Electronic Supplementary Information

for

Chemoselective Acylation of Benzimidazoles with Phenylacetic Acids under Different Cu Catalysts to Fused Five-Membered N-Heterocycles or Tertiary Amides

Shaoyu Mai[a, b], Yingwei Zhao[a] and Qiuling Song[a, c]*

[a] Institute of Next Generation Matter Transformation, College of Chemical Engineering at Huaqiao University

[b] College of Materials Science at Huaqiao University, 668 Jimei Blvd, Xiamen, Fujian, 361021, P. R. China

[c] Beijing National Laboratory for Molecular Sciences, Beijing, 100190, P. R. China
Fax: 86-592-6162990; email: qsong@hqu.edu.cn

Table of Contents

General Considerations

All experiments were conducted with a sealed pressure vessel. Flash column chromatography was performed over silica gel (200-300 mesh). ^{1}H NMR spectra were recorded on a Bruker AVIII-500M spectrometers, Chemical shifts (in ppm) were referenced to $CDCl_3$ (δ =7.26 ppm) or DMSO-d_6 (δ =2.54 ppm) as an internal standard. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.0 ppm) or DMSO-d_6 (δ =40.45 ppm). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Experimental Procedures

1. General procedure for cyclization of benzoimidazoles with *ortho*-halogenated phenyl acetic acids

Condition A: A sealed pressure vessel was charged with 2-fluorophenylacetic acids (0.25 mmol), benzimidazoles (0.35mmol), $Cu(OAc)_2$ (3.6 mg, 0.025 mmol), $BF_3{\cdot}Et_2O$ (7.1 mg, 0.05mmol), K_2CO_3 (69mg, 0.5mmol) and DMF (1 mL). The resulting solution was stirred at 120 ^{o}C under O_2 (O_2 was blowing into the system several times) monitored by TLC and GC for 18 hours. Upon completion of the reaction, the solvens were removed via rotary evaporator and the residue was purified with flash chromatography (silicagel, ethyl acetate: dichloromethane: petroleum ether: =1:1:4-1:1:10).

Condition A': A sealed pressure vessel was charged with 2-bromophenylacetic acid (0.25 mmol), benzimidazole (0.35mmol), CuI (9.5 mg, 0.05 mmol), DMEDA (8.8 mg, 0.1mmol), K_3PO_4 (106mg, 0.5mmol) and DMSO (1 mL). The resulting solution was stirred at 120 ^{o}C under O_2 (O_2 was blowing into the system several times) monitored by TLC and GC for 18 hours. Upon completion of the reaction, the solvents were removed via rotary evaporator and the residue was purified with flash chromatography to give corresponding product **3aa** (22 mg, 40%).(silicagel, ethyl acetate: dichloromethane: petroleum ether: =1:1:4).

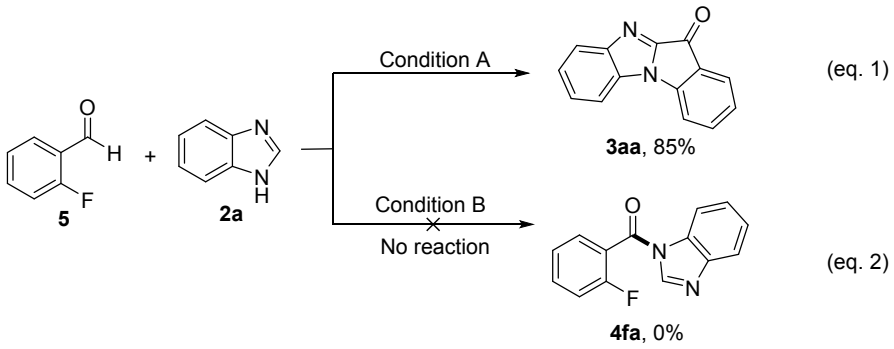
2. General procedure for Decarboxylative Amidation Phenylacetic Acids with Benzimidazoles

Condition B: A sealed pressure vessel was charged with phenylacetic acids (0.25 mmol), benzimidazoles (0.5mmol), CuBr (3.6 mg, 0.025 mmol), pyridine (60 mg, 0.75mmol), and *o*-xylene (1 mL). The resulting solution was stirred at 130 ^{o}C under O_2 (O_2 was blowing into the system several times) monitored by TLC and GC for 24 hours. Upon completion of the

reaction, the solvents were removed via rotary evaporator and the residue was purified with flash chromatography (silicagel, ethyl acetate: petroleum ether=1:4-1:10).

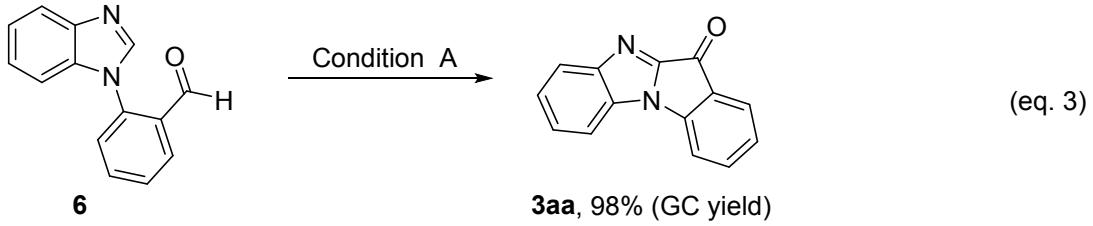
Mechanism Studies

The Mechanism Studies of cyclization of benzoimidazoles with ortho-halogenated phenyl acetic acids

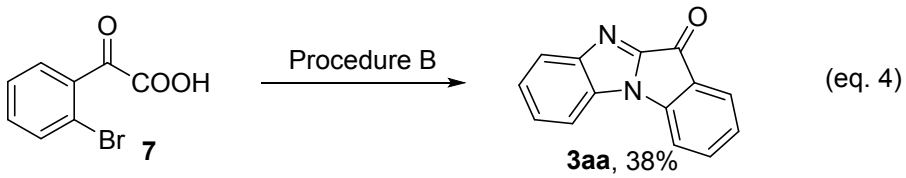


Follow **Condition A**: a sealed pressure vessel was charged with 2-fluorobenzaldehyde (31mg, 0.25 mmol), benzimidazoles (38 mg, 0.35mmol), $Cu(OAc)_2$ (3.6 mg, 0.025 mmol), $BF_3{\cdot}Et_2O$ (7.1 mg, 0.05mmol), K_2CO_3 (69mg, 0.5mmol) and DMF (1 mL). The resulting solution was stirred at 120 ^oC under O_2 (O_2 was blowing into the system several times) monitored by TLC and GC for 18 hours. After cooling to room temperature, solvents were evaporated under reduced pressure and the residue was purified by chromatography on silica gel with ethyl acetate: dichloromethane: petroleum ether (1:1:4) to give corresponding product **3aa** (47 mg, 85%) (eq. 1).

Follow **Condition B**, no aimed amide product **4a′a** was detected. (eq. 2)



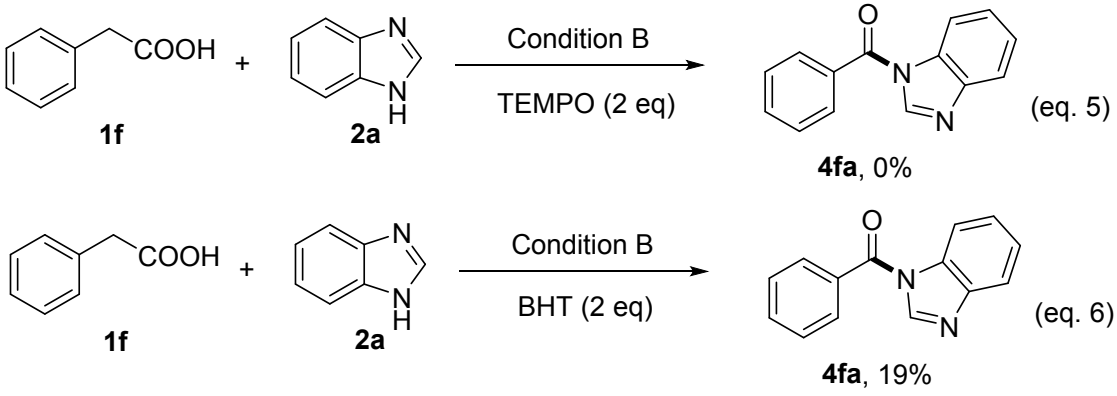
Further study to perform the intramolecular annulation of N-arylation intermediate under Cu/O_2 Condition A afforded **3aa** in nearly quantitative yield (eq. 3).



Follow **Condition A**': A sealed pressure vessel was charged with 2-(2-bromophenyl)-2-oxoacetic acid (**7**) (0.25 mmol), benzimidazole (0.35mmol), CuI (9.5 mg, 0.05 mmol), DMEDA (8.8 mg, 0.1mmol), K_3PO_4 (106mg, 0.5mmol) and DMSO (1 mL). The resulting solution was stirred at 120 °C under O_2 (O_2 was blowing into the system several times) monitored by TLC and GC for 18 hours. Upon completion of the reaction, the solvents were removed via rotary evaporator and the residue was purified with flash chromatography to give corresponding product **3aa** (21 mg, 38%) (silica gel, ethyl acetate: dichloromethane: petroleum ether: =1:1:4) (eq. 4).

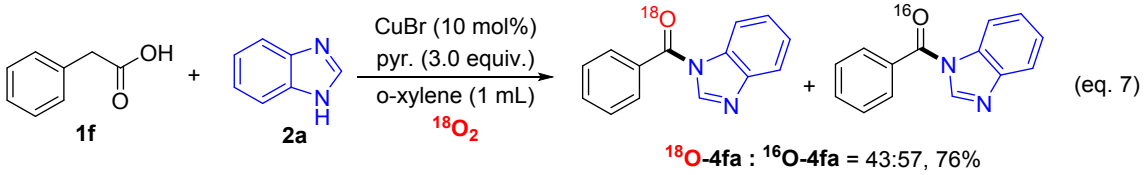
The Mechanism Studies of Decarboxylative Amidation Phenylacetic Acids with Benzimidazoles

1. Radical Trapping Experiments



A sealed pressure vessel was charged with phenylacetic acid (0.25 mmol), benzimidazole (0.5mmol), CuBr (3.6 mg, 0.025 mmol), pyridine (60 mg, 0.75mmol), TEMPO (0.5 mmol) or BHT (0.5 mmol) and *o*-xylene (1 mL) (eq. 5 and 6). The resulting solution was stirred at 130 °C under O_2 monitored by TLC and GC for 24 hours. After cooling down to room temperature, the mixture was measured by GC without further purification. The reactions were mostly inhibited, which indicate that a radical pathway might be involved in this reaction.

2. Labeling Experiments (^{18}O labeling experiment under $^{18}O_2$.)



A sealed pressure vessel was charged with phenylacetic acid **1f** (0.25 mmol), benzimidazole **2a** (0.5mmol), CuBr (3.6 mg, 0.025 mmol), pyridine (60 mg, 0.75mmol), and o-xylene (1 mL). The resulting solution was stirred at 130 °C under $^{18}O_2$ for 24 hours. Upon completion of the reaction, the solvents were removed via rotary evaporator and the residue was purified with flash chromatography (silica gel, ethyl acetate: petroleum ether=1:4) to give 42 mg of **4fa** in 76% isolated yield as a white solid. Then the amide **4fa** was determined by GC-MS and HRMS (Figure **1**). In these cases, part of carbonyl oxygen atom of **4fa** was labeled. The ratio of **4fa**-^{18}O: **4fa**-^{16}O = 43: 57 (eq. 7).

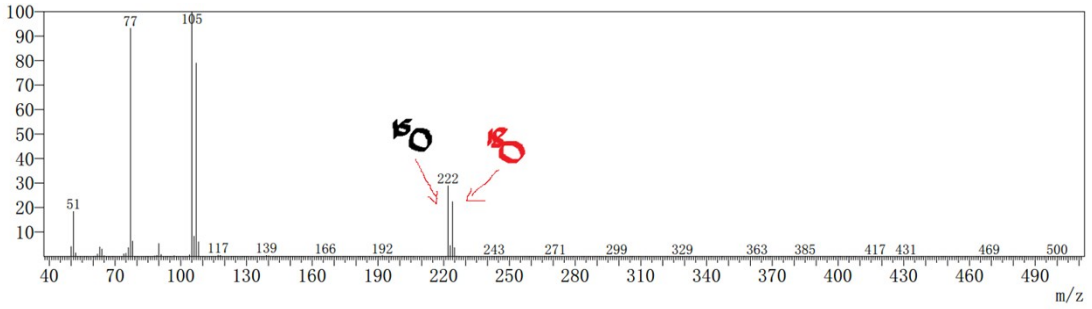
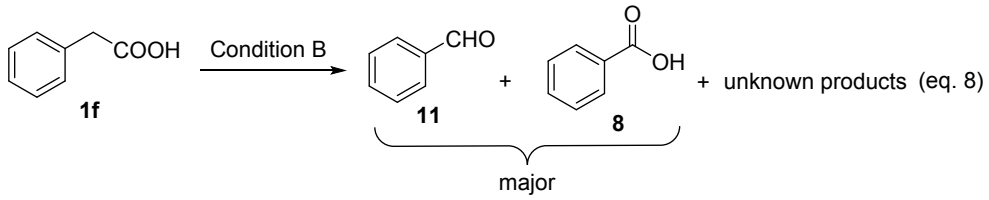
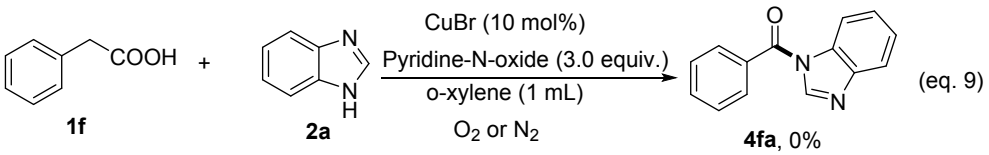


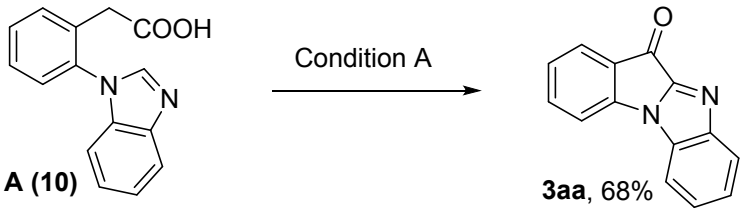
Figure S1. ^{18}O labeling experiment under $^{18}O_2$ measured by GC-MS.

3. Control Experiments

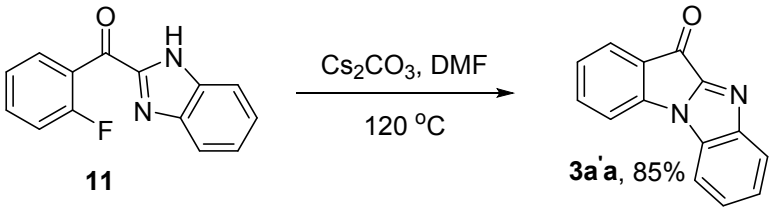




If only phenylacetic acid (**1f**) was exposed under the standard conditions without benzimidazole, benzaldehyde and benzoic acid (**8**) can be detected by GC-MS and some unknown products (eq. 9). Pyridine N-oxide was applied to the phenylacetic acid standard conditions in the presence/absence of dioxygen, yet only trace amount of desired product **4fa** was ever detected, thus it was ruled out as a possible pathway

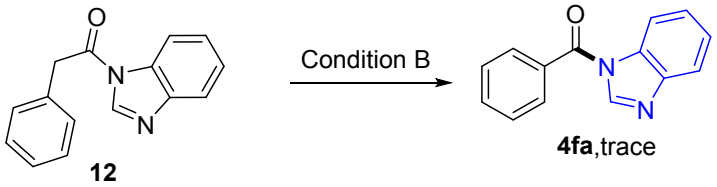


(eq.10)



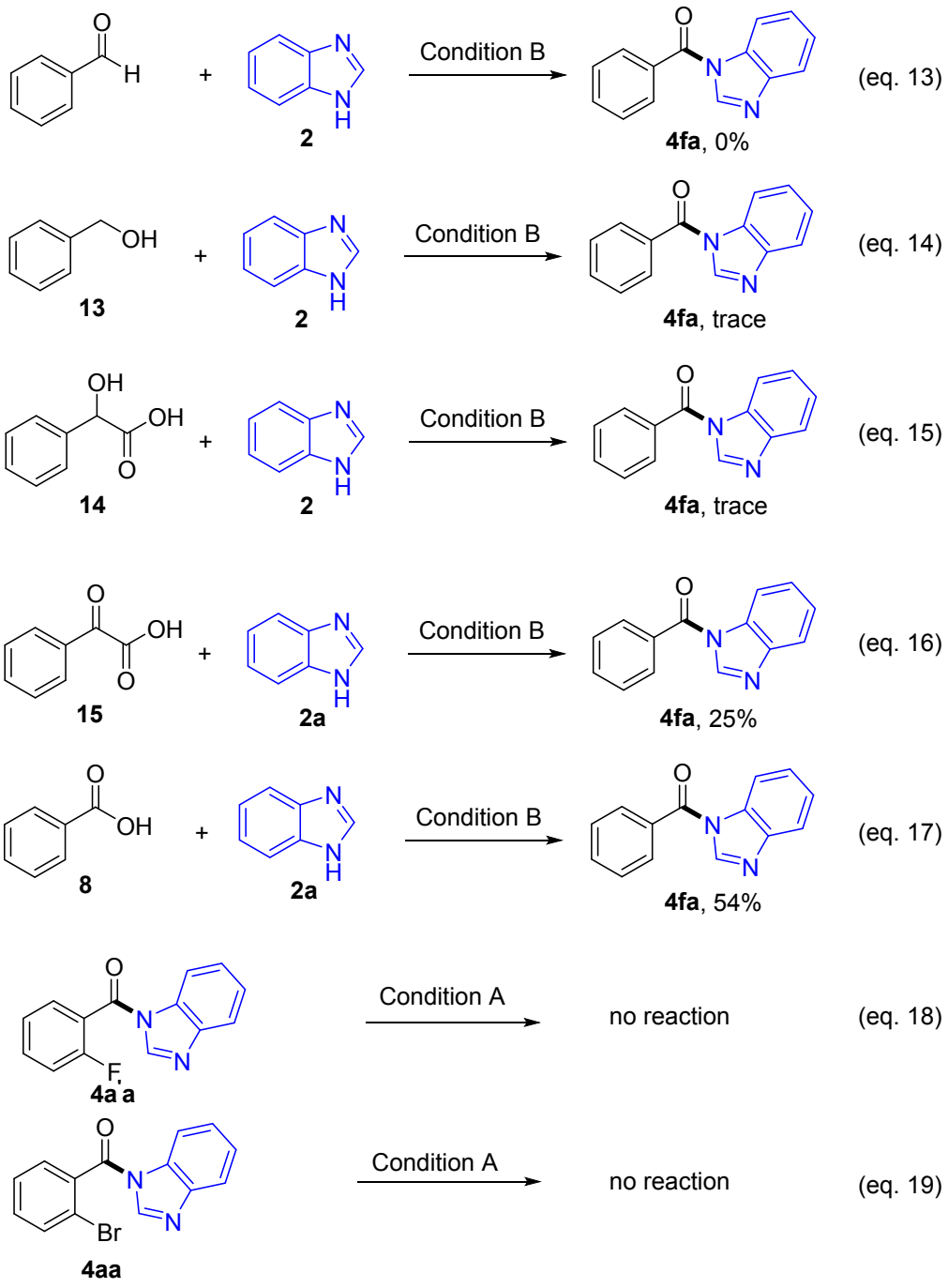
(eq. 11)

In order to figure out which step, S_NAr or aerobic oxidative decarboxylative acylation, occurred first in this tandem process, both compounds **10** and **11** were prepared[19] and subjected to Condition A, desired product were obtained in 68% and 85% yield. However, compound **11** was not observed or detected under either Condition A or Condition B, so we have reasons to believe that SNAr reaction occurred first to lead to C-N bond formation in the tandem process.



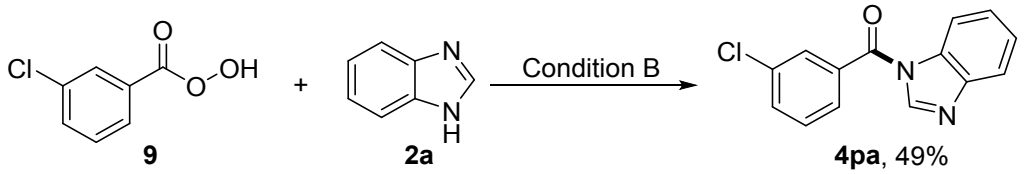
(eq. 12)

Trace amounts of product **4fa** was obtained from compound **12**[2] (eq. 8), suggesting this compound is also not the intermediate.



Furthermore, no desired or trace amounts of product **4fa** was obtained from the reaction between benzaldehyde, benzyl alcohol (**13**), and 2-hydroxyphenylacetic acid (**14**) with benzimidazole (**2a**) (eqs 13-15), revealing that these three compounds are not intermediate for this reaction. The reactions of 2-oxo-2-phenylacetic acid (**15**) and benzoic acid (**8**) with benzimidazole (**2a**) under Condition B were also investigated and the desired product **4fa** was obtained in 25% and 56% yields respectively (eq.s 16 and 17). These two results indicated that they might be the potential intermediates in the reaction transformation. However, the yields were quite low compared with the ones under the standard conditions (79%).

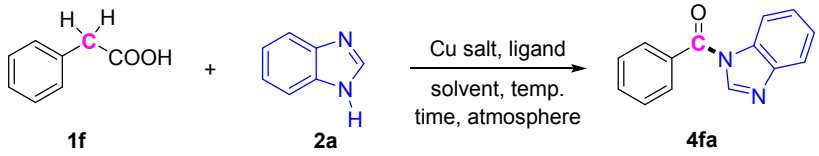
Compounds **4a**'**a** and **4aa** were subjected under Condition A, no reaction occurred (eqs. 18 and 19).



(eq. 18)

In order to figure out whether peroxycarboxylate acts as our key intermediate, the readily available *m*CPBA (3-chloroperoxybenzoic acid) (**9**) was carried out under the standard conditions and corresponding product **4pa** was obtained in 49% (eq 18). Compared to the isolated yield from *m*-Chlorophenylacetic acid (main text, Scheme 3, **4pa**, 41%), we have reasons to believe that the above proposed mechanism is plausible

Optimization of Decarboxylative Amidation Phenylacetic Acids with Benzimidazoles

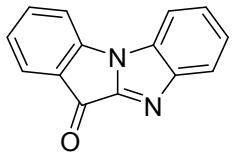


entry	catalyst (mol%)	atmosphere	ligand (equiv.)	temperature	solvent	yield of **3** (%)[b]
1	CuI (10)	O_2	pyridine (3)	130 °C	*p*-Xylene	68
2	CuCl (10)	O_2	pyridine (3)	130 °C	*p*-Xylene	trace
3	CuBr (10)	O_2	pyridine (3)	130 °C	*p*-Xylene	75
4	CuBr (10)	O_2	pyridine (3)	130 °C	*o*-Xylene	91(79)[c]
5	$FeBr_3$ (10)	O_2	pyridine (3)	130 °C	*o*-Xylene	trace
6	CuBr (10)	O_2	Et_3N (3)	130 °C	*o*-Xylene	0
7	CuBr (10)	O_2	bi-pyridine (3)	130 °C	*o*-Xylene	0
8	CuBr (10)	O_2	1, 10-Phen (3)	130 °C	*o*-Xylene	0
9	CuBr (10)	O_2	pyridine (3)	130 °C	PhCl	77
10	CuBr (10)	O_2	pyridine (3)	130 °C	*m*-Xylene	39
11[d]	CuBr (10)	O_2	pyridine (3)	130 °C	*o*-Xylene	81
12	CuBr (10)	O_2	pyridine (3)	120 °C	*o*-Xylene	11
13	CuBr (10)	O_2	pyridine (3)	140 °C	*o*-Xylene	75
14	CuBr (10)	N_2	pyridine (3)	130 °C	*o*-Xylene	no product
15	CuBr (10)	air	pyridine (3)	130 °C	*o*-Xylene	74

Reaction Conditions: [a] phenylacetic acid (**1f**, 0.25 mmol), benzoimidazole (**2a**, 0.5 mmol), Cu salt (10 mol%), ligand, solvent (1 mL), 24 h, temp., corresponding atmosphere. [b] GC yield. [c] Isolated yield. [d] 20 h.

Characterization of Products

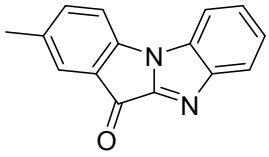
11H-benzo[4,5]imidazo[1,2-a]indol-11-one (CAS:138479-49-9)[3,4]



3aa (3a'a)

A sealed pressure vessel was charged with 2-fluorobenzaldehyde (31mg, 0.25 mmol), benzimidazoles (38mg, 0.35mmol), $Cu(OAc)_2$ (3.6 mg, 0.025 mmol), $BF_3 \cdot Et_2O$ (7.1 mg, 0.05mmol), K_2CO_3 (69mg, 0.5mmol) and DMF (1 mL). The resulting solution was stirred at 120 ^oC under O_2 (O_2 was blowing into the system several times). After cooling to room temperature, solvents were evaporated under reduced pressure and the residue was purified by chromatography on silica gel with ethyl acetate: dichloromethane : petroleum ether (1:1:4) to give **11H-benzo[4,5]imidazo[1,2-a]indol-11-one 3aa** yellow solid (44 mg, 80%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 8.1 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 179.81 (s), 148.95 (s), 148.79 (s), 143.20 (s), 136.76 (s), 129.89 (s), 127.97 (s), 127.34 (s), 125.91 (s), 125.81 (s), 124.40 (s), 123.91 (s), 111.65 (s), 111.13 (s).

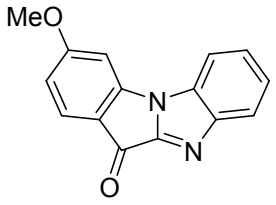
2-methyl-11H-benzo[4,5]imidazo[1,2-a]indol-11-one



3b'a

Yellow solid (32mg, 54%).^1H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.38 – 7.34 (m, 1H), 7.30 (ddd, *J* = 8.3, 7.2, 1.1 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 1H), 2.34 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 180.07 (s), 149.14 (s), 148.70 (s), 141.04 (s), 136.85 (s), 136.03 (s), 129.89 (s), 127.80 (s), 127.43 (s), 126.37 (s), 124.21 (s), 123.86 (s), 111.35 (s), 111.07 (s), 20.99 (s). HRMS m/z (EI) calcd. For $C_{15}H_{10}N_2O$: 234.0790; found: 234.0793.

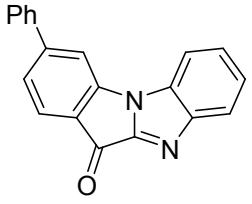
3-methoxy-11H-benzo[4,5]imidazo[1,2-a]indol-11-one (new compound)



3c'a

Yellow solid (31mg, 50%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 1H), 7.49 – 7.44 (m, 1H), 7.32 (ddd, *J* = 8.3, 7.2, 1.1 Hz, 1H), 6.83 (d, *J* = 2.1 Hz, 1H), 6.62 (dd, *J* = 8.4, 2.1 Hz, 1H), 3.95 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 178.53 (s), 166.96 (s), 150.30 (s), 148.75 (s), 145.28 (s), 129.93 (s), 128.02 (s), 127.64 (s), 124.26 (s), 123.87 (s), 120.55 (s), 110.95 (s), 108.77 (s), 99.89 (s), 56.26 (s).HRMS m/z (EI) calcd. For $C_{15}H_{10}N_2O_2$: 250.0749; found: 250.0742

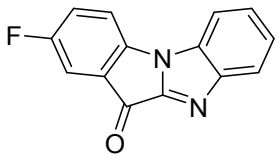
3-phenyl-11H-benzo[4,5]imidazo[1,2-a]indol-11-one



3d'a

Yellow solid (33mg, 45%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.3 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 8.01 (dd, *J* = 11.9, 4.9 Hz, 3H), 7.91 – 7.80 (m, 5H), 7.76 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.69 (dd, *J* = 11.4, 4.1 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 179.48 (s), 150.38 (s), 149.60 (s), 148.92 (s), 144.02 (s), 139.35 (s), 129.28 (s), 129.22 (s), 127.94 (s), 127.24 (s), 126.26 (s), 126.14 (s), 124.64 (s), 124.44 (s), 124.04 (s), 111.20 (s), 110.50 (s). HRMS m/z (EI) calcd. For $C_{20}H_{12}N_2O$: 296.0950; found: 296.0949.

2-fluoro-11H-benzo[4,5]imidazo[1,2-a]indol-11-one

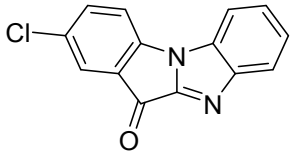


3e'a

Yellow solid (24mg, 40%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 1H), 7.60 – 7.47 (m, 2H), 7.44 – 7.37 (m, 1H), 7.37 – 7.28 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.75 (s), 161.56 (s), 159.58 (s), 149.14 (s), 148.75 (s), 139.37 (s), 129.86 (s), 128.84 (s), 128.32 (s), 124.39 (d, *J* = 53.5 Hz), 122.69 (d, *J* = 24.5 Hz), 113.72 (d, *J* = 25.1 Hz), 112.68

(d, *J* = 7.7 Hz), 110.94 (s). HRMS m/z (EI) calcd. For $C_{14}H_7N_2OF$: 238.0543; found: 238.0542.

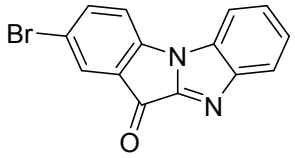
2-chloro-11H-benzo[4,5]imidazo[1,2-a]indol-11-one(CAS: 1632464-25-5) [4]



3f'a

Yellow solid (29mg, 45%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.39 – 7.34 (m, 2H), 7.21 (dd, *J* = 8.0, 1.7 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 178.52 (s), 148.87 (s), 144.00 (s), 142.98 (s), 129.74 (s), 128.32 (s), 126.83 (s), 125.97 (s), 125.77 (s), 124.82 (s), 124.20 (s), 112.55 (s), 111.11 (s). HRMS m/z (EI) calcd. For $C_{14}H_7N_2OCl$: 254.0252; found: 254.0251.

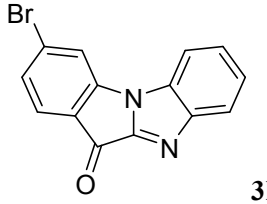
2-bromo-11H-benzo[4,5]imidazo[1,2-a]indol-11-one



3g'a

Yellow solid (46mg, 62%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 1.8 Hz, 1H), 7.74 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.54 (dt, *J* = 15.2, 7.8 Hz, 2H), 7.37 (dd, *J* = 11.2, 4.0 Hz, 1H), 7.27 (s, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 178.41 (s), 148.90 (s), 141.89 (s), 138.99 (s), 129.80 (s), 129.00 (s), 128.81 (s), 128.39 (s), 124.77 (s), 124.23 (s), 118.90 (s), 113.07 (s), 111.13 (s). HRMS m/z (EI) calcd. For $C_{14}H_7N_2OBr$: 297.9745; found: 297.9742.

3-bromo-11H-benzo[4,5]imidazo[1,2-a]indol-11-one (CAS:1632464-23-3)[4]

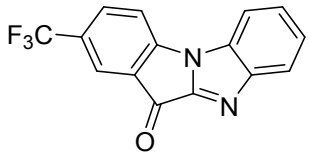


3h'a

Yellow solid (36mg, 48%).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 1H), 7.62 – 7.49 (m, 4H), 7.42 – 7.34 (m, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 178.71 (s), 148.90 (s), 143.88 (s), 131.43 (s), 129.74 (s), 129.02 (s), 128.35 (s), 126.90 (s), 126.20 (s), 124.85 (s),

124.22 (s), 115.33 (s), 111.15 (s).

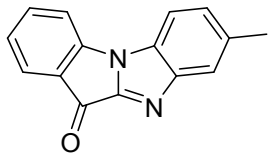
2-(trifluoromethyl)-11H-benzo[4,5]imidazo[1,2-a]indol-11-one



3i'a

Yellow solid (25mg, 35%).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.86 (m, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.26 (s), 149.06 (s), 145.28 (s), 133.99 (dd, *J* = 7.6, 3.9 Hz), 129.80 (s), 128.68 (s), 128.65 (s), 128.38 (s), 127.70 (s), 125.18 (s), 124.41 (s), 124.30 (s), 123.12 (q, *J* = 3.7 Hz), 111.74 (s), 111.24 (s). HRMS m/z (EI) calcd. For $C_{15}H_7N_2OF_3$: 288.0505; found: 288.0510.

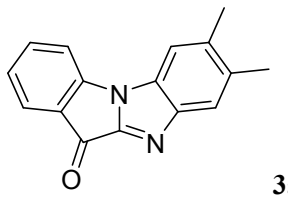
8-methyl-11H-benzo[4,5]imidazo[1,2-a]indol-11-one



3a'b

Yellow solid (44mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 1H), 7.62 (ddd, *J* = 11.7, 5.9, 5.3 Hz, 3H), 7.56 (tdd, *J* = 7.7, 2.2, 1.3 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.32-7.23 (m, 5H), 7.17 (td, *J* = 7.5, 3.2 Hz, 2H), 7.09 (dd, *J* = 8.4, 1.0 Hz, 1H), 2.50 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.85 (s), 179.71 (s), 149.17 (s), 148.93 (s), 148.60 (s), 147.02 (s), 143.23 (s), 143.15 (s), 138.83 (s), 136.61 (s), 136.55 (s), 134.44 (s), 130.15 (s), 129.69 (s), 127.98 (s), 127.52 (s), 127.38 (s), 126.25 (s), 125.82 – 125.59 (m), 123.35 (d, *J* = 8.8 Hz), 111.58 (s), 111.49 (s), 110.92 (s), 110.56 (s), 22.17 (s), 21.58 (s). HRMS m/z (EI) calcd. For $C_{15}H_{10}N_2O$: 234.0785; found: 234.0793.

