Silica gel-promoted practical synthesis of oxindole-nitrones from diazooxindoles and nitrosoarenes under solvent-free conditions

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Supplementary Information

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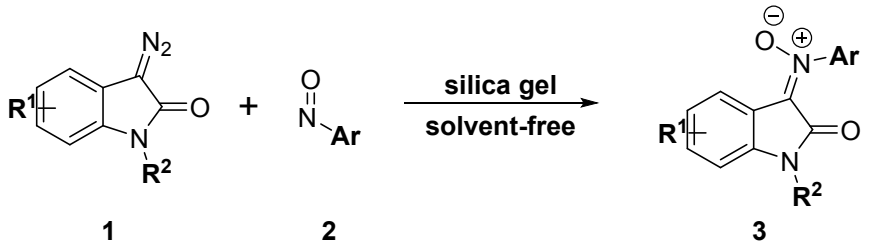
1. General information

All reagents were purchased at the commercial quality and used without further purification. Specially, silica gel (300-400 mesh) used in the reactions was purchased from Yantai Chemical Industry Research Institute. NMR spectra were recorded on a Bruker DPX400 spectrometer (400 MHz) in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Mass spectrometric data were obtained using Bruker Apex IV RTMS.

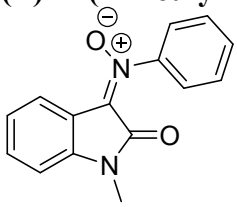
2. General procedure for the synthesis of oxindole-nitrone on silica gel



1 2 3

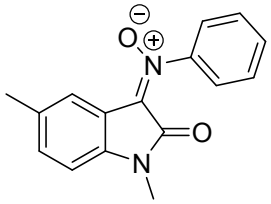
In a round bottom flask diazooxindole **1** (0.1 mmol, 1.0 eq) and nitrosobenzene **2** (0.15 mmol, 1.5 eq) were mixed together, and then silica gel (300–400 mesh, 100 mg) was added at room temperature. The mixture was vigorously stirred at 60 °C or at room temperature. After completion of reaction (monitored by TLC), the mixture was subjected to flash column chromatography and eluted with petroleum/ethyl acetate (1/4) to give the product **3**.

(*E*)-*N*-(1-Methyl-2-oxoindolin-3-ylidene) aniline oxide (3a) [1]



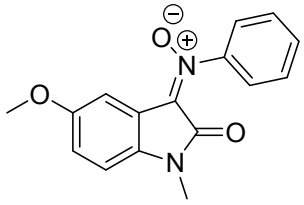
Red-brown solid, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (dd, *J* = 7.6, 0.4 Hz, 1H), 7.55-7.41 (m, 6H), 7.15 (td, *J* = 8.0, 0.8 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 3.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 146.4, 142.1, 134.7, 132.3, 130.7, 129.1, 125.2, 123.7, 123.2, 118.1, 108.0, 26.1.

(*E*)-*N*-(1, 5-Dimethyl-2-oxoindolin-3-ylidene) aniline oxide (3b) [1]



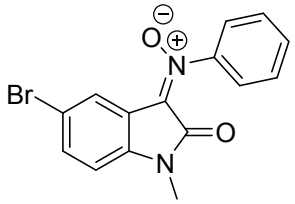
Red-brown solid, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.50-7.45 (m, 5H), 7.23 (d, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 3.16 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 146.4, 140.0, 134.9, 132.8, 132.7, 130.6, 129.1, 125.8, 123.7, 118.0, 107.8, 26.1, 21.1.

(*E*)-*N*-(5-Methoxy-1-methyl-2-oxoindolin-3-ylidene) aniline oxide (3c)



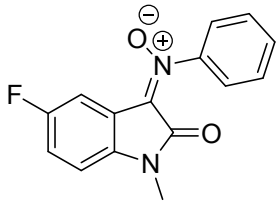
Purple solid, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.4 Hz, 1H), 7.54-7.46 (m, 5H), 6.99 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 3.86 (s, 3H), 3.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 156.1, 146.4, 136.1, 135.2, 130.7, 129.1, 123.7, 118.6, 118.6, 110.4, 108.7, 56.0, 26.1. HRMS (ESI) calcd for: $C_{16}H_{15}N_2O_3$ $[M+H]^+$ 283.1077, found: 283.1080.

(*E*)-*N*-(5-Bromo-1-methyl-2-oxoindolin-3-ylidene) aniline oxide (3d)



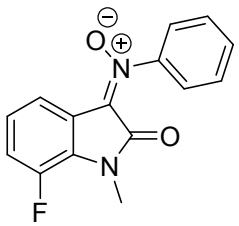
Red-brown solid, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 2.0 Hz, 1H), 7.56-7.45 (m, 6H), 6.73 (d, *J* = 8.4 Hz, 1H), 3.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 146.3, 140.8, 134.6, 133.8, 131.0, 129.1, 127.6, 123.7, 119.6, 115.8, 109.4, 26.2. HRMS (ESI) calcd for: $C_{15}H_{12}BrN_2O_2$ $[M+H]^+$ 331.0077, found: 331.0078.

(*E*)-*N*-(5-Fluoro-1-methyl-2-oxoindolin-3-ylidene) aniline oxide (3e)



Red-brown solid, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.56-7.46 (m, 5H), 7.13 (td, *J* = 8.8, 2.8 Hz, 1H), 6.77 (dd, *J* = 8.8, 4.0 Hz, 1H), 3.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 159.1 (d, *J* =238.9 Hz), 146.3, 138.2, 134.5, 130.9, 129.1, 123.7, 118.9 (d, *J* =10.0 Hz), 118.3 (d, *J* =24.3 Hz), 112.6 (d, *J* =27.3 Hz), 108.4 (d, *J* =8.1 Hz), 26.2. HRMS (ESI) calcd for: $C_{15}H_{12}FN_2O_2$ $[M+H]^+$ 271.0877, found: 271.0878.

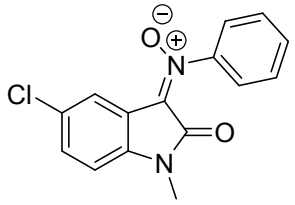
(*E*)-*N*-(7-Fluoro-1-methyl-2-oxoindolin-3-ylidene) aniline oxide (3f) [1]



Pale red-brown solid, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 7.6, 1.2

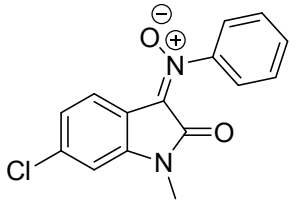
Hz, 1H), 7.54-7.45 (m, 5H), 7.18-7.13 (m, 1H), 7.09-7.04 (m, 1H), 3.39 (d, *J* = 2.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 147.2(d, *J* = 242.2 Hz), 146.3, 134.1, 130.9, 129.1, 128.3 (d, *J* = 9.3 Hz), 123.7, 123.7, 121.0 (d, *J* = 3.2 Hz), 120.7 (d, *J* = 4.4 Hz), 120.1 (d, *J* = 19.3 Hz), 28.7 (d, *J* = 5.6 Hz). HRMS (ESI) calcd for: $C_{15}H_{12}FN_2O_2$ $[M+H]^+$ 271.0877, found: 271.0878.

(*E*)-*N*-(5-Chloro-1-methyl-2-oxoindolin-3-ylidene) aniline oxide (3g) [1]



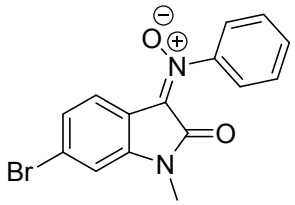
Red-brown solid, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* =2.0 Hz, 1H), 7.56-7.45 (m, 5H), 7.39 (dd, *J* =8.4, 2.0 Hz, 1H), 6.78 (d, *J* =8.0 Hz, 1H), 3.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 146.3, 140.4, 134.0, 131.7, 131.0, 129.0, 128.6, 124.9, 123.7, 119.2, 108.9, 26.2.

(*E*)-*N*-(6-Chloro-1-methyl-2-oxoindolin-3-ylidene) aniline oxide (3h) [1]



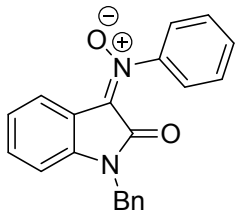
Red-brown solid, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.0 Hz, 1H), 7.54-7.45 (m, 5H), 7.11 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.84 (d, *J* = 1.2 Hz, 1H), 3.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 146.3, 143.1, 137.8, 133.9, 130.9, 129.1, 125.9, 123.7, 123.0, 116.6, 108.8, 26.2. HRMS (ESI) calcd for: $C_{15}H_{12}ClN_2O_2$ $[M+H]^+$ 287.0582, found: 287.0583.

(*E*)-*N*-(6-Bromo-1-methyl-2-oxoindolin-3-ylidene) aniline oxide (3i)



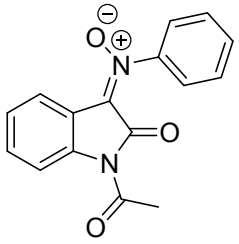
Red-brown solid, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.0 Hz, 1H), 7.56-7.45 (m, 5H), 7.28 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.00 (d, *J* = 1.6 Hz, 1H), 3.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 146.3, 143.0, 134.0, 130.9, 129.1, 126.0, 126.0, 125.9, 123.7, 117.0, 111.6, 26.2. HRMS (ESI) calcd for: $C_{15}H_{12}BrN_2O_2$ $[M+H]^+$ 331.0077, found: 331.0078.

(*E*)-*N*-(1-Benzyl-2-oxoindolin-3-ylidene) aniline oxide (3j) [1]



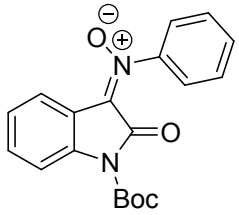
Yellow solid, 89% yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 7.6, 0.4 Hz, 1H), 7.56-7.51 (m, 5H), 7.34-7.25 (m, 6H), 7.12 (td, *J* = 7.6, 0.8 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 4.88 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 146.5, 141.4, 135.5, 134.5, 132.2, 130.8, 129.1, 128.9, 127.8, 127.4, 125.2, 123.8, 123.2, 118.3, 109.0, 43.8.

(*E*)-*N*-(1-Acetyl-2-oxoindolin-3-ylidene) aniline oxide (3k)



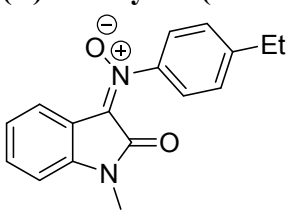
Yellow solid, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 7.6, 0.8 Hz, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 7.60-7.45 (m, 6H), 7.33 (td, *J* = 7.6, 0.8 Hz, 1H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 159.8, 146.6, 138.2, 133.5, 132.8, 131.0, 129.3, 125.7, 124.3, 123.6, 119.1, 116.2, 26.9. HRMS (ESI) calcd for: $C_{16}H_{12}N_2NaO_3$ $[M+Na]^+$ 303.0740, found: 303.0740.

(*E*)-*N*-(1-(*tert*-Butoxycarbonyl)-2-oxoindolin-3-ylidene) aniline oxide (3l)



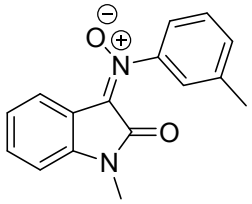
Yellow solid, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.55-7.43 (m, 6H), 7.30-7.26 (m, 1H), 1.60 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.7, 148.7, 146.6, 138.1, 133.4, 132.6, 130.7, 129.2, 124.8, 124.5, 123.7, 118.7, 114.6, 85.0, 28.1. HRMS (ESI) calcd for: $C_{19}H_{18}N_2NaO_4$ $[M+Na]^+$ 361.1159, found: 361.1159.

(*E*)-4-Ethyl-*N*-(1-methyl-2-oxoindolin-3-ylidene) aniline oxide (3m)



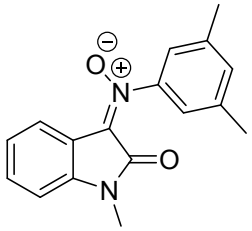
Red-brown solid, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.43-7.32 (m, 5H), 7.14 (td, *J* =7.6, 0.8 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 3.19 (s, 3H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 147.3, 144.3, 142.0, 134.5, 132.1, 128.4, 125.1, 123.6, 123.1, 118.3, 107.9, 28.8, 26.1, 15.2. HRMS (ESI) calcd for: $C_{17}H_{17}N_2O_2$ $[M+H]^+$ 281.1285, found: 281.1284.

(*E*)-3-Methyl-*N*-(1-methyl-2-oxoindolin-3-ylidene) aniline oxide (3n) [1]



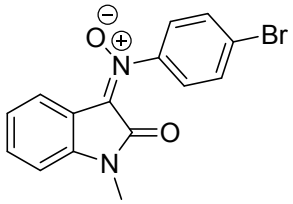
Red solid, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (dd, *J* = 7.6, 0.4 Hz, 1H), 7.44-7.33 (m, 5H), 7.14 (td, *J* = 8.0, 0.4Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 3.19 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 146.5, 142.1, 139.4, 134.6, 132.2, 131.4, 128.8, 125.1, 124.1, 123.1, 120.8, 118.1, 108.0, 26.1, 21.4.

(*E*)-3, 5-Dimethyl-*N*-(1-methyl-2-oxoindolin-3-ylidene) aniline oxide (3o)



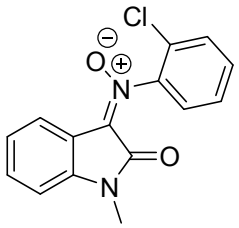
Red-brown solid, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 6.8 Hz, 1H), 7.42 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.15-7.12 (m, 2H), 7.06 (s, 2H), 6.84 (d, *J* = 7.6 Hz, 1H), 3.19 (s, 3H), 2.38 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 146.5, 142.1, 139.0, 134.5, 132.3, 132.1, 125.1, 123.1, 121.1, 118.1, 107.9, 26.1, 21.3. HRMS (ESI) calcd for: $C_{17}H_{17}N_2O_2$ $[M+H]^+$ 281.1285, found: 281.1287.

(*E*)-4-Bromo-*N*-(1-methyl-2-oxoindolin-3-ylidene) aniline oxide (3p) [1]



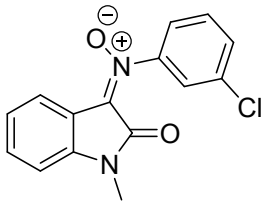
Red solid, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 7.6, 0.4 Hz, 1H), 7.64-7.60 (m, 2H), 7.44-7.34 (m, 3H), 7.12 (td, *J* = 7.6, 0.8 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 3.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 145.1, 142.2, 134.8, 132.5, 132.2, 125.5, 125.2, 124.9, 123.2, 118.0, 108.1, 26.1.

(*E*)-2-Chloro-*N*-(1-methyl-2-oxoindolin-3-ylidene) aniline oxide (3q)



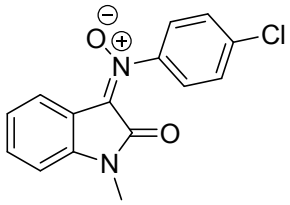
Red solid, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 7.6, 0.4 Hz, 1H), 7.56-7.41 (m, 5H), 7.17 (td, *J* = 7.6, 0.8 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 3.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 144.2, 142.6, 135.9, 132.7, 131.1, 130.5, 128.0, 127.6, 125.5, 125.3, 123.3, 117.3, 108.2, 26.1. HRMS (ESI) calcd for: $C_{15}H_{12}ClN_2O_2$ $[M+H]^+$ 287.0582, found: 287.0583.

(*E*)-3-Chloro-*N*-(1-methyl-2-oxoindolin-3-ylidene) aniline oxide (3r) [1]



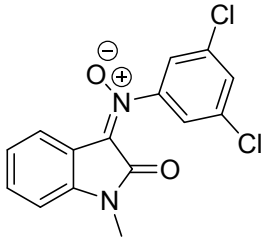
Red-brown solid, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.51-7.38 (m, 5H), 7.15 (td, *J* = 7.6, 0.8 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 3.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 146.9, 142.3, 134.9, 134.7, 132.6, 130.8, 130.1, 125.3, 124.3, 123.3, 122.1, 117.8, 108.1, 26.1.

(*E*)-4-Chloro-*N*-(1-methyl-2-oxoindolin-3-ylidene) aniline oxide (3s)



Red-brown solid, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.49-7.42 (m, 5H), 7.15 (td, *J* = 7.6, 0.8 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 3.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 144.7, 142.2, 136.7, 134.8, 132.5, 129.3, 125.2, 125.2, 123.3, 118.0, 108.1, 26.1. HRMS (ESI) calcd for: $C_{15}H_{12}ClN_2O_2$ $[M+H]^+$ 287.0582, found: 287.0582.

