

Supporting Information

Synthesis of 3,5-bis(fluoroalkyl)pyrazoles/pyrazolines from [3+2] cycloaddition of di/trifluoroacetohydrazonoyl bromides and trifluoromethyl-substituted alkenes

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1. Synthesis of Di/trifluoroacetohydrazonoyl Bromides 1	S2
2. Copies of NMR and HRMS Spectra for Compounds 3 and B	S3
3. X-Ray Crystallographic Data of Compounds 3n and 4j	S118

1. Synthesis Procedure of Di/trifluoroacetohydrazoneyl Bromides 1¹

Step 1: A mixture of hydrazine hydrochlorides (2.0 mmol, 1.0 equiv.), triethylamine (1.0 mmol, 1.0 equiv.), di/trifluoroacetaldehyde ethyl hemiacetal (1.5 mmol, 1.5 equiv.), and freshly activated molecular sieves 4Å in EtOH (8 mL) was stirred at 75 °C in a round-bottom in an oil bath, and the reaction was monitored by TLC. After the reaction was completed, the solvent was removed in vacuo to afford intermediate products, which was used directly for the next step.

Step 2: To a solution of crude mixture from step 1 in DMF (8 mL) was added NBS. The resulting solution was stirred at room temperature, and the reaction was monitored by TLC. After the reaction was completed, the reaction was quenched with sat. NaCl aq., and the mixture was extracted with ethyl acetate (3 x 15 mL), dried over MgSO₄, filtered, and concentrated in vacuo. The resulting products was purified by column chromatography on silica gel (EA)/petroleum ether (PE) (1:8–1:20) to afford di/trifluoroacetohydrazoneyl bromides.

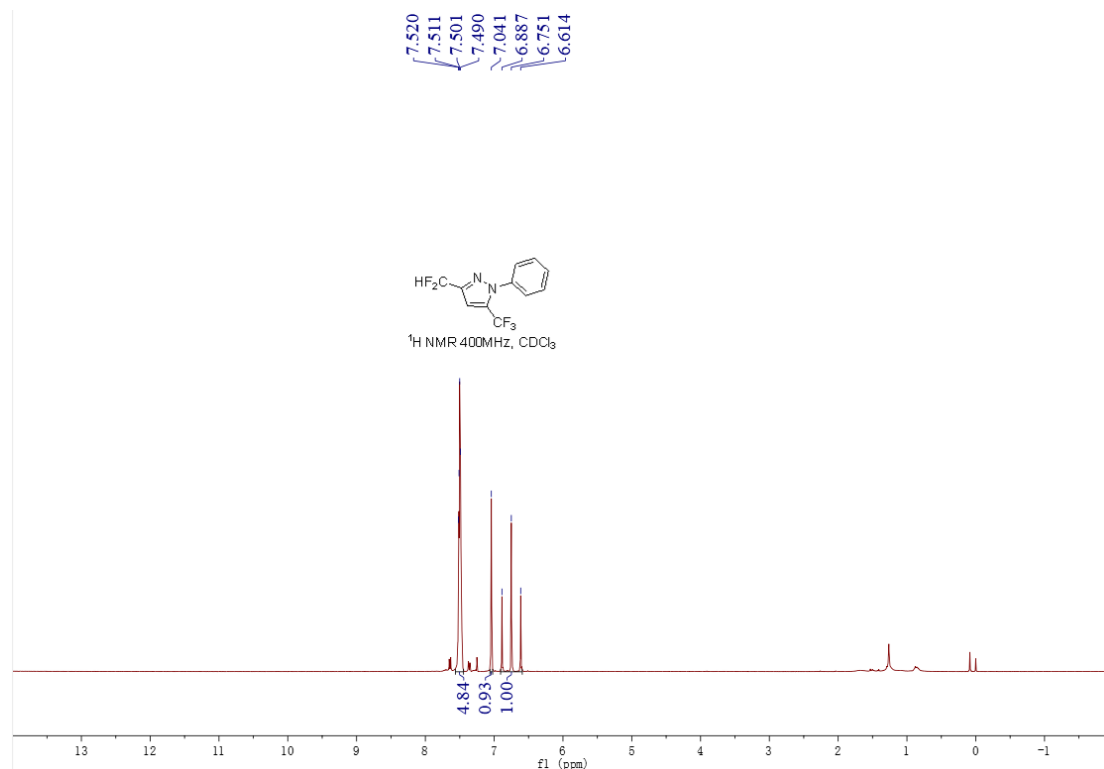
References

- (a) T. Han, K.-H. Wang, M. Yang, P. Zhao, F. Wang, J. Wang, D. Huang and Y. Hu, *J. Org. Chem.*, 2022, **87**, 498–511.
- (b) Y. Ren, R. Ma, Y. Feng, K.-H. Wang, J. Wang, D. Huang, X. Lv and Y. Hu, *Asian J. Org. Chem.*, 2022, e202200438.
- (c) Y. Ren, R. Ma, X. Li, K.-H. Wang, J. Wang, D. Huang, X. Lv and Y. Hu, *Tetrahedron*, 2023, **149**, 133711.
- (d) Y. Feng, Y. Ren, D. Tang, K.-H. Wang, J. Wang, D. Huang, X. Lv and Y. Hu, *Org. Biomol. Chem.*, 2024, **22**, 2797–2812.
- (e) X. Li, D. Huang, Y. Zhou, X. Liu, K. Wang, J. Wang and Y. Hu, *Chin. J. Org. Chem.*, 2024, **44**, 1226–1239.

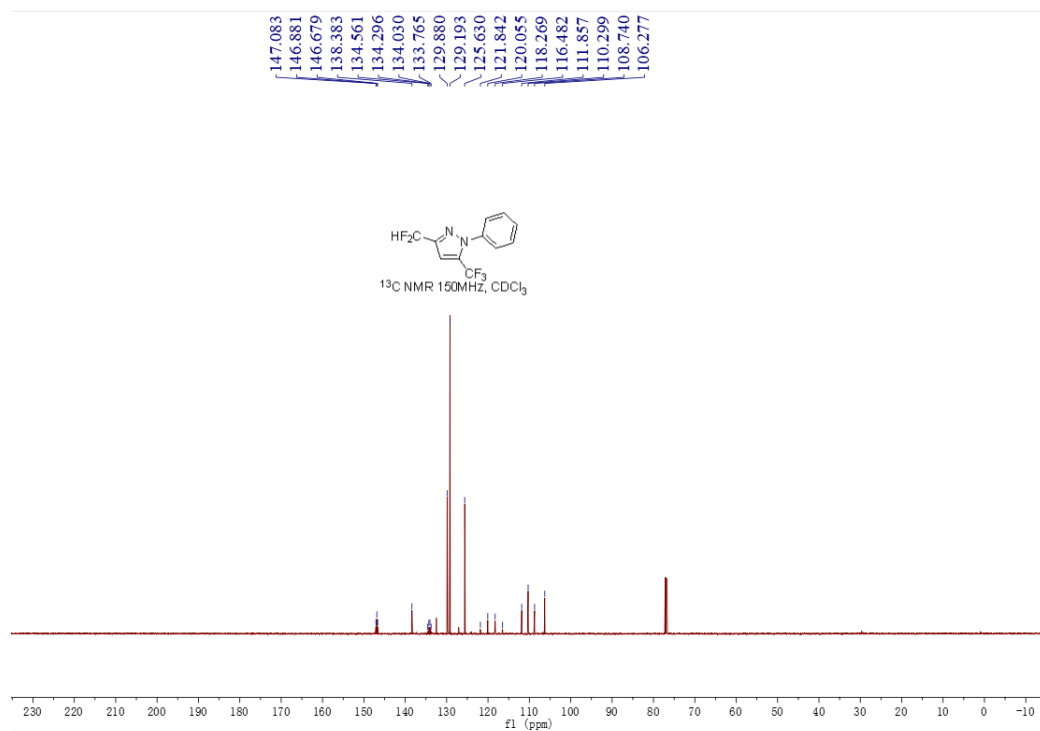
2. Copies of ^1H NMR, ^{13}C NMR of products **3**, **3'**, **4** and **4'**

Spectrogram copies of compound **3a**

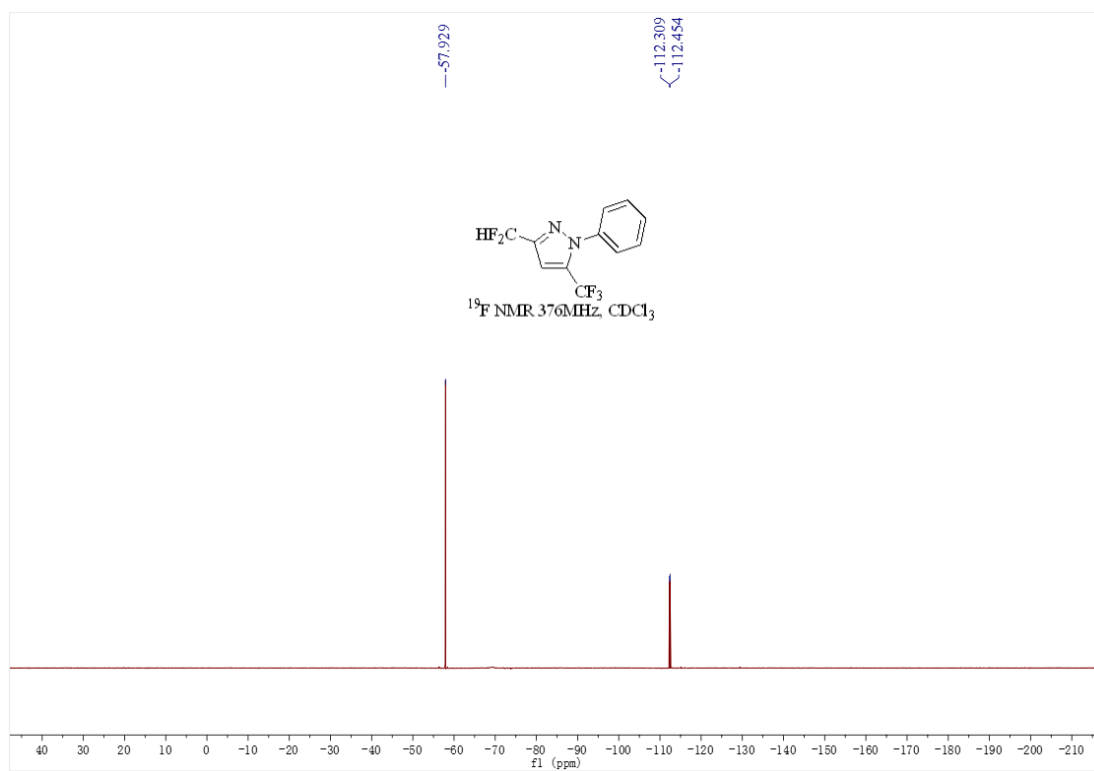
^1H NMR copy of compound **3a**



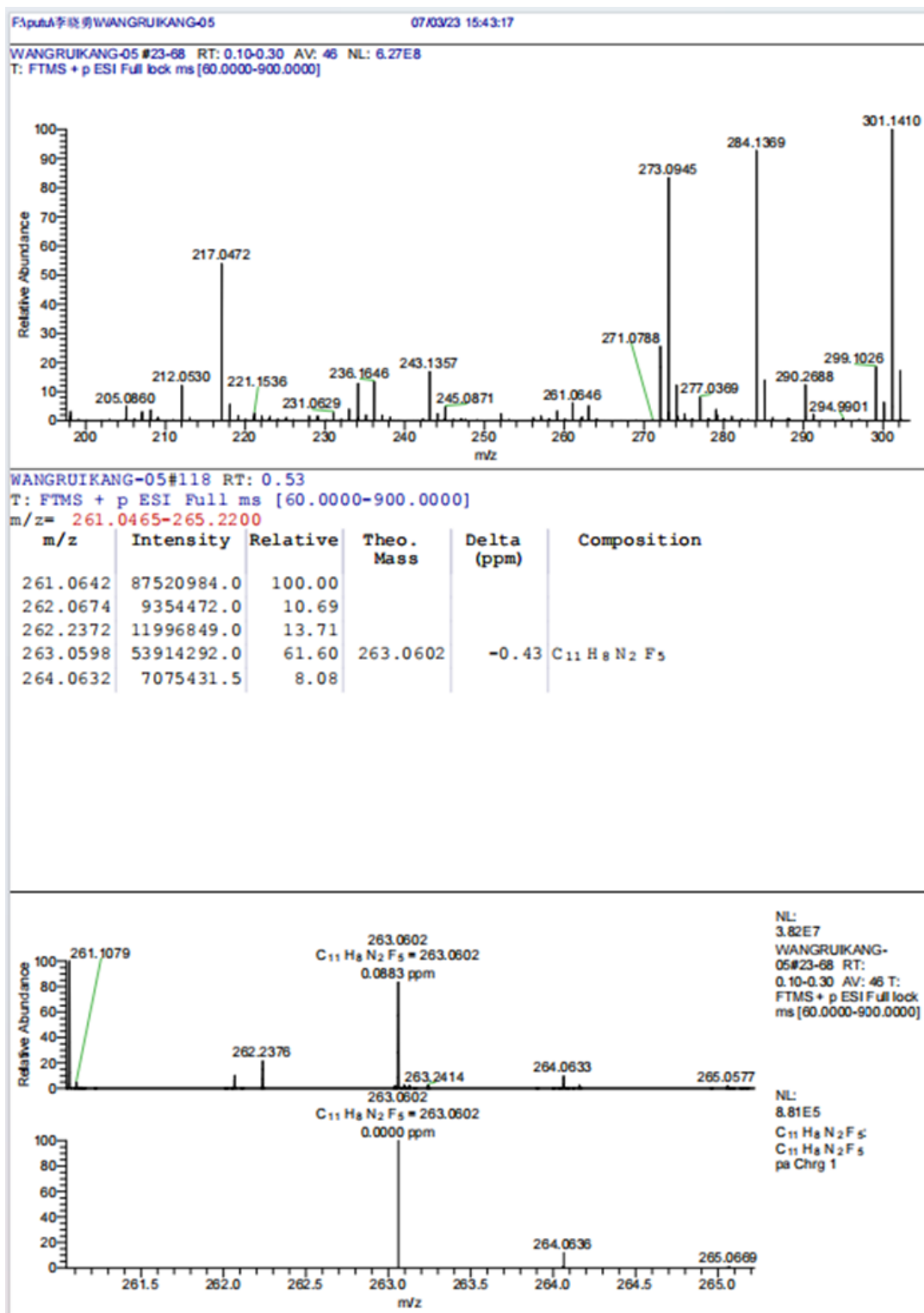
^{13}C NMR copy of compound **3a**



¹⁹F NMR copy of compound **3a**

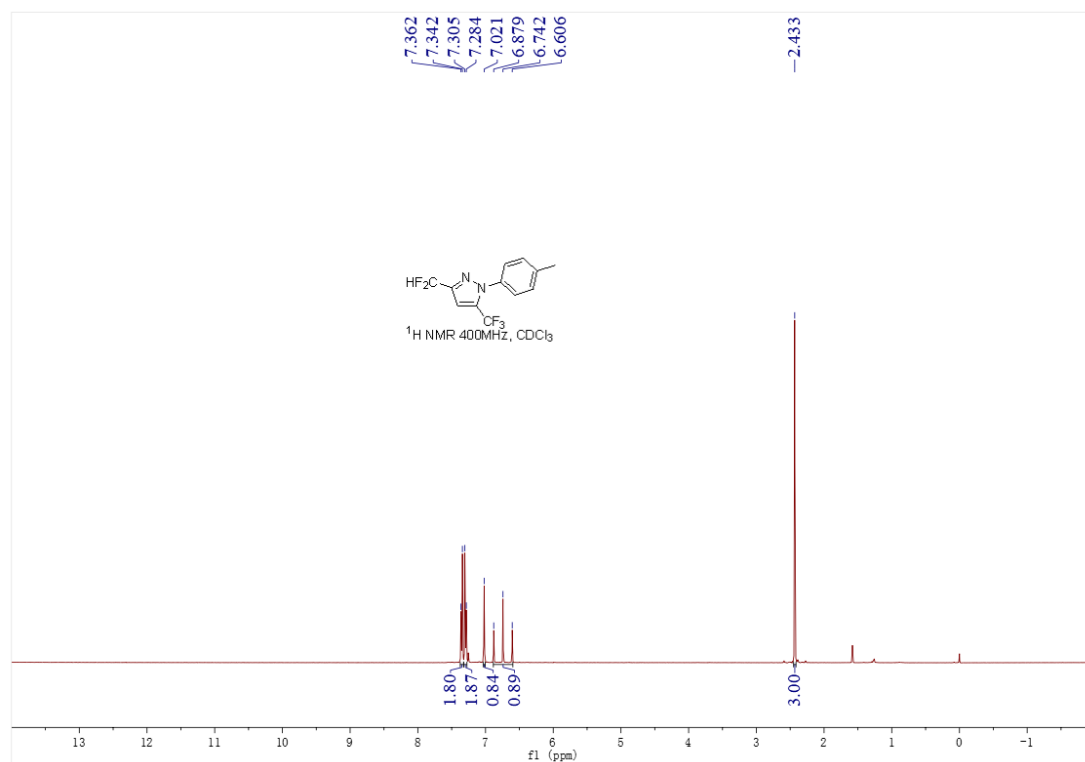


HRMS copy of compound 3a

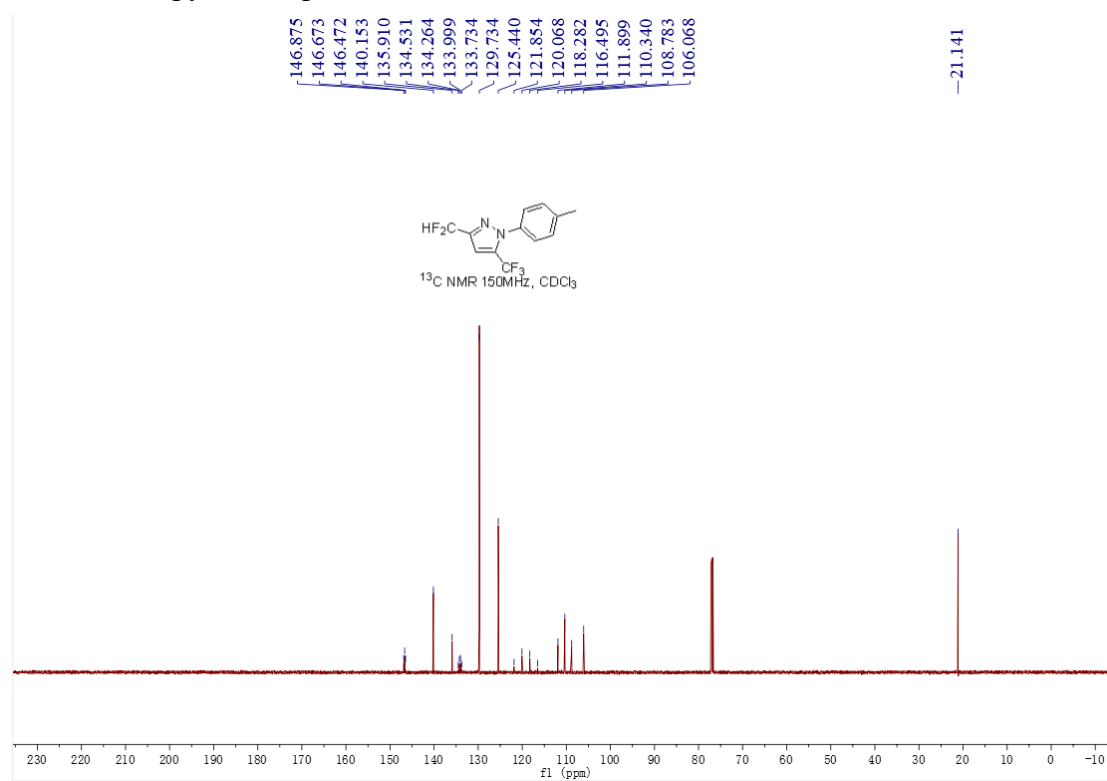


Spectrogram copies of compound **3b**

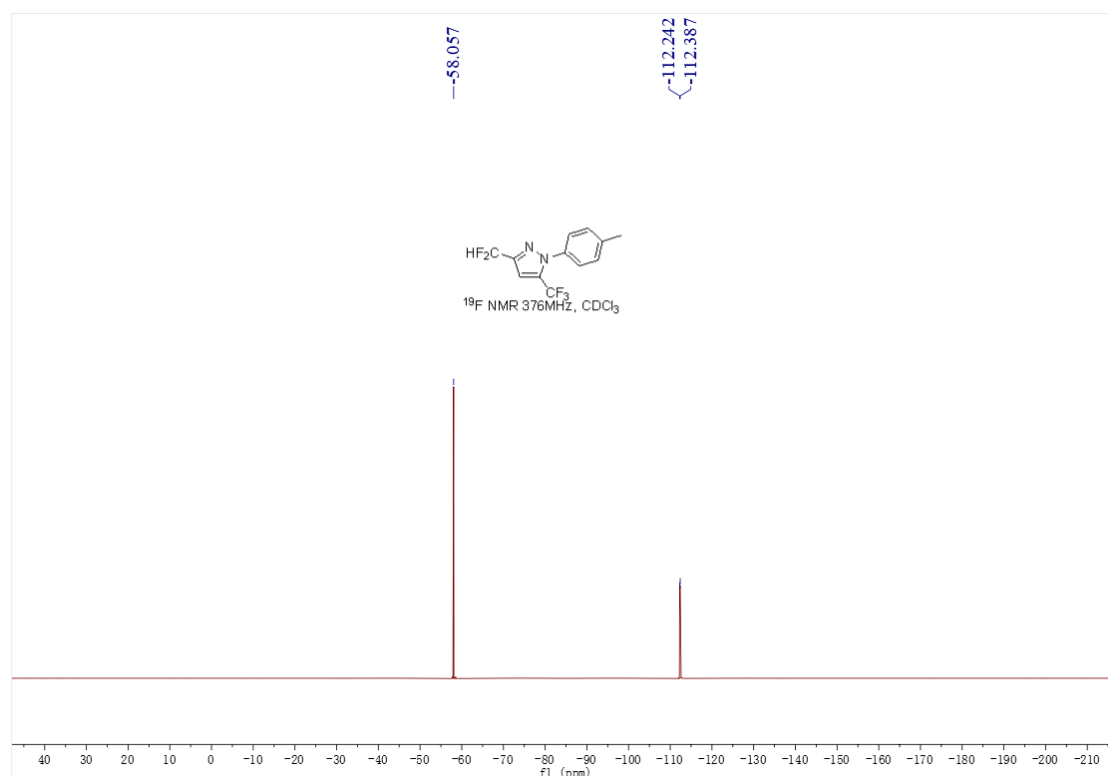
¹H NMR copy of compound **3b**



¹³C NMR copy of compound **3b**



¹⁹F NMR copy of compound **3b**



HRMS copy of compound **3b**

Mass Spectrum SmartFormula Report

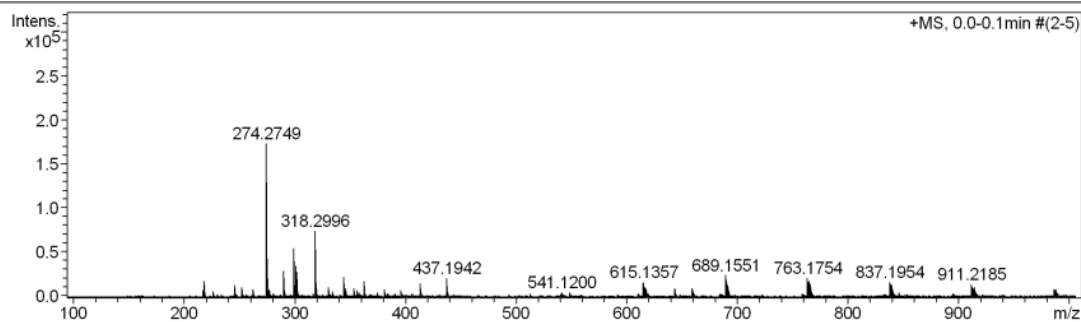
Analysis Info

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 Method tune_low.m
 Sample Name 1
 Comment

Acquisition Date 2024-2-5 9:21:11
 Operator Huyue
 Instrument / Ser# micrOTOF-Q 20453

Acquisition Parameter

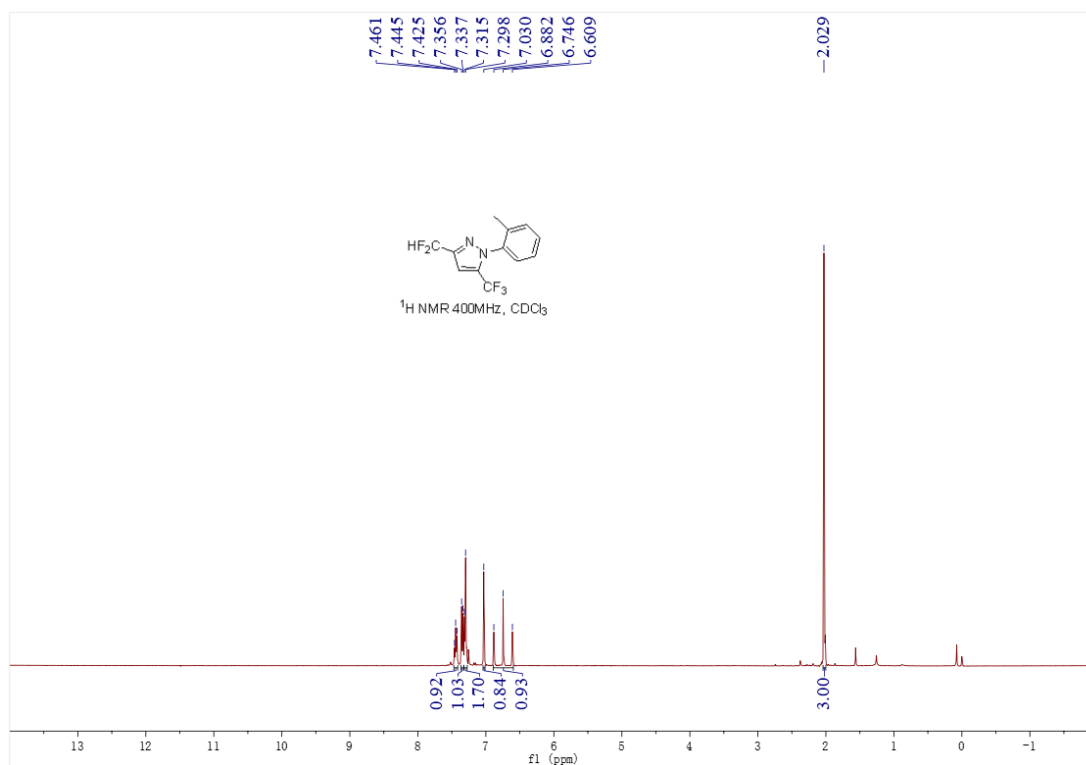
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Scan End	1000 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste



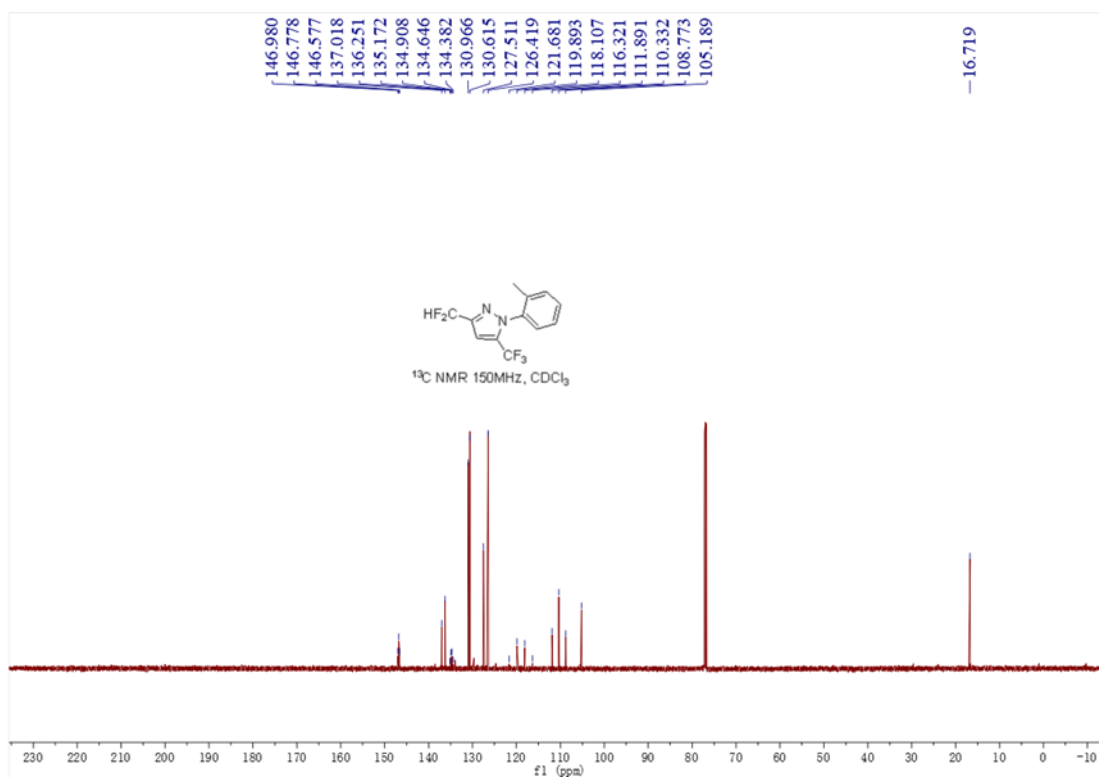
Meas. m/z	#	Formula	m/z	err [ppm]	Me an err [ppm]	rdb	N- Ru le	e j % Conf	mS igma	Std l	Std Me an m/z	Std l Var	Std l m/z Diff	Std Com b Dev
299.0572	1	C 12 H 9 F 5 N 2 Na	299.0578	2.1	1.9	6.5	ok	even	5.4	8.6	0.6	6.4	0.7	842.7

Spectrogram copies of compound **3d**

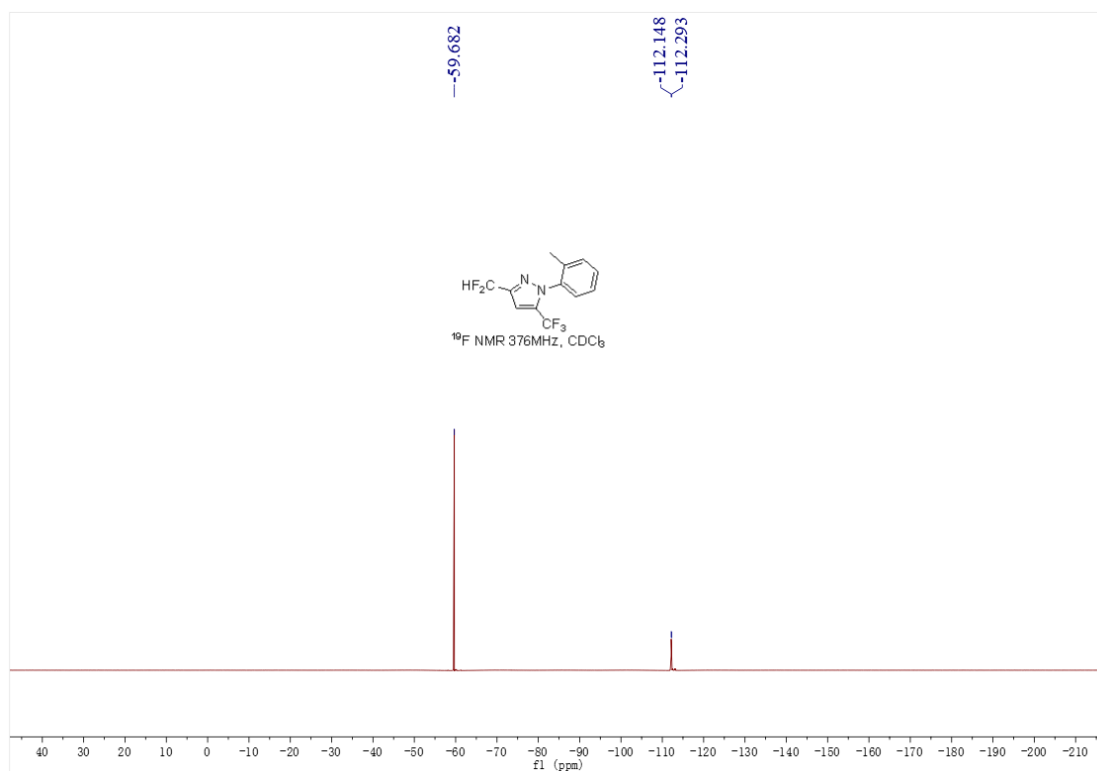
^1H NMR copy of compound **3d**



^{13}C NMR copy of compound **3d**

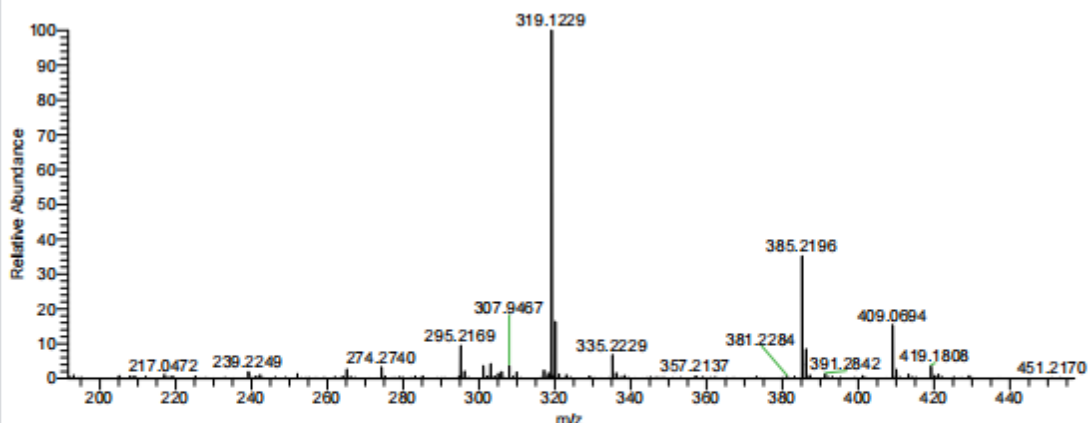


¹⁹F NMR copy of compound **3d**



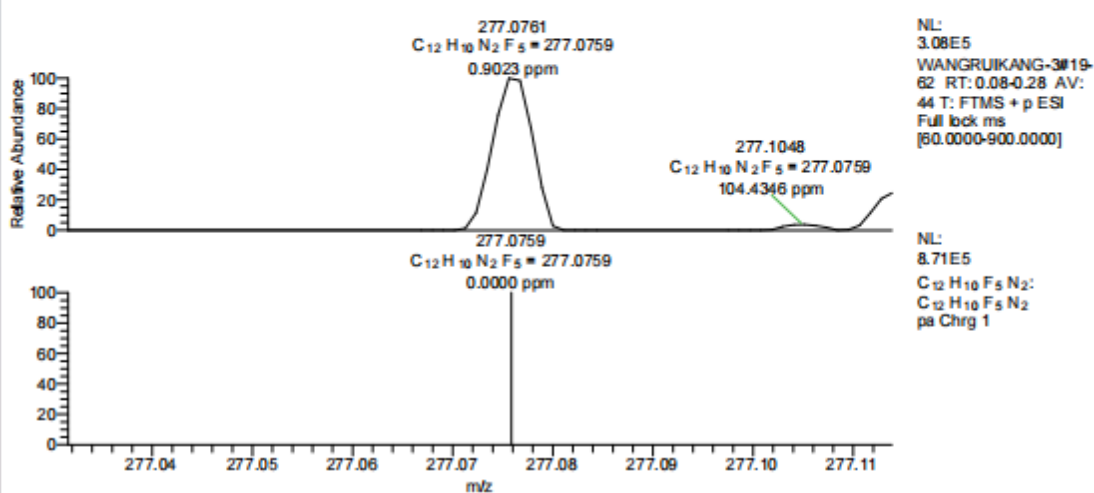
HRMS copy of compound 3d

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T: FTMS + p ESI Full lock ms [60.0000-900.0000]



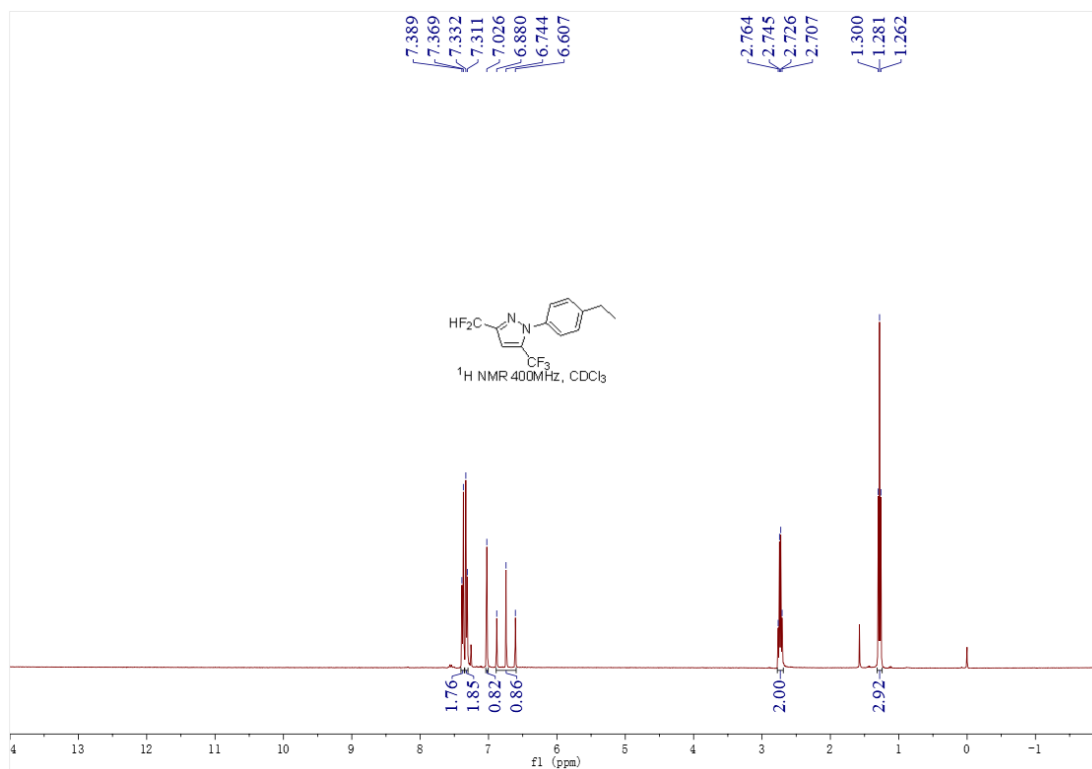
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m/z = 276.8293-277.2937

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
276.9464	16408.6	1.46	277.0759	-129.43	C ₁₂ H ₁₀ N ₂ F ₅
277.0761	315604.8	28.03	277.0759	0.25	C ₁₂ H ₁₀ N ₂ F ₅
277.1144	77138.0	6.85	277.0759	38.58	C ₁₂ H ₁₀ N ₂ F ₅
277.1222	1125918.4	100.00	277.0759	46.33	C ₁₂ H ₁₀ N ₂ F ₅
277.1786	72878.6	6.47	277.0759	102.68	C ₁₂ H ₁₀ N ₂ F ₅

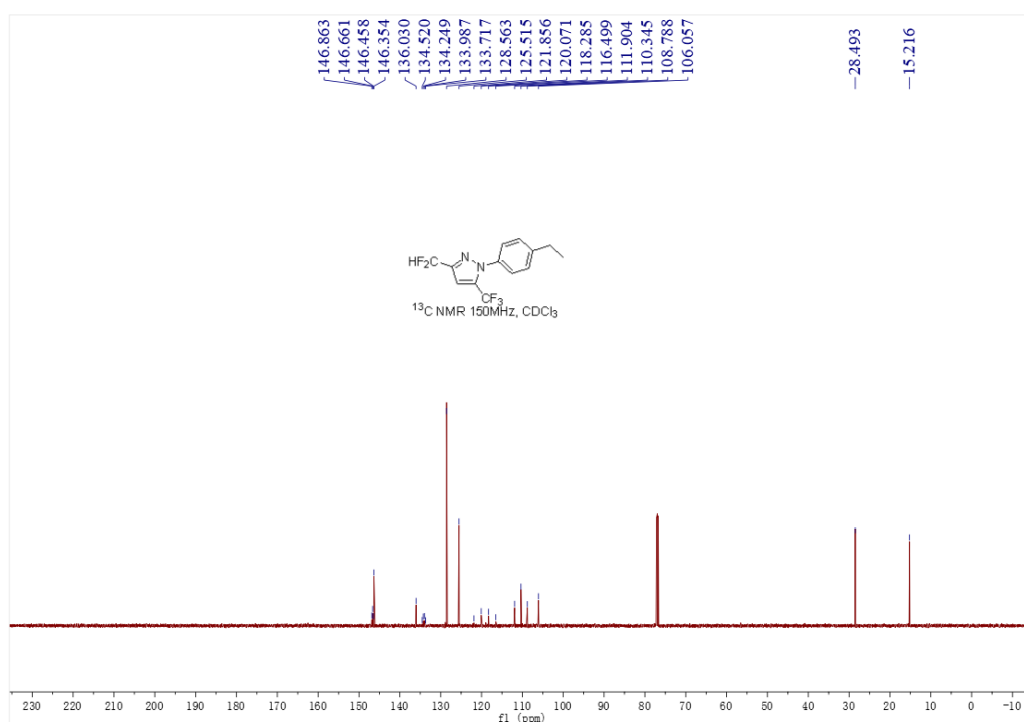


Spectrogram copies of compound **3e**

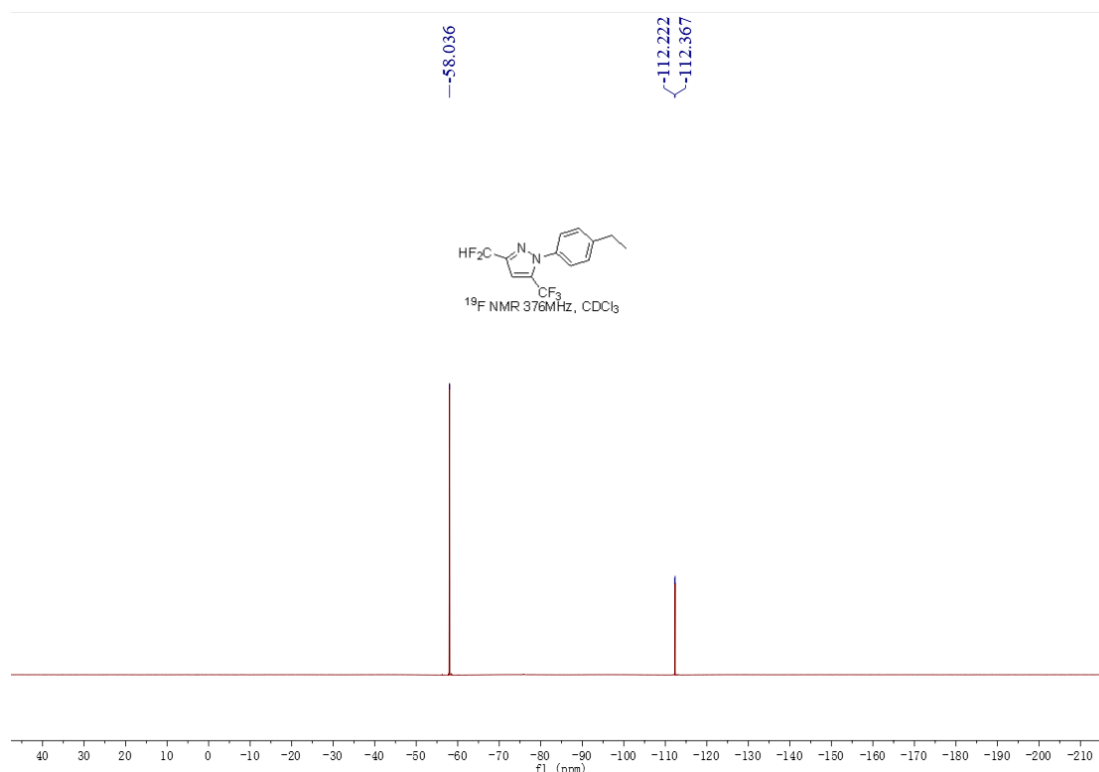
^1H NMR copy of compound **3e**



^{13}C NMR copy of compound **3e**



¹⁹F NMR copy of compound **3e**



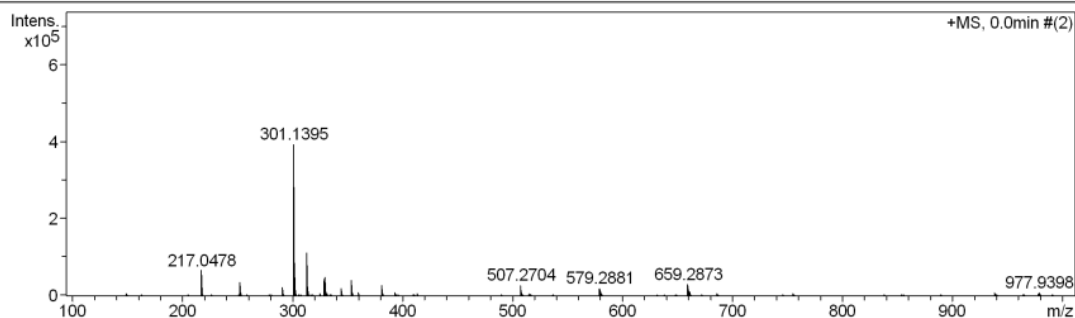
HRMS copy of compound **3e**

Mass Spectrum SmartFormula Report

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Analysis Name D:\Data\user\NWNWU-wangruikang 20240205-10.d	Operator Huyue
Method tune_low.m	Instrument / Ser# micrOTOF-Q 20453
Sample Name 10	
Comment	

Acquisition Parameter

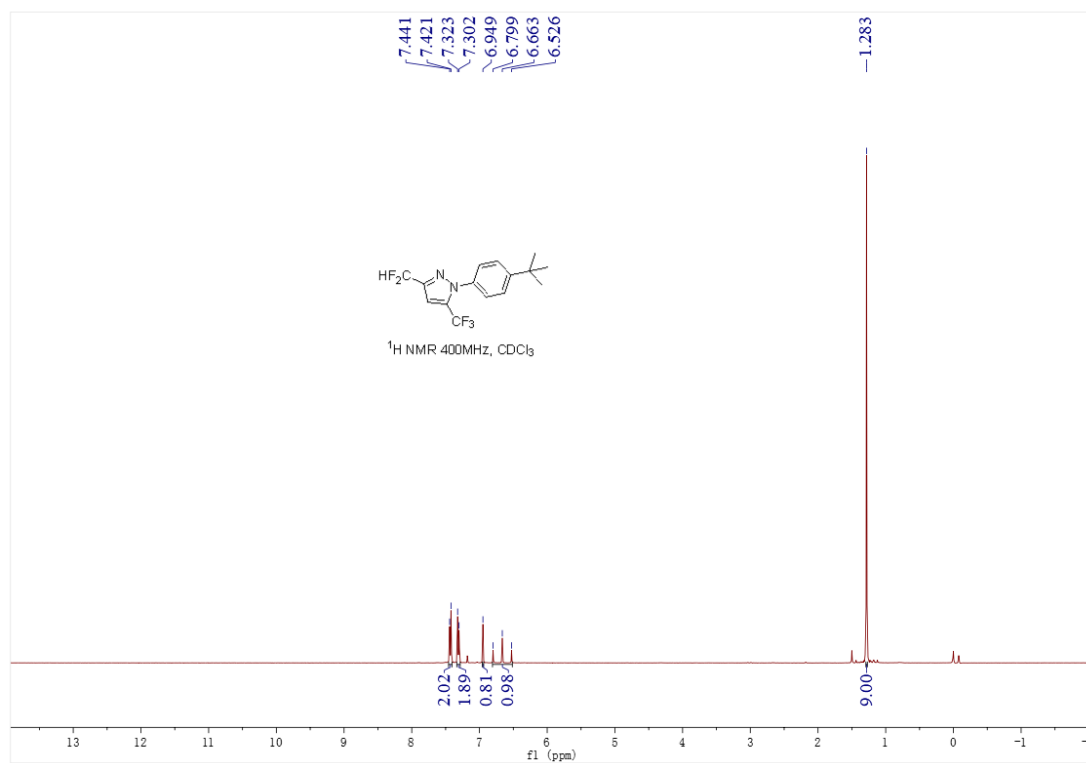
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Focus Active	Set Capillary 4500 V	Set Dry Heater 180 j°C
Scan Begin 100 m/z	Set End Plate Offset -500 V	Set Dry Gas 4.0 l/min
Scan End 1000 m/z	Set Collision Cell RF 300.0 Vpp	Set Divert Valve Waste



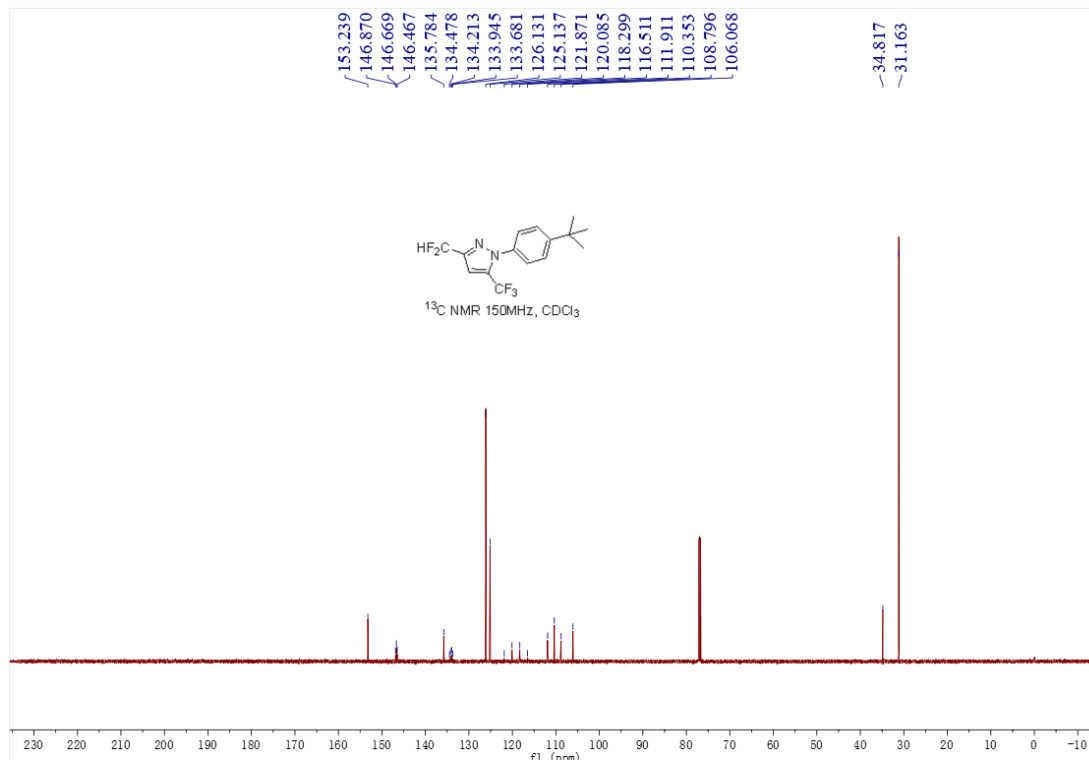
Meas. m/z	#	Formula	m/z	err [ppm]	Me an err [ppm]	rdb	N-Ru le	ej% Conf	mS ig ma	Std l	Std Me an m/z	Std l Var No rm	Std m/ z Diff	Std Com b Dev
313.0734	1	C 13 H 11 F 5 N 2 Na	313.0735	0.1	1.6	6.5	ok	even	8.6	14.8	1.3	8.7	3.9	842.7

Spectrogram copies of compound **3f**

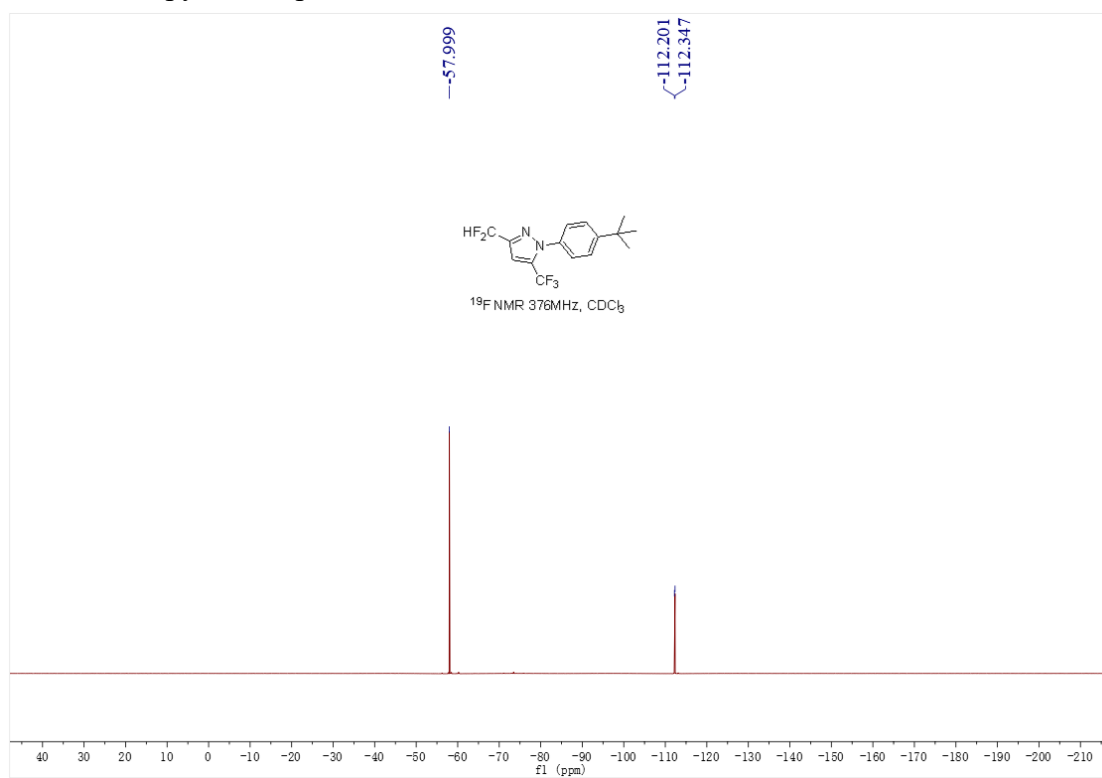
^1H NMR copy of compound **3f**



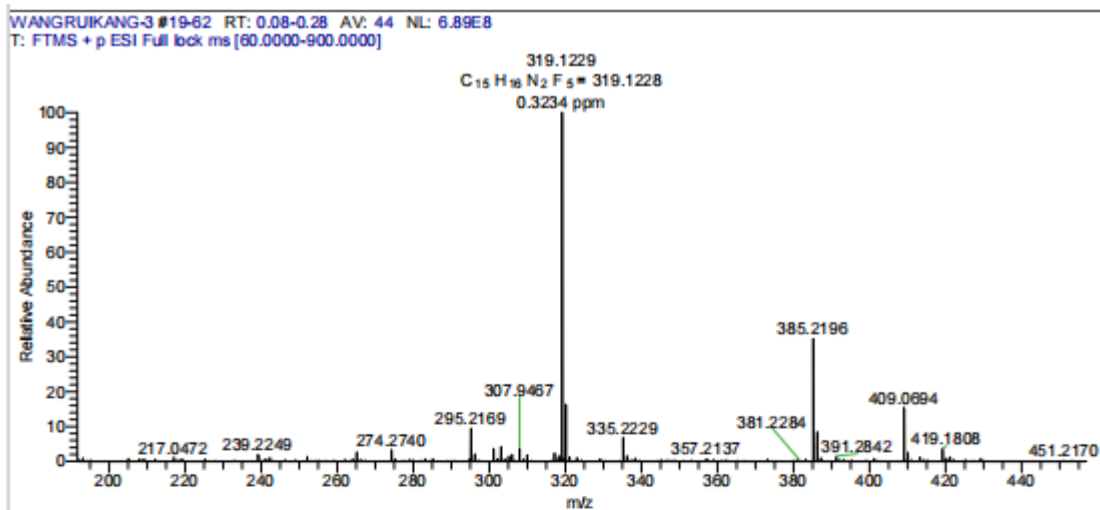
^{13}C NMR copy of compound **3f**



¹⁹F NMR copy of compound **3f**

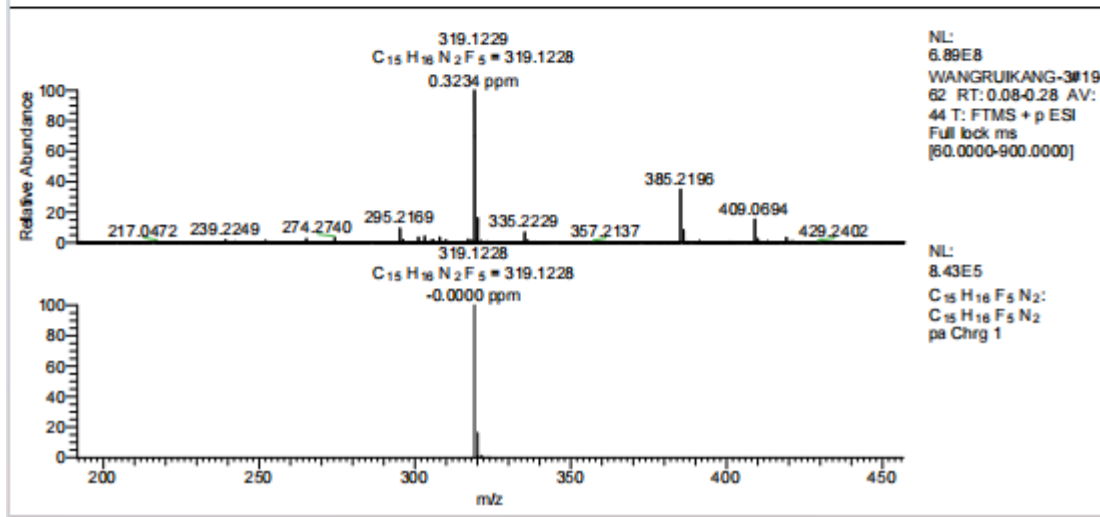


HRMS copy of compound 3f



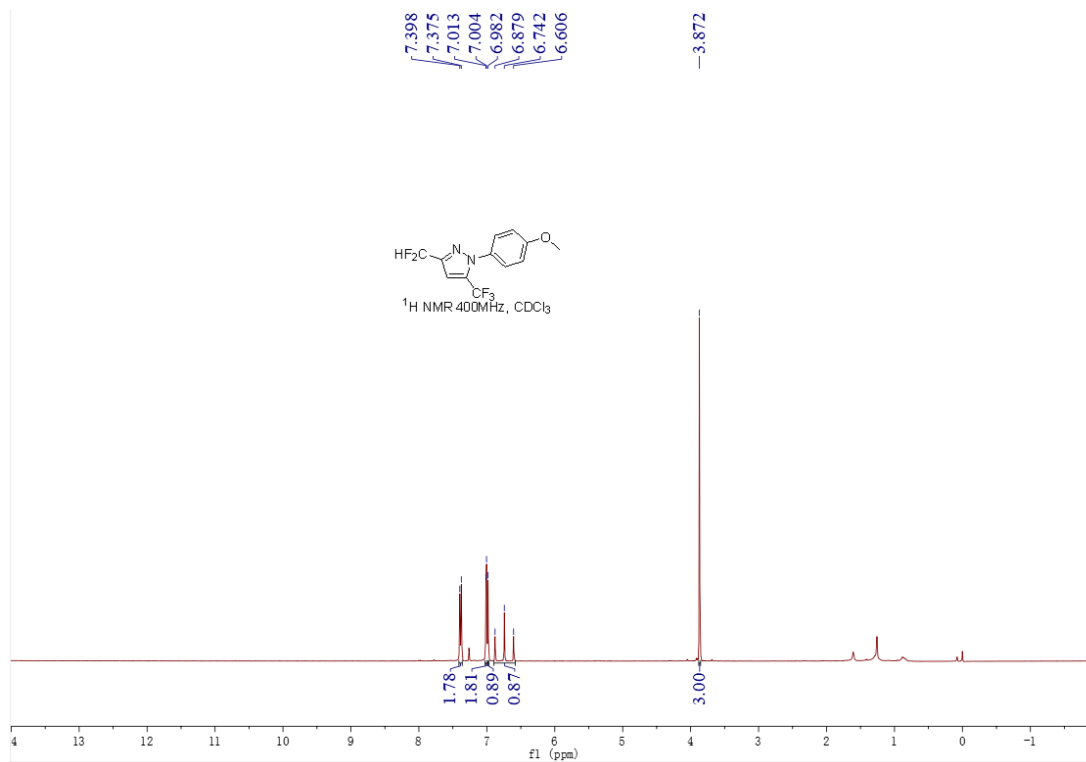
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m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
295.2169	65850368.0	9.33			
319.1229	705573248.0	100.00	319.1228	0.10	C ₁₅ H ₁₆ N ₂ F ₅
320.1263	113023000.0	16.02			
385.2196	246334480.0	34.91			
409.0694	107114928.0	15.18			

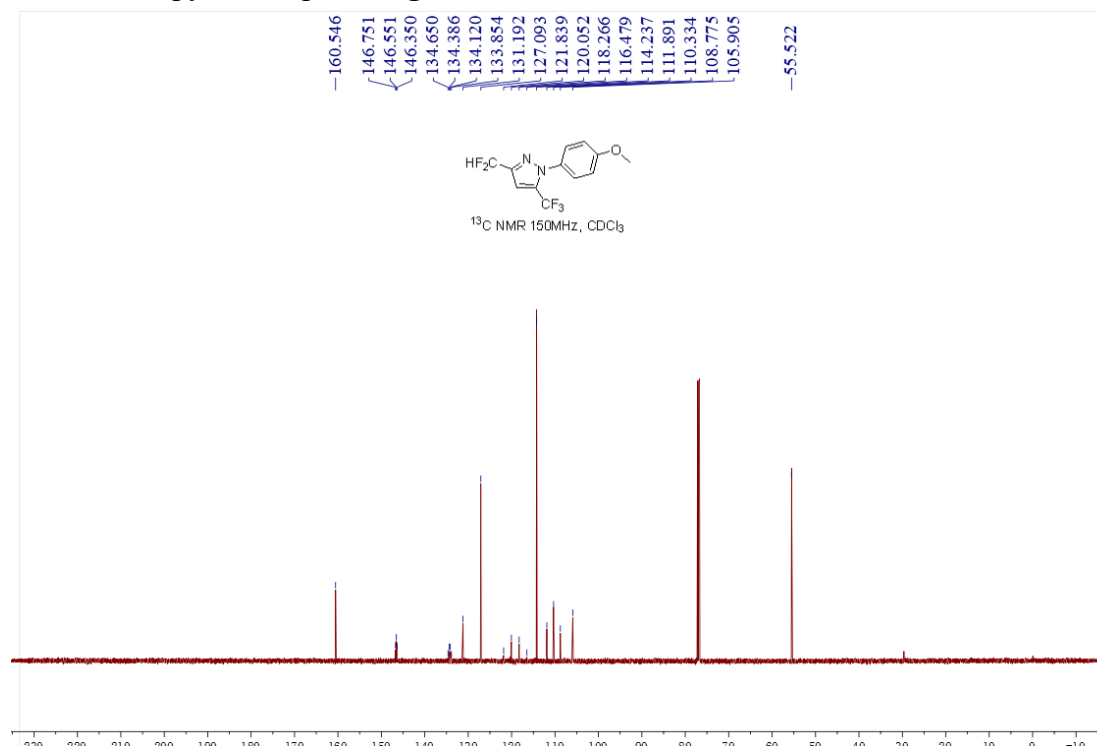


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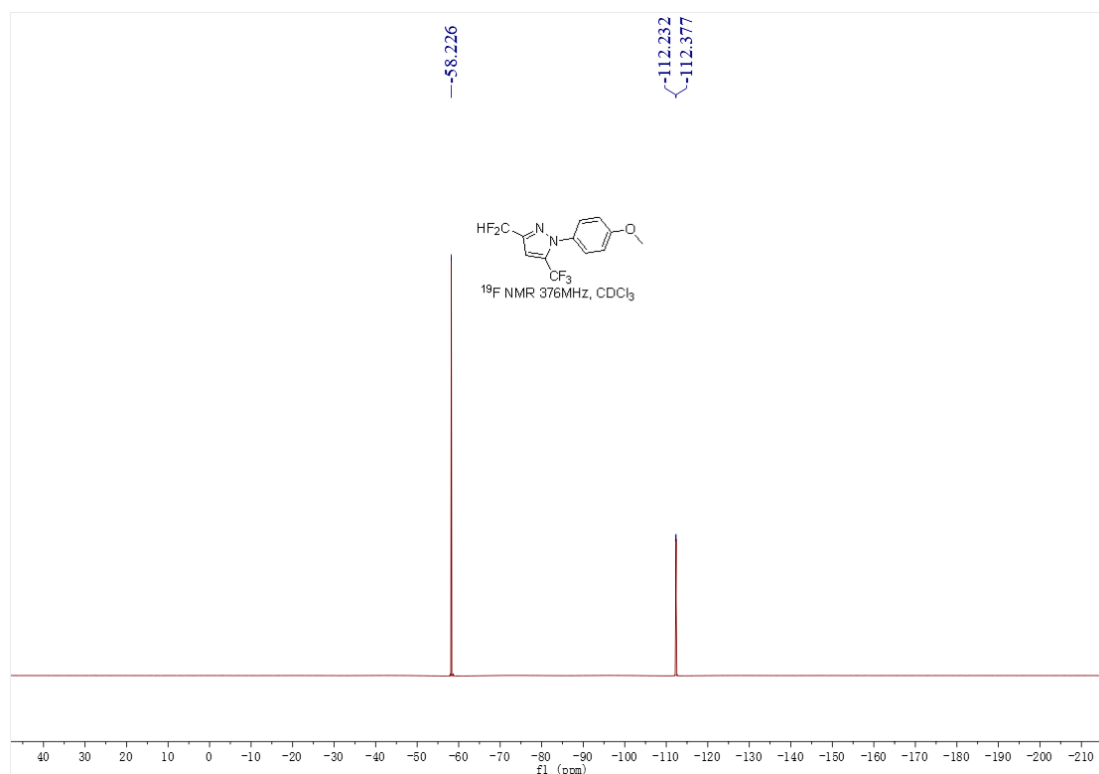
¹H NMR copy of compound **3g**



