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Graphical Abstract

Metal-Free Cross-Dehydrogenative Coupling of Benzimidazoles with Aldehydes to *N*-Acylbenzimidazoles

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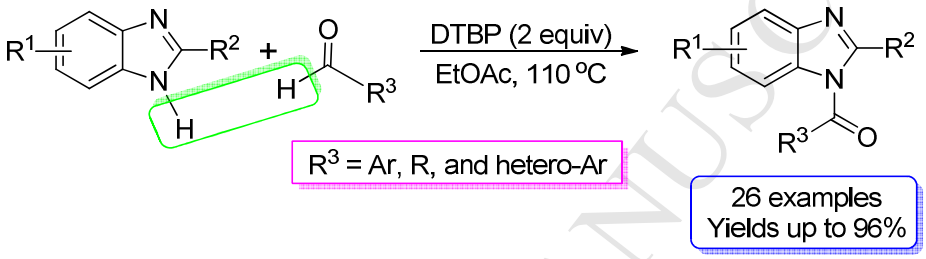

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ABSTRACT

A novel and direct cross-dehydrogenative coupling (CDC) between benzimidazoles with aldehydes promoted by di-*tert*-butyl peroxide (DTBP) was developed. The reactions generated the corresponding *N*-acylbenzimidazoles in good yields under metal-free conditions. This method has broad substrate scope and high efficiency.

1. Introduction

The formation of amide bonds is one of the most significant organic reactions, as the structural motif with amide bonds is a ubiquitous substructure of many biologically relevant molecules, such as proteins, natural products, pharmaceuticals, and synthetic intermediates.[1] Traditionally, amides are prepared from the condensation of carboxylic acids with amines, which generally relies on the use of coupling agents[2] or conversion into more reactive derivatives (acyl halides or anhydrides).[3] Nevertheless, these methods suffer from the use of hazardous or expensive reagents, instability of activated carboxylic acid derivatives, and/or poor atom-efficiency. In the past decade, a number of new strategies for the construction of amide bonds have been developed, such as the modified Staudinger reaction,[4] Schmidt reaction,[5] rearrangement of oximes,[6] amidation of nitriles,[7] oxidative coupling between alcohols and amines,[8] acylation of amines,[9] aminocarbonylation of alkenes,[10] alkynes,[11] and haloarenes,[12] Mn- and Fe-catalyzed C–C bond cleavage,[13] and oxidative amidation of aldehydes.[14] Among the emerging amide formation methods, the direct oxidative amidation of aldehydes with amines is the most elegant atom economic approach, which involves C–H activation of aldehydes and N–H activation of amines, namely, cross-dehydrogenative coupling reaction (CDC). The CDC reaction is one of the most attractive and atom-economic synthetic approaches and has been widely applied in the C–C and C–heteroatom bond formations.[15] Most recently, the synthesis of amides from aldehydes with amines via cross-dehydrogenative coupling reaction under metal-free conditions is a more attractive route because it can overcome the drawbacks of the expensive, poisonous, and air-sensitive properties of metals or organometallics.[14m-u] A variety of metal-free systems, such as *N*-heterocyclic carbene-catalyzed redox systems,[14p-r] *tert*-butyl hydroperoxide (TBHP),[14n,o] diacetoxyiodobenzene (DIB),[14m,s] hydrogen peroxide (H_2O_2),[14t] and NaOCl[14u] have been developed. In the above reactions, aliphatic amines are popular substrates, but aromatic amines are less explored.[14m-u] To date, N–H of aromatic heterocycles, such as pyrroles, pyrazoles, imidazoles, benzimidazoles and indoles used for the cross-dehydrogenative coupling reaction with aldehydes is rarely investigated.

N-Acylation of benzimidazoles are important organic reactions, because acylation not only can provide sufficient protection for benzimidazoles, but also *N*-acylbenzimidazoles are generally considered to be mild acylation agents for kinetic resolution.[16] In the past decades, the synthesis of *N*-acyl aromatic heterocyclic compounds was mainly through the reactions of heterocycles with acyl halides in the presence of a base. However, the methods are not environmentally friendly and atom economical, as they require more than stoichiometric amounts of base and generate halide and/or other wastes. To develop a more environmentally friendly and atom economical route to *N*-acylbenzimidazoles from readily available starting materials is desirable. Herein, we present our recent results on metal-free

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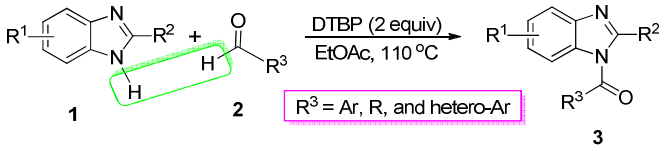
cross-dehydrogenative coupling of benzimidazoles with aldehydes to *N*-acylbenzimidazoles. This direct oxidative coupling of benzimidazoles with aldehydes promoted by di-*tert*-butyl peroxide (DTBP) generated the corresponding products *N*-acylbenzimidazoles in good yields. The method has broad aldehyde scope, including aryl, alkenyl and alkyl aldehydes, and high efficiency (Scheme 1).



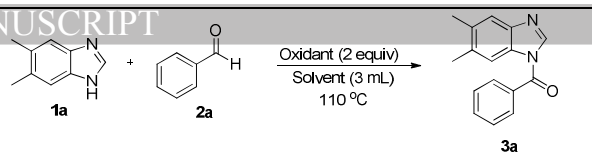
Scheme 1 The direct cross-dehydrogenative coupling of benzimidazoles with aldehydes

2. Results and Discussion

Our initial efforts focused on the direct coupling between 5,6-dimethyl-1*H*-benzo[*d*]imidazole (**1a**) and benzaldehyde (**2a**) to examine suitable reaction conditions and the selected screening results were listed in Table 1. Firstly, various oxidants were tested for the proposed reaction using EtOAc as solvent at 110 °C for 15 h (Table 1, entries 1–7). The oxidant plays an important role in the reaction, and among examined oxidants, di-*tert*-butyl peroxide (DTBP) exhibited the highest reactivity to the reaction, providing 88% yield of the desired product (5,6-dimethyl-1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methanone (**3a**) (Table 1, entry 1). *tert*-Butyl hydroperoxide (TBHP) was subsequently inferior with 84% yield of **3a** (Table 1, entry 2). Moderate yield of **3a** were obtained using *tert*-butyl perbenzoate (TBPB), cumyl hydroperoxide or diacetoxyiodobenzene (DIB) as oxidant (Table 1, entries 3–5). However, trace amounts of **3a** were observed in the presence of cyclohexanone peroxide, $(C_6H_5COO)_2$ or H_2O_2 (Table 1, entries 6–8). No desired product was detected in the absence of oxidant. We also surveyed the effect of solvent on the model reaction and toluene was found to be equally effective as EtOAc (Table 1, entry 9), while CH_3CN, dioxane, C_6H_5Cl, $ClCH_2CH_2Cl$, CH_3NO_2, NMP, DMSO and DMF resulted in diminished yields, providing 23–63% yields of **3a** (Table 1, entries 10–17). When the reaction was conducted in DMA, C_2H_5OH, THF or $CH_3OCH_2CH_2OCH_3$, no desired product was obtained (Table 1, entries 18–21). The addition of 4 Å molecular sieves (50 mg) slightly increased the yield of **3a** up to 93% (Table1, entry 22). For the amount of DTBP used in the reaction, less than 2 equiv of DTBP led to the incompletion of the reaction (Table1, entry 23). Meanwhile, up to 3 equiv of DTBP did not increase the yield of **3a** significantly (Table1, entry 24). The effect of temperature on the reaction was also surveyed and the results indicated that the yield of **3a** was not improved when the reaction temperature was increased to 120 °C (Table1, entry 25), but an obviously lower yield was observed when the reaction was performed at 100 °C (Table1, entry 26). Thus, the optimized reaction conditions for the reaction were found to be DTBP (2 equiv), 4 Å molecular sieves (50 mg) in ethyl acetate at 110 °C for 15 h.

The scope of the substrates toward this direct cross-dehydrogenative coupling of benzimidazoles with aldehydes was further investigated under the optimized reaction conditions, and

Table 1 Optimization of the reaction conditions for the model reaction **1a** with **2a** [a]

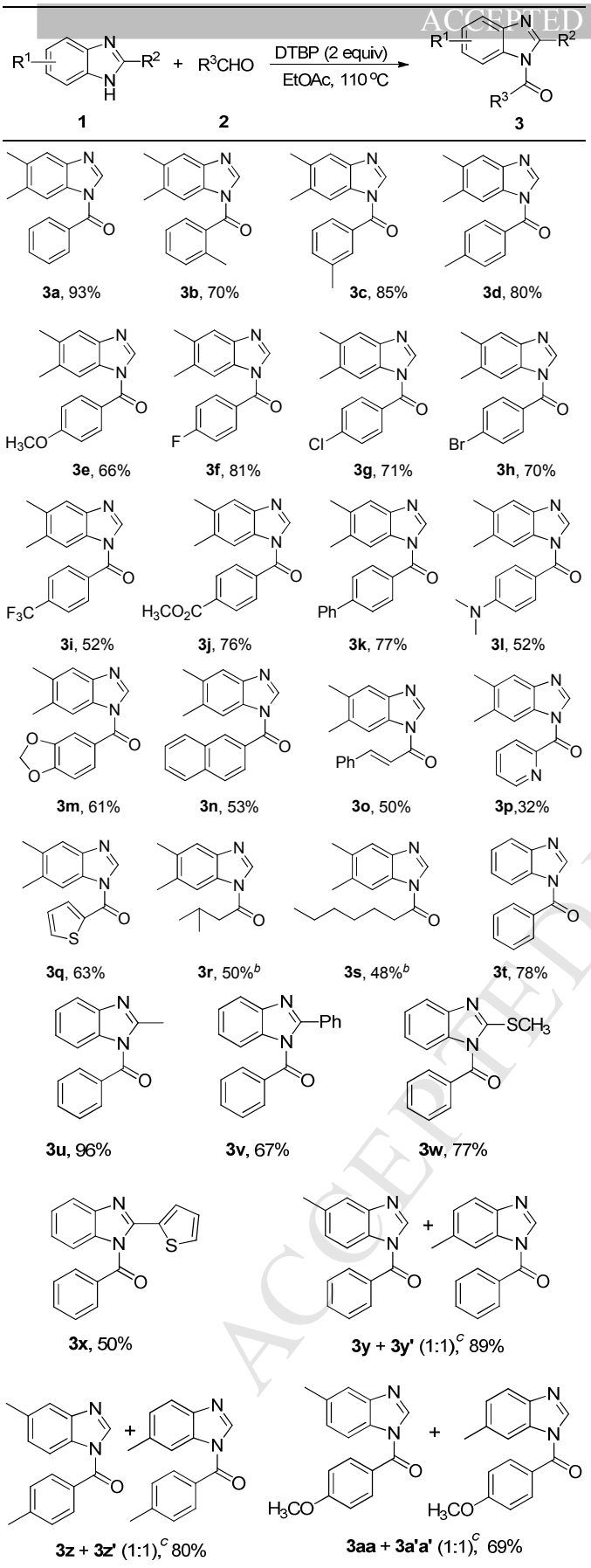


Entry	Oxidant	Solvent	Yield(%) [b]
1	DTBP	EtOAc	88
2	TBHP	EtOAc	84
3	TBPB	EtOAc	63
4	Cumyl hydroperoxide	EtOAc	50
5	DIB	EtOAc	45
6	Cyclohexanone peroxide	EtOAc	Trace
7	$(C_6H_5COO)_2$	EtOAc	Trace
8	H_2O_2	EtOAc	Trace [c]
9	DTBP	Toluene	88
10	DTBP	CH_3CN	63
11	DTBP	Dioxane	53
12	DTBP	C_6H_5Cl	58
13	DTBP	$ClCH_2CH_2Cl$	60
14	DTBP	CH_3NO_2	35
15	DTBP	NMP	30
16	DTBP	DMSO	27
17	DTBP	DMF	23
18	DTBP	DMA	NR
19	DTBP	C_2H_5OH	NR
20	DTBP	THF	NR
21	DTBP	$CH_3OCH_2CH_2OCH_3$	NR
22	DTBP	EtOAc	93 [d]
23	DTBP	EtOAc	56 [e]
24	DTBP	EtOAc	93 [f]
25	DTBP	EtOAc	89 [g]
26	DTBP	EtOAc	64 [h]

[a] Reaction conditions: **1a** (0.50 mmol), **2a** (1.0 mmol), oxidant (2.0 equiv.), solvent (3.0 mL), 110 °C, 15 h, sealed tube, under nitrogen. [b] Isolated yields. [c] 30% H_2O_2 aqueous solution. [d] Addition of 4 Å molecular sieves (50 mg). [e] DTBP (1.0 equiv.). [f] DTBP (3.0 equiv.). [g] 120 °C. [h] 100 °C.

examined in the reaction with 5,6-dimethyl-1*H*-benzo[*d*]imidazole (**1a**), and good to excellent yields of the corresponding products were obtained. Aromatic aldehydes bearing electron-donating groups, such as Me, MeO, *N*,*N*-$(CH_3)_2N$, and OCH_2O, or electron-withdrawing ones including F, Cl, Br, Ph, CF_3, and CO_2CH_3 reacted with **1a** smoothly to afford the desired corresponding products (Table 2, **3b**–**m**). Apparently, the reaction is sensitive to steric hindrance as the reaction with 2-methylbenzaldehyde afforded the corresponding amide **3b** in lower yield than with 3-methylbenzaldehyde or 4-methylbenzaldehyde (**3b** vs **3c** and **3d**). But relatively speaking, benzaldehyde gave much improved yield of the desired product **3a** than in the case of substituted benzaldehydes (Table 2, **3a** vs **3b**–**m**). The substrates 2-naphthaldehyde and cinnamaldehyde also displayed good reactivity, affording **3n** and **3o** in moderate yields. It is noteworthy that heteroaromatic aldehydes, such as picolinaldehyde and thiophene-2-carbaldehyde could react with **1a** and were converted into their corresponding amides in 32% and 63% yields, respectively (Table 2, **3p** and **3q**). However, when aliphatic aldehydes, for example 3-methylbutanal and heptanal, were tested under the optimized reaction conditions, only trace amount of products were detected. Gratifyingly, when 10 mol% $Cu(OAc)_2$ was added, the yields were increased to 50% and 48%, respectively (Table 2, **3r** and **3s**).

Table 2 Oxidative amidation of aldehydes with benzimidazoles[a]

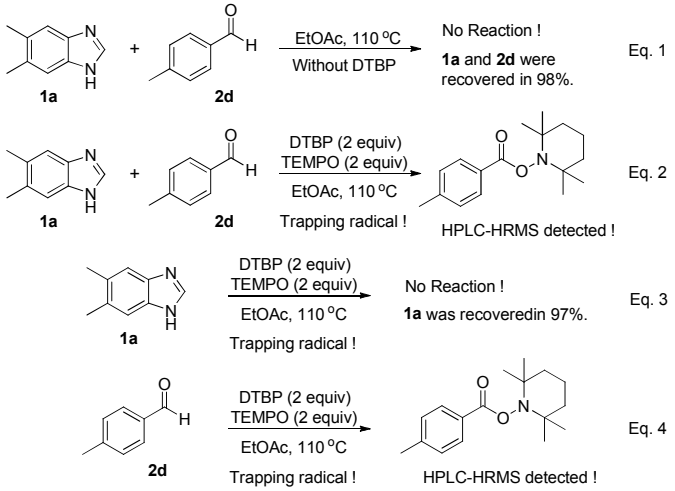


[a] Reaction conditions: benzimidazole (**1**, 0.50 mmol), aldehyde (**2**, 1.0 mmol), DTBP (2.0 equiv), 4 Å molecular sieves (50 mg) in ethyl acetate (3.0 mL) at 110 °C for 15 h, sealed tube, under nitrogen. [b] Addition of 10 mol% $Cu(OAc)_2$. [c] The ratio was determined by ^1H NMR spectra.

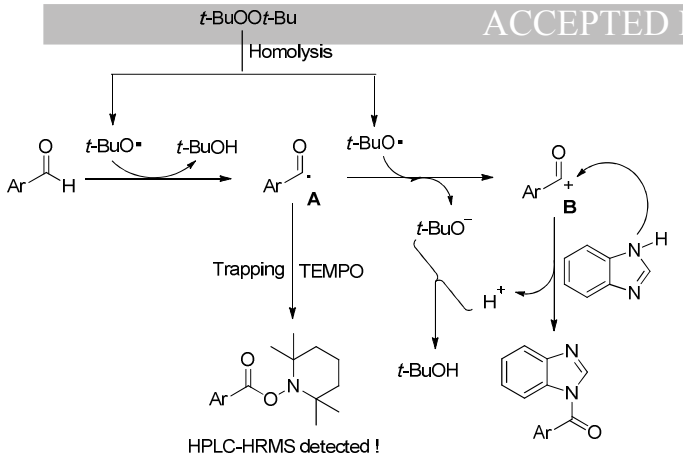
The present reaction conditions were also suitable for the reactions of benzaldehyde with other benzimidazoles. Among the methyl-substituted benzimidazoles, no matter what positions, resulted in high yields of the corresponding products (**3a** and **3u** *vs* **3t**). Especially for the reaction of 2-methyl-1*H*-benzo[*d*]imidazole with benzaldehyde provided the desired product in almost quantitative yield (**3u**). Even if bulky 2-substituted benzimidazoles, such as 2-phenyl-1*H*-benzo[*d*]imidazole, 2-(methylthio)-1*H*-benzo[*d*]imidazole and 2-(thiophen-2-yl)-1*H*-benzo[*d*]imidazole, reacted with benzaldehyde, corresponding *N*-acyl products **3v**, **3w**, and **3x** were isolated in 67%, 77%, and 50% yields, respectively. Owing to the tautomerism, when 5-methyl-1*H*-benzo[*d*]imidazole was engaged in the system, the reactions generated the mixtures of amides isomers with almost 1:1 ratio, which determined by ^1H NMR spectra (Table 2, **3y** and **3y'**, **3z** and **3z'**, **3aa** and **3a'a'**).[17] However, no desired product was obtained for the reactions of 4-hydroxybenzaldehyde or 4-formylbenzoic acid with **1a**, and 1*H*-benzo[*d*]imidazole-5-carboxylic acid with 4-methylbenzaldehyde under the present reaction conditions.

To investigate the reaction mechanism, the related control experiments were conducted, as shown in Scheme 2. No any product was detected when the reaction of **1a** and 4-methylbenzaldehyde (**2d**) was carried out in the absence of oxidant DTPB, and the starting materials were recovered in 98% (Scheme 2, Eq. 1). When 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO, 2.0 equiv), a radical scavenger, was added to the reaction of **1a** with **2d** under the optimized reaction conditions, the coupling product of acyl radical generated from **2d** with TEMPO was confirmed by HPLC-HRMS (Scheme 2, Eq. 2, and SI for detail). It is suggested that TEMPO acts as a radical scavenger and the reaction involves a radical process. On the other hand, from Eq. 3 and Eq. 4 in Scheme 2, it also verified that the formation of the amidation product is not through the direct-cross coupling of the acyl radical from aldehyde and the nitrogen radical from benzimidazole in the presence of DTBP.

Based on our results and literature,[18] a possible mechanism for this reaction was proposed in Scheme 3. Initially, homolysis of DTBP gave the *tert*-butoxy radical. The formed *tert*-butoxy radical abstracted H from aldehyde to generate the corresponding acyl radical **A**, which was further oxidized by *tert*-butoxy radical to afford acyl cation **B**.[18] Finally, the desired amidation product was formed through a nucleophilic reaction of amine (benzimidazole) to intermediate **B**.



Scheme 2 The related control experiments



Scheme 3 Proposed reaction mechanism

3. Conclusions

In conclusion, we have developed a novel and efficient method for the preparation of *N*-acylbenzimidazoles *via* cross-dehydrogenative coupling of benzimidazoles with aldehydes in the presence of di-*tert*-butyl peroxide under metal-free conditions. Compared to previously known approaches, the simplicity of this procedure and the generally satisfactory yields make this method particularly attractive. In addition, the method has broad aldehyde scope, including aryl, alkenyl and alkyl aldehydes and high efficiency. The presence of a diverse range of substituents and functional groups in benzimidazoles and aldehydes also opens an opportunity to acquire many other derivatives. Further studies on the mechanistic details and expansion of the scope of the reaction are currently underway in our laboratory.

4. Experimental section

All reactions were carried out under N_2 atmosphere. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Avance NMR spectrometer (400 MHz or 100 MHz, respectively) with $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane 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) or a Waters Micromass GCT instrument (EI).

Typical procedure for the cross-dehydrogenative coupling of benzimidazoles with aldehydes to N-acylbenzimidazoles

A sealable reaction tube equipped with a magnetic stirrer bar was charged with 5,6-dimethyl-1*H*-benzo[*d*]imidazole (0.50 mmol, 73 mg), benzaldehyde (1.0 mmol, 106 mg), di-*tert*-butyl-peroxide (1.0 mmol, 146 mg), 4 Å molecular sieves (50 mg) and ethyl acetate (3.0 mL). The rubber septum was then replaced by a Teflon-coated screw cap, then the reaction must be under N_2 and the reaction vessel placed in an oil bath at 110 °C. After stirring the mixture at this temperature for 15 h, it was cooled to room temperature and diluted with ethyl acetate then washed with 0.5 mmol/L NaOH aqueous solution (5.0 mL×3), dried over by $MgSO_4$. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/EtOAc, 4:1 to 6:1) to afford the desired product, (5,6-dimethyl-1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methanone (**3a**, 116 mg, 93% yield).

(5,6-Dimethyl-1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methanone (3a): Yellow solid, mp 90.4–92.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (s, 1H), 7.99 (s, 1H), 7.79–7.77 (m, 2H), 7.68–7.65 (m, 1H), 7.58–7.54 (m, 3H), 2.40 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 142.4, 135.0, 134.2, 133.1, 132.9, 130.5, 129.4, 128.9, 120.5, 115.6, 20.5, 20.3. IR (KBr, cm^{-1}): 1700 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{16}H_{15}N_2O$: 251.1184. Found 251.1181.

(5,6-Dimethyl-1*H*-benzo[*d*]imidazol-1-yl)(*o*-tolyl)methanone (3b): Yellow solid, mp 83.6–84.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (s, 1H), 7.84 (s, 1H), 7.58 (s, 1H), 7.52–7.49 (m, 1H), 7.45–7.43 (m, 1H), 7.39–7.34 (m, 2H), 2.42 (s, 3H), 2.41 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6, 142.8, 142.3, 136.6, 135.1, 134.3, 133.3, 131.4, 131.3, 127.8, 126.0, 120.6, 115.7, 20.5, 20.3, 19.4. IR (KBr, cm^{-1}): 1706 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{17}H_{17}N_2O$: 265.1341. Found 265.1338.

(5,6-Dimethyl-1*H*-benzo[*d*]imidazol-1-yl)(*m*-tolyl)methanone (3c): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (s, 1H), 8.00 (s, 1H), 7.59 (s, 1H), 7.57–7.55 (m, 2H), 7.48–7.42 (m, 2H), 2.45 (s, 3H), 2.41 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 142.5, 139.0, 134.9, 134.2, 133.7, 133.1, 130.5, 129.9, 128.7, 126.6, 120.4, 115.6, 21.3, 20.5, 20.3. IR (KBr, cm^{-1}): 1696 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{17}H_{17}N_2O$: 265.1341. Found 265.1339.

(5,6-Dimethyl-1*H*-benzo[*d*]imidazol-1-yl)(*p*-tolyl)methanone (3d): White solid, mp 134.3–135.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (s, 1H), 7.97 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.56 (s, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H), 2.39 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 143.9, 142.5, 142.4, 134.8, 134.0, 130.5, 130.2, 129.7, 129.6, 120.4, 115.6, 21.6, 20.5, 20.3. IR (KBr, cm^{-1}): 1699 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{17}H_{17}N_2O$: 265.1341. Found 265.1335.

(5,6-Dimethyl-1*H*-benzo[*d*]imidazol-1-yl)(4-methoxyphenyl) methanone (3e): Yellow solid, mp 140.3–142.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 1H), 7.94 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.58 (s, 1H), 7.05 (d, *J* = 7.6 Hz, 2H), 3.92 (s, 3H), 2.41 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4, 163.6, 142.5, 142.4, 134.7, 134.0, 132.0, 130.7, 125.0, 120.4, 115.4, 114.3, 55.6, 20.5, 20.3. IR (KBr, cm^{-1}): 1688 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{17}H_{17}N_2O_2$: 281.1290, Found 281.1294.

(5,6-Dimethyl-1*H*-benzo[*d*]imidazol-1-yl)(4-fluorophenyl) methanone (3f): White solid, mp 126.5–127.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (s, 1H), 7.91 (s, 1H), 7.83–7.79 (m, 2H), 7.55 (s, 1H), 7.26–7.22 (m, 2H), 2.38 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8, 165.5 (d, *J* = 254.1 Hz), 142.4, 142.0, 135.0, 134.3, 132.1 (d, *J* = 9.2 Hz), 130.4, 129.2 (d, *J* = 3.3 Hz), 120.5, 116.3 (d, *J* = 22.1 Hz), 115.5, 20.4, 20.2. IR (KBr, cm^{-1}): 1702 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{16}H_{14}FN_2O$: 269.1090. Found 269.1086.

