

Supporting Information

Controllable Synthesis of Trifluoromethyl- or *gem*-Difluorovinyl-containing Analogues of Neonicotinoids by the Reaction of α -(Trifluoromethyl)styrenes with 2-Nitroimino-imidazolidine

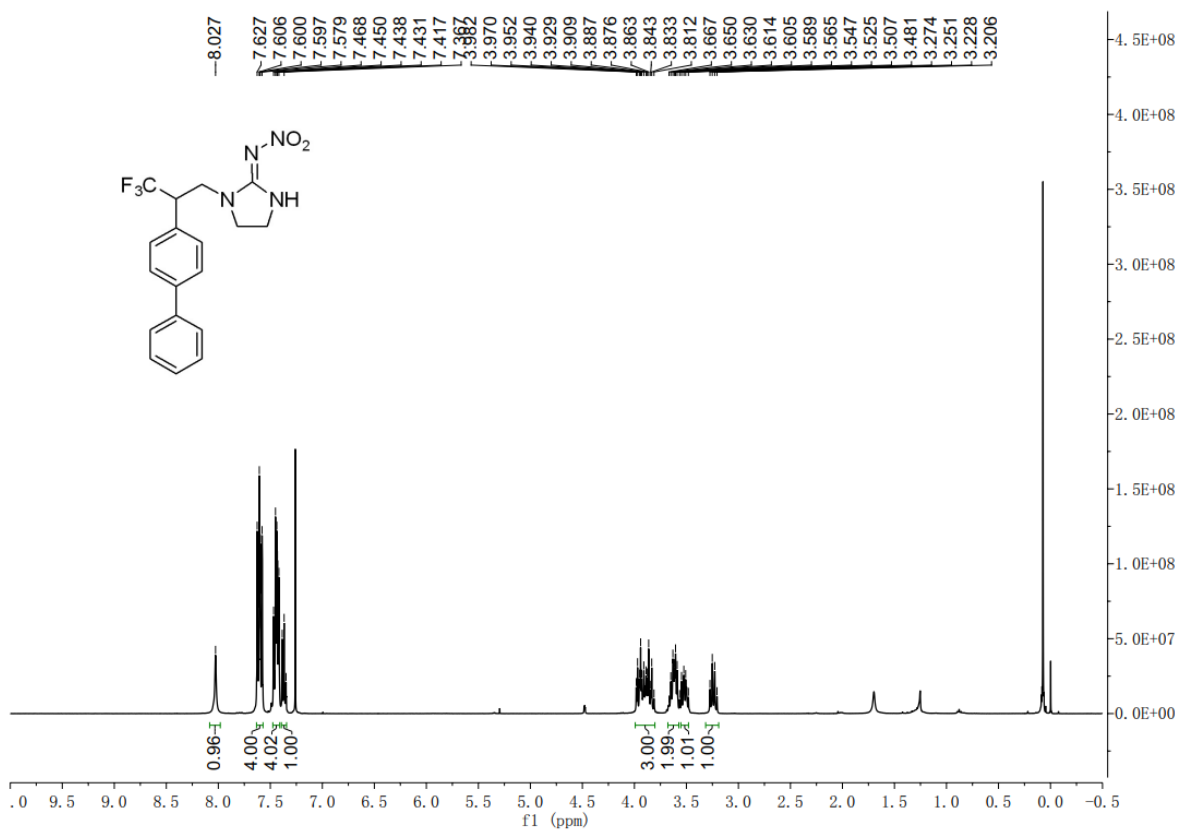
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¹*Shanghai Key Laboratory of Chemical Biology, School of Pharmacy, East China University of Science and Technology (ECUST), Shanghai 200237, China*

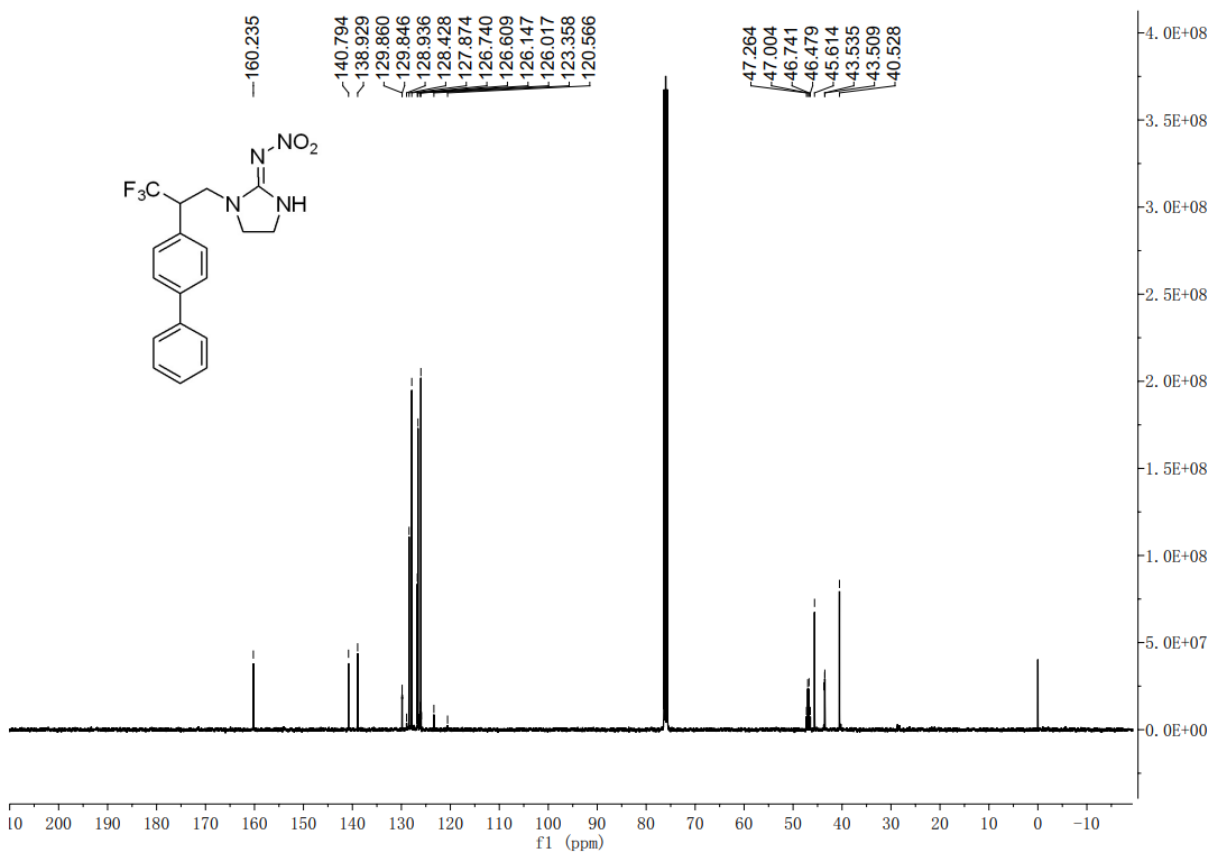
²*Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

¹H, ¹³C, ¹⁹F NMR and HRMS (EI/ESI) spectra of the target compounds

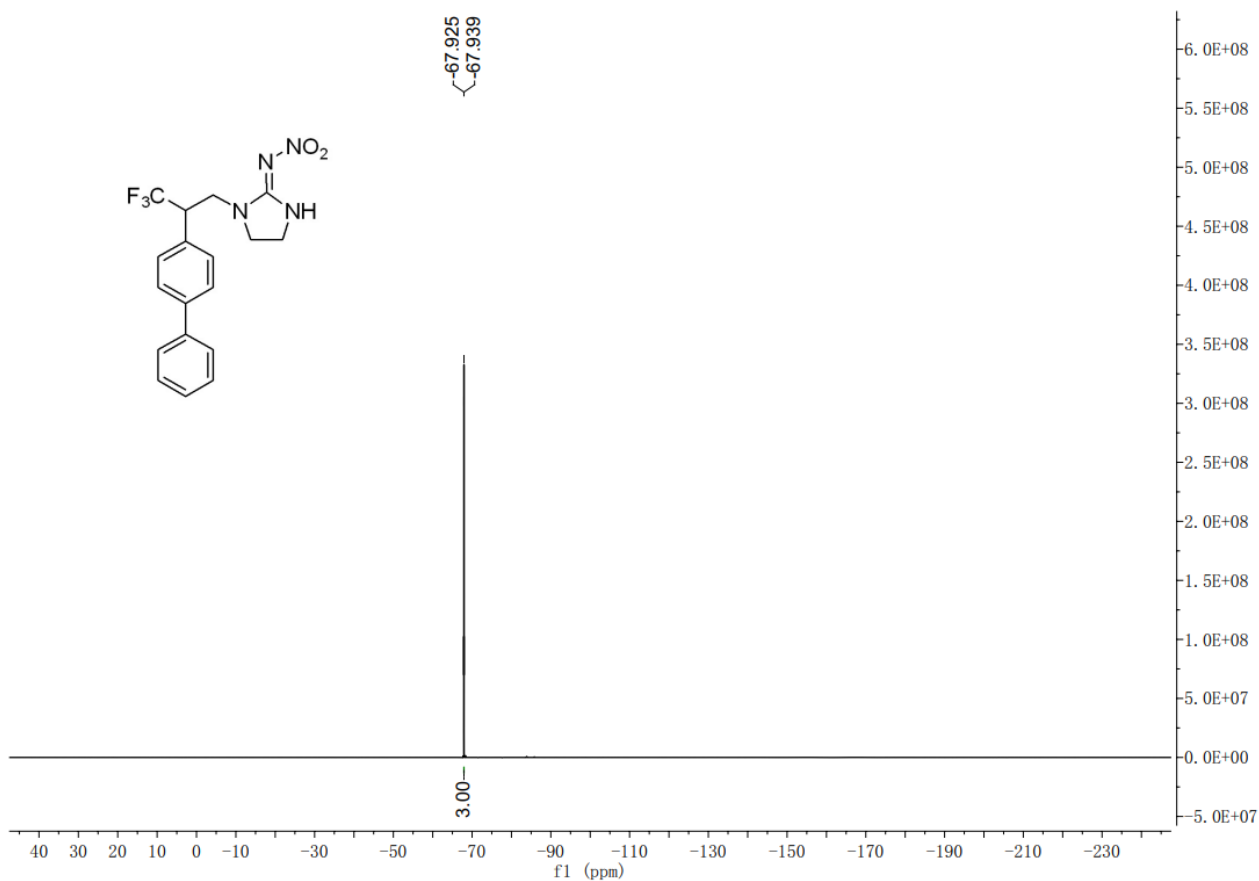
¹H NMR spectrum of 3aa (400 MHz, CDCl₃)



¹³C NMR spectrum of 3aa (100 MHz, CDCl₃)



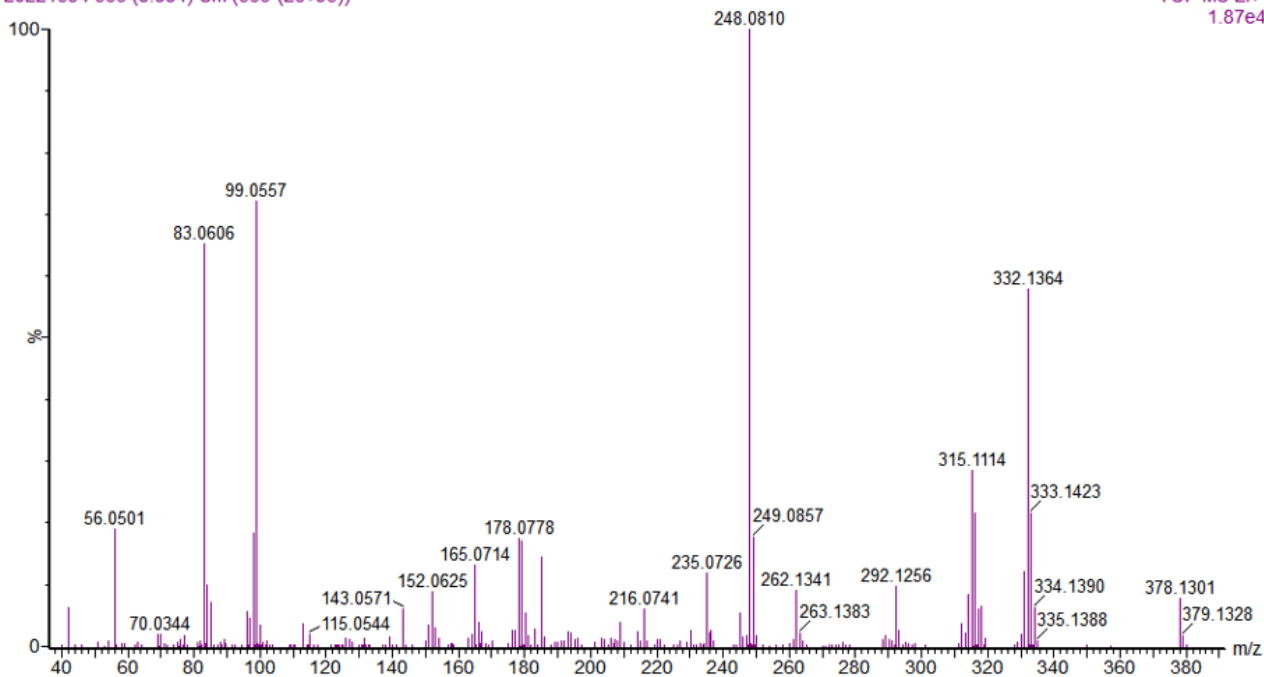
^{19}F NMR spectrum of 3aa (564 MHz, CDCl_3)



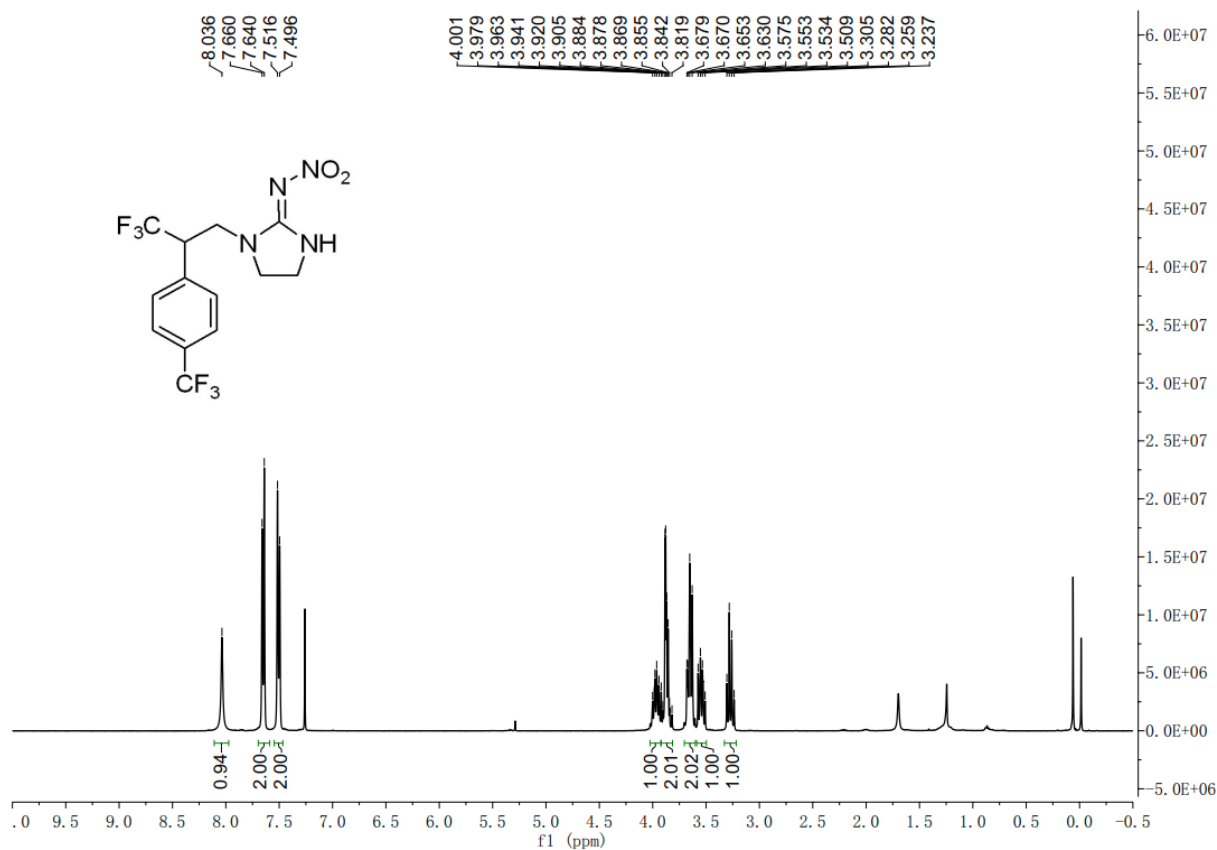
HRMS (EI) spectrum of 3aa

20221594 533 (8.884) Cm (533-(26+93))

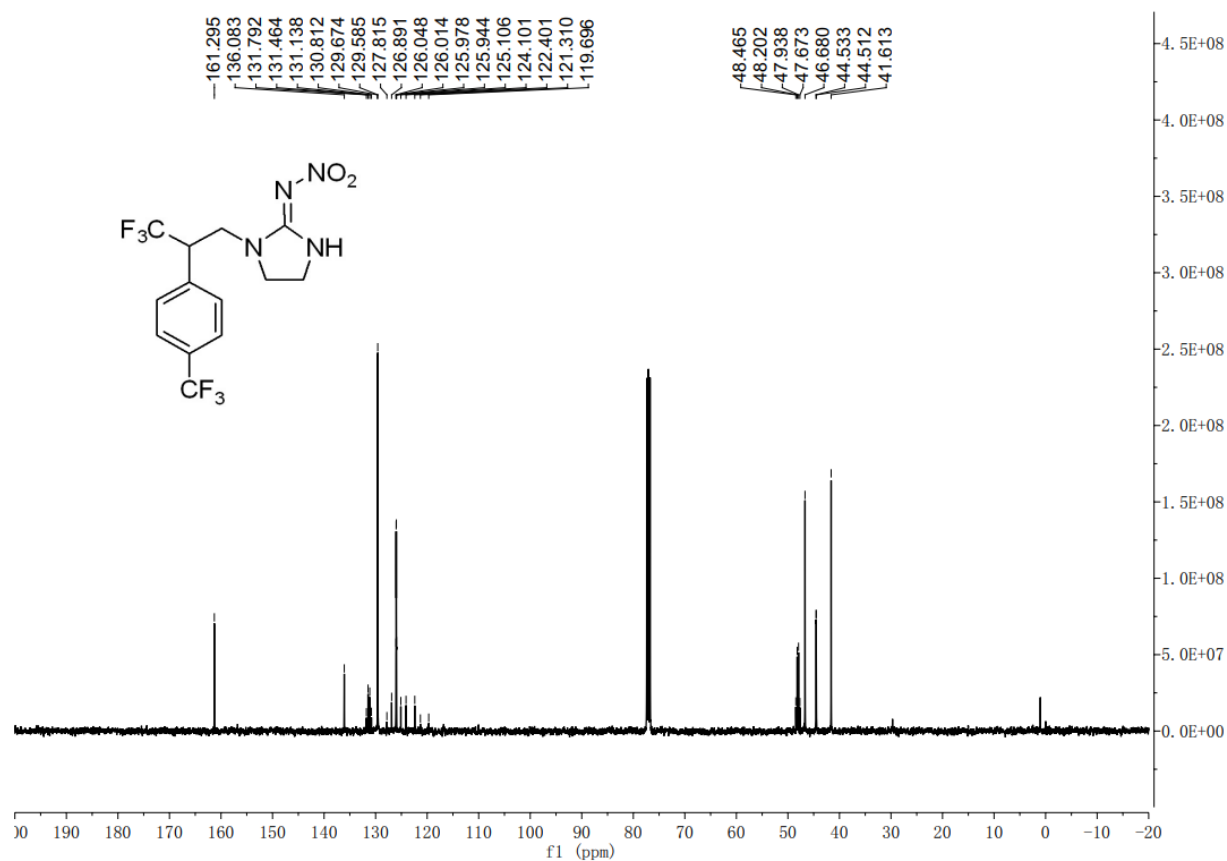
TOF MS EI+
1.87e4



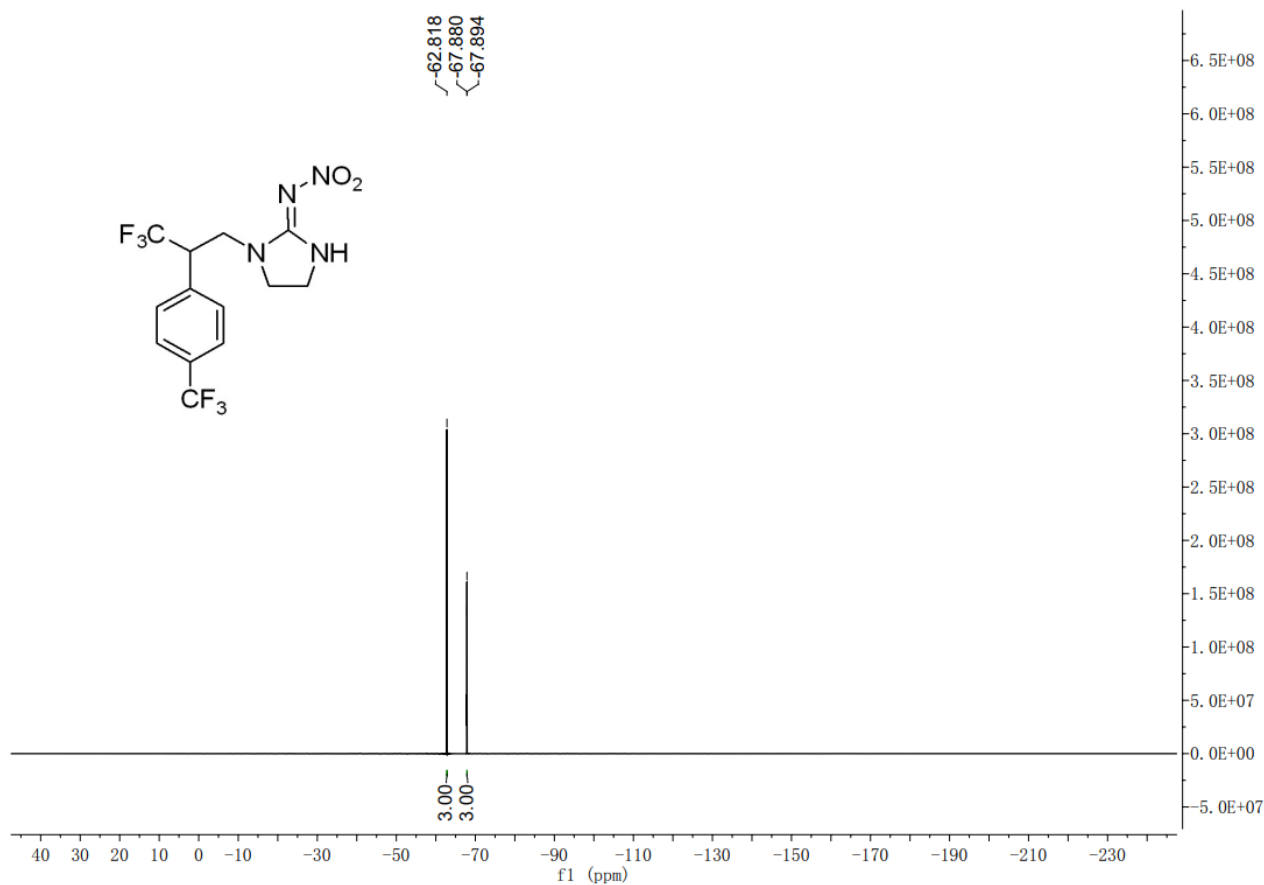
¹H NMR spectrum of 3ba (400 MHz, CDCl₃)



¹³C NMR spectrum of 3ba (100 MHz, CDCl₃)



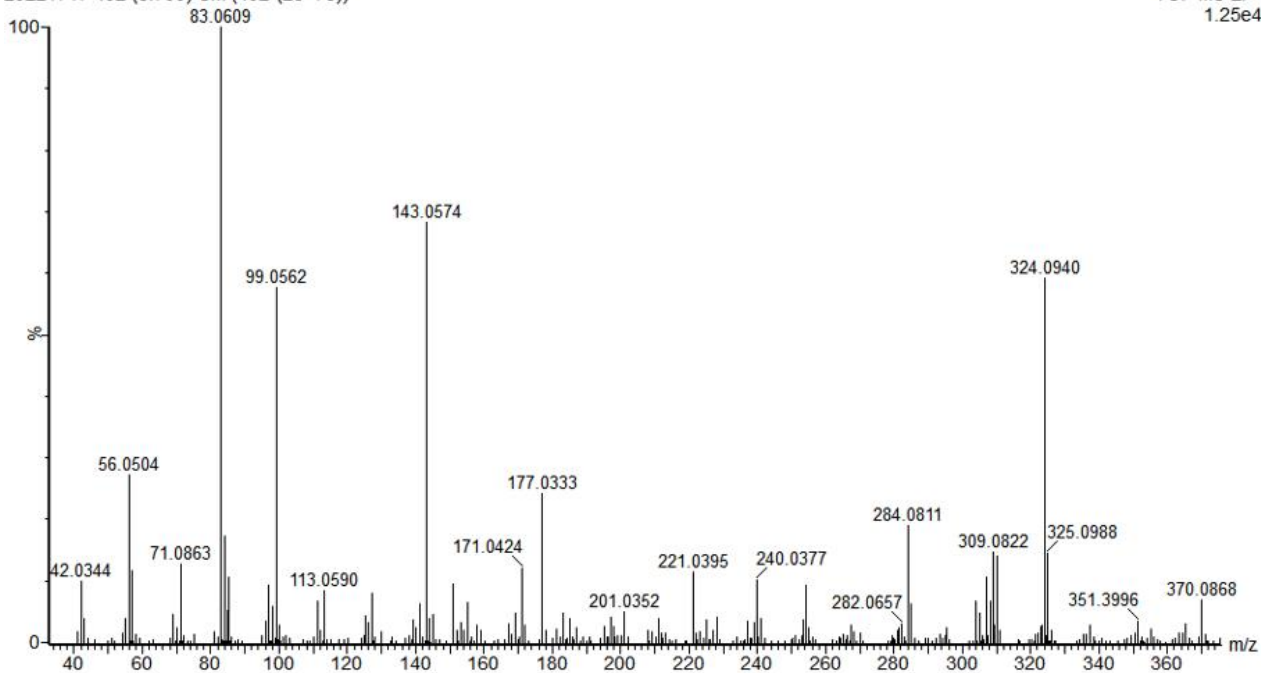
^{19}F NMR spectrum of 3ba (564 MHz, CDCl_3)



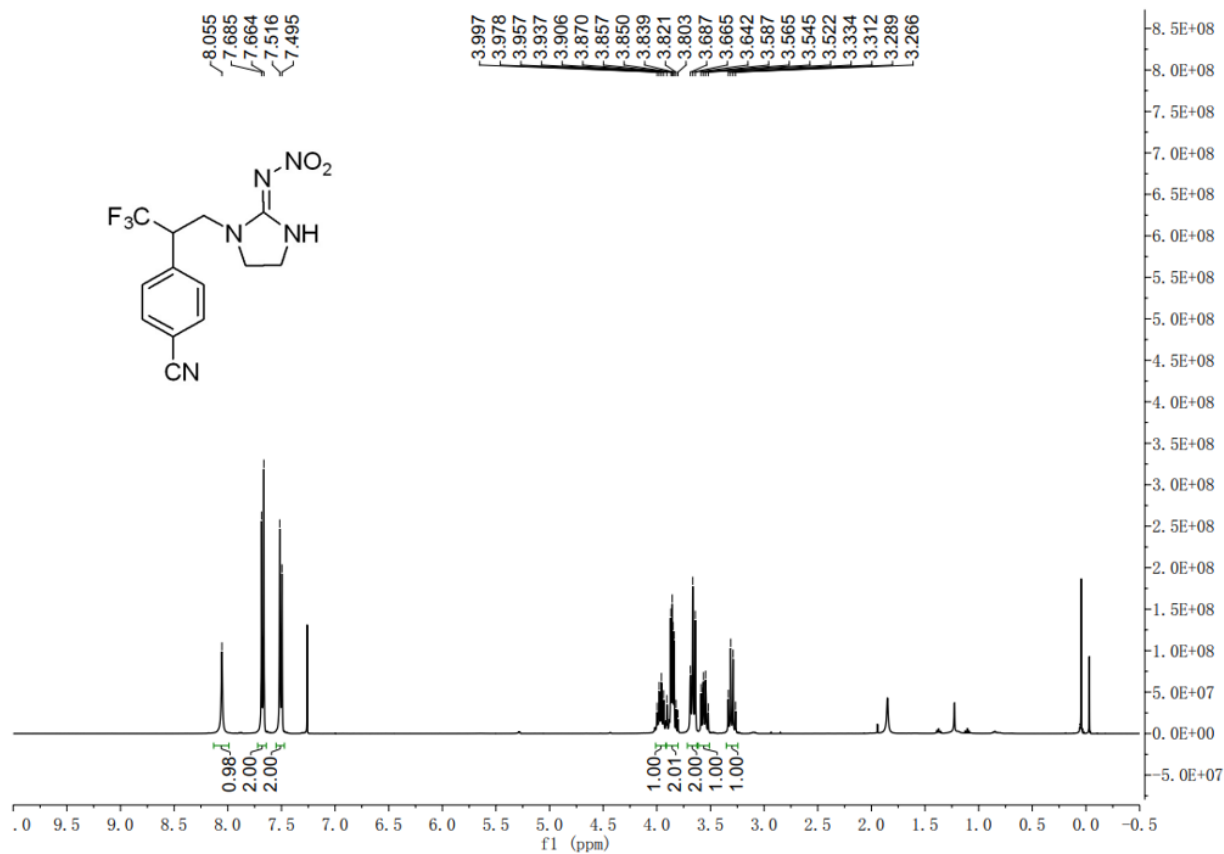
HRMS (EI) spectrum of 3ba

20221717 402 (6.700) Cm (402-(23+76))

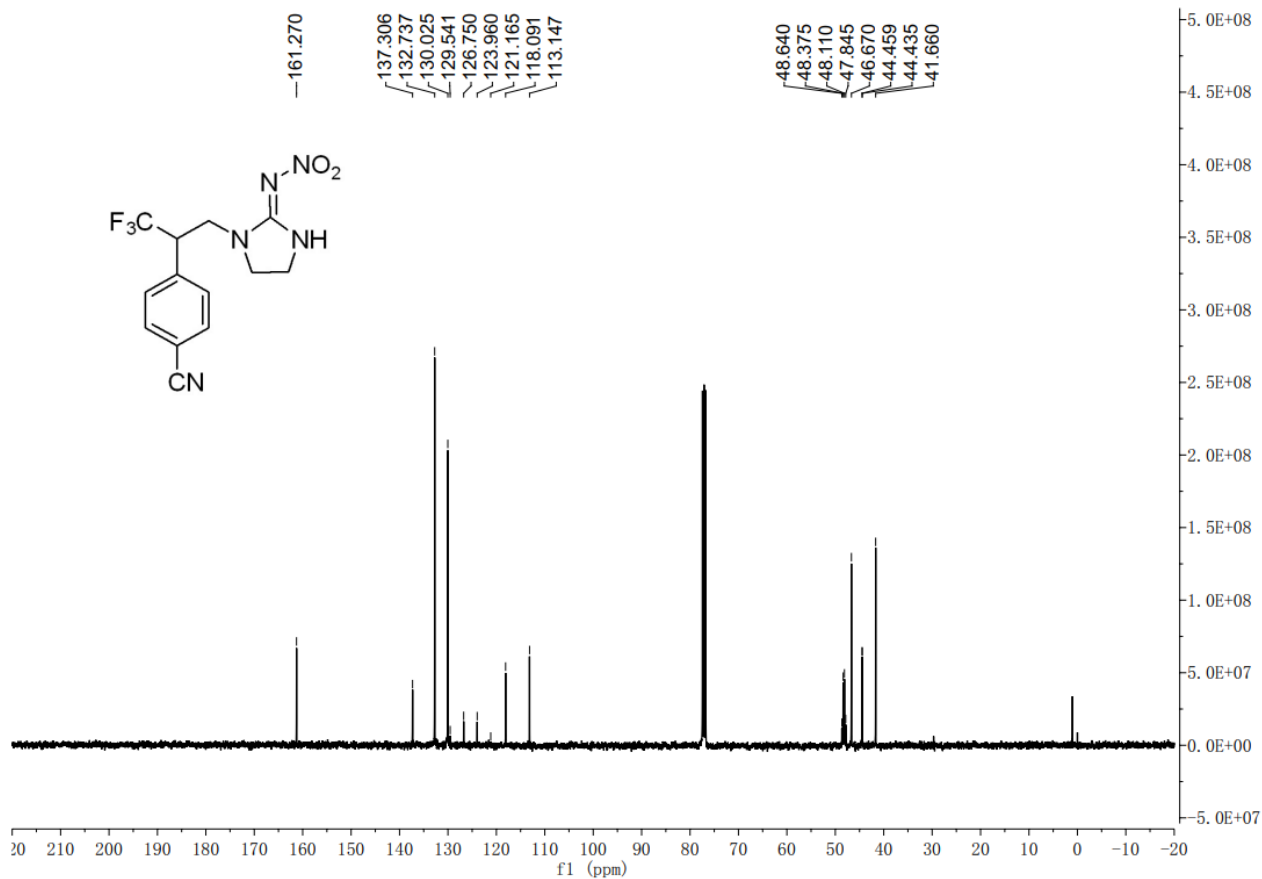
TOF MS EI+
1.25e4



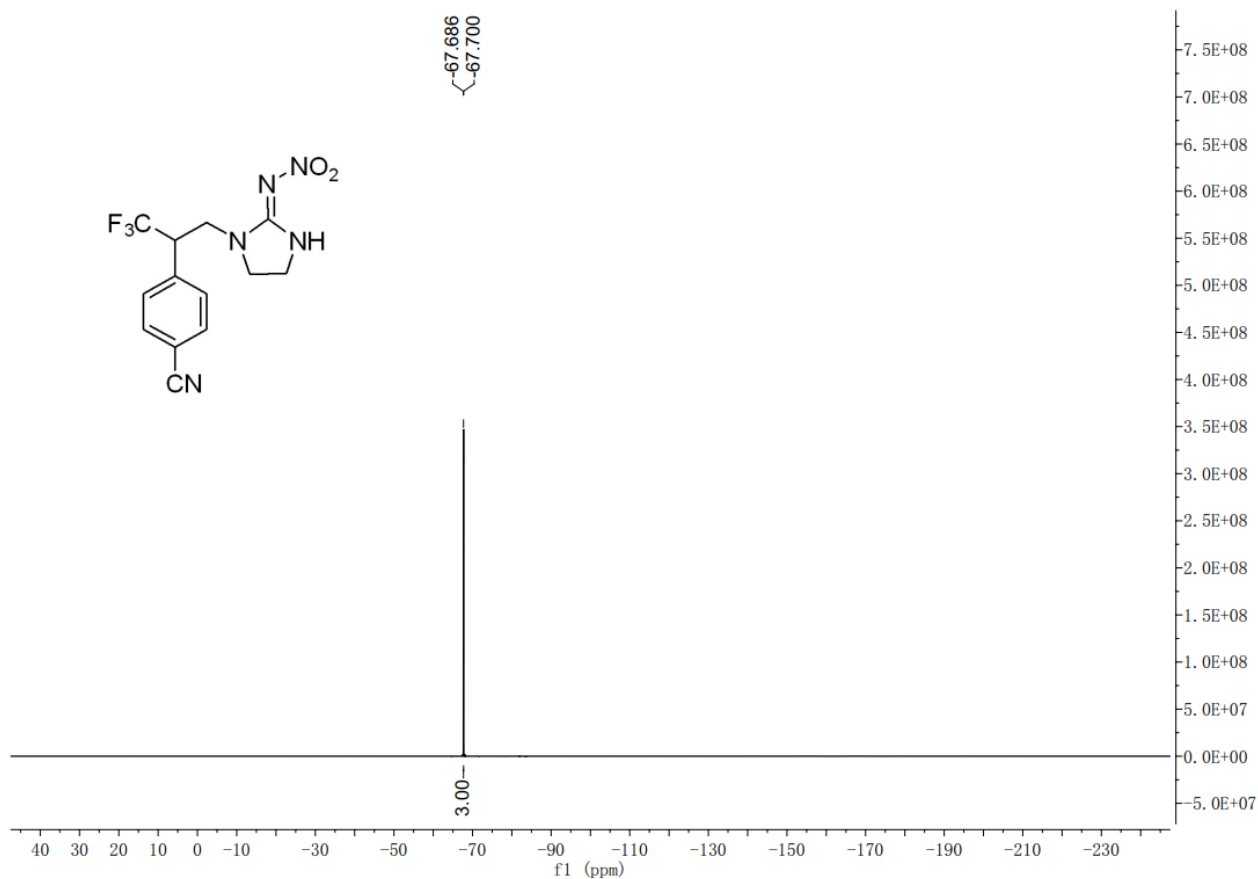
¹H NMR spectrum of 3a (400 MHz, CDCl₃)



¹³C NMR spectrum of 3a (100 MHz, CDCl₃)



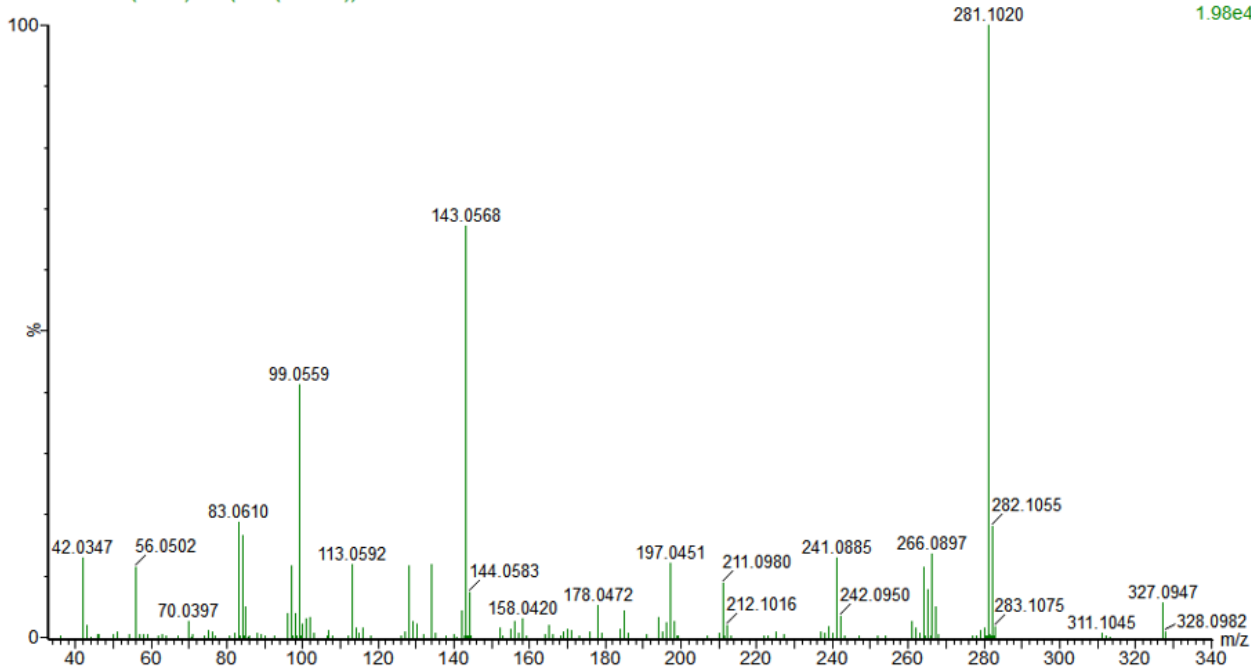
^{19}F NMR spectrum of 3ca (564 MHz, CDCl_3)



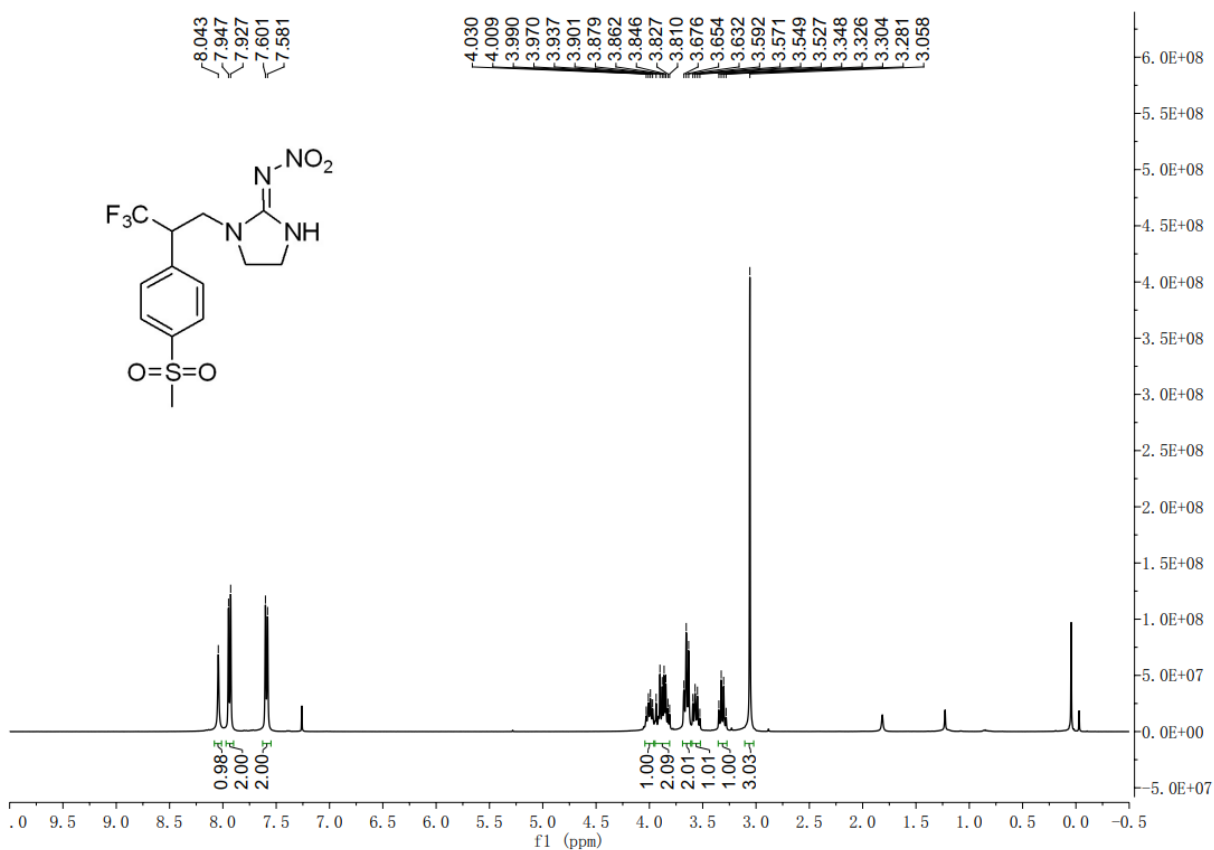
HRMS (EI) spectrum of 3ca

20221598 316 (5.267) Cm (316-(77+555))

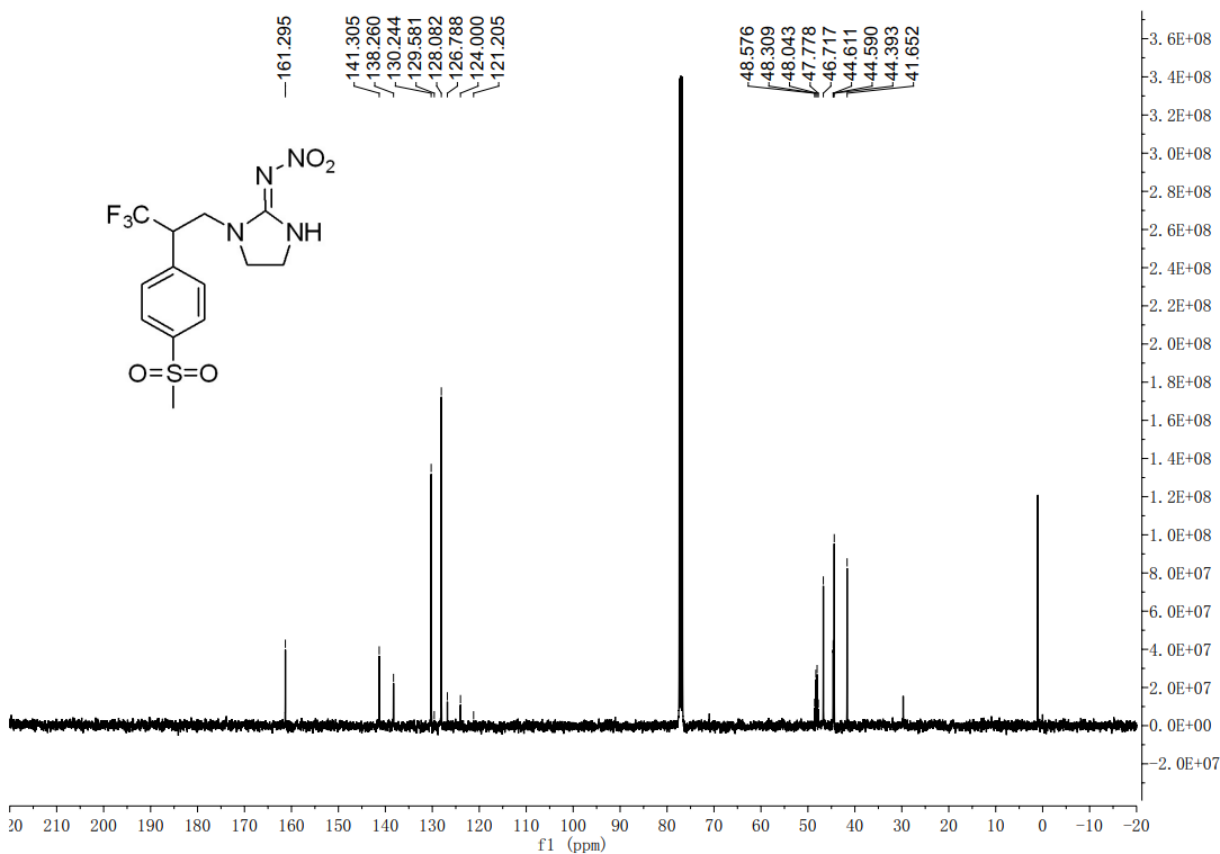
TOF MS EI+
1.98e4



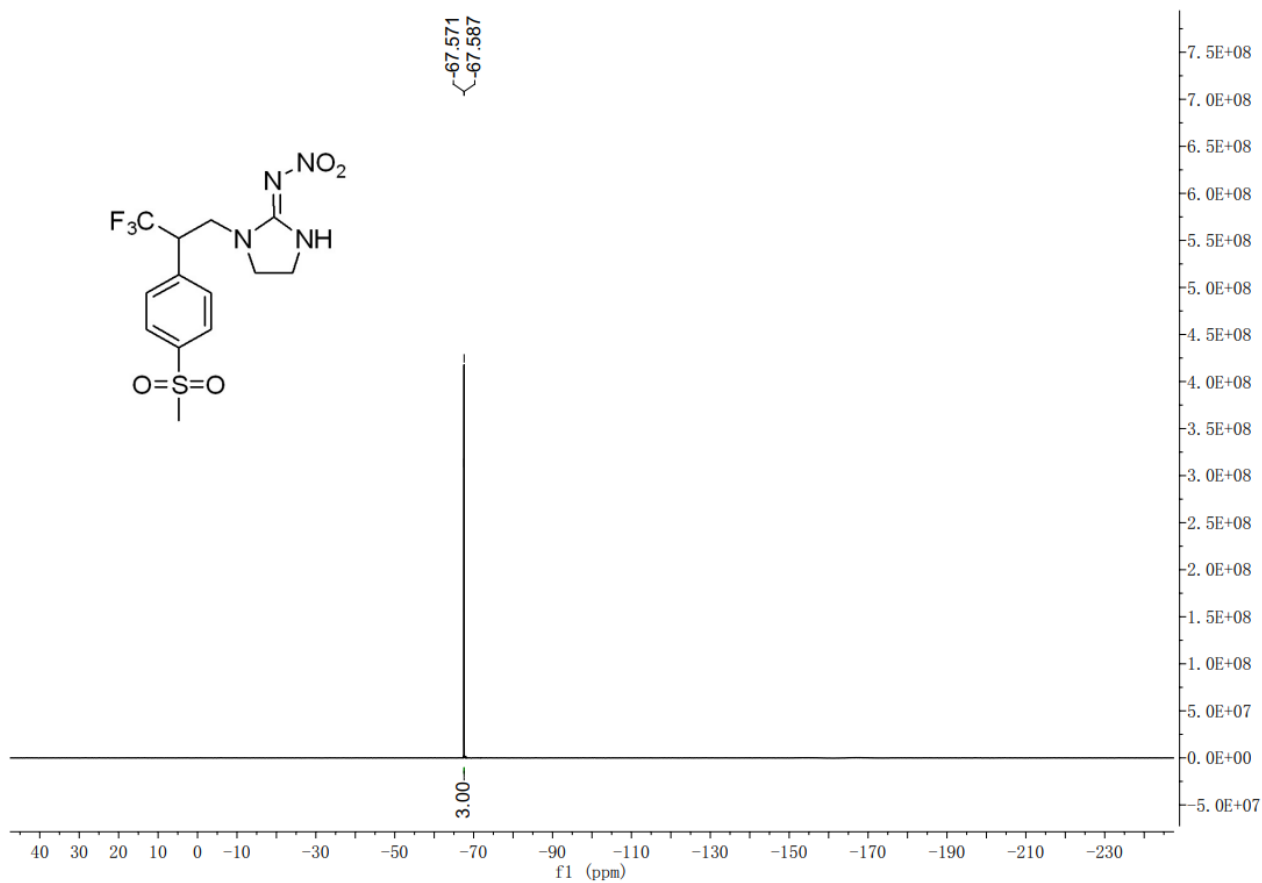
¹H NMR spectrum of 3da (400 MHz, CDCl₃)