¹³C NMR copy of compound **3g**



¹⁹F NMR copy of compound **3g**



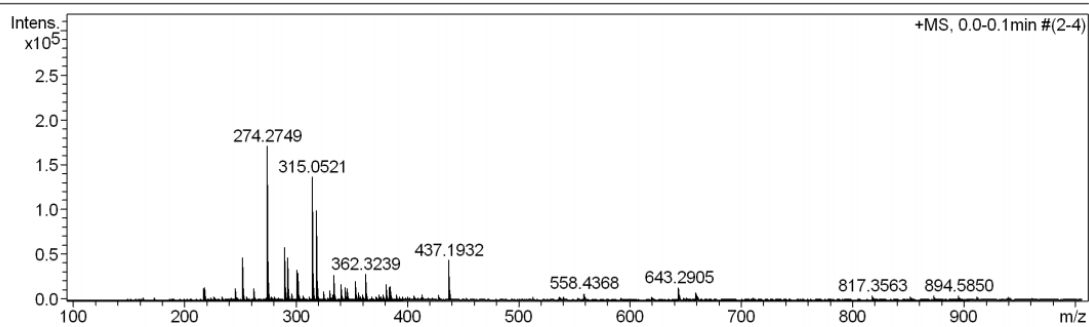
HRMS copy of compound **3g**

Mass Spectrum SmartFormula Report

Analysis Info		Acquisition Date	2024-2-5 9:47:22
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Sample Name	6		
Comment			

Acquisition Parameter

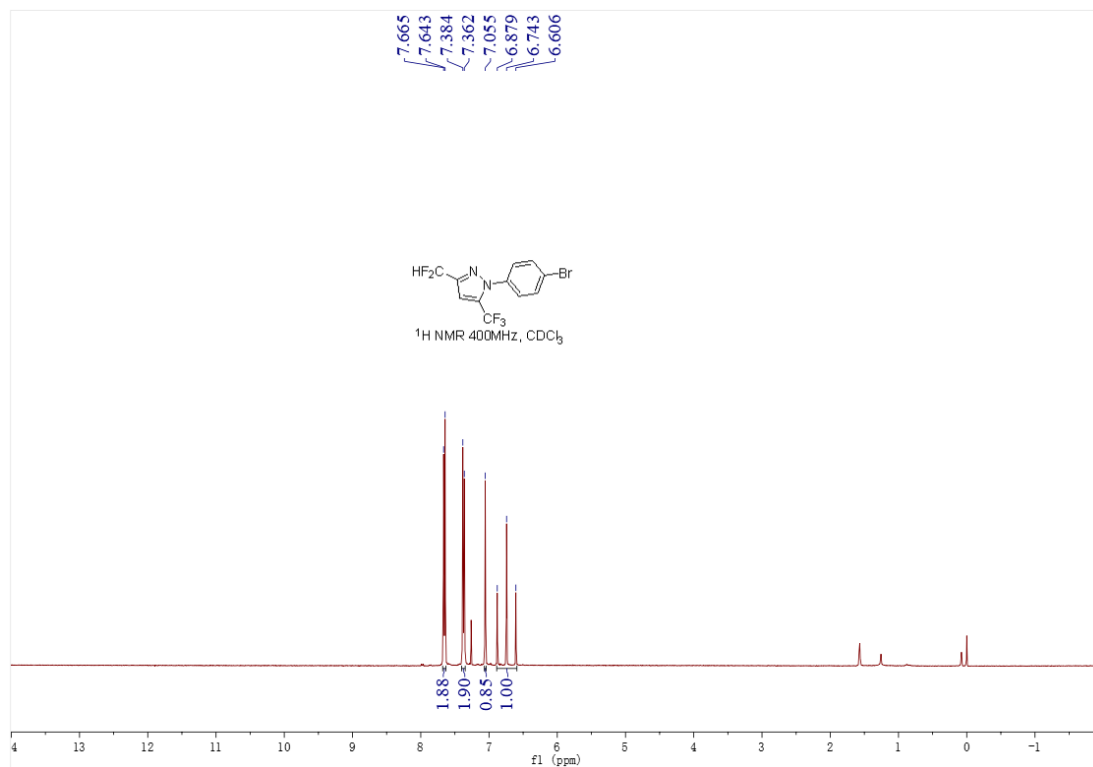
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Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste



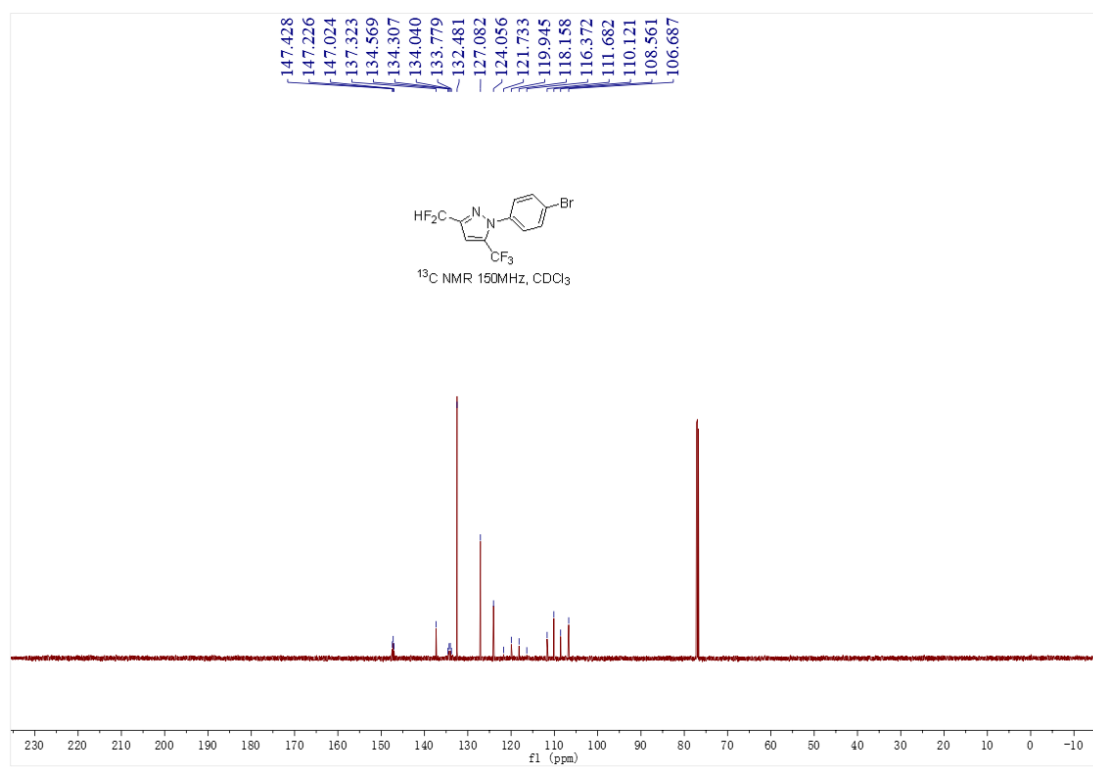
Meas. #	Formula	m/z	err [ppm]	Me an err [ppm]	rdb	N-Ru	ej¥ Conf	mS ig ma	Std I	Std Me an z	Std l Var m/ No rm	Std m/ Diff	Std Com b Dev
315.0521	1 C 12 H 9 F 5 N 2 Na O	315.0527	2.1	2.0	6.5	ok	even	6.7	11.5	0.6	7.1	0.3	842.7

Spectrogram copies of compound **3h**

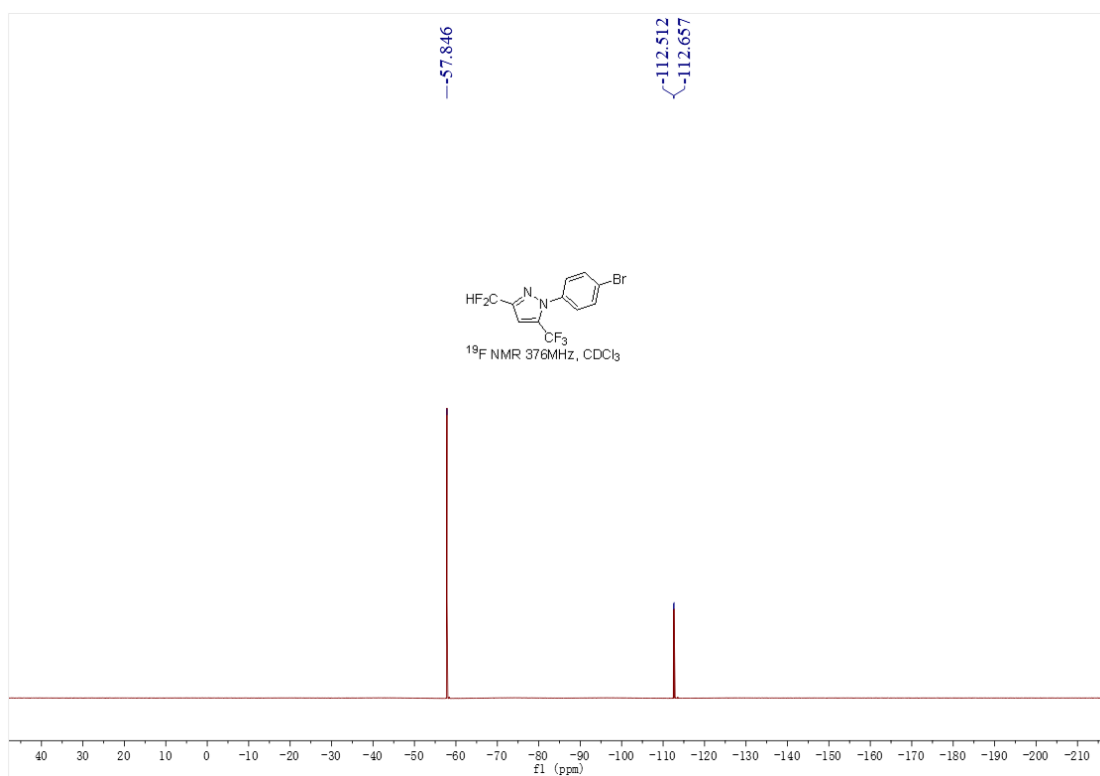
¹H NMR copy of compound **3h**



¹³C NMR copy of compound **3h**

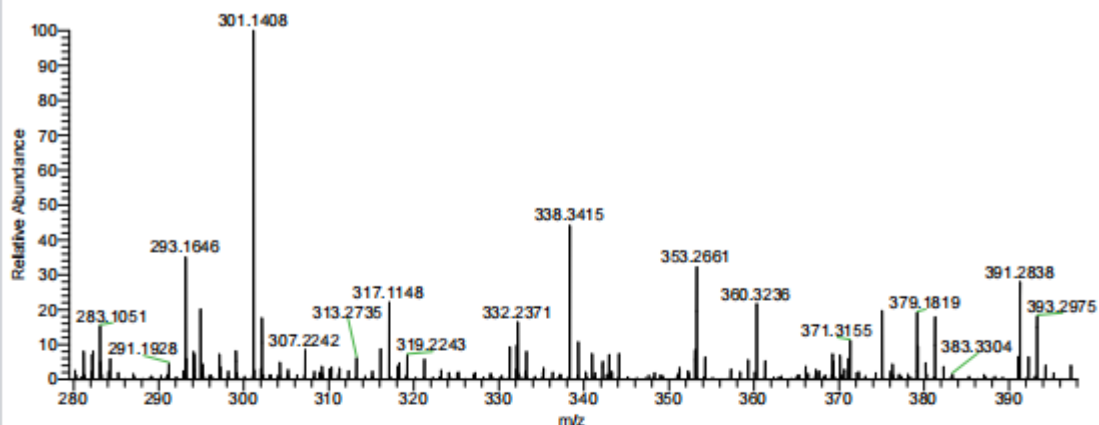


¹⁹F NMR copy of compound **3h**



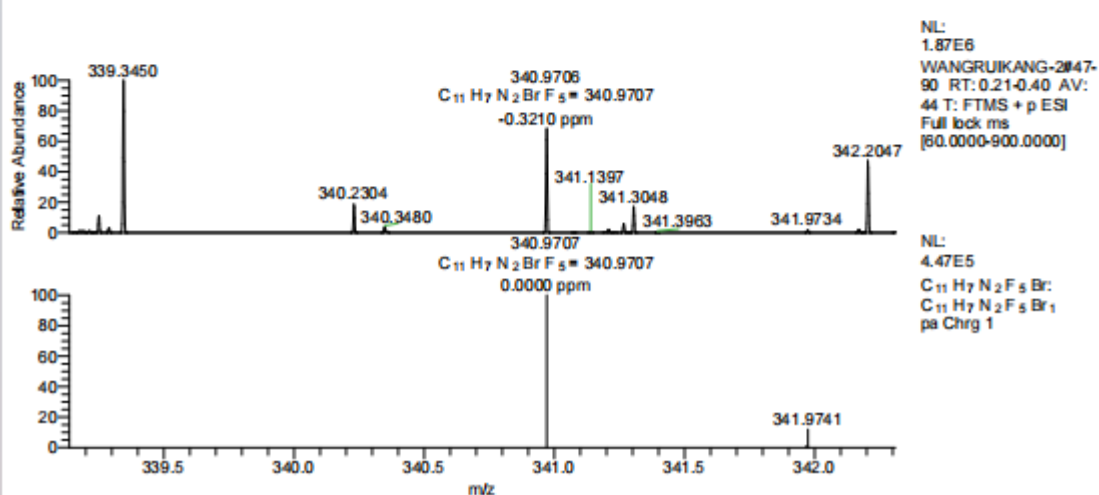
HRMS copy of compound 3h

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T: FTMS + p ESI Full lock ms [60.0000-900.0000]



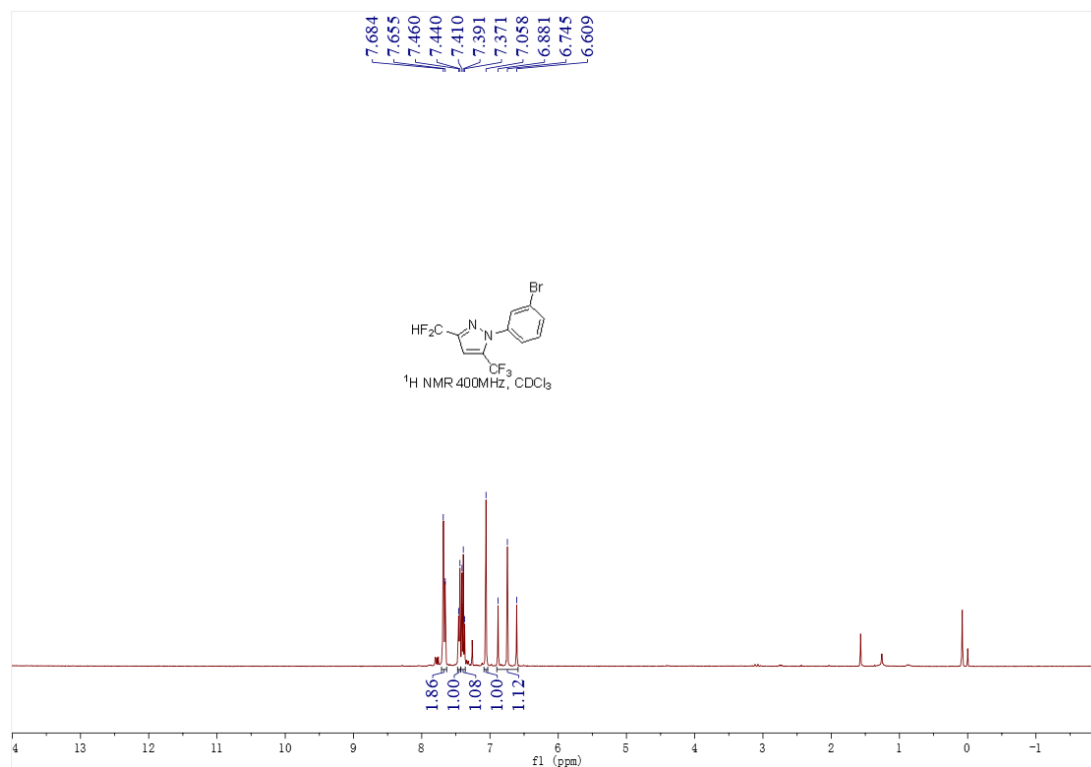
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m/z = 339.1364-342.3095

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
339.3450	1873589.9	100.00			
340.2304	350622.9	18.71			
340.9706	1291521.3	68.93	340.9707	-0.11	C ₁₁ H ₇ N ₂ BrF ₅
341.3048	329300.8	17.58	340.9707	334.10	C ₁₁ H ₇ N ₂ BrF ₅
342.2047	895541.8	47.80			

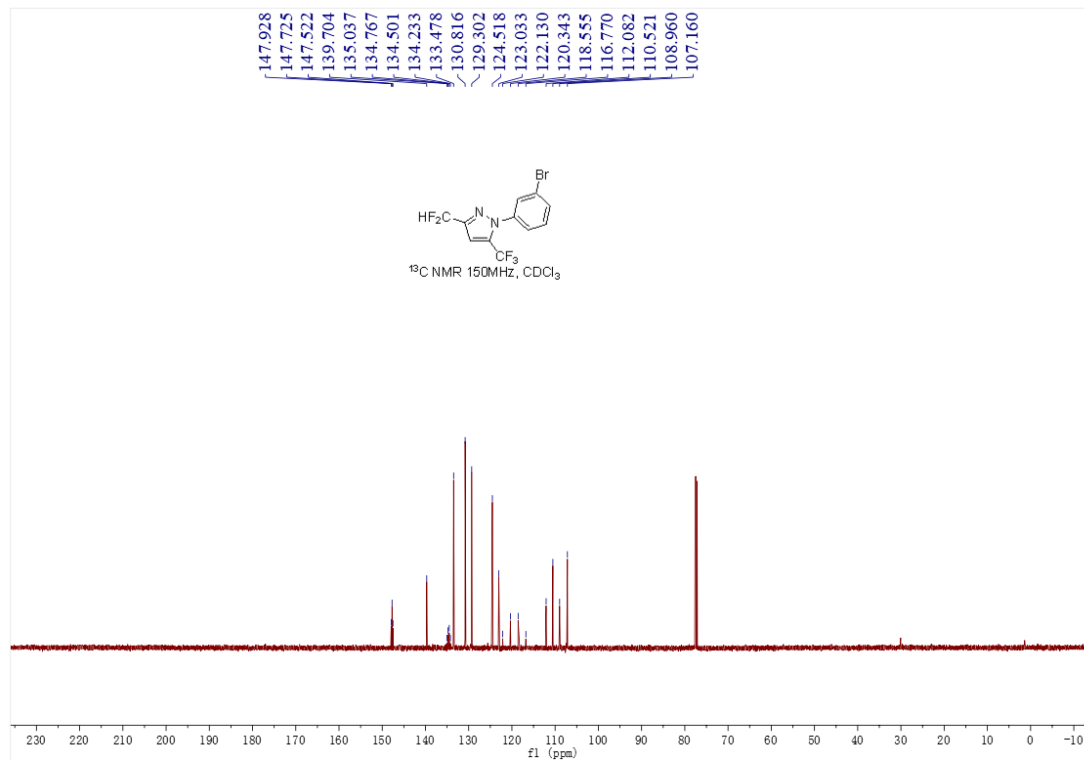


Spectrogram copies of compound **3i**

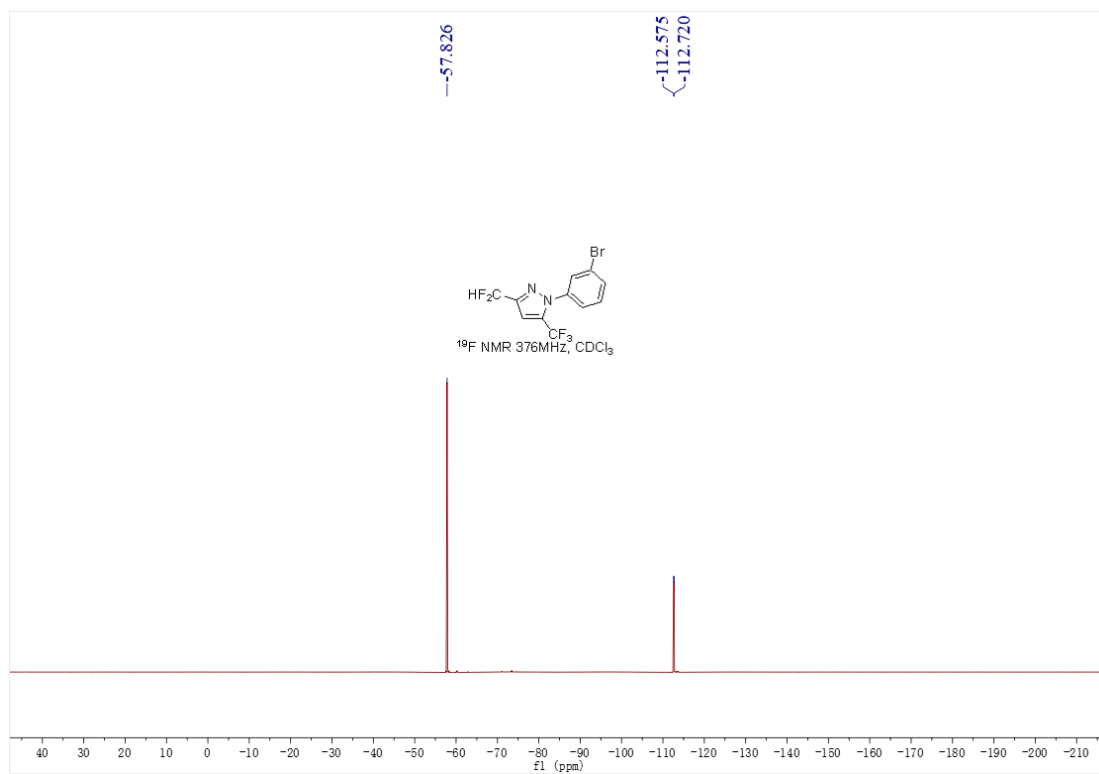
^1H NMR copy of compound **3i**



^{13}C NMR copy of compound **3i**

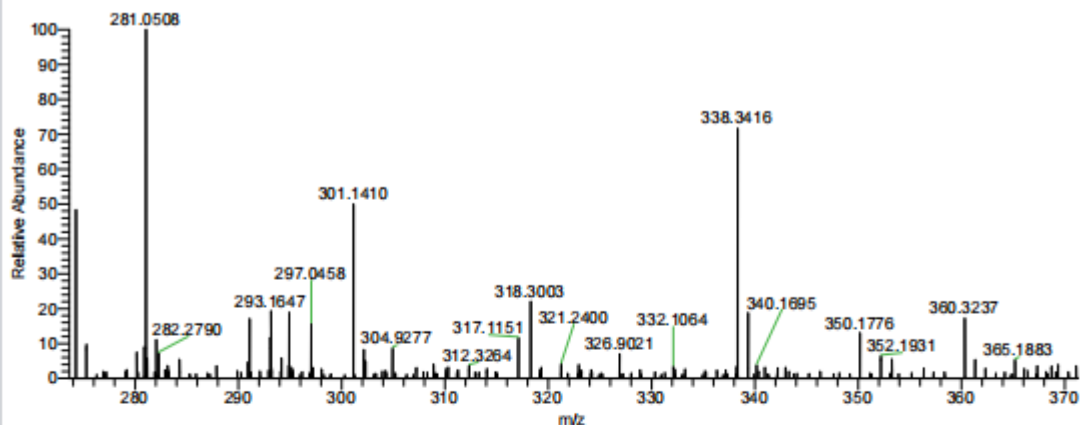


¹⁹F NMR copy of compound **3i**



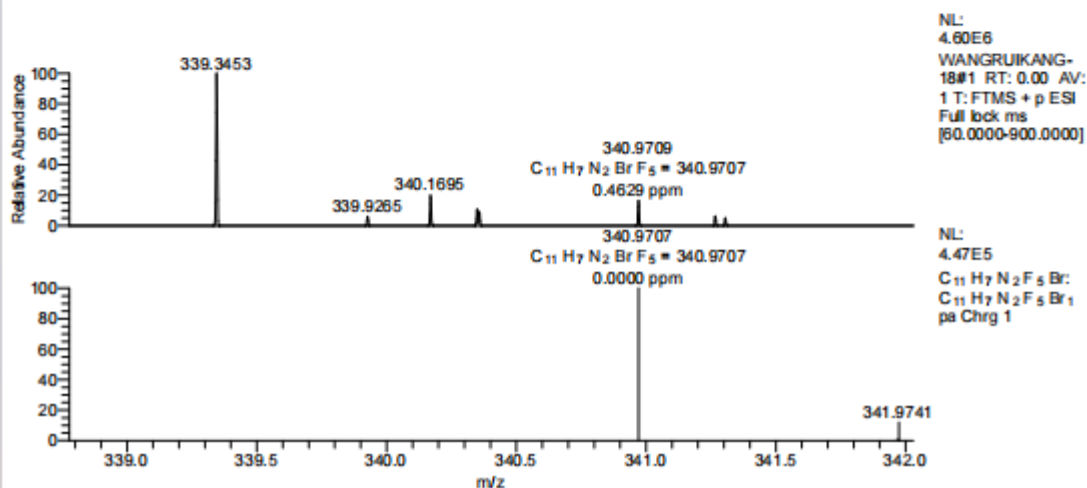
HRMS copy of compound 3i

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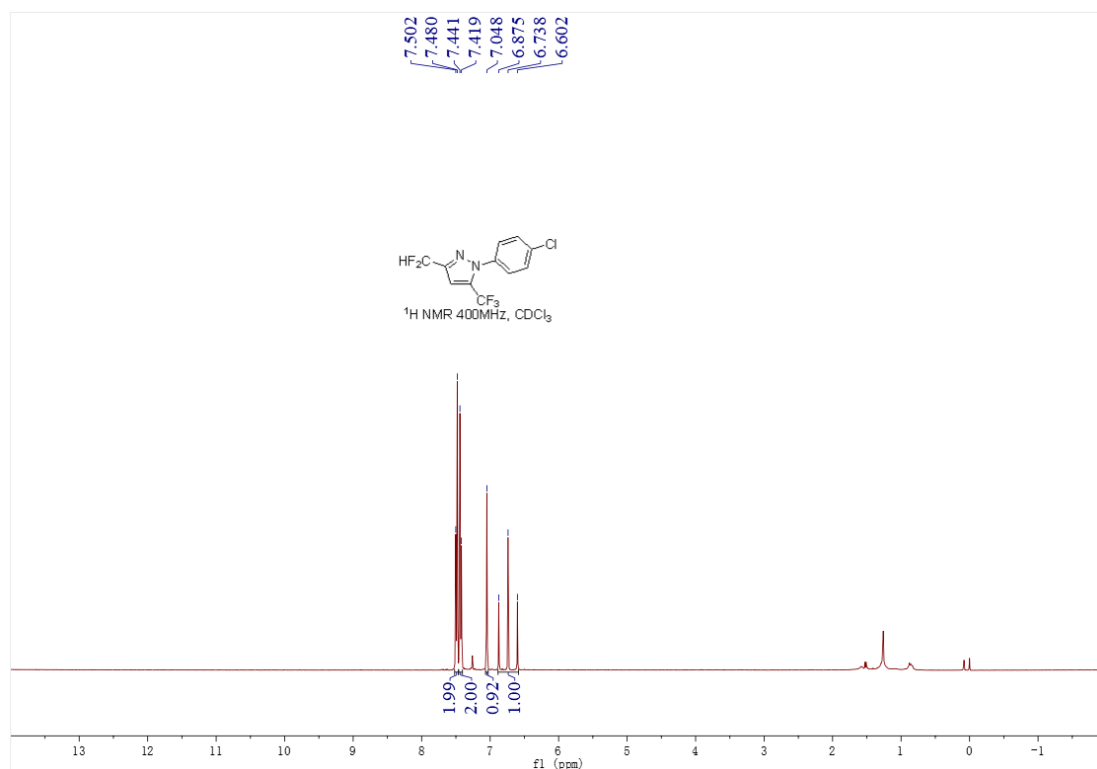
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 m/z = 338.7772-342.0294

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
339.3453	4618260.0	100.00			
340.1695	932057.2	20.18			
340.3485	516863.9	11.19			
340.3577	429236.6	9.29			
340.9709	760309.8	16.46	340.9707	0.16	C ₁₁ H ₇ N ₂ Br F ₅

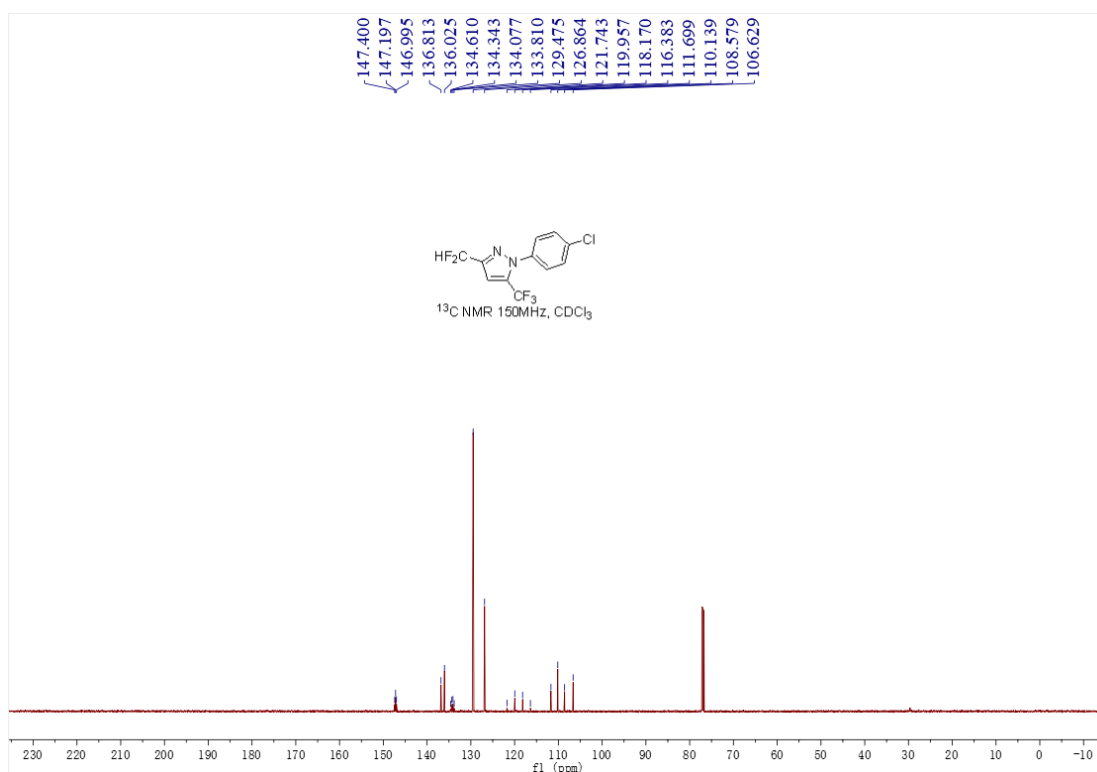


Spectrogram copies of compound **3j**

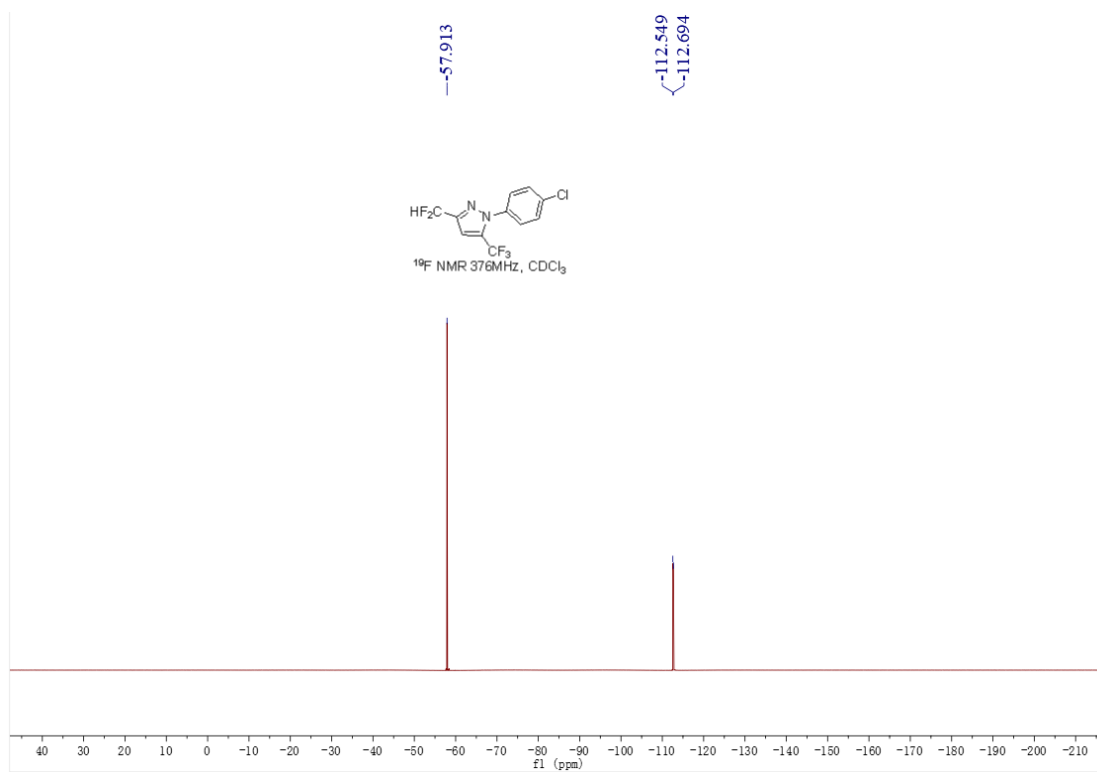
^1H NMR copy of compound **3j**



^{13}C NMR copy of compound **3j**

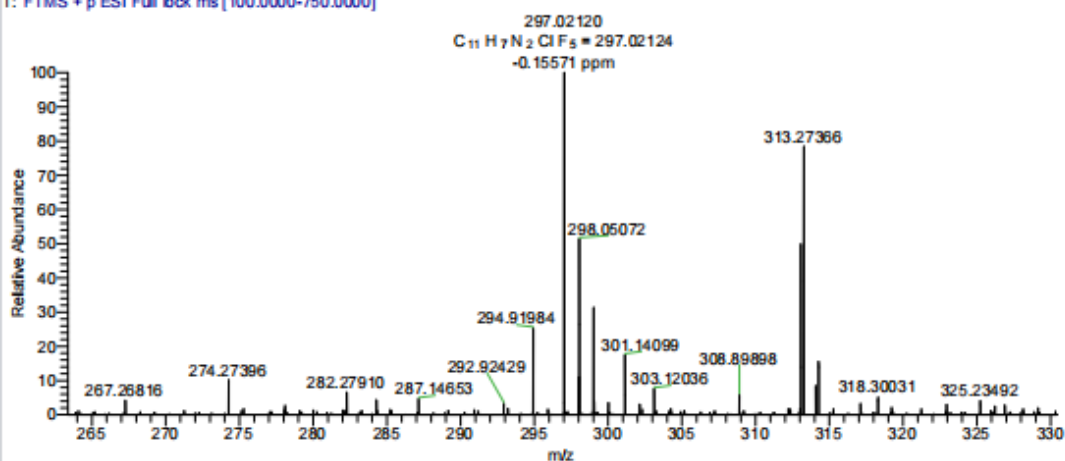


¹⁹F NMR copy of compound **3j**



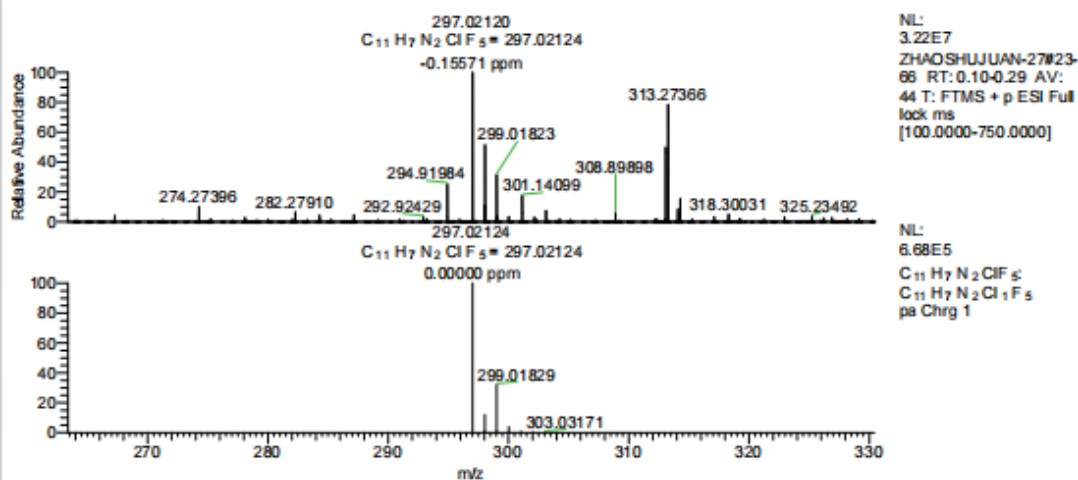
HRMS copy of compound 3j

ZHAOSHUJUAN-27#23-66 RT: 0.10-0.29 AV: 44 NL: 3.22E7
 T: FTMS + p ESI Full lock ms [100.0000-750.0000]



ZHAOSHUJUAN-27#23-66 RT: 0.10-0.29 AV: 44
 T: FTMS + p ESI Full lock ms [100.0000-750.0000]
 m/z = 263.36866-330.41312

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
297.02120	32297652.0	100.00	297.02124	-0.05	C ₁₁ H ₇ N ₂ ClF ₅
298.05072	16630892.0	51.49			
299.01823	10180078.0	31.52			
313.07579	16446007.0	50.92			
313.27366	25305180.0	78.35			

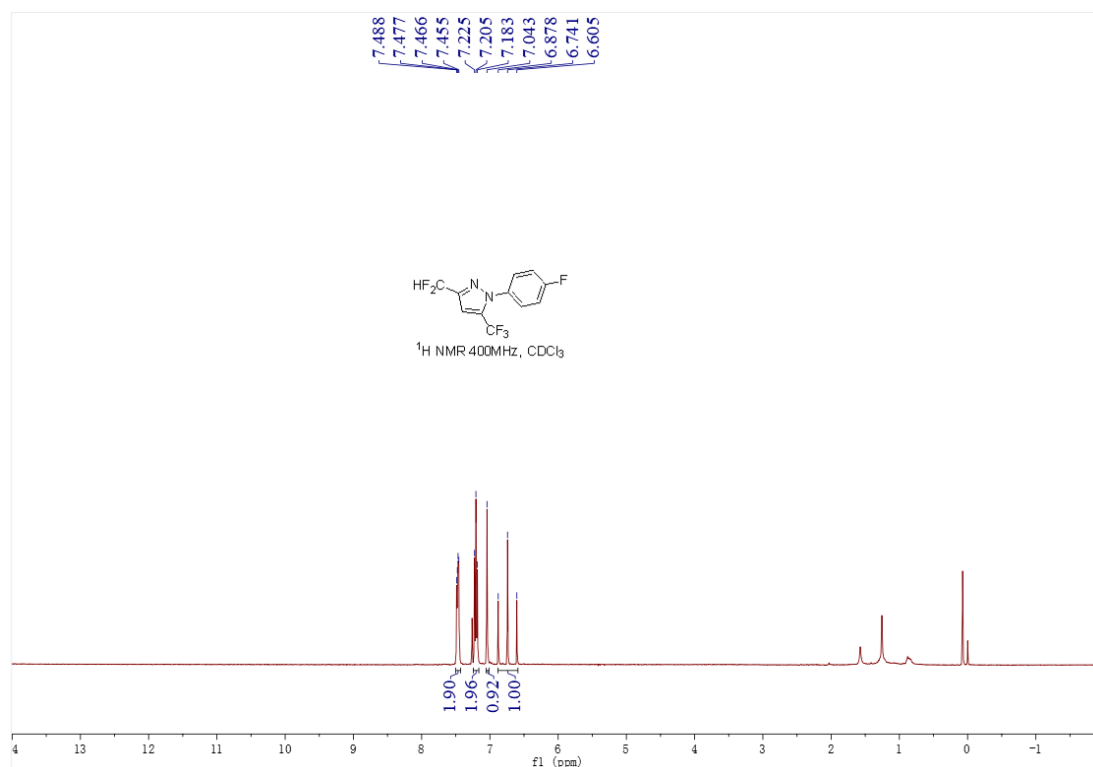


NL: 3.22E7
 ZHAOSHUJUAN-27#23-66 RT: 0.10-0.29 AV: 44 T: FTMS + p ESI Full lock ms [100.0000-750.0000]

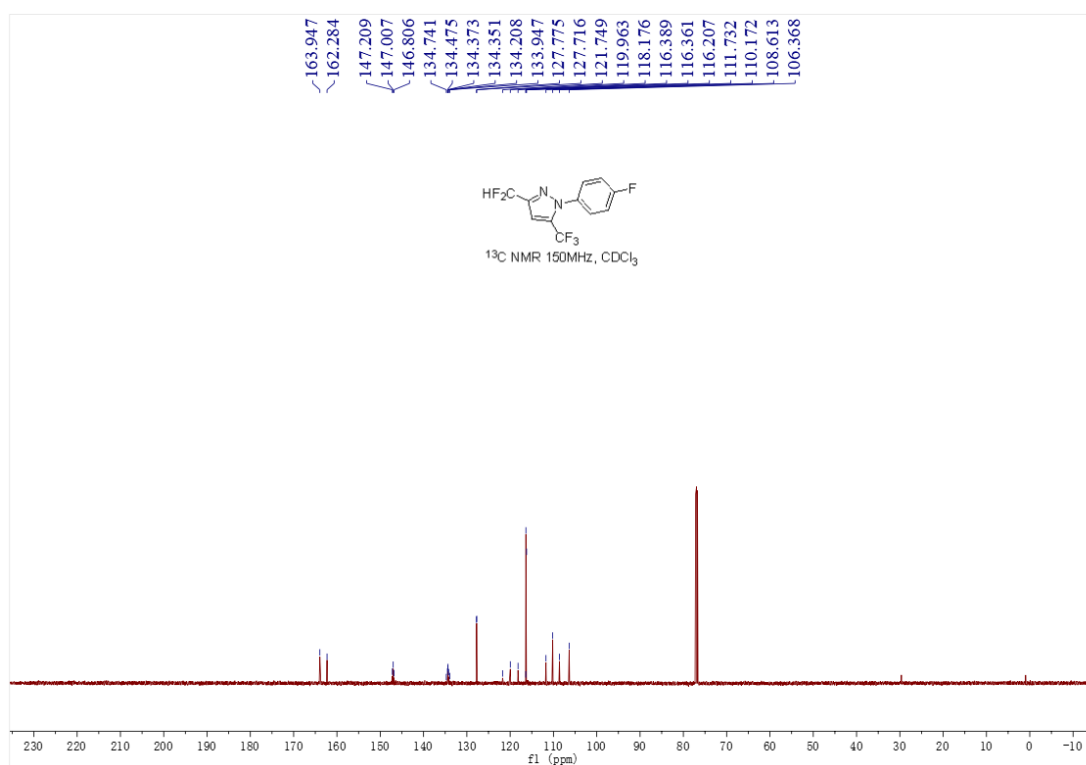
NL: 6.68E5
 C₁₁H₇N₂ClF₅
 C₁₁H₇N₂Cl₁F₅
 pa Chrg 1

Spectrogram copies of compound **3k**

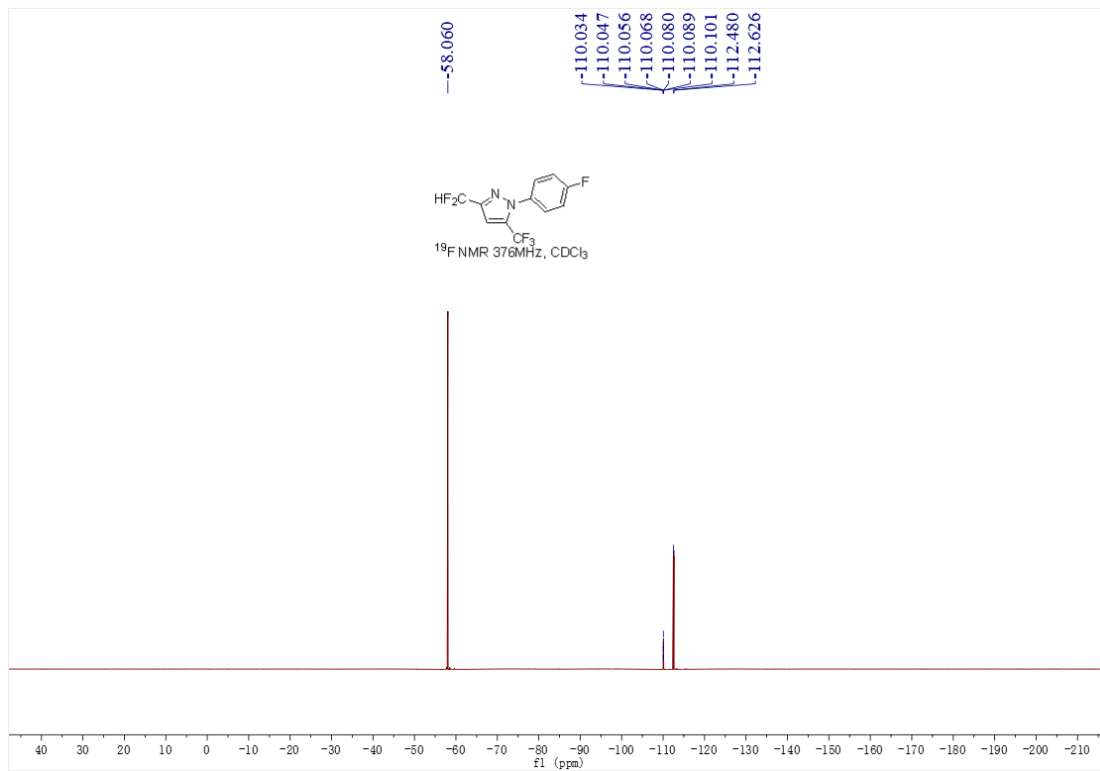
^1H NMR copy of compound **3k**



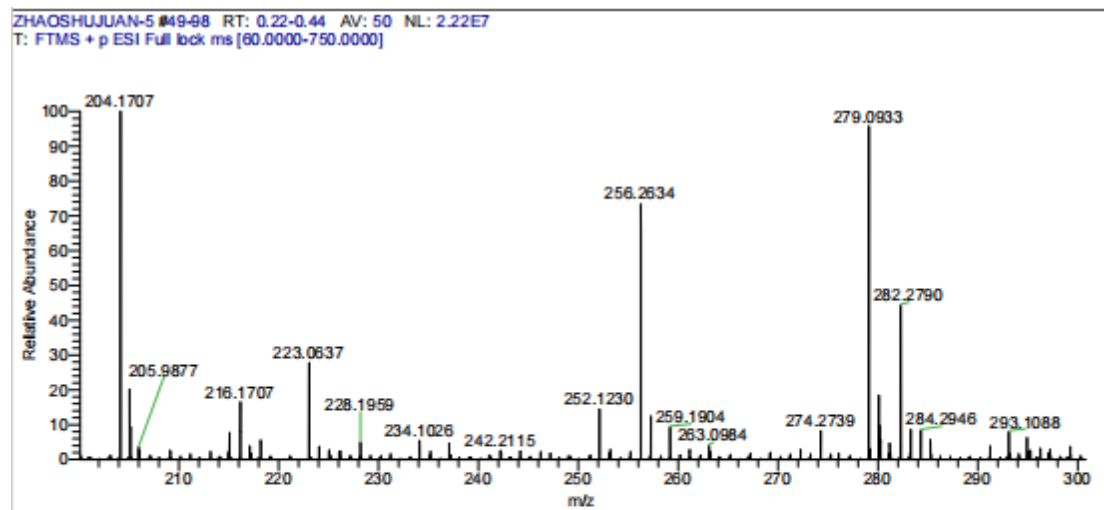
^{13}C NMR copy of compound **3k**



¹⁹F NMR copy of compound **3k**

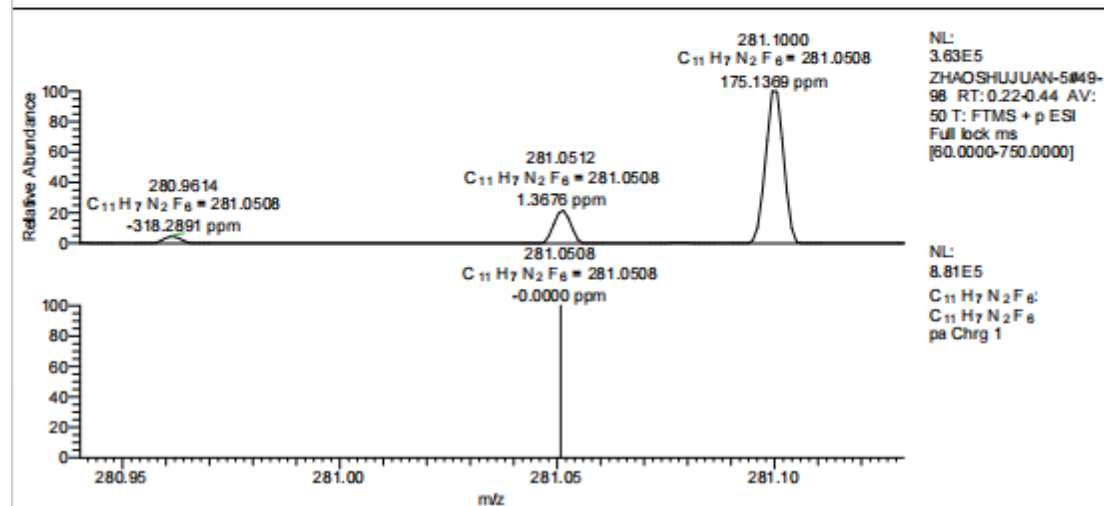


HRMS copy of compound **3k**



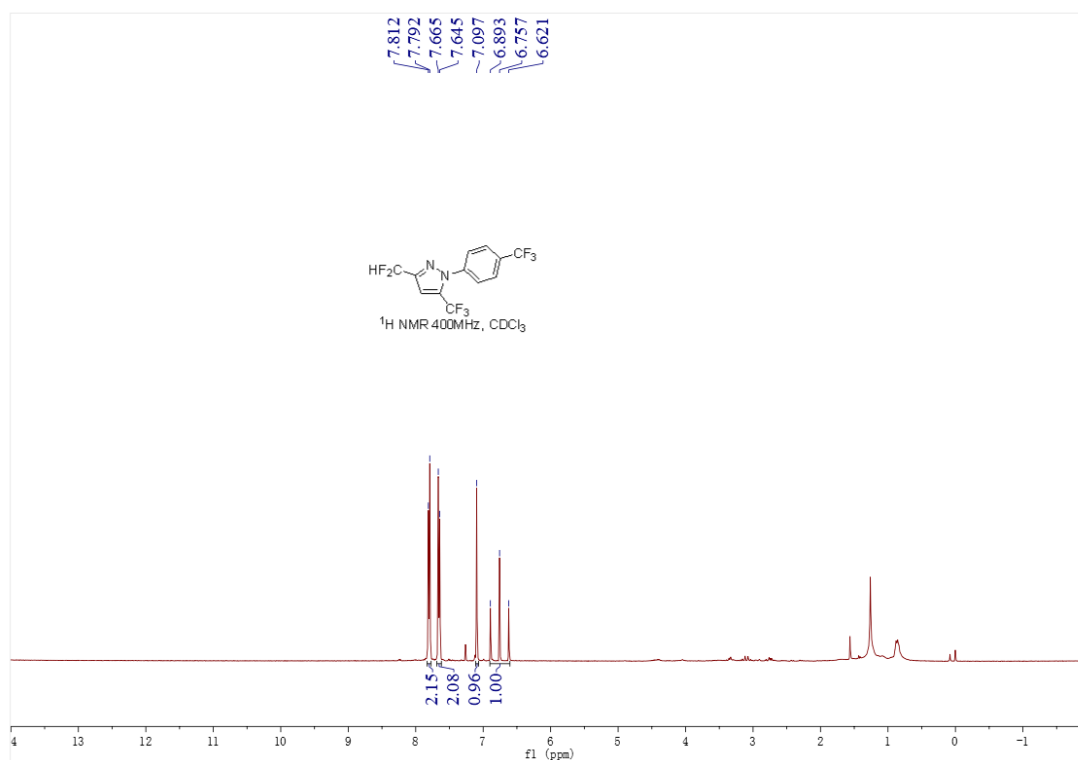
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m/z = 280.9402-281.1298

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
280.9614	16141.6	4.28	281.0508	-89.43	C ₁₁ H ₇ N ₂ F ₆
281.0512	79332.8	21.03	281.0508	0.38	C ₁₁ H ₇ N ₂ F ₆
281.0785	1387.1	0.37	281.0508	27.66	C ₁₁ H ₇ N ₂ F ₆
281.1000	377319.3	100.00	281.0508	49.23	C ₁₁ H ₇ N ₂ F ₆

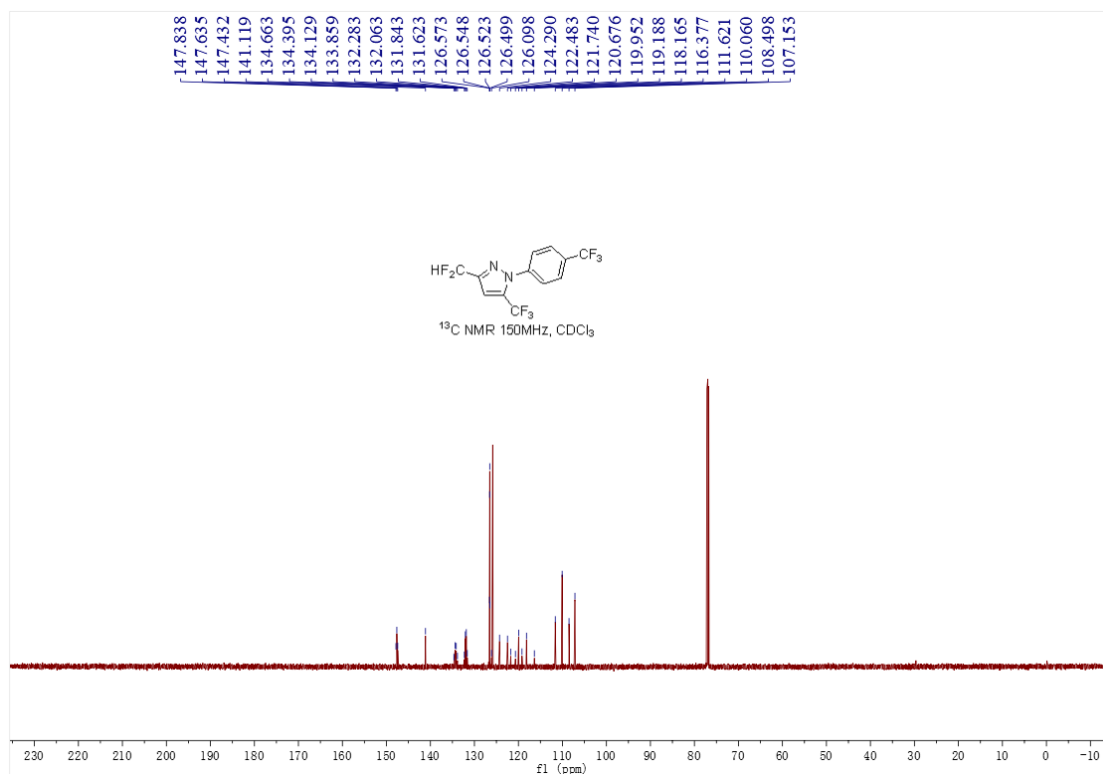


Spectrogram copies of compound **31**

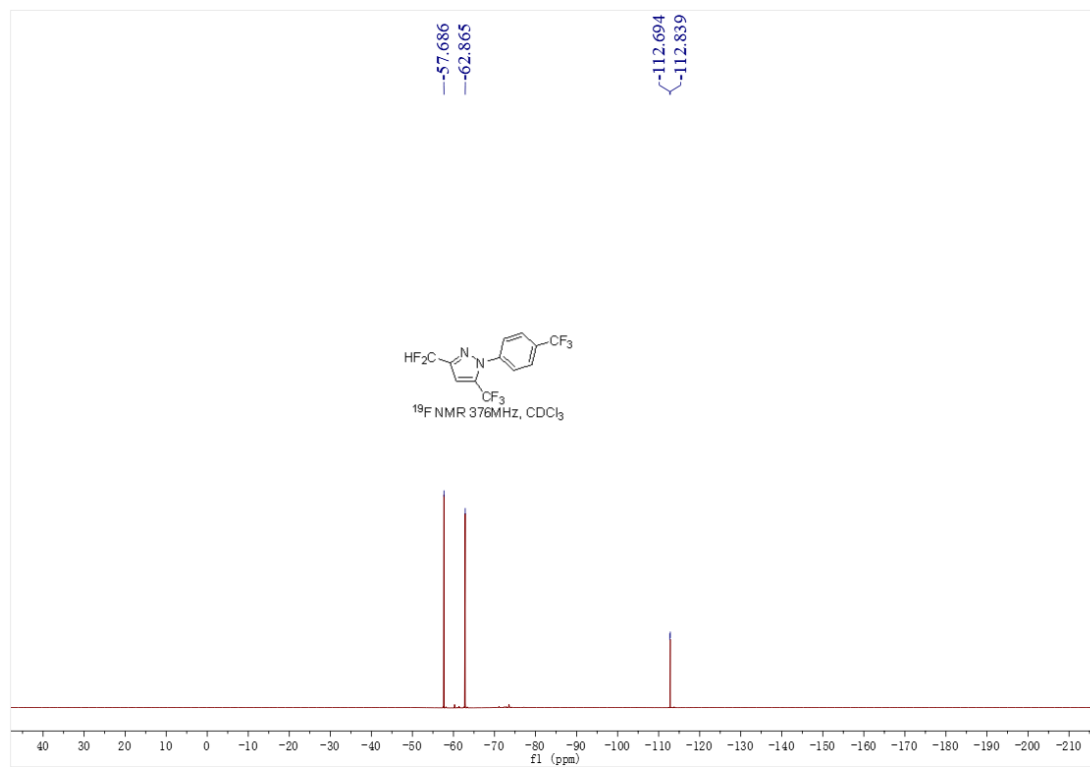
¹H NMR copy of compound **31**



¹³C NMR copy of compound **31**

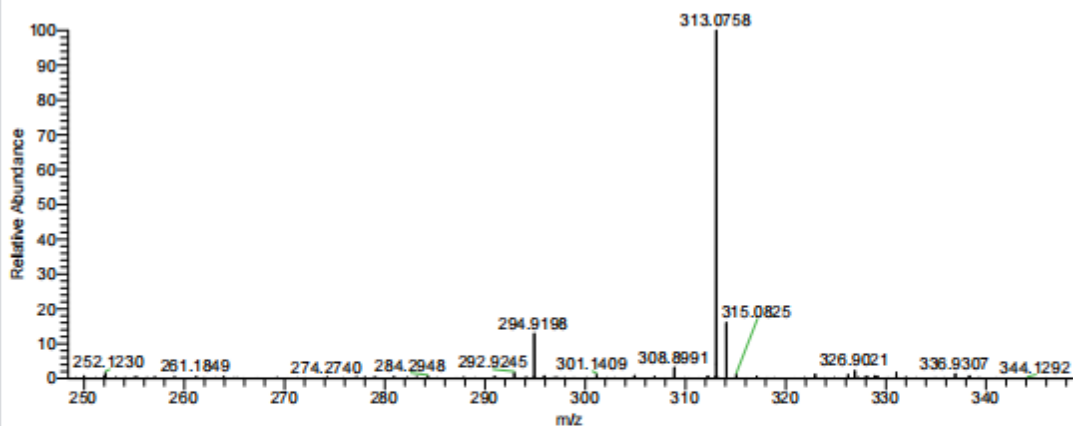


¹⁹F NMR copy of compound **31**



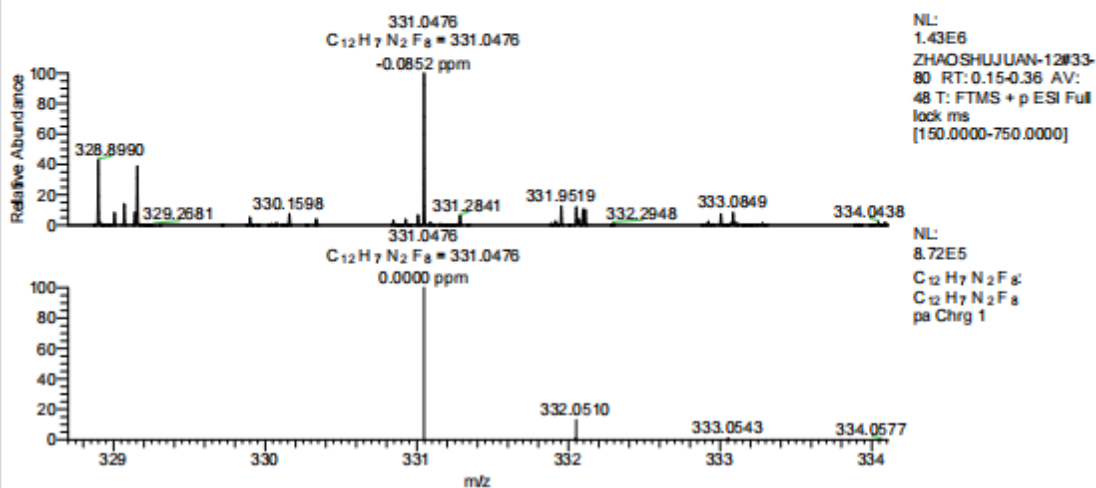
HRMS copy of compound 31

ZHAOSHUJUAN-12#33-80 RT: 0.15-0.36 AV: 48 NL: 8.32E7
T: FTMS + p ESI Full lock ms [150.0000-750.0000]



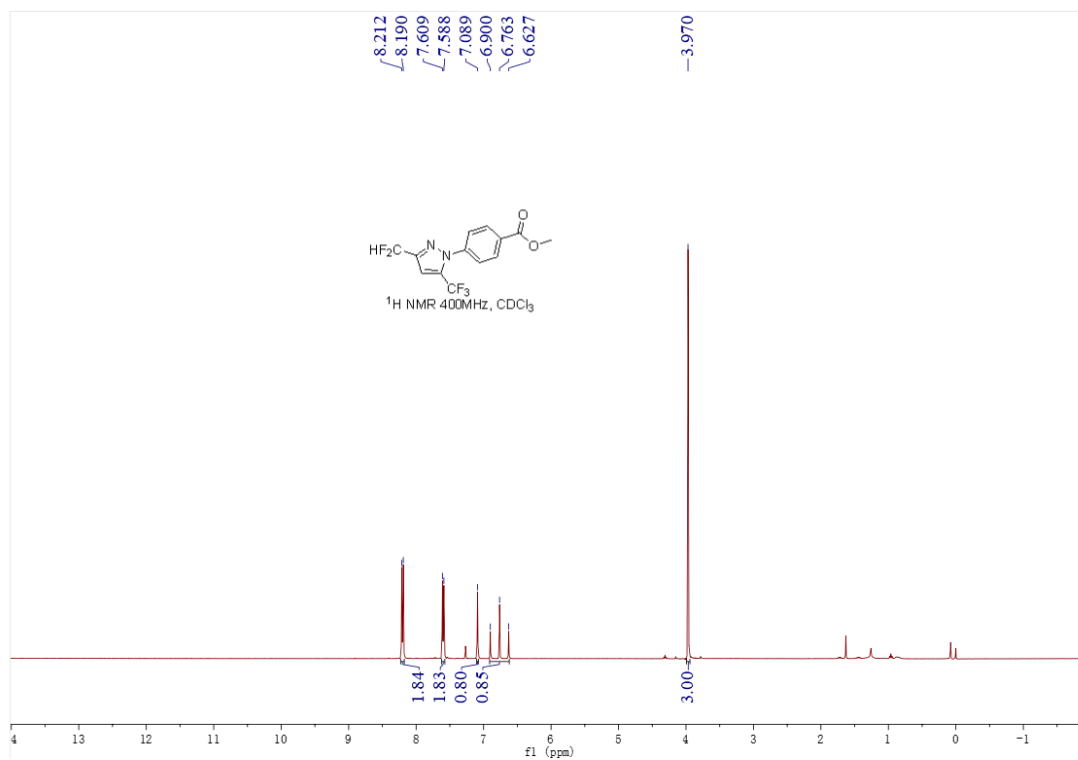
ZHAOSHUJUAN-12#33-80 RT: 0.15-0.36 AV: 48
T: FTMS + p ESI Full lock ms [150.0000-750.0000]
m/z= 328.6993-334.1059