(4-Chlorophenyl)(5,6-dimethyl-1*H*-benzo[*d*]imidazol-1-yl) methanone (3g): White solid, mp 165.2–166.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (s, 1H), 7.95 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.58 (s, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 2.41 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 142.3, 142.0, 135.2, 134.5, 131.3, 130.9, 130.3, 129.3, 128.6, 120.5, 115.6, 20.5, 20.3. IR (KBr, cm^{-1}): 1701 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{16}H_{14}ClN_2O$: 285.0795. Found 285.0799.

(4-Bromophenyl)(5,6-dimethyl-1*H*-benzo[*d*]imidazol-1-yl) methanone (3h): White solid, mp 185.5–186.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (s, 1H), 7.95 (s, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.57 (s, 1H), 2.40 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0, 142.5, 141.9, 135.2, 134.5, 132.3, 131.8, 130.9, 130.3, 128.1, 120.6, 115.6, 20.5, 20.3. IR (KBr, cm^{-1}): 1703 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{16}H_{14}BrN_2O$: 329.0290. Found 329.0285.

(5,6-Dimethyl-1*H*-benzo[*d*]imidazol-1-yl)(4-(trifluoromethyl) phenyl)methanone (3i): Yellow solid, mp 186.3–187.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (s, 1H), 7.96 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.55 (s, 1H), 2.40 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 142.5, 141.7, 136.4, 135.3, 134.7, 134.5 (q, *J* = 32.9 Hz), 130.2, 129.7, 126.0 (q, *J* = 3.7 Hz), 123.3 (q, *J* = 271.2 Hz), 120.6, 115.6, 20.4, 20.2. IR (KBr, cm^{-1}): 1706 ($\nu_{C=O}$). HRMS (EI) ($[M]^+$): Calcd. for $C_{17}H_{13}F_3N_2O$: 318.0980, Found 318.0976.

Methyl 4-(5,6-dimethyl-1H-benzo[d]imidazole-1-carbonyl)benzoate (3j): White solid, mp 191.4–191.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (d, *J* = 8.0 Hz, 2H), 8.04 (s, 1H), 8.00 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.60 (s, 1H), 4.00 (s, 3H), 2.43 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.2, 165.7, 142.6, 141.9, 136.9, 135.3, 134.6, 134.0, 130.3, 130.1, 129.3, 120.7, 115.7, 52.6, 20.5, 20.3. IR (KBr, cm^{-1}): 1731 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{18}H_{17}N_2O_3$: 309.1239, Found 309.1237.

Biphenyl-4-yl(5,6-dimethyl-1*H*-benzo[*d*]imidazol-1-yl) methanone (3k): White solid, mp 186.9–187.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (s, 1H), 8.03 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.60 (s, 1H), 7.53–7.49 (m, 2H), 7.46–7.42 (m, 1H), 2.43 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 145.9, 142.6, 142.3, 139.4, 135.0, 134.2, 131.6, 130.5, 130.1, 129.0, 128.5, 127.5, 127.3, 120.5, 115.7, 20.5, 20.3. IR (KBr, cm^{-1}): 1692 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{22}H_{19}N_2O$: 327.1497, Found 327.1496.

(5,6-Dimethyl-1*H*-benzo[*d*]imidazol-1-yl)(4-(dimethylamino) phenyl)methanone (3l): Yellow solid, mp 197.1–199.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (s, 1H), 7.90 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.58 (s, 1H), 6.73 (d, *J* = 9.2 Hz, 2H), 3.09 (s, 6H), 2.40 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 153.6, 142.6, 142.4, 134.3, 133.4, 132.3, 131.0, 120.2, 118.6, 115.3, 111.0, 40.0, 20.5, 20.2. IR (KBr, cm^{-1}): 1675 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{18}H_{20}N_3O$: 294.1606, Found 294.1601.

Benzo[*d*][1,3]dioxol-5-yl(5,6-dimethyl-1*H*-benzo[*d*]imidazol-1-yl)methanone (3m): Yellow solid, mp 187.9–188.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (s, 1H), 7.92 (s, 1H), 7.56 (s, 1H), 7.35–7.33 (m, 1H), 7.28 (s, 1H), 6.95–6.93 (m, 1H), 6.10 (s, 2H), 2.40 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0, 151.9, 148.3, 142.5, 142.3, 134.8, 134.1, 130.6, 126.6, 125.6, 120.4, 115.4, 109.8, 108.3, 102.2, 20.4, 20.2. IR (KBr, cm^{-1}): 1681 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{17}H_{15}N_2O_3$: 295.1083, Found 295.1082.

(5,6-Dimethyl-1*H*-benzo[*d*]imidazol-1-yl)(naphthalen-2-yl) methanone (3n): Yellow solid, mp 155.0–156.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (s, 1H), 8.18 (s, 1H), 8.04 (s, 1H), 8.02–7.99 (m, 1H), 7.96–7.93 (m, 2H), 7.85–7.83 (m, 1H), 7.68–7.60 (m, 3H), 2.42 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 142.6, 142.5, 135.2, 135.0, 134.2, 132.2, 130.9, 130.6, 130.2, 129.1, 129.0, 128.8, 127.9, 127.4, 125.1, 120.5, 115.7, 20.5, 20.3. IR (KBr, cm^{-1}): 1699 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{20}H_{17}N_2O$: 301.1341, Found 301.1341.

(*E*)-1-(5,6-Dimethyl-1*H*-benzo[*d*]imidazol-1-yl)-3-phenylprop-2-en-1-one (3o): White solid, mp 222.7–223.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (s, 1H), 8.12 (s, 1H), 8.09–8.05 (m, 1H), 7.68–7.67 (m, 2H), 7.58 (s, 1H), 7.48 (s, br, 3H), 7.23–7.19 (m, 1H), 2.43 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.8, 148.4, 142.5, 139.9, 135.0, 134.1, 133.8, 131.3, 130.2, 129.1, 128.6, 120.5, 116.0, 115.8, 20.5, 20.2. IR (KBr, cm^{-1}): 1702 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{18}H_{17}N_2O$: 277.1341, Found 277.1341.

(5,6-Dimethyl-1*H*-benzo[*d*]imidazol-1-yl)(pyidin-2-yl) methanone (3p): Yellow solid, mp 128.9–130.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.27 (s, 1H), 8.79 (d, *J* = 4.4 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 8.19 (s, 1H), 8.00–7.96 (m, 1H), 7.60–7.57 (m, 2H), 2.43 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.0, 150.5, 148.7, 144.0, 141.8, 137.6, 134.7, 134.2, 130.7, 127.0, 126.4, 120.4, 116.4, 20.5, 20.2. IR (KBr, cm^{-1}): 1685 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{15}H_{14}N_3O$: 252.1137, Found 252.1133.

(5,6-Dimethyl-1*H*-benzo[*d*]imidazol-1-yl)(thiophen-2-yl) methanone (3q): Yellow solid, mp 132.5–133.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (s, 1H), 7.97 (s, 1H), 7.80 (d, *J* = 5.2 Hz, 1H), 7.76 (d, *J* = 3.2 Hz, 1H), 7.57 (s, 1H), 7.25–7.23 (m, 1H), 2.41 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 142.4, 141.5, 135.9, 135.0, 134.28, 134.22, 134.0, 130.6, 128.1, 120.5, 115.5, 20.5, 20.3. IR (KBr, cm^{-1}): 1677 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{14}H_{13}N_2OS$: 257.0749, Found 257.0748.

1-(5,6-Dimethyl-1*H*-benzo[*d*]imidazol-1-yl)-3-methylbutan-1-one (3r): Yellow solid, mp 78.1–80.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (s, 1H), 8.02 (s, 1H), 7.52 (s, 1H), 2.82–2.80 (m, 2H), 2.39–2.33 (m, 7H), 1.08 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.7, 142.3, 140.2, 135.0, 133.8, 129.9, 120.4, 115.8, 44.5, 25.4, 22.5, 20.4, 20.1. IR (KBr, cm^{-1}): 1724 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{14}H_{19}N_2O$: 231.1497, Found 231.1493.

1-(5,6-Dimethyl-1*H*-benzo[*d*]imidazol-1-yl)heptan-1-one (3s): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (s, 1H), 8.01 (s, 1H), 7.53 (s, 1H), 2.95 (t, *J* = 7.6 Hz, 2H), 2.38 (s, 3H), 2.36 (s, 3H), 1.88–1.81 (m, 2H), 1.47–1.41 (m, 2H), 1.38–1.33 (m, 4H), 0.92–0.89 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 142.2, 140.2, 135.1, 133.8, 129.8, 120.4, 115.8, 35.8, 31.4, 28.7, 24.3, 22.4, 20.4, 20.1, 13.9. IR (KBr, cm^{-1}): 1698 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{16}H_{23}N_2O$: 259.1810, Found 259.1810.

(1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methanone (3t):[19] Yellow solid, mp 71.7–72.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (s, 1H), 8.19–8.17 (m, 1H), 7.84–7.79 (m, 3H), 7.70–7.66 (m, 1H), 7.59–7.56 (m, 2H), 7.46–7.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 144.0, 143.0, 133.1, 132.9, 132.1, 129.5, 129.0, 125.7, 125.2, 120.5, 115.4. IR (KBr, cm^{-1}): 1699 ($\nu_{C=O}$).

(2-Methyl-1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methanone (3u):[20] Yellow solid, mp 83.3–84.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75–7.74 (m, 2H), 7.70–7.66 (m, 2H), 7.54–7.50 (m, 2H), 7.25–7.23 (m, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.81–6.78 (m, 1H), 2.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.6, 153.1, 142.4, 133.9, 133.8, 133.4, 129.8, 129.0, 123.9, 123.6, 119.4, 113.3, 17.0. IR (KBr, cm^{-1}): 1705 ($\nu_{C=O}$).

Phenyl(2-phenyl-1*H*-benzo[*d*]imidazol-1-yl)methanone (3v):[17] White solid, mp 147.3–149.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.62–7.60

(m, 2H), 7.52–7.46 (m, 2H), 7.41–7.37 (m, 1H), 7.35–7.27 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.1, 154.0, 142.9, 134.9, 134.0, 133.1, 130.5, 130.4, 129.8, 129.2, 128.7, 128.3, 124.6, 124.4, 120.2, 113.1. IR (KBr, cm^{-1}): 1702 ($\nu_{C=O}$).

(2-(Methylthio)-1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methanone (3w): White solid, mp 121.0–122.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73–7.71 (m, 2H), 7.68–7.63 (m, 2H), 7.53–7.49 (m, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.72–6.70 (m, 1H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.9, 156.0, 143.9, 134.4, 133.5, 133.0, 129.5, 128.8, 124.2, 122.8, 118.4, 113.4, 15.6. IR (KBr, cm^{-1}): 1698 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{15}H_{13}N_2OS$: 269.0749, Found 269.0753.

Phenyl(2-(thiophen-3-yl)-1*H*-benzo[*d*]imidazol-1-yl) methanone (3x): Yellow solid, mp 124.6–124.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.84 (m, 1H), 7.78–7.76 (m, 2H), 7.62–7.58 (m, 1H), 7.45–7.41 (m, 2H), 7.38–7.33 (m, 2H), 7.27–7.23 (m, 3H), 6.92–6.90 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.0, 147.9, 142.7, 134.9, 134.4, 132.8, 132.0, 130.6, 130.0, 129.0, 128.9, 127.5, 124.5, 124.4, 120.0, 112.7. IR (KBr, cm^{-1}): 1706 ($\nu_{C=O}$). HRMS (EI) ($[M]^+$): Calcd. for $C_{18}H_{12}N_2OS$: 304.0670, Found 304.0675.

(5-Methyl-1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methanone and (6-methyl-1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methanone (3y and 3y') (1:1 ratio): White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (s, 1H), 8.12 (s, 1H), 8.05–8.03 (m, 2H), 7.79–7.77 (m, 4H), 7.70–7.65 (m, 3H), 7.61 (s, 1H), 7.58–7.54 (m, 4H), 7.26–7.23 (m, 2H), 2.51 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 166.9, 144.3, 143.1, 142.6, 142.0, 136.0, 135.2, 133.07, 133.06, 133.03, 132.9, 132.3, 130.1, 129.5, 129.4, 128.9, 127.0, 126.6, 120.4, 119.9, 115.5, 114.9, 21.8, 21.5. HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{15}H_{13}N_2O$: 237.1028. Found 237.1032.

(5-Methyl-1*H*-benzo[*d*]imidazol-1-yl)(*p*-tolyl)methanone and (6-methyl-1*H*-benzo[*d*]imidazol-1-yl)(*p*-tolyl)methanone (3z and 3z') (1:1 ratio): White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (s, 1H), 8.13 (s, 1H), 8.02–8.00 (m, 2H), 7.69–7.67 (m, 5H), 7.59 (s, 1H), 7.35–7.34 (m, 4H), 7.24–7.21 (m, 2H), 2.50 (s, 3H), 2.49 (s, 3H), 2.46 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 166.9, 144.3, 144.08, 144.06, 143.1, 142.6, 142.1, 135.8, 135.0, 132.4, 130.17, 130.14, 130.0, 129.74, 129.71, 129.6, 126.8, 126.5, 120.3, 119.8, 115.4, 114.8, 21.8, 21.6, 21.5. HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{16}H_{15}N_2O$: 251.1184. Found 251.1188.

(4-Methoxyphenyl)(5-methyl-1*H*-benzo[*d*]imidazol-1-yl) methanone and (4-methoxyphenyl)(6-methyl-1*H*-benzo[*d*]imidazol-1-yl)methanone (3aa and 3a'a') (1:1 ratio): White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (s, 1H), 8.17 (s, 1H), 7.99–7.97 (m, 2H), 7.80–7.78 (m, 4H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.61 (s, 1H), 7.25–7.22 (m, 2H), 7.05–7.03 (m, 4H), 3.91 (s, 6H), 2.51 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 166.3, 163.69, 163.67, 144.3, 143.1, 142.6, 142.1, 135.7, 134.9, 132.5, 132.1, 132.0, 130.2, 126.8, 126.4, 124.95, 124.91, 120.3, 119.8, 115.2, 114.7, 114.3, 55.6, 21.8, 21.5. HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{16}H_{15}N_2O_2$: 267.1134. Found 267.1135.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2014.xx.xxx. These data include MOL files and InChIKeys of the most important compounds described in this article.

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Supplementary Information for Tetrahedron

Metal-Free Cross-Dehydrogenative Coupling of Benzimidazoles with Aldehydes to *N*-Acylbenzimidazoles

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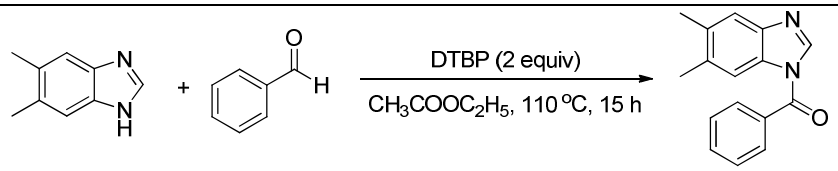
Table of Contents for Supporting Information

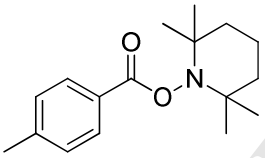
1. Effect of radical scavenger[a]



Entry	TEMPO (mol%)	Yield (%) [b]
1	0	93
2	10	60
3	20	54
4	30	55
5	50	48
6	100	27
7	200	trace
8	300	0

[a] Reaction conditions: benzimidazole (0.50 mmol), aldehyde (1.0 mmol), DTBP (1.0 mmol), 4 Å molecular sieves (50 mg), TEMPO (amount indicated in the above Table), sealed tube, 110 °C, under N_2, 15 h.
[b] Yields of isolated products after flash chromatography.

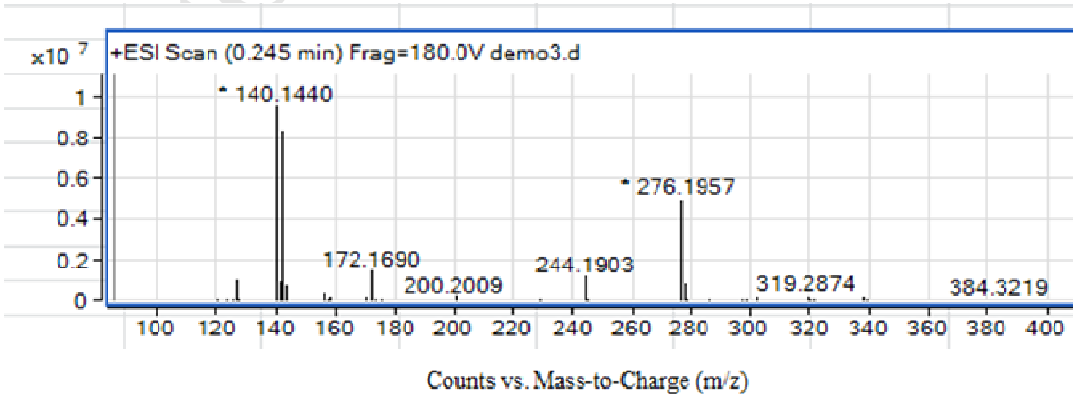
2. HPLC-HRMS of TEMPO with aldehyde



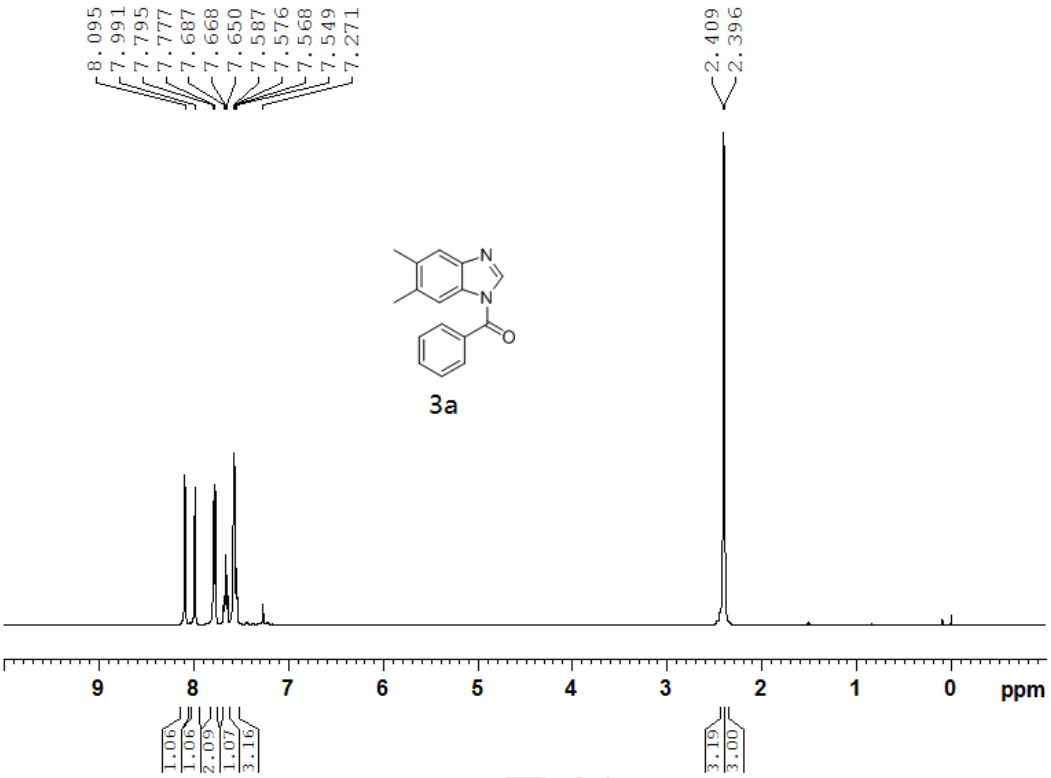
Chemical Formula: $C_{17}H_{25}NO_2$

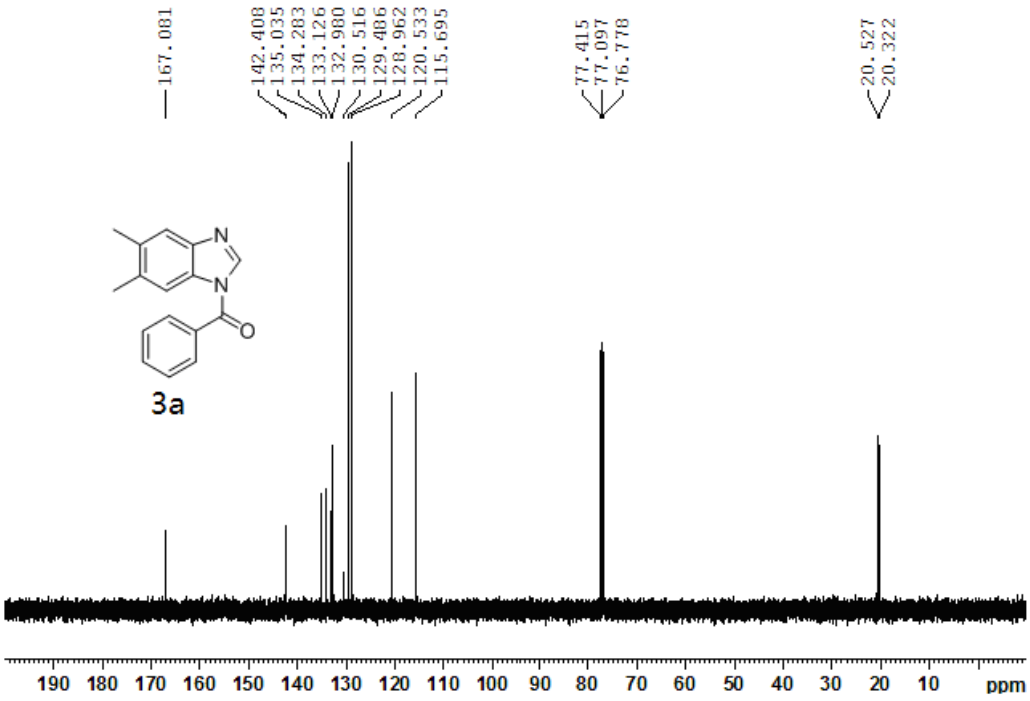
[M+H] = $C_{17}H_{26}NO_2$
Exact Mass: 276.1964
Molecular Weight: 276.3938
m/z: 276.1964 (100.0%), 277.1997 (18.4%), 278.2031 (1.6%)
Elemental Analysis: C, 73.87; H, 9.48; N, 5.07; O, 11.58

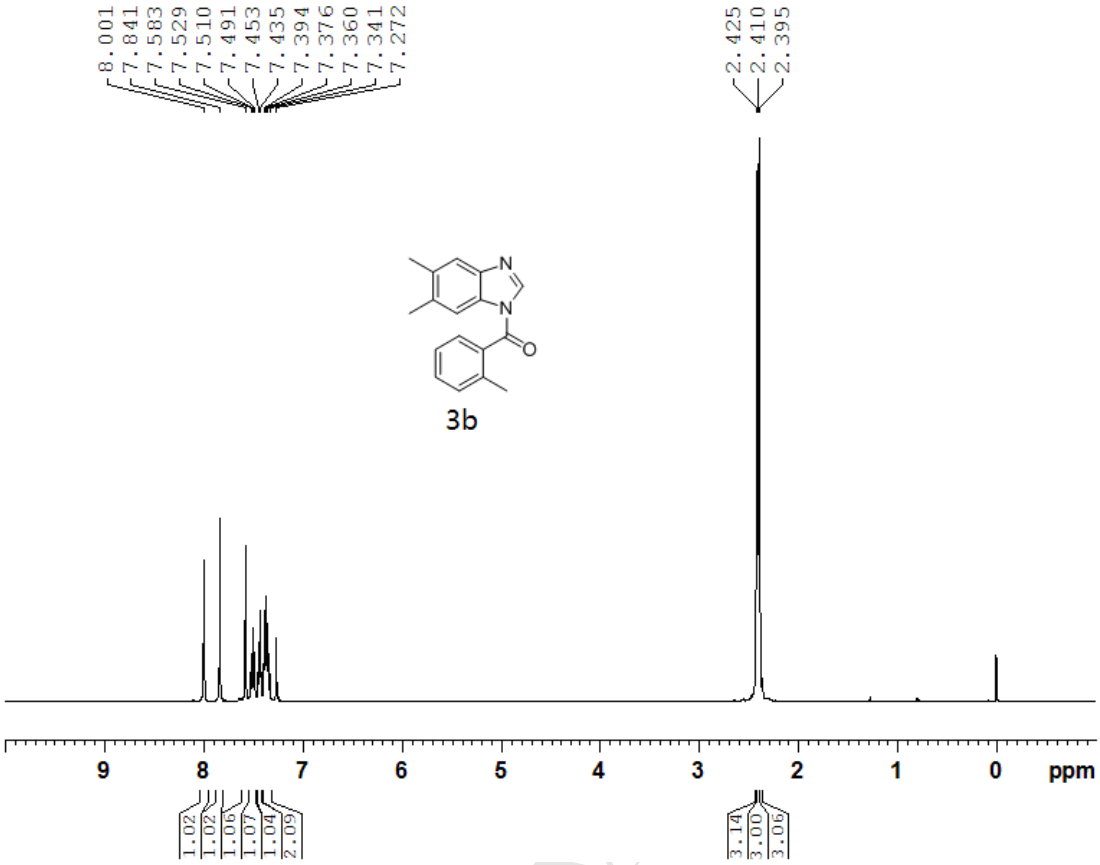
Calculated: [M+H] = 276.1964, Found: [M+H] = 276.1957



