Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Rhodium-Catalyzed Tandem Acylmethylation/Annulation of N-nitrosoanilines with Sulfoxonium Ylides for the Synthesis of Substituted Indazole N-Oxides

State Key Laboratory of Applied Organic Chemistry, Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, Department of Chemistry, Lanzhou University, Lanzhou 730000, China. E-mail: hgs@lzu.edu.cn

Contents

1. General information and materials 2
2. Synthesis of substrates.....3
3. Mechanitic studies.....3
4. Preparation and characterization data of products.....3
5. Copies of ^{1}H and ^{13}C NMR spectrum of products.....23

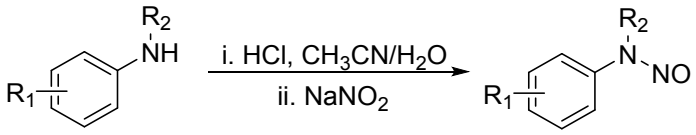
1. General information and materials

Reagent: All the reactions were carried out under inert atmosphere. All the solvents used for the reactions were dried according to standard procedures. All commercial materials were used as received unless otherwise noted. $[Cp^*RhCl_2]_2$, Ag_2O, $Cu(OAc)_2$, were used in Rh-catalyzed reactions. The starting materials N-nitrosoanilines [1], sulfoxonium ylides[2] and [D5]-N-nitrosoanilines [3] were prepared according to the reported procedure. All the reactions were monitored by thin layer chromatography (TLC, Silica gel Merck 60 F 254); The spots were visualized by UV light. Purification of products was conducted by flash chromatography on silica gel.

Instruments: NMR spectra were recorded on Bruker Ultrashield™ 400 MHz. Chemical shifts were given relative to $CDCl_3$ (7.26 ppm for ^1H NMR, 77.00 ppm for ^{13}C NMR). For the characterization of the observed signal multiplicities, the following abbreviations were applied: s (singlet), d (doublet), dd (double doublet), t (triplet), td (triple doublet), q (quartet), m (multiplet), as well as br (broad); High resolution ESI mass experiments were operated on a Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS instrument.

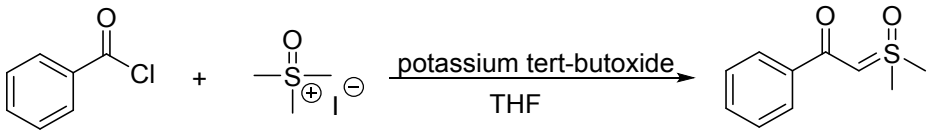
2. Synthesis of Substrates

2.1 General procedure for preparation of N-nitroso aniline substrates[1]



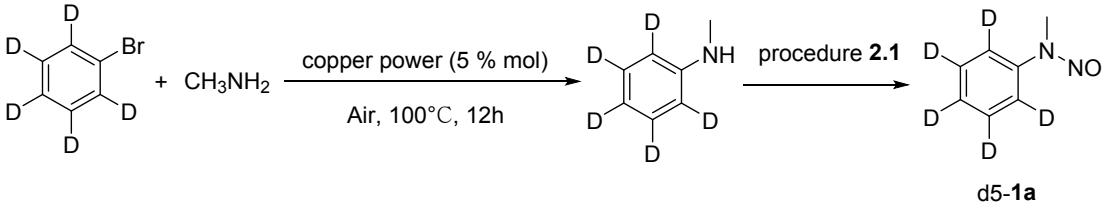
The aniline (0.05 mol, 1.0 equiv) was dissolved in a 1:2 mixture of acetonitrile and water (30.0 mL) and cooled to 0 °C (ice bath). Concentrated aqueous HCl (7.3 mL, 0.24 mol) was added dropwise. The mixture was stirred vigorously for half an hour, while maintained at 0 °C. To this mixture was added an aqueous solution (13.0 mL) of $NaNO_2$ (3.5 g, 0.05 mol) over the course of 10 min. The reaction was allowed to proceed for 1h. The mixture was then extracted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4, concentrated under reduced pressure, and purified by flash silica gel column chromatography (petroleum ether / ethyl acetate = 20:1) to give the corresponding N-nitroso aniline substrates **1**.

2.2 General procedure for preparation of sulfoxonium ylides[2]



In a 250 mL flame-dried round bottom flask attached to a reflux condenser, under argon atmosphere, 6.0 g of potassium tert-butanolate (54.4 mmol, 4.0 equiv) and 60.0 mL of anhydrous THF was added. Then, 8.9 g of trimethylsulfoxonium iodide (40.8 mmol, 3.0 equiv) was added in one portion. The suspension was heated at reflux and maintained for 2 hours. After this time, the mixture was cooled to 0 °C, followed by slow addition of a 1.0 M solution of the benzoyl chlorides (13.6 mmol, 1.0 equiv) in anhydrous THF. The reaction mixture was allowed to warm to room temperature and stirred for additional 3 hours. Next, the solvent was removed on a rotary evaporator, 15.0 mL of water was added and the product extracted with EtOAc (3 ×50 mL). The organic phase was washed with saturated NaCl solution (2 ×10 mL) and dried over with Na_2SO_4. The crude product was purified by recrystallization with EtOAc.

2.3 General procedure for preparation of [D5]-N-nitrosoanilines[3]



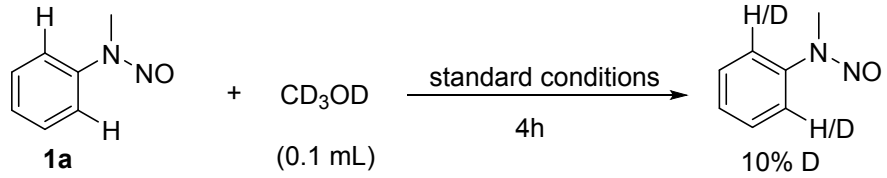
Bromobenzene-d 5 (5 mmol, 0.805 g), 30 % aqueous methylamine solution (2.7 mL,

25 mmol), copper power (0.016 g, 5 mol %) was combined in a 30 mL screwed sealed tube and placed in an oil bath under Air atmosphere. The reaction mixture was magnetically stirred and heated to 100 °C for 12 h. When the reaction completed or underwent to the time, the reaction mixture was cooled to room temperature and ethyl acetate (20 mL) was added to extract the d5 -1a. The organic layer was separated and the aqueous layer was extracted by ethyl acetate (3×10 mL). The combined organic phase was washed with brine and dried over Mg_2SO_4. The organic layer was evaporated in vacuum and the crude product was purified by flash column chromatography (Petroleum ether /EtOAc = 10:1) to give **d5 -1a**.

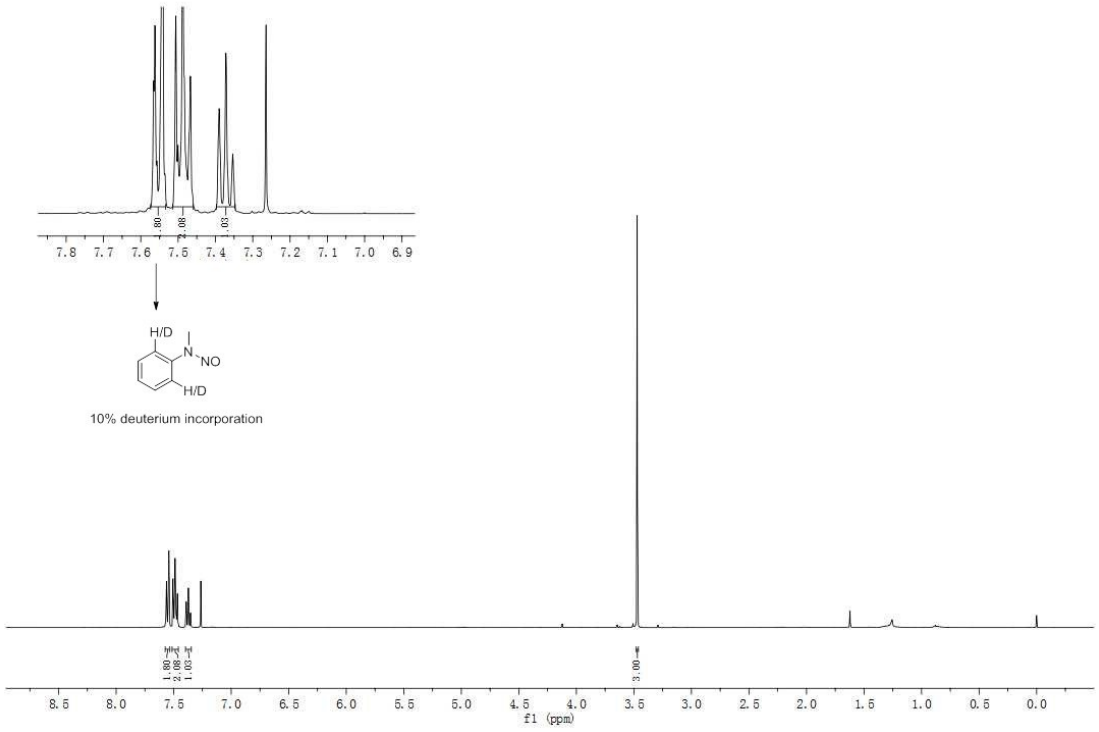
[1] B. Liu, Y. Fan, Y. Gao, C. Sun, C. Xu, J. Zhu, *J. Am. Chem. Soc.* **2013**, *135*, 468.
[2] Barday, M.; Janot, C.; Halcovitch, N. R.; Muir, J.; Aïssa, C. *Angew. Chem. Int. Ed*. 2017, **56**, 13117.
[3] Jiao, J.; Zhang, X. R.; Chang, N. H.; Wang, J.; Wei, J. F.; Shi, X. Y.; Chen, Z. G. *J. Org. Chem*. **2011**, *76*, 1180-1183.

3. Mechanitic studies

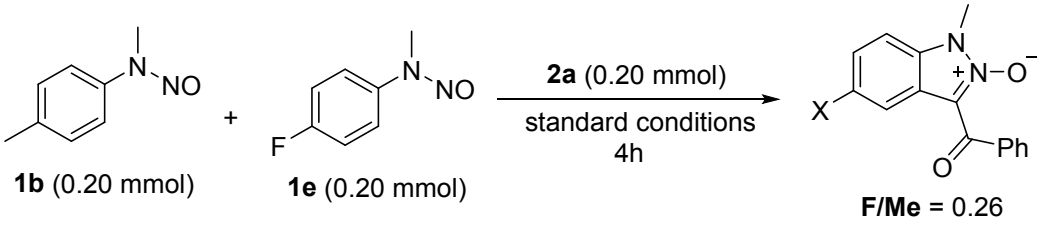
(a) C-H activation reversibility



A mixture of N-methyl-N-phenylnitrous amide (1a, 0.20 mmol), CD_3OD (0.1mL), $Cp^*Rh(OAc)_2 \cdot H_2O$ (10 mol%), $Cu(OAc)_2$ (0.5 equiv), Ag_2O (1.0 equiv) in TFE (2 mL) was stirred at 100 °C for 4 hours. After cooling down, the volatiles were removed and the mixture was purified by flash chromatography of silica gel (eluent: Petroleum ether / Ethyl acetate = 10/1), the deuterium incorporation was estimated to be 10% at ortho position of phenyl by 1H NMR analysis.

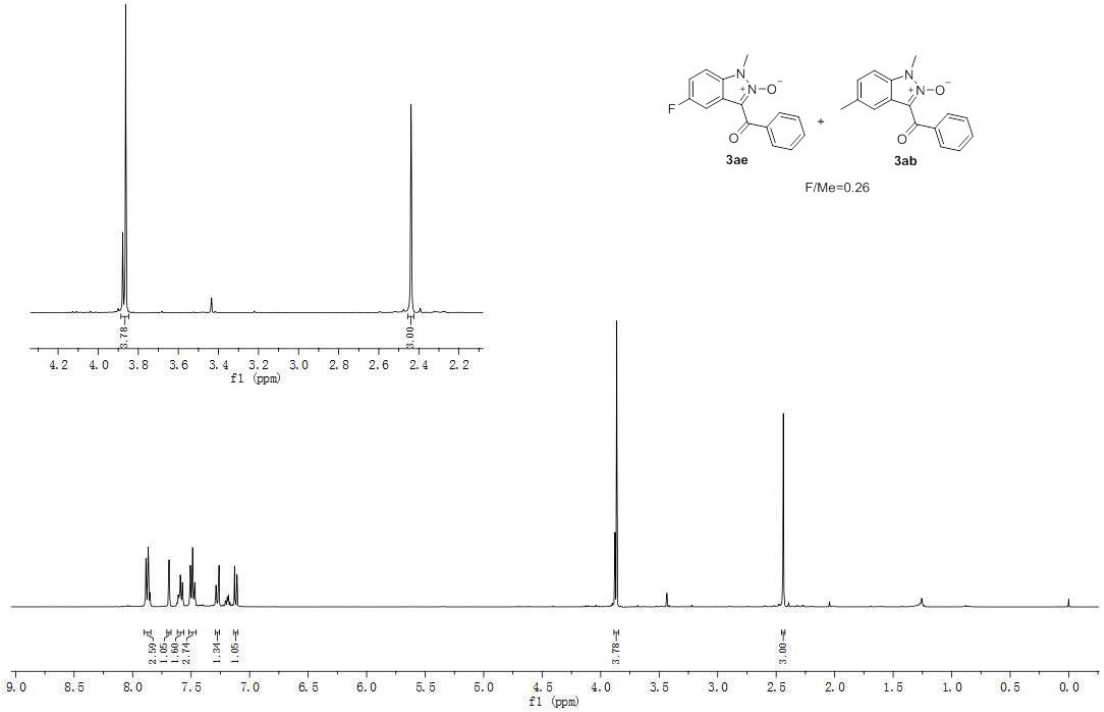


(b) Competition study of substrates with different electronic characteristics

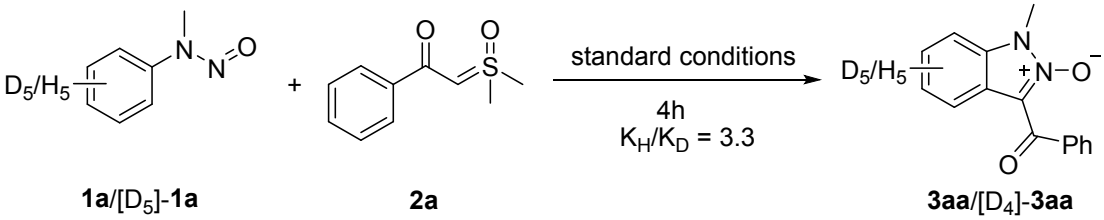


An mixture of **1b** (0.20 mmol), **1e** (0.20 mmol), sulfoxonium ylides **2a** (0.20 mmol), $Cp^*Rh(OAc)_2 \cdot H_2O$ (10 mol%), $Cu(OAc)_2$ (0.5 equiv), Ag_2O (1.0 equiv) in TFE (2 mL)

was stirred at 100 °C for 4 hours. After cooling down, the volatiles were removed and the mixture was purified by flash chromatography of silica gel (eluent: Petroleum ether / Ethyl acetate = 2/1) to give a mixture of products **3ae** and **3ab** at a ratio of 0.26:1.

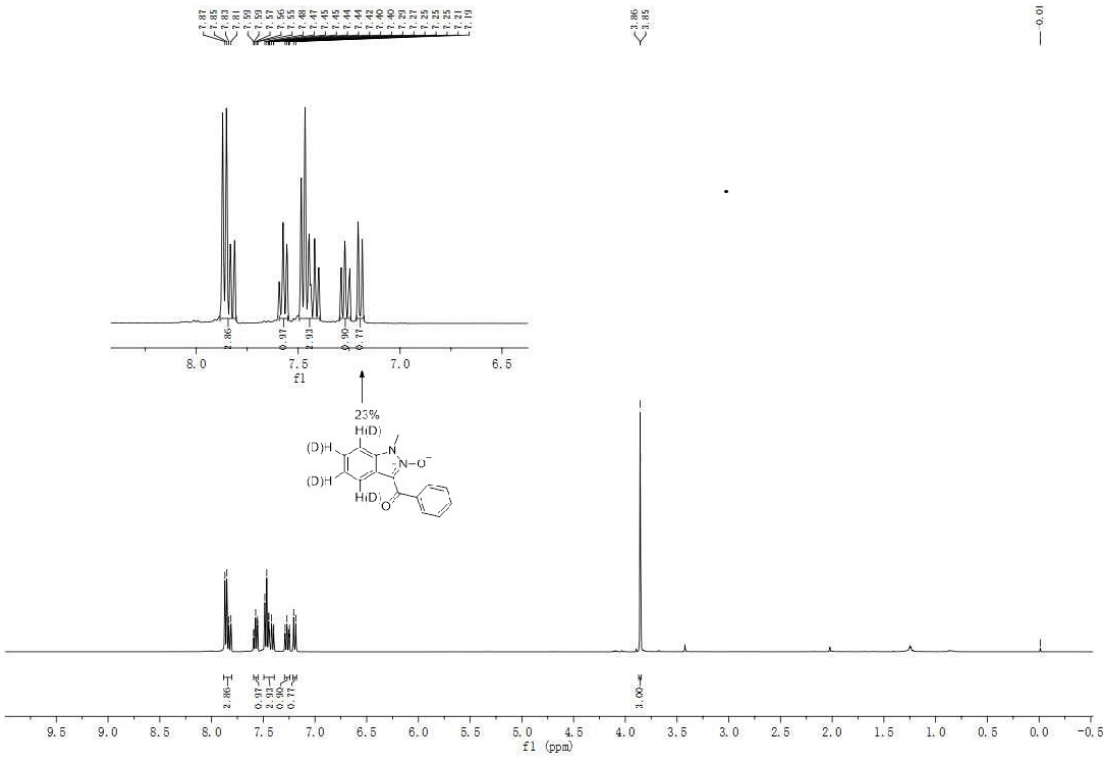


(c) Kinetic isotope study

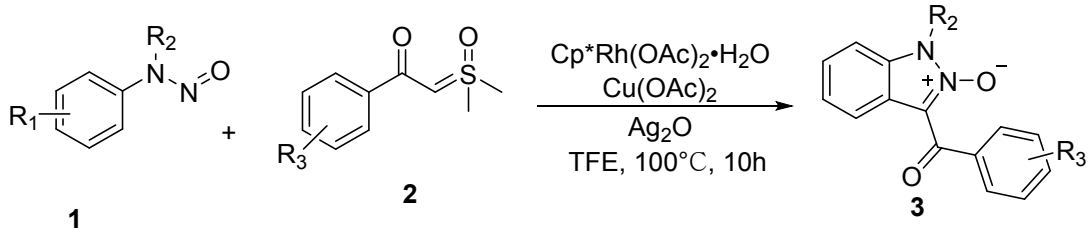


1a/[D_5]-**1a** **2a** **3aa**/[D_4]-**3aa**

An equimolar mixture of **1a** and [D_5]-1a (0.40 mmol in total), sulfoxonium ylide **2a** (0.20 mmol), Cp*Rh(OAc)$_2$ ▪ H_2O (10 mol%), Cu(OAc)$_2$ (0.5 equiv), Ag_2O (1.0 equiv) in TFE (2 mL) was stirred at 100 °C for 4 hours. After cooling down, the volatiles were removed and the mixture was purified by flash chromatography of silica gel (eluent : Petroleum ether / Ethyl acetate = 2/1). KIE value (k_H /k_D = 3.3) was determined on the basis of ^{1}H NMR analysis.

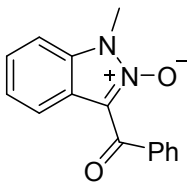


4. Preparation and characterization Data of Products



1a (0.1 mmol), Cp*Rh(OAc)$_2$▪H_2O (10 mol %), Ag_2O (1.0 equiv), Cu(OAc)$_2$ (0.5equiv), and freshly prepared sulfoxonium ylides **2a** (0.15 mmol) were weighed into a pressure tube, to which was added TFE (2.0 mL) under air . The reaction mixture was stirred for 10 h at 100℃. Purification was performed by flash column chromatography on silica gel using EtOAc and petroleum ether to afford the product **3aa** as a yellow oil.

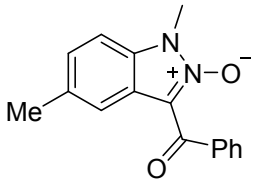
3-benzoyl-1-methyl-1H-indazole 2-oxide (3aa)



Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3aa** as a Yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.91 – 7.82 (m, 3H), 7.63 – 7.56 (m, 1H), 7.52 – 7.41 (m, 3H), 7.29 (m, 1H), 7.22 (d, *J* = 8.1 Hz, 1H), 3.88 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ =185.77 (s), 137.09 (s), 132.91 (s), 130.76 (s), 129.10 (s), 128.16 (s), 126.61 (s), 124.00 (s), 121.47 (s), 120.26 (s), 118.60 (s), 107.14 (s), 28.98 (s).**HRMS (ESI)**: calcd for $C_{15}H_{13}N_2O_2$; $[M+H]^+$ 253.0972, found: 253.0976.

3-benzoyl-1,5-dimethyl-1H-indazole 2-oxide (3ab)

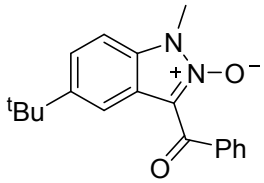


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3ab** as a Yellow solid，mp: 160-163℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.90 – 7.86 (m, 2H), 7.70 (s, 1H), 7.60 (m, 1H), 7.49 (m, 2H), 7.28 (m, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 3.87 (s, 3H), 2.44 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ= 186.03 (s), 137.20 (s), 134.04 (s), 132.87 (s), 129.25 (s), 129.13(s), 128.33 (s), 128.15 (s),121.39 (s), 119.76 (s), 118.87 (s), 106.95 (s), 29.10 (s), 21.49 (s).

HRMS (ESI): calcd for $C_{16}H_{15}N_2O_2$; $[M+H]^+$ 267.1128, found: 267.1133.

3-benzoyl-5-(tert-butyl)-1-methyl-1H-indazole 2-oxide (3ac)

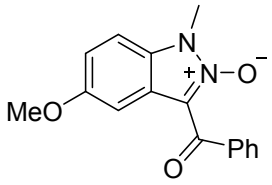


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 1: 1 gave **3ac** as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.88 (d, *J* = 8.4 Hz, 3H), 7.62 – 7.46 (m, 4H), 7.17 (d, *J* = 8.8 Hz, 1H), 3.87 (s, 3H), 1.35 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ= 186.10 (s), 147.57 (s), 137.32 (s), 132.85 (s), 129.26 (s), 129.16 (s), 128.17 (s), 125.08 (s), 121.81 (s), 118.67 (s), 116.27 (s), 106.86 (s), 34.94 (s), 31.48 (s), 29.09 (s).

HRMS (ESI): calcd for $C_{19}H_{20}N_2O_2$; $[M+H]^+$ 309.1598, found: 309.1600.

3-benzoyl-5-methoxy-1-methyl-1H-indazole 2-oxide (3ad)

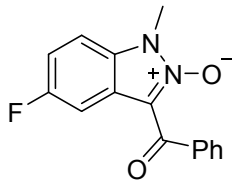


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 1: 1 gave **3ac** as a brown solid, mp: 127-130℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.90 – 7.85 (m, 2H), 7.59 (m, 1H), 7.49 (m, 2H), 7.38 (d, *J* = 2.2 Hz, 1H), 7.11 (m, 2H), 3.87 (s, 3H), 3.84 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ= 186.22 (s), 157.29 (s), 137.26 (s), 132.80 (s), 125.78 (s), 121.84 (s), 119.56 (s), 118.10 (s), 117.50 (s), 108.79 (s), 108.20 (s), 100.69 (s), 55.59 (s), 29.13 (s).

HRMS (ESI): calcd for $C_{16}H_{15}N_2O_3$; $[M+H]^+$ 283.1077, found: 283.1082.

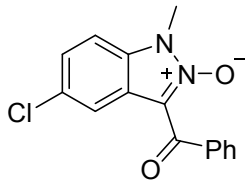
3-benzoyl-5-fluoro-1-methyl-1H-indazole 2-oxide (3ae)



Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3ad** as a light yellow solid, mp: 155-158℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.86 (m, 2H), 7.63 – 7.57 (m, 2H), 7.49 (m, 2H), 7.20 (m, 2H), 3.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ =185.59 (s), 160.04 ($^1J_{C,F}$ =241,d), 136.93 (s), 133.04 (s), 129.08 (s), 128.24 (d, $^2J_{C,F}$ = 14.5 Hz), 127.32 (s), 119.41 (d, $^3J_{C,F}$ = 11.8 Hz), 115.51 (s), 108.43 (s), 106.15 (s),105.76 (s), 29.30 (s). **HRMS (ESI)**: calcd for C_{15} $H_{12}F$ N_2O_2; $[M+H]^+$ 271.0878, found: 271.0877.

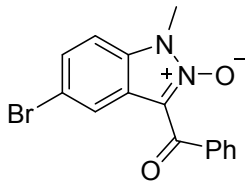
3-benzoyl-5-chloro-1-methyl-1H-indazole 2-oxide (3af)



Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3ae** as a Yellow solid, mp: 190-193℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.87 (m, 3H), 7.60 (m, 1H), 7.49 (m, 2H), 7.39 (m, 1H), 7.15 (m, 1H), 3.86 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ= 185.44 (s), 136.75 (s), 133.08 (s), 129.94 (s), 129.08 (s), 128.13 (s), 127.10 (s), 121.11 (s), 119.75 (s), 108.45 (s), 108.21 (s), 29.20 (s). **HRMS (ESI)**: calcd for C_{15} $H_{12}Cl$ N_2O_2; $[M+H]^+$ 287.0582, found: 287.0586.

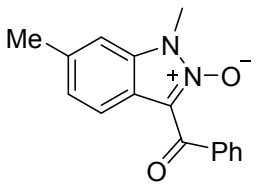
3-benzoyl-5-bromo-1-methyl-1H-indazole 2-oxide (3ag)



Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3af** as a Yellow solid, mp: 208-210℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.06 (d, *J* = 1.8 Hz, 1H), 7.85 (m, 2H), 7.63 – 7.57 (m, 1H), 7.51 (m, 3H), 7.10 (d, *J* = 8.7 Hz, 1H), 3.86 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ= 185.44 (s), 136.72 (s), 133.12 (s), 129.67 (s), 129.38 (s), 129.08 (s), 128.21 (s), 122.76 (s), 120.89 (s), 120.12 (s), 117.35 (s), 108.59 (s), 29.18 (s). **HRMS (ESI)**: calcd for C_{15} $H_{12}Br$ N_2O_2; $[M+H]^+$ 331.0077, found: 331.0083.

3-benzoyl-1,6-dimethyl-1H-indazole 2-oxide (3ah)

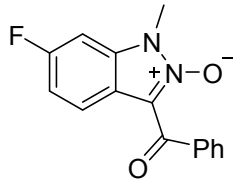


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3ah** as a light yellow solid, mp: 150-154℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.87 (m, 2H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.49 (m, 2H), 7.13 (d, *J* = 8.3 Hz, 1H), 7.02 (s, 1H), 3.86 (s, 3H), 2.50 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ =185.86 (s), 137.25 (s), 132.71 (s), 131.22 (s), 129.15 (s), 128.19 (s), 127.84 (s), 121.60 (s), 119.99 (s), 116.45 (s), 106.55 (s), 106.33 (s), 28.81 (s), 22.12 (s).

HRMS (ESI): calcd for $C_{16}H_{15}N_2O_2$; $[M+H]^+$ 267.1128, found: 267.1132.

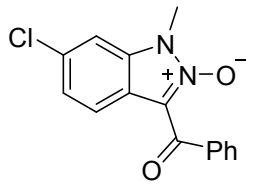
3-benzoyl-6-fluoro-1-methyl-1H-indazole 2-oxide (3ai)



Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3ai** as a light yellow solid, mp: 145-150℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.95 – 7.90 (m, 2H), 7.64 – 7.59 (m, 1H), 7.52 – 7.45 (m, 2H), 7.39 (m, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.94 (m, 1H), 3.91 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ= 184.59 (s), 153.87 (d, $^1J_{C,F}$ =254), 152.60 (s), 136.40 (s), 133.77 (s), 132.74 (d, $^2J_{C,F}$ = 8.3 Hz), 129.68 (s), 128.45 (s), 127.59 (d, $^3J_{C,F}$ = 7.7 Hz), 109.16 (d, $^4J_{C,F}$ = 19.2 Hz), 107.70 ($^5J_{C,F}$ =9.0), 103.39 (s), 77.32 (s), 29.35 (s). **HRMS (ESI)**: calcd for $C_{15}H_{12}FN_2O_2$; $[M+H]^+$ 271.0878, found: 271.0886.

3-benzoyl-6-chloro-1-methyl-1H-indazole 2-oxide (3aj-1)

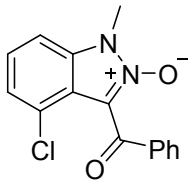


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3aj-1** as a Yellow solid, mp: 112-115℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.89 – 7.85 (m, 2H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.49 (m, 2H), 7.26 (m, 2H), 3.87 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ= 185.68 (s), 136.96 (s), 133.25 (s), 131.38 (s), 129.30 (s), 128.43 (s), 124.93 (s), 121.75 (s), 121.57(s), 117.32 (s), 107.29 (s), 29.23 (s).

HRMS (ESI): calcd for $C_{15}H_{12}ClN_2O_2$; $[M+H]^+$ 287.0582, found: 287.0587.

3-benzoyl-4-chloro-1-methyl-1H-indazole 2-oxide (3aj-2)

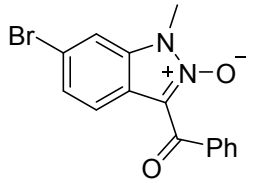


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3aj-2** as a colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.96 – 7.92 (m, 2H), 7.66 – 7.60 (m, 1H), 7.52 – 7.47 (m, 2H), 7.41 – 7.35 (m, 1H), 7.25 – 7.21 (m, 1H), 7.16 (m, 1H), 3.92 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ= 136.60 (s), 134.35 (s), 132.26 (s), 130.03 (s), 128.81 (s), 127.34 (s), 124.90 (s), 124.21 (s), 120.74 (s), 116.59 (s), 105.84 (s), 29.25 (s).

HRMS (ESI): calcd for $C_{15}H_{12}ClN_2O_2$; $[M+H]^+$ 287.0582, found: 287.0581.

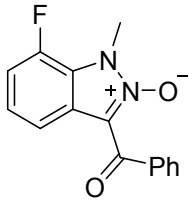
3-benzoyl-6-bromo-1-methyl-1H-indazole 2-oxide (3ak)



Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3ak** as a Yellow solid, mp: 168-170℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.88 – 7.84 (m, 2H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.60 (m, 1H), 7.49 (m, 2H), 7.40 (m, 2H), 3.85 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ =185.47 (s), 136.80 (s), 133.01 (s), 131.47 (s), 129.17 (s), 128.01 (s), 127.10 (s), 121.79 (s), 120.71 (s), 117.52 (s), 110.39 (s), 109.75 (s), 29.02 (s). **HRMS (ESI)**: calcd for $C_{15}H_{12}Br\ N_2O_2$; $[M+H]^+$ 331.0077, found: 331.0082.

3-benzoyl-7-fluoro-1-methyl-1H-indazole 2-oxide (3al)

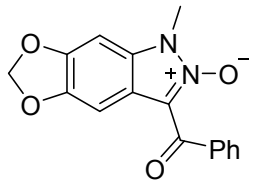


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3al** as a Yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.89 – 7.85 (m, 3H), 7.67 – 7.59 (m, 3H), 7.53 – 7.47 (m, 3H), 7.24 – 7.11 (m, 3H), 4.06 (d, *J* = 0.7 Hz, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ =185.61 (s), 145.88 (d, $^1J_{C,F}$ =244), 144.66 (s), 136.75 (s), 133.19 (s), 129.19 (s), 128.28 (s), 124.13 (d, *J* = 6.0 Hz), 121.72 (s), 121.37 (s), 119.85 (d, *J* = 12.0 Hz), 116.17 (d, *J* = 4.0 Hz), 112.09 (s), 111.92 (s), 31.46 (s).

HRMS (ESI): calcd for $C_{15}H_{12}F\ N_2O_2$; $[M+H]^+$ 271.0878, found: 271.0882.

3-benzoyl-1-methyl-1H-[1,3]dioxolo[4,5-f]indazole 2-oxide (3am)

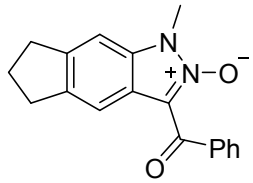


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3am** as a Yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.94 – 7.90 (m, 2H), 7.62 – 7.56 (m, 1H), 7.50 – 7.45 (m, 2H), 7.08 – 7.04 (m, 1H), 6.71 – 6.66 (m, 1H), 6.06 (s, 2H), 3.85 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ =184.72 (s), 144.01 (s), 137.73 (s), 136.53 (s), 133.30 (s), 129.64 (s), 128.15 (s), 119.85 (s), 109.04 (s), 104.60 (s), 102.03 (s), 99.51 (s), 60.37 (s), 29.39 (s).

HRMS (ESI): calcd for $C_{16}H_{13}N_2O_4$; $[M+H]^+$ 297.0870, found: 297.0879.

3-benzoyl-1-methyl-1,5,6,7-tetrahydrocyclopenta[f]indazole 2-oxide (3an)

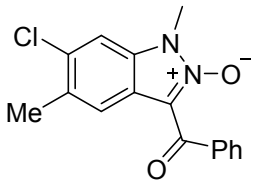


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3an** as a Yellow solid, mp: 185-187℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.87 (m, 2H), 7.68 (s, 1H), 7.61 – 7.55 (m, 1H), 7.48 (m, 2H), 7.06 (s, 1H), 3.85 (s, 3H), 3.02 (m, 2H), 2.96 (m, 2H), 2.12 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ =186.09 (s), 144.50 (s), 141.32 (s), 137.40 (s), 132.75 (s), 130.51 (s), 129.63 (s), 129.14 (s), 128.13 (s), 117.71 (s), 115.21 (s), 102.74 (s), 33.06 (s), 32.42 (s), 28.95 (s), 26.01 (s).

HRMS (ESI): calcd for $C_{18}H_{17}N_2O_2$; $[M+H]^+$ 293.1285, found: 293.1291.

3-benzoyl-6-chloro-1,5-dimethyl-1H-indazole 2-oxide (3ao-1)

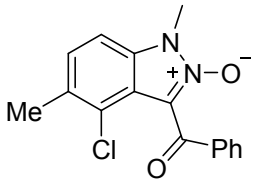


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3ao-1** as a Yellow solid, mp: 195-198℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.89 – 7.85 (m, 4H), 7.78 (s, 2H), 7.64 – 7.58 (m, 2H), 7.49 (m, 4H), 7.26 (d, *J* = 1.2 Hz, 3H), 3.84 (s, 6H), 2.45 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ= 185.76 (s), 136.92 (s), 133.95 (s), 133.07 (s), 132.39 (s), 129.90 (s), 129.14 (s), 128.22 (s), 121.59 (s), 121.24 (s), 117.53 (s), 107.48 (s), 29.20 (s), 20.41 (s).

HRMS (ESI): calcd for $C_{16}H_{14}ClN_2O_2$; $[M+H]^+$ 301.0739, found: 301.0741.

3-benzoyl-4-chloro-1,5-dimethyl-1H-indazole 2-oxide (3ao-2)

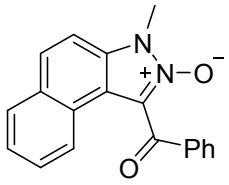


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3ao-2** as a Yellow solid, mp: 185-188℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.95 (m, 2H), 7.66 – 7.60 (m, 1H), 7.53 – 7.47 (m, 2H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 3.90 (s, 3H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ =186.05 (s), 136.58 (s), 134.20 (s), 131.10 (s), 130.63 (s), 129.88 (s), 129.33 (s), 128.77 (s), 123.67 (s), 120.62 (s), 116.87 (s), 105.64 (s), 29.18 (s), 19.54 (s).

HRMS (ESI): calcd for $C_{16}H_{14}ClN_2O_2$; $[M+H]^+$ 301.0739, found: 301.0747.

1-benzoyl-3-methyl-3H-benzo[e]indazole 2-oxide (3ap)

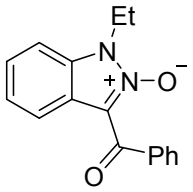


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3ap** as a Yellow solid, mp: 200-203℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.47 (s, 1H), 7.95 – 7.88 (m, 4H), 7.65 – 7.59 (m, 1H), 7.55 – 7.45 (m, 4H), 7.42 (m, 1H), 3.92 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ =185.76 (s), 137.25 (s), 132.84 (s), 132.17 (s), 130.84 (s), 130.64 (s), 129.02 (s), 128.71 (s), 128.18 (s), 127.29 (s), 126.17 (s), 124.55 (s),

120.83 (s), 119.22 (s), 102.52 (s), 29.18 (s). **HRMS (ESI)**: calcd for $C_{19}H_{15}N_2O_2$; $[M+H]^+$ 303.1128, found: 303.1130.

3-benzoyl-1-ethyl-1H-indazole 2-oxide (3aq)

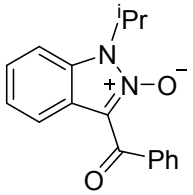


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3aq** as a Yellow solid, mp: 119-123℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.87 (m, 3H), 7.63 – 7.56 (m, 1H), 7.52 – 7.41 (m, 3H), 7.32 – 7.22 (m, 2H), 4.50 – 4.43 (m, 2H), 1.41 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ =185.89 (s), 137.13 (s), 132.86 (s), 129.98 (s), 129.12 (s), 128.12 (s), 126.56 (s), 123.90 (s), 121.52 (s), 120.33 (s), 118.78 (s), 107.07 (s), 37.79 (s), 12.95 (s).

HRMS (ESI): calcd for $C_{16}H_{15}N_2O_2$; $[M+H]^+$ 267.1128, found: 267.1136.

3-benzoyl-1-isopropyl-1H-indazole 2-oxide (3ar)

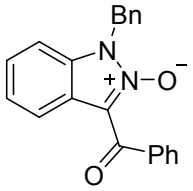


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3ar** as a Yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.90 – 7.85 (m, 3H), 7.59 (m, 1H), 7.49 (m, 2H), 7.43 – 7.41 (m, 2H), 7.31 – 7.25 (m, 1H), 5.52 (m, 1H), 1.68 – 1.63 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ =186.17 (s), 137.18 (s), 132.91 (s), 129.53 (s), 129.15 (s), 128.18 (s), 126.26 (s), 123.48 (s), 121.45 (s), 120.41 (s), 118.88 (s), 108.16 (s), 46.74 (s), 20.04 (s).

HRMS (ESI): calcd for $C_{17}H_{17}N_2O_2$; $[M+H]^+$ 281.1285, found: 281.1289.

3-benzoyl-1-benzyl-1H-indazole 2-oxide (3as)

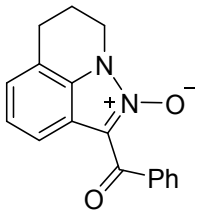


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3as** as a Yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.87 (m, 3H), 7.59 (m, 1H), 7.52 – 7.45 (m, 2H), 7.42 – 7.36 (m, 1H), 7.35 – 7.25 (m, 6H), 7.20 (m, 1H), 5.58 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ= 185.90 (s), 136.97 (s), 134.14 (s), 133.02 (s), 130.57 (s), 129.23 (s), 128.55 (s), 127.80 (s), 126.78 (s), 124.02 (s), 121.44 (s), 120.37 (s), 118.74 (s), 107.54 (s), 45.86 (s).