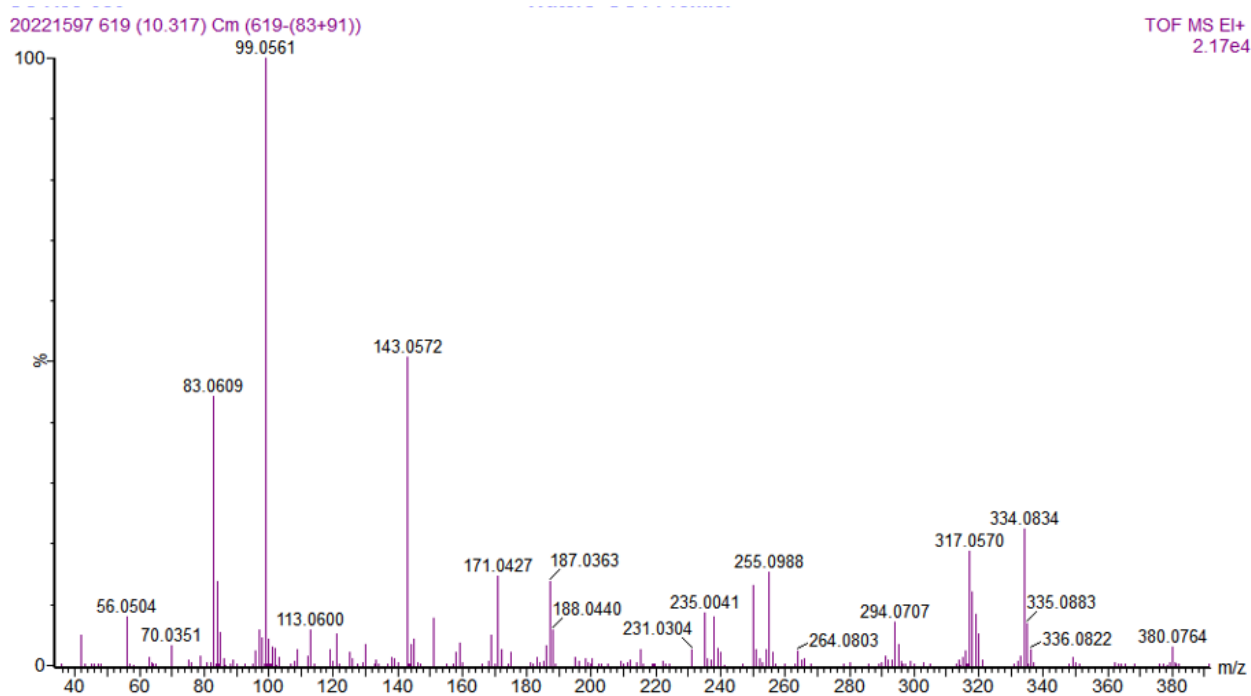
¹³C NMR spectrum of 3da (100 MHz, CDCl₃)



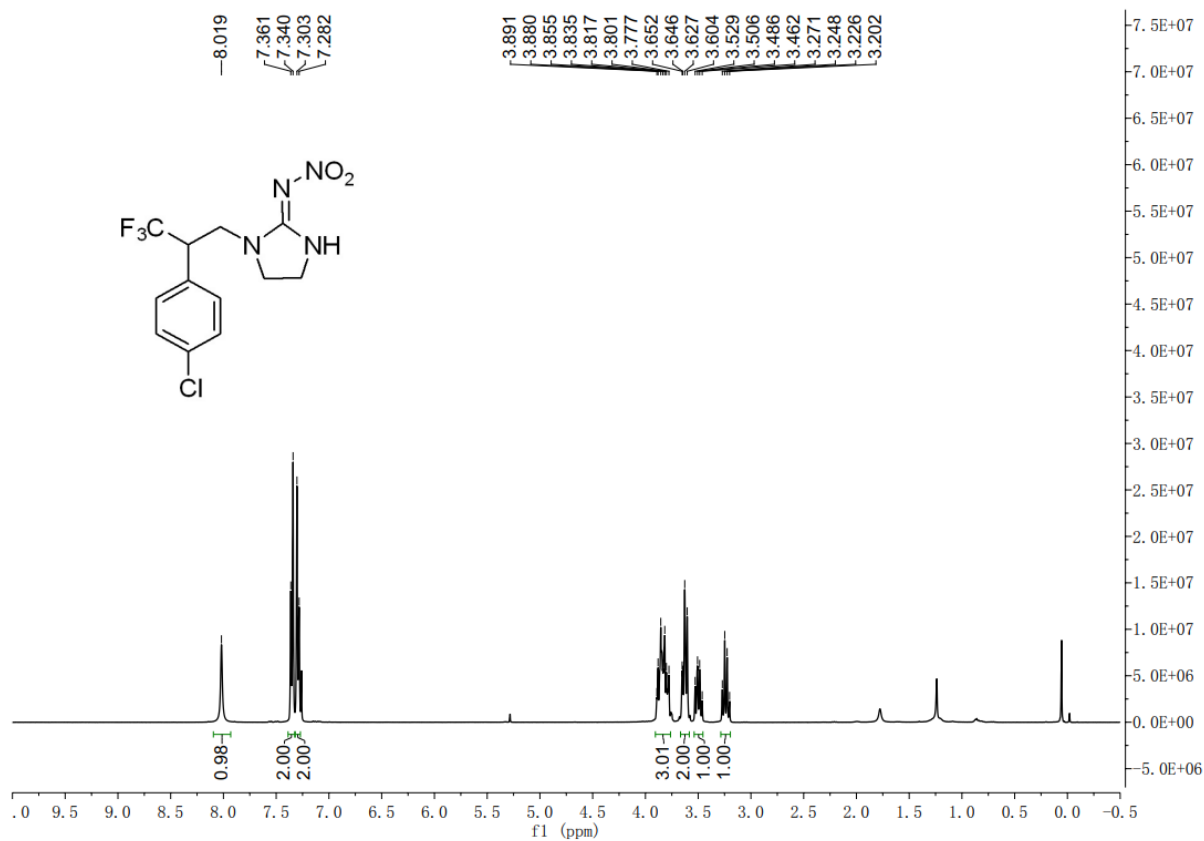
¹⁹F NMR spectrum of 3da (564 MHz, CDCl₃)



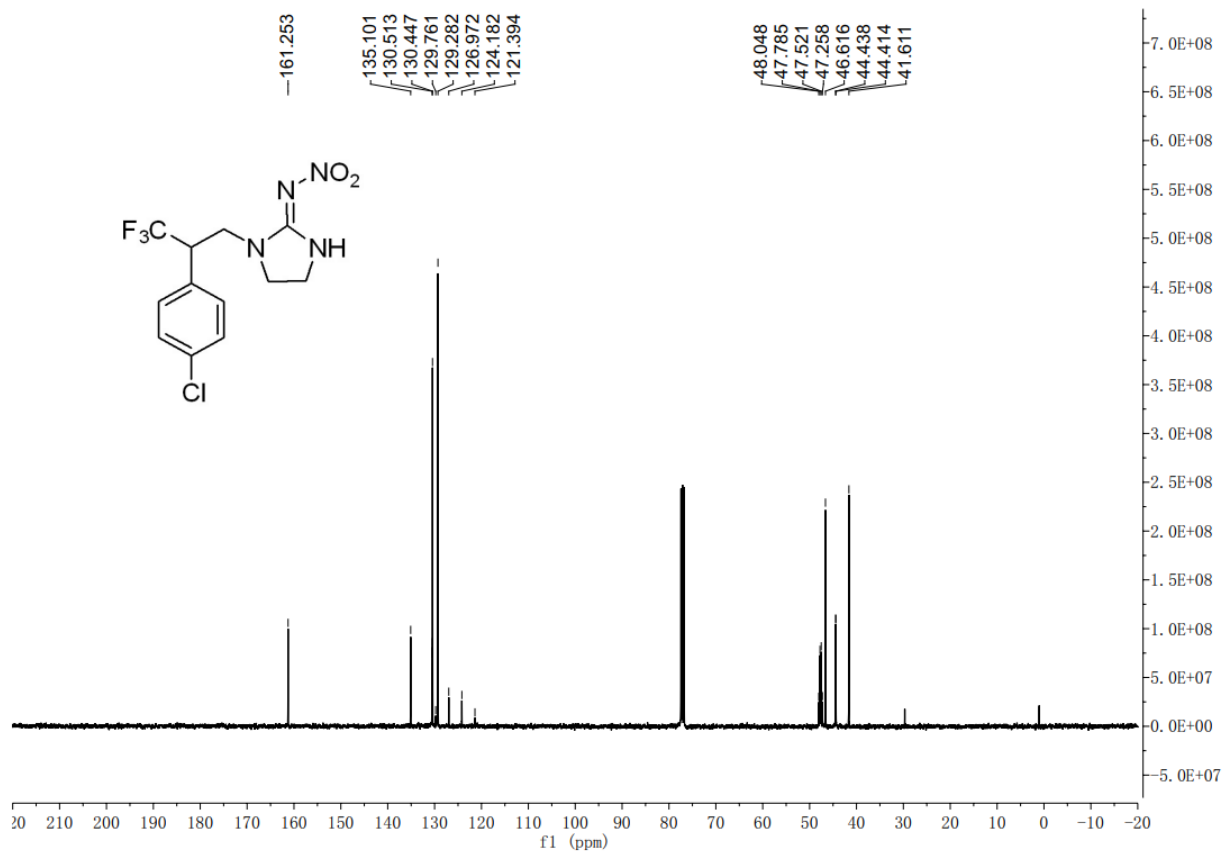
HRMS (EI) spectrum of 3da



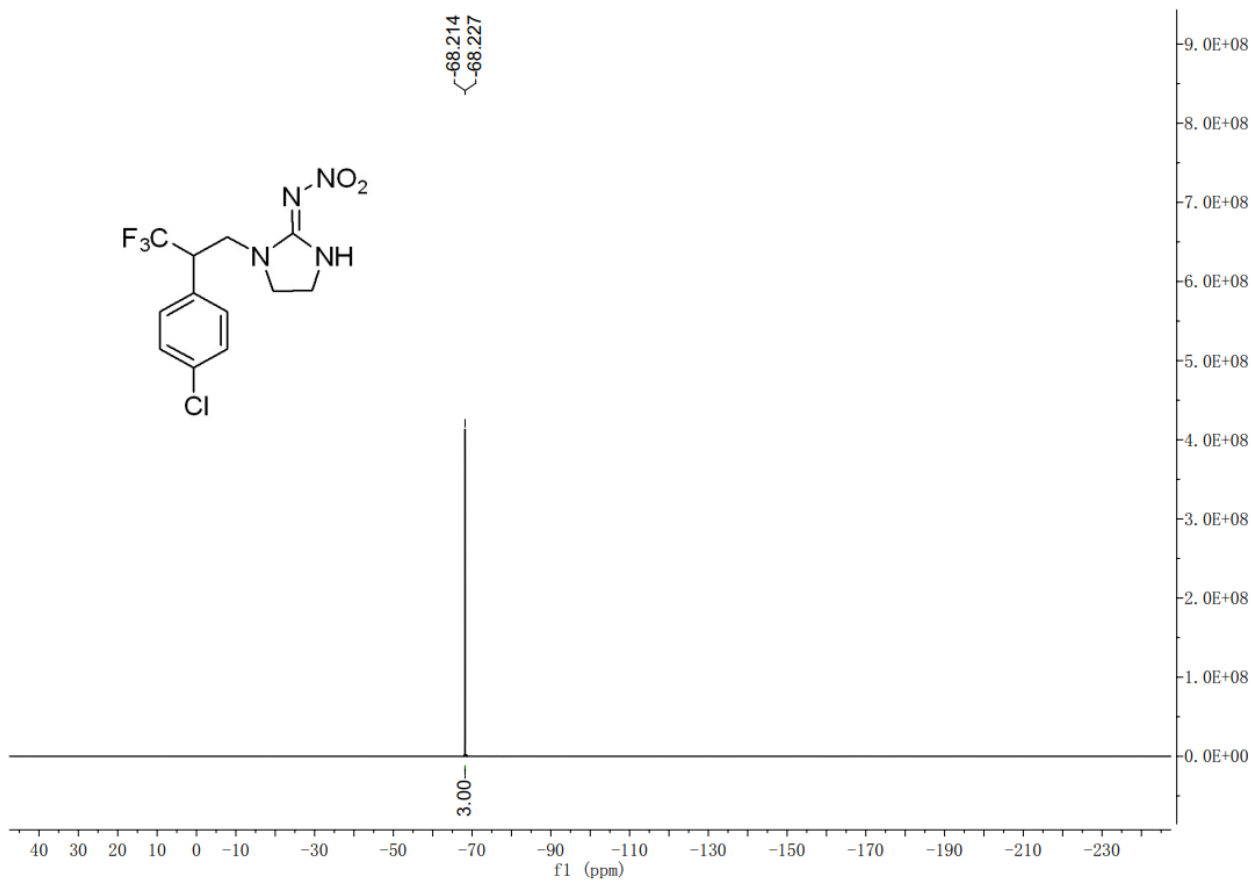
¹H NMR spectrum of 3ea (400 MHz, CDCl₃)



¹³C NMR spectrum of 3ea (100 MHz, CDCl₃)



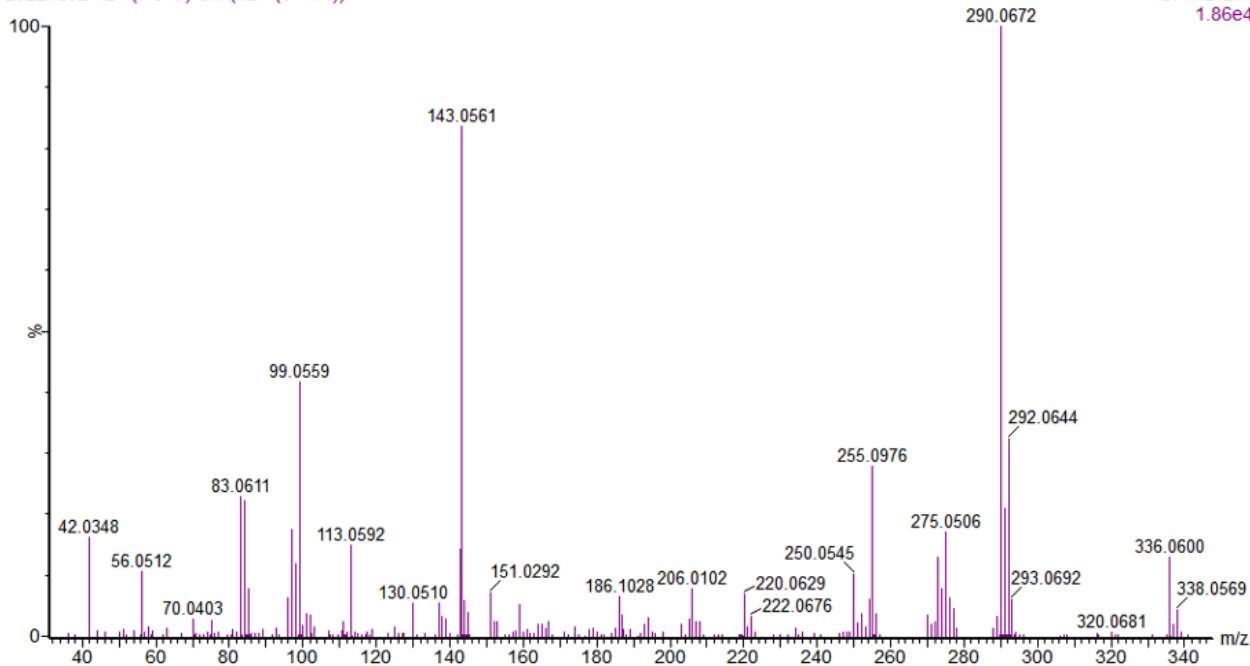
^{19}F NMR spectrum of 3ea (564 MHz, CDCl_3)



HRMS (EI) spectrum of 3ea

20221602 421 (7.019) Cm (421-(5+114))

TOF MS EI+
1.86e4



Chemical structure: Cc1ccc(cc1)C(C#N)C(F)(F)F

¹H NMR spectrum (ppm) showing peaks and integrations:

- Peak at ~8.0 ppm: Integration 0.93
- Peak at ~7.2 ppm: Integration 2.00
- Peak at ~7.1 ppm: Integration 2.00
- Peak at ~3.8 ppm: Integration 1.01
- Peak at ~3.6 ppm: Integration 2.11
- Peak at ~3.4 ppm: Integration 2.04
- Peak at ~3.2 ppm: Integration 1.00
- Peak at ~3.0 ppm: Integration 1.00
- Peak at ~2.4 ppm: Integration 3.01
- Peak at ~0.0 ppm: Integration 1.00

Chemical shift values (ppm) for the inset:

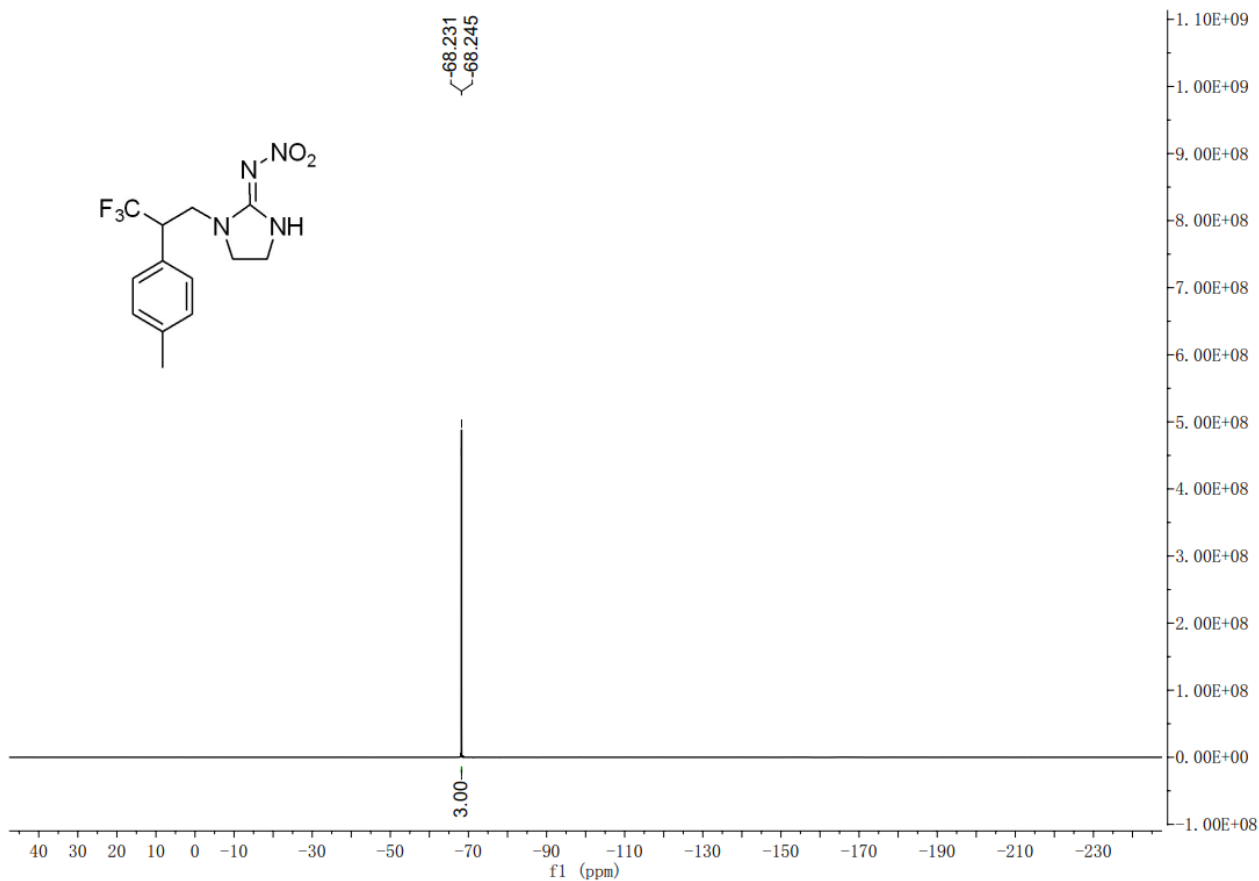
- 3.937, 3.917, 3.907, 3.825, 3.802, 3.788, 3.779, 3.757, 3.734, 3.719, 3.704, 3.630, 3.609, 3.593, 3.584, 3.568, 3.545, 3.474, 3.455, 3.430, 3.407, 3.384, 3.361, 3.161

Chemical structure: Cc1ccc(cc1)C(F)(F)FCCN2C=NC(=O)N2

¹³C NMR peaks (ppm):

- 161.297
- 138.926
- 130.029
- 129.745
- 128.938
- 128.884
- 127.240
- 124.452
- 121.665
- 48.287
- 48.026
- 47.764
- 47.507
- 46.619
- 44.574
- 44.550
- 41.549
- 21.133

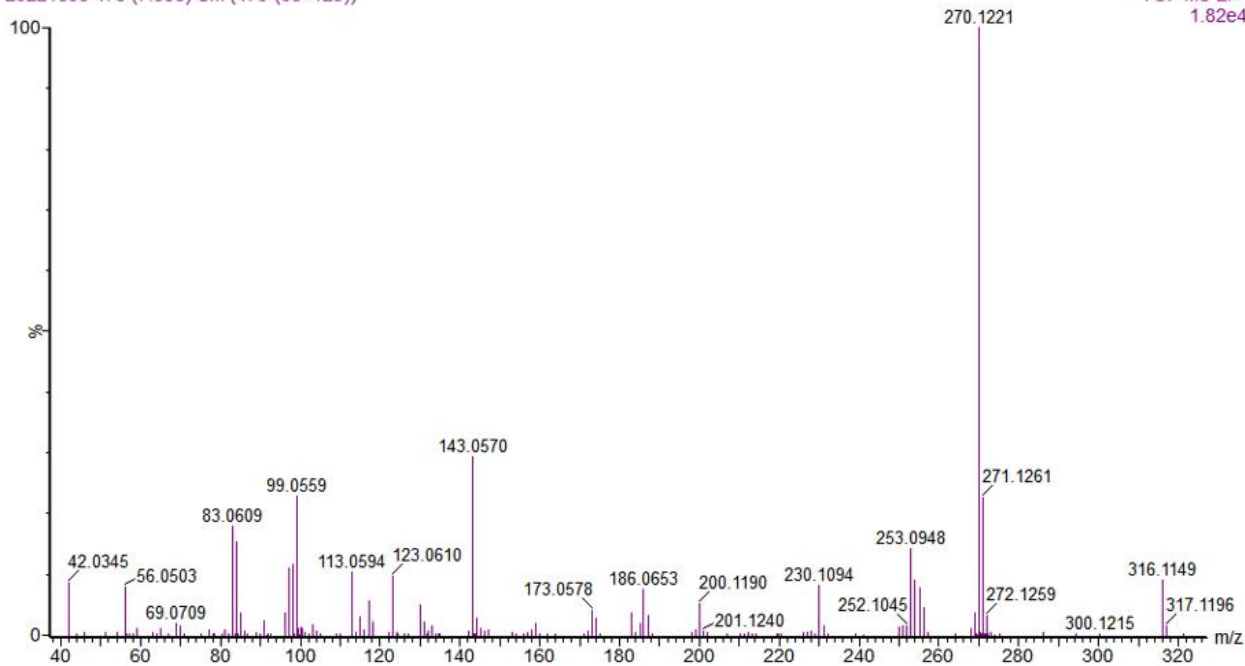
^{19}F NMR spectrum of 3fa (564 MHz, CDCl_3)



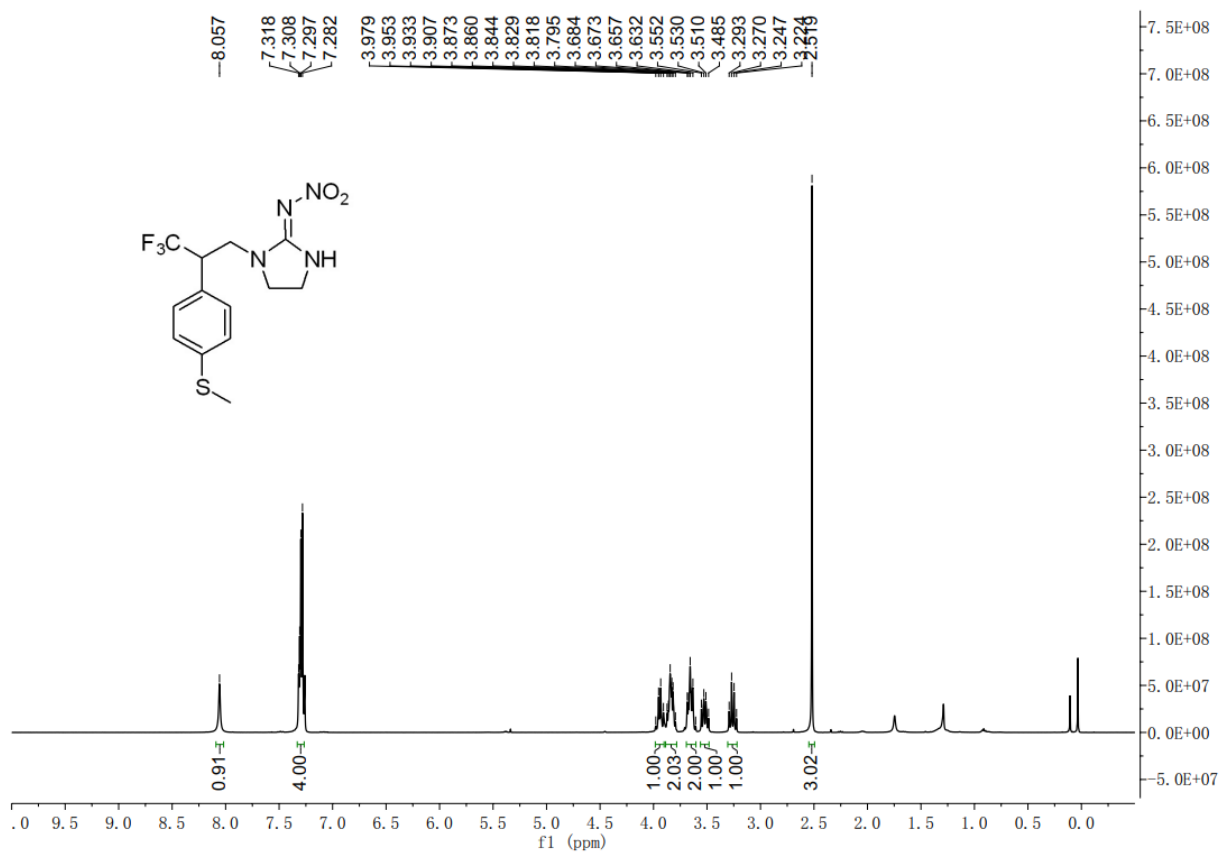
HRMS (EI) spectrum of 3fa

20221595 473 (7.886) Cm (473-(33+129))

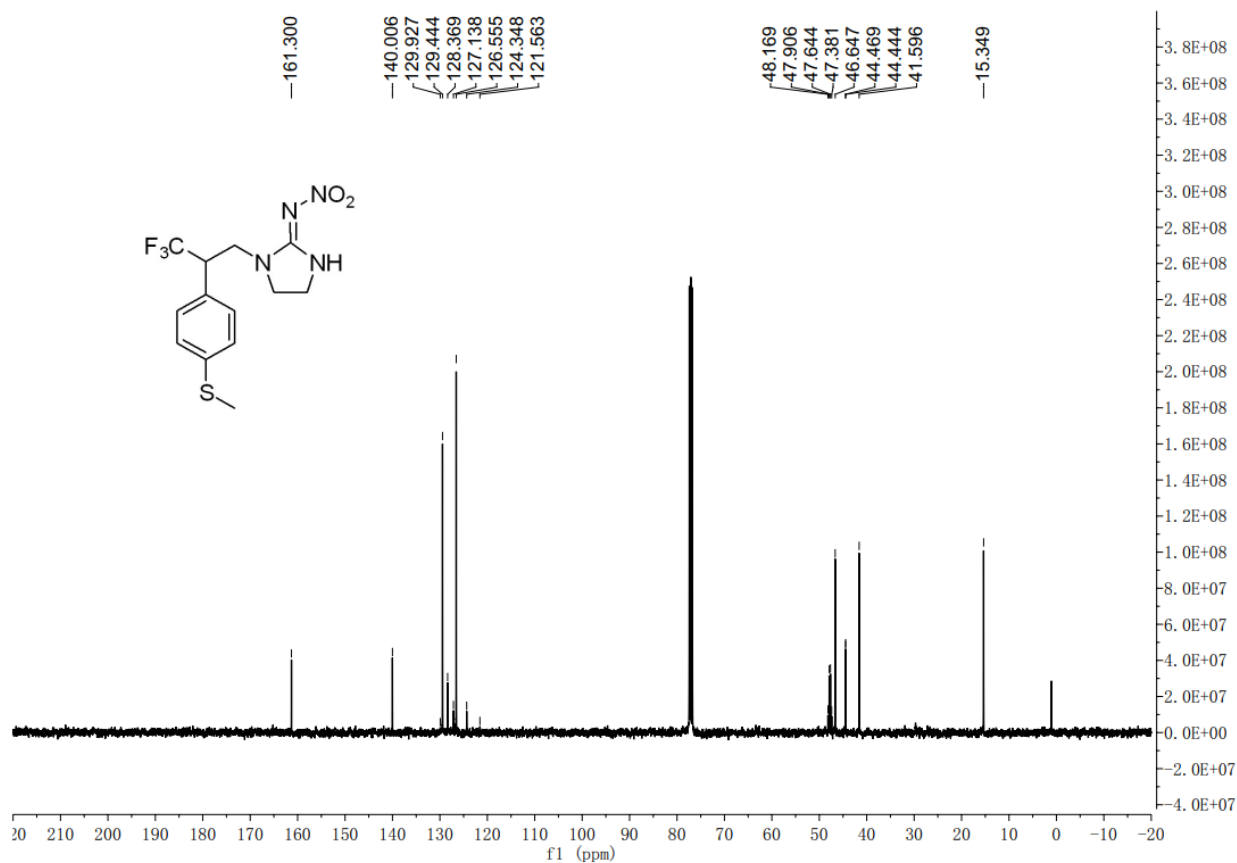
TOF MS EI+
1.82e4



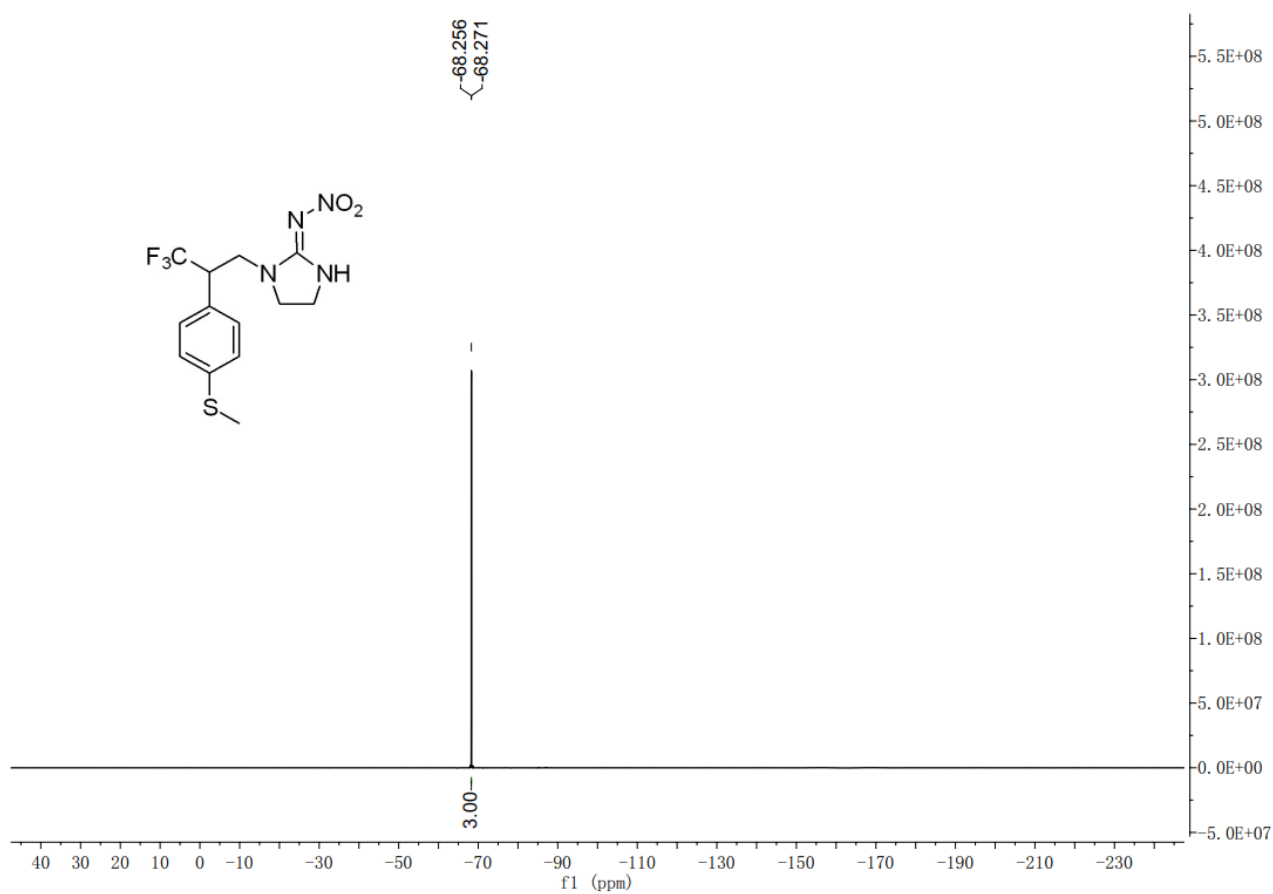
¹H NMR spectrum of 3ga (400 MHz, CDCl₃)



¹³C NMR spectrum of 3ga (100 MHz, CDCl₃)



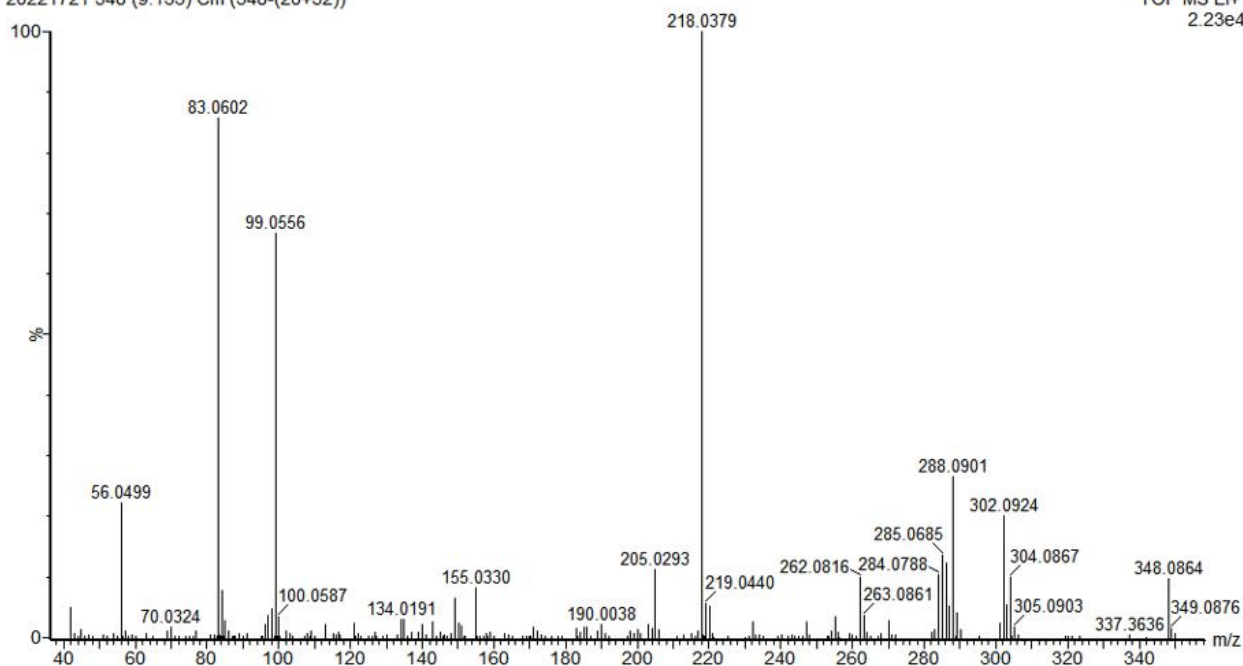
^{19}F NMR spectrum of 3ga (564 MHz, CDCl_3)



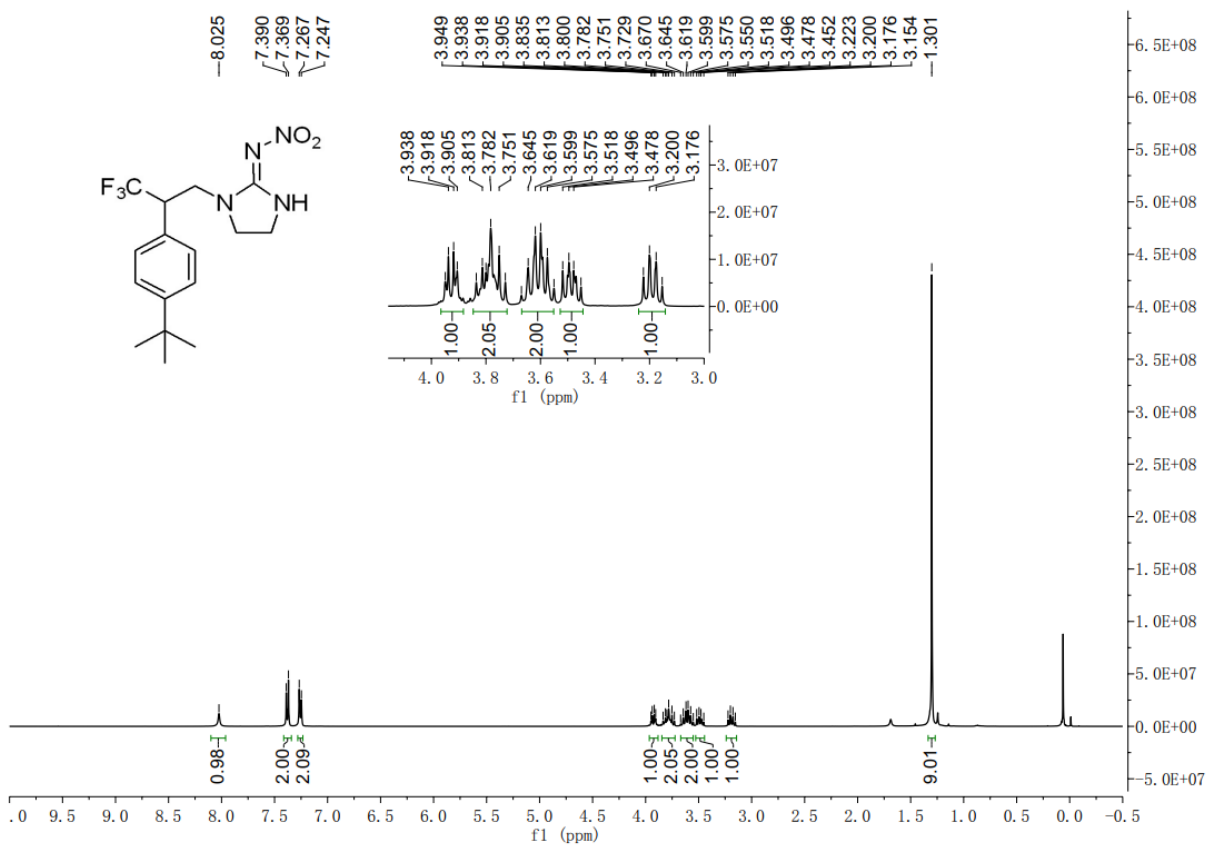
HRMS (EI) spectrum of 3ga

20221721 548 (9.133) Cm (548-(20+52))

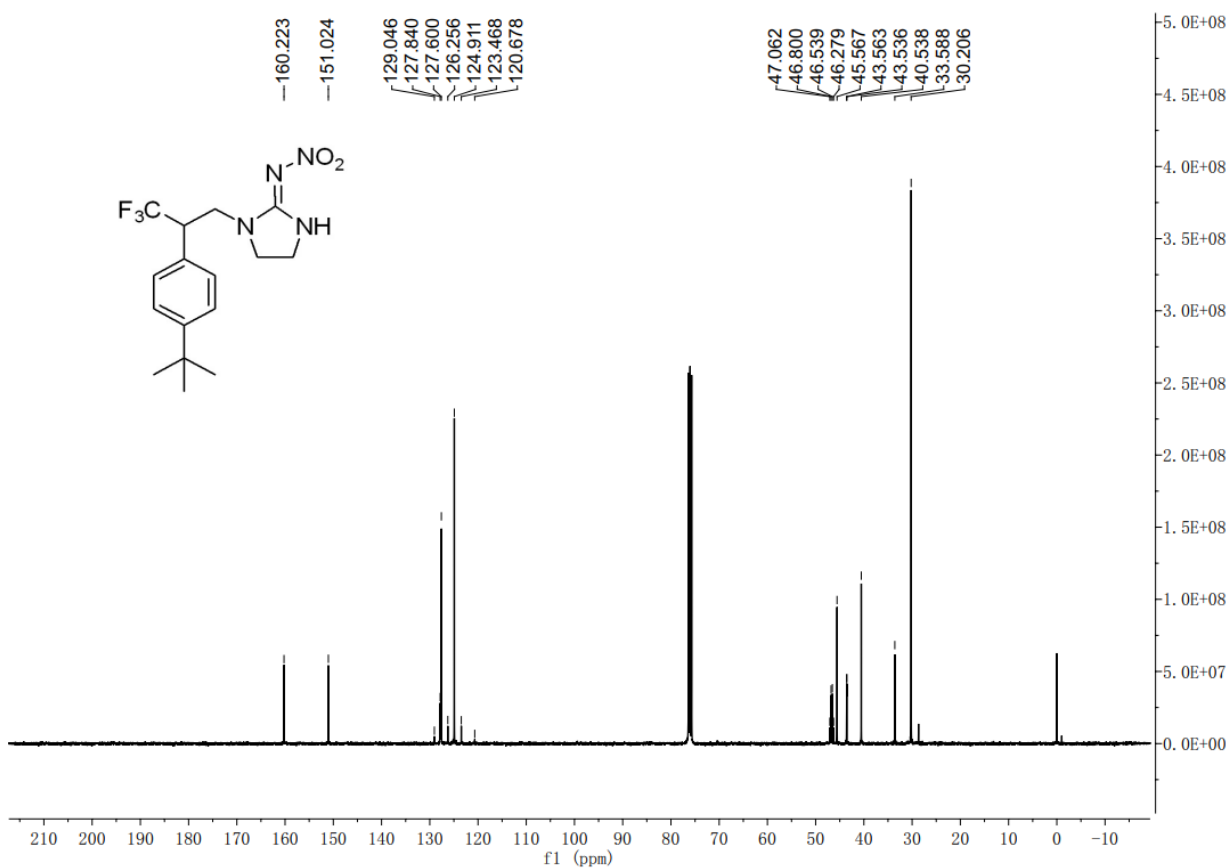
TOF MS EI+
2.23e4



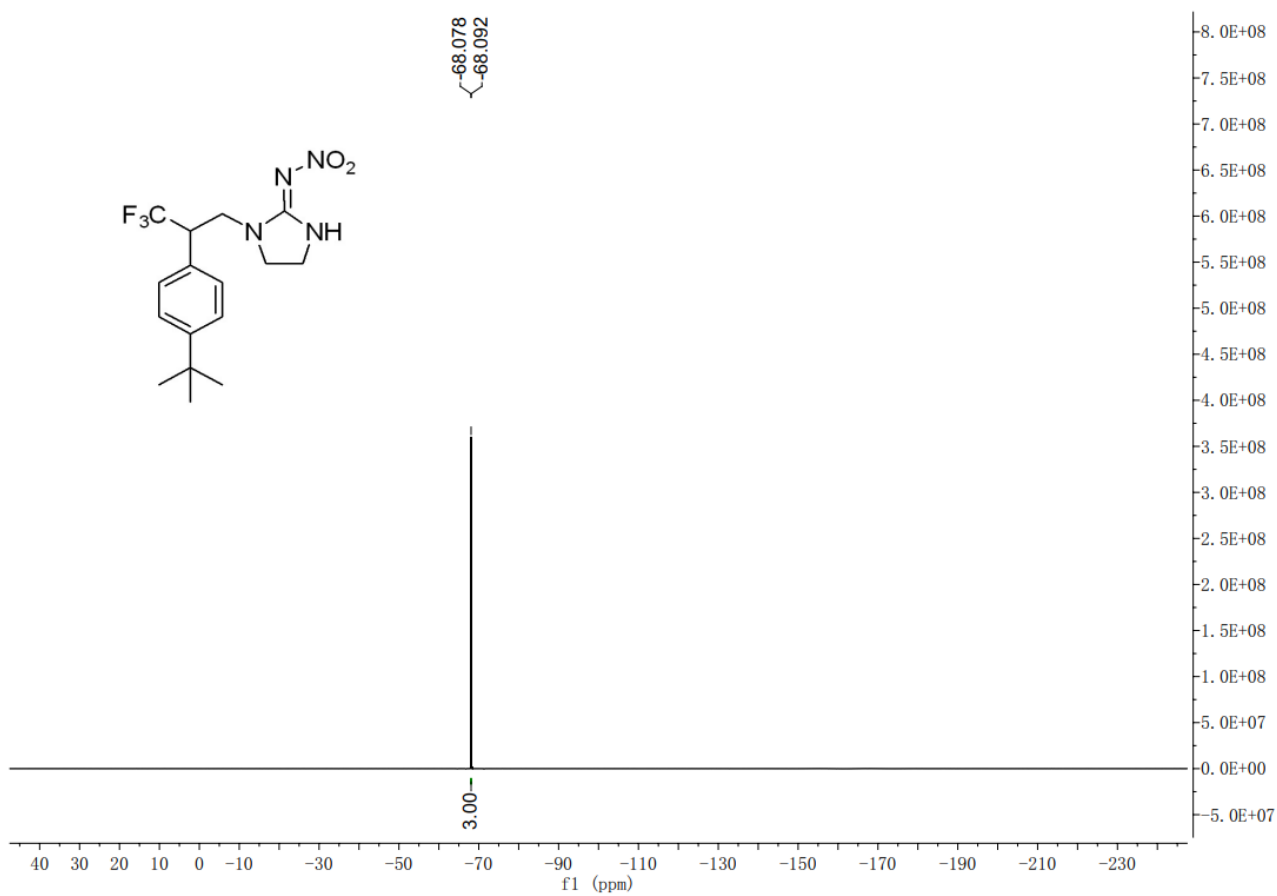
¹H NMR spectrum of 3ha (400 MHz, CDCl₃)



¹³C NMR spectrum of 3ha (100 MHz, CDCl₃)



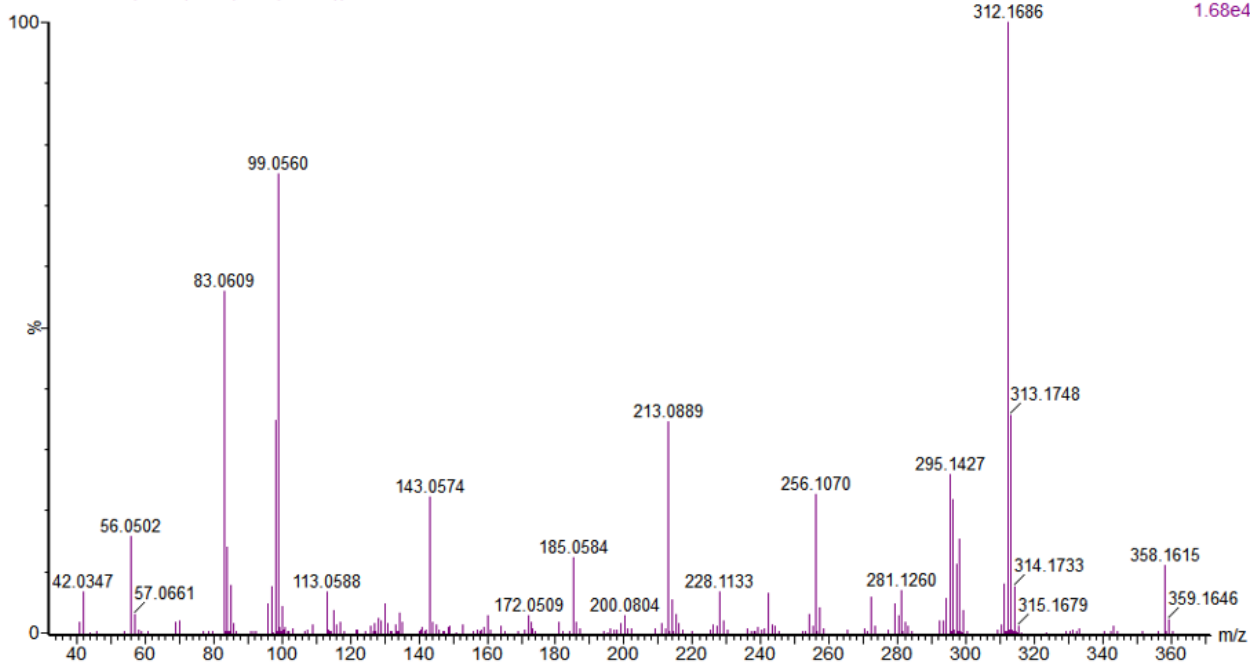
^{19}F NMR spectrum of 3ha (564 MHz, CDCl_3)



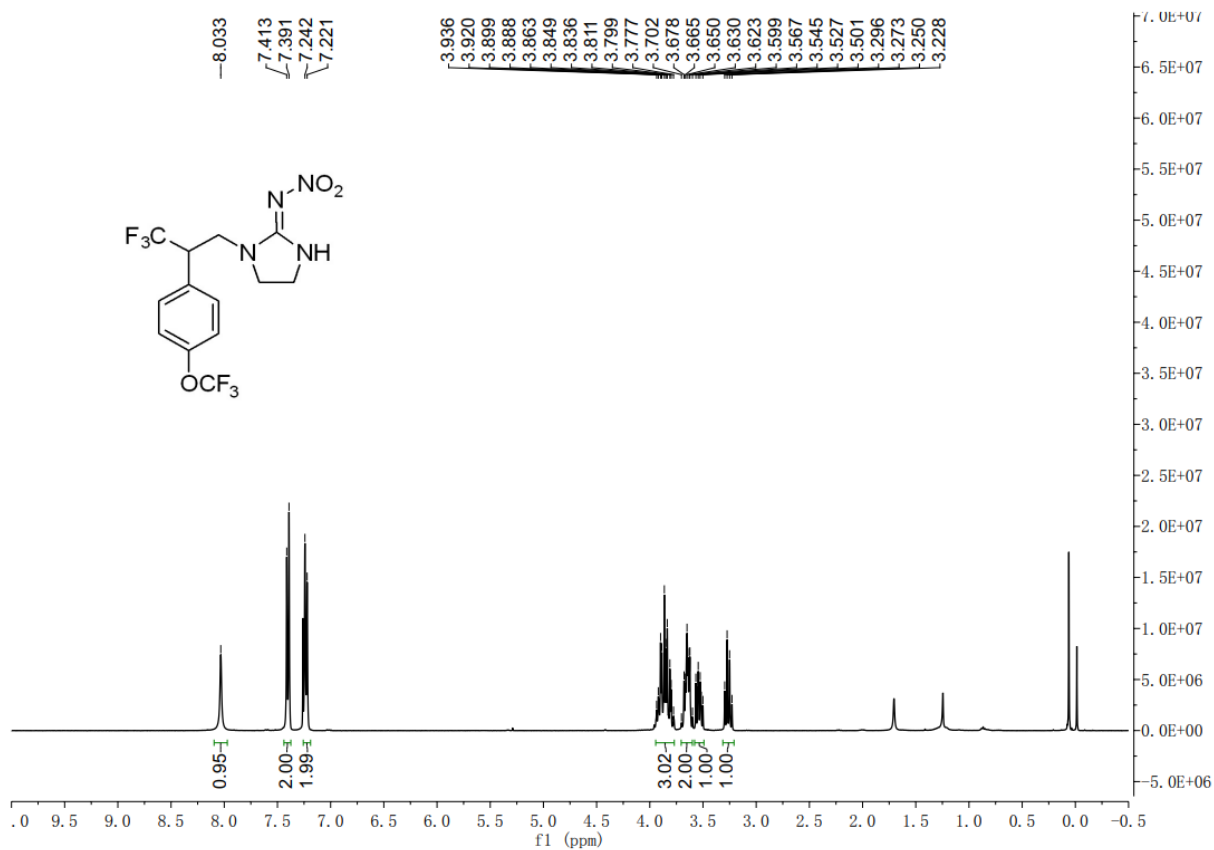
HRMS (EI) spectrum of 3ha

20221596 410 (6.836) Cm (410-(54+97))