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
328.8990	614642.5	42.43			
329.0705	201316.8	13.90			
329.1567	556355.9	38.40			
331.0476	1448706.8	100.00	331.0476	-0.03	C ₁₂ H ₇ N ₂ F ₈
331.9519	181494.6	12.53			

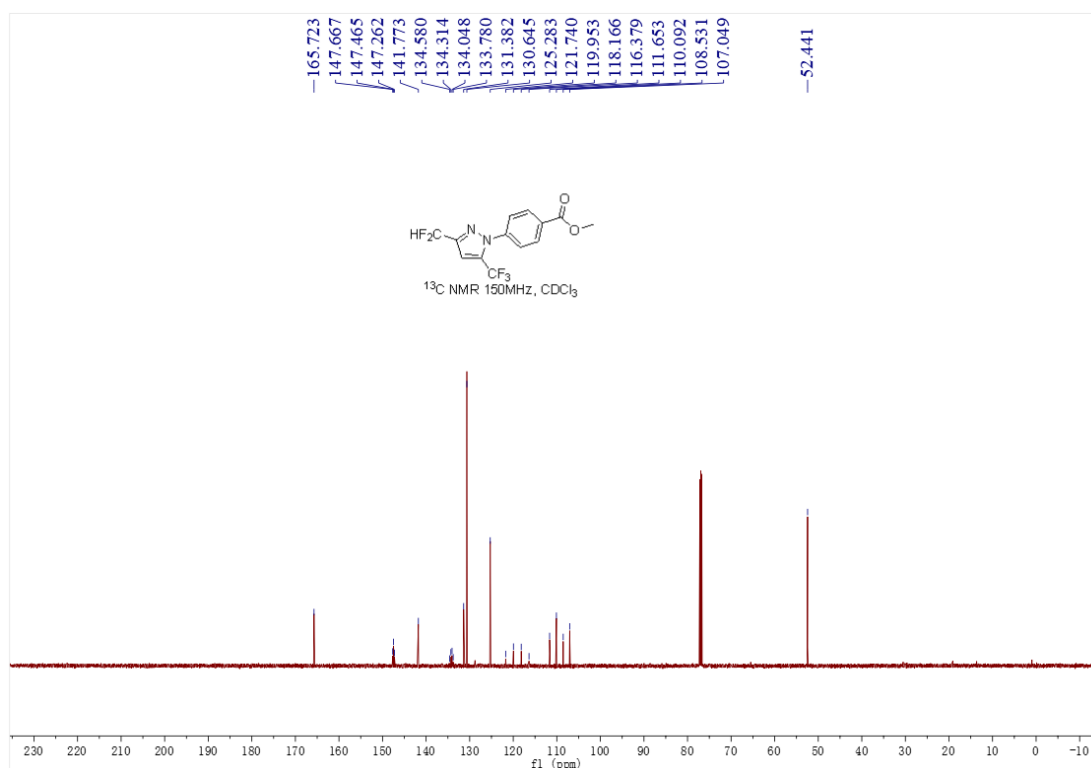


Spectrogram copies of compound **3m**

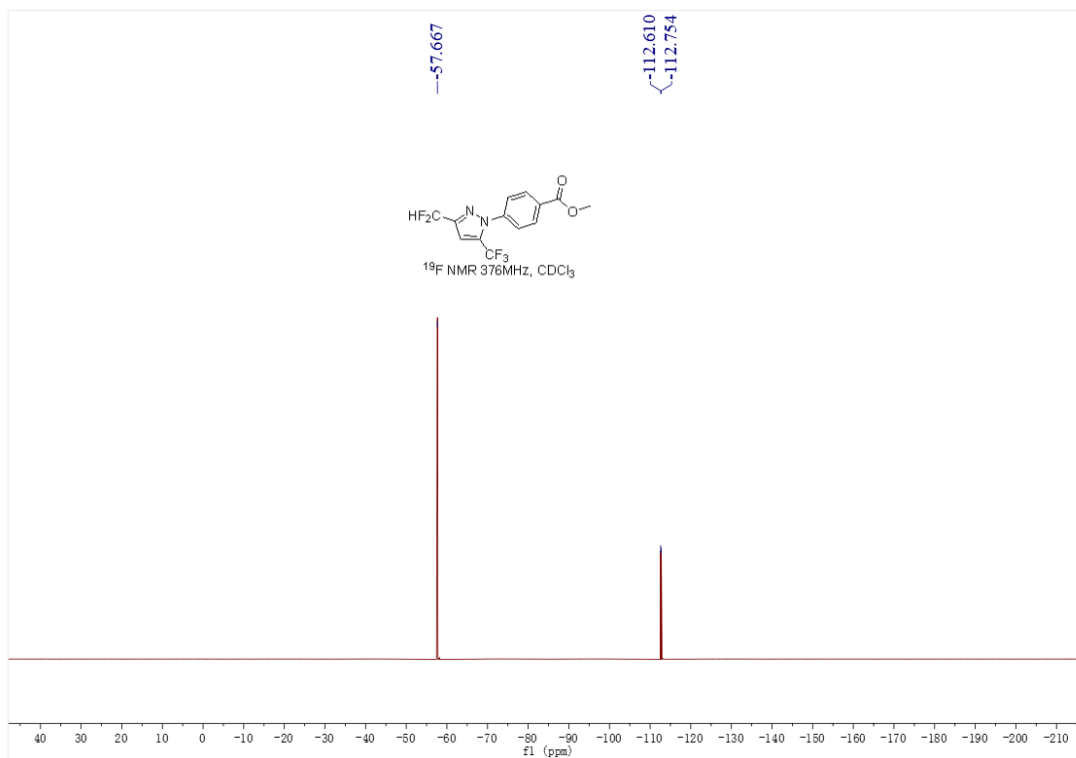
¹H NMR copy of compound **3m**



¹³C NMR copy of compound **3m**

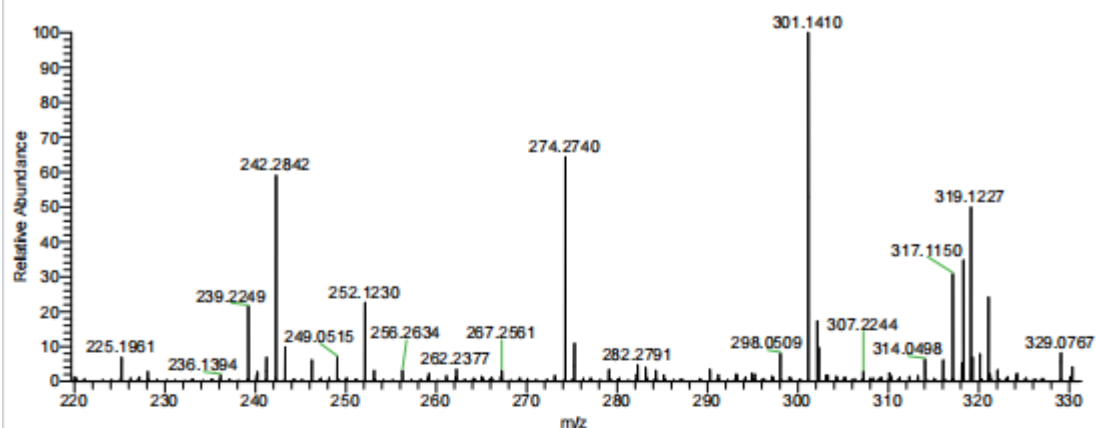


¹⁹F NMR copy of compound **3m**



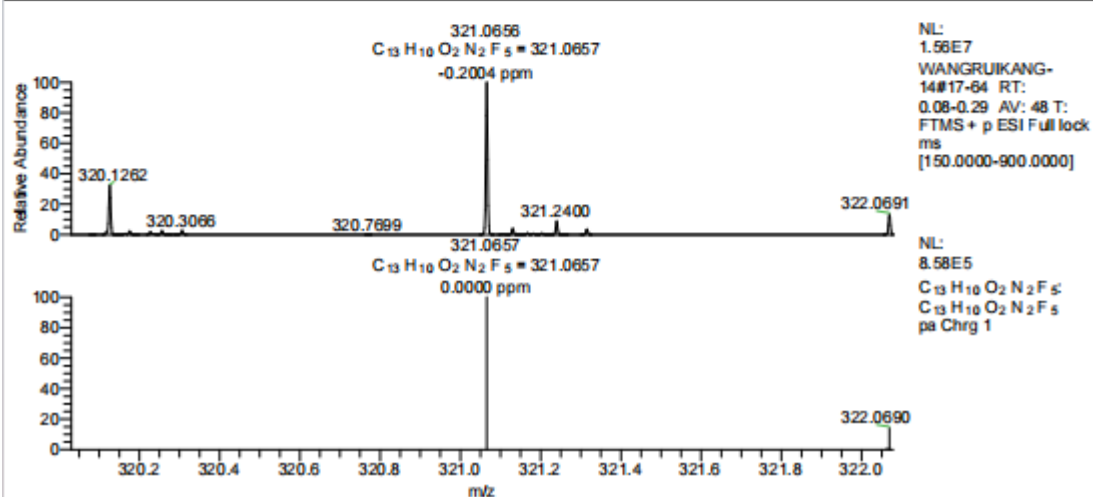
HRMS copy of compound 3m

WANGRUIKANG-14#17-64 RT: 0.08-0.29 AV: 48 NL: 6.46E7
T: FTMS + p ESI Full lock ms [150.0000-900.0000]



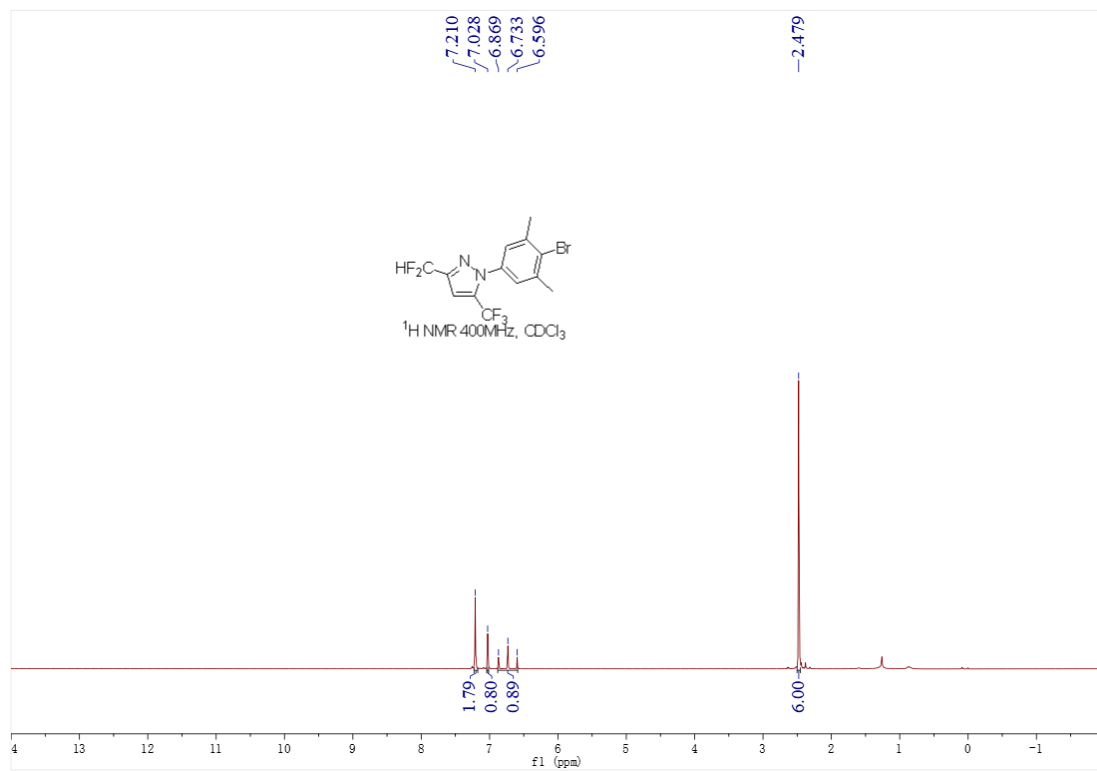
WANGRUIKANG-14#17-64 RT: 0.08-0.29 AV: 48
T: FTMS + p ESI Full lock ms [150.0000-900.0000]
m/z = 320.0302-322.0788

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
320.1262	5061979.0	32.42			
321.0656	15611620.0	100.00	321.0657	-0.06	C ₁₃ H ₁₀ O ₂ N ₂ F ₅
321.1303	633401.8	4.06	321.0657	64.62	C ₁₃ H ₁₀ O ₂ N ₂ F ₅
321.2400	1402895.0	8.99	321.0657	174.33	C ₁₃ H ₁₀ O ₂ N ₂ F ₅
322.0691	2093958.4	13.41			

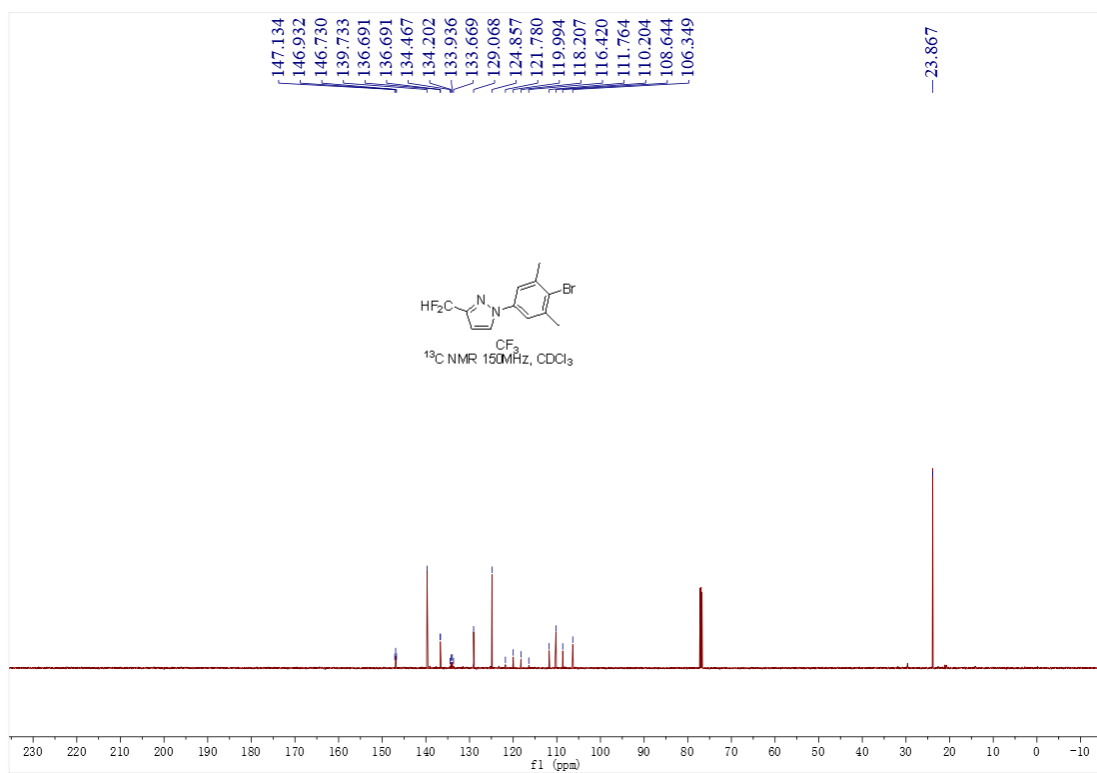


Spectrogram copies of compound **3n**

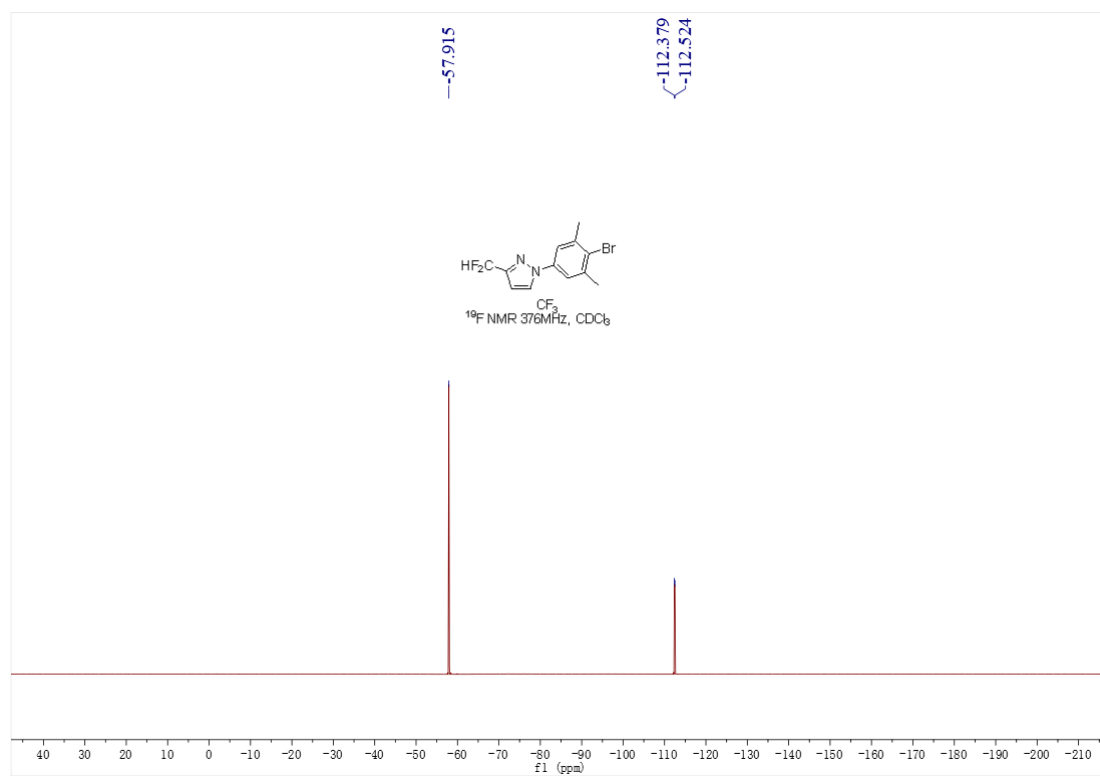
^1H NMR copy of compound **3n**



^{13}C NMR copy of compound **3n**

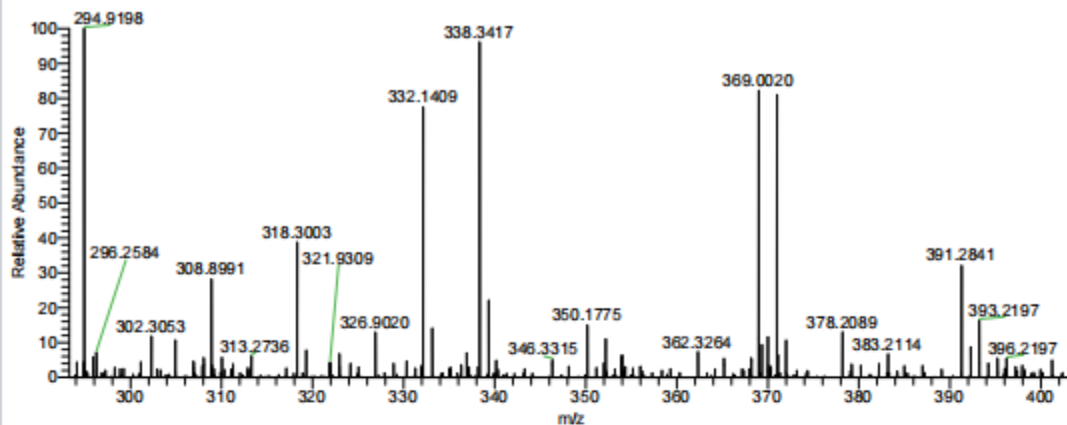


¹⁹F NMR copy of compound **3n**



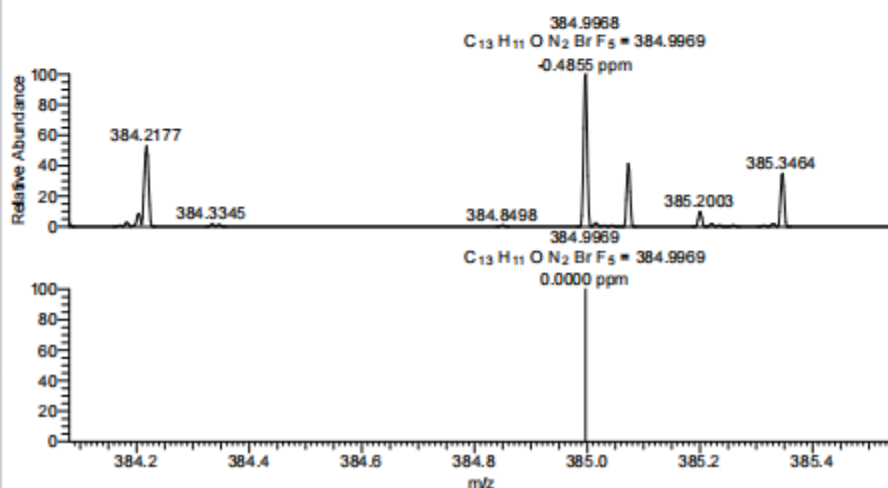
HRMS copy of compound 3n

ZHAOSHUJUAN-8 #18-68 RT: 0.08-0.30 AV: 51 NL: 1.50E7
T: FTMS + p ESI Full lock ms [60.0000-750.0000]



ZHAOSHUJUAN-8 #18-68 RT: 0.08-0.30 AV: 51
T: FTMS + p ESI Full lock ms [60.0000-750.0000]
m/z = 384.0804-385.5453

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
384.2177	258029.2	51.30			
384.9968	503013.9	100.00	384.9969	-0.19	C ₁₃ H ₁₁ O N ₂ Br F ₅
385.0730	202115.4	40.18	384.9969	76.10	C ₁₃ H ₁₁ O N ₂ Br F ₅
385.2003	48659.7	9.67	384.9969	203.32	C ₁₃ H ₁₁ O N ₂ Br F ₅
385.3464	173504.5	34.49	384.9969	349.45	C ₁₃ H ₁₁ O N ₂ Br F ₅

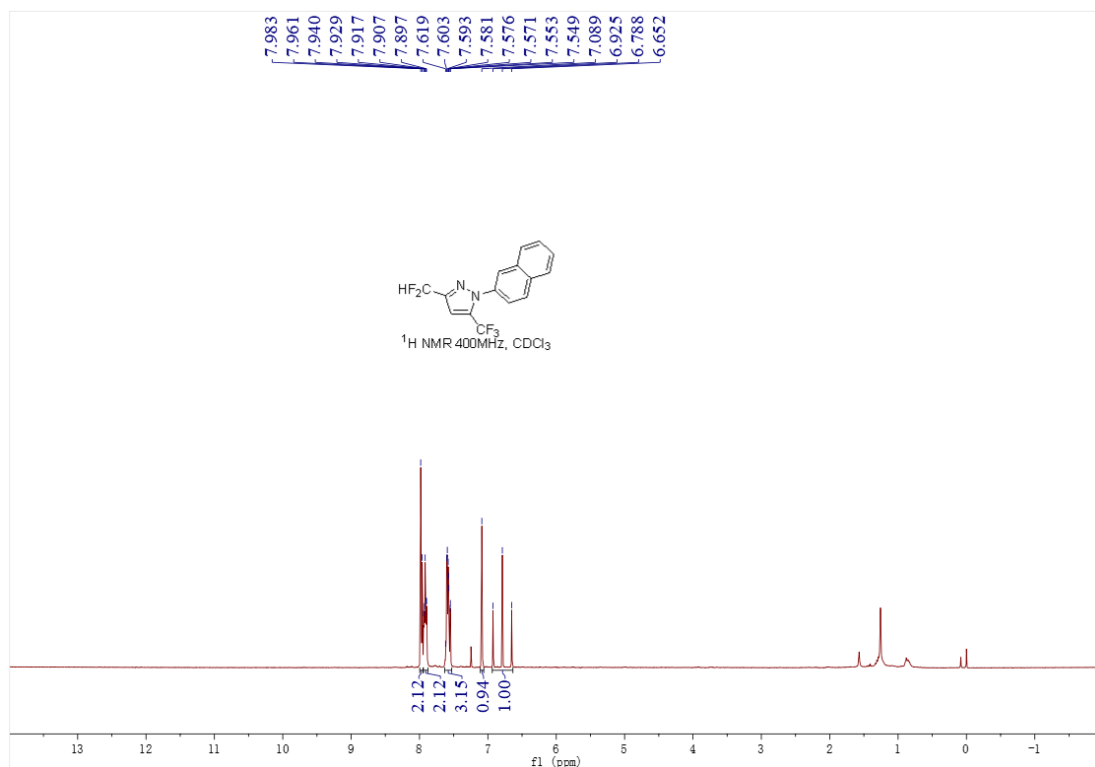


NL:
4.87E5
ZHAOSHUJUAN-8#18-68 RT: 0.08-0.30 AV: 51 T: FTMS + p ESI Full lock ms [60.0000-750.0000]

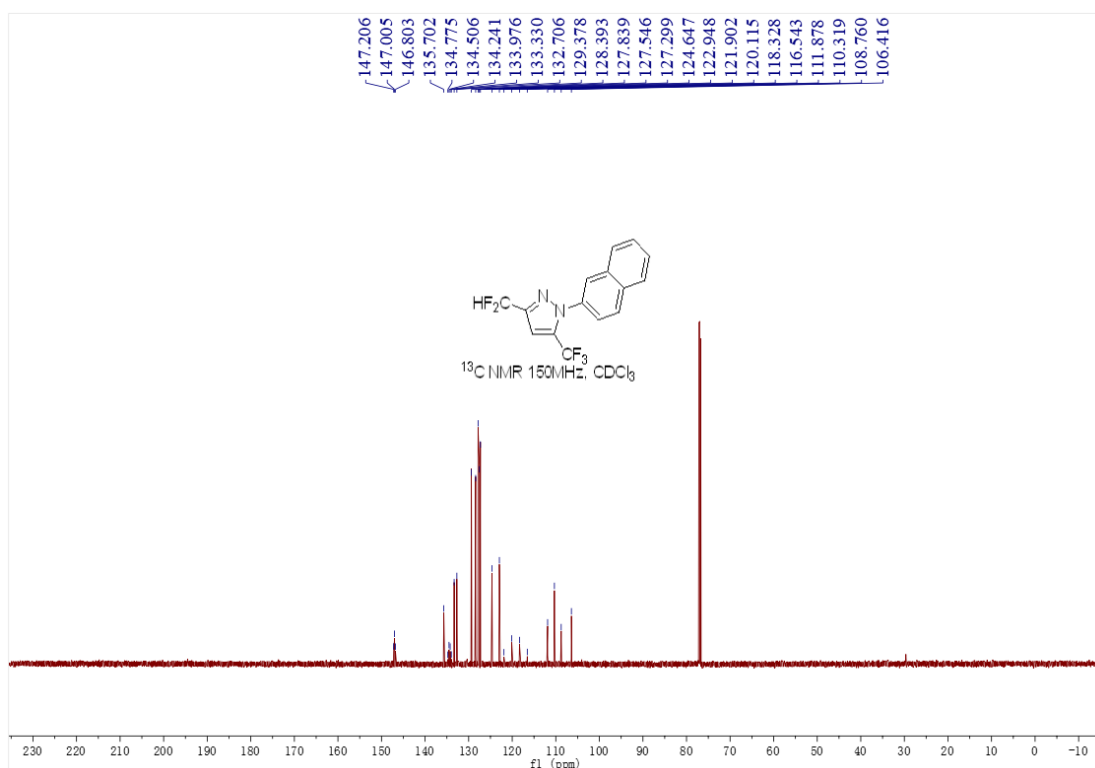
NL:
4.36E5
C₁₃H₁₀N₂BrF₅OH:
C₁₃H₁₁N₂BrF₅O₁
pa Chrg 1

Spectrogram copies of compound **3o**

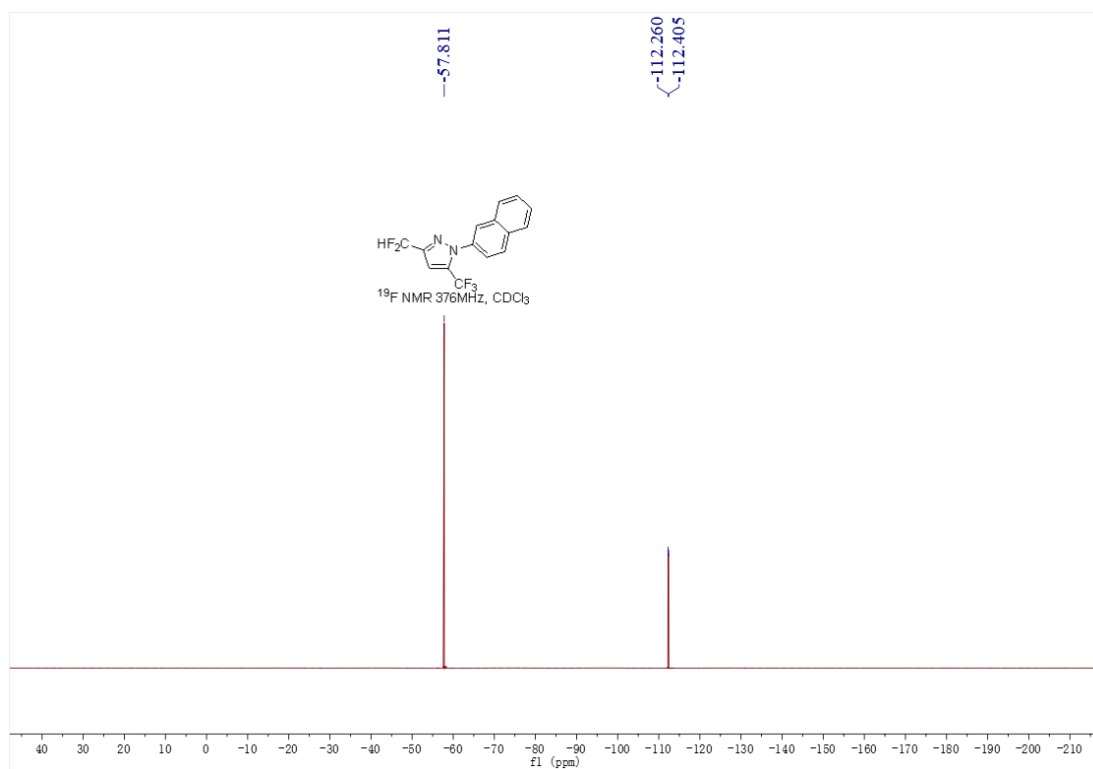
¹H NMR copy of compound **3o**



¹³C NMR copy of compound **3o**

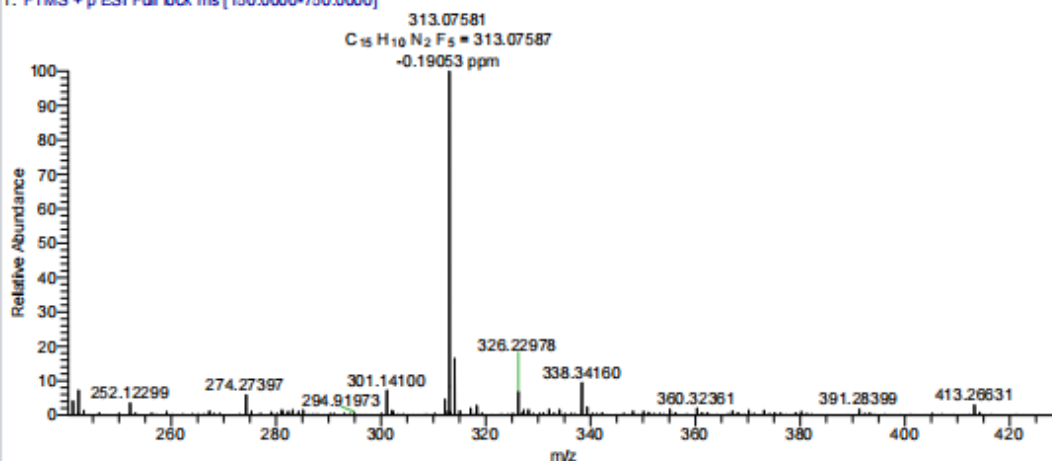


¹⁹F NMR copy of compound **3o**



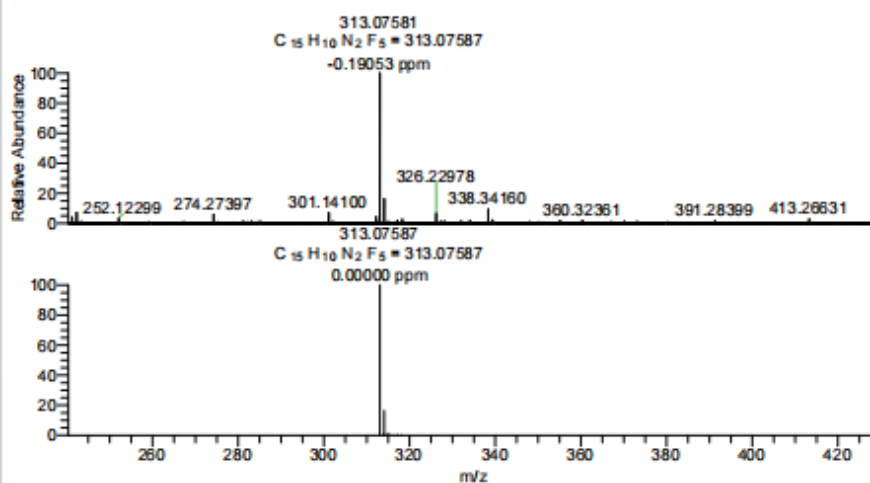
HRMS copy of compound 3o

ZHAOSHUJUAN-9#21-65 RT: 0.09-0.29 AV: 45 NL: 5.73E8
 T: FTMS + p ESI Full lock ms [150.0000-750.0000]



ZHAOSHUJUAN-9#21-65 RT: 0.09-0.29 AV: 45
 T: FTMS + p ESI Full lock ms [150.0000-750.0000]
 m/z= 240.31556-429.87852

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
242.28421	42824316.0	7.31			
301.14100	42620976.0	7.28			
313.07581	585620544.0	100.00	313.07587	-0.06	C ₁₅ H ₁₀ N ₂ F ₅
314.07888	94805536.0	16.19			
338.34160	54612028.0	9.33			

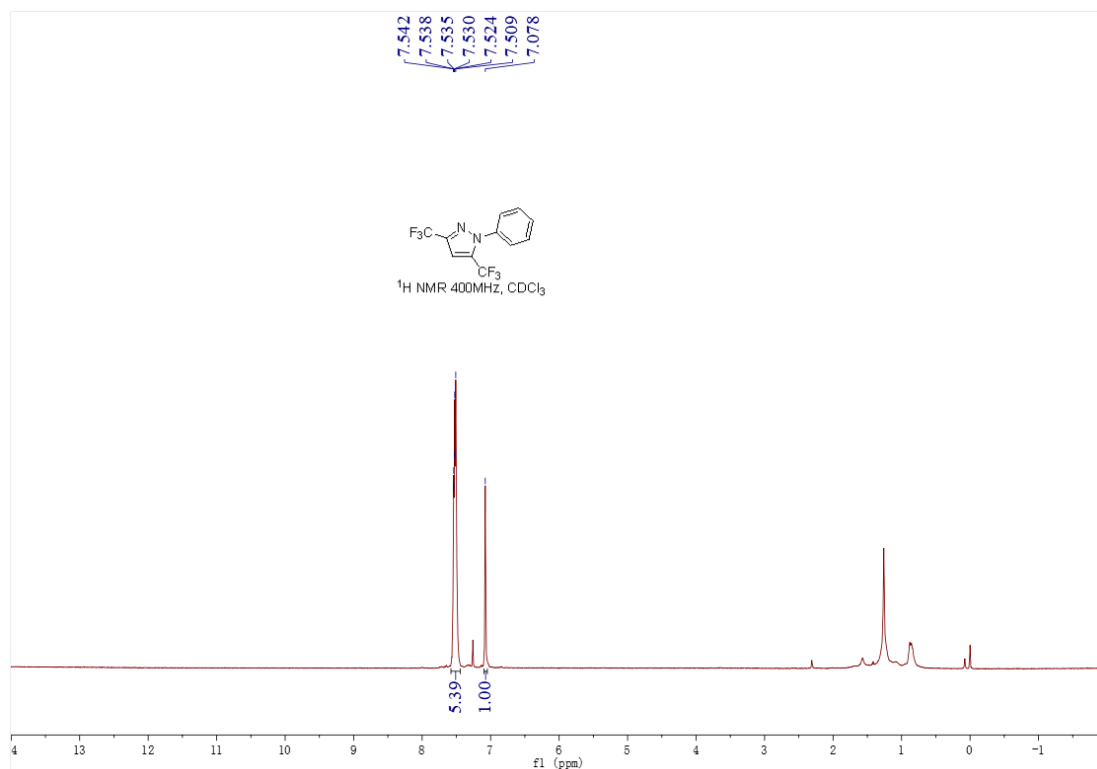


NL:
 5.73E8
 ZHAOSHUJUAN-9#21-
 65 RT: 0.09-0.29 AV:
 45 T: FTMS + p ESI
 Full lock ms
 [150.0000-750.0000]

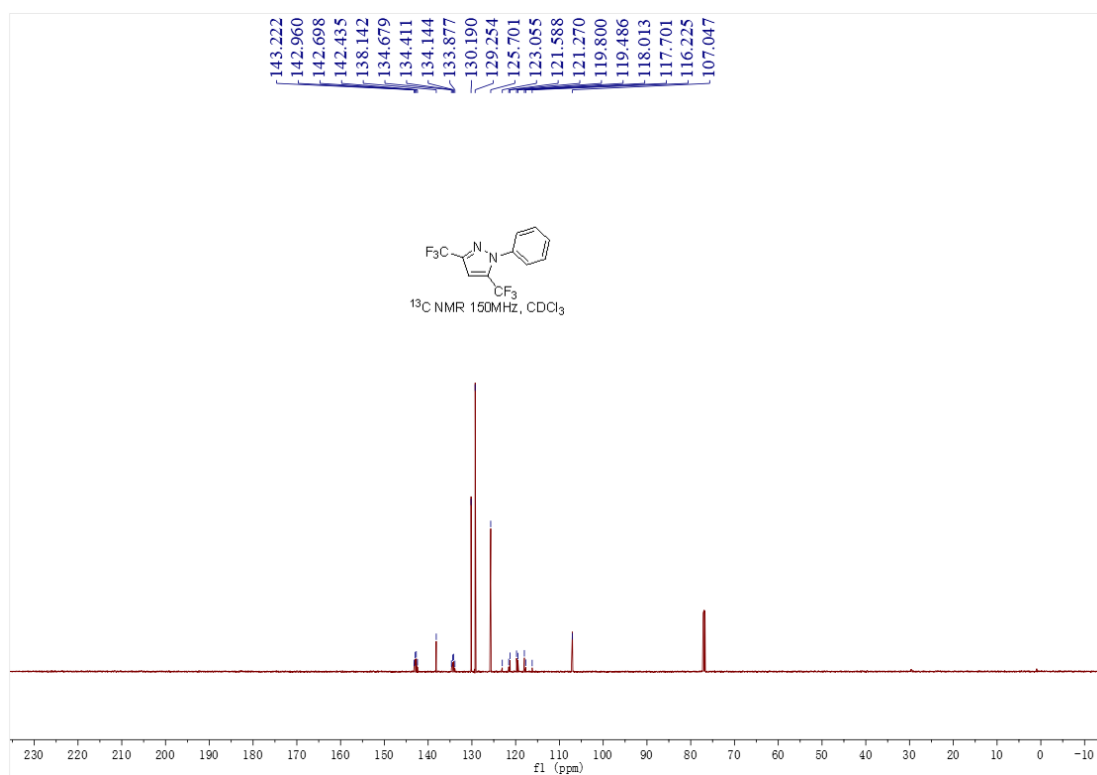
NL:
 8.44E5
 C₁₅H₁₀N₂F₅:
 C₁₅H₁₀N₂F₅
 pa Chrg 1

Spectrogram copies of compound **3a'**

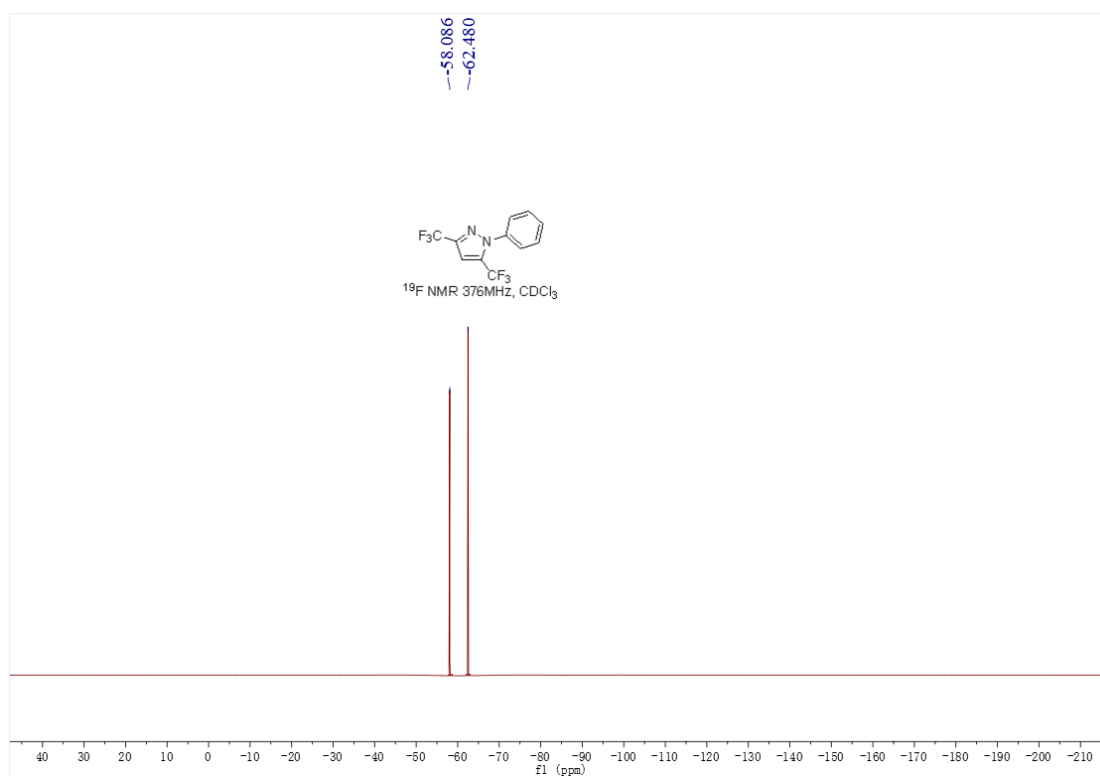
^1H NMR copy of compound **3a'**



^{13}C NMR copy of compound **3a'**

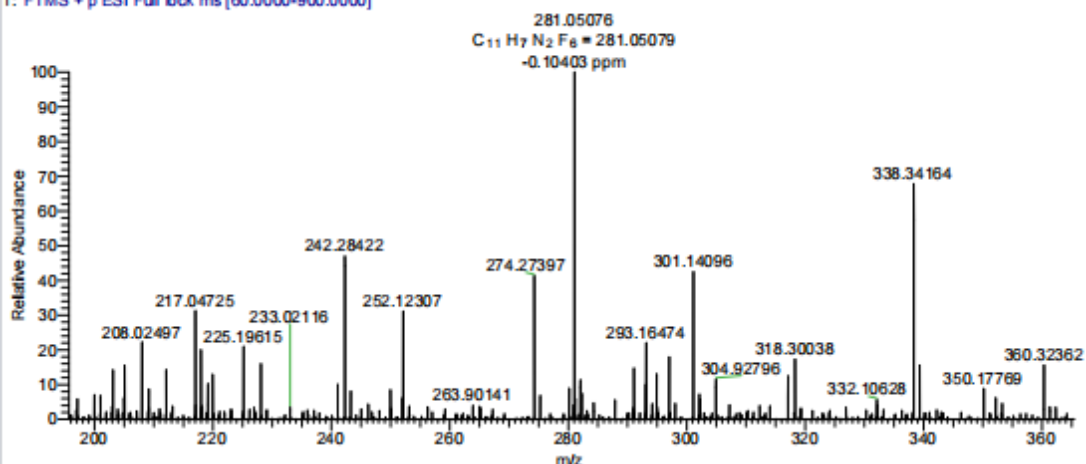


¹⁹F NMR copy of compound **3a'**



HRMS copy of compound 3a'

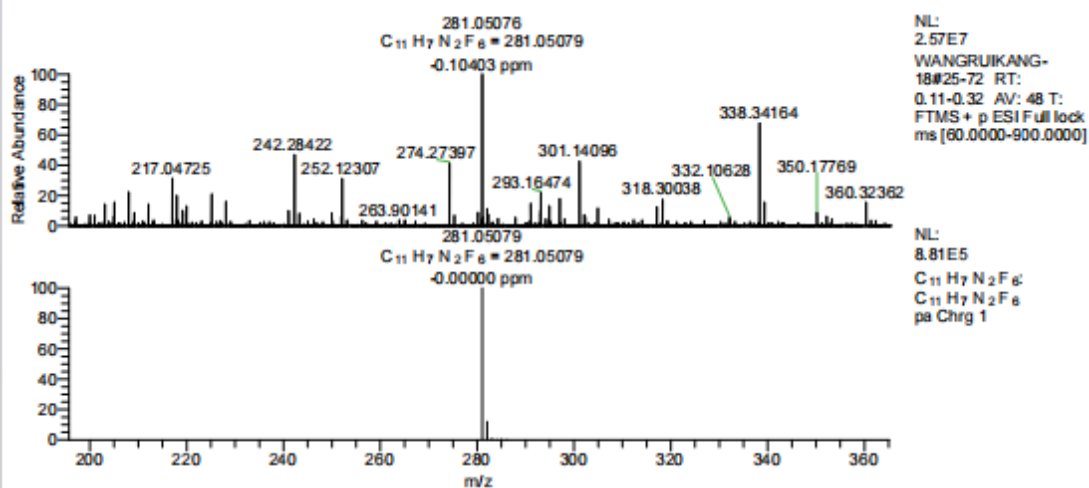
WANGRUIKANG-18#25-72 RT: 0.11-0.32 AV: 48 NL: 2.57E7
 T: FTMS + p ESI Full lock ms [60.0000-900.0000]



WANGRUIKANG-18#25-72 RT: 0.11-0.32 AV: 48
 T: FTMS + p ESI Full lock ms [60.0000-900.0000]

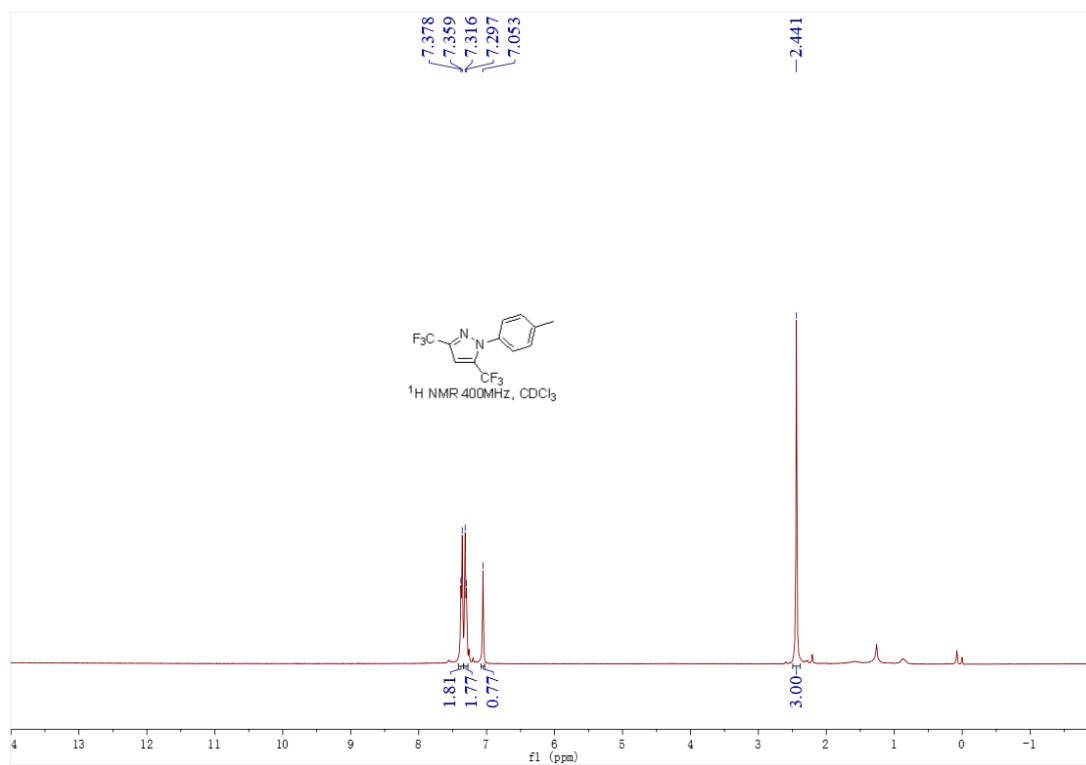
m/z = 195.67604-365.10405

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
242.28422	12262807.0	47.29			
274.27397	10737153.0	41.40			
281.05076	25933474.0	100.00	281.05079	-0.03	C ₁₁ H ₇ N ₂ F ₆
301.14096	11039279.0	42.57			
338.34164	17449414.0	67.29			

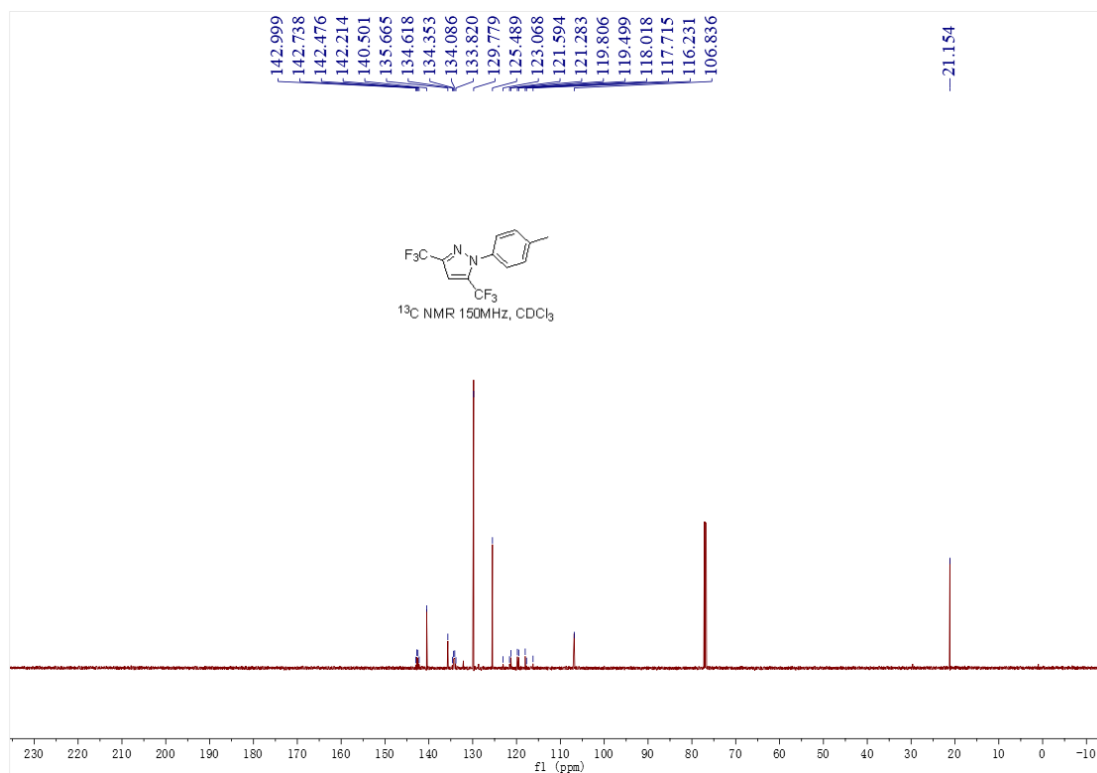


Spectrogram copies of compound **3b'**

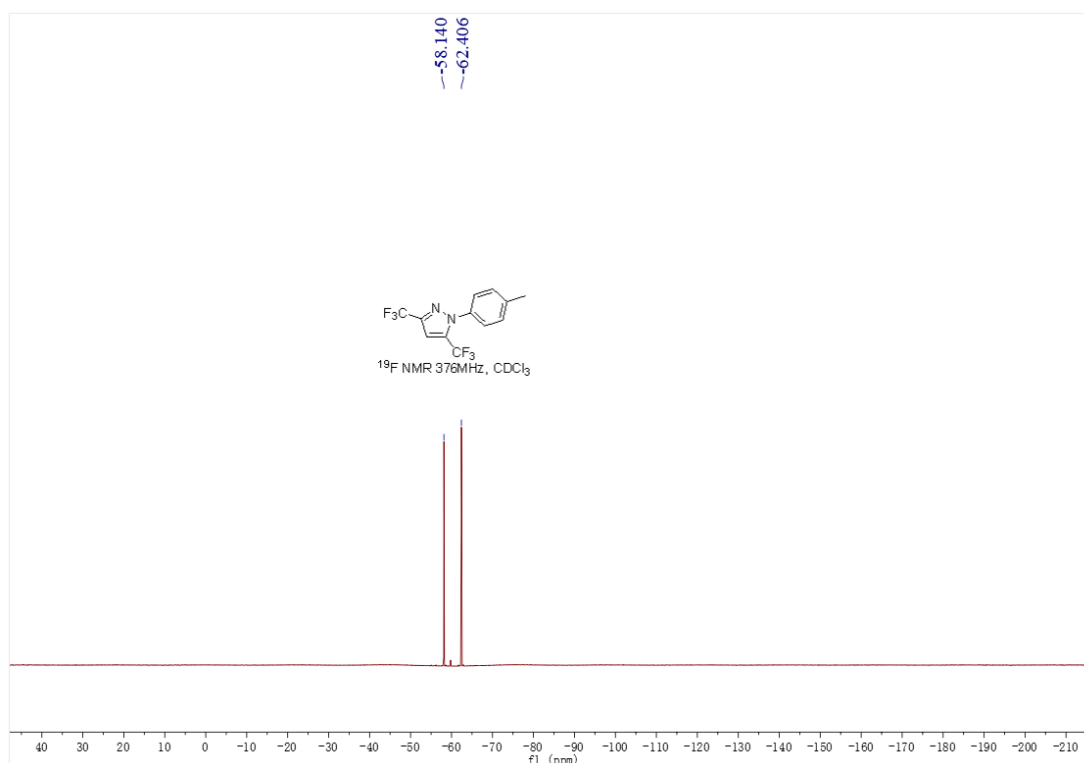
^1H NMR copy of compound **3b'**



^{13}C NMR copy of compound **3b'**



¹⁹F NMR copy of compound **3b'**

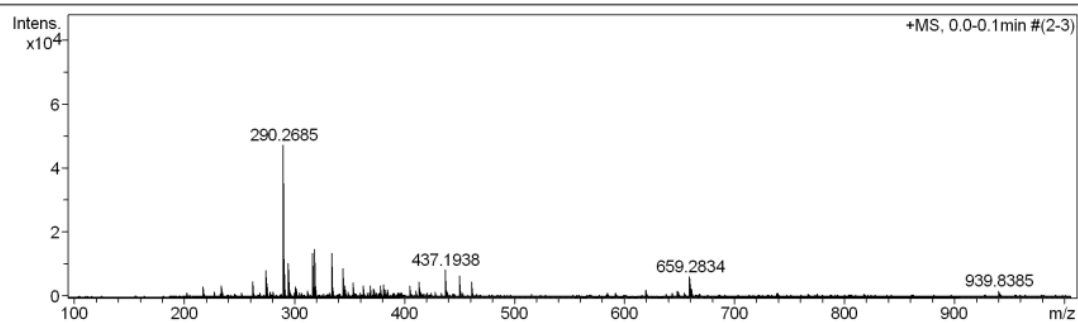


HRMS copy of compound **3b'**

Mass Spectrum SmartFormula Report

Analysis Info		Acquisition Date	
Analysis Name	D:\Data\user\NWNW-wangruikang 20240205--33.d	2024-2-5	10:34:13
Method	tune_low.m	Operator	Huyue
Sample Name	33	Instrument / Ser#	micrOTOF-Q 20453
Comment			

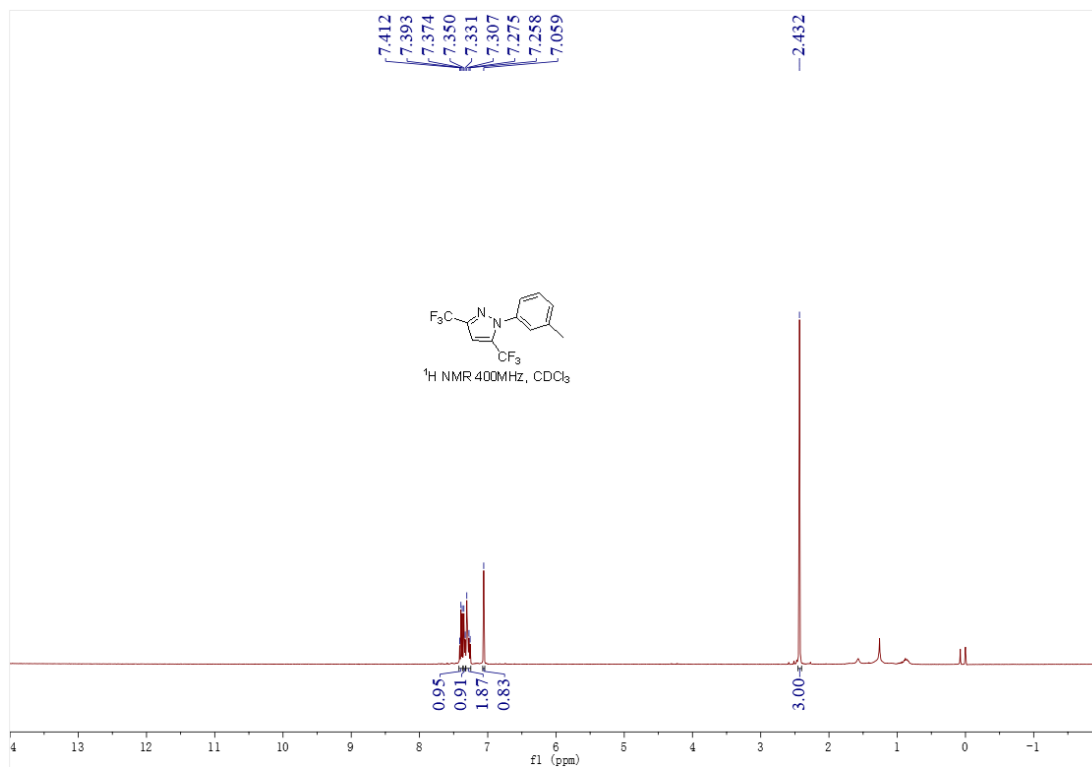
Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 j°C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	400.0 Vpp	Set Divert Valve	Waste



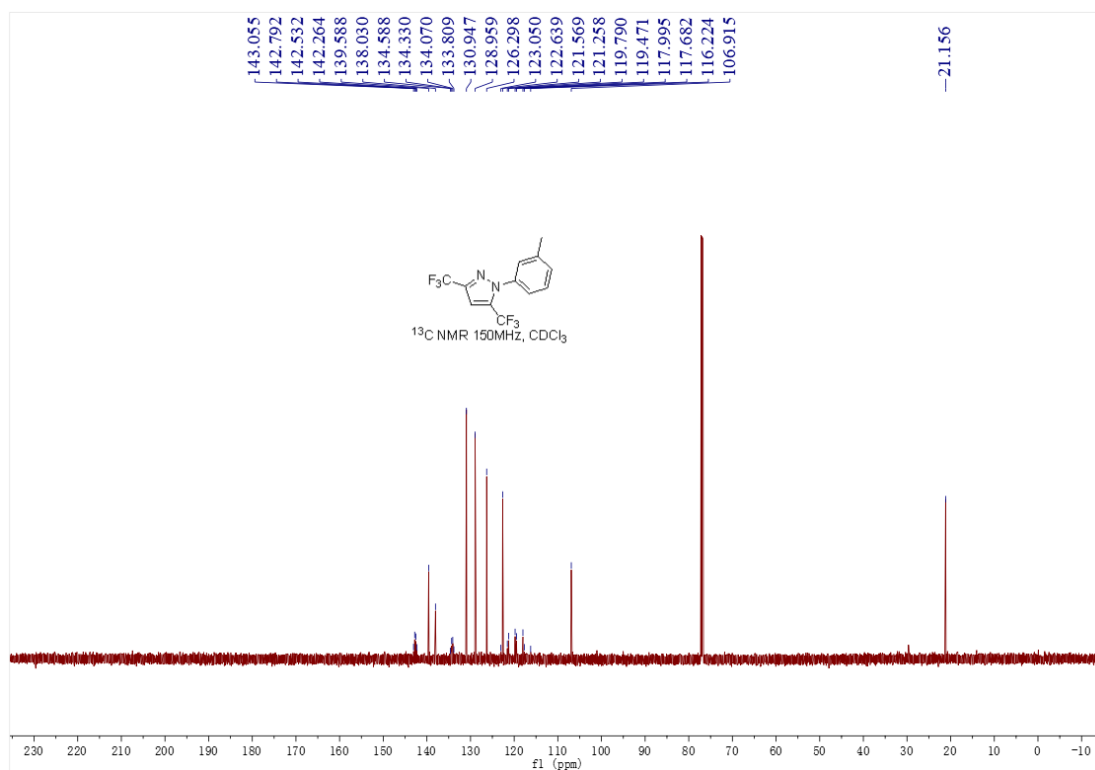
Meas. #	Formula	m/z	err [ppm]	Me an err [ppm]	rdb	N-R	e _j Conf	mSi gma	Std l	Std Me an m/z	Std l Var Nor m	Std m/z Diff	Std Com b Dev
317.0487	1 C ₁₂ H ₈ F ₆ N ₂ Na	317.0484	-0.9	-0.0	6.5	ok	even	11.2	20.8	0.8	10.1	2.7	842.7

Spectrogram copies of compound 3c'

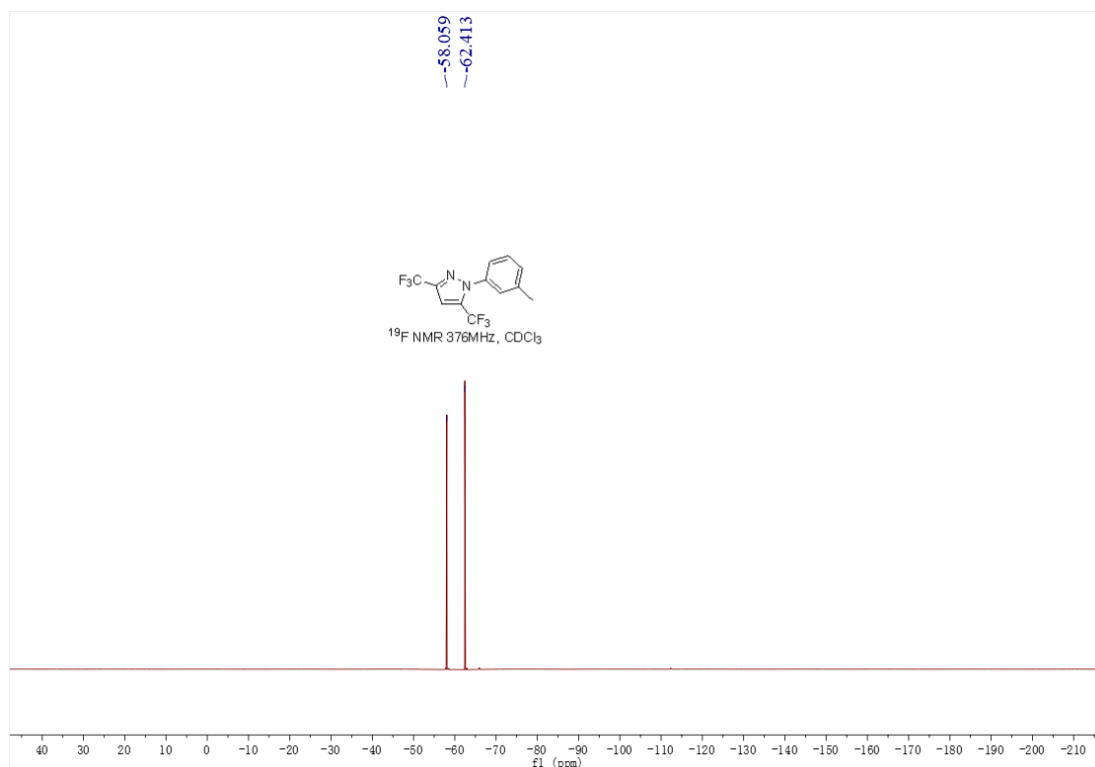
¹H NMR copy of compound 3c'



¹³C NMR copy of compound 3c'



¹⁹F NMR copy of compound 3c'

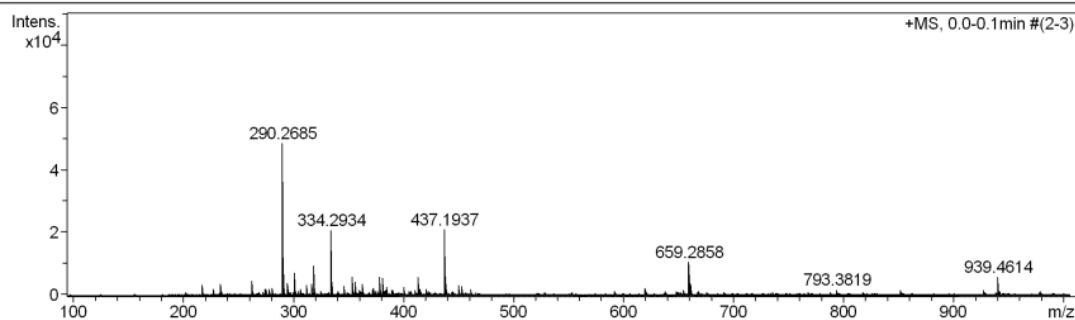


HRMS copy of compound 3c'