HRMS (ESI): calcd for $C_{21}H_{17}N_2O_2$; $[M+H]^+$ 329.1285, found: 329.1290.

2-benzoyl-7,8-dihydro-6H-pyrazolo[4,5,1-ij]quinoline 1-oxide (3at)

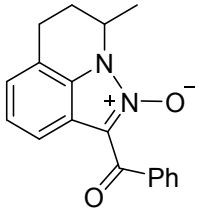


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3at** as a Yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.88 (m, 2H), 7.58 (m, 1H), 7.53 (m, 1H), 7.47 (m, 3H), 7.18 – 7.15 (m, 1H), 4.32 – 4.26 (m, 2H), 3.04 – 2.98 (m, 2H), 2.32 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ =185.76(s), 137.64 (s), 132.88 (s), 129.26 (s), 128.31 (s), 124.46 (s), 123.36 (s), 122.40 (s), 119.20 (s), 117.95 (s), 117.23 (s), 41.22 (s), 23.98 (s), 22.07 (s).

HRMS (ESI): calcd for $C_{17}H_{15}N_2O_2$; $[M+H]^+$ 279.1128, found: 279.1129.

2-benzoyl-8-methyl-7,8-dihydro-6H-pyrazolo[4,5,1-ij]quinoline 1-oxide (3au)

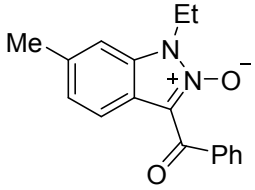


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3au** as a Yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.88 (m, 2H), 7.62 – 7.56 (m, 1H), 7.53 – 7.46 (m, 3H), 7.22 – 7.17 (m, 2H), 5.04 (m, 1H), 3.13 – 2.93 (m, 2H), 2.28 – 2.19 (m, 2H), 1.47 (d, J = 6.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ =185.64 (s), 137.52 (s), 132.68 (s), 129.10 (s), 128.11 (s), 127.19 (s), 124.15 (s), 123.15 (s), 122.19 (s), 118.86 (s), 117.61 (s), 117.11 (s), 47.62 (s), 27.95 (s), 20.16 (s), 17.87 (s).

HRMS (ESI): calcd for $C_{18}H_{17}N_2O_2$; $[M+H]^+$ 293.1285, found: 293.1288.

3-benzoyl-1-ethyl-6-methyl-1H-indazole 2-oxide (3av)

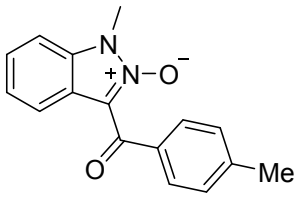


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 4: 1 gave **3av** as a Yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.86 (m, 2H), 7.69 (d, J = 8.2 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.46 (m, 2H), 7.11 – 7.07 (m, 1H), 7.02 (s, 1H), 4.41 (m, 2H), 2.47 (s, 3H), 1.37 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ =186.06 (s), 137.46 (s), 137.30 (s), 132.95 (s), 130.59 (s), 129.33 (s), 128.22 (s), 125.81 (s), 121.77 (s), 120.17 (s), 116.76 (s), 107.22 (s), 37.85 (s), 22.13 (s), 13.09 (s).

HRMS (ESI): calcd for $C_{17}H_{17}N_2O_2$; $[M+H]^+$ 281.1285, found: 281.1285.

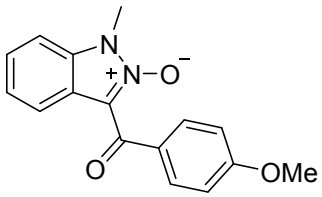
1-methyl-3-(4-methylbenzoyl)-1H-indazole 2-oxide (3ba)



Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3ba** as a Yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.85 – 7.78 (m, 3H), 7.47 – 7.42 (m, 1H), 7.29 (m, 3H), 7.22 (d, *J* = 8.4 Hz, 1H), 3.89 (s, 3H), 2.44 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ =185.42 (s), 143.98 (s), 134.40 (s), 130.83 (s), 129.43 (s), 129.00 (s), 128.94 (s), 126.63 (s), 123.84 (s), 121.66 (s), 120.32 (s), 118.68 (s), 107.17 (s), 29.00 (s), 21.78 (s). **HRMS (ESI)**: calcd for $C_{16}H_{15}N_2O_2$; $[M+H]^+$ 267.1128, found: 267.1136.

3-(4-methoxybenzoyl)-1-methyl-1H-indazole 2-oxide (3ca)

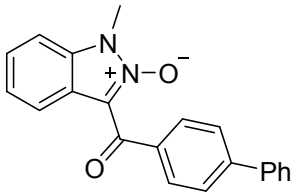


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3ca** as a Yellow solid, mp: 147-150℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.95 – 7.91 (m, 2H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.44 (m, 1H), 7.31 – 7.26 (m, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 6.99 – 6.95 (m, 2H), 3.90 (s, 3H), 3.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ =184.13 (s), 163.76 (s), 131.98 (s), 130.92 (s), 129.52 (s), 126.67 (s), 123.65 (s), 121.75 (s), 120.28 (s), 118.75 (s), 113.66 (s), 107.24 (s), 55.34 (s), 29.12 (s).

HRMS (ESI): calcd for $C_{16}H_{15}N_2O_3$; $[M+H]^+$ 283.1077, found: 283.1080.

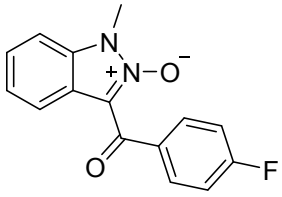
3-([1,1'-biphenyl]-4-carbonyl)-1-methyl-1H-indazole 2-oxide (3da)



Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3da** as a Yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.00 – 7.95 (m, 2H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.72 – 7.68 (m, 2H), 7.67 – 7.62 (m, 2H), 7.45 (m, 3H), 7.38 (m, 1H), 7.30 (m, 1H), 7.25 – 7.20 (m, 1H), 3.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ =185.23 (s), 145.64 (s), 139.93 (s), 135.71 (s), 130.83 (s), 129.86 (s), 128.81 (s), 128.05 (s), 127.21 (s), 126.82 (s), 126.66 (s) 124.01 (s), 121.62 (s), 120.32 (s), 118.66 (s), 107.15 (s), 29.01 (s). **HRMS (ESI)**: calcd for $C_{21}H_{17}N_2O_2$; $[M+H]^+$ 329.1285, found: 329.1292.

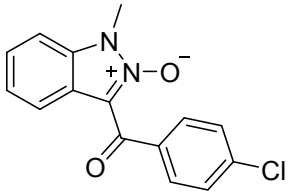
3-(4-fluorobenzoyl)-1-methyl-1H-indazole 2-oxide (3ea)



Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3ea** as a white solid, mp: 194-196℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.97 – 7.88 (m, 3H), 7.51 – 7.44 (m, 1H), 7.32 (m, 1H), 7.28 – 7.21 (m, 1H), 7.21 – 7.14 (m, 2H), 3.90 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ= 184.93 (s), 140.32 (s), 134.19 (s), 133.86 (s), 133.54 (s), 133.21 (s), 130.84 (s), 129.17 (s), 127.01 (s), 125.15 (s), 124.52 (s), 122.29 (s), 121.30 (s), 120.42 (s), 118.49 (s), 107.28 (d, *J* = 12.5 Hz), 29.09 (s). **HRMS (ESI)**: calcd for $C_{15}H_{12}FN_2O_2$; $[M+H]^+$ 271.0878, found: 271.0885.

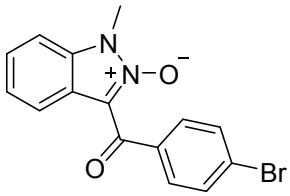
3-(4-chlorobenzoyl)-1-methyl-1H-indazole 2-oxide (3fa)



Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3fa** as a Yellow solid, mp: 188-190℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.93 – 7.88 (m, 1H), 7.85 – 7.80 (m, 2H), 7.49 – 7.43 (m, 3H), 7.33 (m, 1H), 7.24 (m, 1H), 3.89 (d, *J* = 1.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ= 184.54 (s), 139.17 (s), 135.35 (s), 130.82 (s), 130.51 (s), 128.47 (s), 126.81 (s), 124.25 (s), 121.37 (s), 120.32 (s), 118.55 (s), 107.21 (s), 29.06 (s). **HRMS (ESI)**: calcd for $C_{15}H_{12}ClN_2O_2$; $[M+H]^+$ 287.0582, found: 287.0580.

3-(4-bromobenzoyl)-1-methyl-1H-indazole 2-oxide (3ga)

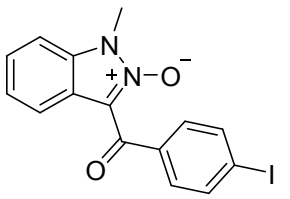


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3ga** as a pale Yellow solid, mp: 152-155℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.92 (d, *J* = 8.0 Hz, 1H), 7.77 – 7.72 (m, 2H), 7.62 (m, 2H), 7.50 – 7.44 (m, 1H), 7.33 (m, 1H), 7.26 – 7.21 (m, 1H), 3.89 (d, *J* = 0.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ= 184.75 (s), 135.83 (s), 131.46 (s), 130.83 (s), 130.69 (s), 127.89 (s), 126.83 (s), 124.30 (s), 121.36 (s), 120.36 (s), 118.57 (s), 107.21 (s), 29.07 (s).

HRMS (ESI): calcd for $C_{15}H_{12}BrN_2O_2$; $[M+H]^+$ 331.0077, found: 331.0081.

3-(4-iodobenzoyl)-1-methyl-1H-indazole 2-oxide (3ha)

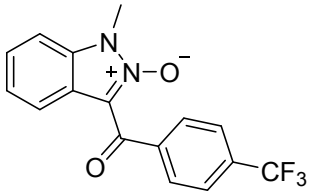


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3ha** as a pale yellow solid, mp: 195-200℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.91 (d, *J* = 8.0 Hz, 1H), 7.87 – 7.82 (m, 2H), 7.61 – 7.58 (m, 2H), 7.47 (m, 1H), 7.33 (m, 1H), 7.23 (d, *J* = 8.3 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ= 185.04 (s), 137.42 (s), 136.41 (s), 130.83 (s), 130.50 (s) 126.81 (s), 124.26 (s), 121.35 (s), 120.37 (s), 118.56 (s), 107.21 (s), 100.71 (s), 29.09 (s). **HRMS (ESI)**: calcd for $C_{15}H_{12}IN_2O_2$; $[M+H]^+$ 378.9938,

found: 378.9946.

1-methyl-3-(4-(trifluoromethyl)benzoyl)-1H-indazole 2-oxide (3ia)

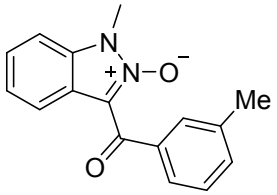


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3ia** as a Yellow solid, mp: 170-173℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ =8.03 – 7.97 (m, 1H), 7.94 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.49 (m, 1H), 7.36 (m, 1H), 7.25 (m, 1H), 3.89 (d, *J* = 1.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ= 184.93 (s), 140.32 (s), 134.19 (t, $^1J_{C,F}$ = 33 Hz), 130.84 (s), 129.17 (s), 127.01 (s), 125.15 (s), 124.52 (s), 122.29 (s), 121.30 (s), 120.42 (s), 118.49 (s), 107.28 (d, $^1J_{C,F}$ = 12.5Hz), 29.09 (s).

HRMS (ESI): calcd for $C_{16}H_{12}F_3N_2O_2$; $[M+H]^+$ 321.0846, found: 321.0850.

1-methyl-3-(3-methylbenzoyl)-1H-indazole 2-oxide (3ja)

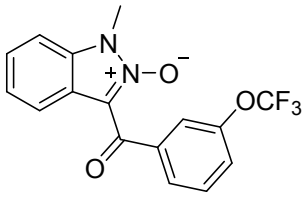


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3ja** as a Yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.81 (d, *J* = 8.0 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.48 – 7.34 (m, 3H), 7.32 – 7.27 (m, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 3.92 – 3.88 (m, 3H), 2.42 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ =185.99 (s), 138.10 (s), 137.20 (s), 133.78 (s), 130.80 (s), 129.45 (s), 128.02 (s), 126.60 (s), 126.45 (s),123.96 (s), 121.60 (s), 120.30 (s), 118.65 (s), 107.13 (s), 29.02 (s), 21.31 (s).

HRMS (ESI): calcd for $C_{16}H_{15}N_2O_2$; $[M+H]^+$ 267.1128, found: 267.1135.

1-methyl-3-(3-(trifluoromethoxy)benzoyl)-1H-indazole 2-oxide (3ka)

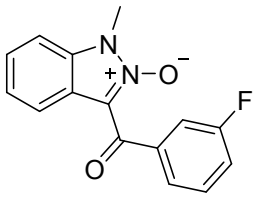


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3ka** as a Yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.96 – 7.91 (m, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.73 (s, 1H), 7.55 – 7.49 (m, 1H), 7.45 (m, 2H), 7.34 (m, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 3.90 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ= 184.24 (s), 148.99 (s), 138.97 (s), 130.84 (s), 129.53 (s), 127.53 (s), 126.99 (s), 125.19 (s), 124.32 (s), 121.57 (s), 121.27 (s), 120.40 (s), 118.57 (s), 107.12 (s), 29.22 (s), 29.01 (s).

HRMS (ESI): calcd for $C_{16}H_{12}F_3N_2O_3$; $[M+H]^+$ 337.0795, found: 337.0799.

3-(3-fluorobenzoyl)-1-methyl-1H-indazole 2-oxide (3la)

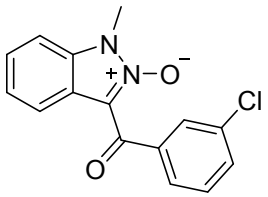


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3la** as a pale Yellow solid, mp: 147-150℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.91 – 7.88 (m, 1H), 7.67 – 7.64 (m, 1H), 7.56 (m, 1H), 7.49 – 7.43 (m, 2H), 7.35 – 7.26 (m, 2H), 7.25 – 7.21 (m, 1H), 3.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ= 184.48 (s), 162.4 (d, $^1J_{C,F}$ =246), 161.17 (s), 139.22 (s), 130.79 (s), 129.74 (s), 126.81 (d, $^2J_{C,F}$ = 16.0 Hz), 124.20 (s), 121.30 (s), 120.28 (s), 119.75 (s), 118.52 (s), 115.63 (s), 107.23 (s), 29.06 (s).

HRMS (ESI): calcd for $C_{15}H_{12}FN_2O_2$; $[M+H]^+$ 271.0878, found: 271.0884.

3-(3-chlorobenzoyl)-1-methyl-1H-indazole 2-oxide (3ma)

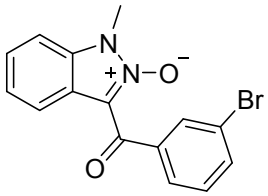


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3ma** as a Yellow solid, mp: 128-130℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.91 (d, *J* = 8.1 Hz, 1H), 7.83 (M, 1H), 7.75 – 7.71 (m, 1H), 7.55 (m, 1H), 7.44 (m, 2H), 7.32 (m, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ= 184.46 (s), 138.84 (s), 134.31 (s), 132.61 (s), 130.85 (s), 129.42 (s), 128.97 (s), 127.18 (s), 126.82 (s), 124.35 (s), 121.28 (s), 120.34 (s), 118.58 (s), 107.20 (s), 29.03 (s).

HRMS (ESI): calcd for $C_{15}H_{12}ClN_2O_2$; $[M+H]^+$ 287.0582, found: 287.0588.

3-(3-bromobenzoyl)-1-methyl-1H-indazole 2-oxide (3na)

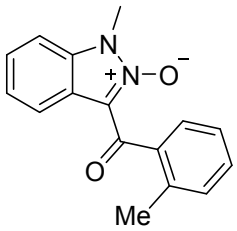


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3na** as a white solid, mp: 177-180℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.99 (m, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.80 – 7.75 (m, 1H), 7.70 (m, 1H), 7.49 – 7.44 (m, 1H), 7.34 (m, 2H), 7.23 (d, *J* = 8.3 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ =184.34 (s), 138.97 (s), 135.52 (s), 131.82 (s), 130.80 (s), 129.66 (s), 127.64 (s), 126.84 (s), 124.36 (s), 122.27 (s), 121.22 (s), 120.31 (s), 118.51 (s), 107.23 (s), 29.11 (s).

HRMS (ESI): calcd for $C_{15}H_{12}BrN_2O_2$; $[M+H]^+$ 331.0077, found: 331.0081.

1-methyl-3-(2-methylbenzoyl)-1H-indazole 2-oxide (3oa)

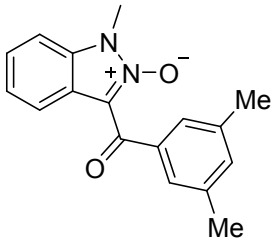


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3oa** as a Yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.88 (d, *J* = 8.1 Hz, 2H), 7.48 – 7.42 (m, 3H), 7.40 (d, *J* = 7.2 Hz, 4H), 7.30 (m, 6H), 7.22 (d, *J* = 8.3 Hz, 2H), 3.85 (s, 6H), 2.40 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ= 187.73 (s), 138.69 (s), 136.06 (s), 130.53 (s), 127.27 (s), 126.80 (s), 125.81 (s), 125.48 (s), 124.24 (s), 122.17 (s), 120.53 (s), 118.20 (s), 107.11 (s), 106.92 (s), 29.03 (s), 19.32 (s).

HRMS (ESI): calcd for $C_{16}H_{15}N_2O_2$; $[M+H]^+$ 267.1128, found: 267.1136.

3-(3,5-dimethylbenzoyl)-1-methyl-1H-indazole 2-oxide (3pa)

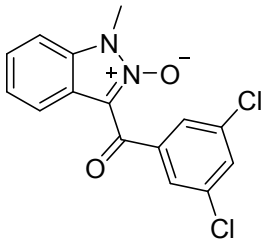


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3pa** as a pale Yellow solid, mp: 205-207℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.76 – 7.73 (m, 1H), 7.46 (s, 2H), 7.45 – 7.40 (m, 1H), 7.29 – 7.24 (m, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 3.88 (s, 3H), 2.35 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ= 186.13 (s), 137.85 (s), 137.32 (s), 134.60 (s), 130.76 (s), 126.79 (s), 123.71 (s), 121.61 (s), 120.21 (s), 118.63 (s), 107.23 (s), 29.10 (s), 28.89 (s), 21.18 (s).

HRMS (ESI): calcd for $C_{17}H_{17}N_2O_2$; $[M+H]^+$ 281.1285, found: 281.1288.

3-(3,5-dichlorobenzoyl)-1-methyl-1H-indazole 2-oxide (3qa)

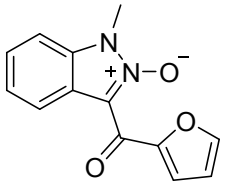


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3qa** as a pale Yellow solid, mp: 233-235℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.97 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 1.9 Hz, 2H), 7.55 (m, 1H), 7.52 – 7.46 (m, 1H), 7.36 (m, 1H), 7.25 (d, *J* = 8.3 Hz, 1H), 3.91 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ= 183.24 (s), 139.82 (s), 134.92 (s), 132.27 (s), 132.12 (s), 130.84 (s), 127.28 (s), 124.59 (s), 121.07 (s), 120.35 (s), 118.47 (s), 107.42 (s), 107.21 (s), 29.31 (s).

HRMS (ESI): calcd for $C_{15}H_{11}Cl_2N_2O_2$; $[M+H]^+$ 321.0192, found: 321.0198.

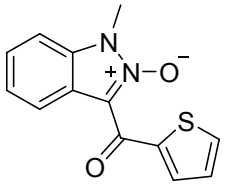
3-(furan-2-carbonyl)-1-methyl-1H-indazole 2-oxide (3ra)



Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3ra** as a Yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.08 – 8.02 (m, 1H), 7.92 (m, 1H), 7.74 – 7.71 (m, 1H), 7.45 (m, 1H), 7.32 (m, 1H), 7.20 (d, *J* = 8.3 Hz, 1H), 6.64 – 6.61 (m, 1H), 3.92 (d, *J* = 0.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ= 171.18 (s), 151.26 (s), 147.46 (s), 130.83 (s), 126.74 (s), 124.02 (s), 121.36 (s), 121.05 (s), 120.67 (s), 118.64 (s), 112.29 (s), 107.04 (s), 77.32 (s), 77.00 (s), 76.68 (s), 29.07 (s). **HRMS (ESI)**: calcd for $C_{13}H_{11}N_2O_3$; $[M+H]^+$ 243.0764, found: 243.0769.

1-methyl-3-(thiophene-2-carbonyl)-1H-indazole 2-oxide (3sa)

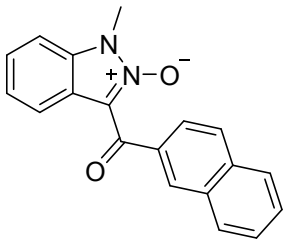


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3sa** as a dark yellow solid, mp: 195-198℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ =8.29 (m, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.76 – 7.72 (m, 1H), 7.49 – 7.41 (m, 1H), 7.36 – 7.28 (m, 1H), 7.24 – 7.16 (m, 2H), 3.93 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ= 176.46 (s), 142.86 (s), 134.96 (s), 130.88 (s), 128.20 (s), 127.83 (s), 126.87 (s),123.88 (s), 121.66 (s), 120.71 (s), 118.69 (s), 106.92 (s), 29.22 (s).

HRMS (ESI): calcd for $C_{13}H_{11}N_2O_2S$; $[M+H]^+$ 259.0536, found: 259.0543.

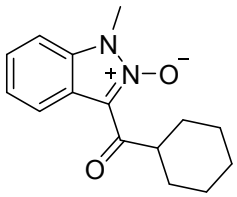
3-(2-naphthoyl)-1-methyl-1H-indazole 2-oxide (3ta)



Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 2: 1 gave **3ta** as a light yellow solid, mp: 182-185℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.43 (s, 1H), 7.92 (m, 3H), 7.86 (m, 2H), 7.58 (m, 1H), 7.51 (m, 1H), 7.44 (m, 1H), 7.28 (m, 1H), 7.21 (d, *J* = 8.3 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 185.59 (s), 135.60 (s), 134.54 (s), 132.43 (s), 131.00 (s), 130.88 (s), 129.58 (s), 128.32 (s), 127.92 (s), 127.75 (s), 126.64 (s), 126.52 (s), 124.90 (s), 124.02 (s), 121.75 (s), 120.33 (s), 118.73 (s), 107.16 (s), 29.01 (s). **HRMS (ESI)**: calcd for $C_{19}H_{15}N_2O_2$; $[M+H]^+$ 303.1128, found: 303.1128.

3-(cyclohexanecarbonyl)-1-methyl-1H-indazole 2-oxide (3ua)

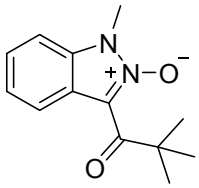


Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 10: 1 gave **3ua** as a light yellow solid, mp: 142-145℃。

^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.34 – 8.30 (m, 1H), 7.44 (m, 1H), 7.33 (m, 1H), 7.17 (m, 1H), 3.90 (s, 3H), 3.82 – 3.74 (m, 1H), 2.06 – 1.98 (m, 2H), 1.91 – 1.82 (m, 2H), 1.50 – 1.43 (m, 4H), 1.33 – 1.21 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ =196.00 (s), 130.75 (s), 126.75 (s), 124.39 (s), 121.96 (s), 121.73 (s), 118.49 (s), 106.78 (s), 47.71 (s), 28.97 (s), 27.97 (s), 26.10 (s), 25.90 (s).

HRMS (ESI): calcd for $C_{15}H_{19}N_2O_2$; $[M+H]^+$ 259.1441, found: 259.1443.

1-methyl-3-pivaloyl-1H-indazole 2-oxide (3va)

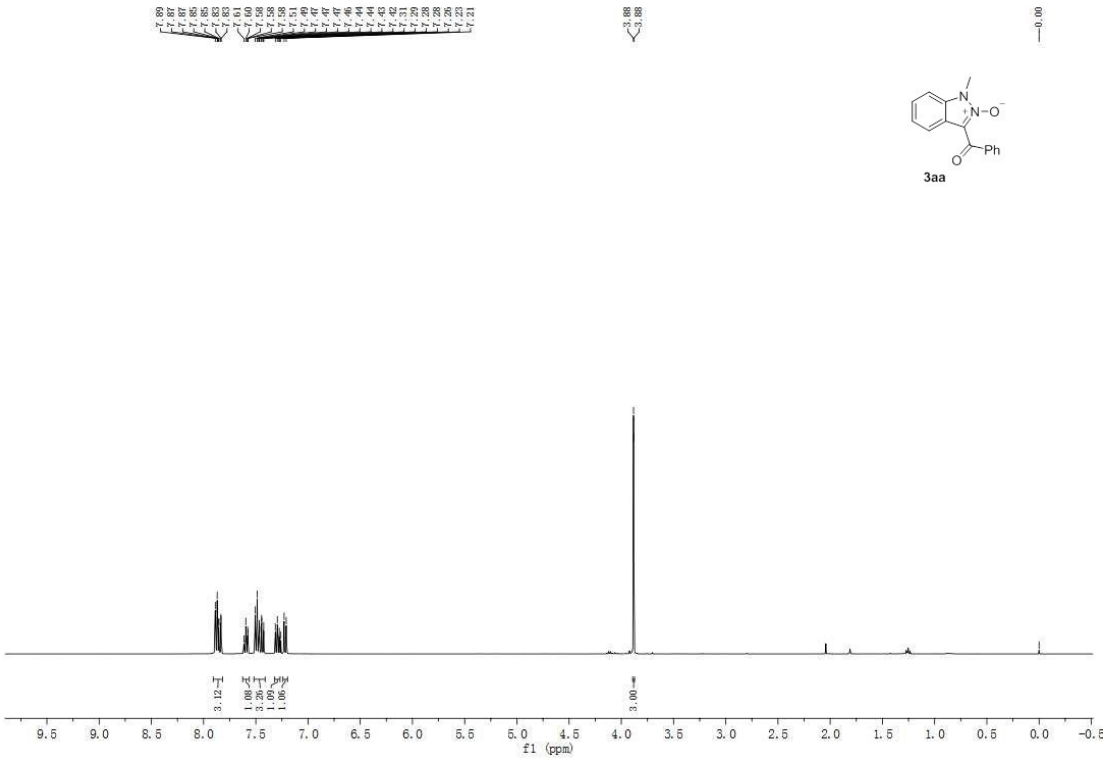


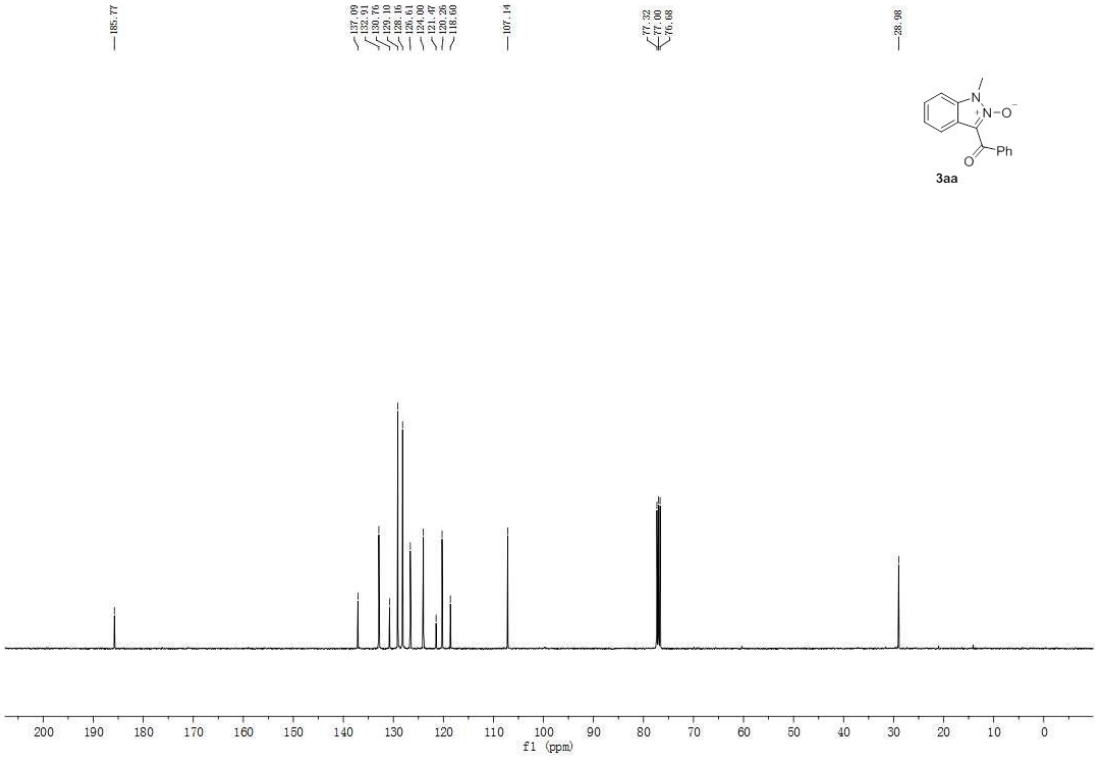
Following the general procedure. A purification by flash chromatography in petroleum ether: ethyl acetate = 10: 1 gave **3va** as a light yellow liquid.

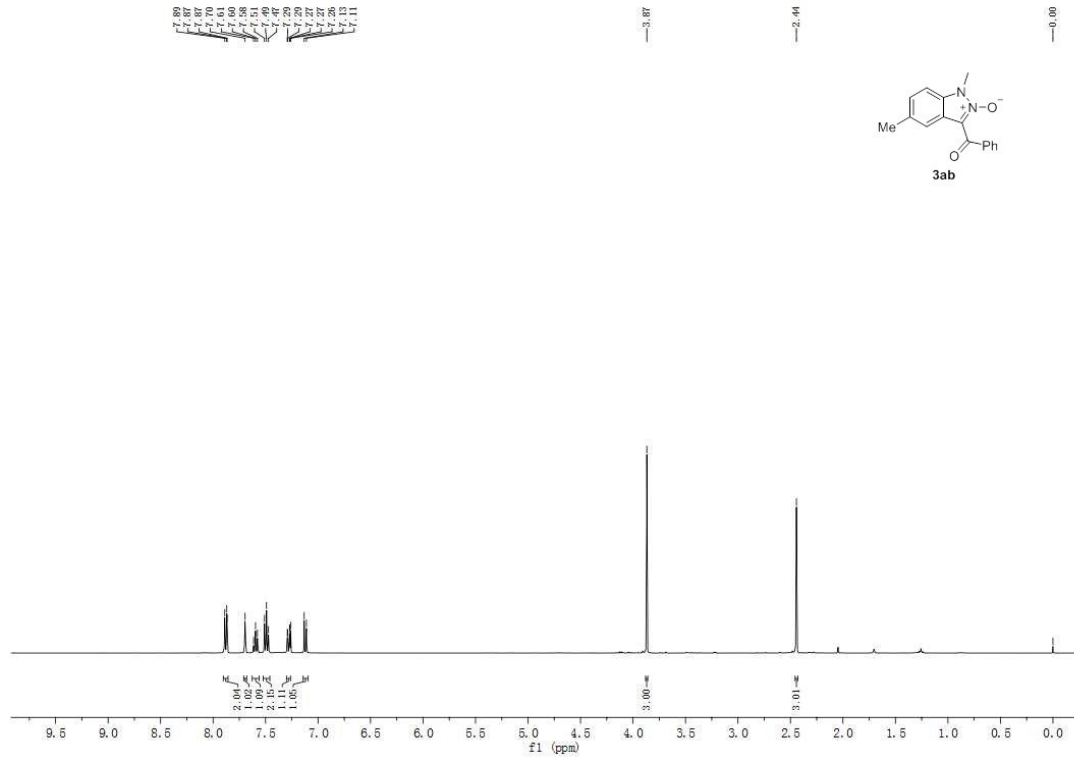
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.14 (d, *J* = 8.1 Hz, 1H), 7.43 (m, 1H), 7.30 (m, 1H), 7.16 (d, *J* = 8.3 Hz, 1H), 3.88 (s, 3H), 1.46 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 198.99 (s), 131.33 (s), 126.60 (s), 123.95 (s), 123.27 (s), 121.59 (s), 119.36 (s), 106.82 (s), 44.30 (s), 29.08 (s), 24.97 (s).

HRMS (ESI): calcd for $C_{13}H_{17}N_2O_2$; $[M+H]^+$ 233.1285, found: 233.1286.