3. ^{1}H NMR and ^{13}C NMR spectra



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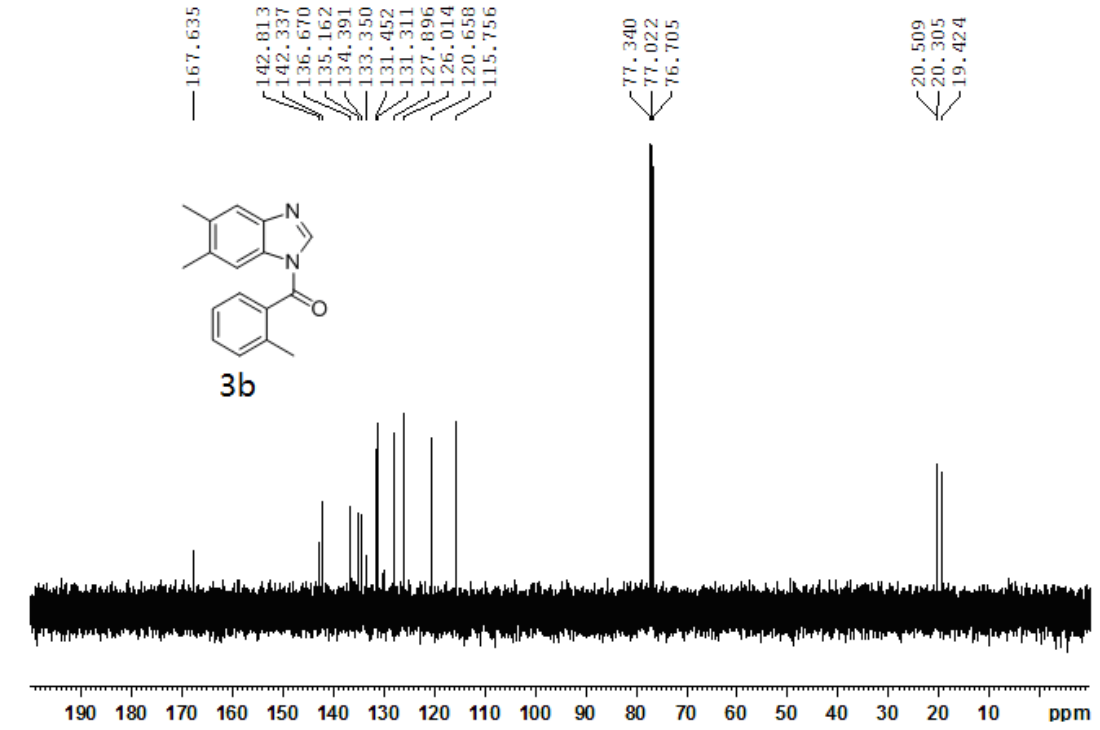
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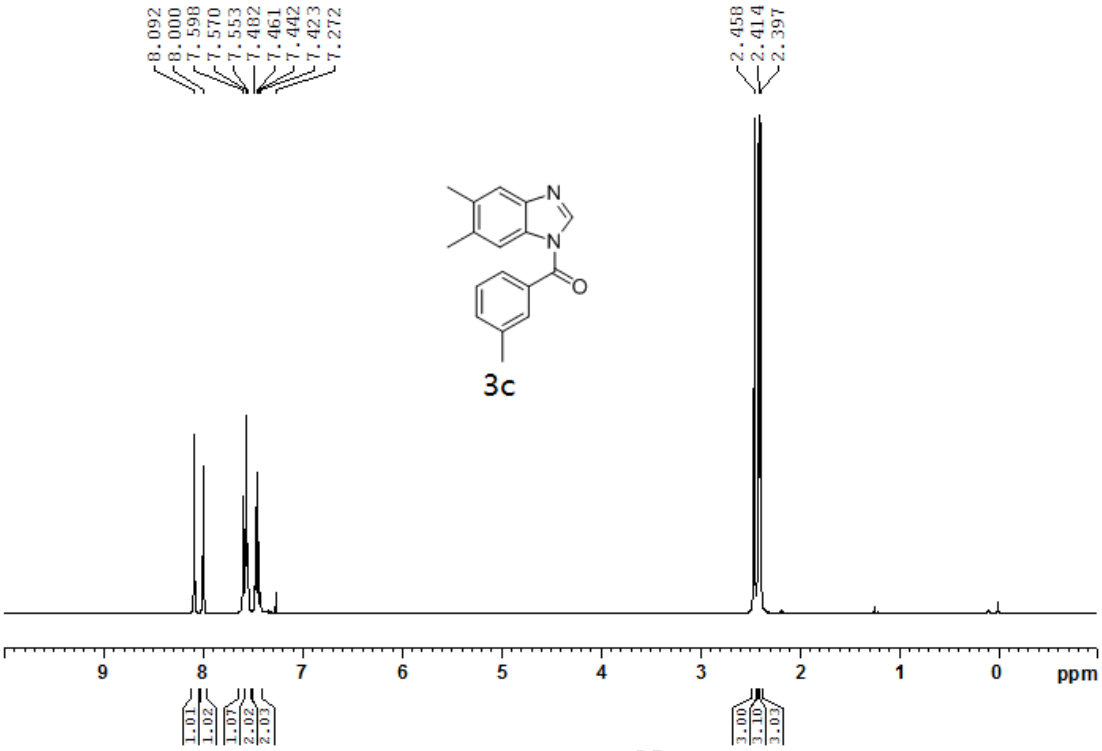
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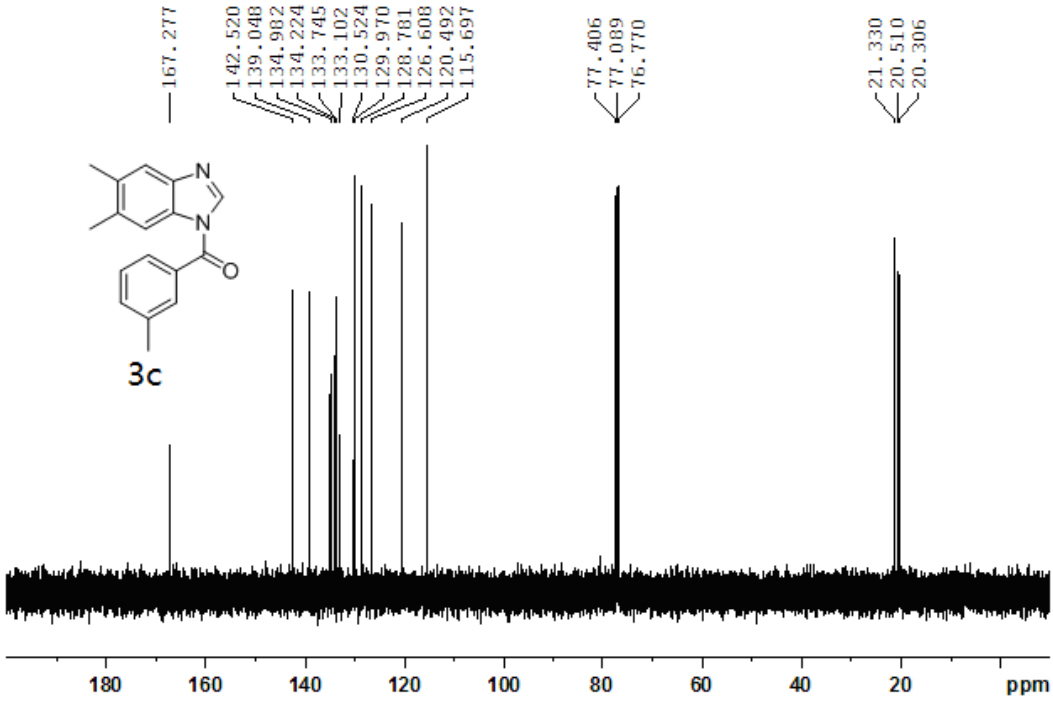
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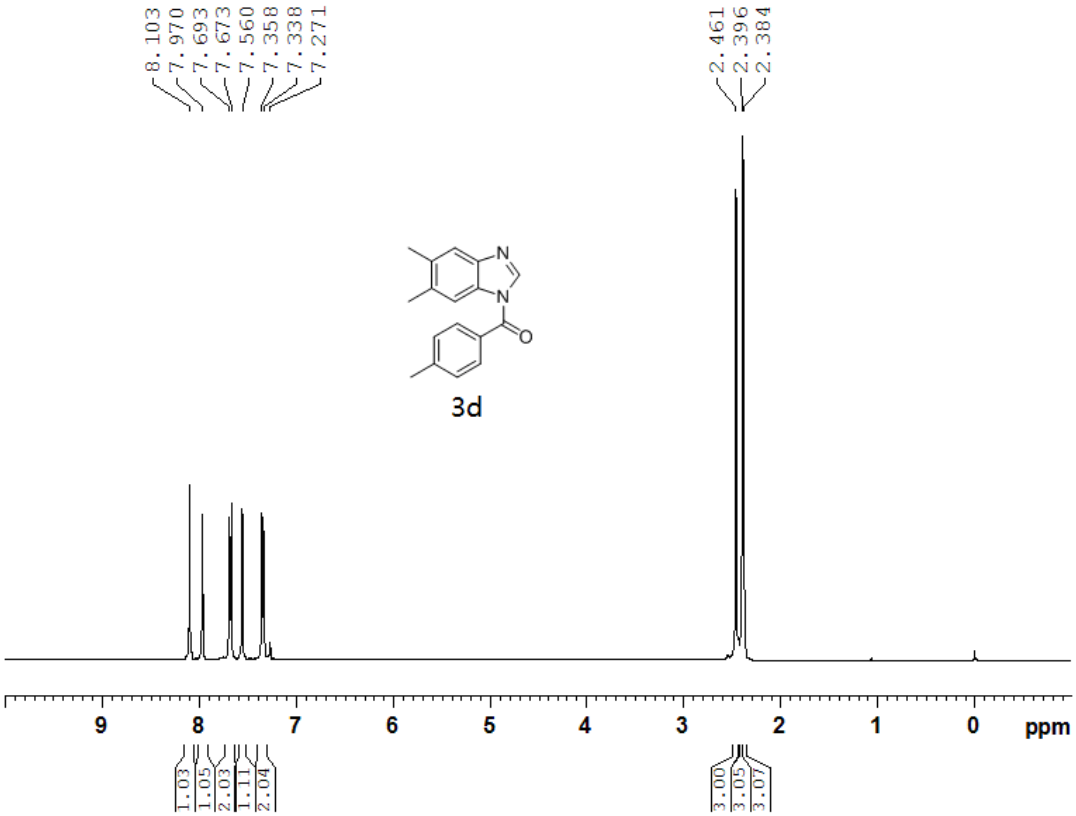
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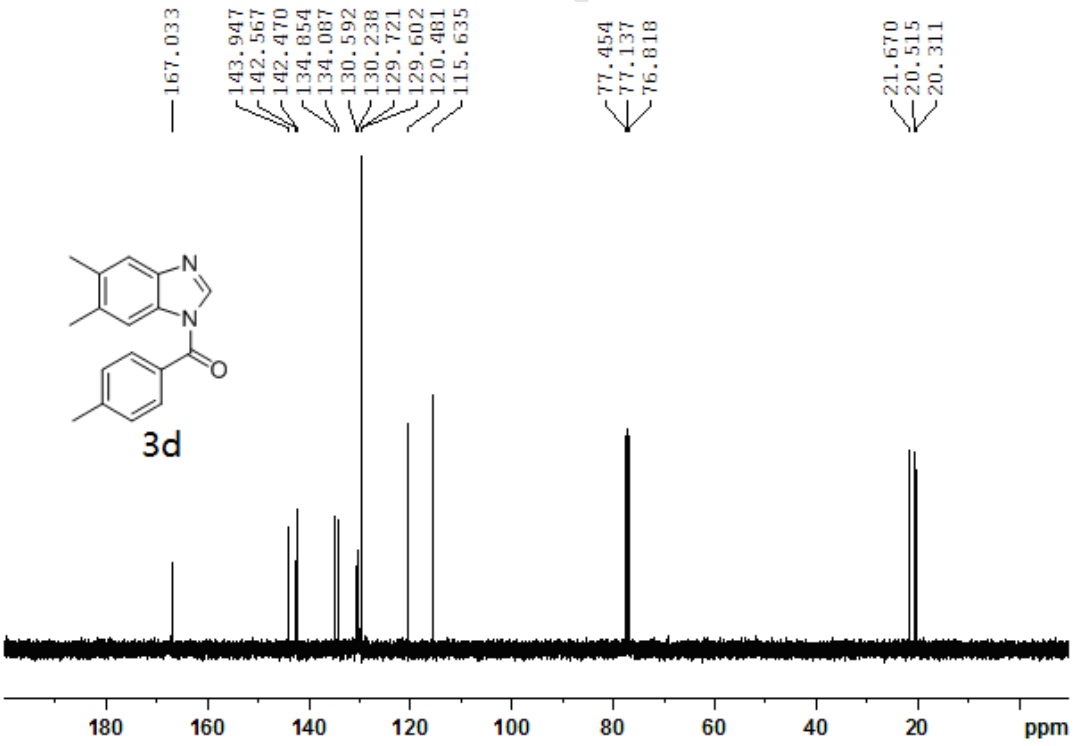
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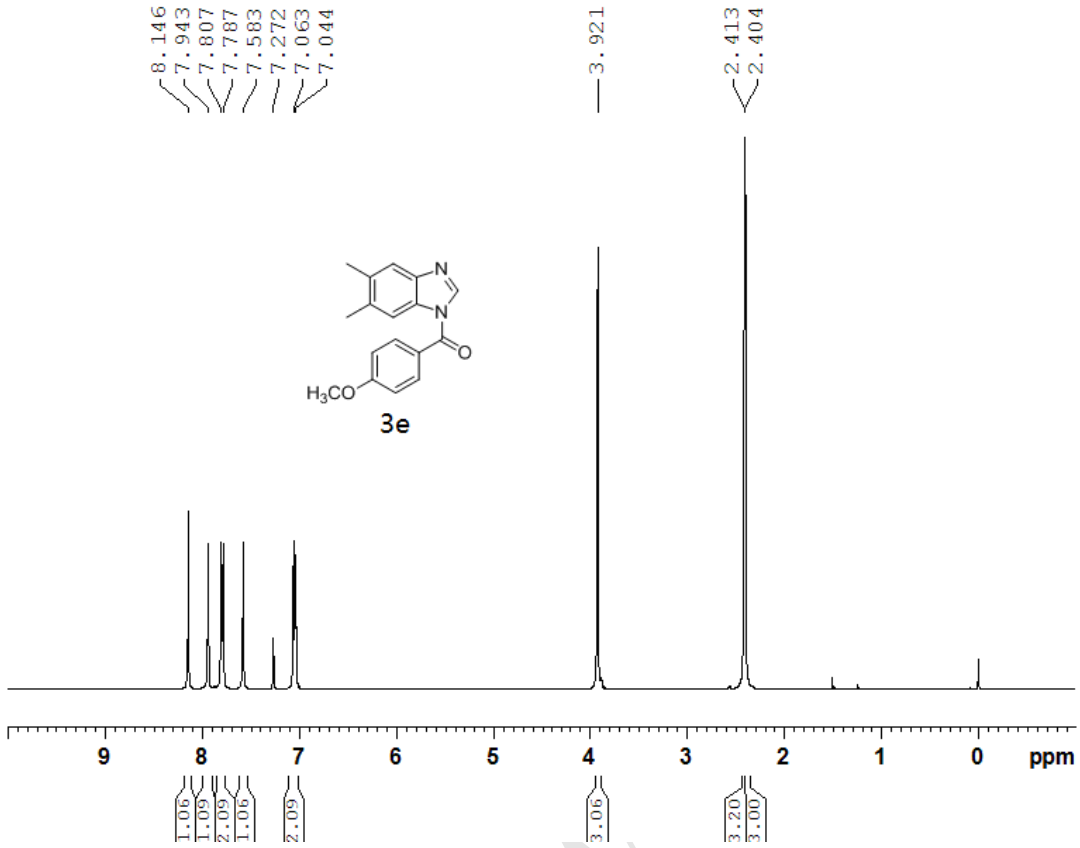
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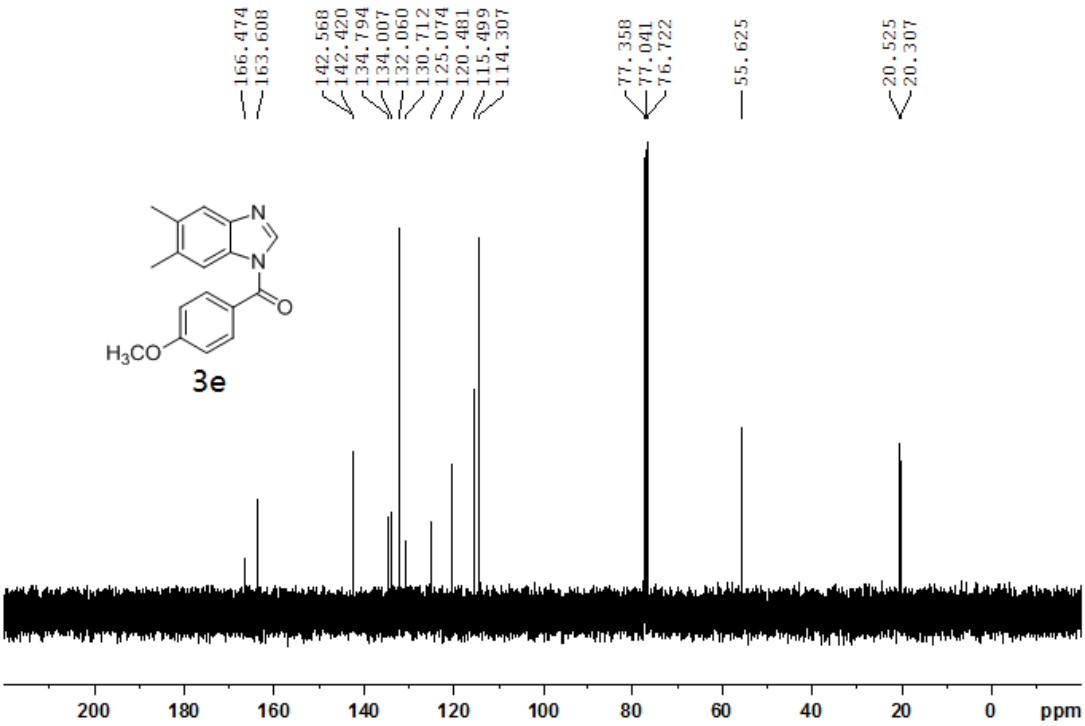
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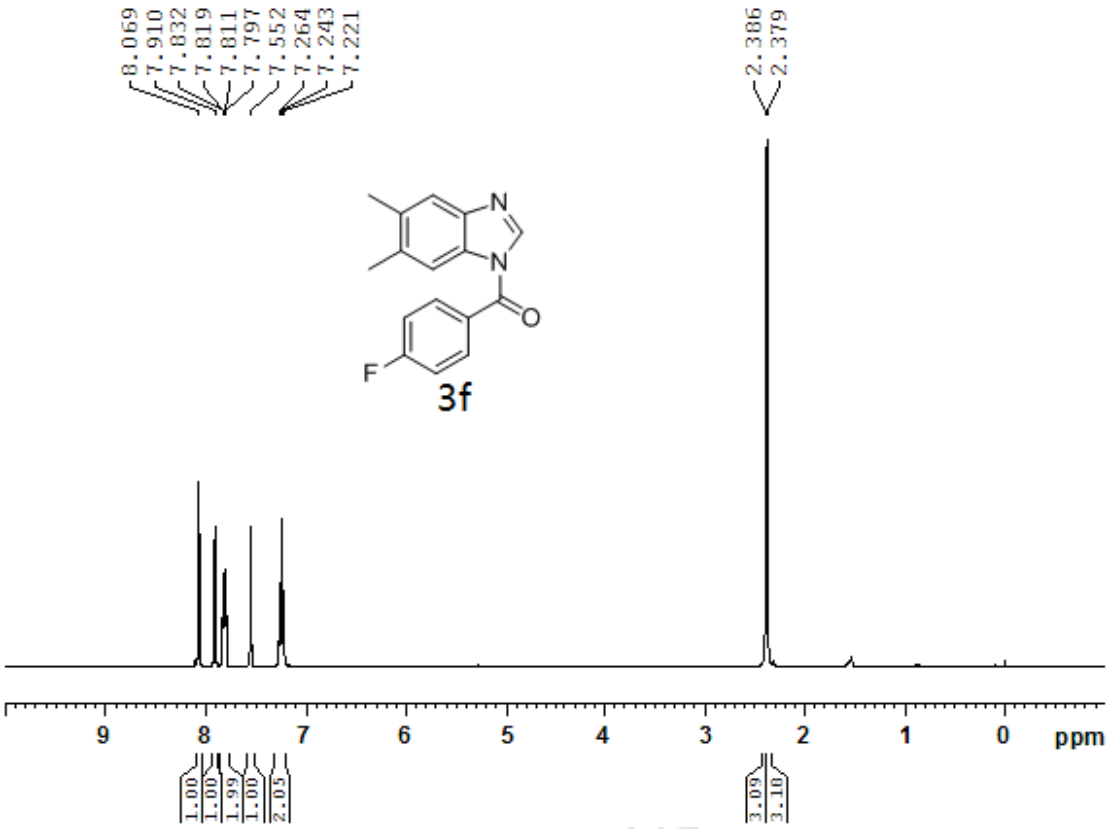
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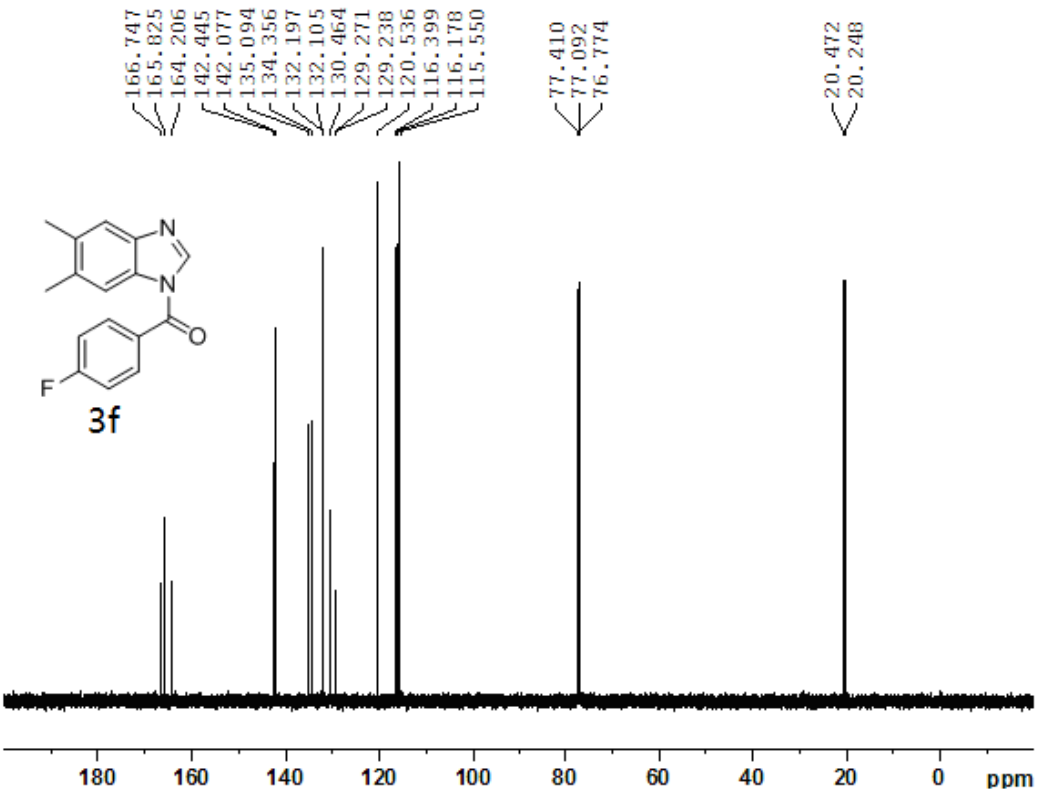
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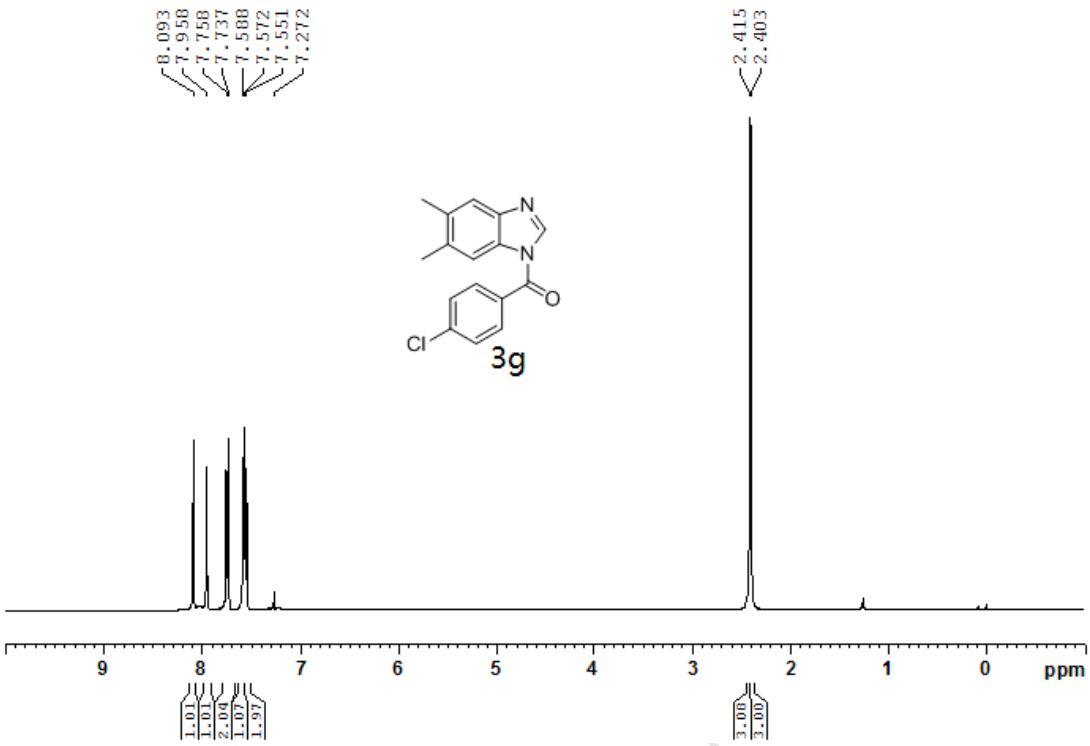
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8
7
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2.04
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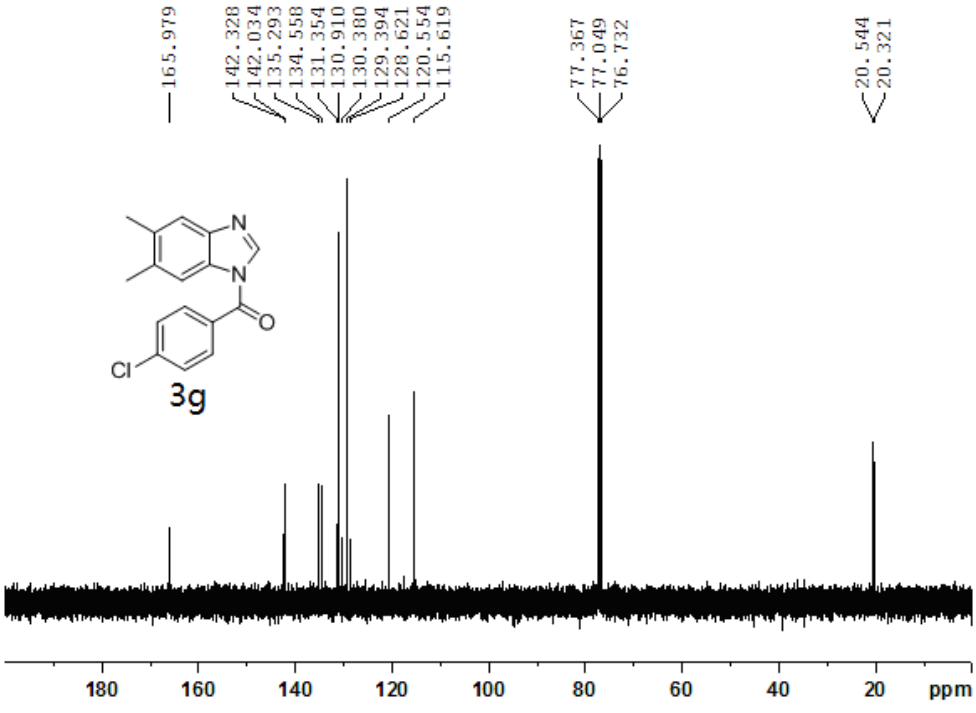
1.97
3.00
3.00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130.380
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128.621
120.554
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77.367
77.049
76.732
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N
N
O
Cl
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140
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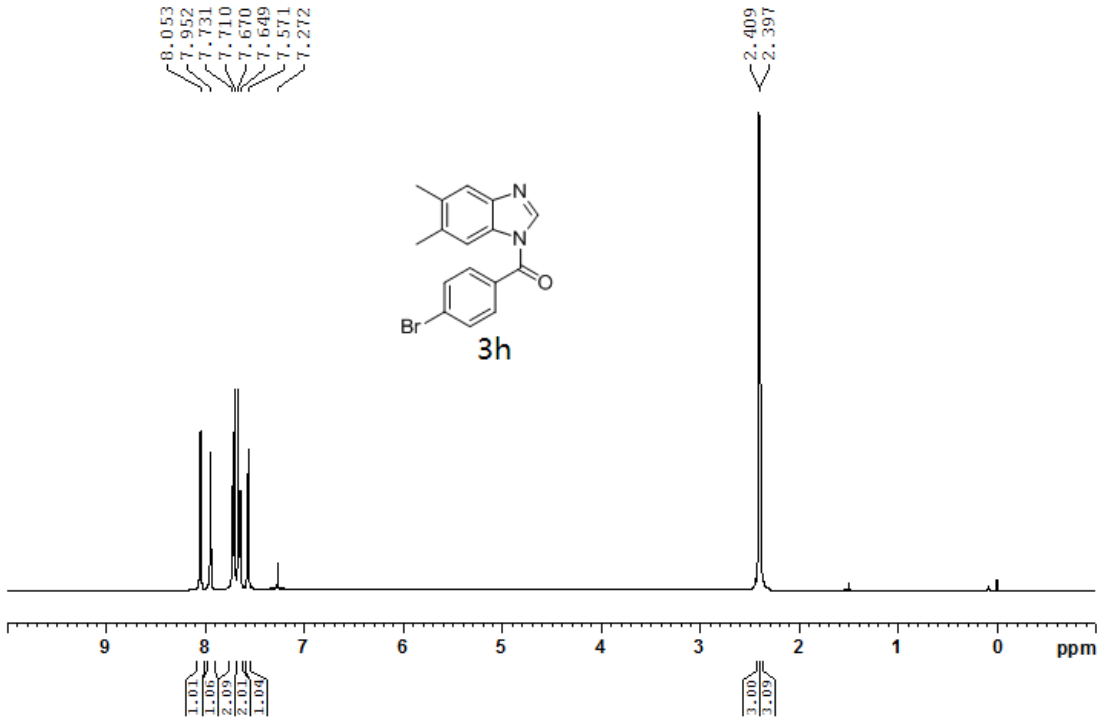
60
40
20
ppm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7.710
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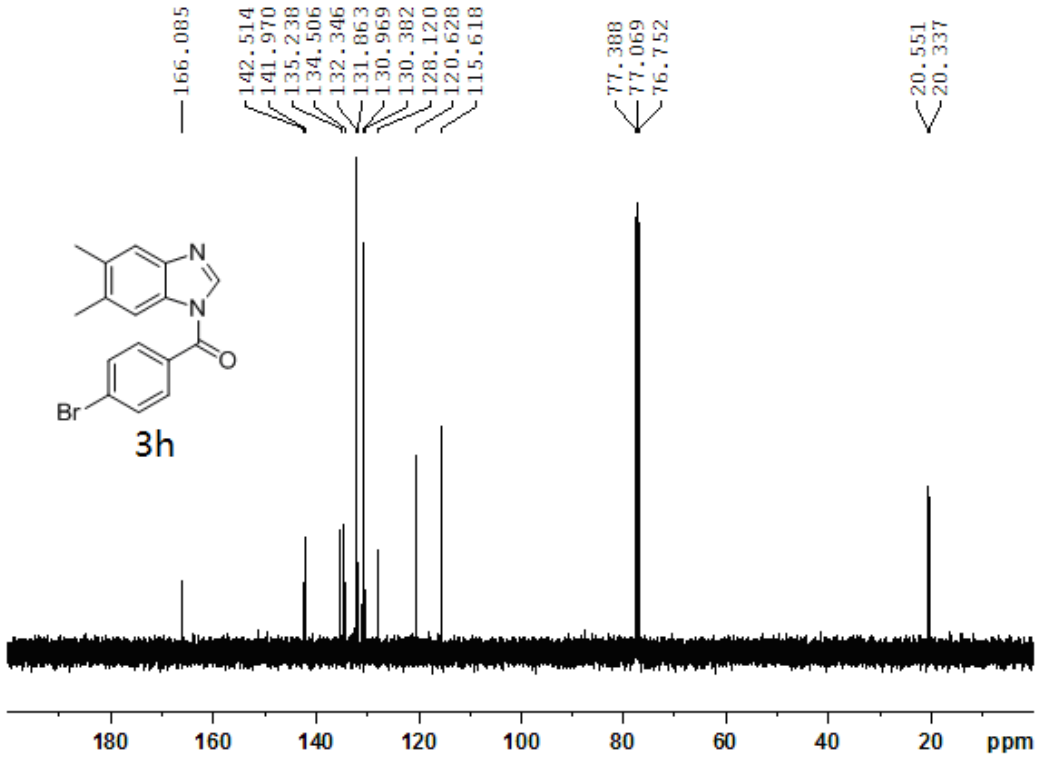
7.571
7.272
2.409
2.397
N
N
O
Br
3h
9
8
7
6
5
4
3
2
1
0
ppm
1.01
1.06
2.09
2.01
1.04
3.00
3.09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132.346
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130.969
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128.120
120.628
115.618
77.388
77.069
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N
N
O
Br
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140
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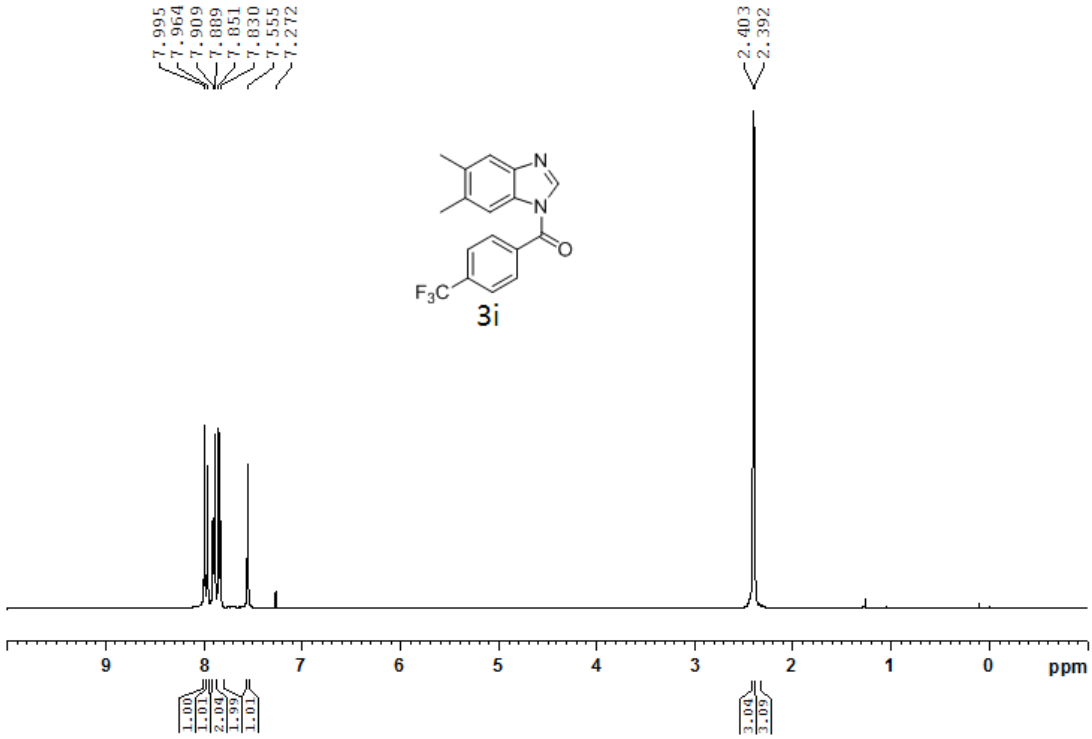
80
60
40
20
ppm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7.909
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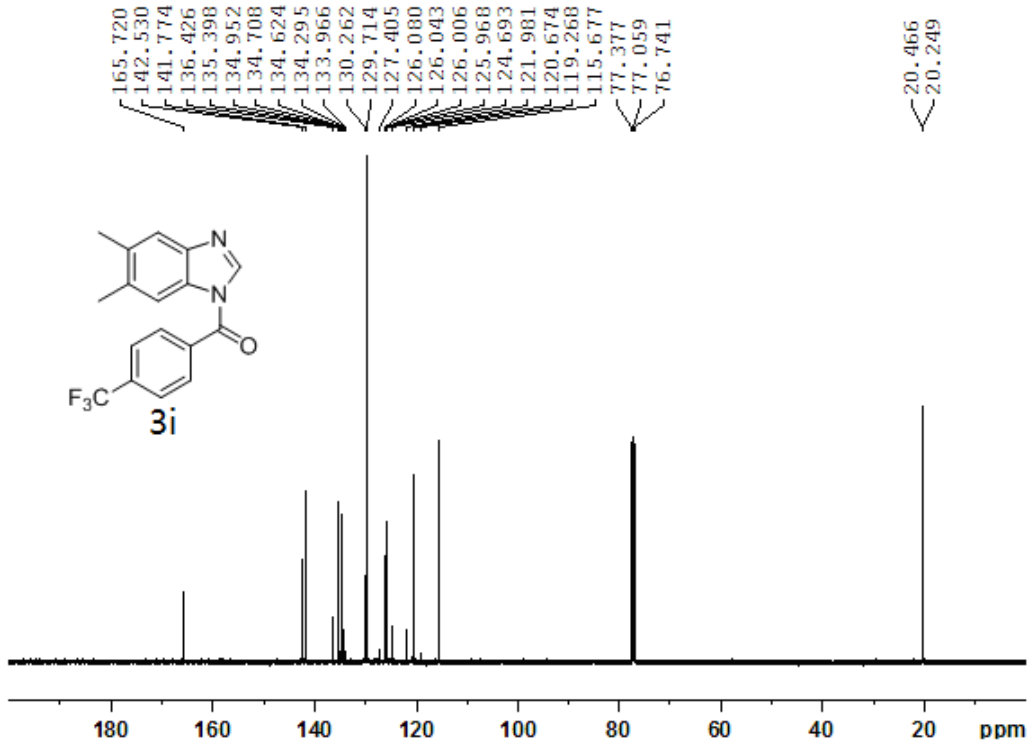
7.851
7.830
7.555
7.272
2.403
2.392
3i
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
2.04
1.99
1.01
3.04
3.09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134.624
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127.405
126.080
126.043
126.006
125.968
124.693
121.981
120.674
119.268
115.677
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20.466
