Supporting Information

Palladium-Catalyzed Intermolecular Carbonylative Cross-Coupling of Heteroaryl C(sp^2)–H Bonds with Amines: An Efficient Strategy for Oxidative Aminocarbonylation of Azoles

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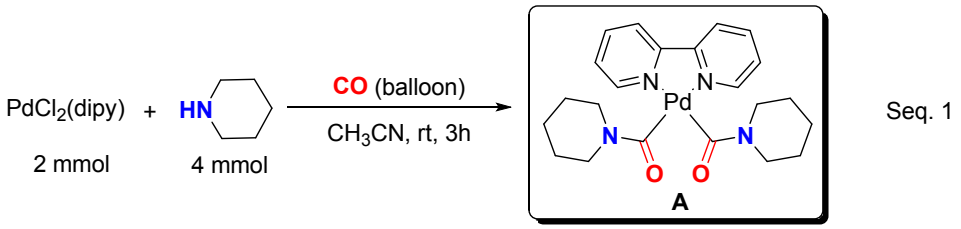
1 General Information

The reagents were purchased from commercial sources and used as received without further purification. The aminocarbonylation of 1,3-diazole were performed in a nitrogen-atmosphere glove box using dry solvents. DMSO was distilled over CaH_2, and stored over 4 ÅMS under N_2 atmosphere. NMR spectra of the products were recorded using a Bruker Avance TM spectrometer operating at 400 MHz for ^1H and 100 MHz for ^{13}C in $CDCl_3$ unless otherwise noted. High resolution mass spectra (HRMS) of the products were obtained on a Bruker Daltonics micro TOF-spectrometer. High-performance liquid chromatography (HPLC) analysis (methanol/H_2O = 60/40, 0.8 mL/min, λ= 258 nm) was performed by Agilent 1260 Infinity with an Agilent ZORBAX C^{18} column using naphthalene as inner standard for benzoxazol-2-yl(morpholino)methanone. Isolated yield for the reaction of 1,3-diazoles with amines was obtained by a Preparative HPLC Equipment with a Hedra C^{18} column (media: 10 μm, size: 30 * 250 mm) made by the Jiangsu Hanbon Science &Technology Company, and a mixture of methanol/H_2O was used as the eluent. Isolated yields for other reactions were obtained by column chromatography (300-400 mesh), and ethyl acetate/petroleum ether was used as the eluent.

2 The Reaction of Carbamoyl-palladium Complexes with Metalated Benzoxazole

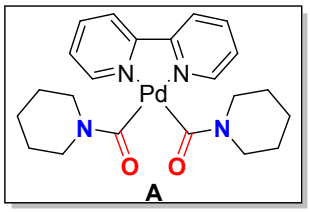
2.1 Synthesis of carbamoyl-palladium complexes[1]



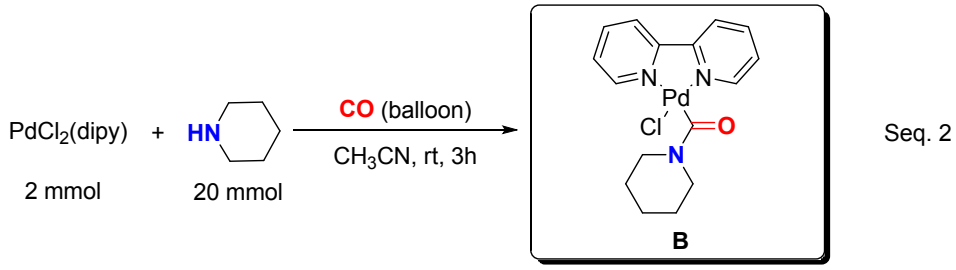
Seq. 1

Complex A was synthesized using the reported method in ref. 1: In a glove box, a solution of freshly prepared $PdCl_2$(dipy) (dipy = 2,2'-dipyridine) (2 mmol) in CH_3CN (15 mL) was added into an 100 mL Schlenk flask. Then piperidine (20 mmol) was added and the resulting mixture was degassed by alternately freezing, evacuating and thawing. Then the mixture was stirred under CO (balloon) at room temperature for about 2 h. The initial yellow color gradually converted into orange. Then the solution was filtered and the mother solution was concentrated to half volume under reduced pressure. The salt that eventually precipitated was eliminated again by filtration. The solution was kept overnight at 278 K to afford impure red crystals of the dicarbamoyl complex. The crude product was suspended in 10 mL of CH_3CN containing 1mL piperidine, and 2.5 mL of a 0.3N solution of CH_3ONa in ethanol was added dropwise under stirring at 273K. The resulting orange suspension was filtered and concentrated to half its volume and kept at 278K overnight. Red crystals of pure dicarbamoyl complex precipitated and were collected by filtration (615 mg, 63%).

Dicarbamoyl palladium complex (A)[1]



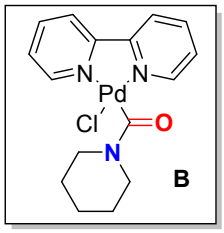
[1]H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.8 Hz, 2H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.99 (td, *J* = 7.9, 1.3 Hz, 2H), 7.50–7.44 (m, 2H), 4.26 (s, 4H), 3.59 (s, 4H), 1.61 (d, *J* = 5.2 Hz, 4H), 1.45 (d, *J* = 5.2 Hz, 8H). [13]C NMR (101 MHz, $CDCl_3$) δ 189.9, 152.3, 149.5, 136.7, 124.6, 119.7, 47.2, 40.0, 25.5, 25.0, 23.8.



Seq. 2

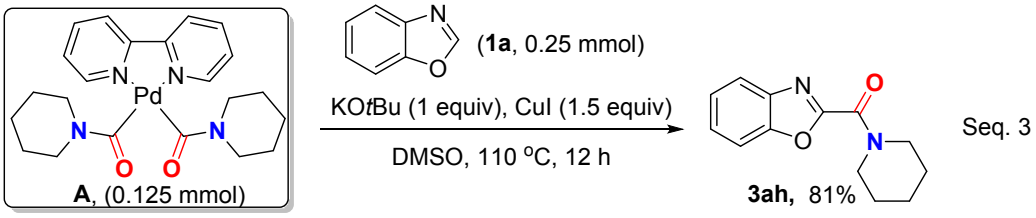
Complex B was synthesized using the reported method in ref. 1: In a glove box, a solution of freshly prepared $PdCl_2$(dipy) (2 mmol) in CH_3CN (15 mL) was added into an 100 mL schlenk flask. Then piperidine (4 mmol) was added and the resulting mixture was degassed by alternately freezing, evacuating and thawing. Then the mixture was stirred under CO (0.1 MPa) at room temperature for about 3 h. The suspension gradually turned to olive green. The product was filtered off, washed with a mixture of CH_3CN/MeOH (10:1) to dissolve impurities of piperidinium chloride and dried in vacuo (602 mg, 73%).

Monocarbamoyl palladium complex (B)[1]

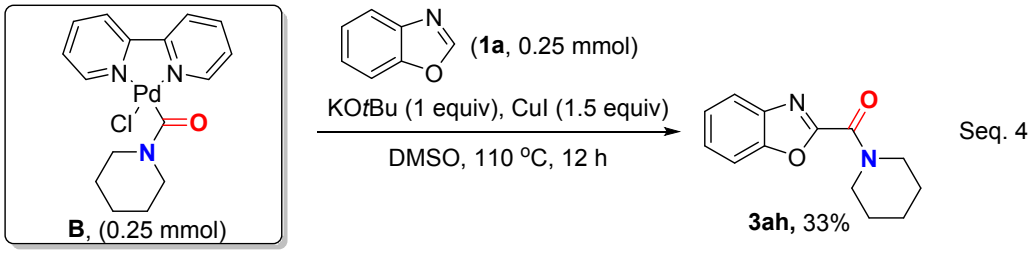


[1]H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.7 Hz, 1H), 8.44–8.40 (m, 3H), 8.12 (t, *J* = 7.8 Hz, 2H), 7.48–7.36 (m, 2H), 4.44–4.17 (m, 2H), 3.79–3.49 (m, 2H), 1.76 (d, *J* = 5.3 Hz, 1H), 1.71–1.53 (m, 3H), 1.49–1.32 (m, 2H). [13]C NMR (100 MHz, $CDCl_3$) δ 174.8, 155.1, 152.5, 151.9, 148.5, 139.9, 139.2, 126.8, 126.1, 123.3, 122.6, 48.9, 44.6, 26.6, 26.4, 25.1.

2.2 The stoichiometric reaction of carbamoyl-palladium complexes with benzoxazole in the presence of base and CuI



Seq. 3

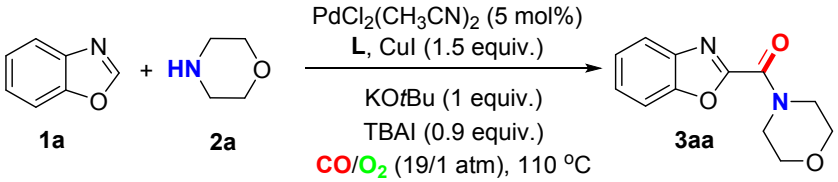


Seq. 4

In a glove box, a mixture of benzoxazole (0.25 mmol), KO*t*Bu (0.25 mmol), CuI (0.375 mmol) and DMSO (1 mL) was added into a 50 mL Schlenk tube. The mixture was stirred for 10 min at room temperature before carbamoyl complex **A** (0.125 mmol) or **B** (0.25 mmol) was added. Then the sealed tube was stirred at 110 °C for 12 h. After cooling to room temperature, the resultant reaction mixture was purified by preparative HPLC equipment to afford the corresponding product. For the reaction of benzoxazole with **A**, 81% yield of **3ah** was obtained. While the reaction of benzoxazole with **B** gave **3ah** in 33% yield. **This result suggested that carbamoyl-palladium complexes are able to react with metalated heteroarenes to furnish the corresponding amides.**

3 Optimization of the Reaction Conditions for the Oxidative Carbonylation of Benzoxazole and Morpholine

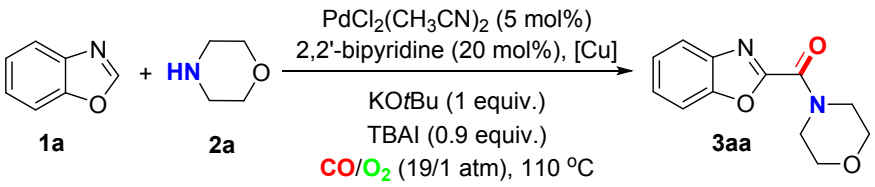
Table S1. Screening of ligands.[a]



Entry [a]	L	Yield (%)
1	$P^tBu_3 \cdot HBF_4$	32
2	PPh_3	70
3	Xantphos	48
4	dppp	54
5	dppf	60
6	2,2'-bipyridine	78
7	L-Proline	54
8	1,10-Phenanthroline	25
9	pyridine	19
10[b]	2,2'-bipyridine	83

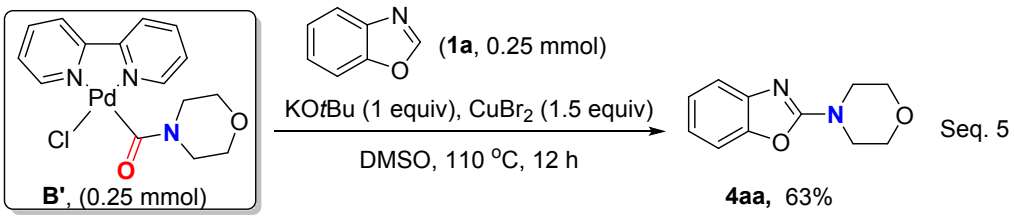
[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.5 mmol), 110 °C, 5.0 mol % of $PdCl_2(CH_3CN)_2$, ligand (10 mol%), CuI (0.375 mmol, 1.5 equiv.), KO*t*Bu (0.25 mmol, 1.0 equiv.), TBAI (0.225 mmol, 0.9 equiv.), CO/O_2 (19/1 atm), DMSO (2 mL), 24 h. The yields were determined by HPLC analysis with naphthalene as an internal standard. [b]20 mol% of 2,2'-pyridine was used.

Table S2. Screening of copper salts.[a]



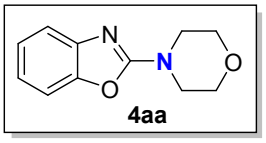
Entry	[Cu]	Yield (%)
1	CuBr	54
2	CuOAc	34
3[b]	$CuBr_2$	n.d.
4[c]	CuI	n.d.
5	---	trace

[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.5 mmol), 110 °C, 5.0 mol % of $PdCl_2(CH_3CN)_2$, 2,2'-bipyridine (20 mol%), Cu salt (0.375 mmol, 1.5 equiv.), KO*t*Bu (0.25 mmol, 1.0 equiv.), TBAI (0.225 mmol, 0.9 equiv.), CO/O_2 (19/1 atm), DMSO (2 mL), 24 h. The yields were determined by HPLC analysis with naphthalene as an internal standard. [b]C–N cross coupling product **4aa** was solely obtained in 64% yield. [c]no Pd catalyst was added, a ring-opening product **5aa** came to be the main product.



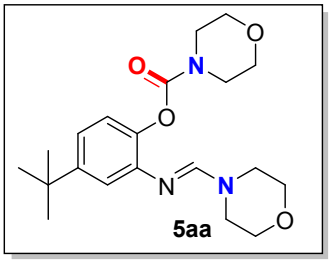
Complex **B′** was synthesized using the reported method in ref. 1. In a glove box, a mixture of 1a (0.25 mmol), KO*t*Bu (0.25 mmol), $CuBr_2$ (0.375 mmol) and DMSO (1 mL) was added into a Schlenk tube with a stir bar. The mixture was stirred for 10 minutes at room temperature before a solution of **B′** (0.25 mmol) in DMSO (1 mL) was added. Then the sealed tube was stirred at 110 °C for 12 h. After cooling to room temperature, the resultant mixture was monitored by GC-MS and purified by preparative thin-layer chromatography to provide the corresponding product. Non-carbonylative C–N cross coupling product **4aa** was obtained in 63% yield while no aminocarbonylation product was observed.

2-morpholinobenzo[d]oxazole (4aa)[2]



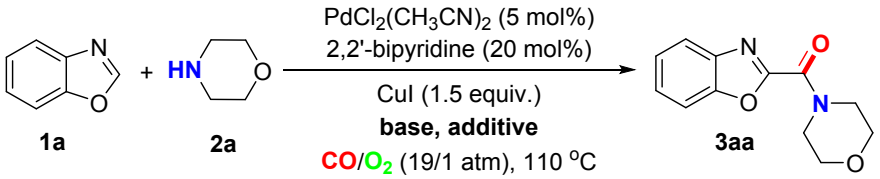
Purified by Preparative HPLC Equipment (methanol/H_2O = 60/40, 10 mL/min); pale yellow solid; 64% yield; *Rf* = 0.25 (5:1 PE/EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.4 Hz, 1H), 7.31–7.23 (m, 1H), 7.18 (td, *J* = 7.7, 1.0 Hz, 1H), 7.04 (td, *J* = 7.8, 1.2 Hz, 1H), 3.87–3.79 (m, 4H), 3.69 (dd, *J* = 6.5, 3.3 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 148.8, 142.9, 124.1, 121.0, 116.5, 108.8, 66.2, 45.7. HRMS (ESI) Calcd for $C_{11}H_{13}N_2O_2$: $[M+H]^+$, 205.0972; Found: 205.0961.

(E)-4-(tert-butyl)-2-((morpholinomethylene)amino)phenyl morpholine-4-carboxylate (5aa)



Purified by Preparative HPLC Equipment (methanol/H_2O = 60/40, 10 mL/min); pale yellow solid; 61% yield; *Rf* = 0.27 (2:1 PE/EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.02 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.89 (d, *J* = 2.1 Hz, 1H), 3.80 – 3.41 (m, 16H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 152.5, 149.3, 143.0, 141.9, 121.7, 120.4, 118.1, 66.7, 45.0, 44.3, 34.5, 31.5. HRMS (ESI) Calcd for $C_{20}H_{29}N_3NaO_4$: $[M+Na]^+$, 398.2050; Found: 398.2055.

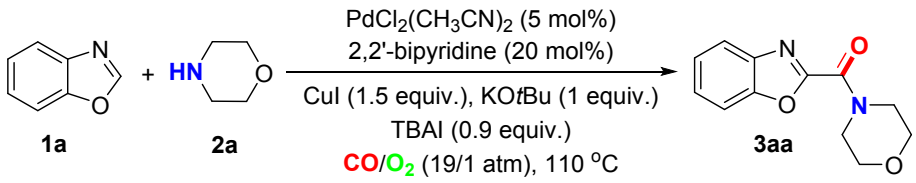
Table S3. Screening of base and additives.[a]



Entry	Base	Additive	Yield (%)
1	NaO*t*Bu	TBAI	43
2	LiO*t*Bu	TBAI	19
3	KO*t*Bu	---	40
4	KO*t*Bu	TBAB	39
5	KO*t*Bu	KI	42

[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.5 mmol), 110 °C, 5.0 mol % of $PdCl_2(CH_3CN)_2$, 2,2'-bipyridine (20 mol%), CuI (0.375 mmol, 1.5 equiv.), base (0.25 mmol, 1.0 equiv.), additive (0.225 mmol, 0.9 equiv.), CO/O_2 (19/1 atm), DMSO (2 mL), 24 h. The yields were determined by HPLC analysis with naphthalene as an internal standard.

Table S4. Screening of solvent.[a]

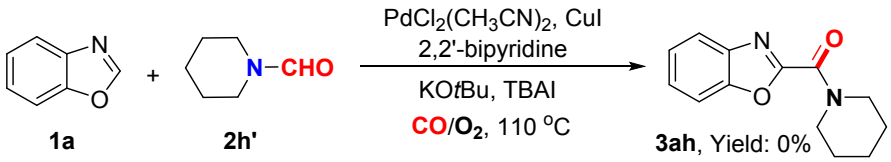


Entry	Solvent	Yield (%)
1	DMF	54
2	THF	45
3	Toluene	32
4[b]	DMSO	96 (84)
5b[c]	DMSO	12

[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.5 mmol), 110 °C, 5.0 mol % of $PdCl_2(CH_3CN)_2$, 2,2'-bipyridine (20 mol%), CuI (0.375 mmol, 1.5 equiv.), base (0.25 mmol, 1.0 equiv.), additive (0.225 mmol, 0.9 equiv.), CO/O_2 (19/1 atm), Solvent (2 mL), 24 h. The yields were determined by HPLC analysis with naphthalene as an internal standard. [b]DMSO (3 mL). [c]CO/air (19/1 atm).

4 Mechanistic Studies

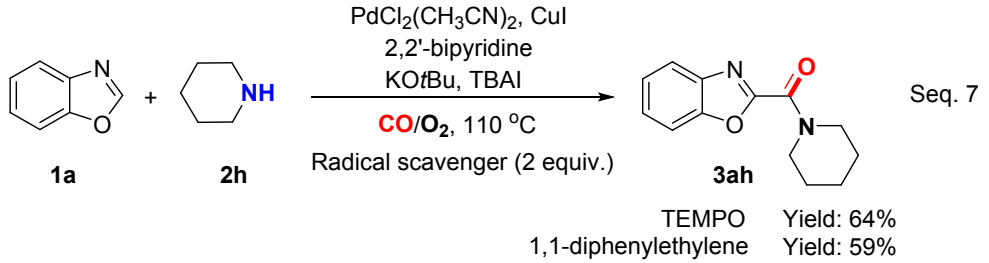
Ruling out formamides as possible intermediates for this aminocarbonylation



Seq. 6

In a glove box, a mixture of **1a** (0.25 mmol), $PdCl_2(CH_3CN)_2$ (5 mol%), 2,2'-bipyridine (20 mol%), CuI (0.375 mmol), TBAI (0.225 mmol), KO*t*Bu (0.25 mmol) and **2h′** (0.5 mmol) in DMSO (3 mL) were added into an 100 mL stainless steel autoclave with a magnetic bar. Flushing the autoclave three times with O_2 before it was finally pressurized with 1.0 atm O_2. Then it was pressurized directly with 19 atm CO without flushing. The mixture was stirred in an oil bath preheated at 110 °C for 24 h. After that, the reactor was cooled to room temperature, degassed carefully and opened. The resultant reaction mixture was monitored by TLC. The desired product was not observed. **This result excludes the possibility of formamides acting as responsible intermediate for the amide formation.**

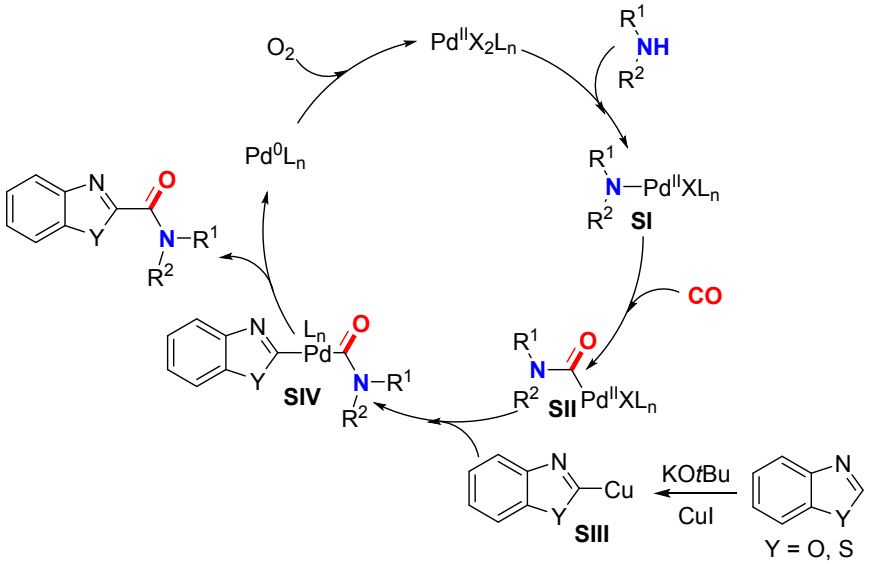
Free-radical trapping experiments



To a 100 mL stainless steel autoclave in glove box was added a mixture of **1a** (0.25 mmol), $PdCl_2(CH_3CN)_2$ (5 mol%), 2,2'-bipyridine (20 mol%), CuI (0.375 mmol), TBAI (0.225 mmol), KO*t*Bu (0.25 mmol), **2h** (0.5 mmol), TEMPO (0.5 mmol) or 1,1-diphenylethylene (0.5 mmol) in DMSO (3 mL). The autoclave was closed and flushed three times with O_2 before it was pressurized with 1.0 atm O_2. After that, 19 atm CO was pressurized directly into the autoclave. The mixture was stirred in an oil bath preheated at 110 °C for 24 h. Afterwards, the autoclave was cooled to room temperature and the excess gas was released carefully. The resultant reaction mixture was purified by Preparative HPLC Equipment to give the desired product **3ah** in 64% and 59% yield, respectively. **This result indicates that the addition of free-radical scavengers doesn't have substantial effect on this aminocarbonylation. So a radical pathway should be ruled out.**

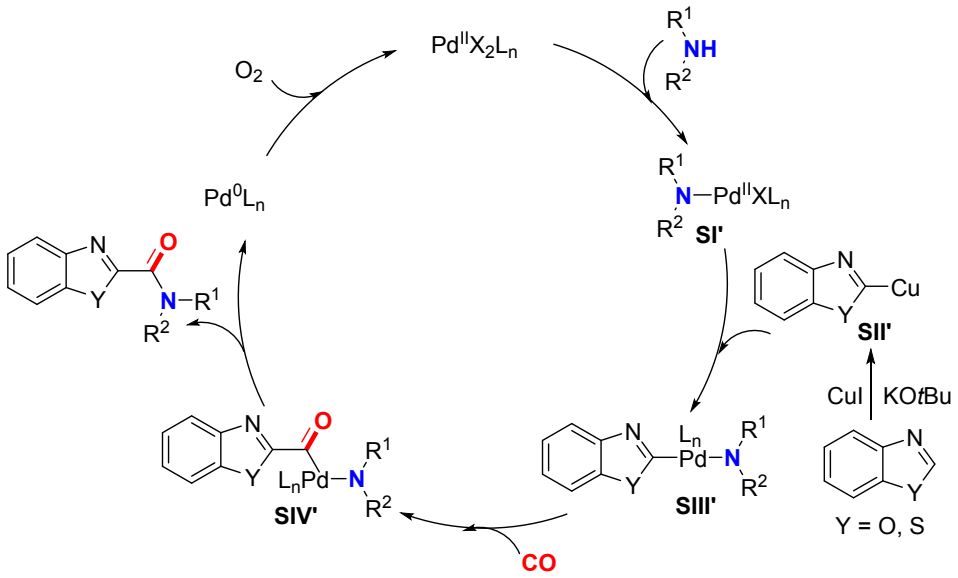
Possible mechanism

path a: A carbamoyl palladium intermediate may be involved in this process (Scheme S1). Firstly, the reaction of amine and Pd^{II} species yielded amino-palladium complex S**I**. Subsequent insertion of CO into S**I** afforded the carbamoyl palladium intermediate S**II**. In the presence of base, metallation of diazole with CuI formed the organocopper intermediate S**III**. Subsequent transmetallation of carbamoyl palladium S**II** with the organocopper intermediate S**III** generated intermediate S**IV**, which finally underwent reductive elimination to give the desired amide product and release Pd^0. In the presence of O_2, Pd^{II} could be regenerated to fulfill the catalytic cycle.



