Supporting Information

A Convenient Synthesis of 1,2,4-Triazino[2,3-b]indazol-3-amine Derivatives via Tandem Abnormal-Staudinger/Aza-Wittig/Isomerization Reaction

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Contents

Table 1. Crystal data and structure refinement for **7a.**

Identification code	**7a**
Empirical formula	C17 H15 N5
Formula weight	289.34
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 9.2337(11) A alpha = 90 deg.
	b = 11.0390(13) A beta = 96.198(3) deg.
	c = 15.7307(16) A gamma = 90 deg.
Volume	1594.1(3) A^3
Z, Calculated density	4, 1.206 Mg/m^3
Absorption coefficient	0.076 mm^-1
F(000)	608
Crystal size	0.14 x 0.06 x 0.05 mm
Theta range for data collection	2.22 to 25.02 deg.
Limiting indices	-10<=h<=10, 0<=k<=13, 0<=l<=18
Reflections collected / unique	2789 / 2789 [R(int) = 0.0000]
Completeness to theta = 25.02	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9962 and 0.9894
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters	2789 / 0 / 201
Goodness-of-fit on F^2	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0945, wR2 = 0.1382
R indices (all data)	R1 = 0.2931, wR2 = 0.1754
Largest diff. peak and hole	0.260 and -0.199 e.A^-3

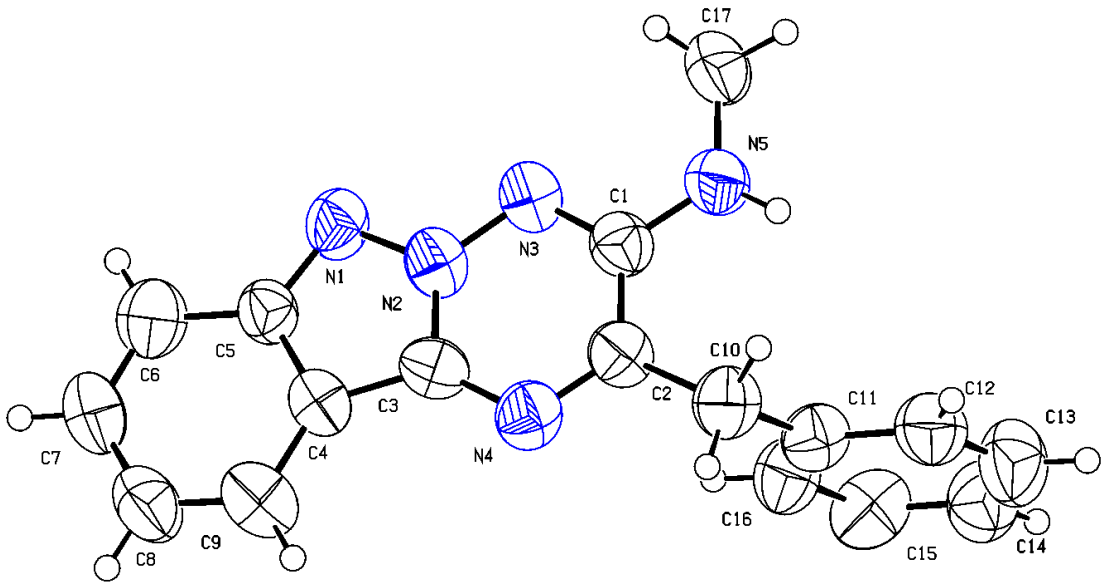
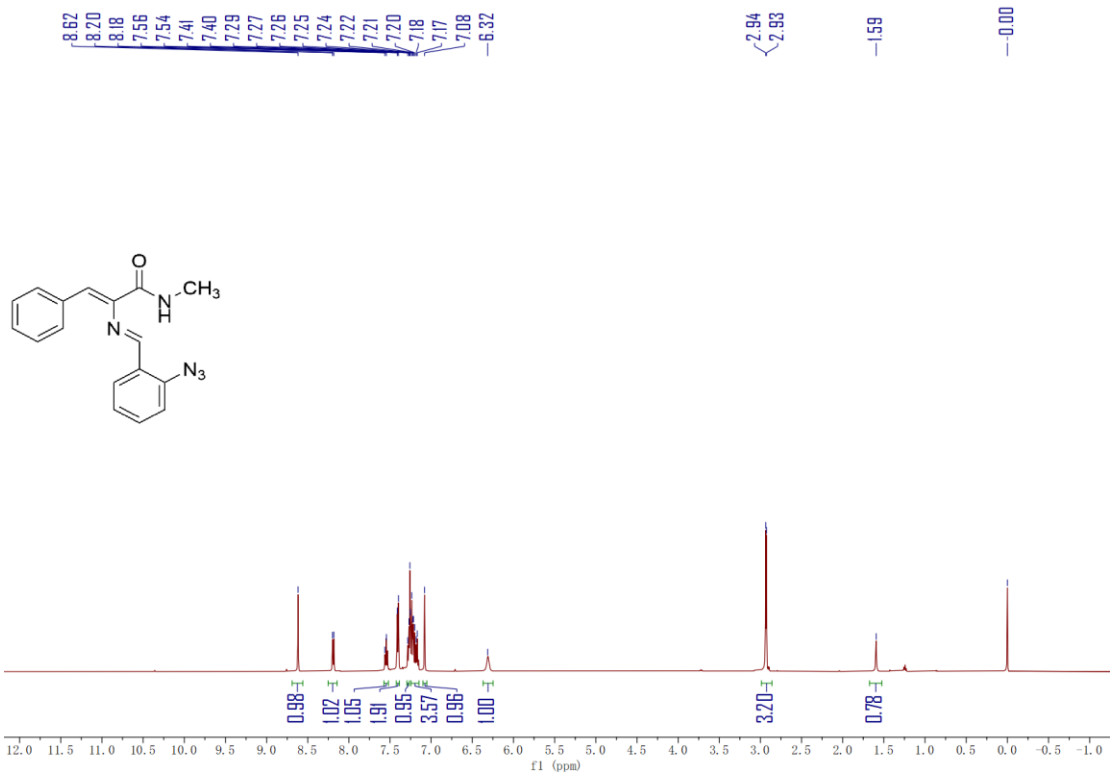
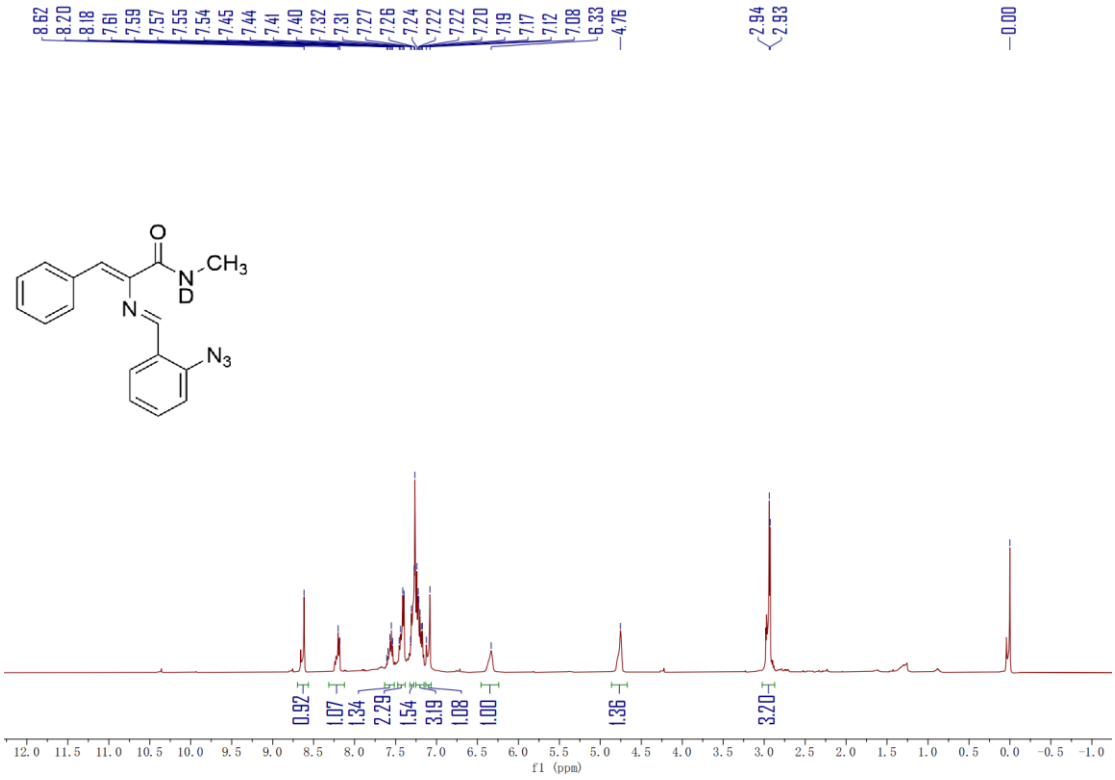


Figure 1 X-ray structures of **7a** CCDC 2281905

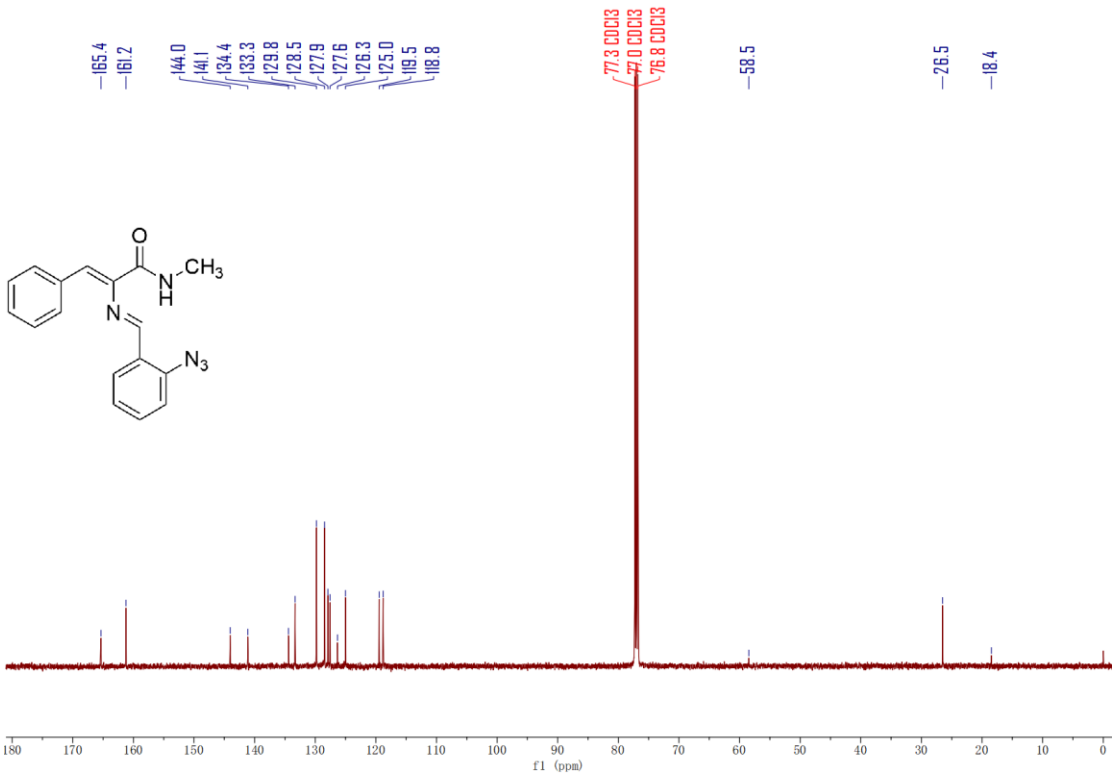
^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound 3a:



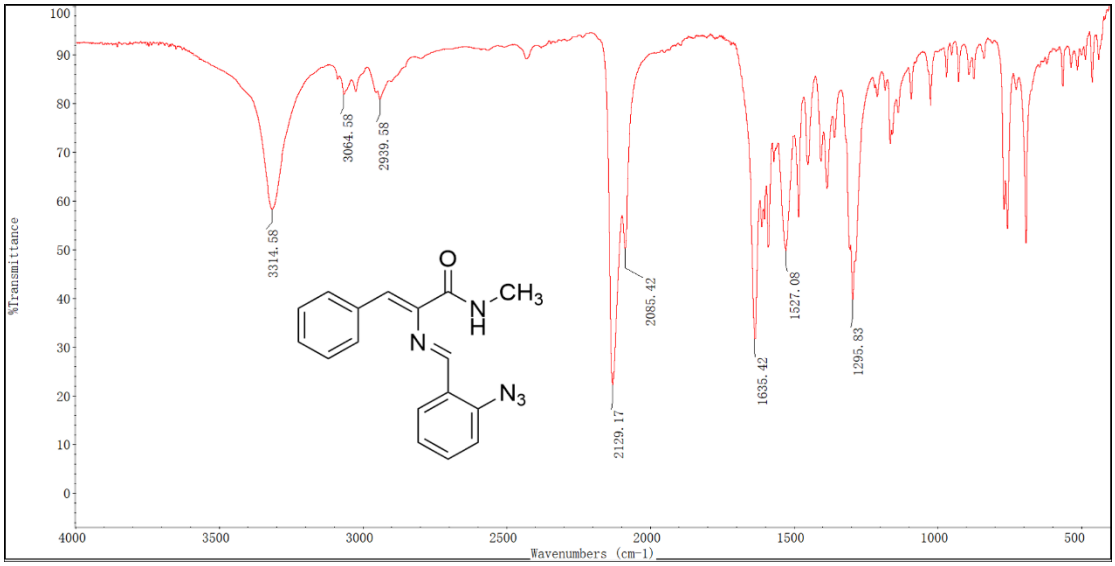
^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound 3a+D_2O



^{13}C NMR (126 MHz,$CDCl_3$) spectra of compound 3a:



IR(3a):

