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ARTICLE

Decarboxylative/Decarbonylative C3-acylation of indoles via photocatalysis: a simple and efficient route to 3-acylindoles

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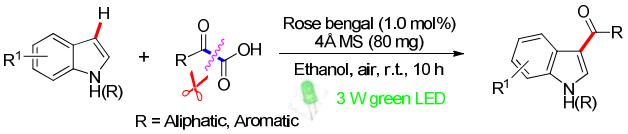
Qing Shi,[a] Pinhua Li,*[a] Xianjin Zhu,[a] and Lei Wang*[a,b]

A simple and efficient strategy for the preparation of 3-acylindoles via visible-light promoted C3-acylation of free (NH)- and *N*-substituted indoles with *α*-oxocarboxylic acids was developed. The reaction tolerates a wide range of functional groups, and the corresponding 3-acylindoles were obtained in high yields under mild conditions.

Introduction

Acylated indoles are ubiquitous in biologically active natural products and pharmaceutical compounds, and are also versatile precursors for the synthesis of alkaloids and other related heterocycles, such as anti-diabetic, anti-cancer, and inhibitor of HIV-1 integrase.[1] Additionally, 3-acylindoles are valuable intermediates in a variety of functional group transformations.[2] The most classic methods for the preparation of 3-acylindoles are Friedel-Crafts reaction,[3] Vilsmeier–Haack reaction,[4] and the reaction of indole with acyl chlorides.[5] Recently, the synthesis of 3-acylindoles has got considerable attention, and some significant approaches have been achieved, such as Ru- and Fe-catalyzed acylation of indoles using anilines as carbonyl sources,[6] Pd-catalyzed acylation of indoles via nitriles as acylating agents,[7] Cu- and Pd-promoted acylation of indoles by α-oxocarboxylic acids,[8] and Pd-catalyzed carbonylation of indoles with CO and arylboronic acids.[9] Moreover, there are a few efficient methods for the synthesis of 3-acylindoles through tandem reactions based on C(sp^3)–H bond activation.[10] However, most of the existing methods are often harmful to the environment. To develop new routes to them from readily available precursors under mild and environmentally friendly conditions is highly desirable.

Visible light is an environmentally benign and infinitely available energy source for activating chemical transformations. Although first proposed by Ciamician a century ago,[11] there was no much attention in this field until 2008 when MacMillan disclosed the visible light photoredox catalysis as a powerful tool in organic synthesis.[12] In the past few years, the visible-light promoted chemical reactions have received considerable attention, and emerged as a hot research topic in organic chemistry.[13] In 2014, Zhou developed a visible-light photoredox synthesis of 3-acylindoles through an intramolecular oxidative cyclization of *o*-alkynylated *N,N*-dialkylamines,[14] and Li reported a simple and efficient visible-light-promoted method for the C3-thiocyanation of indoles.[15] As a continuation of our interest in visible-light photochemistry and inspired by the reported results,[16] we hypothesized that benzoyl radical generated from *α*-oxocarboxylic acids could react with indoles to form 3-acylindoles. We wish to report herein a novel and mild protocol to 3-acylindoles through a visible-light irradiated C3-acylation of free (NH)-indoles and *N*-substituted indoles with *α*-oxocarboxylic acids in the presence of rose bengal as a photocatalyst at ambient conditions (Scheme 1).[17]



Scheme 1 Visible-light irradiated C3-acylation of indoles

Initially, a model reaction of indole (**1a**) with phenylglyoxylic acid (**2a**) was chosen to optimize the reaction conditions. When eosin Y (2.0 mol%) was used as a photoredox catalyst, and the reaction was conducted in ethanol under the irradiation of 3 W green LED in air for 10 h, it was pleasing to find that the reaction does indeed proceed and afforded the desired acylation product **3a** in 31% yield. The structure of **3a** was characterized by ^{1}H and ^{13}C NMR, and further confirmed by X-ray single crystal analysis.[18] An improved yield (51%) of **3a** was obtained when 4Å molecular sieve was added (Table 1, entry 1). A slightly improved yield of **3a** was achieved when an oxygen balloon was used instead of air atmosphere. However, the desired acylation product **3a** was also obtained in 14% yield when the reaction was performed under nitrogen atmosphere (Table 1, entry 2). In the absence of visible-light irradiation, no desired product was formed, and only a trace amount of **3a** was detected without photocatalyst (Table 1, entries 3 and 4). Subsequently, a number of photocatalysts, including Ru- and Ir-complexes and organic dyes (eosin Y, Mes-Acr-Me, fluorescein, methylene blue, acridine red, neutral red), solvents,

[a] *Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, P. R. China; E-mail: pphuali@126.com, leiwang@chnu.edu.cn. Tel.: +86-561-380-2069; fax: +86-561-309-0518*
[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P. R. China*
† Footnotes relating to the title and/or authors should appear here.
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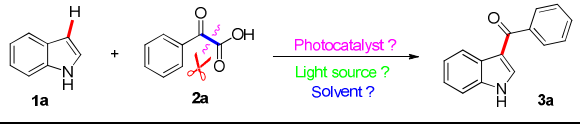
and molar ratio of substrates were examined to improve the reaction efficiency. It should be noted that the colour of light emitting diode (LED) was used to match the absorption wavelength of photocatalyst. Among the photocatalysts examined, rose bengal showed the highest reactivity, which was used widely in visible light promoted organic transformation.[19] Unfortunately, $Ru(bpy)_2Cl_2$ and *fac*-$Ir(ppy)_3$ were no longer the effective catalysts in this reaction (Table 1, entries 5–11). A series of solvents were screened, and ethanol was the most effective medium for the reaction, affording product **3a** in 71% yield (Table 1, entries 12–18). The loading of photocatalyst, the ratio of **1a** to **2a**, as well as the reaction time were optimized, which are also summarized in Table 1 (Table 1, entries 19–21).

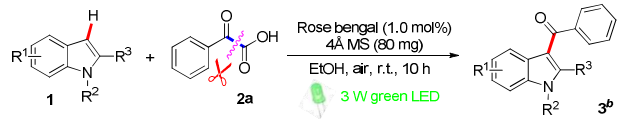
Table 1 Optimization of the reaction conditions[a]

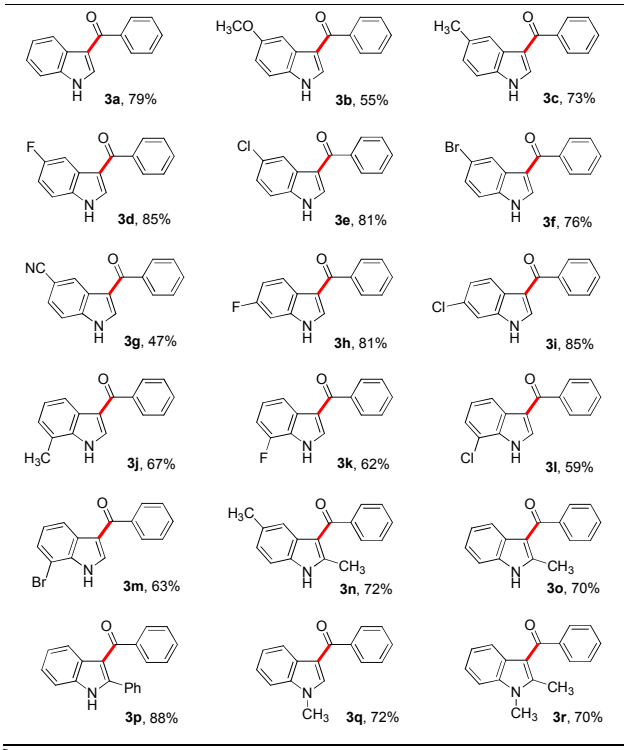


Entry	Photocatalyst	Light source	Solvent	Yield[b] (%)
1	Eosin Y	Green LED	EtOH	31[c], 51
2	Eosin Y	Green LED	EtOH	53[d], 14[e]
3	—	Green LED	EtOH	n.r.[f]
4	Eosin Y	—	EtOH	trace
5	$Ru(bpy)_2Cl_2$	Blue LED	EtOH	trace
6	*fac*-$Ir(ppy)_3$	Green LED	EtOH	trace
7	Mes-Acr-Me	Green LED	EtOH	36[g]
8	Fluorescein	Blue LED	EtOH	15
9	Methylene blue	Visible light	EtOH	40
10	Acridine red	Visible light	EtOH	45
11	Neutral red	Green LED	EtOH	49
12	Rose bengal	Green LED	EtOH	71
13	Rose bengal	Green LED	MeCN	41
14	Rose bengal	Green LED	Toluene	30
15	Rose bengal	Green LED	$CHCl_3$	43
16	Rose bengal	Green LED	$ClCH_2CH_2Cl$	40
17	Rose bengal	Green LED	DMF	n.r.
18	Rose bengal	Green LED	DMSO	n.r.
19	Rose bengal	Green LED	EtOH	35[h], 73[i], 64[j]
20	Rose bengal	Green LED	EtOH	58[k], 79[l]
21	Rose bengal	Green LED	EtOH	51[m], 80[n]

[a]Reaction conditions: **1a** (0.30 mmol), **2a** (0.45 mmol), photocatalyst (2.0 mol%), solvent (2.0 mL), 4Å molecular sieve (80 mg), r.t., air, 3W LED for 10 h. [b]Isolated yield. [c]In the absence of 4Å molecular sieve. [d]Oxygen balloon instead of air. [e]Nitrogen atmosphere. [f]n.r. = no reaction. [g]Mes-Acr-Me = 10-methyl-9-(2,4,6-trimethylphenyl)acridinium perchlorate. [h]Rose bengal (0.5 mol%) was used. [i]Rose bengal (1.0 mol%) was added. [j]Rose bengal (3.0 mol%) was used. [k]**2a** (0.30 mmol) was added. [l]**2a** (0.60 mmol) was used. [m]6 h. [n]15 h.

Table 2 The generality of indoles[a]





[a]Reaction conditions: **1** (0.30 mmol), **2a** (0.60 mmol), rose bengal (1.0 mol%), 4Å molecular sieve (80 mg), ethanol (2.0 mL), 3W green LED, air, r.t., 10 h. [b]Isolated yield.

To explore the generality of this direct acylation reaction, different substituted indoles reacted with phenylglyoxylic acid (**2a**) under the optimized conditions. The results are listed in Table 2. A variety of free (NH)-indoles and *N*-substituted indoles underwent the direct acylation with **2a** smoothly to afford the desired products in good to excellent yields. It should be noted that indoles with an electron-poor group on the phenyl rings gave the higher yields of the corresponding products, while indoles with an electron-rich group on the phenyl rings generated the low yields of the desired products in the most of cases. For example, indoles attached CH_3O and CH_3 on their 5-positions reacted with **2a** to generate the corresponding products **3b** and **3c** in 55% and 73% yields, respectively. On the other hand, the reactions of indoles having F, Cl and Br on their 5-positions or 6-positions with **2a** to afford the desired products (**3d–f**, **3h** and **3i**) in 76–85% yields. However, 5-cyanoindole reacted with **2a** to give the product **3g** in 47% yield. The indoles with both an electron-donating group (CH_3) and an electron-withdrawing group (F, Cl and Br) on their 7-positions showed a comparable reactivity in the reactions with **2a**, providing the 3-acylated indoles (**3j–m**) in a range of 59–67% yields.

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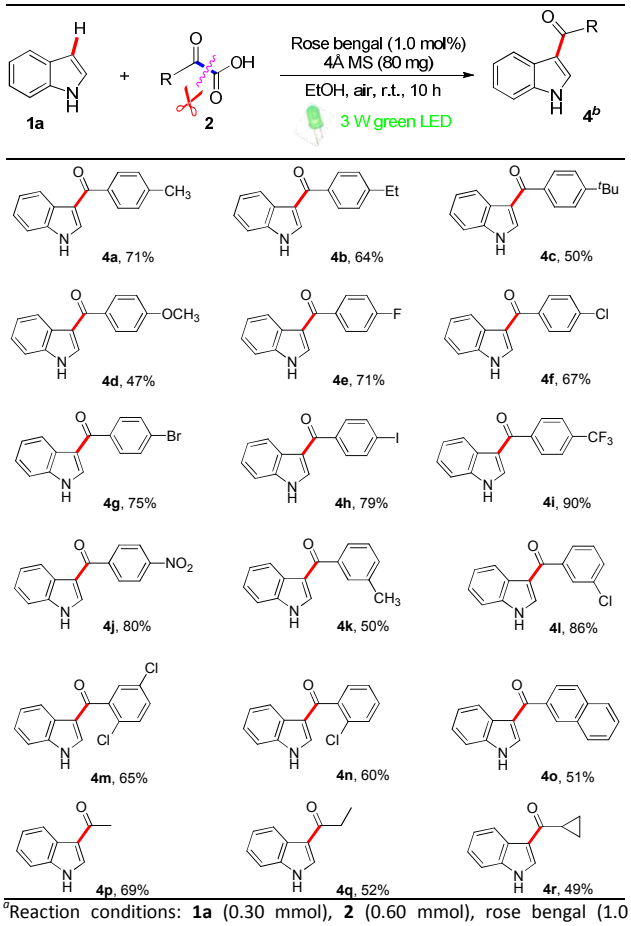
Moreover, 2,6-dimethyl-1*H*-indole, 2-methyl-1*H*-indole, 2-phenyl-1*H*-indole, *N*-methylindole and 2-methyl-*N*-methylindole could also be involved in the acylation reactions, and high yields (70–88%) of the desired products (**3n–r**) were obtained. It should be noted that when 3-methylindole and 3-cyanoindole were subjected to the reaction under the optimized reaction conditions, no reaction was occurred and the starting materials were recovered. To our disappointed, when other electron enriched heterocycles, including pyrrole, *N*-methyl pyrrole, furan, benzofuran, thiophene, thianaphthene, imidazole, benzimidazole, thiazole, benzothiazole and benzoxazole were involved in the reaction, none of the desired products was obtained. In addition, the electron enriched aromatics, such as phenol and *N,N*-dimethylaniline were also failed in this transformation.

Table 3 The scope of α-oxocarboxylic acids[a]



[a]Reaction conditions: **1a** (0.30 mmol), **2** (0.60 mmol), rose bengal (1.0 mol%), 4Å molecular sieve (80 mg), ethanol (2.0 mL), 3W green LED, air, r.t., 10 h. [b]Isolated yield.

Subsequently, the scope of α-oxocarboxylic acids was also investigated under the optimized reaction conditions. As shown in Table 3, a series of functional groups on the phenyl rings in 2-oxo-2-arylacetic acids were tolerated, leading to the desired products in good to excellent yields. It was found that electron- sufficient groups such as *p*-CH_3, *p*-C_2H_5, *p*-$^tC_4H_9$, and *p*-CH_3O showed lower reactivity, providing the products **4a–d** in 47–71% yields, while electron-deficient groups including *p*-F, *p*-Cl, *p*-Br, *p*-I, *p*-CF_3, and *p*-NO_2 exhibited good reactivity and gave high yields of the corresponding products (**4e–j**). *ortho*- and *meta*-Substituted phenylglyoxylic acids reacted with indole **1a** to provide the corresponding products (**4k–n**) in moderate to good yields. 2-Naphthyl-2-oxo-acetic acid also gave the anticipated product **4o** in 52% yield. It is worth noting that aliphatic α-oxocarboxylic acids, such as 2-oxopropanoic acid, 2-oxobutanoic acid and 2-cyclopropyl-2-oxoacetic acid, were also compatible in this reaction, giving fair yields of the desired products (**4p–r**).

To understand this transformation, a numbers of control experiments and analytical survey were conducted. In the presence of rose bengal and 3W green LED irradiation, benzoyl radical derived from **2a** was *in situ* trapped by TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy), affording the corresponding adduct **5** in 52% yield (ESI for detail). In addition, a simultaneous decarboxylation process (release of CO_2) and decarbonylation process (release of CO) was confirmed by FT-IR analysis of the resulting gas during the reaction. The ratio of CO_2/CO was found to be 30.1/1 from the result of FT-IR analysis (ESI, Figure S3 and S4), indicating the decarboxylation process in majority. Further, it is established that the photoexcited rose bengal (RB*) could react with molecular oxygen to generate singlet oxygen ($^1O_2$).[20] In order to determine the active species of oxygen involved in the present reaction, 2,2,6,6-tetramethylpiperidine (TEMP) and 5,5-dimethyl-pyrroline-*N*-oxide (DMPO) were employed to capture $^1O_2$ and $O^{2\bullet-}$, respectively. Irradiation of the ethanol solution of TEMP and rose bengal (RB) in air by green LED resulted in the formation of a strong characteristic signal of $^1O_2$ adduct with TEMP, and this signal decreased obviously as addition of phenylglyoxylic acid (**2a**) into the solution (ESI for detail). It is indicated that **2a** reacted with $^1O_2$ efficiently to consume it rapidly. However, there is no signal of $O^{2\bullet-}$ adduct with DMPO, excluding the formation of $O^{2\bullet-}$ in the reaction system.

On the basis of our observation and literature report, a plausible pathway for the reaction was proposed with indole (**1a**) and phenylglyoxylic acid (**2a**), as shown in Scheme 2. At first, RB was excited to its excited state RB* under green LED irradiation. Then, the formed RB* was interacted with molecular oxygen to generate singlet oxygen $^1O_2$ via the energy transfer,[20] along with the generation of RB to its ground state. Subsequently, the obtained $^1O_2$ reacted with **2a** and followed by a decarboxylation, leading to hydroperoxyl radical (**I**) and benzoyl radical (**II**) along with the release of CO_2. The reaction of benzoyl radical (**II**) occurred through the different transformation pathway simultaneously. In path A, benzoyl radical (**II**) added to the carbon-carbon double bond of indole (**1a**) at C3-position to afford intermediate radical (**III**) and followed by a one-electron oxidation in the presence of the formed hydroperoxyl radical (**I**) to generate intermediate **IV**, which was deprotonated (aromatization process) to give the final product 3-benzoylindole (**3a**). On the other hand (path B), in the presence of the obtained **I**, the free indole (**1a**) was oxidized to indolinium radical cation (**V**) via a singlet electron transfer (SET) process, as the related papers.[21] Subsequently, the generated benzoyl radical (**II**) added to the carbon-carbon double bond of indolinium radical cation (**V**) at C3-position to afford an intermediate **VI**, which was underwent an aromatization process to generate 3-benzoylindole (**3a**) as the final product. It should be noted that the benzoyl radical

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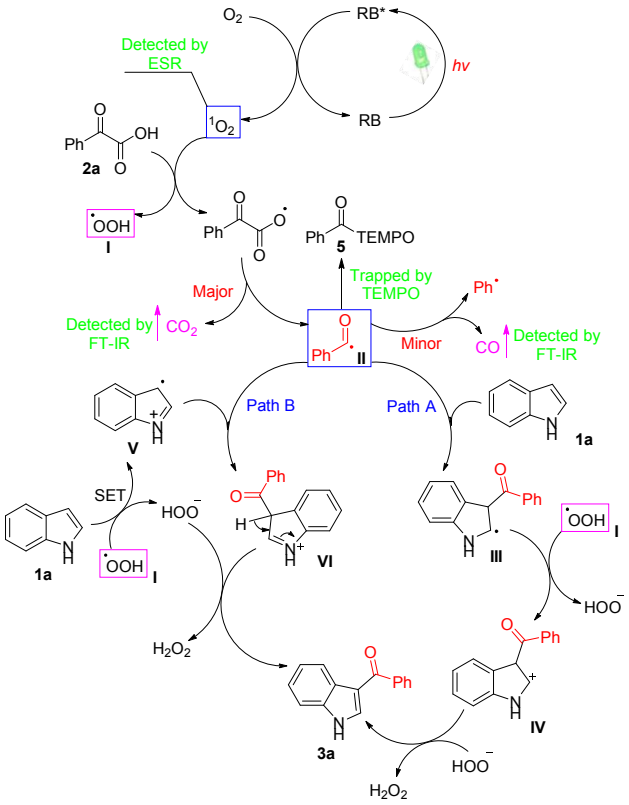
(**II**) could undergoes a decarbonylative process to form phenyl free radical and CO (CO_2/CO = 30.1/1).



Scheme 2 The proposed mechanism

Conclusions

In summary, we have developed a convenient and efficient method for the preparation of 3-acylindoles through visible-light-promoted C3-acylation of free (NH)- and *N*-substituted indoles with *α*-oxocarboxylic acids under mild reaction conditions. Comparing with the existing procedures for the synthesis of 3-acylindoles, this protocol has several advantages, such as the use of an inexpensive, commercial available, and easily degradable organic-dye (rose bengal) as photocatalyst, ethanol as a low toxicity solvent, ambient conditions (room temperature and air atmosphere) and green LED irradiation, and high regioselectivity and good functional group compatibility. Moreover, a plausible reaction mechanism has been proposed on the basis of the control experiments and ESR investigations. An in-depth mechanistic study and further attempts to other visible-light promoted organic transformations through the energy transfer pathway are currently underway in our laboratory.

Experimental section

General remarks

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometers (400 MHz or 100 MHz, respectively). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). Indoles were purchased from Energy Chemical. α-Oxocarboxylic acids were prepared according to the reported methods.[22] All the solvents and commercially available reagents were purchased from commercial suppliers. Products were purified by flash chromatography on 200–300 mesh silica gels, SiO_2.

Typical procedure for C3-acylation of indole with phenylglyoxylic acid

Indole (**1a**, 0.30 mmol), phenylglyoxylic acid (**2a**, 0.6 mmol), rose bengal (0.0030 mmol, 1.0 mol%), 4Å molecular sieve (80 mg) and ethanol (2.0 mL) was added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated using 3 W green LED at room temperature under air atmosphere for 10 h. After the reaction was completed, the reaction solution was concentrated under reduced pressure to yield crude product, which was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give the desired product **3a** in 79% yield as a pale yellow solid.

Characterization data for all products

(1*H*-Indol-3-yl)(phenyl)methanone (**3a**):[8a] Pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.07 (s, 1H), 8.27 (d, *J* = 6.4 Hz, 1H), 7.93 (s, 1H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.62–7.59 (m, 1H), 7.56–7.52 (m, 3H), 7.29–7.22 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 189.94, 140.53, 136.69, 135.69, 130.98, 128.34, 128.32, 126.22, 123.09, 121.86, 121.44, 115.00, 112.20.

(5-Methoxy-1*H*-indol-3-yl)(phenyl)methanone (**3b**):[23] Pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.96 (s, 1H), 7.87 (d, *J* = 2.8 Hz, 1H), 7.81 (d, *J* = 2.4 Hz, 1H), 7.78 (d, *J* = 6.8 Hz, 2H), 7.61–7.57 (m, 1H), 7.55–7.51 (m, 2H), 7.43 (d, *J* = 8.8 Hz, 1H), 6.91 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 189.90, 155.57, 140.65, 135.84, 131.56, 130.88, 128.34, 128.24, 127.06, 114.86, 113.00, 112.95, 103.27, 55.29.

(5-Methyl-1*H*-indol-3-yl)(phenyl)methanone (**3c**):[24] Pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.96 (s, 1H), 8.09 (s, 1H), 7.86 (s, 1H), 7.77 (d, *J* = 7.2 Hz, 2H), 7.61–7.58 (m, 1H), 7.55–7.51 (m, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 189.93, 140.66, 135.70, 135.03, 130.91, 130.73, 128.33, 128.29, 126.52, 124.59, 121.20, 114.66, 111.85, 21.33.

(5-Fluoro-1*H*-indol-3-yl)(phenyl)methanone (**3d**):[6] Pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.19 (s, 1H), 8.03 (s, 1H), 7.97 (dd, J_1 = 10.0 Hz, J_2=2.4 Hz, 1H), 7.80 (d, *J* = 7.2 Hz, 2H), 7.62–7.52 (m, 4H), 7.15–7.10 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 189.78, 158.71 (d, J = 233.2 Hz), 140.21, 137.11, 133.32, 131.12, 128.39, 128.32, 126.91 (d, *J* = 11.0 Hz), 115.07 (d, *J* = 4.5

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Hz), 113.48 (d, *J* = 9.8 Hz), 111.29 (d, *J* = 25.9 Hz), 106.31 (d, *J* = 24.5 Hz).

(5-Chloro-1*H*-indol-3-yl)(phenyl)methanone (**3e**):[6] Pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.25 (s, 1H), 8.26 (d, *J* = 1.6 Hz, 1H), 8.03 (s, 1H), 7.80 (d, *J* = 7.2 Hz, 2H), 7.63–7.59 (m, 1H), 7.57–7.52 (m, 3H), 7.30–7.27 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 189.83, 140.09, 136.93, 135.22, 131.25, 128.44, 128.37, 127.46, 126.68, 123.18, 120.60, 114.59, 113.89.

(5-Bromo-1*H*-indol-3-yl)(phenyl)methanone (**3f**):[24] Pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.25 (s, 1H), 8.41 (s, 1H), 8.01 (d, *J* = 2.8 Hz, 1H), 7.80 (d, *J* = 7.2 Hz, 2H), 7.63–7.60 (m, 1H), 7.56–7.50 (m, 3H), 7.42–7.39 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 189.79, 140.04, 136.76, 135.45, 131.25, 128.43, 128.35, 128.04, 125.72, 123.61, 114.69, 114.44, 114.31.

3-Benzoyl-1*H*-indole-5-carbonitrile (**3g**):[6] Pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.54 (s, 1H), 8.62 (s, 1H), 8.18 (s, 1H), 7.82 (d, *J* = 7.2 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.65–7.61 (m, 2H), 7.57–7.54 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 189.79, 139.69, 138.57, 137.80, 131.53, 128.51, 128.45, 126.51, 126.09, 126.03, 120.12, 115.11, 113.76, 104.16.

(6-Fluoro-1*H*-indol-3-yl)(phenyl)methanone (**3h**): Pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.12 (s, 1H), 8.27–8.24 (m, 1H), 7.95 (s, 1H), 7.80 (d, *J* = 7.2 Hz, 2H), 7.62–7.52 (m, 3H), 7.33–7.31 (m, 1H), 7.13–7.08 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 189.82, 159.40(d, J = 235.7 HZ), 158.23, 140.21, 136.79 (d, *J* = 12.5 Hz), 136.31 (d, *J* = 2.4 Hz), 131.11, 128.36, 128.32, 122.91 (d, *J* = 0.9 Hz), 122.62 (d, *J* = 9.9 Hz), 114.95, 110.17 (d, *J* = 23.6 Hz), 98.43 (d, *J* = 25.6 Hz). HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{15}H_{10}FNO$: 240.0825, Found: 240.0826.

(6-Chloro-1*H*-indol-3-yl)(phenyl)methanone (**3i**): Pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.16 (s, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.99 (s, 1H), 7.80 (d, *J* = 7.2 Hz, 2H), 7.63–7.52 (m, 4H), 7.28–7.25 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 189.81, 140.11, 137.17, 136.54, 131.19, 128.39, 128.34, 127.62, 125.02, 122.75, 122.15, 114.93, 111.94. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{15}H_{10}ClNO$: 256.0524, Found: 256.0524.

(7-Methyl-1*H*-indol-3-yl)(phenyl)methanone (**3j**):[23] White solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.08 (s, 1H), 8.09 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 2.0 Hz, 1H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.62–7.59 (m, 1H), 7.56–7.52 (m, 2H), 7.16–7.13 (m, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 190.01, 140.58, 136.14, 135.19, 130.99, 128.36, 128.34, 126.04, 123.69, 122.08, 121.50, 119.01, 115.40, 16.66.

(7-Fluoro-1*H*-indol-3-yl)(phenyl)methanone (**3k**): Pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.64 (s, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.97 (s, 1H), 7.81 (d, *J* = 7.2 Hz, 2H), 7.63–7.59 (m, 1H), 7.56–7.52 (m, 2H), 7.24–7.19 (m, 1H), 7.14–7.09 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 189.93 (d, *J* = 1.4 Hz), 150.32, 147.89, 140.14, 136.09, 131.28, 129.96 (d, *J* = 4.7 Hz), 128.42 (d, *J* = 0.8 Hz), 124.55 (d, *J* = 13.2 Hz), 122.48 (d, *J* = 6.1 Hz), 117.60 (d, *J* = 3.5 Hz), 115.80 (d, *J* = 1.8 Hz), 108.13 (d, *J* = 15.6 Hz). HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{15}H_{10}FNO$: 240.0819, Found: 240.0819.

(7-Chloro-1*H*-indol-3-yl)(phenyl)methanone (**3l**): Pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.49 (s, 1H), 8.23 (d, *J* = 7.6 Hz, 1H), 7.93 (s, 1H), 7.81 (d, *J* = 6.8 Hz, 2H), 7.64–7.60 (m, 1H), 7.57–7.53 (m, 2H), 7.36 (d, *J* = 7.6 Hz, 1H) 7.27–7.23 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 189.90, 140.02, 136.06, 133.59, 131.34, 128.44, 128.41, 128.16, 123.00, 122.74, 120.42, 116.53, 115.91. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{15}H_{10}ClNO$: 256.0524, Found: 256.0527.

(7-Bromo-1*H*-indol-3-yl)(phenyl)methanone (**3m**): Pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.34 (s, 1H), 8.27 (d, *J* = 7.6 Hz, 1H), 7.89 (s, 1H), 7.81 (d, *J* = 6.8 Hz, 2H), 7.64–7.60 (m, 1H), 7.57–7.49 (m, 3H), 7.22–7.18 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 189.93, 140.00, 136.00, 135.09, 131.33, 128.44, 128.38, 127.92, 125.82, 123.36, 120.88, 115.93, 104.66. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{15}H_{10}BrNO$: 300.0019, Found: 300.0023.

(2,5-Dimethyl-1*H*-indol-3-yl)(phenyl)methanone (**3n**): Pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.81 (s, 1H), 7.61–7.56 (m, 3H), 7.51–7.48 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.22 (s, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 2.33 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 191.66, 144.27, 141.78, 133.29, 130.85, 129.54, 128.25, 127.93, 127.59, 123.20, 119.95, 112.22, 110.82, 21.31, 14.20. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{17}H_{15}NO$: 250.1226, Found: 250.1232.