Scheme S1. One possible mechanism for this oxidative aminocarbonylation

path b: As shown in Scheme S2, the reaction of amine and Pd^{II} species yields amino-palladium complex **SI'**. Meanwhile, in the presence of base, diazole reacts with CuI to form the organocopper intermediate **SII'**. Subsequently, transmetallation of amino-palladium complex **SI'** with **SII'** generates intermediate **SIII'**, which undergoes CO insertion to give intermediate **SIV'**. Finally, reductive elimination of **SIV'** affords the amide product and releases Pd^0 species which is oxidized by O_2 to regenerate Pd^{II} and complete the catalytic cycle.



Scheme S2. Another possible mechanism for this oxidative aminocarbonylation

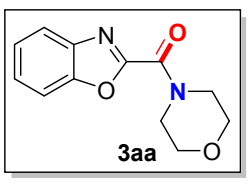
5 Experimental Procedure and Characterization Data for Products

5.1 General procedure for the oxidative carbonylation of 1,3-diazole with amine

1,3-diazole (0.25 mmol), $PdCl_2(CH_3CN)_2$ (5 mol%), 2,2'-bipyridine (20 mol%), CuI (0.375 mmol), TBAI (0.225 mmol), KO*t*Bu (0.25 mmol), amine (0.5 mmol) and DMSO (3 mL) were consecutively added into an 100 mL stainless steel autoclave with a magnetic bar. Then the closed autoclave was vacuumed and flushed three times with O_2 before it was finally pressurized with 1.0 atm O_2 gas. Subsequently, 19 atm CO was inflated directly into the autoclave. Then the reactor was immersed in an oil bath preheated at 110 °C for 24 h. After cooling to room temperature, excess CO/O_2 was released and the resultant reaction mixture was purified by Preparative HPLC Equipment to afford the corresponding product.

5.2 Characterization data for products

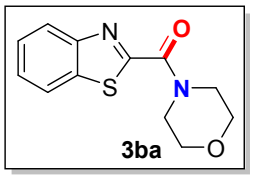
benzo[d]oxazol-2-yl(morpholino)methanone (3aa)



Purified by Preparative HPLC Equipment (methanol/H_2O = 60/40, 10 mL/min); yellow solid; 84% yield; *Rf* = 0.43 (2:1 PE/EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.51–7.41 (m, 2H), 4.36–4.24 (m, 2H), 3.91–3.78 (m, 6H). ^{13}C NMR (100 MHz,

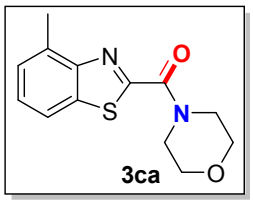
$CDCl_3$) δ 156.1, 154.6, 149.9, 140.1, 127.3, 125.4, 121.3, 111.6, 67.1, 66.8, 47.6, 43.3. HRMS (ESI) Calcd for $C_{12}H_{12}N_2NaO_3$: $[M+Na]^+$, 255.0740; Found: 255.0741.

benzo[d]thiazol-2-yl(morpholino)methanone (3ba)



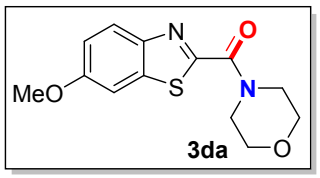
Purified by Preparative HPLC Equipment (methanol/H_2O = 60/40, 10 mL/min); pale yellow solid; 59% yield; *Rf* = 0.39 (5:1 PE/EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15–8.01 (m, 1H), 7.95 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.55–7.46 (m, 2H), 4.63–4.44 (m, 2H), 3.89–3.78 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 159.7, 153.1, 136.2, 126.8, 126.6, 124.6, 121.9, 67.2, 66.9, 47.2, 43.9. HRMS (ESI) Calcd for $C_{12}H_{12}N_2NaO_2S$: $[M+Na]^+$, 271.0512; Found: 271.0506.

(4-methylbenzo[d]thiazol-2-yl)(morpholino)methanone (3ca)



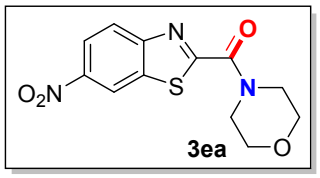
Purified by Preparative HPLC Equipment (methanol/H_2O = 60/40, 10 mL/min); pale yellow solid; 45% yield; *Rf* = 0.69 (5:1 PE/EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.2 Hz, 1H), 4.57 (s, 2H), 3.85 (dd, *J* = 9.8, 4.4 Hz, 6H), 2.73 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 159.8, 152.6, 136.2, 134.7, 126.9, 126.8, 119.2, 67.2, 66.9, 47.3, 44.0, 18.2. HRMS (ESI) Calcd for $C_{13}H_{14}N_2NaO_2S$: $[M+Na]^+$, 285.0668; Found: 285.0662.

(6-methoxybenzo[d]thiazol-2-yl)(morpholino)methanone (3da)



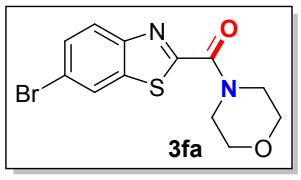
Purified by Preparative HPLC Equipment (methanol/H_2O = 60/40, 10 mL/min); white solid; 46% yield; *Rf* = 0.23 (5:1 PE/EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 9.0 Hz, 1H), 7.37 (d, *J* = 2.5 Hz, 1H), 7.13 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.60–4.51 (m, 2H), 3.90 (s, 3H), 3.83 (d, *J* = 8.5 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 159.7, 159.0, 147.6, 138.0, 125.3, 117.0, 103.3, 67.3, 66.9, 55.8, 47.1, 43.9. HRMS (ESI) Calcd for $C_{13}H_{14}N_2NaO_3S$: $[M+Na]^+$, 301.0617; Found: 301.0621.

morpholino(6-nitrobenzo[d]thiazol-2-yl)methanone (3ea)



Purified by Preparative HPLC Equipment (methanol/H_2O = 60/40, 10 mL/min); yellow solid; 81% yield; *Rf* = 0.19 (5:1 PE/EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 2.2 Hz, 1H), 8.24 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.38 (d, *J* = 9.0 Hz, 1H), 3.89–3.79 (m, 5H), 3.69–3.55 (m, 2H), 3.42–3.35 (m, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 148.1, 144.4, 139.4, 123.9, 122.9, 118.6, 113.4, 66.6, 66.4, 47.7, 45.0. HRMS (ESI) Calcd for $C_{13}H_{14}N_2NaO_2S$: $[M+Na]^+$, 316.0362; Found: 316.0368.

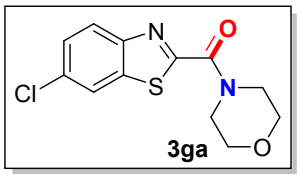
(6-bromobenzo[d]thiazol-2-yl)(morpholino)methanone (3fa)



Purified by Preparative HPLC Equipment (methanol/H_2O = 60/40, 10 mL/min); yellow solid; 54% yield; *Rf* = 0.62 (2:1 PE/EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 1.9 Hz, 1H), 7.92 (d, *J* = 8.7 Hz, 1H), 7.64 (dd, *J* = 8.8, 1.9 Hz, 1H), 4.54–4.49 (m, 2H), 3.84–3.81 (m, 6H).^{13}C

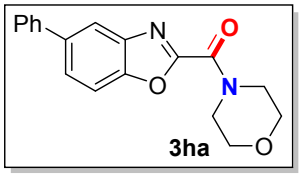
NMR (100 MHz, $CDCl_3$) δ 165.2, 159.2, 151.9, 137.9, 130.3, 125.8, 124.4, 120.9, 67.2, 66.9, 47.1, 44.0. HRMS (ESI) Calcd for $C_{12}H_{11}BrN_2NaO_2S$: $[M+Na]^+$, 348.9617; Found: 348.9589.

(6-chlorobenzo[d]thiazol-2-yl)(morpholino)methanone (3ga)



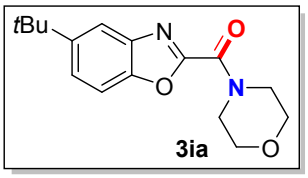
Purified by Preparative HPLC Equipment (methanol/H_2O = 60/40, 10 mL/min); pale yellow solid; 66% yield; *Rf* = 0.33 (5:1 PE/EA). ^1H NMR (400 MHz, $CDCl_3$) δ 7.99–7.93 (m, 2H), 7.49 (dd, *J* = 8.8, 2.0 Hz, 1H), 4.61–4.46 (m, 2H), 3.84–3.81 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 159.2, 151.6, 137.4, 133.1, 127.6, 125.5, 121.5, 67.2, 66.9, 47.1, 44.0. HRMS (ESI) Calcd for $C_{12}H_{11}ClN_2NaO_2S$: $[M+Na]^+$, 305.0122; Found: 305.0135.

morpholino(5-phenylbenzo[d]oxazol-2-yl)methanone (3ha)



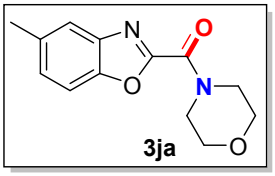
Purified by Preparative HPLC Equipment (methanol/H_2O = 60/40, 10 mL/min); pale yellow solid; 53% yield; *Rf* = 0.23 (5:1 PE/EA). ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.70 (s, 2H), 7.65–7.58 (m, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 4.34–4.26 (m, 2H), 3.93–3.80 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 155.2, 149.4, 140.8, 140.5, 139.4, 129.0, 127.6, 127.5, 119.6, 111.6, 67.1, 66.8, 47.6, 43.4. HRMS (ESI) Calcd for $C_{18}H_{17}N_2O_3$: $[M+H]^+$, 309.1234; Found: 309.1229.

(5-tert-butylbenzo[d]oxazol-2-yl)(morpholino)methanone (3ia)



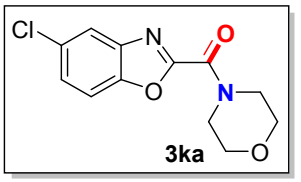
Purified by Preparative HPLC Equipment (methanol/H_2O = 60/40, 10 mL/min); white solid; 48% yield; *Rf* = 0.34 (5:1 PE/EA). ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.56 (s, 2H), 4.35–4.25 (m, 2H), 3.90–3.77 (m, 6H), 1.39 (s, 9H). ^{13}C NMR (10 MHz, $CDCl_3$) δ 156.2, 154.7, 149.1, 148.0, 140.1, 125.4, 117.5, 110.8, 67.1, 66.8, 47.6, 43.3, 35.1, 31.7. HRMS (ESI) Calcd for $C_{16}H_{21}N_2O_3$: $[M+H]^+$, 289.1547; Found: 289.1544.

(5-methylbenzo[d]oxazol-2-yl)(morpholino)methanone (3ja)



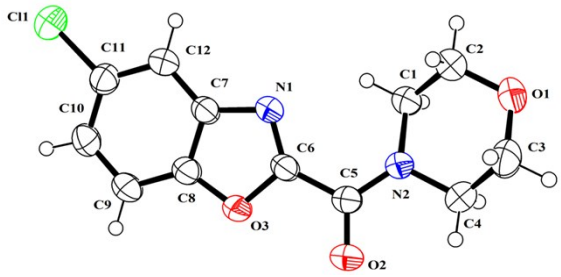
Purified by Preparative HPLC Equipment (methanol/H_2O = 60/40, 10 mL/min); white solid; 57% yield; *Rf* = 0.21 (5:1 PE/EA). ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 and 7.44 (two peaks overlap, 2H), 7.20 (s, 1H), 4.20 (s, 2H), 3.78–3.74 (m, 6H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 154.7, 148.2, 140.3, 135.4, 128.6, 121.0, 111.0, 67.1, 66.8, 47.6, 43.3, 21.5. HRMS (ESI) Calcd for $C_{13}H_{15}N_2O_3$: $[M+H]^+$, 247.1077; Found: 247.1066.

(5-chlorobenzo[d]oxazol-2-yl)(morpholino)methanone (3ka)

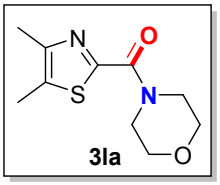


Purified by Preparative HPLC Equipment (methanol/H_2O = 60/40, 10 mL/min); pale yellow solid; 72% yield; *Rf* = 0.42 (2:1 PE/EA). ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 1.9 Hz, 1H), 7.59 (d, *J* = 8.7 Hz, 1H), 7.46 (dd, *J* = 8.7, 1.9 Hz, 1H), 4.28–4.21 (m, 2H), 3.89–3.79 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 155.6, 148.5, 141.1, 131.0, 127.8, 121.2, 112.4, 67.1, 66.7, 47.5, 43.4. HRMS (ESI) Calcd for $C_{12}H_{11}ClN_2NaO_3$: $[M+Na]^+$, 289.0350; Found: 289.0338.

Crystal Structure of **3ka** (CCDC 1534575)

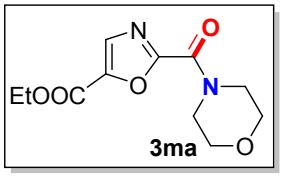


(4,5-dimethylthiazol-2-yl)(morpholino)methanone (3la)



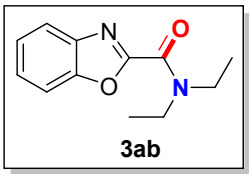
Purified by Preparative HPLC Equipment (methanol/H_2O = 60/40, 10 mL/min); pale yellow solid; 32% yield; *Rf* = 0.50 (2:1 PE/EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.46 (s, 2H), 3.77 (s, 6H), 2.40 and 2.35 (two peaks overlap, s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 159.4, 149.5, 132.6, 67.0, 47.1, 43.6, 29.7, 14.9, 11.5. HRMS (ESI) Calcd for $C_{10}H_{14}N_2NaO_2S$: $[M+Na]^+$, 249.0668; Found: 249.0663.

ethyl 2-(morpholine-4-carbonyl)oxazole-5-carboxylate (3ma)



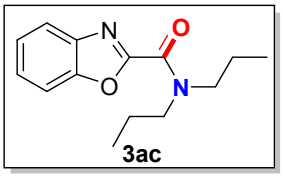
Purified by Preparative HPLC Equipment (methanol/H_2O = 60/40, 10 mL/min); pale yellow solid; 66% yield; *Rf* = 0.09 (5:1 PE/EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.8, 4.42 (d, *J* = 6.5 Hz, 2H), 4.09 (s, 2H), 3.80 and 3.76 (two peaks overlap, 6H), 1.41 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 155.7, 154.8, 143.4, 133.4, 66.9, 66.7, 62.0, 47.4, 43.2, 14.2. HRMS (ESI) Calcd for $C_{11}H_{14}N_2NaO_5$: $[M+Na]^+$, 277.0795; Found: 277.0788.

N,N-diethylbenzo[d]oxazole-2-carboxamide (3ab)



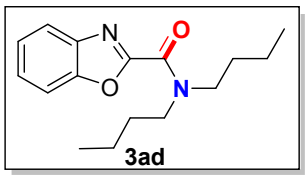
Purified by Preparative HPLC Equipment (methanol/H_2O = 80/20, 10 mL/min); pale yellow solid; 81% yield; *Rf* = 0.77 (5:1 PE/EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.39–7.34 (m, 2H), 3.78 (q, *J* = 7.1 Hz, 2H), 3.55 (q, *J* = 7.1 Hz, 2H), 1.29–1.20 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 155.4, 150.0, 140.4, 126.9, 125.1, 121.3, 111.5, 43.4, 41.3, 14.6, 12.6. HRMS (ESI) Calcd for $C_{12}H_{14}N_2NaO_2$: $[M+Na]^+$, 241.0947; Found: 241.0950.

N,N-dipropylbenzo[d]oxazole-2-carboxamide (3ac)



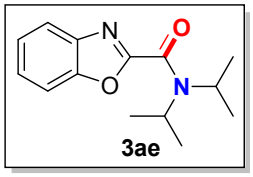
Purified by Preparative HPLC Equipment (methanol/H_2O = 80/20, 10 mL/min); yellow solid; 88% yield; *Rf* = 0.83 (5:1 PE/EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.78 (m, 1H), 7.63 (dd, *J* = 7.4, 0.8 Hz, 1H), 7.48–7.39 (m, 2H), 3.84–3.71 (m, 2H), 3.59–3.46 (m, 2H), 1.79–1.65 (m, 4H), 0.99 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 155.5, 149.9, 140.3, 126.8, 125.1, 121.3, 111.4, 50.5, 48.4, 22.4, 20.6, 11.4, 11.0. HRMS (ESI) Calcd for $C_{14}H_{19}N_2O_2$: $[M+H]^+$, 247.1441; Found: 247.1432.

N,N-dibutylbenzo[d]oxazole-2-carboxamide (3ad)



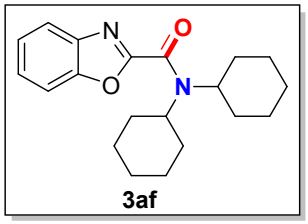
Purified by Preparative HPLC Equipment (methanol/H_2O = 80/20, 10 mL/min); colorless liquid; 87% yield; *Rf* = 0.91 (5:1 PE/EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.75 (m, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.47–7.38 (m, 2H), 3.90–3.73 (m, 2H), 3.64–3.48 (m, 2H), 1.74–1.63 (m, 4H), 1.42–1.40 (m, 2H), 1.32–1.30 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 155.5, 149.9, 140.3, 126.8, 125.1, 121.2, 111.4, 48.7, 46.6, 31.2, 29.4, 20.3, 19.8, 13.9, 13.7. HRMS (ESI) Calcd for $C_{16}H_{22}N_2NaO_2$: $[M+Na]^+$, 297.1573; Found: 297.1587.

N,N-diisopropylbenzo[d]oxazole-2-carboxamide (3ae)



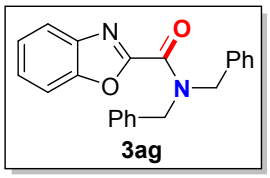
Purified by Preparative HPLC Equipment (methanol/H_2O = 80/20, 10 mL/min); white solid; 82% yield; *Rf* = 0.86 (5:1 PE/EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.49–7.36 (m, 2H), 4.55–4.48 (m, 1H), 3.70–3.63 (m, 1H), 1.56 (d, *J* = 6.8 Hz, 6H), 1.30 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 156.4, 149.8, 140.2, 126.5, 125.0, 121.1, 111.3, 50.7, 46.9, 20.9, 20.1. HRMS (ESI) Calcd for $C_{14}H_{18}N_2NaO_2$: $[M+Na]^+$, 269.1260; Found: 269.1261.

N,N-dicyclohexylbenzo[d]oxazole-2-carboxamide (3af)



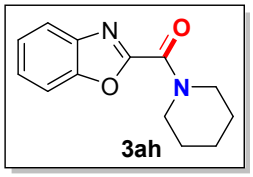
Purified by Preparative HPLC Equipment (methanol/H_2O = 80/20, 10 mL/min); pale yellow solid; 77% yield; *Rf* = 0.92 (5:1 PE/EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.75 (m, 1H), 7.67–7.55 (m, 1H), 7.42 (pd, *J* = 7.4, 1.4 Hz, 2H), 3.92–3.87 (m, 1H), 3.23–3.17 (m, 1H), 2.72–2.49 (m, 2H), 1.98–1.76 (m, 6H), 1.67–1.51 (m, 6H), 1.35–1.05 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 156.6, 149.8, 140.3, 126.4, 124.9, 121.1, 111.3, 59.5, 56.9, 31.2, 29.4, 26.5, 25.6, 25.2, 25.1. HRMS (ESI) Calcd for $C_{20}H_{26}N_2NaO_2$: $[M+Na]^+$, 349.1886; Found: 349.1881.

N,N-dibenzylbenzo[d]oxazole-2-carboxamide (3ag)



Purified by Preparative HPLC Equipment (methanol/H_2O = 80/20, 10 mL/min); white solid; 69% yield; *Rf* = 0.84 (5:1 PE/EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.75 (m, 1H), 7.68–7.62 (m, 1H), 7.50–7.44 (m, 1H), 7.42–7.29 (m, 11H), 5.08 (s, 2H), 4.71 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 155.1, 150.1, 140.2, 136.0, 135.9, 128.9, 128.8, 128.7, 127.9, 121.5, 111.5, 51.0, 48.0. HRMS (ESI) Calcd for $C_{22}H_{18}N_2NaO_2$: $[M+Na]^+$, 365.1260; Found: 365.1243.

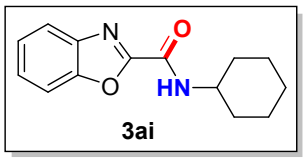
benzo[d]oxazol-2-yl(piperidin-1-yl)methanone (3ah)



Purified by Preparative HPLC Equipment (methanol/H_2O = 60/40, 10 mL/min); white solid; 62% yield; *Rf* = 0.54 (5:1 PE/EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.5 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.48–7.38 (m, 2H), 4.01–3.94 (m, 2H), 3.79 (d, *J* = 5.5 Hz, 2H), 1.72 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 155.4, 149.9, 140.2, 126.9, 125.1, 121.2, 111.5, 48.1, 44.0, 26.7, 25.6, 24.5. HRMS (ESI) Calcd for $C_{13}H_{14}N_2NaO_2$: $[M+Na]^+$, 253.0947; Found:

253.0958.

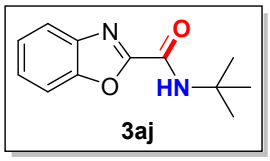
N-cyclohexylbenzo[d]oxazole-2-carboxamide (3ai)



3ai

Purified by Preparative HPLC Equipment (methanol/H_2O = 60/40, 10 mL/min); white solid; 48% yield; *Rf* = 0.36 (5:1 PE/EA). ^{1}H NMR (400 MHz, DMSO) δ 9.13 (d, *J* = 8.3 Hz, 1H), 7.87 (t, *J* = 8.8 Hz, 2H), 7.67–7.13 (m, 2H), 3.85–3.69 (m, 1H), 1.84–1.70 (m, 4H), 1.26–1.44 (m, 6H). ^{13}C NMR (100 MHz, DMSO) δ 155.9, 154.2, 150.1, 139.8, 127.3, 125.5, 120.9, 111.8, 48.6, 33.3, 31.8, 24.8. HRMS (ESI) Calcd for $C_{14}H_{16}N_2NaO_2$: $[M+Na]^+$, 267.1104; Found: 267.1107.