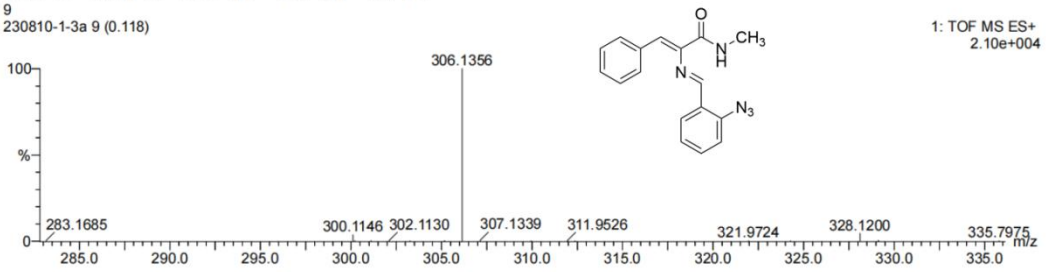


HRMS(3a):

Elemental Composition Report **Page 1**

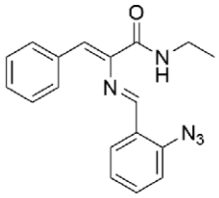
Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

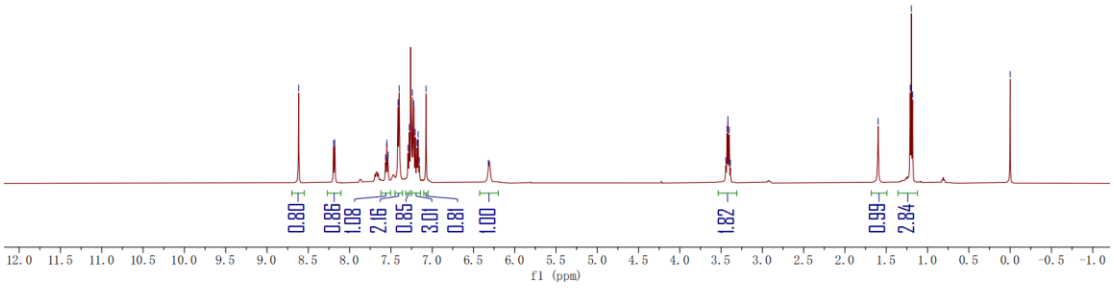
Monoisotopic Mass, Even Electron Ions
385 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 17-17 H: 16-16 N: 0-100 O: 0-100 Na: 0-1
9
230810-1-3a 9 (0.118)



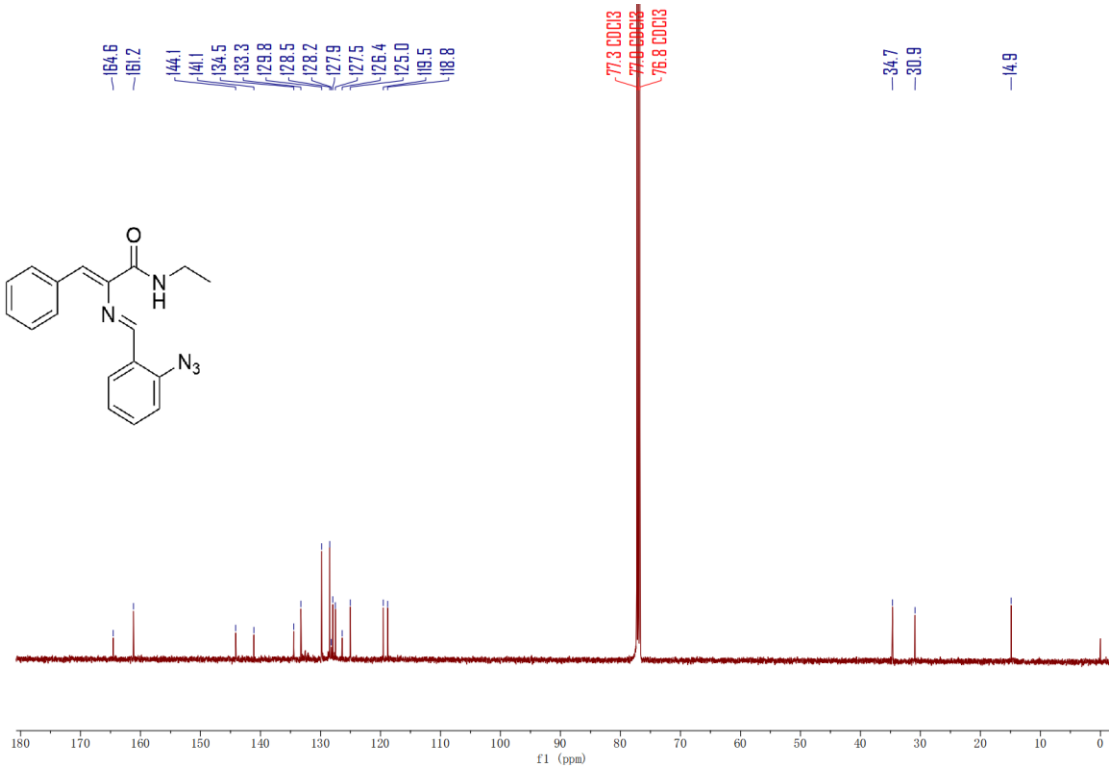
Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
306.1356	306.1355	0.1	0.3	12.5	29.9	n/a	n/a	C17 H16 N5 O

^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound 3b:

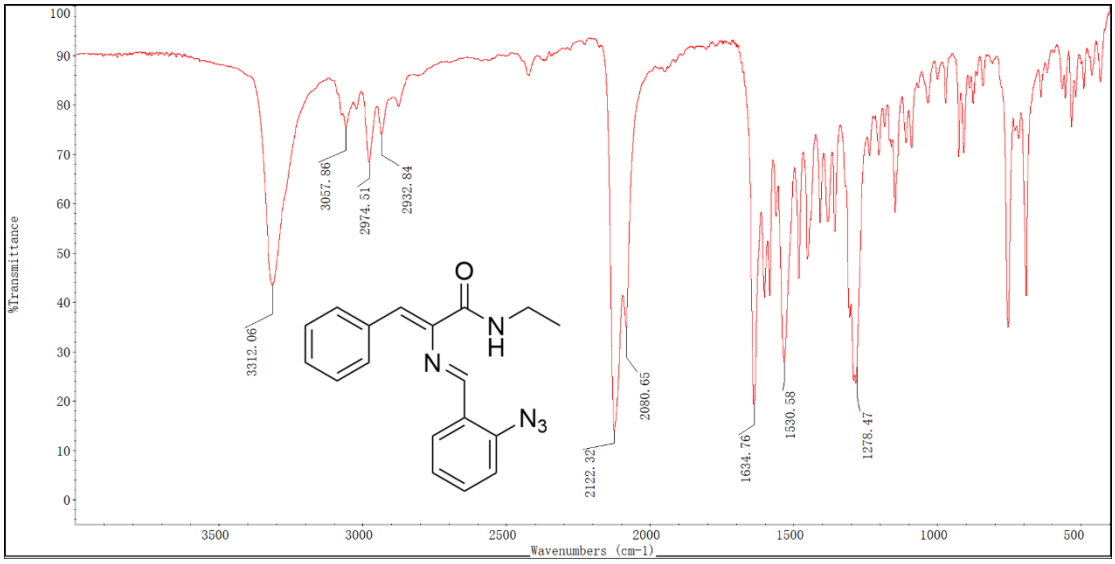




^{13}C NMR (126 MHz,$CDCl_3$) spectra of compound 3b:



IR(3b):

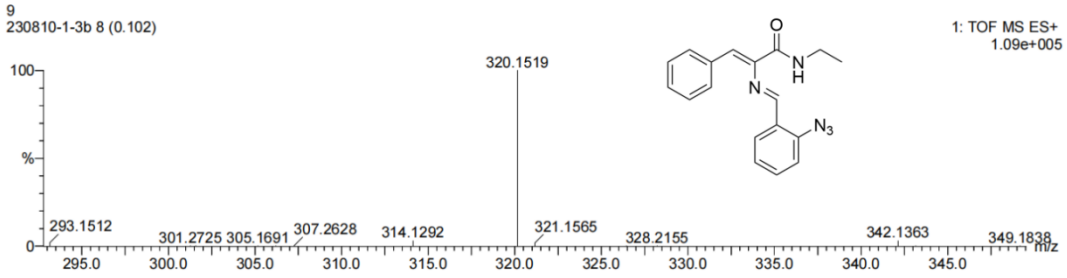


HRMS(3b):

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

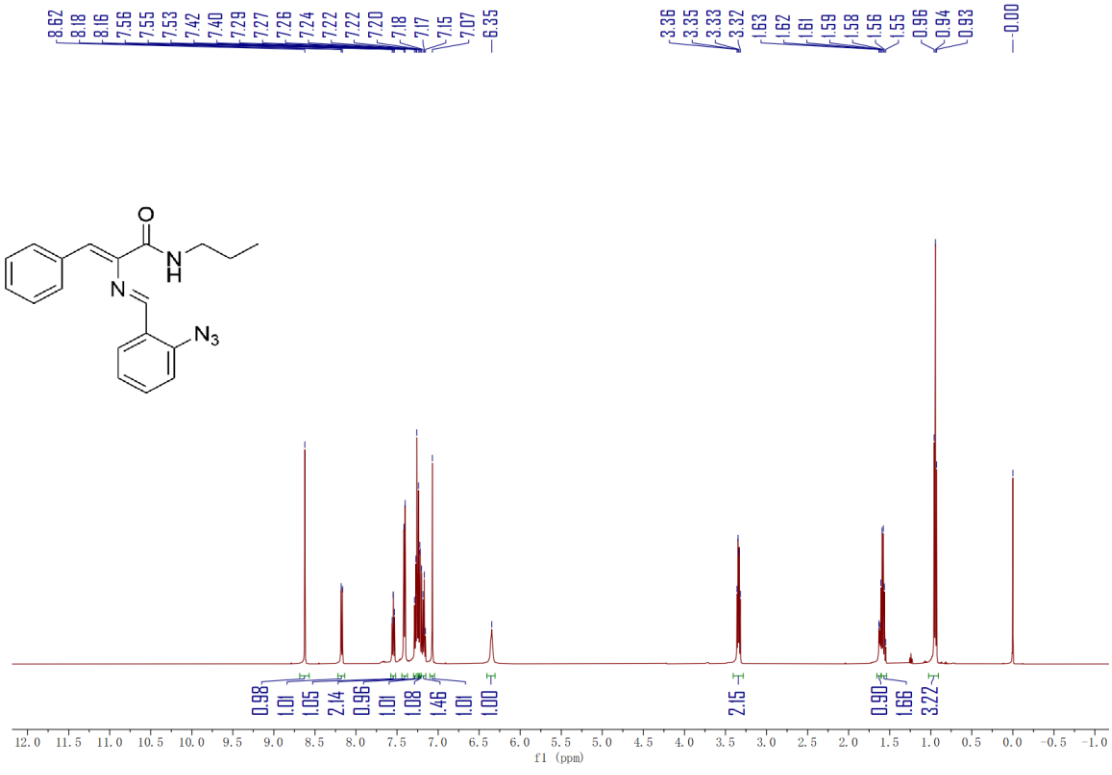
Monoisotopic Mass, Even Electron Ions
422 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 18-18 H: 18-18 N: 0-100 O: 0-100 Na: 0-1
9
230810-1-3b 8 (0.102)



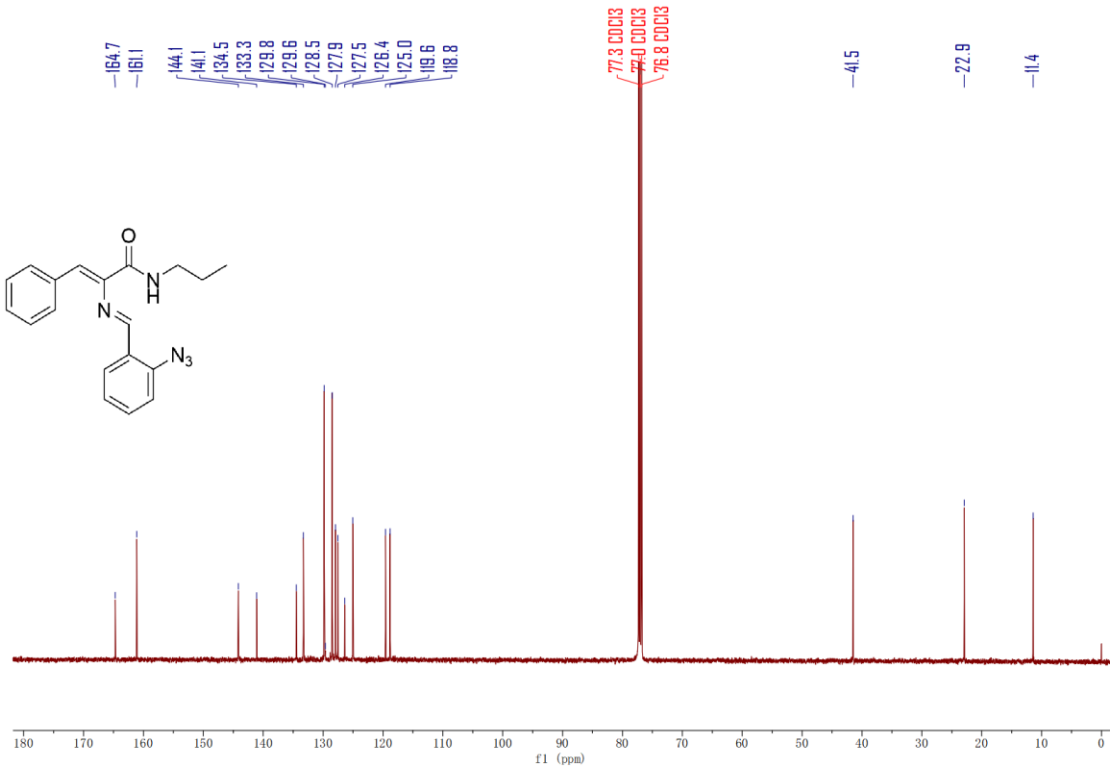
Minimum:			-1.5	
Maximum:		5.0	20.0	50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
320.1519	320.1511	0.8	2.5	12.5	33.8	n/a	n/a	C18 H18 N5 O