(2-Methyl-1*H*-indol-3-yl)(phenyl)methanone (**3o**):[24] Pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.95 (s, 1H), 7.62–7.56 (m, 3H), 7.52–7.48 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.14–7.10 (m, 1H), 7.03–6.99 (m, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 191.71, 144.40, 141.68, 134.97, 130.97, 128.31, 127.98, 127.28, 121.79, 120.91, 120.00, 112.49, 111.22, 14.15.

Phenyl(2-phenyl-1*H*-indol-3-yl)methanone (**3p**):[25] White solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.20 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.54–7.52 (m, 3H), 7.40–7.34 (m, 3H), 7.26–7.14 (m, 7H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 192.13, 144.02, 139.82, 135.83, 131.57, 131.30, 129.50, 129.02, 128.42, 128.17, 127.99, 127.74, 122.82, 121.36, 120.56, 112.17, 111.83.

(1-Methyl-1*H*-indol-3-yl)(phenyl)methanone (**3q**):[8a] Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (d, *J* = 7.6 Hz, 1H), 8.00 (s, 1H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.63–7.53 (m, 4H), 7.36–7.27 (m, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.42, 140.50, 139.39, 137.33, 130.97, 128.35, 128.28, 126.65, 123.15, 122.22, 121.58, 113.82, 110.61, 33.08.

(1,2-Dimethyl-1*H*-indol-3-yl)(phenyl)methanone (**3r**):[8a] White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (d, *J* = 7.2 Hz, 2H), 7.56–7.52 (m, 1H), 7.46–7.42 (m, 2H), 7.32–7.29 (m, 2H), 7.22–7.18 (m, 1H), 7.08–7.04 (m, 1H), 3.37 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.82, 144.64, 141.48, 136.55, 131.37, 129.00, 128.18, 127.07, 122.00, 121.39, 120.95, 113.62, 109.09, 29.63, 12.47.

(1*H*-Indol-3-yl)(*p*-tolyl)methanone (**4a**):[7b] Yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.04 (s, 1H), 8.27–8.25 (m, 1H), 7.94 (d, *J* = 2.8 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.54–7.52 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.28–7.22 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 189.65, 140.96, 137.81, 136.65, 135.27, 128.86, 128.50, 126.30, 122.99, 121.73, 121.44, 115.08, 112.15, 20.98.

(4-Ethylphenyl)(1*H*-indol-3-yl)methanone (**4b**): Yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.05 (s, 1H), 8.28–8.26 (m, 1H), 7.95 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.54–7.52 (m, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.28–7.22 (m, 2H), 2.69 (q, J_1 = 15.2 Hz, J_2 = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 189.64, 147.09, 138.06, 136.65, 135.32, 128.58, 127.68, 126.31, 122.99, 121.73, 121.45, 115.06, 112.14, 28.06, 15.25. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{17}H_{15}NO$: 250.1226, Found: 250.1226.

(4-(*tert*-Butyl)phenyl)(1*H*-indol-3-yl)methanone (**4c**): Yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.03 (s, 1H), 8.28–8.26 (m, 1H), 7.96 (d, *J* = 2.4 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.56–7.51 (m, 3H), 7.28–7.21 (m, 2H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 189.58, 153.83, 137.80, 136.64, 135.41, 128.34, 126.29, 125.10, 123.00, 121.74, 121.45, 115.02, 112.13, 34.60, 30.94. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{19}H_{19}NO$: 278.1539, Found: 278.1532.

(1*H*-Indol-3-yl)(4-methoxyphenyl)methanone (**4d**):[23] Yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.01 (s, 1H), 8.24 (d, *J* = 7.2 Hz, 1H), 7.95 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.27–7.20 (m, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 188.74, 161.69, 136.60, 134.78, 132.95, 130.56, 126.41, 122.92, 121.62, 121.44, 115.06, 113.62, 112.12, 55.35.

(4-Fluorophenyl)(1*H*-indol-3-yl)methanone (**4e**):[7b] White solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.07 (s, 1H), 8.26 (d, *J* = 6.8 Hz, 1H), 7.95 (s, 1H), 7.89–7.86 (m, 2H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.37–7.32 (m, 2H), 7.29–7.22 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 188.48, 163.75 (d, *J* = 247.0 Hz), 137.00 (d, *J* = 3.0 Hz), 136.70, 135.64, 130.96 (d, *J* = 8.8 Hz), 126.23, 123.12, 121.88, 121.41, 115.25 (d, *J* = 21.4 Hz), 114.87, 112.21.

(4-Chlorophenyl)(1*H*-indol-3-yl)methanone (**4f**):[23] White solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.15 (s, 1H), 8.30–8.28 (m, 1H), 7.98 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.58–7.54 (m, 3H), 7.30–7.24 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 188.62, 139.15, 136.76, 135.88, 135.83, 130.21, 128.42, 126.20, 123.21, 122.00, 121.46, 114.87, 112.26.

(4-Bromophenyl)(1*H*-indol-3-yl)methanone (**4g**):[24] Yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.14 (s, 1H), 8.27–8.25 (m, 1H), 7.98 (s, 1H), 7.73 (s, 4H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.29–7.23 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 188.70, 139.47, 136.72, 135.91, 131.35, 130.39, 126.14, 124.67, 123.19, 121.98, 121.40, 114.78, 112.24.

(1*H*-Indol-3-yl)(4-iodophenyl)methanone (**4h**): Pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.12 (s, 1H), 8.26–8.24 (m, 1H), 7.97 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.53–7.51 (m, 1H), 7.29–7.22 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 188.96, 139.76, 137.20, 136.69, 135.86, 130.26, 126.11, 123.16, 121.95, 121.38, 114.74, 112.22, 98.49. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{15}H_{10}INO$: 347.9880, Found: 347.9890.

(1*H*-Indol-3-yl)(4-(trifluoromethyl)phenyl)methanone (**4i**): Pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.21 (s, 1H), 8.30–8.28 (m, 1H), 7.99–7.96 (m, 3H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.56–7.54 (m, 1H), 7.31–7.25 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 188.70, 144.08 (q, J_1 = 2.72 Hz, J_2 = 1.36 Hz), 136.81, 136.51, 130.74 (q, J_1 = 63.3 Hz, J_2 = 31.6 Hz), 128.99, 126.05, 125.32 (q, J_1 = 7.5 Hz, J_2 = 3.7 Hz), 124.00 (q, J_1 = 541.5 Hz, J_2 = 270.8 Hz), 123.33, 122.15, 121.42, 114.82, 112.31. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{16}H_{10}F_3NO$: 290.0787, Found: 290.0791.

(1*H*-Indol-3-yl)(4-nitrophenyl)methanone (**4j**):[24] Pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.25 (s, 1H), 8.35 (d, *J* = 8.8 Hz, 2H), 8.29–8.27 (m, 1H), 8.01–7.98 (m, 3H), 7.56–7.54 (m, 1H), 7.31–7.25 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 188.14, 148.63, 145.94, 136.83, 136.77, 129.50, 125.95, 123.57, 123.47, 122.30, 121.42, 114.84, 112.38.

(1*H*-Indol-3-yl)(*m*-tolyl)methanone (**4k**):[7b] Pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.03 (s, 1H), 8.27–8.25 (m, 1H), 7.93 (d, *J* = 2.8 Hz, 1H), 7.59–7.57 (m, 2H), 7.54–7.52 (m, 1H), 7.44–7.41 (m, 2H), 7.28–7.22 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 190.09, 140.59, 137.67, 136.69, 135.63, 131.59, 128.76, 128.19, 126.24, 125.55, 123.06, 121.82, 121.45, 115.09, 112.19, 20.95.

(3-Chlorophenyl)(1*H*-indol-3-yl)methanone (**4l**): Pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.14 (s, 1H), 8.27–8.25 (m, 1H), 7.99 (s, 1H), 7.77–7.74 (m, 2H), 7.67–7.65 (m, 1H), 7.58–7.54 (m, 2H), 7.30–7.24 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 188.21, 142.43, 136.76, 136.19, 133.23, 130.72, 130.30, 127.84, 126.97, 126.10, 123.24, 122.04, 121.39, 114.71, 112.28. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{15}H_{15}ClNO$: 256.0524, Found: 256.0525.

(2,5-Dichlorophenyl)(1*H*-indol-3-yl)methanone (**4m**): Pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.21 (s, 1H), 8.19–8.17 (m, 1H), 7.77 (s, 1H), 7.63–7.60 (m, 3H), 7.54–7.52 (m, 1H), 7.30–7.25 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 186.39, 141.76, 137.39, 137.06, 131.80, 131.41, 130.43, 128.40, 128.22, 125.30, 123.42, 122.36, 121.11, 115.64, 112.51. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{15}H_9Cl_2NO$: 290.0134, Found: 290.0135.

(2-Chlorophenyl)(1*H*-indol-3-yl)methanone (**4n**): Pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.13 (s, 1H), 8.18–8.16 (m, 1H), 7.65 (d, *J* = 3.2 Hz, 1H), 7.58–7.44 (m, 5H), 7.30–7.24 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 188.20, 140.28, 137.01, 136.83, 130.65, 129.72, 129.61, 128.66, 127.02, 125.40, 123.32, 122.25, 121.14, 116.05, 112.49. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{15}H_{15}ClNO$: 256.0524, Found: 256.0525.

(1*H*-Indol-3-yl)(naphthalen-2-yl)methanone (**4o**): Pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.10 (s, 1H), 8.42 (s, 1H), 8.33–8.31 (m, 1H), 8.12 (d, *J* = 7.6 Hz, 1H), 8.07–8.01 (m, 3H), 7.90

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(d, *J* = 8.0 Hz, 1H), 7.66–7.55 (m, 3H), 7.31–7.25 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 189.86, 137.75, 136.74, 135.90, 134.12, 132.16, 129.15, 128.86, 128.01, 127.55, 126.60, 126.31, 125.24, 123.10, 121.87, 121.47, 115.22, 112.21. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{19}H_{13}NO$: 272.1070, Found: 272.1071.

1-(1*H*-Indol-3-yl)ethanone (**4p**):[7b] Yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.92 (s, 1H), 8.30–8.30 (m, 1H), 8.21 (d, *J* = 7.2 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.23–7.16 (m, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 192.61, 136.65, 134.25, 125.29, 122.68, 121.61, 121.31, 116.81, 112.04, 27.21.

1-(1*H*-Indol-3-yl)propan-1-one (**4q**): Yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ:11.89 (s, 1H), 8.30 (s, 1H), 8.21 (d, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.22–7.15 (m, 2H), 2.87 (q, J_1 = 7.2 Hz, J_2 = 14.4 Hz, 2H), 1.12 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ:195.82, 136.60, 133.39, 125.41, 122.58, 121.52, 121.52, 116.00, 111.99, 31.84, 9.06. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{11}H_{11}NO$: 174.0913, Found: 256.0914.

Cyclopropyl(1*H*-indol-3-yl)methanone (**4r**): Yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.96 (s, 1H), 8.50 (d, *J* = 2.0 Hz, 1H), 8.22 (d, *J* = 7.2 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.23–7.15 (m, 2H), 2.74–2.68 (m, 1H), 0.98 (s, 2H), 0.87–0.85 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 194.19, 136.60, 133.66, 125.24, 122.68, 121.54, 121.40, 117.12, 111.97, 17.11, 9.05. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{12}H_{11}NO$: 186.0913, Found: 186.0914.

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(18) X-ray single crystal structure of **3a** (CCDC: 1449407).

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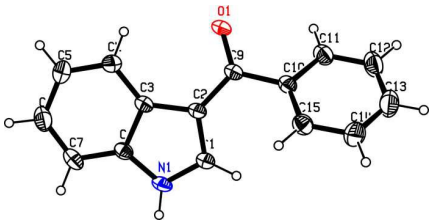

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Supporting Information

Decarboxylative/Decarbonylative C3-acylation of indoles via photocatalysis: a simple and efficient route to 3-acylindoles

Qing Shi,[a] Pinhua Li,*[a] Xianjin Zhu,[a] and Lei Wang*[a,b]

[a] Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, P. R. China, Tel: +86-561-3802-069 Fax: +86-561-3090-518 E-mail: leiwang@chnu.edu.cn

[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P. R. China

Table of Contents for Supporting Information

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1. Reaction mechanism study

1.1 Determination of singlet oxygen

In order to determine the active species of oxygen involved in the present reaction, 2,2,6,6-tetramethylpiperidine (TEMP) and 5,5-dimethyl-pyrroline-*N*-oxide (DMPO) were employed to capture $^1O_2$ and $O^{2\bullet-}$, respectively. Irradiation of the ethanol solution of TEMP and rose bengal (RB) in air by green LED resulted in the formation of a strong characteristic signal of $^1O_2$ adduct with TEMP (Figure S1b *vs* S1a), and this signal decreased obviously as addition of phenylglyoxylic acid (**2a**) into the solution (Figure S1c). It is indicated that **2a** reacted with $^1O_2$ efficiently to consume it rapidly. However, there is no signal of $O^{2\bullet-}$ adduct with DMPO, excluding the formation of $O^{2\bullet-}$ in the reaction system.

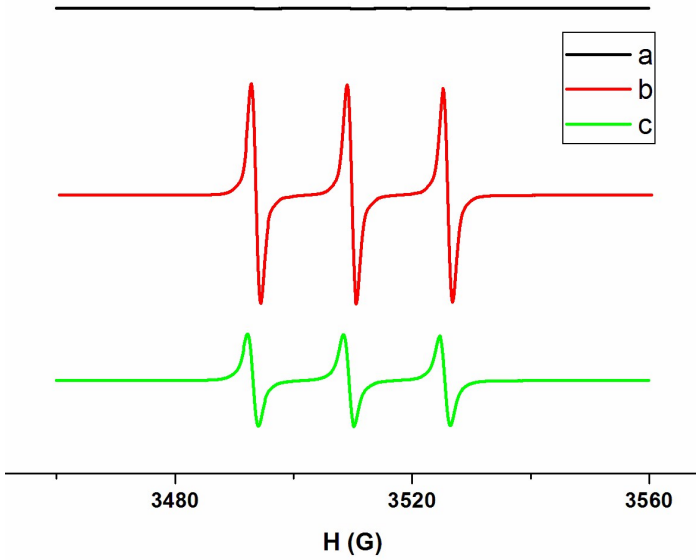

Figure S1. Electron spin resonance (ESR) spectra: (a) a solution of TEMP (0.12 mol/L), rose bengal (1.0 mol%) in air-saturated C_2H_5OH without green LED irradiation; (b) a solution of TEMP (0.12 M), rose bengal (1.0 mol%) in air-saturated C_2H_5OH with green LED irradiation for 30 s; (c) a solution of TEMP (0.12 mol/L), rose bengal (1.0 mol%) in air-saturated C_2H_5OH with green LED irradiation for 30 s, then with addition of **2a** (1.5×10^{-2} mol/L).

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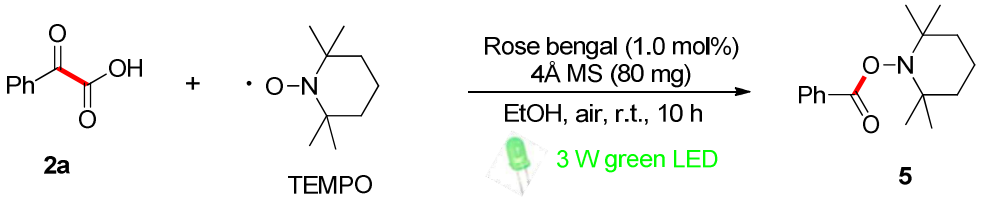
1.2 Benzoyl radical-trapping experiment



Phenylglyoxylic acid (**2a**, 0.30 mmol), 2,2,6,6-tetramethyl-1-oxylpiperidine (TEMPO, 1.0 mmol), rose bengal (RB, 0.003 mmol), 4Å molecular sieve (80 mg) were dissolved in ethanol (2.0 mL) in an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated using green LED at room temperature under air atmosphere for 10 h. After the reaction was carried out, concentrated under reduced pressure to yield the crude product, which was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1 to 10:1), affording the adduct **5** as a colorless solid in 52% yield. 2,2,6,6-Tetramethylpiperidin-1-yl benzoate (**5**) (See: H. Tan, H. Li, W. Ji, L. Wang, *Angew. Chem., Int. Ed.*, 2015, **54**, 8374): White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08 (d, J = 7.6 Hz, 2H), 7.58–7.55 (m, 1H), 7.47–7.44 (m, 2H), 1.81–1.75 (m, 2H), 1.70–1.67 (m, 1H), 1.63–1.57 (m, 2H), 1.47–1.44 (m, 1H), 1.28 (s, 6H), 1.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.15, 132.64, 129.61, 129.36, 128.26, 60.21, 38.92, 31.80, 20.68, 16.84. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{16}H_{24}NO_2$: 262.1802, Found: 262.1805. The following Figure S2 is the HRMS analysis of reaction mixture.

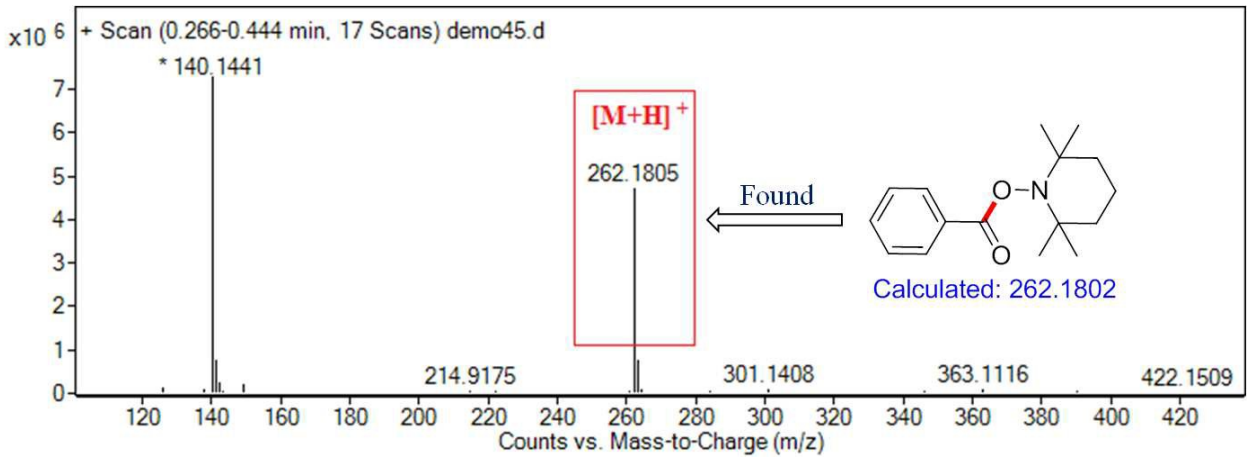


Figure S2. Analysis of reaction mixture by HRMS

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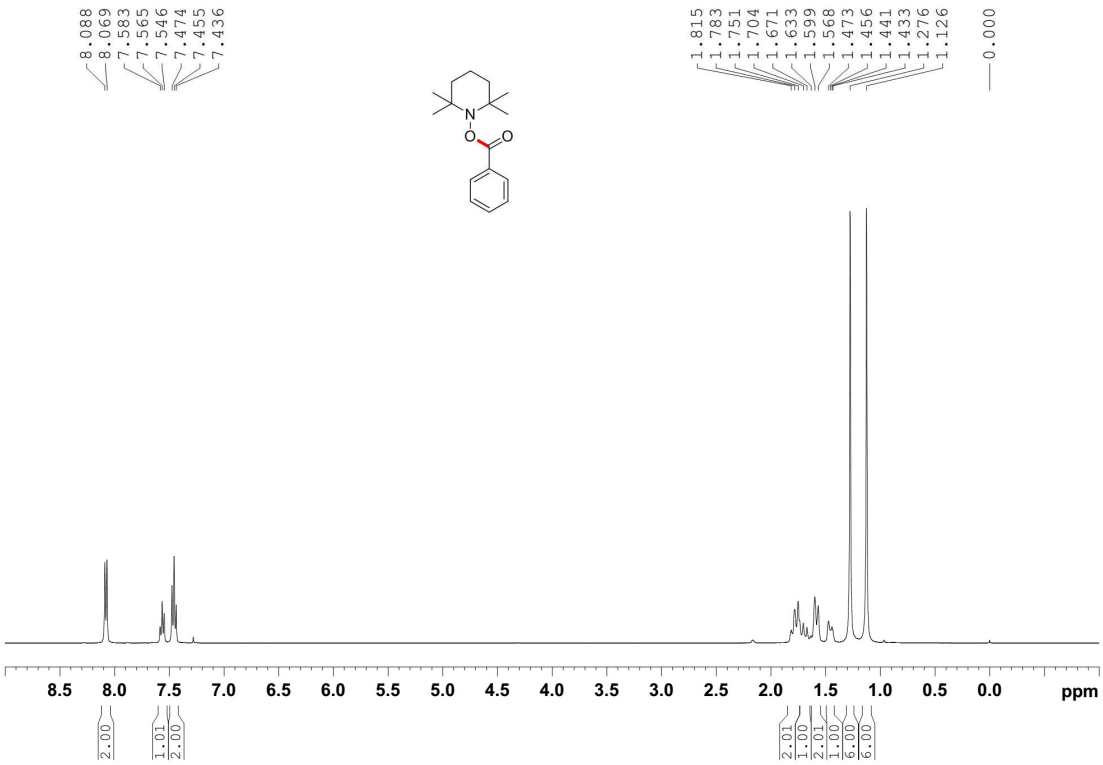

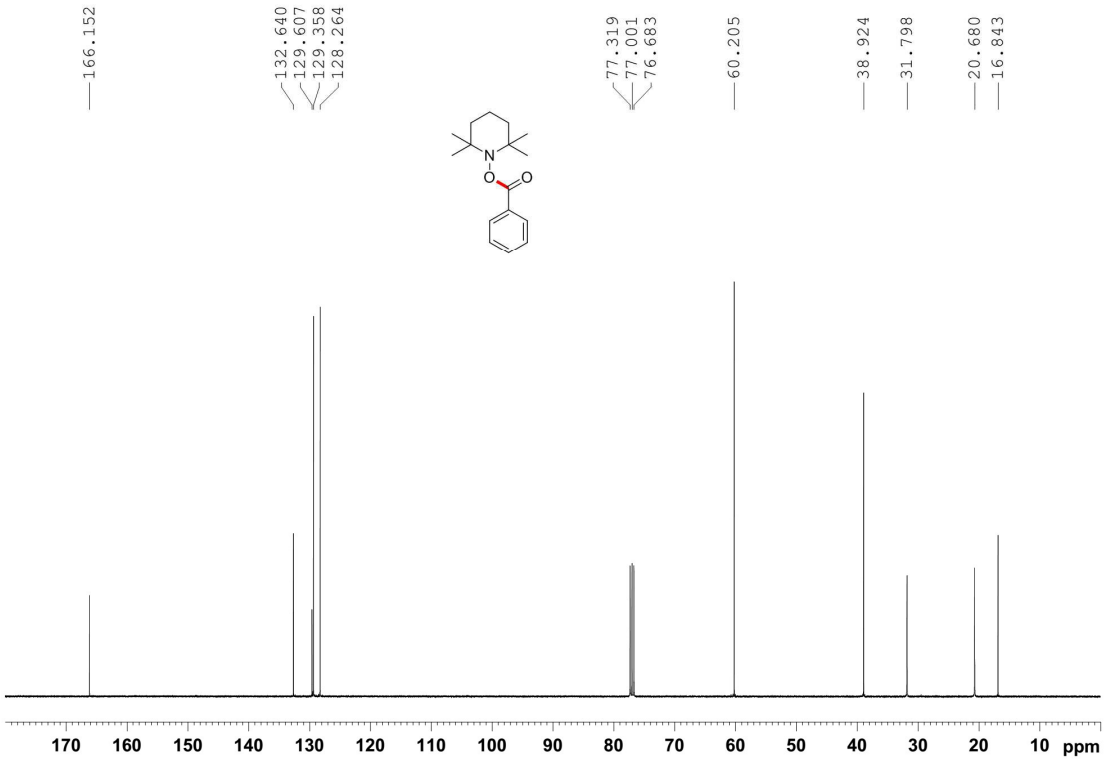

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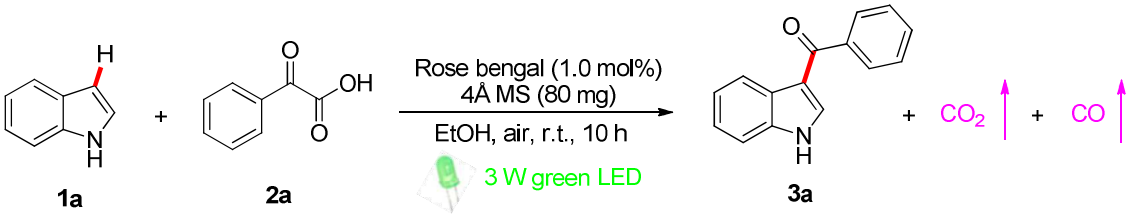
1.3 Determination of CO_2 and CO during the reaction by FT-IR



An Schlenk tube equipped with a magnetic stirrer bar was charged with indole (**1a**, 0.30 mmol), phenylglyoxylic acid (**2a**, 0.6 mmol), rose bengal (1.0 mol%), 4Å molecular sieve (80 mg) and ethanol (2.0 mL). The reaction vessel was exposed to green LED at room temperature for 10 h. After completion of the reaction, the resulting gas from the reaction system was directly determined by a Bruker Tensor 27 FT-IR, and the concentration of CO_2 and CO was found to be 2839.70, and 94.27 ppm (Figure S3 and Figure S4), respectively.

