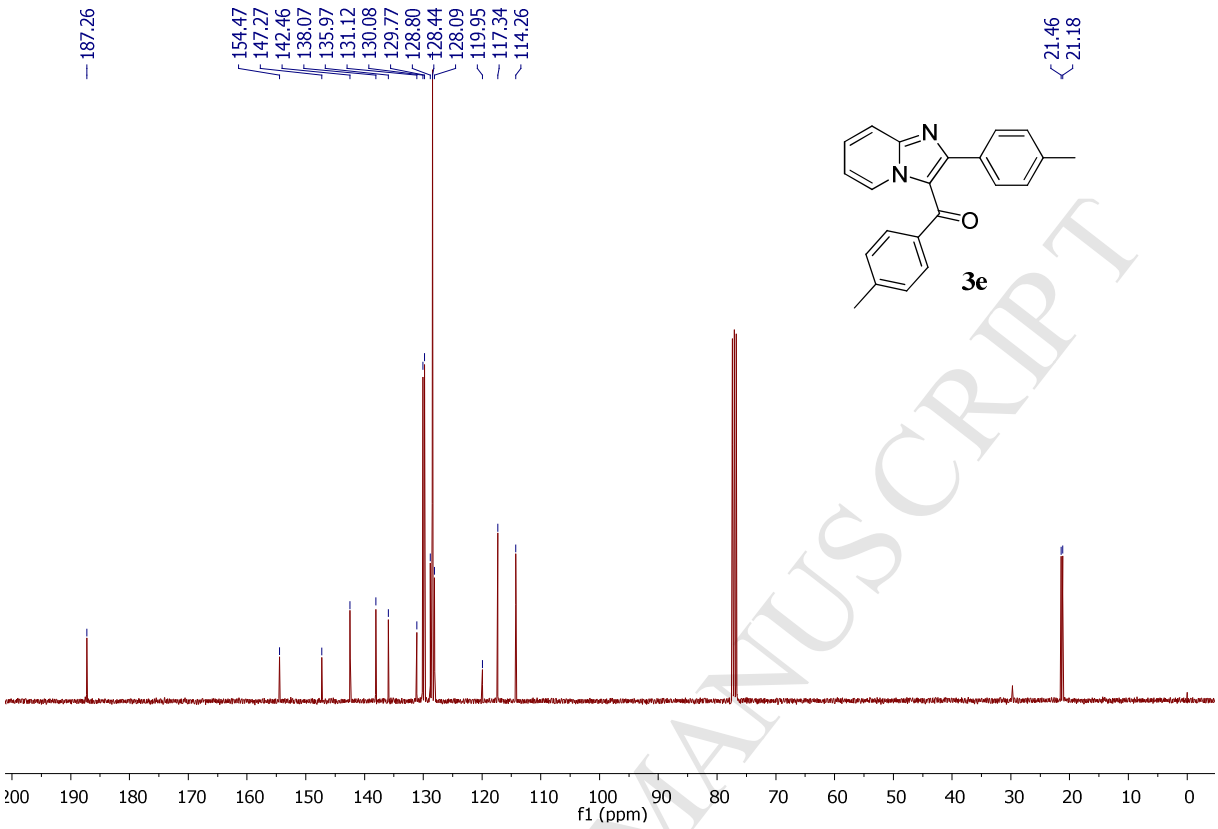

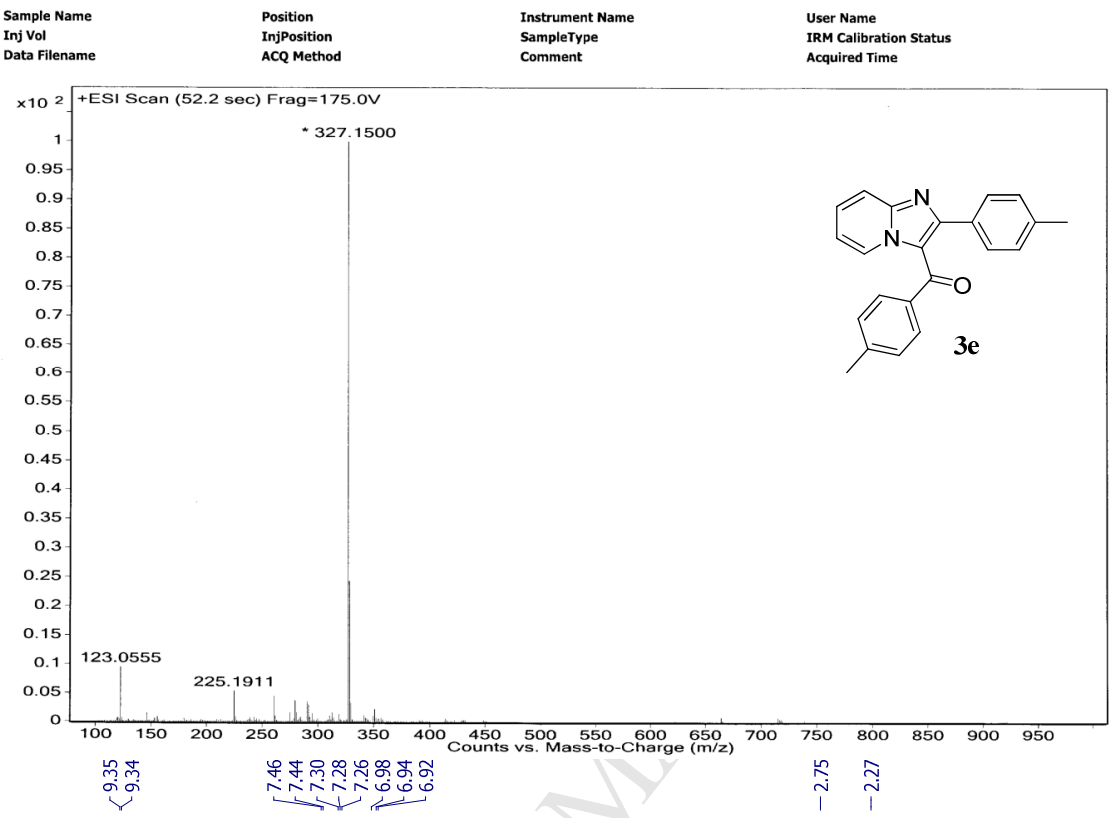

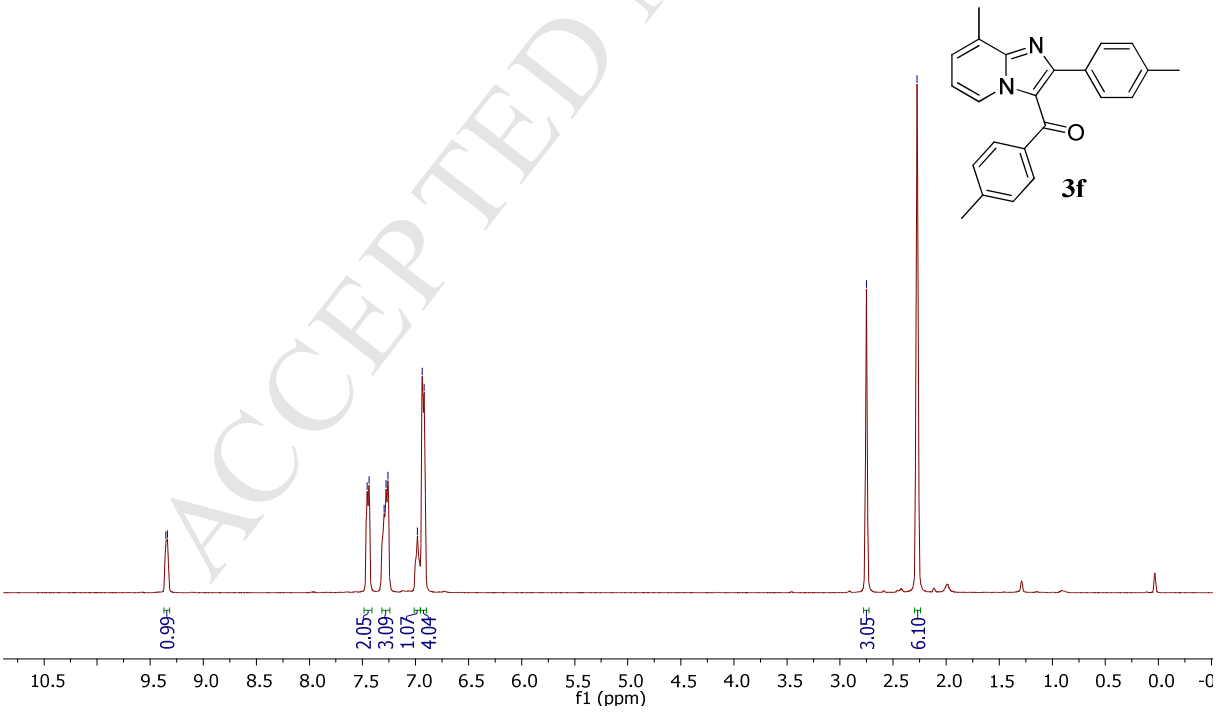

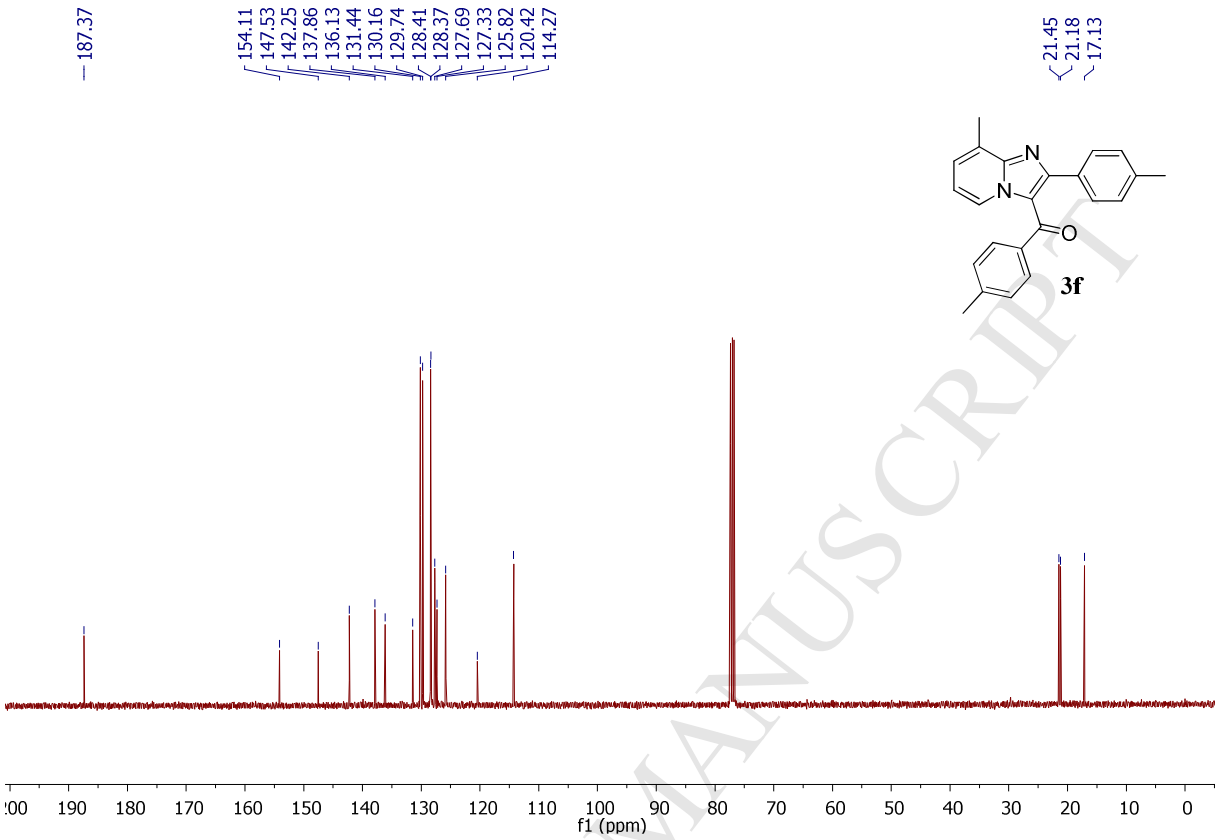
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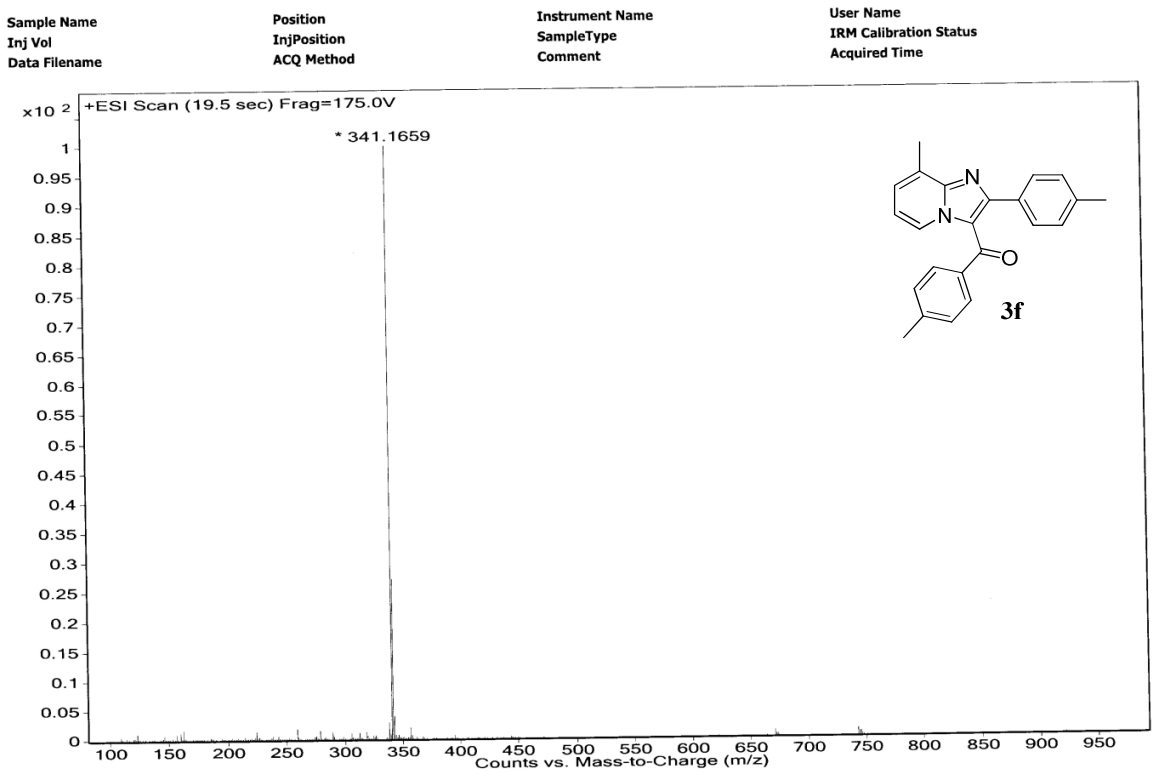
21.18
17.13
N
N
O
3f
f1 (ppm)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Position
InjPosition
