Supporting Information

A regioselective synthesis of 3,4-diaryl-1*H*-pyrazoles through a 1,3-dipolar cycloaddition of tosylhydrazones and nitroalkenes.

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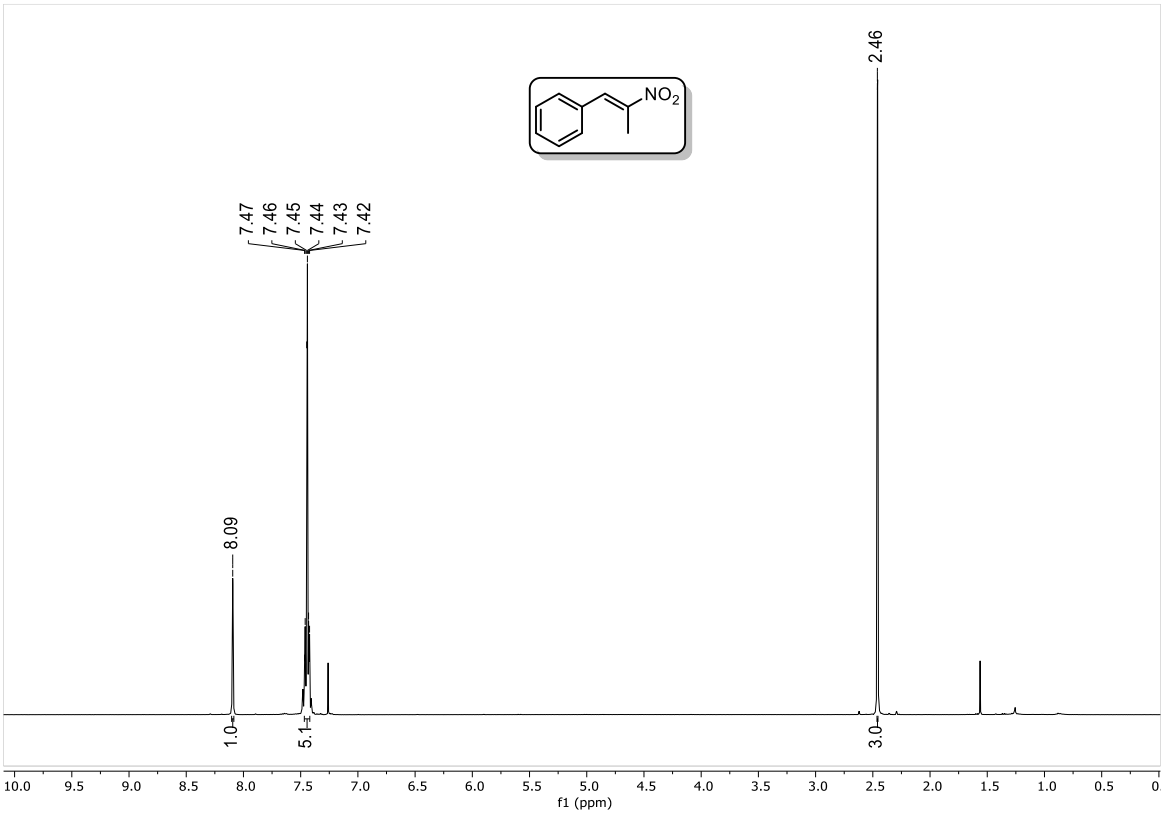
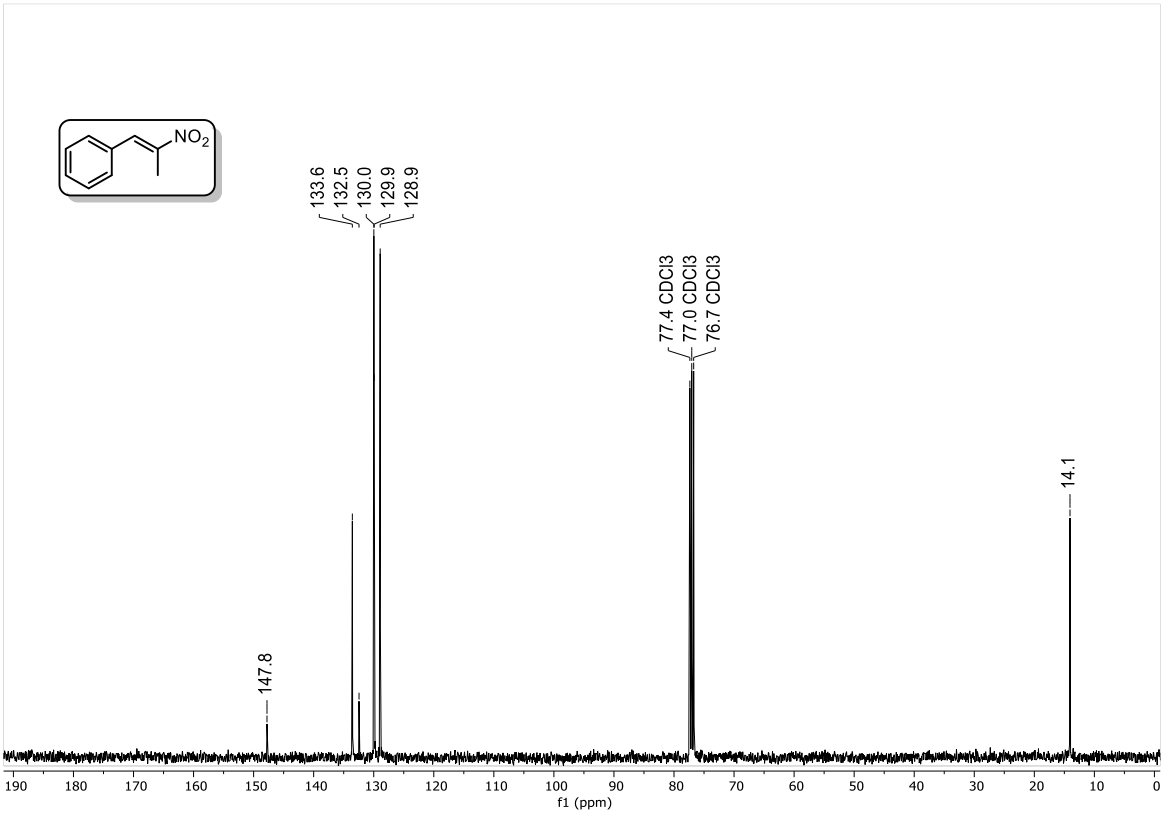
^{1}H-NMR and ^{13}C-NMR and HRMS spectra of the nitroalkenes.



Spectrum 1. ^{1}H-NMR of **6a**.



Spectrum 2. ^{13}C-NMR of **6a**.

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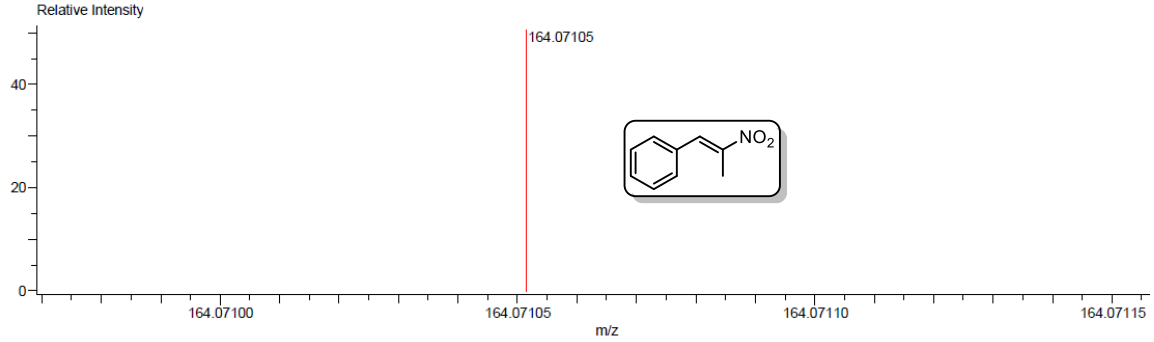
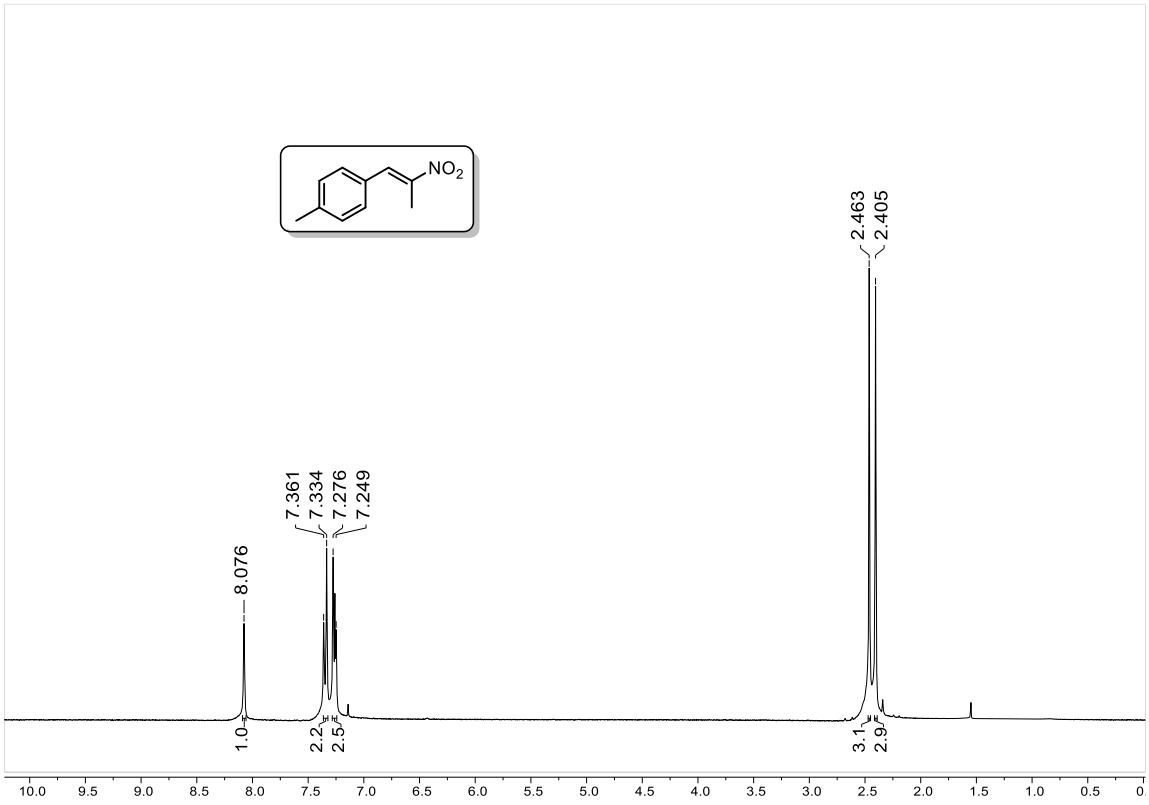
Unsaturation Number:-1.0 .. 60.0 (Fraction:Both)
Element:^{12}C:0 .. 9, ^{1}H:0 .. 50, ^{35}Cl:0 .. 1, ^{14}N:0 .. 1, ^{16}O:0 .. 2, ^{32}S:0 .. 0

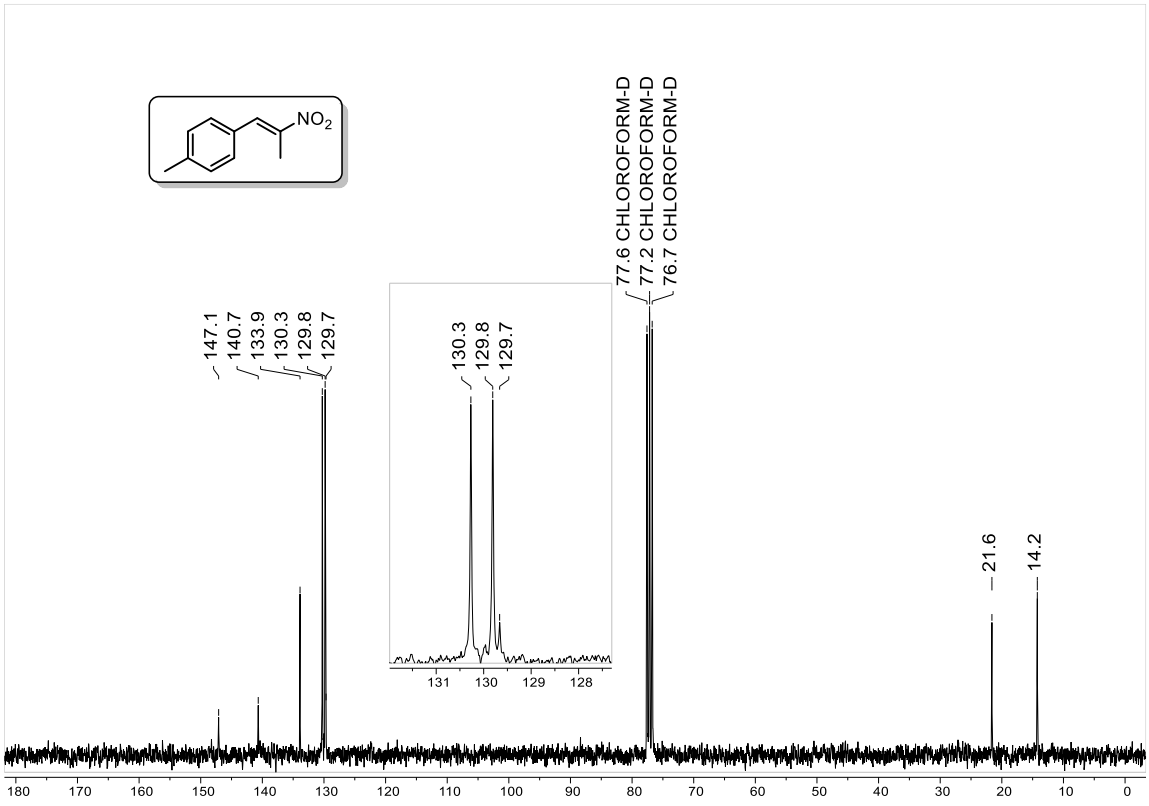


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
164.07105	11180.34	164.07115	-0.10	-0.62	$^{12}C_9{}^{1}H_{10}{}^{14}N_1{}^{16}O_2$	5.5

Spectrum 3. HRMS of **6a**.



Spectrum 4. ^{1}H-NMR of **6b**.



Spectrum 5. ^{13}C-NMR of **6b**.

Description:
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History:Determine m/z[Peak Detect[Centroid,30,Area];Correct Base[];Smooth[5]];Correct Base[5.0%];Average(MS[...

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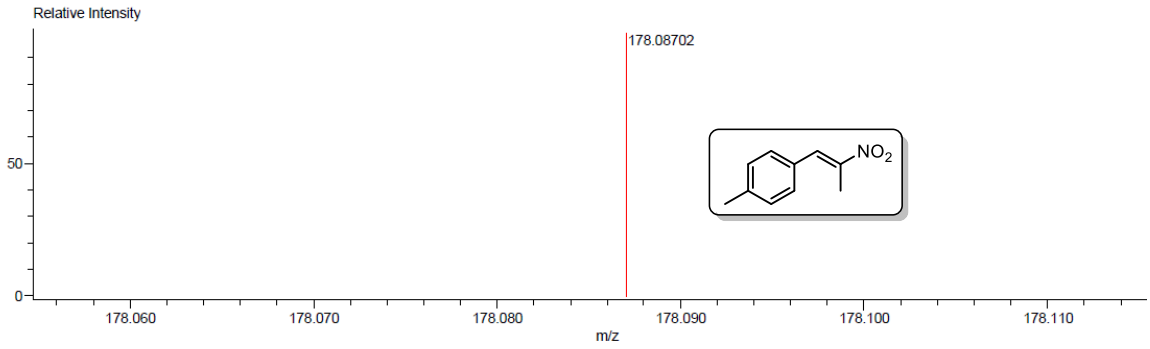
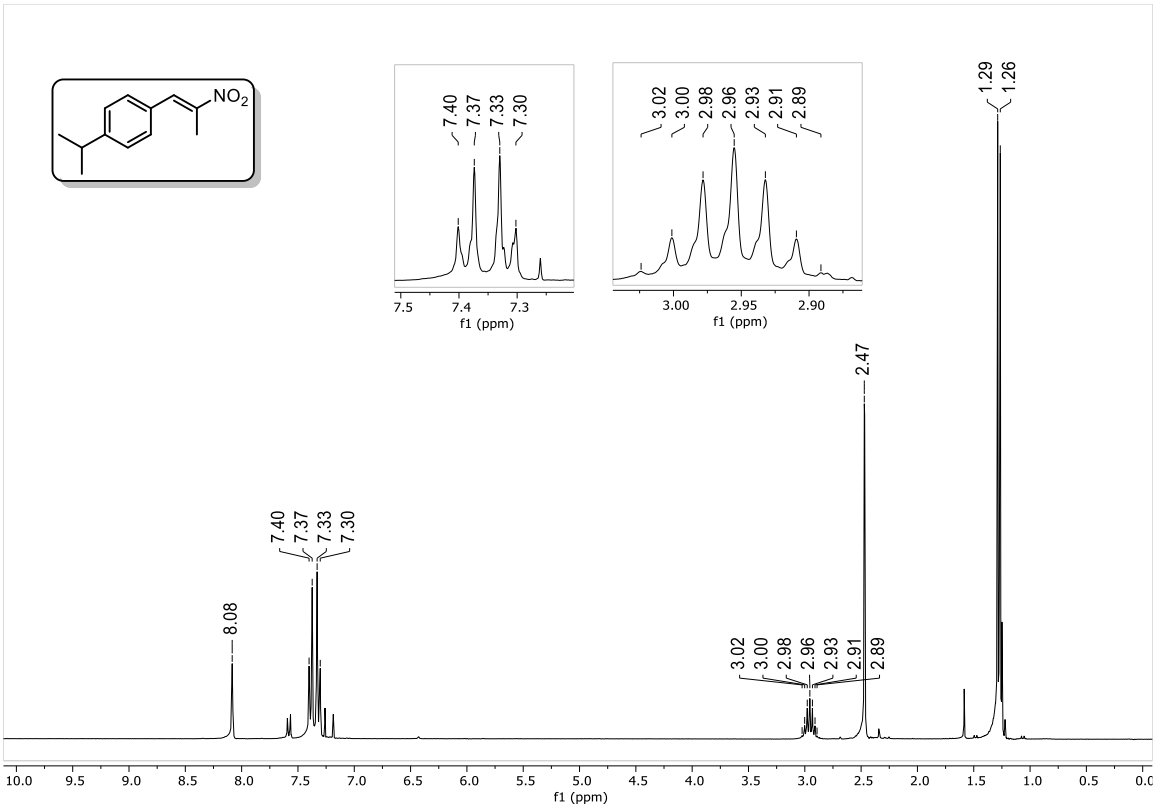
Created by:

Charge number:1
Tolerance:5.00(ppm), 5.00 .. 15.00(mmu)
Unsaturation Number:-1.0 .. 60.0 (Fraction:Both)
Element:^{12}C:0 .. 22, ^{1}H:0 .. 28, ^{35}Cl:0 .. 0, ^{19}F:0 .. 0, ^{14}N:0 .. 1, ^{16}O:0 .. 2, ^{32}S:0 .. 0

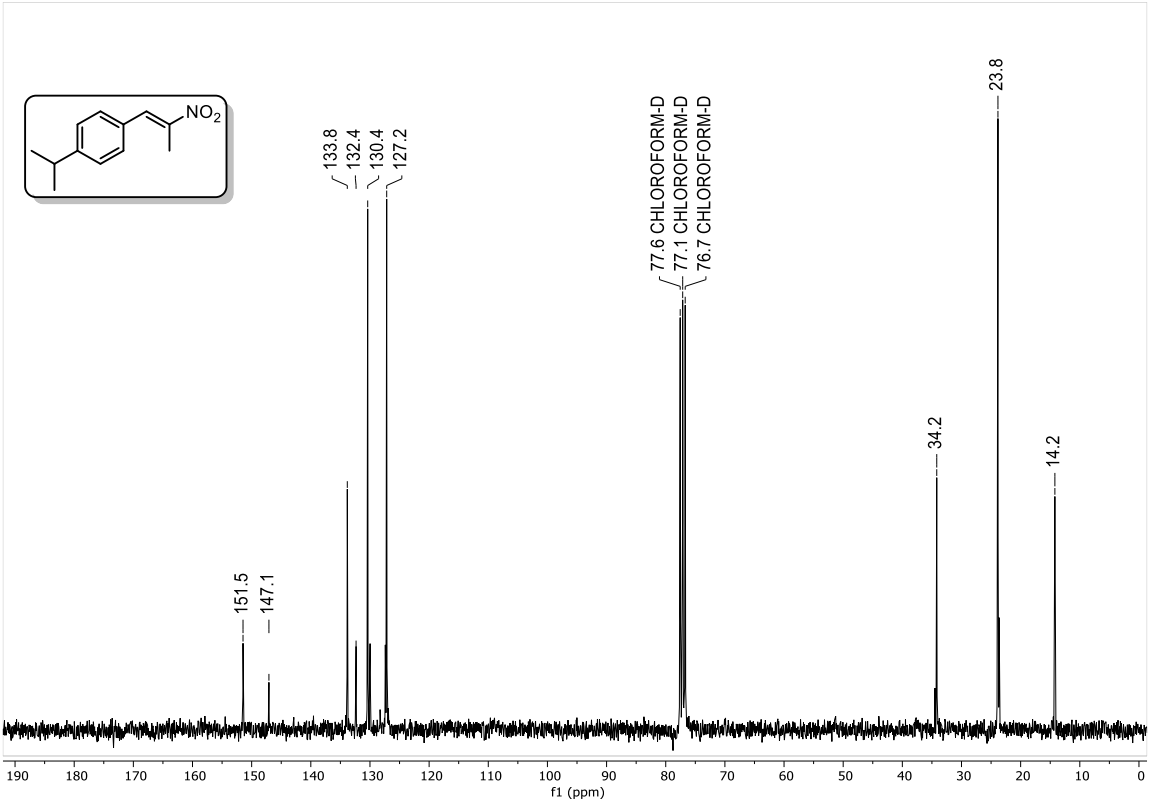


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
178.08702	20008.16	178.08680	0.22	1.23	$^{12}C_{10}{}^{1}H_{12}{}^{14}N_{1}{}^{16}O_{2}$	5.5

Spectrum 6. HRMS of **6b**.



Spectrum 7. ^{1}H-NMR of **6c**.



Spectrum 8. ^{13}C-NMR of **6c**.

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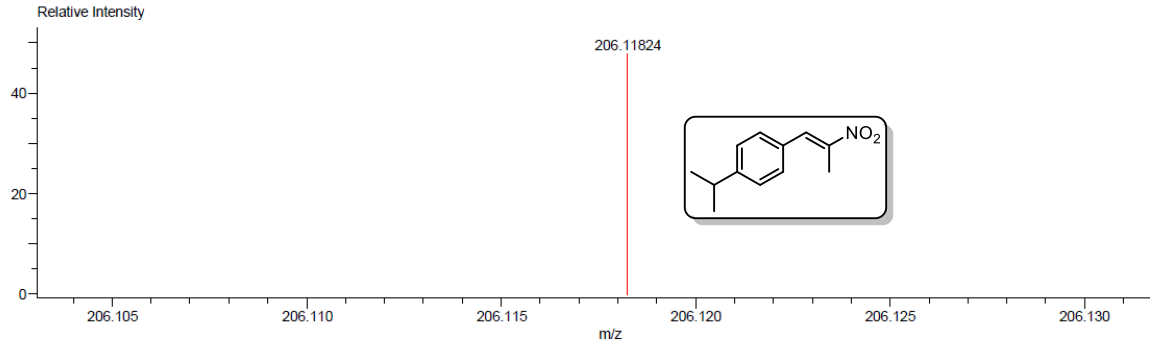
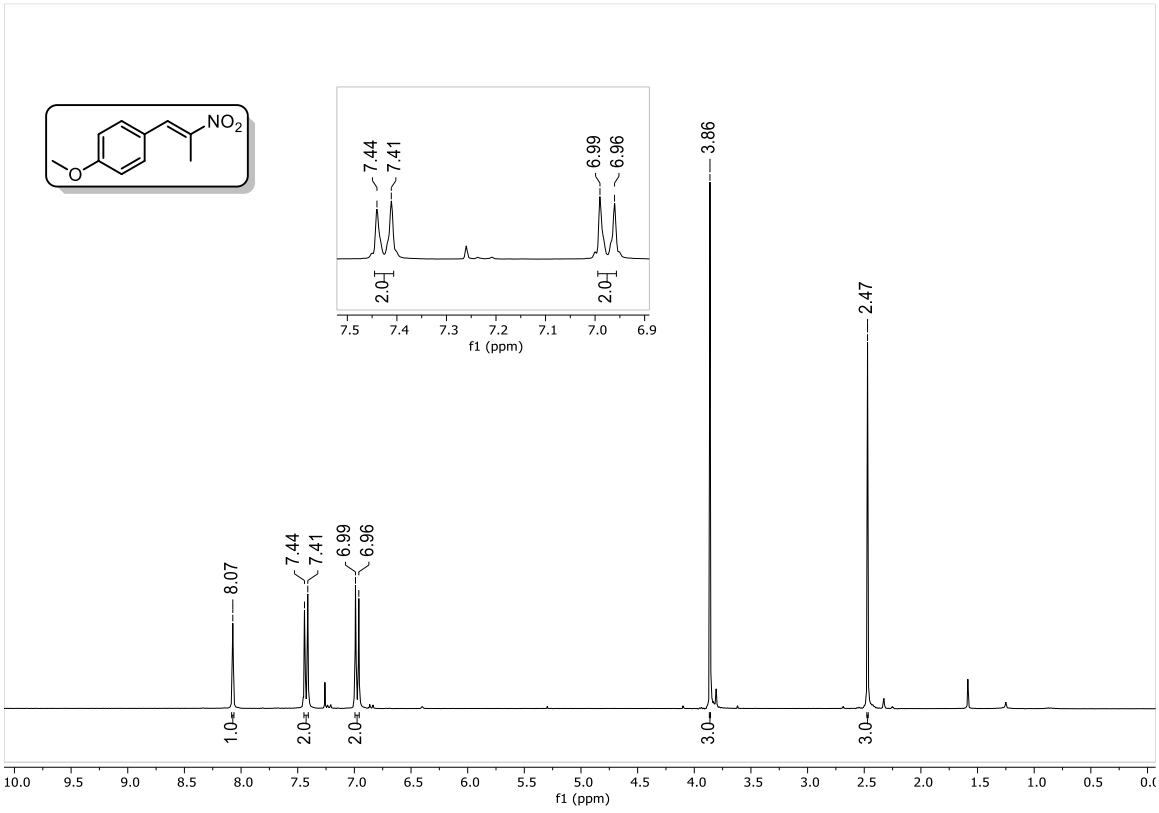
Charge number:1 Tolerance:5.00(ppm), 5.00 .. 15.00(mmu) Unsaturation Number:-1.0 .. 60.0 (Fraction:Both)
Element:^{12}C:0 .. 22, ^{1}H:0 .. 28, ^{35}Cl:0 .. 0, ^{19}F:0 .. 0, ^{14}N:0 .. 1, ^{16}O:0 .. 2, ^{32}S:0 .. 0

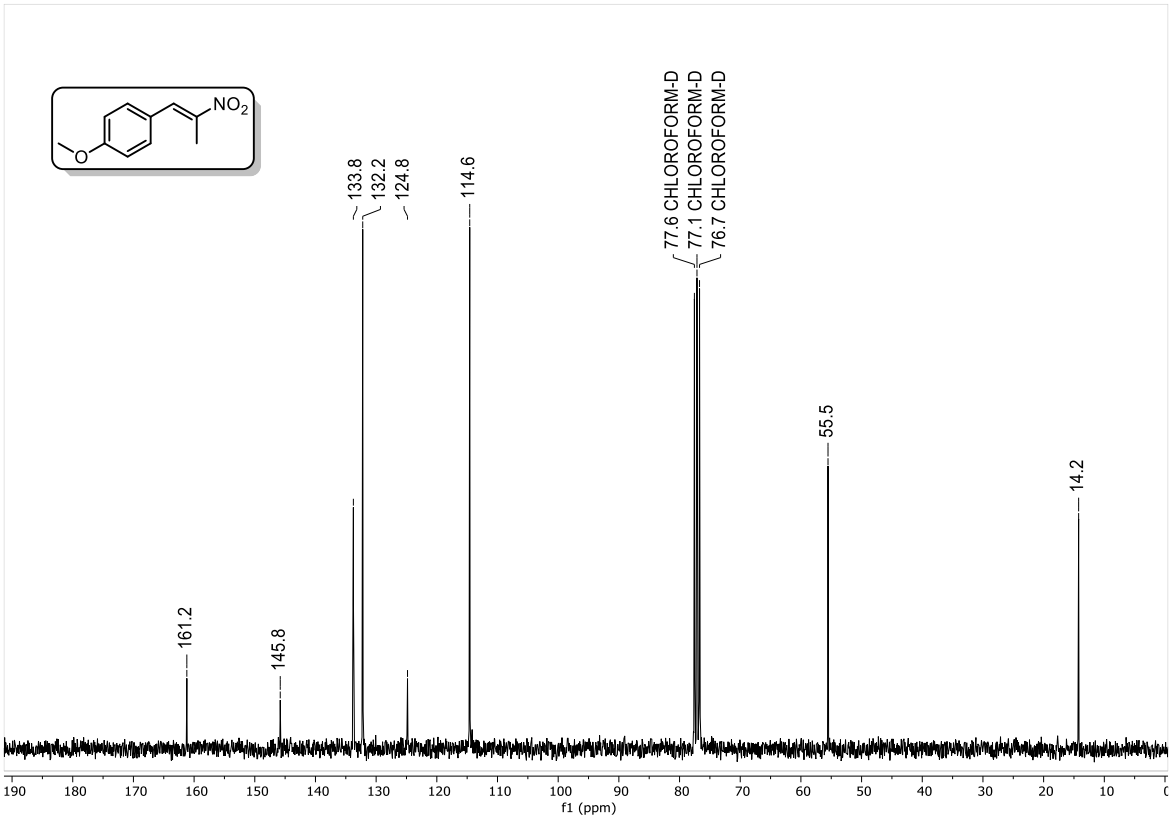


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
206.11824	3006.77	206.11810	0.14	0.68	$^{12}C_{12}{}^{1}H_{16}{}^{14}N_{1}{}^{16}O_{2}$	5.5

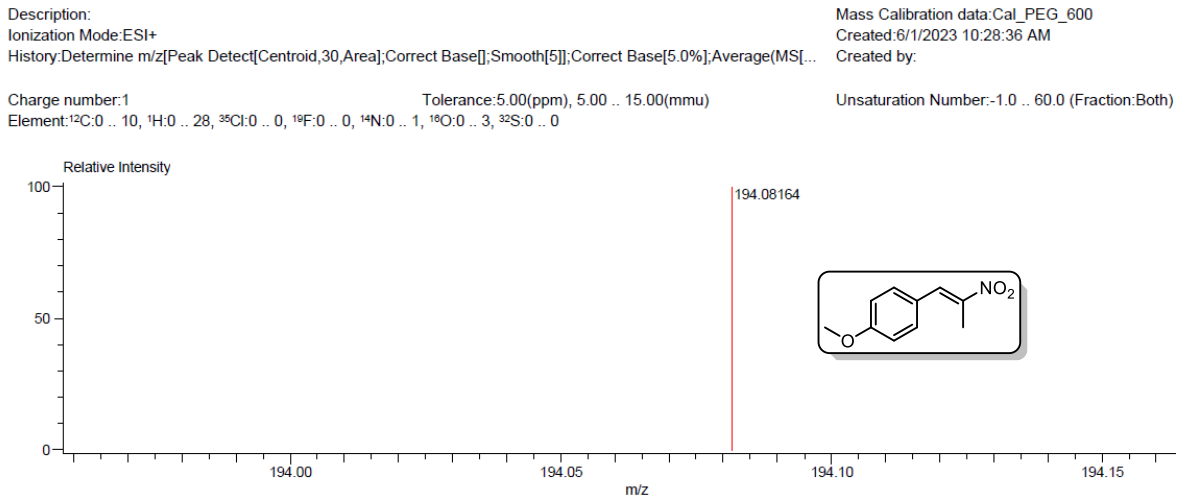
Spectrum 9. HRMS of **6c**.



Spectrum 10. ^{1}H-NMR of **6d**.

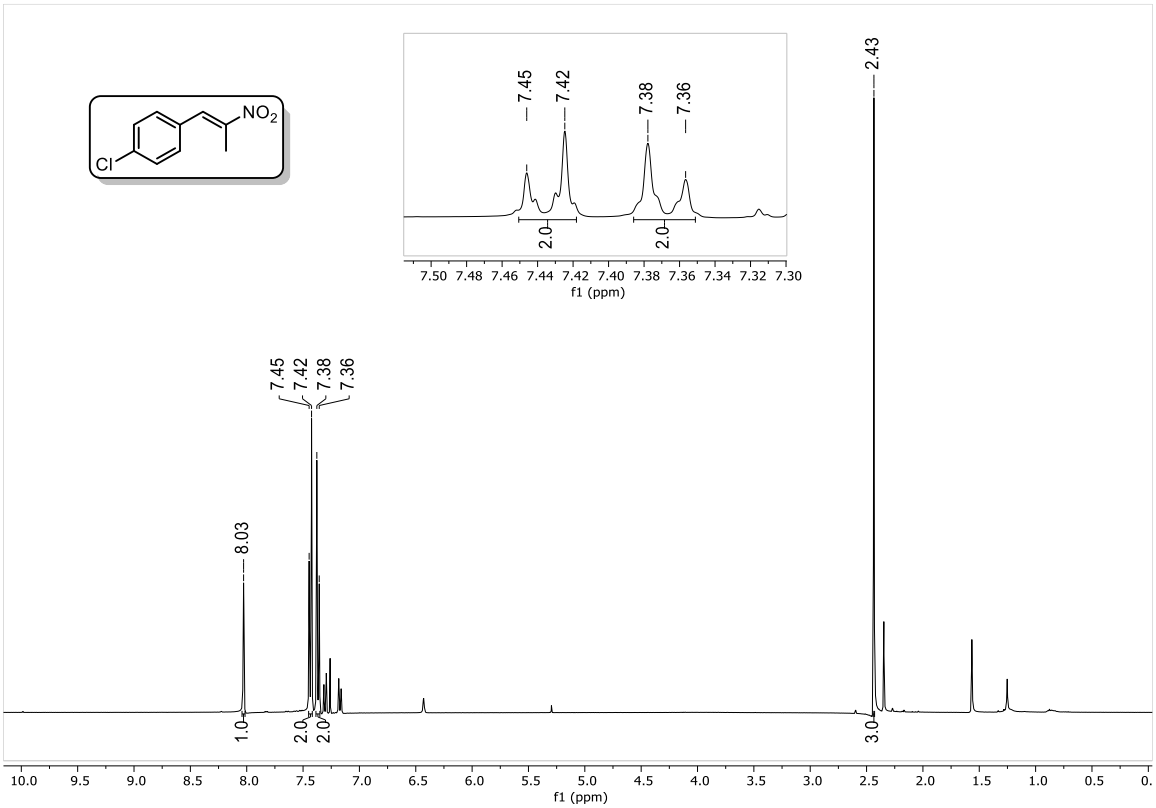


Spectrum 11. ^{13}C-NMR of **6d**.

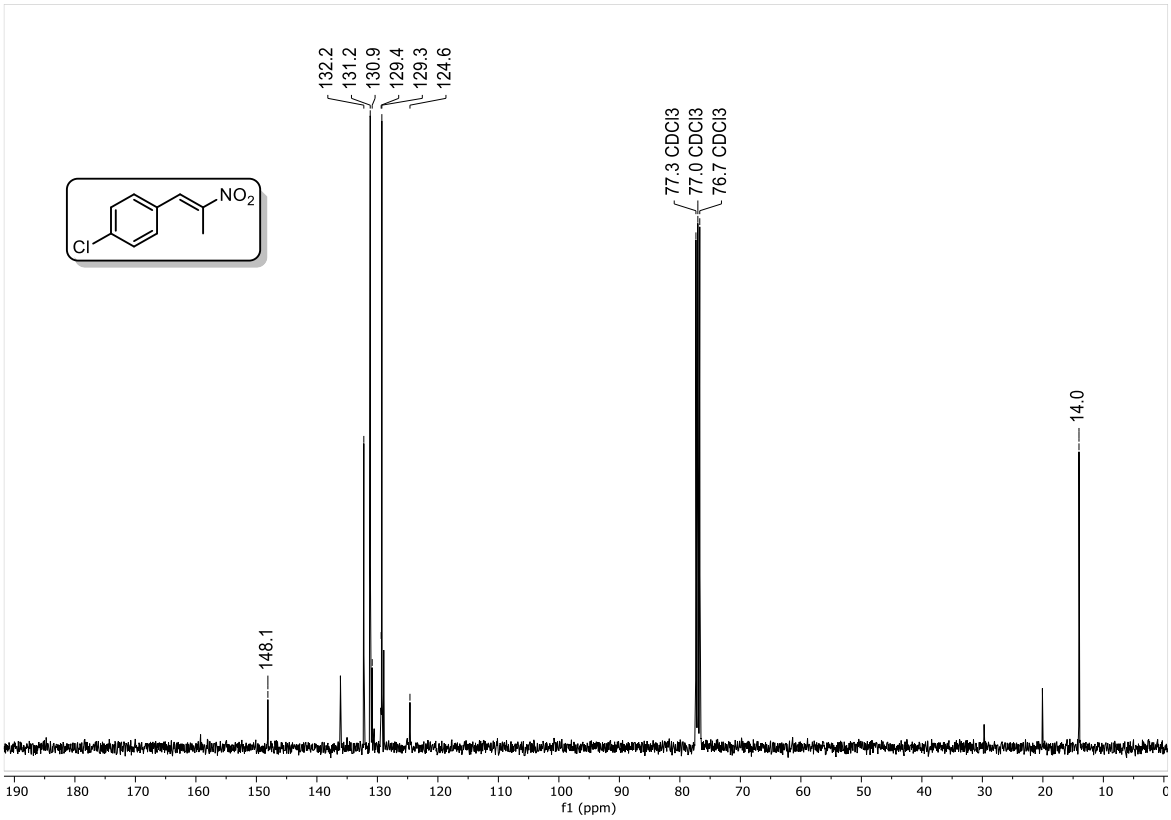


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
194.08164	6888.90	194.08172	-0.07	-0.38	$^{12}C_{10}{}^{1}H_{12}{}^{14}N_{1}{}^{16}O_{3}$	5.5

Spectrum 12. HRMS of **6d**.



Spectrum 13. ^{1}H-NMR of **6e**.



Spectrum 14. ^{13}C-NMR of **6e**.