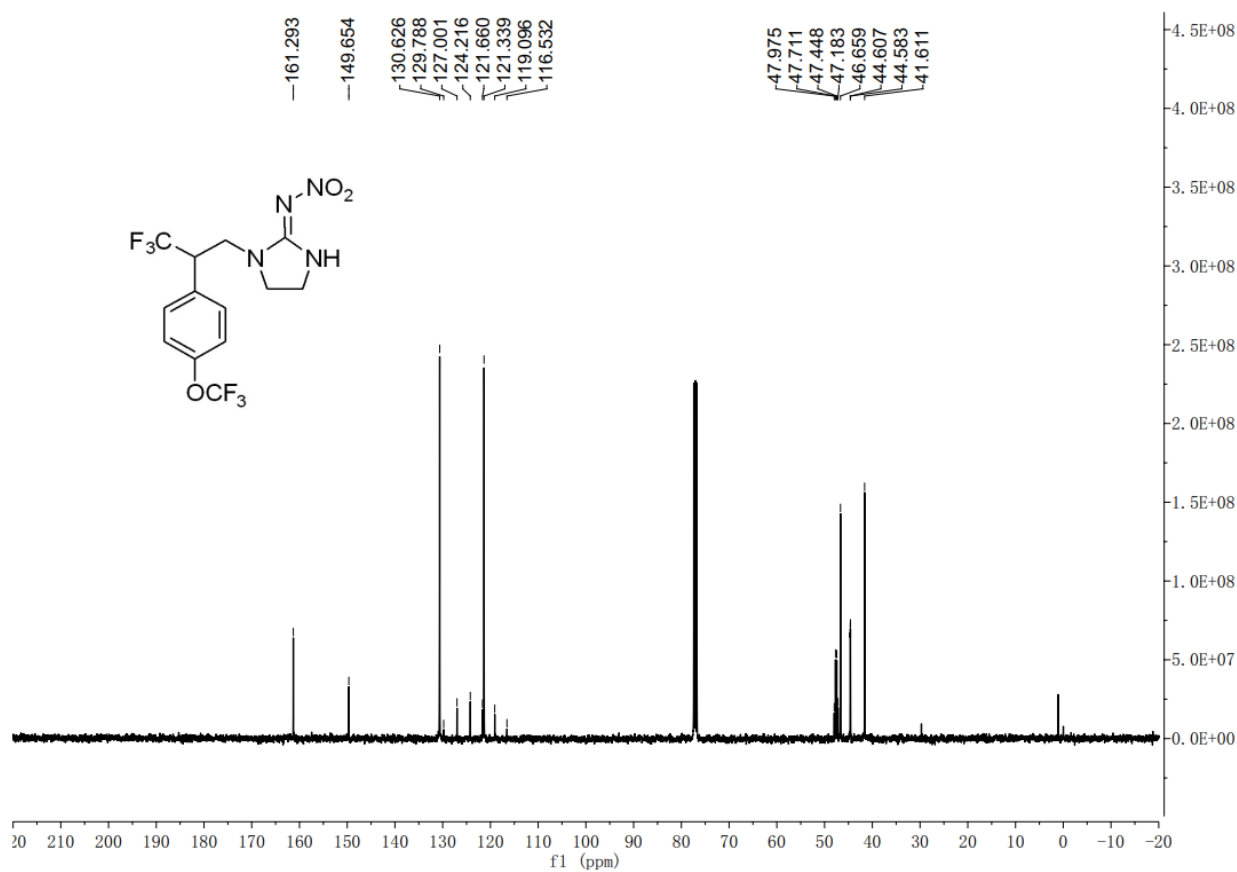
TOF MS EI+
1.68e4



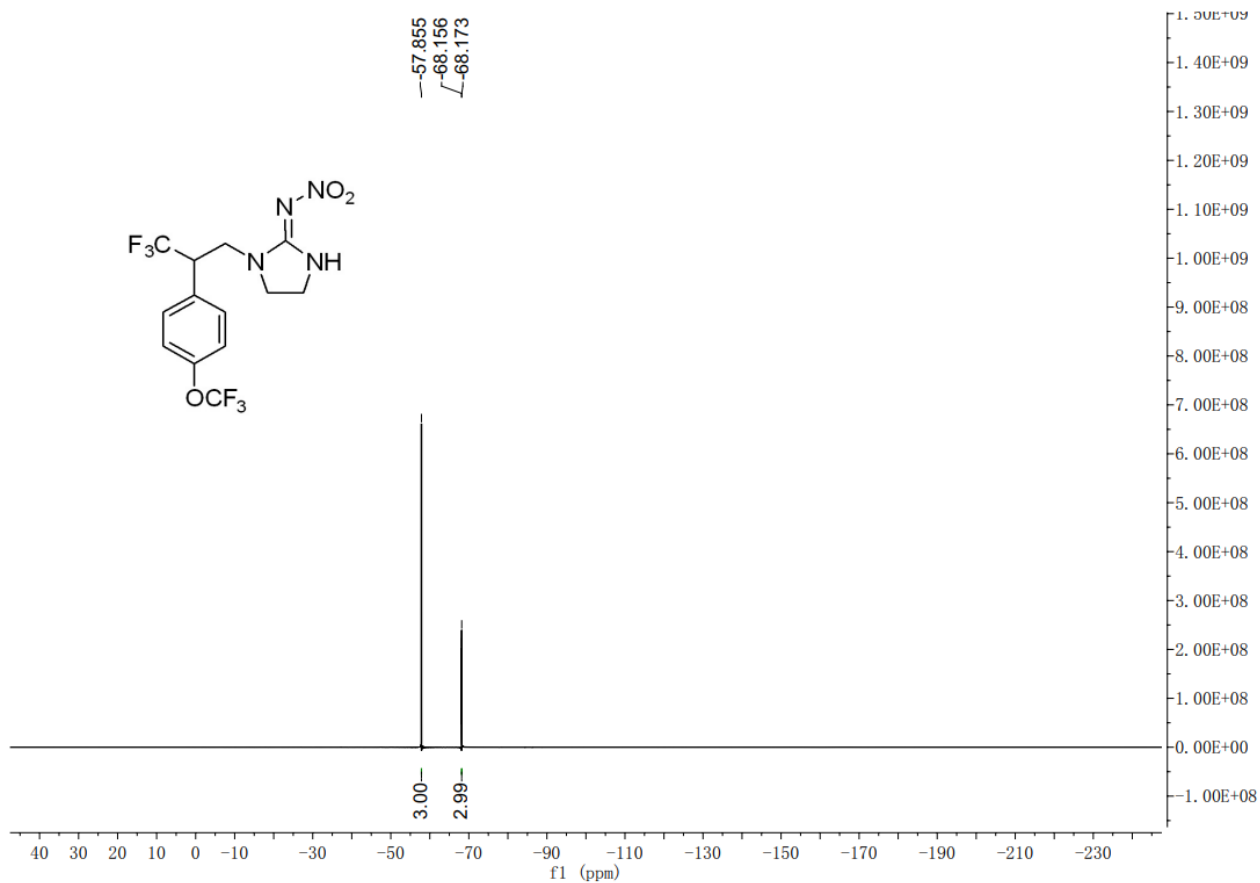
¹H NMR spectrum of 3ia (400 MHz, CDCl₃)



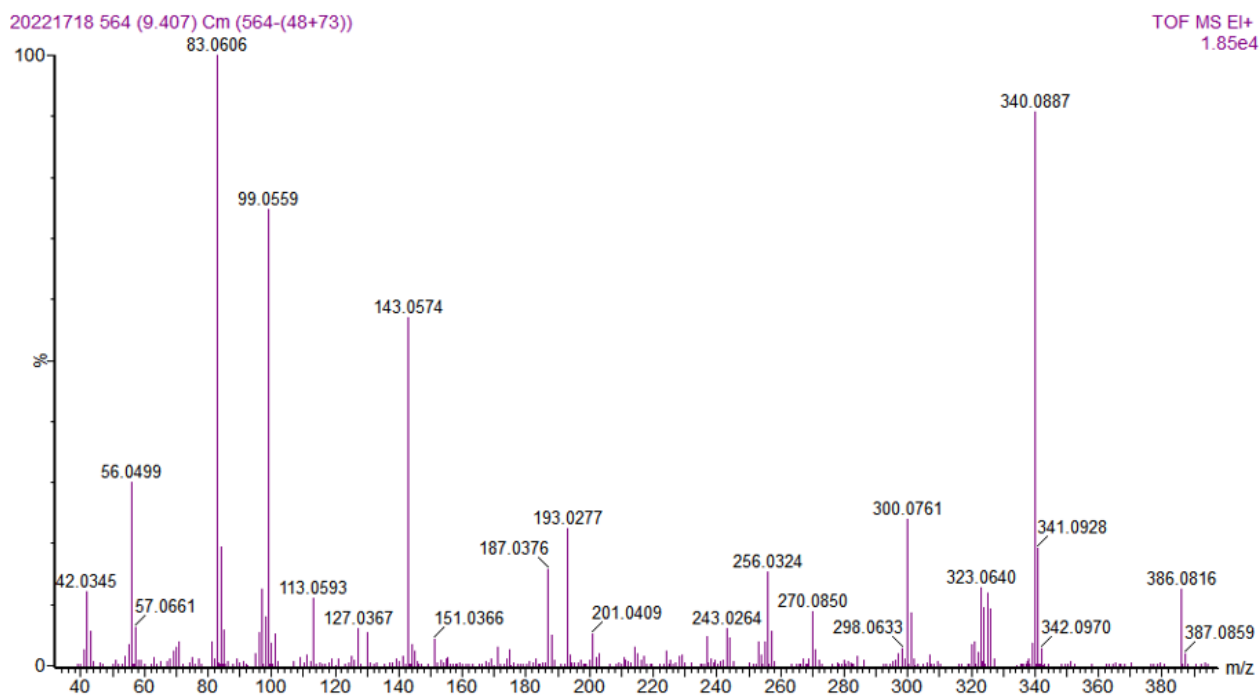
¹³C NMR spectrum of 3ia (100 MHz, CDCl₃)



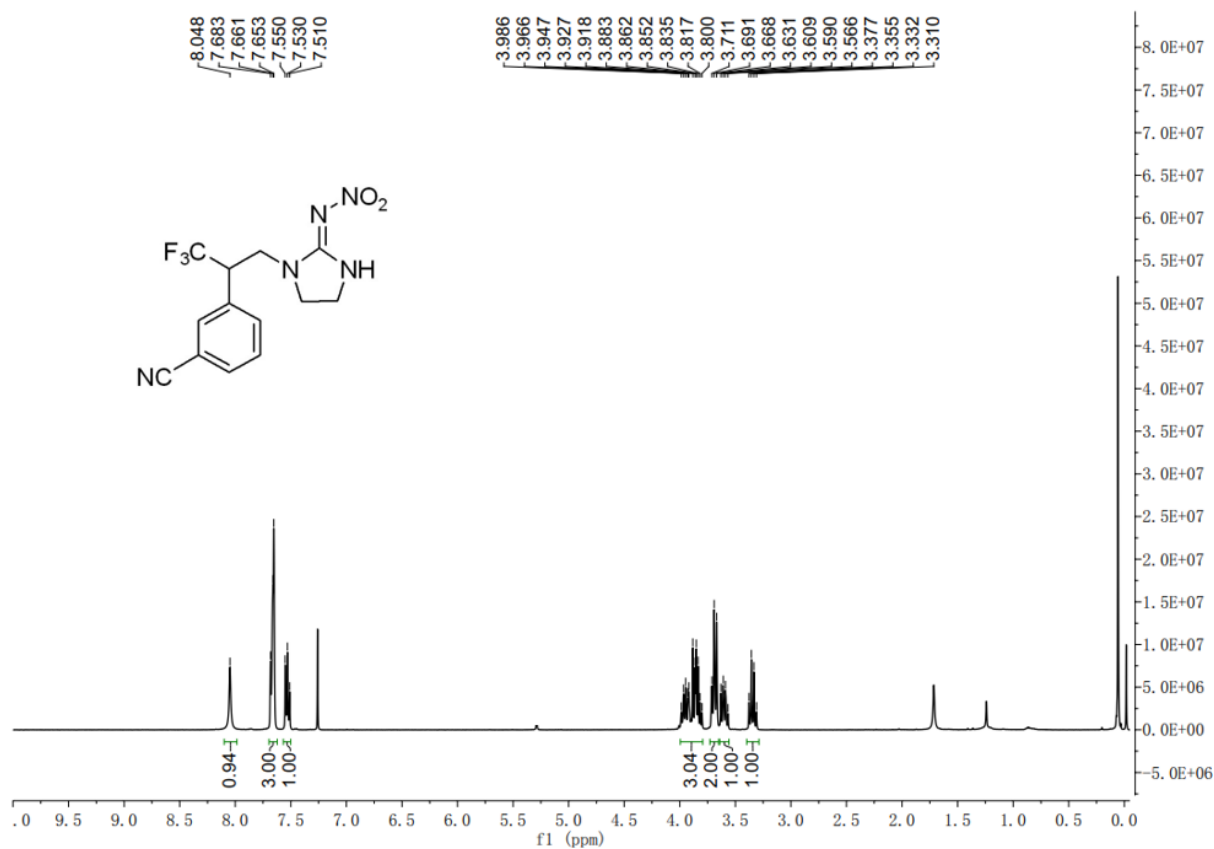
^{19}F NMR spectrum of 3ia (564 MHz, CDCl_3)



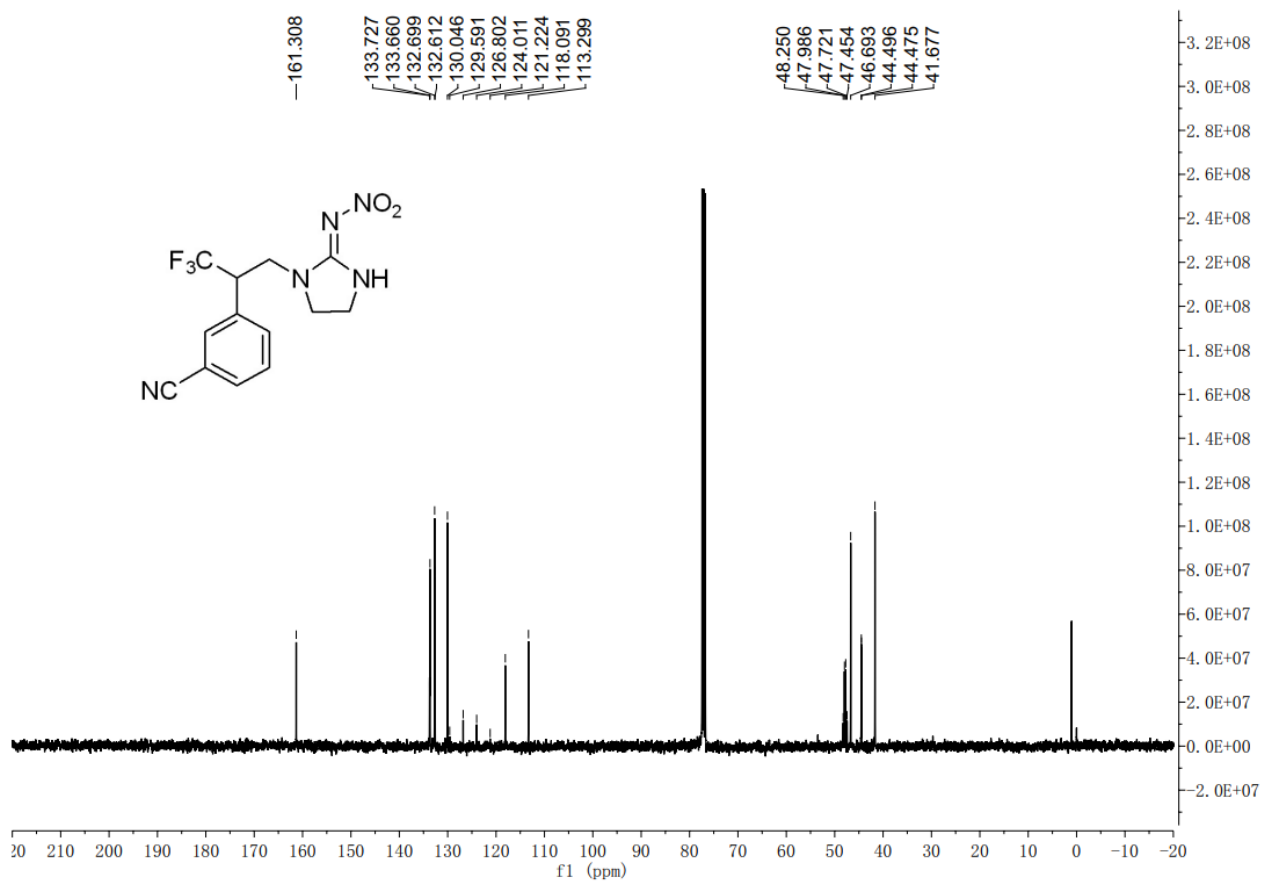
HRMS (EI) spectrum of 3ia



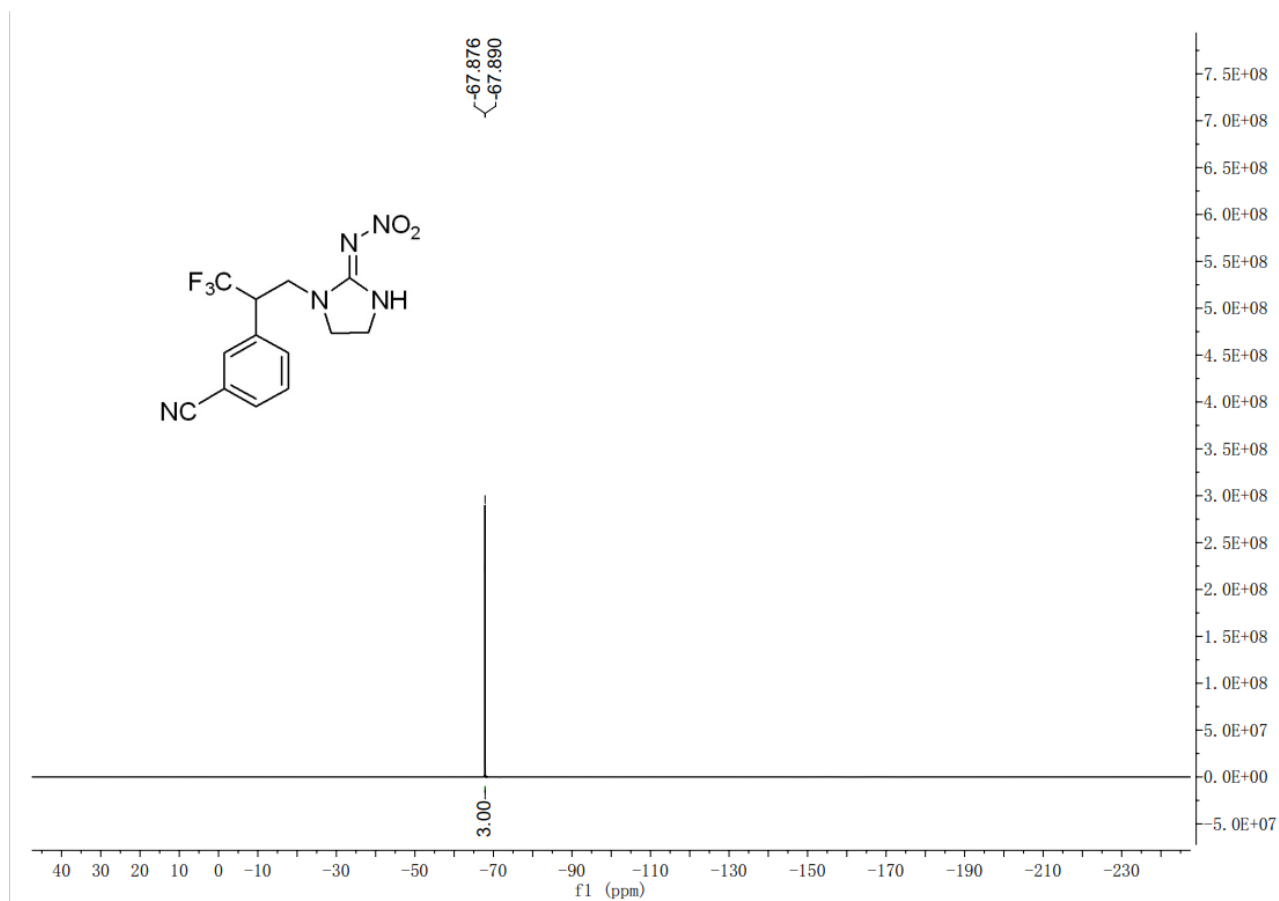
¹H NMR spectrum of 3ja (400 MHz, CDCl₃)



¹³C NMR spectrum of 3ja (100 MHz, CDCl₃)



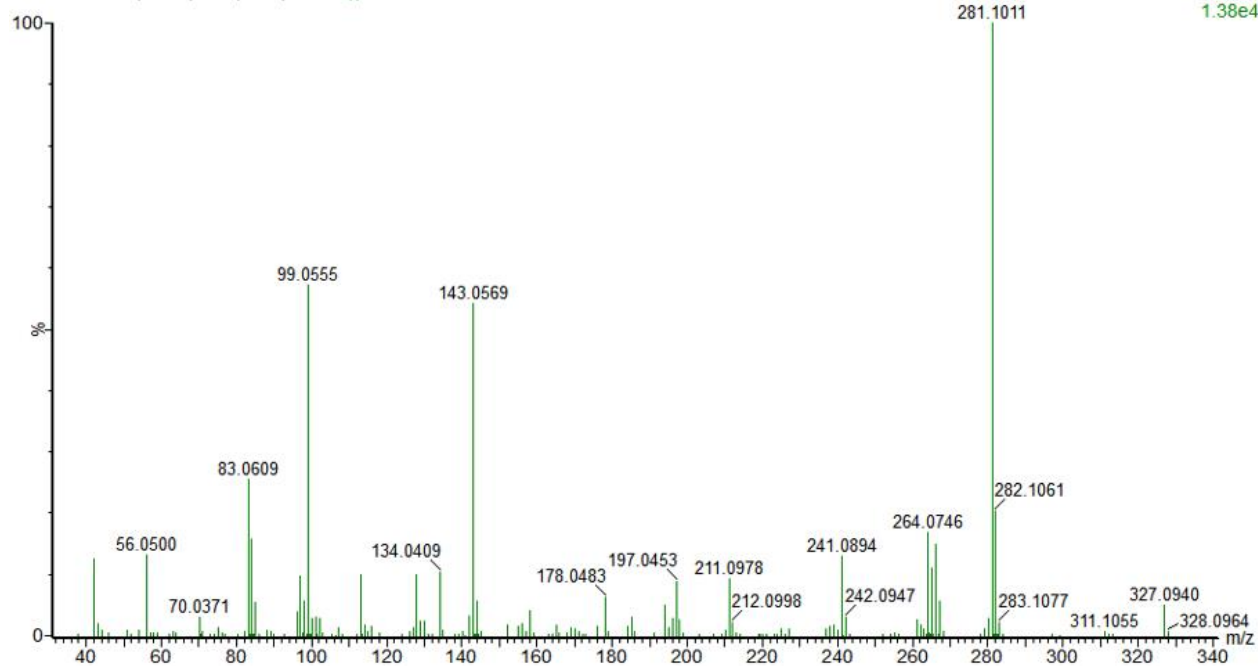
^{19}F NMR spectrum of 3ja (564 MHz, CDCl_3)



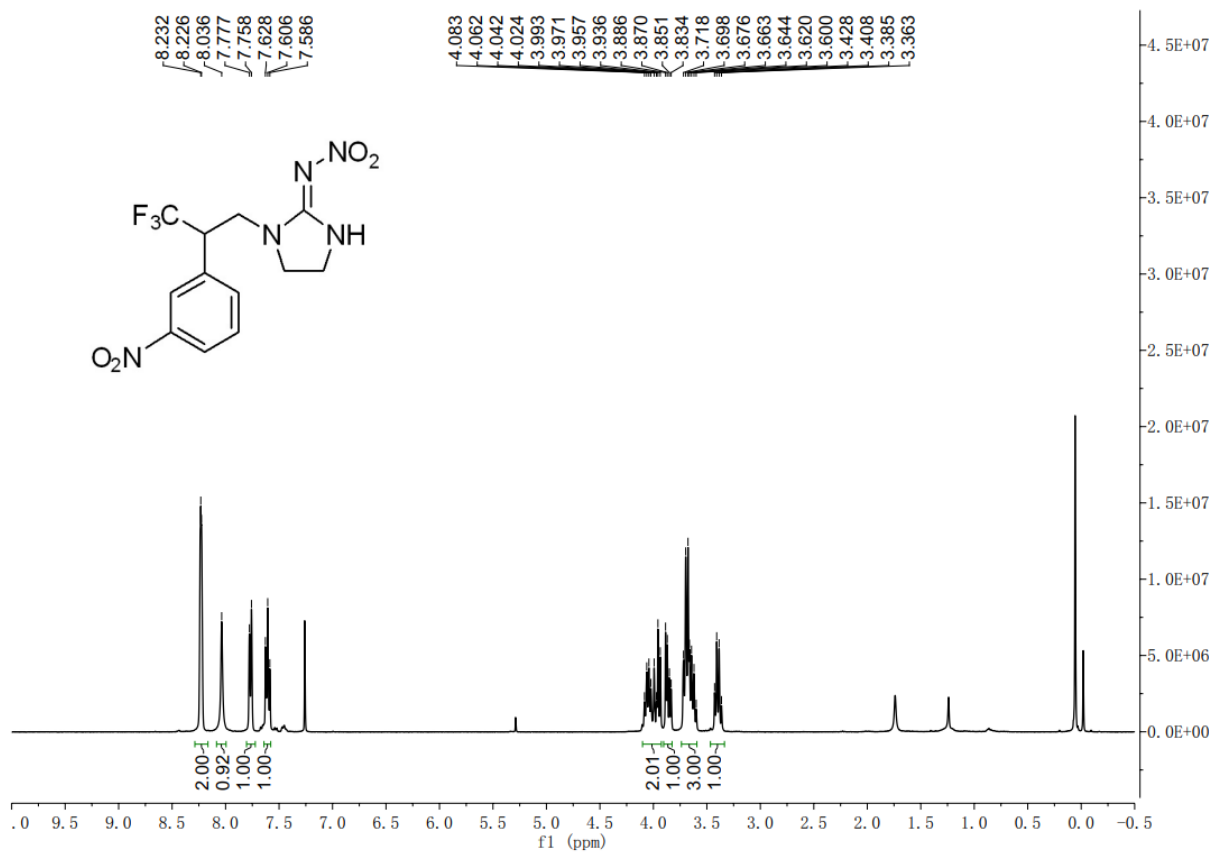
HRMS (EI) spectrum of 3ja

20221599 419 (6.987) Cm (419-(46+716))

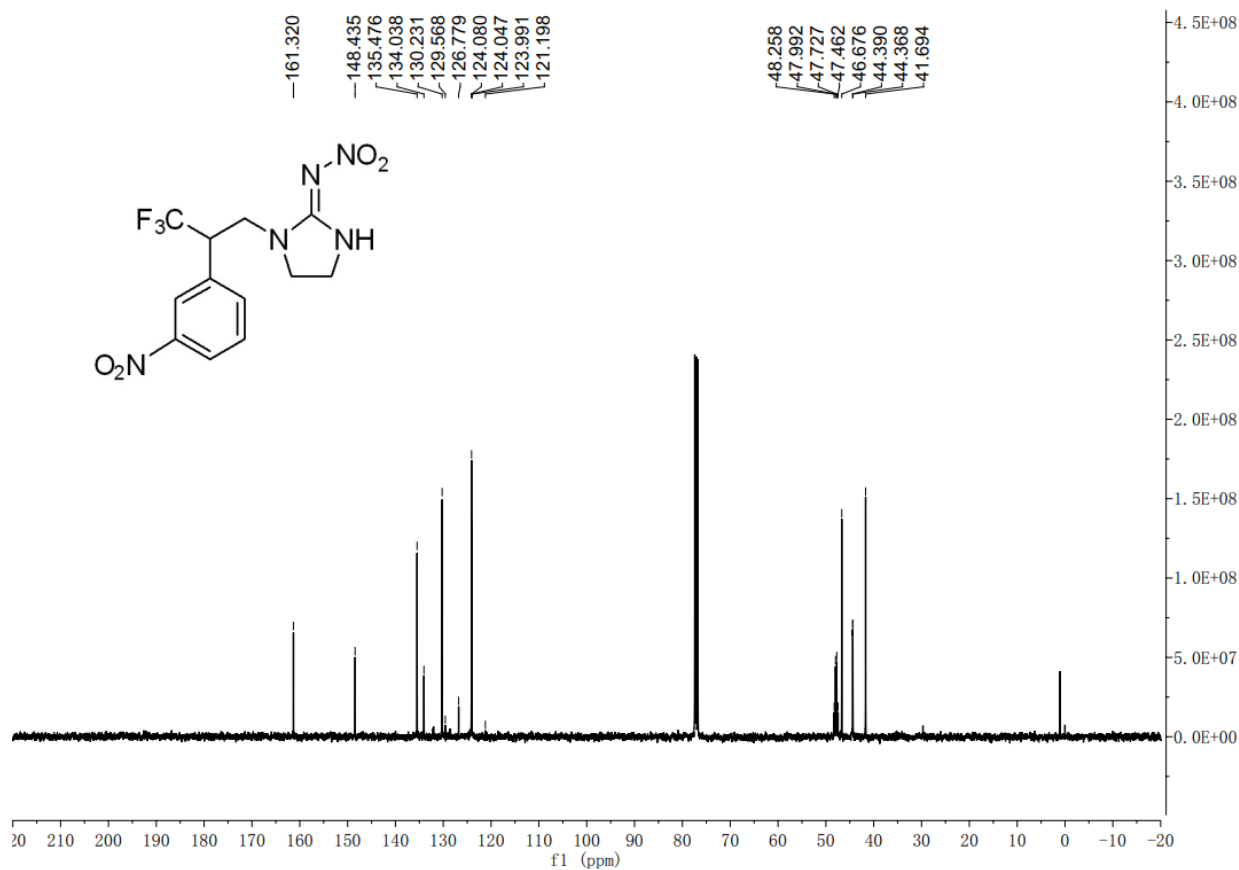
TOF MS EI+
1.38e4



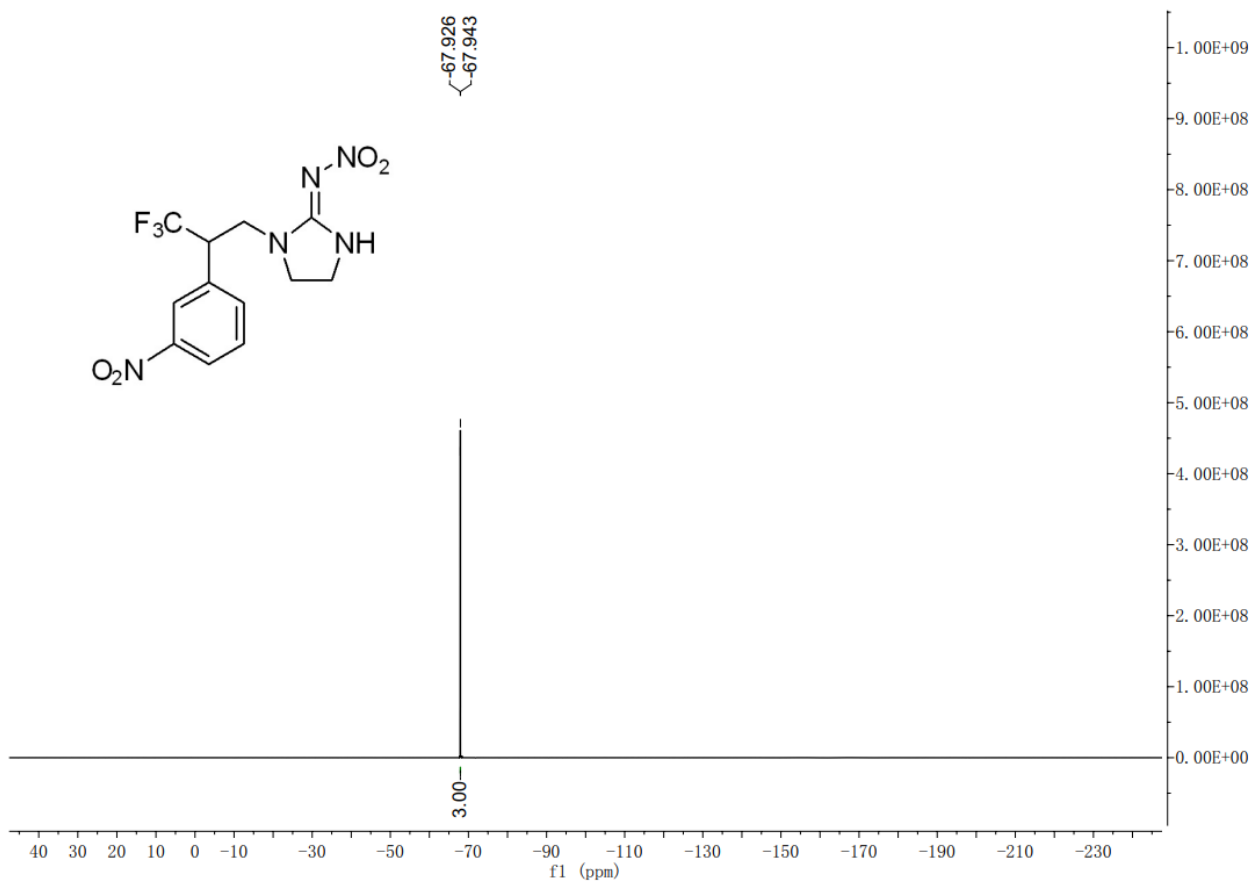
¹H NMR spectrum of 3ka (400 MHz, CDCl₃)



¹³C NMR spectrum of 3ka (100 MHz, CDCl₃)



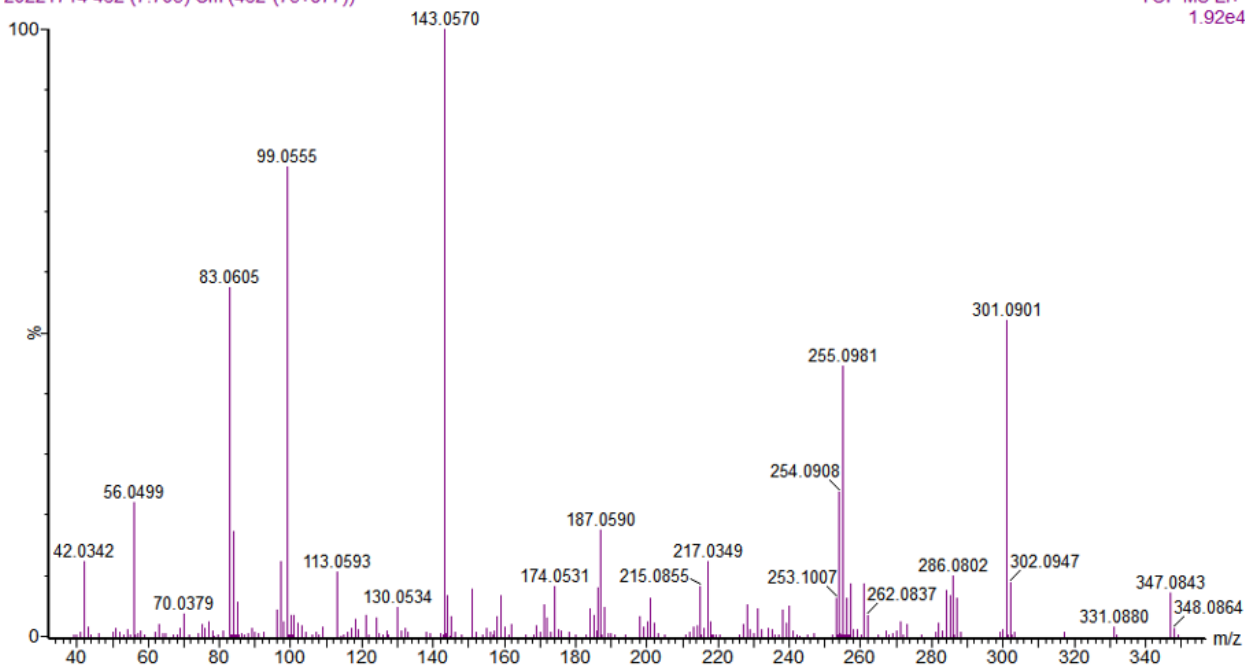
¹⁹F NMR spectrum of 3ka (564 MHz, CDCl₃)



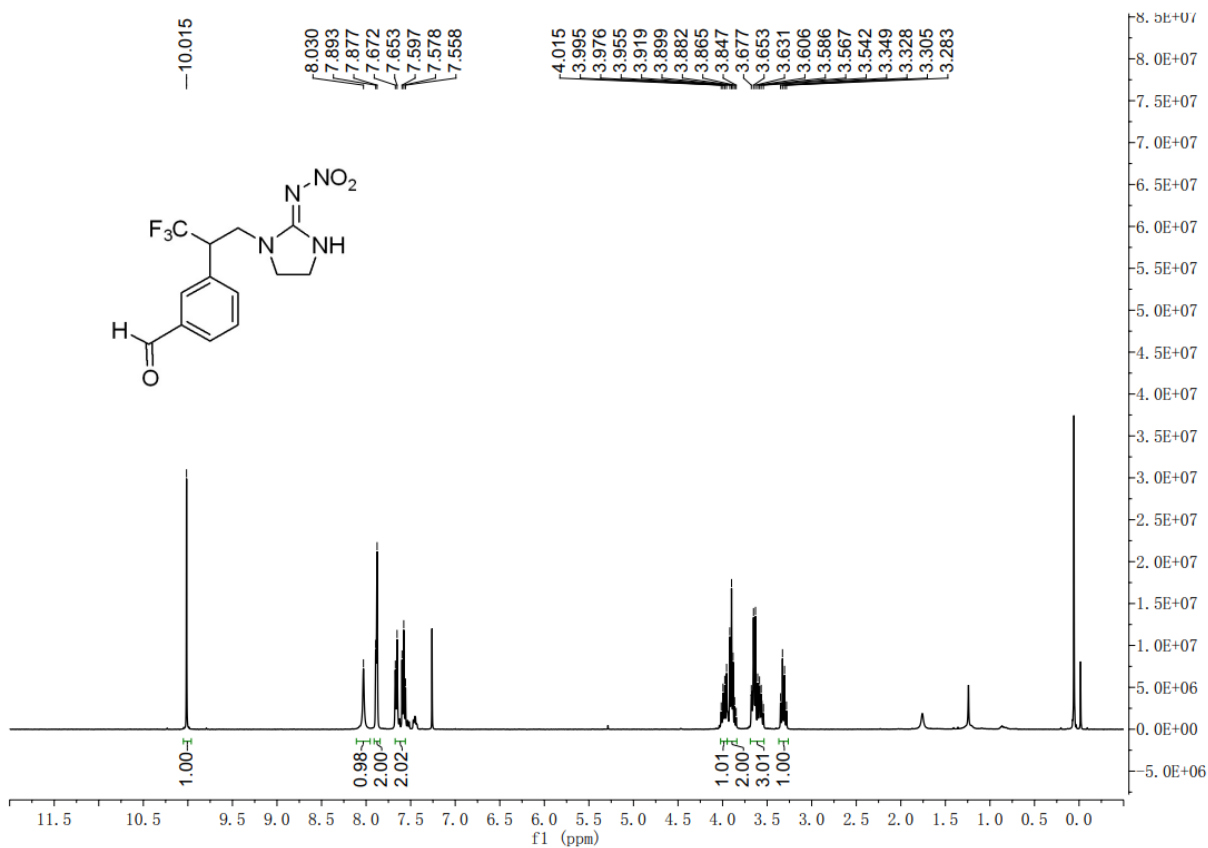
HRMS (EI) spectrum of 3ka

20221714 462 (7.705) Cm (462-(75+877))

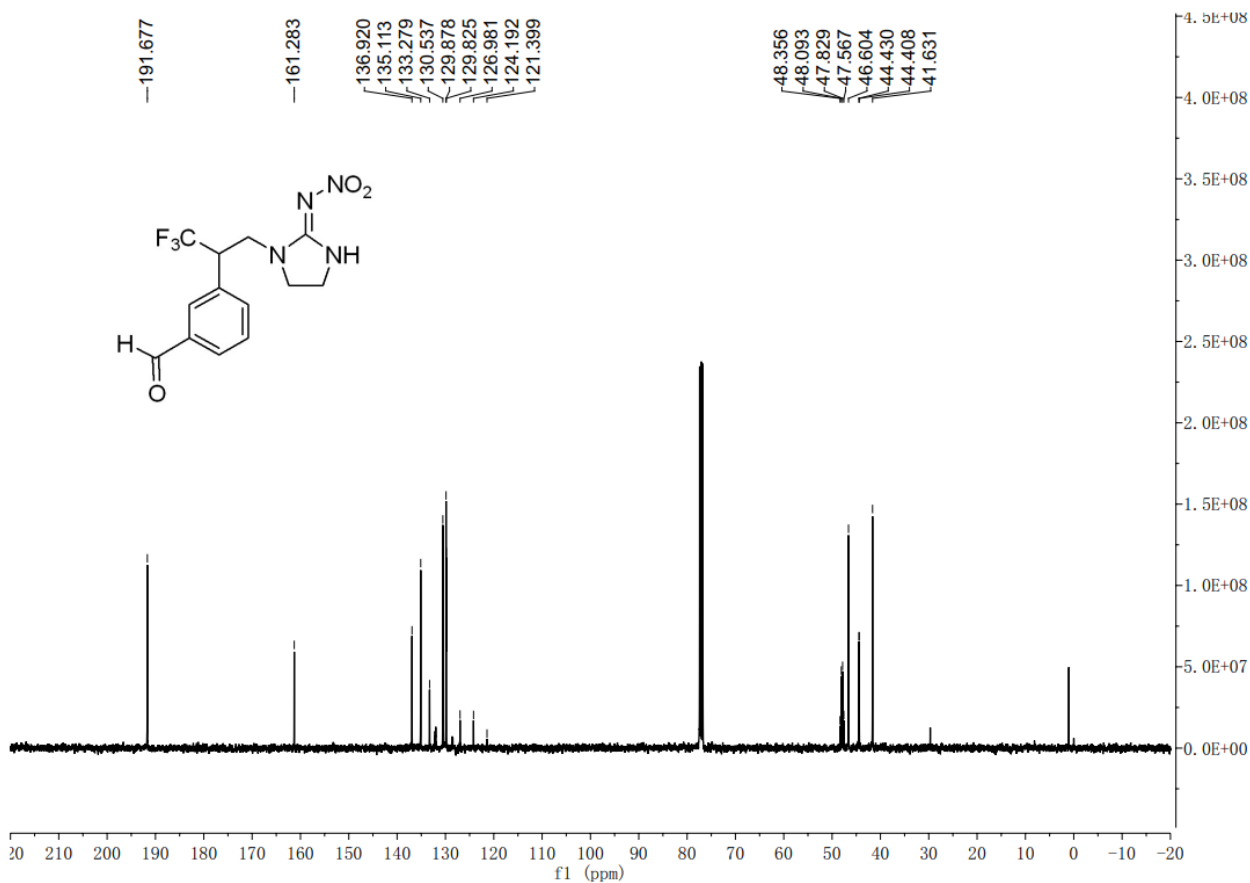
TOF MS EI+
1.92e4



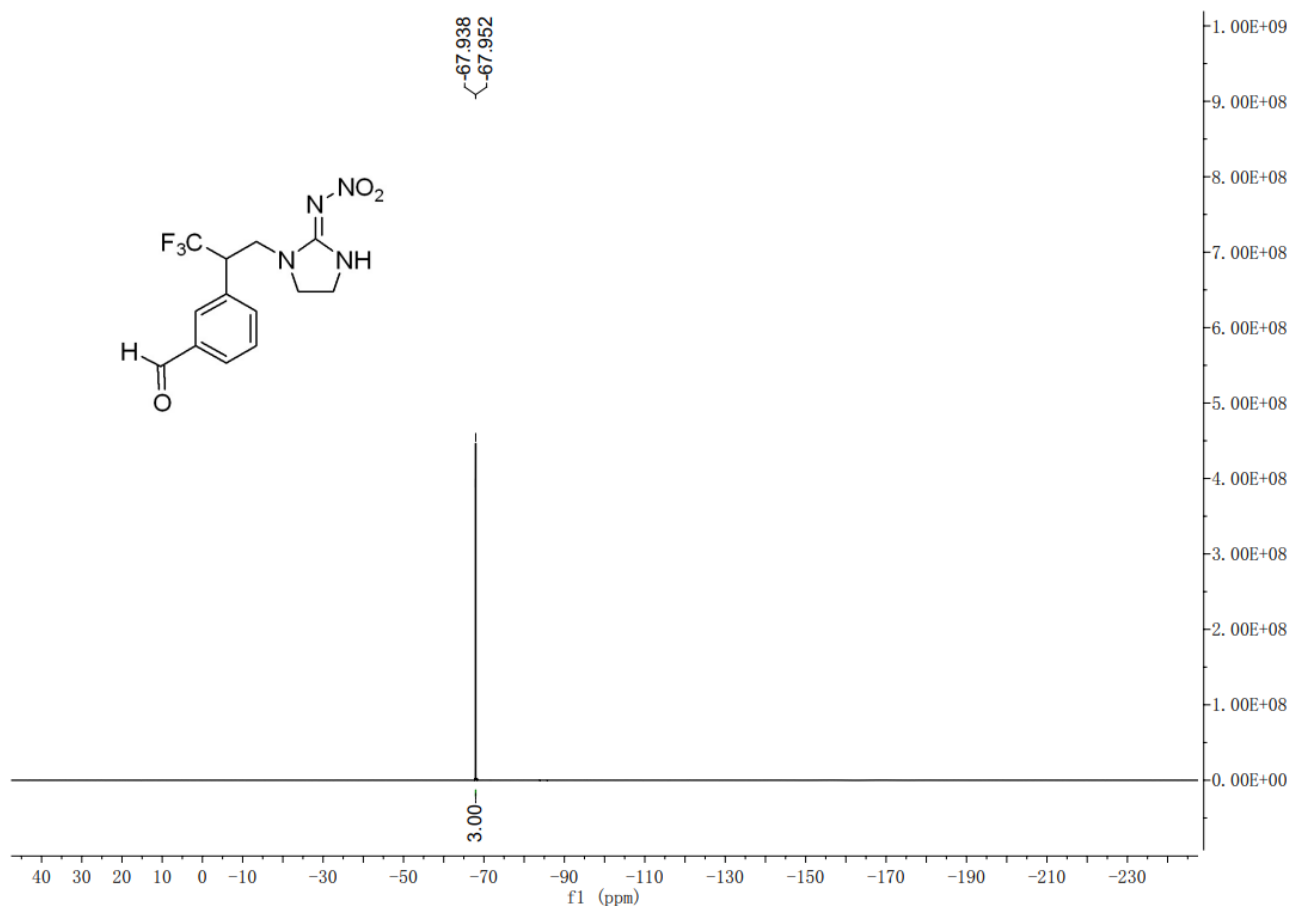
¹H NMR spectrum of 3la (400 MHz, CDCl₃)



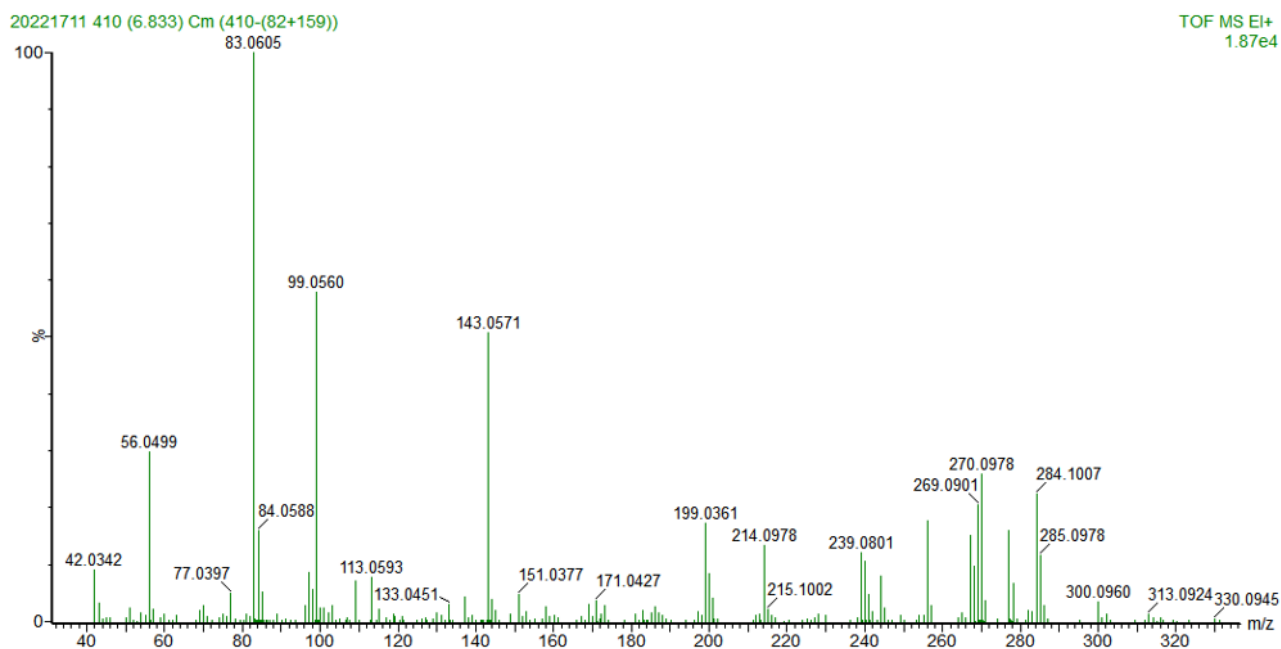
¹³C NMR spectrum of 3la (100 MHz, CDCl₃)