5. Copies of ^{1}H and ^{13}C NMR spectrum of products



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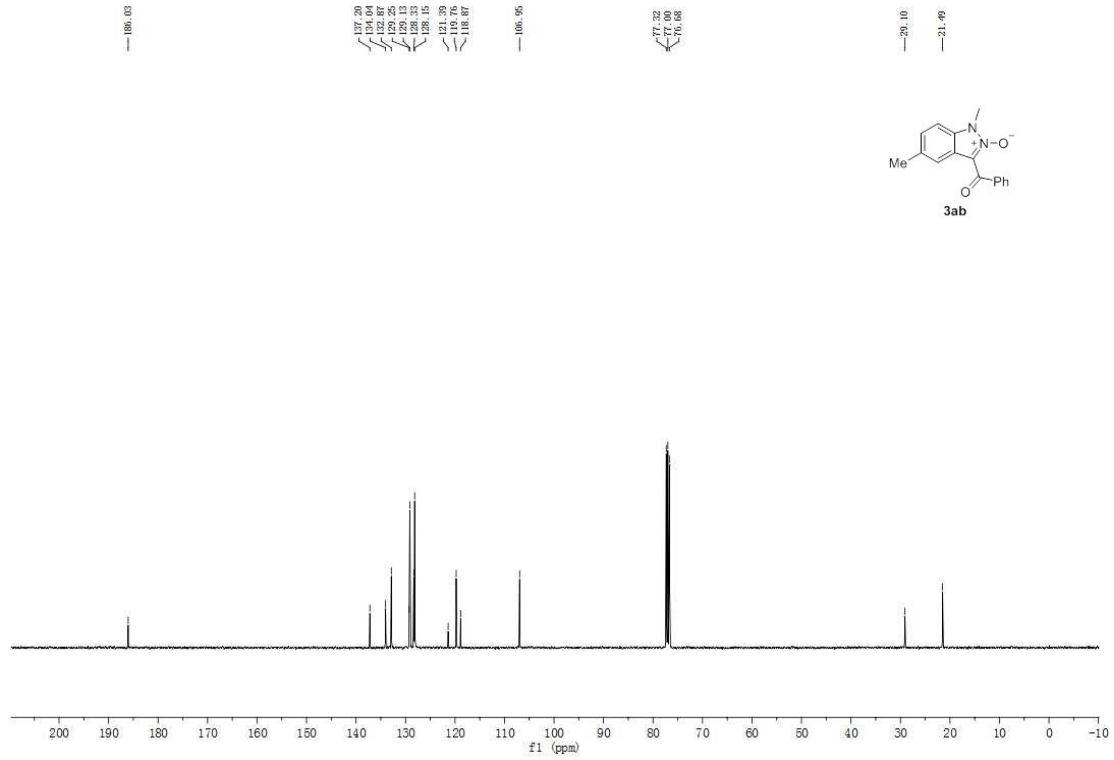
7.27
7.27
7.25
7.13
7.11
3.87
2.44
0.00
Me
N
N-O
O
Ph
3ab
2.04
1.02
1.00
2.15
1.11
1.05
3.00
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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134.04
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129.13
128.33
126.15
121.39
119.76
118.87
106.95
77.32
77.00
76.68
29.10
21.49
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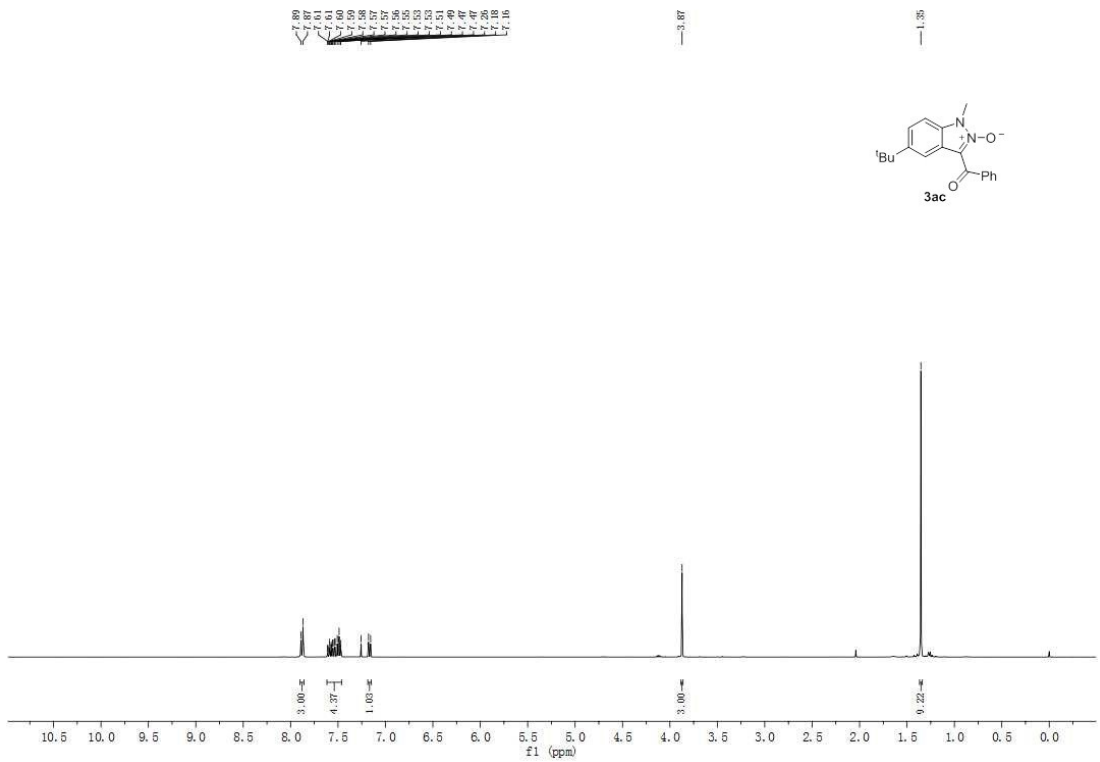
N-O
O
Ph
3ab
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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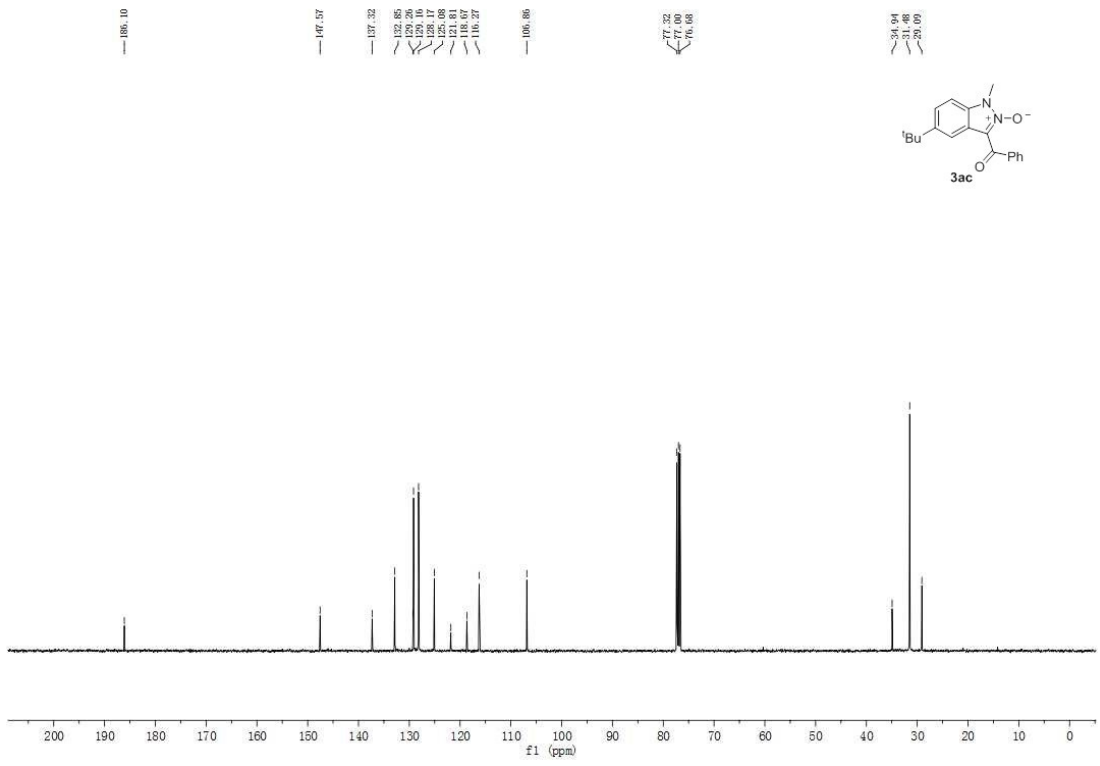
7.51
7.49
7.47
7.47
7.26
7.18
7.16
3.87
1.35
tBu
N
N-O
Ph
O
3ac
3.00
4.37
1.03
3.00
9.22
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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125.08
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106.86
77.32
77.00
76.68
34.94
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N-O
Ph
O
3ac
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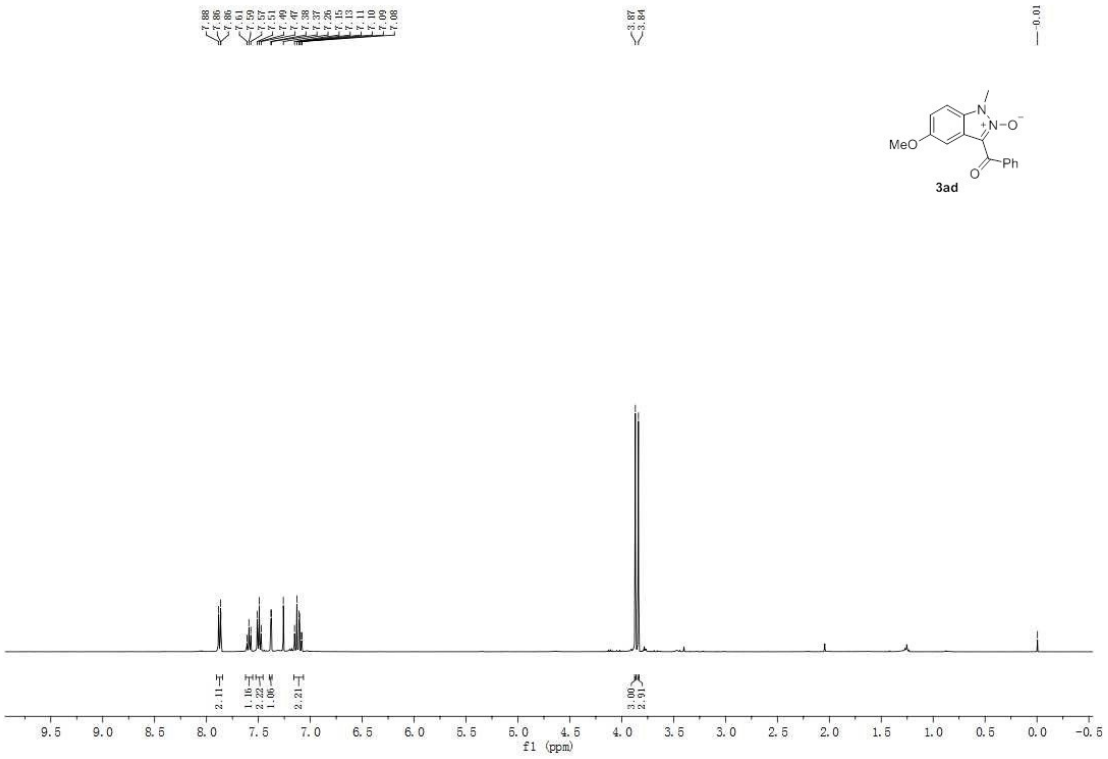
f1 (ppm)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7.10
7.09
7.08
3.87
3.84
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MeO
N
N–O
Ph
O
3ad
2.11
1.16
2.22
1.06
2.21
3.00
2.91
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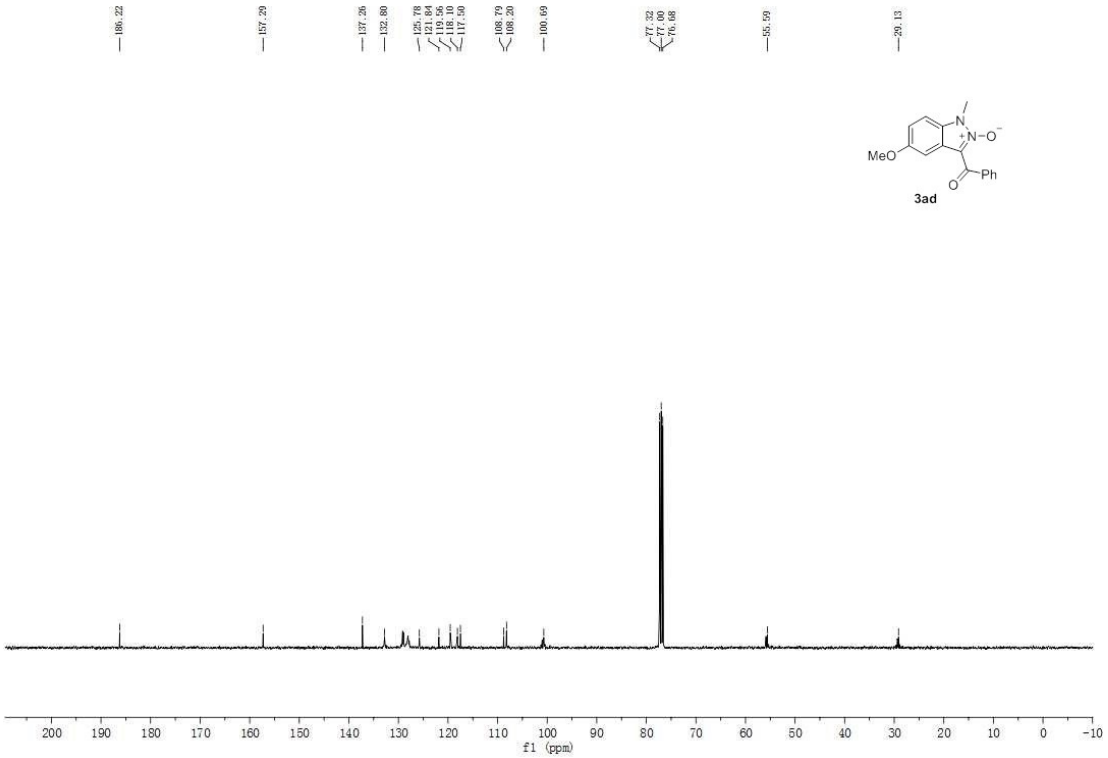
f1 (ppm)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108.79
108.20
100.69
77.32
77.00
76.68
55.59
29.13
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N
N–O
Ph
O
3ad
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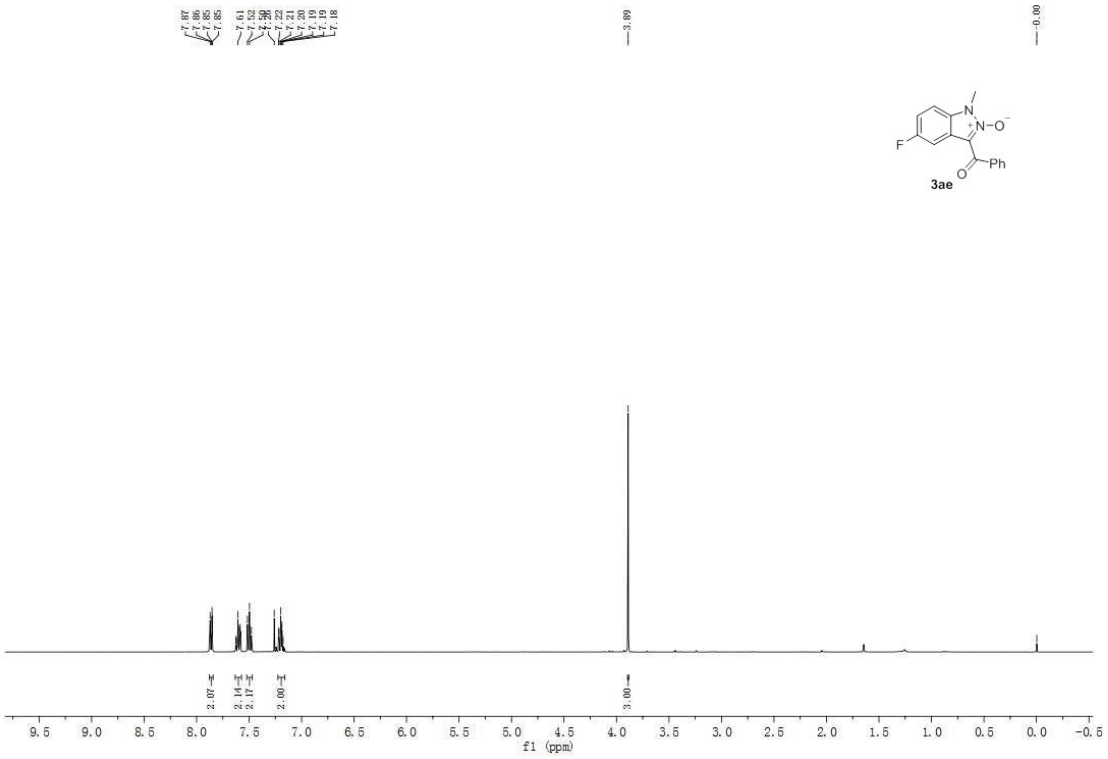
f1 (ppm)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7.20
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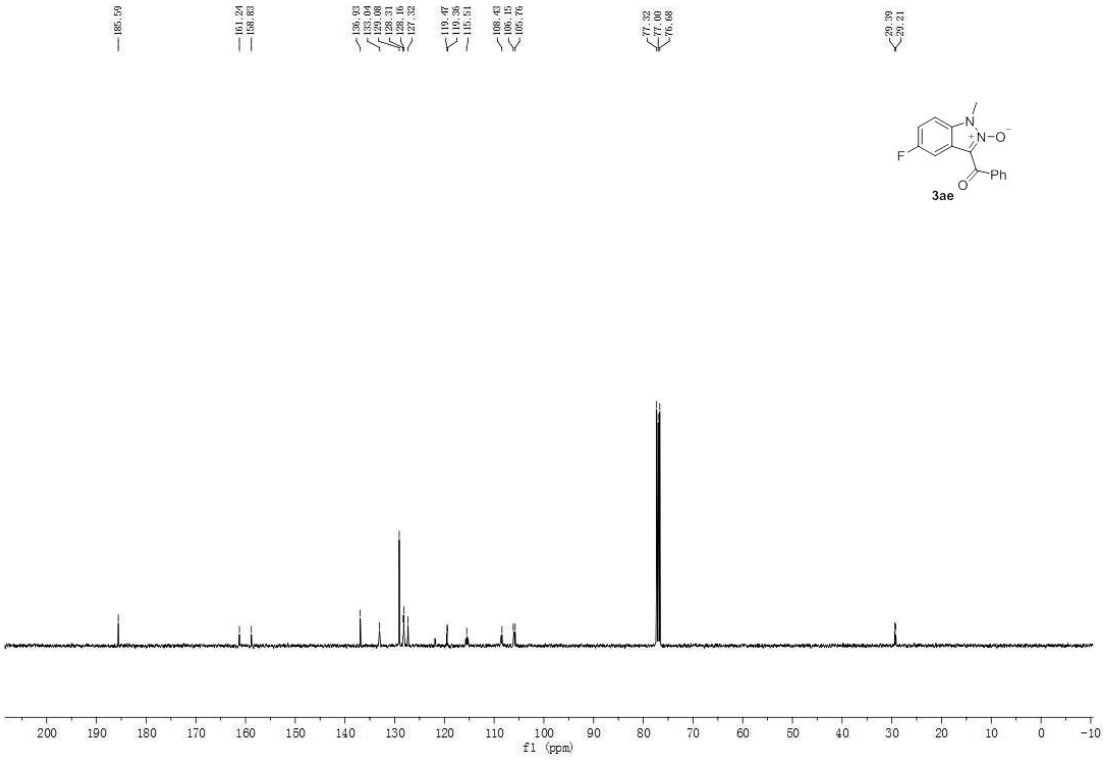
7.18
3.89
0.00
F
N
N-O
O
Ph
3ae
2.07
2.14
2.17
2.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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135.04
129.08
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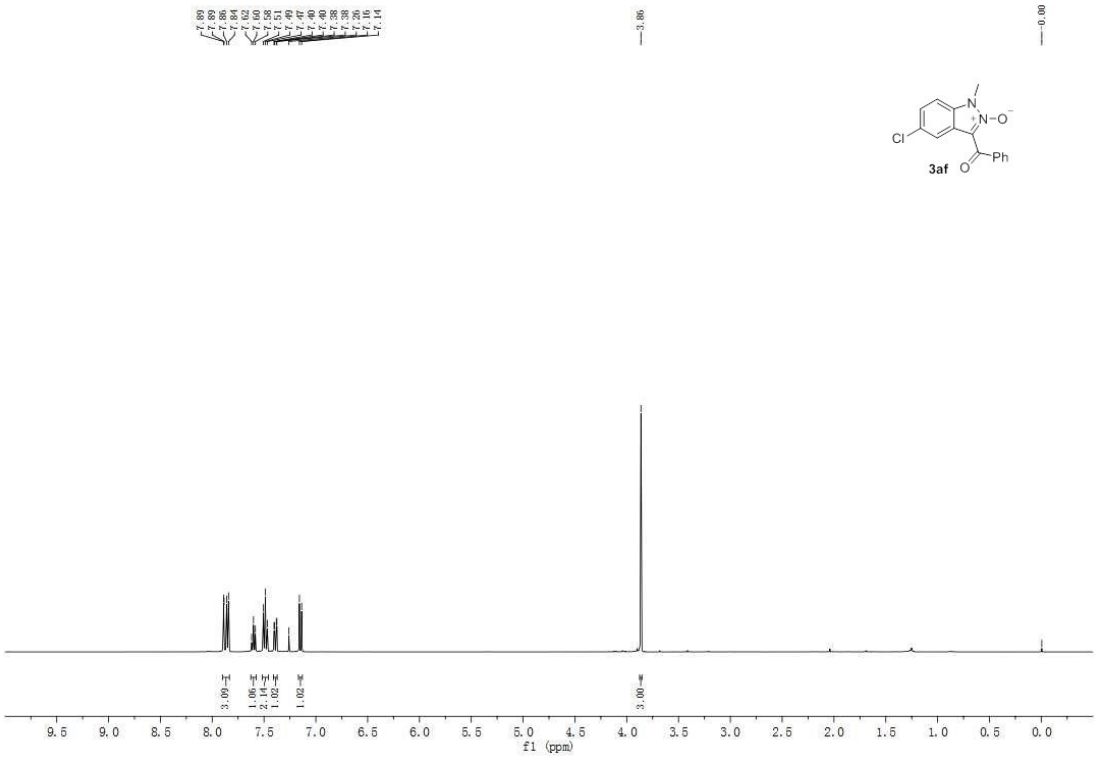
128.16
127.32
119.47
119.36
115.51
108.43
106.15
105.76
77.32
77.00
76.68
29.39
29.21
F
N
N-O
O
Ph
3ae
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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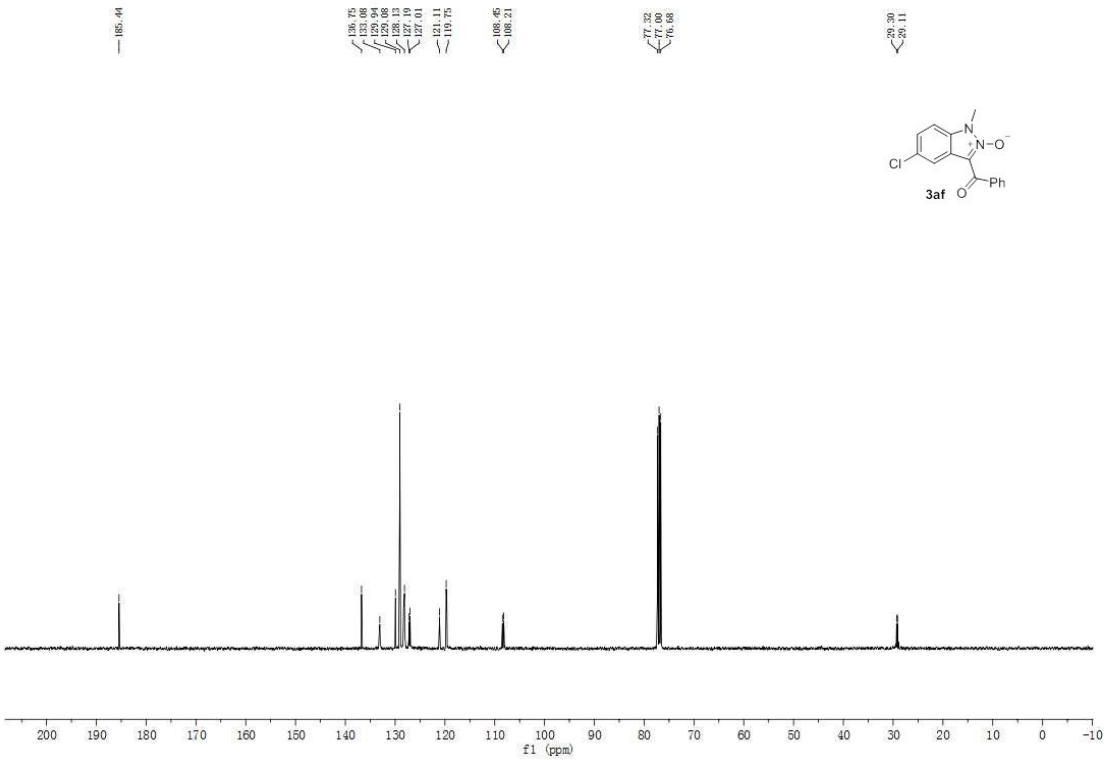
f1 (ppm)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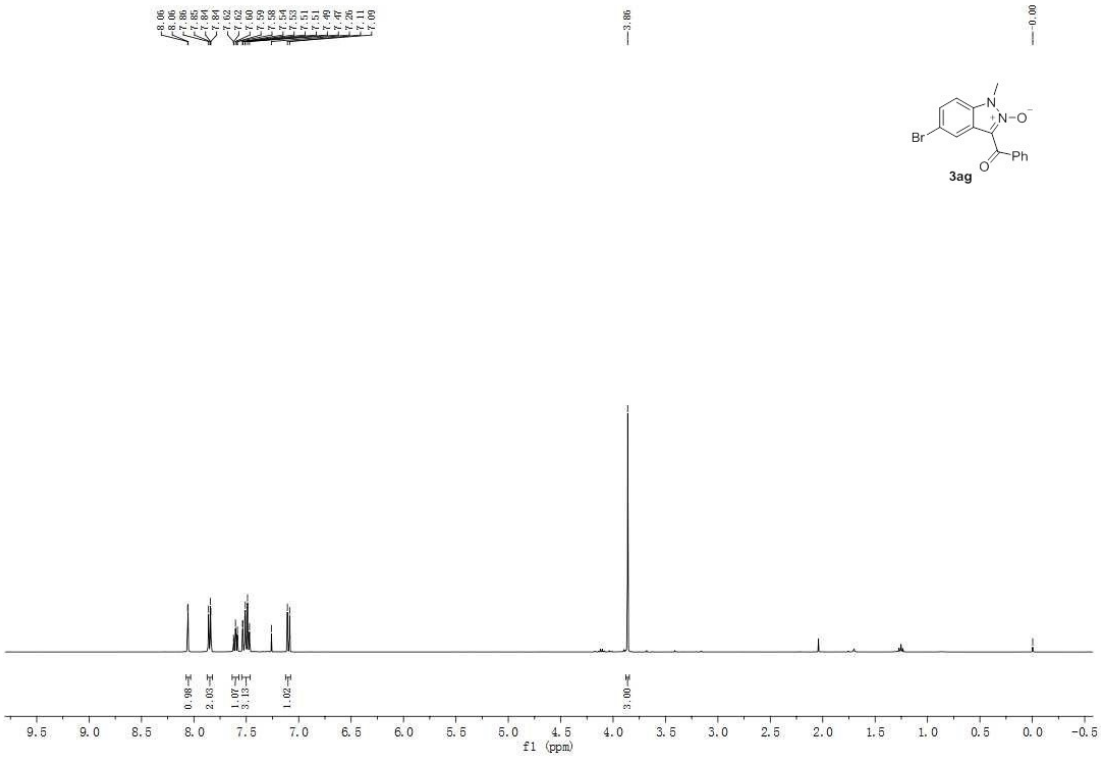
f1 (ppm)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7.84
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7.59
7.58
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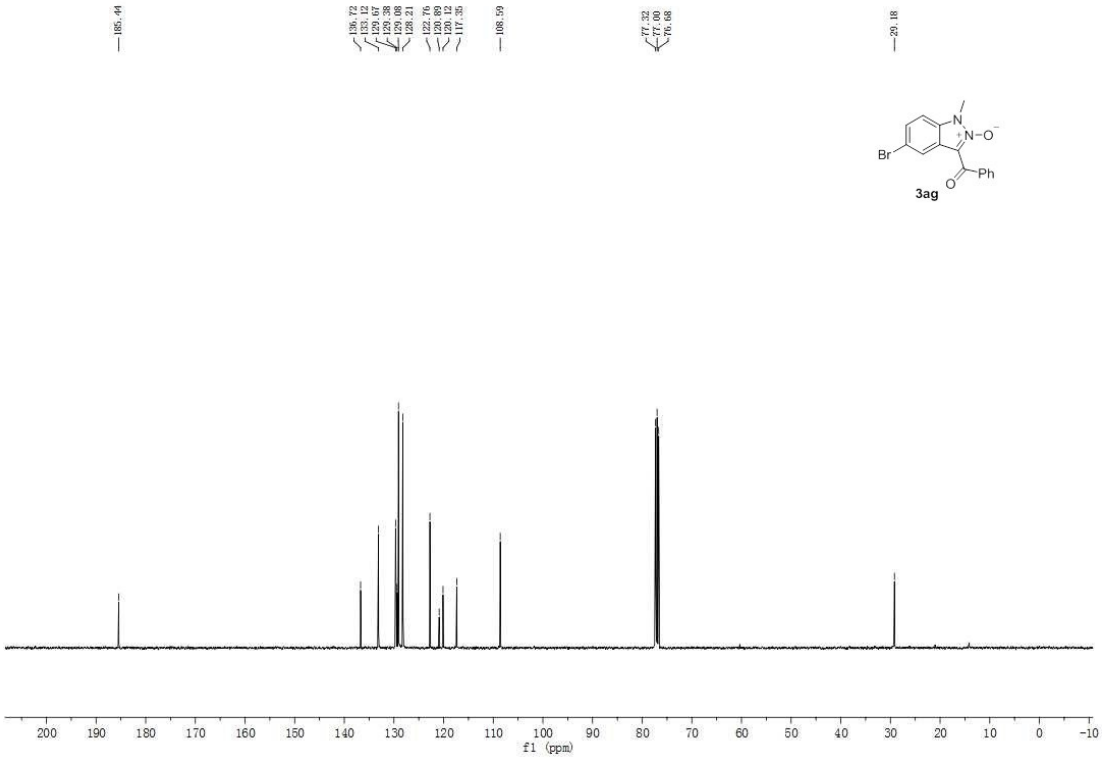
7.53
7.51
7.51
7.49
7.47
7.26
7.11
7.09
3.86
0.00
Br
N
N–O
O
Ph
3ag
0.98
2.03
1.07
3.13
1.02
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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120.12
117.39
108.59
77.32
77.00
76.68
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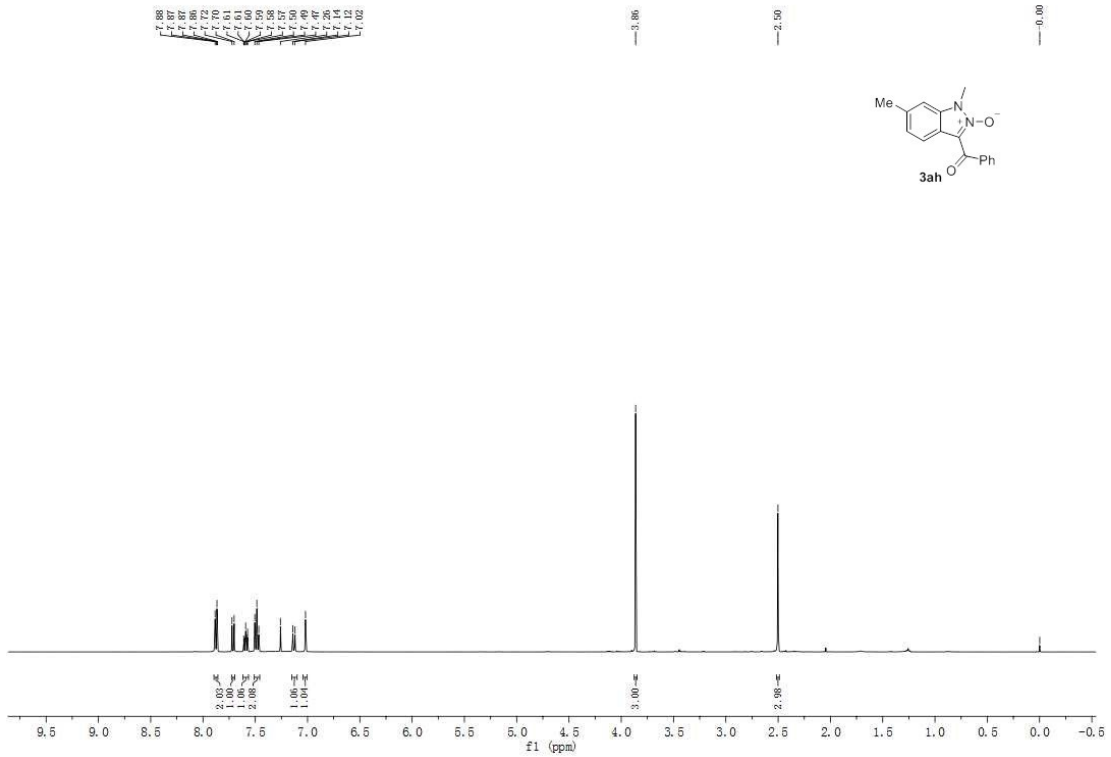
N
N–O
O
Ph
3ag
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.61
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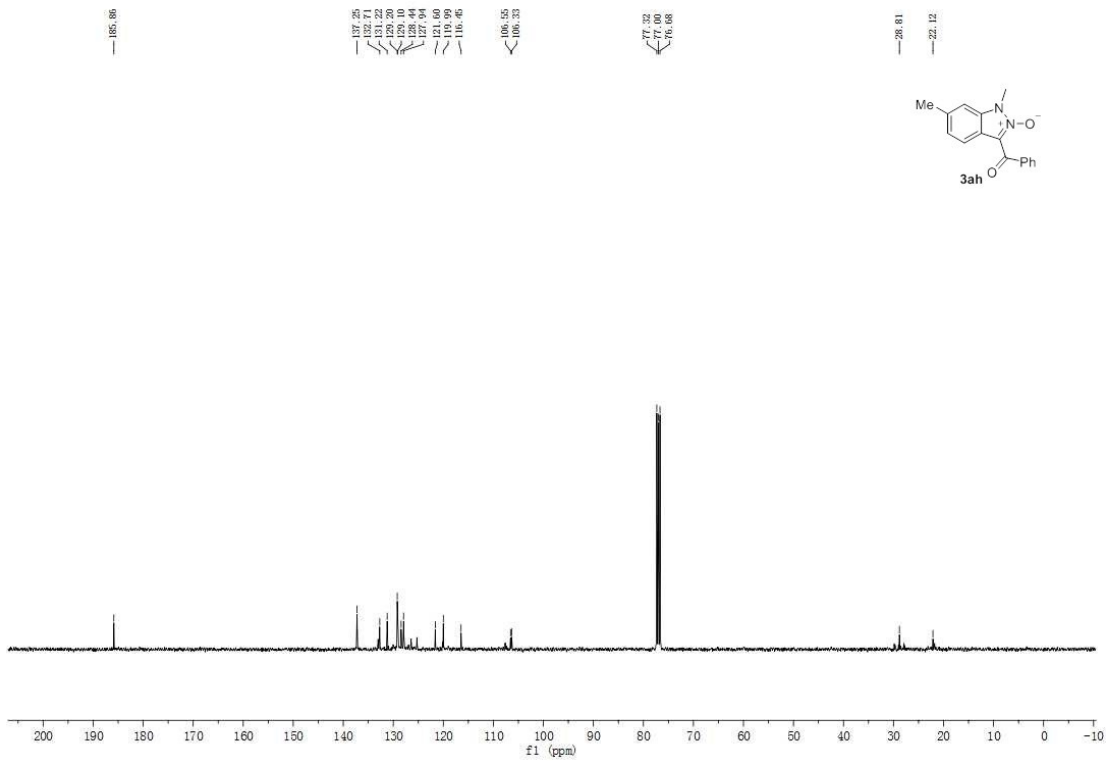
7.59
7.58
7.57
7.50
7.49
7.47
7.25
7.14
7.12
7.02
3.86
2.50
0.00
Me
N
N-O
Ph
O
3ah
2.03
1.00
1.06
2.08
1.06
1.04
3.00
2.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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127.04
121.60
119.99
116.45
106.55
106.33
77.32
77.00
76.68
28.81
22.12
Me
N
N-O
Ph
O
3ah