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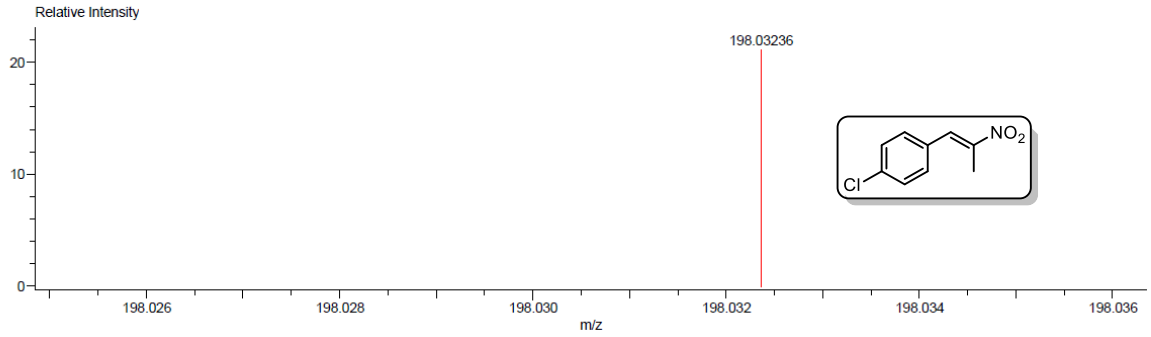
Charge number:1
Element:^{12}C:0 .. 9, ^{1}H:0 .. 50, ^{35}Cl:0 .. 1, ^{14}N:0 .. 1, ^{16}O:0 .. 2, ^{32}S:0 .. 0

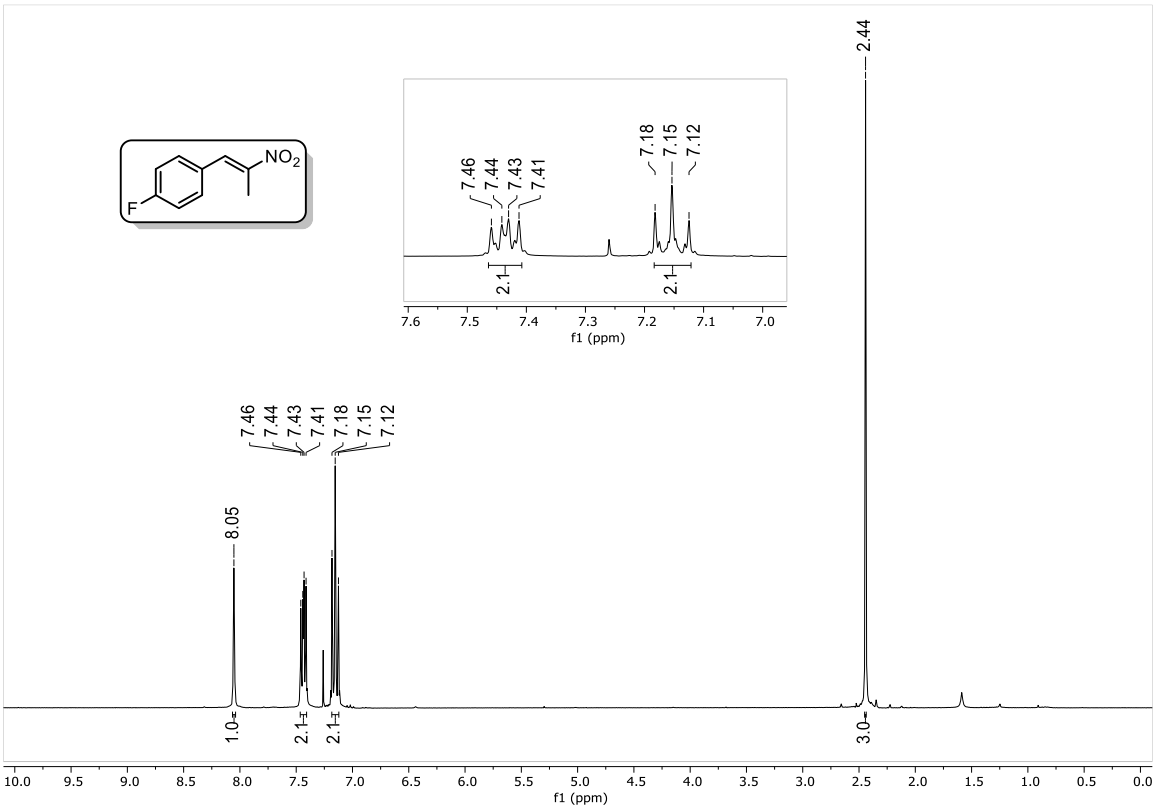
Tolerance:50.00(ppm), 5.00 .. 15.00(mmu)

Unsaturation Number:-1.0 .. 60.0 (Fraction:Both)

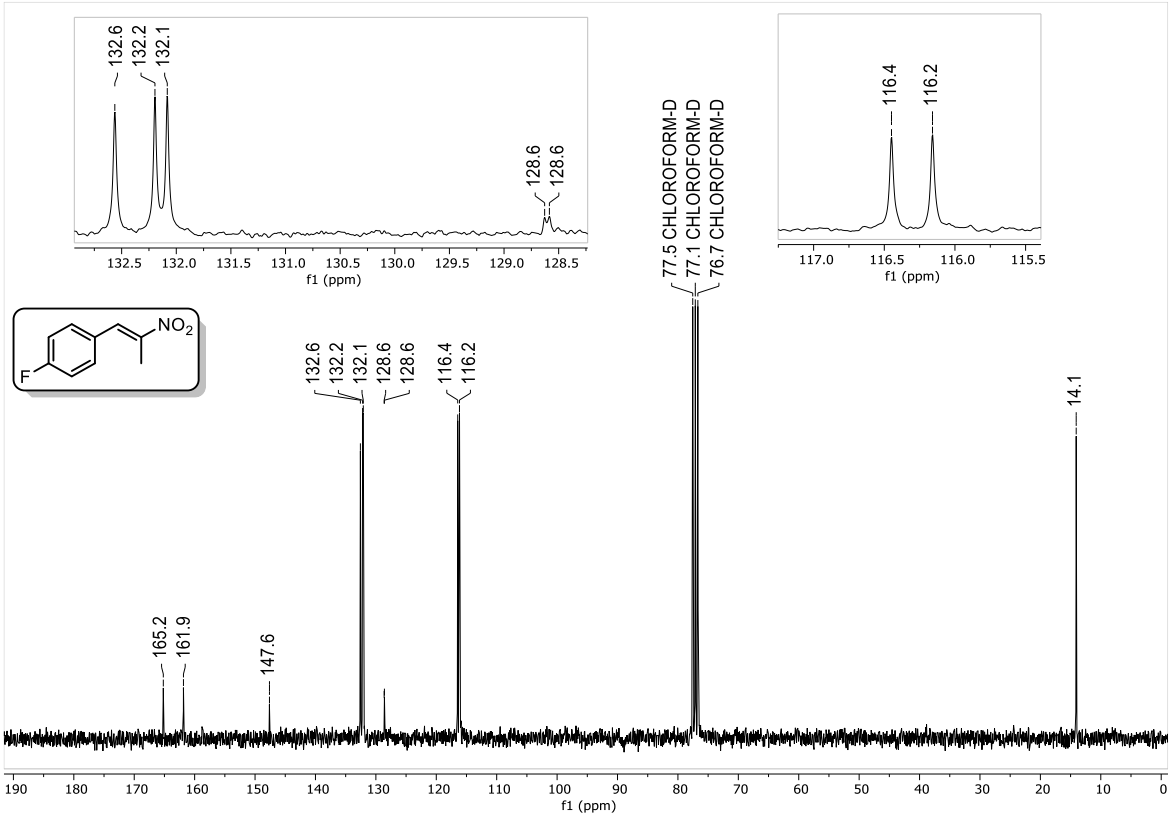


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
198.03236	1682.79	198.03218	0.18	0.91	$^{12}C_9{}^{1}H_9{}^{35}Cl_1{}^{14}N_1{}^{16}O_2$	5.5

Spectrum 15. HRMS of **6e**.



Spectrum 16. ^{1}H-NMR of **6f**.



Spectrum 17. ^{13}C-NMR of **6f**.

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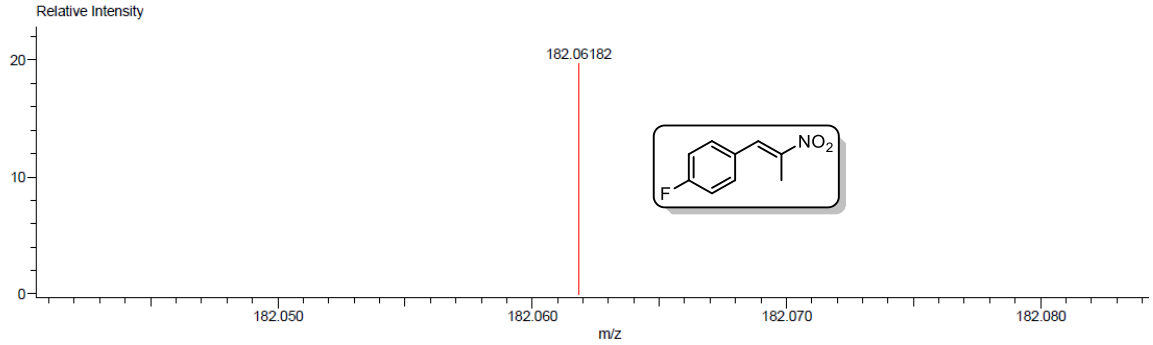
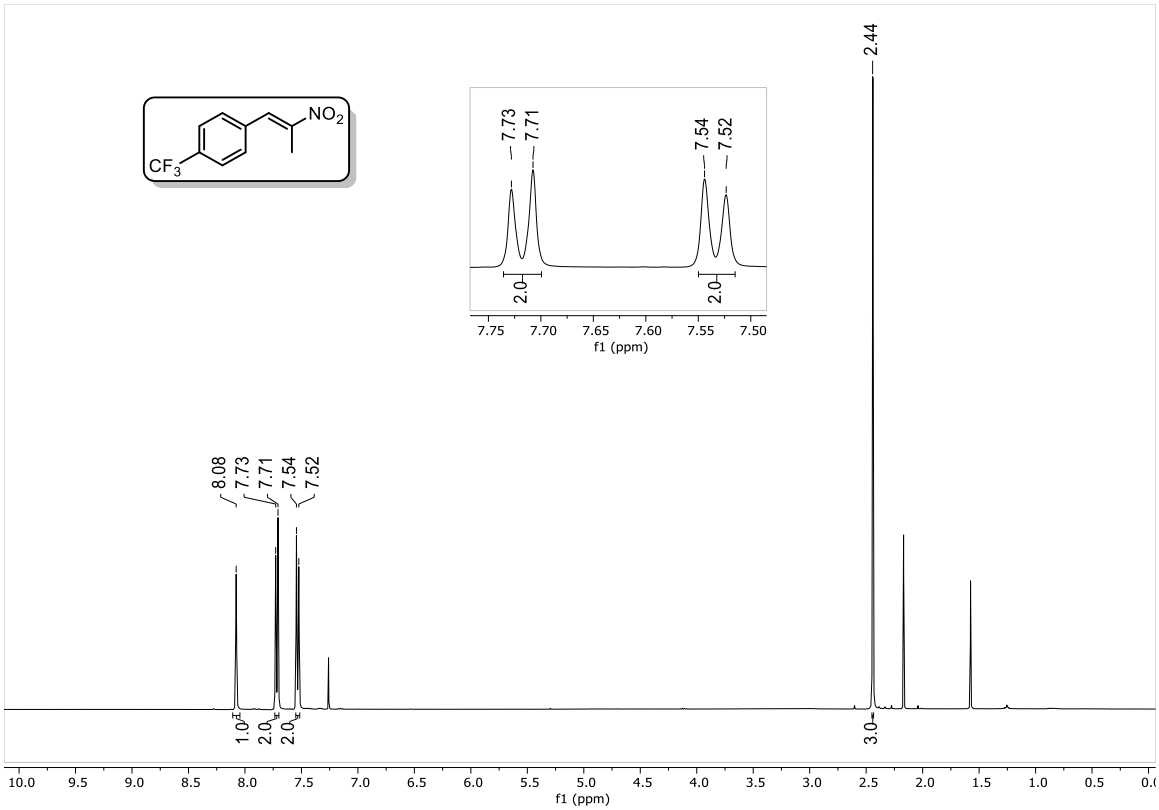
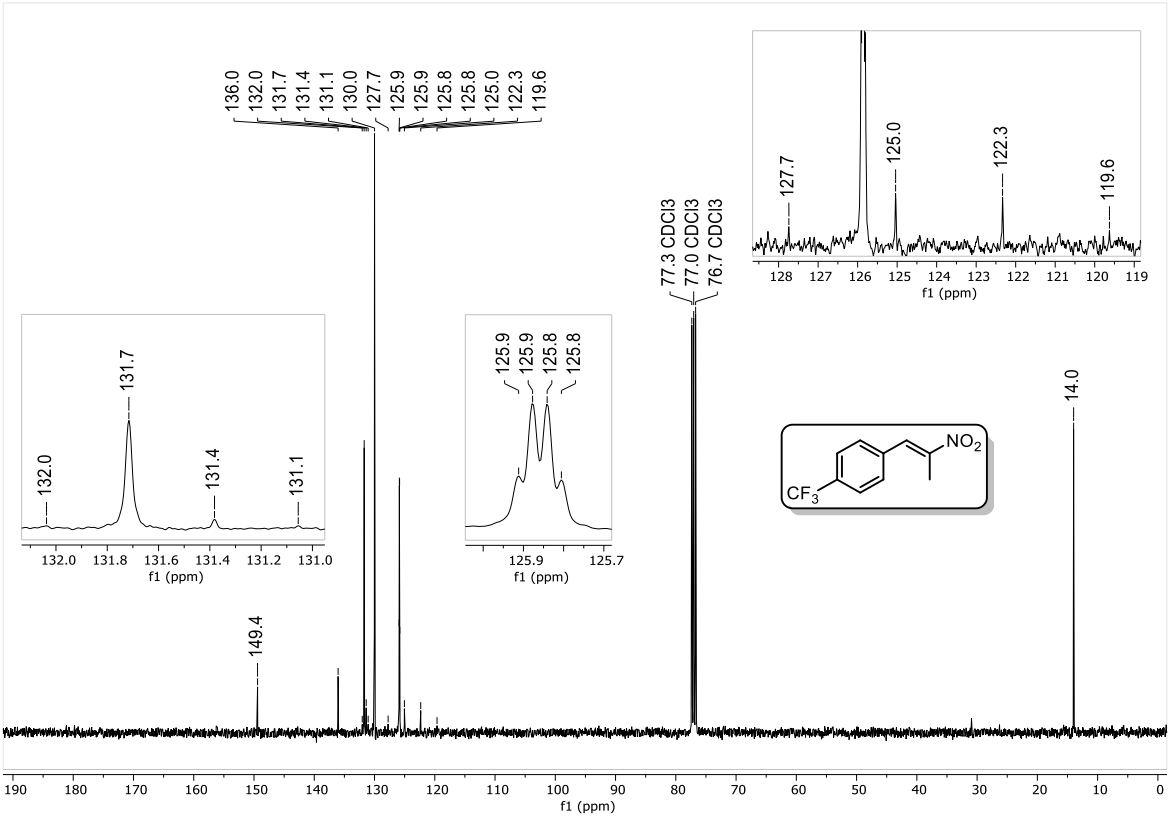


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
182.06182	58399.13	182.06173	0.09	0.49	$^{12}C_9{}^{1}H_9{}^{19}F_1{}^{14}N_1{}^{16}O_2$	5.5

Spectrum 18. HRMS of **6f**.



Spectrum 19. ^{1}H-NMR of **6g**.



Spectrum 20. ^{13}C-NMR of **6g**.

Description:
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History:Determine m/z[Peak Detect[Centroid,30,Area];Correct Base[];Smooth[5]];Correct Base[5.0%];Average(MS[...

Mass Calibration data:Cal_PEG_600
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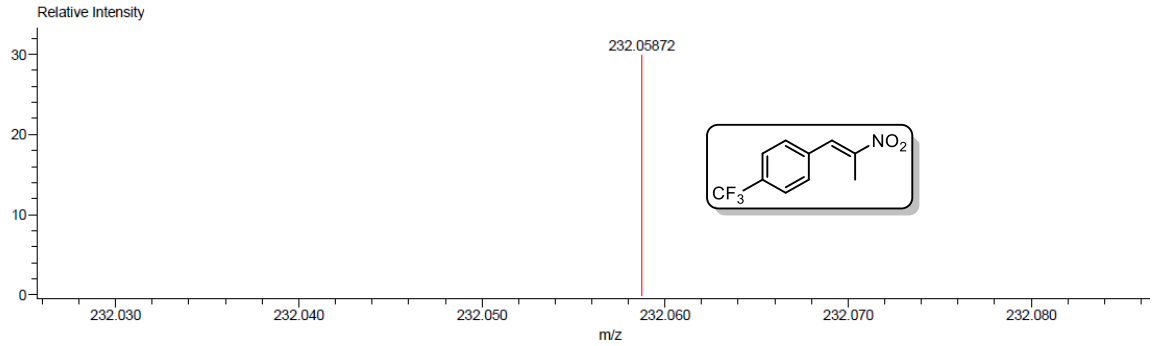
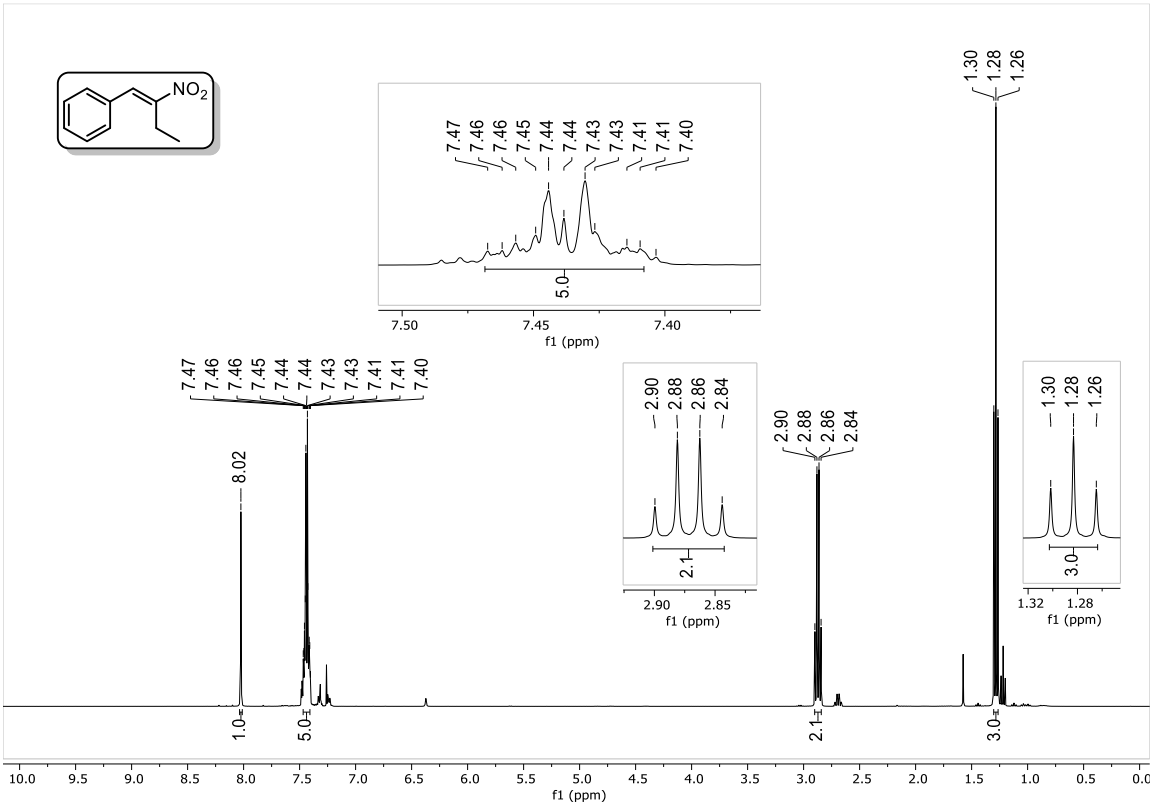
Created by:

Charge number:1 Tolerance:5.00(ppm), 5.00 .. 15.00(mmu) Unsaturation Number:-1.0 .. 60.0 (Fraction:Both)
Element:^{12}C:0 .. 10, ^{1}H:0 .. 28, ^{35}Cl:0 .. 0, ^{19}F:0 .. 3, ^{14}N:0 .. 1, ^{16}O:0 .. 2, ^{32}S:0 .. 0

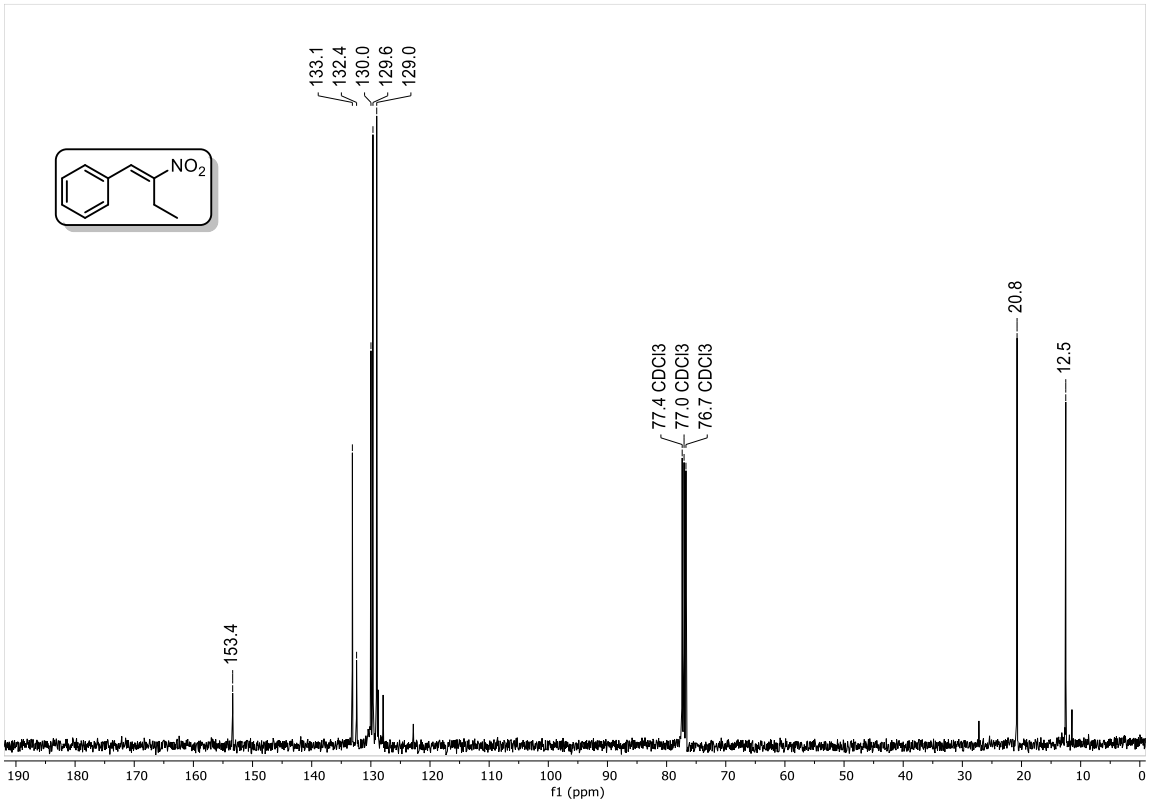


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
232.05872	23637.22	232.05854	0.18	0.79	$^{12}C_{10}{}^{1}H_{9}{}^{19}F_{3}{}^{14}N_{1}{}^{16}O_{2}$	5.5

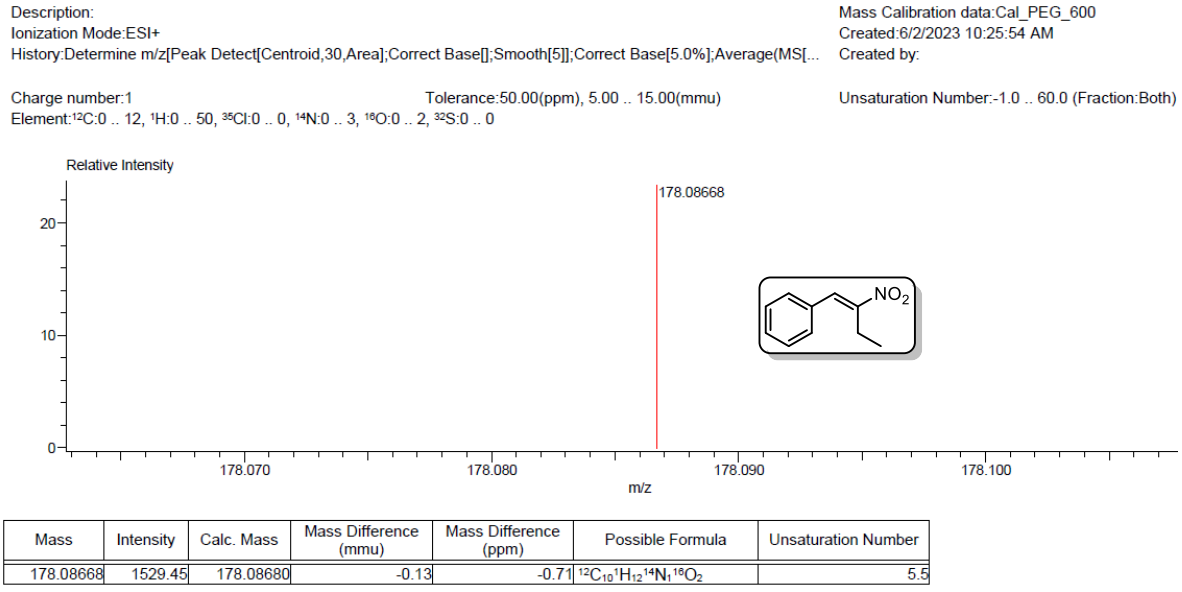
Spectrum 21. HRMS of **6g**.



Spectrum 22. ^{1}H-NMR of **6h**.

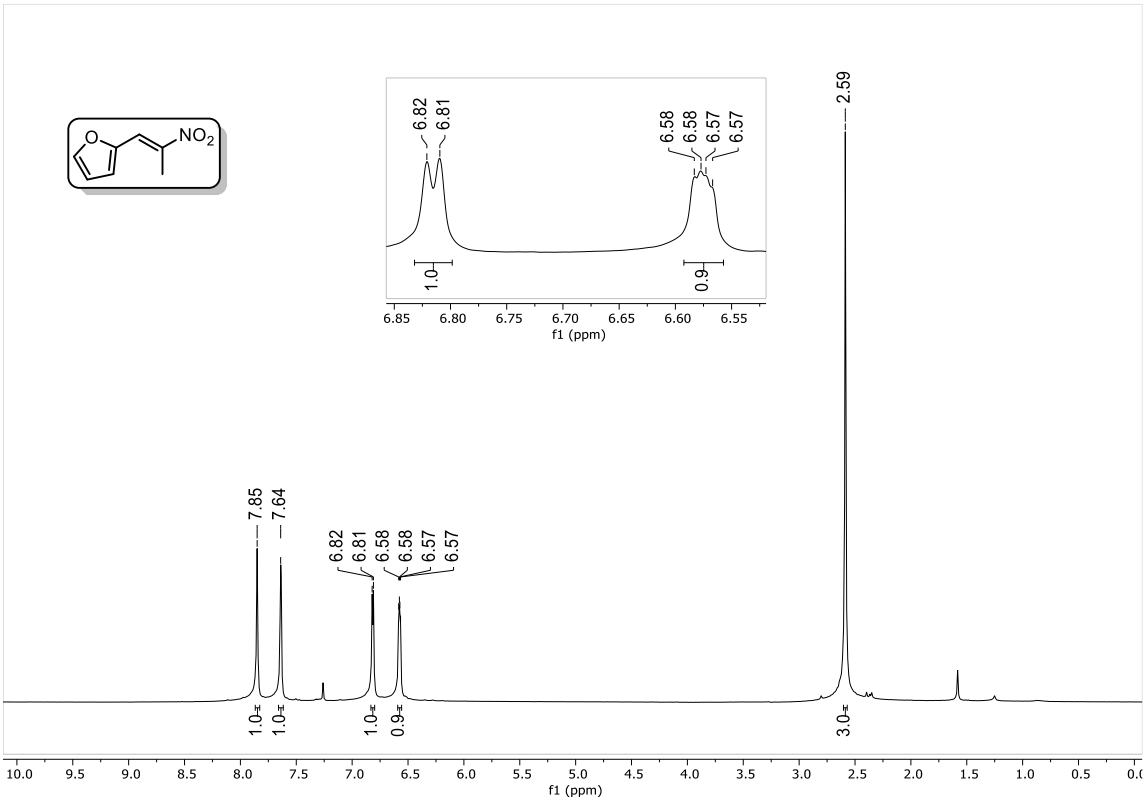


Spectrum 23. ^{13}C-NMR of **6h**.

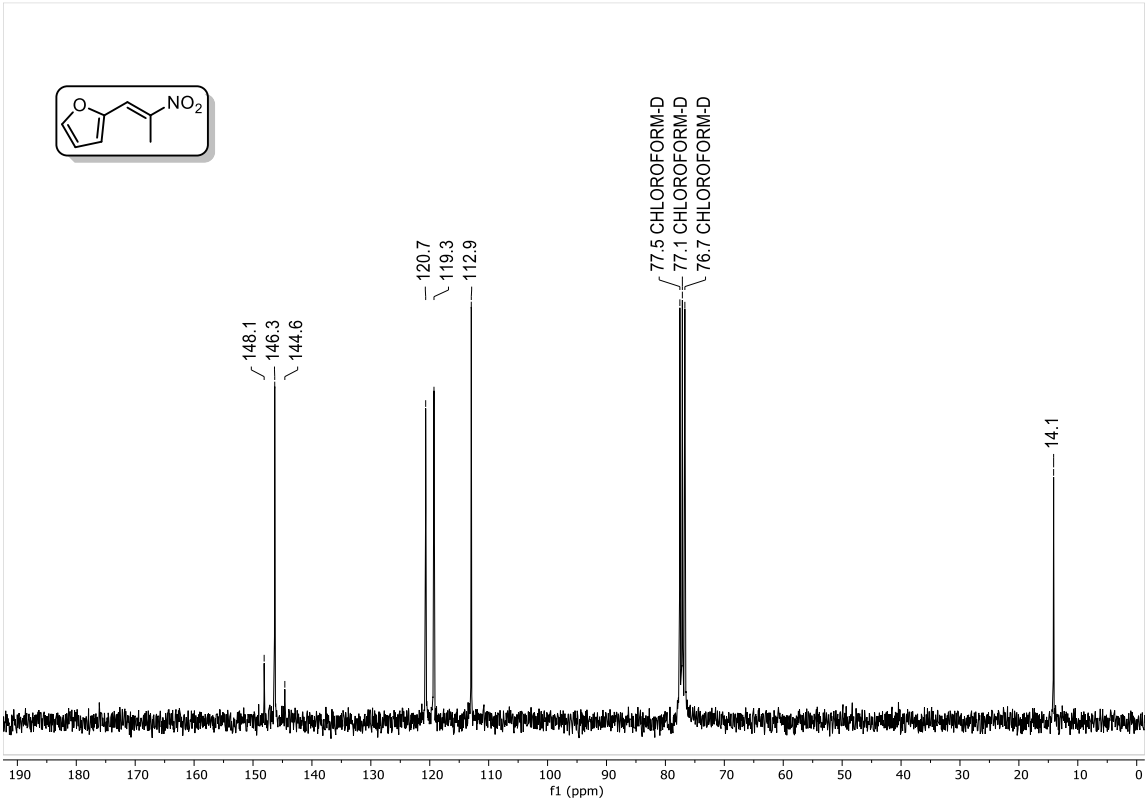


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
178.08668	1529.45	178.08680	-0.13	-0.71	$^{12}C_{10}{}^{1}H_{12}{}^{14}N_{1}{}^{16}O_{2}$	5.5

Spectrum 24. HRMS of **6h**.



Spectrum 25. ^{1}H-NMR of **6j**.



Spectrum 26. ^{13}C-NMR of **6j**.

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History:Determine m/z[Peak Detect[Centroid,30,Area];Correct Base[];Smooth[5]];Correct Base[5.0%];Average(MS[...

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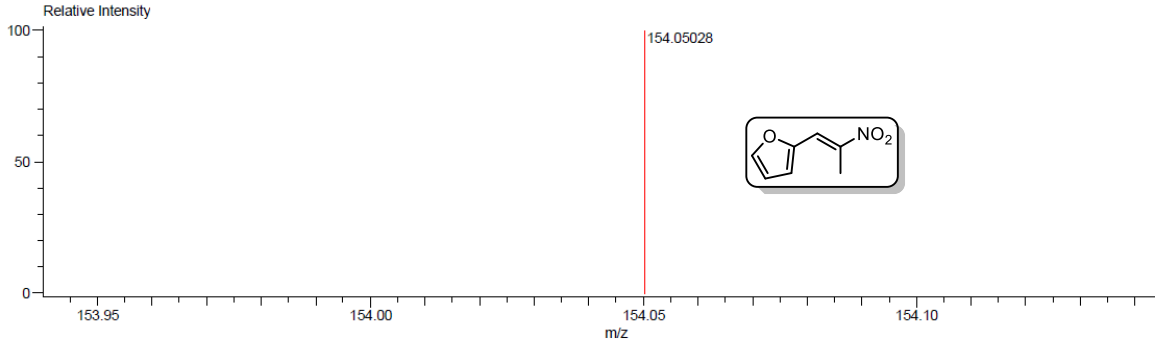
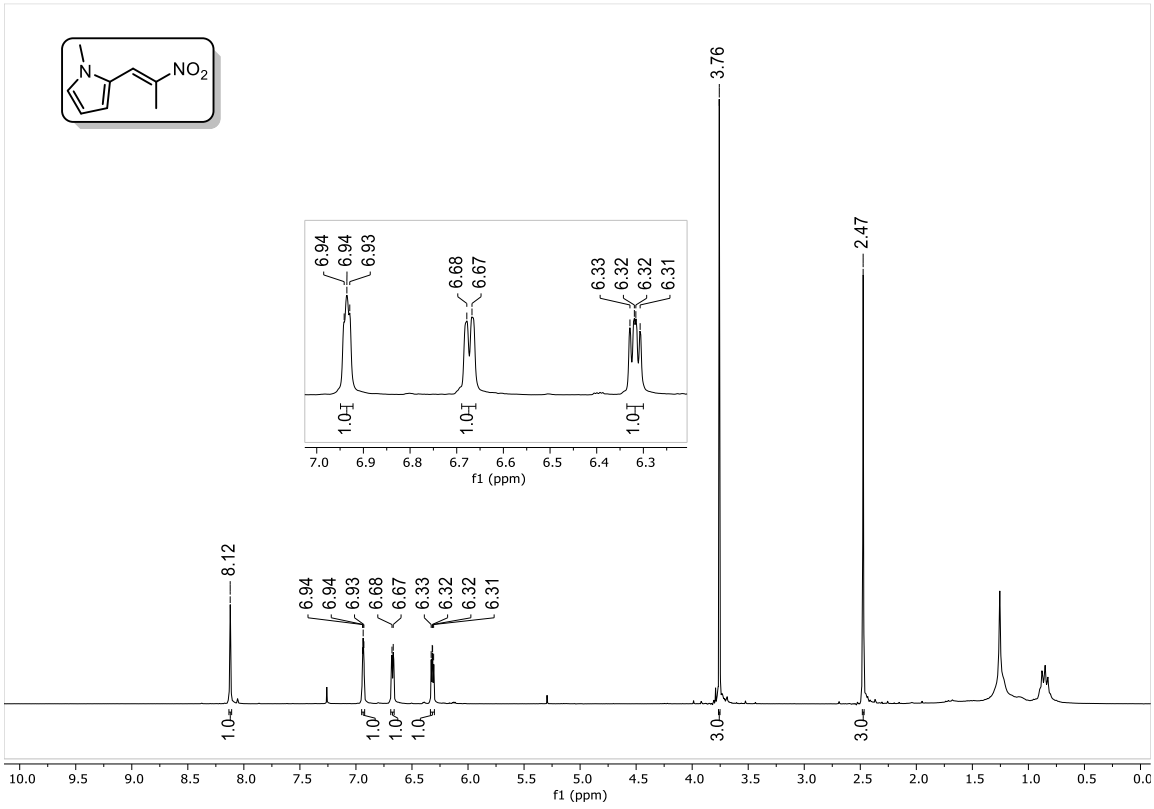
Element:^{12}C:0 .. 7, ^{1}H:0 .. 50, ^{35}Cl:0 .. 0, ^{14}N:0 .. 1, ^{16}O:0 .. 3, ^{32}S:0 .. 0

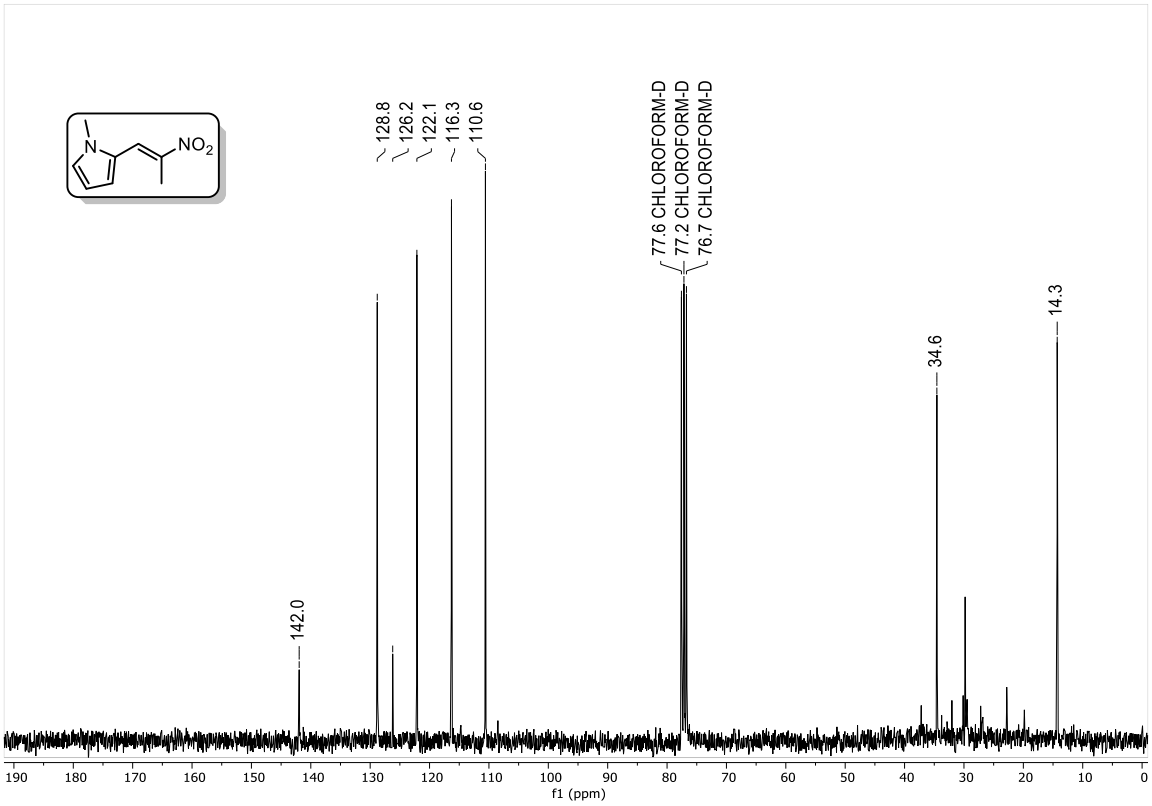


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
154.05028	92551.73	154.05042	-0.13	-0.87	$^{12}C_7{}^{1}H_8{}^{14}N_1{}^{16}O_3$	4.5

Spectrum 27. HRMS of **6j**.



Spectrum 28. ^{1}H-NMR of **6k**.



Spectrum 29. ^{13}C-NMR of **6k**.

Description:
Ionization Mode:ESI+
History:Determine m/z[Peak Detect[Centroid,30,Area];Correct Base[];Smooth[5]];Correct Base[5.0%];Average(MS[...