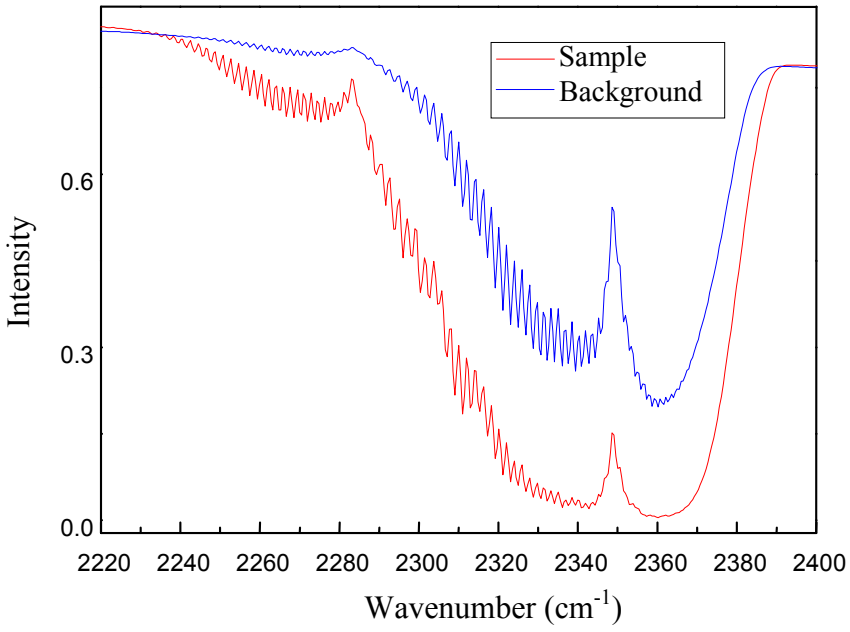


Figure S3. FT-IR analysis of the formation of CO_2 in the reaction

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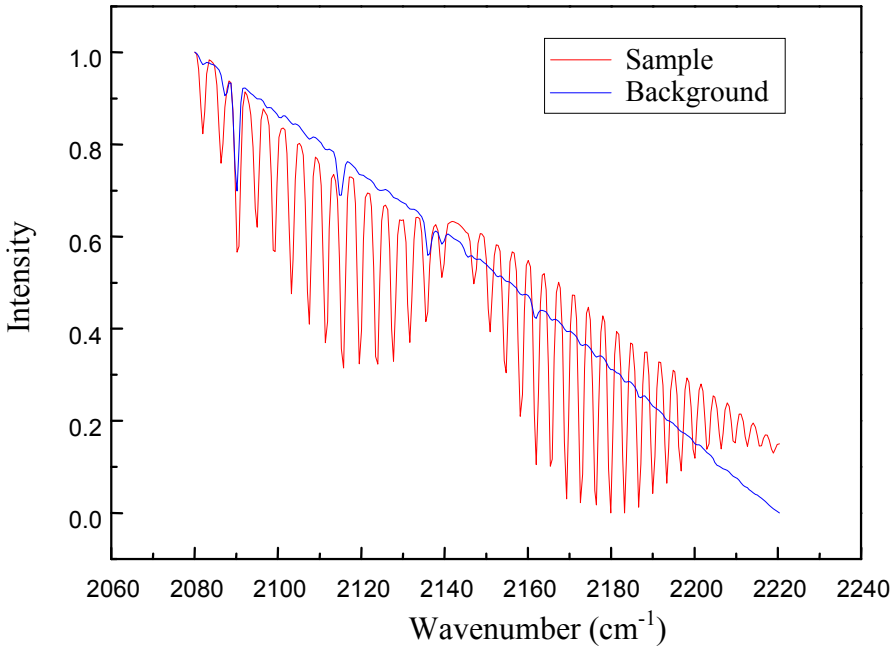

Figure S4. FT-IR analysis of the formation of CO in the reaction

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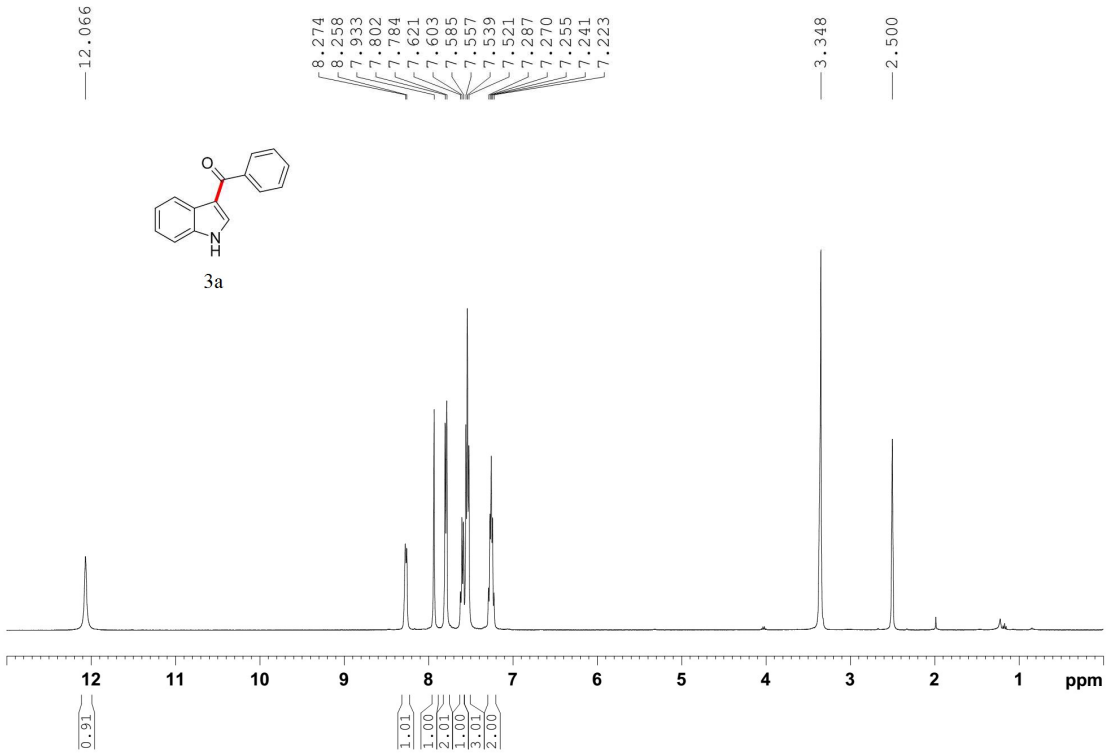
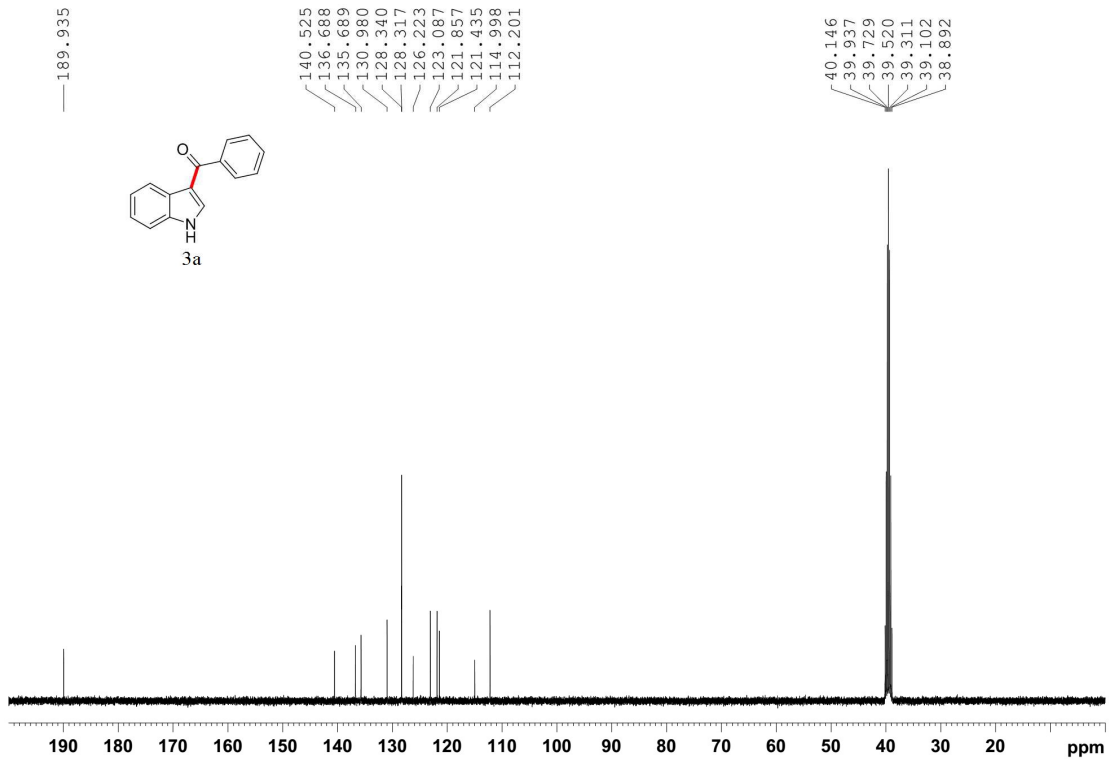
2. ^{1}H and ^{13}C NMR spectra of the products





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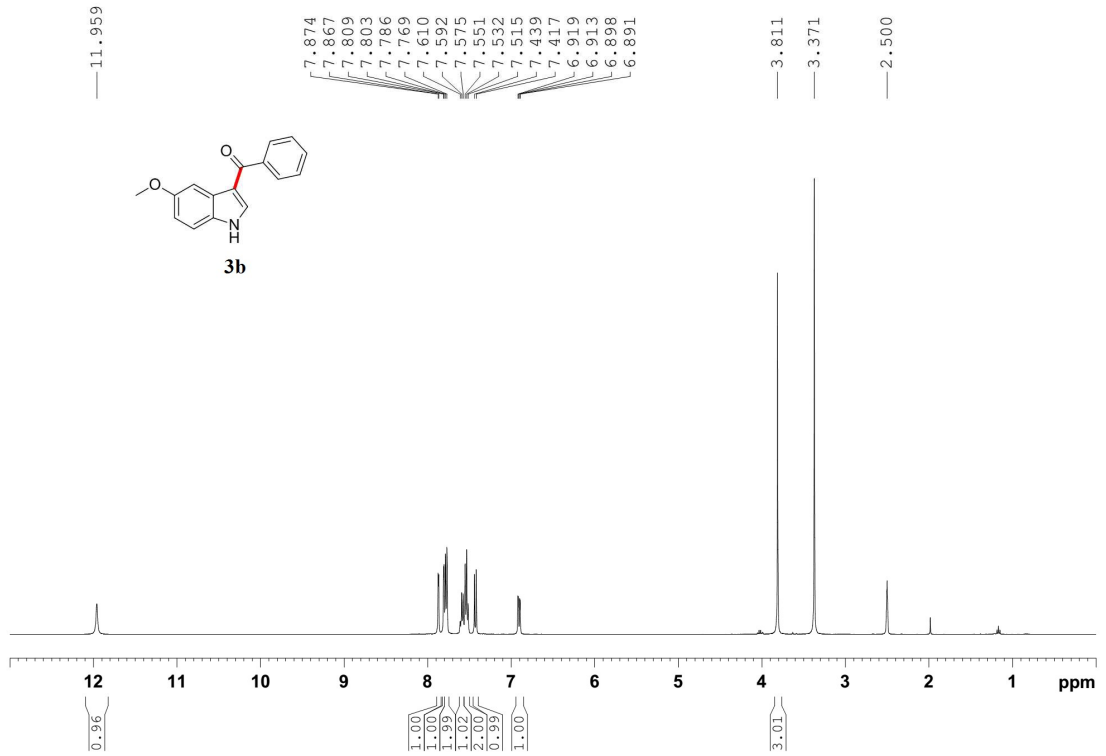

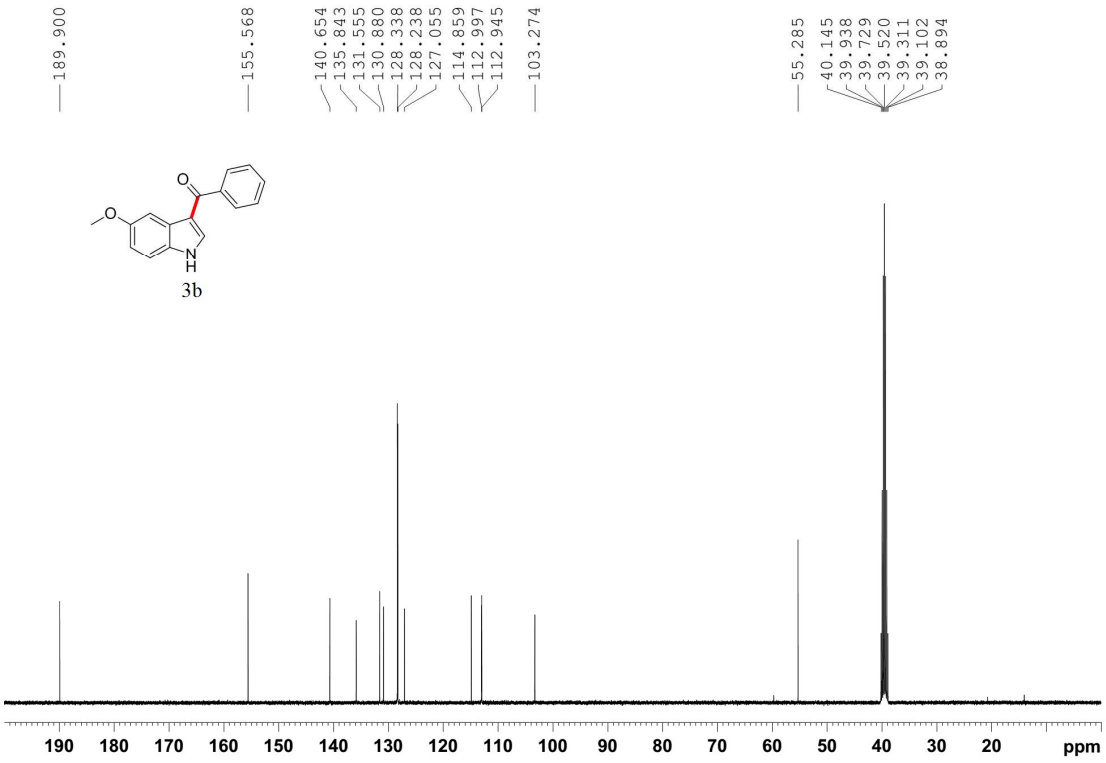

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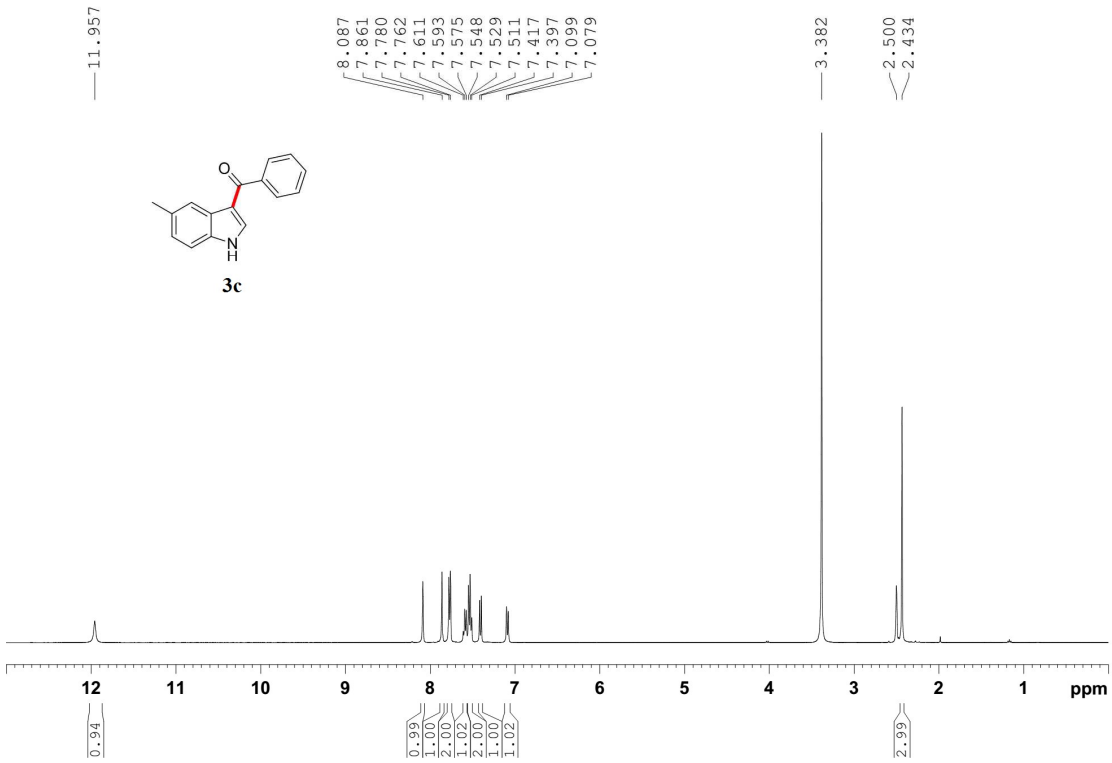

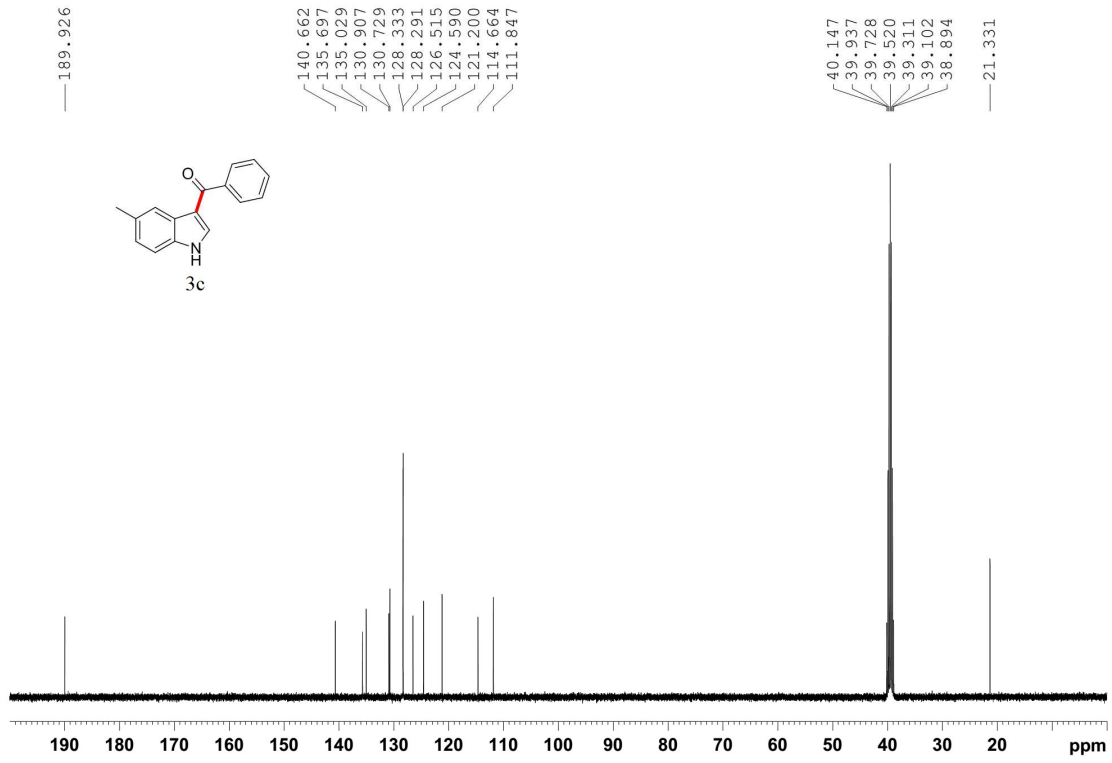

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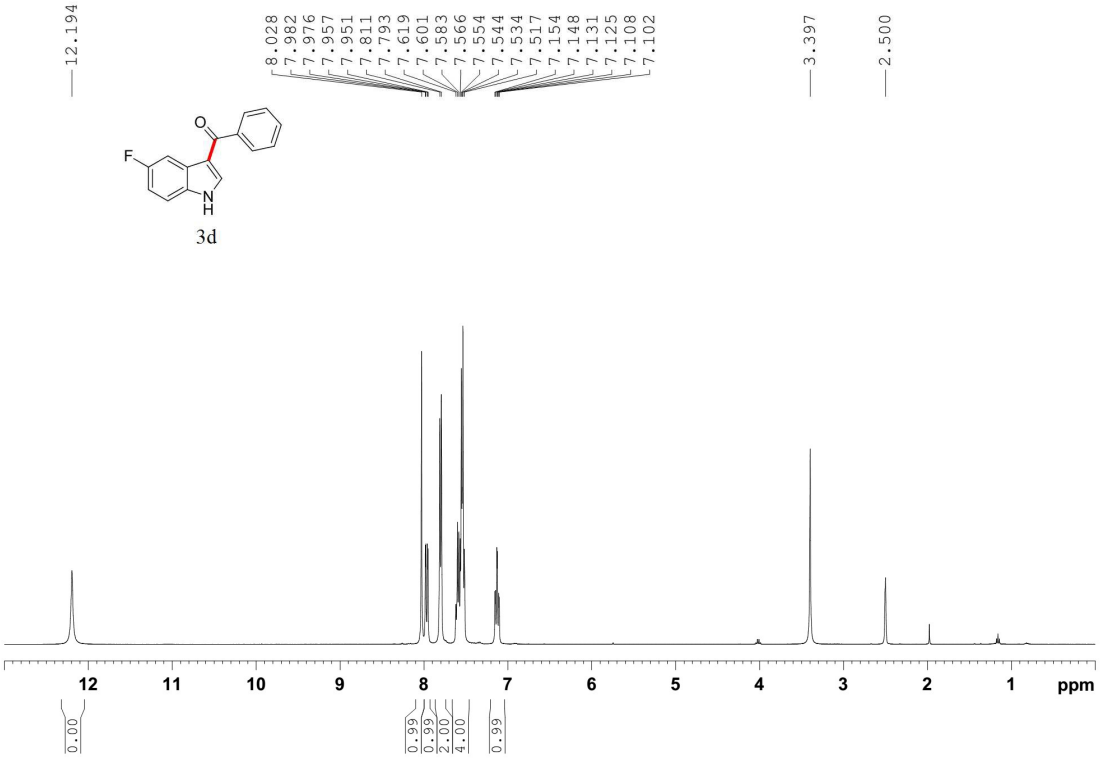

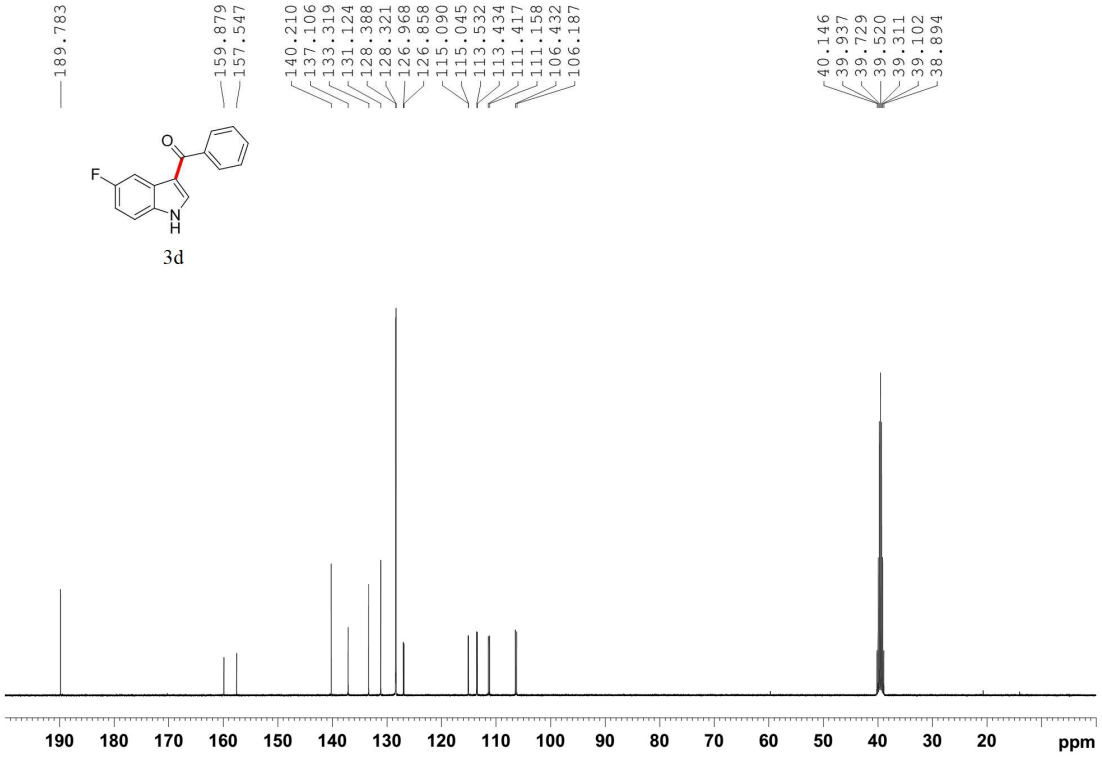

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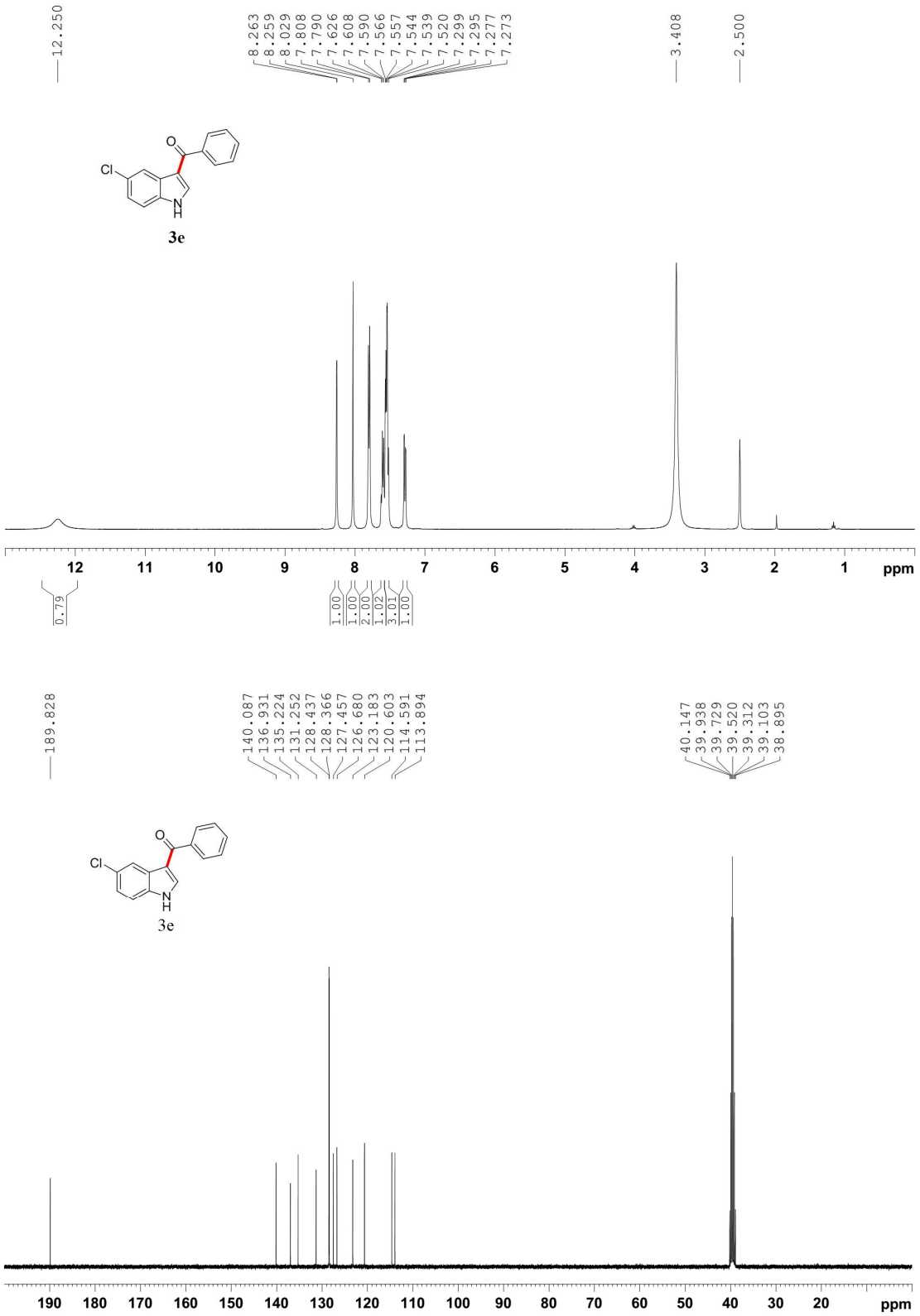

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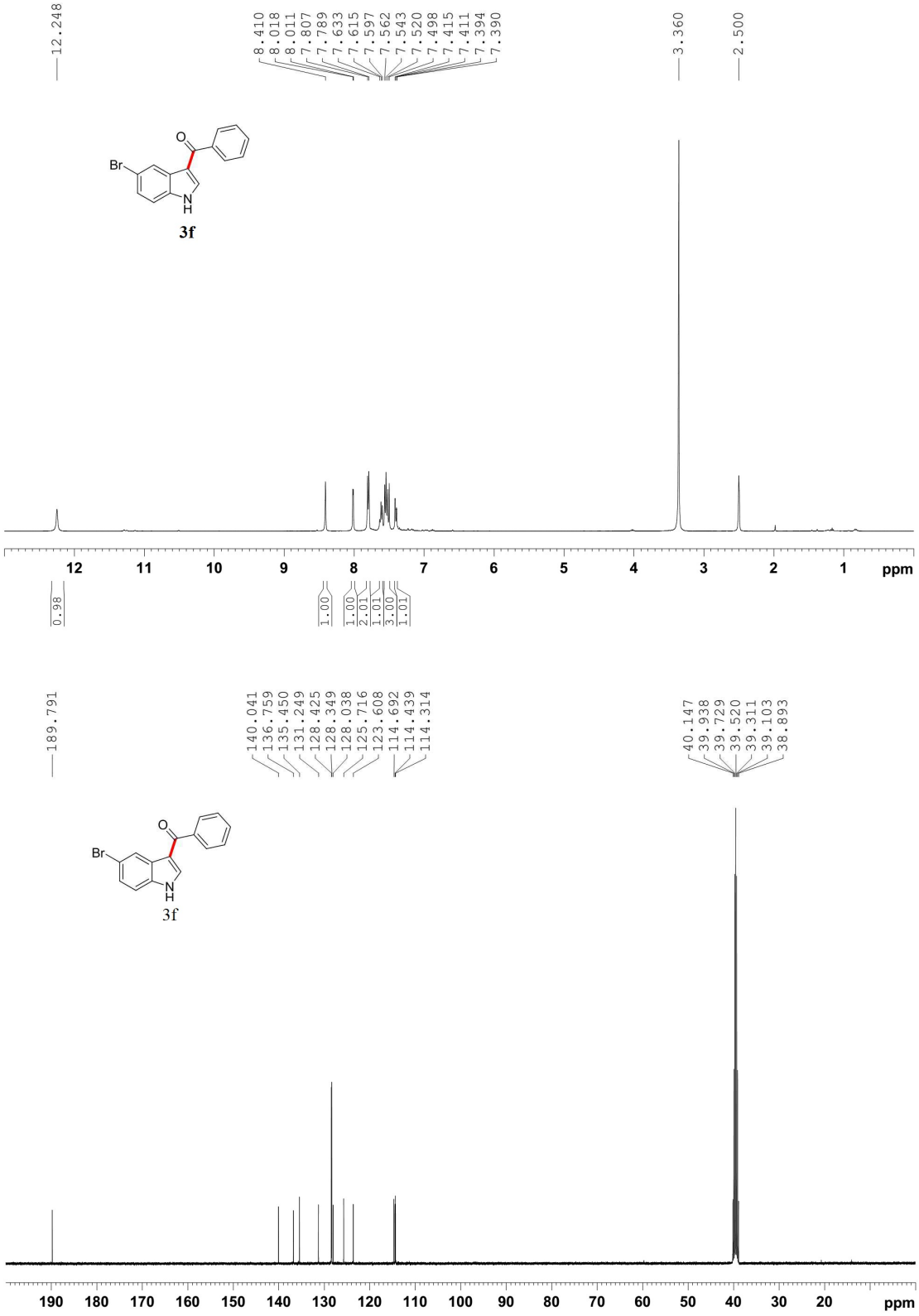

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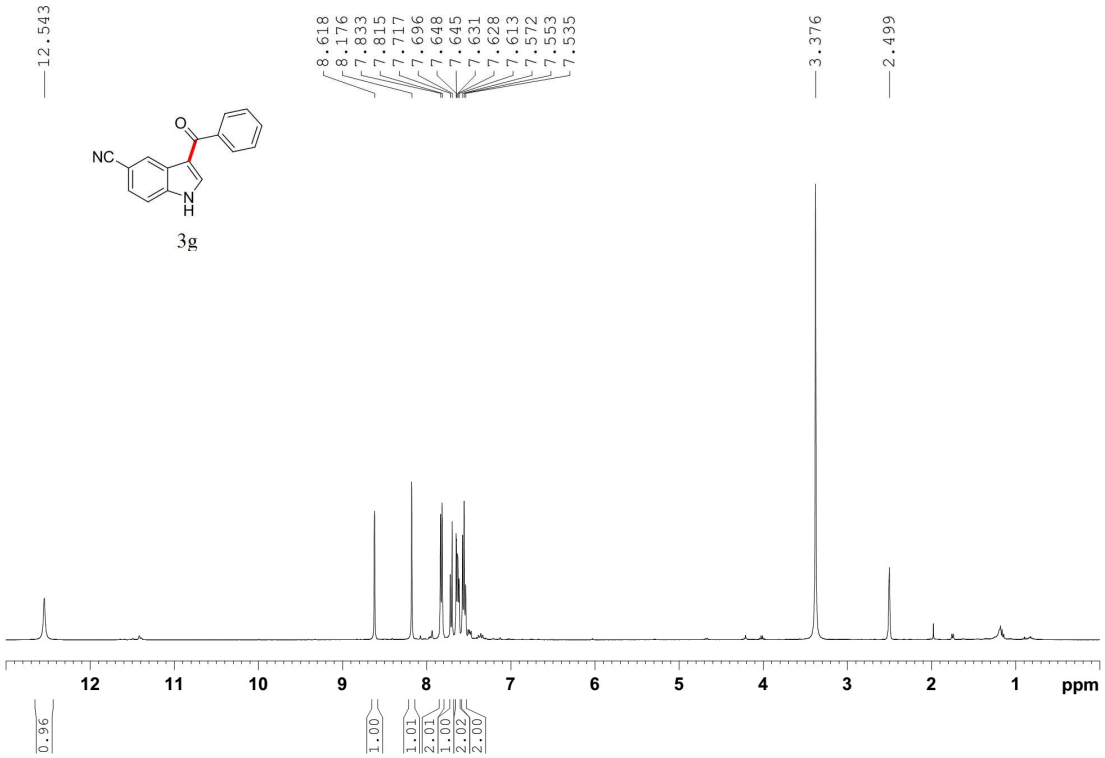