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160
140
120
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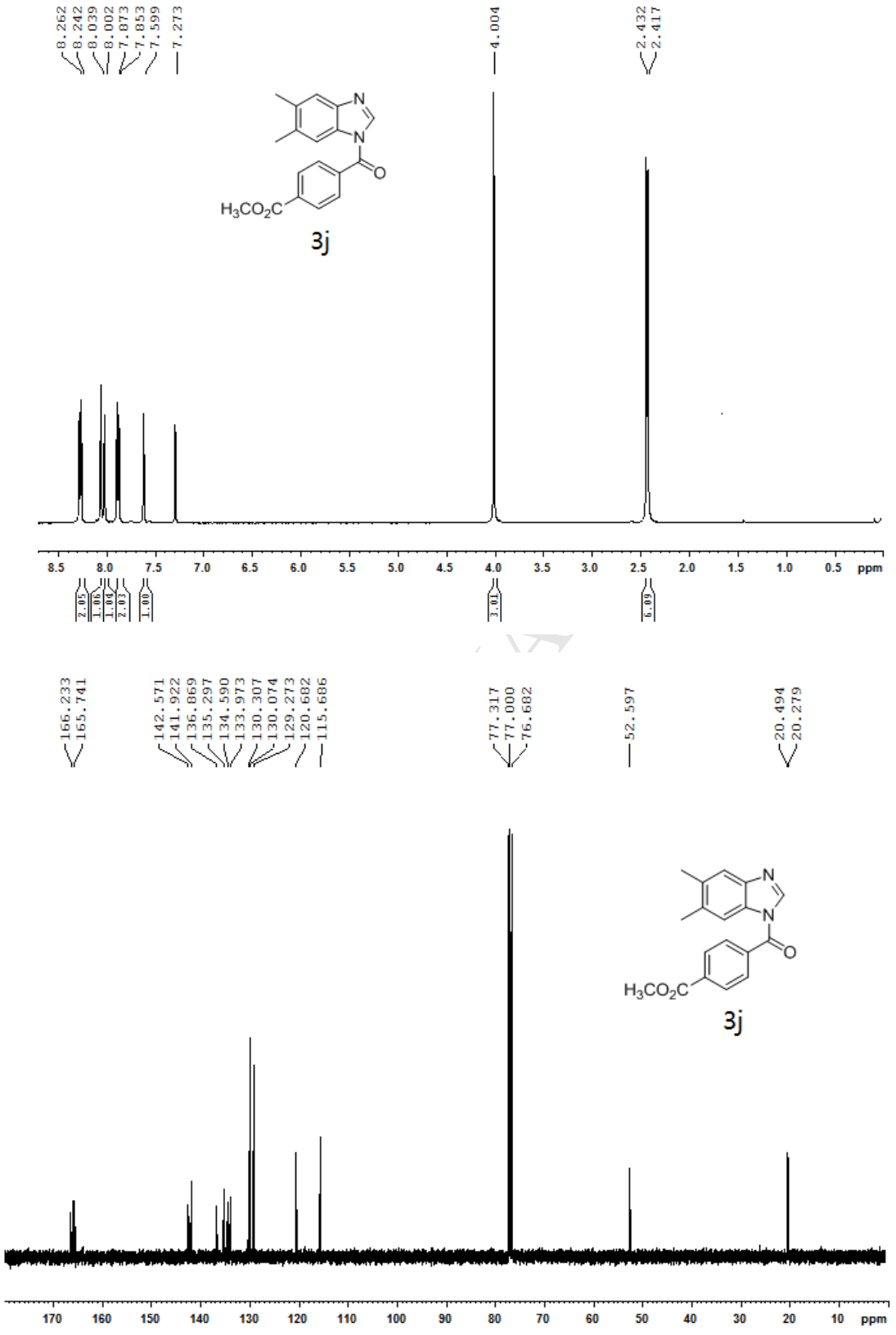
80
60
40
20
ppm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8.242
8.039
8.002
7.873
7.853
7.599
7.273
4.004
2.432
2.417
3j
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.05
1.06
1.04
2.03
1.00
3.01
6.09
166.233
165.741
142.571
141.922
136.869
135.297
134.590
133.973
130.307
130.074
129.273
120.682
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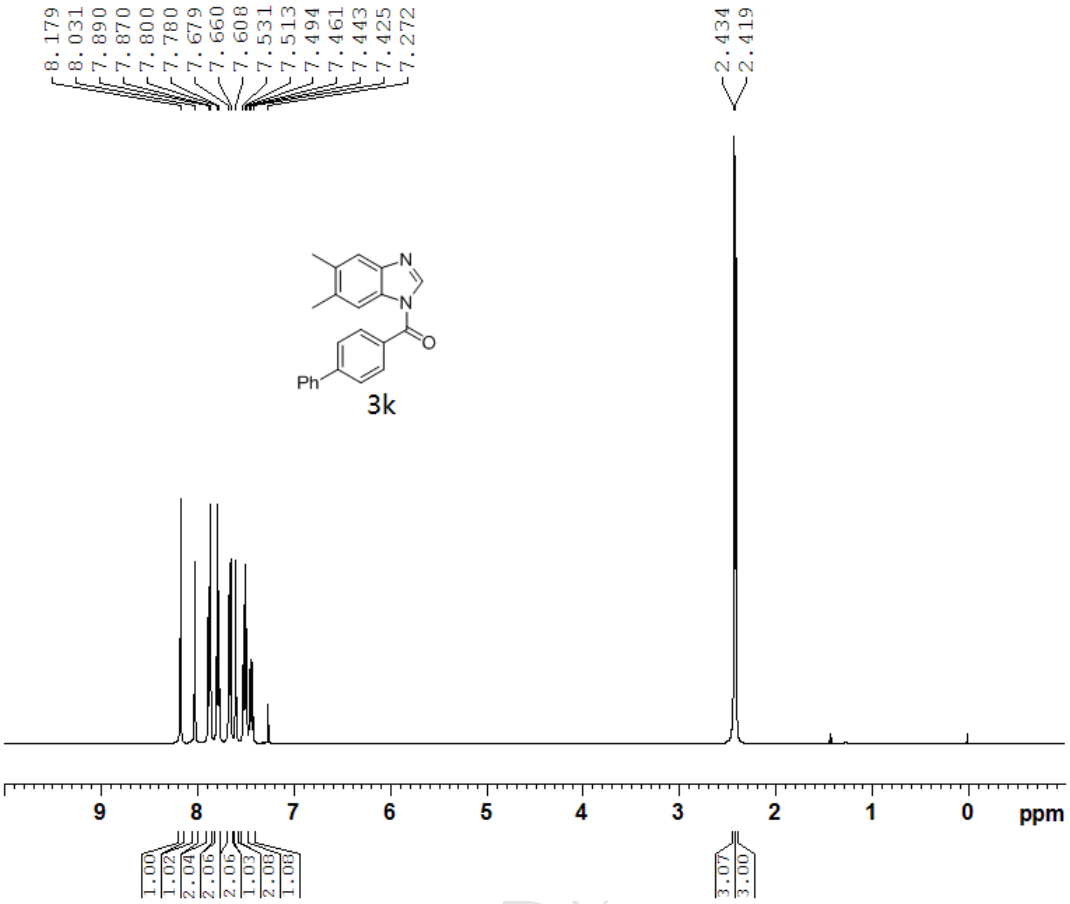
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7.890
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7.660
7.608
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7.513
7.494
7.461
7.443
7.425
7.272
2.434
2.419
N
N
O
Ph
3k
9
8
7
6
5
4
3
2
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ppm
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1.02
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2.06
2.06
1.03
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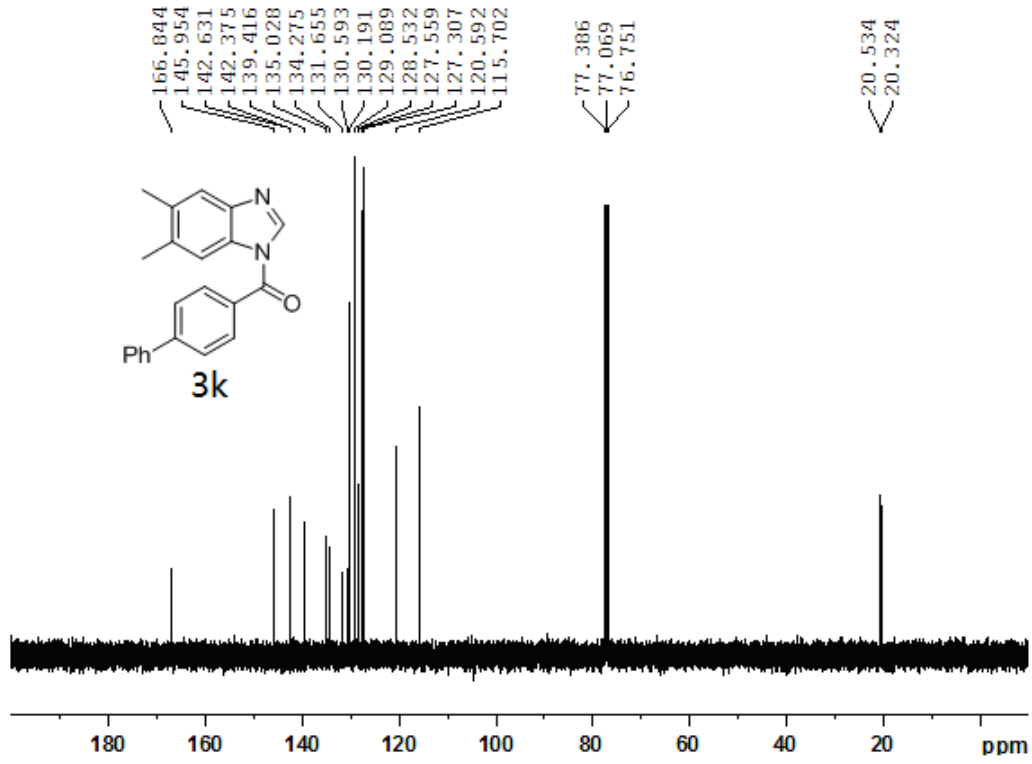
1.08
3.07
3.00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139.416
135.028
134.275
131.655
130.593
130.191
129.089
128.532
127.559
127.307
120.592
115.702
77.386
77.069
76.751
20.534
20.324
N
N
O
Ph
3k
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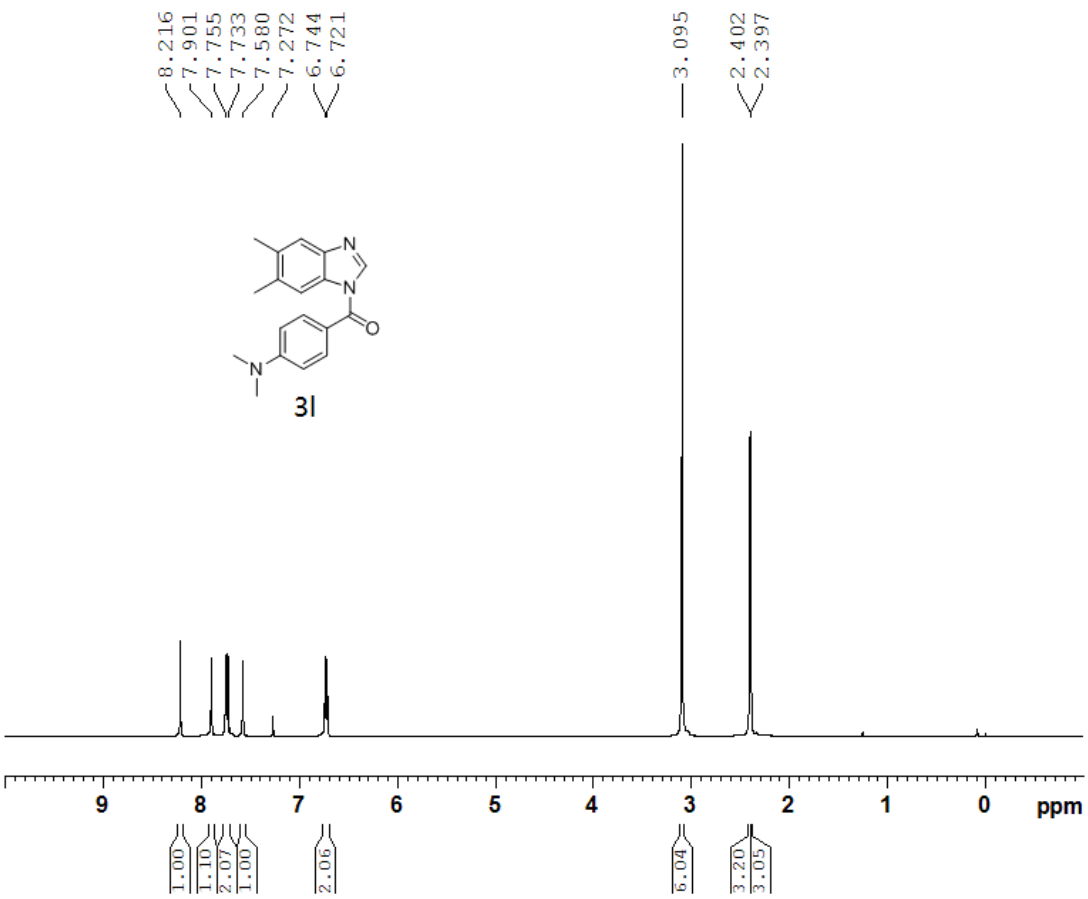
140
120
100
80
60
40
20
ppm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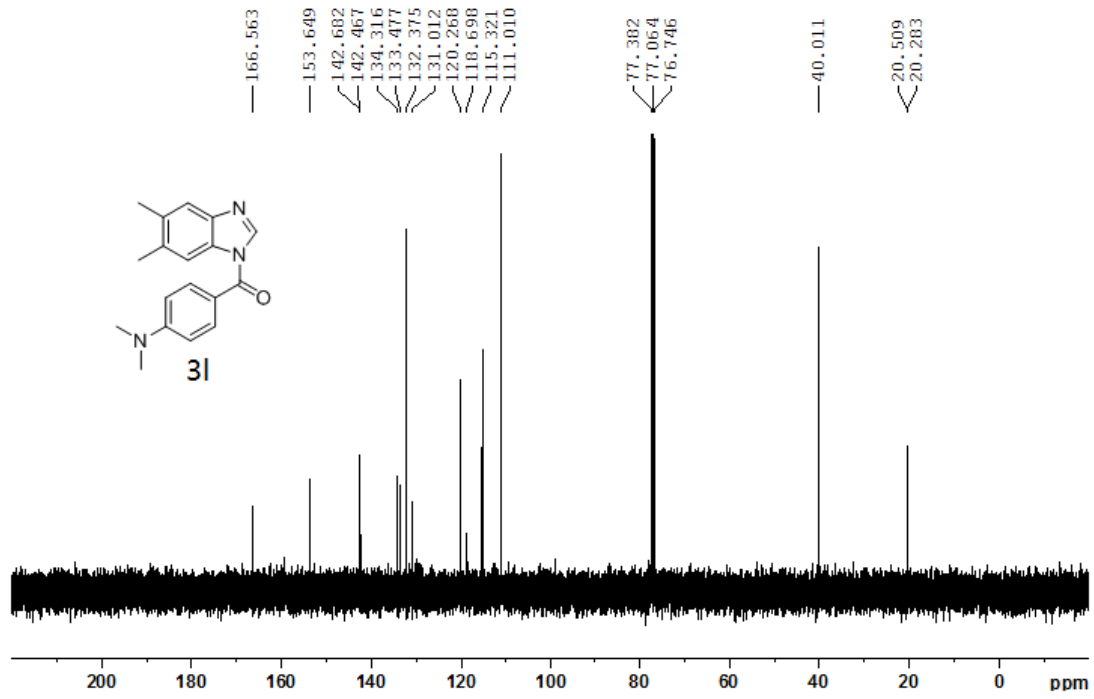
7.901
7.755
7.733
7.580
7.272
6.744
6.721
3.095
2.402
2.397
3l
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.10
2.07
1.00
2.06
6.04
3.20
3.05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134.316
133.477
132.375
131.012
120.268
118.698
115.321
111.010
77.382
77.064
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20.509
20.283
3l
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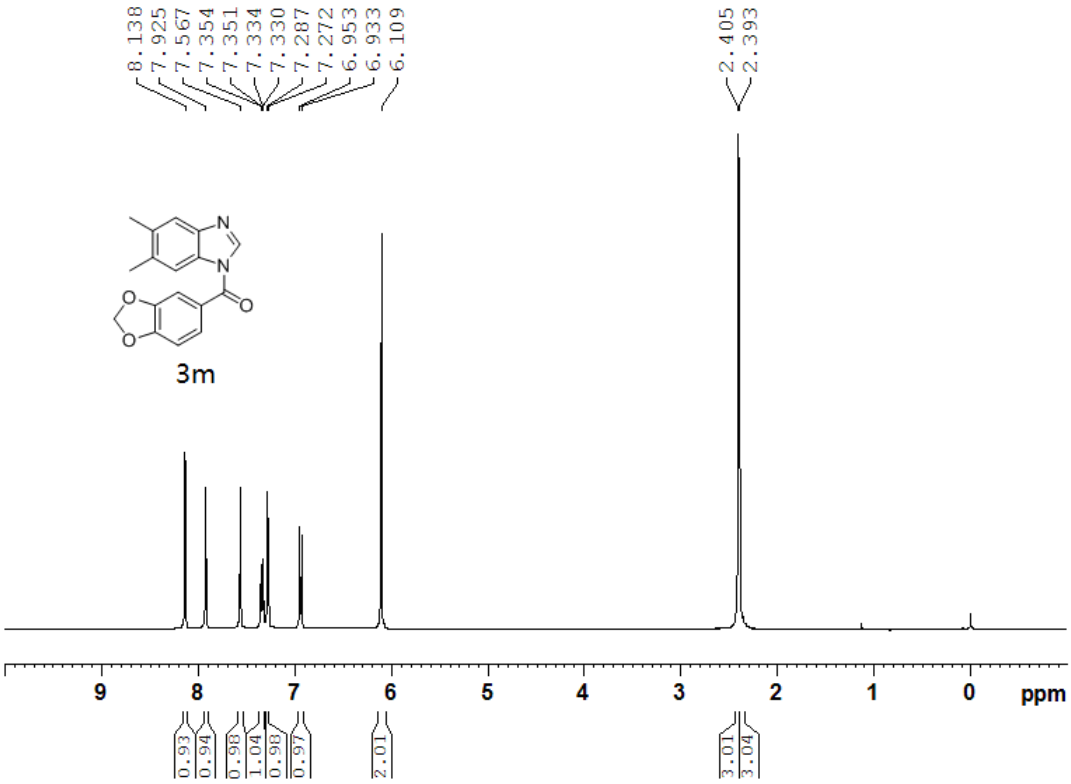
180
160
140
120
100
80
60
40
20
0
ppm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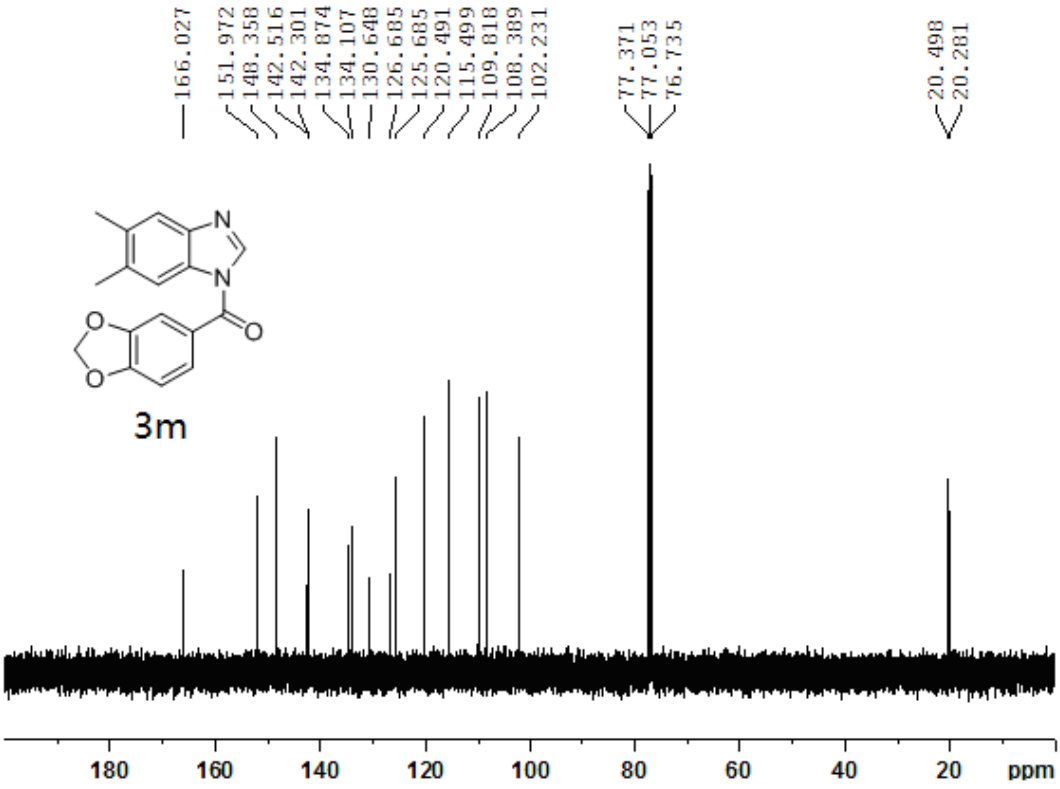
7.567
7.354
7.351
7.334
7.330
7.287
7.272
6.953
6.933
6.109
2.405
2.393
3m
9
8
7
6
5
4
3
2
1
0
ppm
0.93
0.94
0.98
1.04
0.98
0.97
2.01
3.01
3.04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134.107
130.648
126.685
125.685
120.491
115.499
109.818
108.389
102.231
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76.735
20.498
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3m
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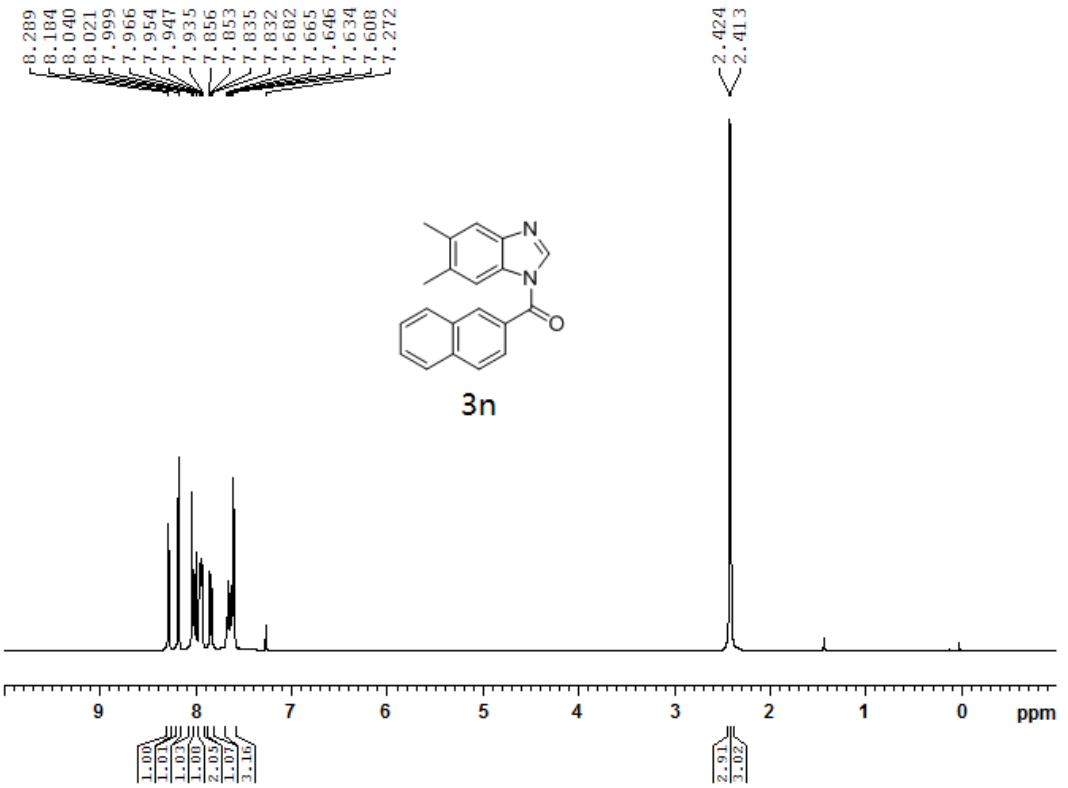
140
120
100
80
60
40
20
ppm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7.947
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7.856
7.853
7.835
7.832
7.682
7.665
7.646
7.634
7.608
7.272
2.424
2.413
N
N
O
3n
9
8
7
6
5
4