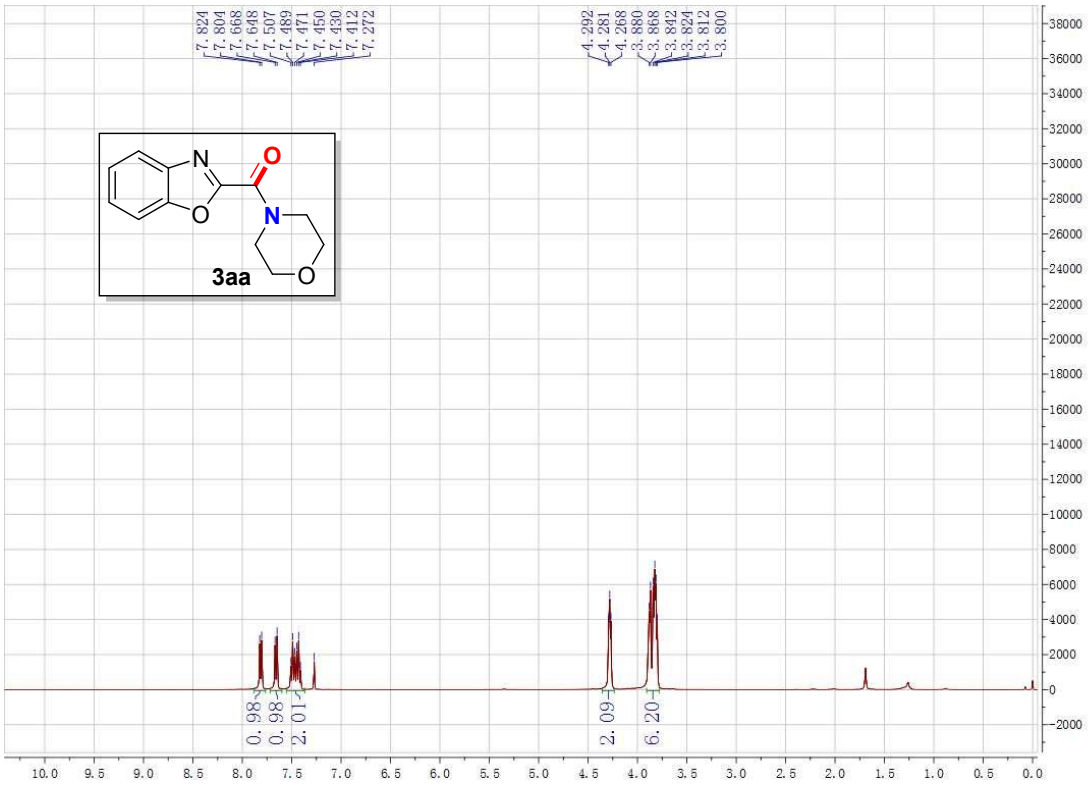
N-tert-butylbenzo[d]oxazole-2-carboxamide (3aj)

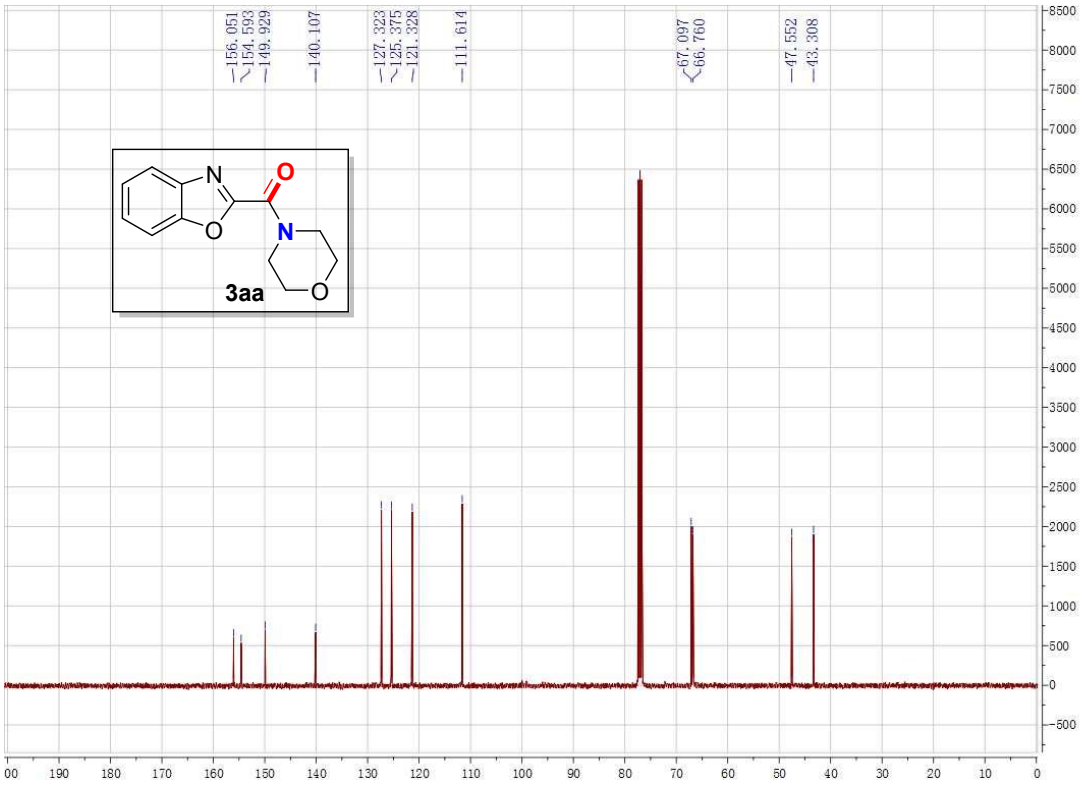


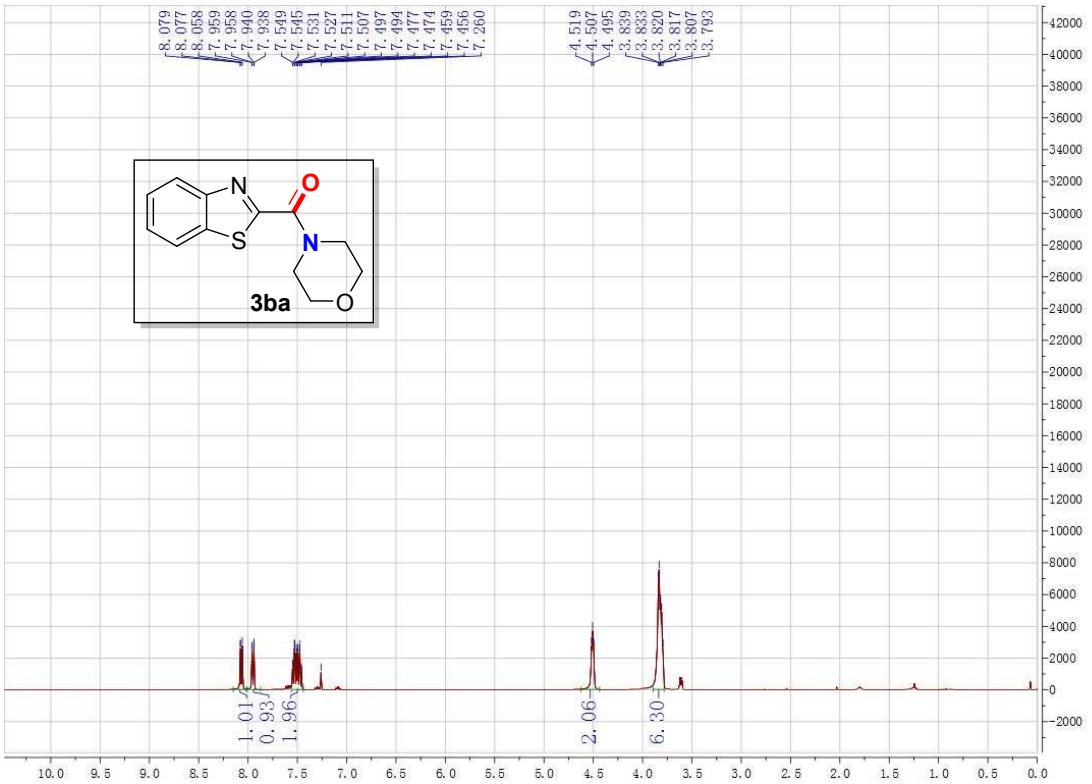
3aj

Purified by Preparative HPLC Equipment (methanol/H_2O = 80/20, 10 mL/min); brown solid; 56% yield; *Rf* = 0.88 (5:1 PE/EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.45 (dt, *J* = 19.1, 7.3 Hz, 2H), 7.17 (s, 1H), 1.52 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 154.8, 151.2, 140.2, 127.2, 125.5, 121.0, 111.9, 52.4, 28.6. HRMS (ESI) Calcd for $C_{12}H_{14}N_2NaO_2$: $[M+Na]^+$, 241.0947; Found: 241.0954.