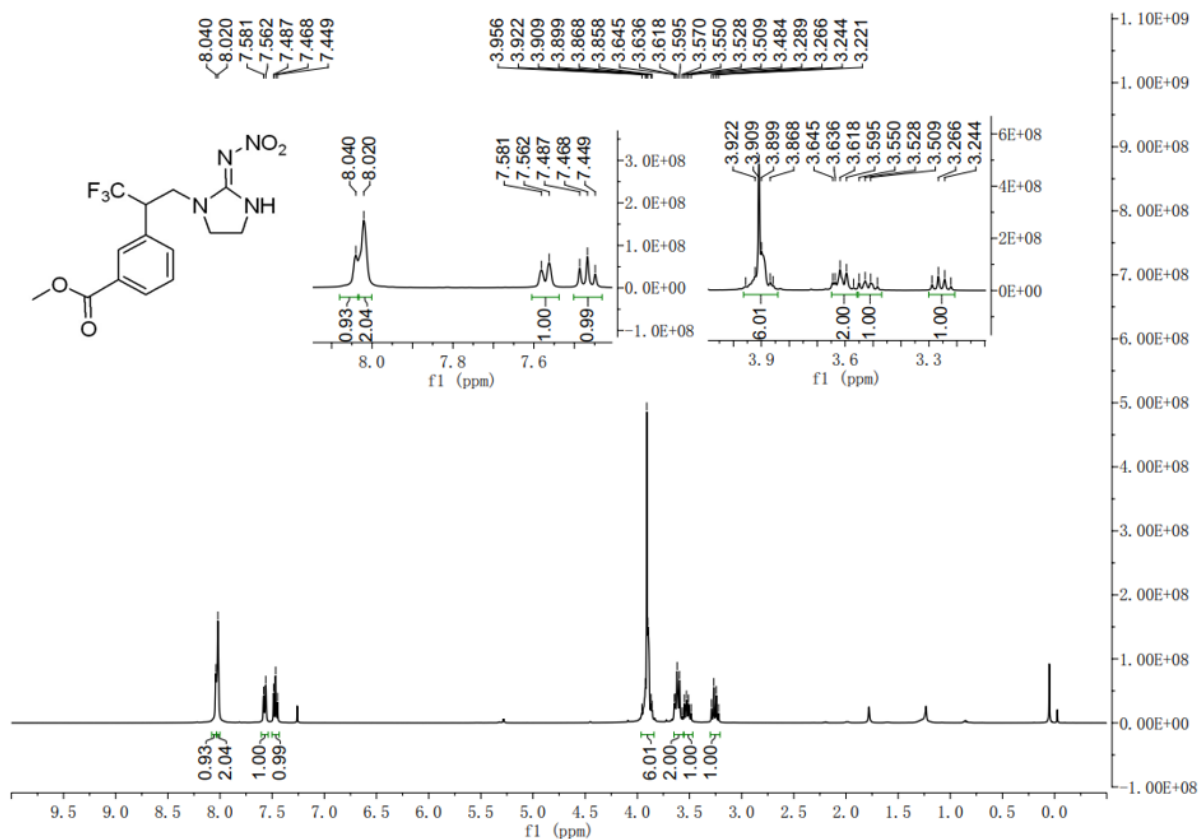
^{19}F NMR spectrum of 3la (564 MHz, CDCl_3)



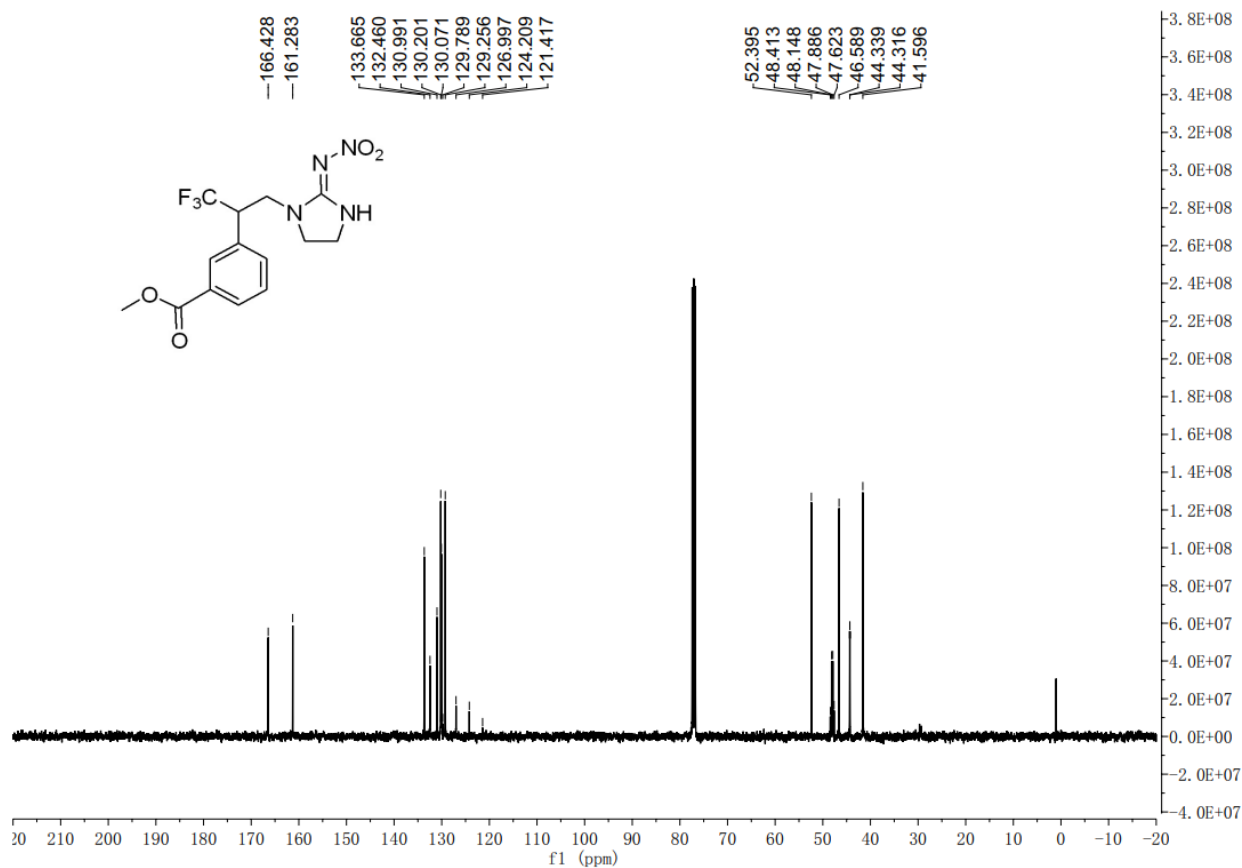
HRMS (EI) spectrum of 3la



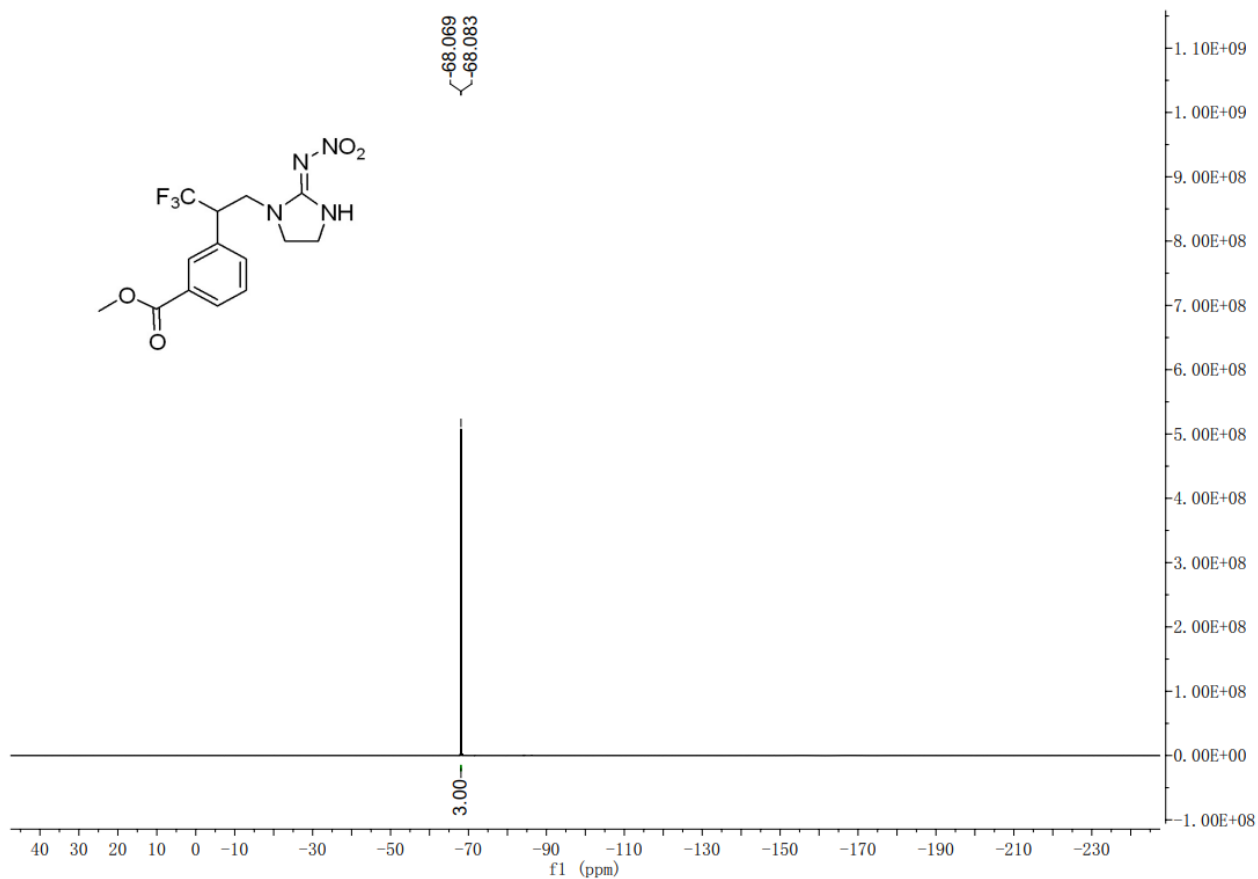
¹H NMR spectrum of 3ma (400 MHz, CDCl₃)



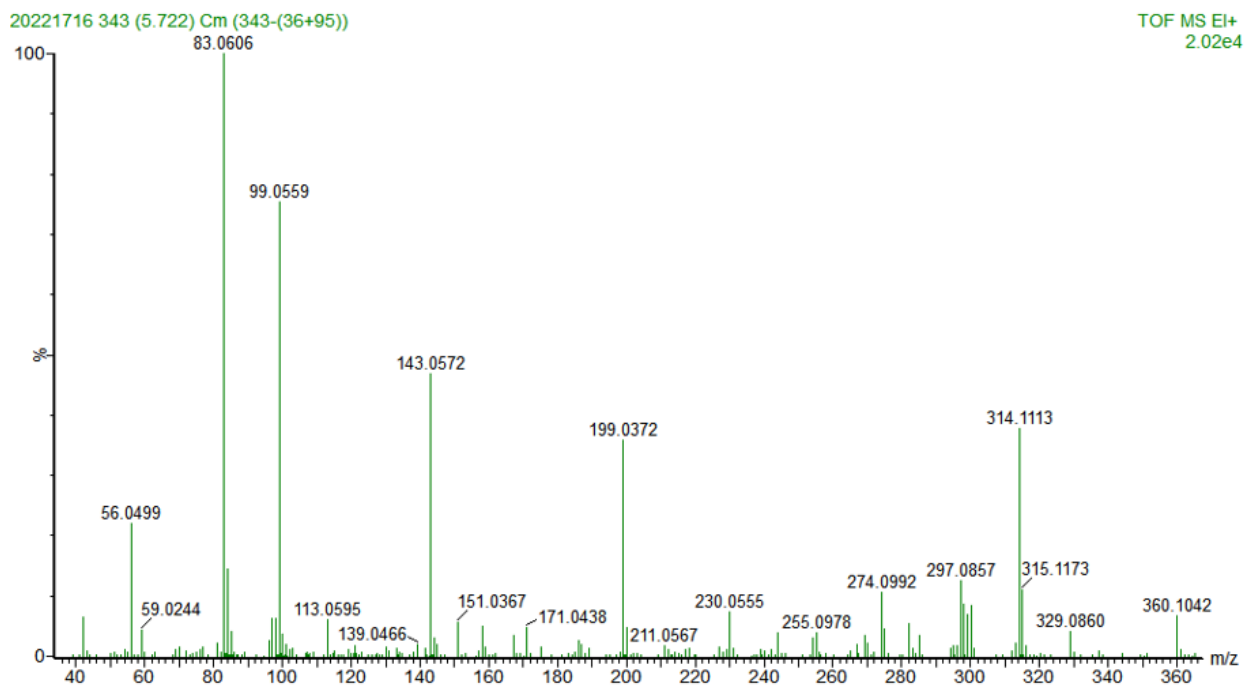
¹³C NMR spectrum of 3ma (100 MHz, CDCl₃)



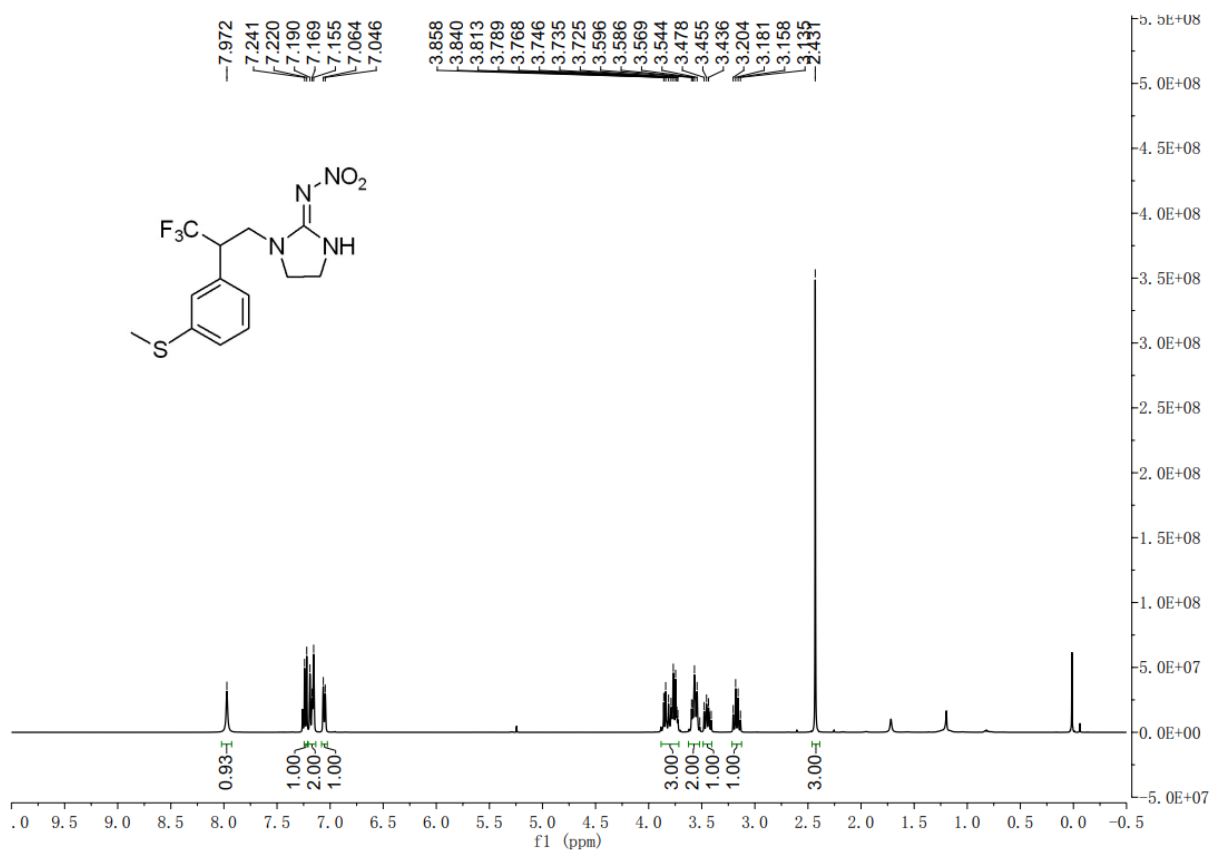
¹⁹F NMR spectrum of 3ma (564 MHz, CDCl₃)



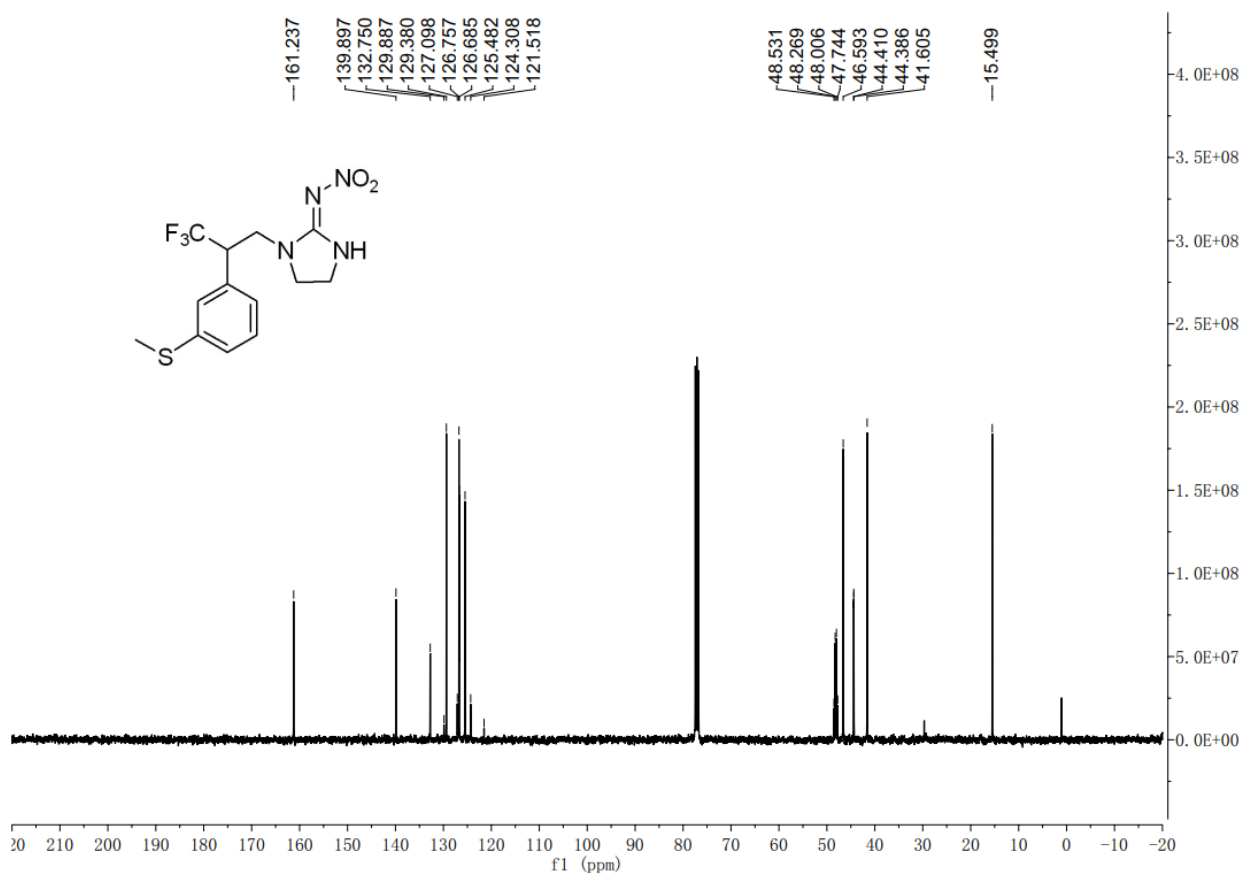
HRMS (EI) spectrum of 3ma



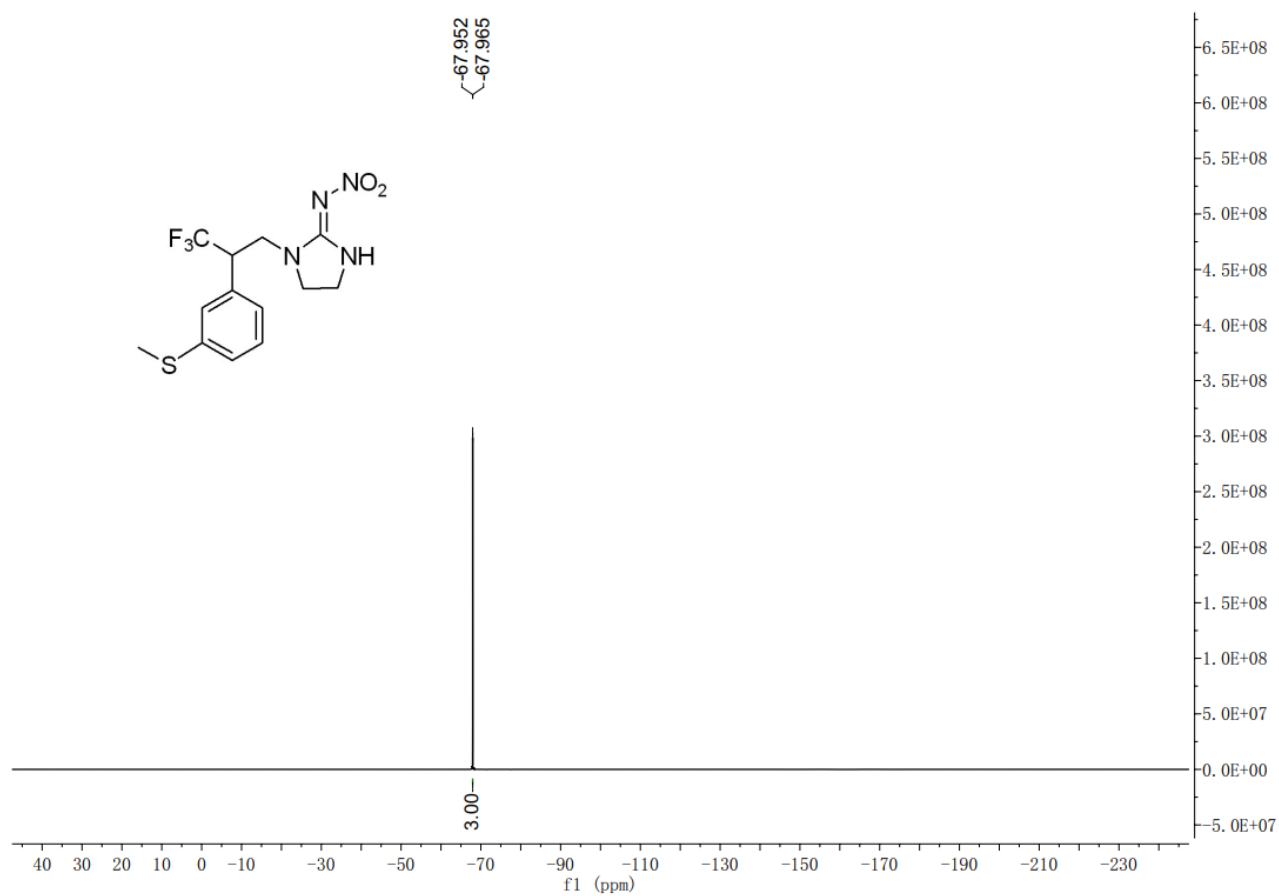
¹H NMR spectrum of 3na (400 MHz, CDCl₃)



¹³C NMR spectrum of 3na (100 MHz, CDCl₃)



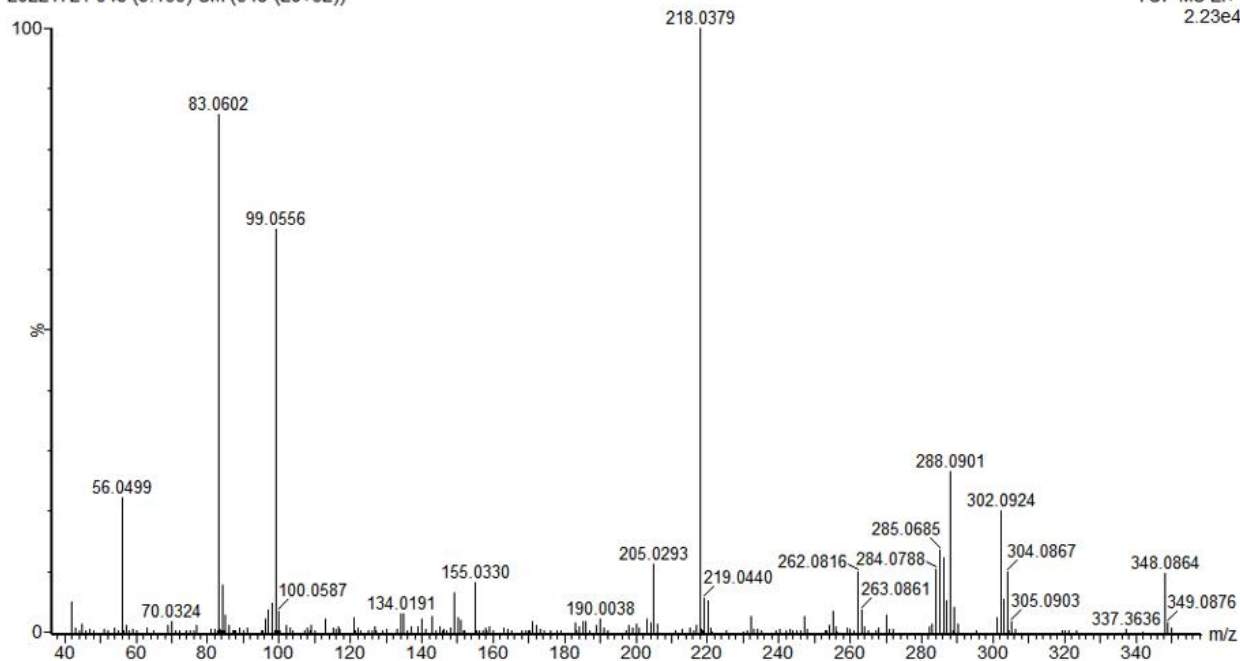
^{19}F NMR spectrum of 3na (564 MHz, CDCl_3)



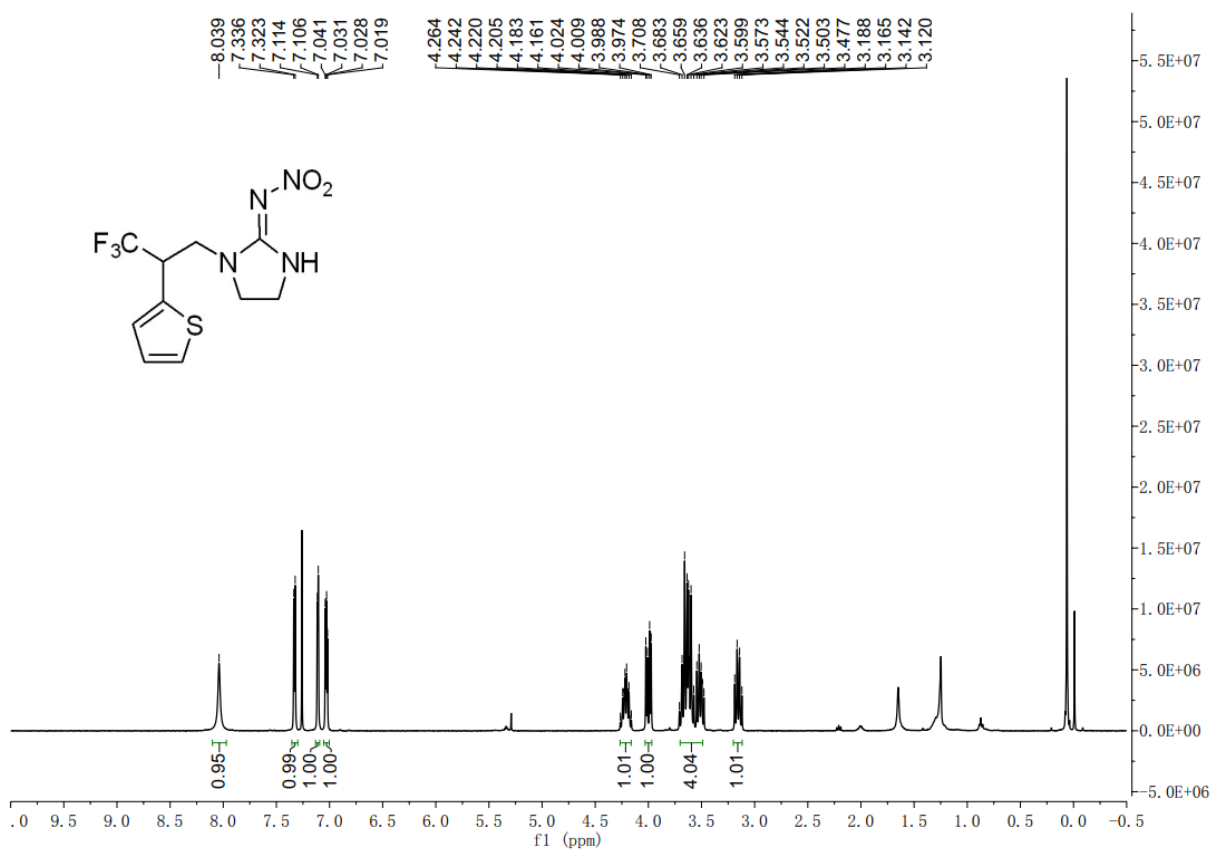
HRMS (EI) spectrum of 3na

20221721 548 (9.133) Cm (548-(20+52))

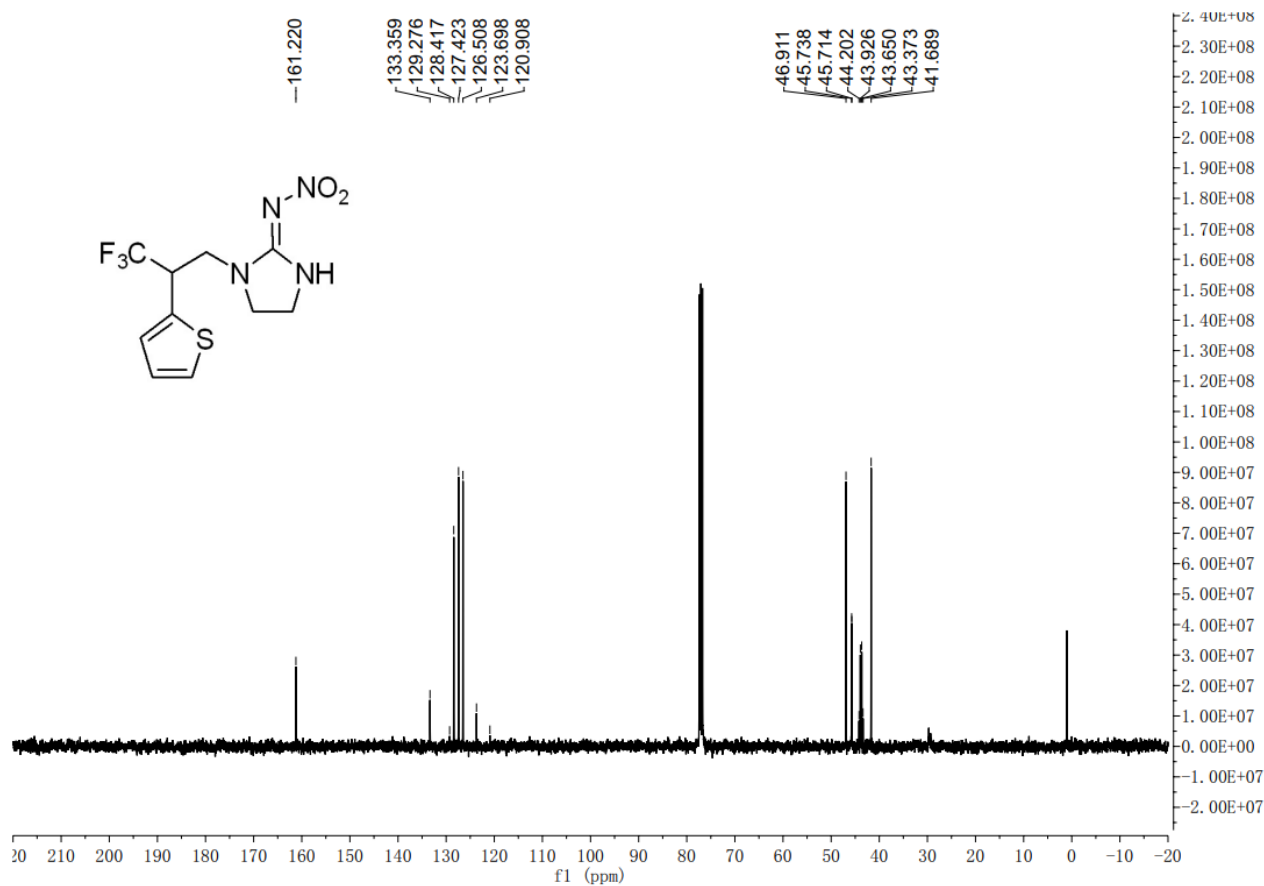
TOF MS EI+
2.23e4



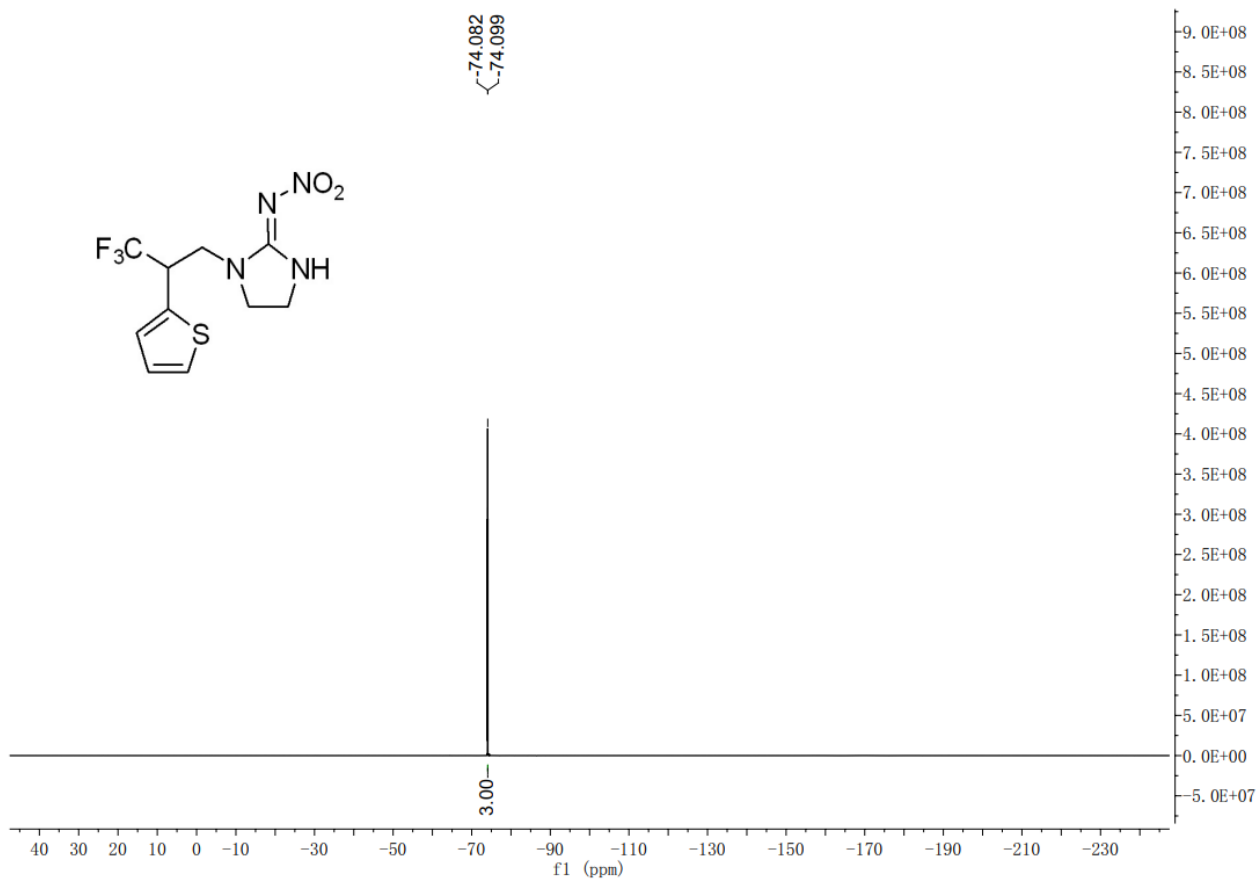
¹H NMR spectrum of 3qa (400 MHz, CDCl₃)



¹³C NMR spectrum of 3qa (100 MHz, CDCl₃)



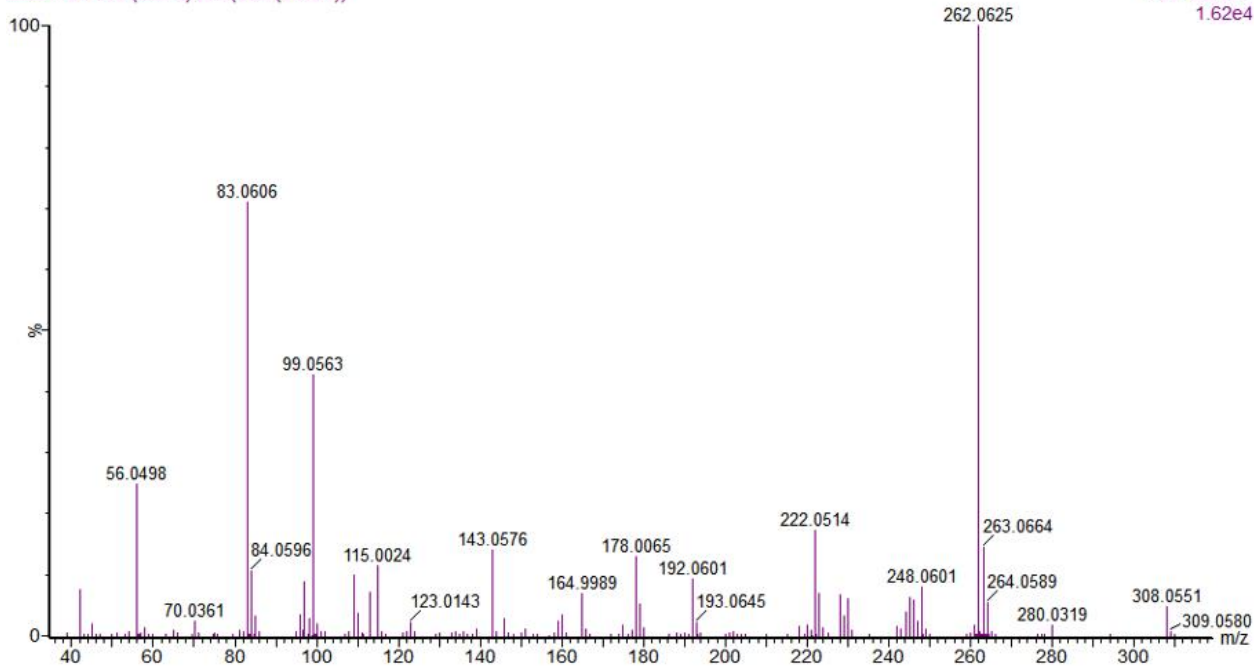
¹⁹F NMR spectrum of 3qa (564 MHz, CDCl₃)



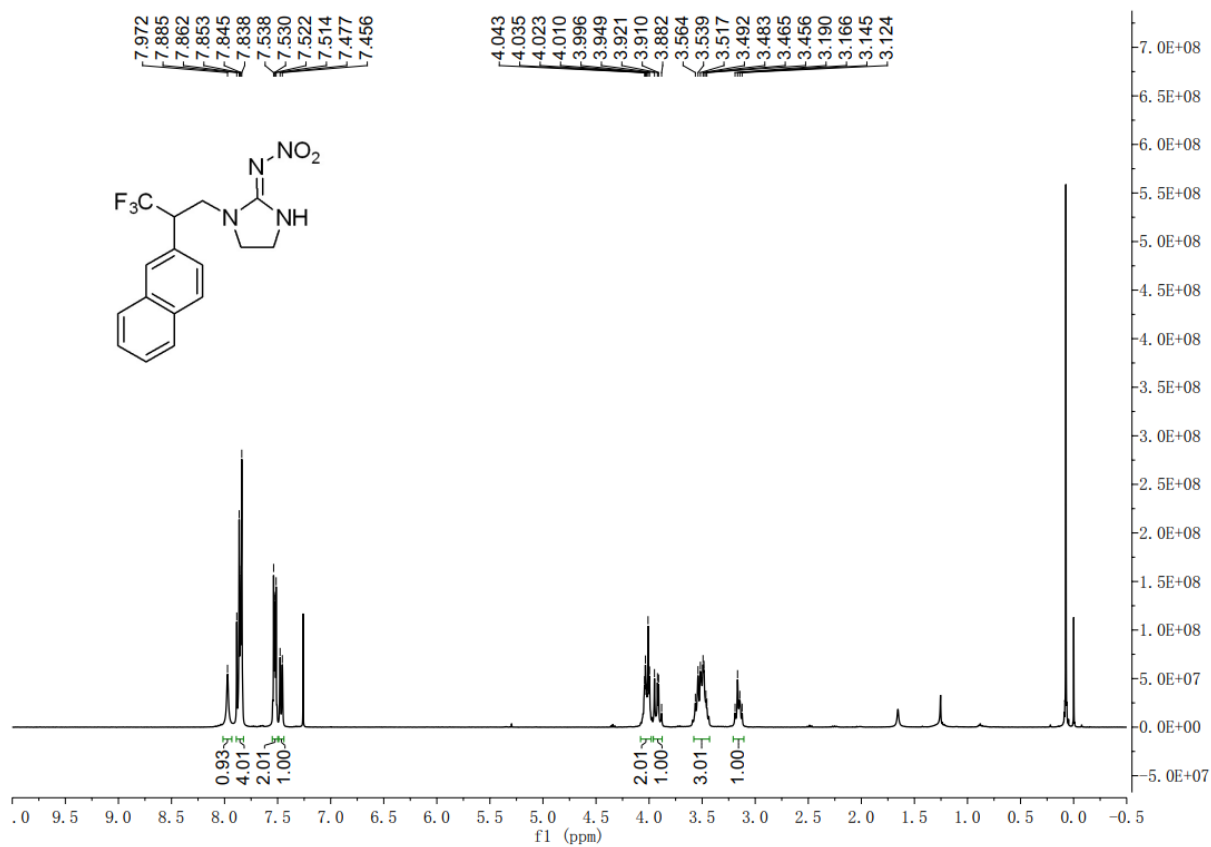
HRMS (EI) spectrum of 3qa

20221709 496 (8.273) Cm (496-(42+91))

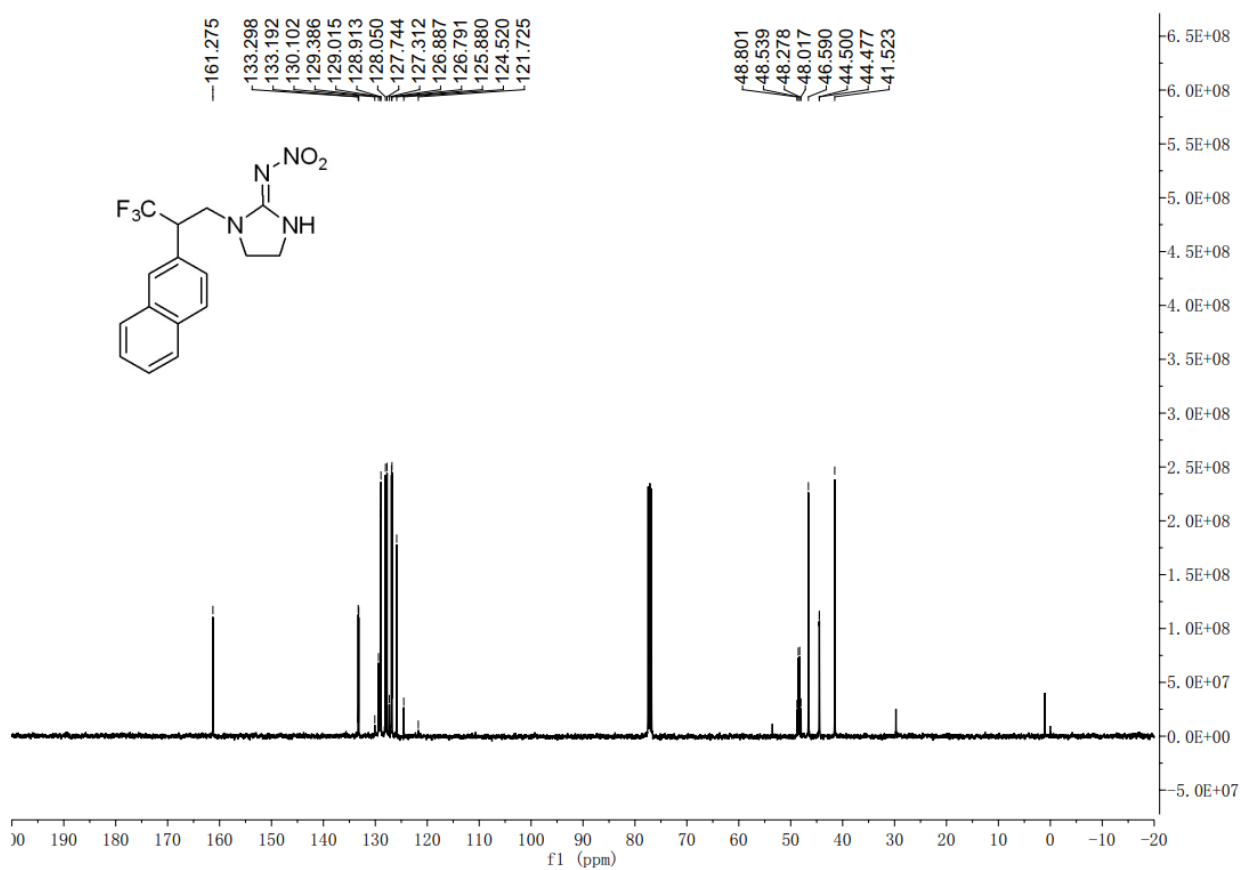
TOF MS EI+
1.62e4



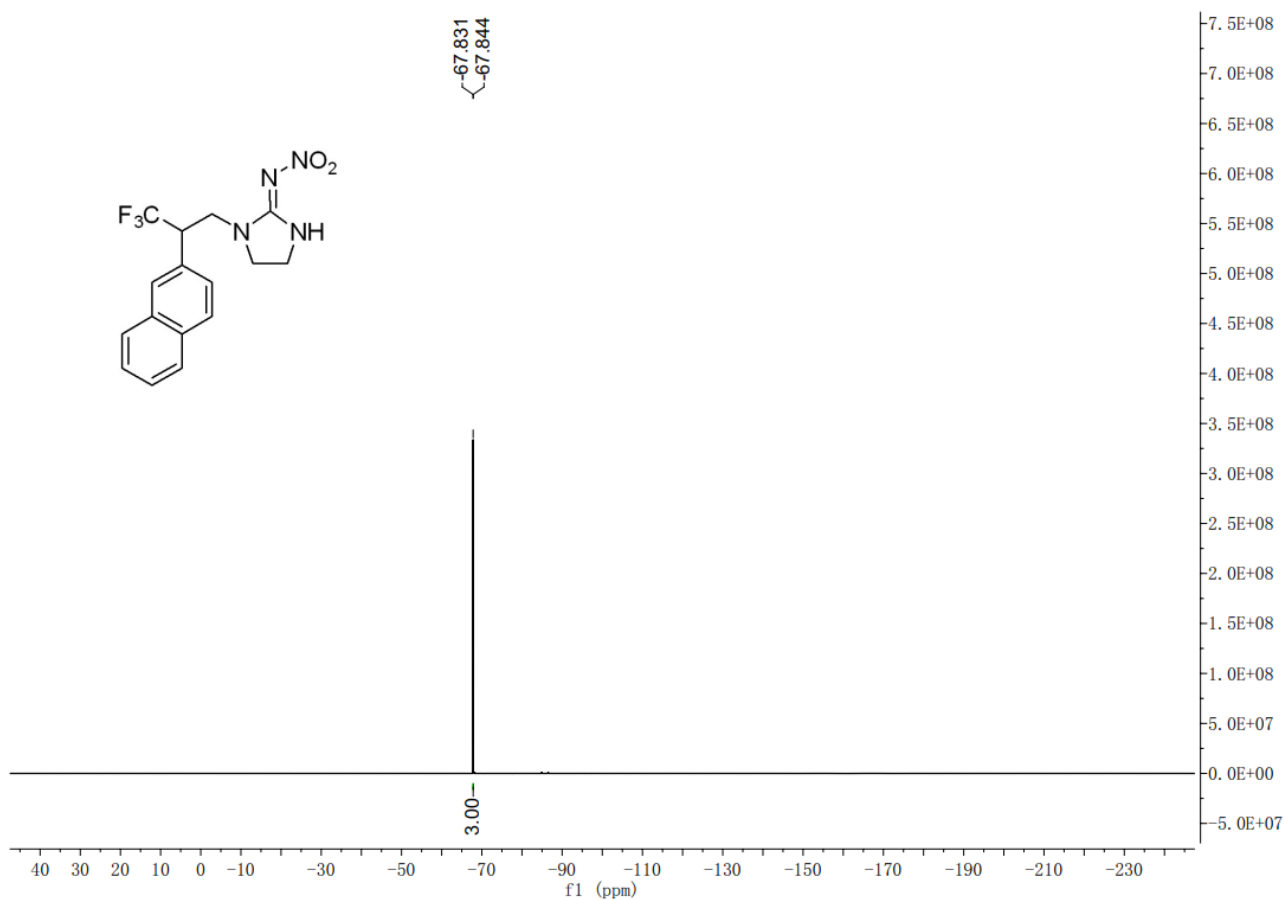
¹H NMR spectrum of 3ra (400 MHz, CDCl₃)



¹³C NMR spectrum of 3ra (100 MHz, CDCl₃)



