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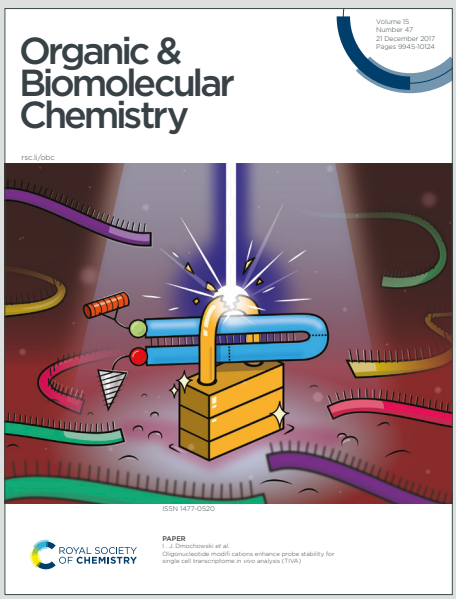

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ARTICLE

Singlet Oxygen Mediated Dual C-C and C-N bond cleavage in Visible Light

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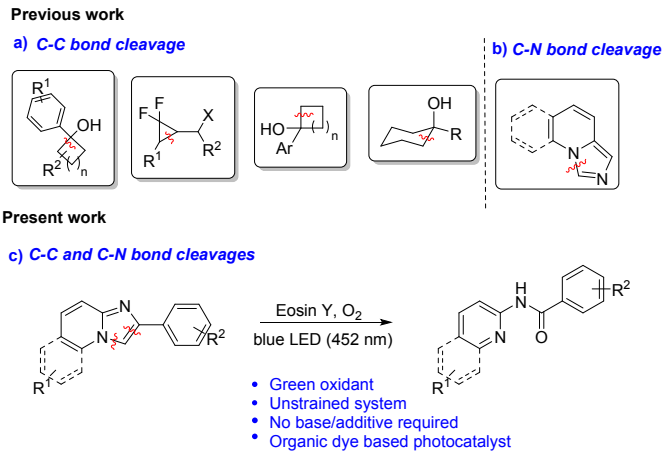
Ritu, Charu Sharma, Sharvan Kumar and Nidhi Jain*

A tandem cleavage of carbon-carbon and carbon-nitrogen bonds in imidazo[1,2-a]pyridines and imidazo[1,2-a]quinolines is reported in presence of Eosin Y and visible light. The ring opening occurs under ambient conditions through singlet oxygen insertion, bond cleavages and CO_2 elimination, and produces *N*-(pyridin-2-yl) amides and *N*-(quinolin-2-yl) amides in high yields. The reaction shows good versatility, and does not require strong external oxidants and additives.

Introduction

Carbon-carbon bond cleavage reactions are ubiquitous in organic transformations, biodegradation and utilization of hydrocarbons in oil and petroleum industry.[1] Though useful, they are difficult to cleave and require harsh conditions like oxidants in stoichiometric amount or toxic metal salts.[2] Like C-C bonds, C-N bonds which are abundantly found in organic molecules are equally cumbersome to cleave. The traditional approach[3] to affect this cleavage involves transition metal mediated oxidative addition to C-N bonds, or transformation to diazonium salts, ammonium salts, triazenes and imidazoles. Some transition-metal free strategies[4] have also been developed, though they necessitate the use of acids, bases, reducing agents, strong oxidants or expensive reagents like CsF. In recent years, visible light has turned into an ideal tool to achieve organic transformations.[5] It enables access to highly active intermediates which can form *in situ* without the use of stoichiometric reagents. The applications of photoredox reactions span a wide range including reduction,[6a,b] oxidation,[6c,d] carbonylation,[6e,f] addition,[6g,h] cross-coupling,[6i] and many more. Recently, light assisted ring opening reactions via C–C bond cleavage have been realised by tapping the high reactivity of strained systems in some cases and using strong oxidants, bases or additives in other (Scheme 1a).[7] Ring opening of imidazo[1,5-*a*]quinolines in visible light through a C-N bond cleavage was recently reported (Scheme 1b).[8]

Scheme 1: Ring opening reactions in light via C-C and C-N bond cleavage



Our intent was to explore photo-assisted oxidative C-C/C-N bond cleavages using molecular oxygen instead of peroxides or toxic metal salts. The cleavage of C-C and C-N bonds together in a single synthetic transformation under conventional conditions has few reports. Zhu (2013)[9a] and Laha (2014)[9b] independently demonstrated metal-free demethylenation in *N*-benzyl-2-aminopyridines and dihydrodiazepines respectively *via* C-C and C-N bond cleavages, and tandem intramolecular C-N bond formation using strong oxidants like phenyliodine diacetate (PIDA) and $K_2S_2O_8$ respectively. Wang[9c] and co-workers demonstrated an oxidative ring opening of imidazopyridines through C-C and C-N bond cleavages at 80°C with TBHP as the oxidant. In all these transformations, requirement of a strong external oxidant in high stoichiometric amount was an inherent limitation. Taking a lead from previous reports and continuing our endeavours towards visible light mediated synthetic transformations,[10] we embarked upon the ring opening reaction of

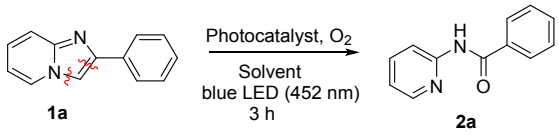
[a] *Department of Chemistry, Indian Institute of Technology, New Delhi-110016, India*
**Corresponding Author Phone: 011-2659-1562. E-mail: njain@chemistry.iitd.ac.in.*
†Electronic Supplementary Information (ESI) available: [Copies of ^{1}H NMR, ^{13}C NMR, and HR-MS for all the synthesized compounds, CV studies, ORTEP and associated X-ray crystallographic data for **4g** have been included]. See DOI: 10.1039/x0xx00000x

imidazopyridines and imidazoquinolines under visible light conditions (Scheme 1c). The reaction took place through a tandem process involving oxidative removal of the methine group via C–C and C–N bond cleavages followed by formation of a new C–O bond.

Results and Discussion

As shown in Table 1, we began our investigation with 2-phenylimidazo[1,2-a]pyridine (**1a**) as the model substrate. Upon irradiation of **1a** with 10 W blue LED under O_2 atmosphere using Eosin Y (2 mol%) as photocatalyst and DMF as solvent, the desired product *N*-(pyridine-2-yl)benzamide (**2a**) was obtained in 50% yield (entry 1). In order to optimize the reaction, various solvents were screened (entries 1-7), and acetonitrile was found to be the solvent of choice (entry 4). Polar aprotic solvents like DMF, DMA and DMSO gave moderate yields (entries 1-3) while polar protic (entry 5) and non-polar solvents (entries 6 and 7) did not promote the reaction. Polar aprotic solvents are known to stabilize high energy intermediates, radicals/ions and charged species while polar protic solvents readily react with such species and form by-products which drastically suppresses the product yield. Ir and Ru based photocatalysts were also tested (Table 1, entries 8 and 9) but gave lower yields due to formation of unidentified side products. Notably, in the absence of light or under nitrogen atmosphere, the reaction did not take place at all (entries 10 and 11) suggesting that the ring opening was an oxidative process triggered only in the presence of light.

Table 1: Optimisation of the reaction conditions[a,b]



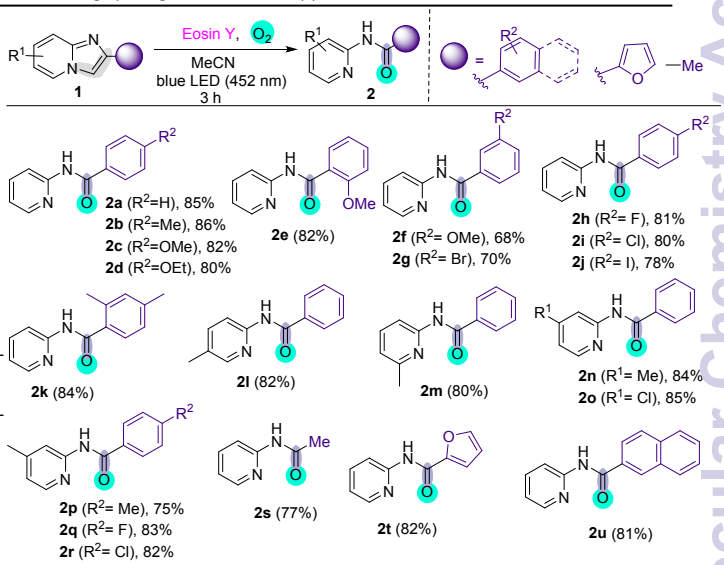
Entry	Catalyst	Solvent	Yield[a,b] [%]
1	Eosin Y	DMF	50
2	Eosin Y	DMA	50
3	Eosin Y	DMSO	40
4	Eosin Y	MeCN	90
5	Eosin Y	MeOH	5
6	Eosin Y	Toluene	7
7	Eosin Y	DCM	3
8	$[Ir\{dF(CF_3)ppy\}_2(dtbpy)]PF_6$	MeCN	75
9	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	MeCN	80
10[c]	Eosin Y	MeCN	NR
11[d]	Eosin Y	MeCN	NR
12[e]	Eosin Y	MeCN	70
13[f]	-	MeCN	50

[a]**1a** (0.5 mmol), photocatalyst (2 mol%), CH_3CN (4 mL), 10 W blue LED (452 nm) irradiation under O_2 atmosphere at room temperature for 3h unless otherwise stated. [b]Yield of product as determined by GC-MS. [c]Reaction performed in dark. [d]Reaction carried out under N_2 atmosphere. [e]Reaction carried out in air. [f]Reaction carried out without photocatalyst.

Replacing O_2 balloon with air declined the conversion to 70% (entry 12). Erosion in product yield was also seen in the absence of Eosin Y (entry 13) due to direct photochemical alteration of the substrate resulting in multiple unidentified side products. Yet, a 50% yield of **2a** without external photosensitizer intrigued us and we investigated if the starting material itself was acting as a photosensitizer. To understand this, electronic properties (UV-vis and fluorescence) of **1a** were studied (SI, Fig. S1), and control reaction of **1a** and α-terpinene was carried out (SI, Fig. S2). The results pointed out towards the potential ability of imidazopyridine to behave as a mild photosensitizer in this reaction. Thus, the best optimized conditions were arrived at with 2 mol% Eosin Y in MeCN under O_2 atmosphere in presence of 10 W blue LED for 3 h.

Following this initial success, we decided to explore the scope of ring opening on various imidazo[1,2-a]pyridines (Table 2). It was found that substrates bearing electron donating and electron withdrawing substituents both on pyridine ring as well on phenyl ring tolerated the reaction conditions well and afforded the corresponding products in good yields. Electron donating groups (such as Me, OMe and OEt) at 4-position of phenyl group of imidazo[1,2-a]pyridines gave the corresponding products (**2b**-**2d**) in 80-86% yields. Moving OMe group to 2-position of phenyl ring didn't alter the reactivity and **2e** was obtained in 82% yield.

Table 2: Ring opening of imidazo[1,2-a]pyridines[a,b]



[a] Reaction conditions: **1** (0.5 mmol), Eosin Y (2 mol%), CH_3CN (4mL), 10 W blue LED (452 nm) irradiation under O_2 atmosphere at room temperature for 3h. [b] Isolated yield.

Notably, changing the substituent position to meta lowered the product yield (**2f** and **2g**). (4-halophenyl)imidazo[1,2-a]pyridines (**1h**-**1j**) also showed good compatibility and gave the respective products (**2h**-**2j**) in 78-81% yields. Ring opening of (2,4-dimethylphenyl)imidazo[1,2-a]pyridine **1k** furnished the dimethyl amide derivative, **2k** in 84% yield. Variations in pyridine ring of imidazo[1,2-a]pyridines were carried out next. With methyl substituent at 6- and 5-positions of imidazo[1,2-a]pyridine, **2l** and **2m** were formed in 82% and 80% yields respectively. With 7-Me and 7-Cl substituted starting material, corresponding products **2n** and **2o** were obtained in good yields. Moreover, when substituents were placed both on pyridine and phenyl ring of **1**, corresponding ring opened products (**2p**-**2r**) were obtained in 75-83% yields. Notably, 2-methyl imidazo[1,2-a]pyridine (**1s**) was amenable to the reaction conditions and gave **2s** in 77% yield. Further, with 2-

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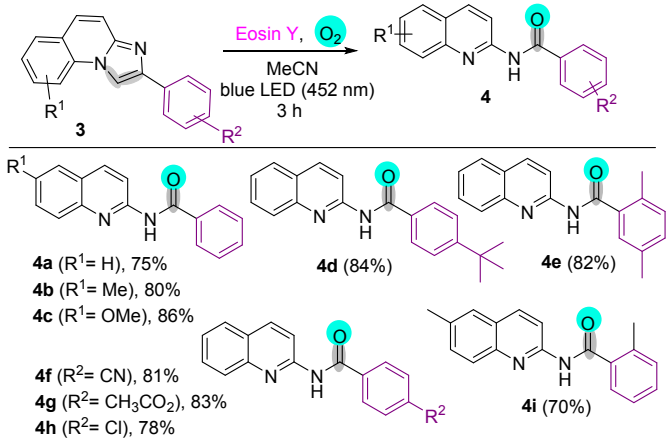
(furan-2-yl)imidazo[1,2-a]pyridine (**1t**), reaction was equally facile and *N*-phenylfuran-2-carboxamide **2t** formed in 82% yield. These derivatives (**2s** and **2t**) upon further synthetic modifications can be translated into molecules of potential biological activity.[11a,b] Our method is advantageous over the previous strategies where products **2s** and **2t** were obtained in very low yields.[9c,d] The reaction also worked with 2-(naphthalene-2-yl)imidazo[1,2-a]pyridine (**1u**) derivative giving the corresponding amide **2u** in 81% yield.

To further expand the reaction scope, we delved into its applicability on 2-phenylimidazo[1,2-a]quinolines (**3**) as substrate, with the results summarised in Table 3. unsubstituted starting material, various substrates bearing both electron donating and withdrawing groups were examined.

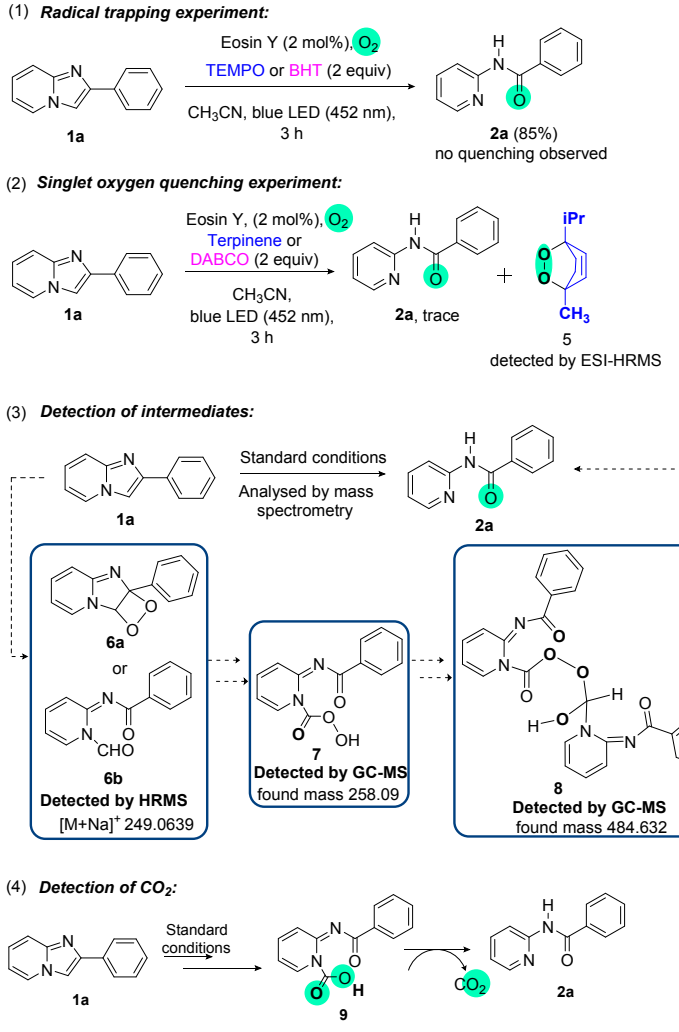
Table 3: Ring opening of 2-phenylimidazo[1,2-a]quinolines[a,b]



[a] Reaction conditions: **3** (0.5 mmol), Eosin Y (2 mol%), CH_3CN (4 mL), 10 W blue LED (452 nm) irradiation under O_2 atmsophere at room temperature for 3 h.
[b] Isolated yield.

Electron donating methyl and methoxy groups at 7-position of imidazo[1,2-a]quinoline, generated products (**4b** and **4c)** in 80-86% yield. Variations on phenyl ring were carried out next. Standard conditions were applicable to 2-(4-(*tert*-butyl)phenyl)imidazoquinoline (**3d**) and 2-(2,5-dimethylphenyl)imidazoquinoline (**3e**), giving products (**4d** and **4e**) in 84 and 82% yields respectively. With electron withdrawing groups such as CN, CH_3CO_2 and Cl, corresponding products (**4f** and **h**) were isolated in 78-83% yields. 7-Methyl-2-(o-tolyl)imidazoquinoline (**3i**) also exhibited good compatibility forming the amide product (**4i**) in moderate yield. It is well known that a photochemical reaction can either be initiated by (i) single electron transfer (SET) process where photoredox catalyst can undergo oxidation or reduction, or by (ii) energy transfer (et) from the excited state photocatalyst to a sensitizer which then induces the reaction or reacts with the substrate leading to product formation. To understand the pathway followed in this reaction, a set of control and trapping experiments were carried out. Having obtained the product in 75% yield (**4a**) with CV and DPV analysis (SI, fig. S3) of 2-phenylimidazopyridine revealed a reduction wave at -1.13 V and an oxidation wave at 1.36 V against SCE. Both redox states lie beyond the excited state reduction, $E_{1/2}$ ($^3EY^*/EY^{\bullet-}$) = -1.11 V and oxidation, $E_{1/2}$ ($EY^{\bullet+}/^3EY^*$) = 0.83 V potential of Eosin Y. This observation neglects the chances of electron transfer between the photocatalyst and substrate.

Scheme 2: Investigations for mechanistic study



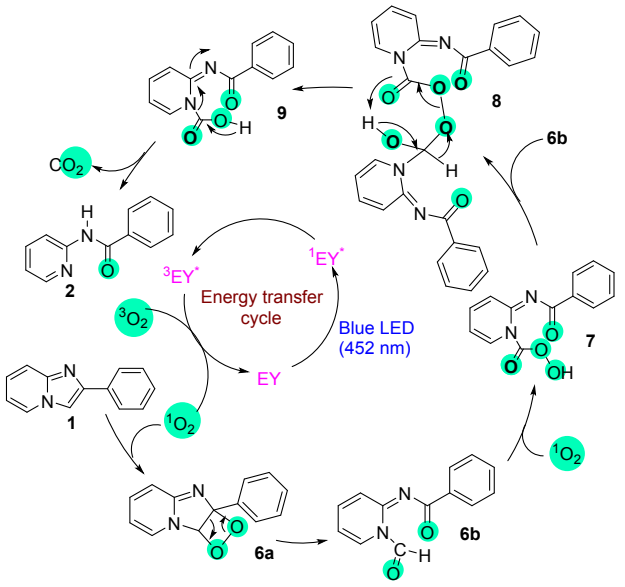
However, the reduction potential of O_2 (-0.75 V vs SCE) is suggestive of a probable reduction of O_2 to $O_2^{\bullet-}$ by Eosin Y.[13] In addition, theoretical calculations from previous reports[14] suggest that triplet energy (ET) of eosin Y (^3EY) = 43.58 kcal/mol is sufficient for the photosensitization of $^3O_2$ to $^1O_2$ [E ($^1\Delta$-$^3\Sigma$) = 22.5 kcal/mol]. Hence, the reaction might proceed via reaction of 2-phenylimidazo[1,2-a]pyridine with $O_2^{\bullet-}$ or with singlet $^1O_2$.

To confirm this, control reaction was performed using radical scavengers TEMPO/BHT (Scheme 2 (1)). No suppression in the product yield was observed which suggested that the reaction proceeded through an energy transfer pathway rather than SET. Further, involvement of singlet oxygen was ascertained when reaction was adequately quenched in presence of α-terpinene and 1,4-diazabicyclo[2.2.2]octane (DABCO). Additionally, the peroxidation product of α-terpinene by $^1O_2$ was detected by HRMS (Scheme 2 (2)). The anticipated intermediates, **6a** or **6b** were confirmed from the HRMS of reaction mixture (Scheme 2

(3)). Further, less stable intermediates **7** and **8**, and CO_2 expelled during the reaction were determined by GC-MS analysis (Scheme 2 (3 and 4)).

Based on previous reports[15] and preliminary investigations, a plausible mechanism for the oxidative ring opening of **1** and **3** is proposed (Scheme 3). Upon irradiation by visible light, Eosin Y (EY) gets excited and undergoes rapid intersystem crossing to reach to its lowest triplet state (^{3}EY*). After that, it comes to ground state by transferring its energy to molecular oxygen by which ground state triplet oxygen ($^3O_2$) gets activated to singlet form ($^1O_2$).

Scheme 3: Proposed mechanism



$^1O_2$ possess sufficient activation energy and selectively reacts with the C=C bond of imidazopyridine forming a 4-membered dioxetane ring (**6a**). Subsequently, the ring opens up and produces (Z)-*N*-(6-formylcyclohexa-2,4-dien-1-ylidene) benzamide(**6b**).[15a,b] Insertion of $^1O_2$ into C-H bond of aldehyde intermediate **6b** generates peracid **7** which further forms an adduct **8** by reacting with another molecule of **6b**. Intermediate **8** decomposes to form **9** which eventually undergoes decarboxylation and aromatisation to afford the ring opened product **2**.[15c,d]

Conclusions

In conclusion, an oxidative ring opening of imidazo[1,2-a]pyridines and imidazo[1,2-a]quinolines is described in presence of oxygen and visible light using Eosin Y as organic photocatalyst. Mechanistic studies suggest an energy transfer pathway involving photochemical generation of singlet oxygen, it's incorporation into C=C, tandem cleavage of C-C and C-N bonds of heterocycle followed by deformylative aromatization into product via expulsion of CO_2. The methodology is metal-free, does not involve use of strong external oxidants or additives, and takes place in visible light under mild conditions.

Experimental

General

All reagents and solvents were of pure analytical grade. Thin layer chromatography (TLC) was performed on 60 F254 silica gel, pre-coated on aluminium plates and revealed with either a UV lamp (λmax= 254 nm). The products were purified by column chromatography on silica gel 230–400 mesh. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz (^{1}H 300MHz,^{13}C 75 MHz), 400 MHz spectrometer (^{1}H 400 MHz, ^{13}C 100 MHz) and 500 MHz spectrometer (^{1}H 500 MHz, ^{13}C 125 MHz) using $CDCl_3$, DMSO and D_2O as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts are in δ (ppm) relative to TMS. The coupling constants (J) are in Hz. High resolution mass spectra (HRMS) were recorded on a mass spectrometer using electrospray ionization-time-of-flight (ESI-TOF) reflectron experiments. Gas quantification was carried out by gas chromatography (GC trace 1110 thermo scientific with carboxen column). All starting materials (**1** and **3**) are known compounds and were synthesized using reported procedures. 2-phenyl imidazo[1,2-*a*]pyridine (**1**) and 2-phenyl imidazo[1,2-*a*]quinoline (**3**) were prepared by following the reported procedure.[16,17]

General procedure for ring opening reaction of 2-phenyl imidazo[1,2-*a*]pyridines (1):

Synthesis of *N*-(pyridine-2-yl)benzamides (2a-2u):

A reaction tube was charged with 2-phenylimidazo[1,2-*a*] pyridine (**1a**) (100 mg, 0.5 mmol) and eosin Y (2 mol %) dissolved in MeCN (4.0 mL). The reaction mixture was stirred under blue LED (10 W) irradiation in O_2 atmosphere at RT for 3h, and monitored by thin layer chromatography. The mixture was extracted with ethyl acetate, dried over Na_2SO_4 and evaporated under reduced pressure. The compound was purified by column chromatography to obtain **2a** (87 mg, 85%) as a white solid.

General procedure for ring opening reaction of 2-phenylimidazo[1,2-*a*]quinolines (3):

Synthesis of *N*-(quinoline-2-yl)benzamides (4a-4i):

A reaction tube was charged with 2-phenylimidazo[1,2-*a*]quinoline (**3a**) (122 mg, 0.5 mmol) and eosin Y (2 mol %) dissolved in MeCN (4.0 mL). The reaction mixture was stirred under blue LED (10 W) irradiation in O_2 atmosphere at RT for 3h, and monitored by thin layer chromatography. The mixture was extracted with ethyl acetate, dried over Na_2SO_4 and evaporated under reduced pressure. The compound was purified by column chromatography to obtain **4a** (93 mg, 75%) as a white solid.

Physical properties and characterization data of synthesized compounds:

***N*-(pyridin-2-yl)benzamide (2a):[18]**

Isolated as White solid in Hexane/EtOAc (93/7), 85% yield, 87 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (br, 1H), 8.41 (d, *J* = 8.4 Hz, 1H), 8.16 (s, 1H), 7.93 (d, *J* = 6.4 Hz, 2H), 7.75 (t, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 6.8 Hz, 1H), 7.48 (t, *J* = 6.6 Hz, 2H), 7.03 (d, *J* = 4.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.0, 151.7, 147.7, 138.5, 134.3, 132.2, 128.8, 127.3, 119.9, 114.4.

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4-methyl-*N*-(pyridin-2-yl)benzamide (2b):[18]
Isolated as White solid in Hexane/EtOAc (93/7), 86% yield, 91 mg. 1H NMR (400 MHz, CDCl3) δ 11.88 (br, 1H), 8.96 (d, J = 8.8 Hz, 1H), 8.30 (d, J = 5.2 Hz, 1H), 8.22 (d, J = 8.4 Hz, 1H), 8.18 (t, J = 8.0 Hz, 2H), 7.38 (d, J = 6.8 Hz, 1H), 7.34 (d, J = 8.4 Hz, 2H), 2.43 (s, 3H). 13C{1H} NMR (75 MHz, CDCl3) δ 166.0, 151.7, 147.8, 138.4, 131.4, 129.5, 127.3, 119.8, 114.2, 21.5.

4-methoxy-*N*-phenylbenzamide (2c):[18]
Isolated as White solid in Hexane/EtOAc (90/10), 82% yield, 93 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.54 (br, 1H), 8.64 (d, *J* = 8.8 Hz, 1H), 8.26 (d, *J* = 4.4 Hz, 1H), 8.09 (d, *J* = 8.8 Hz, 2H), 7.95 (t, *J* = 8.4 Hz, 1H), 7.23 – 7.14 (m, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.7, 163.3,151.0, 142.9, 141.8, 130.1, 124.9, 119.4, 115.7, 114.1, 55.5.

4-ethoxy-*N*-(pyridin-2-yl)benzamide (2d):[19]
Isolated as White solid in Hexane/EtOAc (90/10), 80% yield, 97 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (br, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 8.14 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.65 (s, 1H), 6.94 (s, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.06 – 3.94 (m, 2H), 1.36 (t, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.5, 162.8, 151.9, 148.2, 138.4, 129.1, 126.2, 119.6, 114.5, 114.2, 64.0, 14.6.

2-methoxy-*N*-(pyridin-2-yl)benzamide (2e):[20]
White solid, 82% yield, 93 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.40 (br, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.31 (s, 1H), 8.25 (d, *J* = 7.2 Hz, 1H), 7.71 (s, 1H), 7.47 (s, 1H), 7.09 (d, *J* = 6.8 Hz, 1H), 7.06 – 6.93 (m, 2H), 4.02 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.6, 157.5, 151.9, 147.8, 138.3, 133.7, 132.4, 121.4, 121.3, 119.6, 114.8, 111.5, 56.1.

3-methoxy-*N*-(pyridin-2-yl)benzamide (2f):[20]
Isolated as White solid in Hexane/EtOAc (90/10), 68% yield, 77 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.34 (br, 1H), 8.45 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 4.1 Hz, 1H), 7.80 (t, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 6.8 Hz, 2H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.10 (m, 2H), 3.89 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.8, 160.0, 151.7, 147.5, 138.8, 135.7, 129.8, 119.9, 119.3, 118.8, 114.6, 112.4, 55.4.

3-bromo-*N*-(pyridin-2-yl)benzamide (2g):[20]
Isolated as White solid in Hexane/EtOAc (94/6), 70% yield, 97 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (br, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 8.22 (d, *J* = 3.6 Hz, 1H), 8.11 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.82 – 7.75 (m, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.08 (dd, *J* = 5.2, 6.8 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.5, 151.4, 147.8, 138.7, 136.3, 135.3, 130.7, 130.4, 126.0, 123.2, 120.2, 114.9.

4-fluoro-*N*-(pyridin-2-yl)benzamide (2h):[21]
Isolated as White solid in Hexane/EtOAc (95/5), 81% yield, 87 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (br, 1H), 8.39 (d, *J* = 8.5 Hz, 1H), 8.22 (d, *J* = 4.2 Hz, 1H), 8.00 – 7.94 (m, 2H), 7.81 – 7.75 (m, 1H), 7.18 (t, *J* = 6.8 Hz, 2H), 7.08 (dd, *J* = 7.0, 5.0 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 166.4, 164.8, 163.9, 151.6, 147.8, 138.6, 130.5, 129.8, 120.0, 116.0, 115.8, 114.4.

4-chloro-*N*-phenylbenzamide (2i):[18]
Isolated as White solid in Hexane/EtOAc (95/5), 80% yield, 93 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (br, 1H), 8.37 (d, *J* = 8.5 Hz, 1H), 8.30 (d, *J* = 4.5 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.81 – 7.75 (m, 1H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.10 (dd, *J* = 5.0, 6.5 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.6, 151.4, 147.9, 138.6, 132.6, 129.2, 128.7, 120.2, 114.2.

4-iodo-*N*-(pyridin-2-yl)benzamide (2j):[18]
Isolated as White solid in Hexane/EtOAc (95/5), 78% yield, 126 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (br, 1H), 8.37 (d, *J* = 8.5 Hz, 1H), 8.24 (d, *J* = 4.0 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.80 – 7.73 (m, 1H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.08 (dd, *J* = 5.0, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.0, 151.3, 147.9, 138.5, 138.1, 133.7, 128.8, 120.1, 114.3, 99.5.

2,4-dimethyl-*N*-(pyridin-2-yl)benzamide (2k):[22]
Isolated as White solid in Hexane/EtOAc (93/7), 84% yield, 95 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (br, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 5.6 Hz, 1H), 7.79 – 7.69 (m, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.10 – 7.04 (m, 2H), 7.03 – 6.99 (m, 1H), 2.50 (s, 3H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 167.4, 150.7, 146.8, 139.8, 137.4, 135.8, 131.9, 131.2, 126.0, 125.5, 118.7, 113.0, 20.3, 18.9.

***N*-(5-methylpyridin-2-yl)benzamide (2l):[18]**
Isolated as White solid in Hexane/EtOAc (93/7), 82% yield, 87 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (br, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 8.04 (s, 1H), 7.92 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 2.30 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.8, 149.5, 147.6, 139.2, 134.9, 132.1, 129.3, 128.8, 127.2, 113.9, 17.9.

***N*-(m-tolyl)benzamide (2m):[21]**
Isolated as White solid in Hexane/EtOAc (94/6), 80% yield, 85 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (br, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 7.97 – 7.92 (m, 2H), 7.65 (t, *J* = 7.9 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 6.93 (d, *J* = 7.5 Hz, 1H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.8, 156.8, 150.9, 138.9, 134.3, 132.1, 128.7, 127.3, 119.4, 111.1, 23.8.

***N*-(4-methylpyridin-2-yl)benzamide (2n):[19]**
Isolated as White solid in Hexane/EtOAc (93/7), 84% yield, 89 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (br, 1H), 8.25 (s, 1H), 8.08 (s, 1H), 7.92 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 4.4 Hz, 1H), 2.41 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.8, 151.6, 149.9, 147.5, 134.4, 132.2, 129.0, 127.2, 121.1, 114.7, 21.7.

***N*-(4-chloropyridin-2-yl)benzamide (2o):[19]**
Isolated as White solid in Hexane/EtOAc (95/5), 85% yield, 97 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (br, 1H), 8.52 (d, *J* = 1.5 Hz, 1H), 8.22 (d, *J* = 5.0 Hz, 1H), 7.94 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.0 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.12 (dd, *J* = 5.0, 1.5 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.8, 152.6, 148.5, 146.1, 133.9, 132.5, 128.9, 127.3, 120.3, 114.4.

4-methyl-*N*-(4-methylpyridin-2-yl)benzamide (2p):[18]
Isolated as White solid in Hexane/EtOAc (92/8), 75% yield, 85 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (br, 1H), 8.25 (s, 1H), 8.11 (s, 1H), 7.83 (d, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 2H), 6.88 (s, 1H), 2.42 (s, 3H), 2.40 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.8, 151.7, 150.0, 147.4, 142.8, 131.5, 129.5, 127.3, 121.0, 114.7, 21.5, 21.6.

4-fluoro-*N*-(4-methylpyridin-2-yl)benzamide (2q):[19]
Isolated as White solid in Hexane/EtOAc (94/6), 83% yield, 95 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (br, 1H), 8.23 (s, 1H), 8.00 (d, *J* = 4.4 Hz, 1H), 7.95 (dd, *J* = 5.2, 5.2 Hz, 2H), 7.15 (t, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 4.4 Hz, 1H), 2.40 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.4, 164.9, 163.9, 151.7, 150.2, 147.3, 130.6, 129.7, 121.2, 116.0, 115.7, 114.9, 21.4.