3
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ppm
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1.03
1.00
2.05
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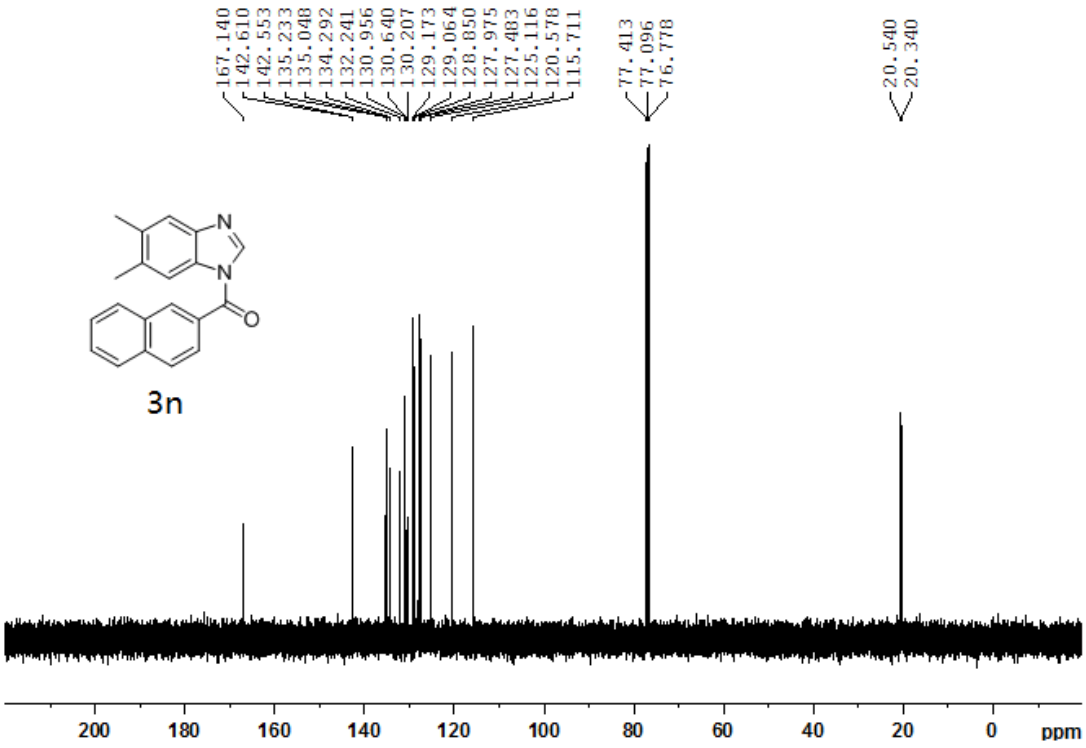
2.91
3.02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130.207
129.173
129.064
128.850
127.975
127.483
125.116
120.578
115.711
77.413
77.096
76.778
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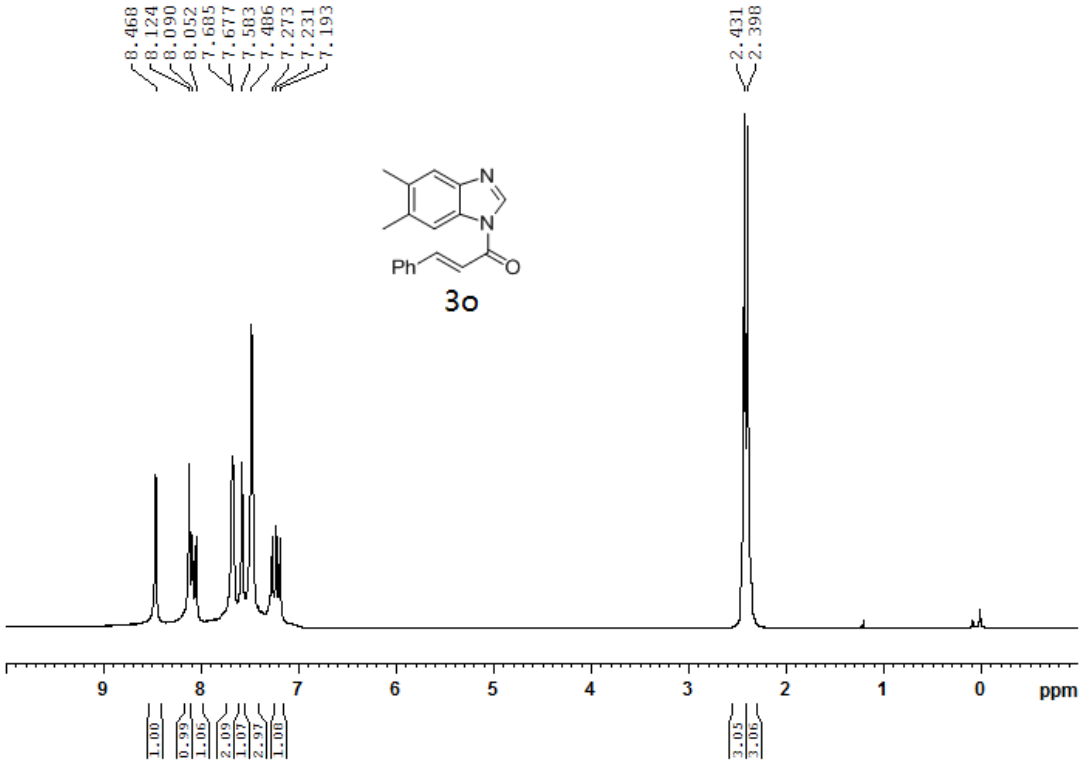
20.340
N
N
O
3n
200
180
160
140
120
100
80
60
40
20
0
ppm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7.583
7.486
7.273
7.231
7.193
2.431
2.398
N
N
Ph
O
3o
9
8
7
6
5
4
3
2
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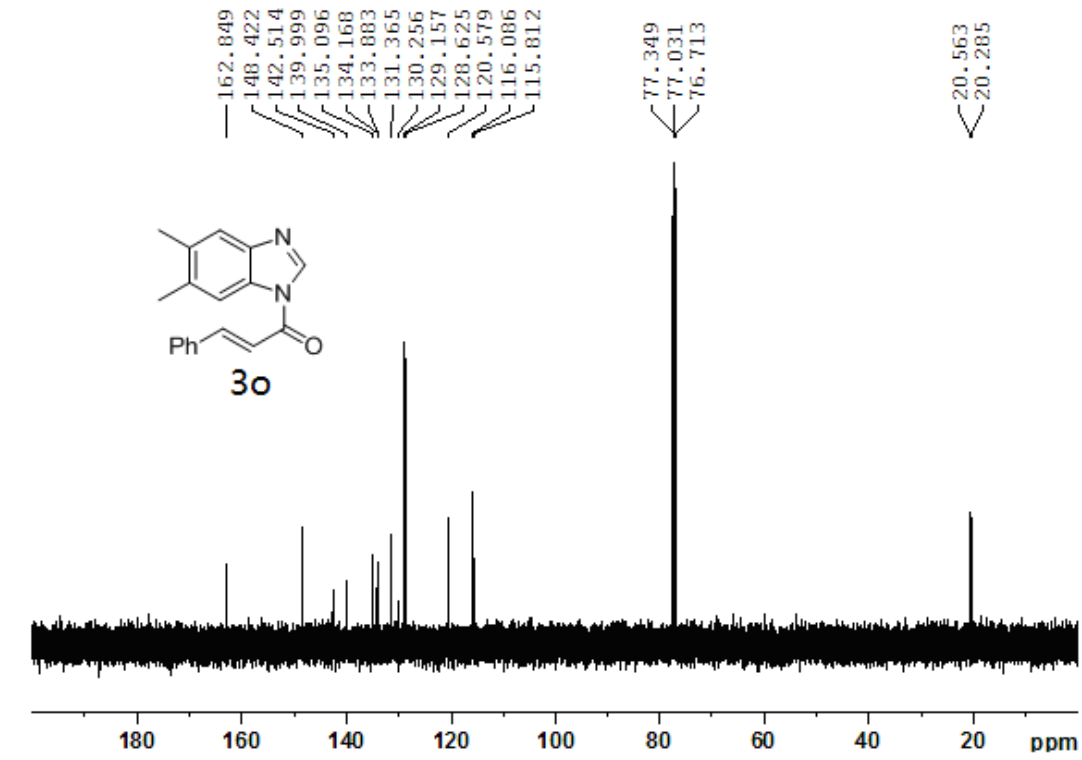
ppm
1.00
0.99
1.06
2.09
1.07
2.97
1.08
3.05
3.06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133.883
131.365
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129.157
128.625
120.579
116.086
115.812
77.349
77.031
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N
Ph
O
3o
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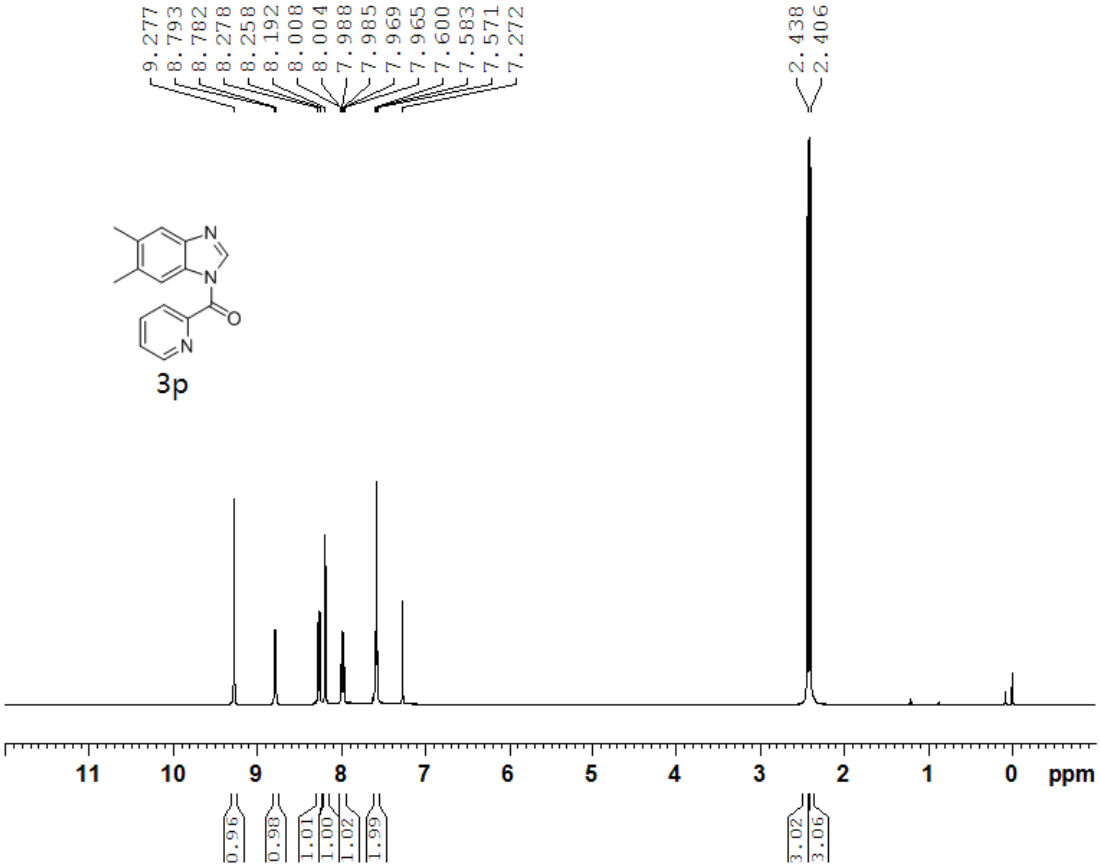
140
120
100
80
60
40
20
ppm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8.004
7.988
7.985
7.969
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7.600
7.583
7.571
7.272
2.438
2.406
3p
11
10
9
8
7
6
5
4
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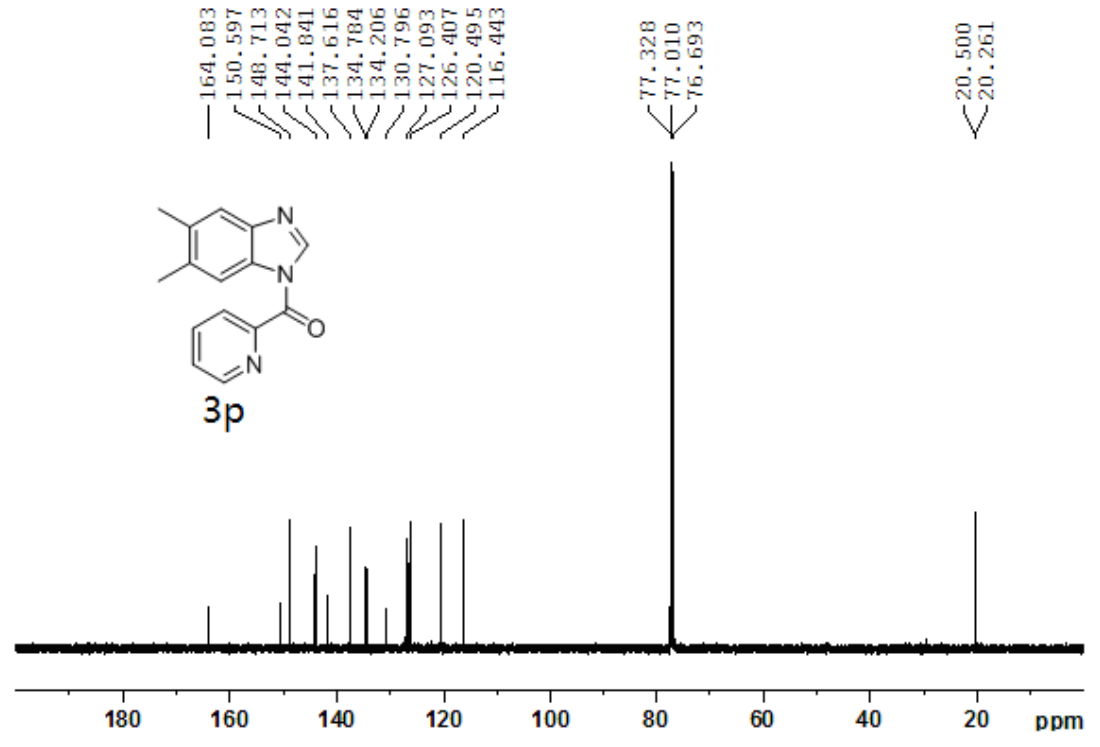
1.00
1.02
1.99
3.02
3.06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134.206
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126.407
120.495
116.443
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76.693
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140
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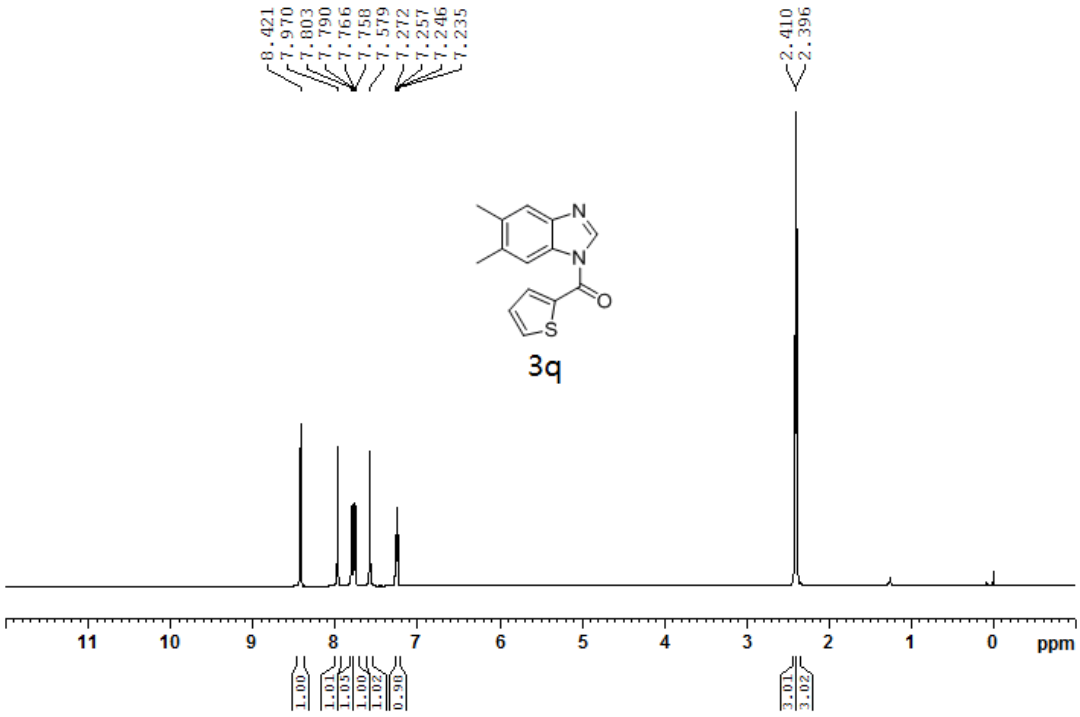
40
20
ppm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7.272
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7.246
7.235
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2.396
3q
11
10
9
8
7
6
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ppm
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1.05
1.00
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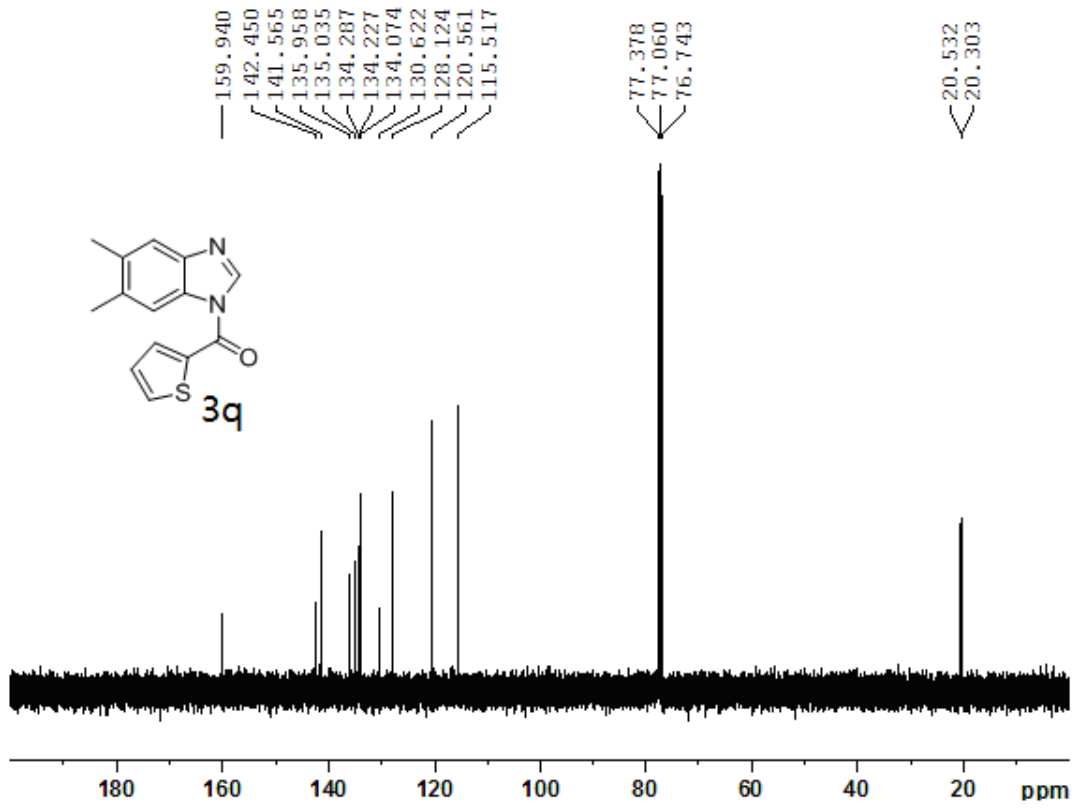
3.02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134.074
130.622
128.124
120.561
115.517
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77.060
76.743
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3q
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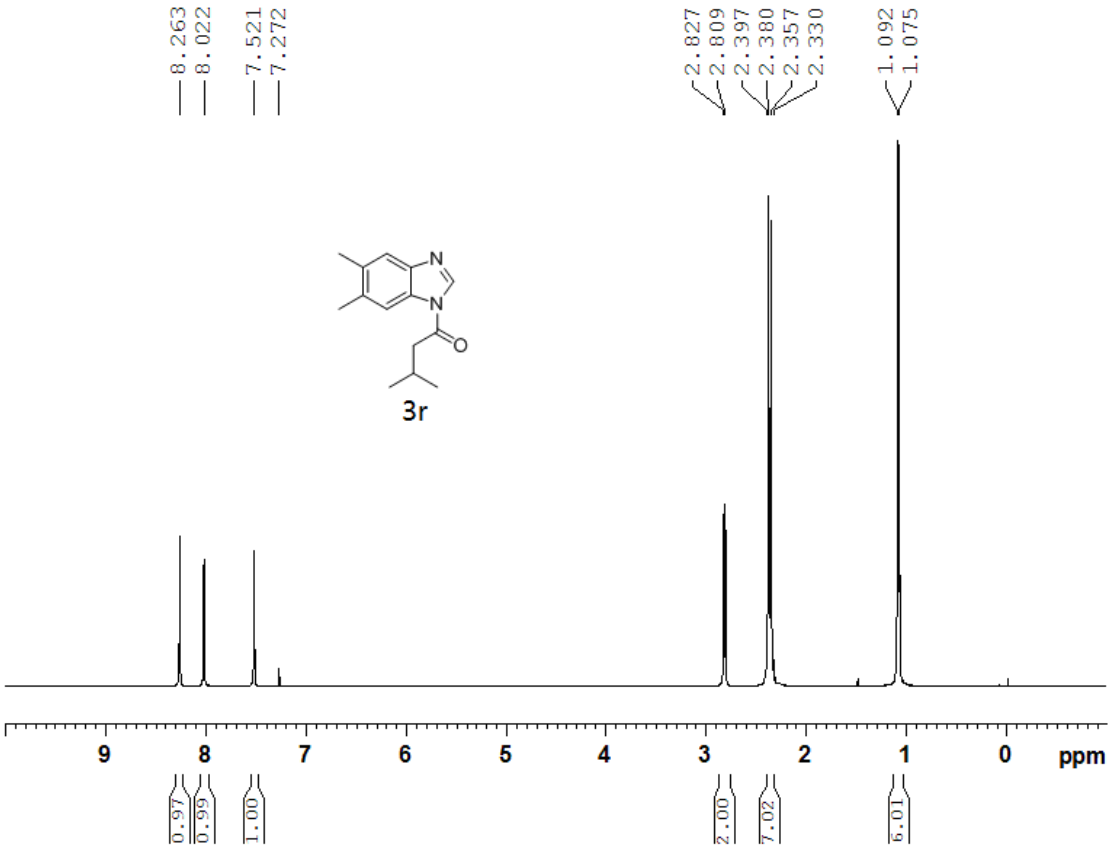
160
140
120
100
80
60
40
20
ppm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2.380
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2.330
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1.075
3r
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8
7
6