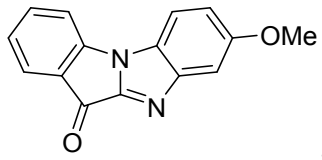
7,8-dimethyl-11H-benzo[4,5]imidazo[1,2-a]indol-11-one (CAS: 138479-56-8)[4]



3a'c

Yellow solid (37mg, 60%).[1]H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.4 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.28 (d, *J* = 7.1 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H). [13]C NMR (126 MHz, $CDCl_3$) δ 179.78 (s), 148.77 – 148.00 (m), 147.60 (s), 143.28 (s), 138.28 (s), 136.44 (s), 133.91 (s), 128.58 (s), 127.65 (s), 125.62 (d, *J* = 3.4 Hz), 123.52 (s), 111.45 (s), 111.16 (s), 20.97 (s), 20.40 (s).

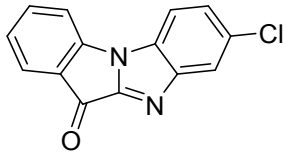
8-methoxy-11H-benzo[4,5]imidazo[1,2-a]indol-11-one



3a'd

Yellow solid (62mg, 84%) [1]H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.9 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 2H), 7.55 (tdd, *J* = 7.7, 4.3, 1.1 Hz, 2H), 7.39 (d, *J* = 8.9 Hz, 1H), 7.26 – 7.21 (m, 3H), 7.17 (dd, *J* = 13.2, 7.4 Hz, 2H), 7.09 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.92 – 6.86 (m, 2H), 3.91 (s, 3H), 3.85 (s, 3H).[13]C NMR (126 MHz, $CDCl_3$) δ179.60 (s), 179.20 (s), 160.53 (s), 157.39 (s), 149.88 (s), 149.08 (s), 148.36 (s), 143.44 (s), 143.14 (s), 142.85 (s), 136.48 (s), 136.32 (s), 130.90 (s), 127.76 (s), 127.37 (s), 125.82 (s), 125.79 (s), 125.69 (s), 125.65 (s), 124.60 (s), 124.51 (s), 119.07 (s), 114.38 (s), 111.47 (s), 111.45 (s), 111.23 (s), 104.58 (s), 93.89 (s), 55.92 (s), 55.73 (s). HRMS m/z (EI) calcd. For $C_{15}H_{10}N_2O_2$: 250.0739; found: 250.0742.

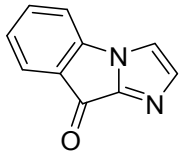
8-chloro-11H-benzo[4,5]imidazo[1,2-a]indol-11-one 9H-imidazo[1,2-a]indol-9-one



3a'e

Yellow solid (32mg, 50%) [1]H NMR (500 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.74 – 7.69 (m, 2H), 7.67 – 7.61 (m, 2H), 7.59 (s, 1H), 7.48 (dd, *J* = 24.9, 8.2 Hz, 2H), 7.37 – 7.29 (m, 3H), 7.28 – 7.21 (m, 2H). [13]C NMR (126 MHz, $CDCl_3$) δ 179.48 (s), 179.41 (s), 149.90 (s), 149.57 (s), 149.47 (s), 147.37 (s), 142.92 (s), 142.79 (s), 136.93 (s), 133.94 (s), 130.25 (s), 130.02 (s), 128.50 (s), 127.31 (s), 127.19 (s), 126.37 (s), 126.35 (s), 126.13 (s), 125.29 (s), 124.76 (s), 123.56 (s), 111.82 (s), 111.78 (s), 111.69 (s), 111.28 (s). HRMS m/z (EI) calcd. For $C_{14}H_7N_2OCl$: 254.0255; found: 254.0247.

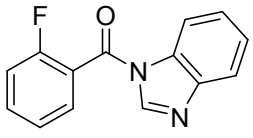
9H-imidazo[1,2-a]indol-9-one (CAS: 120614-25-7)[3,4]



3a'f

Yellow solid (24mg, 56%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.4, 0.7 Hz, 1H), 7.51 (td, *J* = 7.8, 1.2 Hz, 1H), 7.37 (d, *J* = 1.0 Hz, 1H), 7.26 (d, *J* = 1.0 Hz, 1H), 7.22 (td, *J* = 7.8, 0.8 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 177.76 (s), 146.00 (s), 141.41 (s), 137.40 (s), 135.60 (s), 128.27 (s), 127.26 (s), 125.33 (s), 115.19 (s), 111.62 (s).

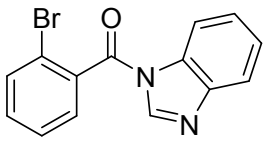
(1H-benzo[d]imidazol-1-yl)(2-fluorophenyl)methanone (CAS:314055-15-7)[5]



4a'a

A sealed pressure vessel was charged with 2-fluorophenylacetic acids (0.25 mmol), benzimidazoles (0.5mmol), CuBr (3.6 mg, 0.025 mmol), pyridine (60 mg, 0.75mmol), and *o*-xylene (1 mL). The resulting solution was stirred at 130 ^{o}C under O_2 (O_2 was blowing into the system several times) for 24 hours. After cooling to room temperature, solvents were evaporated under reduced pressure and the residue was purified by chromatography on silica gel with ethyl acetate: dichloromethane : petroleum ether (1:1:4) to give **4a'a** as white solid (44 mg, 40%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 6.9, 2.0 Hz, 1H), 8.06 (d, *J* = 2.8 Hz, 1H), 7.83 (dd, *J* = 6.8, 2.0 Hz, 1H), 7.71-7.64 (m, 2H), 7.49-7.43 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.32-7.27 (m, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 162.96 (s), 160.21 (s), 158.19 (s), 144.07 (s), 142.70 (d, *J* = 2.8 Hz), 134.45 (d, *J* = 8.3 Hz), 130.50 (d, *J* = 1.9 Hz), 126.01 (s), 125.56 (s), 125.05 (d, *J* = 3.6 Hz), 121.68 (d, *J* = 14.8 Hz), 120.58 (s), 116.80 (d, *J* = 20.9 Hz), 115.47 (s).

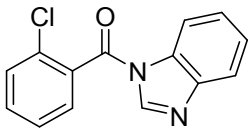
(1H-benzo[d]imidazol-1-yl)(2-bromophenyl)methanone(CAS:326901-39-7)[5]



4aa

Yellow oil (33 mg, 44%).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 5.1 Hz, 1H), 7.90 (s, 1H), 7.86-7.80 (m, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.56-7.44 (m, 5H).^{13}C NMR (126 MHz, $CDCl_3$) δ 165.31 (s), 144.29 (s), 142.71 (s), 135.36 (s), 133.63 (s), 132.71 (s), 131.33 (s), 129.22 (s), 127.93 (s), 126.11 (s), 125.63 (s), 120.67 (s), 119.76 (s), 115.49 (s).

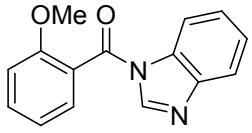
(1H-benzo[d]imidazol-1-yl)(2-chlorophenyl)methanone (CAS:331429-94-8)[5]



4ba

White solid (29 mg, 46%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 5.8 Hz, 1H), 7.91 (s, 1H), 7.83 (dd, *J* = 6.5, 2.3 Hz, 1H), 7.58 (ddd, *J* = 7.9, 6.1, 1.2 Hz, 3H), 7.52-7.43 (m, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 164.61 (s), 144.26 (s), 142.66 (s), 133.18 (s), 132.70 (s), 131.47 (s), 131.35 (s), 130.52 (s), 129.27 (s), 127.43 (s), 126.10 (s), 125.62 (s), 120.66 (s), 115.47 (s).

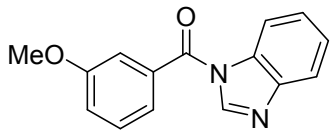
(1H-benzo[d]imidazol-1-yl)(2-methoxyphenyl)methanone(CAS: 816441-32-4)[7]



4ca

White oil (29 mg, 83%). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm) δ 8.27-8.25 (m, 1 H), 7.97 (s, 1 H), 7.81-7.79 (m, 1 H), 7.60 -7.53(m, 2 H), 7.46–7.40 (m, 2 H); 7.15-7.12（m, 1H）, 7.07-7.05 (m, 1H), 3.78(s, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$, ppm).) δ 165.81, 156.49, 144.09, 143.59, 133.48, 131.58, 129.91, 125.68, 125.12, 122.93, 121.15, 120.32, 115.50, 111.60, 55.71.

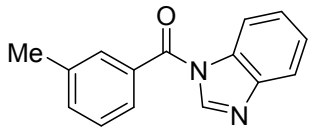
(1H-benzo[d]imidazol-1-yl)(3-methoxyphenyl)methanone (CAS: 349111-08-6)[5]



4da

White solid (47 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.22 – 8.18 (m, 1H), 7.86 – 7.82 (m, 1H), 7.50 – 7.41 (m, 3H), 7.35 – 7.31 (m, 2H), 7.23 – 7.19 (m, 1H), 3.87 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.87 (s), 159.91 (s), 143.97 (s), 143.08 (s), 133.99 (s), 132.05 (s), 130.05 (s), 125.74 (s), 125.27 (s), 121.63 (s), 120.47 (s), 119.34 (s), 115.45 (s), 114.33 (s), 55.54 (s).

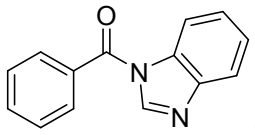
(1H-benzo[d]imidazol-1-yl)(m-tolyl)methanone (CAS:325811-40-3)[5]



4ea

White solid (36 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 6.0, 3.0 Hz, 1H), 7.97 (s, 1H), 7.83 (dd, *J* = 6.0, 3.1 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.47 – 7.41 (m, 3H), 7.37 (dd, *J* = 16.6, 8.1 Hz, 2H), 2.40 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 167.58 (s), 144.20 (s), 143.00 (s), 136.75 (s), 132.94 (s), 131.61 (s), 131.36 (s), 127.92 (s), 126.03 (s), 125.84 (s), 125.34 (s), 120.56 (s), 115.43 (s), 19.47 (s).

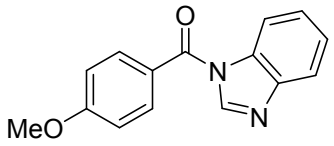
(1H-benzo[d]imidazol-1-yl)(phenyl)methanone（CAS：62573-86-8）[4]



4fa

White solid (44 mg, 79%). ^{1}HNMR: (500 MHz, $CDCl_3$, ppm) δ8.22(s, 1 H), 8.21–8.19 (m, 1 H), 7.85–7.83 (m, 1 H), 7.82-7.80(m, 2 H), 7.71–7.68 (m, 1 H), 7.61–7.58 (m, 2 H), 7.47–7.42 (m, 2 H); ^{13}CNMR: (125 MHz, $CDCl_3$, ppm).) δ 167.1, 144.0, 143.1, 133.2,132.8, 132.1, 129.5, 129.0, 125.8, 125.3, 120.5, 115.4.

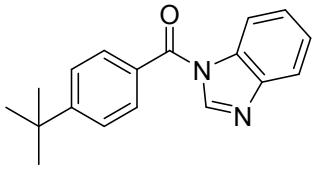
(1H-benzo[d]imidazol-1-yl)(4-methoxyphenyl)methanone (CAS:13361-55-2)[7]



4ga

White solid (54 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.13 (dd, *J* = 6.5, 2.6 Hz, 1H), 7.86 – 7.78 (m, 3H), 7.46 – 7.40 (m, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 3.92 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.41 (s), 163.74 (s), 143.99 (s), 143.08 (s), 132.28 (s), 132.13 (s), 125.50 (s), 124.98 (s), 124.73 (s), 120.45 (s), 115.25 (s), 114.36 (s), 55.64 (s).

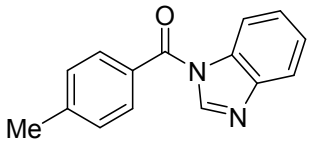
(1H-benzo[d]imidazol-1-yl)(4-(tert-butyl)phenyl)methanone（CAS：20208-57-5）[6]



4ha

White solid (49 mg, 70%) ^{1}HNMR: (500 MHz, $CDCl_3$, ppm)δ8.26 (s, 1 H), 8.23–8.21 (m, 1 H), 7.85-7.83 (m, 1 H), 7.77-7.75(m, 2 H), 7.61–7.59 (m, 2 H), 7.47–7.41 (m, 2 H), 1.39(s, 9 H); ^{13}CNMR: (125 MHz, $CDCl_3$, ppm).) δ 167.1, 157.2, 144.1, 143.2, 132.2, 130.0, 129.7, 126.0, 125.7, 125.1, 120.5, 115.5, 35.3, 31.1.

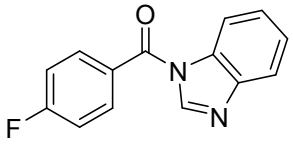
(1H-benzo[d]imidazol-1-yl)(p-tolyl)methanone（CAS：28997-00-4）[6]



4ia

White solid (34 mg, 57%). ^{1}HNMR: (500 MHz, $CDCl_3$, ppm) δ8.24 (s, 1 H), 8.19-8.17 (m, 1 H), 7.84-7.83 (m, 1 H), 7.72-7.71(m, 2 H), 7.46-7.41 (m, 2 H),7.39-7.38 (m, 2 H), 2.49 (s, 1 H); ^{13}CNMR: (125 MHz, $CDCl_3$, ppm).) δ 167.1, 144.3, 144.1, 143.1,132.2, 130.0, 129.8, 129.7, 125.6, 125.1, 120.5, 115.4, 21.7.

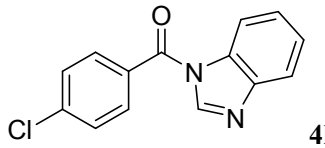
(1H-benzo[d]imidazol-1-yl)(4-fluorophenyl)methanone（CAS：154786-24-0）[6]



4ja

White solid (47 mg, 45%). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm) δ 8.21 (s, 1 H), 8.16-8.14 (m, 1 H), 7.87-7.83 (m, 3 H), 7.48-7.42(m, 2 H), 7.30-7.27 (m, 2 H); ^{13}C NMR: (125 MHz, $CDCl_3$, ppm).) δ165.88, 165.61(d, *J*= 254.63Hz) , 144.06, 142.73, 132.23(d, *J*= 9.13Hz), 132.09, 129.50(d, *J*= 3.38Hz), 125.83, 125.35, 120.64, 116.45(d, *J*= 22.13Hz), 115.34.

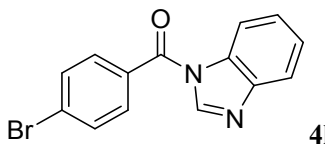
(1H-benzo[d]imidazol-1-yl)(4-chlorophenyl)methanone（CAS:71589-37-2）[6]



4ka

White solid (33 mg, 52%). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm) δ 8.19 (s, 1 H), 8.17–8.15 (m, 1 H), 7.85-7.83 (m, 1 H), 7.78 -7.75(m, 2 H), 7.59–7.57 (m, 2 H); 7.48-7.43 (m, 2H) ; ^{13}C NMR: (125 MHz, $CDCl_3$, ppm).) δ 166.00, 144.00, 142.66, 139.86, 131.96, 131.07, 130.94, 129.46, 125.90, 125.43, 120.63, 115.36.

(1H-benzo[d]imidazol-1-yl)(4-bromophenyl)methanone（CAS：304668-33-5）[6]

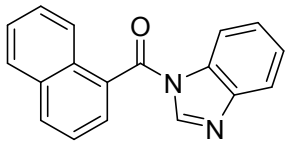


4la

White solid (38 mg, 50%). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm) δ 8.18 (s, 1 H), 8.17-8.13 (m, 1

H), 7.85-7.81 (m, 1 H), 7.75 -7.73(m, 2 H), 7.69-7.66 (m, 2 H); 7.47-7.42（m, 2H）; ^{13}C NMR: (125 MHz, $CDCl_3$, ppm).) δ 166.08, 144.03, 142.61, 132.41, 131.96, 131.58, 130.96, 128.35, 125.88, 125.42, 120.63, 115.35.

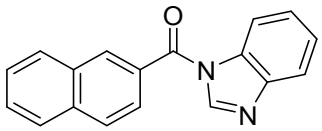
(1H-benzo[d]imidazol-1-yl)(naphthalen-1-yl)methanone（CAS：26670-22-4）[6]



4ma

White solid (41 mg, 60%). ^1H NMR: (500 MHz, $CDCl_3$, ppm) δ 8.32-8.30 (m, 1H), 8.12–8.10 (m, 1H), 8.00-7.96 (m, 3H), 7.86 -7.84(m, 1H), 7.74-7.72 (m, 1H); 7.62-7.55(m, 3H), 7.50-7.46 (m, 2H); ^{13}C NMR: (125 MHz, $CDCl_3$, ppm).) δ 167.06, 144.21, 143.18, 133.57, 132.42, 131.83, 130.58, 130.19, 128.67, 128.13, 127.35, 127.14, 125.90, 125.42, 124.53, 124.48, 120.60, 115.64.

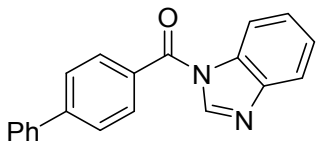
(1H-benzo[d]imidazol-1-yl)(naphthalen-2-yl)methanone（new compound）



4na

White solid (51 mg, 75%). ^1H NMR: (500 MHz, $CDCl_3$, ppm) δ 8.33-8.32 (m, 2 H), 8.23-8.22 (m, 1 H), 8.05-8.04 (m, 1 H), 7.98 -7.96(m, 2 H), 7.88–7.86 (m, 2 H); 7.70-7.67(m, 1H), 7.65-7.62 (m, 1H), 7.49-7.44 (m, 2H); ^{13}C NMR: (125 MHz, $CDCl_3$, ppm).) δ 167.16, 144.03, 143.22, 135.31, 132.20, 131.11, 129.90, 129.19, 128.99, 127.98, 127.56, 125.78, 125.28, 125.03, 120.55, 115.44. HRMS m/z (EI) calcd. for C9H10F3O2 M+ 272.0950, found 272.0953.

[1,1'-biphenyl]-4-yl(1H-benzo[d]imidazol-1-yl)methanone (CAS : 349407-41-6) [6]

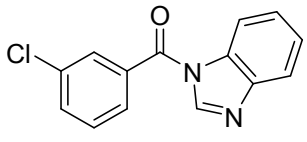


4oa

White solid (46 mg, 62%). ^1H NMR (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.25 – 8.20 (m, 1H), 7.90 (d, J = 8.3 Hz, 2H), 7.88 – 7.84 (m, 1H), 7.81 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 7.2 Hz, 2H), 7.56 – 7.41 (m, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.84, 146.19, 144.09, 143.03,

139.32, 132.17, 131.35, 130.24, 129.09, 128.58, 127.64, 127.30, 125.74, 125.25, 120.56, 115.44.

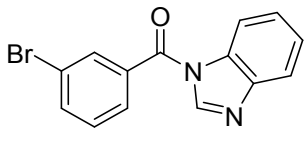
(1H-benzo[d]imidazol-1-yl)(3-chlorophenyl)methanone(CAS :200626-53-5)[7]



4pa

White solid (26 mg, 41%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.21-8.18 (m, 1H), 7.86-7.83 (m, 1H), 7.82-7.79 (m, 2H), 7.72-7.68 (m, 1H), 7.61-7.57 (m, 2H), 7.48-7.41 (m, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 167.08 (s), 144.02 (s), 143.05 (s), 133.20 (s), 132.83 (s), 132.09 (s), 129.51 (s), 129.03 (s), 125.76 (s), 125.27 (s), 120.52 (s), 115.45 (s).

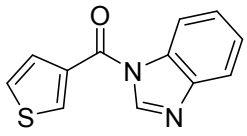
(1H-benzo[d]imidazol-1-yl)(3-bromophenyl)methanone(CAS:299418-27-2)[7]



4qa

White solid (45 mg, 47%).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21-8.15 (m, 2H), 7.96 (t, *J* = 1.6 Hz, 1H), 7.87-7.80 (m, 2H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.49-7.42 (m, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 165.46 (s), 143.99 (s), 142.63 (s), 136.16 (s), 134.66 (s), 132.35 (s), 131.92 (s), 130.53 (s), 127.86 (s), 125.99 (s), 125.53 (s), 123.24 (s), 120.64 (s), 115.43 (s).

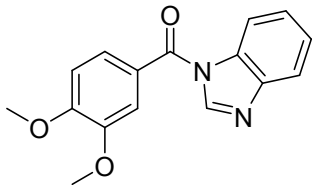
(1H-benzo[d]imidazol-1-yl)(thiophen-3-yl)methanone



4ra

White solid (30 mg, 52%). ^{1}HNMR: (500 MHz, $CDCl_3$, ppm)δ8.404 (s, 1 H), 8.21-8.20(m, 1 H), 8.074-8.066 (m, 1 H), 7.851-7.834(m,1 H), 7.586-7.574 (m, 1 H); 7.542-7.526（m, 1H）, 7.475-7.416(m, 2H); ^{13}CNMR: (125 MHz, $CDCl_3$, ppm).) δ 161.46, 144.02, 142.53, 134.71, 133.22, 132.13, 128.20, 127.60, 125.74, 125.25, 120.56, 115.39. HRMS m/z (EI) calcd. for C9H10F3O2 M+ 228.0357, found 228.0361.

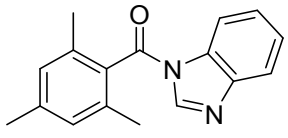
(1H-benzo[d]imidazol-1-yl)(3,4-dimethoxyphenyl)methanone (CAS:333347-80-1)[8]



4sa

White solid (53 mg, 75%).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.12 (dd, *J* = 6.6, 2.2 Hz, 1H), 7.83 (dd, *J* = 6.4, 2.2 Hz, 1H), 7.47-7.36 (m, 4H), 6.99 (d, *J* = 8.2 Hz, 1H), 3.99 (s, 3H), 3.94 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.46 (s), 153.55 (s), 149.46 (s), 144.04 (s), 143.16 (s), 132.34 (s), 125.56 (s), 125.06 (s), 124.87 (s), 124.19 (s), 120.50 (s), 115.28 (s), 112.42 (s), 110.53 (s), 56.25 (s), 56.20 (s).

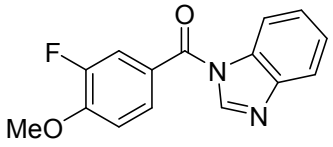
(1H-benzo[d]imidazol-1-yl)(mesityl)methanone (93330-85-9)[9]



4ta

White oil (30 mg, 46%).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 6.3 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.69 (s, 1H), 7.48 (dd, *J* = 17.4, 6.9 Hz, 2H), 6.99 (s, 2H), 2.37 (s, 3H), 2.21 (s, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 168.60 (s), 142.82 (s), 140.69 (s), 134.78 (s), 131.27 (s), 128.80 (s), 126.03 (s), 125.50 (s), 120.58 (s), 115.88 (s), 21.31 (s), 19.21 (s).

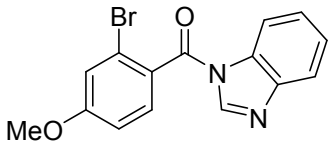
(1H-benzo[d]imidazol-1-yl)(3-fluoro-4-methoxyphenyl)methanone



4ua

White solid (66 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.18-8.14 (m, 1H), 7.86 (dd, *J* = 6.3, 2.5 Hz, 1H), 7.50-7.43 (m, 3H), 7.37 (ddd, *J* = 8.3, 4.2, 2.1 Hz, 1H), 7.28 (t, *J* = 5.2 Hz, 1H), 3.98 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 165.92 (s), 156.45 (s), 154.41 (s), 148.47 (d, *J* = 11.1 Hz), 144.05 (s), 142.79 (s), 132.09 (s), 129.14 (d, *J* = 3.9 Hz), 125.56 (d, *J* = 57.7 Hz), 122.96 (d, *J* = 7.9 Hz), 120.61 (s), 116.47 (d,*J* = 19.4 Hz), 115.31 (s), 114.67 (d, *J* = 3.2 Hz), 56.44 (s).HRMS m/z (EI) calcd. For $C_{15}H_{11}FN_2O_2$: 270.0805, found 270.0807.

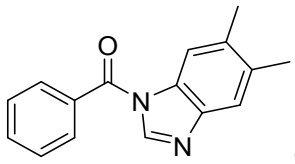
(1H-benzo[d]imidazol-1-yl)(2-bromo-4-methoxyphenyl)methanone



4va

White solid (35 mg, 42%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 6.6, 2.3 Hz, 1H), 7.97 (s, 1H), 7.82 (dd, *J* = 6.4, 2.4 Hz, 1H), 7.49 – 7.41 (m, 3H), 7.25 (d, *J* = 2.4 Hz, 1H), 7.02 (dd, *J* = 8.6, 2.4 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 165.34 (s), 162.30 (s), 144.30 (s), 142.97 (s), 131.49 (s), 130.90 (s), 127.27 (s), 125.95 (s), 125.44 (s), 121.23 (s), 120.58 (s), 119.04 (s), 115.42 (s), 113.79 (s), 55.87 (s).HRMS m/z (EI) calcd. For $C_{15}H_{11}BrN_2O_2$: 330.0004, found 329.9999.

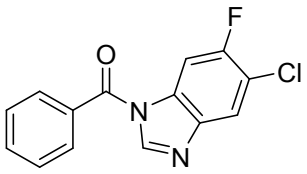
(5,6-dimethyl-1H-benzo[d]imidazol-1-yl)(phenyl)methanone（CAS：16109-46-9）[6]



4fc

White solid (39 mg, 63%). ^{1}HNMR: (500 MHz, $CDCl_3$, ppm) δ8.09 (s, 1 H), 8.00 (s, 1 H), 7.80-7.78 (m, 2 H), 7.69-7.66(m,1 H), 7.59-7.56 (m, 3 H), 2.42(s, 3H), 2.40(s, 3H);^{13}CNMR: (125 MHz, $CDCl_3$, ppm).) δ 167.11, 142.52, 142.37, 135.06, 134.30, 133.08, 132.99, 130.47, 129.46, 128.96, 120.53, 115.67, 20.53, 20.32.

(5-chloro-6-fluoro-1H-benzo[d]imidazol-1-yl)(phenyl)methanone



4fg

White solid (36 mg, 52%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 6.7 Hz, 1H), 8.25 (d, *J* = 5.6 Hz, 2H), 8.07 (d, *J* = 8.9 Hz, 1H), 7.88 (d, *J* = 6.6 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 4H), 7.75 (t, *J* = 7.5 Hz, 2H), 7.63 (dd, *J* = 14.4, 8.2 Hz, 5H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.63 (s)166.58 (s), 157.08 (d, *J* = 45.6 Hz)155.13 (d, *J* = 45.0 Hz), 144.54 (s), 144.10 (d, *J* = 3.4 Hz), 143.08 (s) 143.00 (s), 140.30 (s), 133.60 (d, *J* = 4.3 Hz), 132.11 (d, *J* = 3.2 Hz), 130.83 (s), 129.53 (s)129.19 (s), 128.51 (s), 121.64 (s)116.94 (s), 119.66 (d, *J* = 20.5 Hz)119.03 (d, *J* = 20.5 Hz), 107.61 (d, *J* = 24.3 Hz)103.74 (d, *J* = 29.0 Hz).HRMS m/z (EI) calcd. For $C_{14}H_8ClFN_2O$: 274.0309, found 274.0313.

References

1. Stephen L. Buchwald et al. *J. Am. Chem. Soc.* **2001,** *123*, 7727-7729

2. V. K. A. Kalalbandi et al. *Eur. J. Med. Chem.* **2014**, *79*, 194-202

3. Judi Rosevear and John E K. Wilshire, *Aust. J. Chem.*, **1991**, *44*, 1097-1114.

4. Yang, J. et al. *Chin.Chem.Lett.* **2014**, *27*,340–344

5. Fuwei Li et al. Direct N-acylation of azoles via a metal-freecatalyzed oxidative cross-coupling strategy. *Chem. Comm*. **2014**, *50*, 4751-4754.

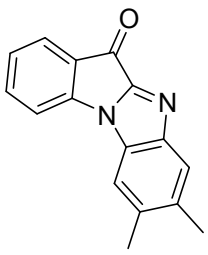
6. Ding, W.; Song, Q. *Org. Chem. Front.* **2015,** *2*, 765-770.

7. Ding, W.; Mai, S.; Song, Q. *Beilstein. J. Org. Chem.* **2015,** *11*, 2158-216

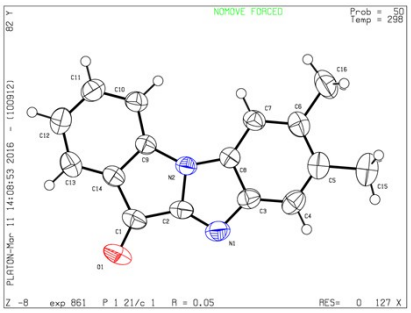
8. Dos Santos, Aurelie; El Kaim, Laurent; Grimaud, Laurence. *Org. Biomol. Chem*. **2013,***11*, 3282-3287.