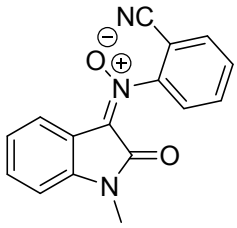
(*E*)-3, 5-Dichloro-*N*-(1-methyl-2-oxoindolin-3-ylidene) aniline oxide (3t)



Red-brown solid, 96% yield. 1H NMR (400 MHz, $CDCl_3$) δ 8.43 (dd, *J* = 7.6, 0.4 Hz, 1H), 7.54 (t, *J* = 1.8 Hz, 1H), 7.48 (td, *J* = 8.0, 1.2 Hz, 1H), 7.40 (d, *J* = 2.0 Hz, 2H),

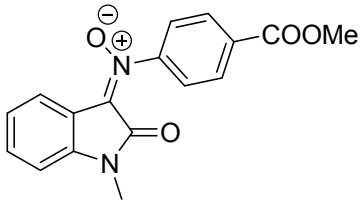
7.17 (td, J = 8.0, 0.8 Hz, 1H), 6.88 (d, J = 7.6 Hz, 1H), 3.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 147.1, 142.4, 135.4, 135.1, 133.0, 130.8, 125.4, 123.4, 122.8, 117.6, 108.2, 26.2. HRMS (ESI) calcd for: $C_{15}H_{11}Cl_2N_2O_2$ $[M+H]^+$ 321.0192, found: 321.0190.

(*E*)-2-Cyano-*N*-(1-methyl-2-oxoindolin-3-ylidene) aniline oxide (3u)



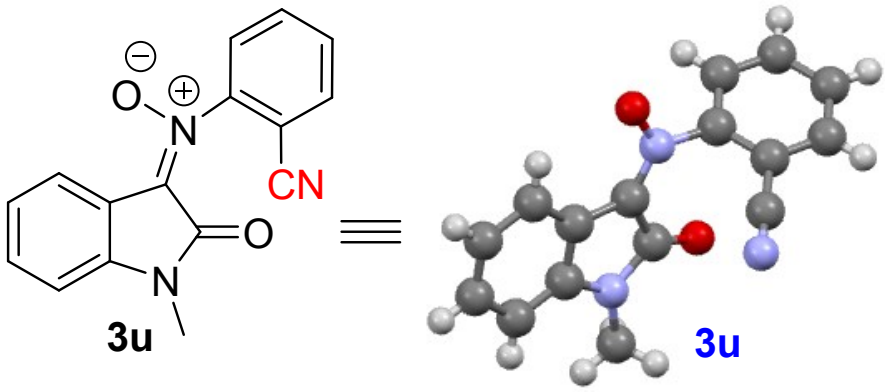
Red-brown solid, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (dd, J = 7.6, 0.4 Hz, 1H), 7.82-7.76 (m, 2H), 7.64 (td, J = 8.0, 1.2 Hz, 1H), 7.55 (dd, J = 8.0, 0.8 Hz, 1H), 7.46 (td, J = 7.6, 1.2 Hz, 1H), 7.16 (td, J = 7.6, 0.8 Hz, 1H), 6.87 (d, J = 7.6 Hz, 1H), 3.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 147.8, 142.8, 136.1, 134.0, 133.4, 133.2, 130.5, 125.7, 125.0, 123.4, 117.2, 114.7, 108.4, 108.3, 26.1. HRMS (ESI) calcd for: $C_{16}H_{12}N_3O_2$ $[M+H]^+$ 278.0924, found: 278.0923.

(*E*)-4-(Methoxycarbonyl)-*N*-(1-methyl-2-oxoindolin-3-ylidene) aniline oxide (3v)



Yellow-brown solid, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 7.2 Hz, 1H), 8.19 (dd, J = 6.8, 1.6 Hz, 2H), 7.55-7.53 (m, 2H), 7.44 (td, J = 8.0, 1.2 Hz, 1H), 7.15 (td, J = 8.0, 0.4 Hz, 1H), 6.85 (d, J = 7.6 Hz, 1H), 3.95 (s, 3H), 3.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 159.4, 149.3, 142.3, 135.0, 132.6, 132.0, 130.6, 125.3, 124.0, 123.3, 117.8, 108.2, 52.5, 26.1. HRMS (ESI) calcd for: $C_{17}H_{15}N_2O_4$ $[M+H]^+$ 311.1026, found: 311.1027.

3. X-ray crystallographic structure of 3u (CCDC 1017177)



EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{16}H_{11}N_3O_2$
Formula Weight	277.28
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.20 X 0.20 X 0.20 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 7.012(4) Å b = 7.844(4) Å c = 12.691(8) Å α = 81.83(4) ^{o} β = 85.86(4) ^{o} γ = 82.76(3) ^{o} V = 684.4(7) Å^3

Space Group	P-1 (#2)
Z value	2
D_{calc}	1.345 g/cm^3
F_{000}	288.00
μ(CuKα)	7.529 cm^{-1}

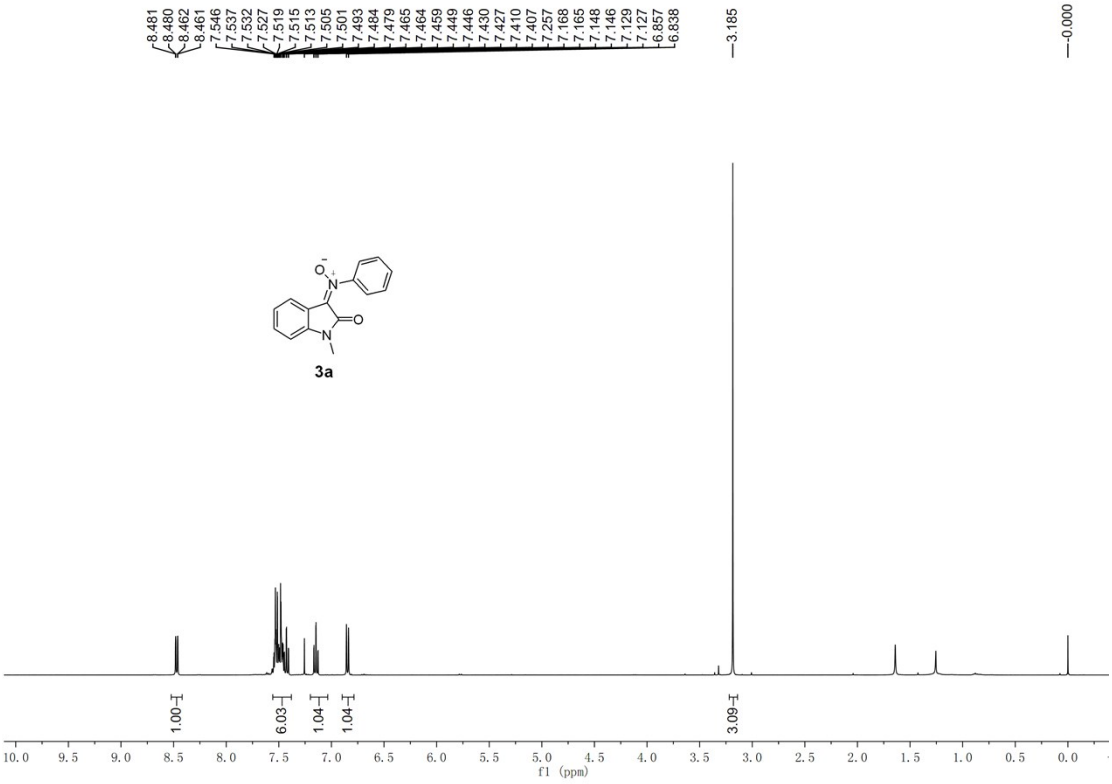
C. Structure Solution and Refinement

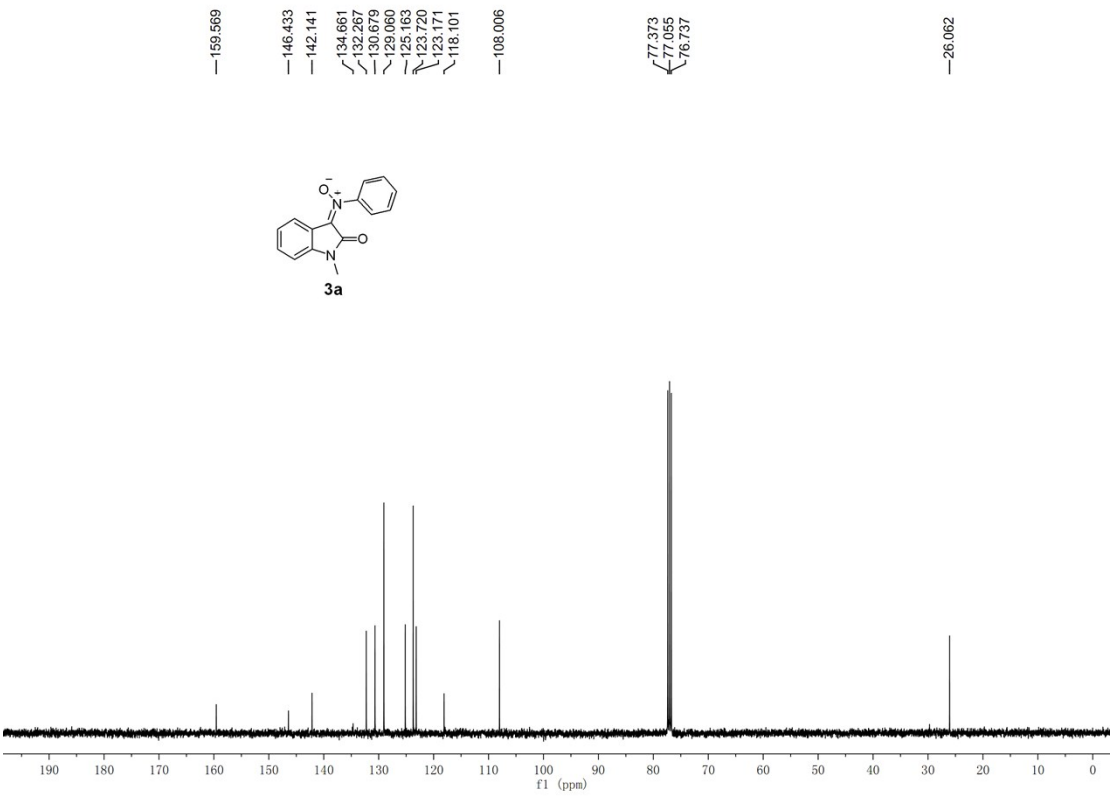
Structure Solution	Direct Methods (SHELX97)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$
Least Squares Weights	w = 1/ [$\sigma^2(Fo^2)$ + (0.1000 · P)^2 + 0.0000 · P] where P = (Max(Fo^2,0) + 2Fc^2)/3
$2\theta_{max}$ cutoff	136.2^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	2435
No. Variables	190
Reflection/Parameter Ratio	12.82
Residuals: R1 (I>2.00σ(I))	0.1344
Residuals: R (All reflections)	0.1607
Residuals: wR2 (All reflections)	0.3650
Goodness of Fit Indicator	2.220
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.35 e^-/Å^3
Minimum peak in Final Diff. Map	-0.64 e^-/Å^3

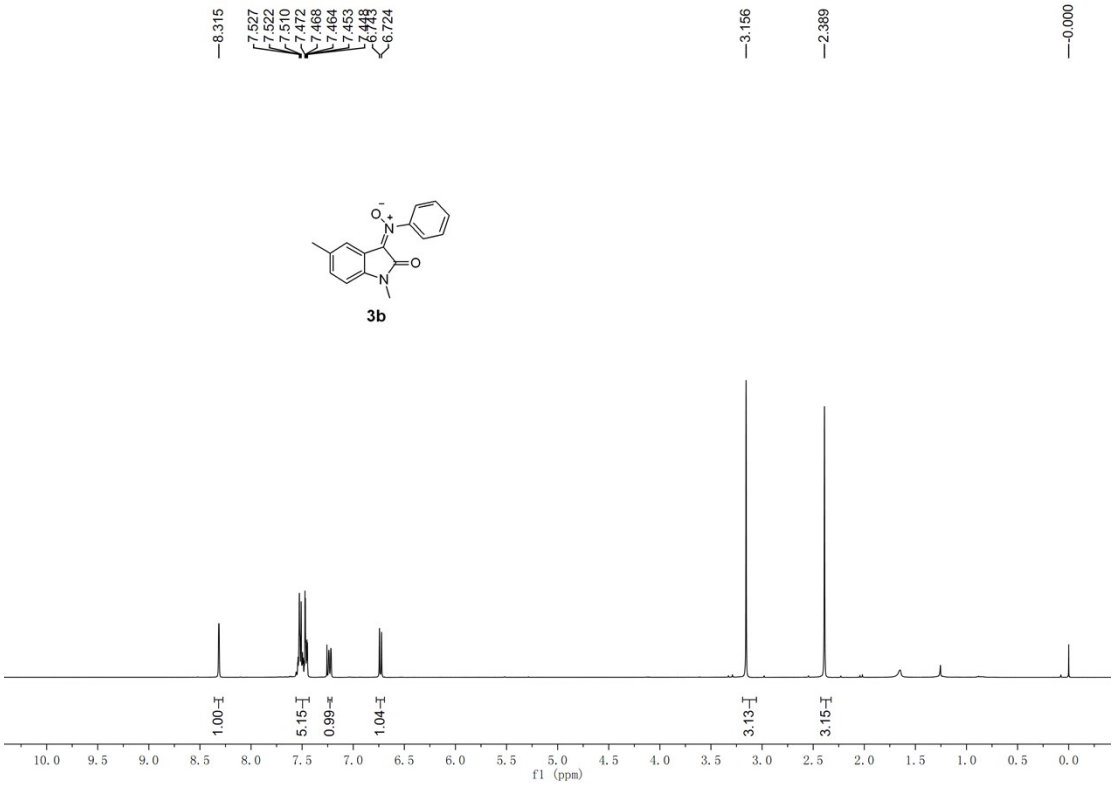
4. Reference:

1 H.-B. Yang and M. Shi, *Org. Biomol.Chem.*, 2012, **10**, 8236.

5. NMR spectra



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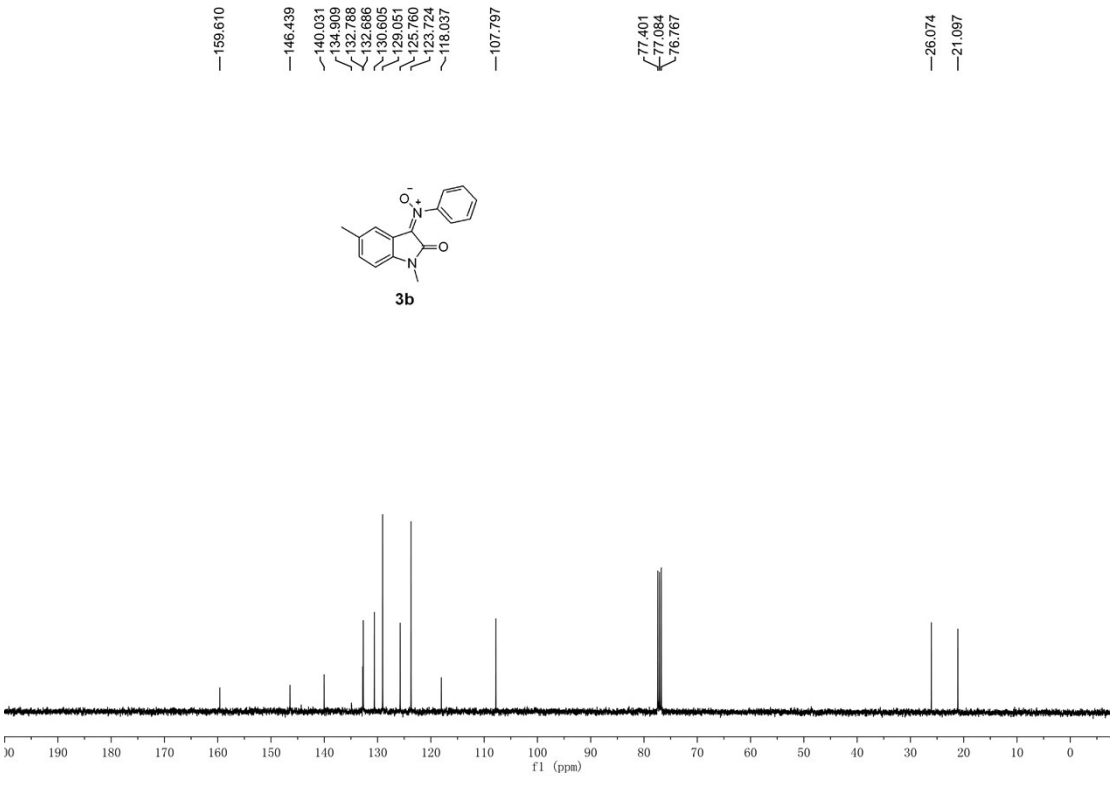
7.527
7.522
7.510
7.472
7.468
7.464
7.453
7.448
7.443
6.724
3.156
2.389
0.000
3b
1.00
5.15
0.99
1.04
3.13
3.15
f1 (ppm)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146.439
140.031
134.909
132.788
132.686
130.605
129.051
125.760
123.724
118.037
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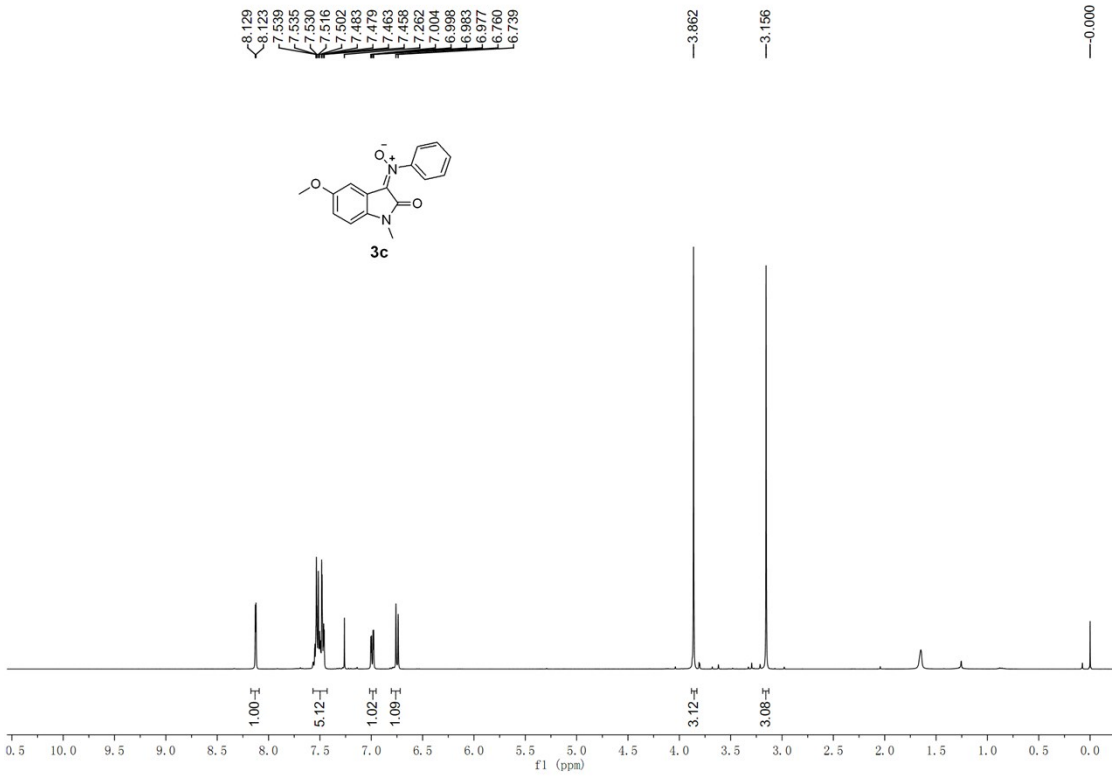
76.767
26.074
21.097
3b
f1 (ppm)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7.535
7.530
7.516
7.502
7.483
7.479
7.463
7.458
7.262
7.004
6.998
6.983
6.977
6.760
6.739
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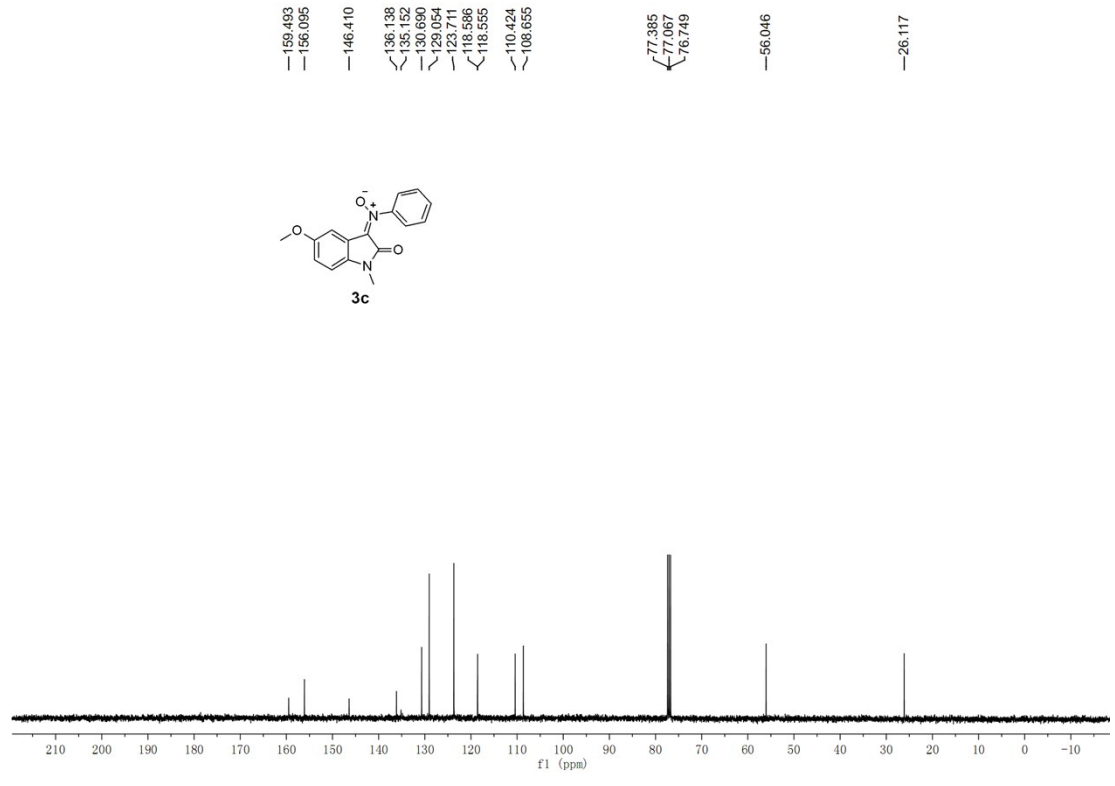
3.156
0.000
3c
1.00
5.12
1.02
1.09
3.12
3.08
f1 (ppm)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146.410
136.138
135.152
130.690
129.054
123.711
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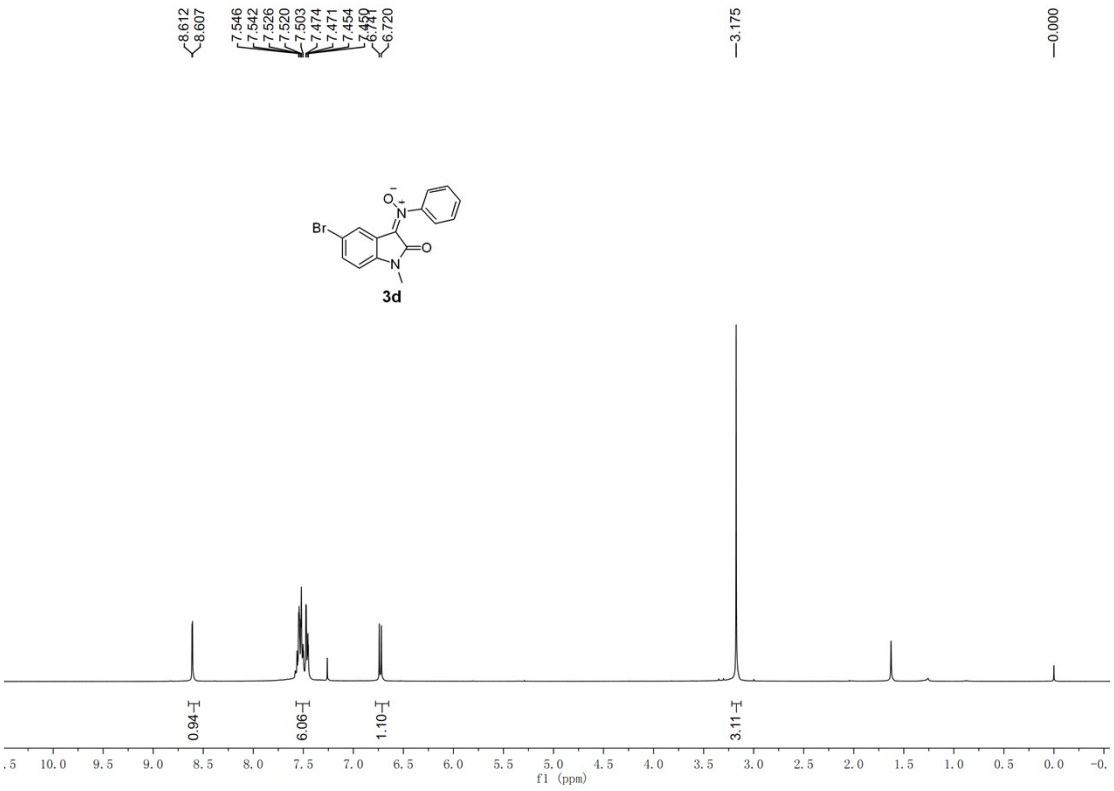
110.424
108.655
77.385
77.067
76.749
56.046
26.117
3c
f1 (ppm)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8.607
7.546
7.542
7.526
7.520
7.503
7.474
7.471
7.454
7.450
6.741
6.720
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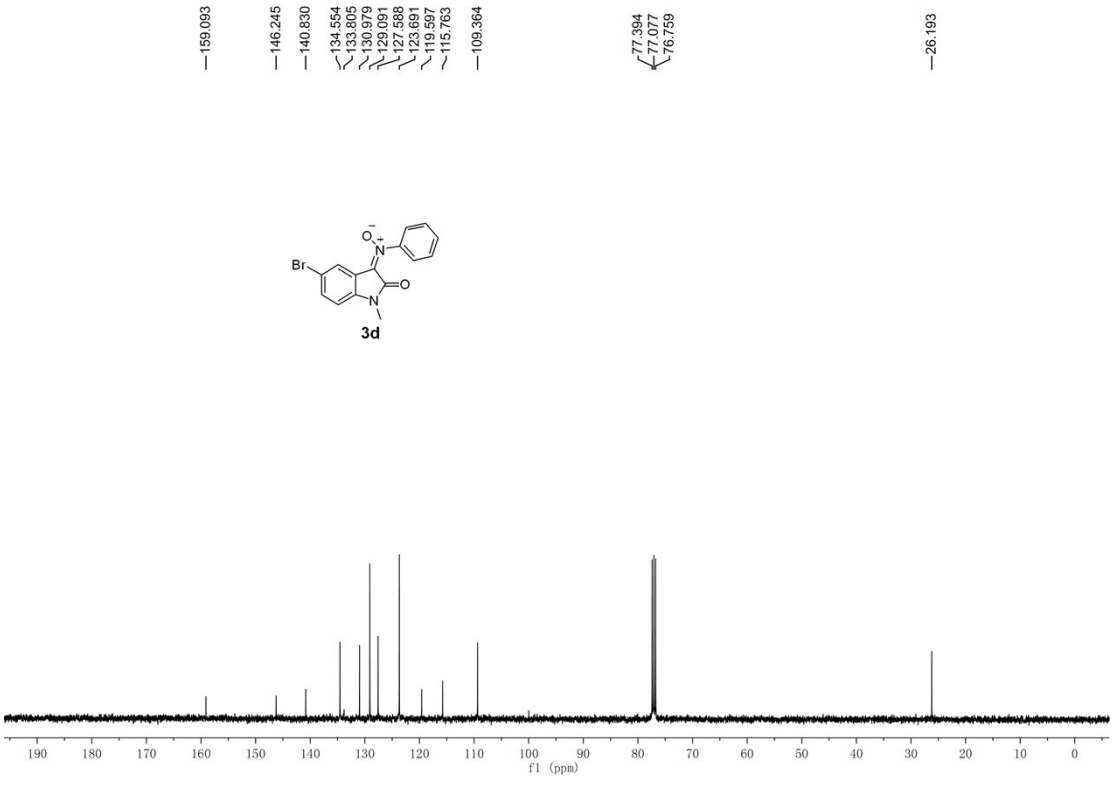
0.000
Br
O
N
O
3d
0.94
6.06
1.10
3.11
f1 (ppm)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140.830
134.554
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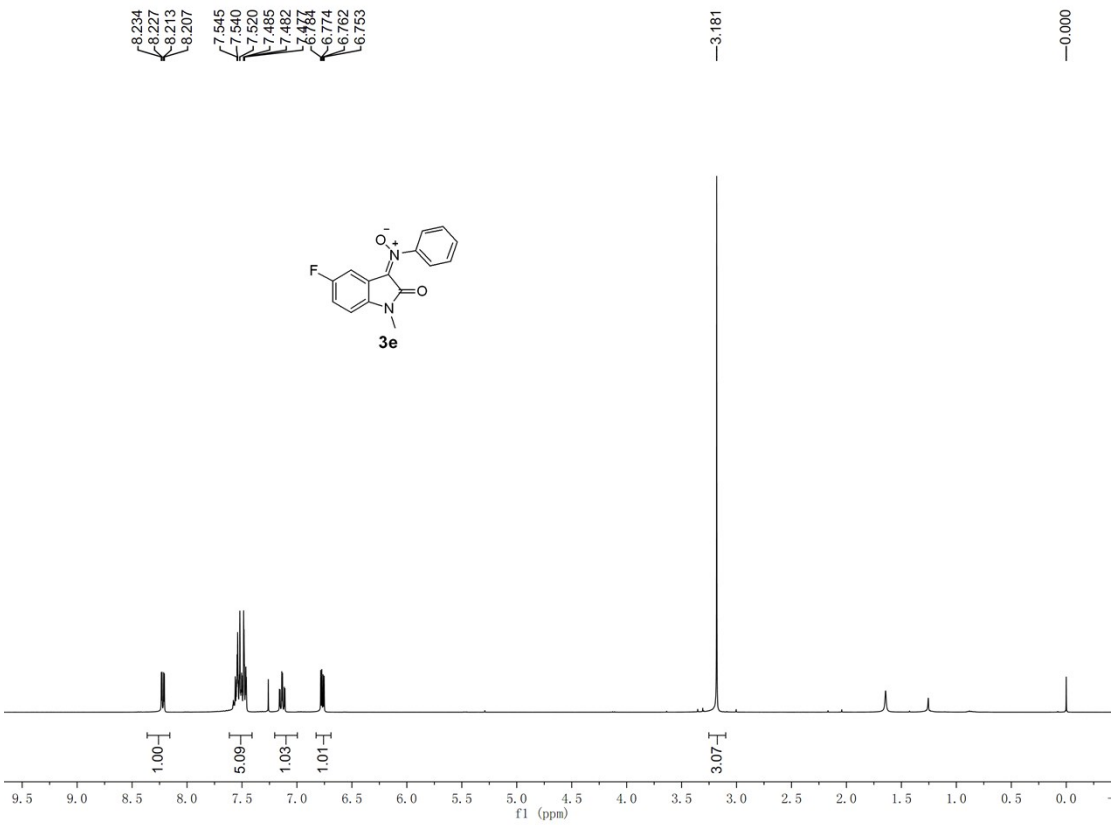
130.979
129.091
127.588
123.691
119.597
115.763
109.364
77.394
77.077
76.759
26.193
Br
O
N
O
3d
f1 (ppm)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8.213
8.207
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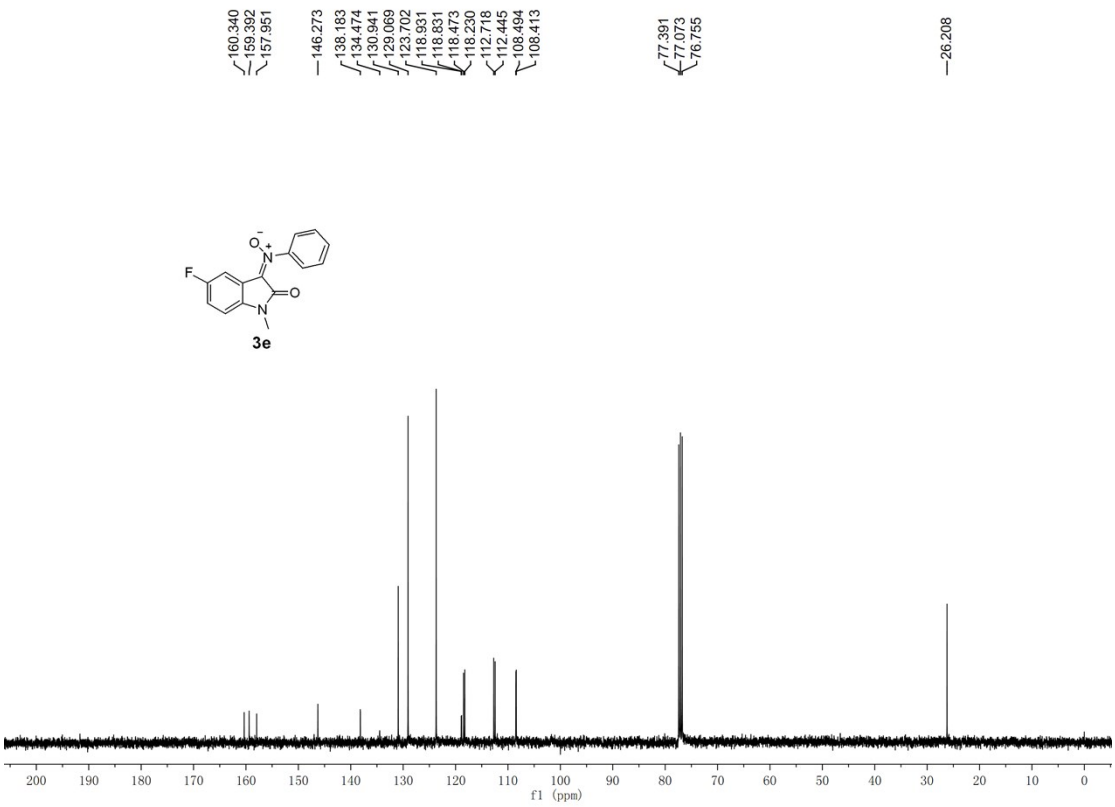
7.540
7.520
7.485
7.482
7.477
6.784
6.774
6.762
6.753
3.181
0.000
F
O
N
3e
1.00
5.09
1.03
1.01
3.07
f1 (ppm)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157.951
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134.474
130.941
129.069
123.702
118.831
118.831
118.473
118.230
112.718
112.445
108.494
108.413
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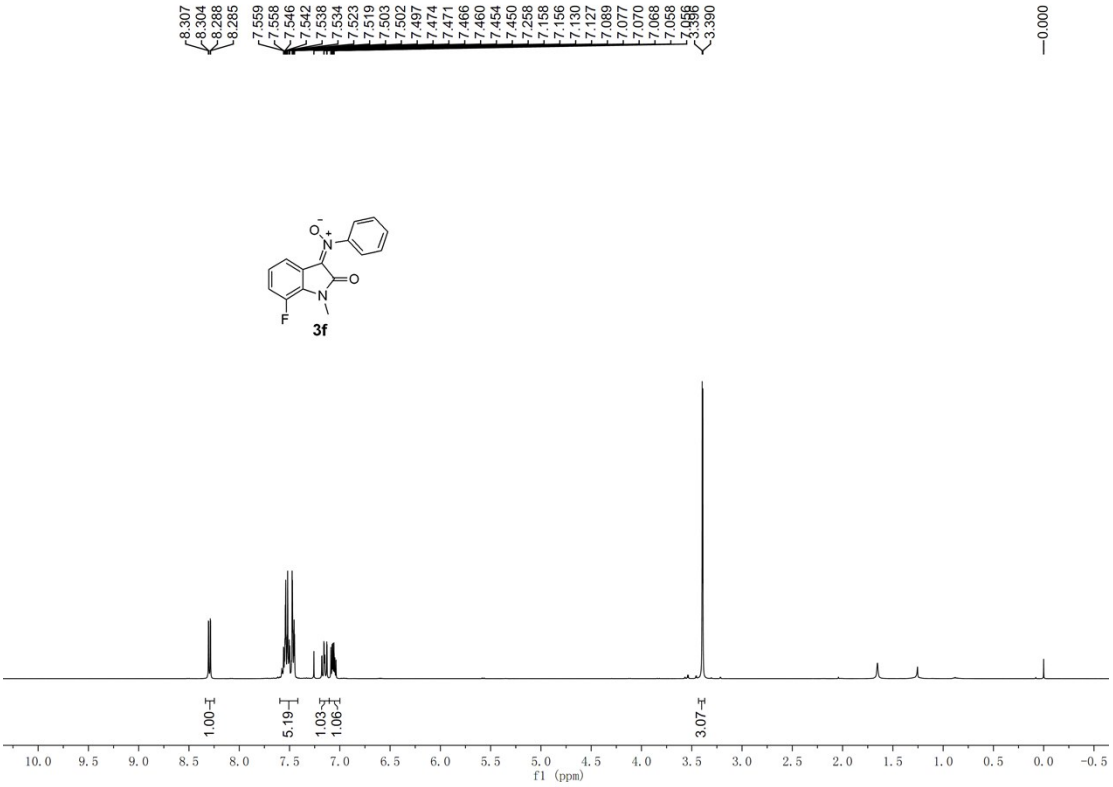
77.073
76.755
26.208
F
O
N
3e
f1 (ppm)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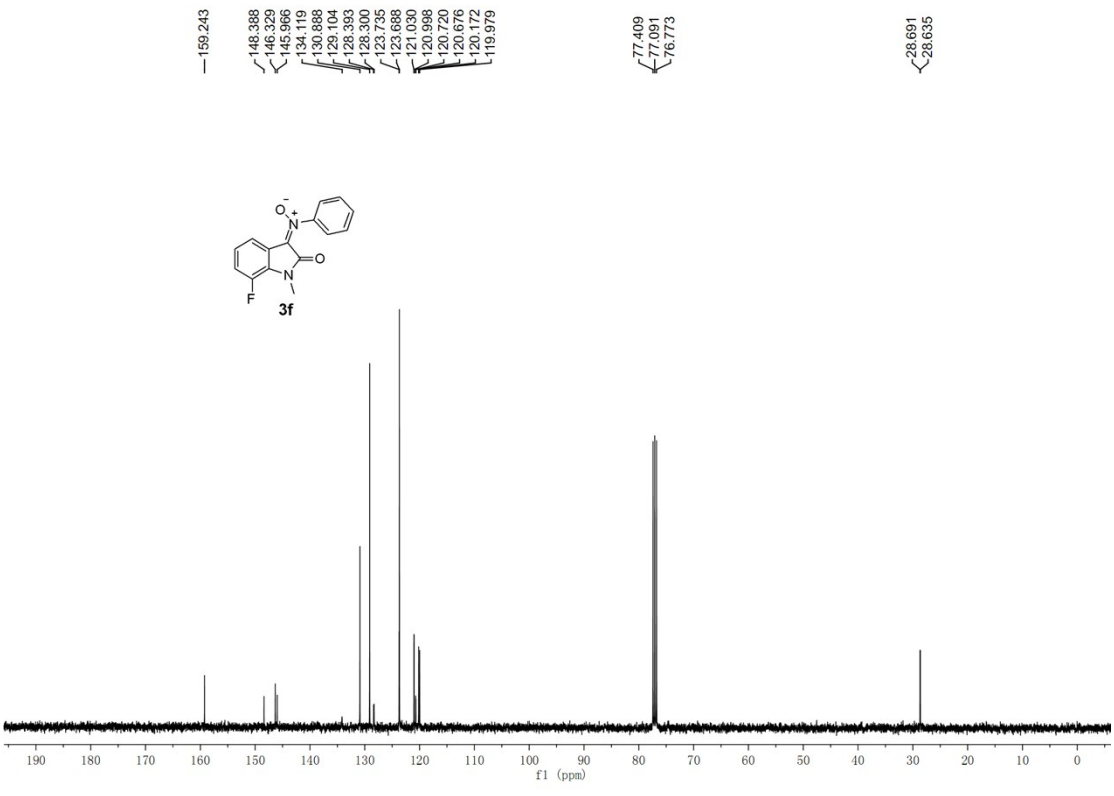
7.558
7.546
7.542
7.538
7.534
7.523
7.519
7.503
7.502
7.497
7.474
7.471
7.466
7.460
7.454
7.450
7.258
7.158
7.156
7.130
7.127
7.089
7.077
7.070
7.068
7.058
7.056
3.396
3.390
0.000
3f
1.00
5.19
1.03
1.06
3.07
f1 (ppm)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128.393
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123.688
121.030
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120.172
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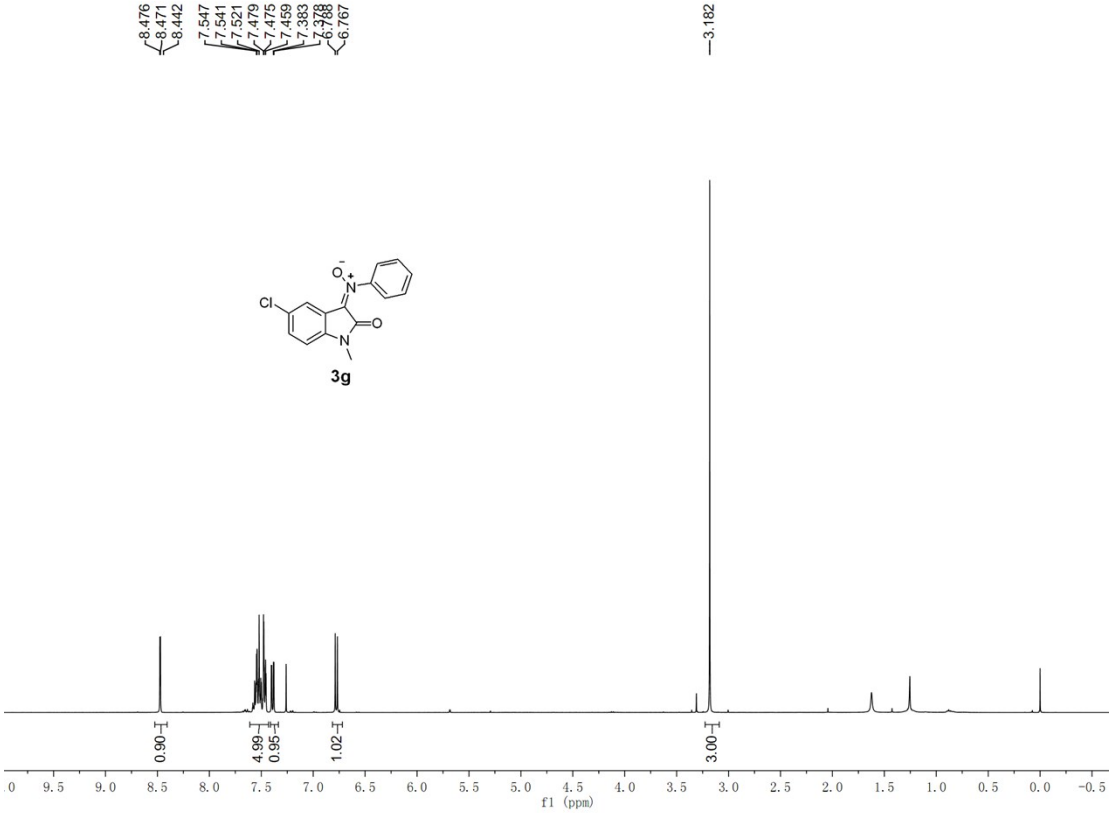
77.091
76.773
28.691
28.635
3f
f1 (ppm)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N
O
N
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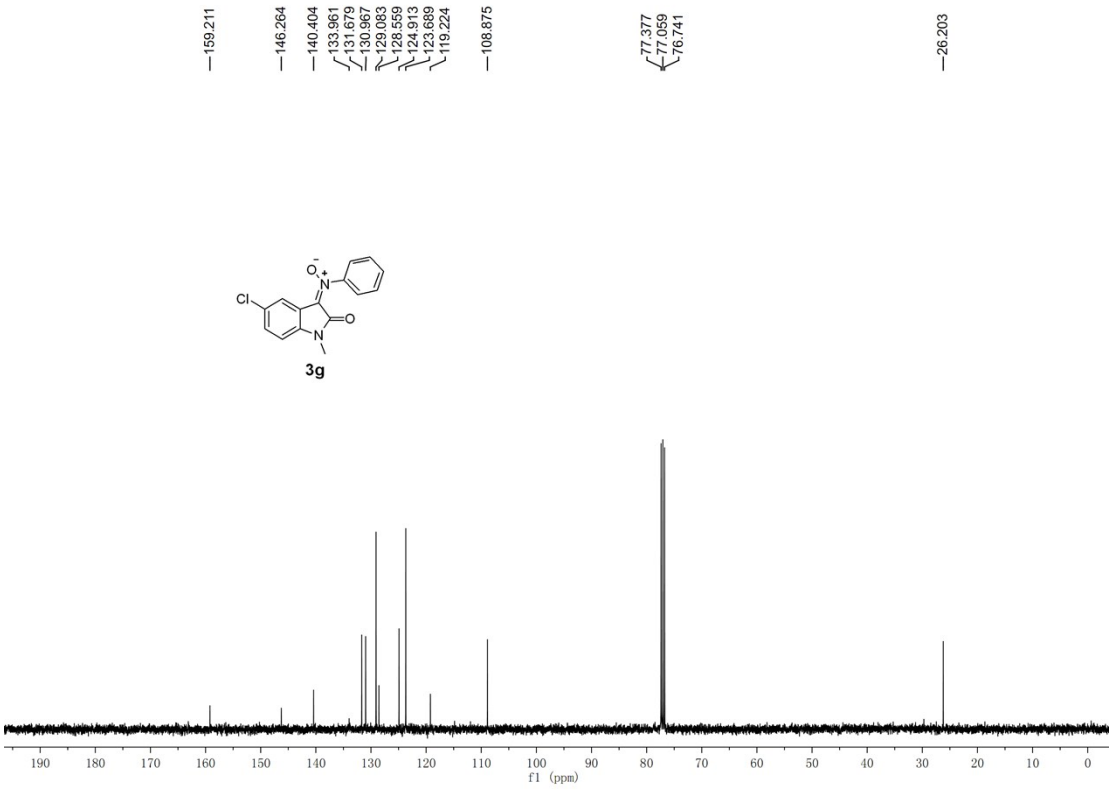
0.95
1.02
3.00
f1 (ppm)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77.377
77.059
76.741
26.203
Cl
O
N
O
N
3g
f1 (ppm)