Mass Calibration data:Cal_PEG_600
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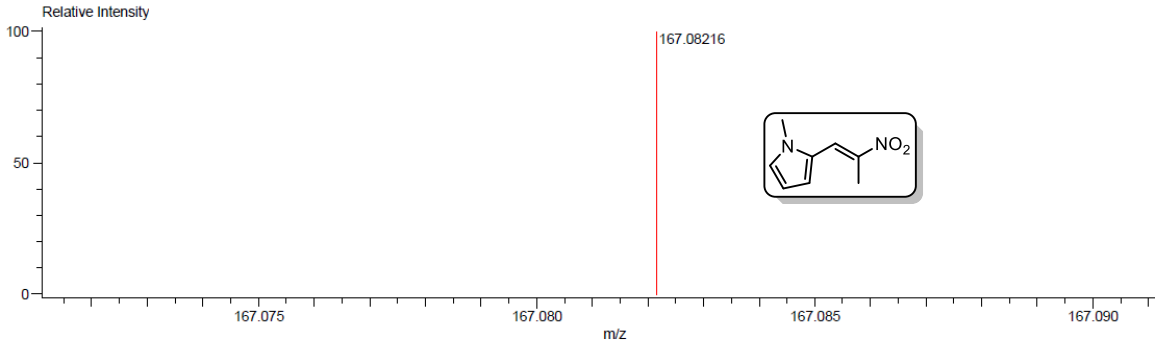
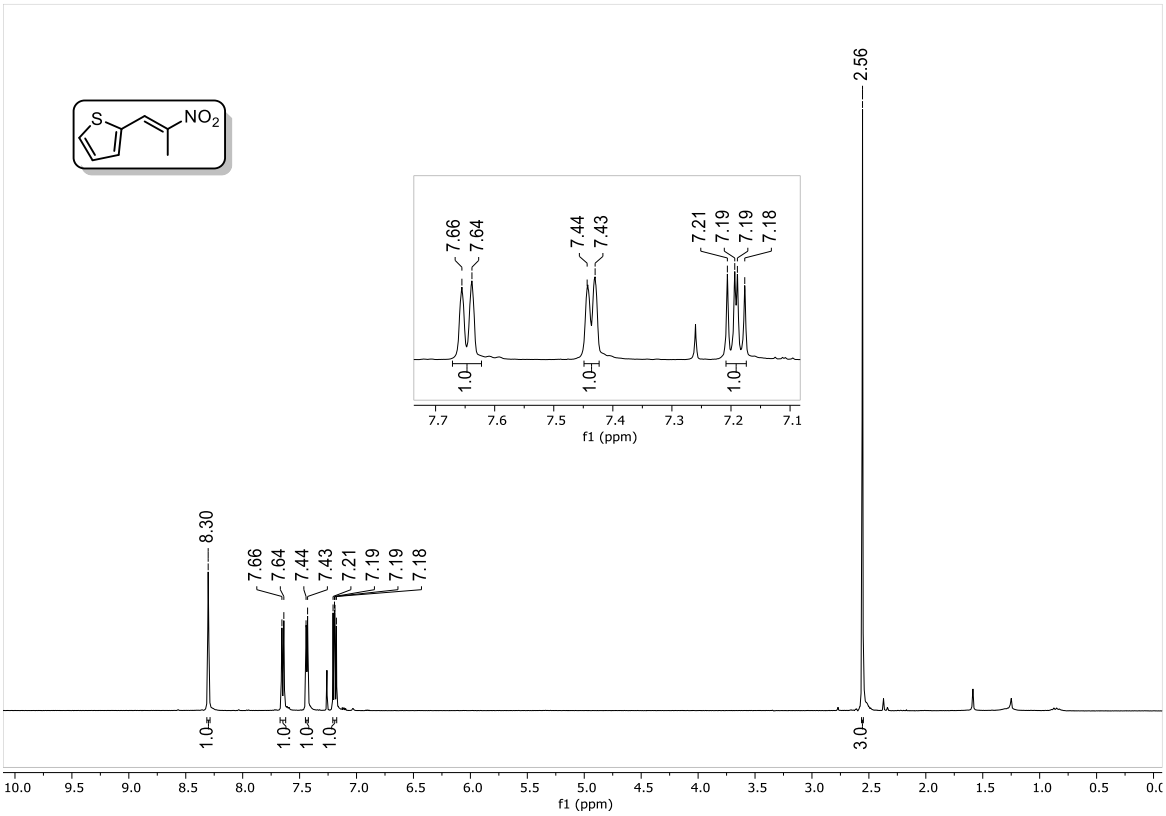
Created by:

Charge number:1 Tolerance:50.00(ppm), 5.00 .. 15.00(mmu) Unsaturation Number:-1.0 .. 60.0 (Fraction:Both)
Element:^{12}C:0 .. 8, ^{1}H:0 .. 50, ^{35}Cl:0 .. 0, ^{14}N:0 .. 2, ^{16}O:0 .. 2, ^{32}S:0 .. 0

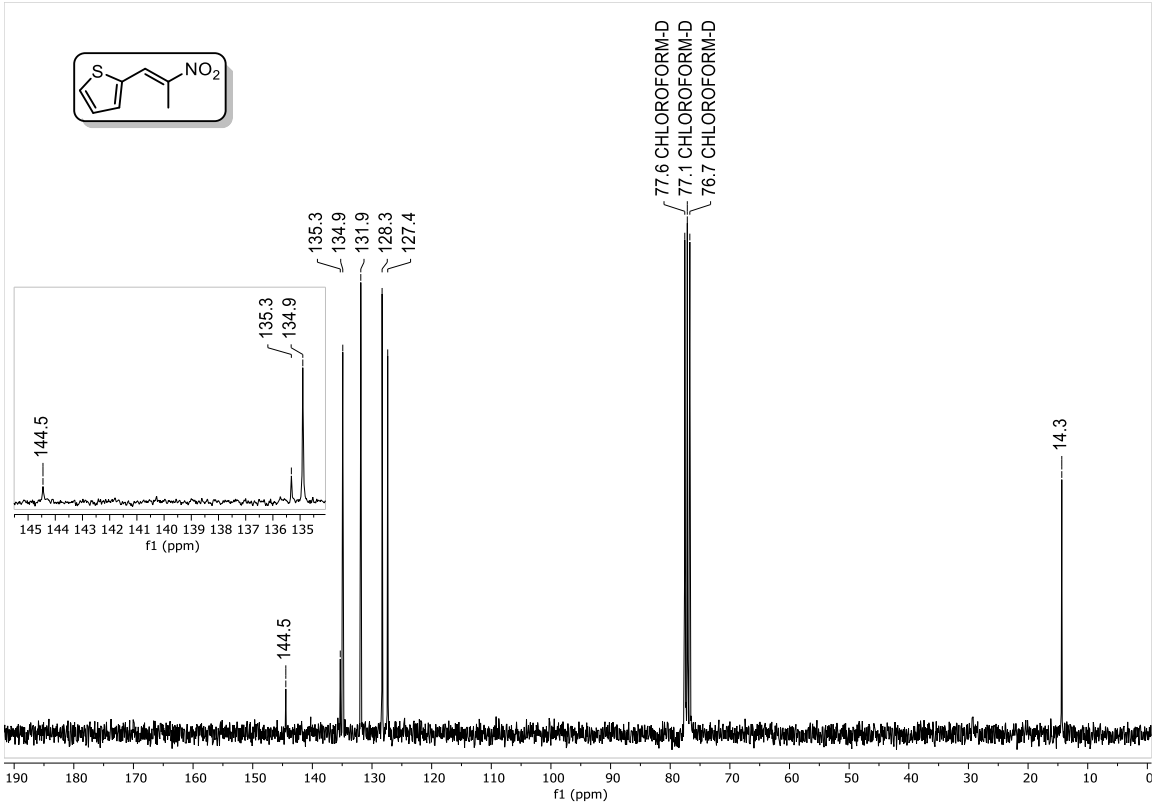


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
167.08216	6406.48	167.08205	0.11	0.66	$^{12}C_8{}^{1}H_{11}{}^{14}N_2{}^{16}O_2$	4.5

Spectrum 30. HRMS of **6k**.



Spectrum 31. ^{1}H-NMR of **6l**.



Spectrum 32. ^{13}C-NMR of **6l**.

Description:
Ionization Mode:ESI+
History:Determine m/z[Peak Detect[Centroid,30,Area];Correct Base[];Smooth[5]];Correct Base[5.0%];Average(MS[...

Mass Calibration data:Cal_PEG_600
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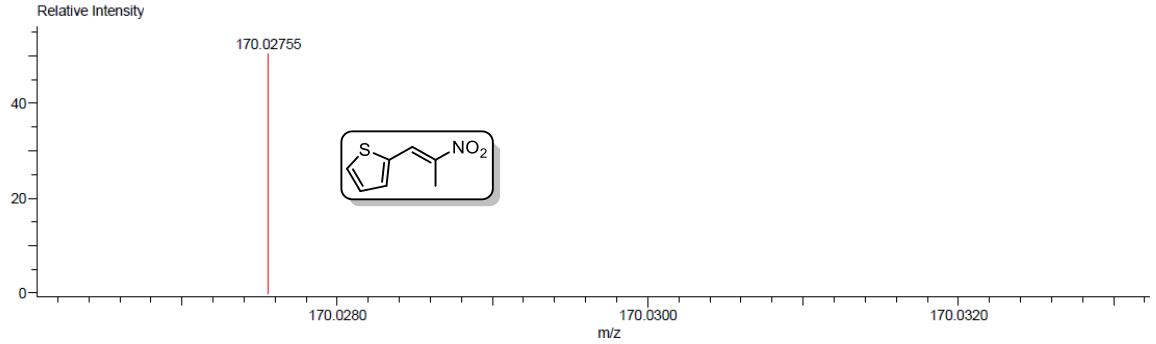
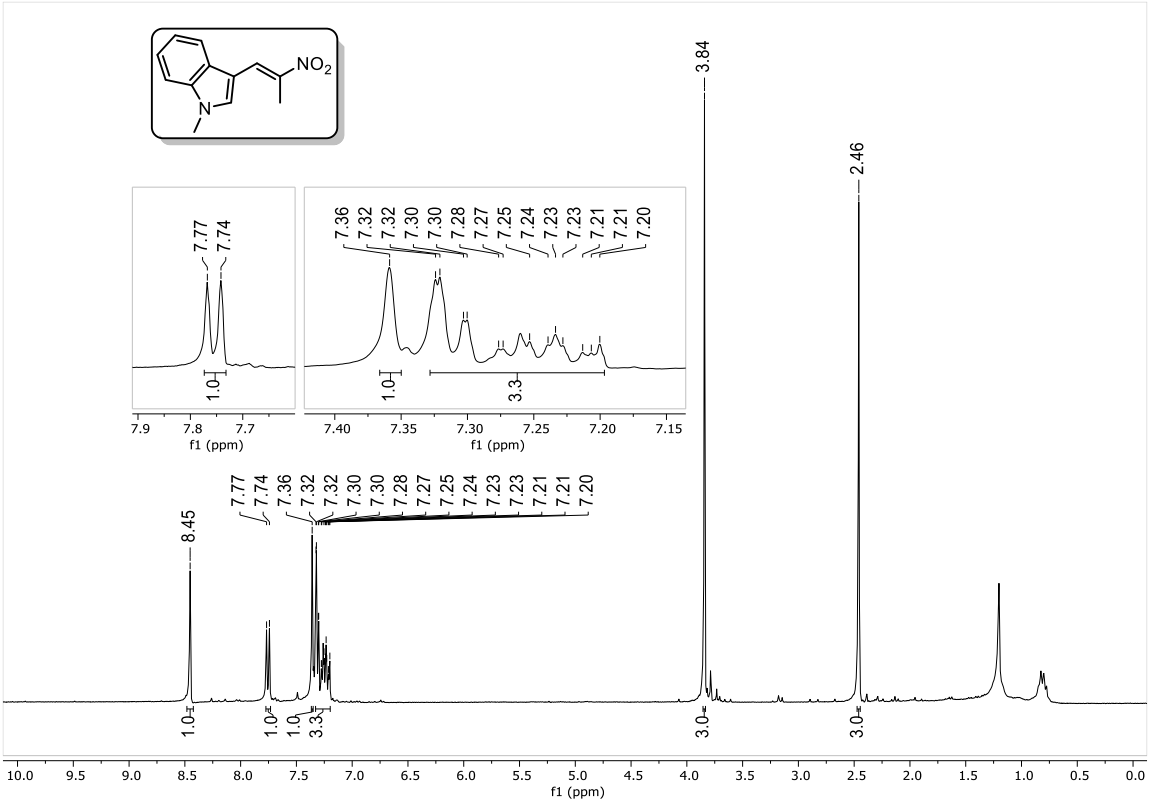
Charge number:1 Tolerance:50.00(ppm), 5.00 .. 15.00(mmu) Unsaturation Number:-1.0 .. 60.0 (Fraction:Both)
Element:^{12}C:0 .. 8, ^{1}H:0 .. 50, ^{35}Cl:0 .. 0, ^{14}N:0 .. 1, ^{16}O:0 .. 2, ^{32}S:0 .. 1

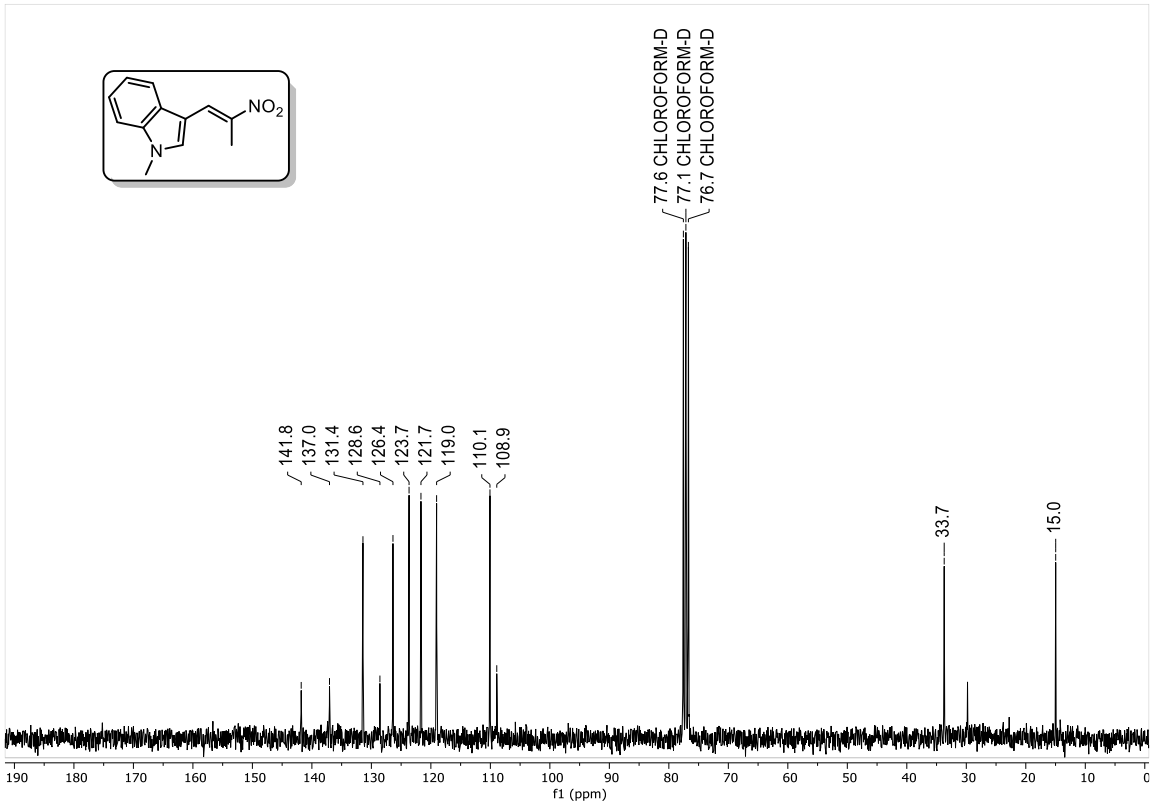


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
170.02755	3602.55	170.02757	-0.02	-0.12	$^{12}C_7{}^{1}H_8{}^{14}N_1{}^{16}O_2{}^{32}S_1$	5.5

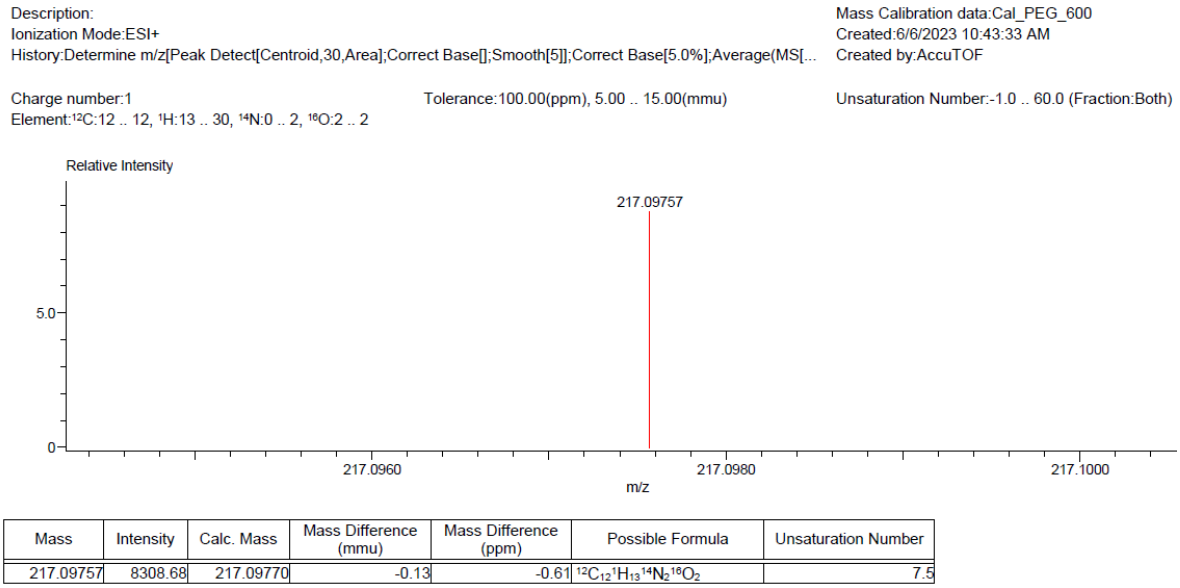
Spectrum 33. HRMS of **6l**.



Spectrum 34. ^{1}H-NMR of **6m**.

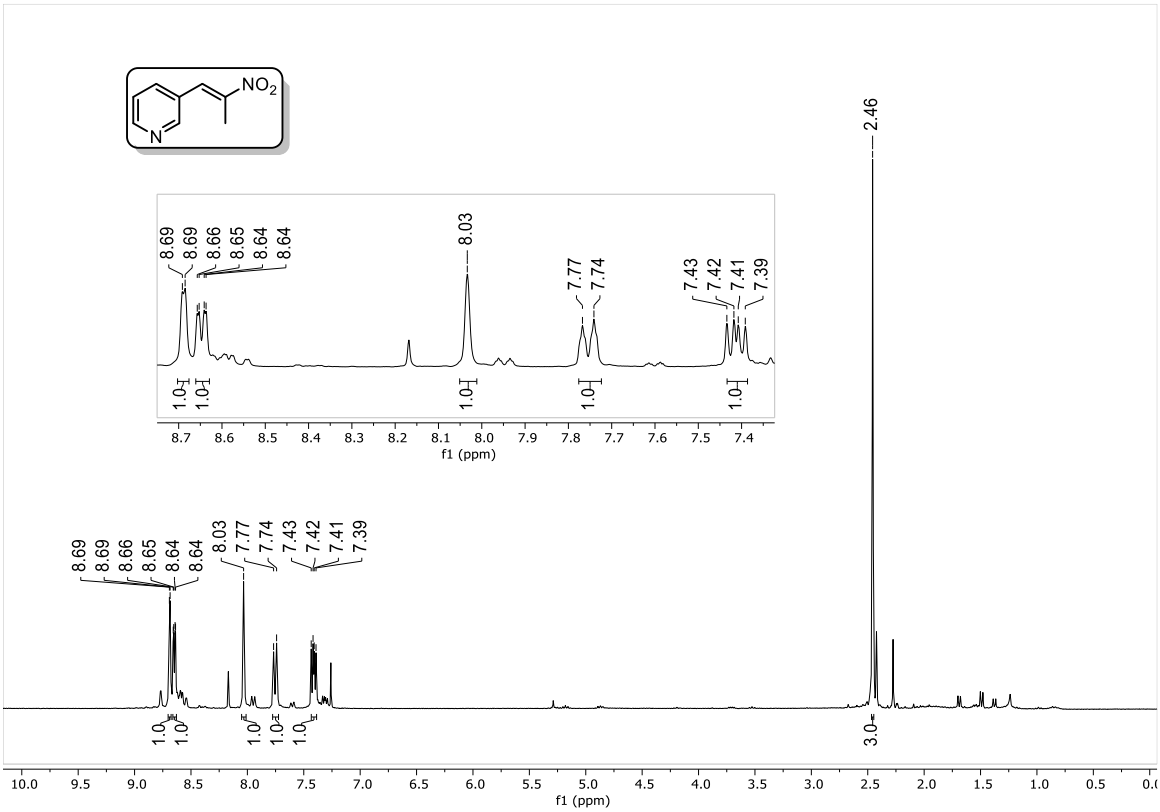


Spectrum 35. ^{13}C-NMR of **6m**.

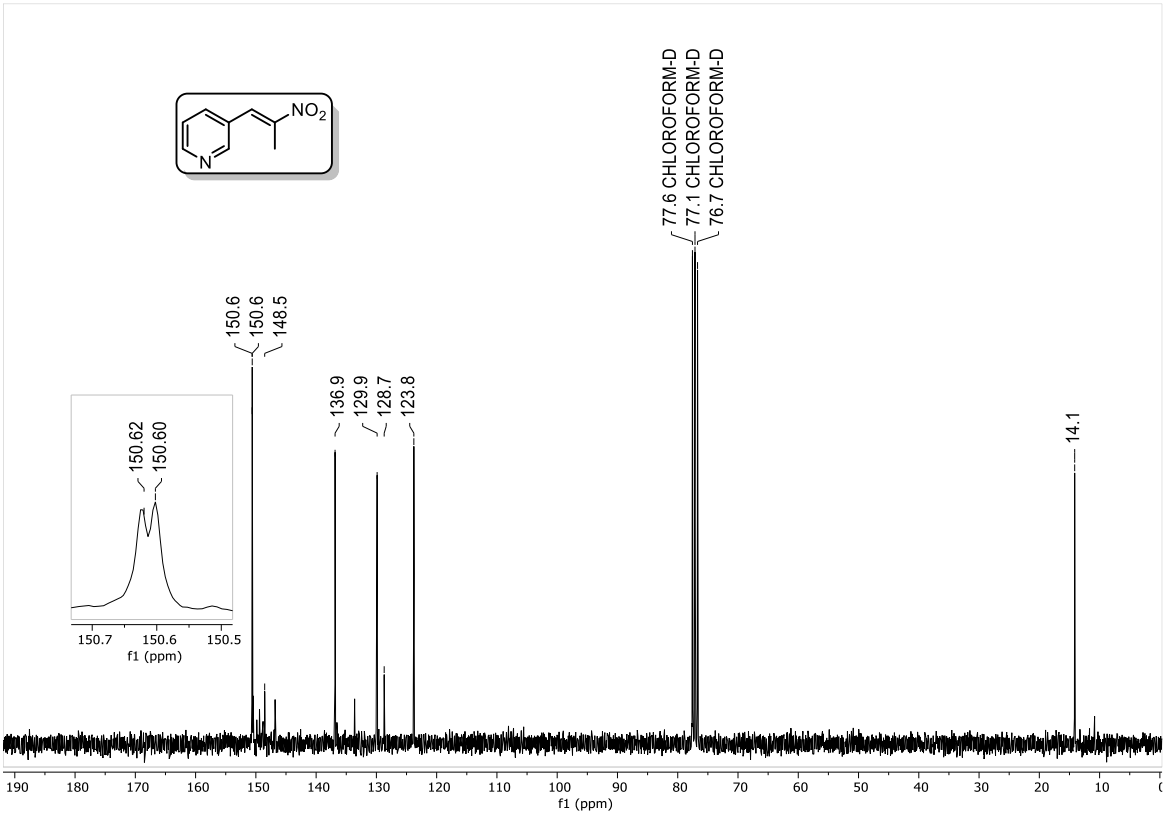


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
217.09757	8308.68	217.09770	-0.13	-0.61	$^{12}C_{12}{}^{1}H_{13}{}^{14}N_2{}^{16}O_2$	7.5

Spectrum 36. HRMS of **6m**.



Spectrum 37. ^{1}H-NMR of **6n**.

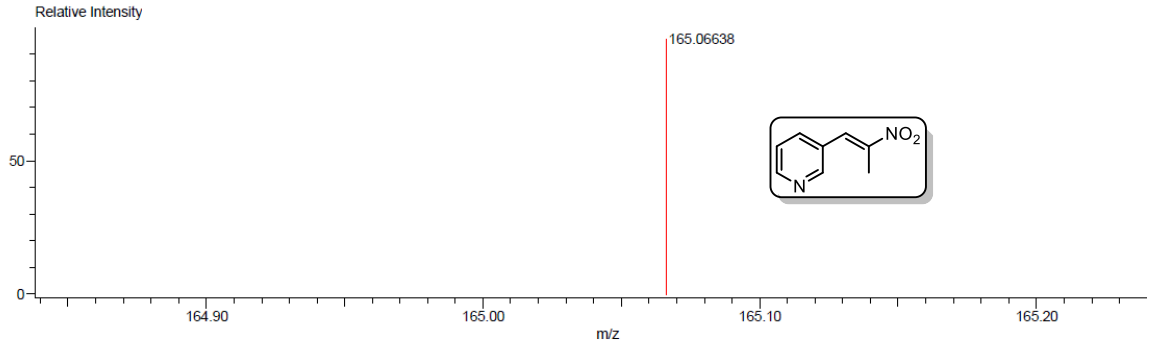


Spectrum 38. ^{13}C-NMR of **6n**.

Description:
Ionization Mode:ESI+
History:Determine m/z[Peak Detect[Centroid,30,Area];Correct Base[];Smooth[5]];Correct Base[5.0%];Average(MS[...

Mass Calibration data:Cal_PEG_600
Created:6/2/2023 10:20:25 AM
Created by:

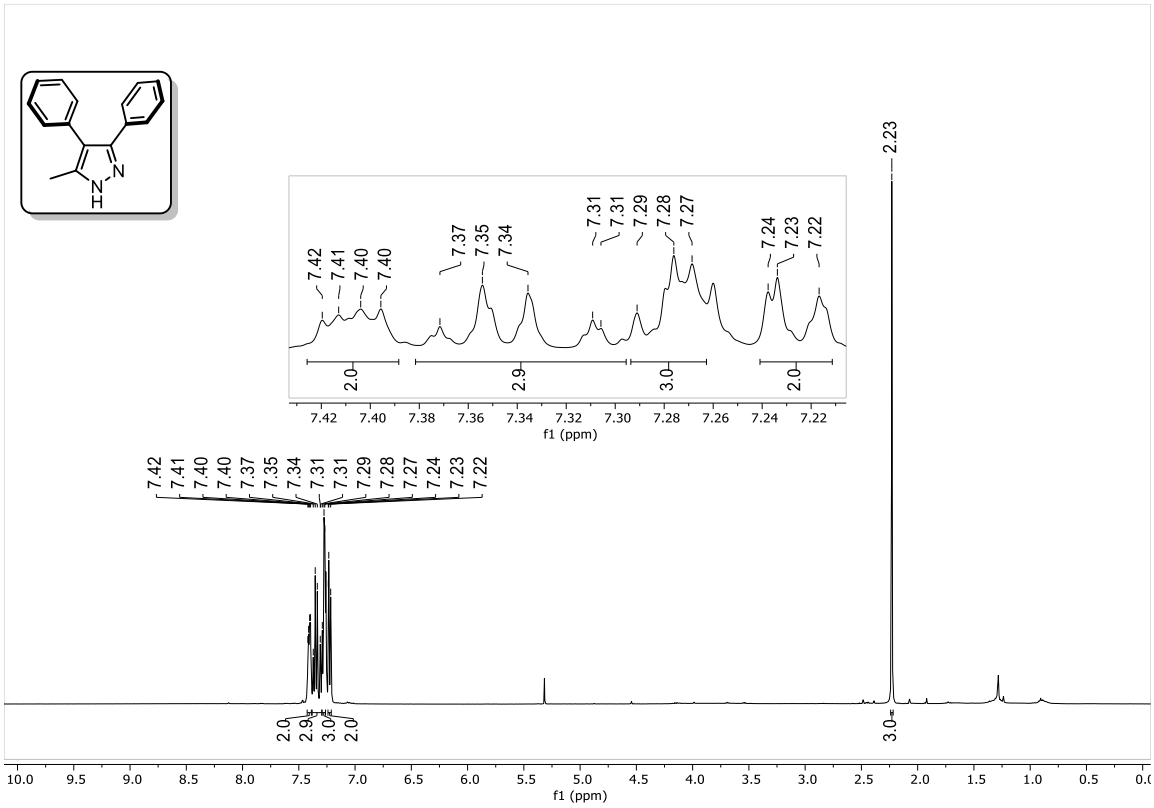
Charge number:1
Tolerance:50.00(ppm), 5.00 .. 15.00(mmu)
Unsaturation Number:-1.0 .. 60.0 (Fraction:Both)
Element:^{12}C:0 .. 12, ^{1}H:0 .. 50, ^{35}Cl:0 .. 0, ^{14}N:0 .. 3, ^{16}O:0 .. 2, ^{32}S:0 .. 0



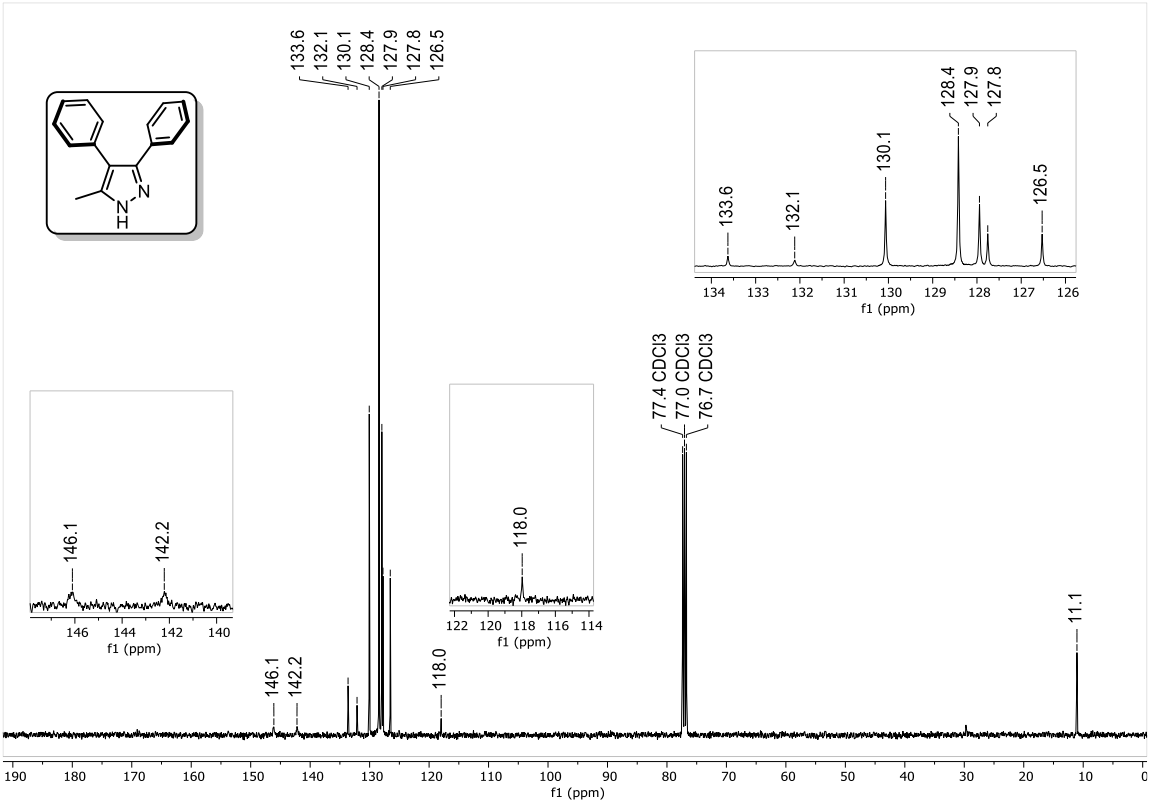
Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
165.06638	3005.60	165.06640	-0.02	-0.11	$^{12}C_8{}^{1}H_9{}^{14}N_2{}^{16}O_2$	5.5

Spectrum 39. HRMS of **6n**.

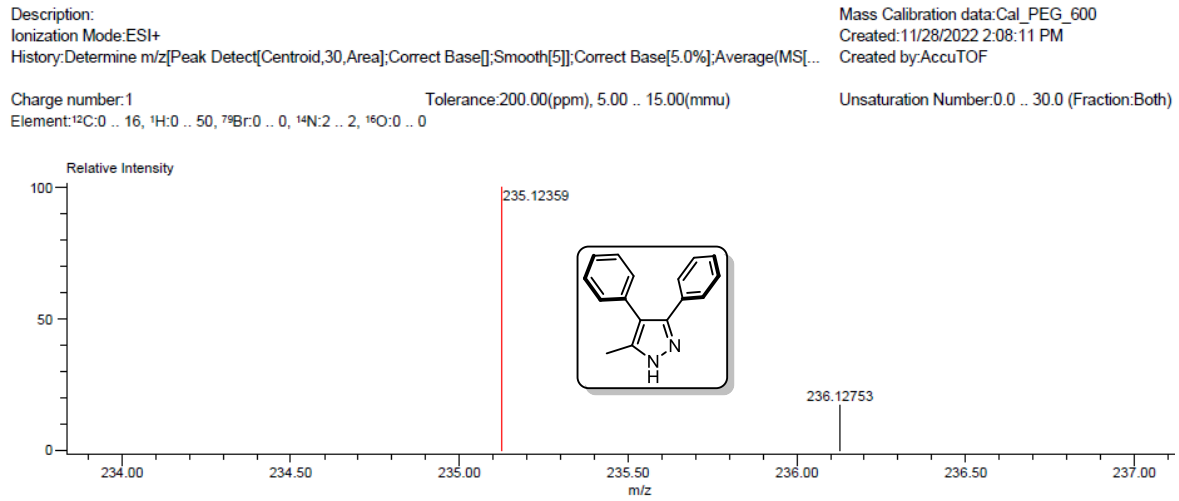
^{1}H-NMR, ^{13}C-NMR, and HRMS spectra of the pyrazoles.



Spectrum 40. ^{1}H-NMR of **8a**.

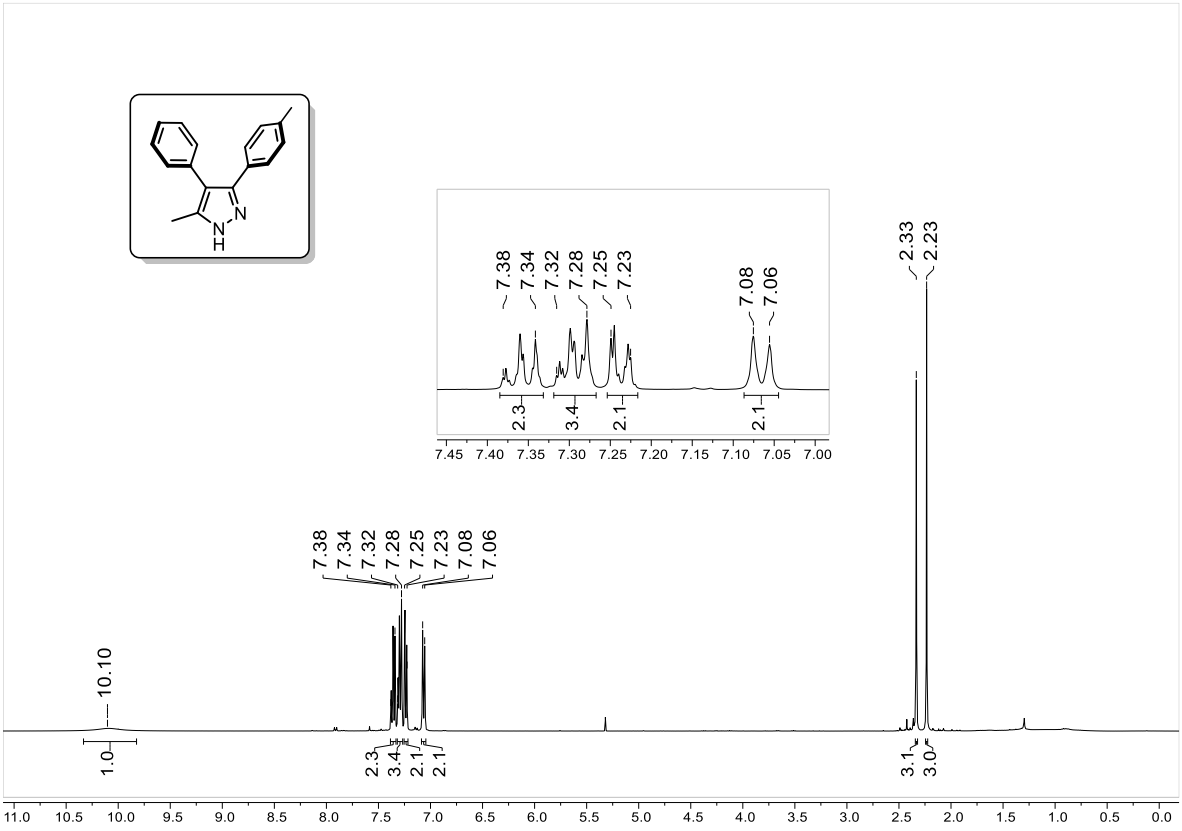


Spectrum 41. ^{13}C-NMR of **8a**.

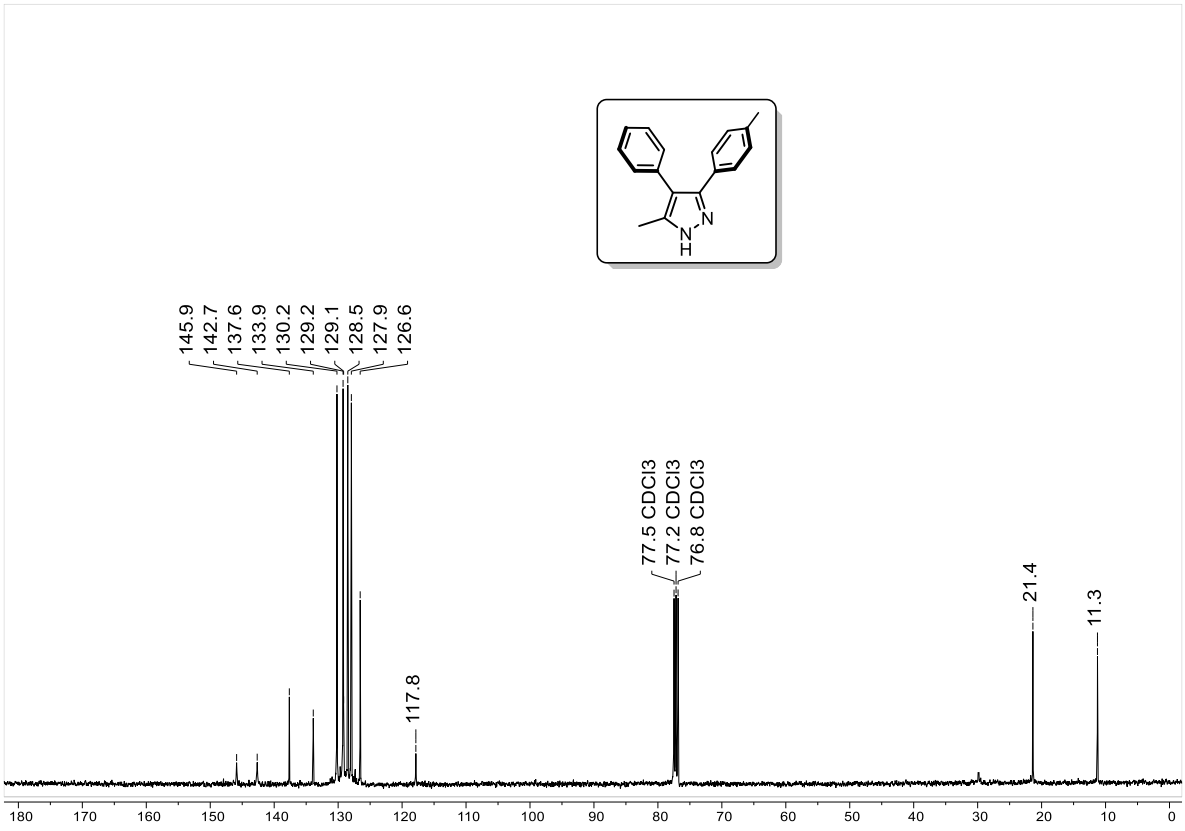


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
235.12359	176868.61	235.12352	0.06	0.27	$^{12}C_{16}{}^{1}H_{15}{}^{14}N_2$	10.5

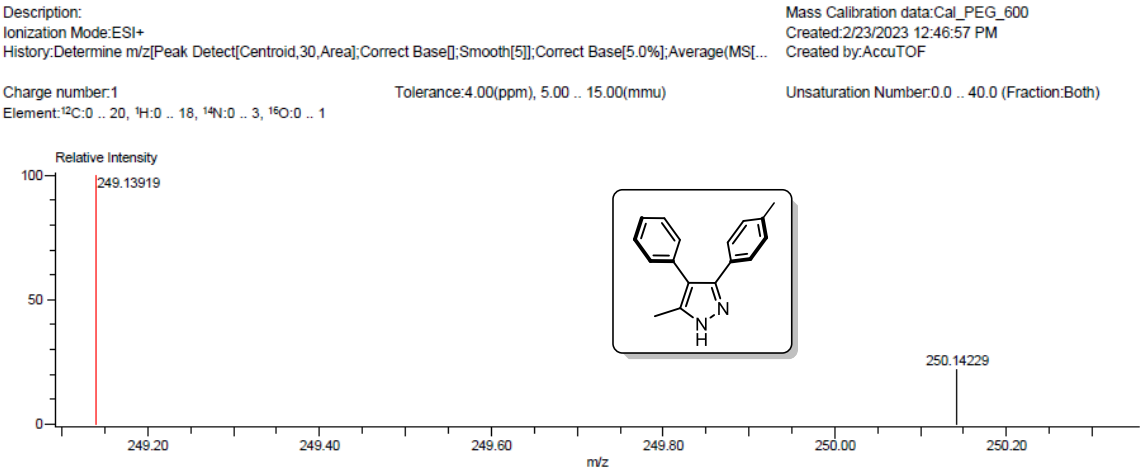
Spectrum 42. HRMS of **8a**.



Spectrum 43. ^{1}H-NMR of **8b**.