4-chloro-*N*-(4-methylpyridin-2-yl)benzamide (2r):[18]
Isolated as White solid in Hexane/EtOAc (94/6), 82% yield, 101 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.25 (br, 1H), 8.79 (s, 1H), 8.28 (d, *J* = 8.4 Hz, 2H), 8.14 (d, *J* = 5.0 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 4.8 Hz, 1H), 2.63 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.3, 159.5, 149.2, 140.2, 137.1, 131.4, 130.1, 129.3, 120.8, 117.2, 22.9.

***N*-phenylacetamide (2s):[23]**
Isolated as White solid in Hexane/EtOAc (88/12), 77% yield, 52 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (br, 1H), 8.26 (d, *J* = 4.4 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 7.71 (t, *J* = 8.4 Hz, 1H), 7.08 – 7.01 (m, 1H), 2.21 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 169.0, 151.7, 147.4, 138.9, 119.7, 114.3, 24.6.

***N*-(pyridin-2-yl)furan-2-carboxamide (2t):[18]**
Isolated as White solid in Hexane/EtOAc (93/7), 82% yield, 77 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.36 – 8.29 (m, 2H), 7.80 – 7.70 (m, 1H), 7.54 (d, *J* = 0.9 Hz, 1H), 7.29 (dd, *J* = 3.5, 0.5 Hz, 1H), 7.13 – 7.02 (m, 1H), 6.58 (dd, *J* = 3.5, 1.5 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 156.2, 151.0, 148.0, 147.4, 144.8, 138.5, 120.0, 115.9, 114.2, 112.7.

***N*-(pyridin-2-yl)-2-naphthamide (2u):[18]**
Isolated as White solid in Hexane/EtOAc (92/8), 81% yield, 101 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (br, 1H), 8.44 (s, 2H), 8.18 (s, 1H), 7.97 (s, 1H), 7.88 (d, *J* = 6.8 Hz, 3H), 7.74 (s, 1H), 7.62 – 7.47 (m, 2H), 7.00 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.0, 151.8, 147.8, 138.6, 135.0, 132.6, 131.5, 129.1, 128.7, 128.1, 127.8, 126.9, 123.7, 119.9, 114.5.

***N*-(quinolin-2-yl)benzamide (4a):[24]**
Isolated as White solid in Hexane/EtOAc (90/10), 75% yield, 93 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.59 (d, *J* = 8.4 Hz, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 7.98 (d, *J* = 6.0 Hz, 2H), 7.81 (t, *J* = 9.6 Hz, 2H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.49 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.1, 151.2, 146.7, 138.7, 134.2, 132.4, 130.1, 128.7, 127.6, 127.4, 126.5, 125.3, 114.4.

***N*-(6-methylquinolin-2-yl)benzamide (4b):[24]**
Isolated as White solid in Hexane/EtOAc (90/10), 80% yield, 105 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.57 (d, *J* = 9.0 Hz, 1H), 8.16 (d, *J* = 9.0 Hz, 1H), 8.00 (d, *J* = 7.5 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.56 – 7.51 (m, 3H), 2.54 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.5, 150.6, 144.9, 138.2, 135.1, 134.3, 132.3, 128.8, 127.4, 126.9, 126.6, 126.5, 114.4, 21.4.

***N*-(6-methoxyquinolin-2-yl)benzamide (4c):[24]**
Isolated as White solid in Hexane/EtOAc (88/12), 86% yield, 119 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.54 (d, *J* = 9.2 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 7.2 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.32 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.08 (d, *J* = 2.0 Hz, 1H), 3.91 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.9, 157.0, 149.3, 142.5, 137.4, 134.3, 132.3, 128.7, 127.3, 122.6, 114.7, 105.5, 55.6.

4-(*tert*-butyl)-*N*-(quinolin-2-yl)benzamide (4d):
New, Isolated as brown liquid in Hexane/EtOAc (92/8), 84% yield, 128 mg. R_f = 0.86 (30% EtOAc/Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.61 (d, *J* = 6.8 Hz, 1H), 8.23 (d, *J* = 7.2 Hz, 1H), 7.93 (d, *J* = 6.8 Hz, 2H), 7.85 (d, *J* = 6.4 Hz, 1H), 7.81 (d, *J* = 7.2 Hz, 1H), 7.68 (t, *J* = 6.0 Hz, 1H), 7.53 (d, *J* = 6.4 Hz, 2H), 7.47 (t, *J* = 6.0 Hz, 1H), 1.37 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.0, 156.2, 151.4, 146.9, 138.6, 131.4, 130.0, 127.7, 127.2, 126.4, 125.8, 125.2, 114.5, 35.0, 31.2. HRMS (ESI, m/z) calcd. for $C_{10}H_{17}O_2$ $[M+Na]^+$ 327.1467, found 327.1467.

2,5-dimethyl-*N*-(quinolin-2-yl)benzamide (4e):
New, Isolated as White solid in Hexane/EtOAc (92/8), 82% yield, 113 mg. R_f = 0.78 (30% EtOAc/Hexane), mp 78-80 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (d, *J* = 9.0 Hz, 1H), 8.56 (s, 1H), 8.25 (d, *J* = 9.0 Hz, 1H), 7.86 – 7.81 (m, 1H), 7.69 (t, *J* = 8.5 Hz, 2H), 7.49 (t, *J* = 6.5 Hz, 1H), 7.43 (s, 1H), 7.24 – 7.16 (m, 2H), 2.54 (s, 3H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.7, 151.1, 146.6, 138.7, 135.6, 135.4, 133.7, 131.5, 131.4, 130.0, 127.6, 127.5, 127.4, 126.5, 125.2, 114.2, 20.8, 19.5. HRMS (ESI, m/z) calcd. for $C_{10}H_{17}O_2$ $[M+H]^+$ 277.1335, found 277.1332.

4-cyano-*N*-(quinolin-2-yl)benzamide (4f):[25]
Isolated as White solid in Hexane/EtOAc (91/9), 81% yield, 111 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 7.6 Hz, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 6.4 Hz, 2H), 7.82 (m, 4H), 7.70 (s, 1H), 7.51 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.8, 165.3, 151.5, 145.4, 139.7, 138.0, 132.4, 130.7, 128.6, 127.8, 126.3, 125.8, 117.9, 115.8, 115.2.

4-(quinolin-2-ylcarbamoyl)phenyl acetate (4g):
New, Isolated as White solid in Hexane/EtOAc (88/12), 83% yield, 127 mg. R_f = 0.86 (30% EtOAc/Hexane), mp 87-89 °C. ^{1}H NMR (400 MHz, DMSO) δ 11.19 (s, 1H), 8.39 (m, *J* = 25.4, 9.0 Hz, 2H), 8.15 (d, *J* = 8.6 Hz, 2H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.78 – 7.69 (m, 1H), 7.52 (dd, J= 14.8, 8 Hz, 1H), 7.32 (m, 2H), 2.32 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, DMSO) δ 169.5, 166.3, 153.9, 152.3, 146.9, 138.6, 131.9, 130.5, 130.3, 128.4, 127.6, 126.3, 125.6, 122.3, 116.0, 21.5. HRMS (ESI, m/z) calcd. for $C_{10}H_{17}O_2$ $[M+H]^+$ 307.1077, found 307.1085.

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4-chloro-*N*-(quinolin-2-yl)benzamide (4h):[24]

Isolated as White solid in Hexane/EtOAc (92/8), 78% yield, 110 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (br, 1H), 8.56 (d, *J* = 6.5 Hz, 1H), 8.26 (d, *J* = 9.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.84 (t, *J* = 8.0 Hz, 2H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 8.5 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 165.6, 151.1, 146.7, 138.9, 138.8, 132.6, 130.2, 129.1, 128.8, 127.7, 127.2, 126.5, 125.4, 114.6.

2-methyl-*N*-(6-methylquinolin-2-yl)benzamide (4i):

New, Isolated as White solid in Hexane/EtOAc (90/10), 70% yield, 97 mg. R_f = 0.72 (30% EtOAc/Hexane), mp 80-82 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.55 (s, 1H), 8.18 (d, *J* = 9.0 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 2H), 2.58 (s, 3H), 2.55 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.5, 150.5, 145.0, 138.1, 136.8, 135.8, 135.1, 132.3, 131.5, 130.6, 127.0, 126.9, 126.6, 126.5, 125.9, 114.3, 21.7, 20.2. HRMS (ESI, m/z) calcd. for $C_{10}H_{17}O_2$ $[M+Na]^+$ 299.1155, found 299.1150.

Conflicts of interest

There are no conflicts to declare.

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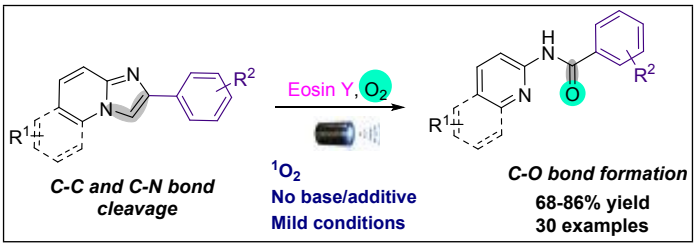
Singlet Oxygen Mediated Dual C-C and C-N bond cleavage in Visible Light

Ritu, Charu Sharma, Sharvan Kumar and Nidhi Jain*



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Supporting Information

Singlet Oxygen Mediated Dual C-C and C-N bond cleavage in Visible Light

Ritu, Charu Sharma, Sharvan Kumar and Nidhi Jain*
Department of Chemistry, Indian Institute of Technology, New Delhi-110016

*E-mail: njain@chemistry.iitd.ac.in; Fax: +91 11 26581102; Tel: +91 11 26591562

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Experimental Details

UV-visible and PL spectroscopy: UV-visible spectra were recorded with a T90+UV-visible spectrophotometer in acetonitrile (ACN) solution (5×10^{-5} M). Photoluminescence spectra were measured using Shimadzu RF5301PC spectrofluorophotometer.

Cyclic and Differential Pulse Voltammetry (CV/DPV): CV and DPV were carried out using a computer controlled potentiostat (CHI 650C) and a standard three electrode arrangement that consisted of both platinum working and auxiliary electrodes and standard calomel electrode (SCE) as reference electrode. All the electrochemical measurements were carried out in Ar-purged solvents with n-Bu_4NPF_6 as the supporting electrolyte. The scan rate for the measurements were typically 200-300 mV/s. DPV was carried out keeping peak amplitude 50 mV, peak width 0.01 sec, pulse period 0.05 sec and increment E at 20 mV.

Crystallographic Description: Data Collection and Refinement Single-crystal X-ray data of compounds was collected on Bruker APEX-II CCD Diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å). Frames were collected at T = 303 K by ω, φ, and 2θ-rotations with full quadrant data collection strategy (four domains each with 600 frames) at 10s per frame. The measured intensities were reduced to F^2 and corrected for absorption with SADABS-2016/2.[1] Structure solution, refinement, and data output were carried out with the SHELXTL package by direct methods.[2,3] Non-hydrogen atoms were refined anisotropically using the Olex2.[4] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as riding atoms using SHELX default parameters. Molecular structures have drawn using ORTEP software. Further information on the crystal structure determination (excluding structure factors) has been given as table S1 and also deposited in the Cambridge Crystallographic Data Centre as CCDC-1946046. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033. e-mail: deposit@ccdc.cam.ac.uk) or via internet.

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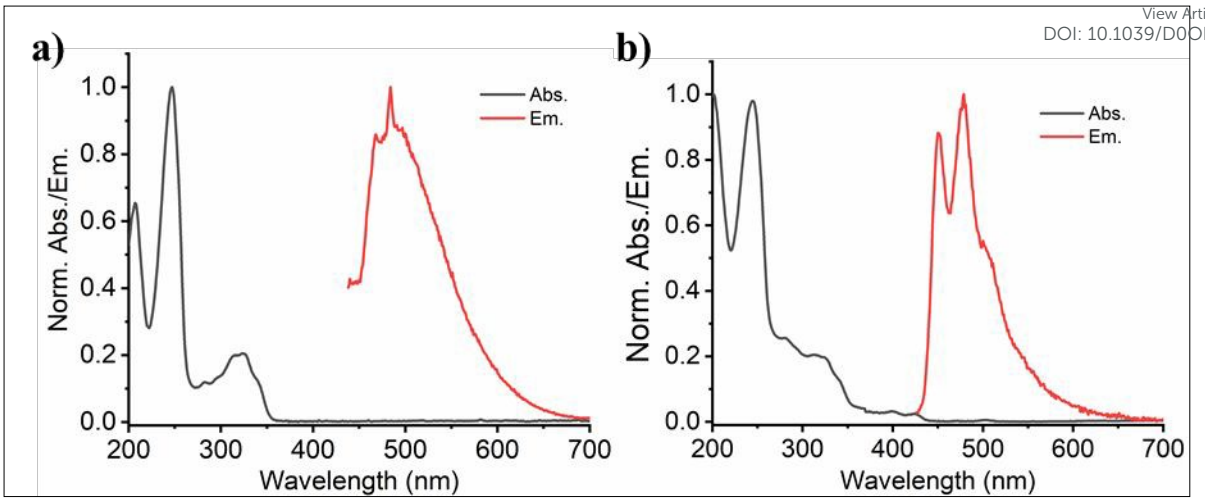

Fig. S1: Normalized absorption (black) and emission (red) spectra of 2-phenylimidazopyridine (**1a)** (a) In acetonitrile excitation wavelength 325 nm. (b) In acetonitrile after 30 min. irradiation of blue LED excitation wavelength 420 nm.

The UV-vis spectra of **1a** in MeCN exhibited absorption bands at 246, 282, 325 nm and a small hump at 340 nm. We found that after 30 minutes of irradiation of the sample in blue light, the absorption spectrum changed and peaks at 240, 281, 325, 399 and 425 nm were observed. On excitation at 420 nm, **1a** gave an emission peak at λ_{max} 480 nm. The above results suggested that imidazo [1,2-a] pyridines can undergo ISC upon excitation and display fluorescence with lifetimes in the millisecond–second. The triplet state energies of some derivatives of imidazo [1,2-a] pyridines are reported in the range of ~46-49 kcal/mol.[5] This energy is significantly larger than that of the $^3O_2$ to $^1O_2$ [E ($^1\Delta$-$^3\Sigma$) = 22.5 kcal/mol and sufficient for photosensitization of $^3O_2$ to $^1O_2$.

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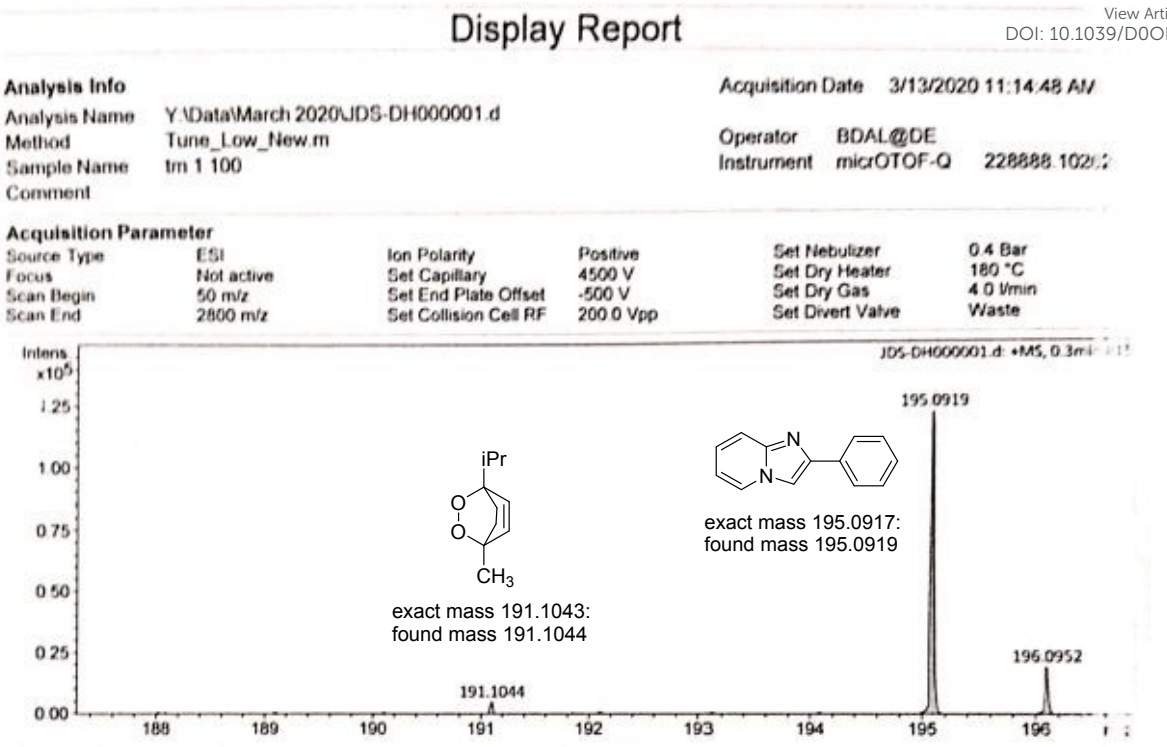

Fig. S2: HRMS spectrum for α-terpinene adduct with singlet oxygen

A control reaction of **1a** and α-terpinene under O_2 atmosphere (in the absence of eosin Y) in blue light quenched the product formation and showed formation of peroxide adduct of α-terpinene.

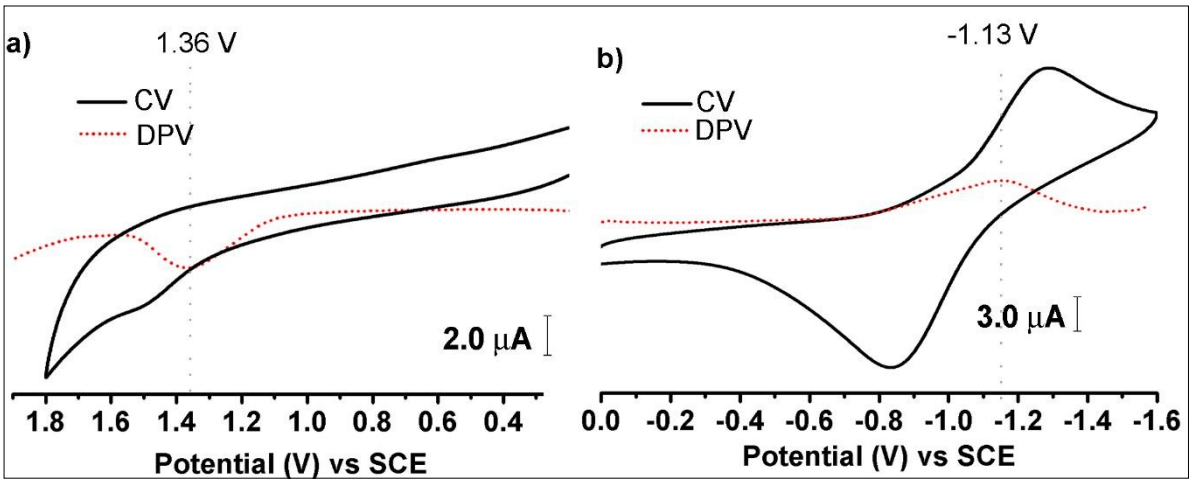

Fig. S3: Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV) shows oxidation and reduction potential values of 2-phenylimidazopyridine (**1a)**.

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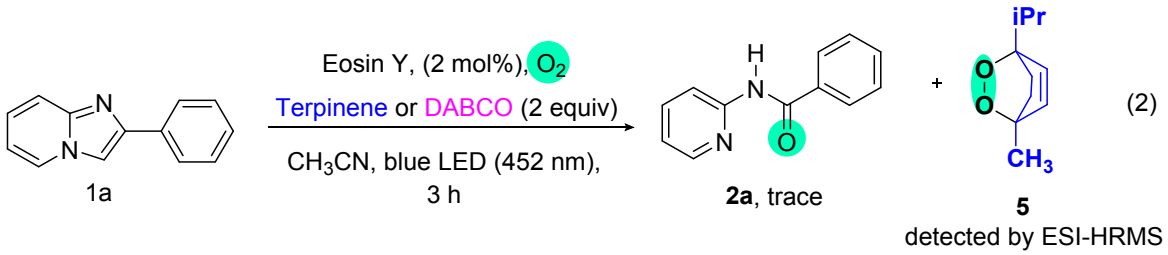
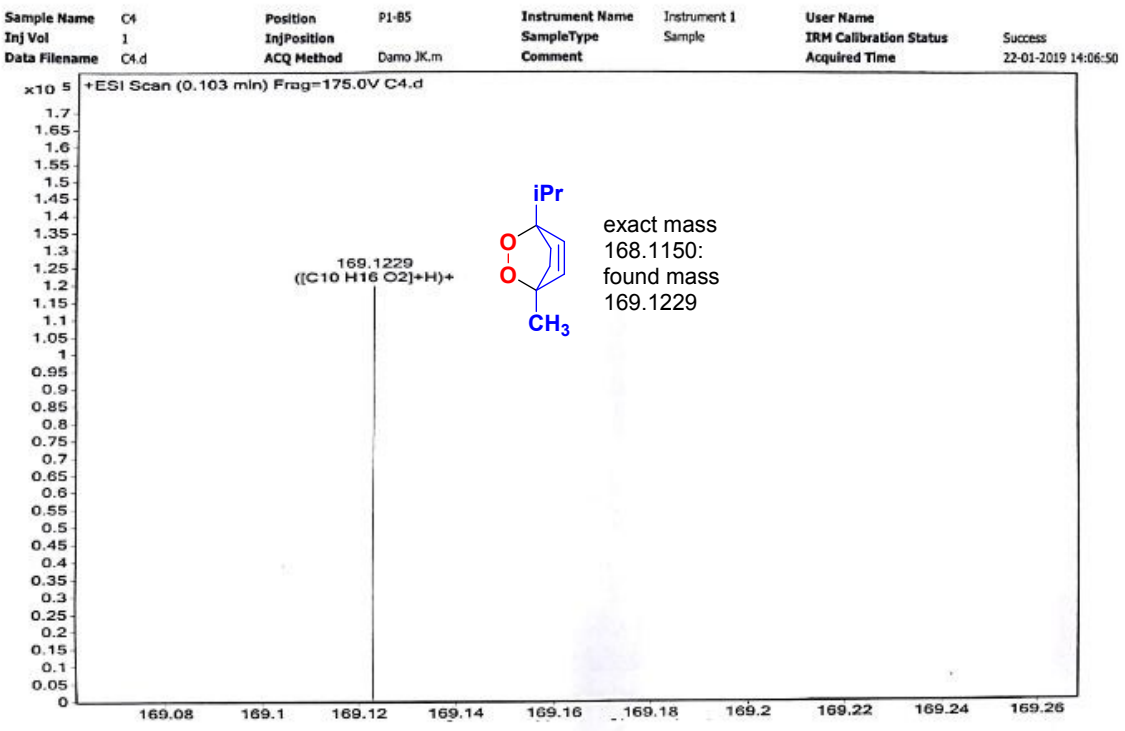
Experiments for mechanistic study

1. Singlet oxygen quenching experiments:

A reaction tube was charged with 2-phenylimidazo[1,2-*a*] pyridine (**1a**) (97 mg, 0.5 mmol), terpinene/DABCO (136 mg/112 mg, 1.0 mmol) and eosin Y (2 mol%) dissolved in MeCN (4.0 mL). The reaction mixture was stirred under blue LED (10 W) irradiation in O_2 atmosphere at RT for 3 h. The reaction mixture was monitored by thin layer chromatography. The desired product **2a** was formed in trace. Further, a small aliquot of the reaction mixture was injected into the mass spectrometer. Peak corresponding to terpinene adduct (**5**) was seen in the mass spectrum given below. HRMS (ESI, m/z) calcd. for $C_{10}H_{17}O_2$ $[M+H]^+$ 169.1223, found 169.1229.



(2)



2. Experimental procedure for analysis of reaction mixture by mass spectrometry

A reaction tube was charged with 2-phenylimidazo[1,2-*a*] pyridine (**1a**) (97 mg, 0.5 mmol) and eosin Y (2 mol %) dissolved in MeCN (4.0 mL). The reaction mixture was stirred under blue LED (10 W) irradiation in O_2 atmosphere at RT for 1 h. 30 µL of the mixture was quickly taken out into a small tube and analysed by HRMS and GCMS (**Fig. S4, S5 and S6**).

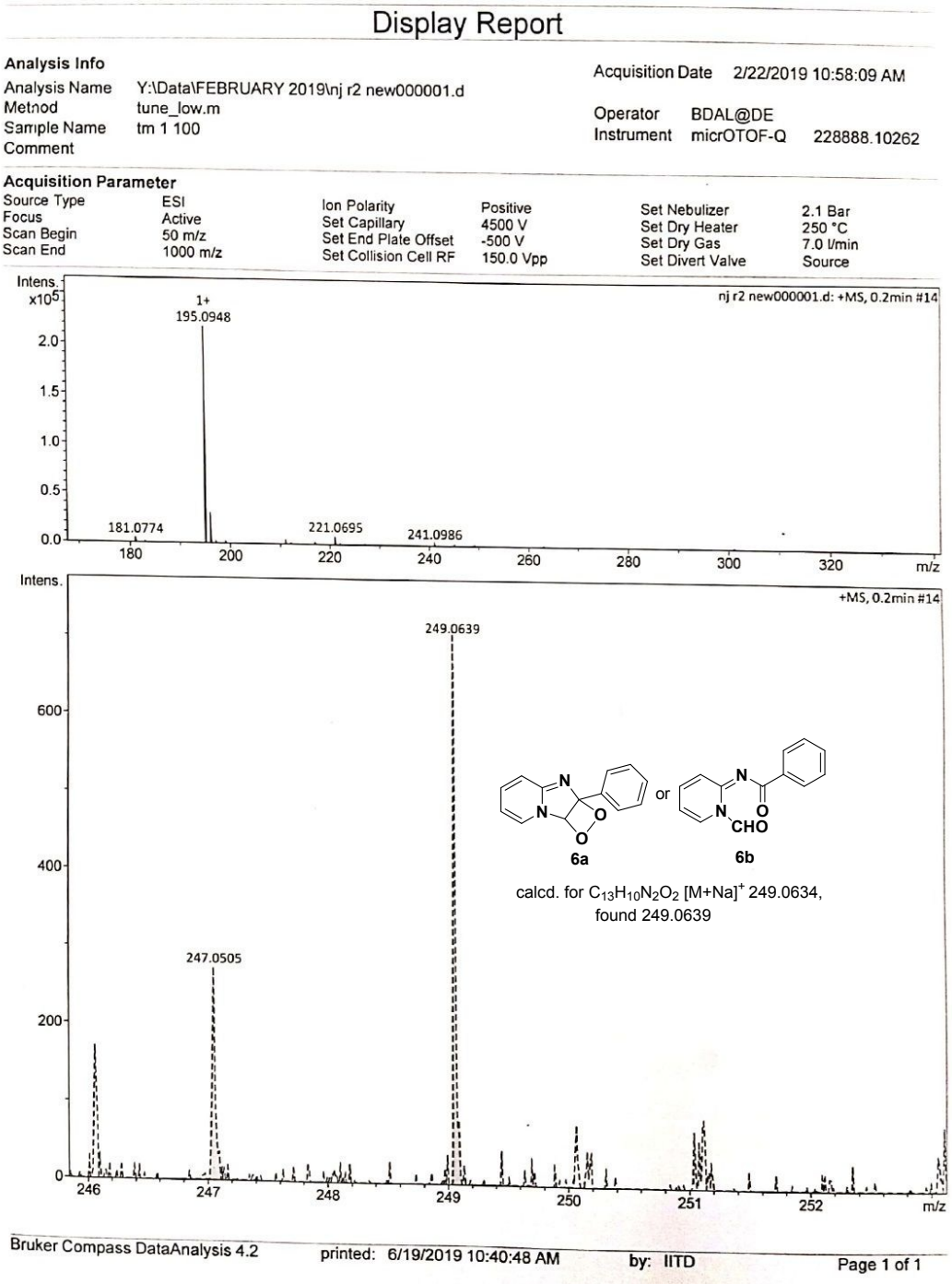


Fig. S4: HRMS spectrum of the reaction mixture.

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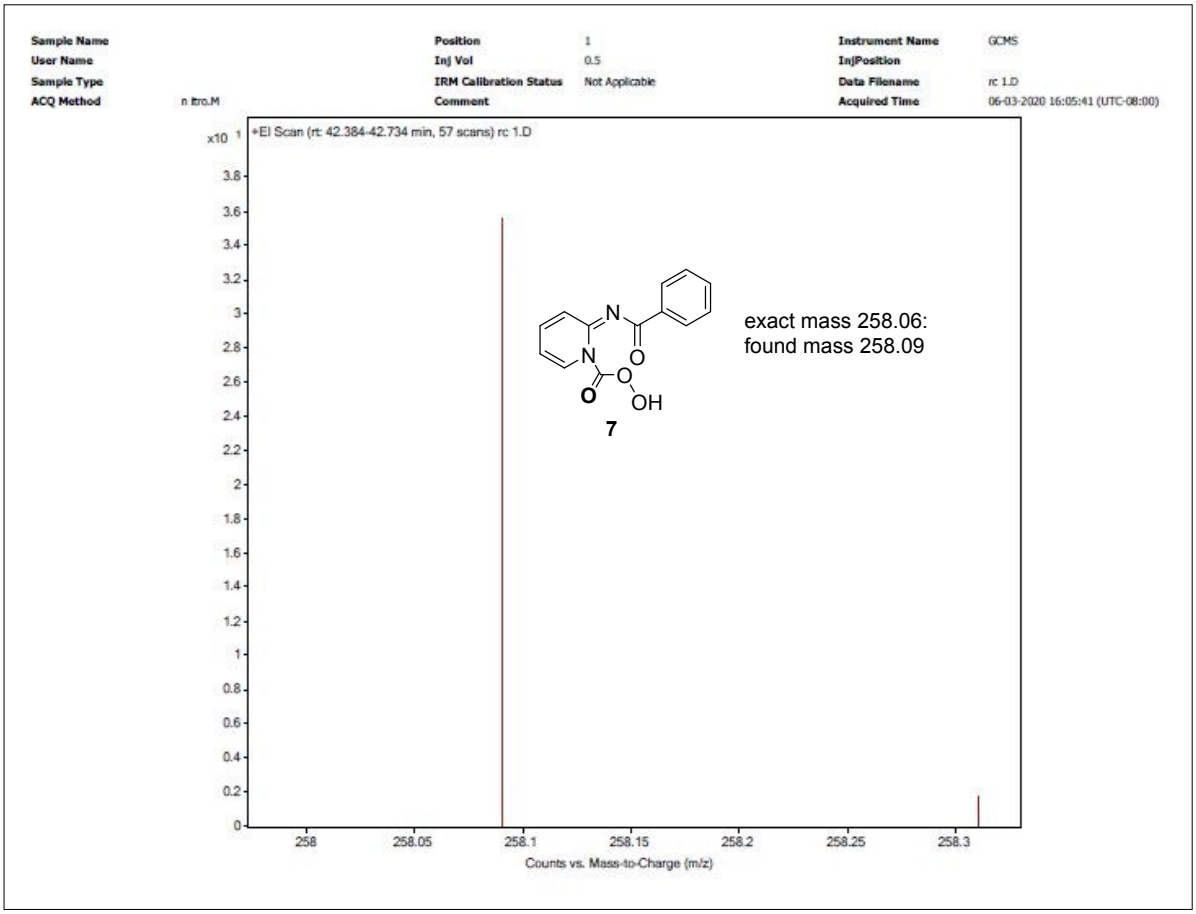

Fig. S5: GCMS spectrum of the reaction mixture after 1 h.

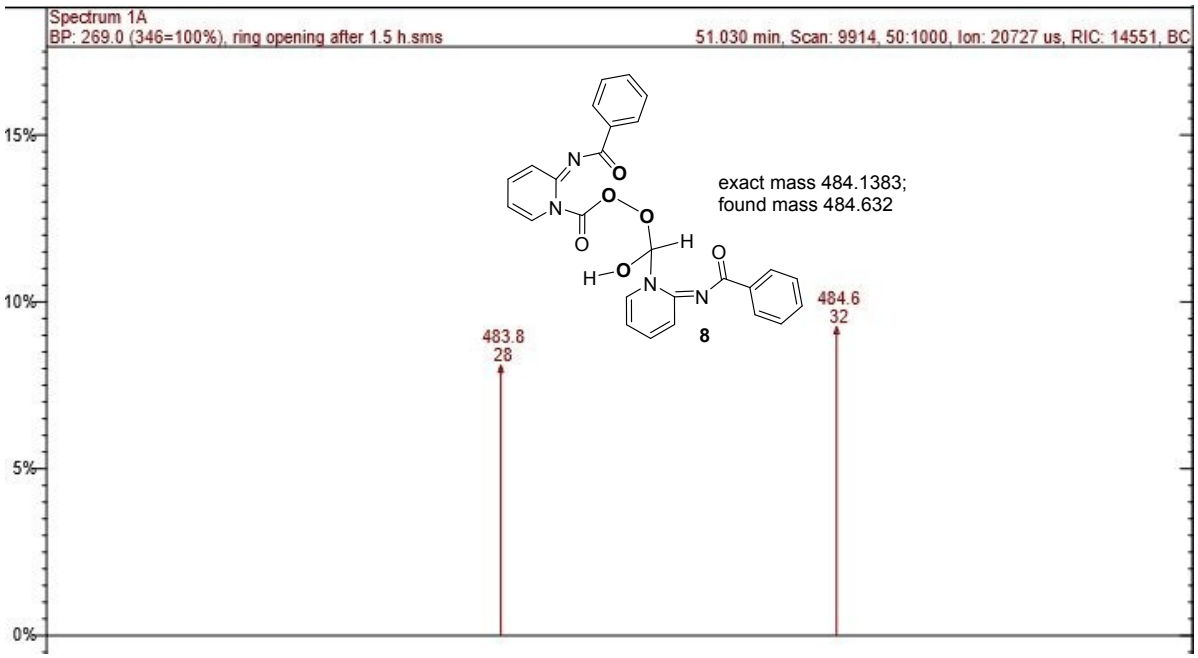

Fig. S6: GCMS spectrum of the reaction mixture after 1 h.