8.324
8.304
7.556
7.543
7.539
7.534
7.528
7.518
7.513
7.497
7.492
7.479
7.476
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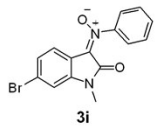
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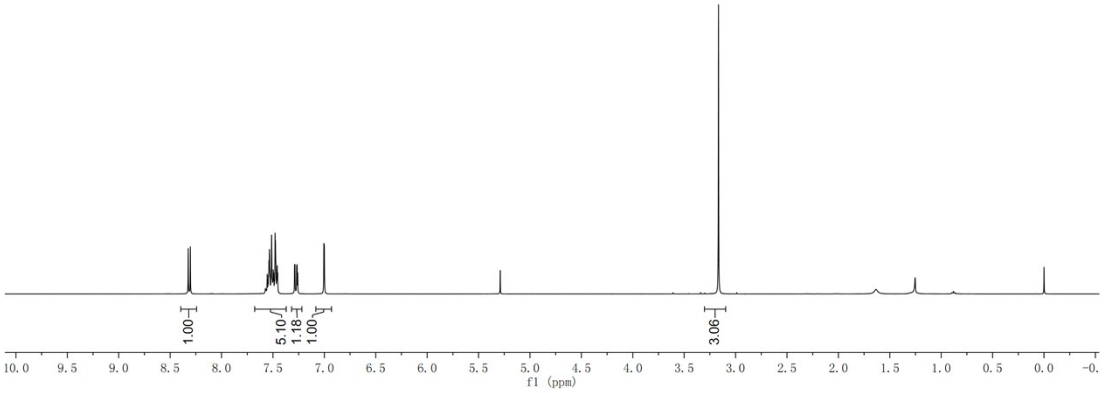
N
O
N

3i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5.10
1.18
1.00
3.06
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.
f1 (ppm)


159.317
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142.980
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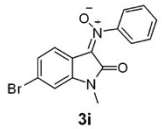
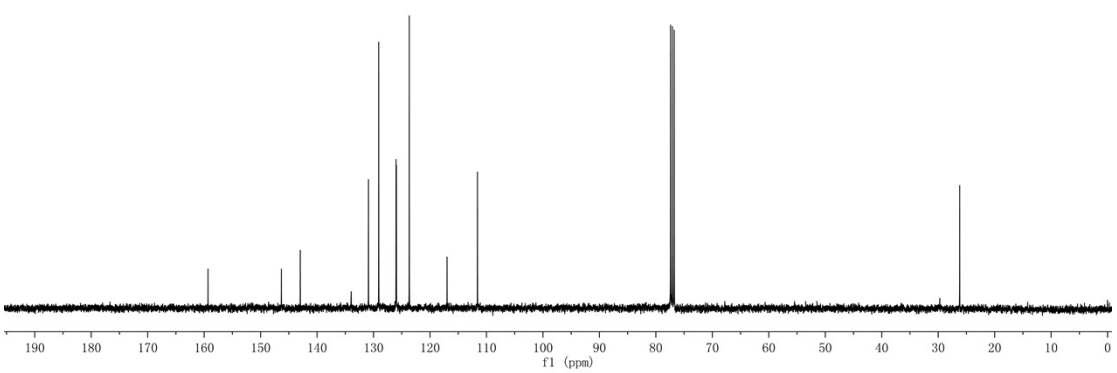
77.076
76.758
26.192