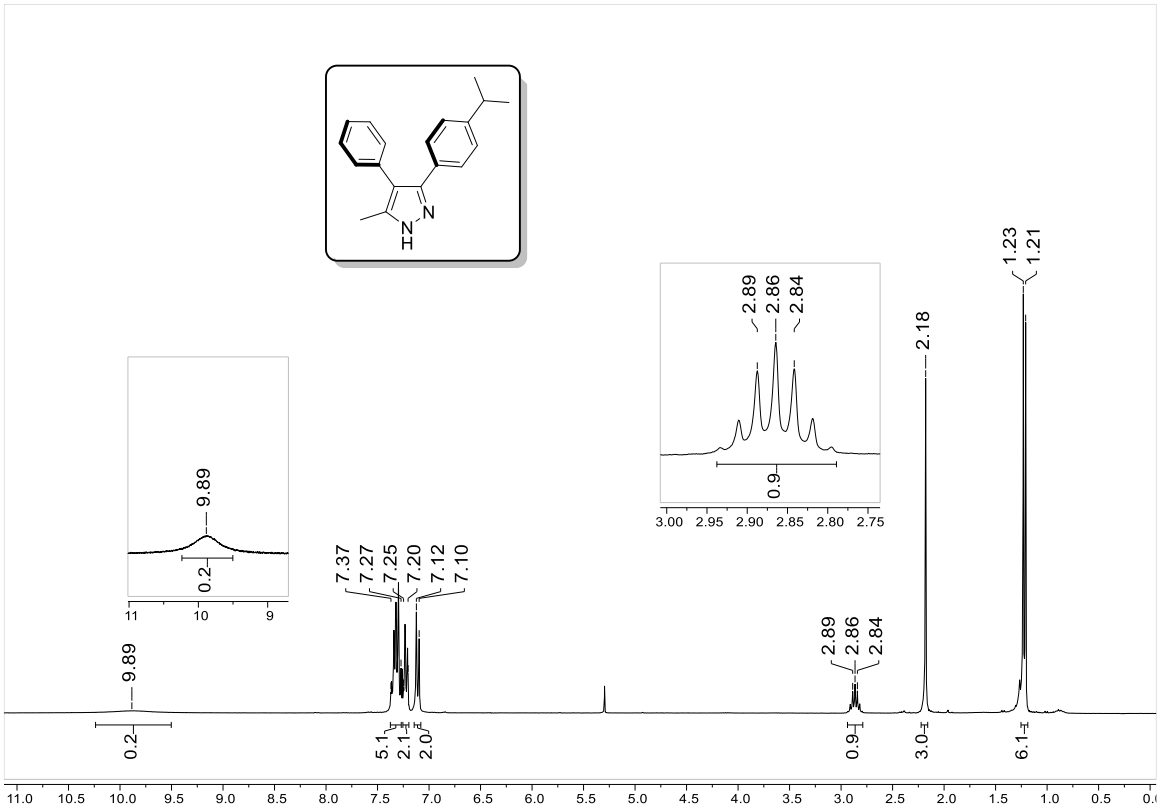


Spectrum 44. ^{13}C-NMR of **8b**.

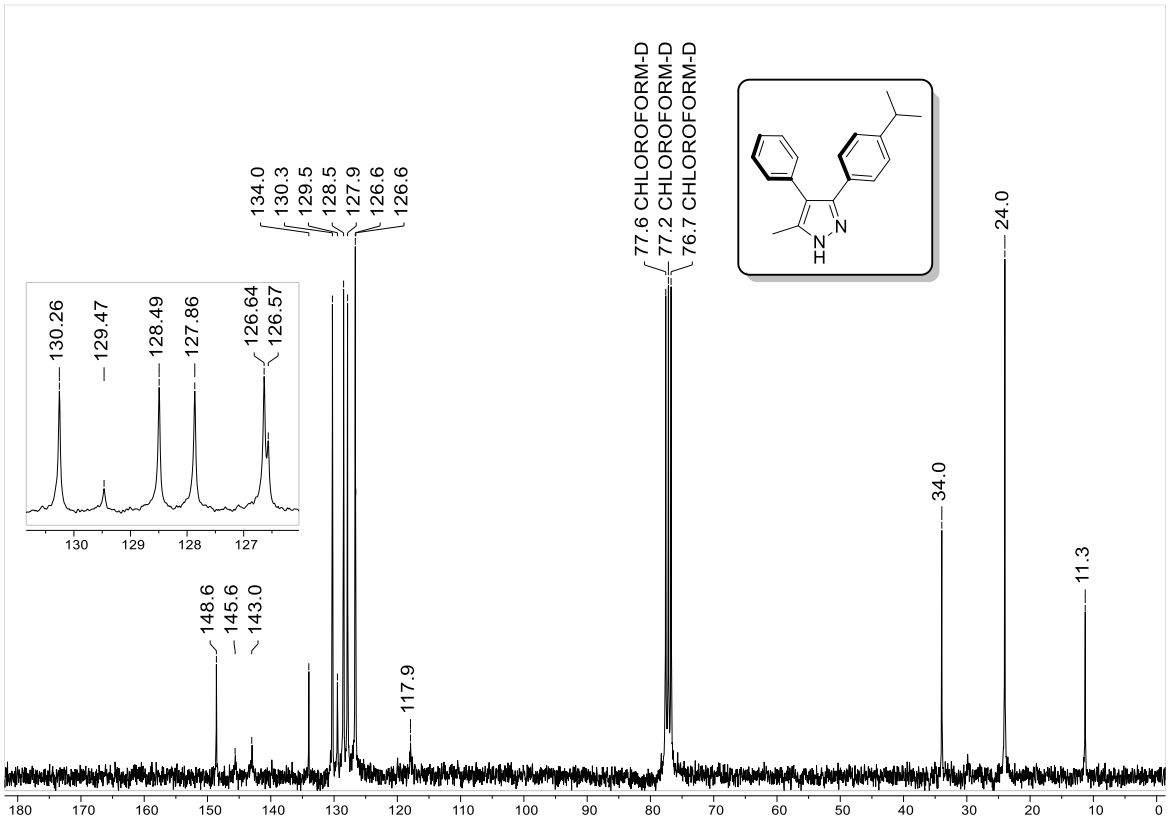


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
249.13919	5395.11	249.13917	0.02	0.07	$^{12}C_{17}{}^{1}H_{17}{}^{14}N_2$	10.5

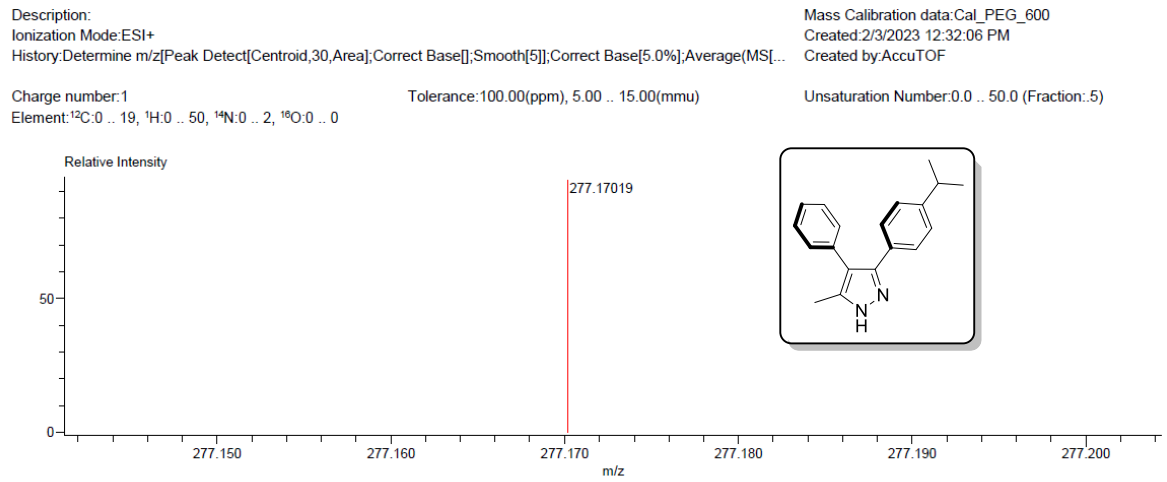
Spectrum 45. HRMS of **8b**.



Spectrum 46. ^{1}H-NMR of **8c**.

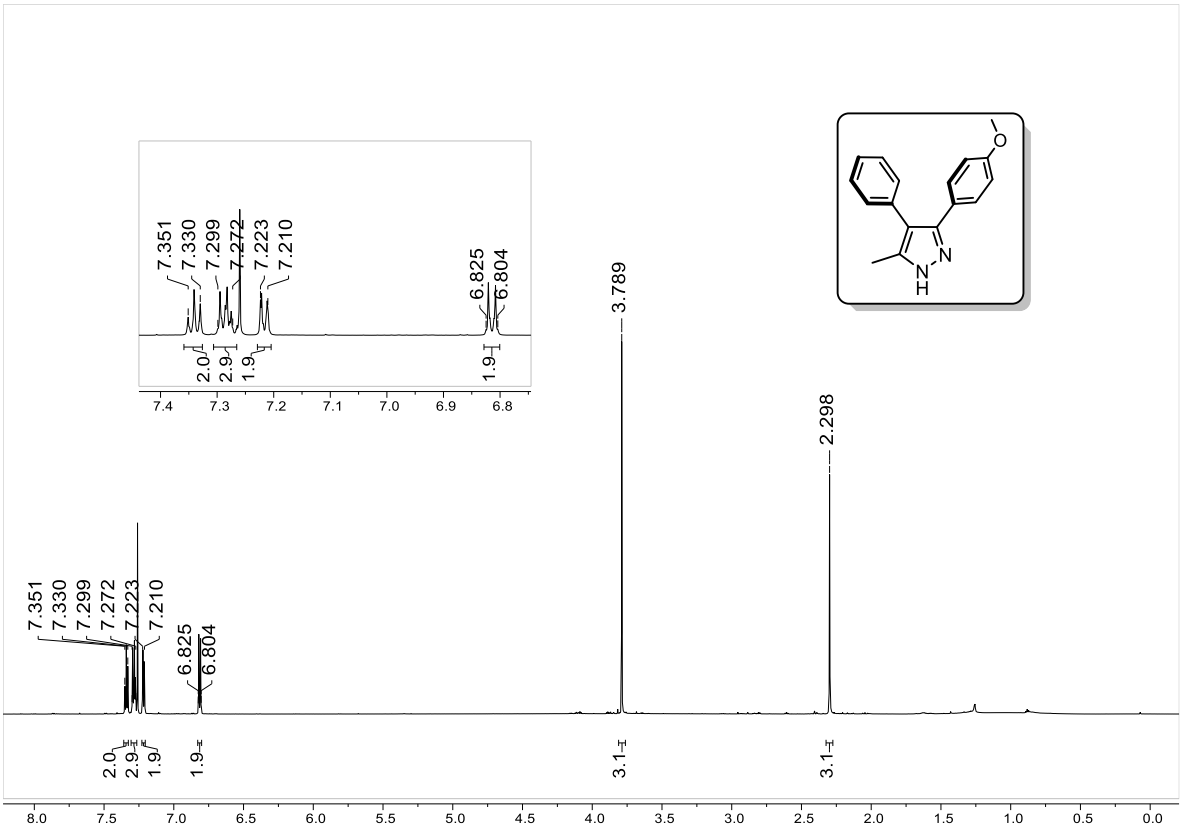


Spectrum 47. ^{13}C-NMR of **8c**.

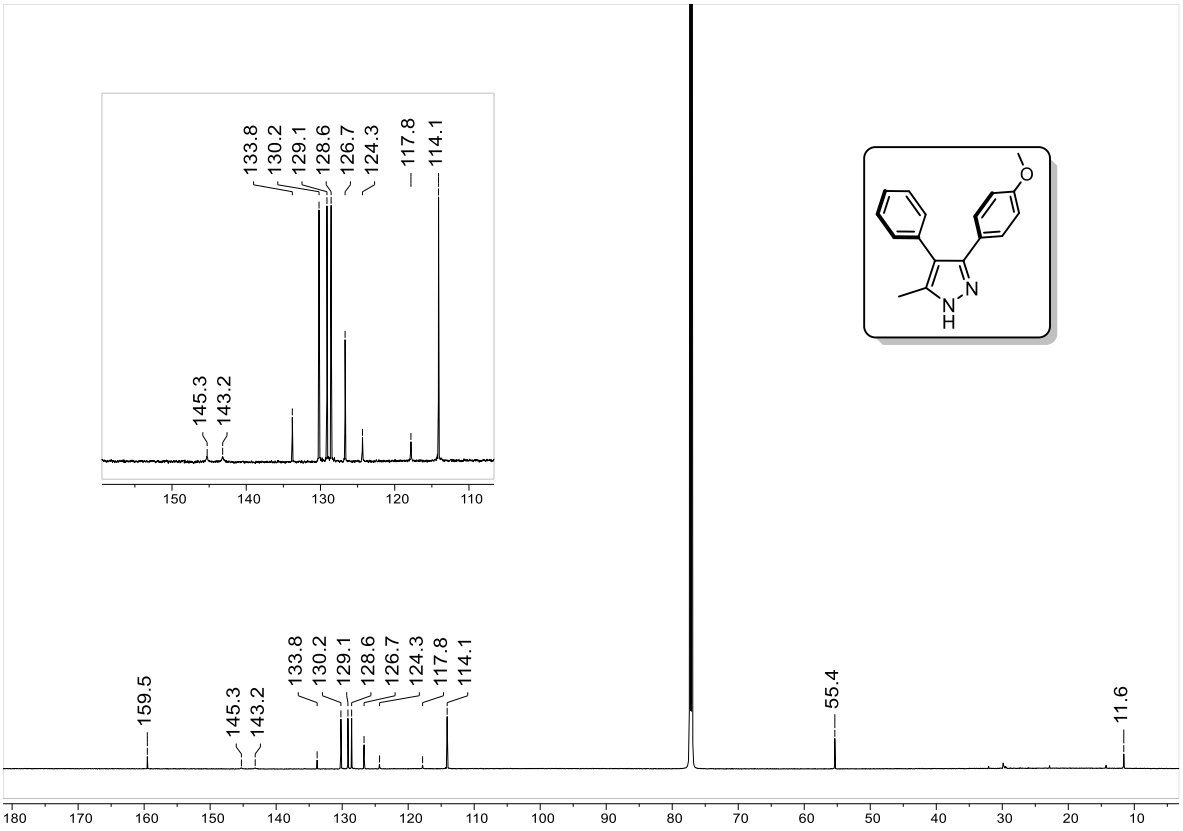


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
277.17019	3715.29	277.17047	-0.28	-1.01	$^{12}C_{19}{}^{1}H_{21}{}^{14}N_2$	10.5

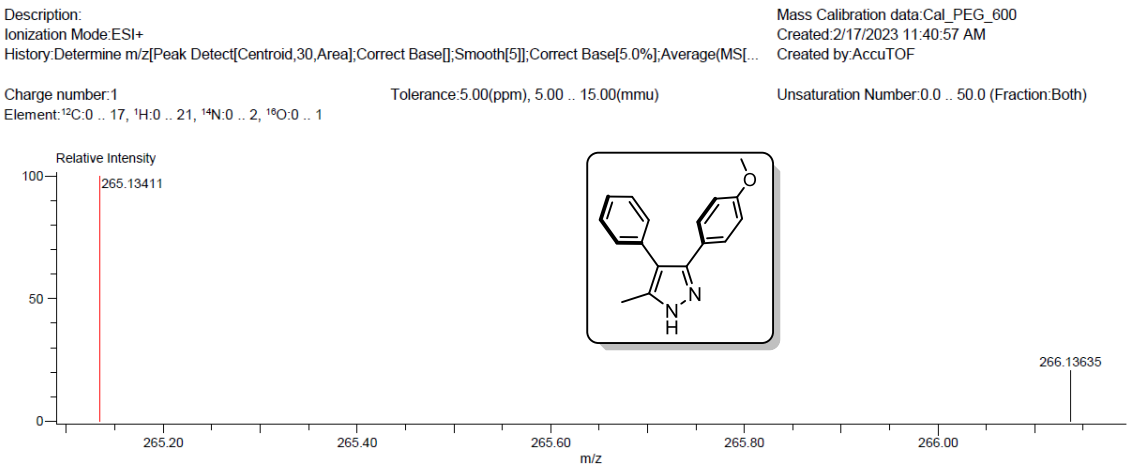
Spectrum 48. HRMS of **8c**.



Spectrum 49. ^{1}H-NMR of **8d**.

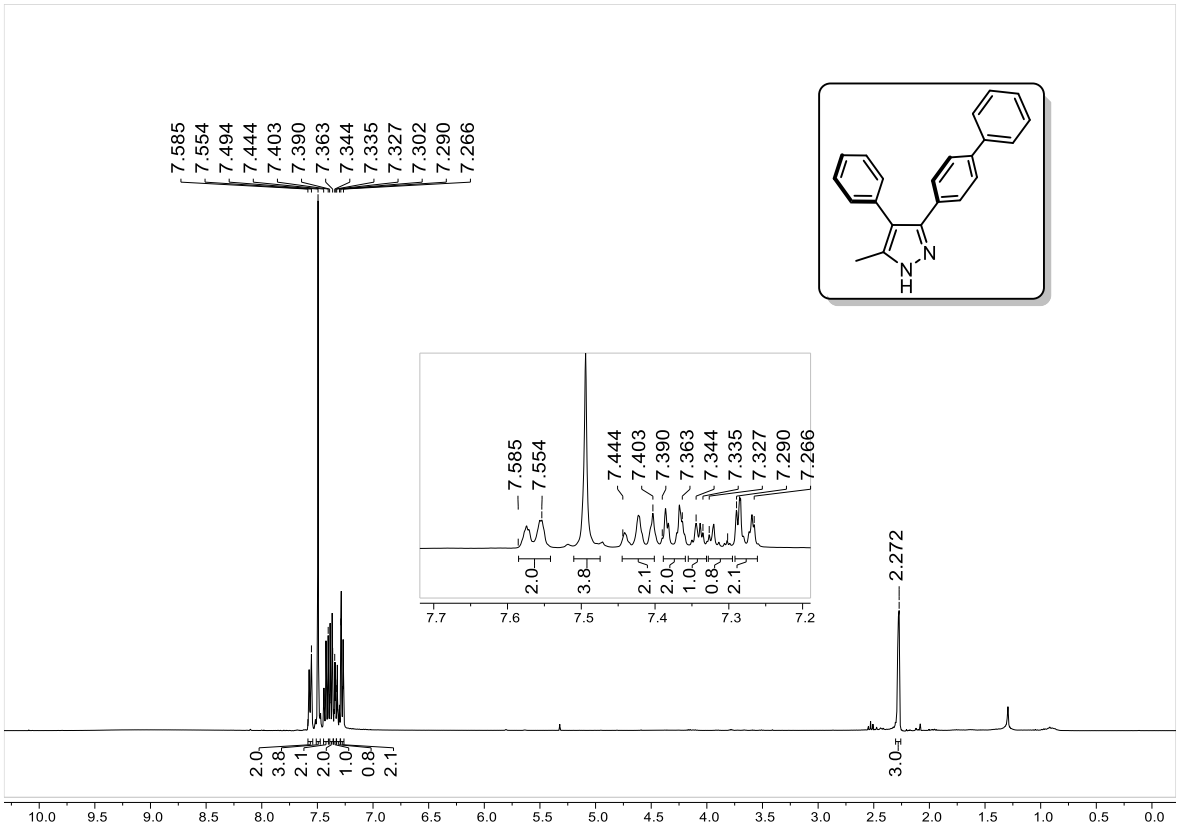


Spectrum 50. ^{13}C-NMR of **8d**.

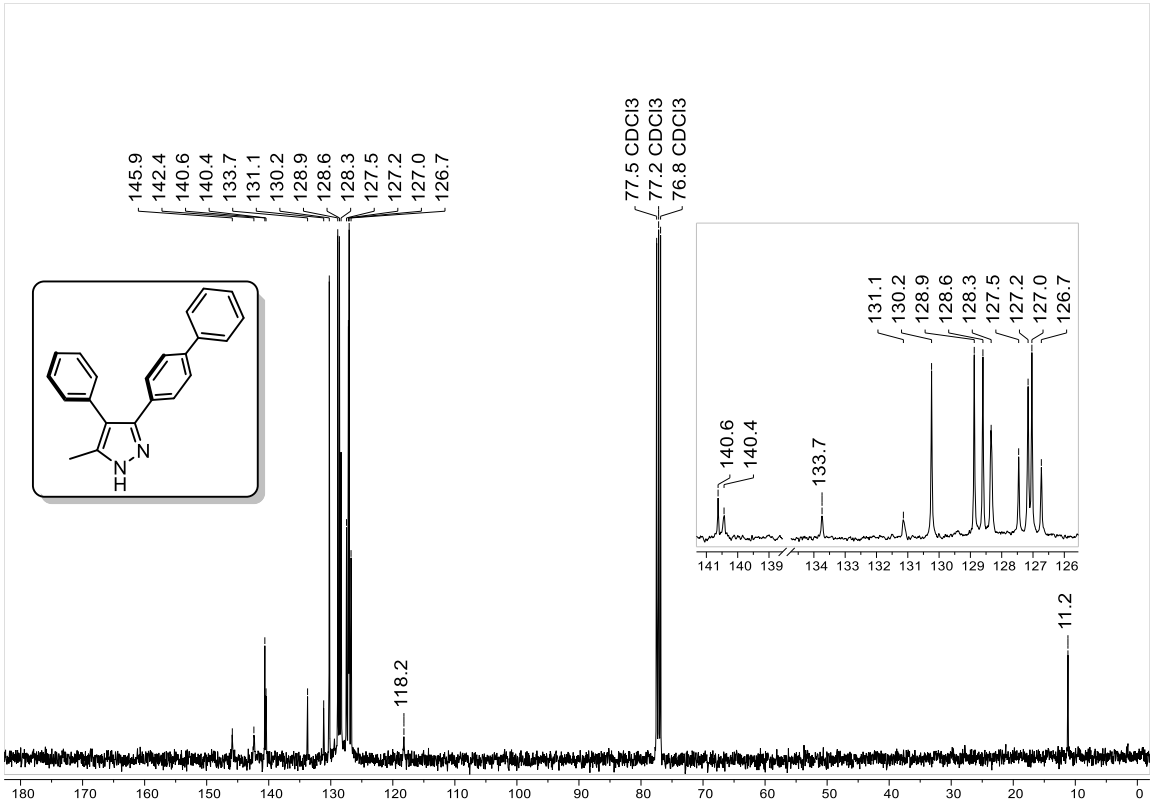


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
265.13411	13136.52	265.13409	0.02	0.08	$^{12}C_{17}{}^{1}H_{17}{}^{14}N_{2}{}^{16}O_{1}$	10.5

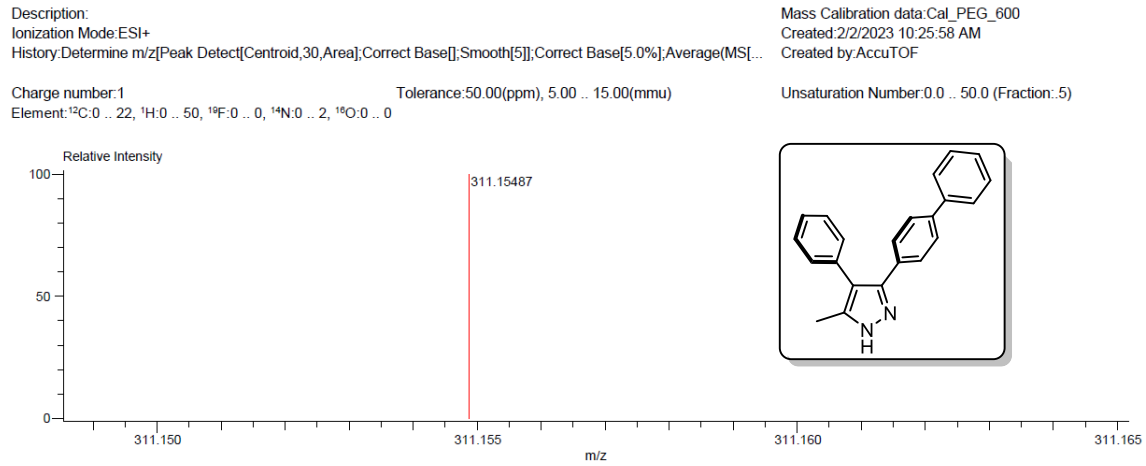
Spectrum 51. HRMS of **8d**.



Spectrum 52. ^{1}H-NMR of **8e**.

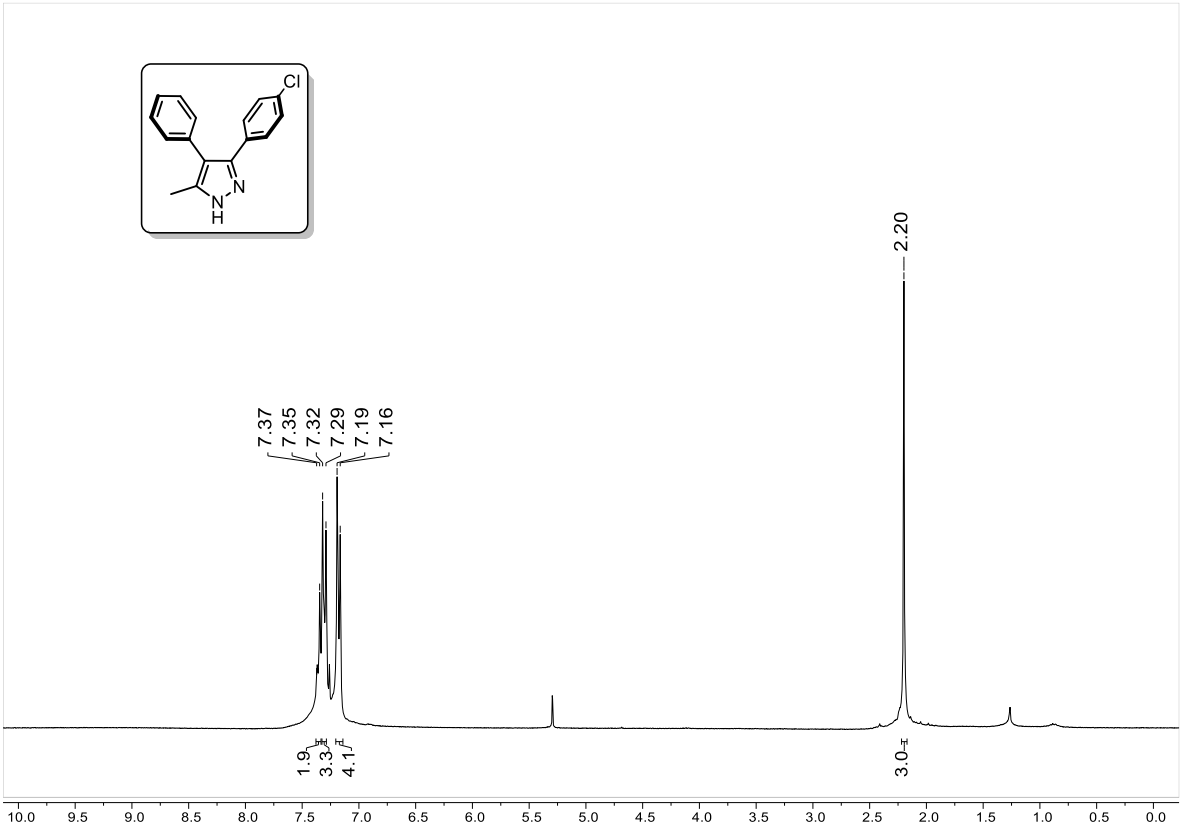


Spectrum 53. ^{13}C-NMR of **8e**.

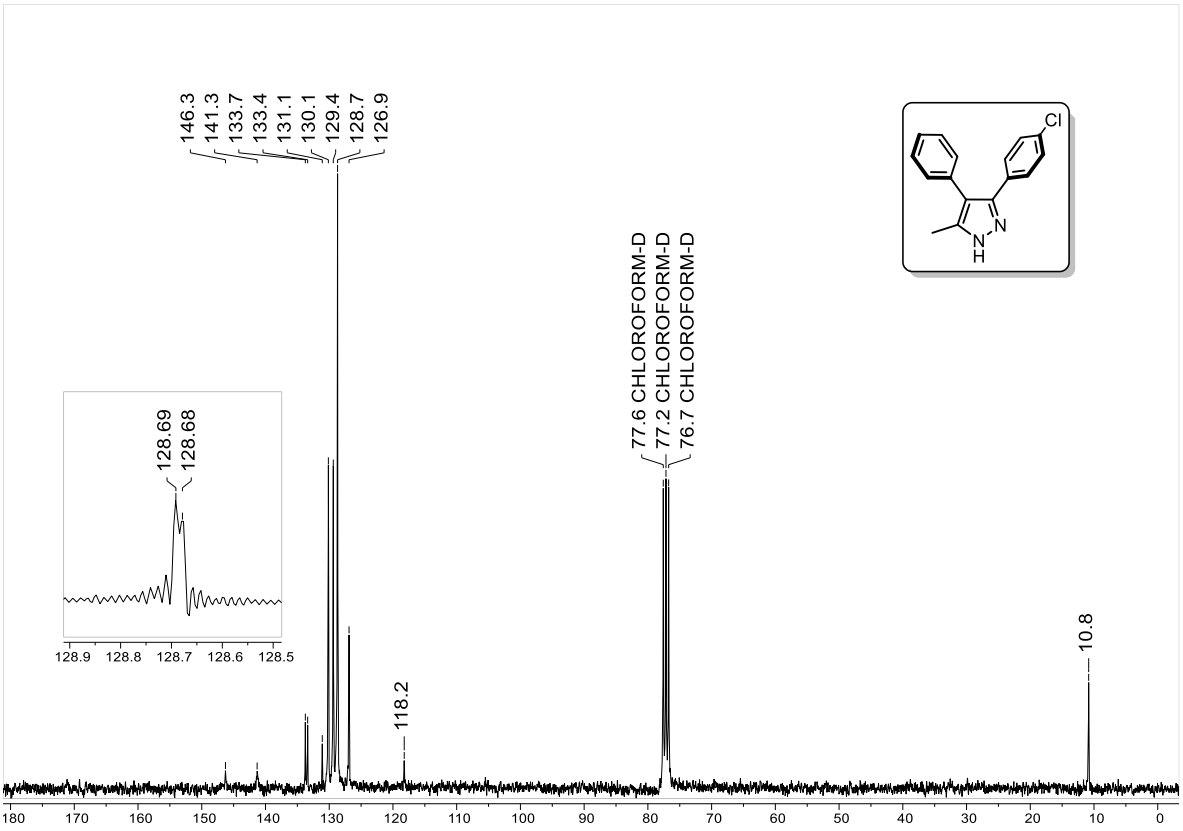


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
311.15487	265293.61	311.15482	0.05	0.15	$^{12}C_{22}{}^{1}H_{19}{}^{14}N_2$	14.5

Spectrum 54. HRMS of **8e**.



Spectrum 55. ^{1}H-NMR of **8f**.



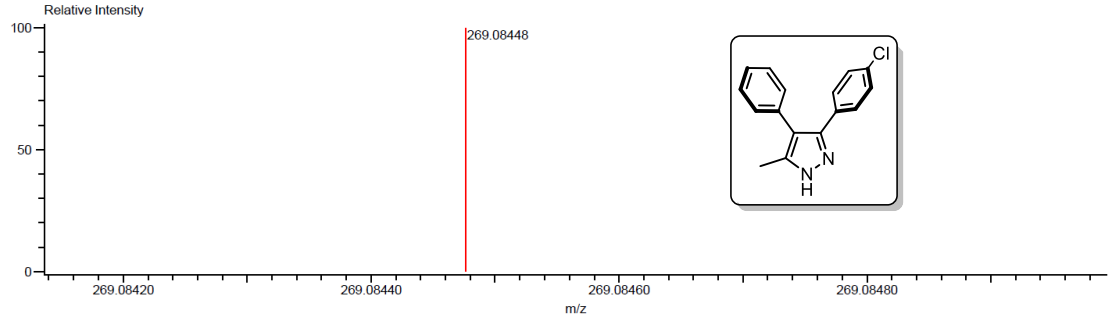
Spectrum 56. ^{13}C-NMR of **8f**.

Description:
Ionization Mode:ESI+
History:Determine m/z[Peak Detect[Centroid,30,Area];Correct Base[];Smooth[5];Correct Base[5.0%];Average(MS[...

Mass Calibration data:Cal_PEG_600
Created:2/3/2023 12:43:22 PM
Created by:AccuTOF

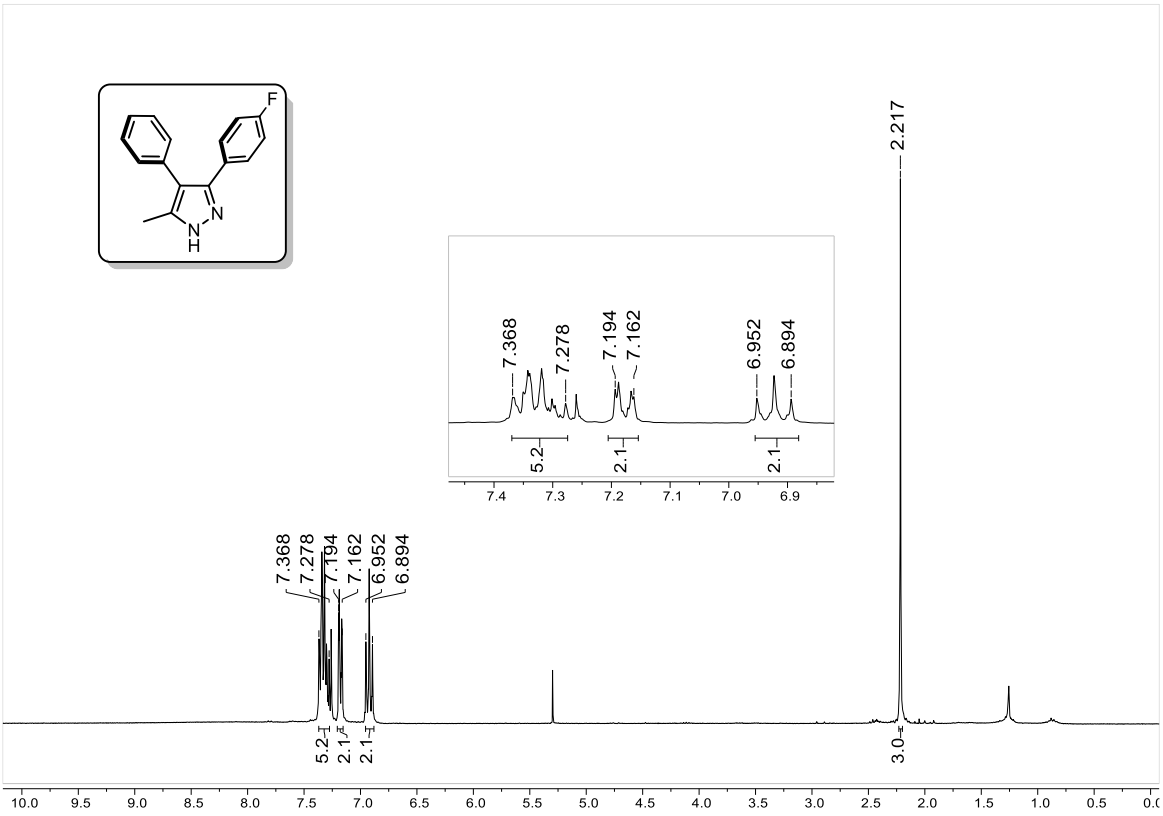
Charge number:1 Tolerance:100.00(ppm), 5.00 .. 15.00(mmu)
Element:^{12}C:0 .. 19, ^{1}H:0 .. 50, ^{35}Cl:0 .. 1, ^{19}F:0 .. 0, ^{14}N:0 .. 2, ^{16}O:0 .. 0

Unsaturation Number:0.0 .. 50.0 (Fraction:.5)

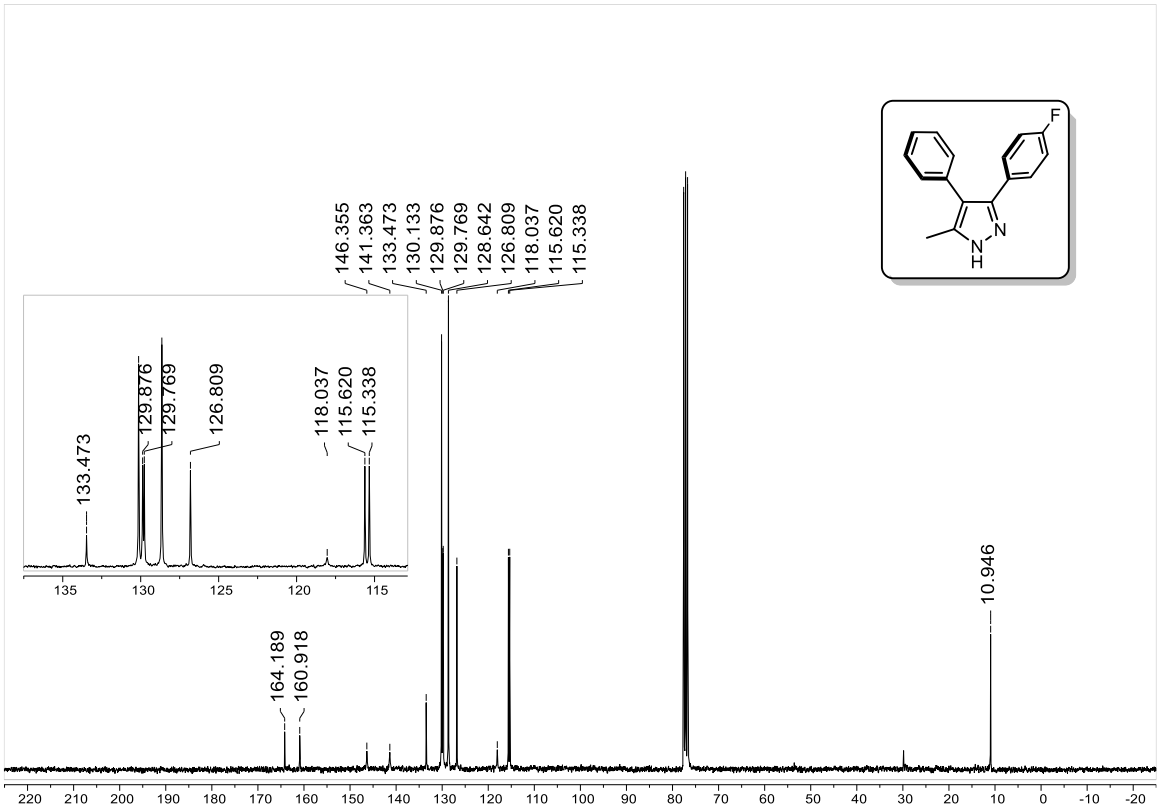


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
269.08448	878215.03	269.08455	-0.07	-0.28	$^{12}C_{16}{}^{1}H_{14}{}^{35}Cl_{1}{}^{14}N_{2}$	10.5

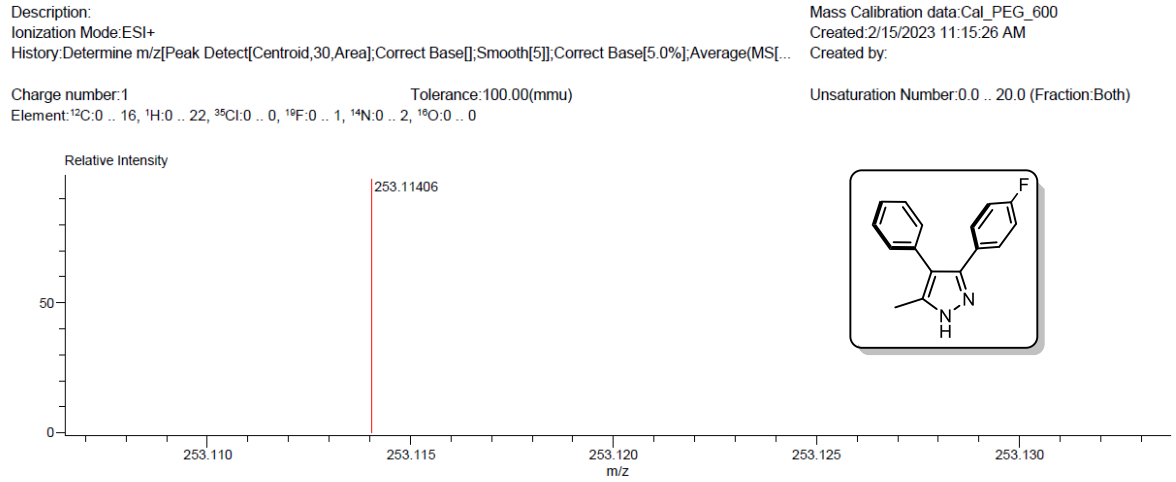
Spectrum 57. HRMS of **8f**.



Spectrum 58. ^{1}H-NMR of **8g**.

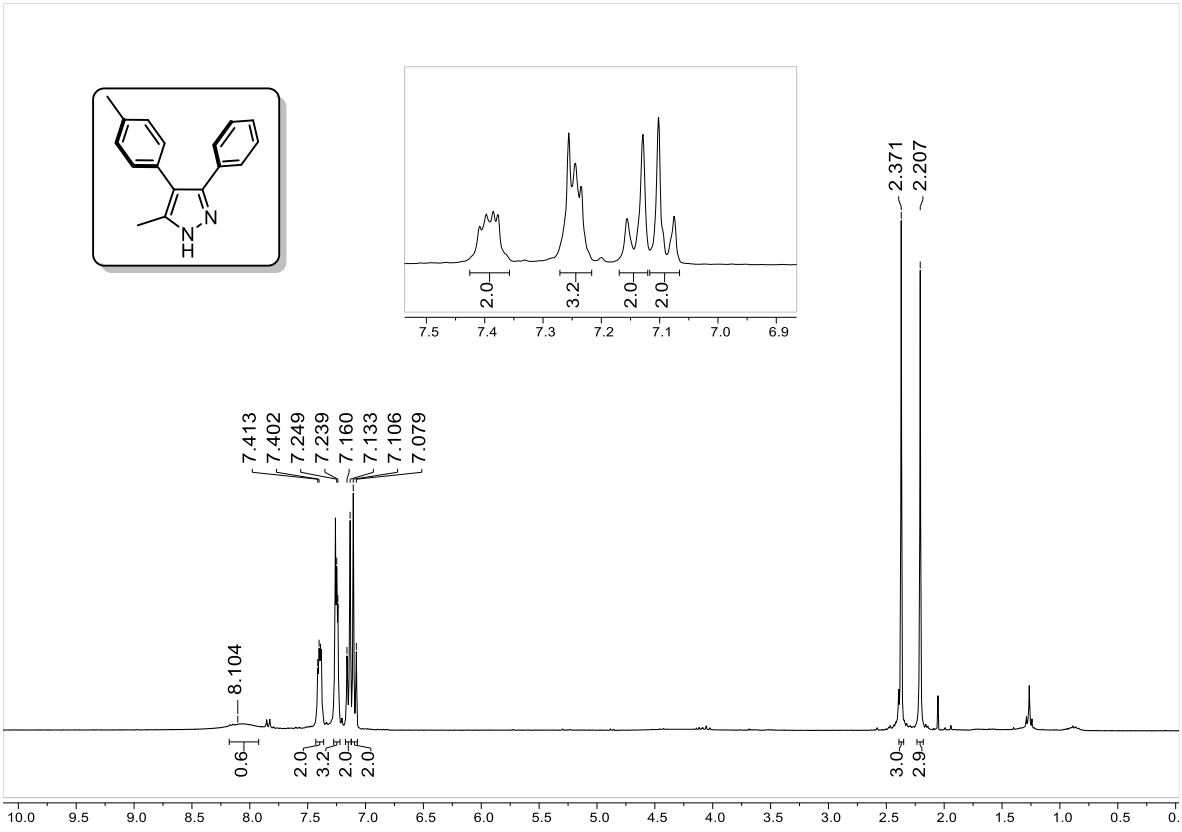


Spectrum 59. ^{13}C-NMR of **8g**.