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3. Detection of CO_2.

A sealed tube was charged with 2-phenylimidazo[1,2-*a*] pyridine (**1a**) (97 mg, 0.5 mmol) and eosin Y (2 mol %) dissolved in MeCN (4.0 mL). The reaction mixture was stirred under blue LED (10 W) irradiation in O_2 atmosphere at RT. The gases produced in the reaction mixture were taken into 1 ml syringe from headspace and injected into a glass chromatograph. A calibration curve was drawn between concentration of CO_2 injected and area of the CO_2 peak obtained at different concentrations (**Fig. S7**).

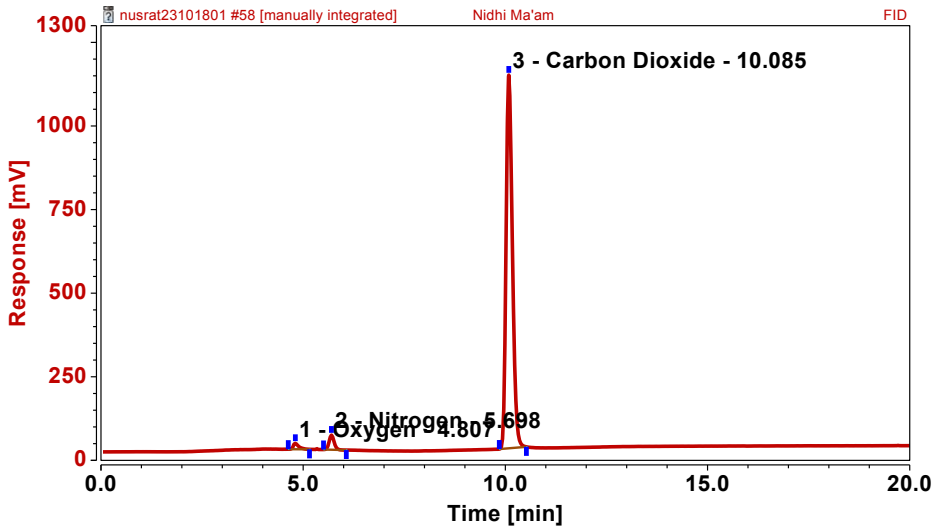

Fig. S7: Calibration curve for CO_2 estimation.

The area obtained in the test sample was equal to a concentration of 5000 ppm CO_2 in the standard samples. Presence of O_2 and N_2 may be due to their natural abundance in atmospheric air.

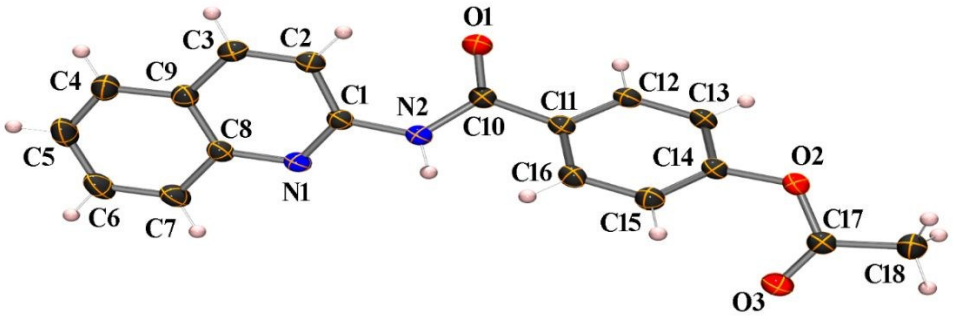

Fig. S8: Single crystal X-ray molecular structure of compound **4g**. Thermal ellipsoids are set at 50% probability.

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Crystallographic description of 4-(quinolin-2-ylcarbamoyl)phenyl acetate (4g) (Table S1):

Identification code	new7_1_0m_a	
Empirical formula	C18 H14 N2 O3	
Formula weight	306.31	
Temperature	303 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 9.5310 (5) Å	a= 90°.
	b = 7.0315 (4) Å	b= 93.267 (2)°.
	c = 21.6758 (12) Å	g = 90°.
Volume	1450.29 (14) $Å^3$	
Z	4	
Density (calculated)	1.403 Mg/m^3	
Absorption coefficient	0.097 mm^{-1}	
F(000)	640.0	
Crystal size	0.16 x 0.10 x 0.08 mm^3	
Theta range for data collection	3.12 to 24.99°.	
Index ranges	-12<=h<=12, -9<=k<=9, -28<=l<=28	
Reflections collected	9023	
Independent reflections	3304 [R(int) = 0.0510]	
Completeness to theta = 28.30°	98.6 %	
Absorption correction	Multi-scan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3561 / 0 / 210	
Goodness-of-fit on F^2	1.069	
Final R indices [I>2sigma(I)]	R1 = 0.0538, wR2 = 0.1454	
R indices (all data)	R1 = 0.0510, wR2 = 0.1482	

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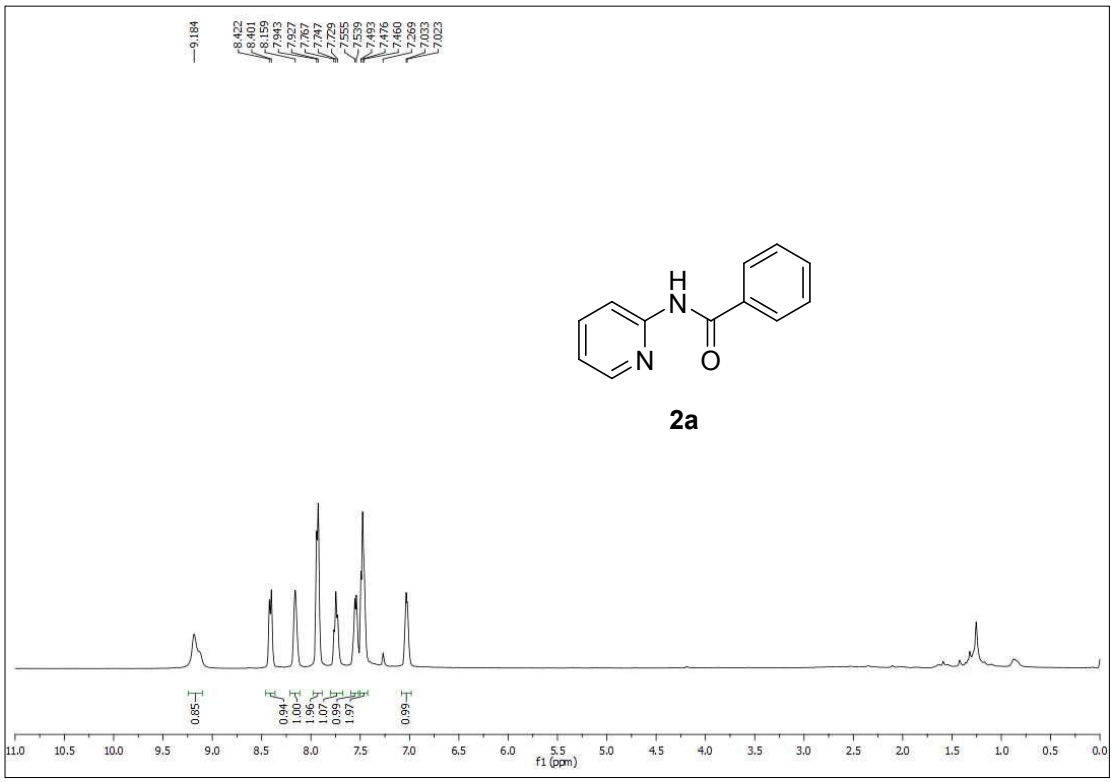
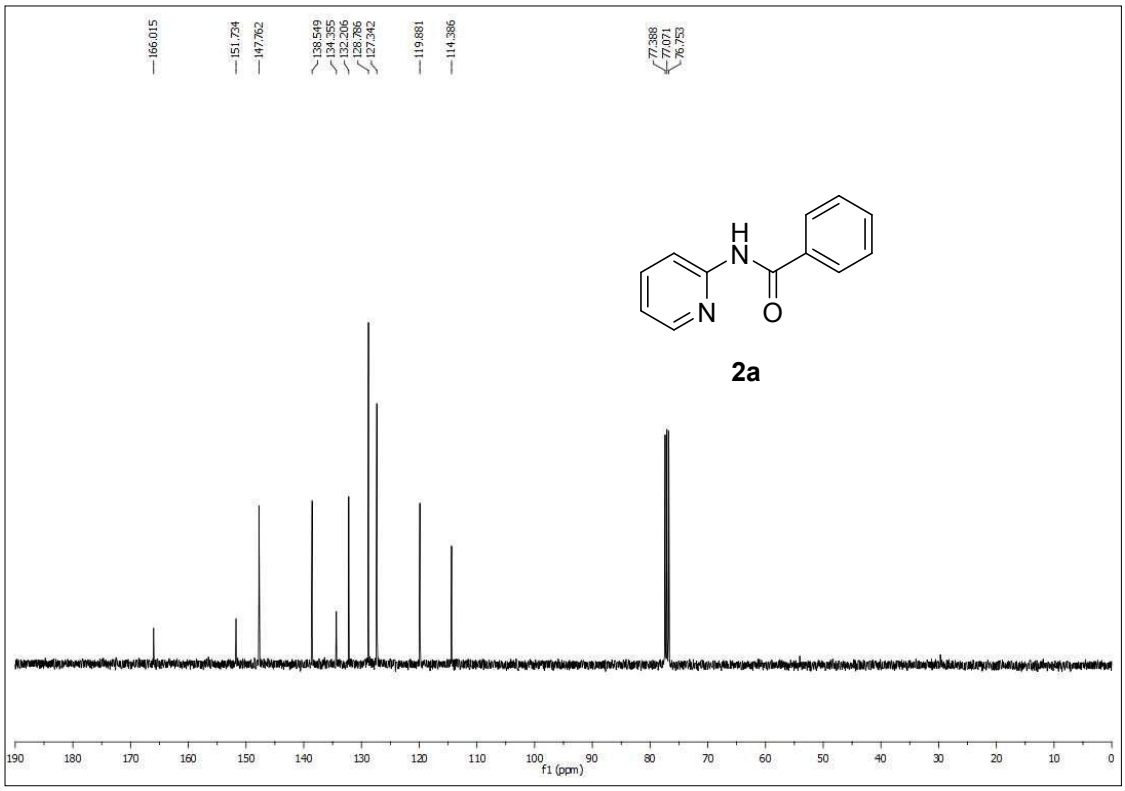
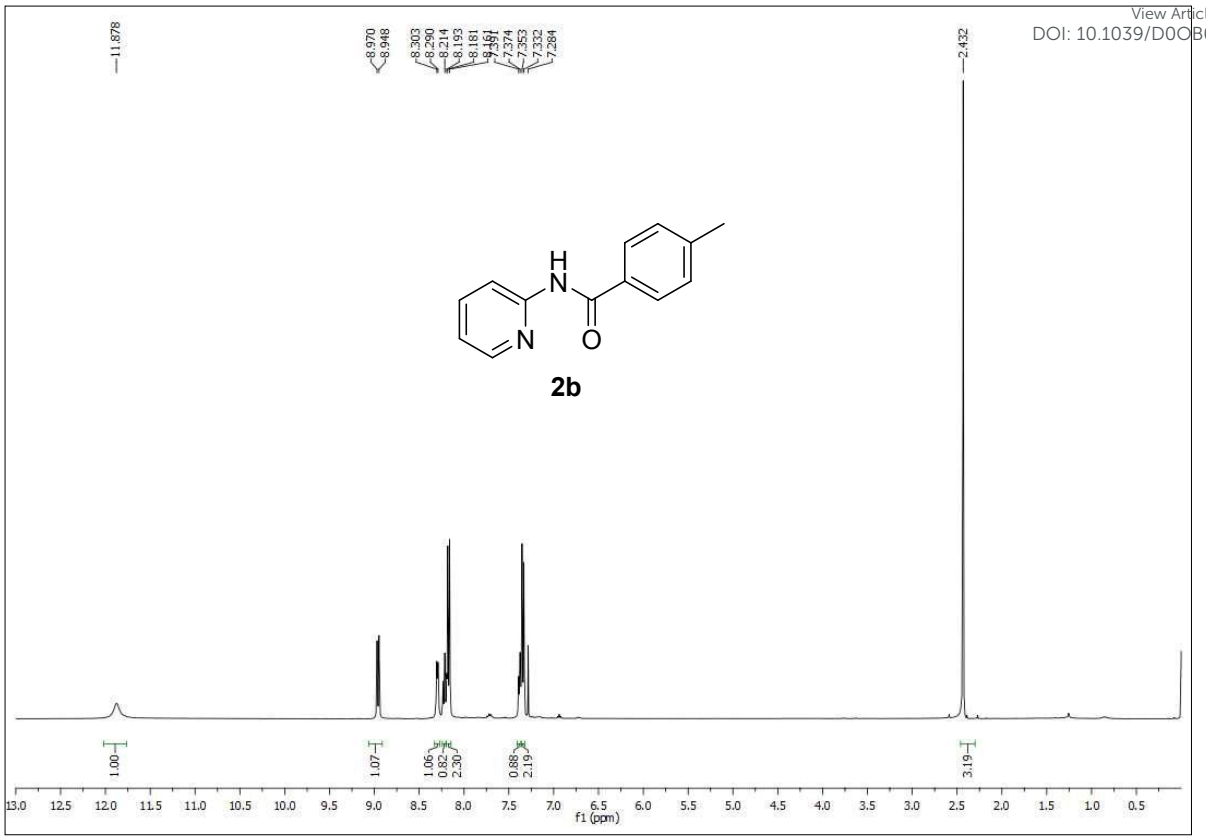
Copies of ^{1}H and ^{13}C NMR spectra.







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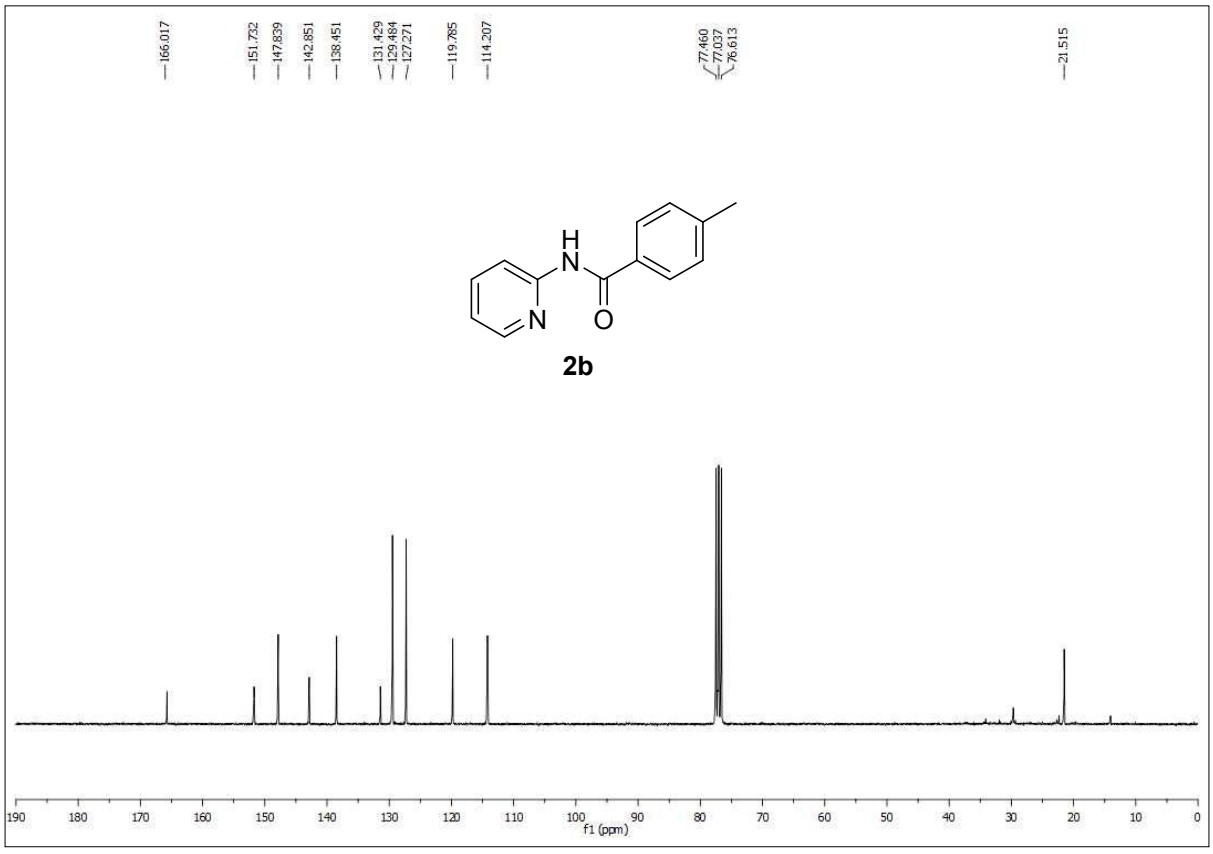

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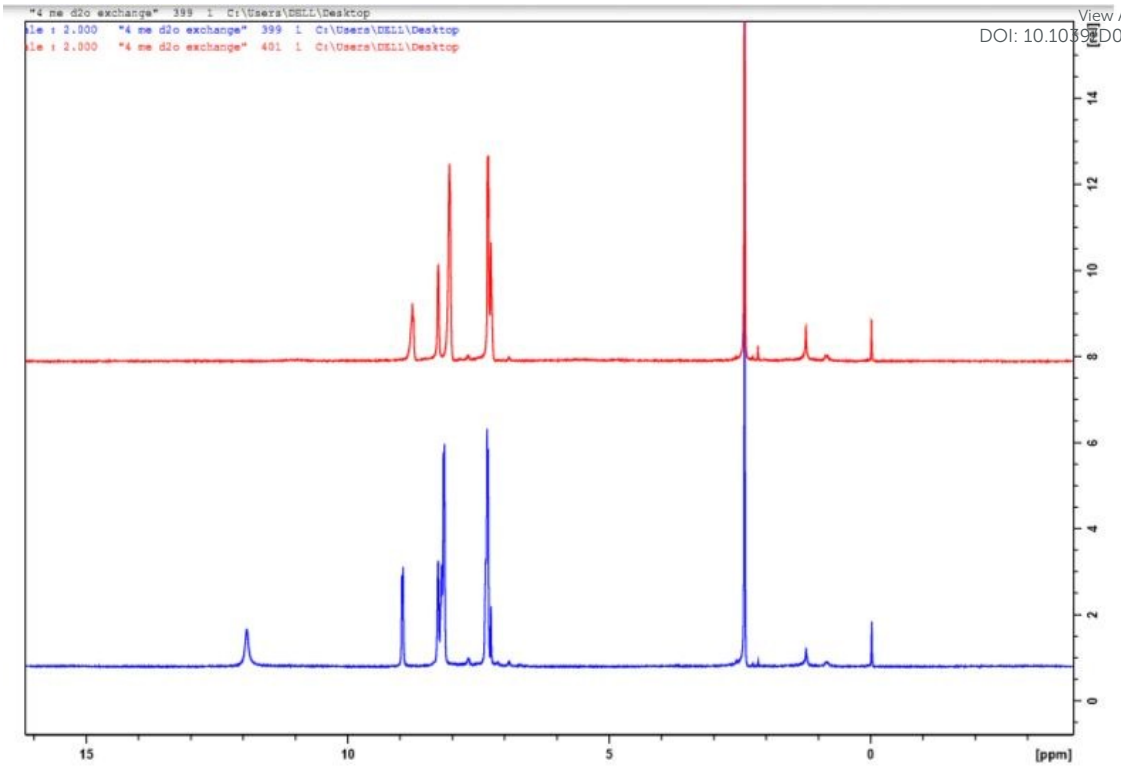
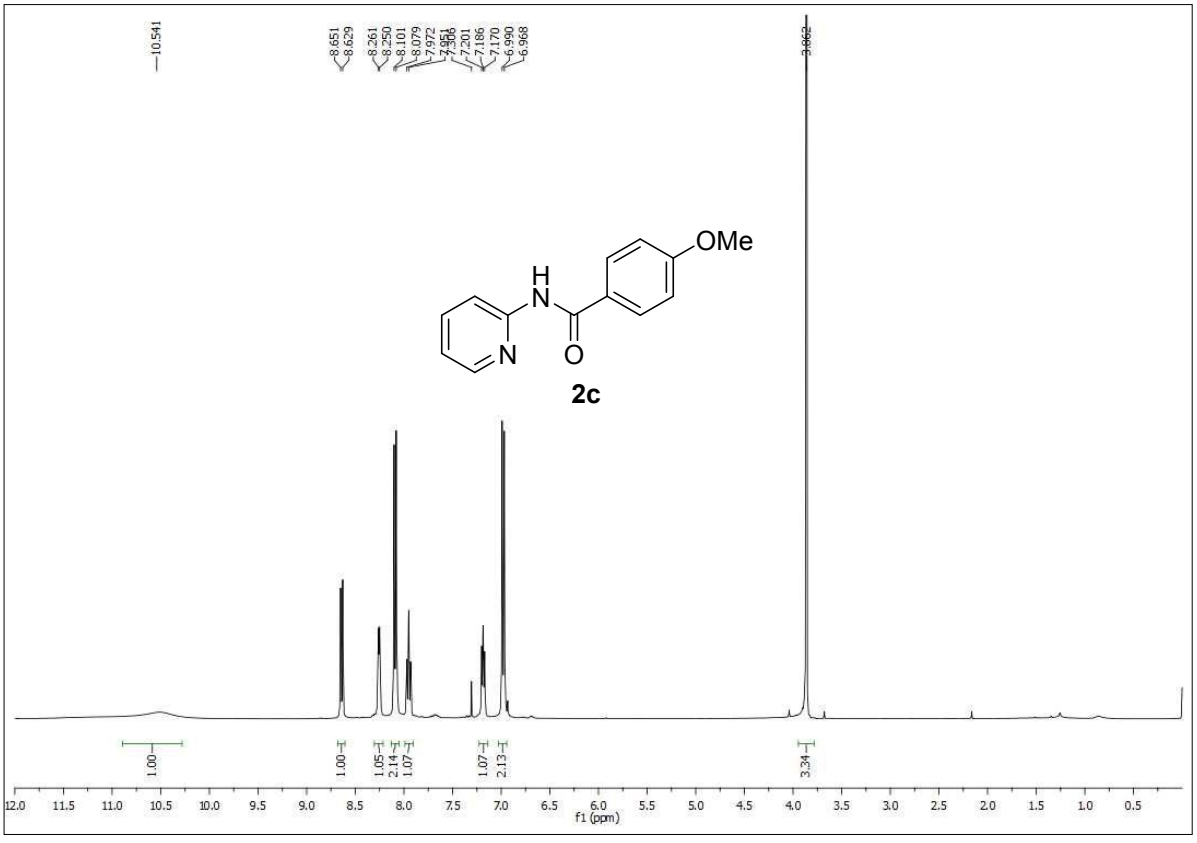


Fig. S7: Top Spectrum- ^{1}H NMR of compound **2b** (After D_2O exchange). Bottom Spectrum- ^{1}H NMR of compound **2b** (Before D_2O exchange).



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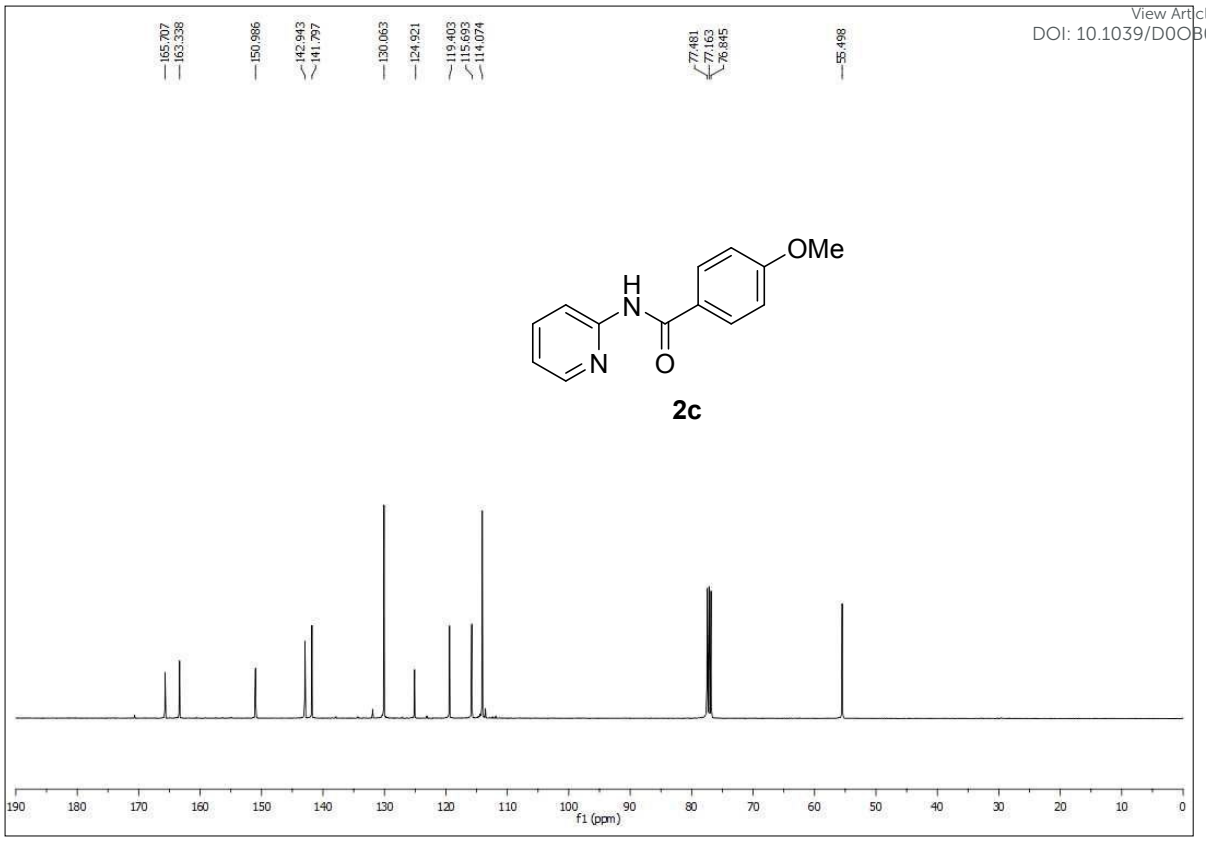

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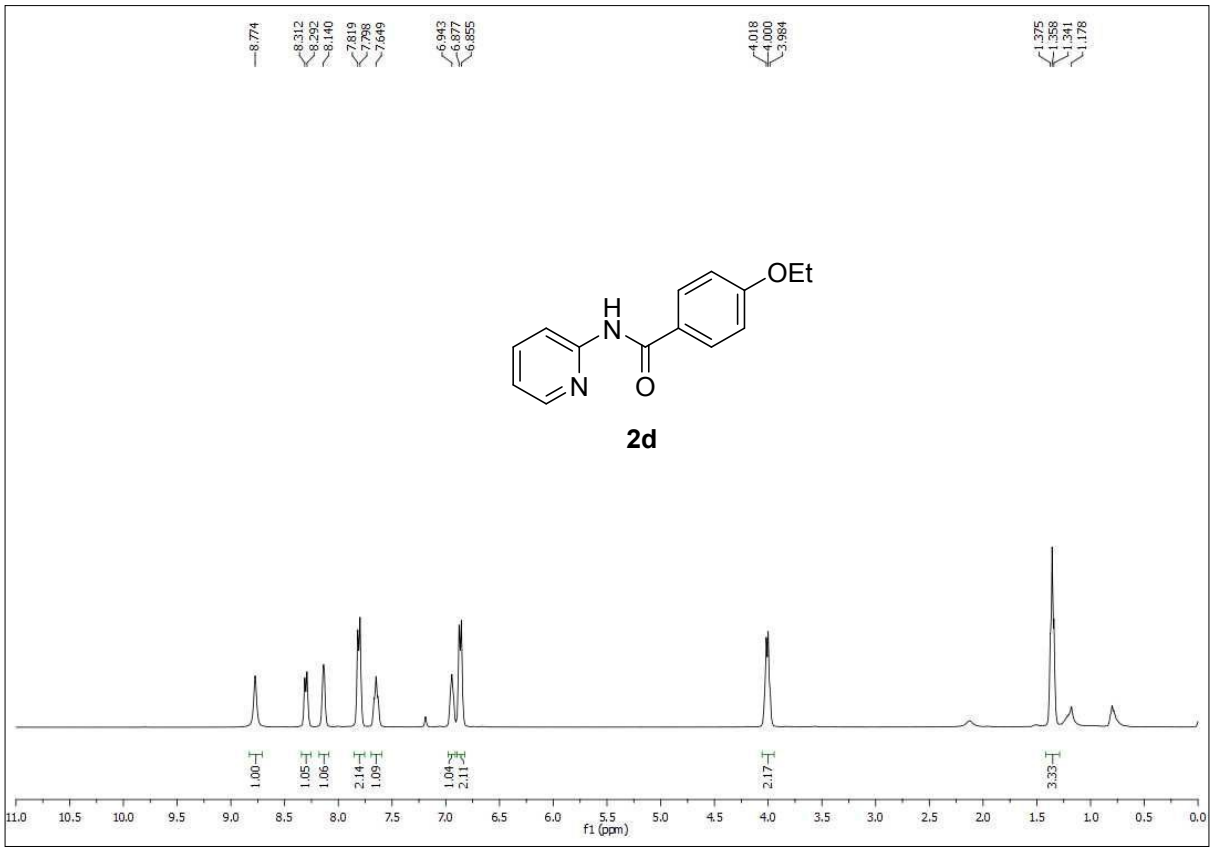

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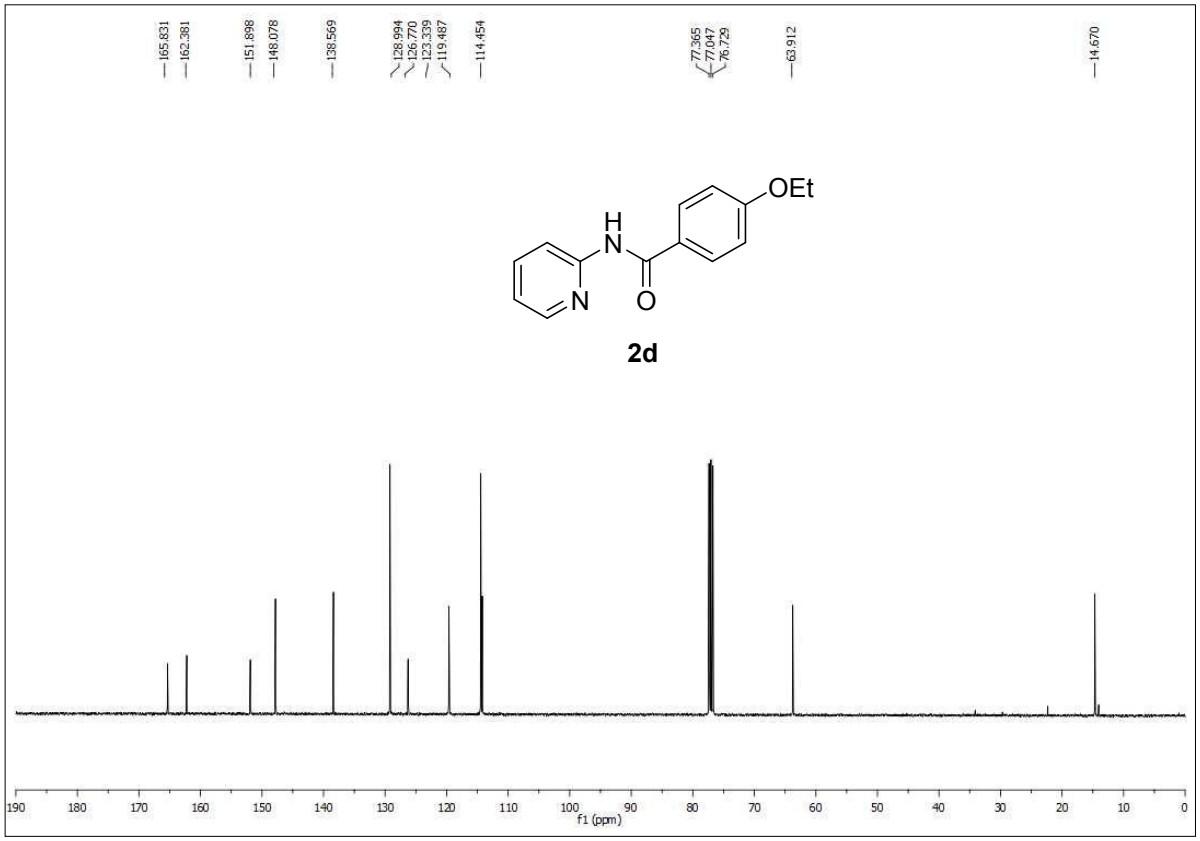