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Instrument Name
SampleType
Comment
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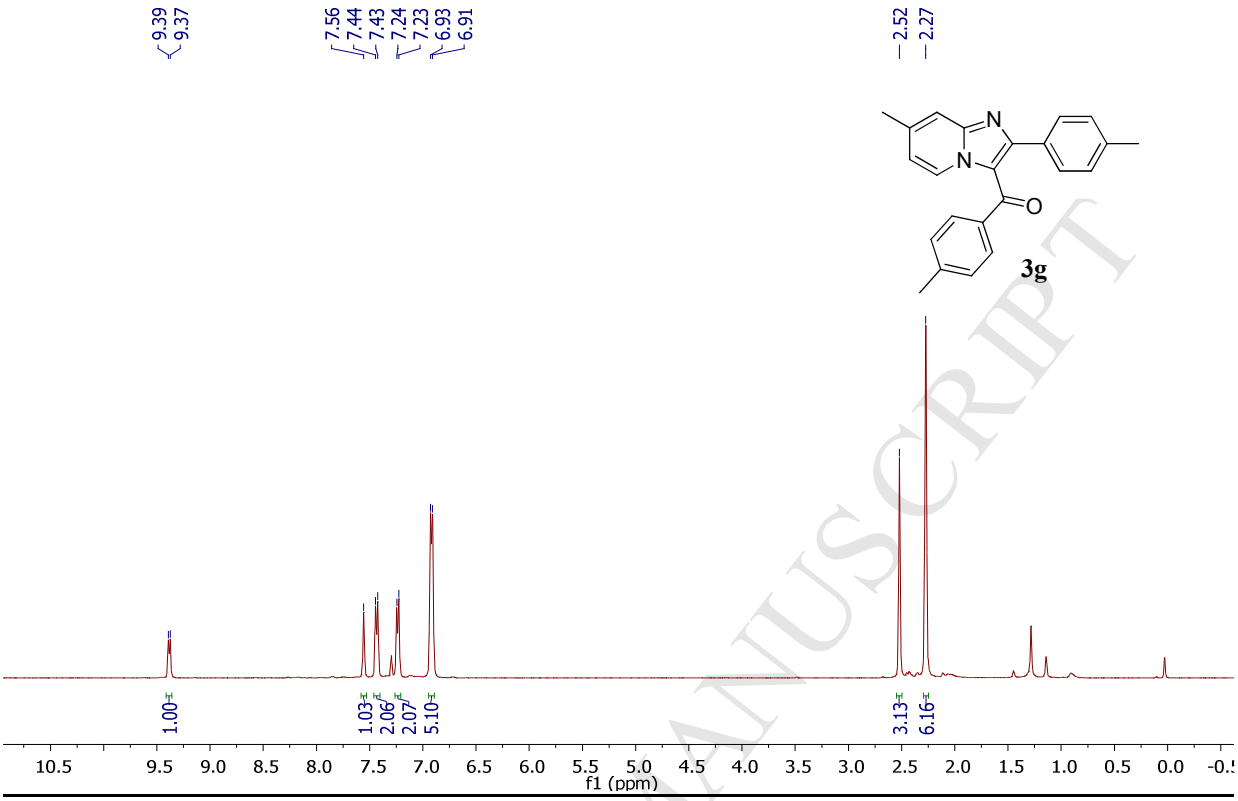
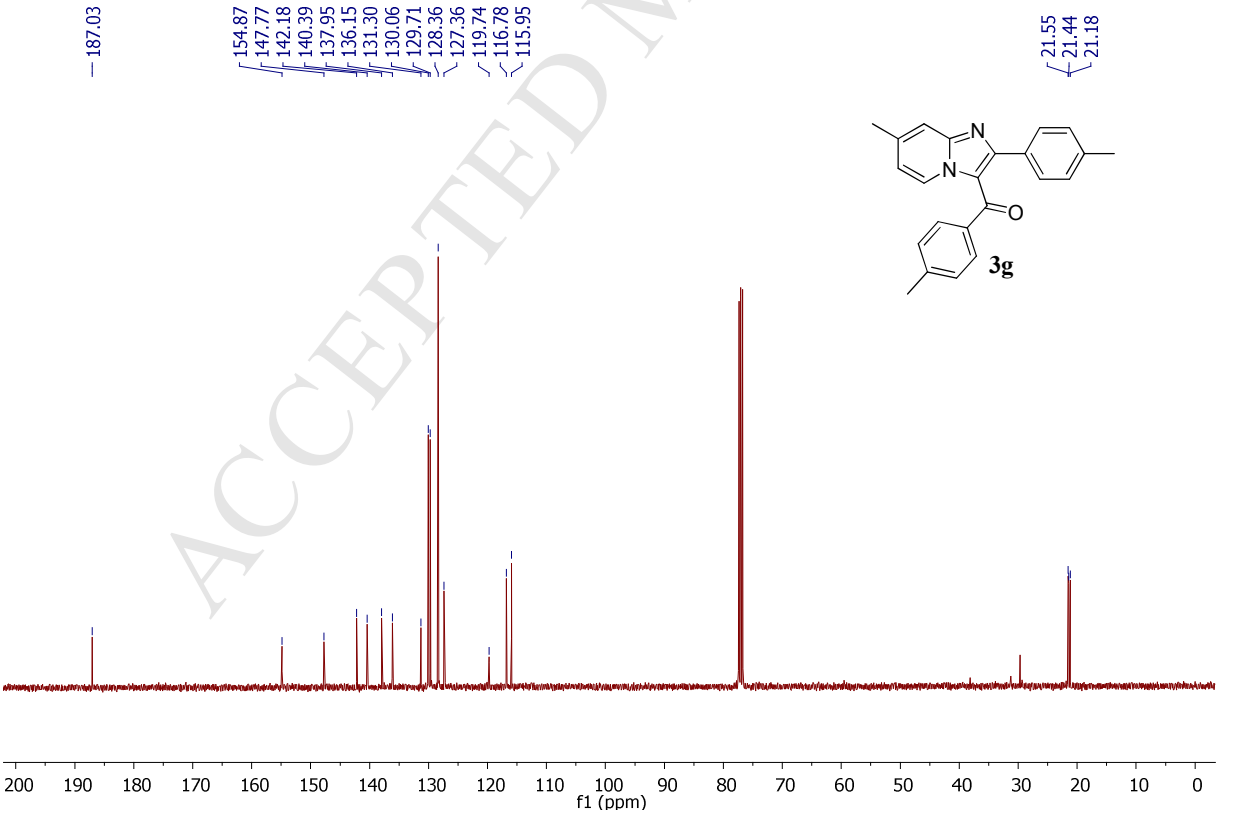
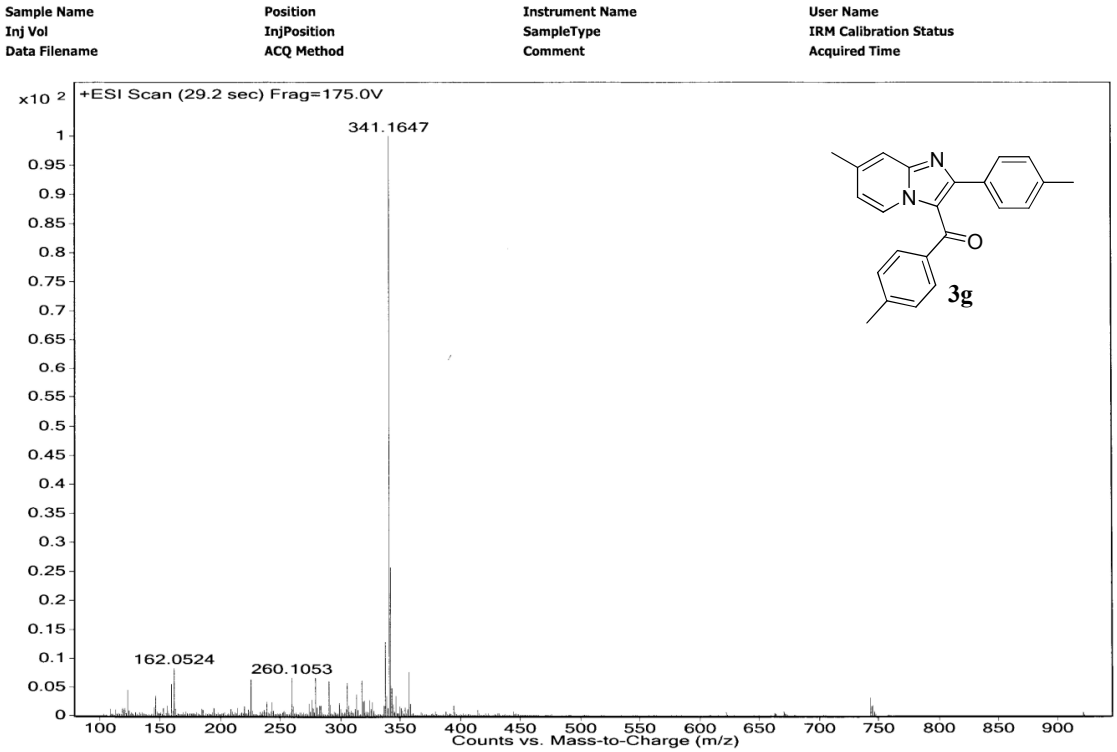
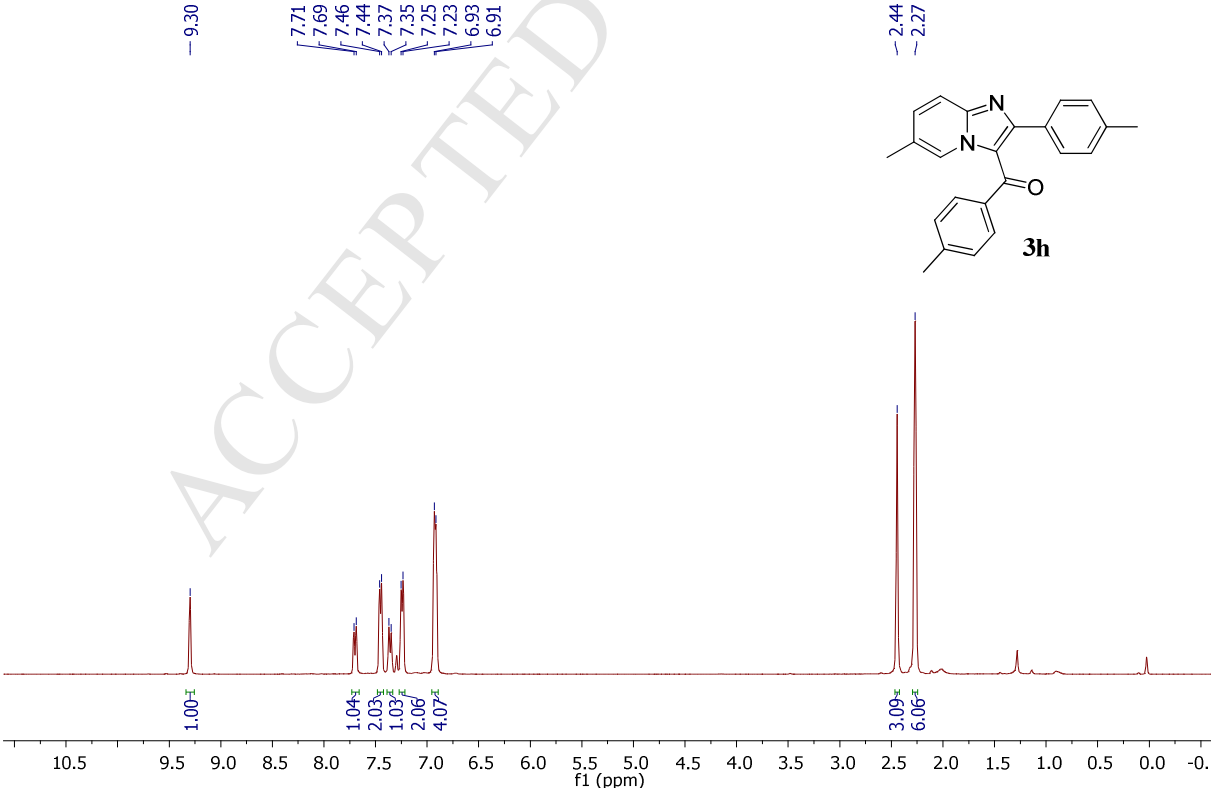
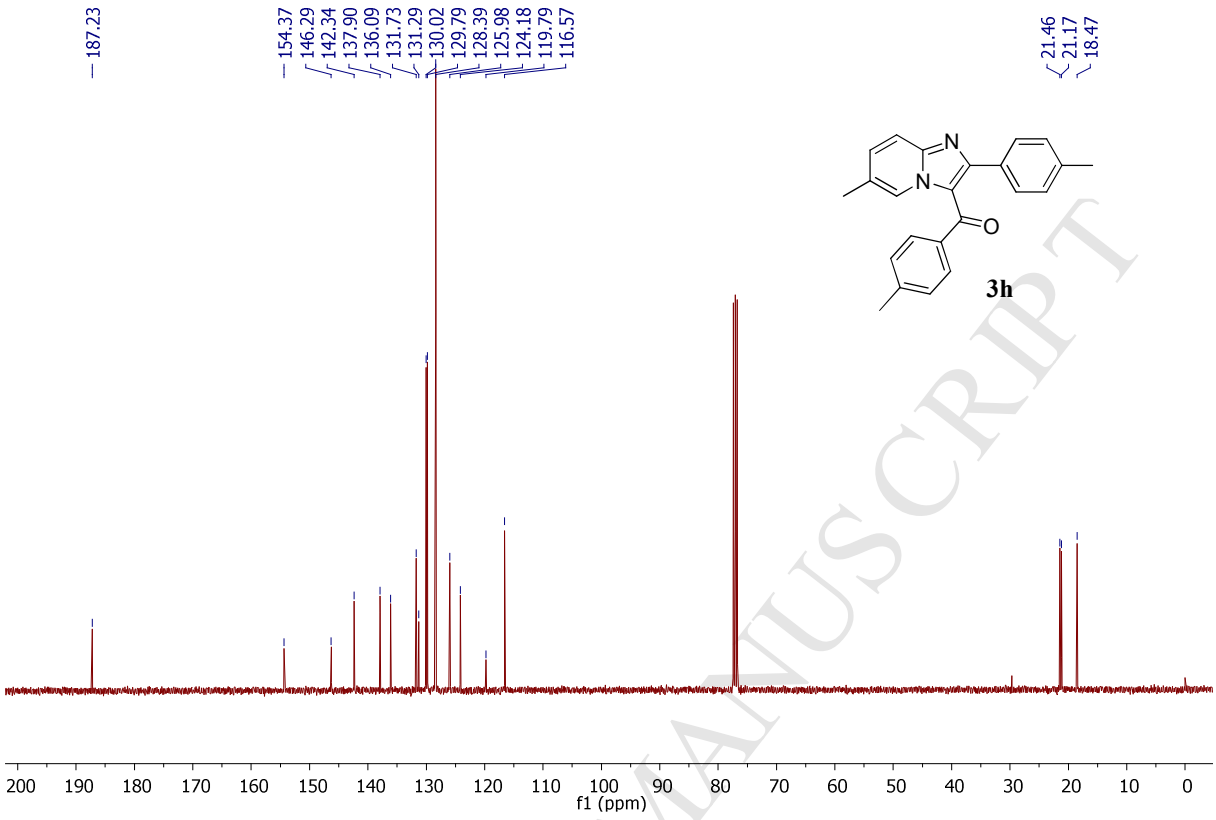
N
O
3f
Counts vs. Mass-to-Charge (m/z)











