Supplementary information

Indolizine Synthesis via Radical Cyclization and Demethylation of Sulfoxonium Ylides and 2-(Pyridin-2-yl)acetate Derivatives

Kexin Su, [a] Xin Guo,[b] Liangwei Zhu,[a] Yafeng Liu, [b] Yixuan Lu, [a] and Baohua Chen*[a]

[a] State Key Laboratory of Applied Organic Chemistry, Department of Chemistry, Lanzhou University, Lanzhou, Gansu, China.
E-mail: chbh@lzu.edu.cn; Fax: +0931-8912596
[b] School of Chemistry and Chemical Engineering, North Minzu University, Yinchuan, China

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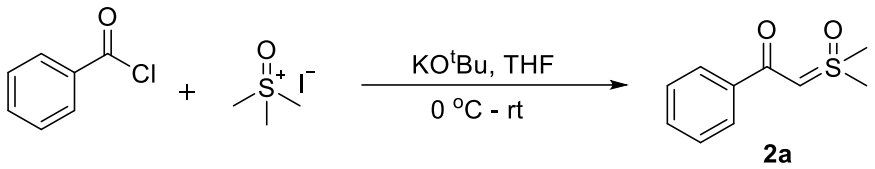
General information

Unless otherwise indicated, all commercial regents and solvents were used without additional purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on Mercury 300 M and Bruker 400M in $CDCl_3$. All ^{1}H NMR and ^{13}C NMR chemical shifts were given as δ value(ppm) with reference to tetramethylsilane (TMS) as an internal standard. All compounds were further characterized by MS; copies of their ^{1}H NMR and ^{13}C NMR spectra were provided. Products were purified by flash chromatography on 200–300 mesh silica gels. All melting points were determined without correction. All reagents were purchased commercially and used as received, unless otherwise noted.

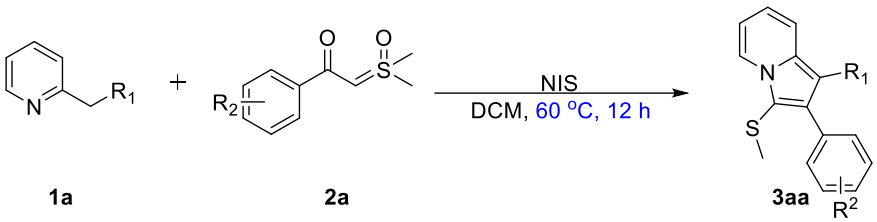
General procedure for the synthesis of sulfoxonium ylides



2a

Sulfoxonium ylides **2a** were prepared according to a literature procedure. Trimethylsulfoxonium iodide (5.0 g, 20.6 mmol) was added to a stirred solution of potassium tert-butoxide (3.0 g, 27.2 mmol) in THF (30 mL) at room temperature. The resulting mixture was refluxed for 2 h, then cooled to 0 ºC, followed by addition of acyl chlorides (7 mmol) in THF (5 mL) and stirred for another 3 h at room temperature. Next, the solvent was evaporated under vacuum, afterwards water (15 mL) and ethyl acetate (20 mL) were added to the resulting slurry. The aqueous layer was separated and washed with ethyl acetate (2 × 30 mL), and combined with the organic layers. The organic solution was dried over anhydrous sodium sulphate (Na_2SO_4), filtered over a sintered funnel and evaporated to dryness. The crude product was finally purified by flash chromatography over silica gel with EtOAc/MeOH (95:5) to afford the corresponding sulfoxonium ylides.

General procedure for the 3-(methylthio)-2-phenylindolizine-1-carboxylate



1a **2a** **3aa**

The substrate sulfoxonium ylides (**2a**, 0.2 mmol) and NIS (0.4 mmol) were added to a 10 mL Schlenk tube, followed by addition of DCM (1.5 mL), then a certain amount of ethyl pyridin-2-ylacetates (**1a**, 0.2 mmol) were added into the liquor. The mixture was stirred at 60 ºC for 12 h under air. After cooled down, the solvent was removed, filtered and evaporated under vacuum. Then the residue was purified by silica gel chromatography using ethylacetate/petroleum ether (15:1) to afford product **3aa** as white solid (36.8 mg, 62% yield).

X-ray single data

An amount of 25 mg **3aa** were dissolved in petroleum ether / DCM (5:1) on the brown small reagent bottle (5 mL) and the cap is covered with a thin film. The crystal was obtained by slow evaporation of the solution at low temperature.

The data were collected at 296.15 K using a Bruker APEX II area detectordiffractometer equipped with a graphite monochromated Mo Kα radiation source (λ = 0.71073 Å) operation at 50 kV and 0.8 mA. Using Olex2, the structure was solved with the ShelXS-1997 structure solution program using Direct Methods and refined with the olex2.refine refinement package using Gauss-Newton minimisation. Nonhydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All hydrogen atoms were placed by geometrical considerations and were added to the structure factor calculations.

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 2067793).

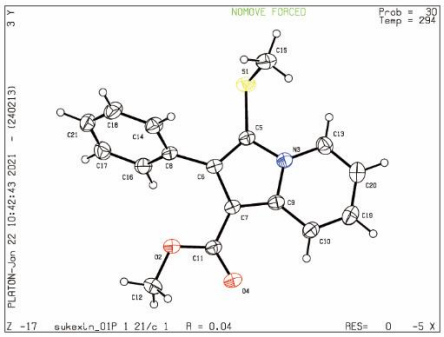


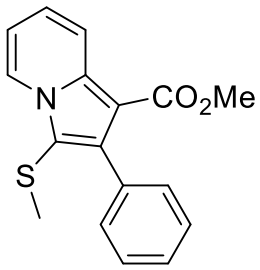
Figure 2. X-ray structure of **3aa**

Table 1 Crystal data and structure refinement for **3aa**.

Identification code	sukexin_0116
Empirical formula	$C_{17}H_{15}NO_2S$
Formula weight	297.36
Temperature/K	293.78(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.0441(4)
b/Å	18.6223(6)
c/Å	8.2831(4)
α/°	90
β/°	110.227(5)
γ/°	90
Volume/Å^3	1453.76(11)
Z	4
ρ_{calc}g/cm^3	1.359

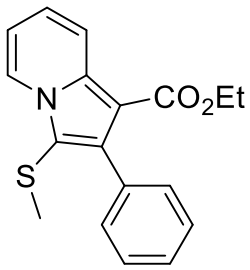
μ/mm^{-1}	2.006
F(000)	624.0
Crystal size/mm^3	0.17 × 0.14 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.384 to 133.152
Index ranges	-9 ≤ h ≤ 11, -22 ≤ k ≤ 18, -9 ≤ l ≤ 9
Reflections collected	5264
Independent reflections	2562 [R_{int} = 0.0265, R_{sigma} = 0.0344]
Data/restraints/parameters	2562/0/192
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0419, wR_2 = 0.1087
Final R indexes [all data]	R_1 = 0.0530, wR_2 = 0.1164
Largest diff. peak/hole / e Å^{-3}	0.23/-0.27

Characterization data for the products



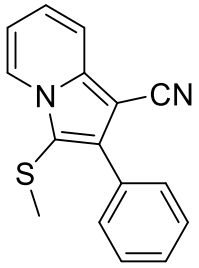
methyl 3-(methylthio)-2-phenylindolizine-1-carboxylate (3aa)

White solid, mp: 118-121 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (s, 1H), 8.32 (s, 1H), 7.42 (d, *J* = 11.9 Hz, 5H), 7.21 (d, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 1H), 3.70 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.03, 138.60, 137.77, 134.96, 130.49, 127.39, 127.33, 124.48, 123.98, 120.23, 115.65, 113.19, 102.89, 50.69, 18.58. ESI calcd for $C_{17}H_{15}NO_2S$ $[M+H]^+$ 297.0823; found: 297.1258.



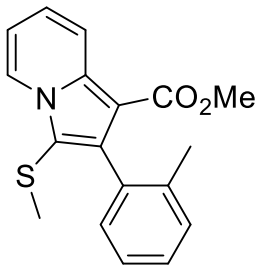
ethyl 3-(methylthio)-2-phenylindolizine-1-carboxylate (3ba)

White solid, mp: 116-119 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 9.9 Hz, 1H), 8.32 (d, *J* = 9.7 Hz, 1H), 7.43 – 7.37 (m, 5H), 7.19 (s, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 4.19 – 4.13 (m, 2H), 2.08 (s, 3H), 1.10 (d, *J* = 7.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.63, 138.59, 137.78, 135.19, 130.51, 127.32, 127.25, 124.43, 123.88, 120.17, 113.15, 103.23, 59.37, 18.63, 14.15. ESI calcd for $C_{18}H_{17}NO_2S$ $[M+H]^+$ 311.0980; found: 311.1959.



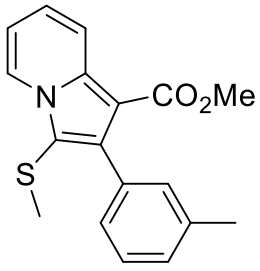
3-(methylthio)-2-phenylindolizine-1-carbonitrile (3ca)

Yellow solid, mp: 132-134 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.59 (dt, *J* = 7.0, 1.1 Hz, 1H), 7.75 – 7.69 (m, 3H), 7.54 – 7.48 (m, 2H), 7.44 (d, *J* = 7.3 Hz, 1H), 7.25 – 7.19 (m, 1H), 6.95 (td, *J* = 6.9, 1.3 Hz, 1H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.61, 137.67, 132.05, 129.83, 128.59, 128.44, 124.99, 124.12, 117.87, 116.46, 113.69, 18.39. ESI calcd for $C_{16}H_{12}N_2S$ $[M+H]^+$ 264.0721; found: 264.1318.



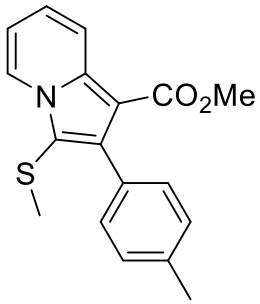
methyl 3-(methylthio)-2-(*o*-tolyl)indolizine-1-carboxylate (3ab)

White solid, mp: 104-105 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.59 (d, *J* = 7.0 Hz, 1H), 8.31 (d, *J* = 9.0 Hz, 1H), 7.30 – 7.23 (m, 3H), 7.18 (dd, *J* = 20.1, 4.6 Hz, 2H), 6.94 – 6.88 (m, 1H), 3.66 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 165.06, 137.86, 137.10, 135.32, 130.06, 129.49, 127.79, 125.11, 124.63, 124.05, 120.27, 115.45, 113.24, 103.36, 50.91, 20.45, 18.57. ESI calcd for $C_{18}H_{17}NO_2S$ $[M+H]^+$ 311.0980; found: 311.1427.



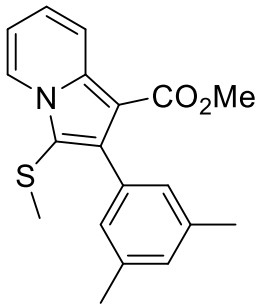
methyl 3-(methylthio)-2-(*m*-tolyl)indolizine-1-carboxylate (3ac)

White solid, mp: 109-111 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.59 (dt, *J* = 7.0, 1.2 Hz, 1H), 8.30 (dt, *J* = 9.1, 1.2 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.19 (dt, *J* = 7.2, 2.1 Hz, 4H), 6.90 (td, *J* = 6.8, 1.3 Hz, 1H), 3.71 (s, 3H), 2.42 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.18, 138.93, 137.85, 136.89, 134.95, 131.28, 128.30, 127.68, 127.39, 124.60, 124.08, 120.34, , 113.29, 50.86, 21.84, 18.80. ESI calcd for $C_{18}H_{17}NO_2S$ $[M+H]^+$ 311.0980; found: 311.1419.



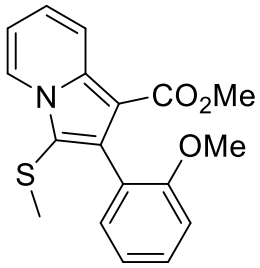
methyl 3-(methylthio)-2-(*p*-tolyl)indolizine-1-carboxylate (3ad)

White solid, mp: 129-130 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 6.9 Hz, 1H), 8.28 (d, *J* = 9.0 Hz, 1H), 7.27 (d, *J* = 12.8 Hz, 4H), 7.19 (dd, *J* = 9.1, 6.6 Hz, 1H), 6.90 (d, *J* = 7.0 Hz, 1H), 3.72 (s, 3H), 2.43 (s, 3H), 2.09 (s, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.05, 138.72, 137.73, 136.95, 131.83, 130.34, 128.23, 124.49, 124.44, 123.89, 120.24, 120.20, 113.11, 102.89, 50.76, 21.52, 18.60. ESI calcd for $C_{18}H_{17}NO_2S$ $[M+H]^+$ 311.0980; found:311.1700.



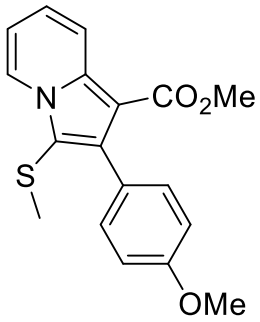
methyl 2-(3,5-dimethylphenyl)-3-(methylthio)indolizine-1-carboxylate (3ae)

White solid, mp: 121-123 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.60 – 8.56 (m, 1H), 8.28 (d, *J* = 9.0 Hz, 1H), 7.19 (s, 1H), 7.02 (s, 1H), 6.99 (s, 2H), 6.89 (d, *J* = 8.3 Hz, 1H), 3.71 (s, 3H), 2.38 (s, 6H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.03, 138.97, 137.68, 136.54, 134.71, 129.14, 128.25, 124.44, 123.84, 120.19, 113.08, 102.96, 50.69, 21.55, 18.70. ESI calcd for $C_{19}H_{19}NO_2S$ $[M+H]^+$ 325.1136; found: 325.1754.



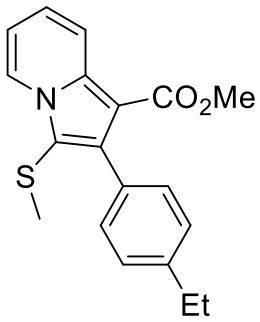
methyl 2-(2-methoxyphenyl)-3-(methylthio)indolizine-1-carboxylate (3af)

Yellow solid, mp: 135-136 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.56 (s, 1H), 8.28 (d, *J* = 8.9 Hz, 1H), 7.39 (d, *J* = 1.7 Hz, 1H), 7.22 (t, *J* = 3.4 Hz, 1H), 7.19 – 7.14 (m, 1H), 7.04 (s, 1H), 7.00 (d, *J* = 9.4 Hz, 1H), 6.87 (s, 1H), 3.75 (s, 3H), 3.67 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.01, 157.52, 137.69, 134.82, 131.71, 129.03, 124.44, 124.40, 123.55, 120.18, 120.04, 115.70, 112.89, 110.65, 103.64, 55.65, 50.65, 18.20. ESI calcd for $C_{18}H_{17}NO_3S$ $[M+H]^+$ 327.0929; found: 327.1910.



methyl 2-(4-methoxyphenyl)-3-(methylthio)indolizine-1-carboxylate (3ag)

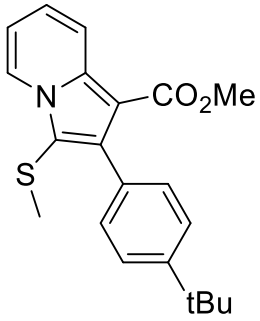
Yellow solid, mp: 116-118 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 (dd, *J* = 7.1, 1.4 Hz, 1H), 8.22 (dd, *J* = 8.8, 1.4 Hz, 1H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.15 – 7.09 (m, 1H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.83 (td, *J* = 6.9, 1.4 Hz, 1H), 3.80 (s, 3H), 3.66 (s, 3H), 2.02 (s, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.56, 156.42, 135.77, 129.13, 124.47, 121.93, 121.36, 117.66, 113.05, 110.57, 110.41, 100.29, 52.71, 48.18, 15.99. ESI calcd for $C_{18}H_{17}NO_3S$ $[M+H]^+$ 327.0929; found: 327.1640.



methyl 2-(4-ethylphenyl)-3-(methylthio)indolizine-1-carboxylate (3ah)

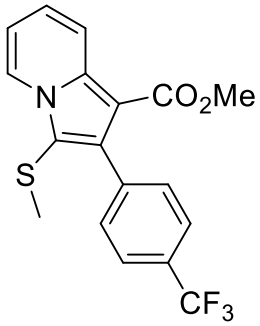
Yellow solid, mp: 84-87 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (d, *J* = 6.8 Hz, 1H), 8.28 (dd, *J* = 9.1, 1.2 Hz, 1H), 7.33 – 7.26 (m, 4H), 7.21 – 7.17 (m, 1H), 6.89 (dd, *J* = 7.5, 6.3 Hz, 1H), 3.72 (s, 3H), 2.74 (q, *J* = 7.7 Hz, 2H), 2.09 (s, 3H), 1.31 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*)

δ 165.07, 143.11, 138.74, 137.74, 131.97, 130.40, 126.92, 124.47, 123.89, 120.23, 113.10, 102.86, 50.73, 28.75, 18.59, 15.31. ESI calcd for $C_{19}H_{19}NO_2S$ $[M+H]^+$ 325.1136; found: 325.1673.