Mass Spectrum SmartFormula Report

Analysis Info		Acquisition Date	2024-2-5 10:35:36
Analysis Name	D:\Data\user\NWNWU-wangruikang 20240205-34.d	Operator	Huyue
Method	tune_low.m	Instrument / Ser#	micrOTOF-Q 20453
Sample Name	34		
Comment			

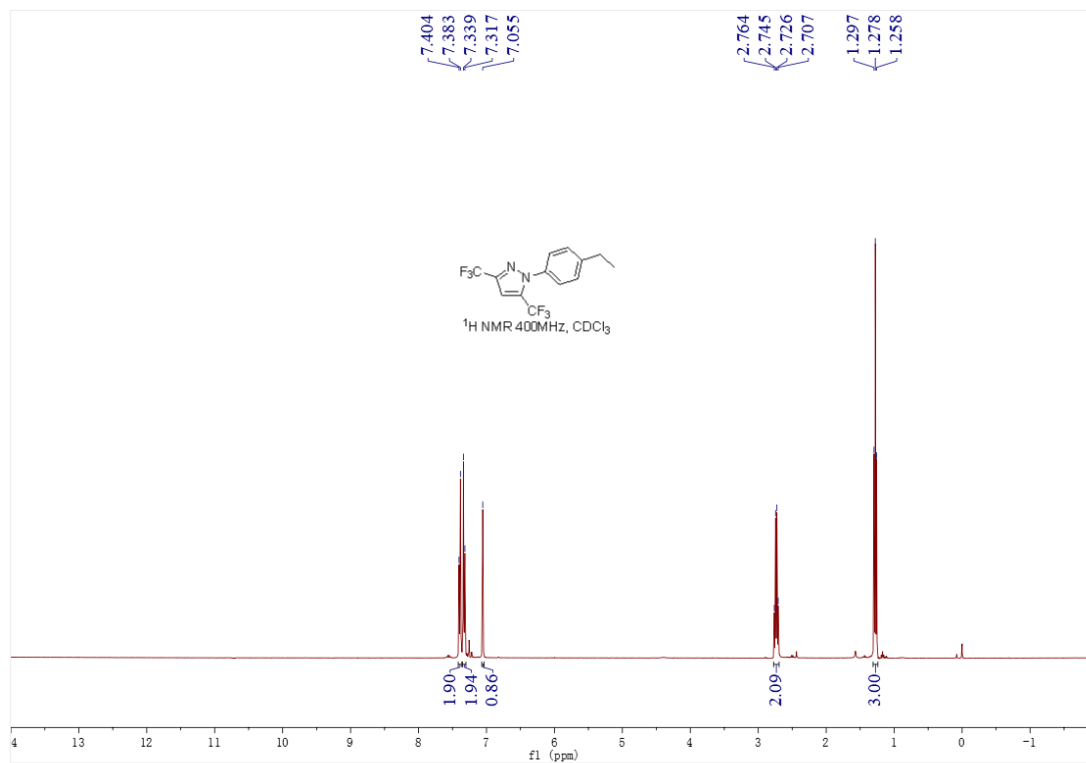
Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 j°C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	400.0 Vpp	Set Divert Valve	Waste



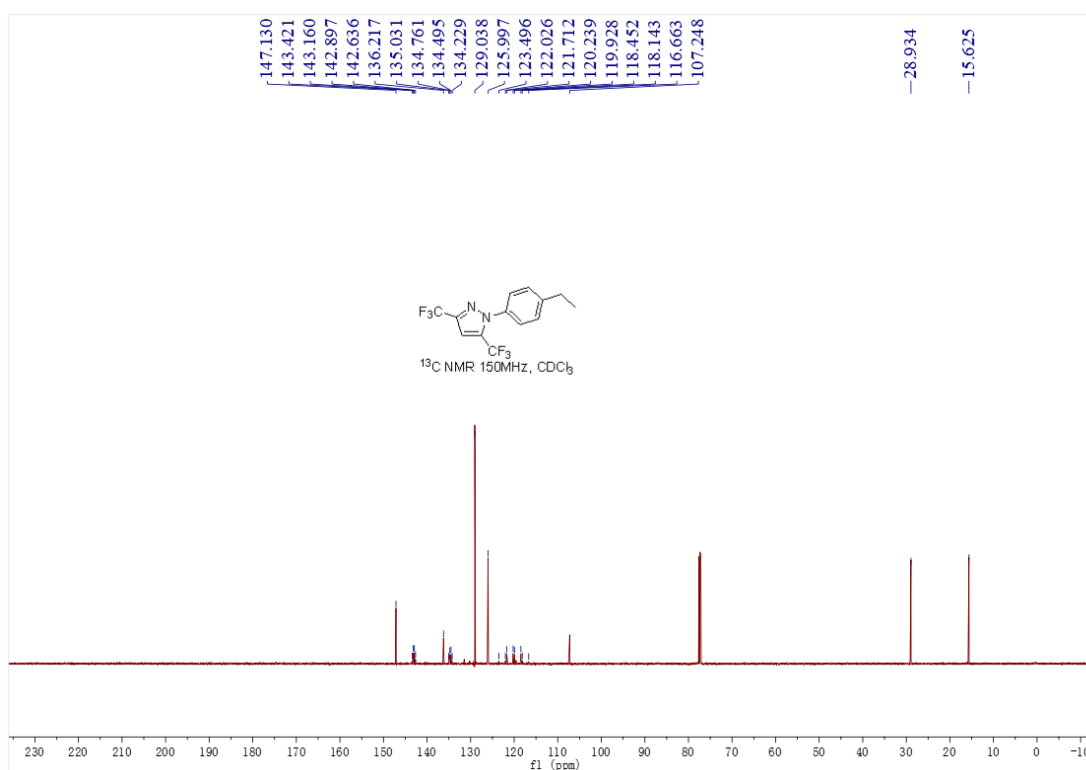
Meas. m/z	#	Formula	m/z	err [ppm]	Me an err [ppm]	rdb	N-Ru le	ej≠ Conf	mSi gma	Std l	Std Me an m/z	Std l Var Nor m	Std m/z Diff	Std Com b Dev
295.0656	1	C 12 H 9 F 6 N 2	295.0664	2.8	2.8	6.5	ok	even	79.4	137.2	0.8	68.9	0.8	842.7

Spectrogram copies of compound **3e'**

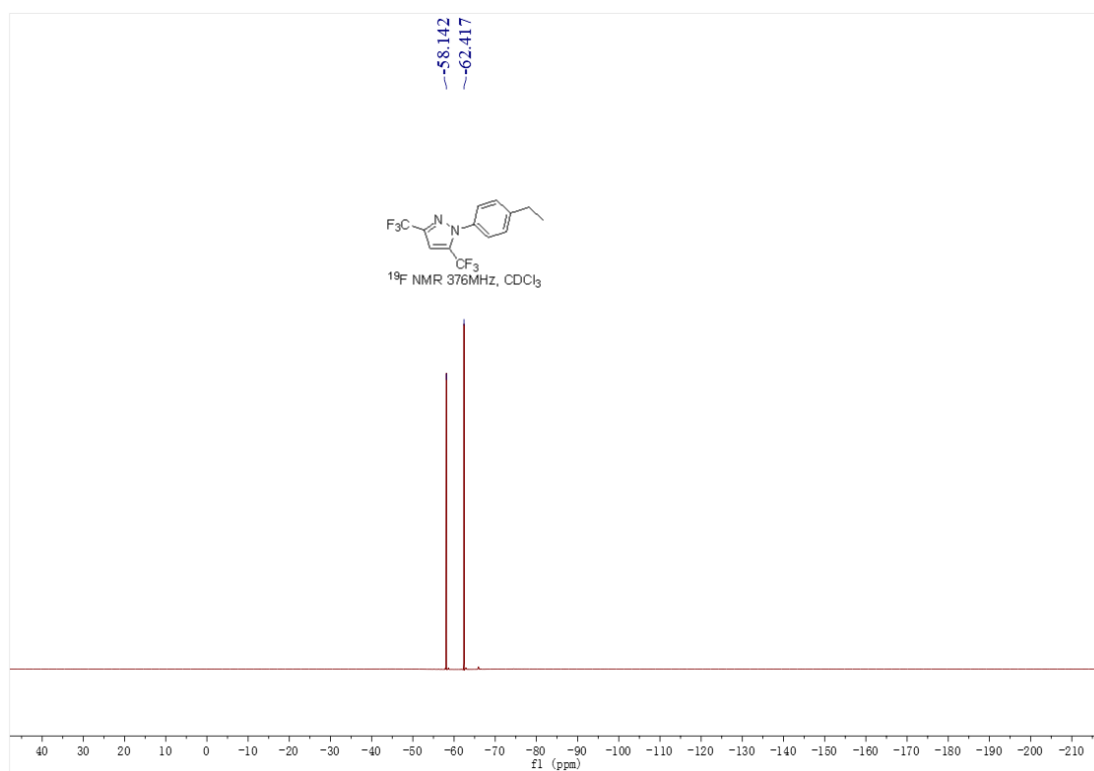
^1H NMR copy of compound **3e'**



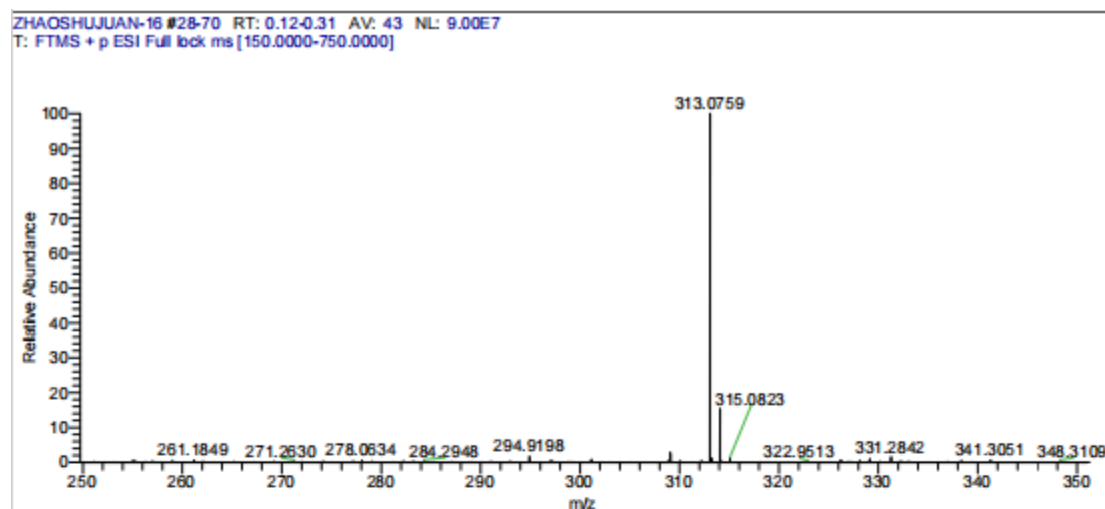
^{13}C NMR copy of compound **3e'**



¹⁹F NMR copy of compound **3e'**

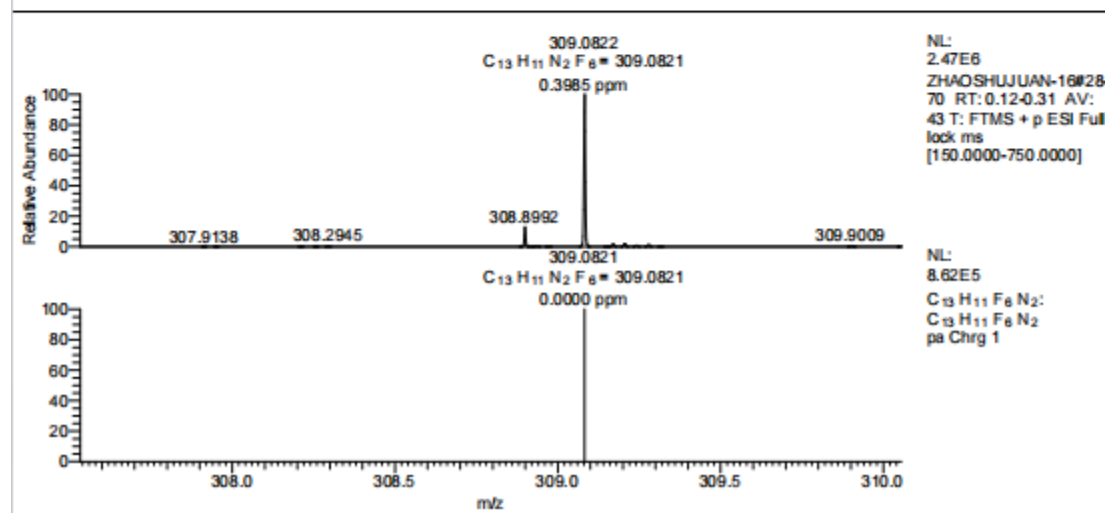


HRMS copy of compound 3e'



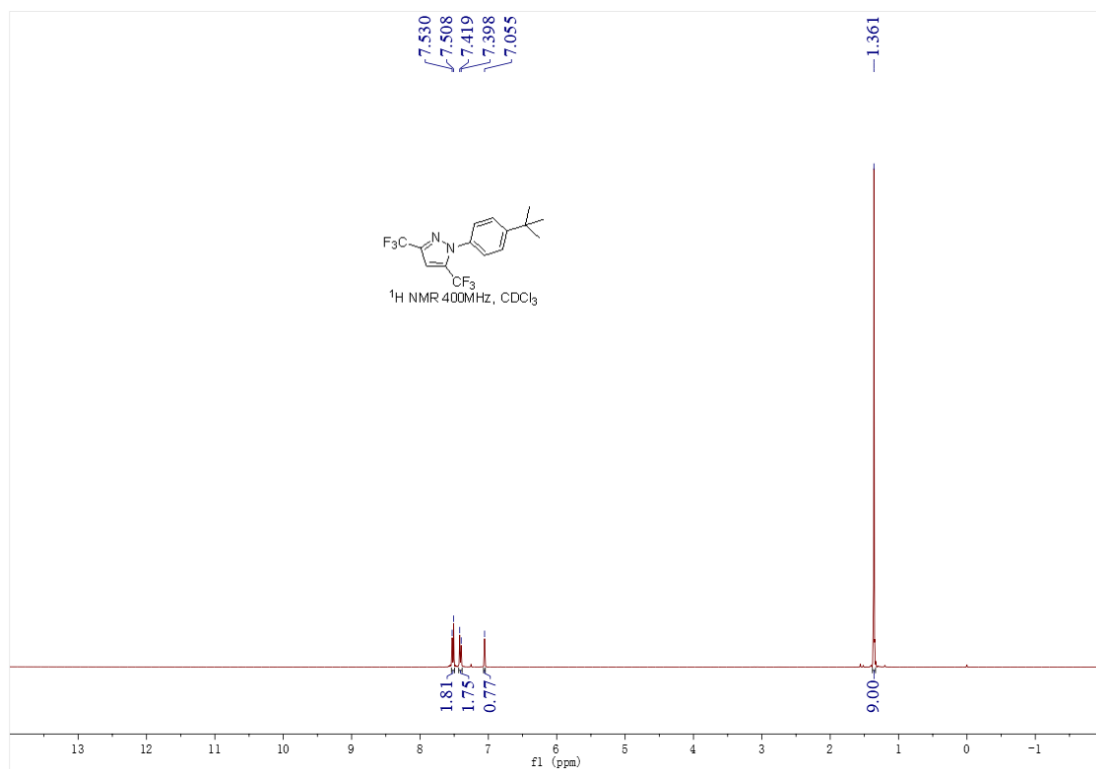
ZHAOSHUJUAN-16#28-70 RT: 0.12-0.31 AV: 43
T: FTMS + p ESI Full lock ms [150.0000-750.0000]
m/z = 307.5329-310.0554

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
308.8992	323639.2	13.02	309.0821	-182.89	C ₁₃ H ₁₁ N ₂ F ₆
309.0822	2484776.0	100.00	309.0821	0.12	C ₁₃ H ₁₁ N ₂ F ₆
309.1700	40907.3	1.65	309.0821	87.94	C ₁₃ H ₁₁ N ₂ F ₆
309.2053	50479.8	2.03	309.0821	123.19	C ₁₃ H ₁₁ N ₂ F ₆
309.2794	31769.7	1.28	309.0821	197.28	C ₁₃ H ₁₁ N ₂ F ₆

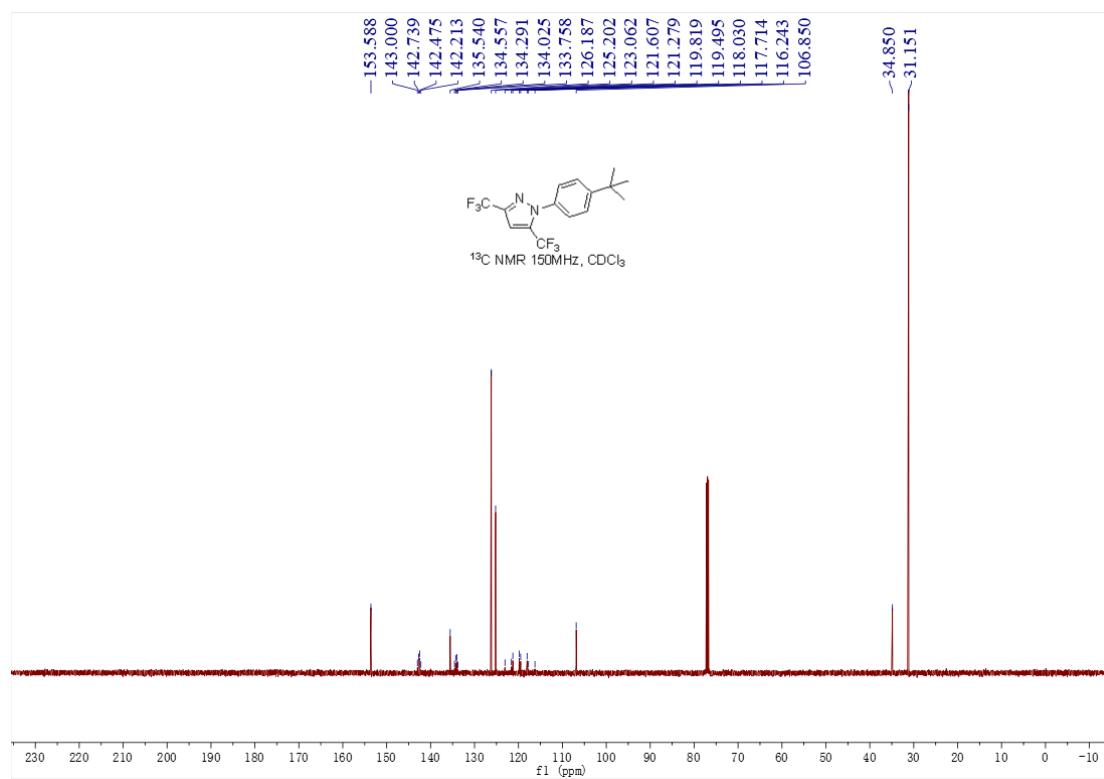


Spectrogram copies of compound **3f'**

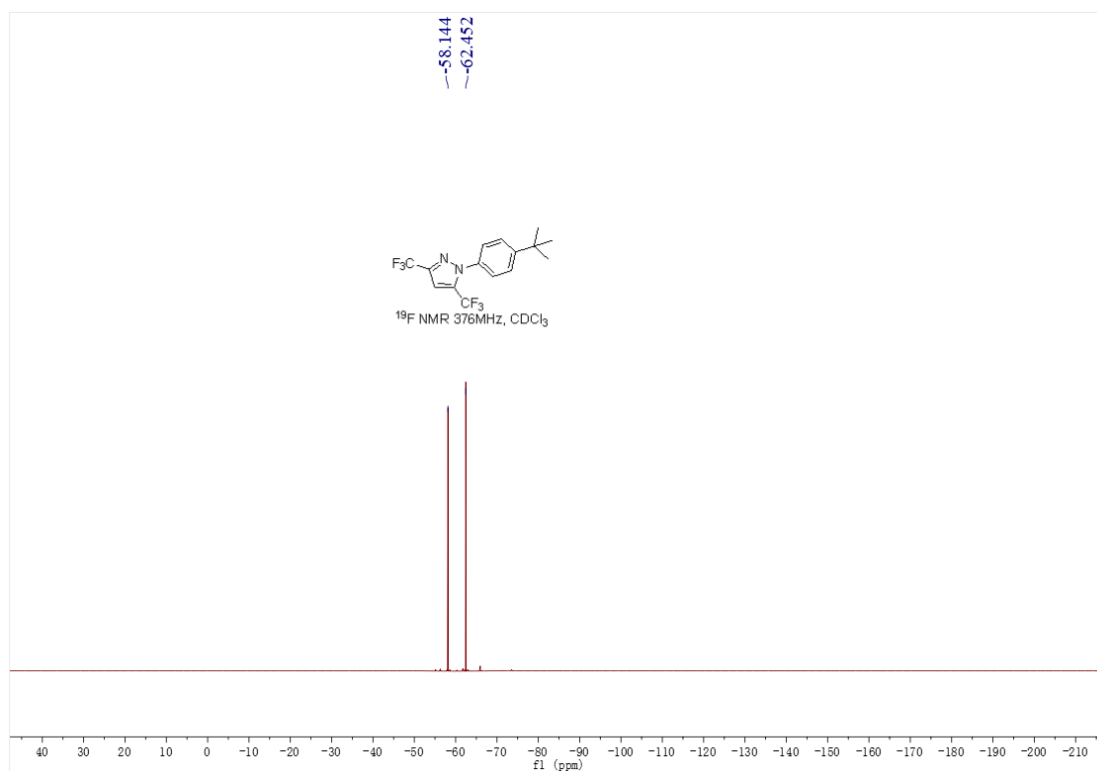
¹H NMR copy of compound **3f'**



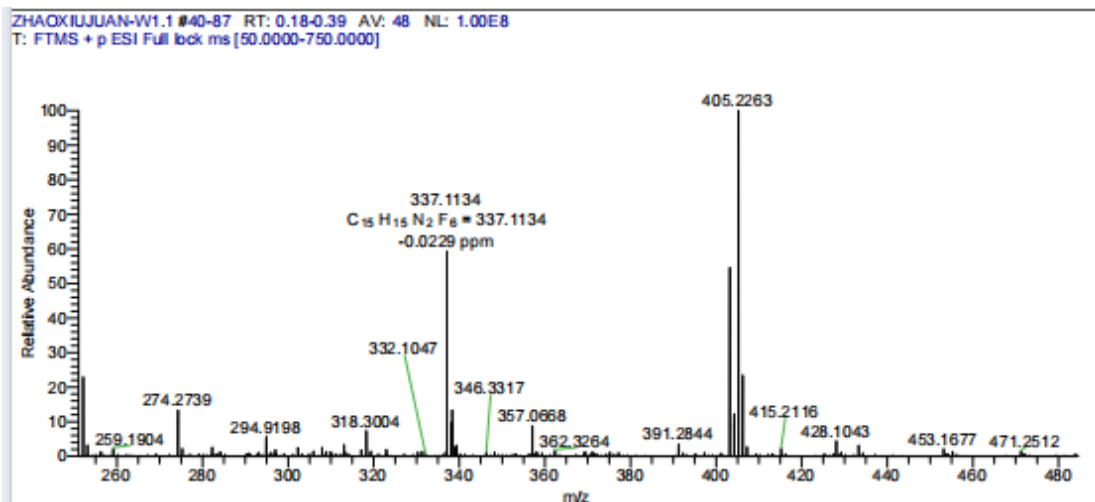
¹³C NMR copy of compound **3f'**



¹⁹F NMR copy of compound **3f'**

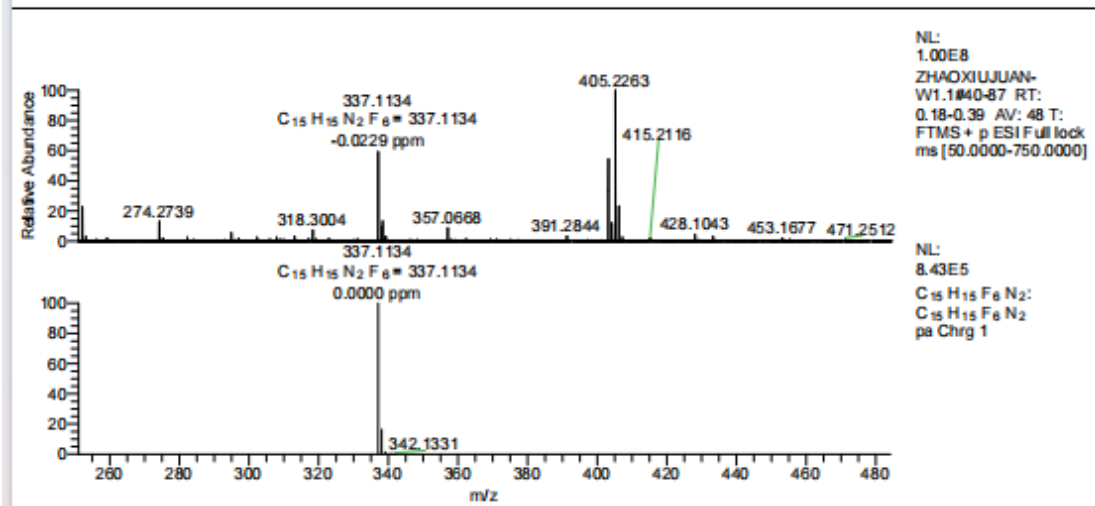


HRMS copy of compound 3f'



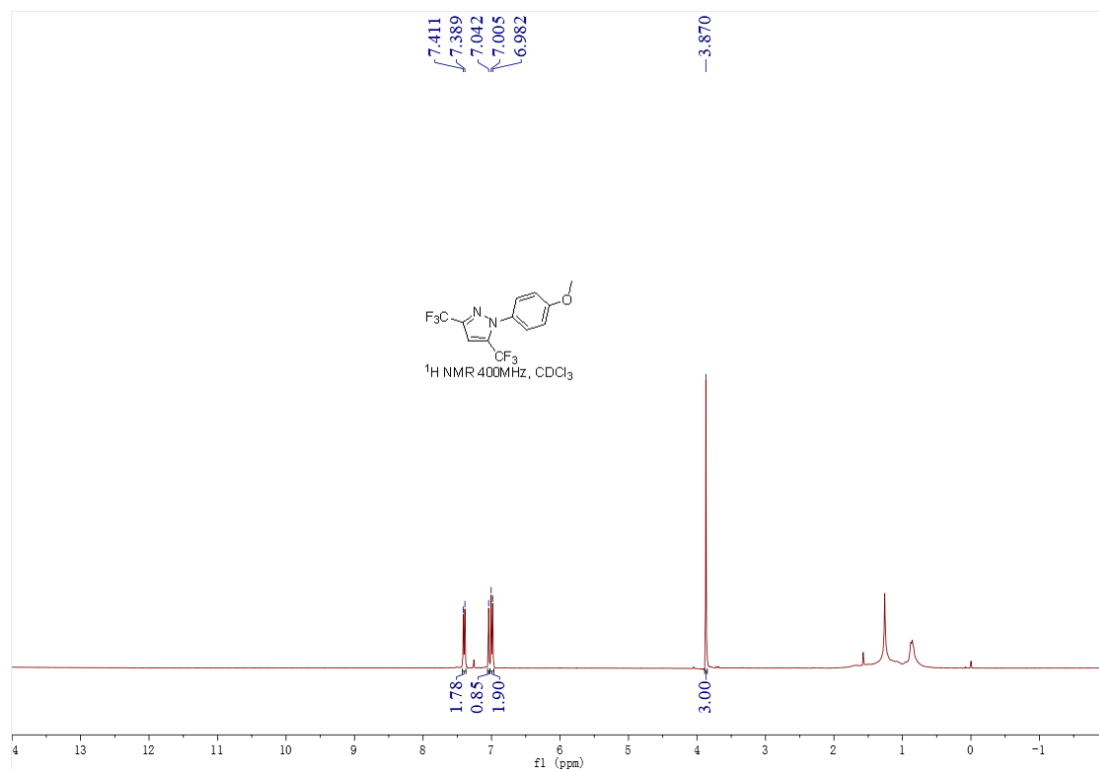
ZHAOXIUJUAN-W1.1#40-87 RT: 0.18-0.39 AV: 48
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 251.0216-484.2023

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
252.1230	22941646.0	22.66			
337.1134	61712468.0	60.94	337.1134	-0.01	C ₁₅ H ₁₅ N ₂ F ₆
403.2106	55402504.0	54.71			
405.2263	101265192.0	100.00			
406.2299	23837218.0	23.54			

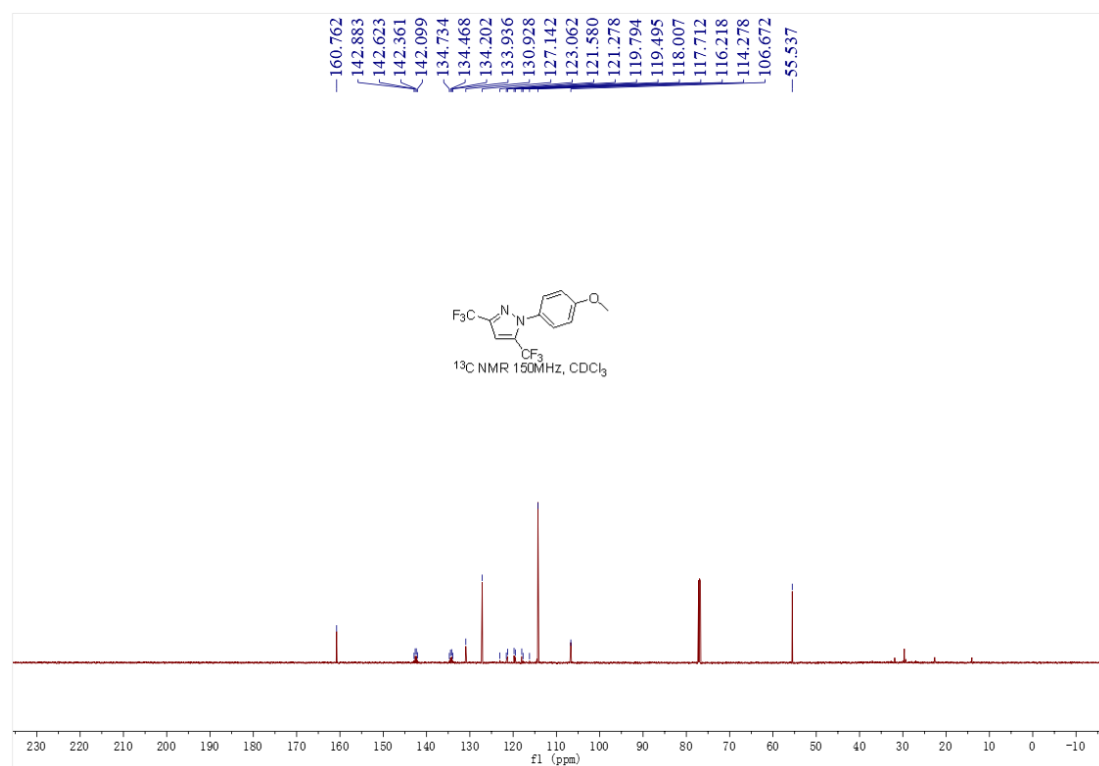


Spectrogram copies of compound **3g'**

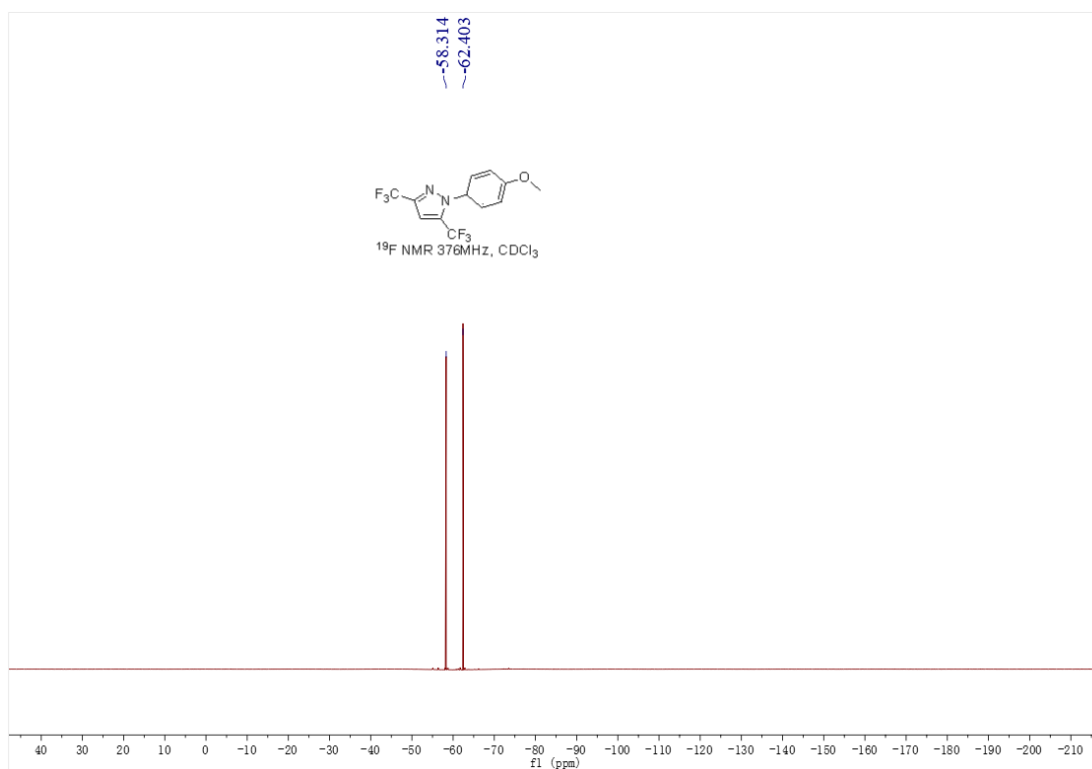
^1H NMR copy of compound **3g'**



^{13}C NMR copy of compound **3g'**

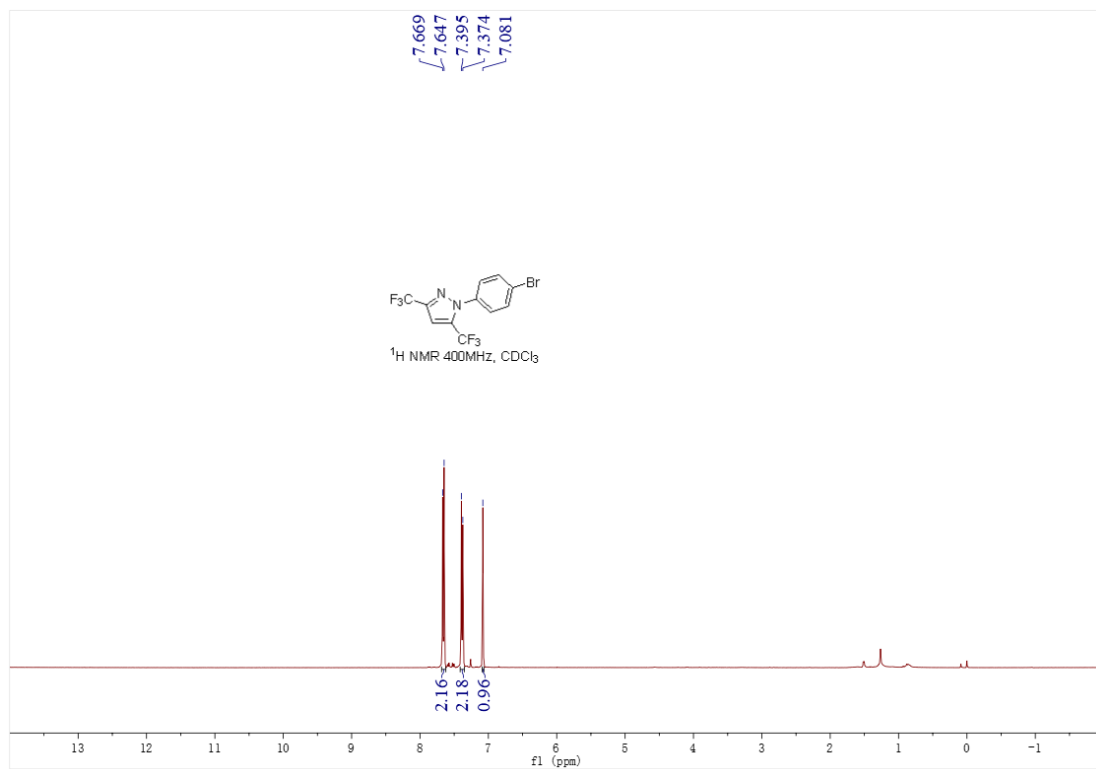


¹⁹F NMR copy of compound **3g'**

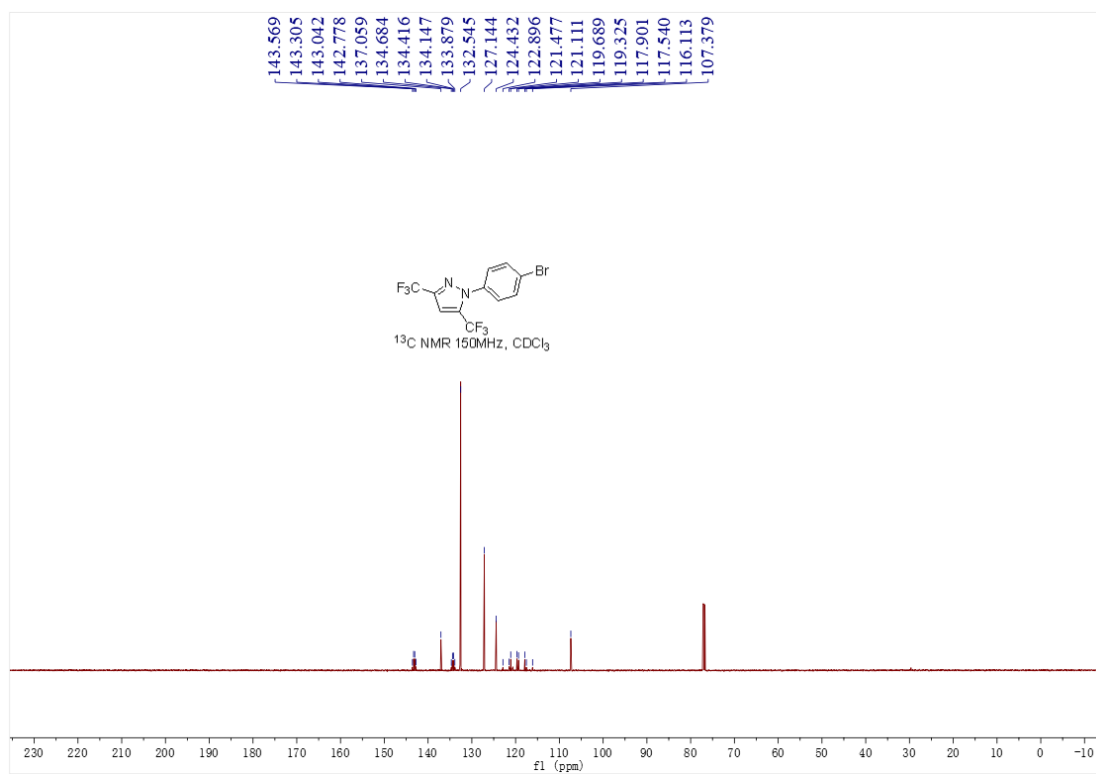


Spectrogram copies of compound **3h'**

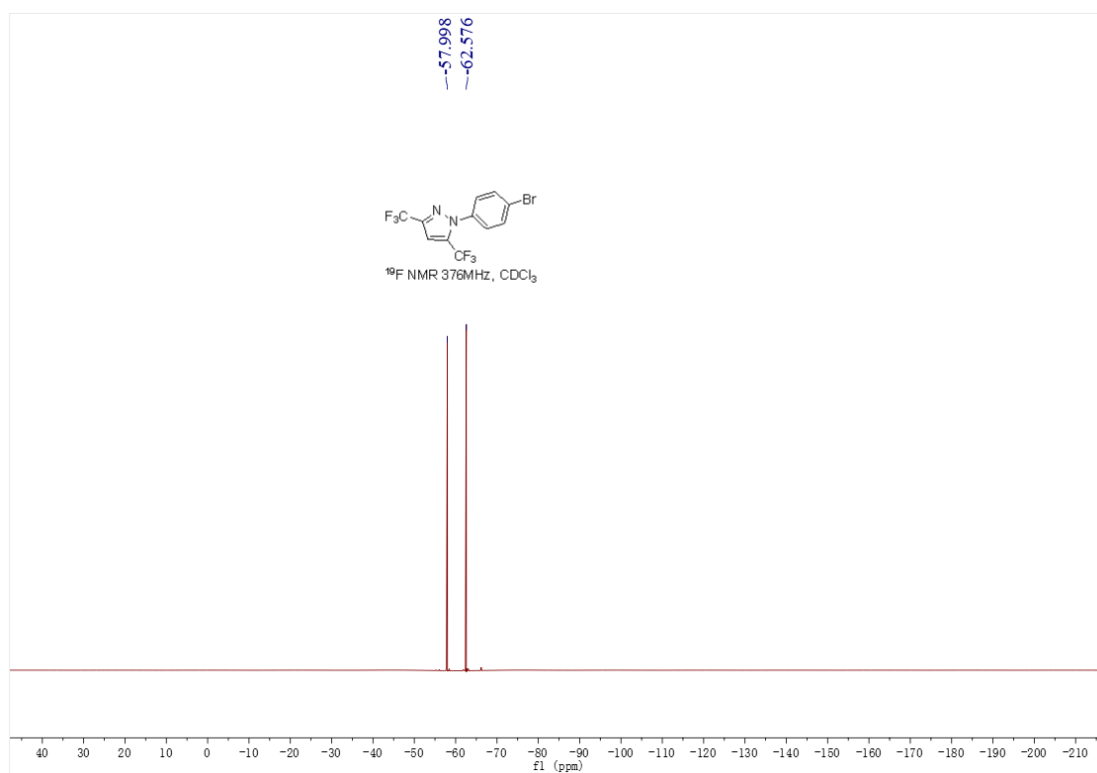
¹H NMR copy of compound **3h'**



¹³C NMR copy of compound **3h'**

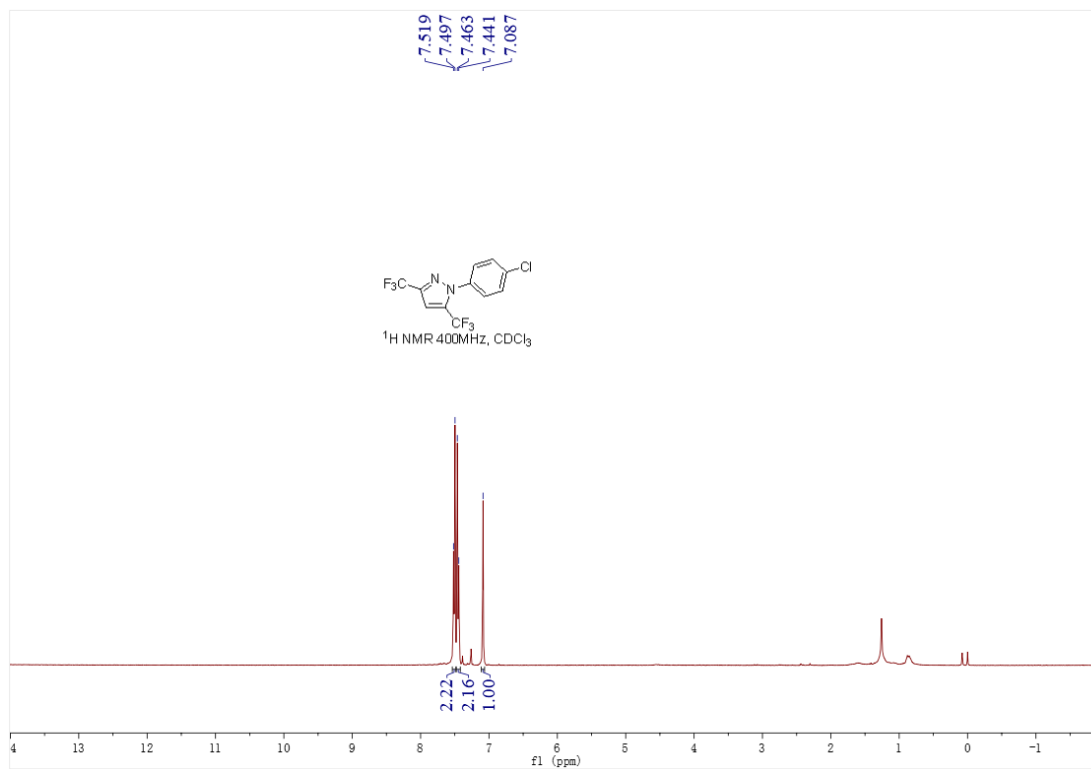


¹⁹F NMR copy of compound **3h'**

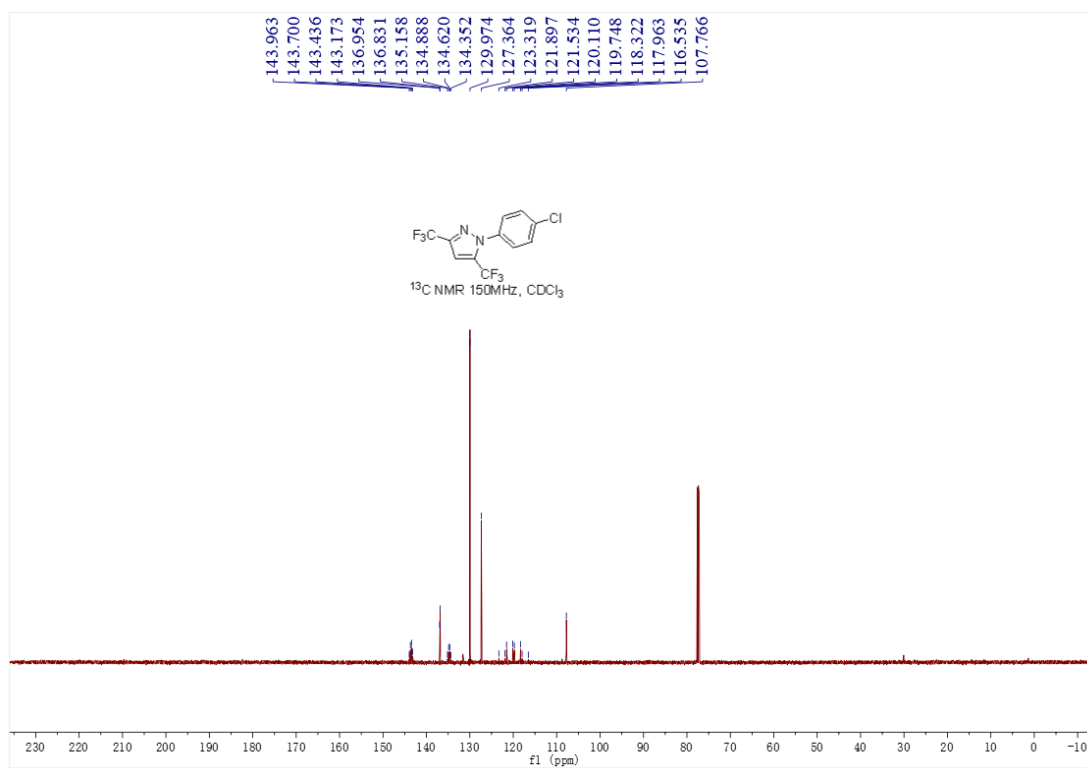


Spectrogram copies of compound **3j'**

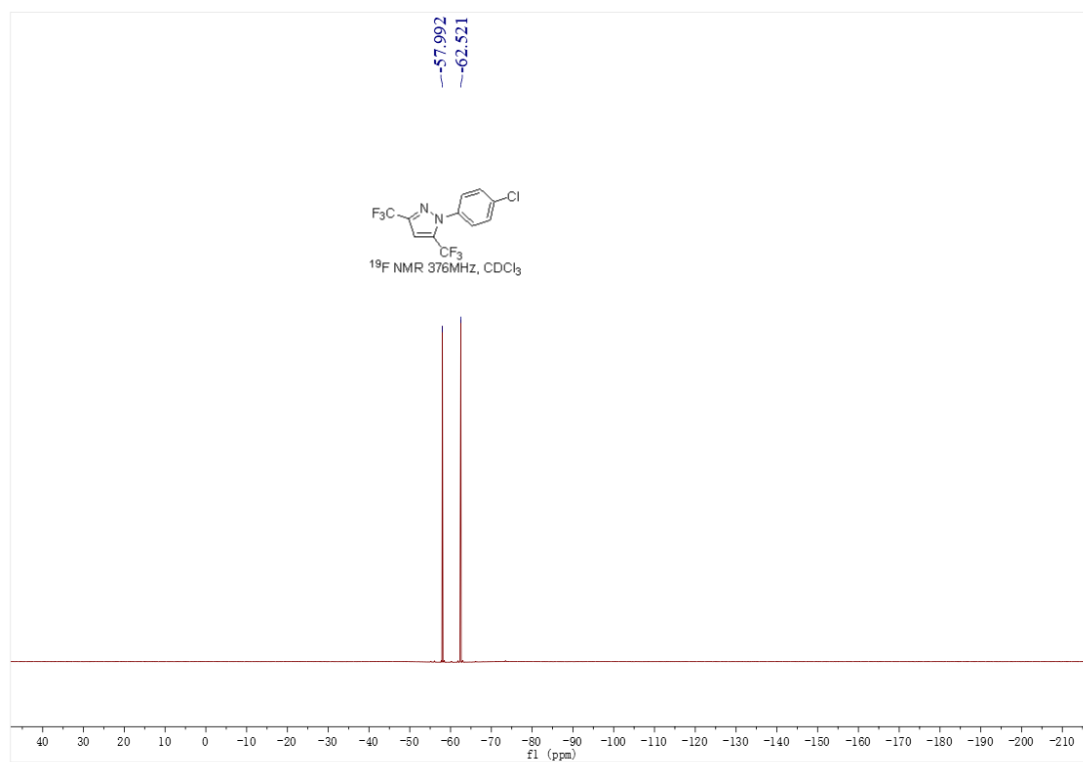
^1H NMR copy of compound **3j'**



^{13}C NMR copy of compound **3j'**

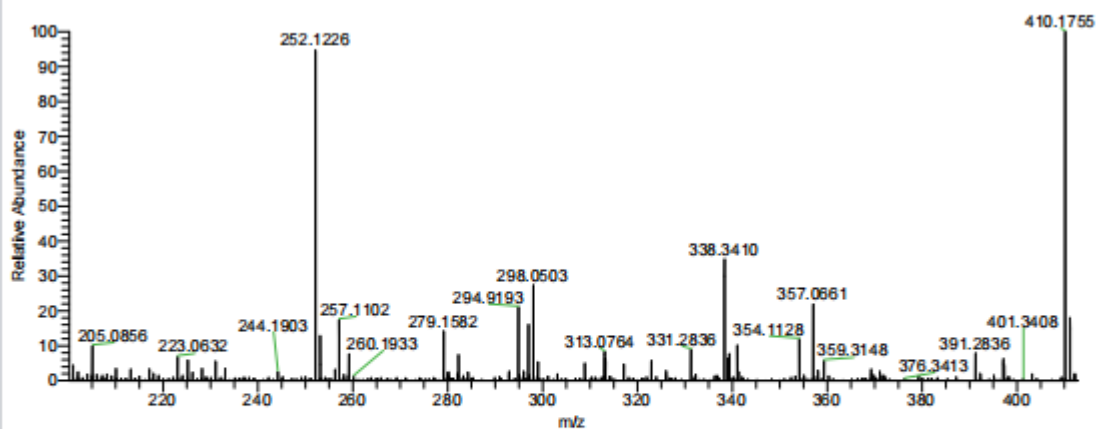


¹⁹F NMR copy of compound **3j'**



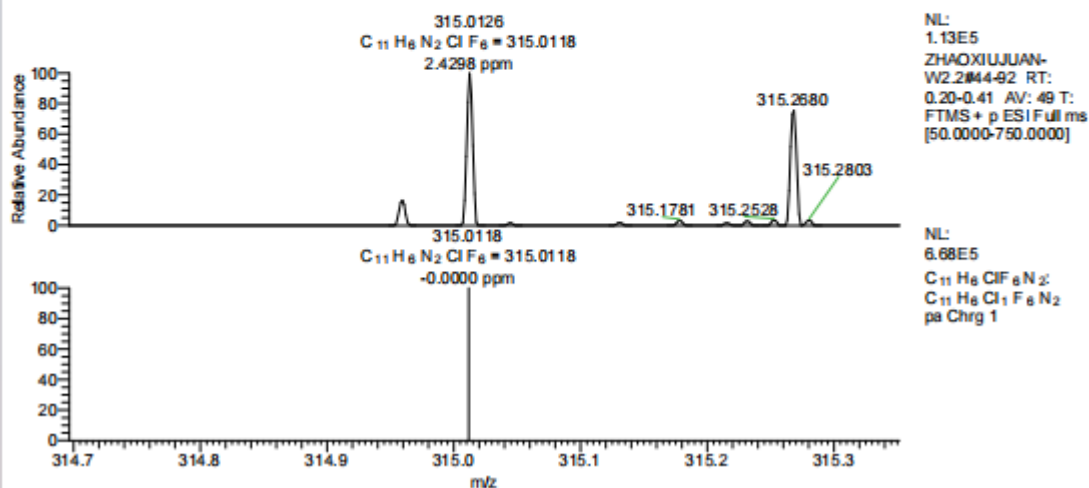
HRMS copy of compound 3j'

ZHAOXIUJUAN-W2.2#44-92 RT: 0.20-0.41 AV: 49 NL: 3.48E7
T: FTMS + p ESI Full ms [50.0000-750.0000]



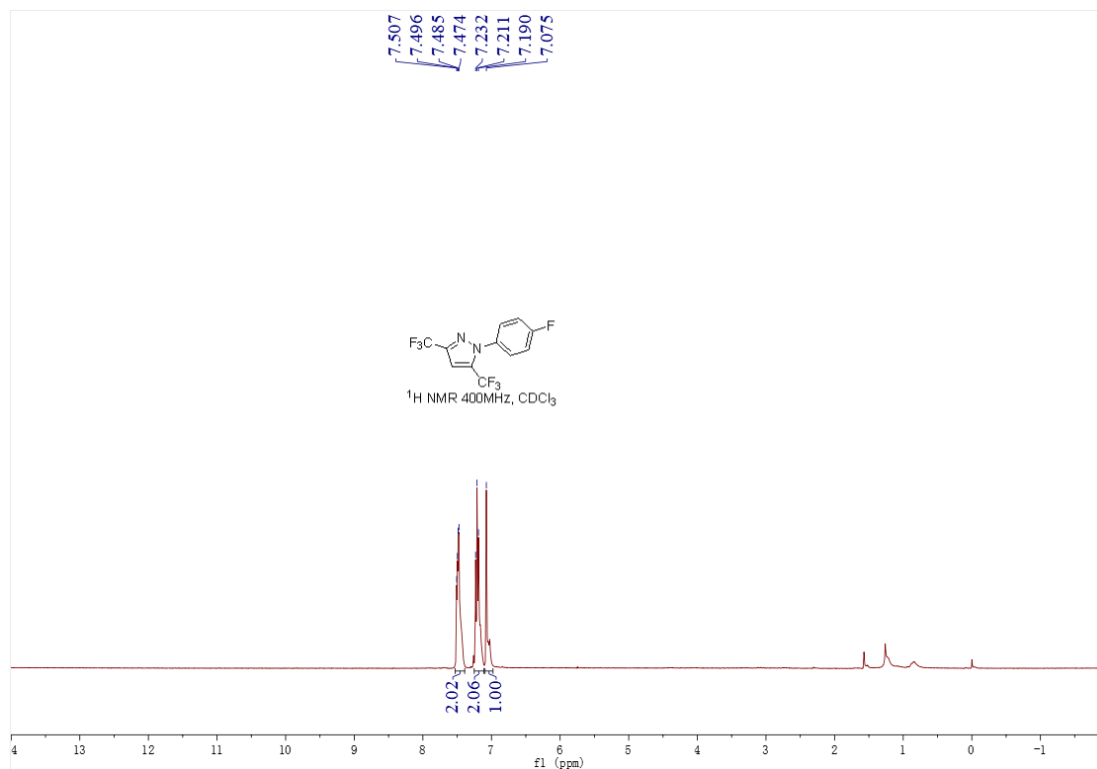
ZHAOXIUJUAN-W2.2#44-92 RT: 0.20-0.41 AV: 49
T: FTMS + p ESI Full ms [50.0000-750.0000]
m/z = 314.6966-315.3515

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
314.9593	18781.8	16.57	315.0118	-52.56	C ₁₁ H ₆ N ₂ ClF ₆
315.0126	113321.9	100.00	315.0118	0.77	C ₁₁ H ₆ N ₂ ClF ₆
315.2528	4064.1	3.59	315.0118	240.95	C ₁₁ H ₆ N ₂ ClF ₆
315.2680	87073.8	76.84	315.0118	256.16	C ₁₁ H ₆ N ₂ ClF ₆
315.2803	3831.5	3.38	315.0118	268.48	C ₁₁ H ₆ N ₂ ClF ₆

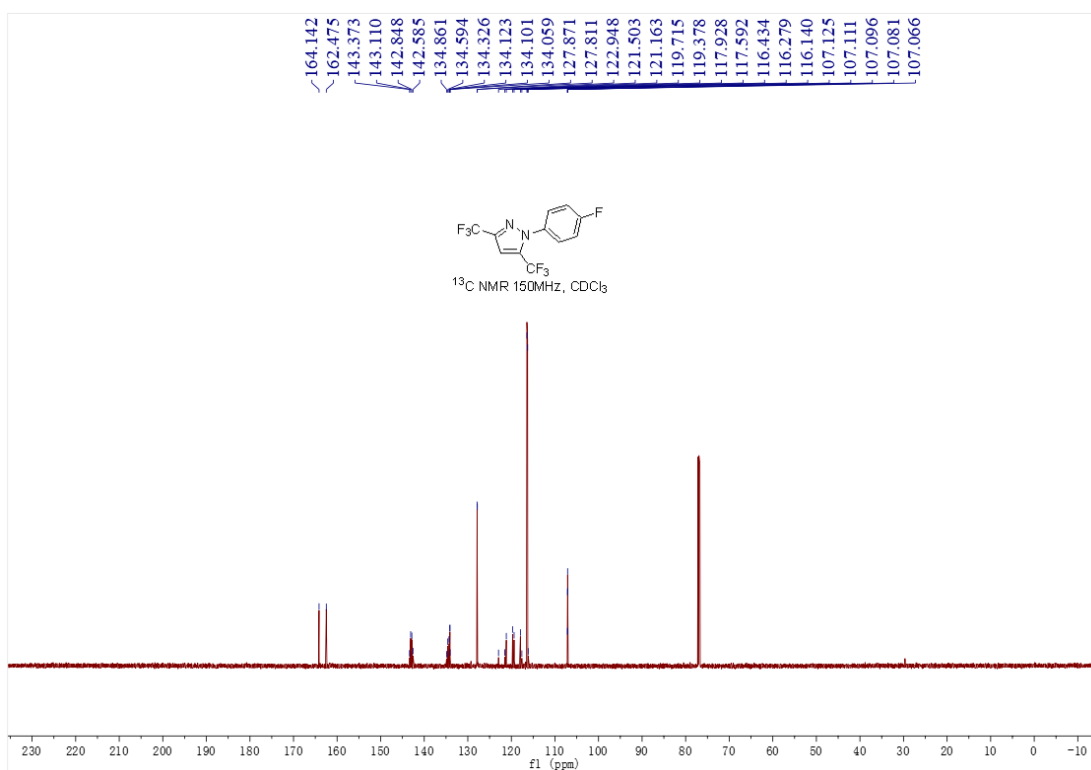


Spectrogram copies of compound **3k'**

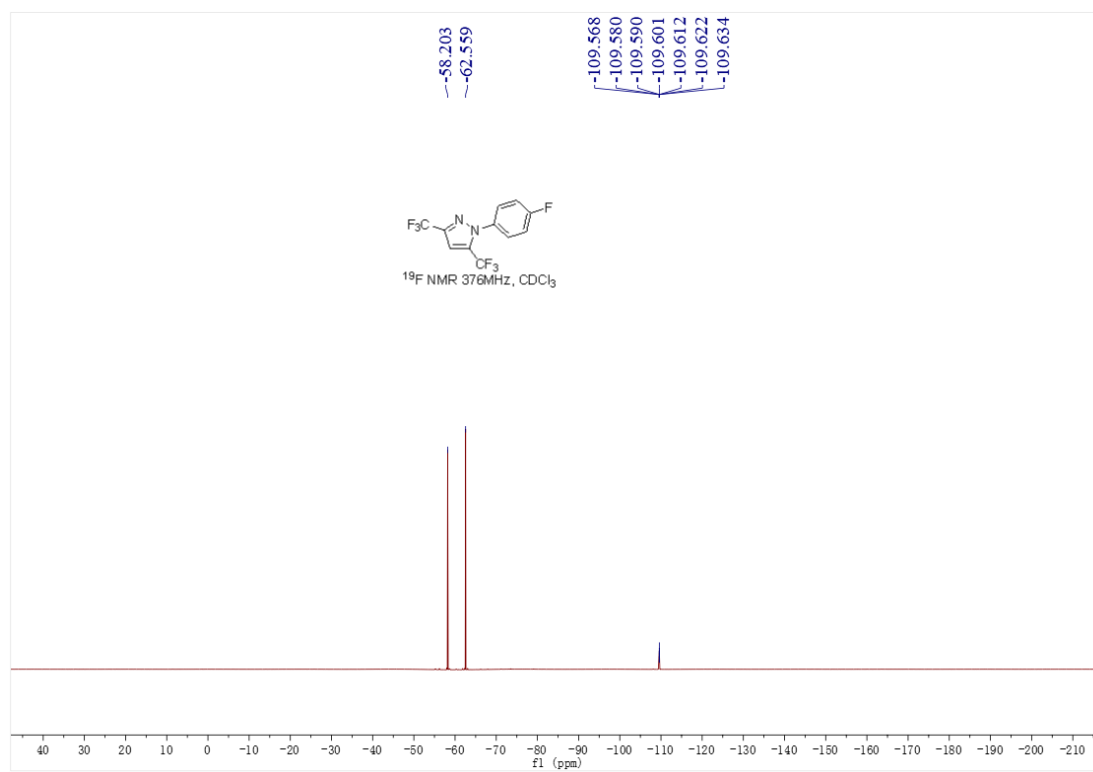
¹H NMR copy of compound **3k'**



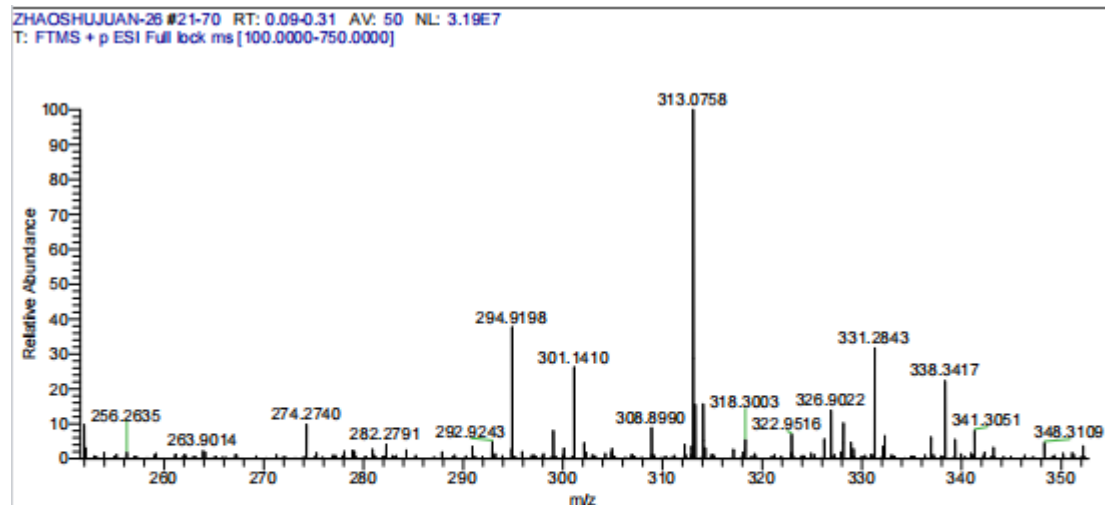
¹³C NMR copy of compound **3k'**



¹⁹F NMR copy of compound **3k'**

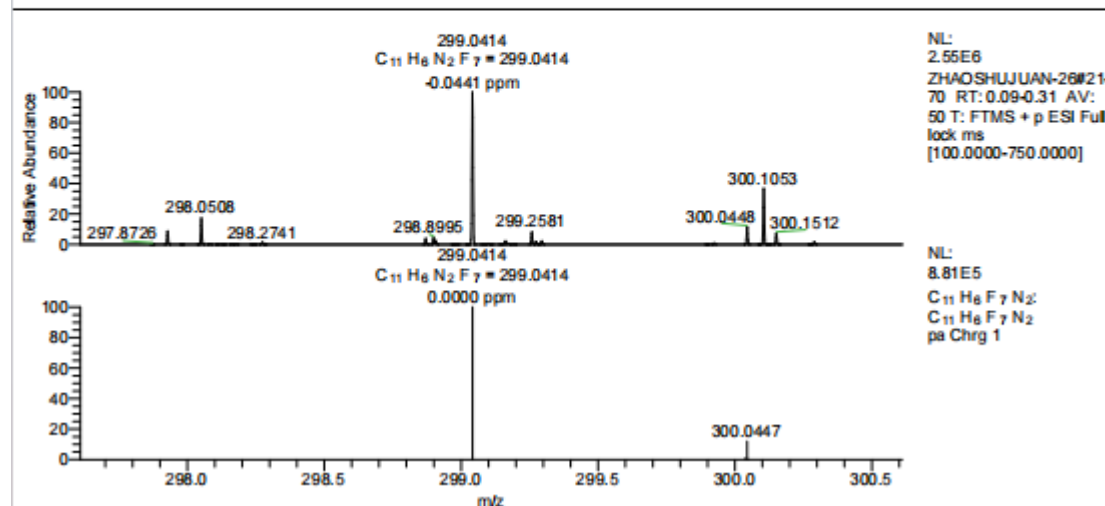


HRMS copy of compound 3k'