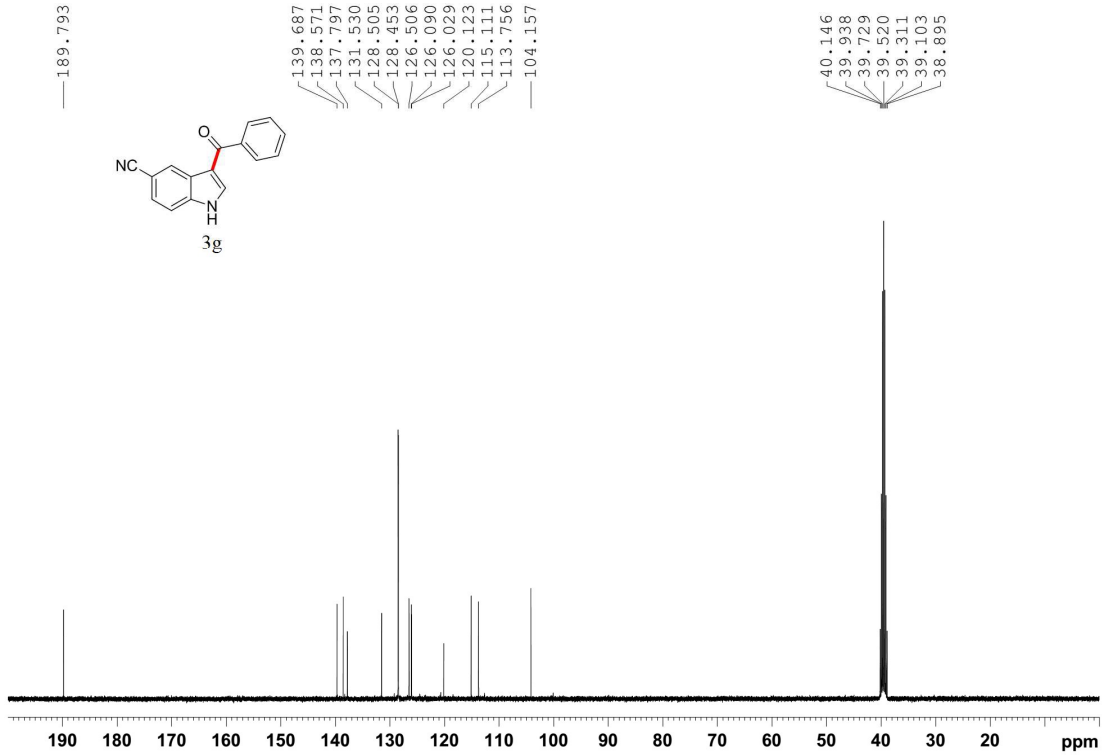

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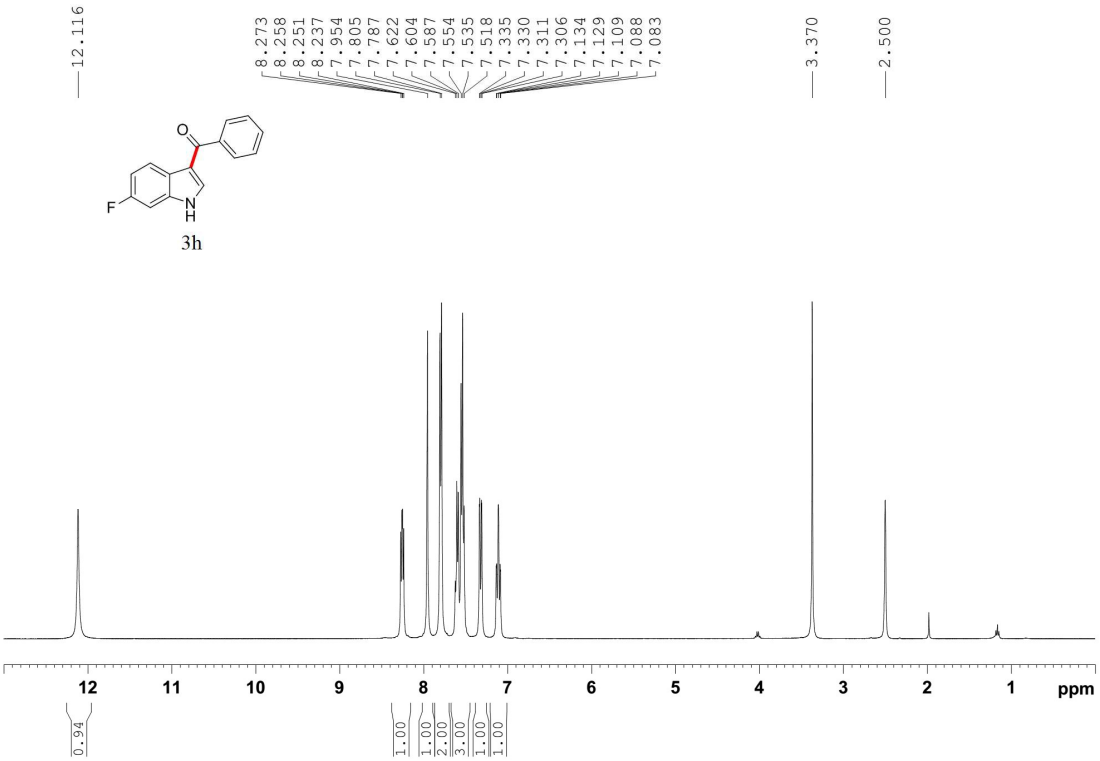

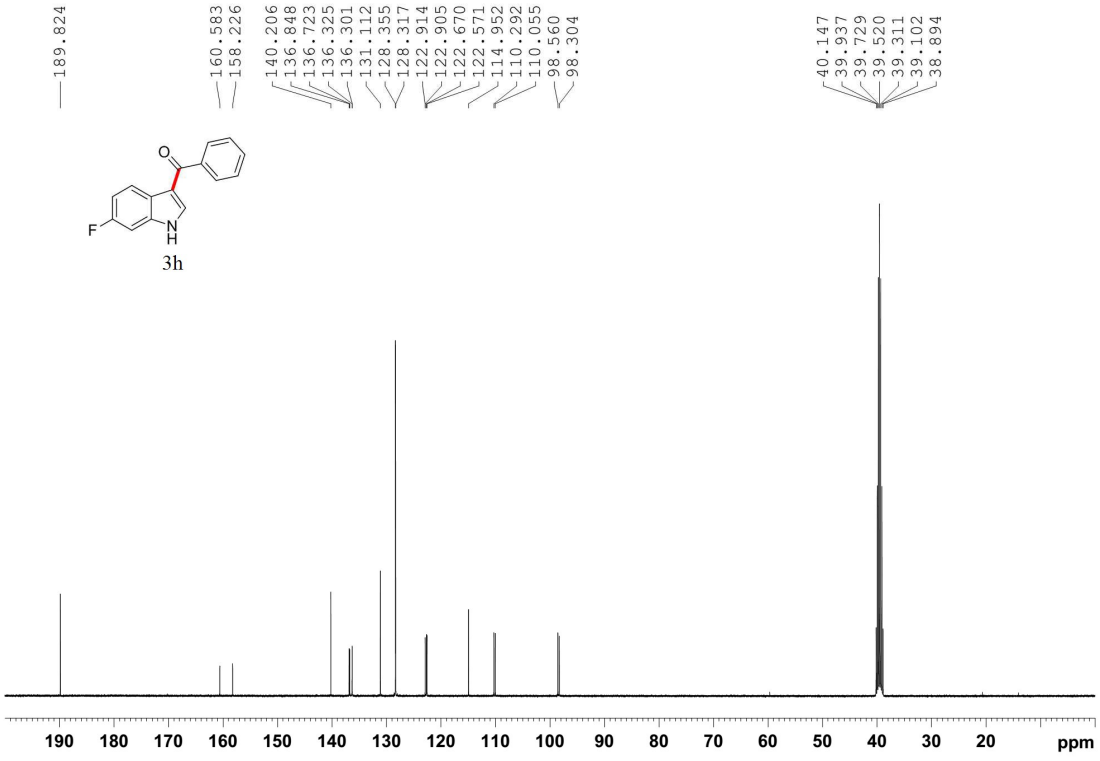

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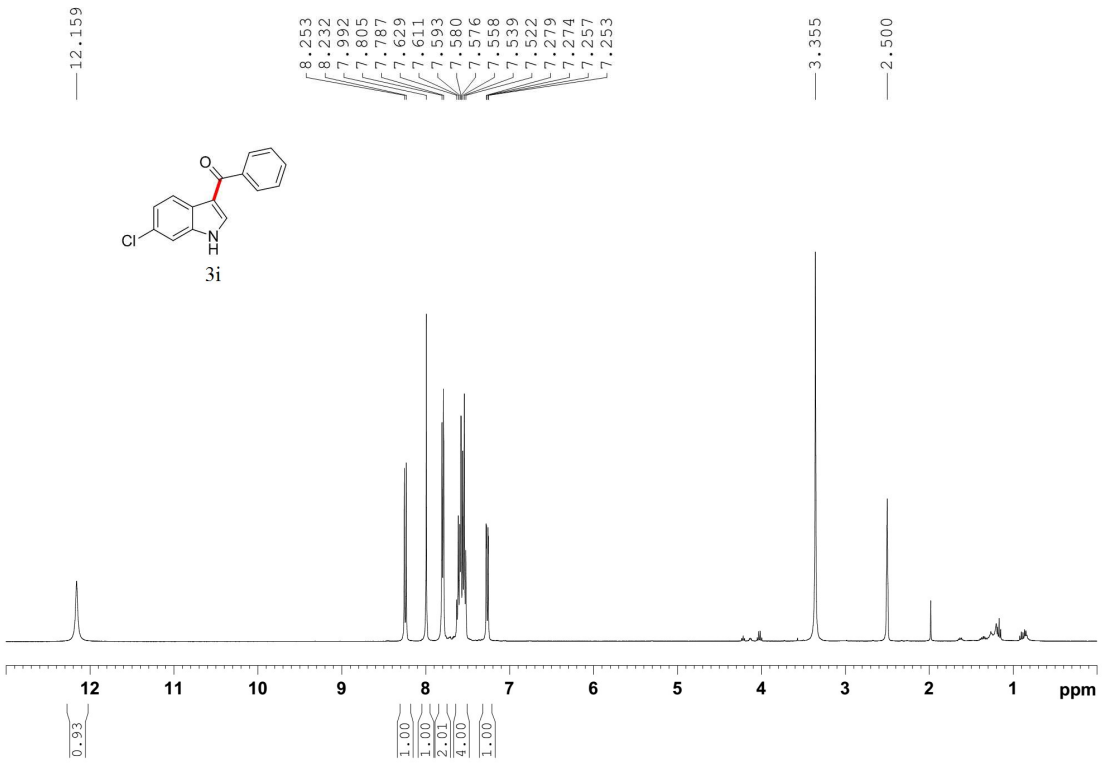

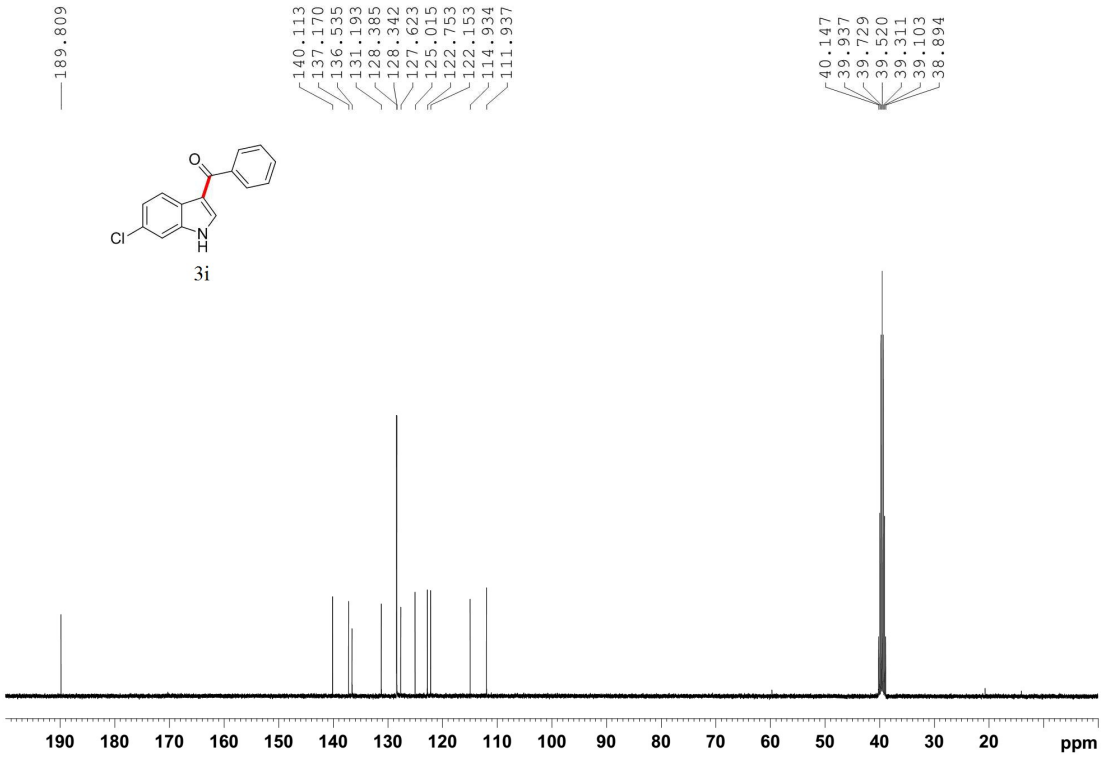

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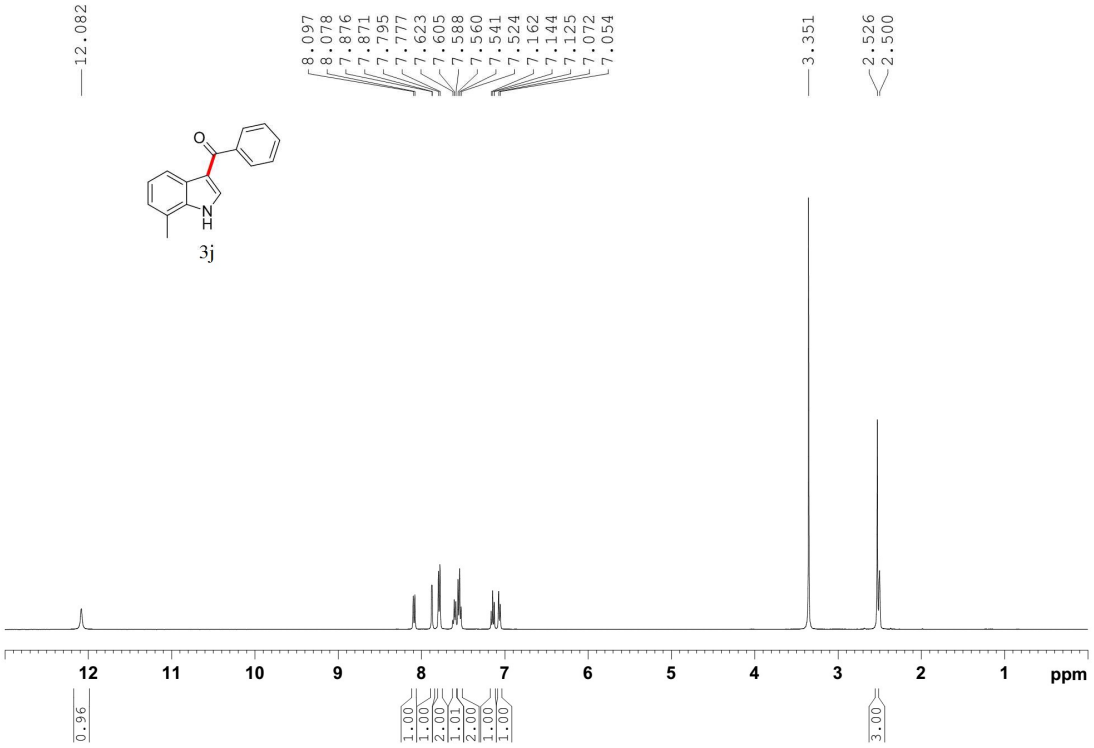

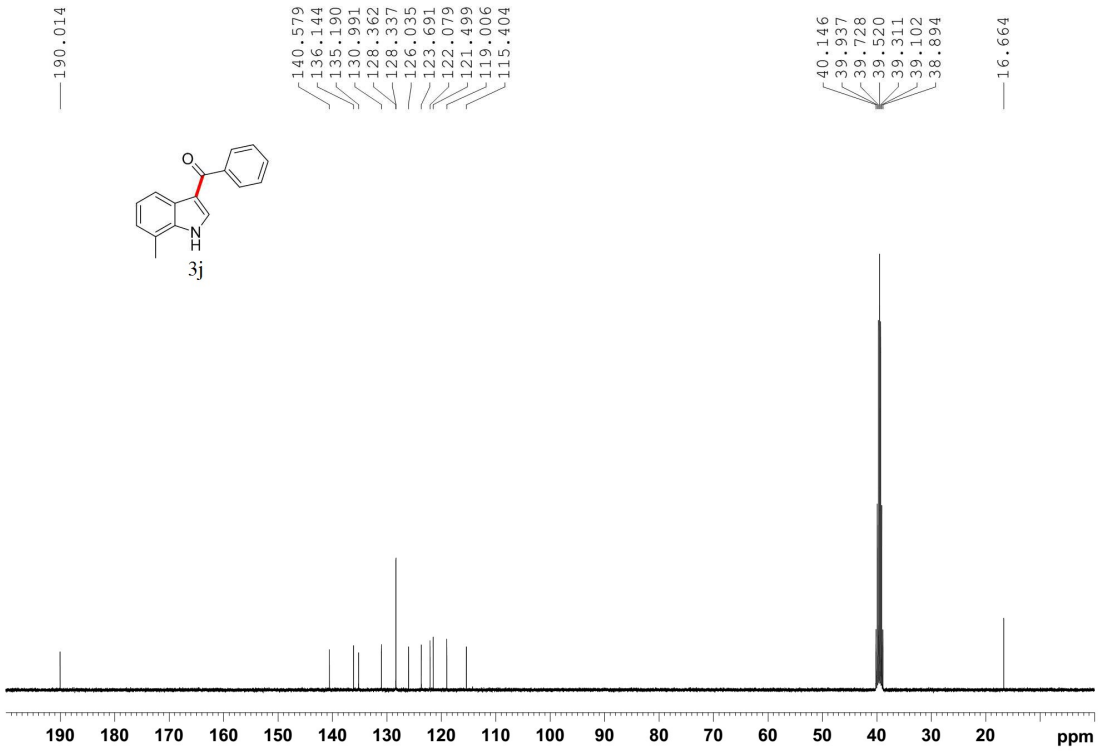

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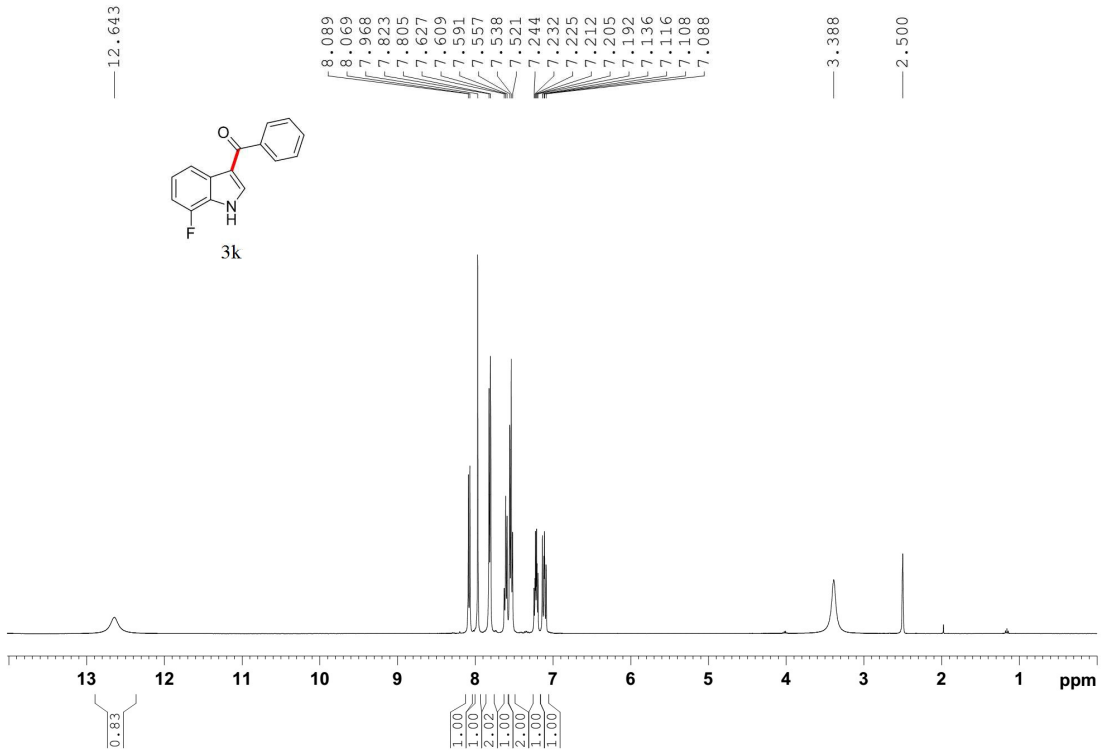

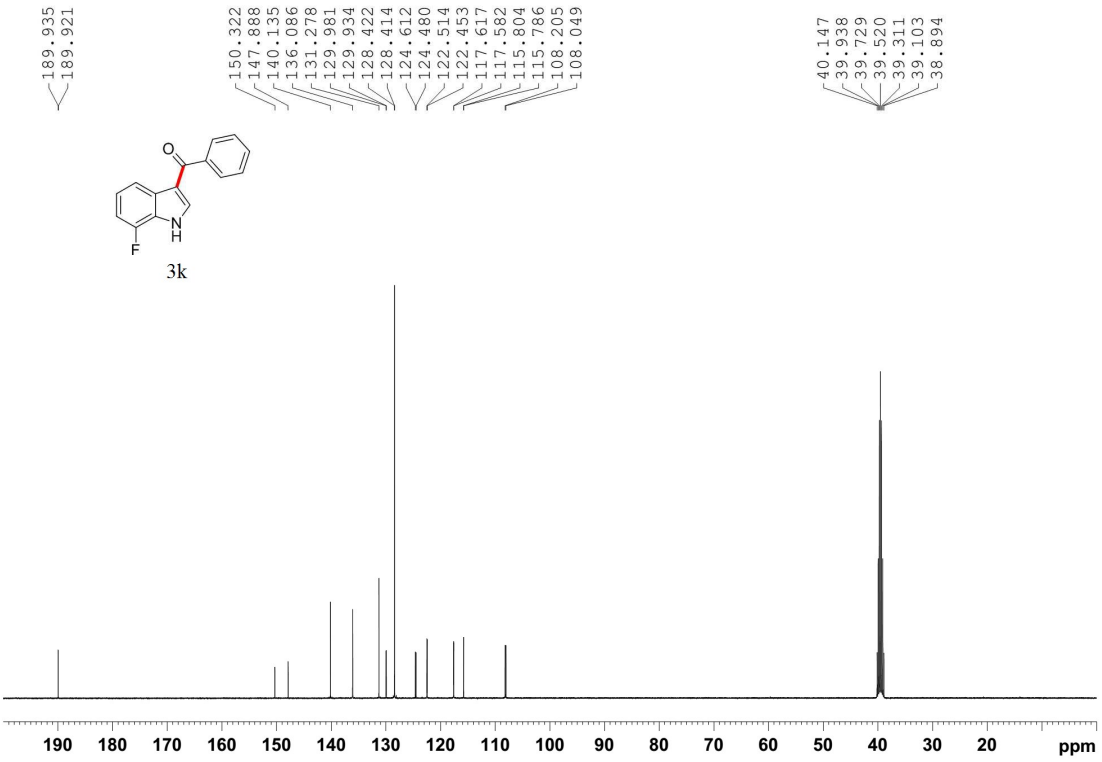

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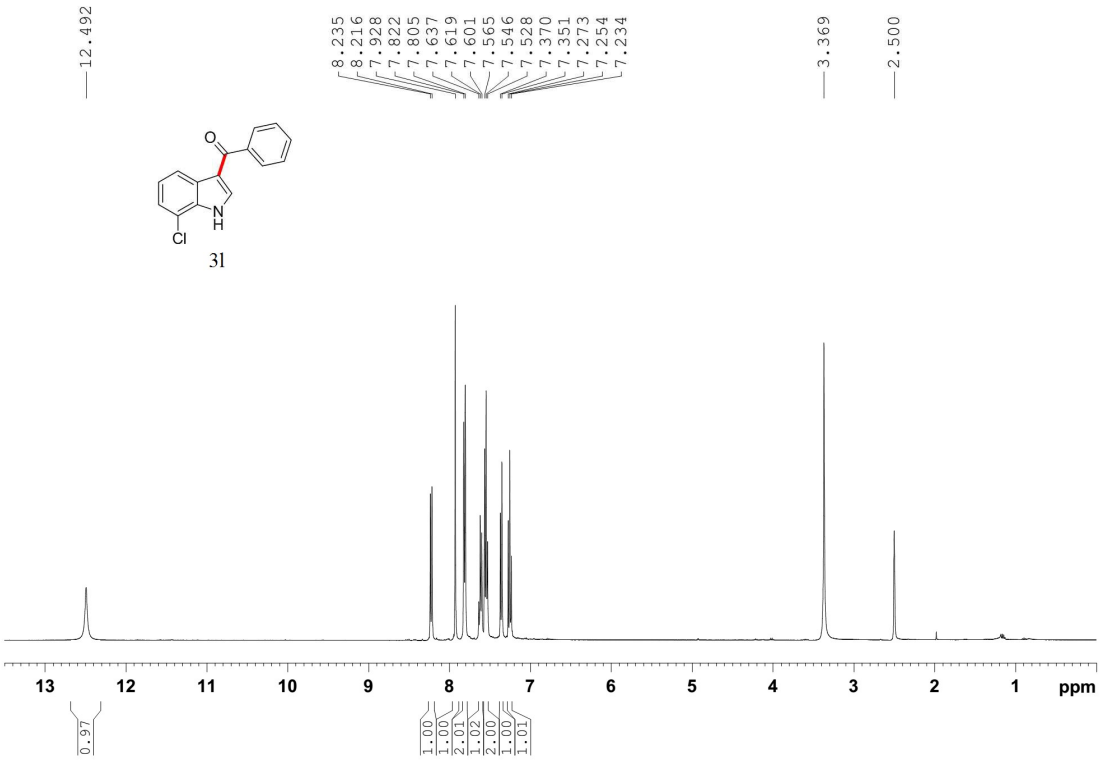