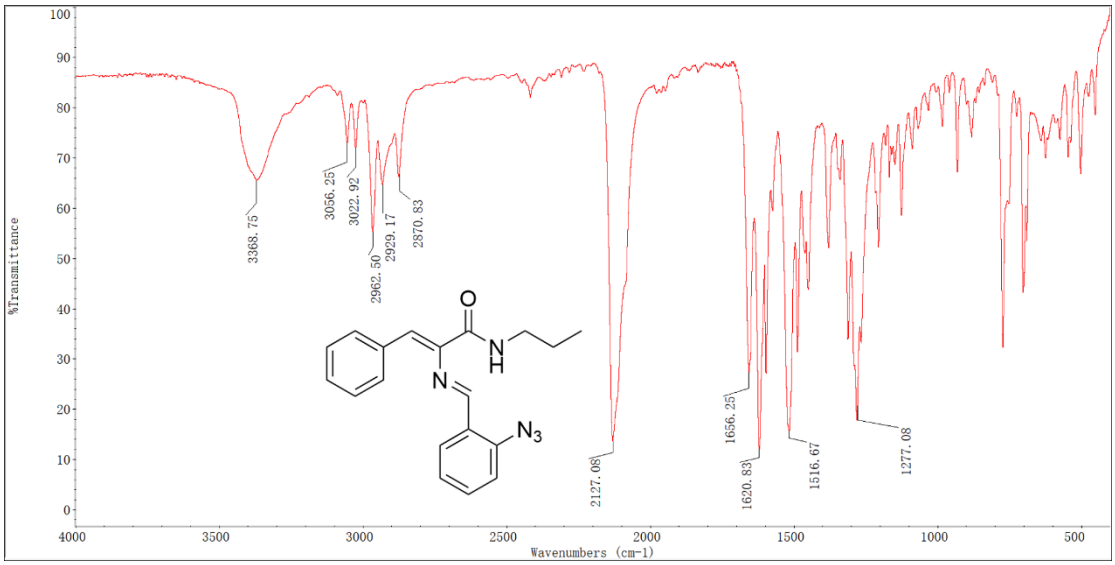
^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound 3c:



^{13}C NMR (126 MHz,$CDCl_3$) spectra of compound 3c:



IR(3c):

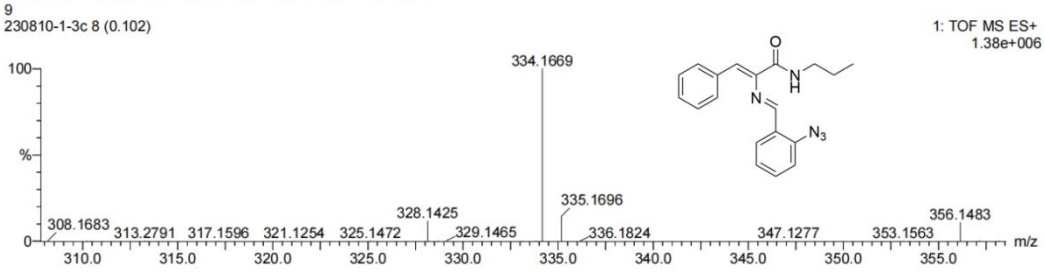


HRMS(3c):

Elemental Composition Report **Page 1**

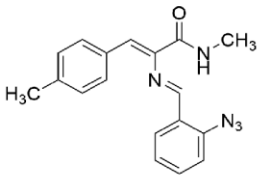
Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

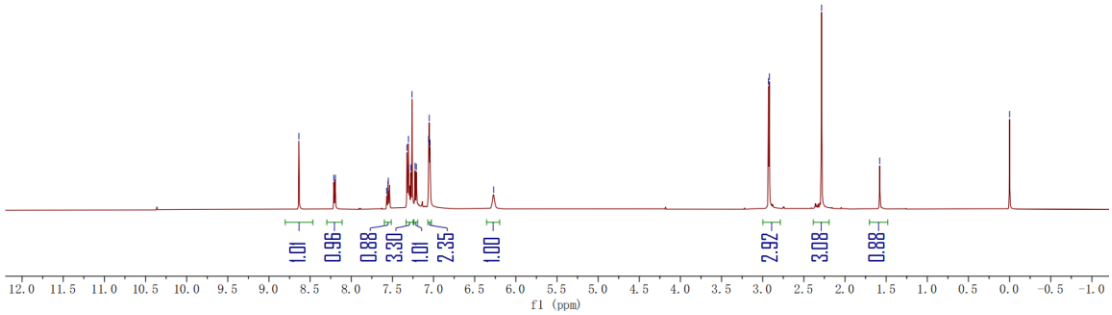
Monoisotopic Mass, Even Electron Ions
459 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 19-19 H: 20-20 N: 0-100 O: 0-100 Na: 0-1
9
230810-1-3c 8 (0.102)



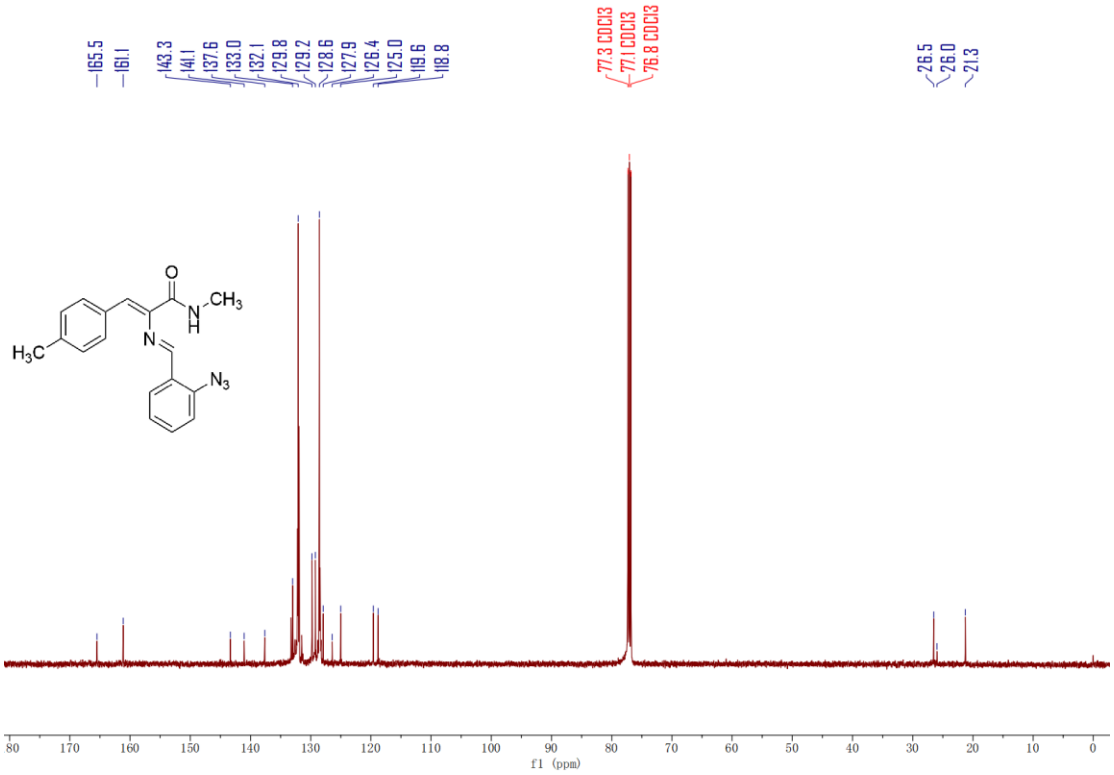
Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
334.1669	334.1668	0.1	0.3	12.5	48.3	n/a	n/a	C19 H20 N5 O

^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound 3d:





^{13}C NMR (126 MHz,$CDCl_3$) spectra of compound 3d:



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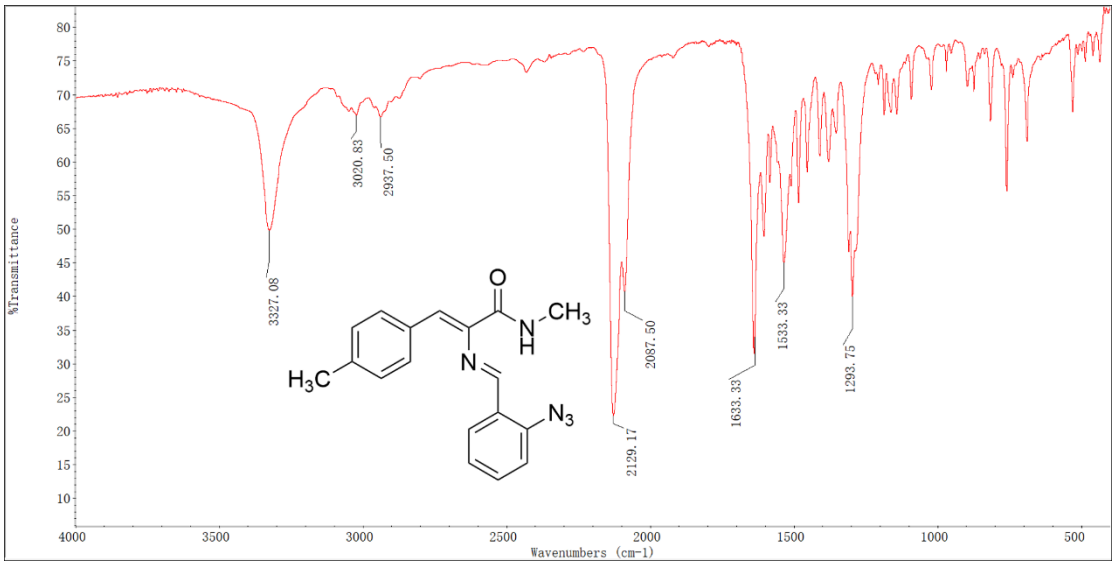
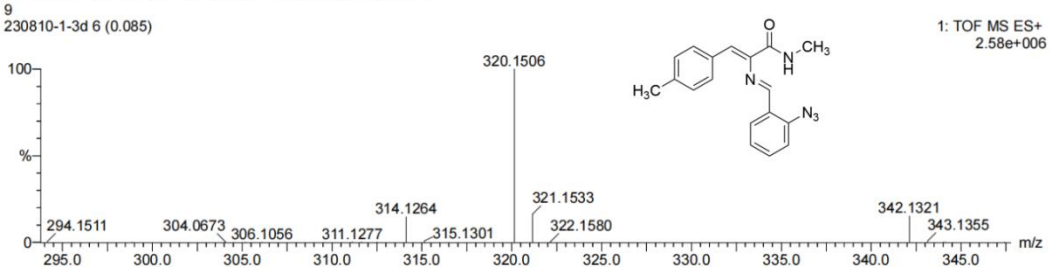


HRMS(3d):

Elemental Composition Report **Page 1**

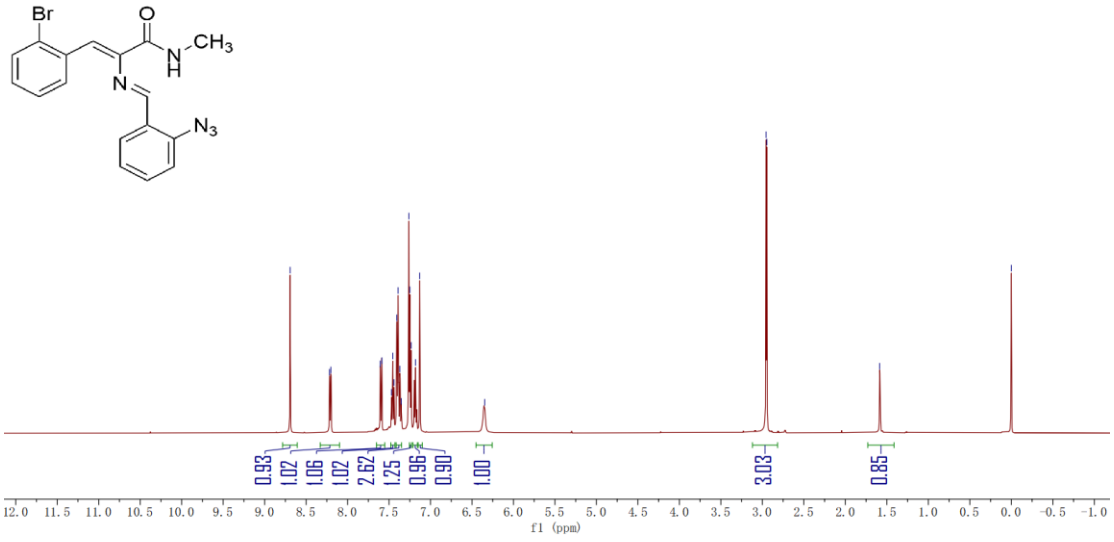
Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
422 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 18-18 H: 18-18 N: 0-100 O: 0-100 Na: 0-1
9
230810-1-3d 6 (0.085)

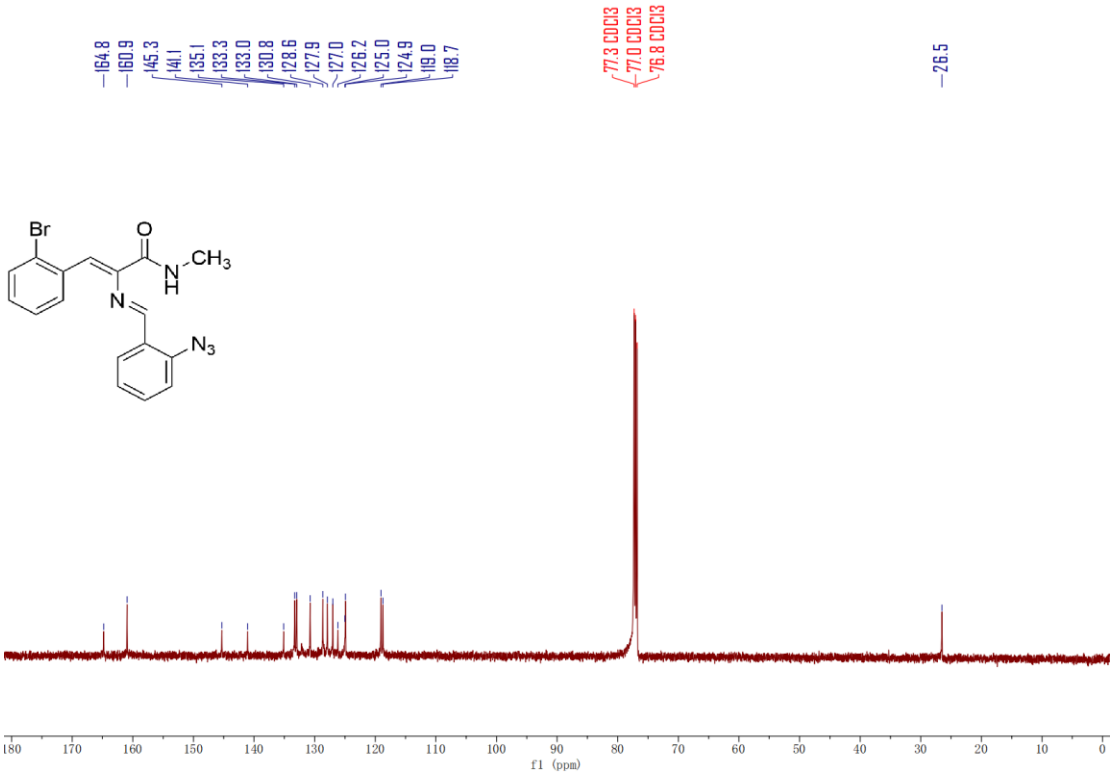


Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
320.1506	320.1511	-0.5	-1.6	12.5	44.1	n/a	n/a	C18 H18 N5 O