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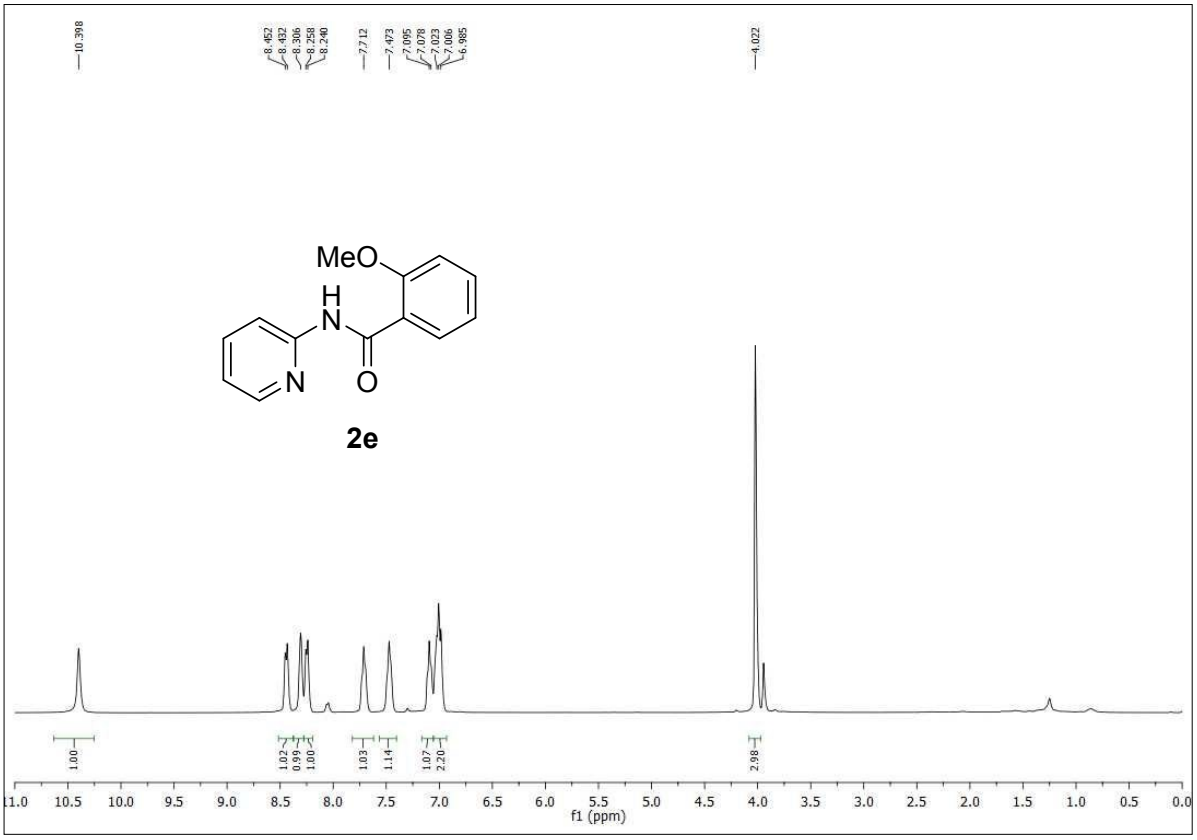

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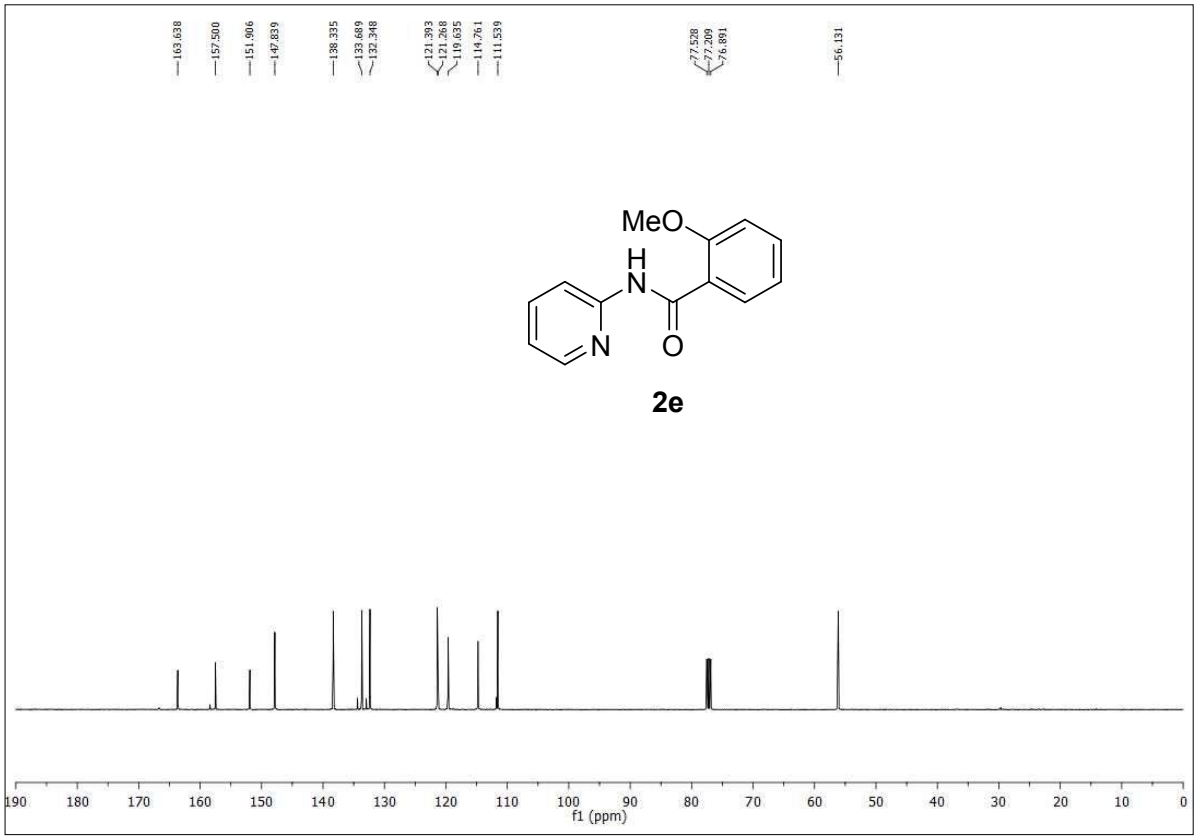

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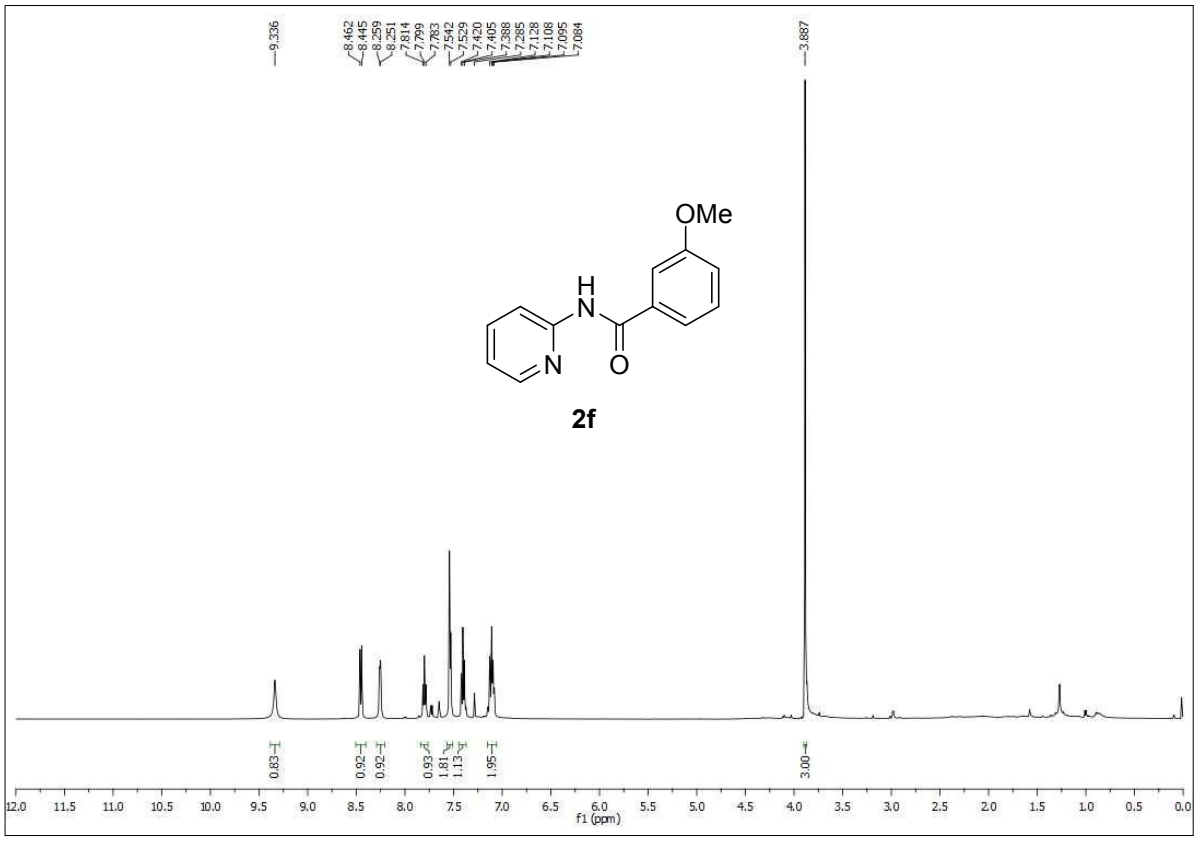

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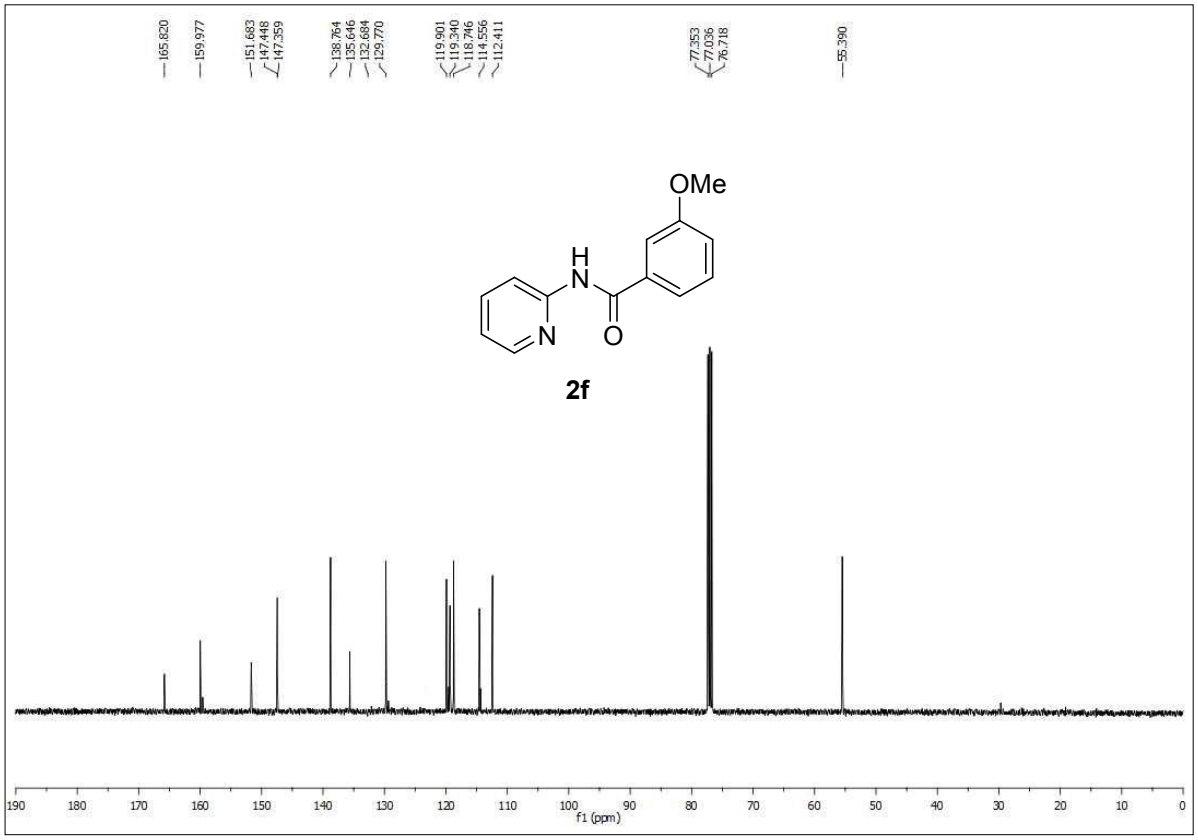

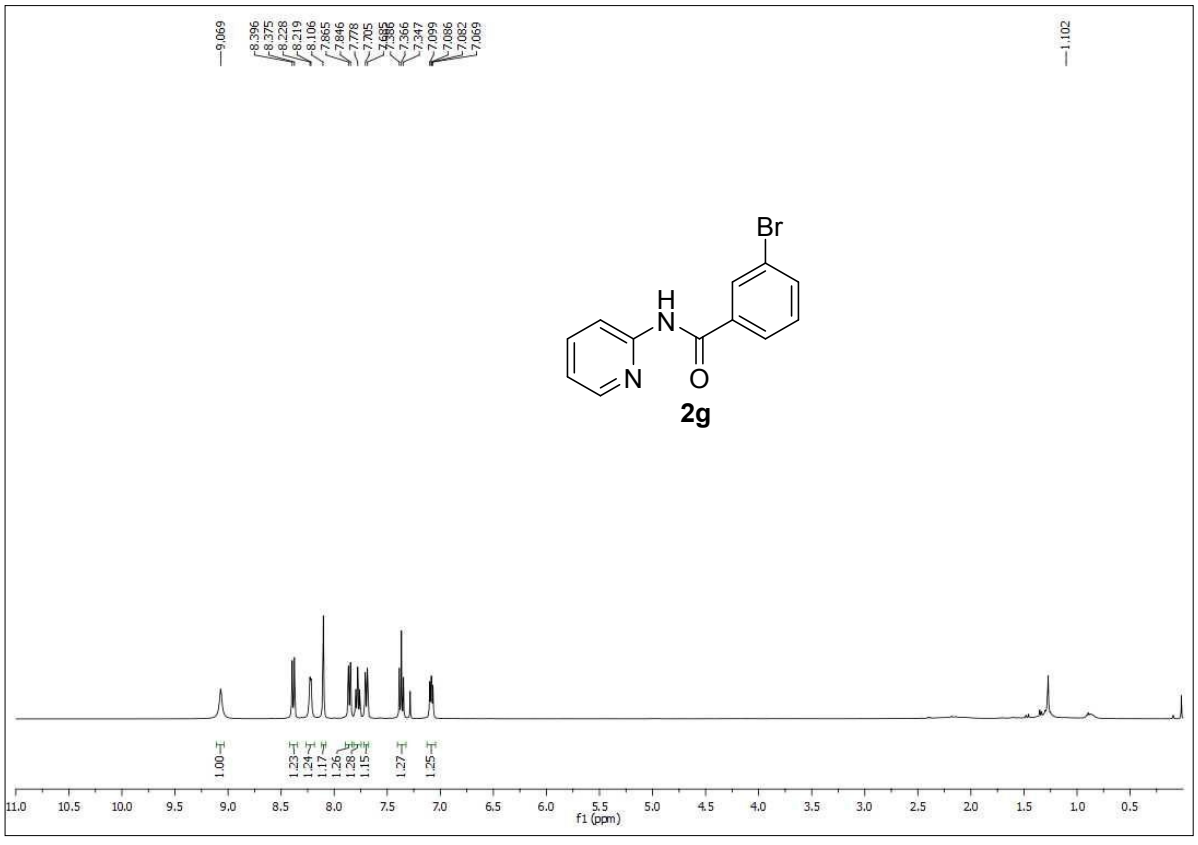

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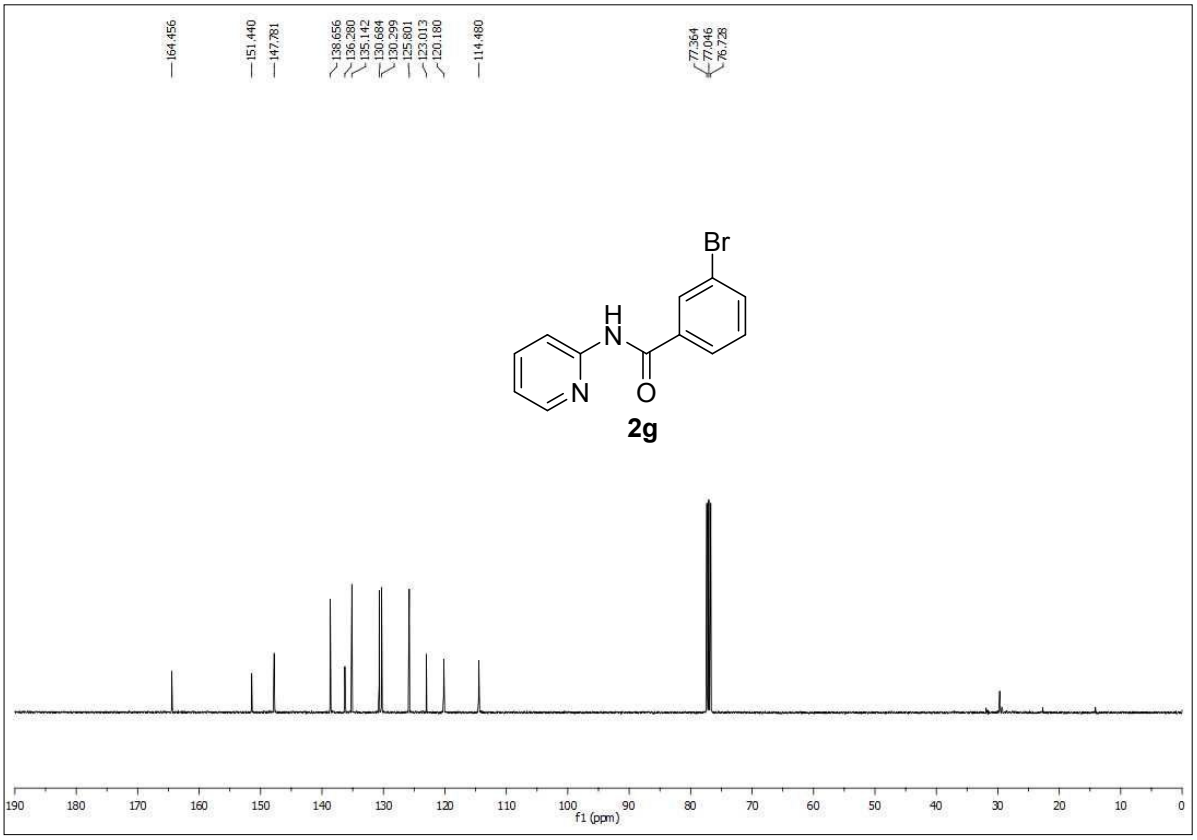

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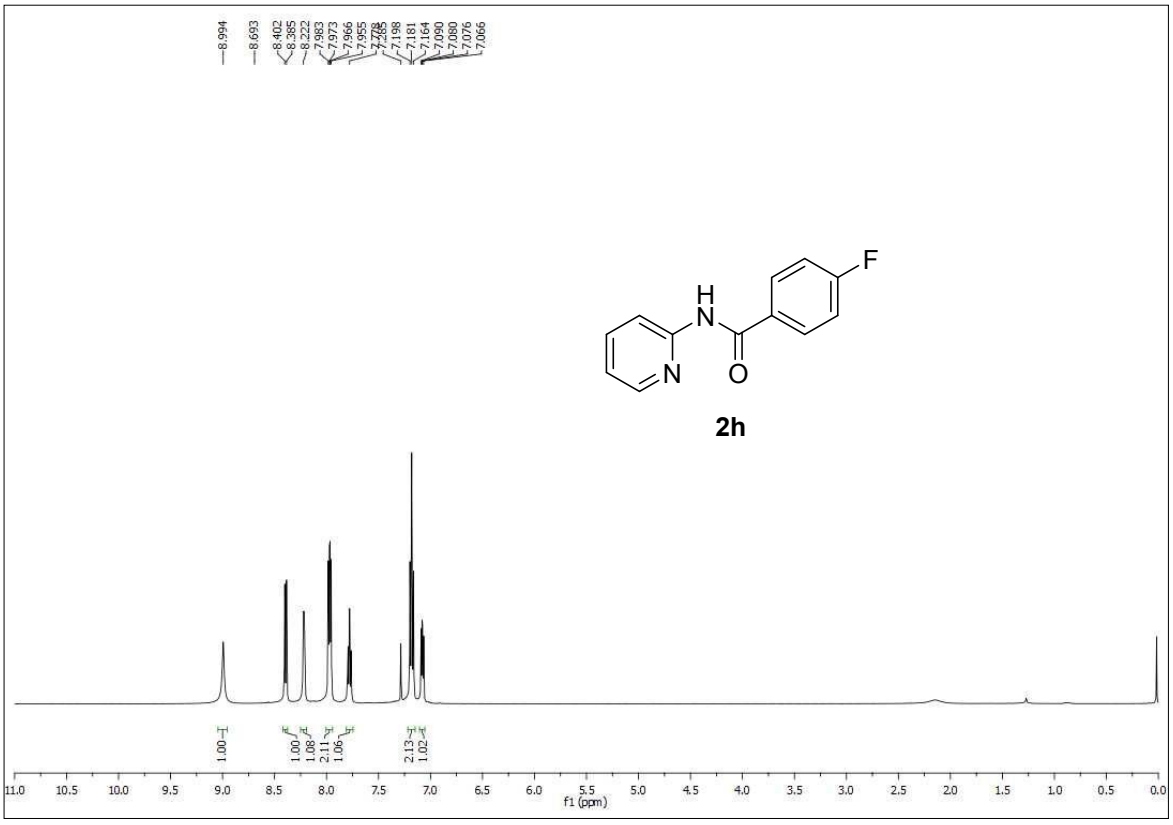

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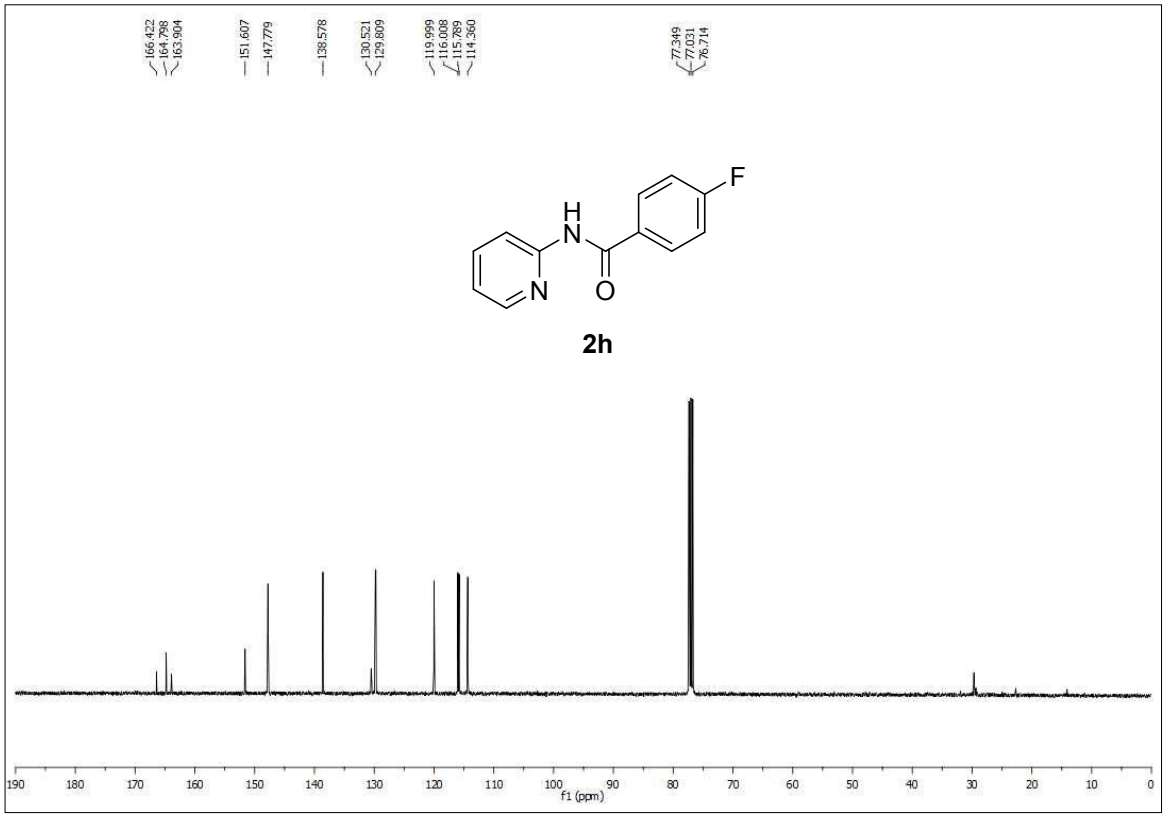

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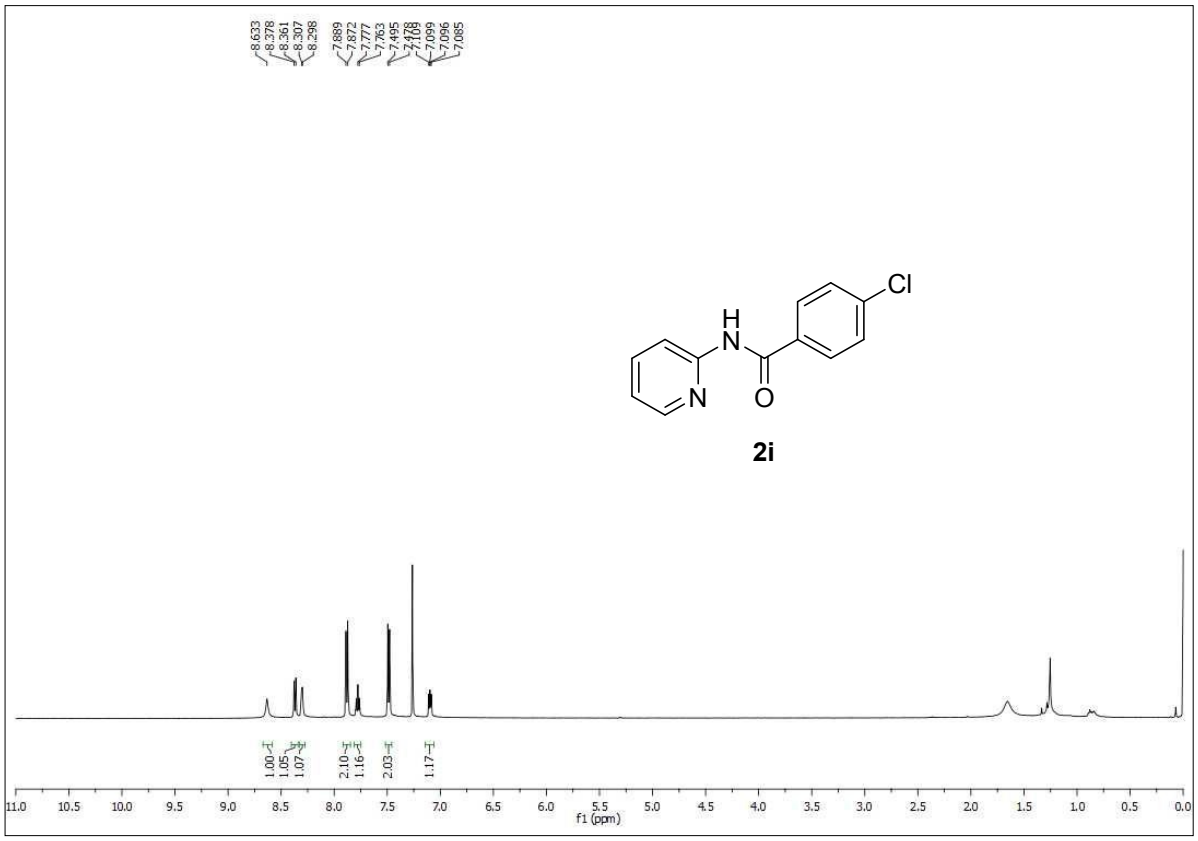

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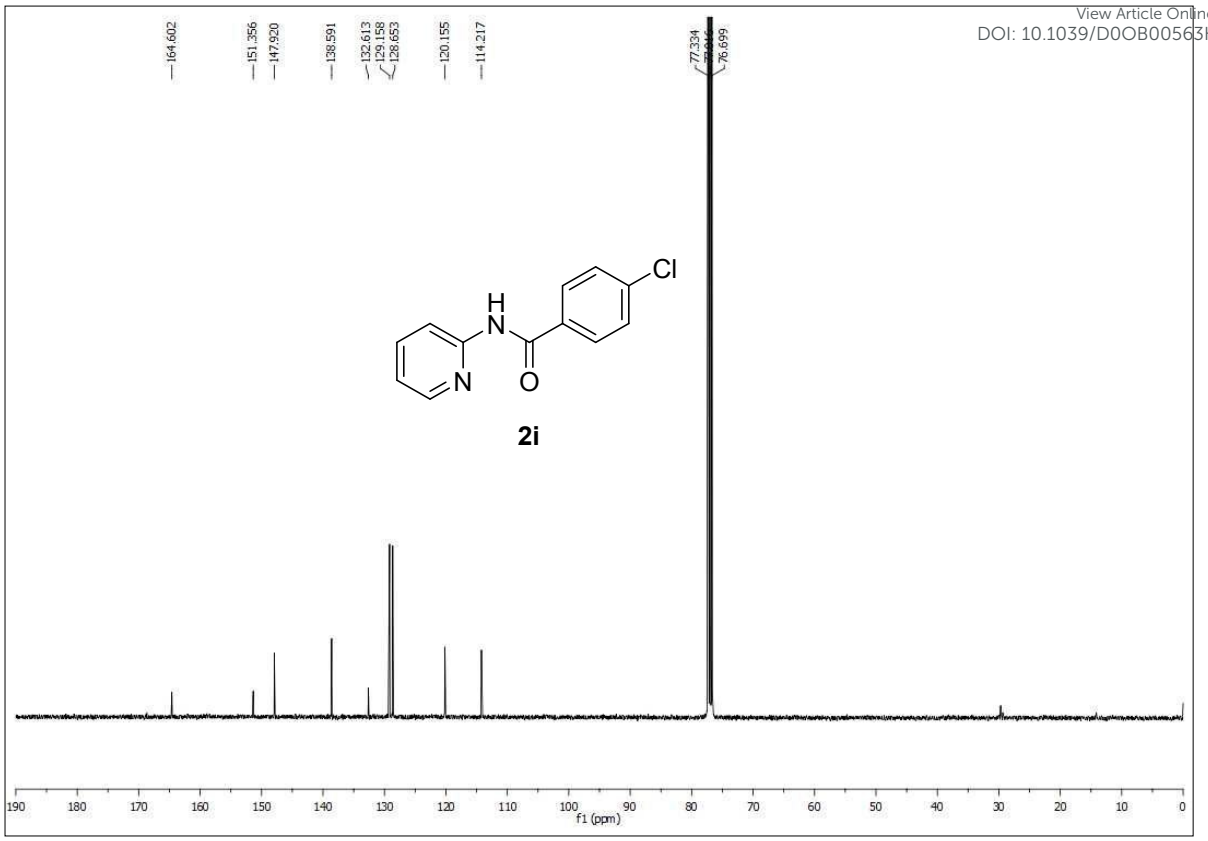