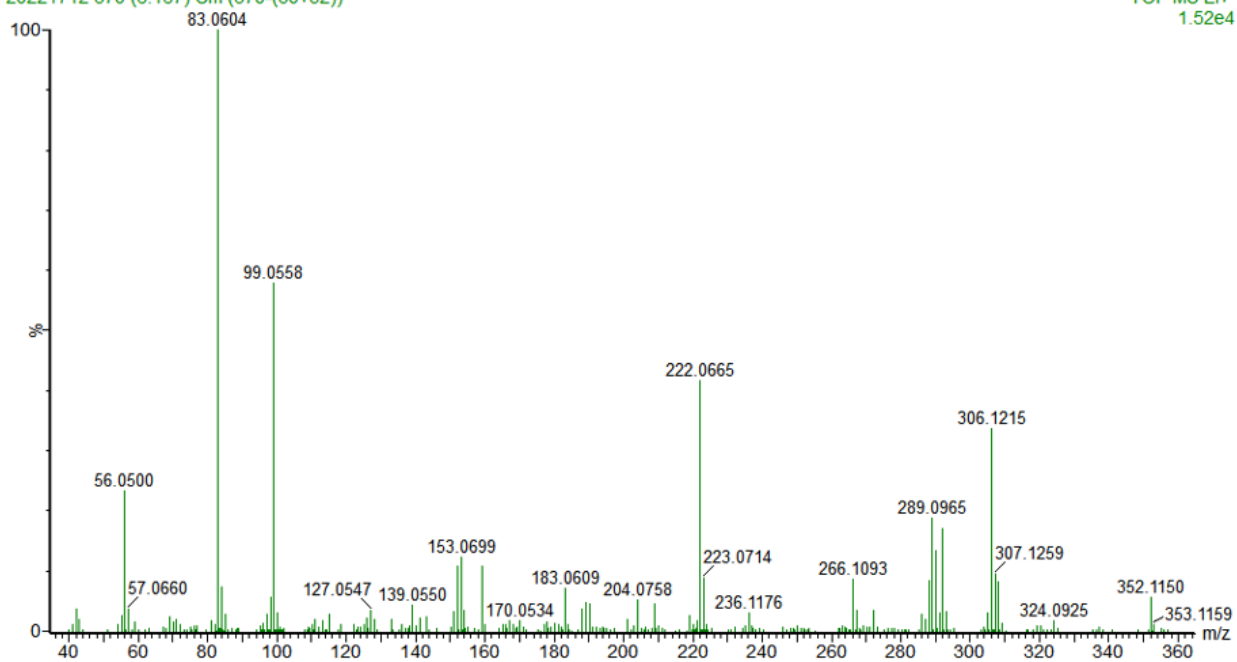
^{19}F NMR spectrum of 3ra (564 MHz, CDCl_3)



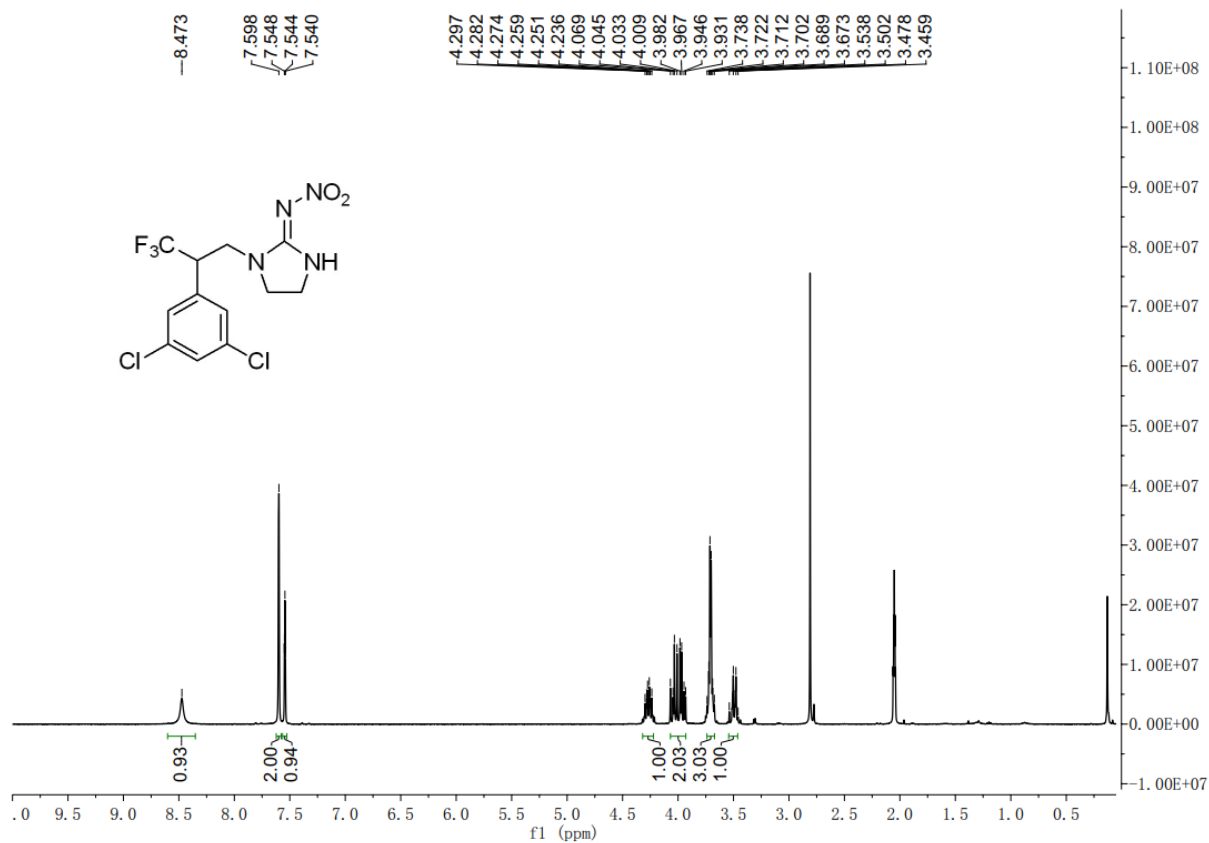
HRMS (EI) spectrum of 3ra

20221712 370 (6.167) Cm (370-(30+52))

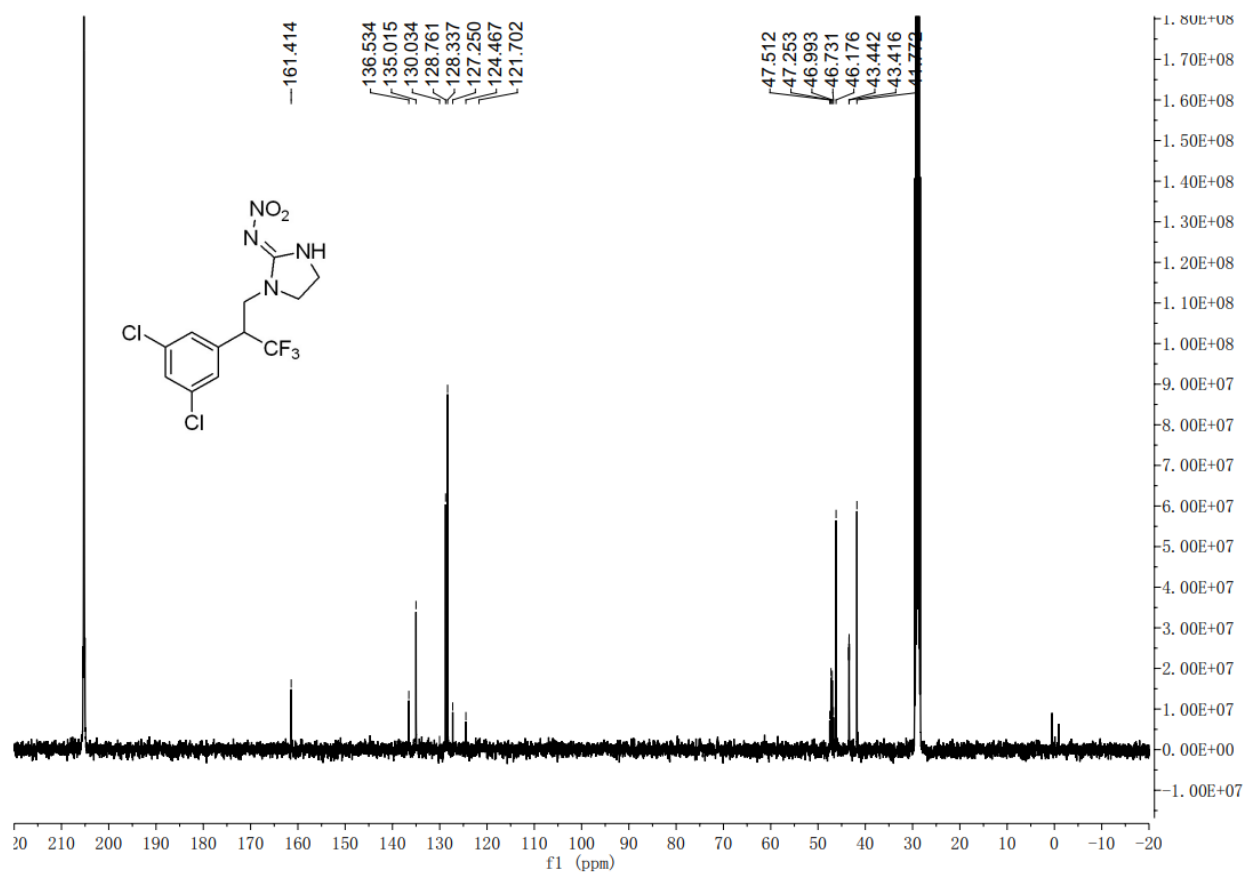
TOF MS EI+
1.52e4



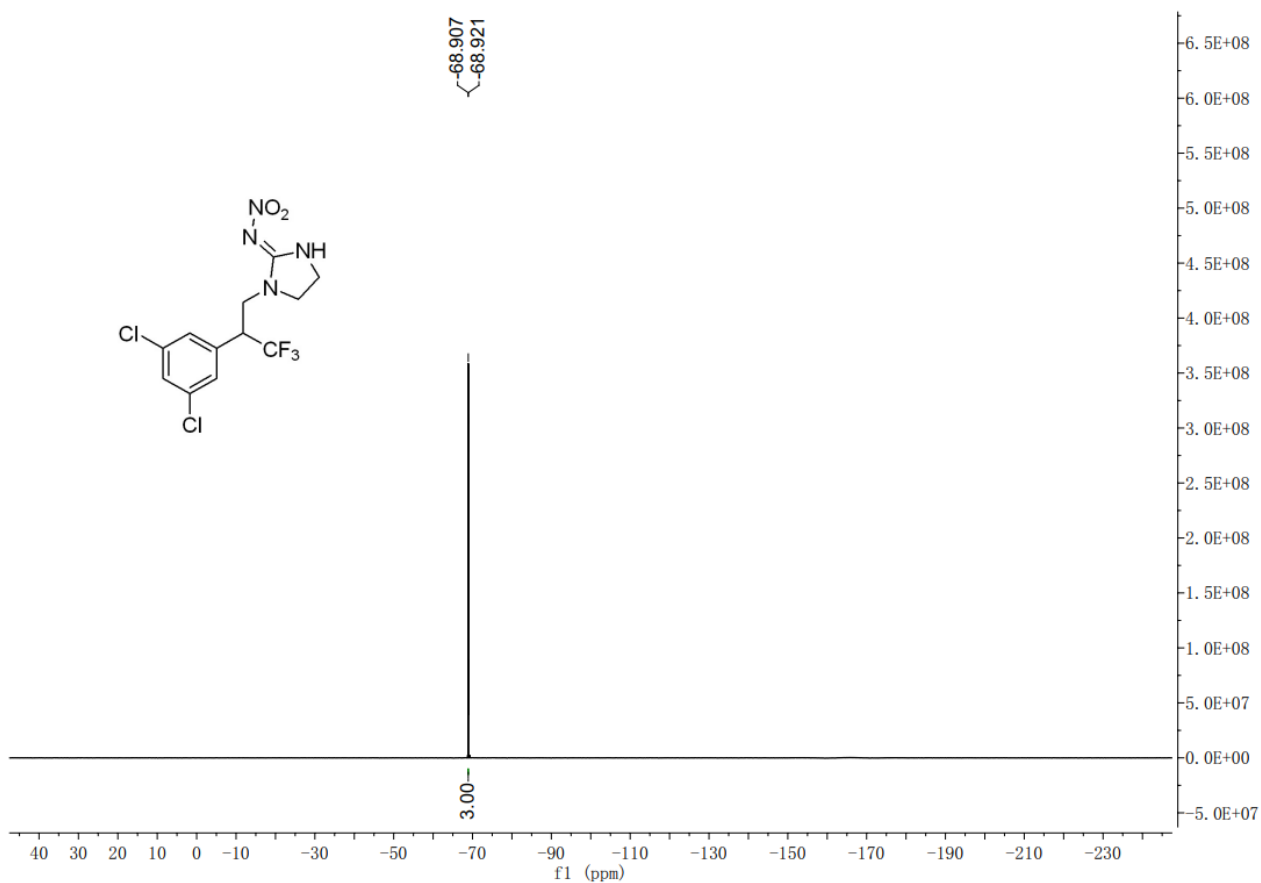
¹H NMR spectrum of 3sa (400 MHz, acetone-*d*₆)



¹³C NMR spectrum of 3sa (100 MHz, acetone-*d*₆)



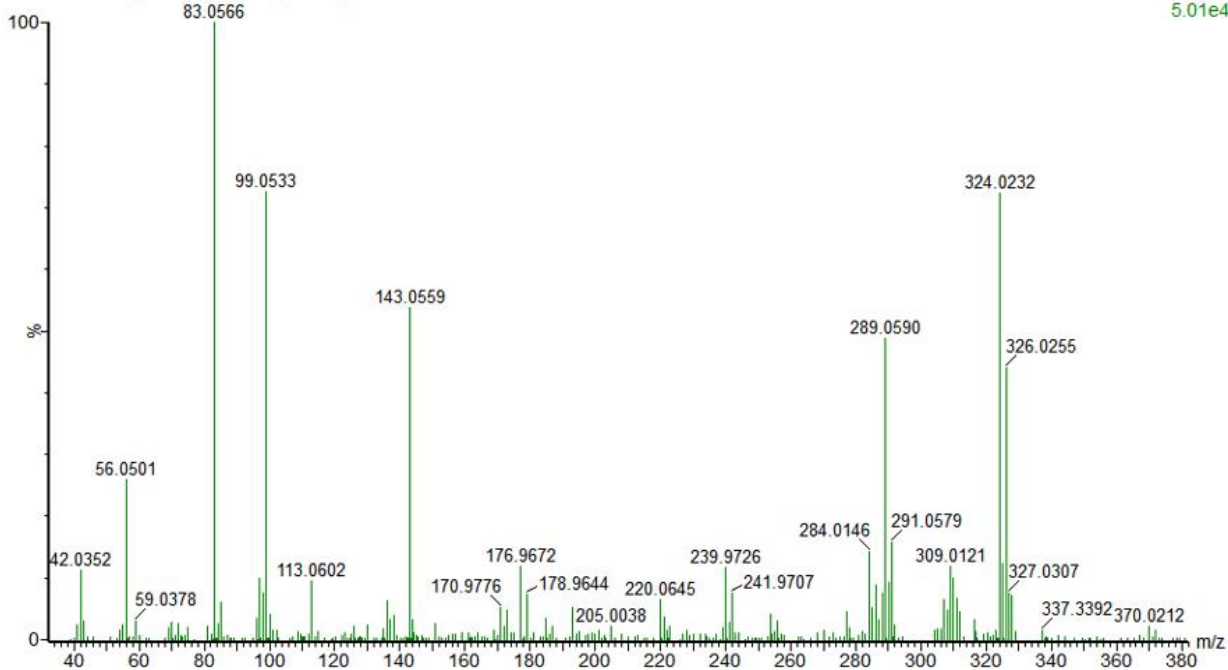
¹⁹F NMR spectrum of 3sa (564 MHz, acetone-*d*₆)



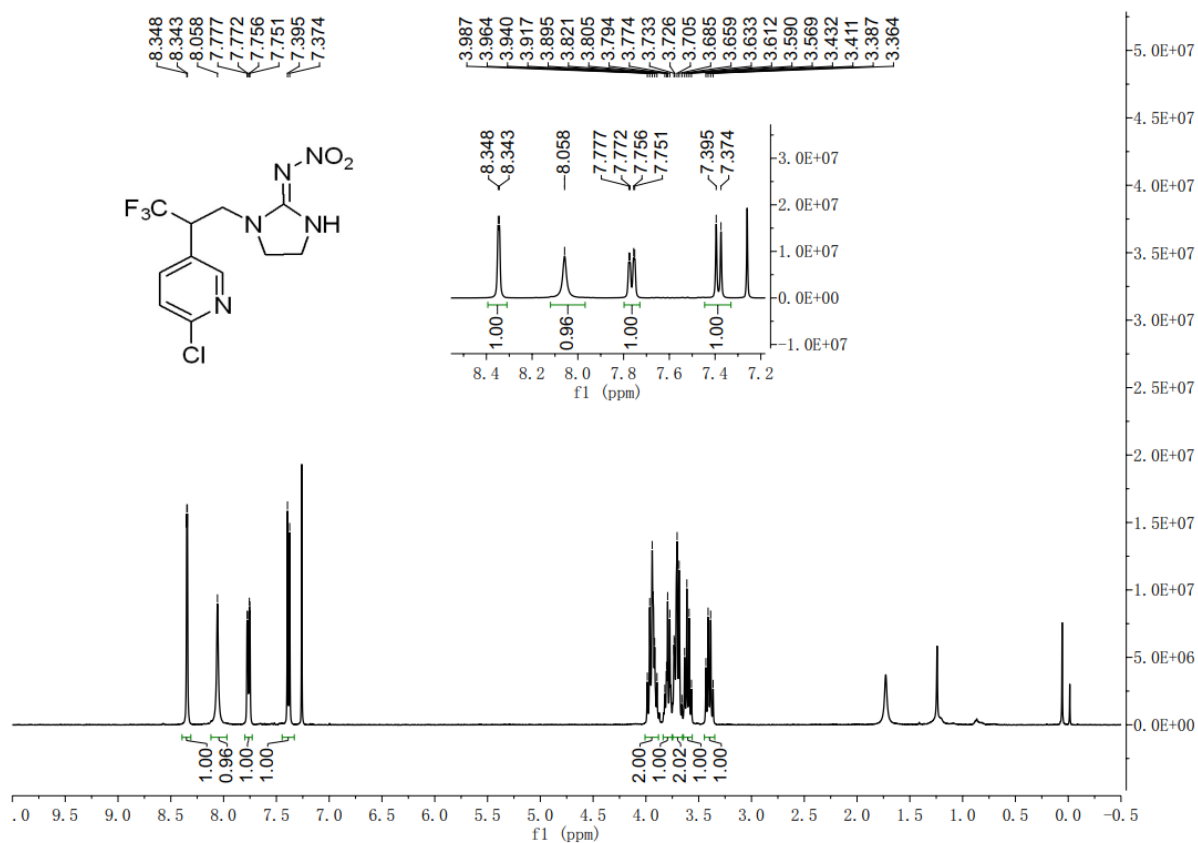
HRMS (EI) spectrum of 3sa

20221713 575 (9.591) Cm (575-(25+81))

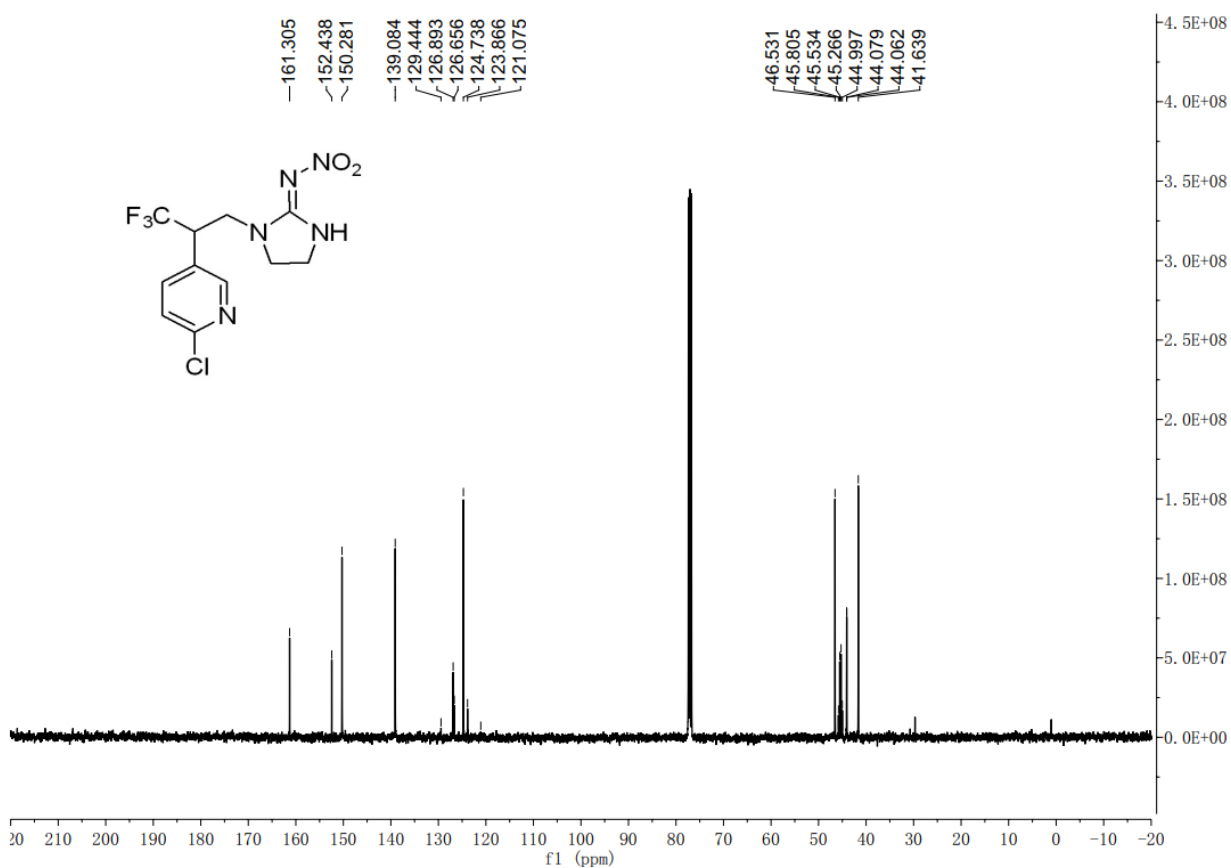
TOF MS EI+
5.01e4



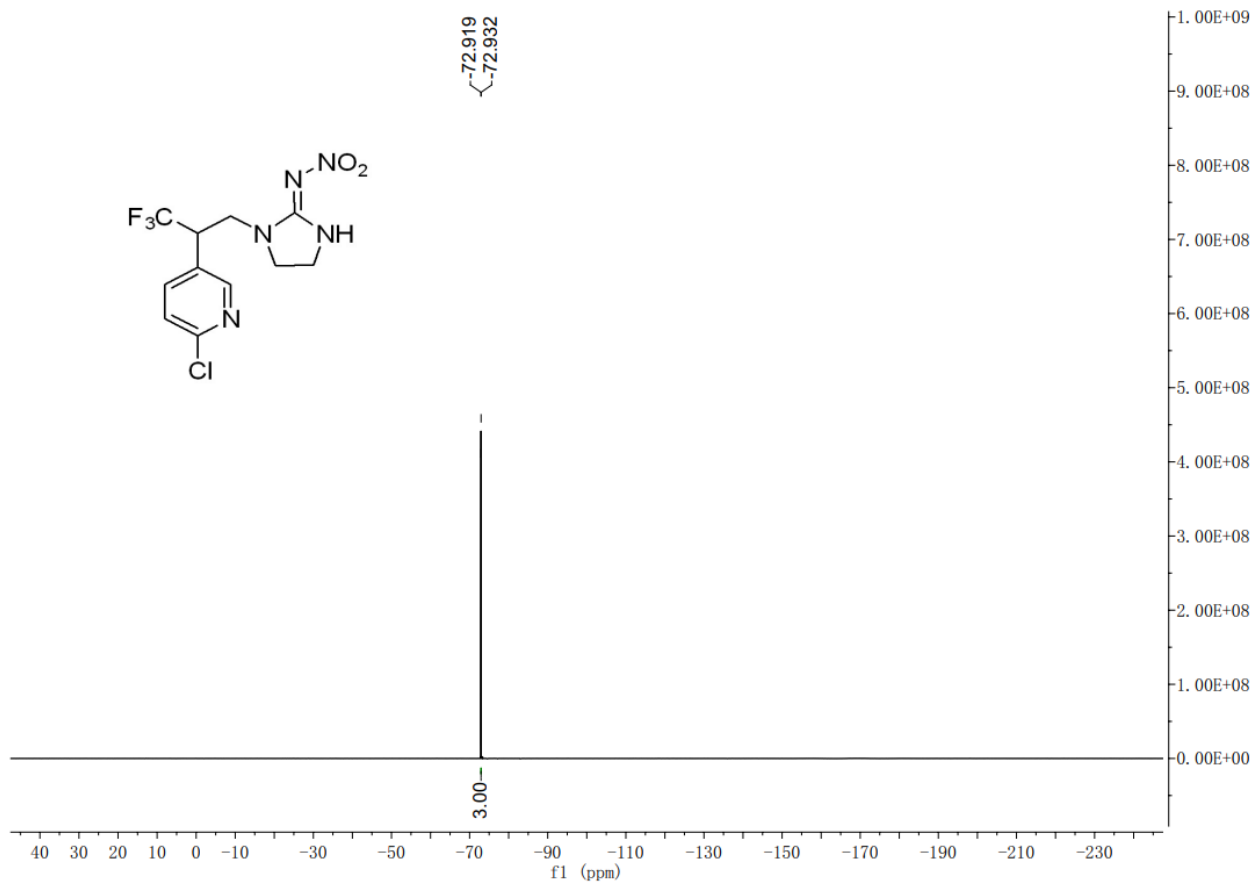
¹H NMR spectrum of 3ta (400 MHz, CDCl₃)



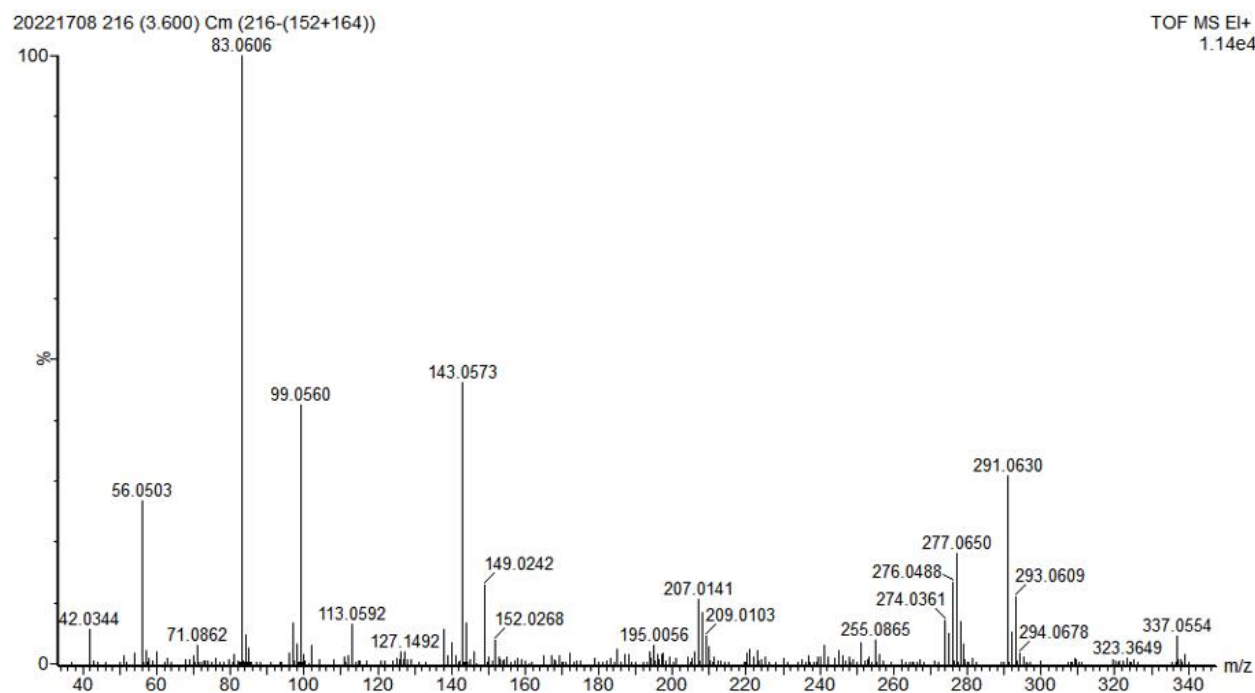
¹³C NMR spectrum of 3ta (100 MHz, CDCl₃)



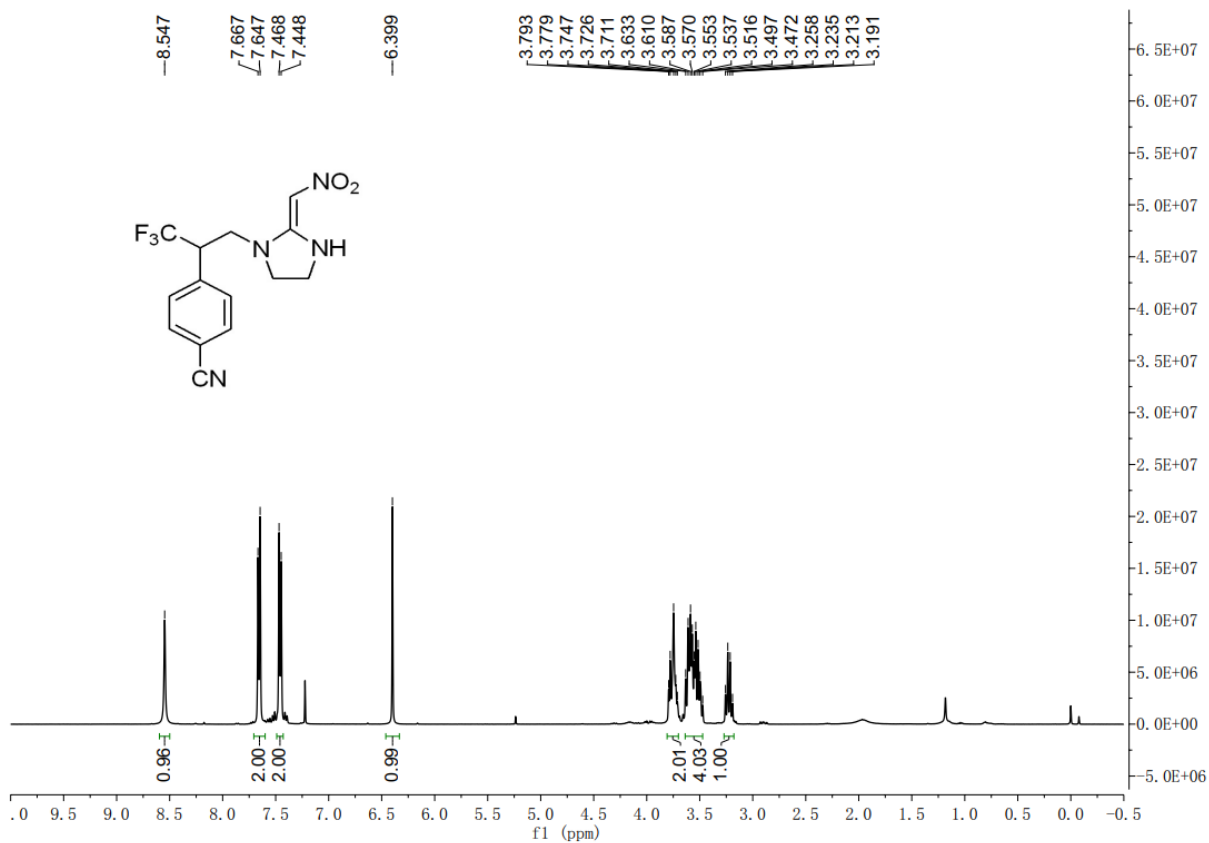
^{19}F NMR spectrum of 3ta (564 MHz, CDCl_3)



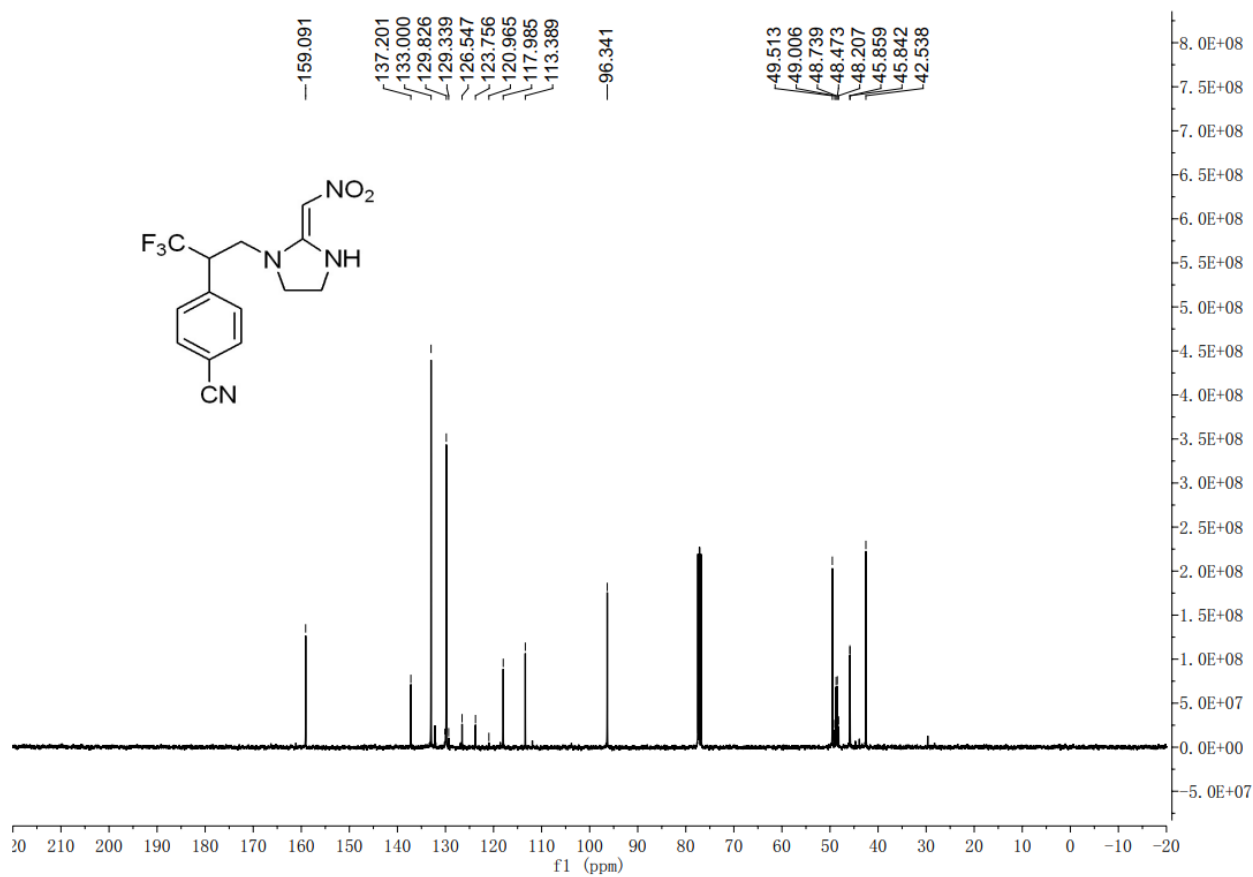
HRMS (EI) spectrum of 3ta



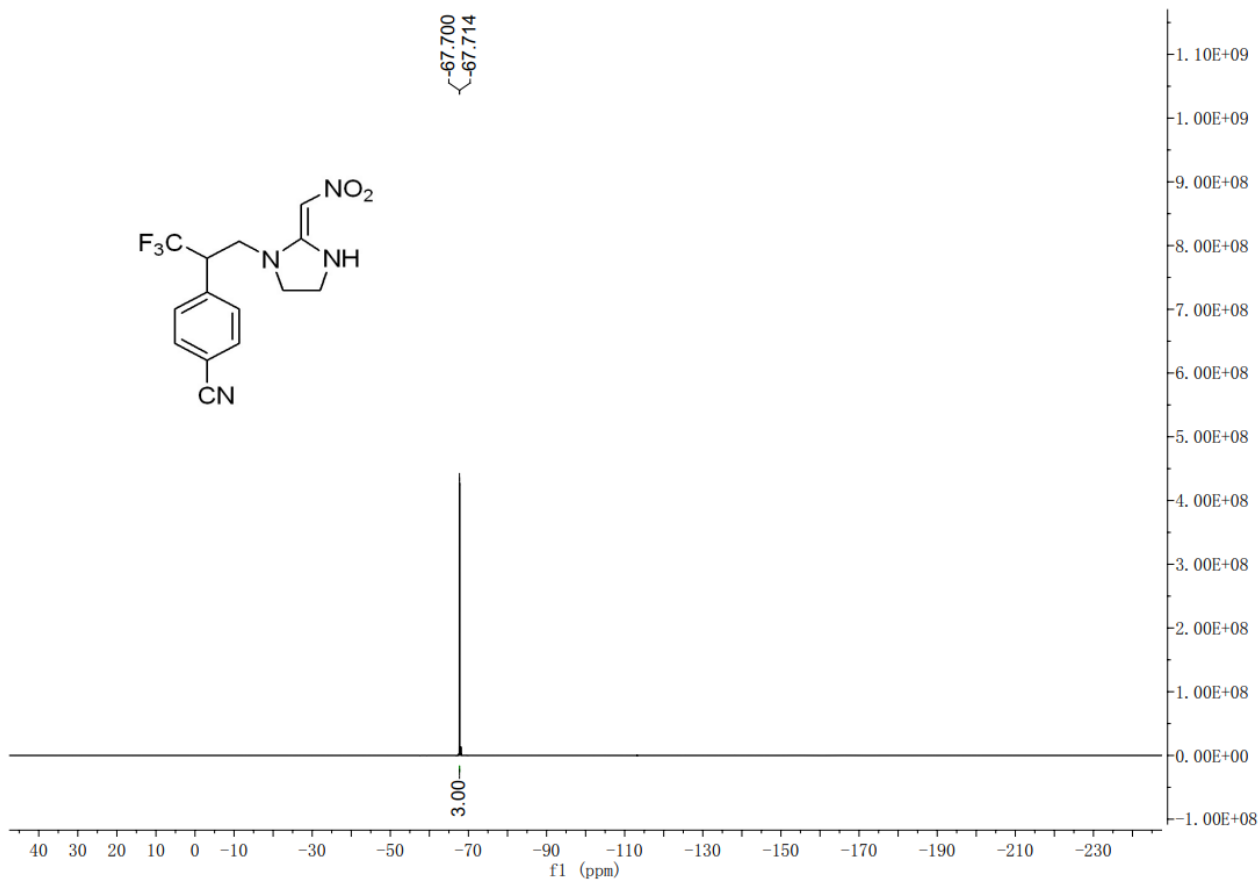
¹H NMR spectrum of 3cb (400 MHz, CDCl₃)



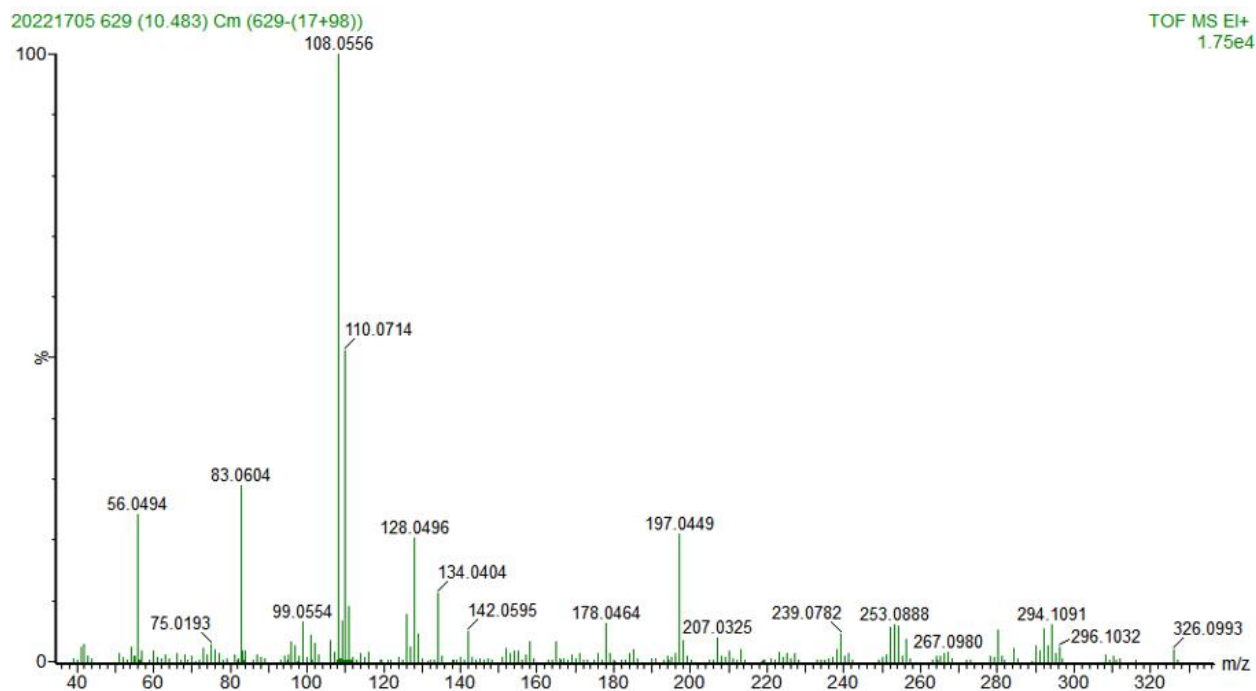
¹³C NMR spectrum of 3cb (100 MHz, CDCl₃)



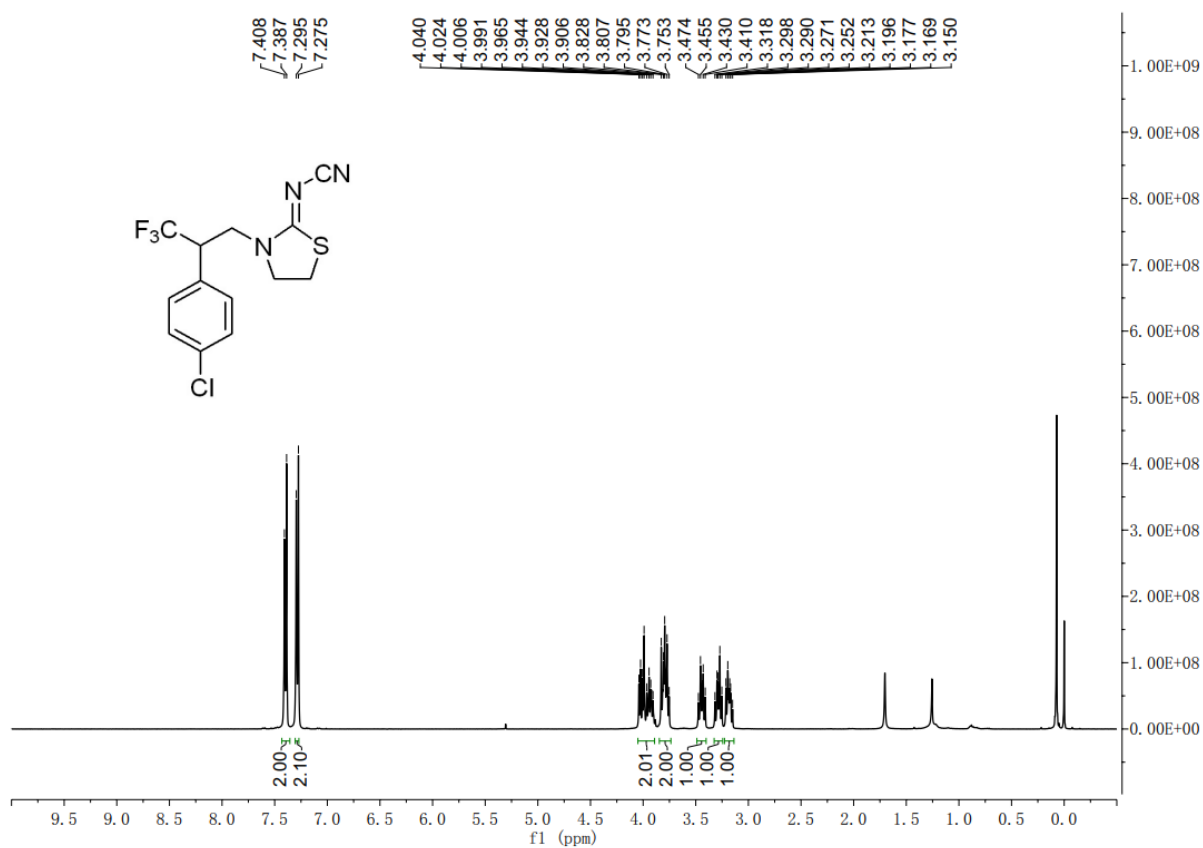
^{19}F NMR spectrum of 3cb (564 MHz, CDCl_3)



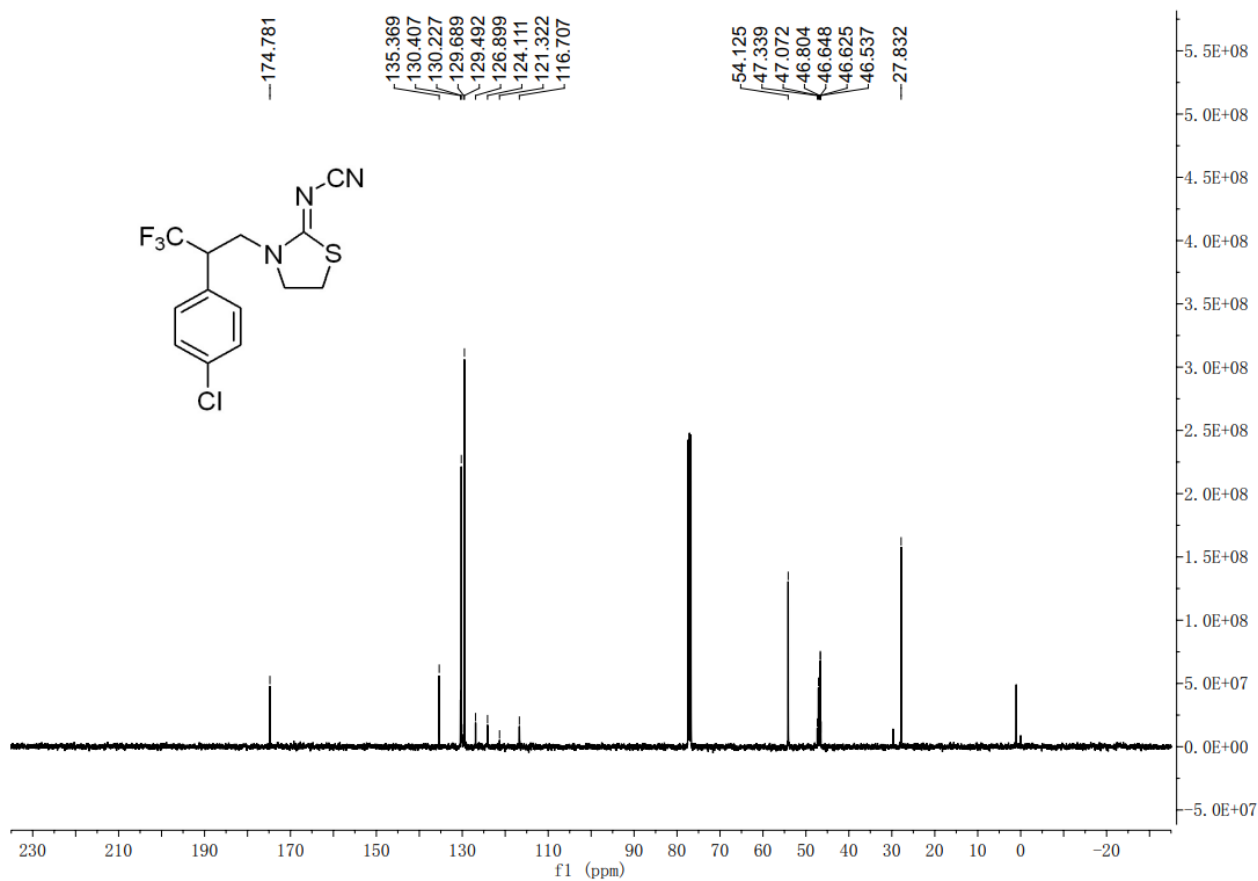
HRMS (EI) spectrum of 3cb



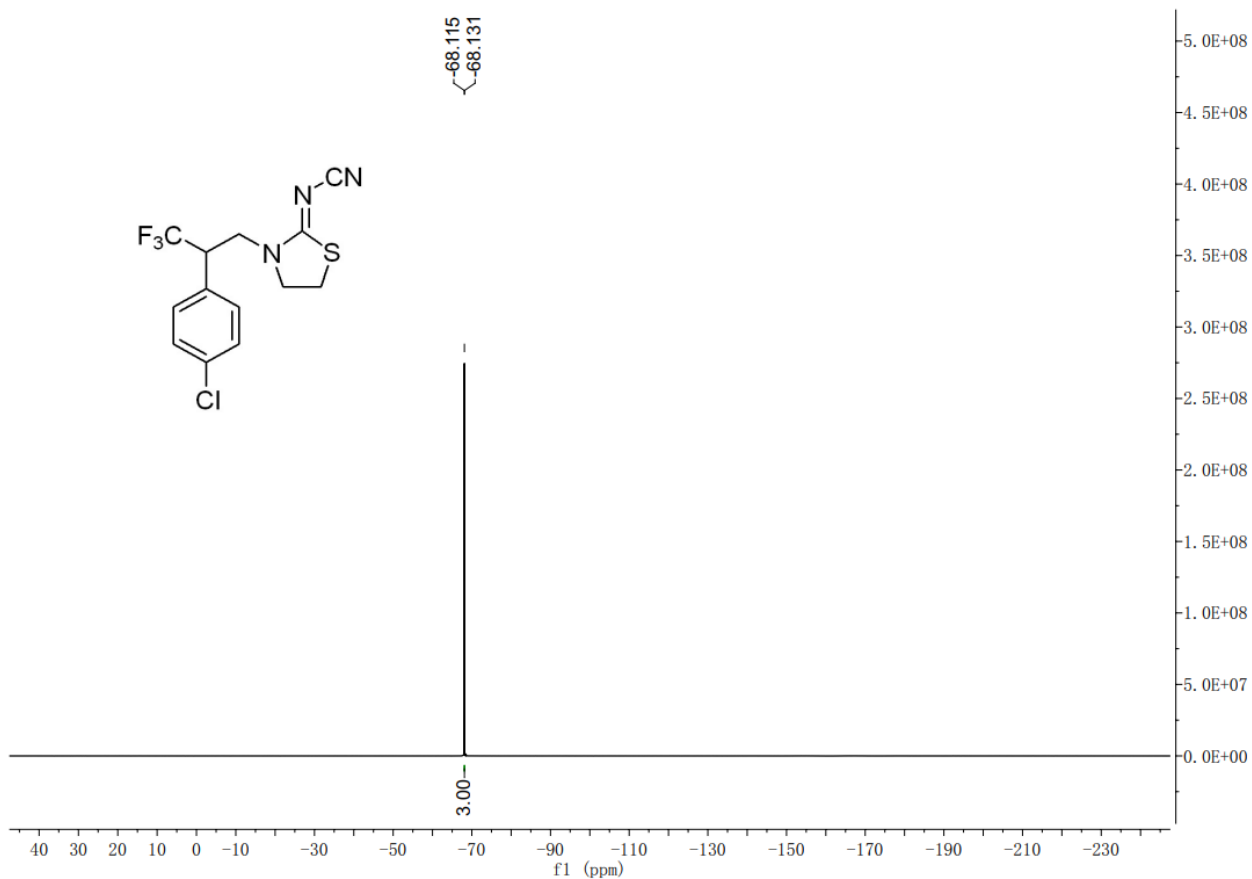
¹H NMR spectrum of 3ec (400 MHz, CDCl₃)



