Supporting Information

N-Heterocyclic Carbene-Catalyzed [3 + 3] Cycloaddition of *α*-Bromoenals with *β*-Nitro Enamines: Synthesis of Nitro-containing *δ*-Lactams

Yarui Li,[a,b] Xiaoxia Huang,[a,b] Shiyong Peng,[a] Jian Wang*[a] and Ming Lang*[a,b]

[a] School of Biotechnology and Health Sciences, Wuyi University, Jiangmen, 529020, People's Republic of China
[b] International Healthcare Innovation Institute (Jiangmen), Jiangmen 529040, People's Republic of China.

E-mail: wangjian2012@tsinghua.edu.cn; langm2019@163.com

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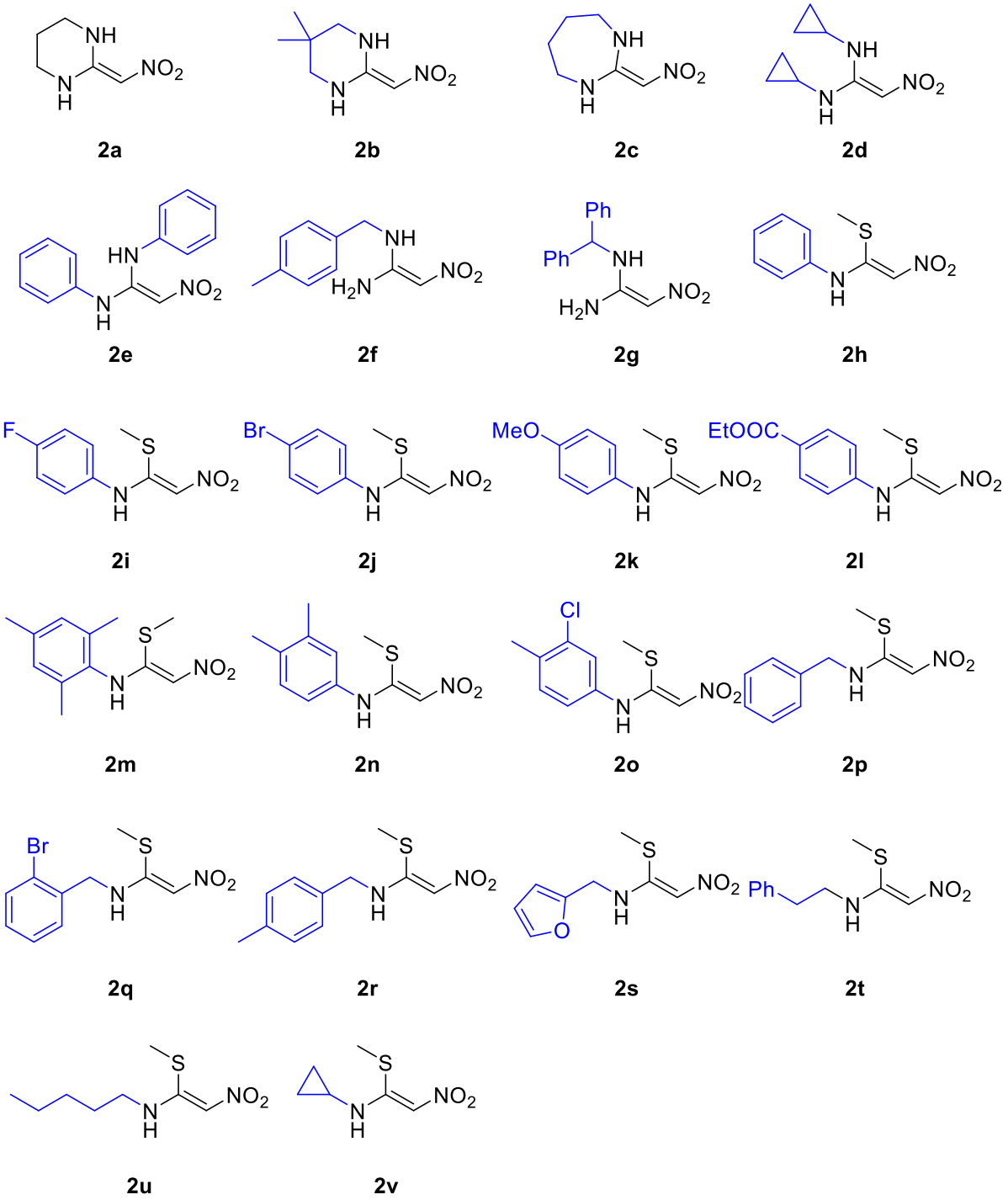
1. General information

Unless otherwise noted, all the materials and solvents were purchased from commercial suppliers and used without further purification. Reactions were conducted in dry glassware using anhydrous solvent. Thin-layer chromatography (TLC) was conducted on plates (GF254) supplied by Qingdao Weinaxipu New Material co., Ltd. and visualized using a combination of UV, iodine and Phosphomolybdic acid staining. Column chromatography was performed with silica gel (200-300 mesh). Melting points were determined with an SGW X-4B melting point apparatus and are uncorrected. NMR spectra were recorded on a Bruker Ascend™ 500 spectrometer for ^{1}H at 500 MHz, ^{13}C NMR at 126 MHz, ^{19}F NMR at 471 MHz using TMS as internal standard. The peaks were internally referenced to residual undeuterated chloroform in $CDCl_3$ (7.26 ppm for ^{1}H NMR, 77.16 ppm for ^{13}C NMR) or DMSO in DMSO-d_6 (2.50 ppm for ^{1}H NMR, 39.52 ppm for ^{13}C NMR). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, dt = doublet of triplets, td = triplet of doublets, m = multiplet or unresolved, br = broad signal. Coupling constants were reported in Hertz (Hz). High resolution mass spectroscopy data of the products were collected on a Thermo Scientific Q Exactive UHMR (Ultra-High Mass Range) Hybrid Quadrupole-Orbitrap™ mass spectrometer using ESI ionization.

2. Synthesis of substrates

2.1 General experimental procedure for the Synthesis of *β*-Nitro Enamines (2)

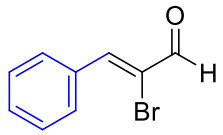
All substrates were prepared according to literature procedures.[1]



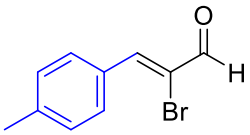
Scheme 1. Chemical structures of substrates **2a-2v**

2.2 General experimental procedure for the synthesis of *α*-bromoenals (1)

All *α*-bromoenals were prepared from the corresponding enals according to procedures previously reported by our group.[2]



1a



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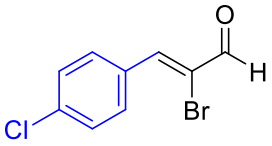

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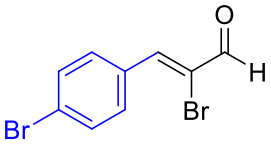

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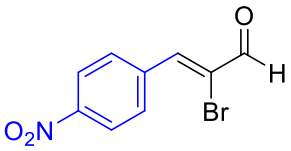

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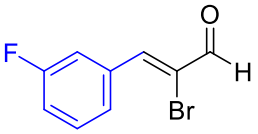

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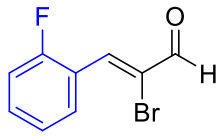
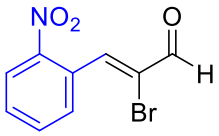
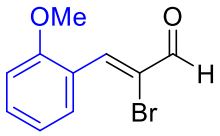


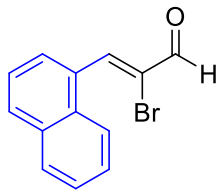
1g



1h



1i



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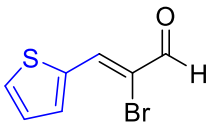
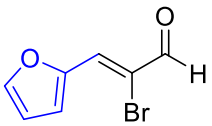
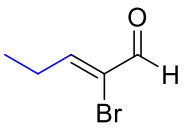


1k



1l



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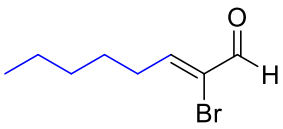
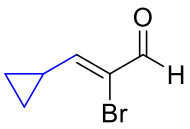
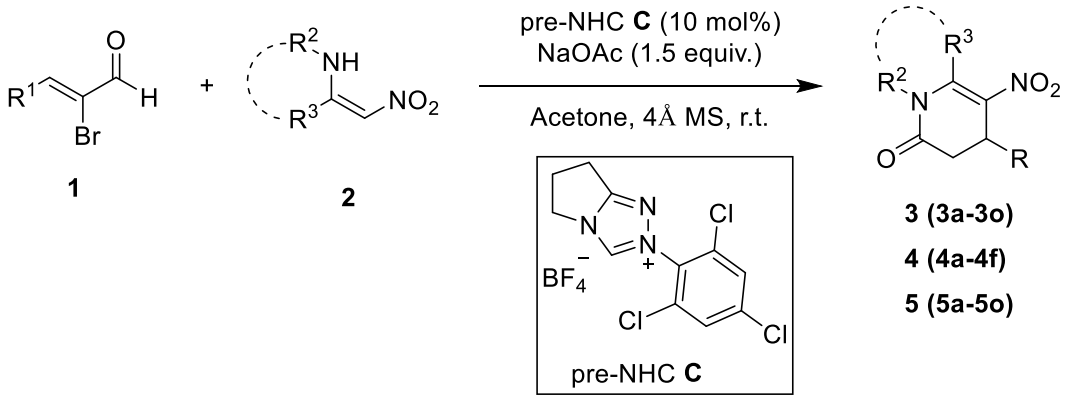


1n



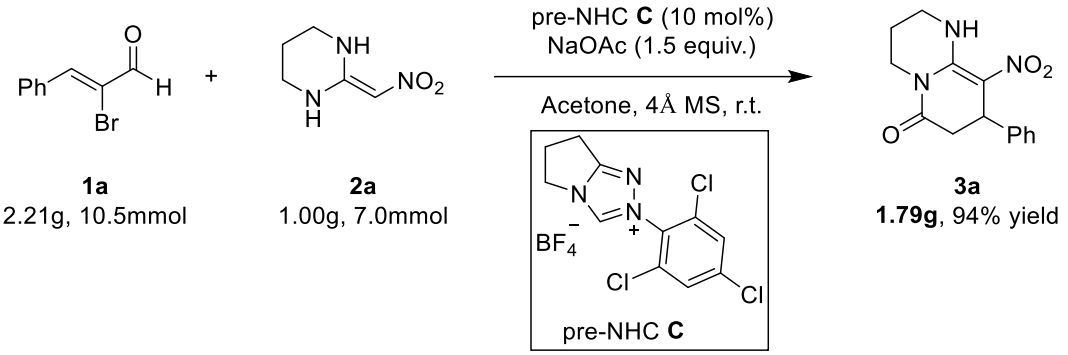
1o

3. Synthesis of target compounds 3 (3a-3o), 4 (4a-4f) and 5 (5a-5o)



A mixture of α-bromoenals (**1**, 0.3 mmol), β-nitro enamines (**2**, 0.2 mmol), pre-NHC **C** (0.02 mmol), NaOAc (0.3 mmol), 4Å molecular sieve (50 mg) in acetone (2.0 mL) was stirred at room temperature until complete conversion of the starting material as indicated by TLC. The solvent was removed under reduced pressure and the crude product was directly purified by column chromatography on silica gel to afford the desired product **3**, **4** or **5**.

4. Scale-up experiment

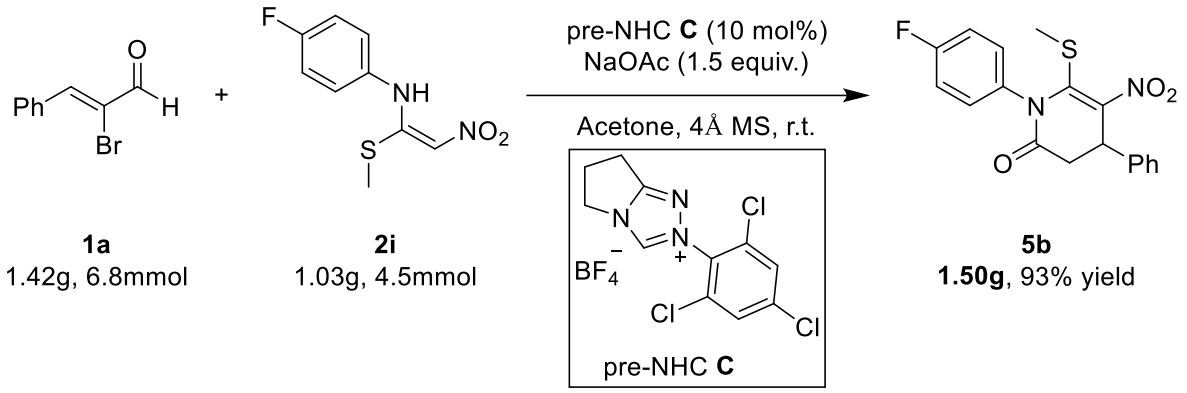


1a
2.21g, 10.5mmol

2a
1.00g, 7.0mmol

3a
1.79g, 94% yield

A mixture of **1a** (2.21g, 10.5 mmol), **2a** (1.00g, 7.0 mmol), pre-NHC **C** (263mg, 0.7 mmol), NaOAc (861mg, 10.5 mmol), 4Å molecular sieve (1.0g) in acetone (40 mL) was stirred at room temperature until complete conversion of the starting material as indicated by TLC. The solvent was removed under reduced pressure and the crude product was directly purified by column chromatography on silica gel to afford the desired product **3a** (1.79g, 94% yield) as a white solid.



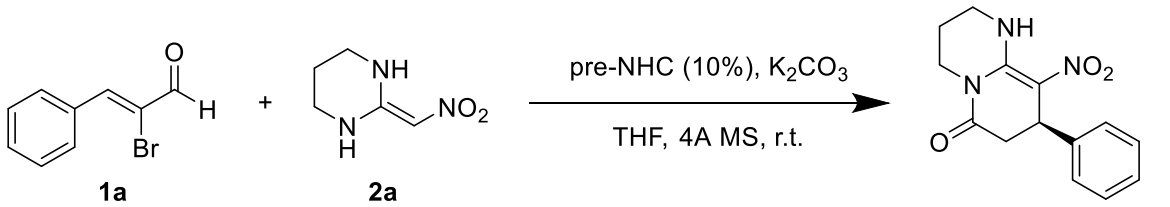
1a
1.42g, 6.8mmol

2i
1.03g, 4.5mmol

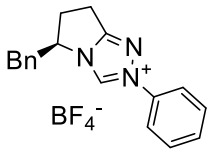
5b
1.50g, 93% yield

A mixture of **1a** (1.42g, 6.8 mmol), **2i** (1.03g, 4.5 mmol), pre-NHC **C** (169mg, 0.45 mmol), NaOAc (558mg, 6.8 mmol), 4Å molecular sieve (1.0g) in acetone (30 mL) was stirred at room temperature until complete conversion of the starting material as indicated by TLC. The solvent was removed under reduced pressure and the crude product was directly purified by column chromatography on silica gel to afford the desired product **5b** (1.50g, 93% yield) as a white solid.

5. Preliminary exploration on enantioselective version

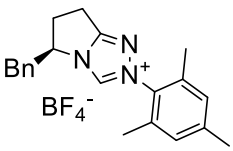


1a **2a**



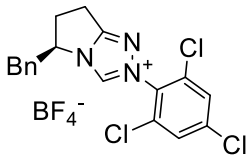
G

41%, 6% *ee*



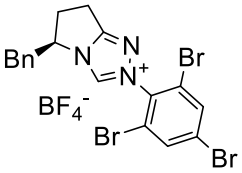
H

40%, 28% *ee*



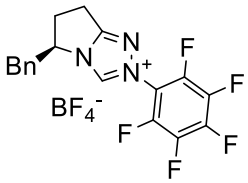
I

39%, 37% *ee*



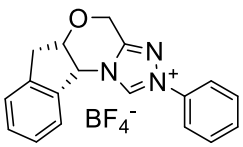
J

49%, 37% *ee*



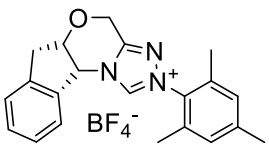
K

42%, 13% *ee*



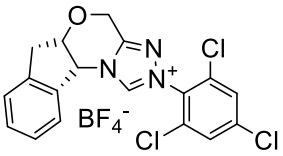
L

72%, 11% *ee*



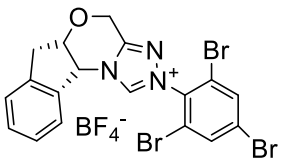
M

50%, 4% *ee*



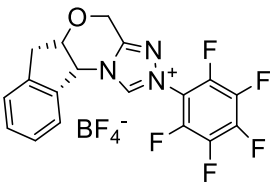
N

72%, 10% *ee*



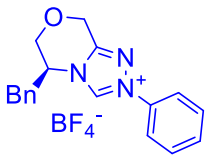
O

71%, 16% *ee*



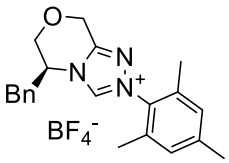
P

74%, 16% *ee*



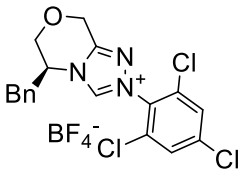
Q

49%, 44% *ee*



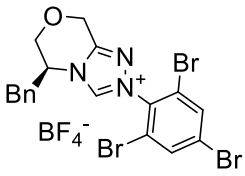
R

15%, 7% *ee*



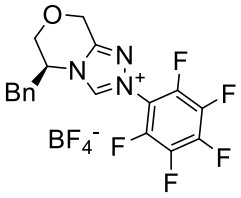
S

13%, 26% *ee*



T

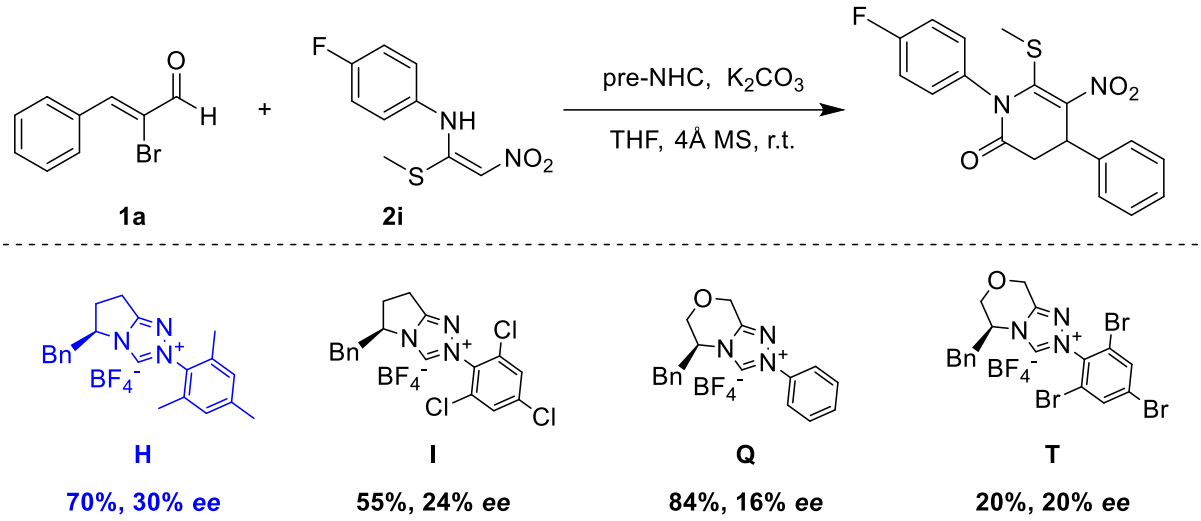
11%, 33% *ee*



U

24%, 8% *ee*

Reaction conditons: **1a** (0.3 mmol), **2a** (0.2 mmol), pre-NHC (0.02 mmol), K_2CO_3 (0.3 mmol), 4Å MS (50 mg) and THF (2.0 mL) at room temperature.



Reaction conditons: **1a** (0.3 mmol), **2i** (0.2 mmol), pre-NHC (0.02 mmol), K_2CO_3 (0.3 mmol), 4Å MS (50 mg) and THF (2.0 mL) at room temperature.

6. X-ray structure and crystal data of 3a and 5b

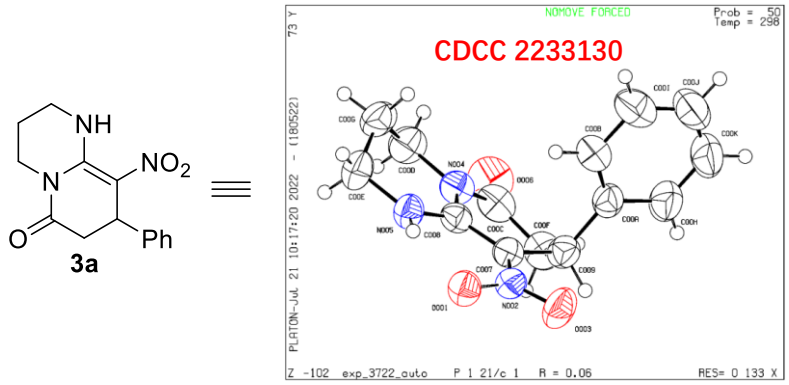


Table 1 Crystal data and structure refinement for 3a.

Identification code	3a
Empirical formula	$C_{14}N_3O_3H_{0.25}$
Formula weight	258.42
Temperature/K	298.37(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	6.2441(3)
b/Å	25.3839(8)
c/Å	8.4223(3)
α/°	90
β/°	101.995(4)
γ/°	90
Volume/Å^3	1305.78(9)
Z	4
ρ_{calc}g/cm^3	1.315
μ/mm^{-1}	0.824
F(000)	517.0
Crystal size/mm^3	? × ? × ?
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.964 to 154.524
Index ranges	$-7 \le h \le 7$, $-31 \le k \le 17$, $-9 \le l \le 10$
Reflections collected	8613
Independent reflections	2622 [R_{int} = 0.0460, R_{sigma} = 0.0475]
Data/restraints/parameters	2622/0/181
Goodness-of-fit on F^2	1.091
Final R indexes [I>=2σ (I)]	R_1 = 0.0610, wR_2 = 0.1812
Final R indexes [all data]	R_1 = 0.0689, wR_2 = 0.1889
Largest diff. peak/hole / e Å^{-3}	0.24/-0.21

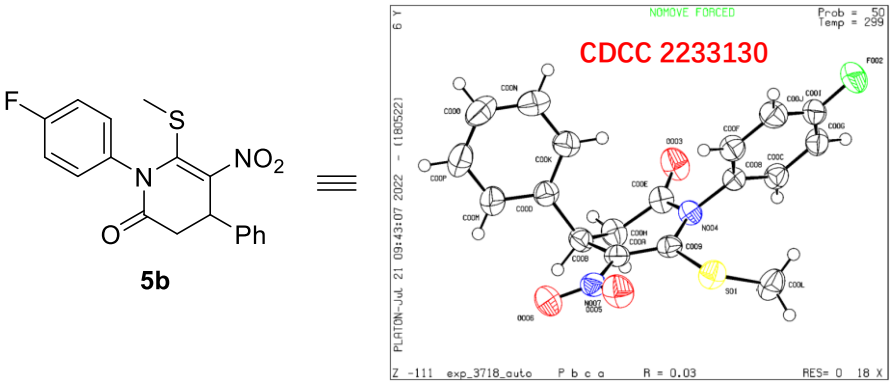
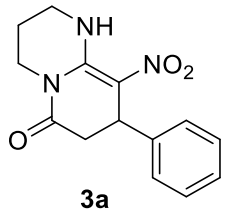


Table 1 Crystal data and structure refinement for 5b.

Identification code	5b
Empirical formula	$C_{18}H_{15}FN_2O_3S$
Formula weight	358.38
Temperature/K	298.98(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	8.17910(10)
b/Å	19.9839(3)
c/Å	20.2957(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3317.34(8)
Z	8
ρ_{calc}g/cm^3	1.435
μ/mm^{-1}	2.015
F(000)	1488.0
Crystal size/mm^3	? × ? × ?
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.714 to 154.744
Index ranges	-6 ≤ h ≤ 9, -23 ≤ k ≤ 24, -24 ≤ l ≤ 24
Reflections collected	12990
Independent reflections	3297 [R_{int} = 0.0329, R_{sigma} = 0.0294]
Data/restraints/parameters	3297/0/228
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0349, wR_2 = 0.0953
Final R indexes [all data]	R_1 = 0.0392, wR_2 = 0.0987
Largest diff. peak/hole / e Å^{-3}	0.18/-0.18

7. Analytical data



3a

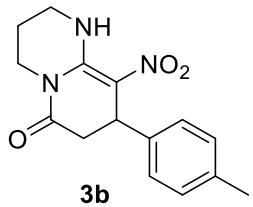
99% yield, white solid;

m.p. = 216 – 217 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.81 (s, 1H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.22 (d, *J* = 7.1 Hz, 1H), 7.15 (d, *J* = 7.1 Hz, 2H), 4.80 (dd, *J* = 7.5, 2.1 Hz, 1H), 4.09 – 4.00 (m, 1H), 3.65 (dt, *J* = 13.4, 5.6 Hz, 1H), 3.61 – 3.43 (m, 2H), 3.05 (dd, *J* = 16.4, 7.3 Hz, 1H), 2.97 (dd, *J* = 16.4, 2.2 Hz, 1H), 2.12 – 2.00 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 152.7, 140.4, 129.1, 127.5, 126.5, 109.7, 39.5, 39.3, 38.3, 36.1, 20.0.

HRMS (ESI): exact mass calculated for $C_{14}H_{16}N_3O_3$ $[M + H]^+$ 274.1186, found 274.1180.



3b

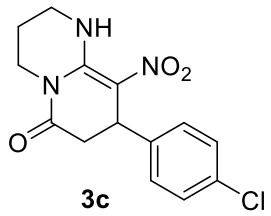
61% yield, white solid;

m.p. = 221 – 222 ℃;

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.61 (s, 1H), 7.09 (d, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 4.57 (dd, *J* = 7.3, 2.0 Hz, 1H), 3.87 (ddd, *J* = 12.8, 7.8, 4.7 Hz, 1H), 3.65 – 3.41 (m, 3H), 3.20 (dd, *J* = 16.0, 7.3 Hz, 1H), 2.67 (dd, *J* = 16.0, 2.0 Hz, 1H), 2.24 (s, 3H), 2.01 – 1.91 (m, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 168.5, 152.5, 138.4, 136.0, 129.2, 126.3, 108.7, 38.5, 35.7, 20.6, 19.2.

HRMS (ESI): exact mass calculated for $C_{15}H_{18}N_3O_3$ $[M + H]^+$: 288.1343, found 288.1338.



3c

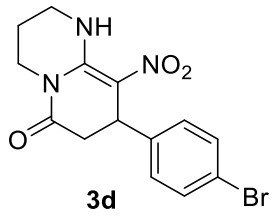
99% yield, white solid;

m.p. = 251 – 252 ℃;

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.58 (s, 1H), 7.38 – 7.31 (m, 2H), 7.21 – 7.15 (m, 2H), 4.62 (dd, *J* = 7.5, 2.0 Hz, 1H), 3.92 – 3.83 (m, 1H), 3.65 – 3.52 (m, 2H), 3.51 – 3.43 (m, 1H), 3.24 (dd, *J* = 16.0, 7.5 Hz, 1H), 2.69 (dd, *J* = 16.1, 2.0 Hz, 1H), 2.03 – 1.90 (m, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 168.7, 152.9, 141.0, 131.9, 129.1, 128.9, 108.7, 39.8, 38.7, 36.1, 19.6.

HRMS (ESI) xx; **HRMS** (ESI): exact mass calculated for $C_{14}H_{15}ClN_3O_3$ $[M + H]^+$: 308.0796, found 308.0791.



3d

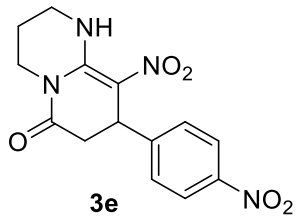
94% yield, white solid;

m.p. = 234 – 235 ℃;

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.57 (s, 0H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 4.60 (dd, *J* = 7.5, 2.0 Hz, 1H), 3.91 – 3.83 (m, 1H), 3.65 – 3.52 (m, 2H), 3.51 – 3.42 (m, 1H), 3.23 (dd, *J* = 16.1, 7.5 Hz, 1H), 2.69 (dd, *J* = 16.1, 2.1 Hz, 1H), 2.04 – 1.89 (m, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 168.3, 152.5, 141.0, 131.6, 128.9, 120.0, 108.2, 38.2, 35.7, 19.1.

HRMS (ESI): exact mass calculated for $C_{14}H_{15}BrN_3O_3$ $[M + H]^+$: 353.0325, found 353.0321.



3e

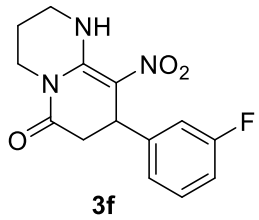
99% yield, white solid;

m.p. = 201 – 202 ℃;

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.57 (s, 1H), 8.15 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.8 Hz, 2H), 4.77 (dd, J = 7.9, 2.0 Hz, 1H), 3.94 – 3.83 (m, 1H), 3.67 – 3.56 (m, 2H), 3.54 – 3.44 (m, 1H), 3.32 (dd, J = 16.5, 8.0 Hz, 1H), 2.74 (dd, J = 16.2, 2.0 Hz, 1H), 2.05 – 1.92 (m, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 168.3, 153.8, 152.1, 142.3, 110.4, 106.9, 105.5, 39.3, 39.1, 35.6, 30.8, 19.1.

HRMS (ESI): exact mass calculated for $C_{14}H_{15}N_4O_5$ $[M + H]^+$: 319.1037, found 319.1033.



3f

95% yield, white solid;

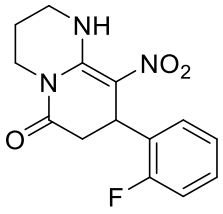
m.p. = 198 – 199 ℃;

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.59 (s, 1H), 7.40 – 7.30 (m, 1H), 7.09 – 6.96 (m, 3H), 4.64 (dd, J = 7.5, 2.0 Hz, 1H), 3.95 – 3.83 (m, 1H), 3.66 – 3.53 (m, 2H), 3.52 – 3.43 (m, 1H), 3.25 (dd, J = 16.1, 7.6 Hz, 1H), 2.72 (dd, J = 16.2, 2.1 Hz, 1H), 2.01 – 1.91 (m, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 168.2, 162.4 (d, J = 244.0 Hz), 152.5, 144.6 (d, J = 6.6 Hz), 130.7 (d, J = 8.3 Hz), 122.4 (d, J = 2.6 Hz), 113.8 (d, J = 20.9 Hz), 113.5 (d, J = 21.5 Hz), 108.1, 39.3, 39.0, 38.2, 36.0, 19.1.

^{19}F NMR (471 MHz, DMSO-d_6) δ -112.8.

HRMS (ESI): exact mass calculated for $C_{14}H_{15}FN_3O_3$ $[M + H]^+$: 292.1092, found 292.1086.



3g

91% yield, white solid;

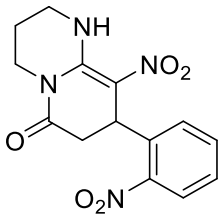
m.p. = 210 – 211 ℃;

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.59 (s, 1H), 7.34 – 7.26 (m, 1H), 7.20 (dd, J = 10.8, 8.2 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 7.04 (td, J = 7.8, 1.8 Hz, 1H), 4.86 – 4.81 (m, 1H), 3.93 – 3.85 (m, 1H), 3.66 – 3.56 (m, 2H), 3.52 – 3.45 (m, 1H), 3.31 (dd, J = 16.0, 7.8 Hz, 1H), 2.57 (dd, J = 16.1, 1.8 Hz, 1H), 2.03 – 1.97 (m, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 167.9, 160.2 (d, J = 244.1 Hz), 152.8, 129.1 (d, J = 8.2 Hz), 128.1 (d, J = 14.2 Hz), 127.6 (d, J = 4.1 Hz), 124.7 (d, J = 3.3 Hz), 115.7 (d, J = 21.6 Hz), 106.9, 37.2, 30.9 (d, J = 3.2 Hz), 19.1.

^{19}F NMR (471 MHz, DMSO-d_6) δ -119.0.

HRMS (ESI): exact mass calculated for $C_{14}H_{15}FN_3O_3$ $[M + H]^+$: 292.1092, found 292.1087.



3h

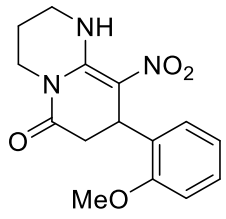
95% yield, white solid;

m.p. = 243 – 244 ℃;

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.53 (s, 1H), 7.96 (dd, J = 8.1, 1.4 Hz, 1H), 7.62 (td, J = 7.5, 1.4 Hz, 1H), 7.52 (td, J = 7.7, 1.4 Hz, 1H), 7.29 (dd, J = 7.9, 1.3 Hz, 1H), 4.93 (dd, J = 8.6, 1.6 Hz, 1H), 3.98 – 3.89 (m, 1H), 3.74 – 3.66 (m, 1H), 3.67 – 3.58 (m, 1H), 3.55 – 3.46 (m, 1H), 3.43 (dd, J = 16.3, 8.7 Hz, 1H), 2.66 (dd, J = 16.3, 1.7 Hz, 1H), 2.13 – 1.95 (m, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 167.7, 152.7, 149.0, 136.3, 134.0, 128.6, 127.7, 124.8, 107.9, 39.4, 39.3, 37.1, 32.7, 19.0.

HRMS (ESI): exact mass calculated for $C_{14}H_{15}N_4O_5$ $[M + H]^+$: 319.1037, found 319.1032.



3i

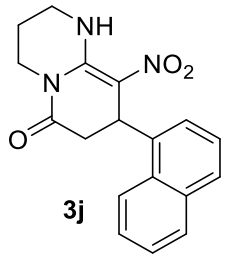
92% yield, white solid;

m.p. = 230 – 231 ℃;

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.67 (s, 1H), 7.26 – 7.19 (m, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.89 – 6.78 (m, 2H), 4.78 (dd, *J* = 7.9, 1.8 Hz, 1H), 3.93 – 3.83 (m, 1H), 3.81 (s, 3H), 3.68 – 3.53 (m, 2H), 3.52 – 3.43 (m, 1H), 3.16 (dd, *J* = 16.0, 7.9 Hz, 1H), 2.59 (dd, *J* = 16.0, 1.8 Hz, 1H), 2.03 – 1.94 (m, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 168.5, 156.7, 152.9, 128.5, 128.3, 126.3, 120.3, 111.1, 107.5, 55.3, 39.2, 39.1, 36.6, 31.7, 19.2.

HRMS (ESI): exact mass calculated for $C_{15}H_{18}N_3O_4$ $[M + H]^+$: 304.1292, found 304.1292.



3j

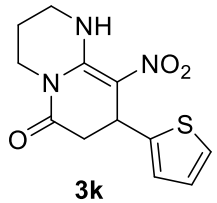
99% yield, white solid;

m.p. = 220 – 221 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.93 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.88 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.55 – 7.48 (m, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 7.1 Hz, 1H), 5.59 (dd, *J* = 7.6, 1.9 Hz, 1H), 4.06 – 3.97 (m, 1H), 3.73 – 3.60 (m, 2H), 3.58 – 3.50 (m, 1H), 3.18 (dd, *J* = 16.1, 7.7 Hz, 1H), 3.08 (dd, *J* = 16.2, 1.9 Hz, 1H), 2.15 – 2.06 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 153.4, 135.4, 134.6, 130.8, 129.4, 128.6, 126.7, 126.0, 125.3, 122.8, 121.9, 108.7, 39.5, 39.4, 38.0, 33.2, 20.2.

HRMS (ESI): exact mass calculated for $C_{18}H_{18}N_3O_3$ $[M + H]^+$: 324.1343, found 324.1338.



3k

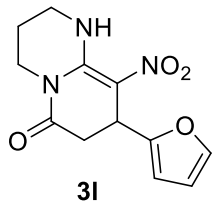
94% yield, white solid;

m.p. = 173 – 174 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.66 (s, 1H), 7.13 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.93 – 6.81 (m, 2H), 5.08 (dd, *J* = 6.5, 2.5 Hz, 1H), 4.08 (ddd, *J* = 13.1, 8.0, 4.7 Hz, 1H), 3.71 – 3.49 (m, 3H), 3.14 – 2.99 (m, 2H), 2.16 – 2.00 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 152.1, 143.8, 126.9, 124.4, 124.1, 110.3, 39.5, 39.3, 38.3, 32.3, 20.0.

HRMS (ESI): exact mass calculated for $C_{12}H_{14}N_3O_3S$ $[M + H]^+$: 280.0750, found 280.0747.



3l

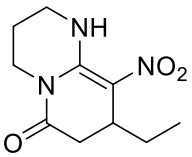
96% yield, white solid;

m.p. = 211 – 212 ℃;

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.47 (s, 1H), 7.53 (d, *J* = 1.6 Hz, 1H), 6.33 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.09 (d, *J* = 3.1 Hz, 1H), 4.71 (dd, *J* = 7.1, 2.0 Hz, 1H), 3.94 – 3.85 (m, 1H), 3.63 – 3.51 (m, 2H), 3.49 – 3.40 (m, 1H), 3.17 (dd, *J* = 16.1, 7.0 Hz, 1H), 2.76 (dd, *J* = 16.1, 2.0 Hz, 1H), 2.03 – 1.85 (m, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 168.3, 153.8, 152.1, 142.3, 110.4, 106.9, 105.5, 39.3, 39.1, 35.6, 30.8, 19.1.

HRMS (ESI): exact mass calculated for $C_{12}H_{14}N_3O_4$ $[M + H]^+$: 264.0979, found 264.0975.



3m

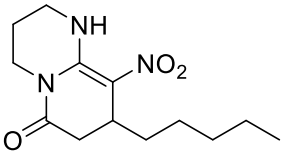
71% yield, white solid;

m.p. = 167 – 168 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.88 (s, 1H), 4.16 – 4.03 (m, 1H), 3.71 – 3.43 (m, 4H), 2.81 – 2.67 (m, 2H), 2.12 – 2.06 (m, 2H), 1.71 – 1.59 (m, 1H), 1.42 – 1.29 (m, 1H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2, 152.3, 110.8, 39.3, 39.2, 35.0, 32.4, 24.9, 20.0, 11.1.

HRMS (ESI): exact mass calculated for $C_{10}H_{16}N_3O_3$ $[M + H]^+$: 226.1186, found 226.1182.



3n

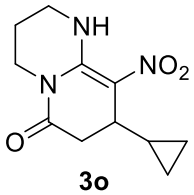
84% yield, white solid;

m.p. = 153 – 154 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.86 (s, 1H), 4.12 – 4.04 (m, 1H), 3.71 – 3.50 (m, 4H), 2.79 – 2.66 (m, 2H), 2.08 (dd, *J* = 9.7, 4.9 Hz, 2H), 1.58 (dq, *J* = 13.6, 5.5, 4.6 Hz, 1H), 1.39 – 1.23 (m, 7H), 0.86 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2, 152.2, 111.1, 39.3, 39.2, 35.3, 31.8, 31.7, 31.0, 26.3, 22.6, 20.0, 14.1.

HRMS (ESI): exact mass calculated for $C_{13}H_{22}N_3O_3$ $[M + H]^+$: 268.1656, found 268.1651.



3o

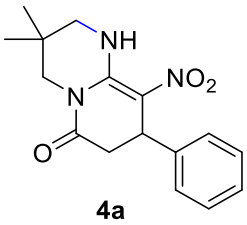
84% yield, white solid;

m.p. = 199 – 200 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.80 (s, 1H), 4.14 – 4.06 (m, 1H), 3.72 – 3.58 (m, 2H), 3.58 – 3.50 (m, 1H), 3.28 – 3.21 (m, 1H), 2.83 – 2.71 (m, 2H), 2.15 – 2.02 (m, 2H), 0.81 – 0.71 (m, 1H), 0.65 – 0.55 (m, 1H), 0.47 – 0.36 (m, 2H), 0.16 – 0.06 (m, *J* = 5.2, 4.7 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3, 152.4, 109.9, 39.4, 39.3, 37.1, 34.3, 20.1, 14.5, 3.4, 2.5.

HRMS (ESI): exact mass calculated for $C_{11}H_{16}N_3O_3$ $[M + H]^+$: 238.1186, found 238.1182.



4a

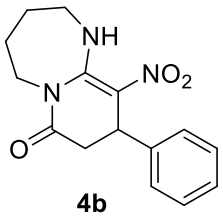
99% yield, white solid;

m.p. = 183 – 184 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.82 (s, 1H), 7.31 – 7.27 (m, 2H), 7.25 – 7.20 (m, 1H), 7.19 – 7.14 (m, 2H), 4.84 (dd, *J* = 7.3, 2.2 Hz, 1H), 3.77 (d, *J* = 13.2 Hz, 1H), 3.37 (d, *J* = 13.7 Hz, 1H), 3.31 – 3.21 (m, 2H), 3.09 (dd, *J* = 16.5, 7.2 Hz, 1H), 3.02 (dd, *J* = 16.4, 2.2 Hz, 1H), 1.11 (d, *J* = 3.2 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 151.8, 140.3, 129.0, 127.5, 126.4, 109.5, 50.8, 50.2, 38.3, 36.1, 27.6, 24.1, 23.9.

HRMS (ESI): exact mass calculated for $C_{16}H_{20}N_3O_3$ $[M + H]^+$: 302.1499, found 302.1495.



4b

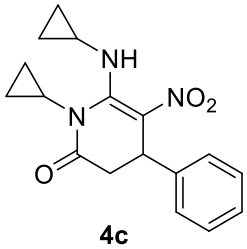
67% yield, white solid;

m.p. = 148 – 149 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.22 (s, 1H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 4.88 (dd, *J* = 6.6, 2.2 Hz, 1H), 4.56 – 4.50 (m, 1H), 3.75 – 3.69 (m, 1H), 3.48 – 3.42 (m, 1H), 3.31 – 3.23 (m, 1H), 3.04 (dd, *J* = 16.2, 6.6 Hz, 1H), 2.97 (dd, *J* = 16.1, 2.4 Hz, 1H), 1.99 – 1.79 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8, 158.1, 139.3, 129.0, 127.5, 126.5, 113.9, 46.0, 45.7, 39.2, 36.0, 25.4, 25.4.

HRMS (ESI): exact mass calculated for $C_{15}H_{18}N_3O_3$ $[M + H]^+$: 288.1343, found 288.1339.



4c

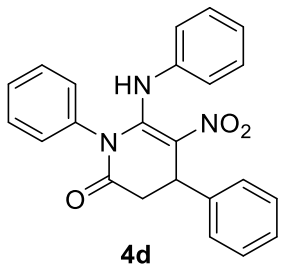
62% yield, white solid;

m.p. = 197 – 198 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.28 (s, 1H), 7.30 – 7.24 (m, 2H), 7.24 – 7.19 (m, 1H), 7.09 – 7.04 (m, 2H), 4.89 (dd, *J* = 6.0, 2.4 Hz, 1H), 3.16 – 3.03 (m, 3H), 2.95 (dd, *J* = 16.6, 5.9 Hz, 1H), 1.05 – 0.88 (m, 5H), 0.83 – 0.74 (m, 1H), 0.68 – 0.59 (m, 1H), -0.03 – -0.12 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 158.0, 138.7, 128.9, 127.5, 126.2, 115.3, 38.9, 35.1, 29.7, 27.9, 11.7, 9.3, 9.2.

HRMS (ESI): exact mass calculated for $C_{15}H_{17}N_2O_3S$ $[M + H]^+$: 314.1499, found 314.1494.



4d

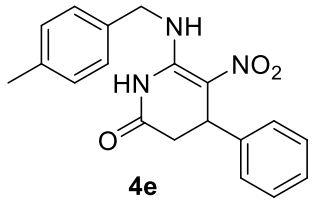
85% yield, white solid;

m.p. = 201 – 202 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.97 (s, 1H), 7.36 – 7.28 (m, 4H), 7.28 – 7.21 (m, 1H), 7.09 – 6.95 (m, 6H), 6.74 – 6.69 (m, 4H), 5.12 (dd, *J* = 6.8, 2.3 Hz, 1H), 3.37 (dd, *J* = 15.7, 6.7 Hz, 1H), 3.20 (dd, *J* = 15.7, 2.3 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 154.7, 139.1, 136.7, 136.4, 129.2, 129.1, 128.4, 127.8, 127.8, 127.1, 126.7, 125.7, 117.6, 39.3, 36.2.

HRMS (ESI): exact mass calculated for $C_{23}H_{20}N_3O_3$ $[M + H]^+$: 386.1499, found 386.1492.



4e

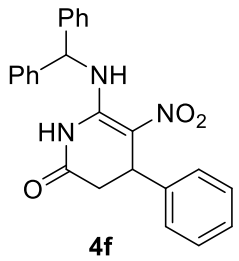
64% yield, white solid;

m.p. = 172 – 173 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.23 (t, *J* = 5.8 Hz, 1H), 8.87 (s, 1H), 7.30 – 7.19 (m, 3H), 7.16 (d, *J* = 8.1 Hz, 6H), 4.82 (dd, *J* = 7.8, 1.9 Hz, 1H), 4.60 (qd, *J* = 15.5, 5.9 Hz, 2H), 3.03 (dd, *J* = 16.5, 7.7 Hz, 1H), 2.82 (dd, *J* = 16.5, 1.9 Hz, 1H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 151.7, 140.4, 138.7, 131.6, 130.1, 129.1, 127.6, 127.2, 126.5, 109.7, 45.9, 38.4, 37.0, 21.3.

HRMS (ESI): exact mass calculated for $C_{19}H_{20}N_3O_3$ $[M + H]^+$: 338.1499, found 338.1493.



4f

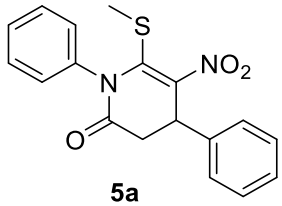
76% yield, white solid;

m.p. = 120 – 121 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.56 (d, *J* = 6.9 Hz, 1H), 8.41 (s, 1H), 7.41 – 7.20 (m, 13H), 7.17 – 7.12 (m, 2H), 6.02 (d, *J* = 6.9 Hz, 1H), 4.82 (dd, *J* = 7.8, 1.8 Hz, 1H), 3.01 (dd, *J* = 16.5, 7.7 Hz, 1H), 2.81 (dd, *J* = 16.6, 1.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 150.8, 140.3, 139.2, 138.8, 129.7, 129.5, 129.1, 129.0, 128.8, 127.7, 127.0, 126.9, 126.5, 110.1, 60.7, 38.4, 37.1.

HRMS (ESI): exact mass calculated for $C_{24}H_{22}N_3O_3$ $[M + H]^+$: 400.1656, found 400.1650.



5a

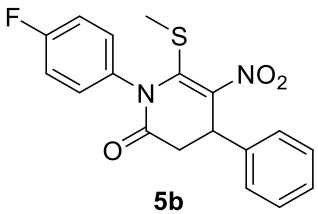
99% yield, white solid;

m.p. = 165 – 166 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.20 (m, 10H), 4.97 (d, *J* = 4.9 Hz, 1H), 3.35 (dd, *J* = 15.9, 7.1 Hz, 1H), 3.12 (dd, *J* = 15.9, 2.2 Hz, 1H), 1.95 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 153.4, 139.5, 138.0, 137.8, 129.4, 128.8, 128.4, 128.1, 126.5, 38.6, 38.2, 18.1.

HRMS (ESI): exact mass calculated for $C_{18}H_{17}N_2O_3S$ $[M + H]^+$: 341.0954, found 341.0951.