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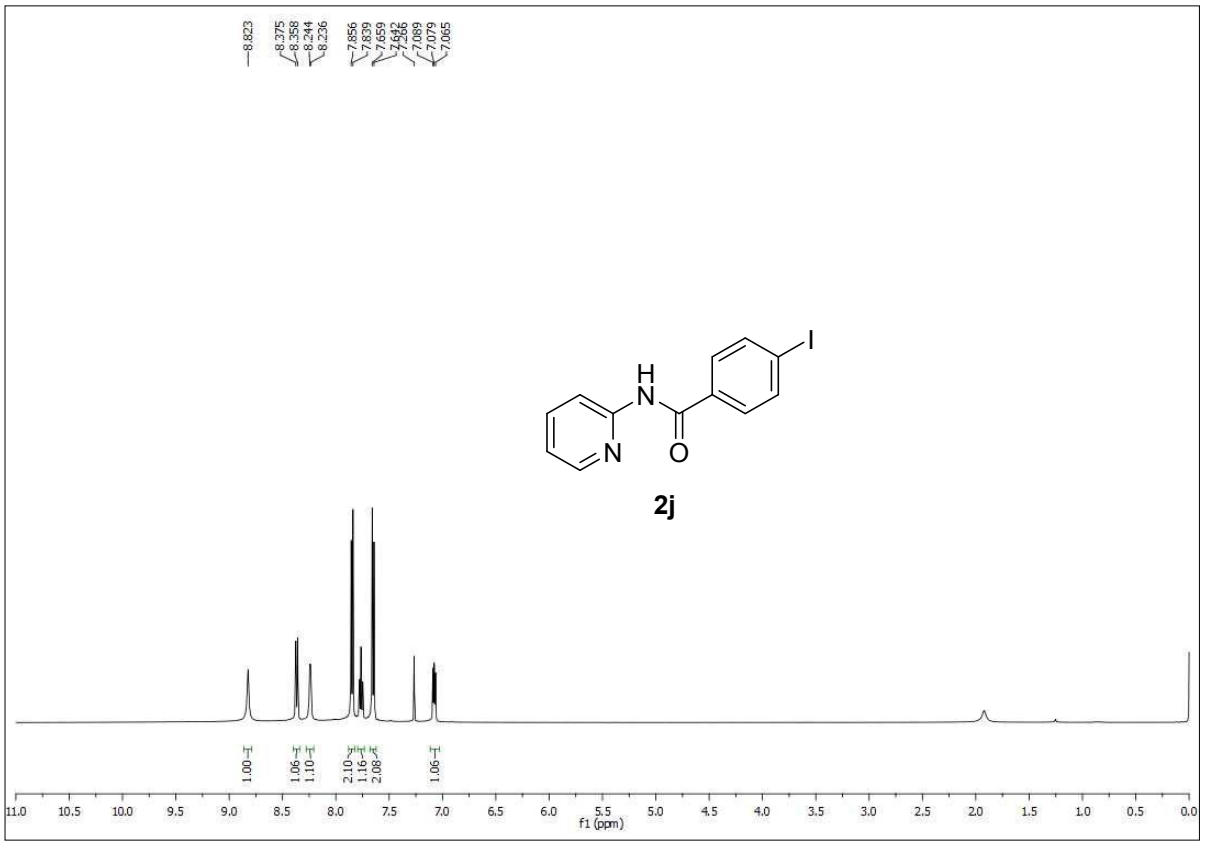

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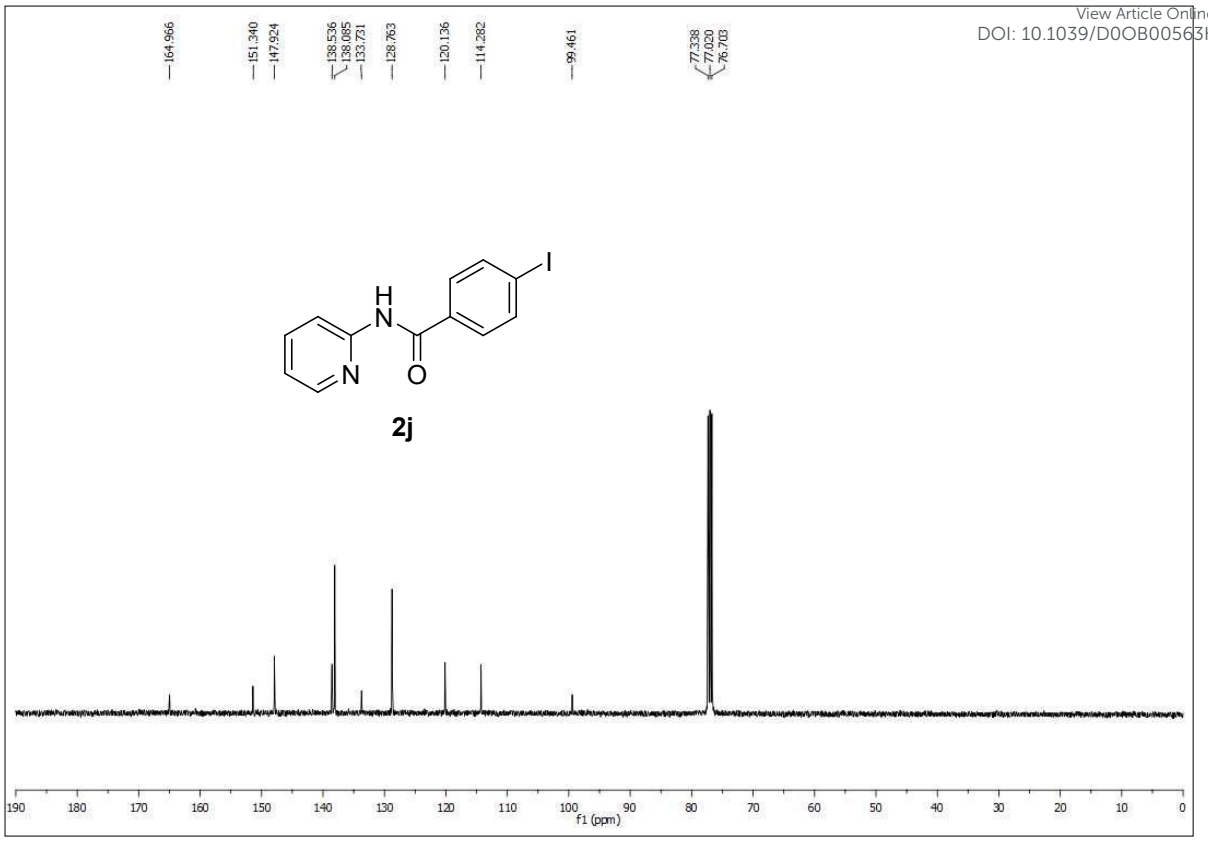

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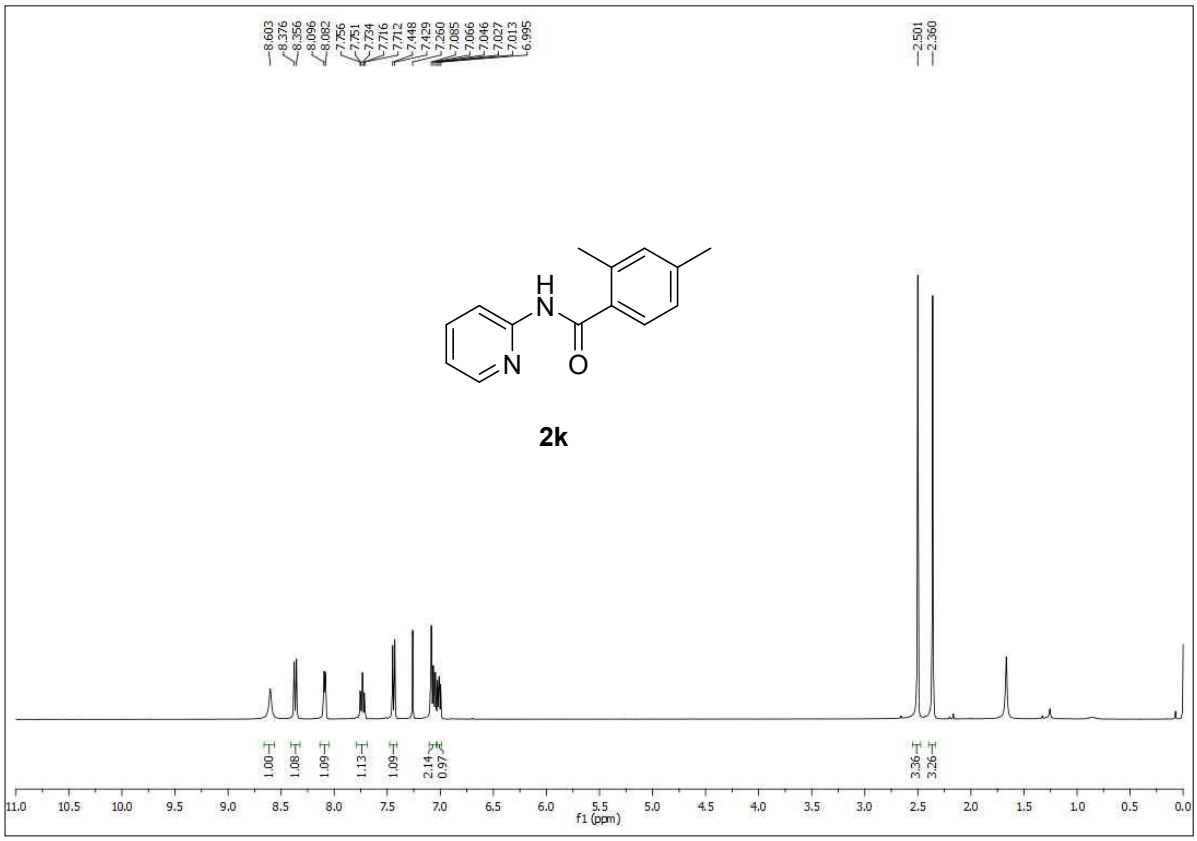

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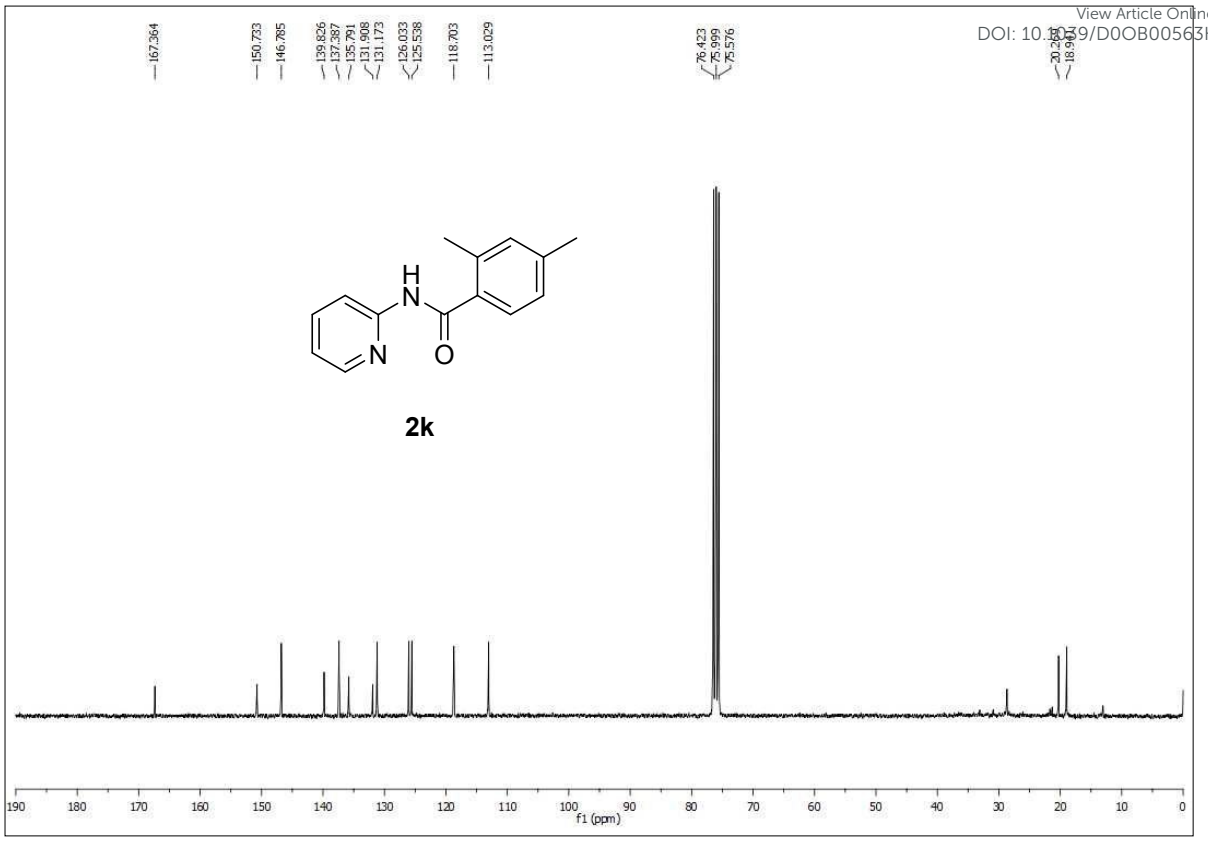

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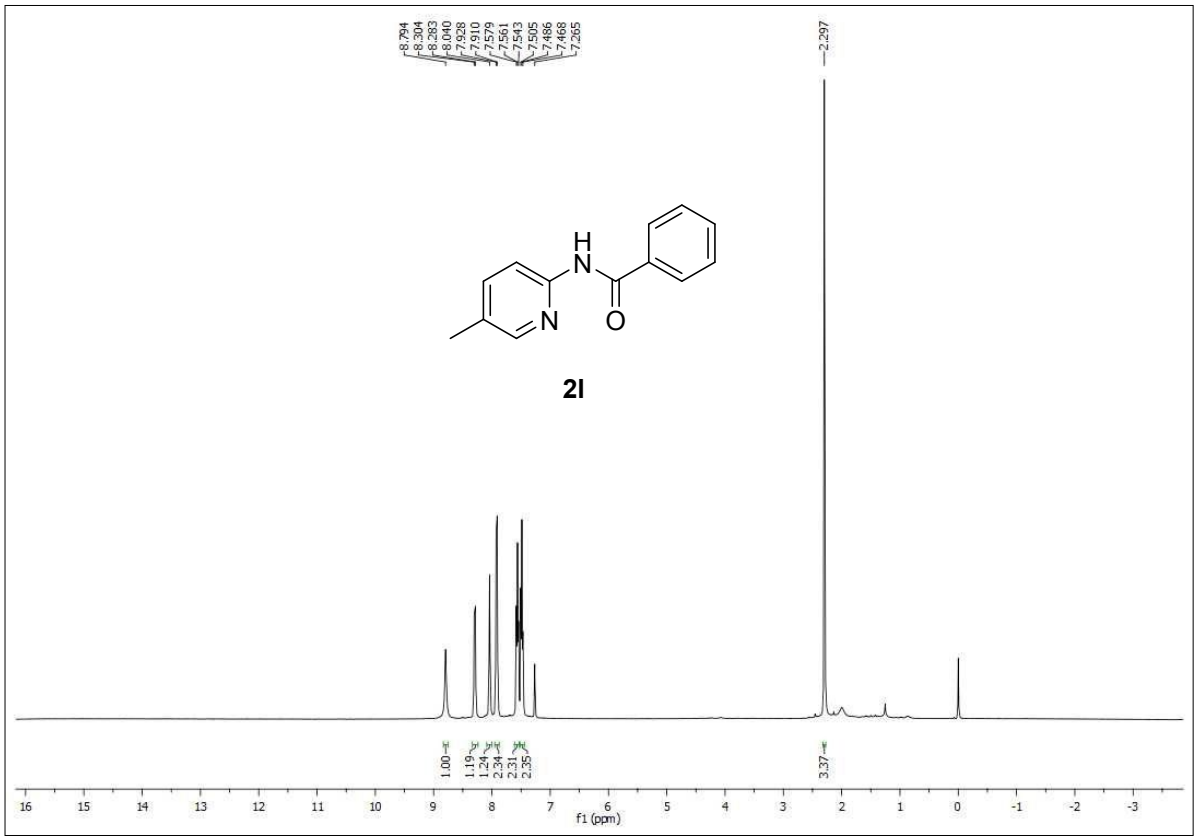

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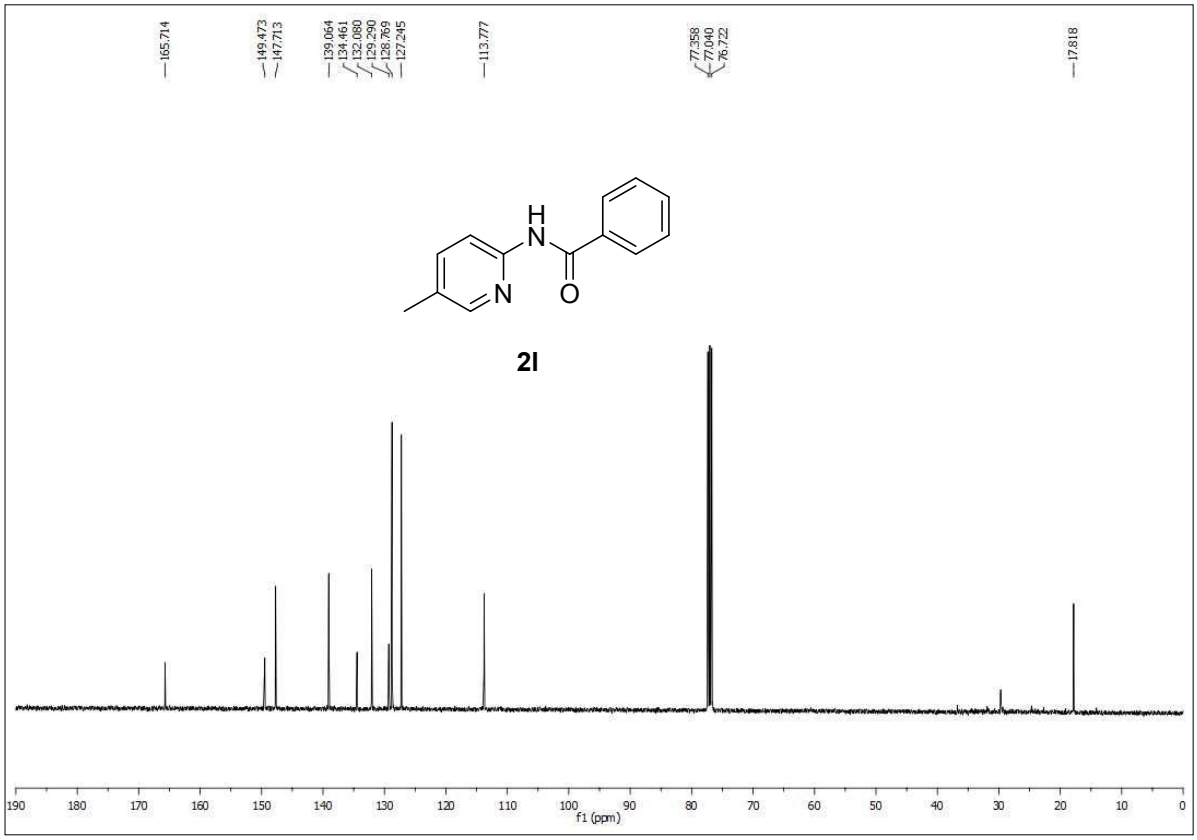

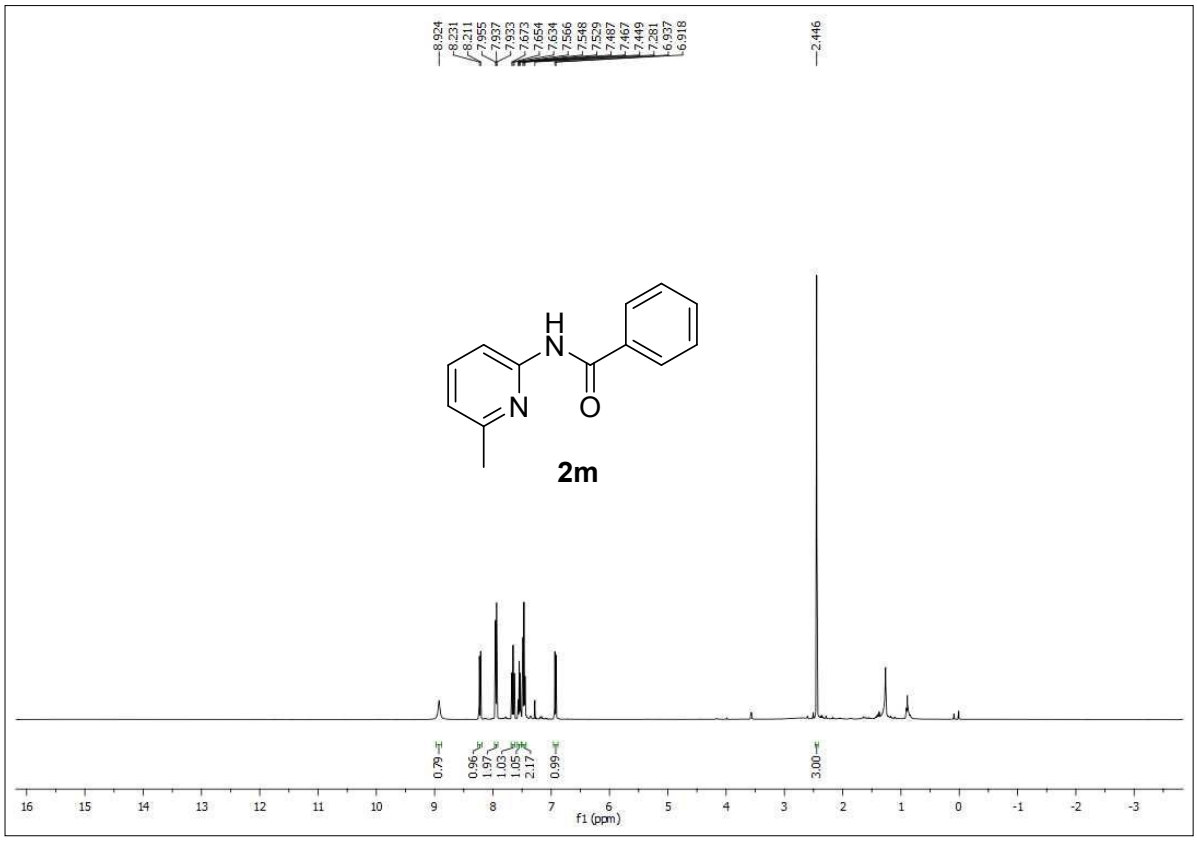

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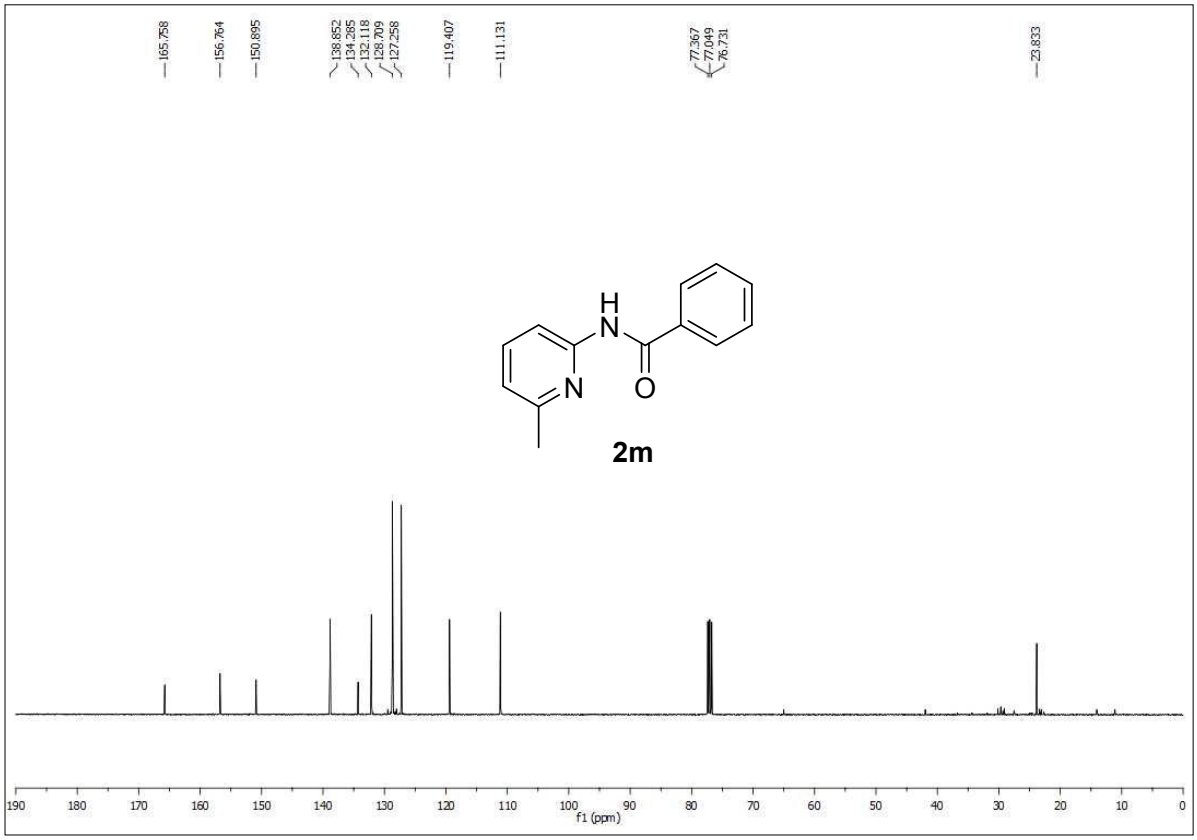

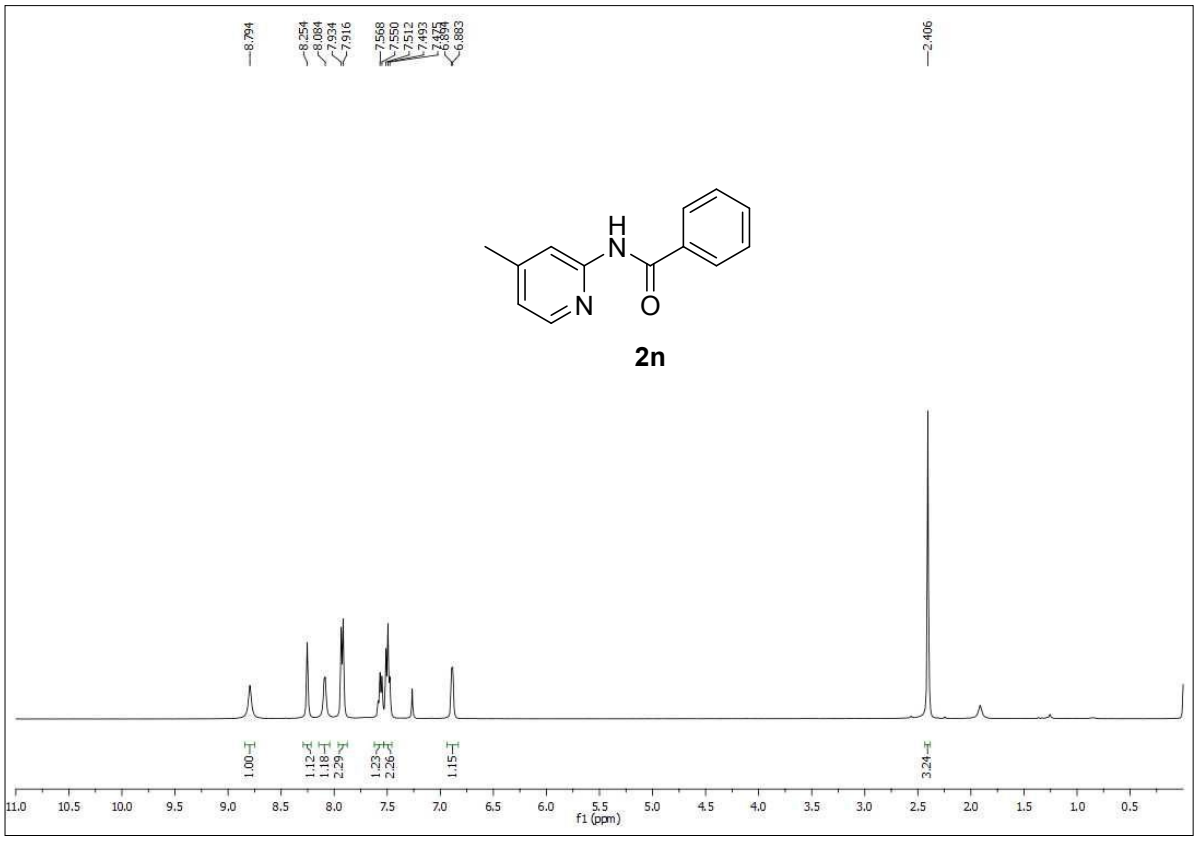

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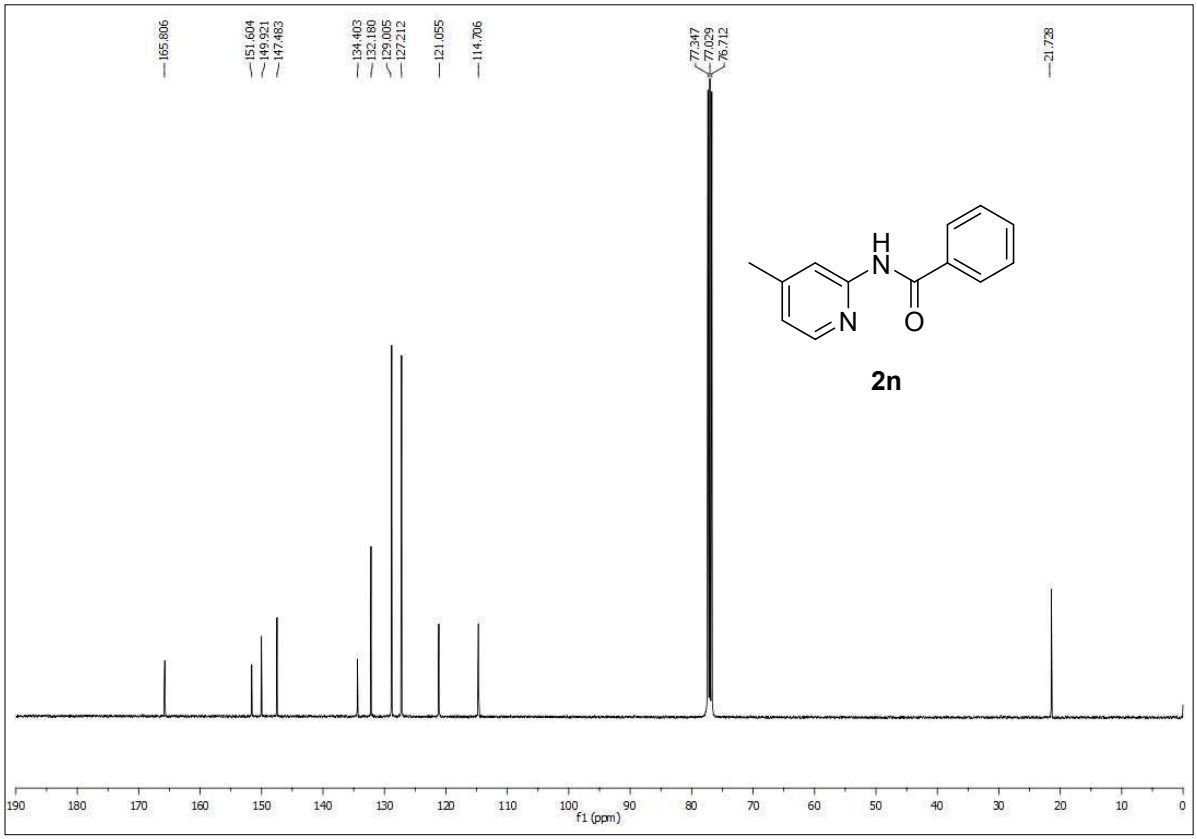

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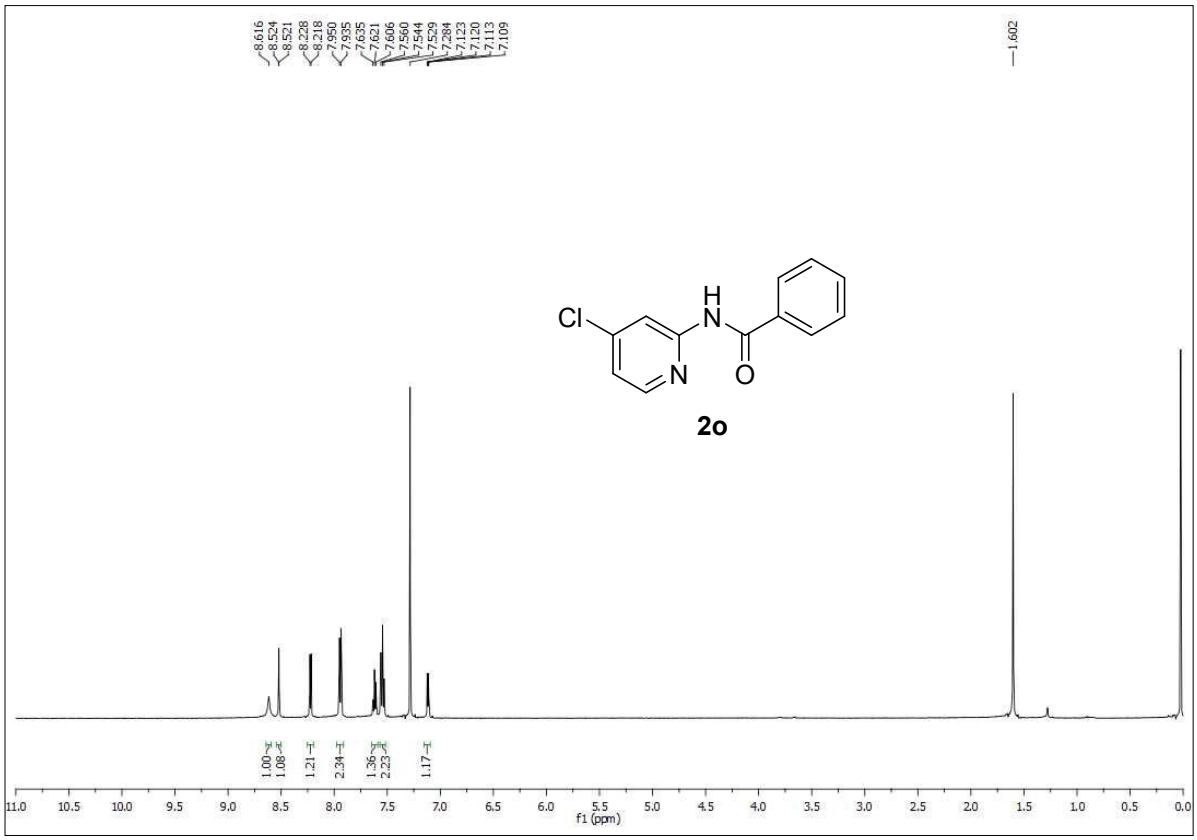