6 ^{1}H NMR and ^{13}C NMR Copies of Products



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7.507
7.497
7.494
7.477
7.474
7.459
7.456
7.260
4.519
4.507
4.495
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3.817
3.807
3.793
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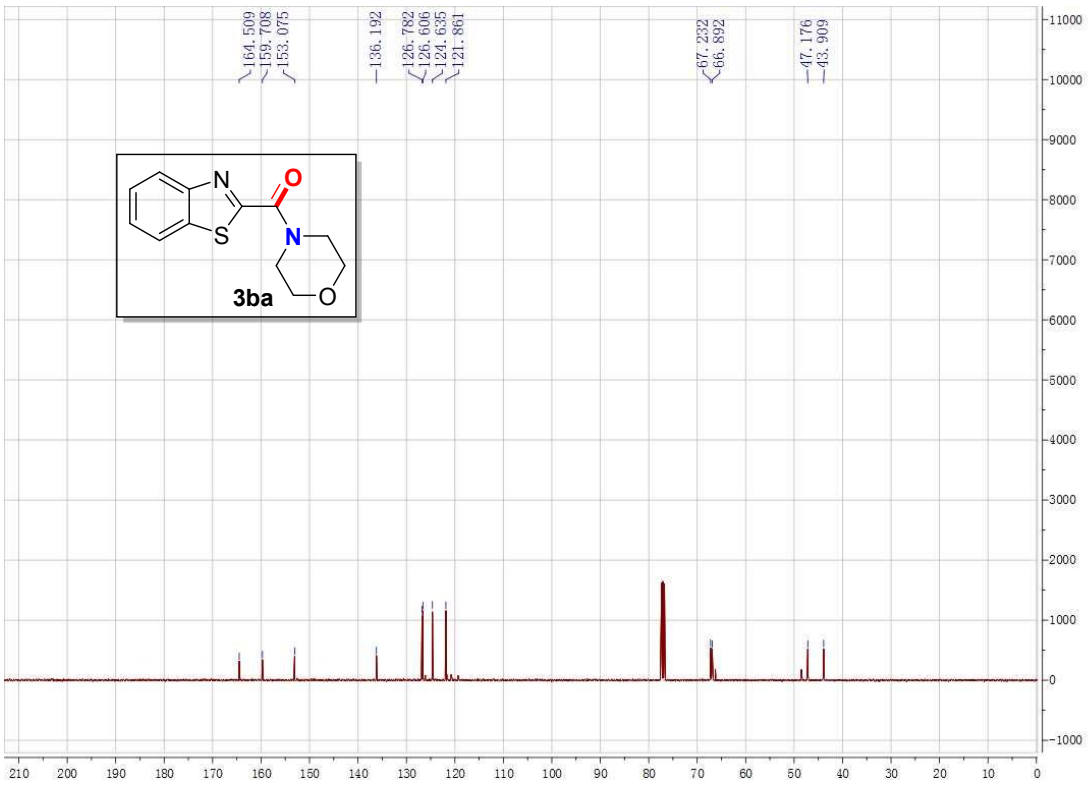
0.93
1.96
2.06
6.30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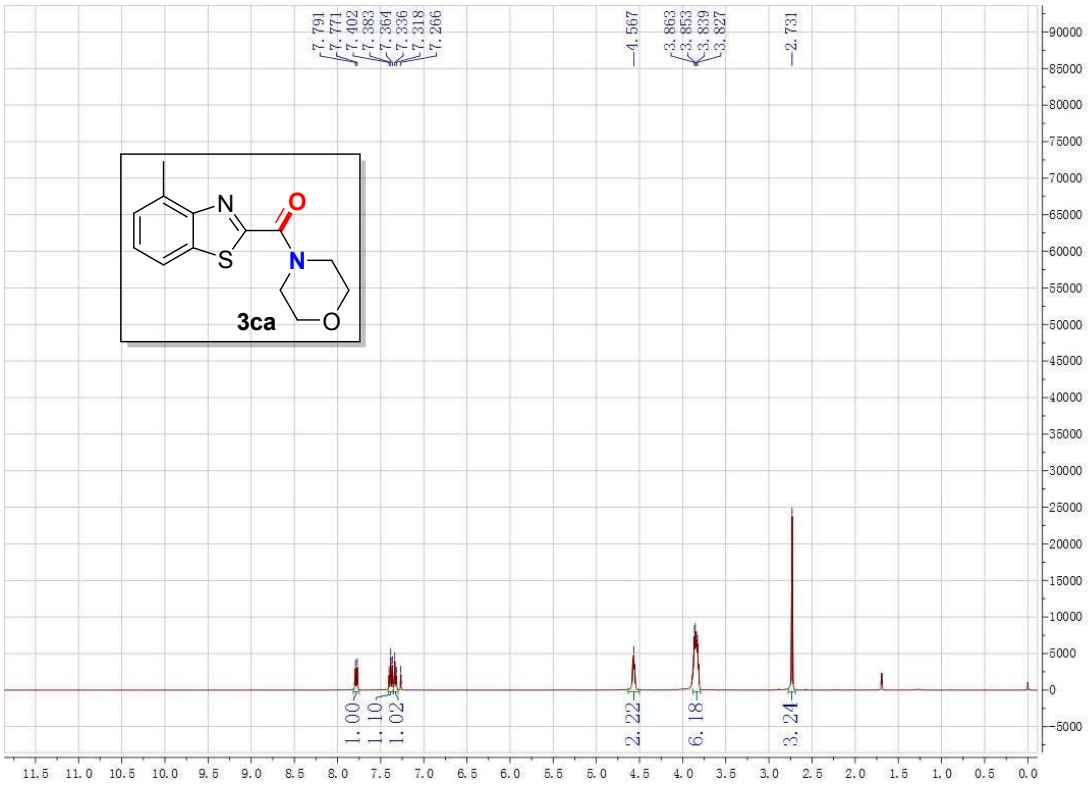
3ba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S
N
O
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1.10
1.02
2.22
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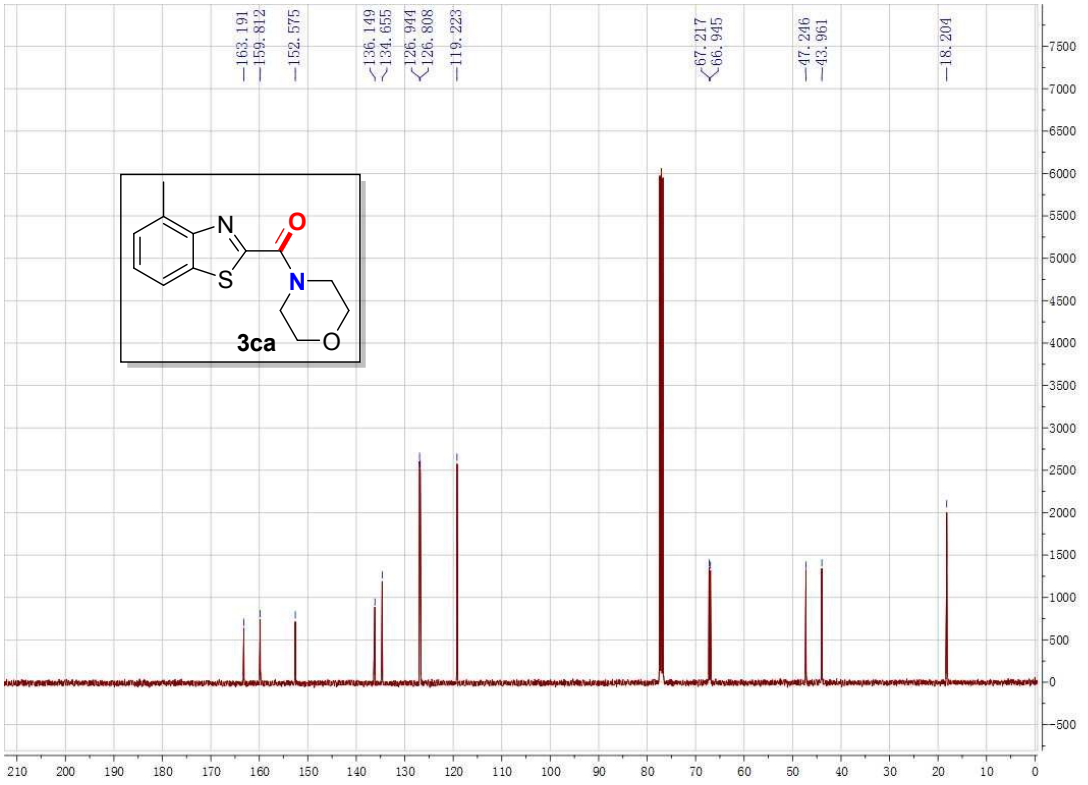
3.24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O
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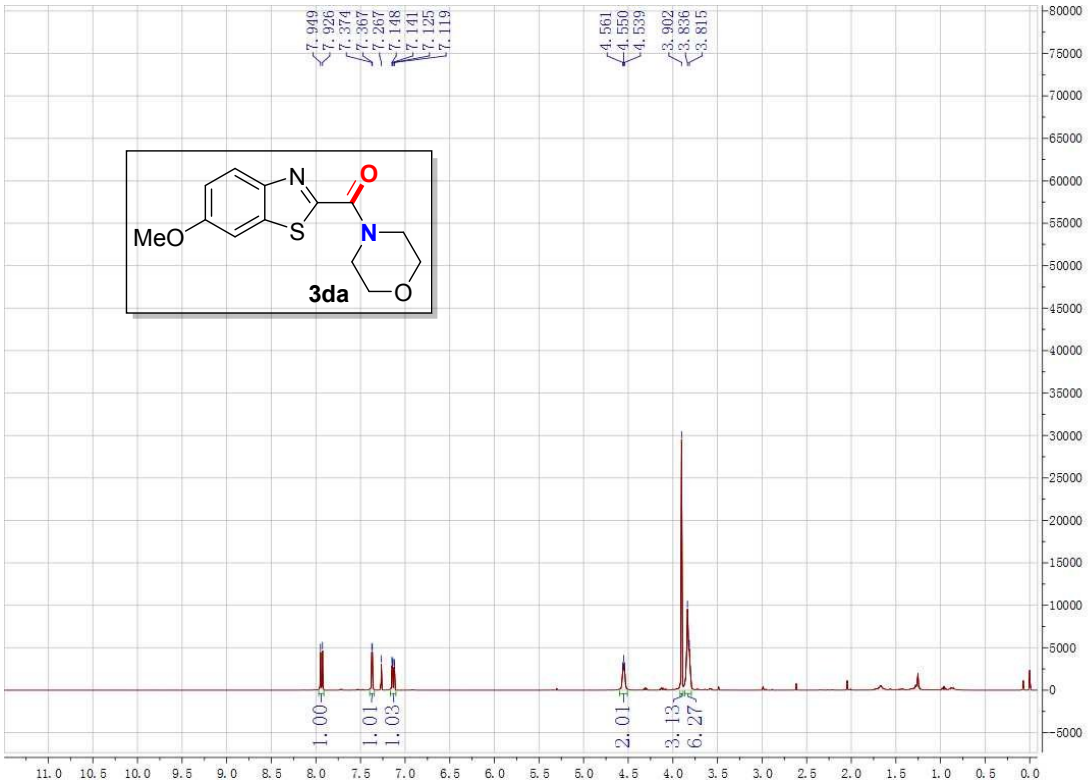
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3.836
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S
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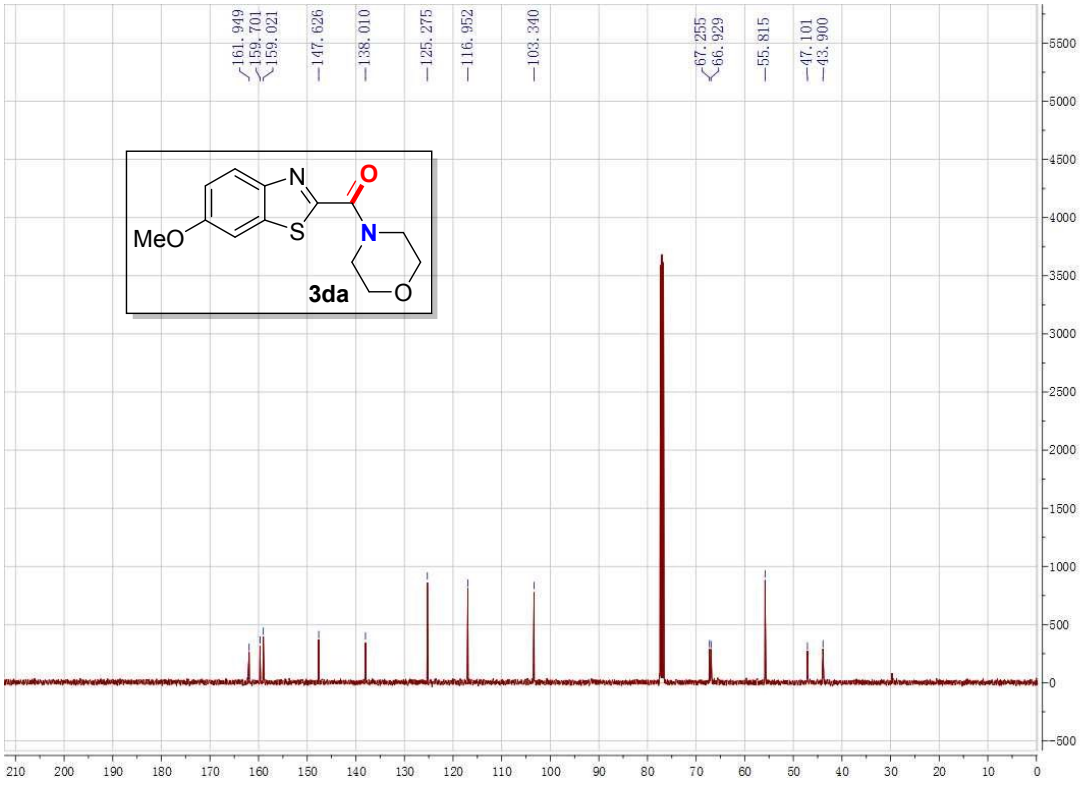
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S
N
O
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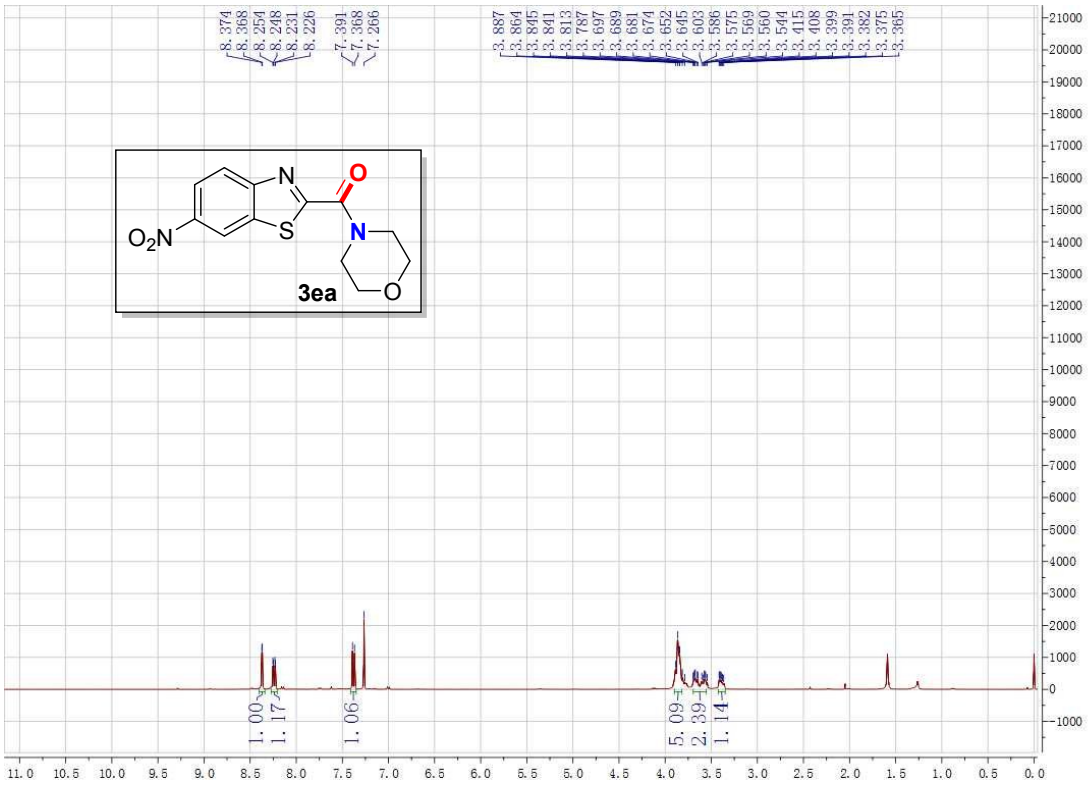
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3.841
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3.787
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3.689
3.681
3.674
3.652
3.645
3.603
3.586
3.575
3.569
3.560
3.544
3.415
3.408
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1.06
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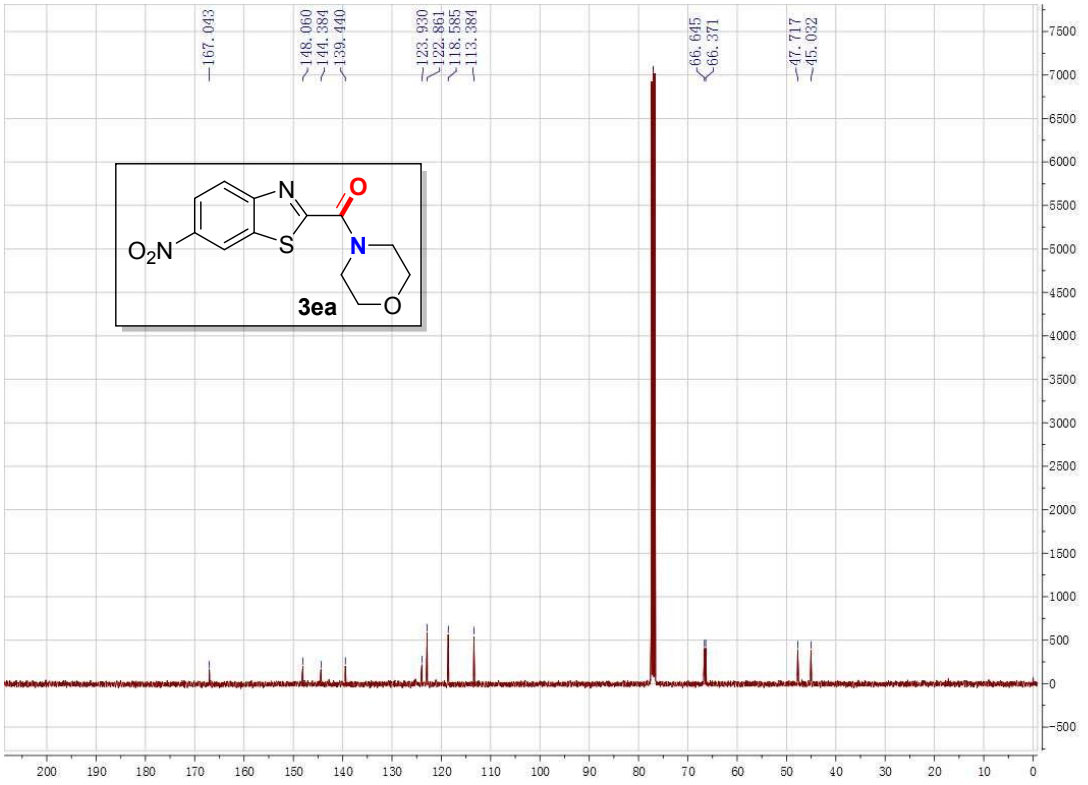
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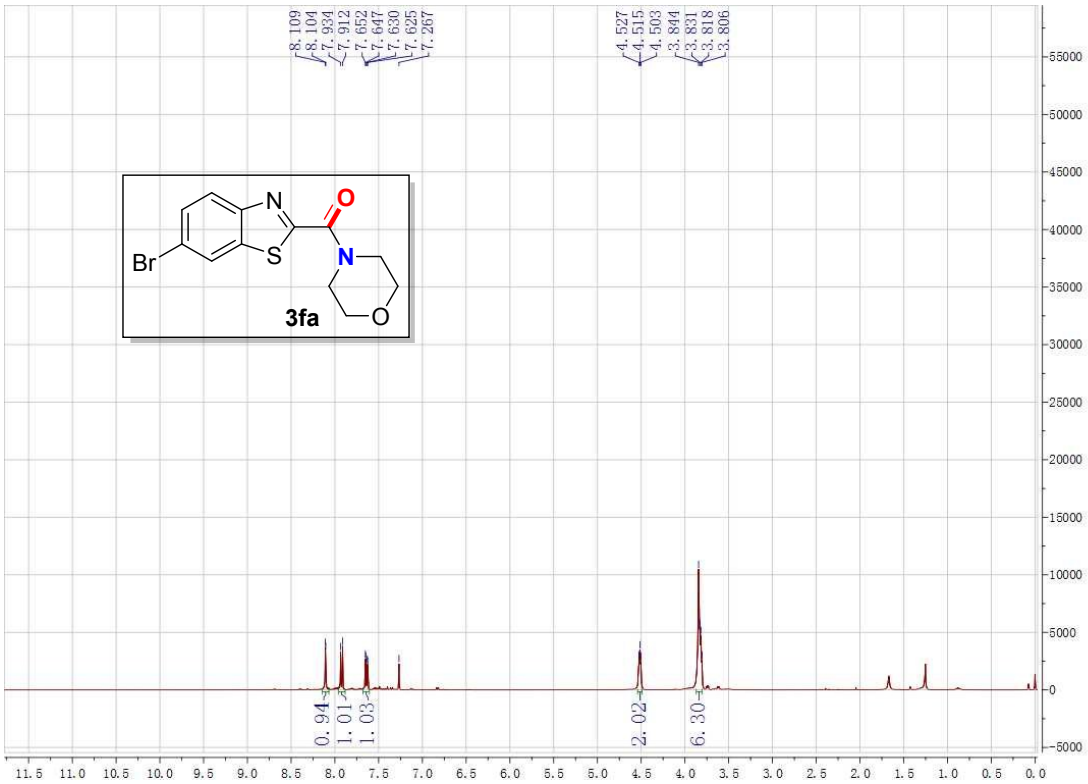
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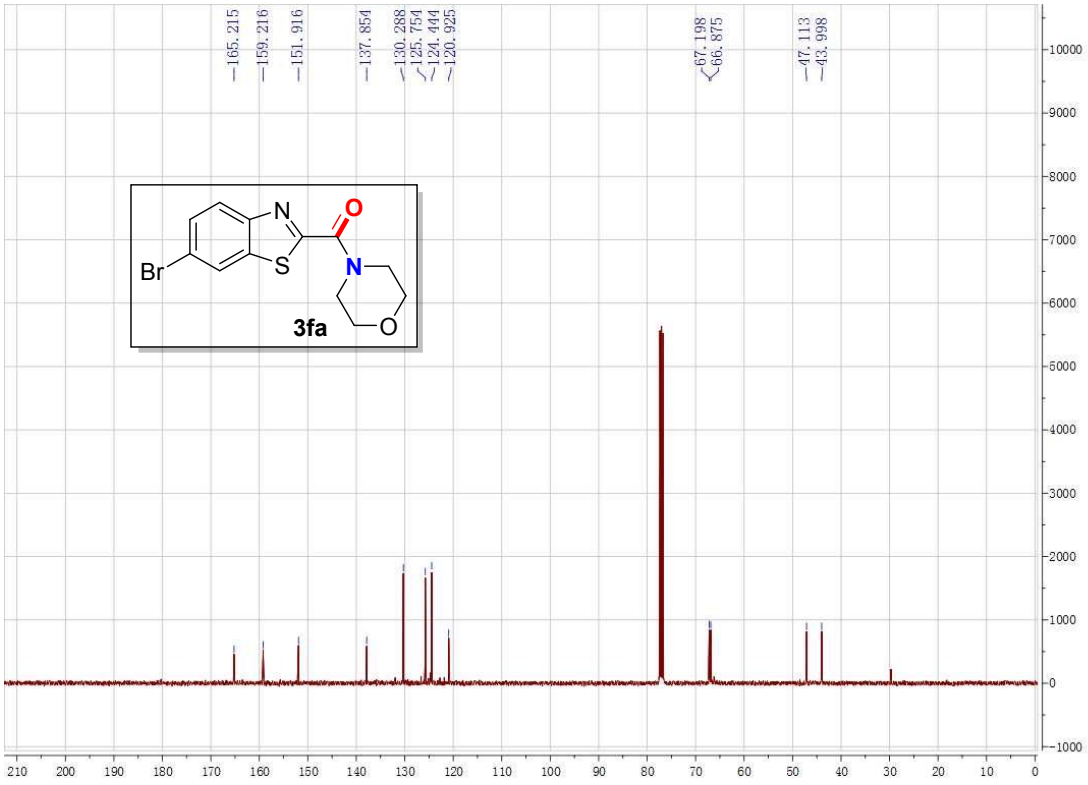
2.02
6.30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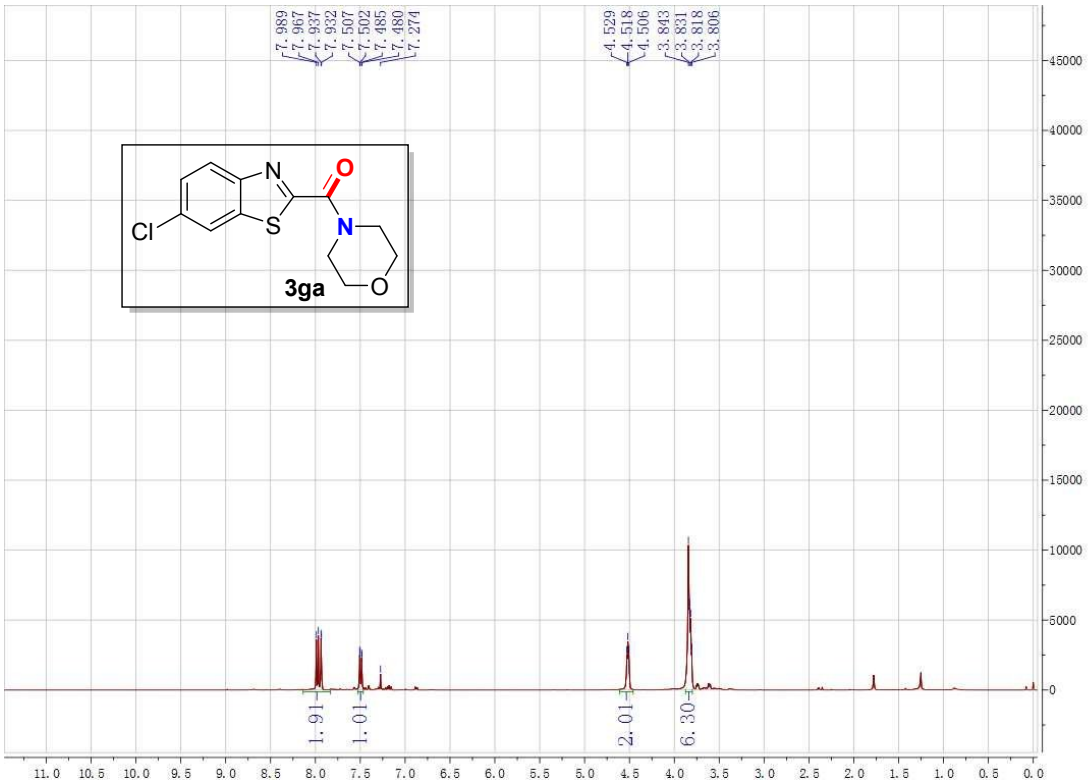