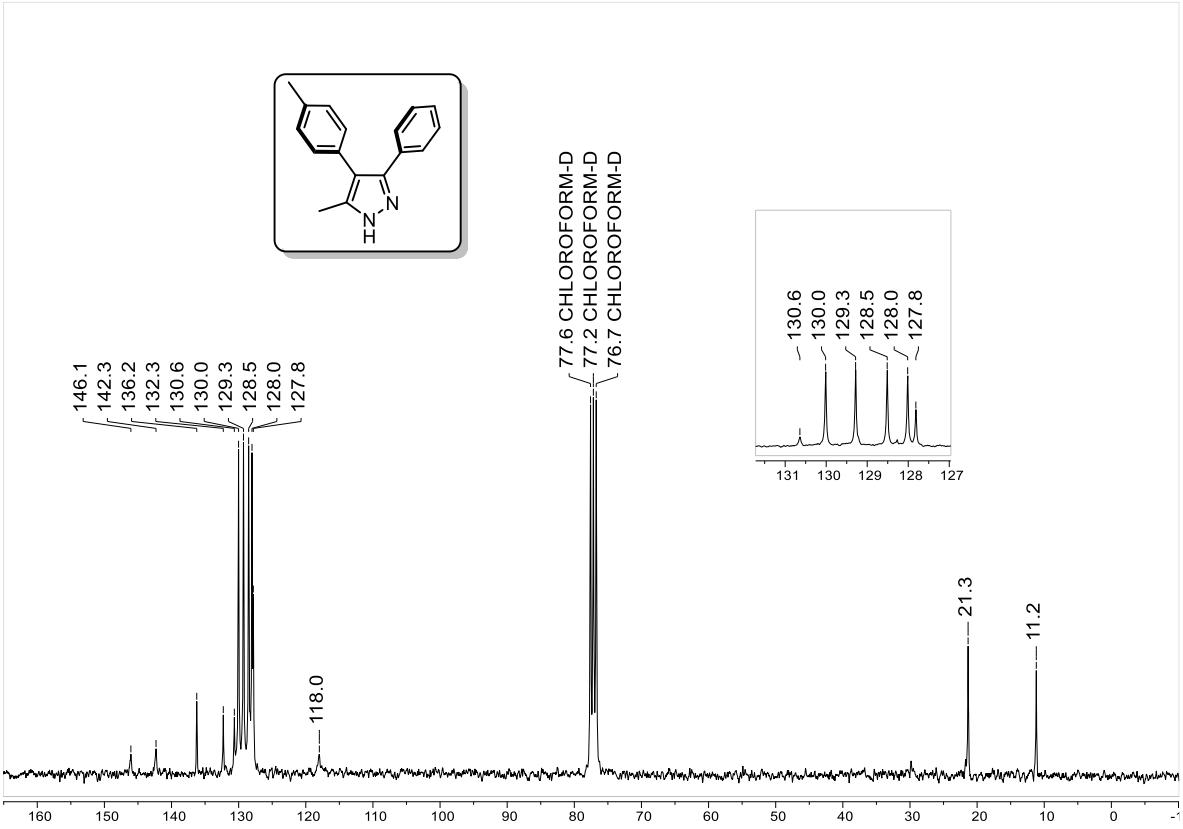


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
253.11406	762947.17	253.11410	-0.04	-0.17	$^{12}C_{16}{}^{1}H_{14}{}^{19}F_{1}{}^{14}N_{2}$	10.5

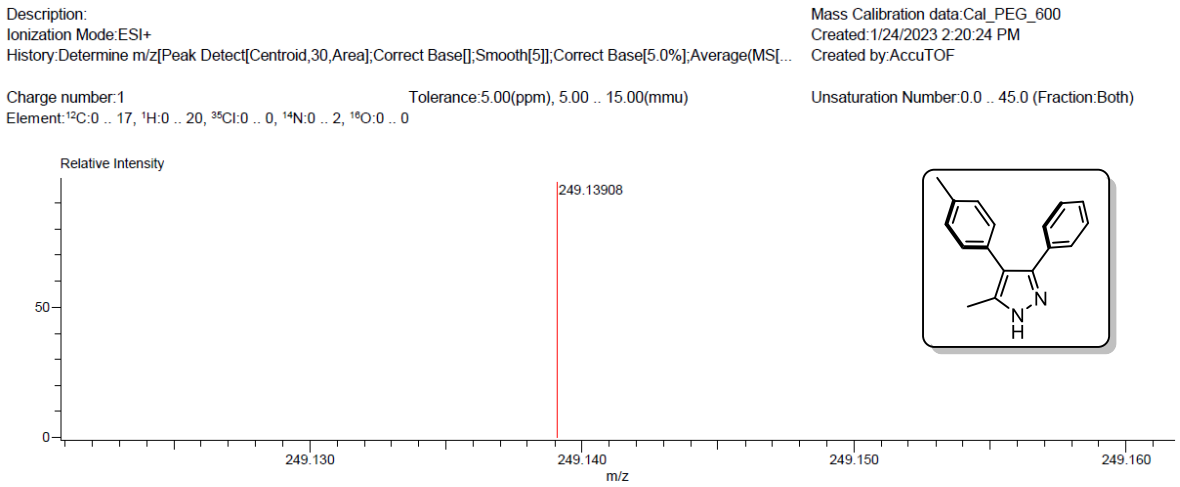
Spectrum 60. HRMS of **8g**.



Spectrum 61. ^{1}H-NMR of **8h**.

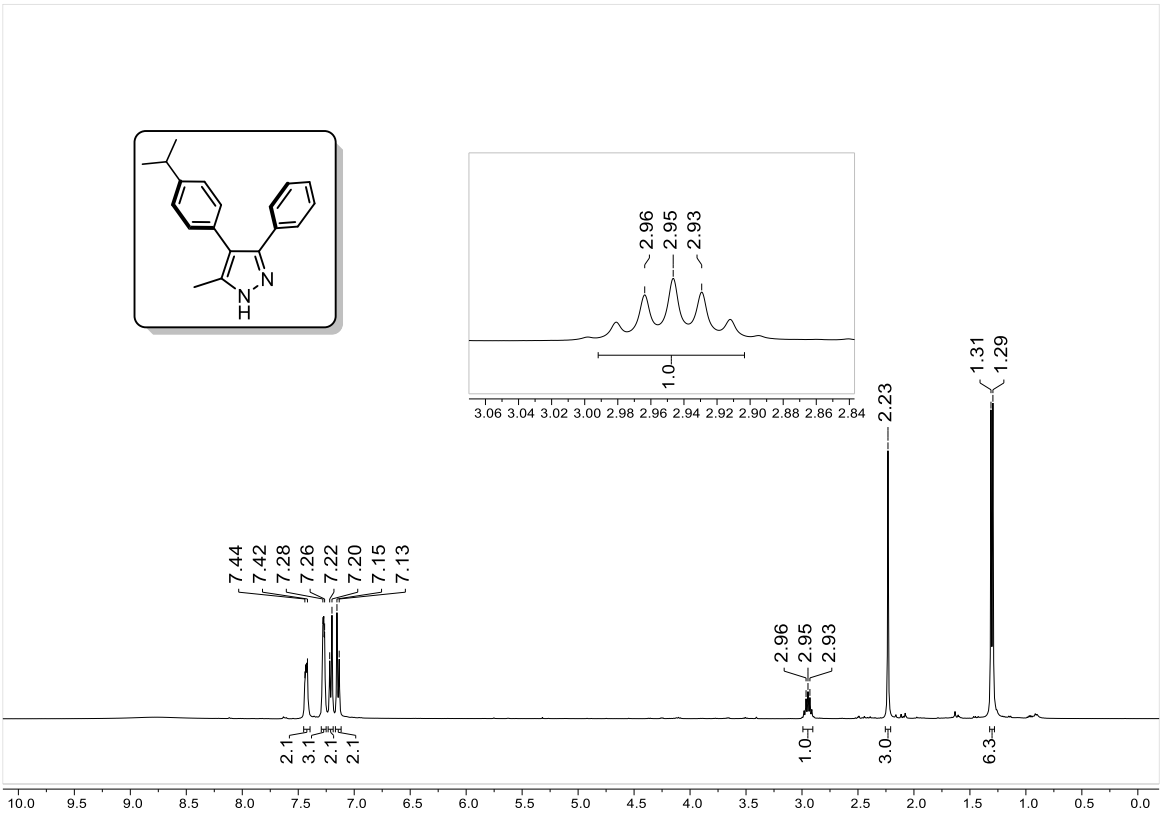


Spectrum 62. ^{13}C-NMR of **8h**.

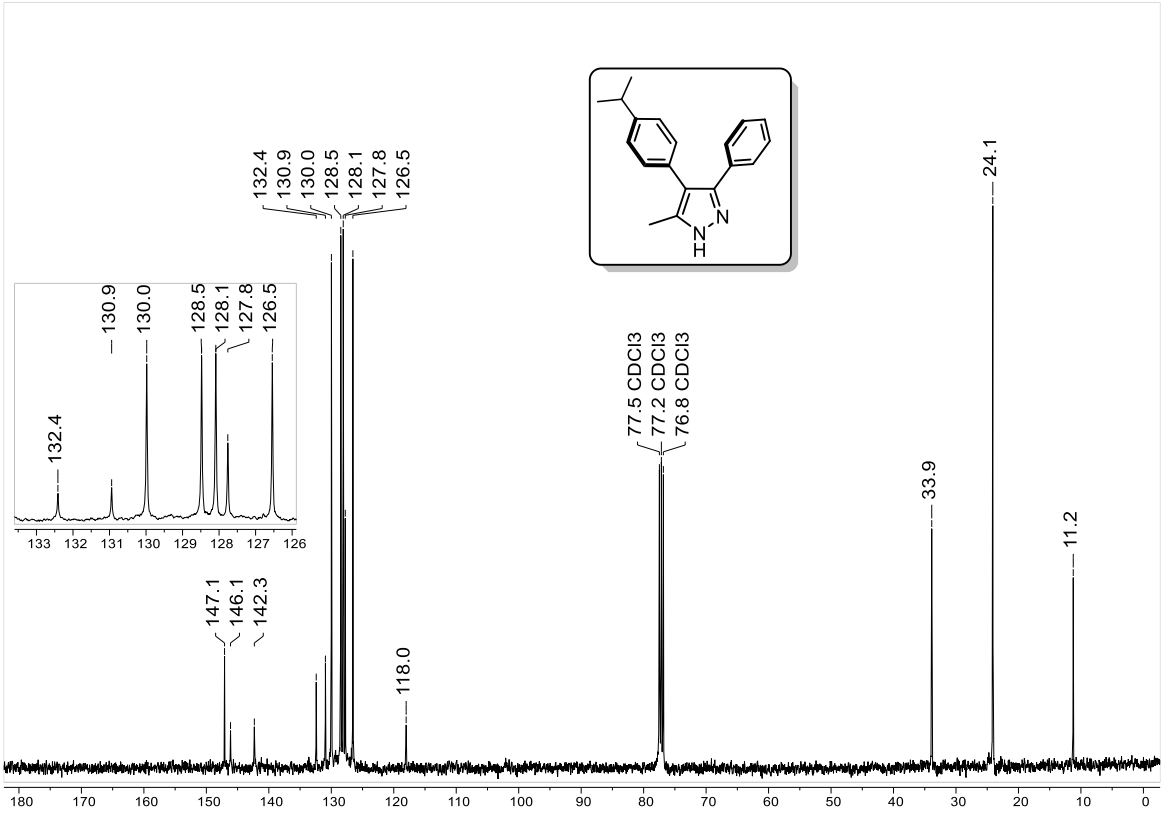


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
249.13908	3737.98	249.13917	-0.09	-0.37	$^{12}C_{17}{}^{1}H_{17}{}^{14}N_2$	10.5

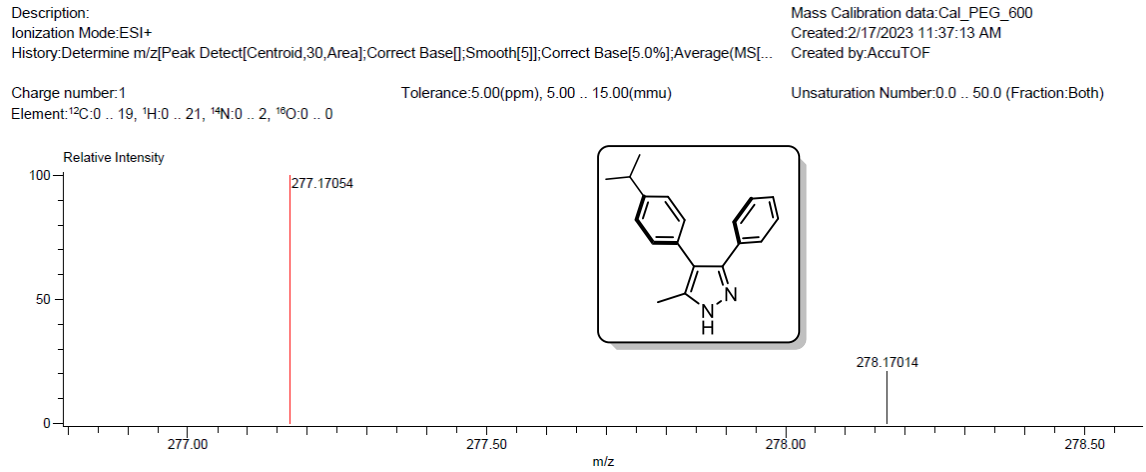
Spectrum 63. HRMS of **8h**.



Spectrum 64. ^{1}H-NMR of **8i**.

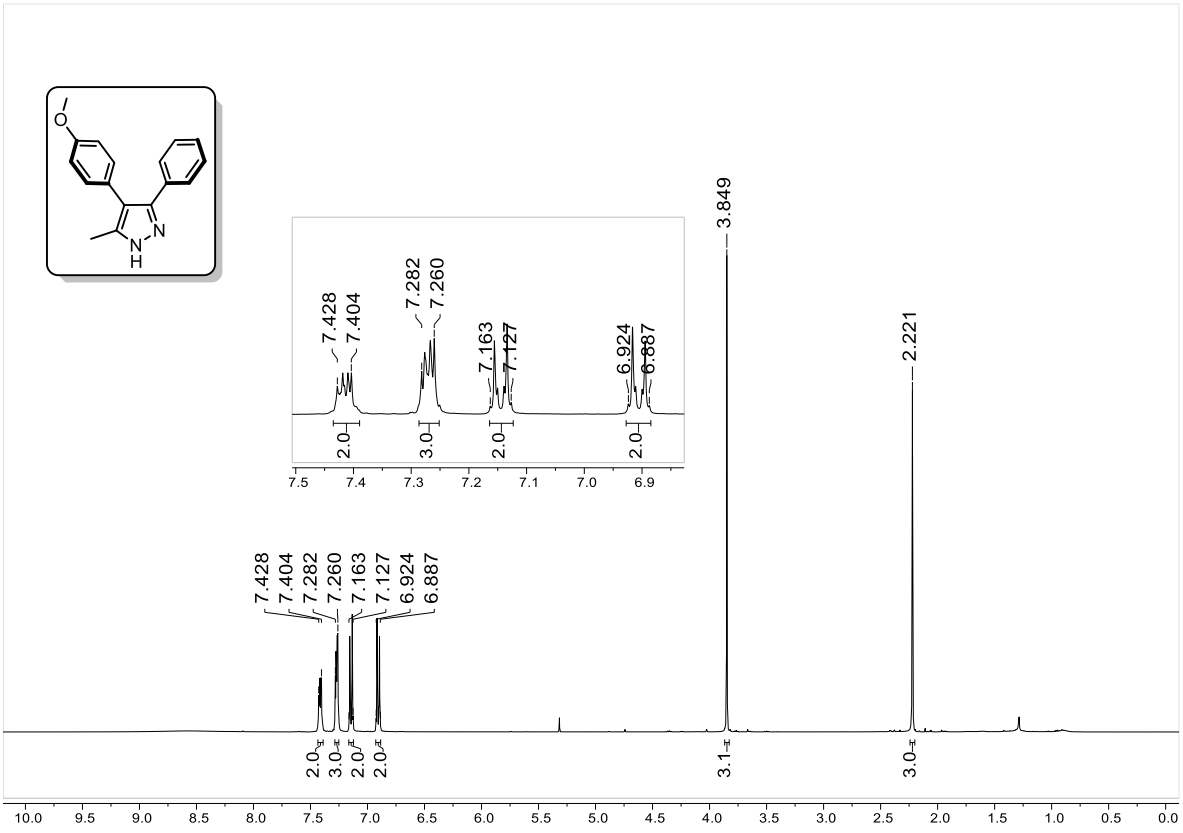


Spectrum 65. ^{13}C-NMR of **8i**.

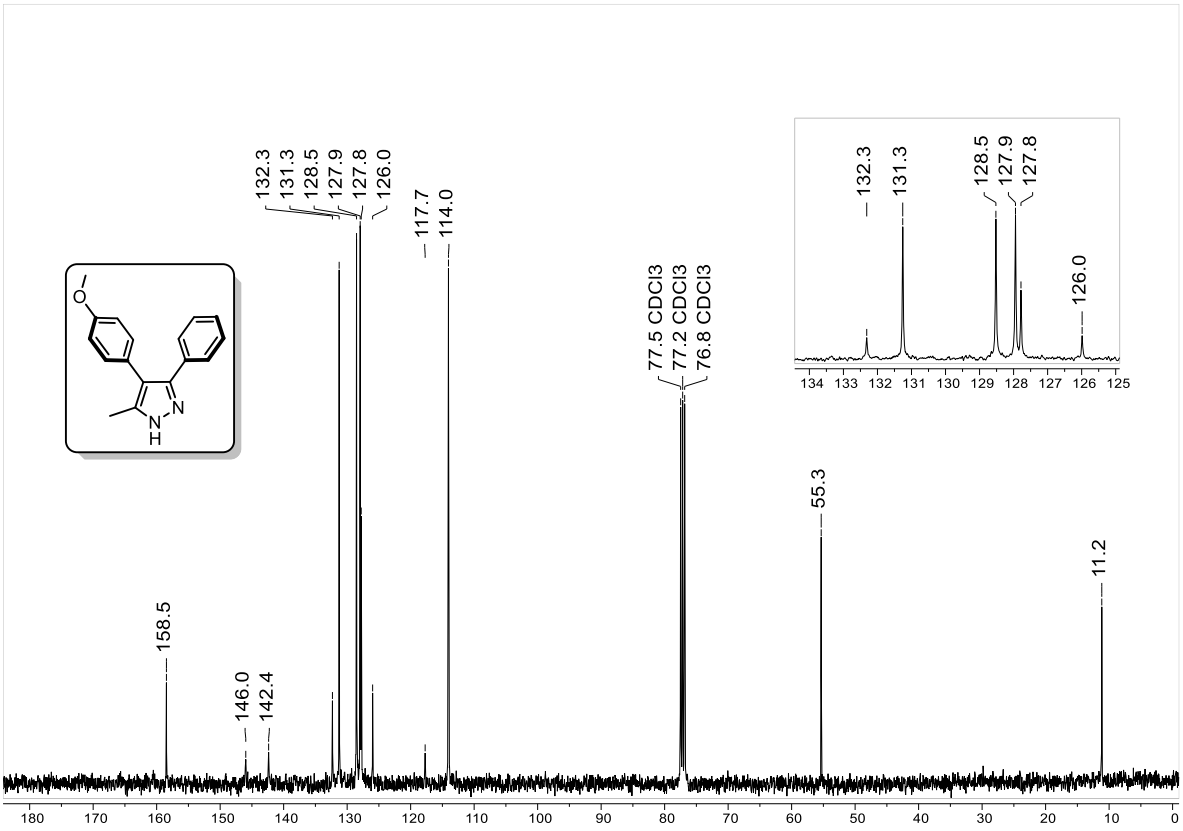


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
277.17054	8995.62	277.17047	0.07	0.24	$^{12}C_{19}{}^{1}H_{21}{}^{14}N_2$	10.5

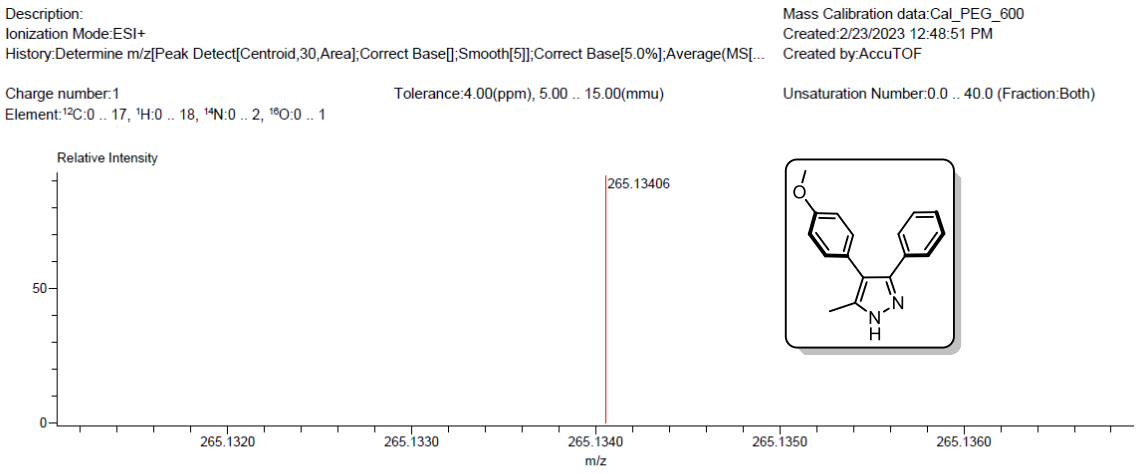
Spectrum 66. HRMS of **8i**.



Spectrum 67. ^{1}H-NMR of **8j**.

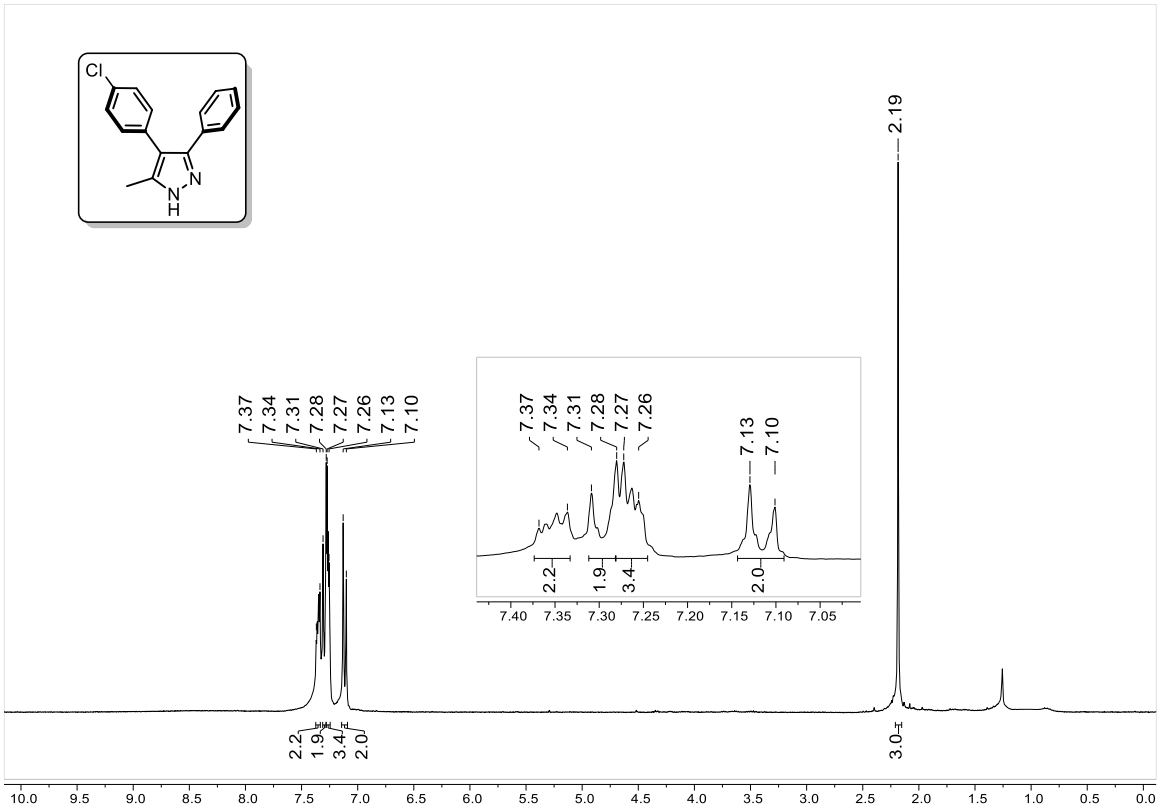


Spectrum 68. ^{13}C-NMR of **8j**.

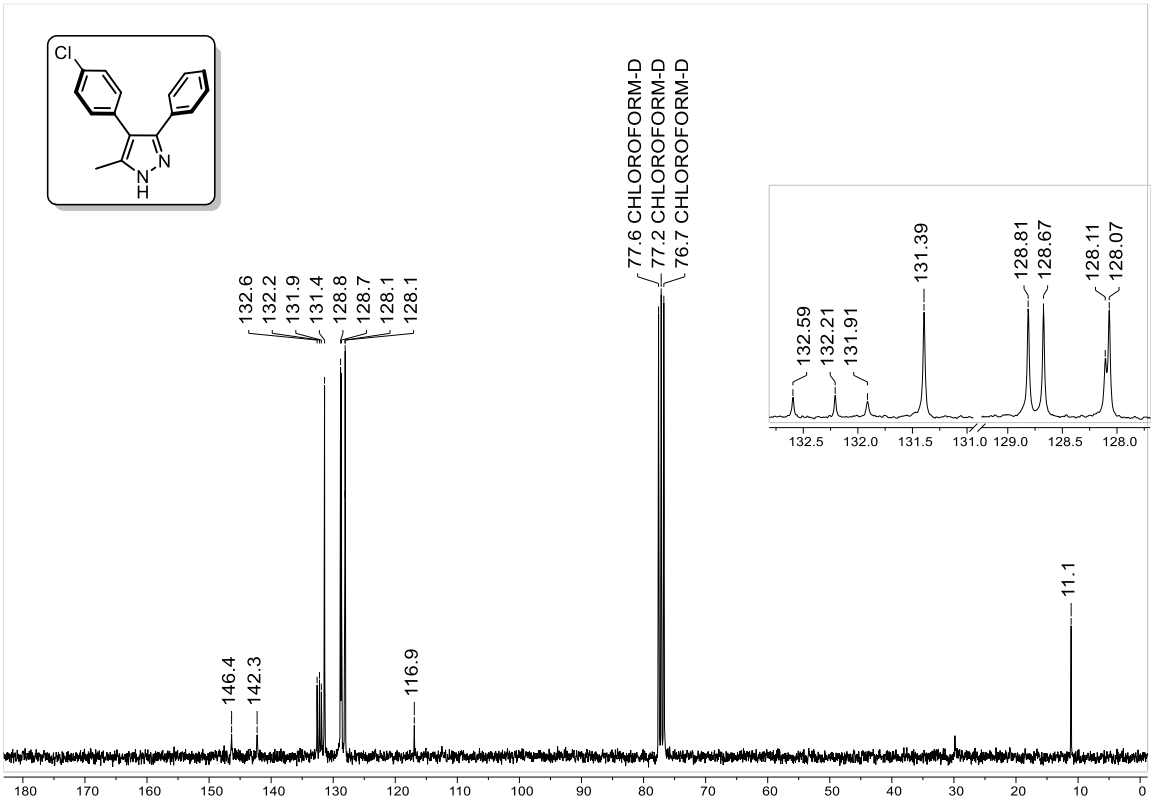


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
265.13406	3779.12	265.13409	-0.03	-0.12	$^{12}C_{17}{}^{1}H_{17}{}^{14}N_{2}{}^{16}O_{1}$	10.5

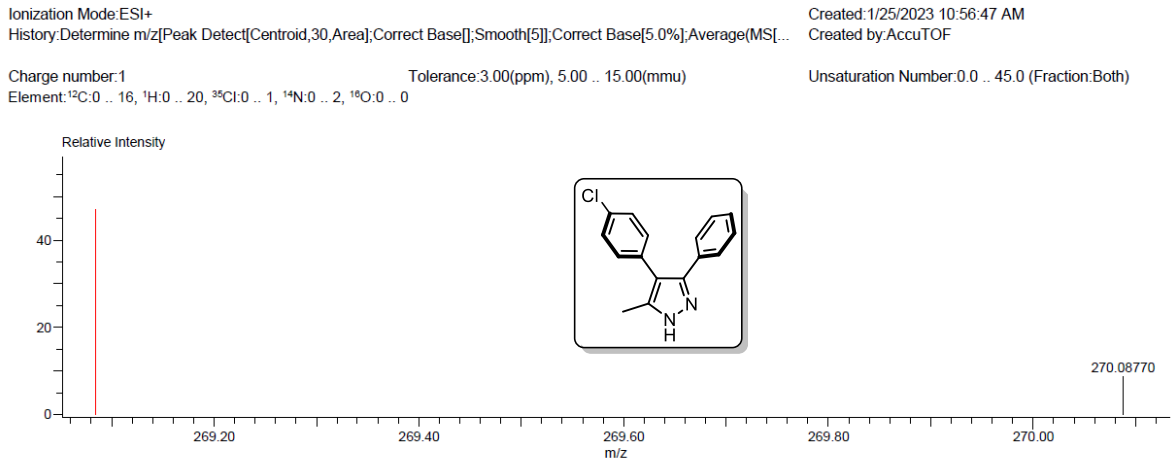
Spectrum 69. HRMS of **8j**.



Spectrum 70. ^{1}H-NMR of **8k**.

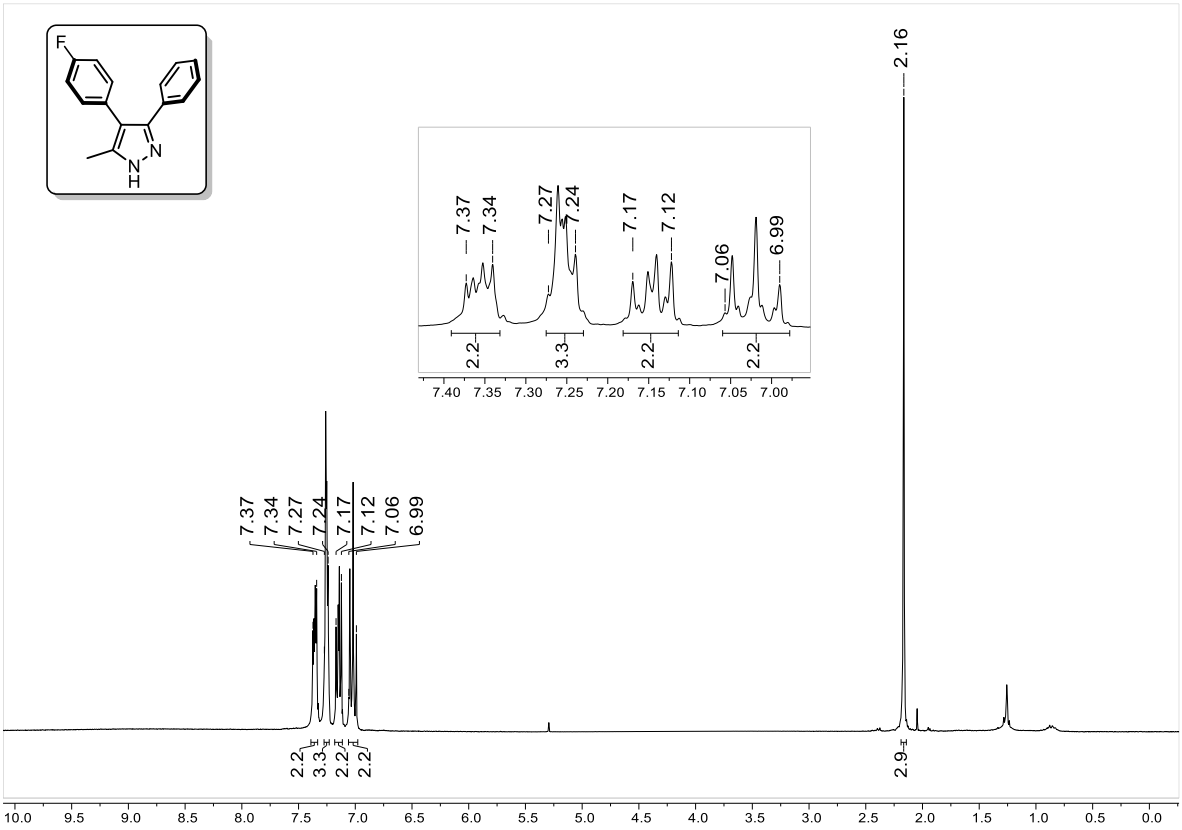


Spectrum 71. ^{13}C-NMR of **8k**.

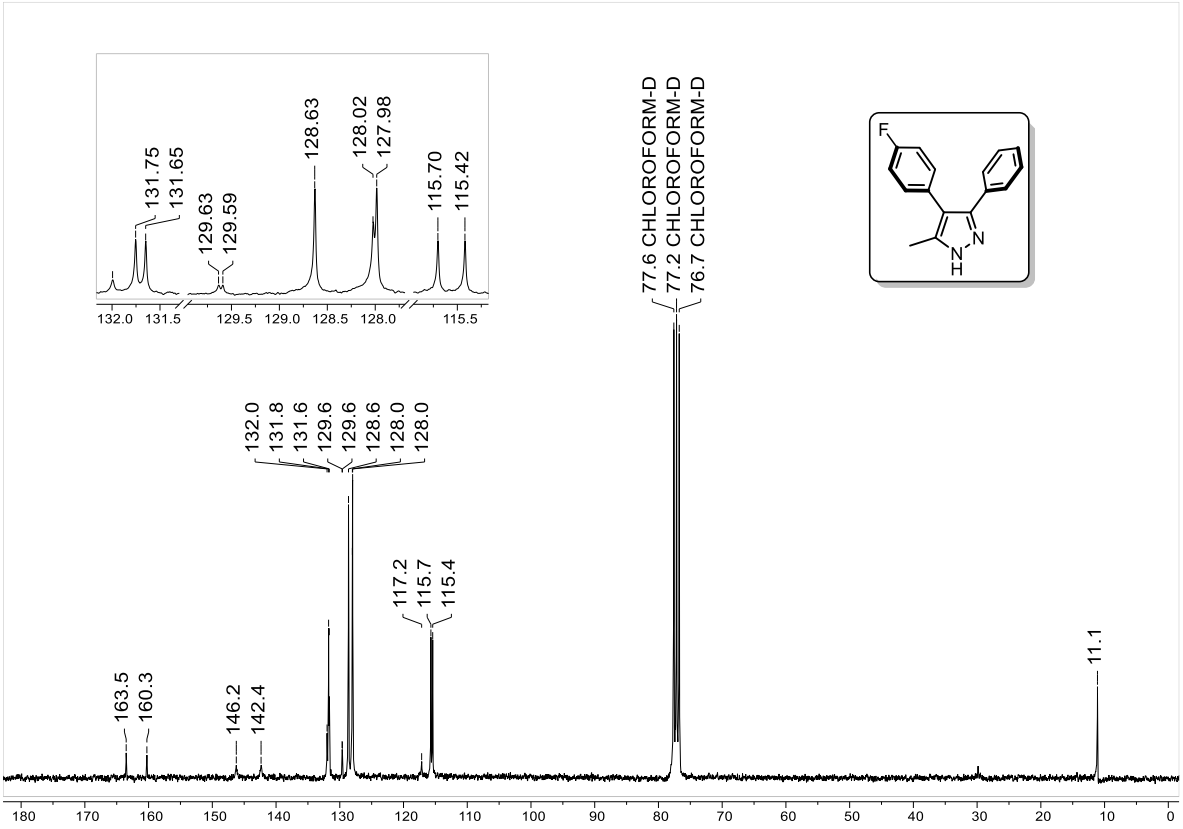


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
269.08460	6551.40	269.08455	0.05	0.18	$^{12}C_{16}{}^{1}H_{14}{}^{35}Cl_{1}{}^{14}N_{2}$	10.5

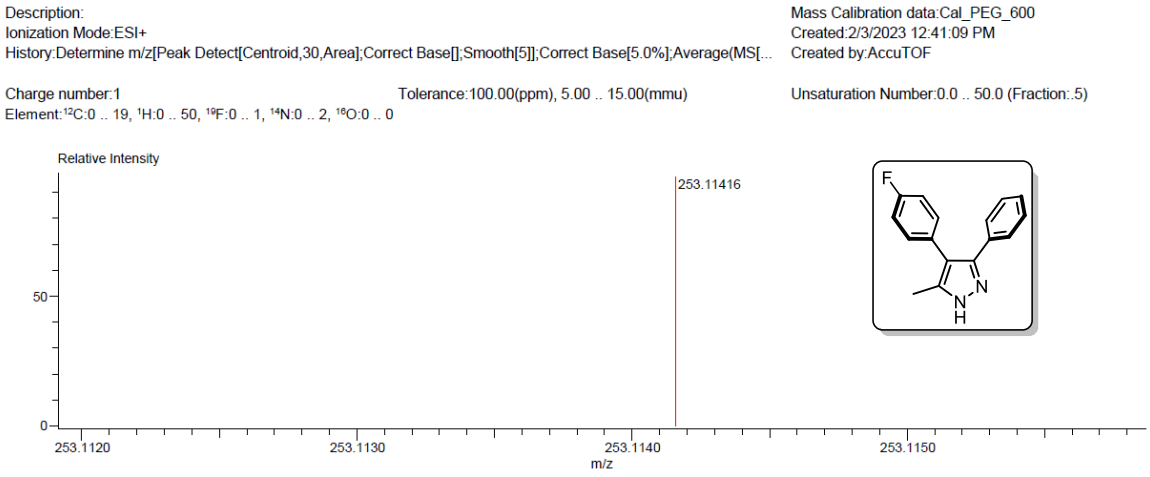
Spectrum 72. HRMS of **8k**.



Spectrum 73. ^{1}H-NMR of **8l**.

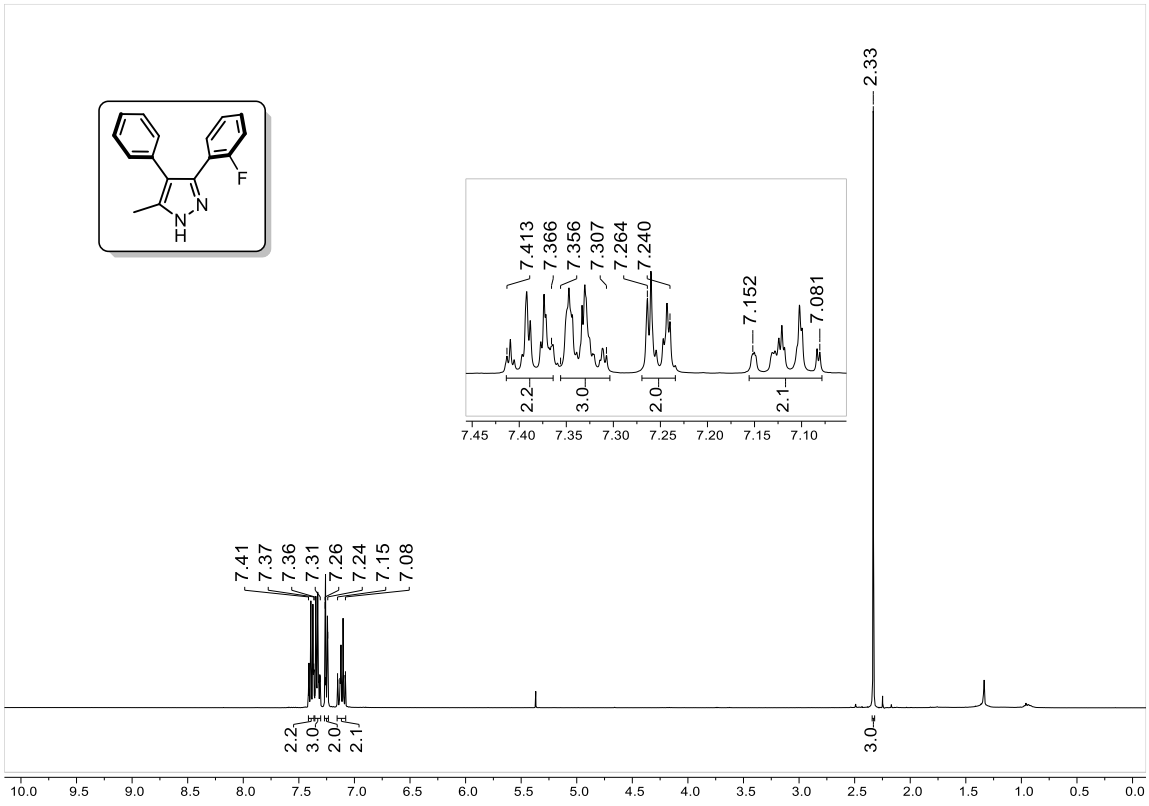


Spectrum 74. ^{13}C-NMR of **8l**.