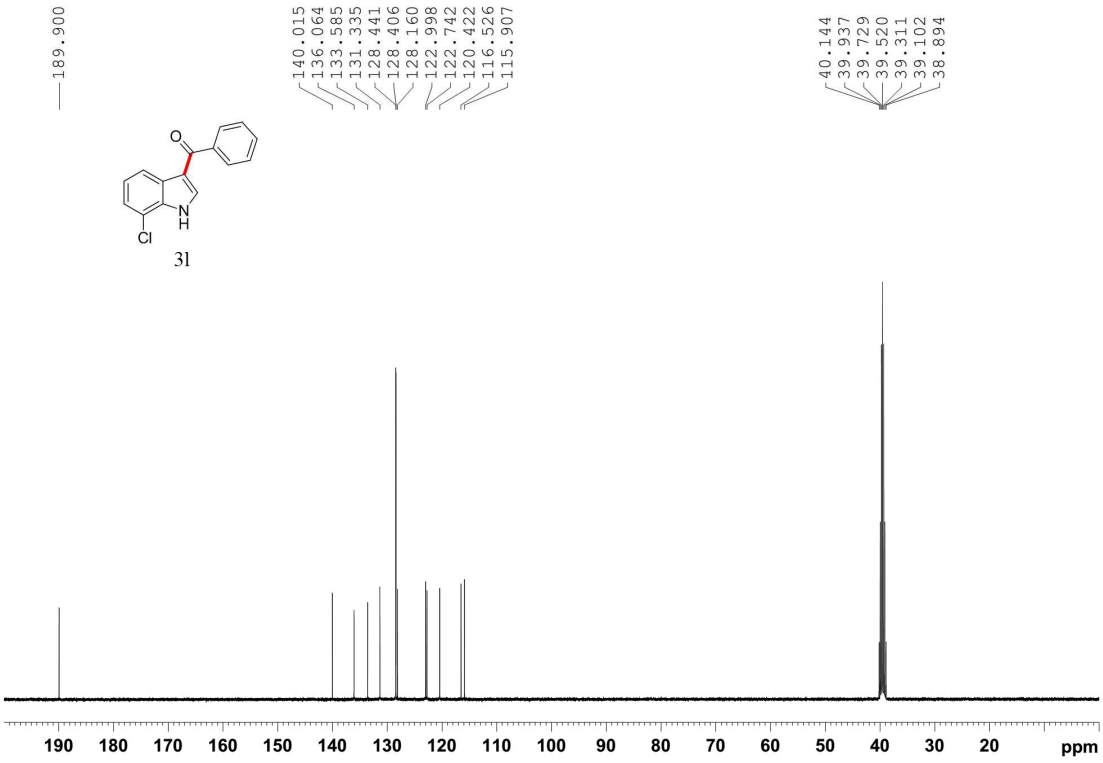

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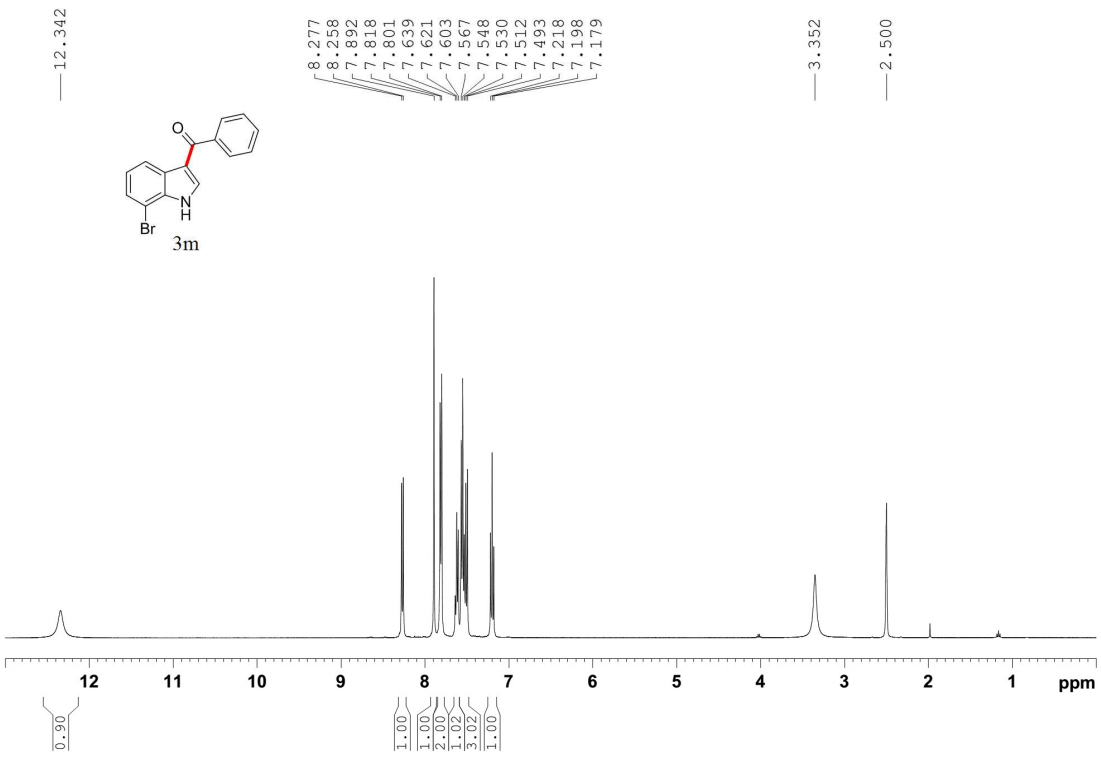

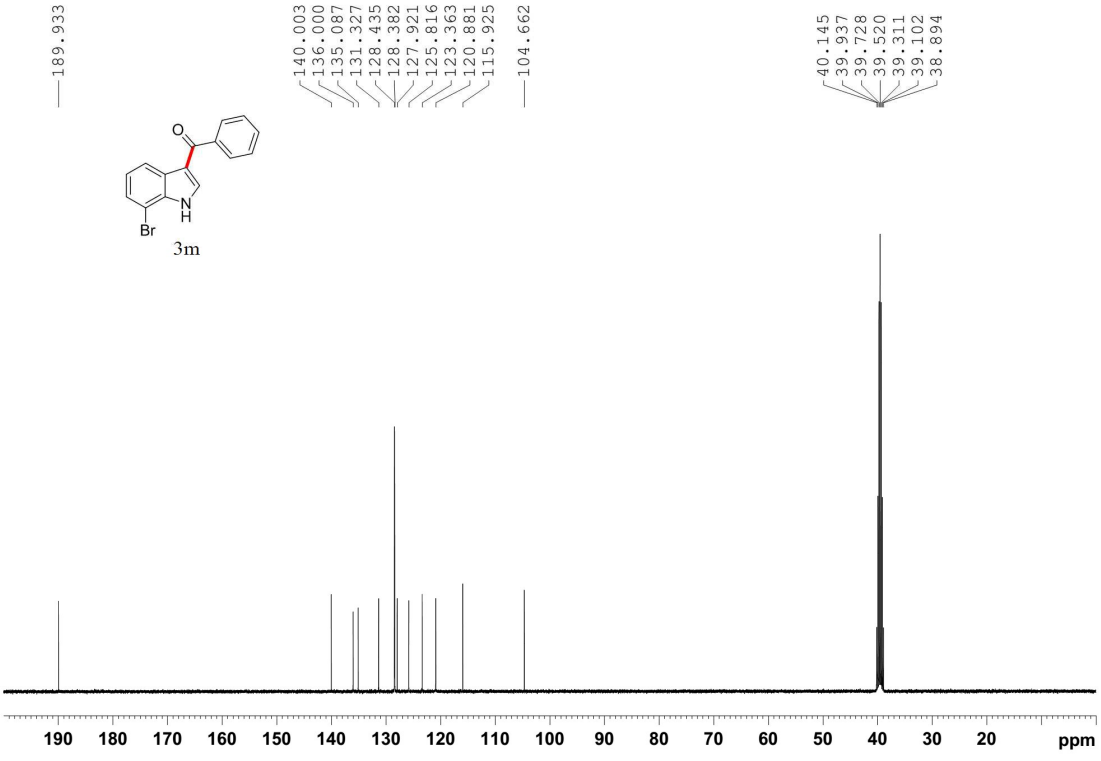

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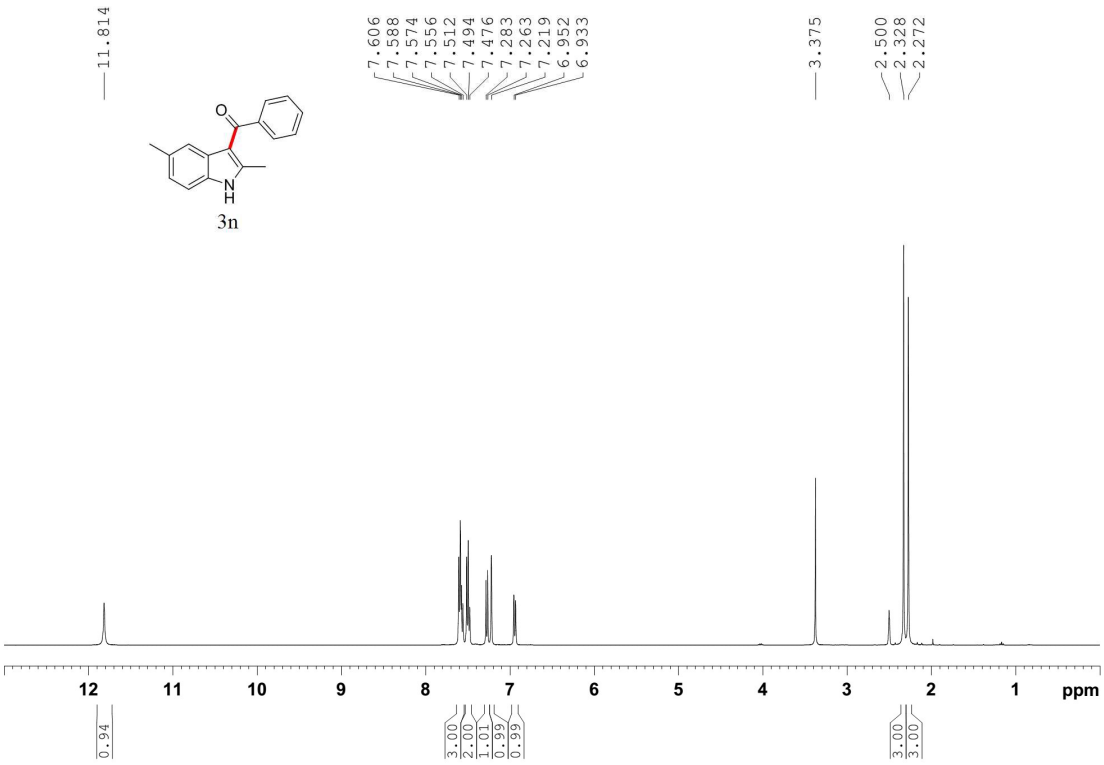

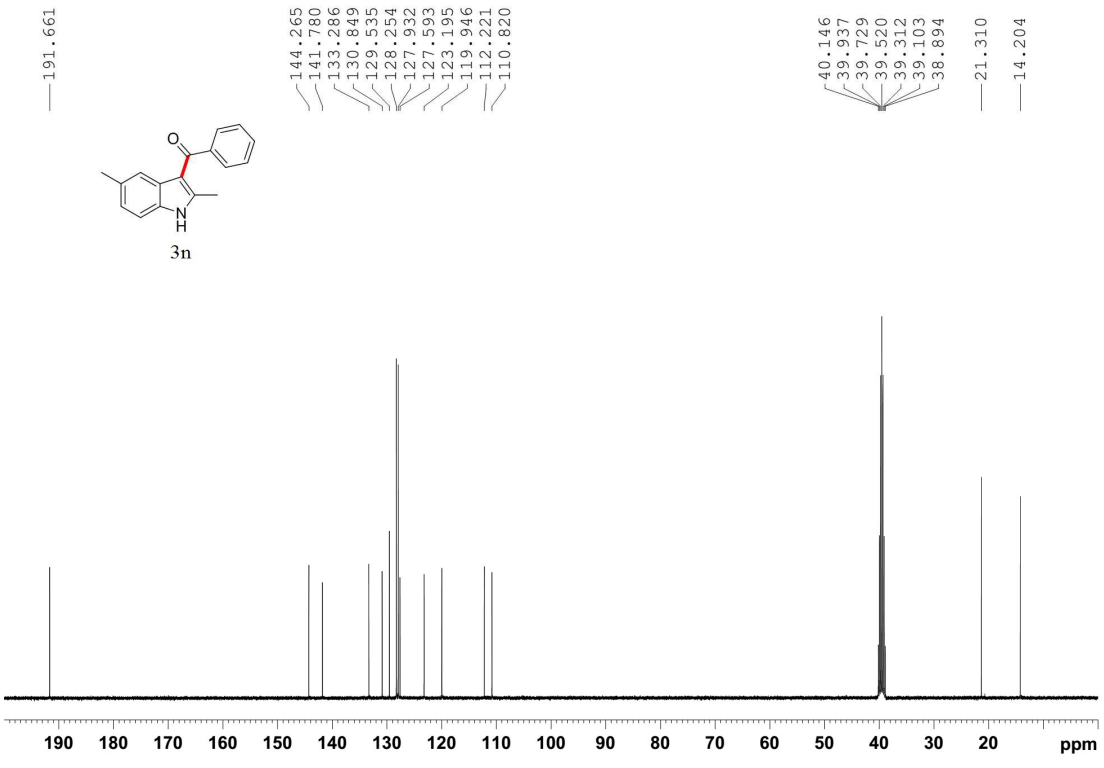

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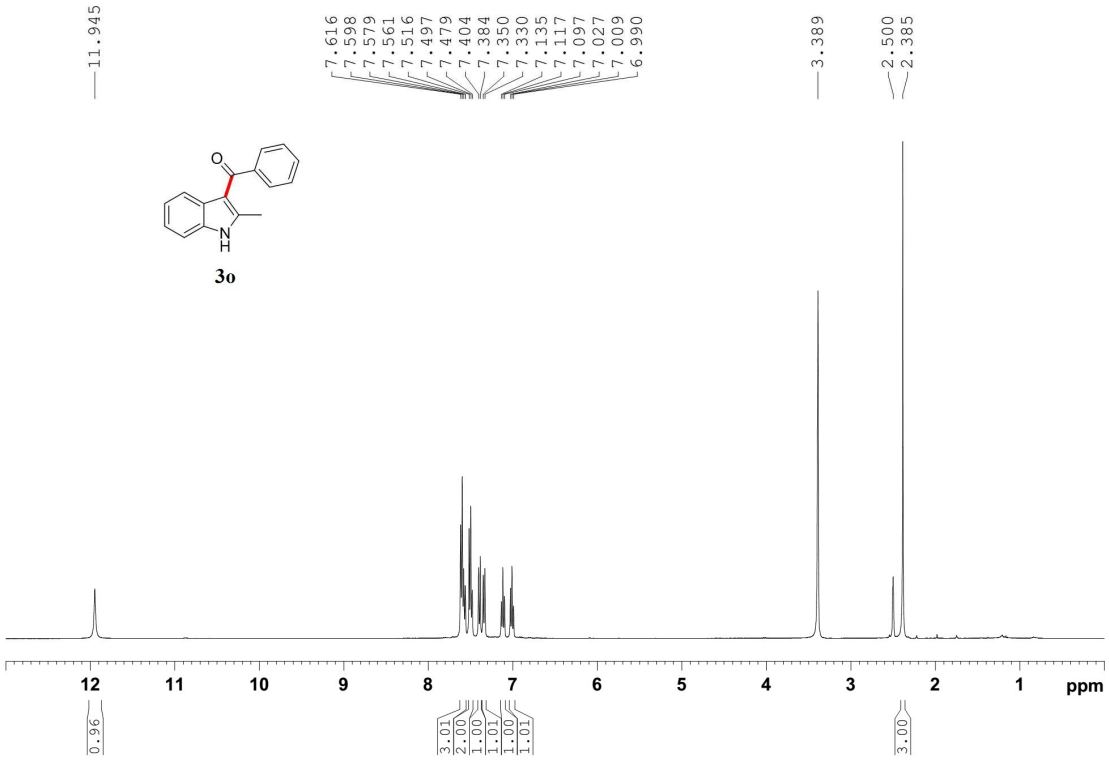

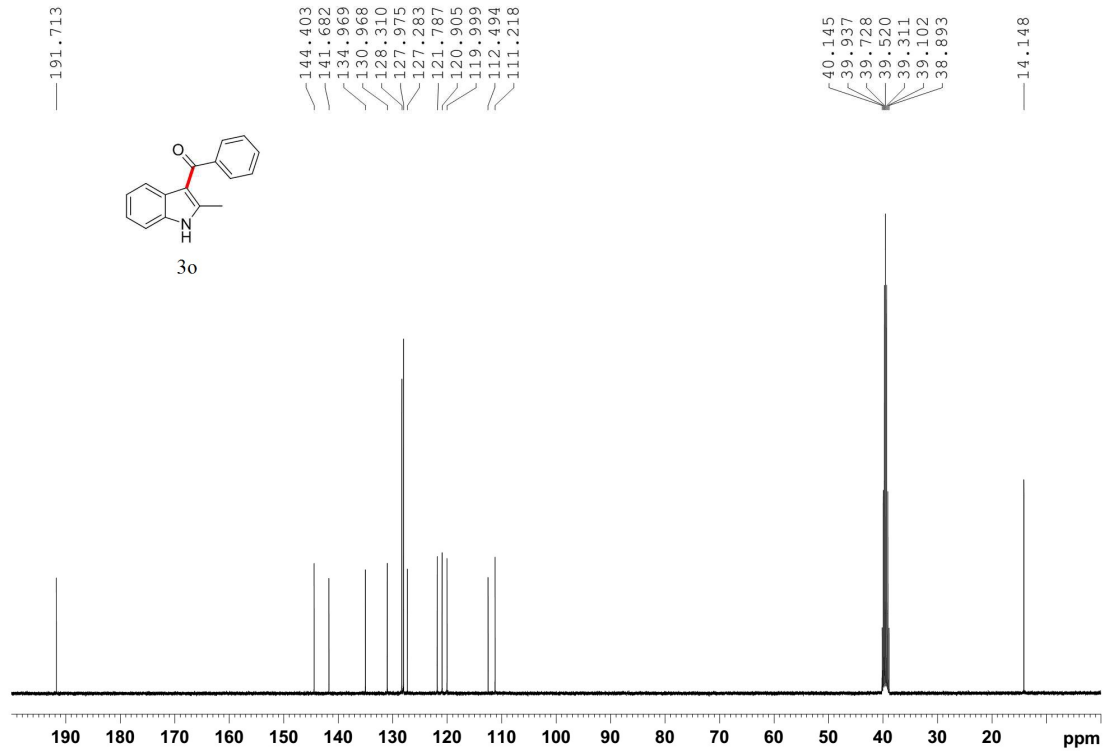

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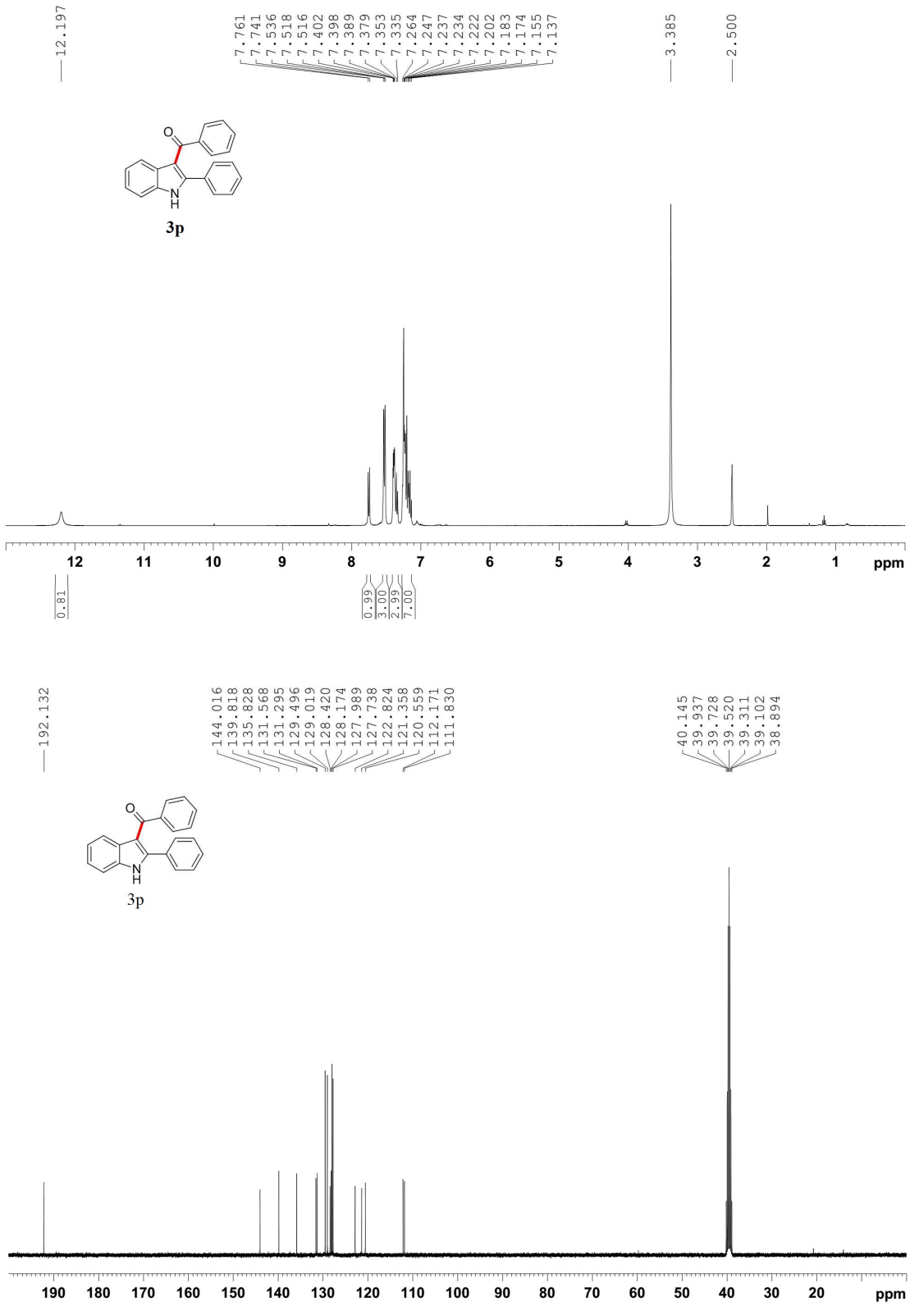

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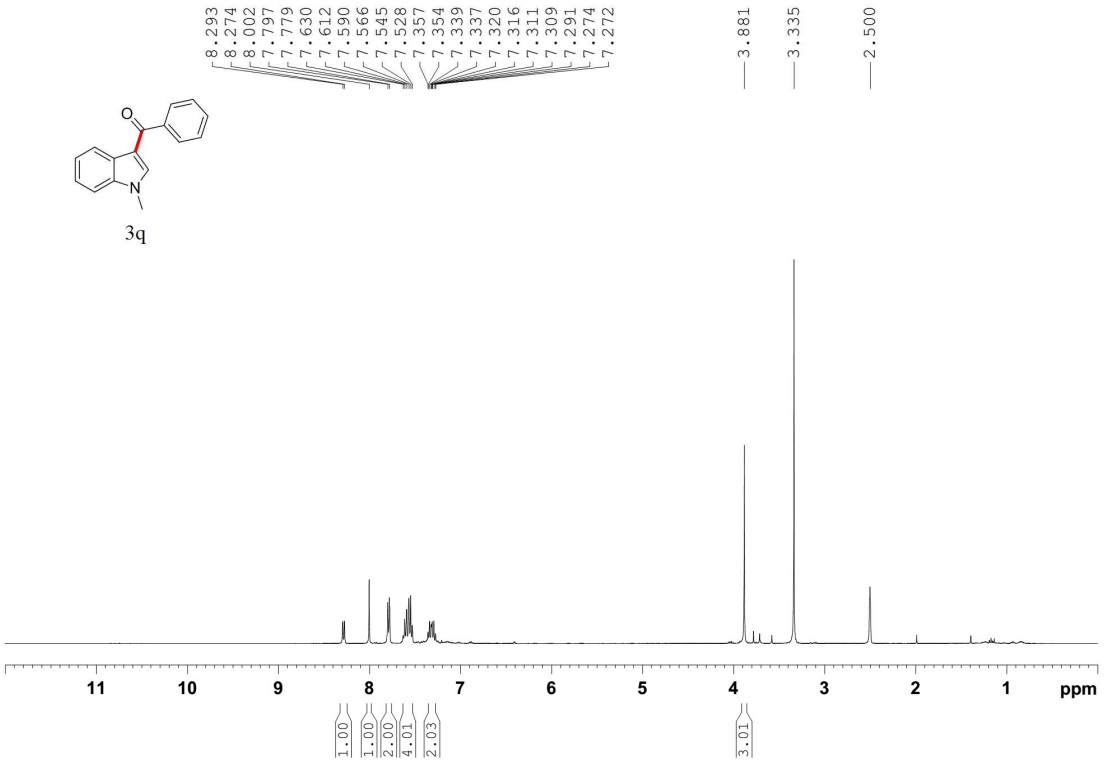

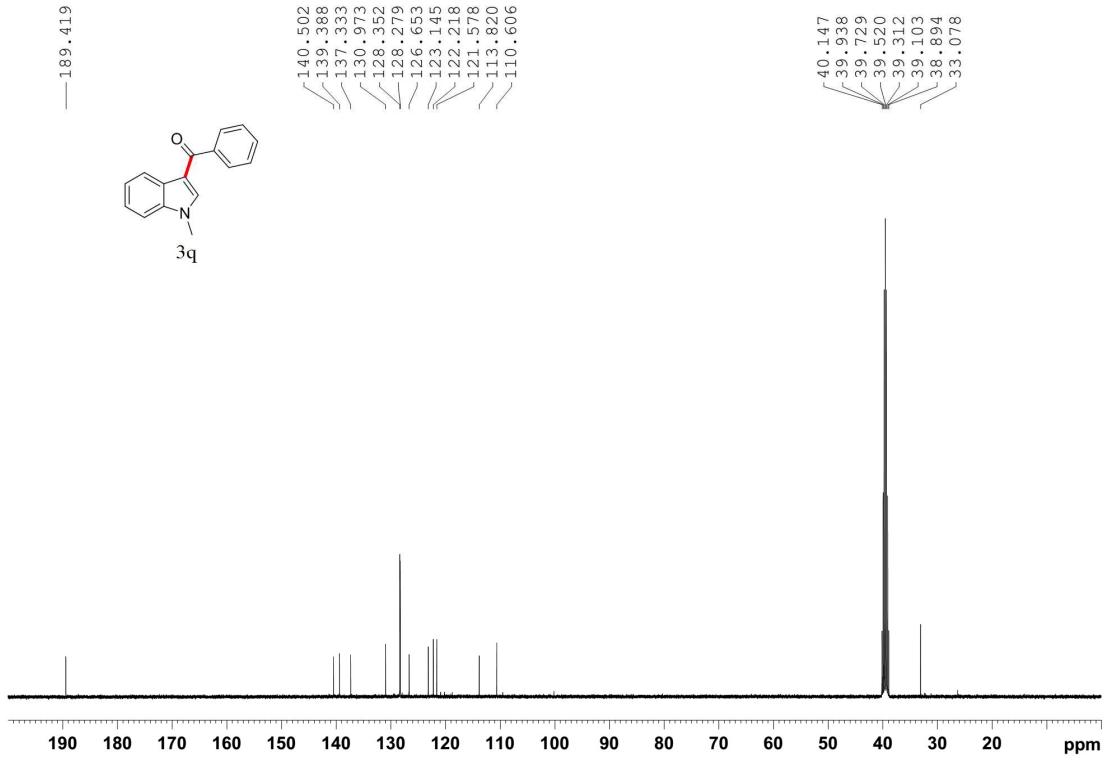

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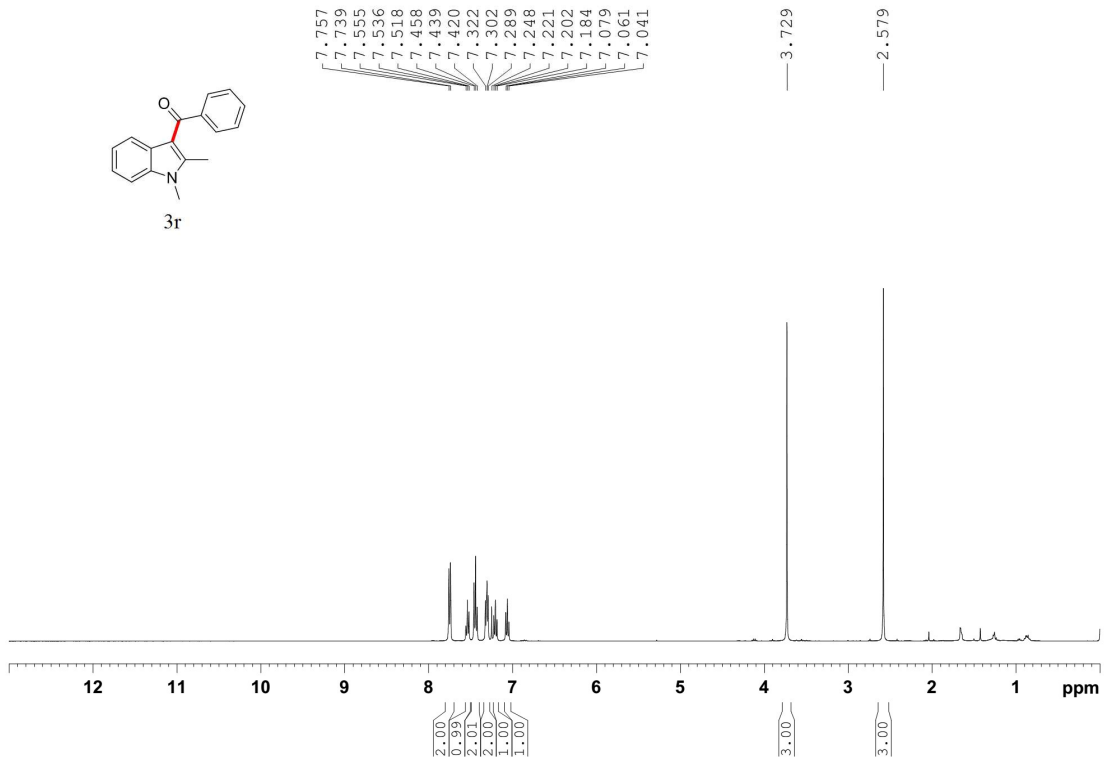