9. Mannschreck, A.; Staab, H. A.; Wurmb-Gerlich, D. *Tetrahedron Lett.* **1963,** *29,* 2003-2008

Crystal Structure of Product 3a’c



3a’c (CCDC1464636**)**



Crystal data and structure refinement for **3a’c.**

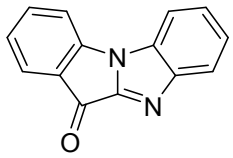
Identification code	3a’ c
Empirical formula	$C_{16}H_{12}N_2O$
Formula weight	248.28
Temperature/K	298.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.0964(5)
b/Å	11.9998(8)
c/Å	14.4434(11)
α/°	90
β/°	98.551(6)
γ/°	90
Volume/Å^3	1216.27(15)
Z	4
ρ_{calc}g/cm^3	1.356
μ/mm^{-1}	0.087
F(000)	520.0
Crystal size/mm^3	0.1 × 0.1 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.64 to 57.908
Index ranges	-9 ≤ h ≤ 9, -14 ≤ k ≤ 16, -18 ≤ l ≤ 18
Reflections collected	8165
Independent reflections	2835 [R_{int} = 0.0303, R_{sigma} = 0.0384]

Data/restraints/parameters	2835/0/175
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0528, wR_2 = 0.1149
Final R indexes [all data]	R_1 = 0.0793, wR_2 = 0.1286
Largest diff. peak/hole / e $Å^{-3}$	0.16/-0.15

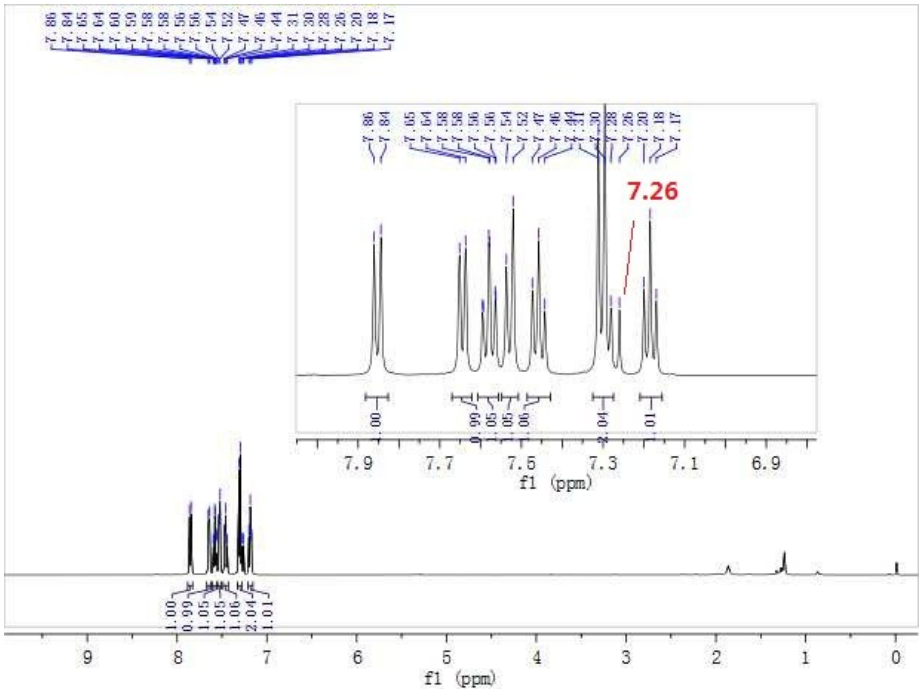
CCDC-

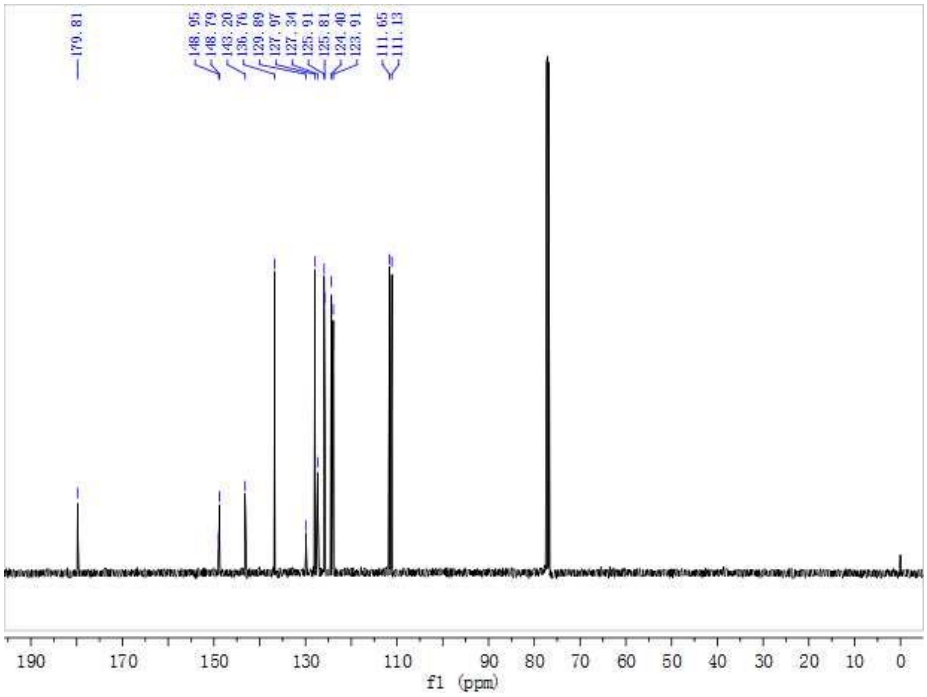
1464636 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallo graphic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

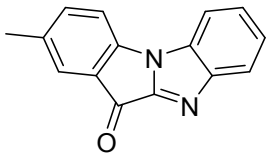
NMR Spectra of Products



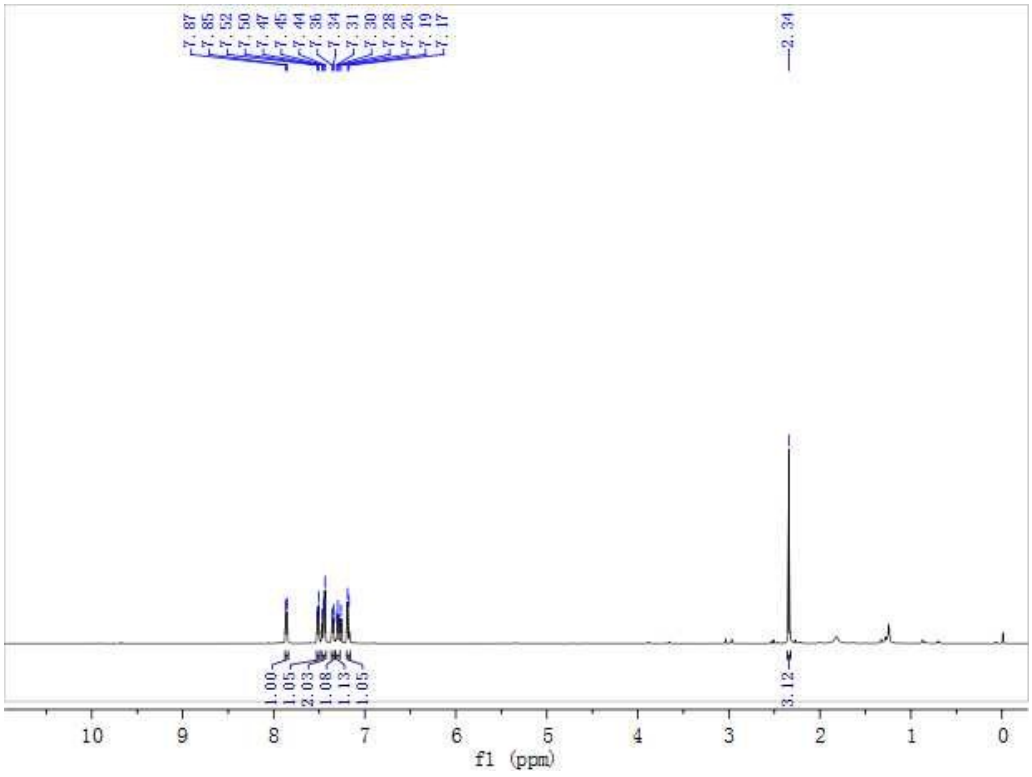
3a'a

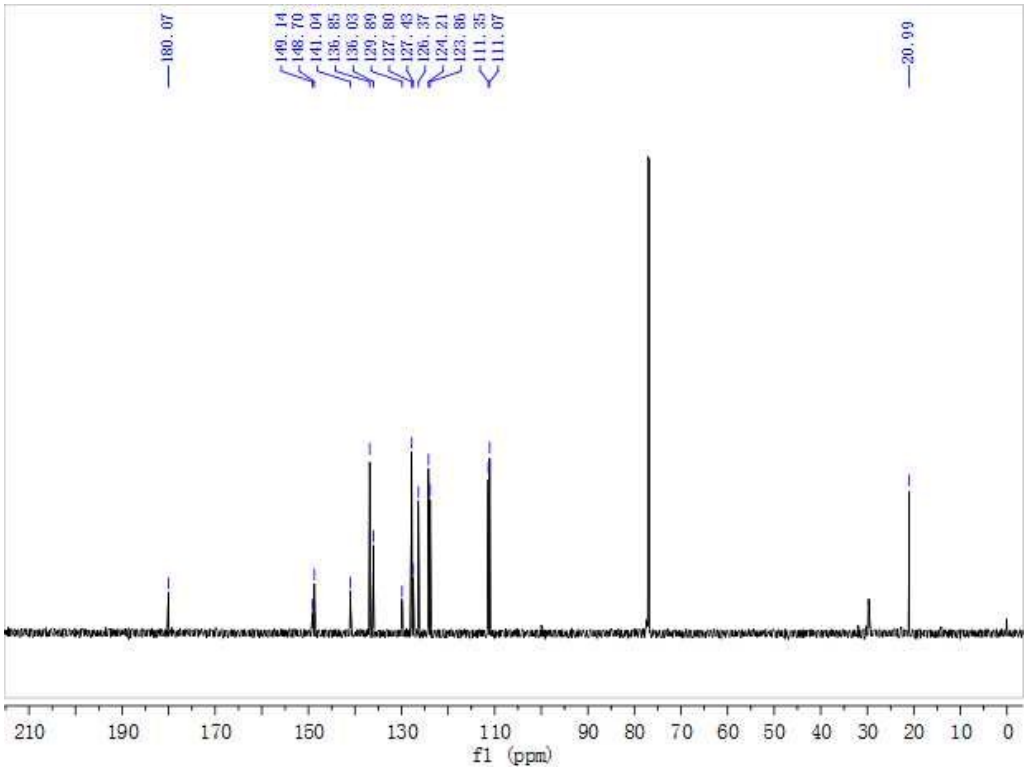


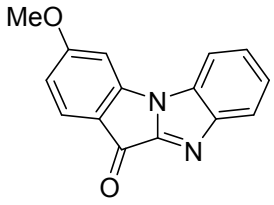

179.81
148.95
148.79
143.20
136.76
129.89
127.97
127.34
125.91
125.81
124.40
123.91
111.65
111.13
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
N
O

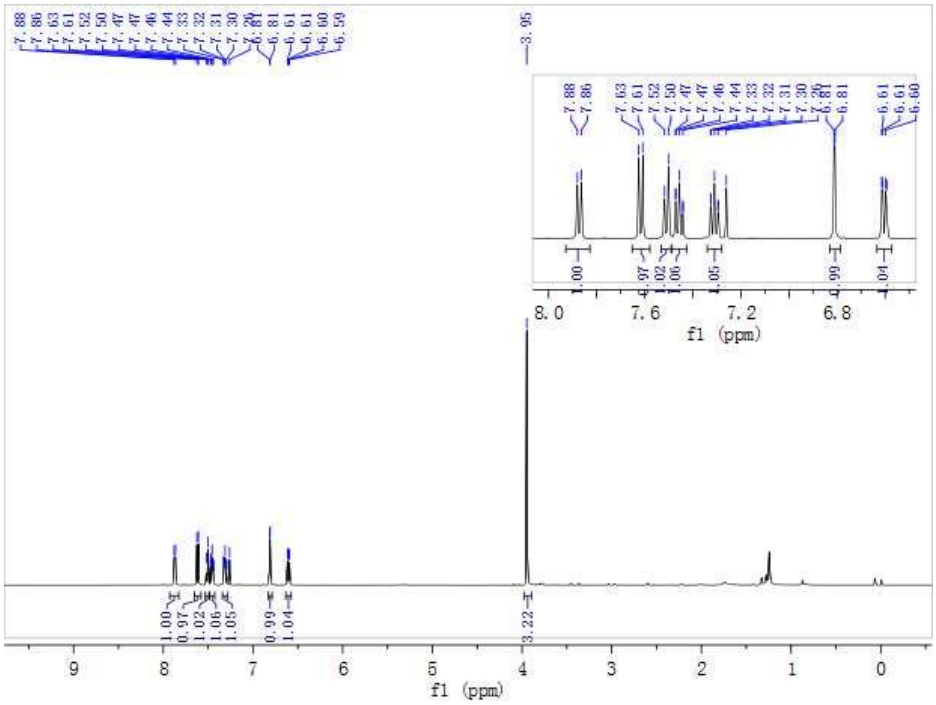
3b'a

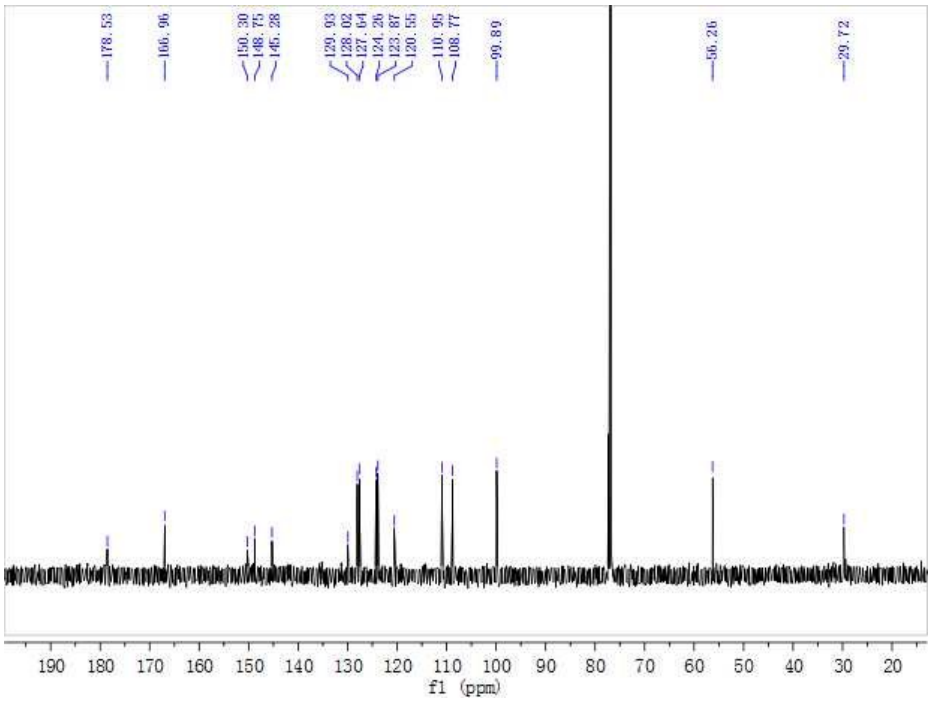

7.87
7.85
7.52
7.50
7.47
7.45
7.44
7.36
7.34
7.31
7.30
7.28
7.26
7.19
7.17
2.34
1.00
1.05
2.03
1.08
1.13
1.05
3.12
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

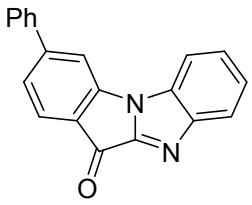

180.07
149.14
148.70
141.04
136.85
136.03
129.89
127.80
127.43
126.37
124.21
123.86
111.35
111.07
20.99
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


MeO
N
N
O

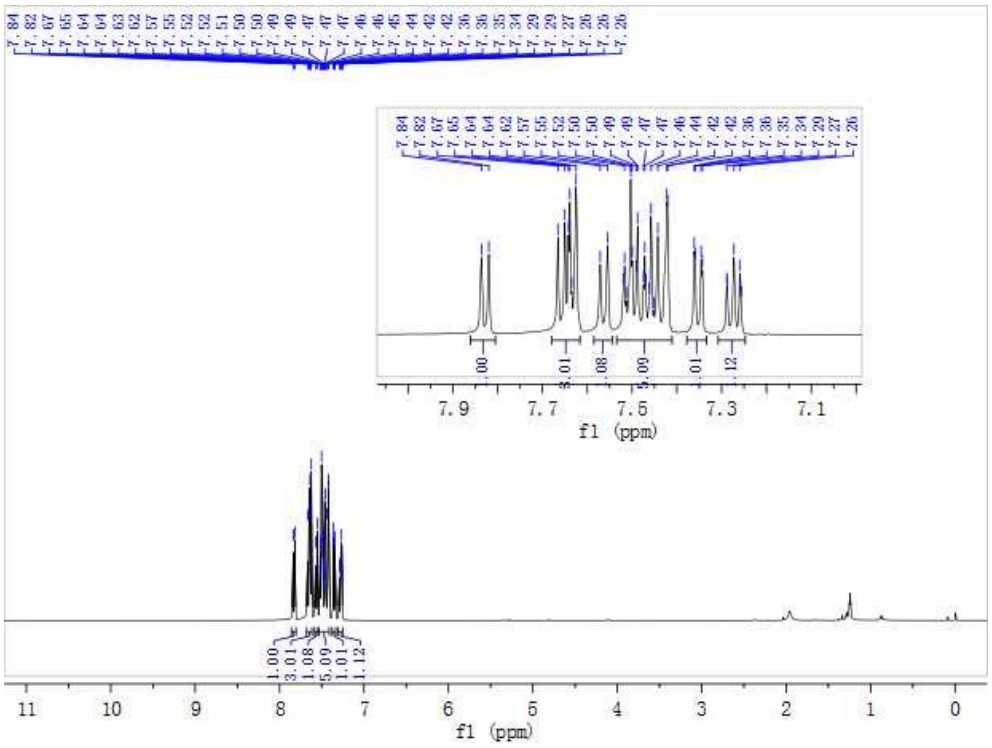
3c'a

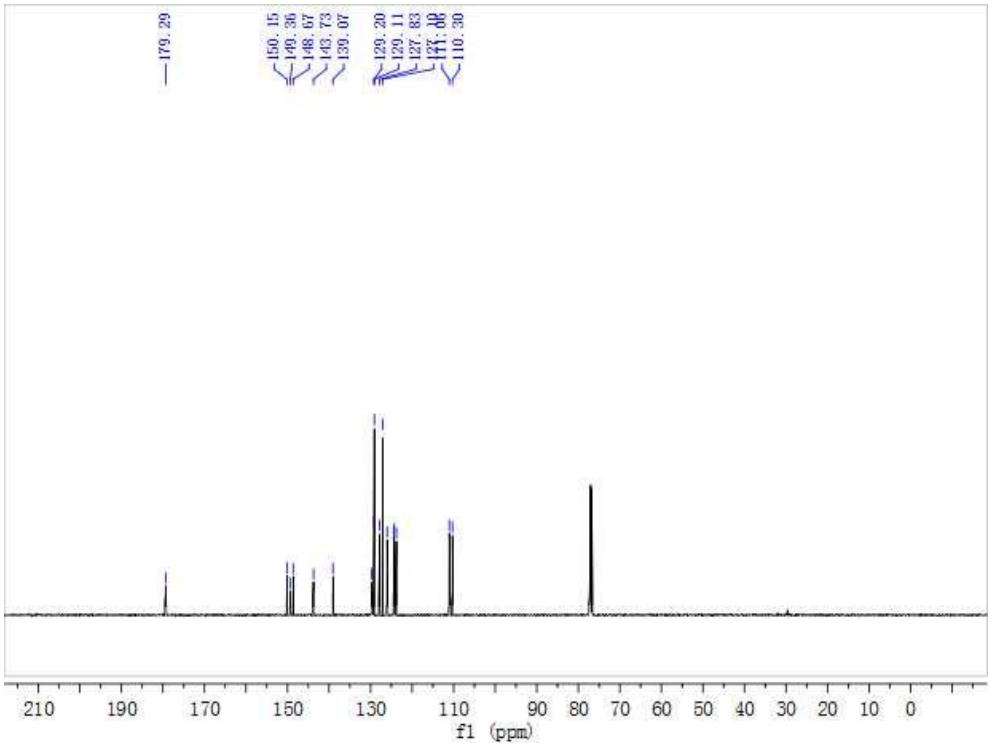


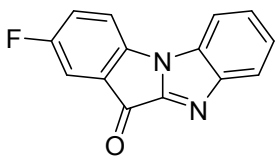




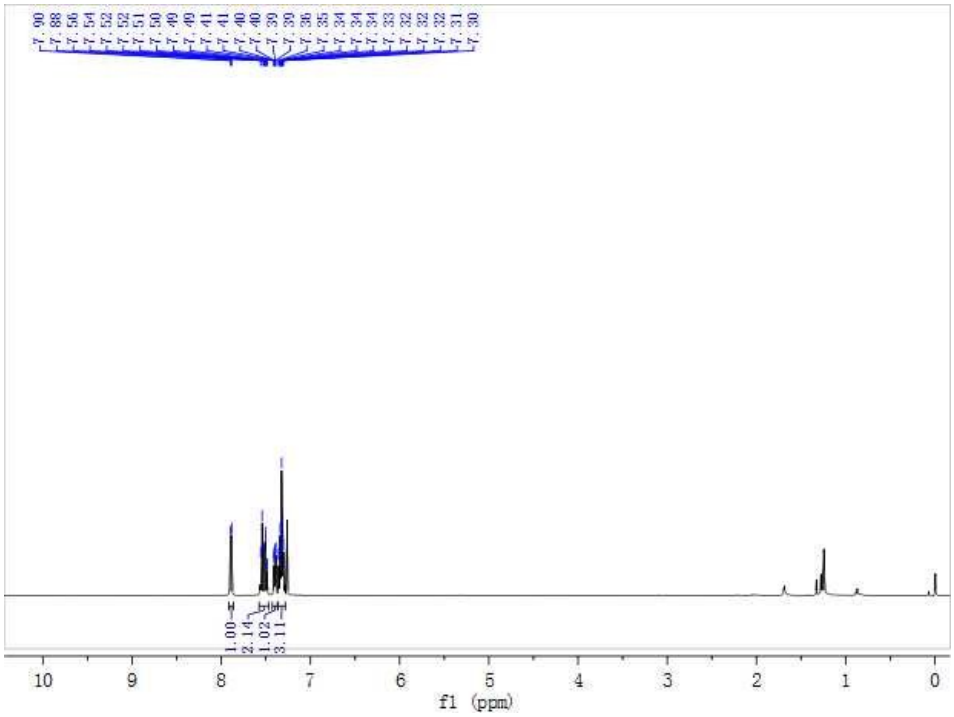
3d'a

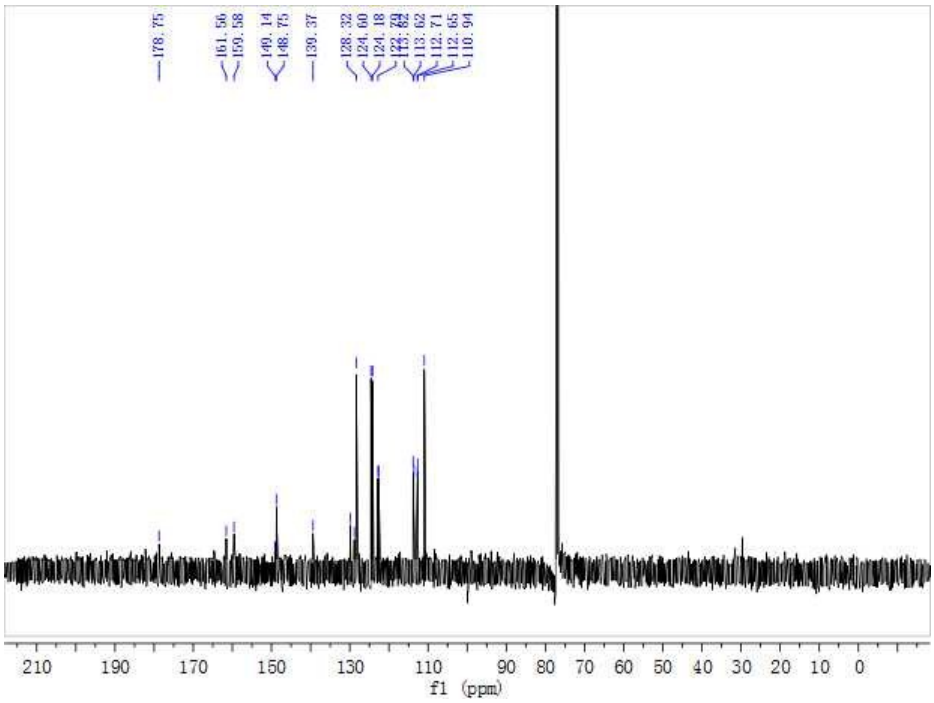


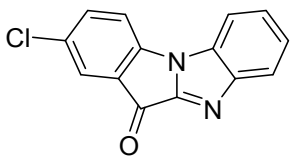




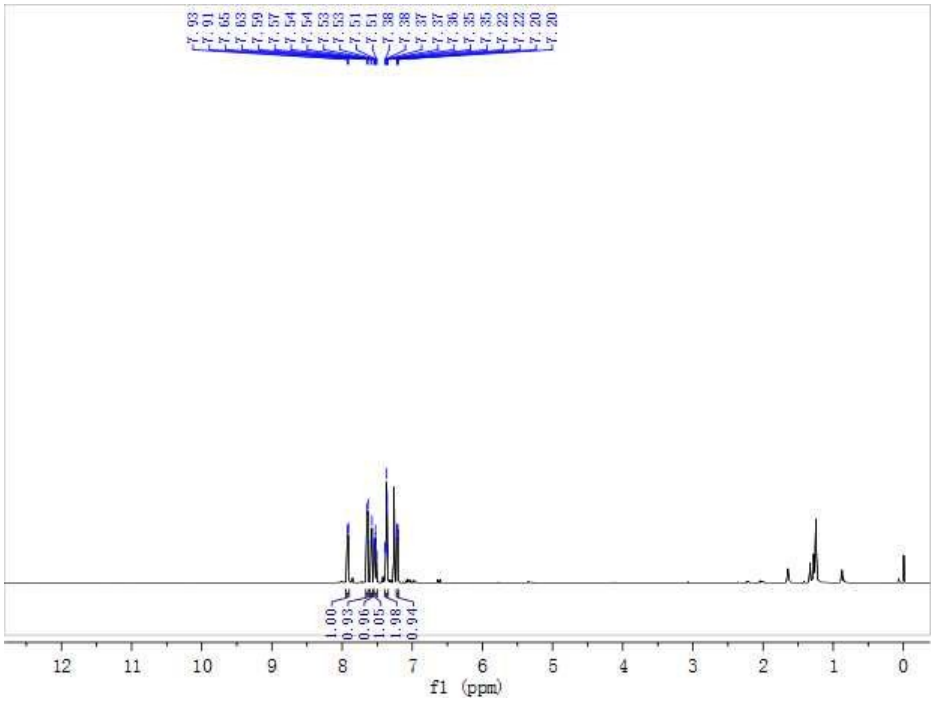
3e'a

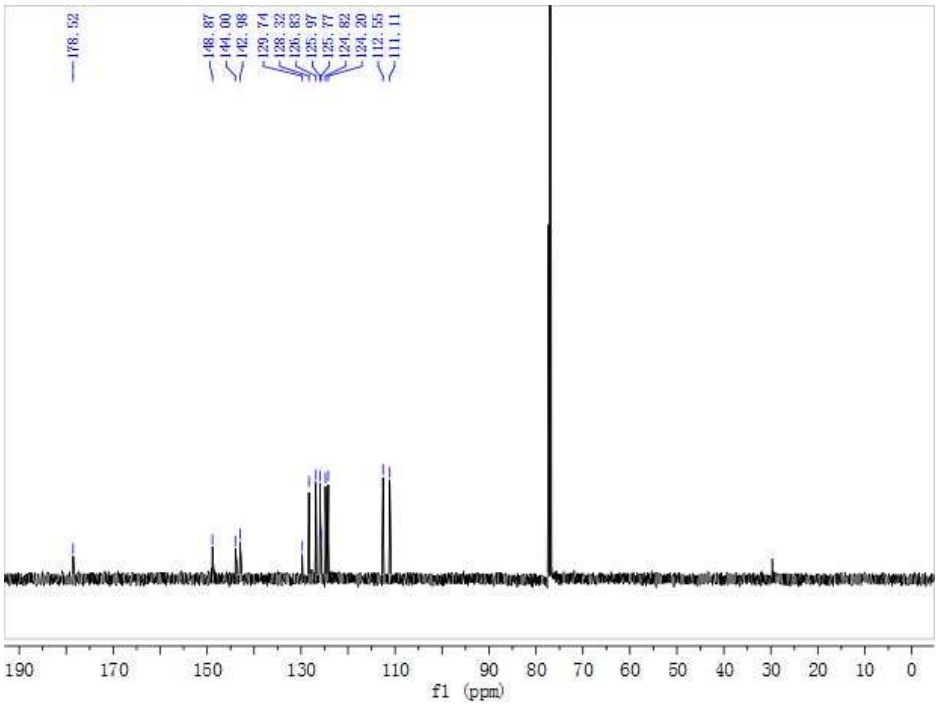

7.90
7.88
7.56
7.54
7.52
7.52
7.51
7.50
7.49
7.49
7.41
7.41
7.40
7.40
7.39
7.39
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.30
1.00
2.14
1.02
3.11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

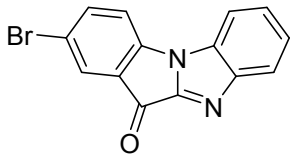

178.75
161.56
159.58
149.14
148.75
139.37
128.32
124.60
124.18
113.62
112.71
112.65
110.94
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Cl
N
N
O

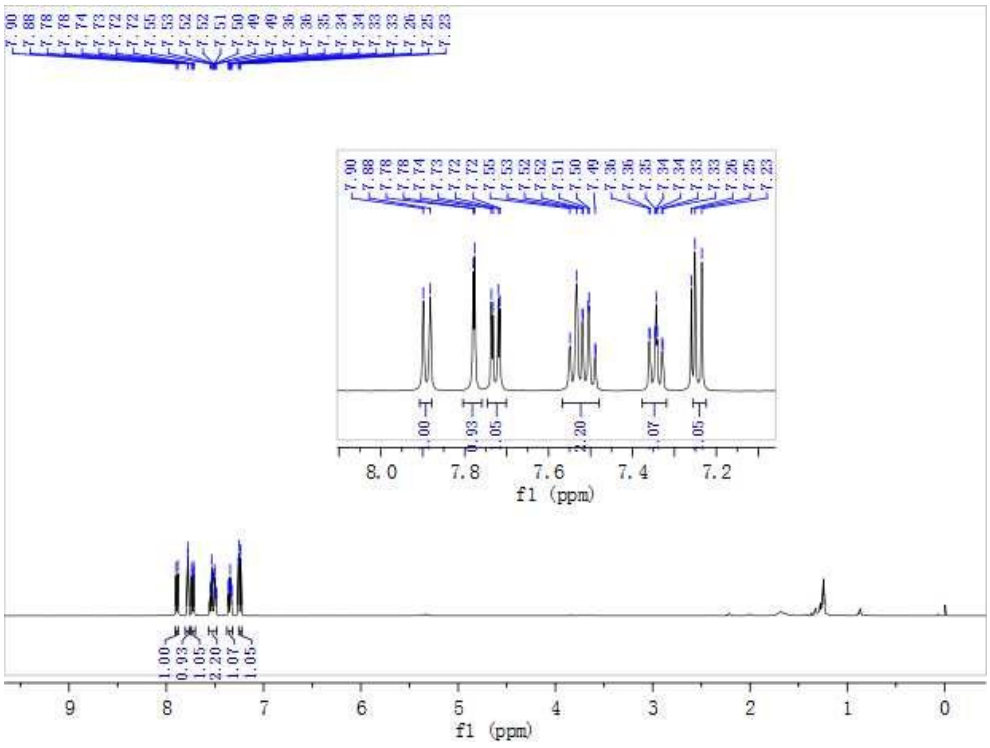
3f'a

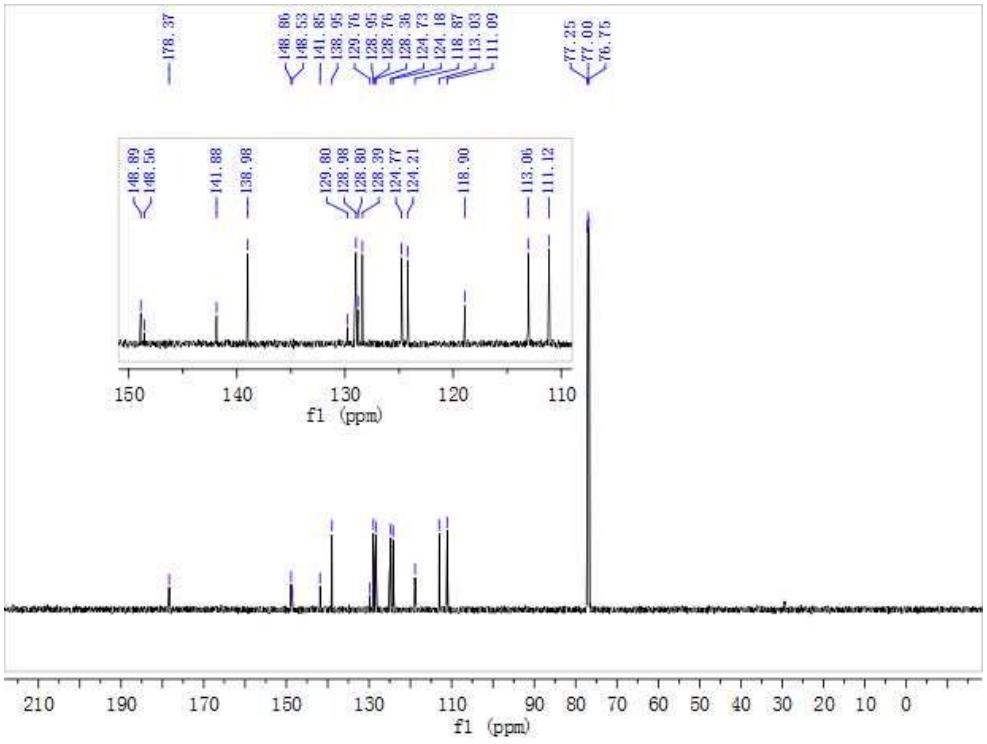

7.93
7.91
7.65
7.63
7.59
7.57
7.54
7.54
7.53
7.53
7.51
7.51
7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.22
7.20
7.20
1.00
0.93
0.96
1.05
1.98
0.94
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

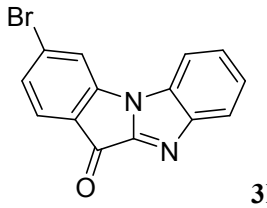

178.52
148.87
144.00
142.98
129.74
128.32
126.83
125.97
125.77
124.82
124.20
112.55
111.11
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Br
N
N
O

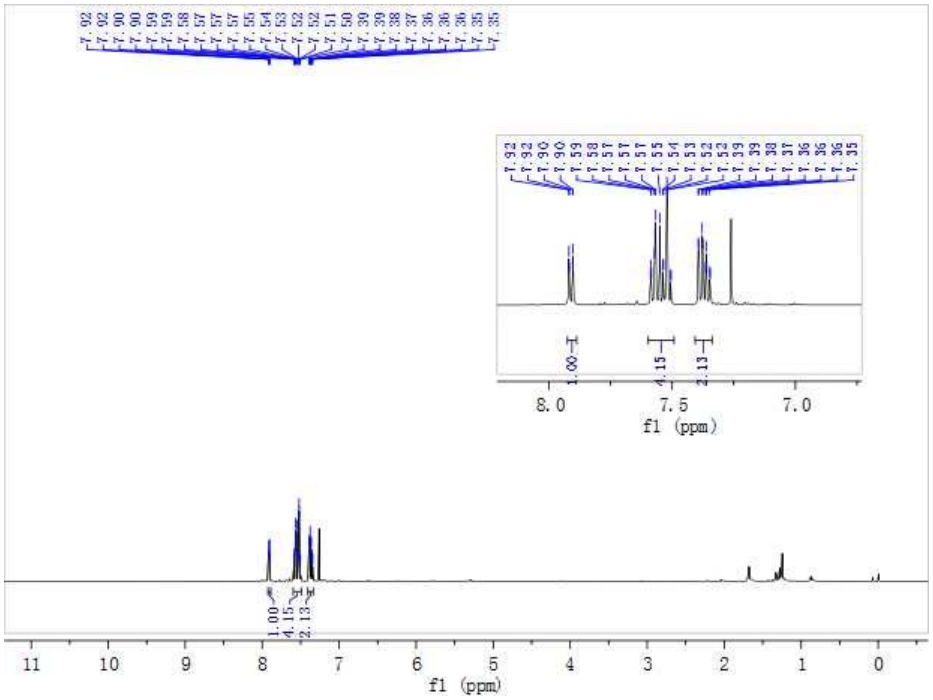
3g'a

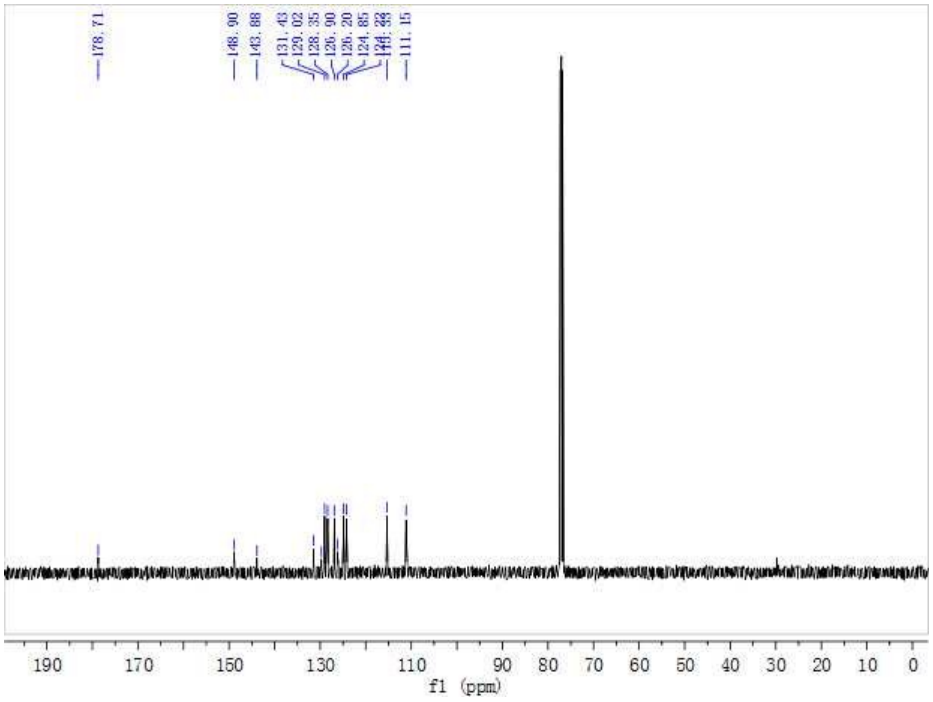

f1 (ppm)