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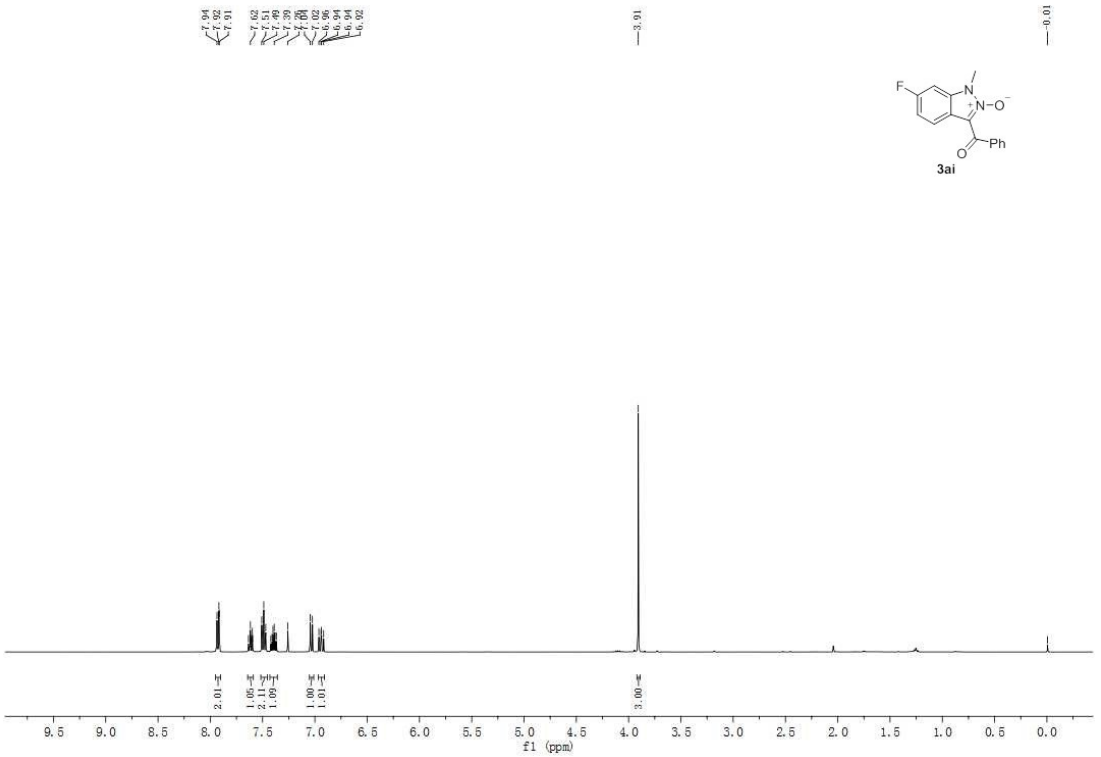
f1 (ppm)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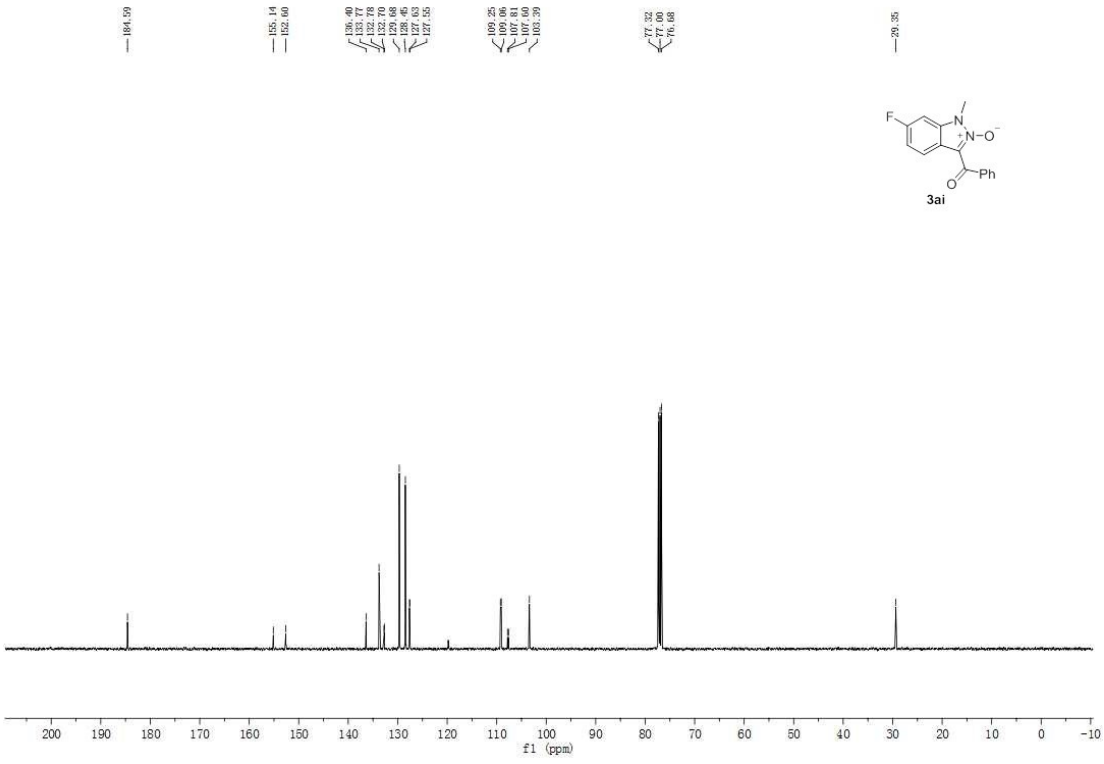
7.91
7.62
7.51
7.49
7.39
7.37
7.02
6.96
6.94
6.92
3.91
-0.01
F
N
N-O
Ph
O
3ai
2.01
1.05
2.11
1.09
1.00
1.01
3.00
f1 (ppm)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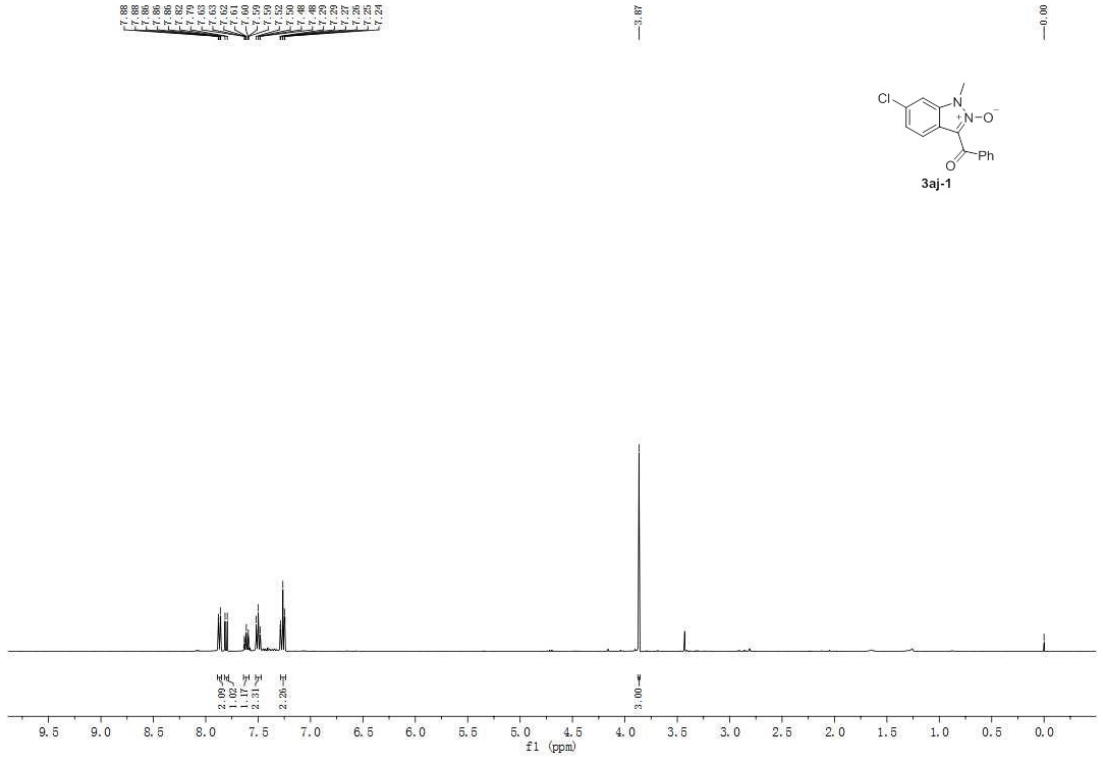
127.63
127.55
109.25
109.06
107.81
107.60
103.39
77.32
77.00
76.68
29.35
F
N
N-O
Ph
O
3ai
f1 (ppm)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7.86
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7.62
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7.59
7.52
7.50
7.48
7.48
7.29
7.29
7.27
7.26
7.25
7.24
3.87
0.00
Cl
N
N-O
Ph
O
3aj-1
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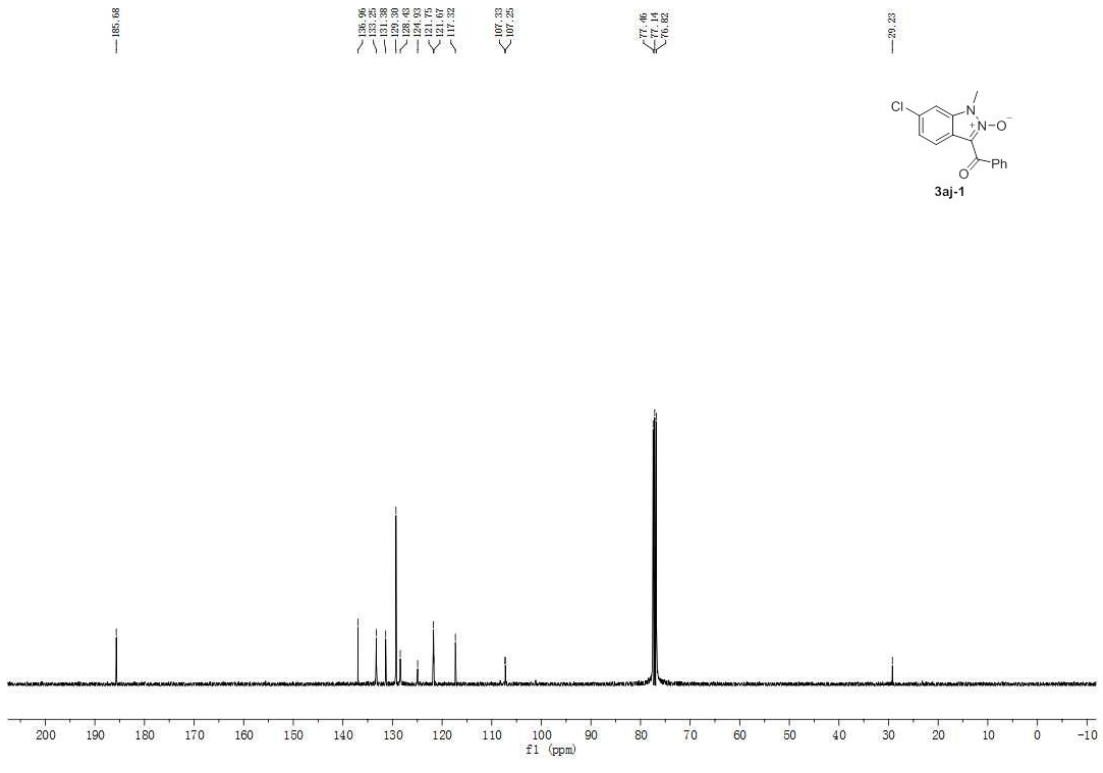
1.02
1.17
2.01
2.26
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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107.33
107.25
77.46
77.14
76.82
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N-O
Ph
O
3aj-1
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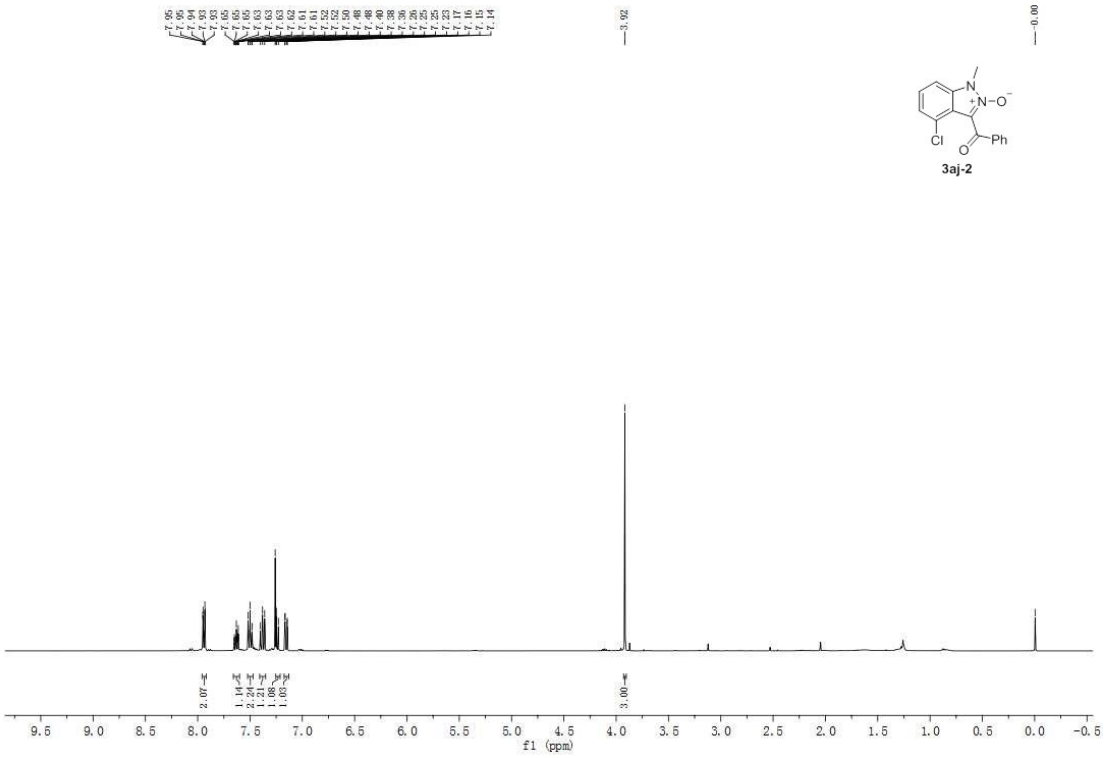
f1 (ppm)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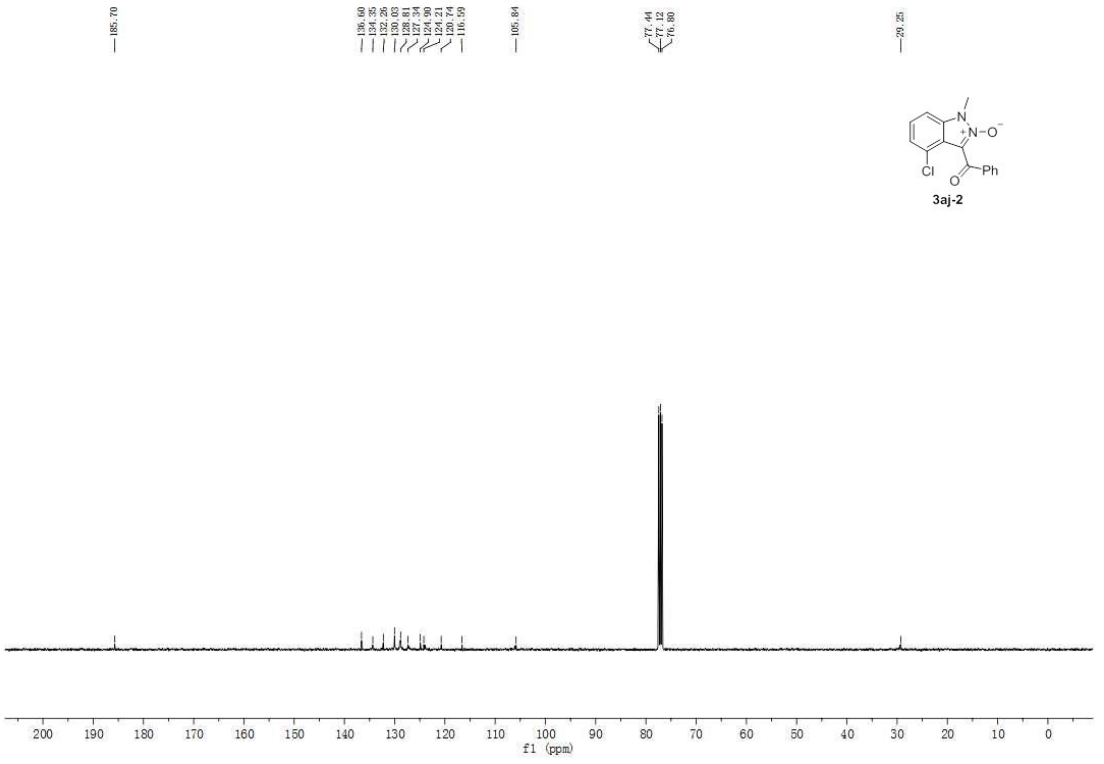
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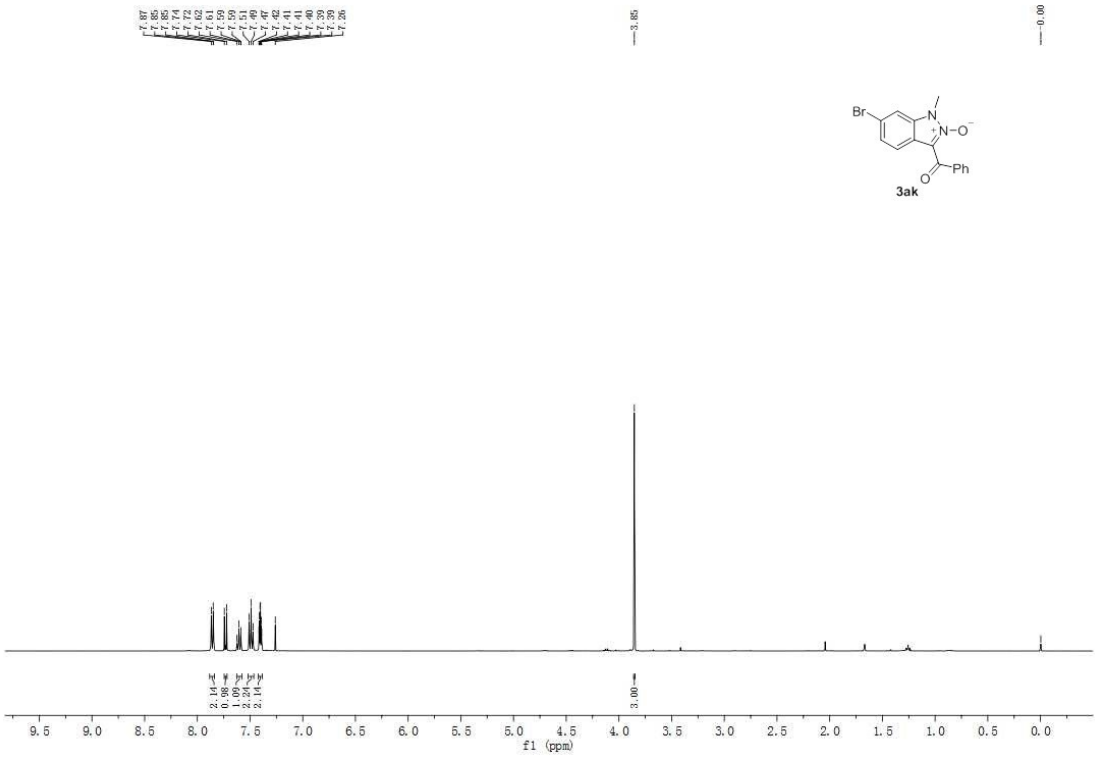
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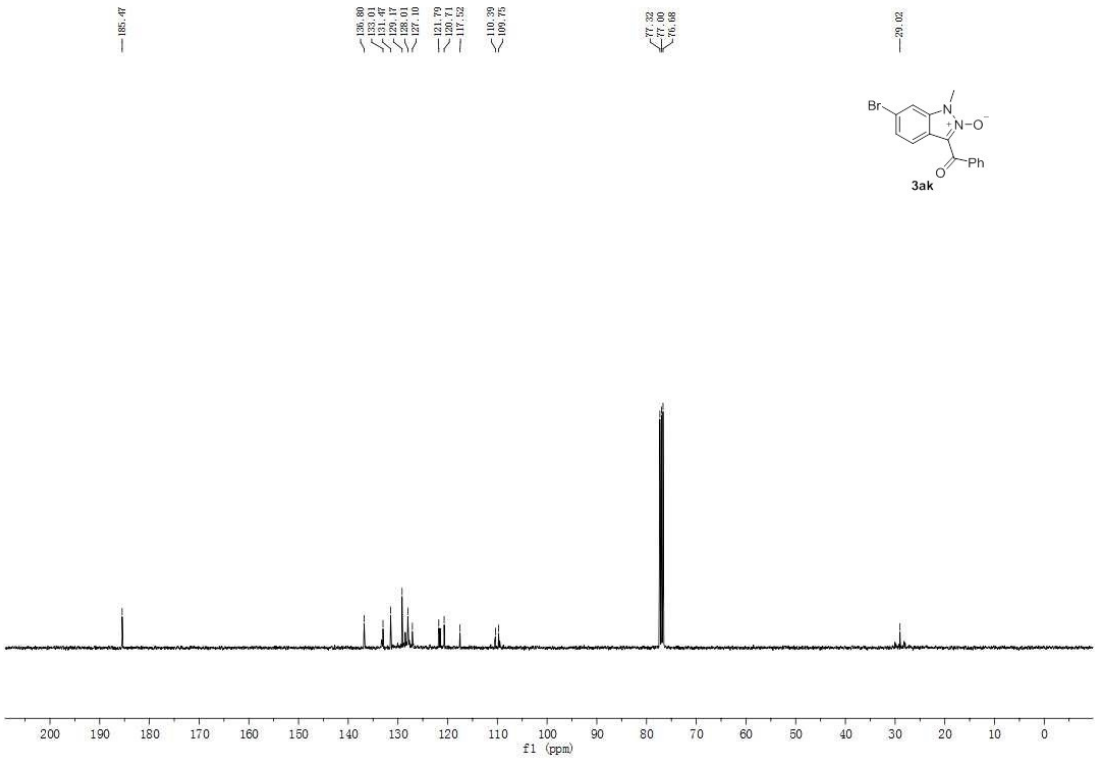
7.41
7.40
7.39
7.26
3.85
0.00
Br
N
N-O
Ph
O
3ak
2.14
0.98
1.09
2.24
2.14
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.32
77.00
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29.02
Br
N
N-O
Ph
O
3ak
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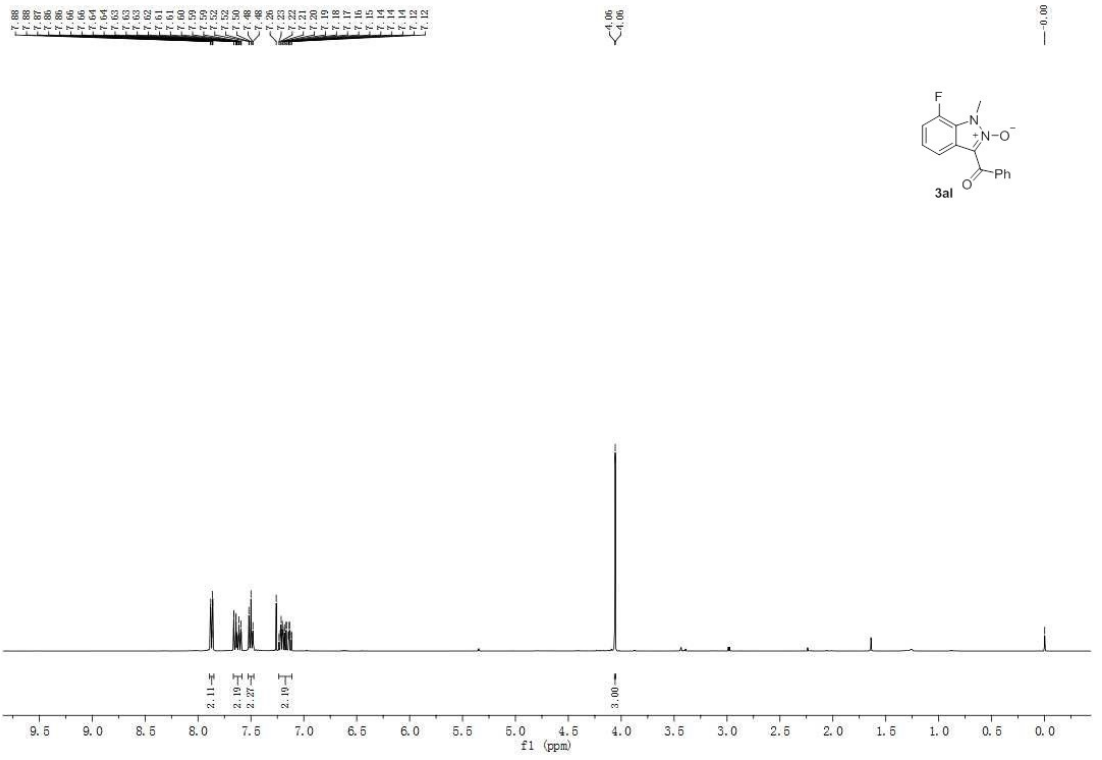
f1 (ppm)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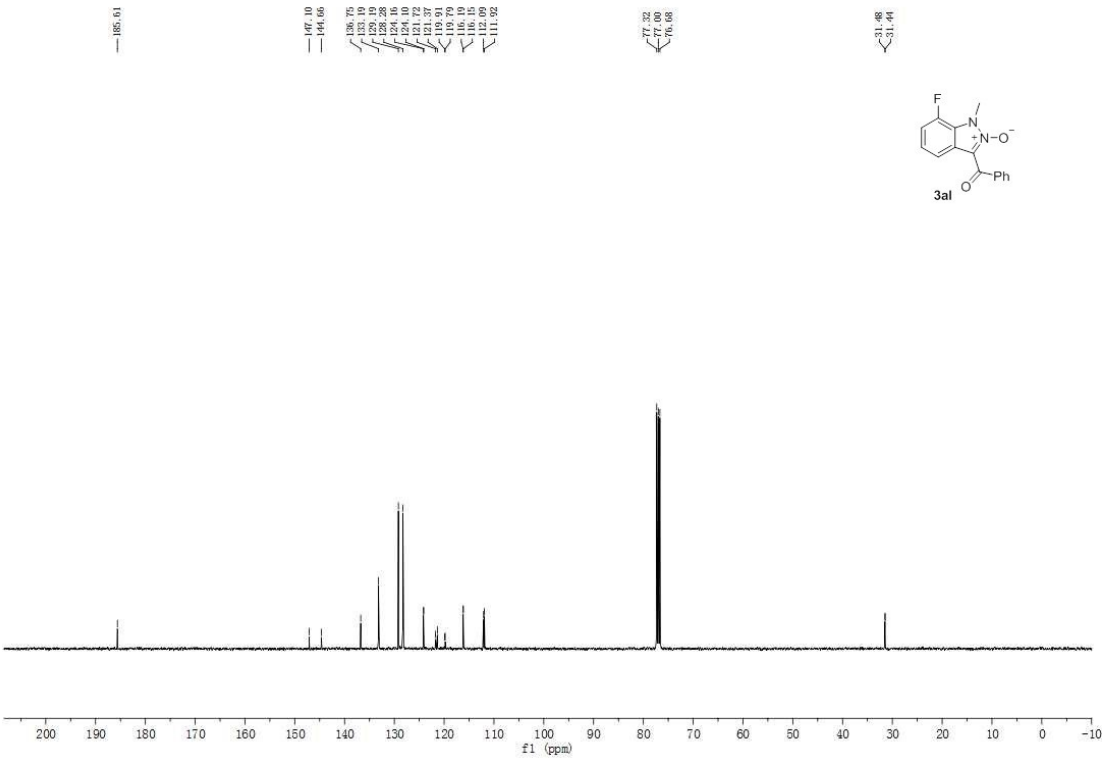
7.62
7.61
7.60
7.59
7.52
7.50
7.48
7.26
7.23
7.22
7.21
7.20
7.19
7.18
7.17
7.16
7.15
7.14
7.14
7.12
7.12
4.06
4.06
0.00
F
N
+N–O⁻
O
Ph
3al
2.11
2.19
2.27
2.19
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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119.79
116.19
116.15
112.09
111.92
77.32
77.00
76.68
31.48
31.44
F
N
+N–O⁻
O
Ph
3al
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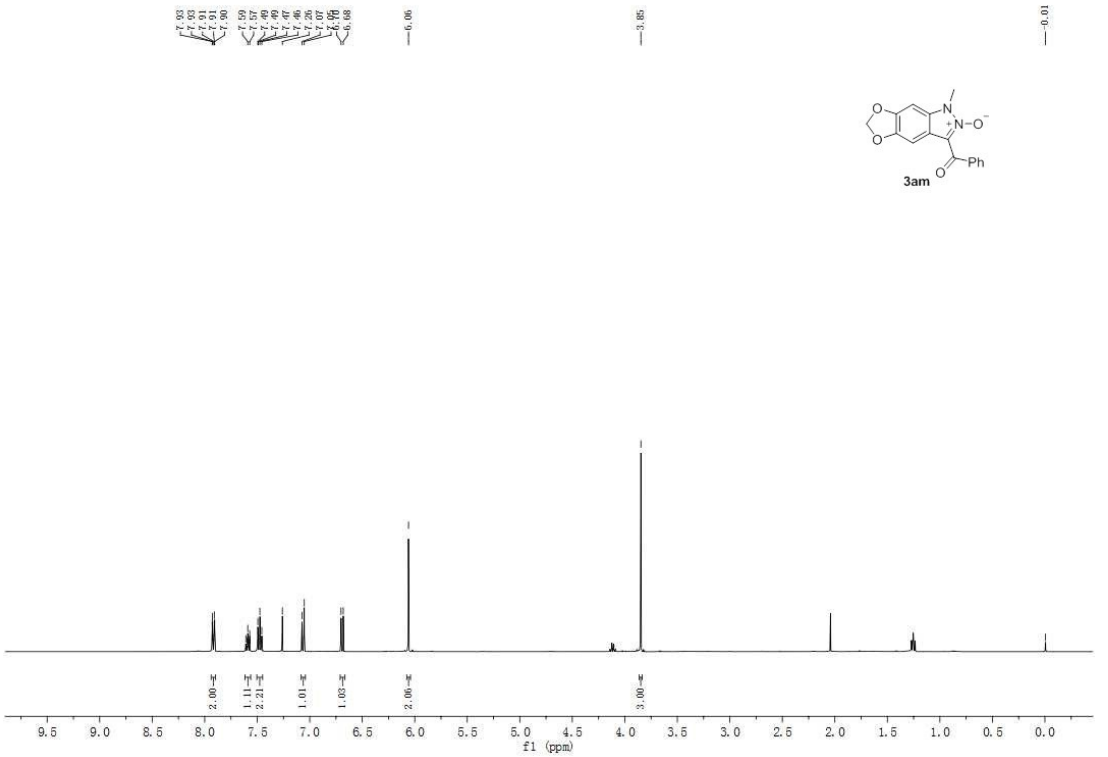
f1 (ppm)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7.47
7.47
7.46
7.46
7.07
7.07
6.68
6.06
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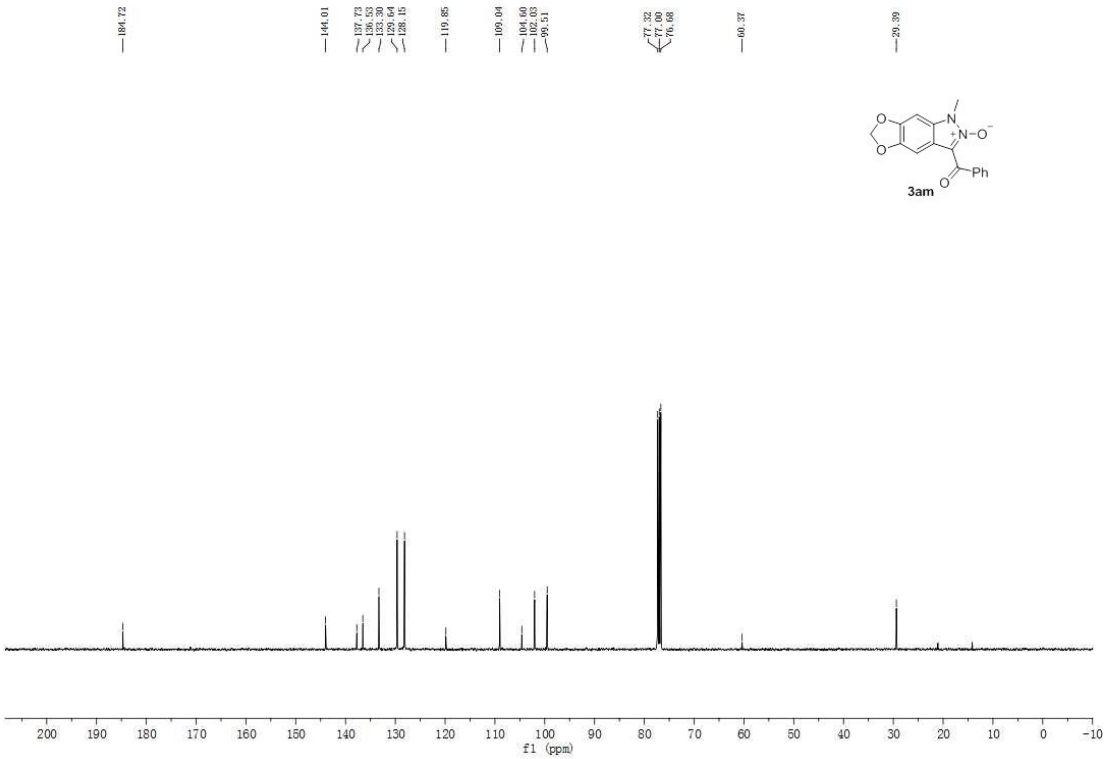
3am
2.00
1.11
2.21
1.01
1.03
2.06
3.00
f1 (ppm)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109.04
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103.03
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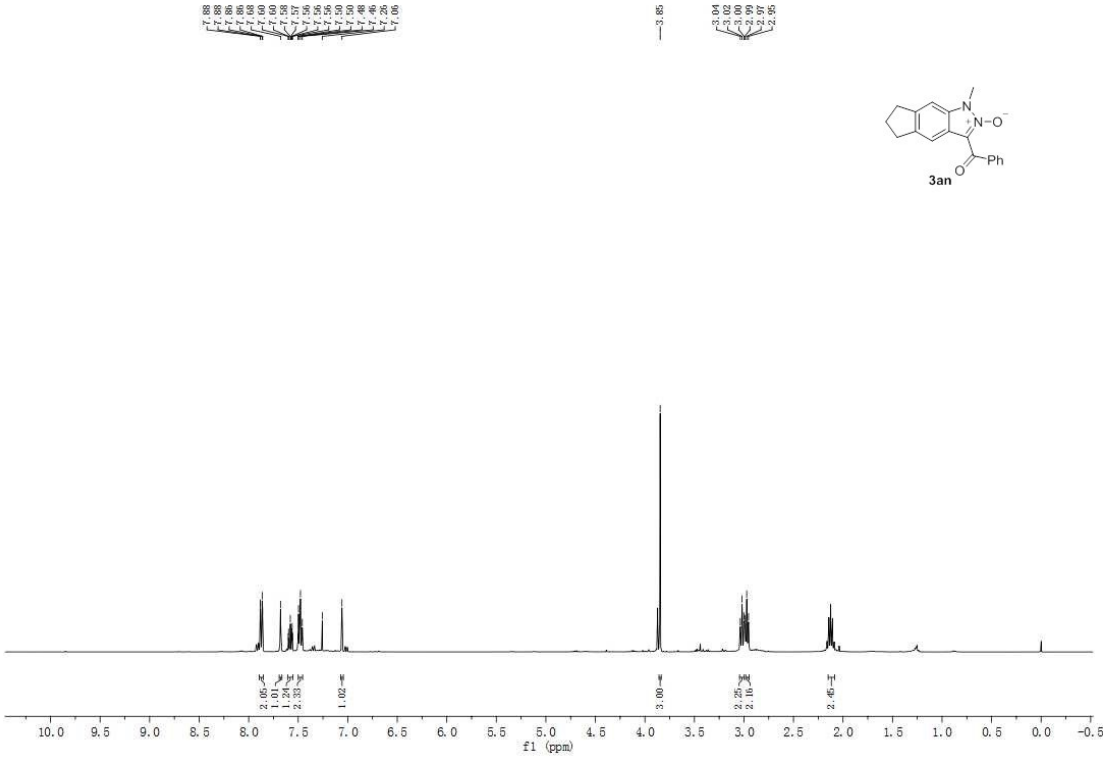
76.68
60.37
29.39
3am
f1 (ppm)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7.58
7.57
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7.56
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7.50
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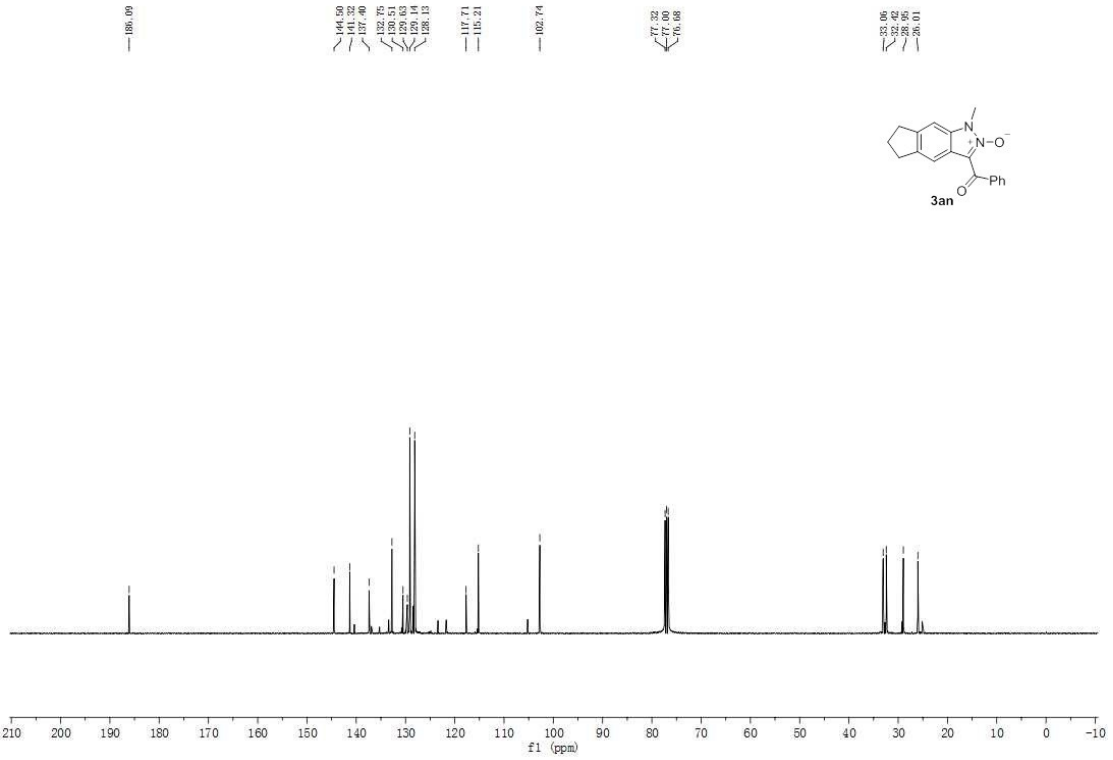
7.46
7.26
7.06
3.85
3.04
3.02
3.00
2.99
2.97
2.95
N
N-O
O
Ph
3an
2.05
1.01
1.24
2.33
1.02
3.00
2.25
2.16
2.45
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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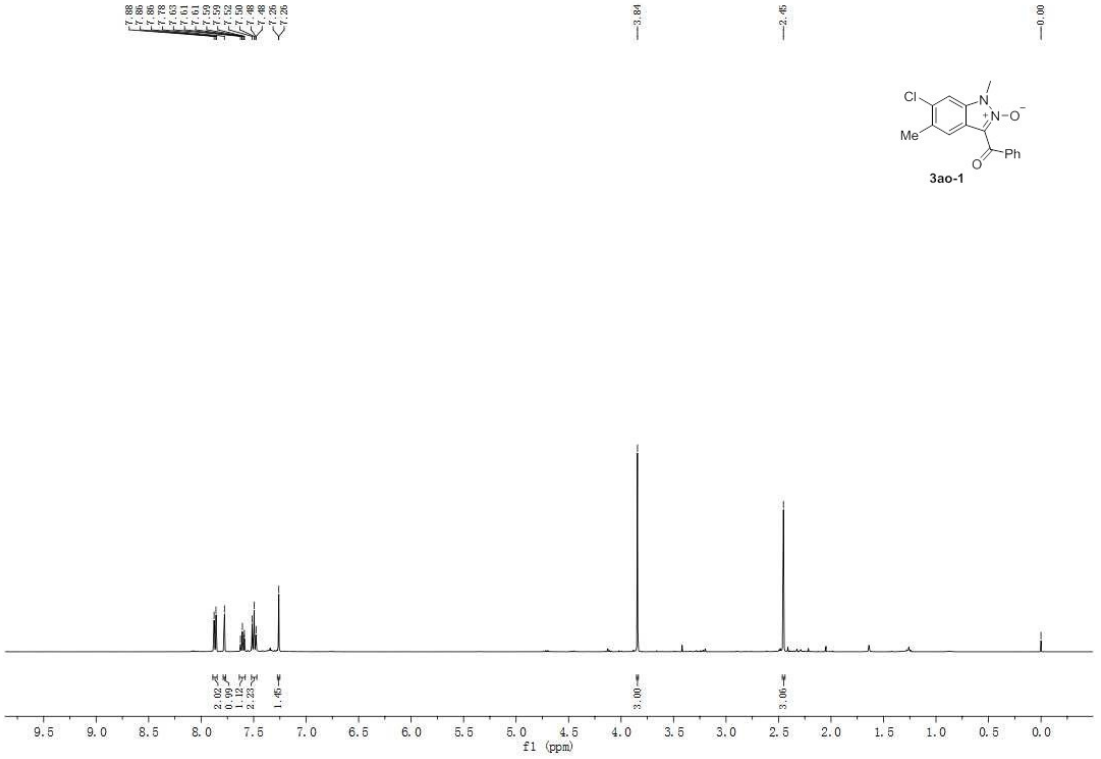
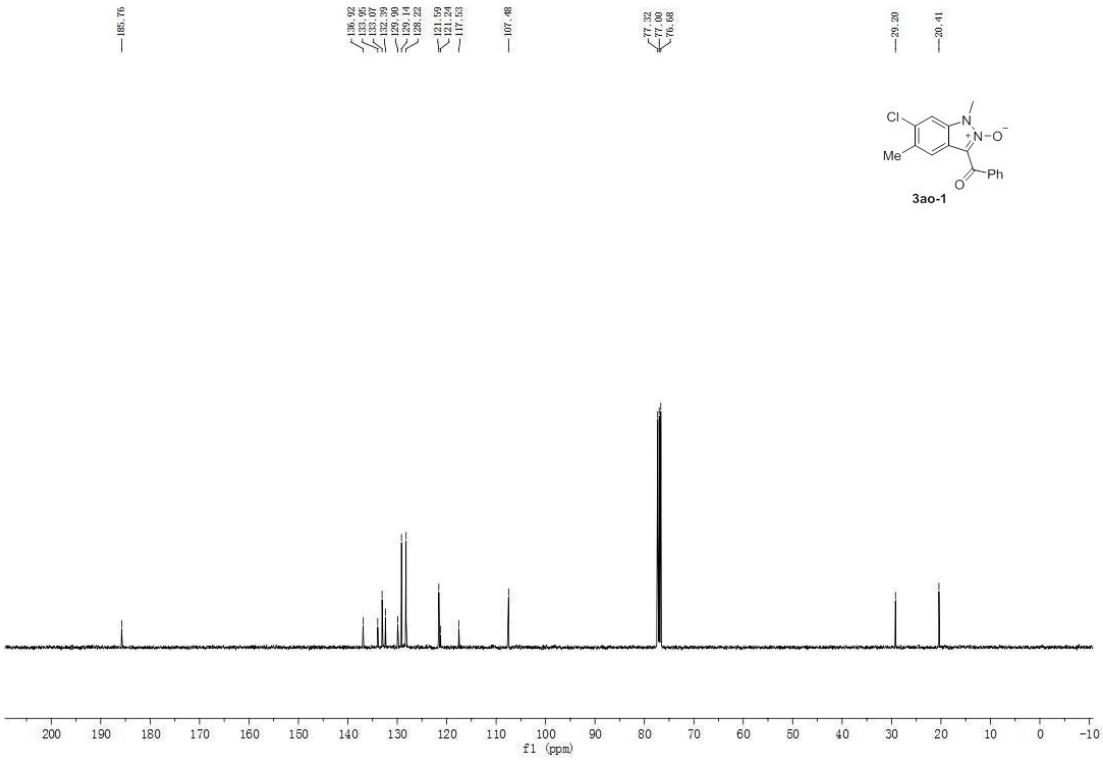
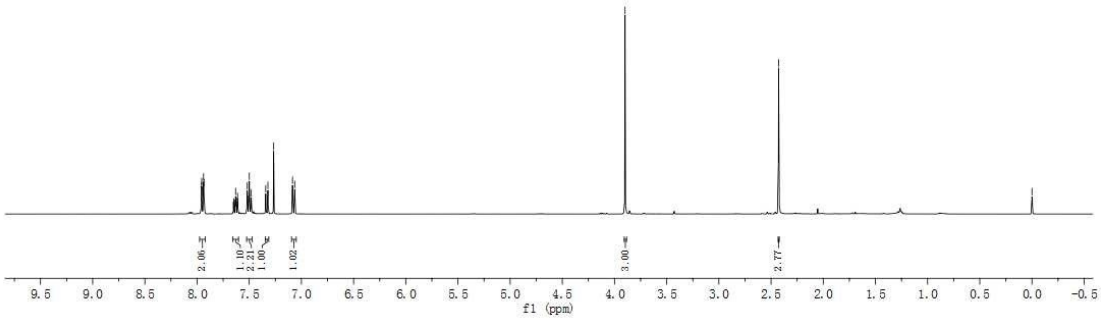
144.50
141.32
137.40
132.75
130.51
129.63
129.14
128.13
117.71
115.21
102.74
77.32
77.00
76.68
33.06
32.42
28.95
26.01
N
N-O
O
Ph
3an
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