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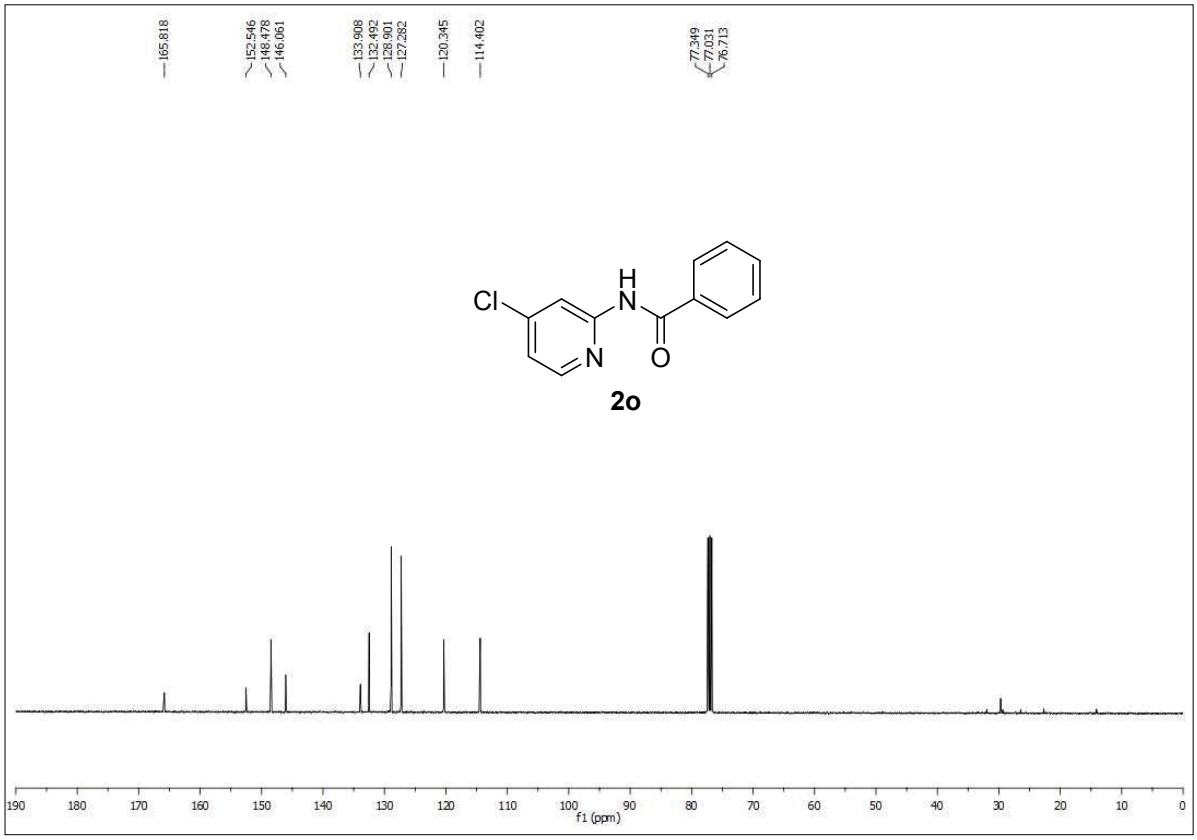

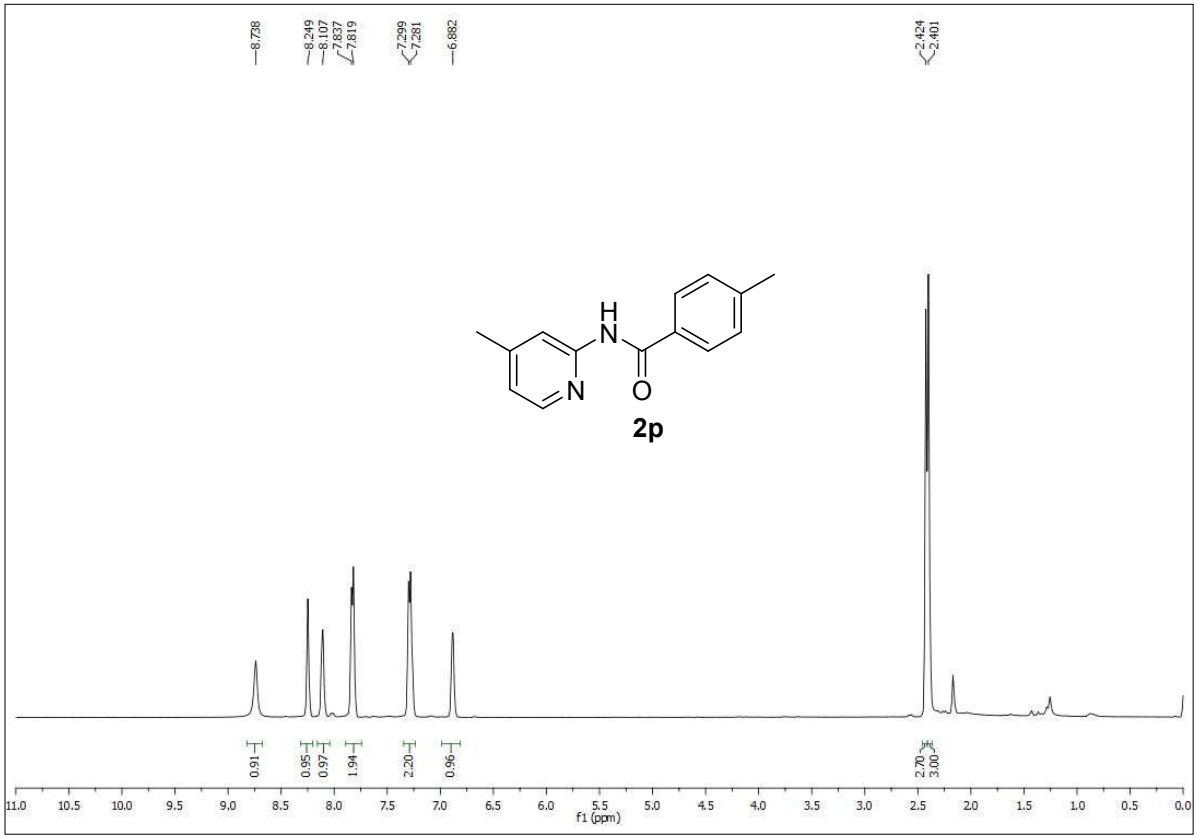

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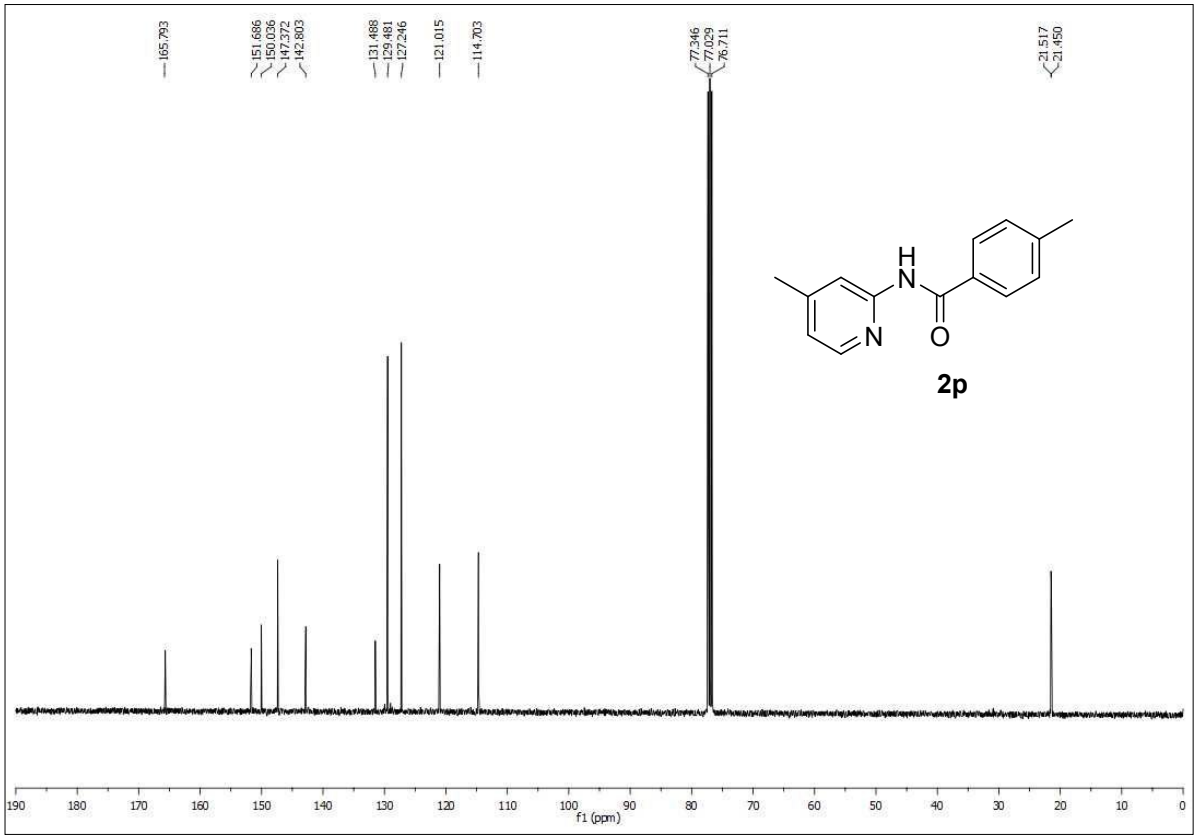

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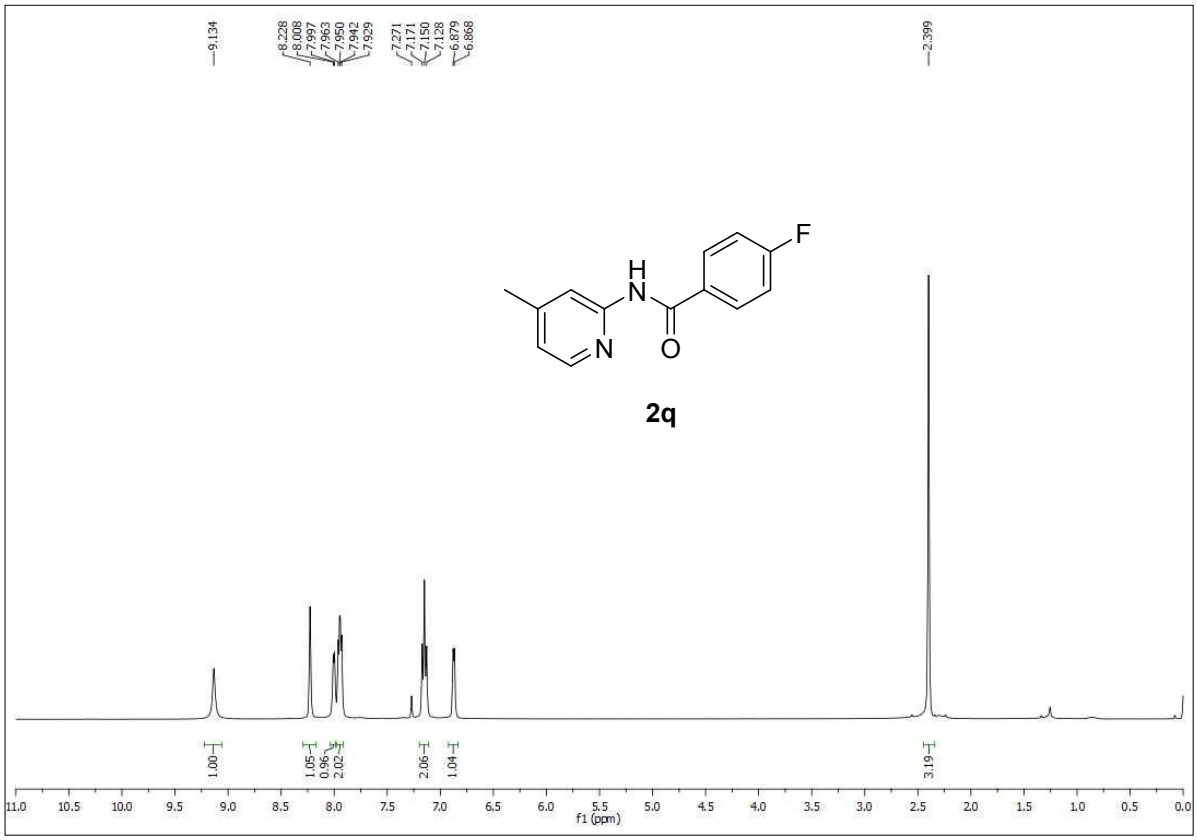

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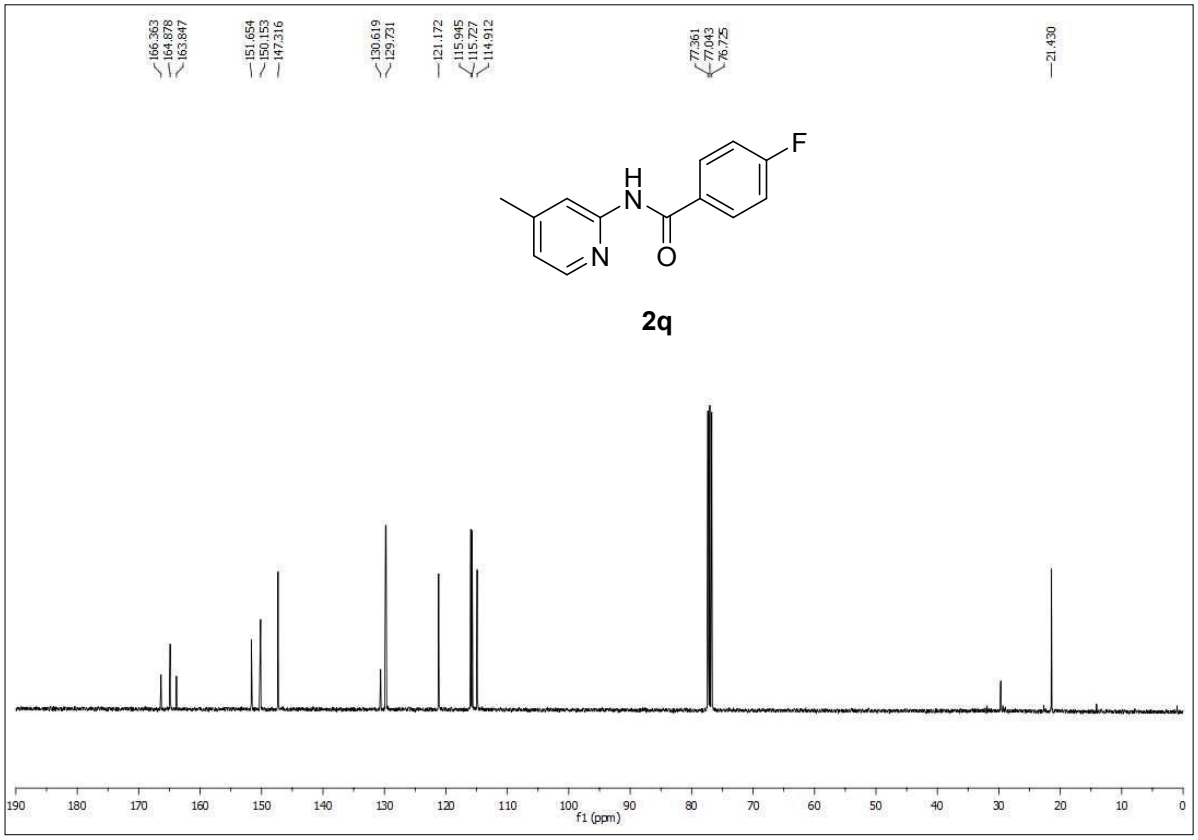

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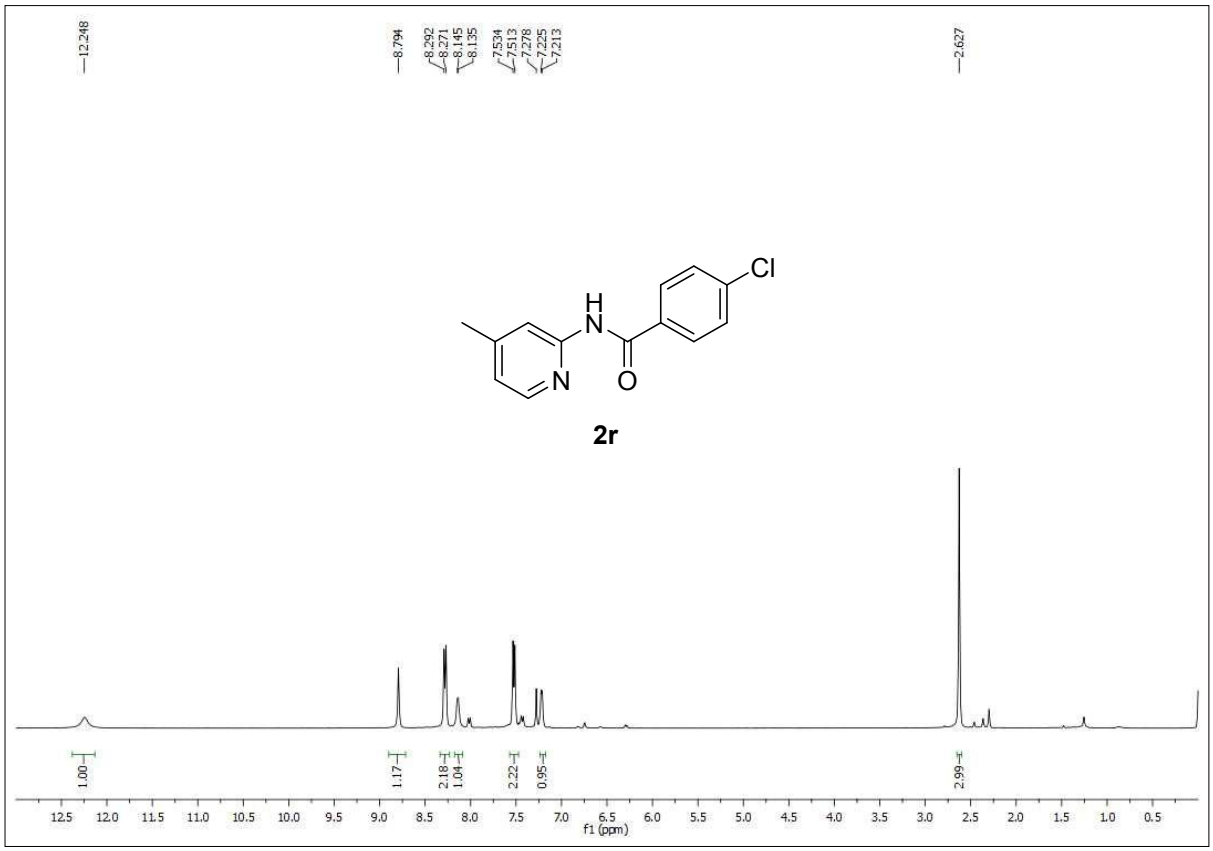

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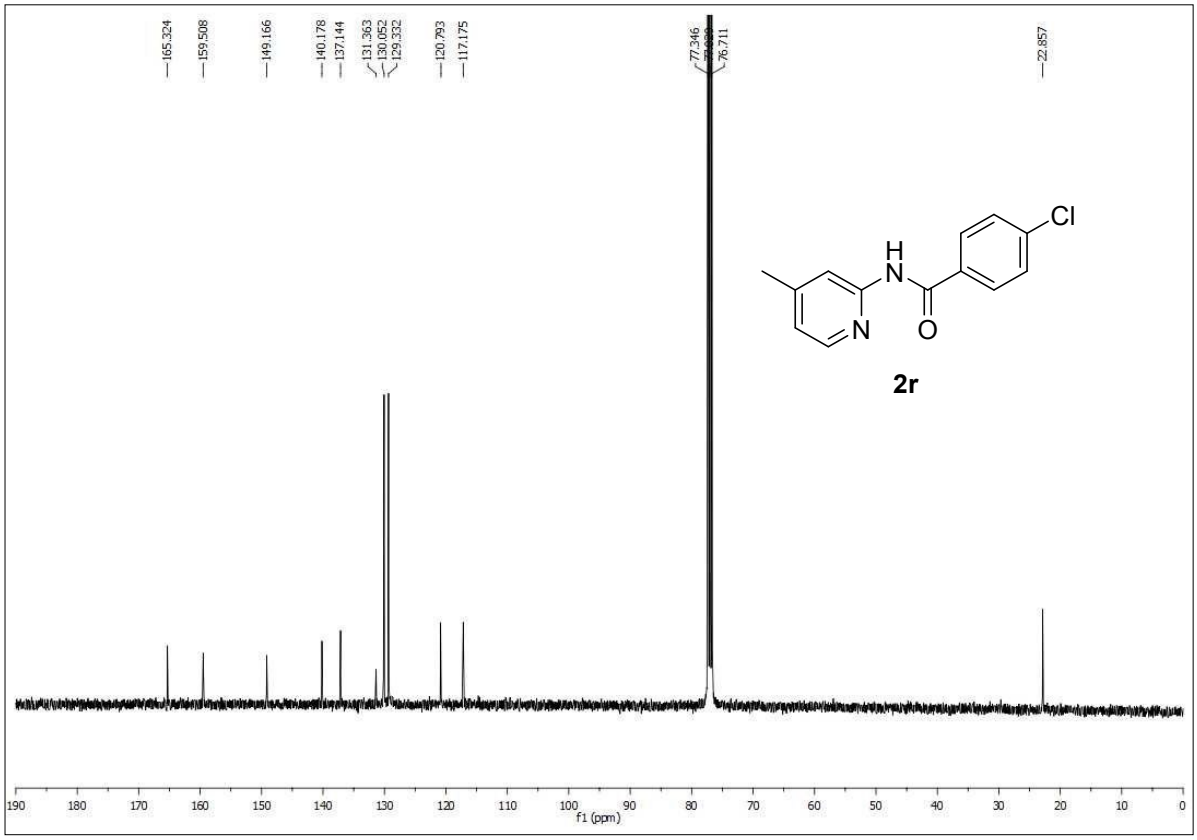

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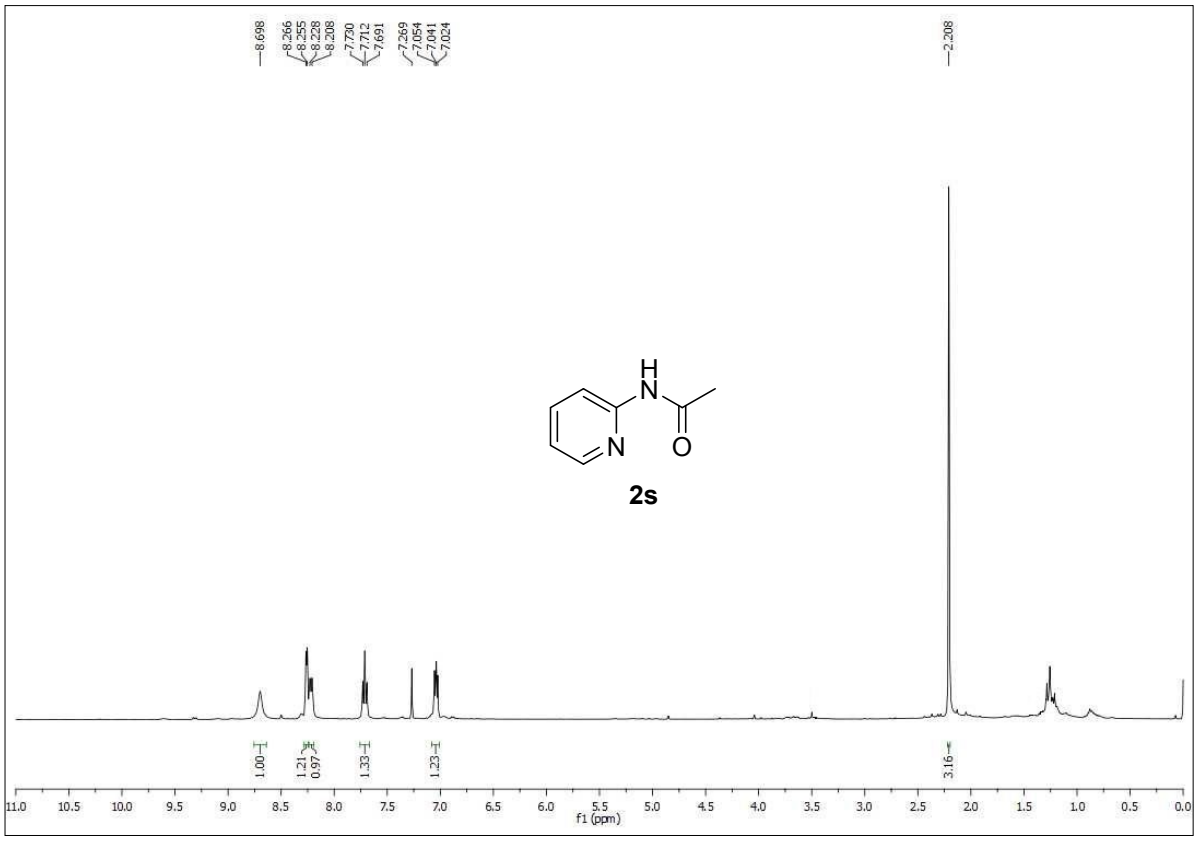

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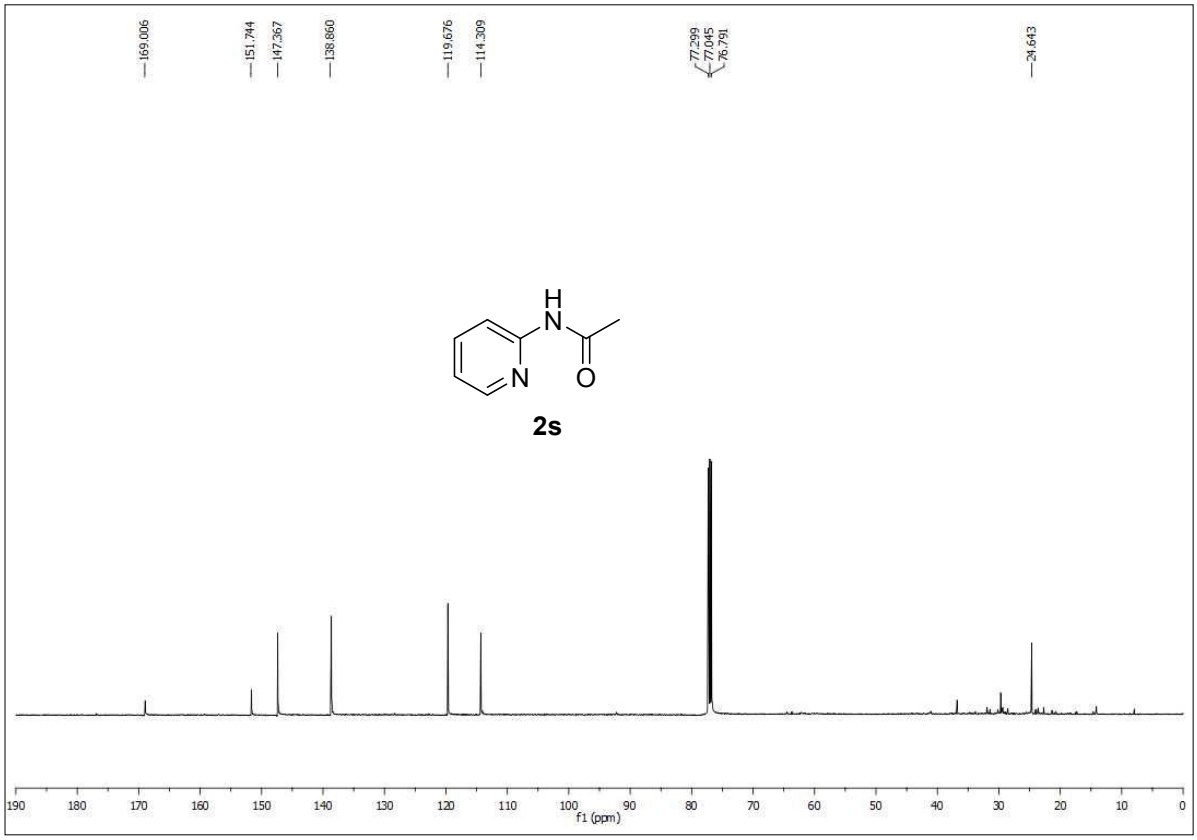

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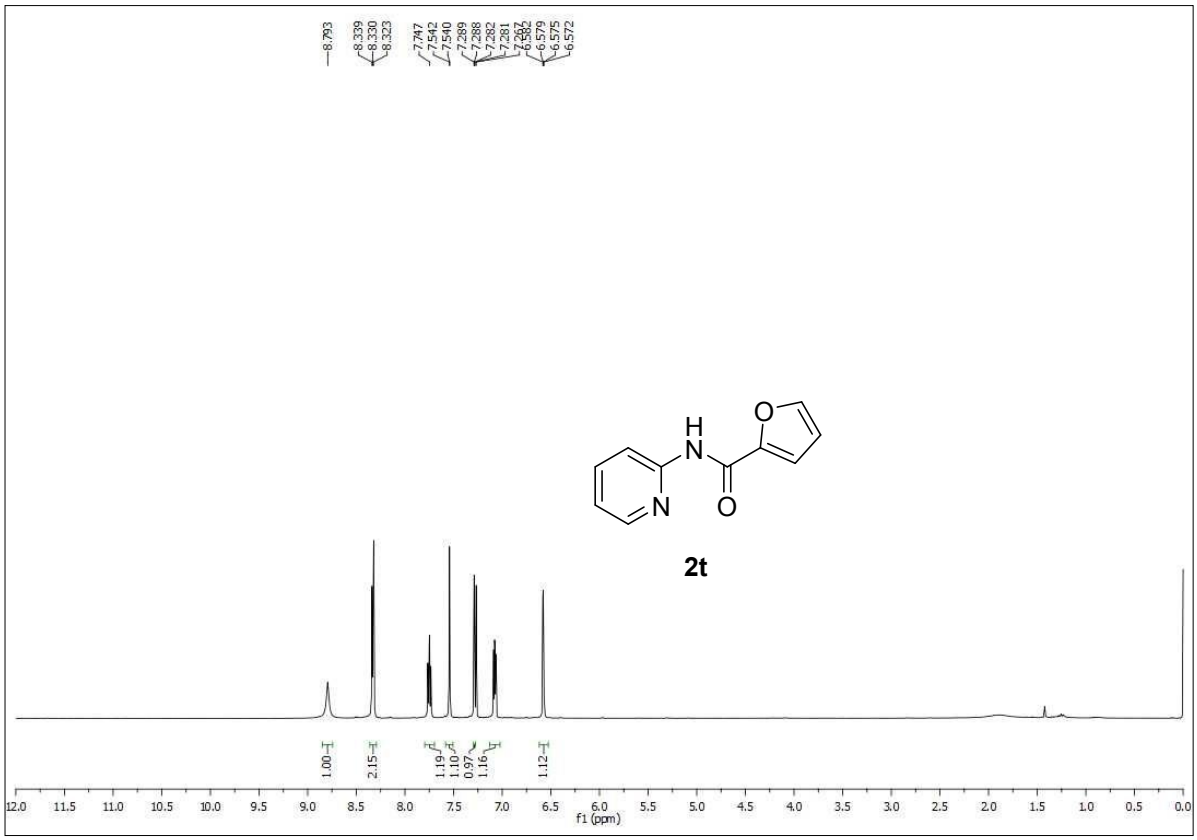

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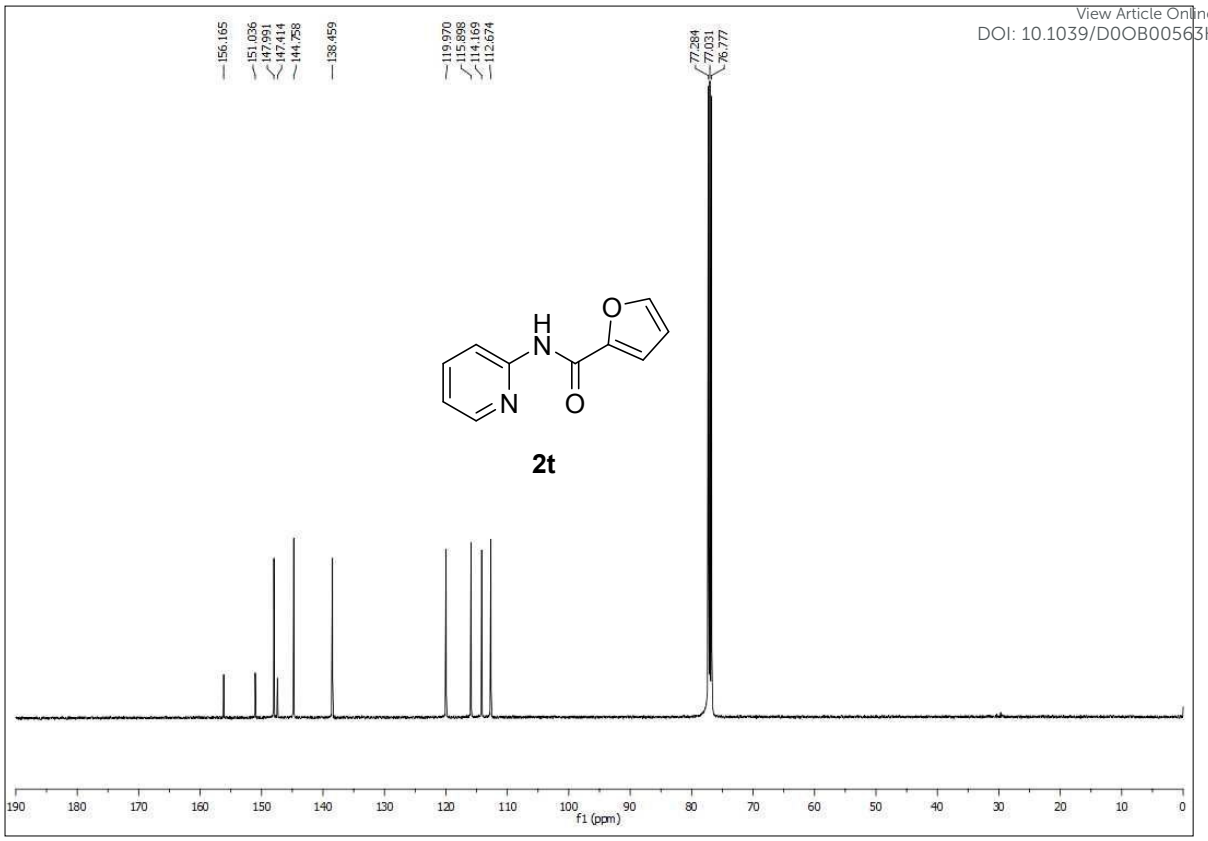