5b

96% yield, white solid;

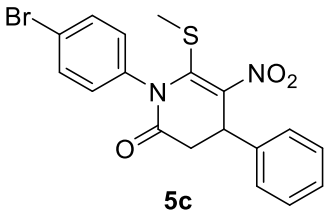
m.p. = 170 – 171 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.18 (m, 7H), 7.10 (t, *J* = 8.3 Hz, 2H), 4.96 (dd, *J* = 7.0, 2.2 Hz, 1H), 3.35 (dd, *J* = 16.0, 7.0 Hz, 1H), 3.14 (dd, *J* = 16.0, 2.2 Hz, 1H), 1.99 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 162.0 (d, *J* = 249.5 Hz), 152.4, 139.8, 137.7, 133.7 (d, *J* = 3.4 Hz), 130.1, 129.4, 128.2, 126.5, 115.9 (d, *J* = 23.0 Hz), 38.5, 38.2, 18.1.

^{19}F NMR (471 MHz, $CDCl_3$) δ -112.0.

HRMS (ESI): exact mass calculated for $C_{18}H_{16}FN_2O_3S$ $[M + H]^+$: 359.0860, found 359.0855.



5c

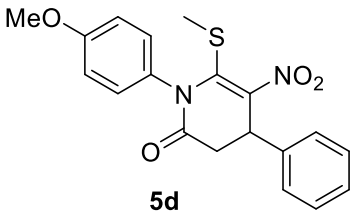
93% yield, white solid;

m.p. = 151 – 152 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.7 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.28 – 7.23 (m, 1H), 7.22 – 7.17 (m, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 4.96 (dd, *J* = 7.0, 2.2 Hz, 1H), 3.33 (dd, *J* = 15.9, 7.0 Hz, 1H), 3.13 (dd, *J* = 16.0, 2.2 Hz, 1H), 1.97 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 152.2, 140.1, 137.6, 136.9, 132.0, 129.8, 129.4, 128.2, 126.4, 122.3, 38.5, 38.1, 18.1.

HRMS (ESI): exact mass calculated for $C_{18}H_{16}BrN_2O_3S$ $[M + H]^+$: 420.0093, found 420.0085.



5d

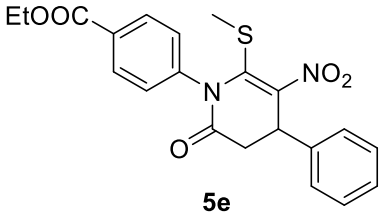
99% yield, white solid;

m.p. = 141 – 142 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.1, 6.6 Hz, 2H), 7.28 – 7.19 (m, 3H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 9.2 Hz, 2H), 4.94 (dd, *J* = 7.1, 2.2 Hz, 1H), 3.82 (s, 3H), 3.33 (dd, *J* = 15.9, 7.1 Hz, 1H), 3.11 (dd, *J* = 15.9, 2.2 Hz, 1H), 1.99 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 159.2, 153.6, 139.1, 137.9, 130.5, 129.3, 128.0, 126.5, 114.0, 55.6, 38.6, 38.2, 18.2.

HRMS (ESI): exact mass calculated for $C_{19}H_{19}N_2O_4S$ $[M + H]^+$: 371.1060, found 371.1057.



5e

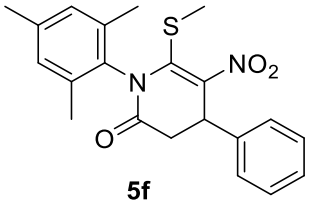
99% yield, white solid;

m.p. = 123 – 124 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.7 Hz, 1H), 7.92 (s, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.45 – 7.19 (m, 6H), 5.00 – 4.95 (m, 1H), 4.46 – 4.32 (m, 2H), 3.37 (dd, *J* = 15.9, 7.1 Hz, 1H), 3.16 (dd, *J* = 15.9, 2.3 Hz, 1H), 1.98 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 165.5, 151.9, 140.0, 138.1, 137.6, 131.5, 129.5, 129.4, 128.9, 128.2, 126.5, 61.6, 38.6, 38.3, 18.2, 14.4.

HRMS (ESI): exact mass calculated for $C_{21}H_{21}N_2O_5S$ $[M + H]^+$: 413.1166, found 413.1160.



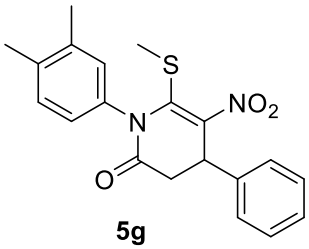
5f

90% yield, colorless oil;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 4H), 7.31 – 7.26 (m, 1H), 6.93 (s, 1H), 6.86 (s, 1H), 4.82 (t, *J* = 4.9 Hz, 1H), 3.29 (d, *J* = 4.9 Hz, 2H), 2.29 (d, *J* = 1.8 Hz, 6H), 2.08 (s, 3H), 1.68 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 152.0, 139.4, 138.4, 136.7, 136.3, 135.3, 132.7, 129.7, 129.3, 129.1, 128.0, 126.7, 39.3, 37.5, 21.2, 19.2, 18.1, 17.9.

HRMS (ESI): exact mass calculated for $C_{21}H_{23}N_2O_3S$ $[M + H]^+$: 383.1424, found 383.1419.



5g

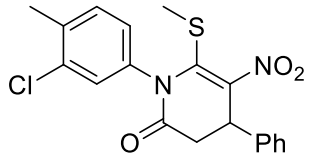
97% yield, white solid;

m.p. = 158 – 159 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.0, 6.5 Hz, 2H), 7.27 – 7.21 (m, 3H), 7.16 (d, *J* = 8.1 Hz, 1H), 7.00 – 6.94 (m, 2H), 4.94 (dd, *J* = 7.2, 2.2 Hz, 1H), 3.33 (dd, *J* = 15.9, 7.2 Hz, 1H), 3.11 (dd, *J* = 15.9, 2.2 Hz, 1H), 2.27 (s, 3H), 2.26 (s, 3H), 2.00 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 153.7, 139.1, 138.0, 137.4, 137.3, 135.5, 129.9, 129.3, 128.0, 126.6, 38.6, 38.3, 20.0, 19.6, 18.4.

HRMS (ESI): exact mass calculated for $C_{20}H_{21}N_2O_3S$ $[M + H]^+$: 369.1267, found 369.1261.



5h

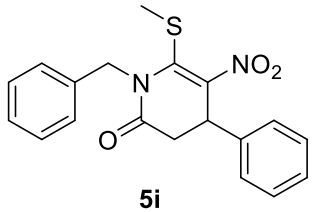
95% yield, white solid;

m.p. = 102 – 104 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.18 (m, 7H), 7.06 – 7.01 (m, 1H), 4.94 (dd, *J* = 7.1, 2.2 Hz, 1H), 3.33 (dd, *J* = 15.9, 7.1 Hz, 1H), 3.13 (dd, *J* = 15.9, 2.3 Hz, 1H), 2.39 (s, 3H), 2.02 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 152.3, 139.9, 137.6, 136.8, 136.4, 134.3, 130.8, 129.4, 128.9, 128.2, 126.5, 38.6, 38.2, 20.0, 18.2.

HRMS (ESI): exact mass calculated for $C_{19}H_{18}ClN_2O_3S[M + H]^+$: 389.0721, found 389.0714.



5i

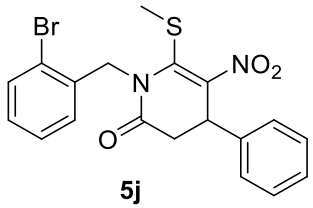
95% yield, white solid;

m.p. = 91 – 92 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.13 (m, 6H), 7.09 (t, *J* = 7.6 Hz, 2H), 6.84 (d, *J* = 7.6 Hz, 2H), 5.44 (d, *J* = 14.5 Hz, 1H), 4.90 (d, *J* = 14.5 Hz, 1H), 4.68 (dd, *J* = 7.3, 2.5 Hz, 1H), 3.15 (dd, *J* = 16.3, 7.2 Hz, 1H), 3.04 (dd, *J* = 16.2, 2.6 Hz, 1H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 147.8, 141.6, 137.1, 136.3, 129.1, 128.7, 128.7, 128.0, 127.8, 126.6, 48.4, 38.5, 38.1, 18.9.

HRMS (ESI): exact mass calculated for $C_{19}H_{19}N_2O_3S$ $[M + H]^+$: 355.1111, found 355.1106.



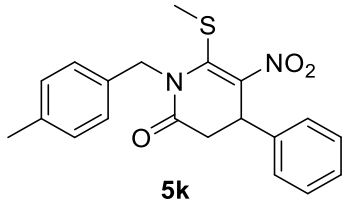
5j

69% yield, colorless oil;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.33 – 7.22 (m, 3H), 7.20 – 7.13 (m, 2H), 7.05 (td, *J* = 7.6, 1.7 Hz, 1H), 6.98 (td, *J* = 7.6, 1.3 Hz, 1H), 6.56 (dd, *J* = 7.8, 1.7 Hz, 1H), 5.32 (d, *J* = 16.1 Hz, 1H), 5.13 (d, *J* = 16.2 Hz, 1H), 4.75 (t, *J* = 4.9 Hz, 1H), 3.21 (d, *J* = 5.0 Hz, 2H), 2.32 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 147.8, 140.7, 137.3, 135.4, 133.0, 129.2, 128.9, 128.0, 128.0, 127.5, 126.7, 122.7, 48.6, 38.4, 37.5, 19.4.

HRMS (ESI): exact mass calculated for $C_{19}H_{18}BrN_2O_3S$ $[M + H]^+$: 433.0216, found 433.0210.



5k

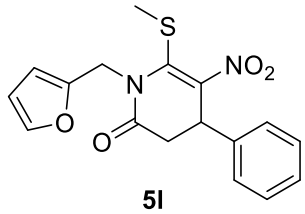
85% yield, white solid;

m.p. = 125 – 126 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.4 Hz, 1H), 7.06 (t, *J* = 8.1 Hz, 4H), 6.99 (d, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 7.5 Hz, 2H), 5.41 (d, *J* = 14.4 Hz, 1H), 4.84 (d, *J* = 14.5 Hz, 1H), 4.67 (dd, *J* = 7.3, 2.5 Hz, 1H), 3.13 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.02 (dd, *J* = 16.2, 2.5 Hz, 1H), 2.36 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 148.2, 141.6, 137.7, 137.2, 133.3, 129.3, 129.0, 128.7, 127.6, 126.6, 48.4, 38.5, 38.1, 21.3, 18.9.

HRMS (ESI): exact mass calculated for $C_{20}H_{21}N_2O_3S$ $[M + H]^+$: 369.1267, found 369.1263.



5l

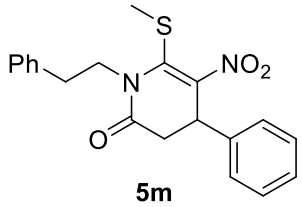
89% yield, white solid;

m.p. = 116 – 117 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 1H), 7.20 – 7.11 (m, 3H), 6.86 – 6.81 (m, 2H), 6.25 (dd, *J* = 16.6, 2.8 Hz, 2H), 5.43 (d, *J* = 15.1 Hz, 1H), 4.95 (d, *J* = 15.1 Hz, 1H), 4.66 (dd, *J* = 7.4, 2.3 Hz, 1H), 3.13 (dd, *J* = 16.2, 7.4 Hz, 1H), 2.96 (dd, *J* = 16.2, 2.3 Hz, 1H), 2.42 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 149.5, 147.4, 142.5, 141.6, 137.2, 129.2, 127.7, 126.5, 110.6, 110.1, 41.4, 38.8, 38.4, 18.8.

HRMS (ESI): exact mass calculated for $C_{17}H_{17}N_2O_4$ $[M + H]^+$: 345.0904, found 345.0899.



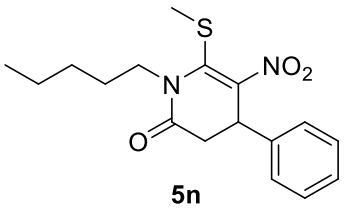
5m

82% yield, colorless oil;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.14 (m, 10H), 4.75 (dd, *J* = 6.3, 3.5 Hz, 1H), 4.40 – 4.31 (m, 1H), 3.94 – 3.83 (m, 1H), 3.16 – 3.04 (m, 2H), 2.66 (td, *J* = 12.0, 11.5, 5.1 Hz, 1H), 2.56 (td, *J* = 12.0, 5.4 Hz, 1H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 148.2, 140.9, 137.8, 137.4, 129.2, 128.9, 128.7, 128.1, 126.8, 126.5, 47.5, 38.3, 38.0, 35.2, 18.8.

HRMS (ESI): exact mass calculated for $C_{20}H_{21}N_2O_3S$ $[M + H]^+$: 369.1267, found 369.1262.



5n

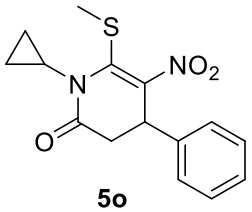
99% yield, white solid;

m.p. = 129 – 130 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 3H), 7.17 – 7.11 (m, 2H), 4.75 (dd, *J* = 5.6, 3.8 Hz, 1H), 4.22 – 4.12 (m, 1H), 3.67 – 3.57 (m, 1H), 3.14 – 3.01 (m, 2H), 2.38 (s, 3H), 1.37 – 1.30 (m, 2H), 1.23 – 1.16 (m, 2H), 1.14 – 1.05 (m, 2H), 0.80 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 149.2, 140.7, 137.4, 129.1, 127.9, 126.5, 46.2, 38.1, 37.9, 28.9, 22.3, 18.7, 13.9.

HRMS (ESI): exact mass calculated for $C_{17}H_{23}N_2O_3S$ $[M + H]^+$: 335.1424, found 335.1417.



5o

80% yield, white solid;

m.p. = 121 – 122 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 3H), 7.05 – 7.00 (m, 2H), 4.93 (t, *J* = 4.2 Hz, 1H), 3.10 (d, *J* = 4.3 Hz, 2H), 2.94 – 2.89 (m, 1H), 2.52 (s, 3H), 0.99 – 0.94 (m, 2H), 0.84 – 0.78 (m, 1H), -0.02 – -0.10 (m, 1H).

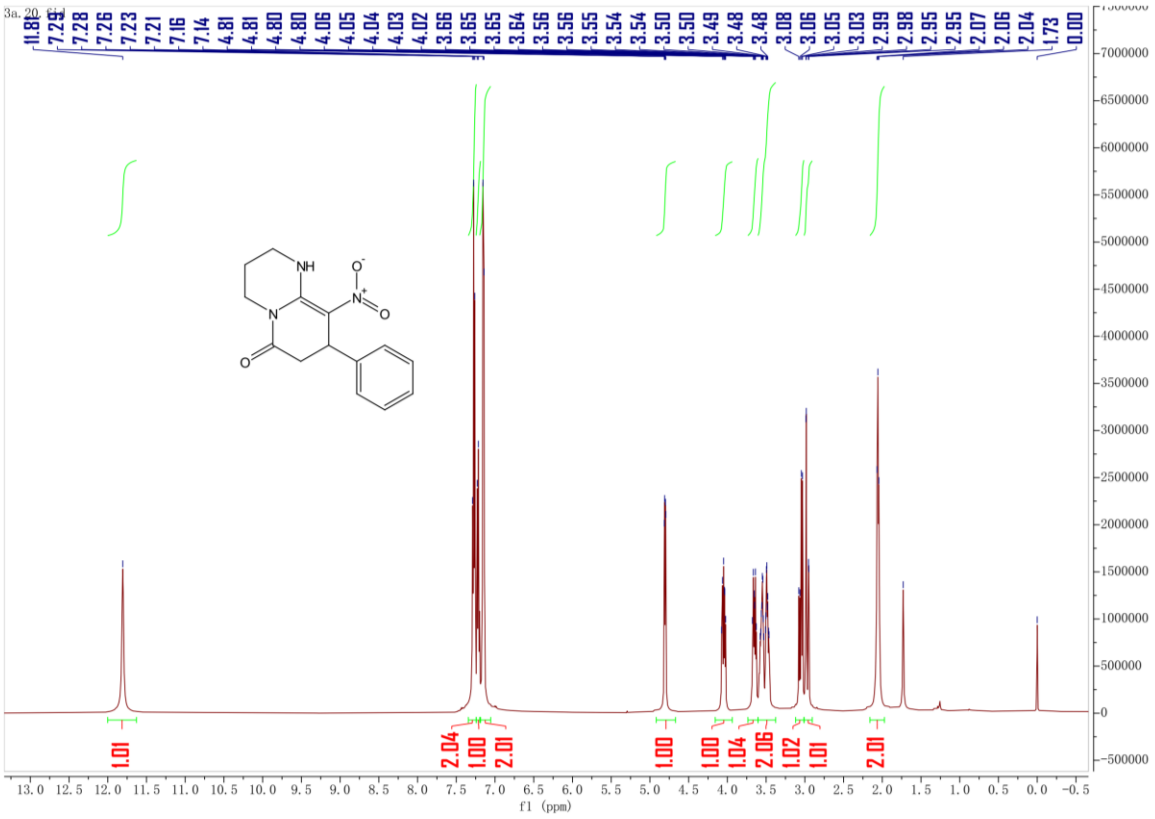
^{13}C NMR (126 MHz, $CDCl_3$) δ 171.2, 156.6, 138.5, 137.4, 129.1, 127.9, 126.2, 38.3, 36.4, 30.6, 18.6, 11.4, 9.1.

HRMS (ESI): exact mass calculated for $C_{15}H_{17}N_2O_3S$ $[M + H]^+$: 305.0954, found 305.0950.

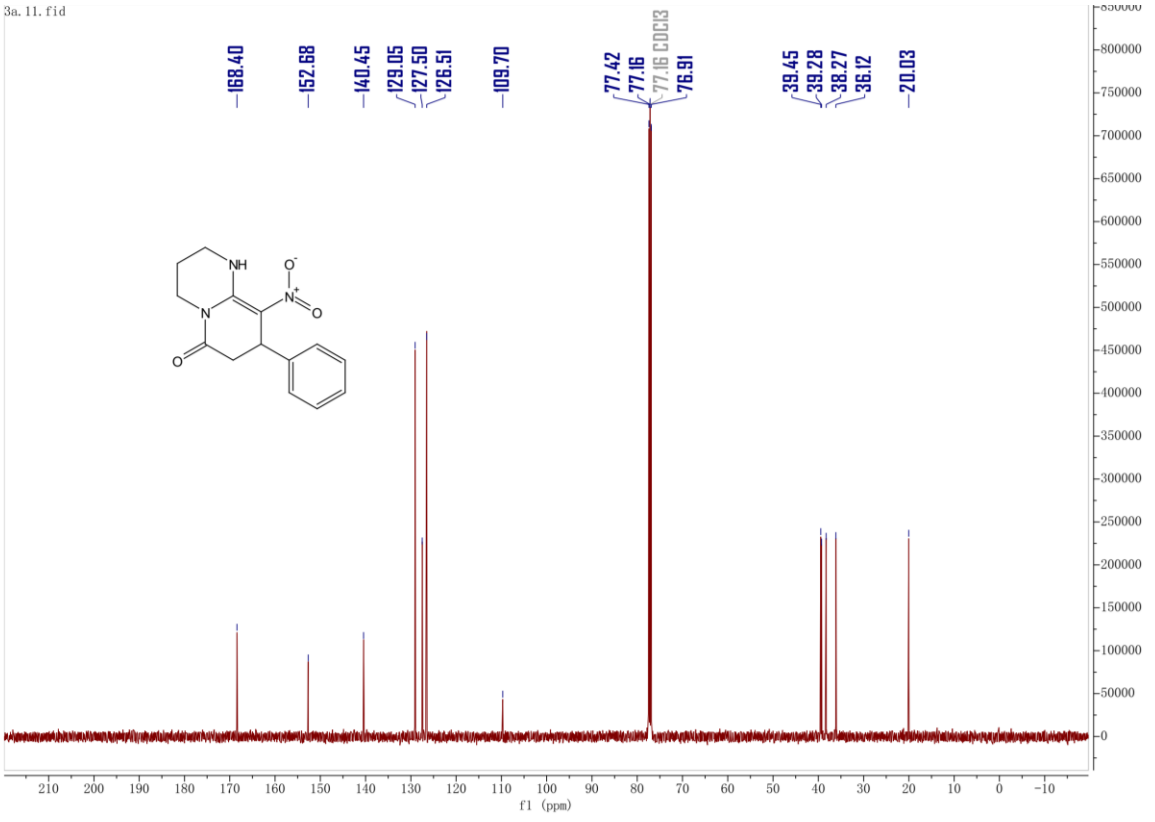
8. Reference

1. (a) E. Safari, A. Maryamabadi and A. Hasaninejad, Highly efficient, one-pot synthesis of novel bis-spirooxindoles with skeletal diversity via sequential multi-component reaction in PEG-400 as a biodegradable solvent, *RSC Adv.*, 2017, **7**, 39502; (b) C. Venkatesh, B. Singh, P. K. Mahata, H. Ila and H. Junjappa, Heteroannulation of nitroketene N,S-arylaminoacetals with $POCl_3$: a novel highly regioselective synthesis of unsymmetrical 2,3-substituted quinoxalines, *Org. Lett.*, 2005, **7**, 2169; (c) Q. X. Zi, C. L. Yang, K. Li, Q. Luo, J. Lin and S. J. Yan, Multicomponent Cascade Reaction by Metal-Free Aerobic Oxidation for Synthesis of Highly Functionalized 2-Amino-4-coumarinyl-5-arylpyrroles, *J. Org. Chem.*, 2020, **85**, 327.
2. M. Lang and J. Wang, N-Heterocyclic Carbene-Catalyzed Enantioselective *β*-Amination of *α*-Bromoenals Enabled by a Proton-Shuttling Strategy, *Eur. J. Org. Chem.*, 2018, **2018**, 2958.

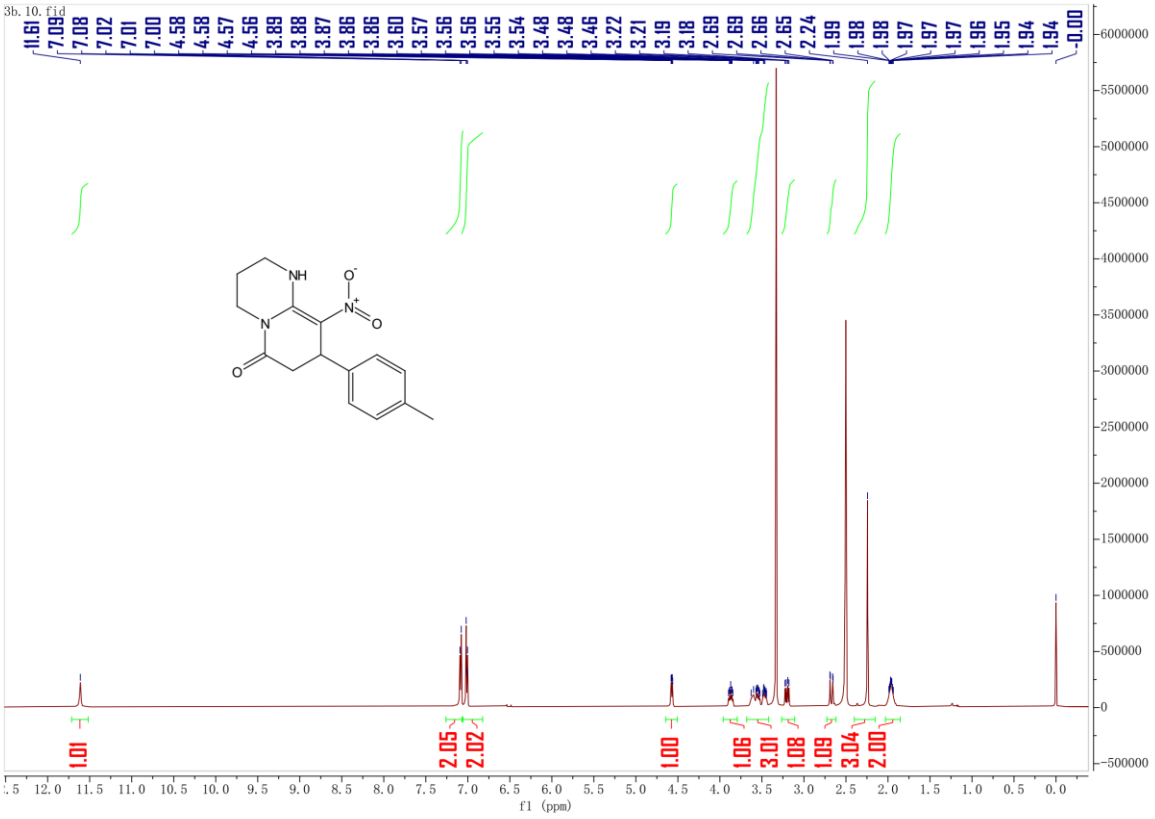
9. Copies of NMR spectra



^{1}H NMR spectrum of 3a



^{13}C NMR spectrum of 3a



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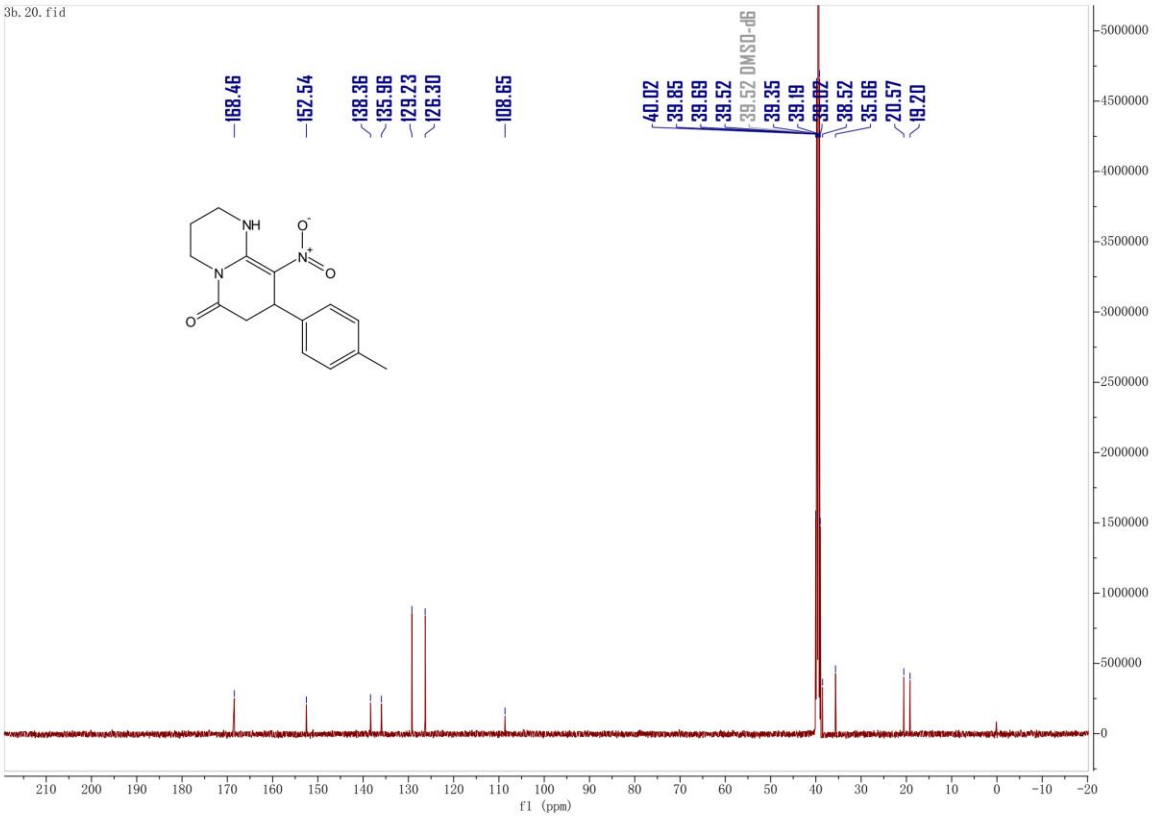

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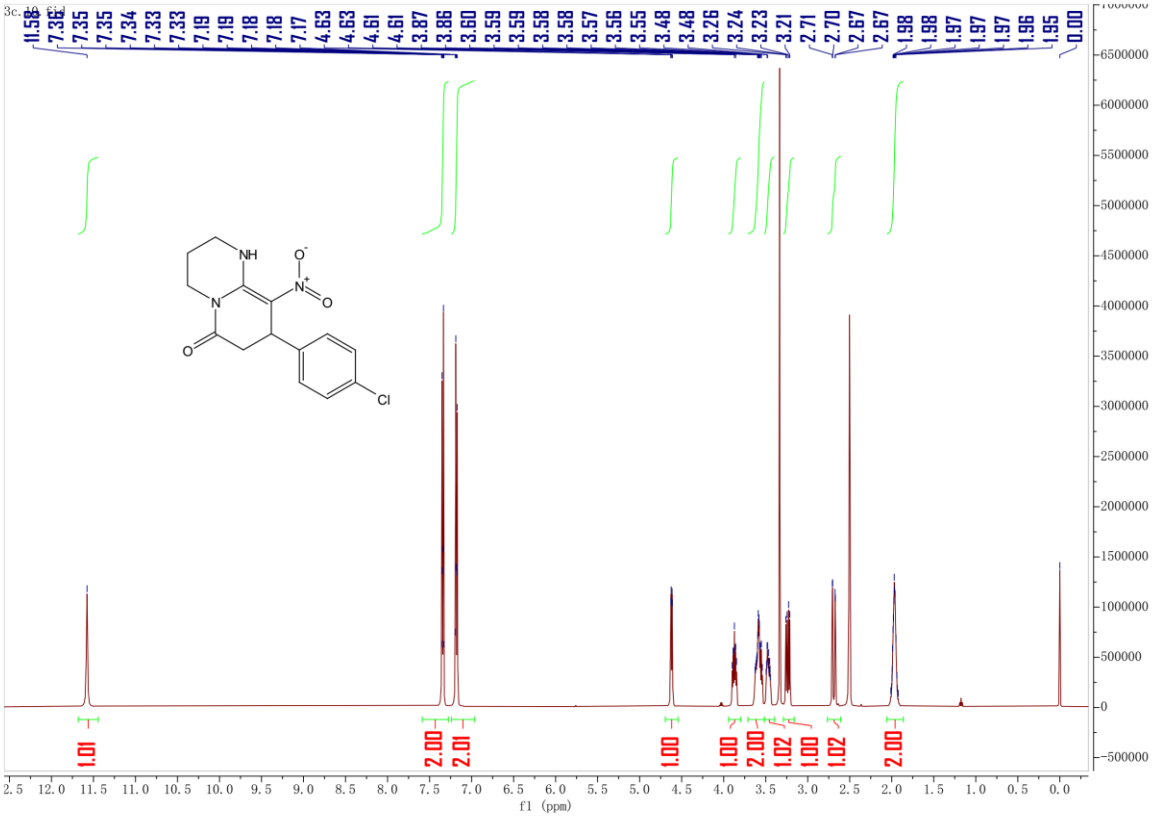

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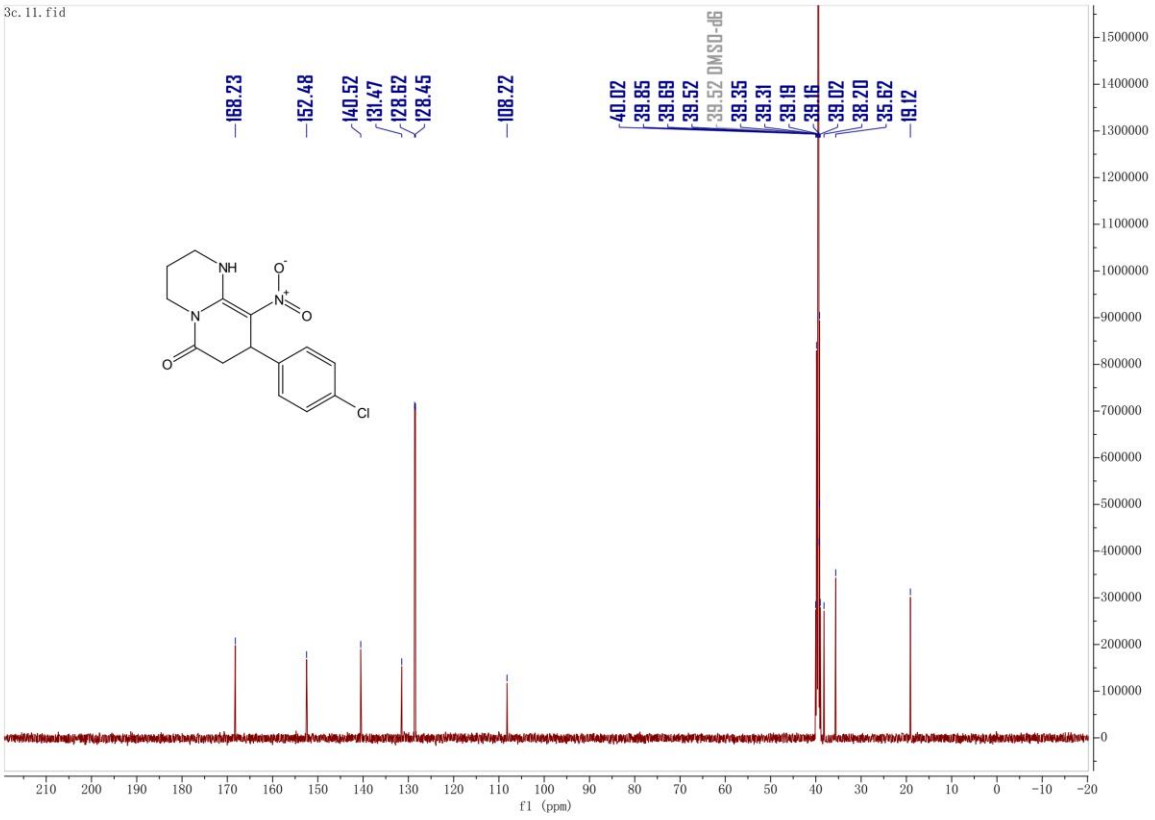

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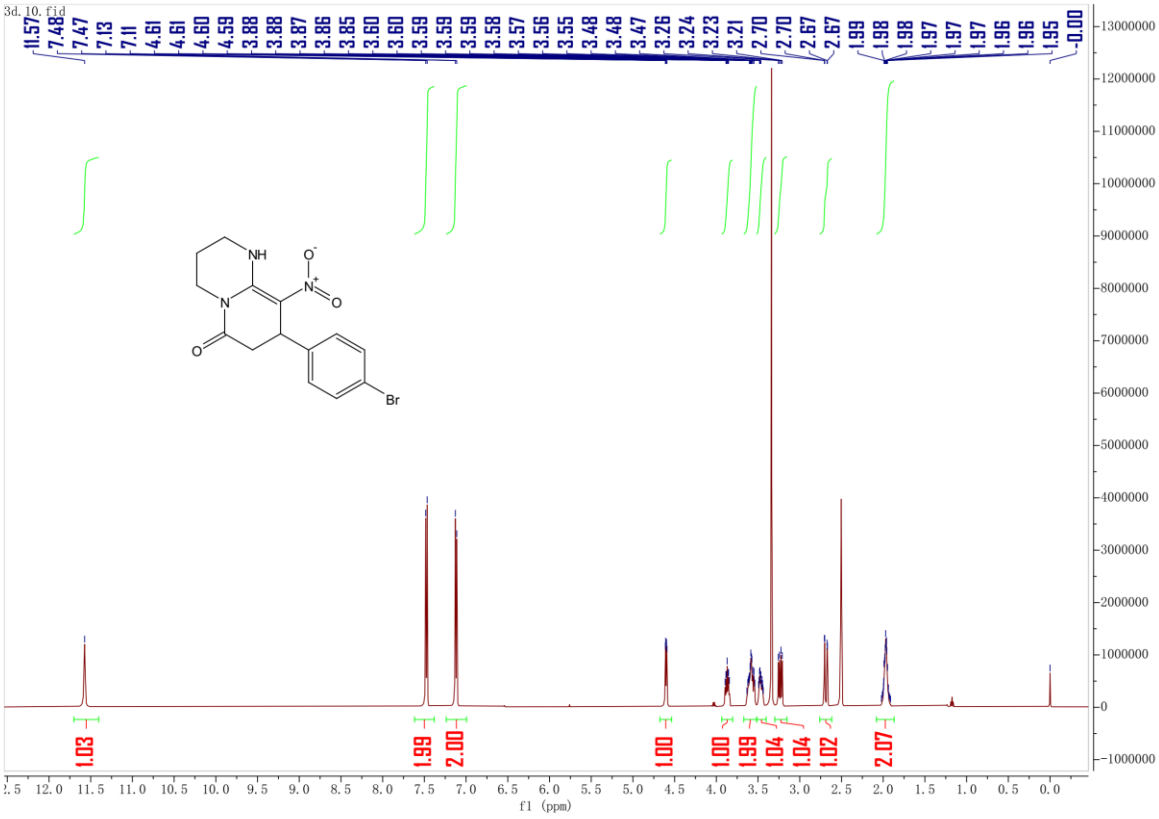

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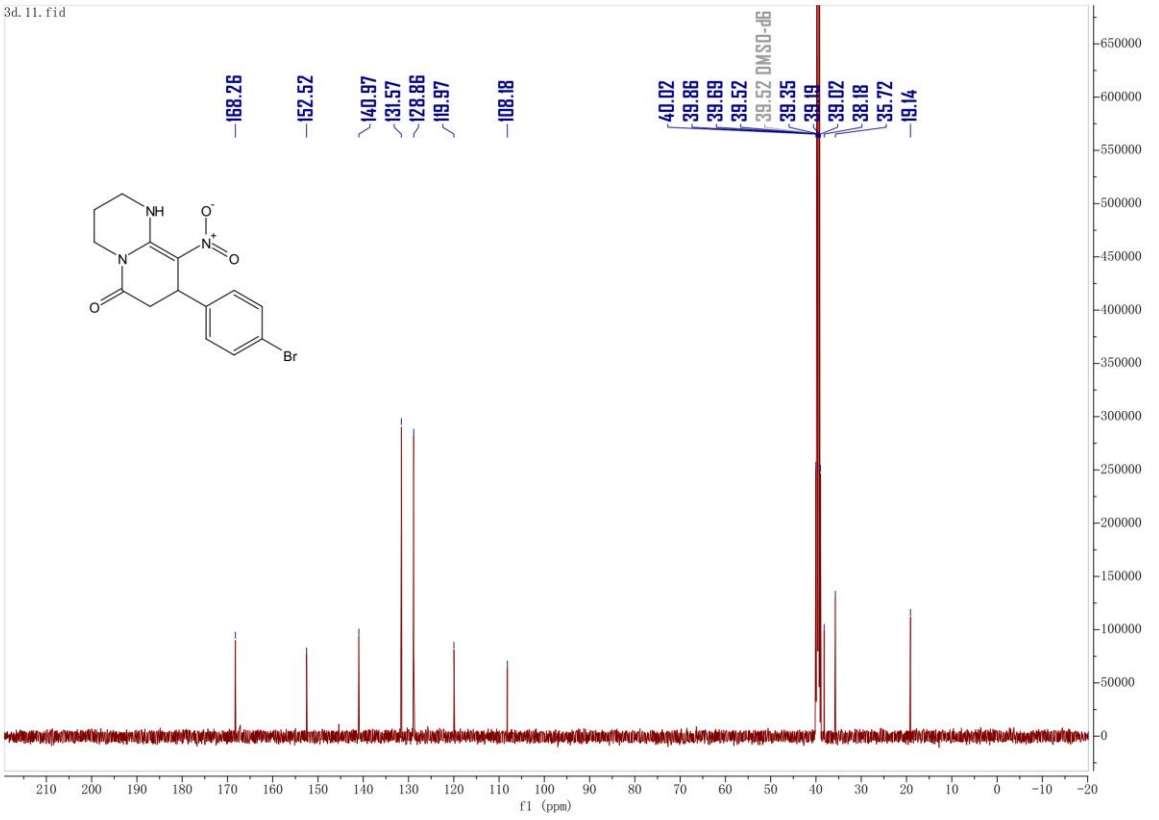

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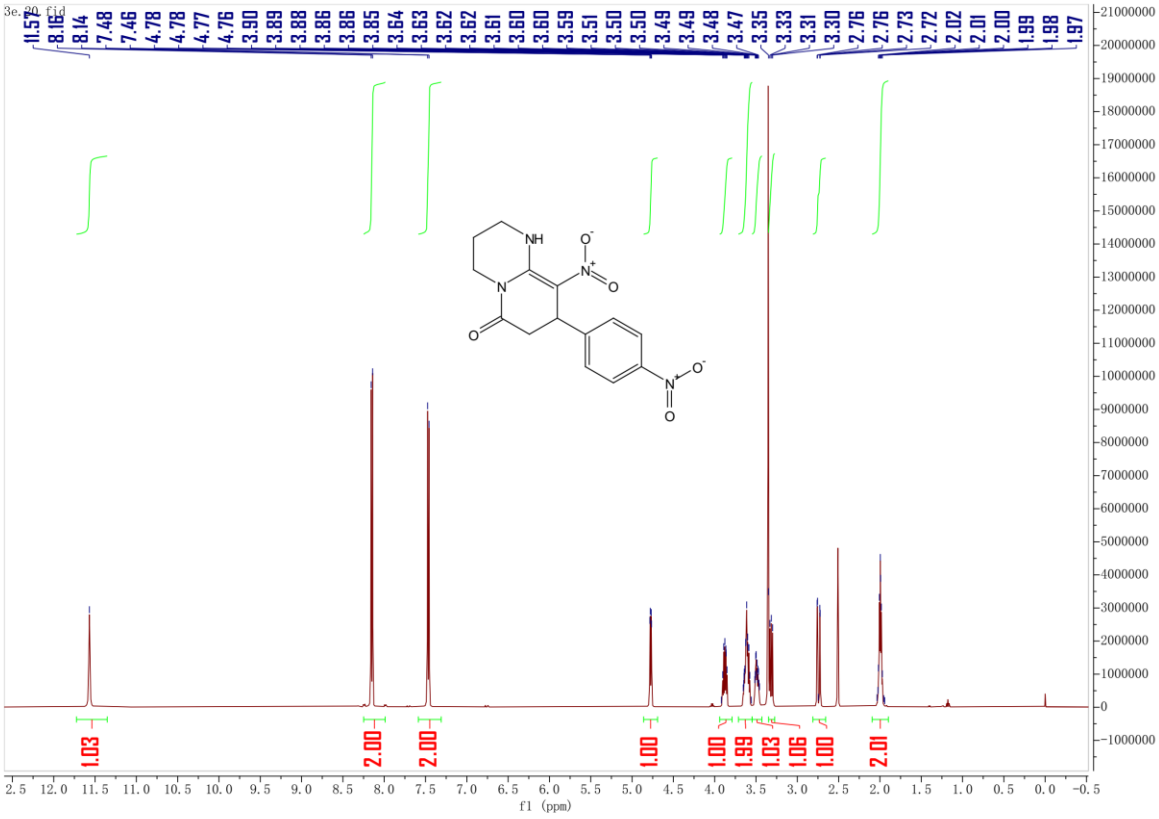
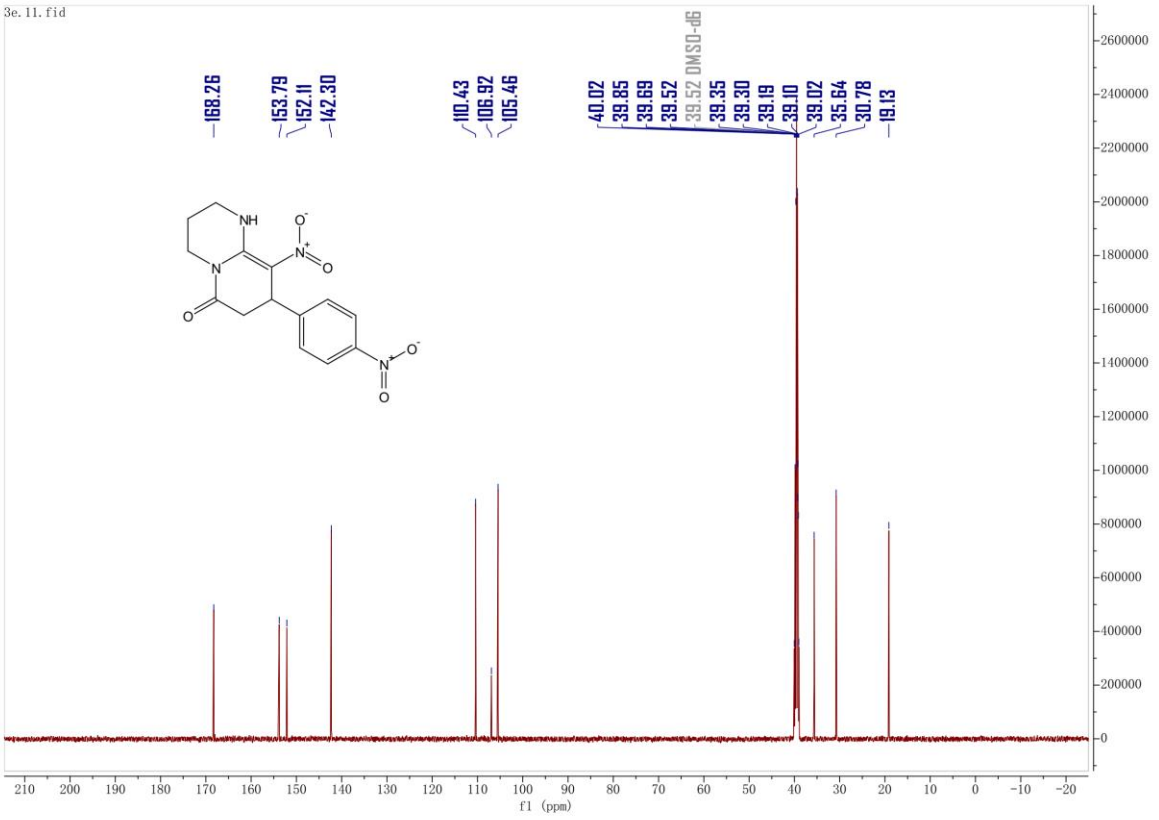


^{1}H NMR spectrum of 3e



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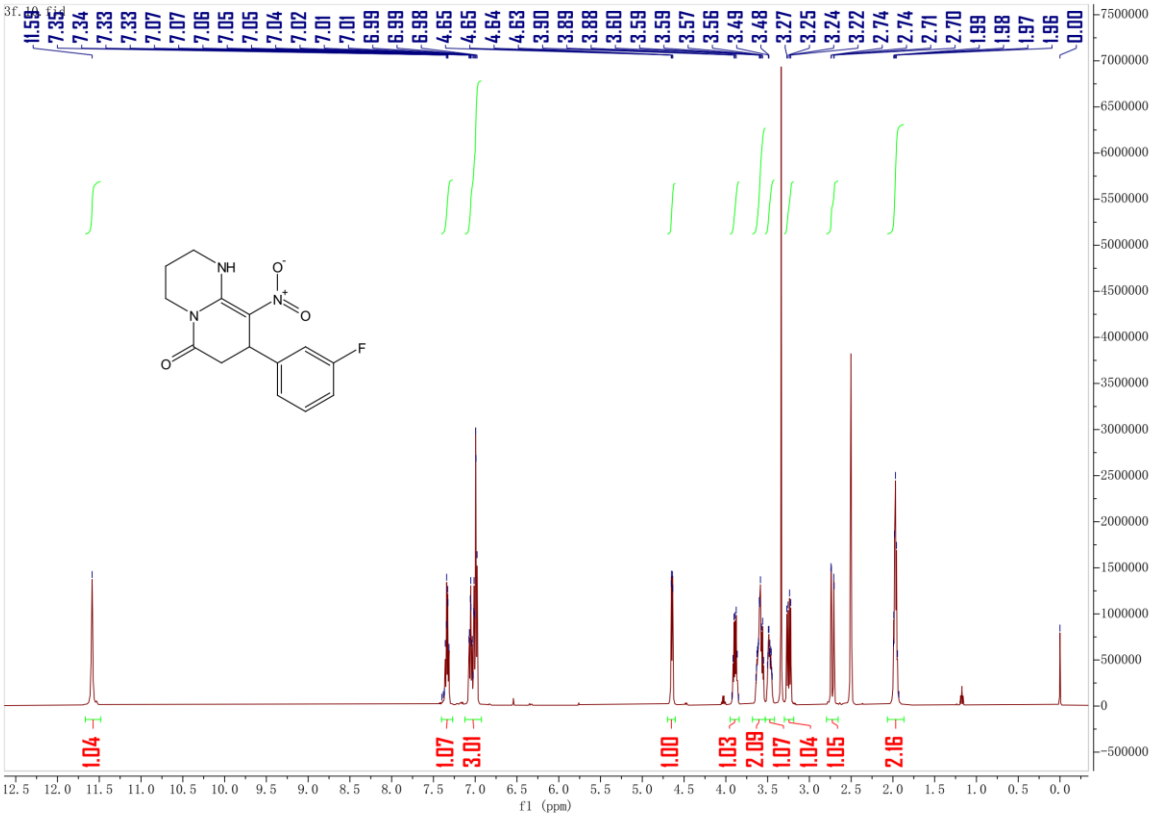