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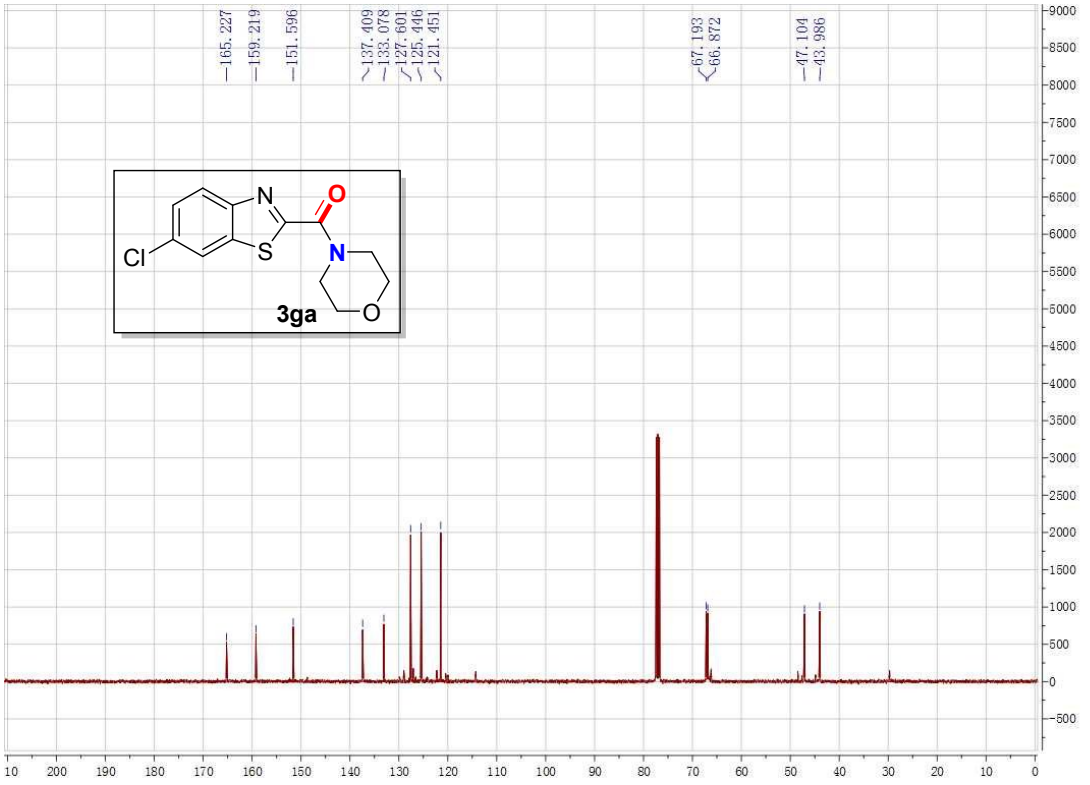
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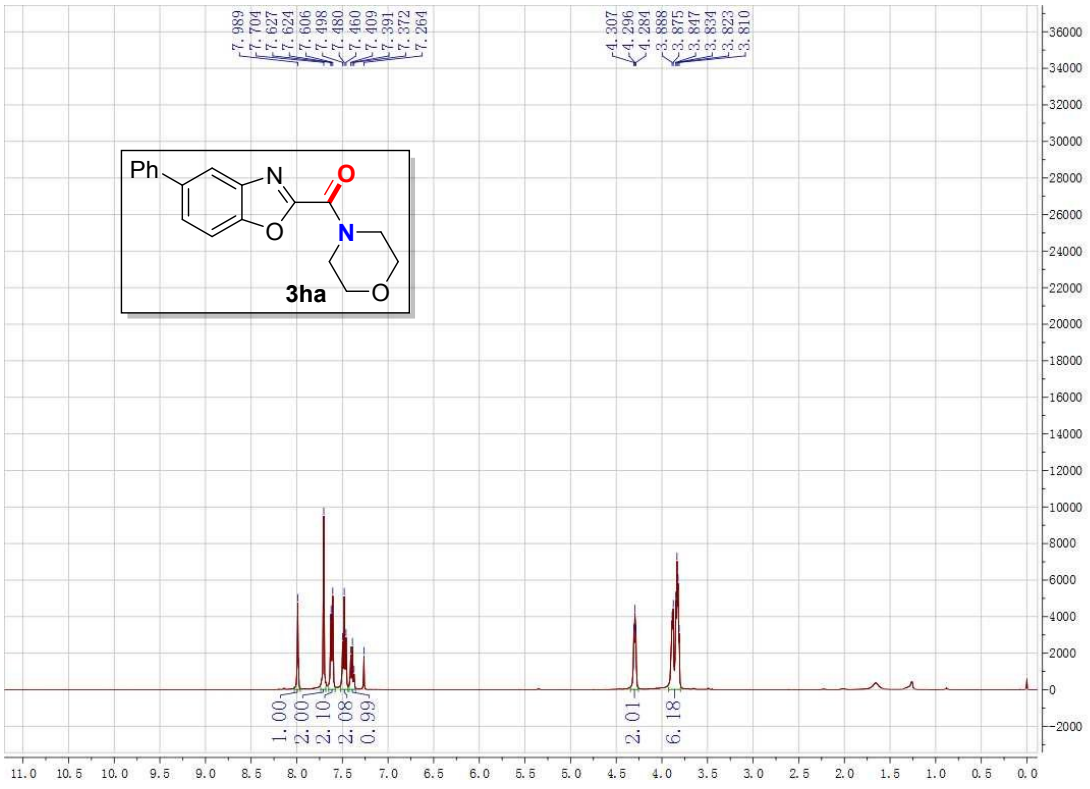
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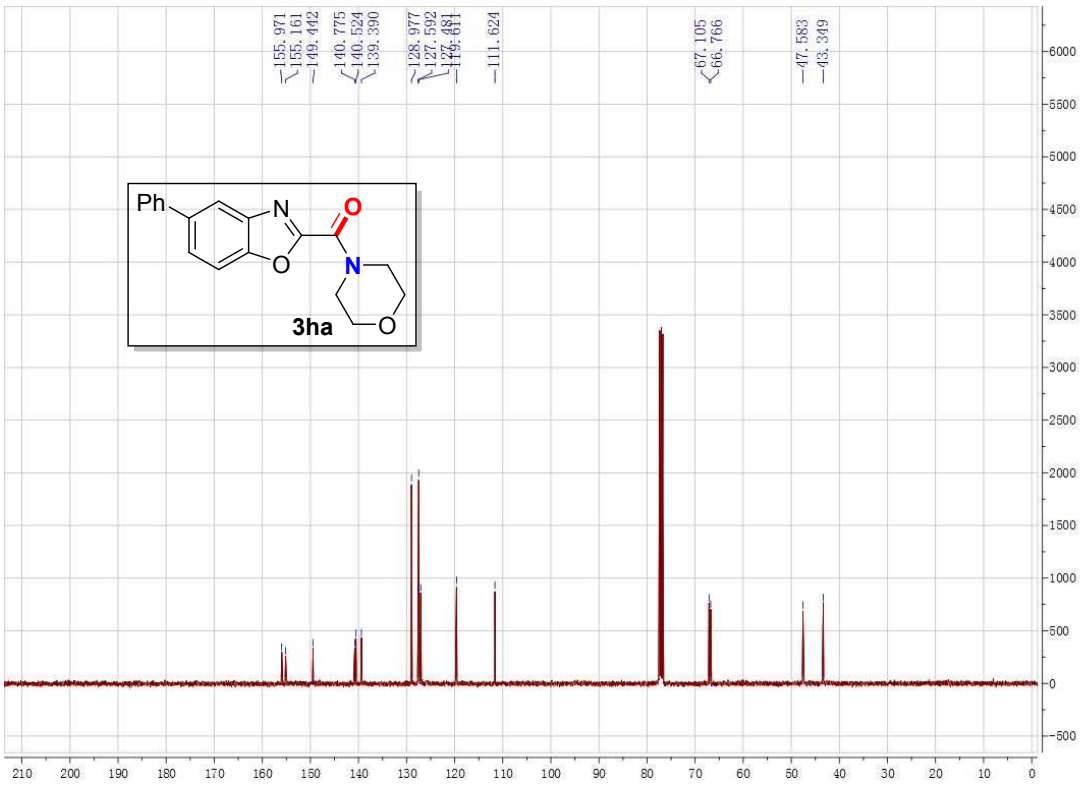
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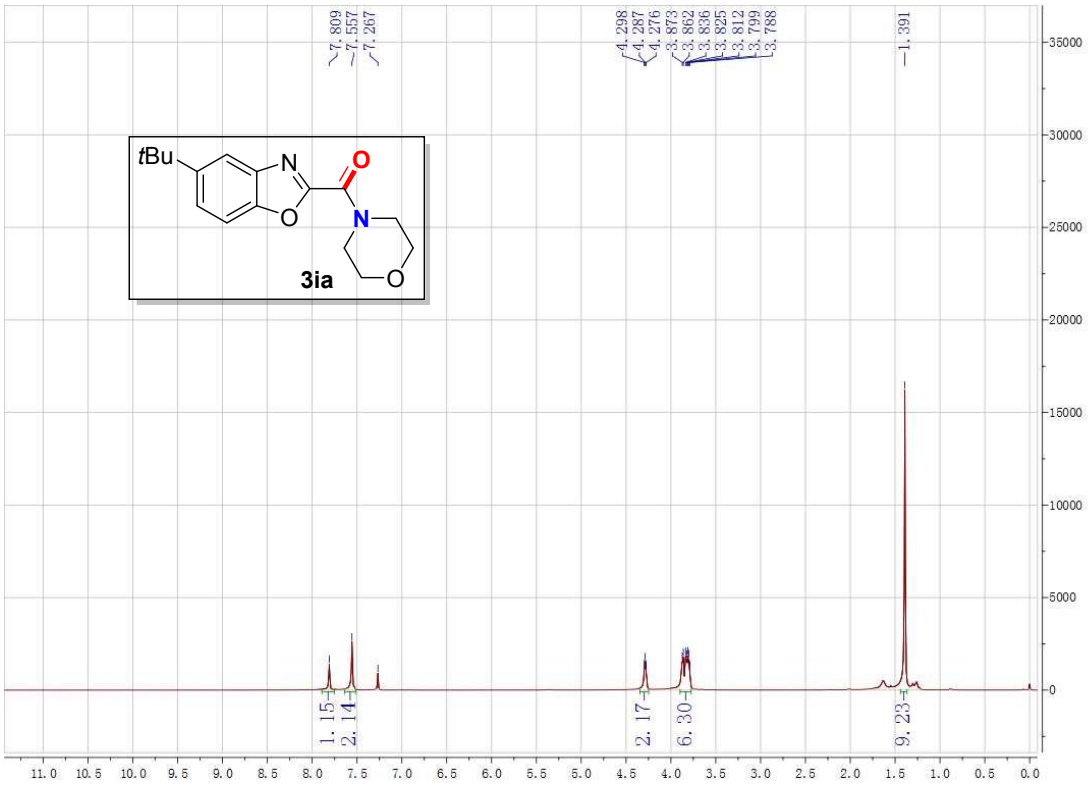
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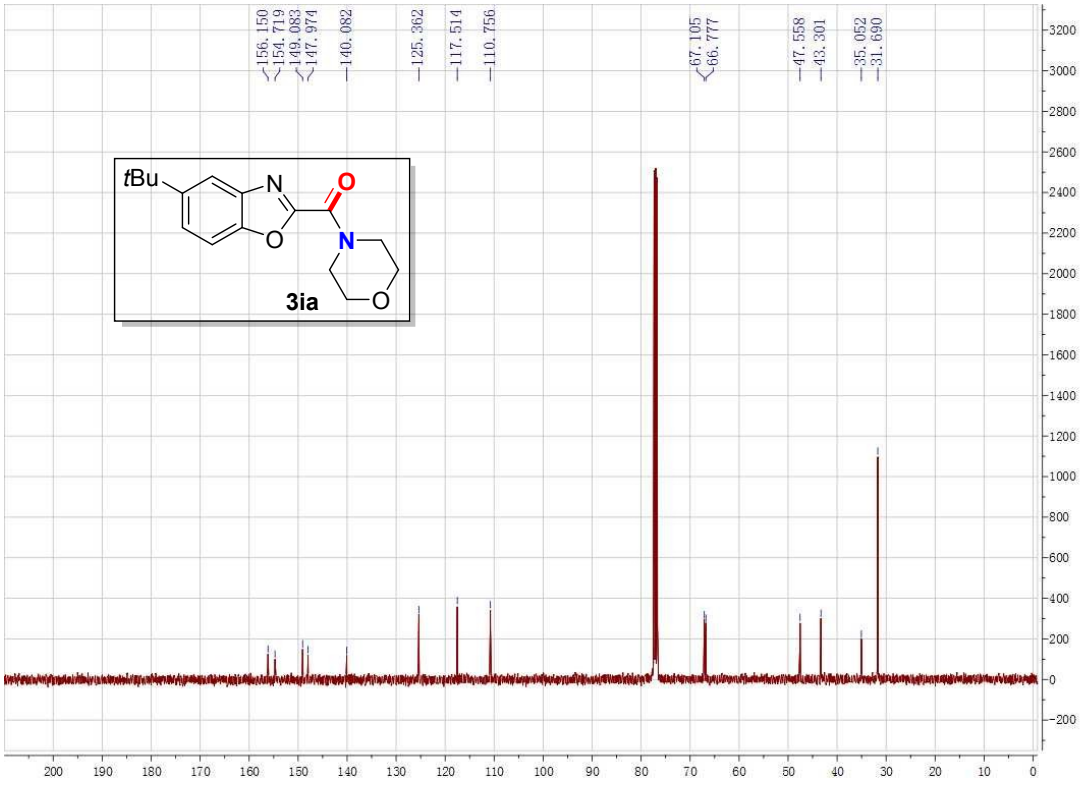
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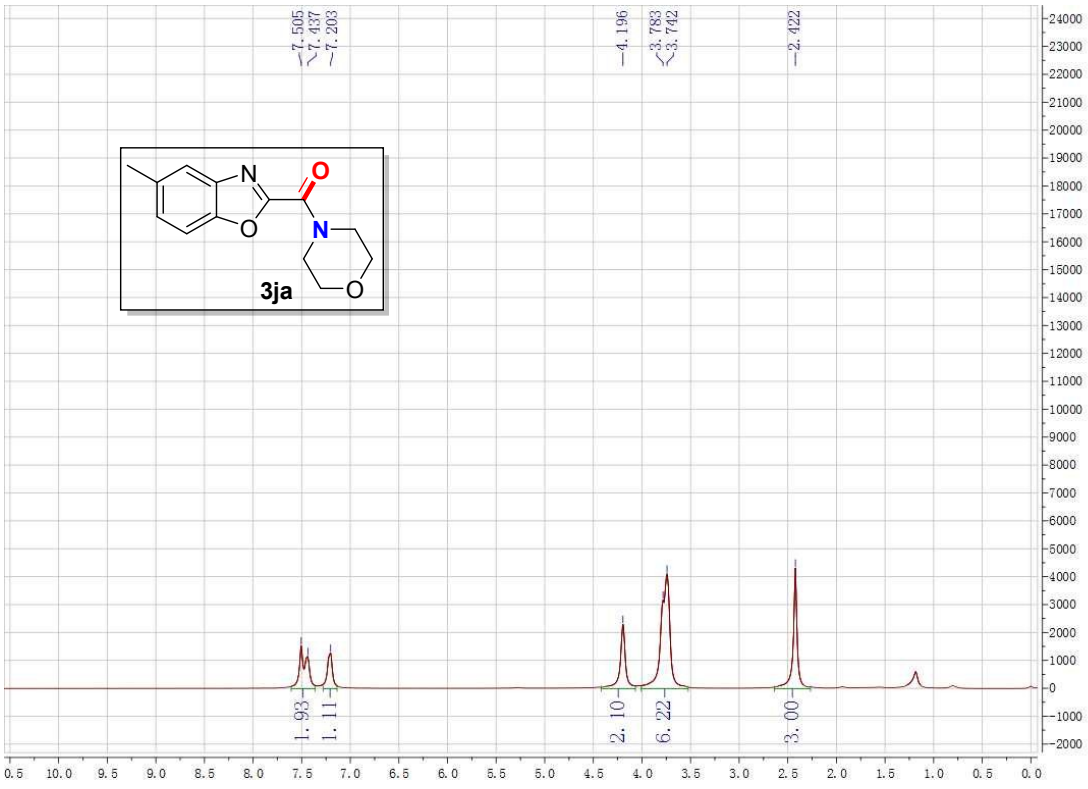
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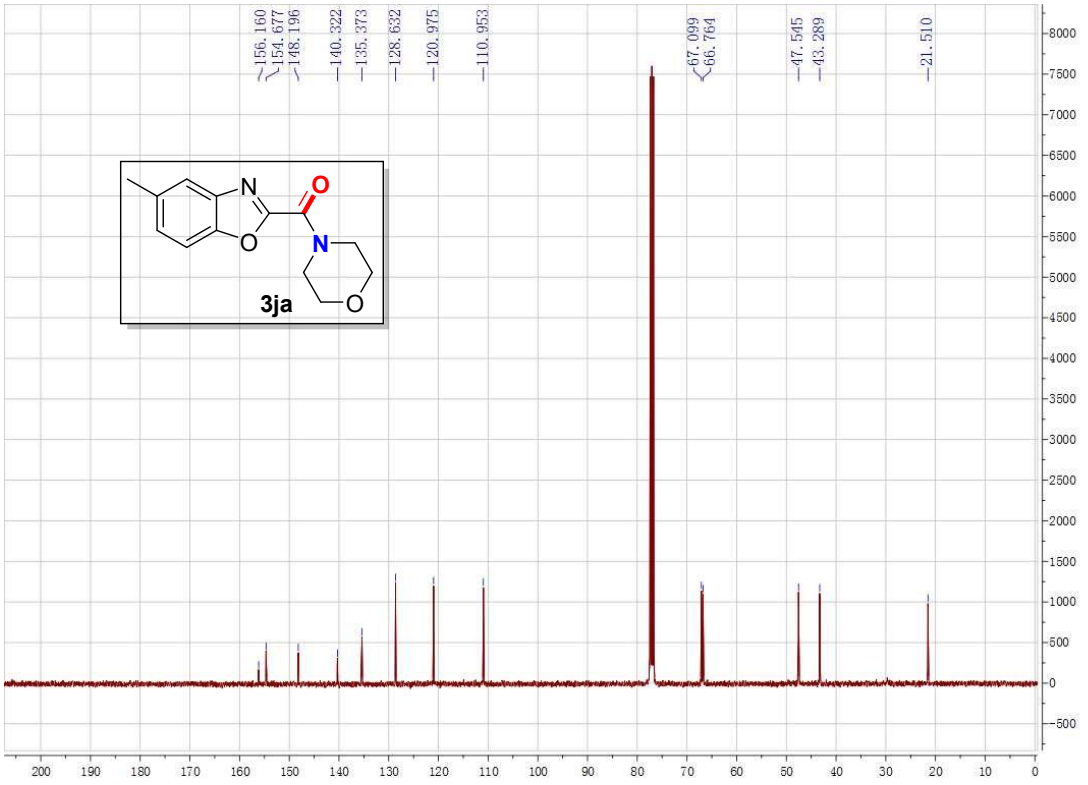
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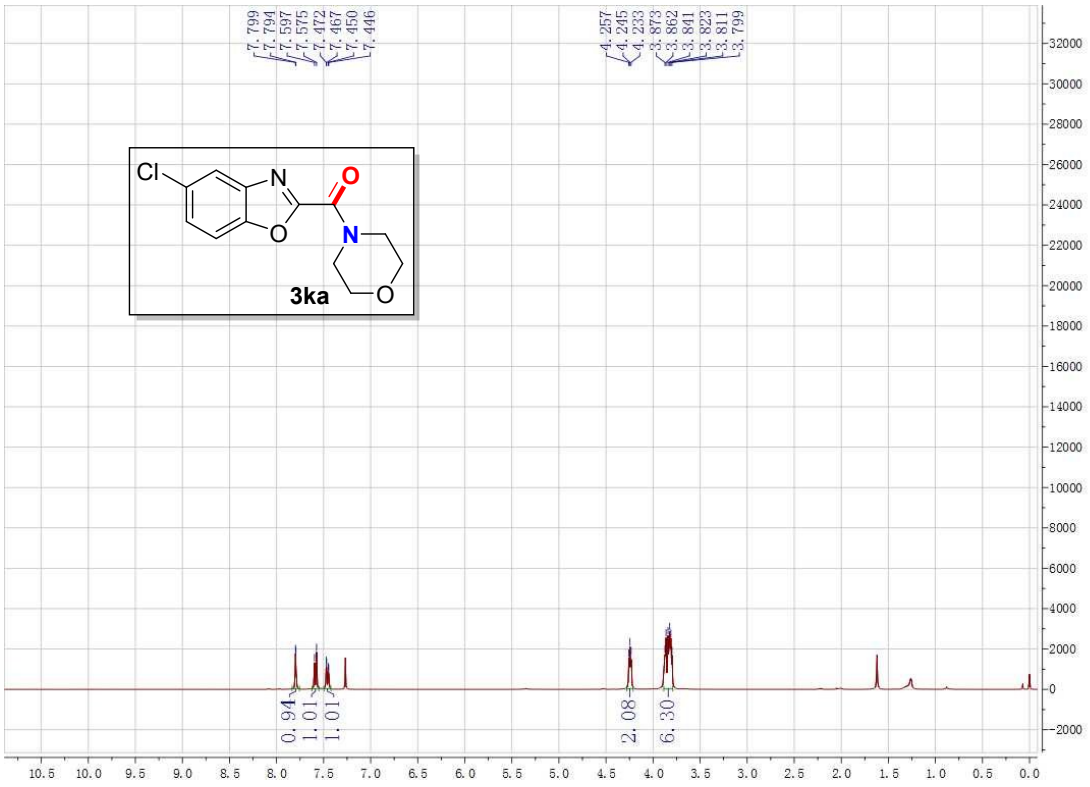
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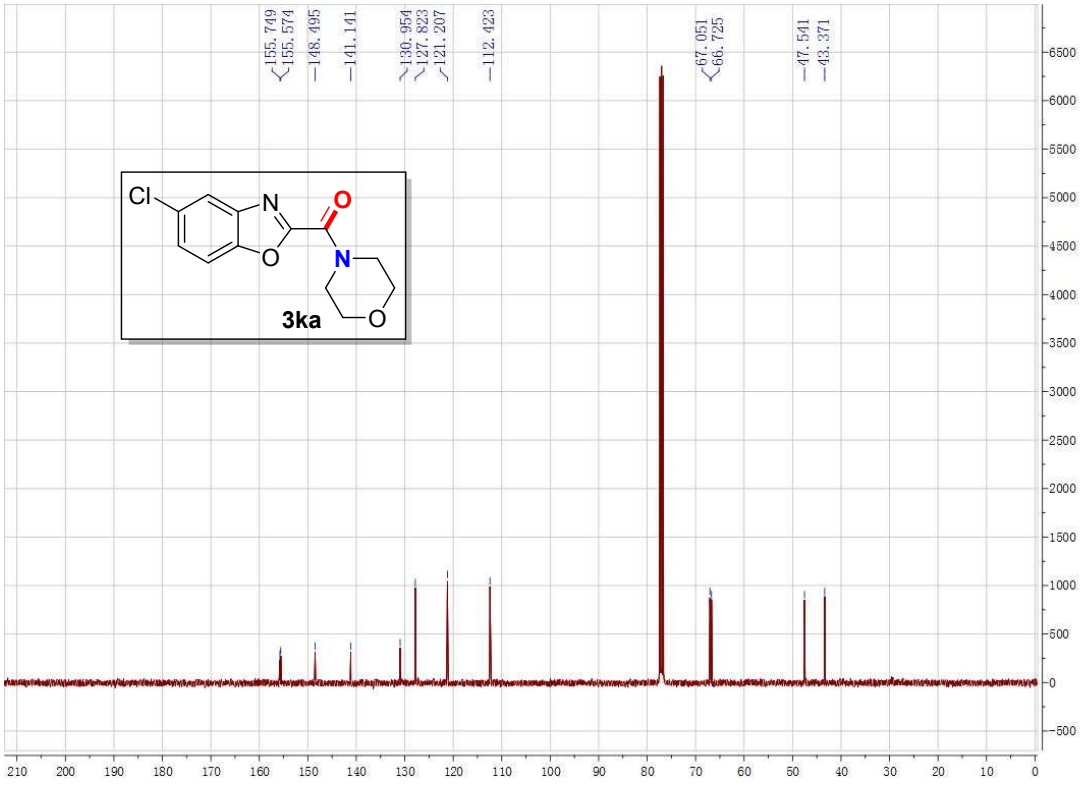
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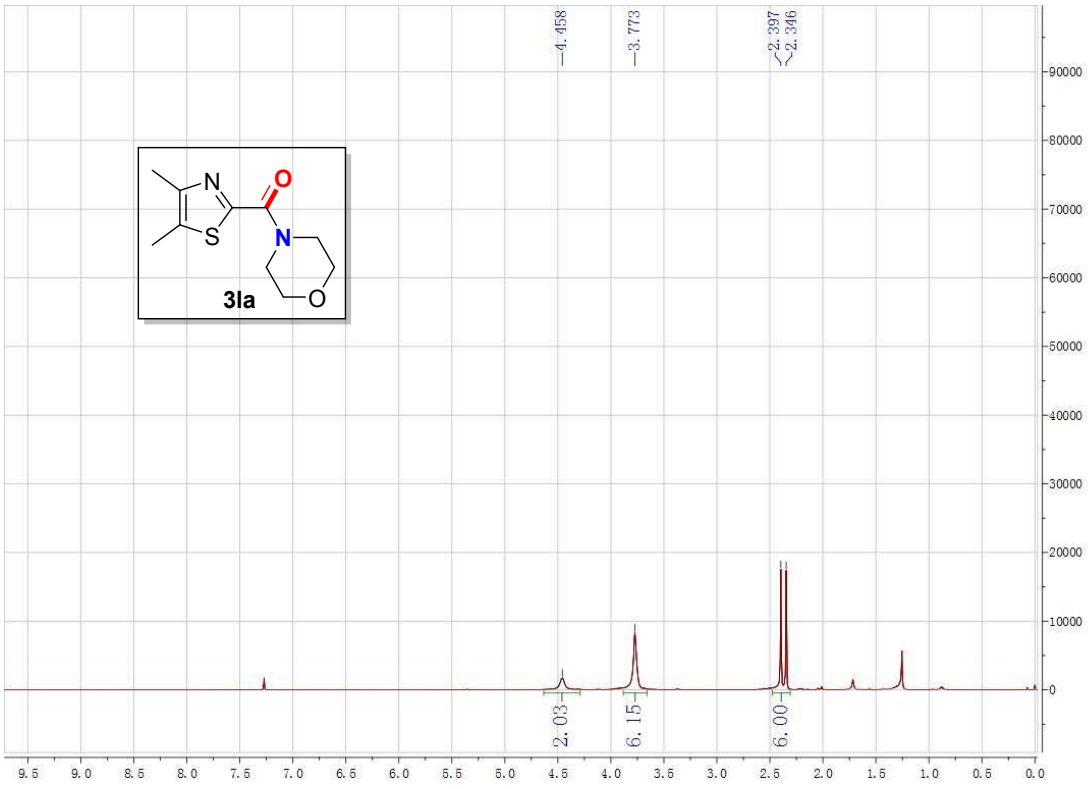
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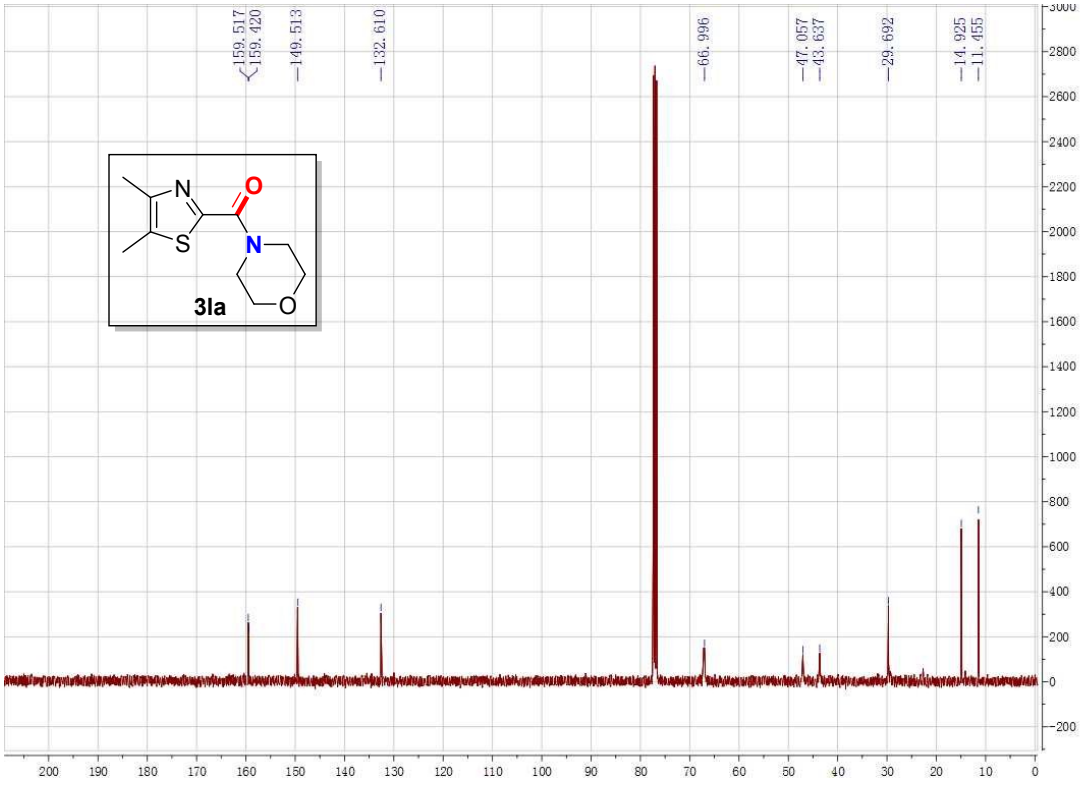
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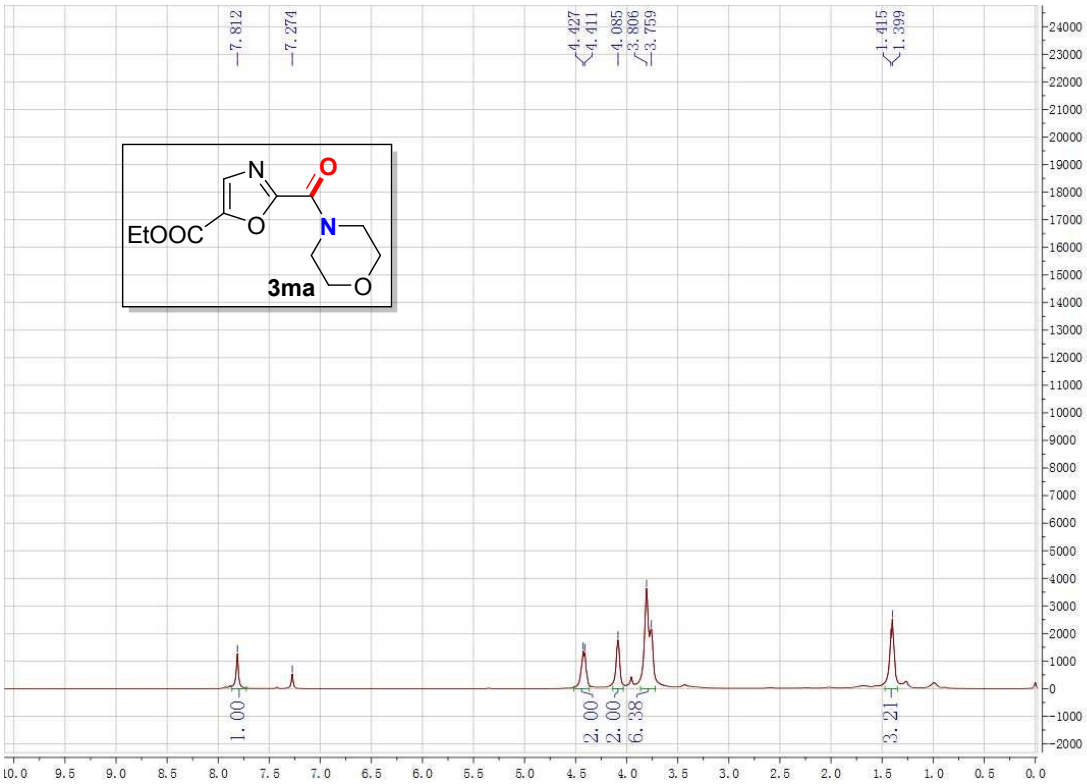
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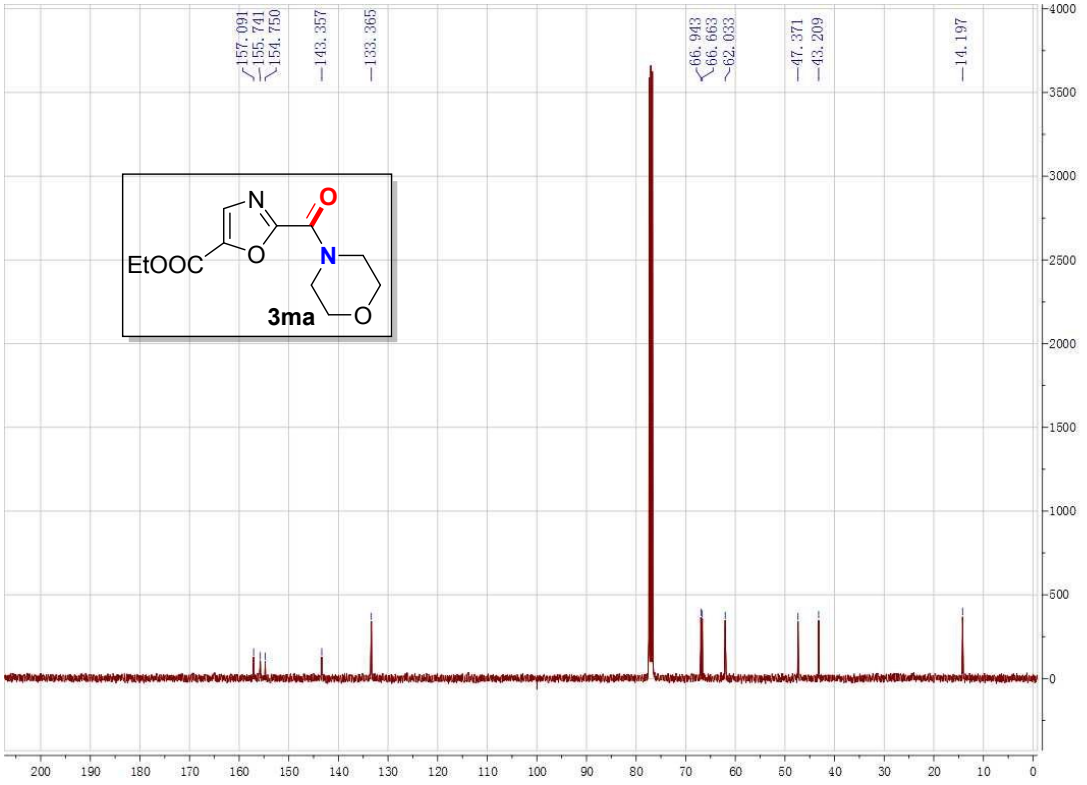
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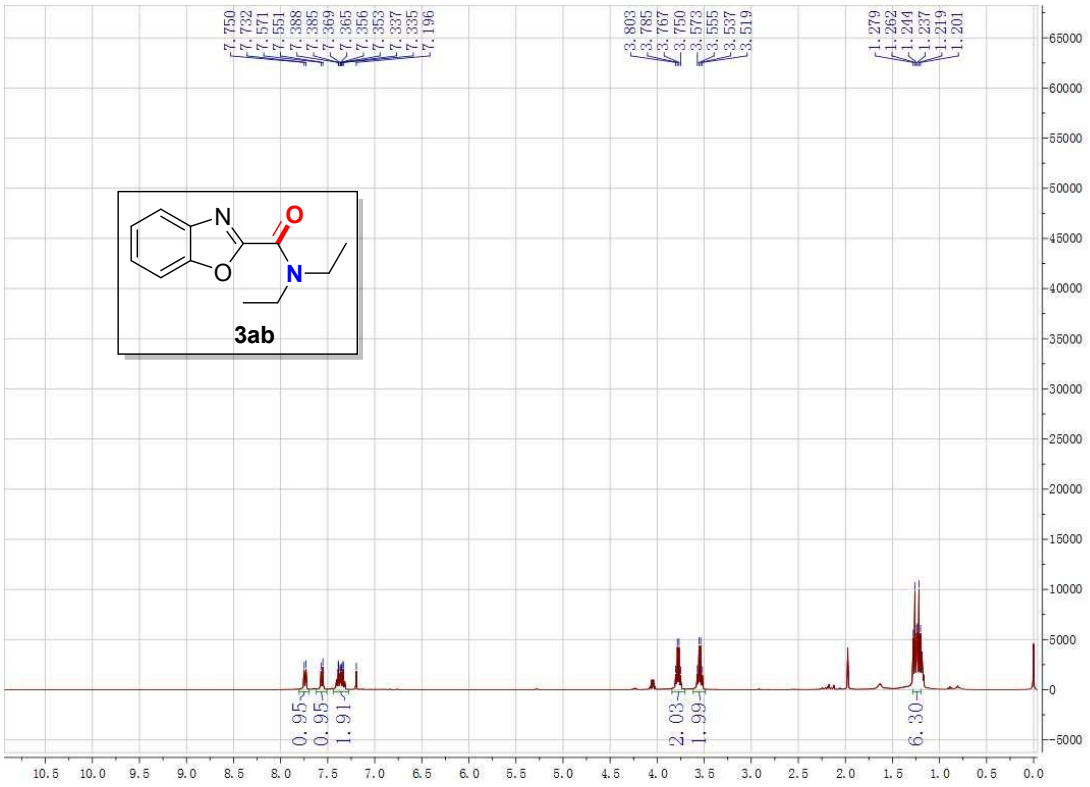
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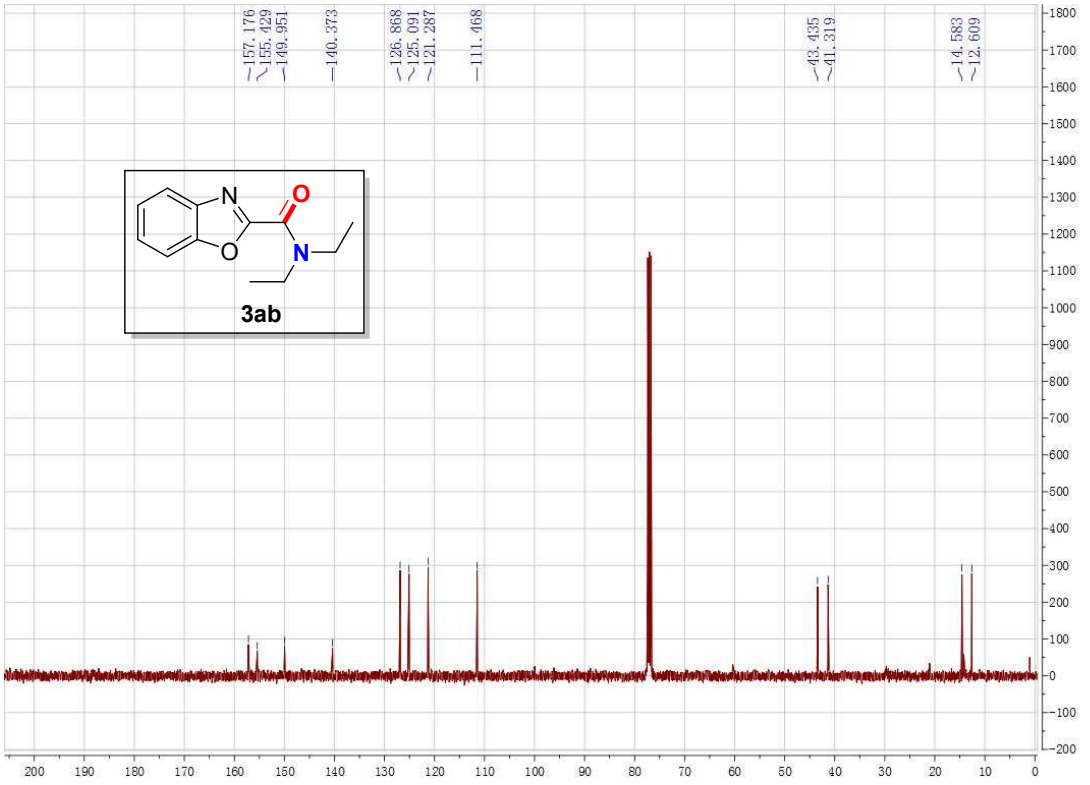
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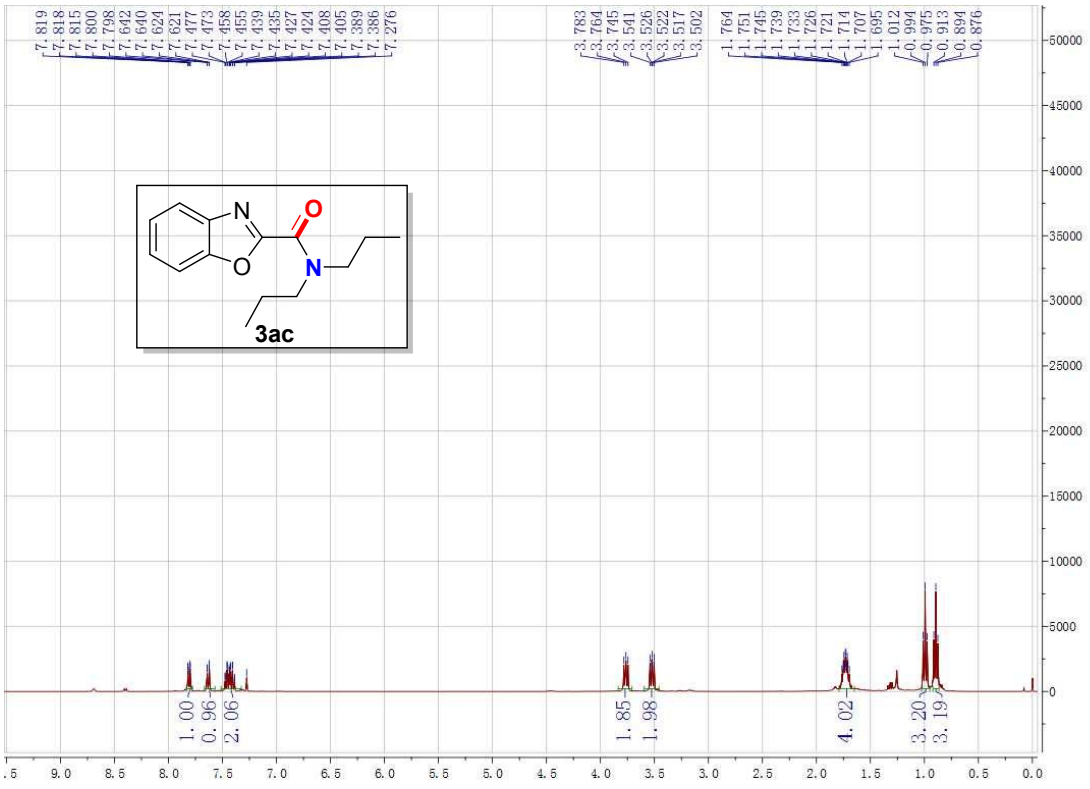
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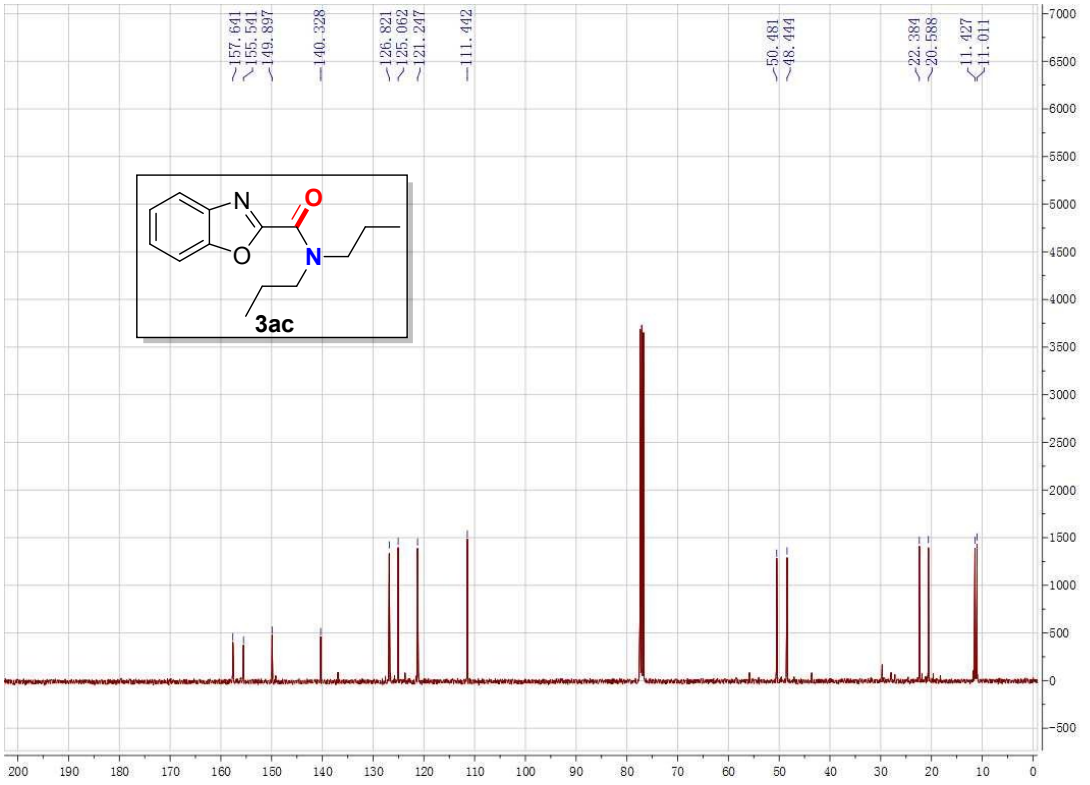
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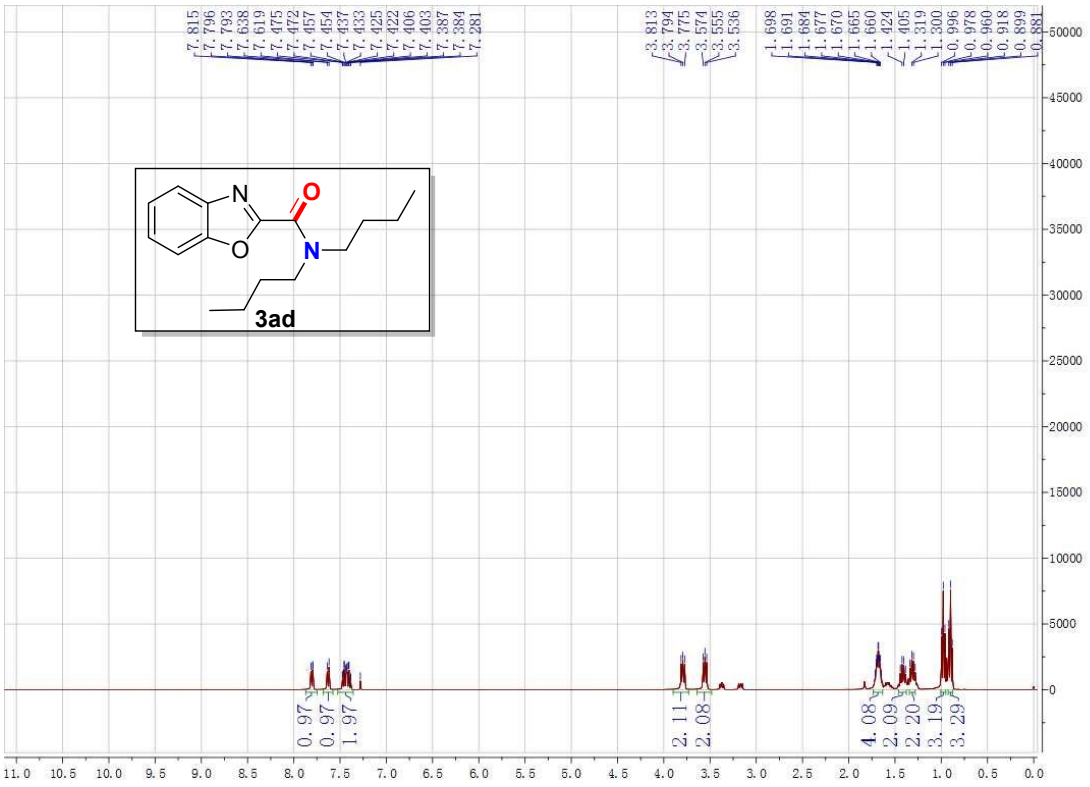
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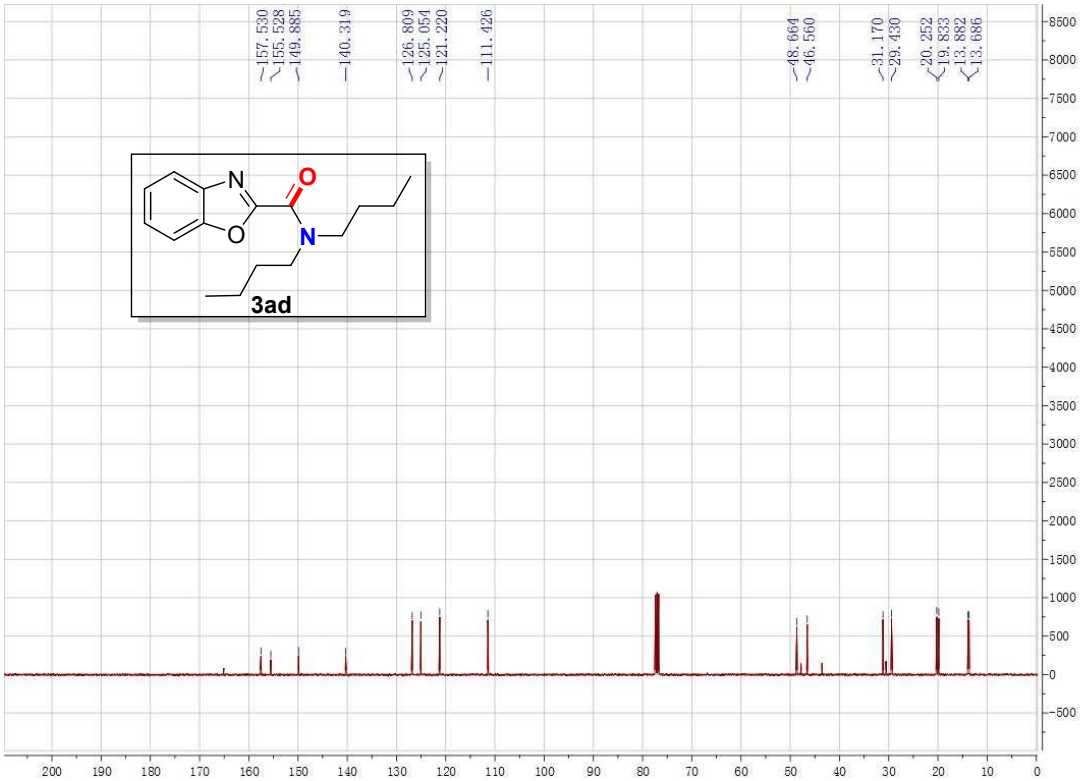
3.29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20.252
19.833
13.882
13.686