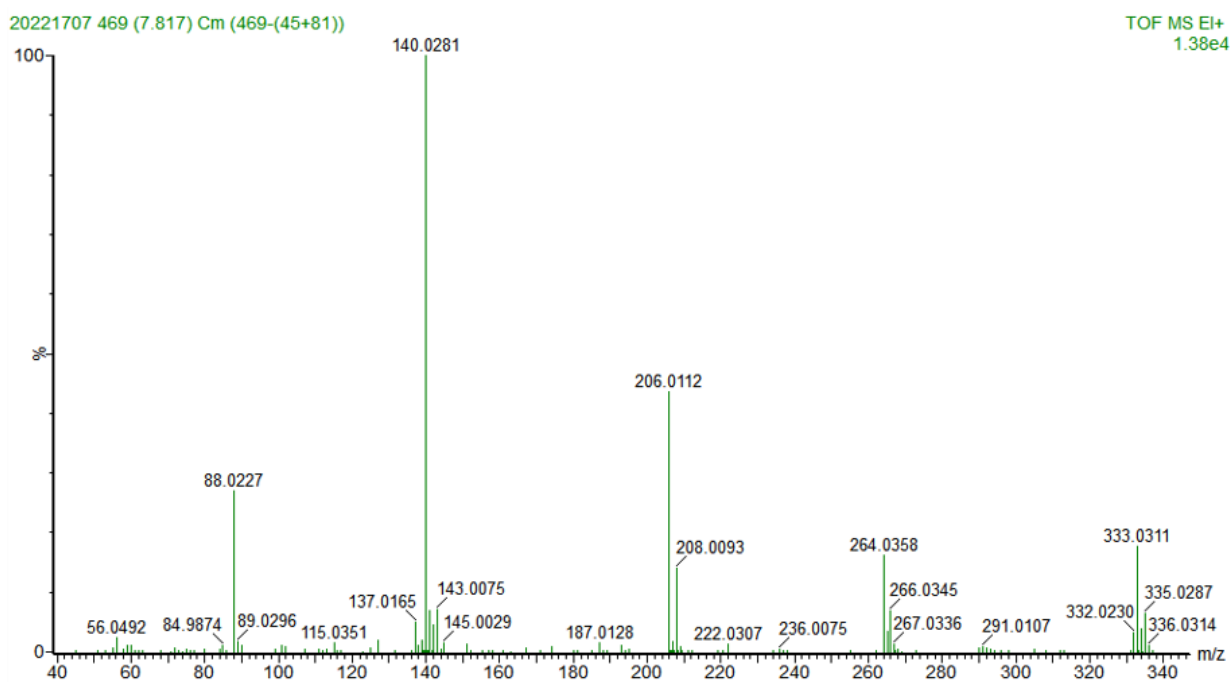
¹³C NMR spectrum of 3ec (100 MHz, CDCl₃)



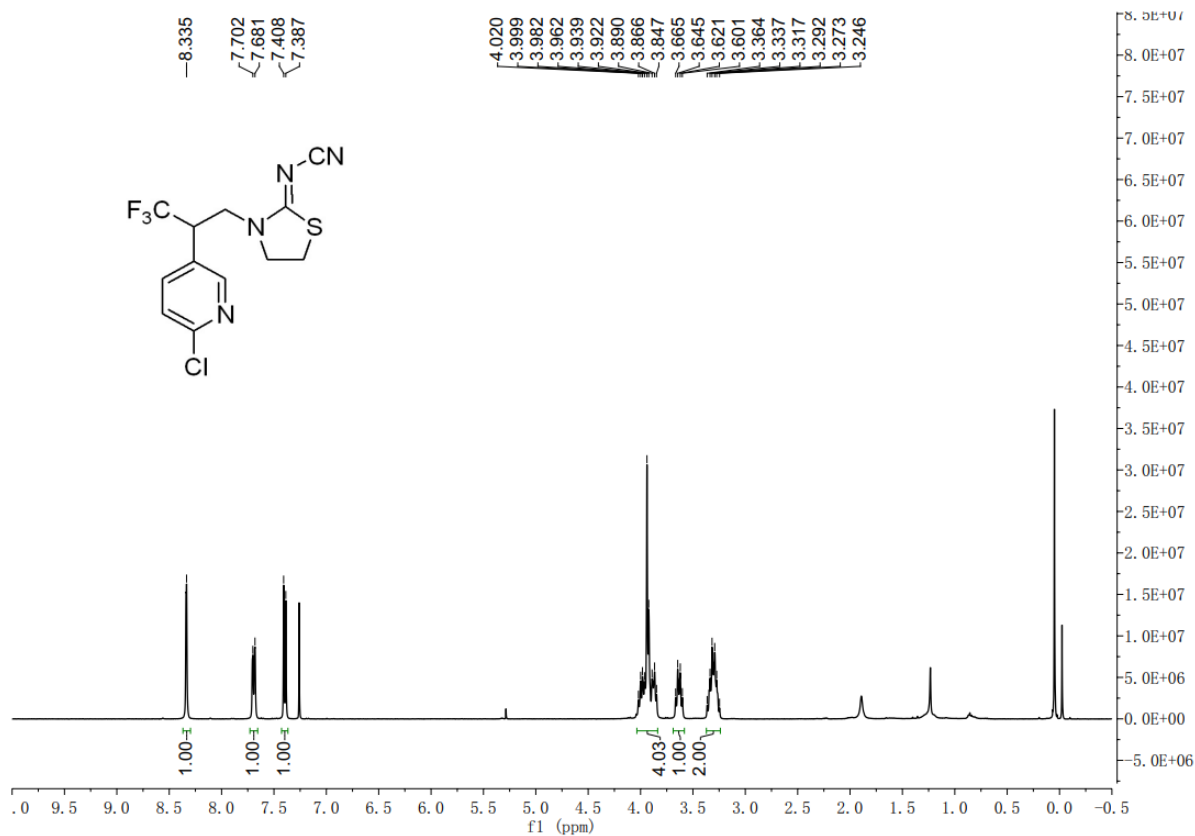
^{19}F NMR spectrum of 3ec (564 MHz, CDCl_3)



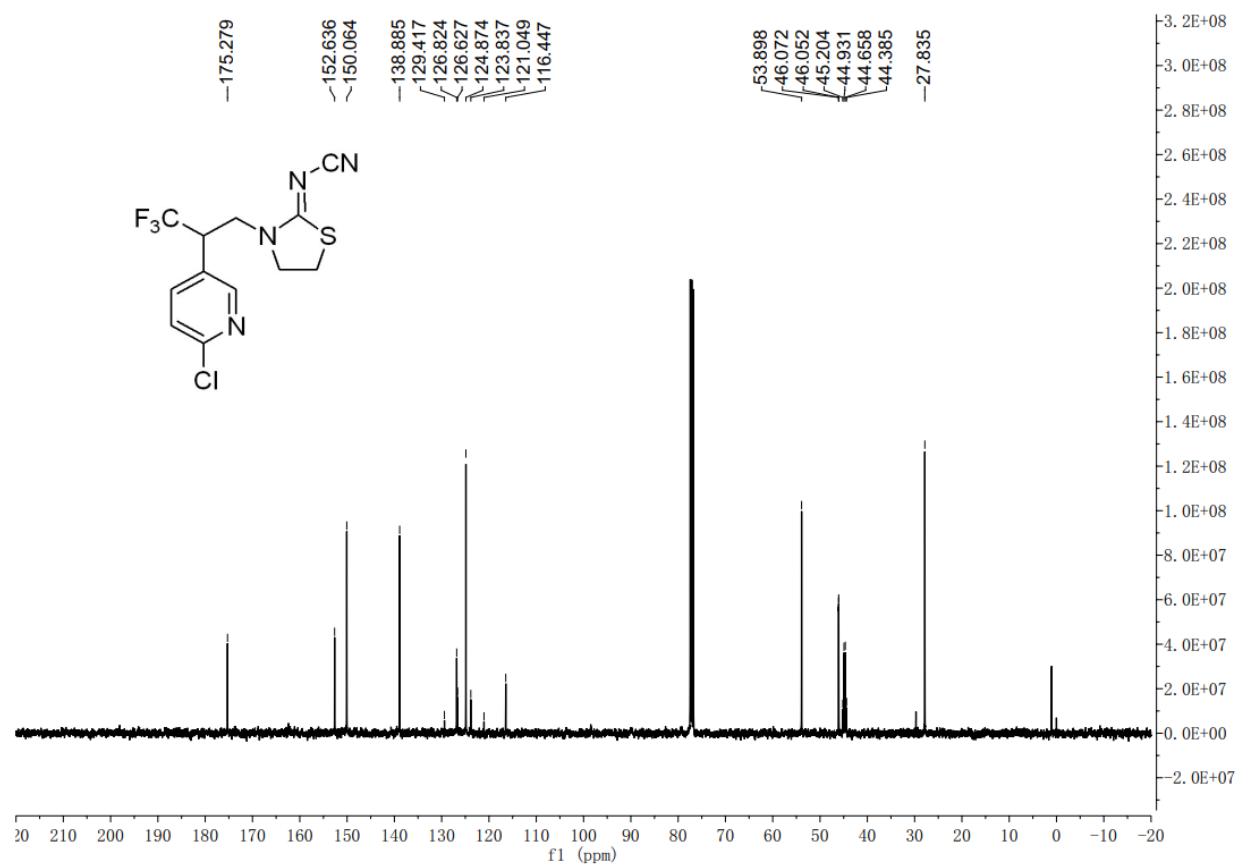
HRMS (EI) spectrum of 3ec



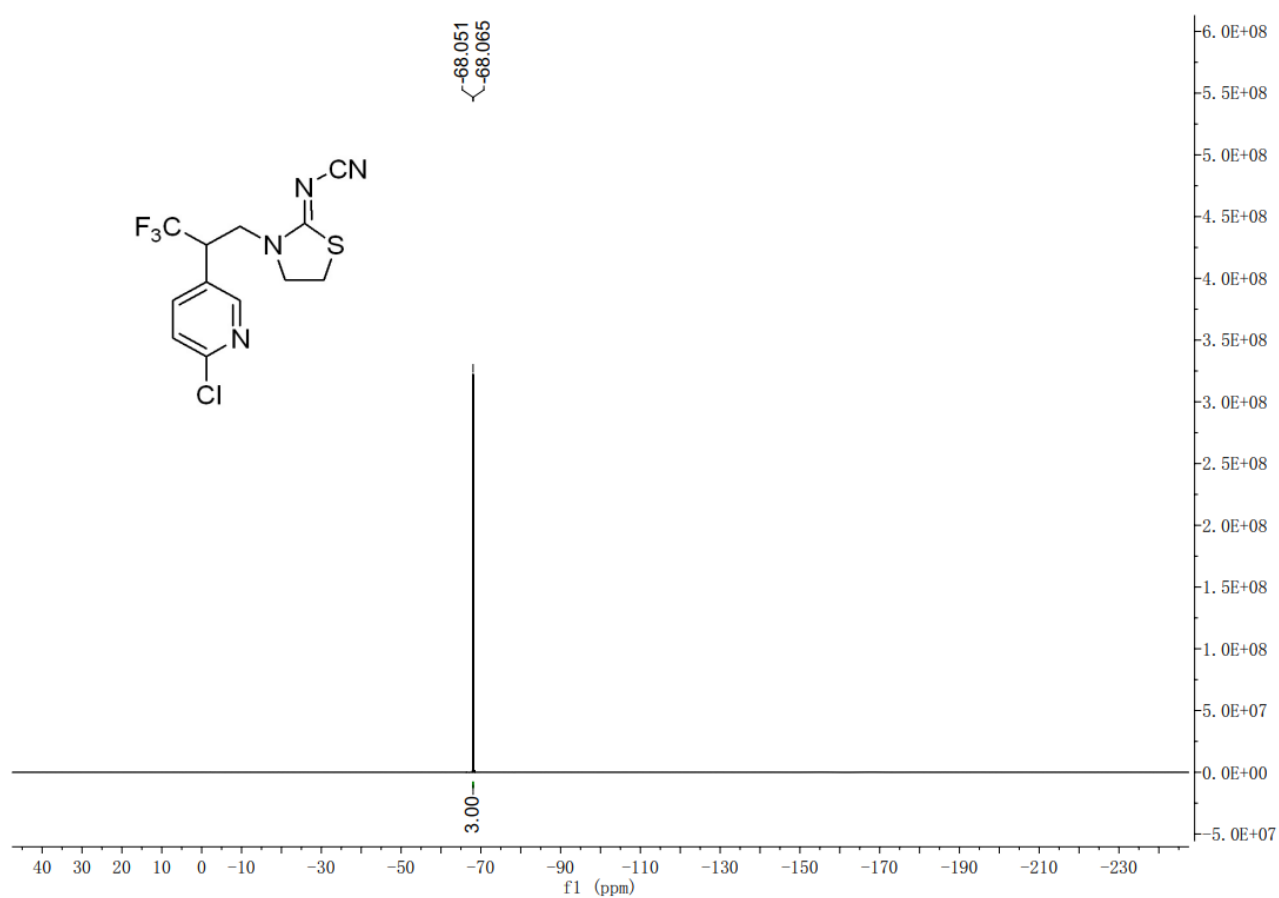
¹H NMR spectrum of 3tc (400 MHz, CDCl₃)



¹³C NMR spectrum of 3tc (100 MHz, CDCl₃)



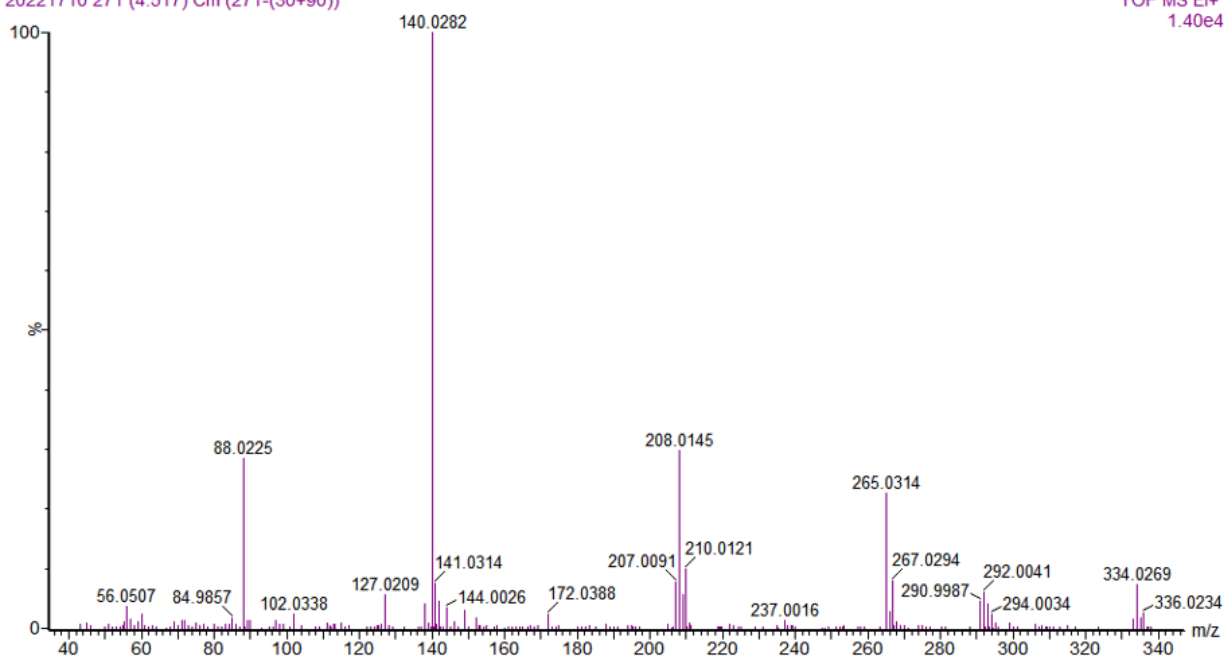
^{19}F NMR spectrum of 3tc (564 MHz, CDCl_3)



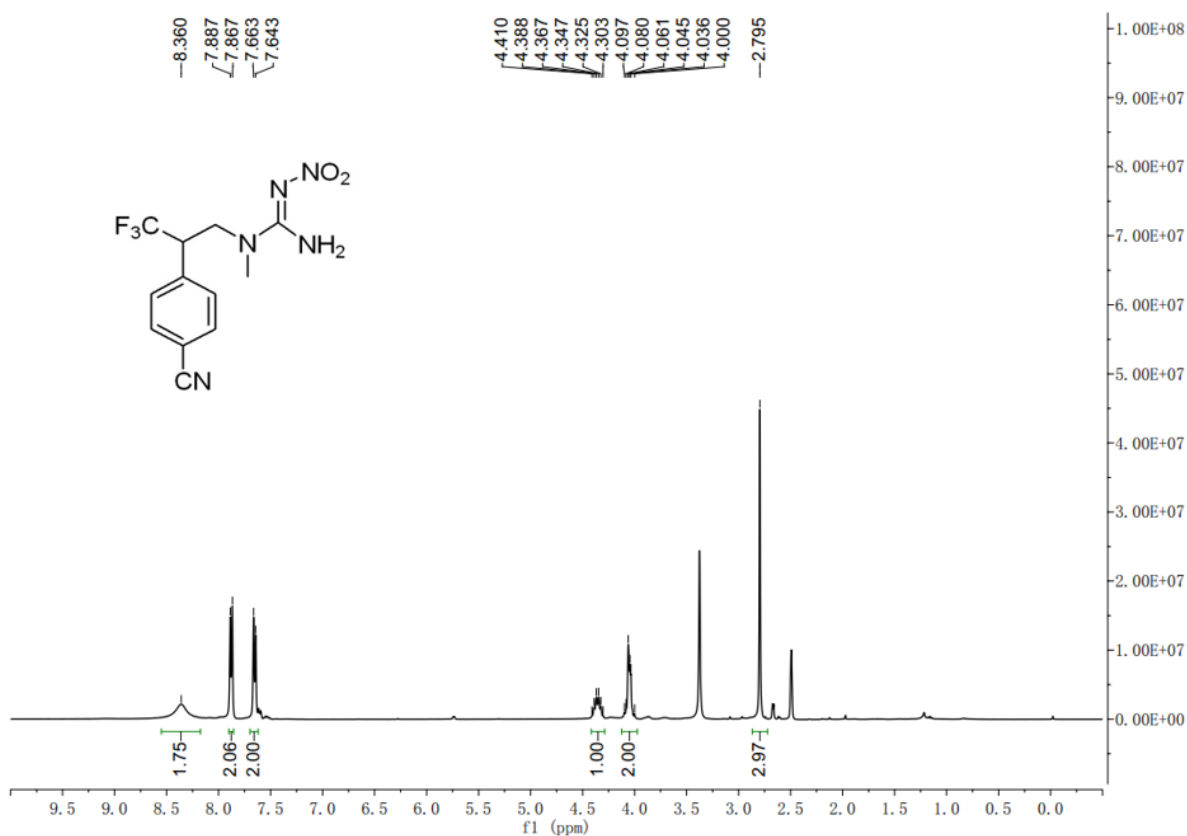
HRMS (EI) spectrum of 3tc

20221710 271 (4.517) Cm (271-(30+90))

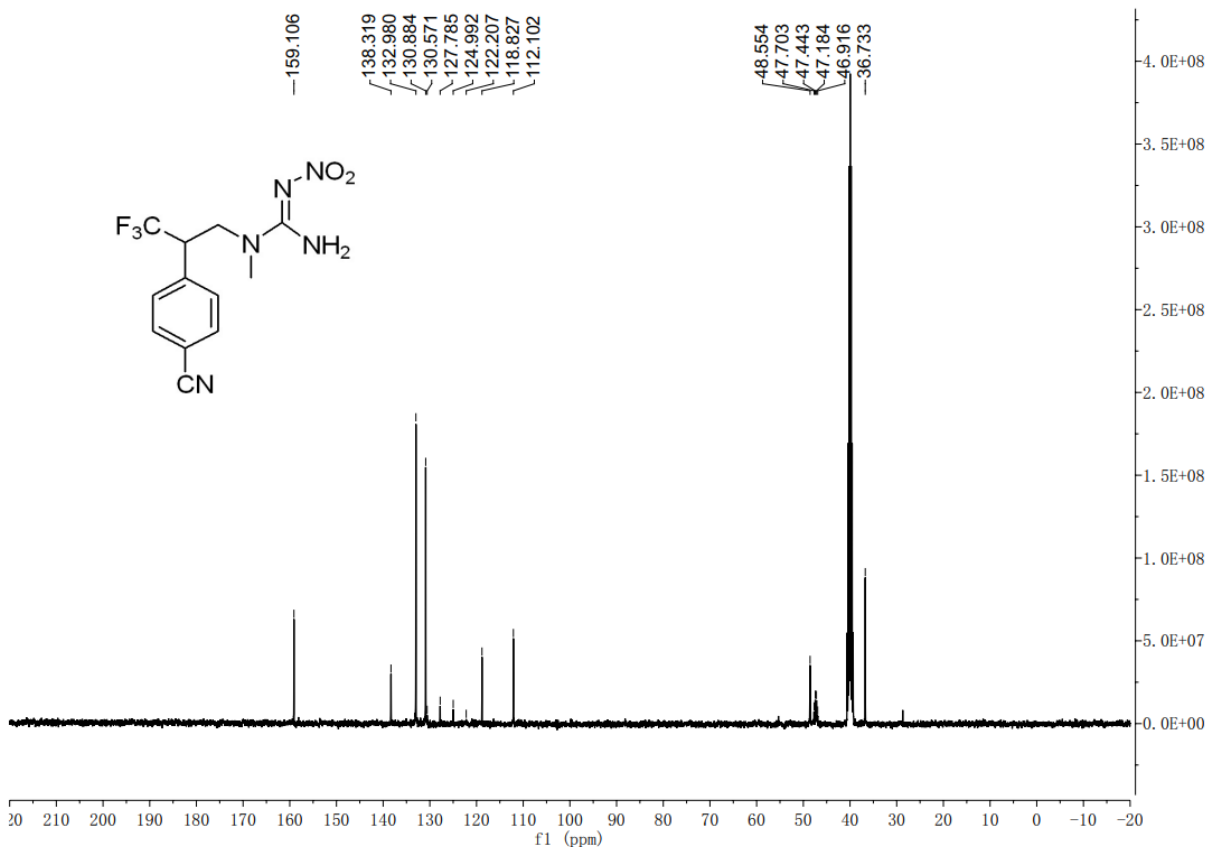
TOF MS EI+
1.40e4



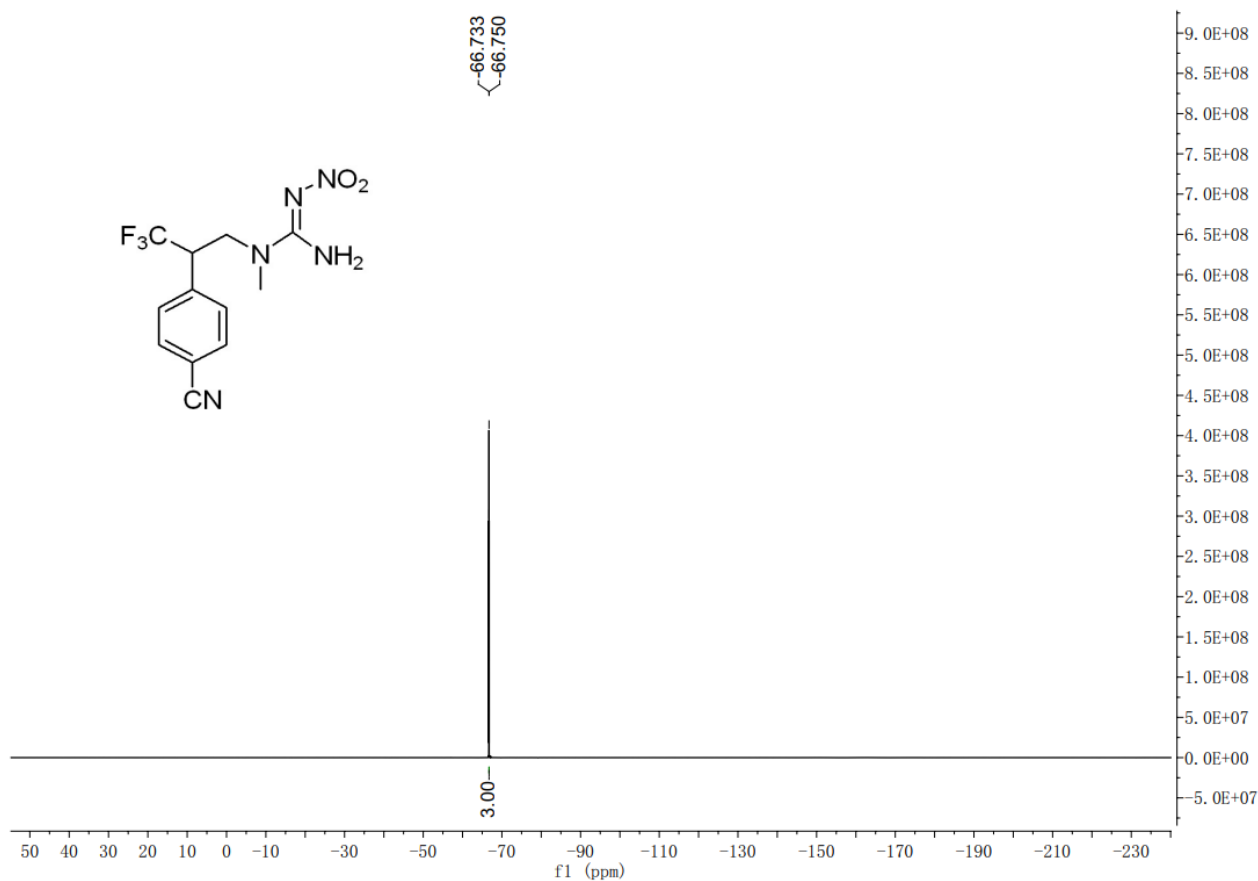
¹H NMR spectrum of 3cd (400 MHz, DMSO-*d*₆)



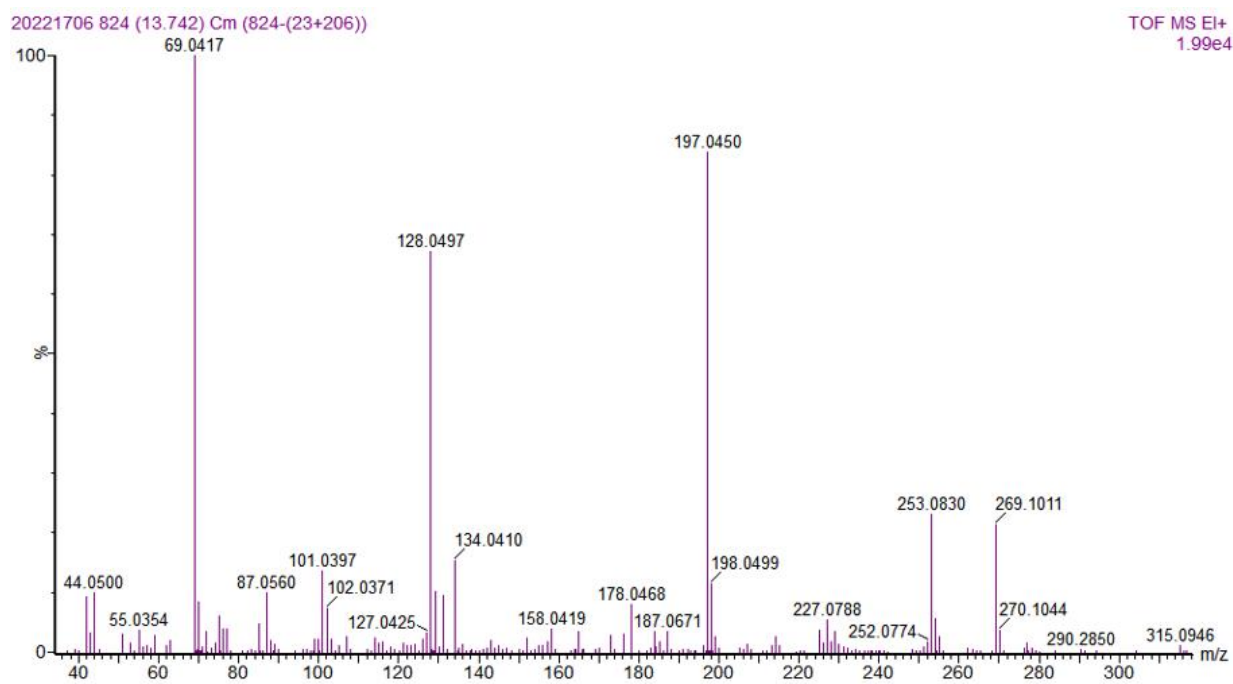
¹³C NMR spectrum of 3cd (100 MHz, DMSO-*d*₆)



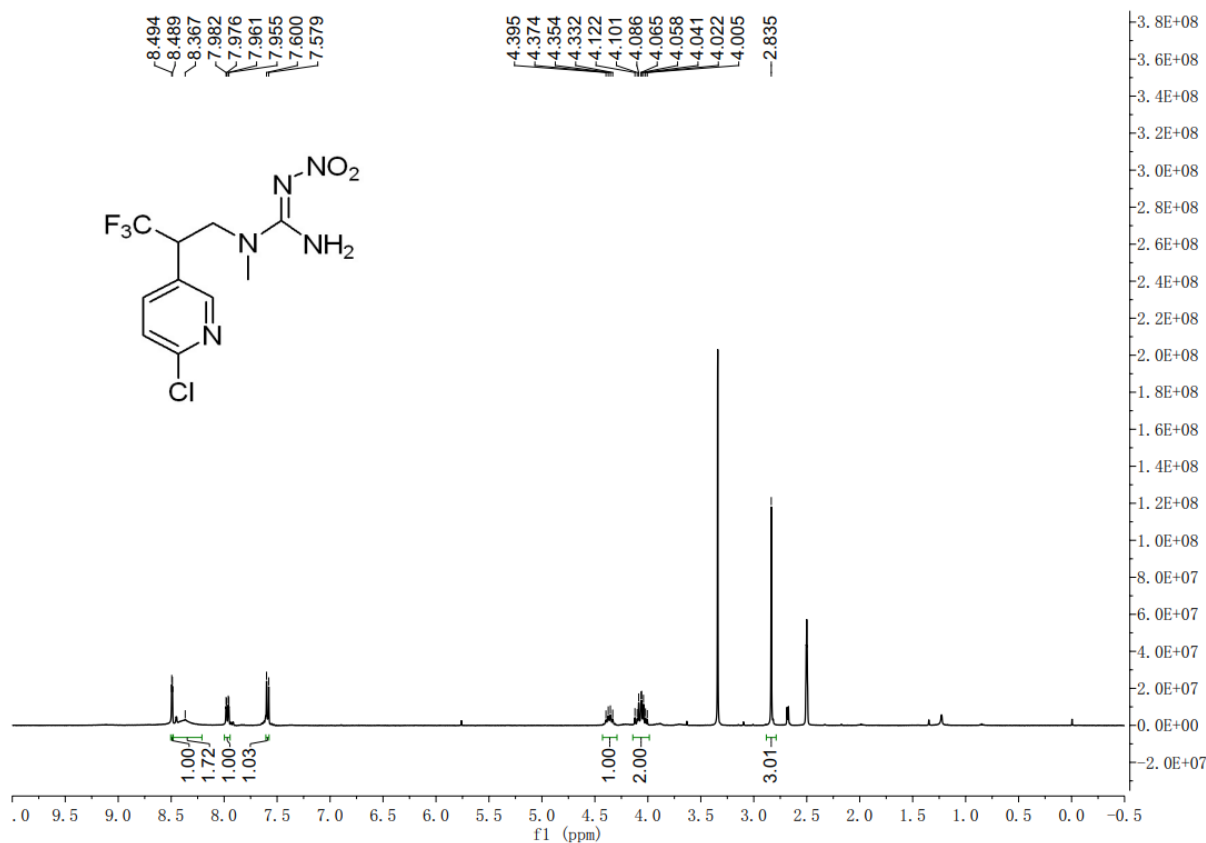
^{19}F NMR spectrum of 3cd (564 MHz, $\text{DMSO}-d_6$)



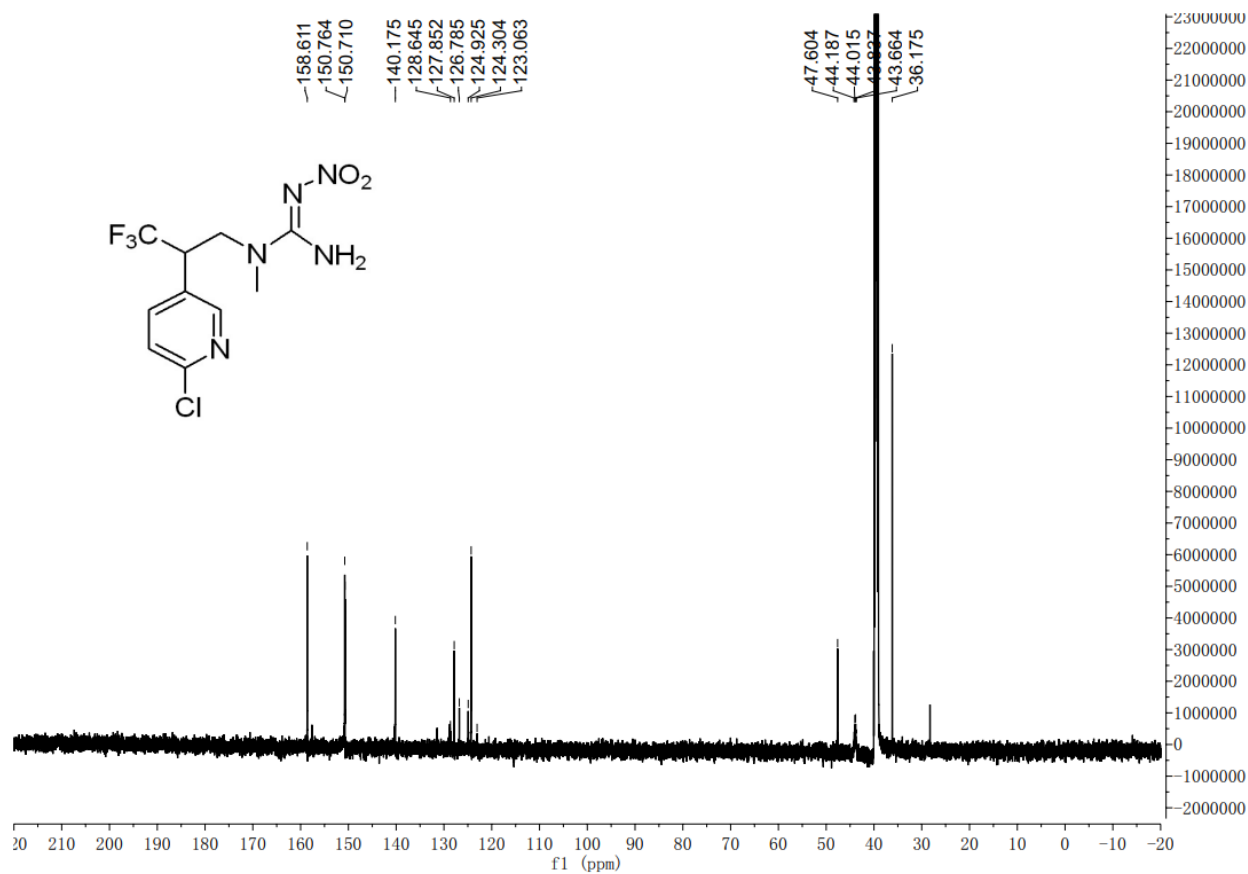
HRMS (EI) spectrum of 3cd



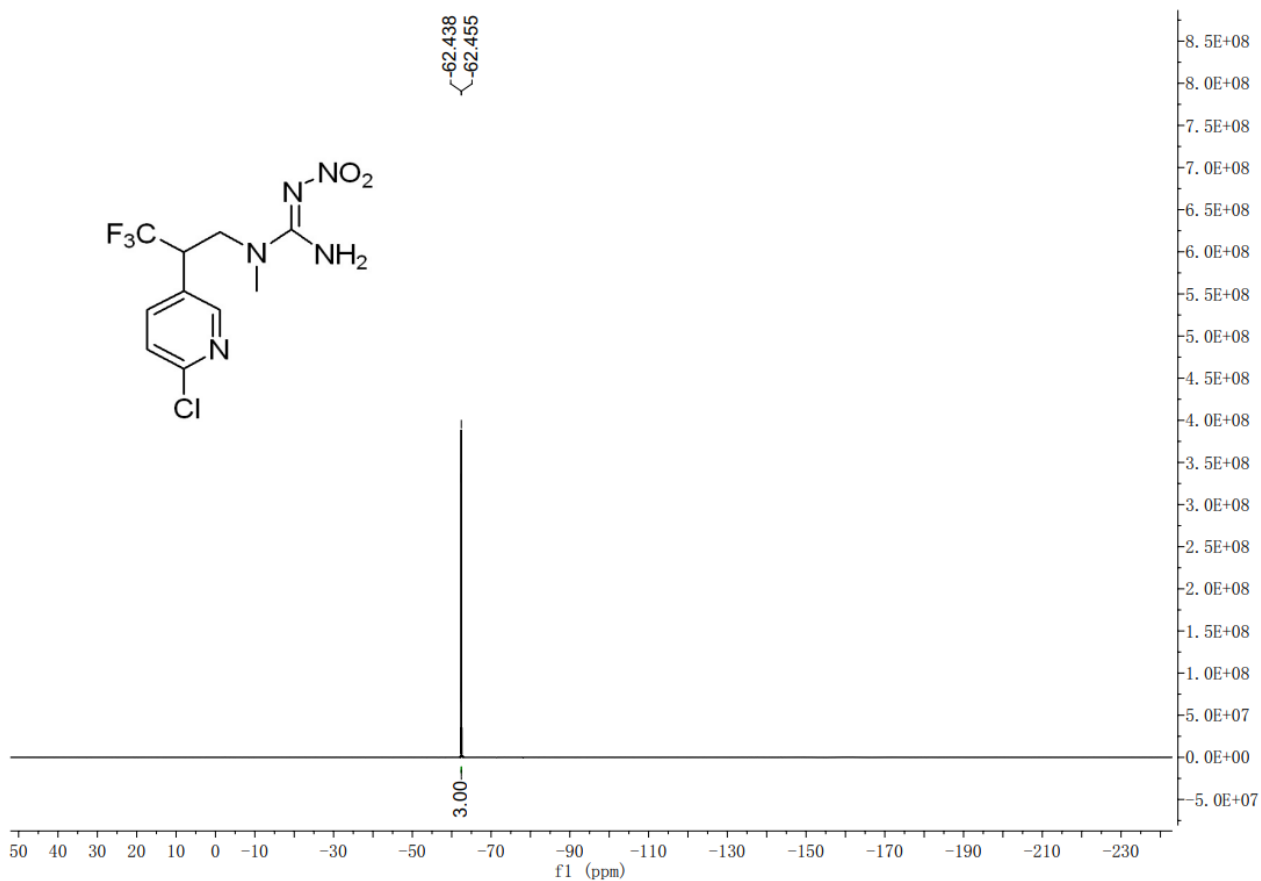
¹H NMR spectrum of 3td (400 MHz, DMSO-*d*₆)



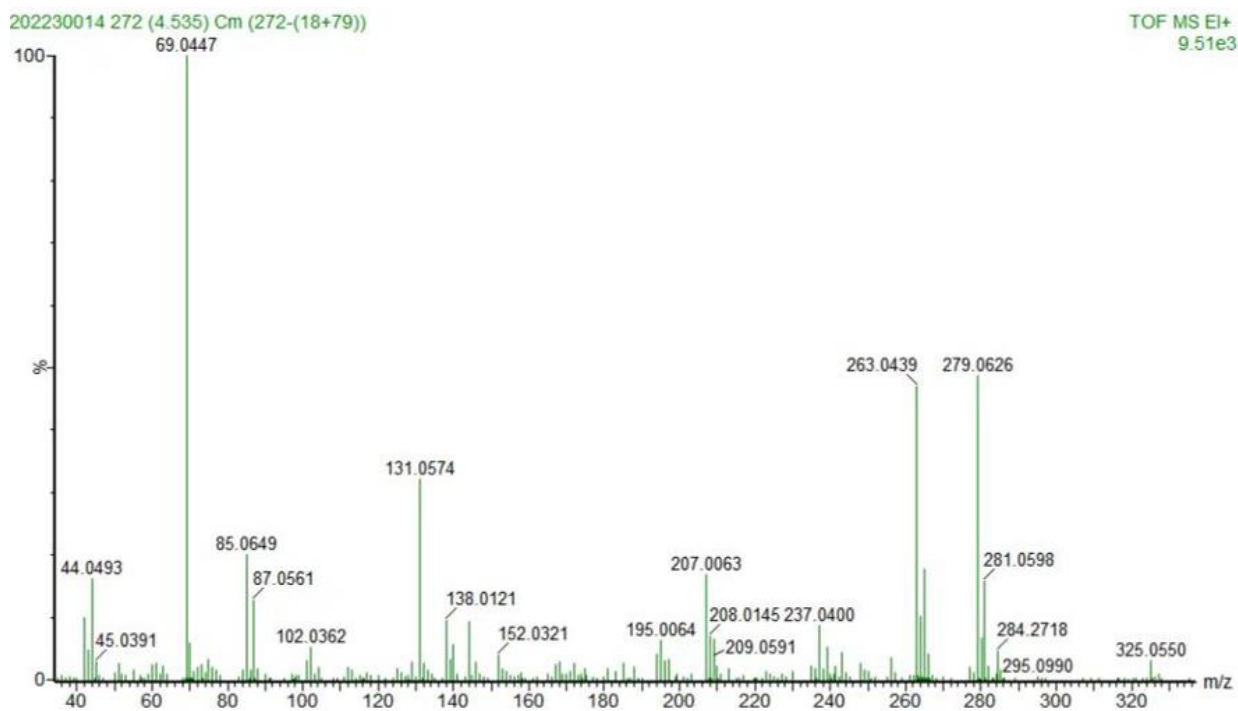
¹³C NMR spectrum of 3td (150 MHz, DMSO-*d*₆)



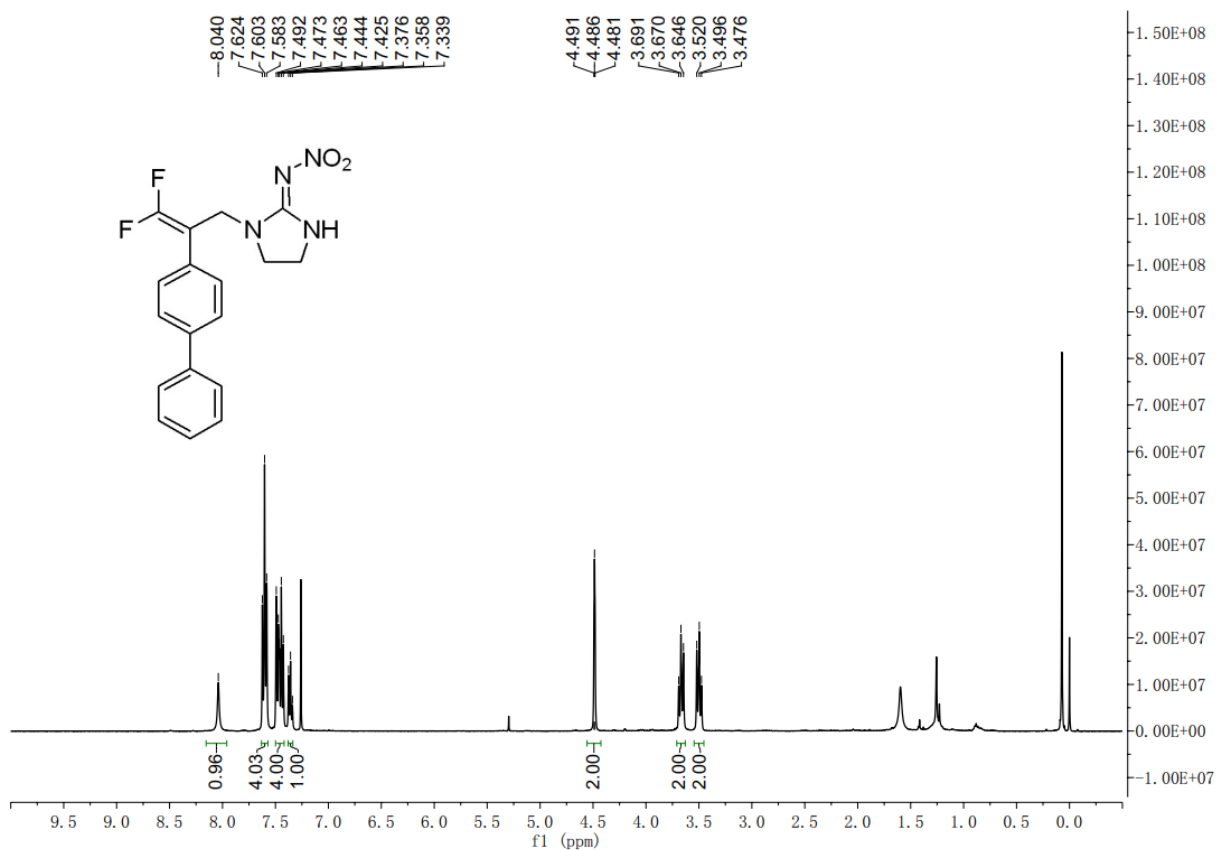
^{19}F NMR spectrum of 3td (564 MHz, $\text{DMSO-}d_6$)



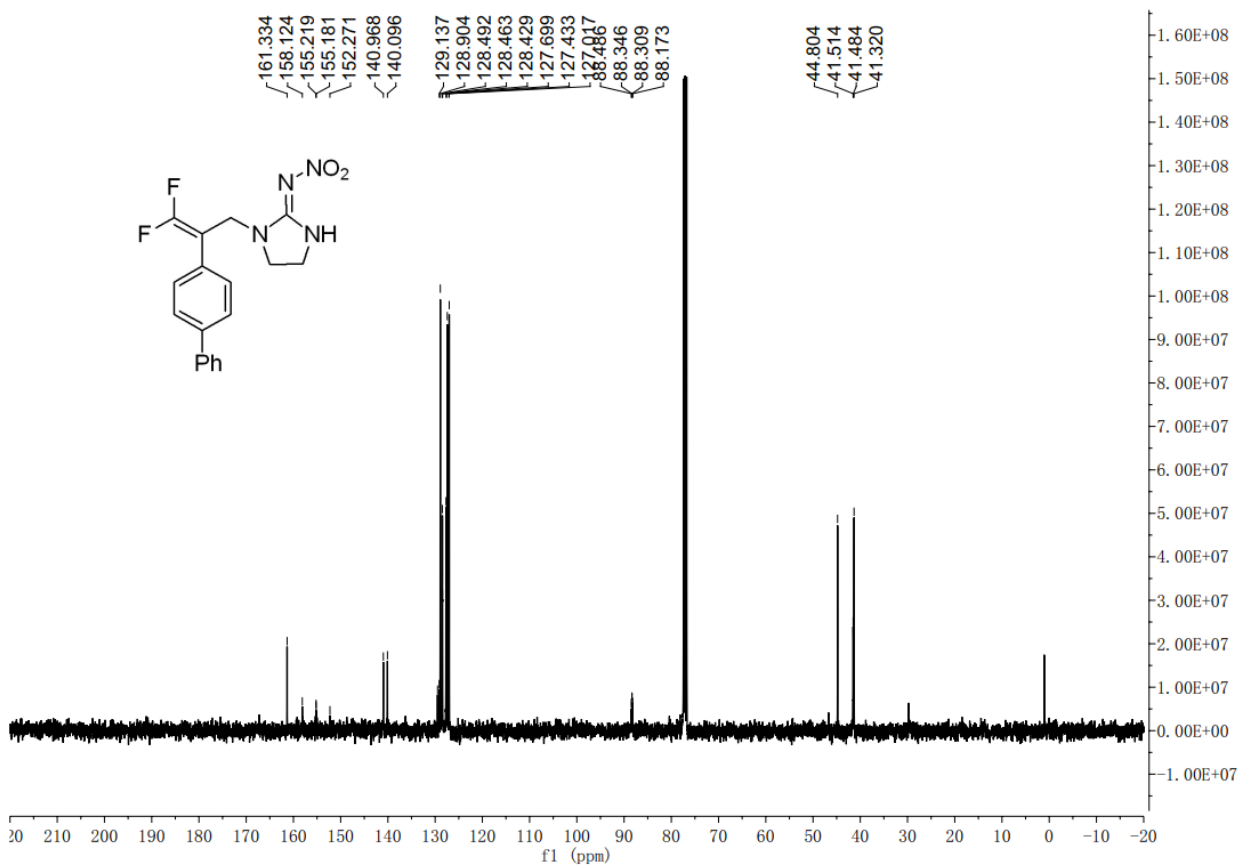
HRMS (EI) spectrum of 3td



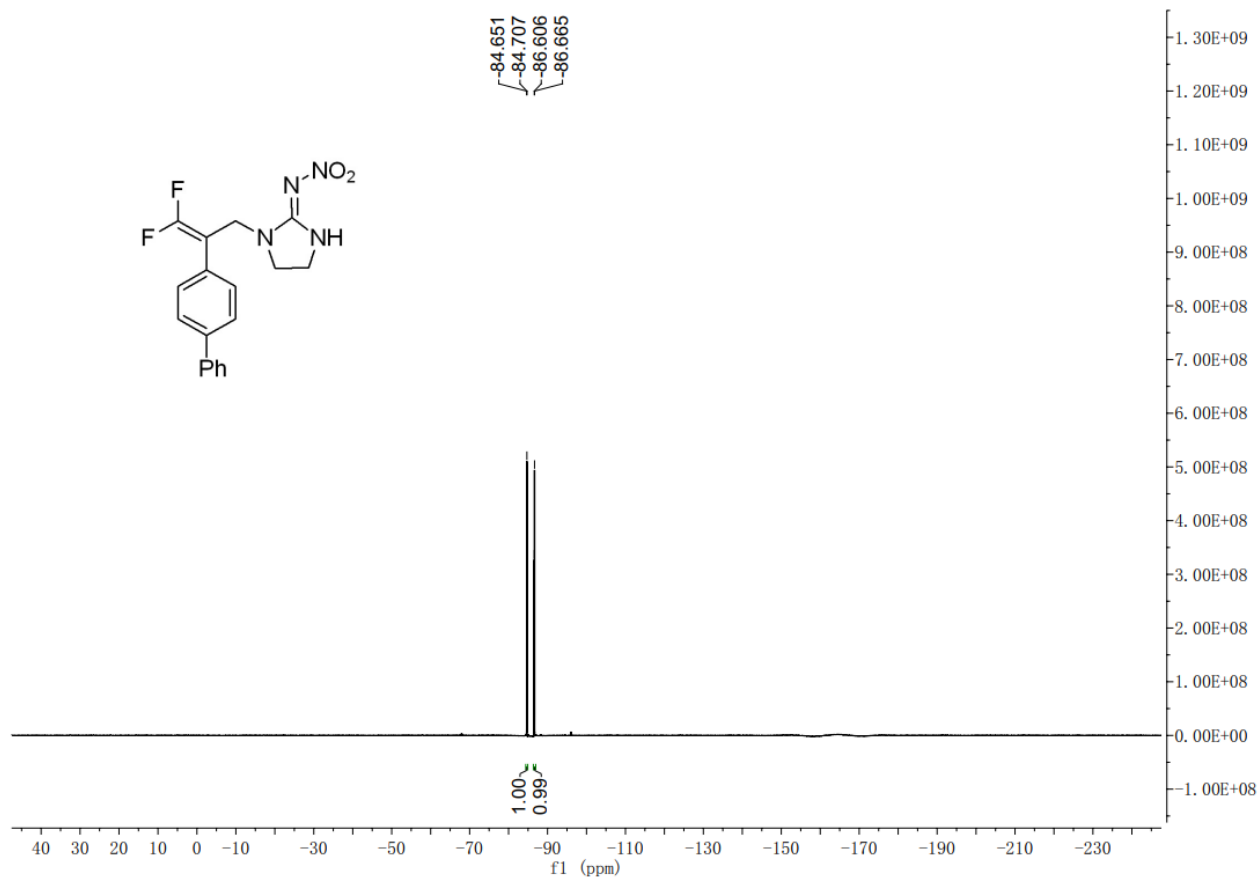
¹H NMR spectrum of 4aa (400 MHz, CDCl₃)