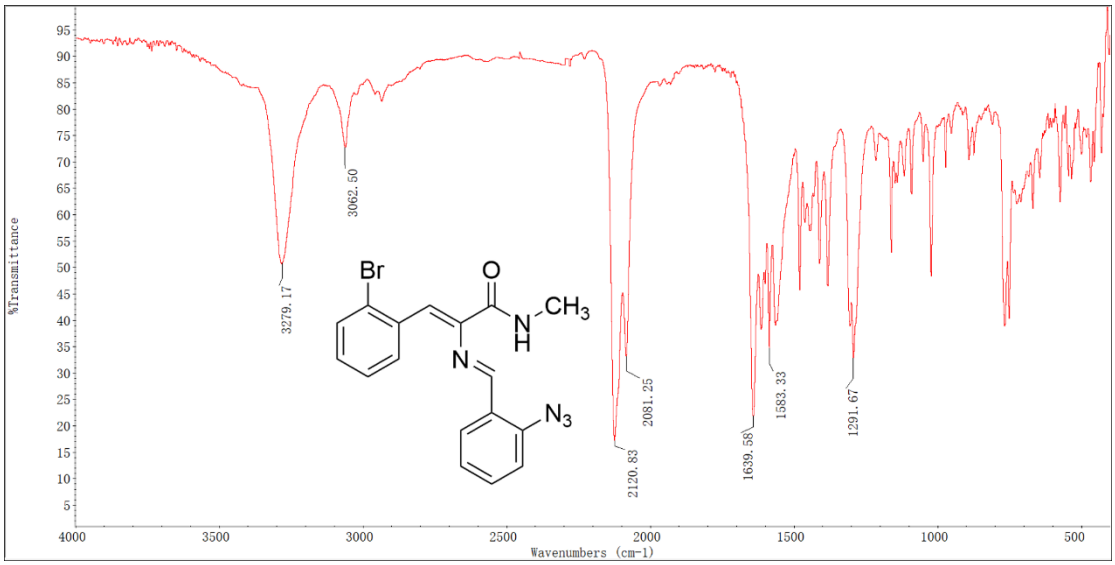
^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound 3e:



^{13}C NMR (126 MHz,$CDCl_3$) spectra of compound 3e:



IR of compound 3e:



HRMS(3e):

Elemental Composition Report **Page 1**

Single Mass Analysis
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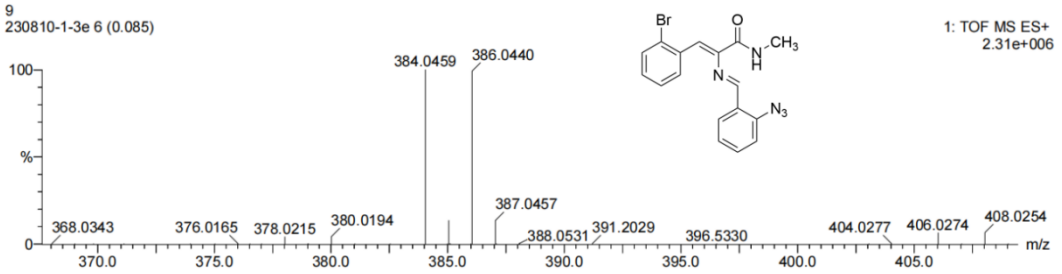
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

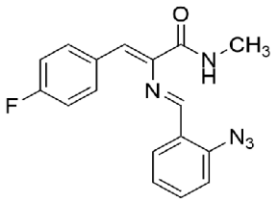
Monoisotopic Mass, Even Electron Ions
718 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 17-17 H: 15-15 N: 0-100 O: 0-100 Na: 0-1 Br: 1-3

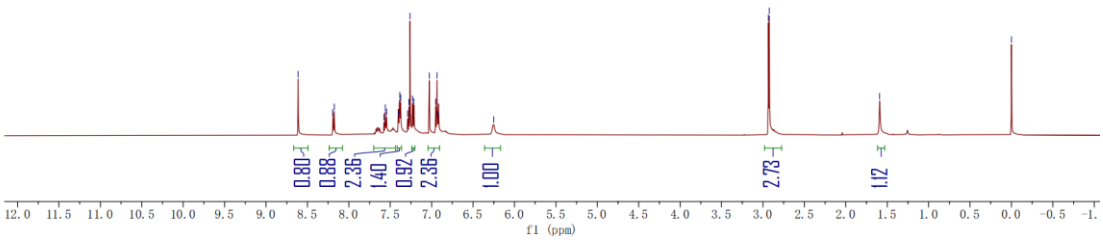
9
230810-1-3e 6 (0.085)



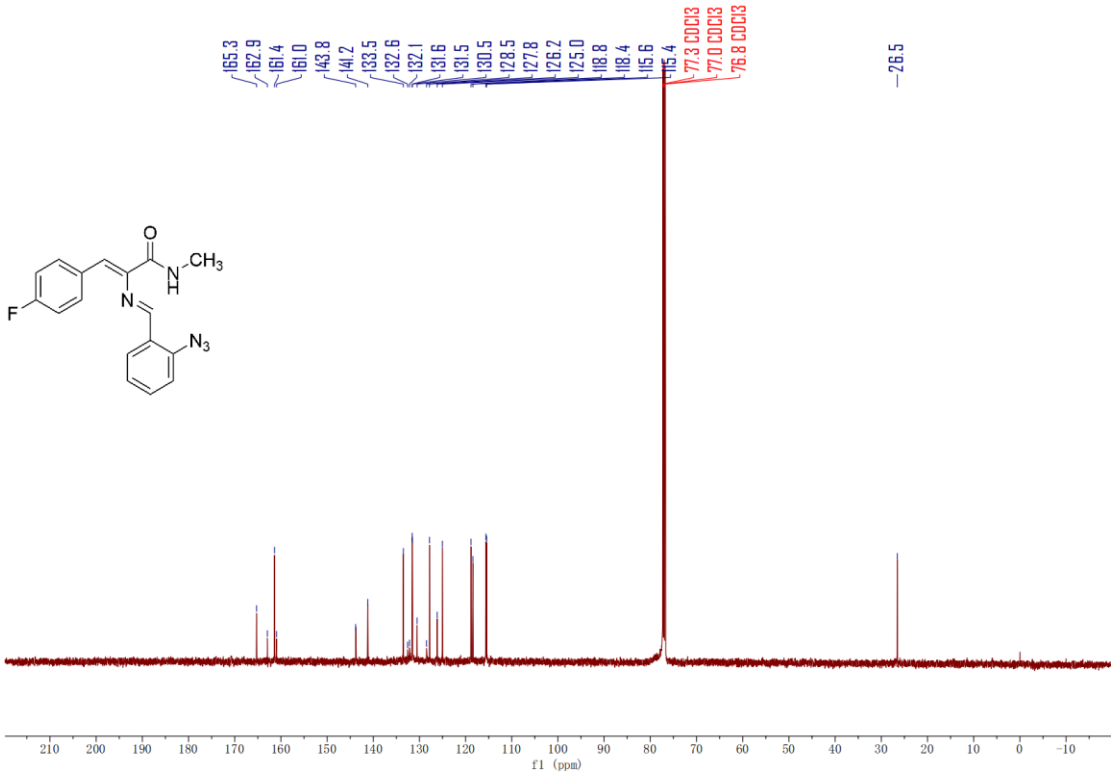
Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
384.0459	384.0460	-0.1	-0.3	12.5	57.8	n/a	n/a	C17 H15 N5 O Br

^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound 3f:

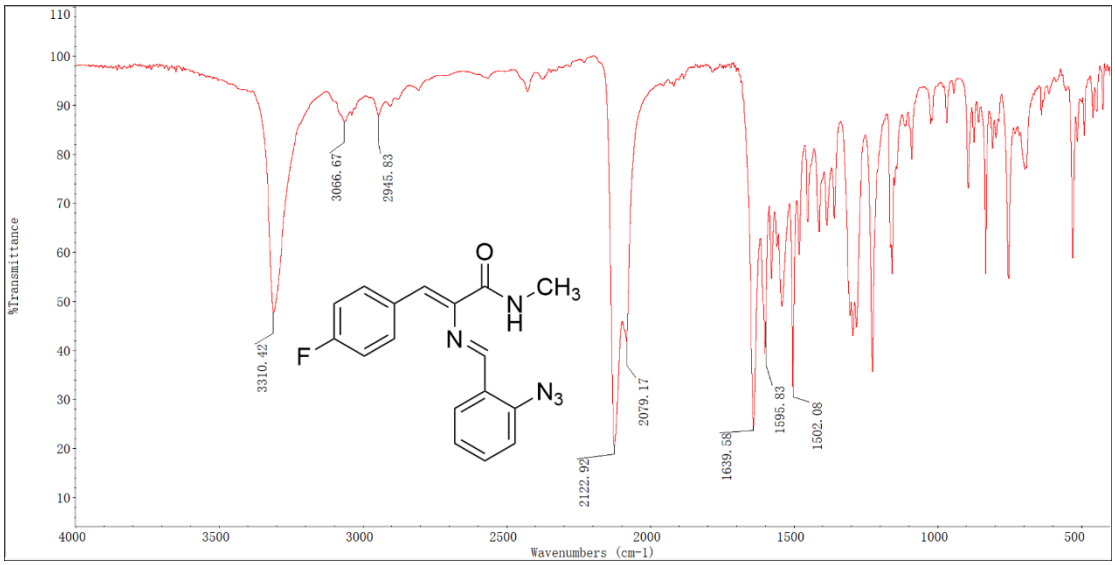




^{13}C NMR (126 MHz,$CDCl_3$) spectra of compound 3f:



IR of compound 3f:



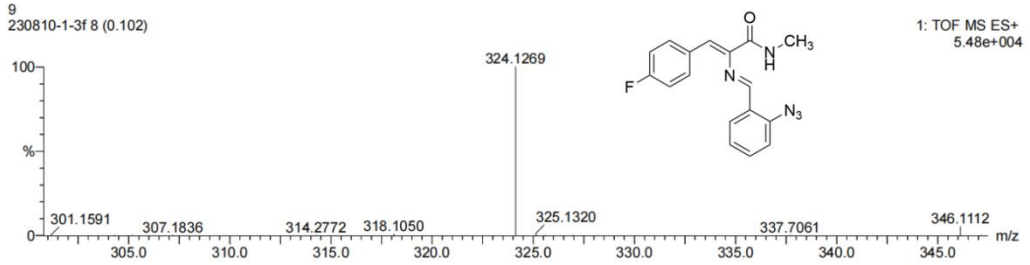
HRMS(3f):

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

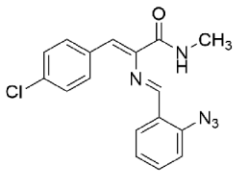
Monoisotopic Mass, Even Electron Ions
384 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 17-17 H: 15-15 N: 0-100 O: 0-100 Na: 0-1 F: 1-1

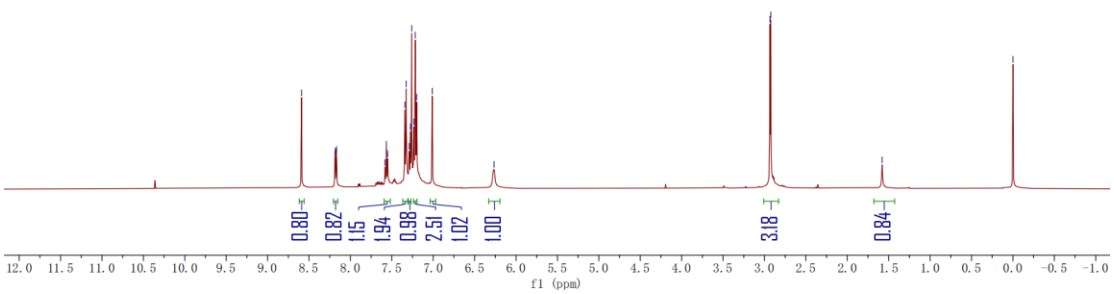
9
230810-1-3f 8 (0.102)