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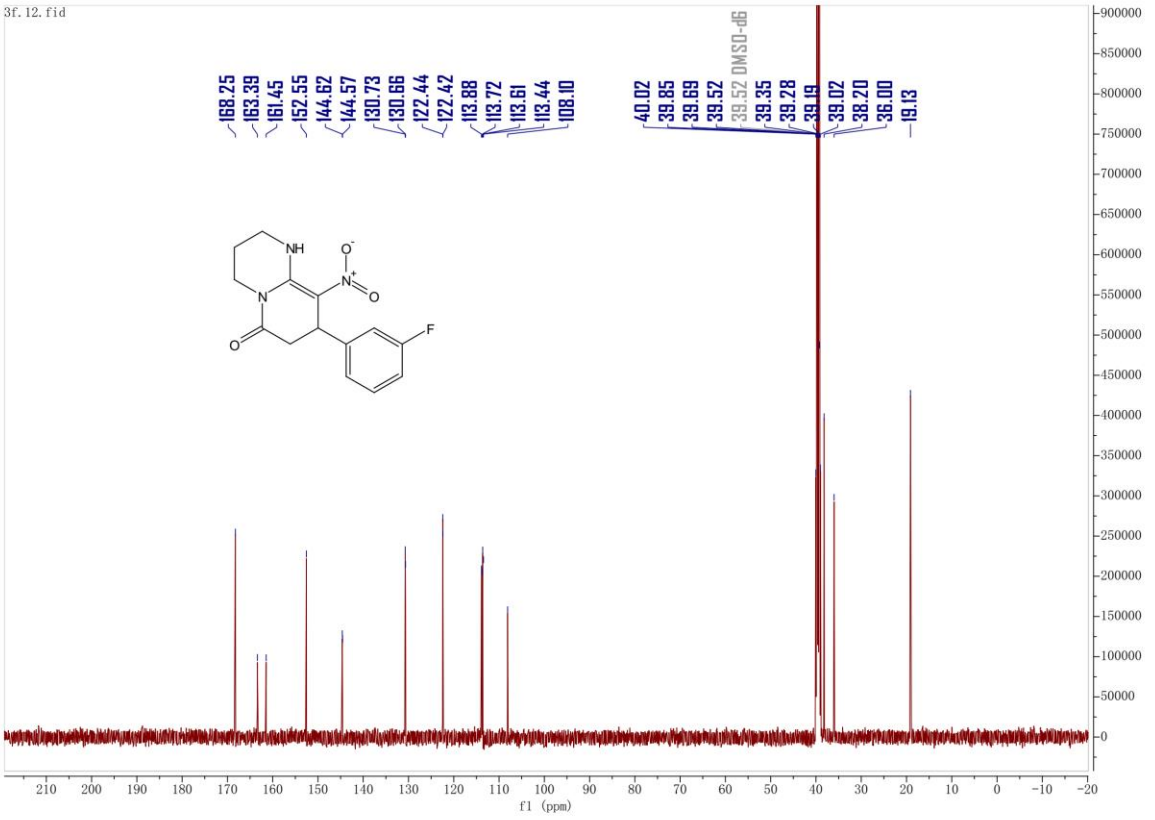
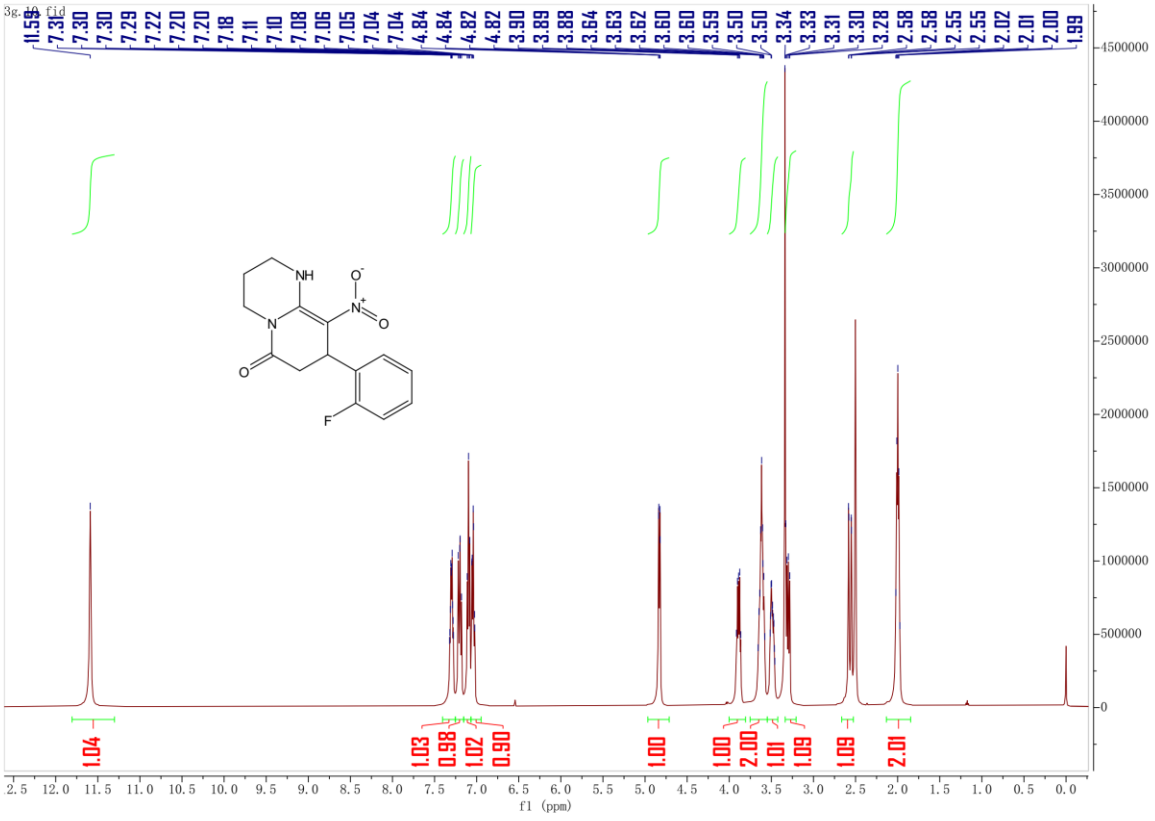


^{13}C NMR spectrum of 3f

^{19}F NMR spectrum of 3f



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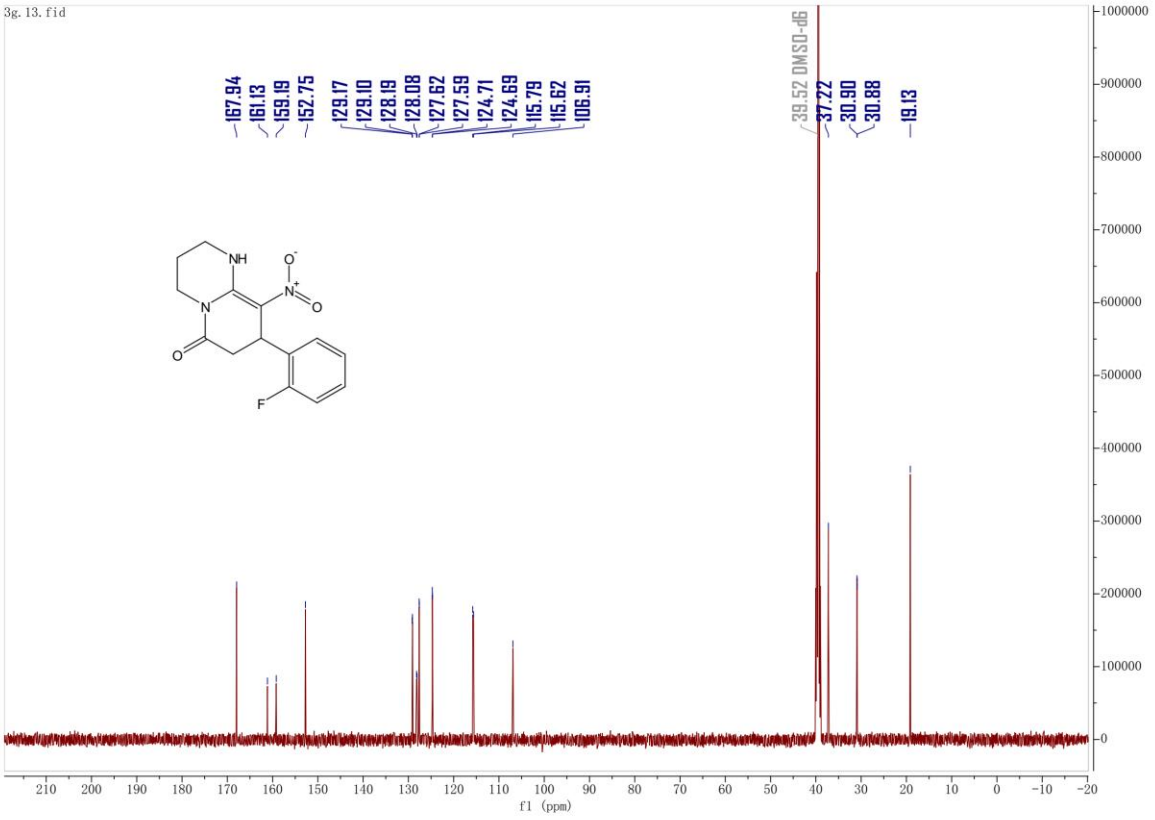

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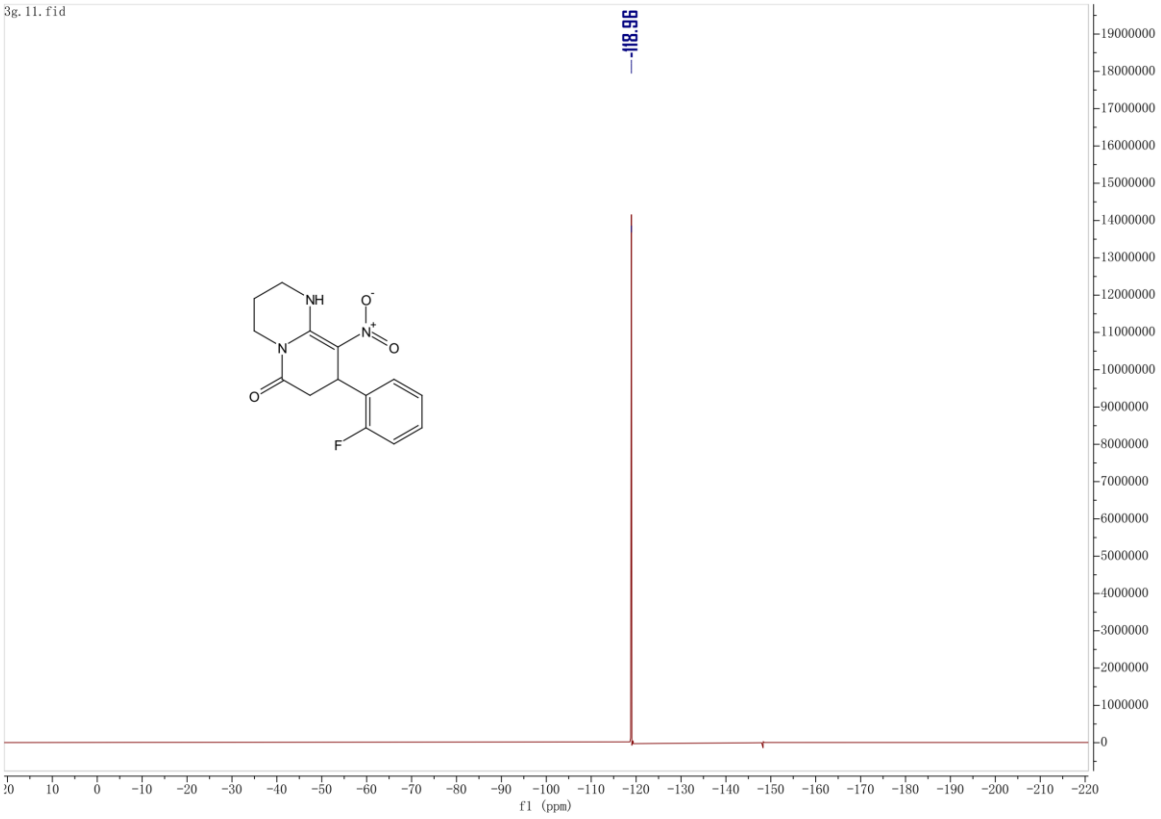

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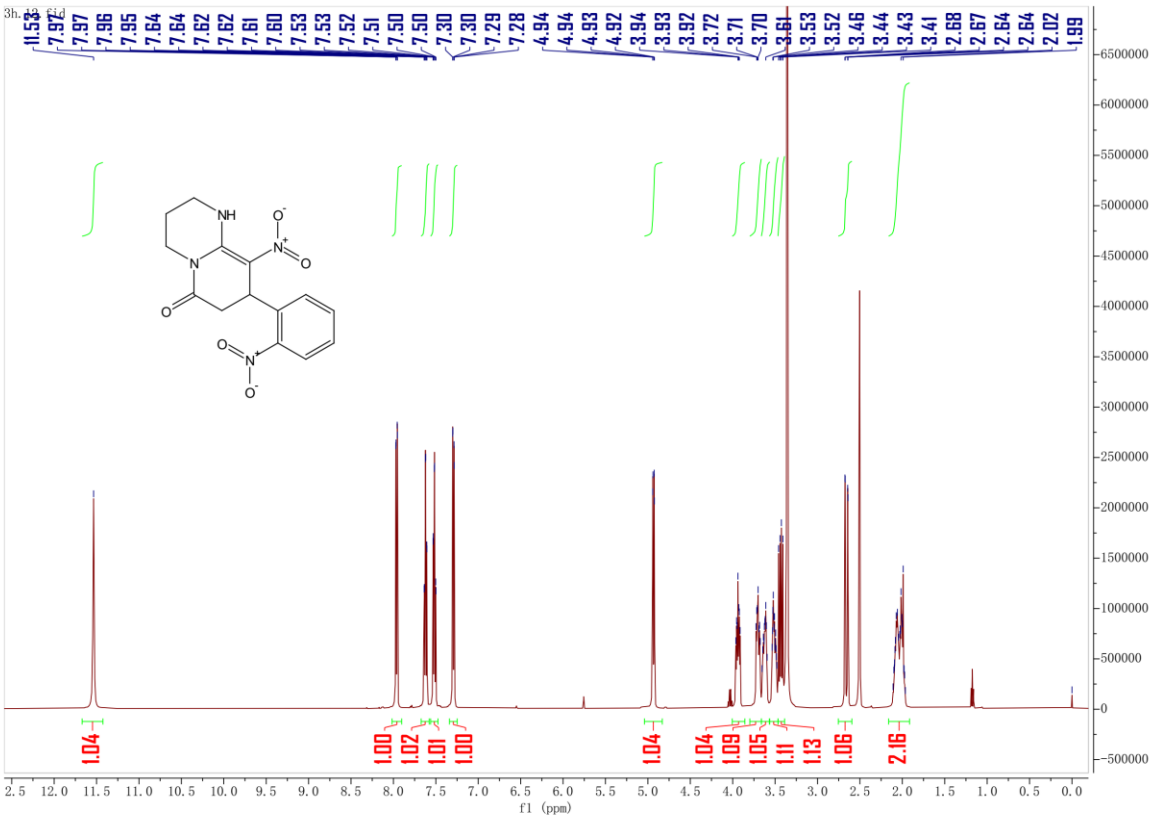
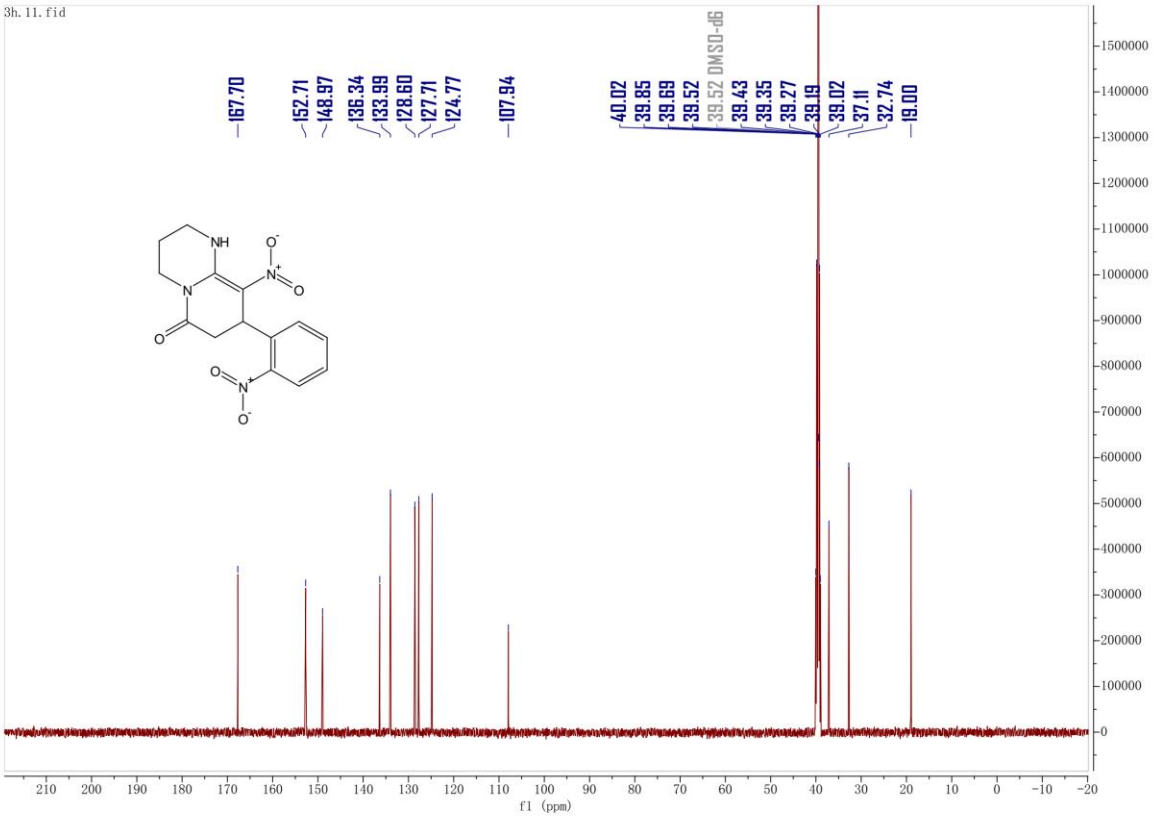
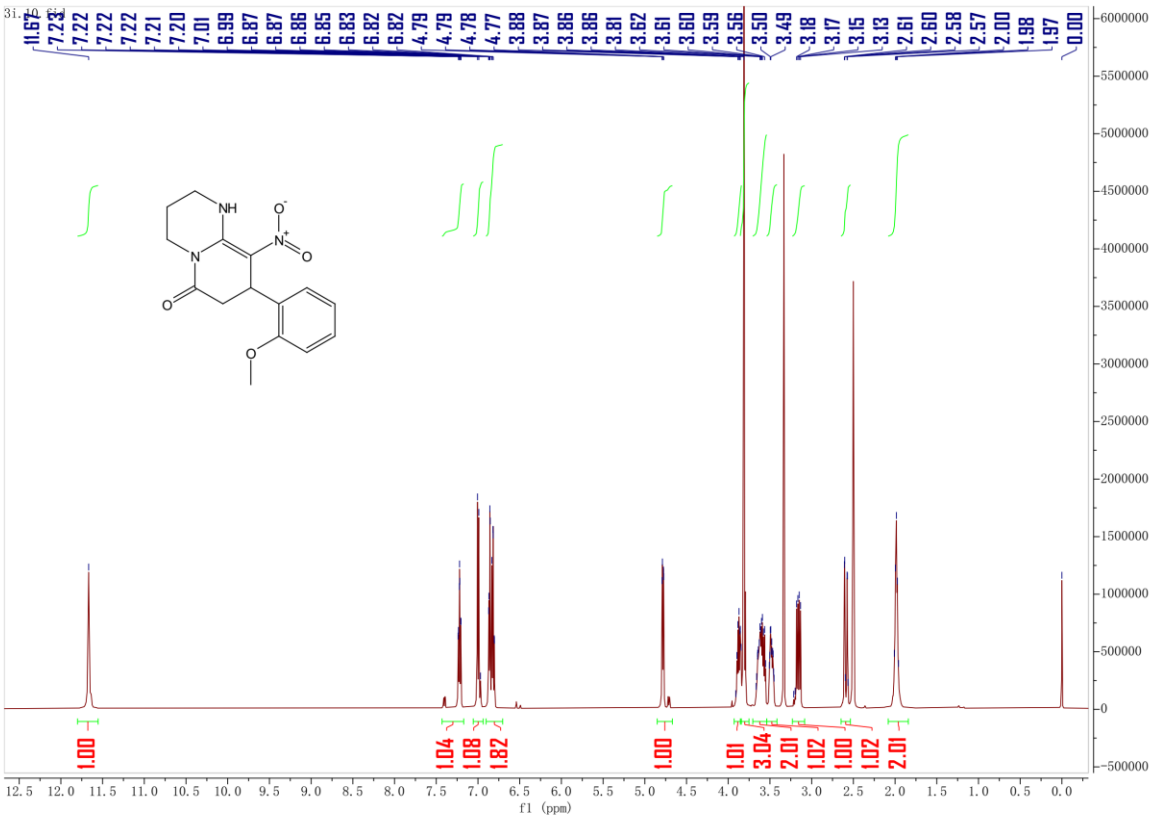


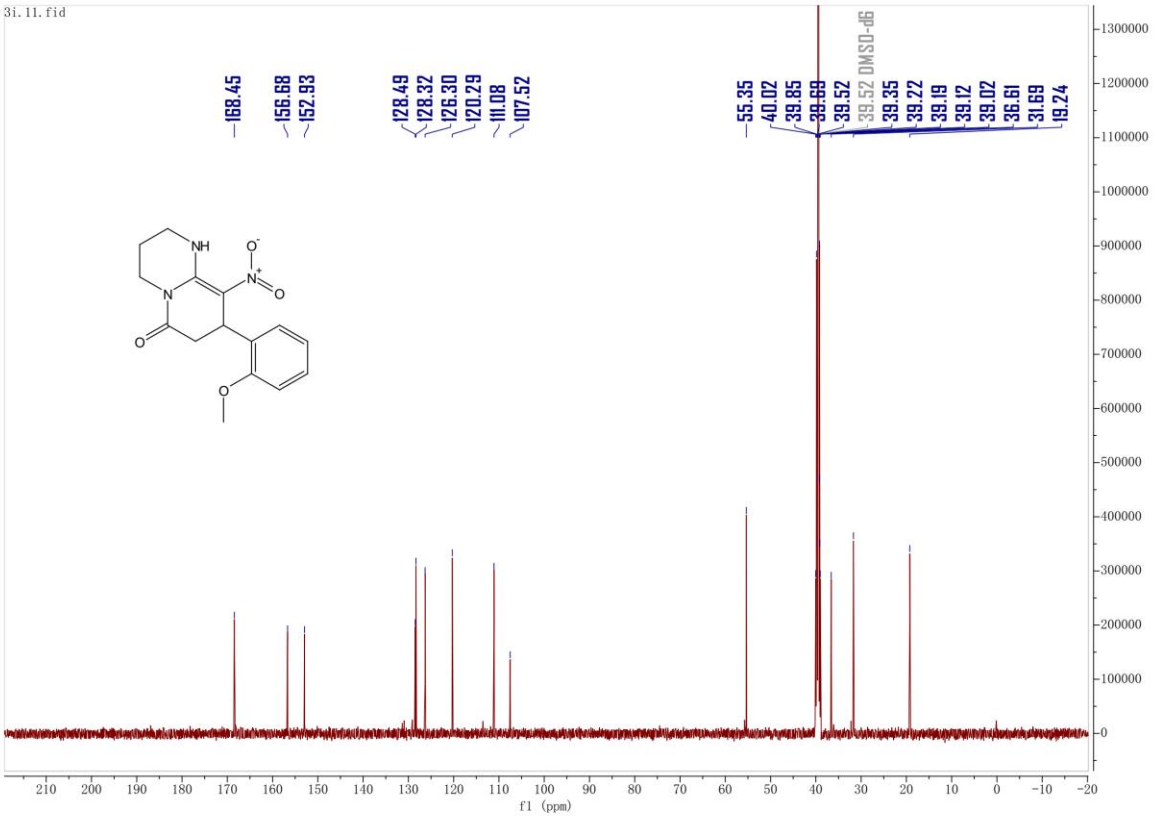
^{1}H NMR spectrum of 3h



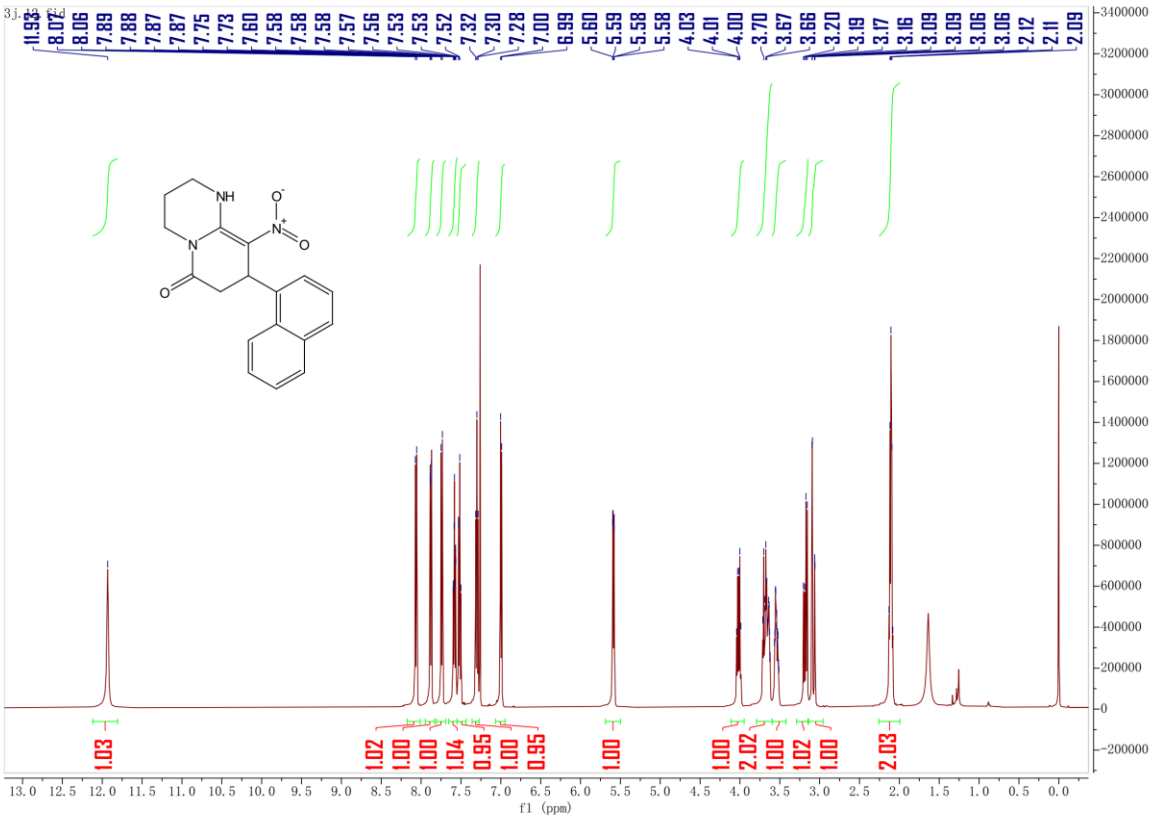
^{13}C NMR spectrum of 3h



^{1}H NMR spectrum of 3i



^{13}C NMR spectrum of 3i



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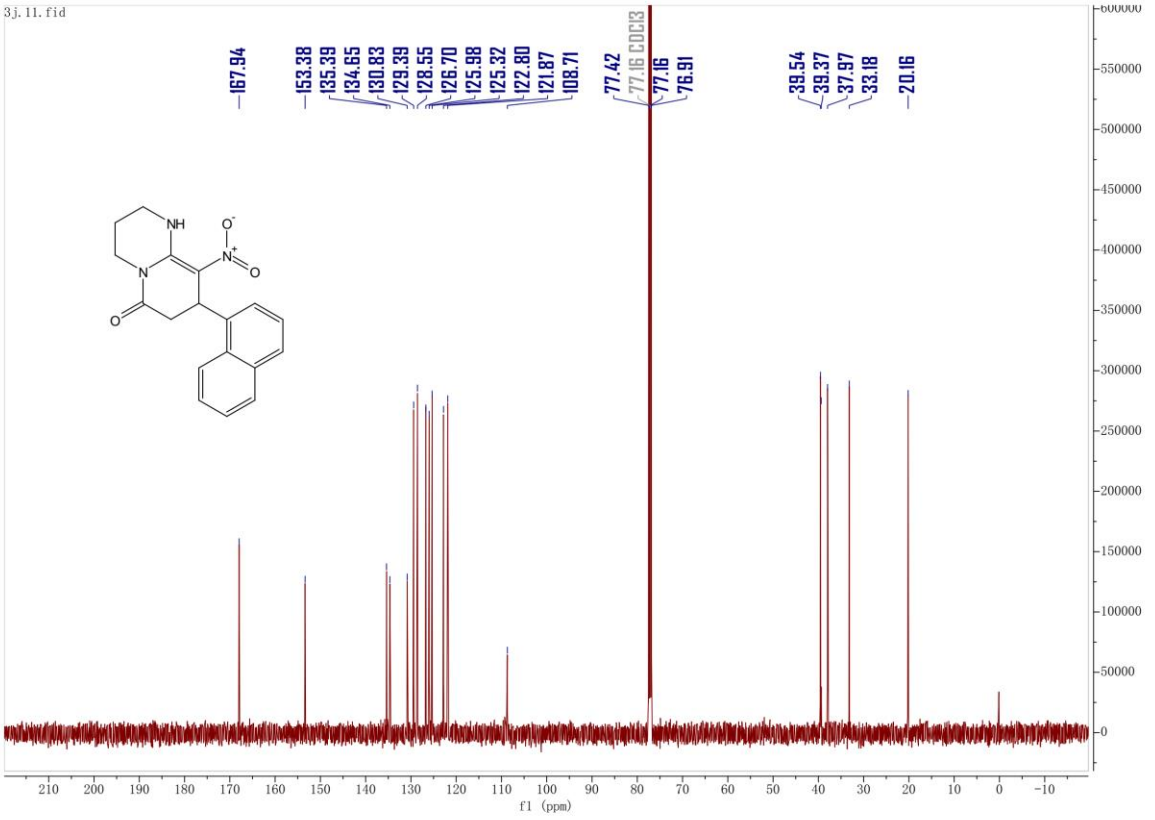

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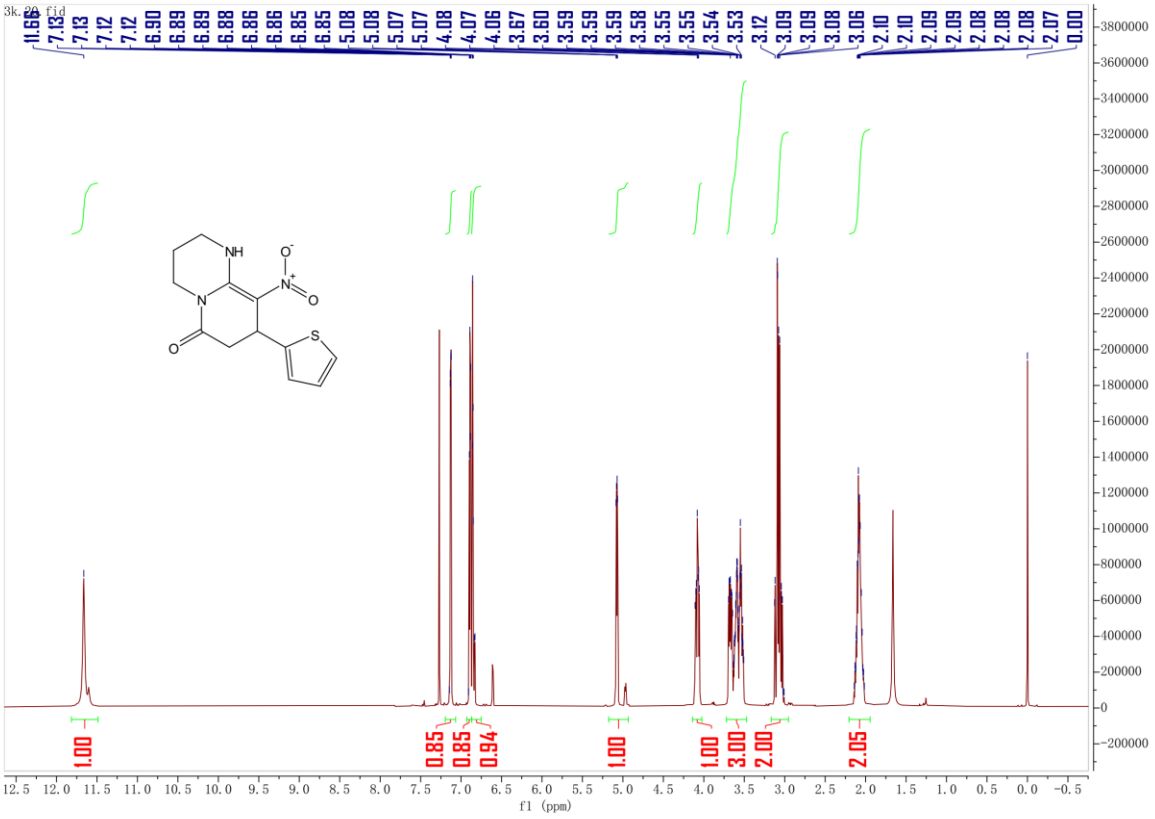

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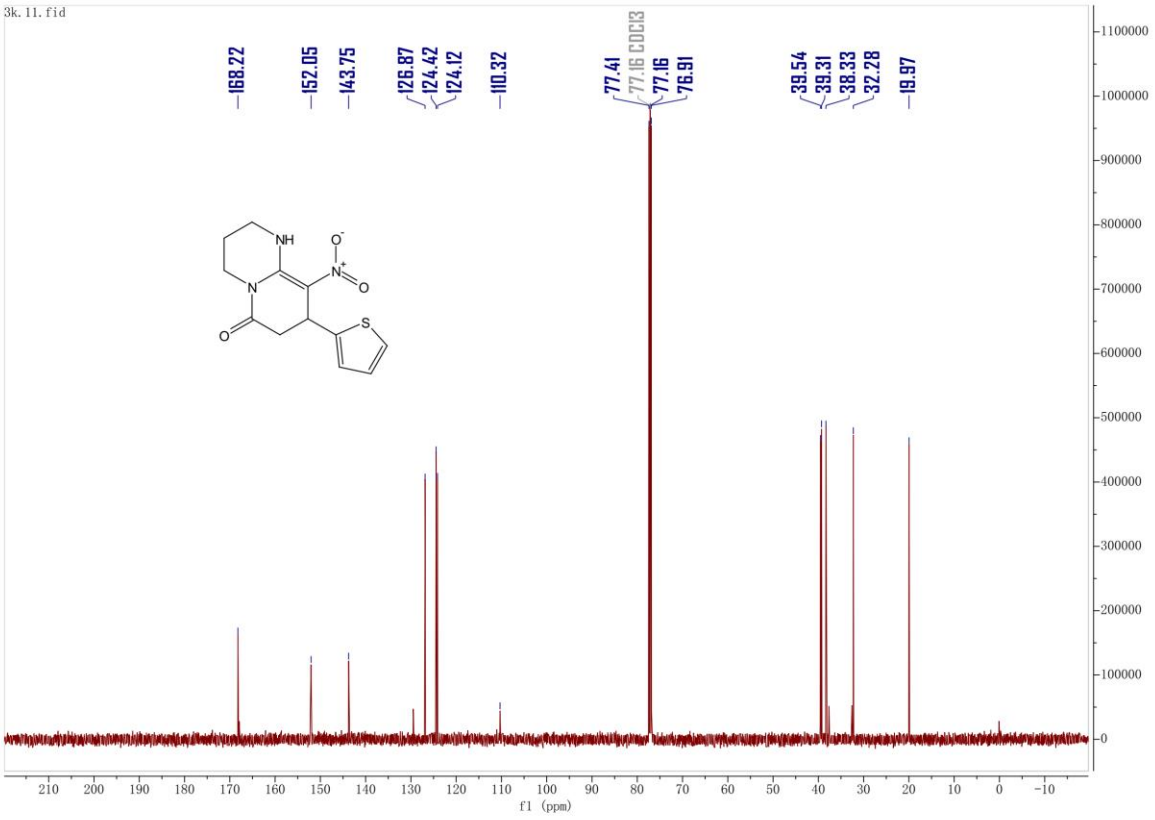
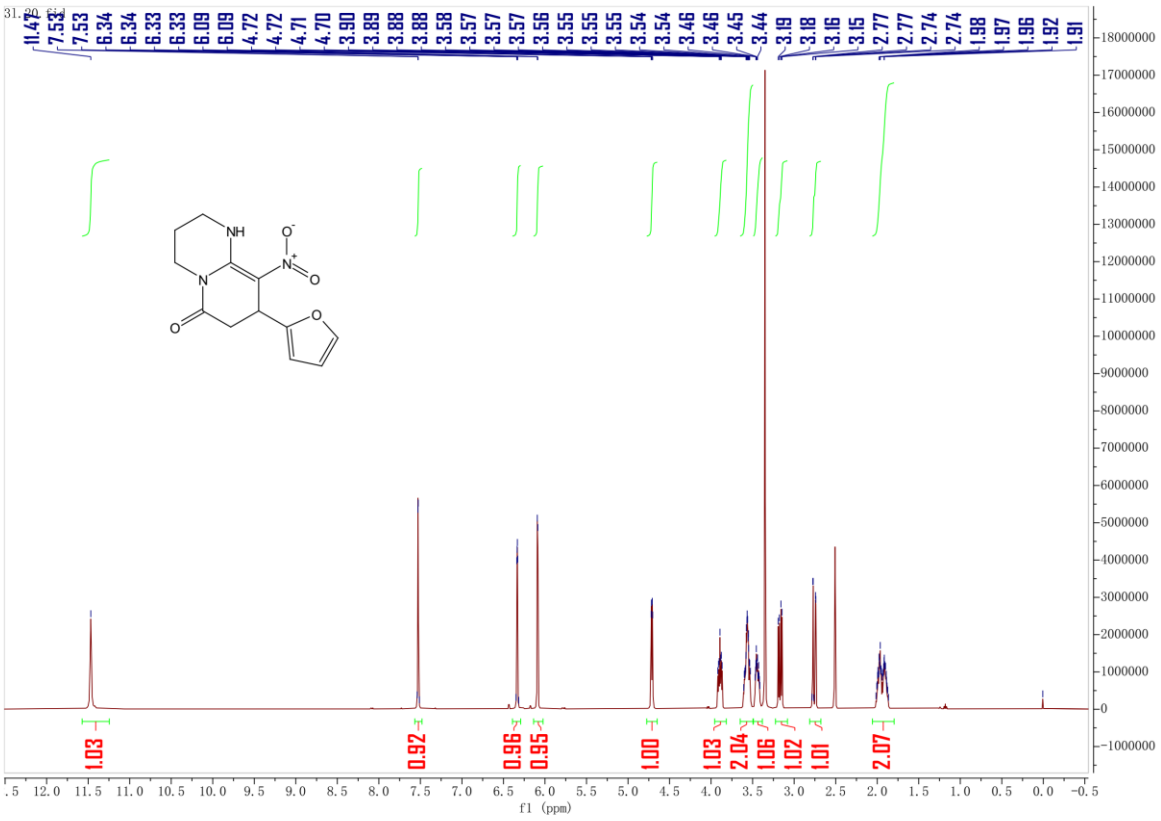


^{13}C NMR spectrum of 3k



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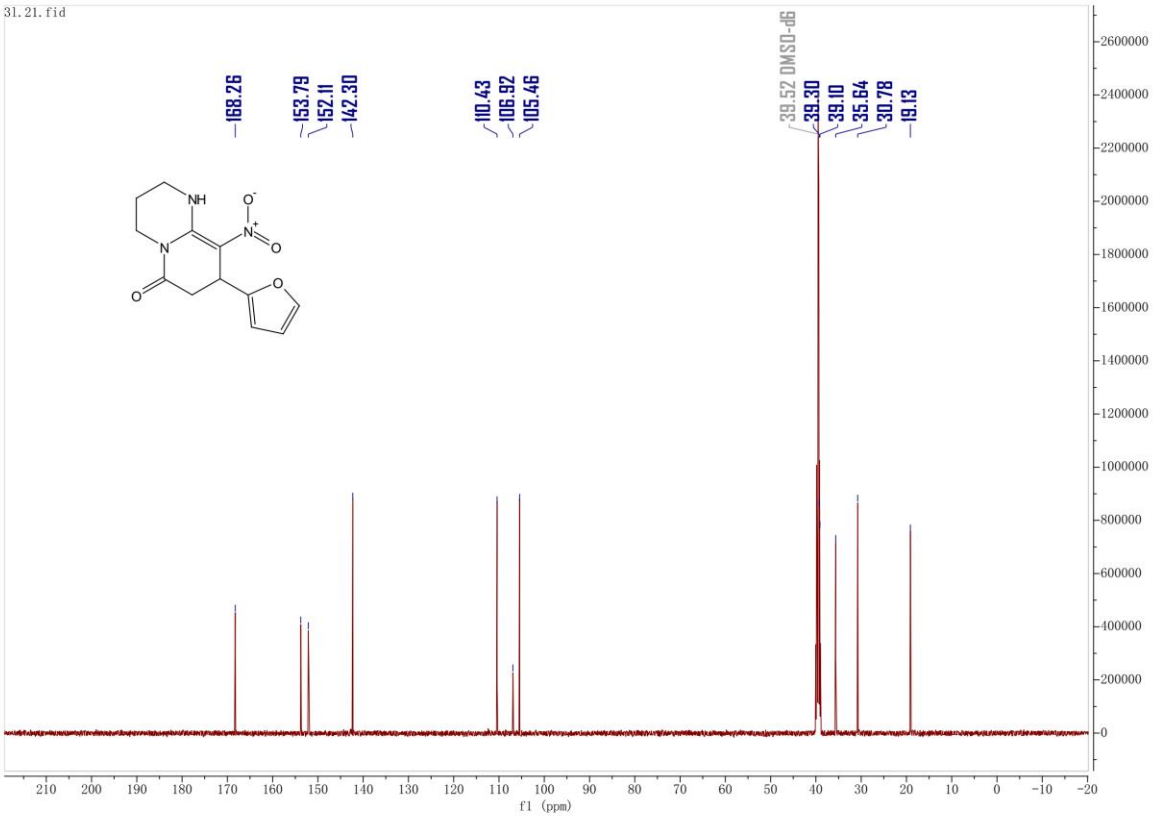
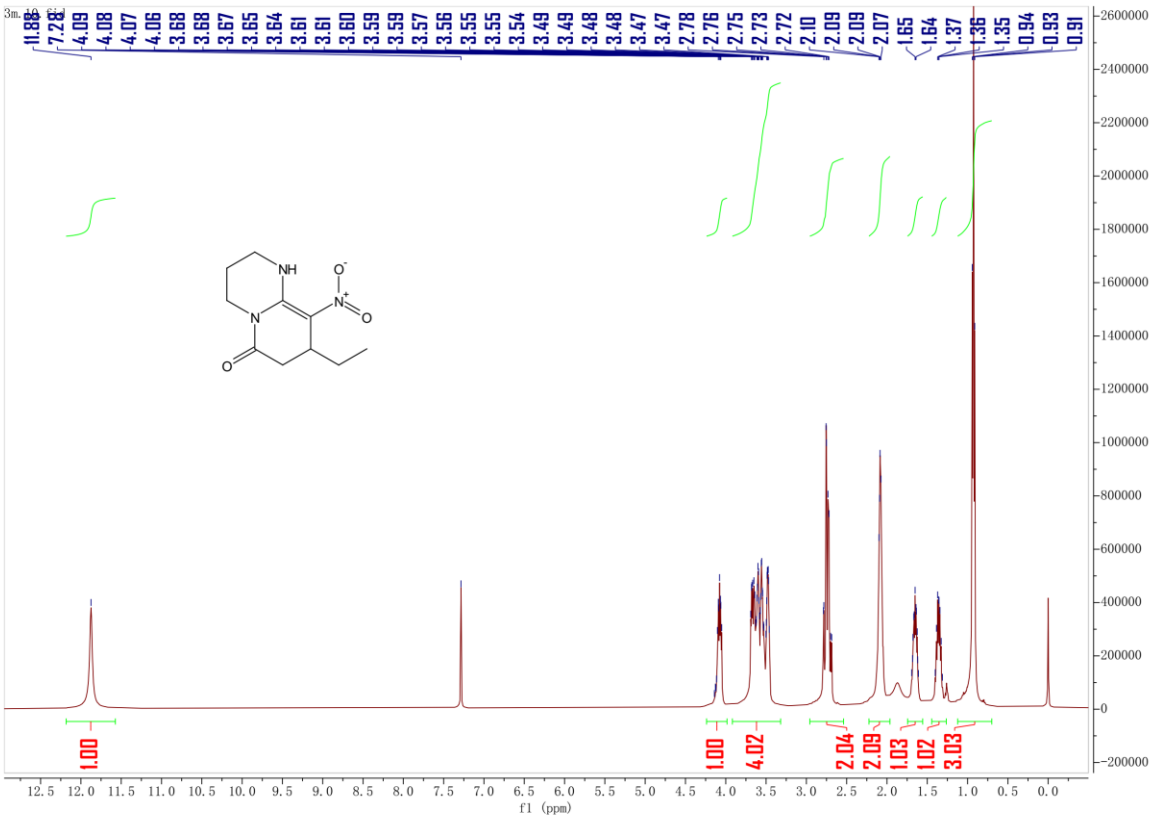