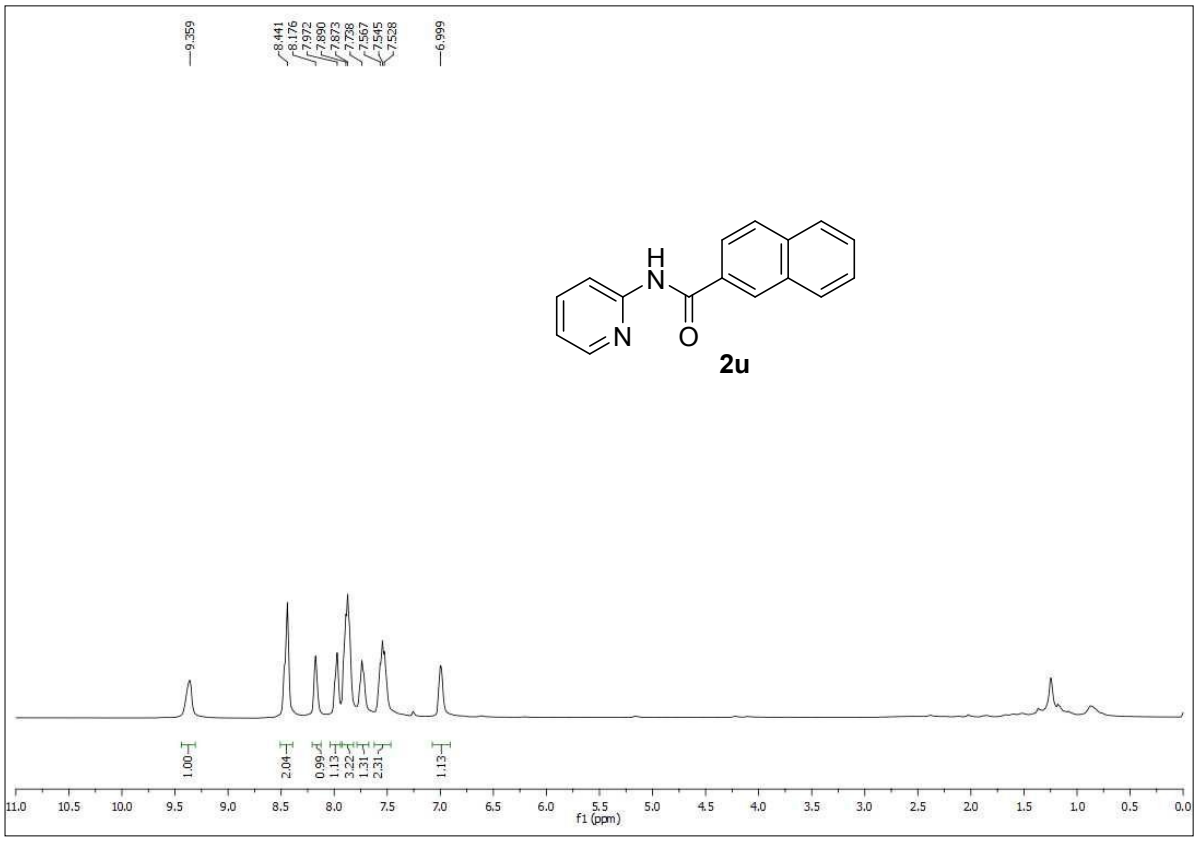

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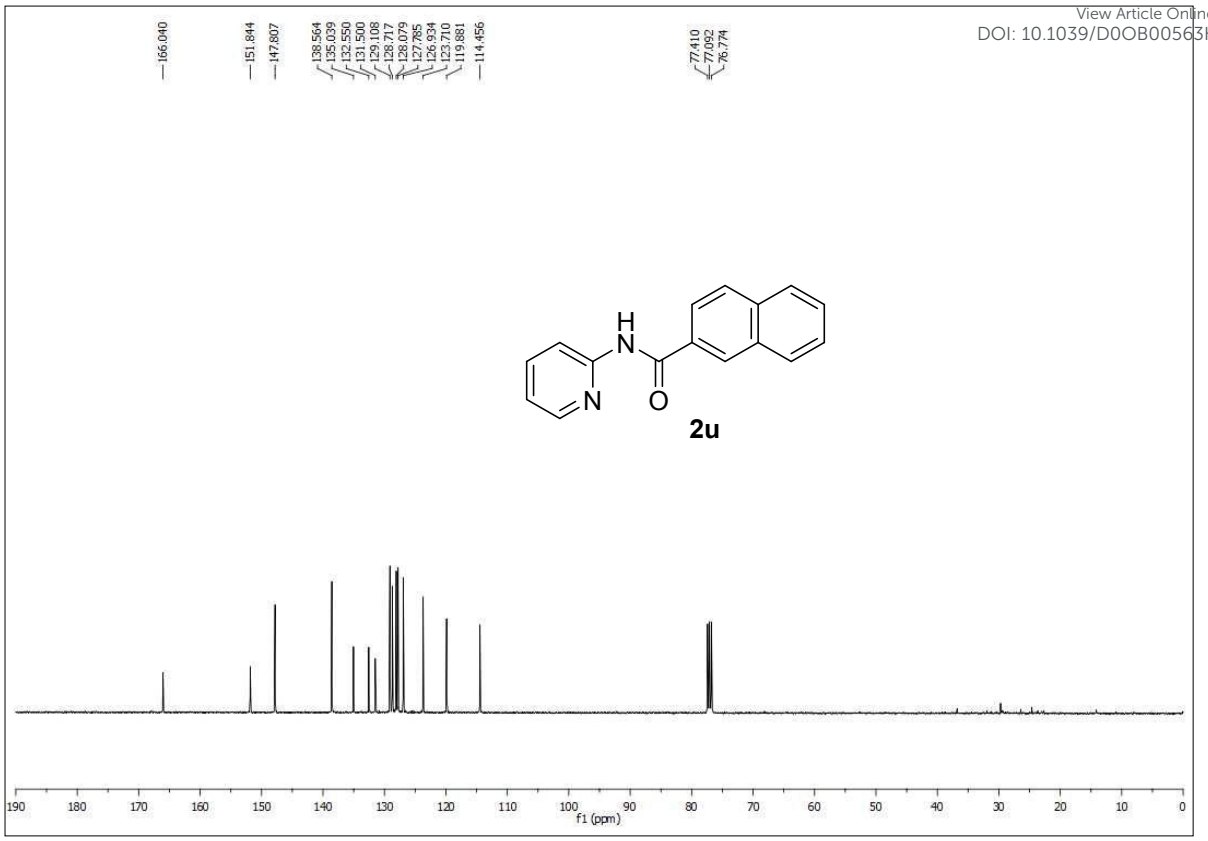

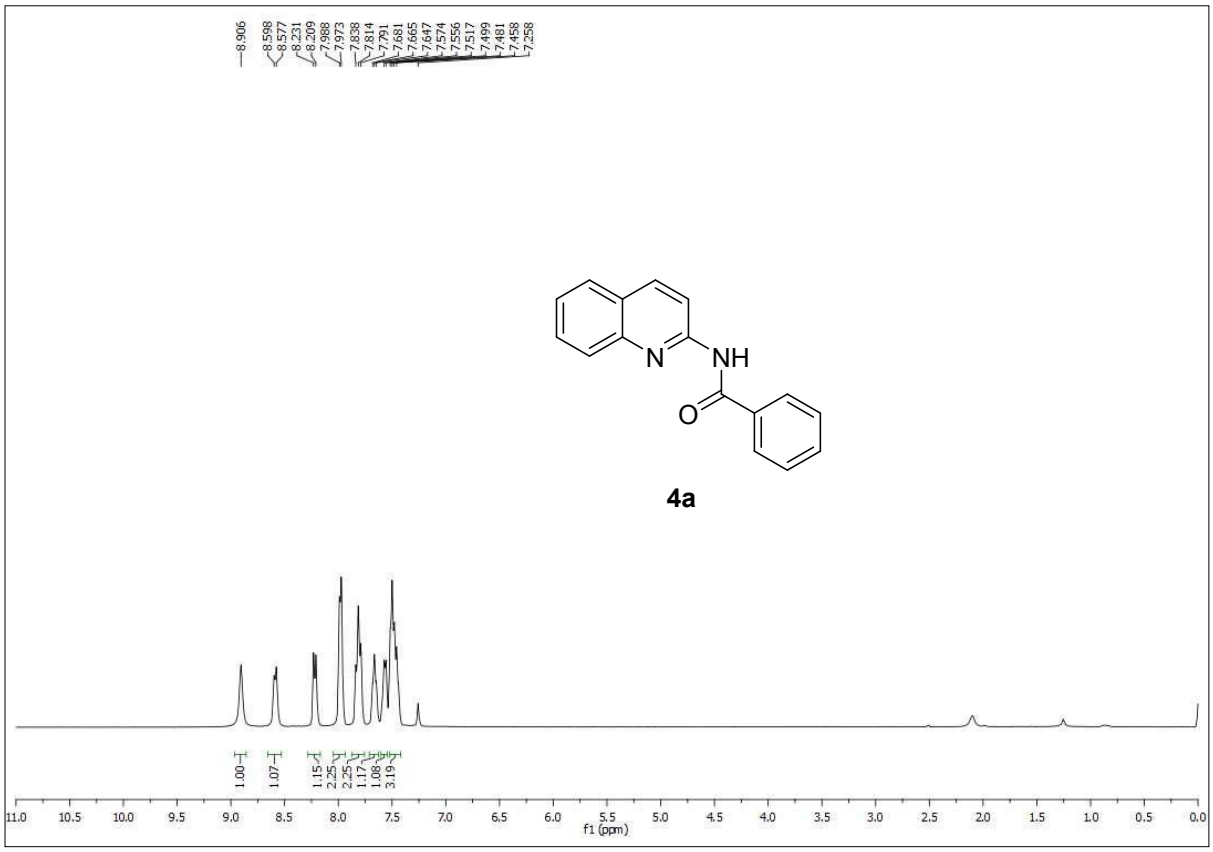

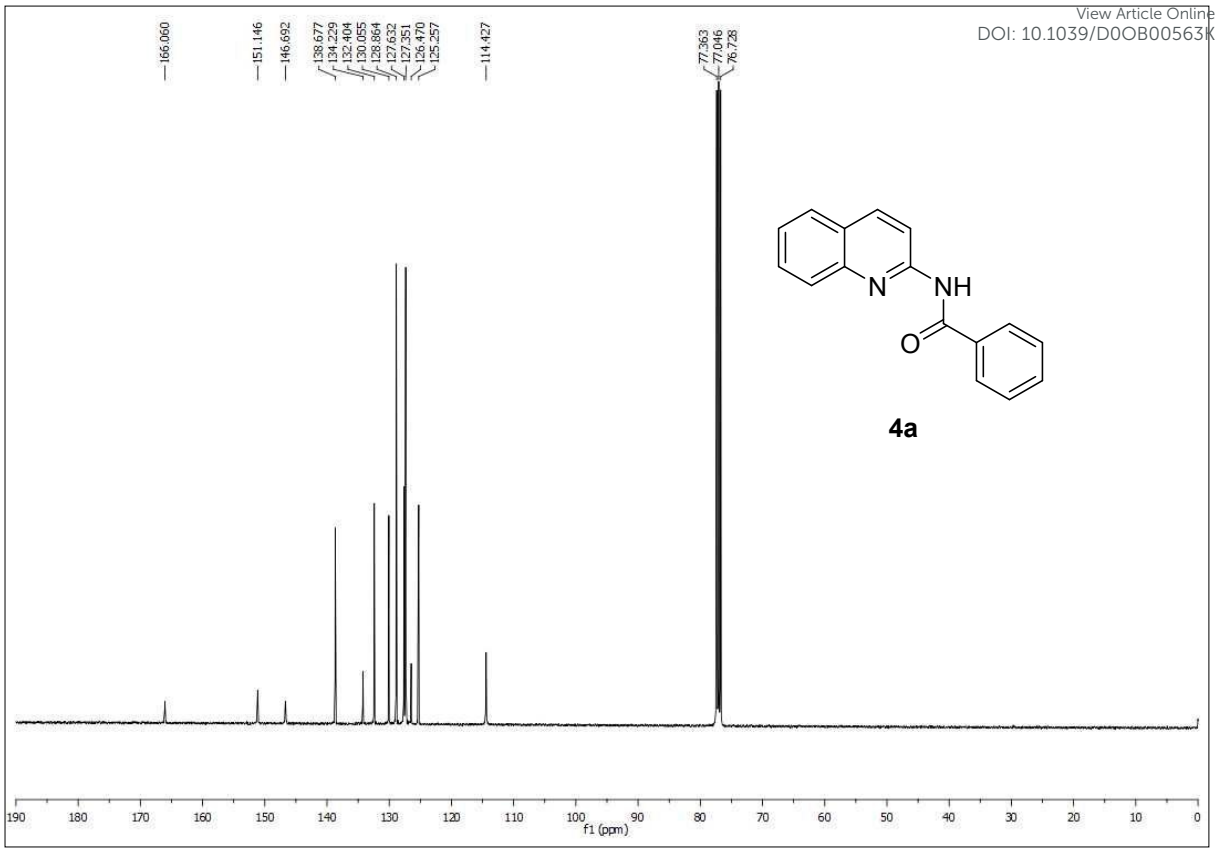

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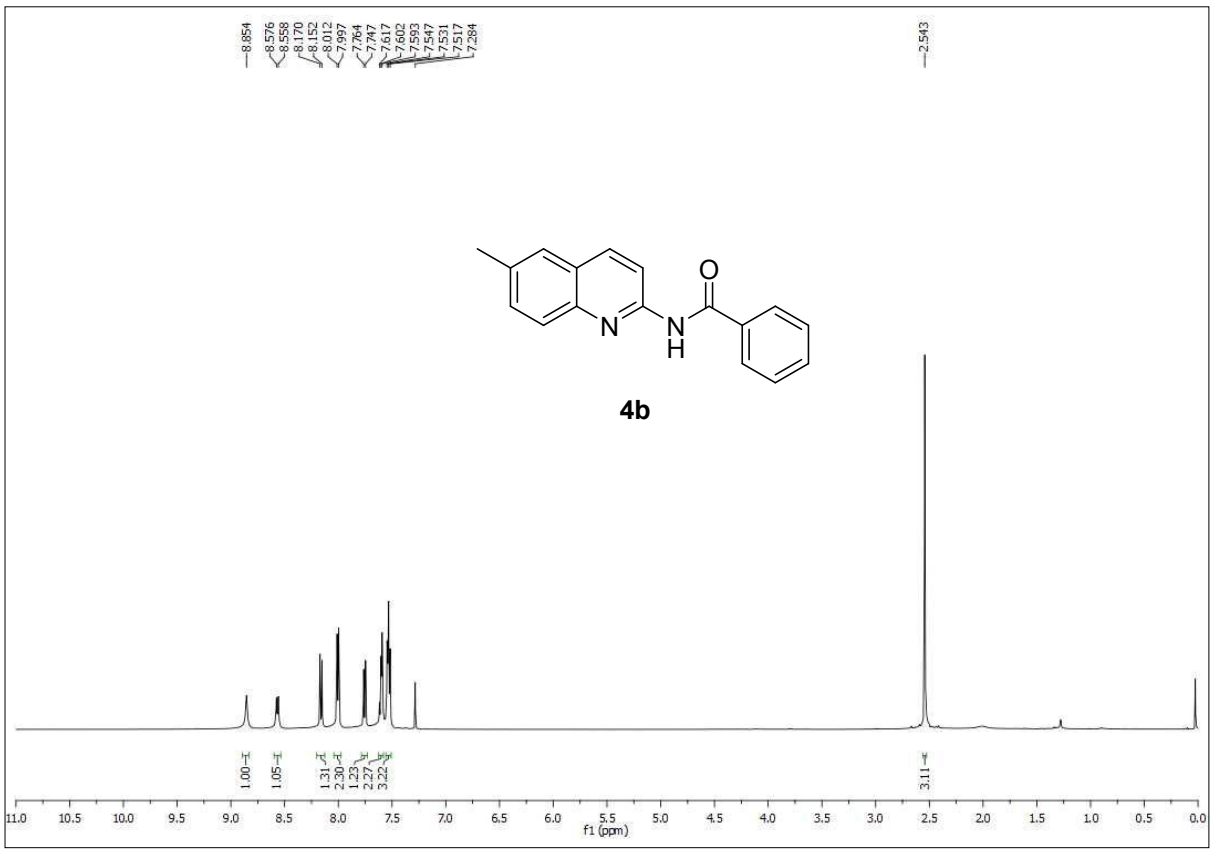

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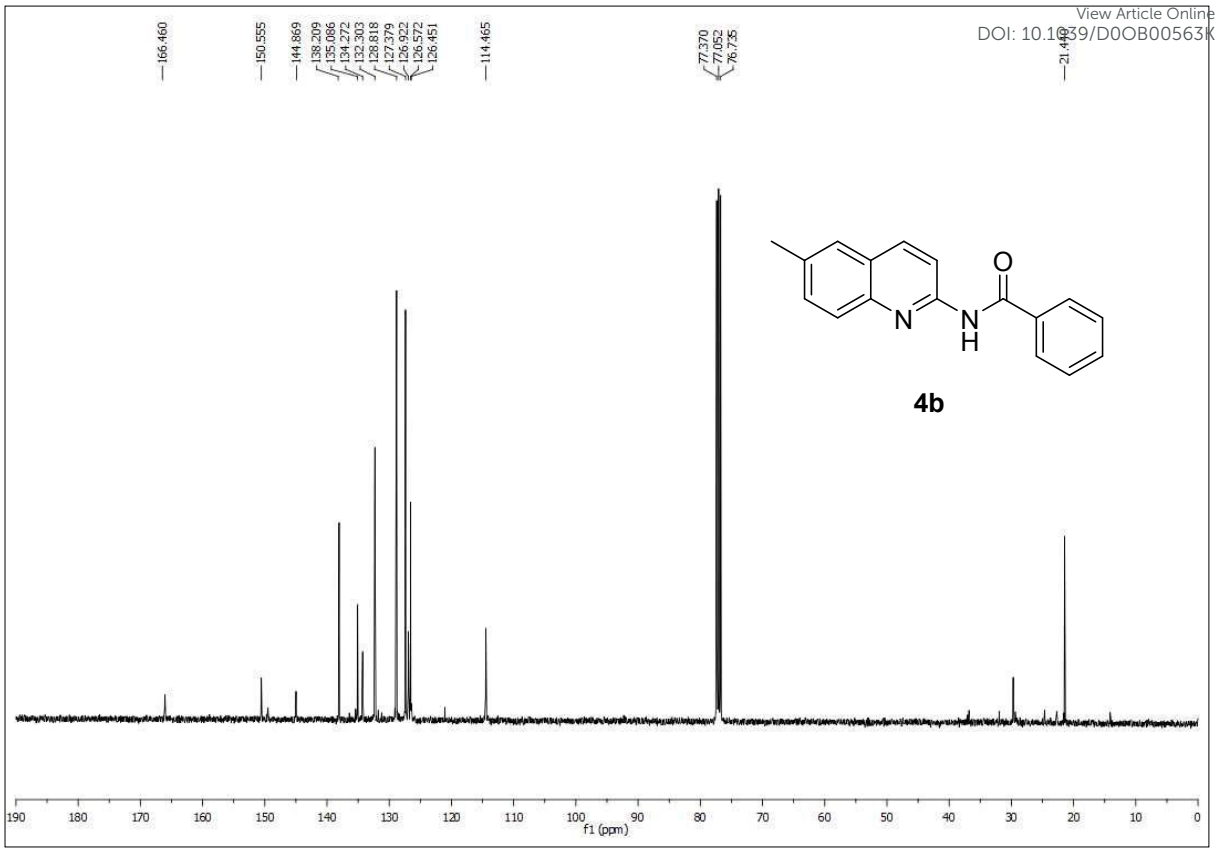

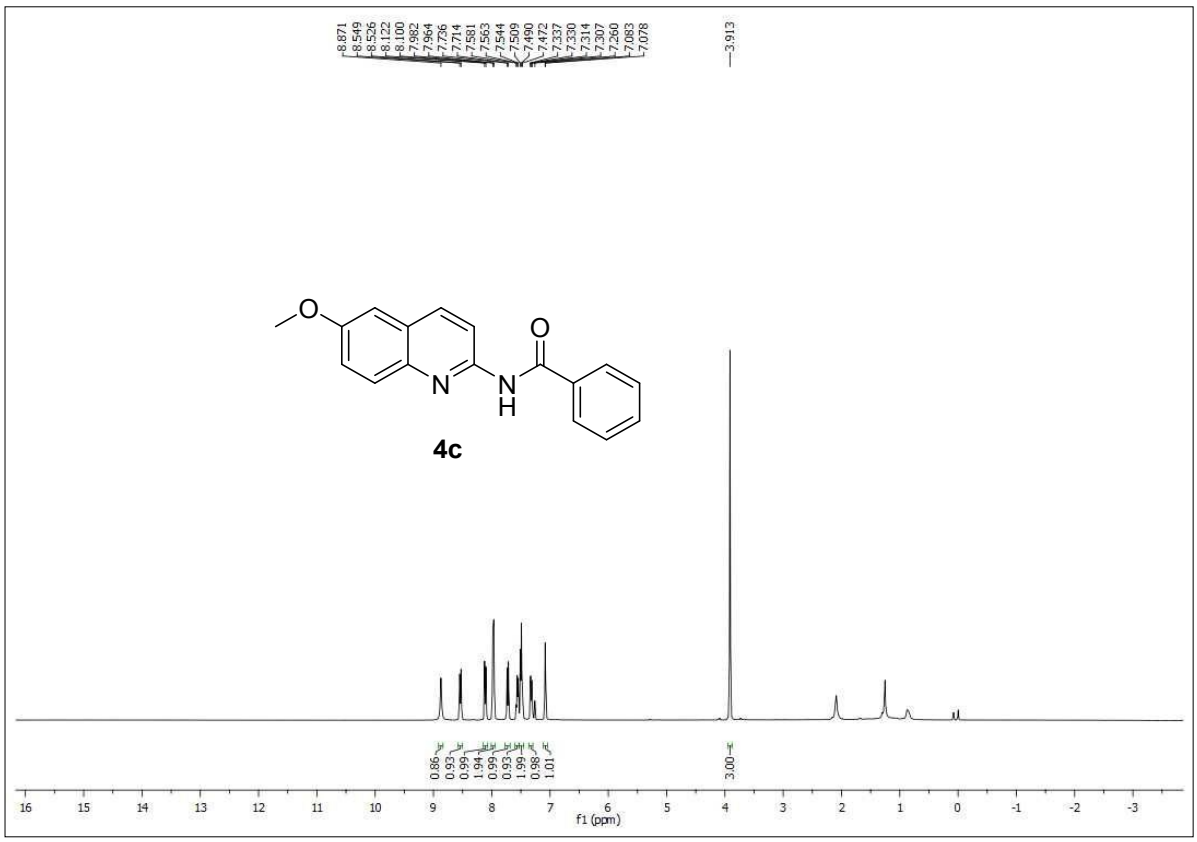

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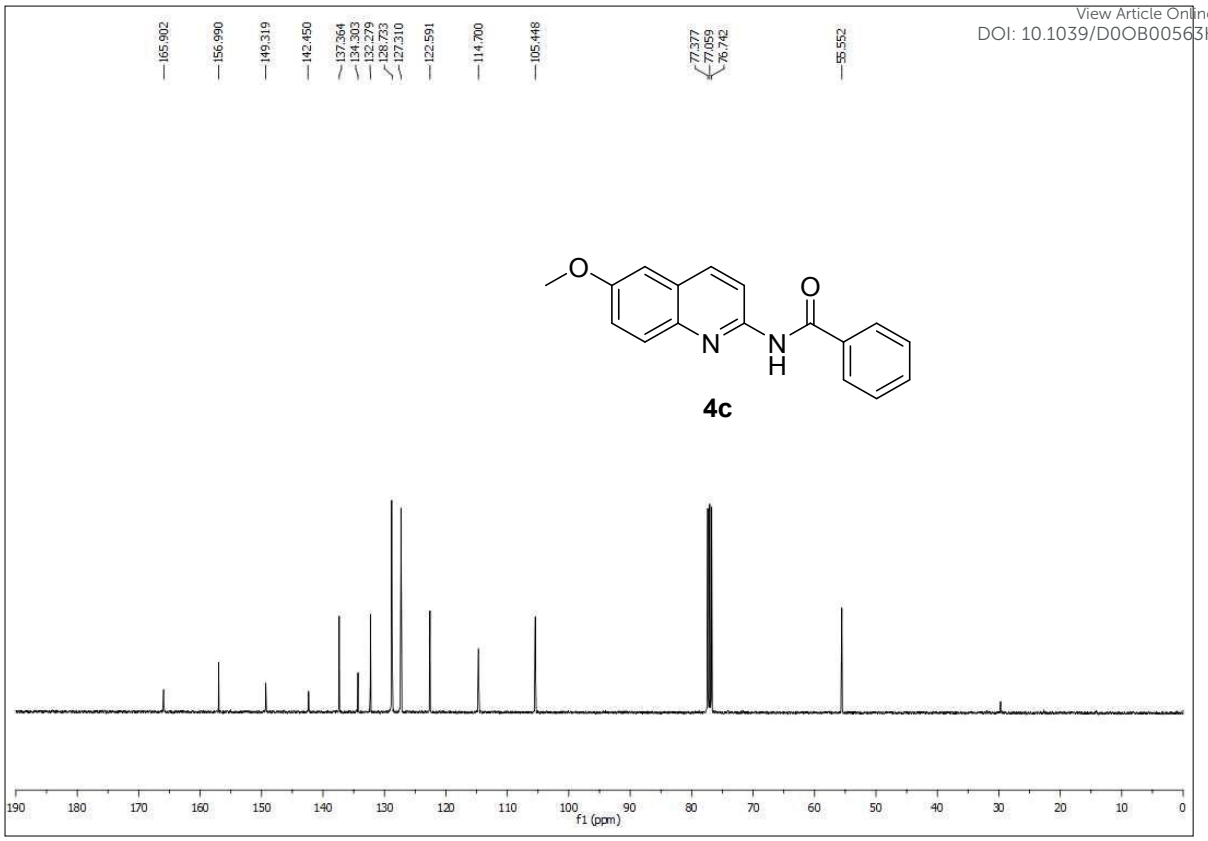