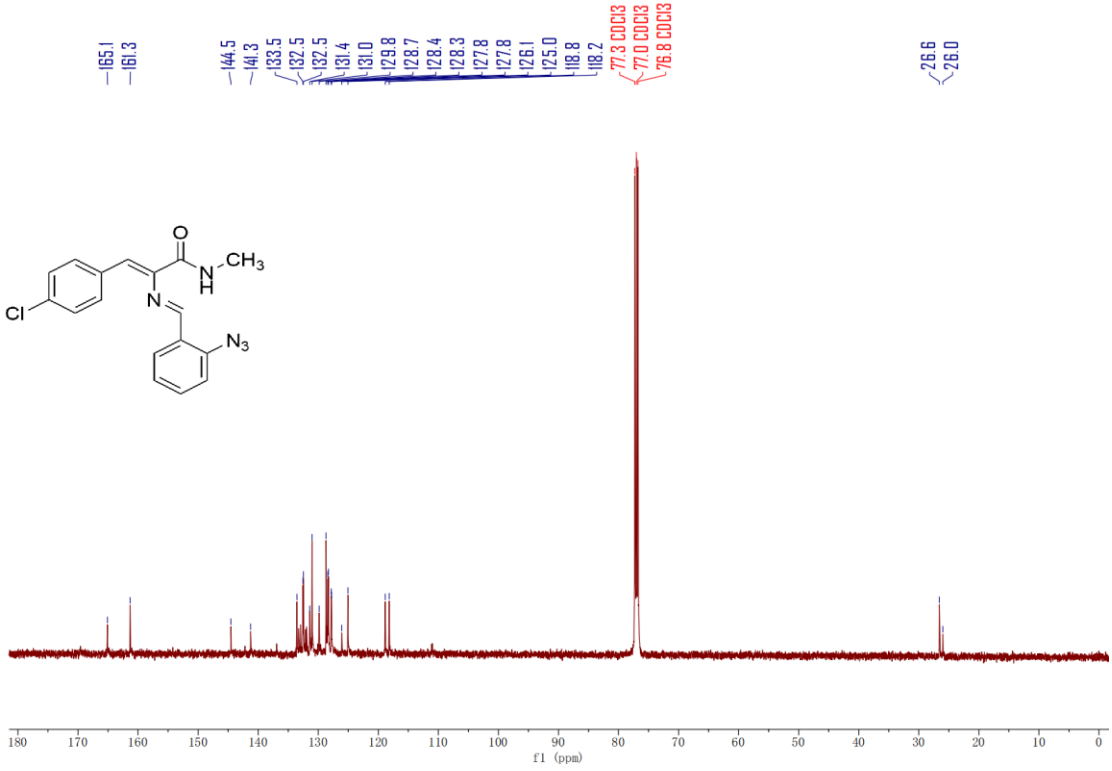
Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
324.1269	324.1261	0.8	2.5	12.5	43.7	n/a	n/a	C17 H15 N5 O F

^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound 3g:

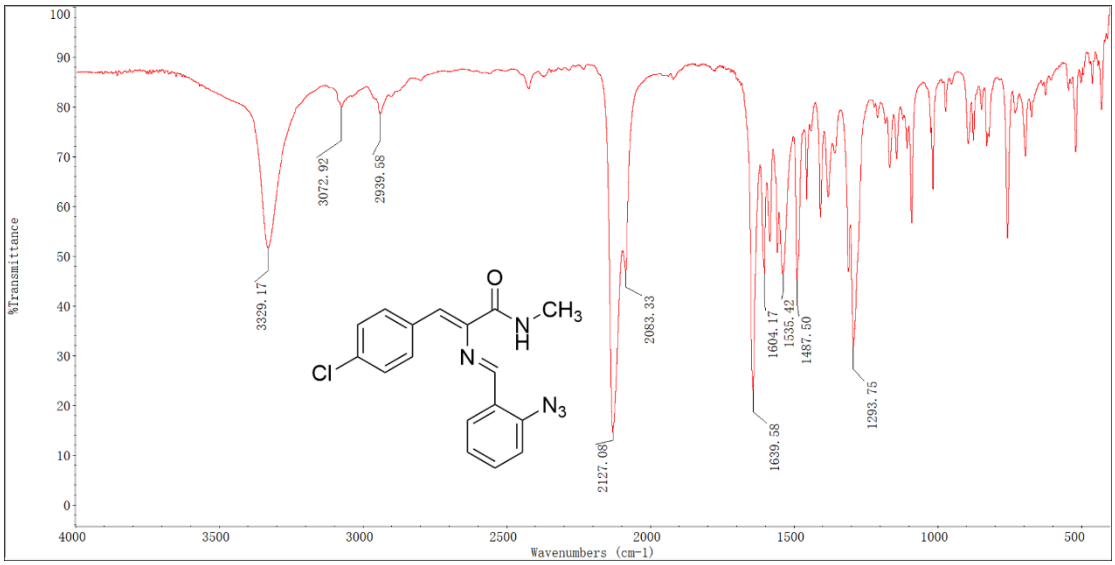




^{13}C NMR (126 MHz,$CDCl_3$) spectra of compound 3g:



IR of compound 3g:

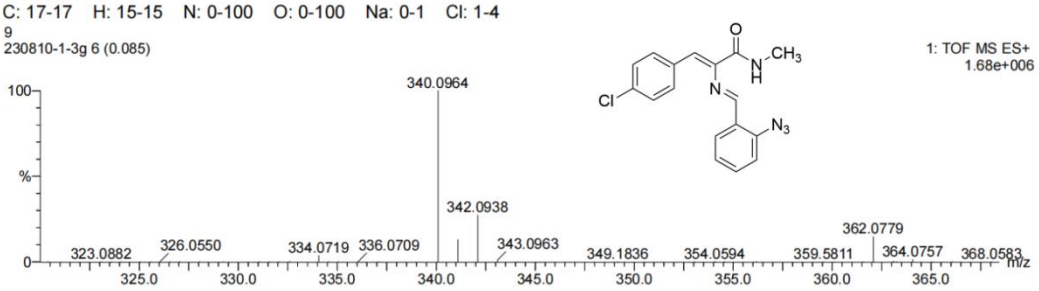


HRMS(3g):

Elemental Composition Report **Page 1**

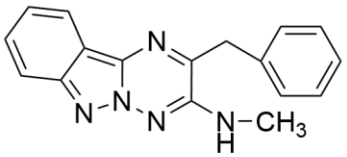
Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

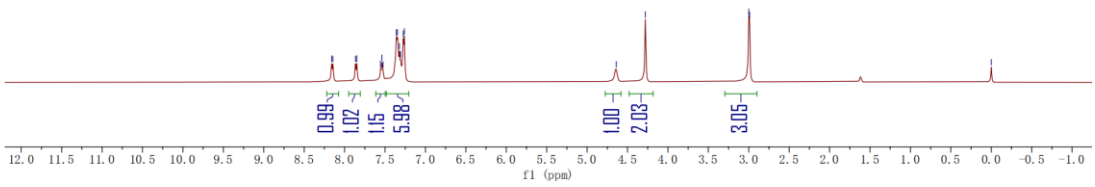
Monoisotopic Mass, Even Electron Ions
1129 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 17-17 H: 15-15 N: 0-100 O: 0-100 Na: 0-1 Cl: 1-4
9
230810-1-3g 6 (0.085)



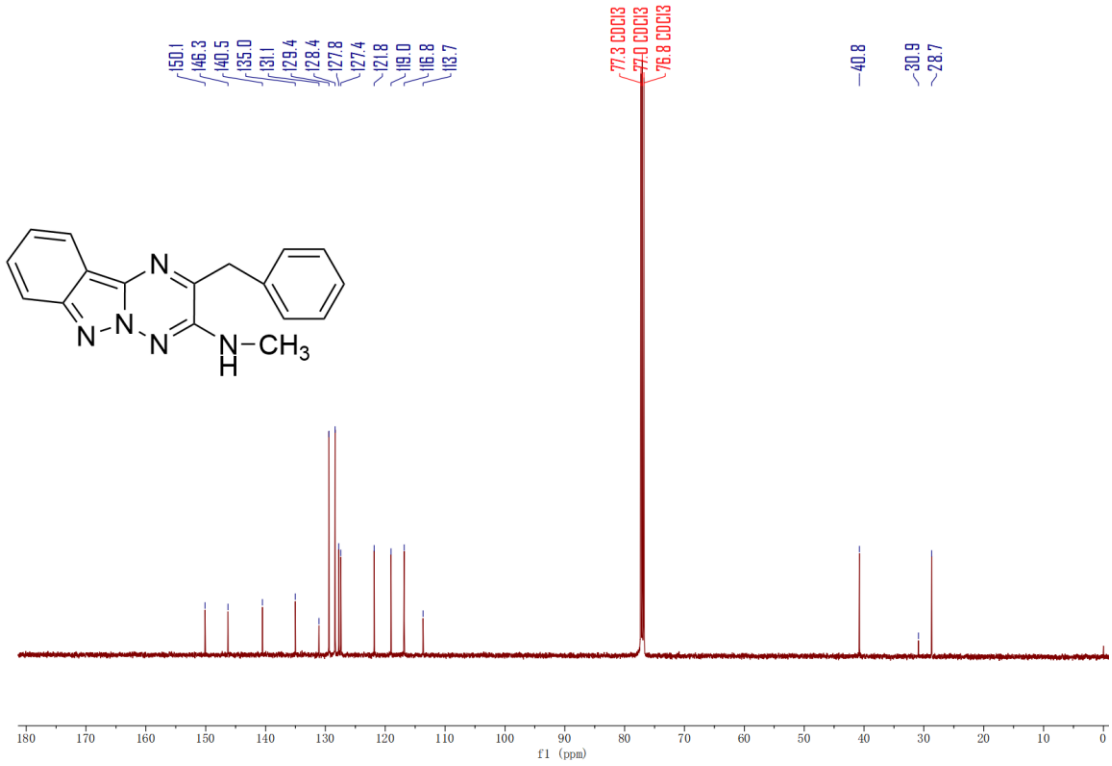
Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
340.0964	340.0965	-0.1	-0.3	12.5	29.1	n/a	n/a	C17 H15 N5 O Cl

^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound 7a:

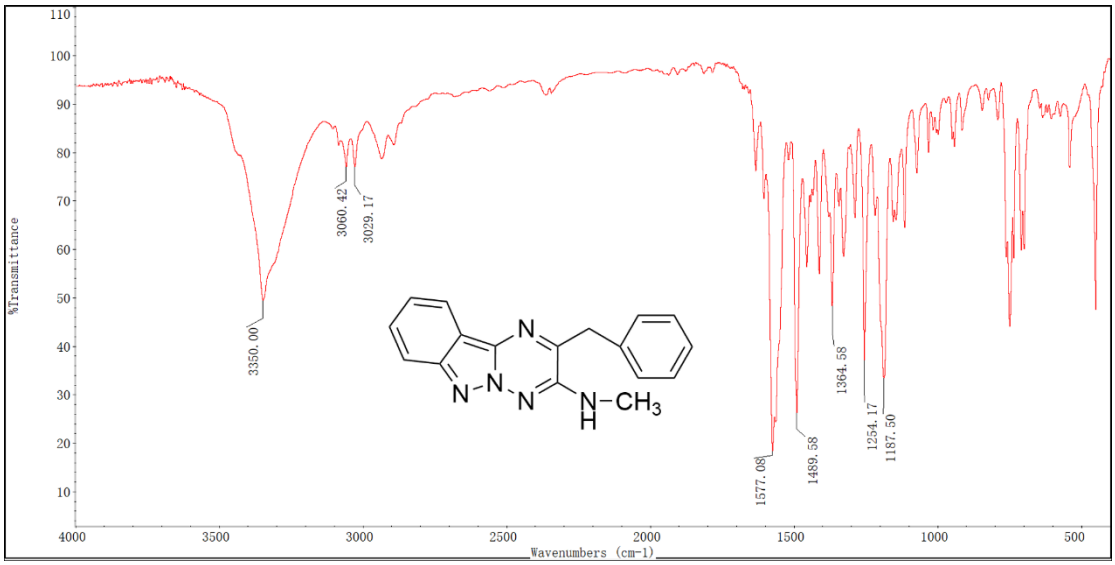




^{13}C NMR (126 MHz,$CDCl_3$) spectra of compound 7a:



IR(7a):



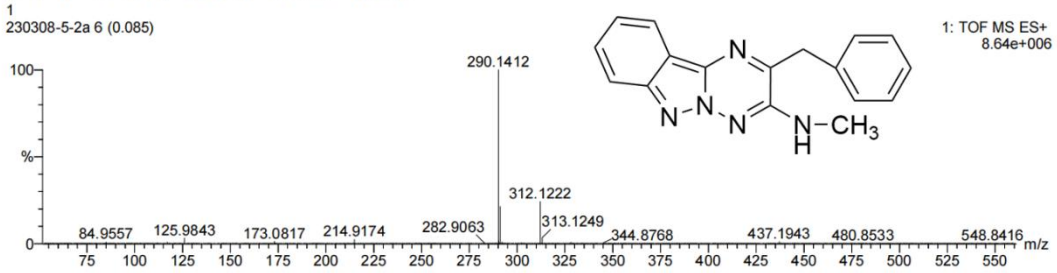
HRMS(7a):

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

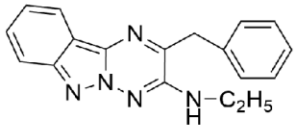
Monoisotopic Mass, Even Electron Ions
614 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 17-17 H: 16-16 N: 0-40 O: 0-40 Na: 0-3

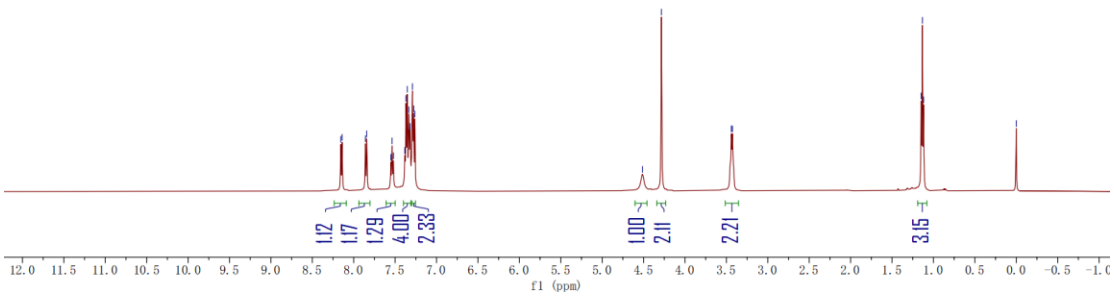
1
230308-5-2a 6 (0.085)