Br
O
N
O
N

3i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f1 (ppm)


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8.506
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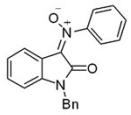
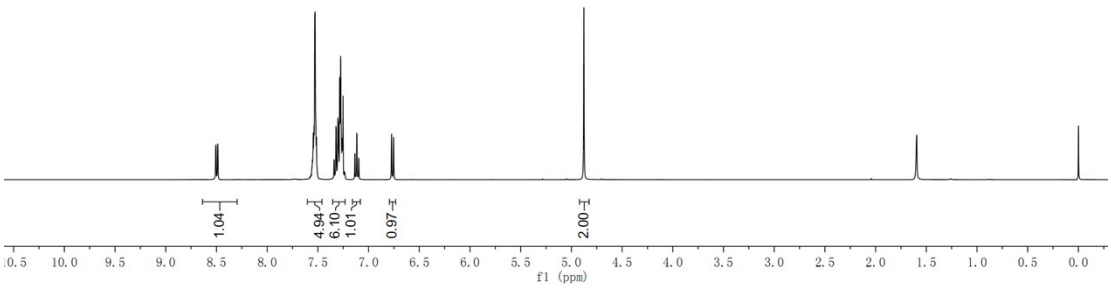


3j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f1 (ppm)


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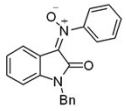
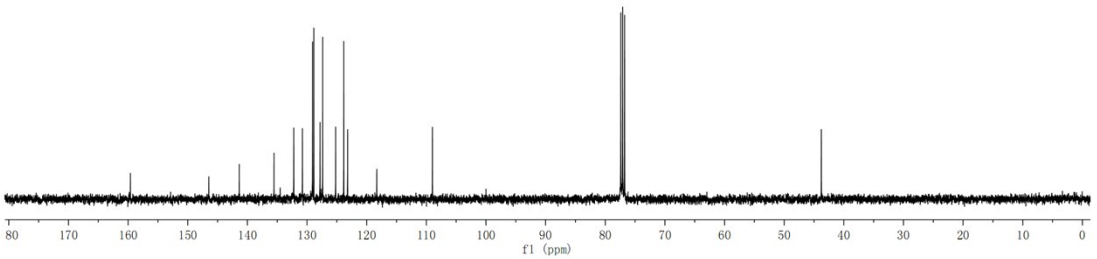
43.771



3j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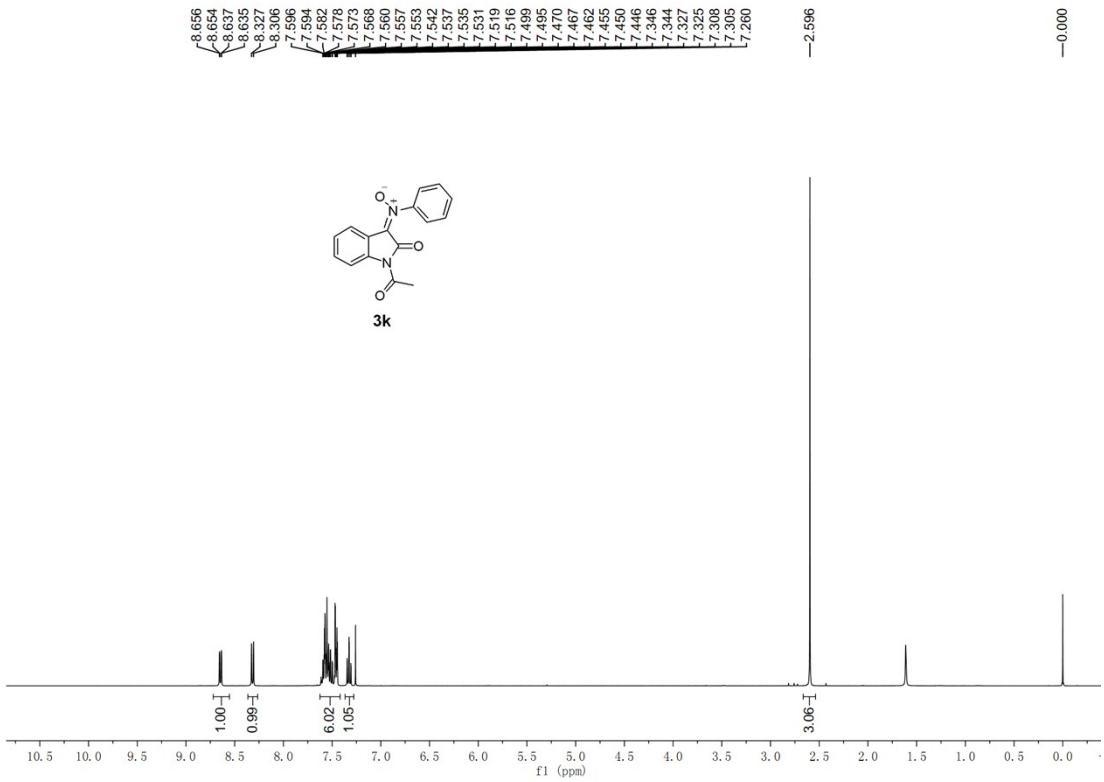
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7.594
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7.560
7.557
7.553
7.542
7.537
7.535
7.531
7.519
7.516
7.499
7.495
7.470
7.467
7.462
7.455
7.450
7.446
7.346
7.344
7.327
7.325
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3k
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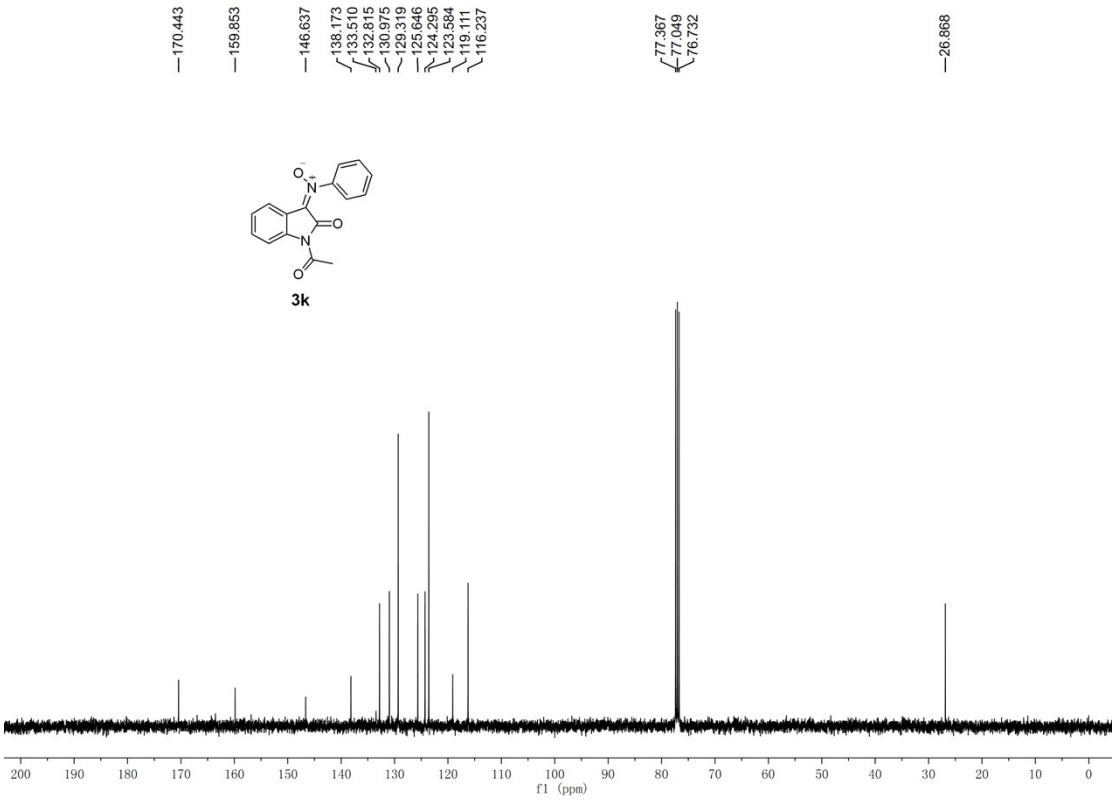
6.02
1.05
3.06
f1 (ppm)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132.815
130.975
129.319
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123.584
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116.237
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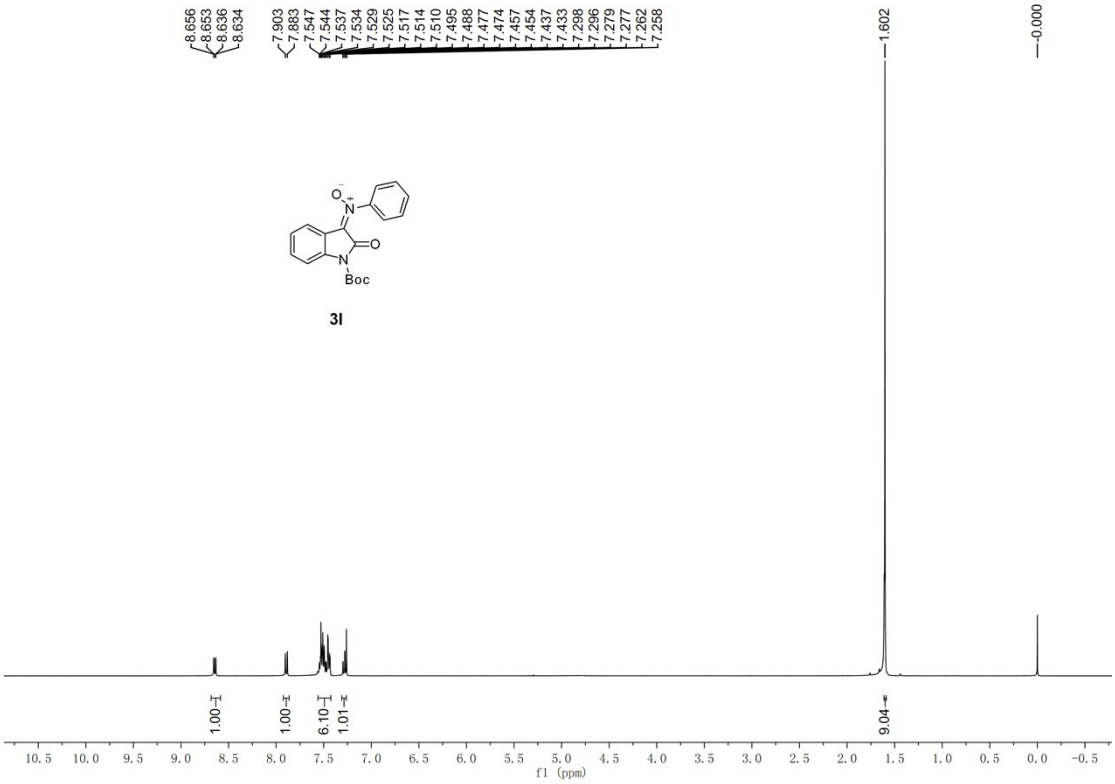
77.049
76.732
26.868
3k
f1 (ppm)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7.534
7.529
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7.510
7.495
7.488
7.477
7.474
7.457
7.454
7.437
7.433
7.298
7.296
7.279
7.277
7.262
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0.000
Boc
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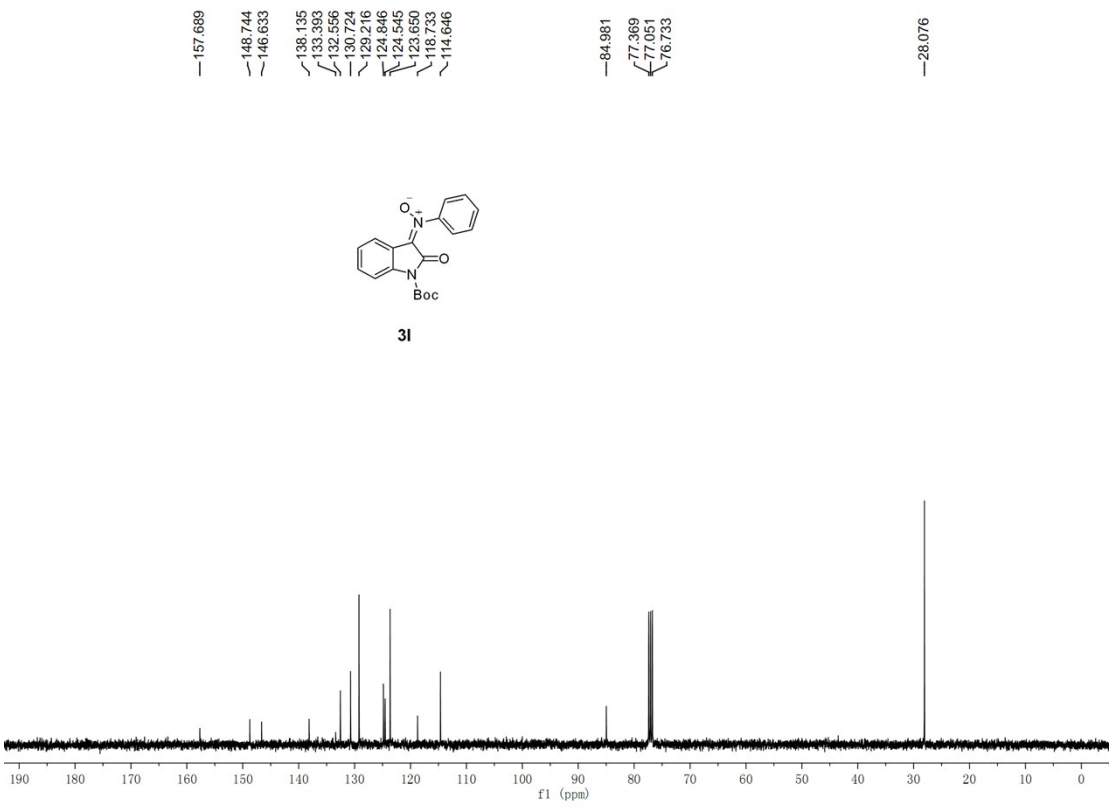
1.00
6.10
1.01
9.04
f1 (ppm)

3l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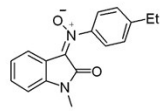
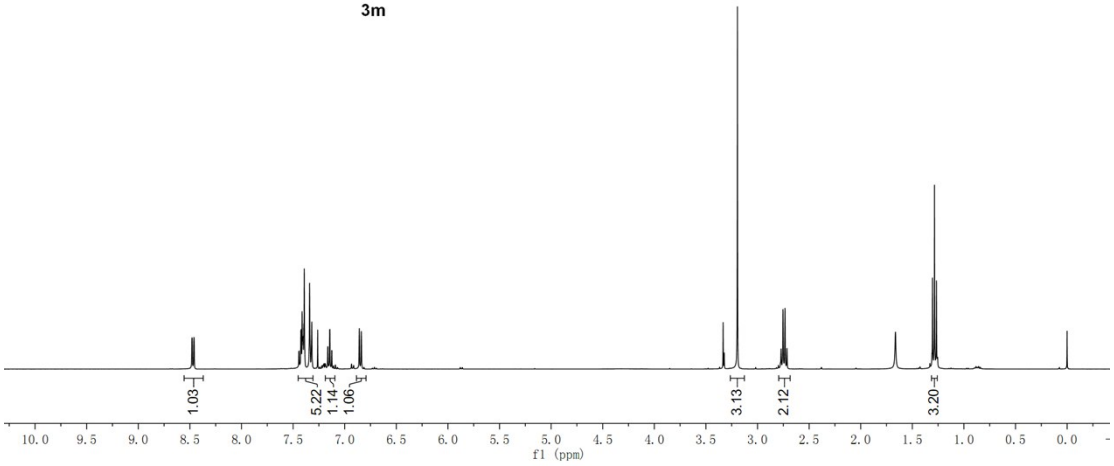
114.646
84.981
77.369
77.051
76.733
28.076
Boc
f1 (ppm)

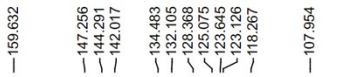
3l

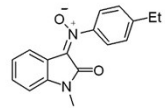

8.480
8.478
8.461
8.459
7.425
7.422
7.412
7.406
7.402
7.396
7.391
7.340
7.319
7.262
7.164
7.162
7.145
7.143
7.126
7.124
6.858
6.839
3.195
2.772
2.753
2.734
2.715
1.304
1.285
1.266
0.000