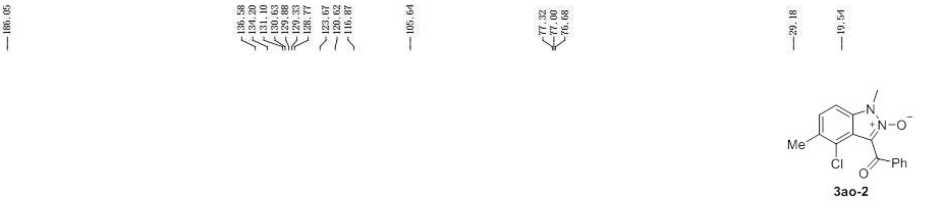

7.88
7.86
7.78
7.63
7.61
7.59
7.52
7.50
7.48
7.26
3.84
2.45
0.00
Cl
Me
N
N-O
Ph
O
3ao-1
2.02
0.99
1.13
2.23
1.45
3.00
3.06
f1 (ppm)


185.76
136.92
133.95
133.07
132.39
129.90
129.14
128.22
121.59
111.24
117.53
107.48
77.32
77.00
76.68
29.20
20.41
Cl
Me
N
N-O
Ph
O
3ao-1
f1 (ppm)

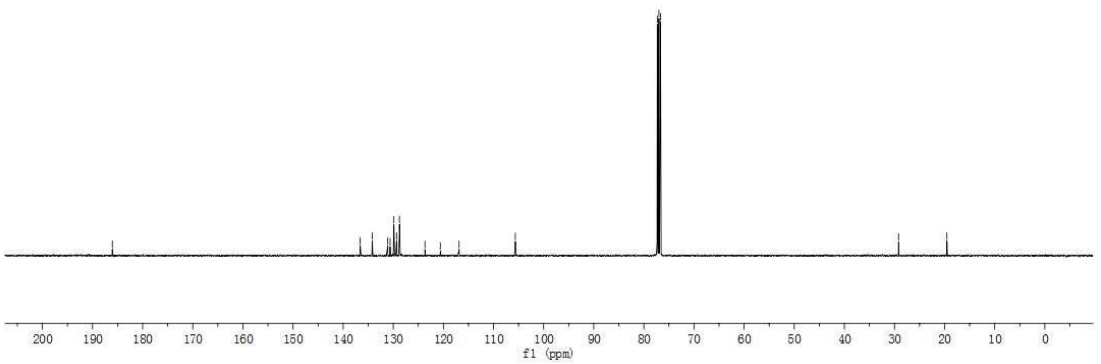

7.96
7.96
7.94
7.93
7.65
7.65
7.63
7.63
7.62
7.62
7.61
7.61
7.52
7.52
7.50
7.48
7.48
7.32
7.27
7.09
7.06
3.90
2.43
0.00
Me
Cl
N
N−O
Ph
O

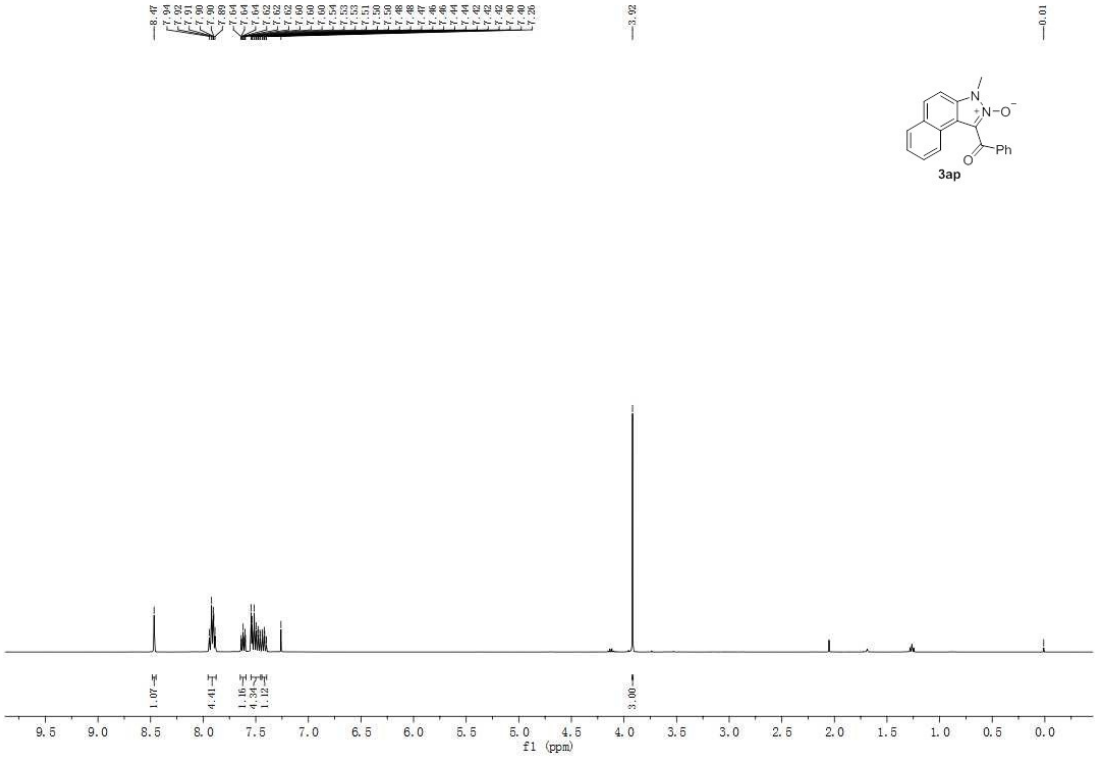
3ao-2

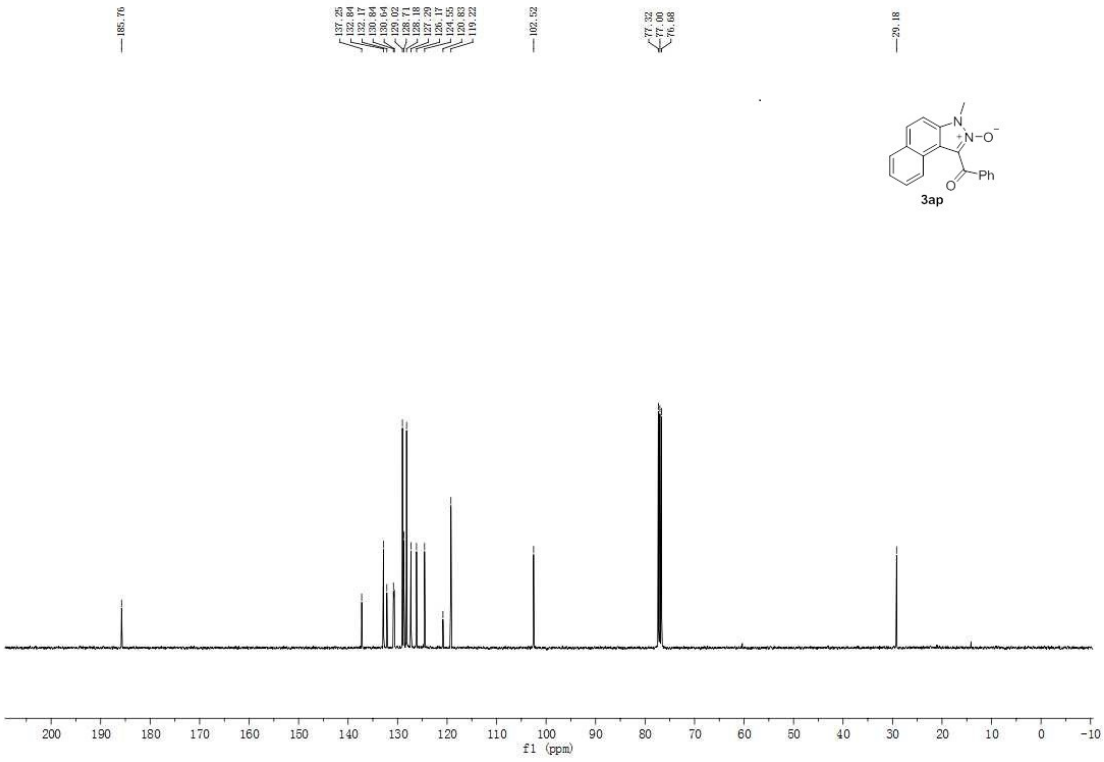

2.06
1.10
2.21
1.00
1.02
3.00
2.77
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

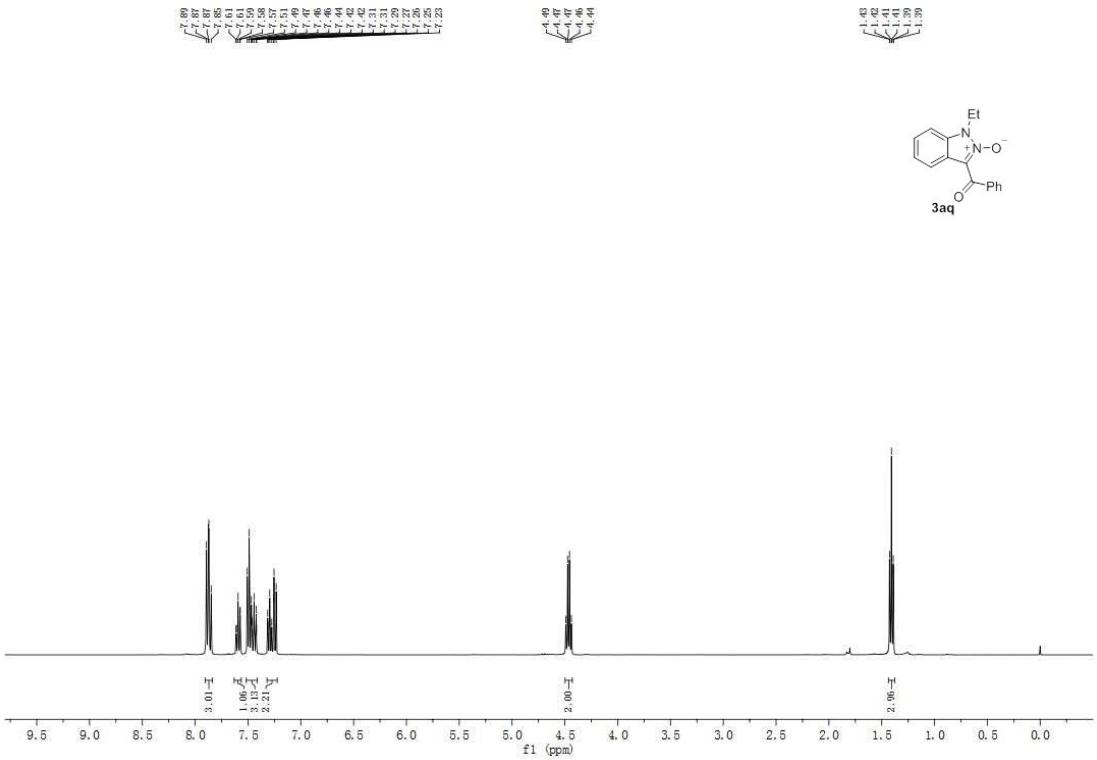

186.05
136.58
134.20
131.10
130.53
129.88
129.33
128.77
123.67
120.62
116.87
105.64
77.32
77.00
76.68
29.18
19.54
Me
Cl
N
N−O
Ph
O

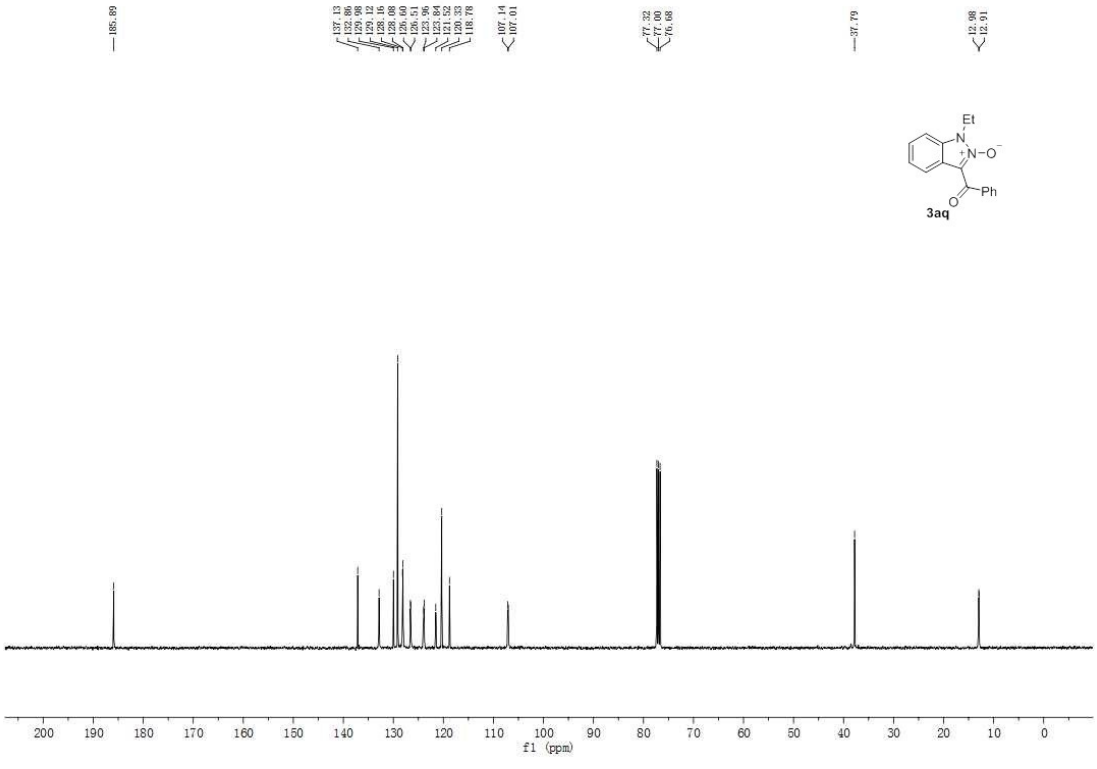
3ao-2

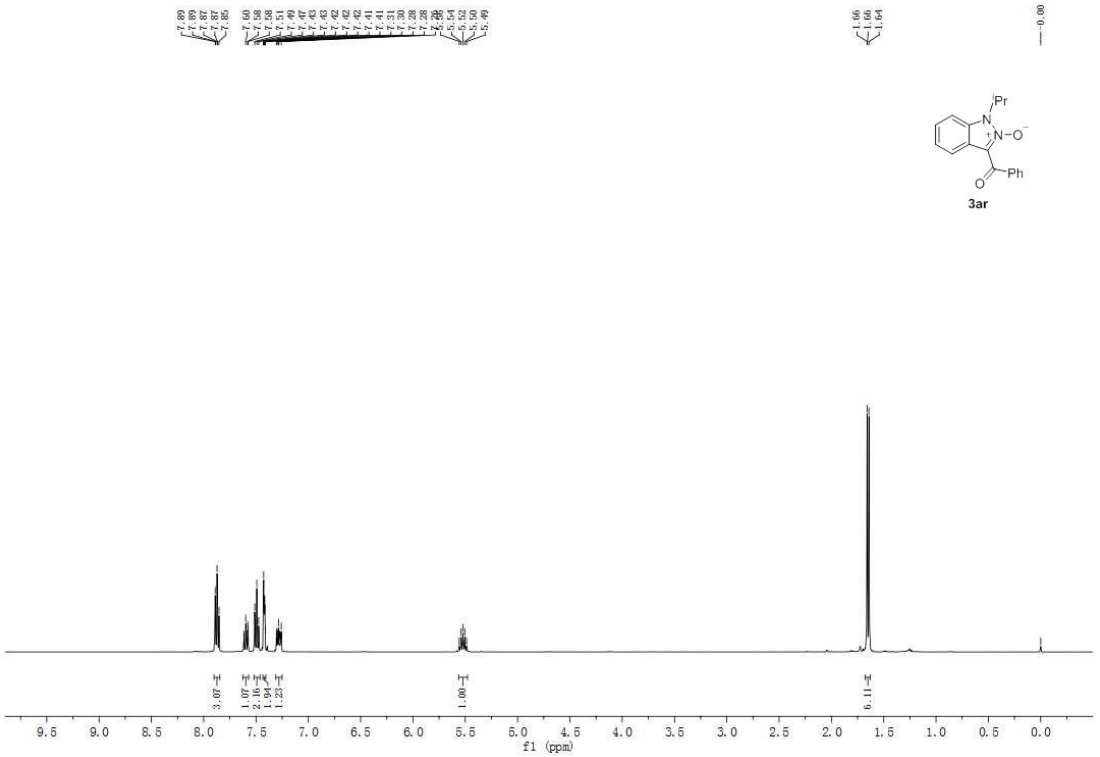

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

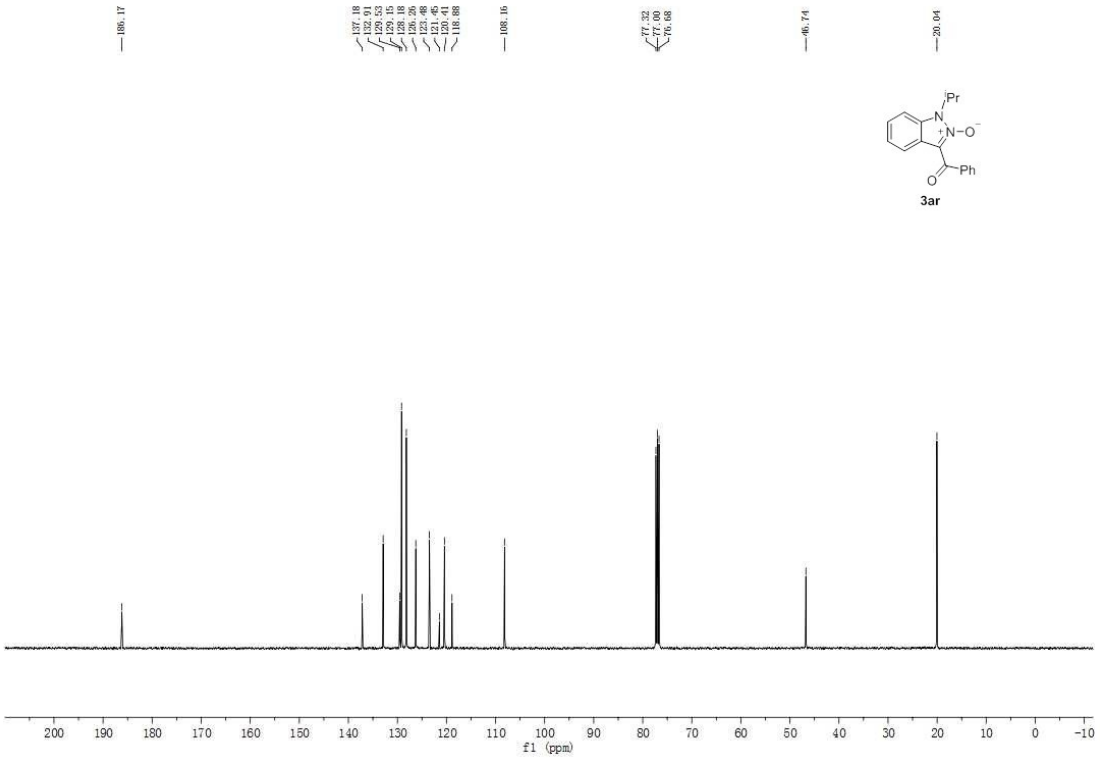

8.47
7.94
7.92
7.91
7.90
7.89
7.89
7.64
7.64
7.62
7.62
7.62
7.60
7.60
7.59
7.54
7.53
7.53
7.51
7.50
7.50
7.48
7.48
7.47
7.46
7.46
7.44
7.44
7.42
7.42
7.40
7.40
7.26
3.92
0.01
1.07
4.41
1.16
4.39
1.12
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
N
N−O
Ph
O
3ap

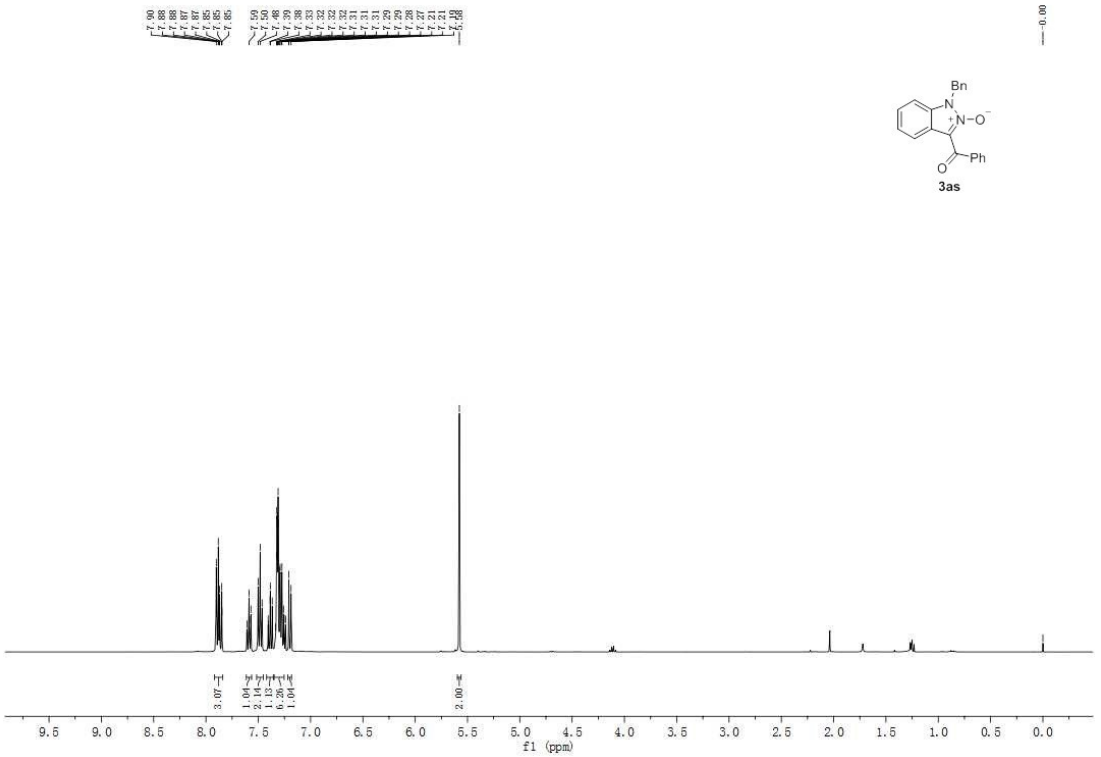

185.76
137.25
132.84
132.17
130.84
130.64
129.02
128.71
128.18
127.29
126.17
124.55
120.85
119.22
102.52
77.32
77.00
76.68
29.18
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)
N
N−O
Ph
O
3ap

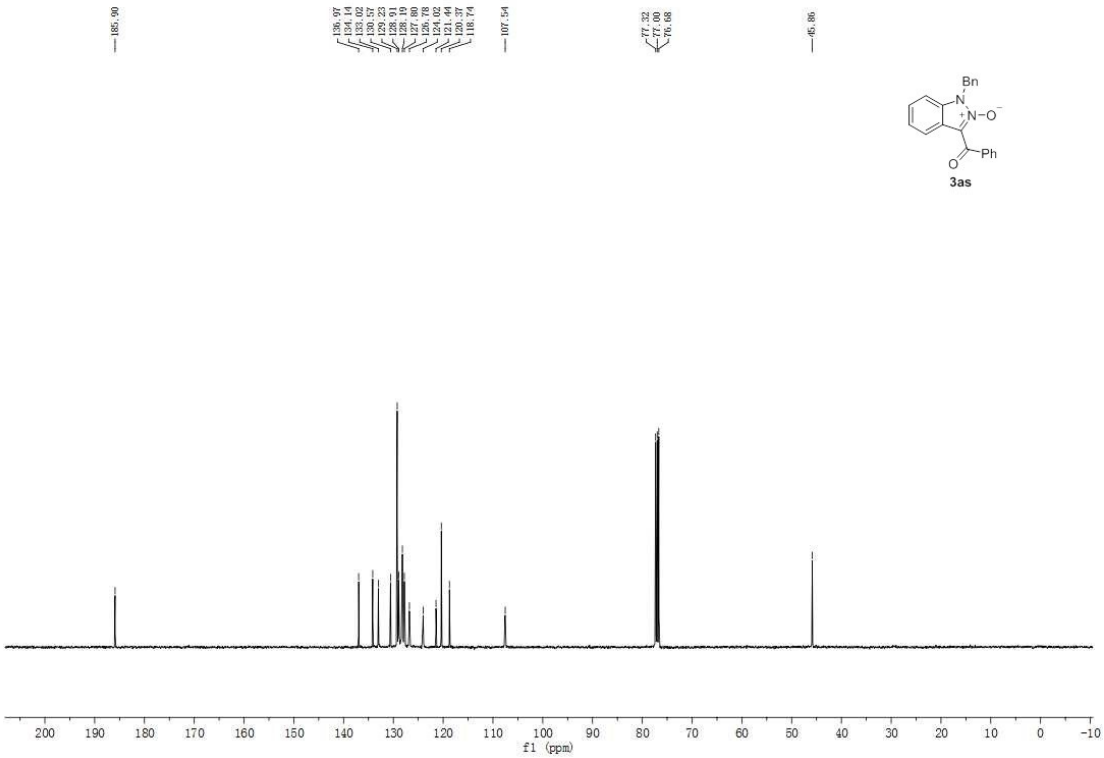

7.89
7.87
7.85
7.61
7.59
7.58
7.57
7.51
7.49
7.47
7.46
7.44
7.42
7.31
7.29
7.27
7.26
7.25
7.23
4.49
4.47
4.46
4.44
1.43
1.42
1.41
1.39
1.39
Et
N
N–O
Ph
O
3aq
3.01
1.06
3.13
2.21
2.00
2.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

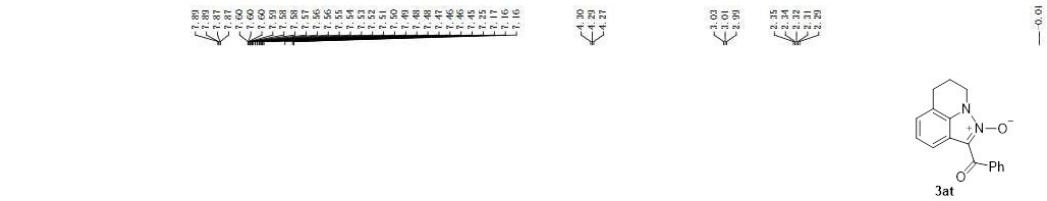

185.89
137.13
132.86
129.98
129.12
128.16
128.00
126.60
126.51
123.96
122.84
121.52
120.33
118.78
107.14
107.01
77.32
77.00
76.68
37.79
12.98
12.91
Et
N
N–O
Ph
O
3aq
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.89
7.89
7.87
7.87
7.85
7.60
7.58
7.58
7.51
7.51
7.49
7.47
7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.31
7.30
7.28
7.28
5.54
5.52
5.50
5.49
1.66
1.66
1.64
1.64
0.00
iPr
N
+
N–O
−
Ph
O
3ar
3.07
1.07
2.16
1.94
1.25
1.00
6.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

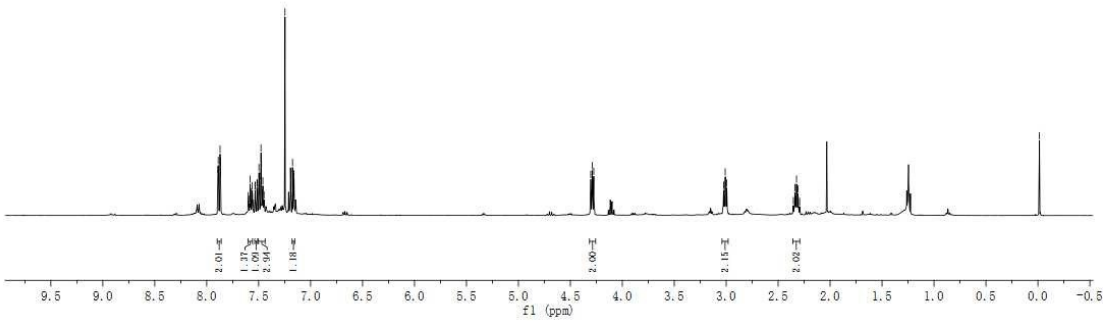

186.17
137.18
132.91
129.52
129.15
128.18
126.26
123.48
121.45
120.41
118.88
108.16
77.32
77.00
76.68
46.74
20.04
iPr
N
+
N–O
−
Ph
O
3ar
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

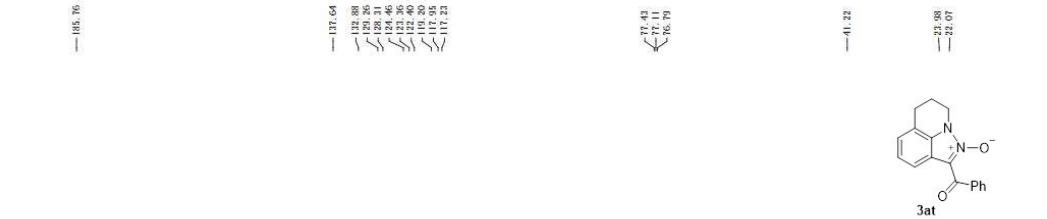

Bn
N
+N–O⁻
O
Ph
3as
f1 (ppm)


Bn
N
+N–O⁻
O
Ph
3as
f1 (ppm)

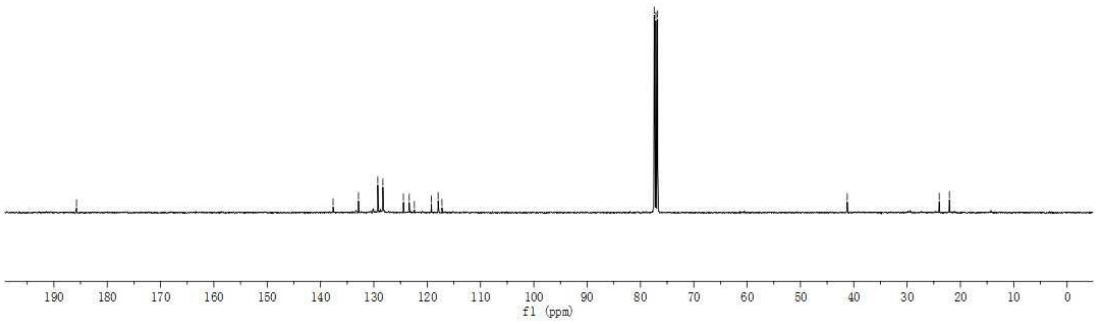


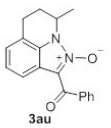
N
N—O⁻
Ph
O
3at


2.01
1.37
1.09
2.94
1.18
2.00
2.15
2.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

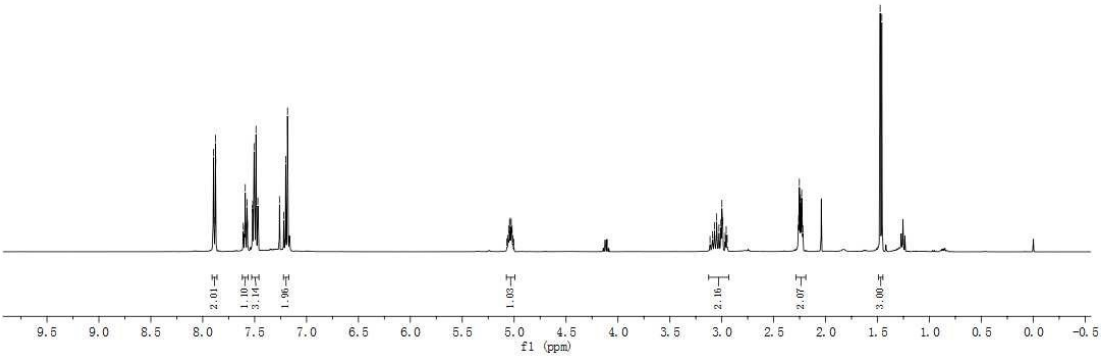


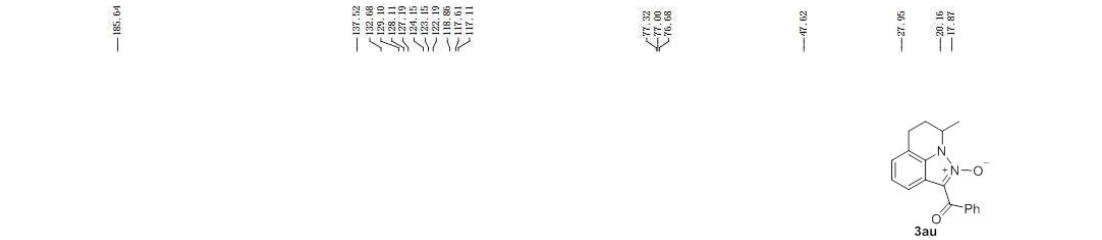
N
N—O⁻
Ph
O
3at


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


N
+N—O⁻
O
Ph

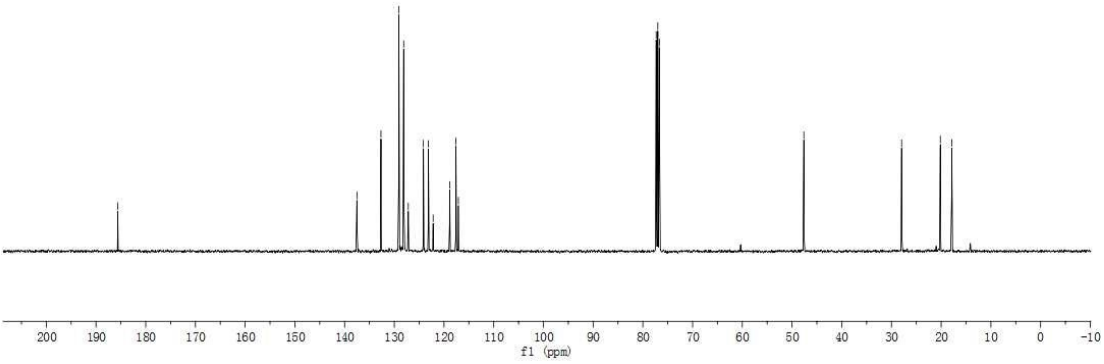
3au

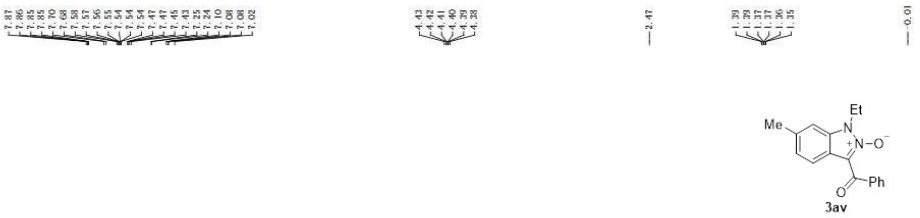

2.01
1.10
3.14
1.96
1.03
2.16
2.07
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



N
+N—O⁻
O
Ph

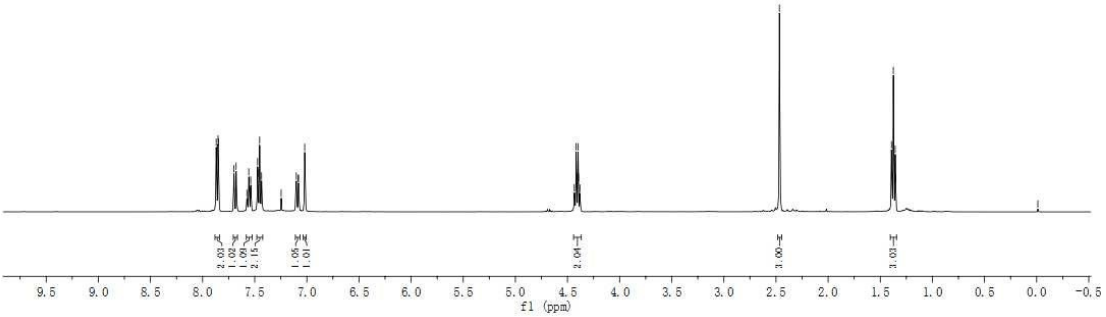
3au

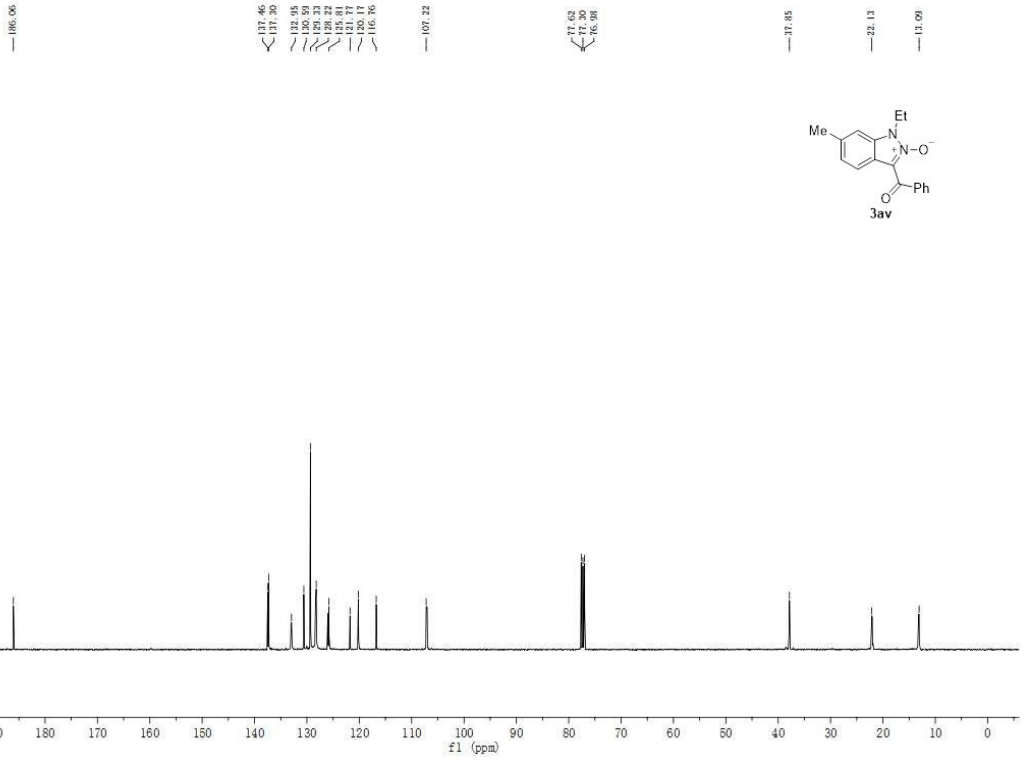

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



Et
Me
N
N–O
Ph
O

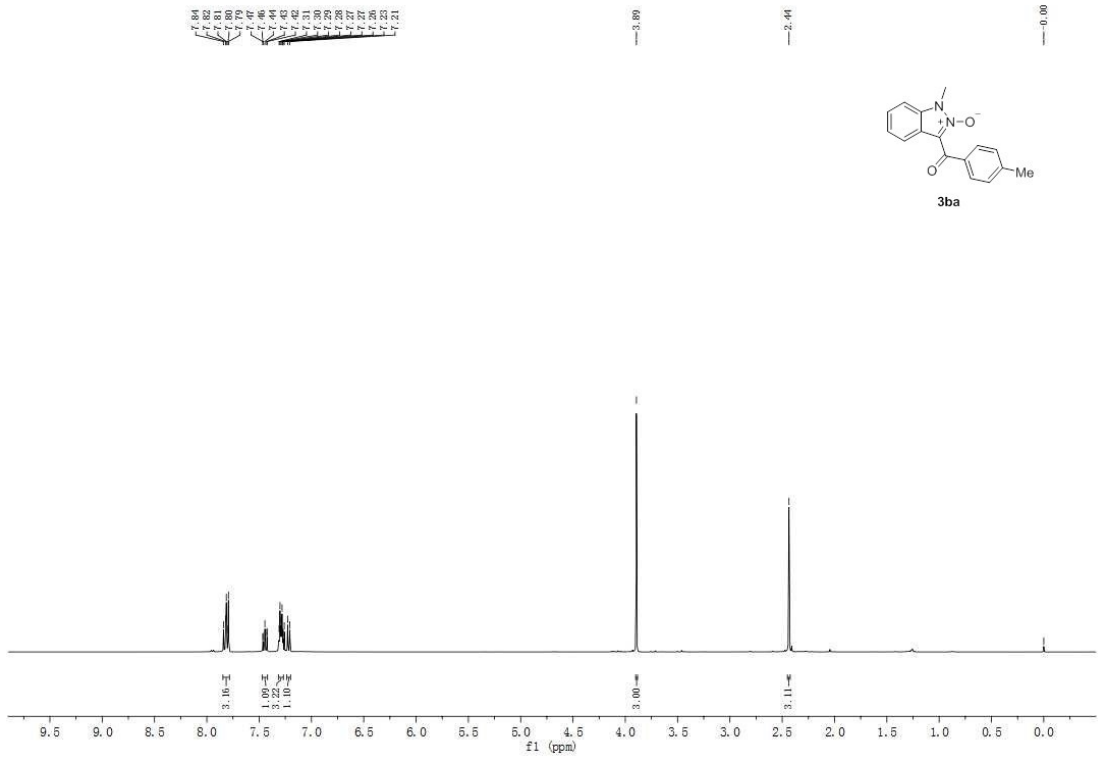
3av

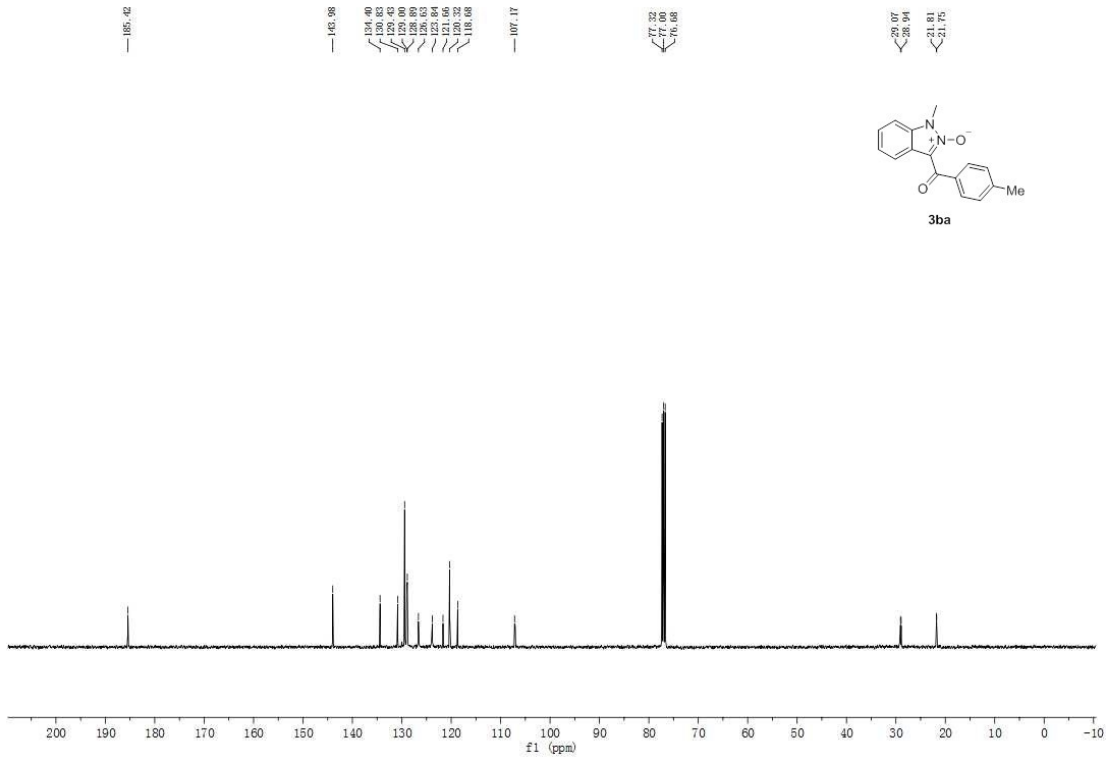

2.03
1.02
1.09
2.15
1.05
1.01
2.04
3.00
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