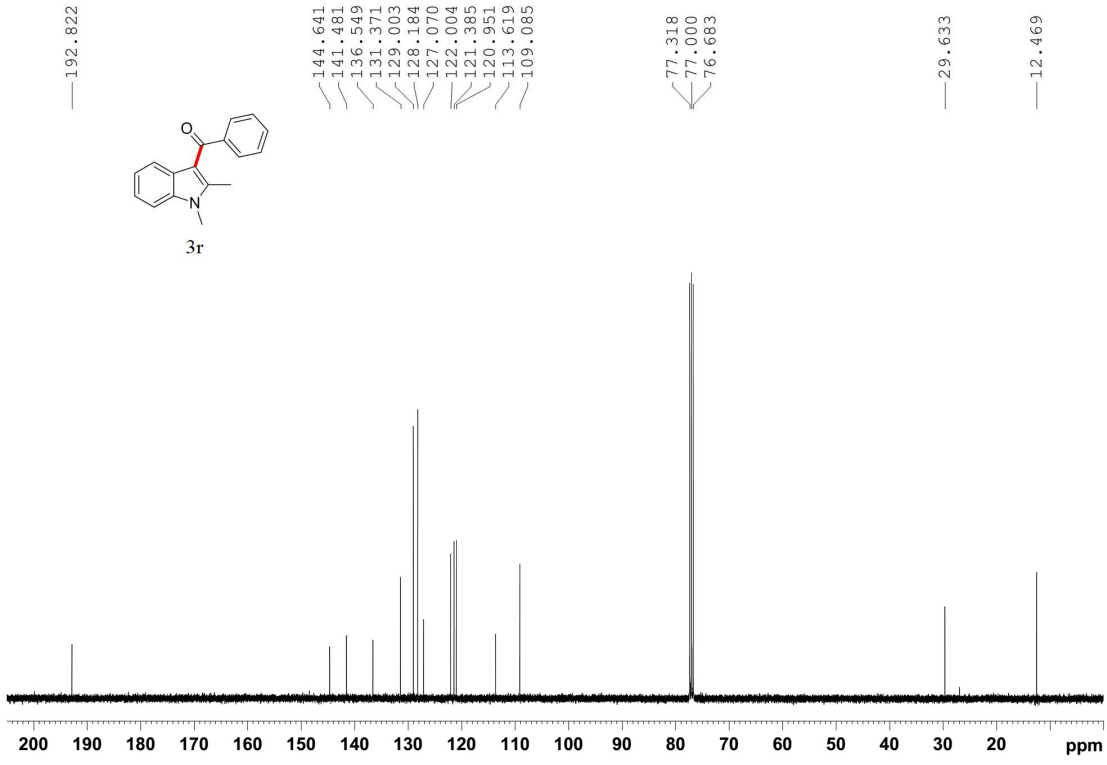

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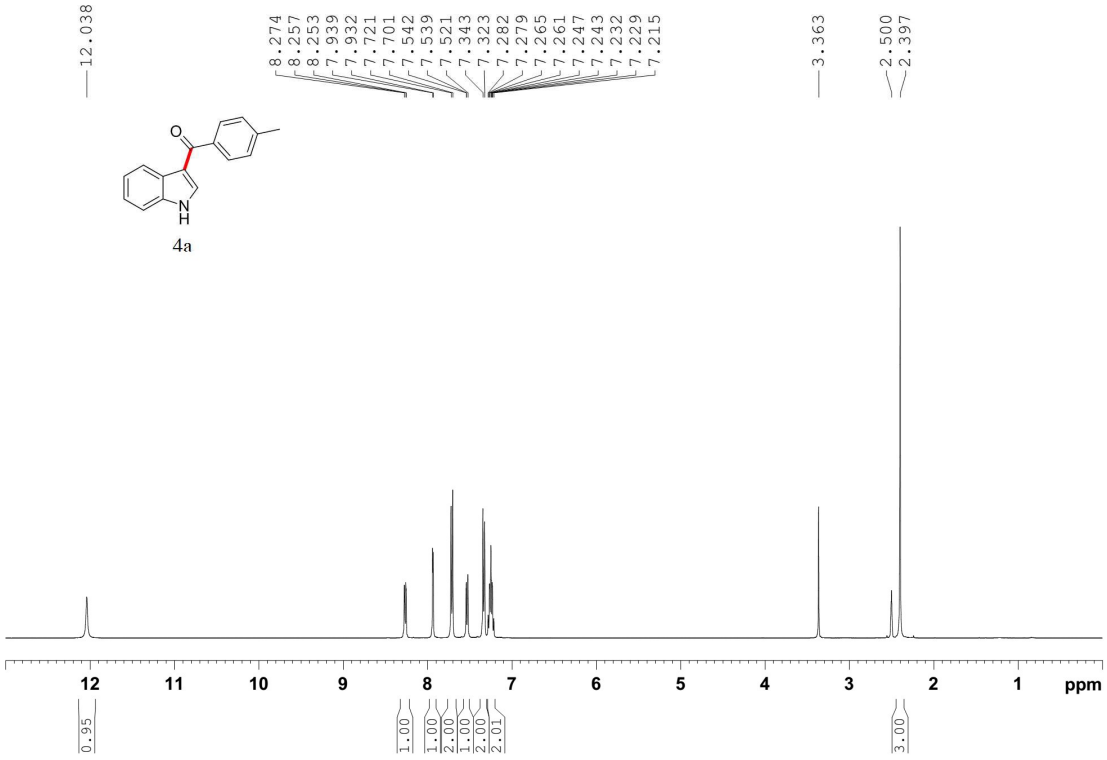

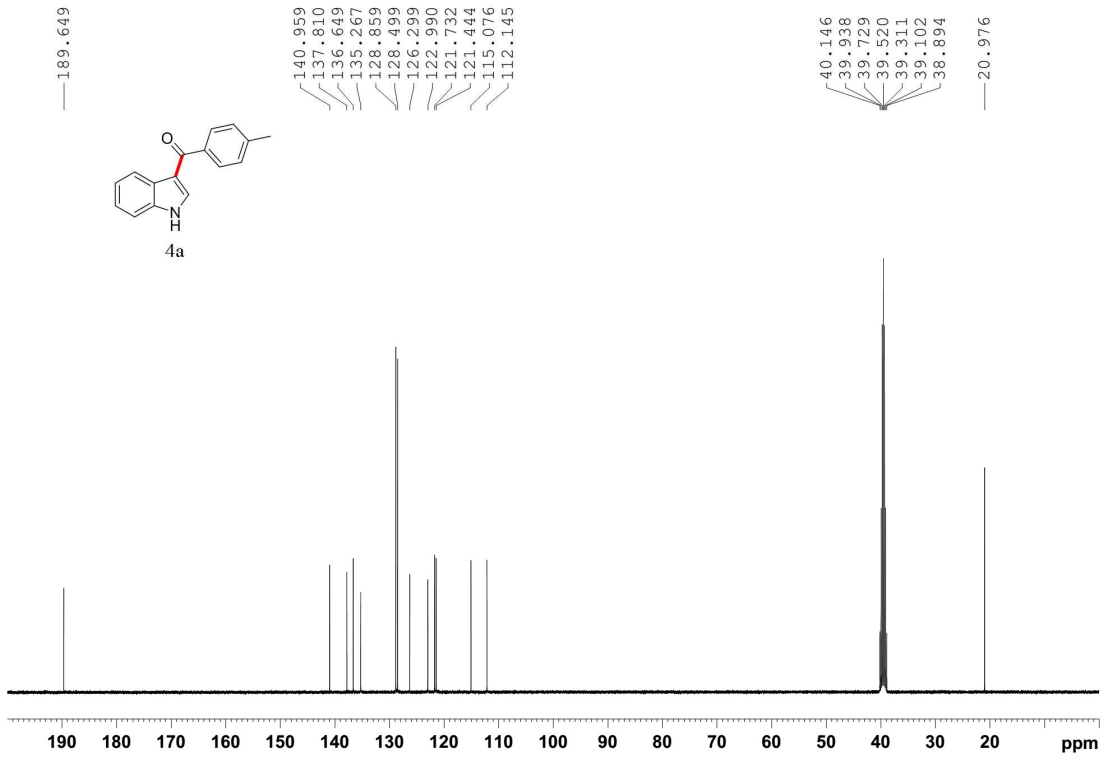

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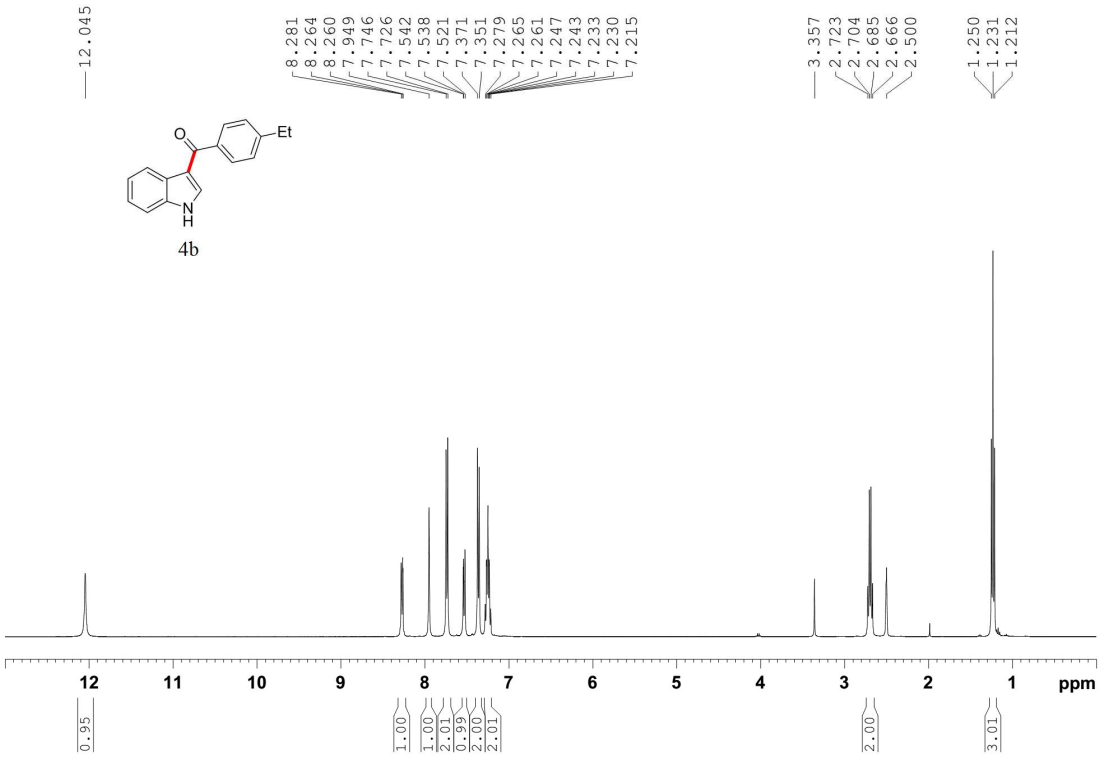

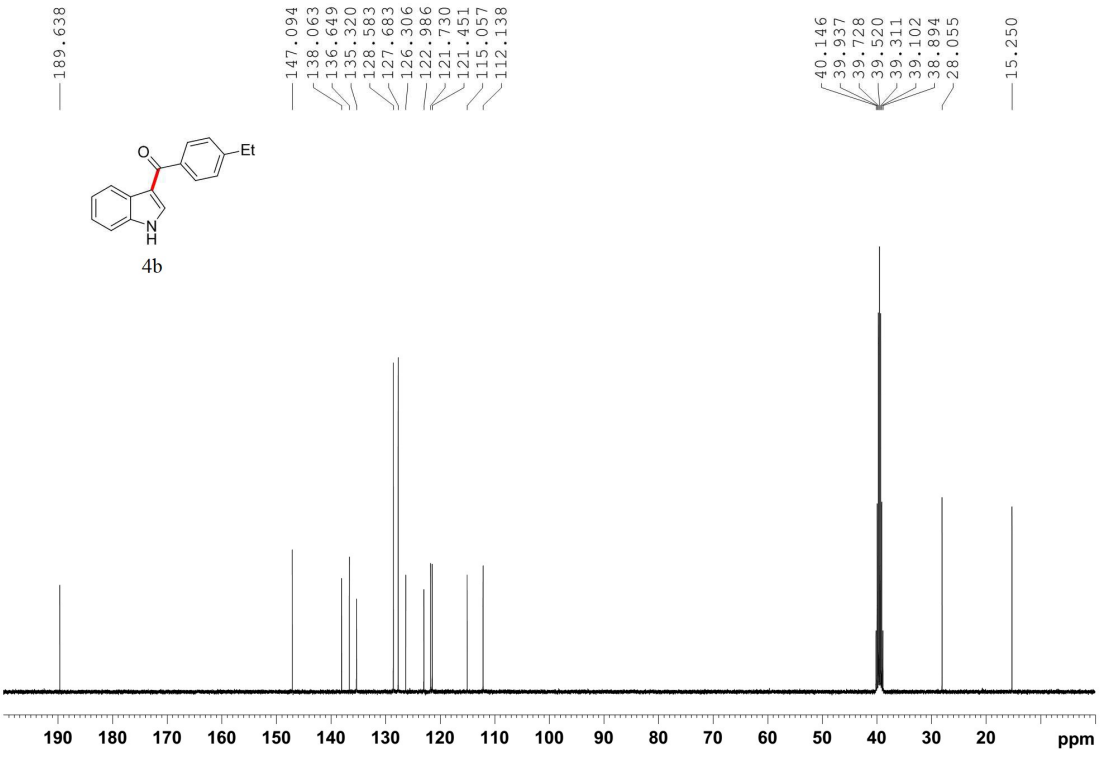

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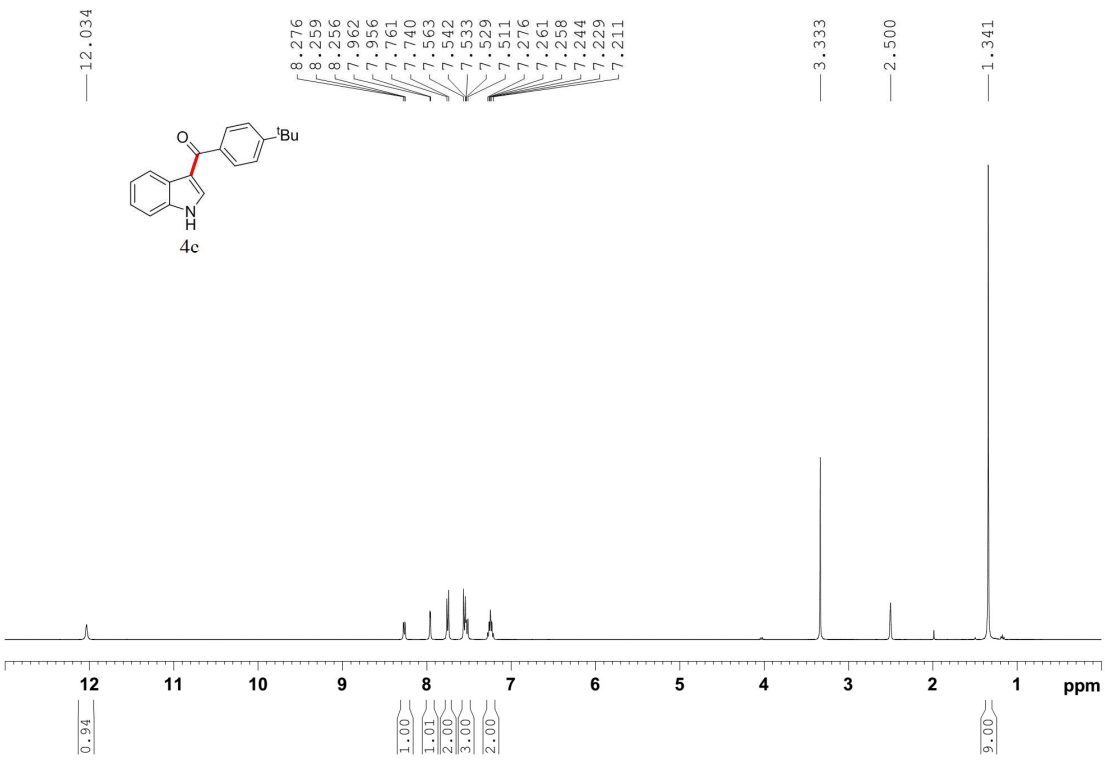

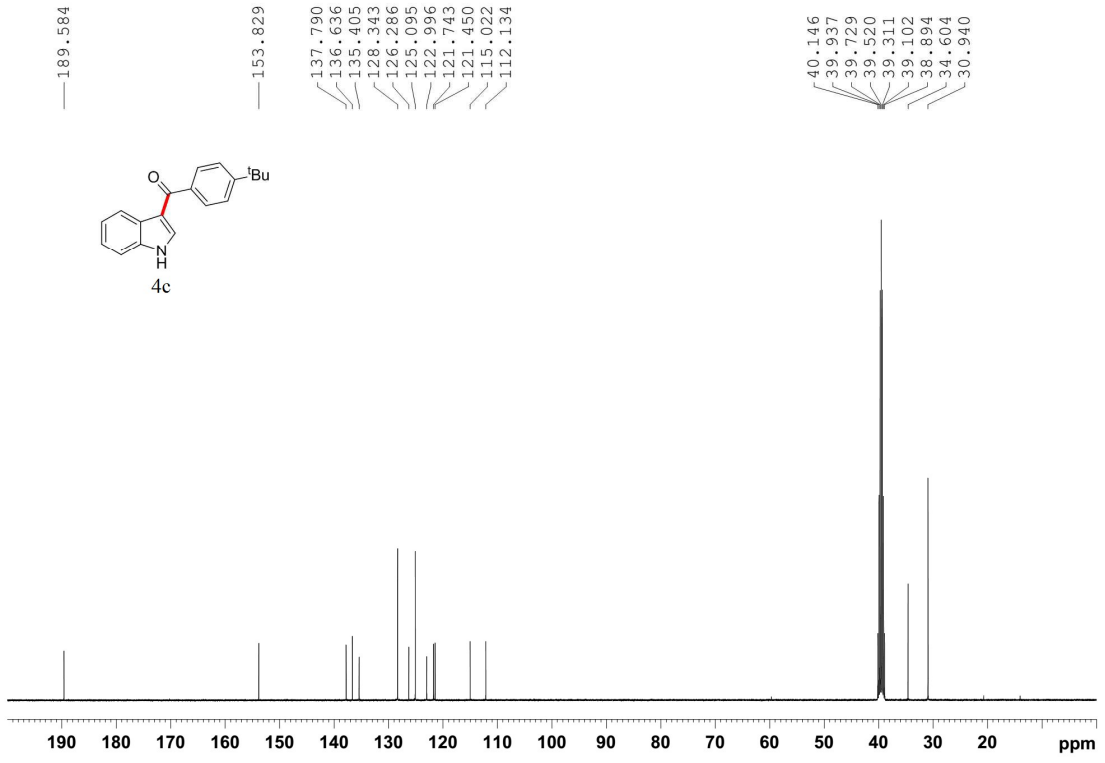

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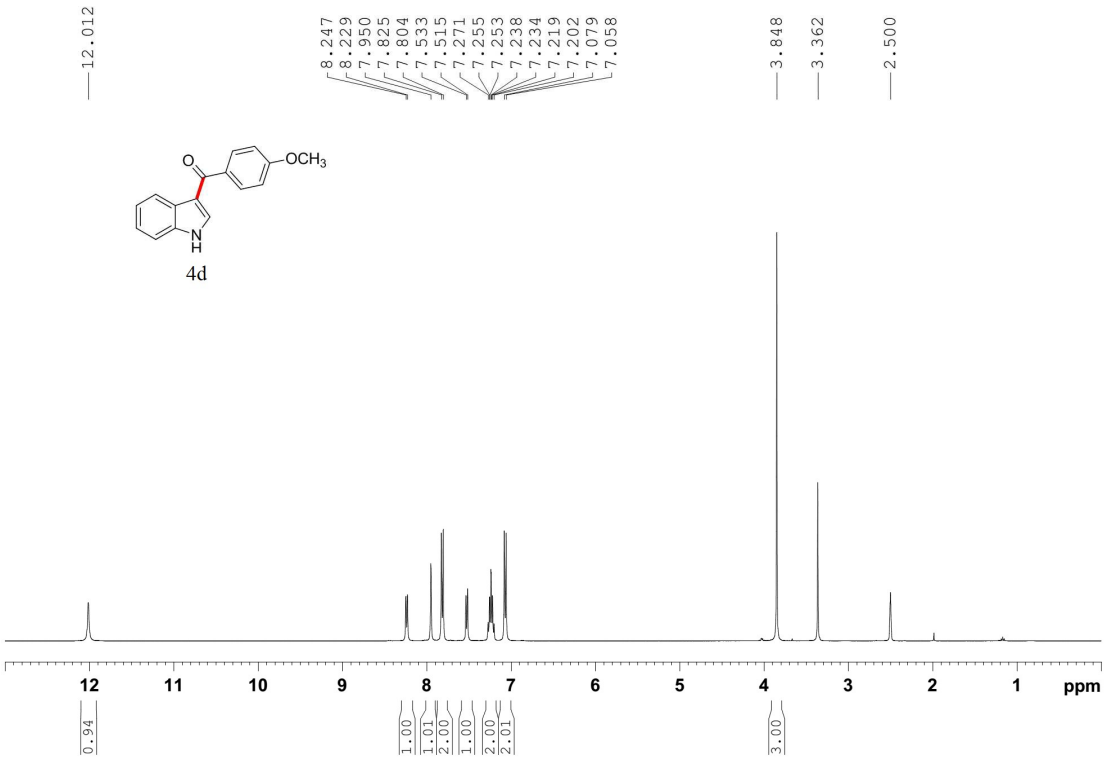

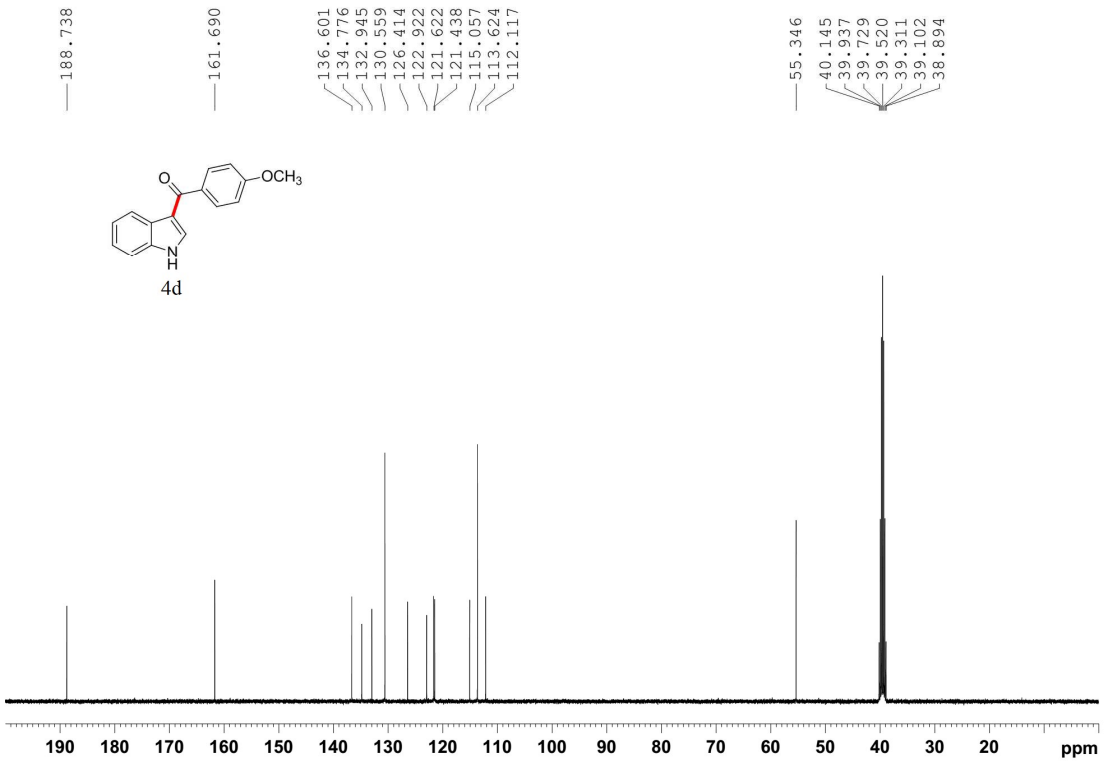

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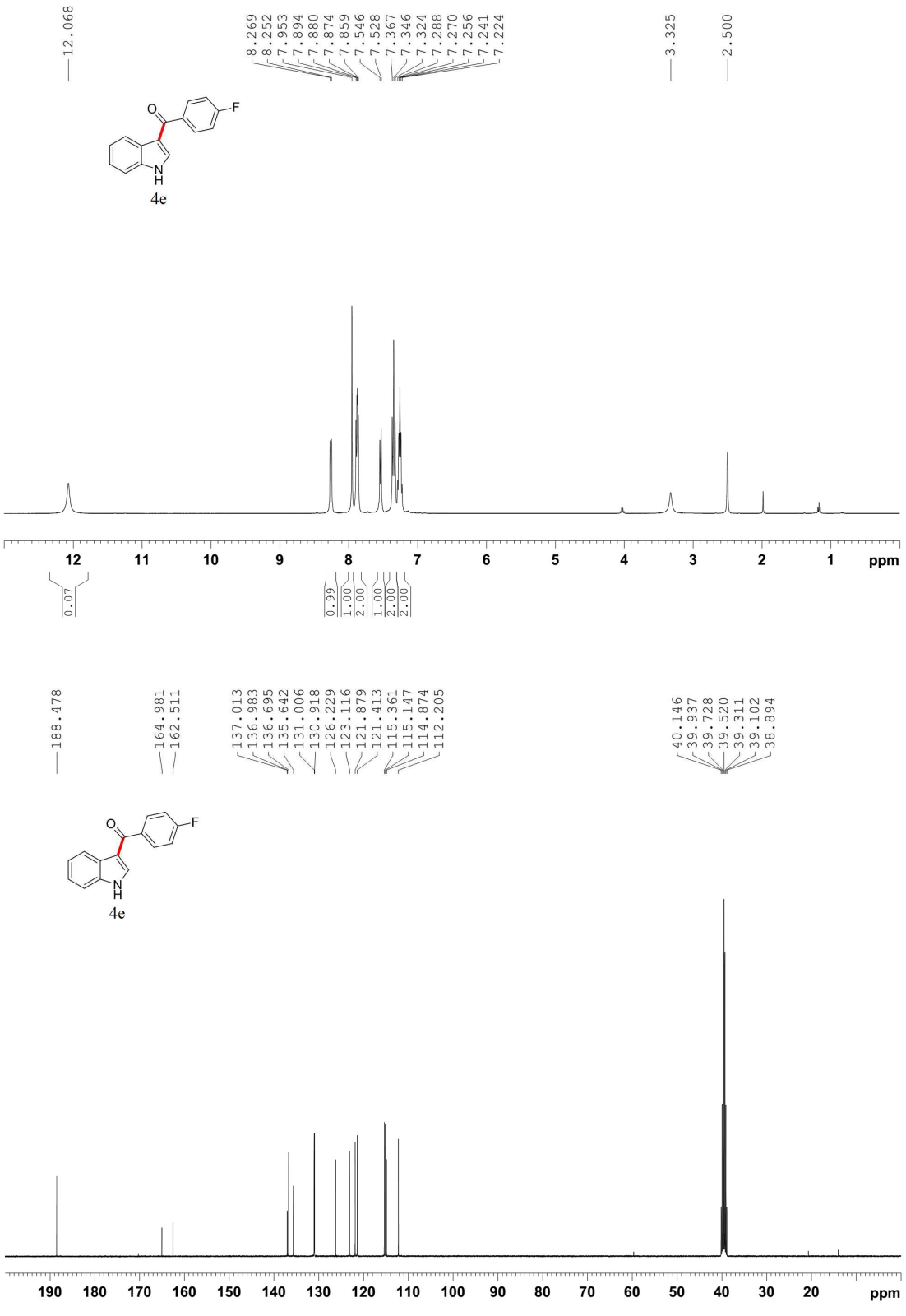

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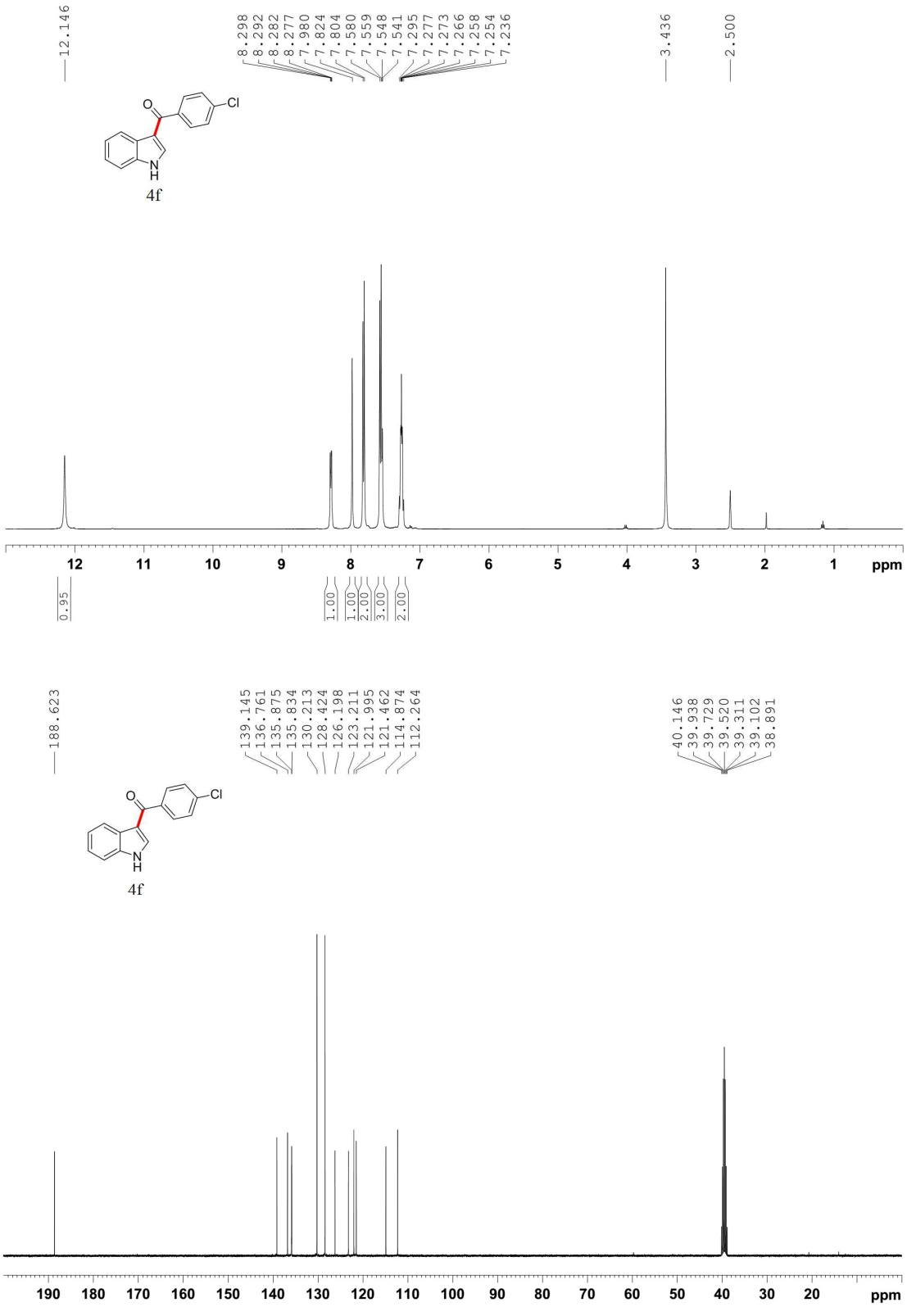