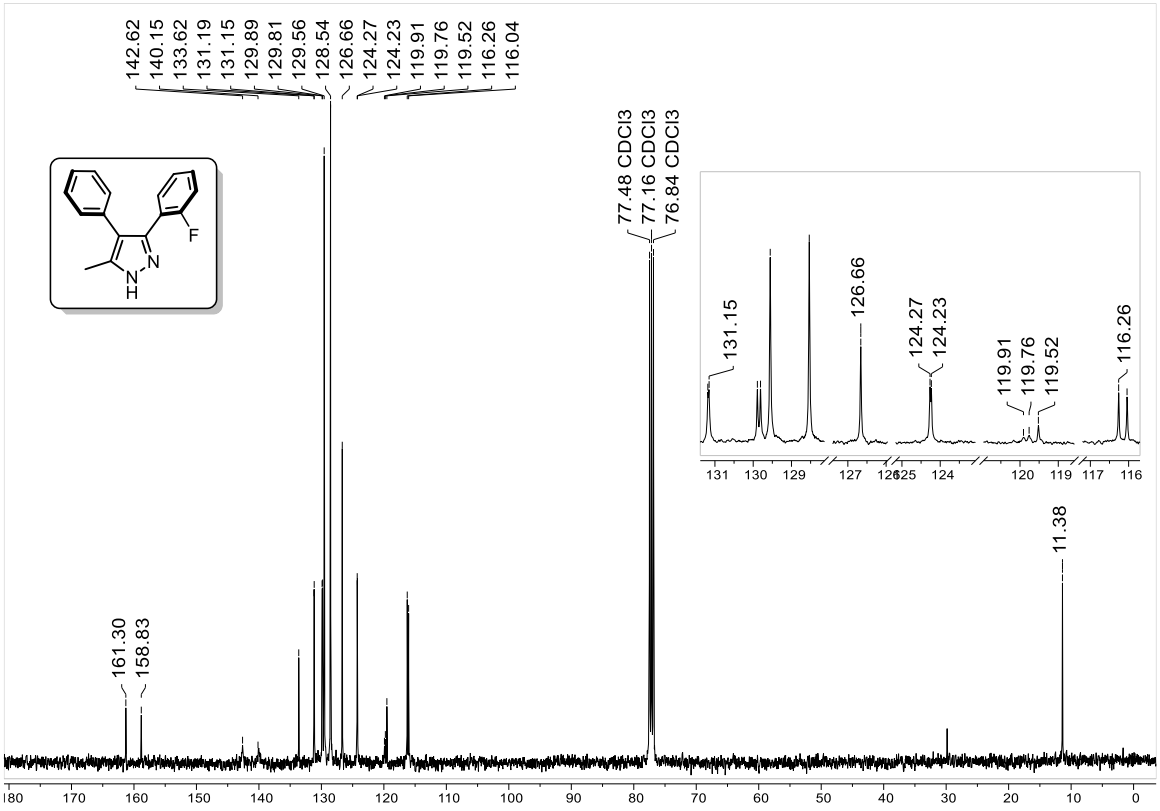


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
253.11416	844768.97	253.11410	0.06	0.23	$^{12}C_{16}{}^{1}H_{14}{}^{19}F_{1}{}^{14}N_{2}$	10.5

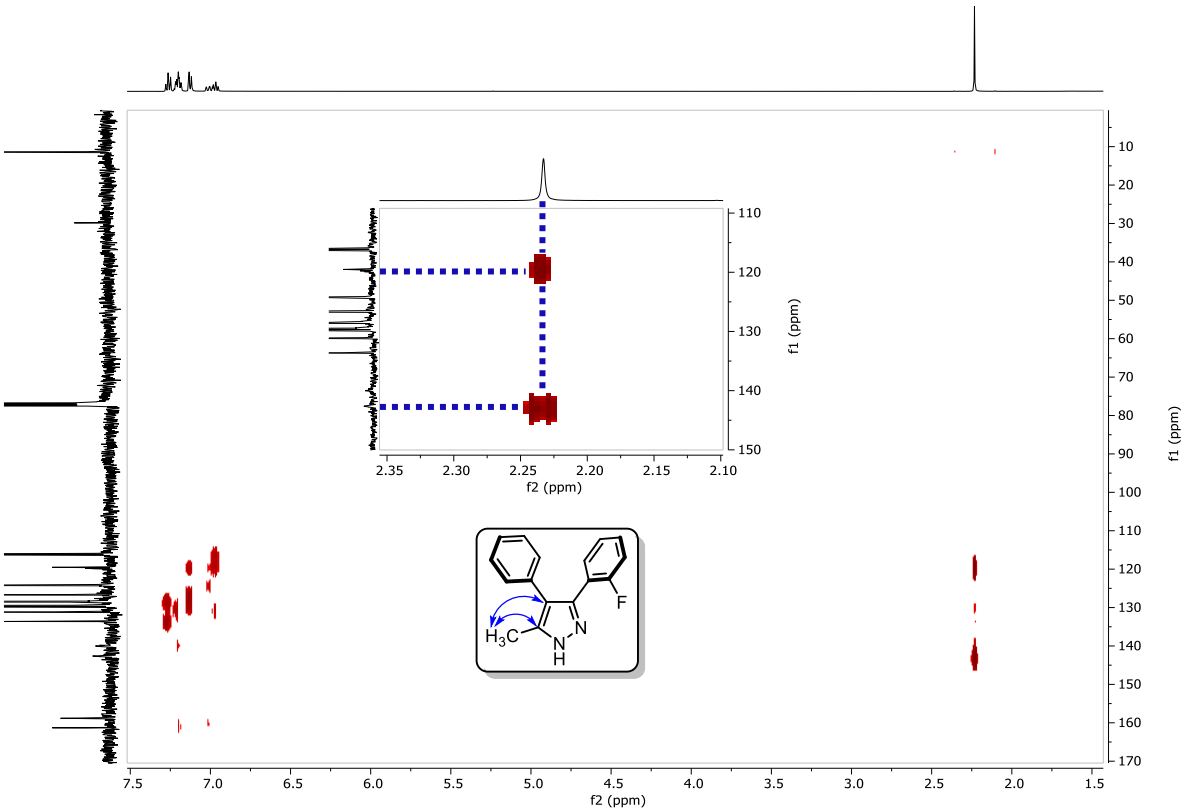
Spectrum 75. HRMS of **8l**.



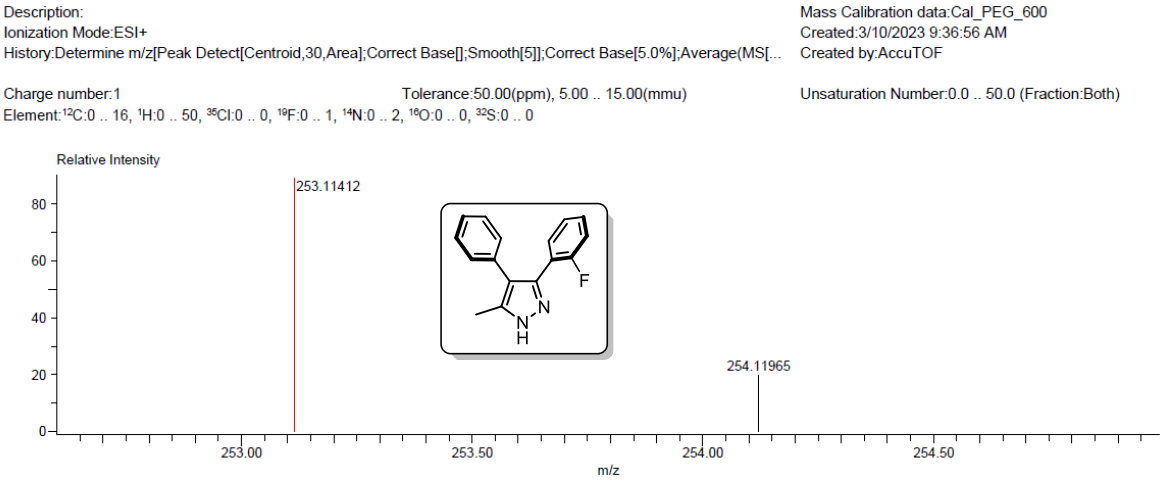
Spectrum 76. ^{1}H-NMR of **8m**.



Spectrum 77. ^{13}C-NMR of **8m**.

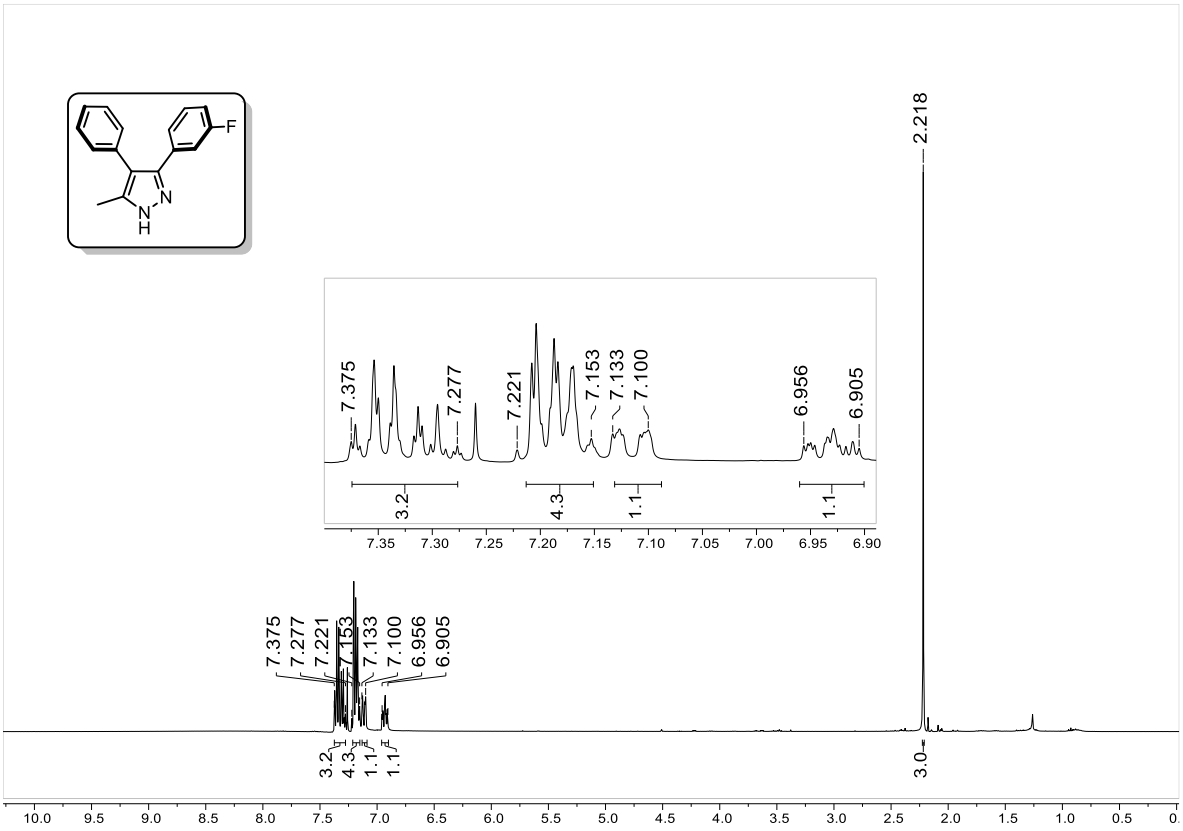


Spectrum 78. HMBC of **8m**.

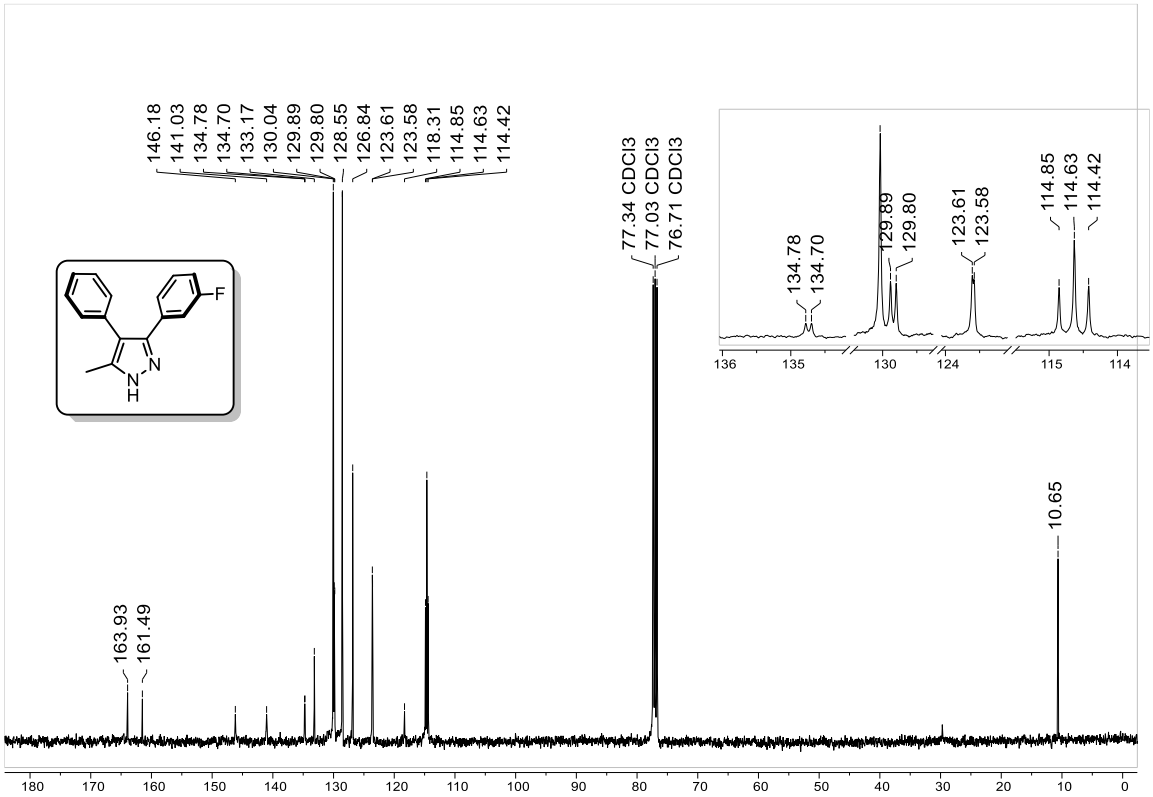


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
253.11412	14151.66	253.11410	0.02	0.06	$^{12}C_{16}{}^{1}H_{14}{}^{19}F_{1}{}^{14}N_{2}$	10.5

Spectrum 79. HRMS of **8m**.



Spectrum 80. ^{1}H-NMR of **8n**.

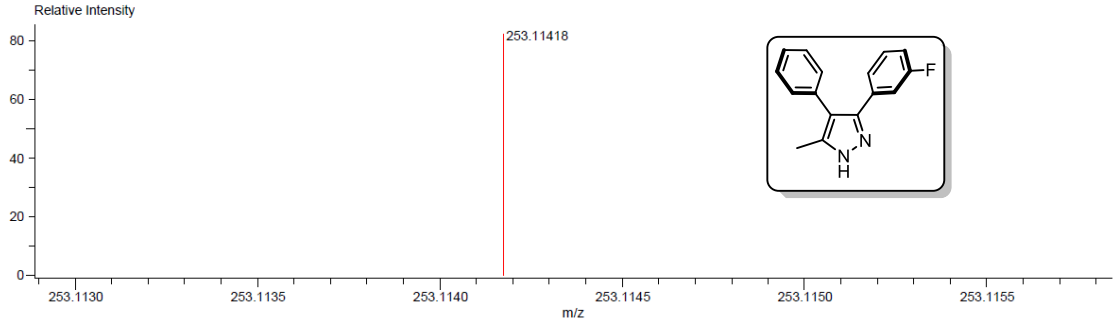


Spectrum 81. ^{13}C-NMR of **8n**.

Description:
Ionization Mode:ESI+
History:Determine m/z[Peak Detect[Centroid,30,Area];Correct Base[];Smooth[5]];Correct Base[5.0%];Average(MS[...

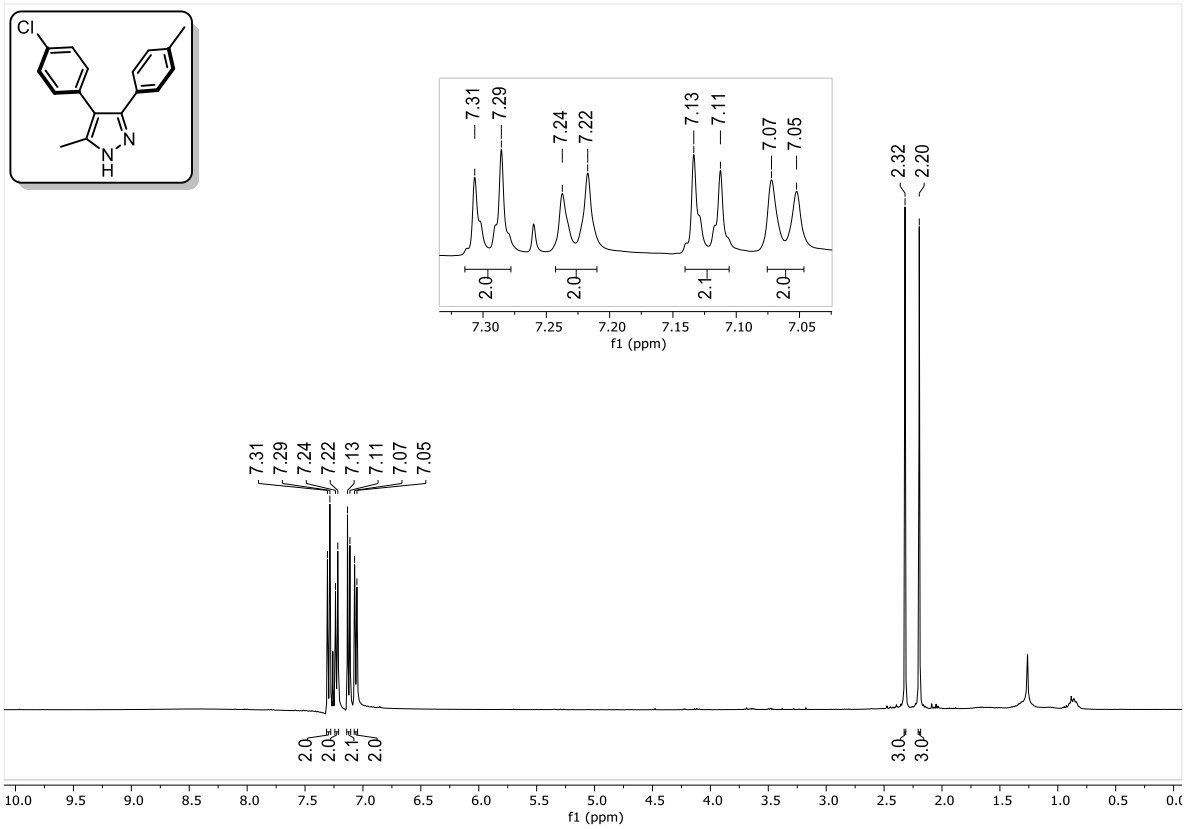
Mass Calibration data:Cal_PEG_600
Created:2/27/2023 2:14:34 PM
Created by:AccuTOF

Charge number:1
Tolerance:200.00(ppm), 5.00 .. 15.00(mmu)
Unsaturation Number:0.0 .. 30.0 (Fraction:Both)
Element:^{12}C:0 .. 16, ^{1}H:0 .. 20, ^{35}Cl:0 .. 1, ^{19}F:1 .. 1, ^{14}N:2 .. 2

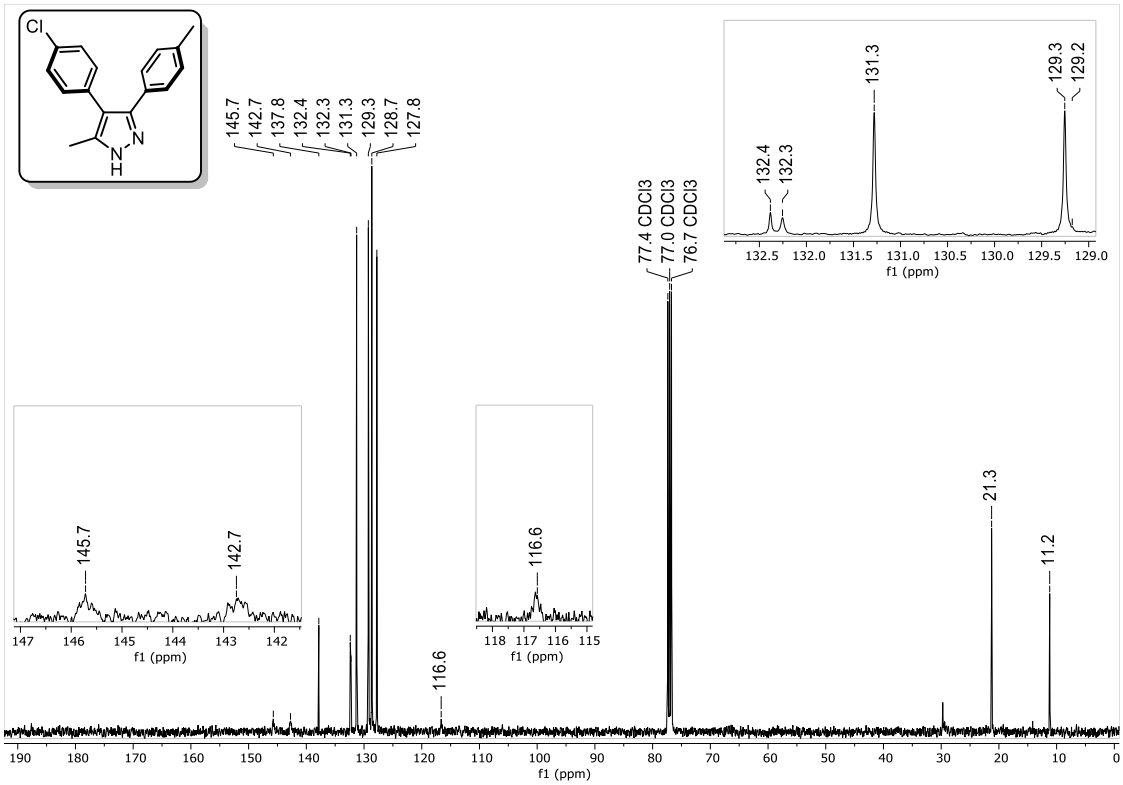


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
253.11418	62940.07	253.11410	0.07	0.29	$^{12}C_{16}{}^{1}H_{14}{}^{19}F_{1}{}^{14}N_{2}$	10.5

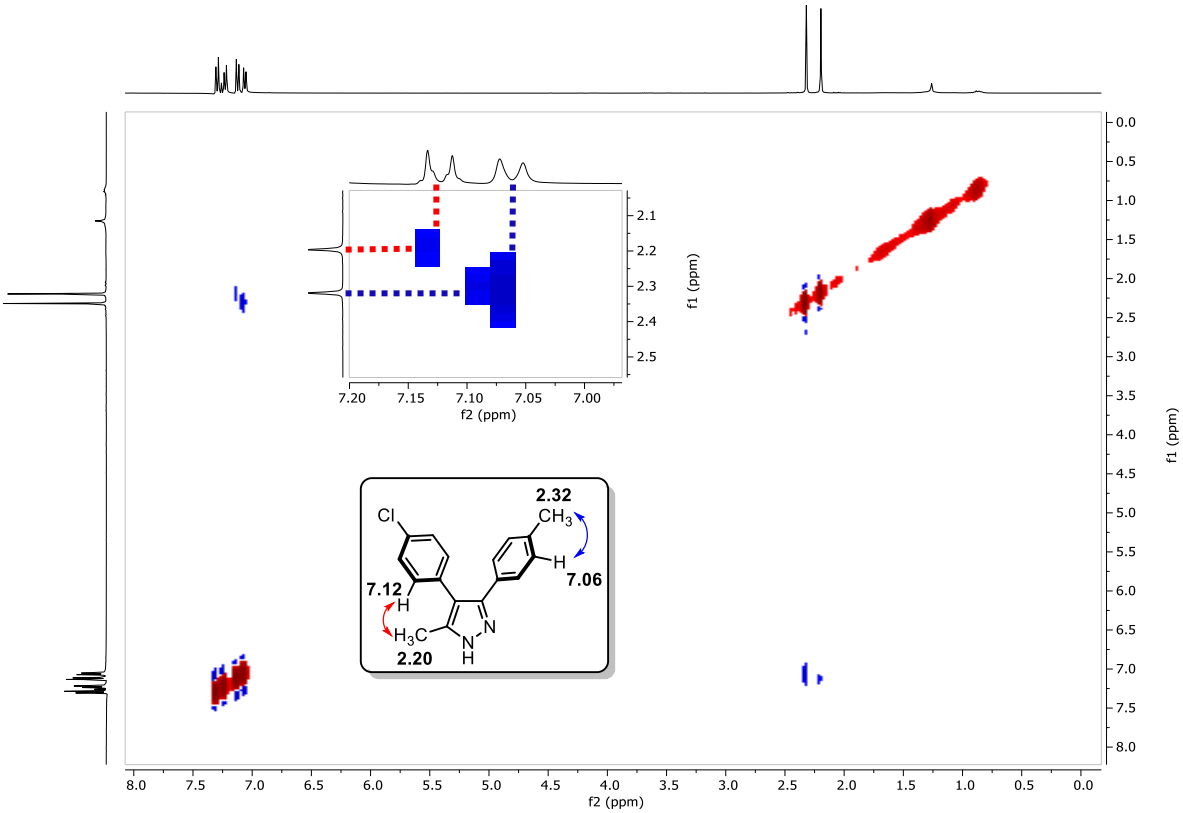
Spectrum 82. HRMS of **8n**.



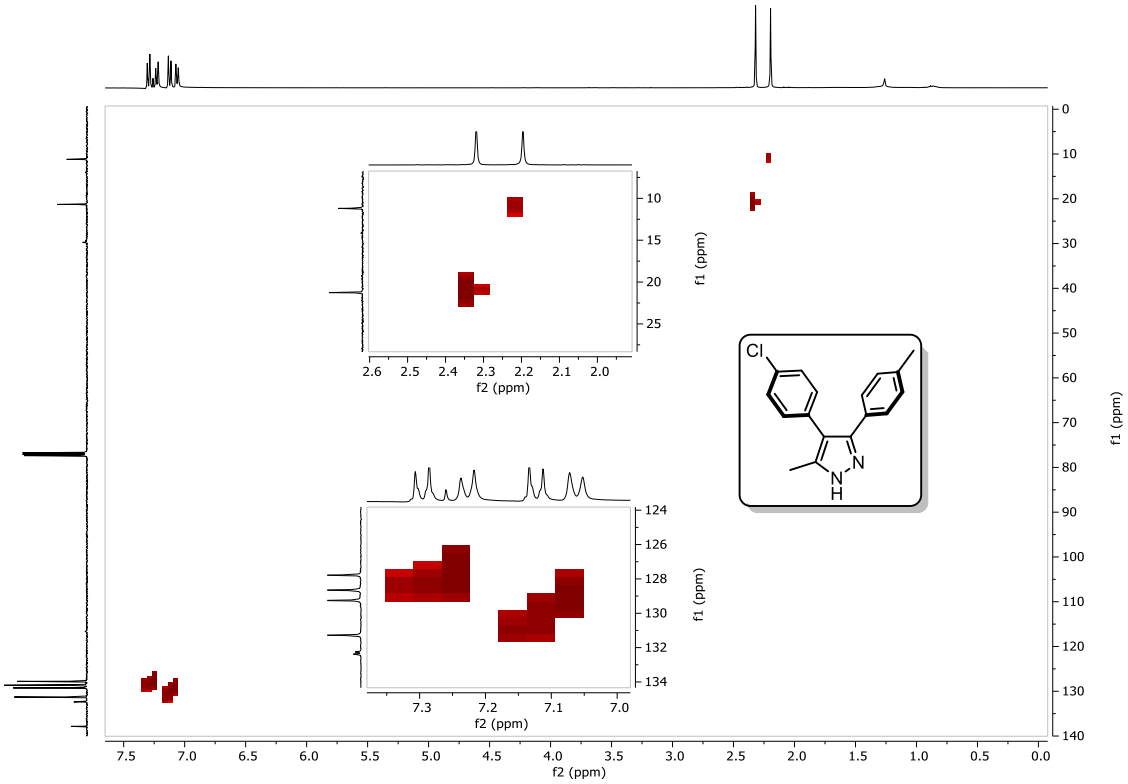
Spectrum 83. ^{1}H-NMR of **8o**.



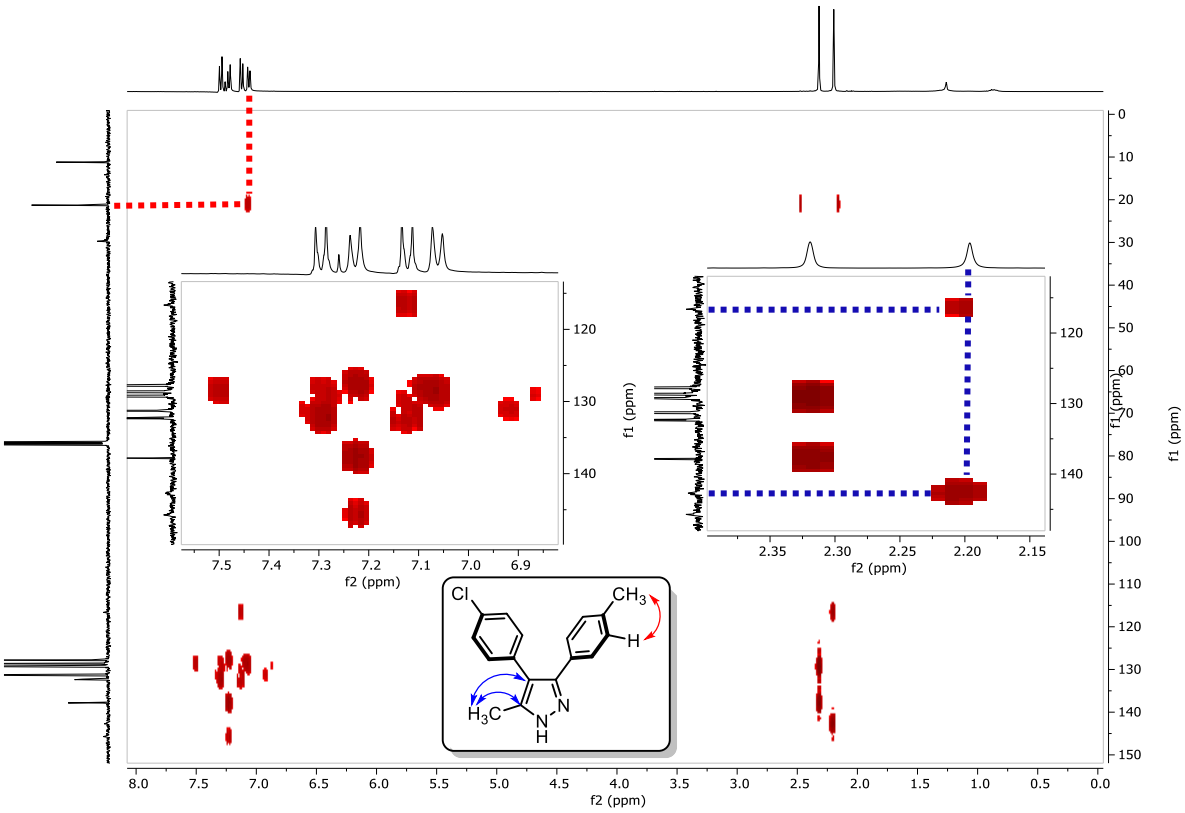
Spectrum 84 ^{13}C-NMR of **8o**.



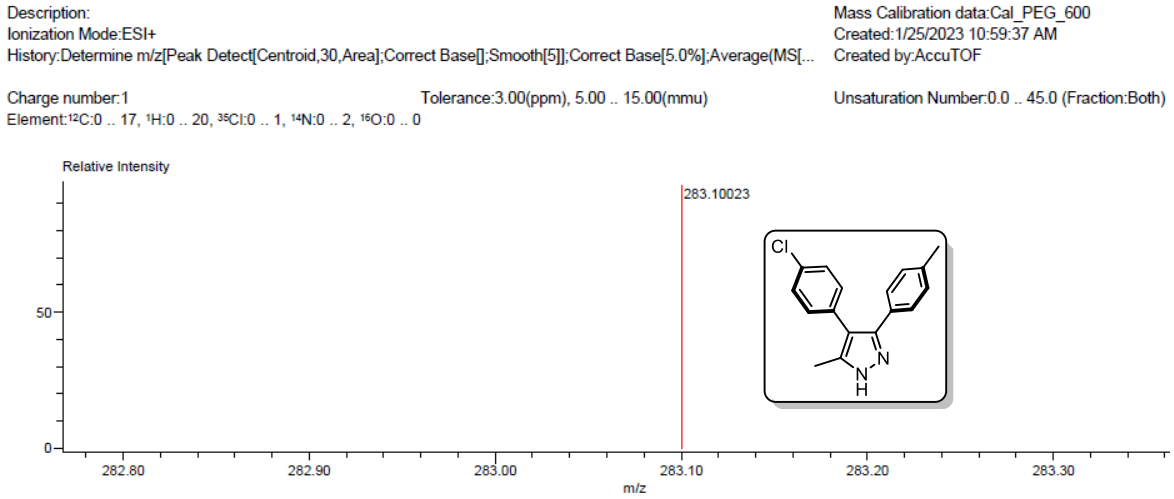
Spectrum 85. 2D-NOESY of **8o**.



Spectrum 86. HSQC of **8o**.

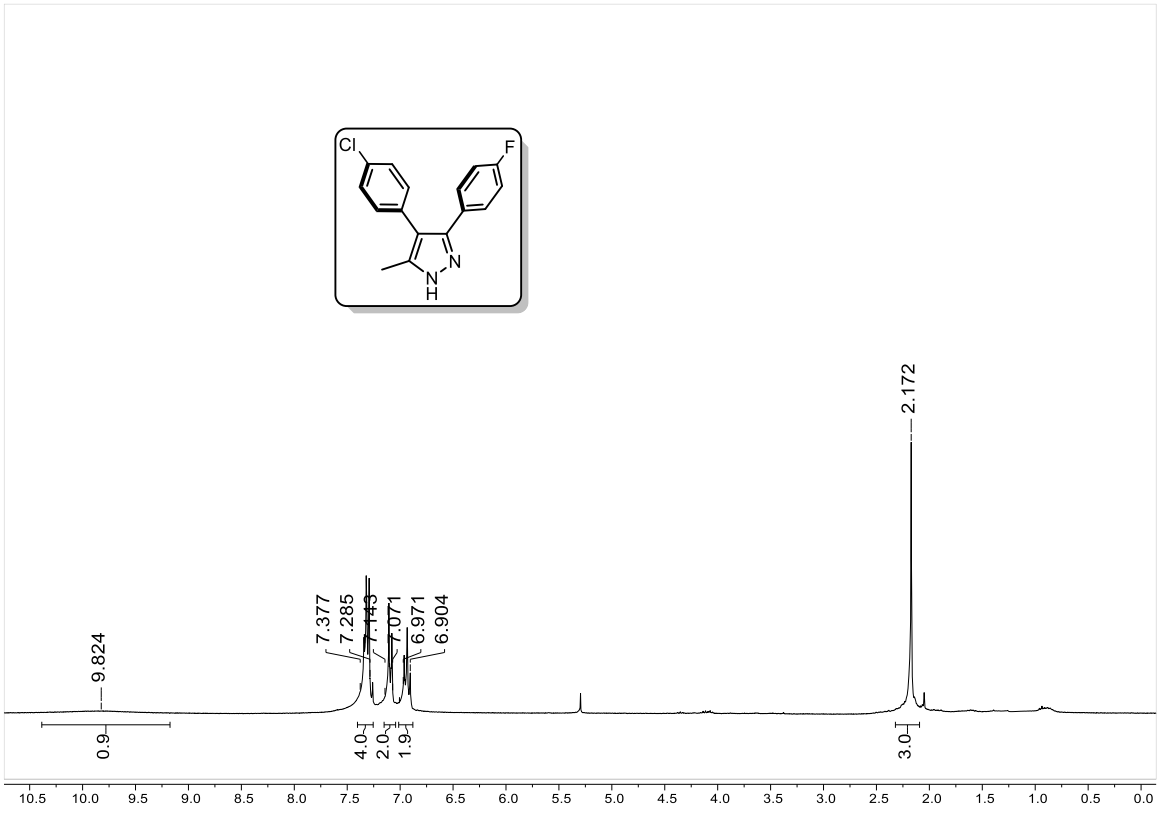


Spectrum 87. HMBC of **8o**.

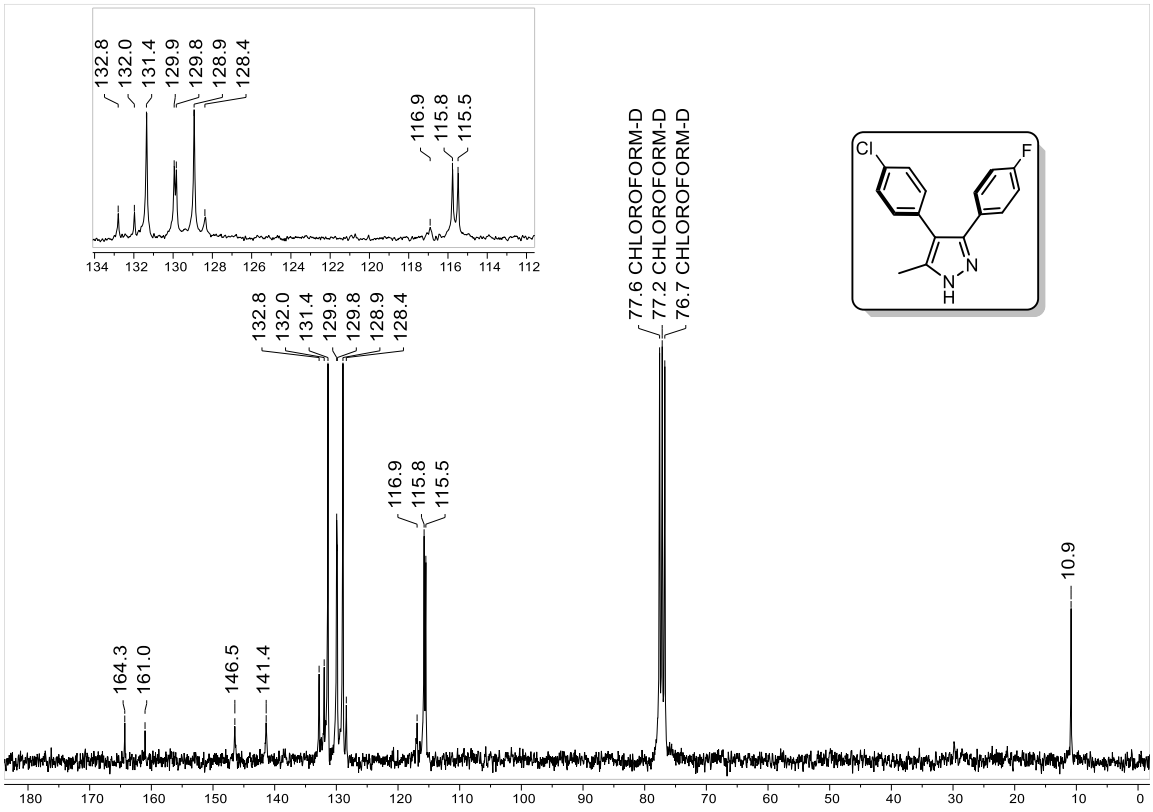


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
283.10023	1926911.20	283.10020	0.03	0.11	$^{12}C_{17}{}^{1}H_{16}{}^{35}Cl_{1}{}^{14}N_{2}$	10.5

Spectrum 88. HRMS of **8o**.



Spectrum 89. ^{1}H-NMR of **8p**.