Et
O
N
O
N

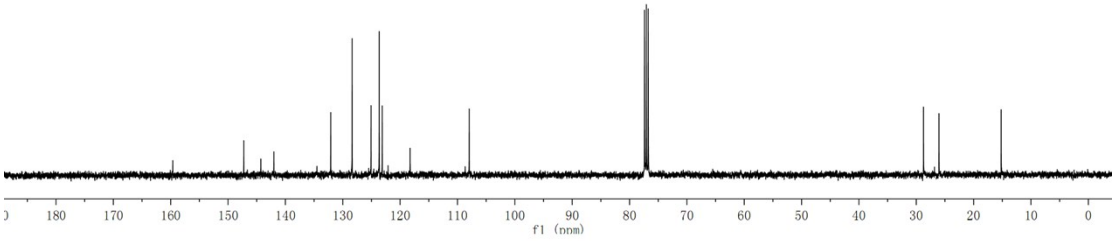
3m

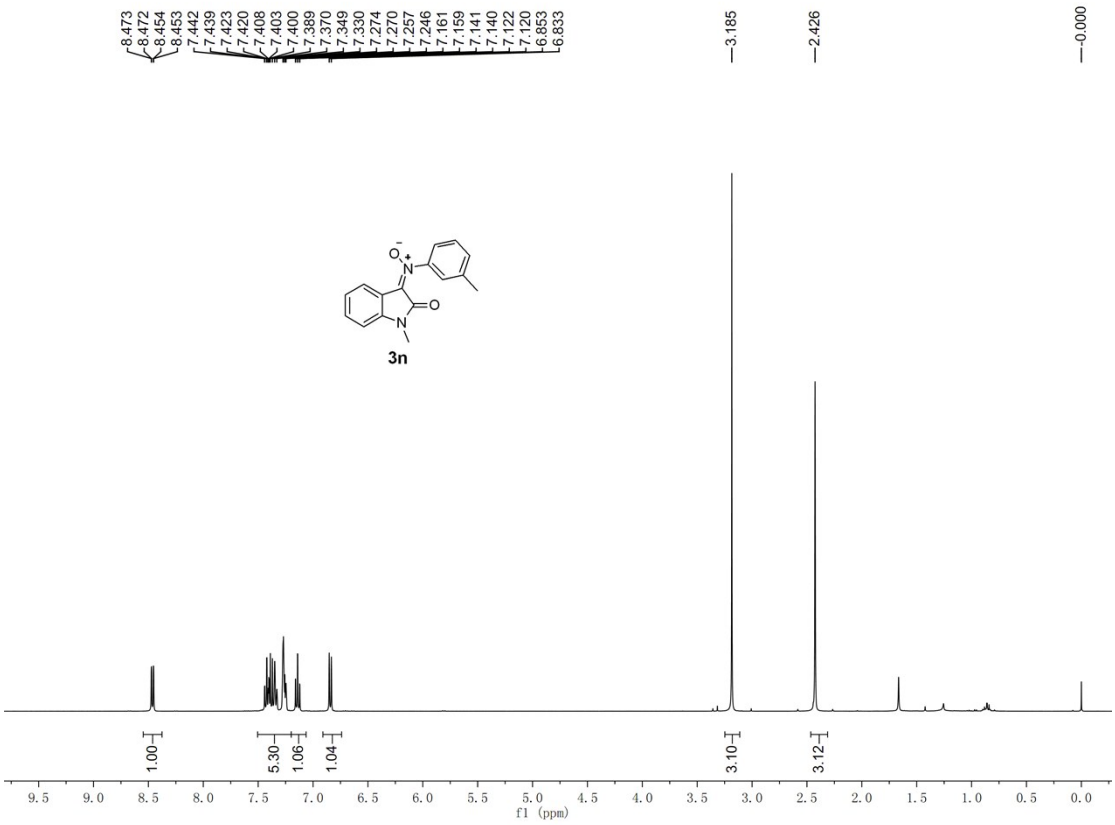

1.03
5.22
1.14
1.06
3.13
2.12
3.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

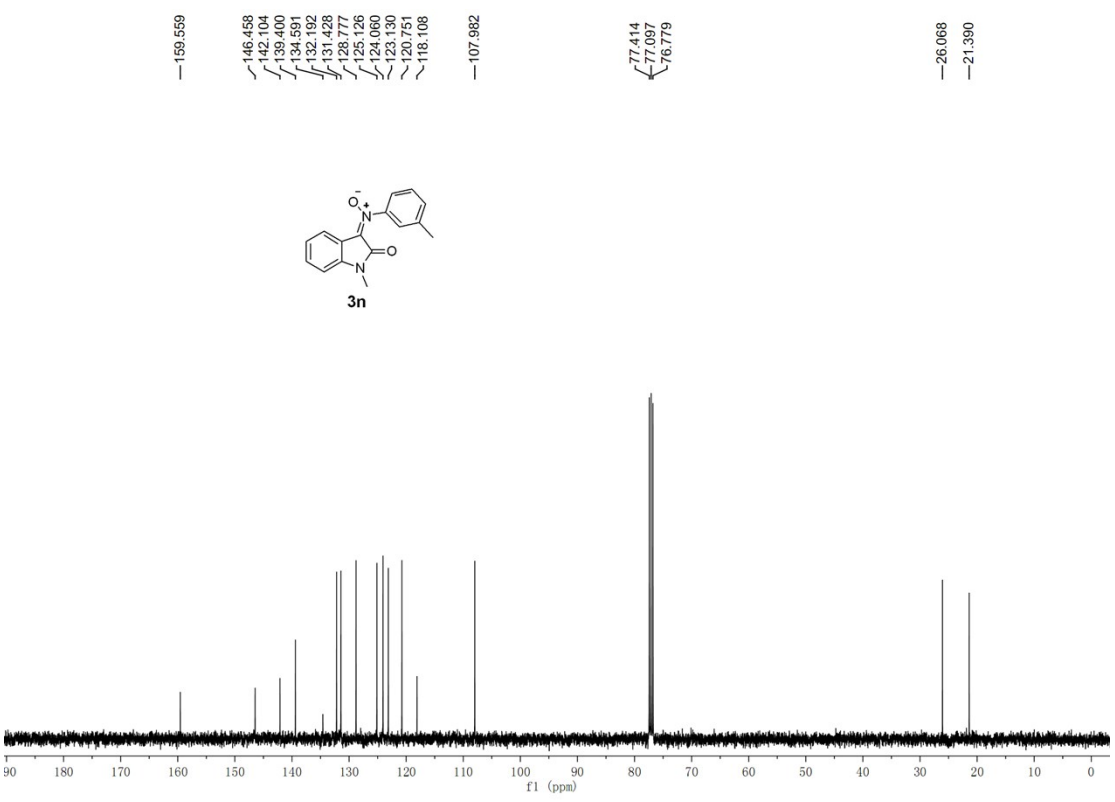

159.632
147.256
144.291
142.017
134.483
132.105
128.368
125.075
123.645
123.126
118.267
107.954
77.384
77.067
76.749
28.746
26.055
15.204

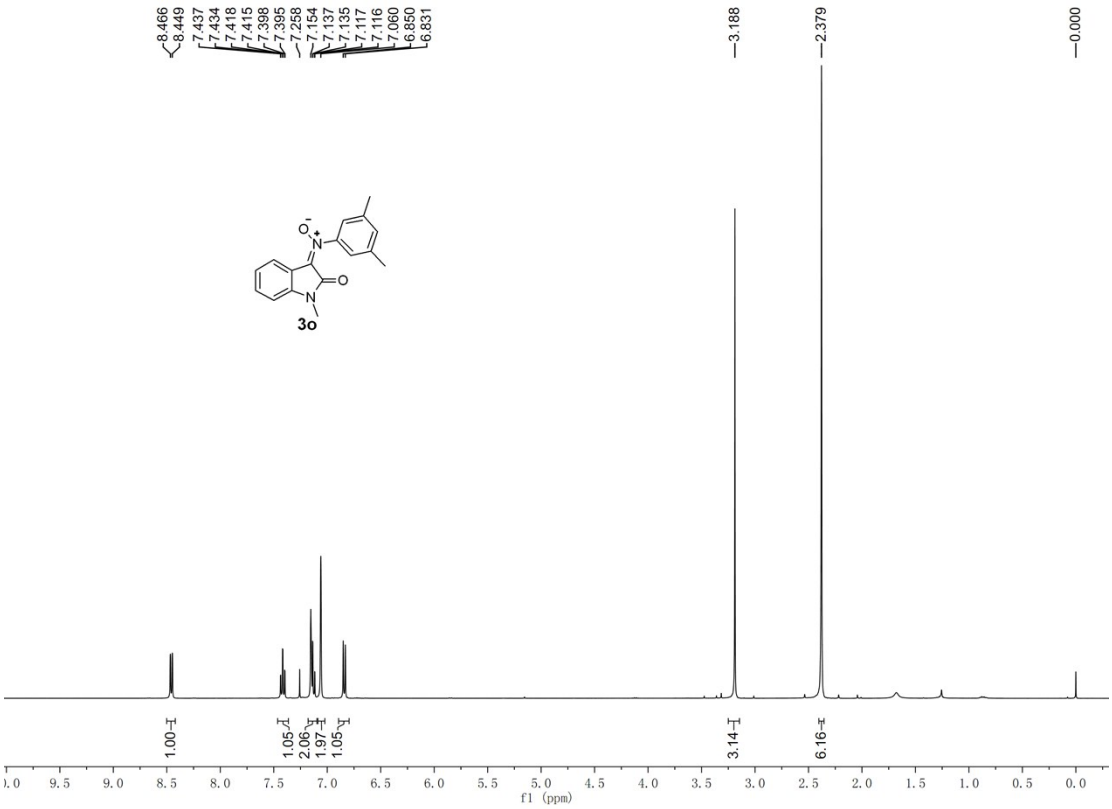

Et
O
N
O
N

3m

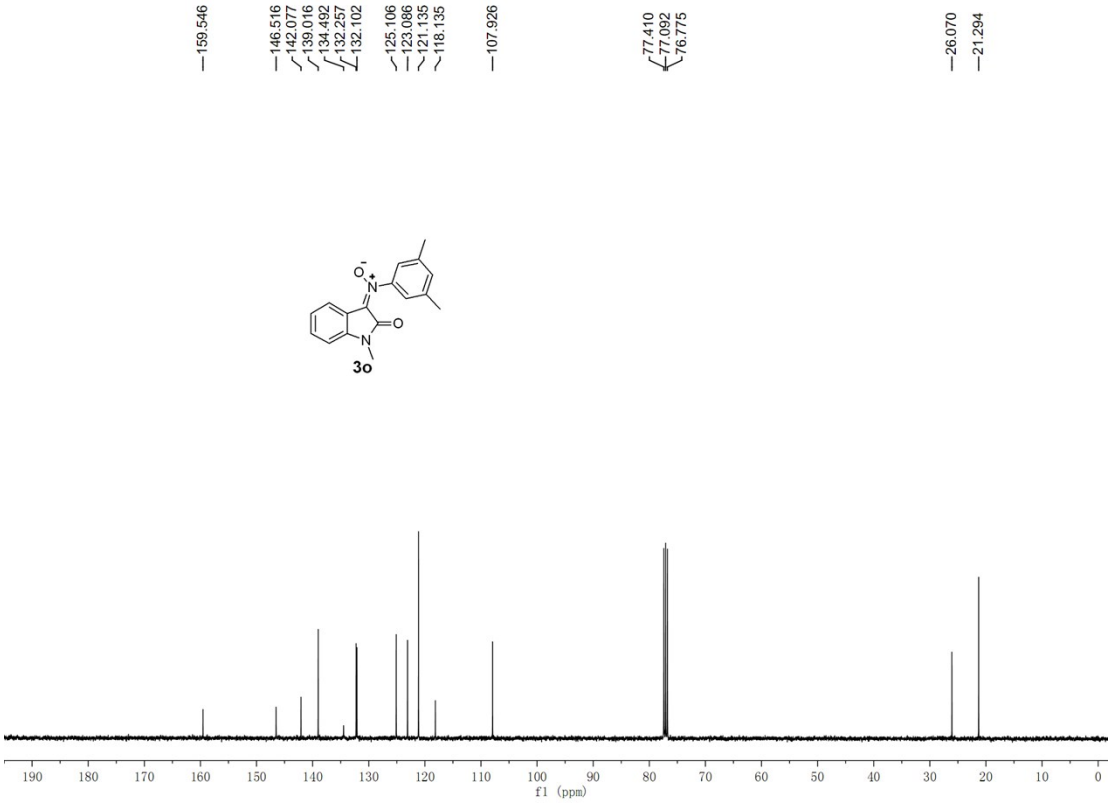

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.473
8.472
8.454
8.453
7.442
7.439
7.423
7.420
7.408
7.403
7.400
7.389
7.370
7.349
7.330
7.274
7.270
7.257
7.246
7.161
7.159
7.141
7.140
7.122
7.120
6.853
6.833
3.185
2.426
0.000
3n
1.00
5.30
1.06
1.04
3.10
3.12
f1 (ppm)

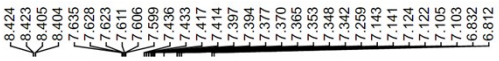

159.559
146.458
142.104
139.400
134.591
132.192
131.428
128.777
125.126
124.060
123.130
120.751
118.108
107.982
77.414
77.097
76.779
26.068
21.390
3n
f1 (ppm)

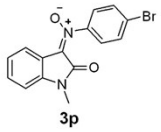

8.466
8.449
7.437
7.434
7.418
7.415
7.398
7.395
7.258
7.154
7.137
7.135
7.117
7.116
7.060
6.850
6.831
3.188
2.379
0.000
1.00
1.05
2.06
1.97
1.05
3.14
6.16
f1 (ppm)

3o

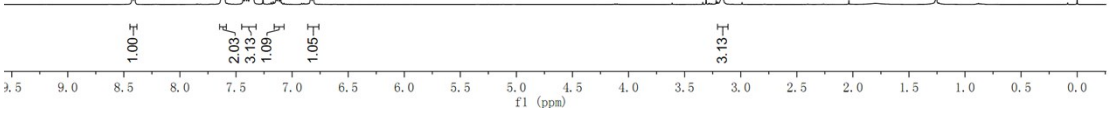

159.546
146.516
142.077
139.016
134.492
132.257
132.102
125.106
123.086
121.135
118.135
107.926
77.410
77.092
76.775
26.070
21.294
f1 (ppm)

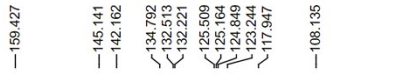
3o

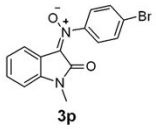

8.424
8.423
8.405
8.404
7.635
7.628
7.623
7.611
7.606
7.599
7.436
7.433
7.417
7.414
7.397
7.394
7.377
7.370
7.365
7.353
7.348
7.342
7.259
7.143
7.141
7.124
7.122
7.105
7.103
6.832
6.812
3.165
0.000


Br
O
N
O
N

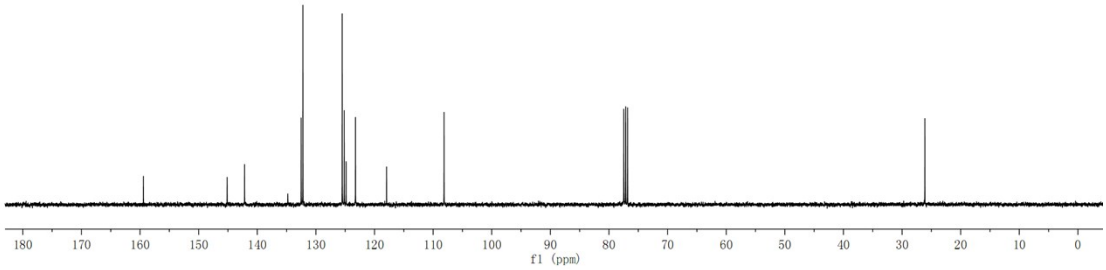
3p

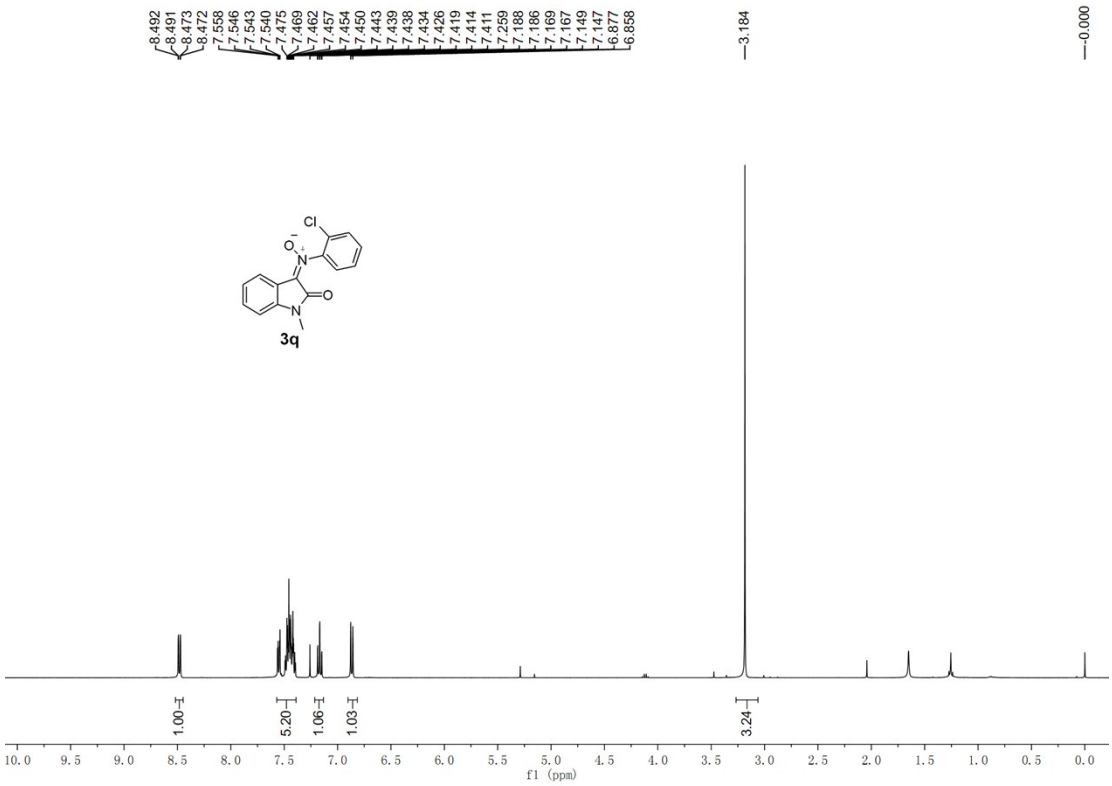

1.00
2.03
3.13
1.09
1.05
3.13
f1 (ppm)