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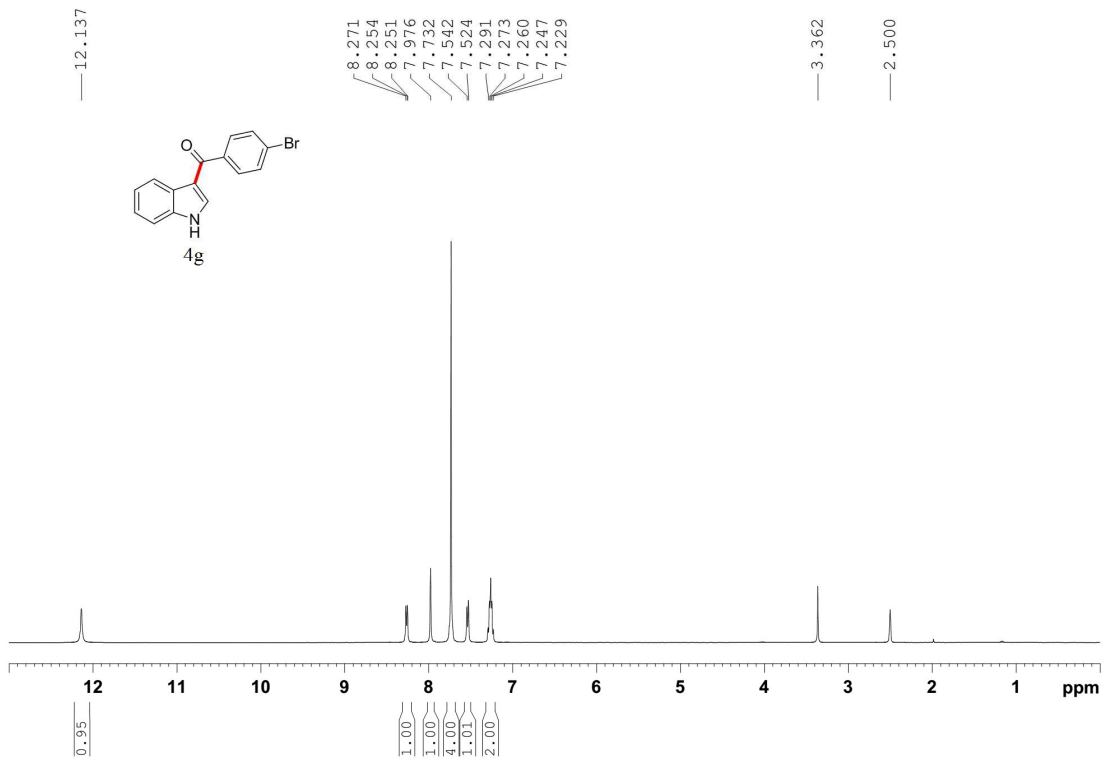

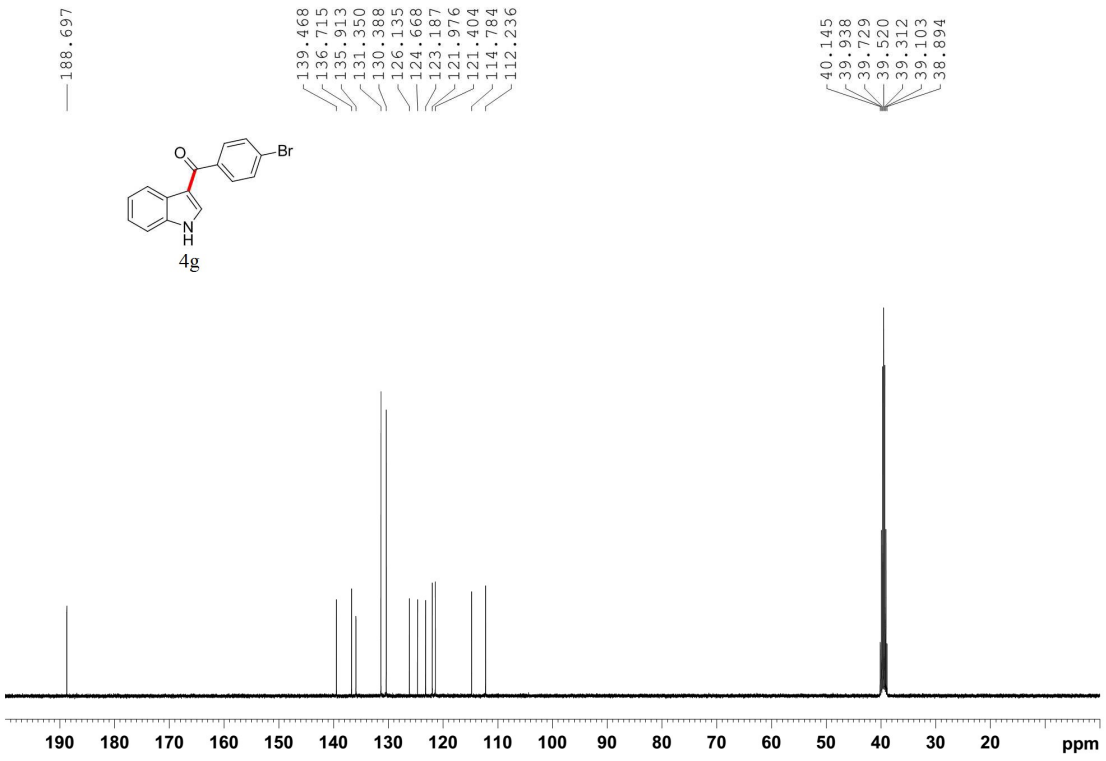

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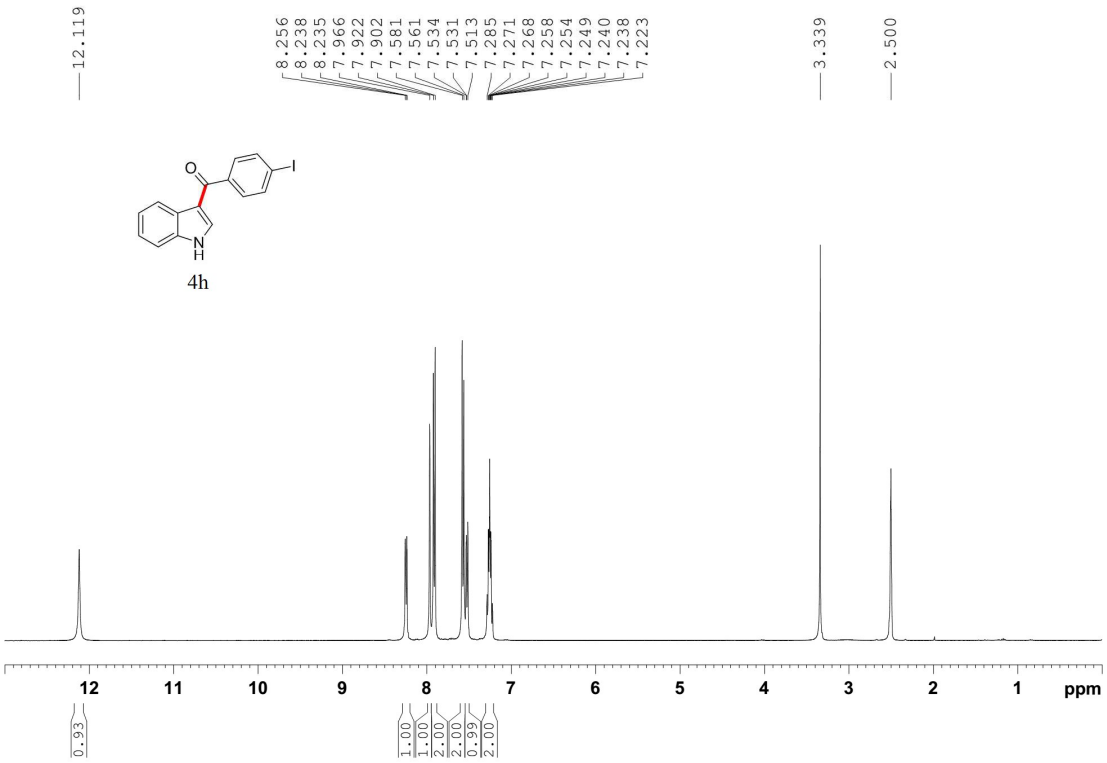

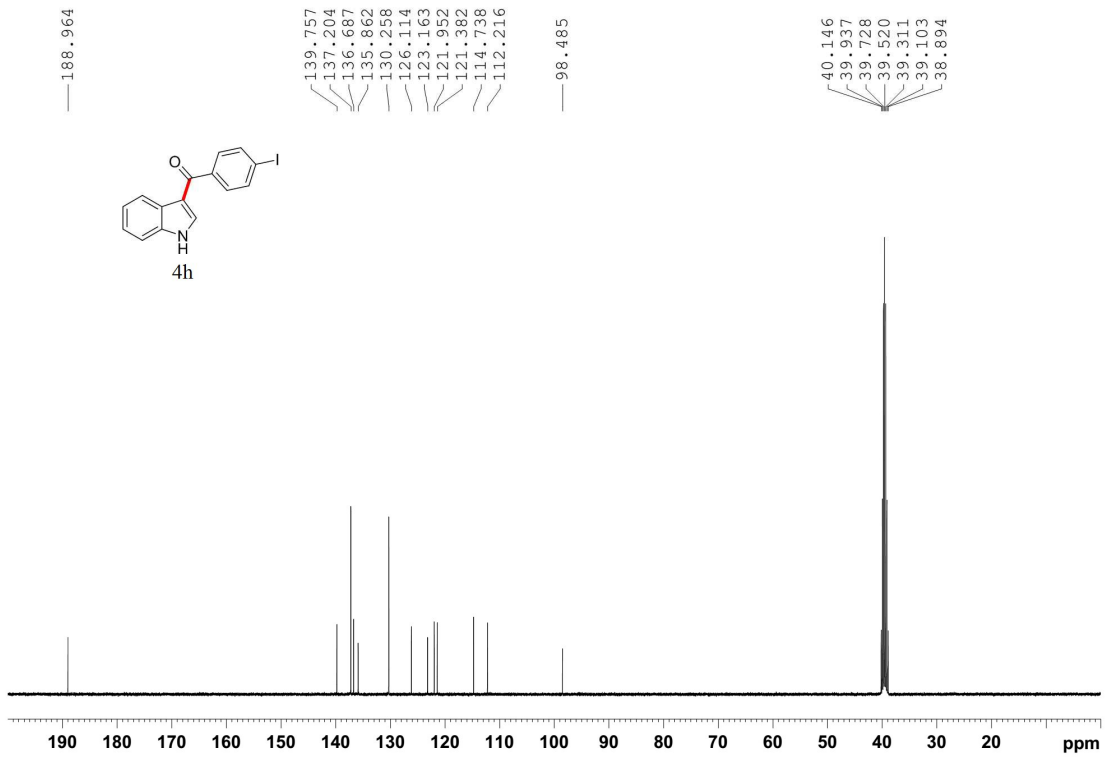

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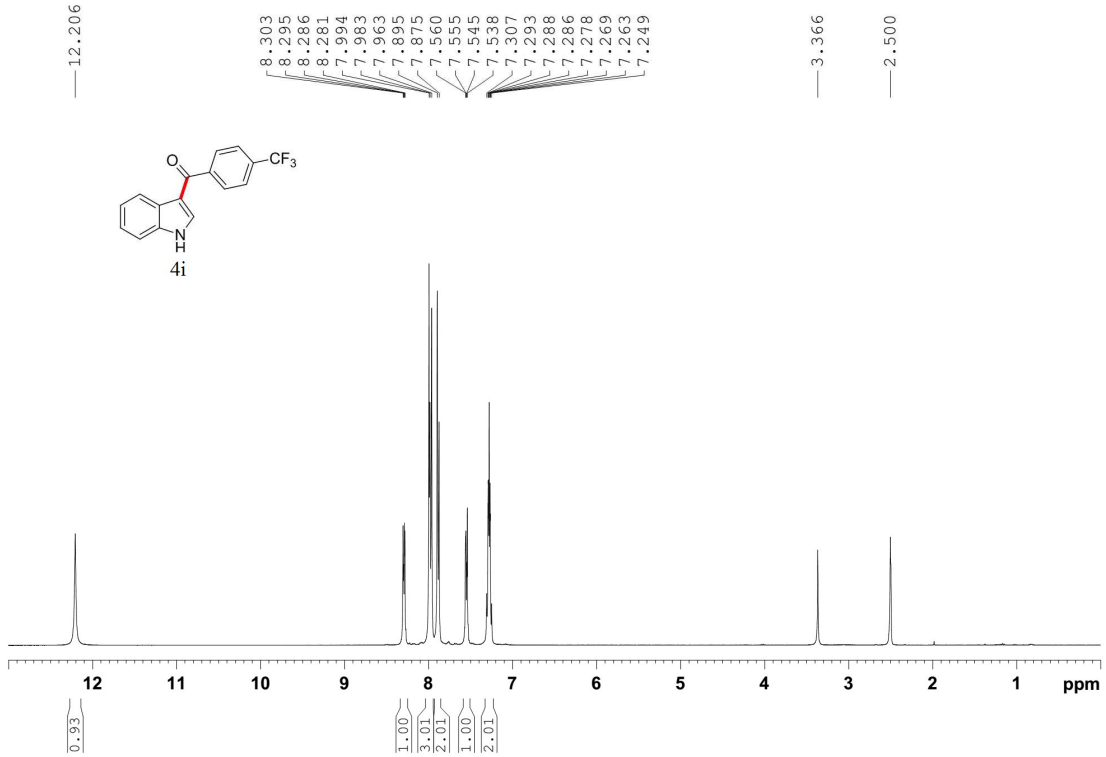

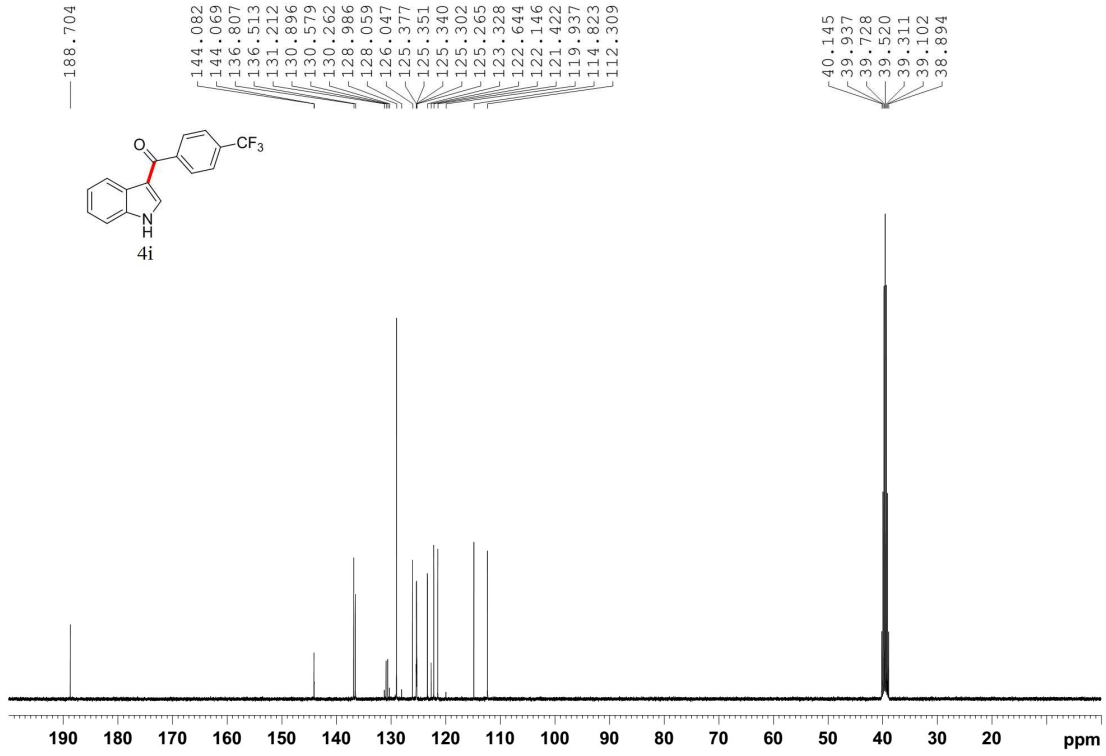

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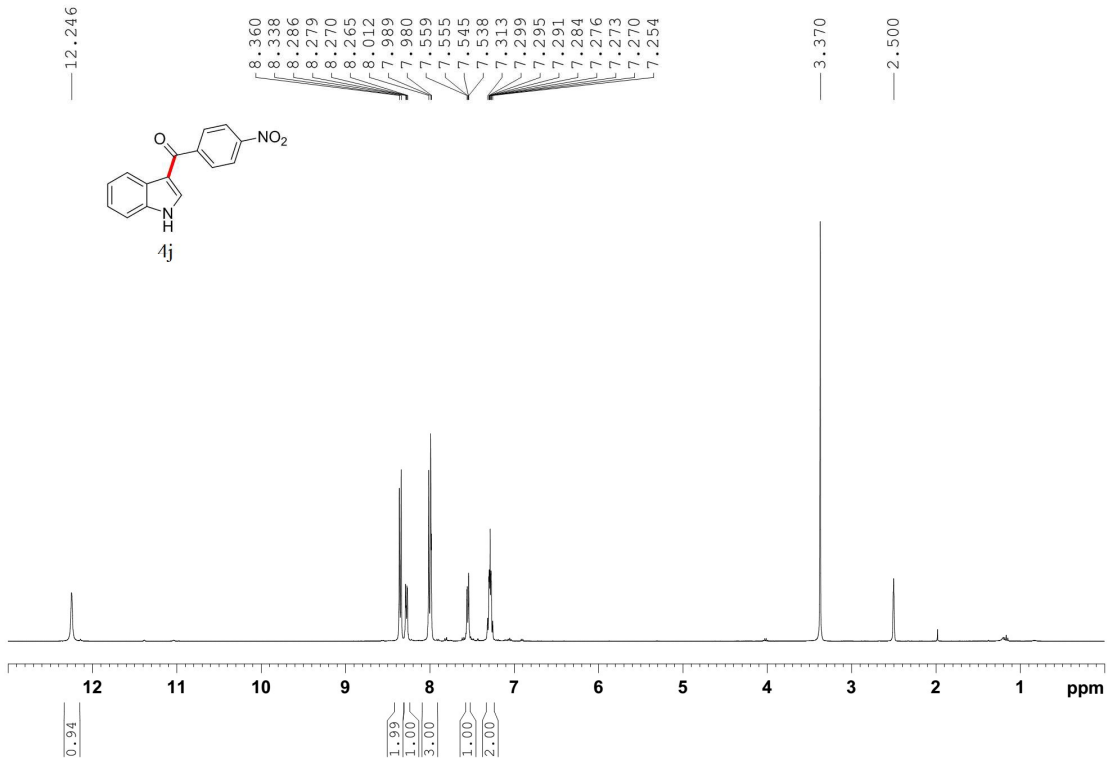

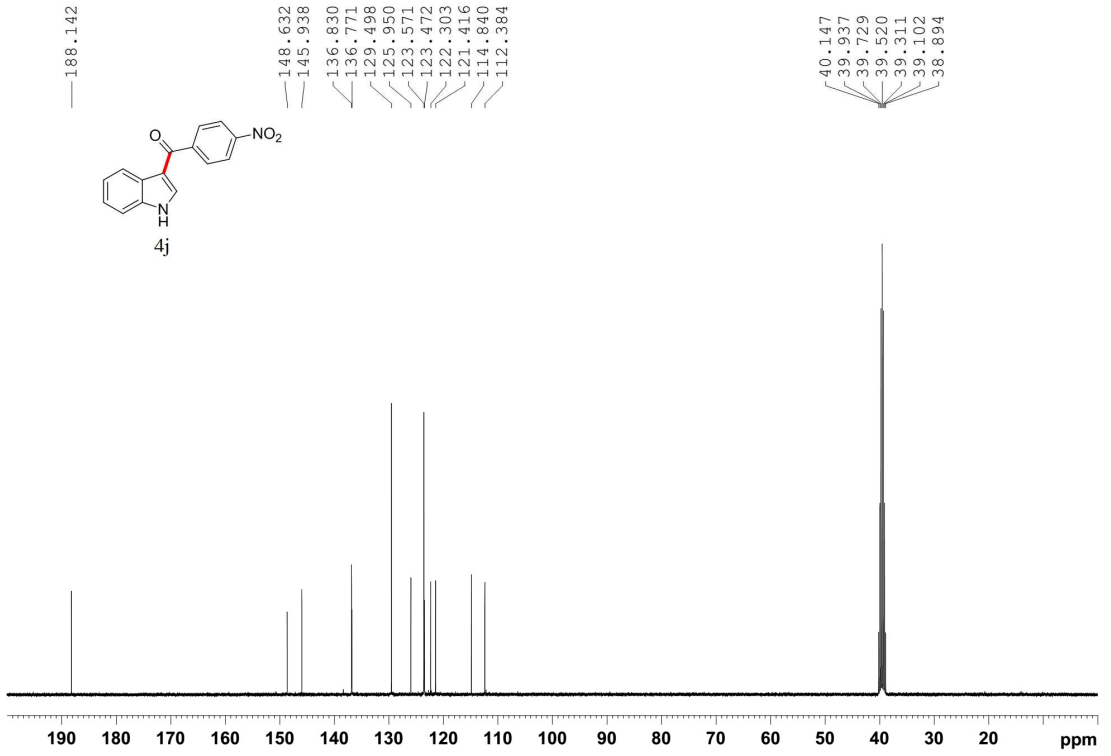

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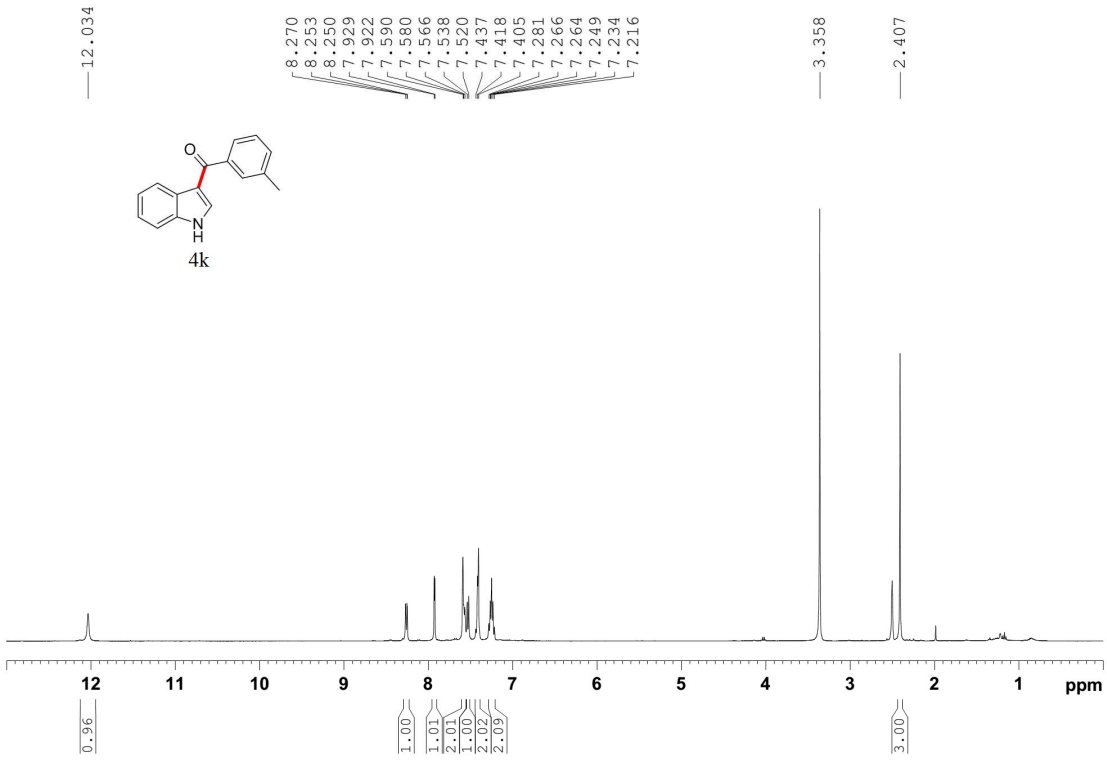

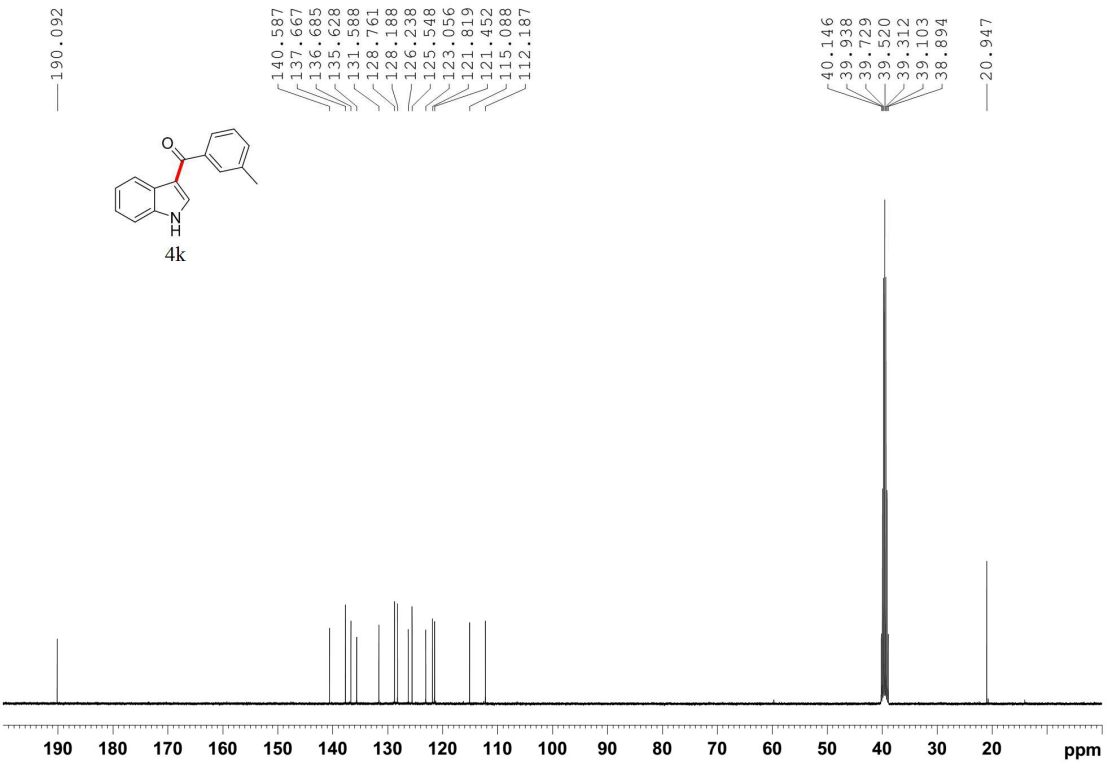

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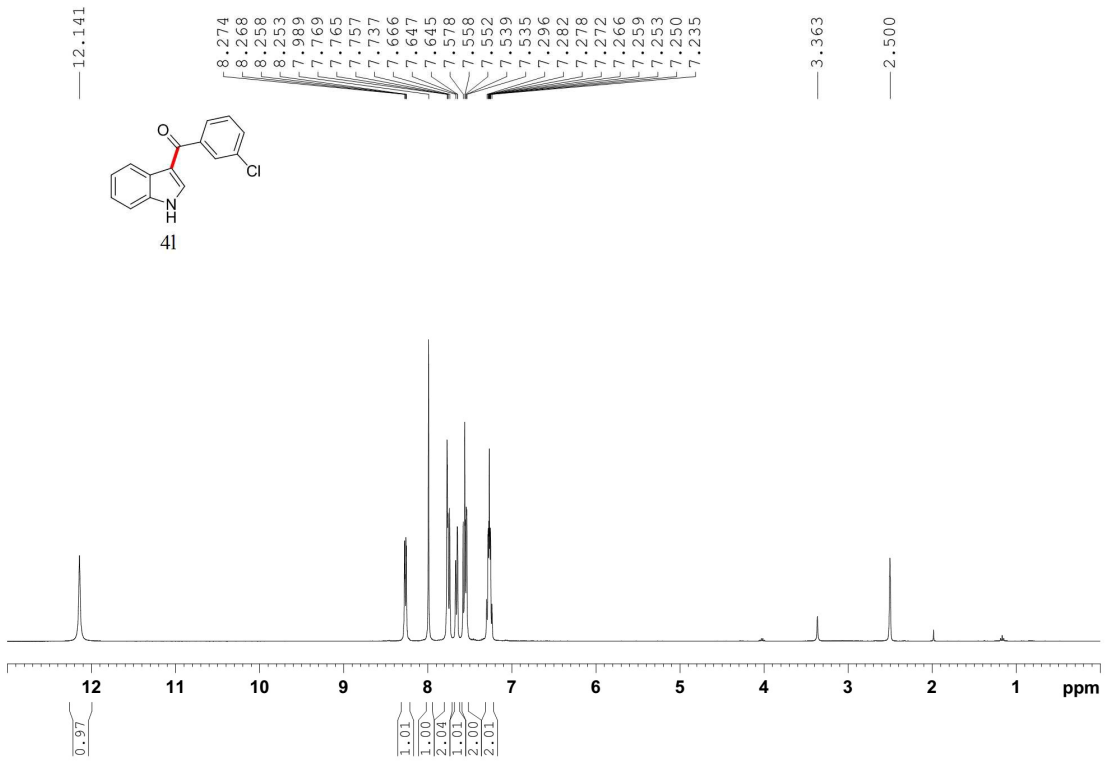