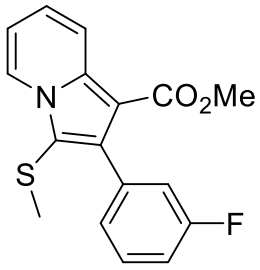
methyl 2-(4-(tert-butyl)phenyl)-3-(methylthio)indolizine-1-carboxylate (3ai)

White solid, mp: 92-95 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (d, *J* = 7.7 Hz, 1H), 8.28 (d, *J* = 9.3 Hz, 1H), 7.46 (s, 2H), 7.36 (s, 2H), 7.19 (d, *J* = 1.9 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 3.72 (s, 3H), 2.10 (s, 3H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.10, 149.96, 138.64, 137.77, 131.59, 130.18, 124.31, 123.88, 120.25, 115.59, 113.09, 102.82, 50.70, 34.69, 18.59. ESI calcd for $C_{21}H_{23}NO_2S$ $[M+H]^+$ 353.1449; found: 353.1527.



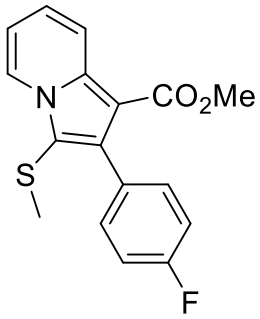
methyl 3-(methylthio)-2-(4-(trifluoromethyl)phenyl)indolizine-1-carboxylate (3aj)

Yellow solid, mp: 114-117 ºC. ^{1}H NMR (300 MHz, Chloroform-d) δ 8.60 (d, J = 7.0 Hz, 1H), 8.31 (d, J = 9.1 Hz, 1H), 7.69 (d, J = 7.9 Hz, 2H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.25 (q, *J* = 2.8, 2.3 Hz, 1H), 6.95 (s, 1H), 3.72 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 194.50, 138.38, 137.43, 135.81, 130.39, 128.18, 127.96, 125.46, 124.19, 121.00, 114.15, 113.82, 30.60, 18.68. ESI calcd for $C_{18}H_{14}F_3NO_2S$ $[M+H]^+$ 365.0697; found: 365.1475.



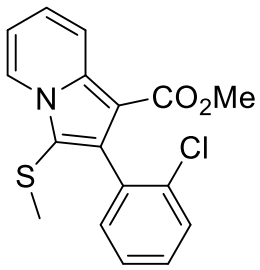
methyl 2-(3-fluorophenyl)-3-(methylthio)indolizine-1-carboxylate (3ak)

Yellow solid, mp: 94-96 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.59 (d, *J* = 7.0 Hz, 1H), 8.31 (d, *J* = 9.1 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.26 – 7.18 (m, 2H), 7.16 – 7.09 (m, 2H), 6.96 – 6.90 (m, 1H), 3.72 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.82, 162.14 (d, J=245.4Hz), 137.75, 137.21, 128.79, 128.71, 126.35, 124.36 (d, J=28.28Hz), 120.27, 117.66, 117.45, 115.72, 114.17 (d, J=21.21Hz), 113.39, 102.82, 50.76, 18.59. ESI calcd for $C_{17}H_{14}FNO_2S$ $[M+H]^+$ 315.0729; found: 315.1426.



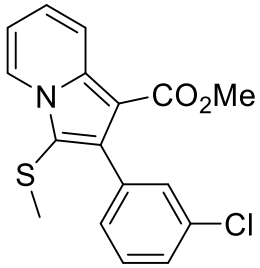
methyl 2-(4-fluorophenyl)-3-(methylthio)indolizine-1-carboxylate (3al)

Yellow solid, mp: 117-119 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.60 (s, 1H), 8.29 (d, *J* = 9.0 Hz, 1H), 7.37 (d, *J* = 10.1 Hz, 2H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 9.3 Hz, 2H), 6.92 (d, *J* = 7.7 Hz, 1H), 3.72 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.94, 163.59, 137.77, 137.54, 132.19, 132.11, 130.73, 124.50, 124.15, 120.25, 114.54, 114.32, 113.31, 102.84, 50.74, 18.52. ESI calcd for $C_{17}H_{14}FNO_2S$ $[M+H]^+$ 315.0729; found: 315.1262.



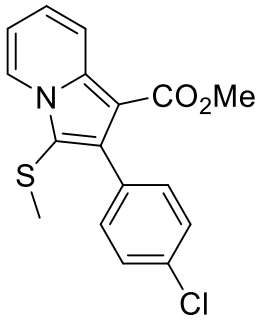
methyl 2-(2-chlorophenyl)-3-(methylthio)indolizine-1-carboxylate (3am)

Yellow solid, mp: 107-110 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 6.8 Hz, 1H), 8.31 (d, *J* = 8.9 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.37 – 7.32 (m, 2H), 7.30 – 7.27 (m, 1H), 7.24 – 7.19 (m, 1H), 6.92 (td, *J* = 6.9, 1.3 Hz, 1H), 3.68 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.68, 137.56, 134.80, 134.31, 131.78, 128.98, 128.90, 126.07, 124.47, 123.98, 120.28, 113.25, 103.49, 50.83, 18.21. ESI calcd for $C_{17}H_{14}ClNO_2S$ $[M+H]^+$ 331.0434; found: 331.1052.



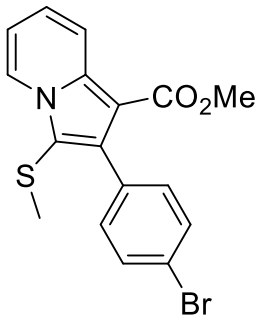
methyl 2-(3-chlorophenyl)-3-(methylthio)indolizine-1-carboxylate (3an)

Yellow solid, mp: 104-106 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (d, *J* = 6.9 Hz, 1H), 8.31 (d, *J* = 9.2 Hz, 1H), 7.39 (d, *J* = 1.9 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.30 – 7.26 (m, 1H), 7.22 (dd, *J* = 9.0, 6.7 Hz, 1H), 6.92 (t, *J* = 6.9 Hz, 1H), 3.71 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.79, 137.79, 137.00, 136.79, 133.17, 130.59, 128.85, 128.58, 127.45, 124.50, 124.25, 120.29, 113.42, 102.81, 50.78, 18.60. ESI calcd for $C_{17}H_{14}ClNO_2S$ $[M+H]^+$ 331.0434; found: 331.1157.



methyl 2-(4-chlorophenyl)-3-(methylthio)indolizine-1-carboxylate (3ao)

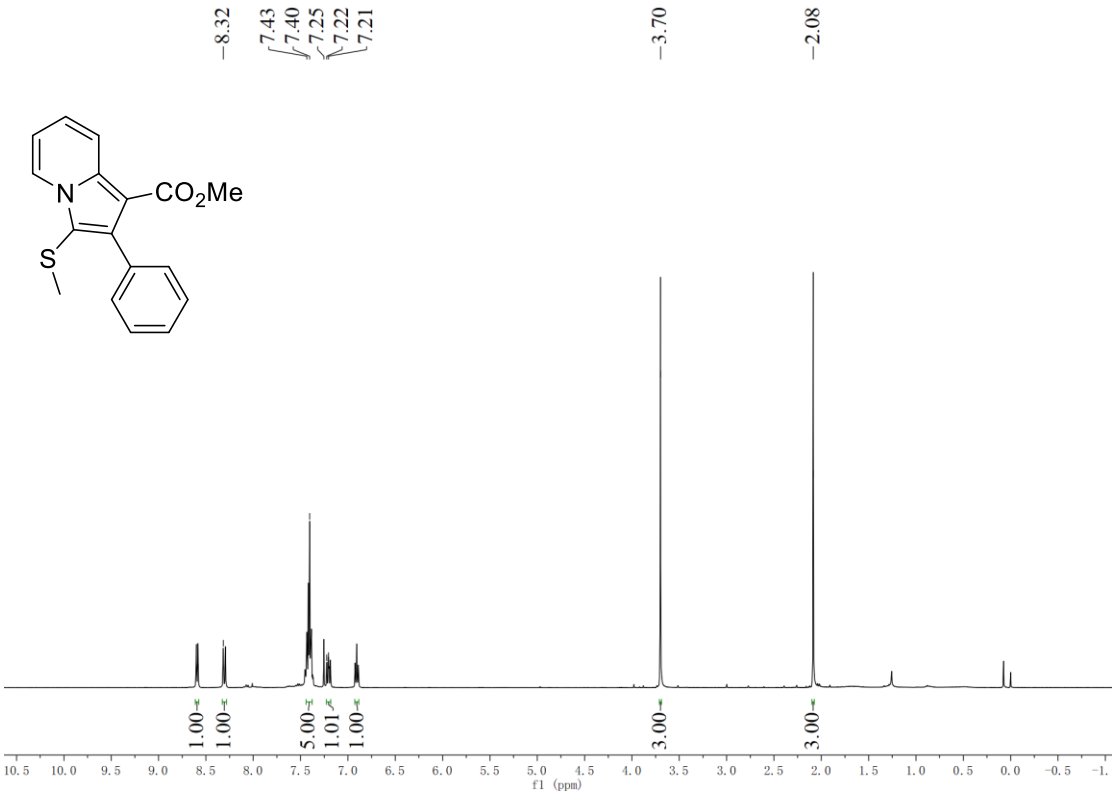
Yellow solid, mp: 117-118 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (d, *J* = 6.9 Hz, 1H), 8.30 (d, *J* = 9.1 Hz, 1H), 7.42 – 7.32 (m, 4H), 7.22 (dd, *J* = 8.8, 6.7 Hz, 1H), 6.92 (t, *J* = 6.9 Hz, 1H), 3.72 (s, 3H), 2.08 (s, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.87, 137.80, 137.30, 133.40, 133.37, 124.46, 120.30, 115.69, 113.33, 102.76, 50.82, 50.72, 18.55. ESI calcd for $C_{17}H_{14}ClNO_2S$ $[M+H]^+$ 331.0434; found: 331.1142.



methyl 2-(4-bromophenyl)-3-(methylthio)indolizine-1-carboxylate (3ap)

Yellow solid, mp: 127-128 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 6.9 Hz, 1H), 8.29 (d, *J* = 9.0 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.22 (dd, *J* = 9.0, 6.7 Hz, 1H), 6.92 (t, *J* = 6.8 Hz, 1H), 3.72 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.86, 137.81, 137.29, 133.86, 132.23, 130.62, 124.50, 124.23, 121.69, 120.27, 115.64, 113.38, 102.72, 50.77, 18.55. ESI calcd for $C_{17}H_{14}BrNO_2S$ $[M+H]^+$ 374.9929; found: 376.0459.

3aa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S
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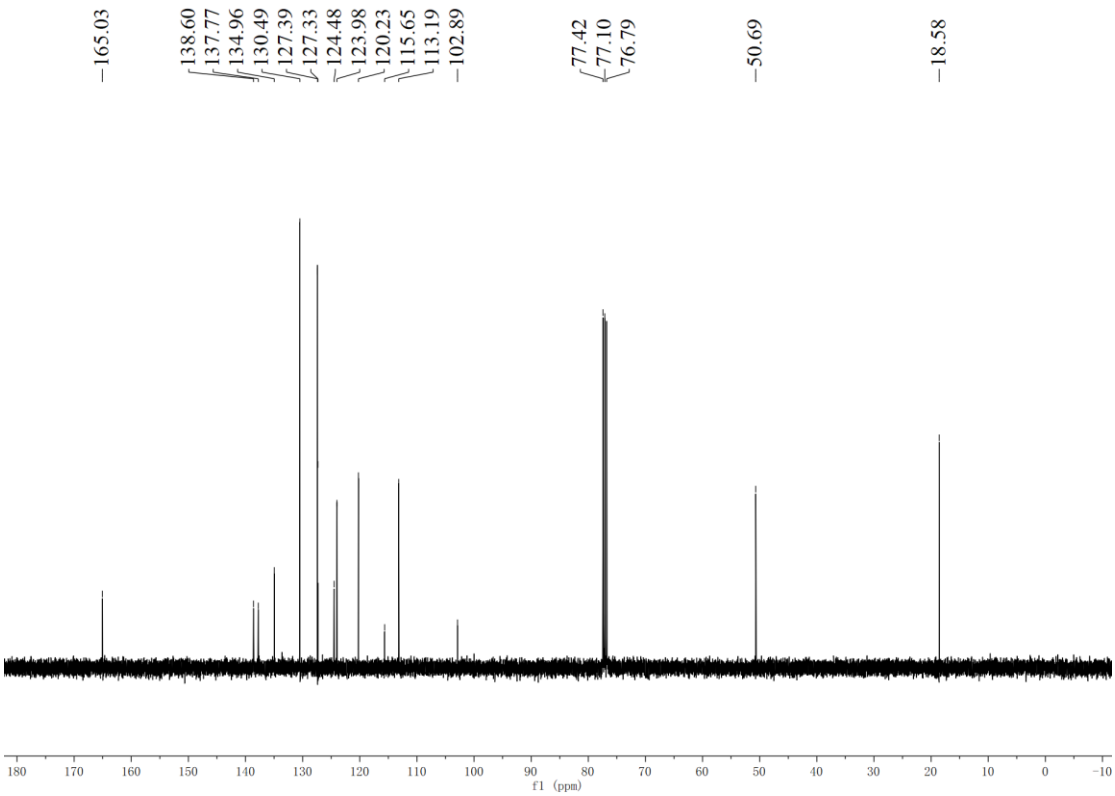
1.00
3.00
3.00
f1 (ppm)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113.19
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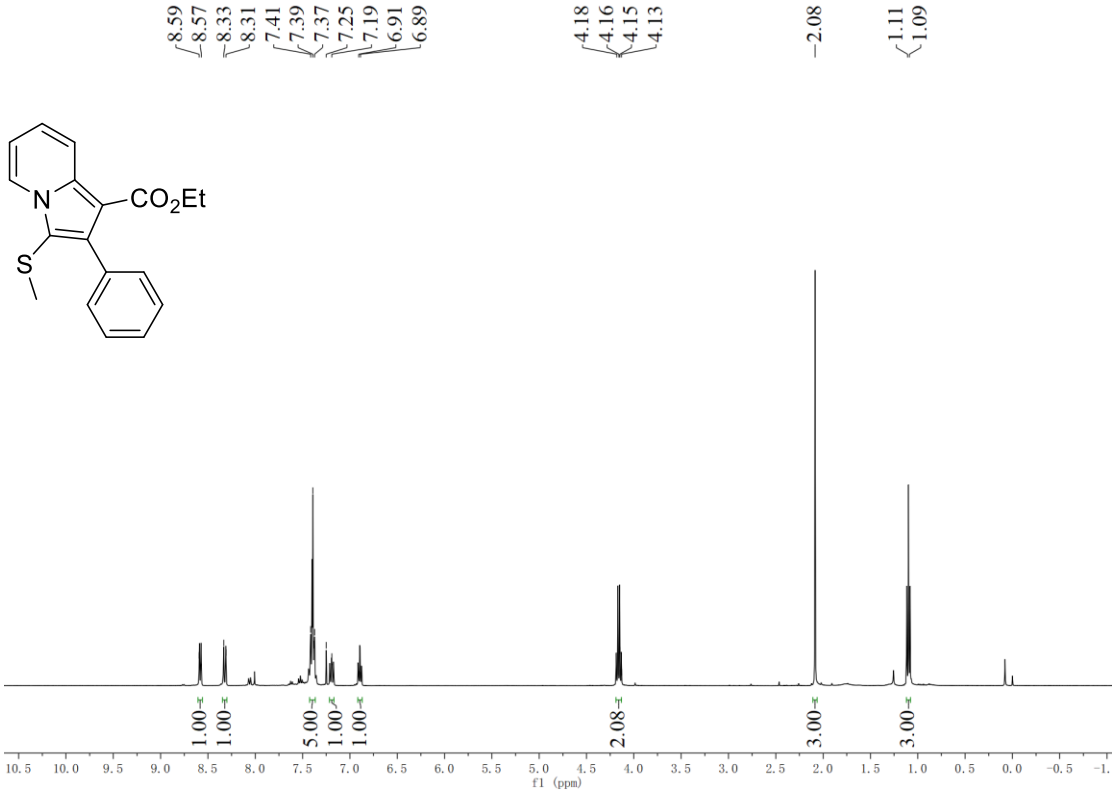
18.58
f1 (ppm)