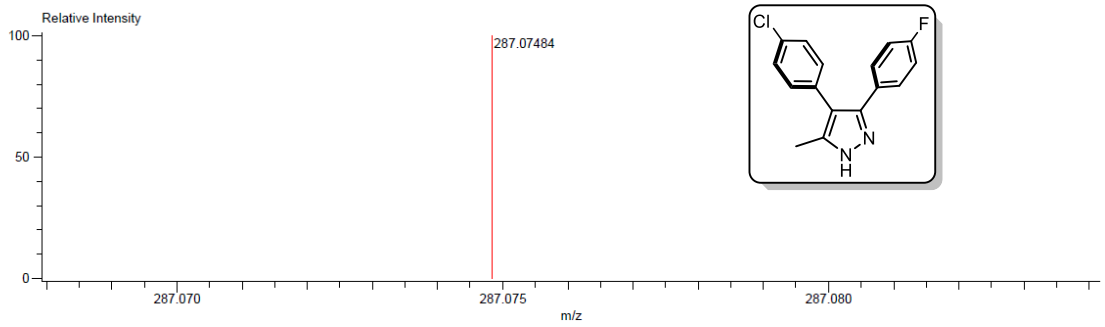
Spectrum 90. ^{13}C-NMR of **8p**.

Description:
Ionization Mode:ESI+
History:Determine m/z[Peak Detect[Centroid,30,Area];Correct Base[];Smooth[5]];Correct Base[5.0%];Average(MS[...

Mass Calibration data:Cal_PEG_600
Created:2/15/2023 11:00:07 AM
Created by:

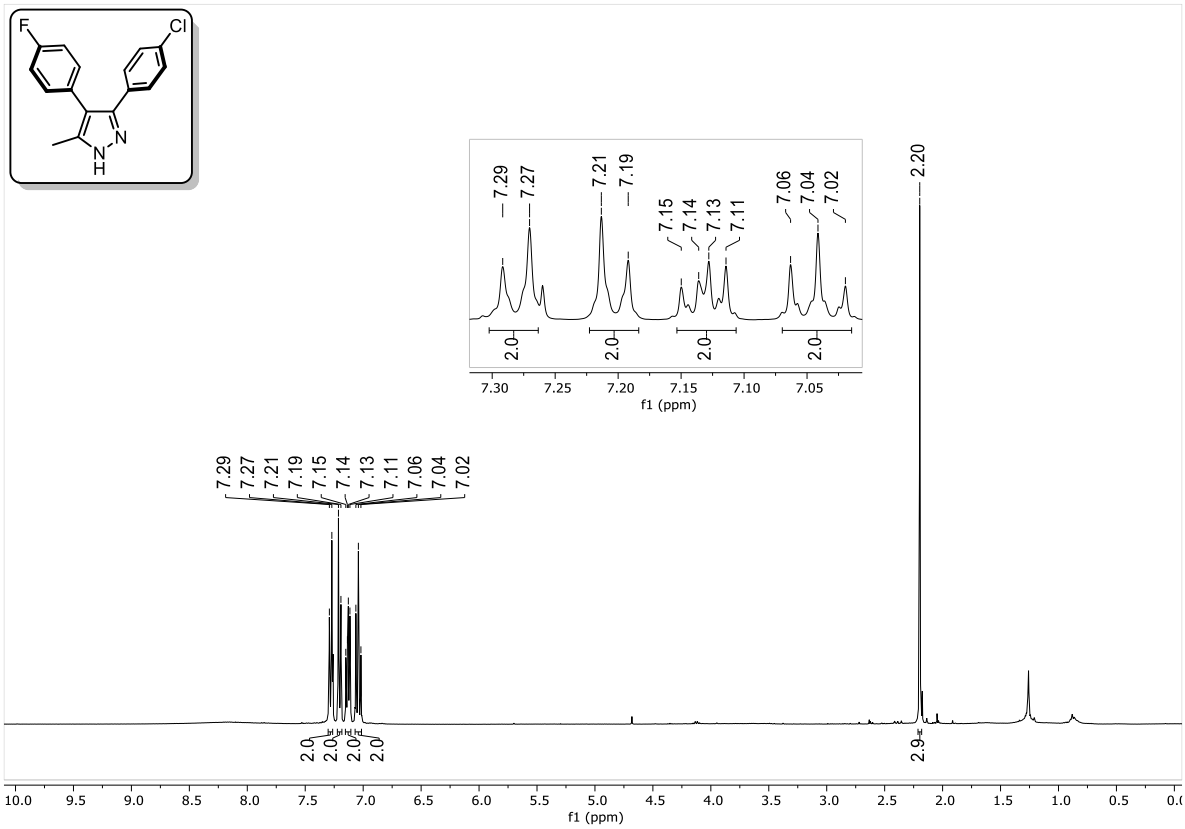
Charge number:1 Tolerance:100.00(mmu)
Element:^{12}C:0 .. 16, ^{1}H:0 .. 22, ^{35}Cl:0 .. 1, ^{19}F:0 .. 1, ^{14}N:0 .. 2, ^{16}O:0 .. 0

Unsaturation Number:0.0 .. 20.0 (Fraction:Both)

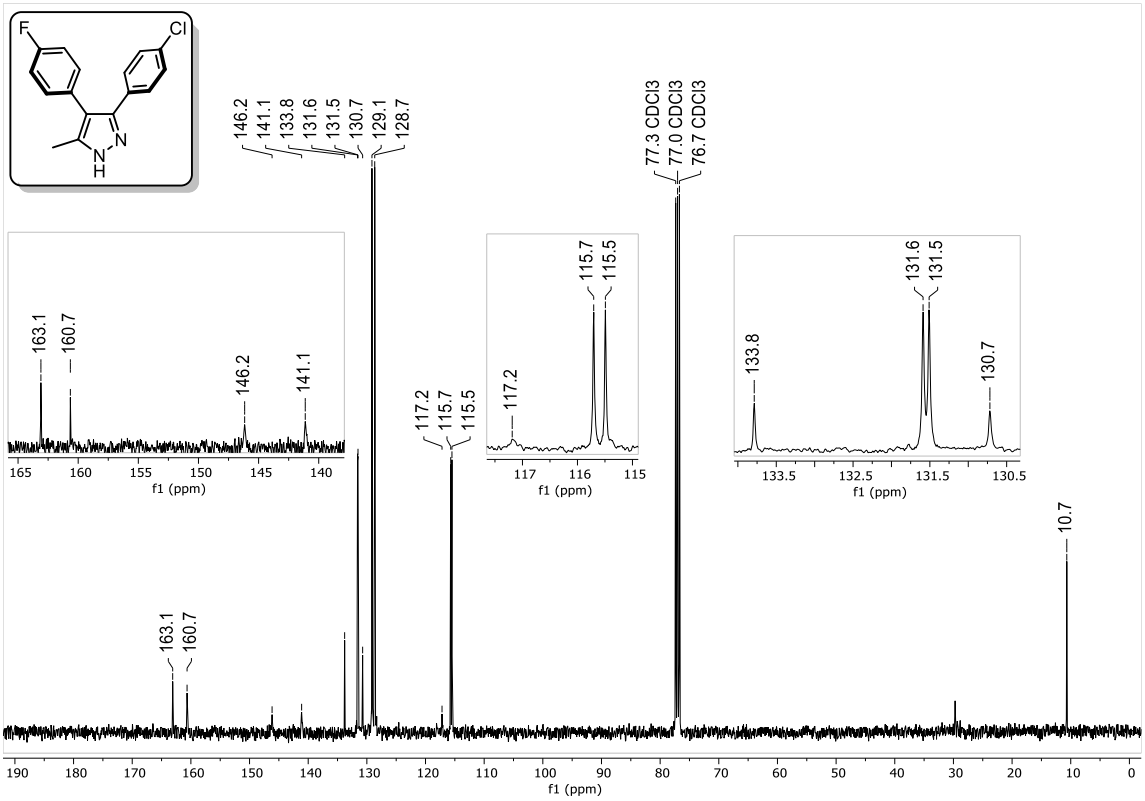


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
287.07484	14179.37	287.07513	-0.29	-1.00	$^{12}C_{16}{}^{1}H_{13}{}^{35}Cl_{1}{}^{19}F_{1}{}^{14}N_{2}$	10.5

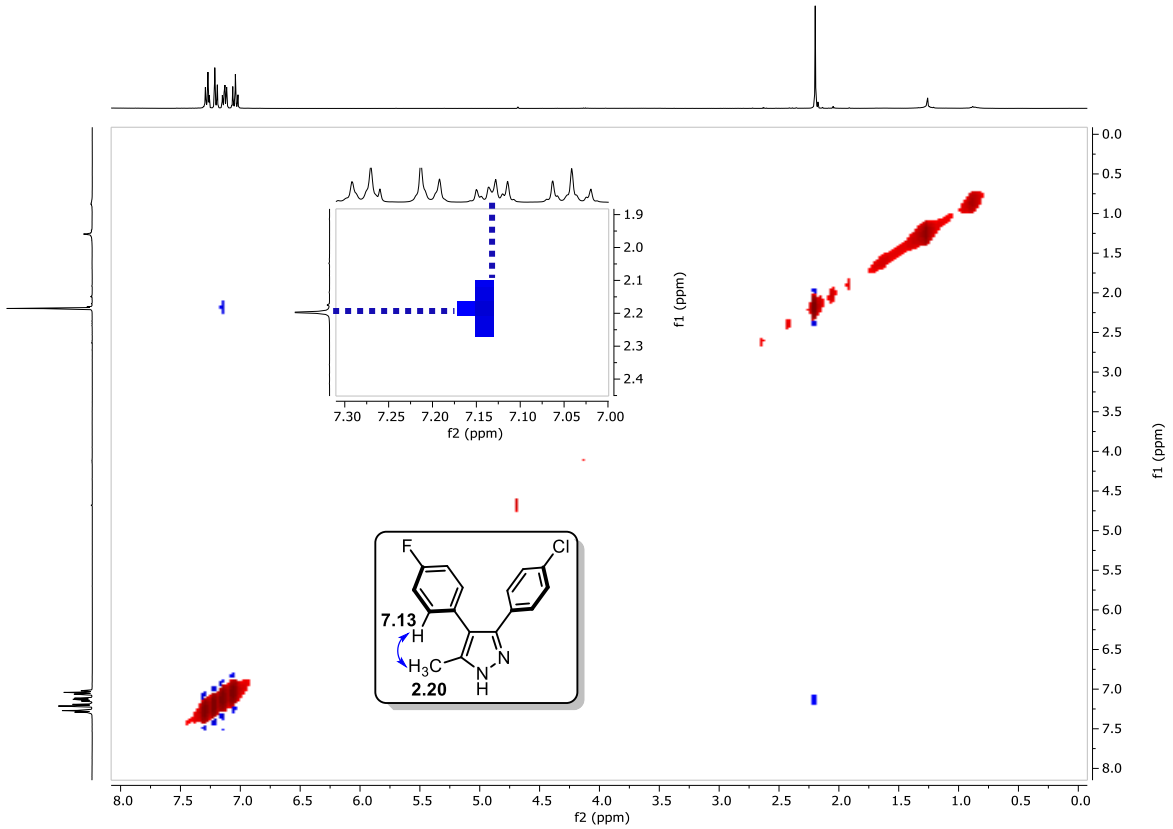
Spectrum 91. HRMS of **8p**.



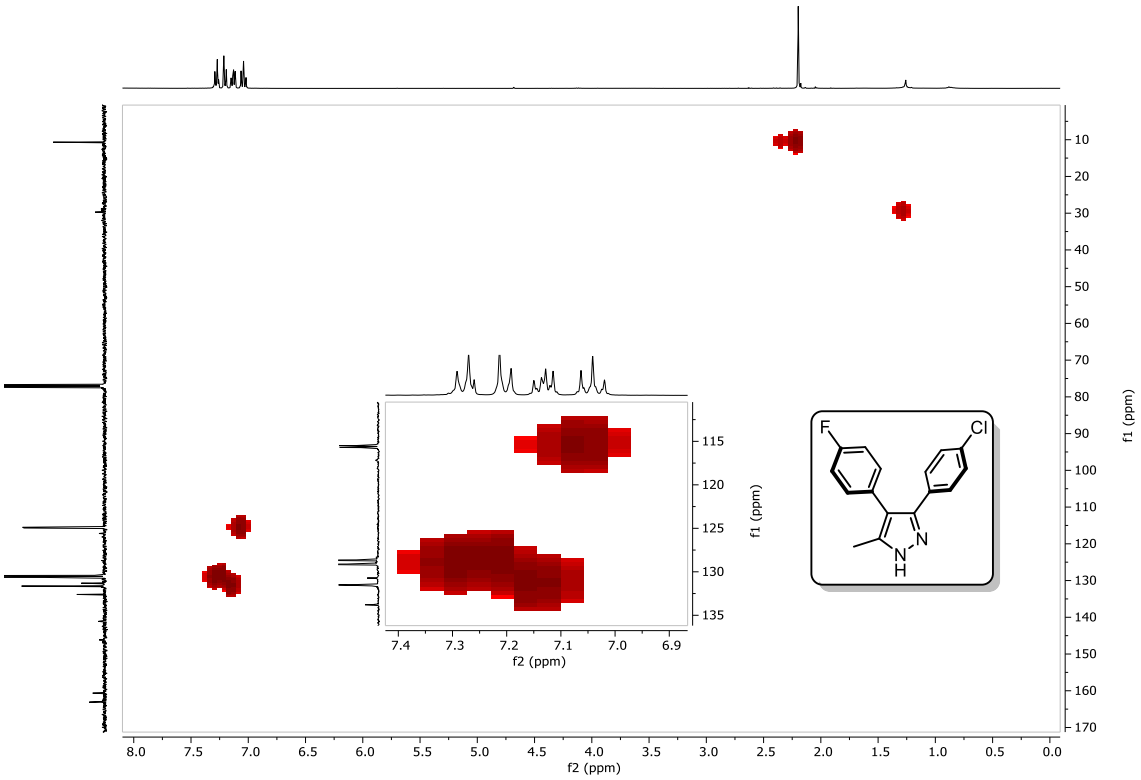
Spectrum 92. ^{1}H-NMR of **8q**.



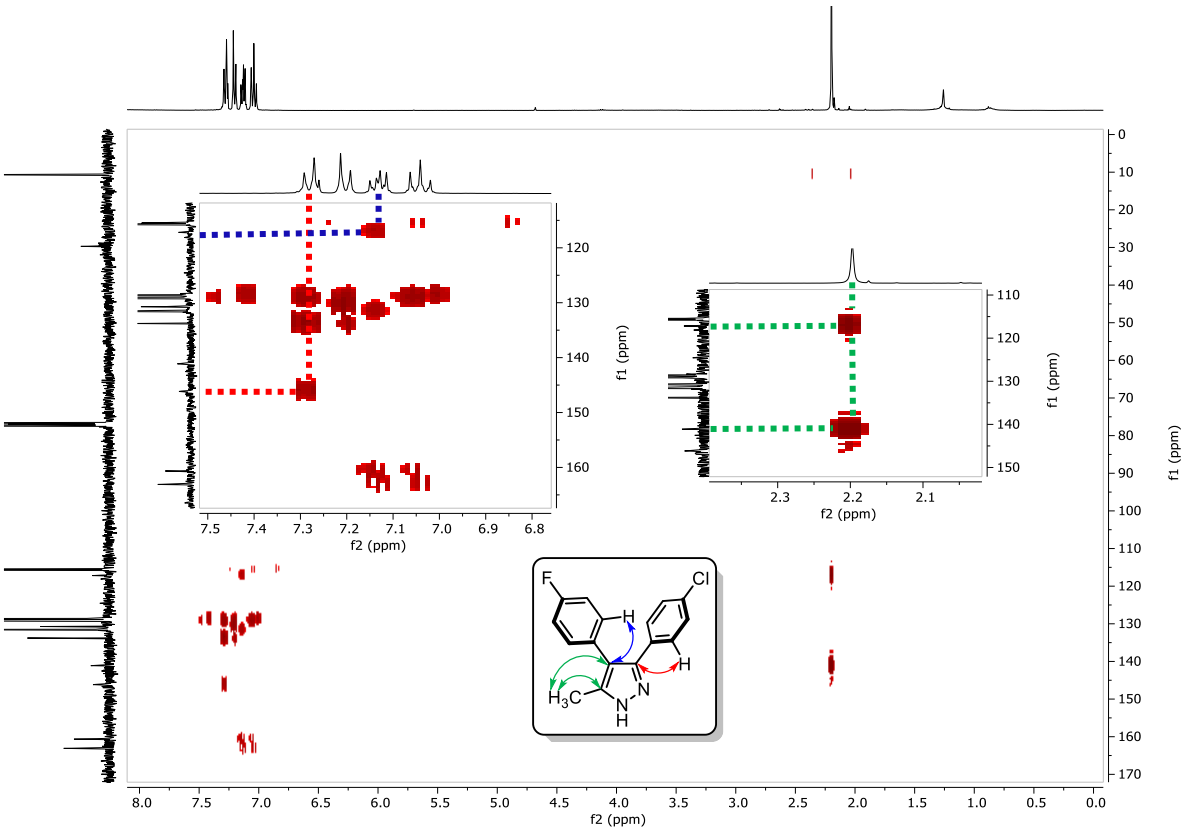
Spectrum 93. ^{13}C-NMR of **8q**.



Spectrum 94. 2D-NOESY of **8q**.



Spectrum 95. HSQC of **8q**.

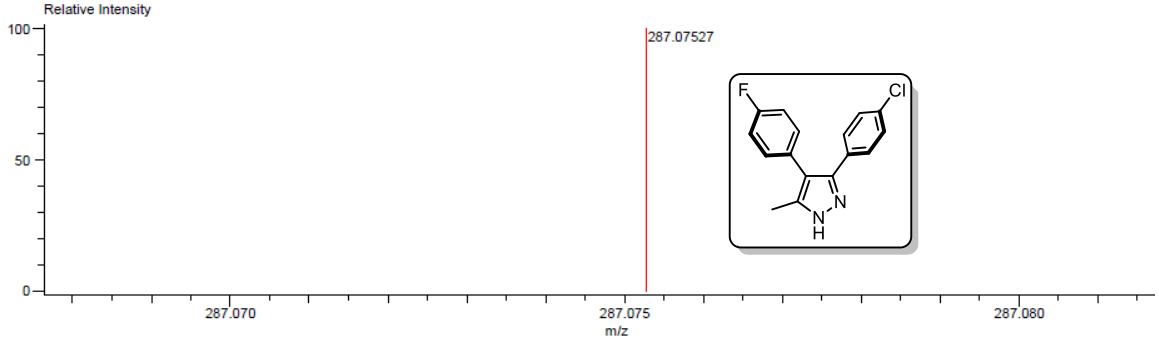


Spectrum 96. HMBC of **8q**.

Description:
Ionization Mode:ESI+
History:Determine m/z[Peak Detect[Centroid,30,Area];Correct Base[];Smooth[5]];Correct Base[5.0%];Average(MS[...

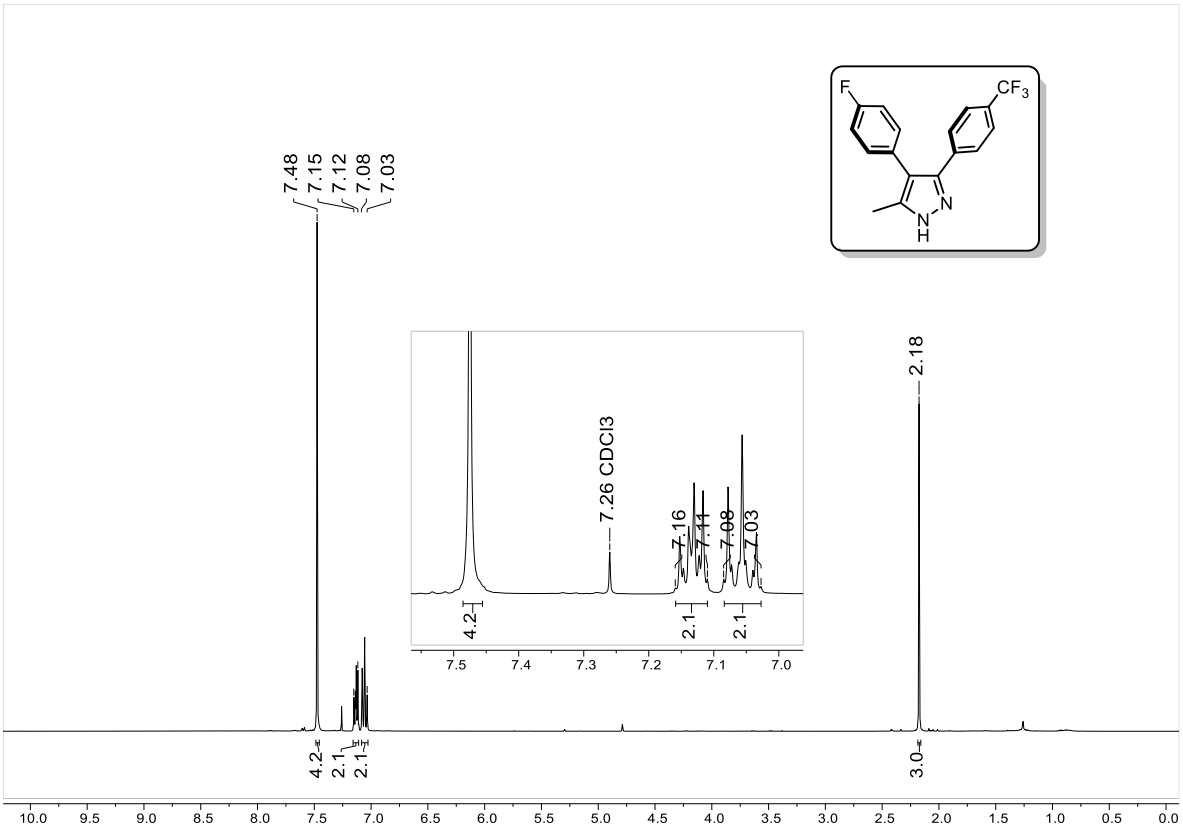
Mass Calibration data:Cal_PEG_600
Created:1/25/2023 11:02:36 AM
Created by:AccuTOF

Charge number:1
Tolerance:3.00(ppm), 5.00 .. 15.00(mmu)
Unsaturation Number:0.0 .. 45.0 (Fraction:Both)
Element:^{12}C:0 .. 16, ^{1}H:0 .. 20, ^{35}Cl:0 .. 1, ^{19}F:1 .. 1, ^{14}N:0 .. 2, ^{16}O:0 .. 0

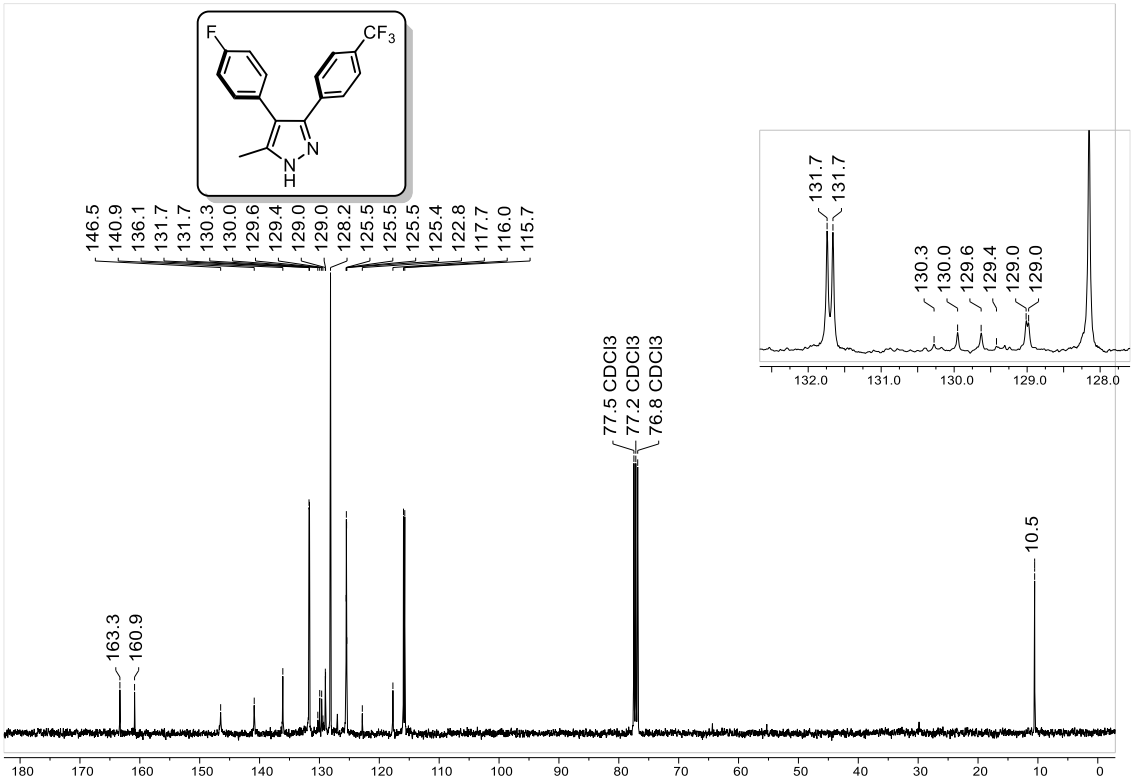


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
287.07527	17703.09	287.07513	0.14	0.49	$^{12}C_{16}{}^{1}H_{13}{}^{35}Cl_{1}{}^{19}F_{1}{}^{14}N_{2}$	10.5

Spectrum 97. HRMS of **8q**.



Spectrum 98. ^{1}H-NMR of **8r**.

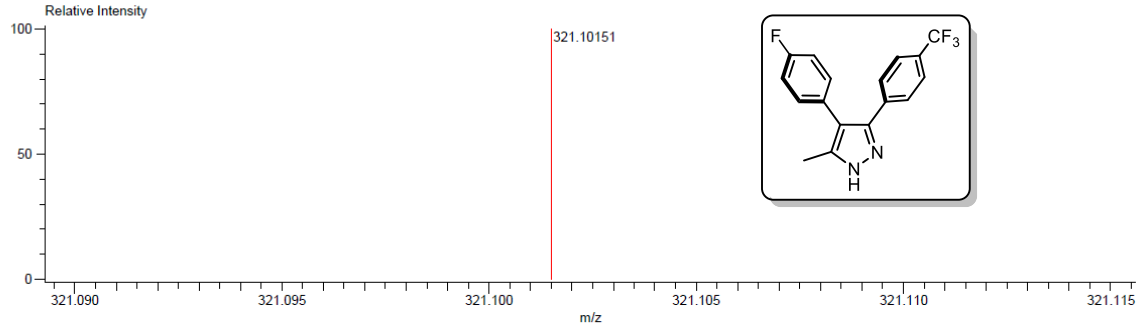


Spectrum 99. ^{13}C-NMR of **8r**.

Description:
Ionization Mode:ESI+
History:Determine m/z[Peak Detect[Centroid,30,Area];Correct Base[];Smooth[5]];Correct Base[5.0%];Average(MS[...

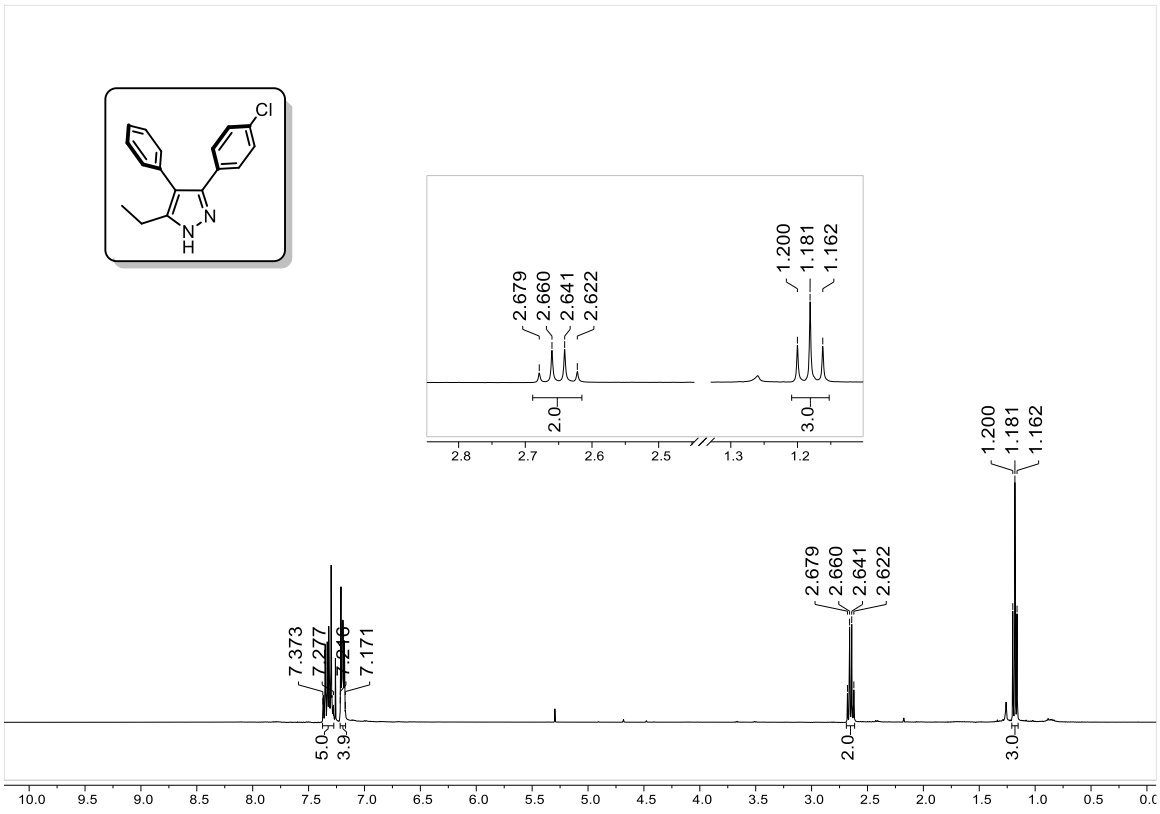
Mass Calibration data:Cal_PEG_600
Created:2/2/2023 10:33:12 AM
Created by:AccuTOF

Charge number:1
Tolerance:50.00(ppm), 5.00 .. 15.00(mmu)
Unsaturation Number:0.0 .. 50.0 (Fraction:.5)
Element:^{12}C:0 .. 17, ^{1}H:0 .. 50, ^{19}F:0 .. 4, ^{14}N:0 .. 2, ^{16}O:0 .. 0

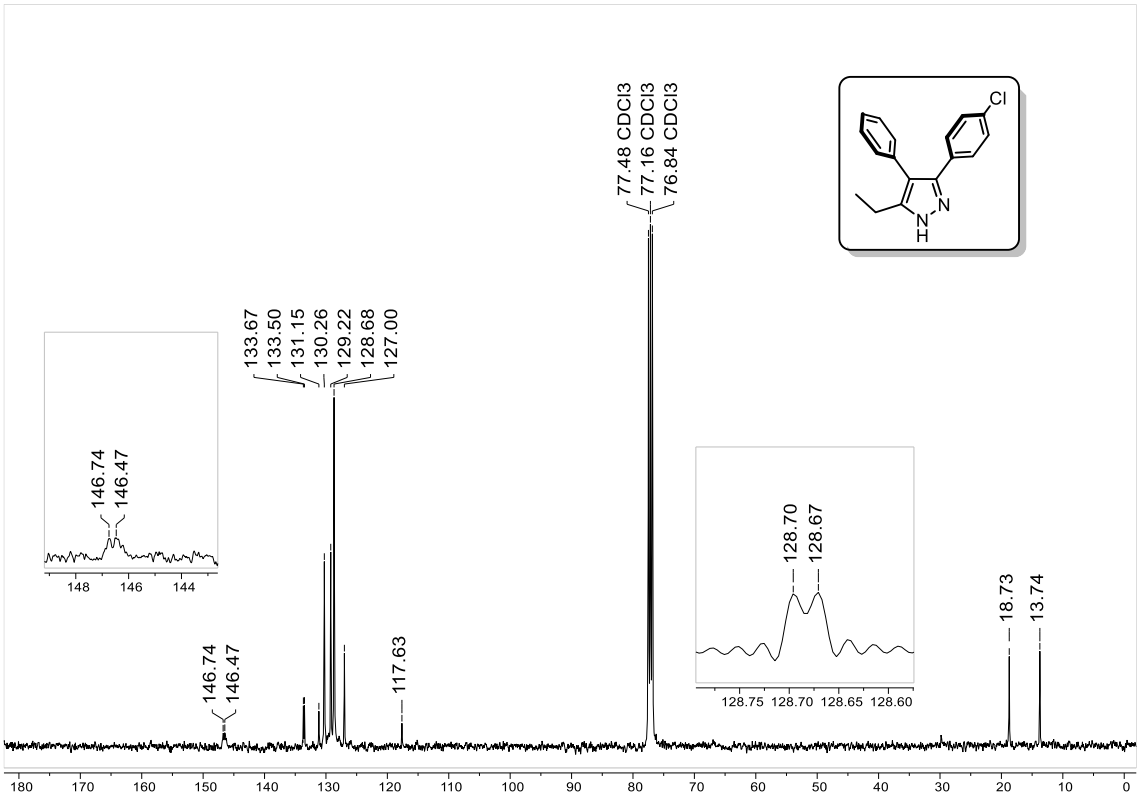


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
321.10151	4047.61	321.10149	0.02	0.07	$^{12}C_{17}{}^{1}H_{13}{}^{19}F_{4}{}^{14}N_{2}$	10.5

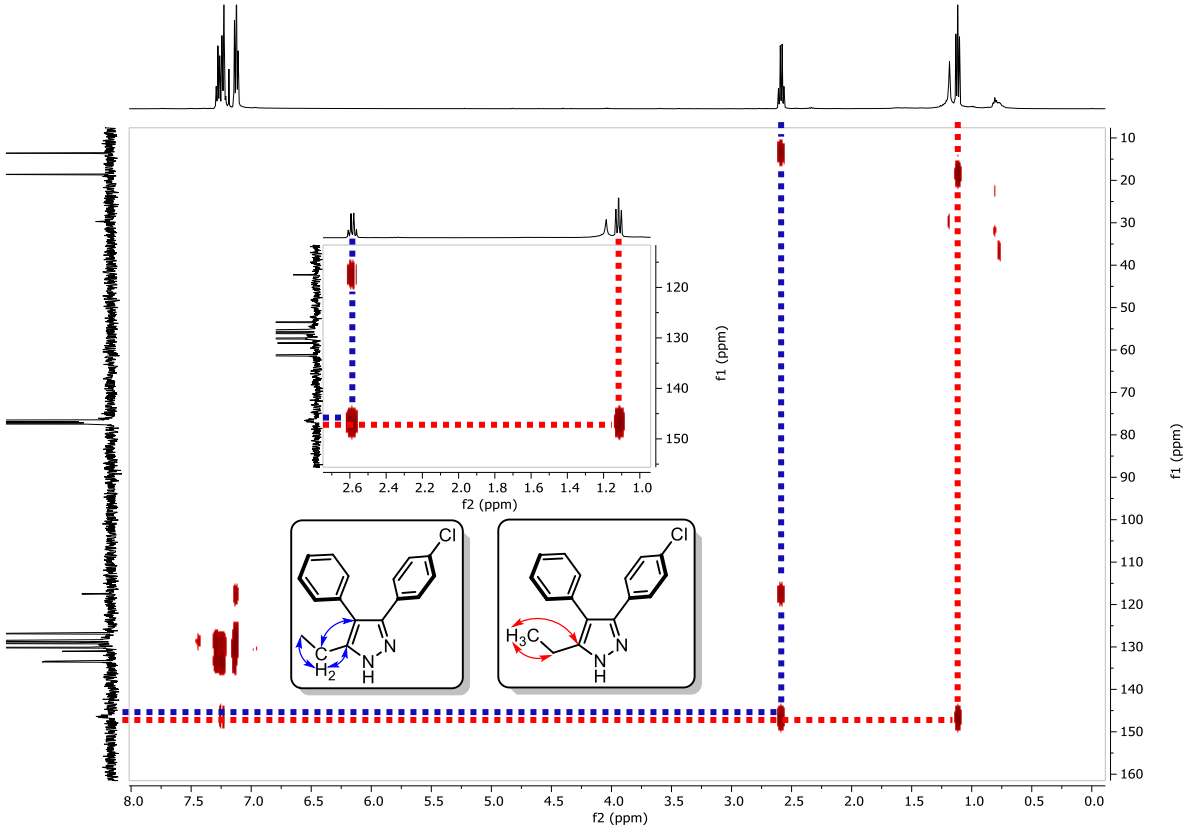
Spectrum 100. HRMS of **8r**.



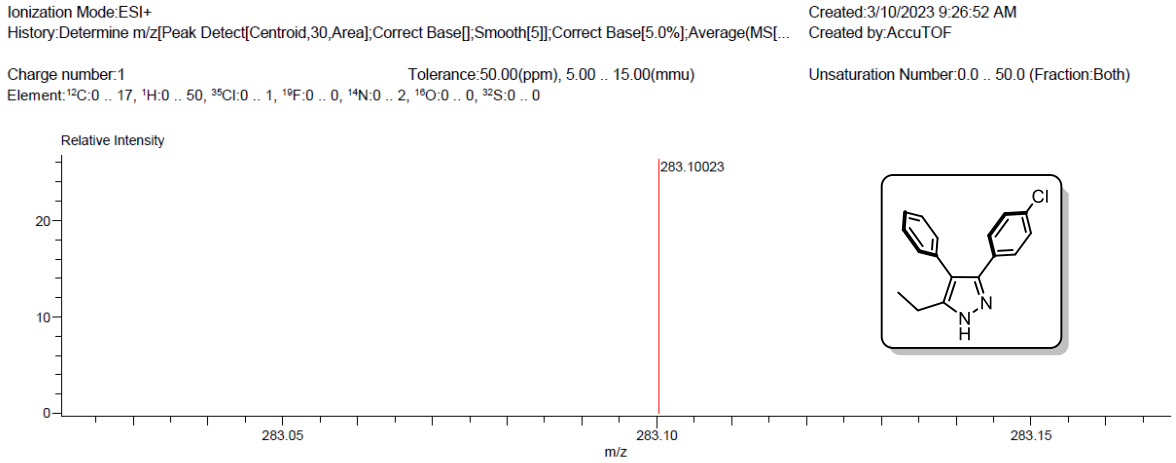
Spectrum 101. ^{1}H-NMR of **8s**.



Spectrum 102. ^{13}C-NMR of **8s**.

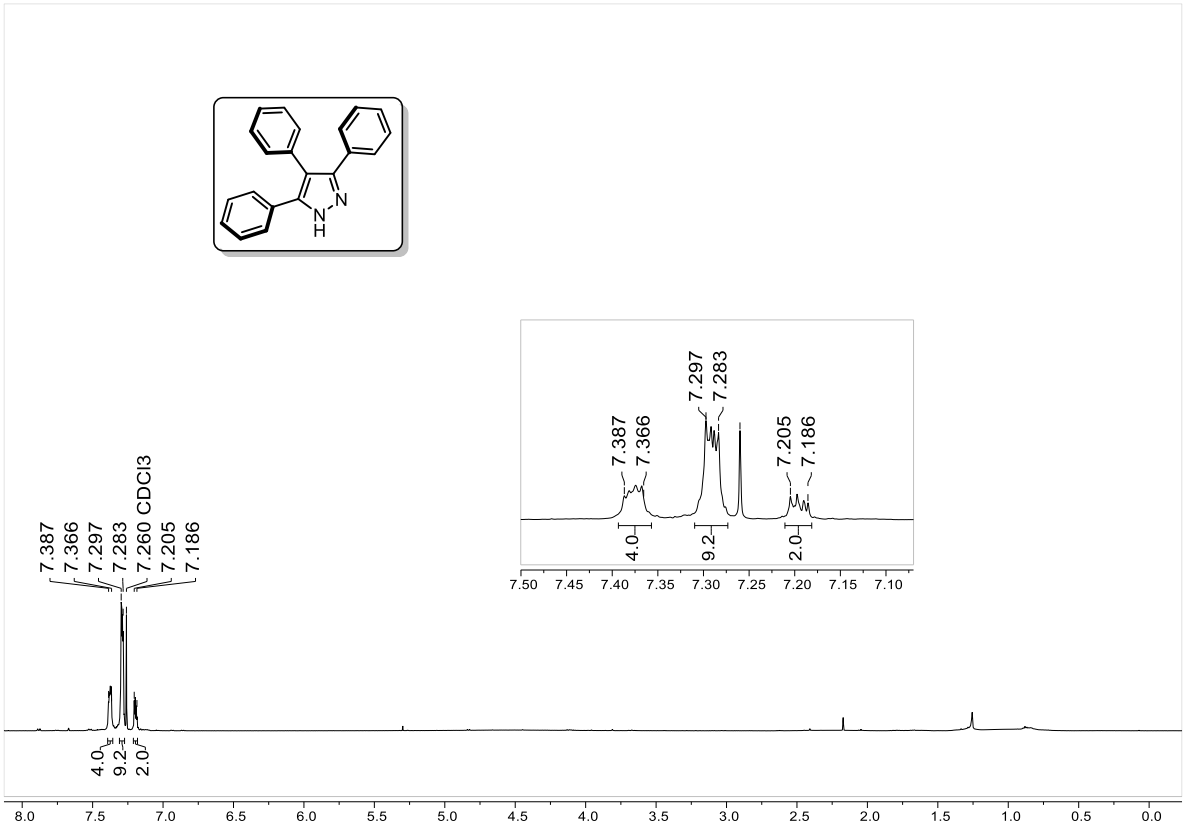


Spectrum 103. HMBC of **8s**.