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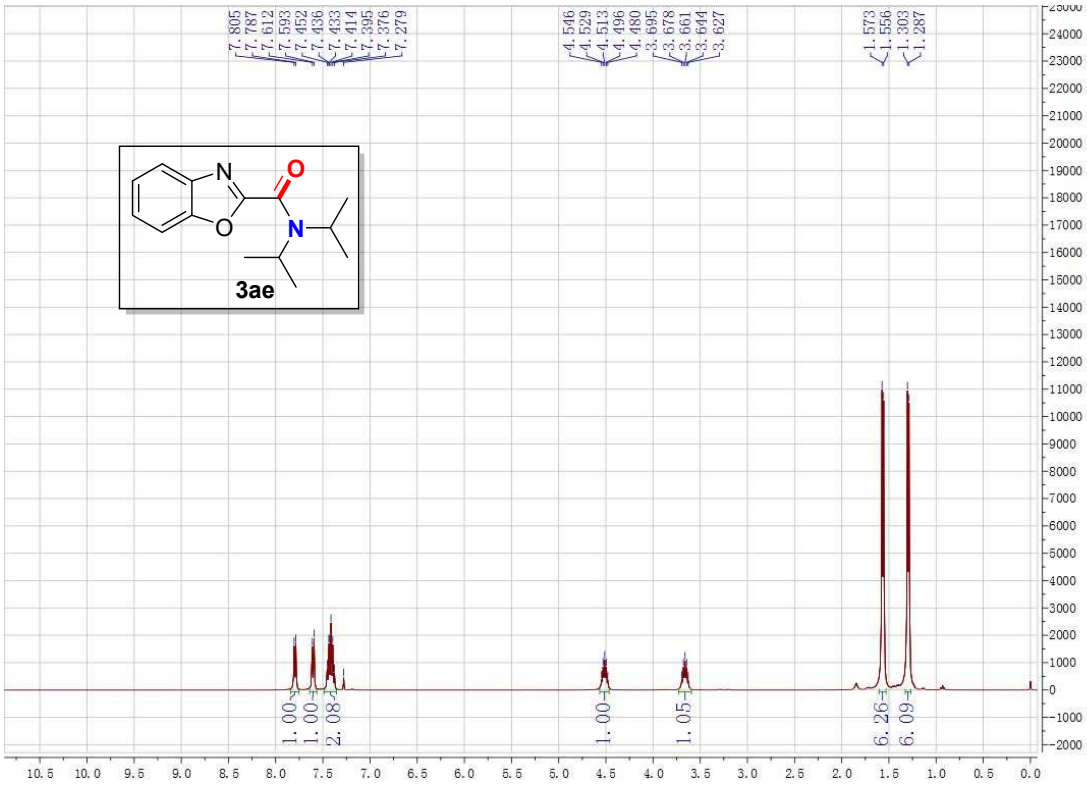
O
O
N
3ad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7.433
7.414
7.395
7.376
7.279
4.546
4.529
4.513
4.496
4.480
3.695
3.678
3.661
3.644
3.627
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1.556
1.303
1.287
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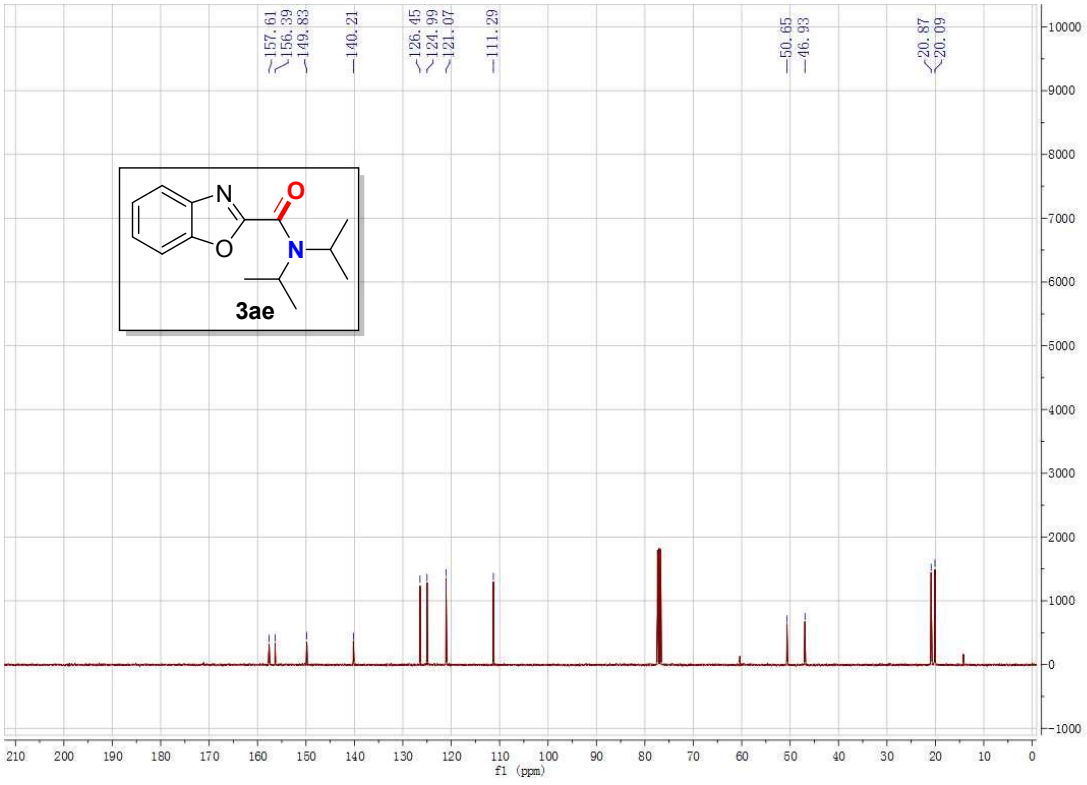
1.00
2.08
1.00
1.05
6.26
6.09
3ae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156.39
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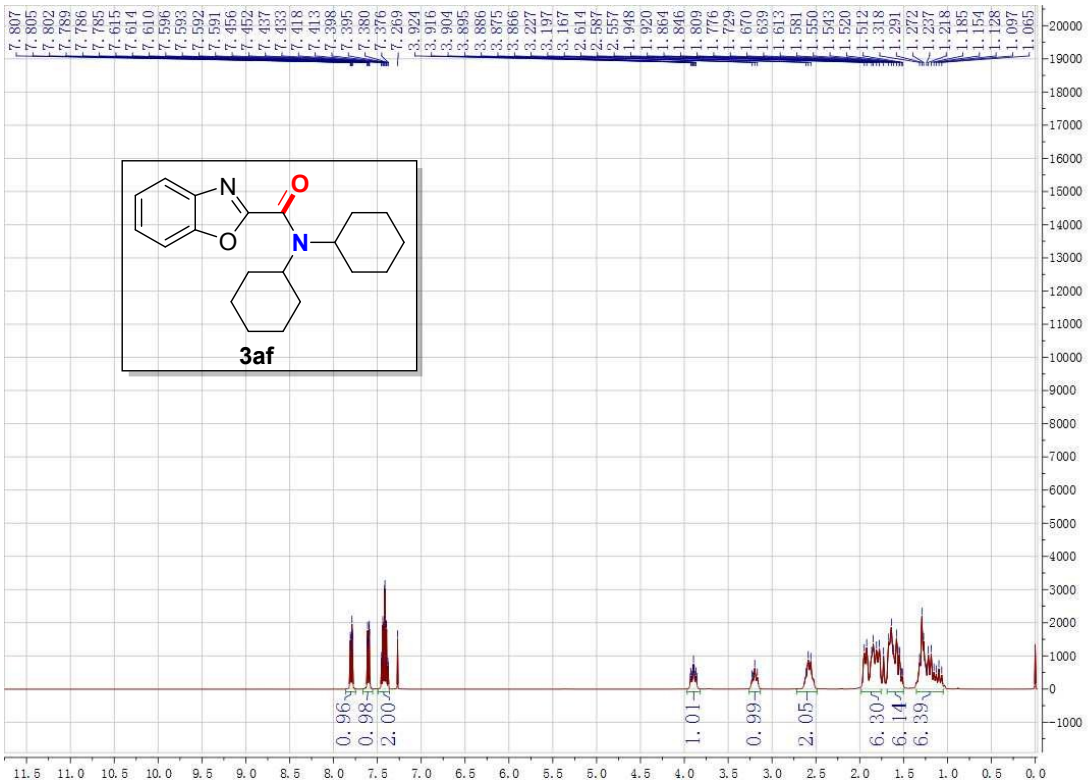
140.21
126.45
124.99
121.07
111.29
50.65
46.93
20.87
20.09
3ae
f1 (ppm)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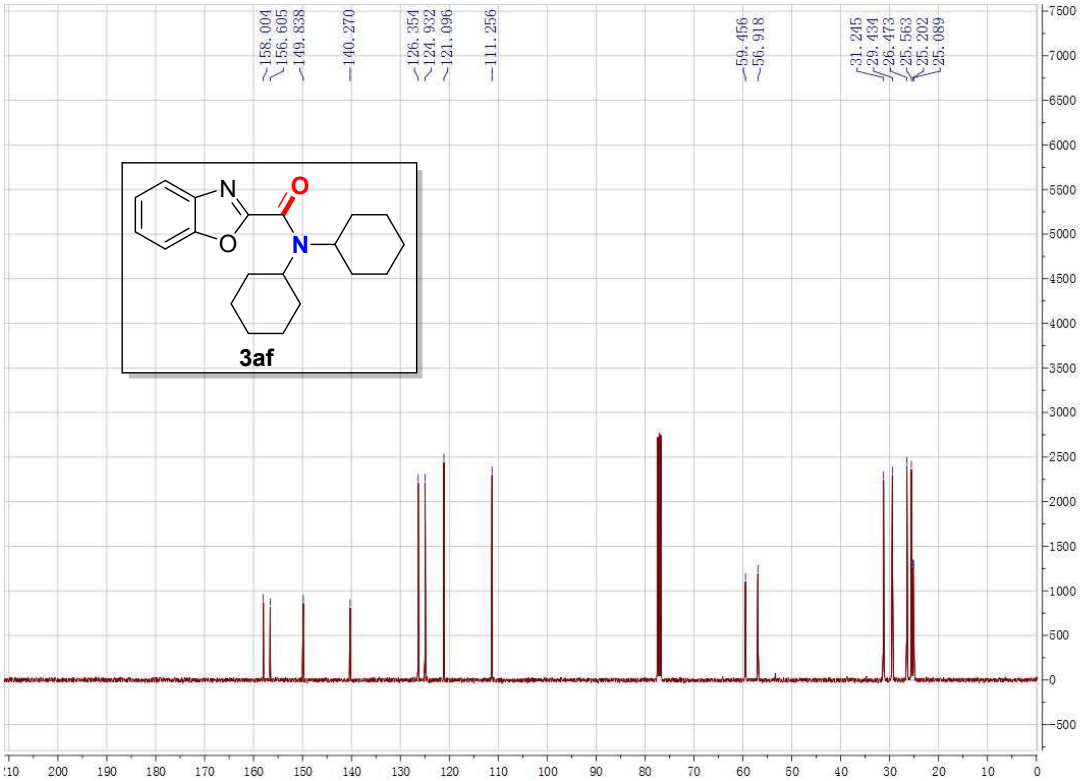
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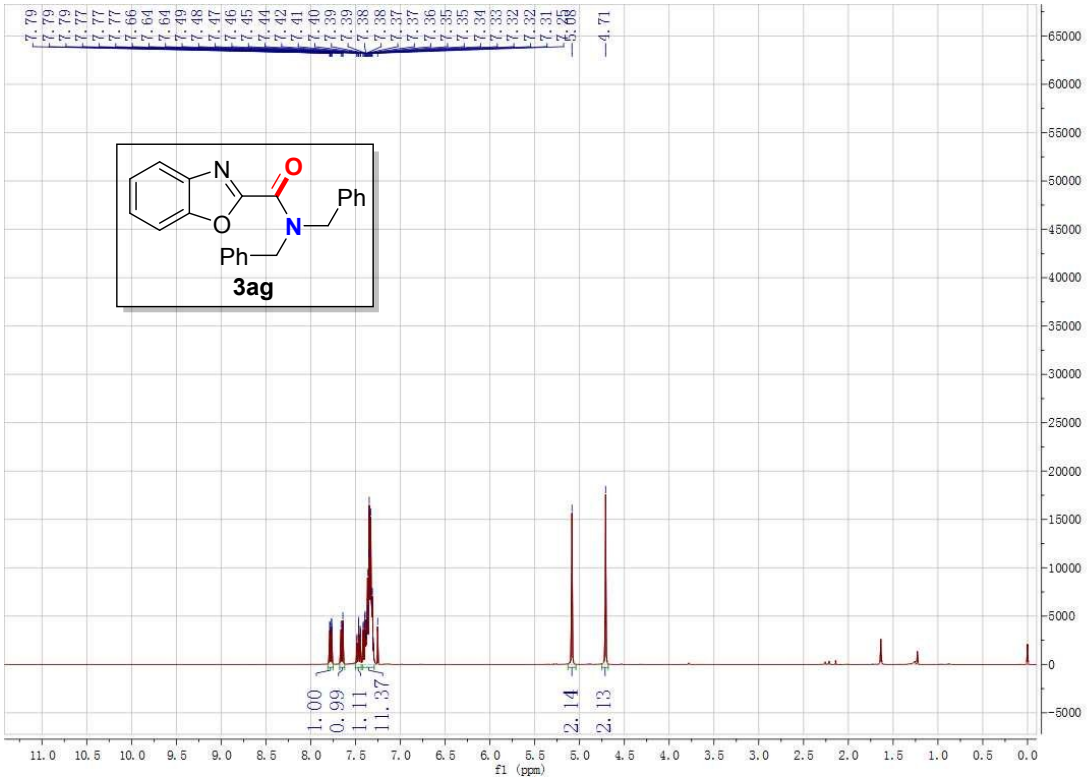
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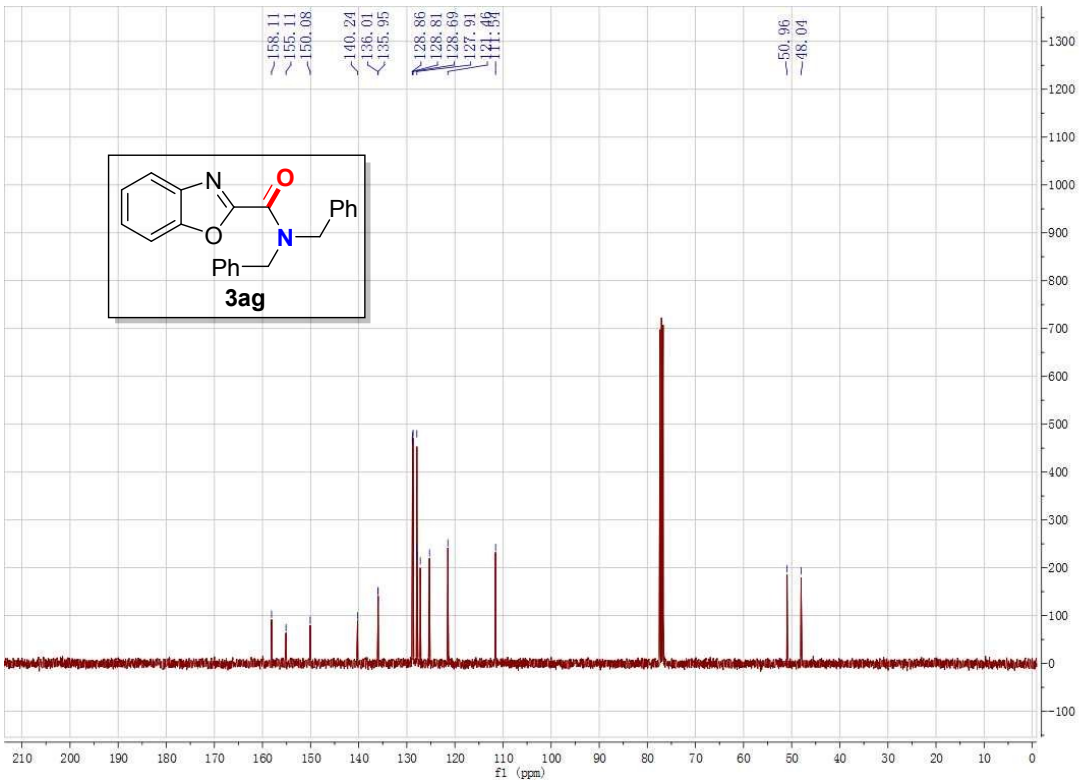
7.79
7.79
7.77
7.77
7.77
7.66
7.64
7.49
7.48
7.47
7.46
7.45
7.44
7.42
7.41
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.34
7.33
7.32
7.31
5.68
4.71
N
O
Ph
N
Ph
3ag
1.00
0.99
1.11
11.37
2.14
2.13
f1 (ppm)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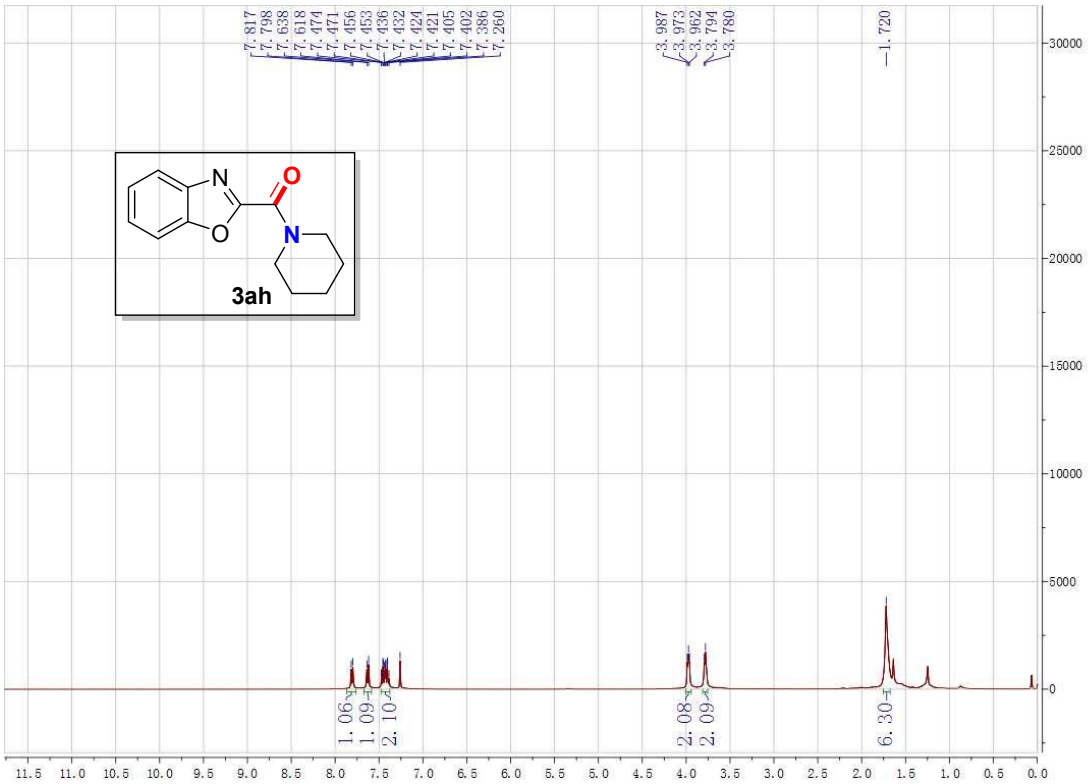
155.11
150.08
140.24
136.01
135.95
128.86
128.81
128.69
127.91
121.46
111.94
50.96
48.04
N
O
Ph
N
Ph
3ag
f1 (ppm)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7.638
7.618
7.474
7.471
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7.453
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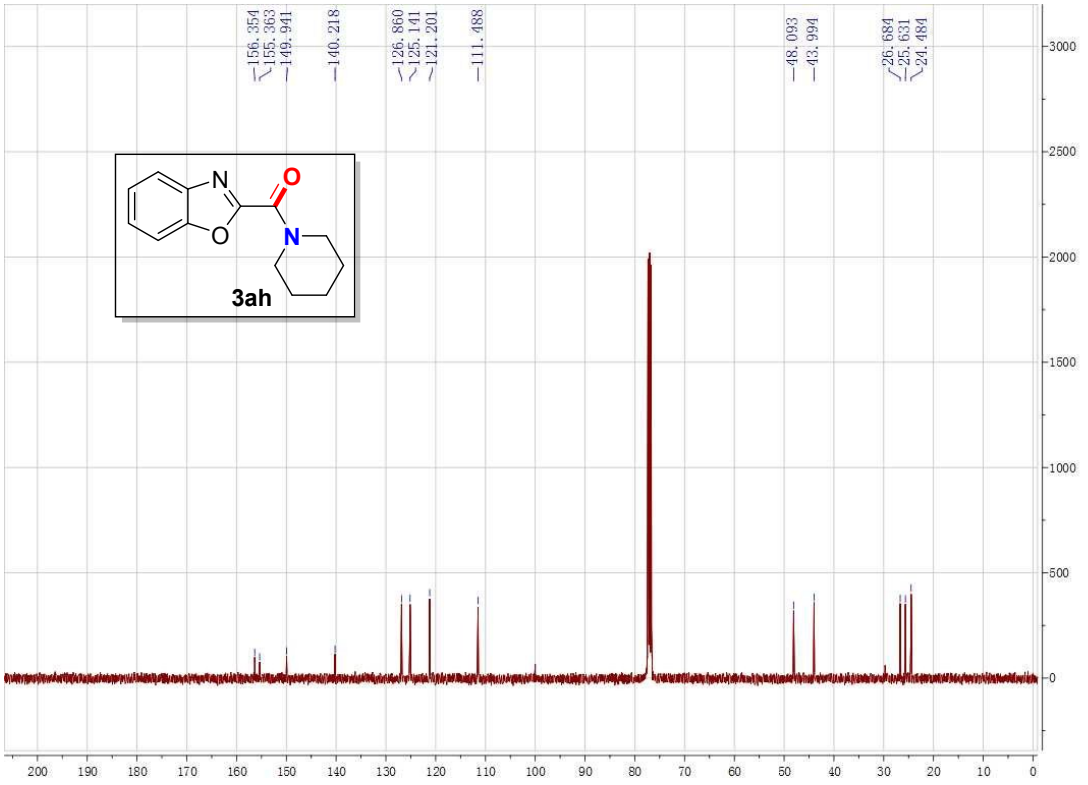
7.432
7.424
7.421
7.405
7.402
7.386
7.260
3.987
3.973
3.962
3.794
3.780
1.720
3ah
1.06
1.09
2.10
2.08
2.09
6.30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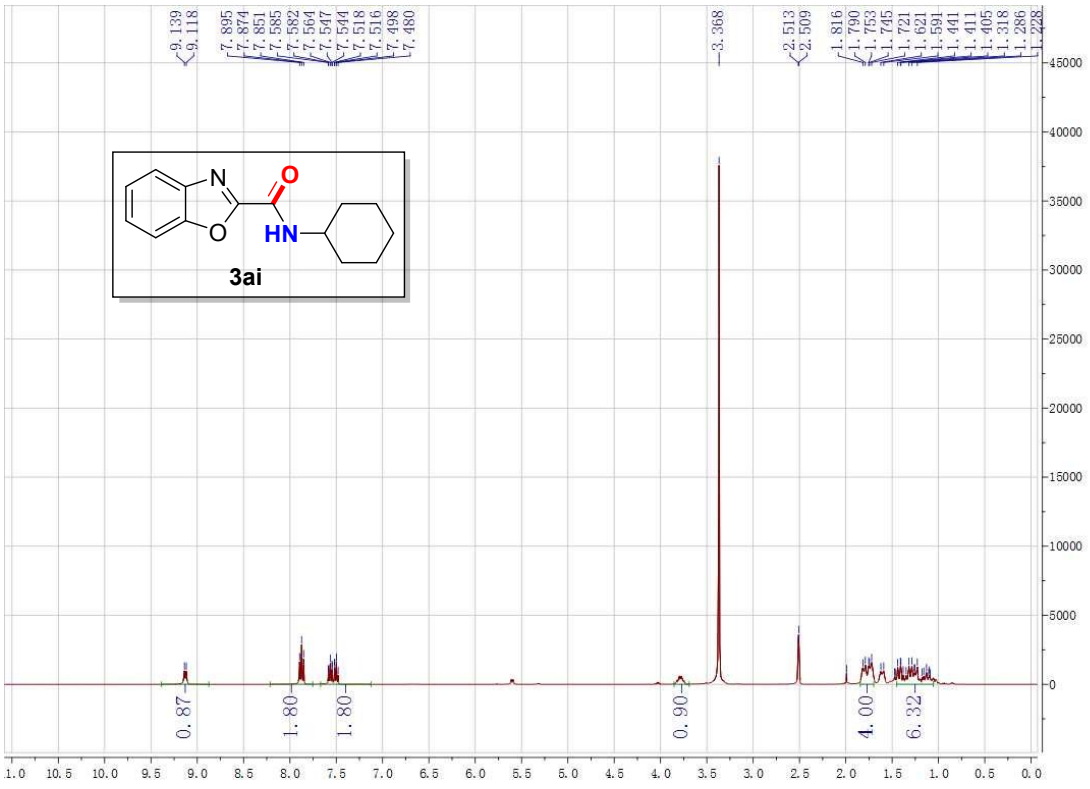
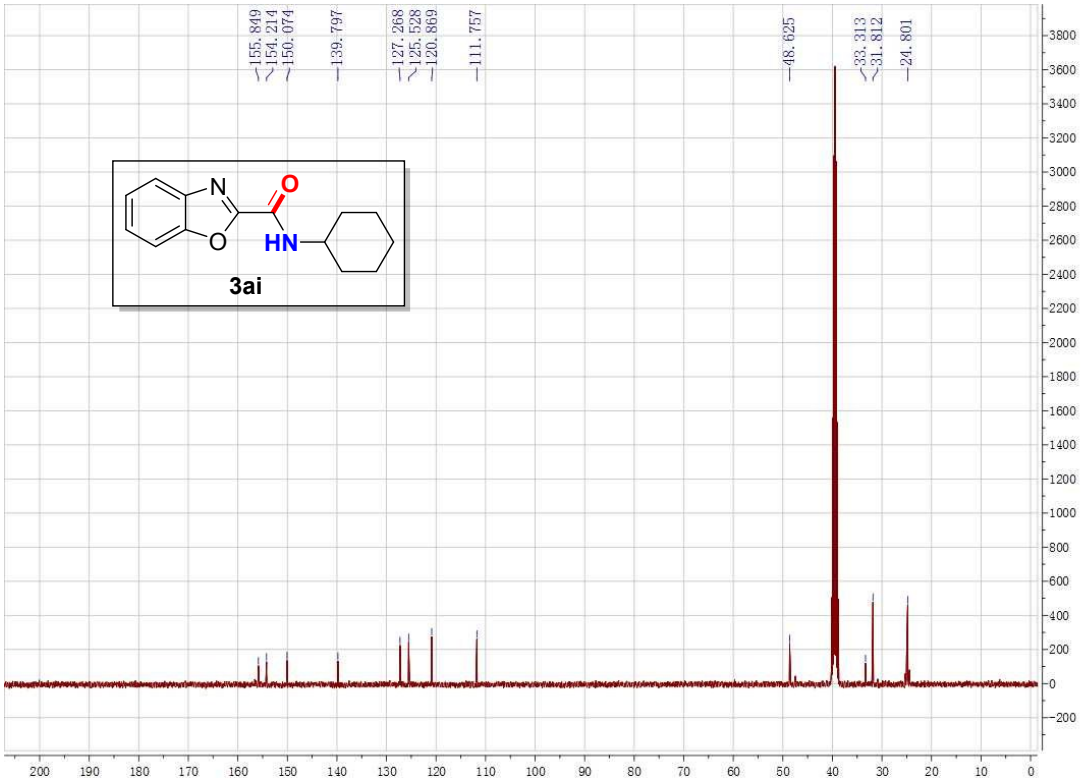
111.488
48.093
43.994
26.684
25.631
24.484
3ah