3ba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4.16
4.15
4.13
2.08
1.11
1.09
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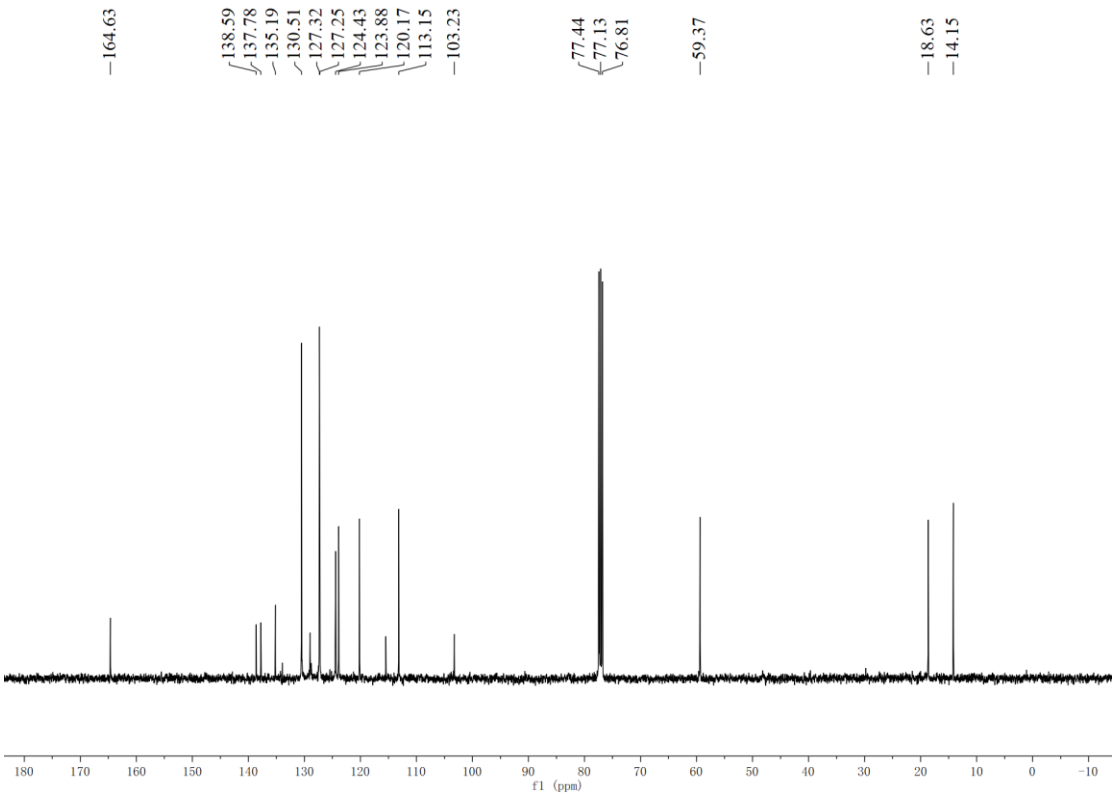
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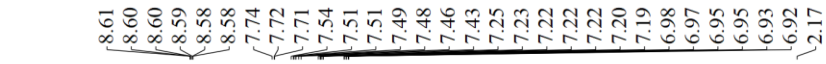
59.37
18.63
14.15
f1 (ppm)

3ca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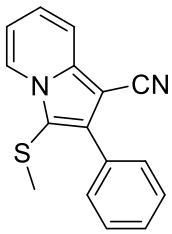
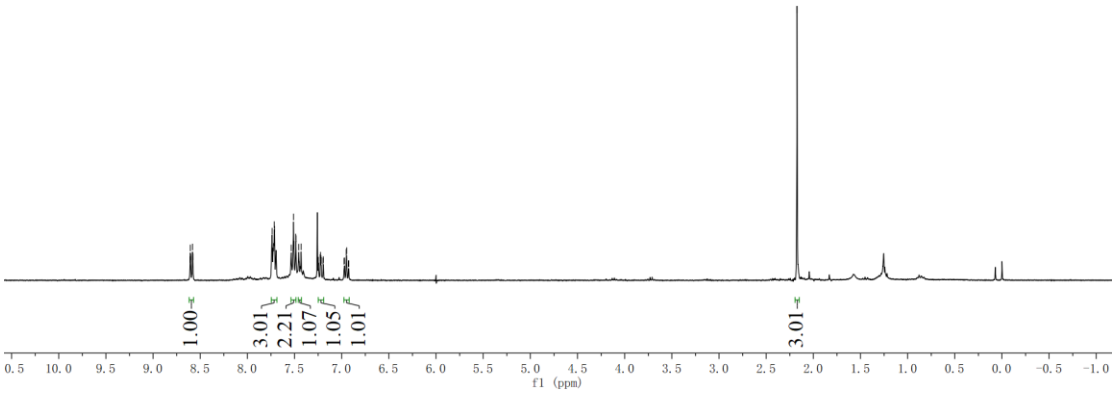
6.93
6.92
2.17


N
CN
S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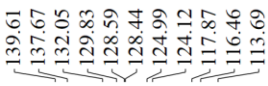
f1 (ppm)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113.69


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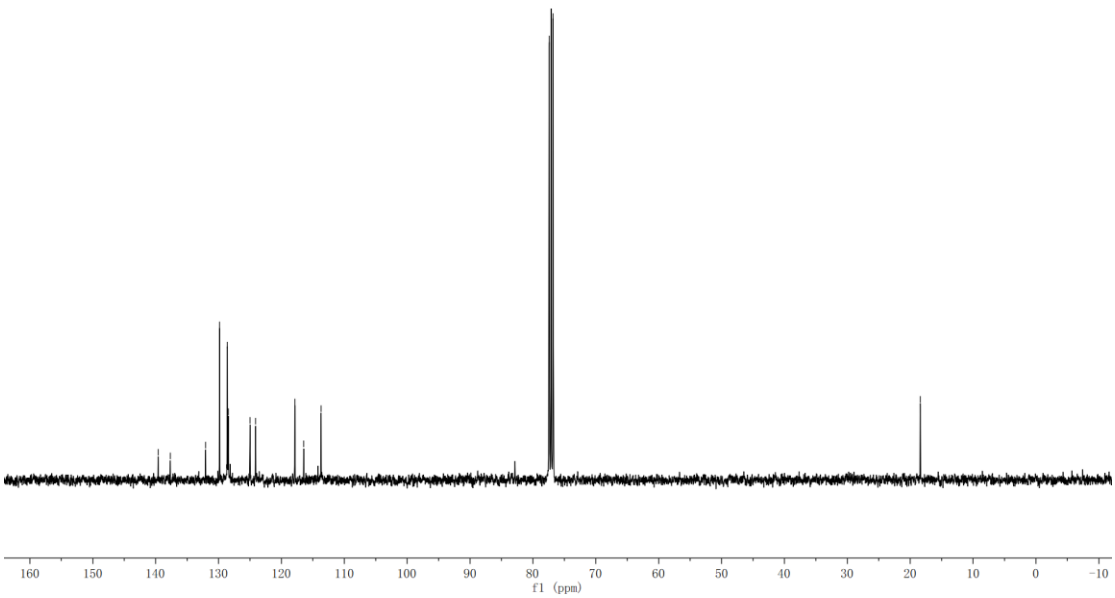
77.10
76.78


18.39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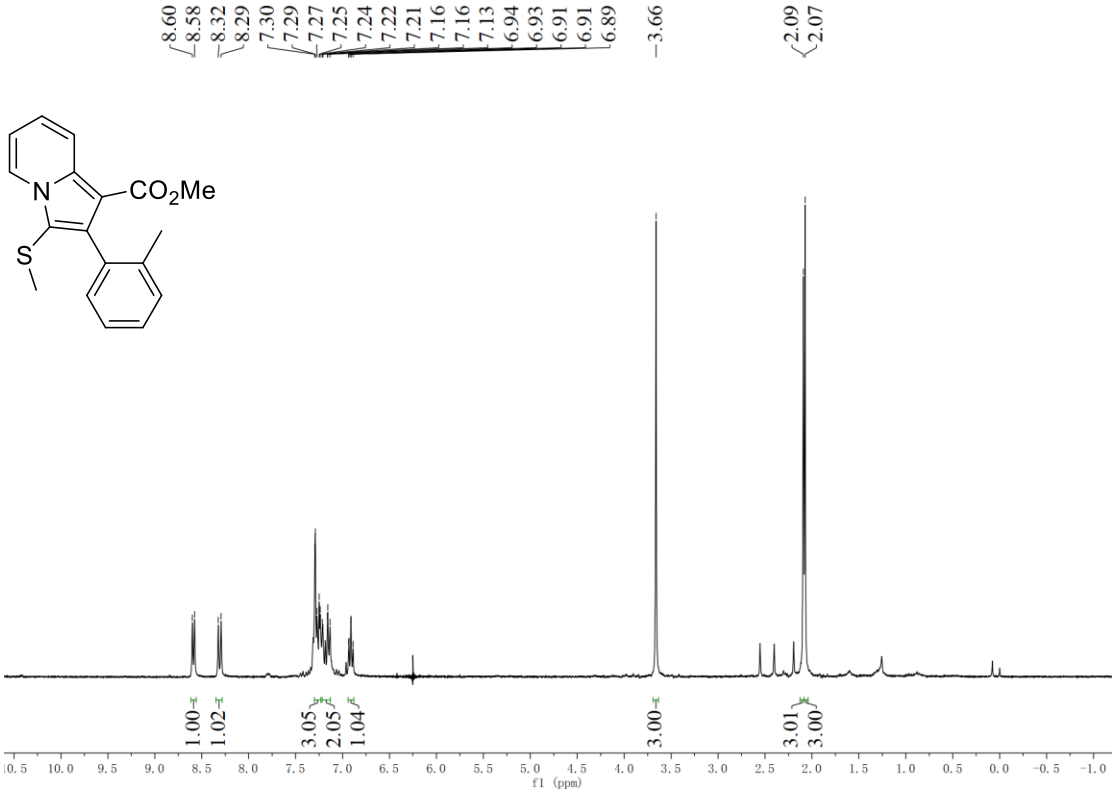
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7.16
7.13
6.94
6.93
6.91
6.91
6.89
3.66
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3.05
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1.04
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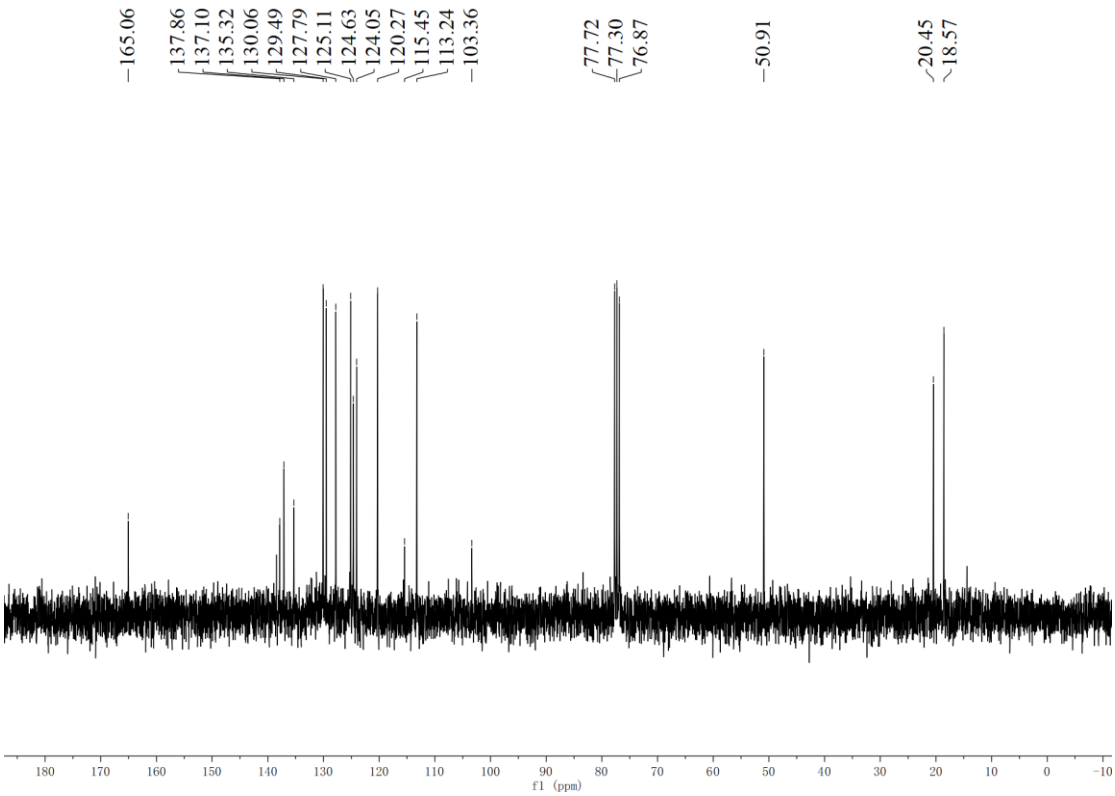
f1 (ppm)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50.91
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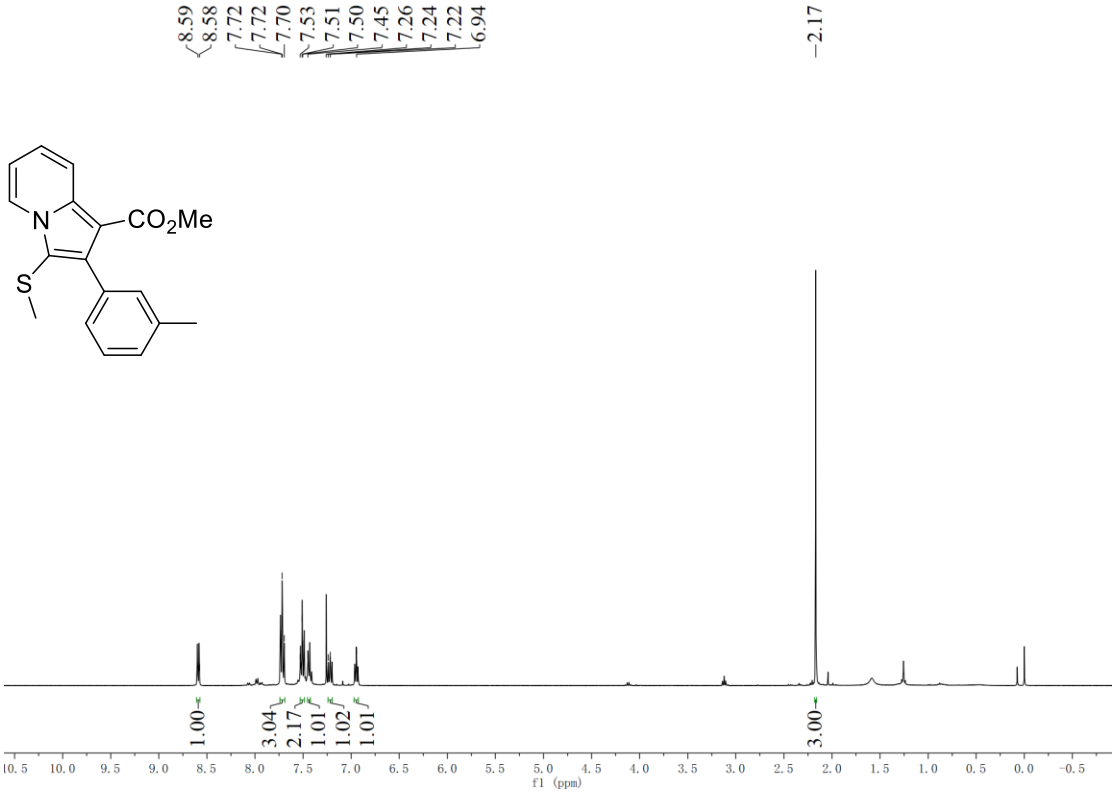
f1 (ppm)