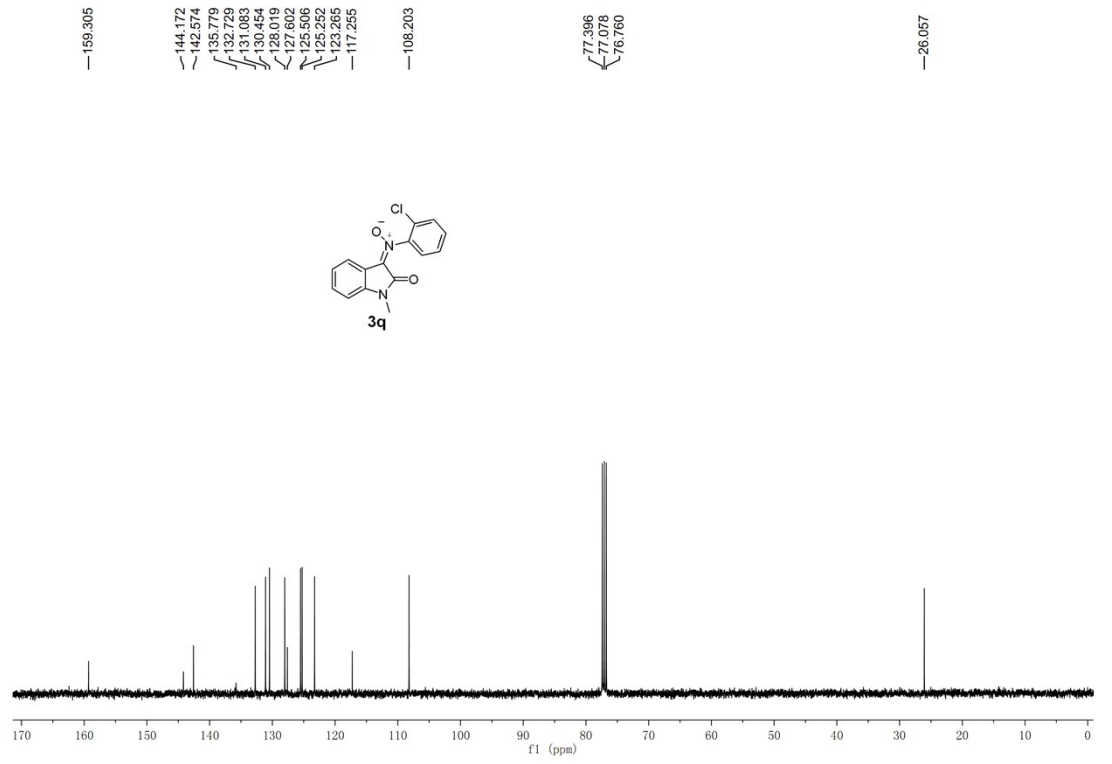

159.427
145.141
142.162
134.792
132.513
132.221
125.509
125.164
124.849
123.244
117.947
108.135
77.471
77.153
76.834
26.107

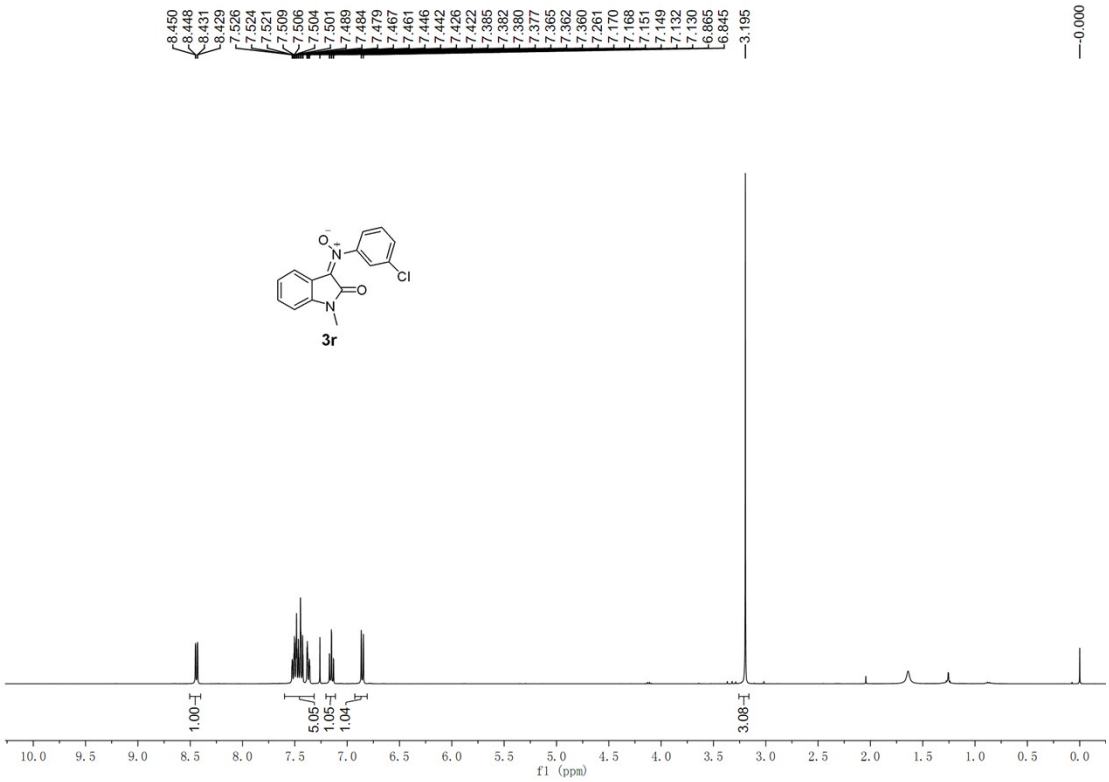

Br
O
N
O
N

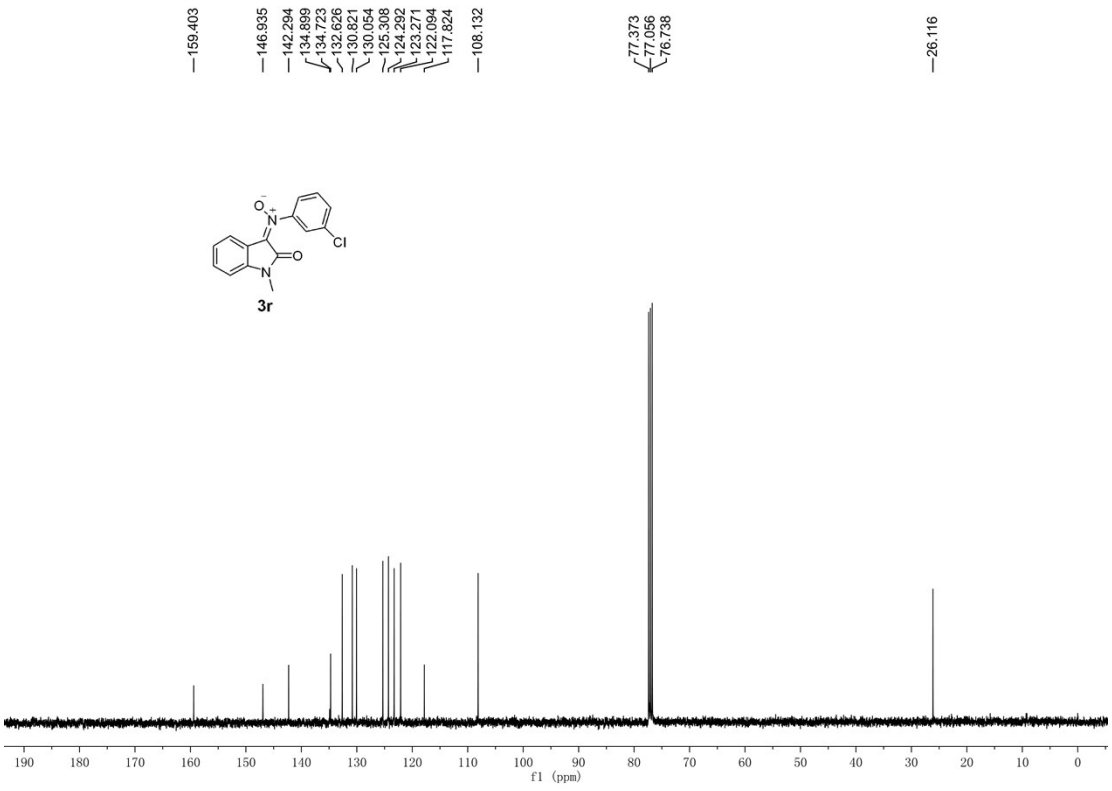
3p

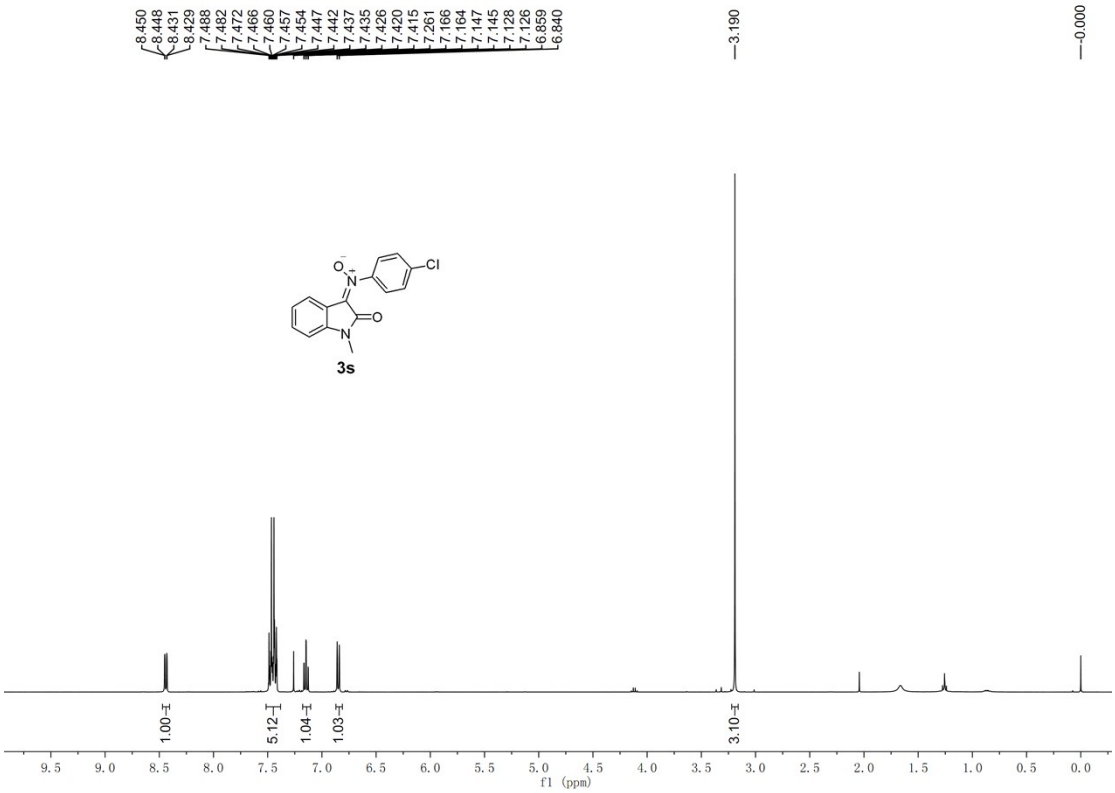

f1 (ppm)

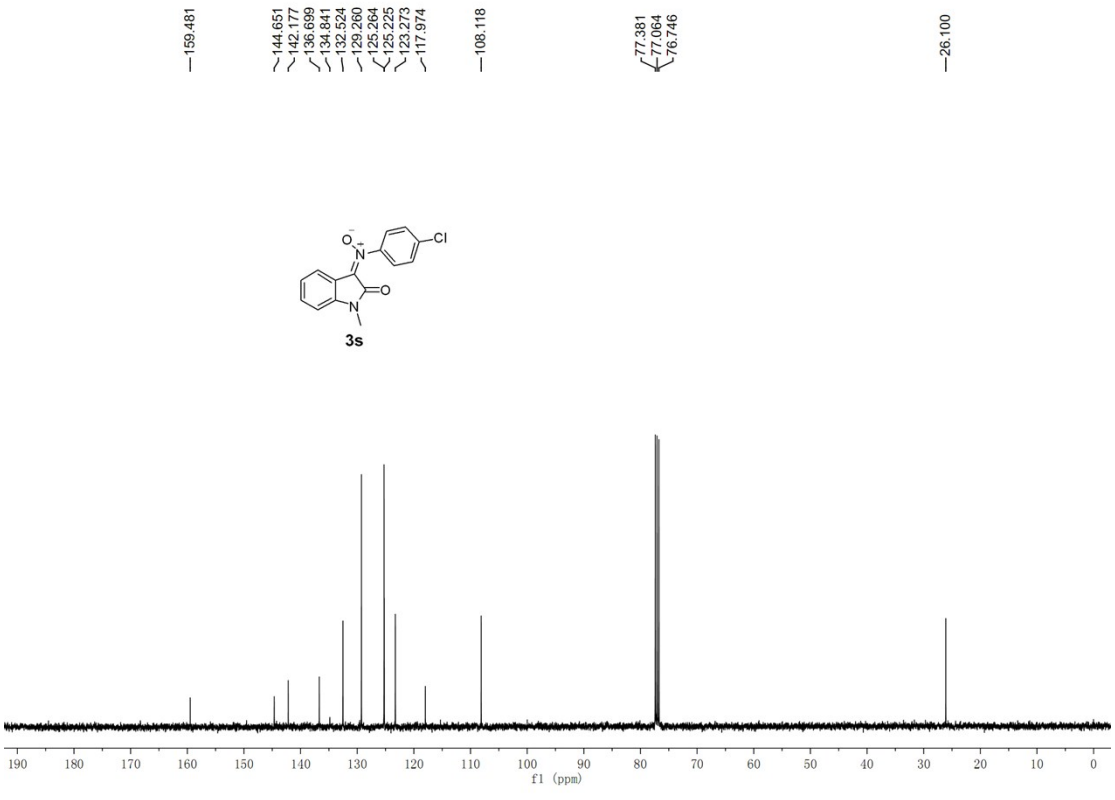

8.492
8.491
8.473
8.472
7.558
7.546
7.543
7.540
7.475
7.469
7.462
7.457
7.454
7.450
7.443
7.439
7.438
7.434
7.426
7.419
7.414
7.411
7.259
7.188
7.186
7.169
7.167
7.149
7.147
6.877
6.858
3.184
0.000
Cl
O
N
O
N
3q
1.00
5.20
1.06
1.03
3.24
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


159.305
144.172
142.574
135.779
132.729
131.083
130.454
128.019
127.602
125.506
125.252
123.265
117.255
108.203
77.396
77.078
76.760
26.057
Cl
O
N
O
N
3q
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.450
8.448
8.431
8.429
7.526
7.524
7.521
7.509
7.506
7.504
7.501
7.489
7.484
7.479
7.467
7.461
7.446
7.442
7.426
7.422
7.385
7.382
7.380
7.377
7.365
7.362
7.360
7.261
7.170
7.168
7.151
7.149
7.132
7.130
6.865
6.845
3.195
0.000
3r
1.00
5.05
1.05
1.04
3.08
f1 (ppm)