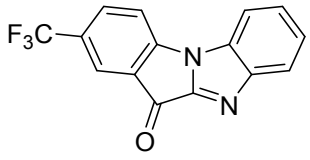

f1 (ppm)


Br
N
N
O

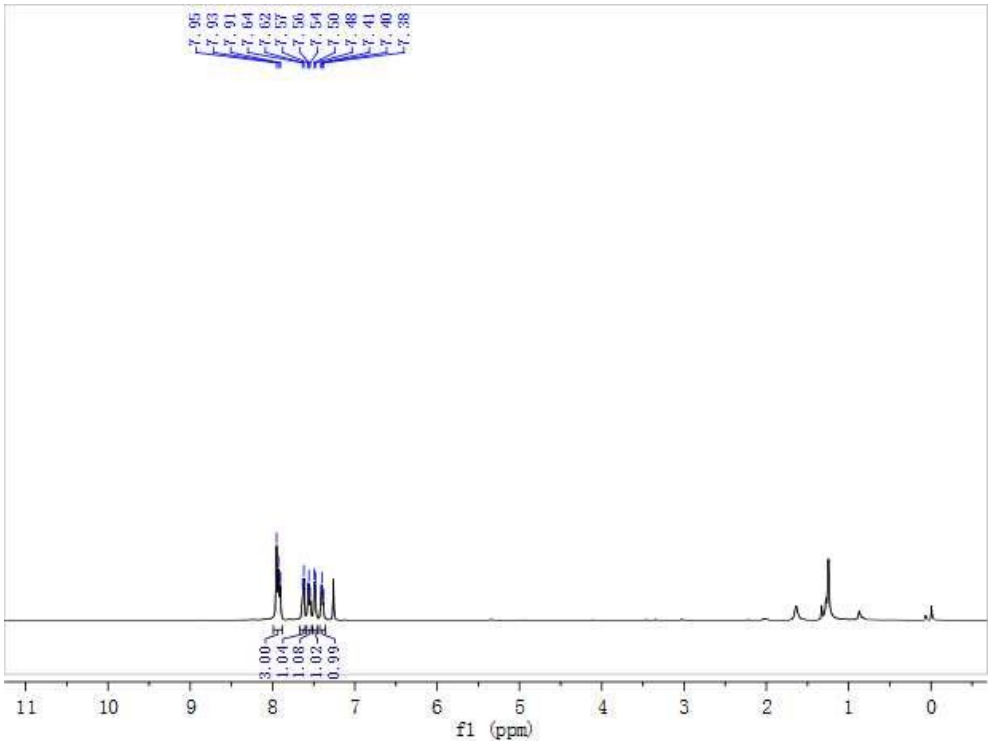
3h'a

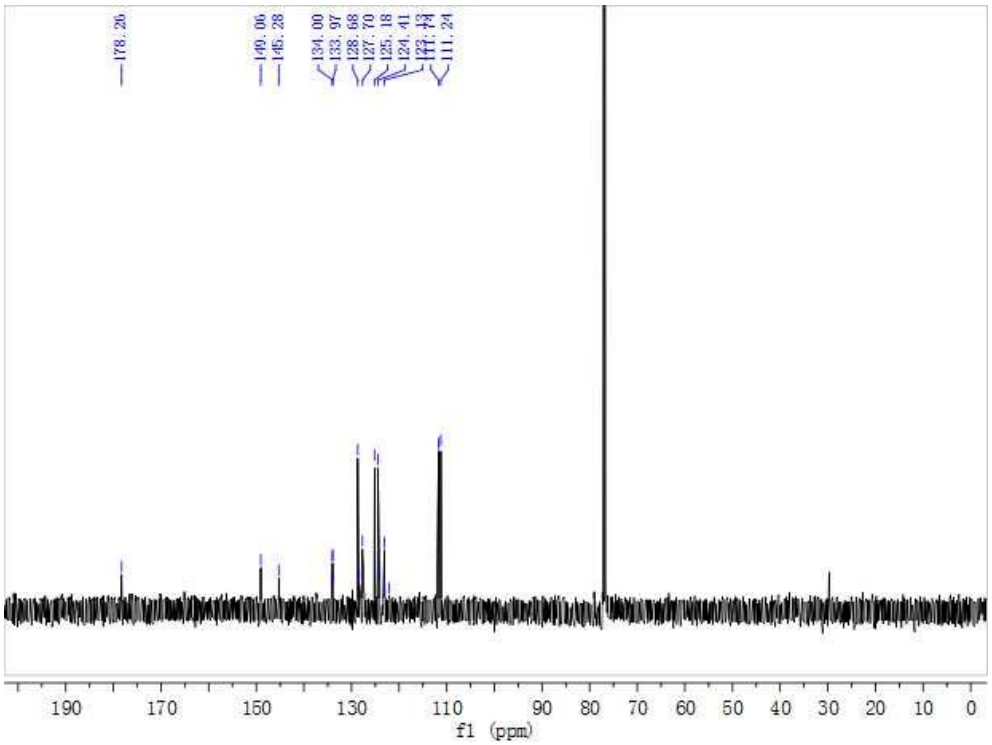

7.92
7.92
7.90
7.90
7.59
7.59
7.58
7.57
7.57
7.57
7.55
7.54
7.53
7.52
7.52
7.51
7.50
7.39
7.39
7.38
7.37
7.36
7.36
7.36
7.35
7.35
1.00
4.15
2.13
8.0
7.5
7.0
f1 (ppm)
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

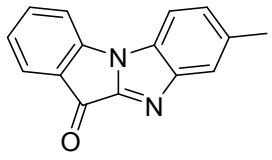

178.71
148.90
143.88
131.43
129.02
128.35
126.90
126.20
124.85
111.15
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F3C
N
N
O

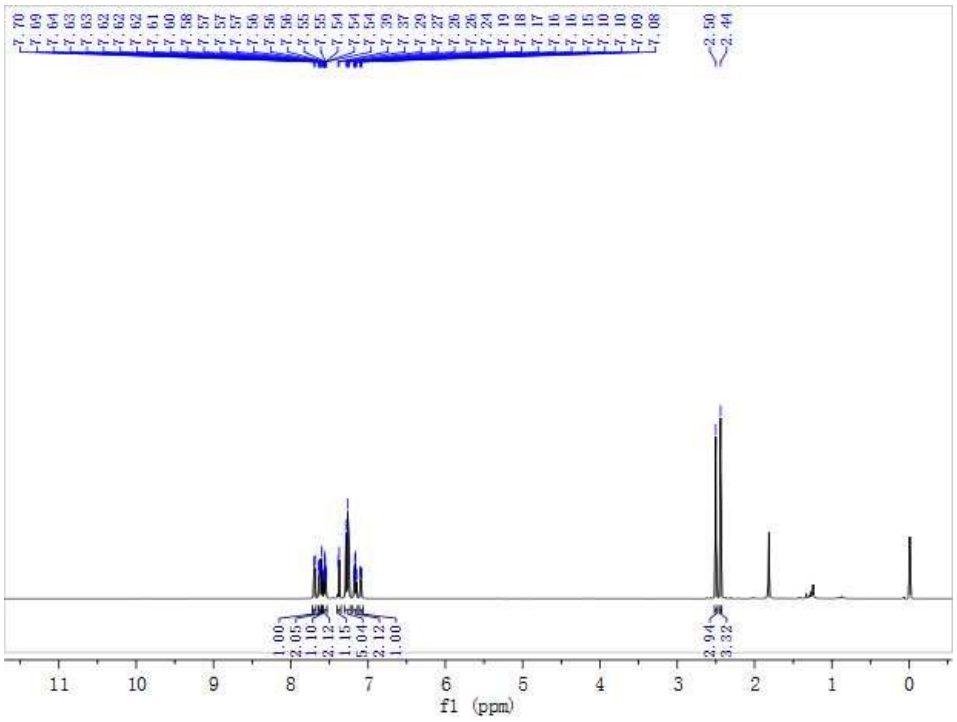
3i'a

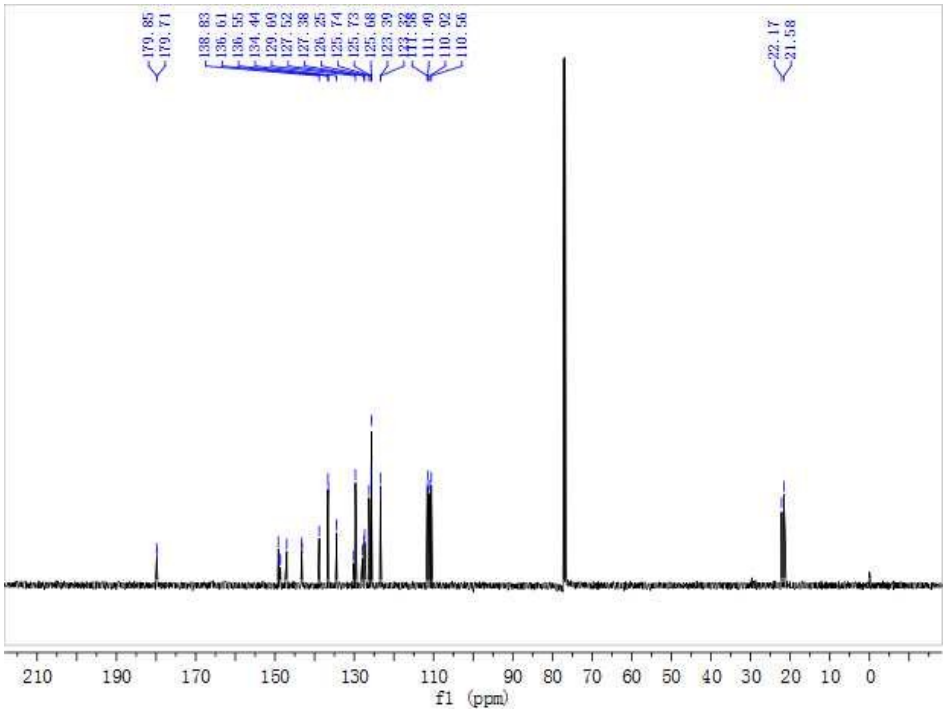

7.95
7.93
7.91
7.64
7.62
7.57
7.56
7.54
7.50
7.48
7.41
7.40
7.38
3.00
1.04
1.08
1.02
0.99
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

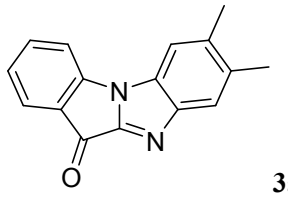

178.26
149.06
145.28
134.00
133.97
128.68
127.70
125.18
124.41
111.24
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



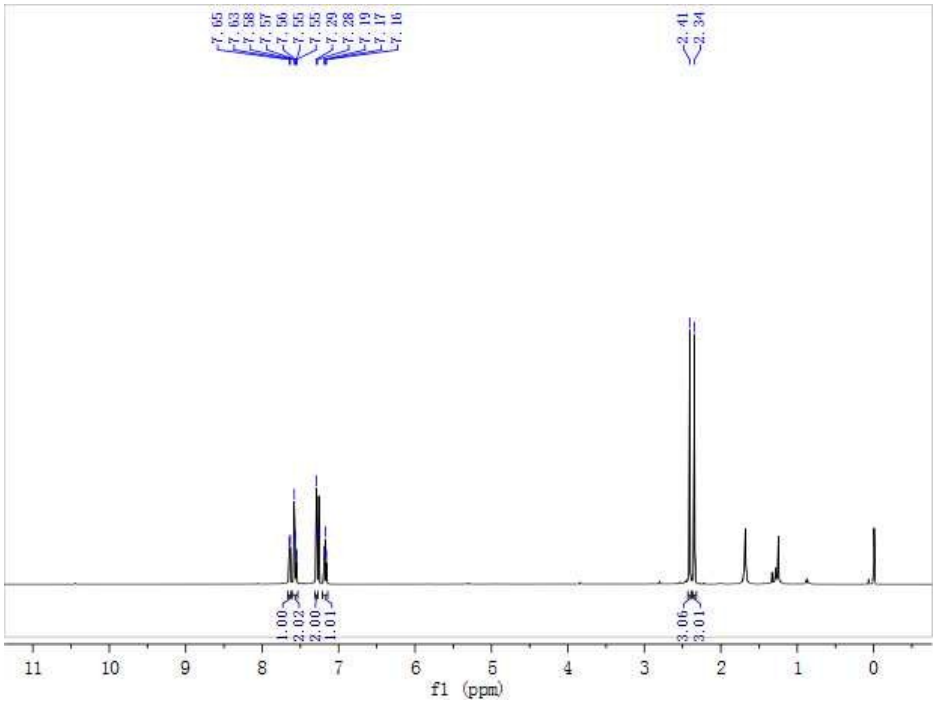
3a'b

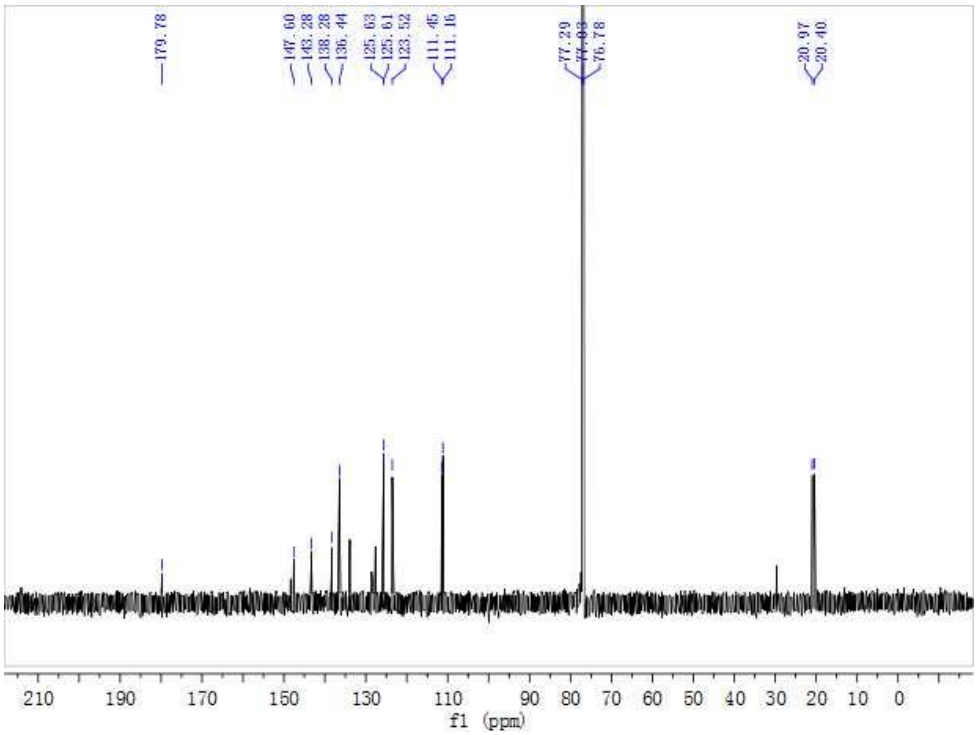


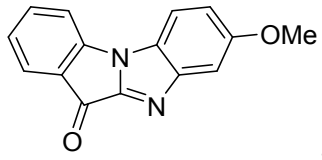




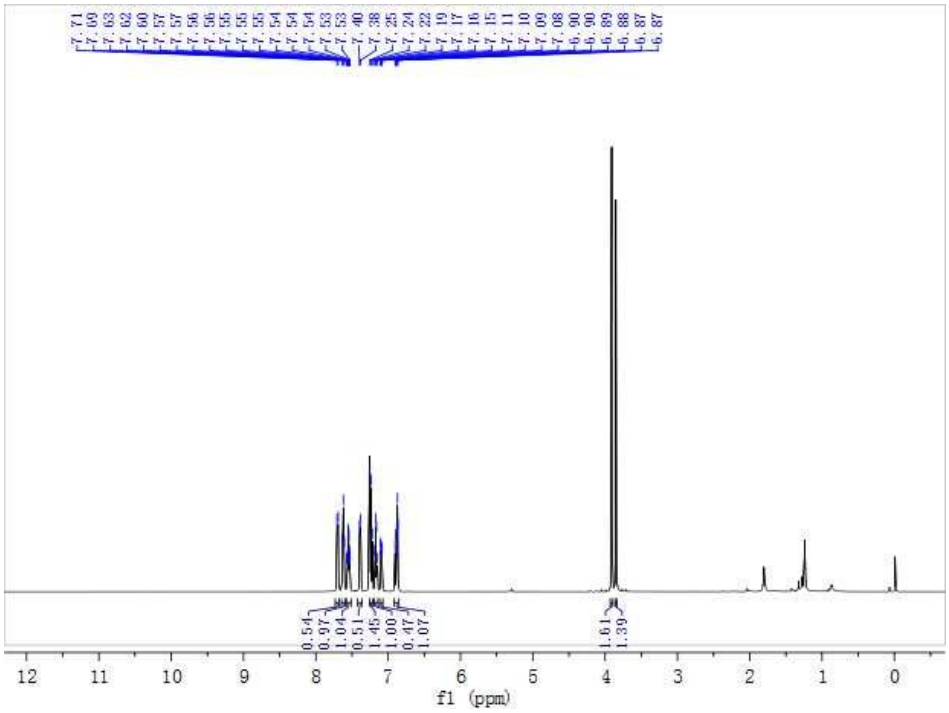
3a'c

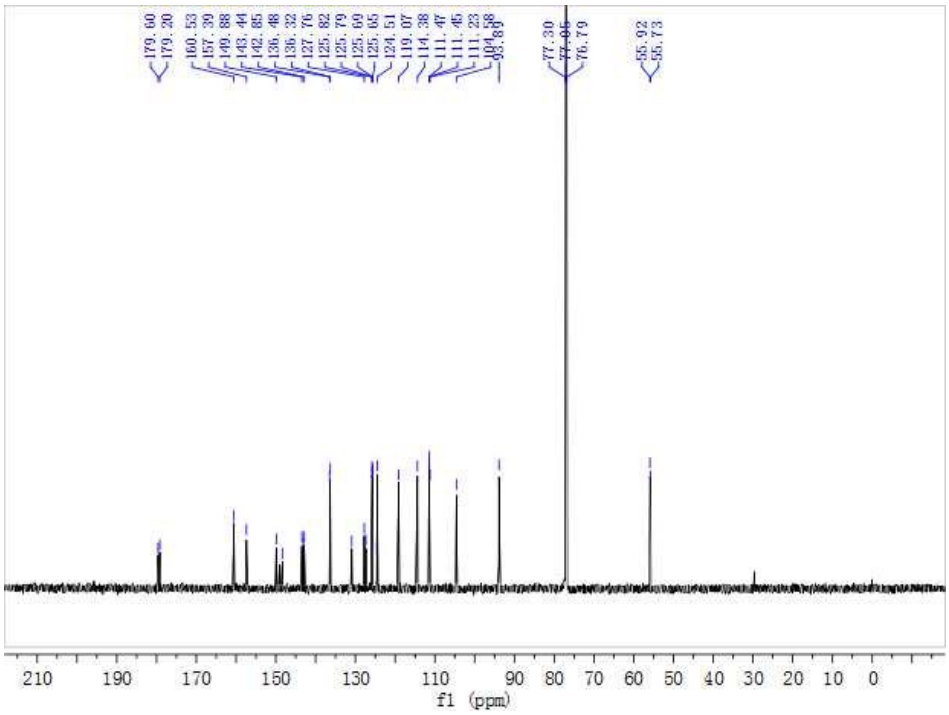

7.65
7.63
7.58
7.57
7.56
7.55
7.55
7.29
7.28
7.19
7.17
7.16
2.41
2.34
1.00
2.02
2.00
1.01
3.06
3.01
f1 (ppm)

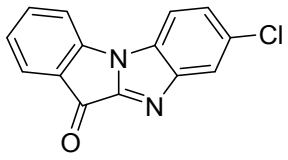

179.78
147.60
143.28
138.28
136.44
125.63
125.61
123.52
111.45
111.16
77.29
77.03
76.78
20.97
20.40
f1 (ppm)



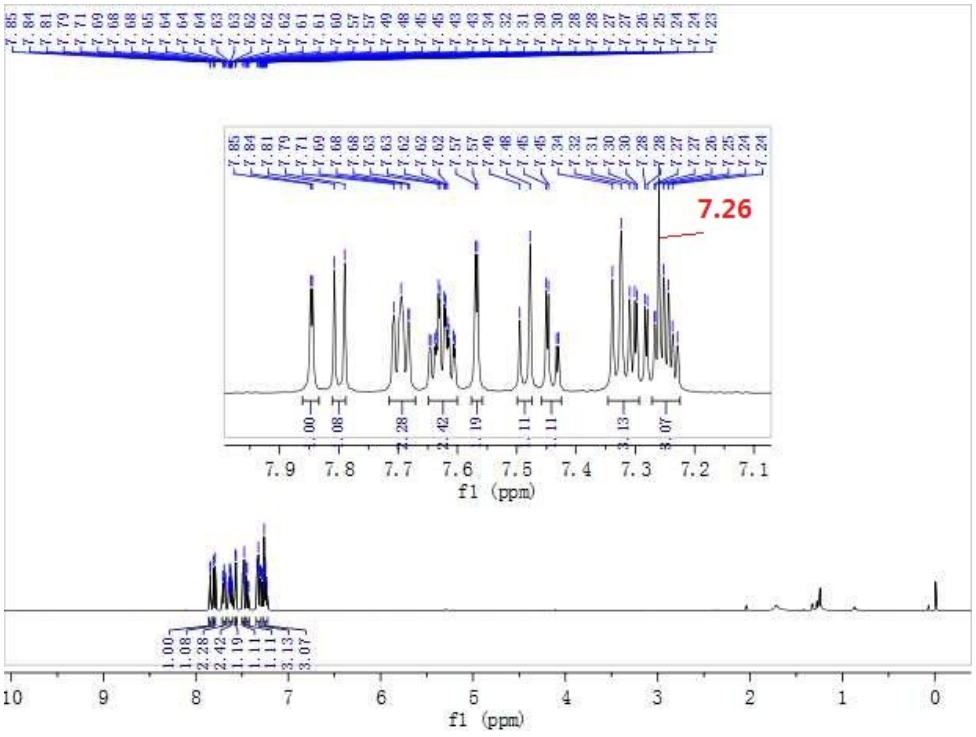
3a'd

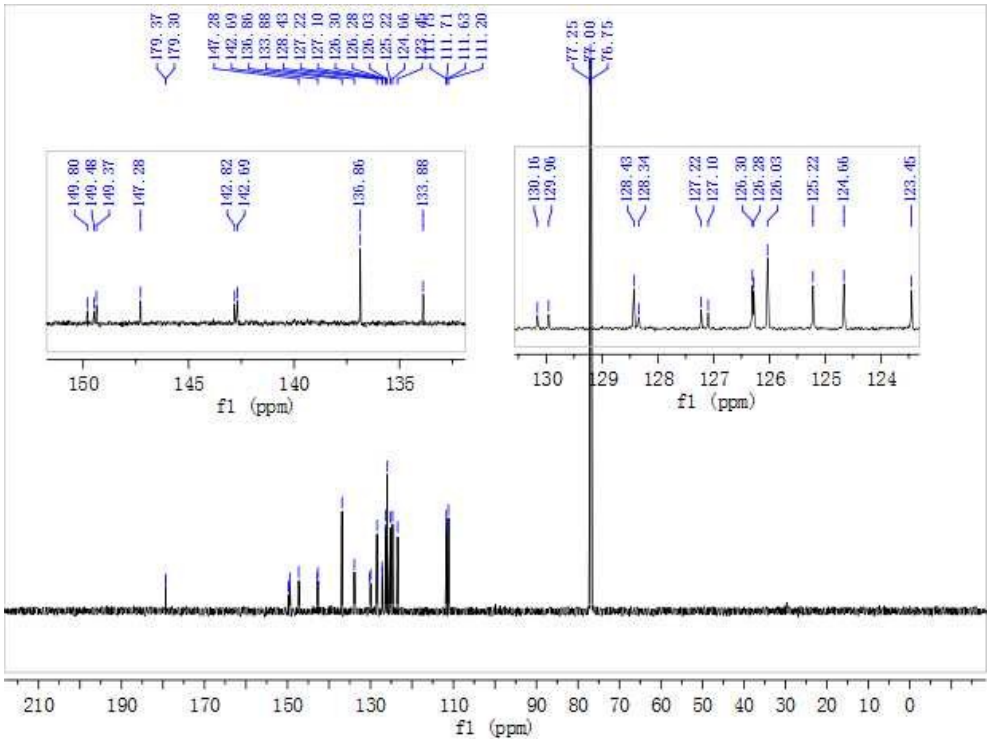


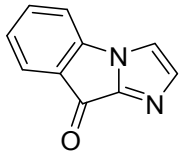




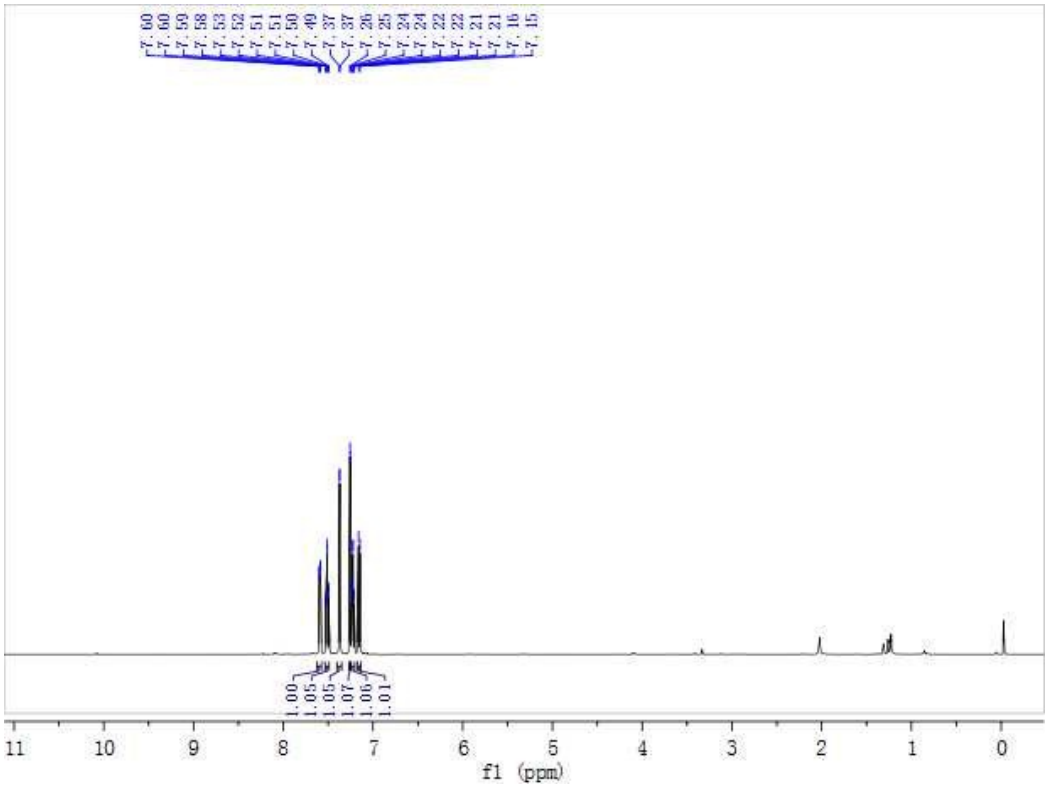
3a'e

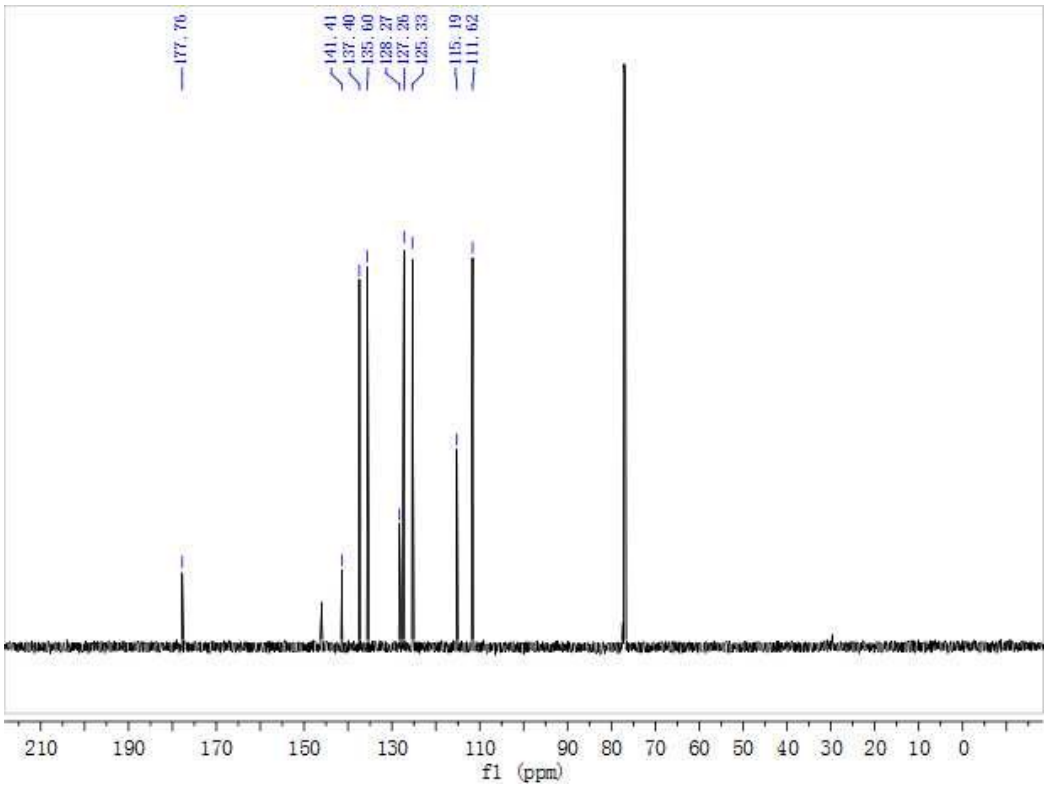


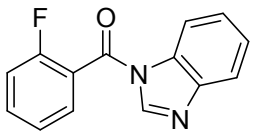




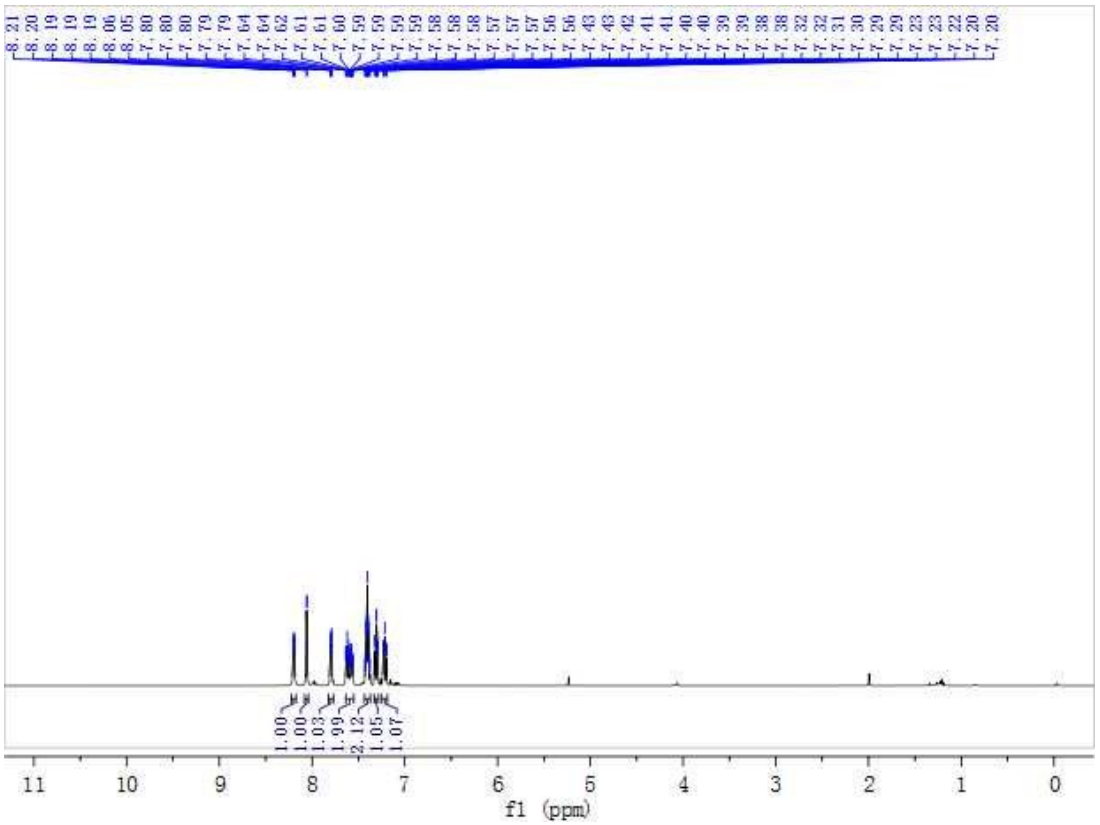
3a'f

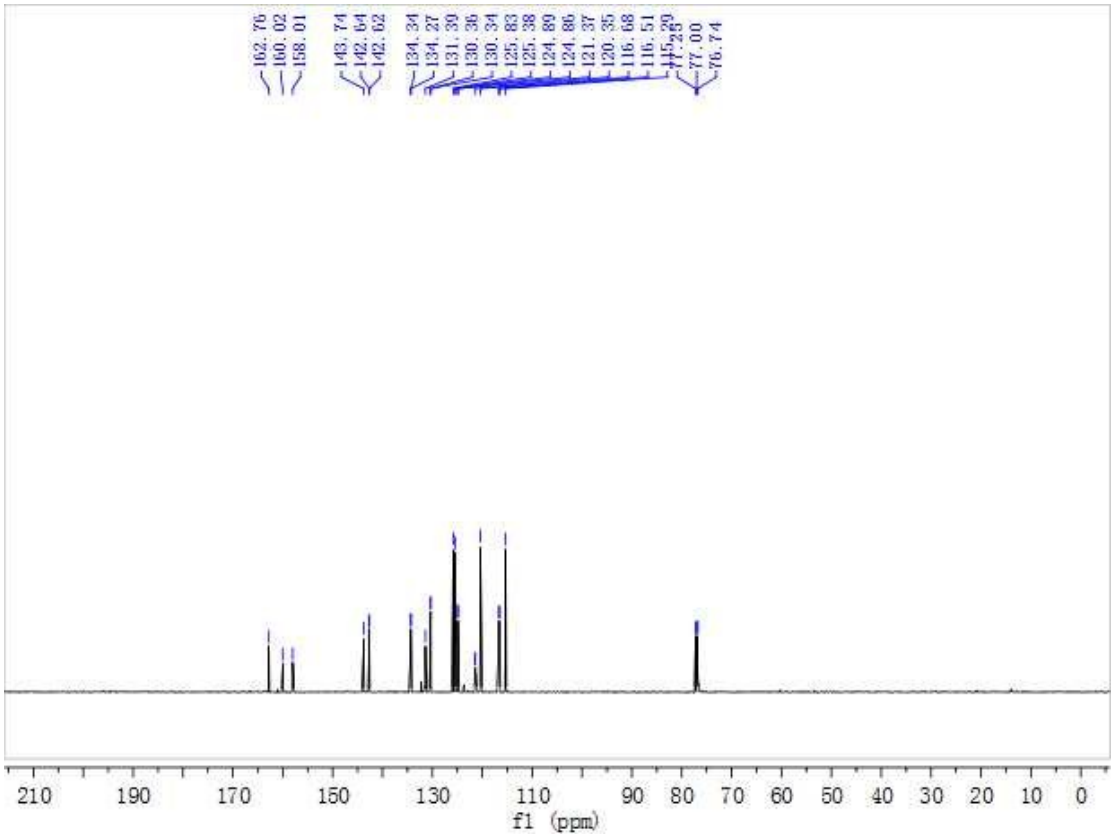

7.60
7.60
7.59
7.58
7.53
7.52
7.51
7.51
7.50
7.49
7.37
7.37
7.26
7.25
7.24
7.24
7.22
7.22
7.21
7.21
7.16
7.15
1.00
1.05
1.05
1.07
1.06
1.01
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