3ac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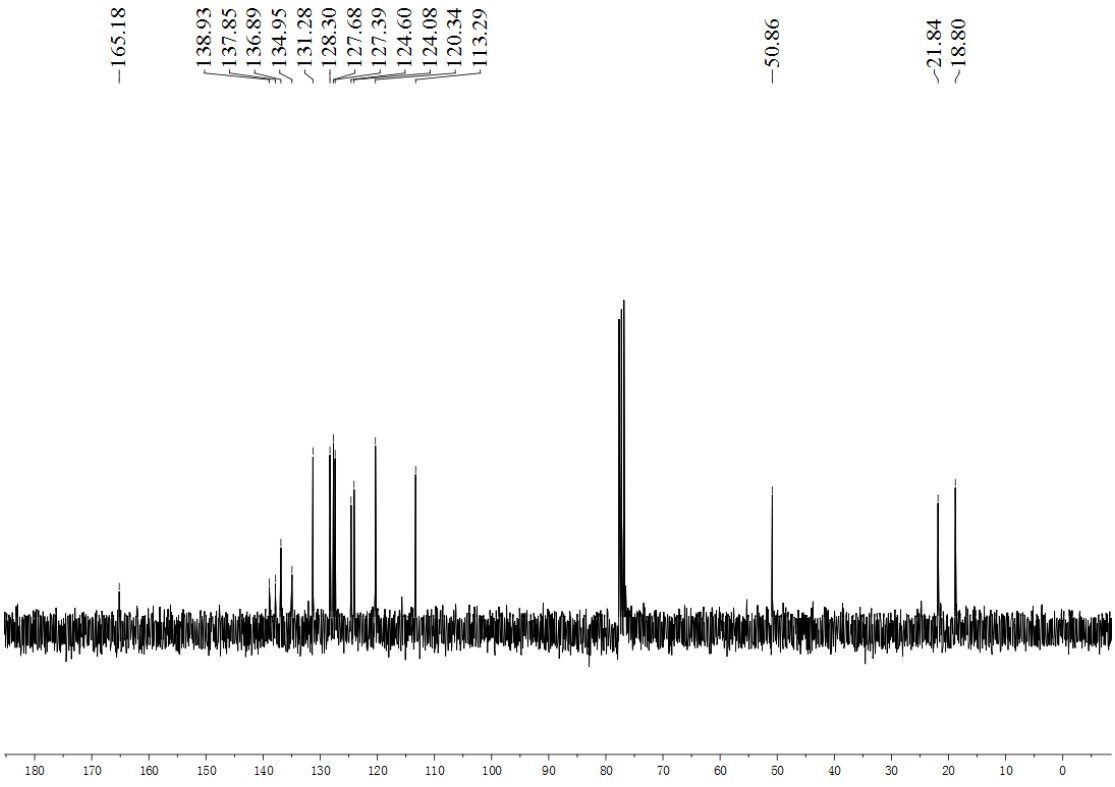
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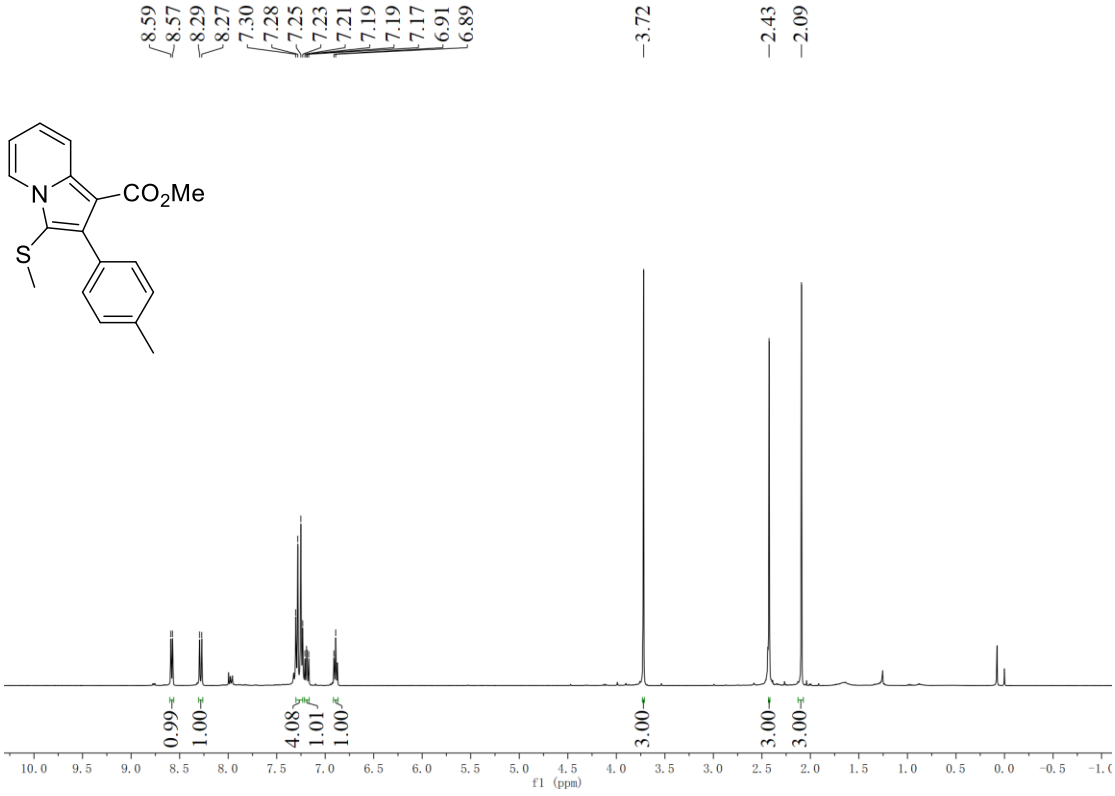
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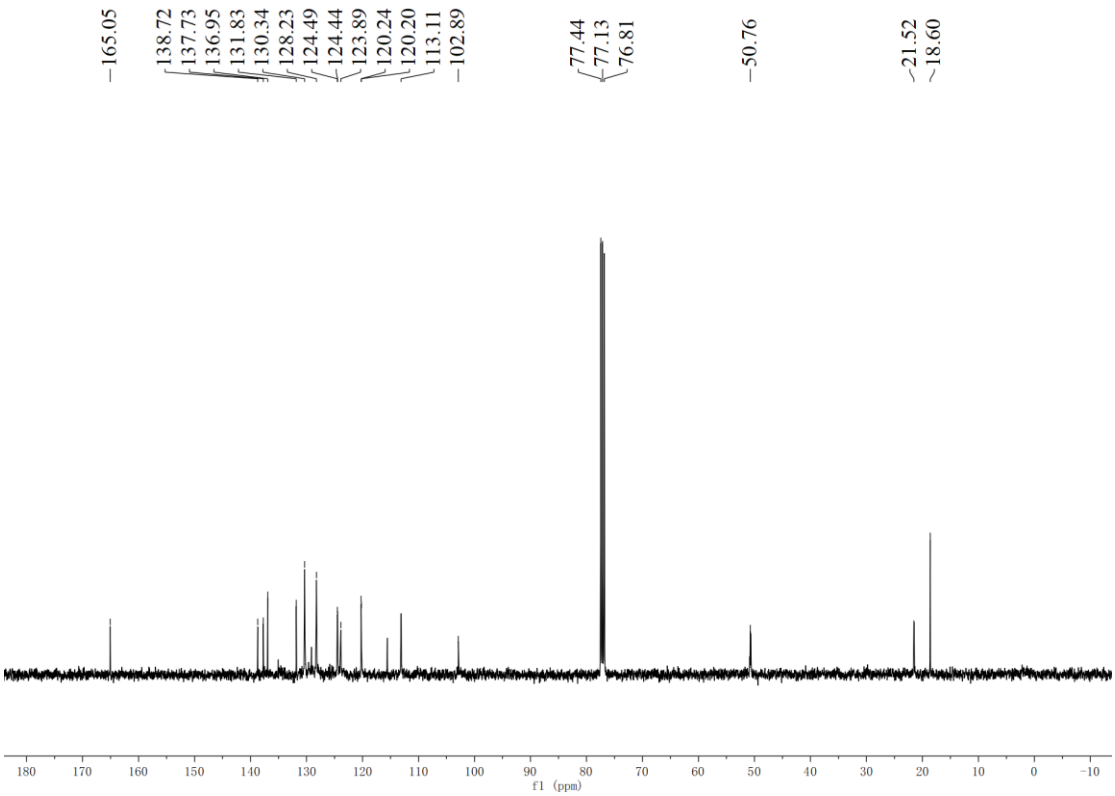
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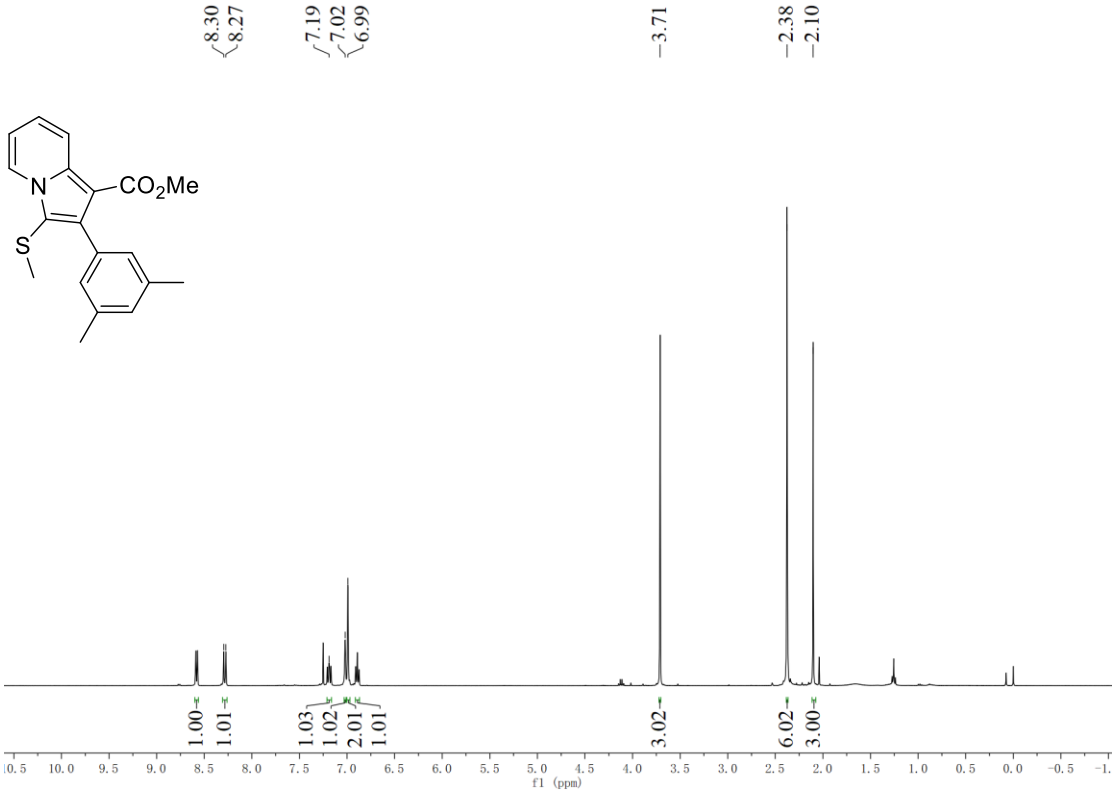
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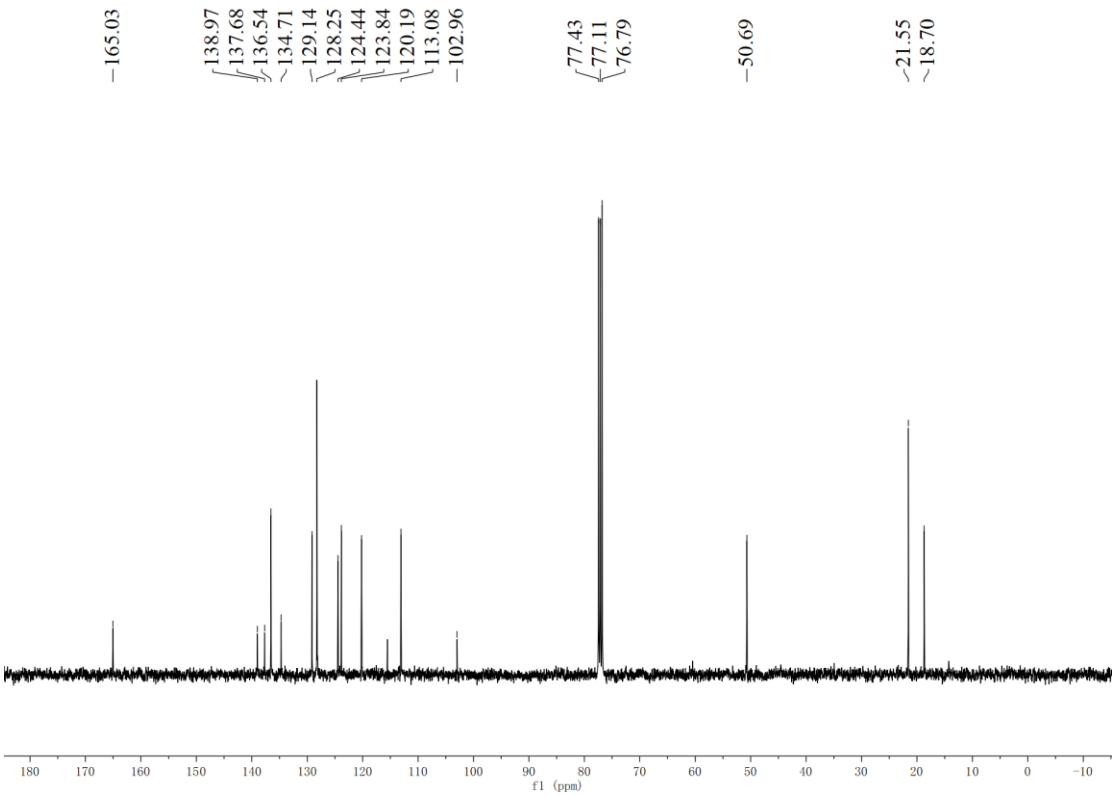
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f1 (ppm)