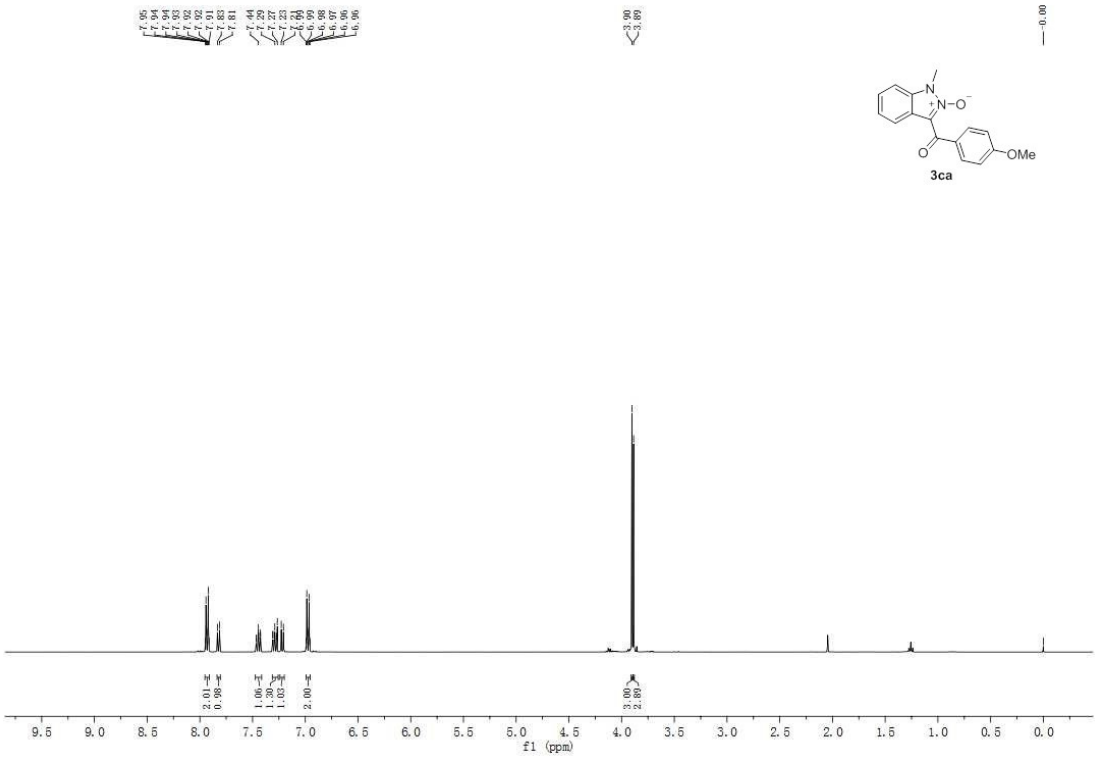

186.06
137.46
137.30
132.95
130.59
130.33
129.22
128.81
121.77
120.17
116.76
107.22
77.63
77.30
76.98
37.85
22.13
13.09
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

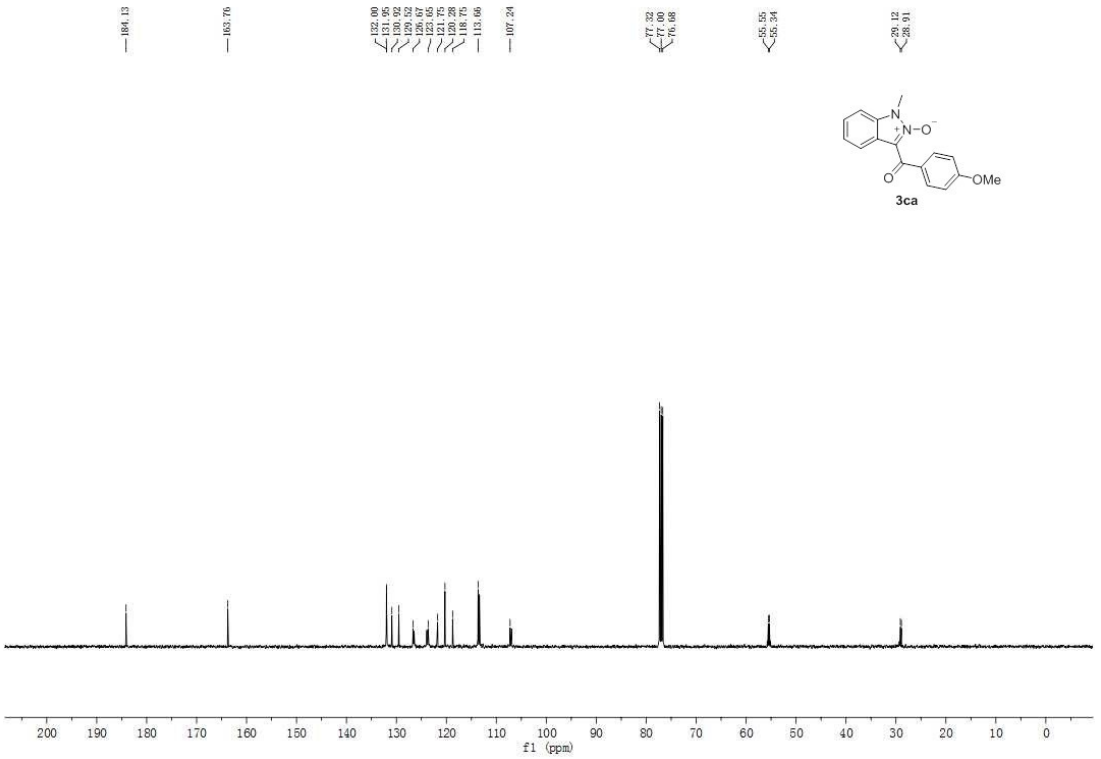
Et
Me
N
N–O
Ph
O

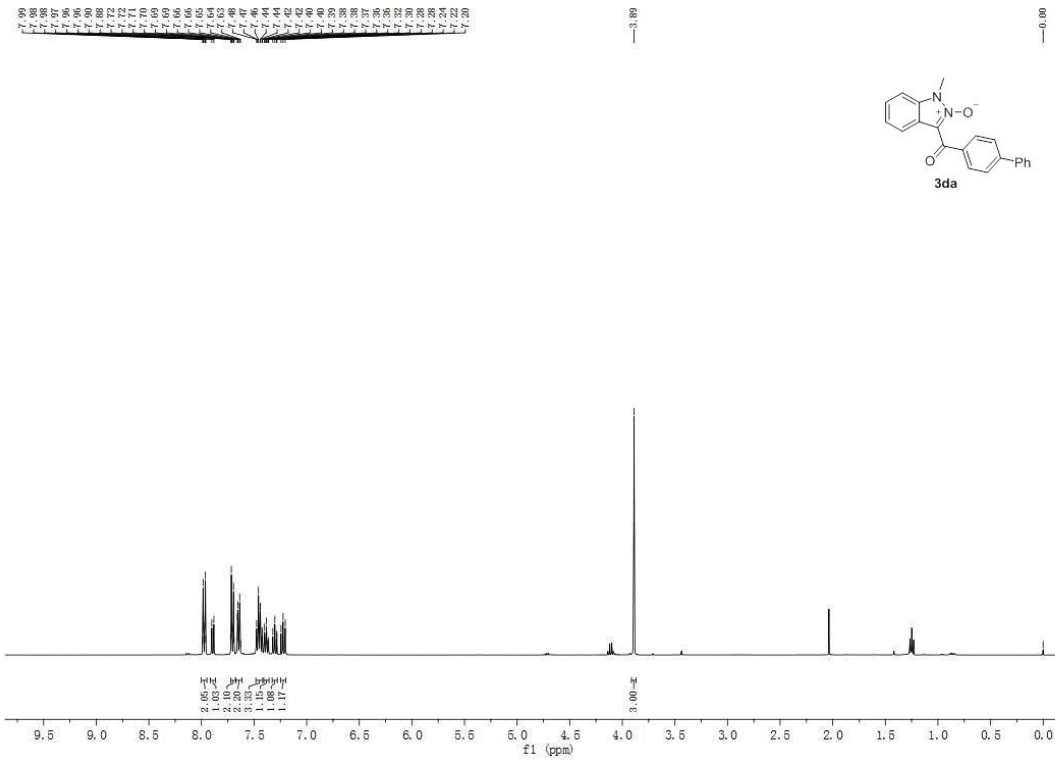
3av


7.84
7.82
7.81
7.80
7.79
7.47
7.46
7.44
7.43
7.42
7.31
7.30
7.29
7.28
7.27
7.26
7.23
7.21
3.89
2.44
0.00
N
+N–O⁻
O
Me
3ba
3.16
1.09
3.22
1.10
3.00
3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


185.42
145.98
134.40
130.83
129.43
129.00
126.89
126.65
123.84
121.66
120.32
118.68
107.17
77.32
77.00
76.68
29.07
28.94
21.81
21.75
N
+N–O⁻
O
Me
3ba
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.95
7.94
7.94
7.93
7.92
7.92
7.91
7.83
7.81
7.44
7.29
7.27
7.23
7.04
6.99
6.98
6.97
6.96
6.96
3.90
3.89
0.00
N
N–O
O
OMe
3ca
2.01
0.98
1.06
1.30
1.03
2.00
3.00
2.89
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


184.13
163.76
132.00
131.95
130.92
129.52
126.67
123.65
121.75
120.28
116.75
113.66
107.24
77.32
77.00
76.68
55.55
55.34
29.12
28.91
N
N–O
O
OMe
3ca
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.99
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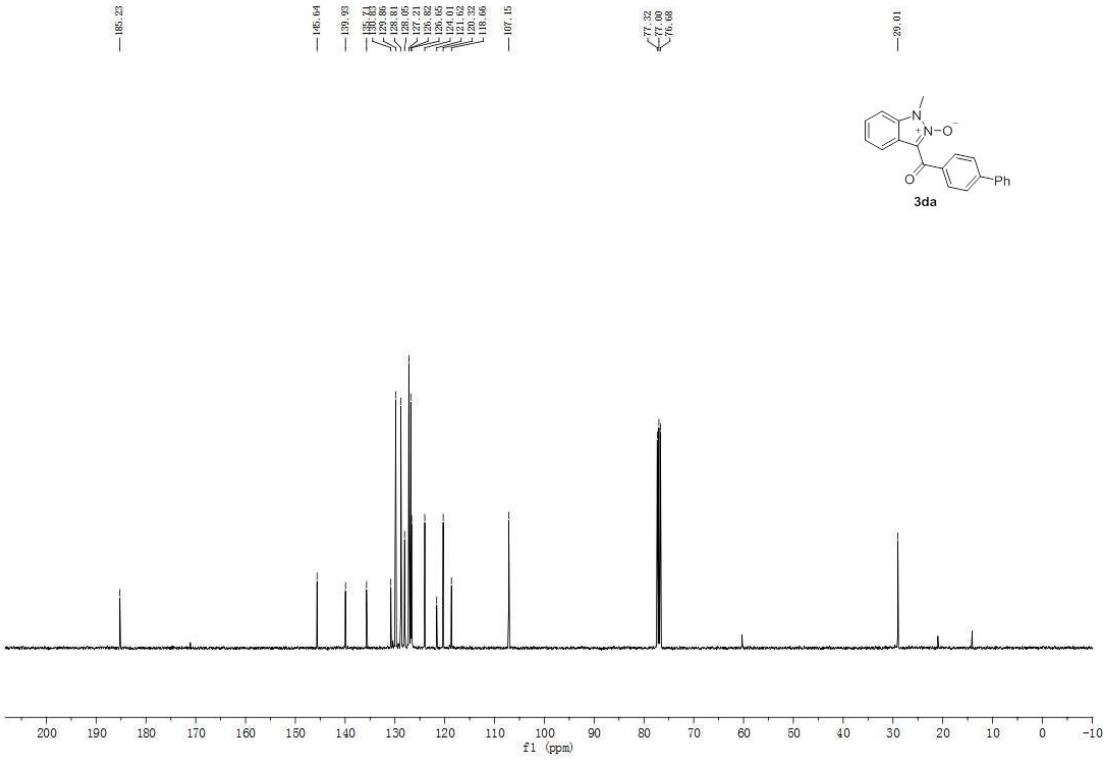
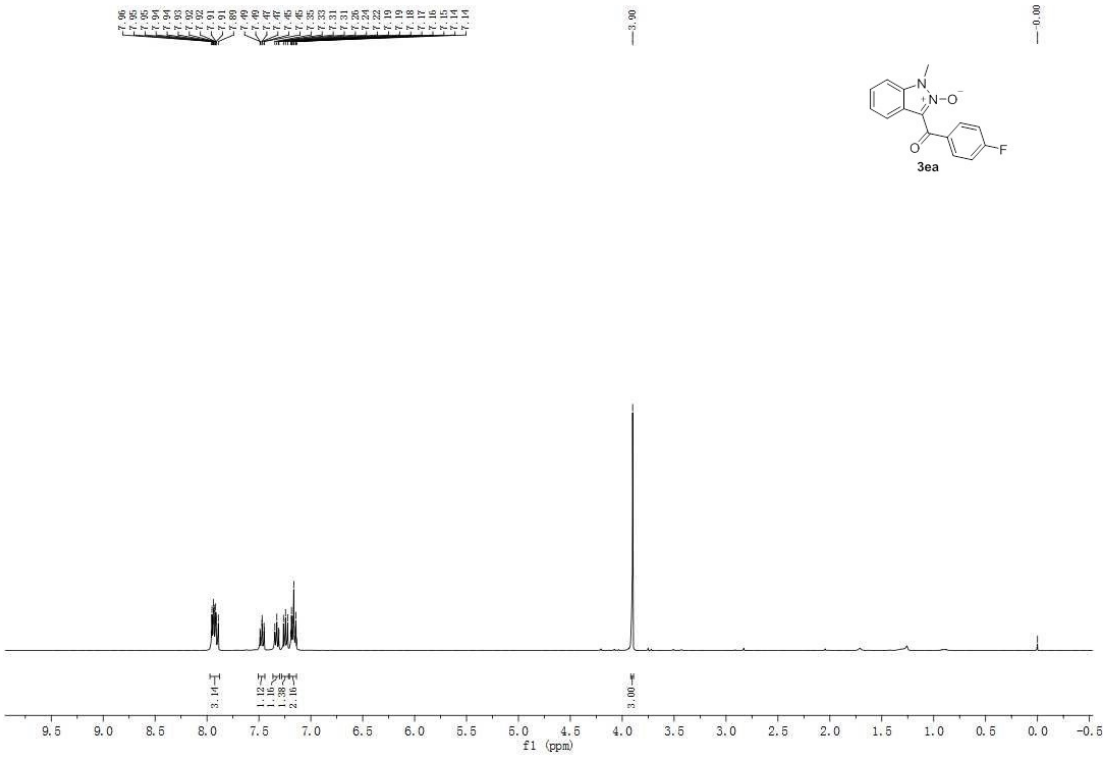
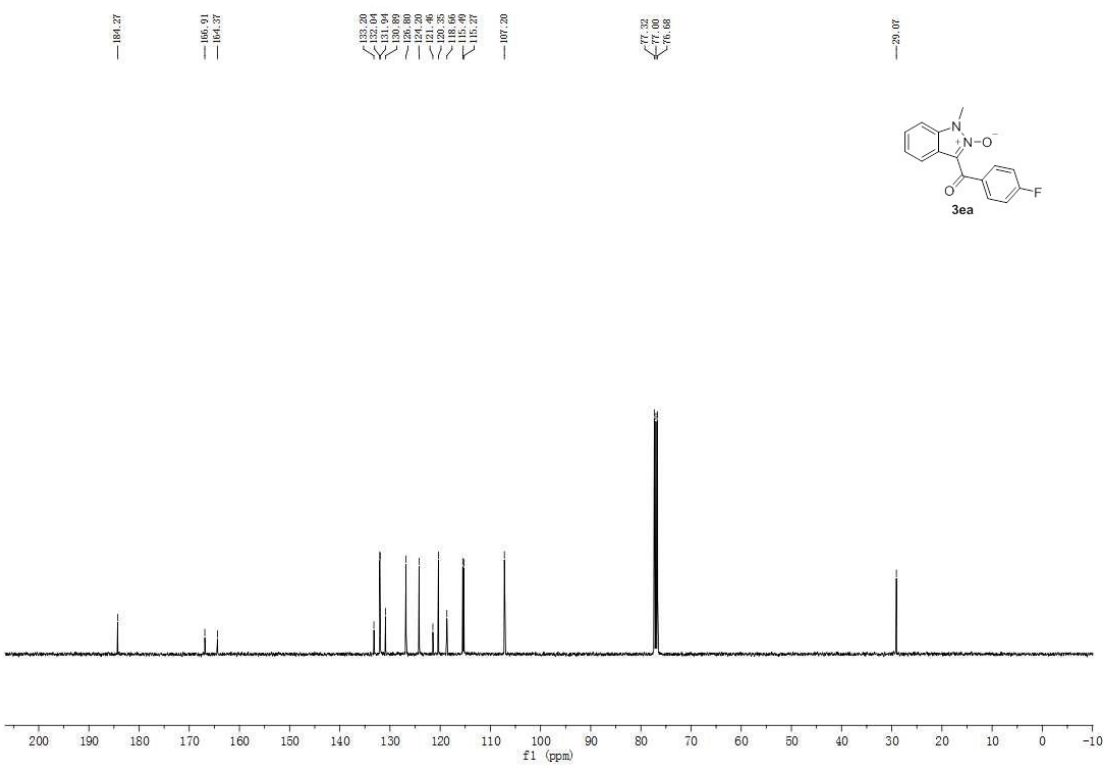
7.98
7.97
7.96
7.96
7.90
7.88
7.72
7.72
7.71
7.70
7.69
7.69
7.66
7.65
7.64
7.63
7.48
7.47
7.46
7.44
7.44
7.42
7.42
7.40
7.40
7.39
7.38
7.38
7.37
7.36
7.32
7.30
7.28
7.24
7.22
7.20
3.89
0.00
N
N-O
O
Ph
3da
2.05
1.03
2.10
2.20
3.33
1.15
1.08
1.17
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


185.23
145.64
139.93
135.74
135.41
129.86
128.81
128.05
127.21
126.82
126.65
121.01
121.02
120.32
118.66
107.15
77.32
77.00
76.68
29.01
N
N-O
O
Ph
3da
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


3ea
f1 (ppm)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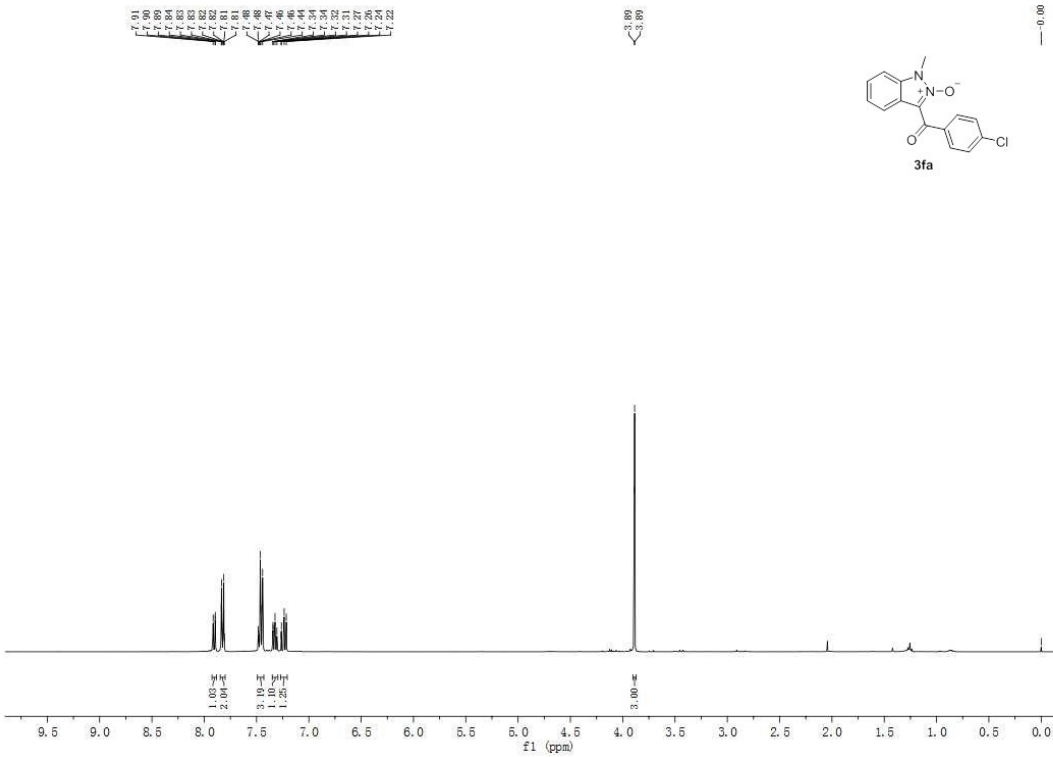
f1 (ppm)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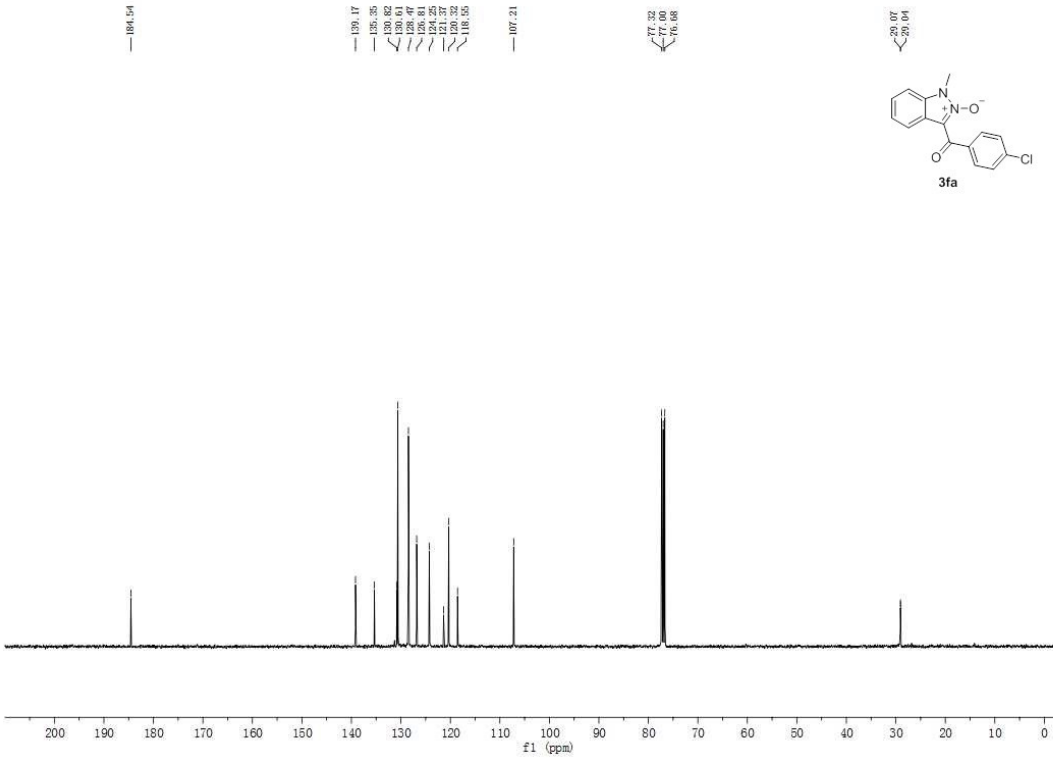
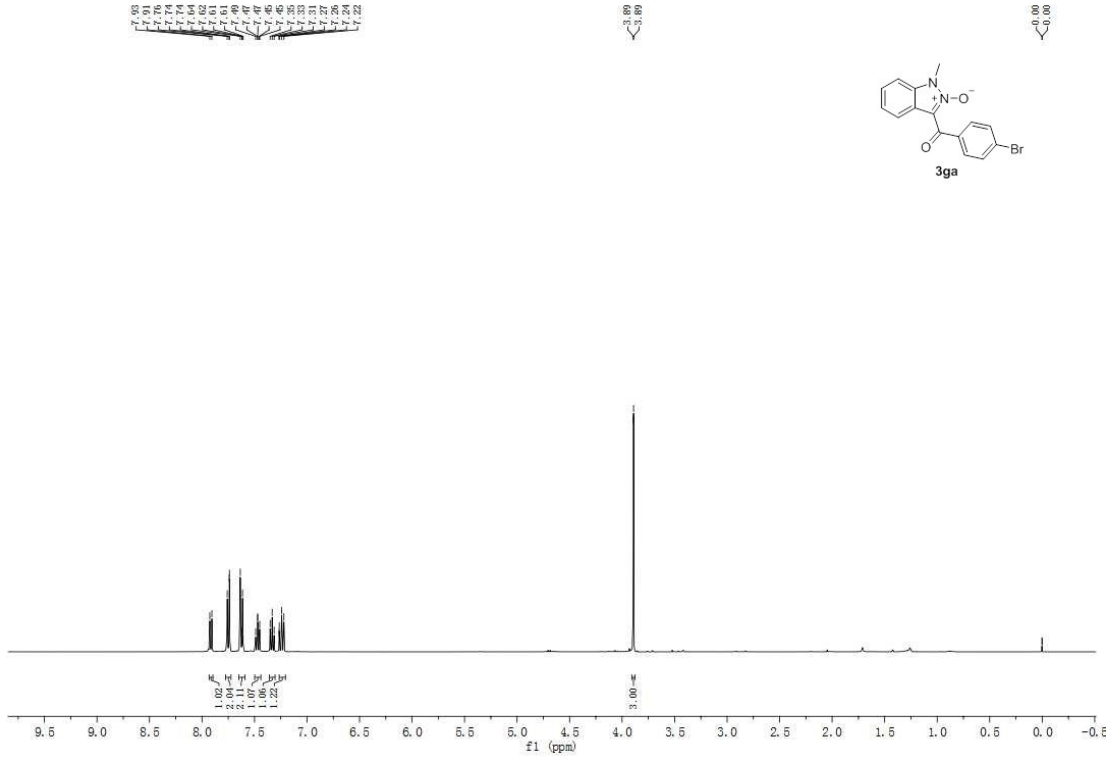
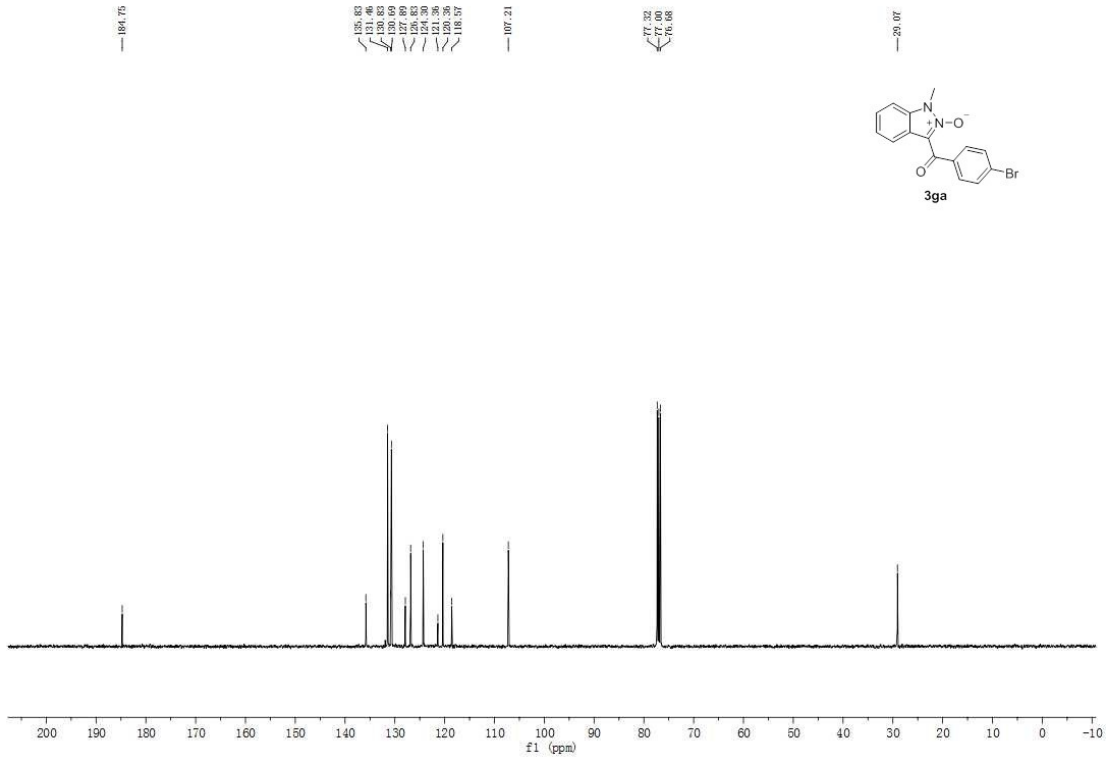
7.90
7.89
7.84
7.83
7.83
7.82
7.82
7.81
7.81
7.48
7.48
7.47
7.47
7.46
7.46
7.44
7.34
7.34
7.32
7.31
7.27
7.26
7.24
7.22
3.89
3.89
0.00
1.03
2.04
3.19
1.10
1.25
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
3fa


184.54
139.17
135.35
130.82
130.61
128.47
126.61
125.25
121.37
120.32
118.55
107.21
77.32
77.00
76.68
29.07
29.04
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
3fa


7.93
7.91
7.76
7.74
7.74
7.64
7.62
7.61
7.49
7.47
7.47
7.46
7.45
7.33
7.31
7.27
7.26
7.24
7.22
3.89
3.89
0.00
0.00
3ga
1.02
2.04
2.11
1.07
1.06
1.22
3.00
f1 (ppm)