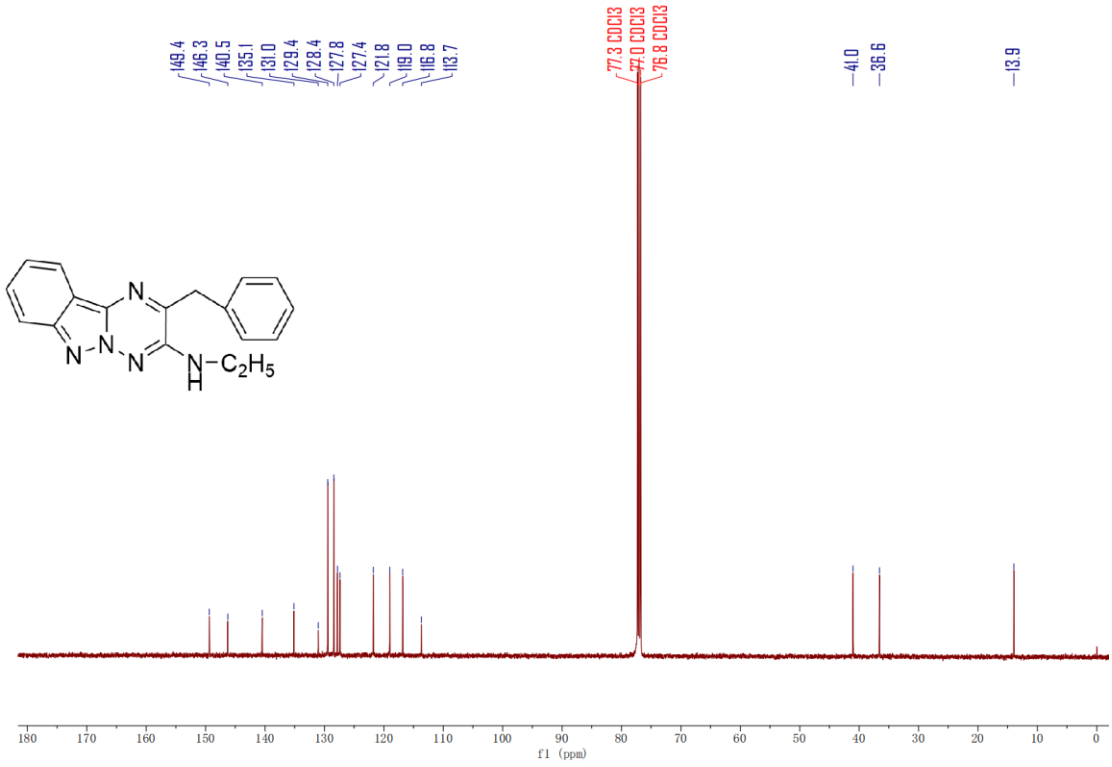
Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
290.1412	290.1406	0.6	2.1	12.5	379.4	n/a	n/a	C17 H16 N5

^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound 7b:

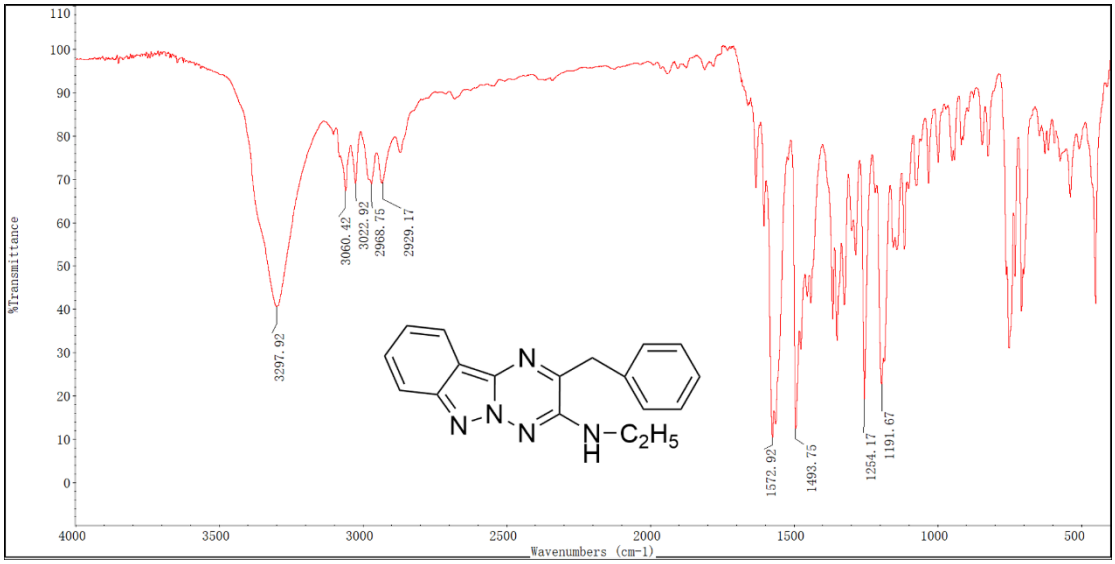




^{13}C NMR (126 MHz,$CDCl_3$) spectra of compound 7b:



IR of compound 7b:



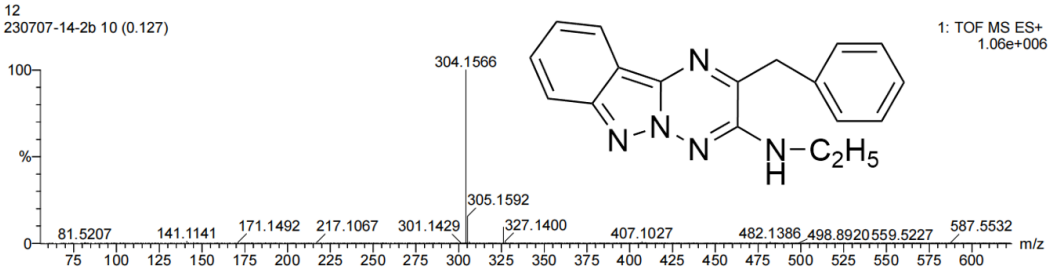
HRMS(7b):

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

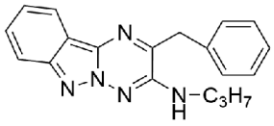
Monoisotopic Mass, Even Electron Ions
206 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 18-18 H: 18-18 N: 0-100 O: 0-100

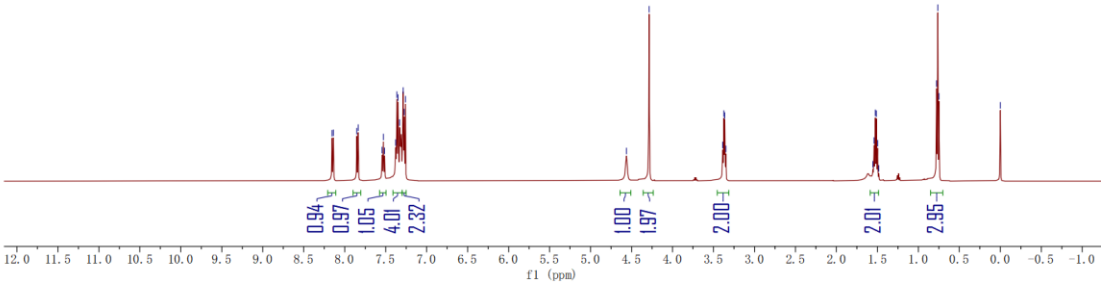
12
230707-14-2b 10 (0.127)



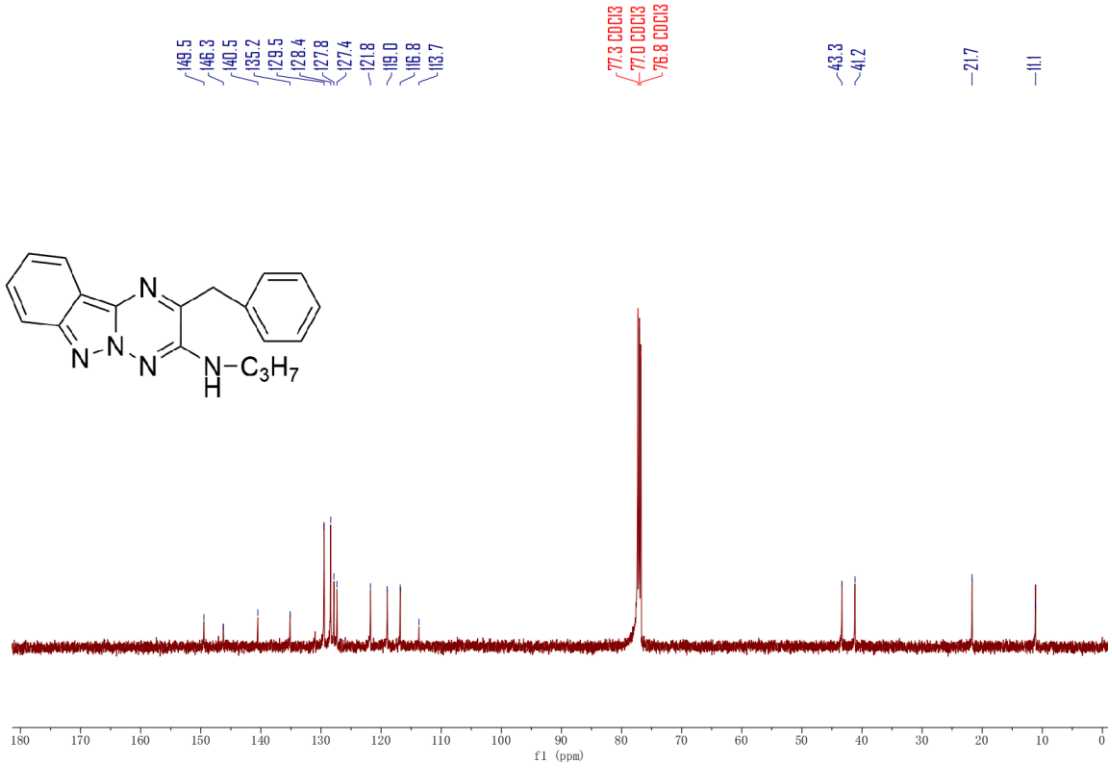
Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
304.1566	304.1562	0.4	1.3	12.5	260.0	n/a	n/a	C18 H18 N5

^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound 7c:

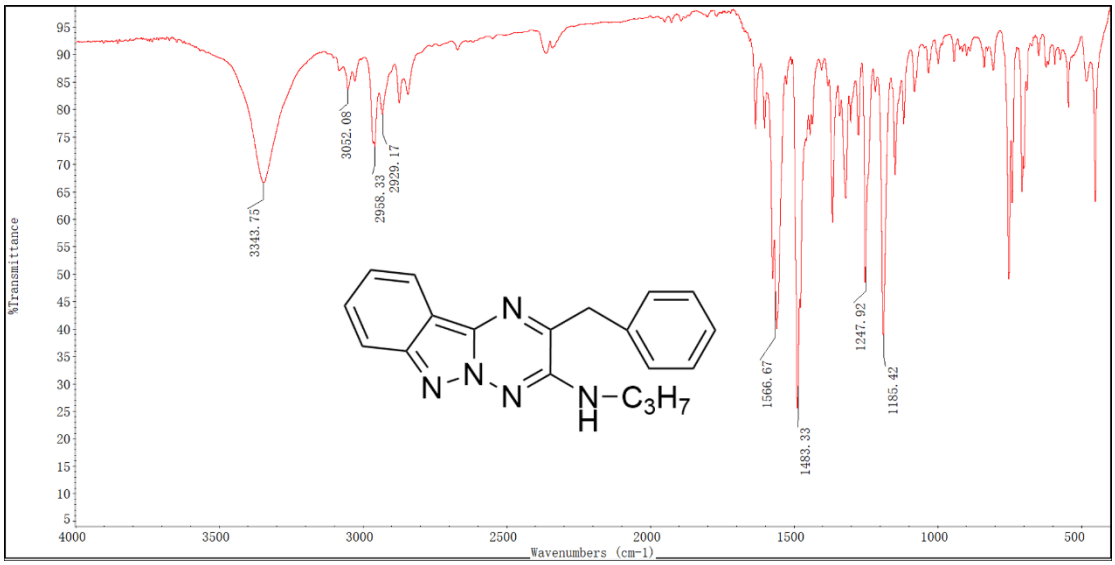




^{13}C NMR (126 MHz,$CDCl_3$) spectra of compound 7c:



IR of compound 7c:



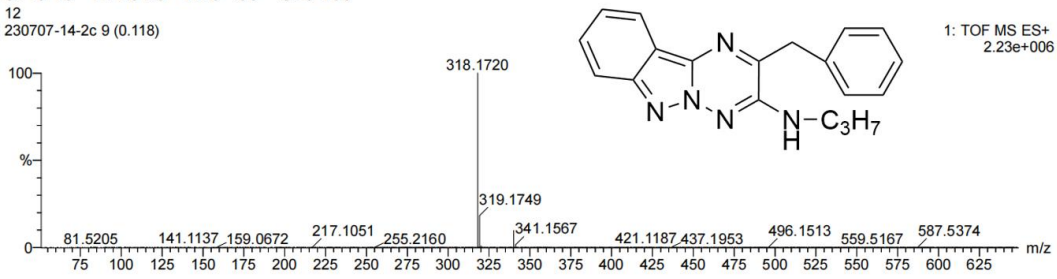
HRMS(7c):

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

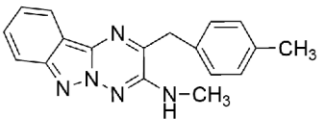
Monoisotopic Mass, Even Electron Ions
225 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 19-19 H: 20-20 N: 0-100 O: 0-100

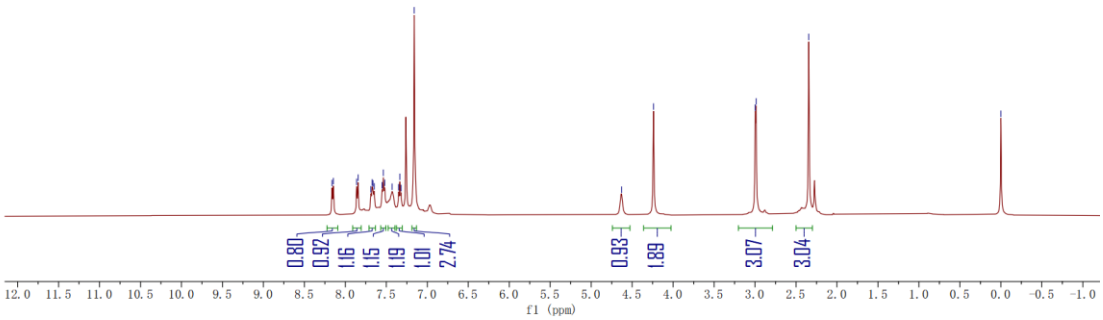
12
230707-14-2c 9 (0.118)