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4
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0.99
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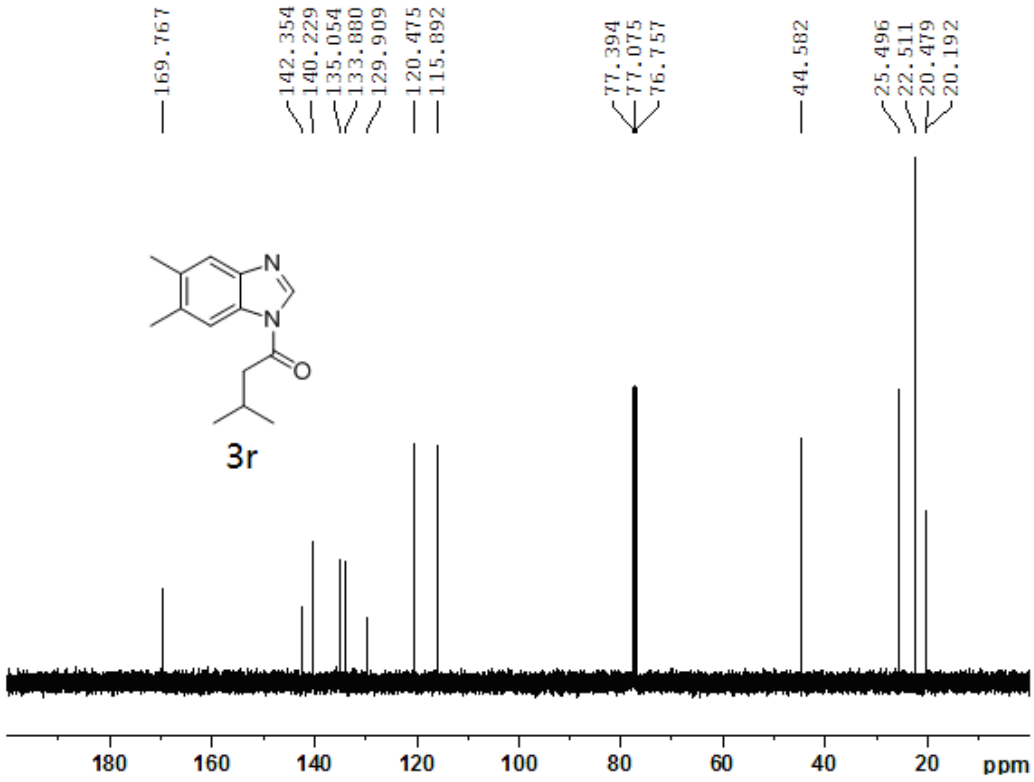
2.00
7.02
6.01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77.075
76.757
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140
120
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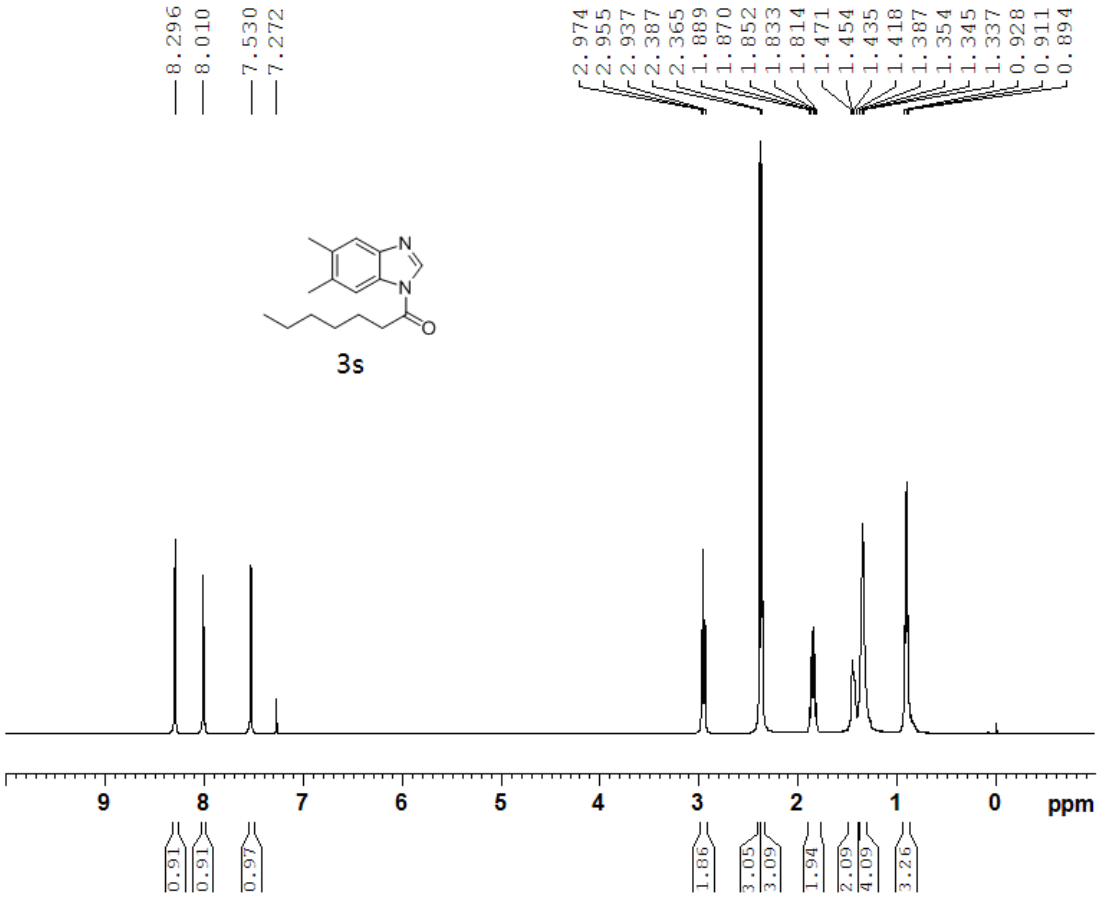
80
60
40
20
ppm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2.387
2.365
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1.870
1.852
1.833
1.814
1.471
1.454
1.435
1.418
1.387
1.354
1.345
1.337
0.928
0.911
0.894
3s
9
8
7
6
5
4
3
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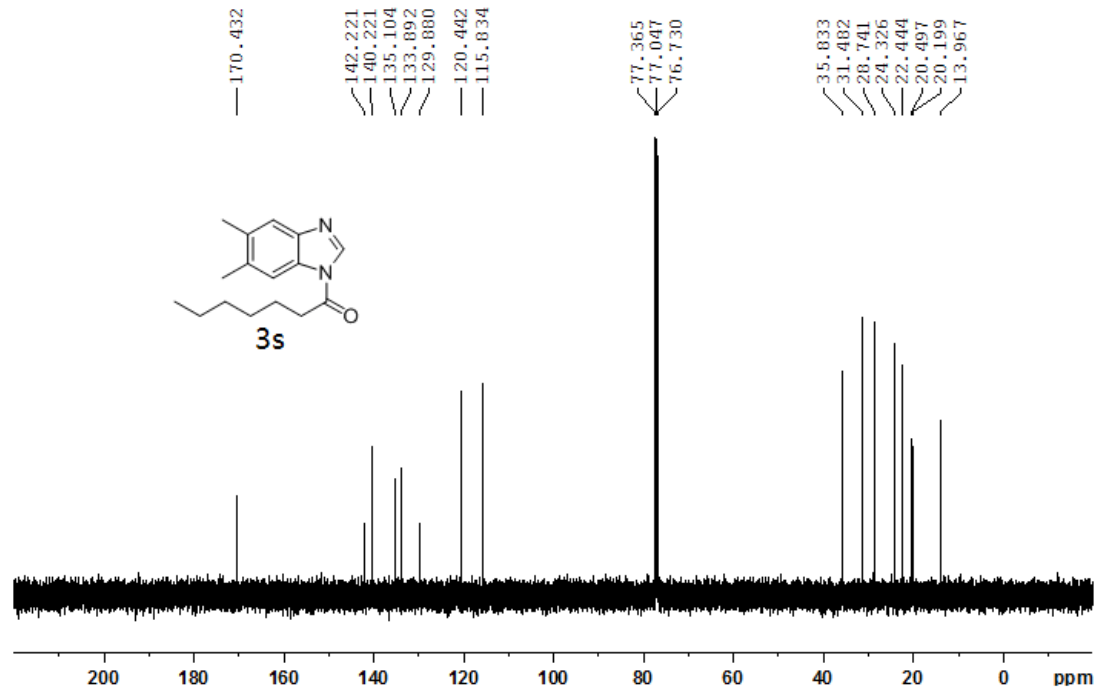
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77.047
76.730
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31.482
28.741
24.326
22.444
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13.967
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140
120
100
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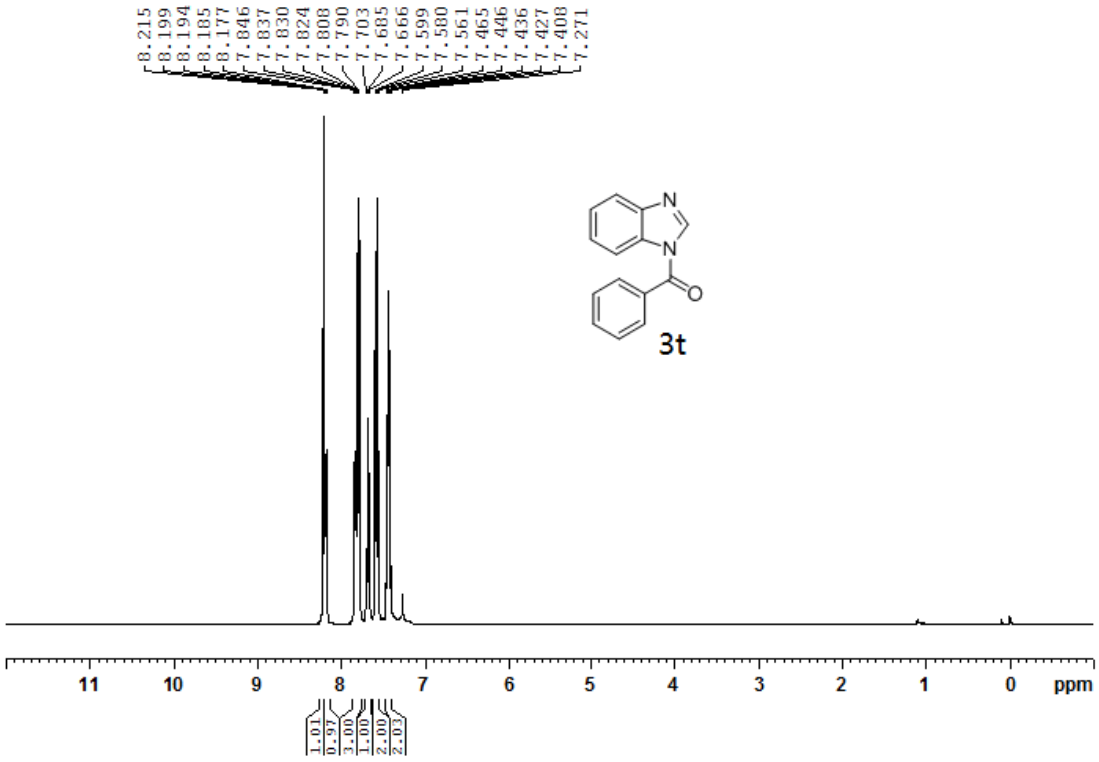
40
20
0
ppm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7.830
7.824
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7.790
7.703
7.685
7.666
7.599
7.580
7.561
7.465
7.446
7.436
7.427
7.408
7.271
3t
11
10
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8
7
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5
4
3
2
1
0
ppm
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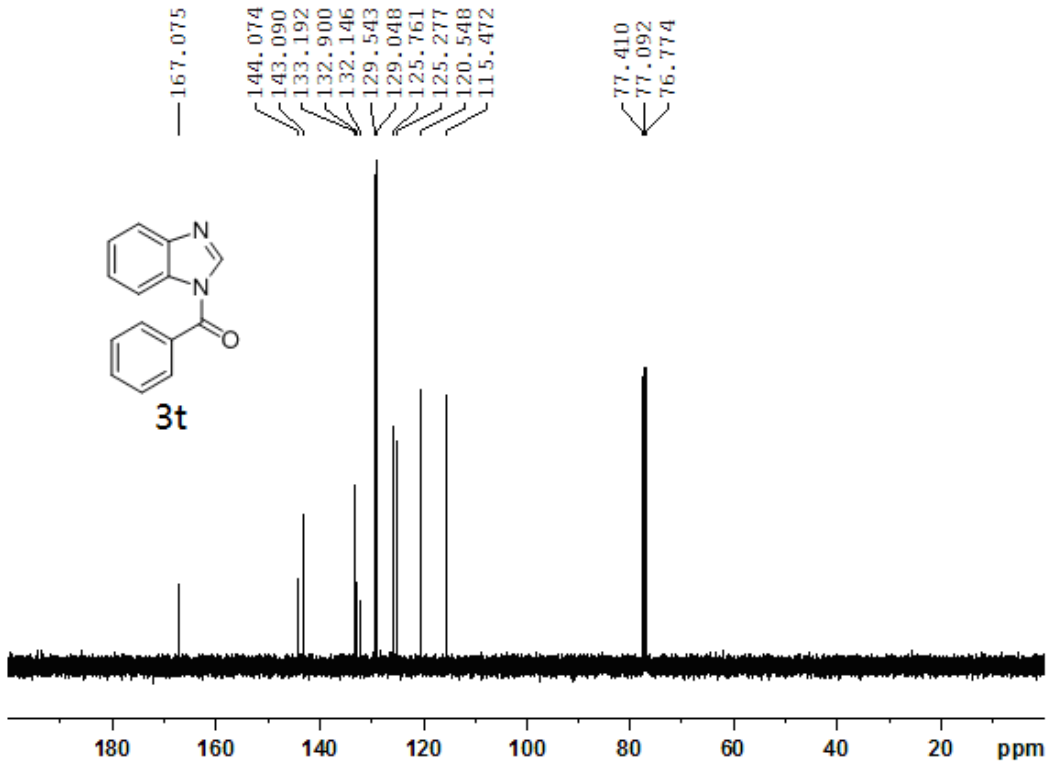
0.97
3.00
1.00
2.00
2.03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129.048
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125.277
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140
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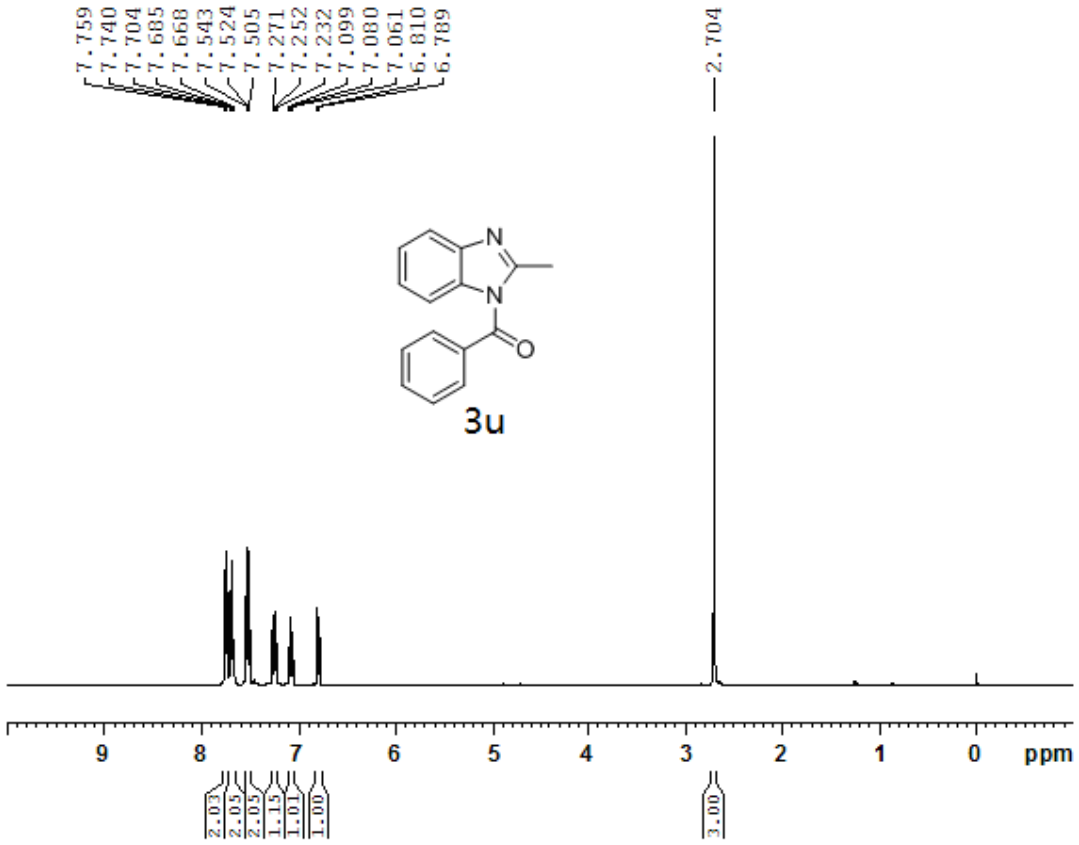
20
ppm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7.271
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7.232
7.099
7.080
7.061
6.810
6.789
2.704
N
N
O
3u
9
8
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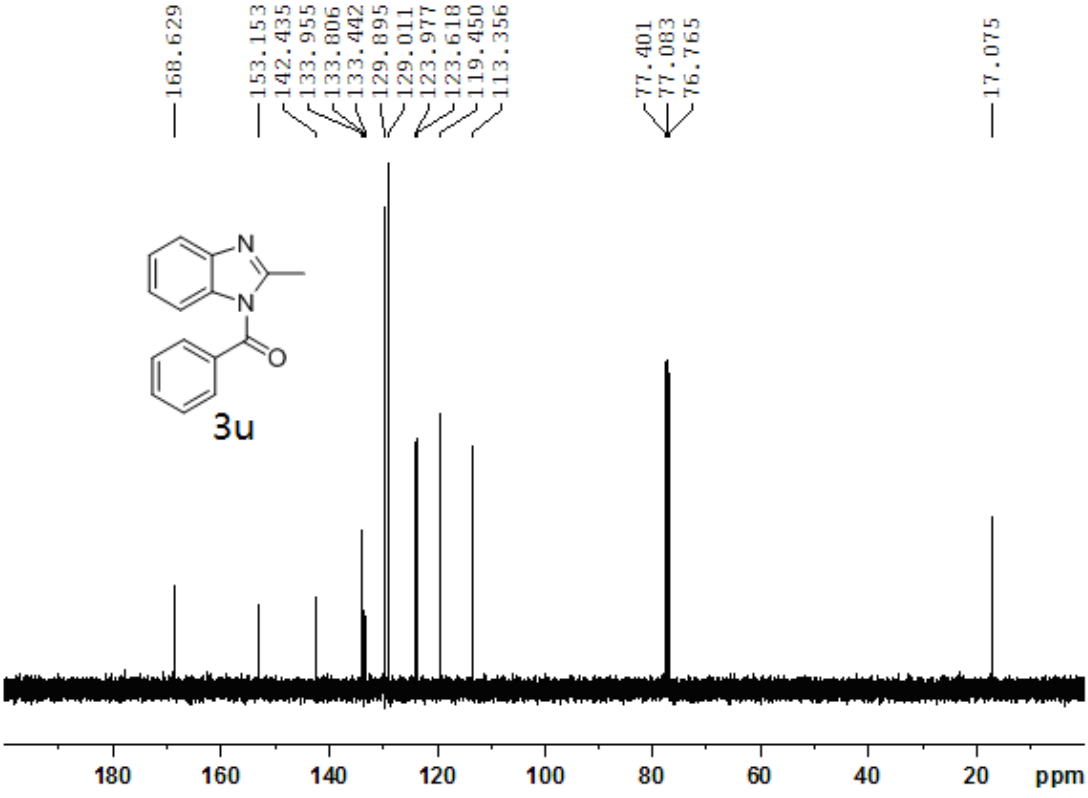
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123.618
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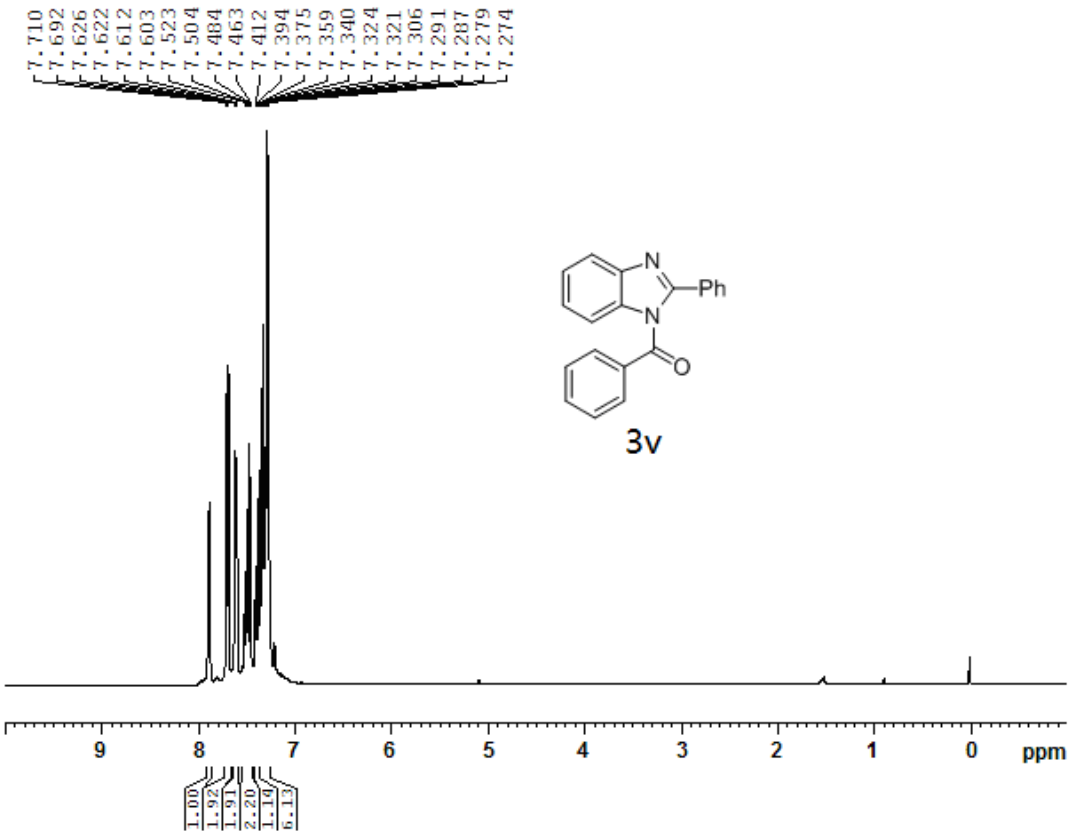
77.401
77.083
76.765
17.075
N
N
O
3u
180
160
140
120
100
80
60
40
20
ppm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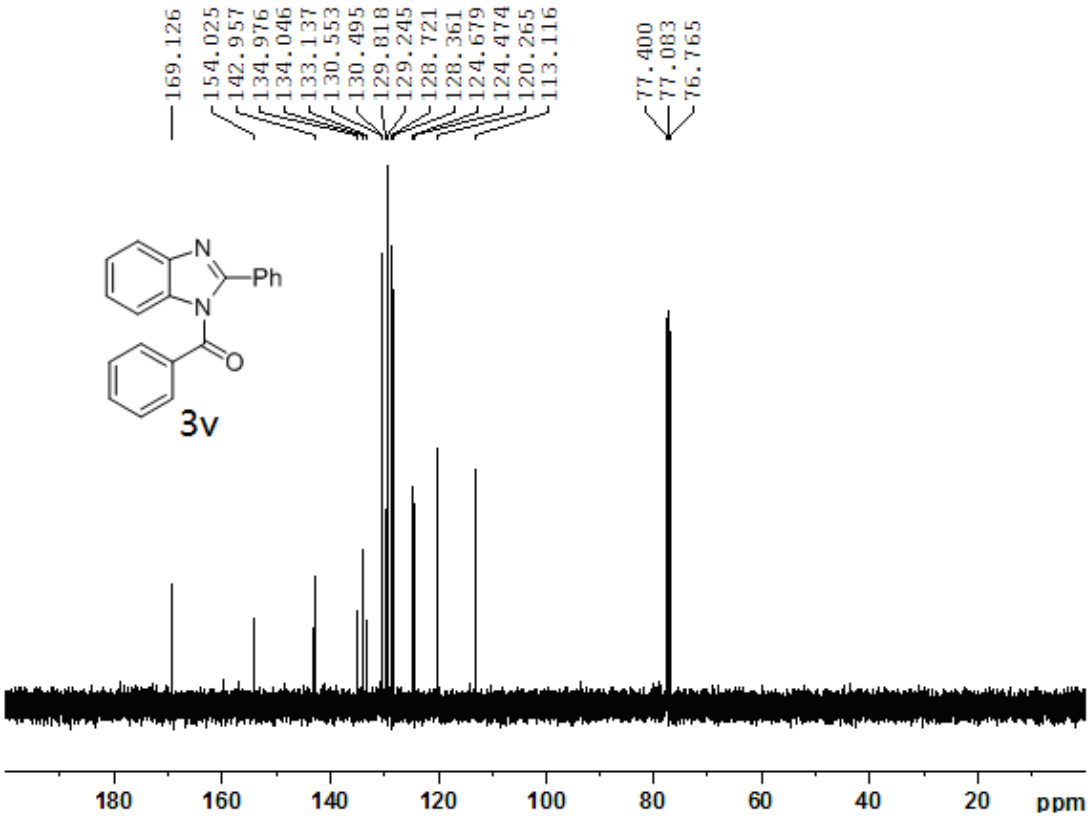
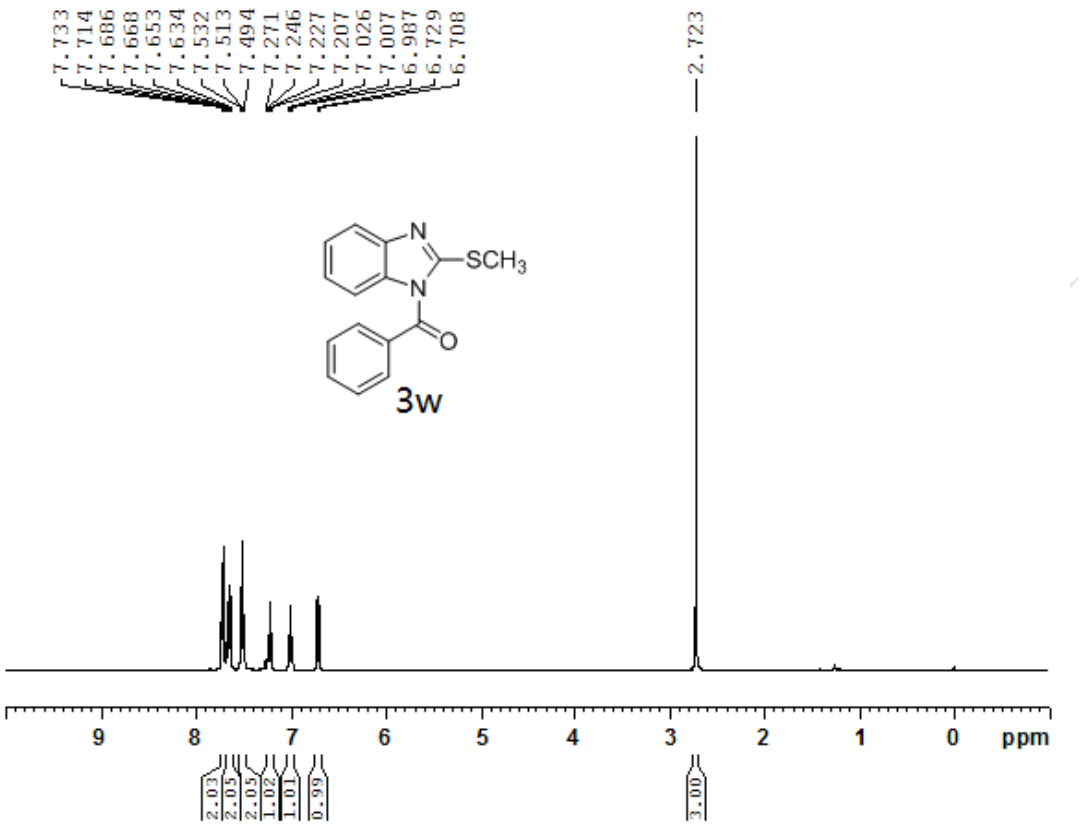
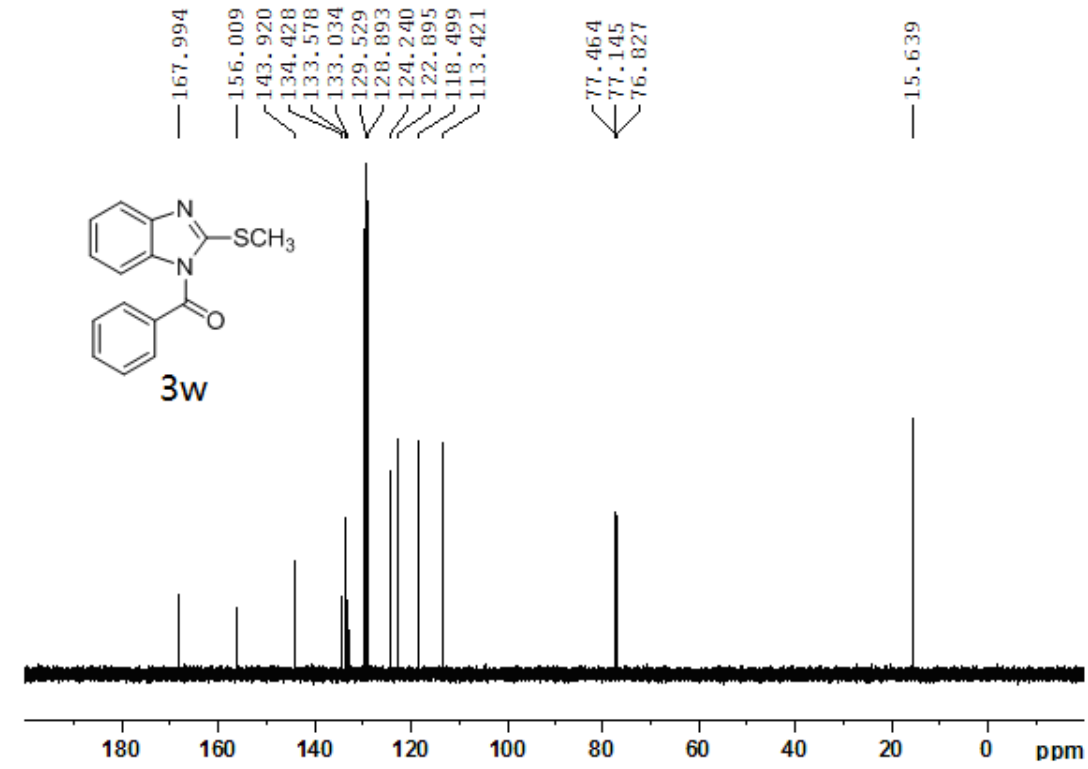
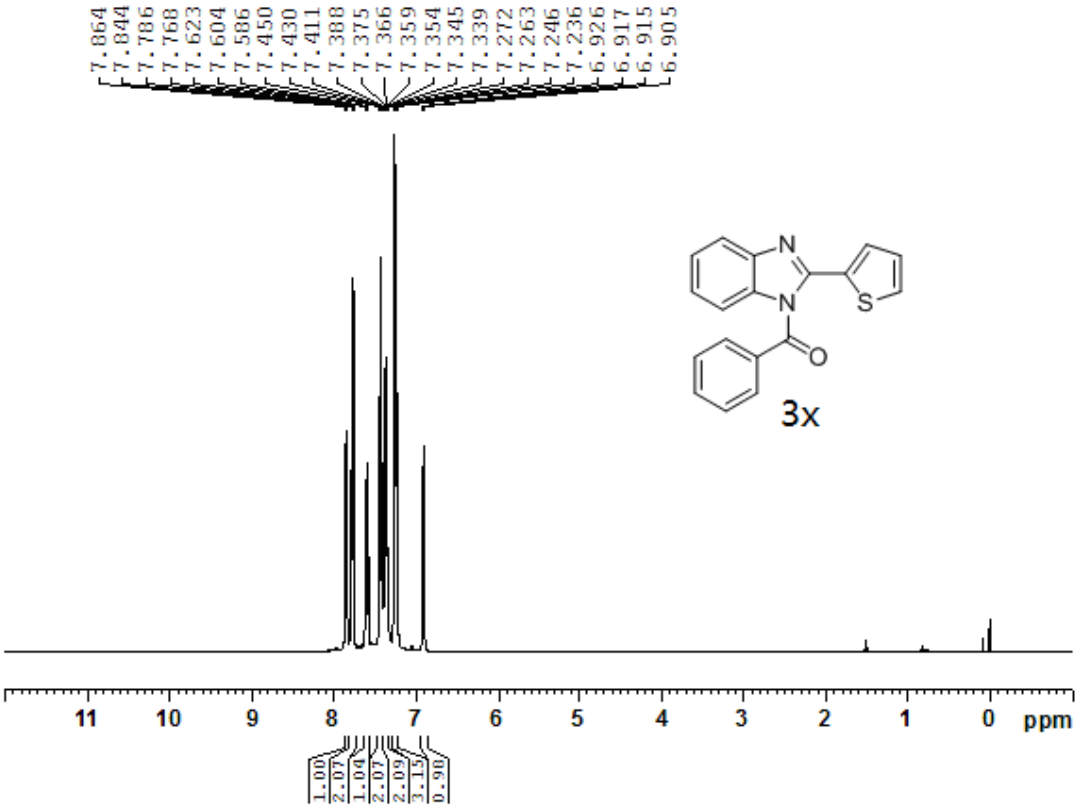
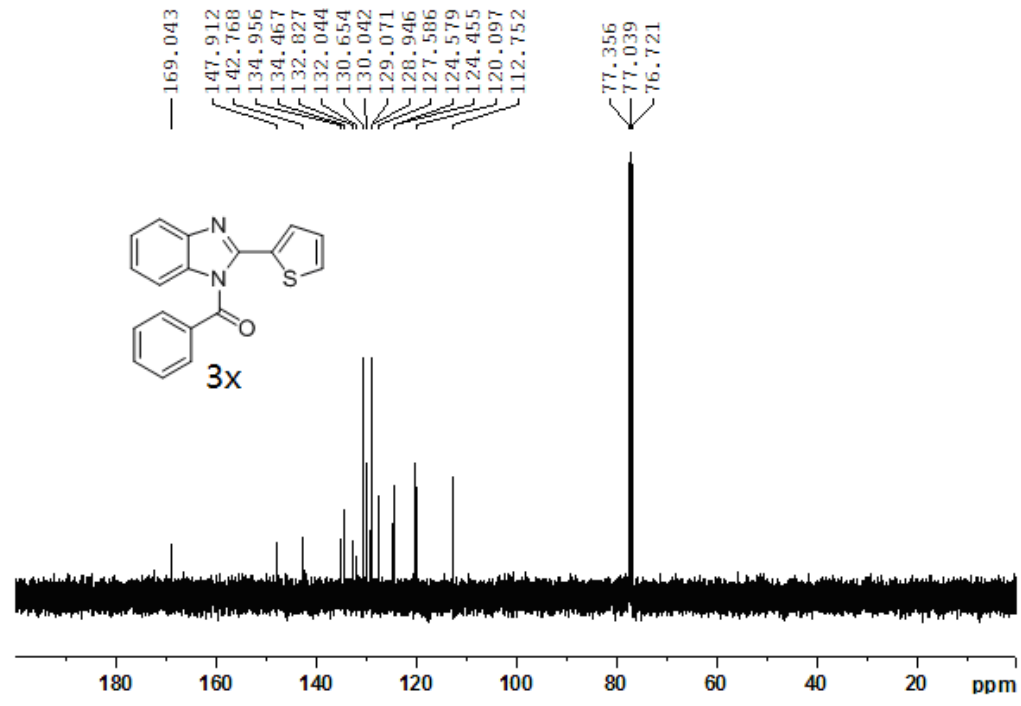
7.692
7.626
7.622
7.612
7.603
7.523
7.504
7.484
7.463
7.412
7.394
7.375
7.359
7.340
7.324
7.321
7.306
7.291
7.287
7.279
7.274
N
Ph
N
O
3v
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.92
1.91
2.20
1.10
6.13