^{13}C NMR spectrum of 3l



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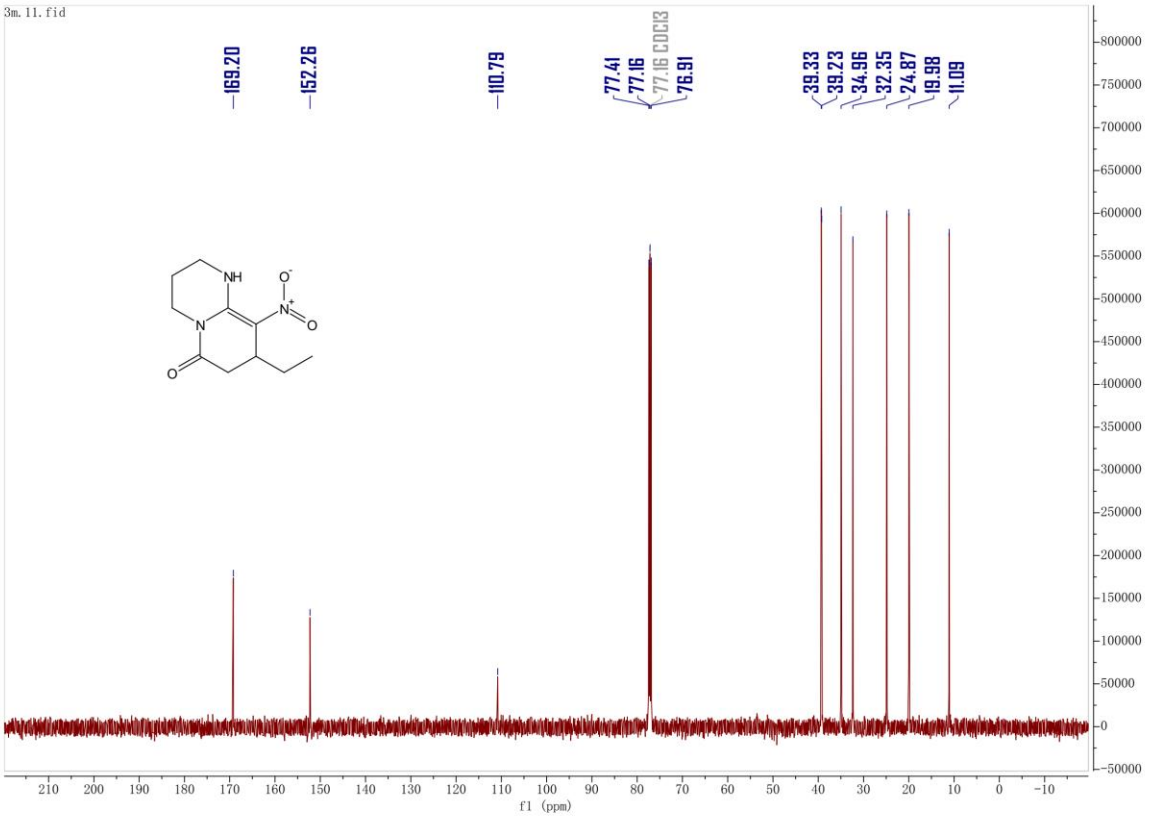
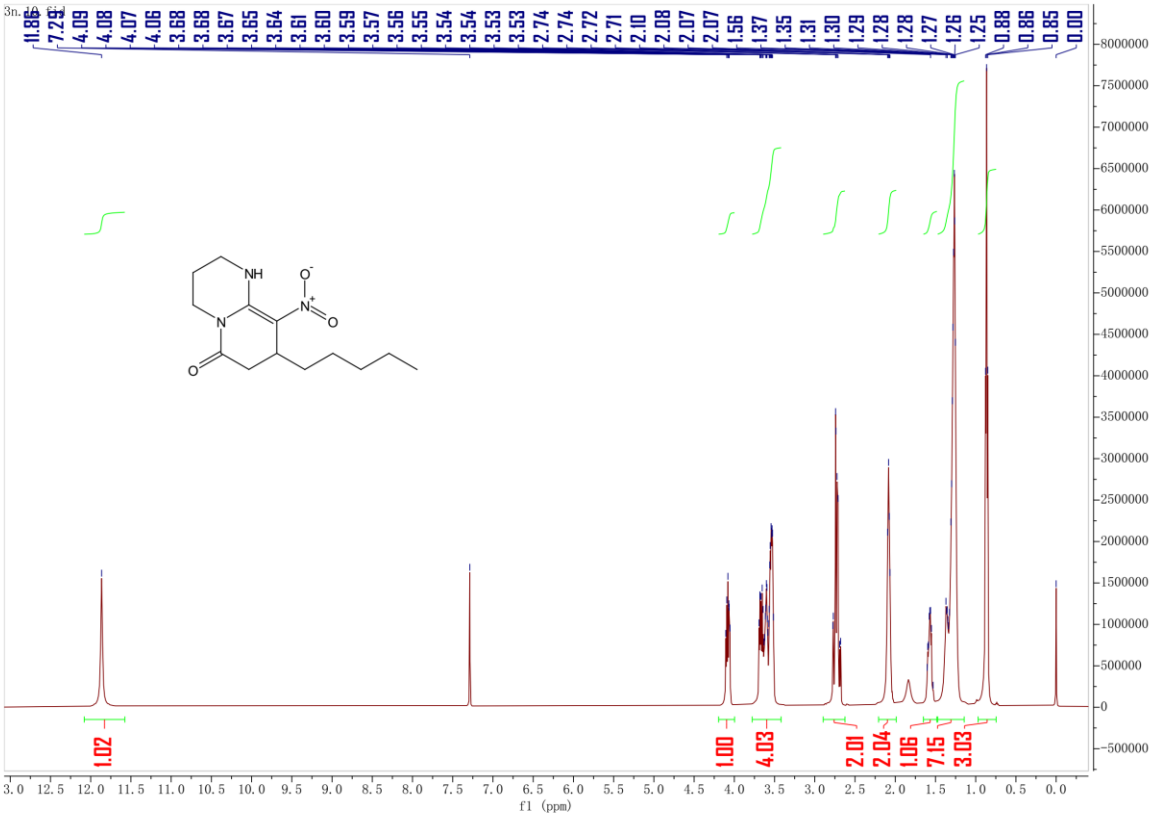
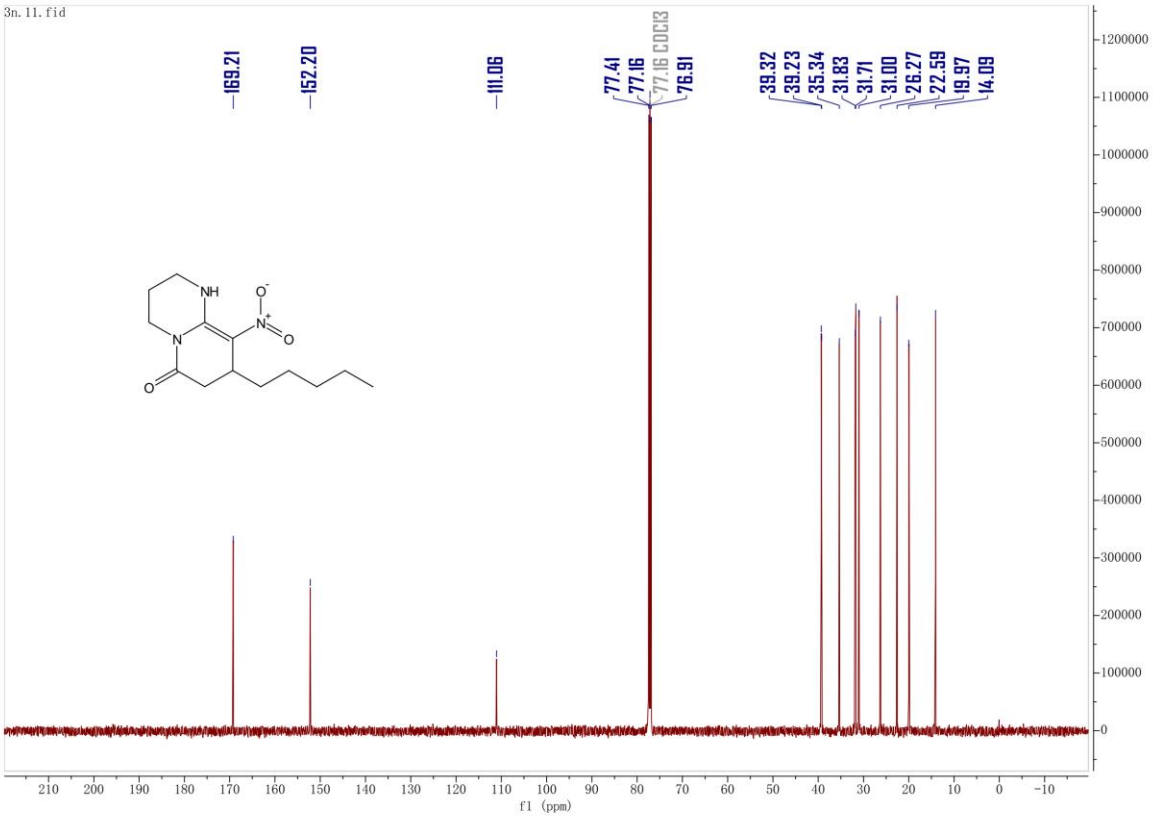


^{13}C NMR spectrum of 3m



^{1}H NMR spectrum of 3n



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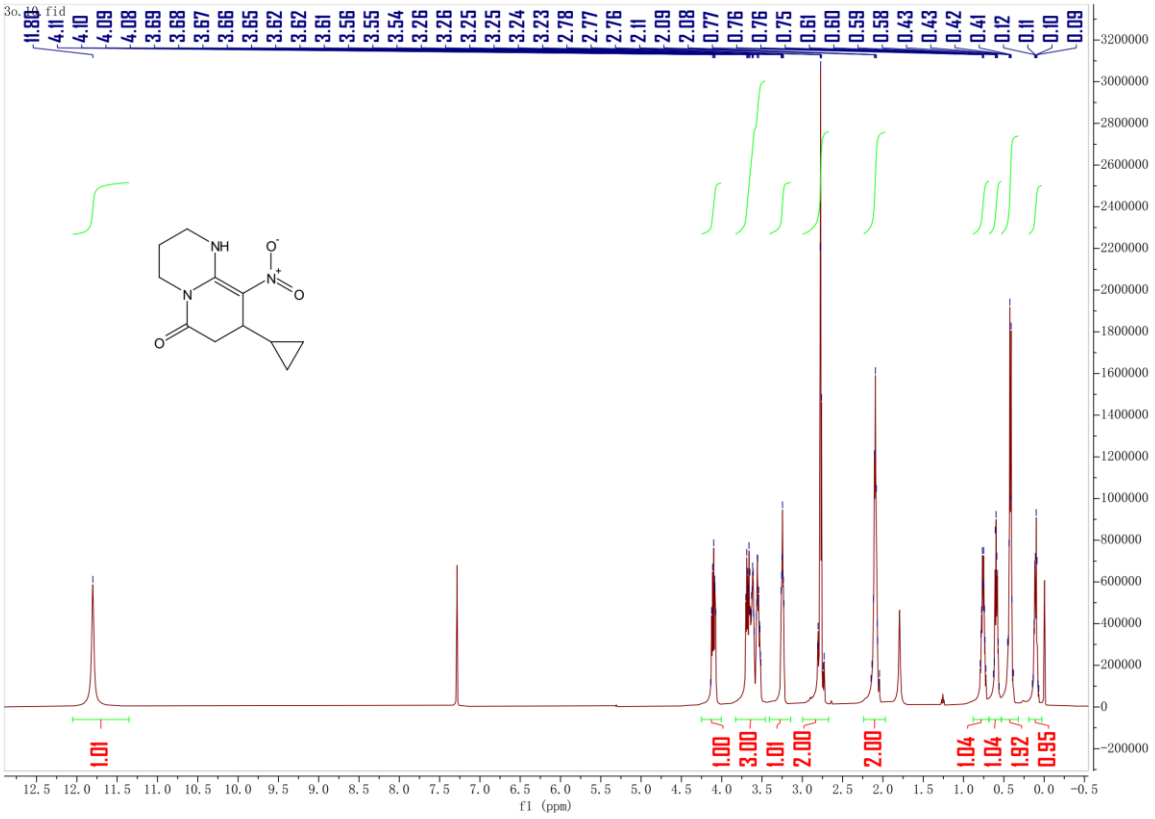

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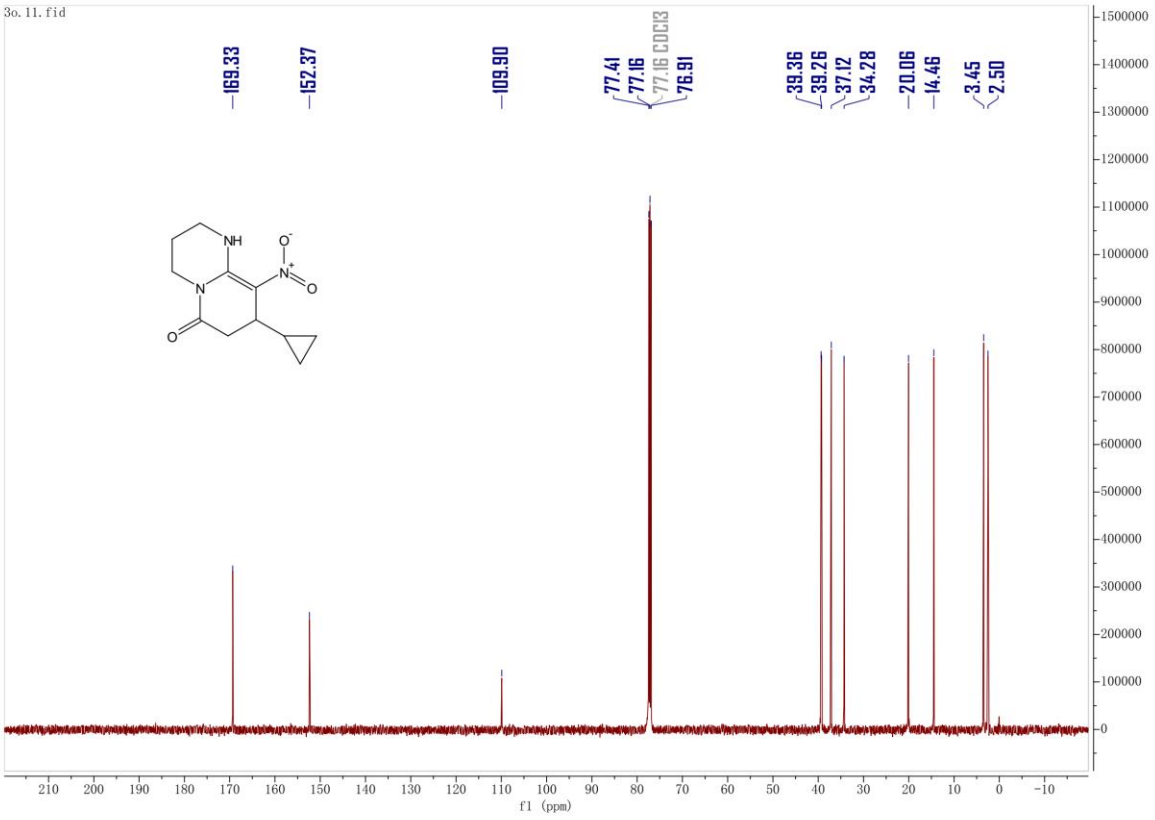

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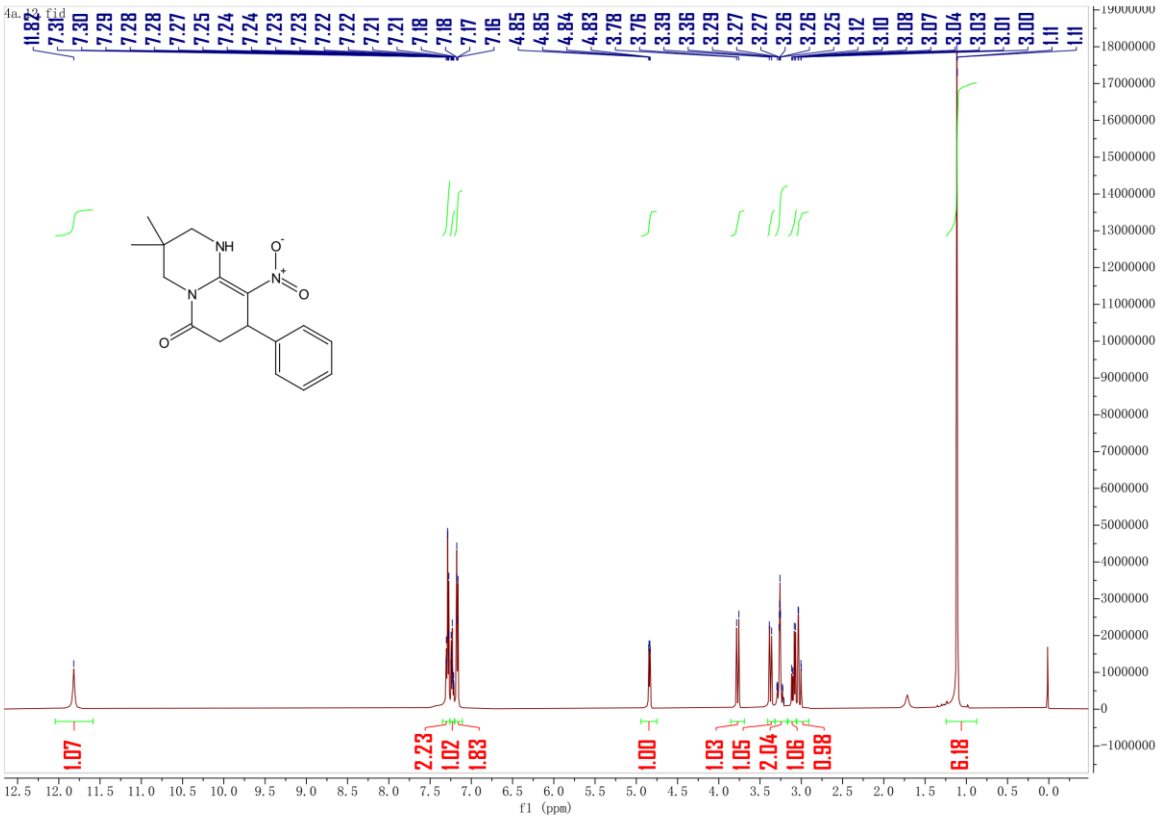

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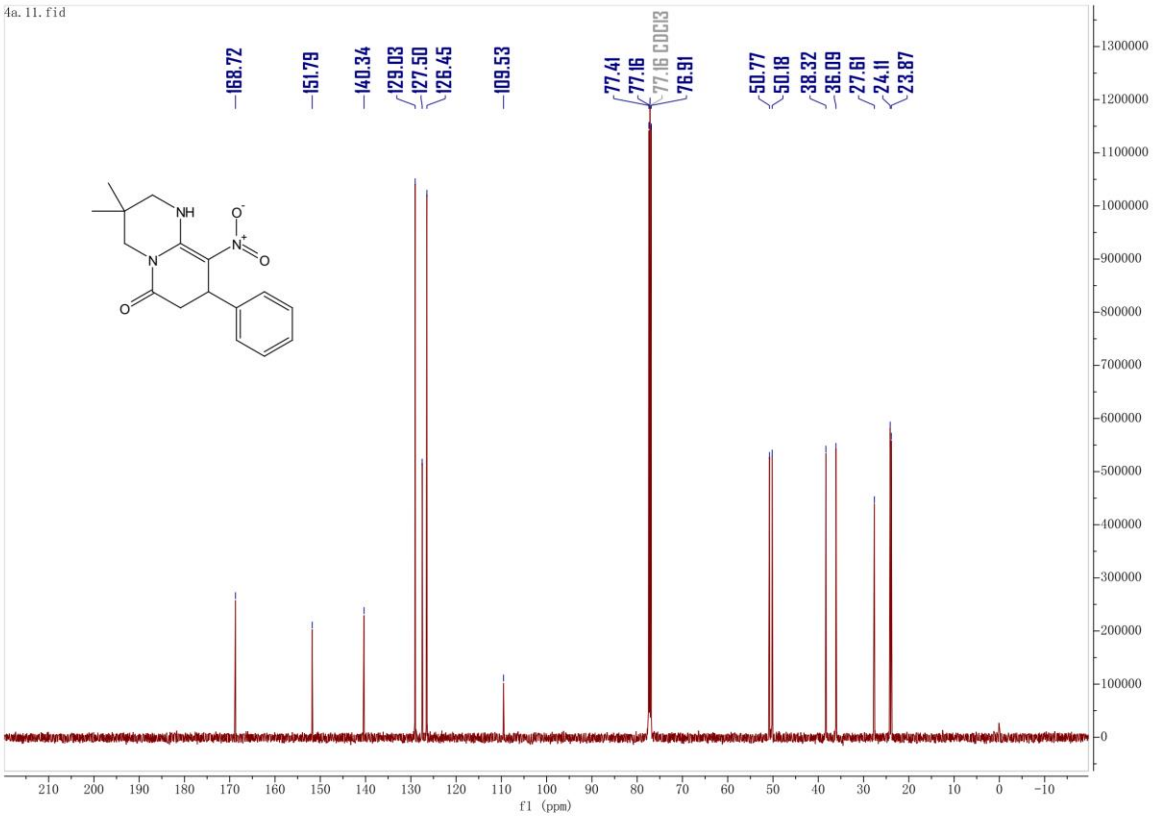

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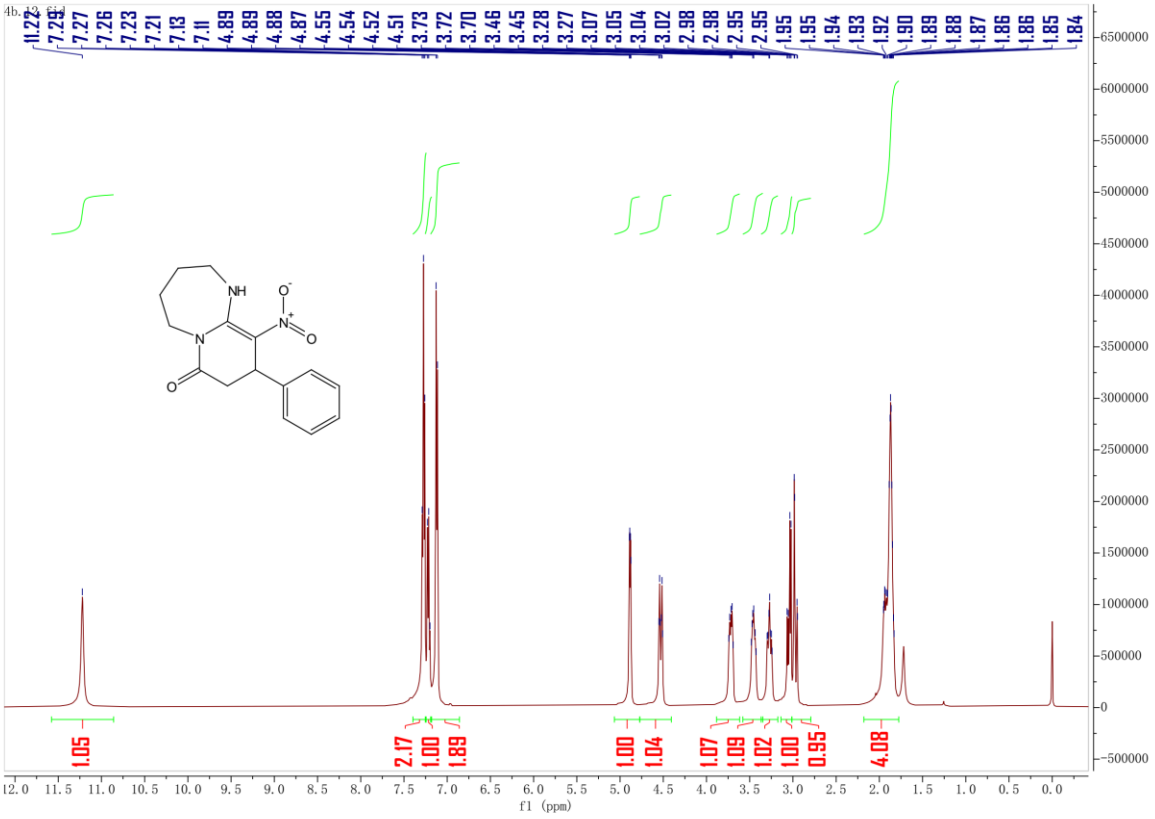

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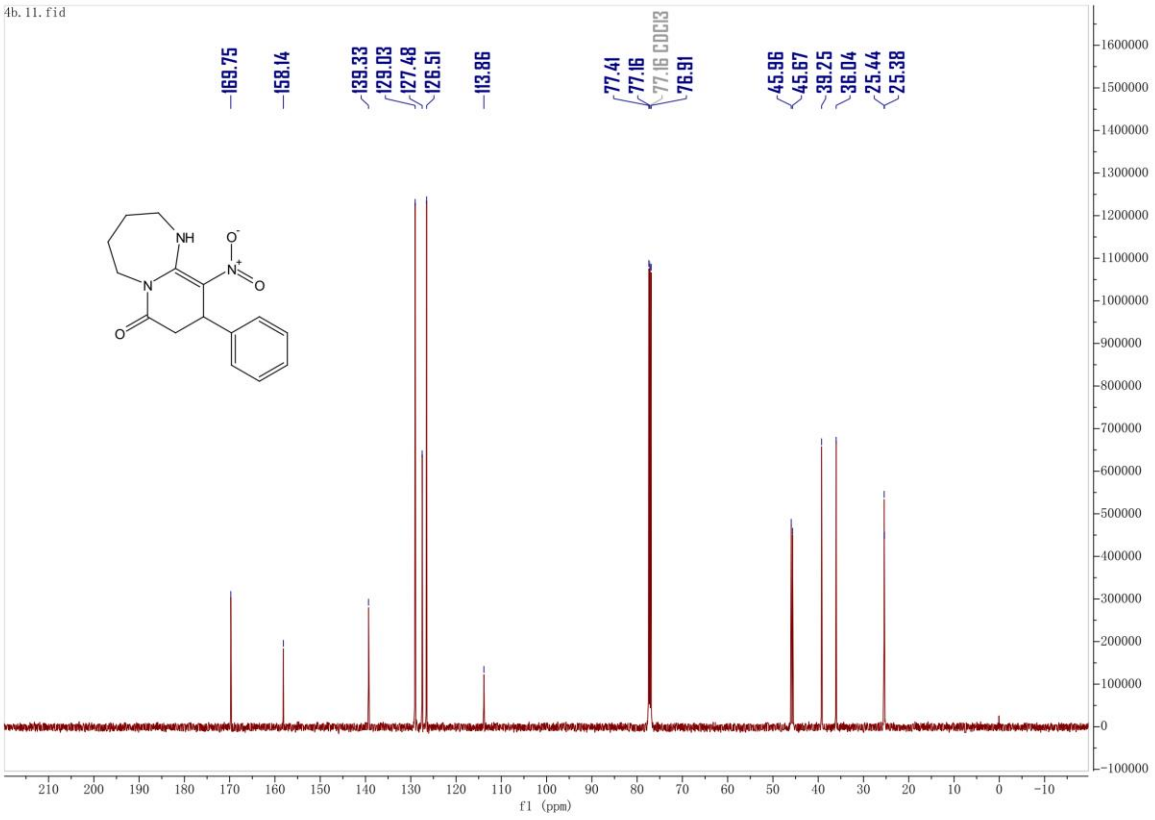

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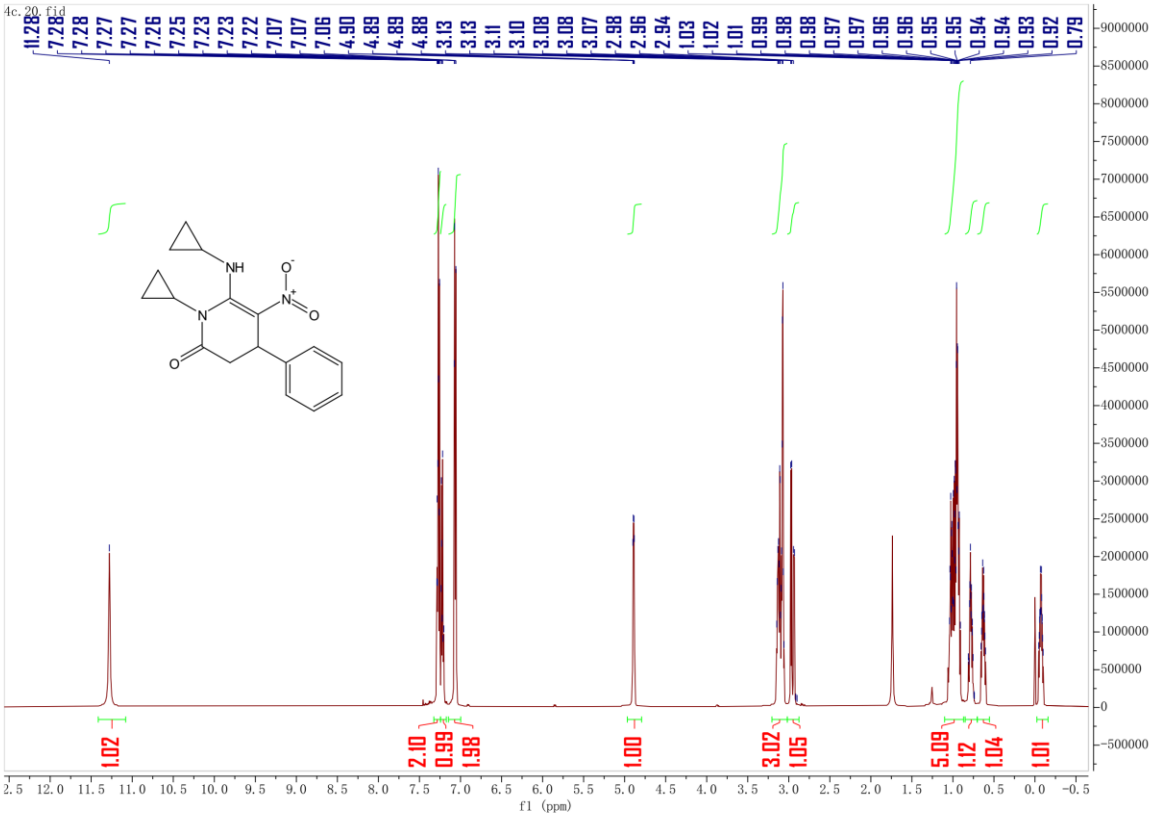

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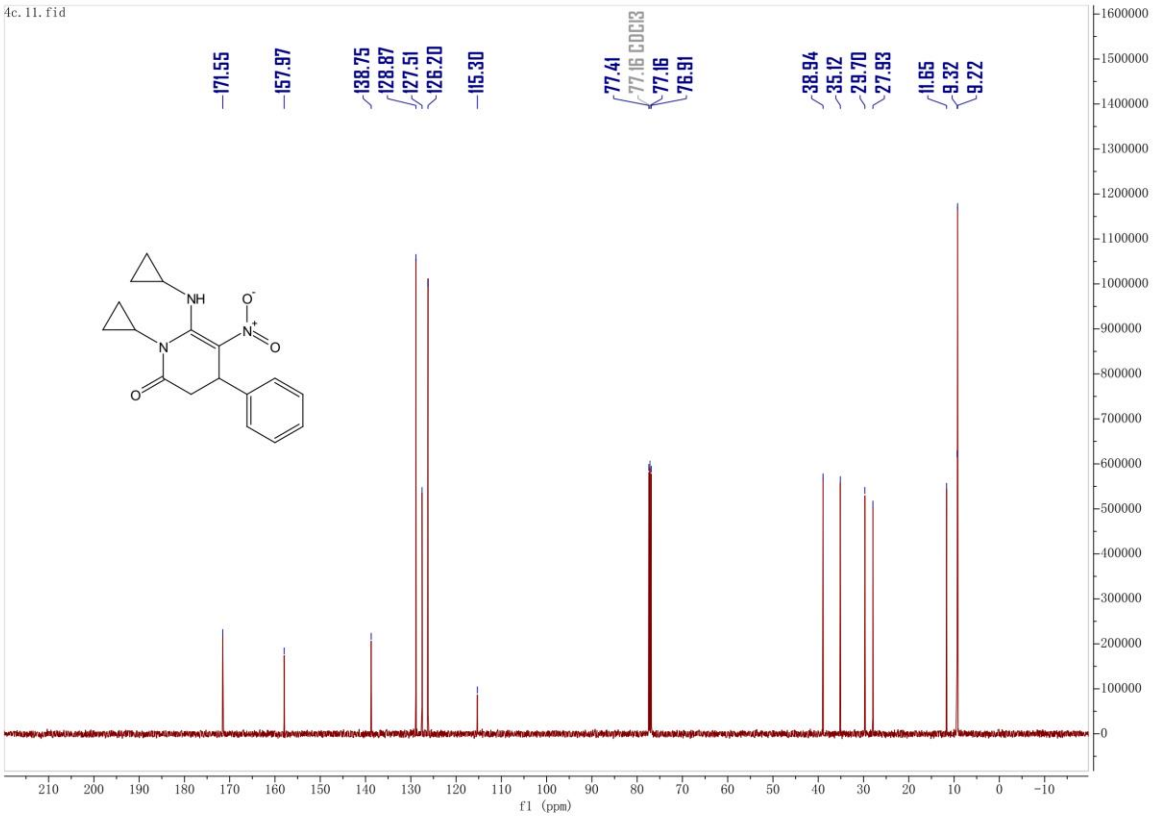

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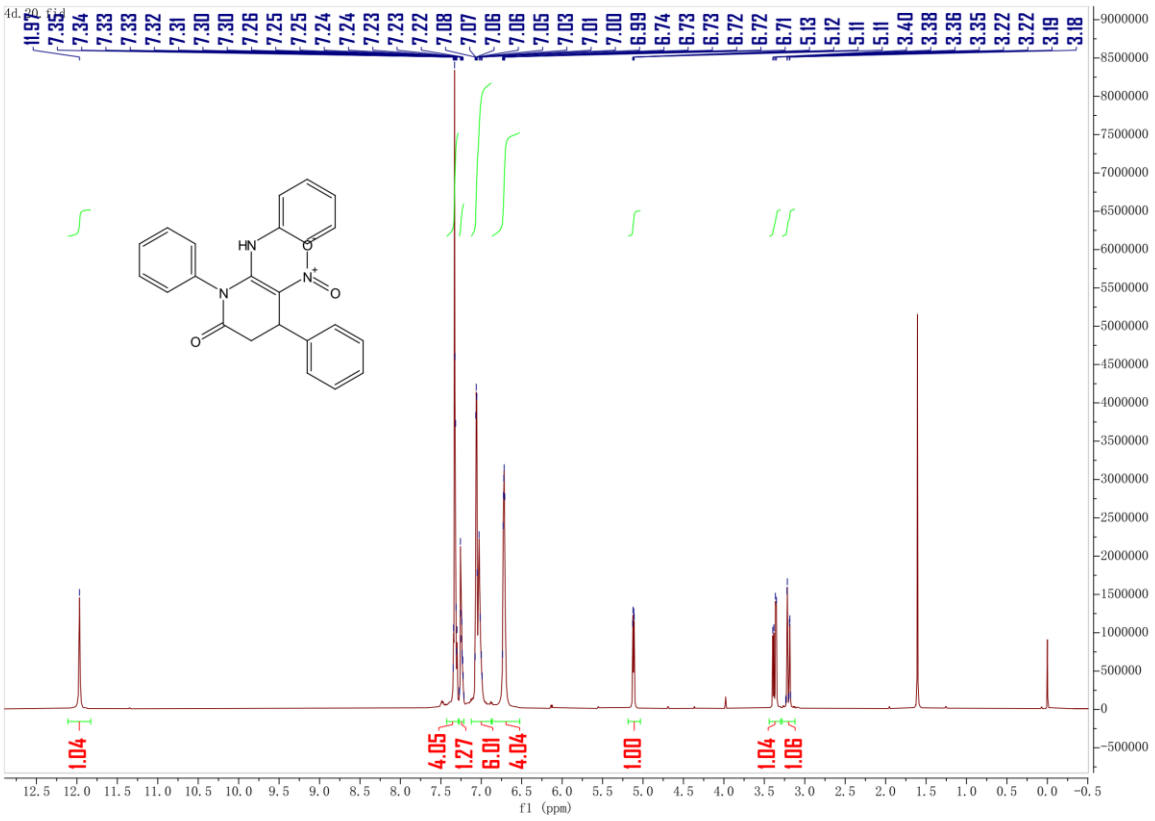

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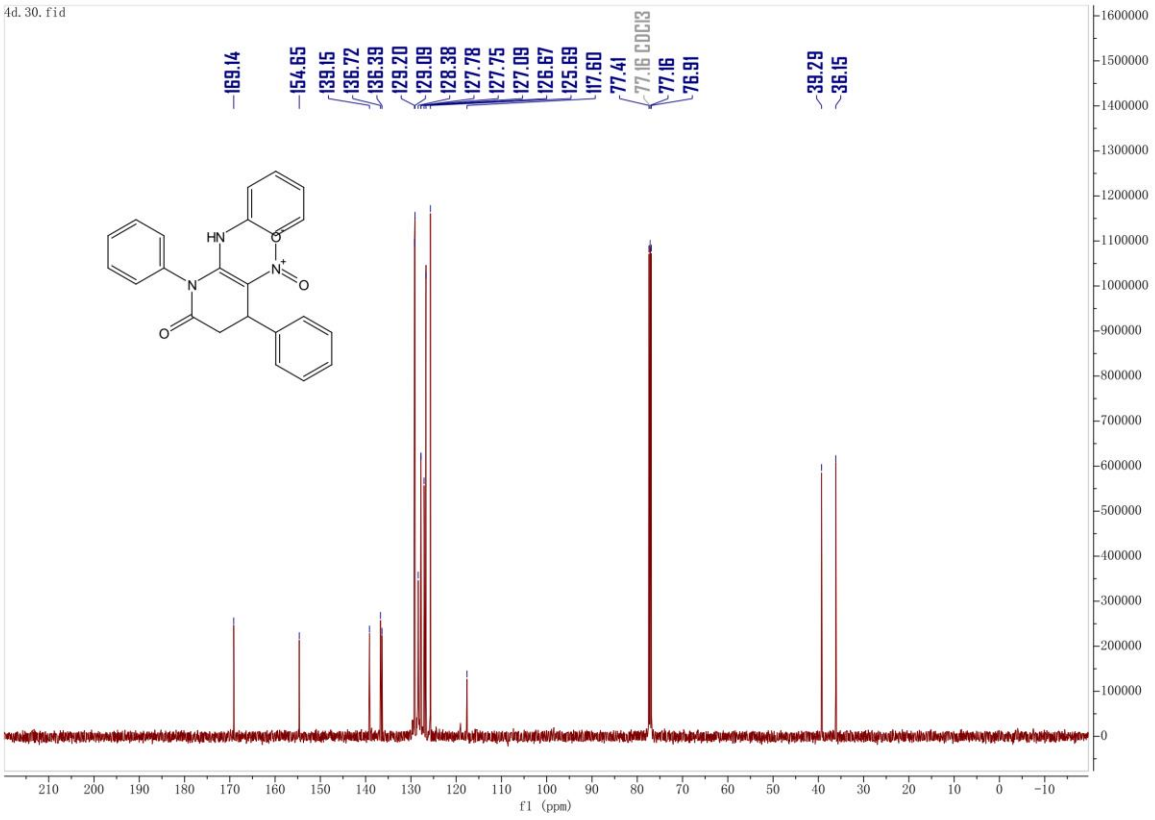

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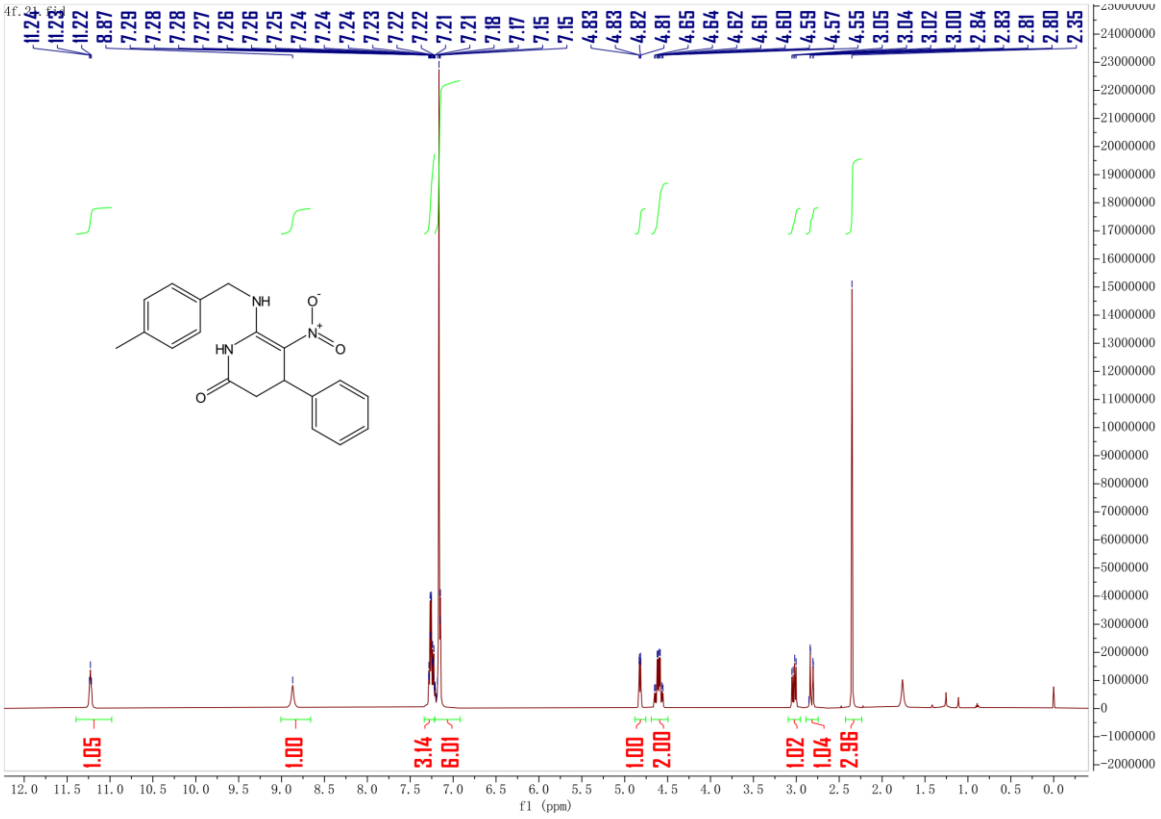

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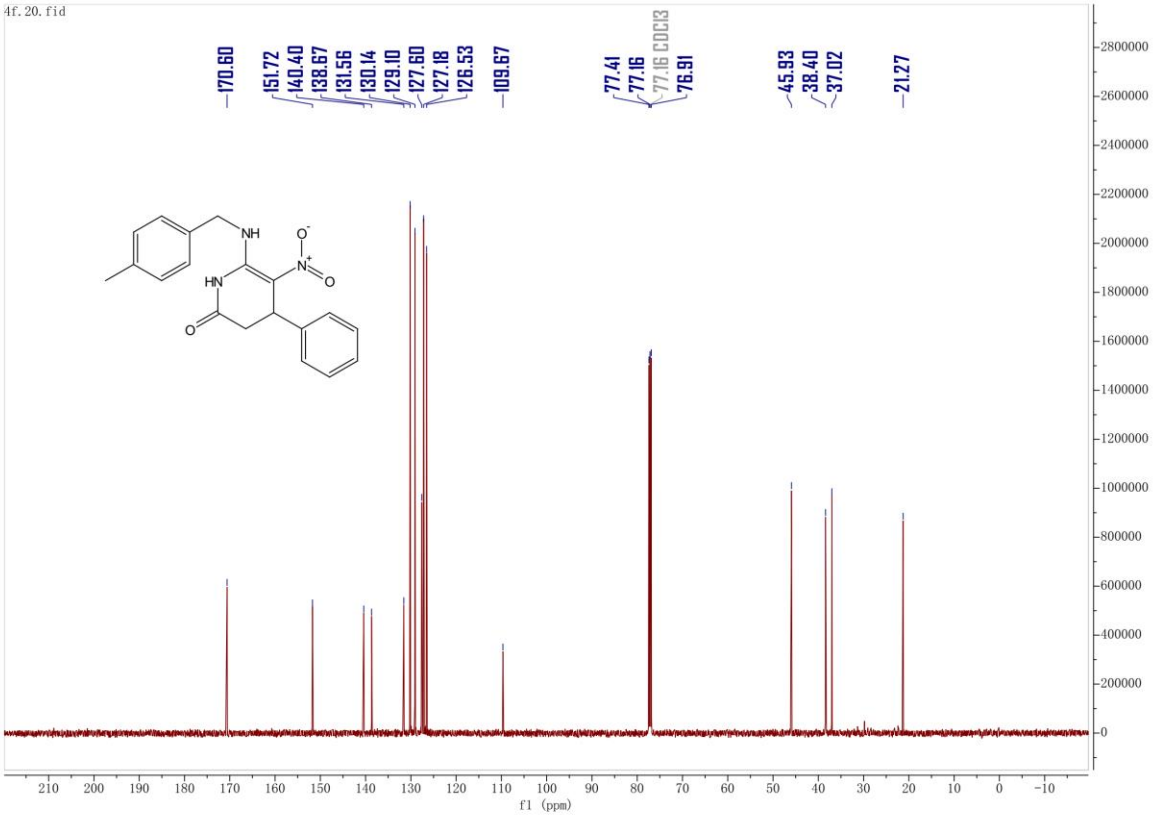

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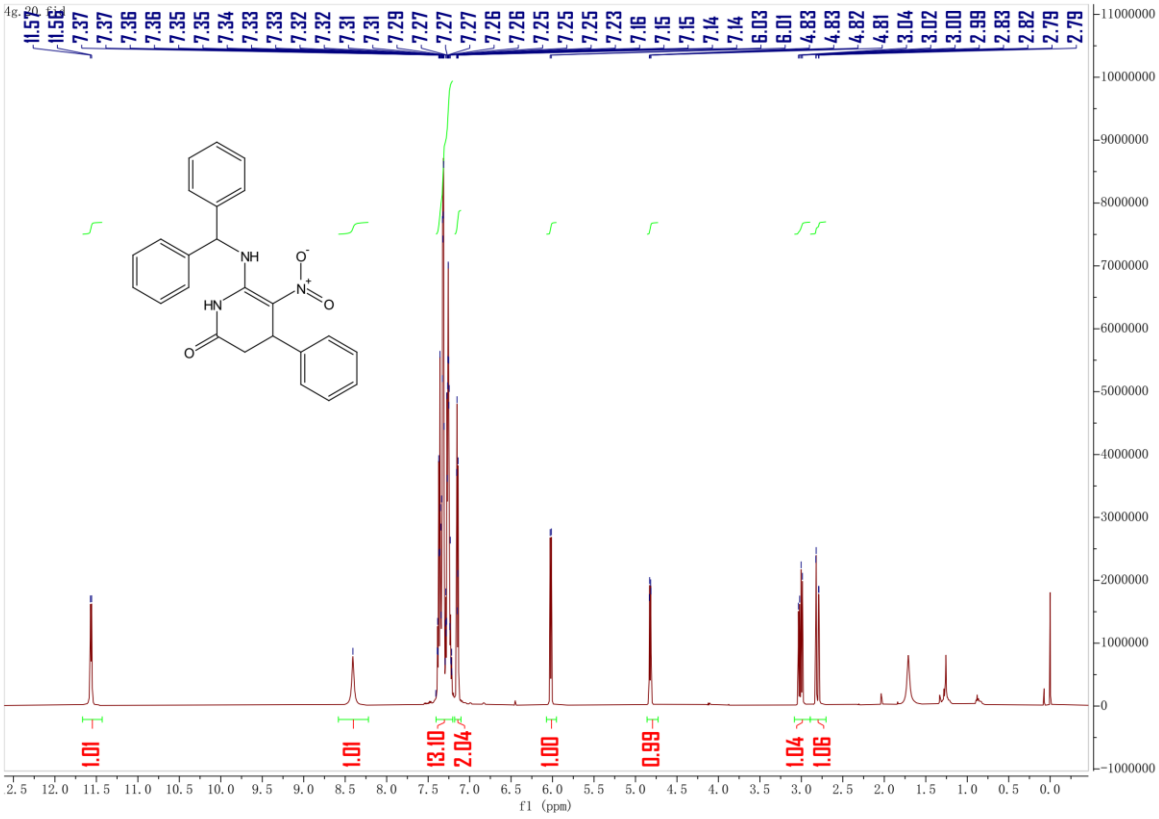