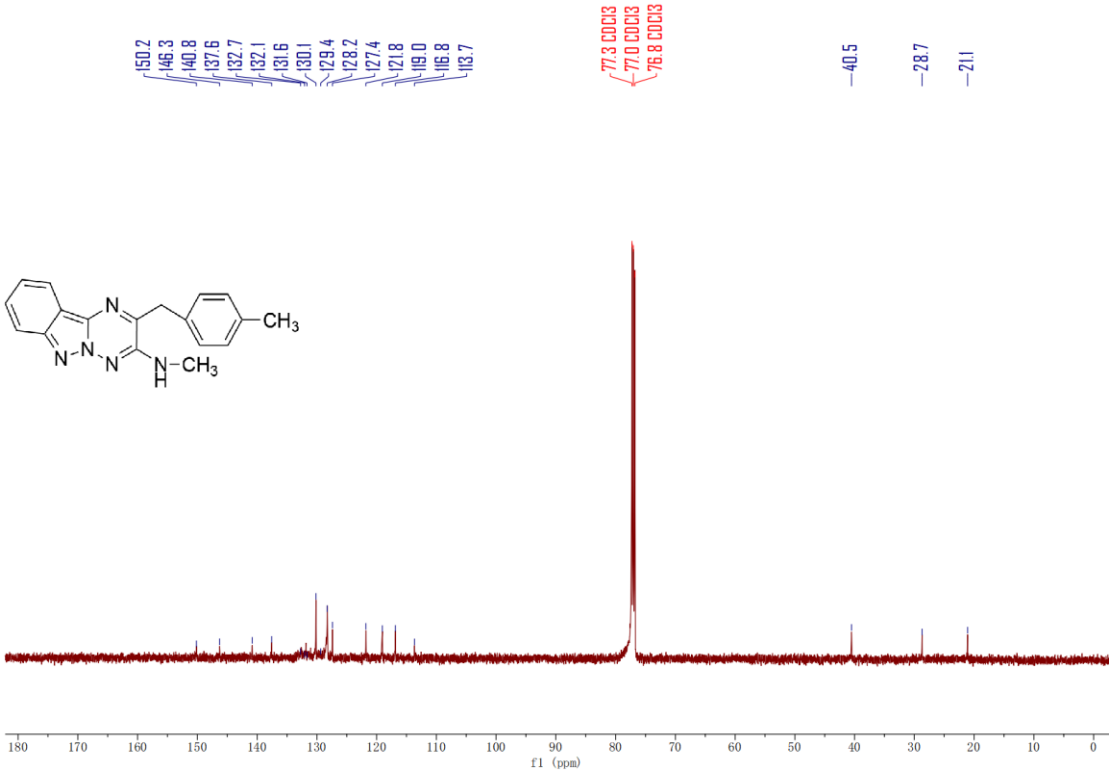
Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
318.1720	318.1719	0.1	0.3	12.5	328.6	n/a	n/a	C19 H20 N5

^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound 7d:

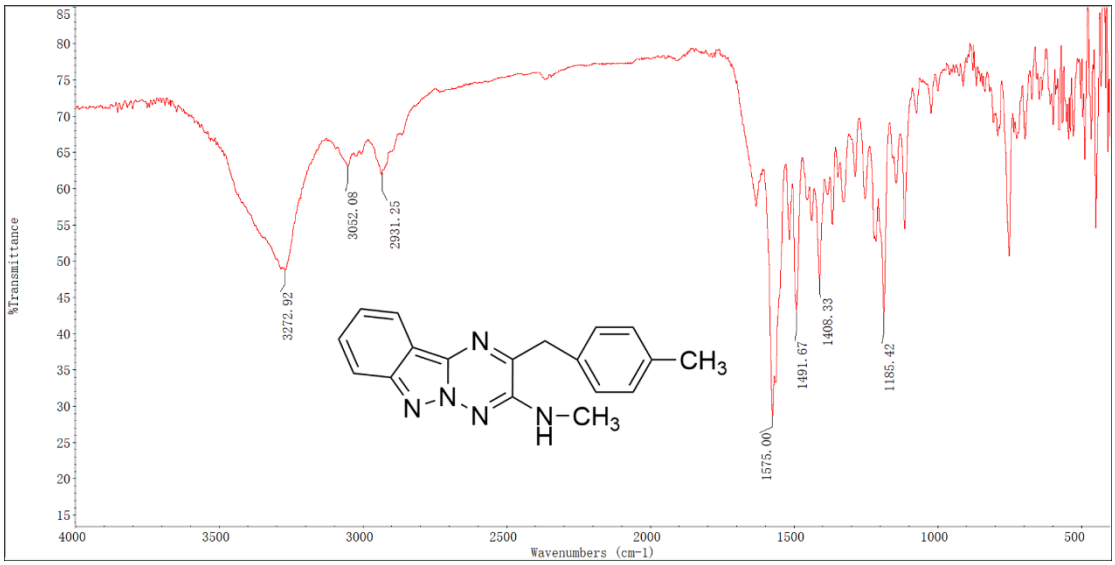




^{13}C NMR (126 MHz,$CDCl_3$) spectra of compound 7d:



IR of compound 7d:



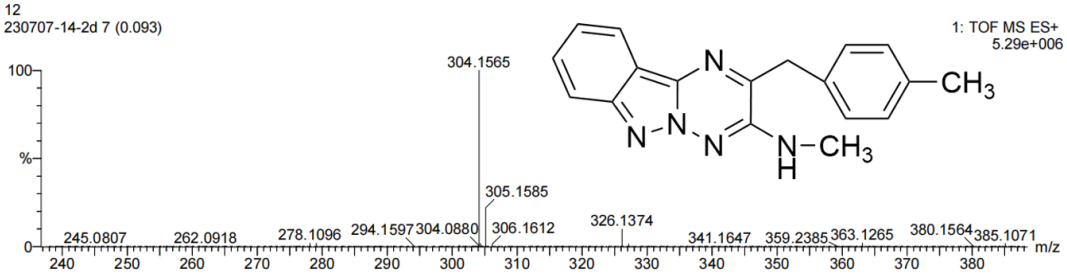
HRMS(7d):

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

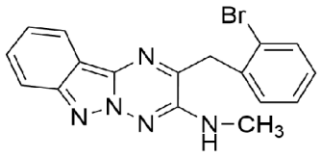
Monoisotopic Mass, Even Electron Ions
206 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 18-18 H: 18-18 N: 0-100 O: 0-100

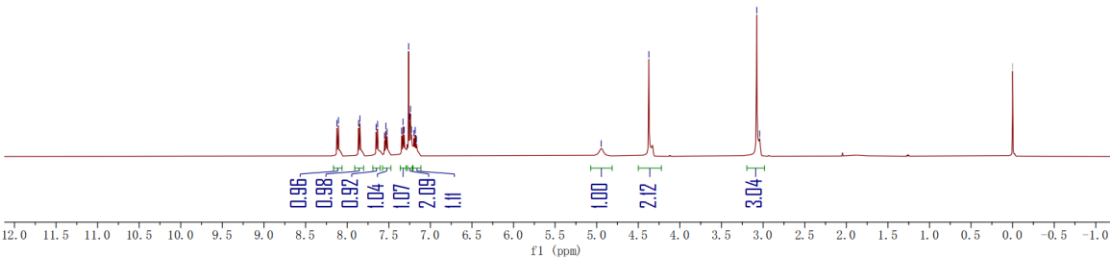
12
230707-14-2d 7 (0.093)



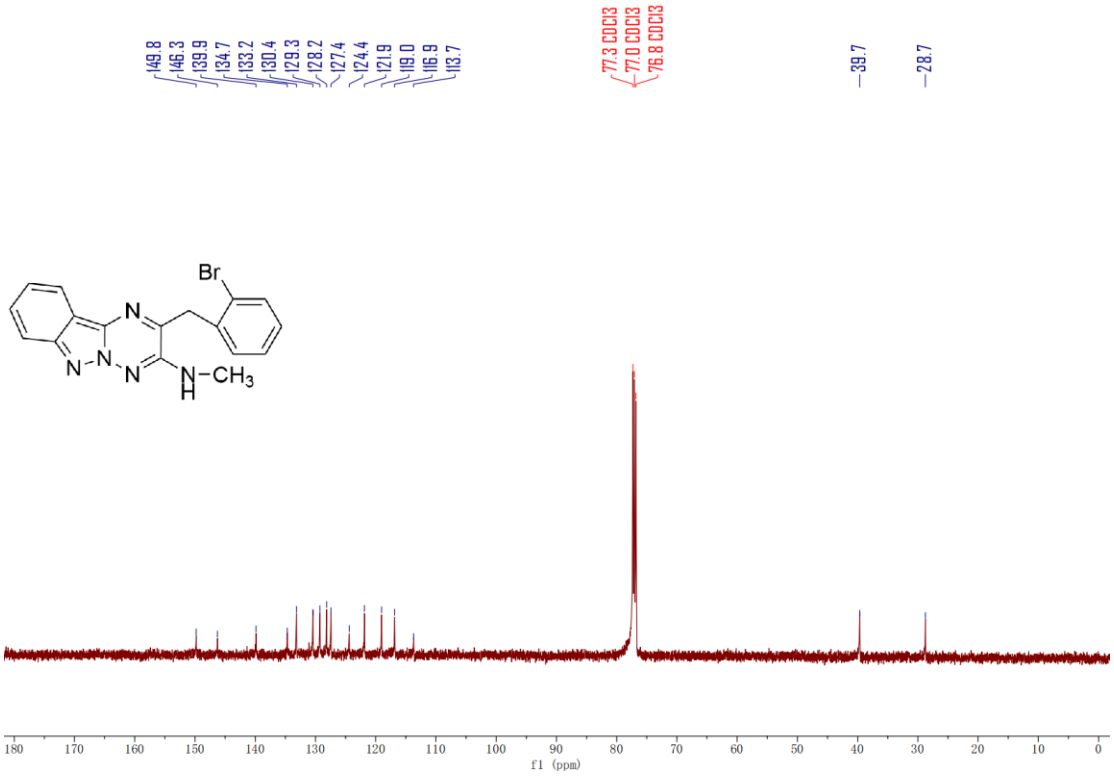
Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
304.1565	304.1562	0.3	1.0	12.5	476.3	n/a	n/a	C18 H18 N5

^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound 7e:

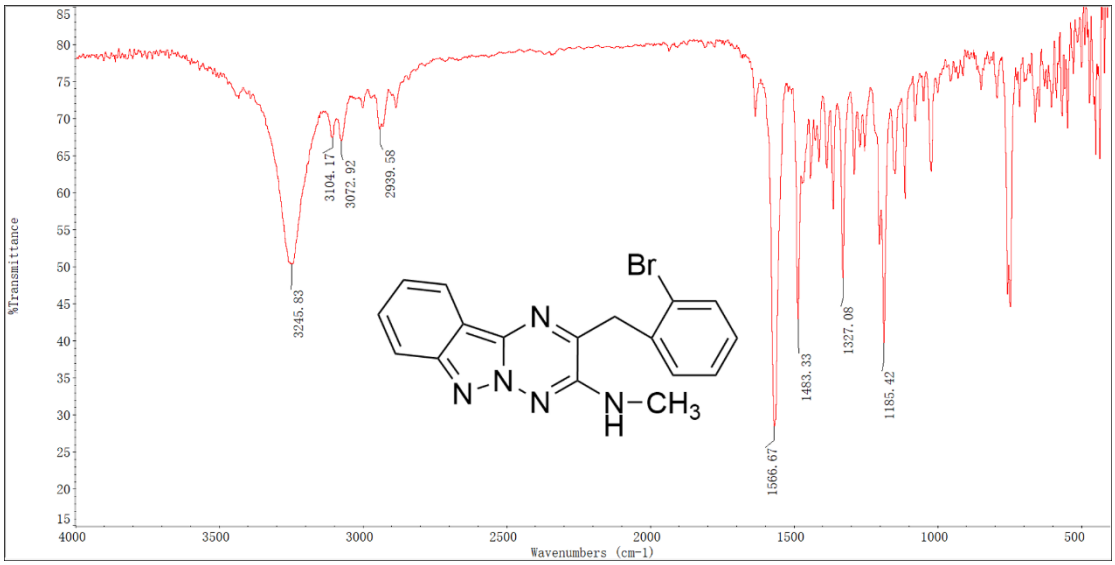




^{13}C NMR (126 MHz,$CDCl_3$) spectra of compound 7e:



IR(7e):

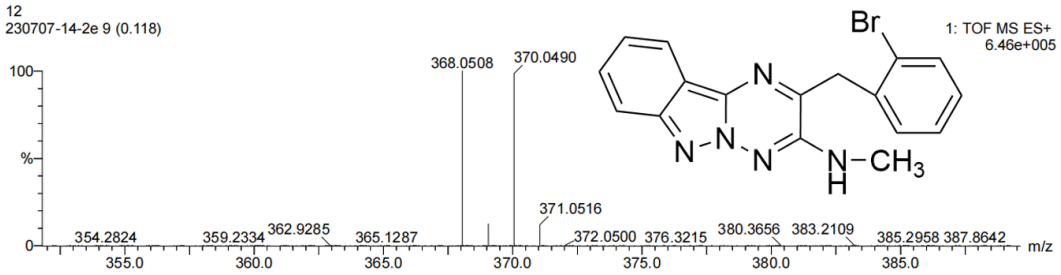


HRMS(7e):

Elemental Composition Report **Page 1**

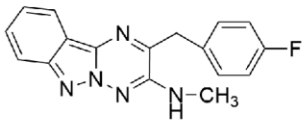
Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