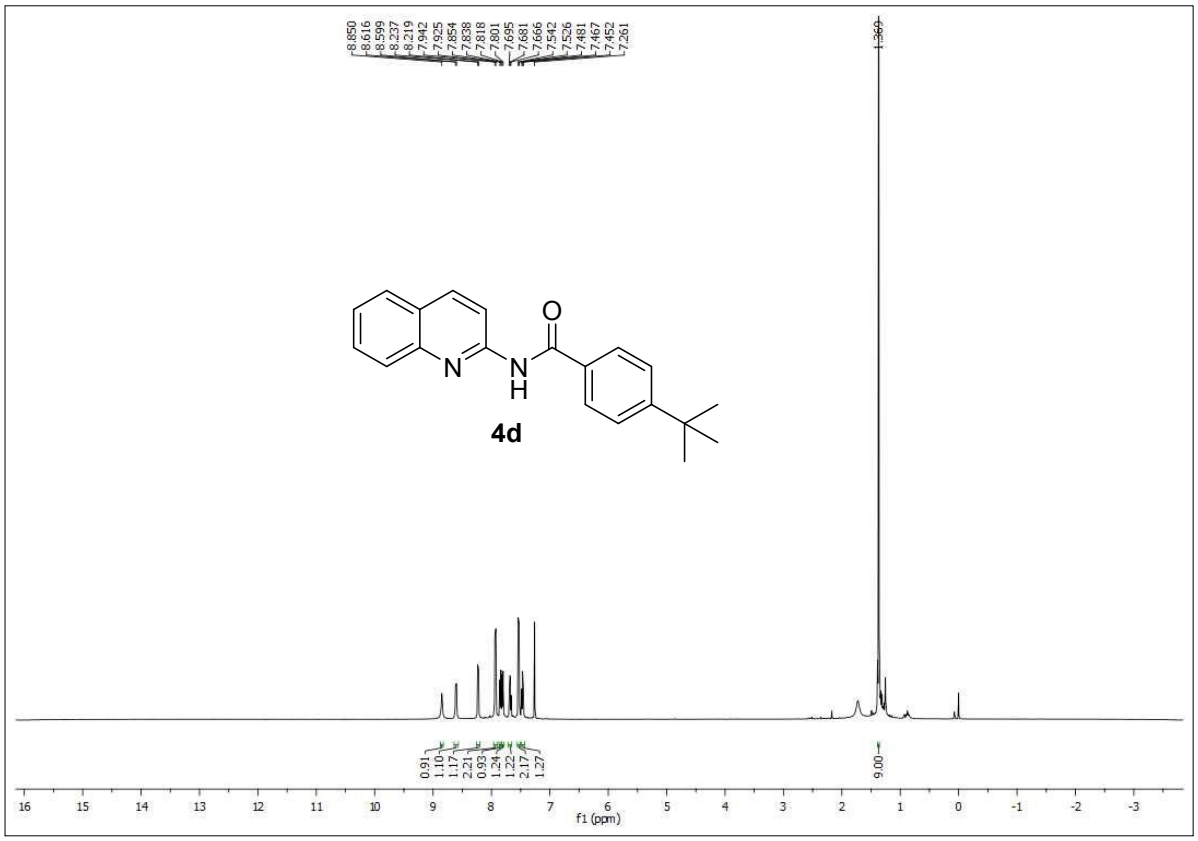

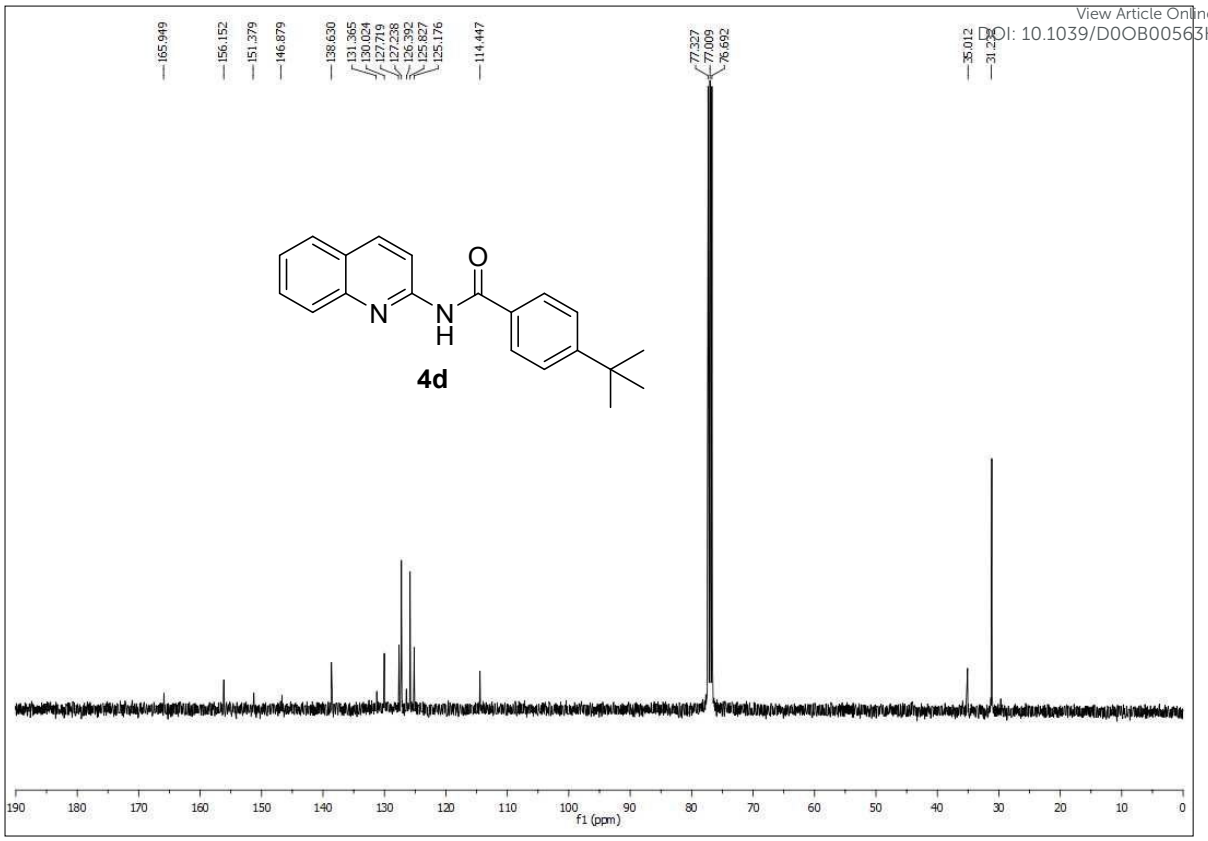

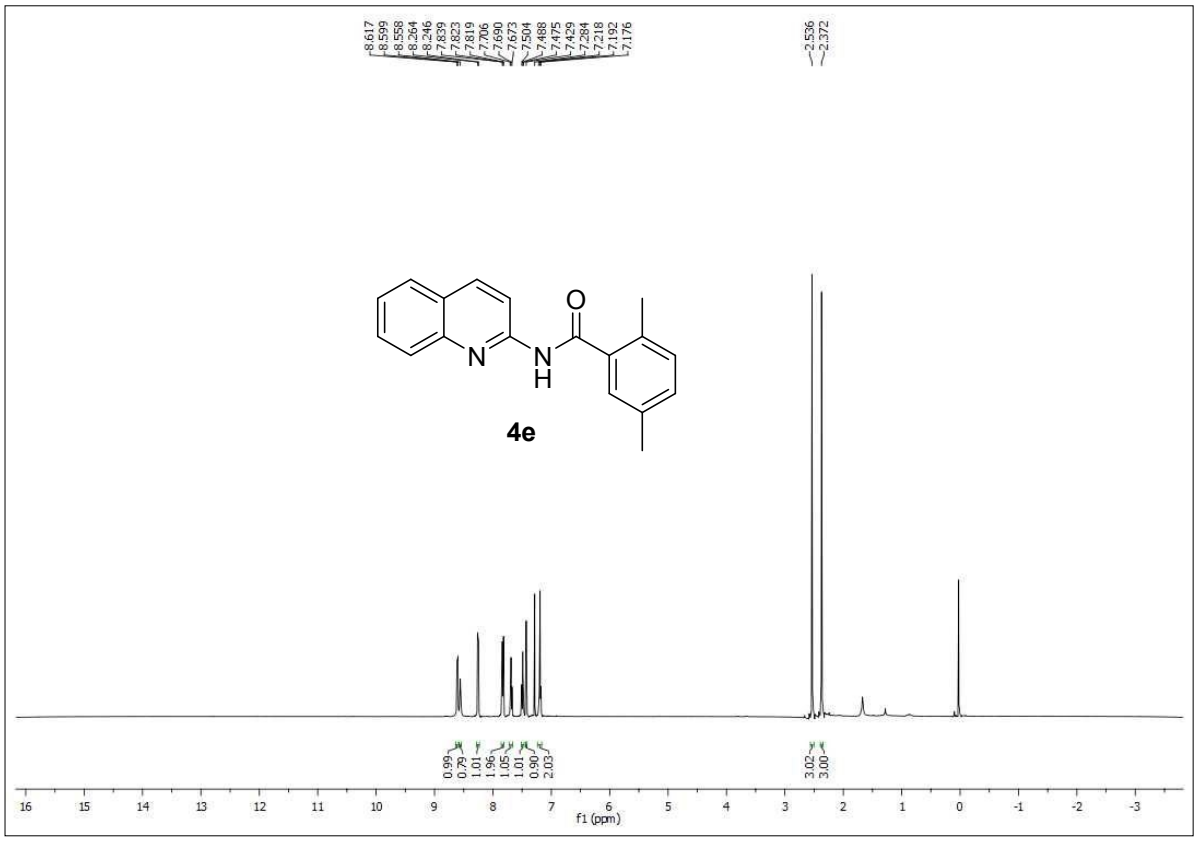

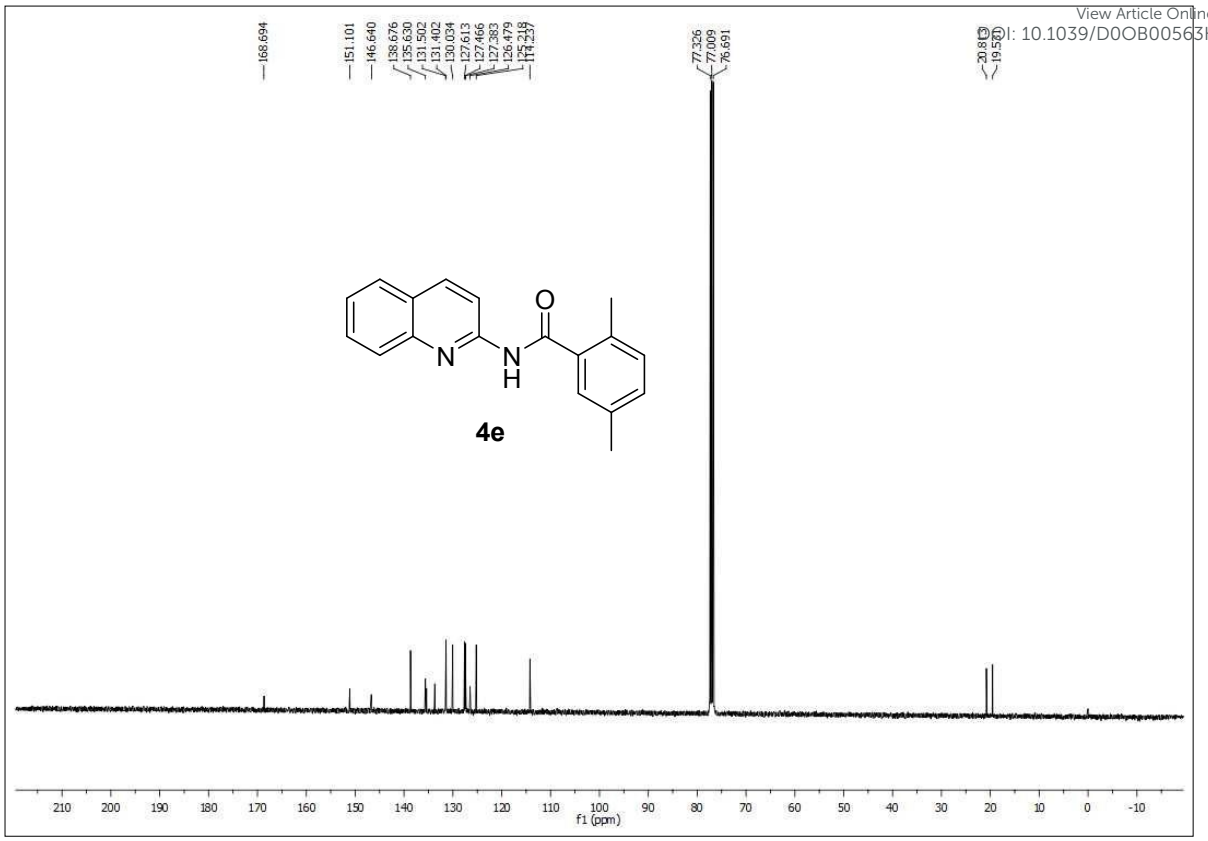

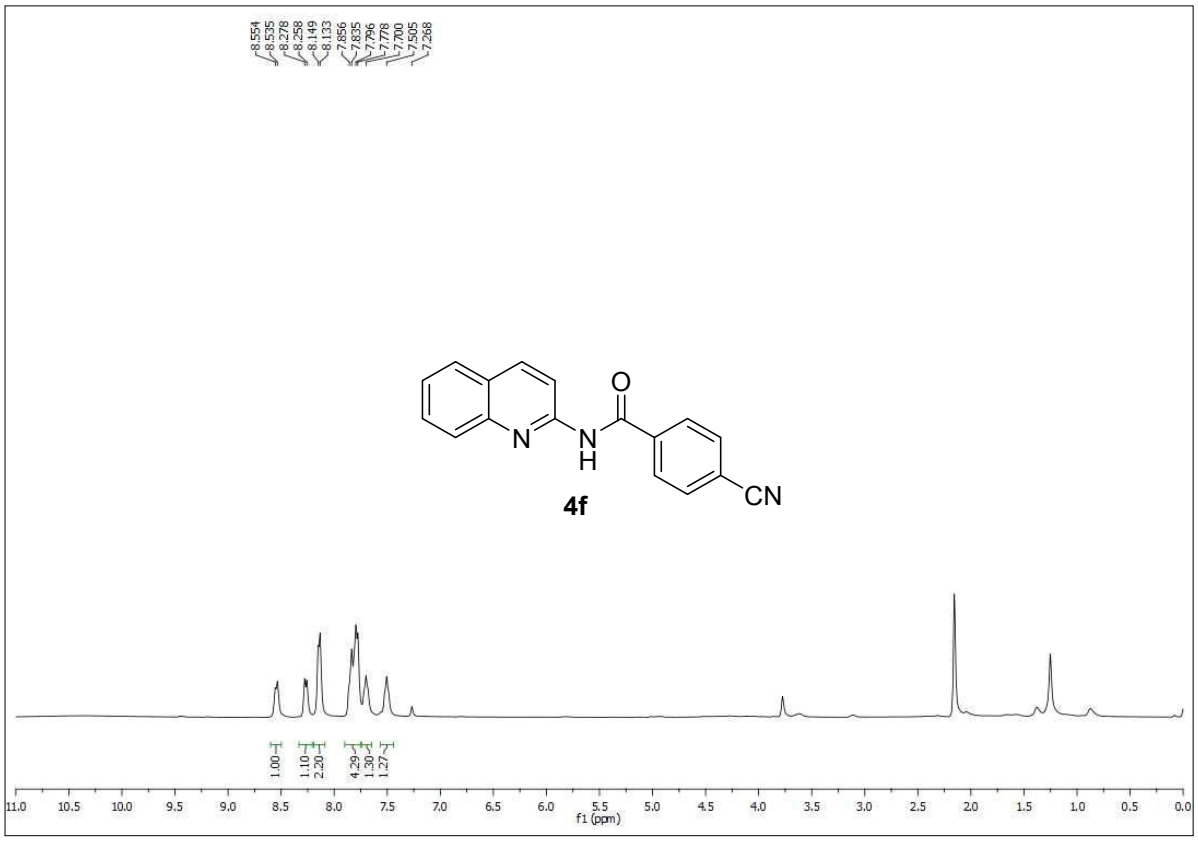

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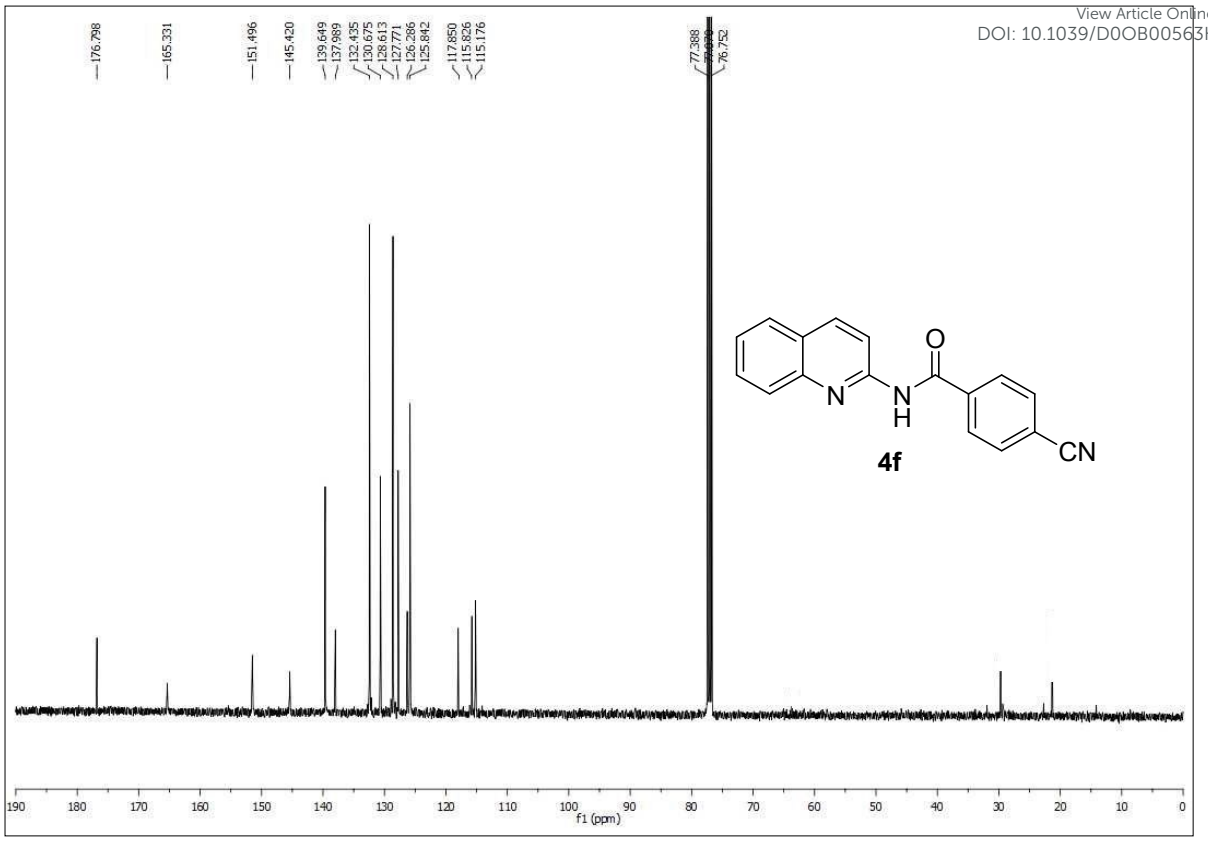

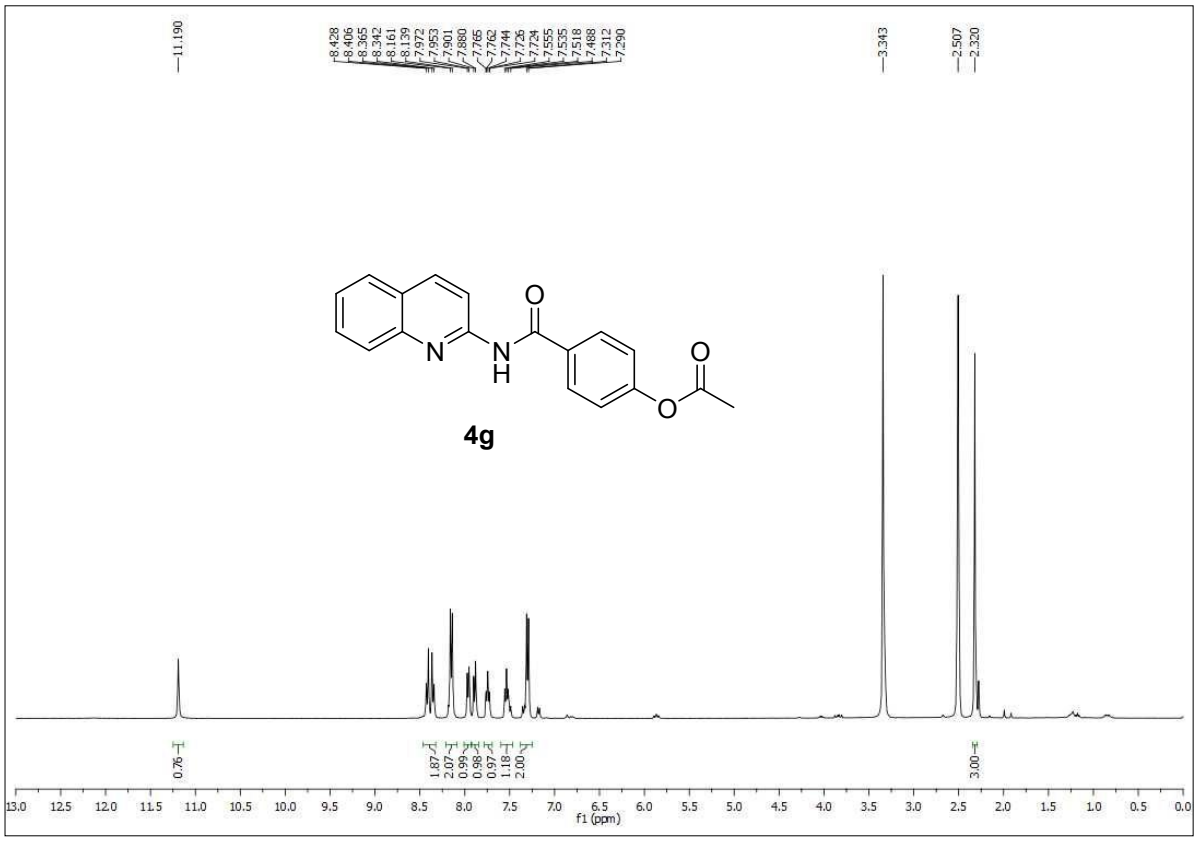

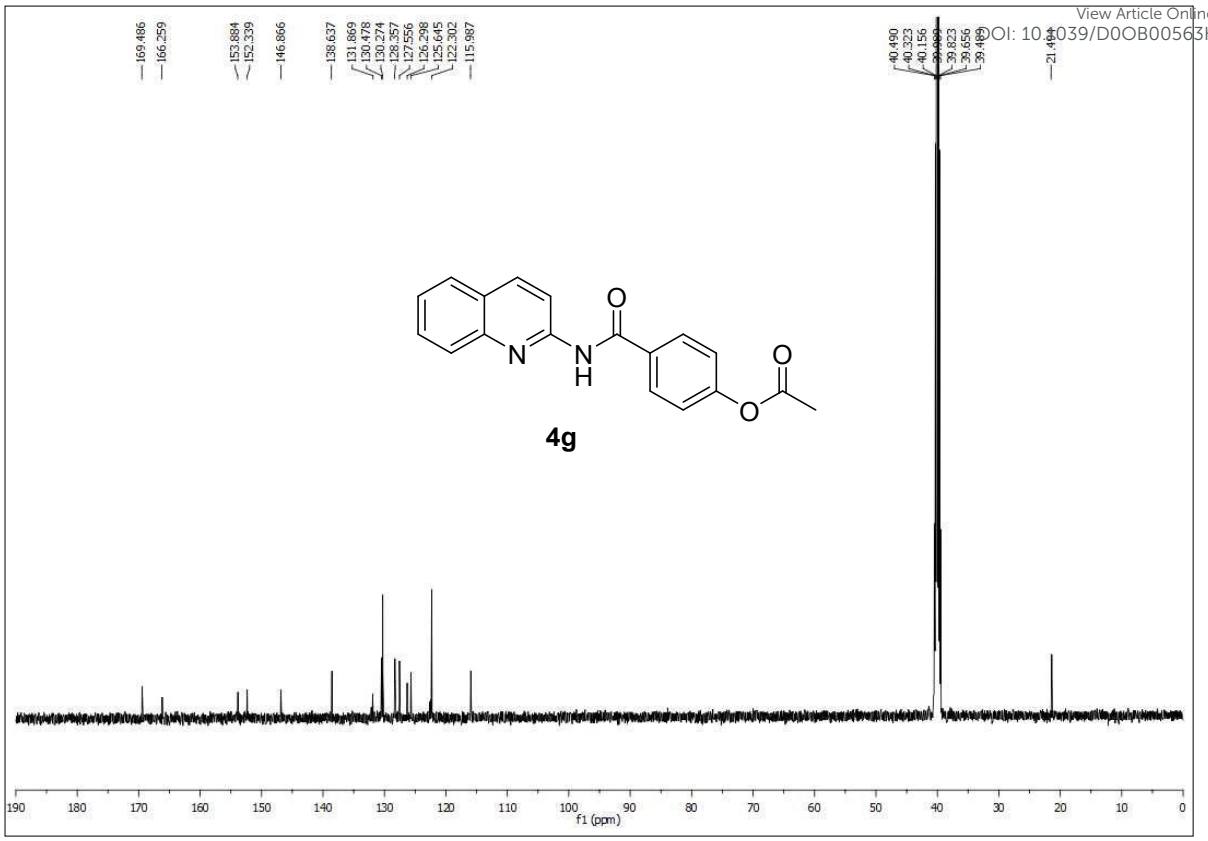

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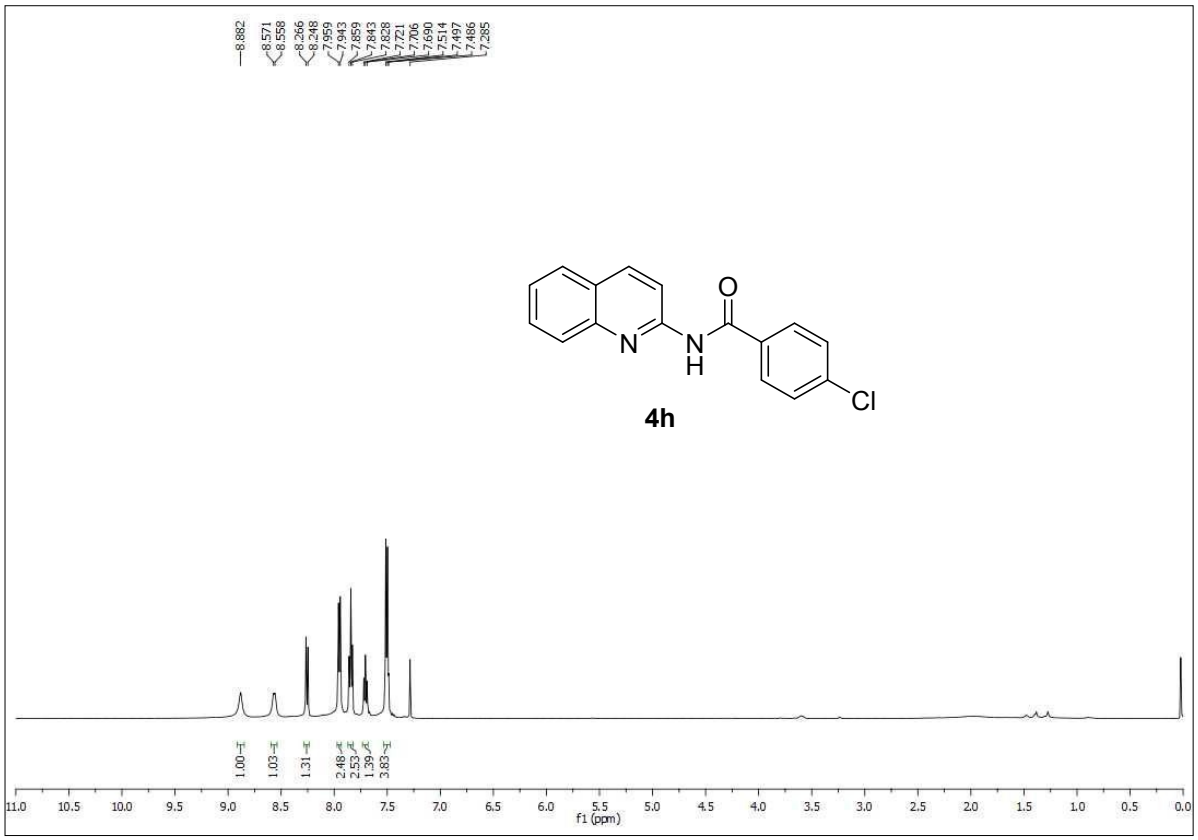

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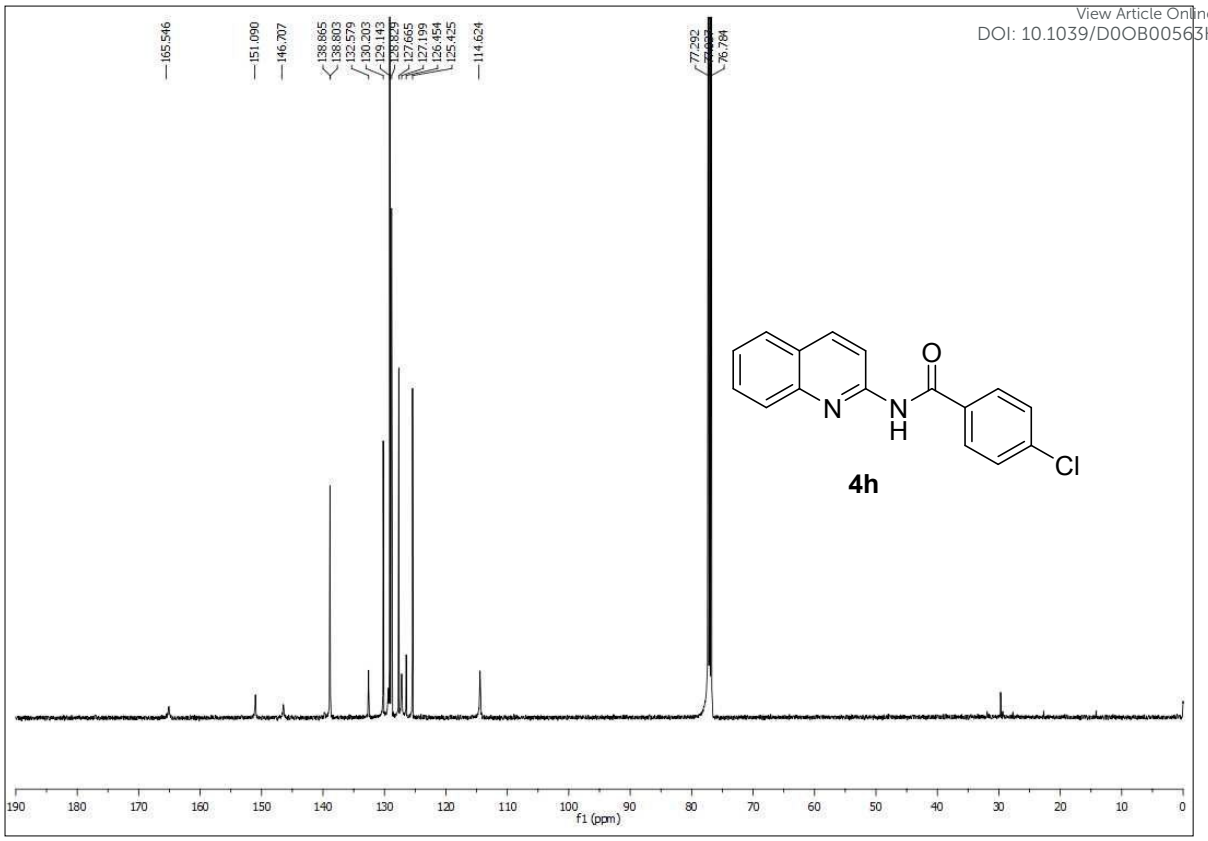

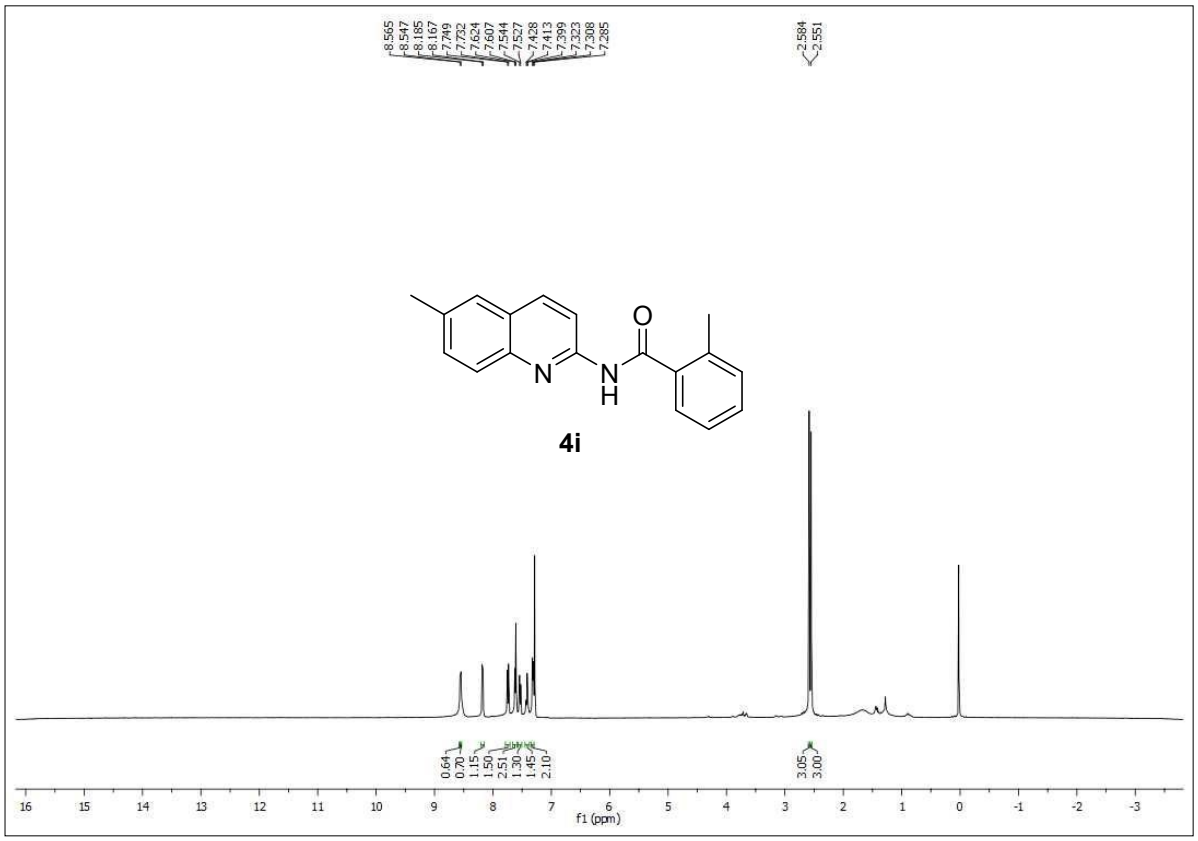

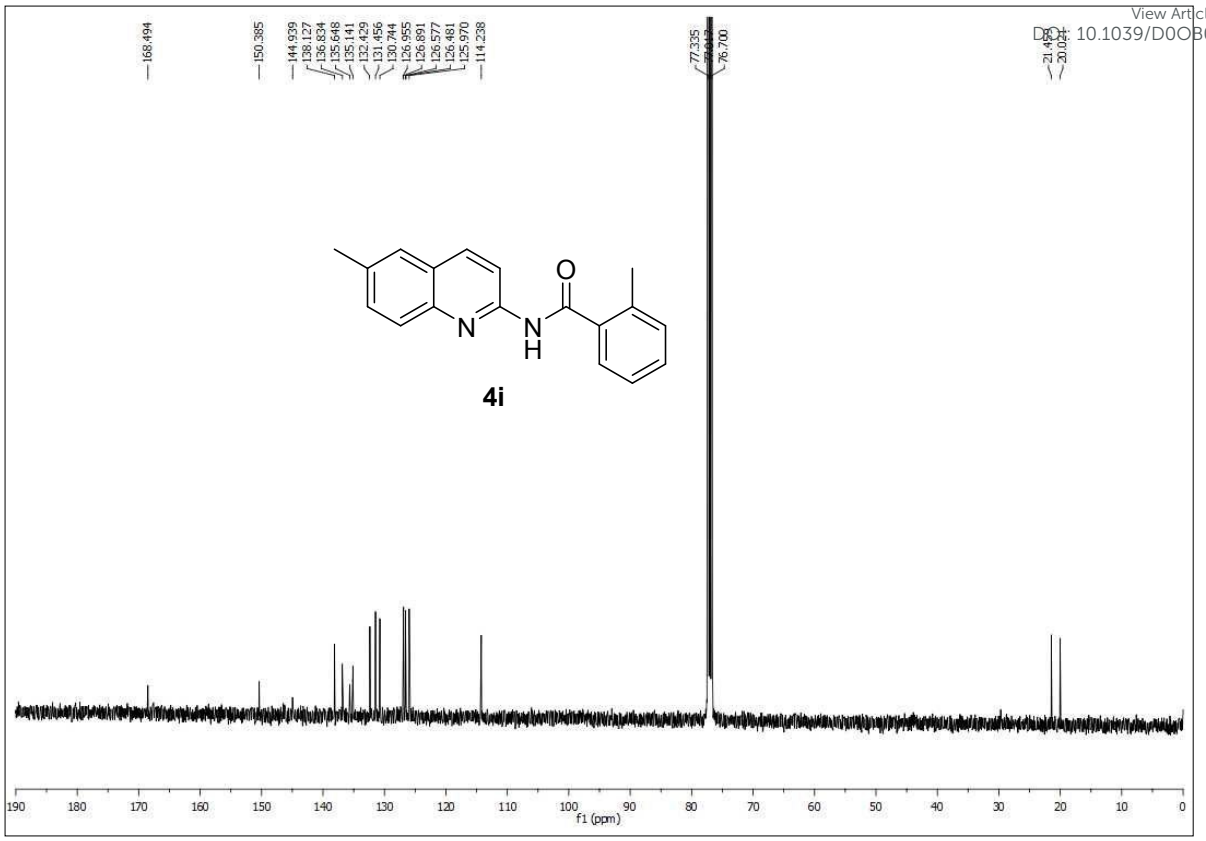

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