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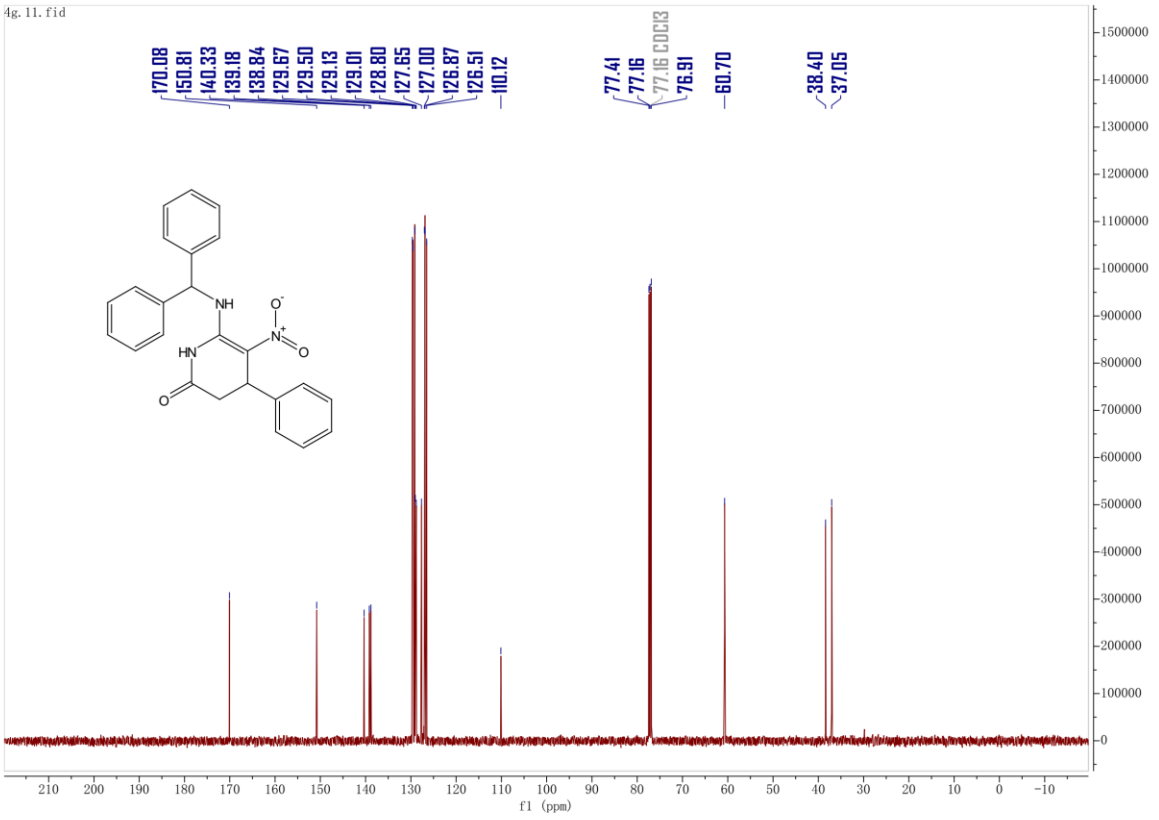

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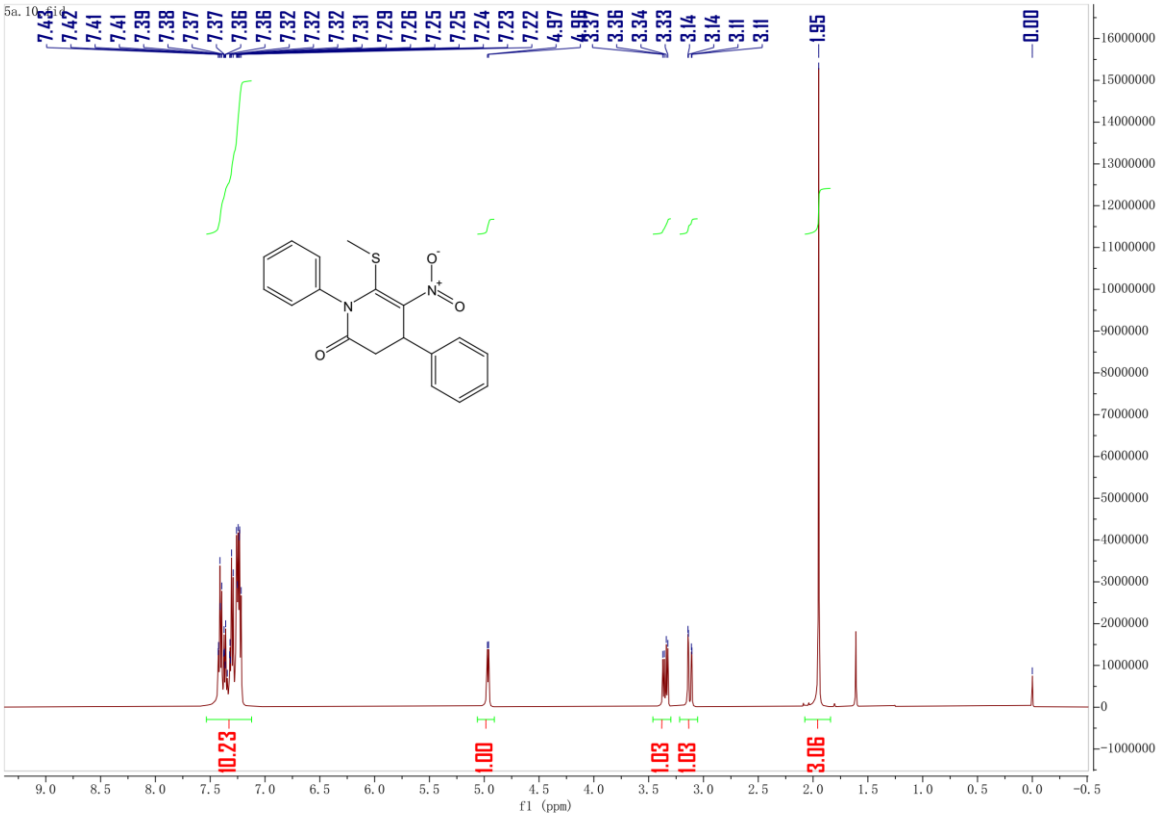

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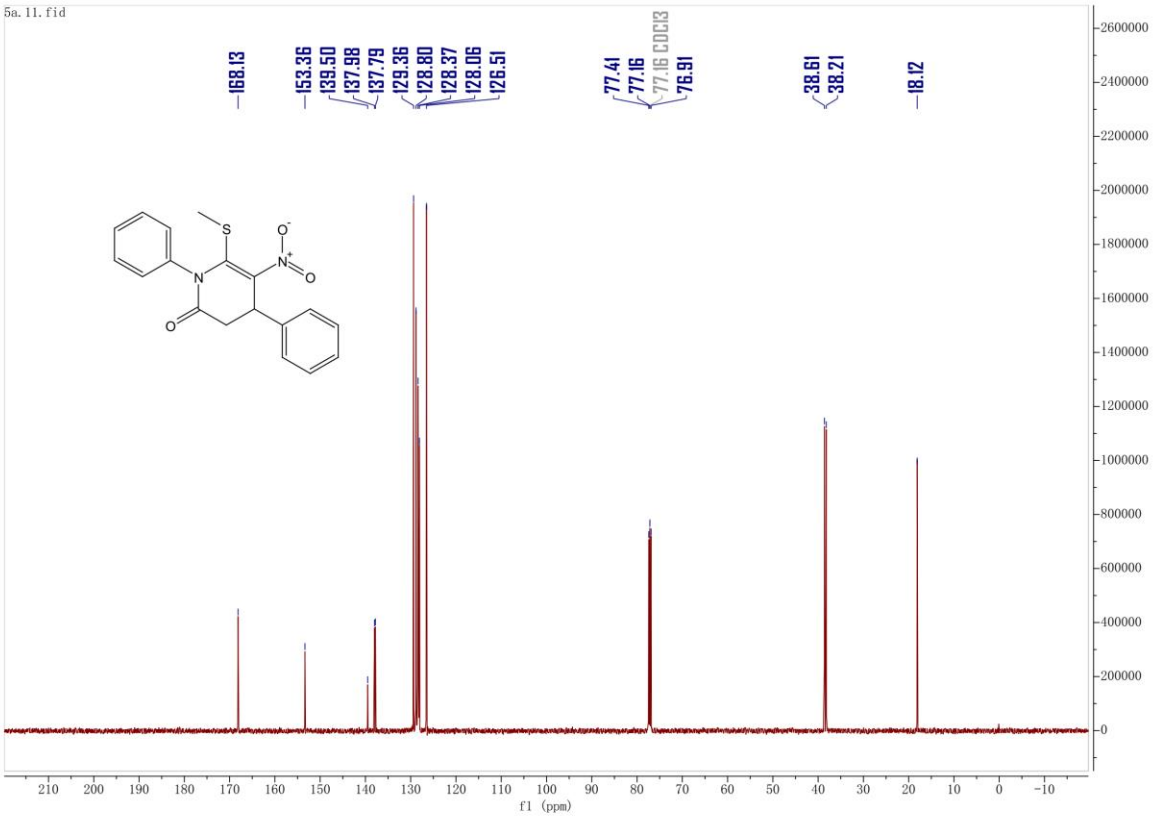

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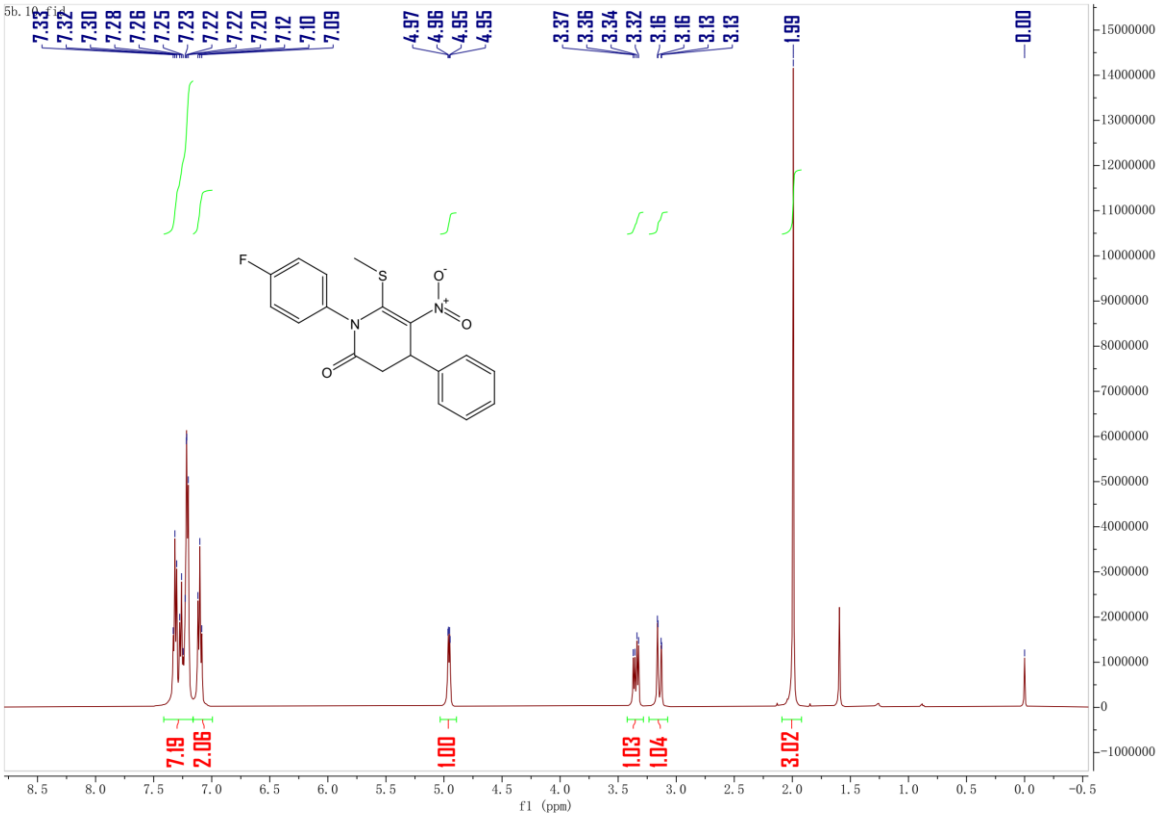

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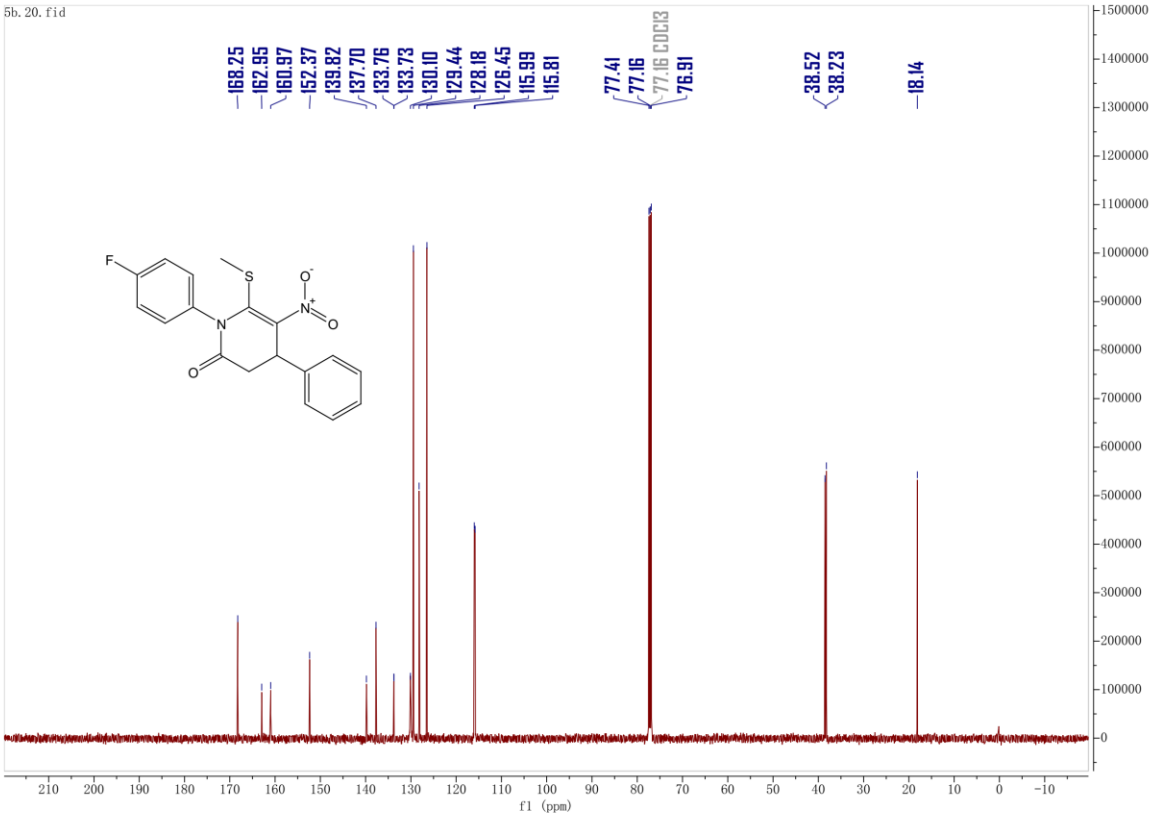

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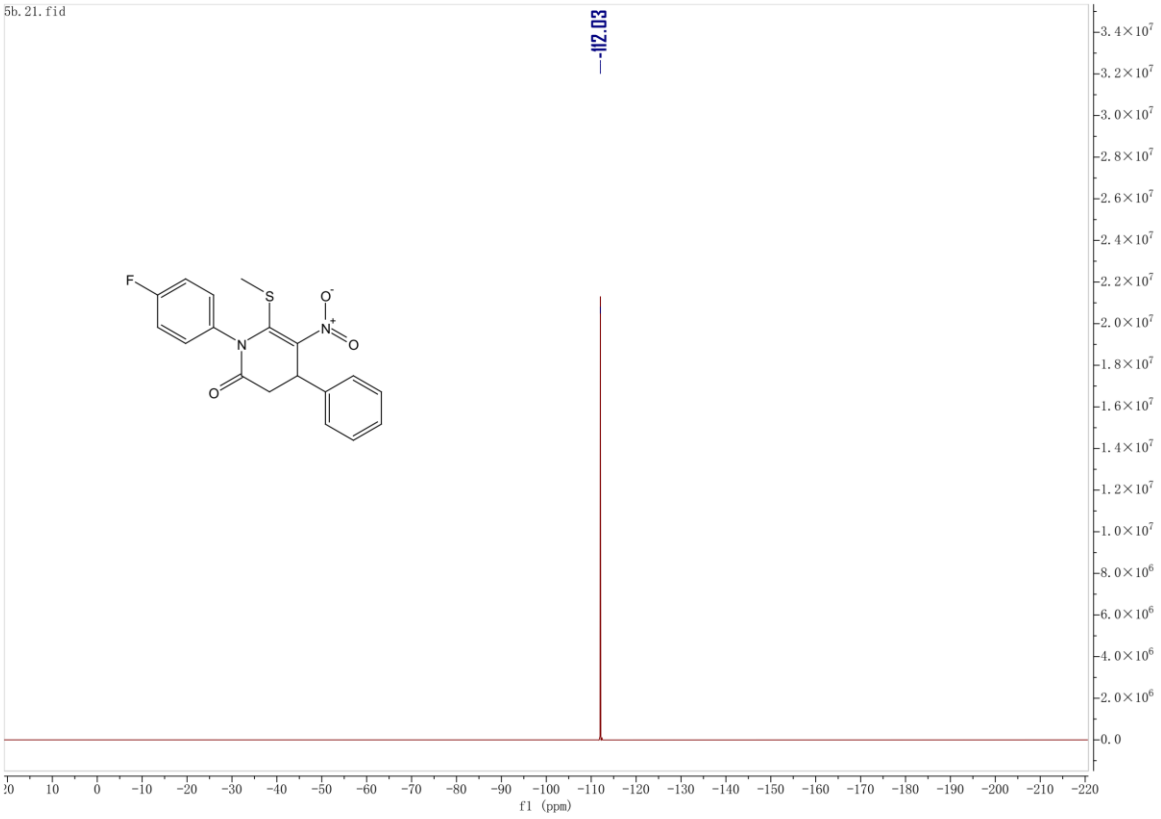

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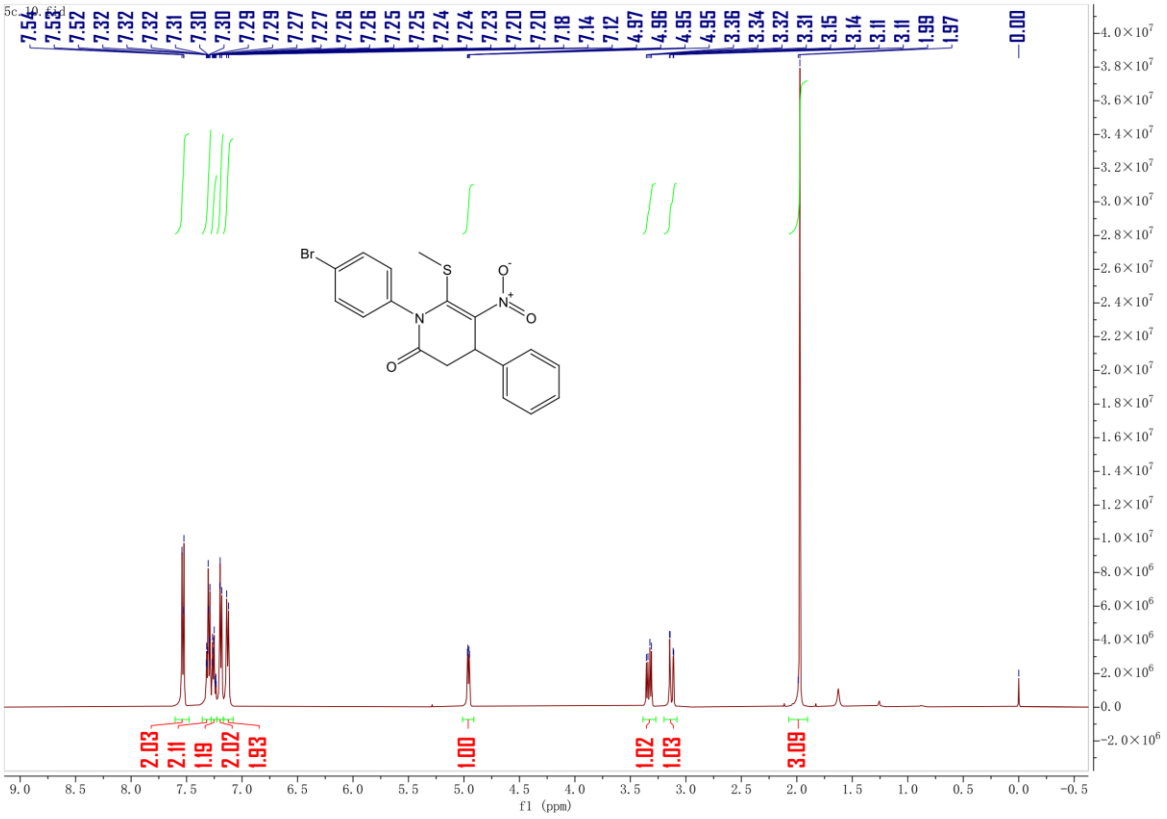

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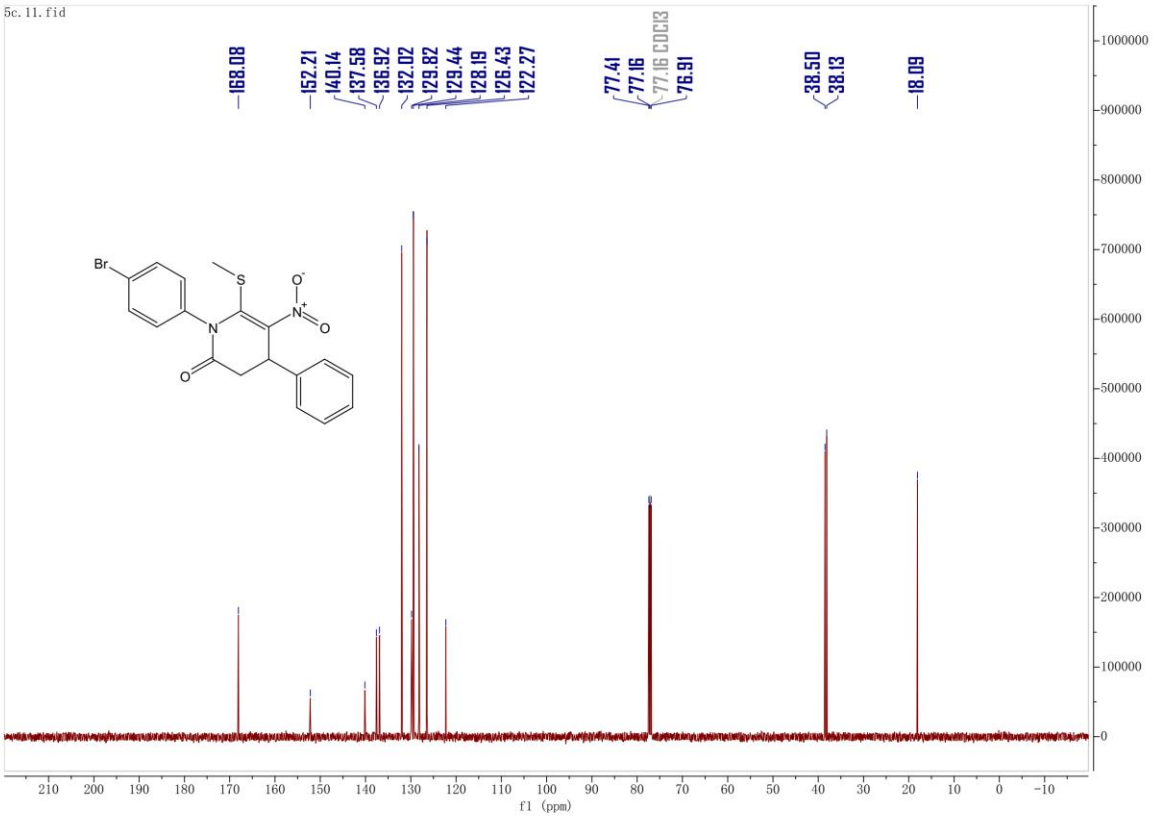

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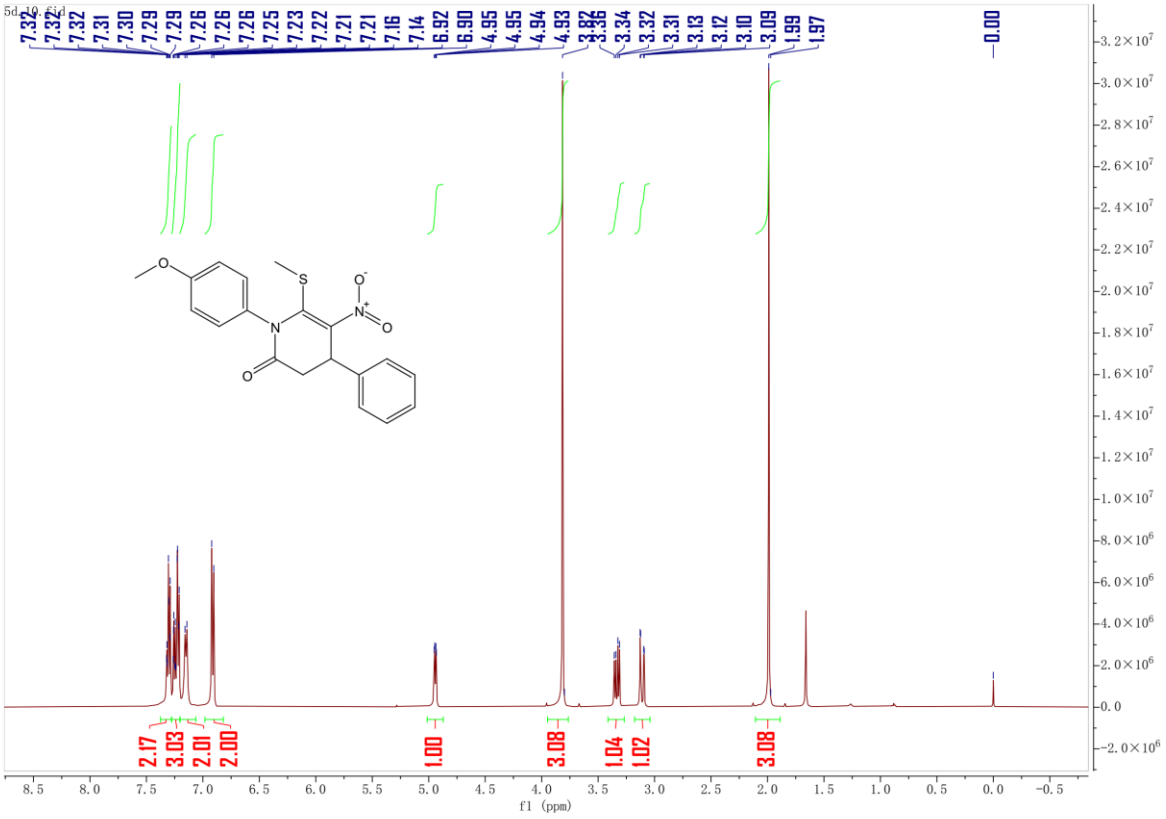

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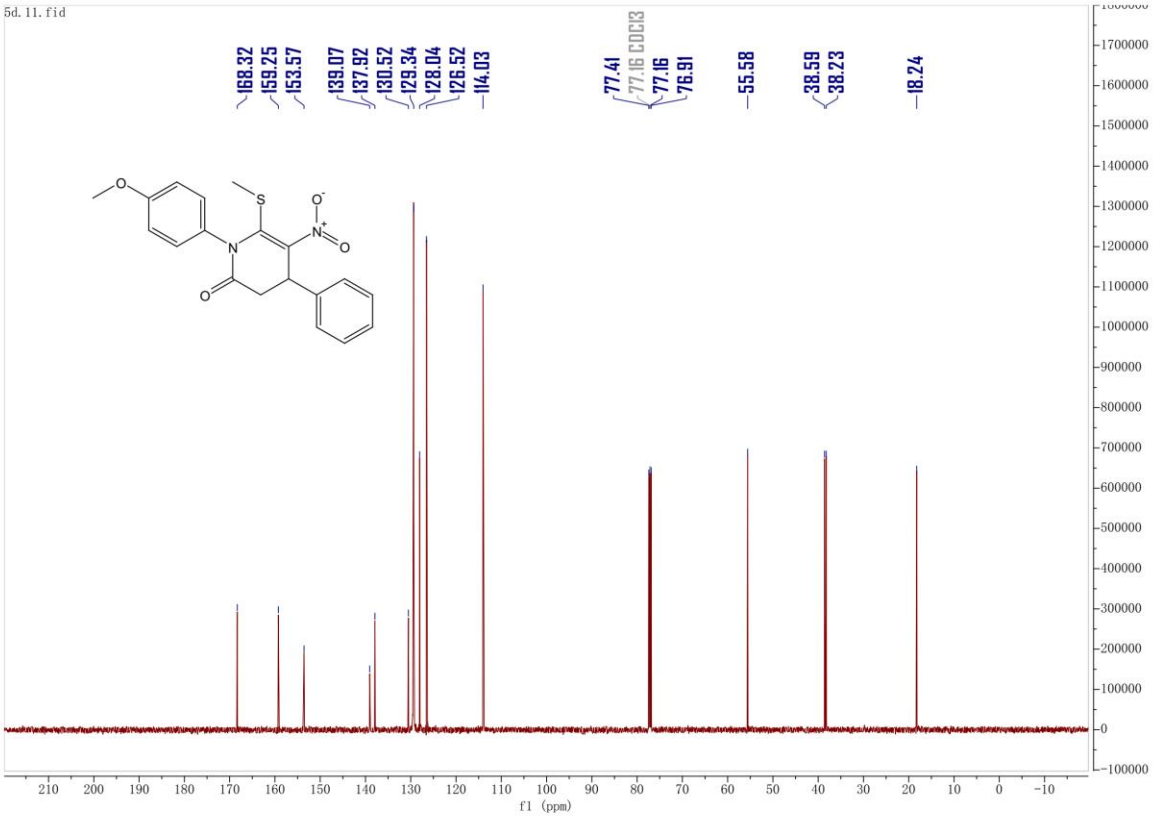

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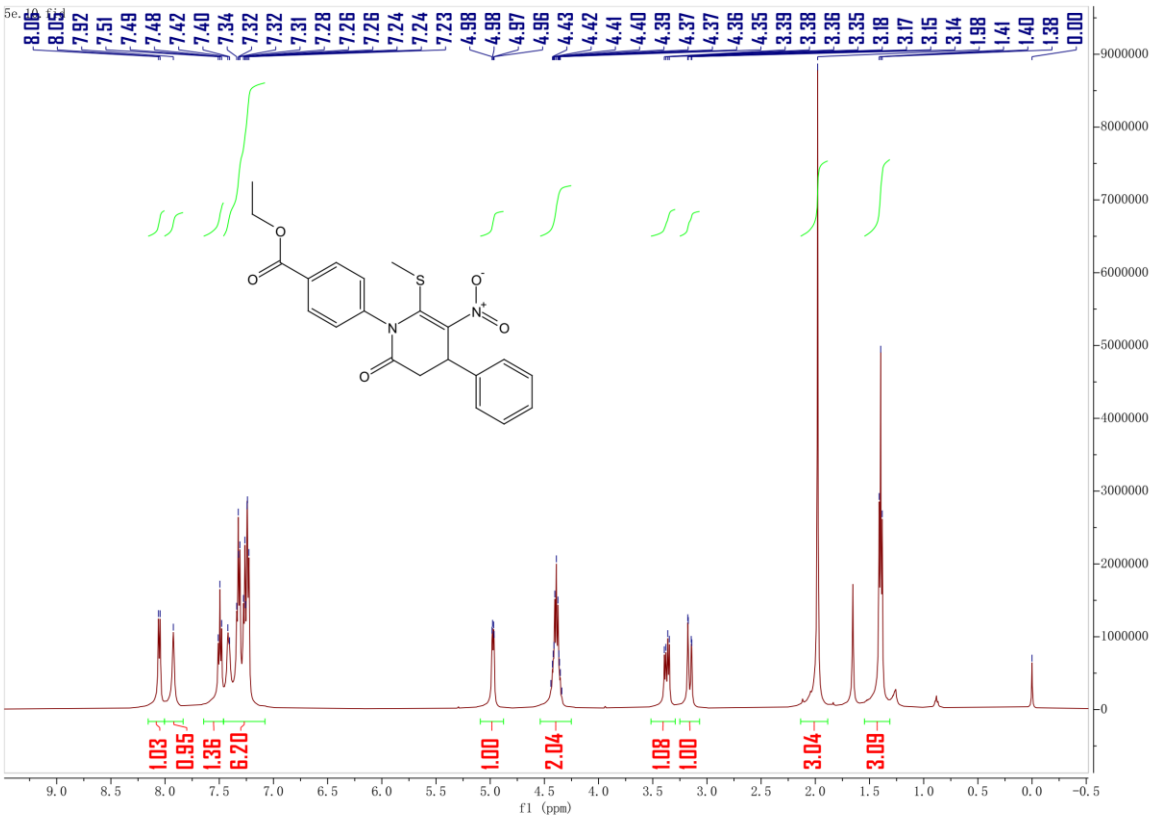

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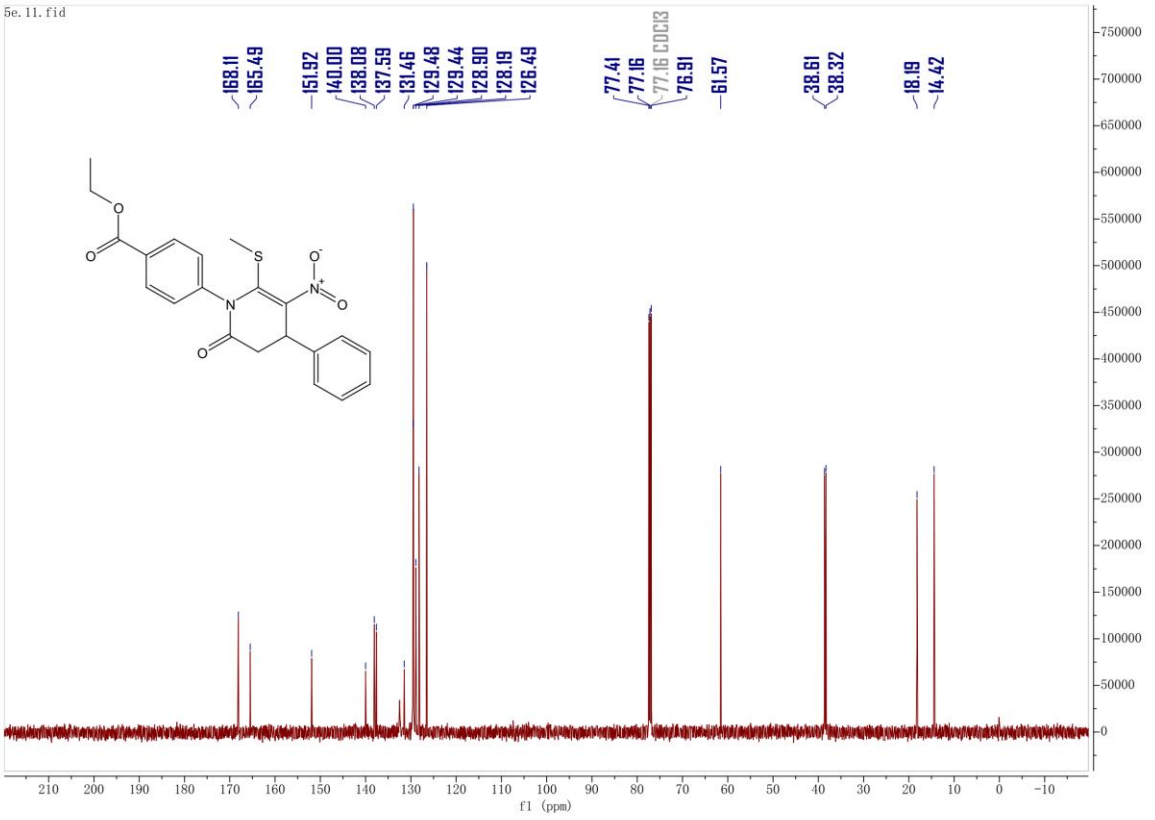

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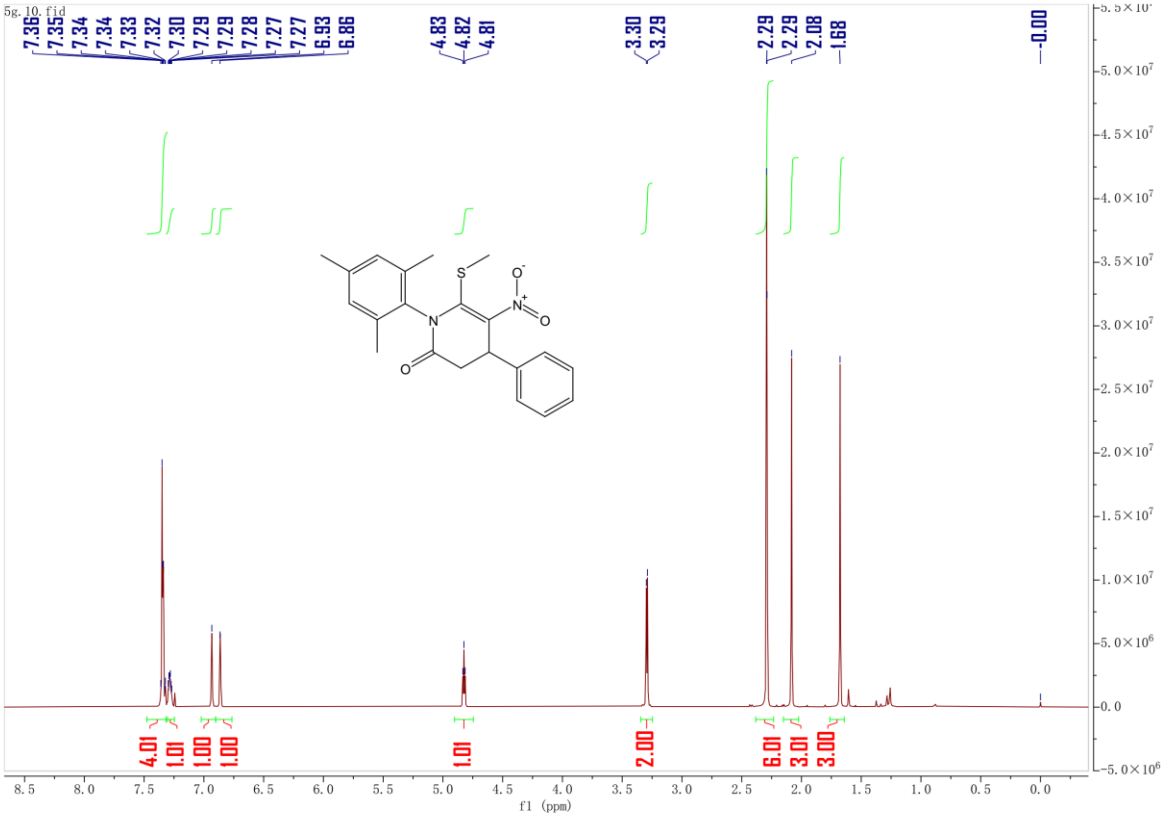
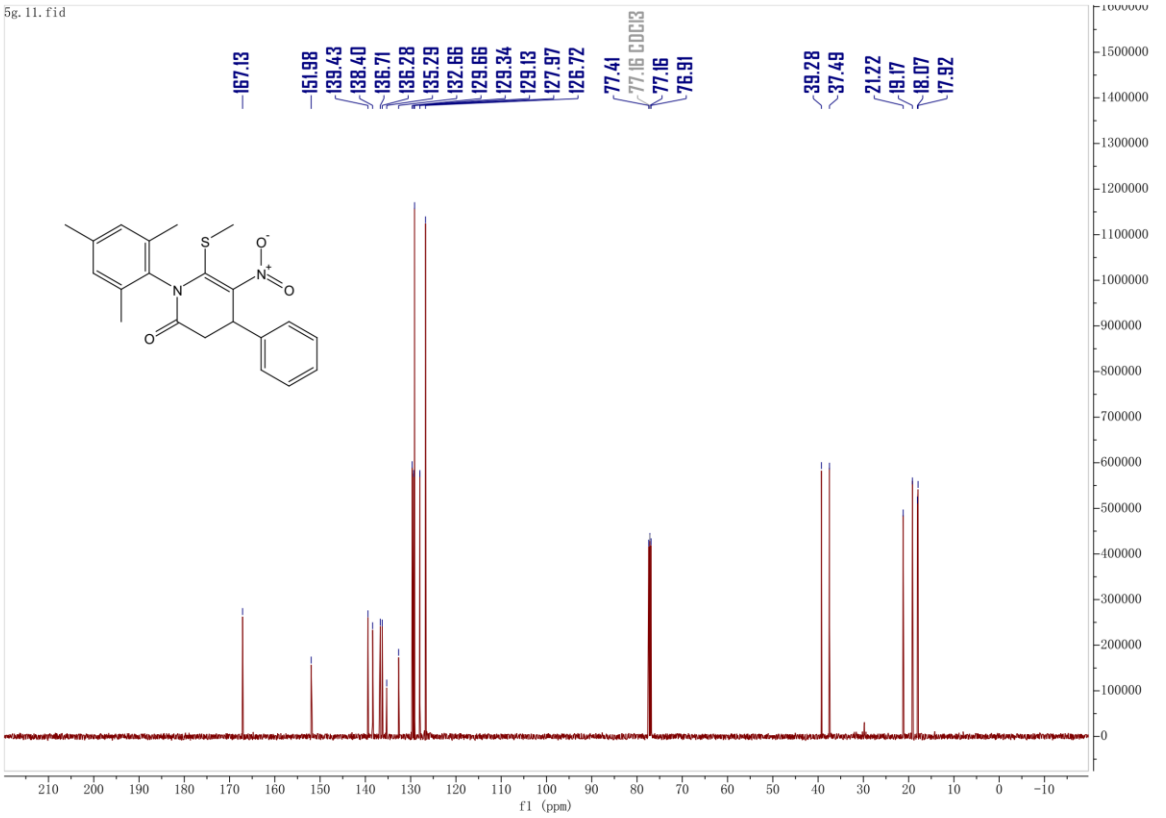
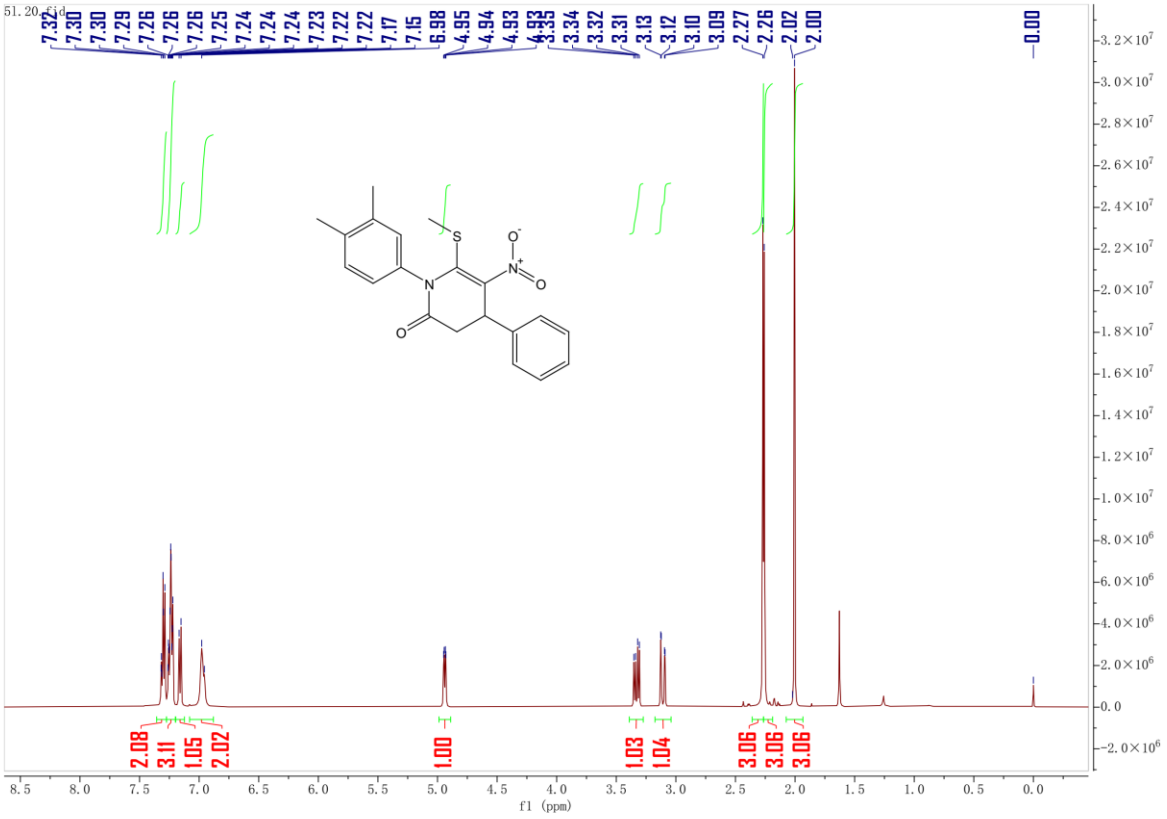