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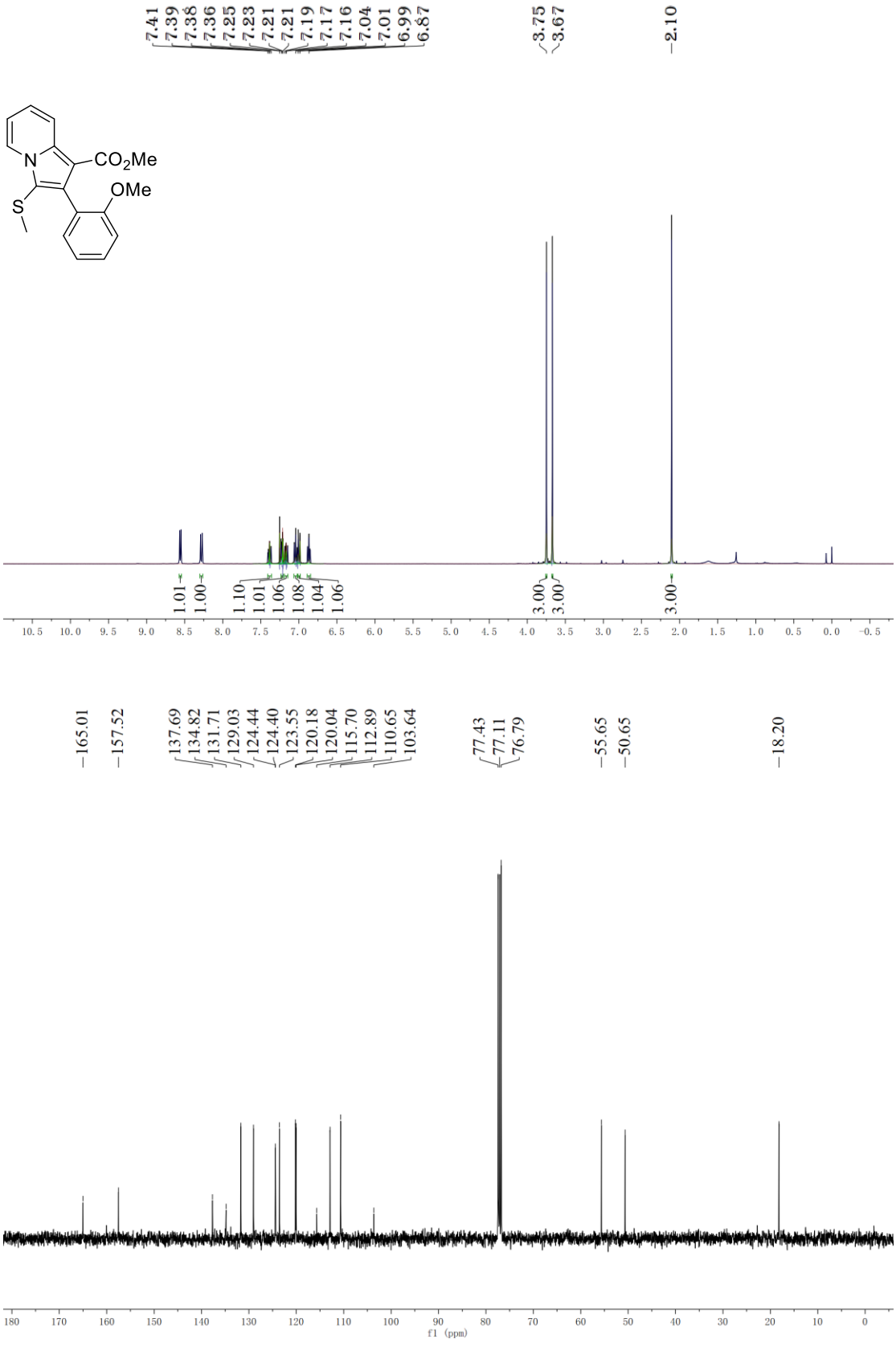
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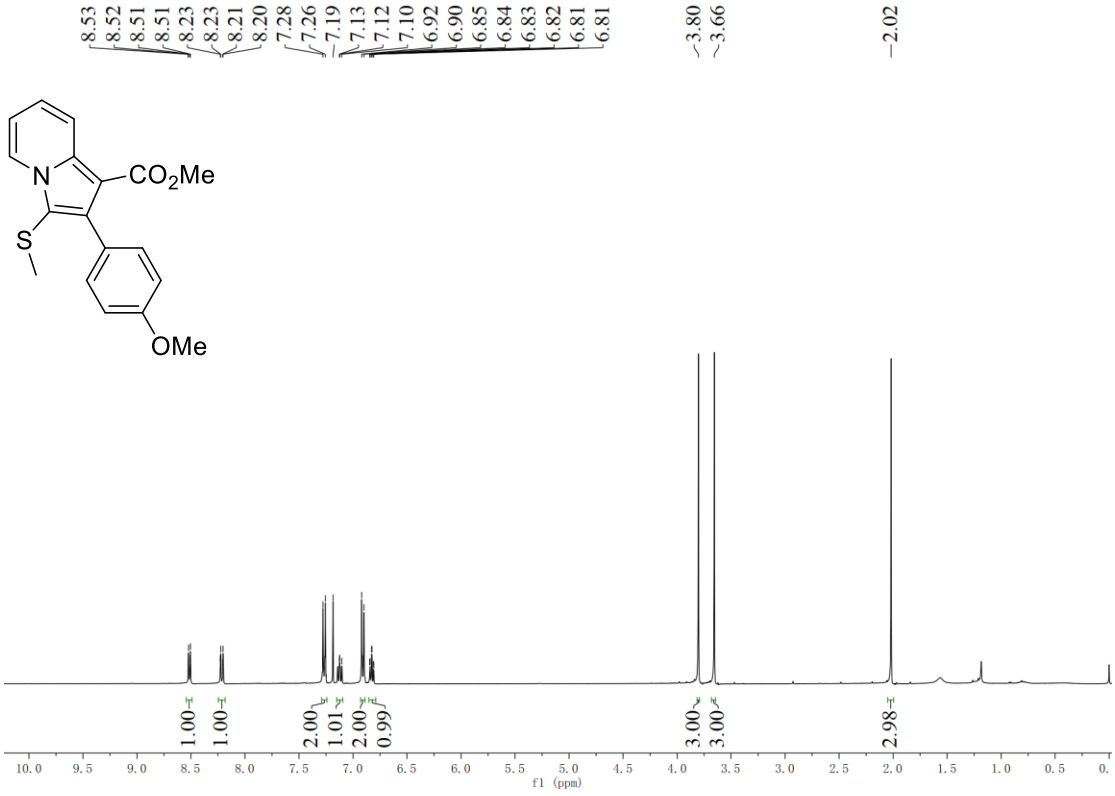
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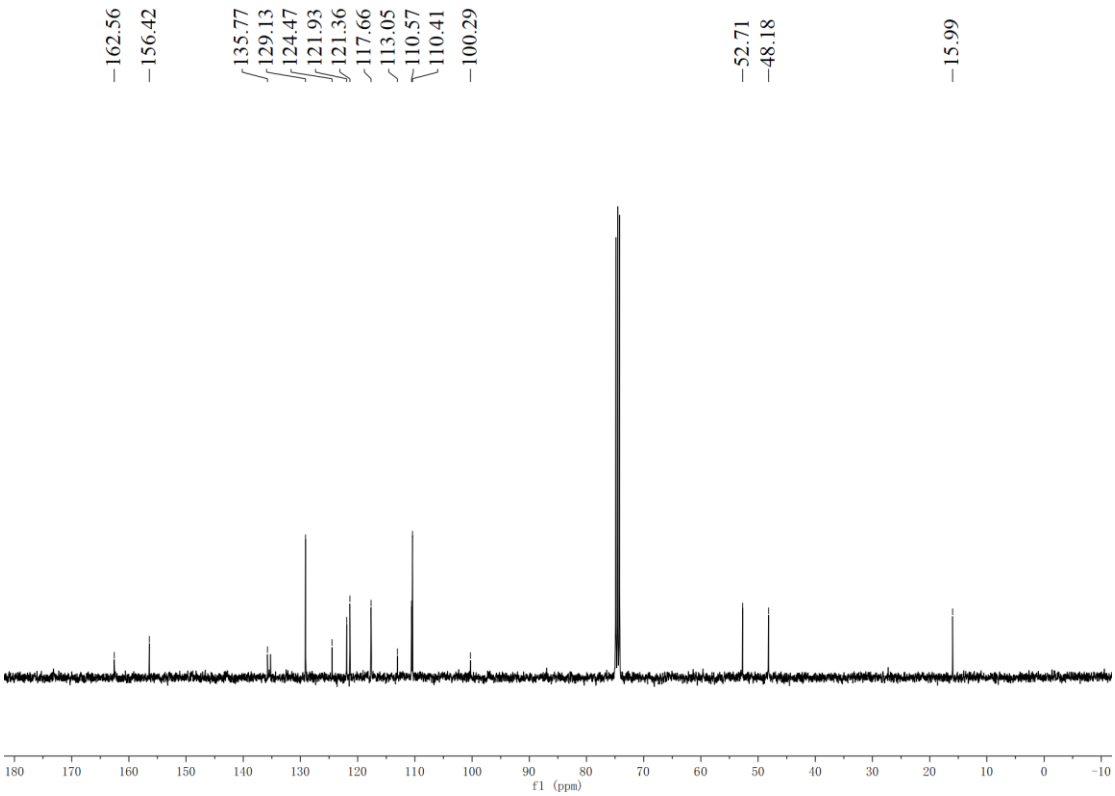
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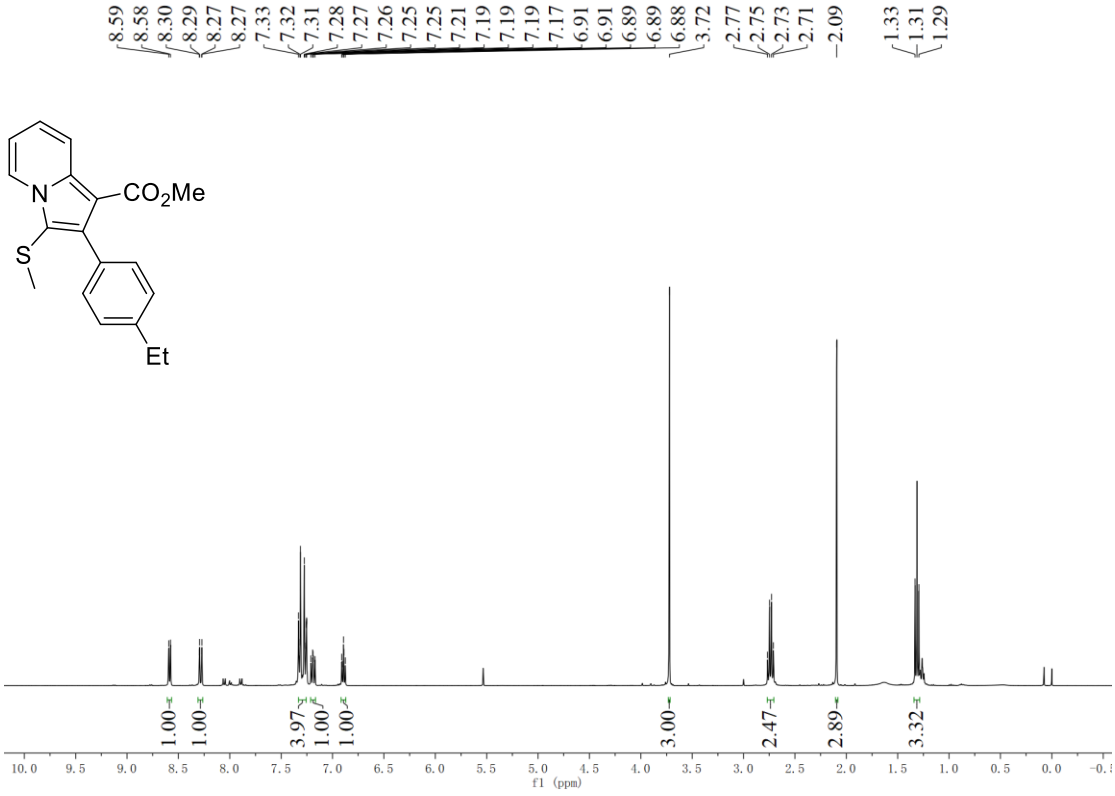
3ah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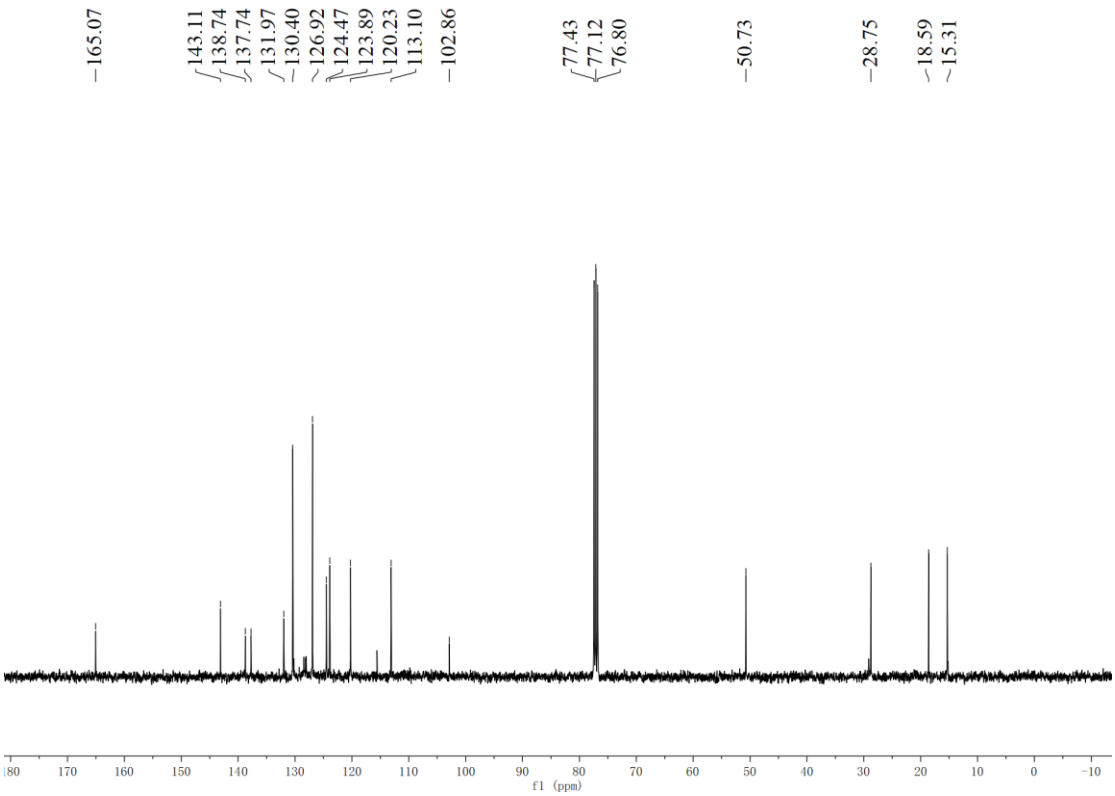
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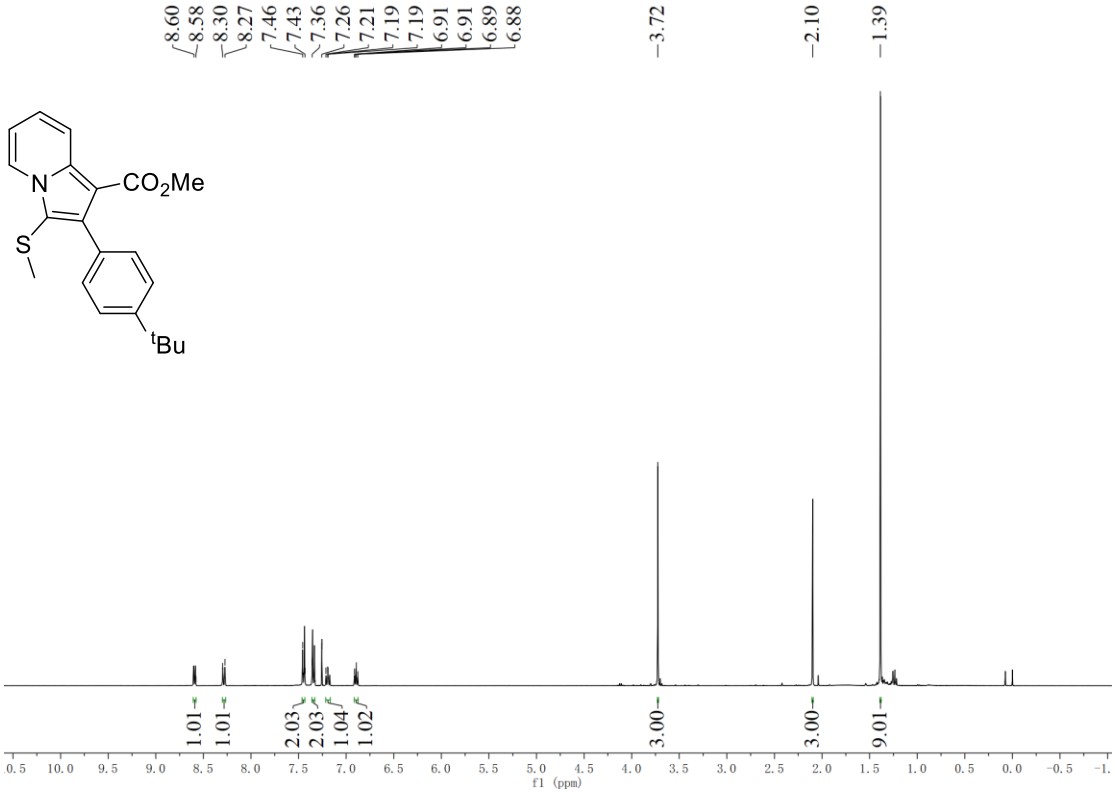
3ai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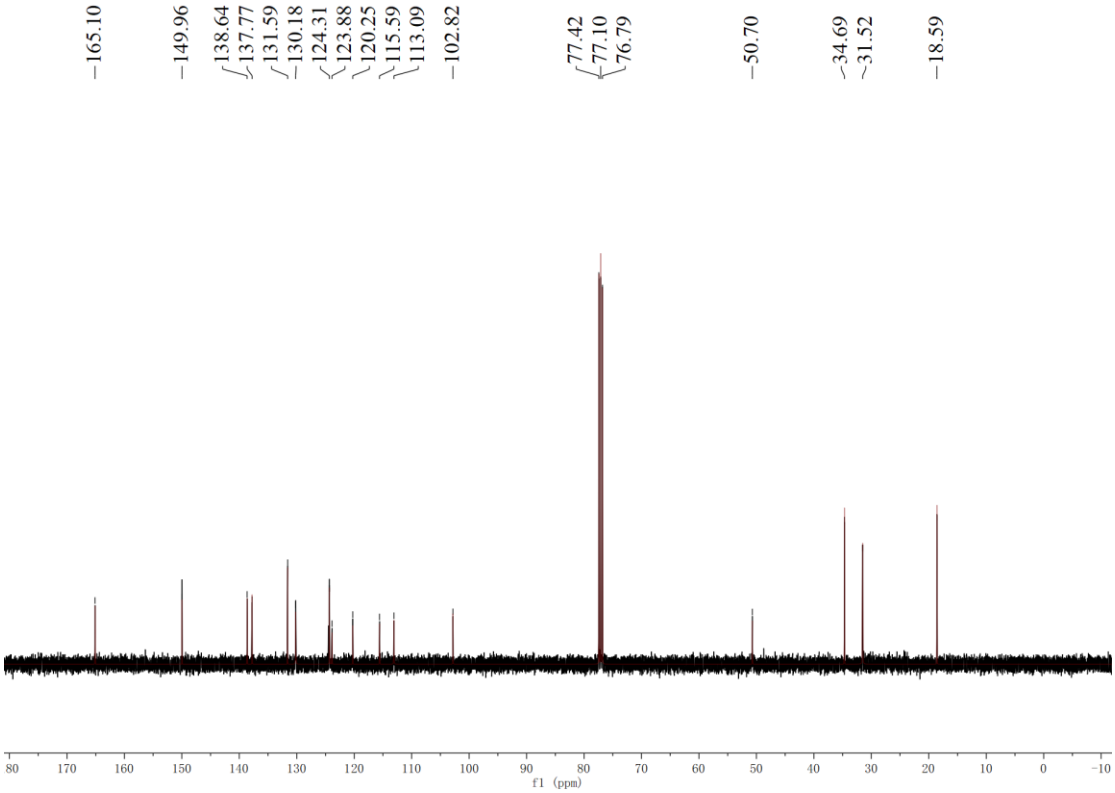
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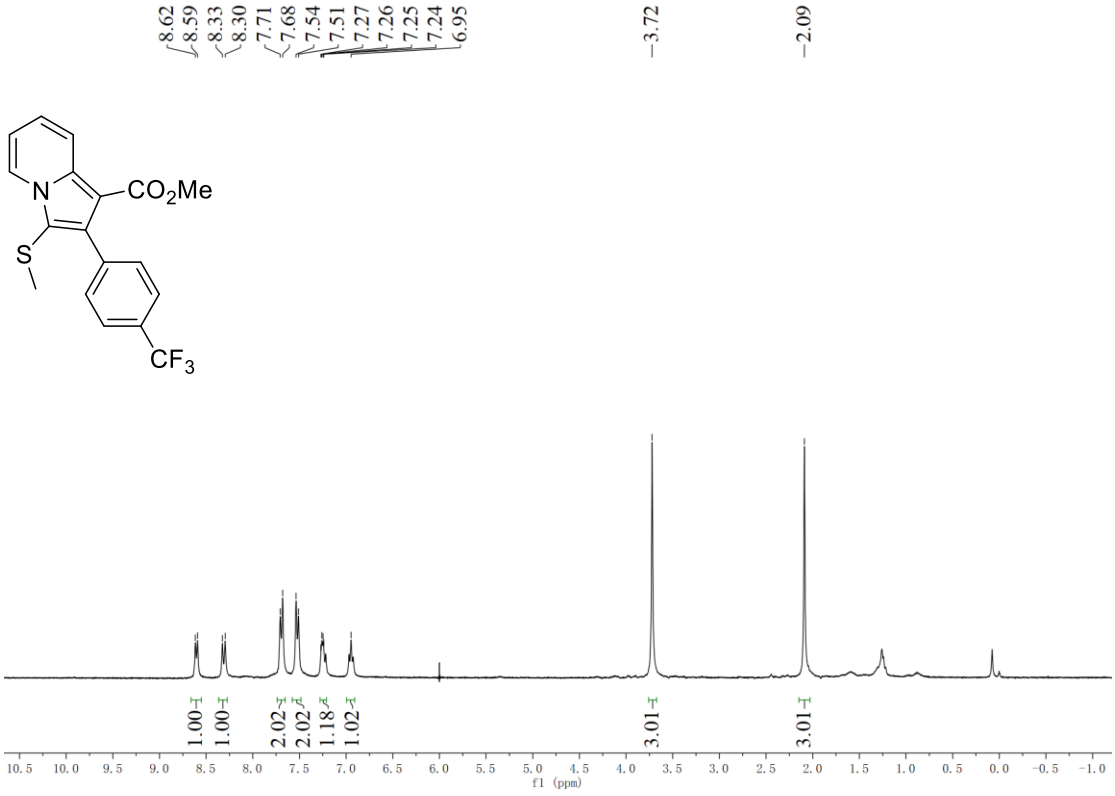
f1 (ppm)