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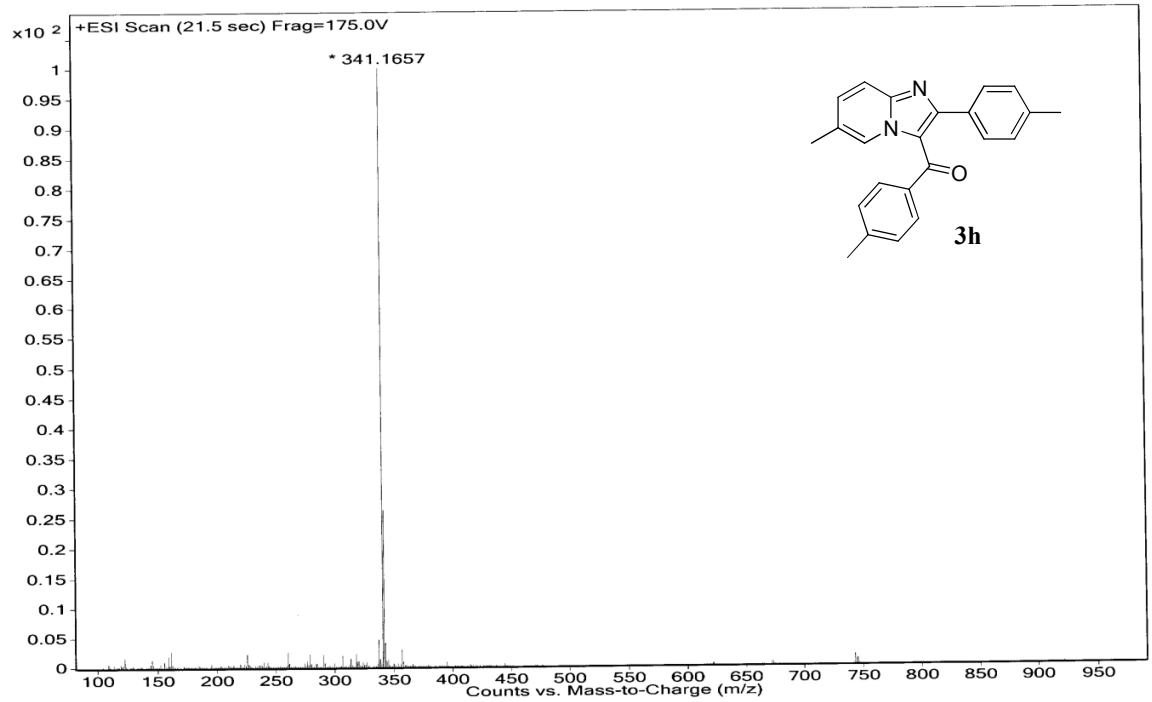
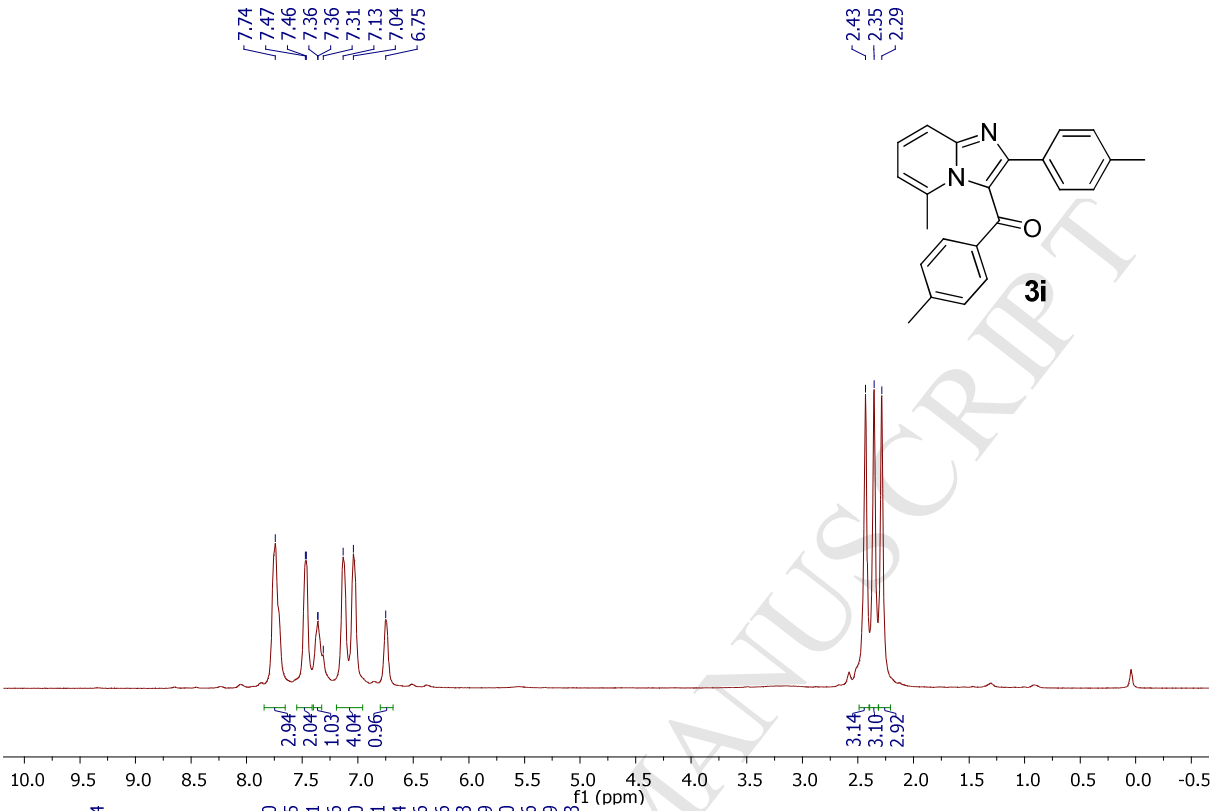
Inj Vol
Data Filename

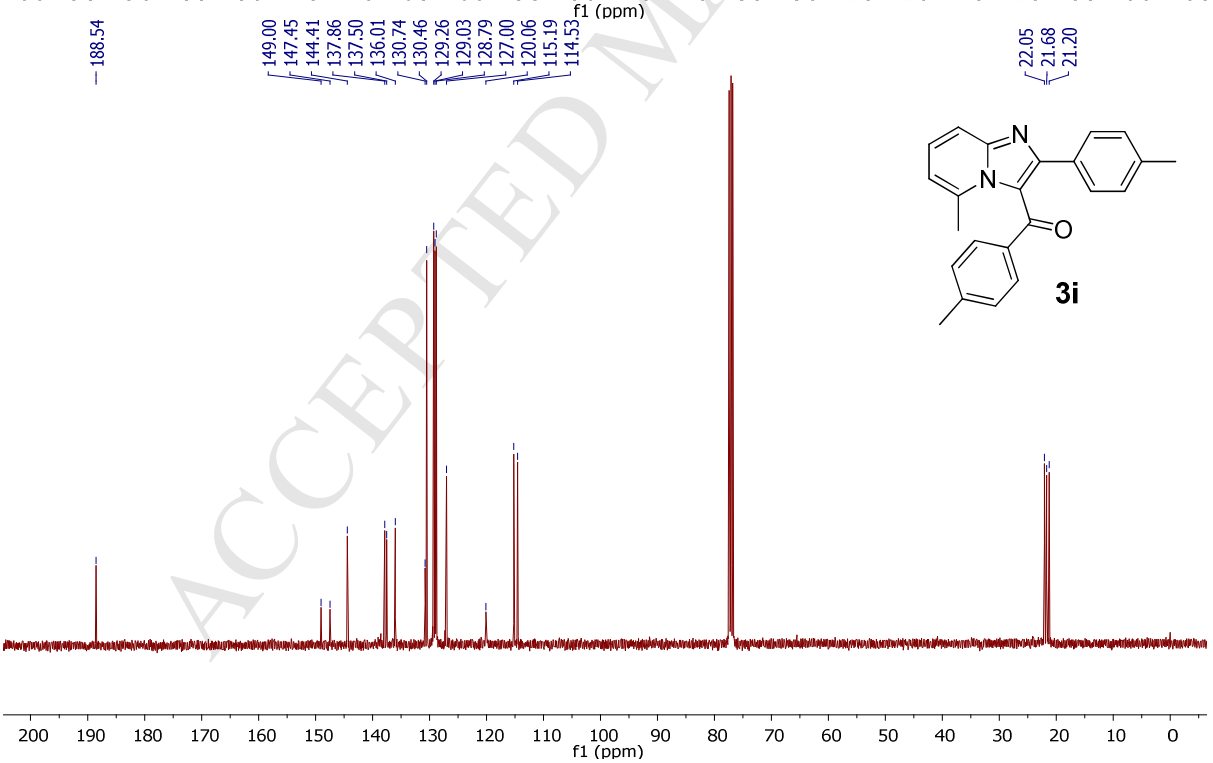
Position
InjPosition
ACQ Method

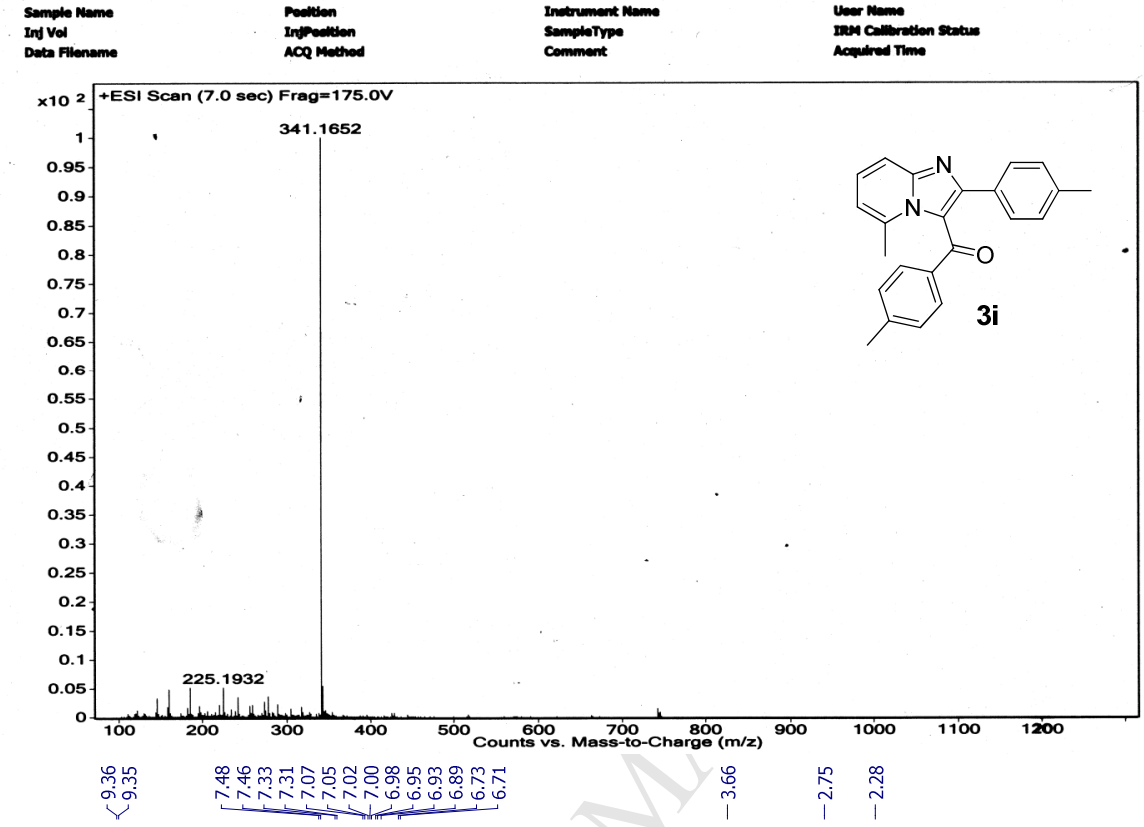
Instrument Name
SampleType
Comment

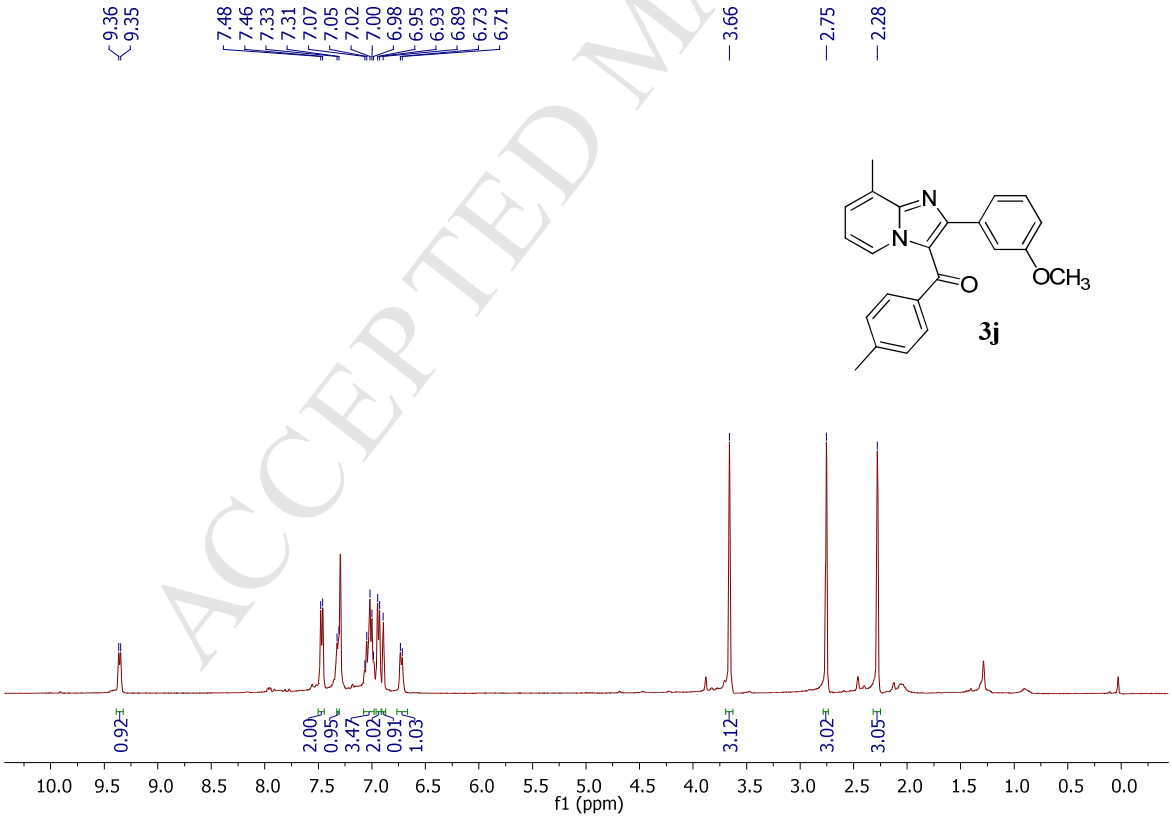
User Name
IRM Calibration Status
Acquired Time