9.139
9.118
7.895
7.874
7.851
7.585
7.582
7.564
7.547
7.544
7.518
7.516
7.498
7.480
3.368
2.513
2.509
1.816
1.790
1.753
1.745
1.721
1.621
1.591
1.441
1.411
1.405
1.318
1.286
1.228
N
O
O
HN
3ai
0.87
1.80
1.80
0.90
4.00
6.32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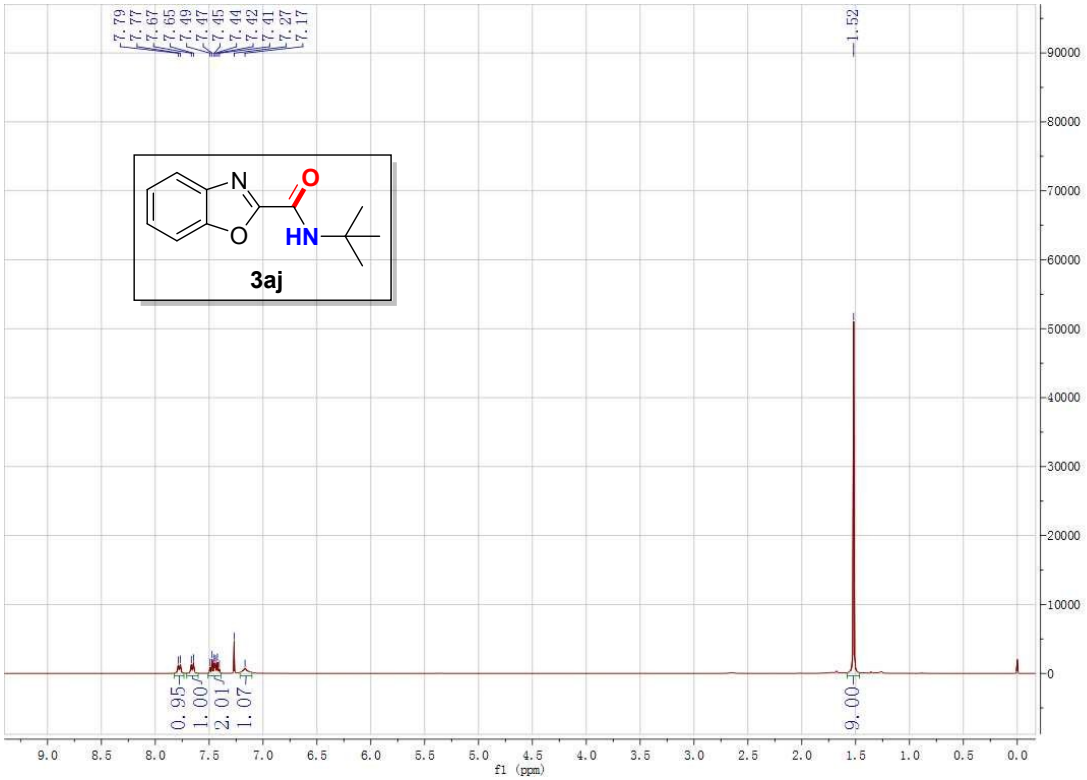
150.074
139.797
127.268
125.528
120.869
111.757
48.625
33.313
31.812
24.801
N
O
O
HN
3ai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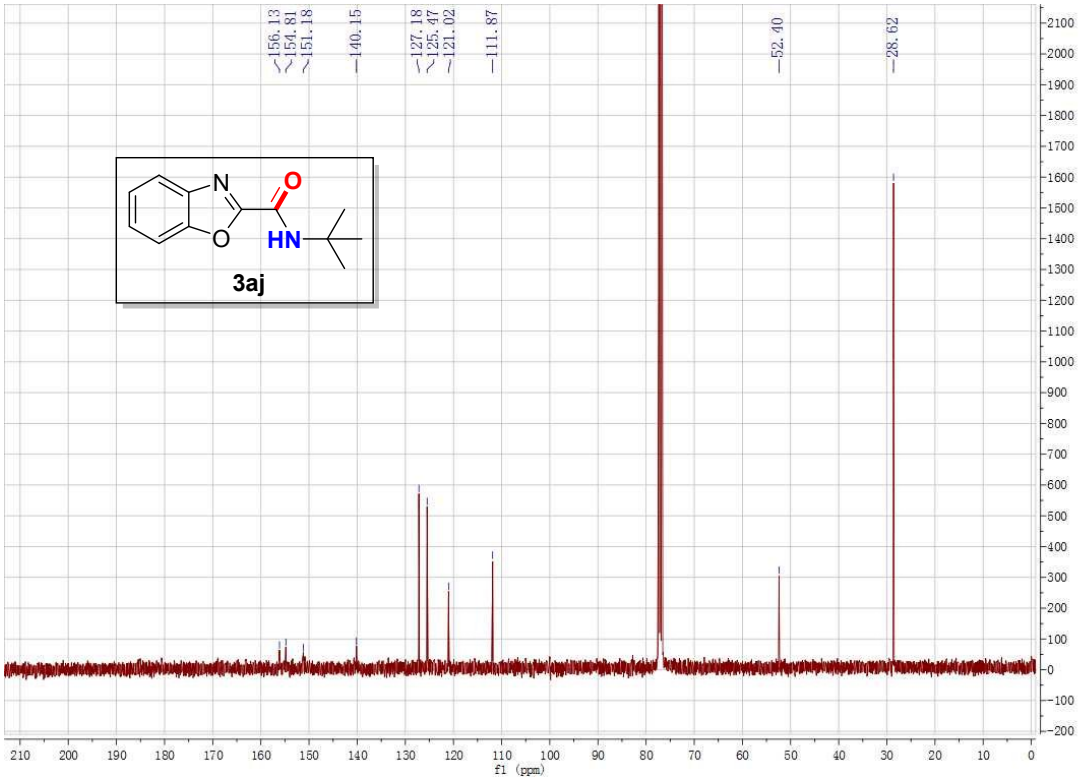
7.77
7.67
7.65
7.49
7.47
7.45
7.44
7.42
7.41
7.27
7.17
1.52
N
O
O
HN
3aj
0.95
1.00
2.01
1.07
9.00
f1 (ppm)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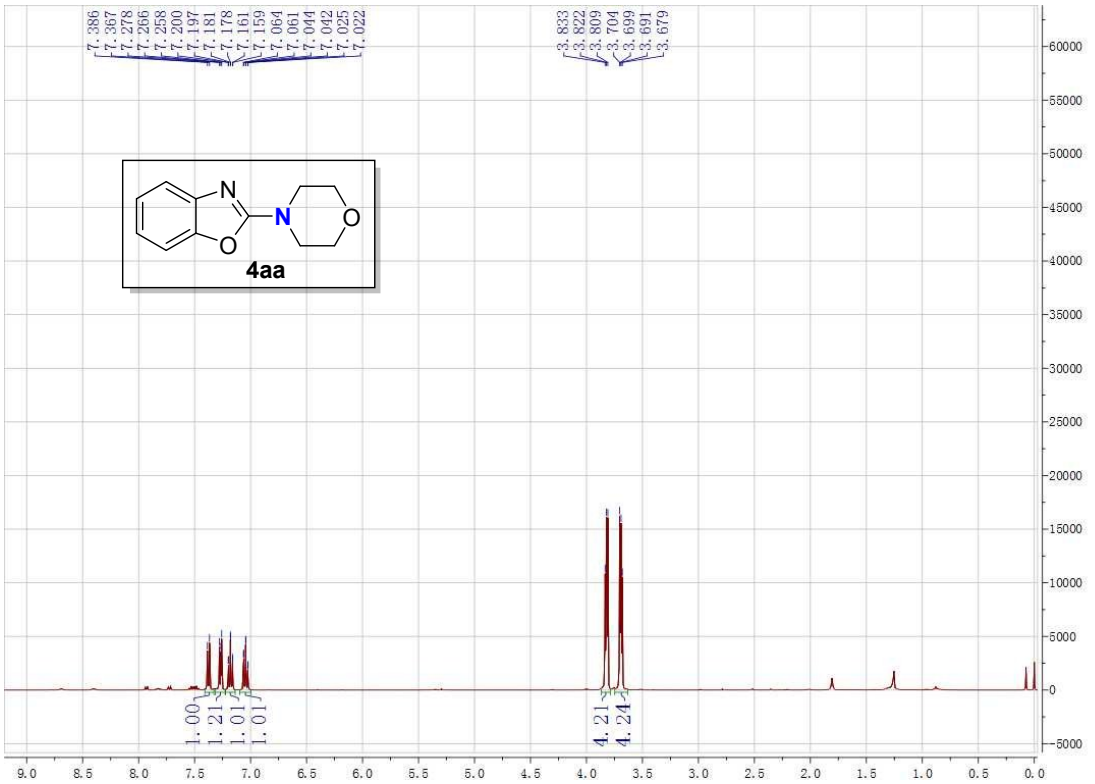
154.81
151.18
140.15
127.18
125.47
121.02
111.87
52.40
28.62
N
O
O
HN
3aj
f1 (ppm)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7.278
7.266
7.258
7.200
7.197
7.181
7.178
7.161
7.159
7.064
7.061
7.044
7.042
7.025
7.022
3.833
3.822
3.809
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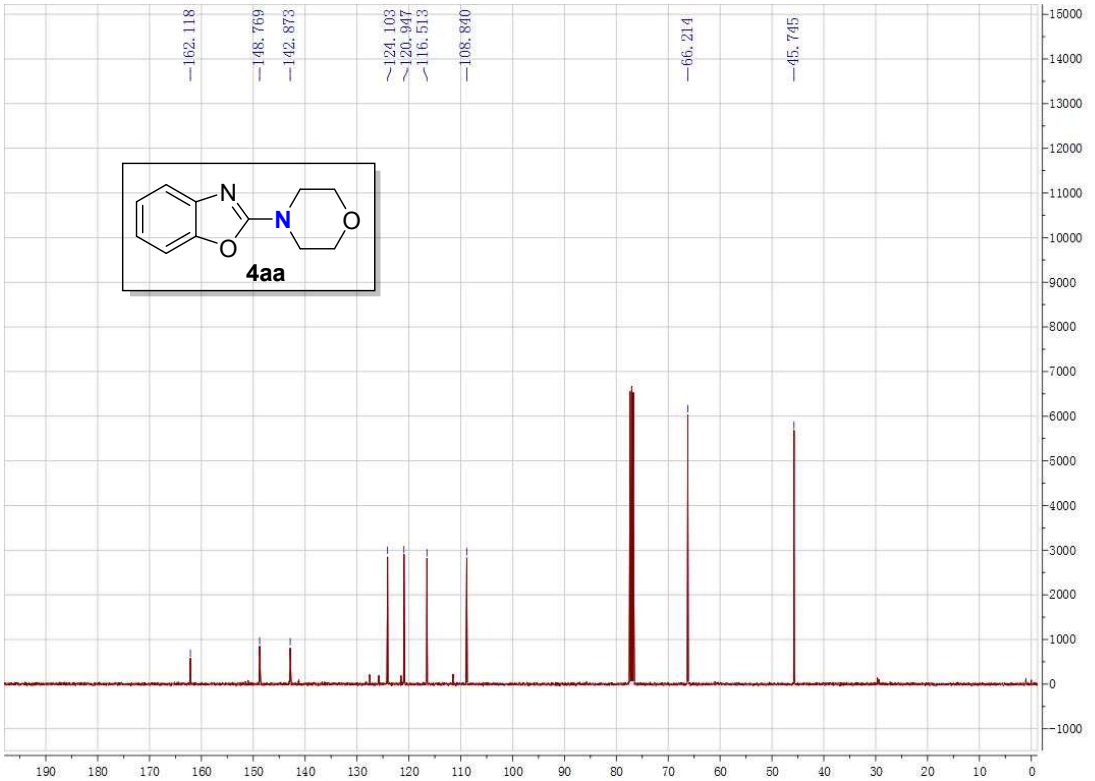
3.699
3.691
3.679
4aa
1.00
1.21
1.01
1.01
4.21
4.24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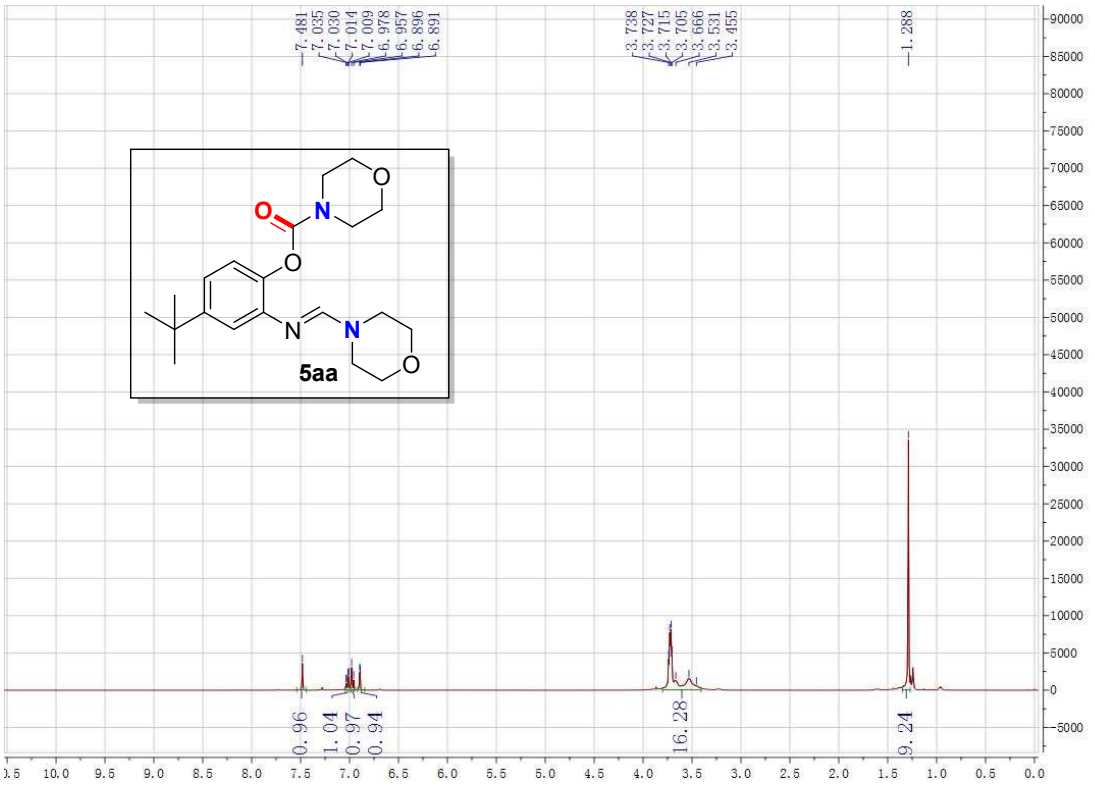
108.840
66.214
45.745
4aa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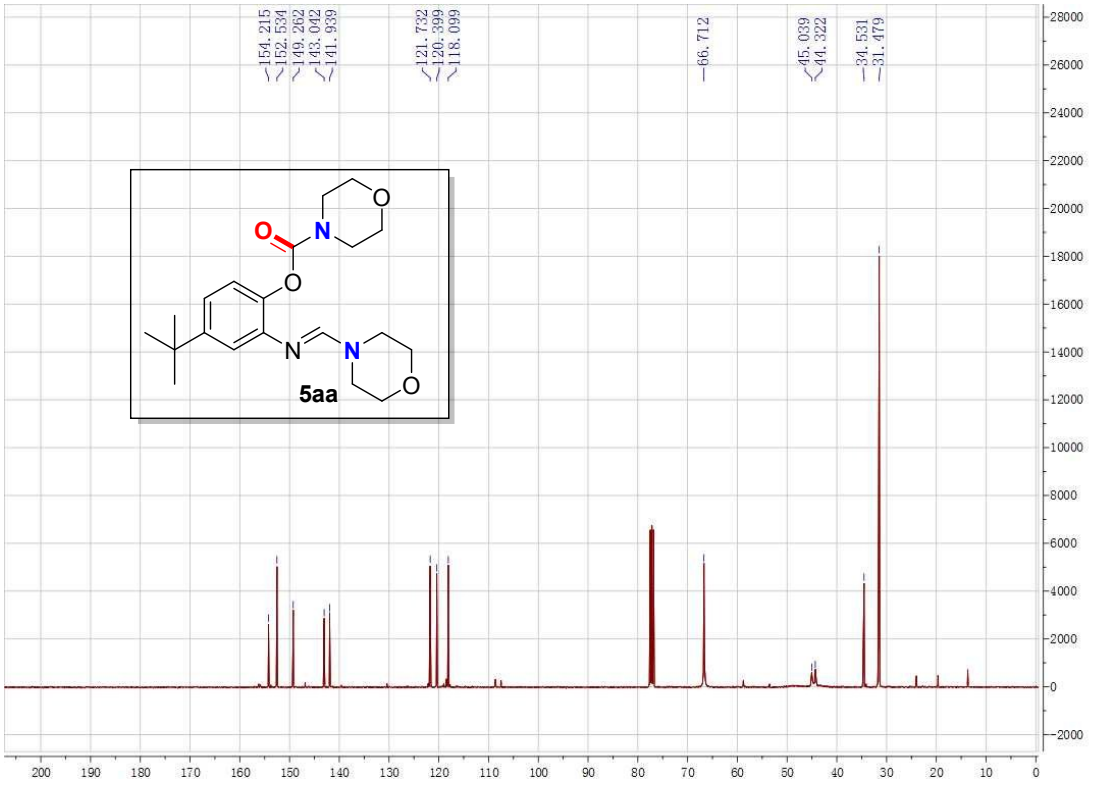
7.009
6.978
6.957
6.896
6.891
3.738
3.727
3.715
3.705
3.666
3.531
3.455
1.288
5aa
0.96
1.04
0.97
0.94
16.28
9.24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118.099
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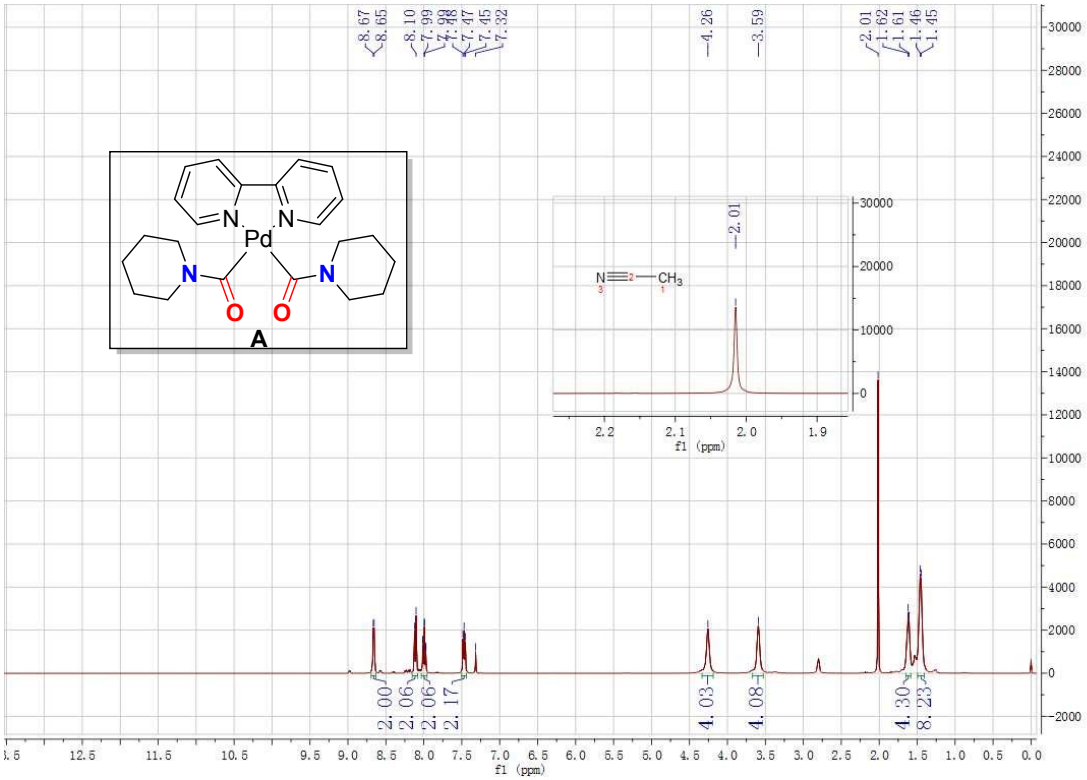
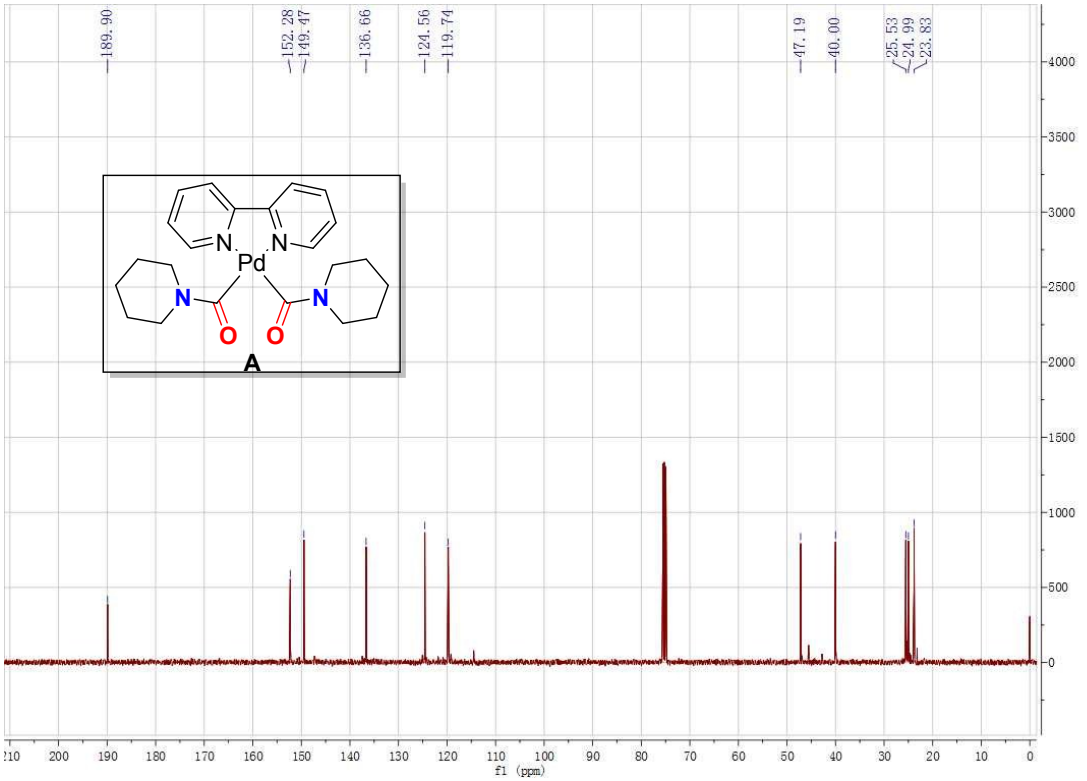
34.531
31.479
5aa