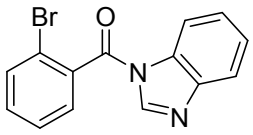

177.76
141.41
137.40
135.60
128.27
127.26
125.33
115.19
111.62
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
O
N
N

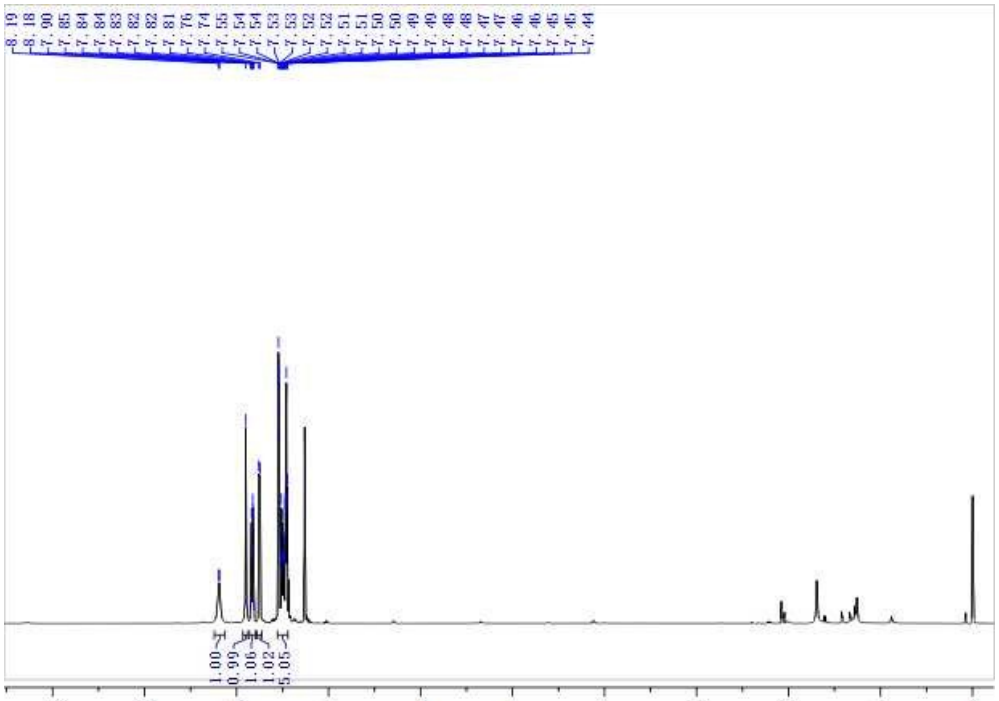
4a'a

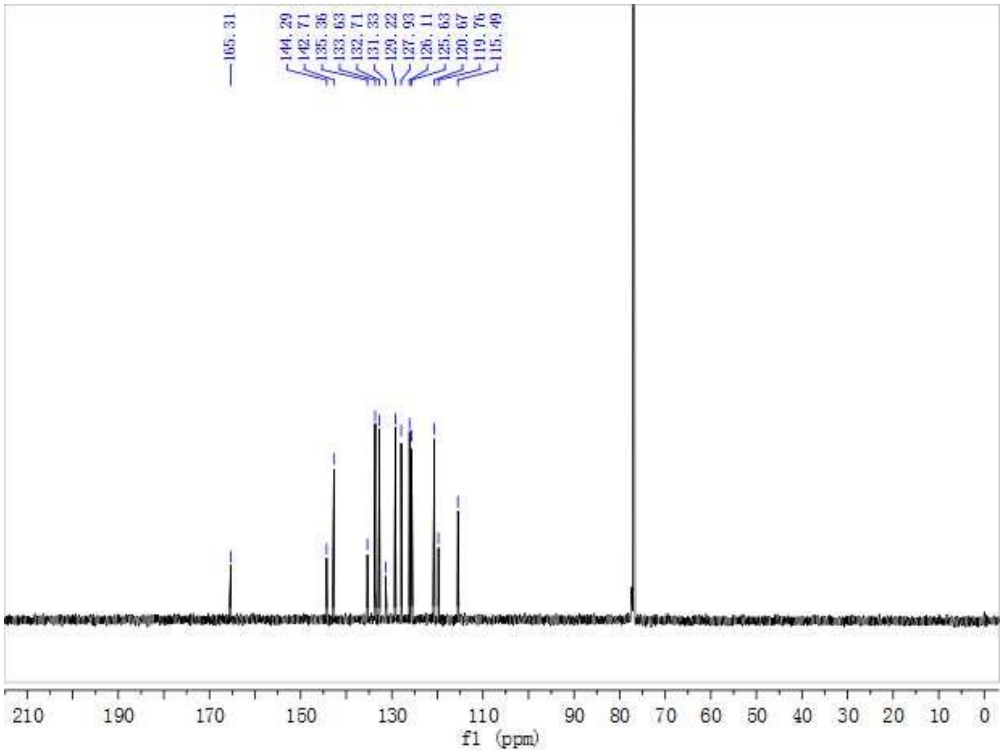

8.21 8.20 8.19 8.19 8.19 8.06 8.05 7.80 7.80 7.80 7.79 7.79 7.64 7.64 7.62 7.61 7.61 7.60 7.59 7.59 7.59 7.59 7.58 7.58 7.58 7.57 7.57 7.57 7.56 7.56 7.43 7.42 7.41 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.32 7.32 7.31 7.30 7.29 7.29 7.23 7.22 7.20 7.20
1.00 1.00 1.03 1.99 2.12 1.05 1.07
11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

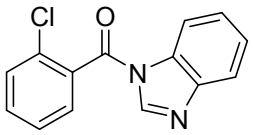

162.76 160.02 158.01 143.74 142.64 142.62 134.34 134.27 131.30 130.36 130.34 125.83 125.38 124.89 124.80 121.37 120.35 116.68 116.51 77.25 77.00 76.74
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Br
O
N
N

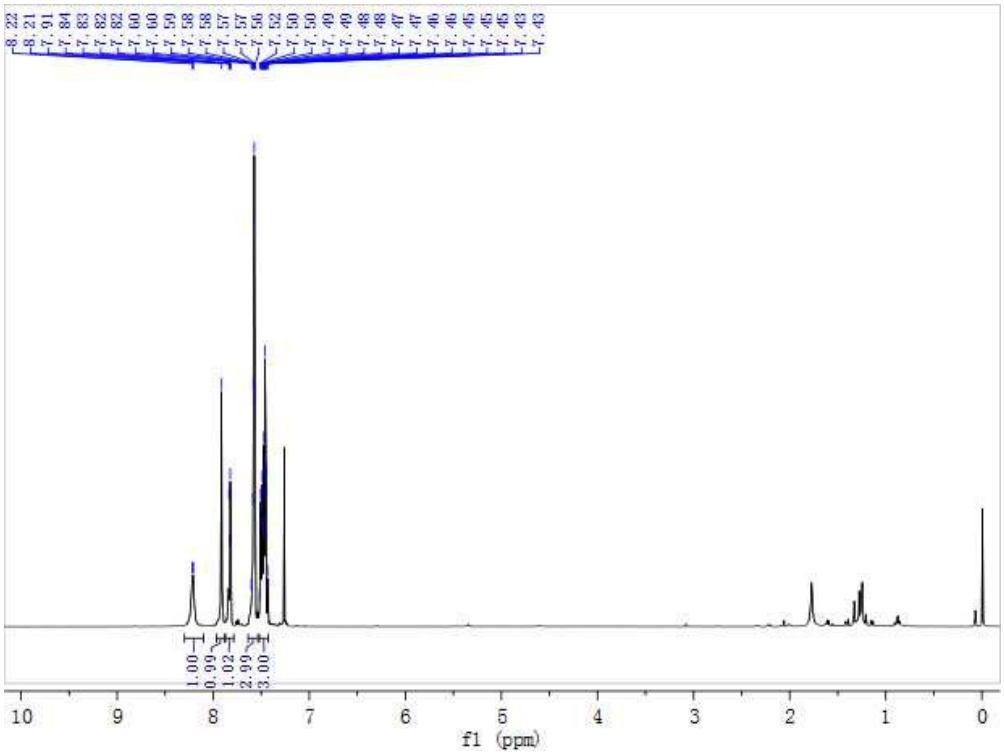
4aa

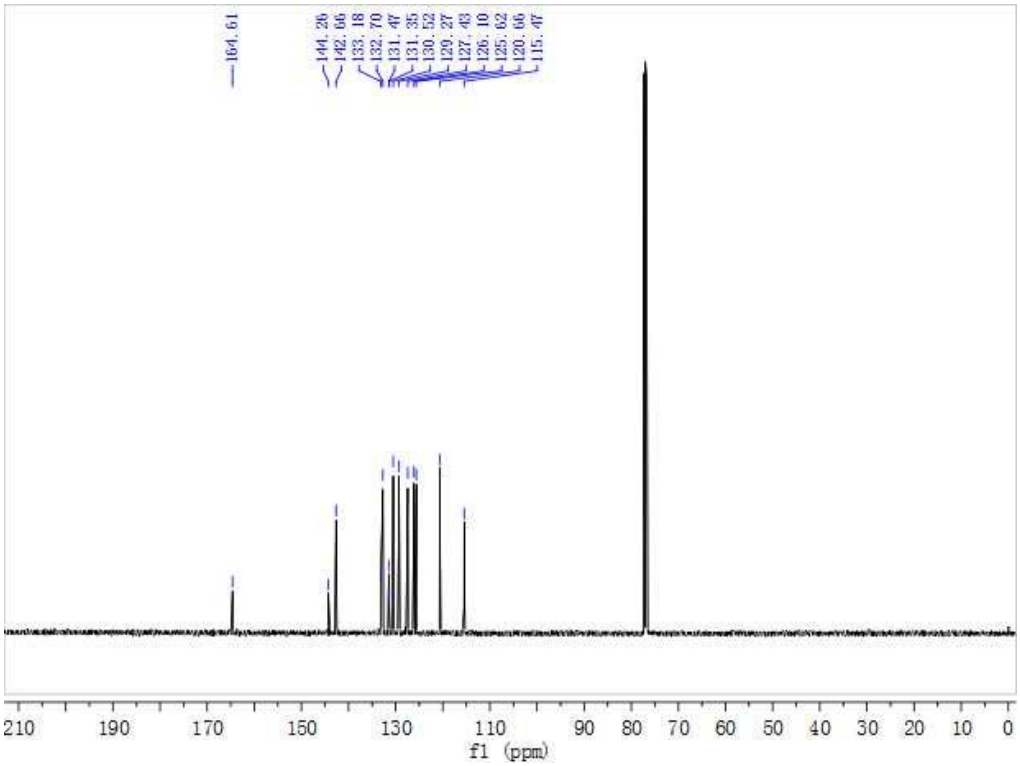

8.19
8.18
7.90
7.85
7.84
7.84
7.83
7.82
7.82
7.81
7.76
7.74
7.55
7.54
7.54
7.53
7.53
7.52
7.52
7.51
7.51
7.50
7.50
7.49
7.49
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.44
1.00
0.99
1.06
1.02
5.05
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

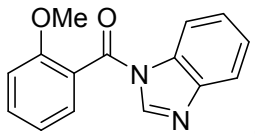

165.31
144.29
142.71
135.36
133.63
132.71
131.33
129.22
127.93
126.11
125.63
120.67
119.76
115.49
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Cl
O
N
N

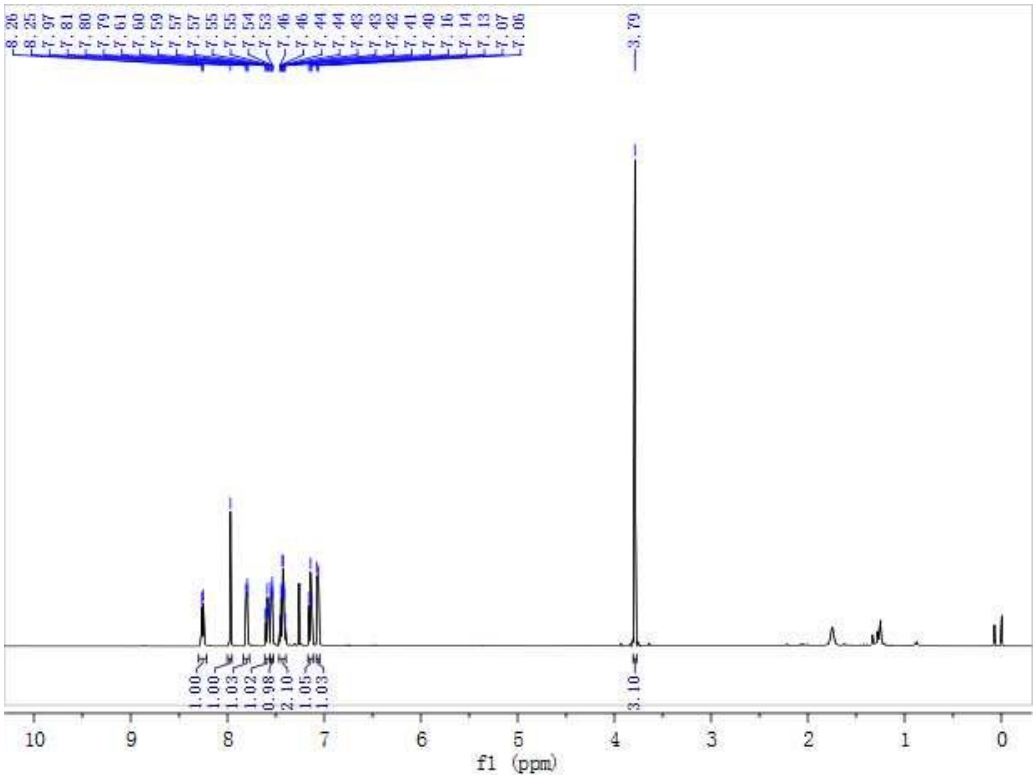
4ba

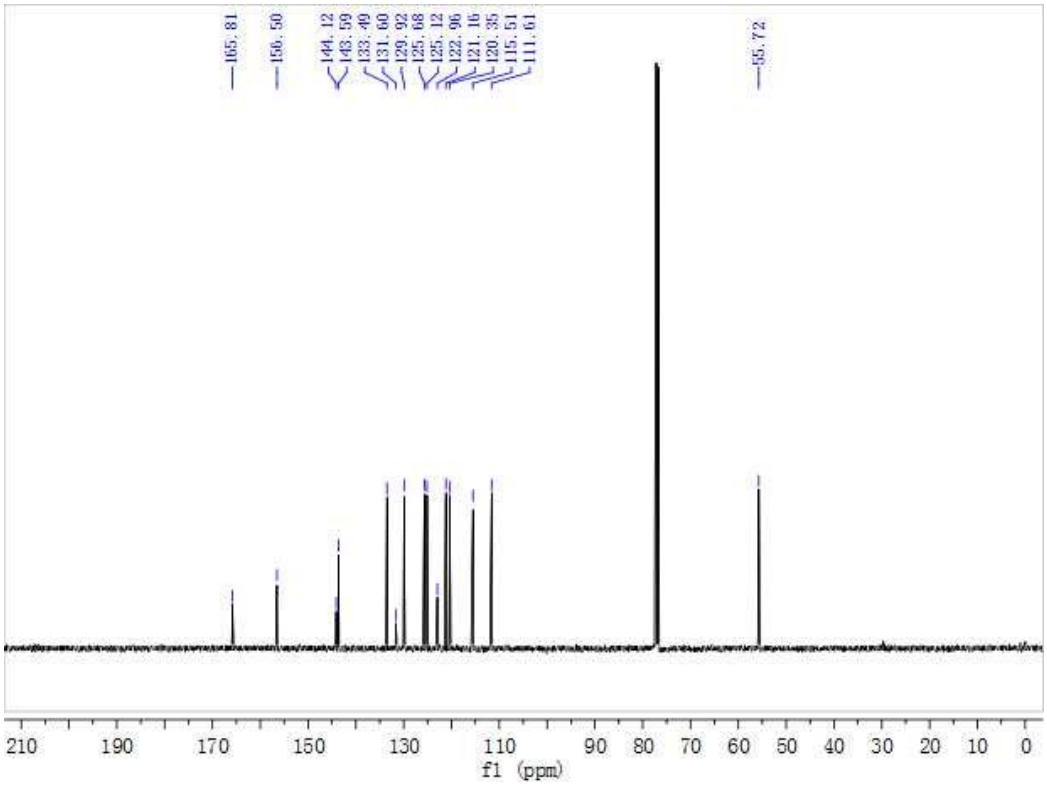

8.22
8.21
7.91
7.84
7.83
7.82
7.82
7.60
7.60
7.59
7.58
7.58
7.57
7.57
7.56
7.52
7.50
7.50
7.49
7.49
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.43
7.43
1.00
0.99
1.02
2.99
3.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

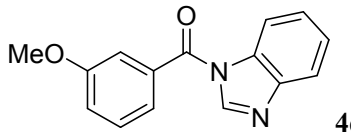

164.61
144.26
142.66
133.18
132.70
131.47
131.35
130.52
129.27
127.43
126.10
125.62
120.66
115.47
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OMe
O
N
N

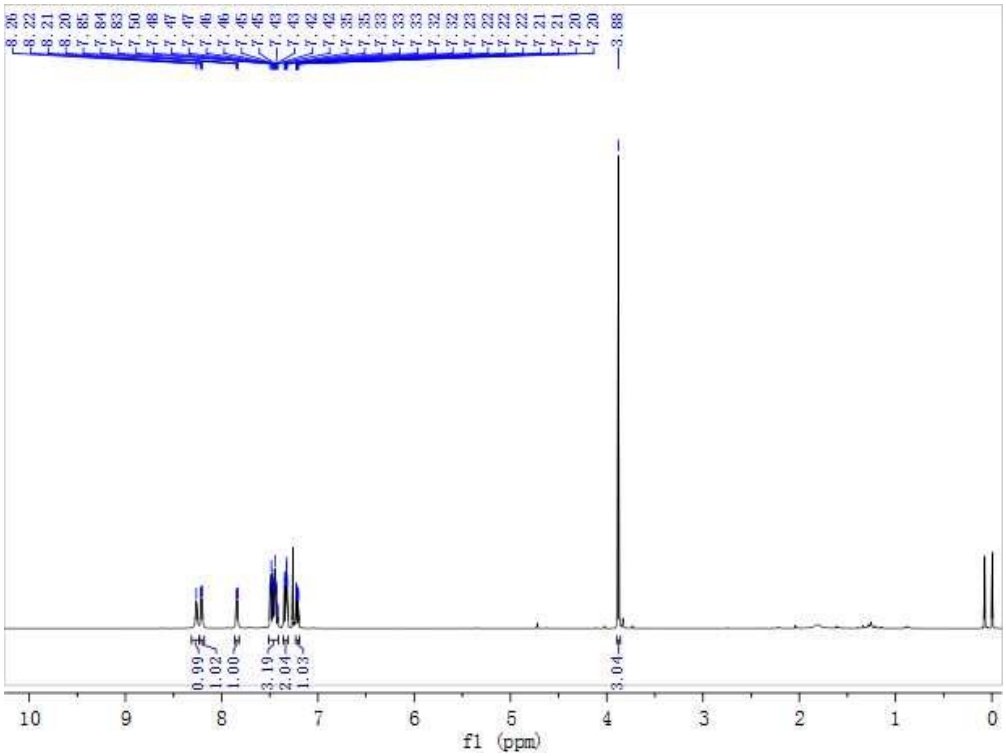
4ca

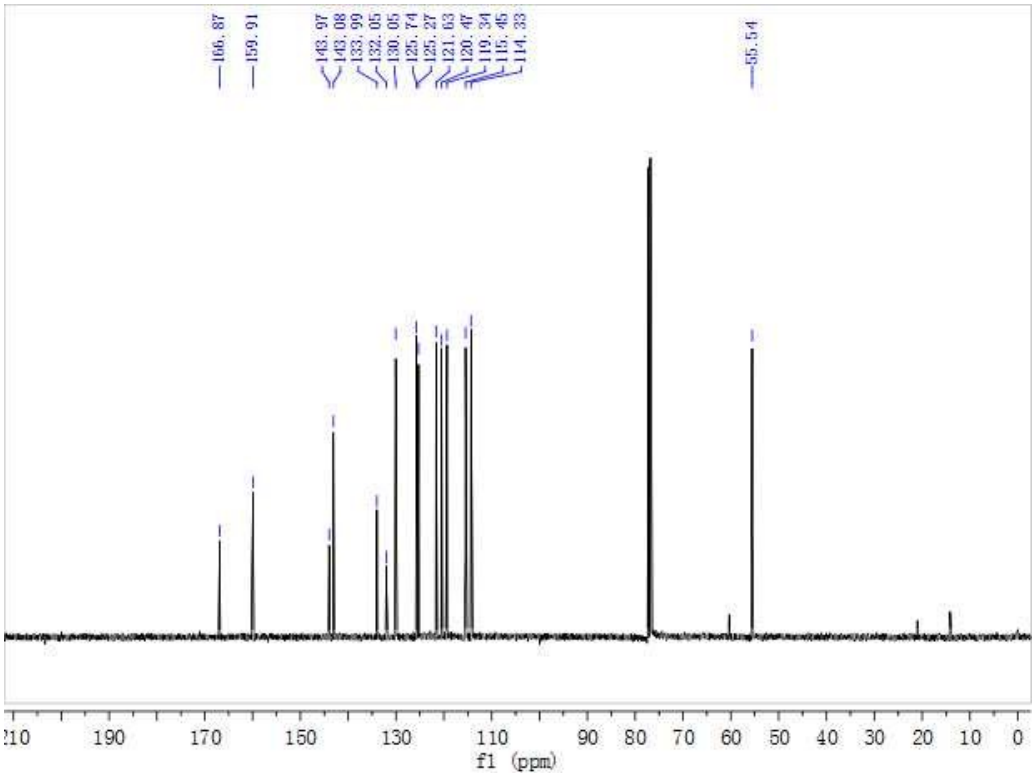

8.26
8.25
7.97
7.81
7.80
7.79
7.61
7.60
7.59
7.57
7.57
7.55
7.55
7.54
7.53
7.46
7.46
7.44
7.44
7.43
7.43
7.42
7.41
7.40
7.16
7.14
7.13
7.07
7.06
3.79
1.00
1.00
1.03
1.02
0.98
2.10
1.05
1.03
3.10
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

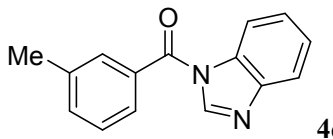

165.81
150.50
144.12
143.59
133.49
131.60
129.92
125.68
125.12
122.96
121.16
120.35
115.51
111.61
55.72
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


MeO
O
N
N

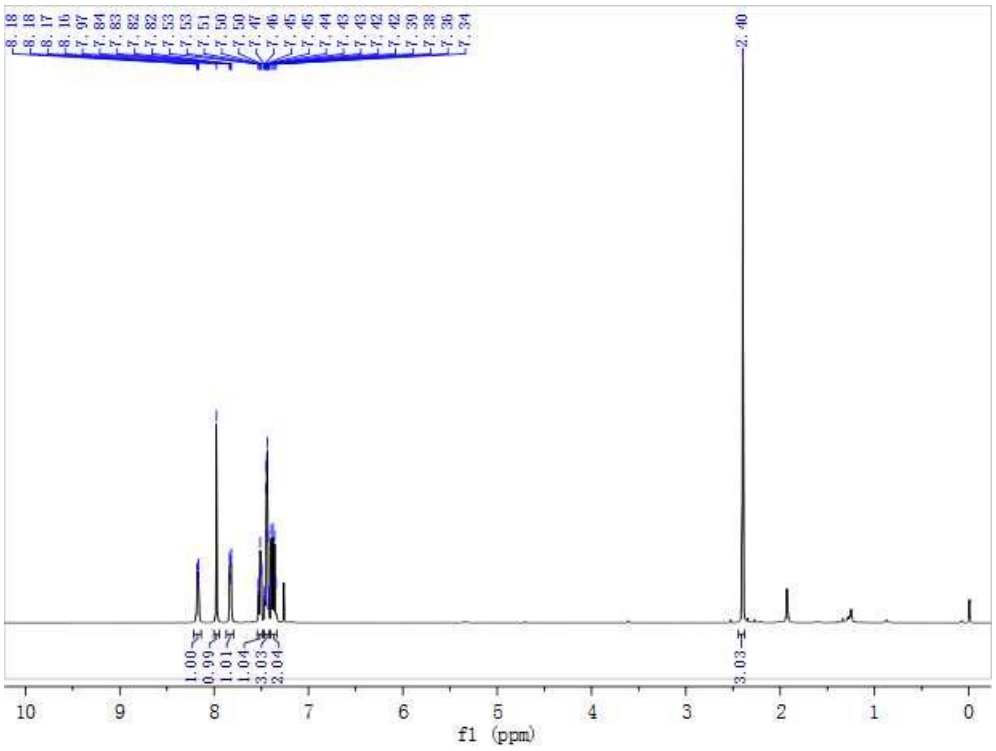
4da

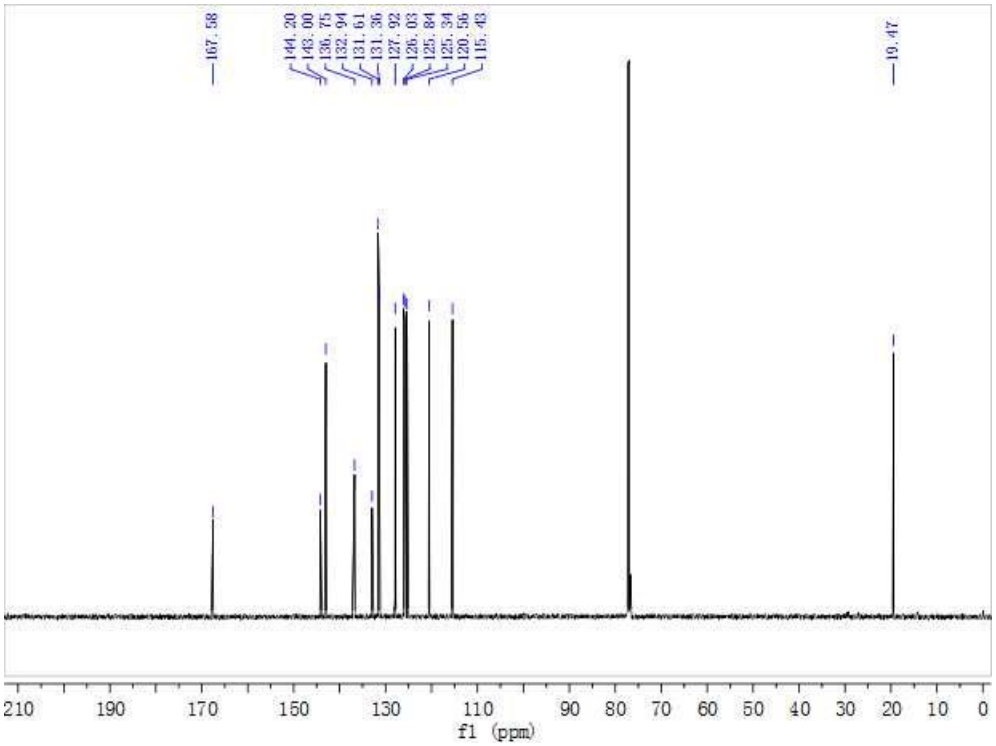

8.26
8.22
8.21
8.20
7.85
7.84
7.83
7.50
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.43
7.43
7.42
7.42
7.35
7.35
7.33
7.33
7.33
7.32
7.32
7.23
7.22
7.22
7.22
7.21
7.21
7.20
7.20
3.88
0.99
1.02
1.00
3.19
2.04
1.03
3.04
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

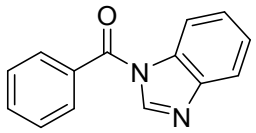

166.87
159.91
143.97
143.08
133.99
132.05
130.05
125.74
125.27
121.63
120.47
119.34
115.45
114.33
55.54
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
O
N
N