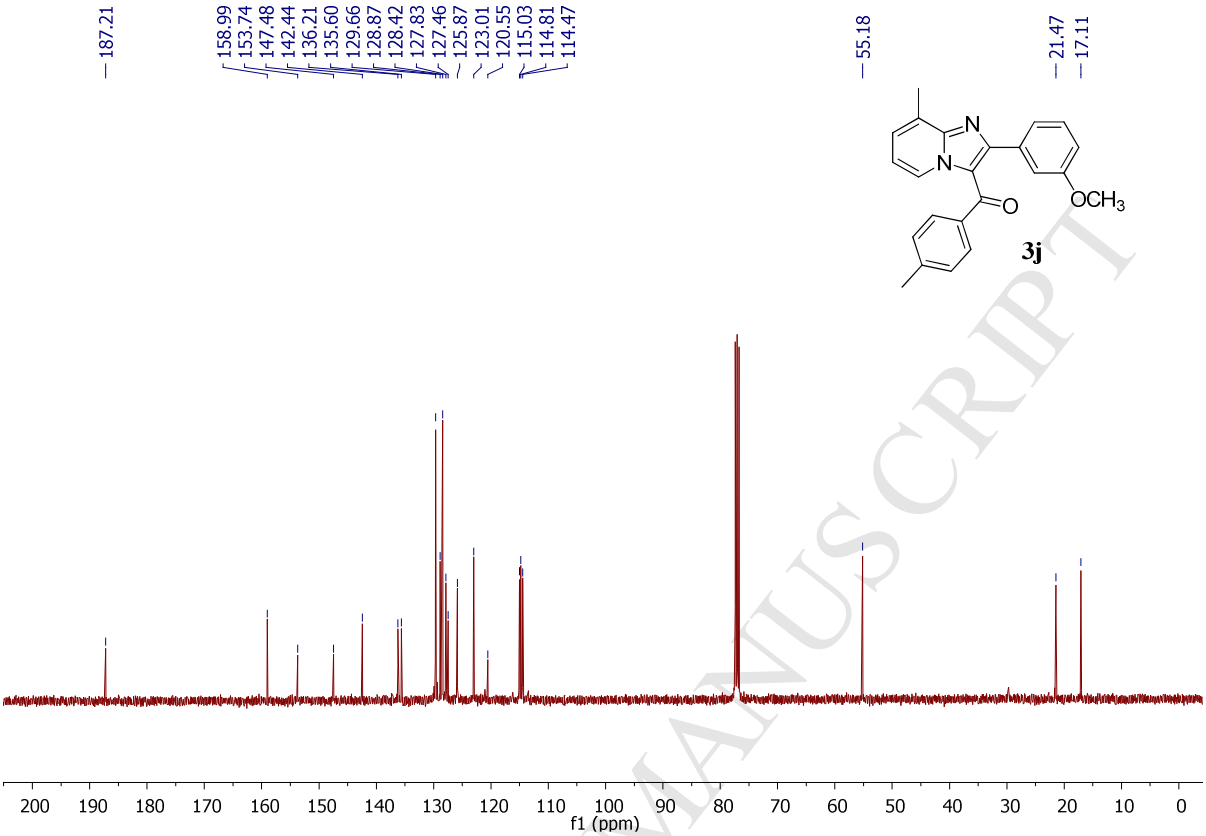








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153.74
147.48
142.44
136.21
135.60
129.66
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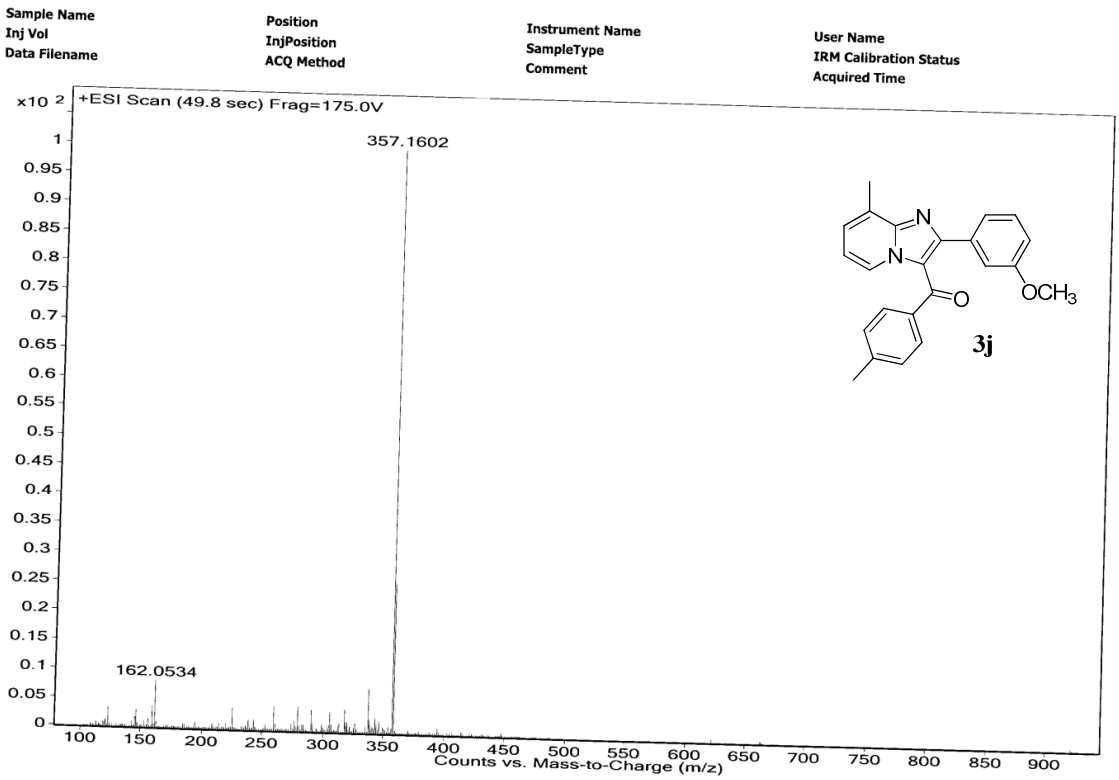
128.42
127.83
127.46
125.87
123.01
120.55
115.03
114.81
114.47
55.18
21.47
17.11
N
N
O
OCH3
3j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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InjPosition
ACQ Method
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SampleType
Comment
User Name
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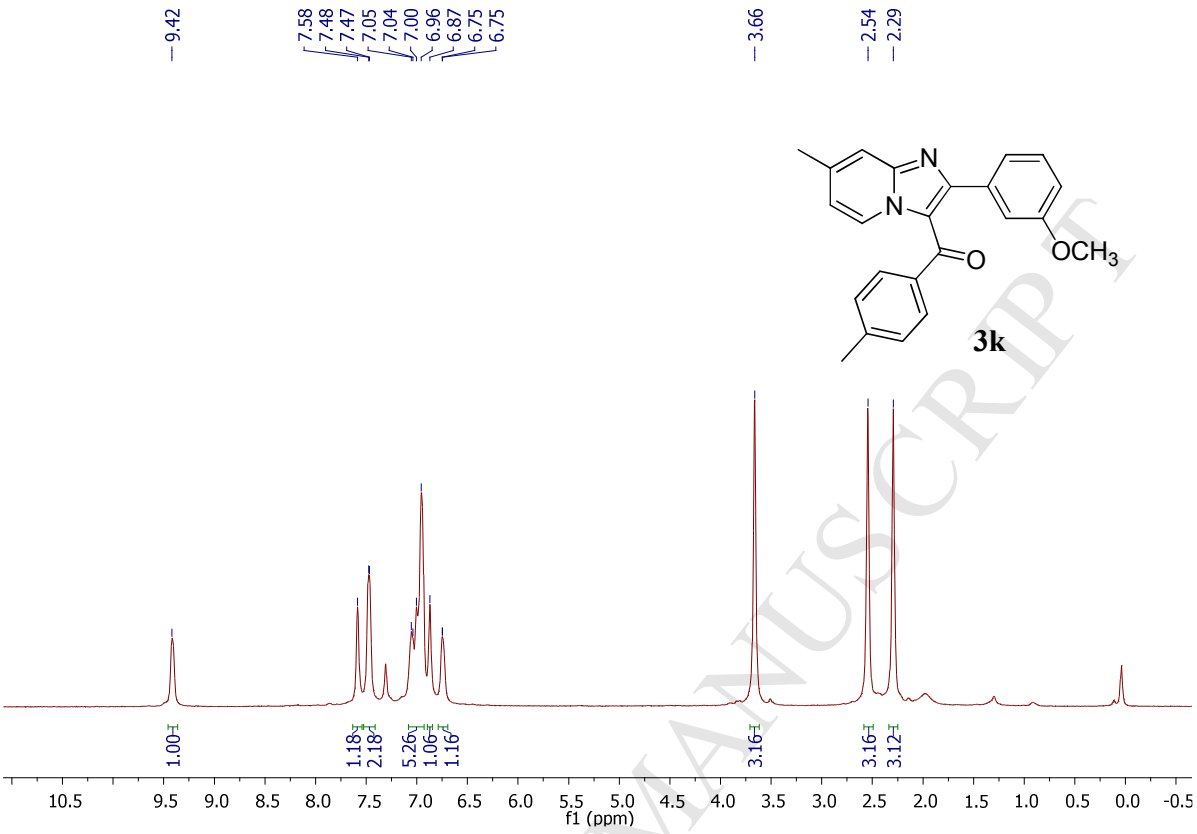
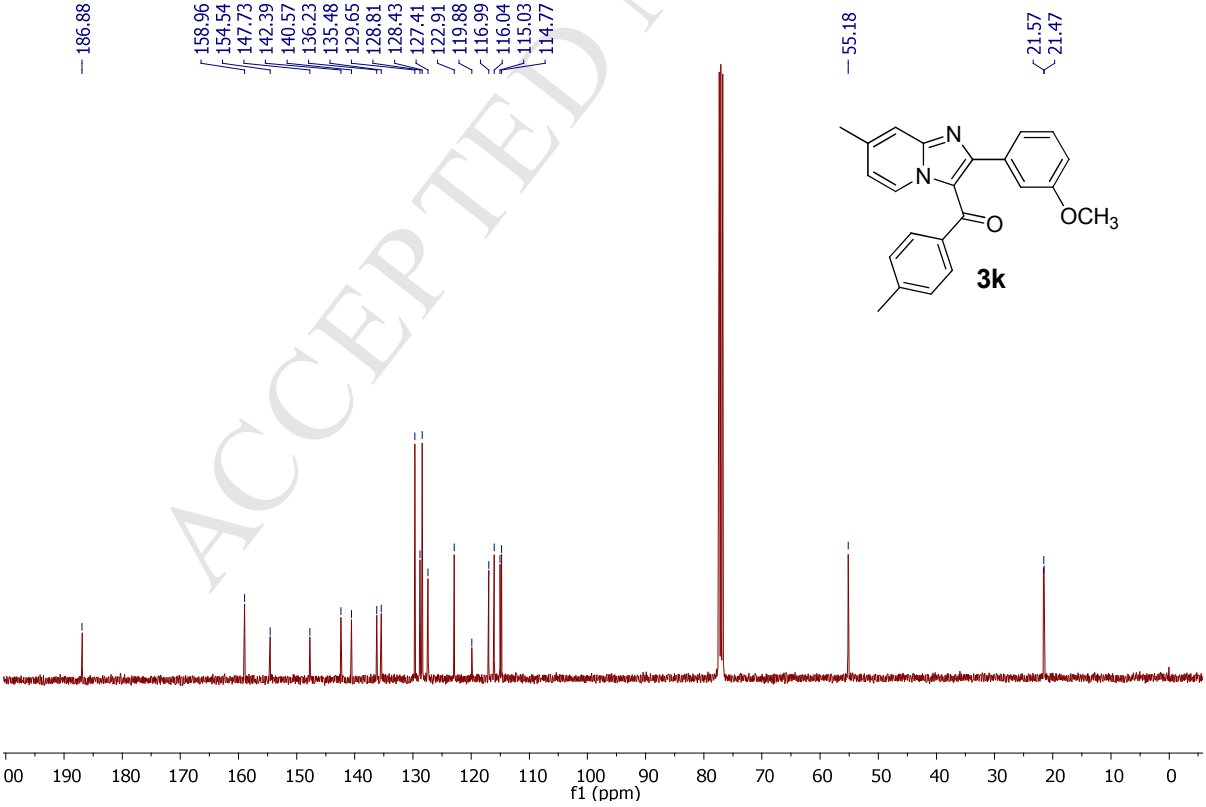
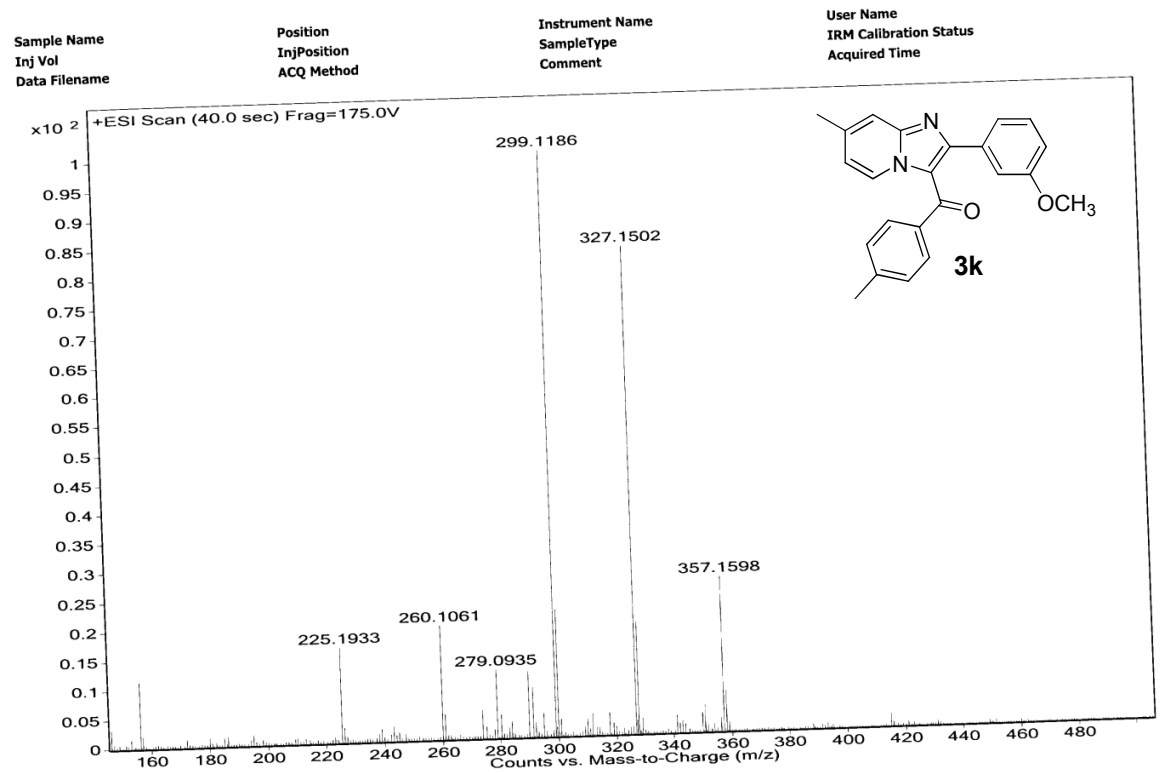
N
O
OCH3
3j
Counts vs. Mass-to-Charge (m/z)