3aj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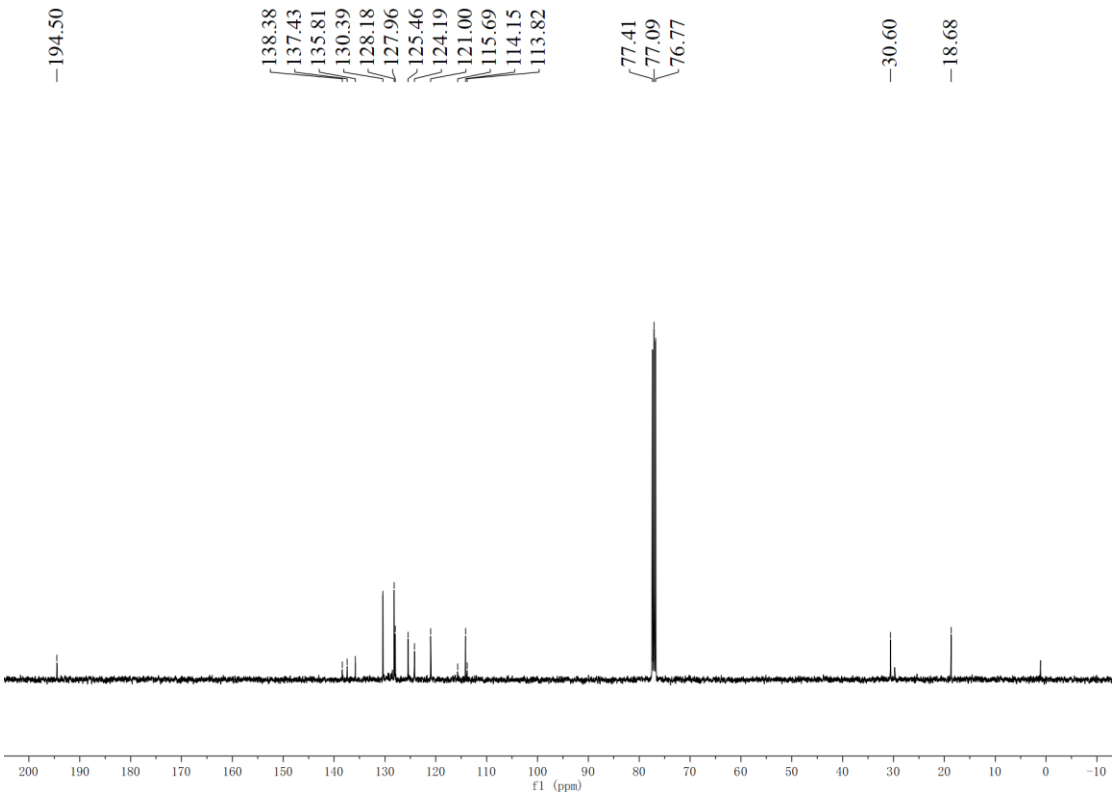
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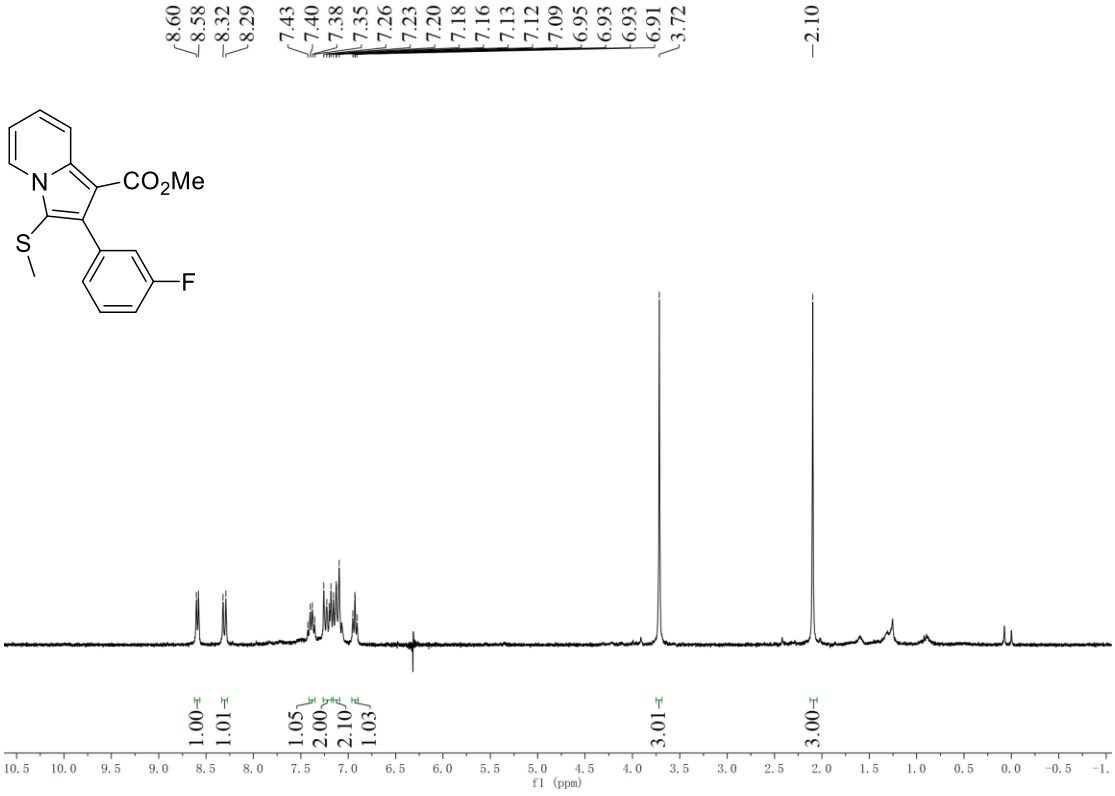
77.41
77.09
76.77
30.60
18.68
f1 (ppm)