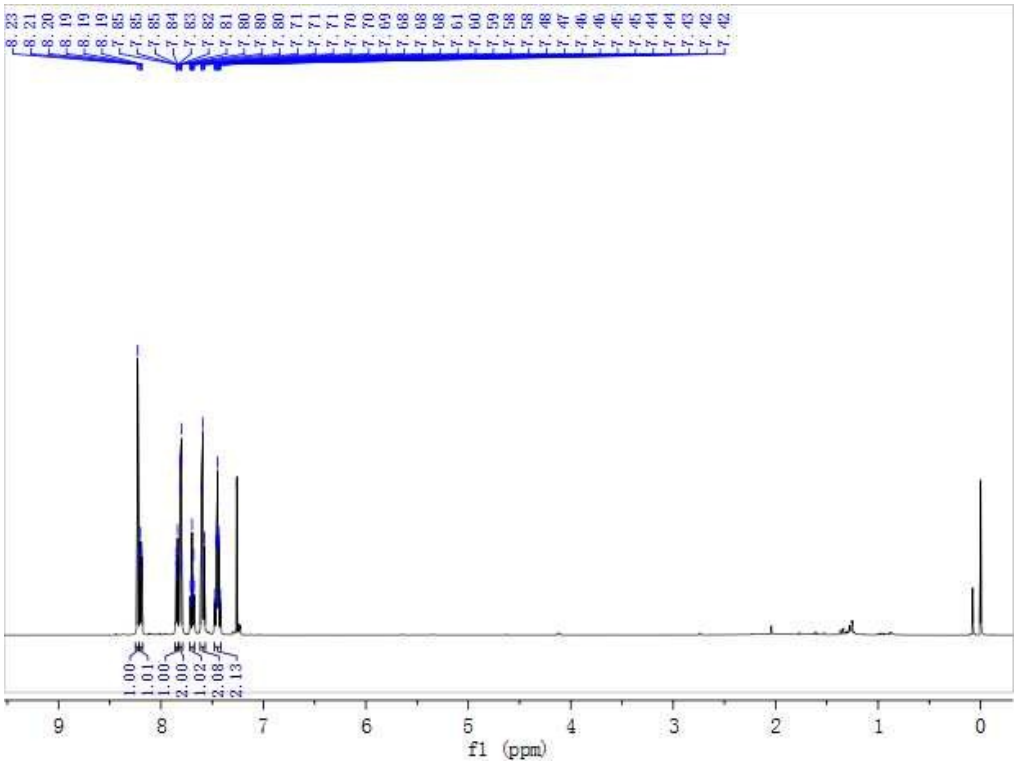
4ea

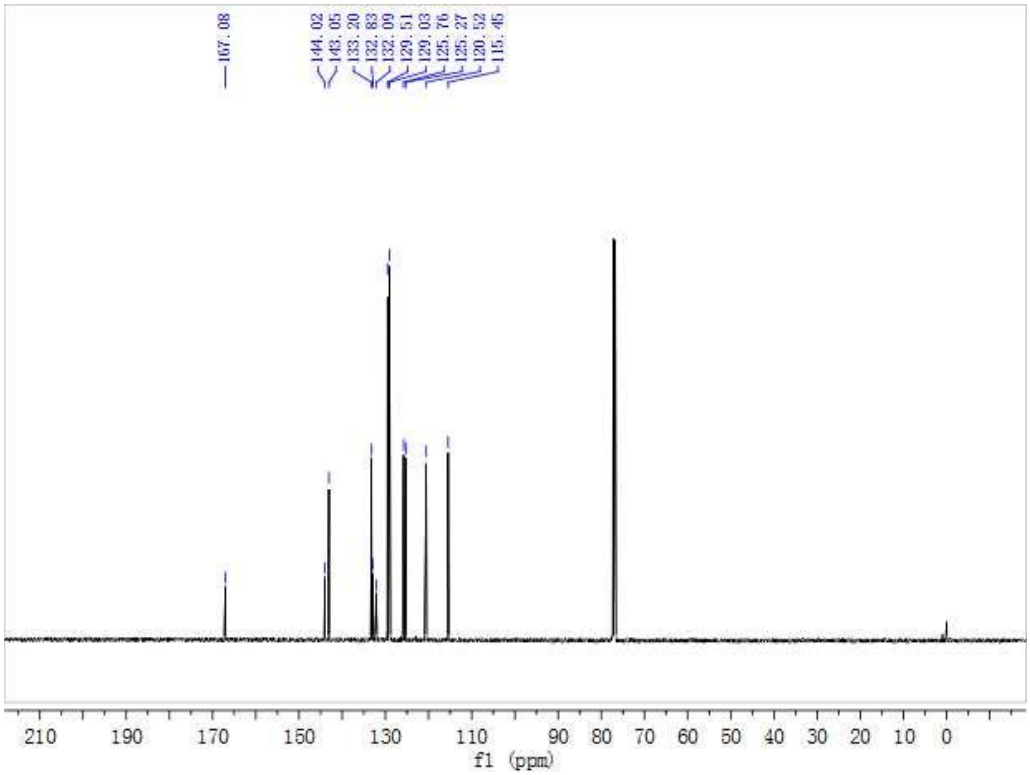

8.18
8.18
8.17
8.16
7.97
7.84
7.83
7.82
7.82
7.53
7.53
7.51
7.50
7.50
7.47
7.46
7.45
7.45
7.44
7.43
7.43
7.42
7.42
7.39
7.38
7.36
7.34
2.40
1.00
0.99
1.01
1.04
3.03
2.04
3.03
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

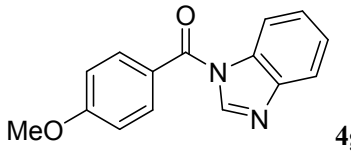

167.58
144.20
143.00
136.75
132.94
131.61
131.36
127.92
126.03
125.84
125.34
120.56
115.43
19.47
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



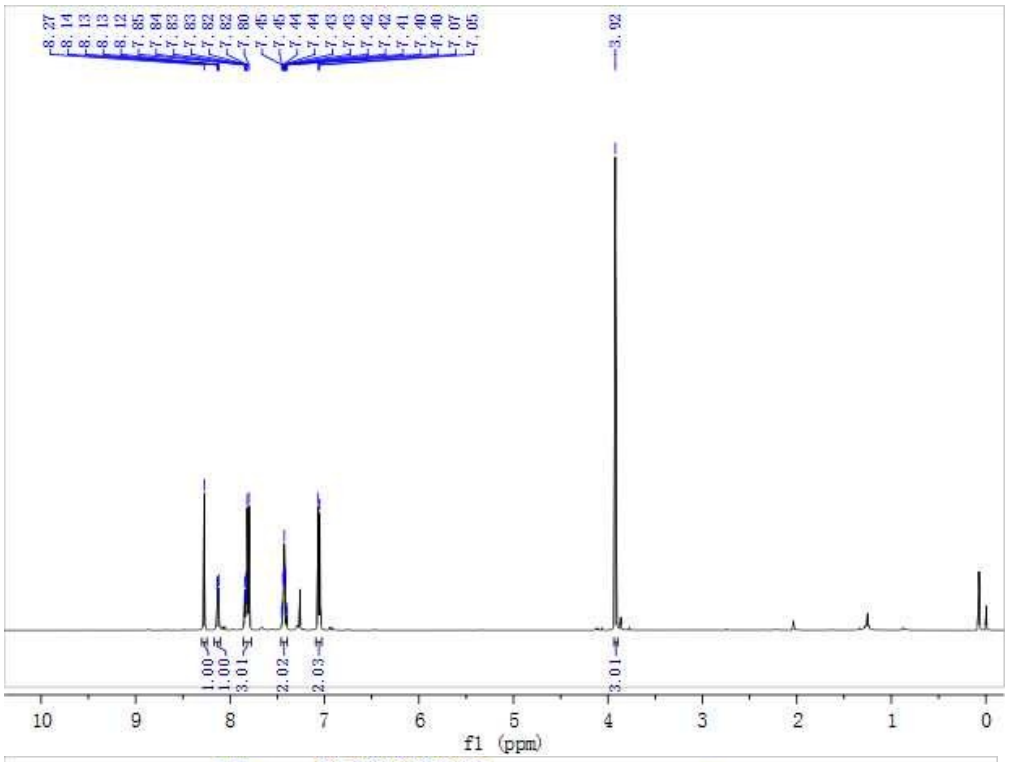
4fa

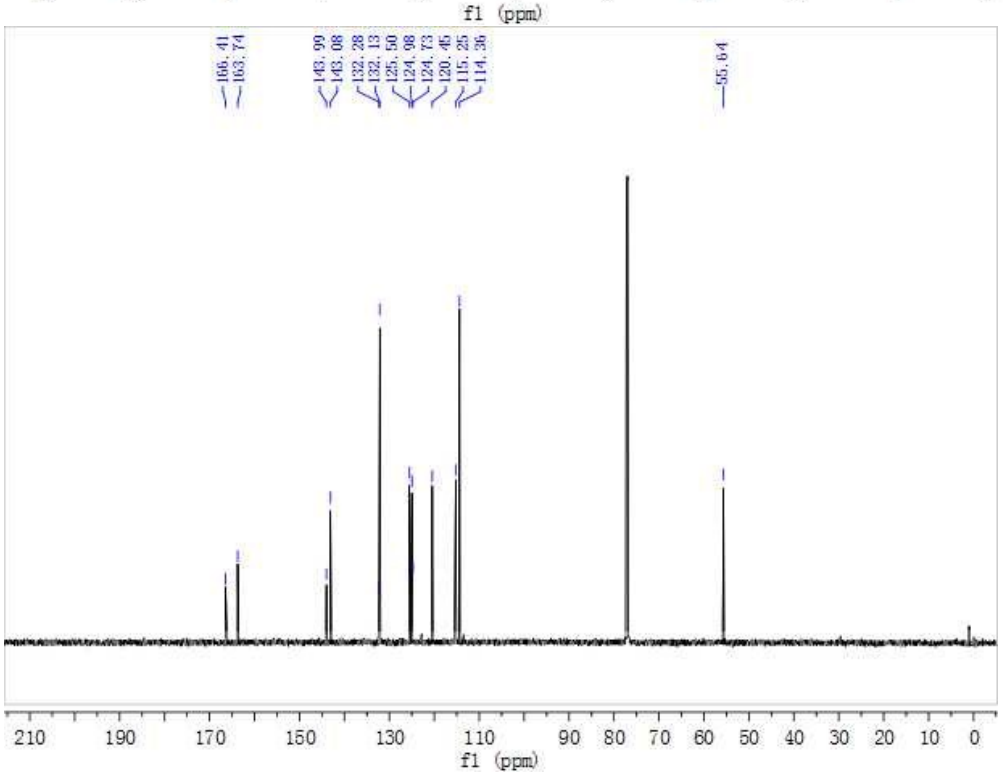

8.23
8.21
8.20
8.19
8.19
8.19
7.85
7.85
7.84
7.83
7.82
7.81
7.80
7.80
7.71
7.71
7.71
7.70
7.70
7.69
7.68
7.68
7.61
7.60
7.59
7.58
7.58
7.48
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.42
7.42
1.00
1.01
1.00
2.00
1.02
2.08
2.13
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

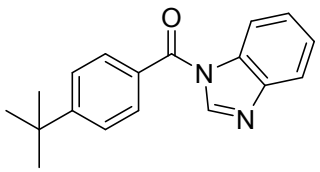

167.08
144.02
143.05
133.20
132.83
132.09
129.51
129.03
125.76
125.27
120.52
115.45
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
N
N
MeO

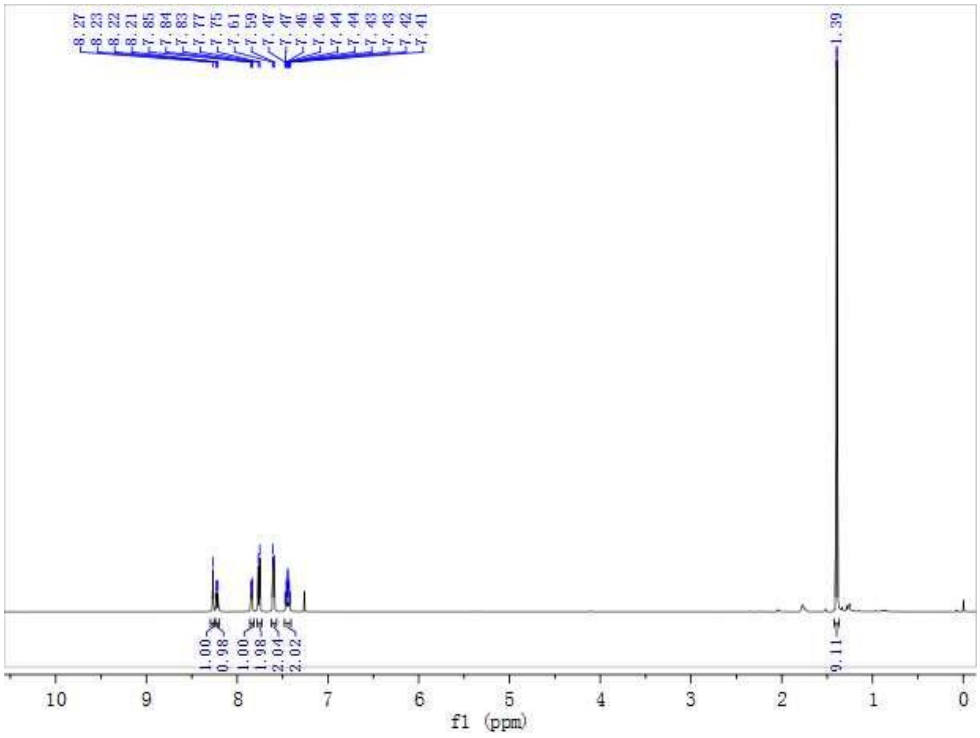
4ga

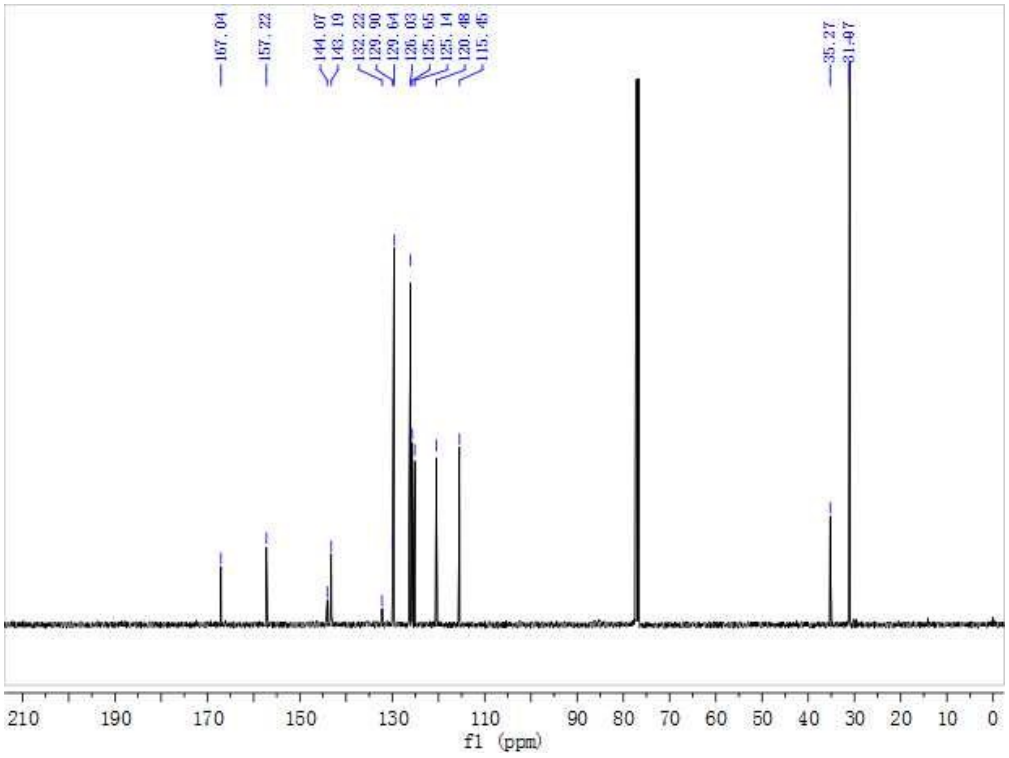

8.27
8.14
8.13
8.13
8.12
7.85
7.84
7.83
7.82
7.82
7.80
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.41
7.40
7.40
7.07
7.05
3.92
1.00
1.00
3.01
2.02
2.03
3.01
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

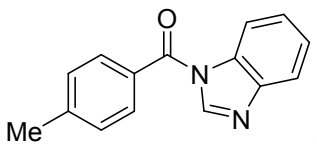

166.41
163.74
143.99
143.08
132.28
132.13
125.50
124.98
124.73
120.45
115.25
114.36
55.64
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



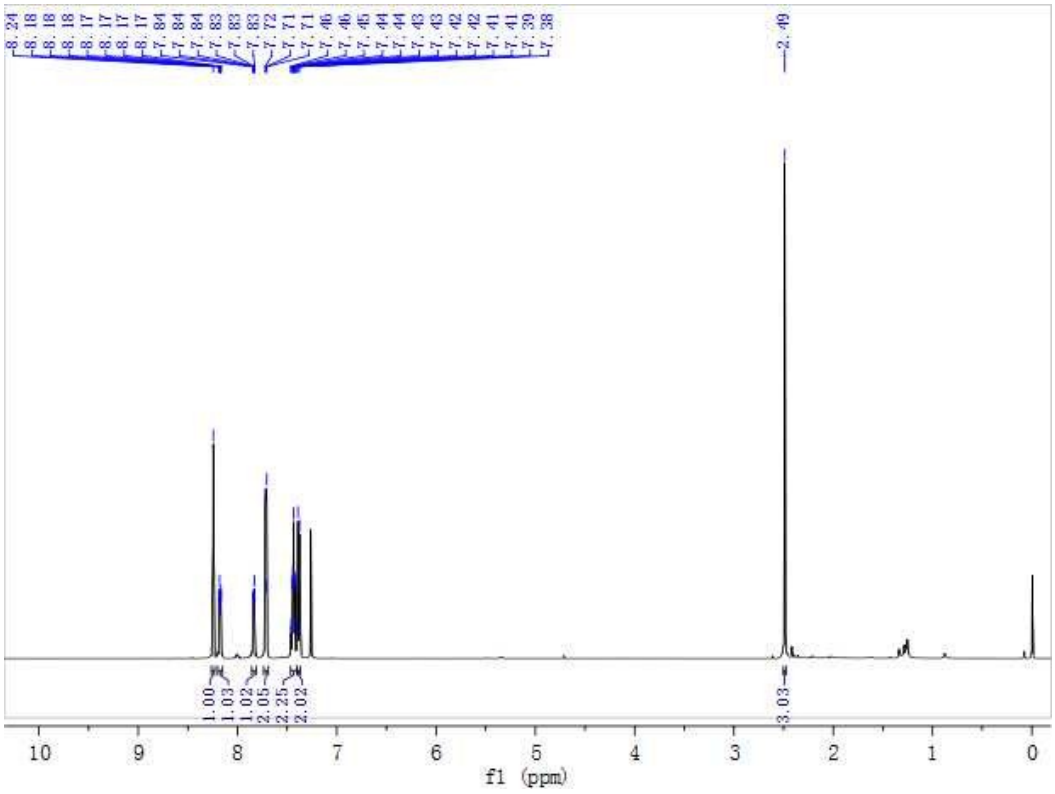
4ha

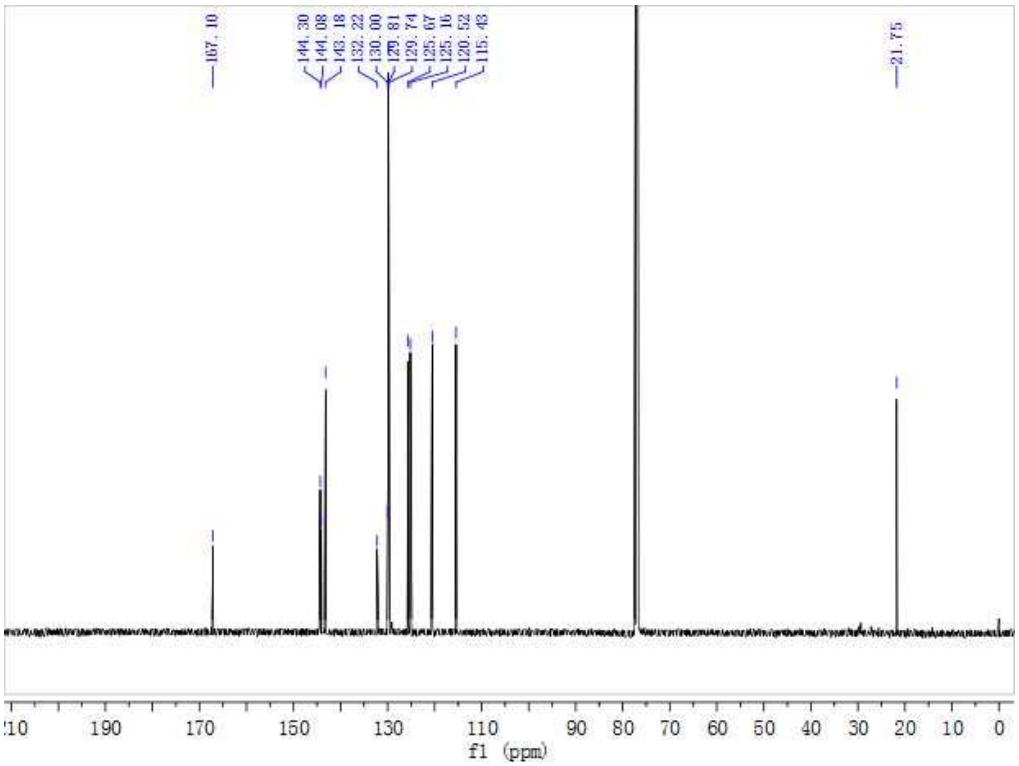

8.27
8.23
8.22
8.21
7.85
7.84
7.83
7.77
7.75
7.61
7.59
7.47
7.47
7.46
7.46
7.44
7.44
7.43
7.43
7.42
7.41
1.39
1.00
0.98
1.00
1.98
2.04
2.02
9.11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

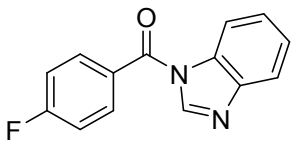

167.04
157.22
144.07
143.19
132.22
129.90
129.64
126.03
125.65
125.14
120.48
115.45
35.27
31.07
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
N
N
Me

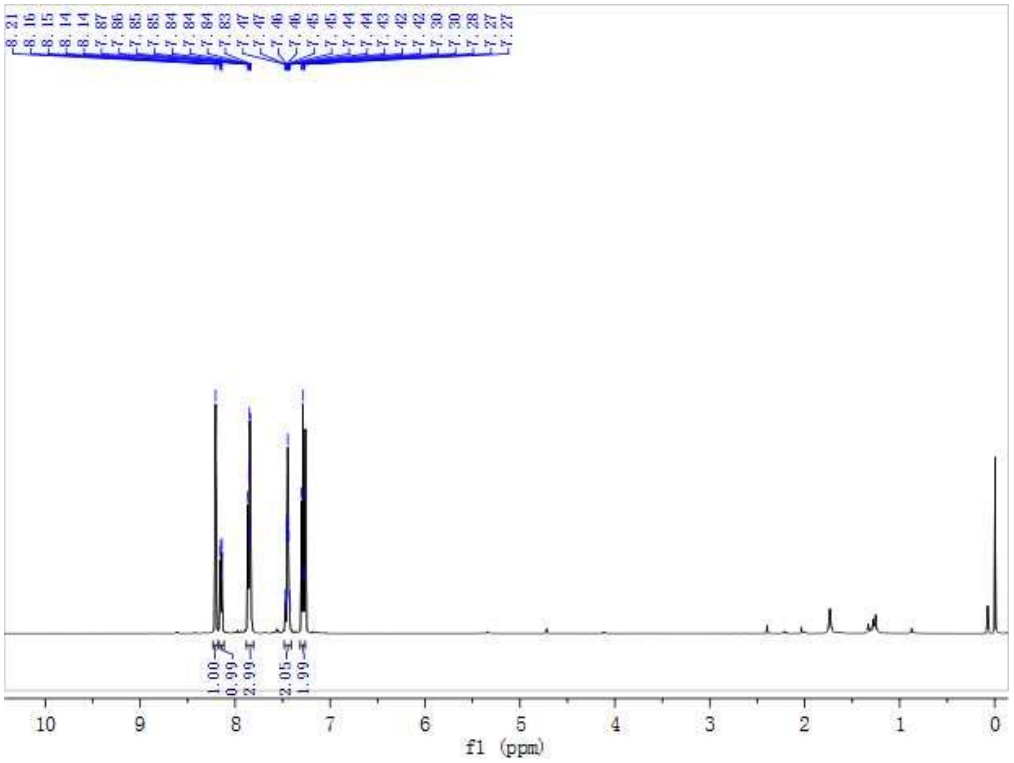
4ia

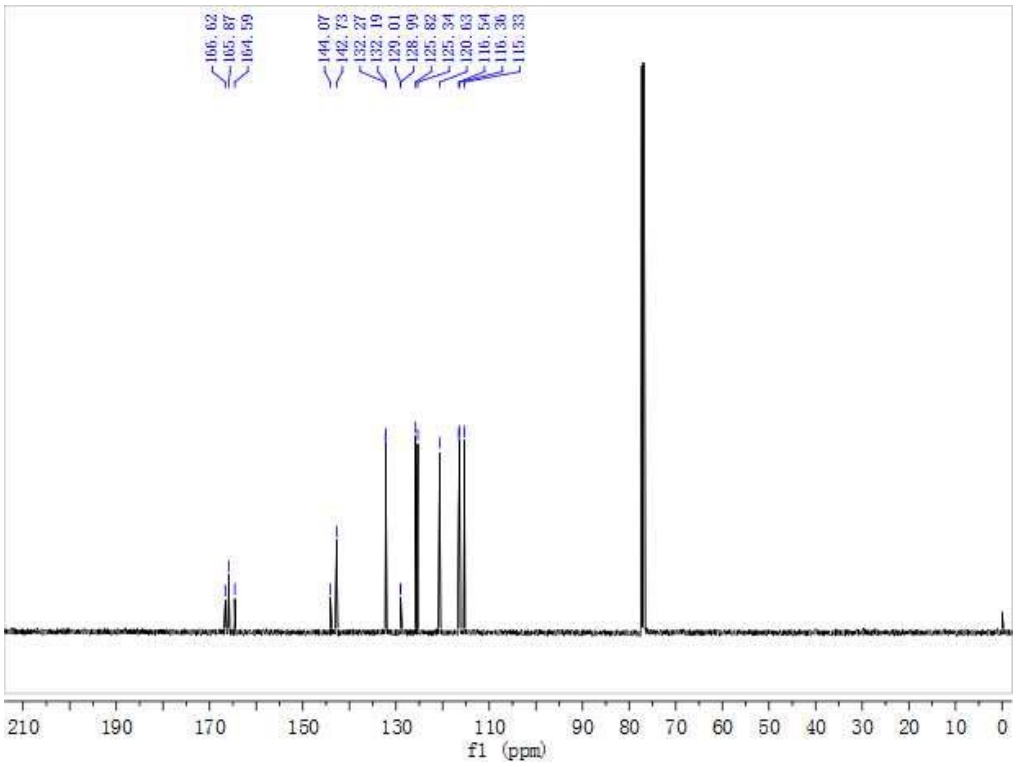

8.24
8.18
8.18
8.18
8.17
8.17
8.17
8.17
7.84
7.84
7.84
7.83
7.83
7.83
7.72
7.71
7.71
7.46
7.46
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.39
7.38
2.49
1.00
1.03
1.02
2.05
2.25
2.02
3.03
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

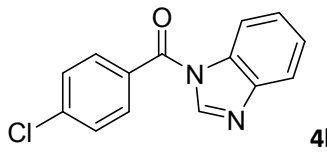

167.10
144.30
144.08
143.18
132.22
130.00
129.81
129.74
125.67
125.16
120.52
115.43
21.75
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
N
N
F

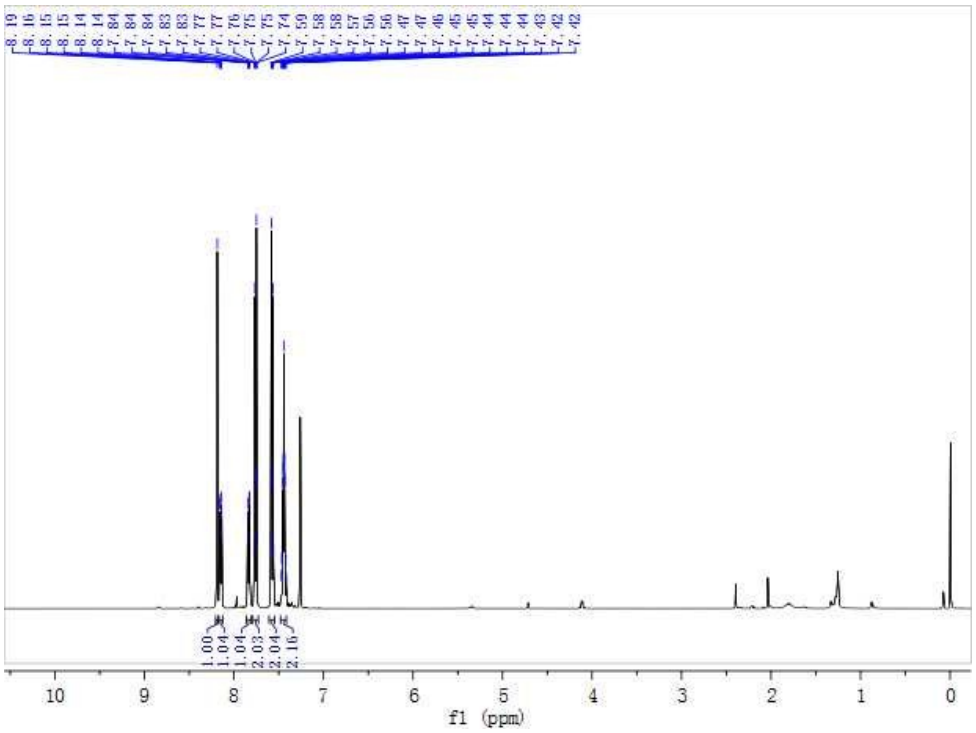
4ja

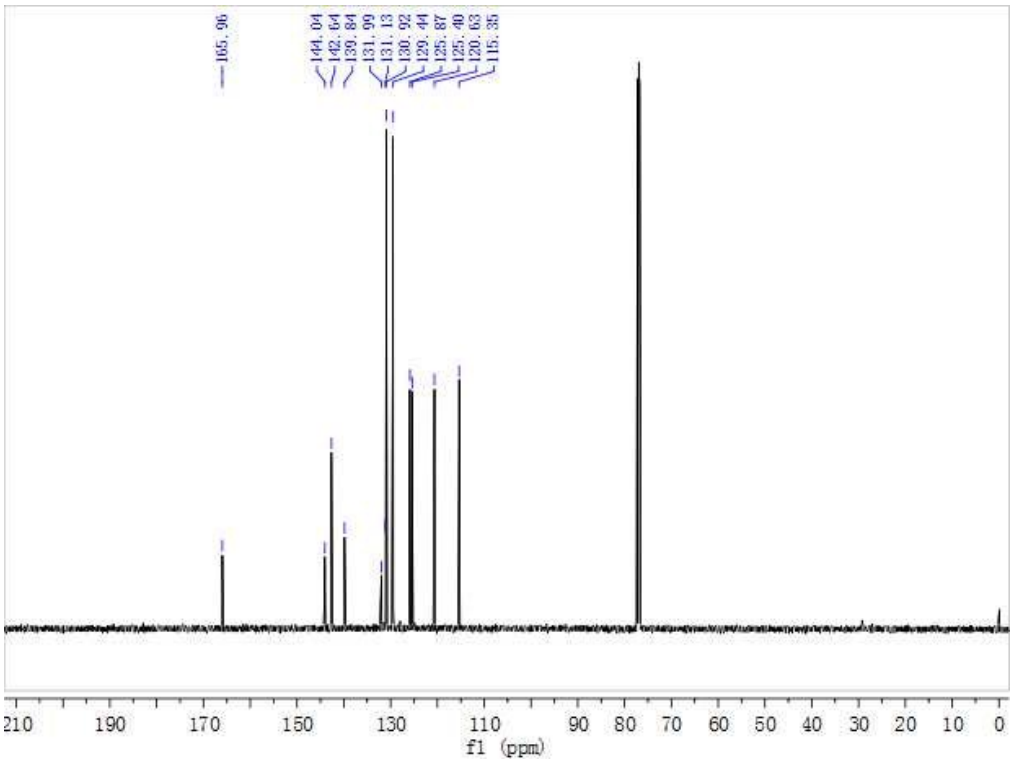

8.21
8.16
8.15
8.14
8.14
7.87
7.86
7.85
7.85
7.84
7.84
7.84
7.83
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.42
7.42
7.30
7.30
7.28
7.27
7.27
1.00
0.99
2.99
2.05
1.99
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

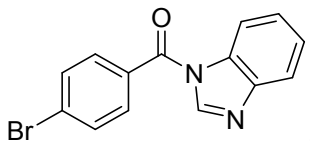

166.62
165.87
164.59
144.07
142.73
132.27
132.19
129.01
128.99
125.82
125.34
120.63
116.54
116.36
115.33
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
N
N
Cl

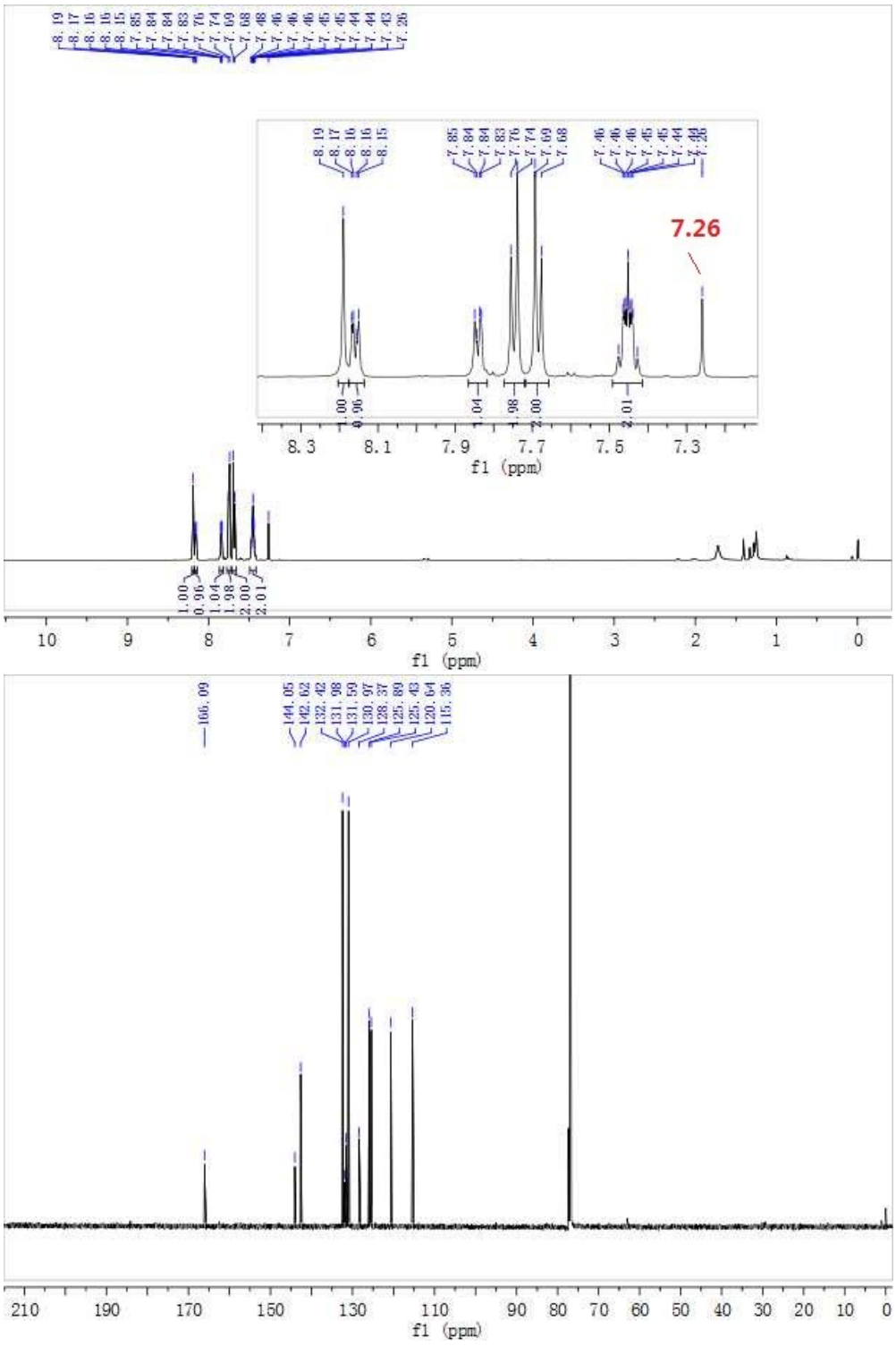
4ka

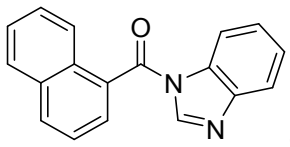

8.19
8.16
8.15
8.15
8.14
8.14
7.84
7.84
7.84
7.83
7.77
7.77
7.76
7.75
7.75
7.74
7.59
7.58
7.57
7.56
7.56
7.47
7.47
7.46
7.45
7.45
7.44
7.44
7.43
7.42
7.42
1.00
1.04
1.04
2.03
2.04
2.16
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