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User Name
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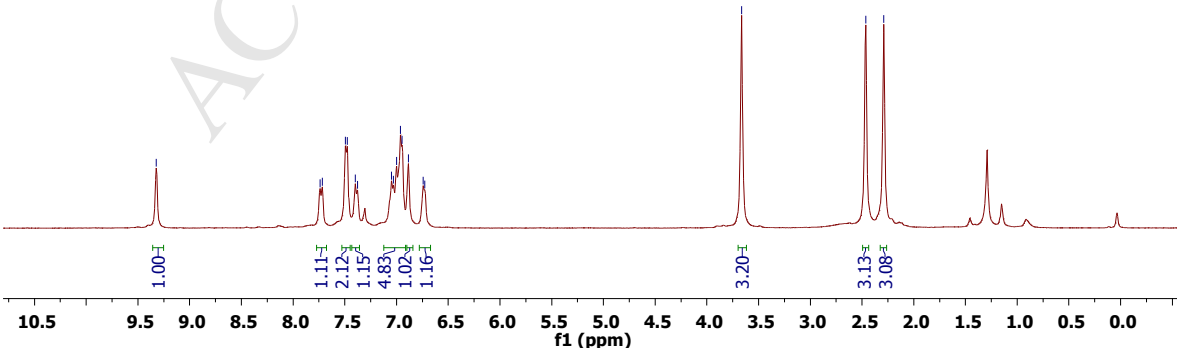
357.1598
260.1061
225.1933
279.0935
Counts vs. Mass-to-Charge (m/z)
OCH3
3k


9.32
7.74
7.72
7.49
7.48
7.40
7.38
7.05
7.03
7.00
6.96
6.95
6.89
6.74
6.73
3.66
2.46
2.29

OCH3
3l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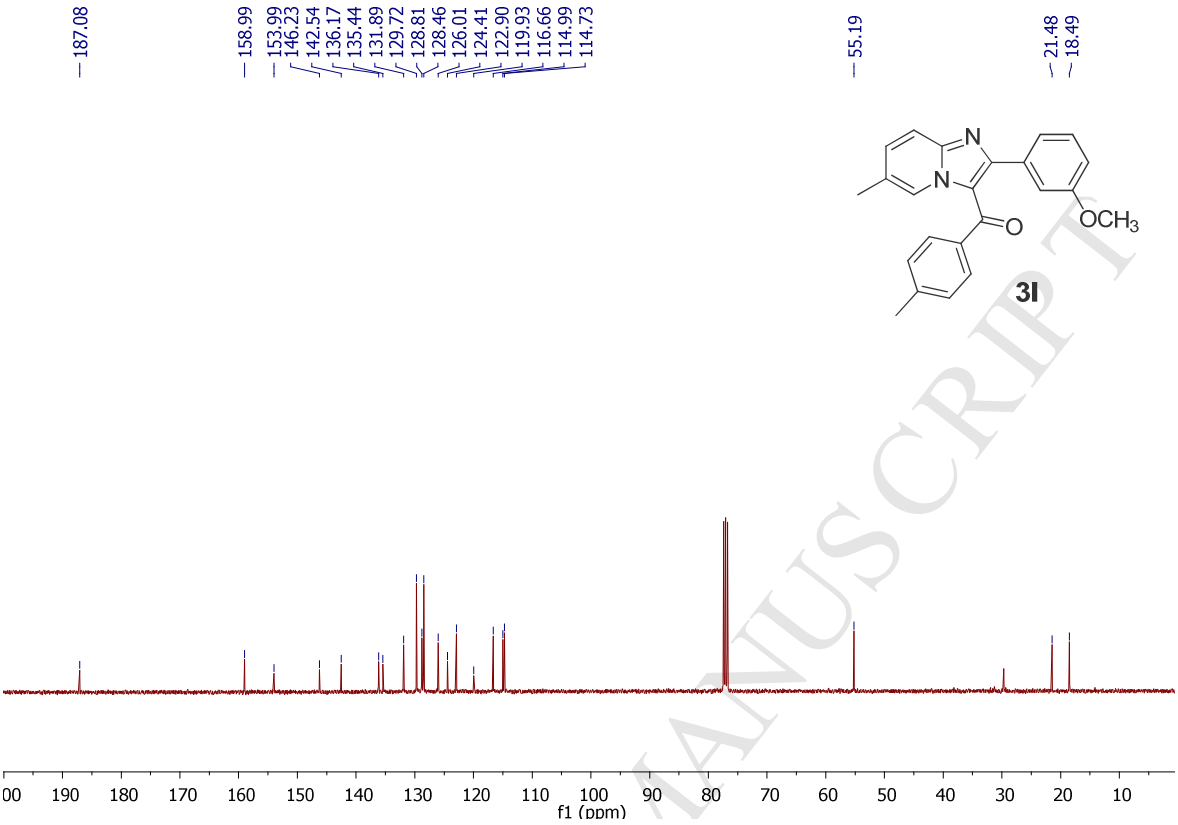
4.83
1.02
1.16
3.20
3.13
3.08
f1 (ppm)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124.41
122.90
119.93
116.66
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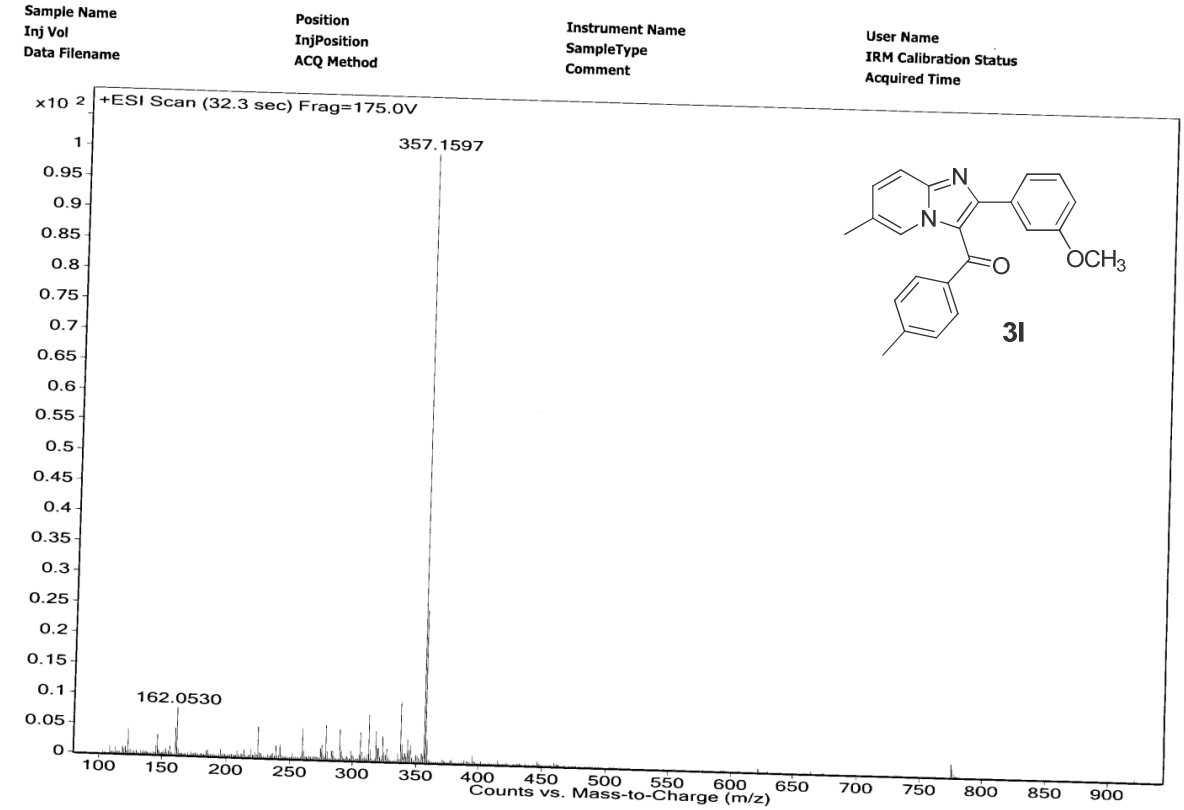
114.73
55.19
21.48
18.49
N
N
O
OCH3
3l
f1 (ppm)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SampleType
Comment
User Name
IRM Calibration Status
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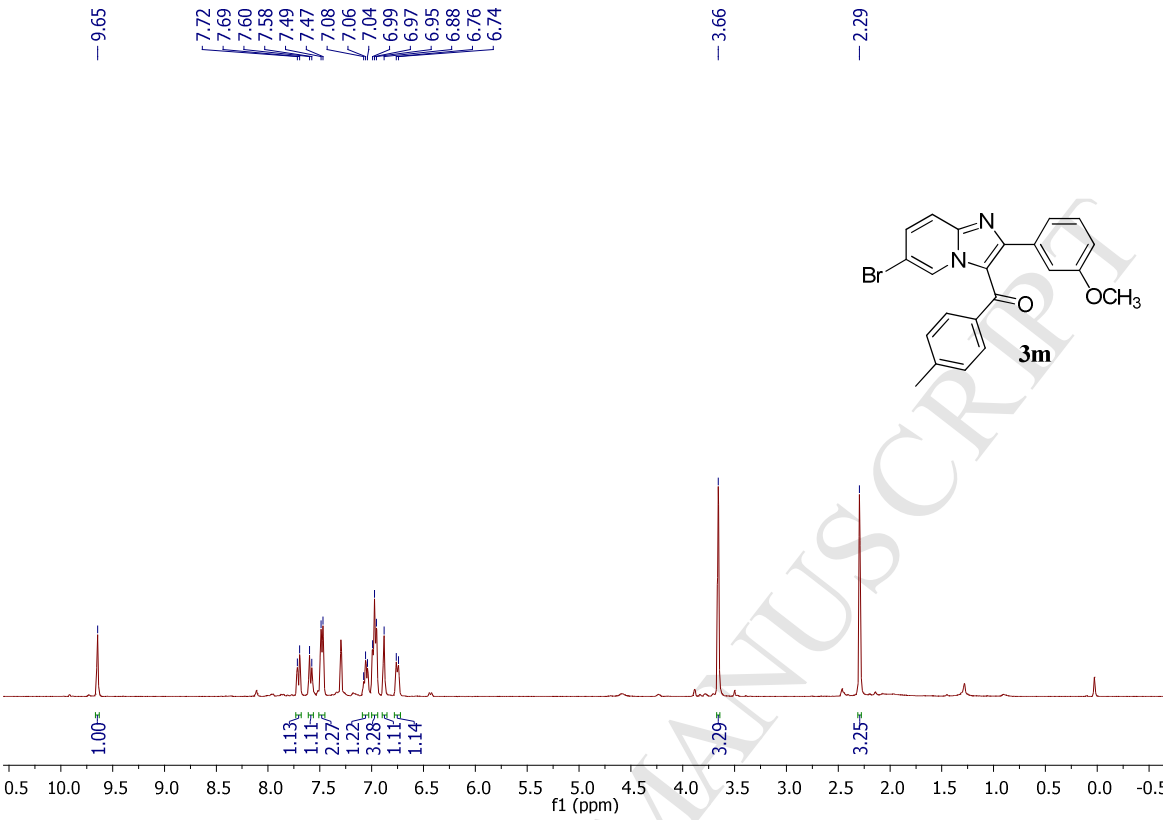
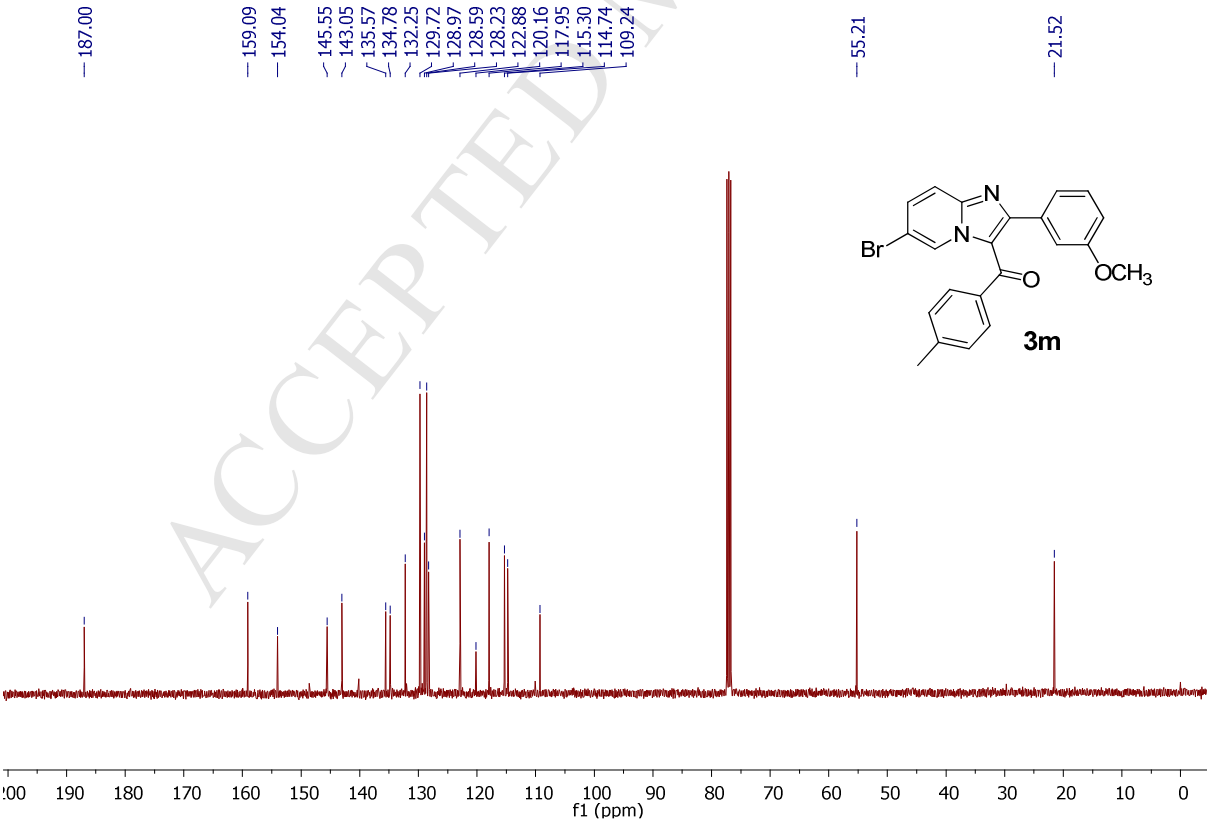
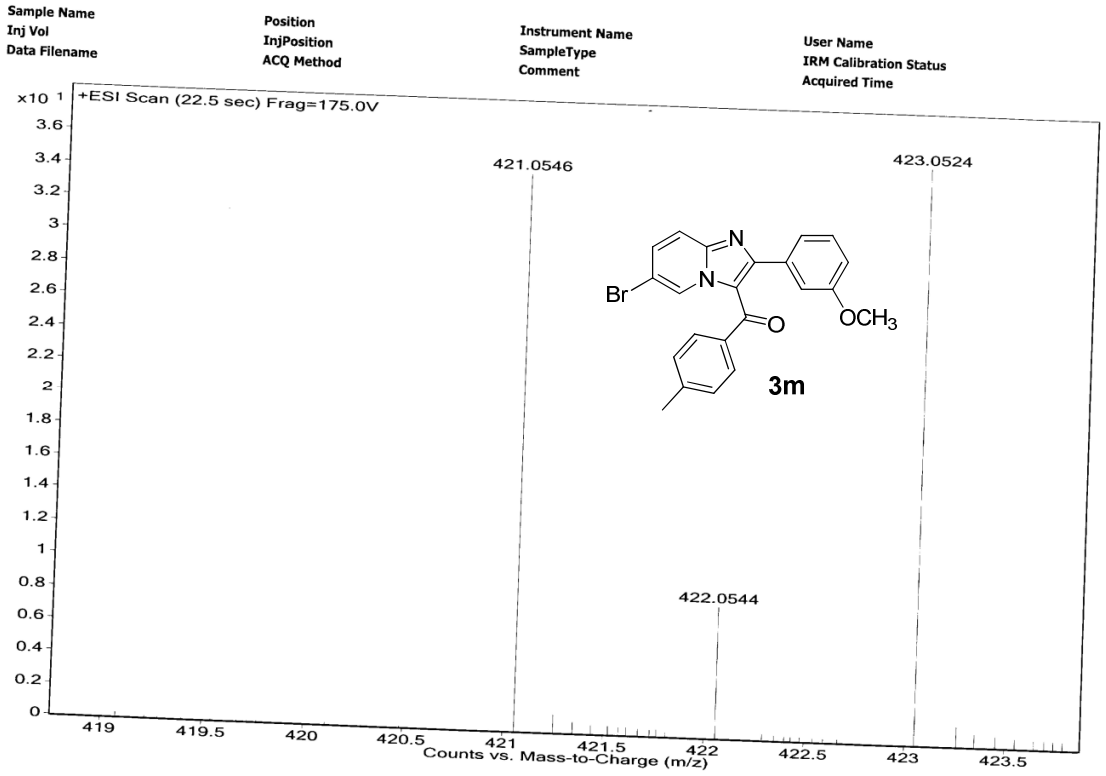
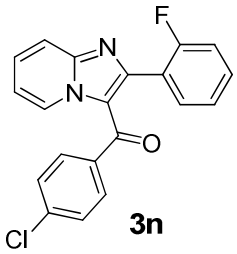
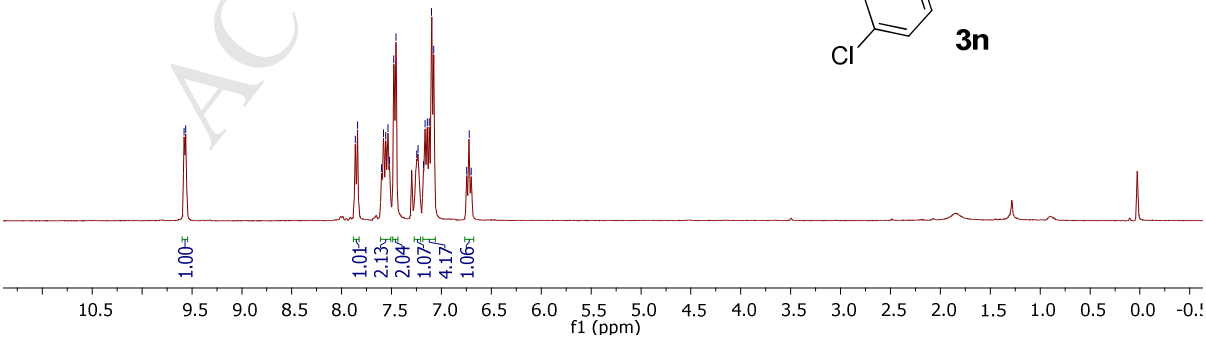
N
O
OCH3
3l
Counts vs. Mass-to-Charge (m/z)