3ak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8.32
8.29
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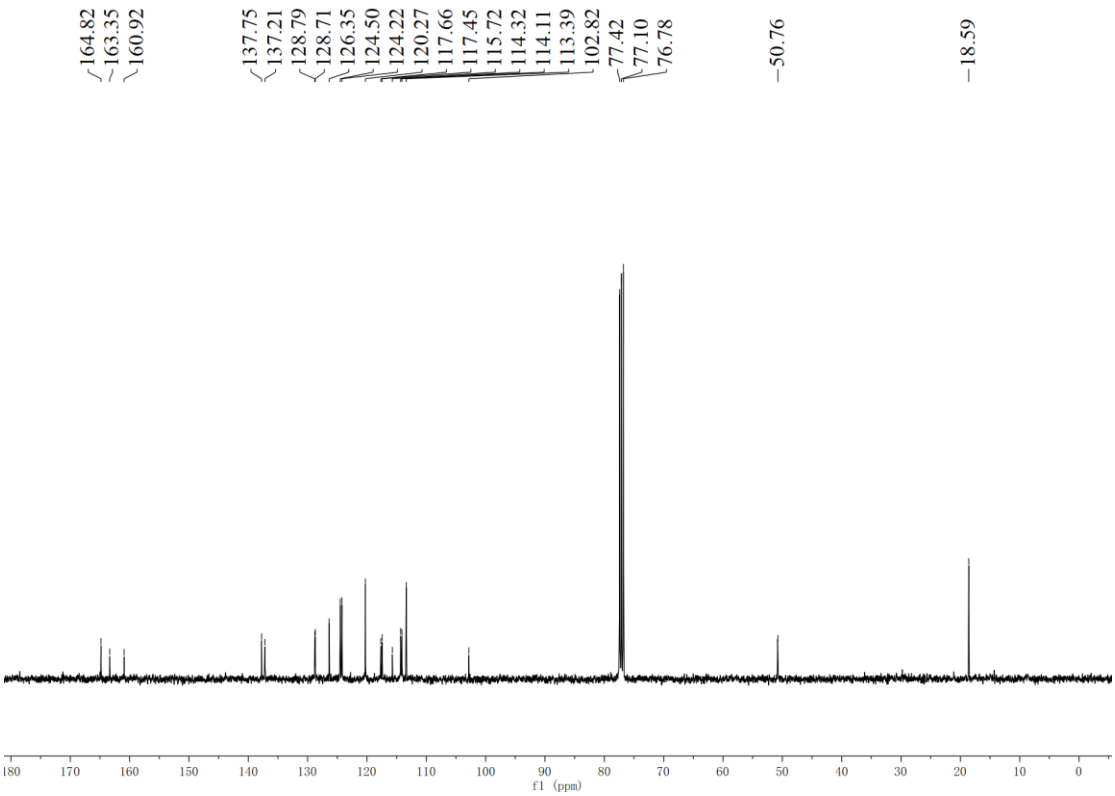
7.40
7.38
7.35
7.26
7.23
7.20
7.18
7.16
7.13
7.12
7.09
6.95
6.93
6.93
6.91
3.72
2.10
N
CO2Me
S
F
1.00
1.01
1.05
2.00
2.10
1.03
3.01
3.00
f1 (ppm)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160.92
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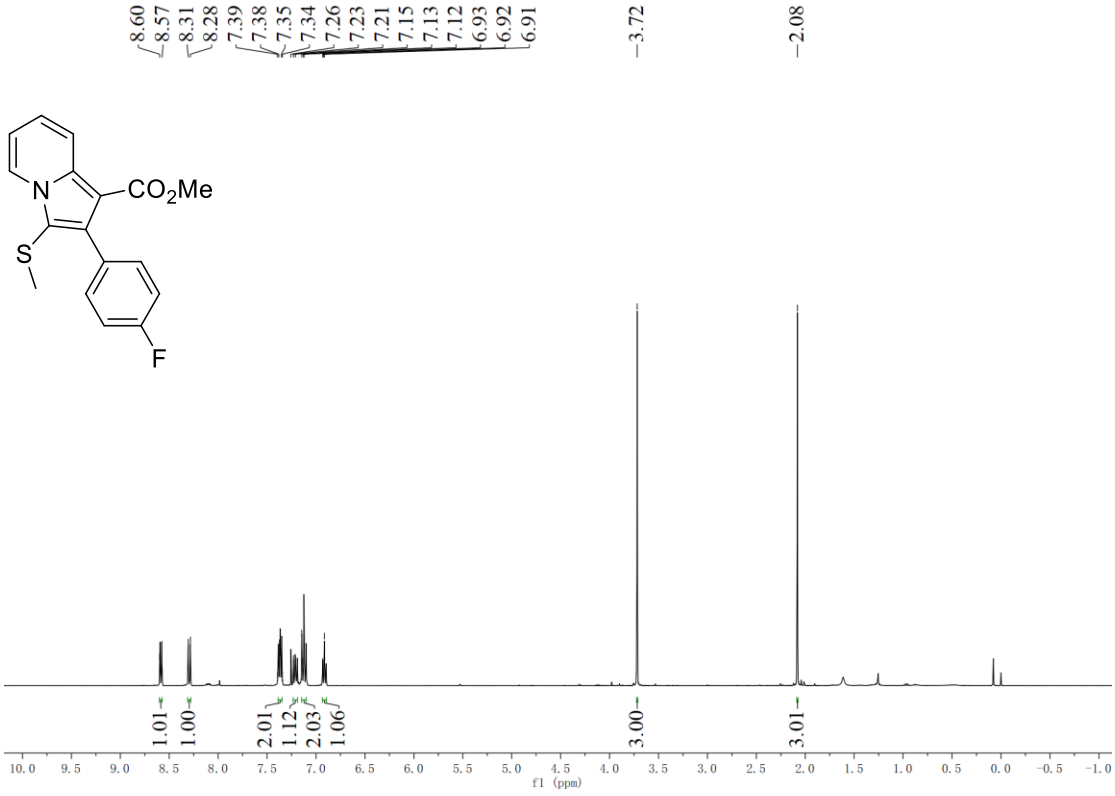
137.21
128.79
128.71
126.35
124.50
124.22
120.27
117.66
117.45
115.72
114.32
114.11
113.39
102.82
77.42
77.10
76.78
50.76
18.59
f1 (ppm)

3al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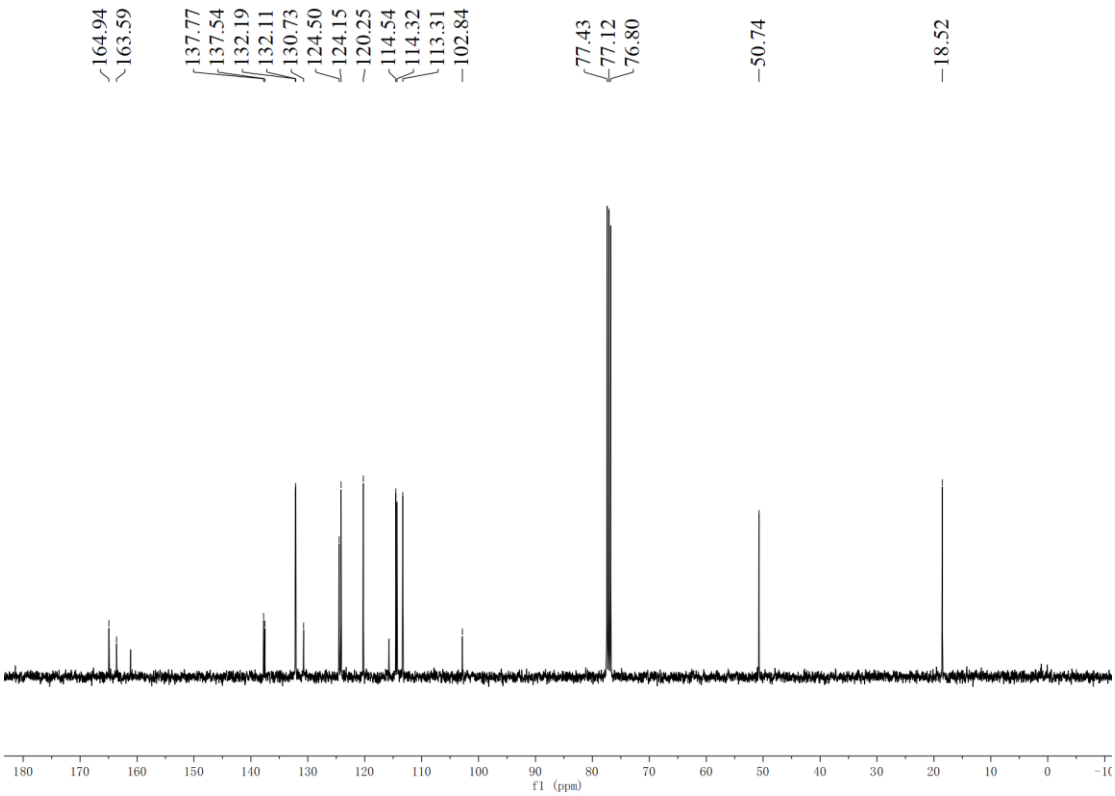
8.57
8.31
8.28
7.39
7.38
7.35
7.34
7.26
7.23
7.21
7.15
7.13
7.12
6.93
6.92
6.91
3.72
2.08
CO2Me
N
S
F
1.01
1.00
2.01
1.12
2.03
1.06
3.00
3.01
f1 (ppm)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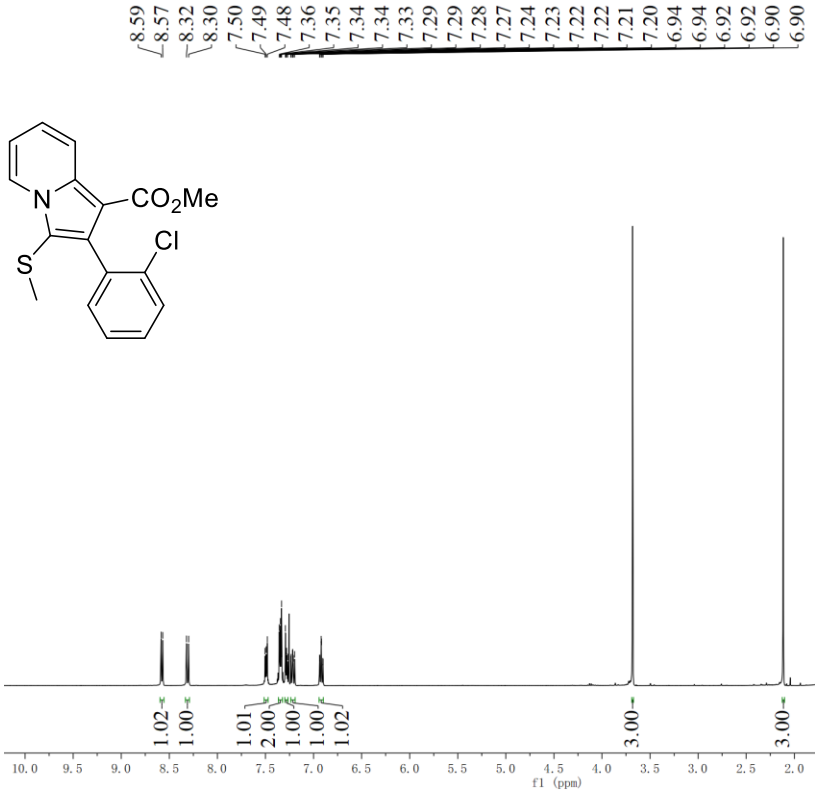
163.59
137.77
137.54
132.19
132.11
130.73
124.50
124.15
120.25
114.54
114.32
113.31
102.84
77.43
77.12
76.80
50.74
18.52
f1 (ppm)

3am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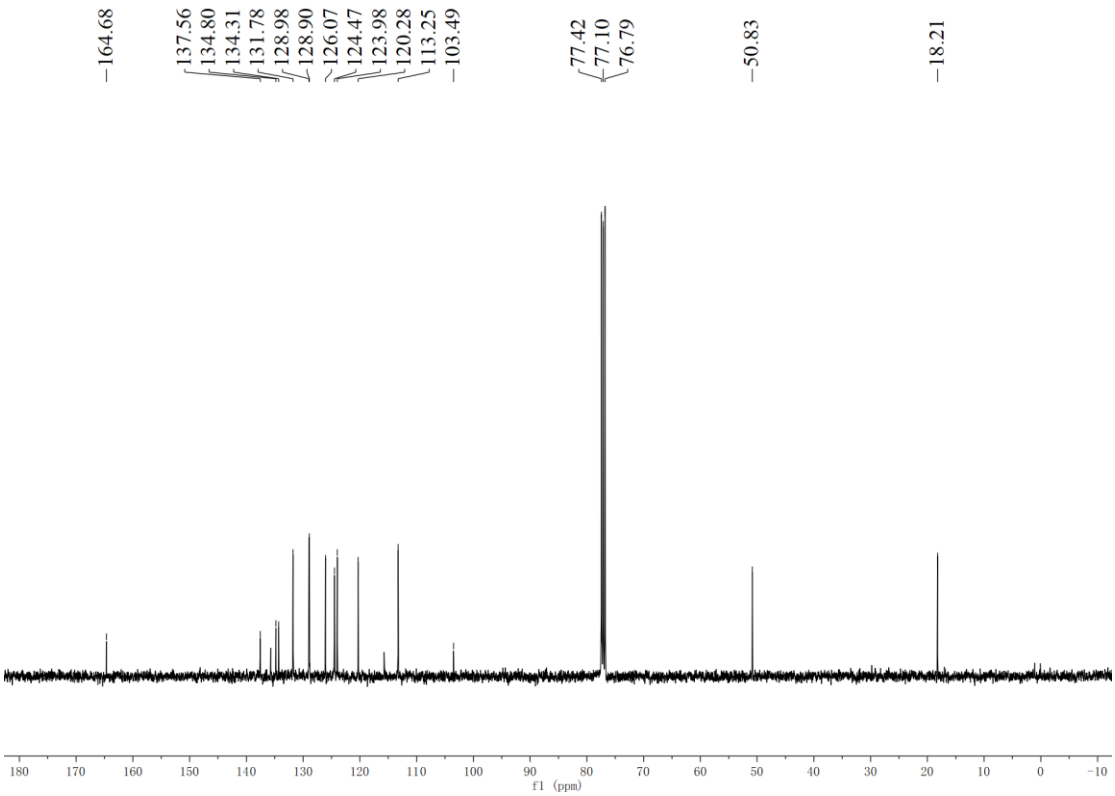
8.57
8.32
8.30
7.50
7.49
7.48
7.36
7.35
7.34
7.34
7.33
7.29
7.29
7.28
7.27
7.24
7.23
7.22
7.22
7.21
7.20
6.94
6.94
6.92
6.92
6.90
6.90
N
CO2Me
Cl
S
1.02
1.00
1.01
2.00
1.00
1.00
1.02
3.00
3.00
f1 (ppm)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134.31
131.78
128.98
128.90
126.07
124.47
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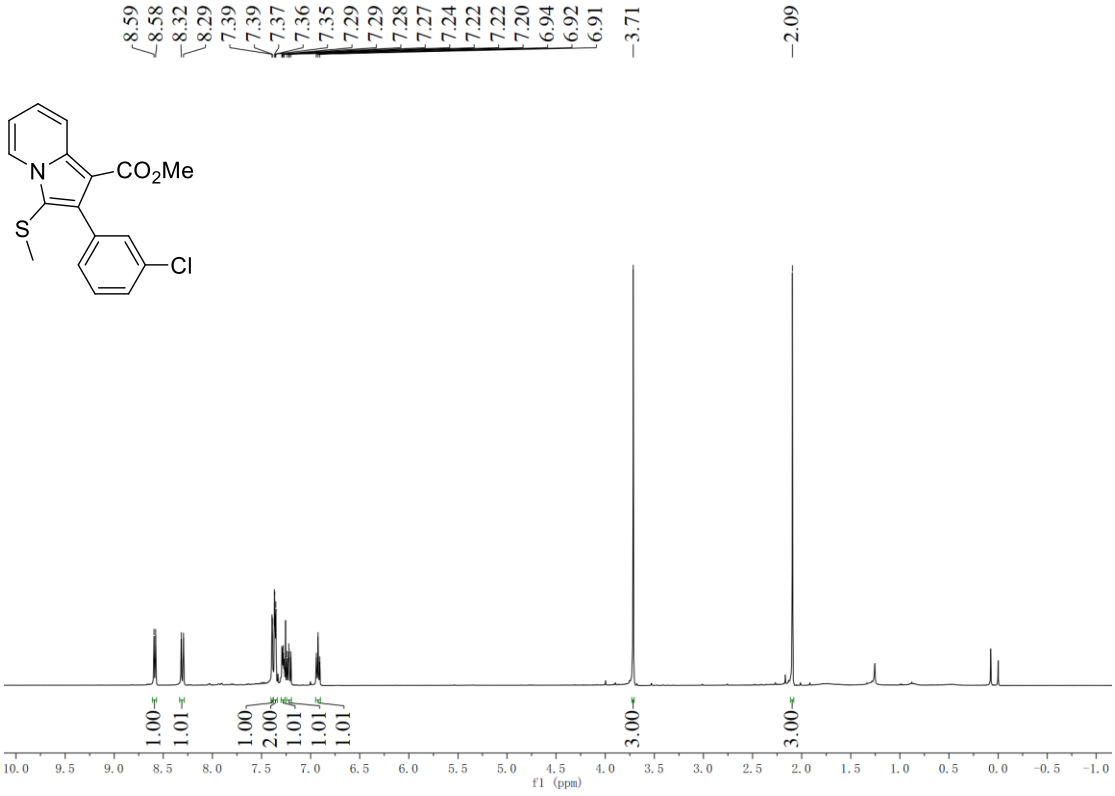
77.42
77.10
76.79
50.83
18.21
f1 (ppm)