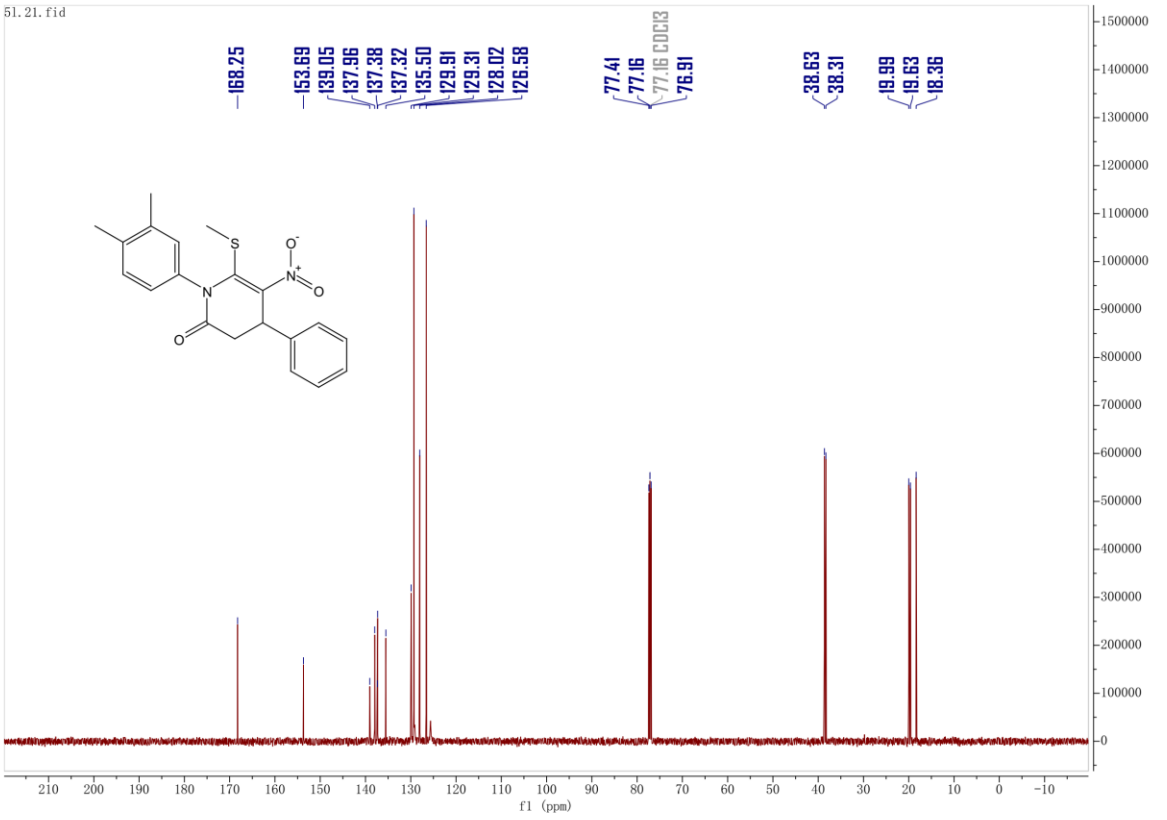
^{1}H NMR spectrum of 5f



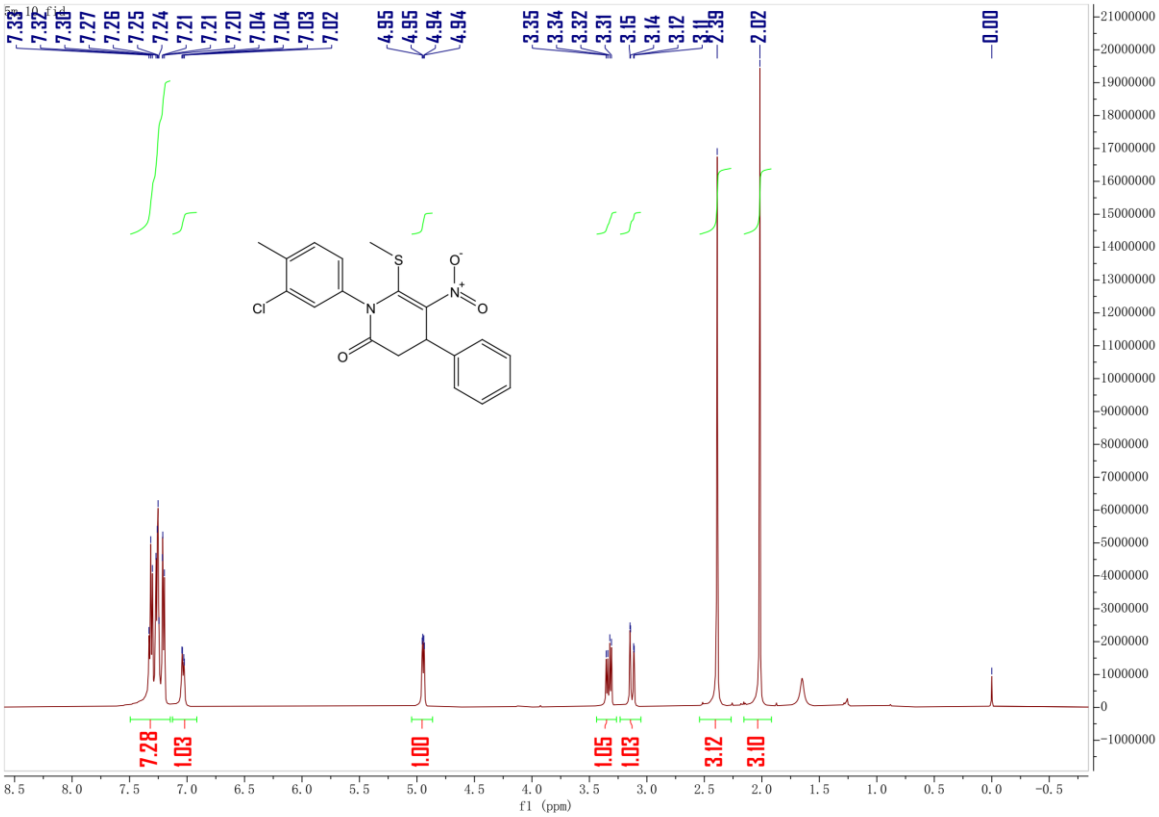
^{13}C NMR spectrum of 5f



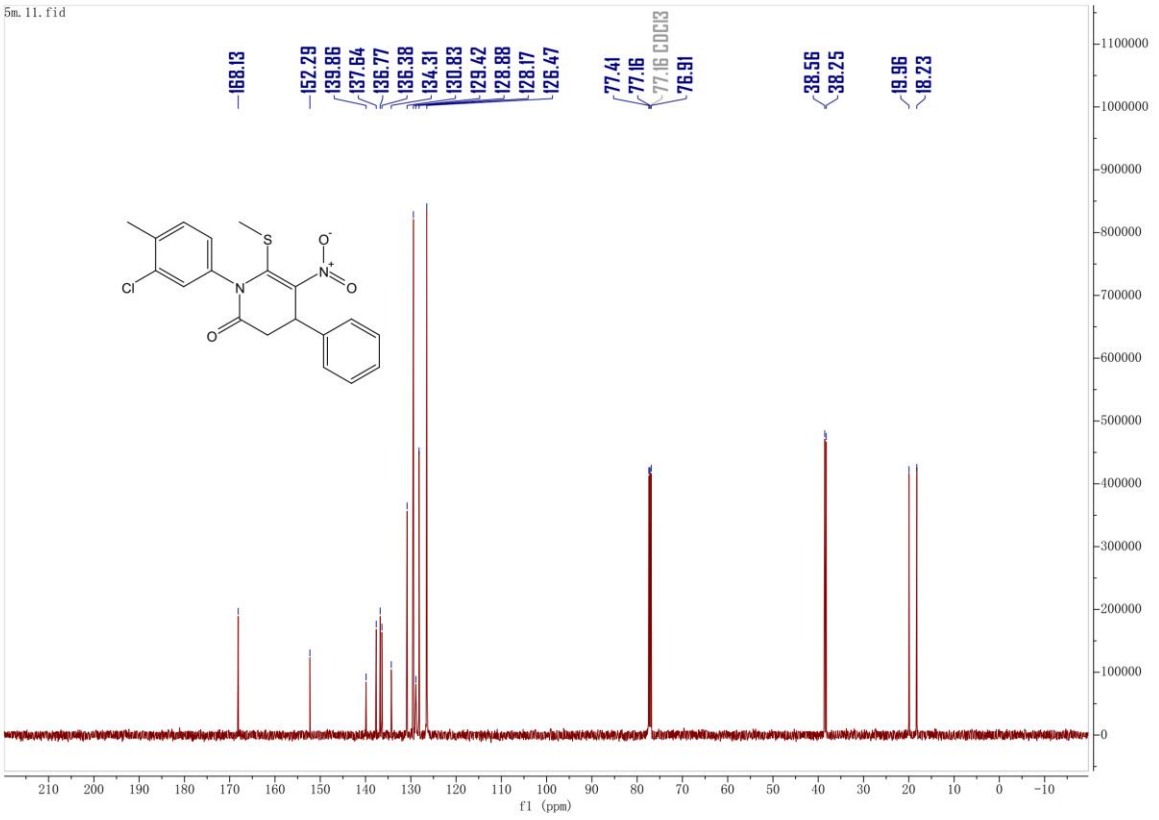
^{1}H NMR spectrum of 5g



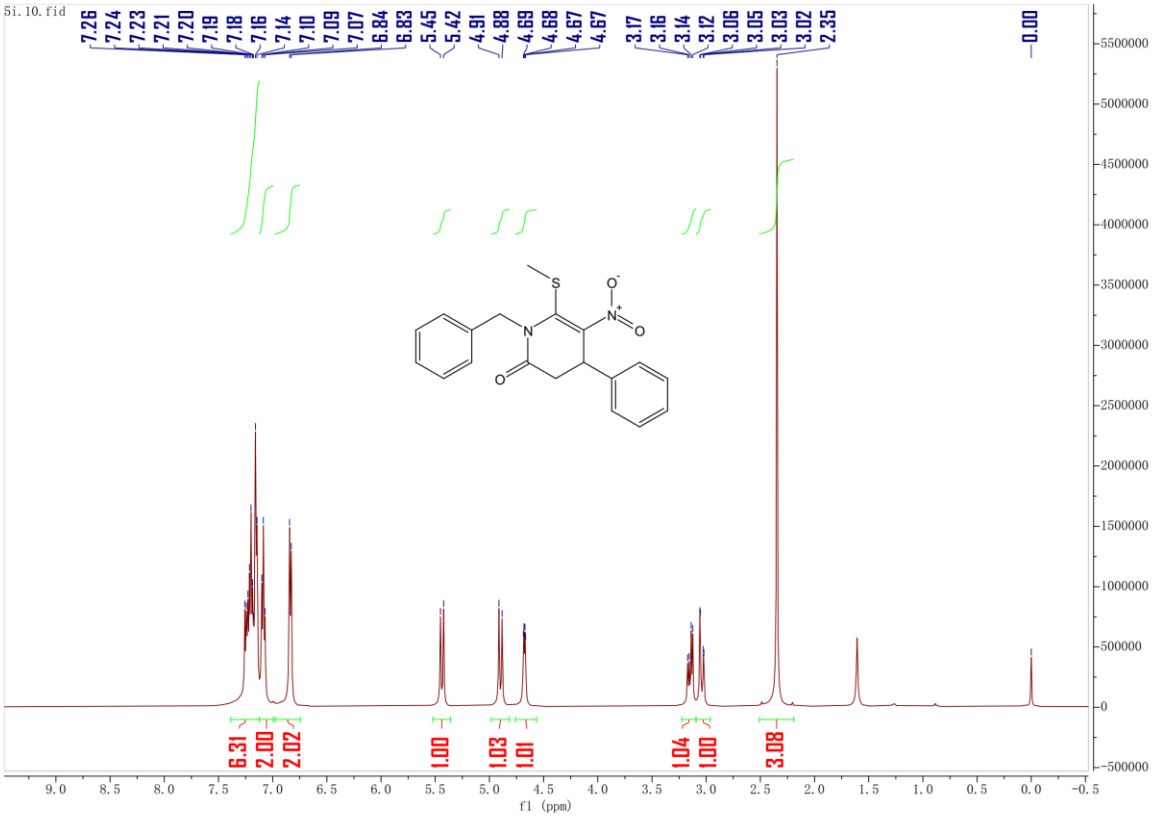
^{13}C NMR spectrum of 5g



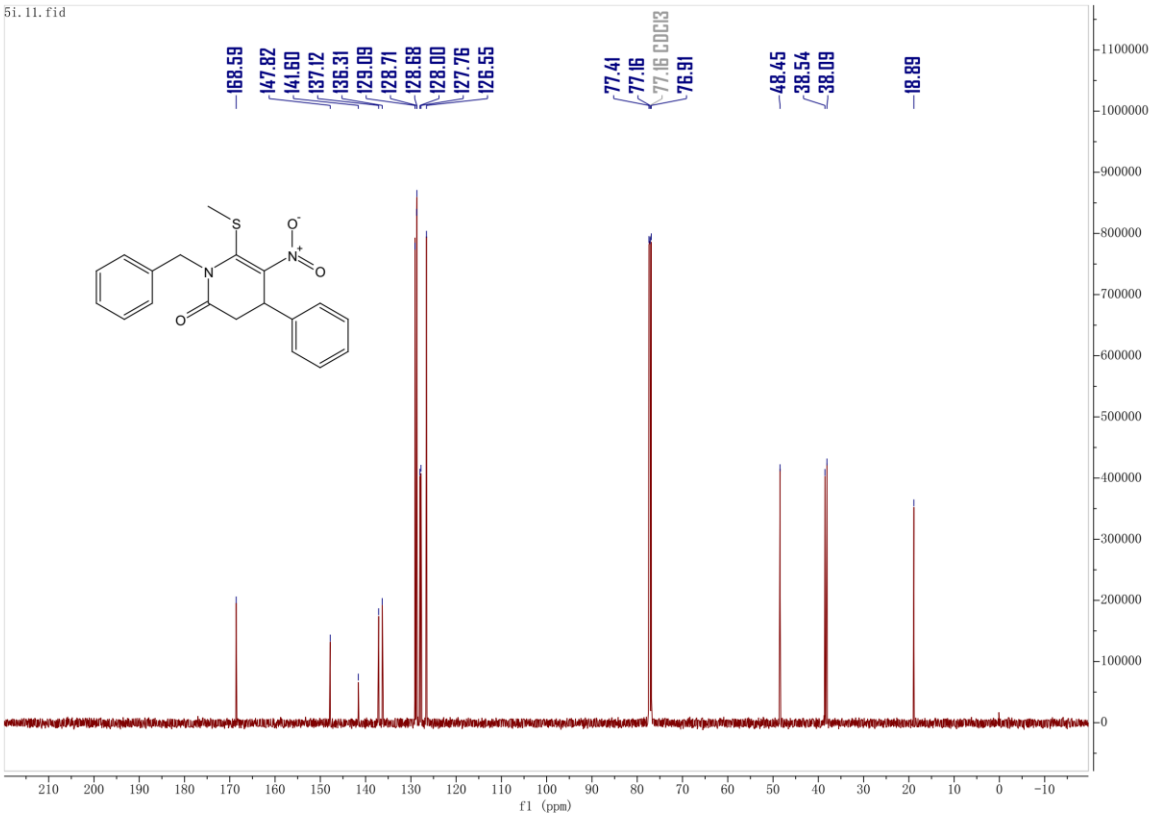
^{1}H NMR spectrum of 5h



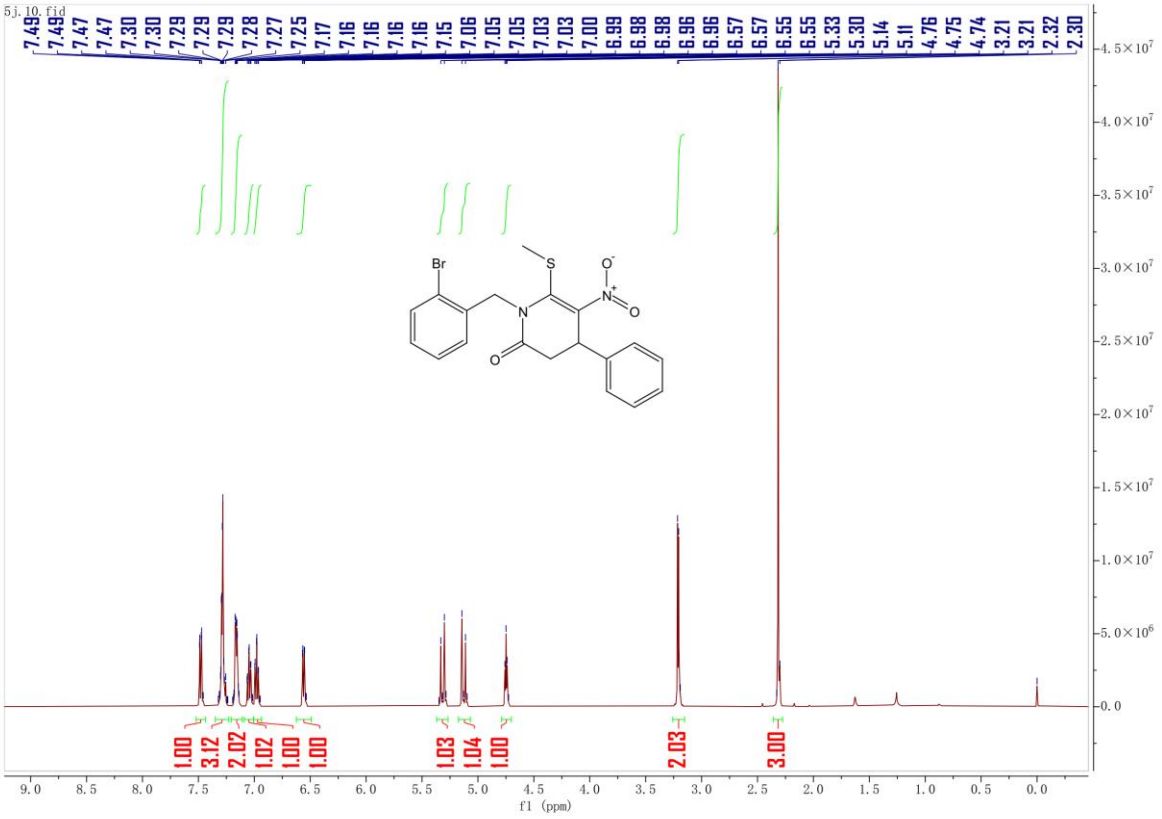
^{13}C NMR spectrum of 5h



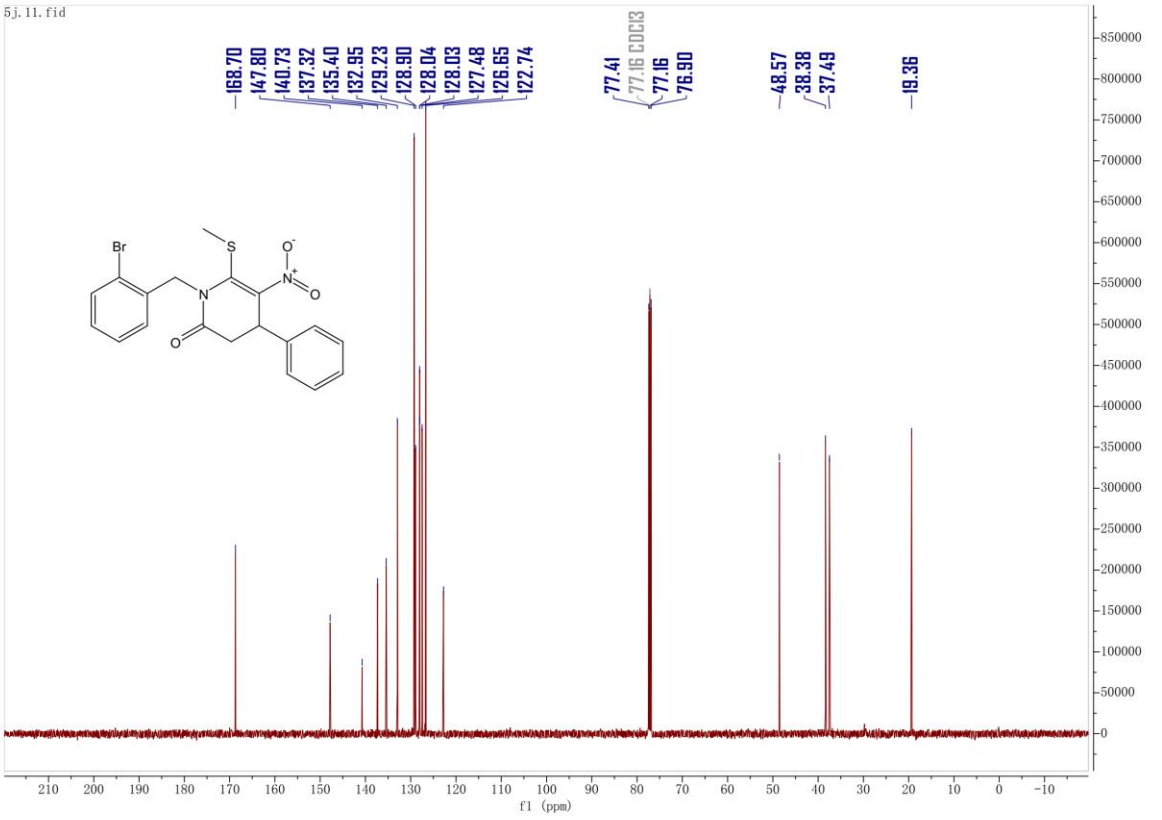
^{1}H NMR spectrum of 5i



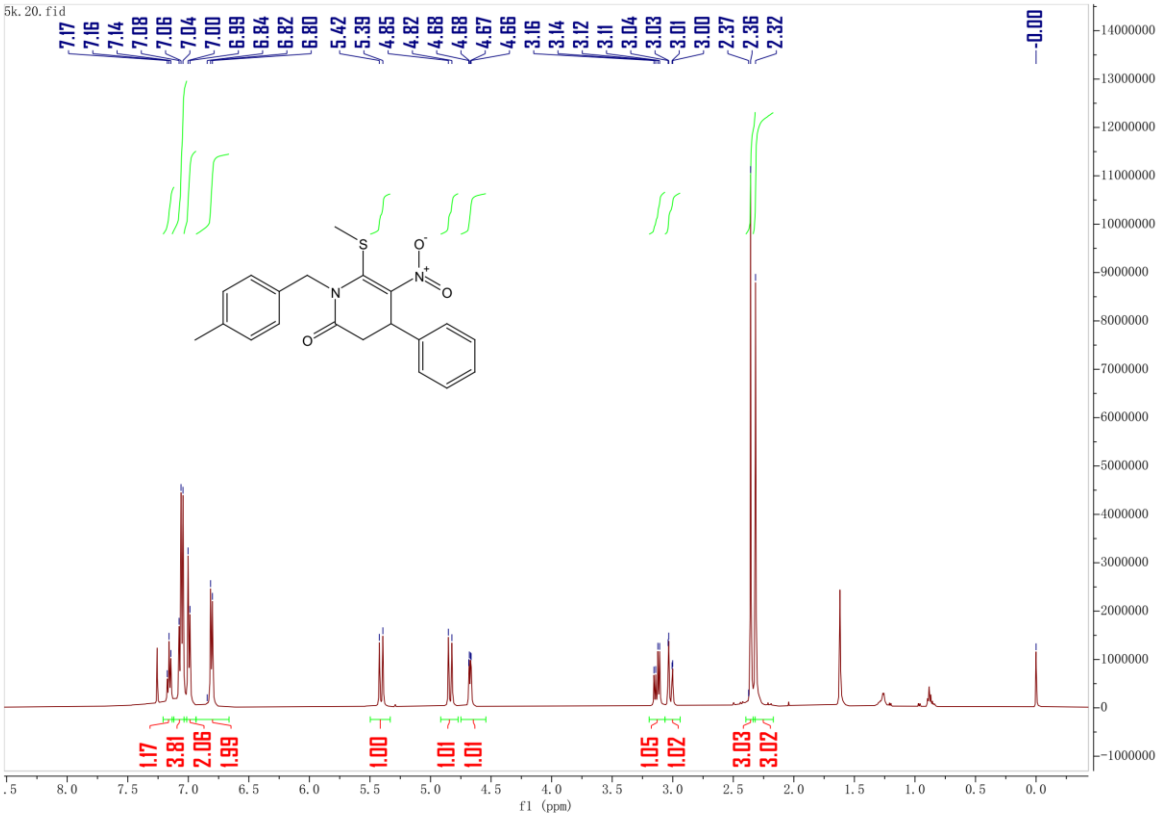
^{13}C NMR spectrum of 5i



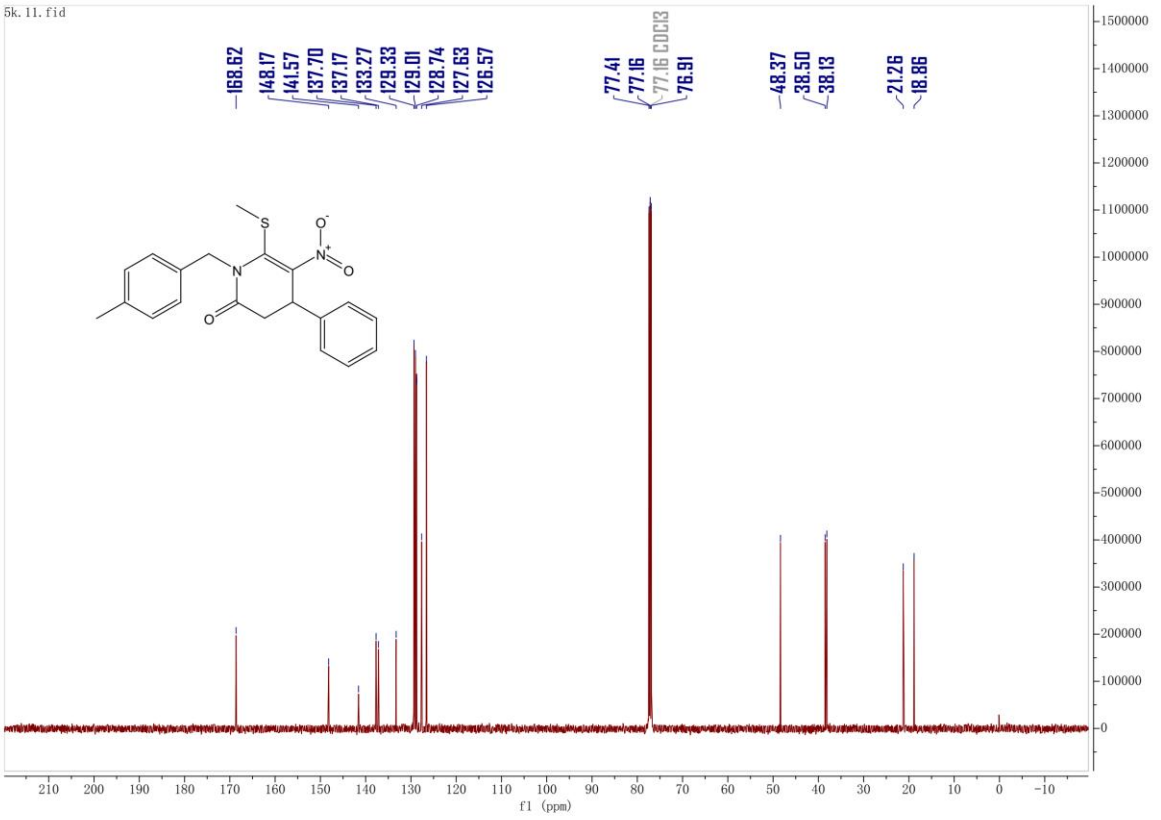
^{1}H NMR spectrum of 5j



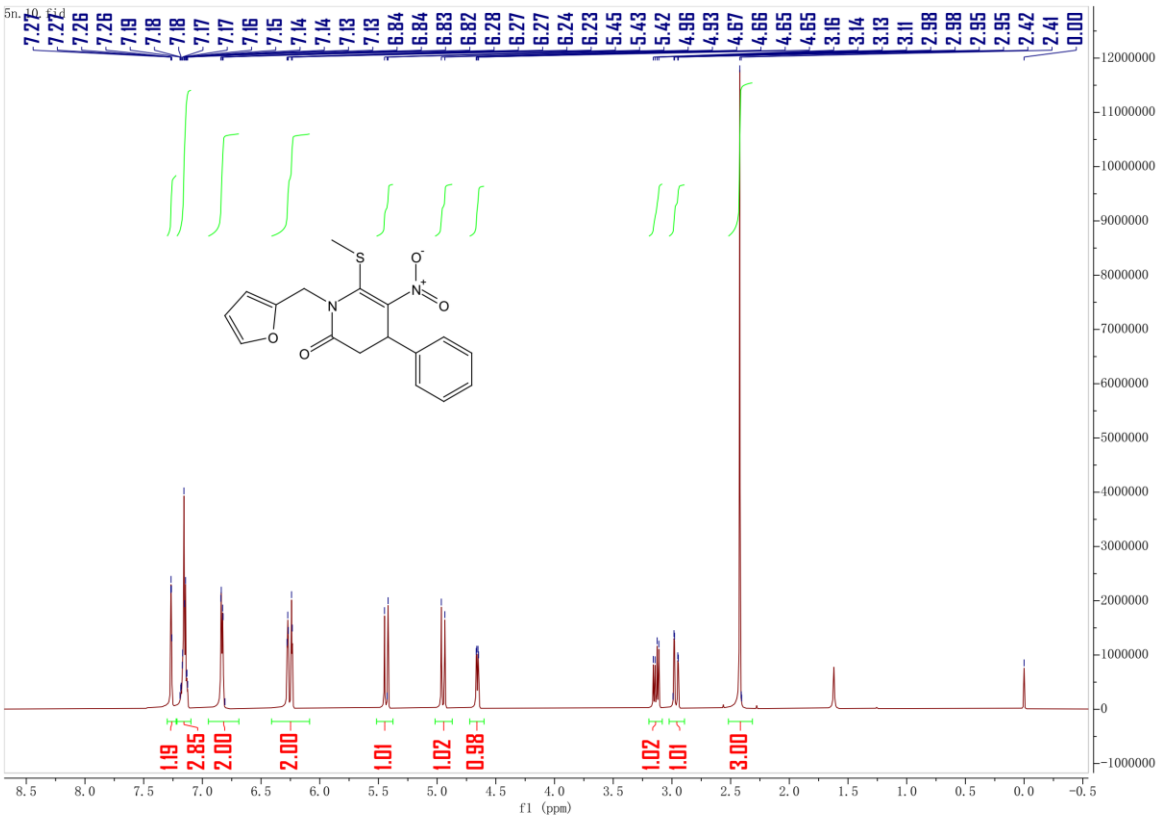
^{13}C NMR spectrum of 5j



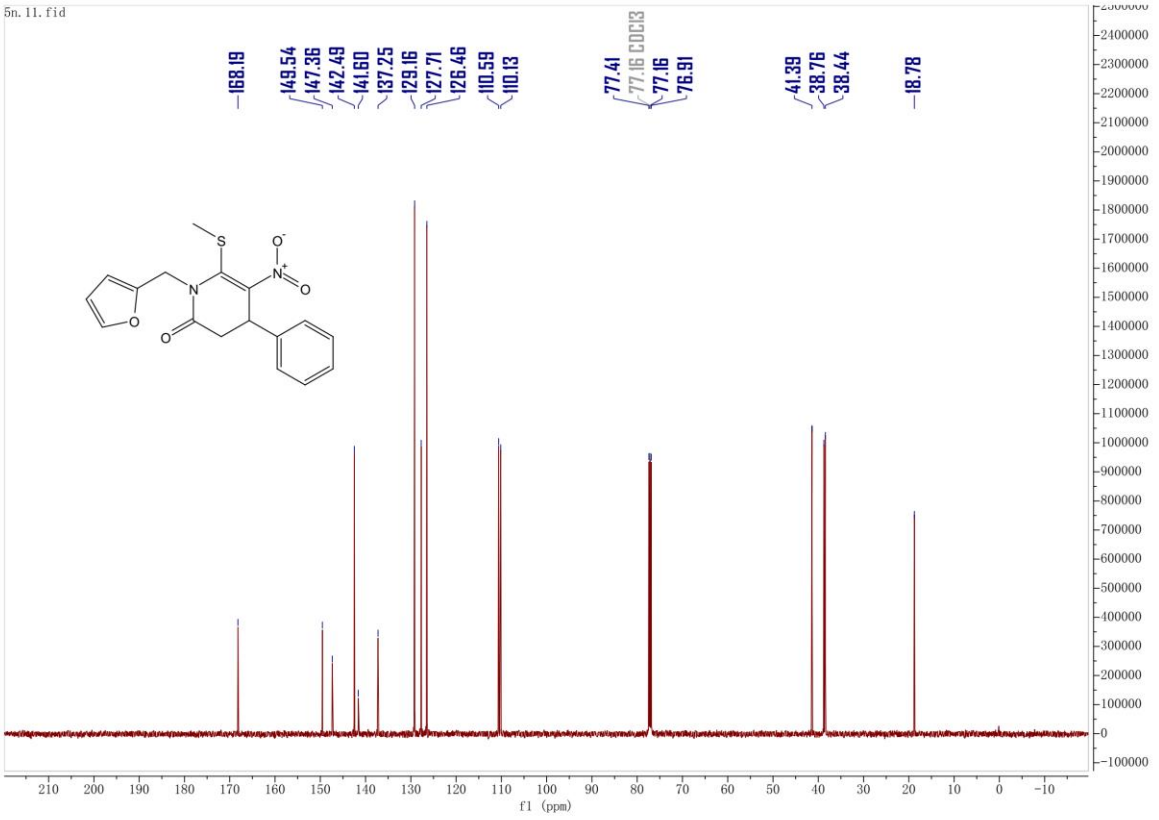
^{1}H NMR spectrum of 5k



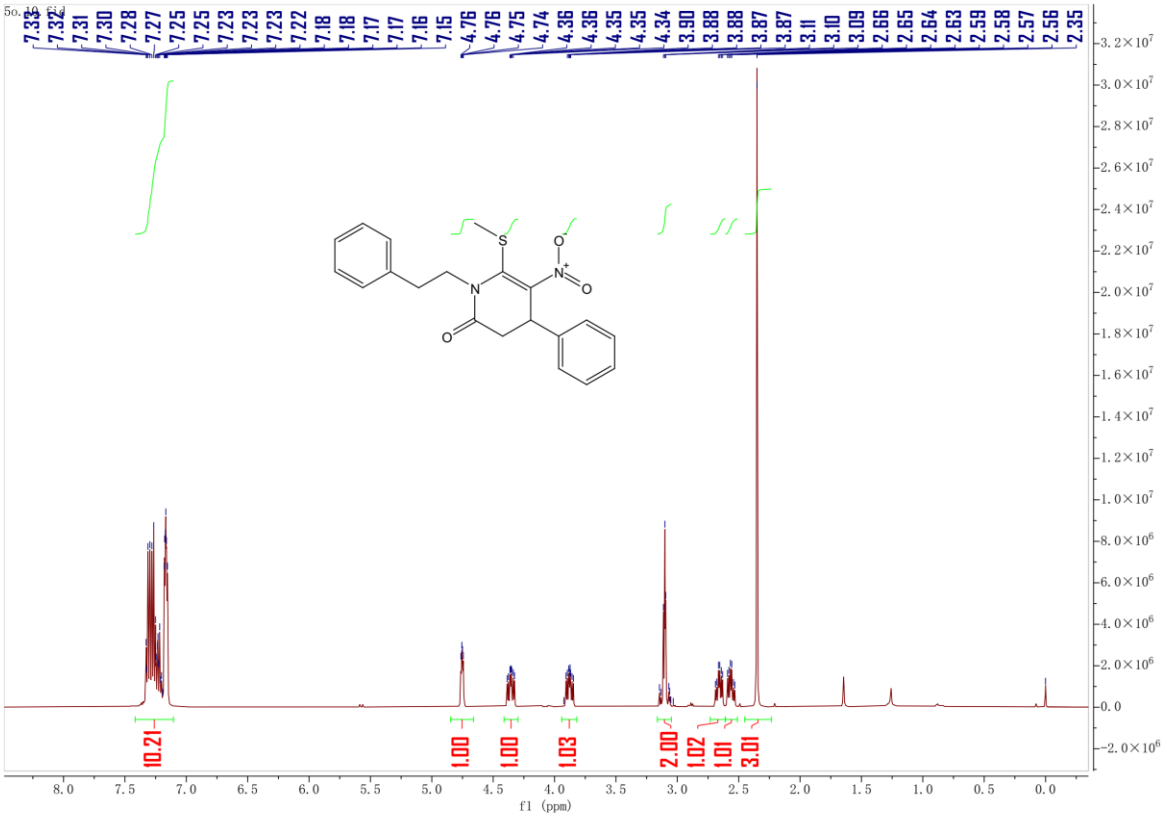
^{13}C NMR spectrum of 5k



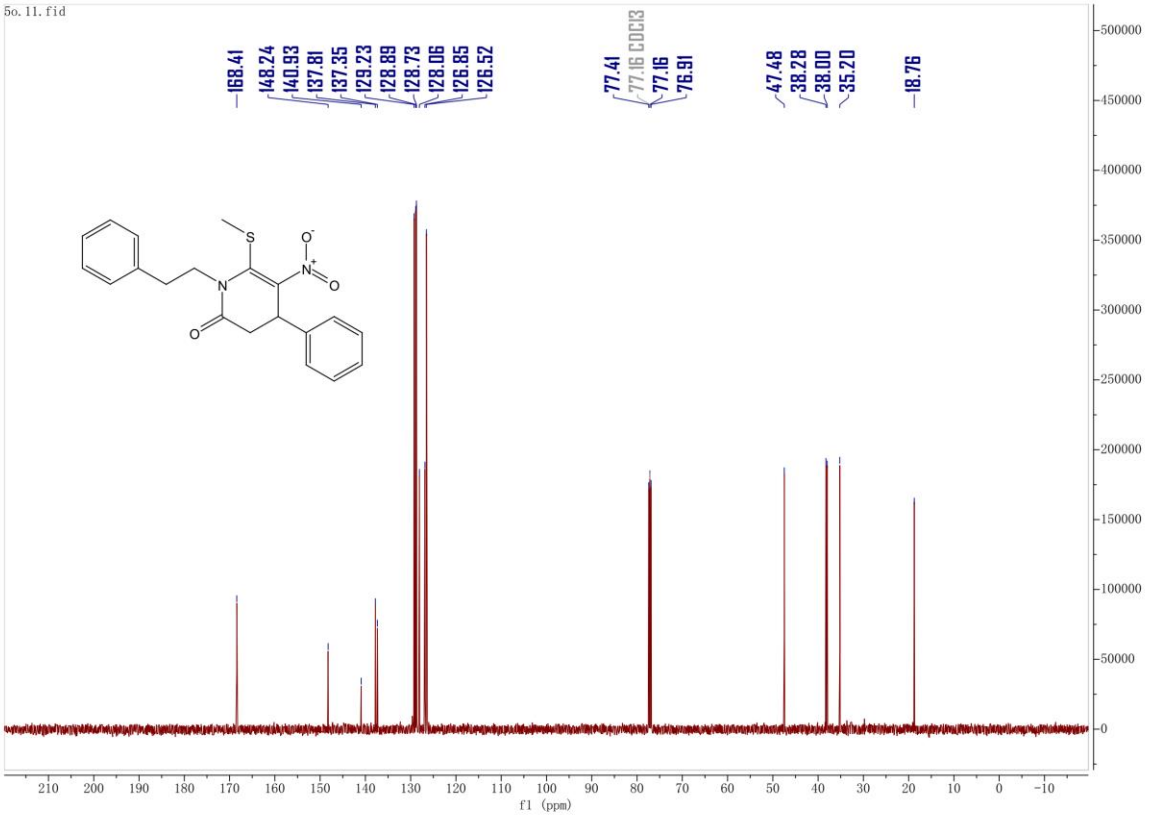
^{1}H NMR spectrum of 5l



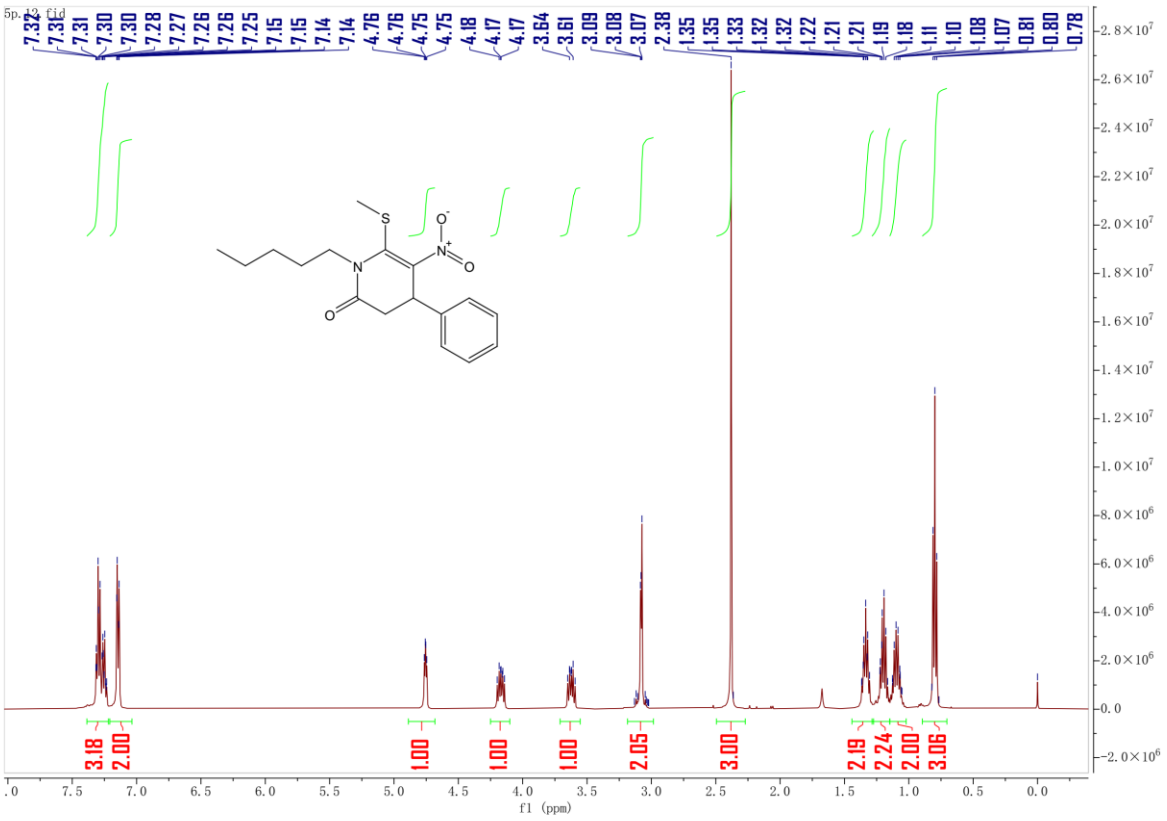
^{13}C NMR spectrum of 5l



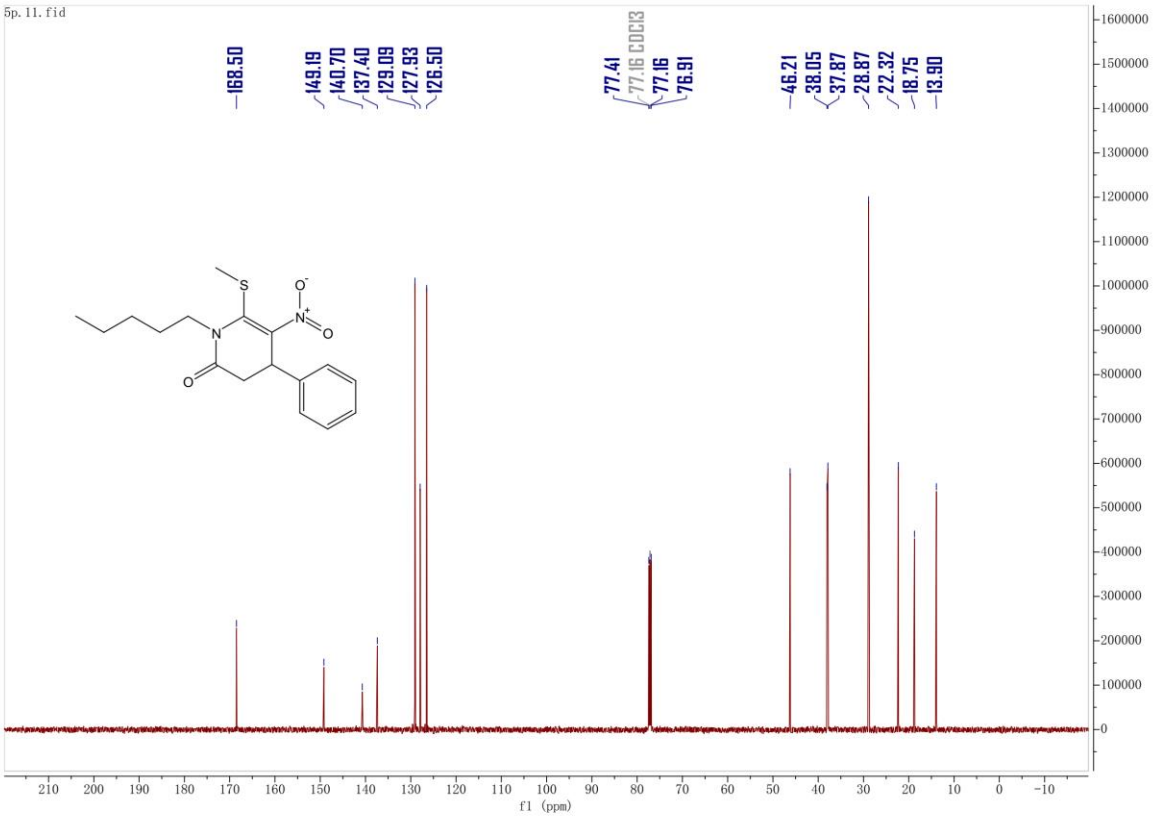
^{1}H NMR spectrum of 5m



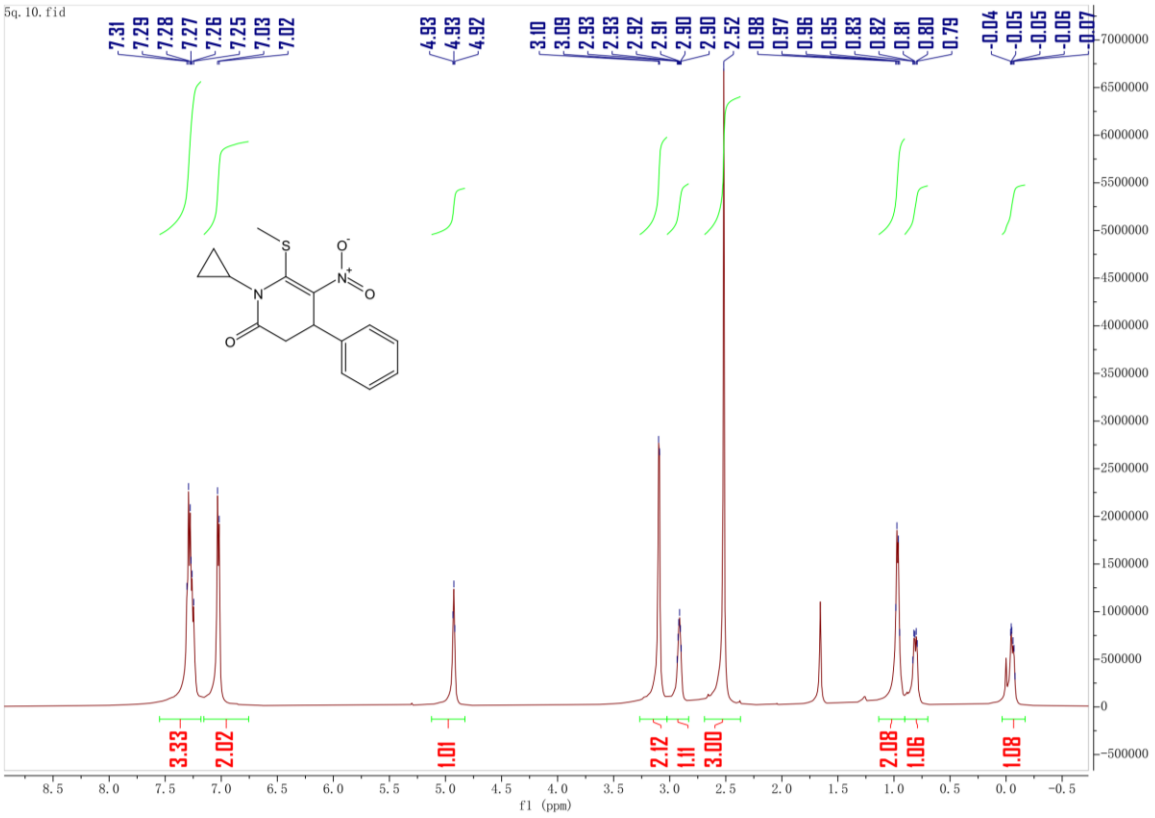
^{13}C NMR spectrum of 5m



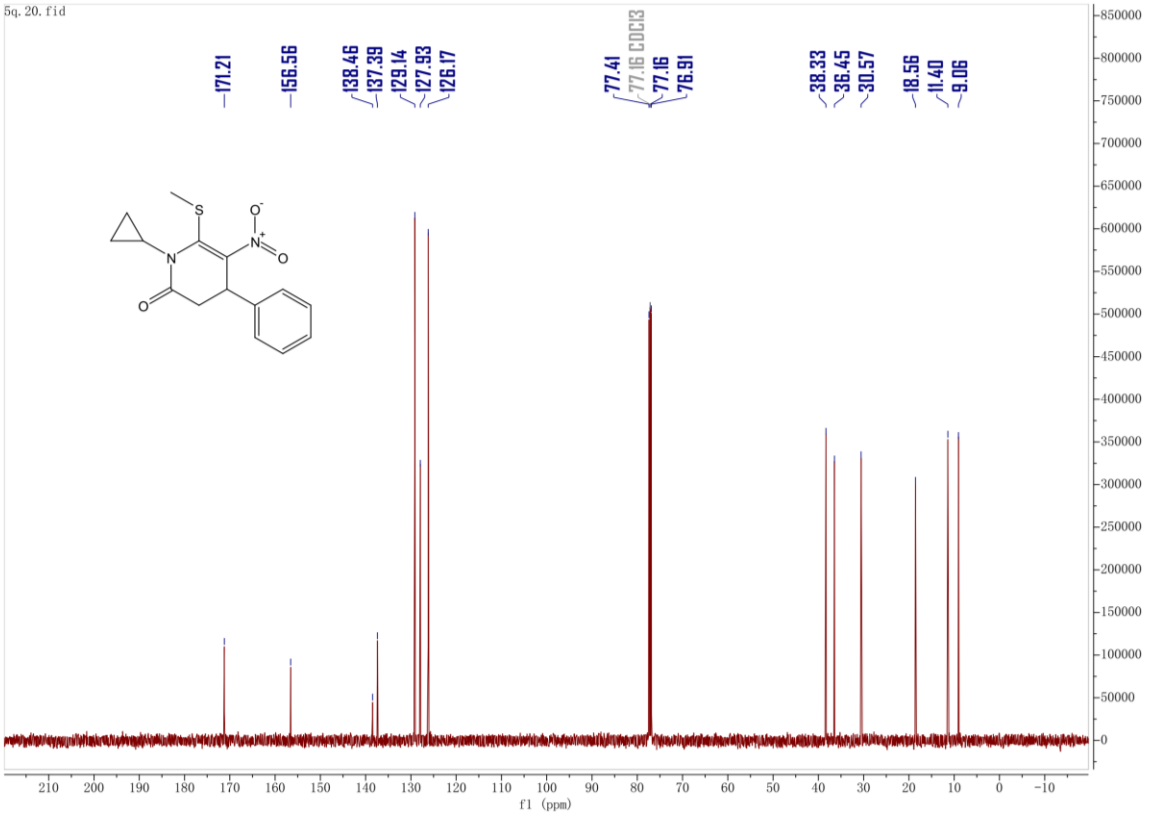
^{1}H NMR spectrum of 5n



^{13}C NMR spectrum of 5n

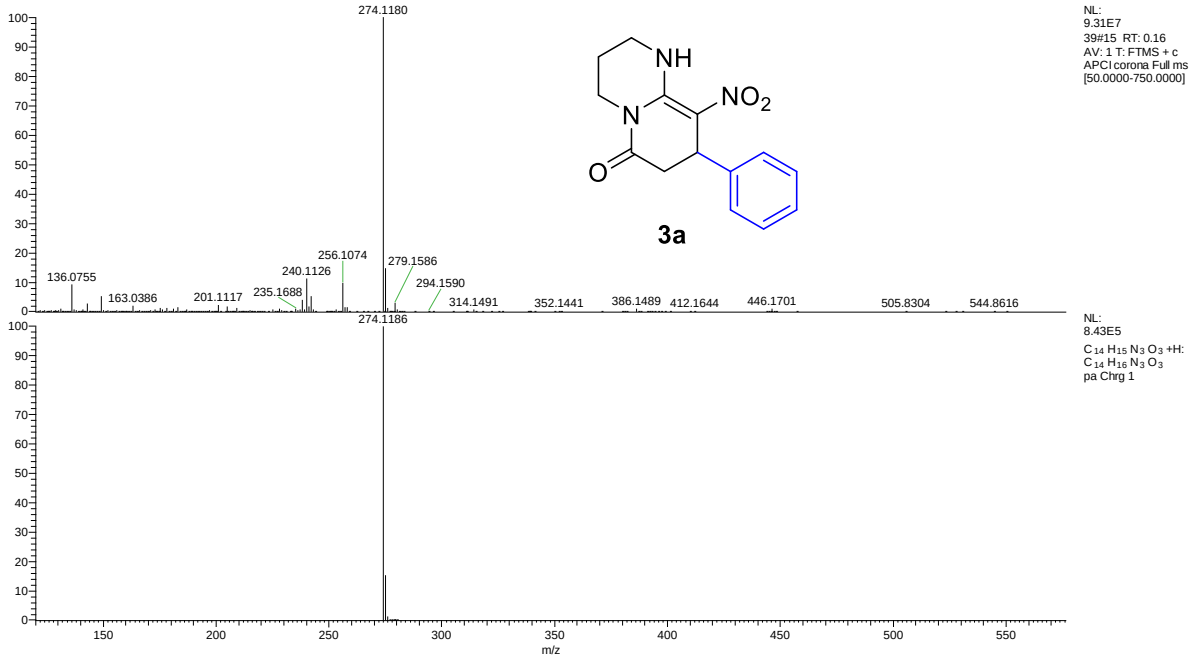


^{1}H NMR spectrum of 5o

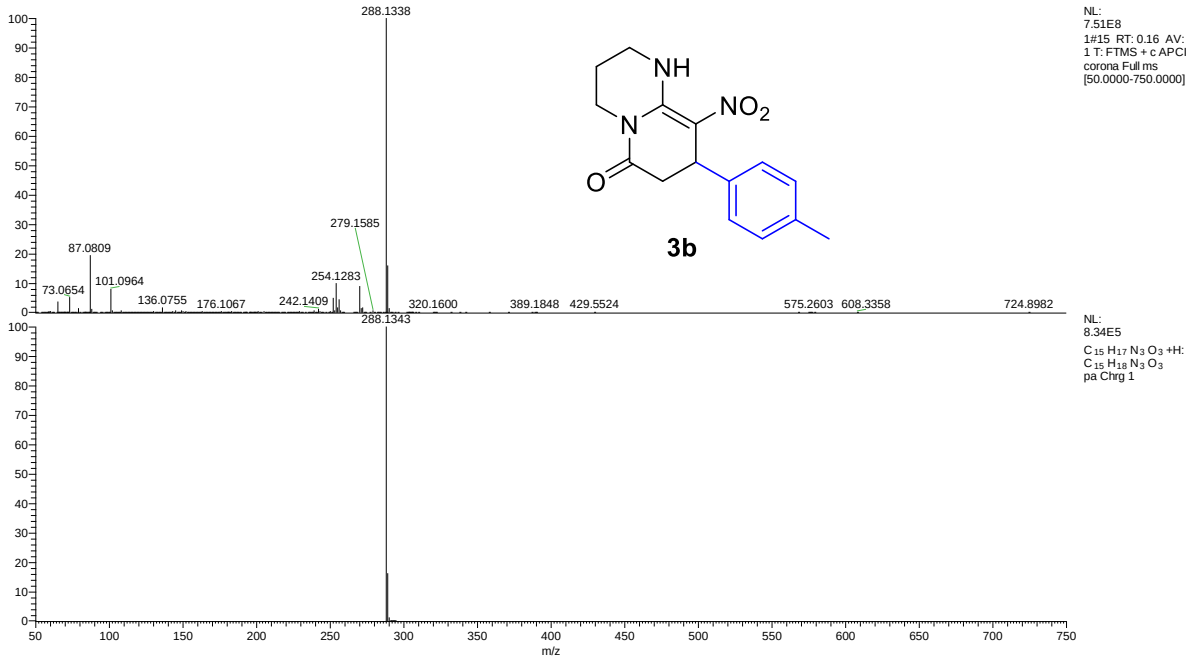


^{13}C NMR spectrum of 5o

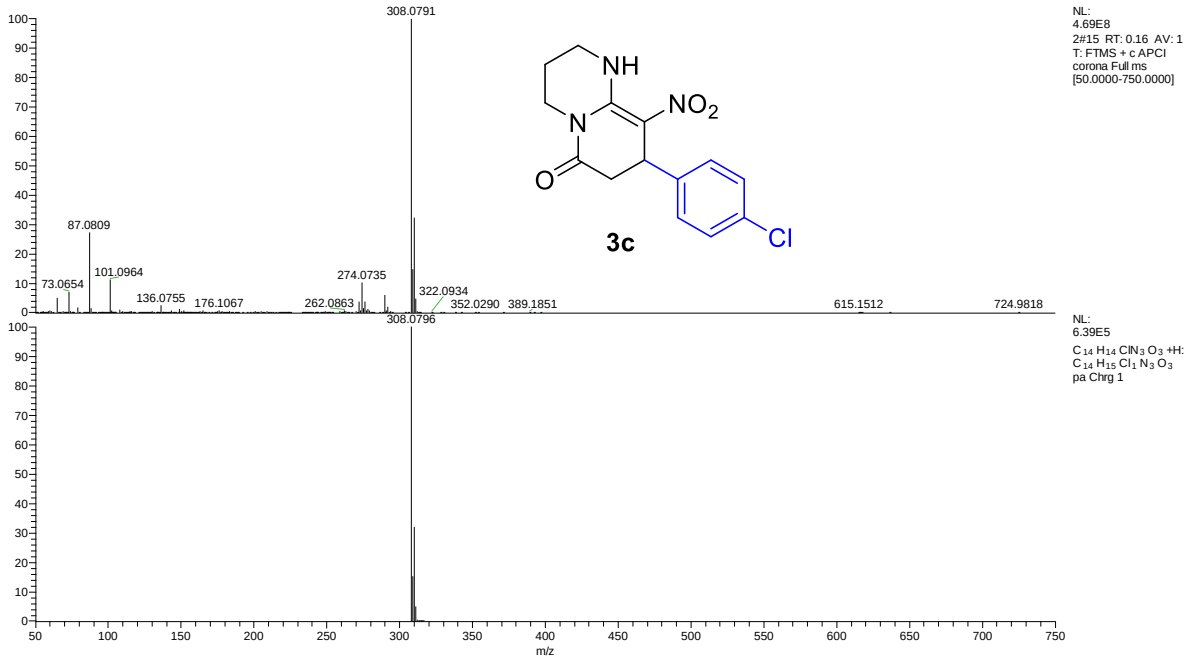
10.Copies of HRMS spectra



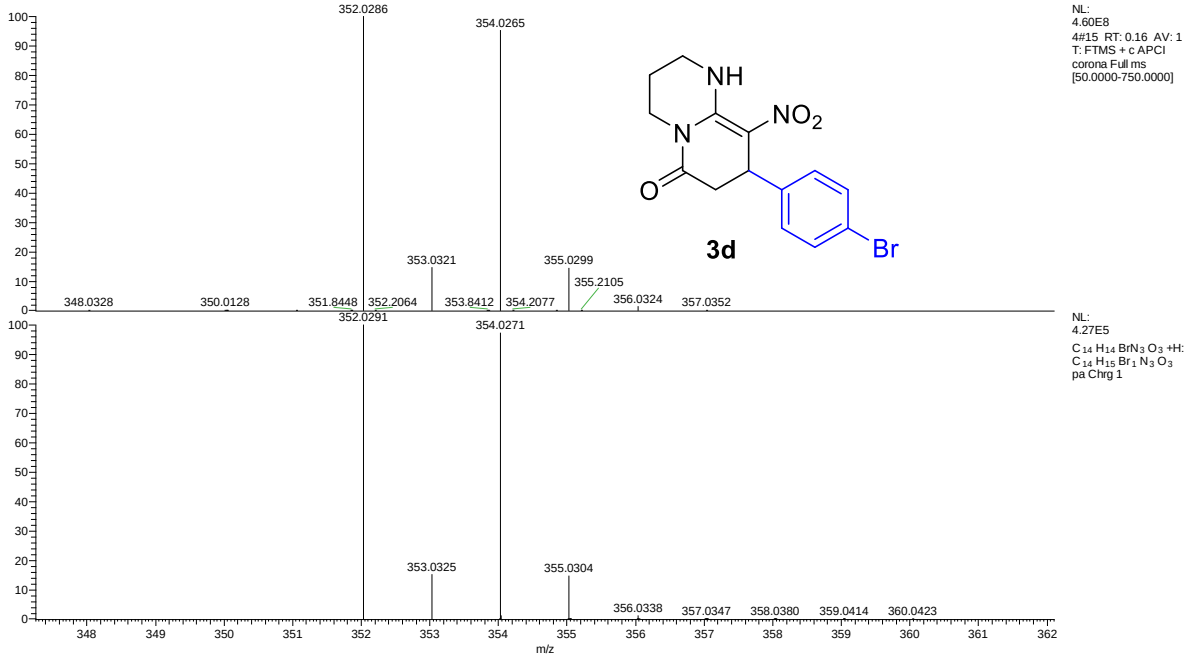
HRMS (ESI): exact mass calculated for $C_{14}H_{16}N_3O_3$ $[M + H]^+$ 274.1186, found 274.1180.



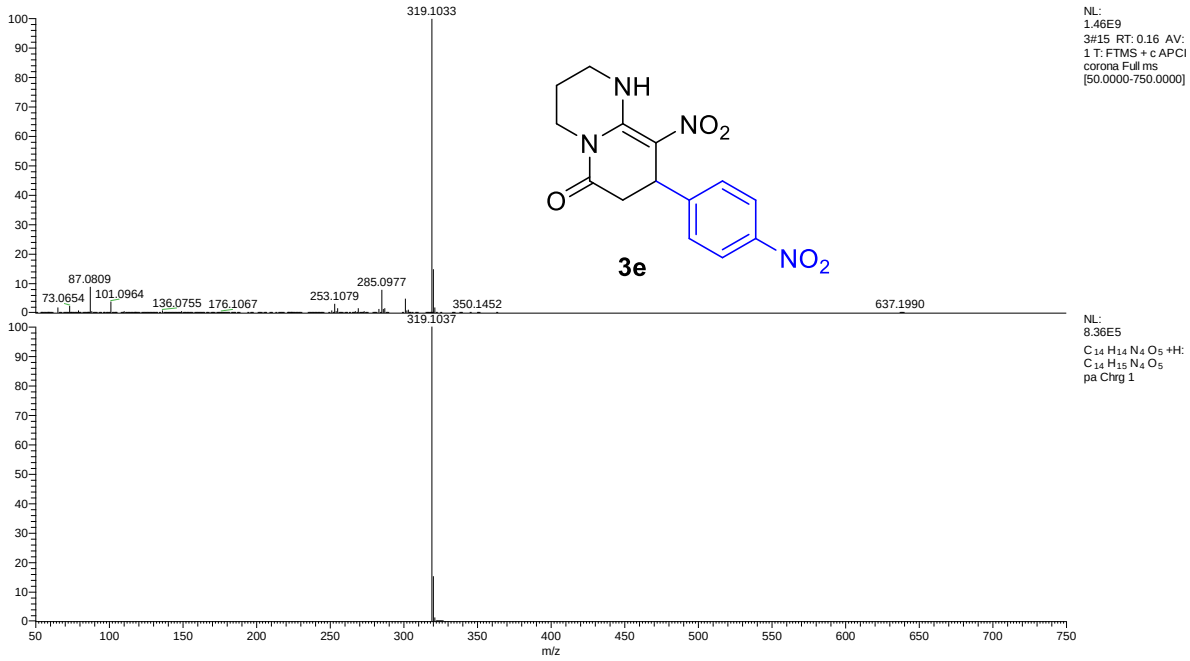
HRMS (ESI): exact mass calculated for $C_{15}H_{18}N_3O_3$ $[M + H]^+$: 288.1343, found 288.1338.



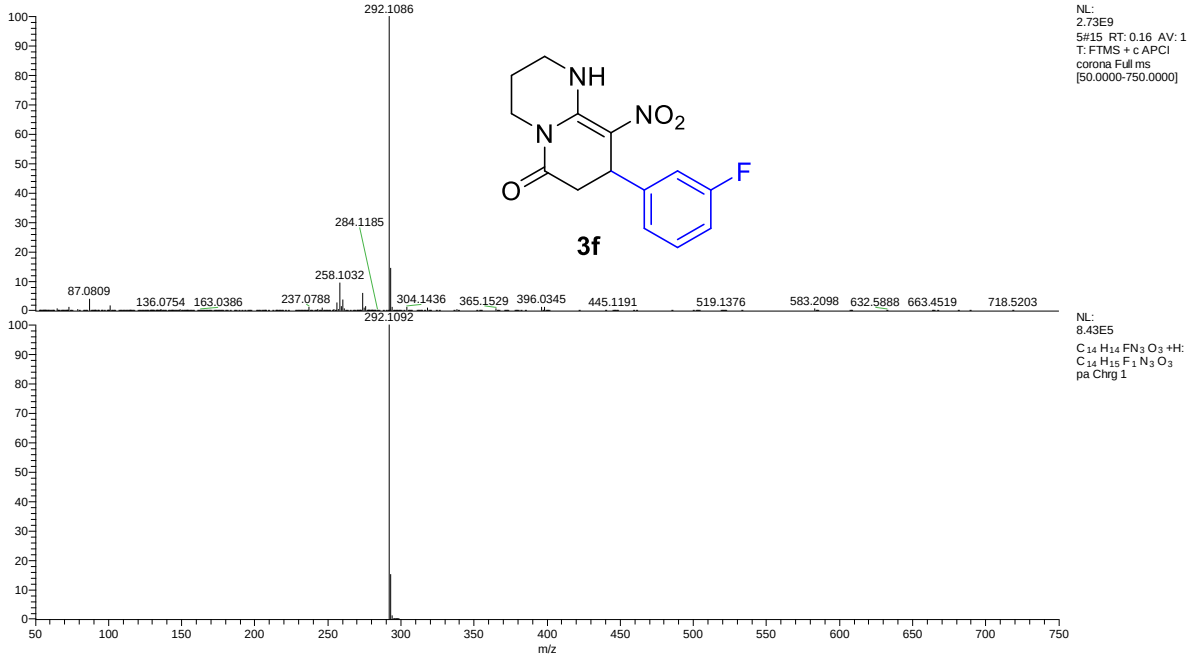