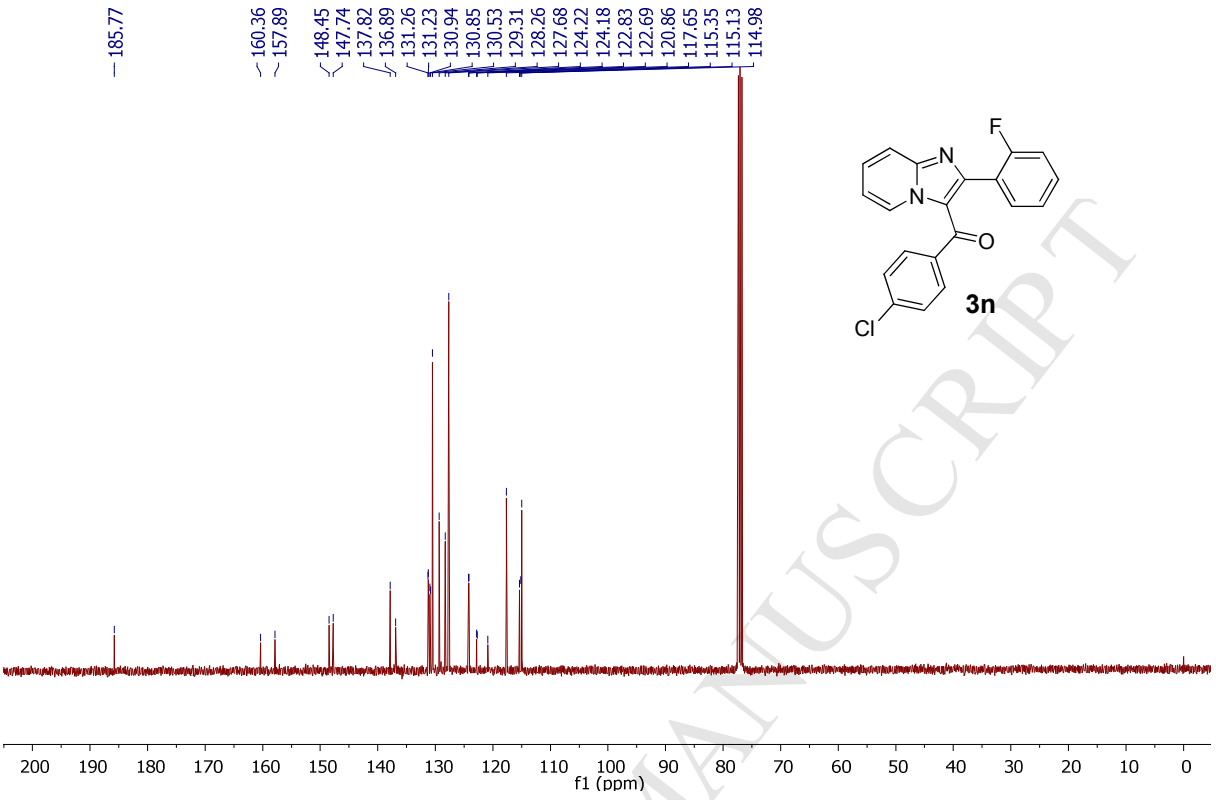


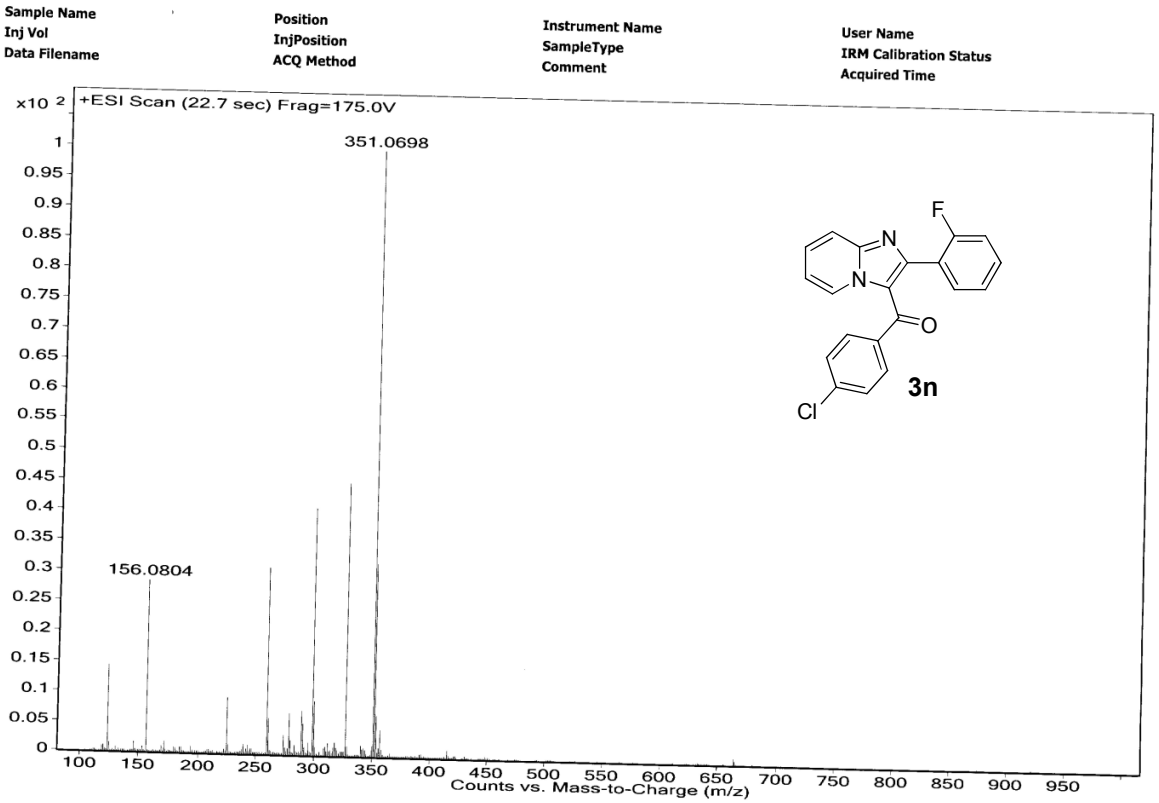


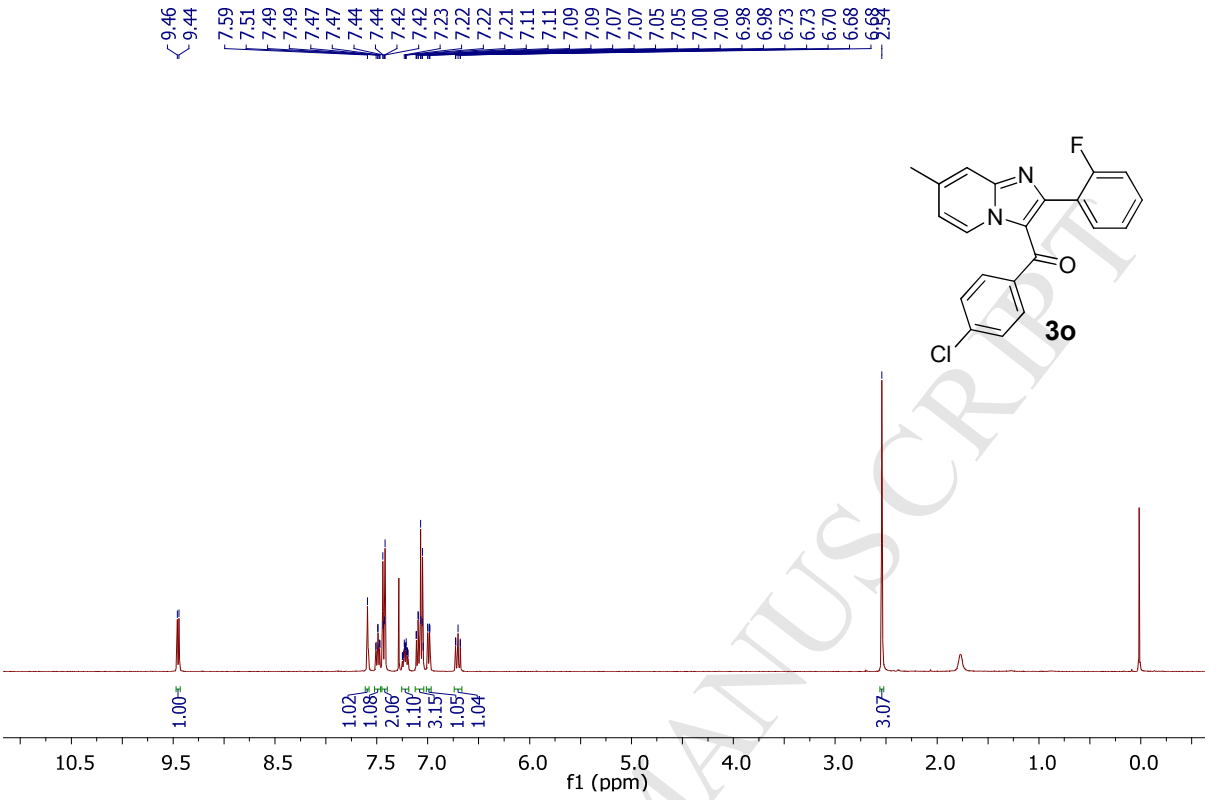


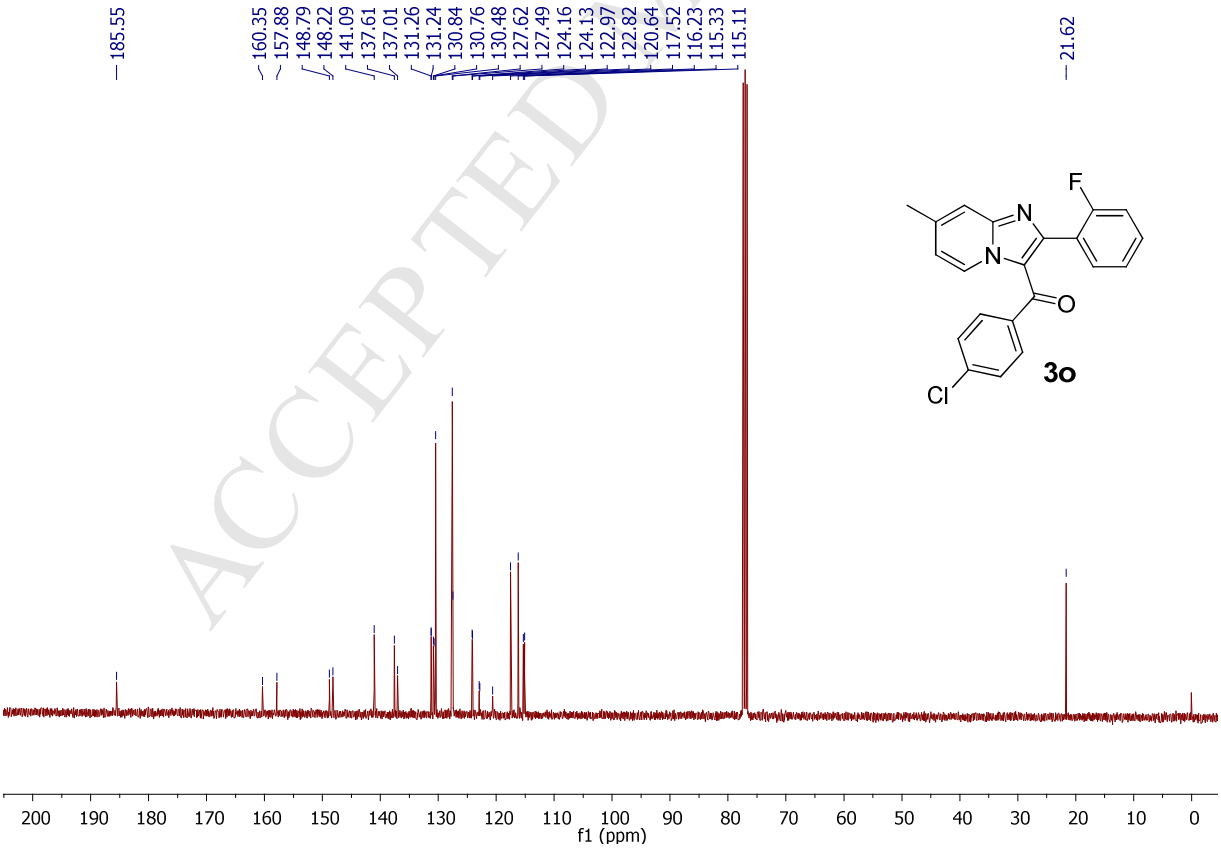


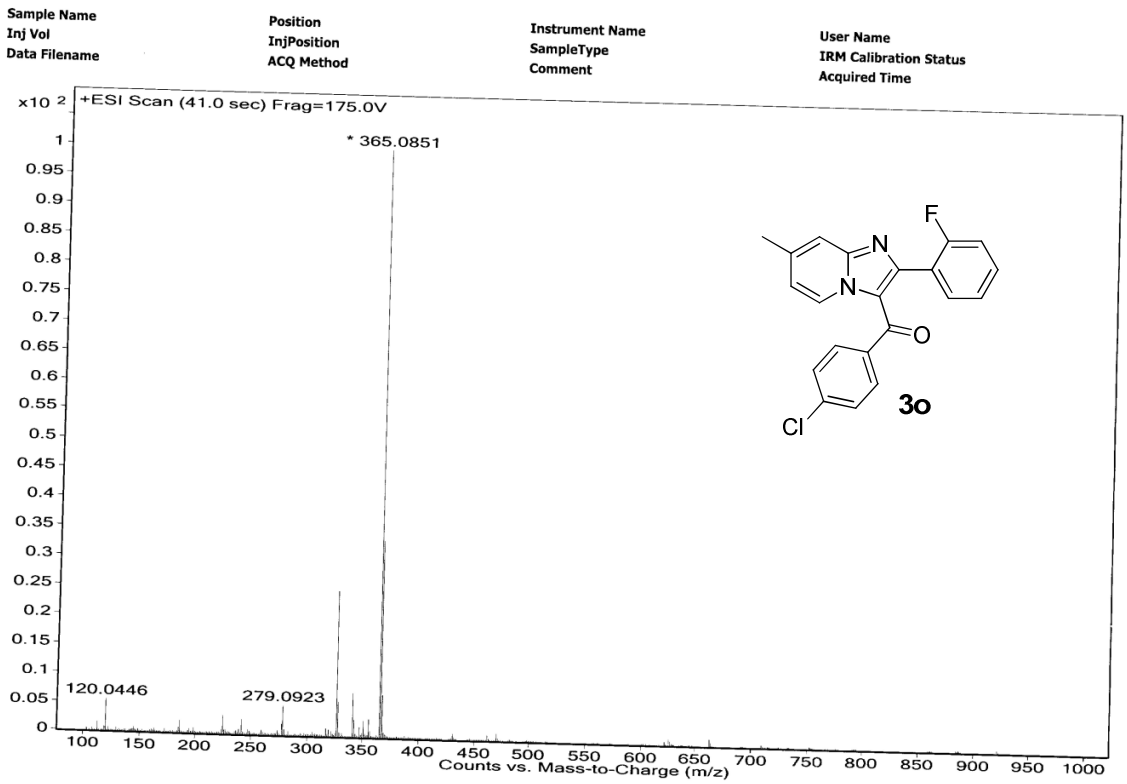



185.77
160.36
157.89
148.45
147.74
137.82
136.89
131.26
131.23
130.94
130.85
130.53
129.31
128.26
127.68
124.22
124.18
122.83
122.69
120.86
117.65
115.35
115.13
114.98
F
N
N
O
Cl
3n
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

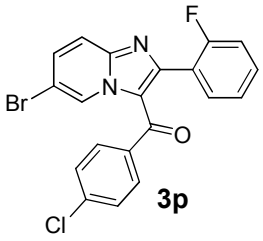

Sample Name
Inj Vol
Data Filename
Position
InjPosition
ACQ Method
Instrument Name
SampleType
Comment
User Name
IRM Calibration Status