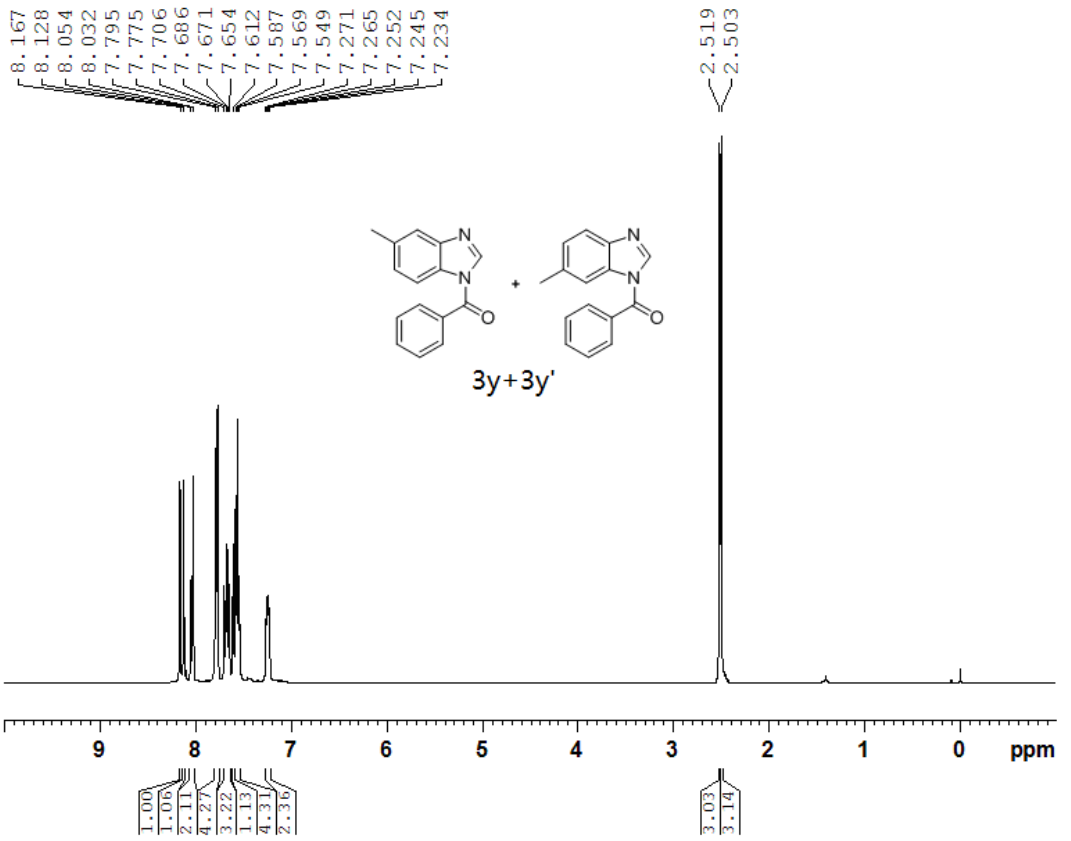

169.126
154.025
142.957
134.976
134.046
133.137
130.553
130.495
129.818
129.245
128.721
128.361
124.679
124.474
120.265
113.116
77.400
77.083
76.765
N
Ph
N
O
3v
180
160
140
120
100
80
60
40
20
ppm