184.75
135.83
131.46
130.55
130.69
127.89
126.83
124.30
121.36
120.36
118.57
107.21
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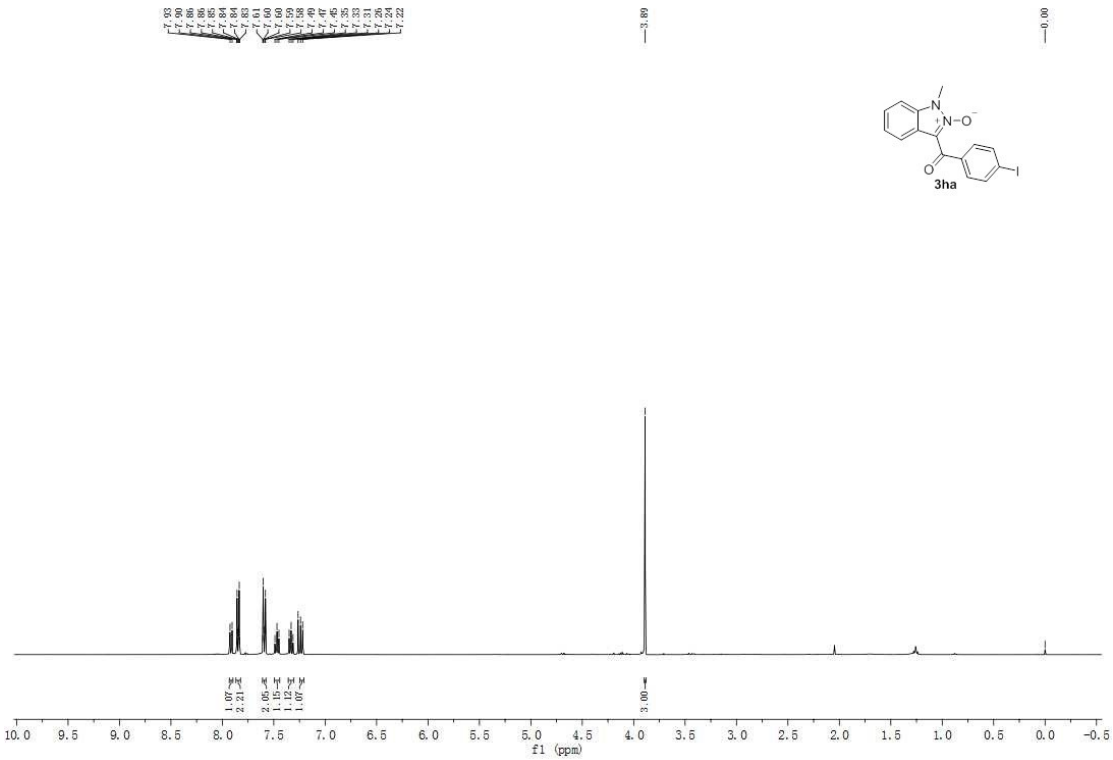
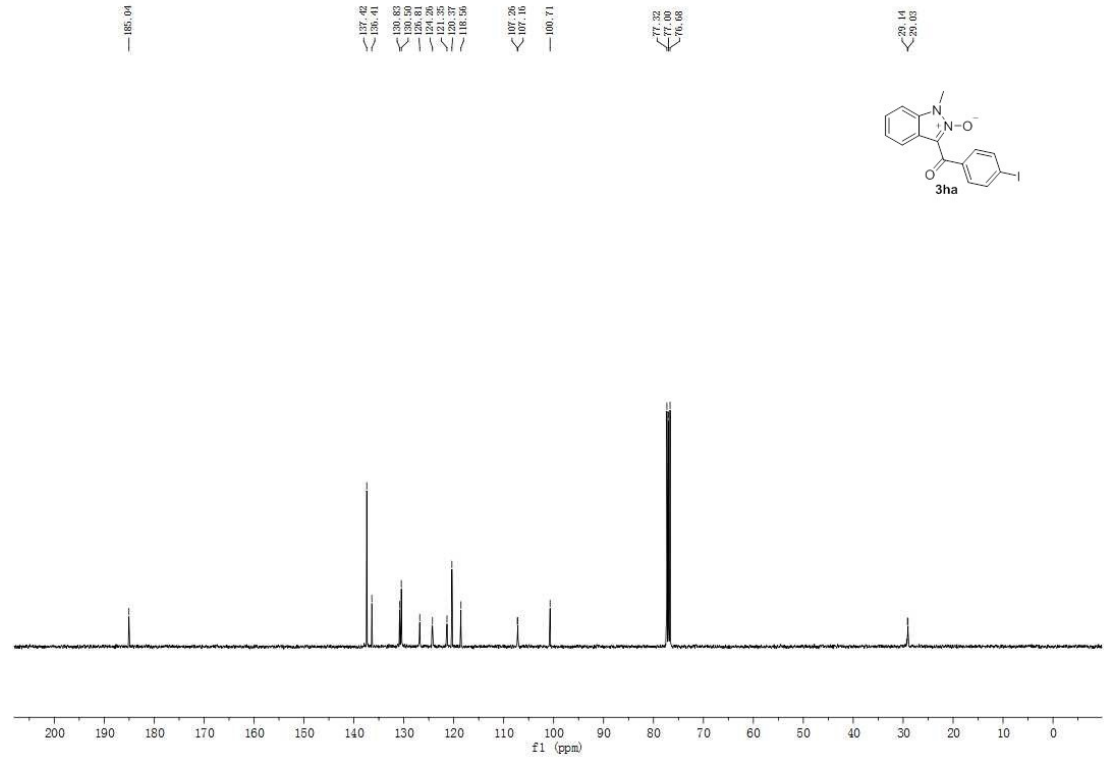
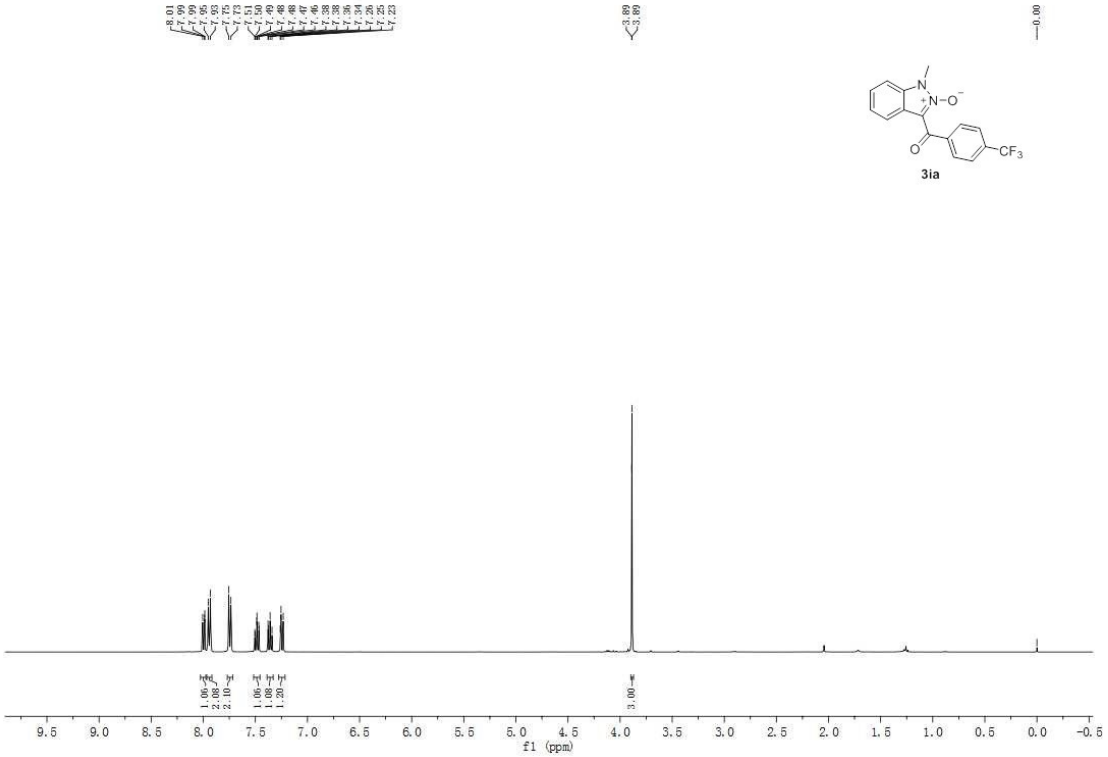
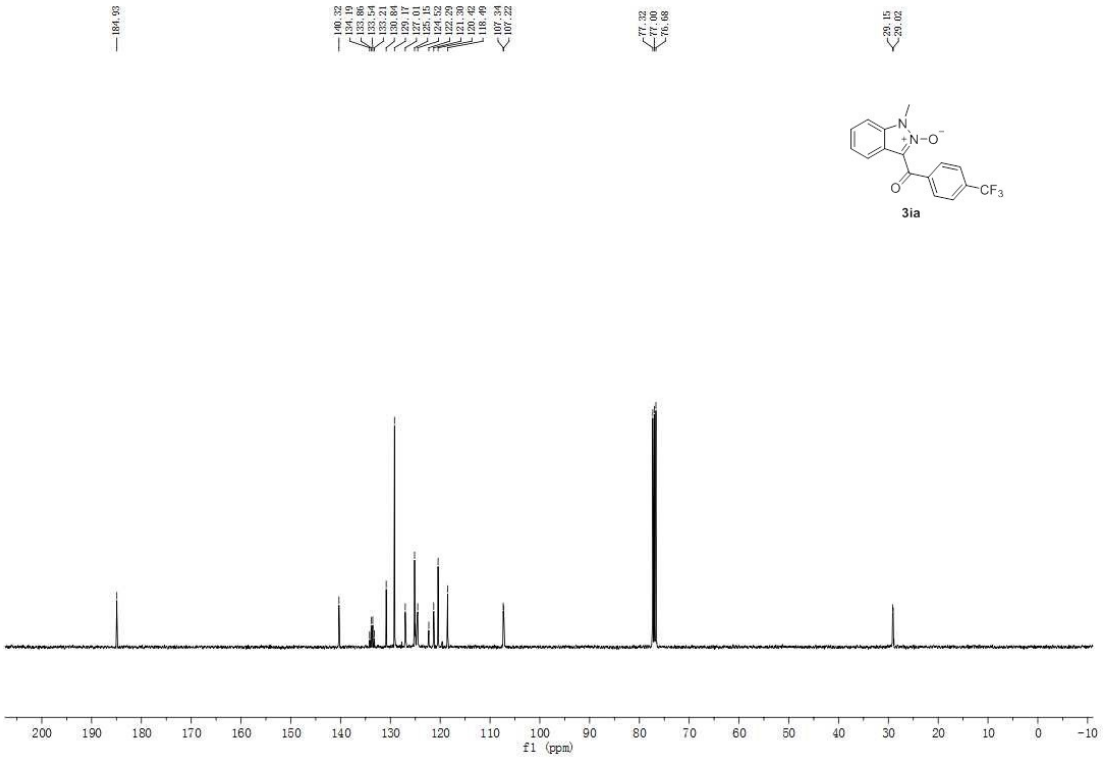
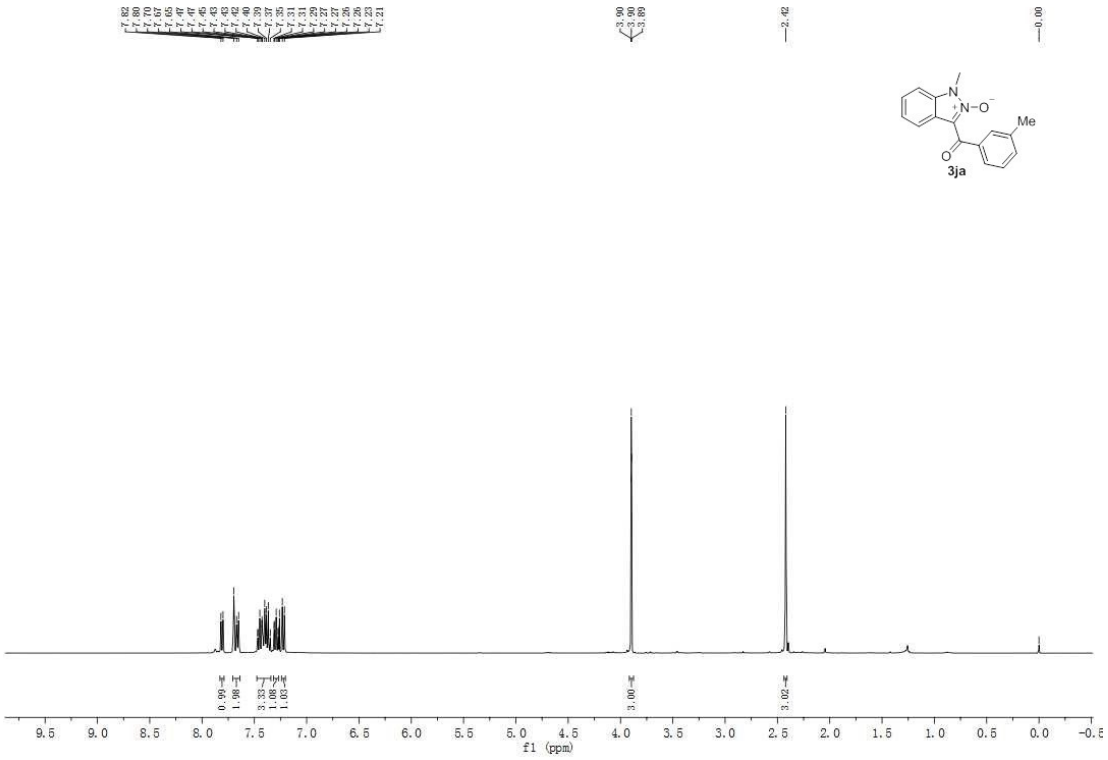
77.00
76.68
29.07
3ga
f1 (ppm)


7.93
7.90
7.88
7.86
7.85
7.84
7.84
7.83
7.61
7.60
7.59
7.59
7.58
7.58
7.49
7.47
7.45
7.35
7.33
7.31
7.26
7.24
7.22
3.89
0.00
3ha
1.07
2.21
2.05
1.15
1.12
1.07
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


185.04
137.42
136.41
130.83
130.50
126.81
124.26
121.35
120.37
118.56
107.26
107.16
100.71
77.32
77.00
76.68
29.14
29.03
3ha
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.01
7.99
7.95
7.93
7.75
7.73
7.51
7.50
7.49
7.48
7.47
7.46
7.38
7.36
7.34
7.25
7.23
3.89
3.89
0.00
3ia
1.06
2.08
2.10
1.06
1.08
1.20
3.00
f1 (ppm)


184.93
140.32
136.19
133.86
133.54
133.21
130.84
130.17
127.01
125.15
124.52
122.29
121.30
120.42
118.49
107.34
107.22
77.32
77.00
76.68
29.15
29.02
3ia
f1 (ppm)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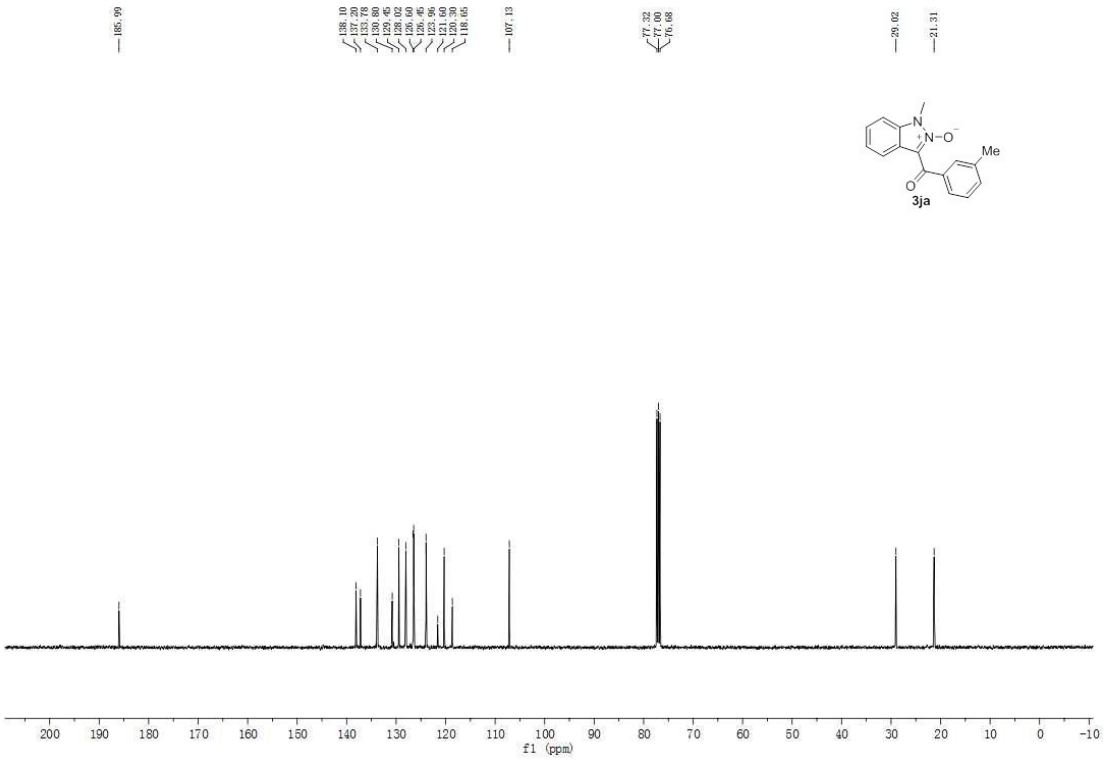
7.80
7.70
7.67
7.65
7.49
7.47
7.45
7.43
7.42
7.40
7.39
7.37
7.35
7.31
7.29
7.27
7.26
7.23
7.21
3.90
3.88
2.42
0.00
N
N-O
Me
O
3ja
0.99
1.98
3.33
1.08
1.03
3.00
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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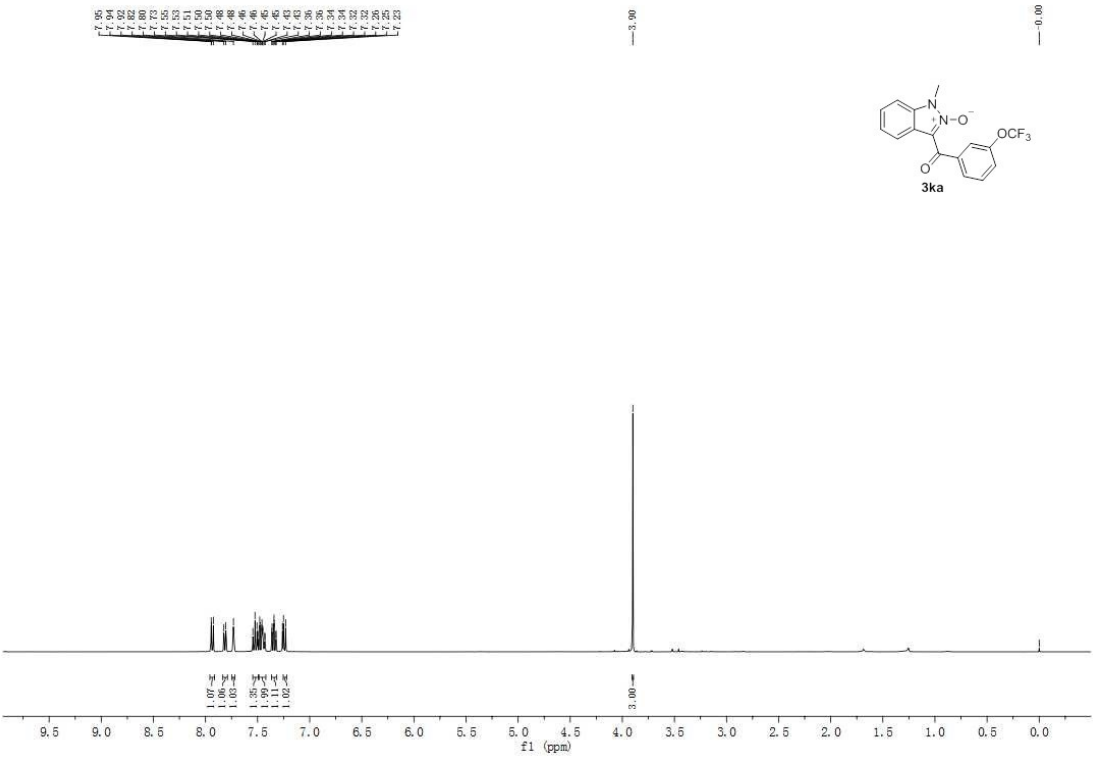
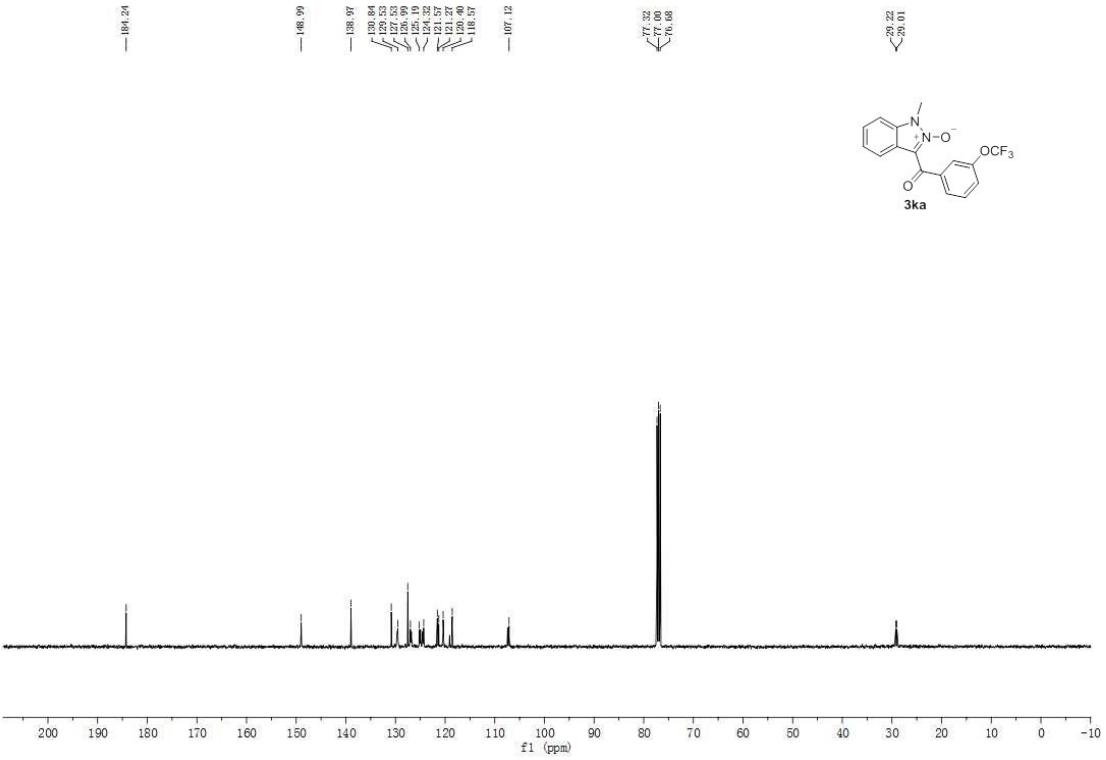
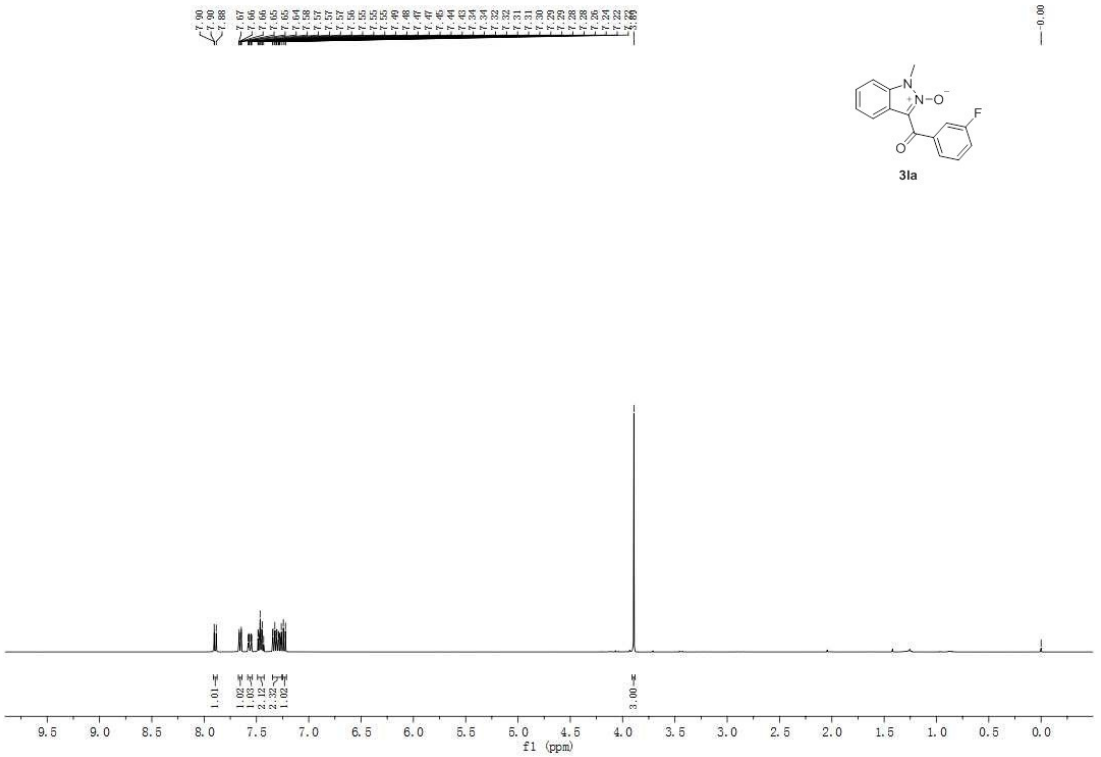
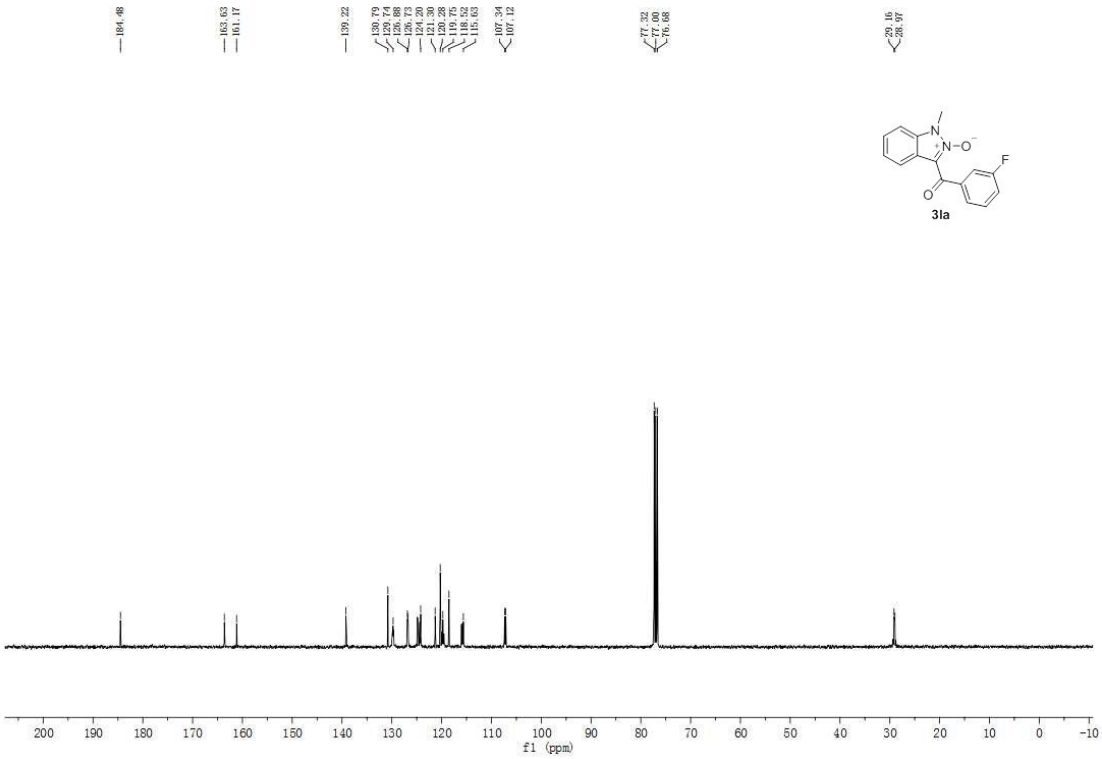
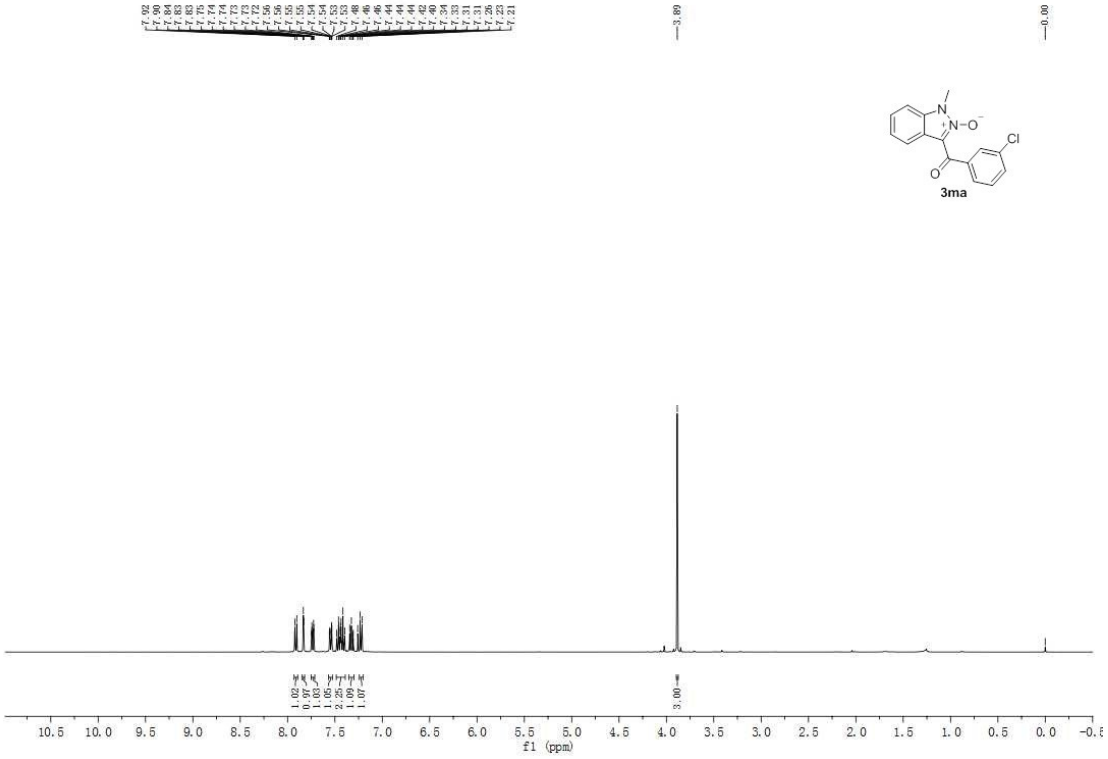
138.10
137.20
133.79
130.88
129.45
128.02
126.60
126.46
123.96
121.60
120.30
118.65
107.13
77.32
77.00
76.68
29.02
21.31
N
N-O
Me
O
3ja
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


3ka
f1 (ppm)


3ka
f1 (ppm)


3la
1.01
1.02
1.03
2.12
2.32
1.02
3.00
f1 (ppm)


3la
f1 (ppm)


7.92
7.90
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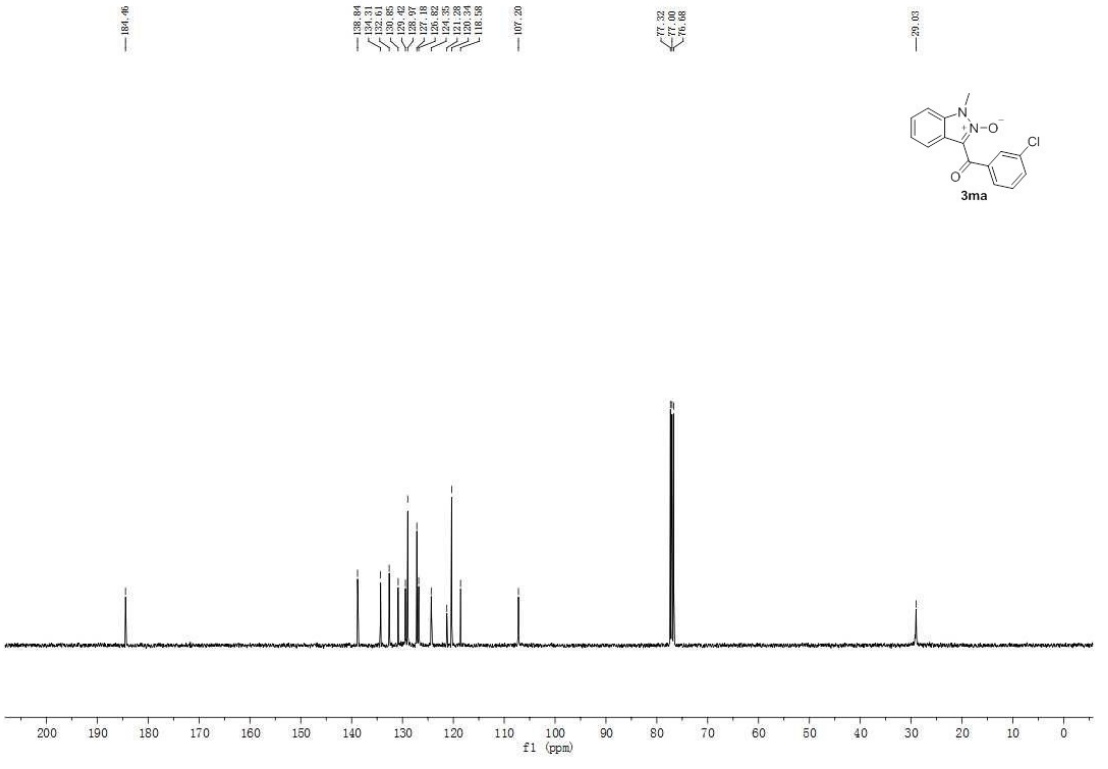
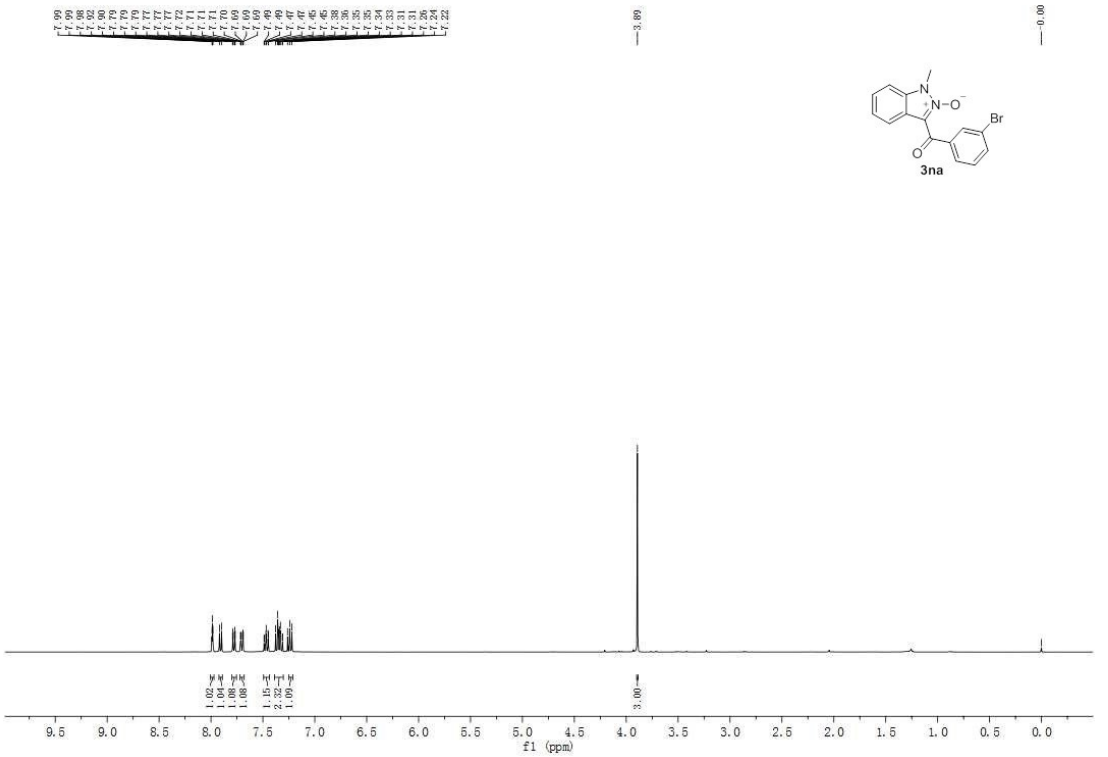
7.83
7.75
7.74
7.74
7.73
7.73
7.72
7.56
7.56
7.55
7.55
7.54
7.54
7.53
7.53
7.48
7.46
7.46
7.44
7.44
7.42
7.40
7.34
7.33
7.31
7.31
7.26
7.23
7.21
3.89
0.00
1.02
0.97
1.03
1.05
2.25
1.00
1.07
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
3ma


184.46
138.84
134.31
132.61
130.85
129.42
128.97
127.18
126.52
124.35
121.28
120.34
116.58
107.20
77.32
77.00
76.68
29.03
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
3ma


7.99
7.98
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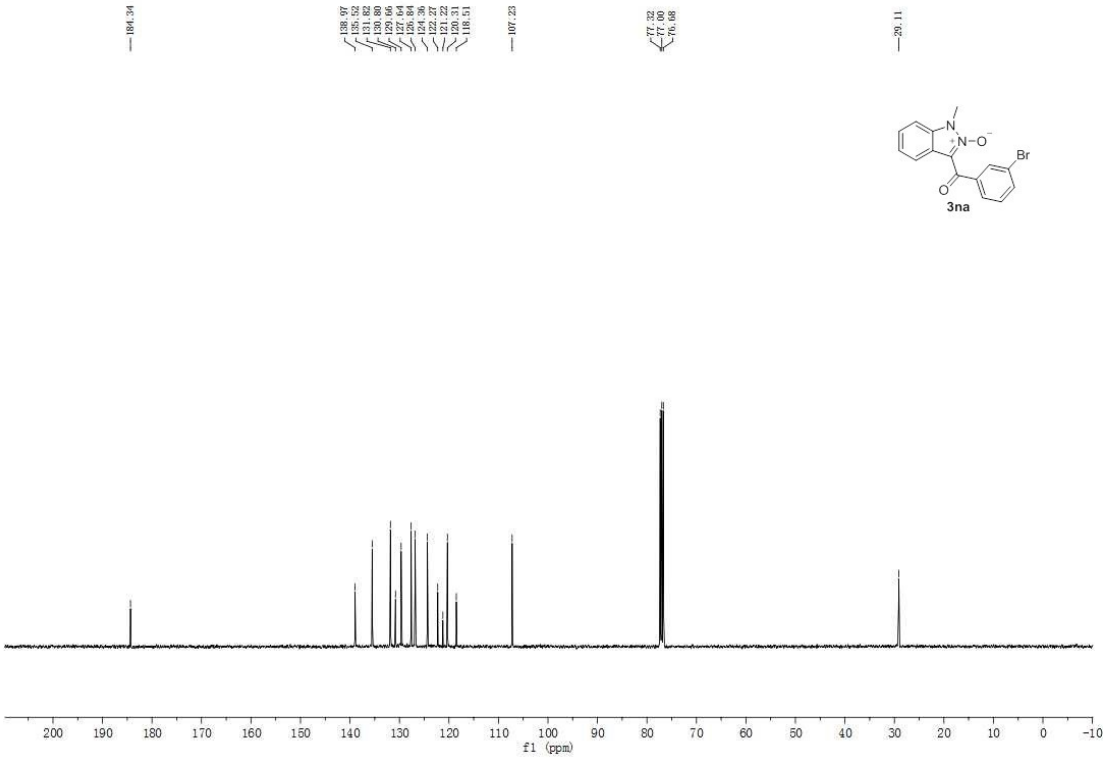
7.90
7.79
7.77
7.72
7.71
7.70
7.69
7.49
7.47
7.45
7.38
7.35
7.34
7.33
7.31
7.26
7.24
7.22
3.89
0.00
Br
3na
1.02
1.04
1.08
1.08
1.15
2.32
1.09
3.00
f1 (ppm)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131.82
130.80
129.66
127.64
126.84
123.39
122.27
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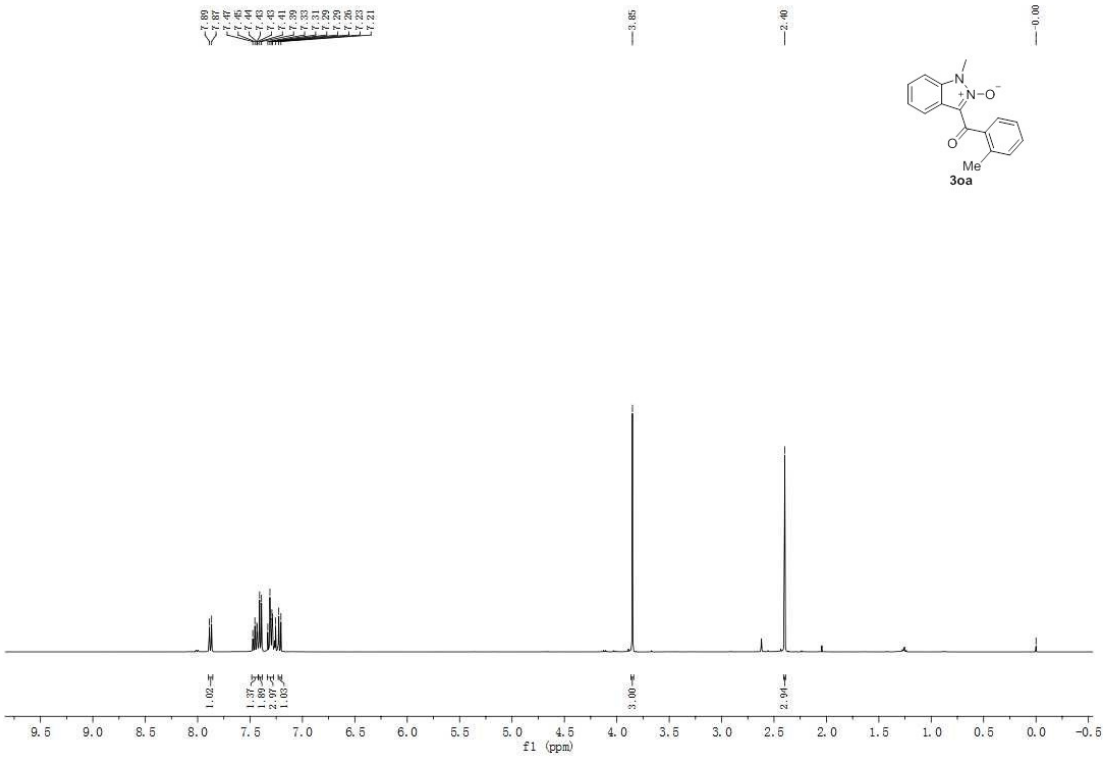
120.31
118.51
107.23
77.32
77.00
76.68
29.11
Br
3na
f1 (ppm)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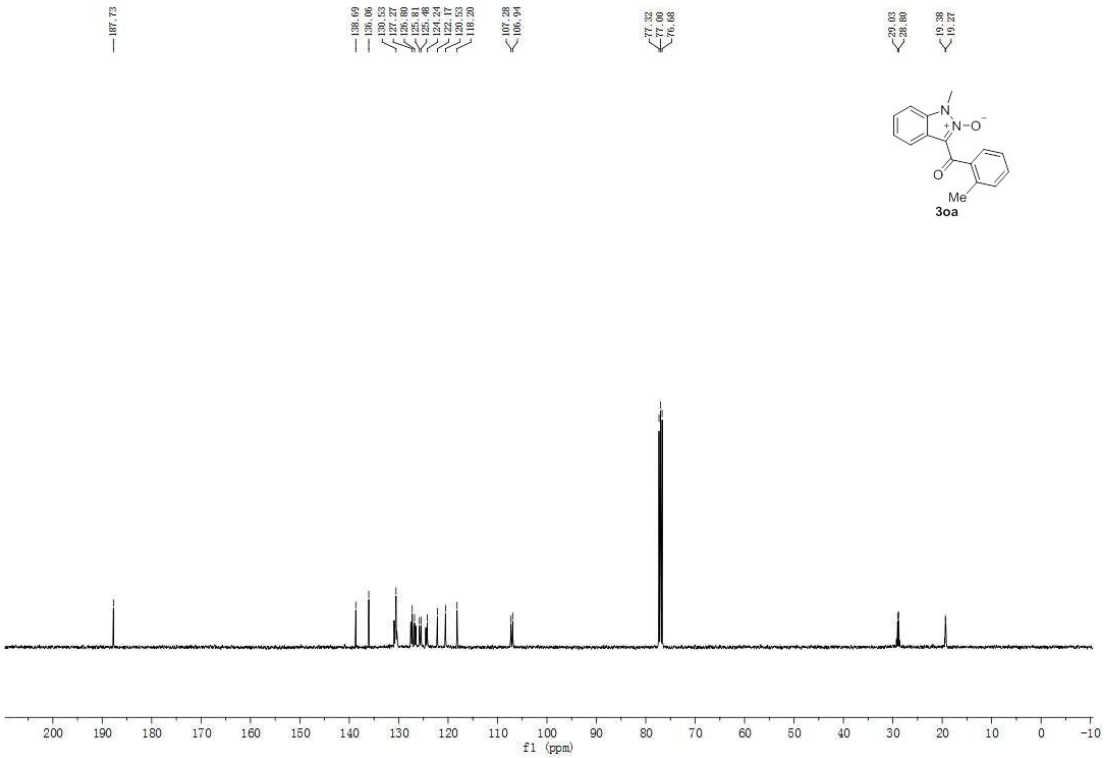
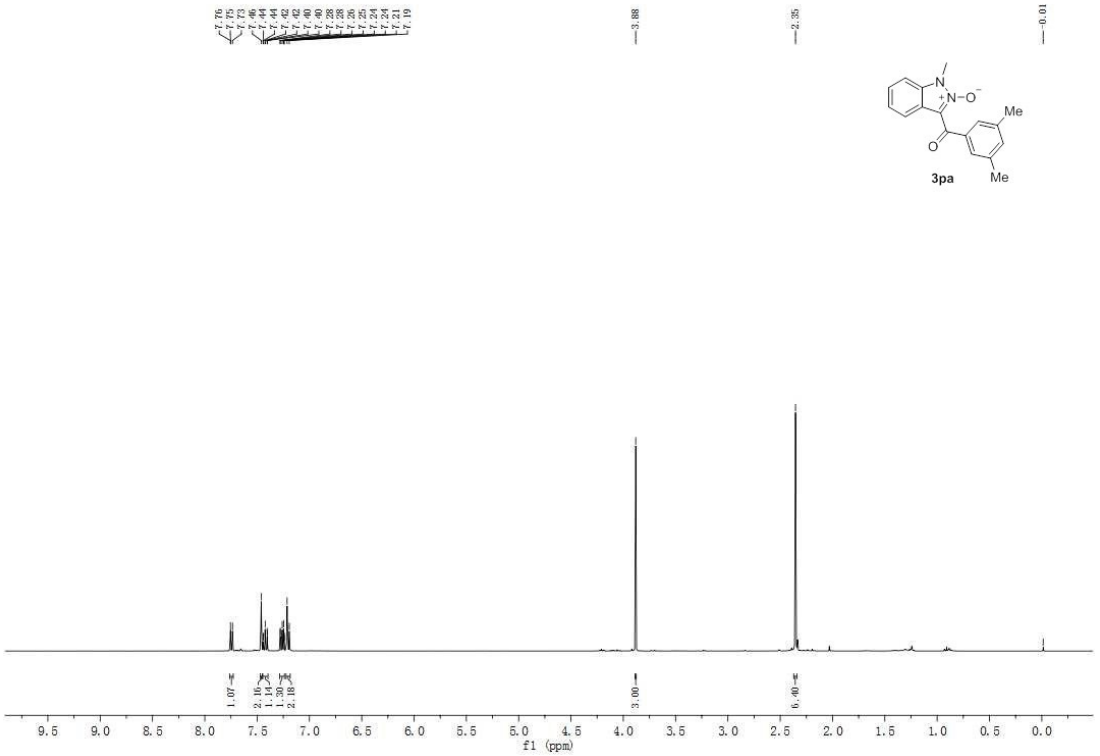
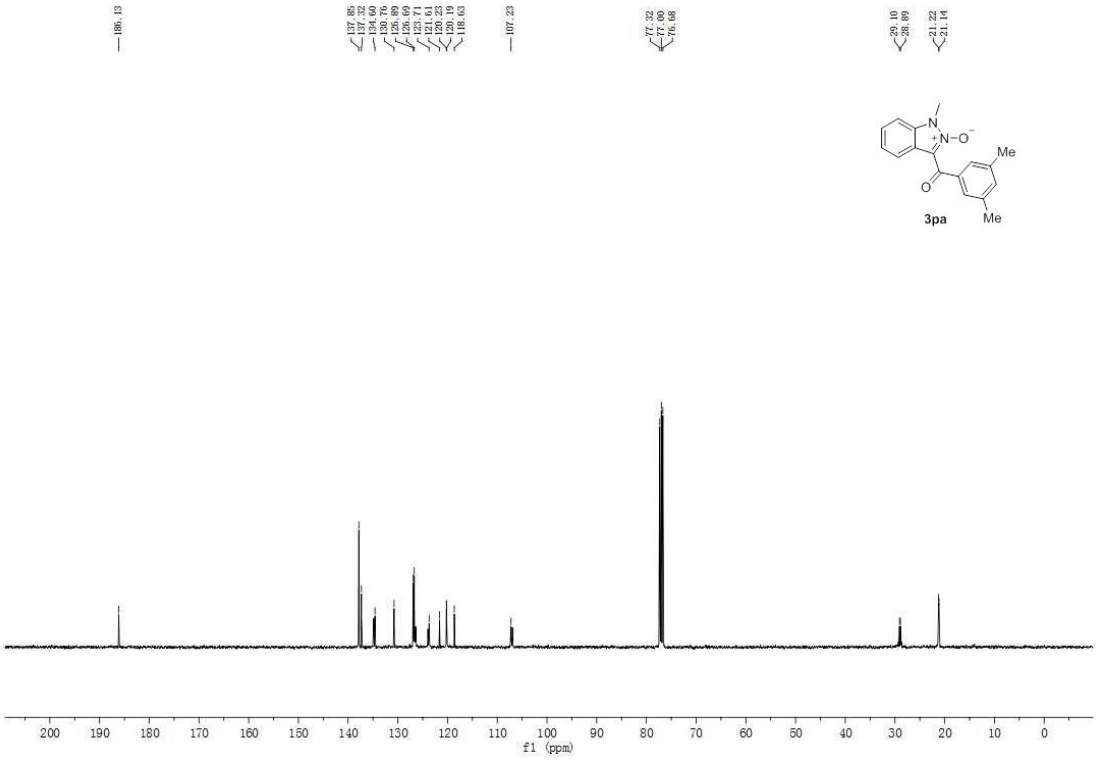
7.47
7.45
7.44
7.43
7.41
7.33
7.31
7.29
7.26
7.23
7.21
3.85
2.40
0.00
Me
3oa
1.02
1.37
1.89
2.97
1.03
3.00
2.94
f1 (ppm)