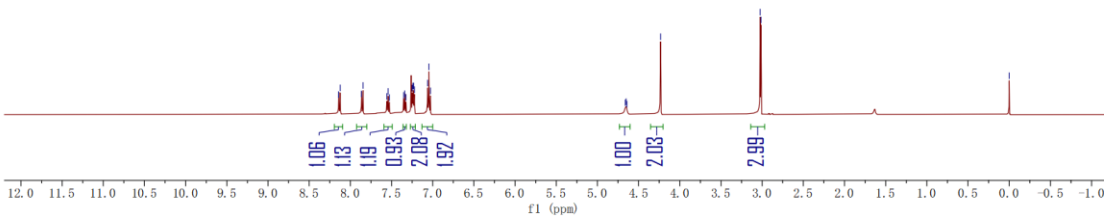
Monoisotopic Mass, Even Electron Ions
300 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 17-17 H: 15-15 N: 0-100 O: 0-100 Br: 1-2



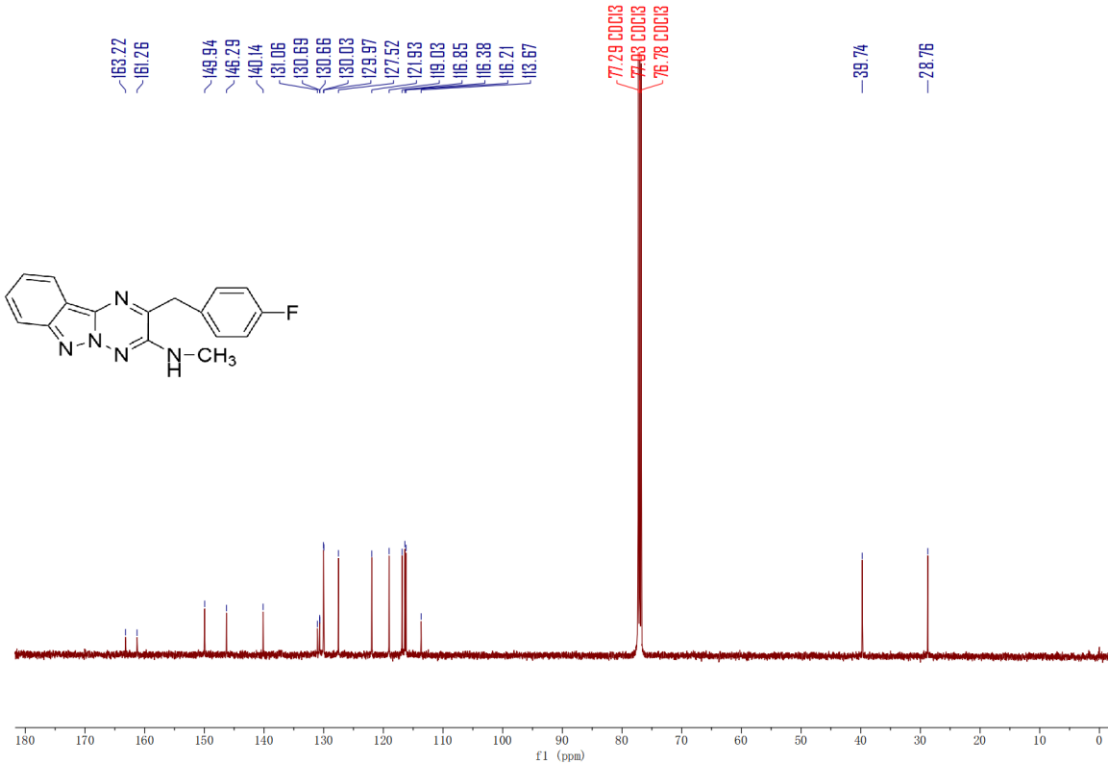
Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
368.0508	368.0511	-0.3	-0.8	12.5	433.3	n/a	n/a	C17 H15 N5 Br

^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound 7f:

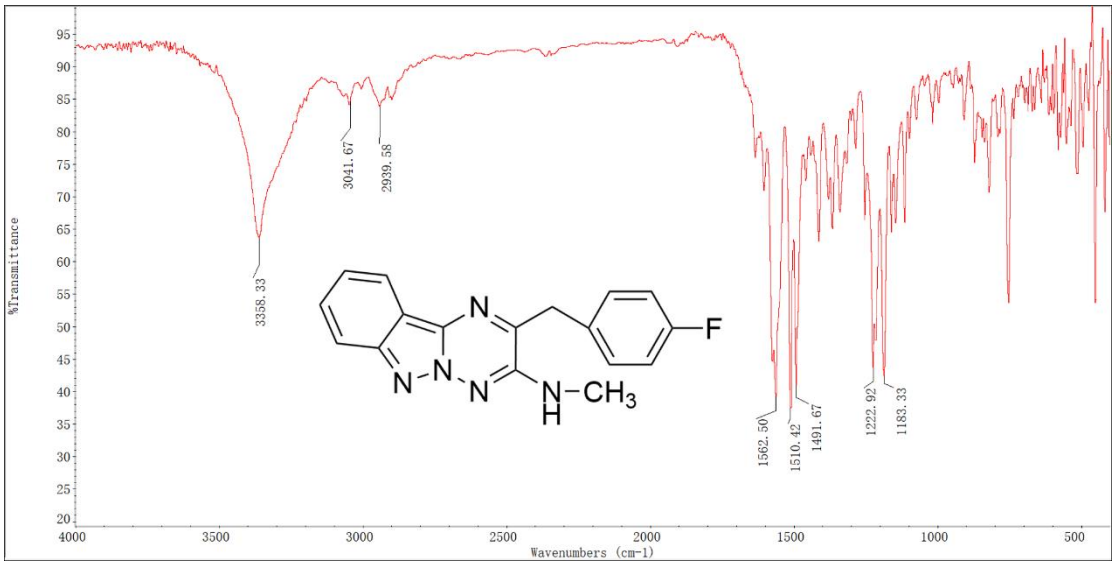




^{13}C NMR (126 MHz,$CDCl_3$) spectra of compound 7f:



IR of compound 7f:



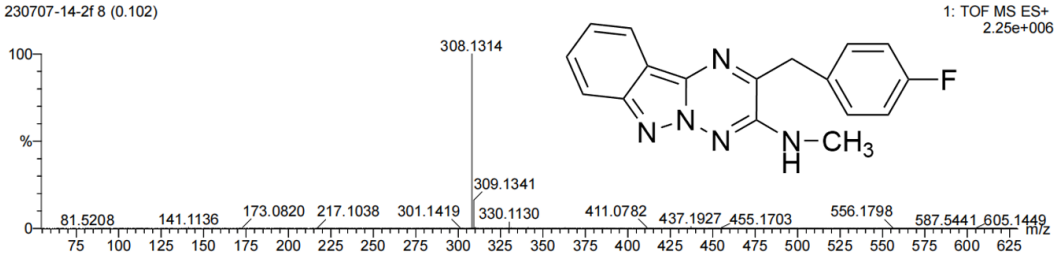
HRMS(7f):

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

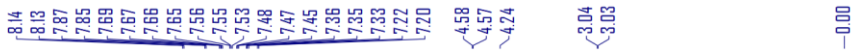
Monoisotopic Mass, Even Electron Ions
187 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 17-17 H: 15-15 N: 0-100 O: 0-100 F: 1-1

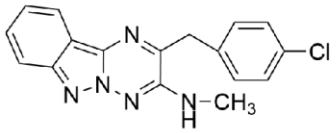
12
230707-14-2f 8 (0.102)

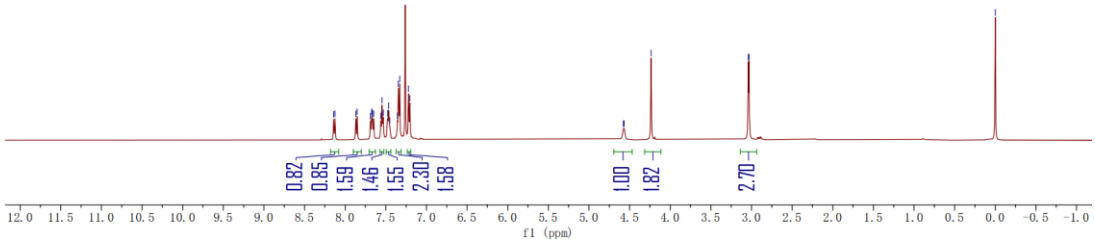


Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
308.1314	308.1311	0.3	1.0	12.5	332.4	n/a	n/a	C17 H15 N5 F

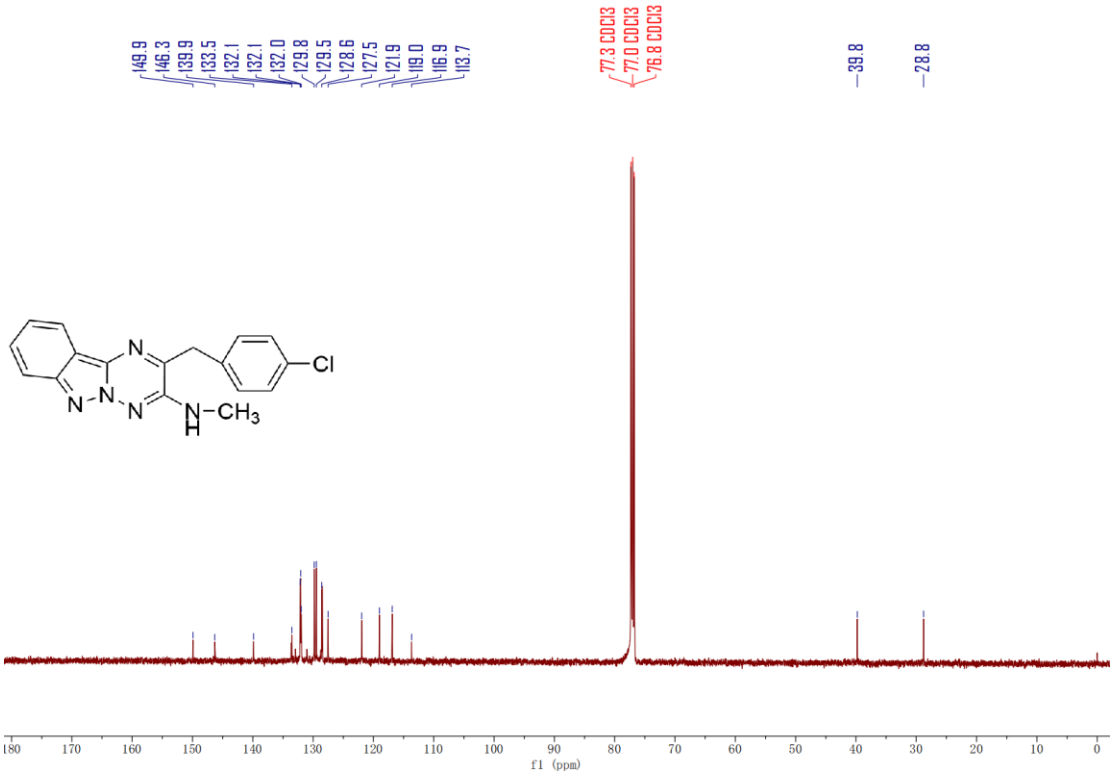
^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound 7g:



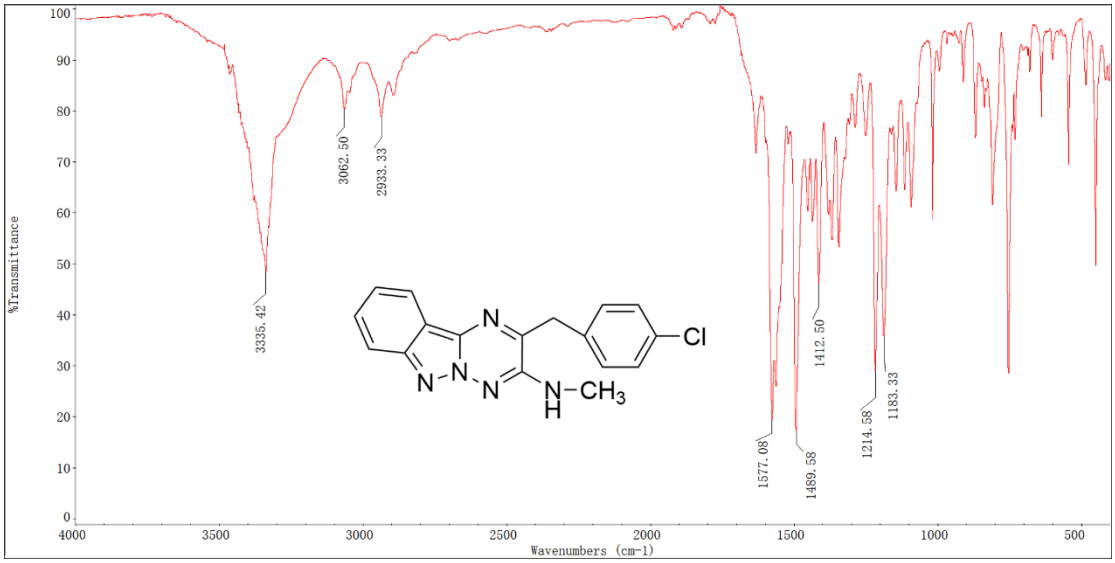




^{13}C NMR (126 MHz,$CDCl_3$) spectra of compound 7g:



IR (7g:)

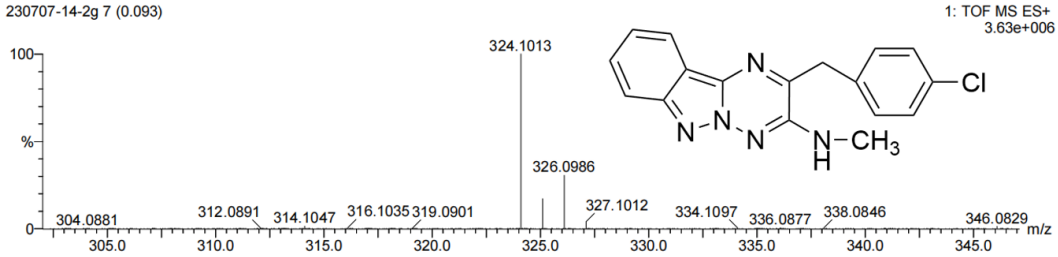


HRMS(7g):

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
187 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 17-17 H: 15-15 N: 0-100 O: 0-100 Cl: 1-1
12
230707-14-2g 7 (0.093)



Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
324.1013	324.1016	-0.3	-0.9	12.5	423.5	n/a	n/a	C17 H15 N5 Cl