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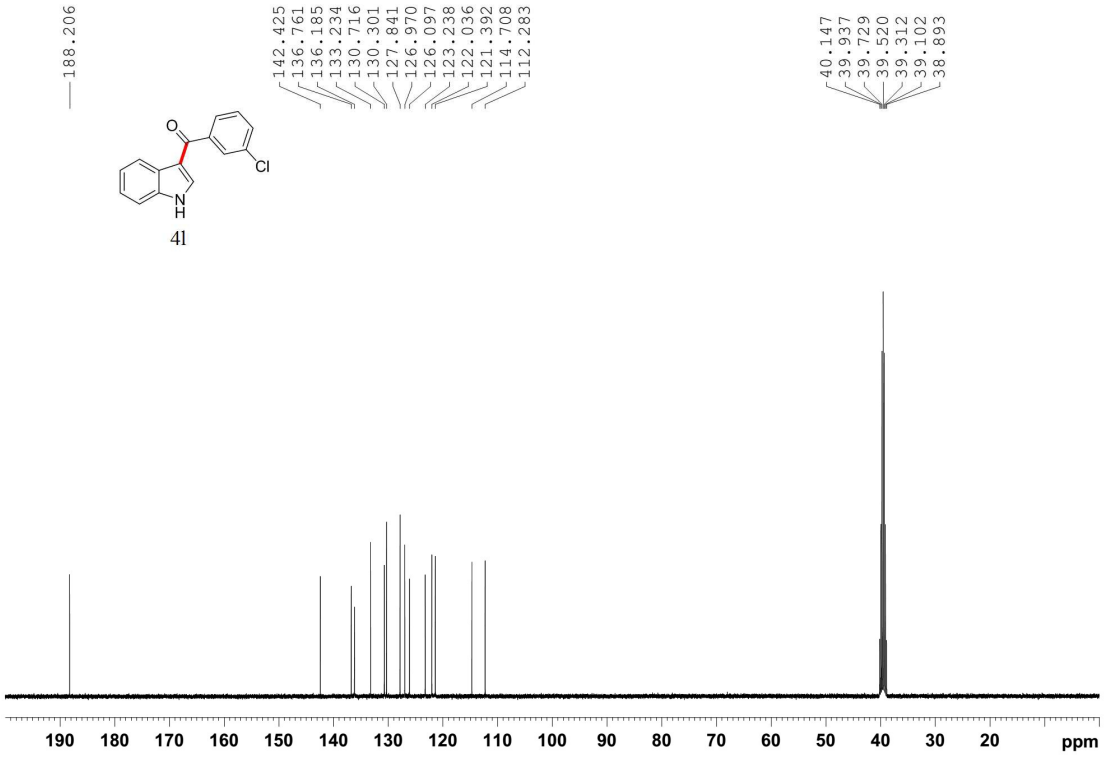

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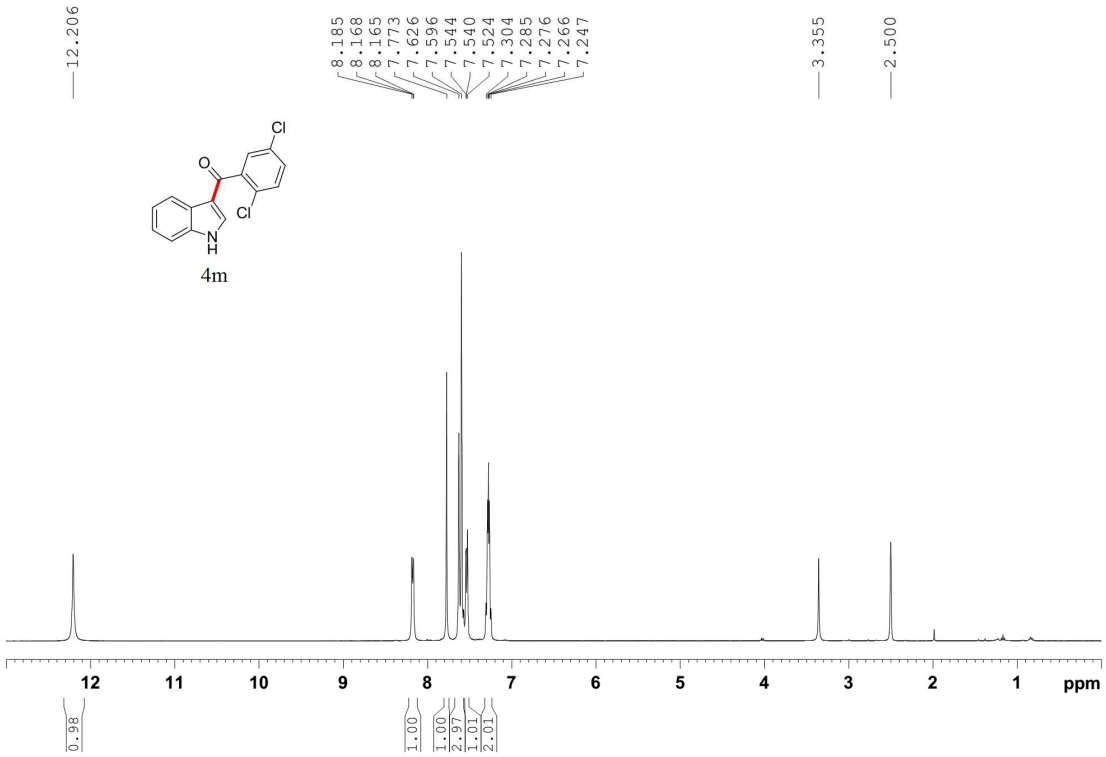

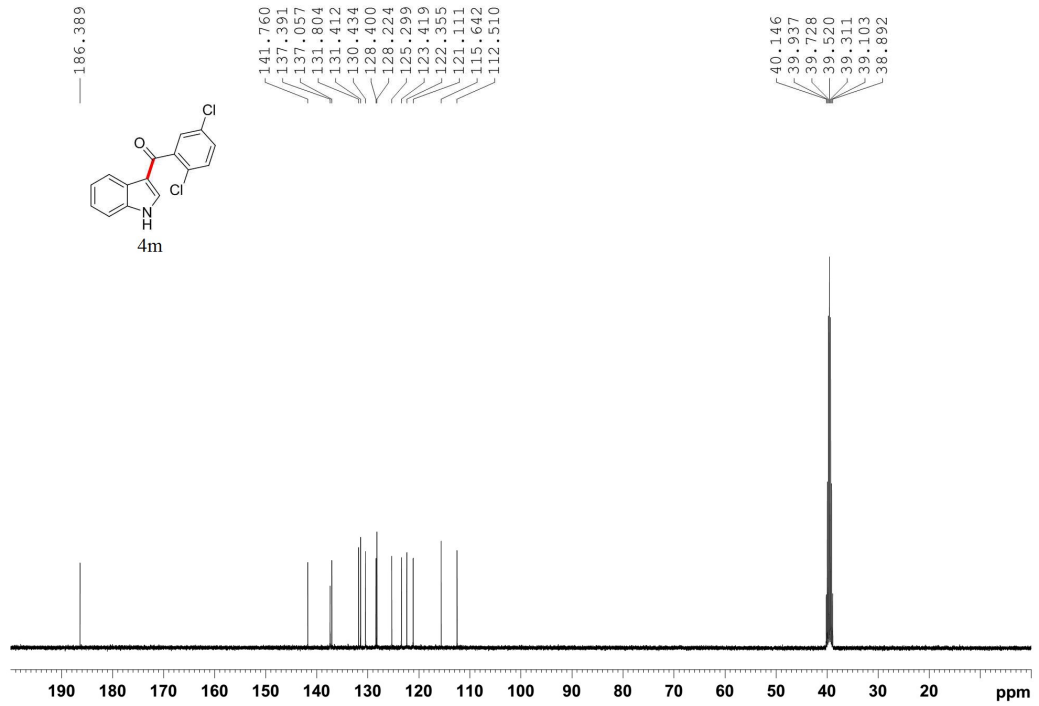

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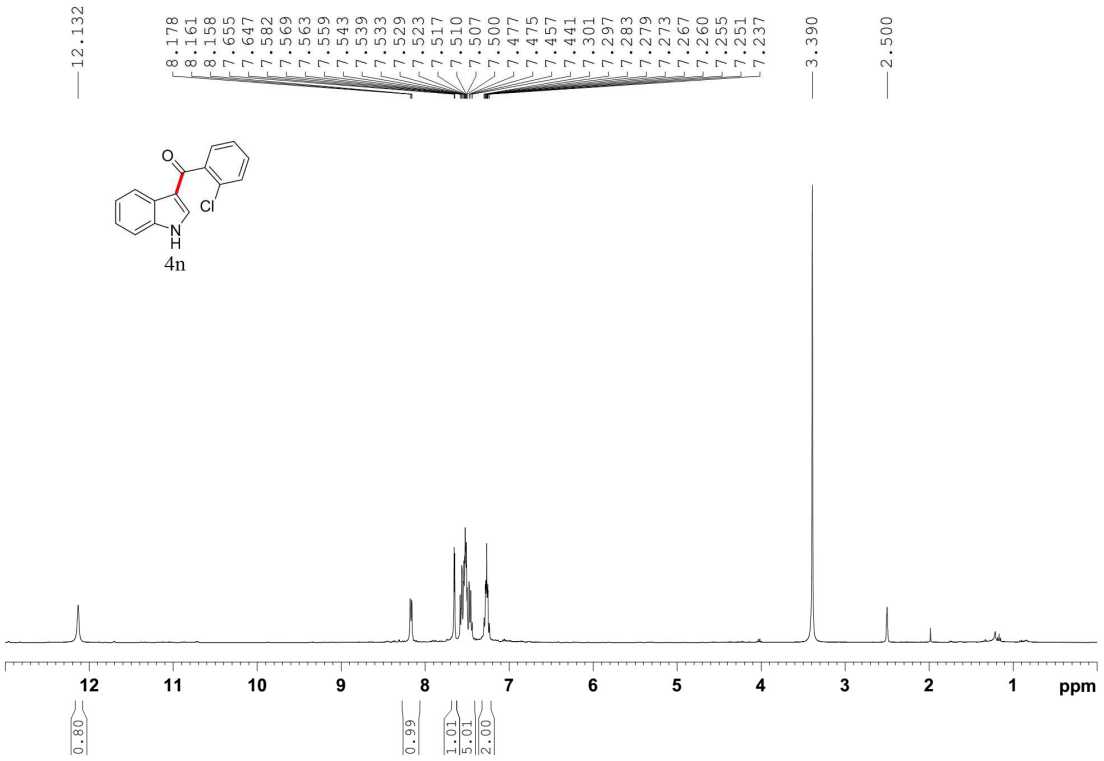

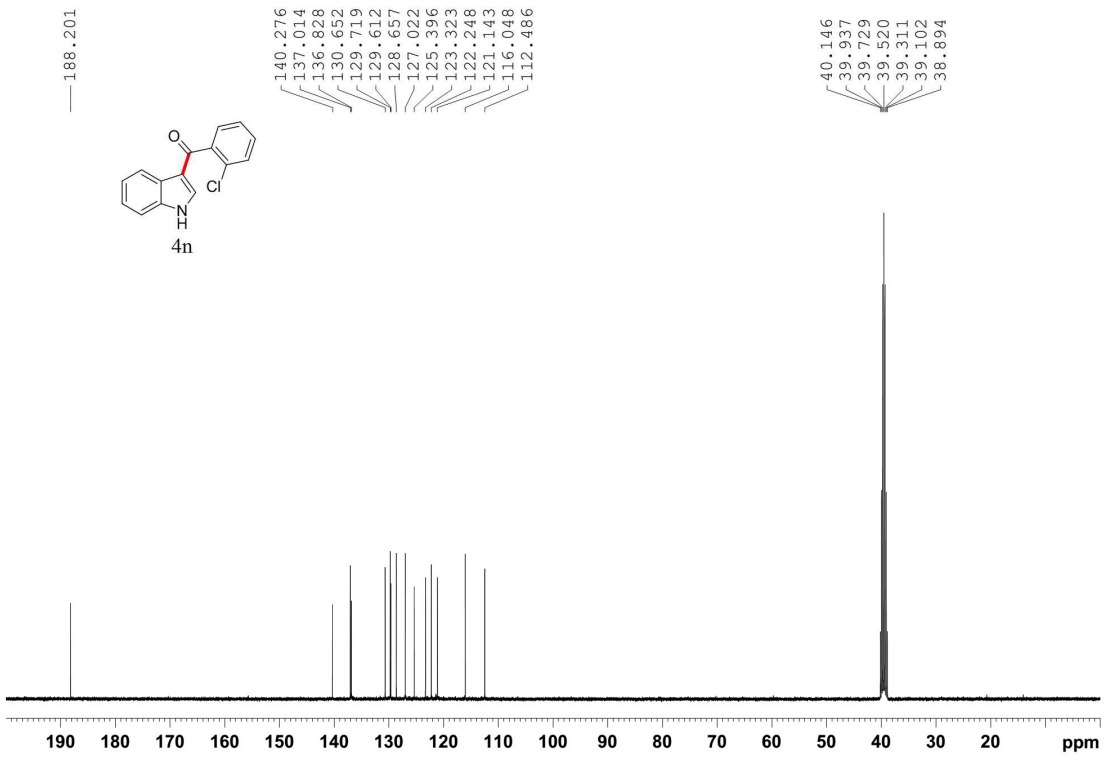

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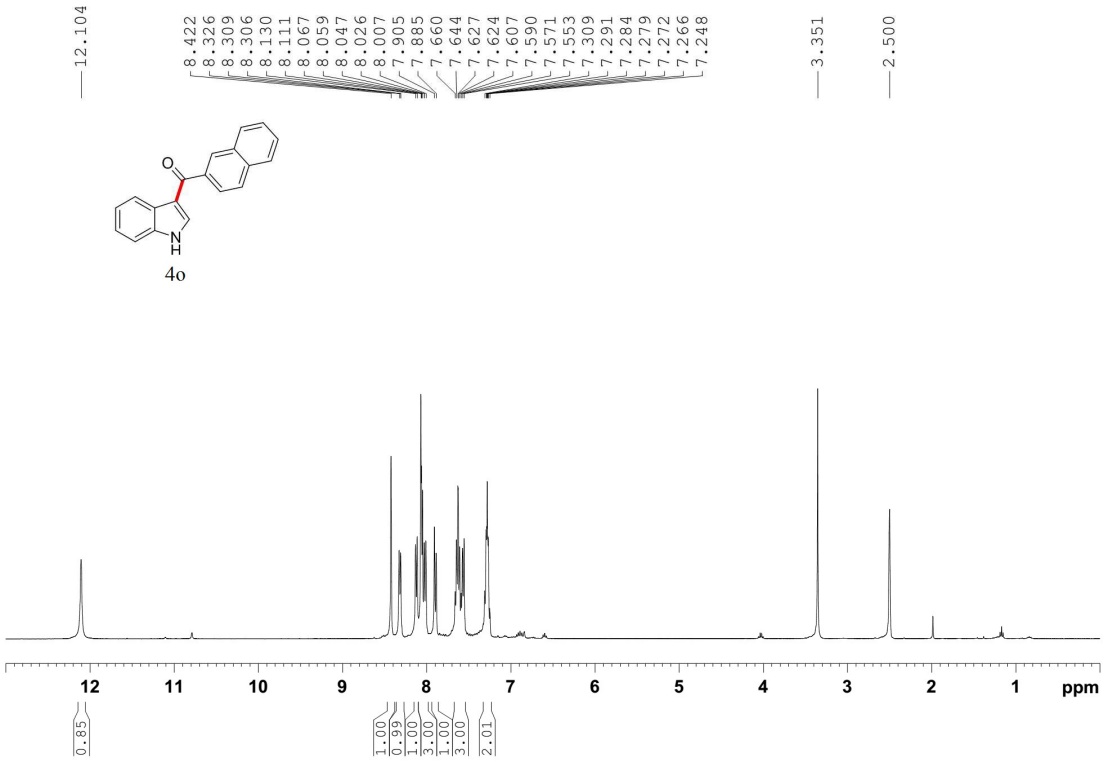

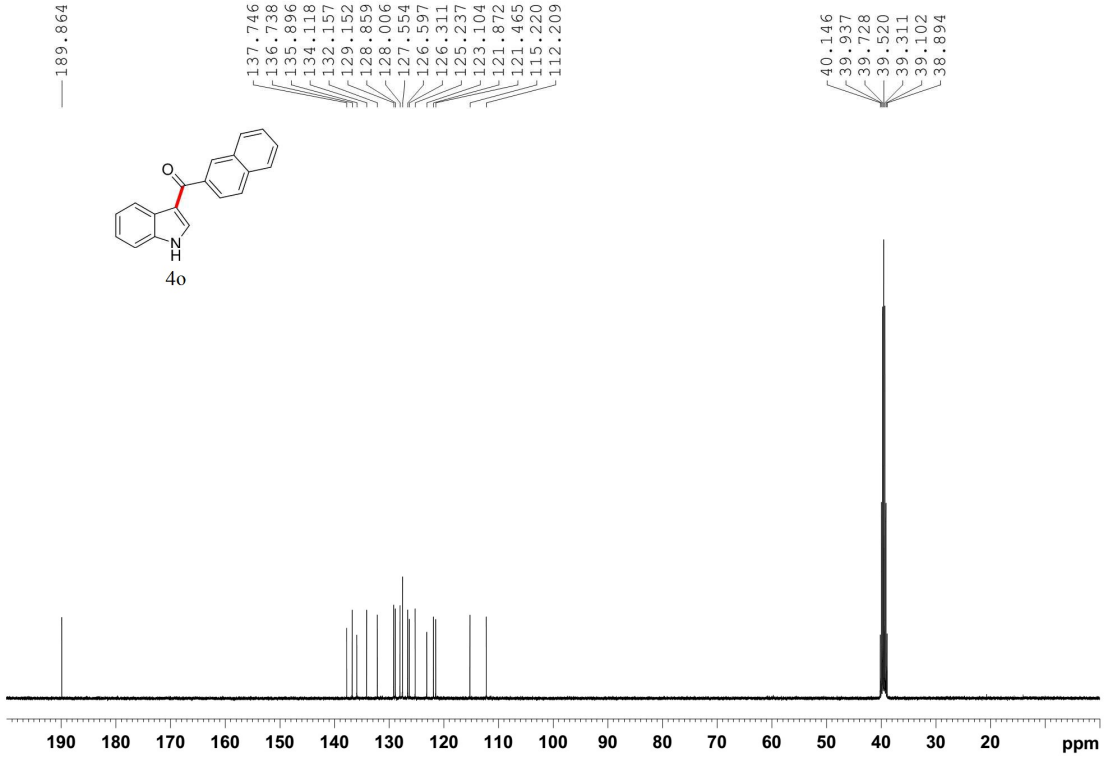

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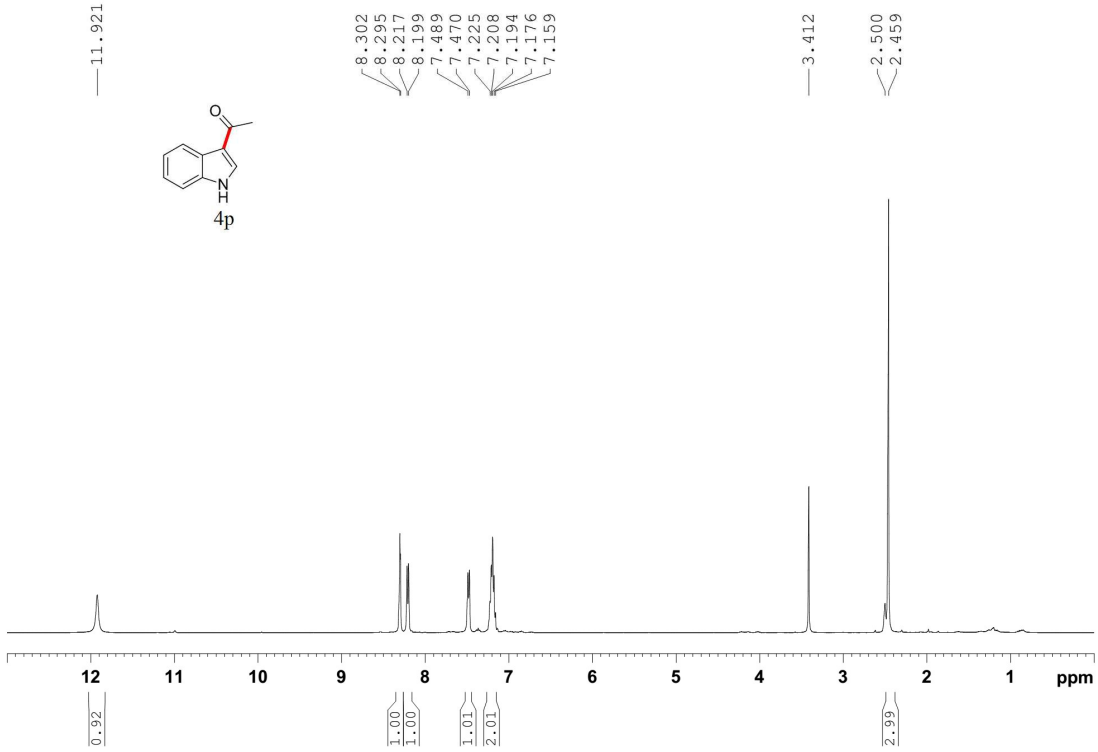

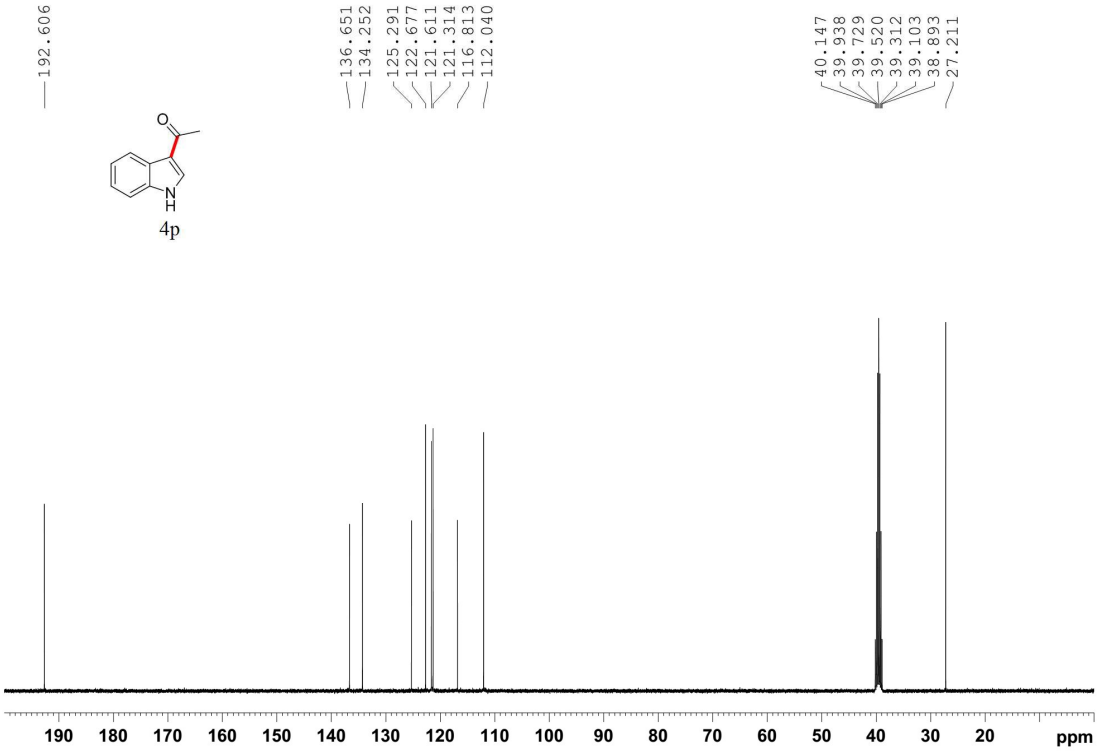

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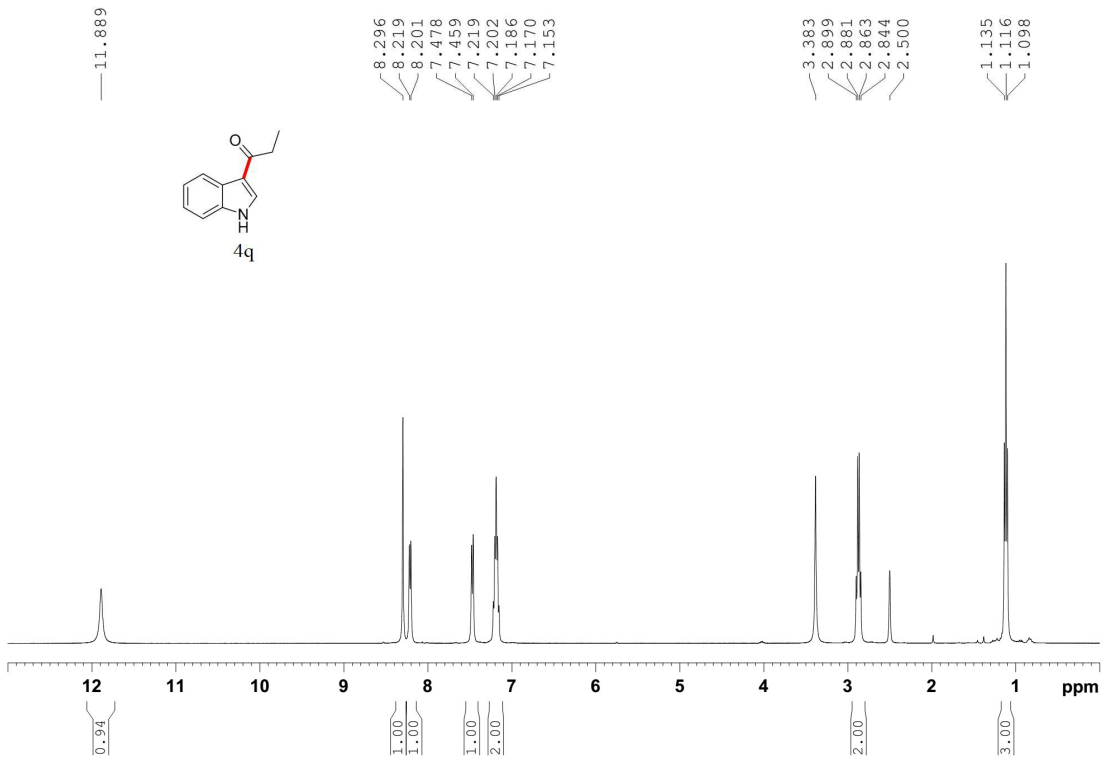

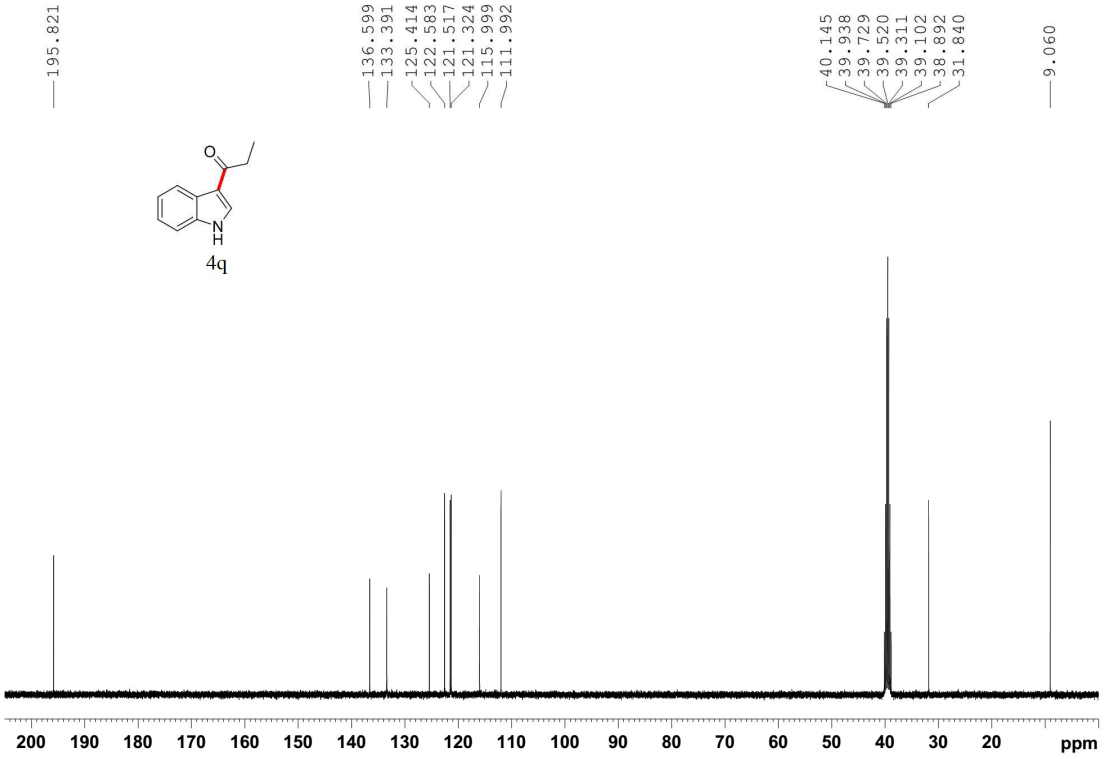

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