¹³C NMR spectrum of 4aa (100 MHz, CDCl₃)



¹⁹F NMR spectrum of 4aa (564 MHz, CDCl₃)



HRMS (ESI) spectrum of 4aa

Monoisotopic Mass, Even Electron Ions

78 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

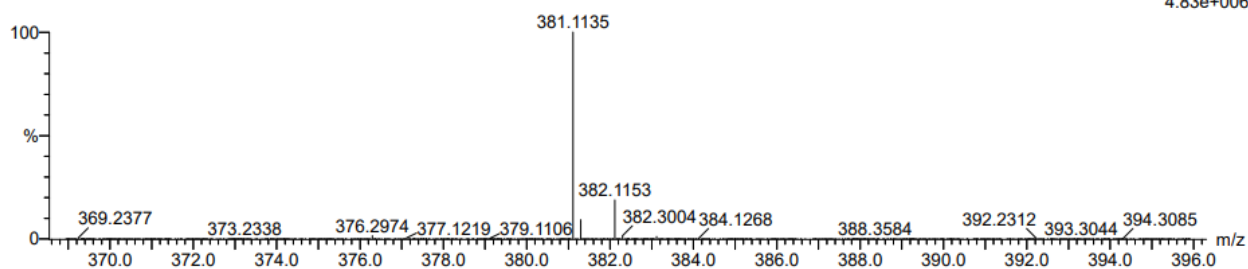
Elements Used:

C: 18-18 H: 16-16 N: 0-8 O: 0-6 F: 2-3 Na: 1-1

15

221219-2-1-- 21 (0.135)

1: TOF MS ES+
4.83e+006

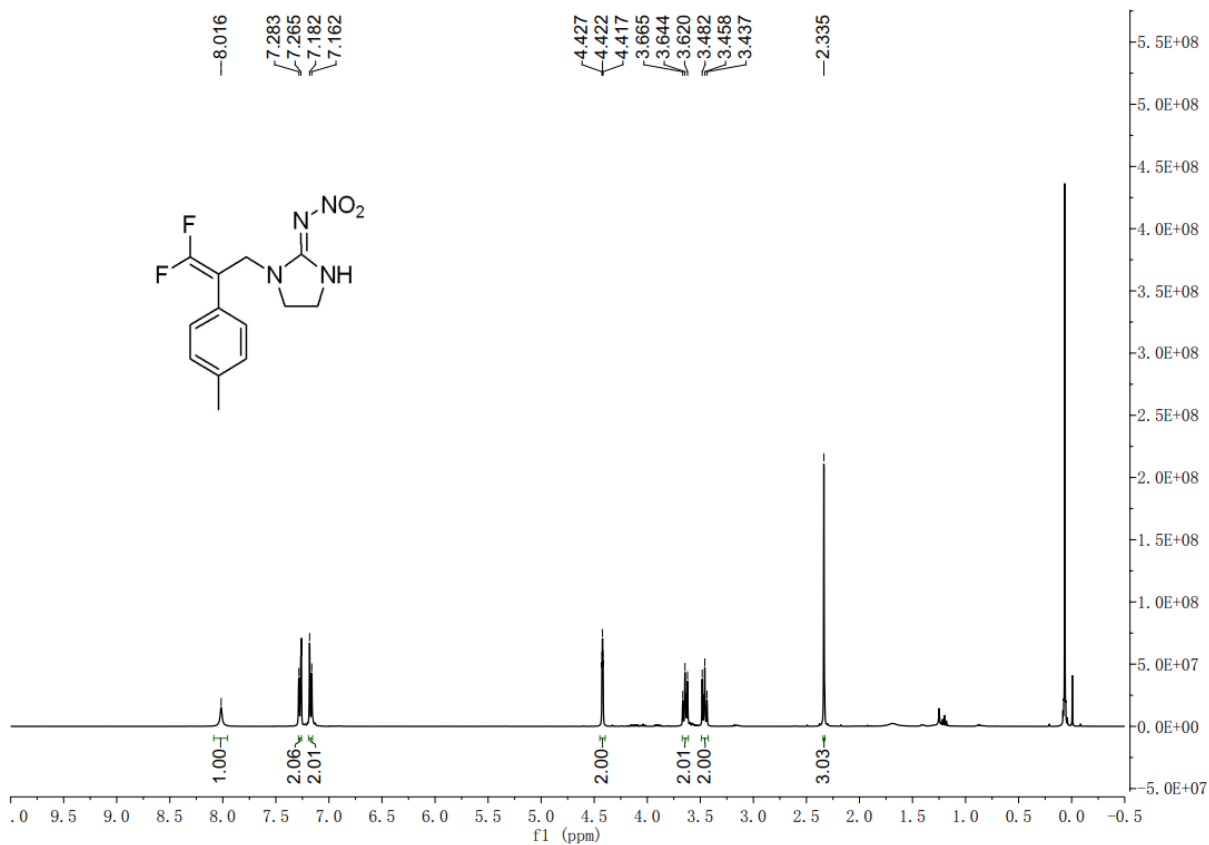


Minimum:

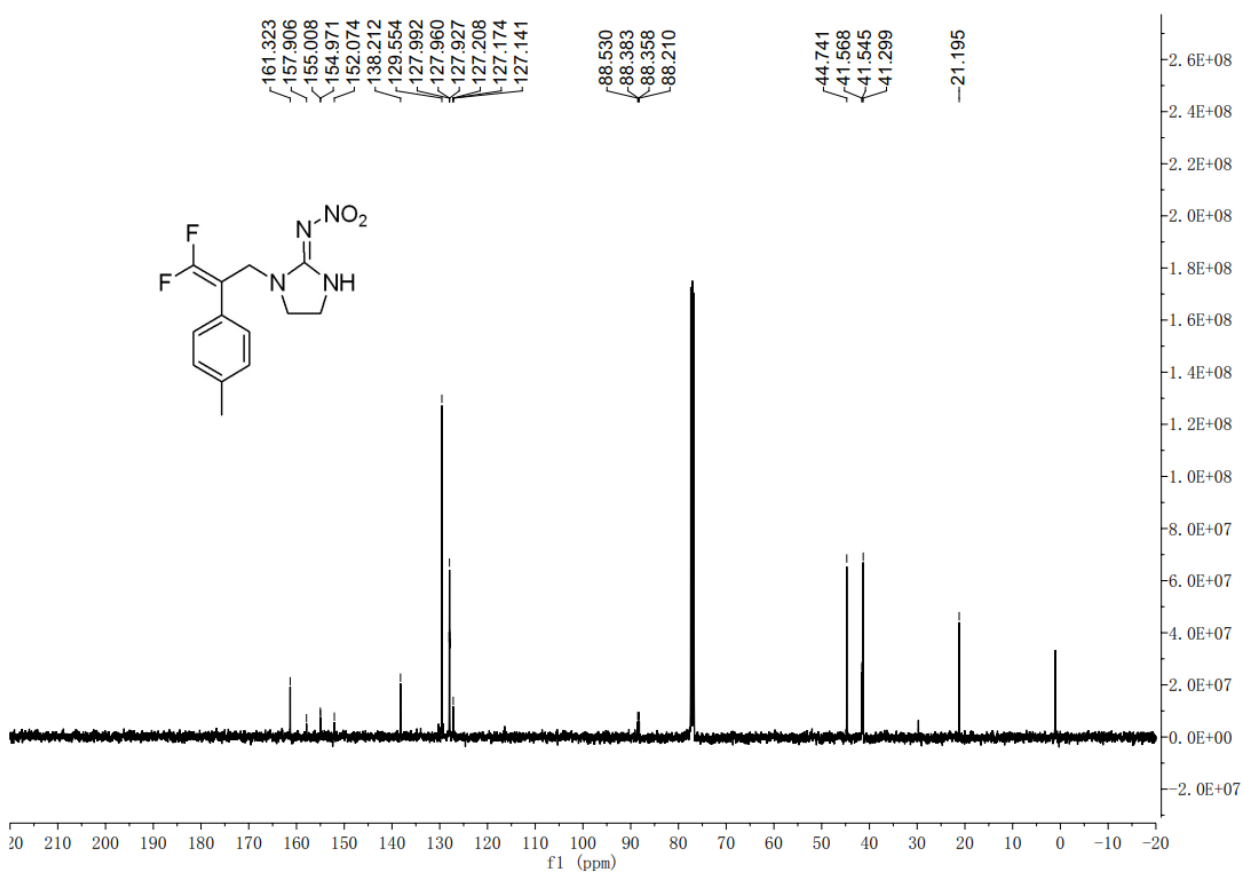
Maximum: 5.0 50.0 -1.5

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
381.1135	381.1139	-0.4	-1.0	11.5	767.1	n/a	n/a	C18 H16 N4 O2 F2 Na

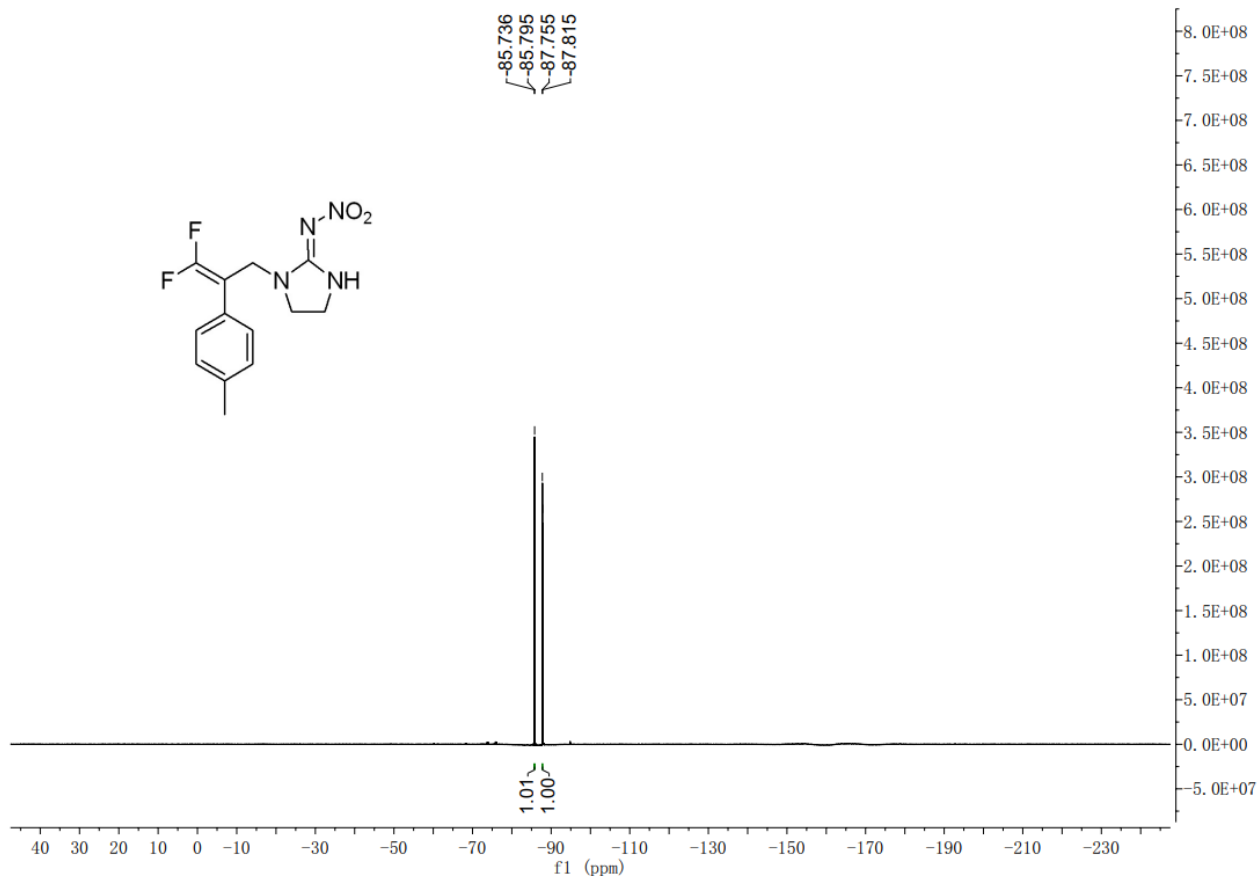
¹H NMR spectrum of 4fa (400 MHz, CDCl₃)



¹³C NMR spectrum of 4fa (100 MHz, CDCl₃)



¹⁹F NMR spectrum of 4fa (564 MHz, CDCl₃)



HRMS (ESI) spectrum of 4fa

Monoisotopic Mass, Even Electron Ions

86 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

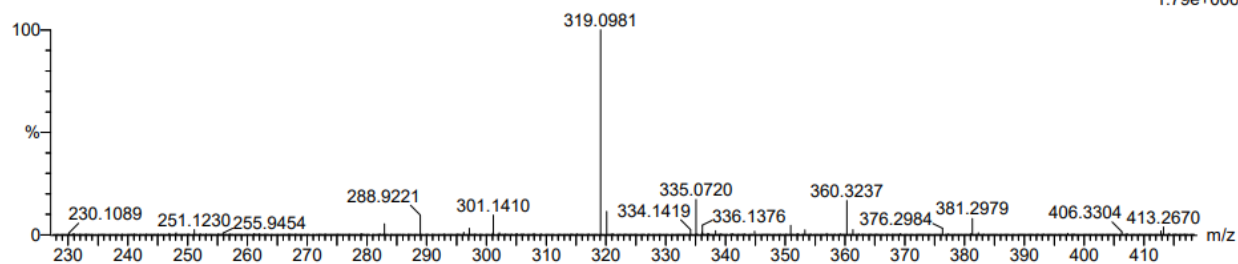
Elements Used:

C: 13-13 H: 14-16 N: 0-8 O: 0-6 F: 2-3 Na: 1-1

15

221219-2-4 26 (0.161)

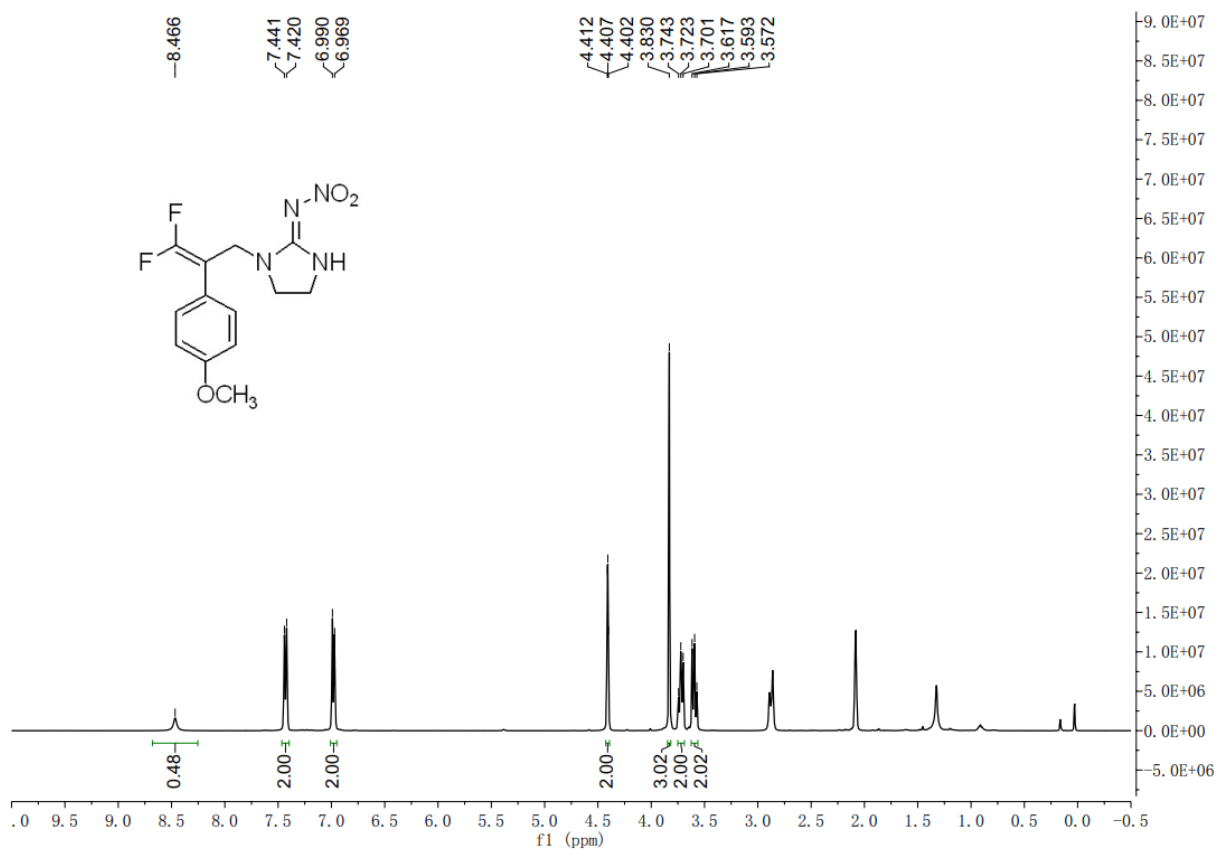
1: TOF MS ES+
1.79e+006



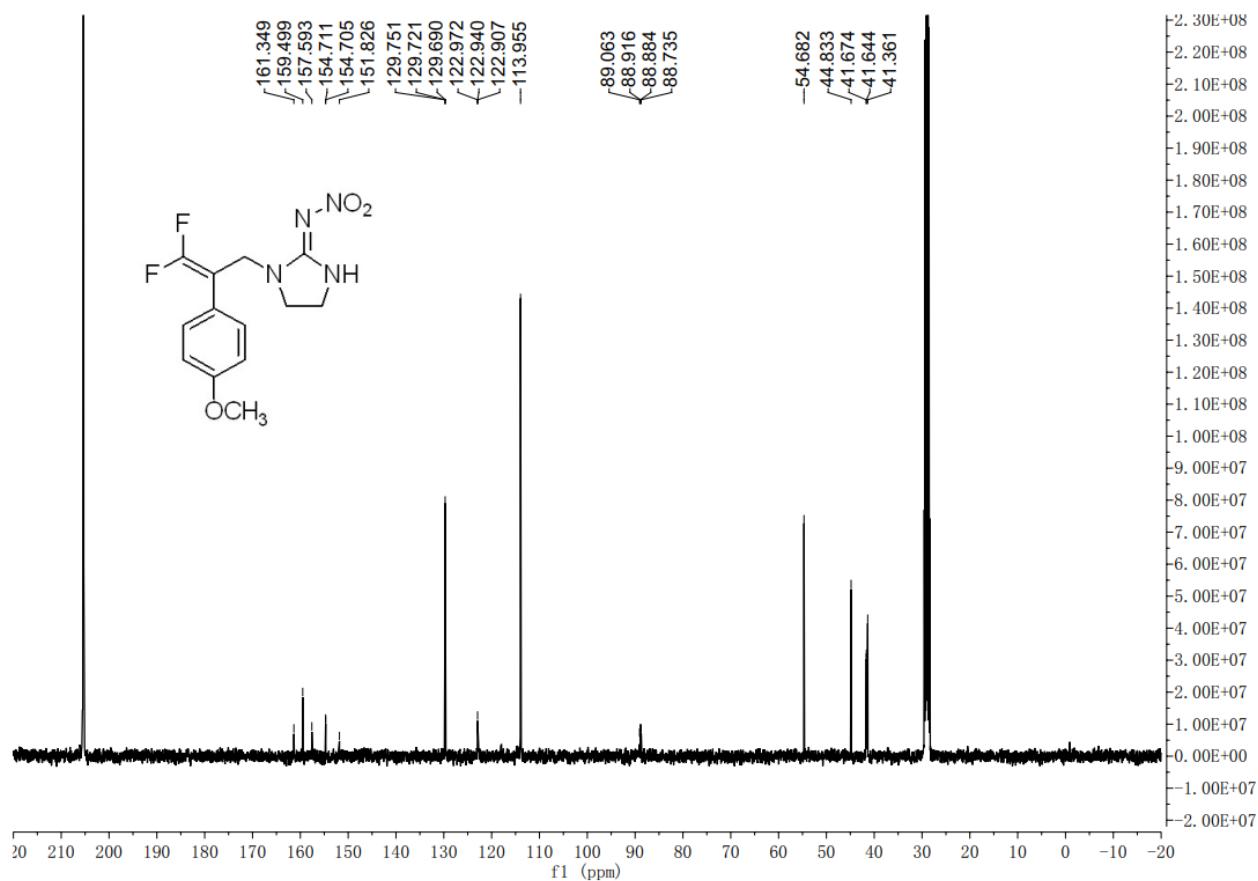
Minimum: -1.5
Maximum: 5.0 50.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
319.0981	319.0983	-0.2	-0.6	7.5	664.0	n/a	n/a	C13 H14 N4 O2 F2 Na

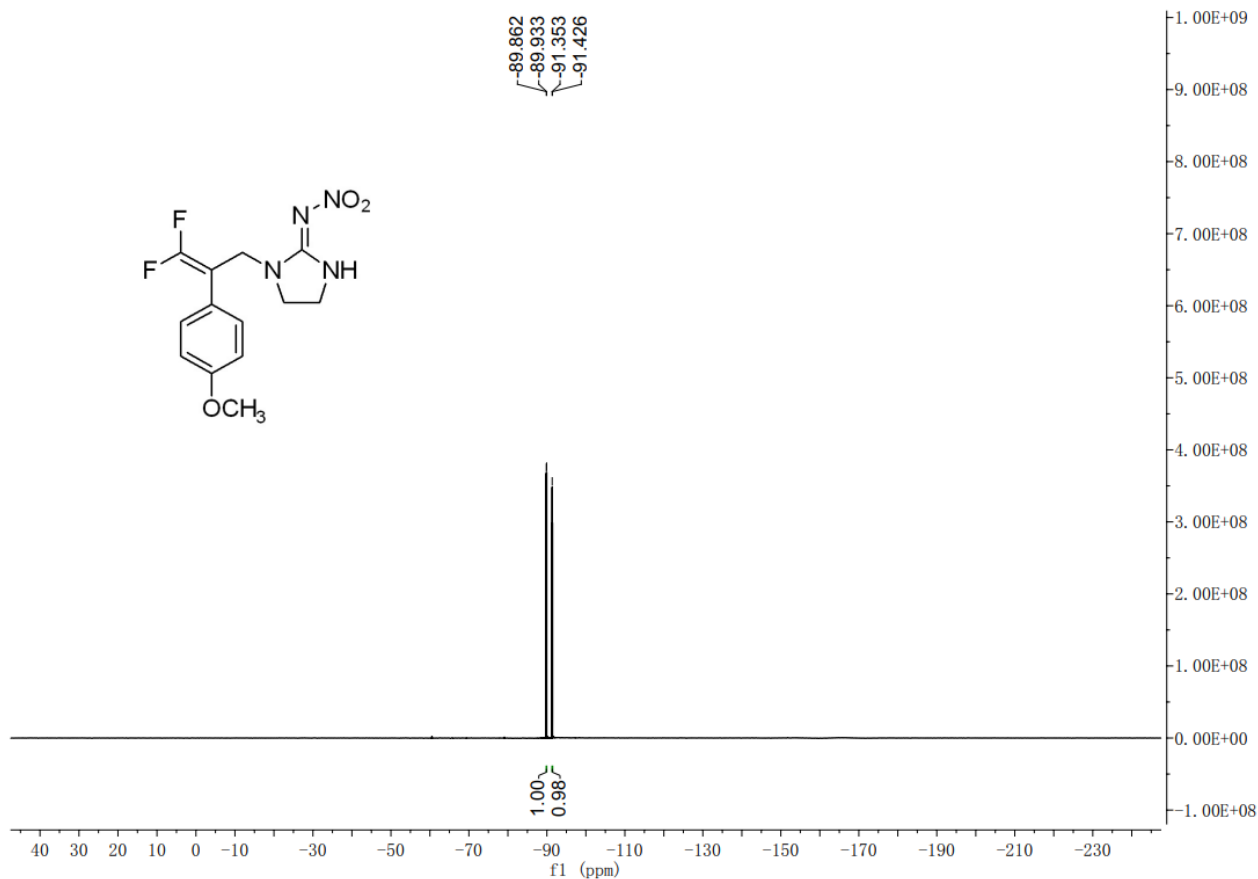
¹H NMR spectrum of 4ua (400 MHz, acetone-*d*₆)



¹³C NMR spectrum of 4ua (100 MHz, acetone-*d*₆)



¹⁹F NMR spectrum of 4ua (564 MHz, acetone-*d*₆)



HRMS (ESI) spectrum of 4ua

Monoisotopic Mass, Even Electron Ions

60 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

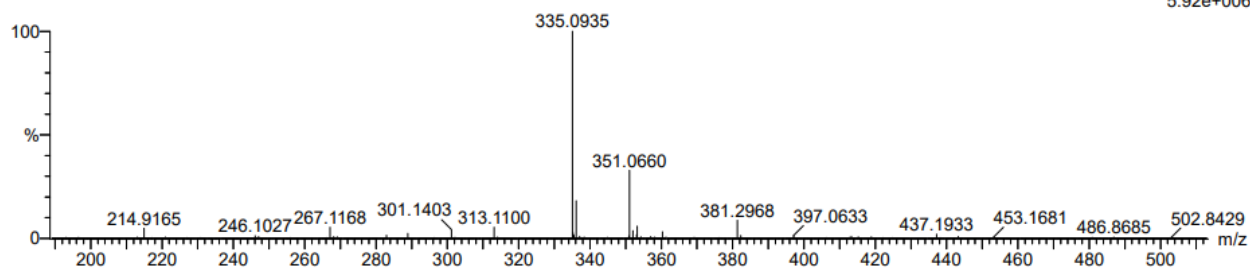
Elements Used:

C: 13-13 H: 0-45 N: 0-8 O: 0-6 F: 2-2 Na: 1-1

10

221219-2-1 17 (0.114)

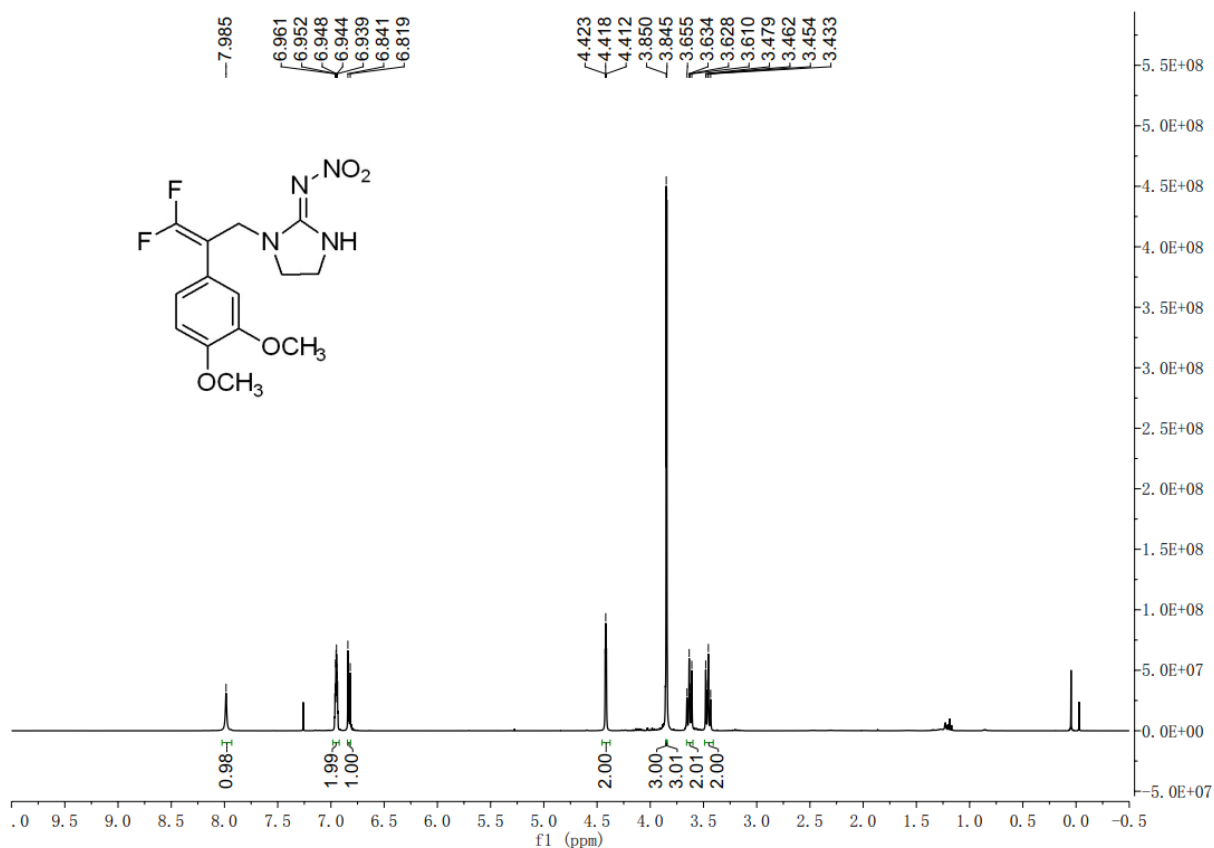
1: TOF MS ES+
5.92e+006



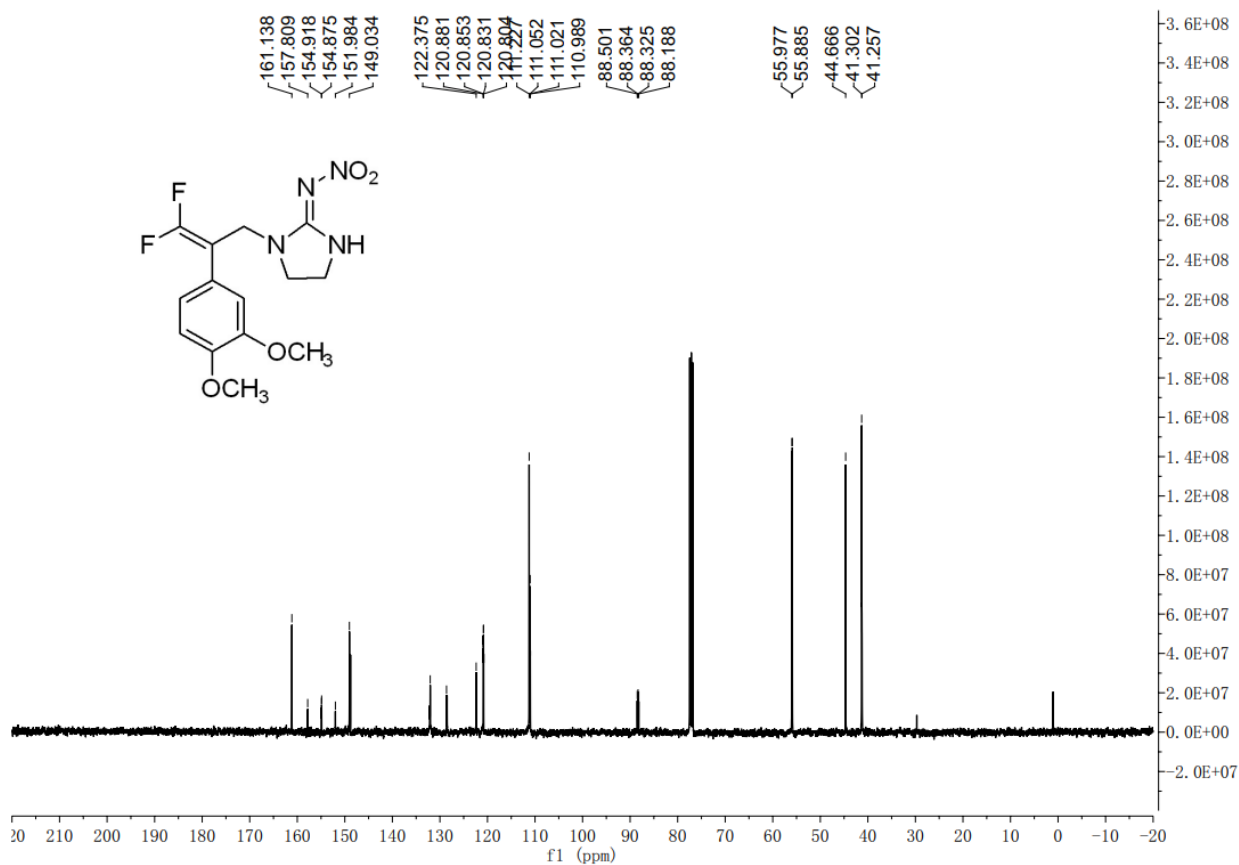
Min imum: -1.5
Max imum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
335.0935	335.0932	0.3	0.9	7.5	701.1	n/a	n/a	C13 H14 N4 O3 F2 Na

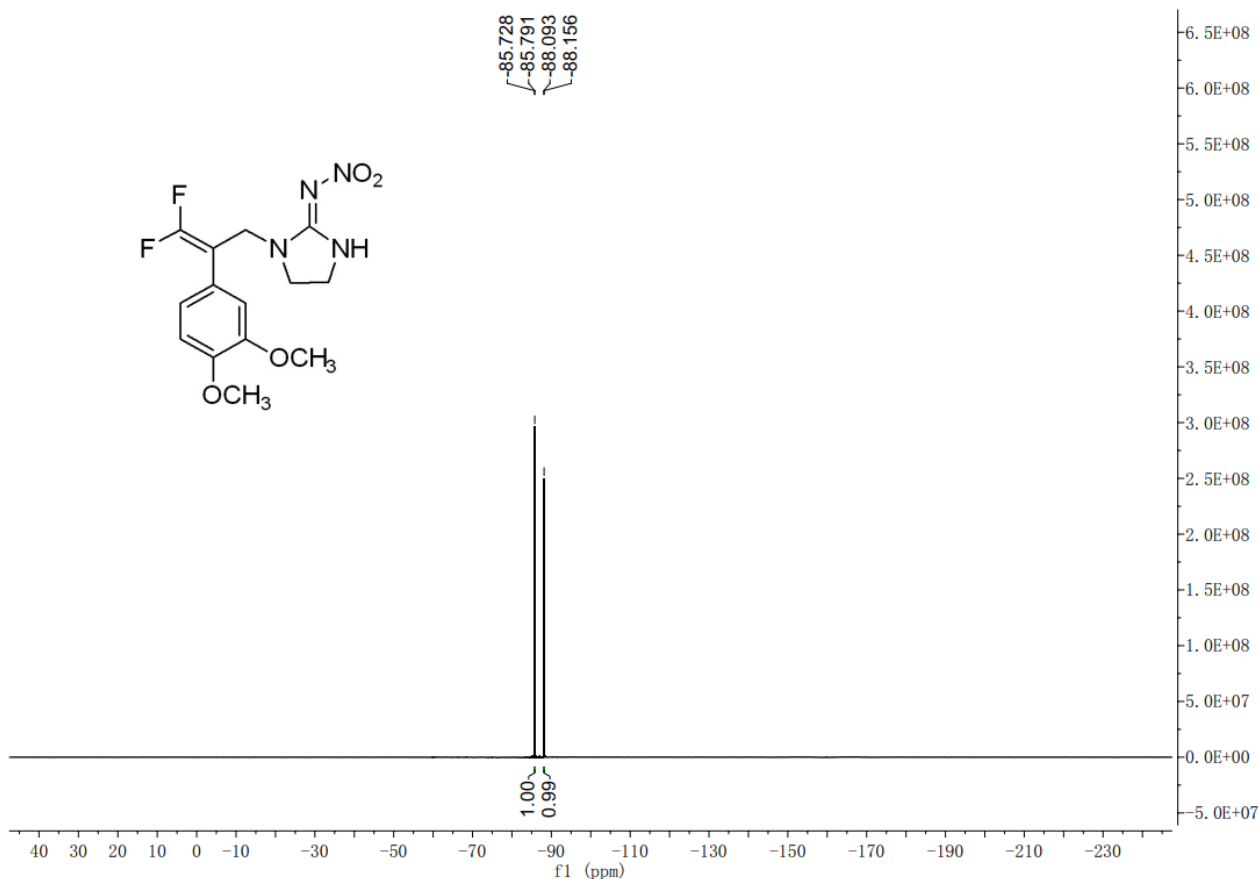
¹H NMR spectrum of 4va (400 MHz, CDCl₃)



¹³C NMR spectrum of 4va (100 MHz, CDCl₃)



¹⁹F NMR spectrum of 4va (564 MHz, CDCl₃)



HRMS (ESI) spectrum of 4va

Monoisotopic Mass, Even Electron Ions

78 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

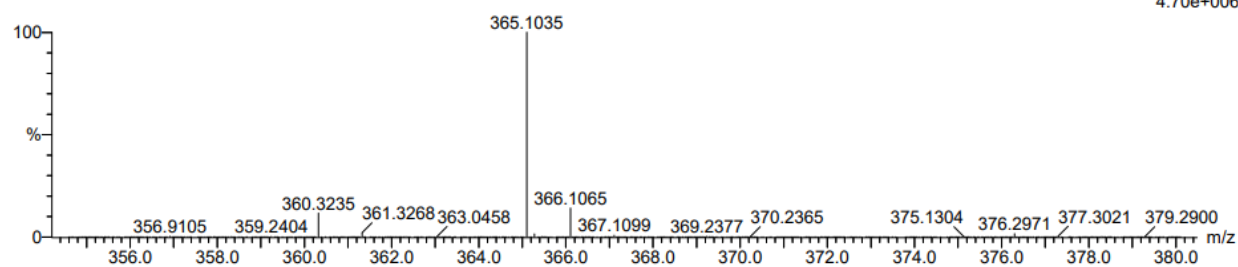
Elements Used:

C: 14-14 H: 14-16 N: 0-8 O: 0-6 F: 2-3 Na: 1-1

15

221219-2-3 21 (0.135)

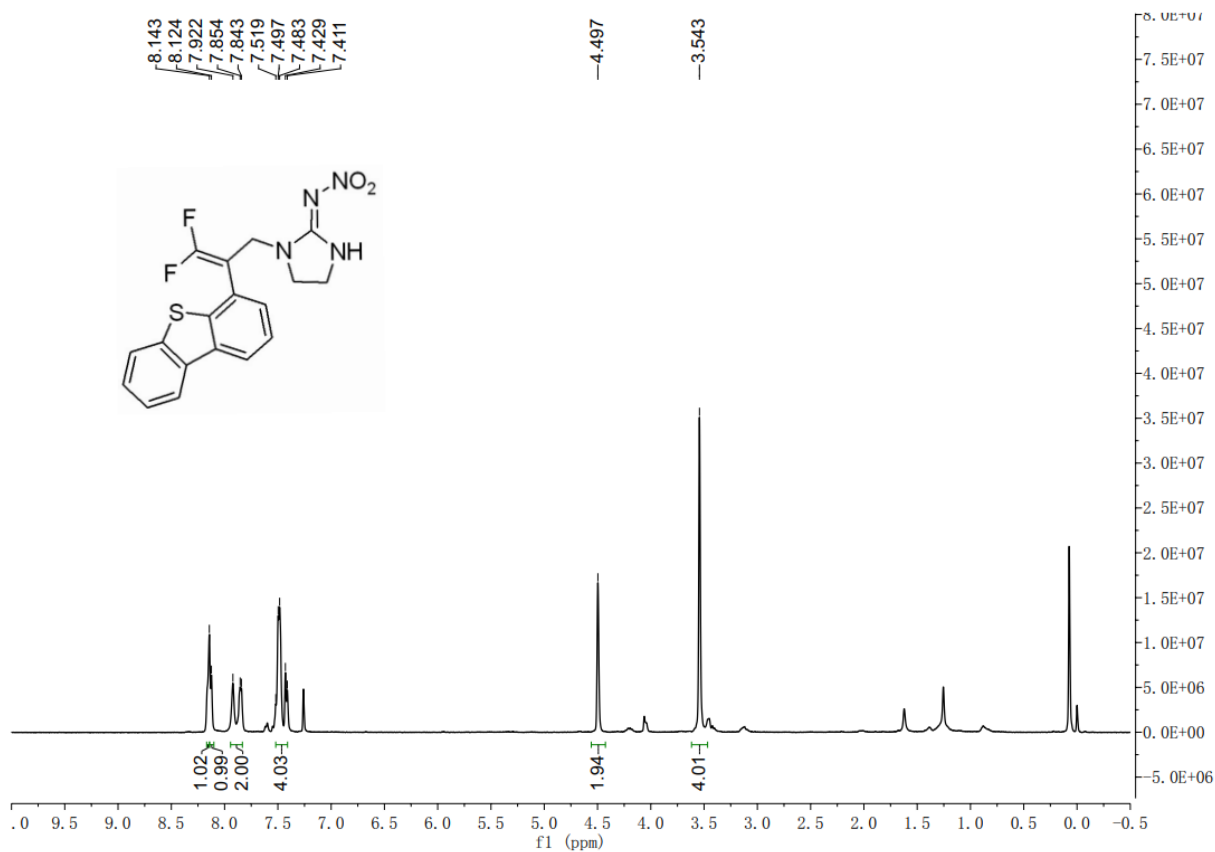
1: TOF MS ES+
4.70e+006



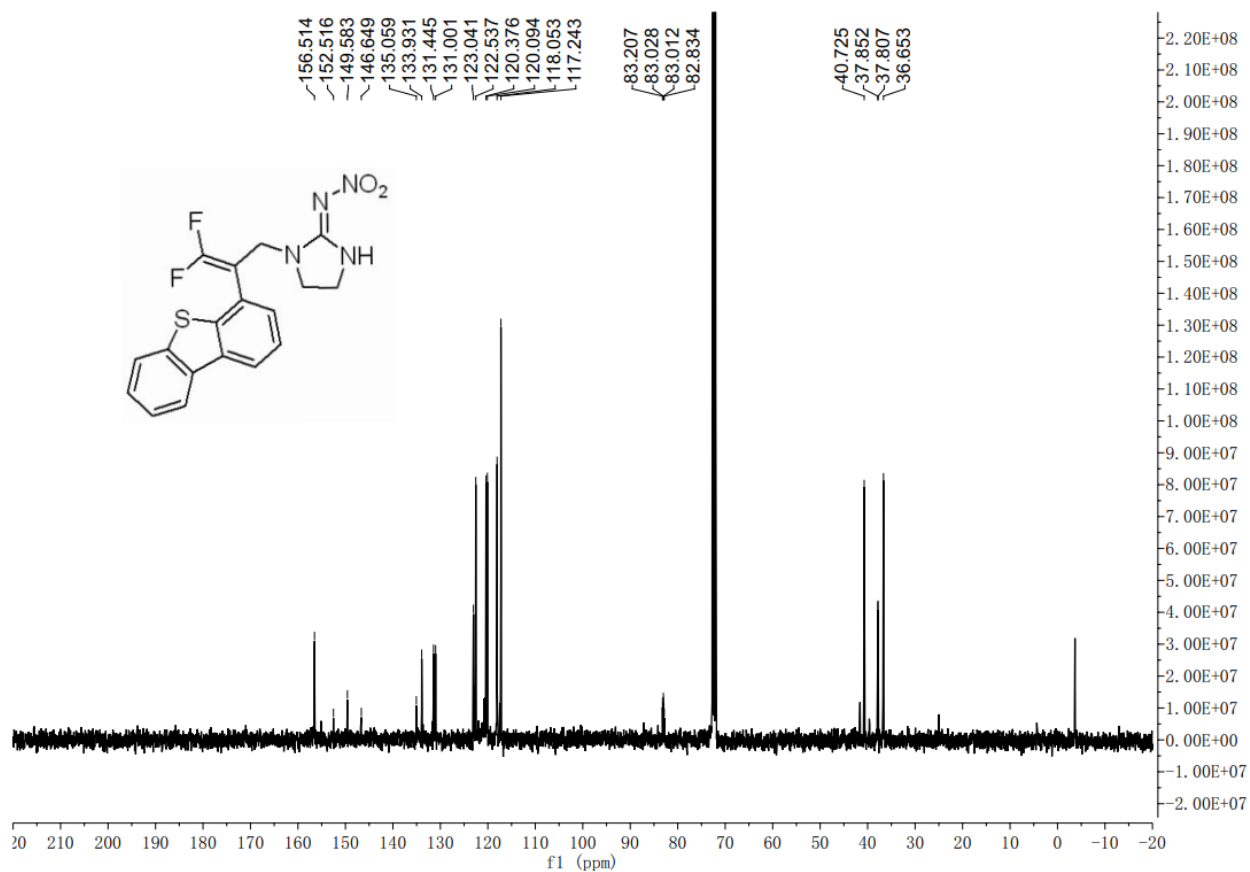
Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
365.1035	365.1037	-0.2	-0.5	7.5	710.5	n/a	n/a	C14 H16 N4 O4 F2 Na

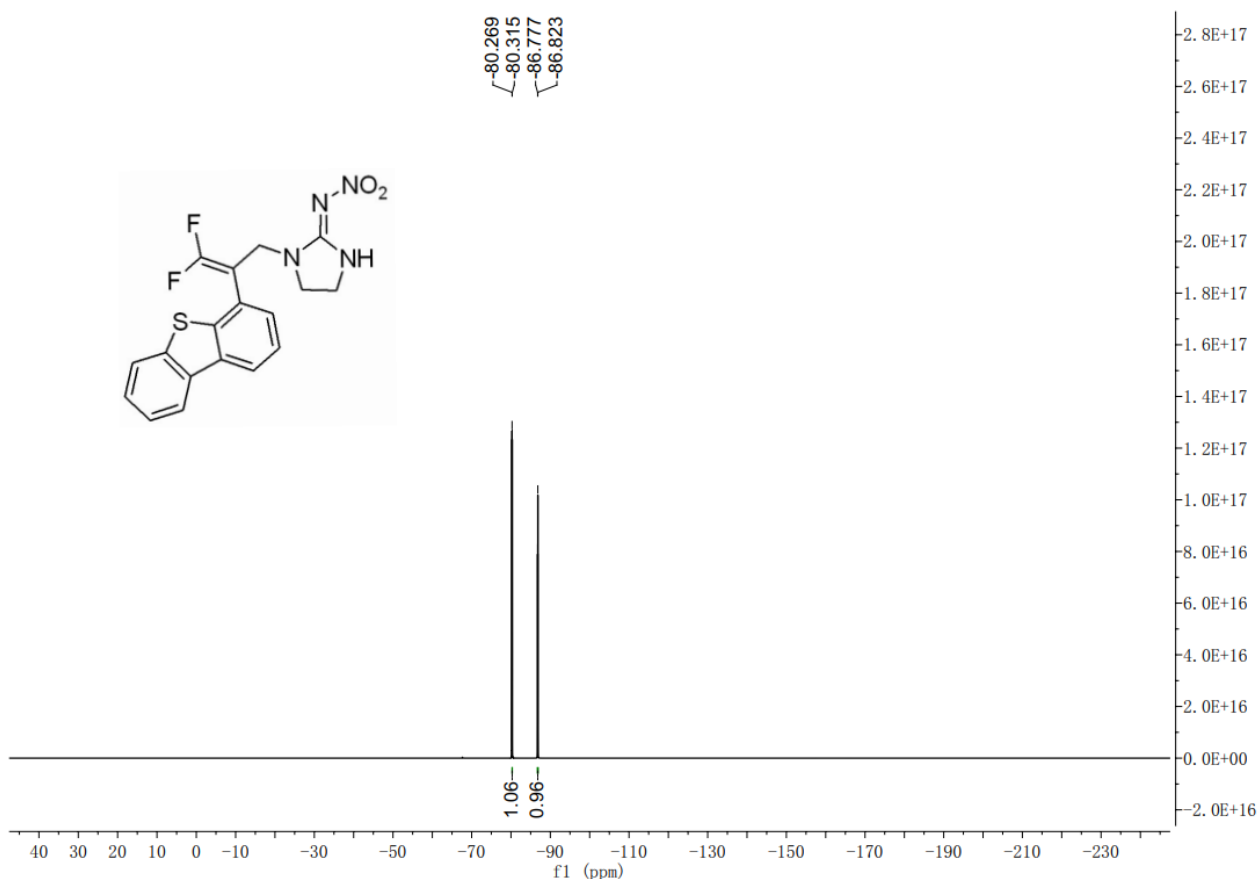
¹H NMR spectrum of 4wa (400 MHz, CDCl₃)



¹³C NMR spectrum of 4wa (100 MHz, CDCl₃)



¹⁹F NMR spectrum of 4wa (564 MHz, CDCl₃)



HRMS (ESI) spectrum of 4wa

Monoisotopic Mass, Even Electron Ions

81 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

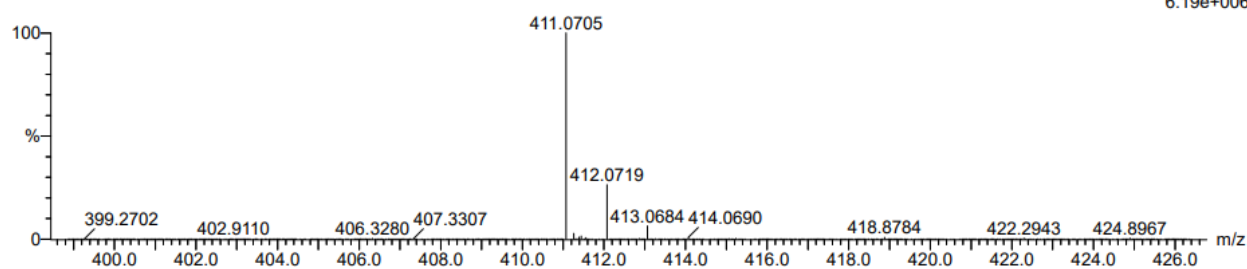
Elements Used:

C: 18-18 H: 14-16 N: 0-8 O: 0-6 F: 2-3 Na: 1-1 S: 1-1

15

221219-2-2 20 (0.130)

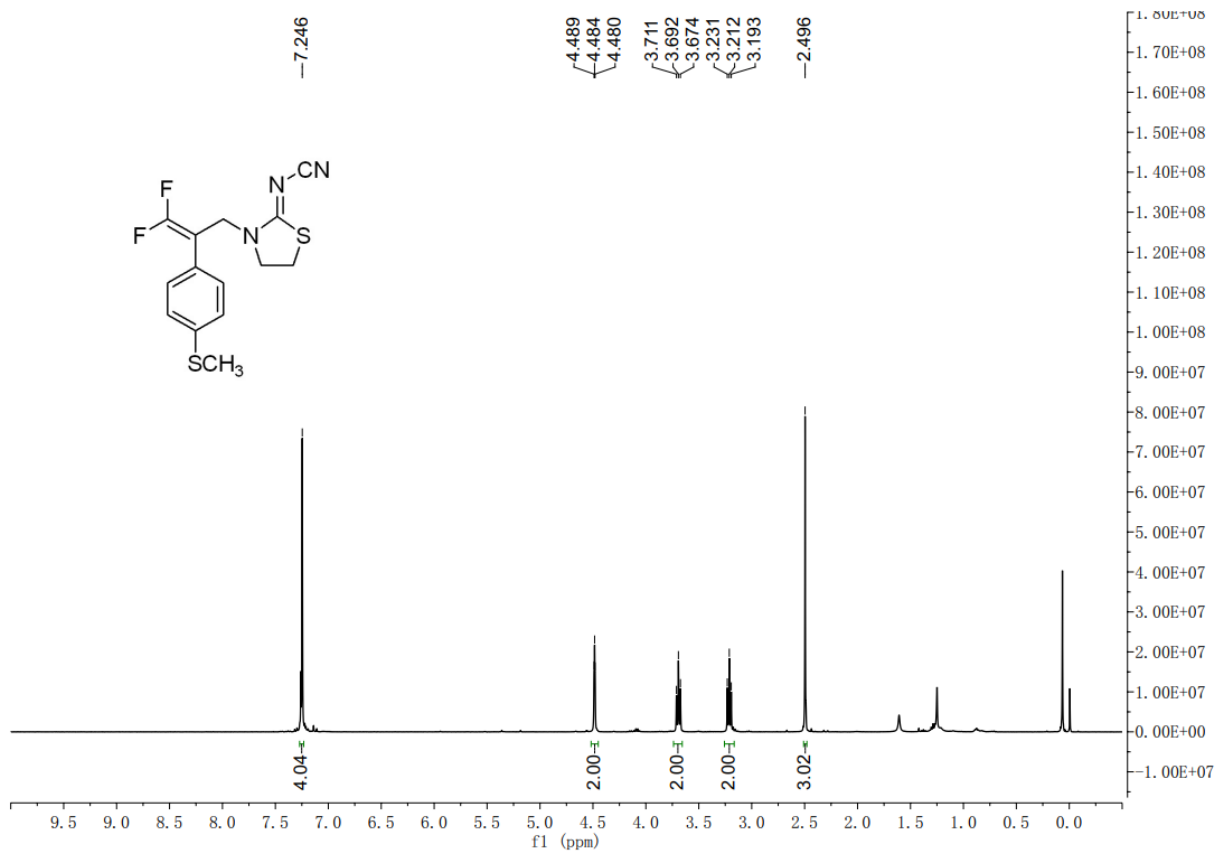
1: TOF MS ES+
6.19e+006



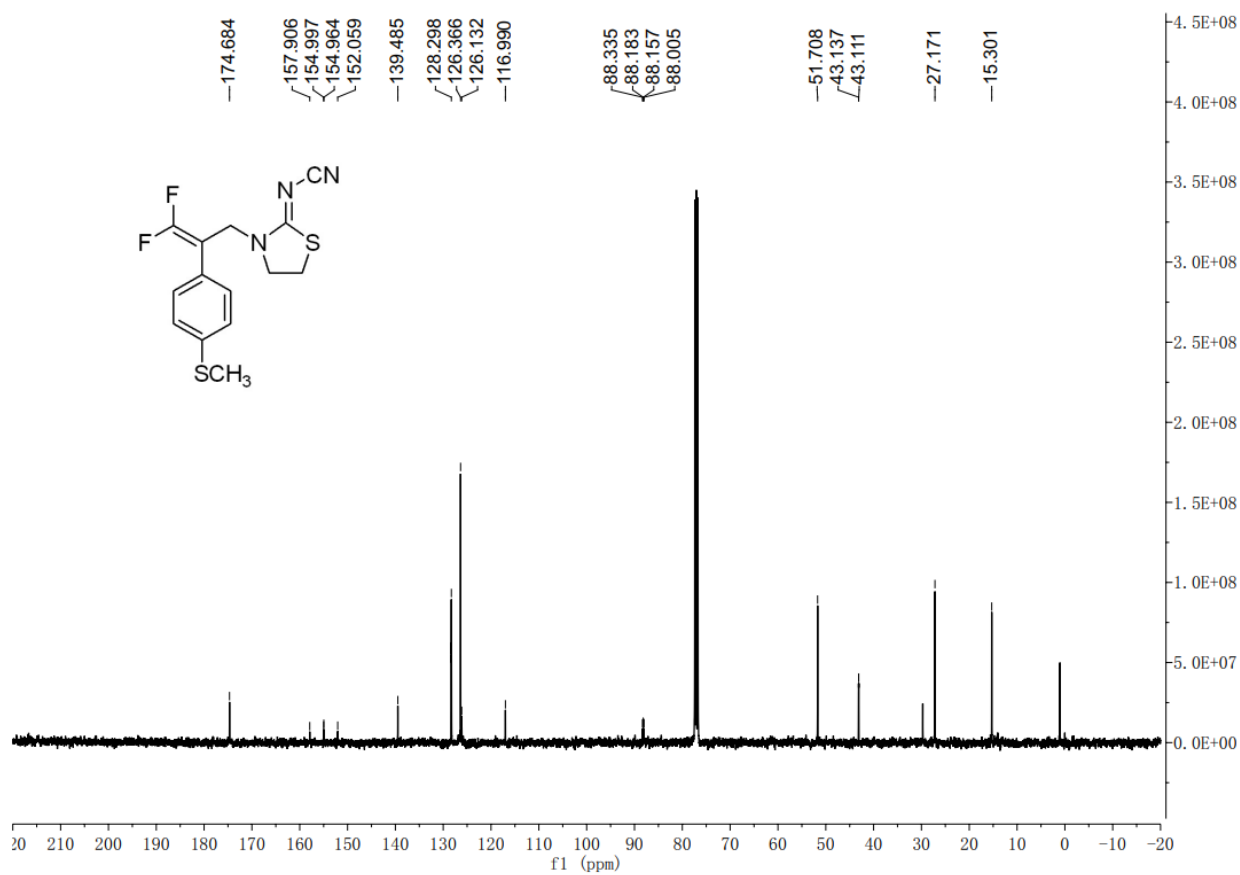
Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
411.0705	411.0703	0.2	0.5	12.5	571.9	n/a	n/a	C ₁₈ H ₁₄ N ₄ O ₂ F ₂ NaS

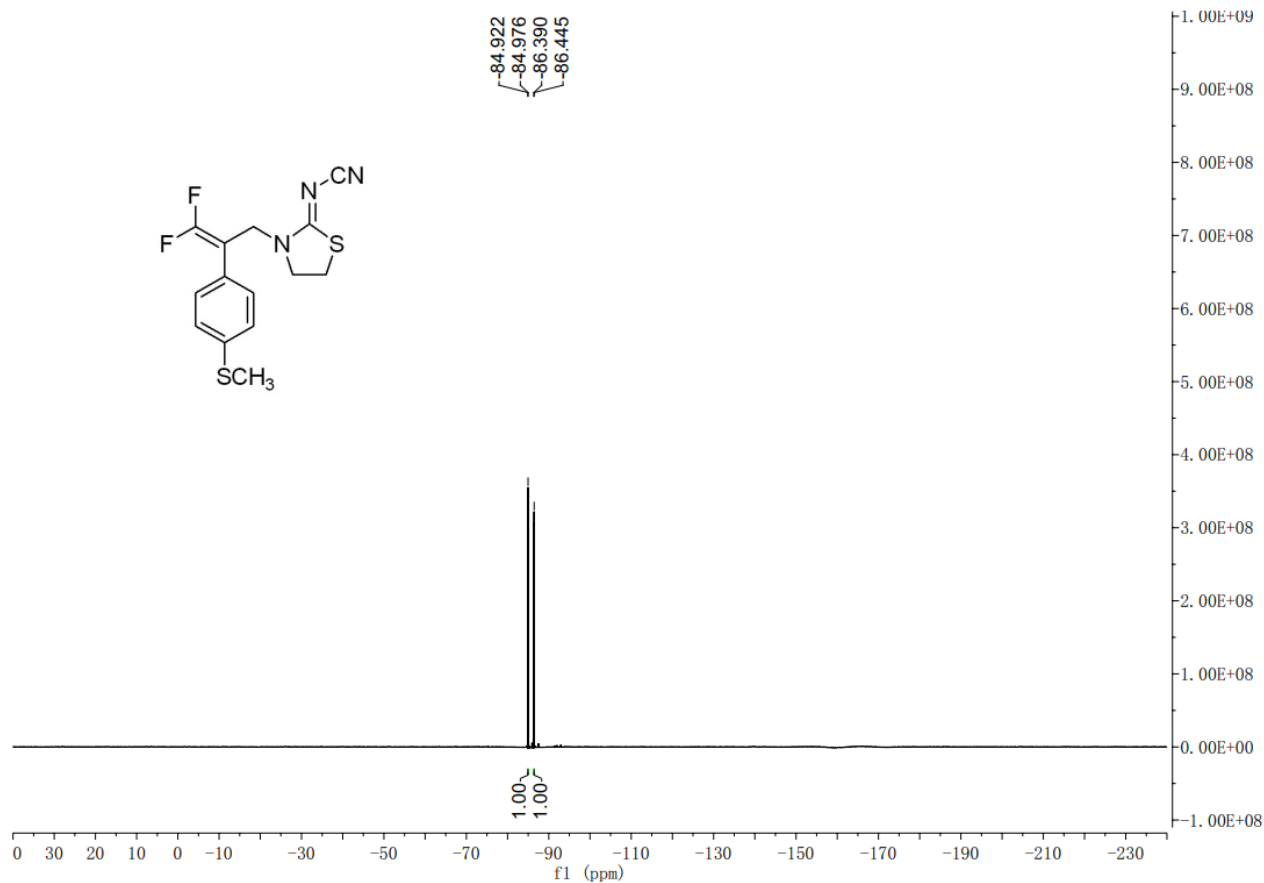
¹H NMR spectrum of 4gc (400 MHz, CDCl₃)



¹³C NMR spectrum of 4gc (100 MHz, CDCl₃)

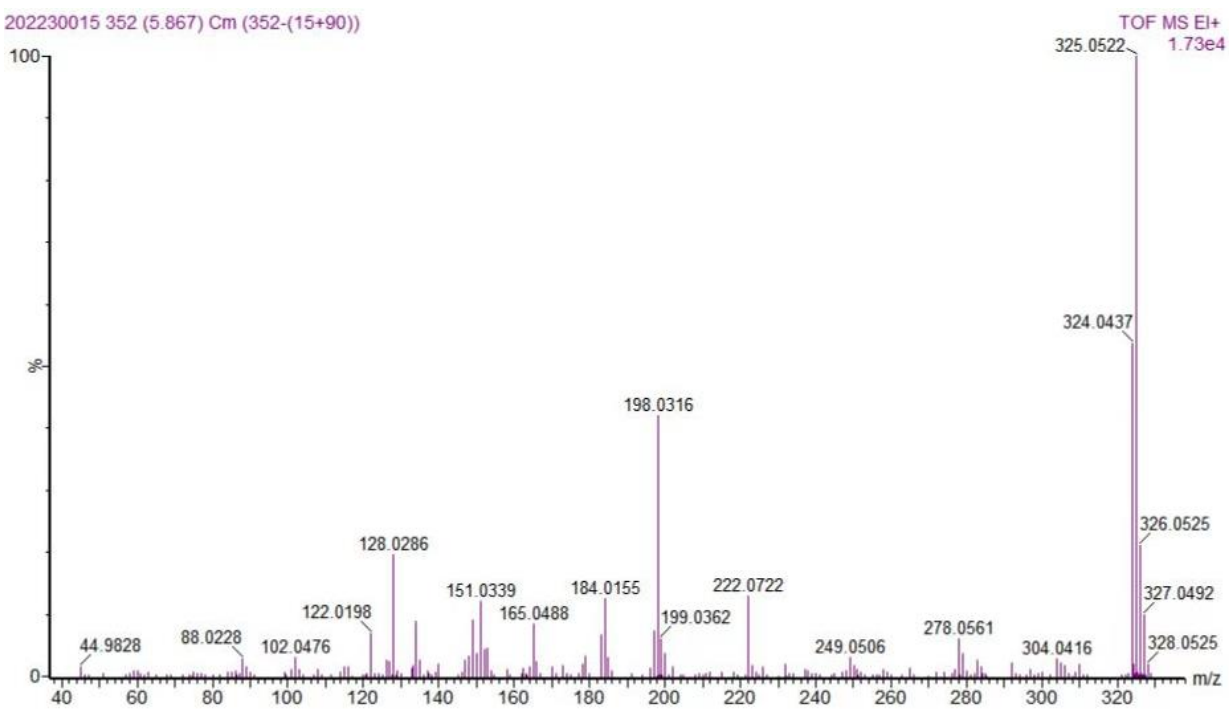


¹⁹F NMR spectrum of 4gc (564 MHz, CDCl₃)

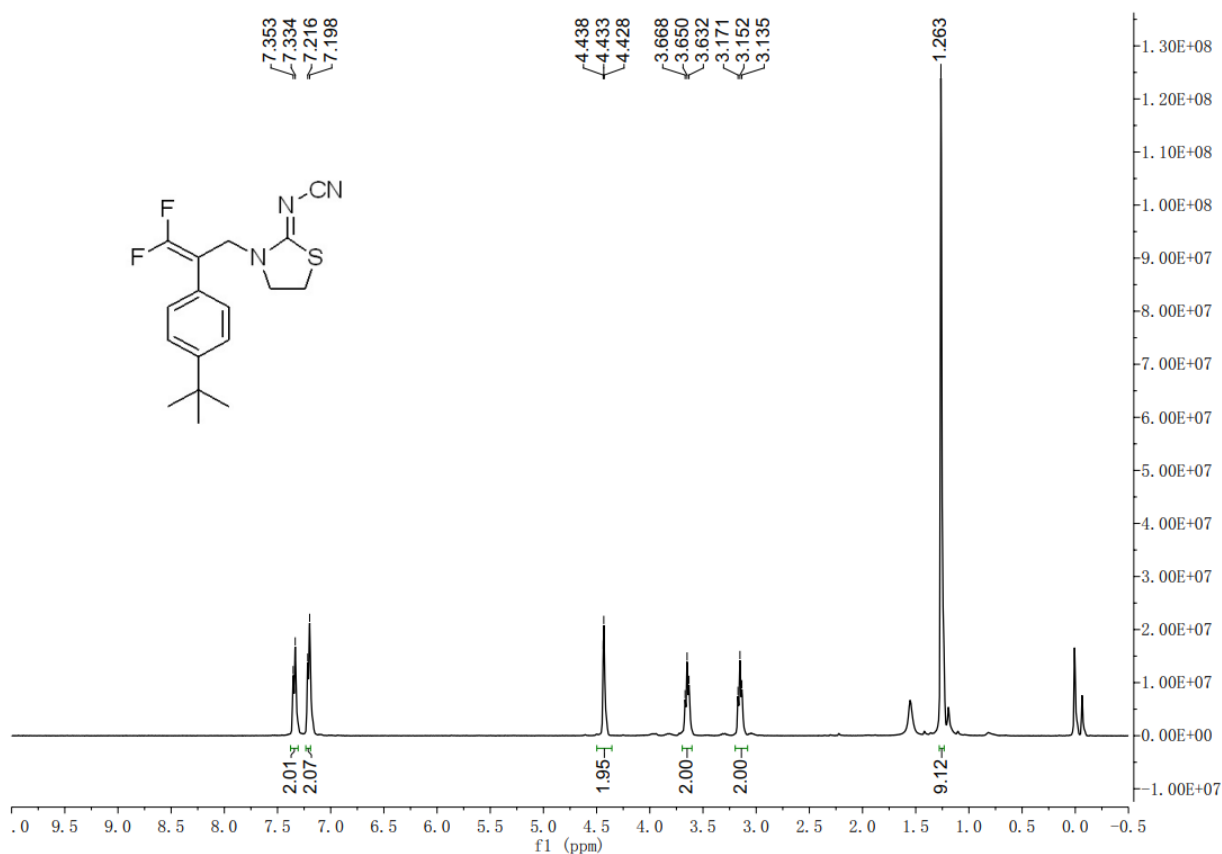


HRMS (EI) spectrum of 4gc

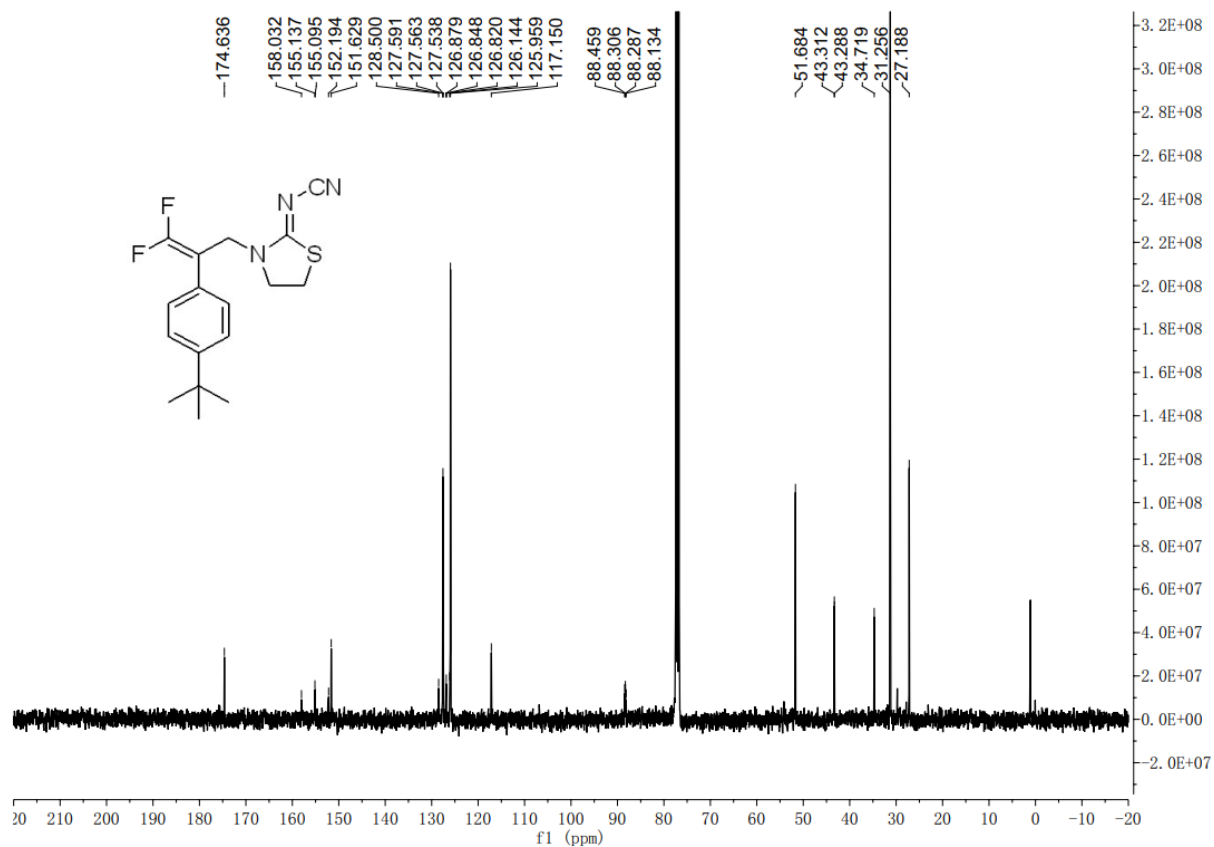
202230015 352 (5.867) Cm (352-(15+90))



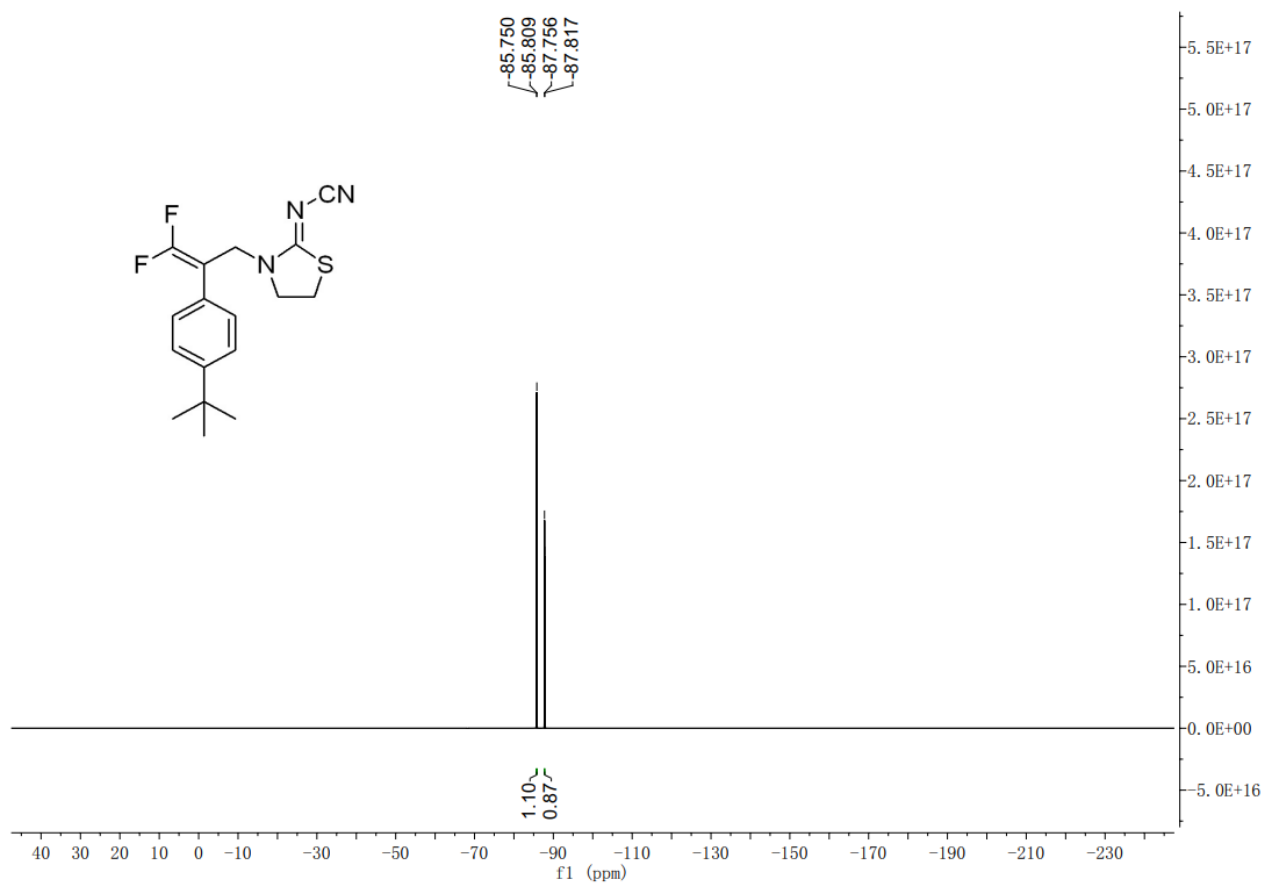
¹H NMR spectrum of 4hc (400 MHz, CDCl₃)



¹³C NMR spectrum of 4hc (100 MHz, CDCl₃)

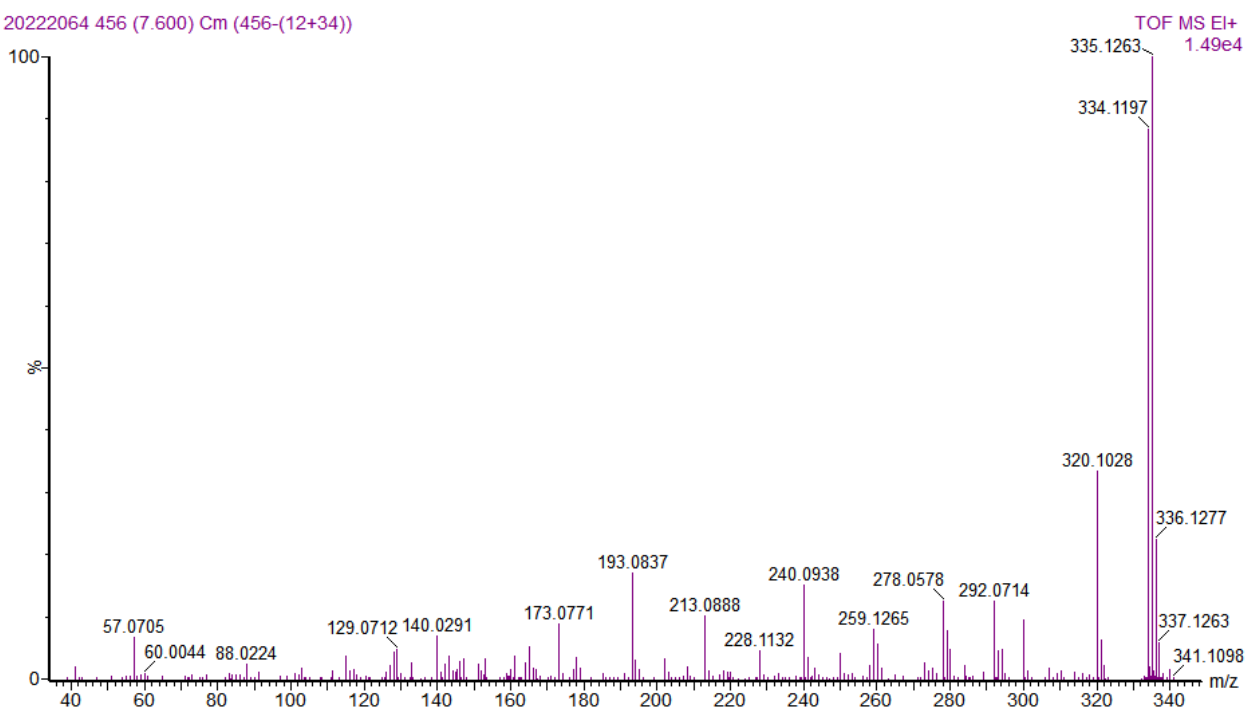


^{19}F NMR spectrum of 4hc (564 MHz, CDCl_3)

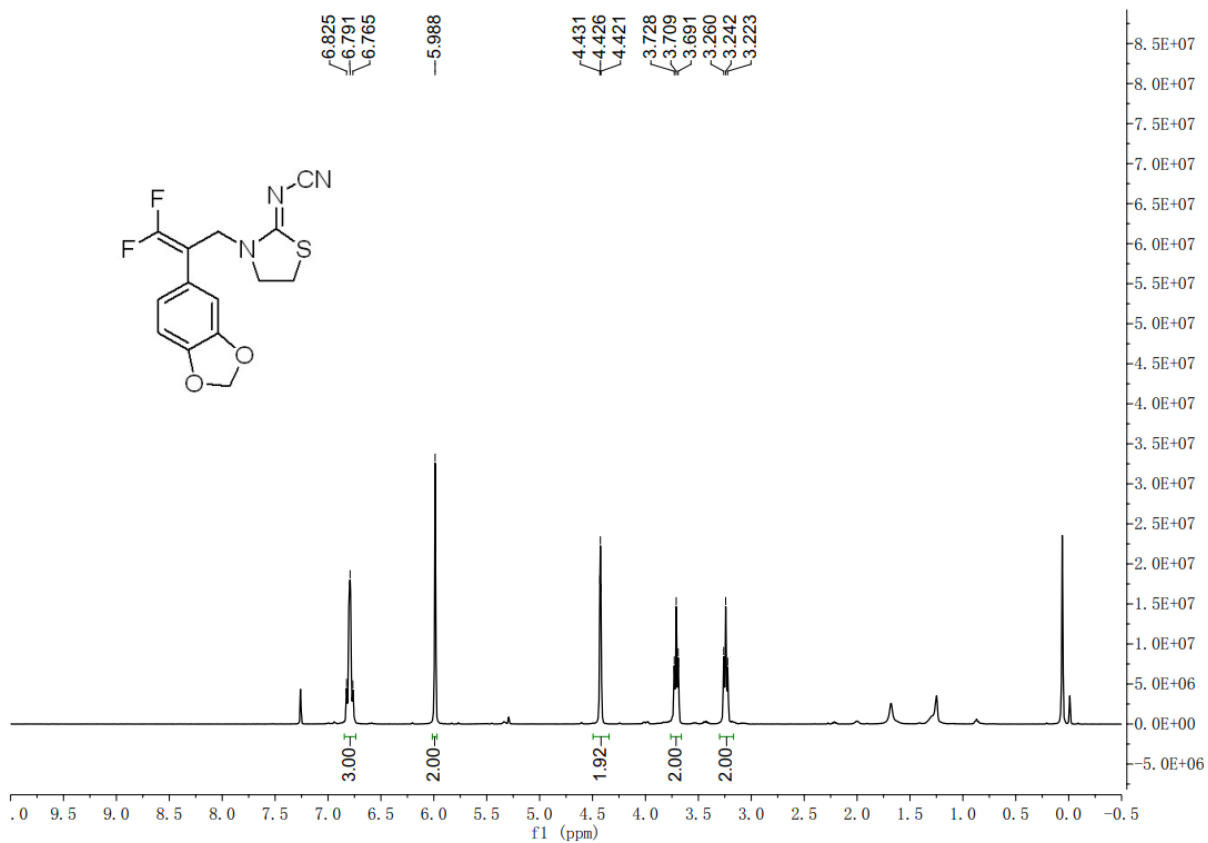


HRMS (EI) spectrum of 4hc

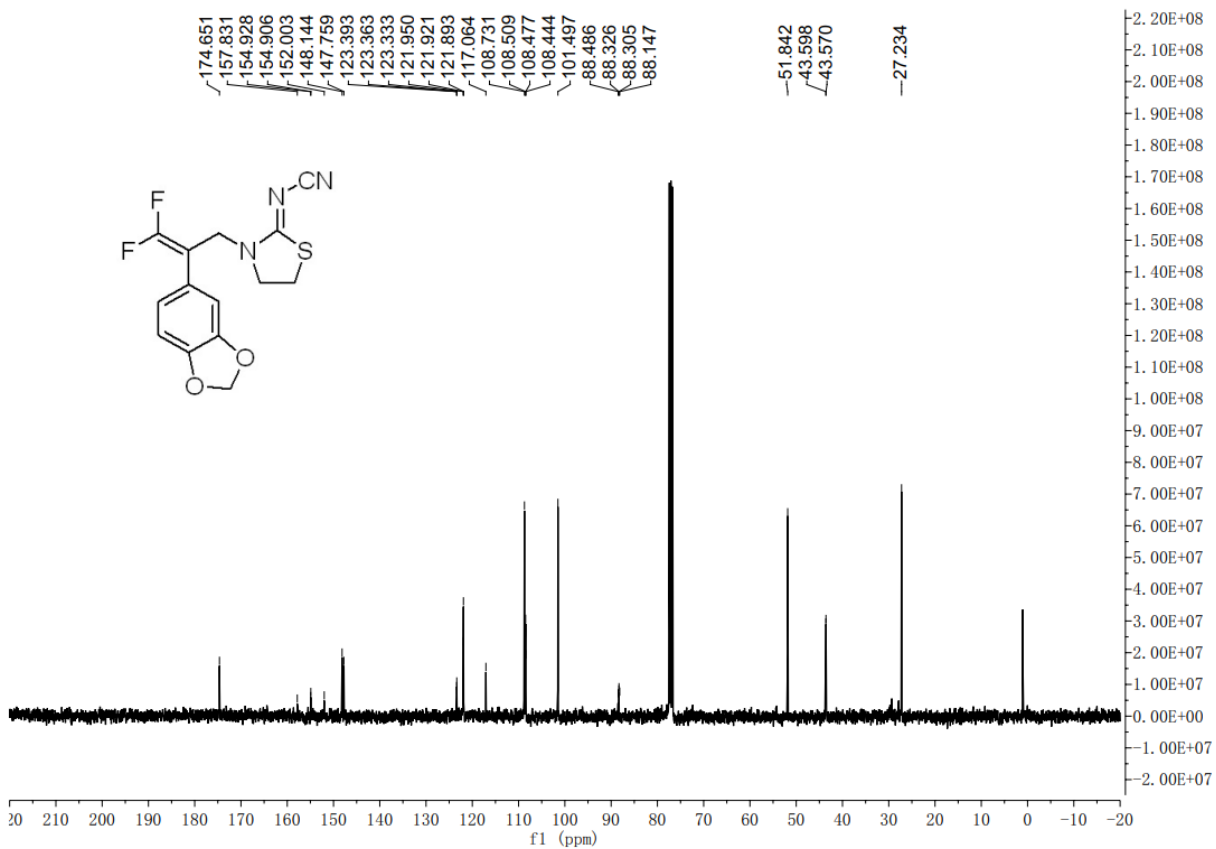
20222064 456 (7.600) Cm (456-(12+34))



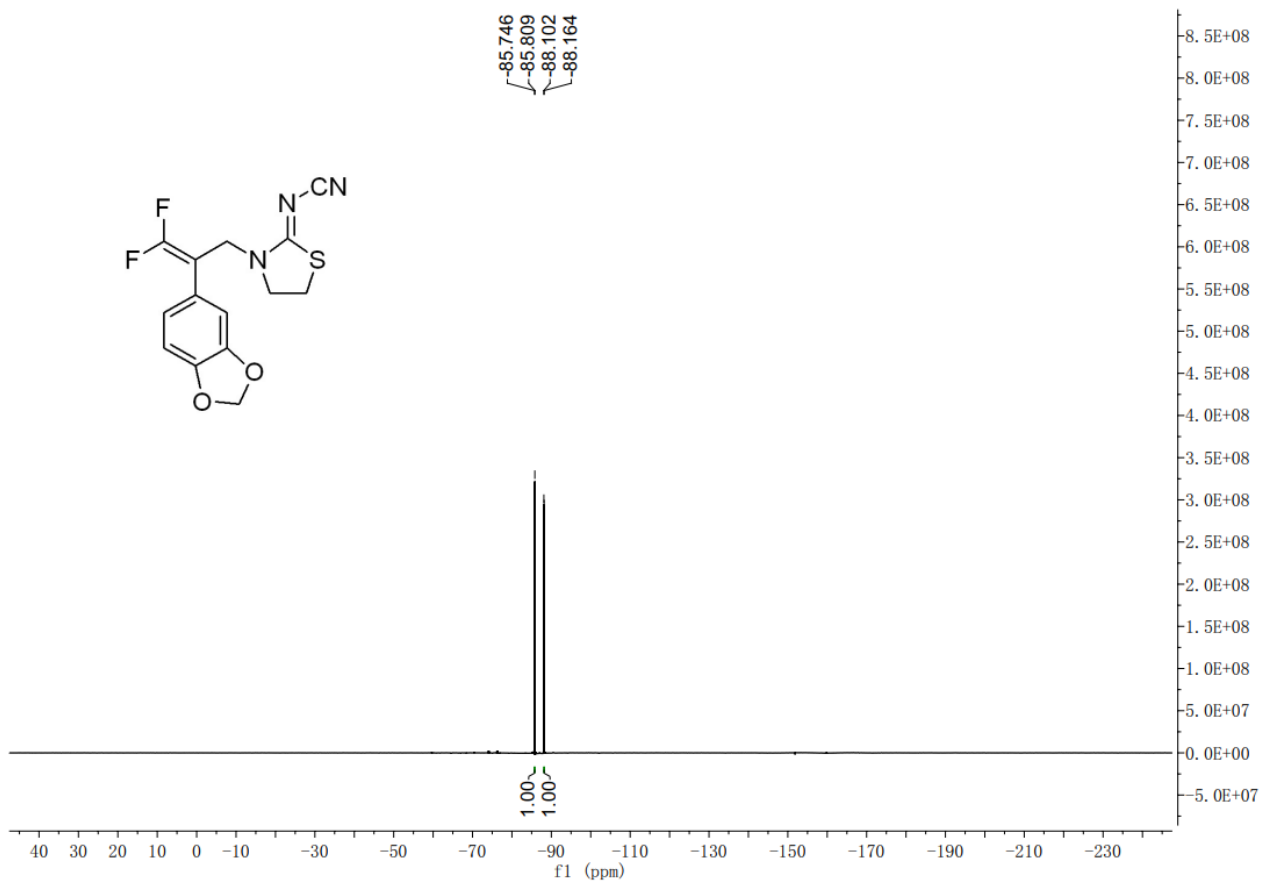
¹H NMR spectrum of 4xc (400 MHz, CDCl₃)



¹³C NMR spectrum of 4xc (100 MHz, CDCl₃)

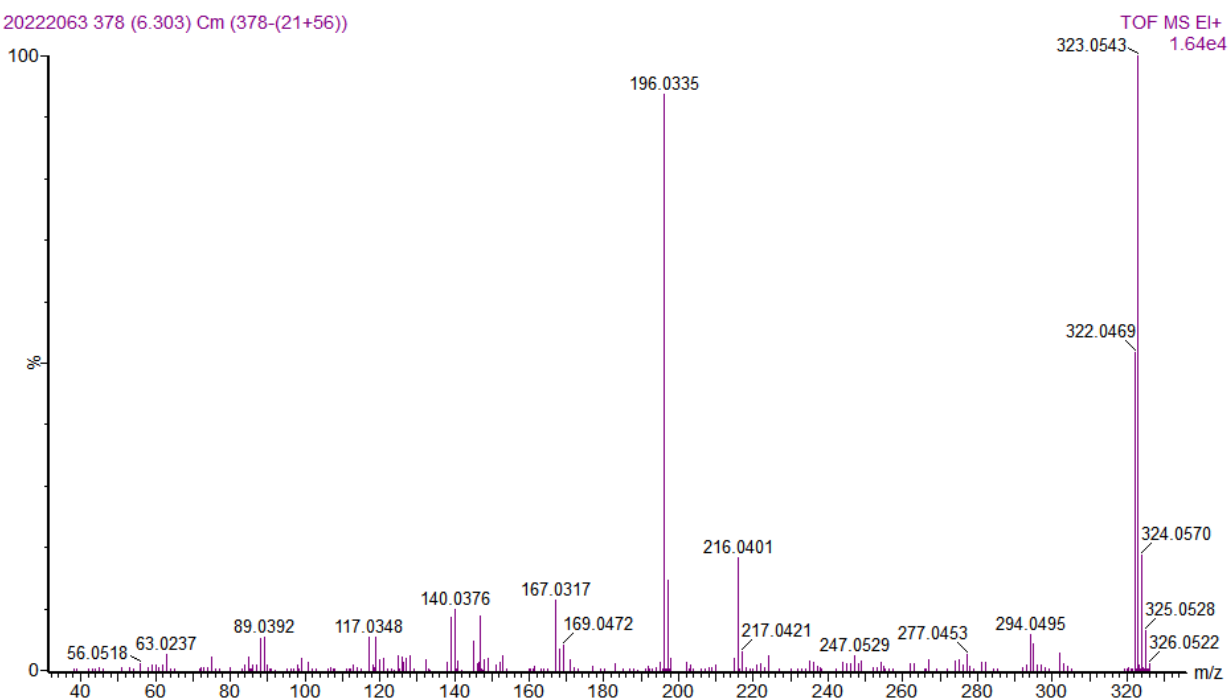


¹⁹F NMR spectrum of 4xc (564 MHz, CDCl₃)

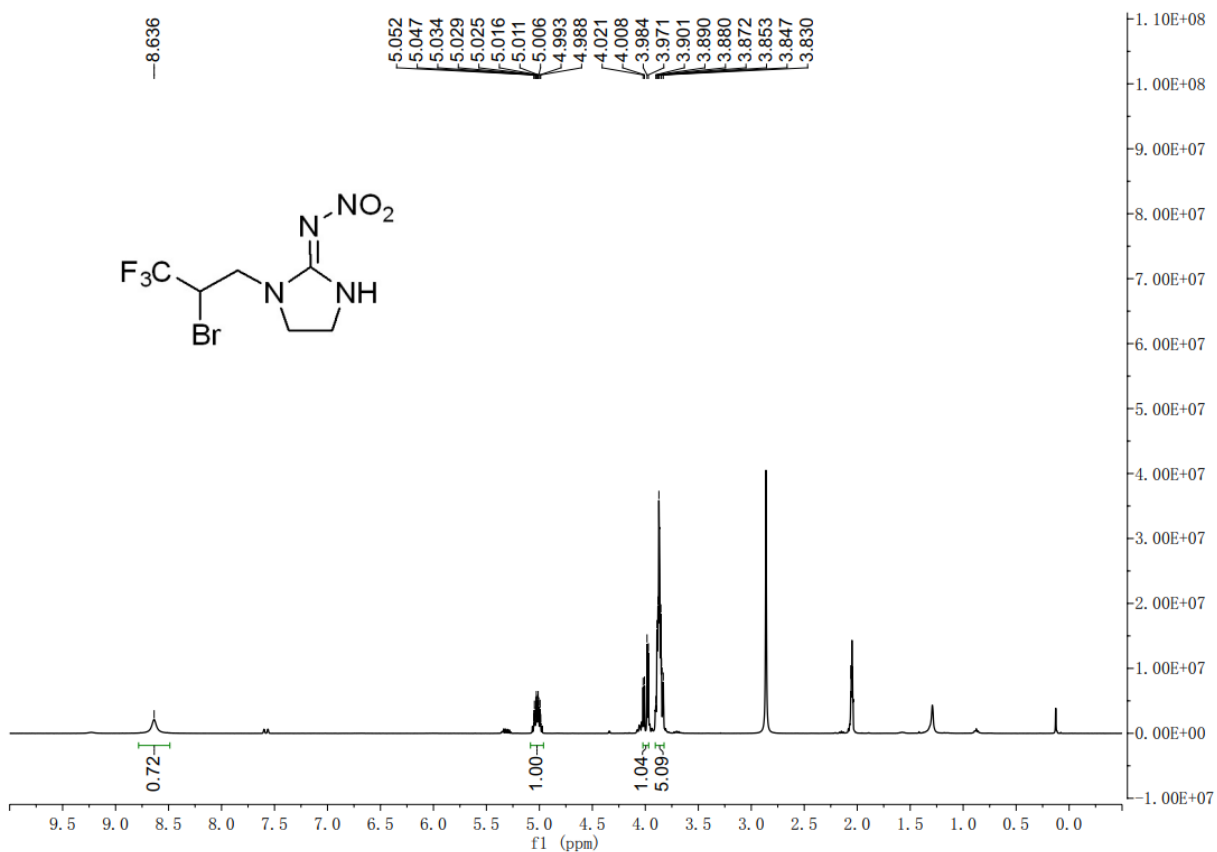


HRMS (EI) spectrum of 4xc

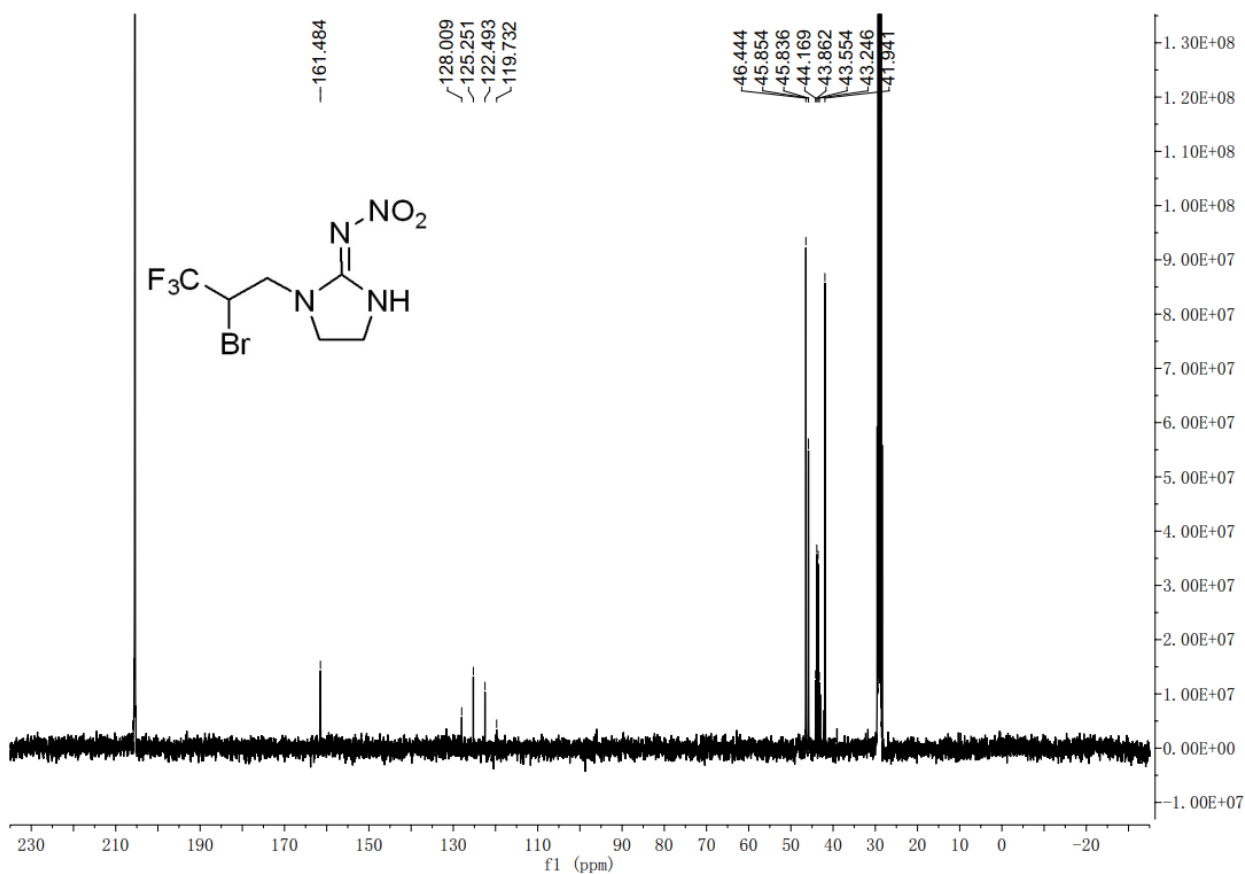
20222063 378 (6.303) Cm (378-(21+56))



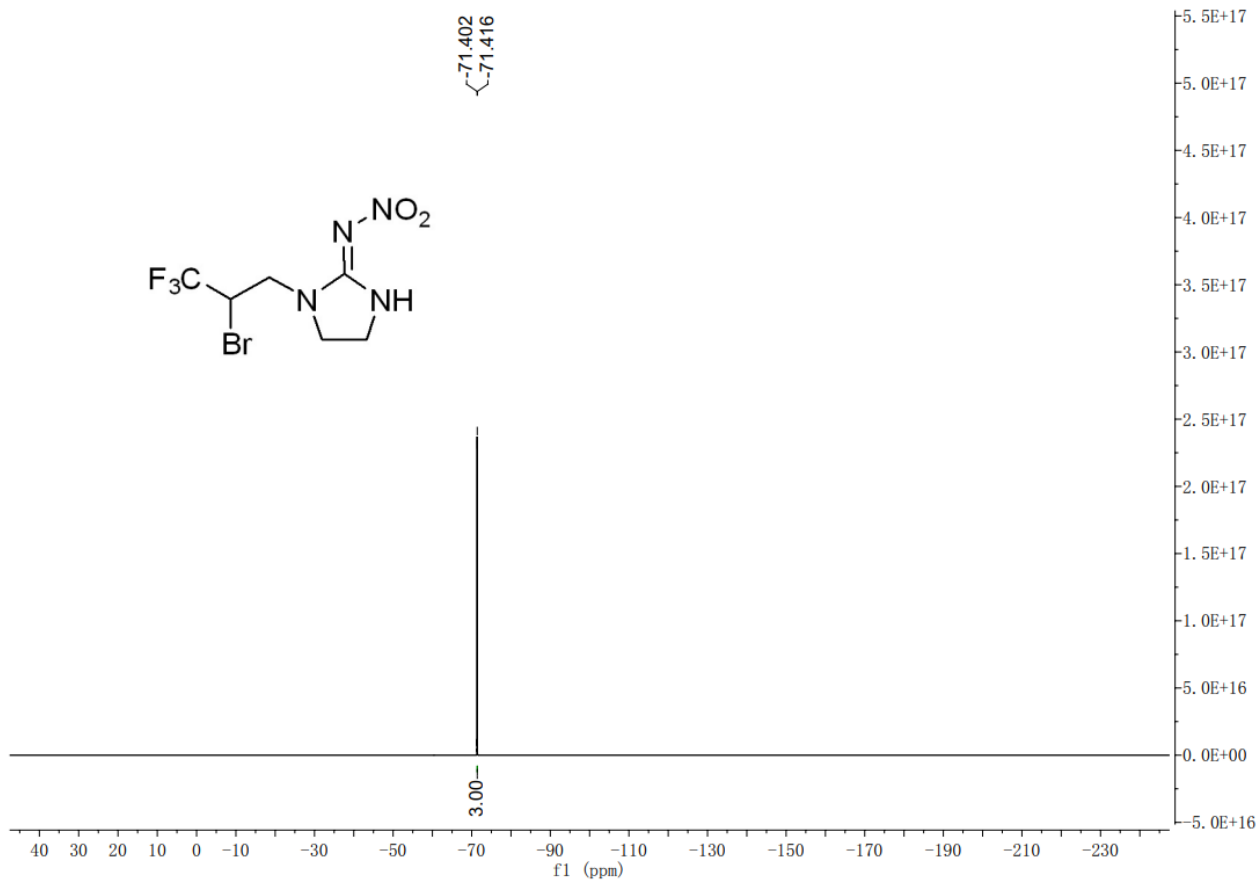
¹H NMR spectrum of 6 (400 MHz, acetone-*d*₆)



¹³C NMR spectrum of 6 (100 MHz, acetone-*d*₆)



^{19}F NMR spectrum of 6 (564 MHz, acetone- d_6)



HRMS (EI) spectrum of 6

20221832 377 (6.283) Cm (377-(19+114))

TOF MS EI+
1.84e4