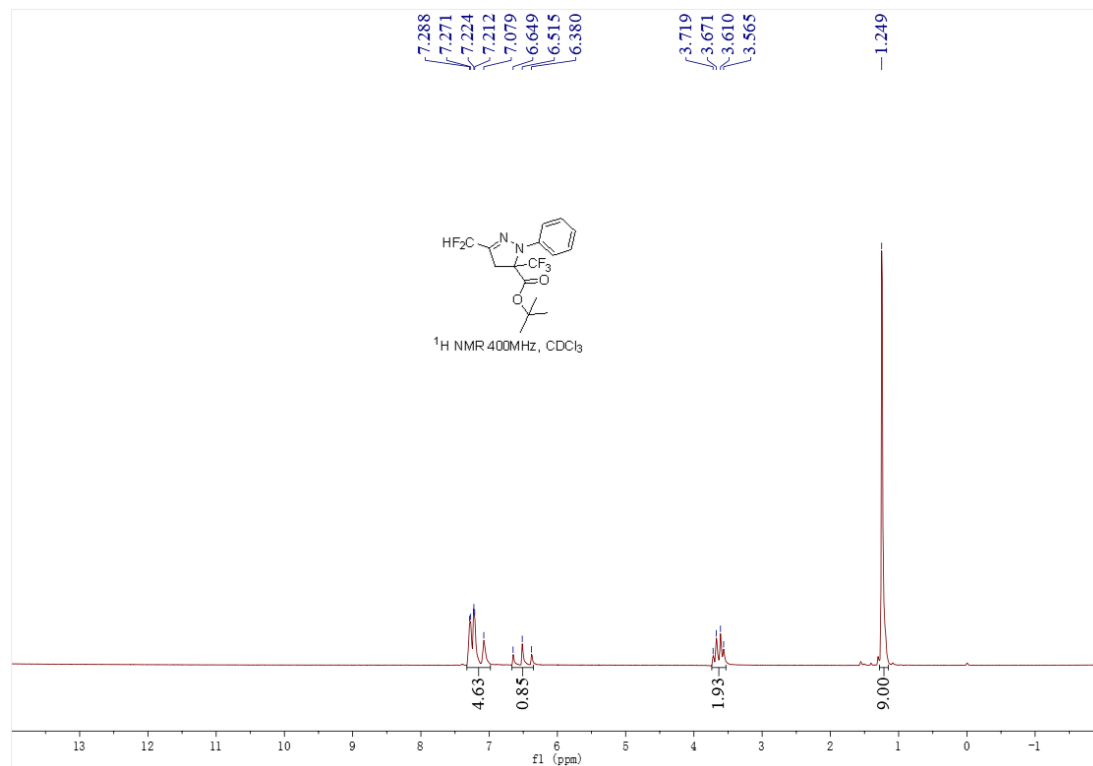
ZHAOSHUJUAN-26#21-70 RT: 0.09-0.31 AV: 50
T: FTMS + p ESI Full lock ms [100.0000-750.0000]
m/z = 297.6086-300.6112

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
297.9278	230327.2	9.00			
298.0508	448310.4	17.52			
299.0414	2558502.0	100.00	299.0414	-0.01	C ₁₁ H ₆ N ₂ F ₇
300.0448	309293.0	12.09			
300.1053	976387.5	38.16			

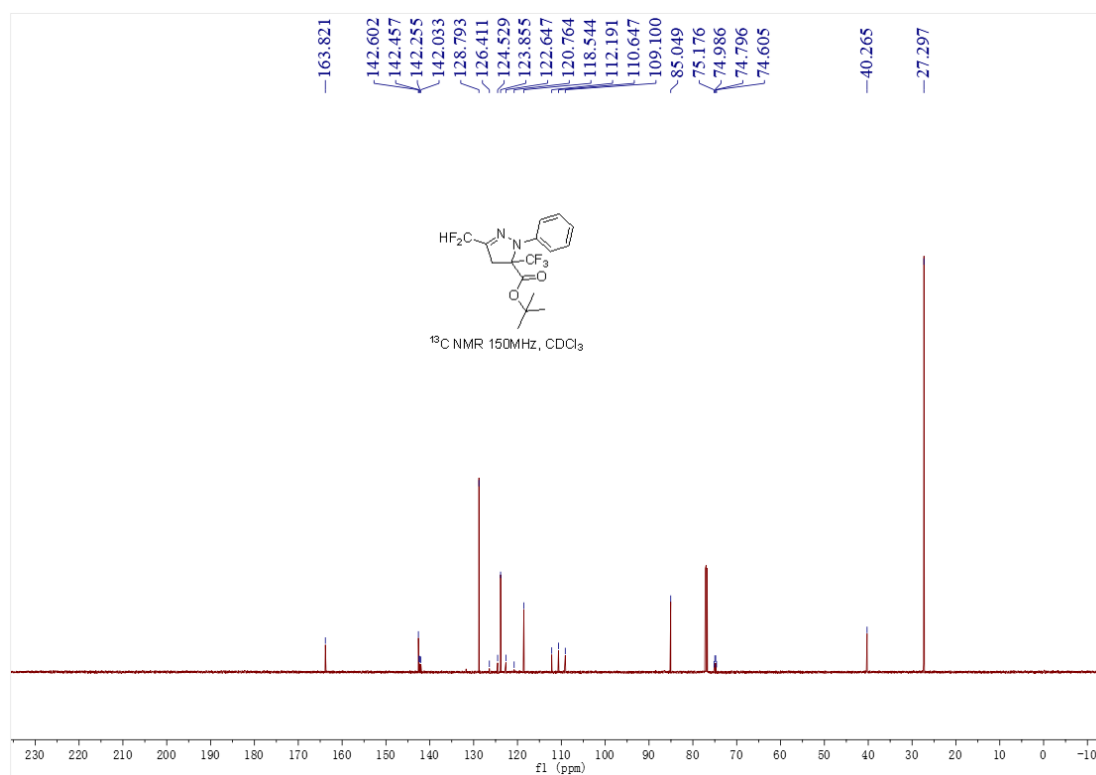


Spectrogram copies of compound **4a**

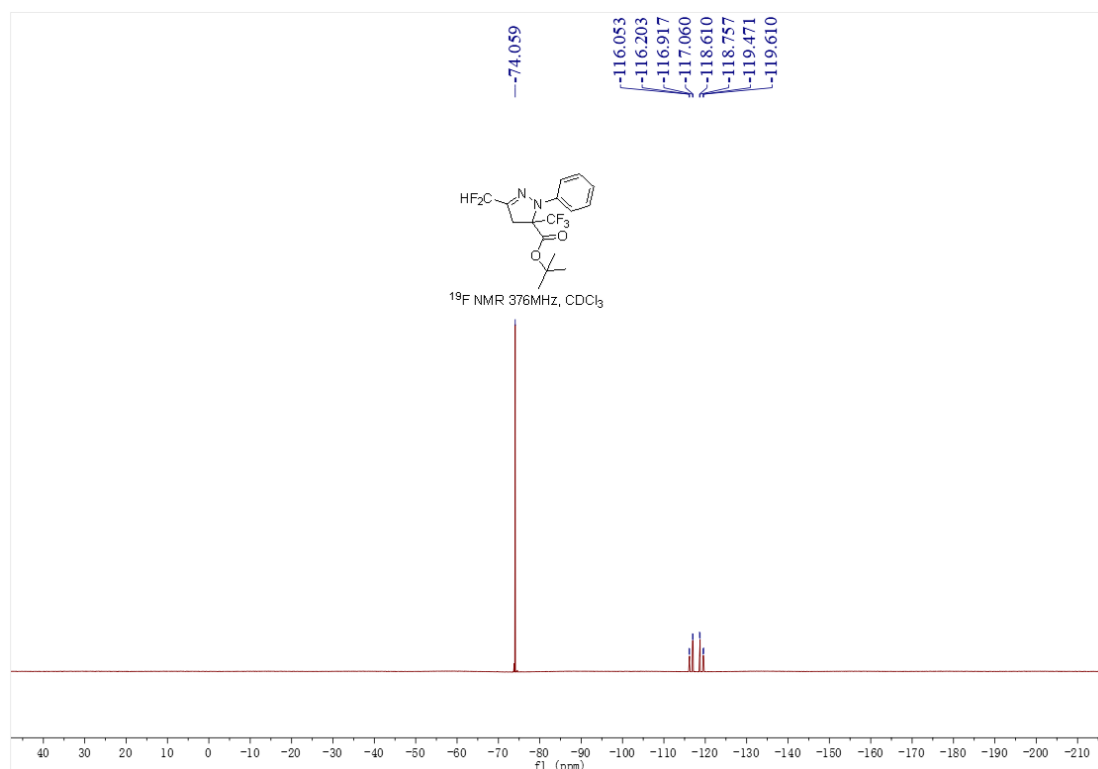
¹H NMR copy of compound **4a**



¹³C NMR copy of compound **4a**



¹⁹F NMR copy of compound 4a



HRMS copy of compound 4a

Mass Spectrum SmartFormula Report

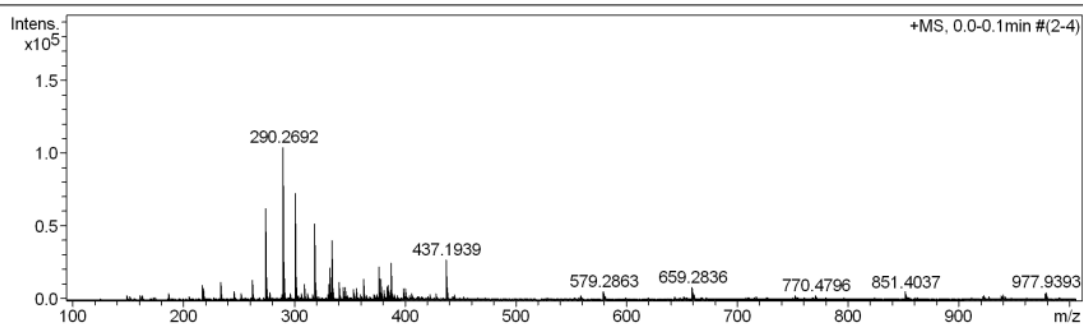
Analysis Info

Analysis Name D:\Data\user\NWNW-wangruikang 20240205-11.d
 Method tune_low.m
 Sample Name 11
 Comment

Acquisition Date 2024-2-5 9:58:12
 Operator Huyue
 Instrument / Ser# micrOTOF-Q 20453

Acquisition Parameter

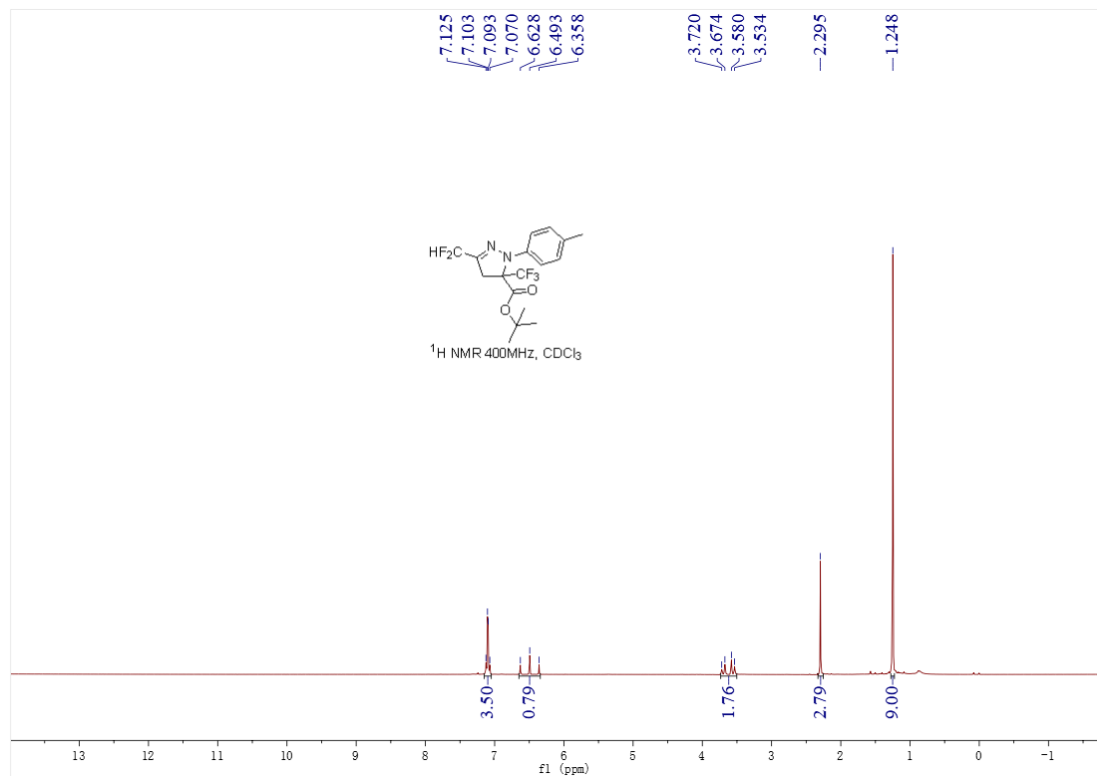
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 j°C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste



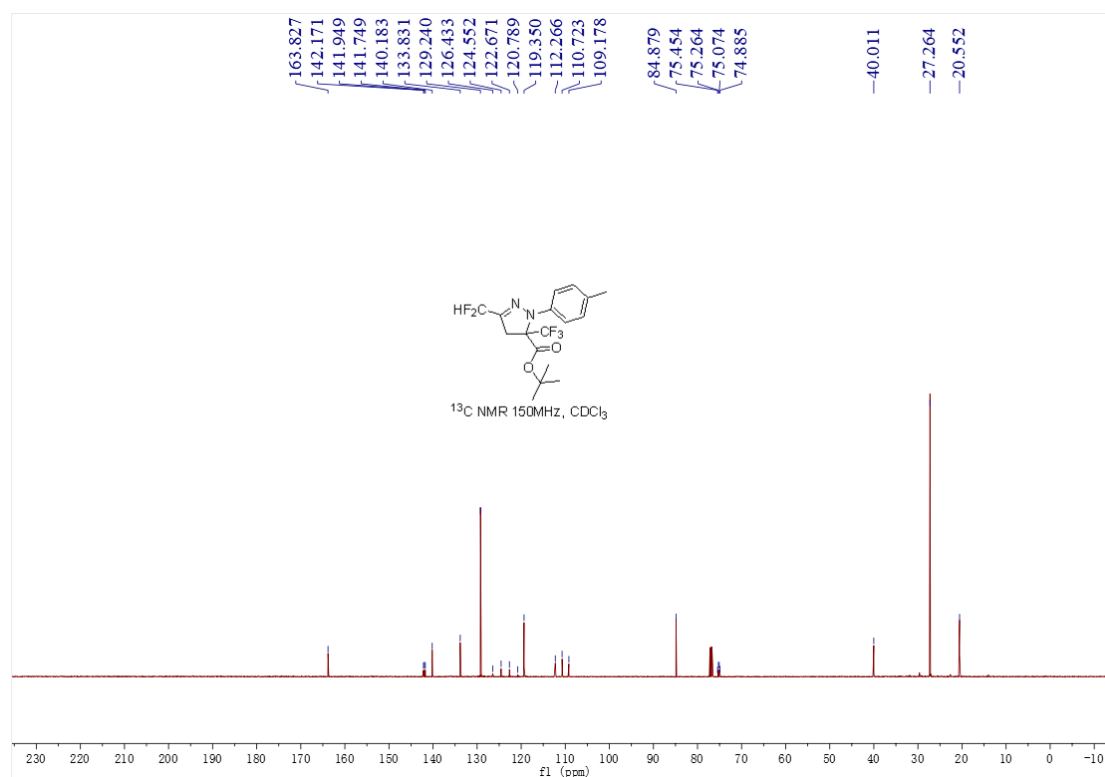
Meas. #	Formula	m/z	err [ppm]	Me an err [ppm]	rdb	N-R	ej# Conf	mSi gm a	Std l	Std d Me an m/z	Std Var m/ m	Std l Nor m	Std d z Dif f	Std Com b Dev
387.1093	1 C ₁₆ H ₁₇ F ₅ N ₂ NaO ₂	387.1102	2.4	3.2	6.5	ok	even	12.6	19.2	1.5	14.1	2.3	842.7	

Spectrogram copies of compound **4b**

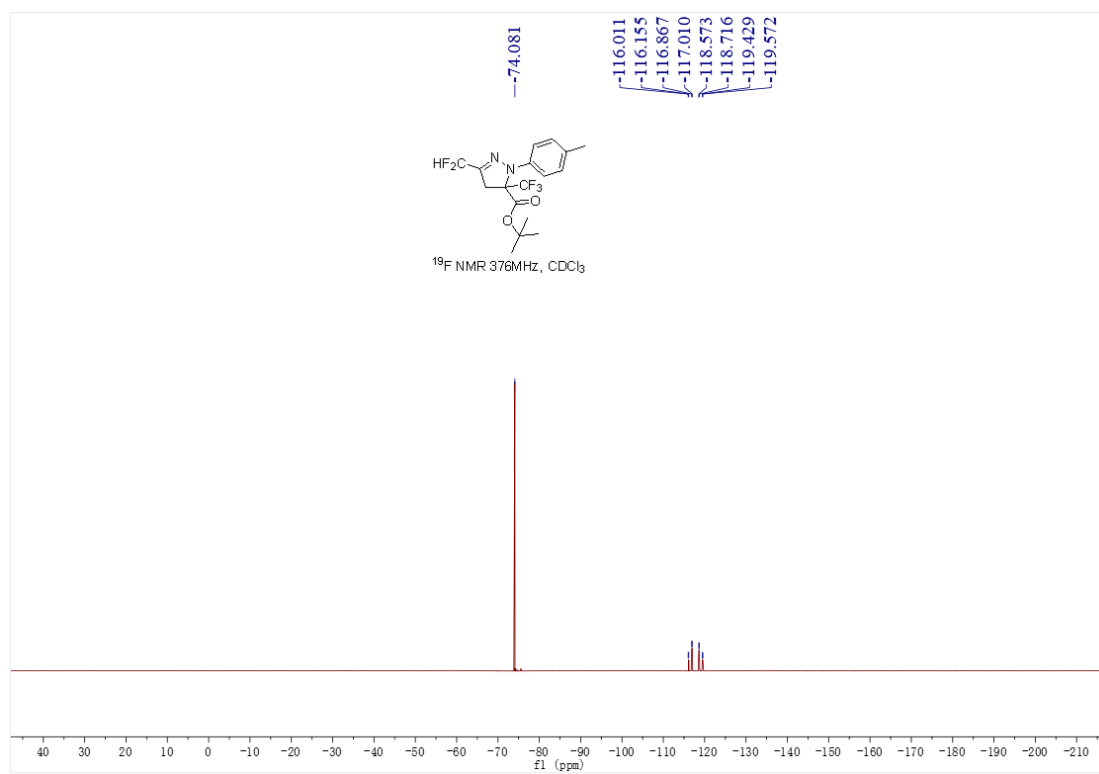
¹H NMR copy of compound **4b**



¹³C NMR copy of compound **4b**

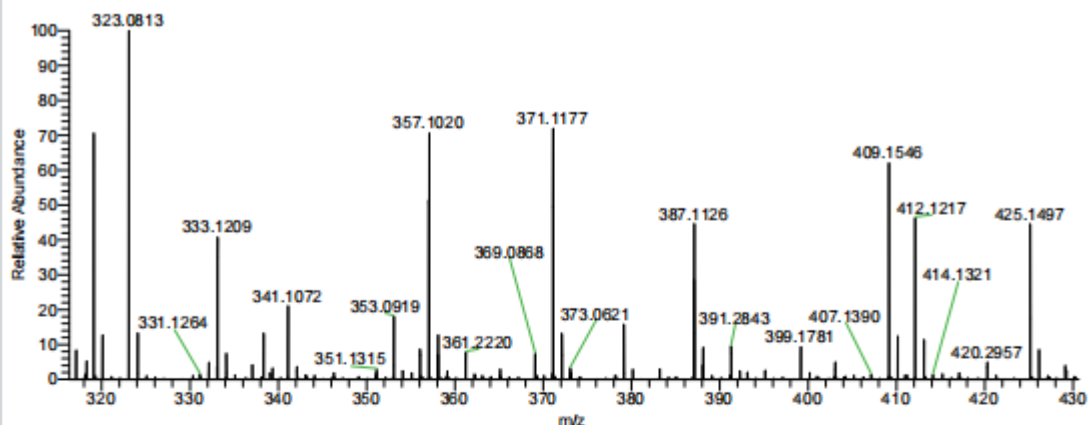


¹⁹F NMR copy of compound **4b**



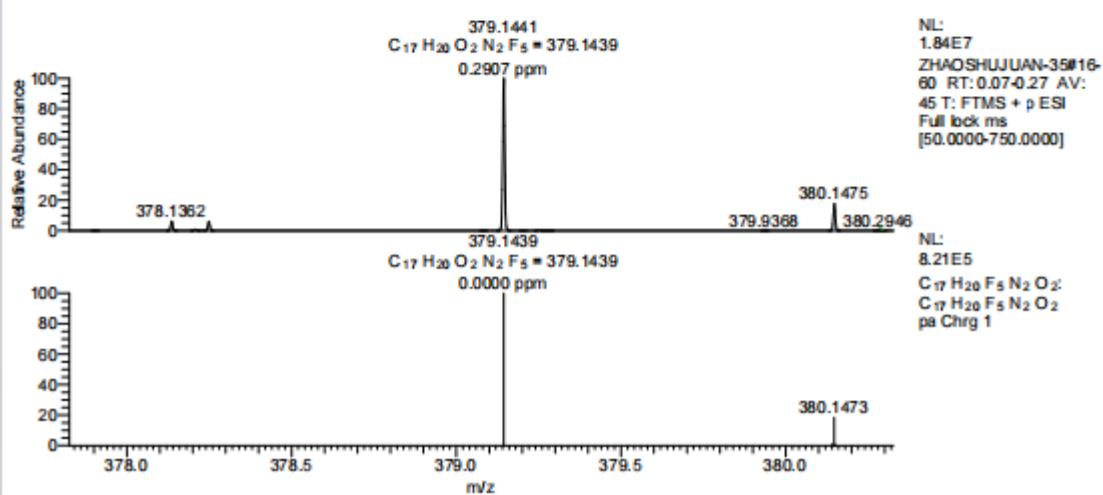
HRMS copy of compound 4b

ZHAOSHUJUAN-35#16-60 RT: 0.07-0.27 AV: 45 NL: 1.17E8
 T: FTMS + p ESI Full lock ms [50.0000-750.0000]



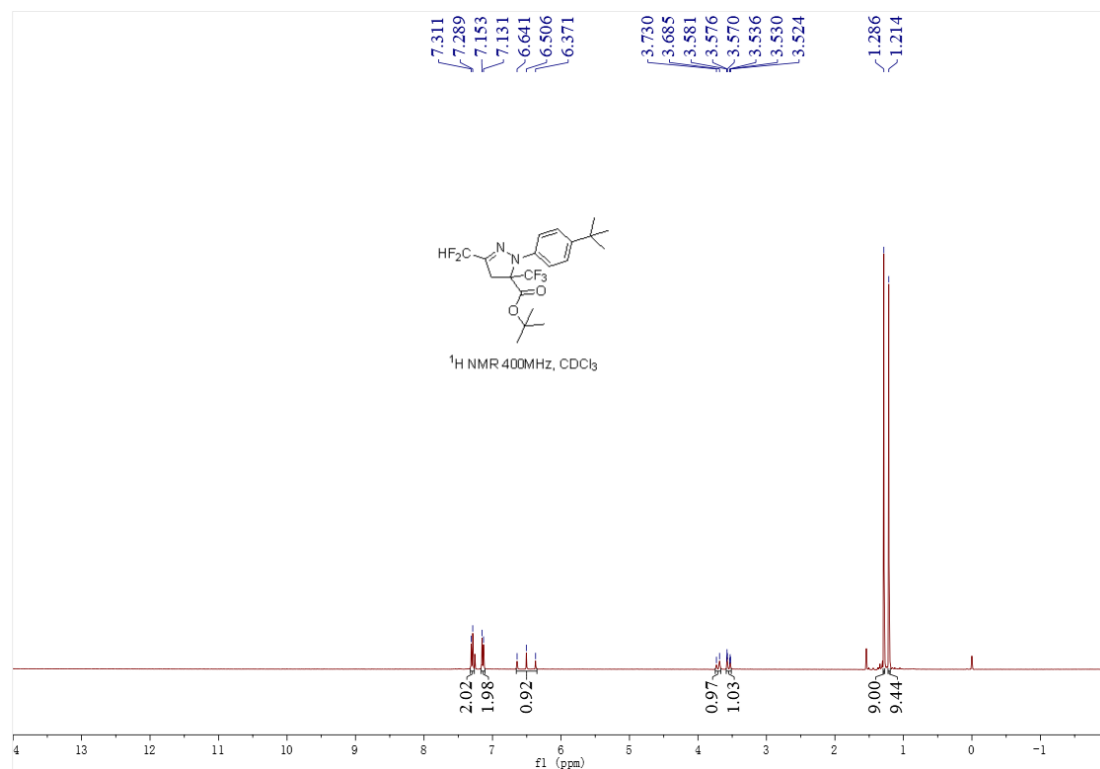
ZHAOSHUJUAN-35#16-60 RT: 0.07-0.27 AV: 45
 T: FTMS + p ESI Full lock ms [50.0000-750.0000]
 m/z = 377.8250-380.3262

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
378.1362	1165817.4	6.21			
378.2089	150825.8	0.80			
378.2487	1131236.6	6.03			
379.1441	18758398.0	100.00	379.1439	0.11	C ₁₇ H ₂₀ O ₂ N ₂ F ₅
380.1475	3280600.3	17.49			

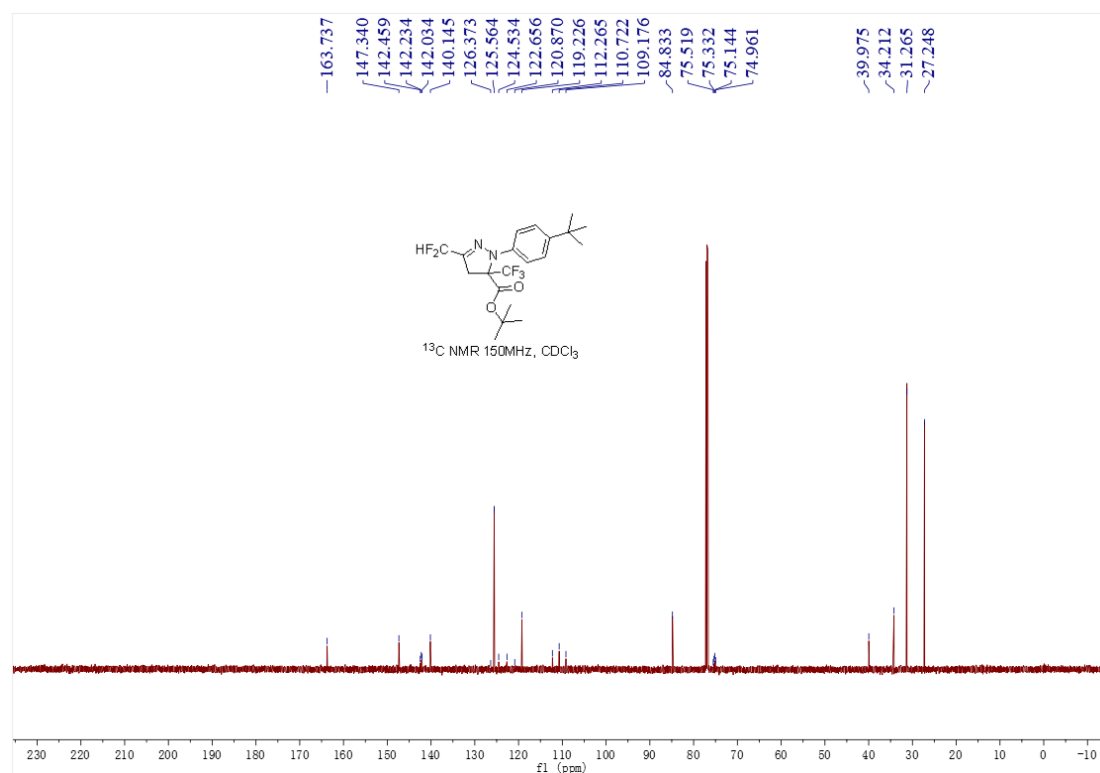


Spectrogram copies of compound **4c**

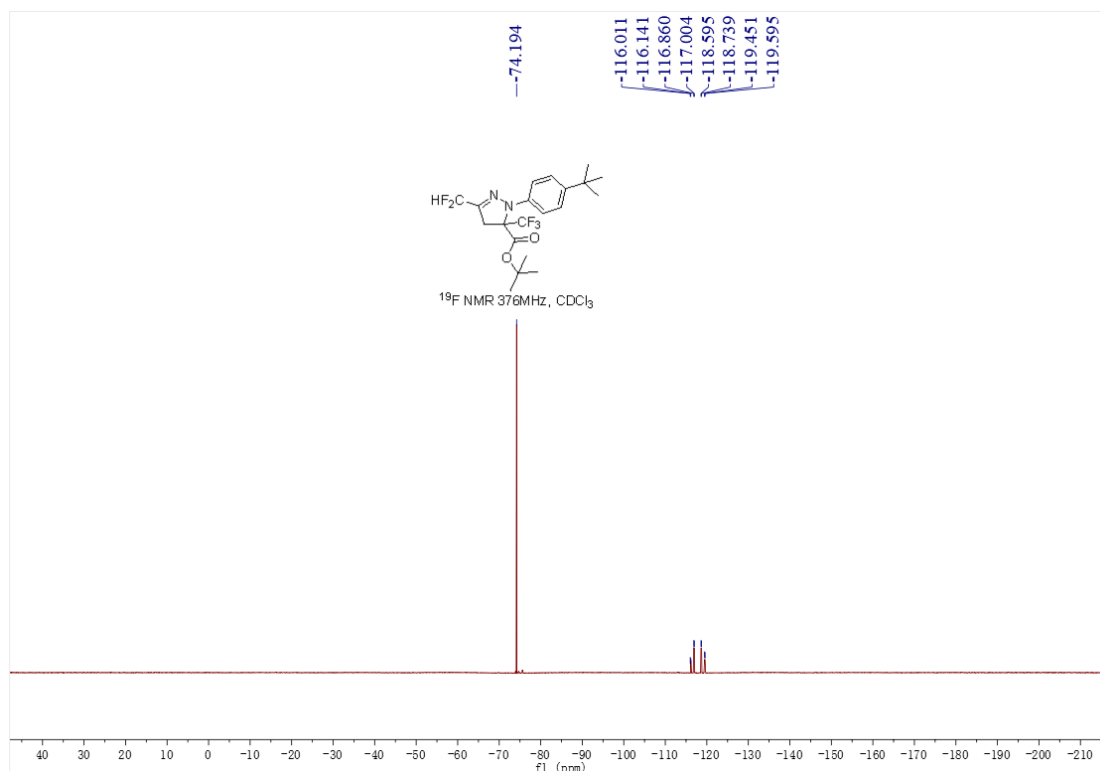
^1H NMR copy of compound **4c**



^{13}C NMR copy of compound **4c**



¹⁹F NMR copy of compound 4c

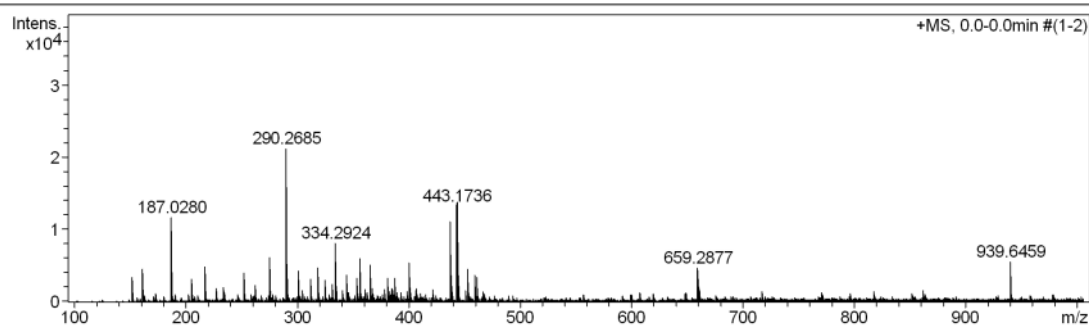


HRMS copy of compound 4c

Mass Spectrum SmartFormula Report

Analysis Info		Acquisition Date	
Analysis Name	D:\Data\user\NWNW-wangruikang 20240205-22.d	2024-2-5 10:15:36	
Method	tune_low.m	Operator	Huyue
Sample Name	22	Instrument / Ser#	micrOTOF-Q 20453
Comment			

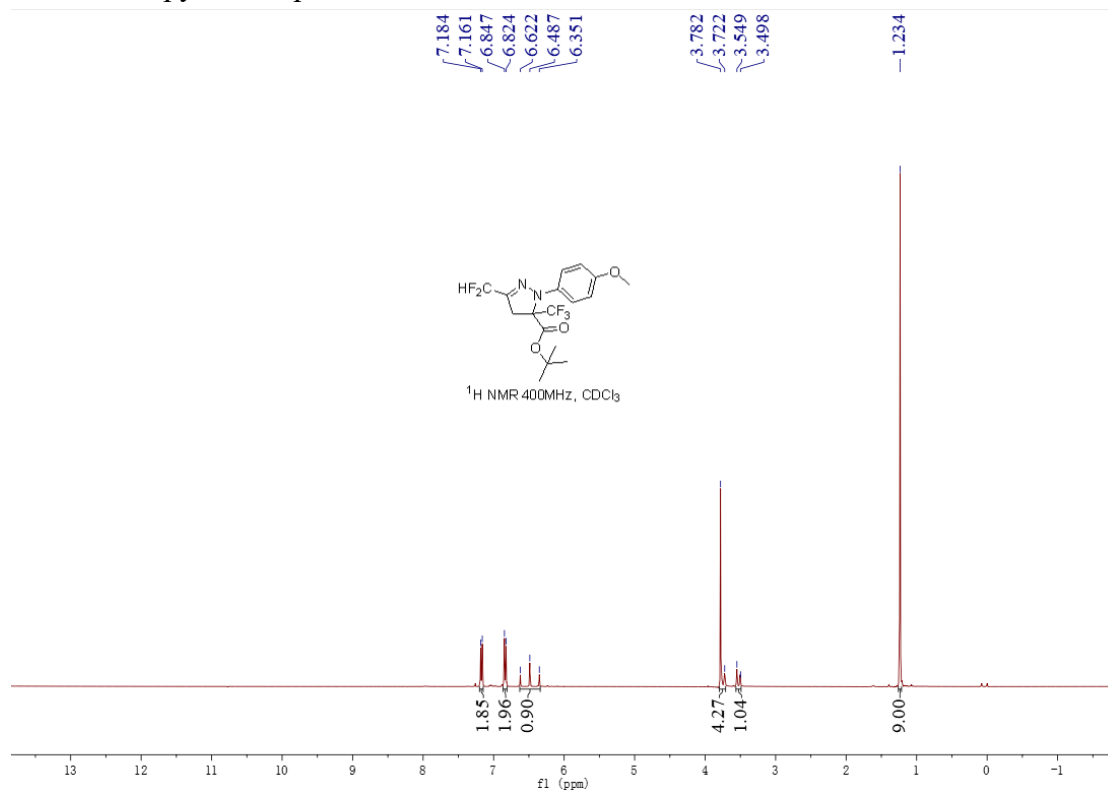
Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 j̄aC
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste



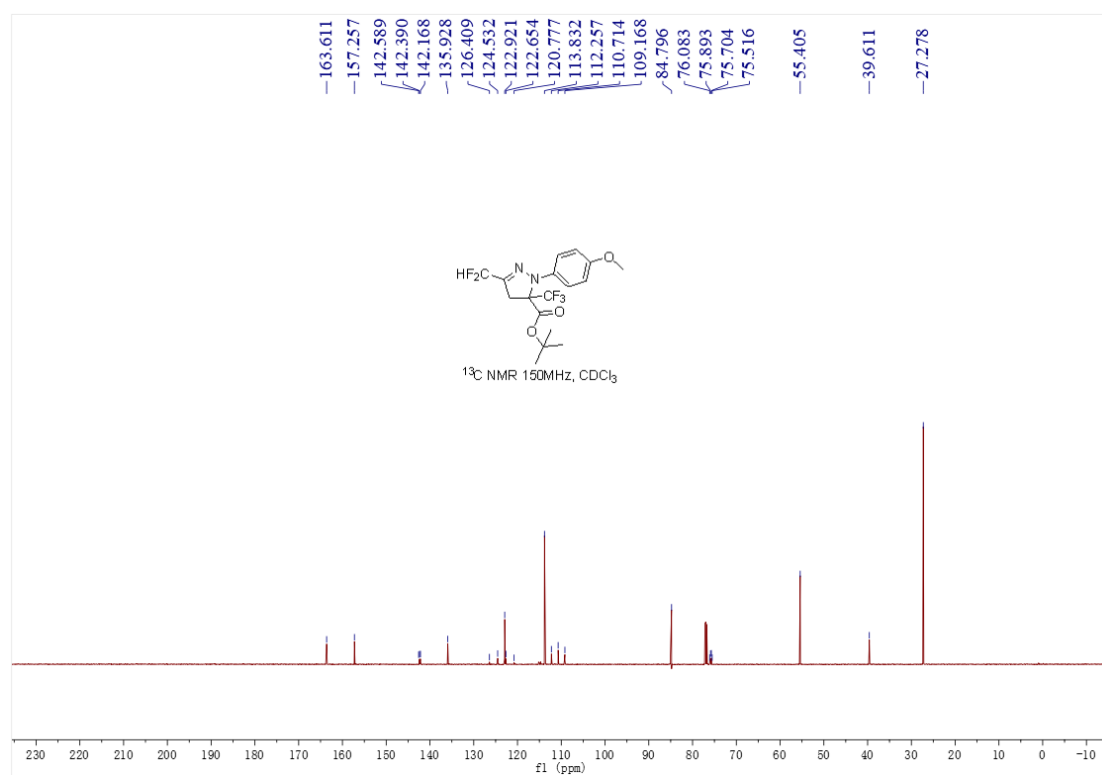
Meas. #	Formula	m/z	err [ppm]	Me an err [ppm]	rd b	N- R ul f e	e j % Con	mSi gm a	Std l	St d Me an m/z	Std l Var m	Std l Dif f	Std Com b Dev
443.1736	1 C ₂₀ H ₂₅ F ₅ N ₂ NaO ₂	443.1728	-1.7	-1.7	6.5	ok	even	39.2	60.1	0.8	29.5	0.1	842.7

Spectrogram copies of compound **4d**

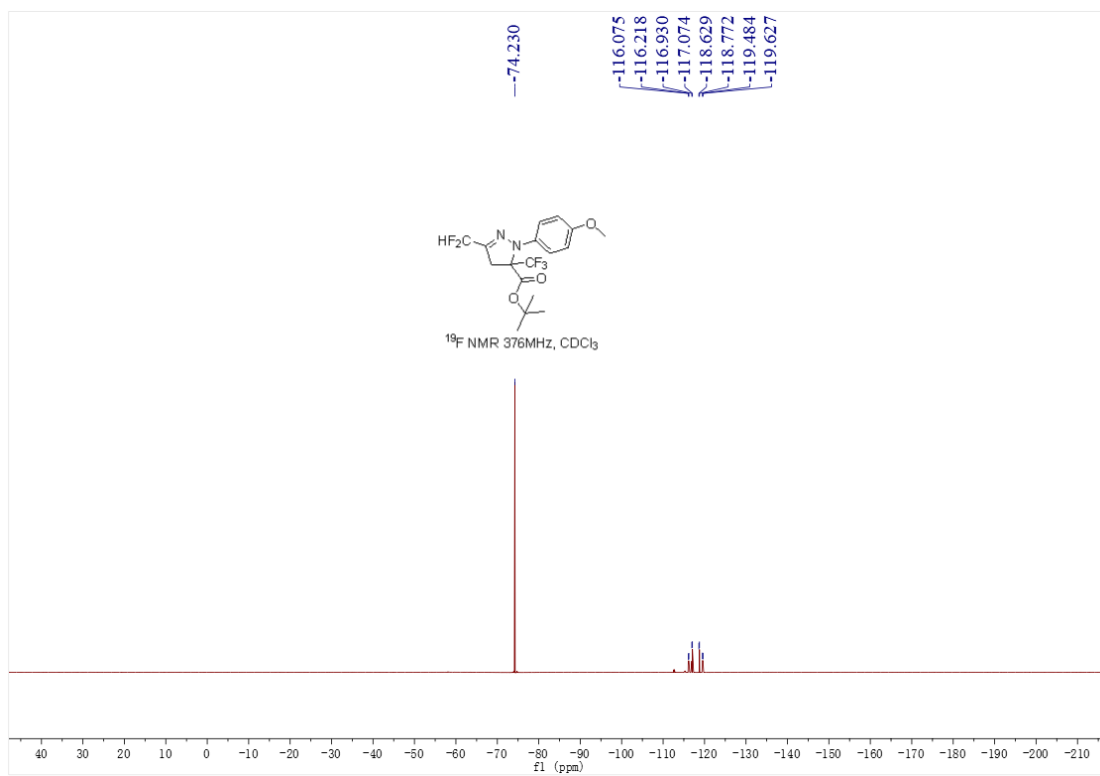
¹H NMR copy of compound **4d**



¹³C NMR copy of compound **4d**

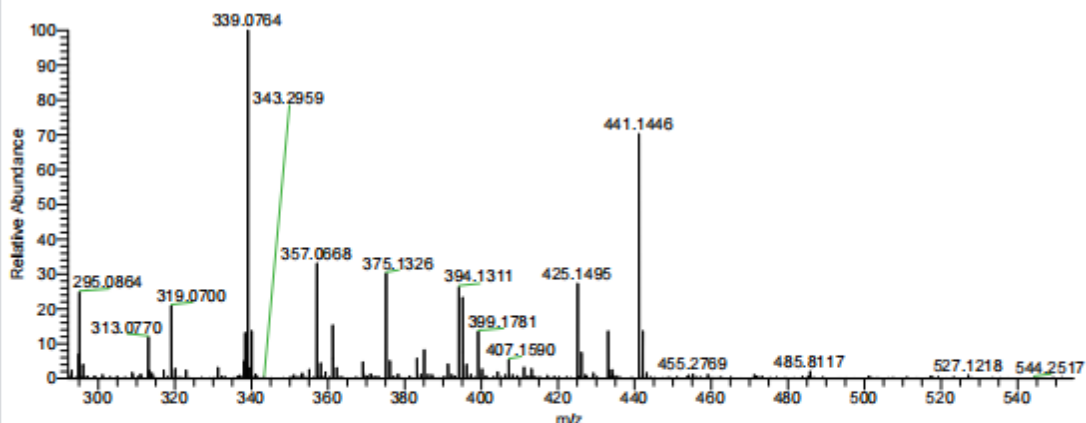


¹⁹F NMR copy of compound **4d**



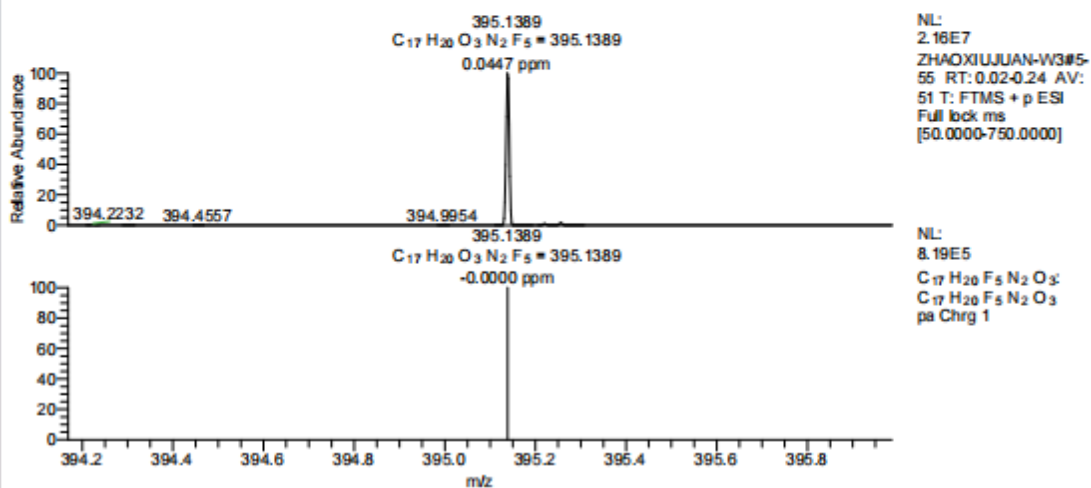
HRMS copy of compound 4d

ZHAOXIUJUAN-W3#5-55 RT: 0.02-0.24 AV: 51 NL: 9.27E7
T: FTMS + p ESI Full lock ms [50.0000-750.0000]



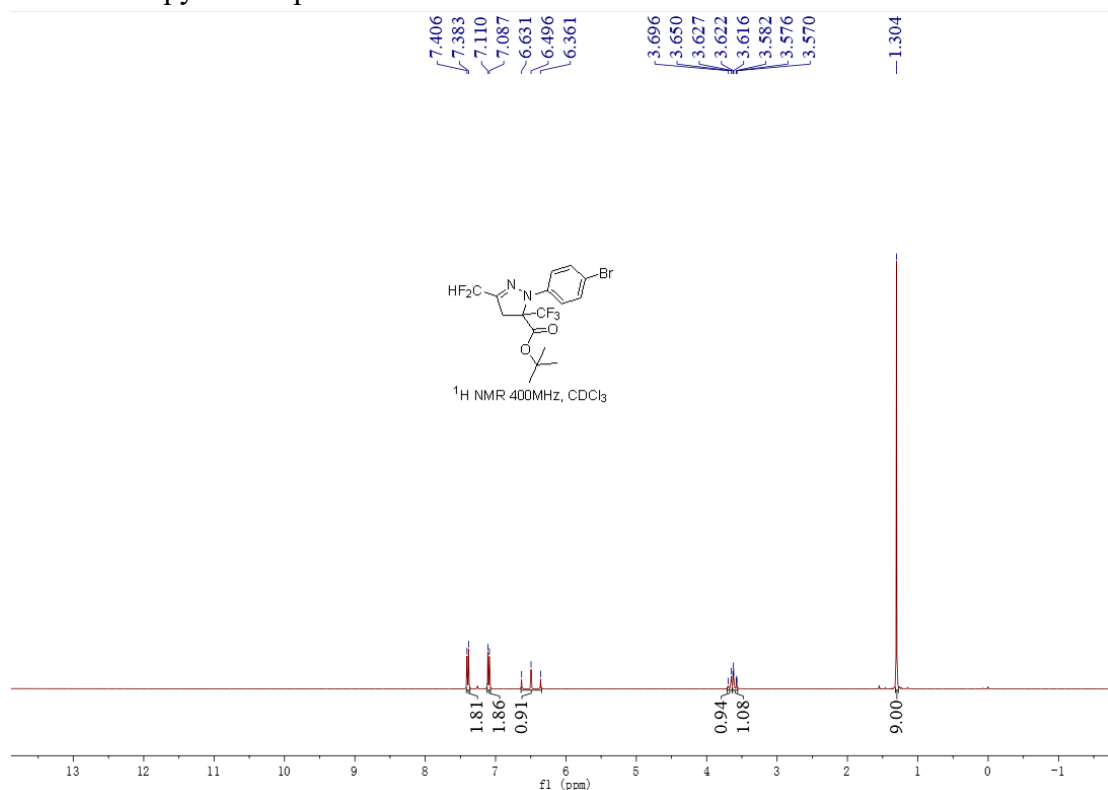
ZHAOXIUJUAN-W3#5-55 RT: 0.02-0.24 AV: 51
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 392.2451-399.1363

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
392.2877	1000421.0	4.06			
394.1311	24638958.0	100.00			
395.1389	22091790.0	89.66	395.1389	0.02	C ₁₇ H ₂₀ O ₃ N ₂ F ₅
396.1427	3790185.8	15.38			
397.2723	1065636.3	4.33			

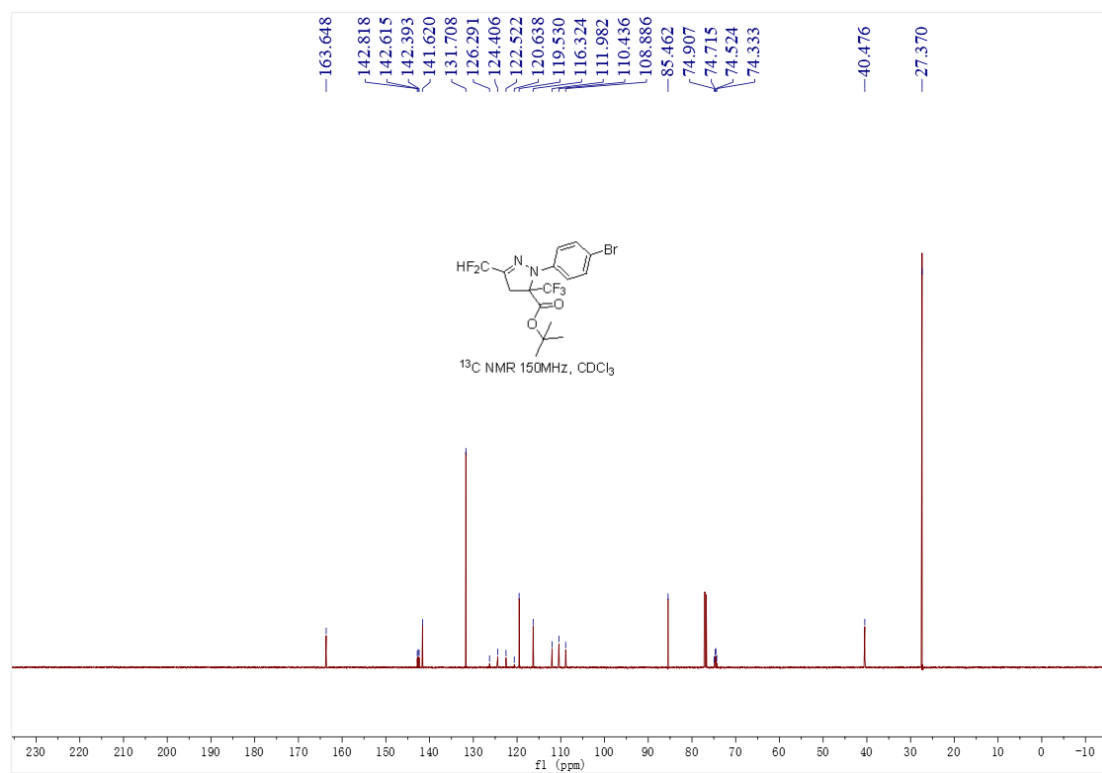


Spectrogram copies of compound **4e**

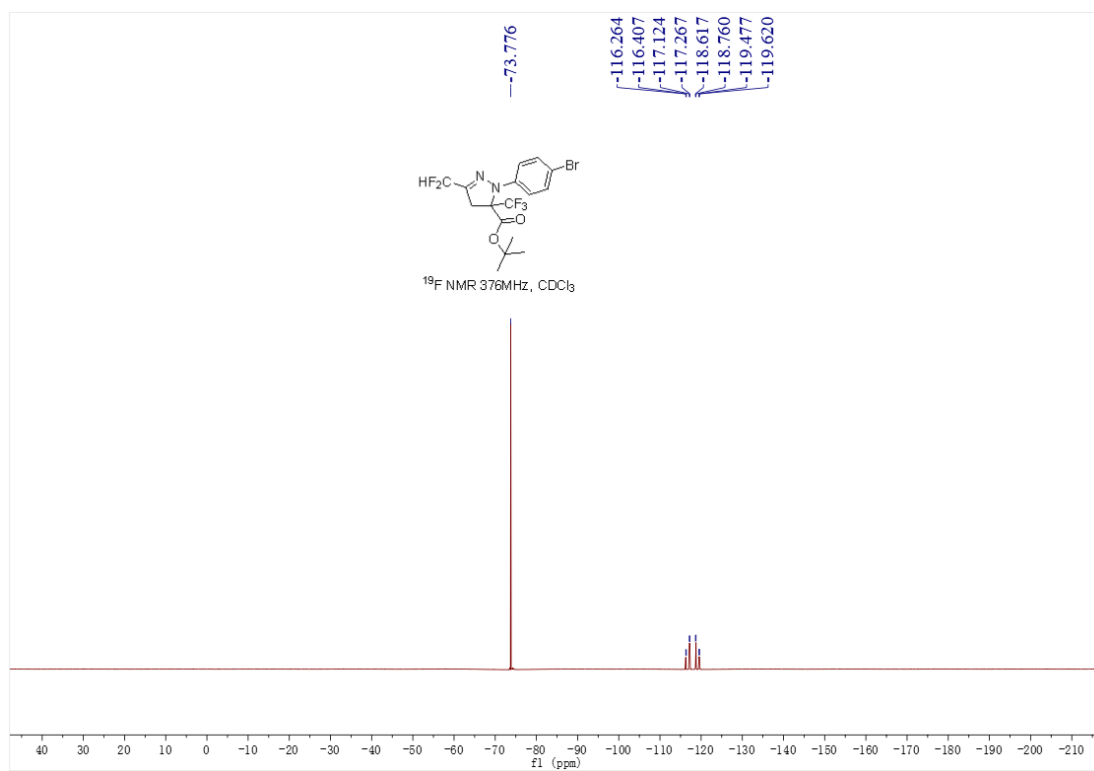
^1H NMR copy of compound **4e**



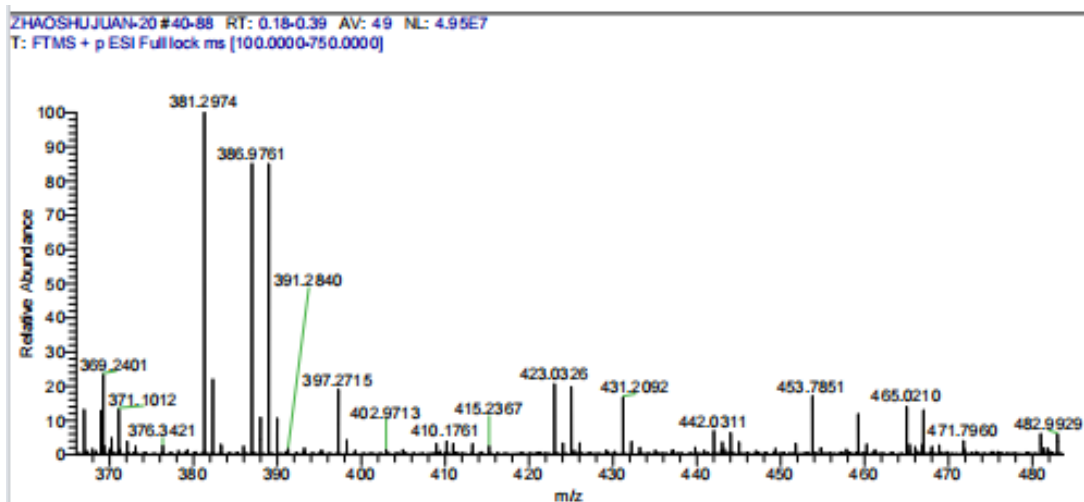
^{13}C NMR copy of compound **4e**



¹⁹F NMR copy of compound 4e

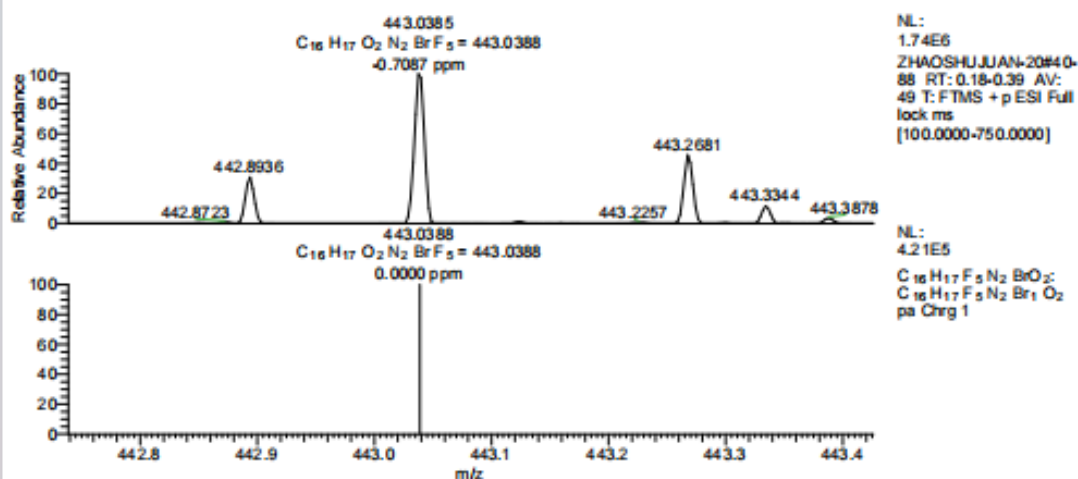


HRMS copy of compound 4e



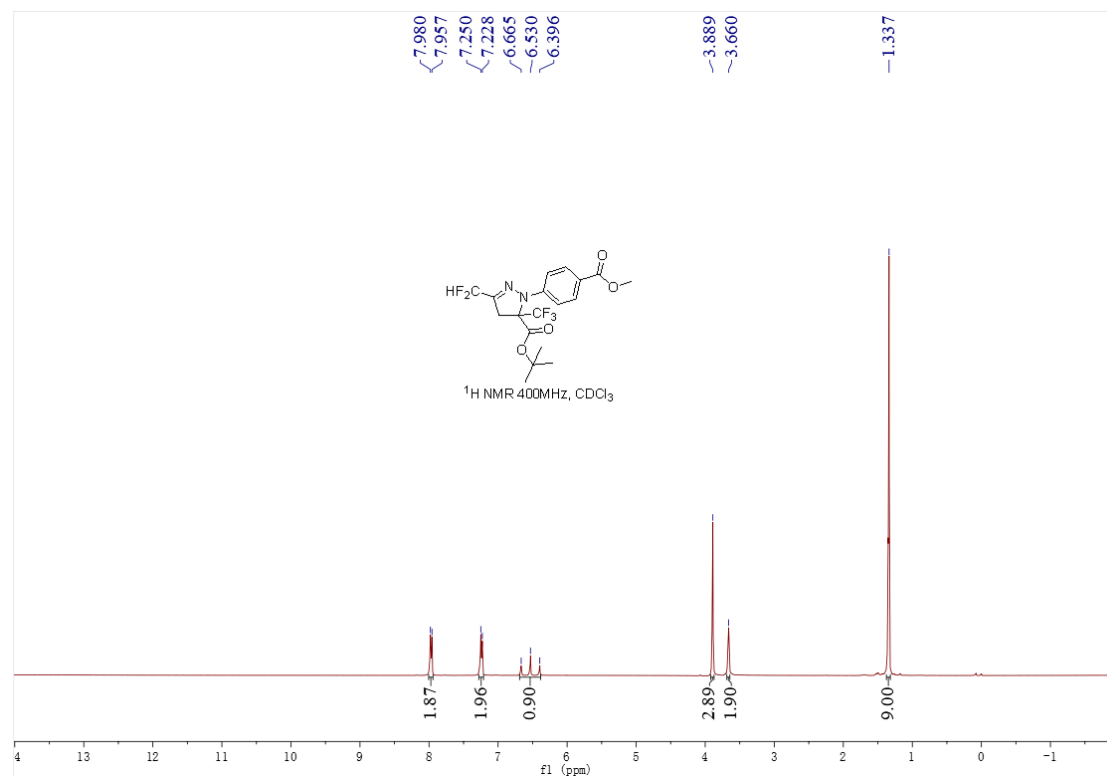
ZHAOSHUJUAN-20#40-88 RT: 0.18-0.39 AV: 49
T: FTMS + p ESI Full lock ms [100.0000-750.0000]
m/z = 442.7385-443.4259

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
442.8936	540896.4	30.26	443.0388	-145.20	C ₁₆ H ₁₇ O ₂ N ₂ BrF ₅
443.0385	1787463.1	100.00	443.0388	-0.31	C ₁₆ H ₁₇ O ₂ N ₂ BrF ₅
443.2681	804456.9	45.01	443.0388	229.27	C ₁₆ H ₁₇ O ₂ N ₂ BrF ₅
443.3344	204813.8	11.46	443.0388	295.57	C ₁₆ H ₁₇ O ₂ N ₂ BrF ₅
443.3878	59548.9	3.33			

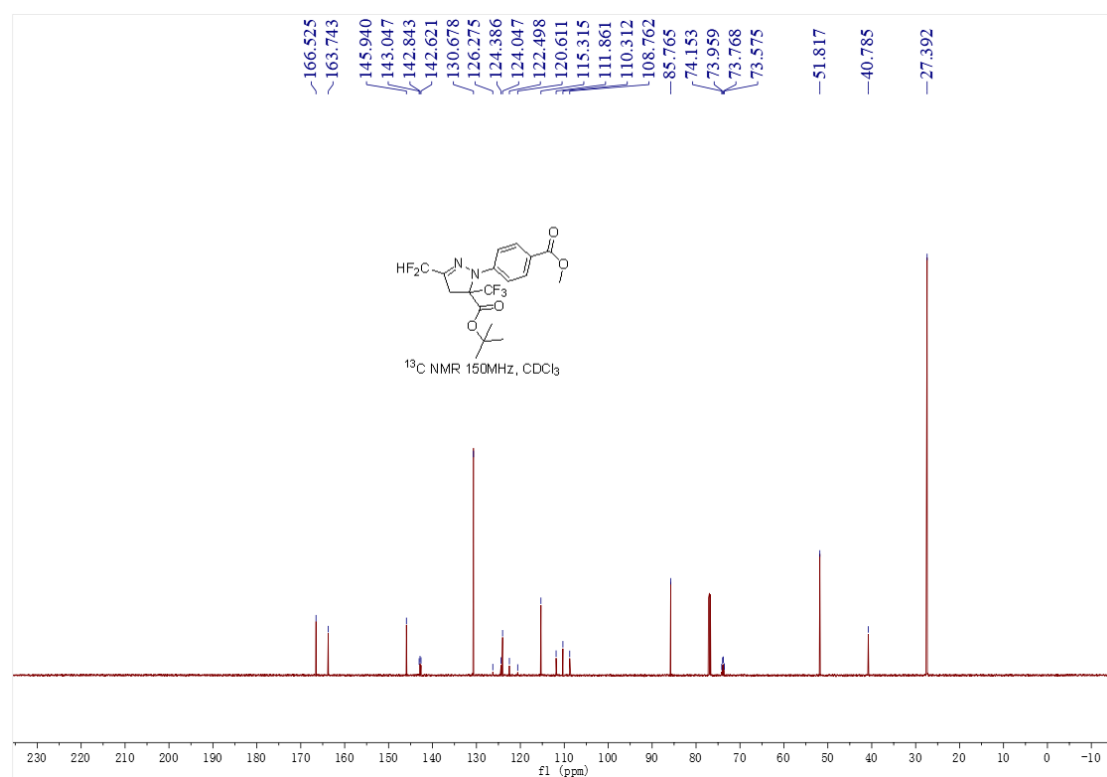


Spectrogram copies of compound **4f**

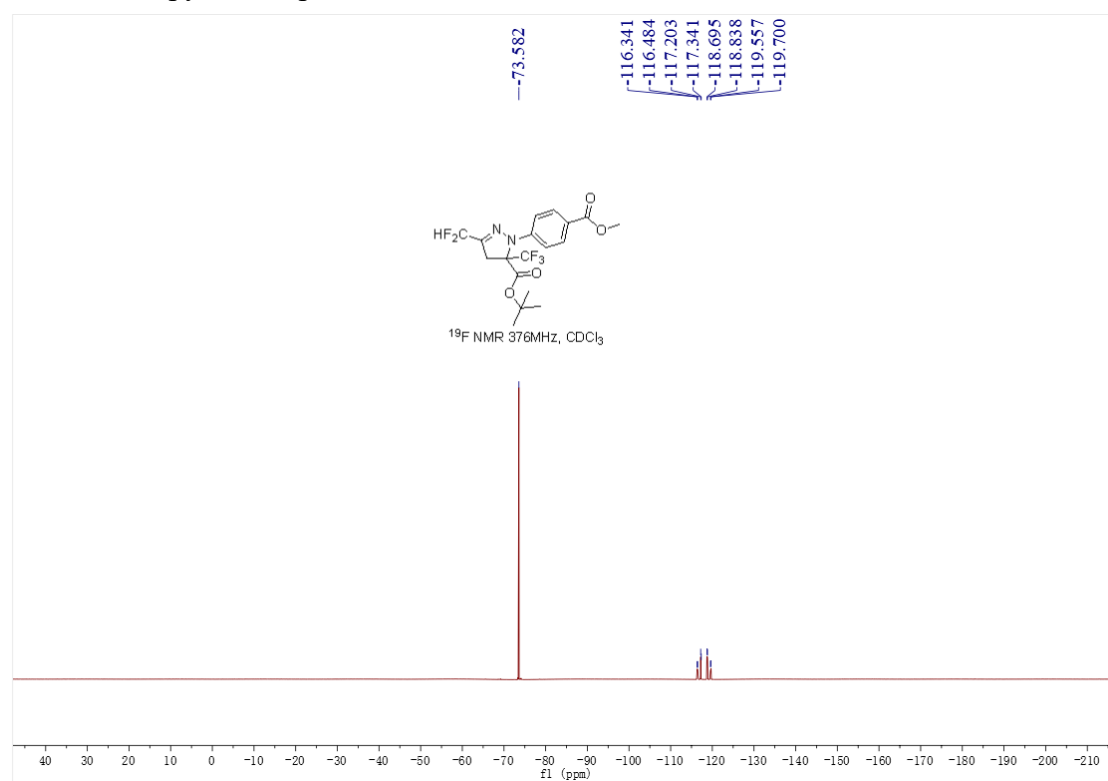
¹H NMR copy of compound **4f**



¹³C NMR copy of compound **4f**



¹⁹F NMR copy of compound **4f**



HRMS copy of compound **4f**

Mass Spectrum SmartFormula Report

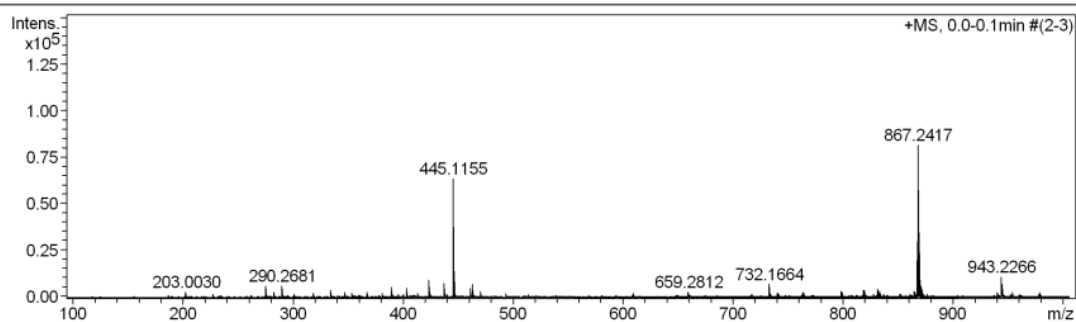
Analysis Info

Analysis Name D:\Data\user\NWNW-wangruikang 20240205-29.d
 Method tune_low.m
 Sample Name 29
 Comment