165.96
144.04
142.64
139.84
131.99
131.13
130.92
129.44
125.87
125.40
120.63
115.35
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

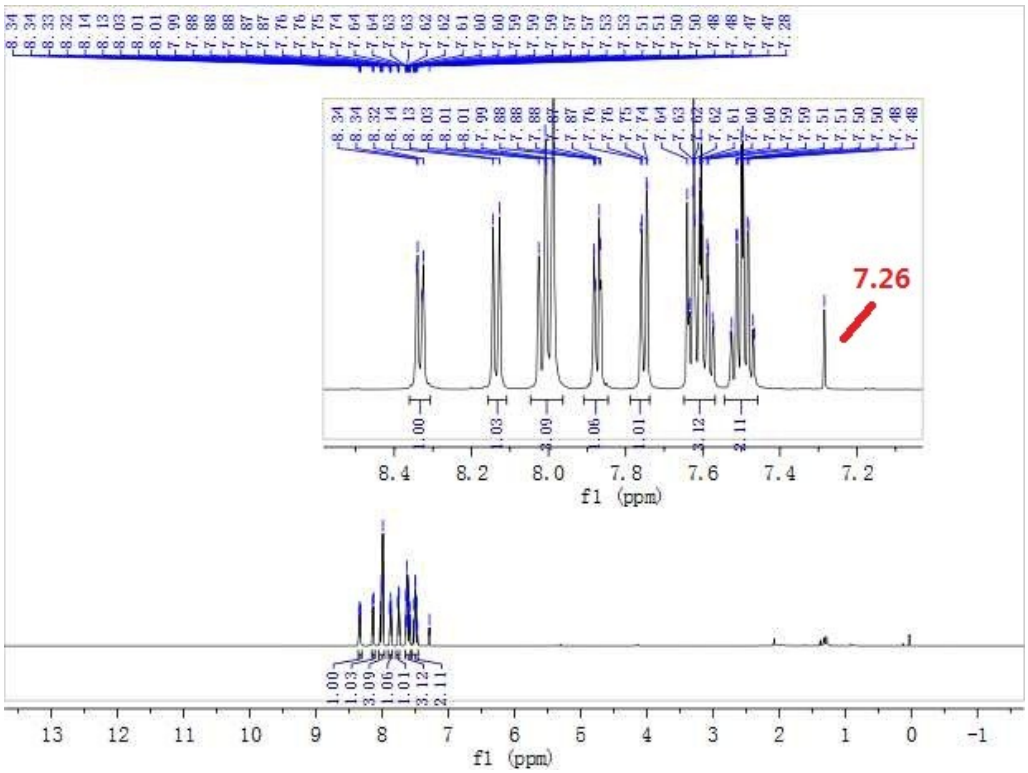


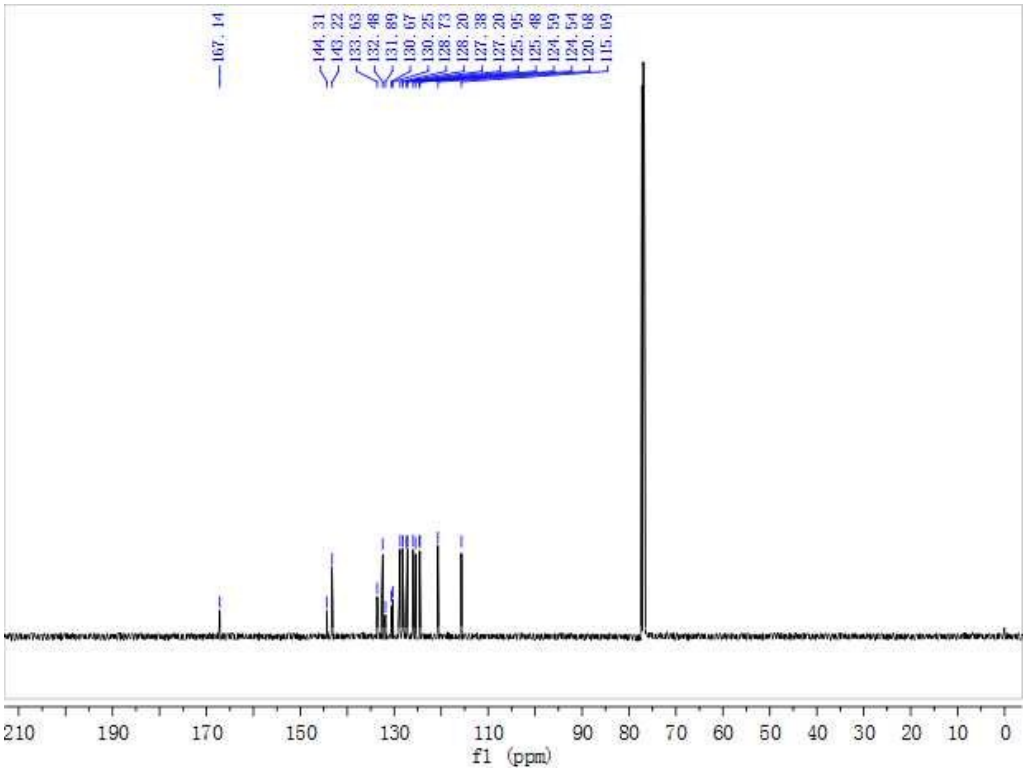
4la

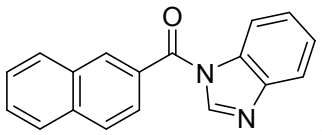




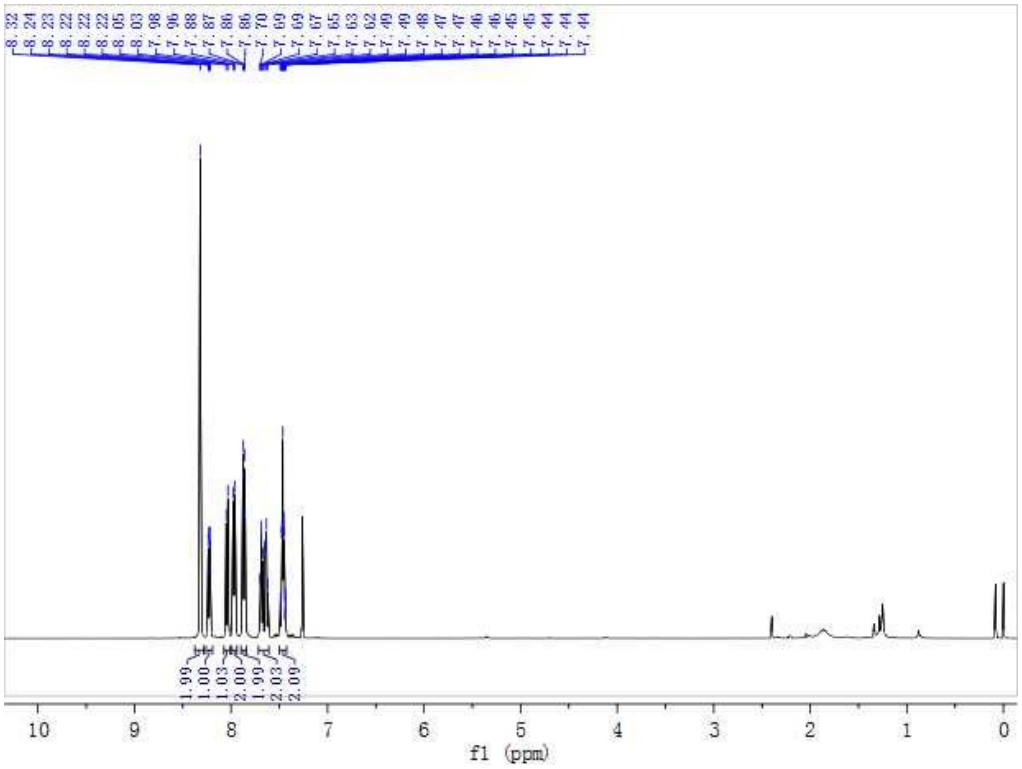
4ma

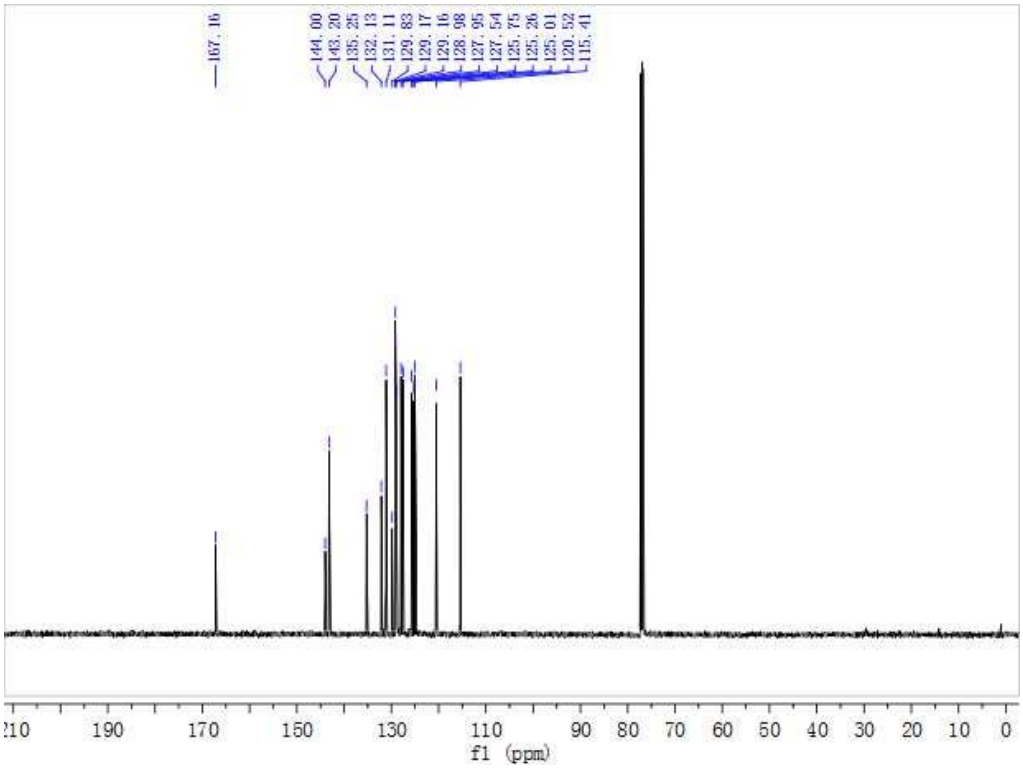

7.26
1.00
1.03
3.09
1.06
1.01
3.12
2.11
f1 (ppm)

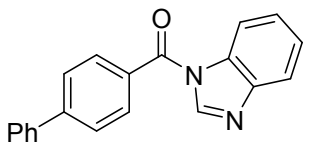

167.14
144.31
143.22
133.63
132.48
131.89
130.67
130.25
128.73
128.20
127.38
127.20
125.95
125.48
124.59
124.54
120.68
115.69
f1 (ppm)



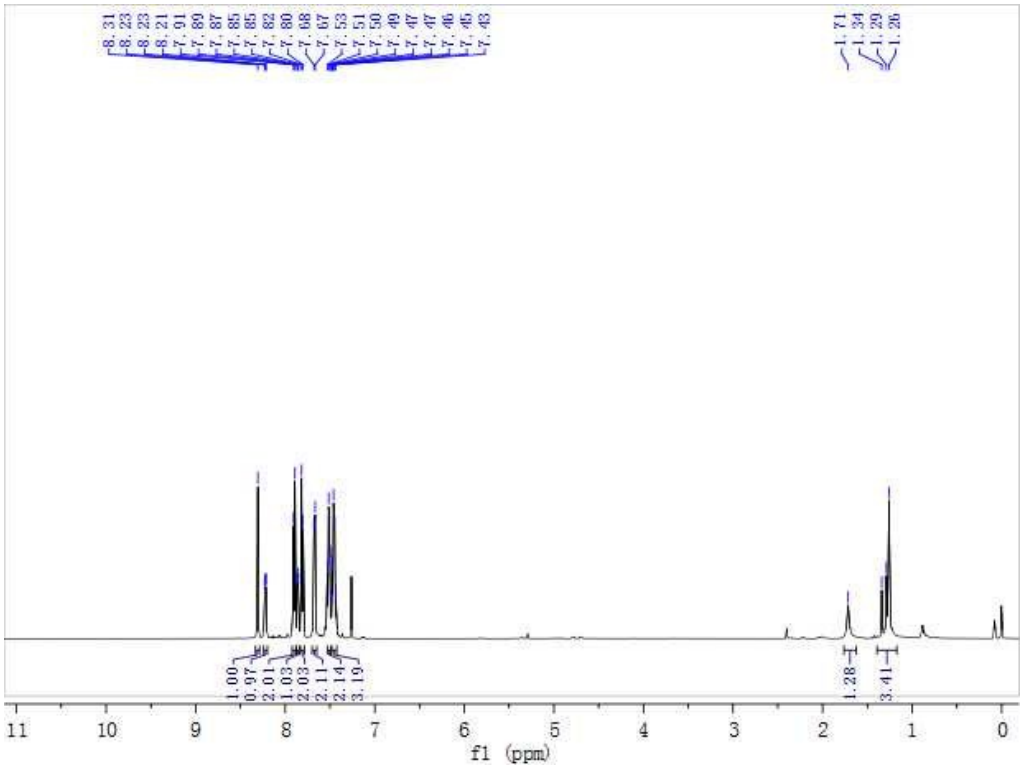
4na

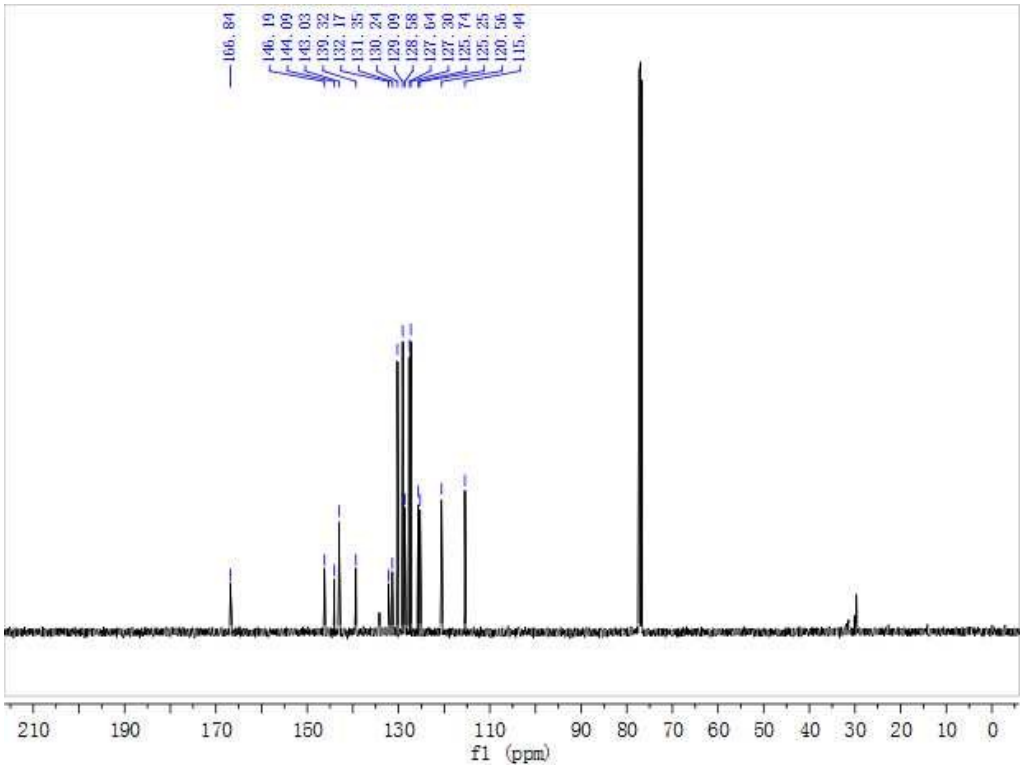

8.32
8.24
8.23
8.22
8.22
8.22
8.05
8.03
7.98
7.96
7.88
7.87
7.86
7.86
7.70
7.69
7.69
7.67
7.65
7.63
7.62
7.49
7.49
7.48
7.47
7.47
7.46
7.46
7.45
7.44
7.44
7.44
1.99
1.00
1.03
2.00
1.99
2.03
2.09
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

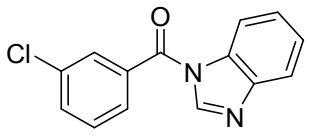

167.16
144.00
143.20
135.25
132.13
131.11
129.83
129.17
129.16
128.98
127.95
127.54
125.75
125.26
125.01
120.52
115.41
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
N
N
Ph

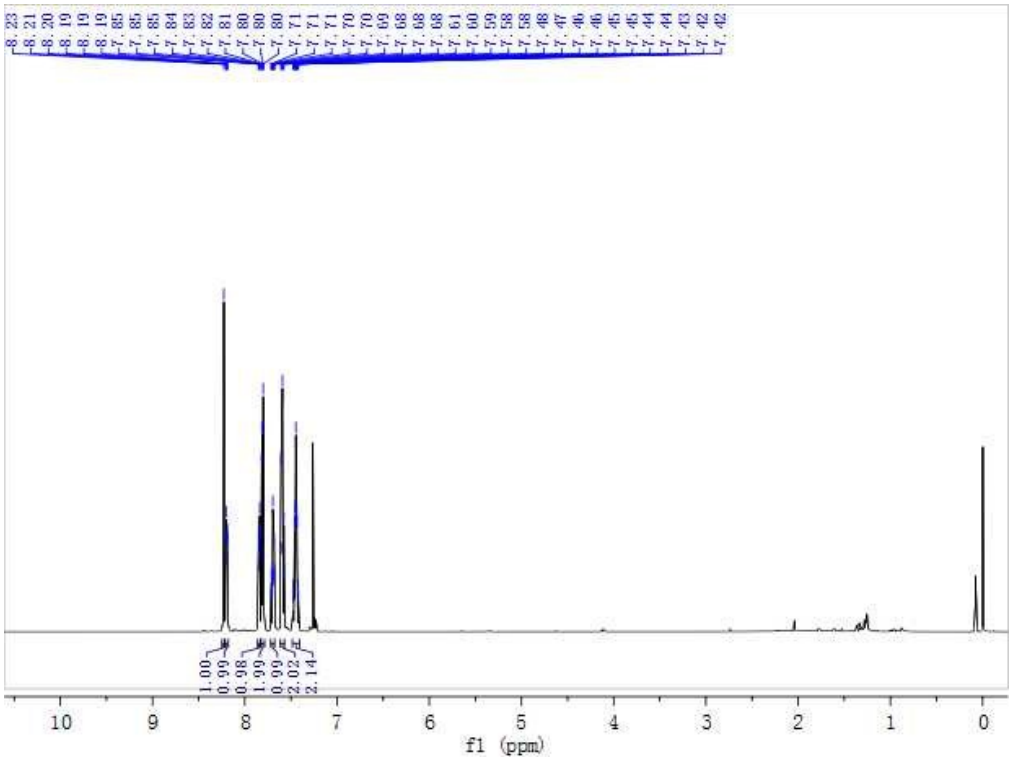
4oa

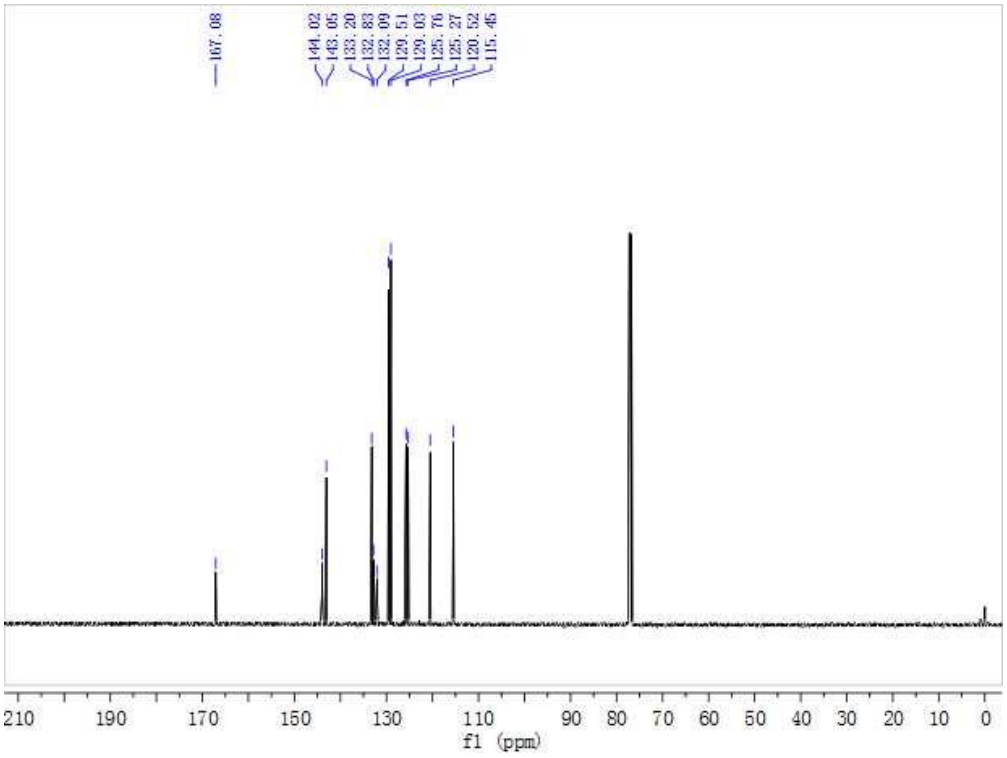

8.31
8.23
8.23
8.21
7.91
7.89
7.87
7.85
7.85
7.82
7.80
7.68
7.67
7.53
7.51
7.50
7.49
7.47
7.47
7.46
7.45
7.43
1.71
1.34
1.29
1.26
1.00
0.97
2.01
1.03
2.03
2.11
2.14
3.19
1.28
3.41
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

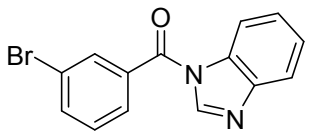

166.84
146.19
144.09
143.03
139.32
132.17
131.35
130.24
129.09
128.58
127.64
127.30
125.74
125.25
120.56
115.44
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
Cl
N
N

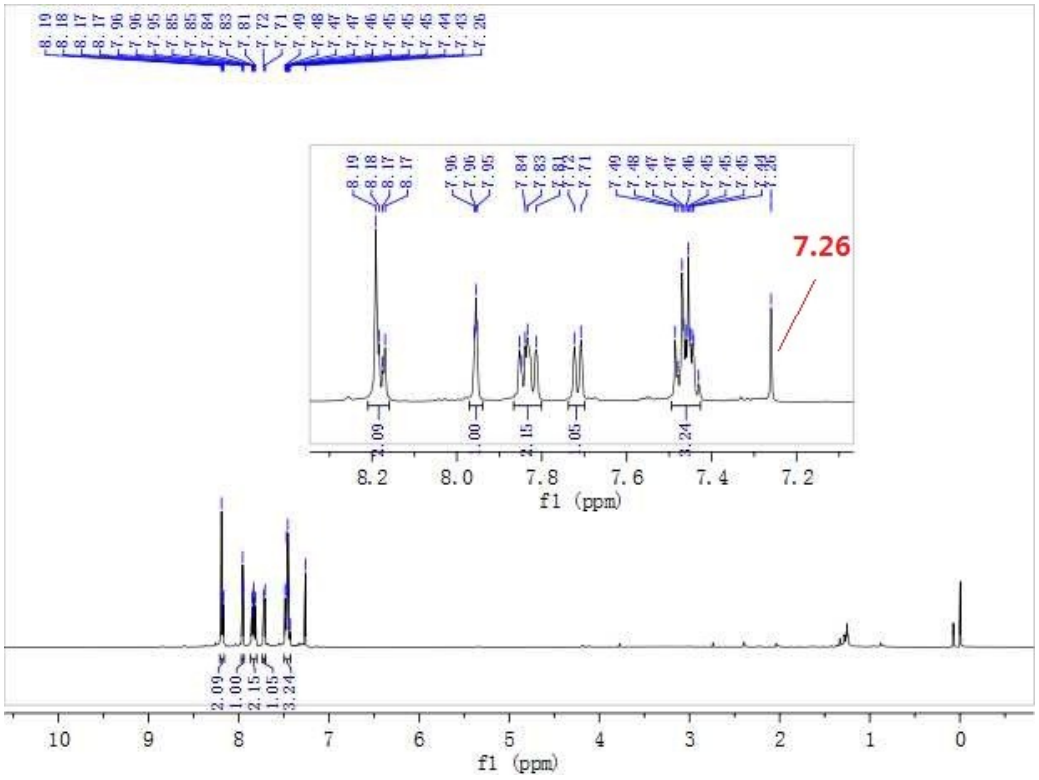
4pa

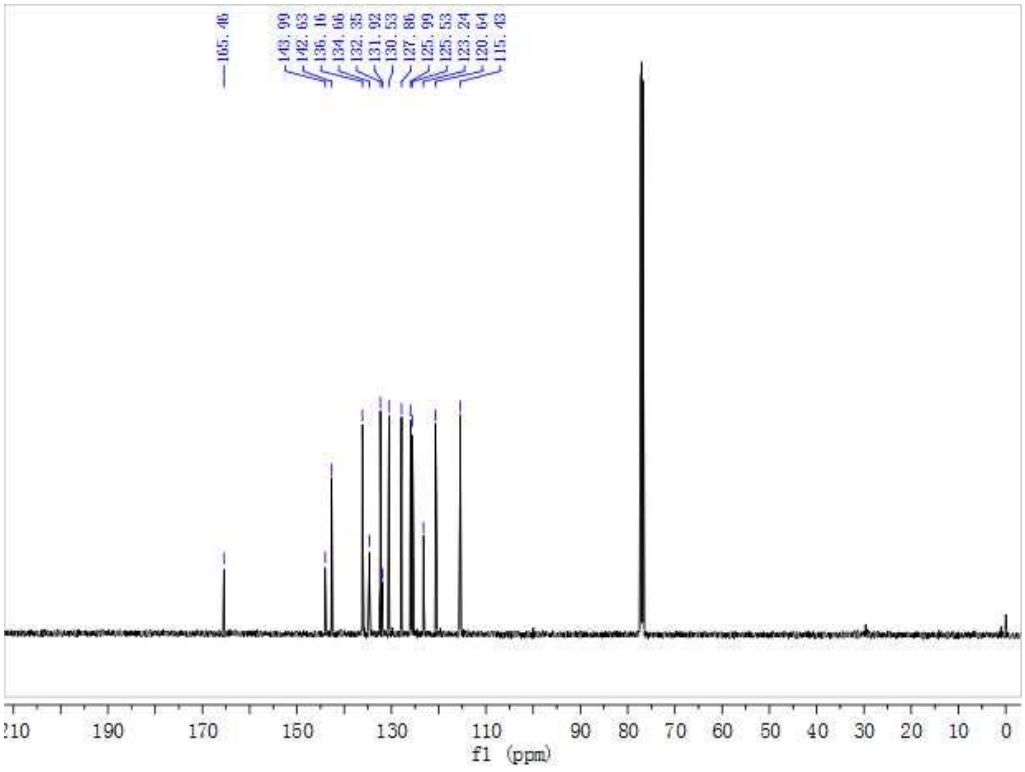

8.23
8.21
8.20
8.19
8.19
8.19
7.85
7.85
7.85
7.84
7.83
7.82
7.81
7.80
7.80
7.80
7.71
7.71
7.71
7.70
7.70
7.69
7.68
7.68
7.68
7.61
7.60
7.59
7.58
7.58
7.48
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.42
7.42
1.00
0.99
0.98
1.99
0.99
2.02
2.14
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

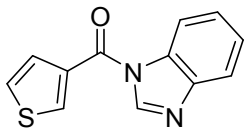

167.08
144.02
143.05
133.20
132.83
132.09
129.51
129.03
125.76
125.27
120.52
115.45
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
Br
N
N

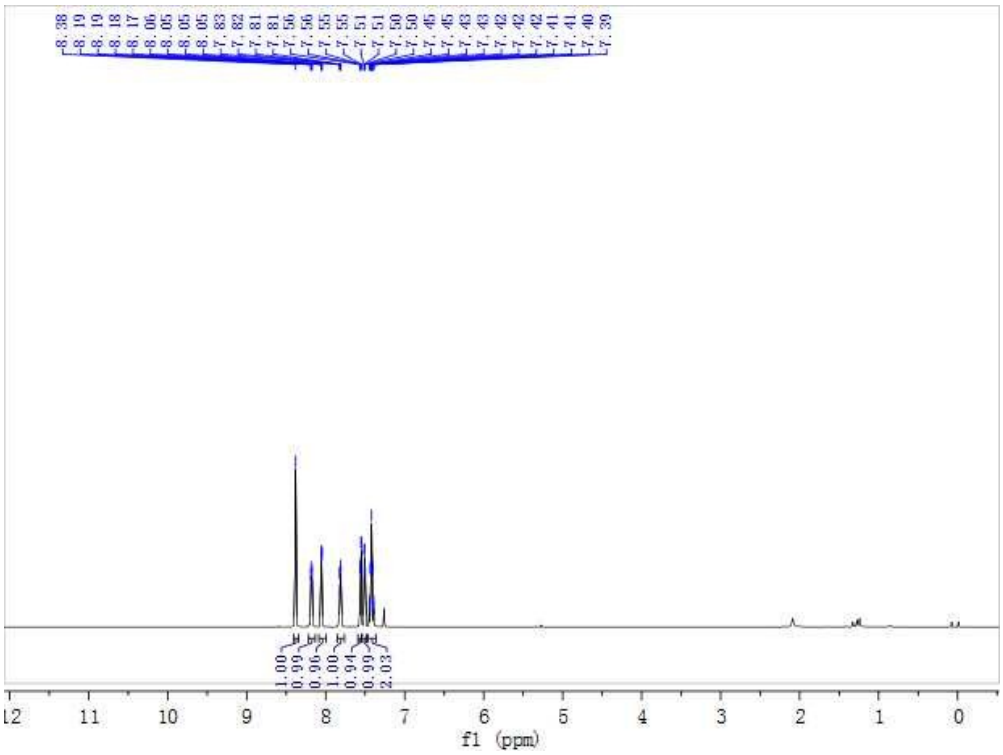
4qa

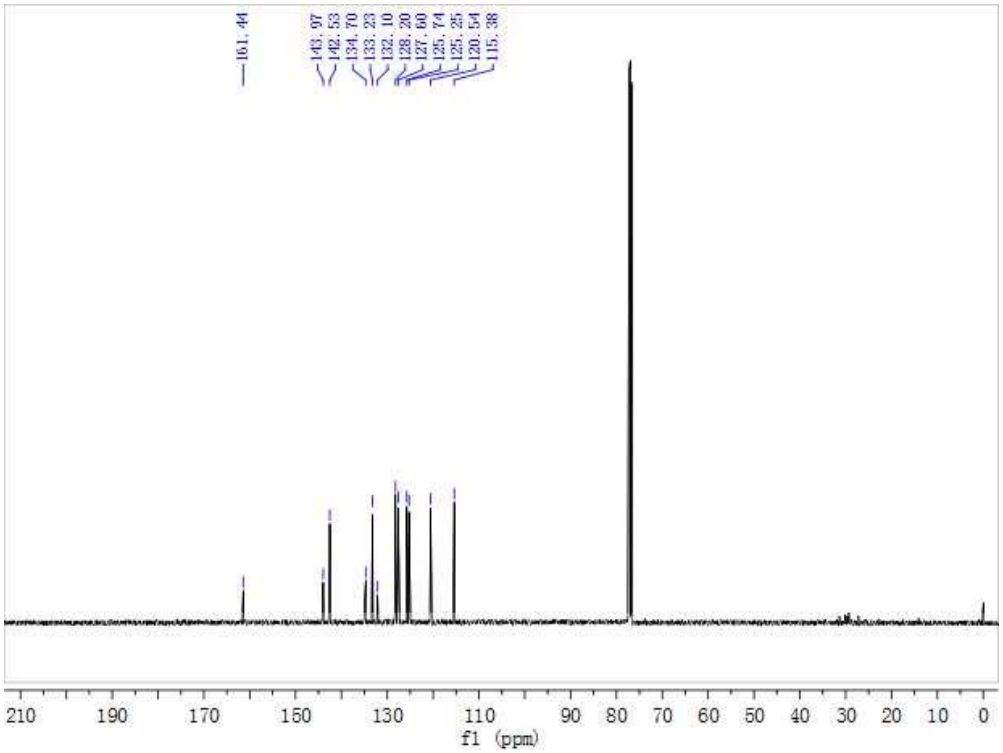

7.26
2.09
1.00
2.15
1.05
3.24
f1 (ppm)