Acquired Time
x10 2
+ESI Scan (22.7 sec) Frag=175.0V
351.0698
156.0804
F
N
N
O
Cl
3n
Counts vs. Mass-to-Charge (m/z)

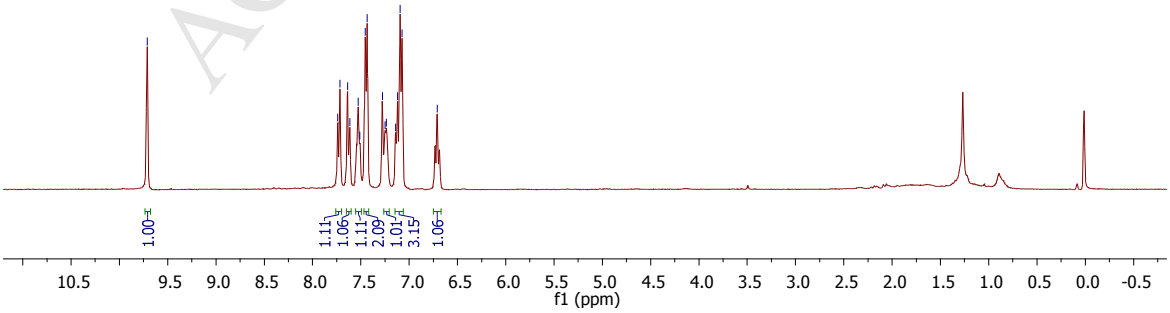


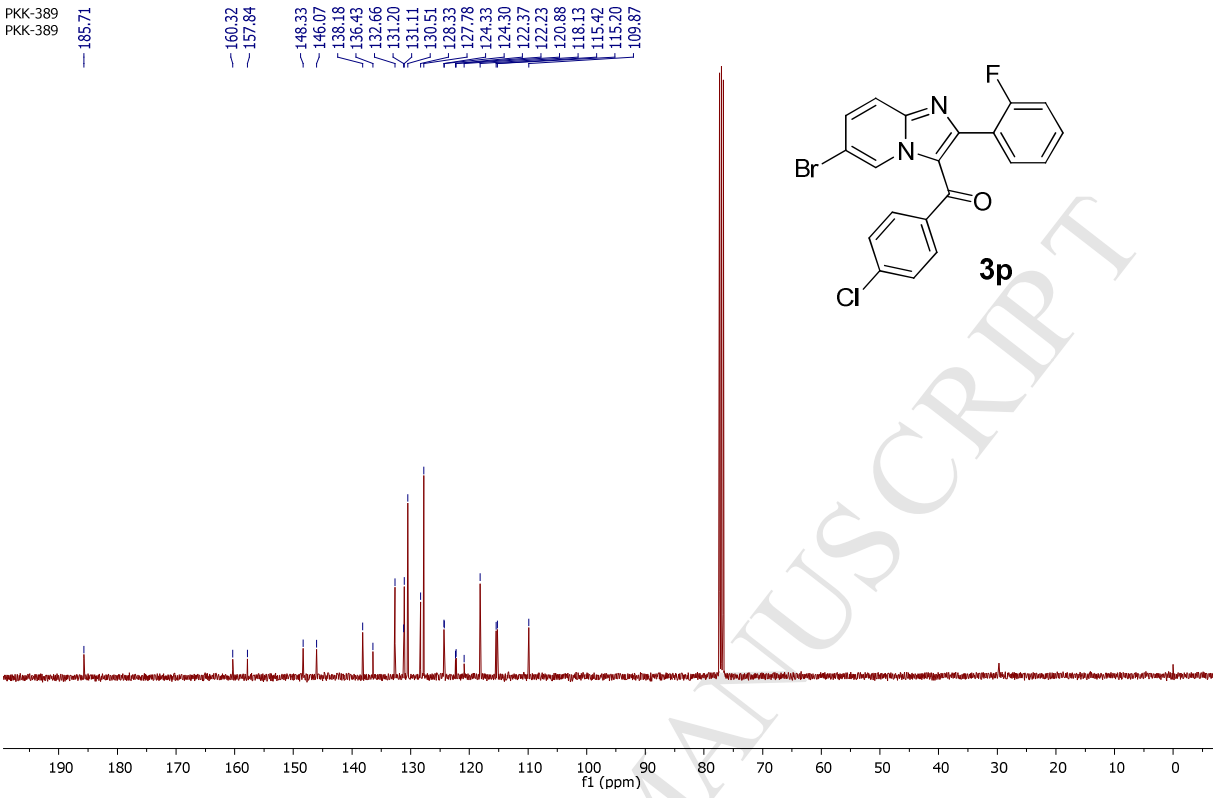


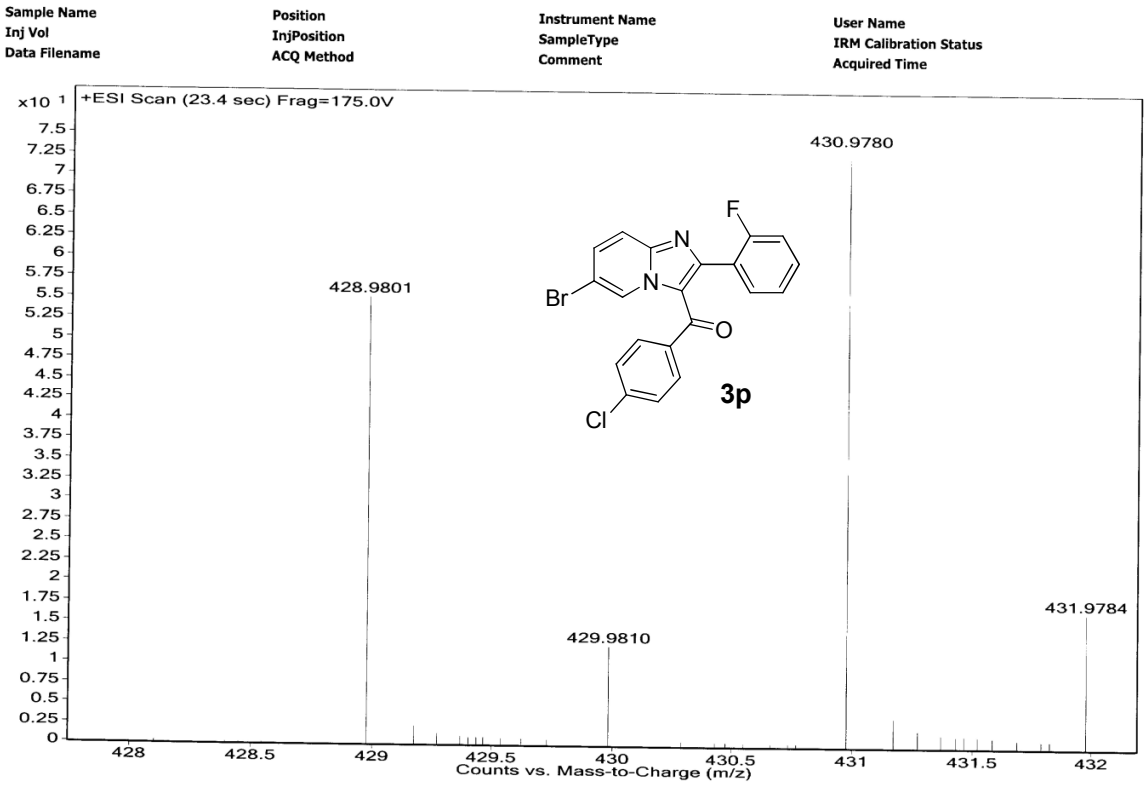

Sample Name
Inj Vol
Data Filename
Position
InjPosition
ACQ Method
Instrument Name
SampleType
Comment
User Name
IRM Calibration Status
Acquired Time
x10 2
+ESI Scan (41.0 sec) Frag=175.0V
* 365.0851
120.0446
279.0923
Counts vs. Mass-to-Charge (m/z)
F
N
N
O
Cl
3o

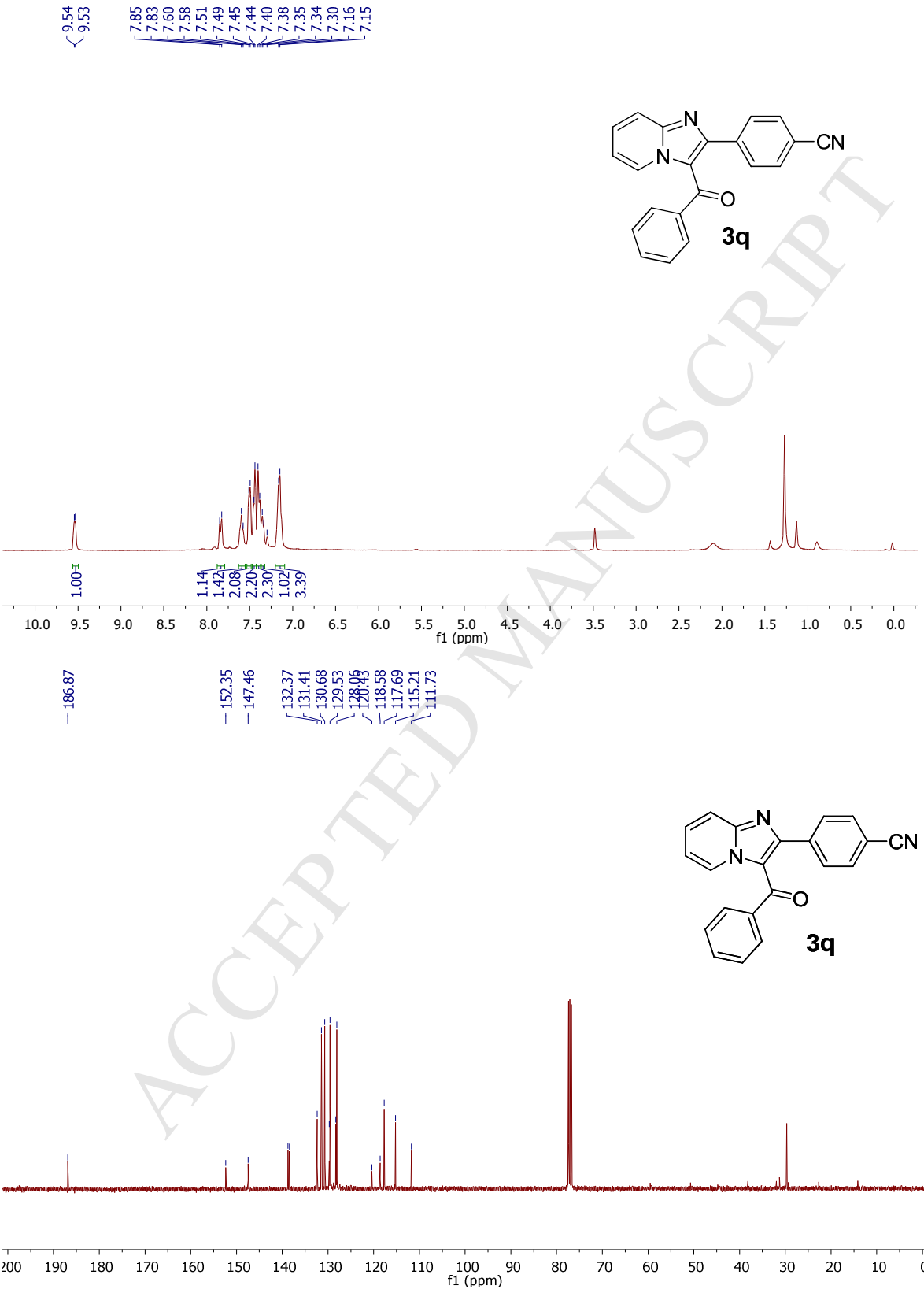

9.71
7.74
7.72
7.64
7.62
7.53
7.51
7.45
7.44
7.28
7.25
7.24
7.14
7.12
7.09
7.07
6.71