Acquisition Date 2024-2-5 10:28:05
 Operator Huyue
 Instrument / Ser# micrOTOF-Q 20453

Acquisition Parameter

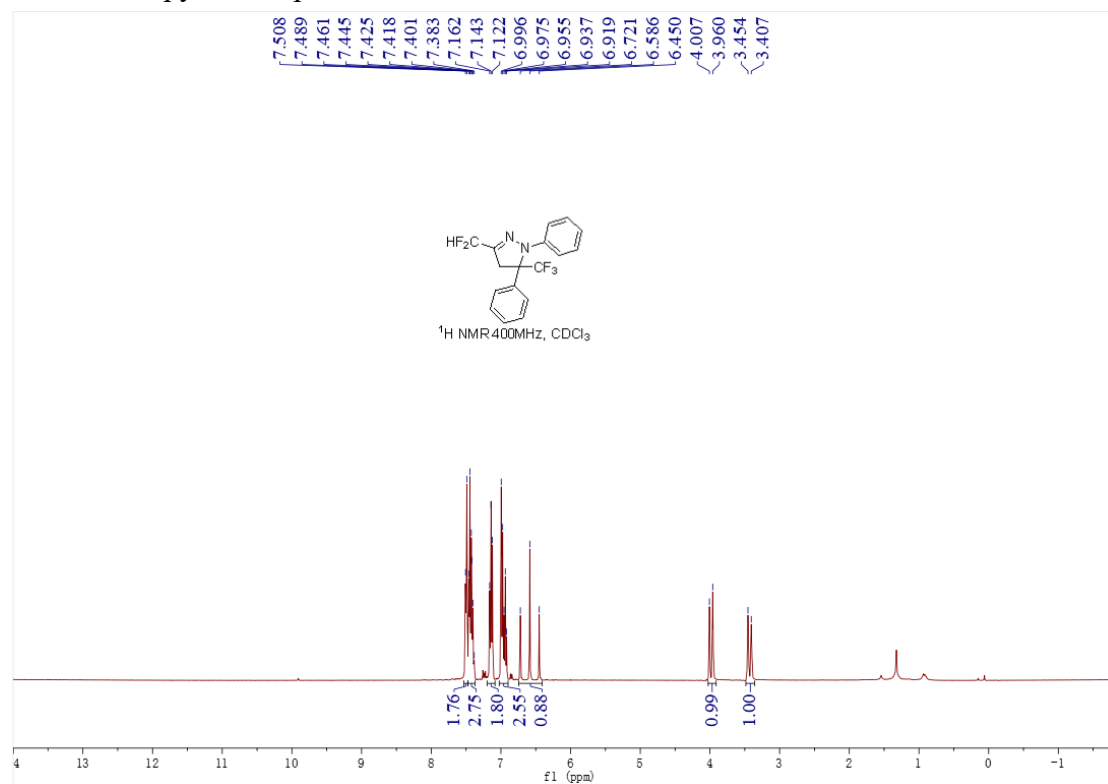
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 j°C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	400.0 Vpp	Set Divert Valve	Waste



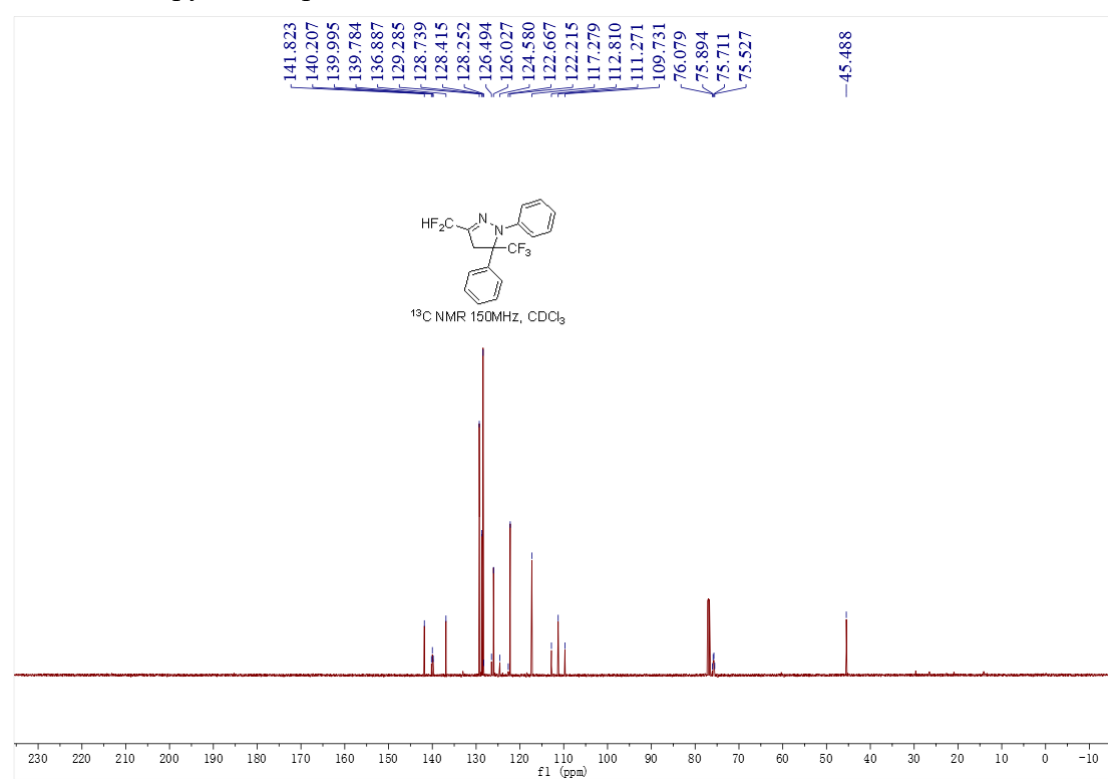
Meas. #	Formula	m/z	err [ppm]	Me an err [ppm]	rdb	N-R ul e	ej% Conf	mS ig ma	Std l	Std Me an m/z	Std Va rN or m	Std m/z Diff	Std Com b Dev
445.1155	1 C 18 H 19 F 5 N 2 Na O 4	445.1157	0.6	0.8	7.5	ok	even	9.3	17.0	0.7	7.3	0.0	842.7

Spectrogram copies of compound **4h**

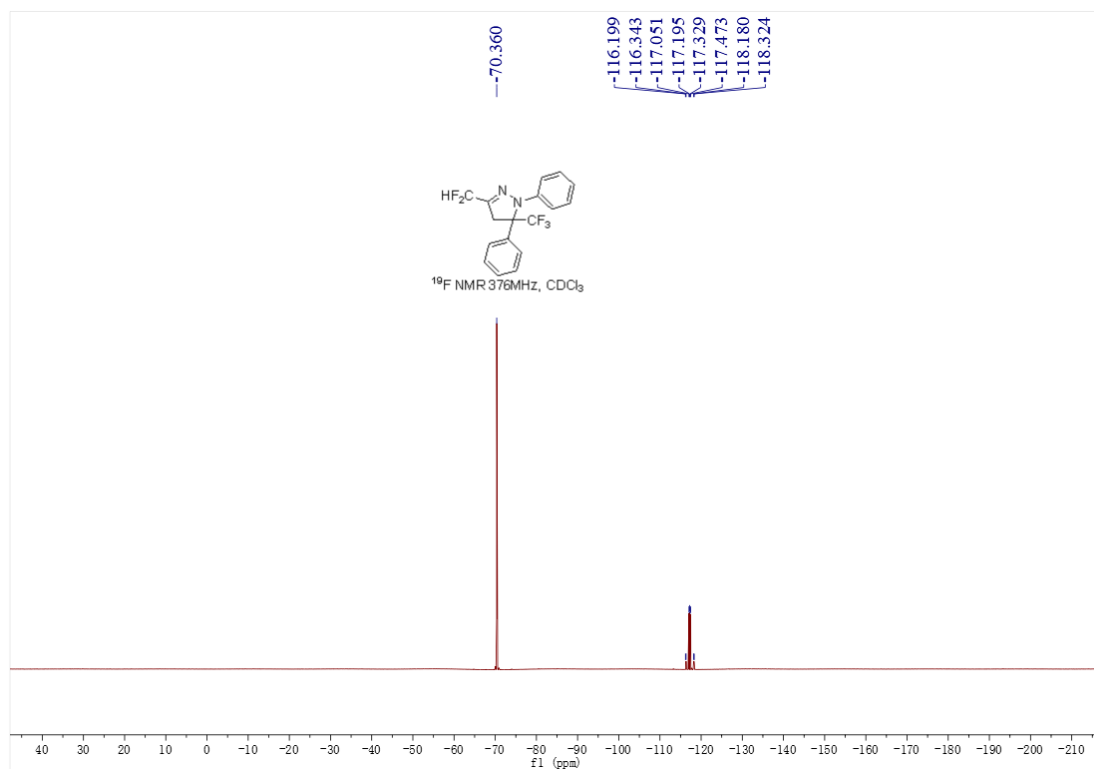
¹H NMR copy of compound **4h**



¹³C NMR copy of compound **4h**

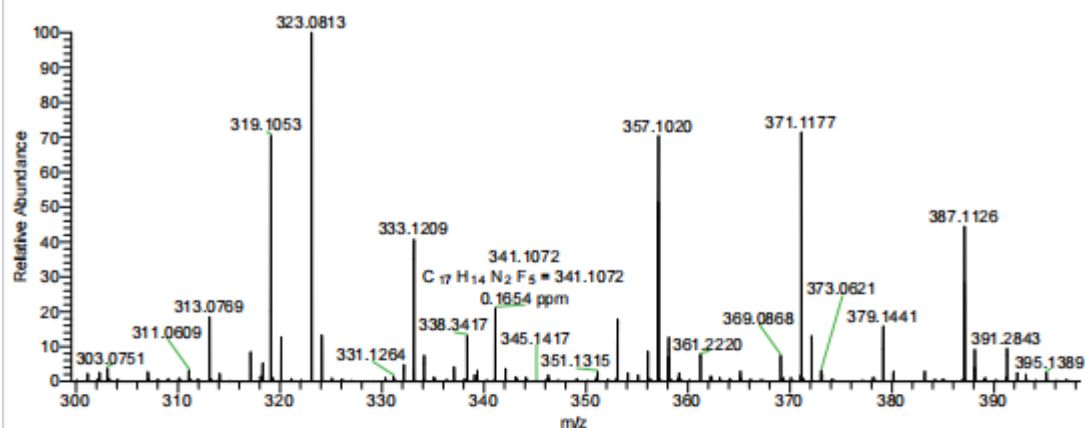


¹⁹F NMR copy of compound **4h**



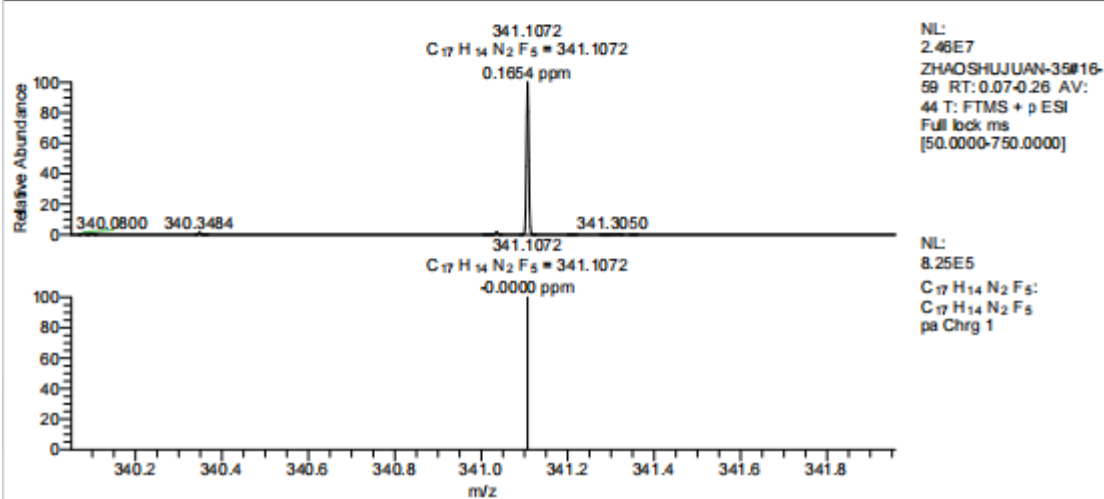
HRMS copy of compound 4h

ZHAOSHUJUAN-35#16-59 RT: 0.07-0.26 AV: 44 NL: 1.17E8
T: FTMS + p ESI Full lock ms [50.0000-750.0000]



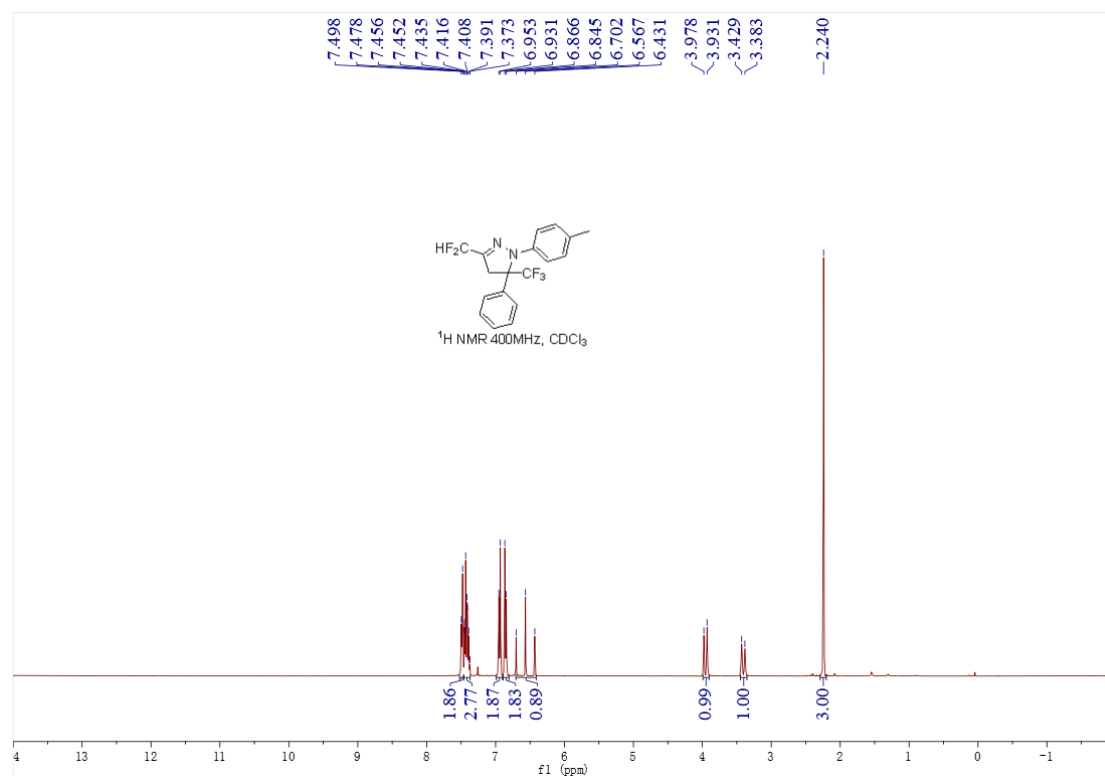
ZHAOSHUJUAN-35#16-59 RT: 0.07-0.26 AV: 44
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z = 340.0514-341.9577

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
340.0800	214961.9	0.87			
340.0996	214800.3	0.87			
340.3484	347972.5	1.41			
341.0357	411597.9	1.67	341.1072	-71.50	C ₁₇ H ₁₄ N ₂ F ₅
341.1072	24594608.0	100.00	341.1072	0.06	C ₁₇ H ₁₄ N ₂ F ₅

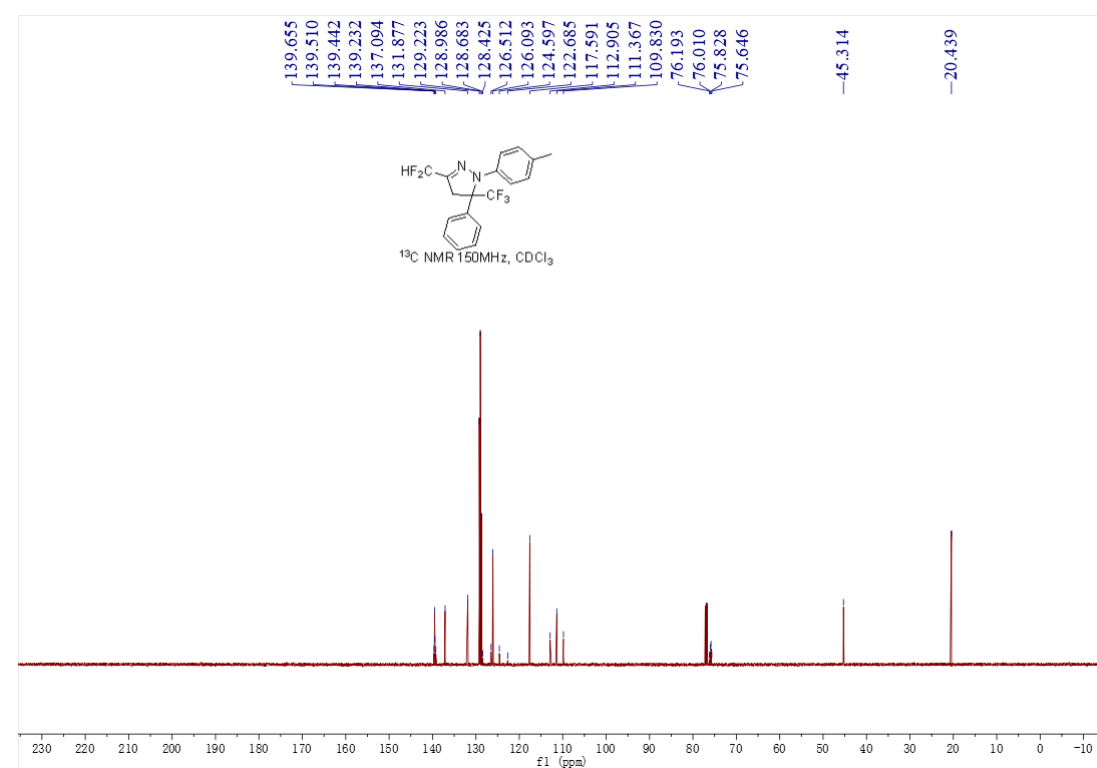


Spectrogram copies of compound **4i**

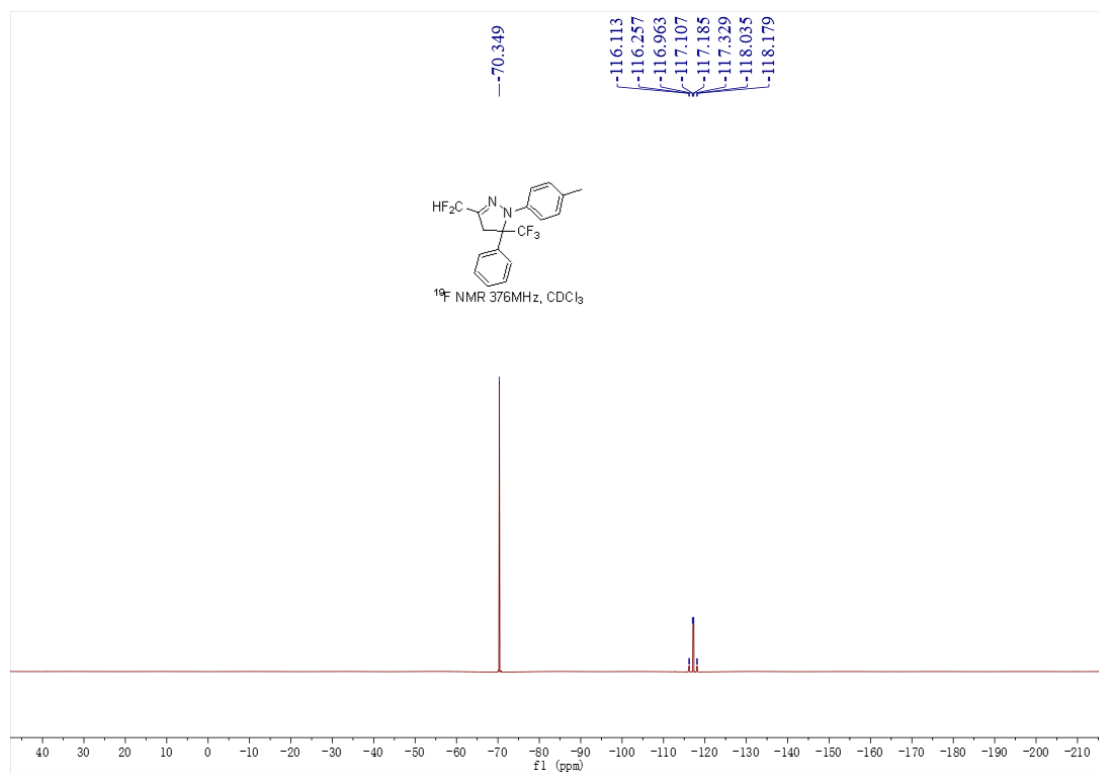
¹H NMR copy of compound **4i**



¹³C NMR copy of compound **4i**

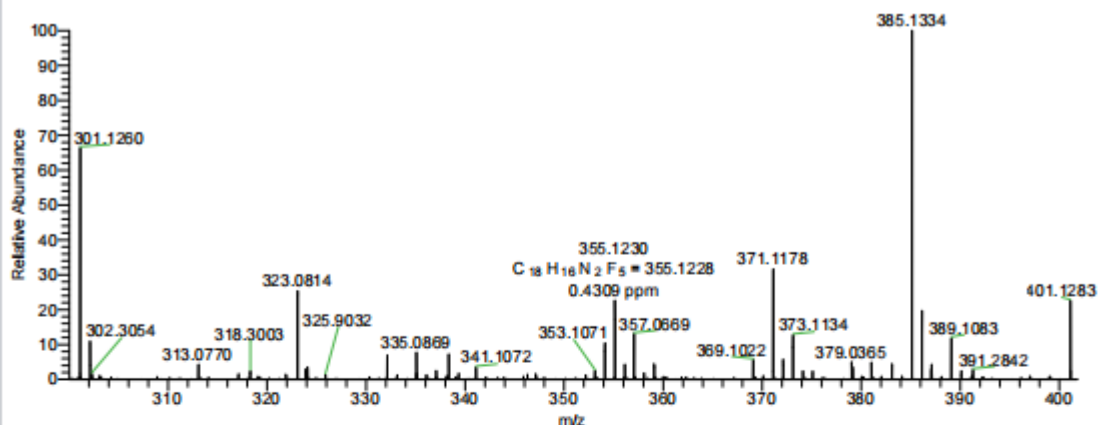


¹⁹F NMR copy of compound **4i**



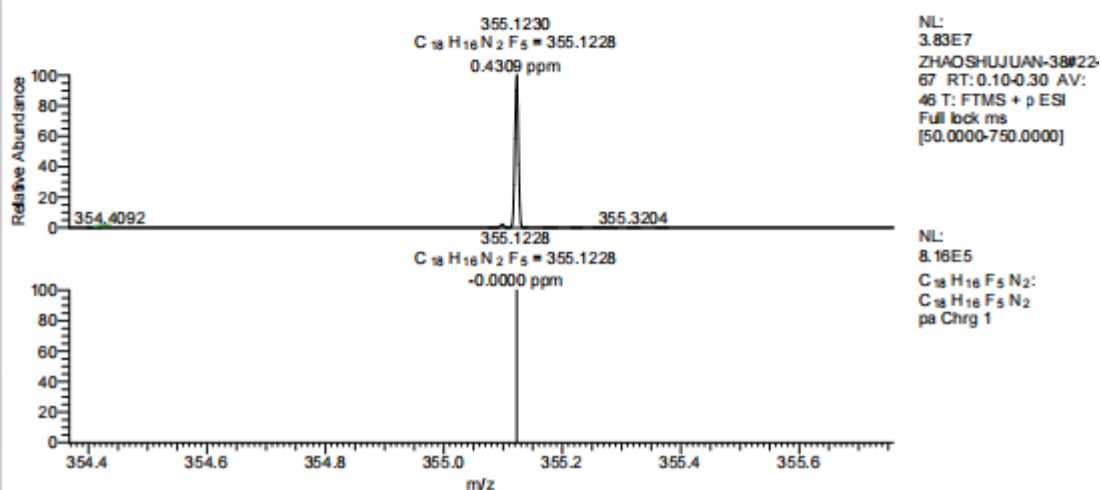
HRMS copy of compound 4i

ZHAOSHUJUAN-38#22-67 RT: 0.10-0.30 AV: 46 NL: 1.69E8
T: FTMS + p ESI Full lock ms [50.0000-750.0000]



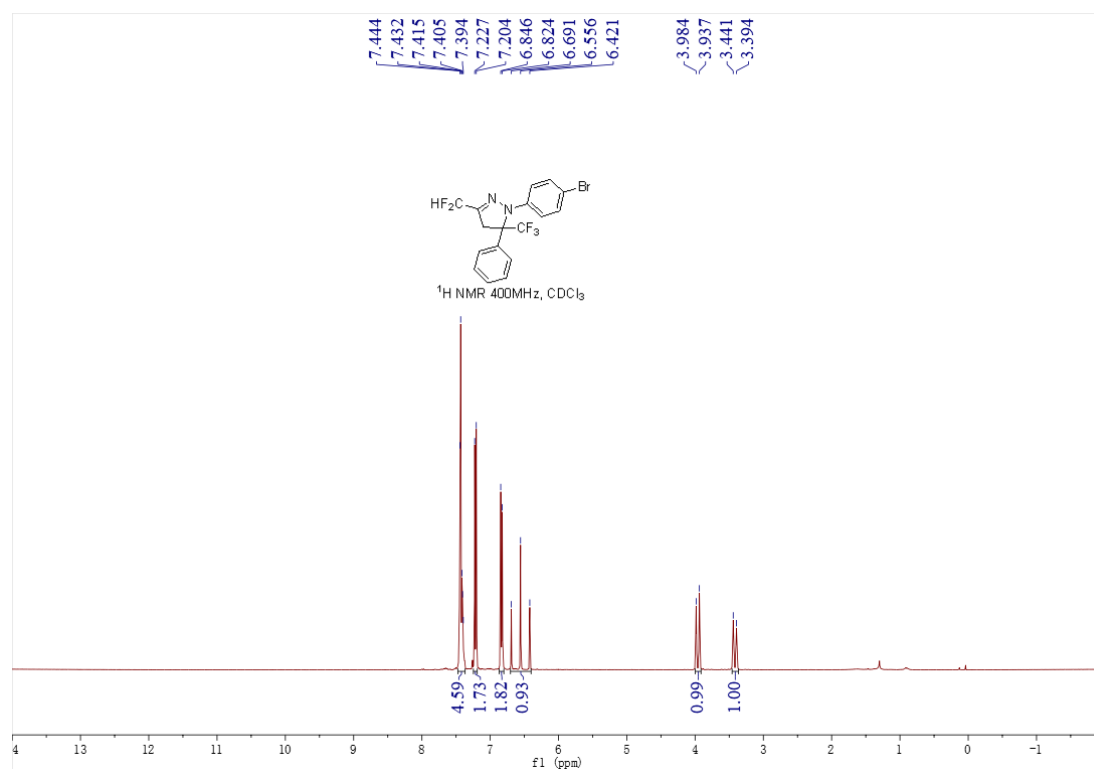
ZHAOSHUJUAN-38#22-67 RT: 0.10-0.30 AV: 46
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z = 354.3676-355.7585

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
354.4092	29261.1	0.08			
355.0988	837586.1	2.17	355.1228	-24.05	C ₁₈ H ₁₆ N ₂ F ₅
355.1230	38525624.0	100.00	355.1228	0.15	C ₁₈ H ₁₆ N ₂ F ₅
355.1799	16670.2	0.04	355.1228	57.05	C ₁₈ H ₁₆ N ₂ F ₅
355.3204	28856.3	0.07	355.1228	197.55	C ₁₈ H ₁₆ N ₂ F ₅

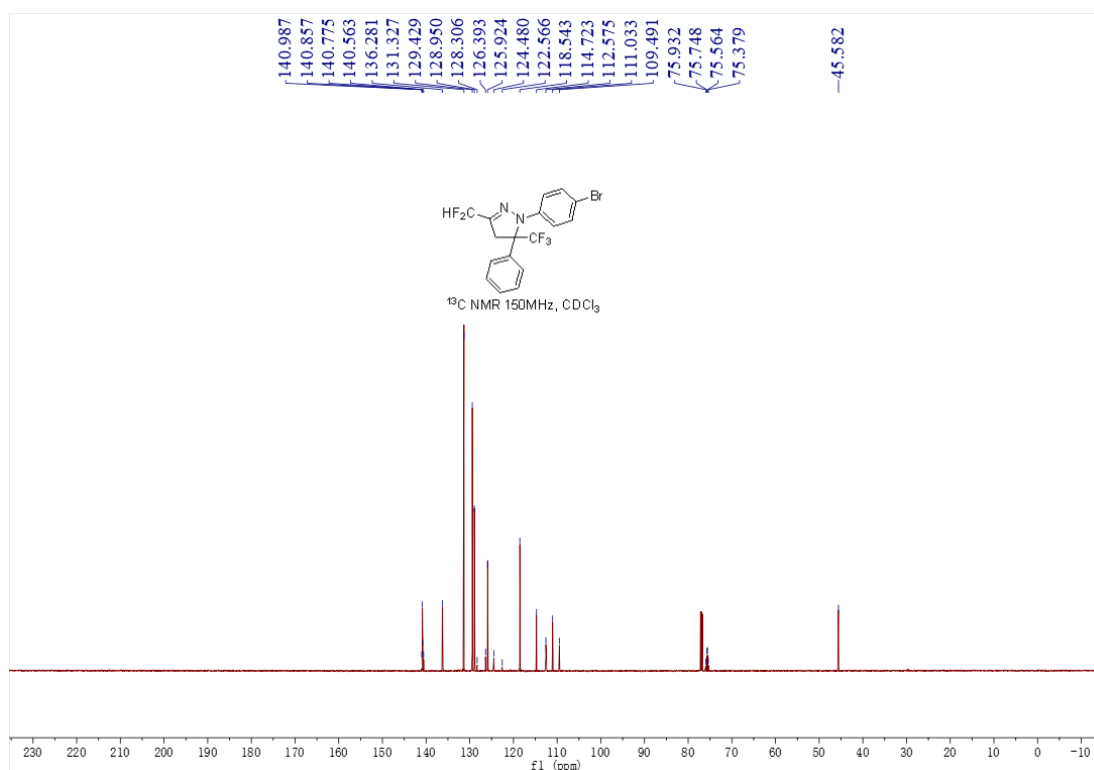


Spectrogram copies of compound **4j**

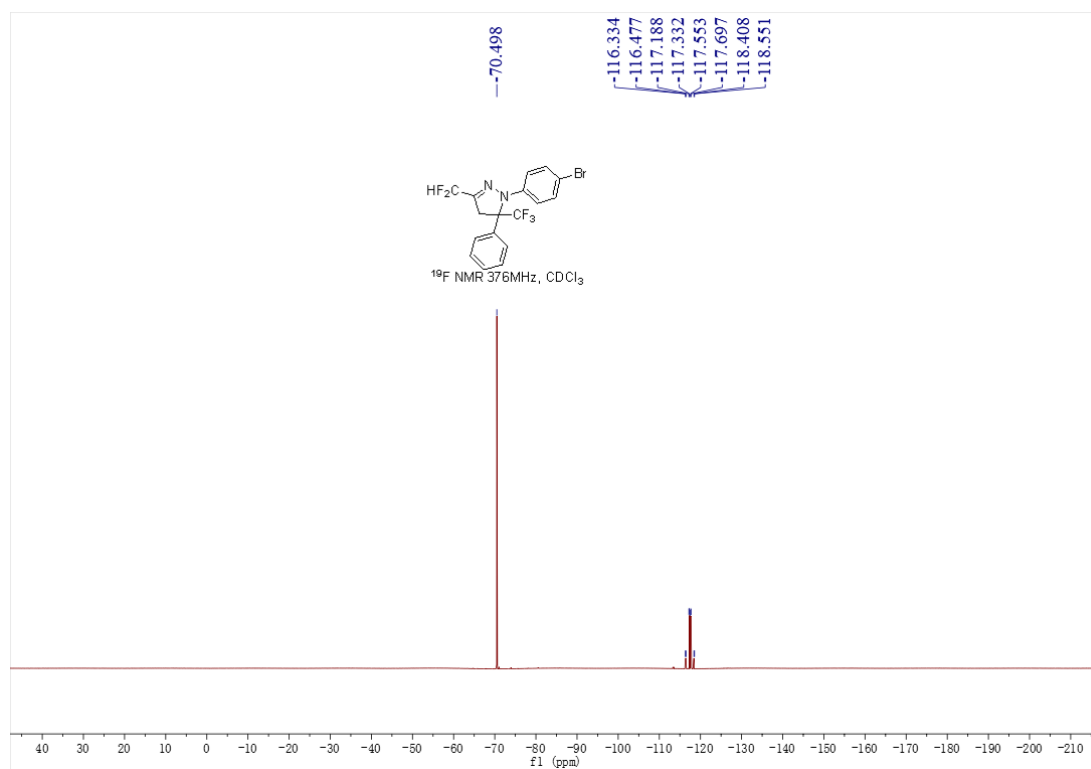
^1H NMR copy of compound **4j**



^{13}C NMR copy of compound **4j**

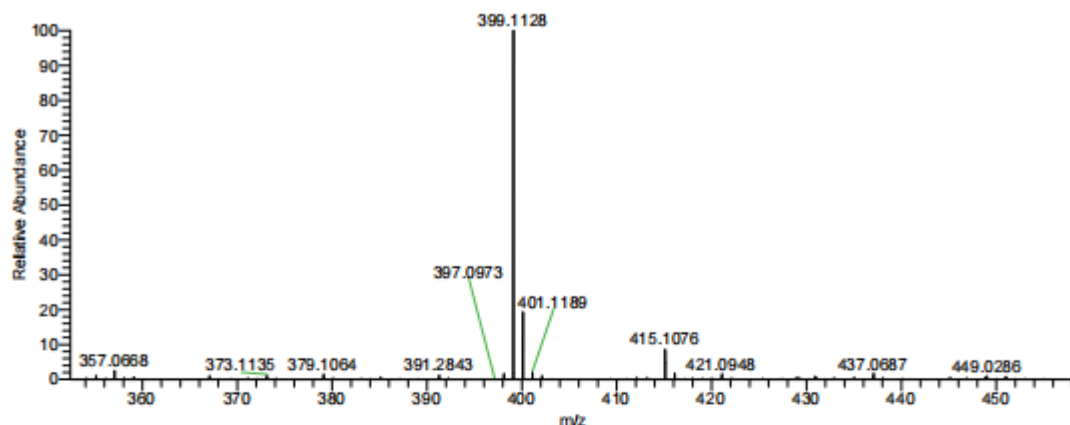


¹⁹F NMR copy of compound **4j**



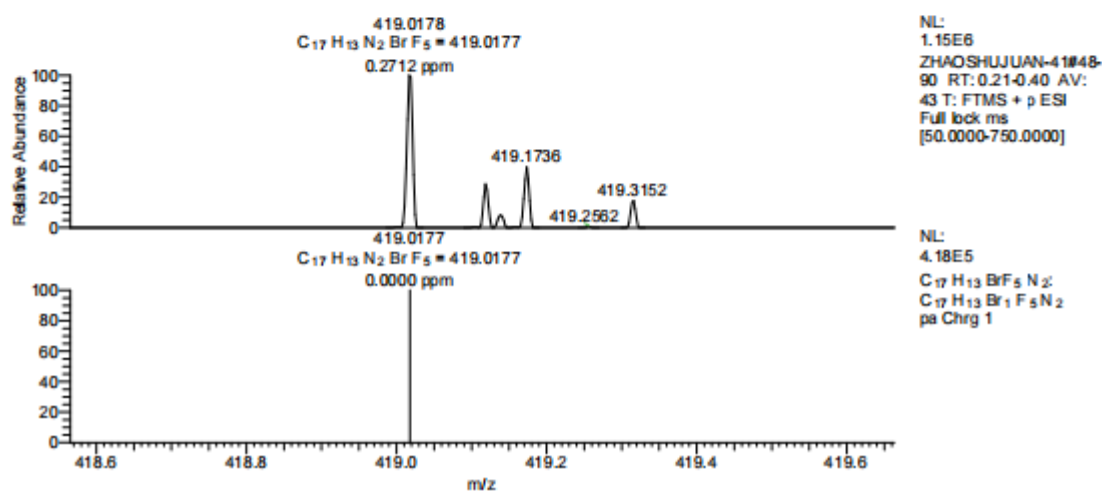
HRMS copy of compound 4j

ZHAOSHUJUAN-41 #48-90 RT: 0.21-0.40 AV: 43 NL: 5.95E8
 T: FTMS + p ESI Full lock ms [50.0000-750.0000]



ZHAOSHUJUAN-41#48-90 RT: 0.21-0.40 AV: 43
 T: FTMS + p ESI Full lock ms [50.0000-750.0000]
 m/z = 418.5653-419.6632

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
419.0178	1188991.6	100.00	419.0177	0.11	C ₁₇ H ₁₃ N ₂ BrF ₅
419.1190	332982.2	28.01	419.0177	101.28	C ₁₇ H ₁₃ N ₂ BrF ₅
419.1387	95017.9	7.99	419.0177	121.00	C ₁₇ H ₁₃ N ₂ BrF ₅
419.1736	457920.0	38.51	419.0177	155.88	C ₁₇ H ₁₃ N ₂ BrF ₅
419.3152	207181.4	17.42	419.0177	297.54	C ₁₇ H ₁₃ N ₂ BrF ₅

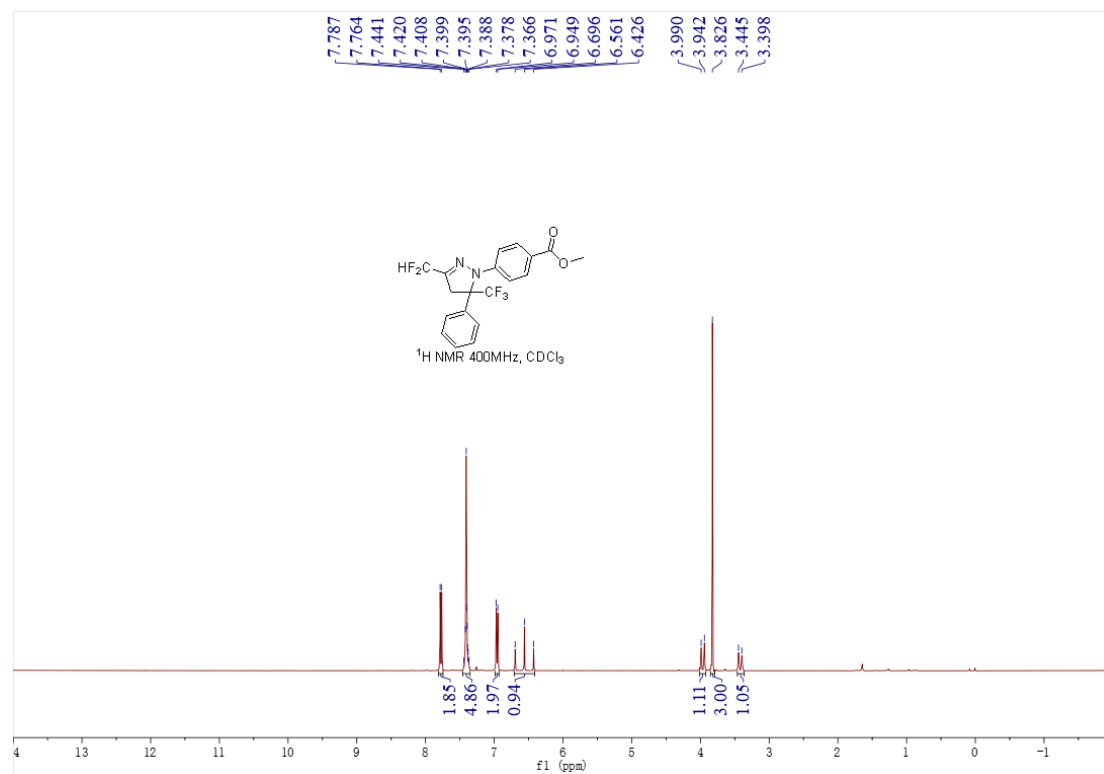


NL:
 1.15E6
 ZHAOSHUJUAN-41#48-90 RT: 0.21-0.40 AV: 43 T: FTMS + p ESI Full lock ms [50.0000-750.0000]

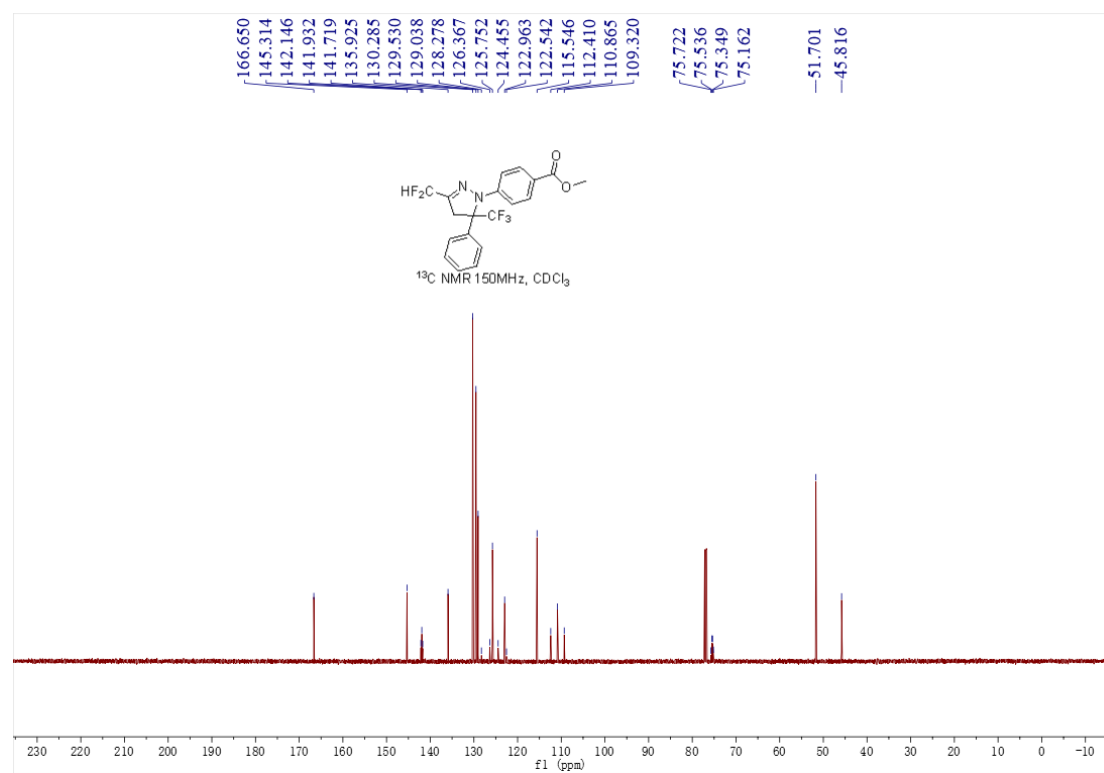
NL:
 4.18E5
 C₁₇H₁₃BrF₅N₂
 C₁₇H₁₃Br₁F₅N₂
 pa Chrg 1

Spectrogram copies of compound **4k**

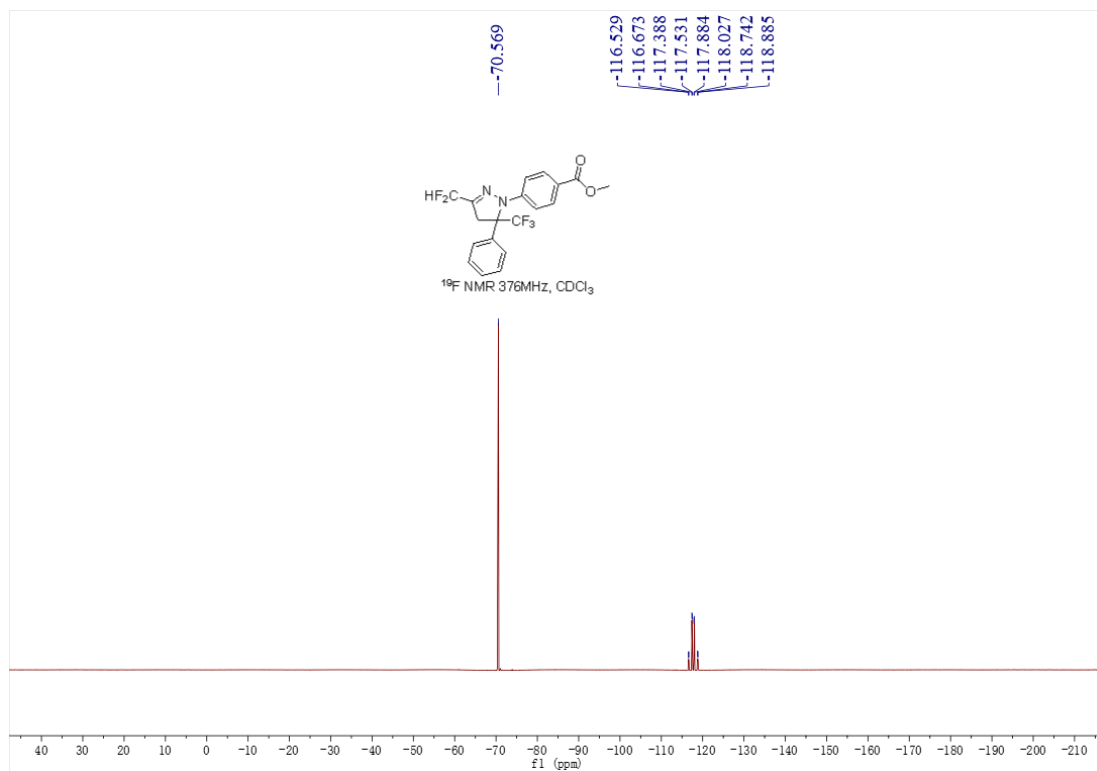
¹H NMR copy of compound **4k**



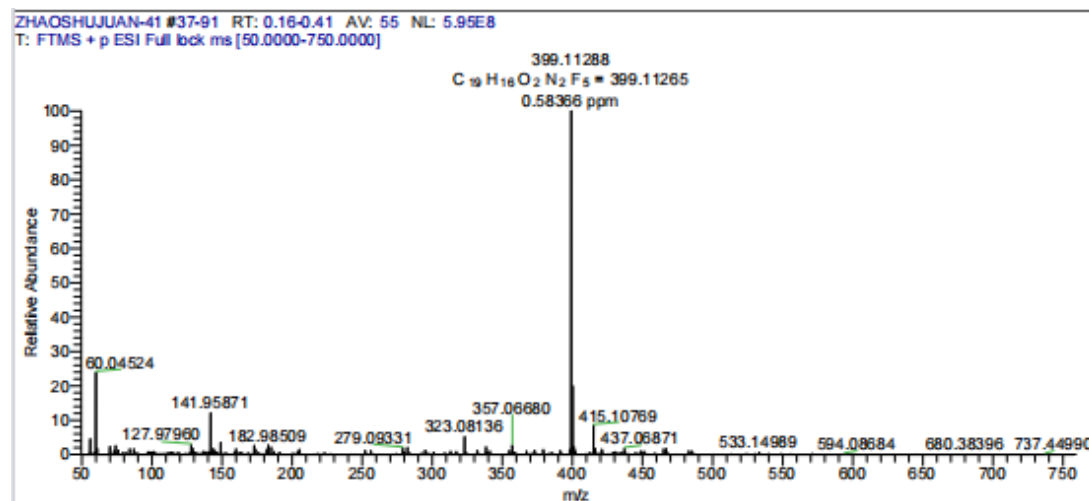
¹³C NMR copy of compound **4k**



¹⁹F NMR copy of compound **4k**

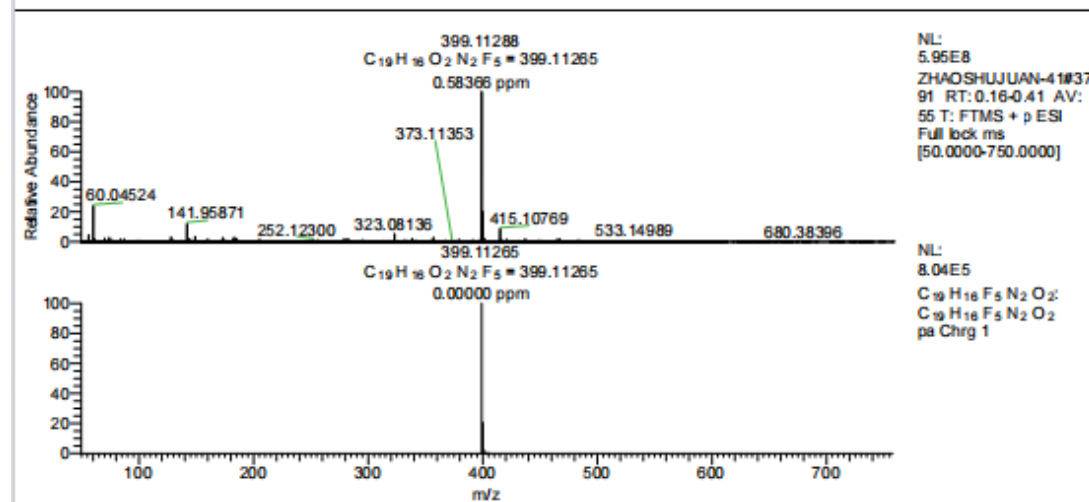


HRMS copy of compound 4k



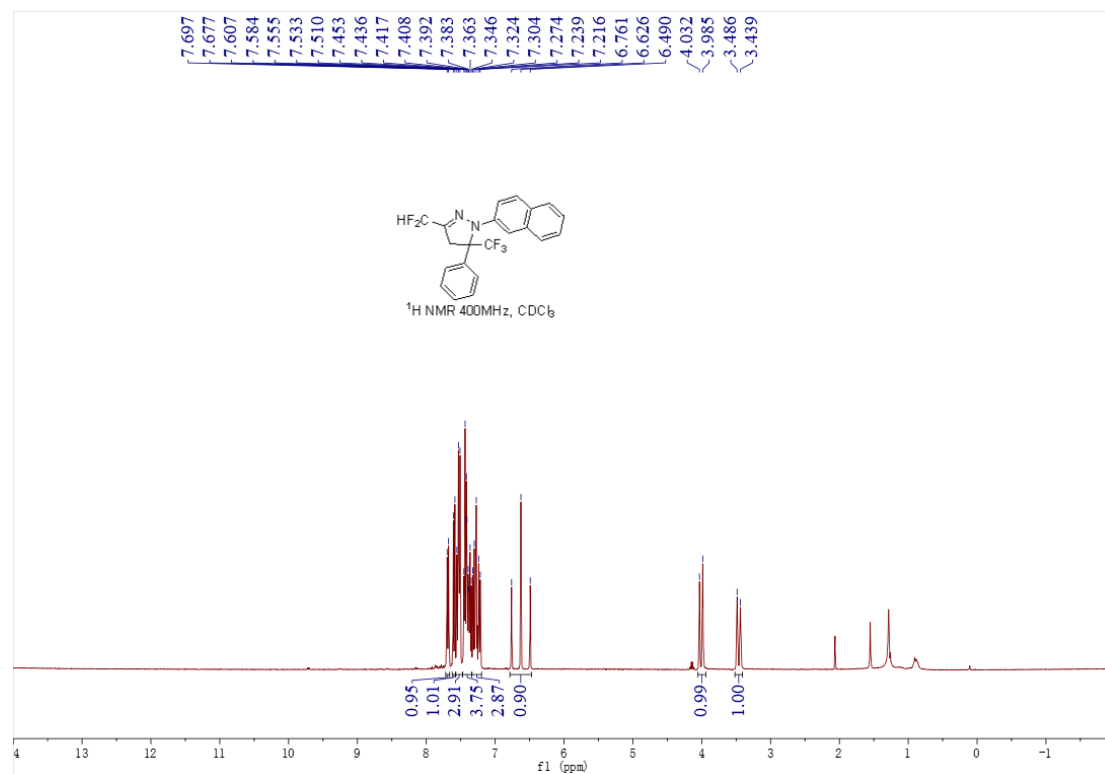
ZHAOSHUJUAN-41#37-91 RT: 0.16-0.41 AV: 55
T: FTMS + p ESI Full lock ms [50.0000-750.0000]

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
60.04524	141937632.0	23.55			
141.95871	72073048.0	11.96			
399.11288	602749760.0	100.00	399.11265	0.23	C ₁₉ H ₁₆ O ₂ N ₂ F ₅
400.11614	121922736.0	20.23			
415.10769	50507616.0	8.38			

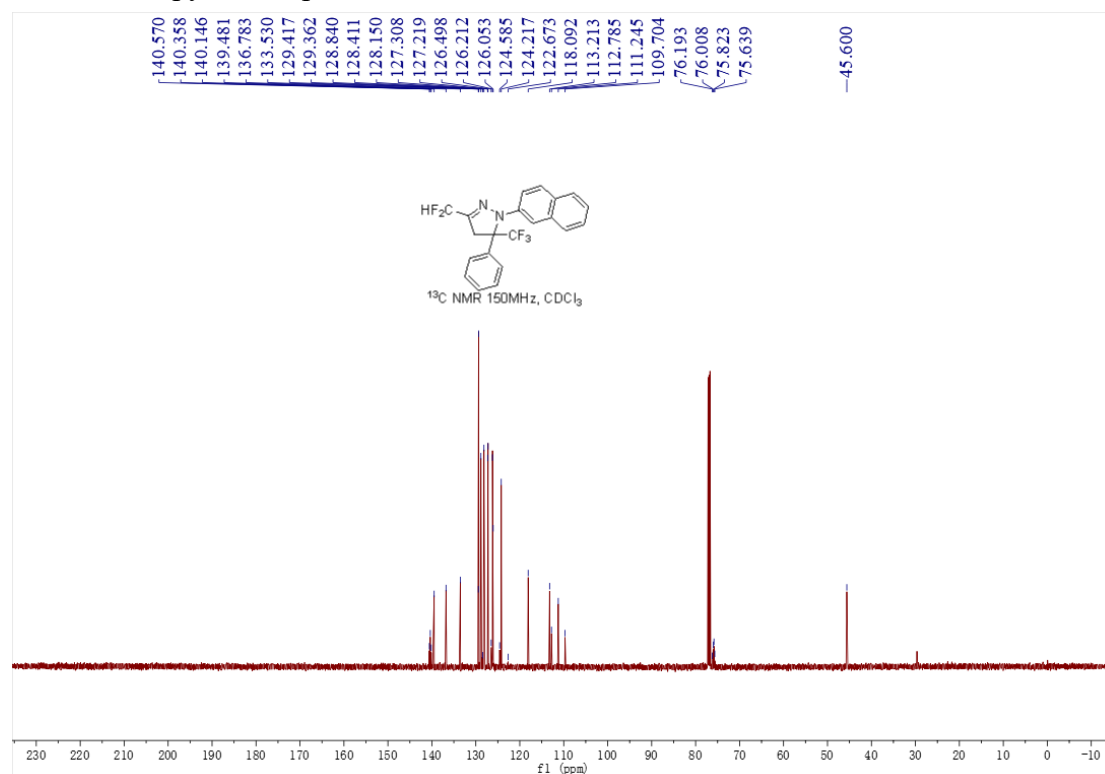


Spectrogram copies of compound **4l**

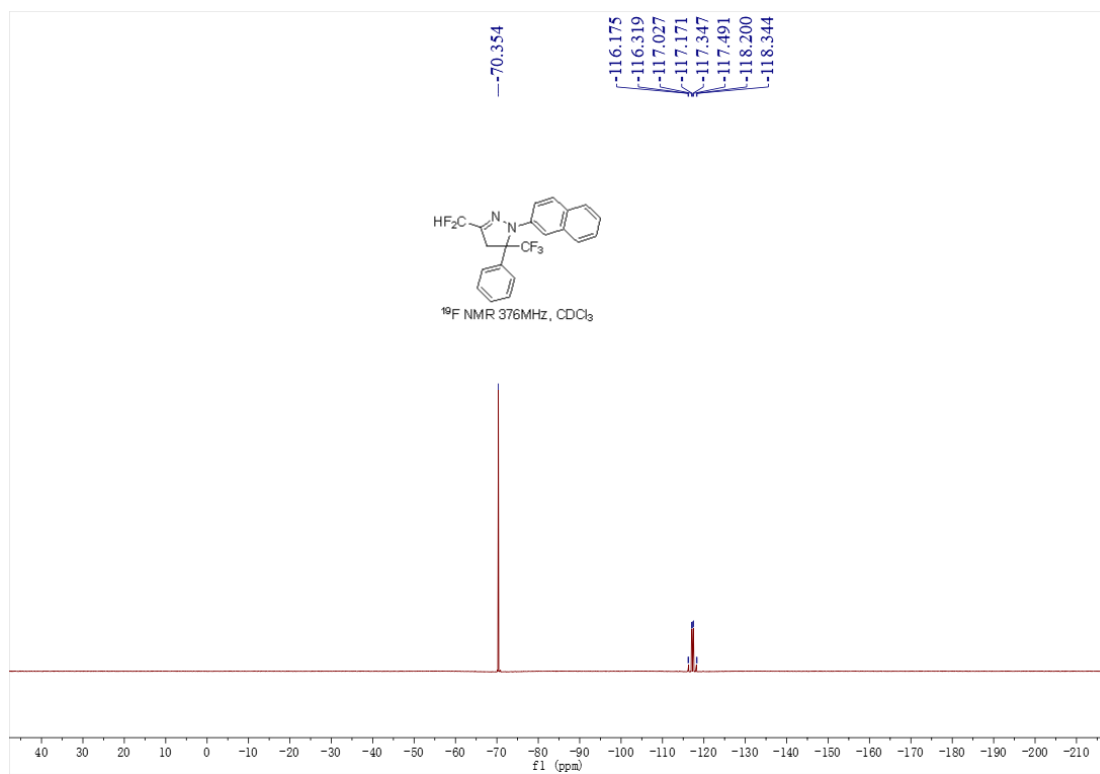
¹H NMR copy of compound **4l**



¹³C NMR copy of compound **4l**

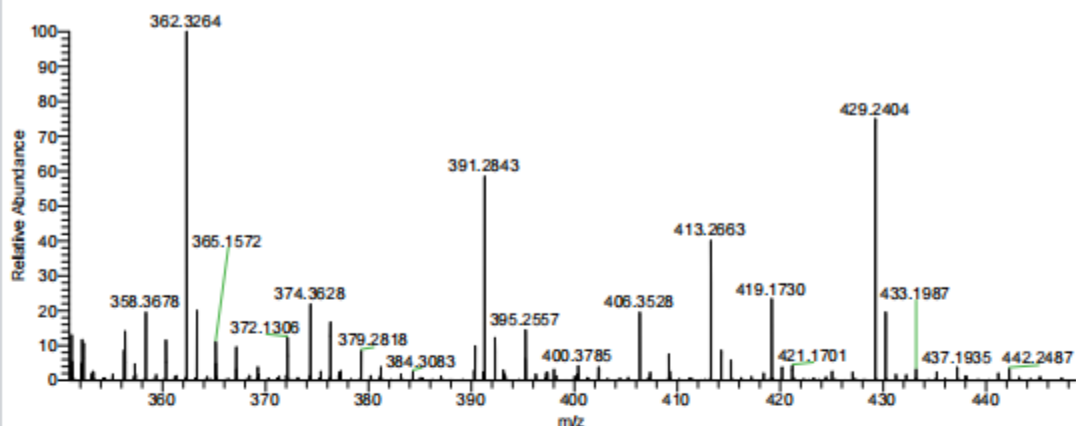


¹⁹F NMR copy of compound **41**



HRMS copy of compound 4l

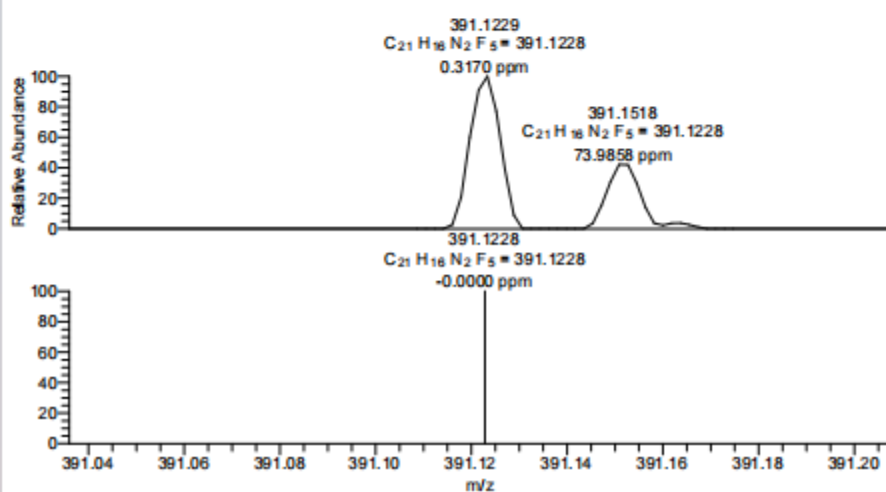
ZHAOSHUJUAN-44#24-68 RT: 0.11-0.30 AV: 45 NL: 2.23E5
T: FTMS + p ESI Full lock ms [50.0000-750.0000]



ZHAOSHUJUAN-44#24-68 RT: 0.11-0.30 AV: 45
T: FTMS + p ESI Full lock ms [50.0000-750.0000]

m/z = 391.0360-391.2080

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
391.1229	5243.9	100.00	391.1228	0.12	C ₂₁ H ₁₆ N ₂ F ₅
391.1518	2262.2	43.14	391.1228	28.94	C ₂₁ H ₁₆ N ₂ F ₅
391.1629	195.8	3.73	391.1228	40.12	C ₂₁ H ₁₆ N ₂ F ₅