HRMS (ESI): exact mass calculated for $C_{14}H_{15}ClN_3O_3$ $[M + H]^+$: 308.0796, found 308.0791.



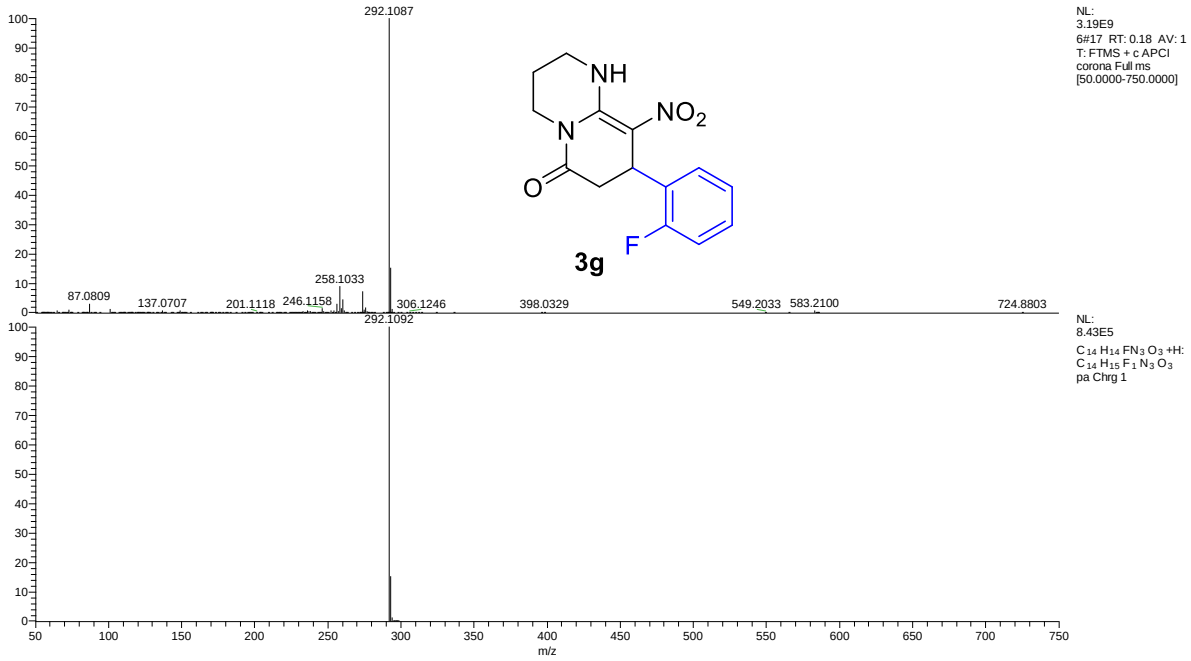
HRMS (ESI): exact mass calculated for $C_{14}H_{15}BrN_3O_3$ $[M + H]^+$: 353.0325, found 353.0321.



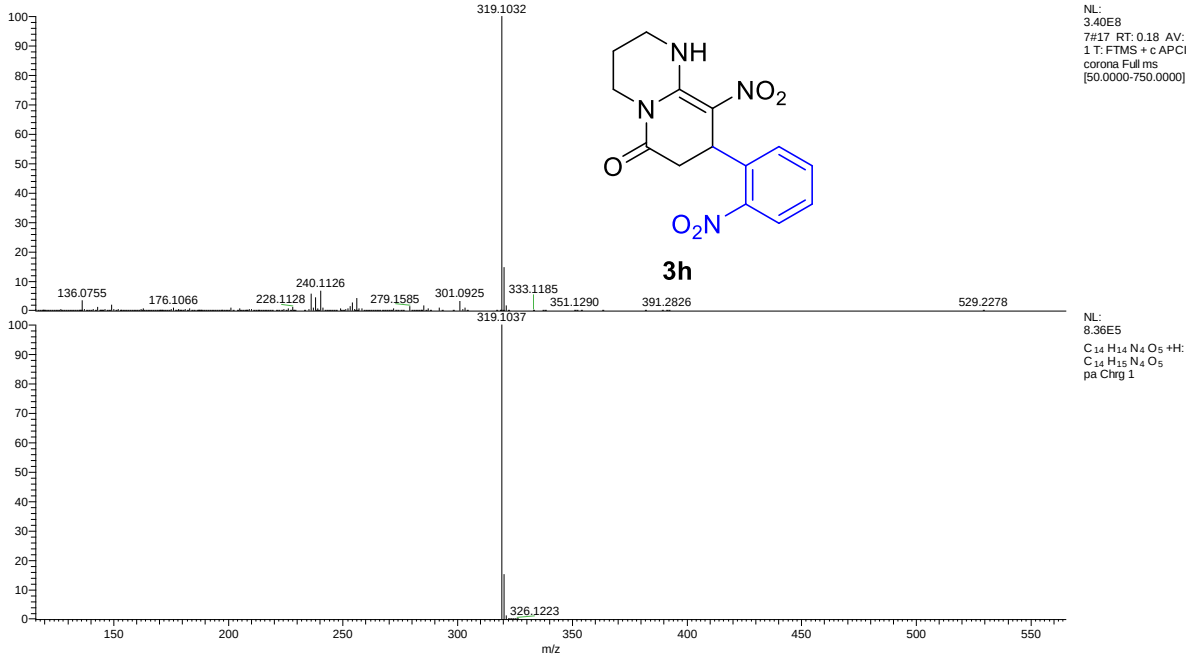
HRMS (ESI): exact mass calculated for $C_{14}H_{15}N_4O_5$ $[M + H]^+$: 319.1037, found 319.1033.



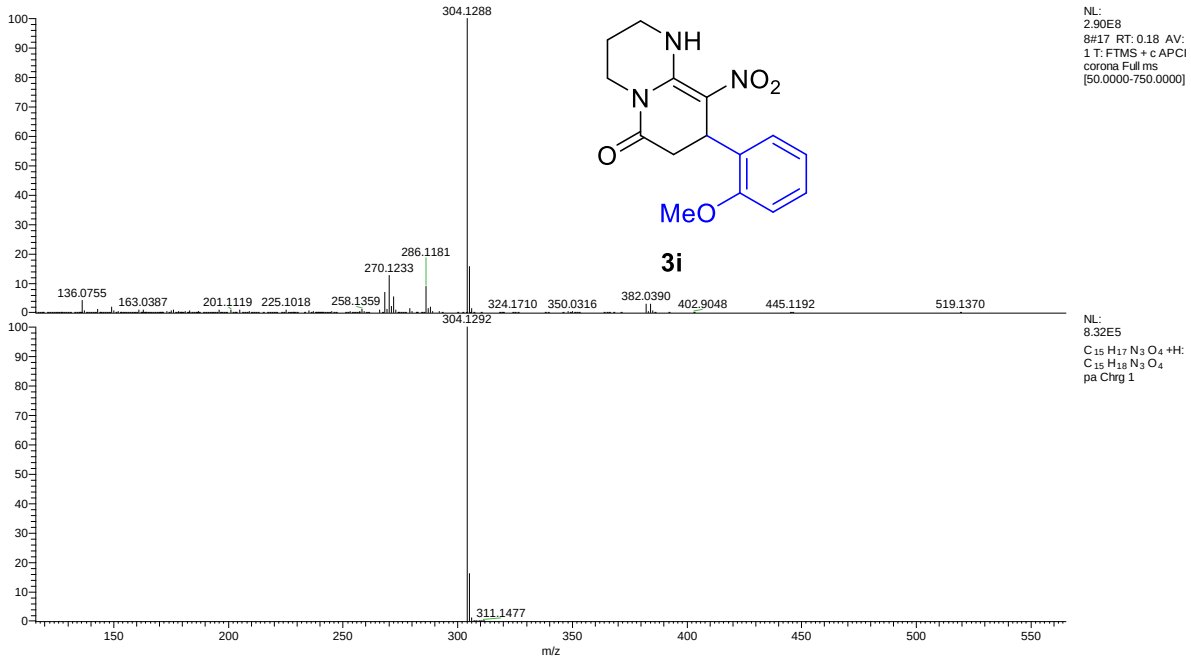
HRMS (ESI): exact mass calculated for $C_{14}H_{15}FN_3O_3$ $[M + H]^+$: 292.1092, found 292.1086.



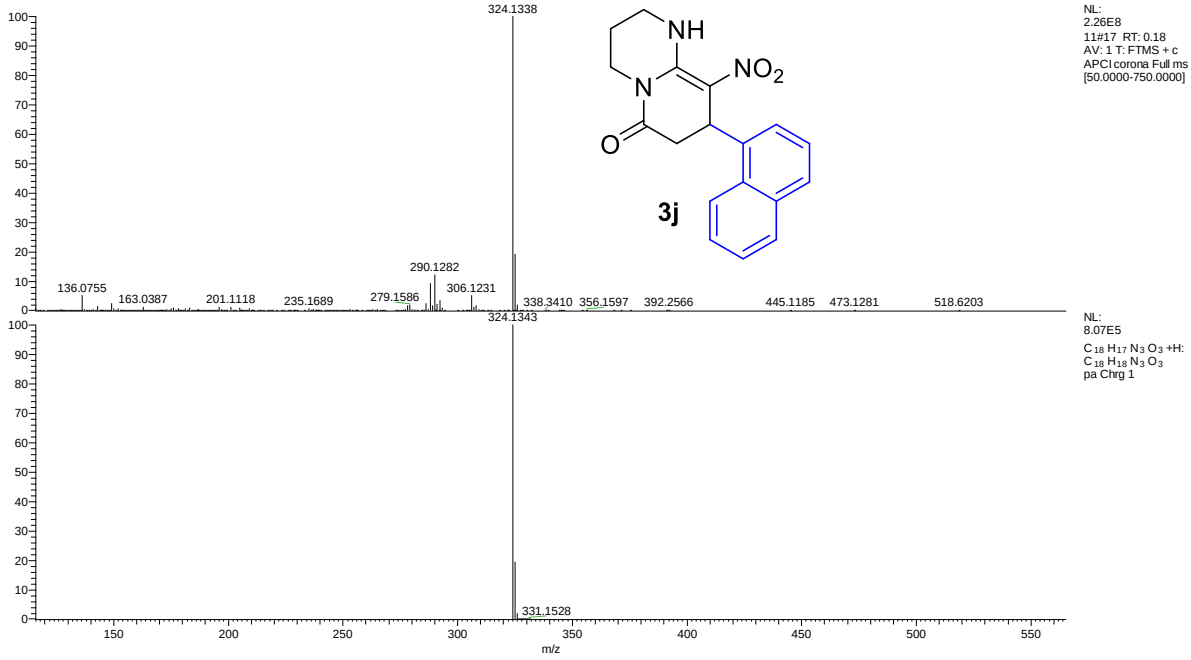
HRMS (ESI): exact mass calculated for $C_{14}H_{15}FN_3O_3$ $[M + H]^+$: 292.1092, found 292.1087.



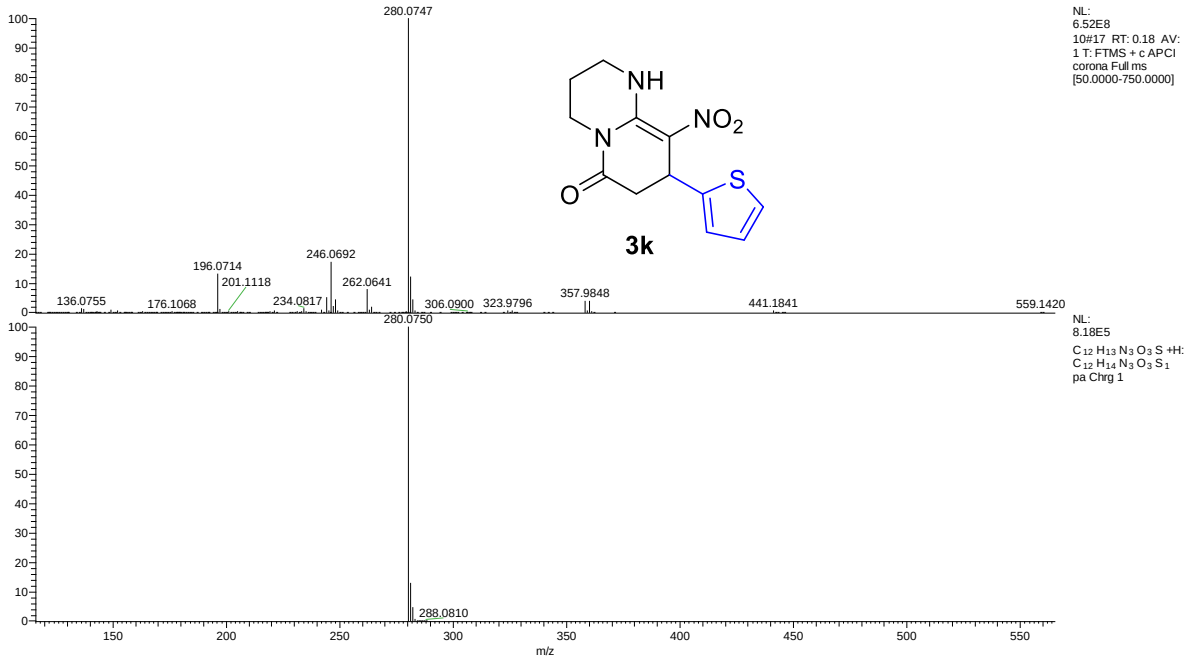
HRMS (ESI): exact mass calculated for $C_{14}H_{15}N_4O_5$ $[M + H]^+$: 319.1037, found 319.1032.



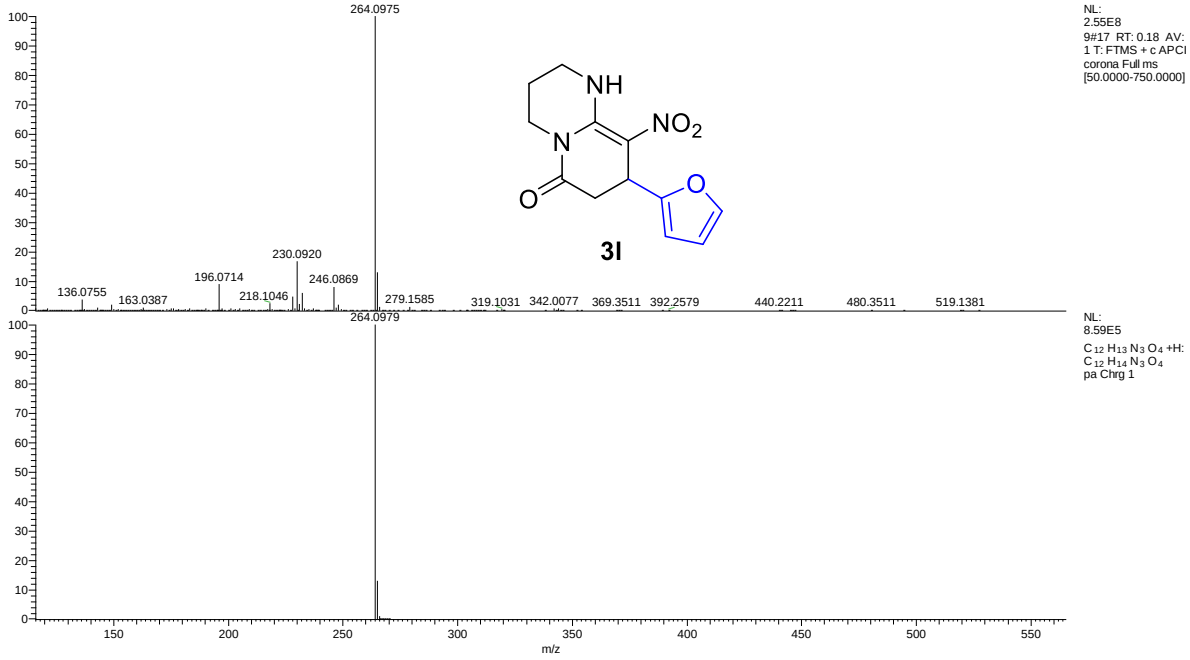
HRMS (ESI): exact mass calculated for $C_{15}H_{18}N_3O_4$ $[M + H]^+$: 304.1292, found 304.1292.



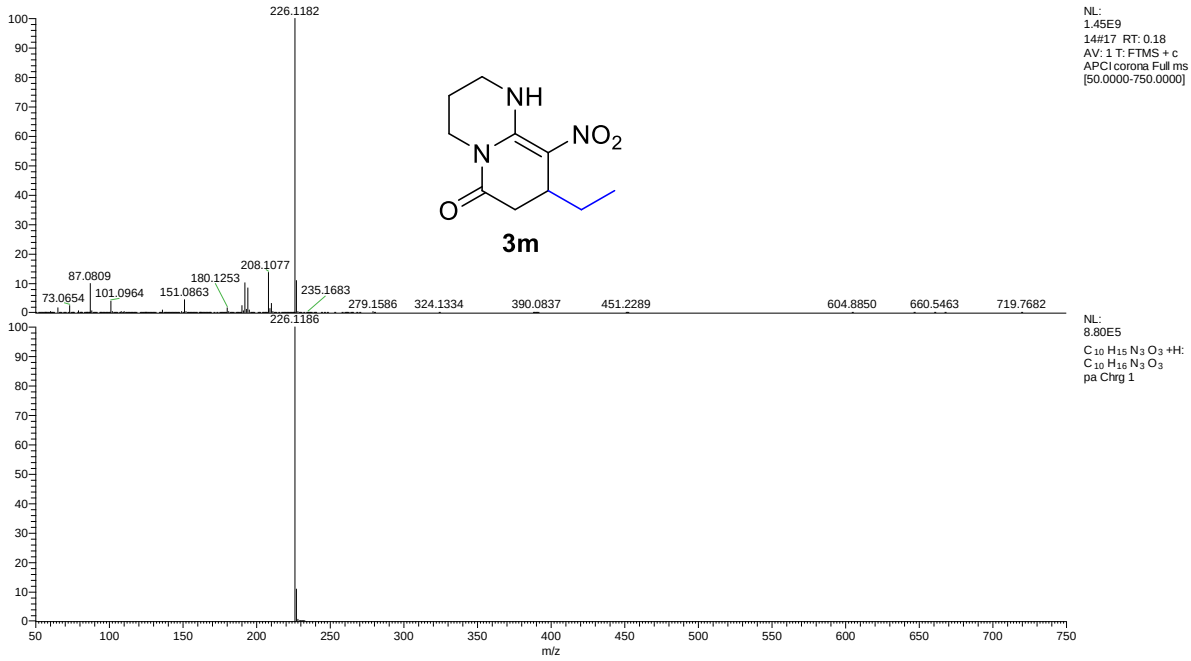
HRMS (ESI): exact mass calculated for $C_{18}H_{18}N_3O_3$ $[M + H]^+$: 324.1343, found 324.1338.



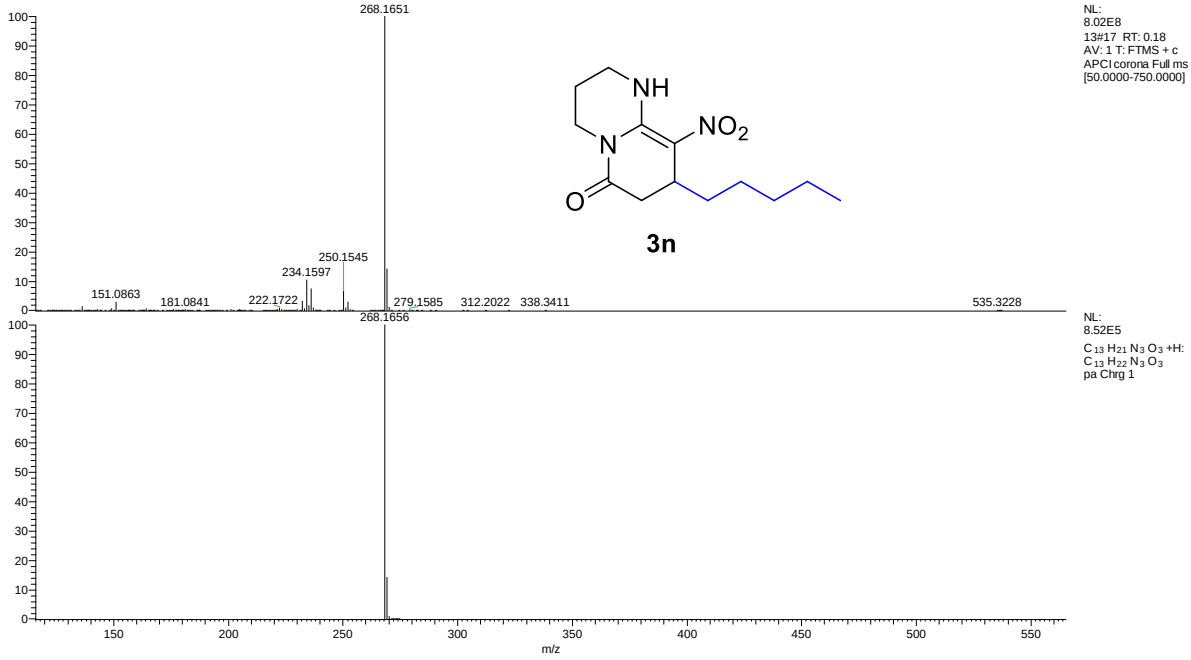
HRMS (ESI): exact mass calculated for $C_{12}H_{14}N_3O_3S$ $[M + H]^+$: 280.0750, found 280.0747.



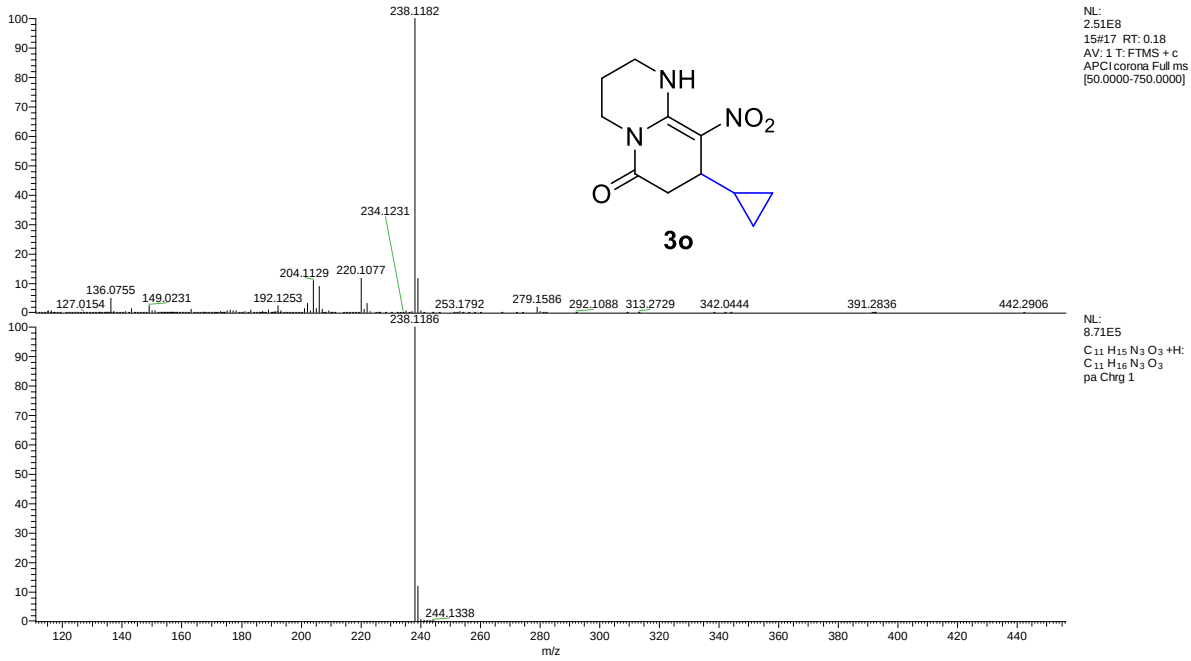
HRMS (ESI): exact mass calculated for $C_{12}H_{14}N_3O_4$ $[M + H]^+$: 264.0979, found 264.0975.



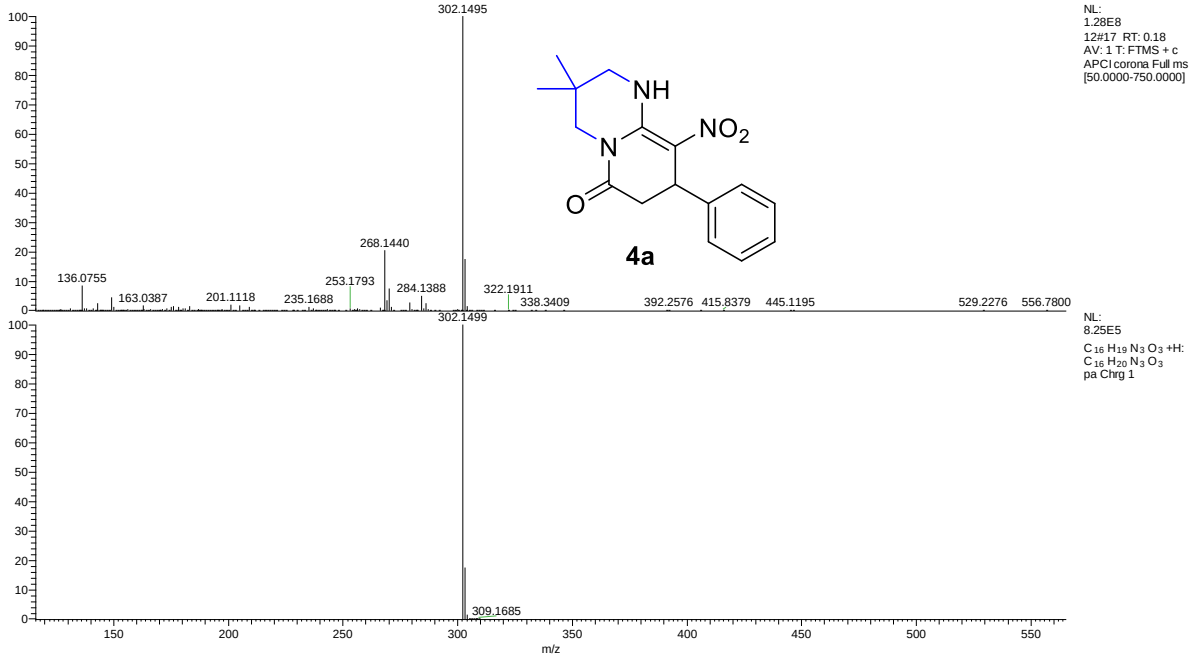
HRMS (ESI): exact mass calculated for $C_{10}H_{16}N_3O_3$ $[M + H]^+$: 226.1186, found 226.1182.



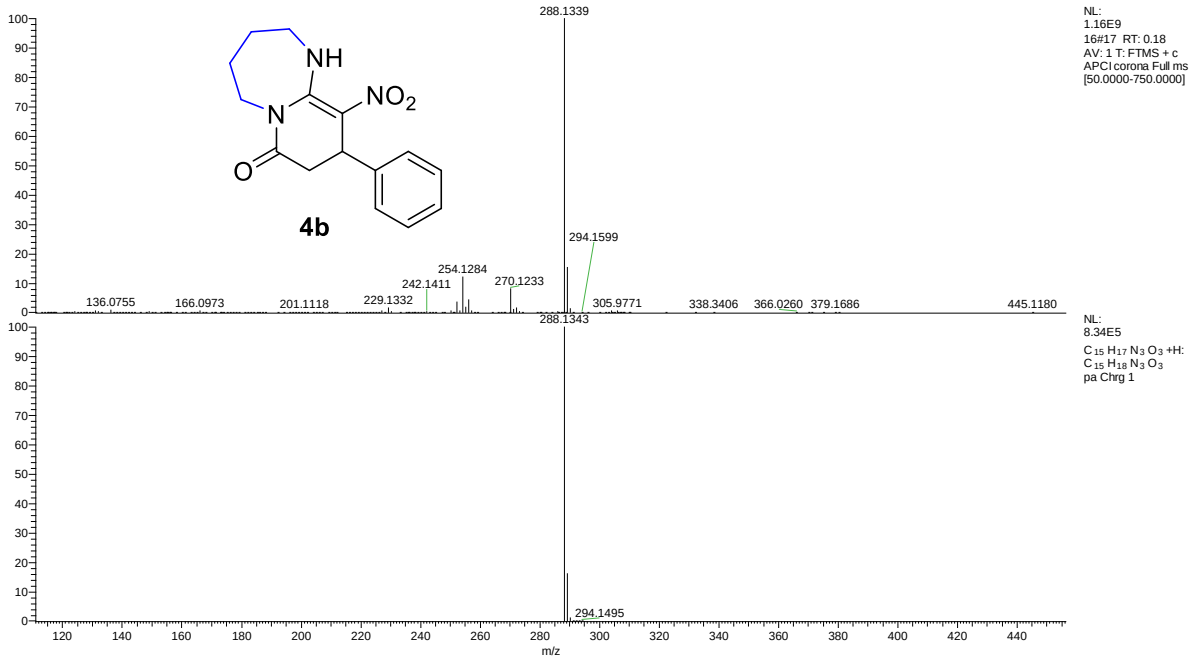
HRMS (ESI): exact mass calculated for $C_{13}H_{22}N_3O_3$ $[M + H]^+$: 268.1656, found 268.1651.



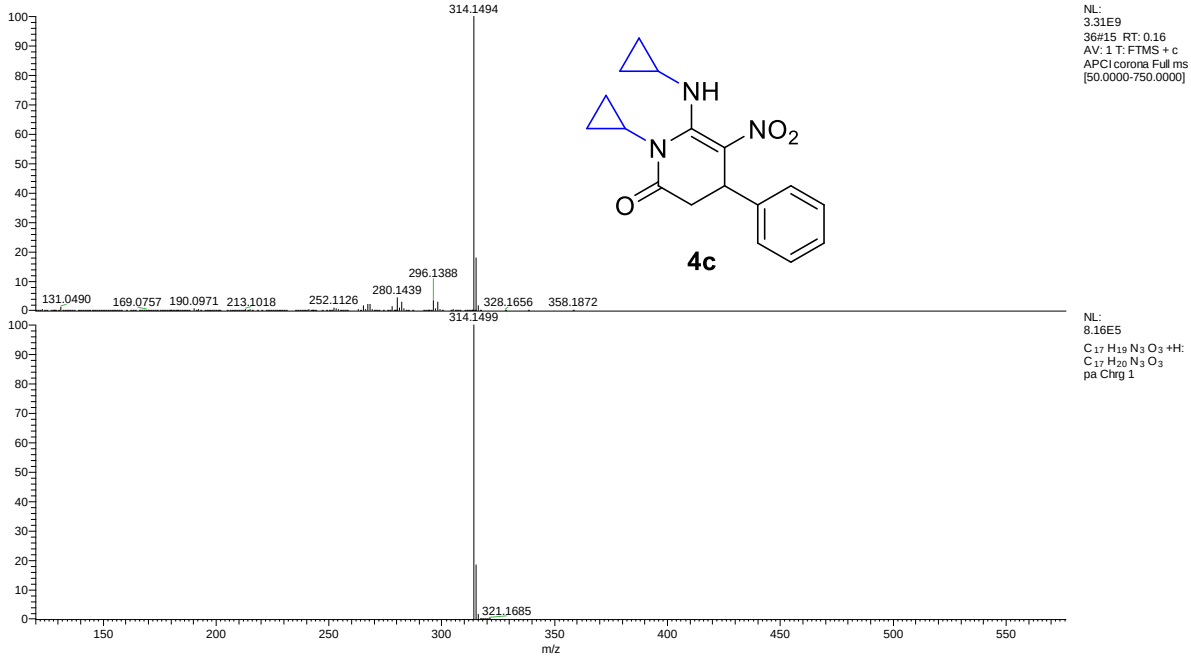
HRMS (ESI): exact mass calculated for $C_{11}H_{16}N_3O_3$ $[M + H]^+$: 238.1186, found 238.1182.