159.403
146.935
142.294
134.899
134.723
132.626
130.821
130.054
125.308
124.292
123.271
122.094
117.824
108.132
77.373
77.056
76.738
26.116
3r
f1 (ppm)


8.450
8.448
8.431
8.429
7.488
7.482
7.472
7.466
7.460
7.457
7.454
7.447
7.442
7.437
7.435
7.426
7.420
7.415
7.261
7.166
7.164
7.147
7.145
7.128
7.126
6.859
6.840
3.190
0.000
Cl
O
N
O
3s
1.00
5.12
1.04
1.03
3.10
f1 (ppm)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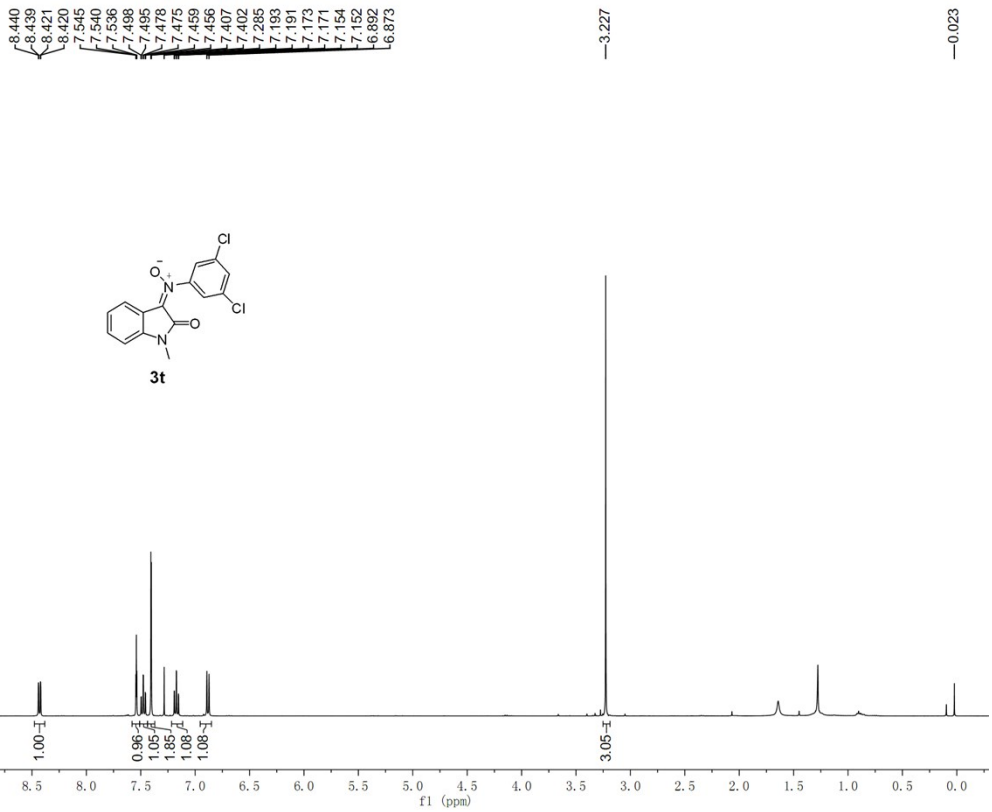
142.177
136.699
134.841
132.524
129.260
125.264
125.225
123.273
117.974
108.118
77.381
77.064
76.746
26.100
Cl
O
N
O
3s
f1 (ppm)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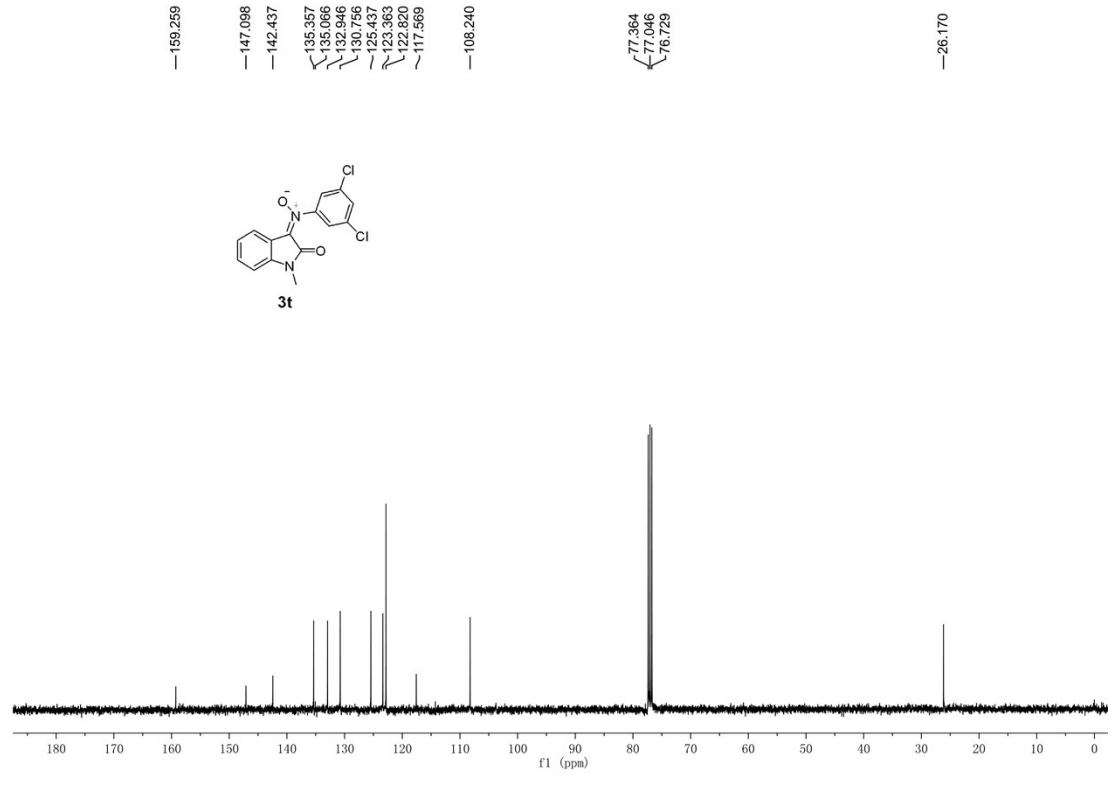
8.439
8.421
8.420
7.545
7.540
7.536
7.498
7.495
7.478
7.475
7.459
7.456
7.407
7.402
7.285
7.193
7.191
7.173
7.171
7.154
7.152
6.892
6.873
3.227
0.023
Cl
Cl
O
N
O
3t
1.00
0.96
1.05
1.85
1.08
1.08
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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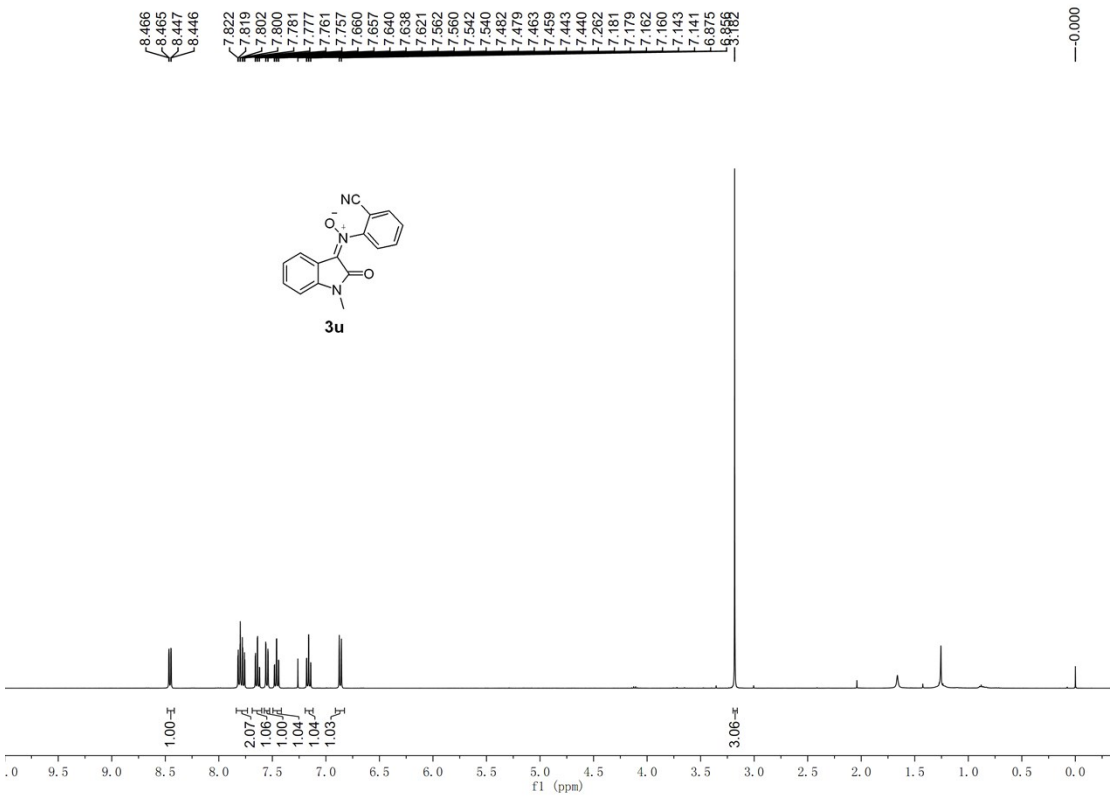
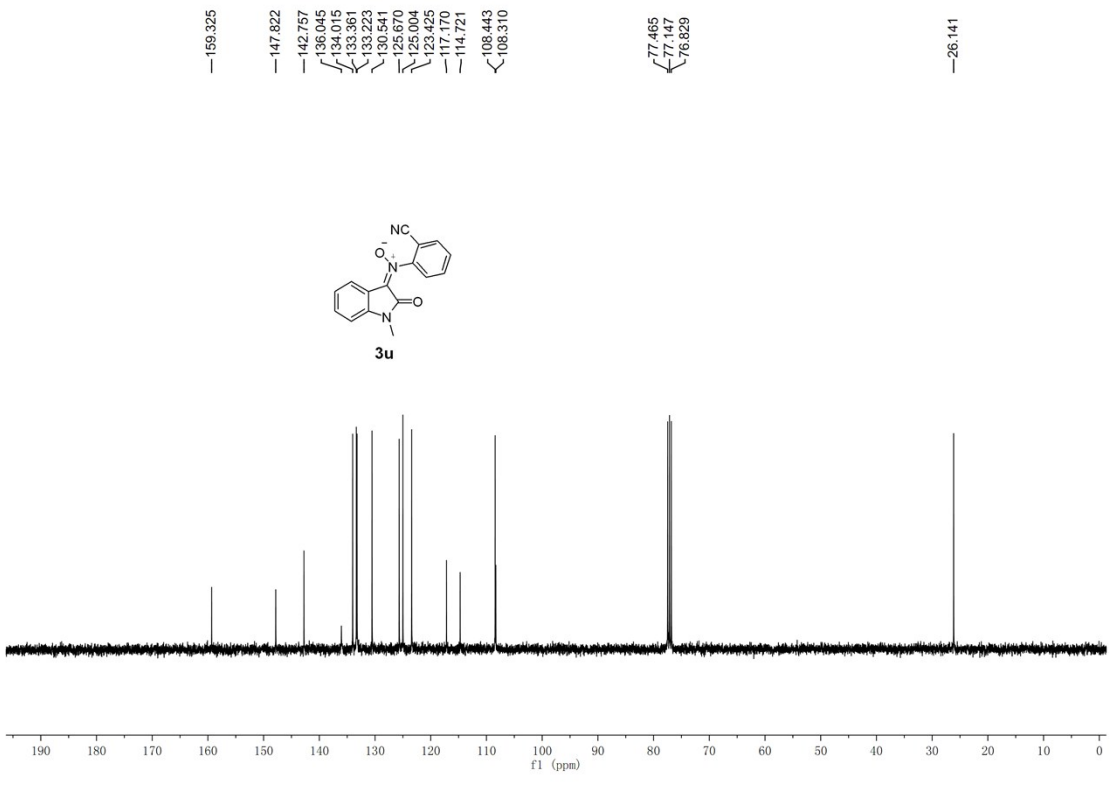
142.437
135.357
135.066
132.946
130.756
125.437
123.363
122.820
117.569
108.240
77.364
77.046
76.729
26.170
Cl
Cl
O
N
O
3t
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.466
8.465
8.447
8.446
7.822
7.819
7.802
7.800
7.781
7.777
7.761
7.757
7.660
7.657
7.640
7.638
7.621
7.562
7.560
7.542
7.540
7.482
7.479
7.463
7.459
7.443
7.440
7.262
7.181
7.179
7.162
7.160
7.143
7.141
6.875
6.856
3.182
0.000
NC
O
N
O
N
3u
1.00
2.07
1.06
1.00
1.04
1.04
1.03
3.06
f1 (ppm)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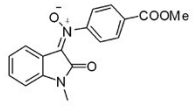
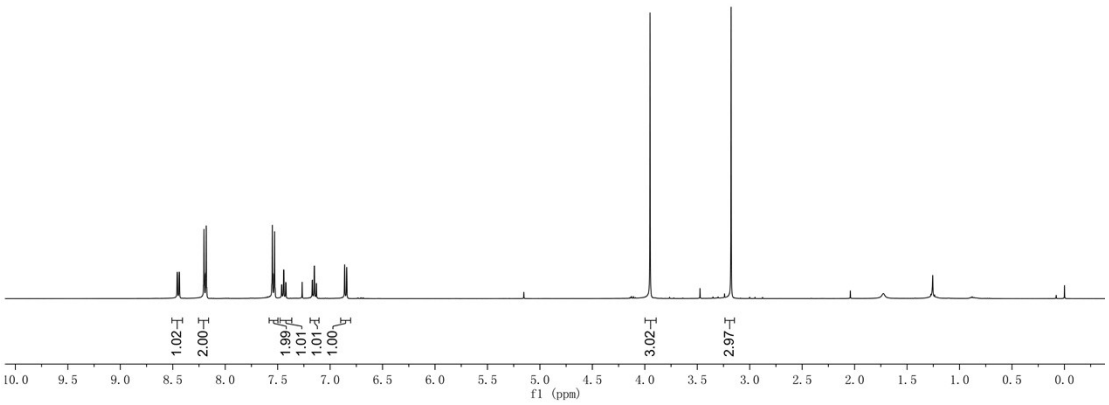
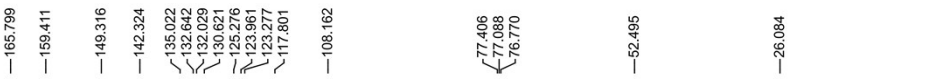
147.822
142.757
136.045
134.015
133.361
133.223
130.541
125.670
125.004
123.425
117.170
114.721
108.443
108.310
77.465
77.147
76.829
26.141
NC
O
N
O
N
3u
f1 (ppm)


8.456
8.438
8.202
8.198
8.185
8.181
7.551
7.546
7.534
7.529
7.463
7.460
7.443
7.440
7.424
7.421
7.267
7.171
7.169
7.151
7.150
7.132
7.131
6.861
6.842
3.950
3.178
0.000


COOMe
O
N
O
N

3v


1.02
2.00
1.99
1.01
1.01
1.00
3.02
2.97
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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159.411
149.316
142.324
135.022
132.642
132.029
130.621
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123.961
123.277
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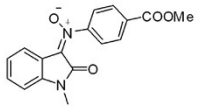
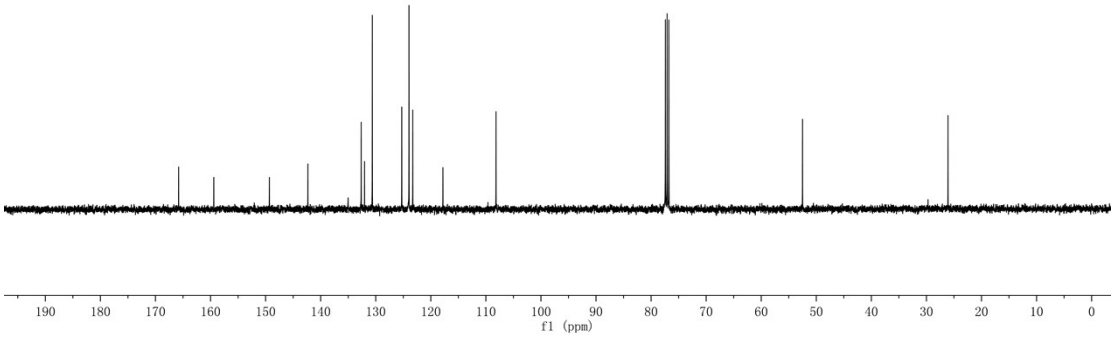
108.162
77.406
77.088
76.770
52.495
26.084


COOMe
O
N
O
N

3v


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