187.73
138.69
136.06
130.53
127.27
126.80
125.81
125.48
124.24
122.17
120.53
118.20
107.28
100.94
77.32
77.00
76.68
29.03
28.80
19.38
19.27
Me
3oa
f1 (ppm)


7.76
7.75
7.73
7.46
7.44
7.42
7.42
7.42
7.40
7.28
7.25
7.25
7.24
7.24
7.21
7.19
3.88
2.35
0.01
3pa
Me
Me
1.07
2.16
1.14
1.39
2.18
3.00
6.40
f1 (ppm)


188.13
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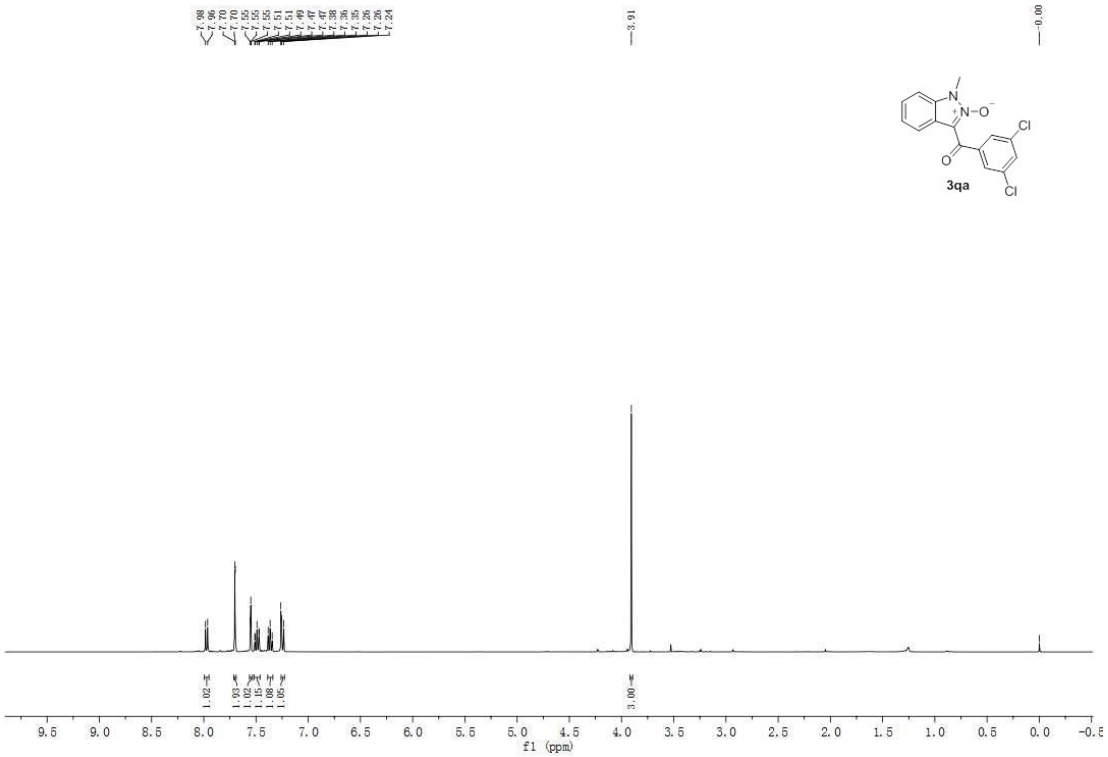
137.32
134.60
130.76
126.89
126.60
123.71
121.61
120.23
120.19
110.65
107.23
77.32
77.00
76.68
29.10
28.89
21.22
21.14
3pa
Me
Me
f1 (ppm)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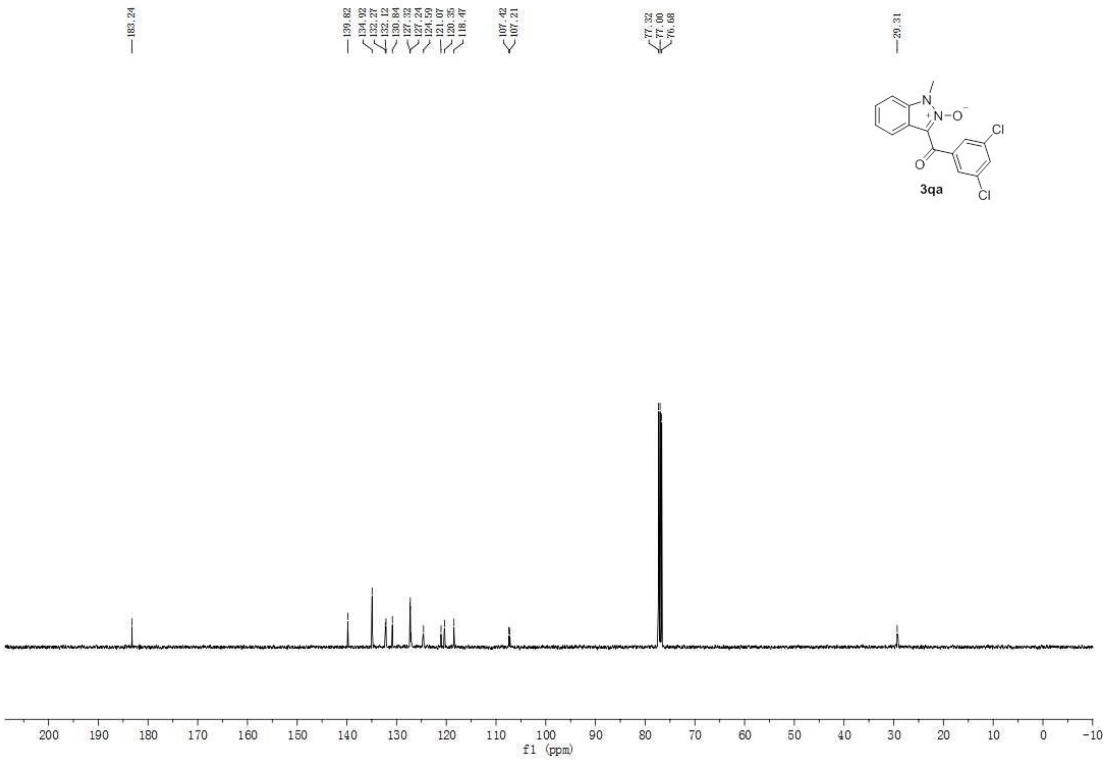
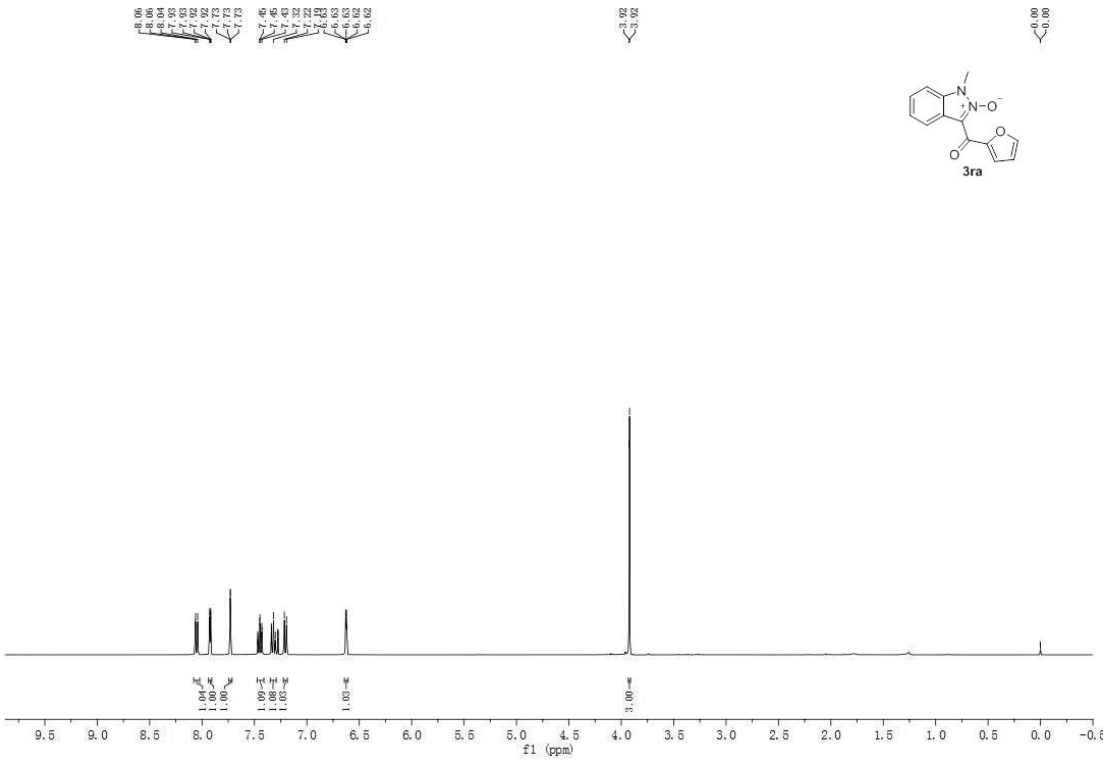
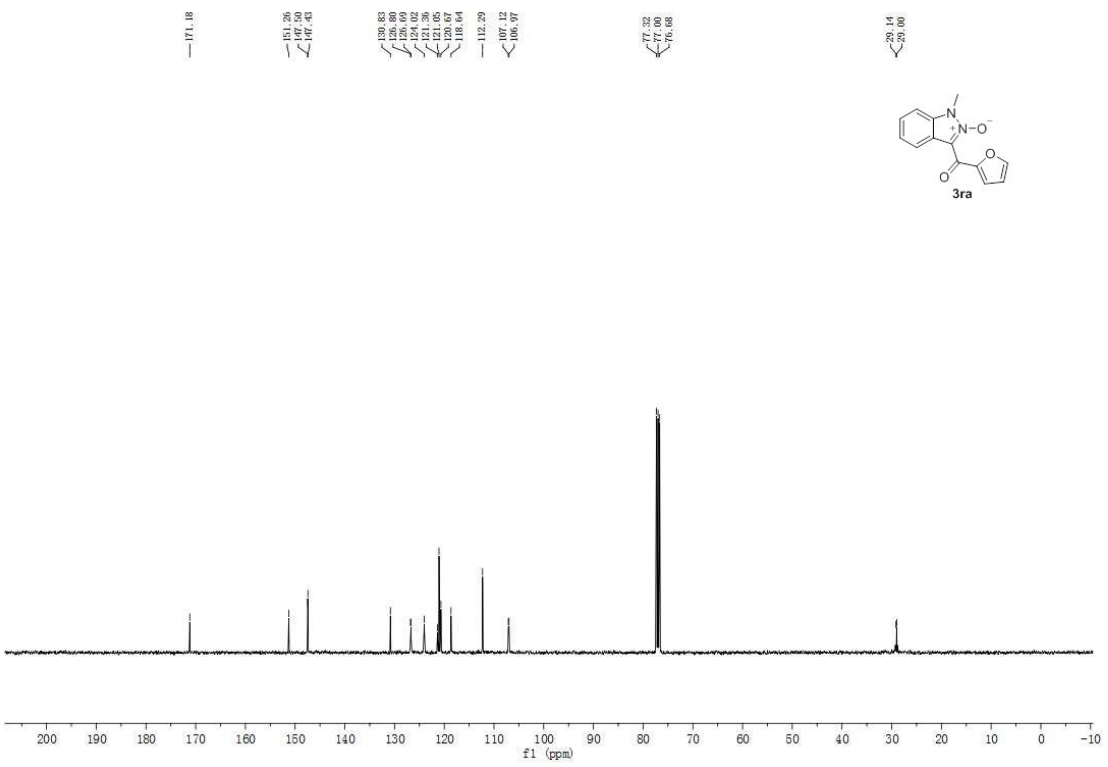
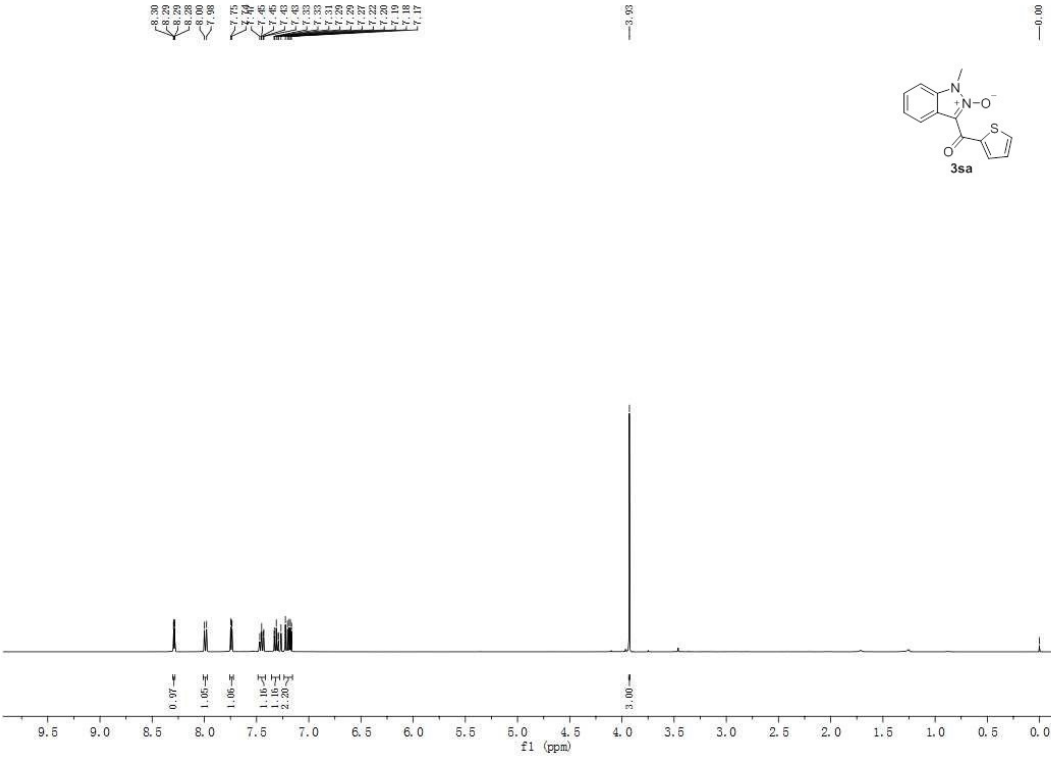
7.70
7.70
7.55
7.55
7.55
7.55
7.51
7.51
7.49
7.47
7.47
7.38
7.36
7.35
7.26
7.26
7.24
3.91
0.00
3qa
1.02
1.93
1.02
1.15
1.08
1.05
3.00
f1 (ppm)


183.24
139.82
134.92
132.27
132.12
130.84
127.32
127.24
124.59
121.07
120.35
116.47
107.42
107.21
77.32
77.00
76.68
29.31
3qa
f1 (ppm)


3ra
f1 (ppm)


3ra
f1 (ppm)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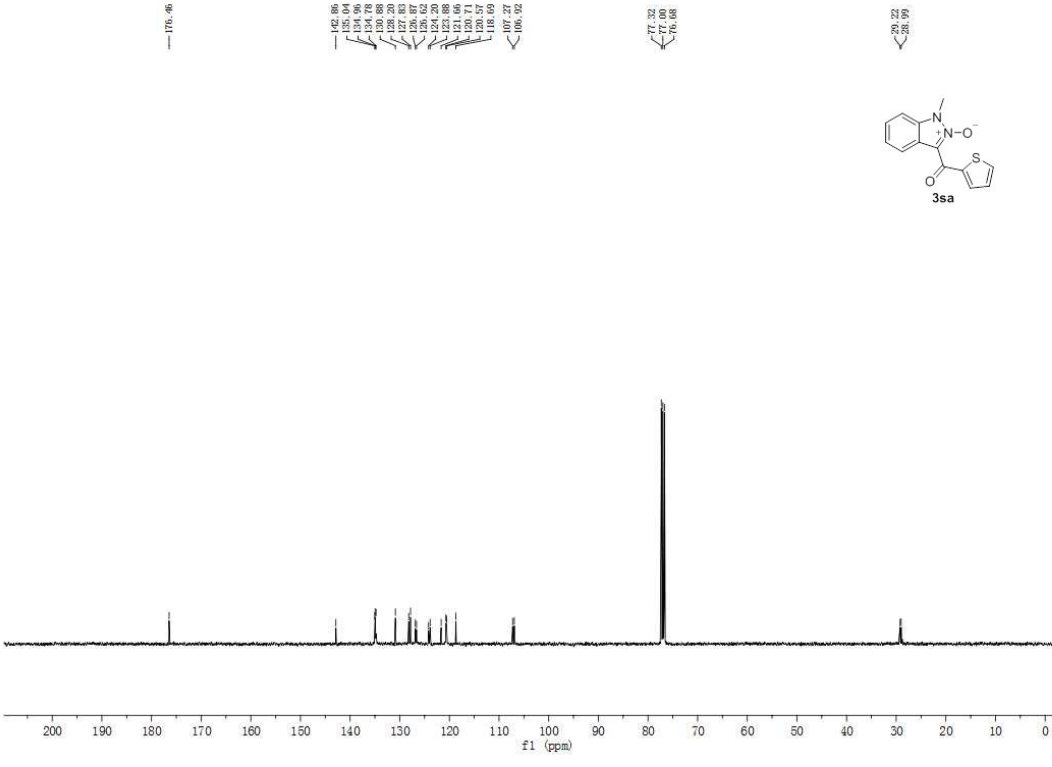
8.28
8.00
7.98
7.75
7.45
7.43
7.33
7.31
7.29
7.27
7.22
7.20
7.19
7.18
7.17
3.93
0.00
3sa
0.97
1.05
1.06
1.16
1.16
2.20
3.00
f1 (ppm)


176.46
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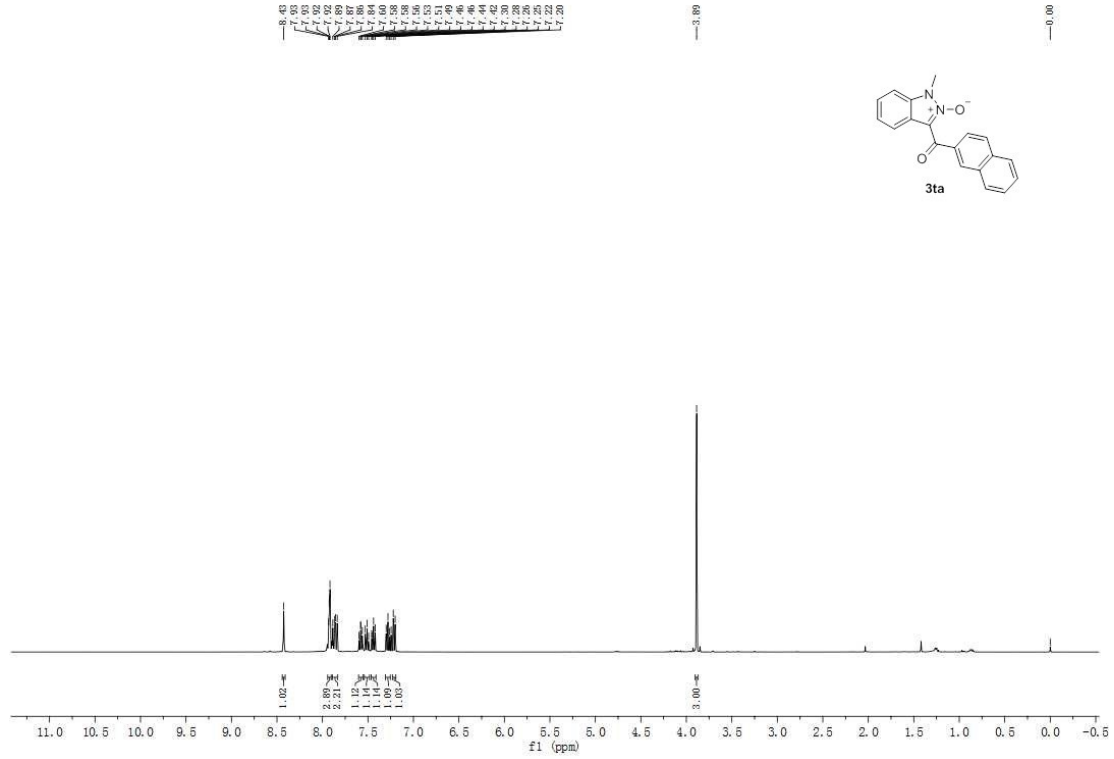
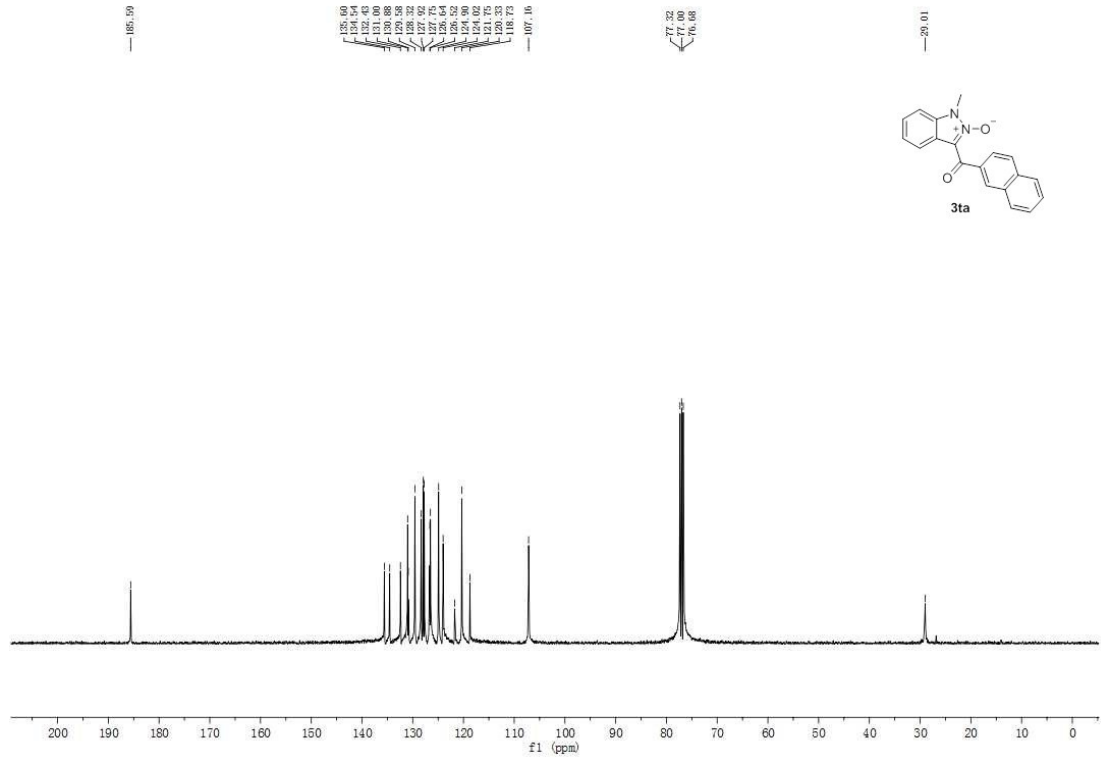
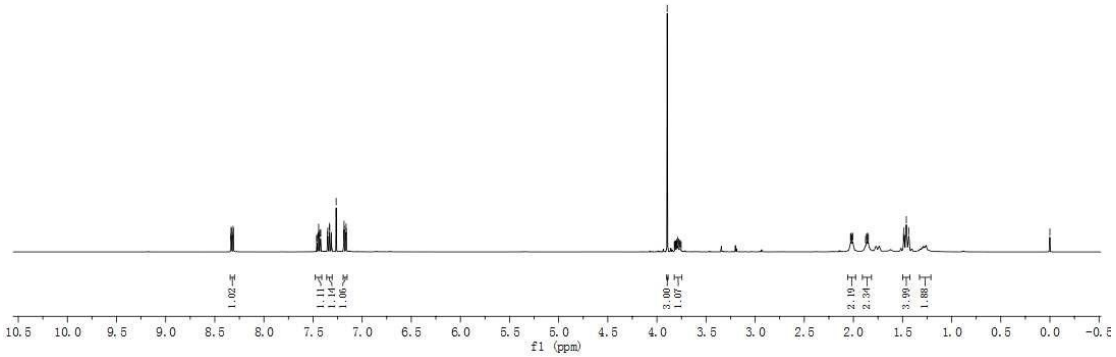
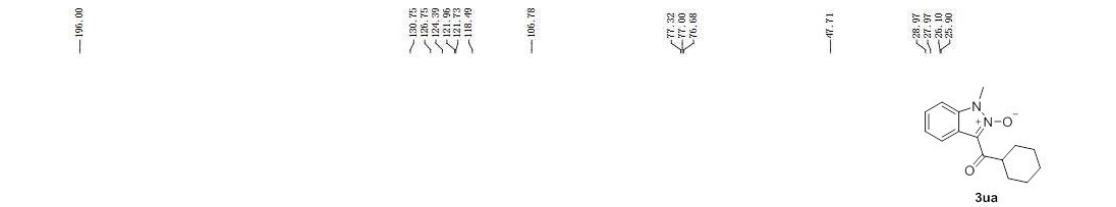
135.04
134.96
134.78
130.88
129.20
127.83
126.87
126.62
124.39
123.88
121.66
120.71
120.57
118.69
107.27
106.92
77.32
77.00
76.68
29.22
28.99
3sa
f1 (ppm)


8.43
7.93
7.92
7.92
7.89
7.87
7.86
7.64
7.60
7.58
7.56
7.53
7.51
7.49
7.46
7.46
7.44
7.42
7.30
7.28
7.26
7.25
7.22
7.20
3.89
0.00
3ta
1.02
2.89
2.21
1.12
1.14
1.14
1.09
1.03
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

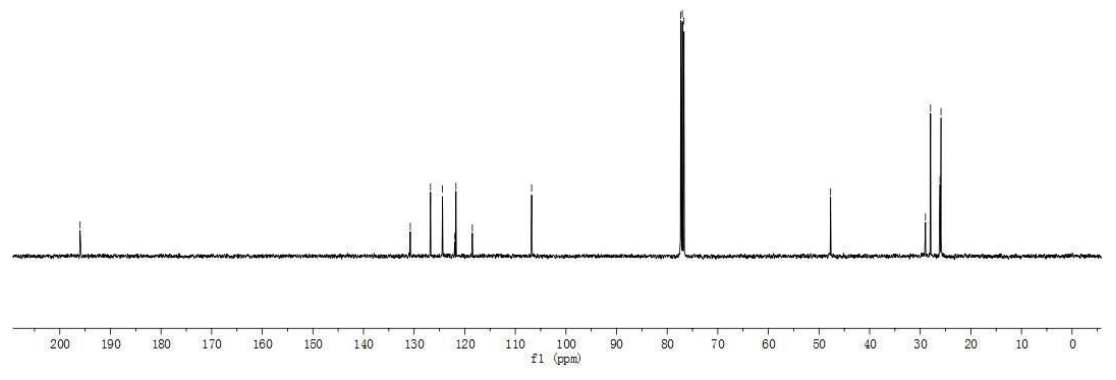

185.59
135.60
134.54
132.43
131.00
130.88
129.58
128.32
127.92
127.75
126.64
126.52
124.96
124.02
121.75
120.33
118.73
107.16
77.32
77.00
76.68
29.01
3ta
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

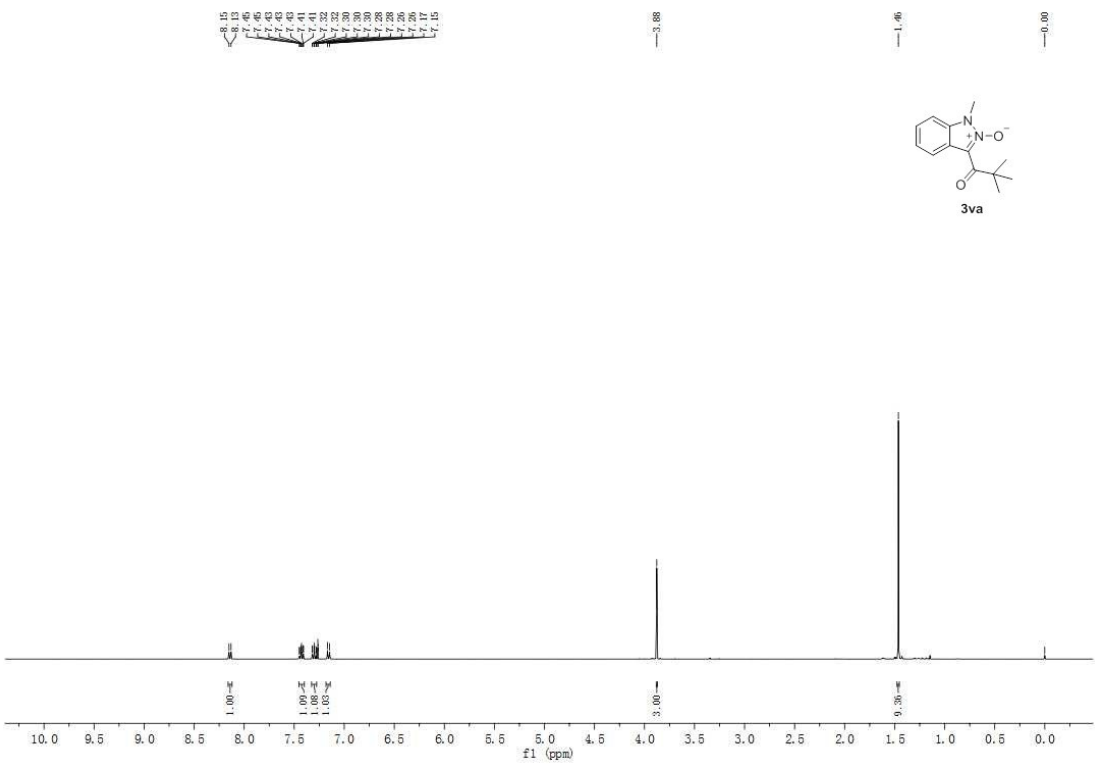
3ua

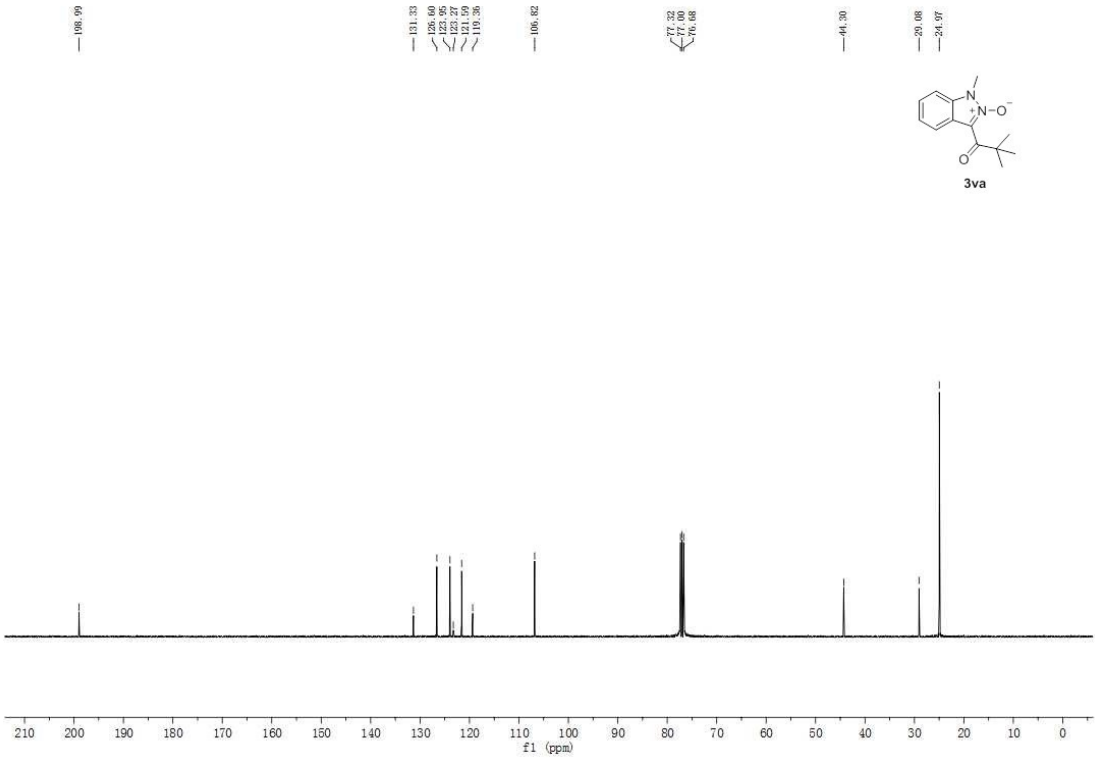




3ua




8.15
8.13
7.45
7.43
7.41
7.32
7.30
7.28
7.26
7.17
7.15
3.88
1.46
0.00
3va
1.00
1.09
1.08
1.03
3.00
9.36
f1 (ppm)


198.99
131.33
126.60
123.95
123.27
121.59
119.36
106.82
77.32
77.00
76.68
44.30
29.08
24.97
3va
f1 (ppm)