3an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8.58
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7.29
7.29
7.28
7.27
7.24
7.22
7.22
7.20
6.94
6.92
6.91
3.71
2.09
CO2Me
N
S
Cl
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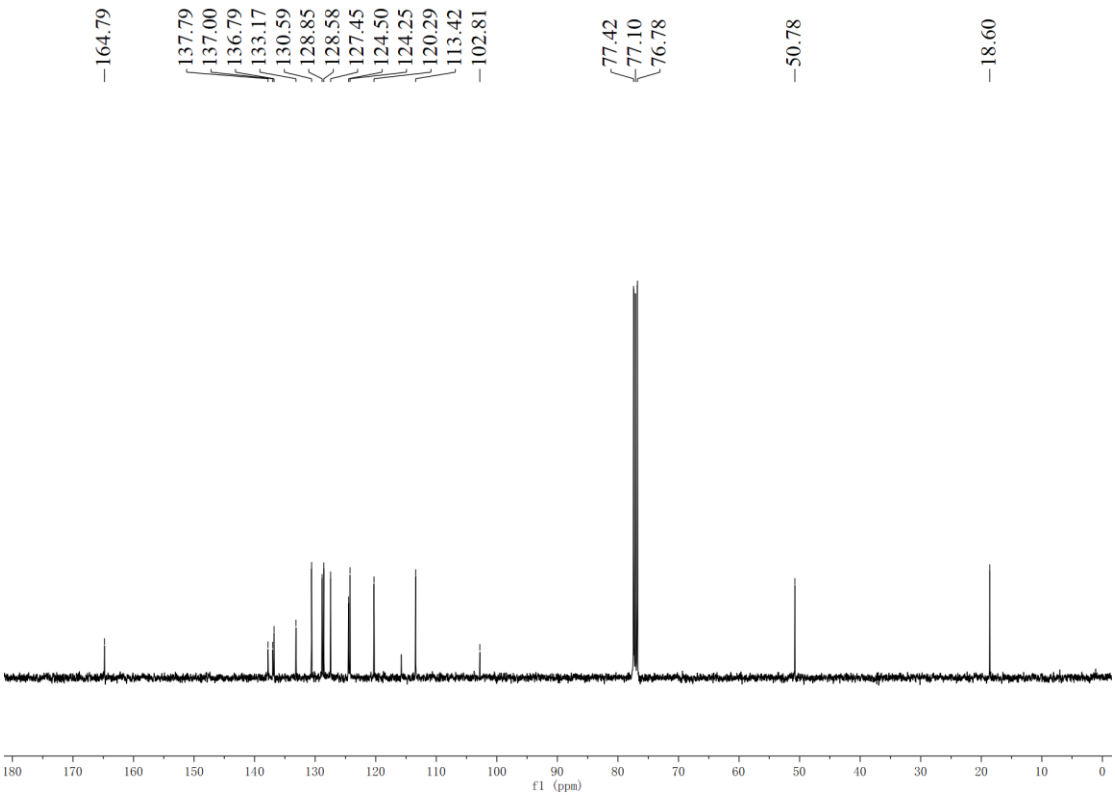
1.01
1.00
2.00
1.01
1.01
1.01
3.00
3.00
f1 (ppm)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133.17
130.59
128.85
128.58
127.45
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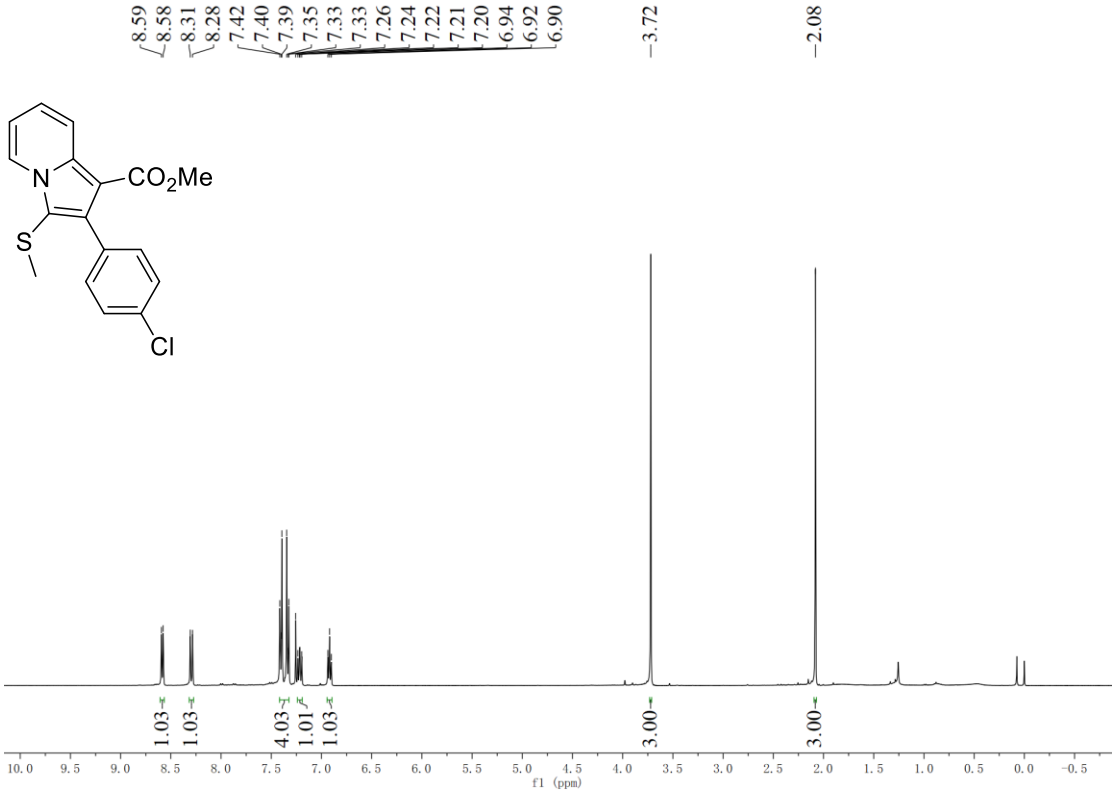
124.25
120.29
113.42
102.81
77.42
77.10
76.78
50.78
18.60
f1 (ppm)

3ao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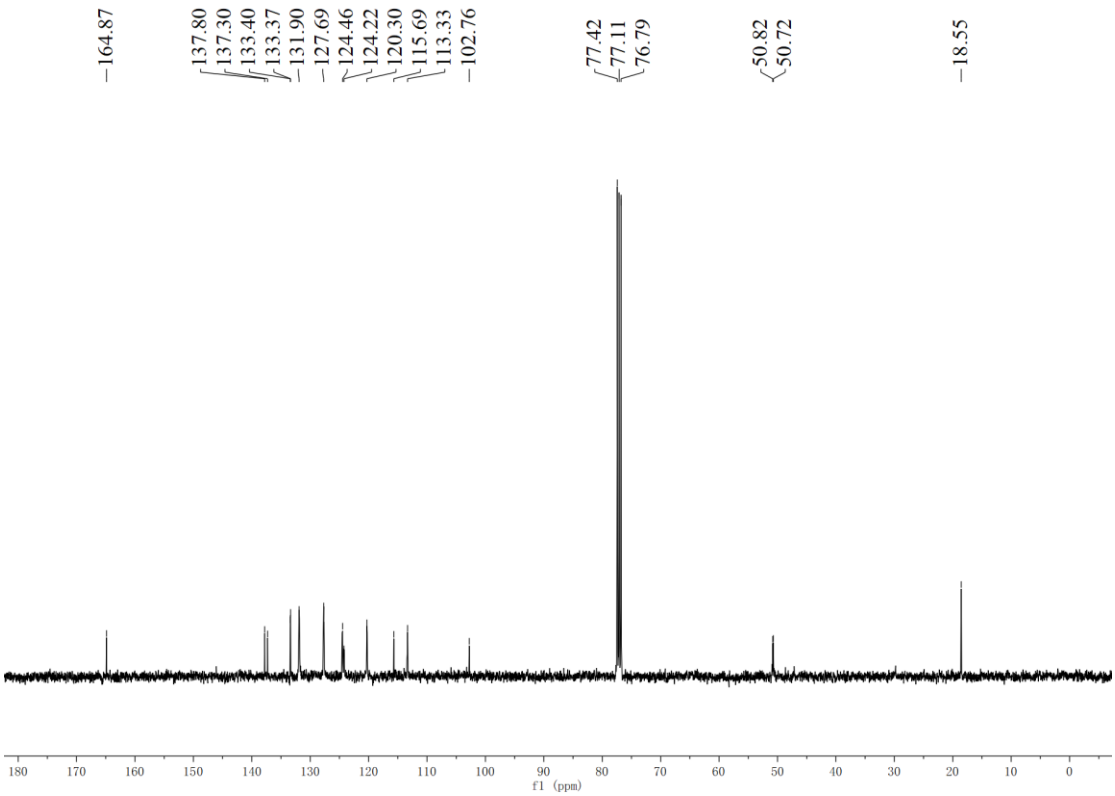
7.42
7.40
7.39
7.35
7.33
7.33
7.26
7.24
7.22
7.21
7.20
6.94
6.92
6.90
3.72
2.08
N
CO2Me
S
Cl
1.03
1.03
4.03
1.01
1.03
3.00
3.00
f1 (ppm)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131.90
127.69
124.46
124.22
120.30
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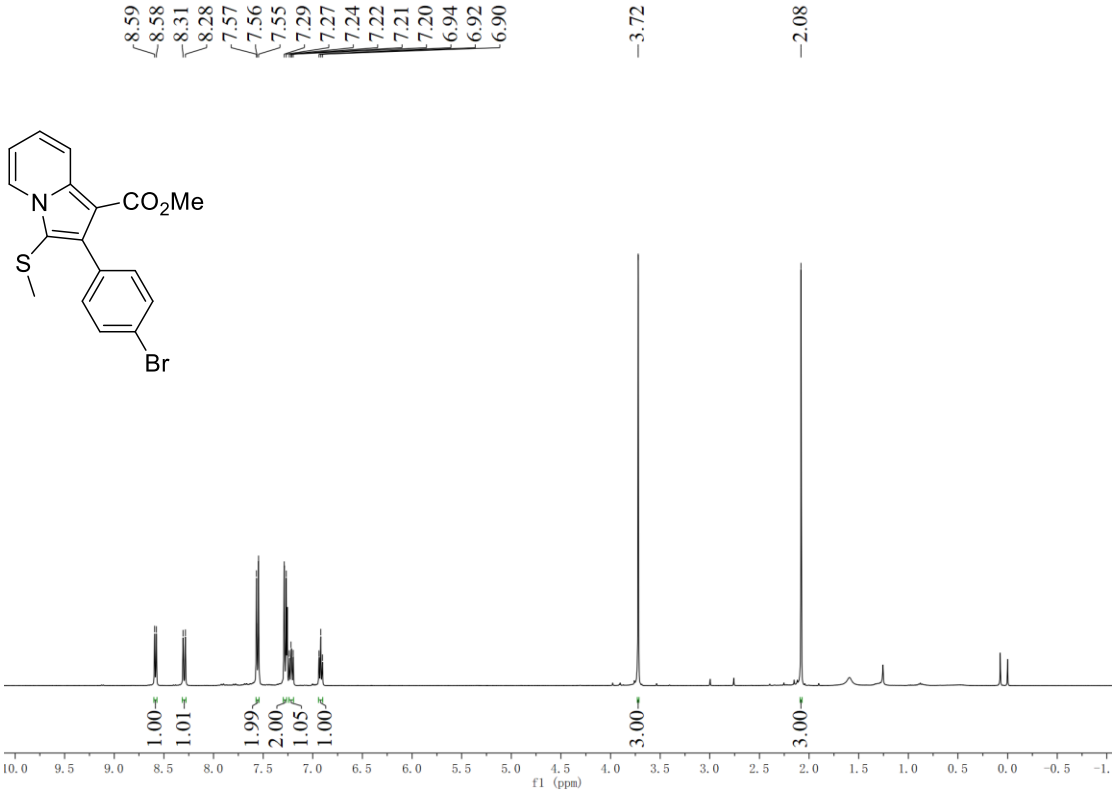
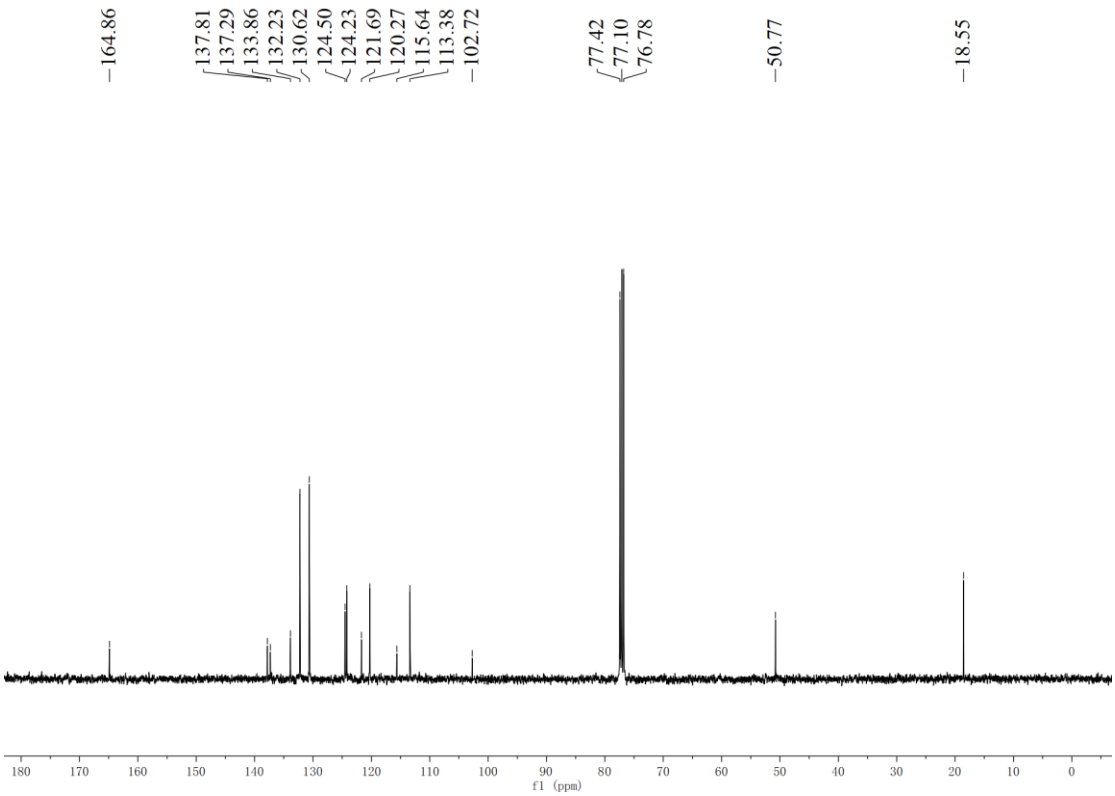
113.33
102.76
77.42
77.11
76.79
50.82
50.72
18.55
f1 (ppm)

3ap


8.59
8.58
8.31
8.28
7.57
7.56
7.55
7.29
7.27
7.24
7.22
7.21
7.20
6.94
6.92
6.90
3.72
2.08
CO2Me
N
S
Br
1.00
1.01
1.99
2.00
1.05
1.00
3.00
3.00
f1 (ppm)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124.50
124.23
121.69
120.27
115.64
113.38
102.72
77.42
77.10
76.78
50.77
18.55
f1 (ppm)

GC-MS spectrum of formaldehyde