8.67
8.65
8.10
7.99
7.98
7.47
7.45
7.32
4.26
3.59
2.01
1.62
1.61
1.46
1.45
Pd
N
O
A
2.01
CH3
f1 (ppm)
2.00
2.06
2.06
2.17
4.03
4.08
4.30
8.23
f1 (ppm)


189.90
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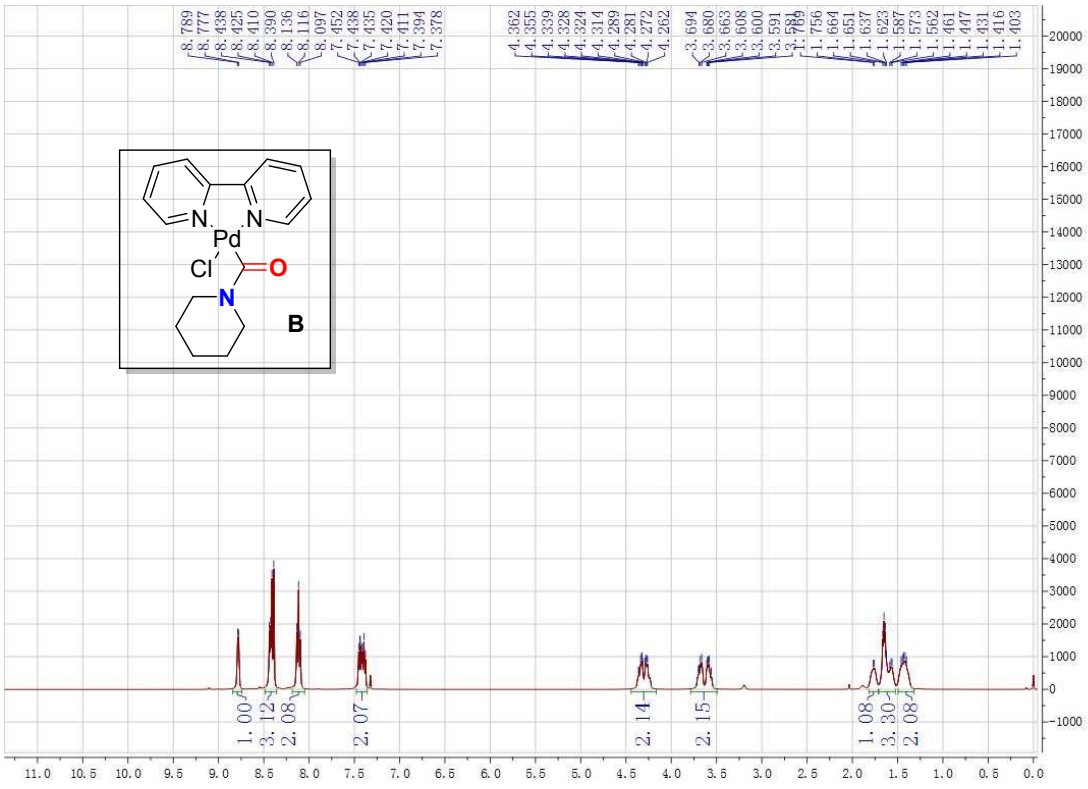
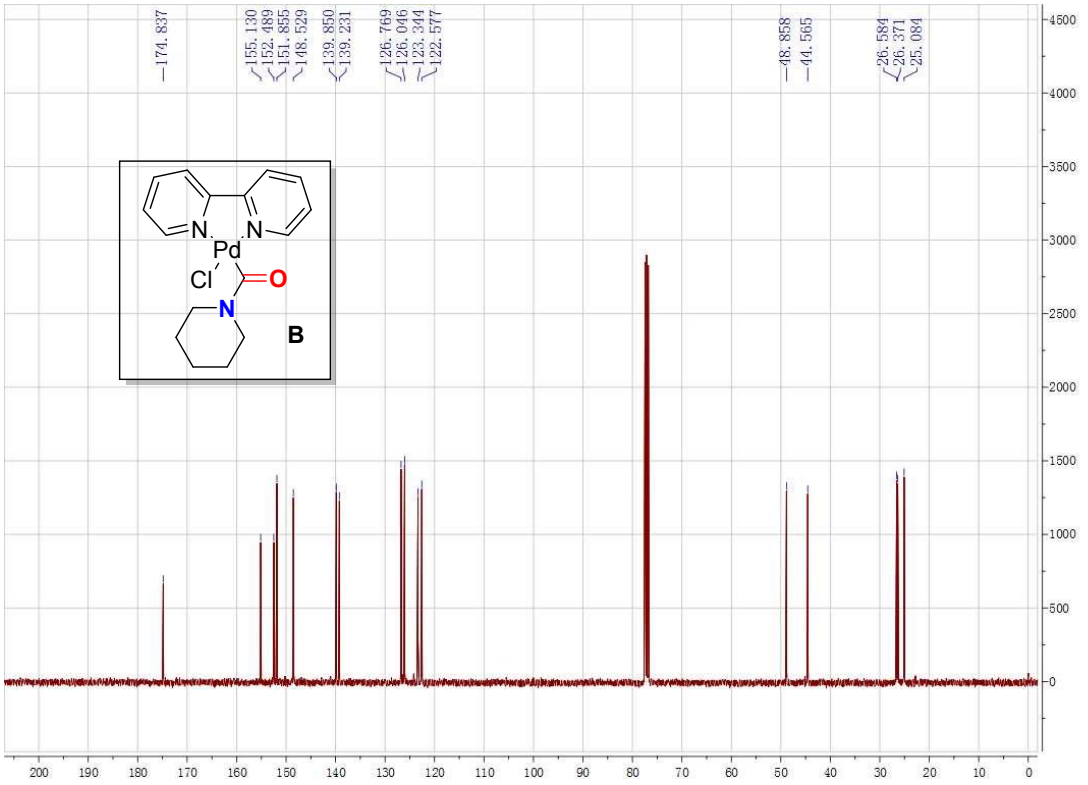
47.19
40.00
25.53
24.99
23.83
Pd
N
O
A
f1 (ppm)





7 References

1. Aresta, M.; Giannoccaro, P.; Tommasi, I.; Dibenedetto, A.; Lanfredi, A. M. M.; Ugozzoli, F. *Organometallics* **2000**, *19*, 3879-3889.
2. He, T.; Li, H. J.; Li, P. H.; Wang, L. *Chem. Commun.* **2011**, *47*, 8946-8948.