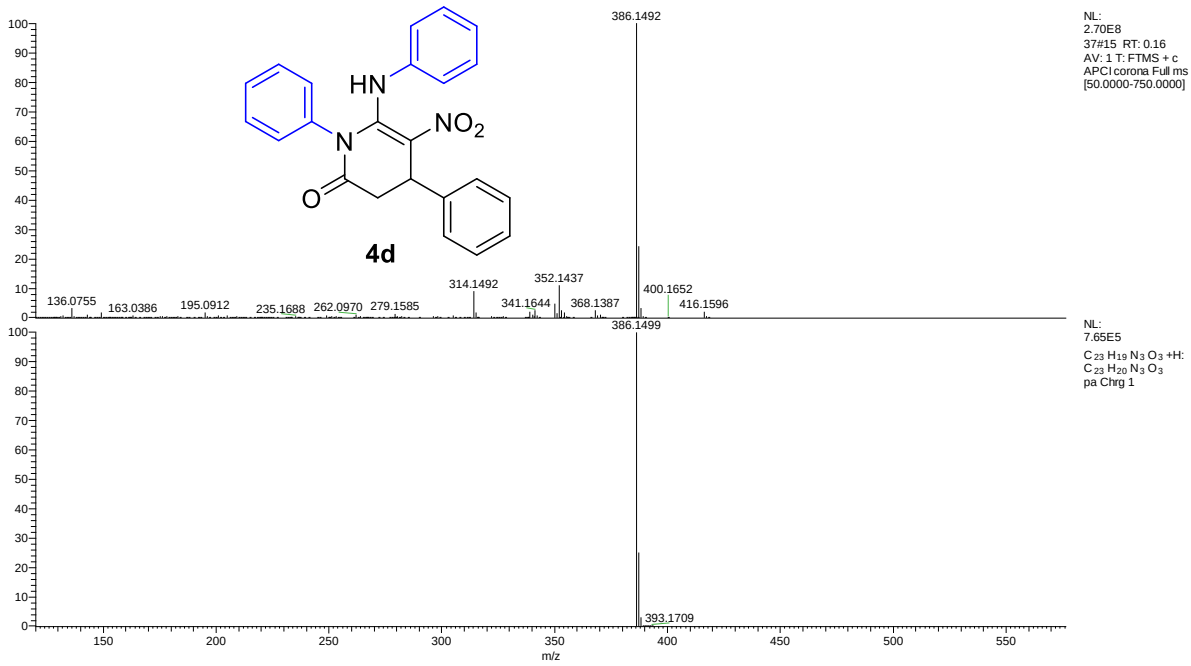
HRMS (ESI): exact mass calculated for $C_{16}H_{20}N_3O_3$ $[M + H]^+$: 302.1499, found 302.1495.



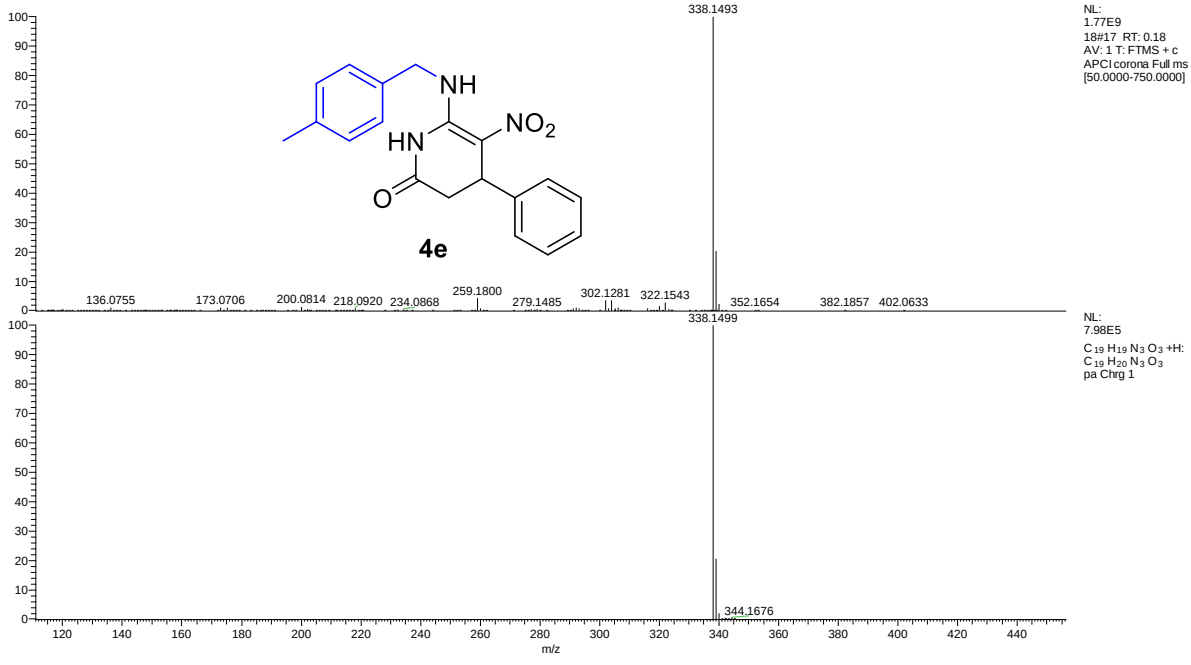
HRMS (ESI): exact mass calculated for $C_{15}H_{18}N_3O_3$ $[M + H]^+$: 288.1343, found 288.1339.



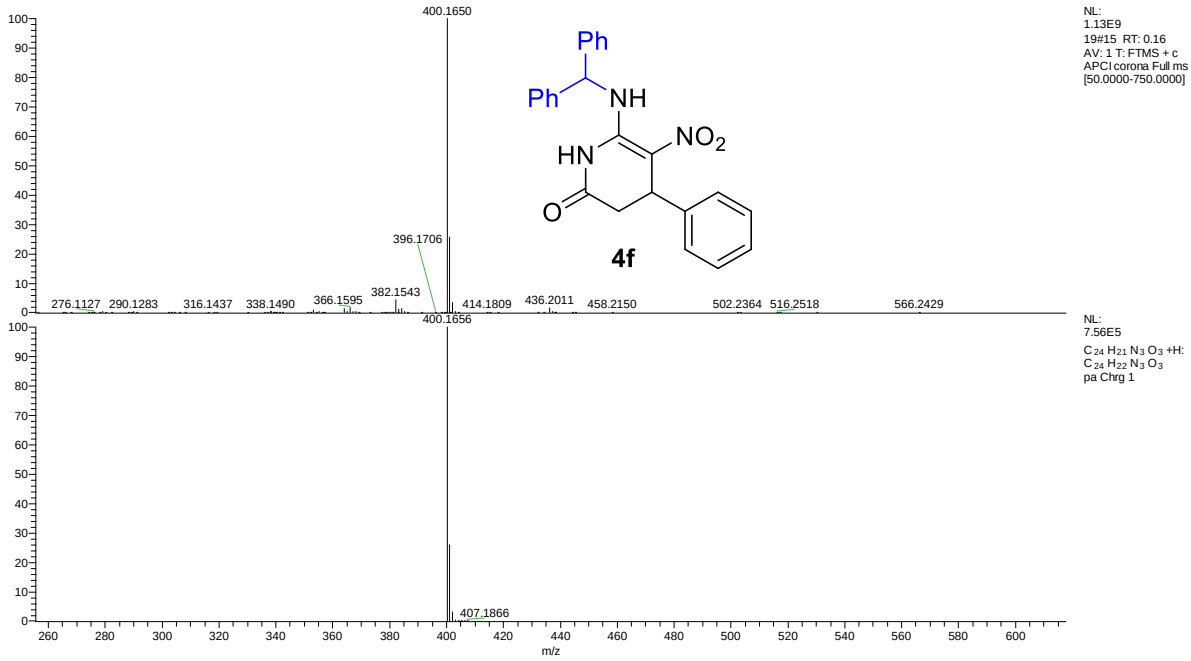
HRMS (ESI): exact mass calculated for $C_{15}H_{17}N_2O_3S$ $[M + H]^+$: 314.1499, found 314.1494.



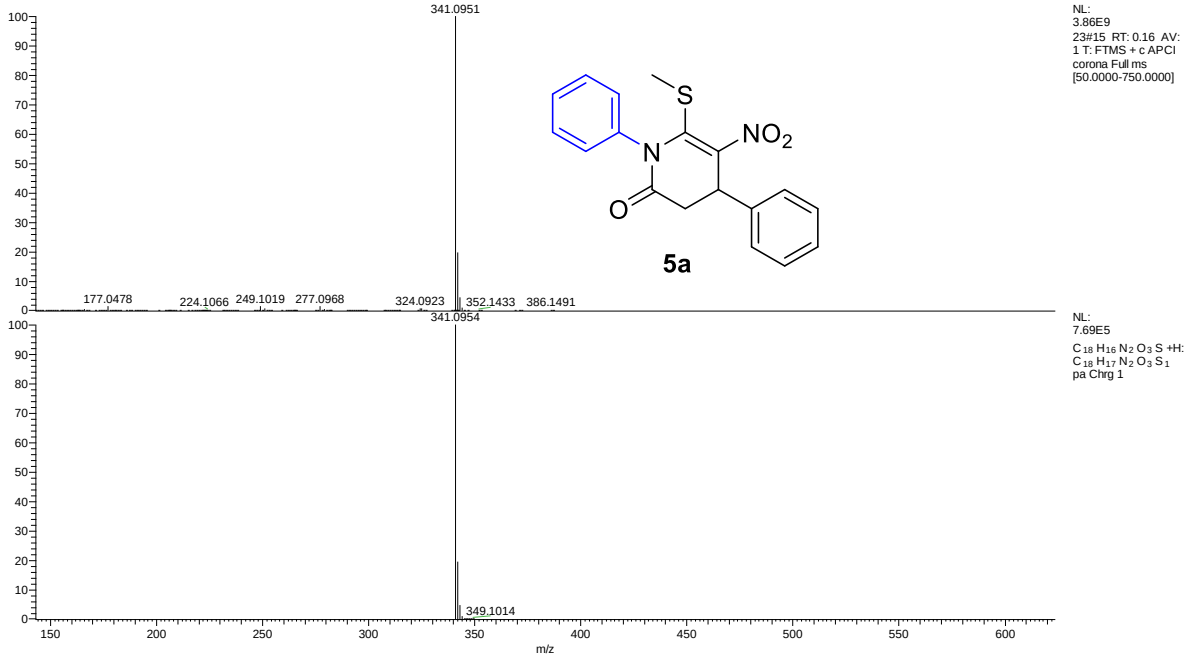
HRMS (ESI): exact mass calculated for $C_{23}H_{20}N_3O_3$ $[M + H]^+$: 386.1499, found 386.1492.



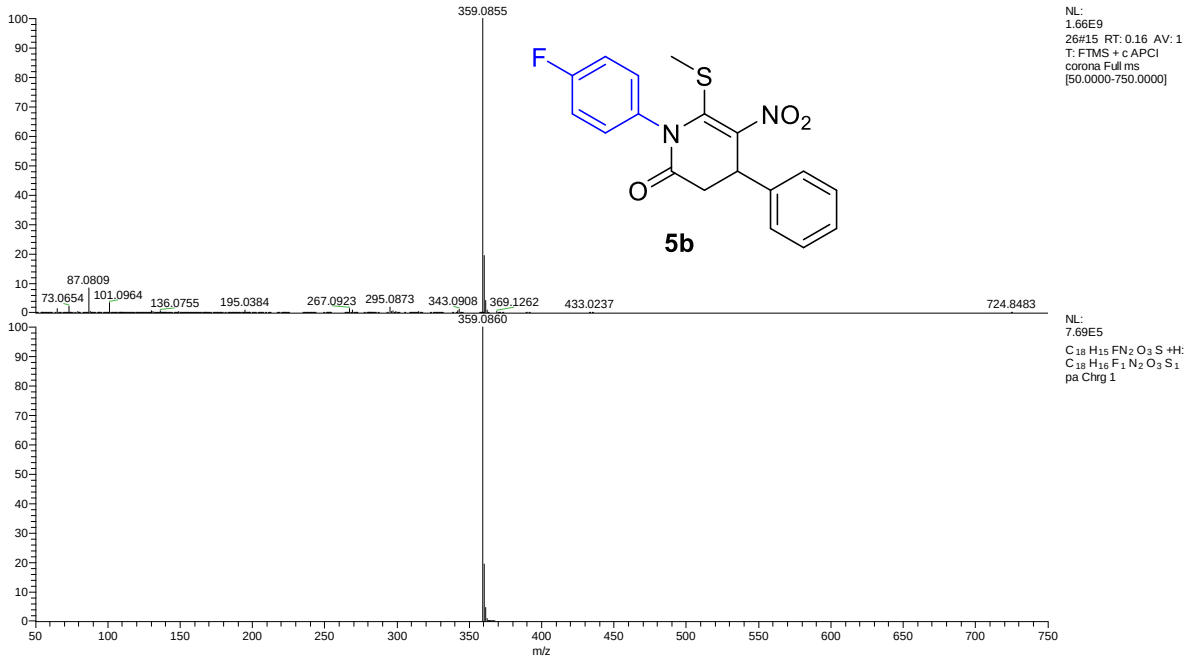
HRMS (ESI): exact mass calculated for $C_{19}H_{20}N_3O_3$ $[M + H]^+$: 338.1499, found 338.1493.



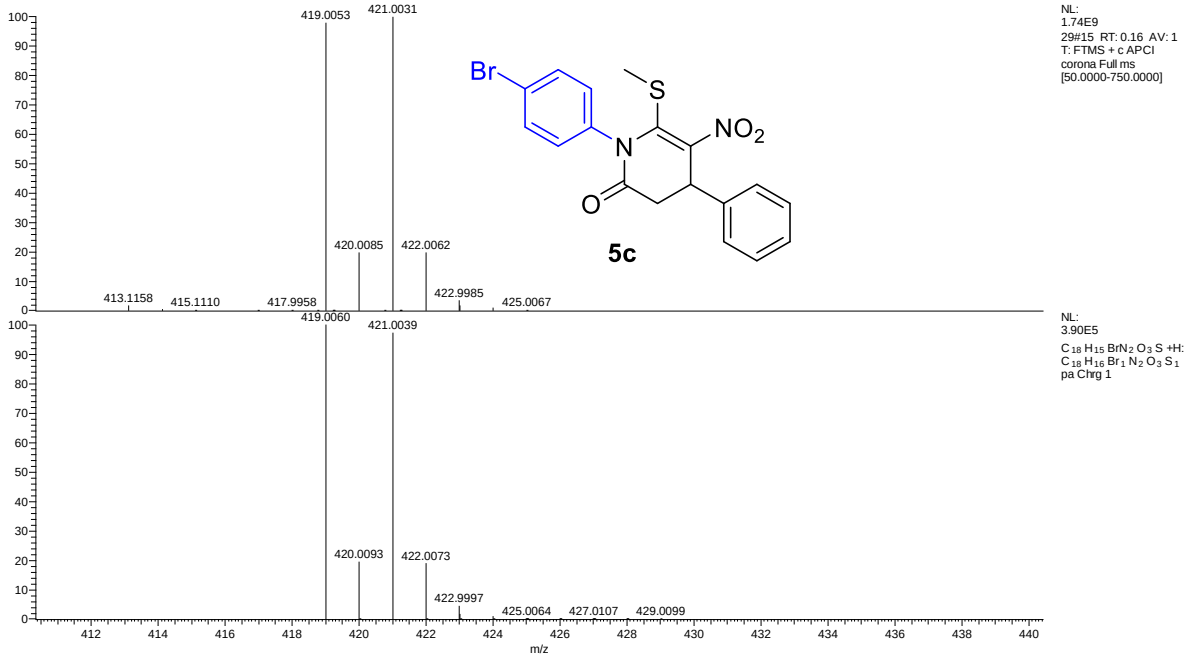
HRMS (ESI): exact mass calculated for $C_{24}H_{22}N_3O_3$ $[M + H]^+$: 400.1656, found 400.1650.



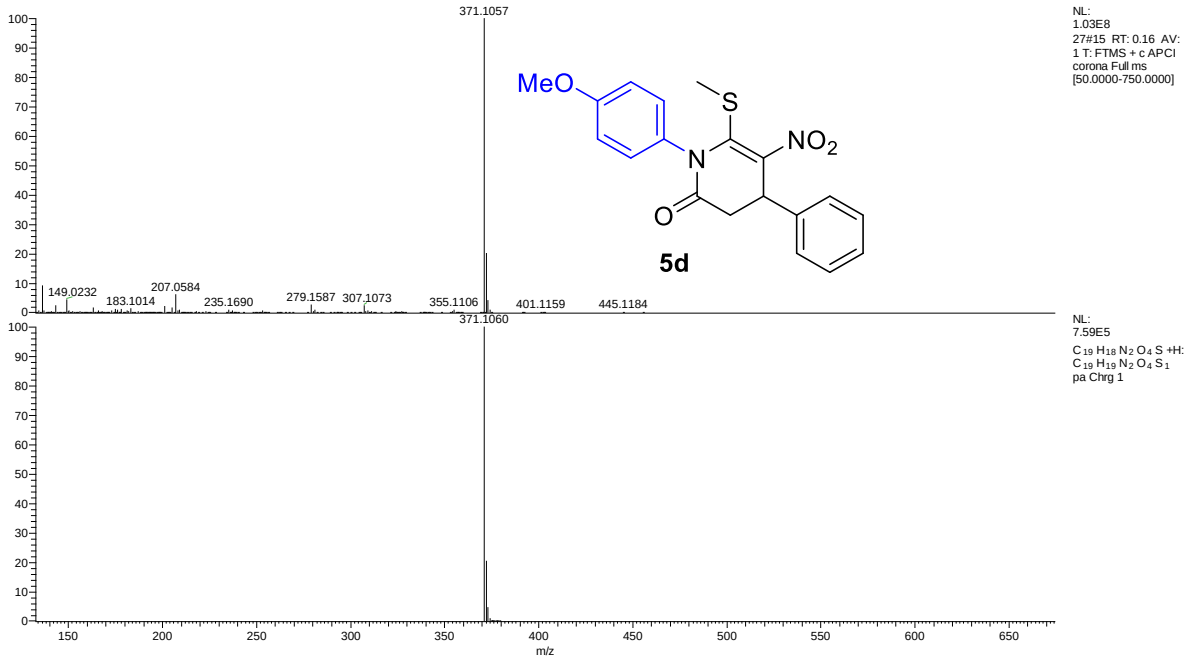
HRMS (ESI): exact mass calculated for $C_{18}H_{17}N_2O_3S$ $[M + H]^+$: 341.0954, found 341.0951.



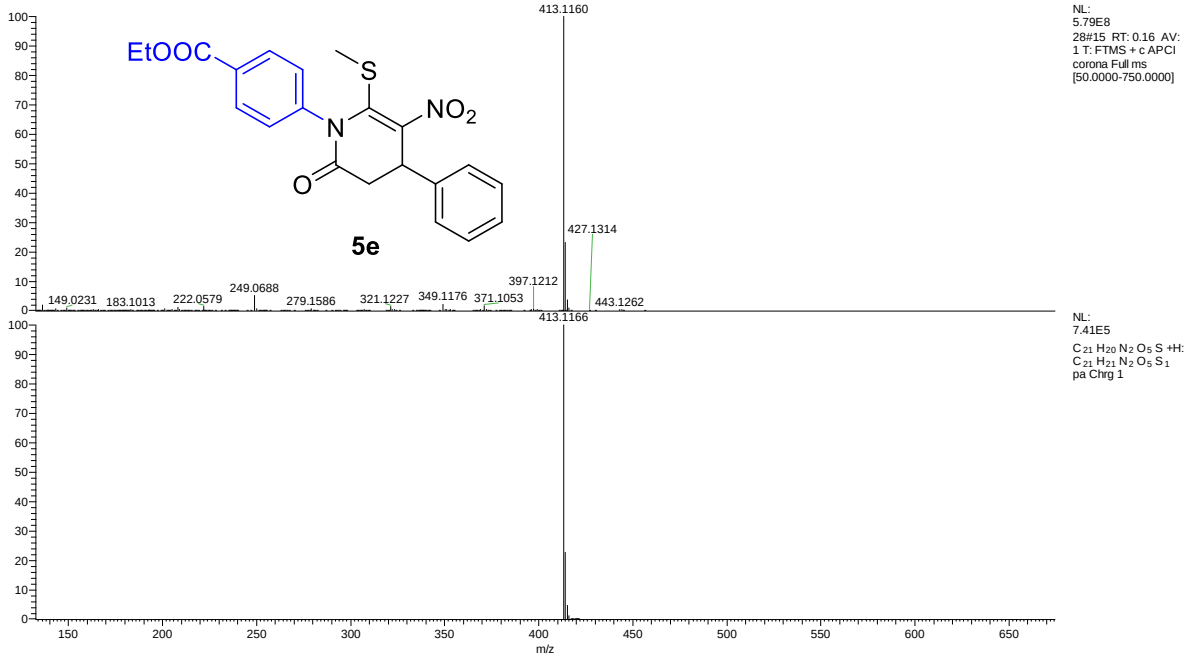
HRMS (ESI): exact mass calculated for $C_{18}H_{16}FN_2O_3S$ $[M + H]^+$: 359.0860, found 359.0855.



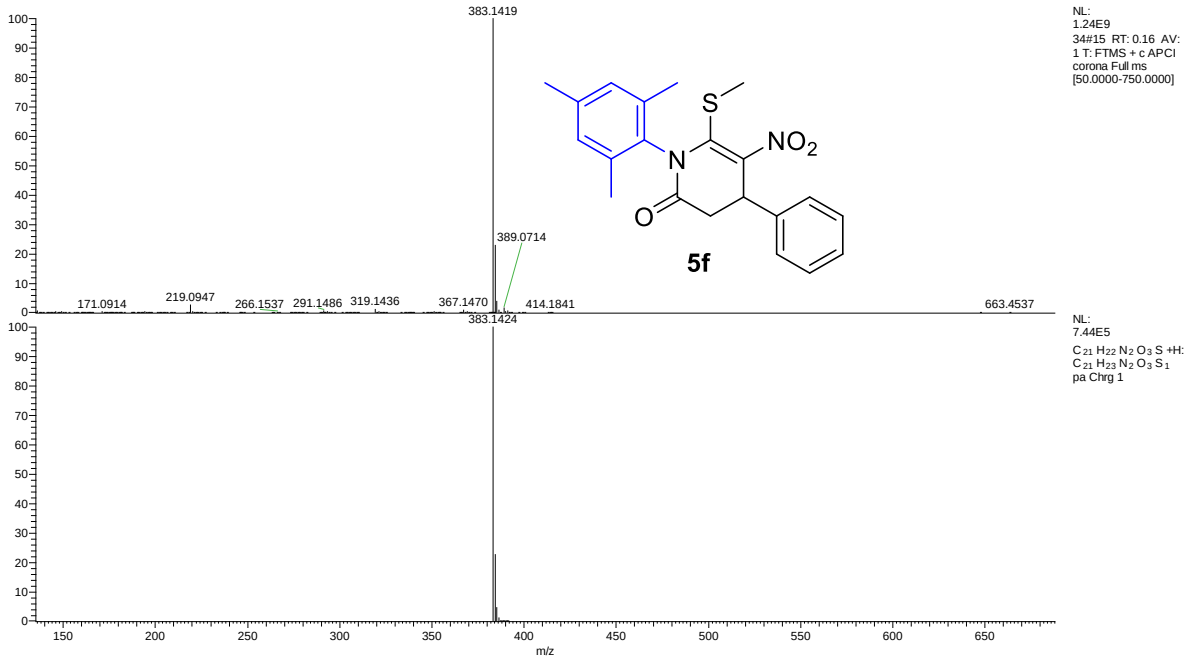
HRMS (ESI): exact mass calculated for $C_{18}H_{16}BrN_2O_3S$ $[M + H]^+$: 420.0093, found 420.0085.



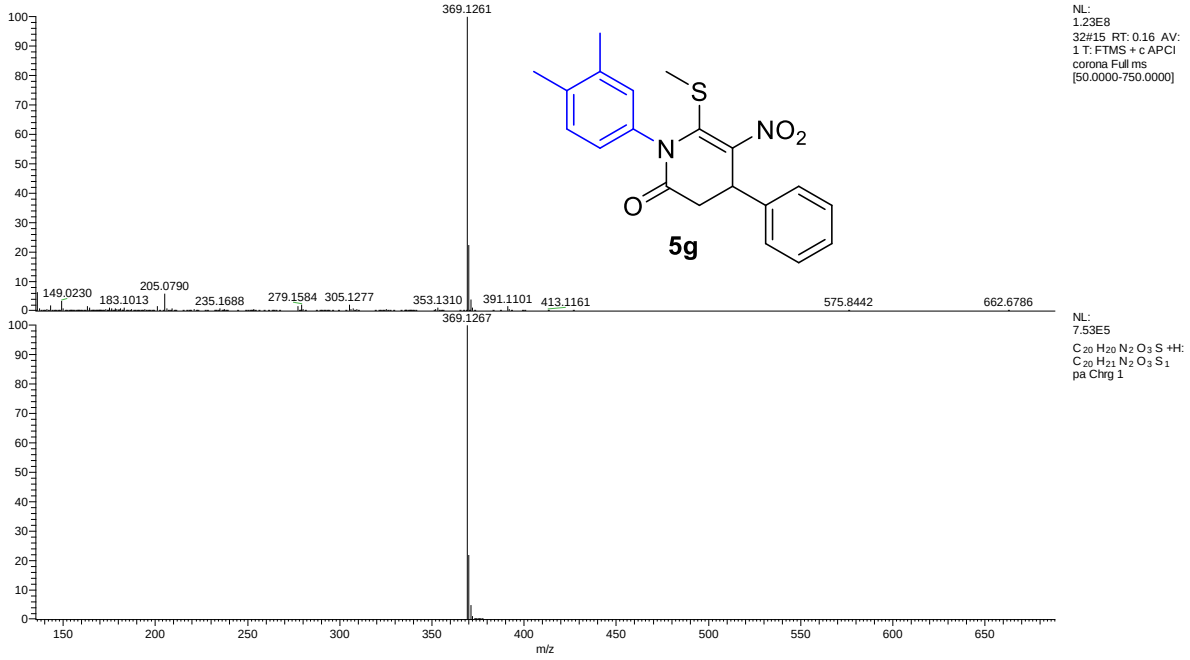
HRMS (ESI): exact mass calculated for $C_{19}H_{19}N_2O_4S$ $[M + H]^+$: 371.1060, found 371.1057.



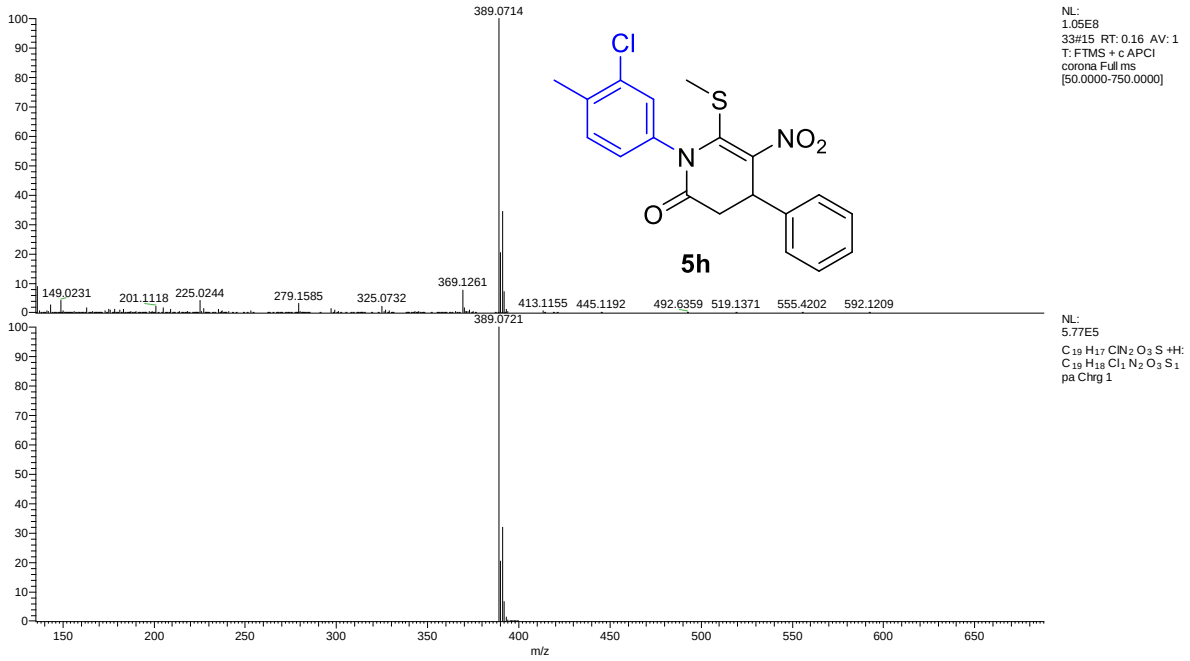
HRMS (ESI): exact mass calculated for $C_{21}H_{21}N_2O_5S$ $[M + H]^+$: 413.1166, found 413.1160.



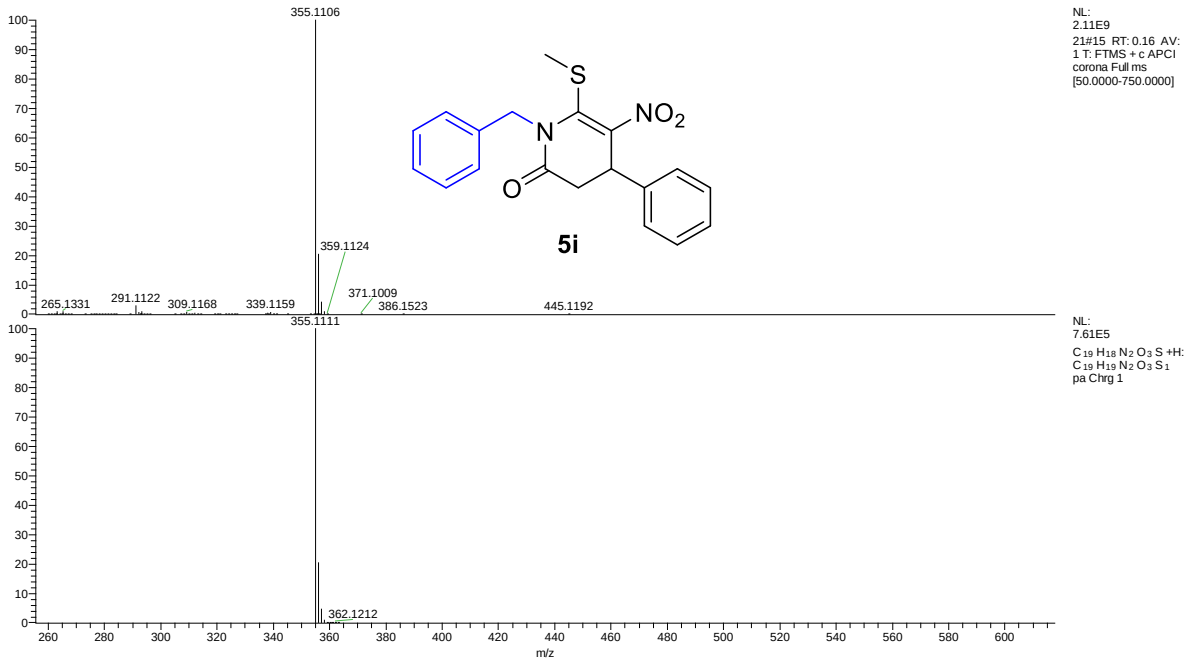
HRMS (ESI): exact mass calculated for $C_{21}H_{23}N_2O_3S$ $[M + H]^+$: 383.1424, found 383.1419.



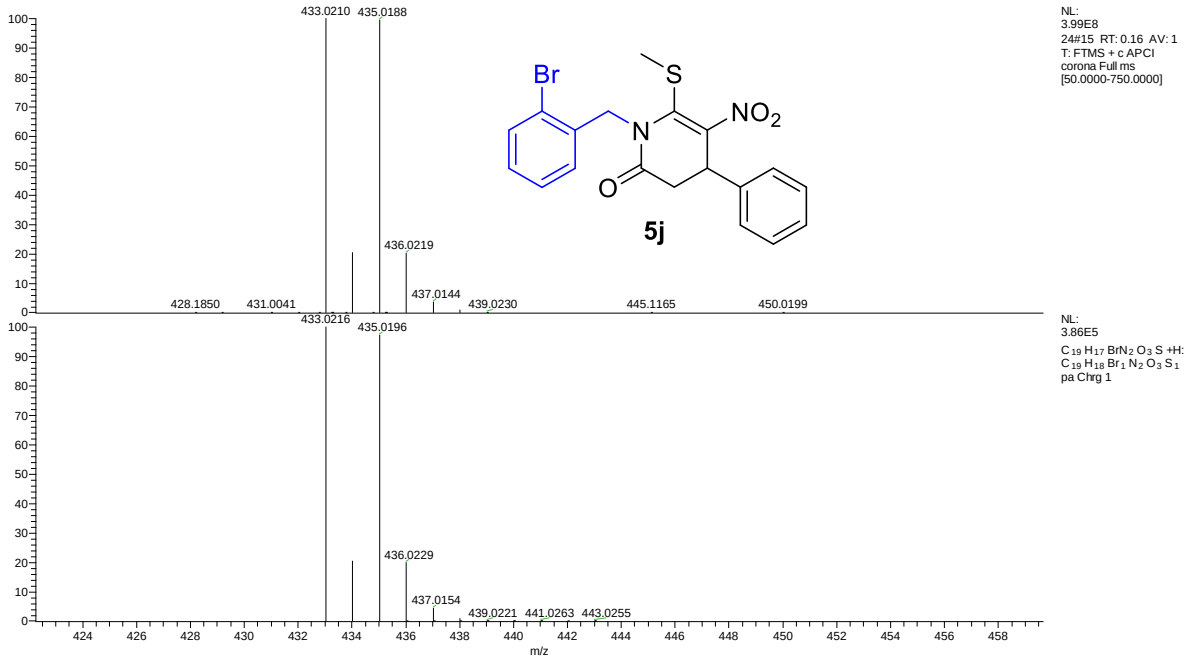
HRMS (ESI): exact mass calculated for $C_{20}H_{21}N_2O_3S$ $[M + H]^+$: 369.1267, found 369.1261.



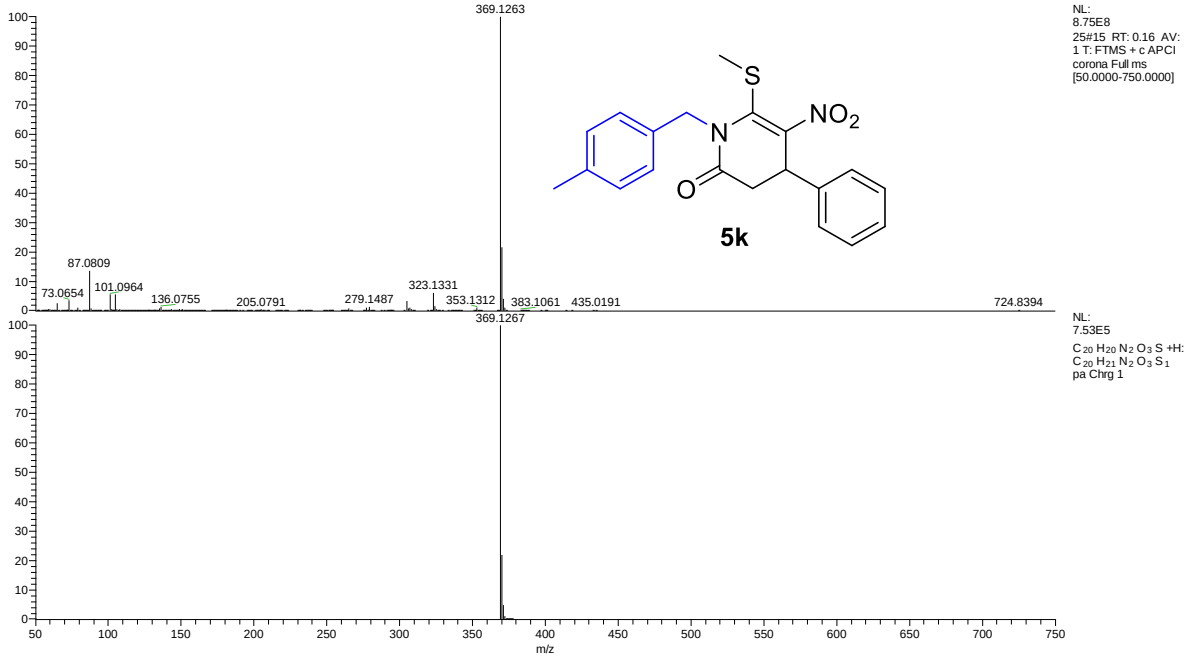
HRMS (ESI): exact mass calculated for $C_{19}H_{18}ClN_2O_3S[M + H]^+$: 389.0721, found 389.0714.



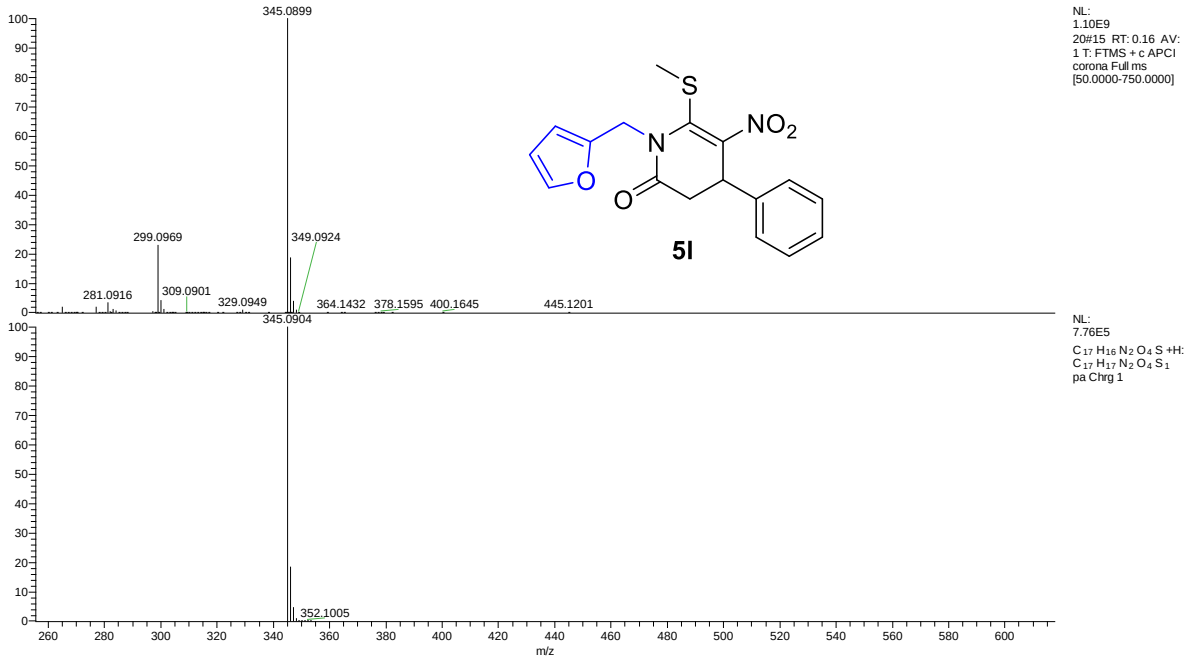
HRMS (ESI): exact mass calculated for $C_{19}H_{19}N_2O_3S$ $[M + H]^+$: 355.1111, found 355.1106.



HRMS (ESI): exact mass calculated for $C_{19}H_{18}BrN_2O_3S$ $[M + H]^+$: 433.0216, found 433.0210.

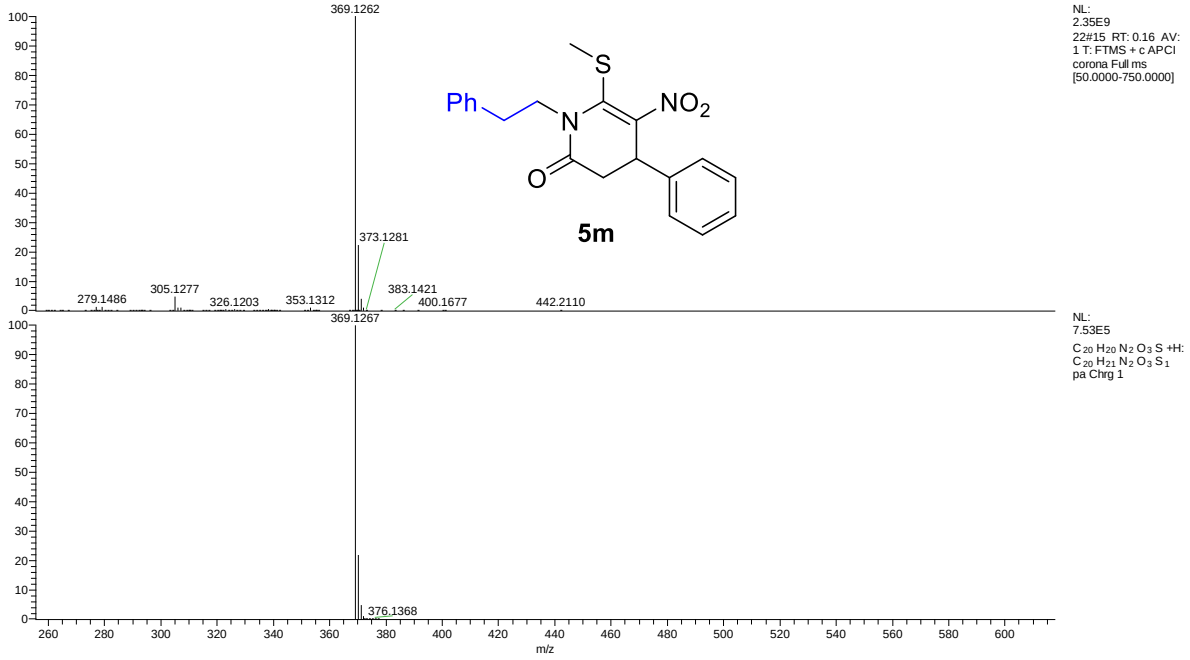


HRMS (ESI): exact mass calculated for $C_{20}H_{21}N_2O_3S$ $[M + H]^+$: 369.1267, found 369.1263.



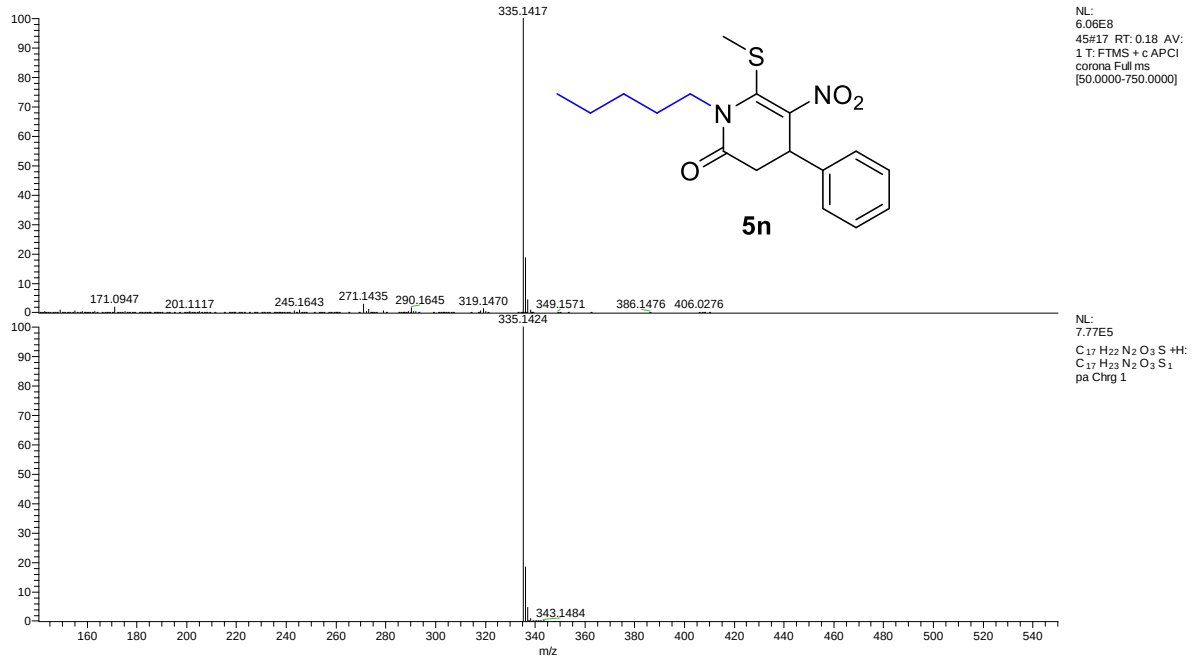
5l

HRMS (ESI): exact mass calculated for $C_{17}H_{17}N_2O_4$ $[M + H]^+$: 345.0904, found 345.0899.

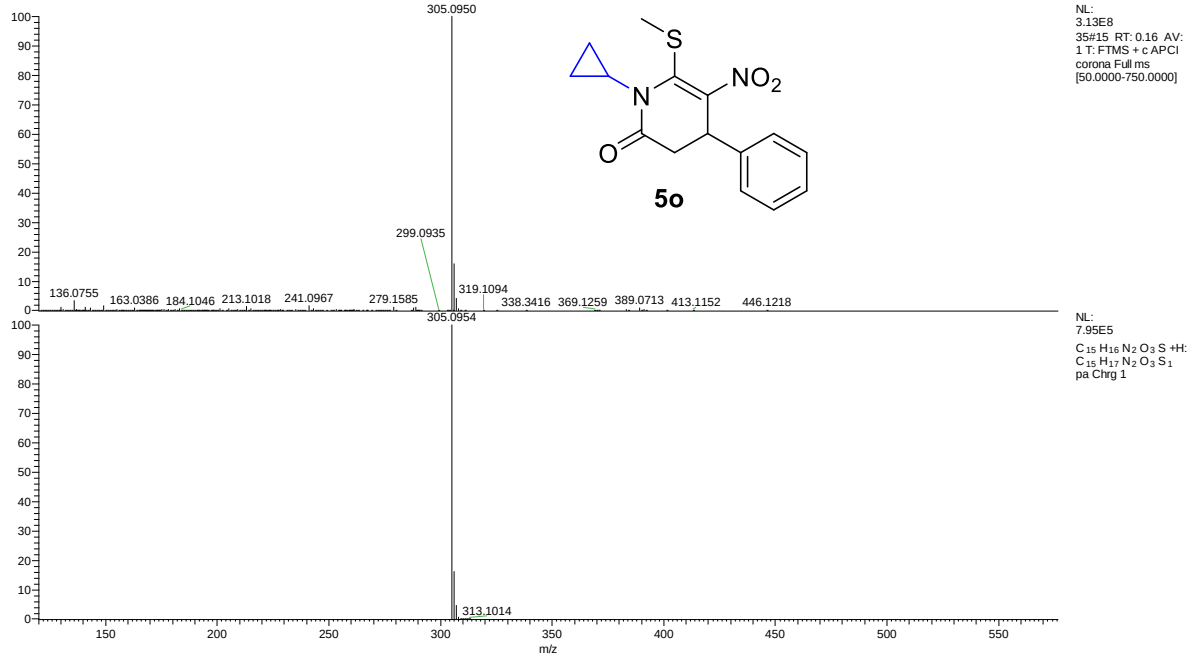


5m

HRMS (ESI): exact mass calculated for $C_{20}H_{21}N_2O_3S$ $[M + H]^+$: 369.1267, found 369.1262.



HRMS (ESI): exact mass calculated for $C_{17}H_{23}N_2O_3S$ $[M + H]^+$: 335.1424, found 335.1417.



HRMS (ESI): exact mass calculated for $C_{15}H_{17}N_2O_3S$ $[M + H]^+$: 305.0954, found 305.0950.