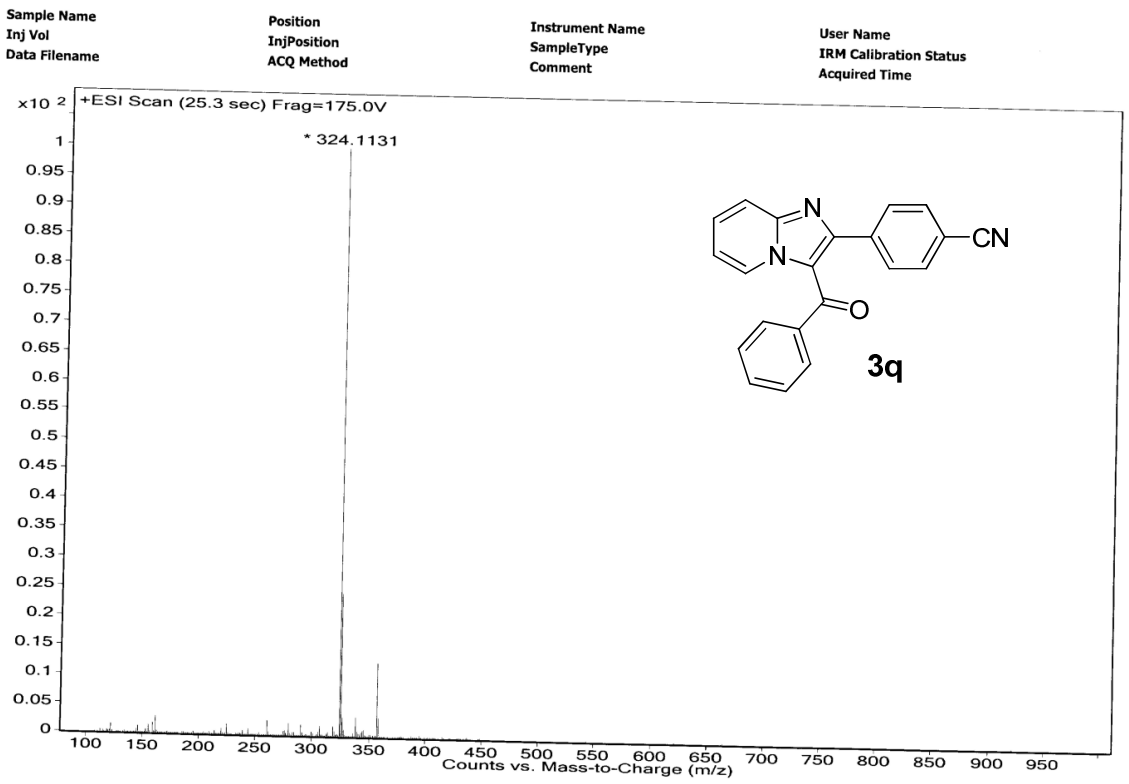

F
N
N
Br
O
Cl
3p

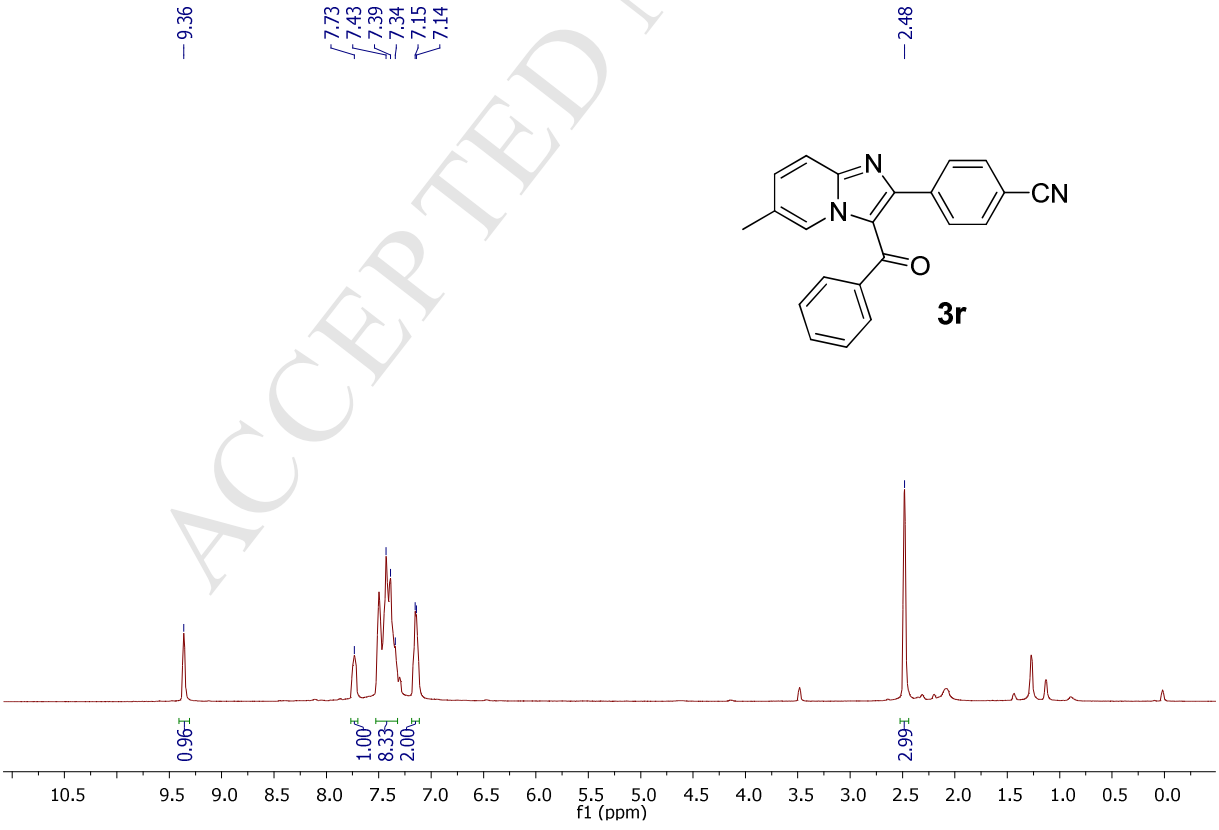

1.00
1.11
1.06
1.11
2.09
1.01
3.15
1.06
f1 (ppm)

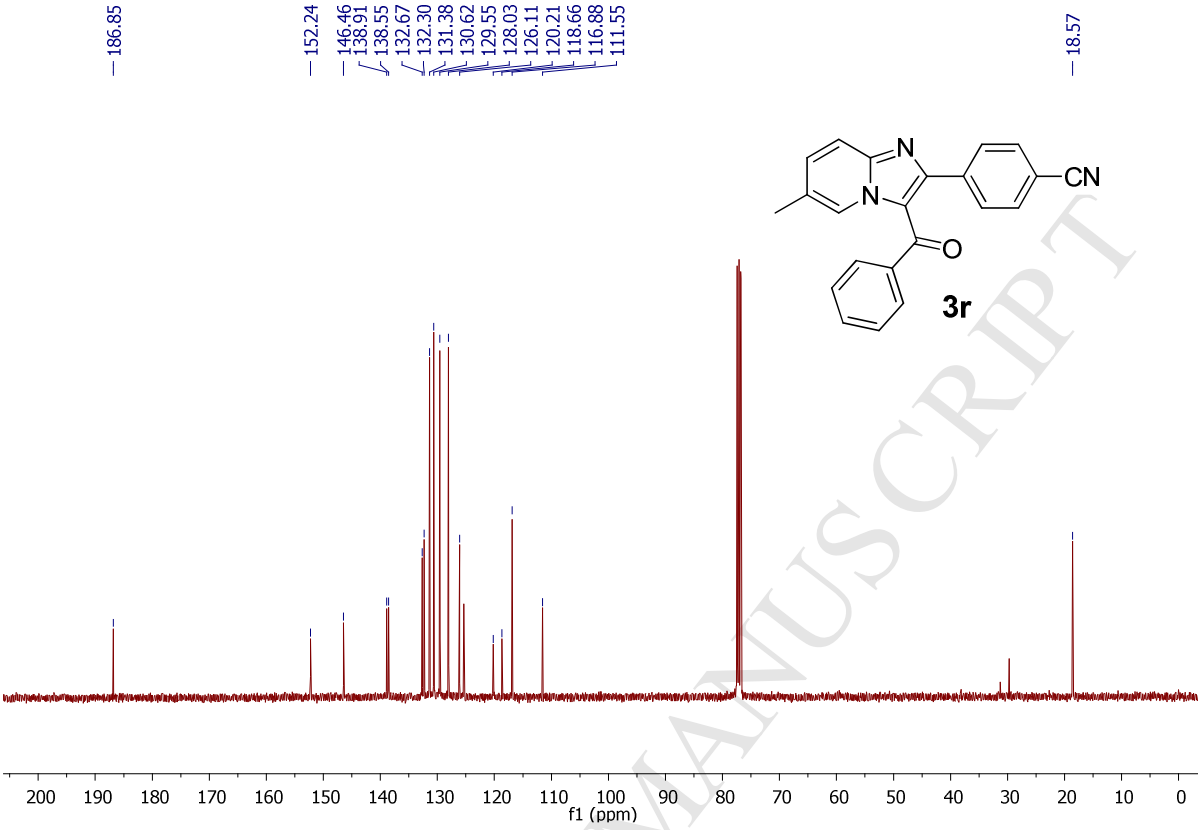

PKK-389
PKK-389
185.71
160.32
157.84
148.33
146.07
138.18
136.43
132.66
131.20
131.11
130.51
128.33
127.78
124.33
124.30
122.37
122.23
120.88
118.13
115.42
115.20
109.87
F
N
N
Br
O
Cl
3p
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

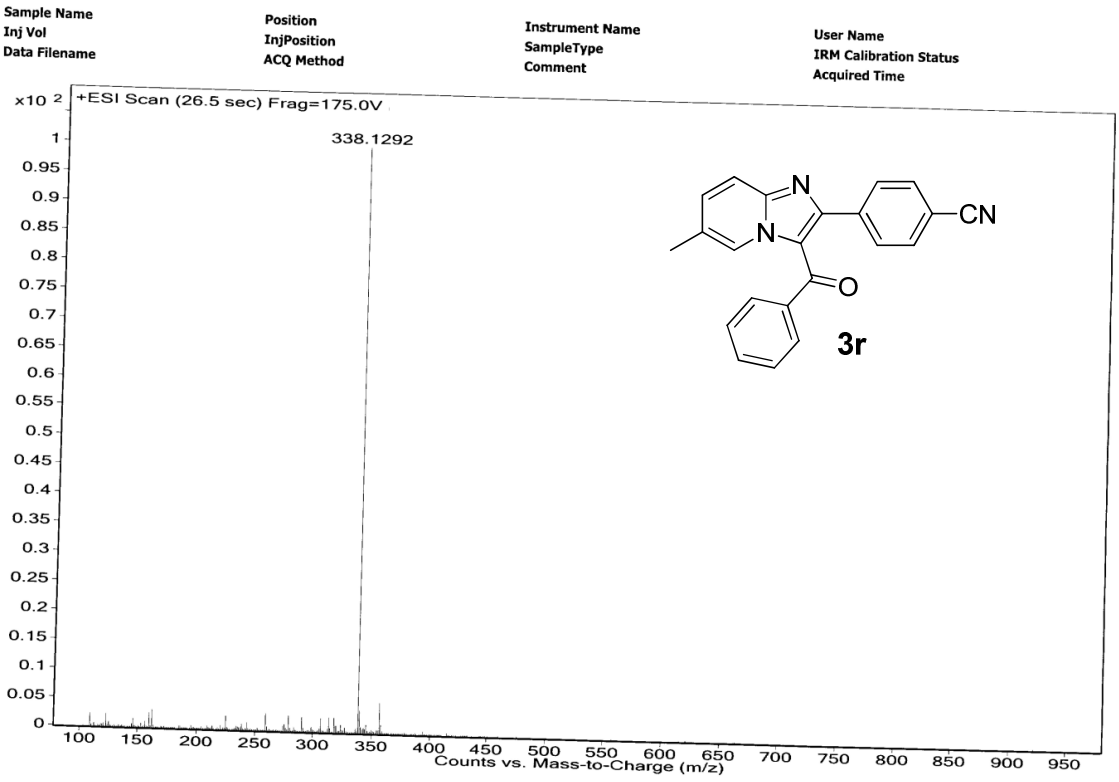

Sample Name
Inj Vol
Data Filename
Position
InjPosition
ACQ Method
Instrument Name
SampleType
Comment
User Name
IRM Calibration Status
Acquired Time
x10 1
+ESI Scan (23.4 sec) Frag=175.0V
7.5
7.25
7
6.75
6.5
6.25
6
5.75
5.5
5.25
5
4.75
4.5
4.25
4
3.75
3.5
3.25
3
2.75
2.5
2.25
2
1.75
1.5
1.25
1
0.75
0.5
0.25
0
428.9801
429.9810
430.9780
431.9784
F
N
N
Br
O
Cl
3p
428 428.5 429 429.5 430 430.5 431 431.5 432
Counts vs. Mass-to-Charge (m/z)








186.85
152.24
146.46
138.91
138.55
132.67
132.30
131.38
130.62
129.55
128.03
126.11
120.21
118.66
116.88
111.55
18.57
N
N
CN
O
3r
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Sample Name
Inj Vol
Data Filename
Position
InjPosition
ACQ Method
Instrument Name
SampleType
Comment
User Name
IRM Calibration Status
Acquired Time
x10 2
+ESI Scan (26.5 sec) Frag=175.0V
338.1292
N
N
CN
O
3r
Counts vs. Mass-to-Charge (m/z)