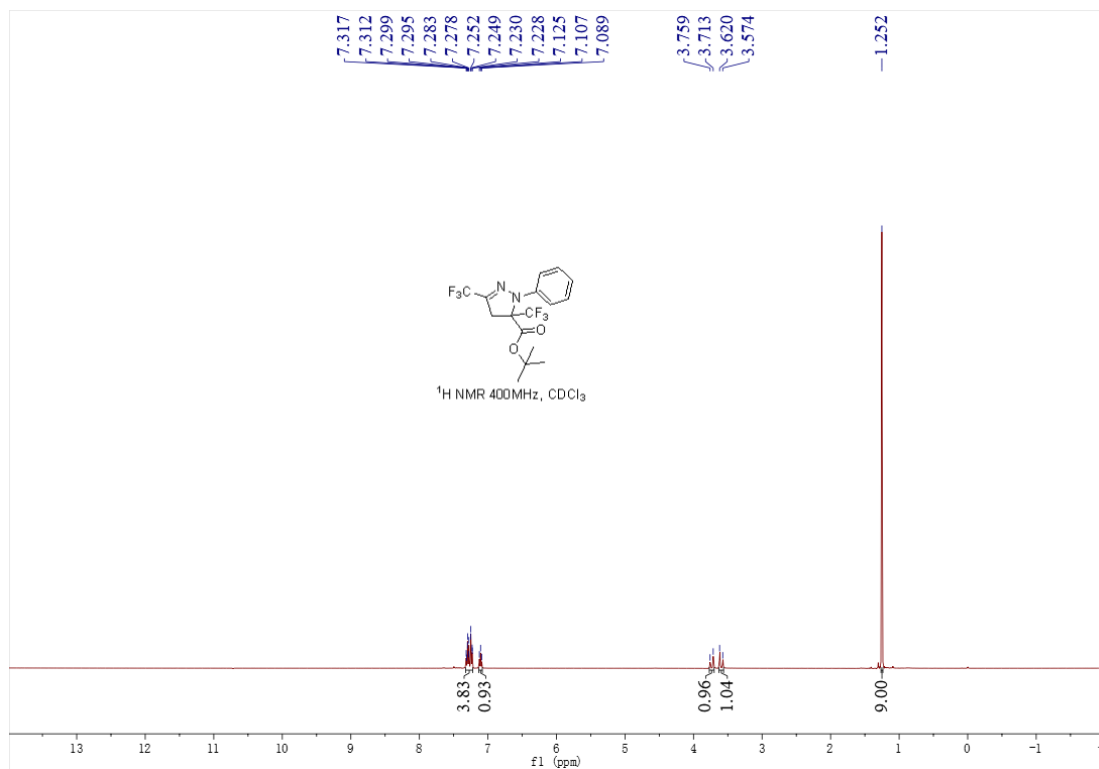


NL:
5.20E3
ZHAOSHUJUAN-44#24-
68 RT: 0.11-0.30 AV:
45 T: FTMS + p ESI
Full lock ms
[50.0000-750.0000]

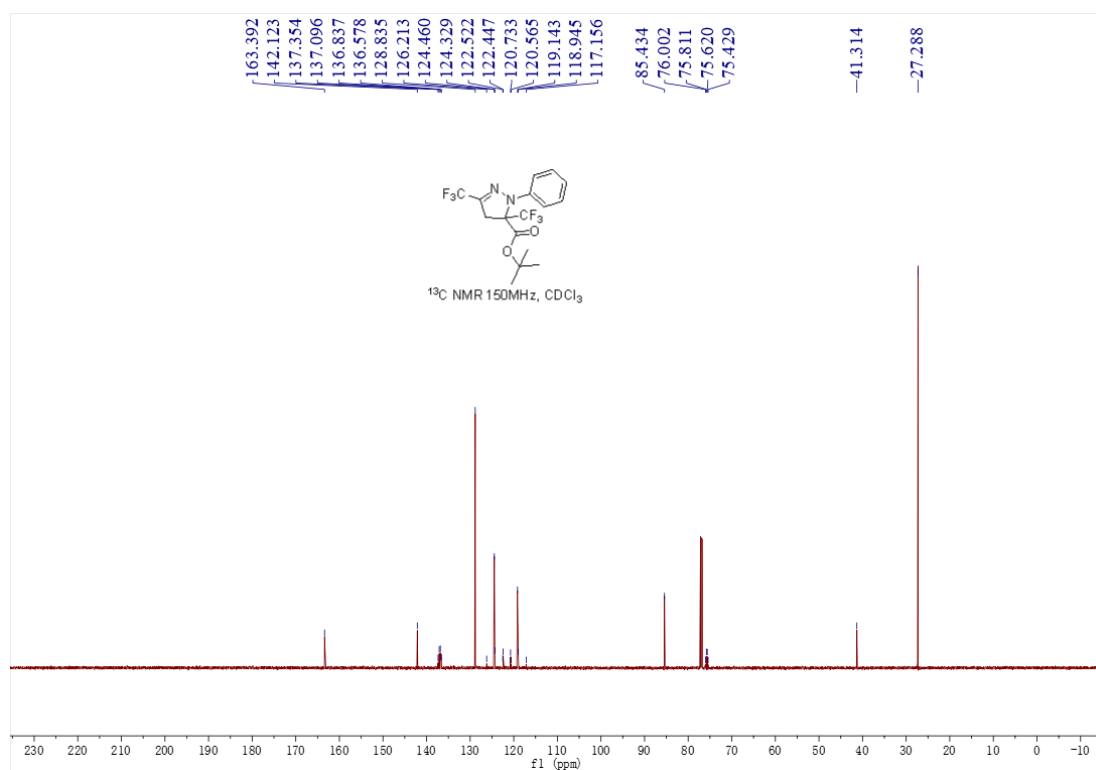
NL:
7.90E5
C₂₁H₁₆F₅N₂:
C₂₁H₁₆F₅N₂
pa Chrg 1

Spectrogram copies of compound **4a'**

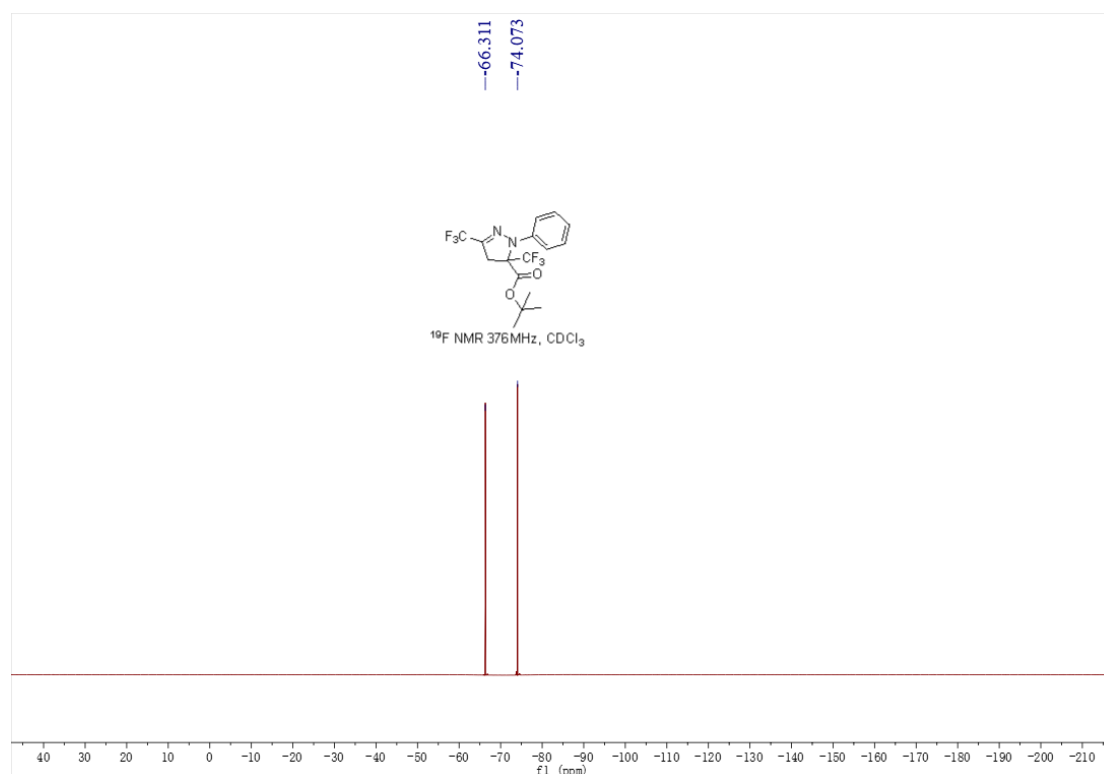
^1H NMR copy of compound **4a'**



^{13}C NMR copy of compound **4a'**



¹⁹F NMR copy of compound **4a'**

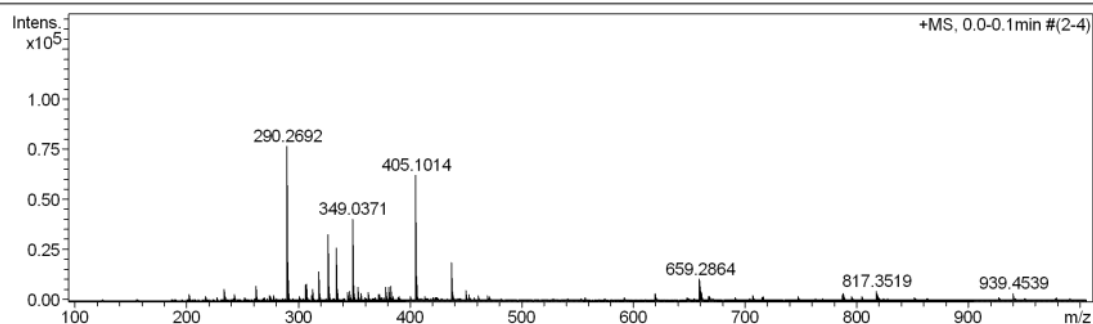


HRMS copy of compound **4a'**

Mass Spectrum SmartFormula Report

Analysis Info		Acquisition Date	2024-2-5 10:31:42
Analysis Name	D:\Data\user\NWNWU-wangruikang 20240205-32.d	Operator	Huyue
Method	tune_low.m	Instrument / Ser#	micrOTOF-Q 20453
Sample Name	32		
Comment			

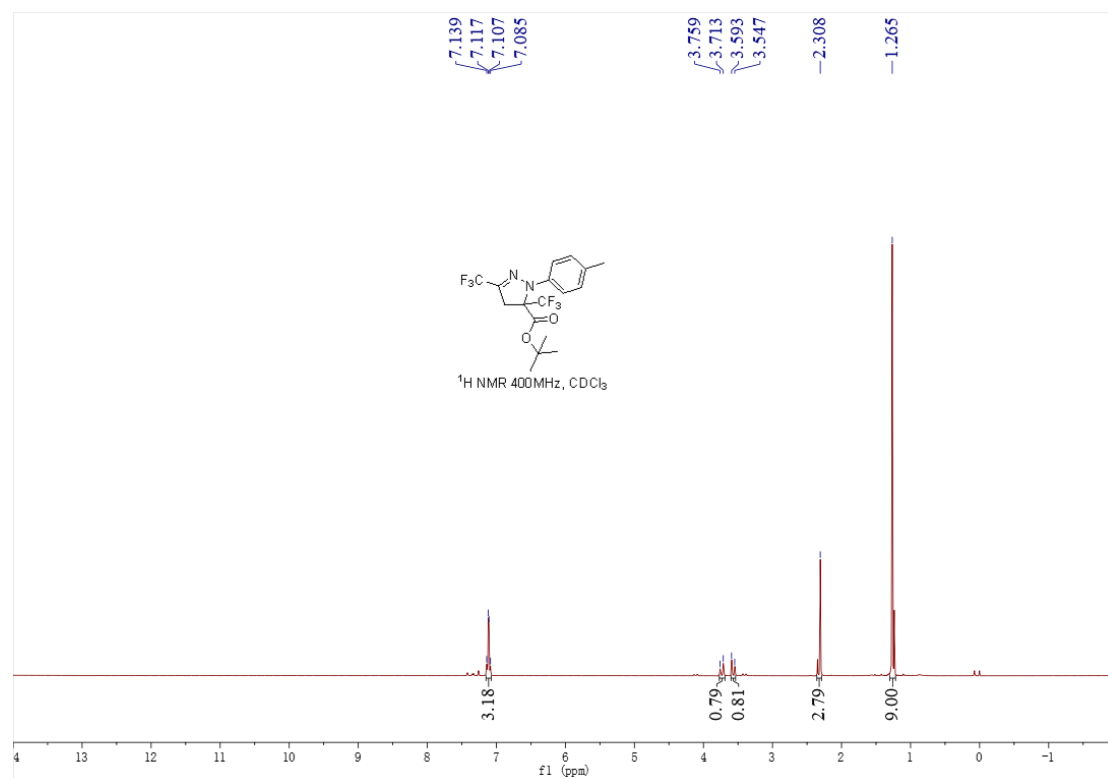
Acquisition Parameter		Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Source Type	ESI	Set Capillary	4500 V	Set Dry Heater	180 j°C
Focus	Active	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan Begin	100 m/z	Set Collision Cell RF	400.0 Vpp	Set Divert Valve	Waste
Scan End	1000 m/z				



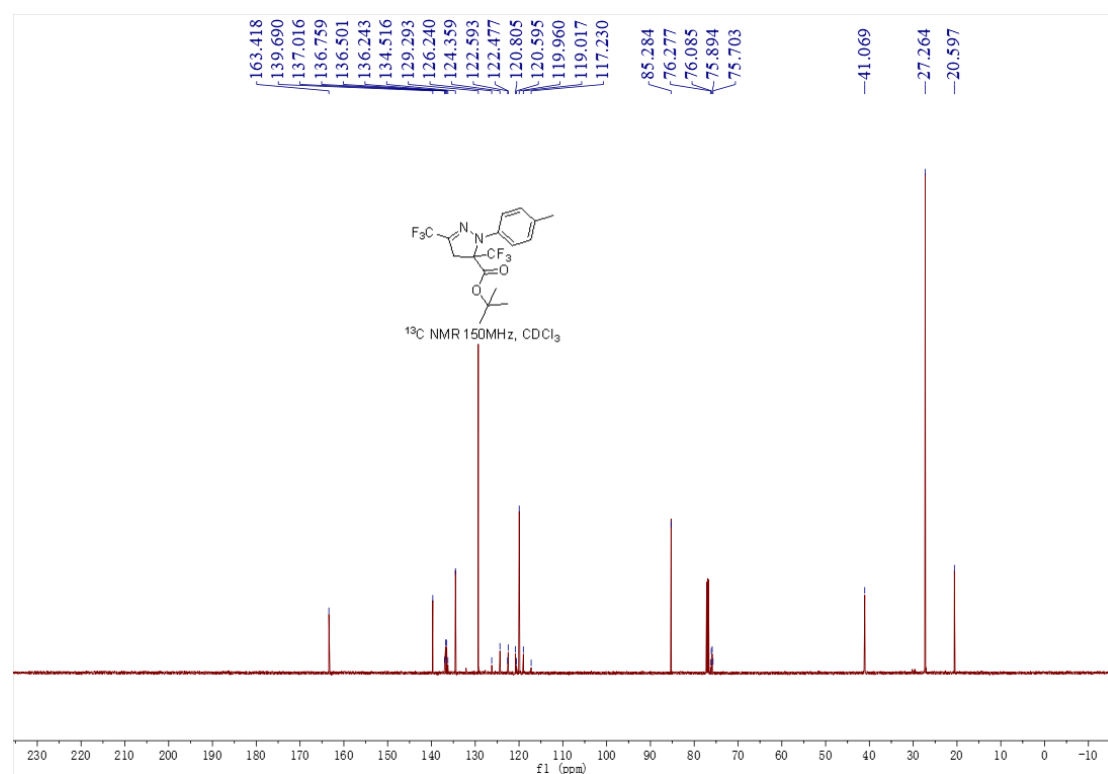
Meas. #	Formula	m/z	err [ppm]	Me an err [ppm]	rd b	N- R ul f e	e j % Con	mSi gm a	Std l	St d Me an m/ z	Std Var m Nor m Dif	Std l m/ z	Std d f	Std Com b Dev
405.1014	1 C ₁₆ H ₁₆ F ₆ N ₂ NaO ₂	405.1008	-1.4	-0.9	6.5	ok	even	13.7	21.3	0.5	14.6	1.1	842.7	

Spectrogram copies of compound **4b'**

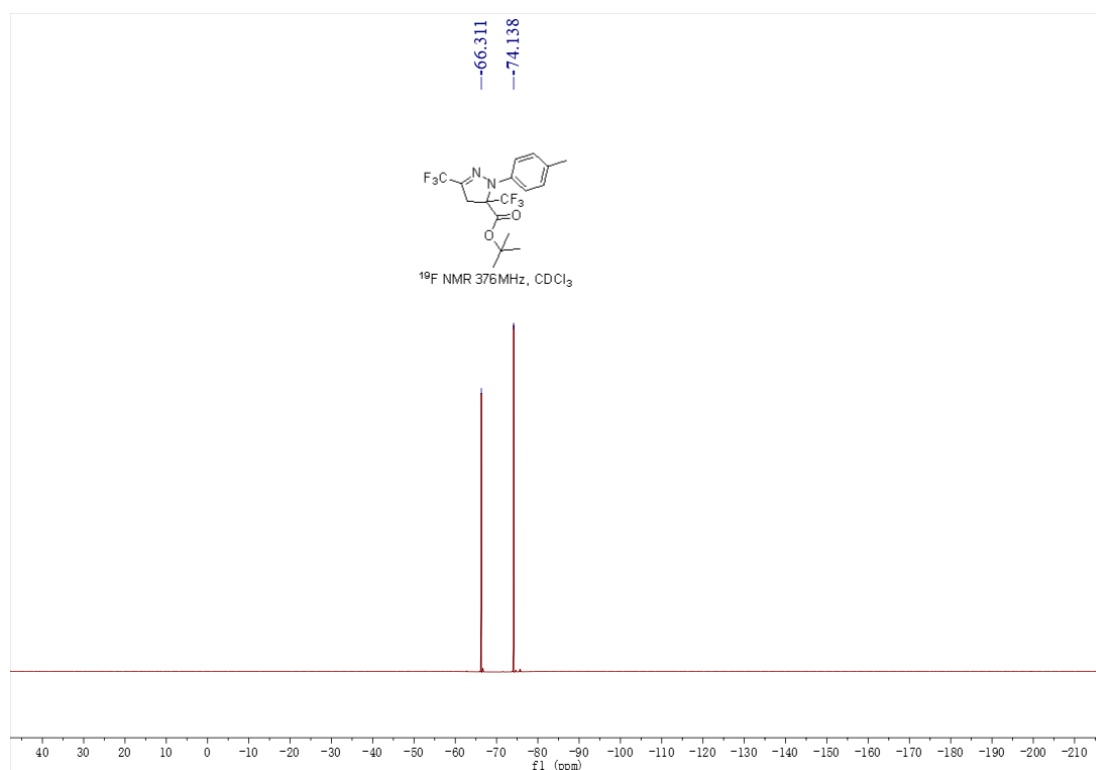
^1H NMR copy of compound **4b'**



^{13}C NMR copy of compound **4b'**



¹⁹F NMR copy of compound **4b'**

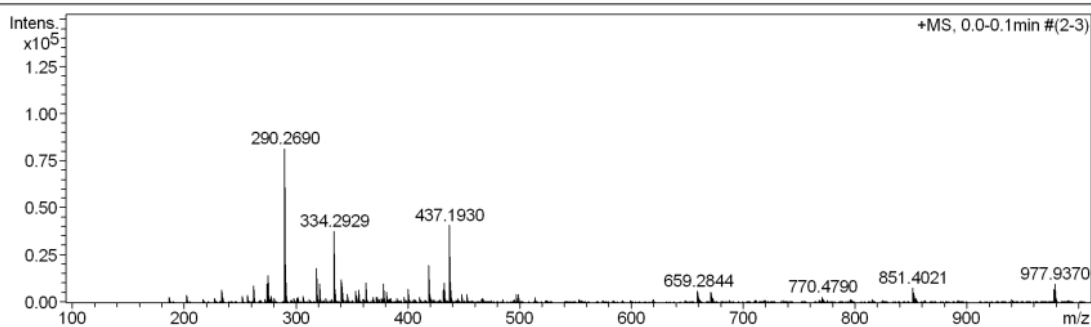


HRMS copy of compound **4b'**

Mass Spectrum SmartFormula Report

Analysis Info		Acquisition Date
Analysis Name	D:\Data\user\NWNWU-wangruikang 20240205-30.d	2024-2-5 10:29:09
Method	tune_low.m	Operator Huyue
Sample Name	30	Instrument / Ser# micrOTOF-Q 20453
Comment		

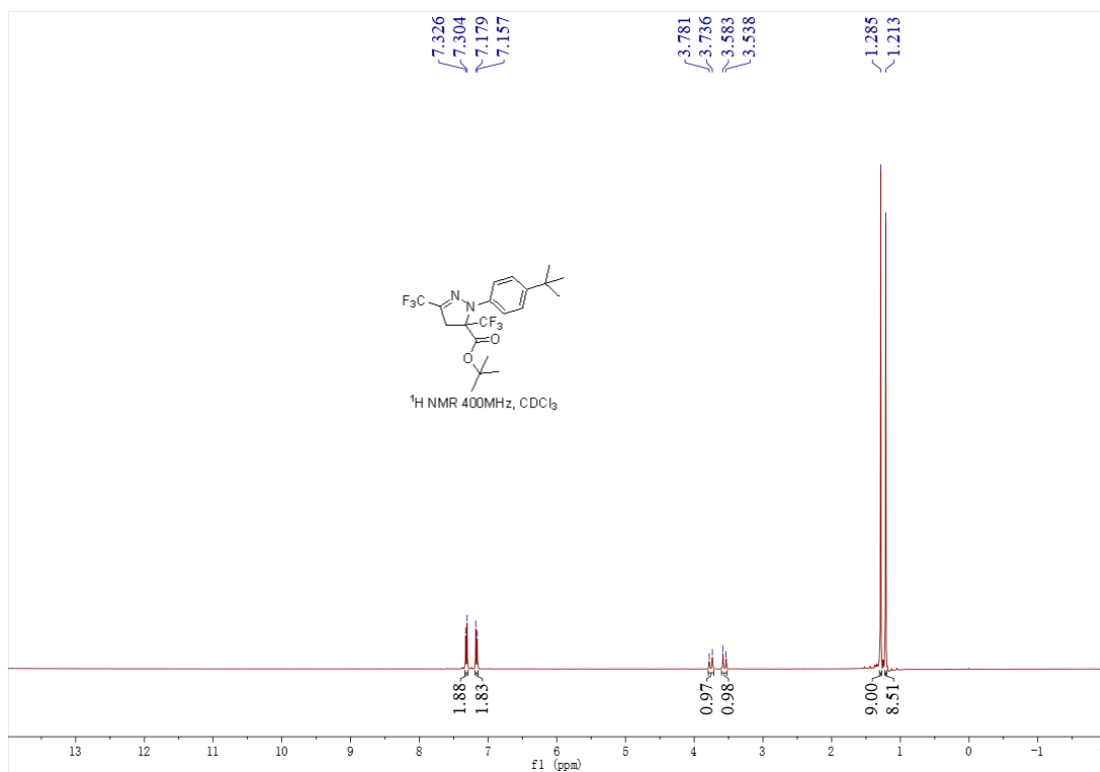
Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 j̄C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	400.0 Vpp	Set Divert Valve	Waste



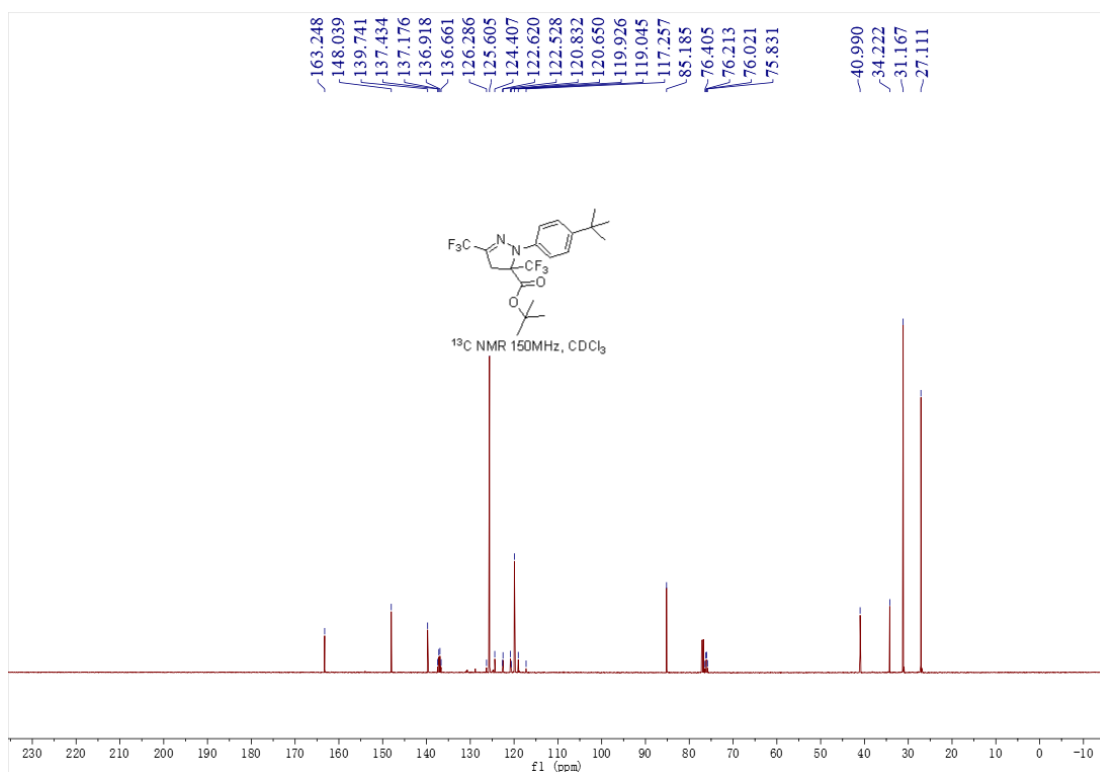
Meas. #	Formula	m/z	err [ppm]	Me an err [ppm]	rd b	N- R ul f e	e j % Con	mSi gm a	Std l	St d Me an m/z	Std Var Nor m	St d m/ Dif f	Std Com b Dev
419.1168	1 C ₁₇ H ₁₈ F ₆ N ₂ NaO ₂	419.1165	-0.9	-0.3	6.5	ok	even	32.6	53.1	0.5	24.9	1.2	842.7

Spectrogram copies of compound **4c'**

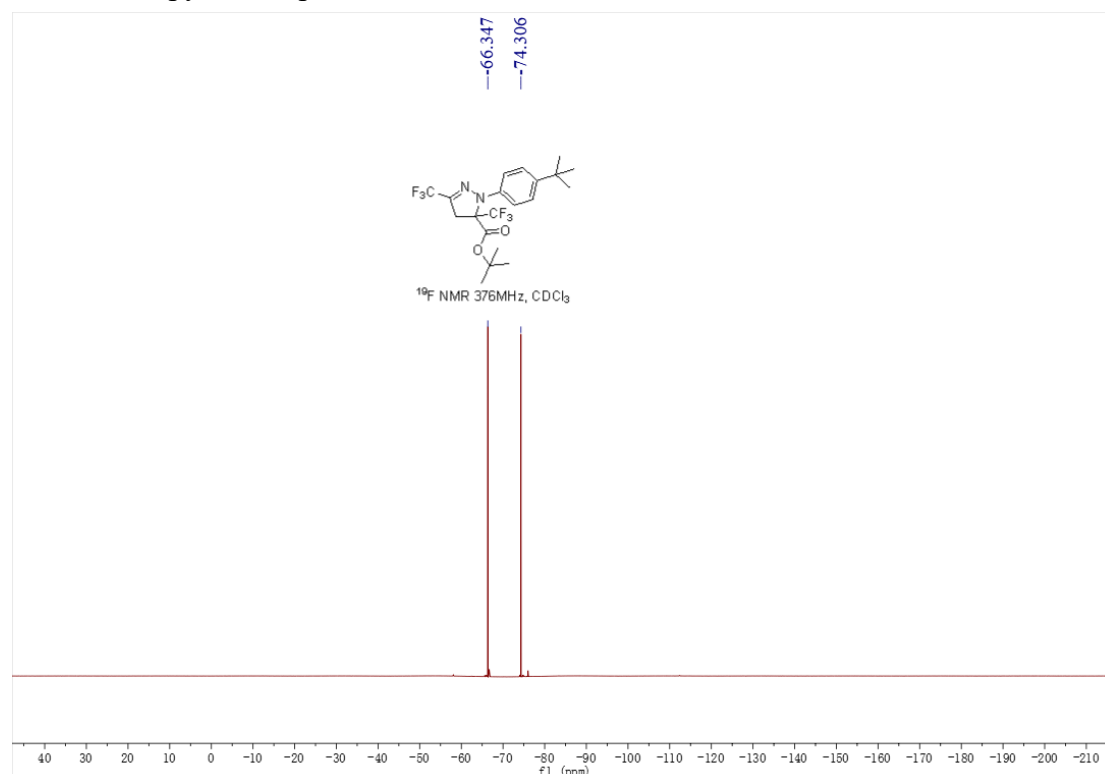
^1H NMR copy of compound **4c'**



^{13}C NMR copy of compound **4c'**



¹⁹F NMR copy of compound **4c'**



HRMS copy of compound **4c'**

Mass Spectrum SmartFormula Report

Analysis Info

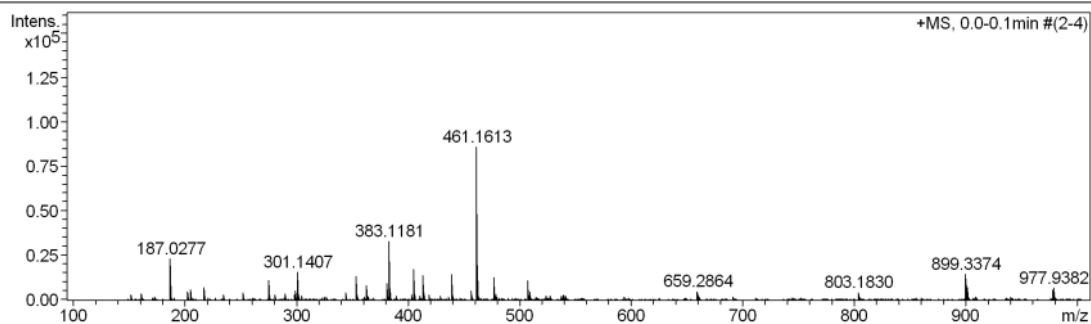
Analysis Name D:\Data\user\NWNWU-wangruikang 20240205-21.d
 Method tune_low.m
 Sample Name 21
 Comment

Acquisition Date 2024-2-5 10:14:12

Operator Huyue
 Instrument / Ser# micrOTOF-Q 20453

Acquisition Parameter

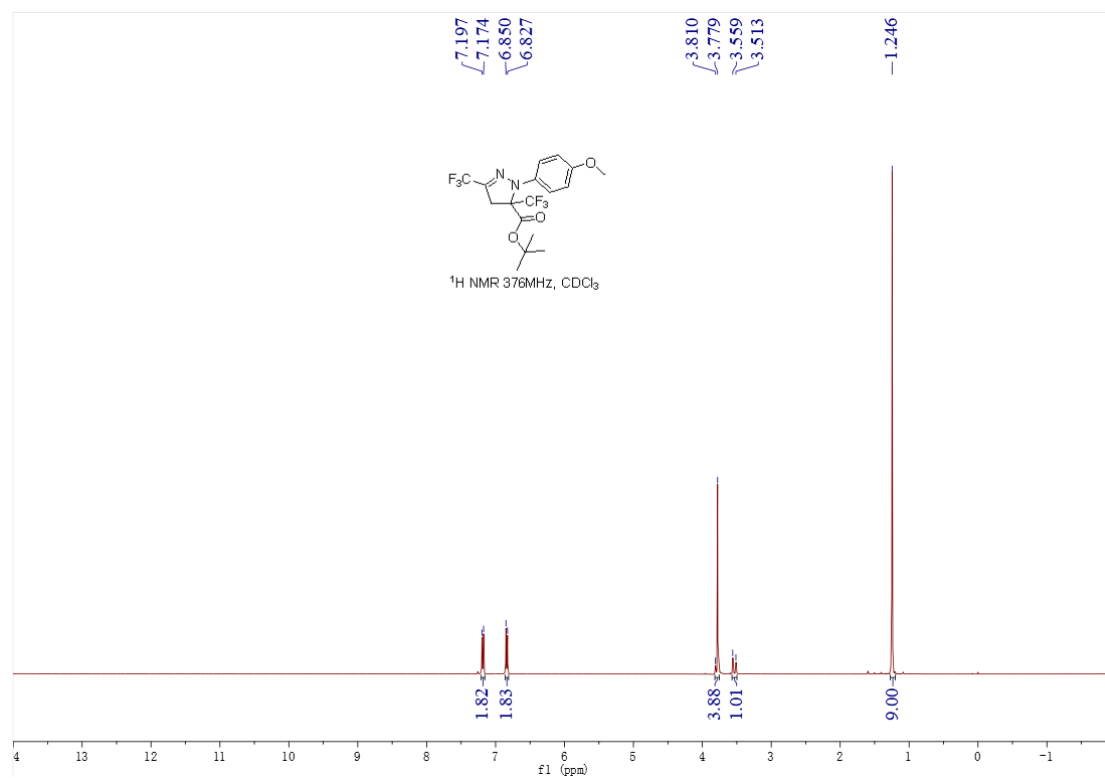
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 j°C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste



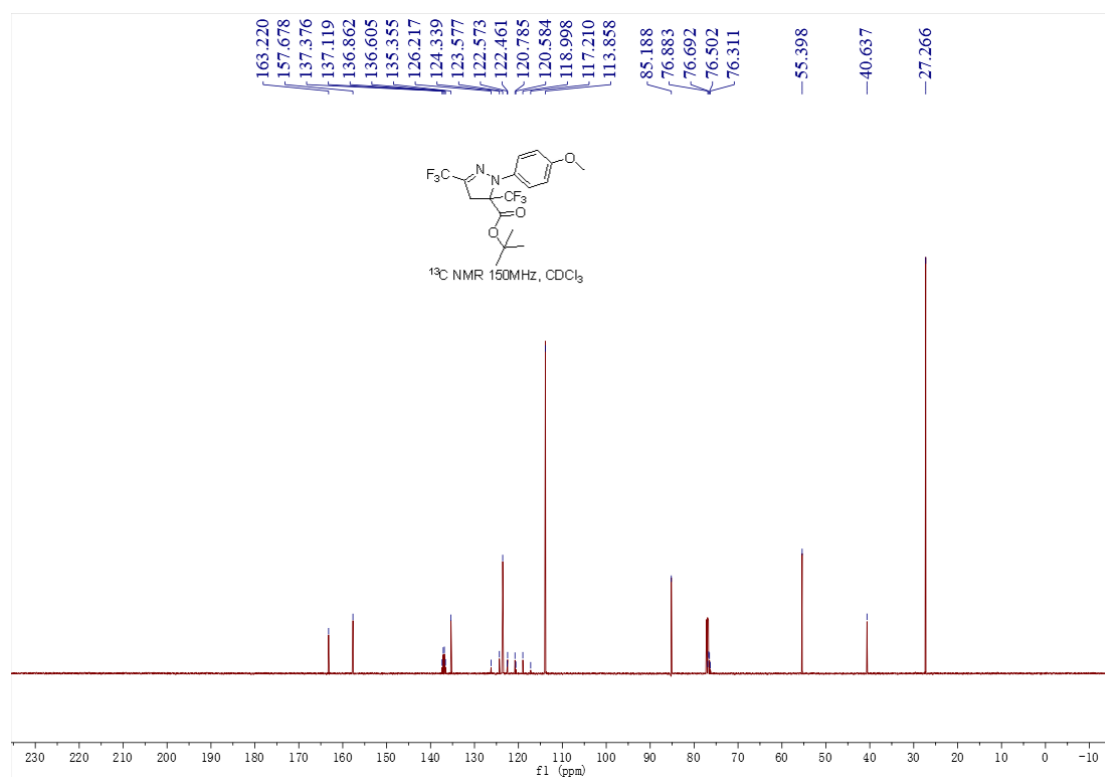
Meas. #	m/z	Formula	m/z	err [ppm]	Me an err [ppm]	rdb	N-R	ej% Conf	mS	Std	Std	Std	Std	Std
461.1613	1	C ₂₀ H ₂₄ F ₆ N ₂ NaO ₂	461.1634	4.6	3.5	6.5	ok	even	2.7	4.6	2.0	1.9	2.0	842.7

Spectrogram copies of compound **4d'**

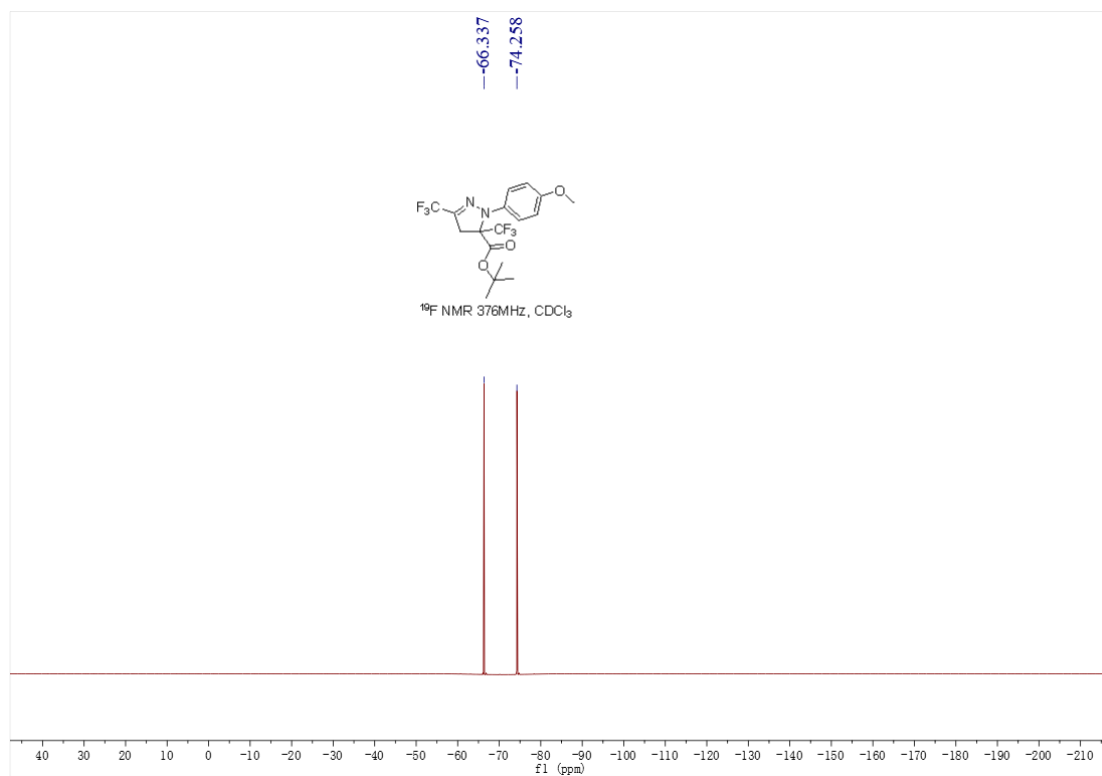
^1H NMR copy of compound **4d'**



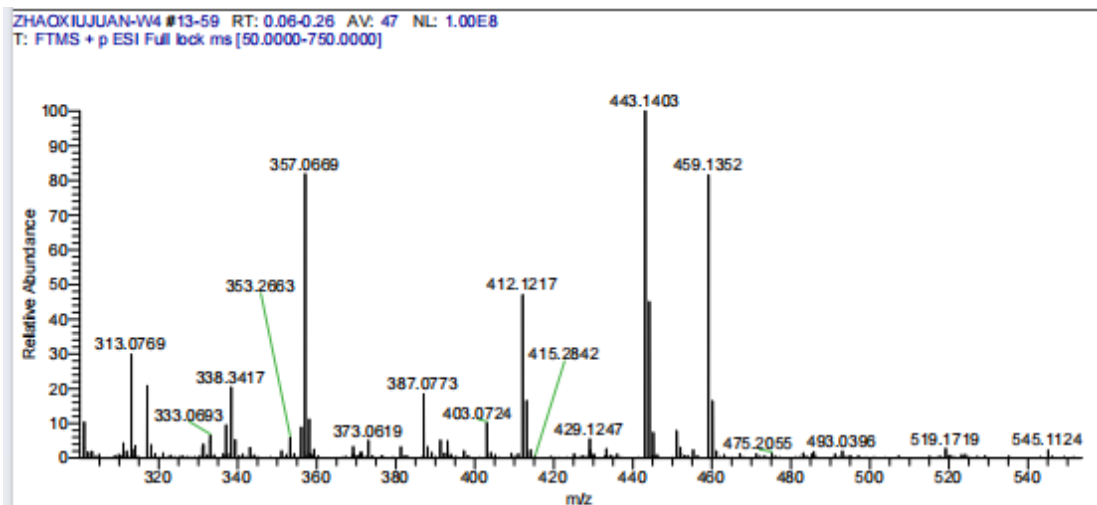
^{13}C NMR copy of compound **4d'**



¹⁹F NMR copy of compound **4d'**

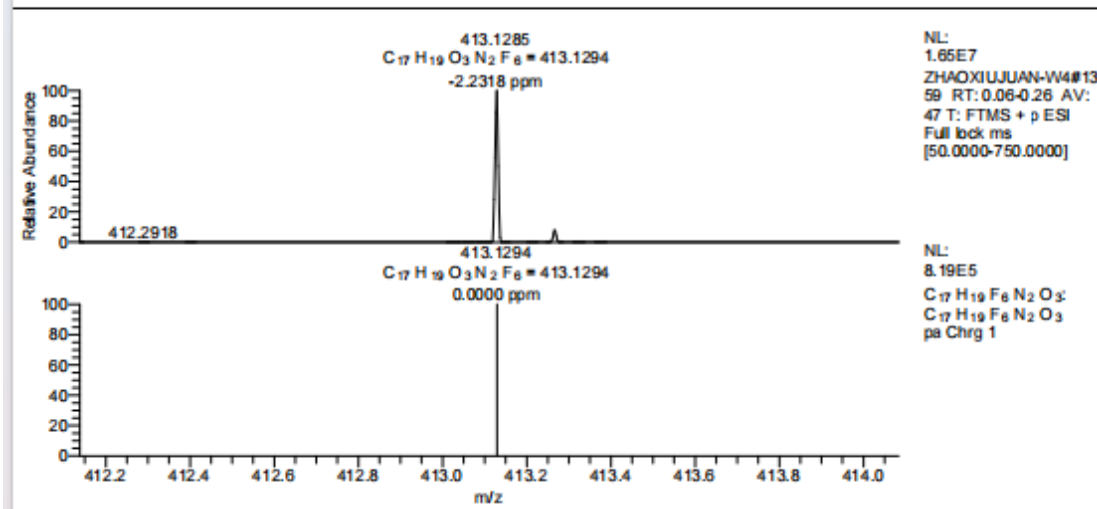


HRMS copy of compound **4d'**



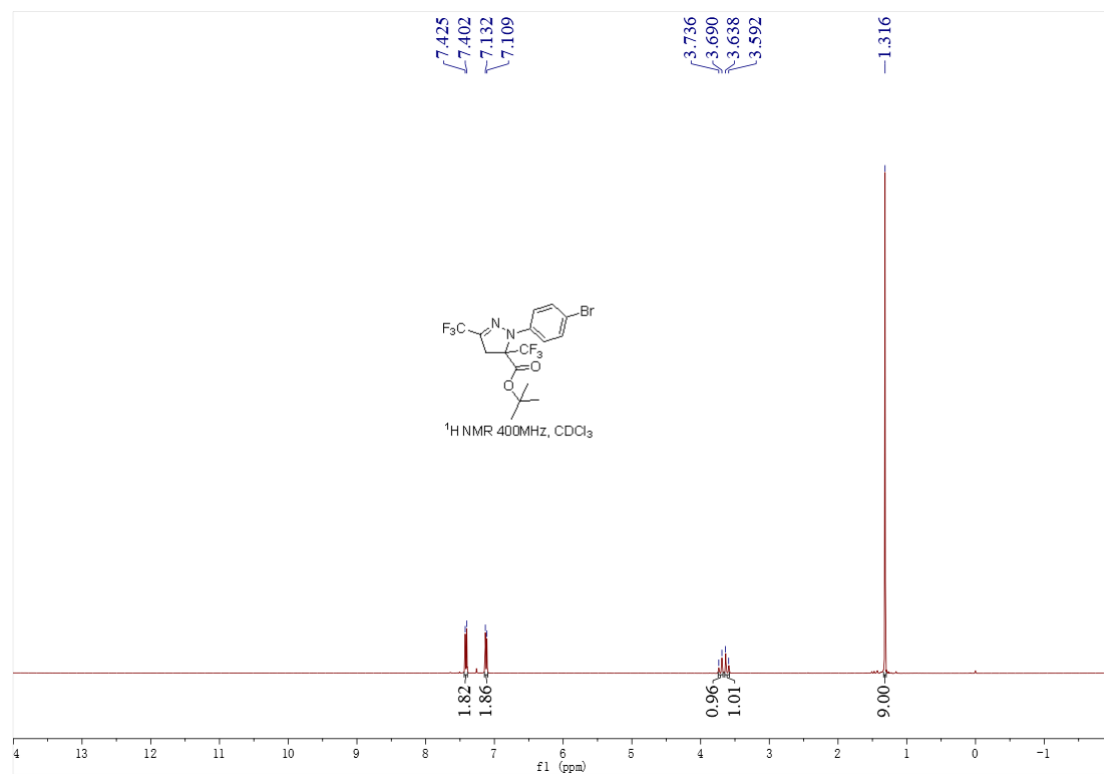
ZHAOXIUJUAN-W4#13-59 RT: 0.06-0.26 AV: 47
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 412.1380-414.0835

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
413.0257	7711.2	0.05	413.1294	-103.69	C ₁₇ H ₁₉ O ₃ N ₂ F ₆
413.0607	5299.9	0.03	413.1294	-68.72	C ₁₇ H ₁₉ O ₃ N ₂ F ₆
413.1285	16494018.0	100.00	413.1294	-0.92	C ₁₇ H ₁₉ O ₃ N ₂ F ₆
413.1474	11668.0	0.07	413.1294	17.96	C ₁₇ H ₁₉ O ₃ N ₂ F ₆
413.2664	1316181.3	7.98	413.1294	136.94	C ₁₇ H ₁₉ O ₃ N ₂ F ₆

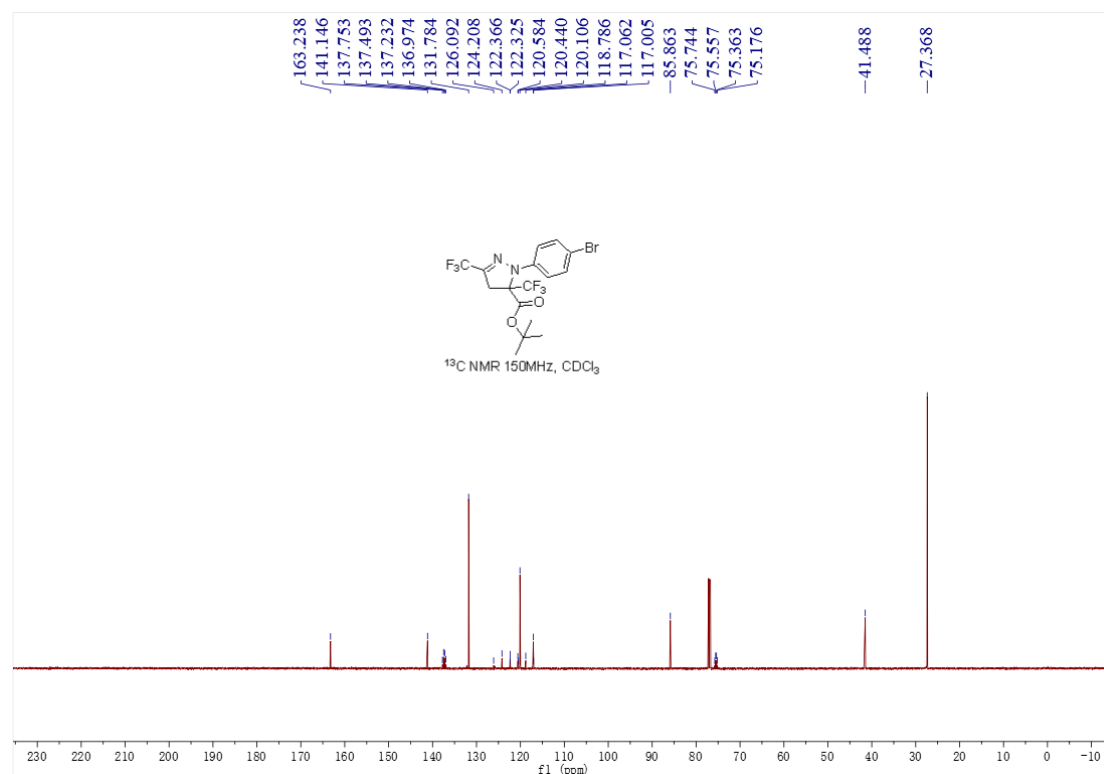


Spectrogram copies of compound **4e'**

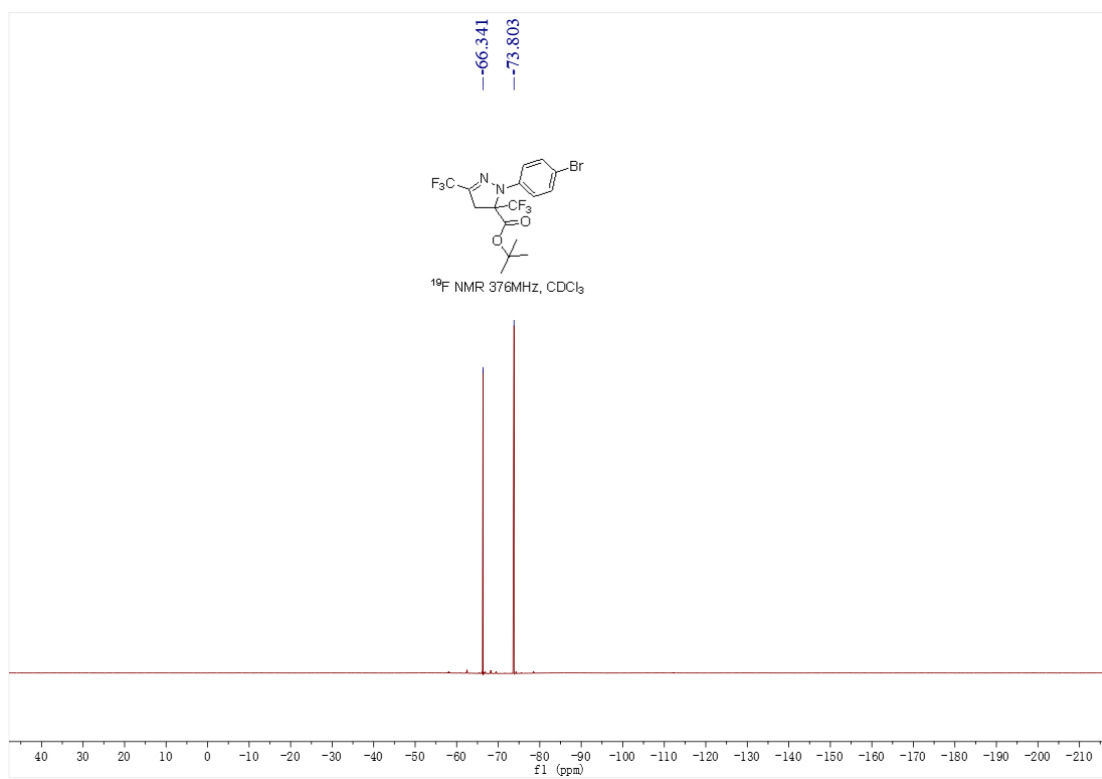
^1H NMR copy of compound **4e'**



^{13}C NMR copy of compound **4e'**

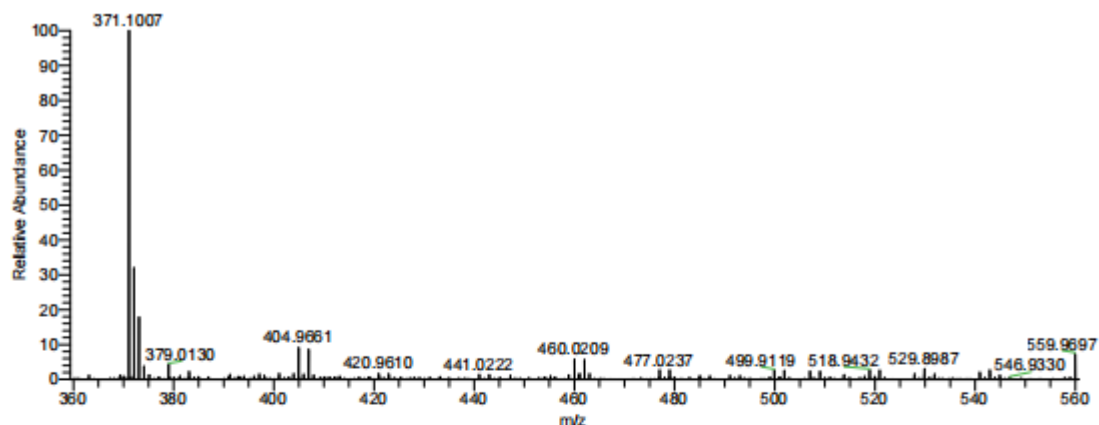


¹⁹F NMR copy of compound 4e'



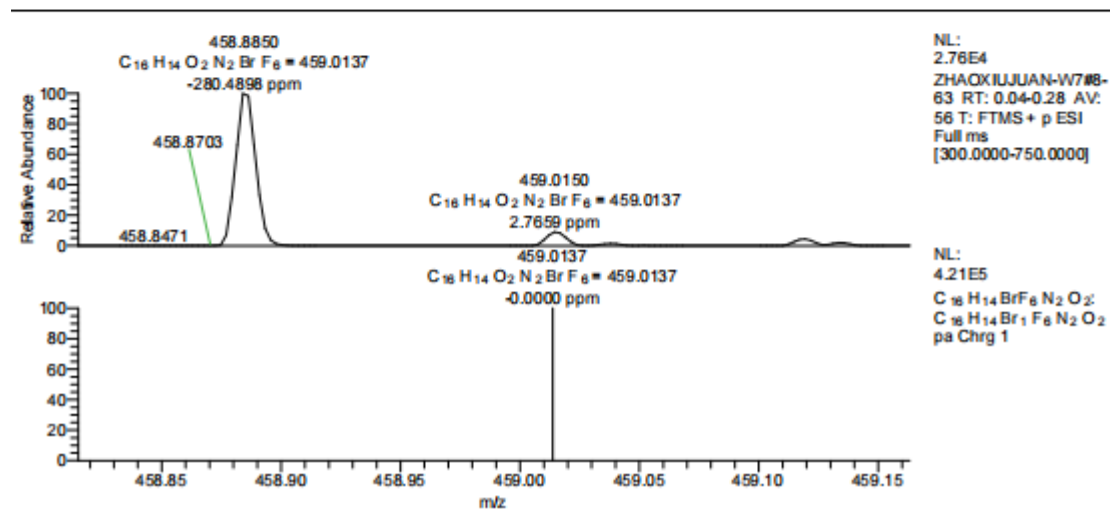
HRMS copy of compound 4e'

ZHAOXIUJUAN-W7#8-63 RT: 0.04-0.28 AV: 56 NL: 2.28E6
 T: FTMS + p ESI Full ms [300.0000-750.0000]



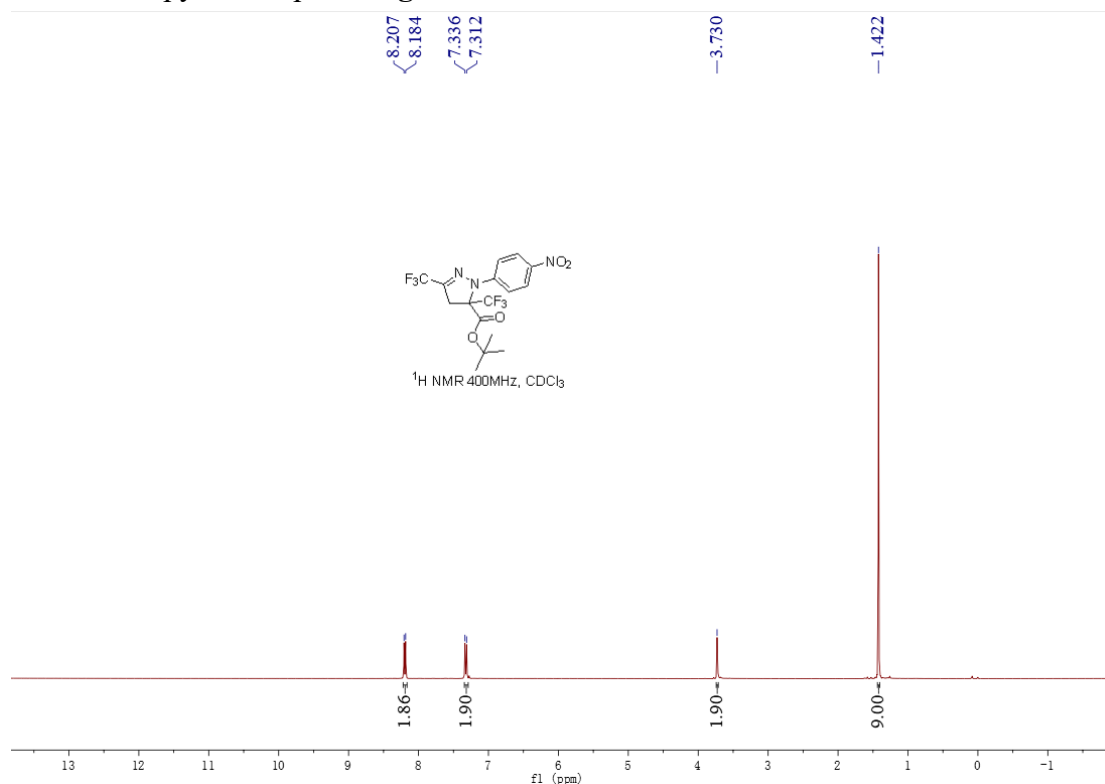
ZHAOXIUJUAN-W7#8-63 RT: 0.04-0.28 AV: 56
 T: FTMS + p ESI Full ms [300.0000-750.0000]
 m/z = 458.8151-459.1631

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
458.8850	28625.3	100.00	459.0137	-128.71	C ₁₆ H ₁₄ O ₂ N ₂ BrF ₆
459.0150	2516.9	8.79	459.0137	1.27	C ₁₆ H ₁₄ O ₂ N ₂ BrF ₆
459.0380	375.5	1.31	459.0137	24.30	C ₁₆ H ₁₄ O ₂ N ₂ BrF ₆
459.1190	1214.9	4.24	459.0137	105.24	C ₁₆ H ₁₄ O ₂ N ₂ BrF ₆
459.1341	557.4	1.95	459.0137	120.36	C ₁₆ H ₁₄ O ₂ N ₂ BrF ₆

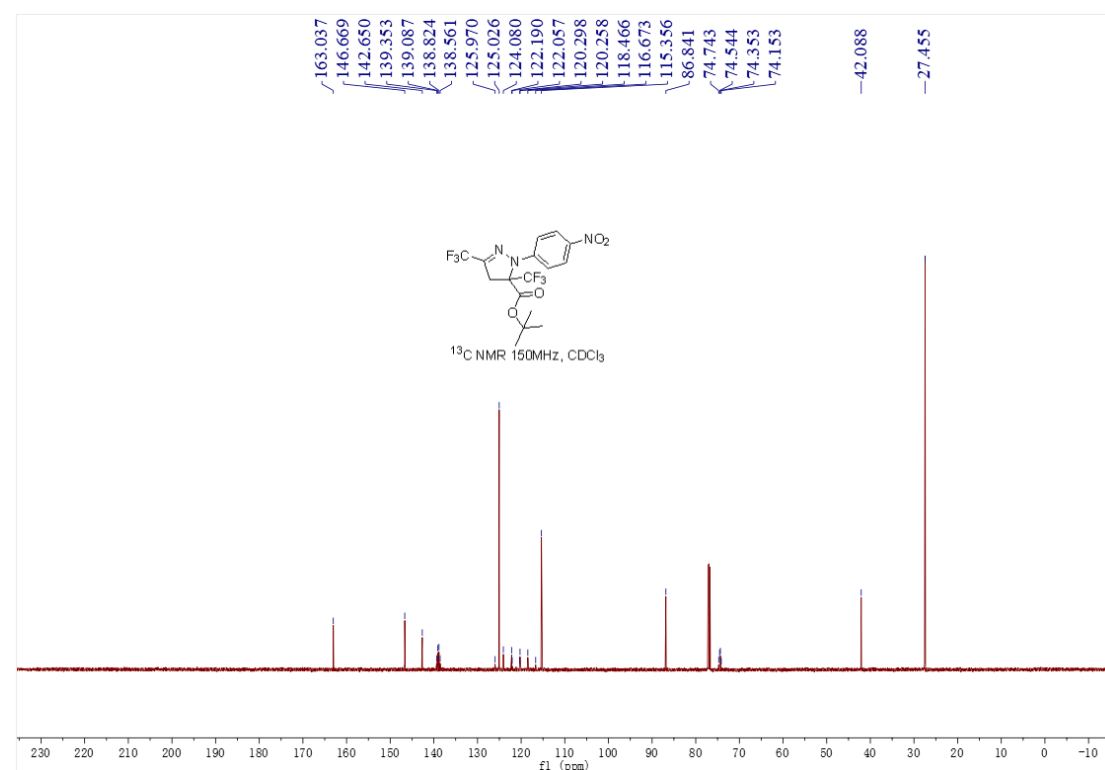


Spectrogram copies of compound **4g'**

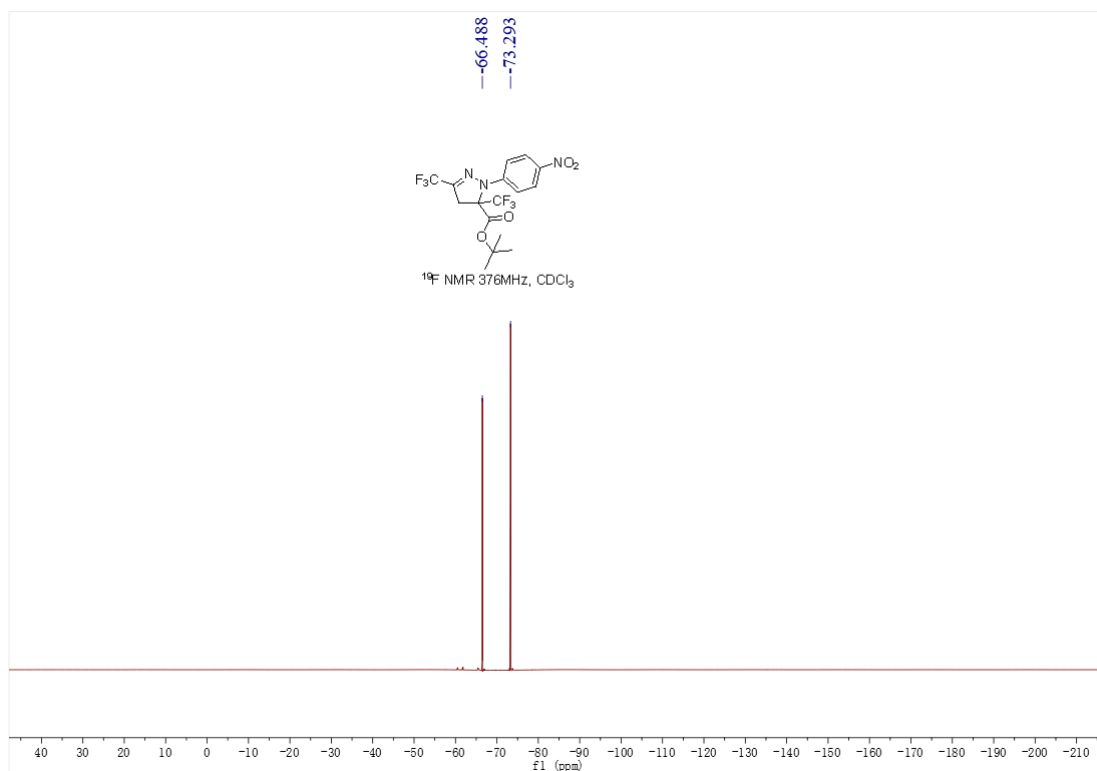
¹H NMR copy of compound **4g'**



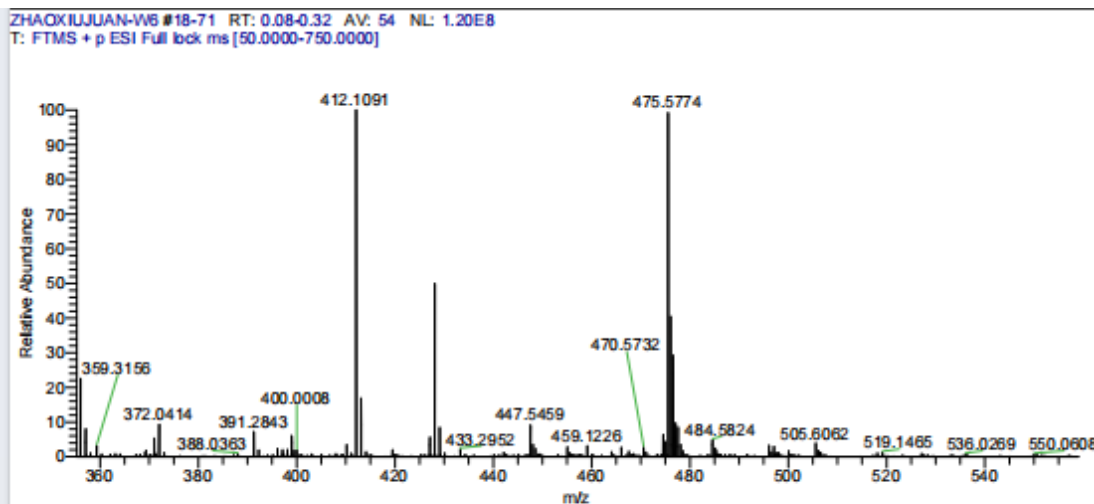
¹³C NMR copy of compound **4g'**



¹⁹F NMR copy of compound **4g'**

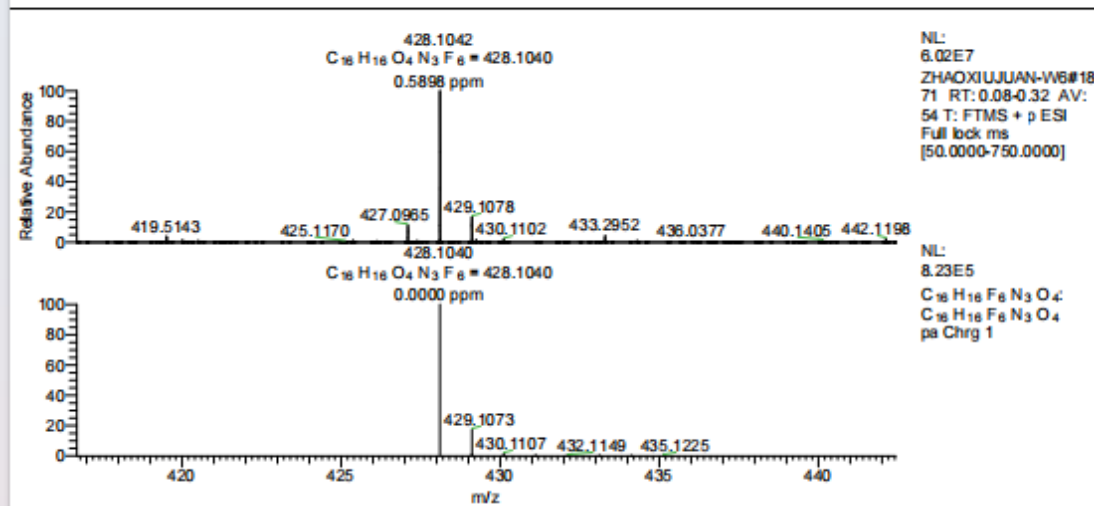


HRMS copy of compound 4g'