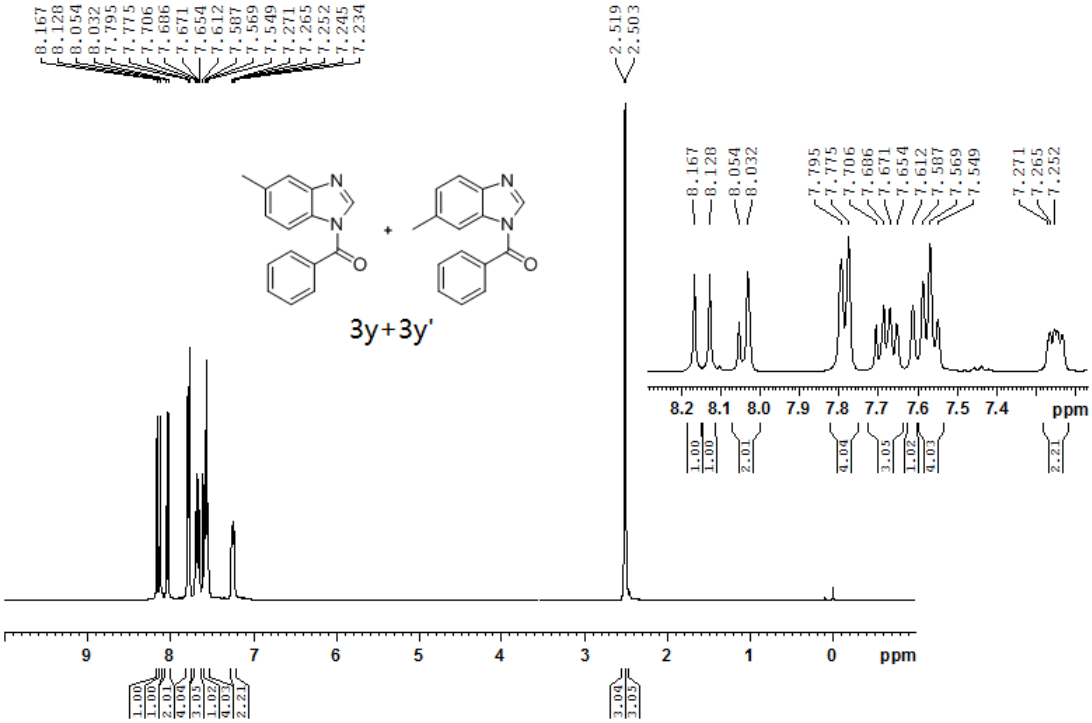

7.733
7.714
7.686
7.668
7.653
7.634
7.532
7.513
7.494
7.271
7.246
7.227
7.207
7.026
7.007
6.987
6.729
6.708
2.723
N
SCH3
N
O
3w
9
8
7
6
5
4
3
2
1
0
ppm
2.03
2.05
2.05
1.02
1.01
0.99
3.00

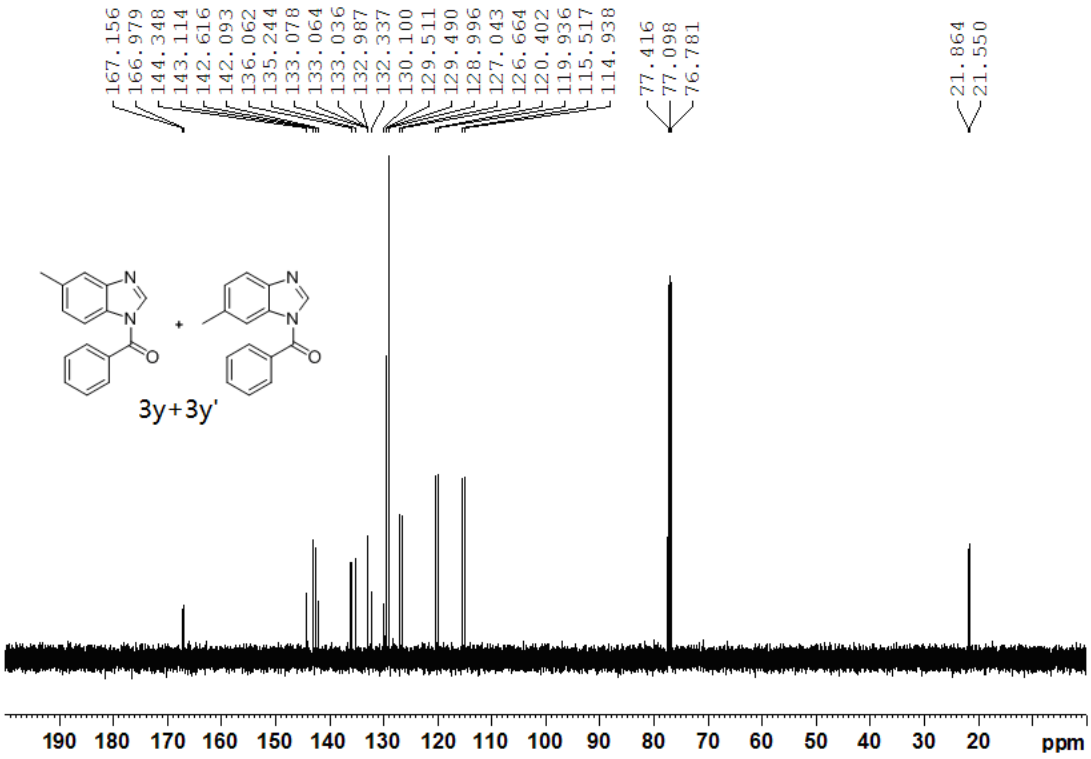

167.994
156.009
143.920
134.428
133.578
133.034
129.529
128.893
124.240
122.895
118.499
113.421
77.464
77.145
76.827
15.639
N
SCH3
N
O
3w
180
160
140
120
100
80
60
40
20
0
ppm

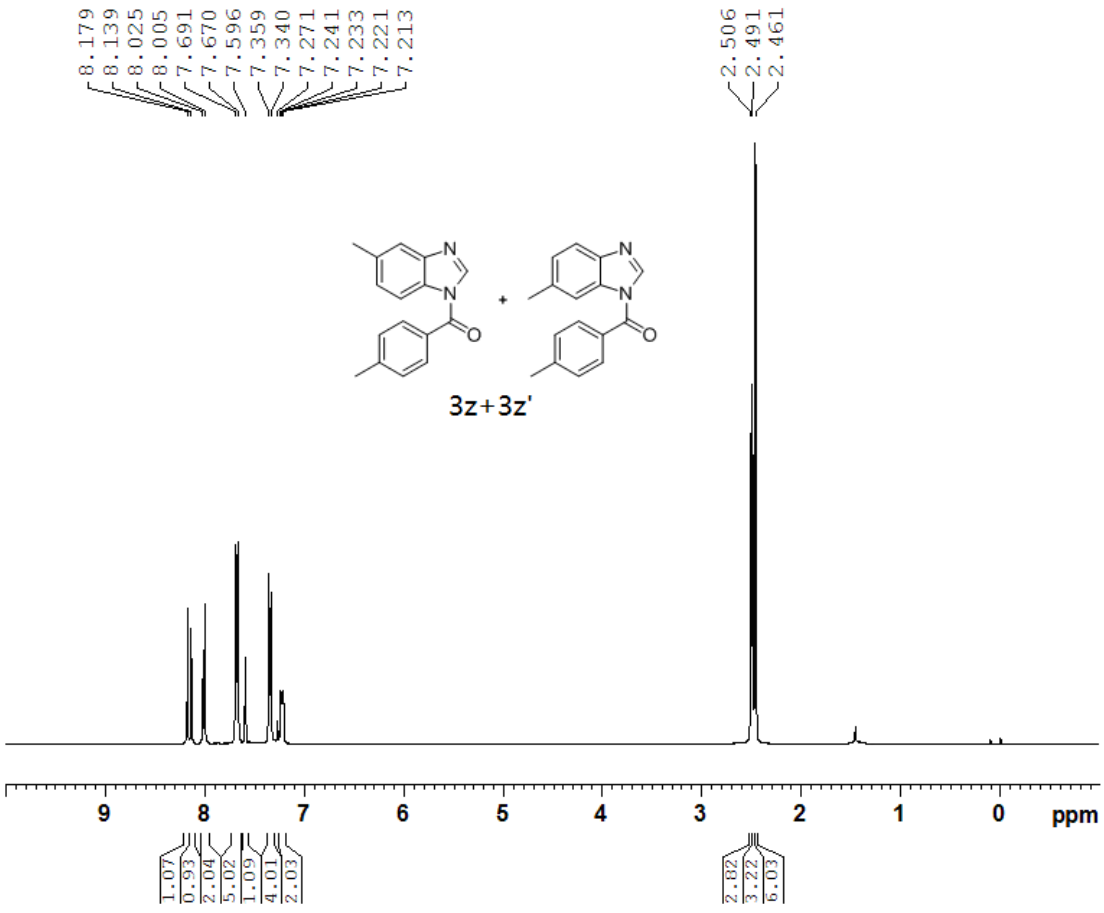

7.864
7.844
7.786
7.768
7.623
7.604
7.586
7.450
7.430
7.411
7.388
7.375
7.366
7.359
7.354
7.345
7.339
7.272
7.263
7.246
7.236
6.926
6.917
6.915
6.905
N
N
S
O
3x
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.07
1.04
2.07
2.09
3.15
0.90

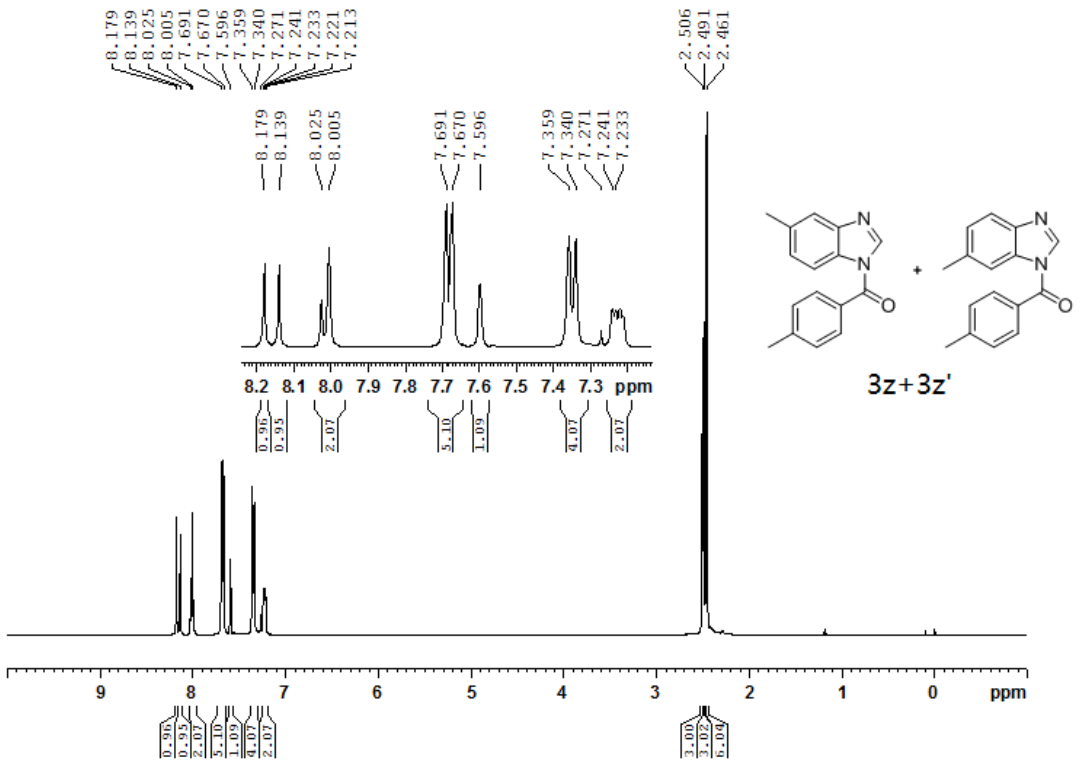

169.043
147.912
142.768
134.956
134.467
132.827
132.044
130.654
130.042
129.071
128.946
127.586
124.579
124.455
120.097
112.752
77.356
77.039
76.721
N
N
S
O
3x
180
160
140
120
100
80
60
40
20
ppm

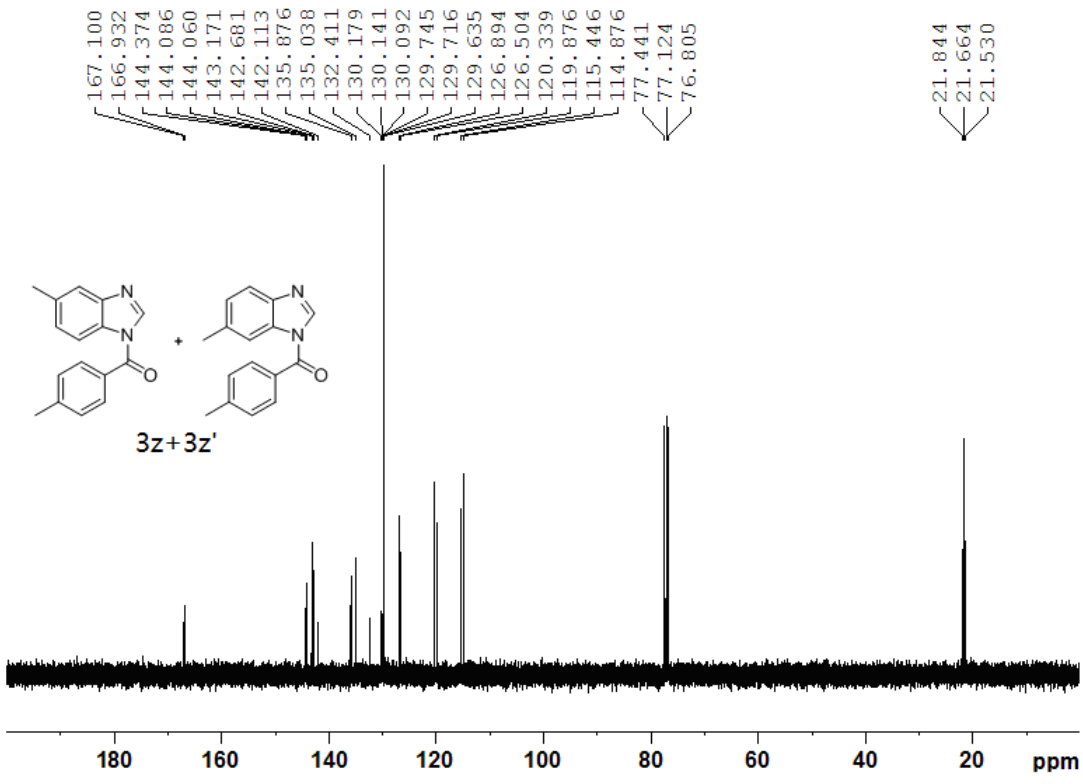

8.167
8.128
8.054
8.032
7.795
7.775
7.706
7.686
7.671
7.654
7.612
7.587
7.569
7.549
7.271
7.265
7.252
7.245
7.234
2.519
2.503
3y+3y'
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.06
2.11
4.27
3.22
1.13
4.31
2.36
3.03
3.14

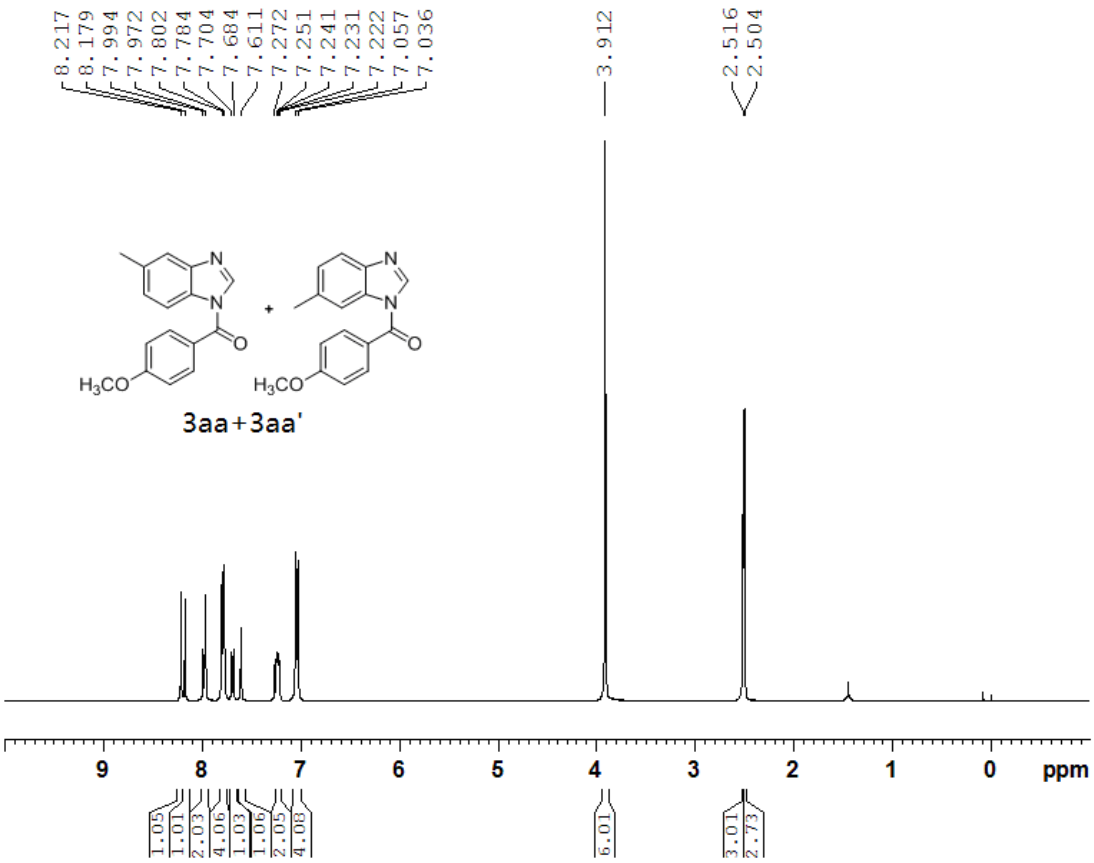

8.167
8.128
8.054
8.032
7.795
7.775
7.706
7.686
7.671
7.654
7.612
7.587
7.569
7.549
7.271
7.265
7.252
7.245
7.234
2.519
2.503
3y+3y'
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
ppm
1.00
1.00
2.01
4.04
3.05
1.02
4.03
2.21
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
2.01
4.04
3.05
1.02
4.03
2.21
3.04
3.05


167.156
166.979
144.348
143.114
142.616
142.093
136.062
135.244
133.078
133.064
133.036
132.987
132.337
130.100
129.511
129.490
128.996
127.043
126.664
120.402
119.936
115.517
114.938
77.416
77.098
76.781
21.864
21.550
3y+3y'
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.179
8.139
8.025
8.005
7.691
7.670
7.596
7.359
7.340
7.271
7.241
7.233
7.221
7.213
2.506
2.491
2.461
3z+3z'
9 8 7 6 5 4 3 2 1 0 ppm
1.07
0.93
2.04
5.02
1.09
4.01
2.03
2.82
3.22
6.03


8.179
8.139
8.025
8.005
7.691
7.670
7.596
7.359
7.340
7.271
7.241
7.233
7.221
7.213
2.506
2.491
2.461
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 ppm
0.96
0.95
2.07
5.10
1.09
4.07
2.07
3.00
3.02
6.04
9 8 7 6 5 4 3 2 1 0 ppm
3z+3z'


167.100
166.932
144.374
144.086
144.060
143.171
142.681
142.113
135.876
135.038
132.411
130.179
130.141
130.092
129.745
129.716
129.635
126.894
126.504
120.339
119.876
115.446
114.876
77.441
77.124
76.805
21.844
21.664
21.530
3z+3z'
180 160 140 120 100 80 60 40 20 ppm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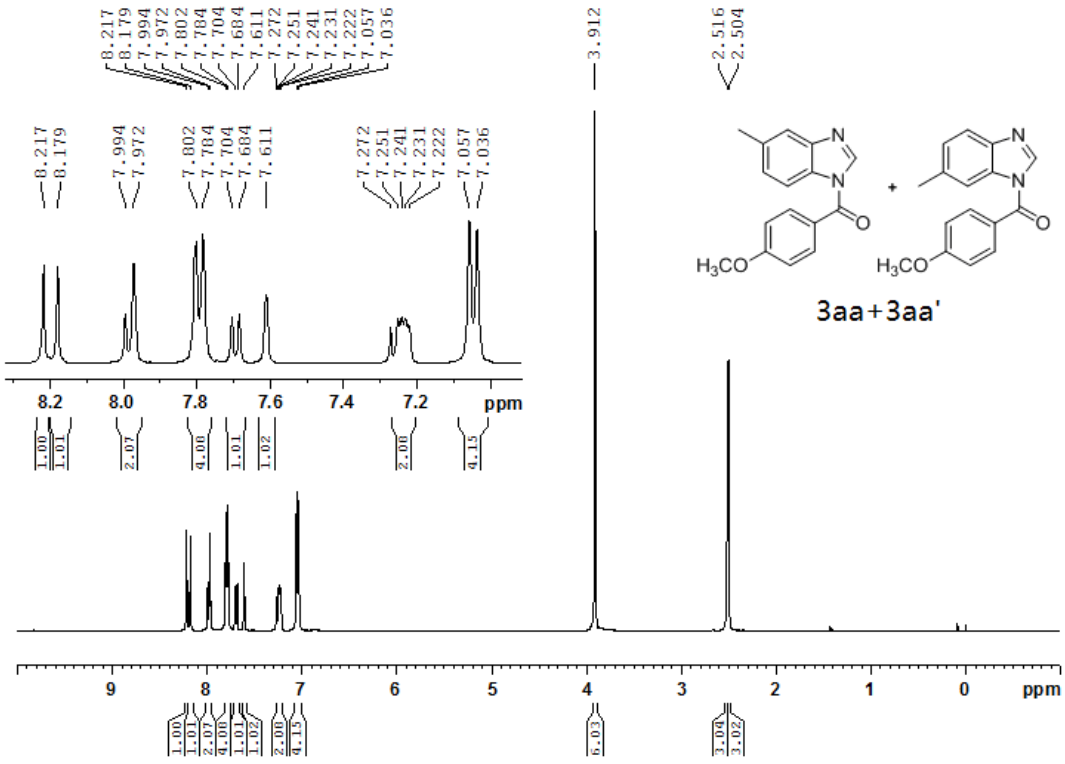
8.179
7.994
7.972
7.802
7.784
7.704
7.684
7.611
7.272
7.251
7.241
7.231
7.222
7.057
7.036
3.912
2.516
2.504
3aa+3aa'
ppm


8.217
8.179
7.994
7.972
7.802
7.784
7.704
7.684
7.611
7.272
7.251
7.241
7.231
7.222
7.057
7.036
3.912
2.516
2.504
3aa+3aa'
ppm