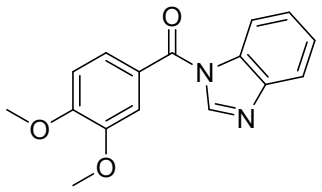

165.46
143.99
142.63
136.16
134.66
132.35
131.92
130.53
127.86
125.99
125.53
123.24
120.64
115.43
f1 (ppm)


O
N
N
S

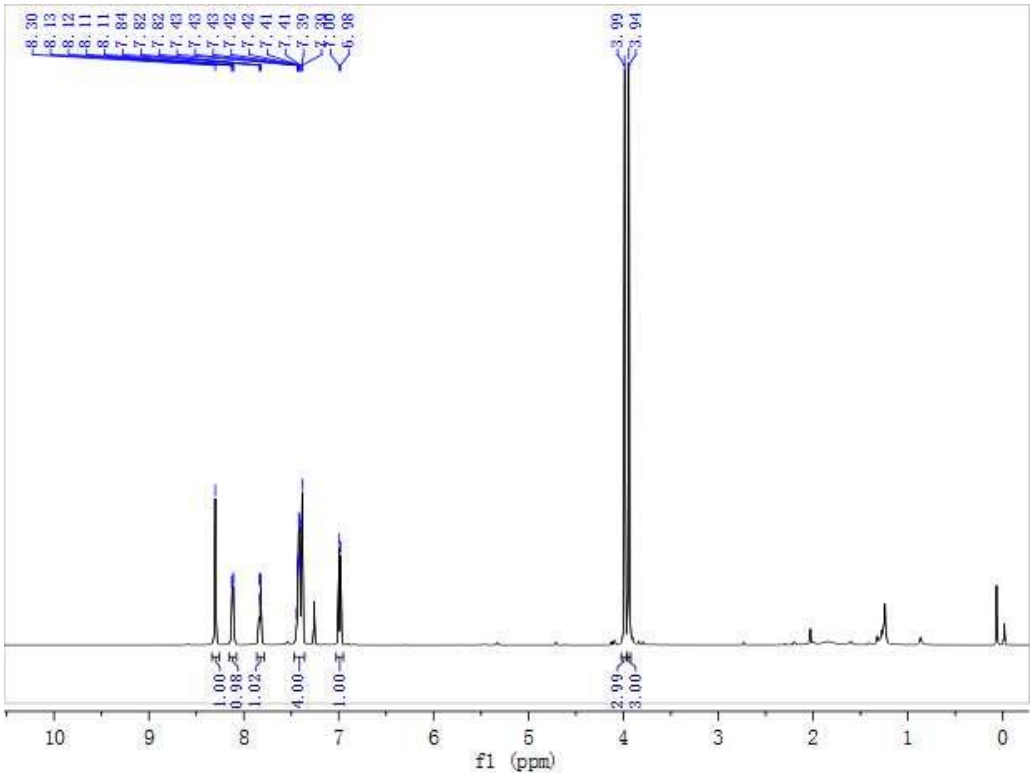
4ra

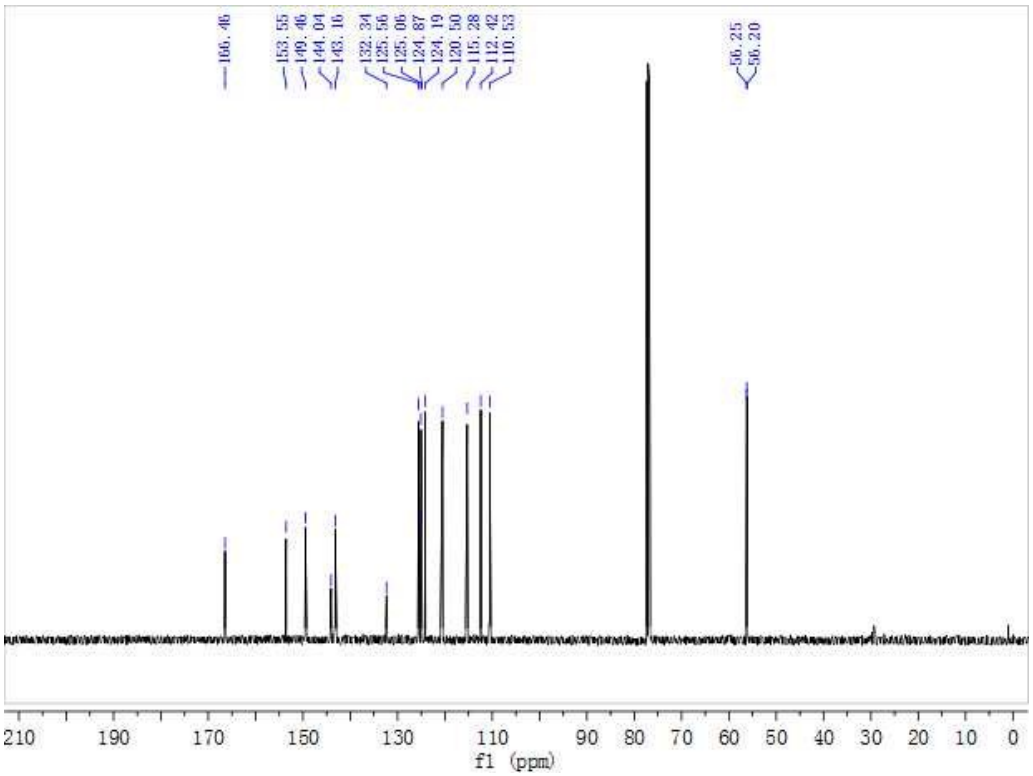

8.38
8.19
8.19
8.18
8.17
8.06
8.05
8.05
8.05
7.83
7.82
7.81
7.81
7.56
7.56
7.55
7.55
7.51
7.51
7.50
7.50
7.45
7.45
7.43
7.43
7.42
7.42
7.42
7.42
7.41
7.41
7.40
7.39
1.00
0.99
0.96
1.00
0.94
0.99
2.03
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

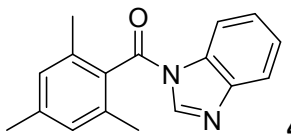

161.44
143.97
142.53
134.70
133.23
132.10
128.20
127.60
125.74
125.25
120.54
115.38
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



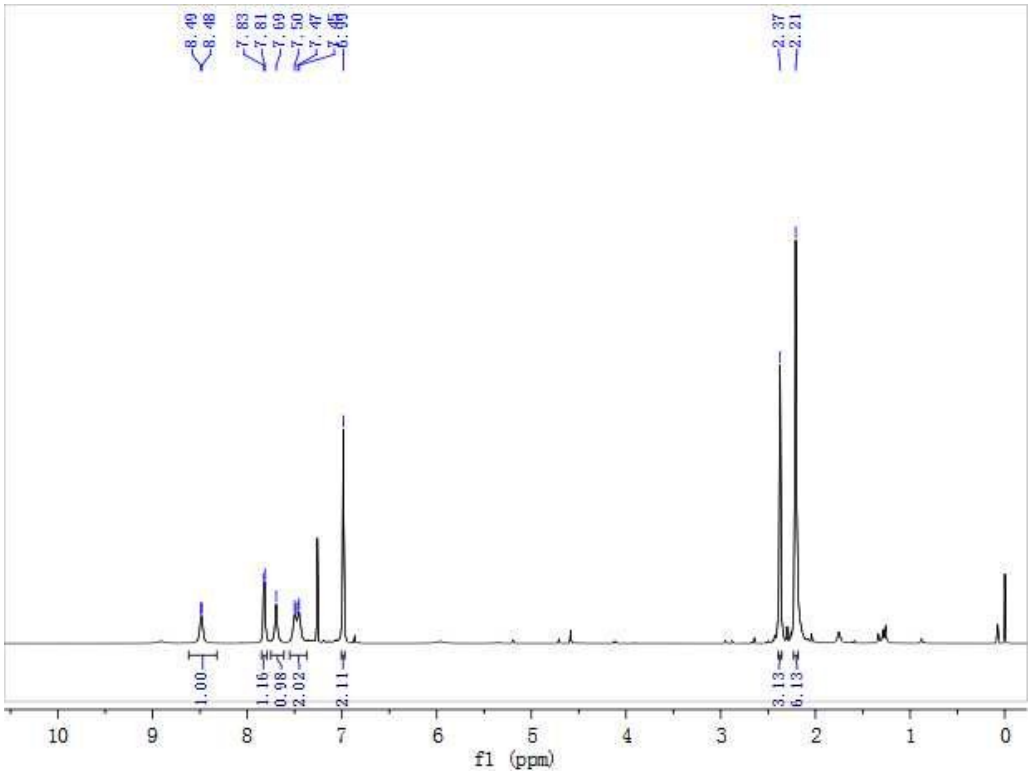
4sa

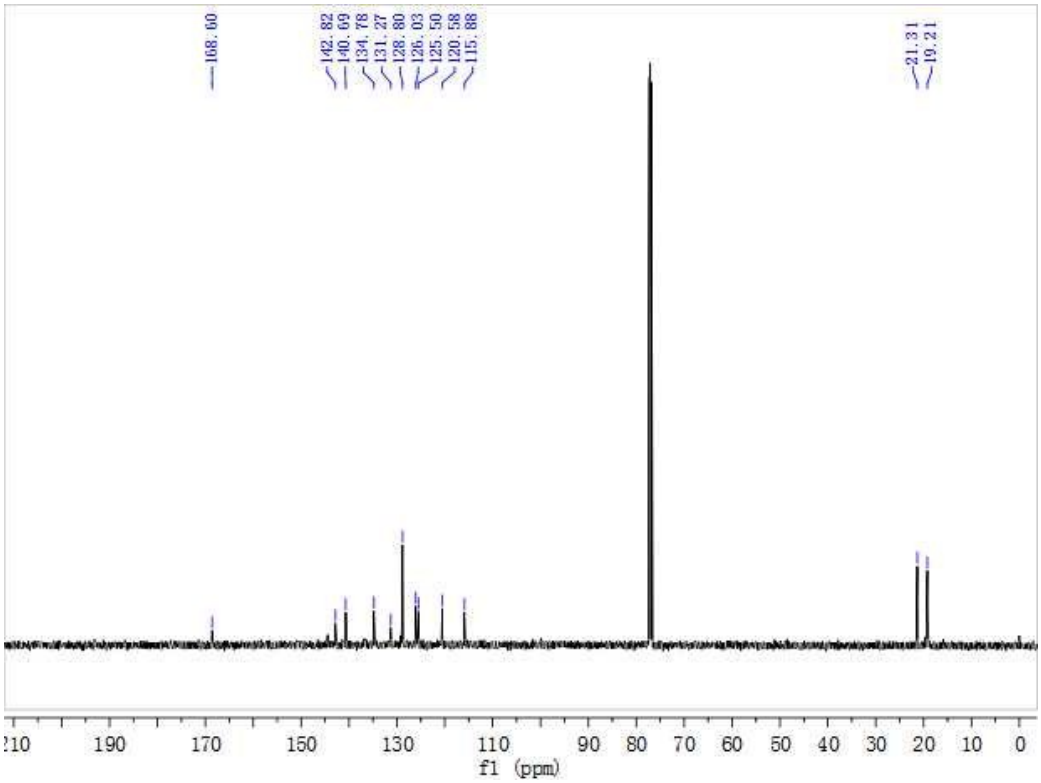

8.30
8.13
8.12
8.11
8.11
7.84
7.82
7.82
7.43
7.43
7.43
7.42
7.42
7.41
7.41
7.39
7.38
6.98
3.99
3.94
1.00
0.98
1.02
4.00
1.00
2.99
3.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

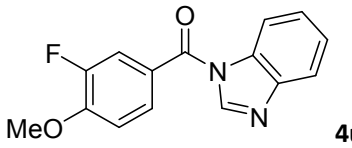

166.46
153.55
149.46
144.04
143.16
132.34
125.56
125.06
124.87
124.19
120.50
115.28
112.42
110.53
56.25
56.20
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
N
N

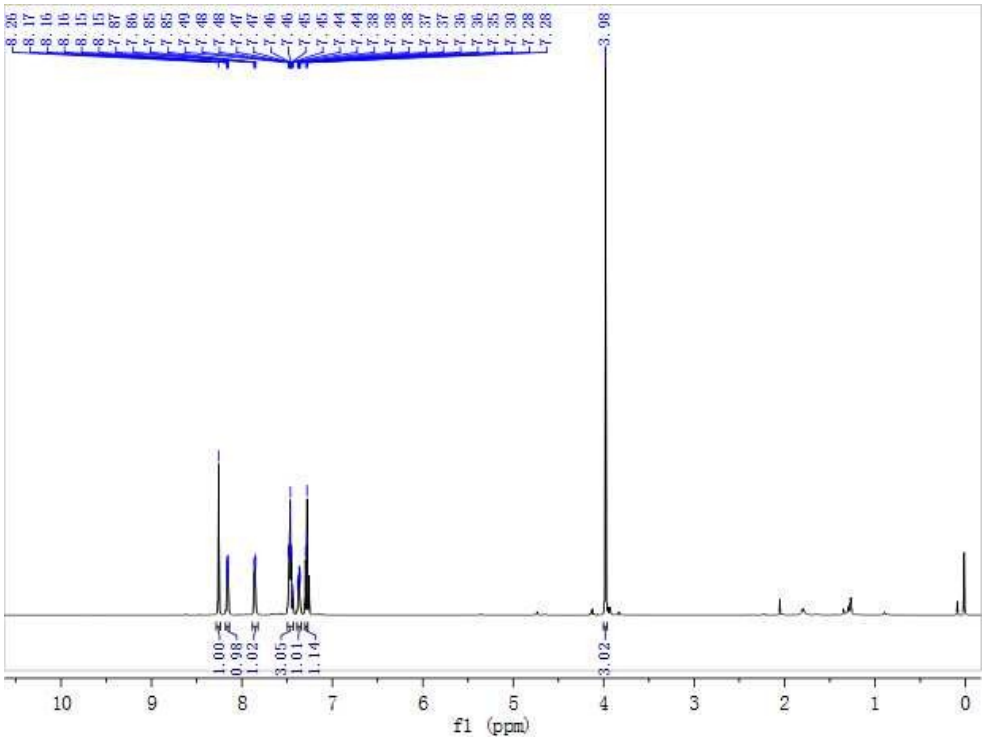
4ta

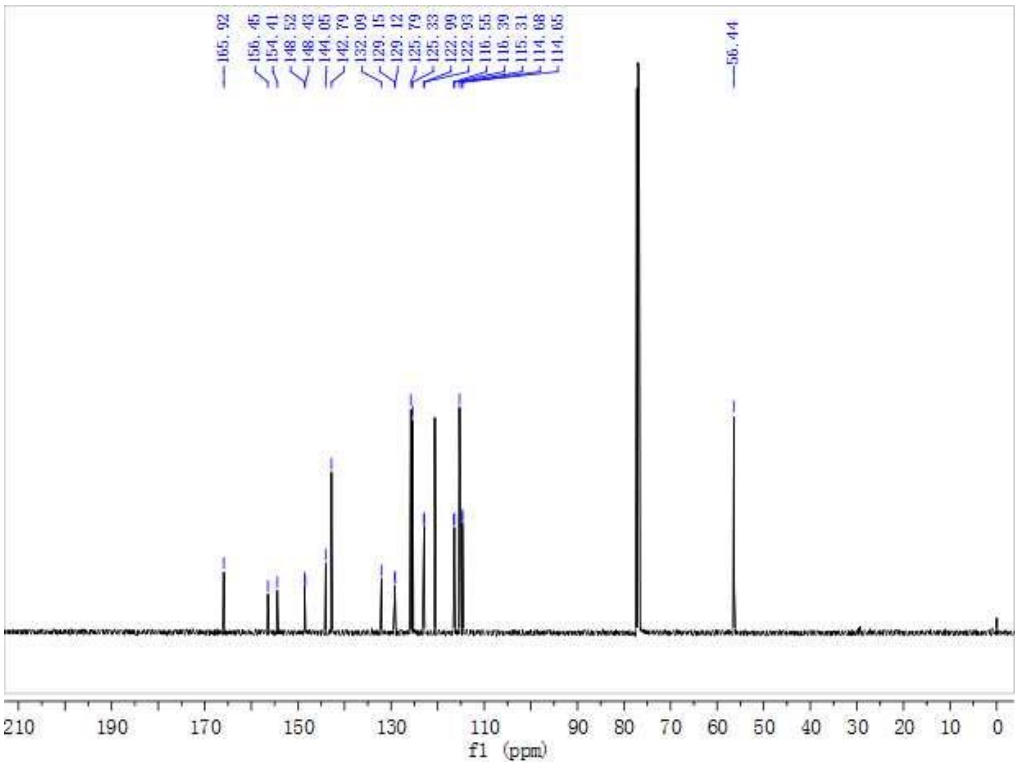

8.49
8.48
7.83
7.81
7.69
7.50
7.47
2.37
2.21
1.00
1.16
0.98
2.02
2.11
3.13
6.13
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

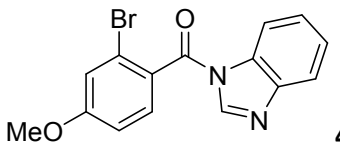

168.60
142.82
140.69
134.78
131.27
128.80
126.03
125.50
120.58
115.88
21.31
19.21
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
F
N
N
MeO

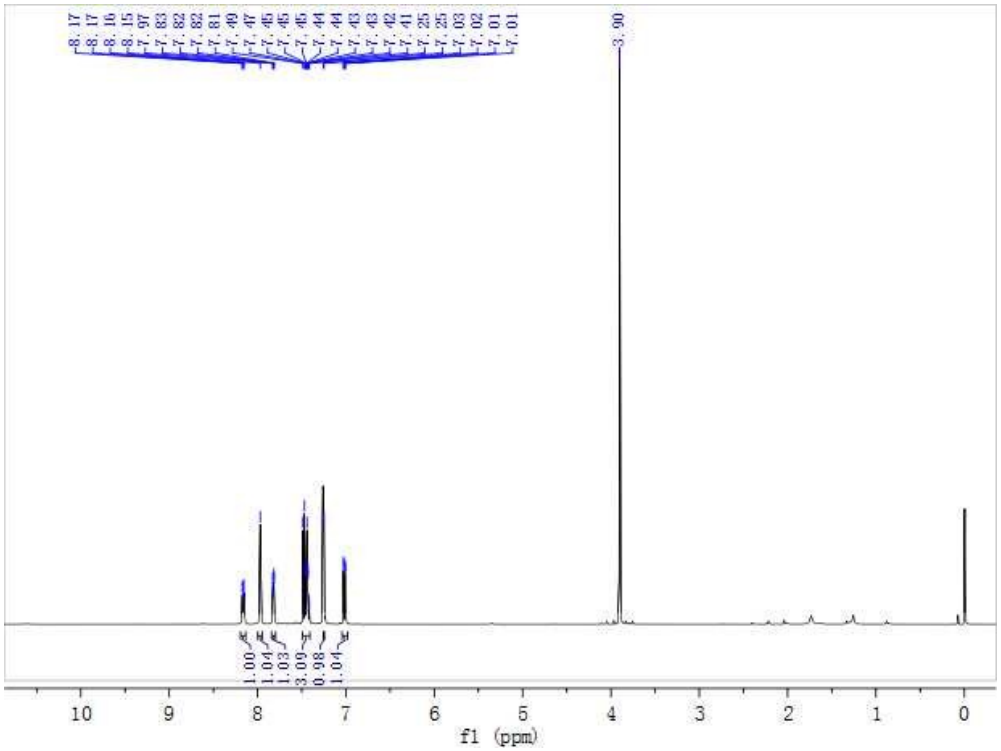
4ua

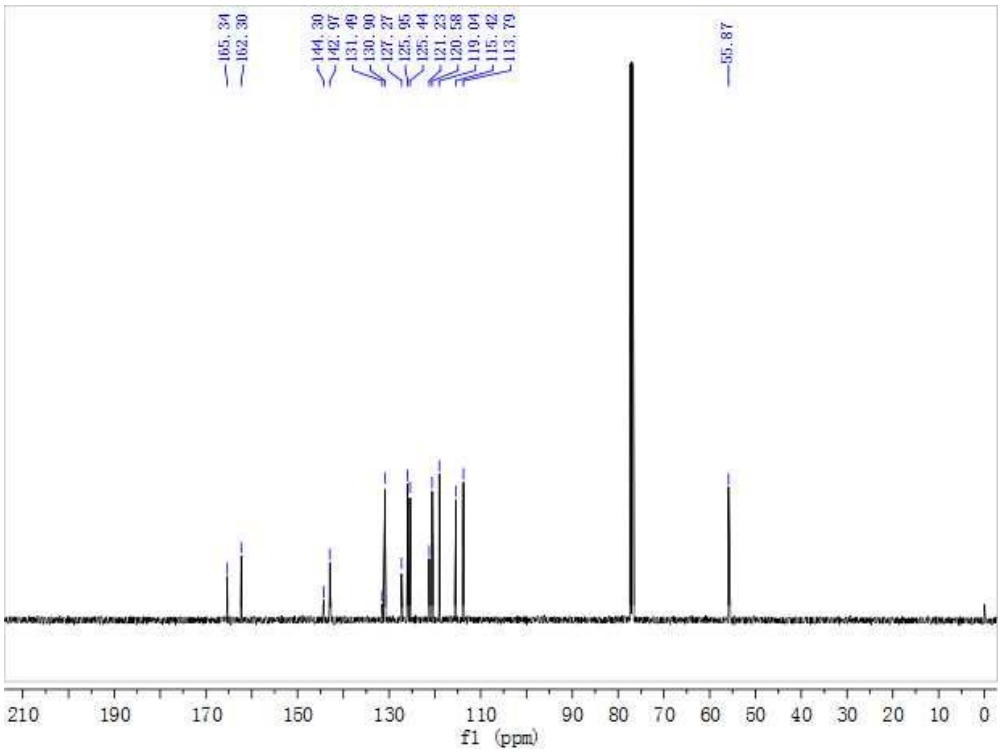

8.20
8.17
8.16
8.16
8.15
8.15
7.87
7.86
7.85
7.85
7.49
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.30
7.28
7.28
3.98
1.00
0.98
1.02
3.05
1.01
1.14
3.02
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

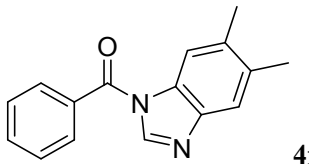

165.92
156.45
154.41
148.52
148.43
144.05
142.79
132.09
129.15
129.12
125.79
125.33
122.99
122.93
116.55
116.39
115.31
114.68
114.65
56.44
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Br
O
N
N
MeO

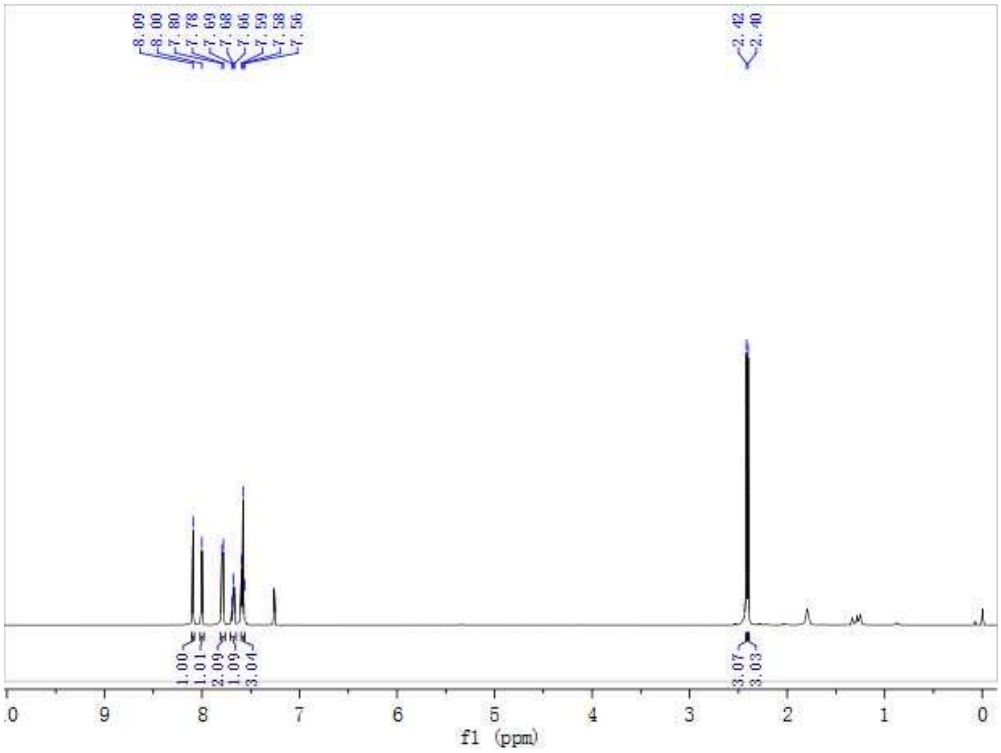
4va

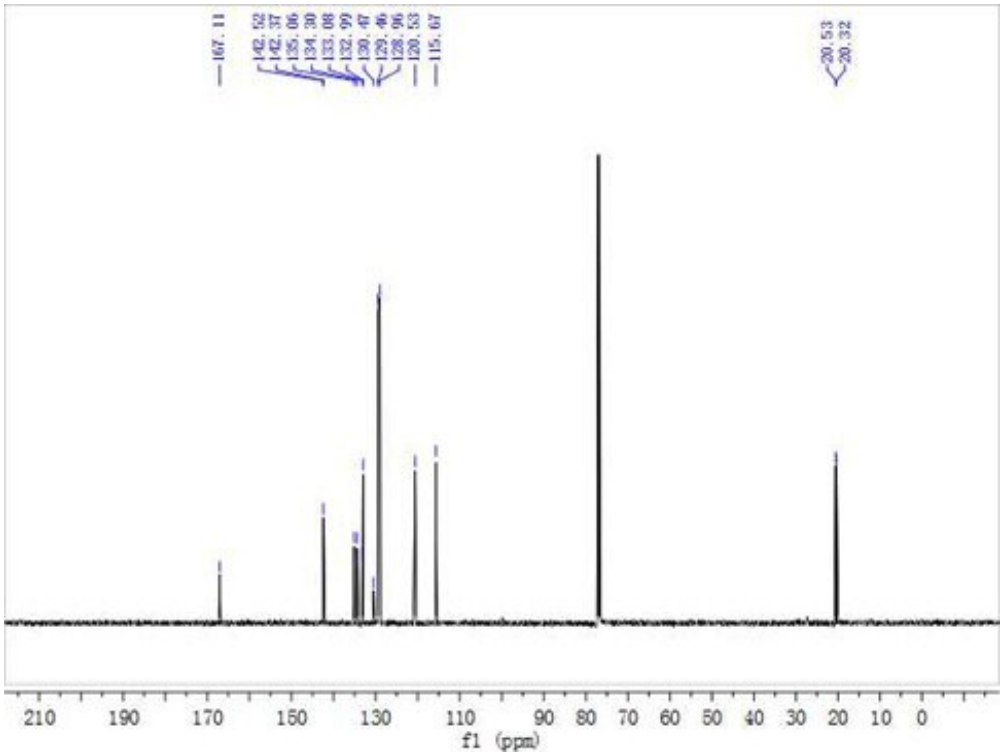

8.17
8.17
8.16
8.15
7.97
7.83
7.82
7.82
7.81
7.49
7.47
7.45
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.41
7.25
7.03
7.02
7.01
7.01
3.90
1.00
1.04
1.03
3.09
0.98
1.04
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

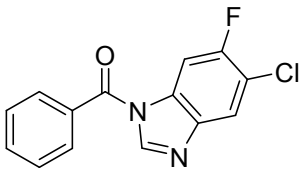

165.34
162.30
144.30
142.97
131.49
130.90
127.27
125.95
125.44
121.23
120.58
119.04
115.42
113.79
55.87
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



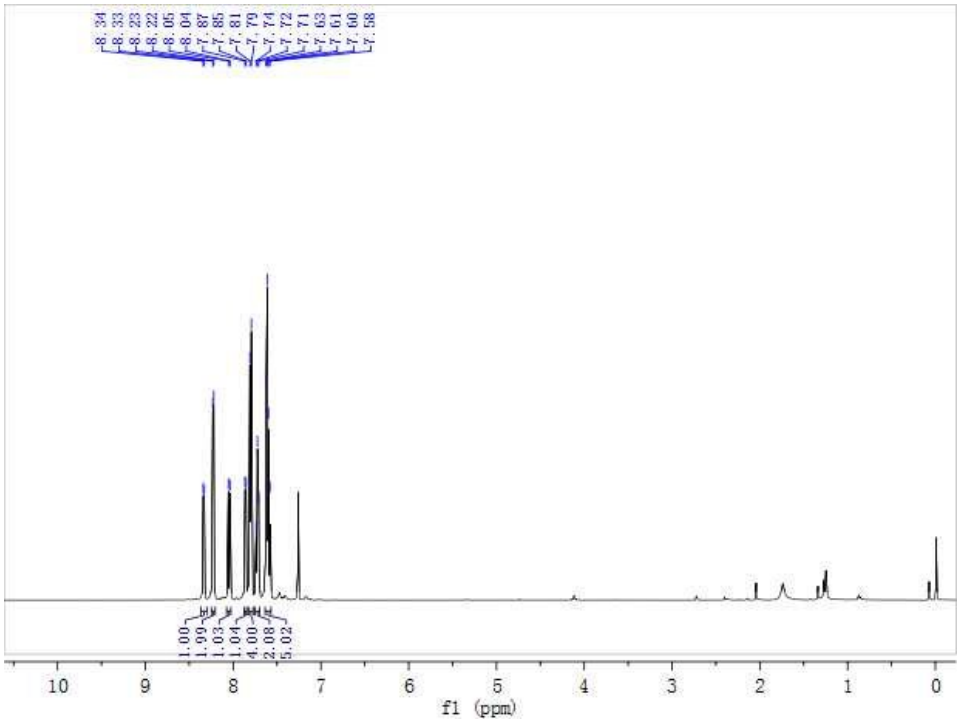
4fc

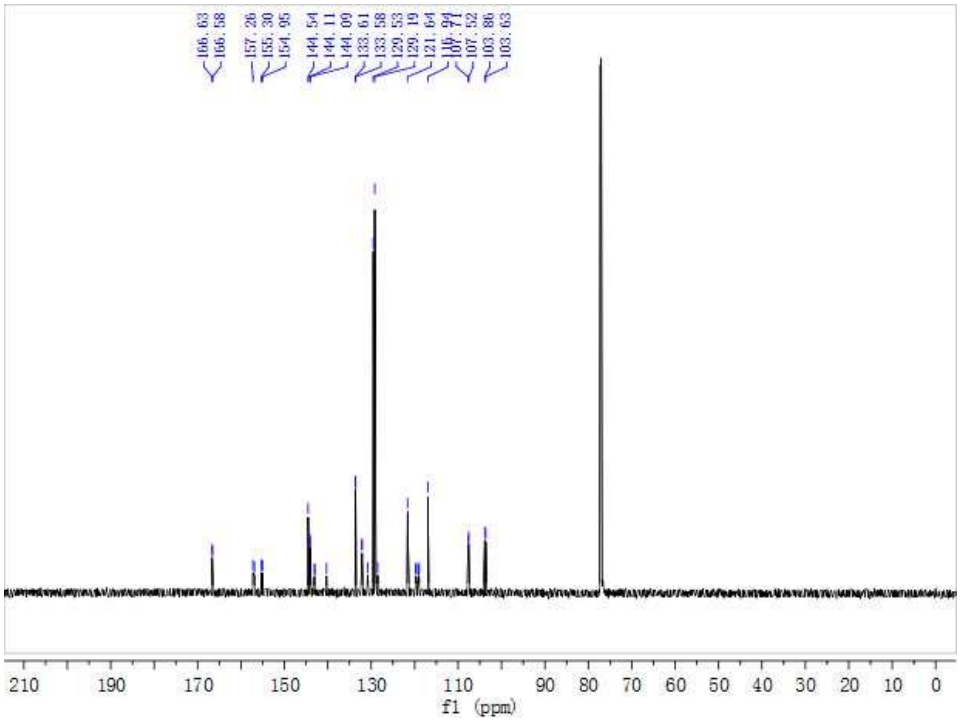

8.09
8.00
7.80
7.78
7.69
7.68
7.66
7.59
7.58
7.56
2.42
2.40
1.00
1.01
2.09
1.09
3.04
3.07
3.03
f1 (ppm)


167.11
142.52
142.37
135.06
134.30
133.08
132.99
130.47
129.46
128.96
120.53
115.67
20.53
20.32
f1 (ppm)


F
O
Cl
N
N

4fg


8.34
8.33
8.23
8.22
8.05
8.04
7.87
7.85
7.81
7.79
7.74
7.72
7.71
7.63
7.61
7.60
7.58
1.00
1.99
1.03
1.04
4.00
2.08
5.02
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


166.63
166.58
157.26
155.30
154.95
144.54
144.11
144.09
133.61
133.58
129.53
129.19
121.64
110.94
110.77
107.52
103.86
103.63
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)