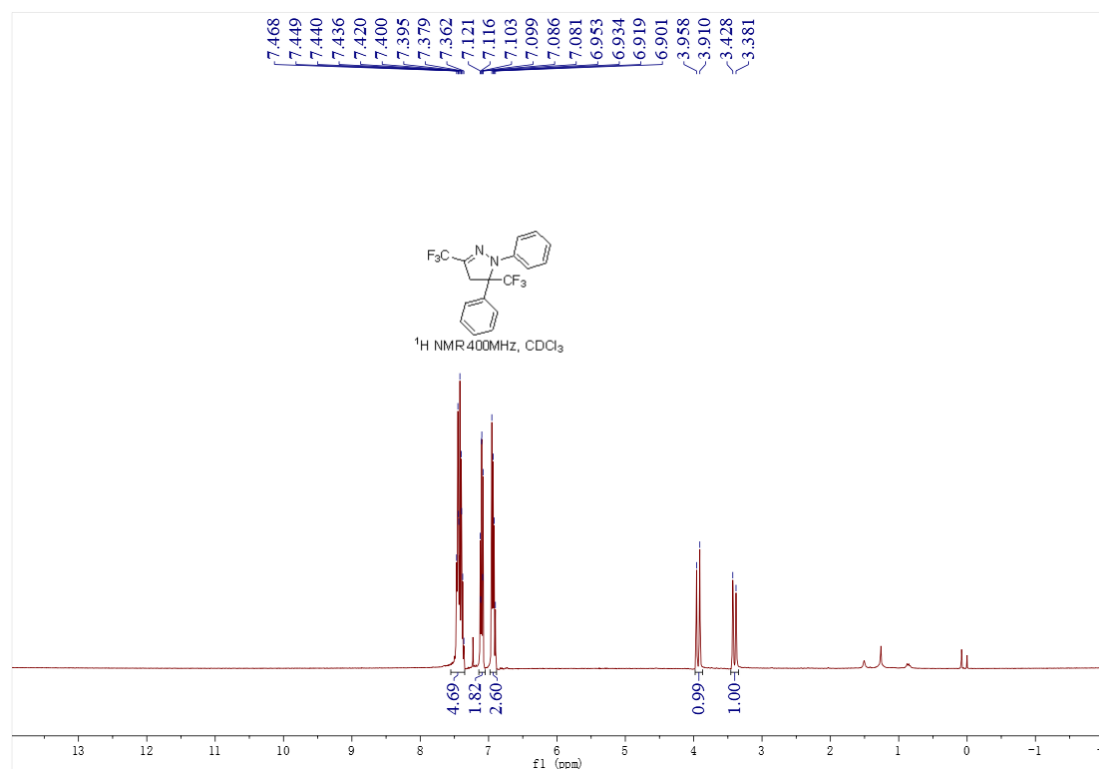
ZHAOXIUJUAN-W6#18-71 RT: 0.08-0.32 AV: 54
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z = 416.6898-442.4248

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
419.5143	2368459.0	3.85			
427.0965	6849721.5	11.12			
428.1042	61583512.0	100.00	428.1040	0.25	C ₁₆ H ₁₆ O ₄ N ₃ F ₆
429.1078	10322933.0	16.76			
433.2952	2611551.0	4.24			

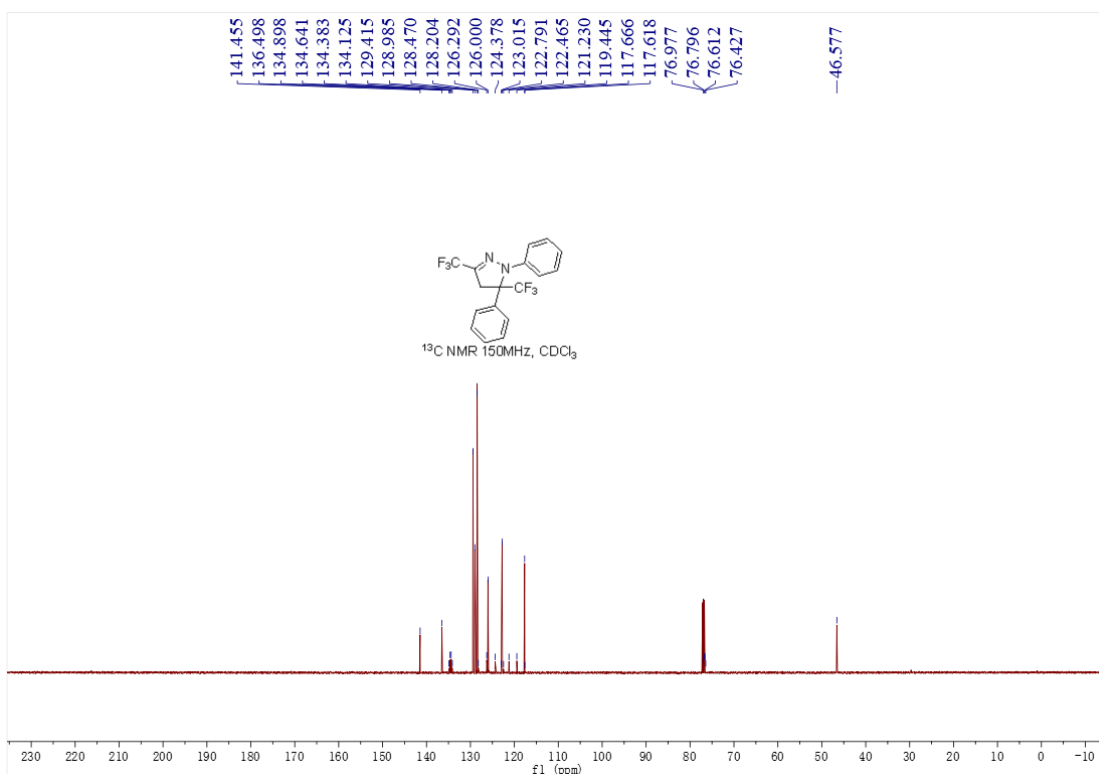


Spectrogram copies of compound **4h'**

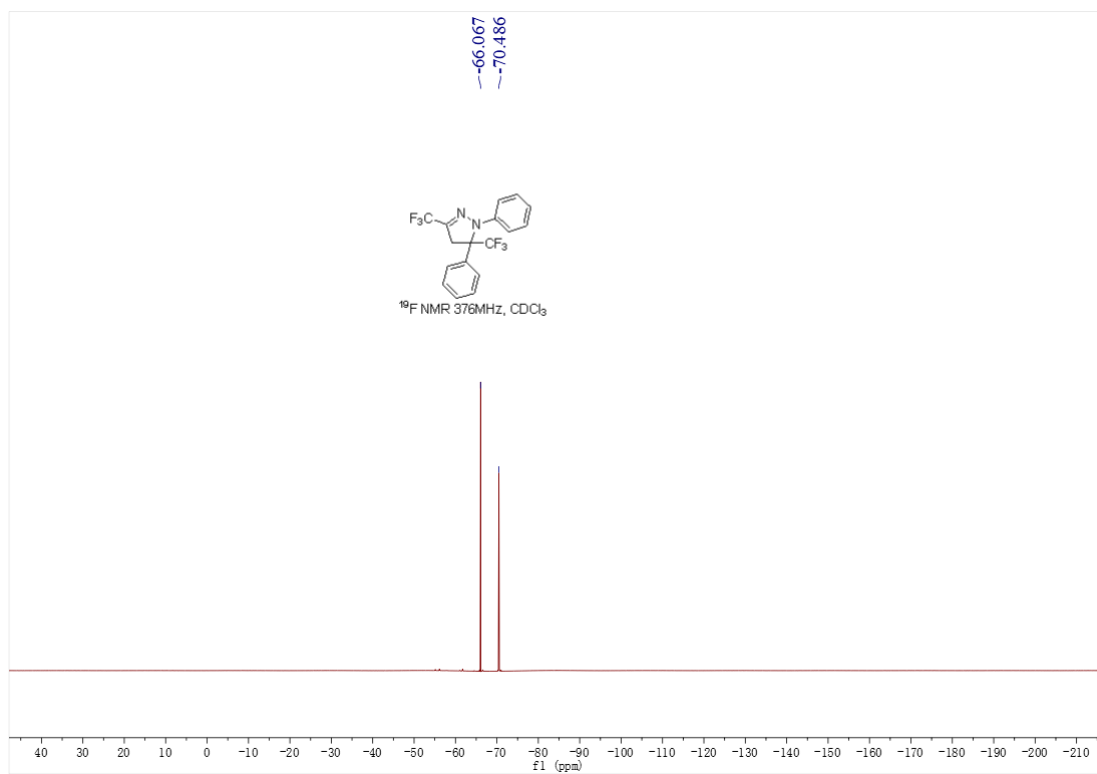
¹H NMR copy of compound **4h'**



¹³C NMR copy of compound **4h'**

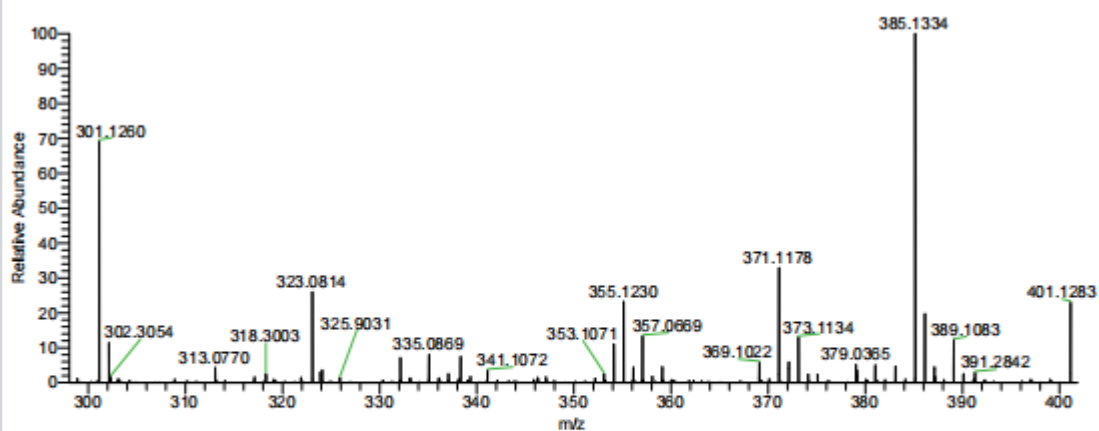


¹⁹F NMR copy of compound **4h'**



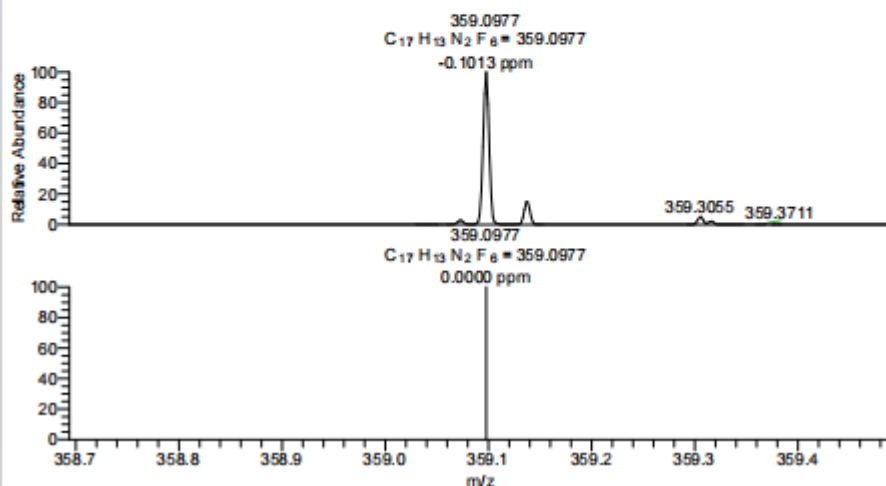
HRMS copy of compound 4h'

ZHAOSHUJUAN-38 #25-71 RT: 0.11-0.32 AV: 47 NL: 1.63E8
T: FTMS + p ESI Full lock ms [50.0000-750.0000]



ZHAOSHUJUAN-38#25-71 RT: 0.11-0.32 AV: 47
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z = 358.6937-359.4923

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
359.0729	199744.6	2.72	359.0977	-24.86	C ₁₇ H ₁₃ N ₂ F ₆
359.0977	7339133.0	100.00	359.0977	-0.04	C ₁₇ H ₁₃ N ₂ F ₆
359.1373	1124881.5	15.33	359.0977	39.60	C ₁₇ H ₁₃ N ₂ F ₆
359.3055	376228.3	5.13	359.0977	207.72	C ₁₇ H ₁₃ N ₂ F ₆
359.3159	157297.0	2.14	359.0977	218.13	C ₁₇ H ₁₃ N ₂ F ₆

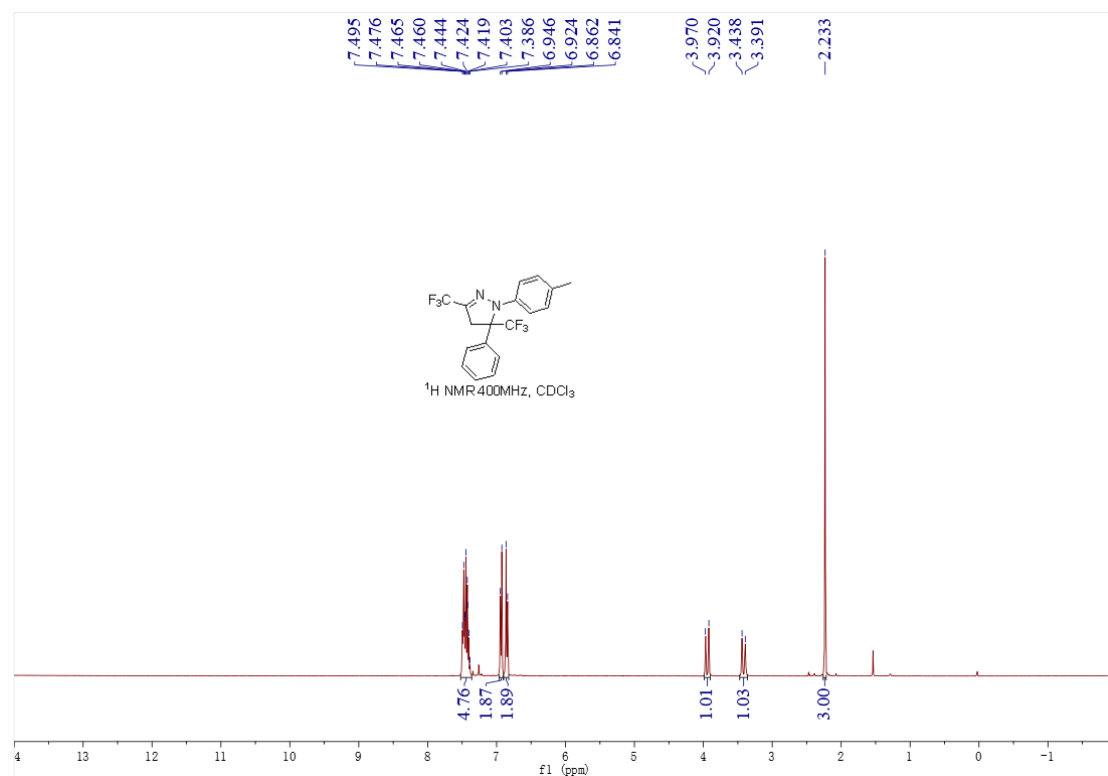


NL:
7.33E6
ZHAOSHUJUAN-38#25-71 RT: 0.11-0.32 AV: 47 T: FTMS + p ESI Full lock ms [50.0000-750.0000]

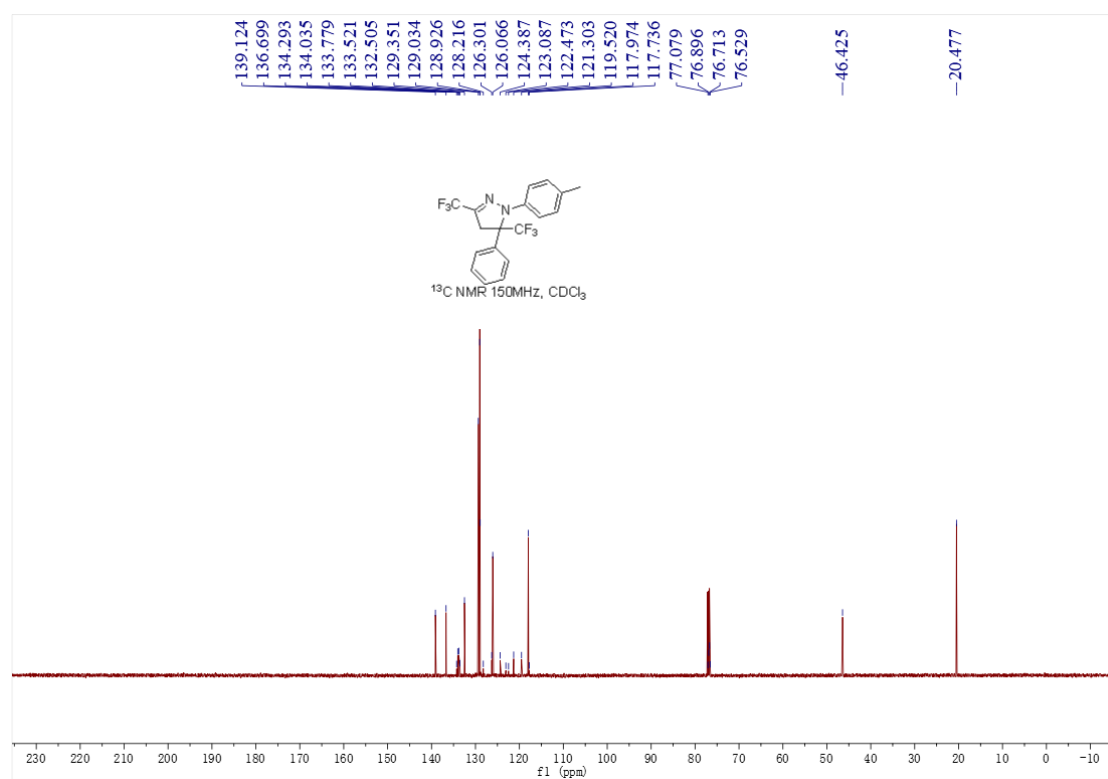
NL:
8.26E5
C₁₇H₁₃F₆N₂:
C₁₇H₁₃F₆N₂:
pa Chrg 1

Spectrogram copies of compound **4i'**

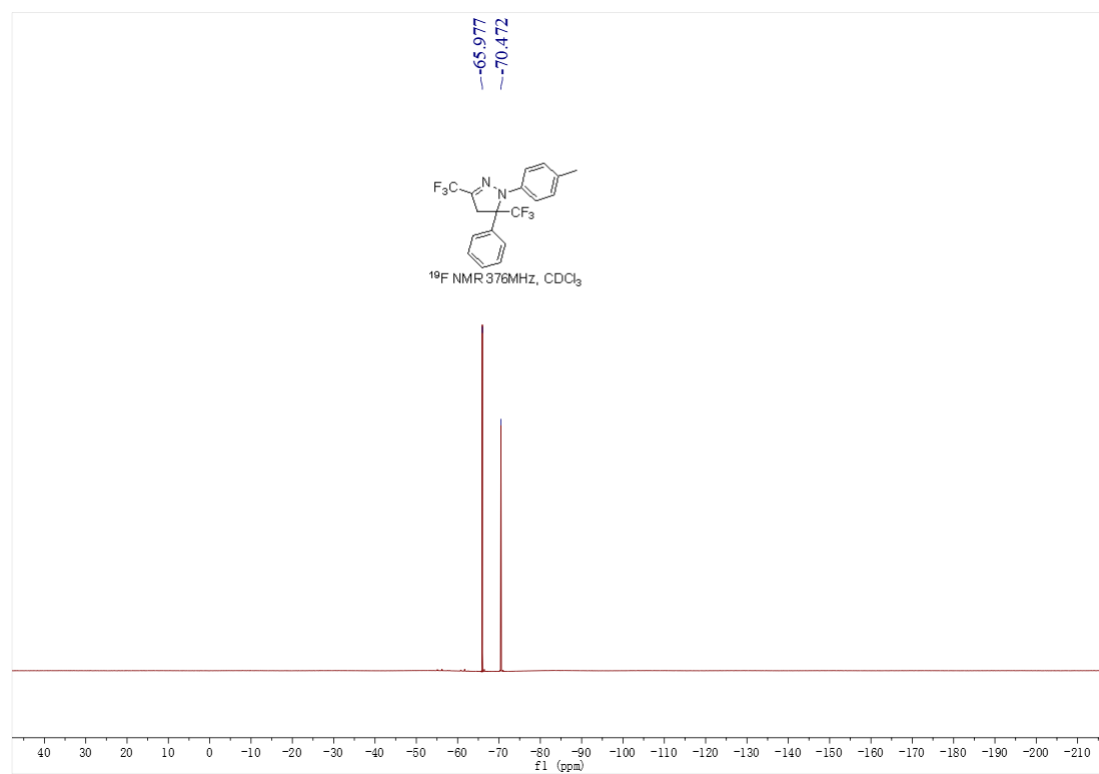
¹H NMR copy of compound **4i'**



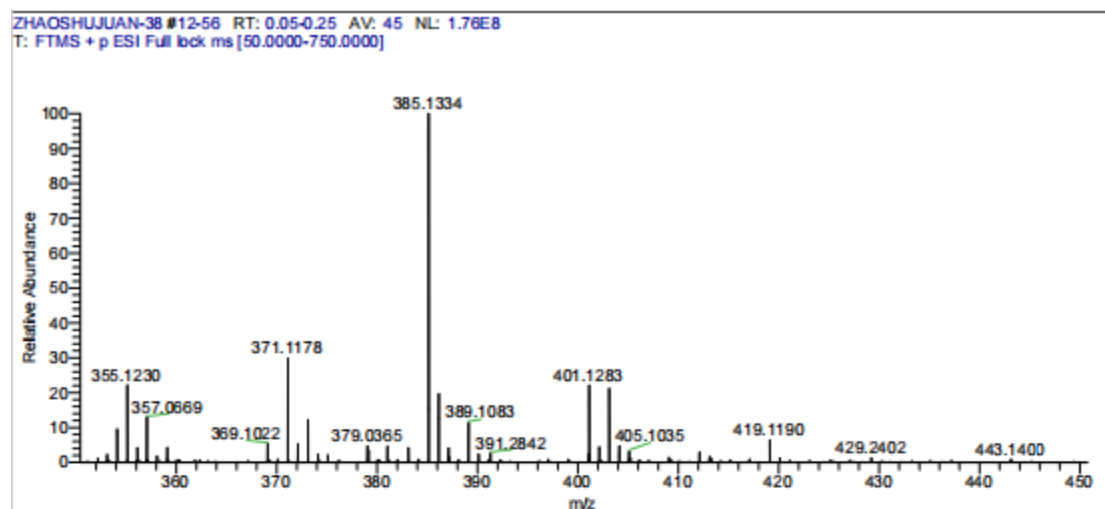
¹³C NMR copy of compound **4i'**



¹⁹F NMR copy of compound **4i'**

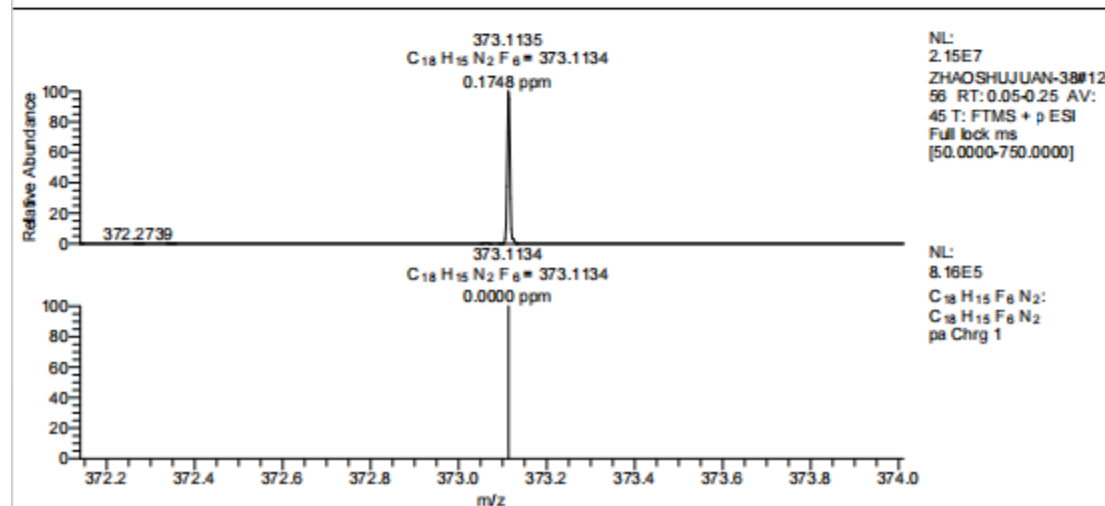


HRMS copy of compound 4i'



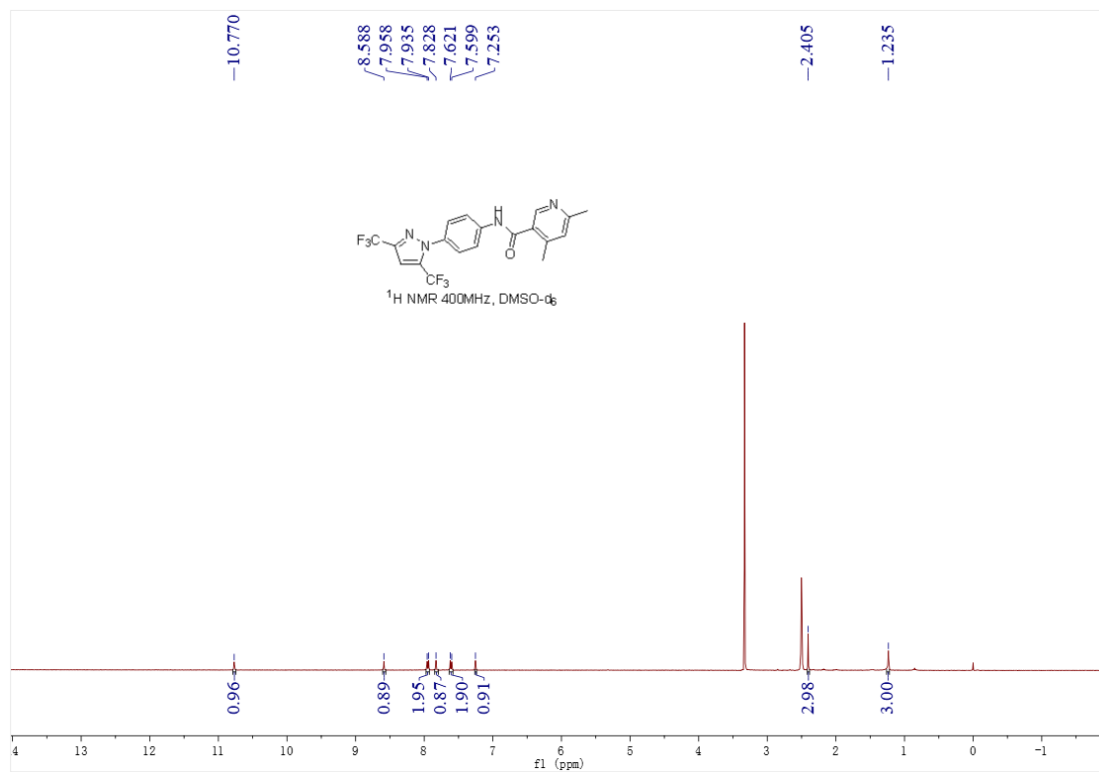
ZHAOSHUJUAN-38#12-56 RT: 0.05-0.25 AV: 45
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z = 372.1398-374.0108

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
372.2739	21883.6	0.10			
372.3475	4559.2	0.02			
373.0620	107603.9	0.49	373.1134	-51.42	C ₁₈ H ₁₅ N ₂ F ₆
373.0998	31789.6	0.15	373.1134	-13.60	C ₁₈ H ₁₅ N ₂ F ₆
373.1135	21883934.0	100.00	373.1134	0.07	C ₁₈ H ₁₅ N ₂ F ₆

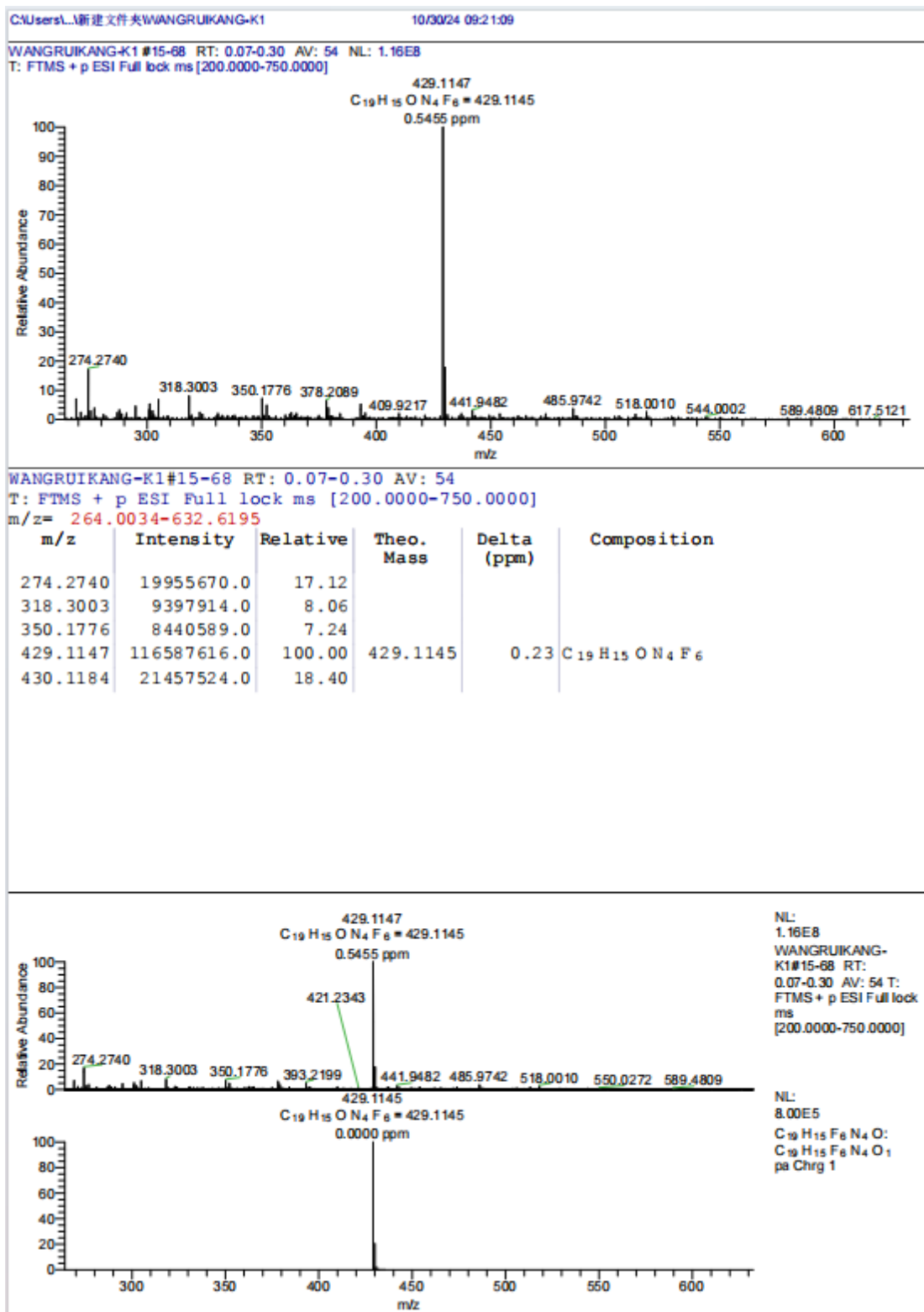


Spectrogram copies of compound **B**

^1H NMR copy of compound **B**



HRMS copy of compound B



3. X-Ray Crystallographic Data of Compounds **3n** and **4j**

Compound **3n**

Thermal ellipsoids are set at a 50% probability level. Crystal data have been deposited to CCDC, number 2313274.

Crystallization Details

The obtained compound **3n** (35 mg) was dissolved in THF (0.2 mL) in a NMR tube at room temperature. Then petroleum ether (2 mL) was added to the solution slowly along the tube wall, resulting in a two-phase mixture. The colorless crystal of **3n** was formed after the two-phase mixture has diffused.

Experimental

A suitable crystal was selected and placed on a ROD, Synergy Custom system, HyPix diffractometer. The crystal was kept at 150.00(10) K during data collection. Using Olex², the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation.

Experimental

A suitable crystal was selected and compound **3n** on a ROD, Synergy Custom system, HyPix diffractometer. The crystal was kept at 300.27(10) K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst.* 42, 339-341.
2. Sheldrick, G.M. (2015). *Acta Cryst.* A71, 3-8.
3. Sheldrick, G.M. (2015). *Acta Cryst.* C71, 3-8.

Crystal structure determination of compound 3n

Crystal Data for $C_{13}H_{10}BrF_5N_2$ ($M = 369.14$ g/mol): monoclinic, space group P2/n (no. 13), $a = 17.6937(9)$ Å, $b = 4.5126(2)$ Å, $c = 18.7442(10)$ Å, $\beta = 105.041(5)$, $V = 1445.35(13)$ Å³, $Z = 4$, $T = 300.27(10)$ K, $\mu(\text{Cu K}\alpha) = 4.376$ mm⁻¹, $D_{\text{calc}} = 1.696$ g/cm³, 8115 reflections measured ($6.122^\circ \leq 2\Theta \leq 154.342^\circ$), 2870 unique ($R_{\text{int}} = 0.0543$, $R_{\text{sigma}} = 0.0641$) which were used in all calculations. The final R_1 was 0.0619 ($I > 2\sigma(I)$) and wR_2 was 0.1963 (all data).

Refinement model description

Number of restraints - 24, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups, All C(H,H) groups

At 1.5 times of:

All C(H,H,H) groups

2. Uiso/Uanis restraints and constraints

$U_{\text{anis}}(\text{F4}) \approx U_{\text{eq}}$, $U_{\text{anis}}(\text{F4B}) \approx U_{\text{eq}}$, $U_{\text{anis}}(\text{F5}) \approx U_{\text{eq}}$, $U_{\text{anis}}(\text{F5B})$

$\approx U_{\text{eq}}$: with sigma of 0.004 and sigma for terminal atoms of 0.002

3. Others

Fixed Sof: F4(0.7) F4B(0.3) F5(0.5) F5B(0.5) H5A(0.5) H5B(0.5)

4.a Ternary CH refined with riding coordinates:

C5(H5A), C5(H5B)

4.b Aromatic/amide H refined with riding coordinates:

C2(H2), C6(H6), C12(H12)

4.c Idealised Me refined as rotating group:

C3(H3A,H3B,H3C), C11(H11A,H11B,H11C)

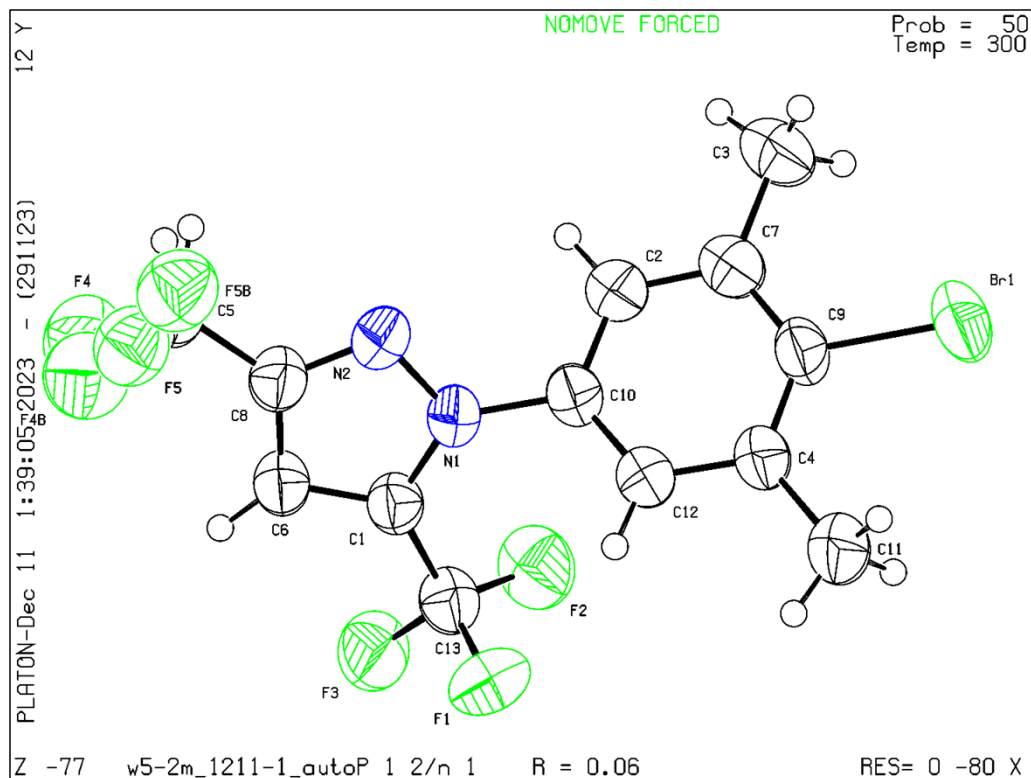


Table S1 Crystal data and structure refinement for compound 3n.	
Identification code	compound 3n
Empirical formula	C ₁₃ H ₁₀ BrF ₅ N ₂
Formula weight	369.14
Temperature/K	300.27(10)
Crystal system	monoclinic
Space group	P2/n
a/Å	17.6937(9)
b/Å	4.5126(2)
c/Å	18.7442(10)
α/°	90
β/°	105.041(5)
γ/°	90
Volume/Å ³	1445.35(13)
Z	4
ρ _{calc} /g/cm ³	1.696
μ/mm ⁻¹	4.376
F(000)	728.0
Crystal size/mm ³	0.15 × 0.06 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	6.122 to 154.342
Index ranges	-22 ≤ h ≤ 21, -5 ≤ k ≤ 2, -23 ≤ l ≤ 23
Reflections collected	8115
Independent reflections	2870 [R _{int} = 0.0543, R _{sigma} = 0.0641]
Data/restraints/parameters	2870/24/210
Goodness-of-fit on F ²	1.107
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0619, wR ₂ = 0.1805
Final R indexes [all data]	R ₁ = 0.0764, wR ₂ = 0.1962
Largest diff. peak/hole / e Å ⁻³	0.62/-0.60

Table S2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for compound 3n. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
Br1	8698.7(3)	1227.0(15)	6755.0(3)	85.9(3)
F1	4973.6(19)	3181(6)	4349.6(17)	78.0(8)
F2	5571(2)	-886(6)	4303(2)	87.3(9)
F3	4567.2(19)	284(8)	3435.9(18)	90.7(9)
F4	5749(4)	4838(14)	1331(3)	108.4(16)
F4B	5674(9)	6870(40)	1485(9)	110(4)
F5	6133(5)	8730(14)	1812(4)	86.0(17)
F5B	6638(6)	8787(15)	2029(5)	96(2)
N1	6486(2)	3380(7)	3741.2(19)	55.6(8)
N2	6787(2)	4588(9)	3213(2)	62.8(9)
C1	5710(2)	2831(8)	3472(2)	52.2(8)
C2	7685(3)	1273(9)	4508(3)	61.1(10)
C3	8950(3)	-905(15)	5236(4)	91.1(17)
C4	7312(3)	3422(9)	5777(2)	58.7(9)
C5	6329(4)	5965(12)	1924(3)	75.8(13)
C6	5496(3)	3731(9)	2754(2)	58.9(10)
C7	8201(3)	760(10)	5186(3)	64.5(10)
C8	6190(3)	4802(10)	2626(2)	61.6(10)
C9	8001(3)	1877(10)	5807(2)	59.8(10)
C10	7001(2)	2836(9)	4459(2)	54.9(9)
C11	7098(4)	4572(15)	6450(3)	84.4(15)
C12	6816(3)	3906(9)	5079(2)	58.8(10)
C13	5211(3)	1378(8)	3895(3)	58.0(9)

Table S3 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for compound 3n. The Anisotropic displacement factor exponent takes the form: $2 \pi^2 [h^2 a^{*2} U_{11} + 2hka^* b^* U_{12} + \dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	68.9(4)	109.8(5)	63.3(4)	4.7(3)	-10.9(3)	11.2(3)
F1	89(2)	77.7(15)	80.6(19)	-10.6(13)	45.4(17)	-8.3(14)
F2	93(2)	67.9(14)	99(2)	28.3(14)	21.5(18)	-0.8(14)
F3	70.1(18)	126(2)	69.3(19)	-5.3(17)	6.8(14)	-33.3(17)
F4	115(2)	114(2)	95(2)	8.4(17)	24.7(17)	-8.7(17)
F4B	110(4)	113(4)	108(4)	4(2)	29(2)	3(2)
F5	95(2)	81(2)	83(2)	8.1(17)	25.5(18)	-0.1(18)
F5B	102(3)	95(2)	94(3)	6.8(18)	31.5(19)	-2.2(18)
N1	53.1(18)	68.8(18)	43.2(17)	9.2(14)	9.6(14)	2.8(14)
N2	61(2)	81(2)	48.3(19)	8.3(16)	17.8(16)	-0.1(17)
C1	52(2)	55.9(18)	45.8(19)	-1.0(16)	8.1(16)	1.7(16)
C2	54(2)	73(2)	56(2)	-0.6(19)	13.5(19)	3.1(18)
C3	63(3)	118(4)	88(4)	0(3)	12(3)	29(3)
C4	52(2)	72(2)	47(2)	-2.4(17)	4.6(17)	2.4(17)
C5	85(3)	86(3)	55(3)	13(2)	17(2)	14(2)
C6	59(2)	69(2)	46(2)	1.7(17)	7.7(18)	7.2(18)
C7	53(2)	72(2)	66(3)	0(2)	12(2)	5.7(19)
C8	66(3)	68(2)	50(2)	7.9(18)	15.2(19)	10.6(19)
C9	51(2)	72(2)	49(2)	5.4(18)	-1.0(17)	-0.9(17)
C10	50(2)	63(2)	49(2)	3.6(17)	6.4(17)	1.3(16)
C11	74(3)	122(4)	53(3)	-7(3)	8(2)	17(3)
C12	52(2)	72(2)	51(2)	1.3(18)	10.0(18)	8.4(18)
C13	58(2)	55.8(19)	56(2)	4.1(17)	8.7(19)	-3.5(16)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C9	1.905(4)	C1	C6	1.363(6)
F1	C13	1.323(5)	C1	C13	1.483(6)
F2	C13	1.335(5)	C2	C7	1.378(7)
F3	C13	1.332(5)	C2	C10	1.383(6)
F4	C5	1.398(9)	C3	C7	1.506(7)
F4B	C5	1.301(16)	C4	C9	1.393(6)
F5	C5	1.297(8)	C4	C11	1.500(7)
F5B	C5	1.380(9)	C4	C12	1.390(6)
N1	N2	1.354(5)	C5	C8	1.495(7)
N1	C1	1.357(5)	C6	C8	1.396(7)
N1	C10	1.436(5)	C7	C9	1.395(7)
N2	C8	1.317(6)	C10	C12	1.375(6)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	N1	C1	110.8(3)	C2	C7	C9	117.2(4)
N2	N1	C10	118.6(3)	C9	C7	C3	122.5(5)
C1	N1	C10	130.7(3)	N2	C8	C5	118.8(4)
C8	N2	N1	104.9(4)	N2	C8	C6	112.4(4)
N1	C1	C6	107.9(4)	C6	C8	C5	128.7(4)
N1	C1	C13	124.6(4)	C4	C9	Br1	117.6(3)
C6	C1	C13	127.5(4)	C4	C9	C7	123.7(4)
C7	C2	C10	120.5(4)	C7	C9	Br1	118.6(3)
C9	C4	C11	123.2(4)	C2	C10	N1	118.8(4)
C12	C4	C9	116.6(4)	C12	C10	N1	119.9(4)
C12	C4	C11	120.1(4)	C12	C10	C2	121.2(4)
F4	C5	C8	108.5(5)	C10	C12	C4	120.7(4)
F4B	C5	F5B	93.2(8)	F1	C13	F2	106.6(4)
F4B	C5	C8	110.1(8)	F1	C13	F3	106.4(4)
F5	C5	F4	96.4(6)	F1	C13	C1	113.9(3)
F5	C5	C8	112.5(5)	F2	C13	C1	112.5(4)
F5B	C5	C8	110.4(5)	F3	C13	F2	106.7(3)
C1	C6	C8	104.0(4)	F3	C13	C1	110.3(4)
C2	C7	C3	120.2(5)				

Table S6 Torsion Angles for compound 3n.										
A	B	C	D	Angle/°	A	B	C	D	Angle/°	
F4	C5	C8	N2	154.4(5)	C1	C6	C8	C5	177.0(5)	
F4	C5	C8	C6	-22.4(7)	C2	C7	C9	Br1	-179.8(3)	
F4B	C5	C8	N2	-160.6(9)	C2	C7	C9	C4	1.0(7)	
F4B	C5	C8	C6	22.7(10)	C2	C10	C12	C4	-0.5(7)	
F5	C5	C8	N2	-100.2(7)	C3	C7	C9	Br1	-0.8(7)	
F5	C5	C8	C6	83.0(8)	C3	C7	C9	C4	-180.0(5)	
F5B	C5	C8	N2	-59.1(7)	C6	C1	C13	F1	-102.2(5)	
F5B	C5	C8	C6	124.2(6)	C6	C1	C13	F2	136.3(4)	
N1	N2	C8	C5	-177.7(4)	C6	C1	C13	F3	17.3(6)	
N1	N2	C8	C6	-0.5(5)	C7	C2	C10	N1	178.7(4)	
N1	C1	C6	C8	0.4(4)	C7	C2	C10	C12	-0.2(7)	
N1	C1	C13	F1	80.7(5)	C9	C4	C12	C10	1.4(6)	
N1	C1	C13	F2	-40.7(6)	C10	N1	N2	C8	179.6(4)	
N1	C1	C13	F3	-159.7(4)	C10	N1	C1	C6	-179.4(4)	
N1	C10	C12	C4	-179.4(4)	C10	N1	C1	C13	-1.8(7)	
N2	N1	C1	C6	-0.7(5)	C10	C2	C7	C3	-179.1(5)	
N2	N1	C1	C13	176.9(4)	C10	C2	C7	C9	0.0(7)	
N2	N1	C10	C2	-51.5(5)	C11	C4	C9	Br1	-0.2(6)	
N2	N1	C10	C12	127.5(4)	C11	C4	C9	C7	179.0(5)	
C1	N1	N2	C8	0.7(5)	C11	C4	C12	C10	-179.3(5)	
C1	N1	C10	C2	127.1(5)	C12	C4	C9	Br1	179.1(3)	
C1	N1	C10	C12	-53.9(6)	C12	C4	C9	C7	-1.6(7)	
C1	C6	C8	N2	0.1(5)	C13	C1	C6	C8	-177.1(4)	

Table S7 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for compound 3n.

Atom	x	y	z	U(eq)
H2	7797.6	563.3	4081.71	73
H3A	8936.42	-1769.23	4765.03	137
H3B	9007.58	-2442	5600.41	137
H3C	9385.13	436.11	5375.22	137
H5A	6858.97	5559.18	1880.52	91
H5B	6623.46	4606.43	1689.4	91
H6	5002.85	3650.54	2424.58	71
H11 A	6614.97	5649.64	6302.42	127
H11B	7504.56	5862.27	6718.36	127
H11C	7038.78	2939.06	6758.91	127
H12	6354.96	4965.76	5031.12	71

Table S8 Atomic Occupancy for compound 3n.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
F4	0.7	F4B	0.3	F5	0.5
F5B	0.5	H5A	0.5	H5B	0.5

Compound 4j

Thermal ellipsoids are set at a 50% probability level. Crystal data have been deposited to CCDC, number 2380999.

Crystallization Details

The obtained compound **4j** (30 mg) was dissolved in THF (0.2 mL) in a NMR tube at room temperature. Then petroleum ether (2 mL) was added to the solution slowly along the tube wall, resulting in a two-phase mixture. The colorless crystal of compound **4j** was formed after the two-phase mixture has diffused.

Experimental

Single crystals of $C_{17}H_{12}BrF_5N_2$ [**compound 4j**] were []. A suitable crystal was selected and [] on a **XtaLAB Synergy R, DW system, HyPix** diffractometer. The crystal was kept at 149.99(10) K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst.* 42, 339-341.
2. Sheldrick, G.M. (2015). *Acta Cryst.* A71, 3-8.
3. Sheldrick, G.M. (2015). *Acta Cryst.* C71, 3-8.

Crystal structure determination of [compound 4j]

Crystal Data for $C_{17}H_{12}BrF_5N_2$ ($M = 419.20$ g/mol): triclinic, space group P-1 (no. 2), $a = 7.4520(4)$ Å, $b = 10.0443(4)$ Å, $c = 11.7716(5)$ Å, $\alpha = 86.890(3)$, $\beta = 73.961(4)$, $\gamma = 70.172(4)$, $V = 795.85(7)$ Å³, $Z = 2$, $T = 149.99(10)$ K, $\mu(\text{Cu K}\alpha) = 4.064$ mm⁻¹, $D_{\text{calc}} = 1.749$ g/cm³, 8425 reflections measured ($7.822^\circ \leq 2\theta \leq 151.838^\circ$), 3125 unique ($R_{\text{int}} = 0.0251$, $R_{\text{sigma}} = 0.0198$) which were used in all calculations. The final R_1 was 0.0300 ($I > 2\sigma(I)$) and wR_2 was 0.0750 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups, All C(H,H) groups

2.a Ternary CH refined with riding coordinates:

C3(H3)

2.b Secondary CH2 refined with riding coordinates:

C5(H5A,H5B)

2.c Aromatic/amide H refined with riding coordinates:

C2(H2), C6(H6), C7(H7), C8(H8), C11(H11), C14(H14), C15(H15), C16(H16),

C17(H17)

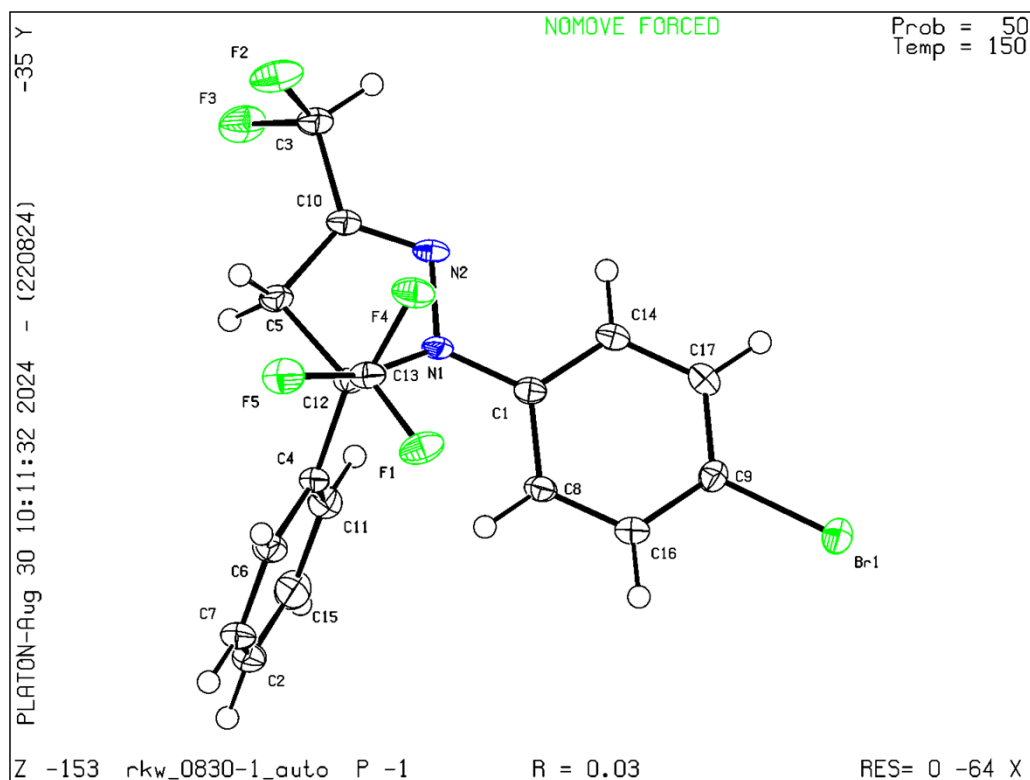


Table S9 Crystal data and structure refinement for compound 4j.	
Identification code	compound 4j
Empirical formula	C ₁₇ H ₁₂ BrF ₅ N ₂
Formula weight	419.20
Temperature/K	149.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.4520(4)
b/Å	10.0443(4)
c/Å	11.7716(5)
α/°	86.890(3)
β/°	73.961(4)
γ/°	70.172(4)
Volume/Å ³	795.85(7)
Z	2
ρ _{calc} /cm ³	1.749
μ/mm ⁻¹	4.064
F(000)	416.0
Crystal size/mm ³	0.18 × 0.15 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7.822 to 151.838
Index ranges	-8 ≤ h ≤ 9, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14
Reflections collected	8425
Independent reflections	3125 [R _{int} = 0.0251, R _{sigma} = 0.0198]
Data/restraints/parameters	3125/0/226
Goodness-of-fit on F ²	1.076
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0300, wR ₂ = 0.0748
Final R indexes [all data]	R ₁ = 0.0306, wR ₂ = 0.0750
Largest diff. peak/hole / e Å ⁻³	0.39/-0.56

Table S10 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for compound 4j. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
Br1	2735.6(3)	3553.2(2)	6780.0(2)	25.57(9)
F1	3987.0(17)	9335.9(13)	7659.0(11)	26.0(3)
F2	9209(2)	8349.8(15)	10819.8(12)	34.9(3)
F3	11976.8(18)	7174.9(16)	9581.3(12)	32.7(3)
F4	4684.7(18)	9022.5(14)	9327.4(10)	26.5(3)
F5	5293.8(19)	10697.4(12)	8234.6(11)	27.0(3)
N1	7535(2)	6868.5(17)	7962.2(14)	17.4(3)
N2	8340(2)	6463.0(18)	8909.9(14)	18.5(3)
C1	6413(3)	6106(2)	7700.1(16)	16.2(4)
C2	9631(4)	8567(3)	3844.1(19)	29.1(5)
C3	10084(3)	7200(2)	10054.1(18)	20.8(4)
C4	8141(3)	8451(2)	6289.3(16)	16.8(4)
C5	8879(3)	8580(2)	8271.6(18)	20.6(4)
C6	7345(3)	9652(2)	5698.2(18)	21.5(4)
C7	8089(3)	9698(2)	4483.4(19)	26.7(5)
C8	5611(3)	6449(2)	6732.7(17)	18.2(4)
C9	4223(3)	4584(2)	7166.0(17)	18.4(4)
C10	9068(3)	7386(2)	9099.6(17)	18.4(4)
C11	9705(3)	7311(2)	5639.1(18)	21.7(4)
C12	7447(3)	8329(2)	7628.4(16)	16.2(4)
C13	5327(3)	9352(2)	8208.8(17)	19.9(4)
C14	6121(3)	4978(2)	8380.1(17)	18.0(4)
C15	10439(3)	7371(3)	4429(2)	28.2(5)
C16	4503(3)	5696(2)	6479.5(17)	19.4(4)
C17	5034(3)	4216(2)	8114.0(18)	20.3(4)

Table S11 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for compound 4j. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	30.21(14)	24.72(14)	28.68(14)	4.02(9)	-12.24(10)	-15.06(10)
F1	19.9(6)	30.7(7)	23.9(6)	-5.8(5)	-10.0(5)	0.0(5)
F2	35.3(7)	42.0(8)	21.7(6)	-10.0(6)	-11.3(5)	-1.3(6)
F3	18.1(6)	48.1(8)	30.4(7)	1.5(6)	-10.3(5)	-6.3(6)
F4	26.4(6)	33.5(7)	14.7(6)	-0.1(5)	-2.5(5)	-6.3(5)
F5	33.5(7)	17.1(6)	26.0(6)	-3.2(5)	-10.2(5)	-0.7(5)
N1	23.2(8)	17.8(8)	14.8(8)	6.0(6)	-11.3(6)	-7.2(6)
N2	19.8(8)	21.0(8)	13.7(8)	4.1(6)	-9.0(6)	-2.7(6)
C1	16.2(8)	16.4(9)	13.1(8)	-0.8(7)	-3.1(7)	-2.4(7)
C2	35.7(12)	46.4(14)	14.7(9)	4.5(9)	-6.1(9)	-26.8(11)
C3	20.6(9)	24.1(10)	18.0(9)	2.9(8)	-9.2(8)	-5.1(8)
C4	18.8(9)	19.6(9)	13.8(9)	3.0(7)	-6.7(7)	-7.5(7)
C5	24.6(10)	21.4(10)	19.5(9)	4.5(8)	-12.9(8)	-7.6(8)
C6	25.2(10)	20.6(10)	20.3(10)	5.3(8)	-10.9(8)	-6.7(8)
C7	34.6(11)	34.0(12)	21.1(10)	11.9(9)	-16.5(9)	-18.1(10)
C8	22.7(9)	18.3(9)	13.9(9)	3.2(7)	-6.8(7)	-6.2(7)
C9	18.2(9)	18.5(9)	19.2(9)	-1.7(7)	-4.4(7)	-7.2(7)
C10	18.2(9)	21.4(9)	14.8(9)	2.5(7)	-7.2(7)	-3.9(7)
C11	19.3(9)	22.9(10)	22.2(10)	2.2(8)	-6.1(8)	-6.0(8)
C12	19.6(9)	15.0(9)	14.2(9)	2.8(7)	-7.3(7)	-4.5(7)
C13	23.4(9)	20.1(9)	15.0(9)	-0.4(7)	-7.5(7)	-3.8(8)
C14	18.6(9)	18.7(9)	14.9(9)	2.8(7)	-5.5(7)	-3.4(7)
C15	24.1(10)	35.6(12)	23.5(11)	-6.1(9)	0.9(8)	-13.1(9)
C16	20.9(9)	20.9(9)	15.4(9)	1.2(7)	-6.5(7)	-4.7(8)
C17	21.1(9)	19.1(9)	19.1(9)	4.3(7)	-3.9(8)	-6.7(7)

Table S12 Bond Lengths for compound 4j.					
Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C9	1.9007(19)	C3	C10	1.490(3)
F1	C13	1.336(2)	C4	C6	1.394(3)
F2	C3	1.360(2)	C4	C11	1.397(3)
F3	C3	1.358(2)	C4	C12	1.529(3)
F4	C13	1.336(2)	C5	C10	1.498(3)
F5	C13	1.345(2)	C5	C12	1.557(3)
N1	N2	1.388(2)	C6	C7	1.388(3)
N1	C1	1.408(3)	C8	C16	1.388(3)
N1	C12	1.483(2)	C9	C16	1.383(3)
N2	C10	1.278(3)	C9	C17	1.387(3)
C1	C8	1.402(3)	C11	C15	1.384(3)
C1	C14	1.395(3)	C12	C13	1.548(3)
C2	C7	1.381(4)	C14	C17	1.388(3)
C2	C15	1.388(3)			

Table S13 Bond Angles for compound 4j.							
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	N1	C1	118.18(15)	N2	C10	C3	120.32(18)
N2	N1	C12	111.54(15)	N2	C10	C5	114.85(17)
C1	N1	C12	127.07(15)	C3	C10	C5	124.79(18)
C10	N2	N1	108.63(16)	C15	C11	C4	120.5(2)
C8	C1	N1	120.47(17)	N1	C12	C4	112.39(15)
C14	C1	N1	120.61(17)	N1	C12	C5	101.33(14)
C14	C1	C8	118.91(18)	N1	C12	C13	108.40(15)
C7	C2	C15	119.3(2)	C4	C12	C5	112.08(16)
F2	C3	C10	109.87(16)	C4	C12	C13	113.71(15)
F3	C3	F2	104.96(17)	C13	C12	C5	108.13(15)
F3	C3	C10	109.54(16)	F1	C13	F5	107.00(16)
C6	C4	C11	118.80(18)	F1	C13	C12	113.87(16)
C6	C4	C12	123.47(18)	F4	C13	F1	106.99(16)
C11	C4	C12	117.69(17)	F4	C13	F5	107.12(16)
C10	C5	C12	101.00(15)	F4	C13	C12	110.45(16)
C7	C6	C4	120.2(2)	F5	C13	C12	111.08(17)
C2	C7	C6	120.8(2)	C17	C14	C1	120.64(18)
C16	C8	C1	120.25(18)	C11	C15	C2	120.4(2)
C16	C9	Br1	119.02(15)	C9	C16	C8	120.03(18)
C16	C9	C17	120.44(18)	C9	C17	C14	119.72(18)
C17	C9	Br1	120.54(15)				

Table S14 Torsion Angles for compound 4j.									
A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C9	C16	C8	-178.94(14)	C4	C12	C13	F5	-72.2(2)
Br1	C9	C17	C14	179.80(14)	C5	C12	C13	F1	173.85(16)
F2	C3	C10	N2	-123.6(2)	C5	C12	C13	F4	-65.7(2)
F2	C3	C10	C5	58.9(3)	C5	C12	C13	F5	53.0(2)
F3	C3	C10	N2	121.6(2)	C6	C4	C11	C15	-0.5(3)
F3	C3	C10	C5	-55.9(3)	C6	C4	C12	N1	146.01(18)
N1	N2	C10	C3	-178.43(17)	C6	C4	C12	C5	-100.6(2)
N1	N2	C10	C5	-0.7(2)	C6	C4	C12	C13	22.4(3)
N1	C1	C8	C16	-179.86(17)	C7	C2	C15	C11	0.2(3)
N1	C1	C14	C17	-179.27(17)	C8	C1	C14	C17	-0.8(3)
N1	C12	C13	F1	-77.1(2)	C10	C5	C12	N1	-14.57(18)
N1	C12	C13	F4	43.3(2)	C10	C5	C12	C4	-134.60(16)
N1	C12	C13	F5	162.05(15)	C10	C5	C12	C13	99.28(17)
N2	N1	C1	C8	-178.30(17)	C11	C4	C6	C7	0.6(3)
N2	N1	C1	C14	0.2(3)	C11	C4	C12	N1	-36.4(2)
N2	N1	C12	C4	135.75(16)	C11	C4	C12	C5	77.0(2)
N2	N1	C12	C5	15.94(19)	C11	C4	C12	C13	-159.98(17)
N2	N1	C12	C13	-97.71(17)	C12	N1	N2	C10	-10.3(2)
C1	N1	N2	C10	-171.56(17)	C12	N1	C1	C8	23.7(3)
C1	N1	C12	C4	-65.1(2)	C12	N1	C1	C14	-157.80(18)
C1	N1	C12	C5	175.11(17)	C12	C4	C6	C7	178.25(19)
C1	N1	C12	C13	61.5(2)	C12	C4	C11	C15	-178.22(19)
C1	C8	C16	C9	-1.4(3)	C12	C5	C10	N2	10.4(2)
C1	C14	C17	C9	-0.3(3)	C12	C5	C10	C3	-172.01(18)
C4	C6	C7	C2	-0.4(3)	C14	C1	C8	C16	1.6(3)
C4	C11	C15	C2	0.1(3)	C15	C2	C7	C6	0.0(3)
C4	C12	C13	F1	48.7(2)	C16	C9	C17	C14	0.5(3)
C4	C12	C13	F4	169.10(16)	C17	C9	C16	C8	0.4(3)

Table S15 Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for compound 4j.

Atom	x	y	z	U(eq)
H2	10133.47	8605.98	3012.89	35
H3	10061.5	6313.65	10479.18	25
H5A	10174.86	8510.79	7711.31	25
H5B	8295.64	9512.39	8706.14	25
H6	6289.84	10440.16	6127.73	26
H7	7531.42	10518.36	4087.01	32
H8	5826.72	7198.54	6248.87	22
H11	10269.75	6488.32	6030.96	26
H14	6671.22	4728.6	9031.7	22
H15	11502.01	6588.99	3995.62	34
H16	3936.29	5945.75	5834.31	23
H17	4847.28	3445.91	8579.08	24