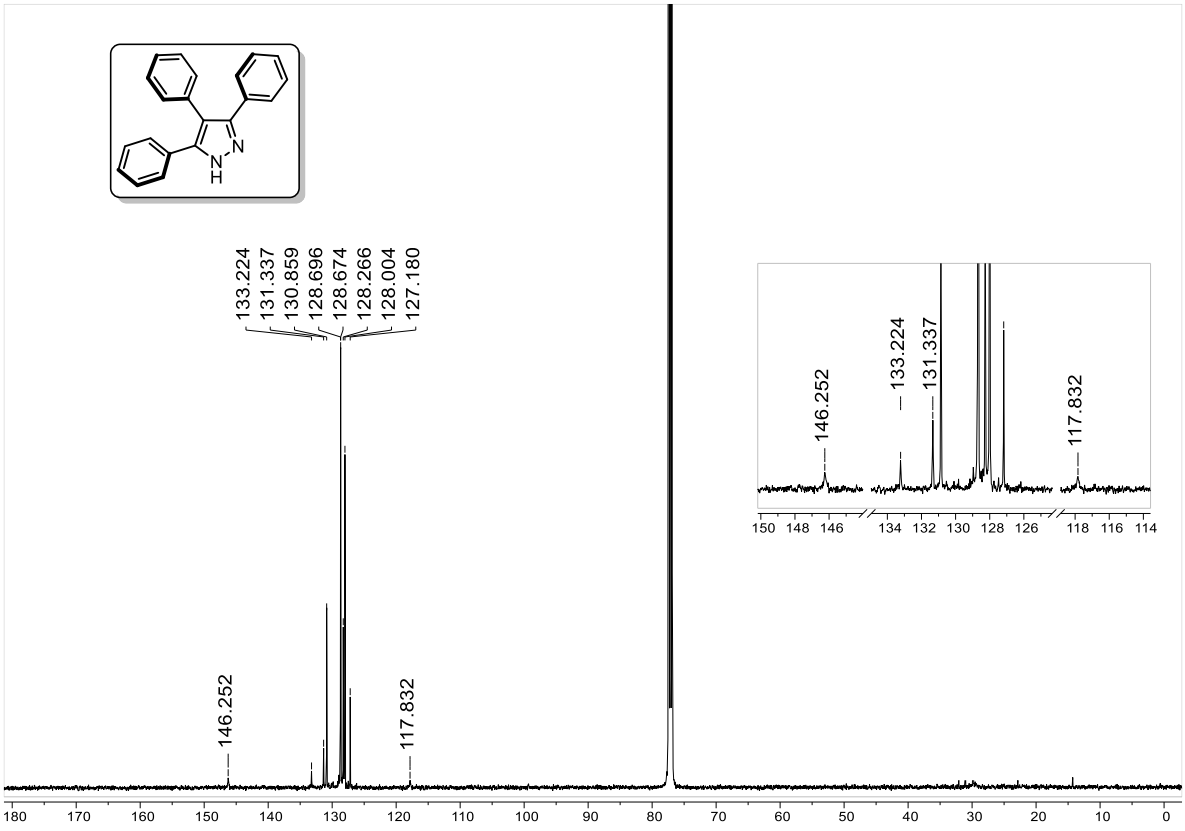


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
283.10023	377996.21	283.10020	0.03	0.12	$^{12}C_{17}{}^{1}H_{16}{}^{35}Cl_{1}{}^{14}N_{2}$	10.5

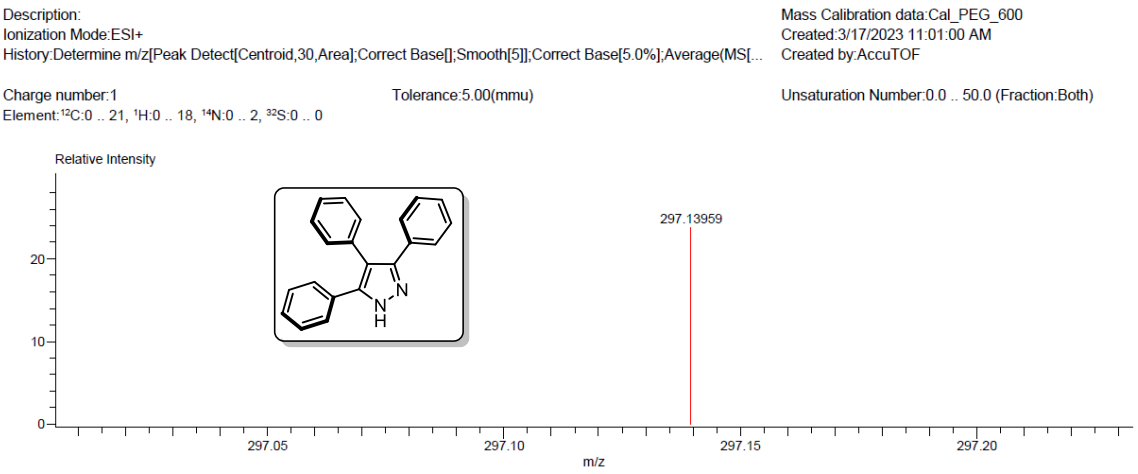
Spectrum 104. HRMS of **8s**.



Spectrum 105. ^{1}H-NMR of **8t**.

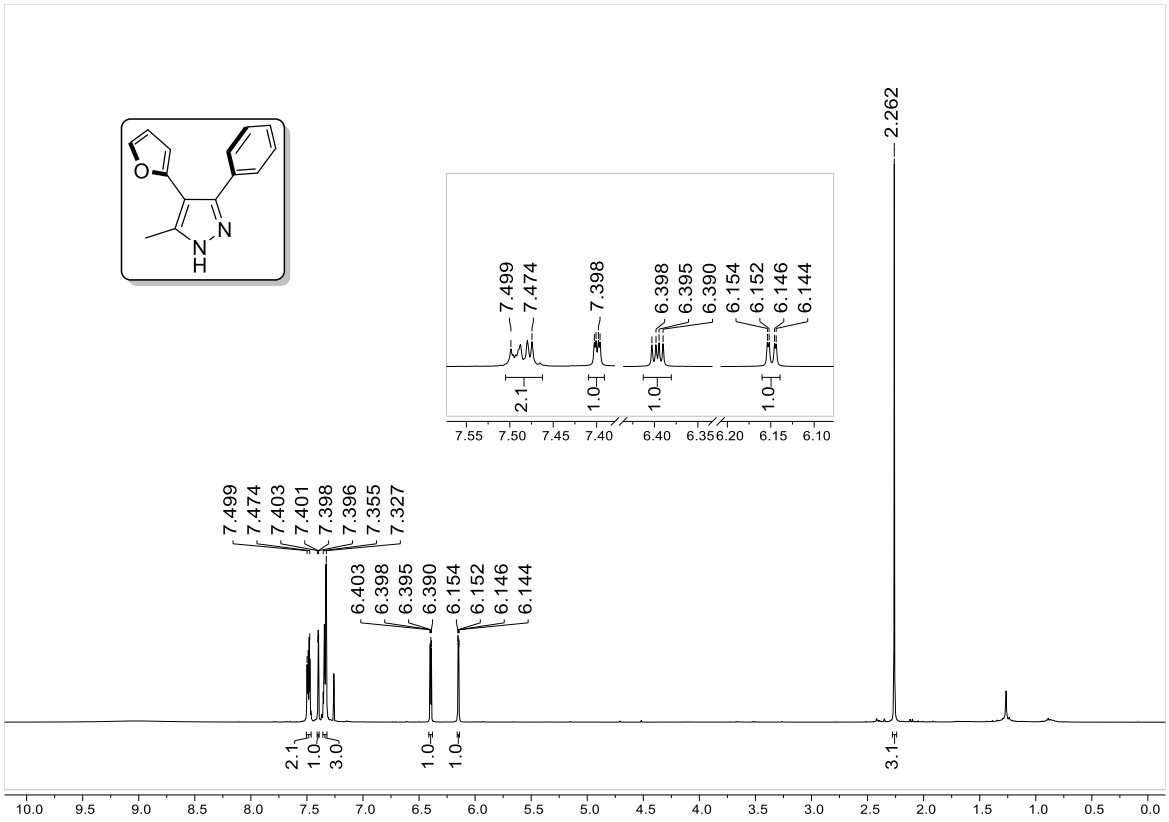


Spectrum 106. ^{13}C-NMR of **8t**.

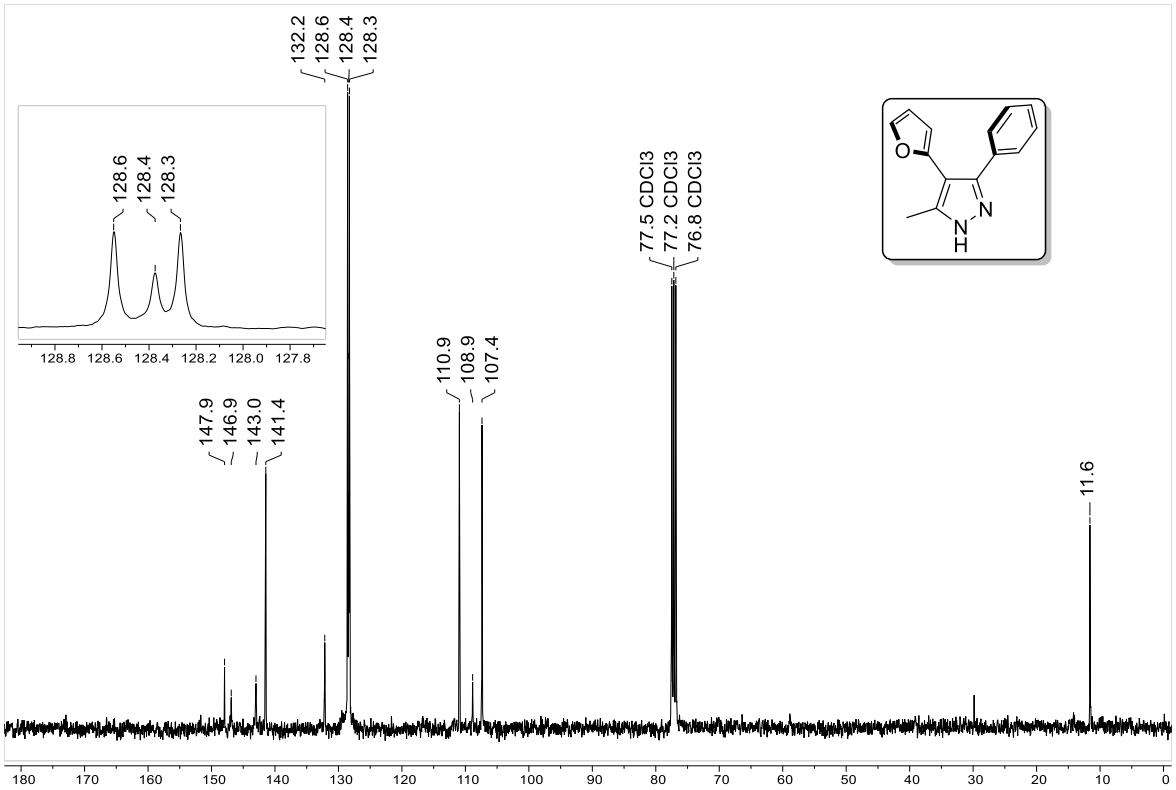


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
297.13959	22230.20	297.13917	0.42	1.42	$^{12}C_{21}{}^{1}H_{17}{}^{14}N_2$	14.5

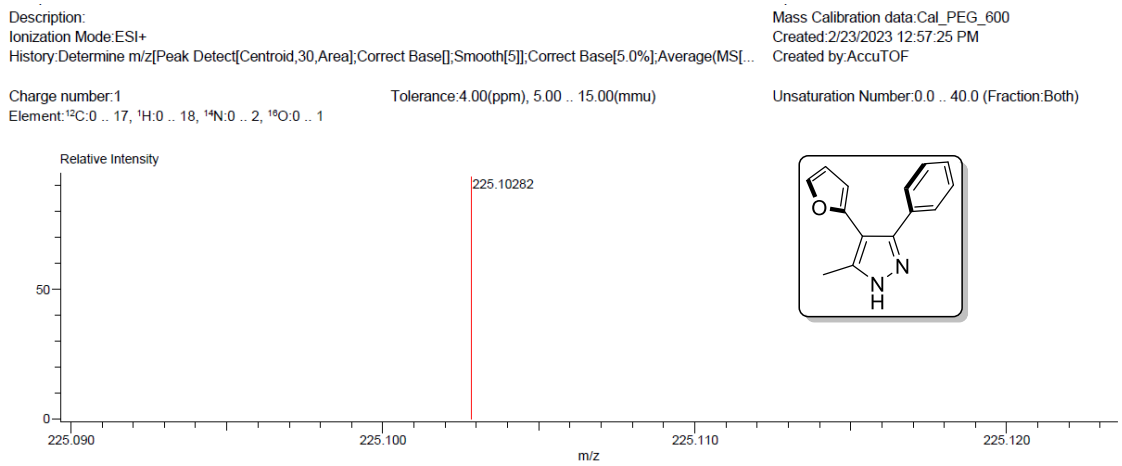
Spectrum 107. HRMS of **8t**.



Spectrum 108. ^{1}H-NMR of **8u**.

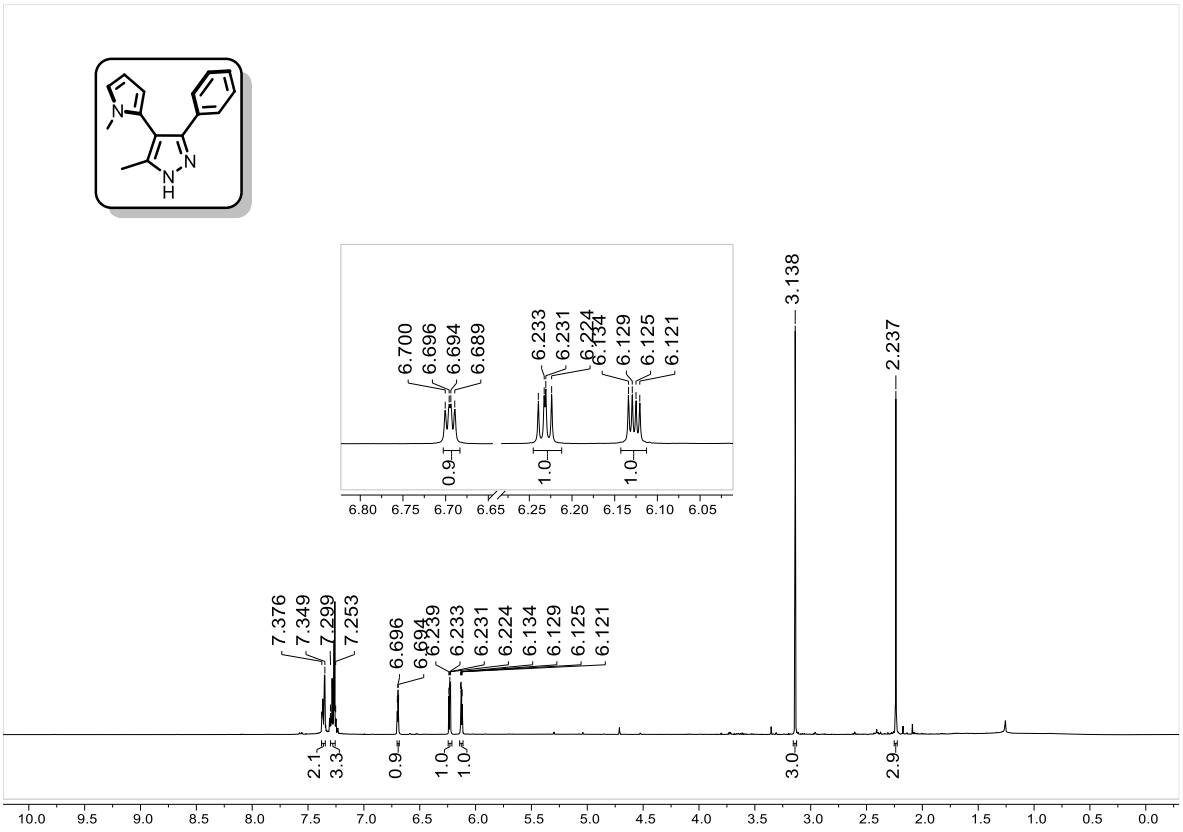


Spectrum 109. ^{13}C-NMR of **8u**.

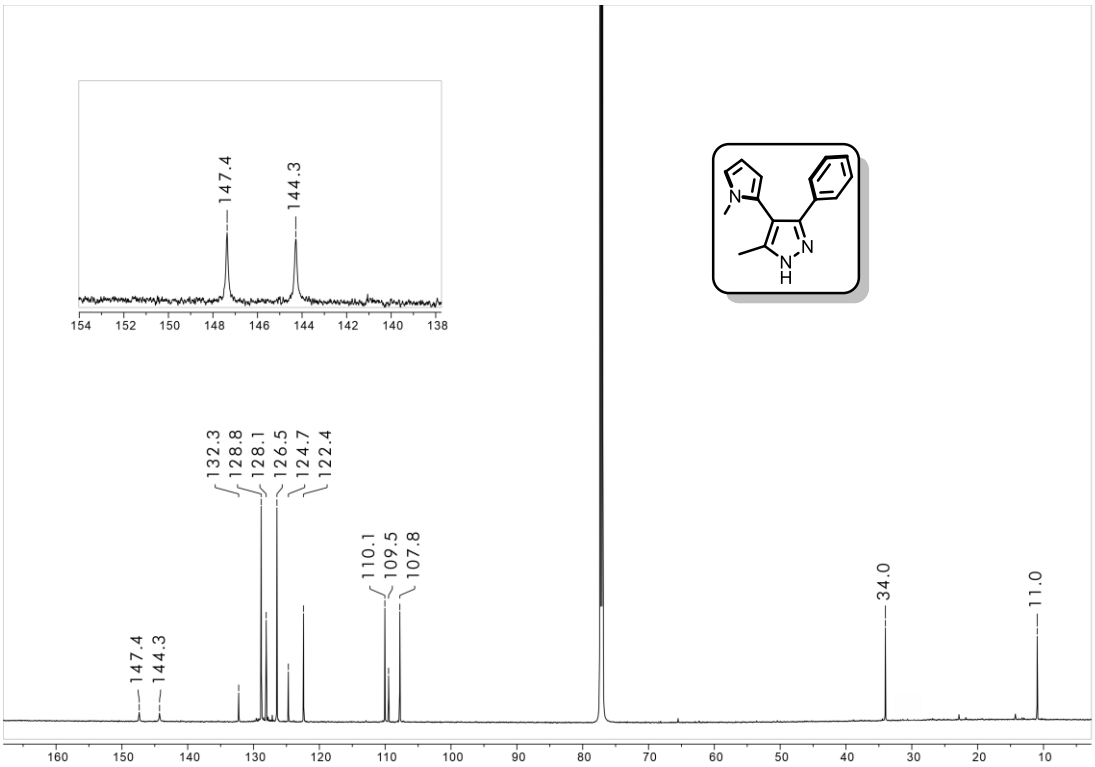


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
225.10282	5968.48	225.10279	0.03	0.14	$^{12}C_{14}{}^{1}H_{13}{}^{14}N_{2}{}^{16}O_{1}$	9.5

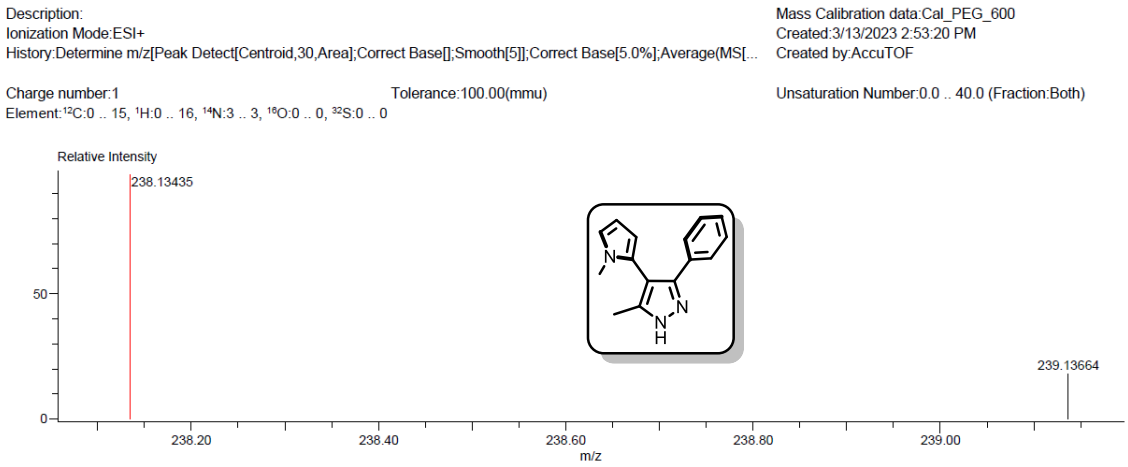
Spectrum 110. HRMS of **8u**.



Spectrum 111. ^{1}H-NMR of **8v**.

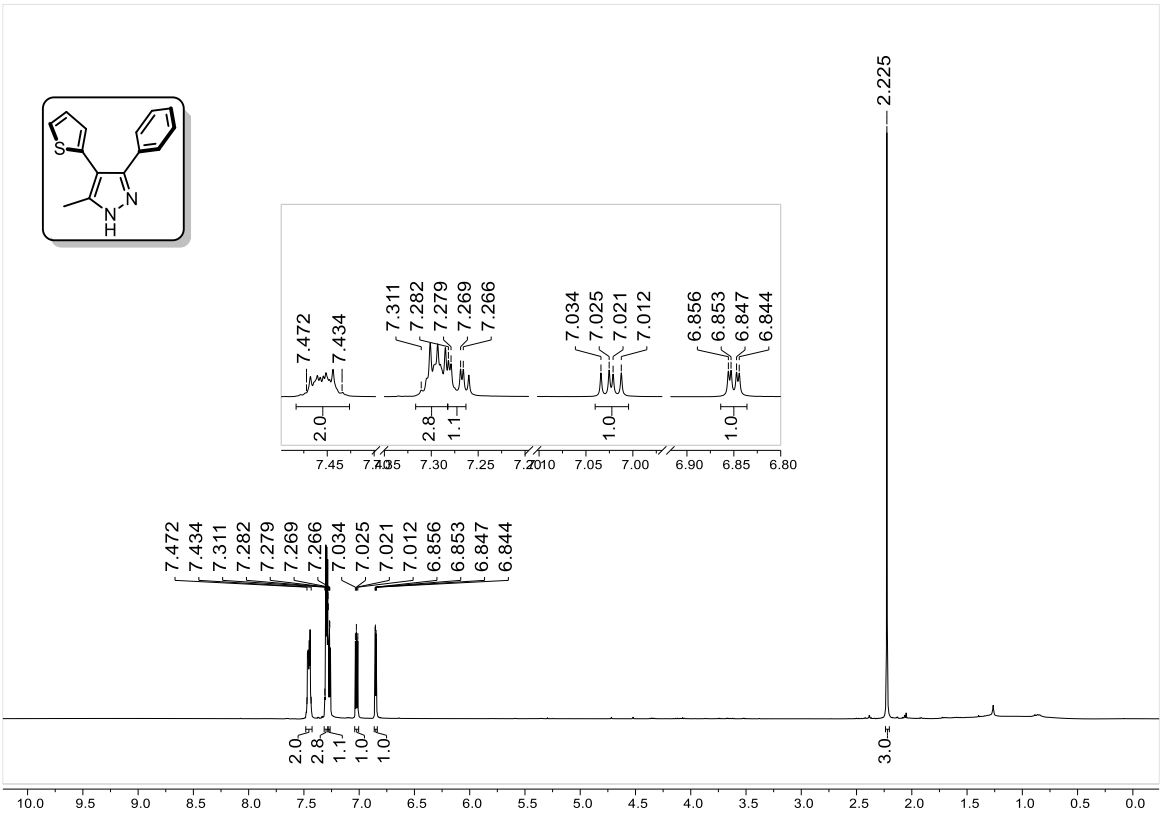


Spectrum 112. ^{13}C-NMR of **8v**.

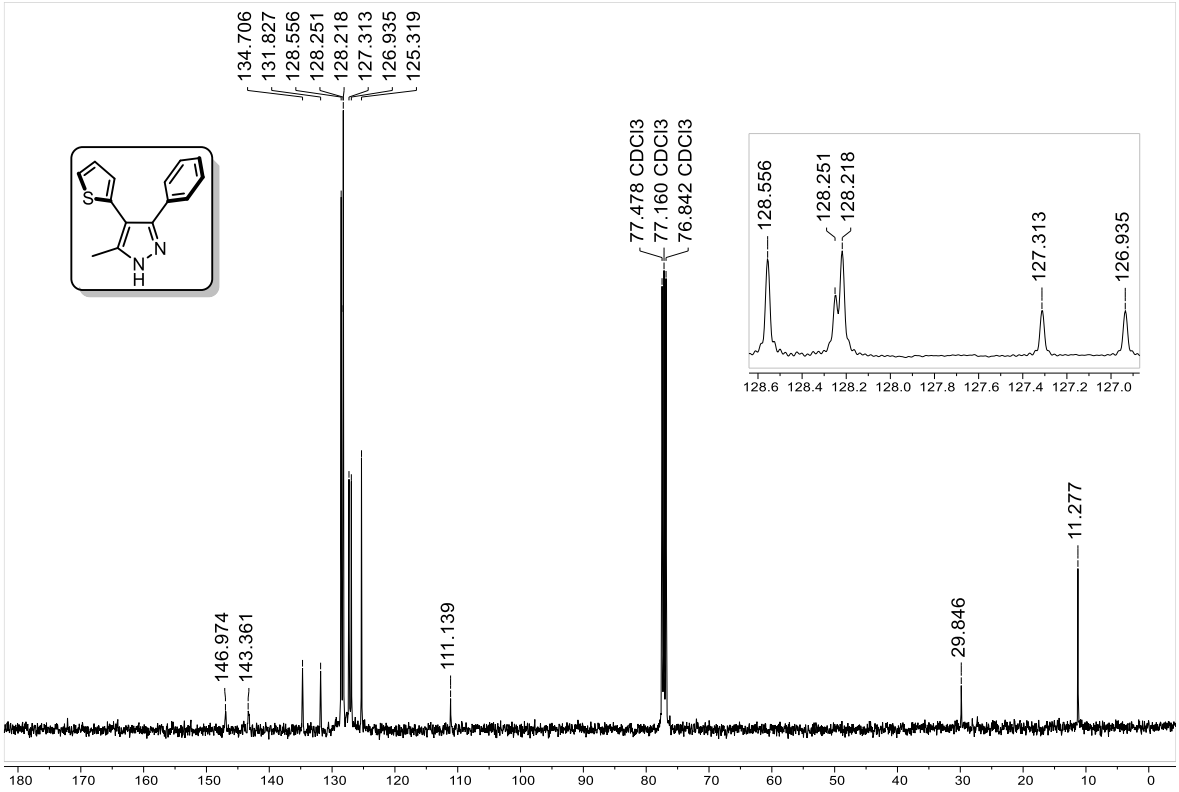


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
238.13435	21076.71	238.13442	-0.07	-0.29	$^{12}C_{15}{}^{1}H_{16}{}^{14}N_3$	9.5

Spectrum 113. HRMS of **8v**.



Spectrum 114. ^{1}H-NMR of **8w**.

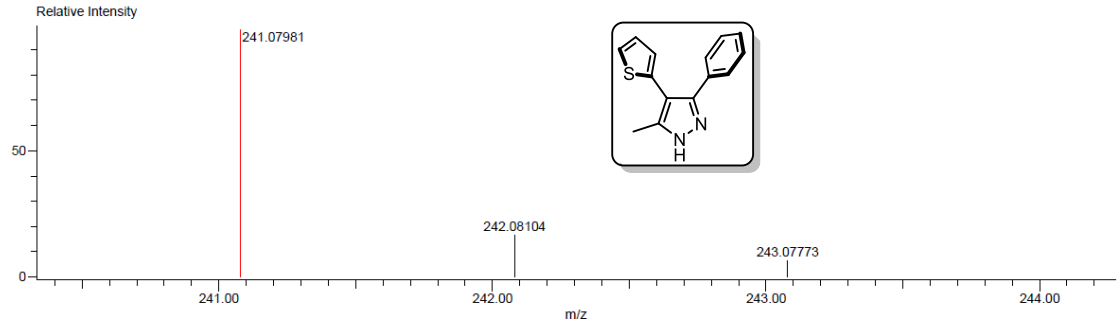


Spectrum 115. ^{13}C-NMR of **8w**.

Description:
Ionization Mode:ESI+
History:Determine m/z[Peak Detect[Centroid,30,Area];Correct Base[];Smooth[5]];Correct Base[5.0%];Average(MS[...

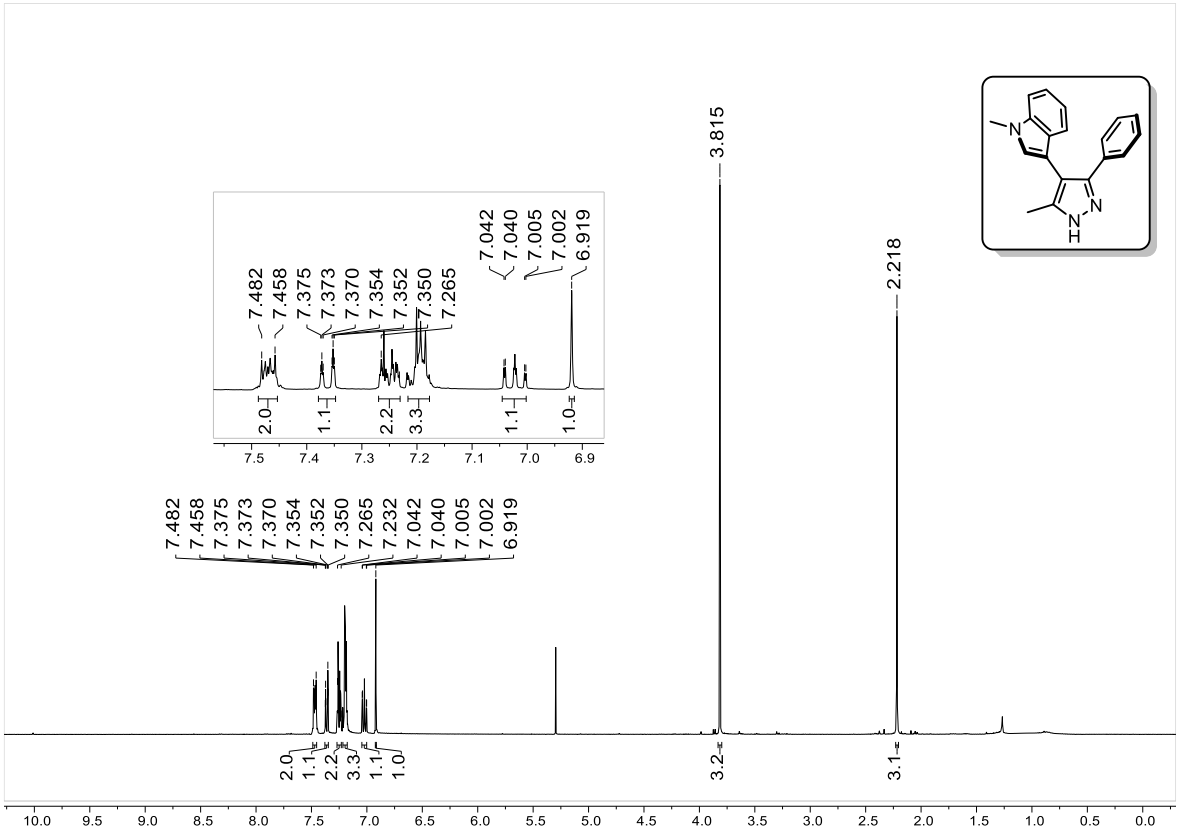
Mass Calibration data:Cal_PEG_600
Created:3/10/2023 9:16:20 AM
Created by:AccuTOF

Charge number:1 Tolerance:50.00(ppm), 5.00 .. 15.00(mmu) Unsaturation Number:0.0 .. 50.0 (Fraction:Both)
Element:^{12}C:0 .. 14, ^{1}H:0 .. 50, ^{35}Cl:0 .. 0, ^{19}F:0 .. 0, ^{14}N:0 .. 2, ^{16}O:0 .. 0, ^{32}S:0 .. 1

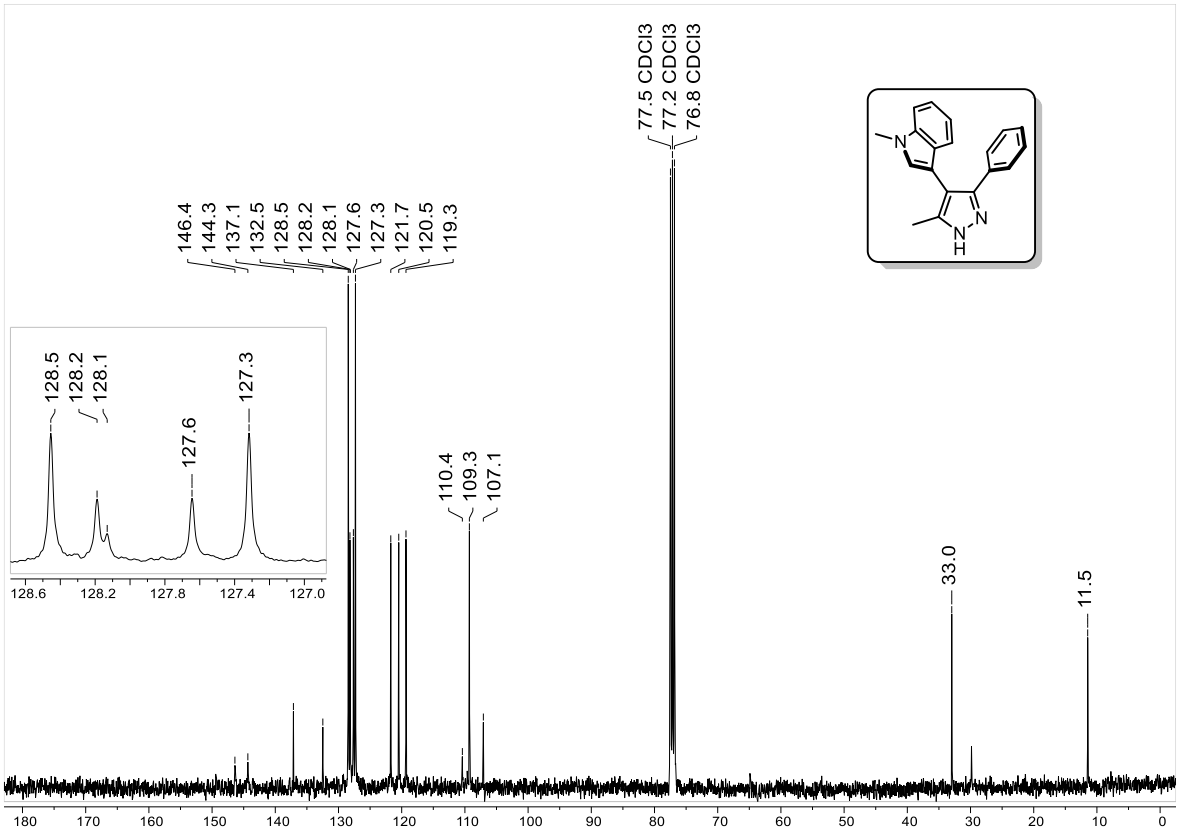


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
241.07981	20510.44	241.07994	-0.13	-0.55	$^{12}C_{14}{}^{1}H_{13}{}^{14}N_{2}{}^{32}S_{1}$	9.5

Spectrum 116. HRMS of **8w**.



Spectrum 117. ^{1}H-NMR of **8x**.



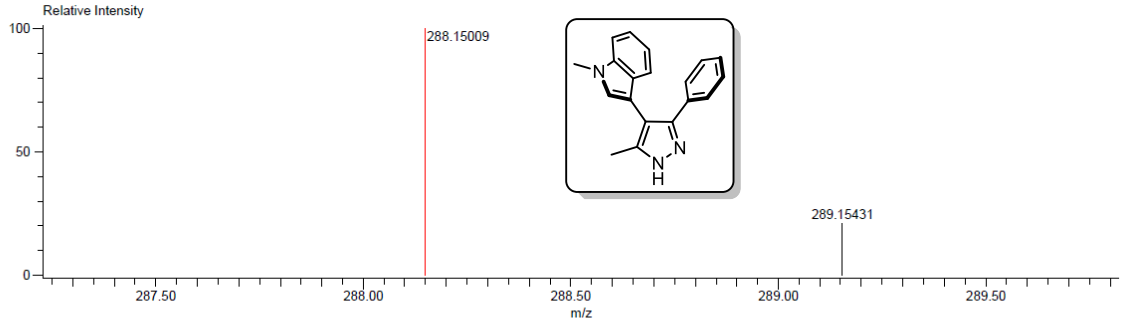
Spectrum 118. ^{13}C-NMR of **8x**.

Description:
Ionization Mode:ESI+
History:Determine m/z[Peak Detect[Centroid,30,Area];Correct Base[];Smooth[5]];Correct Base[5.0%];Average(MS[...

Mass Calibration data:Cal_PEG_600
Created:3/1/2023 10:40:03 AM
Created by:AccuTOF

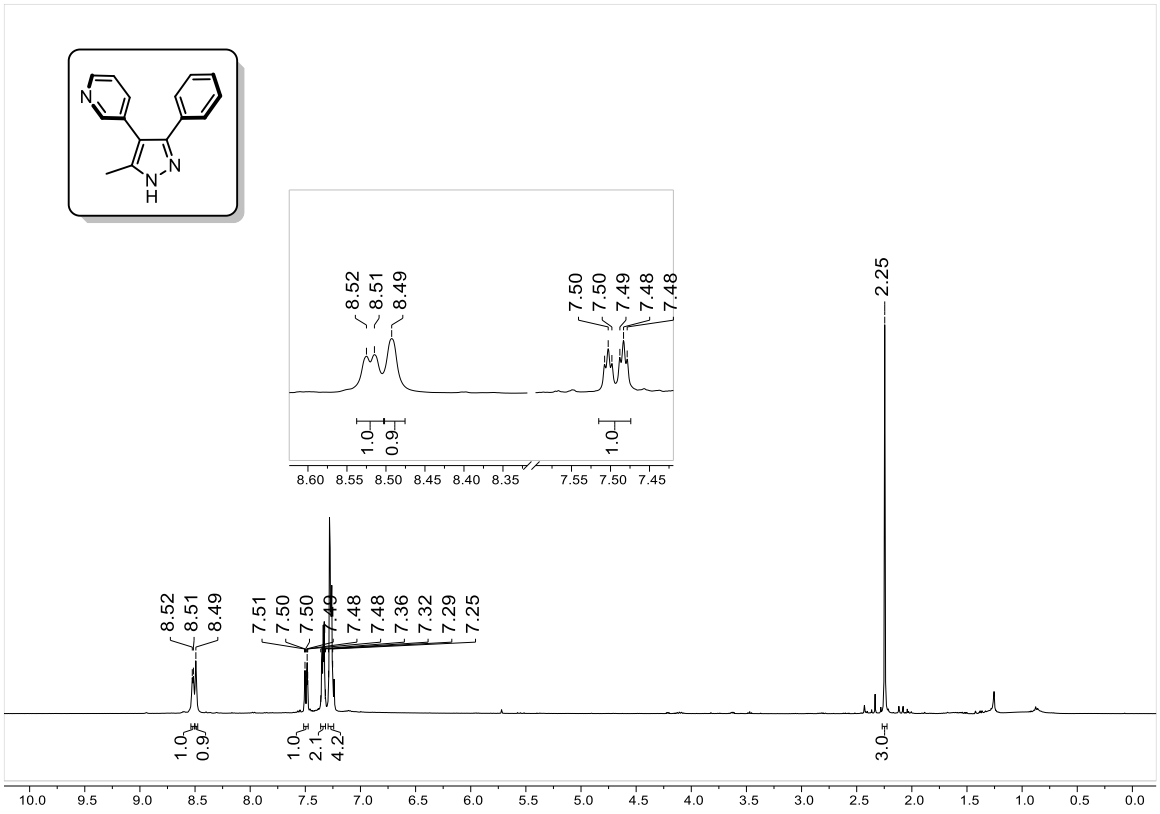
Charge number:1
Tolerance:3.00(mmu)
Element:^{12}C:0 .. 19, ^{1}H:0 .. 20, ^{79}Br:0 .. 0, ^{81}Br:0 .. 0, ^{14}N:0 .. 3, ^{15}N:0 .. 0, ^{16}O:0 .. 0, ^{32}S:0 .. 0

Unsaturation Number:0.0 .. 30.0 (Fraction:Both)

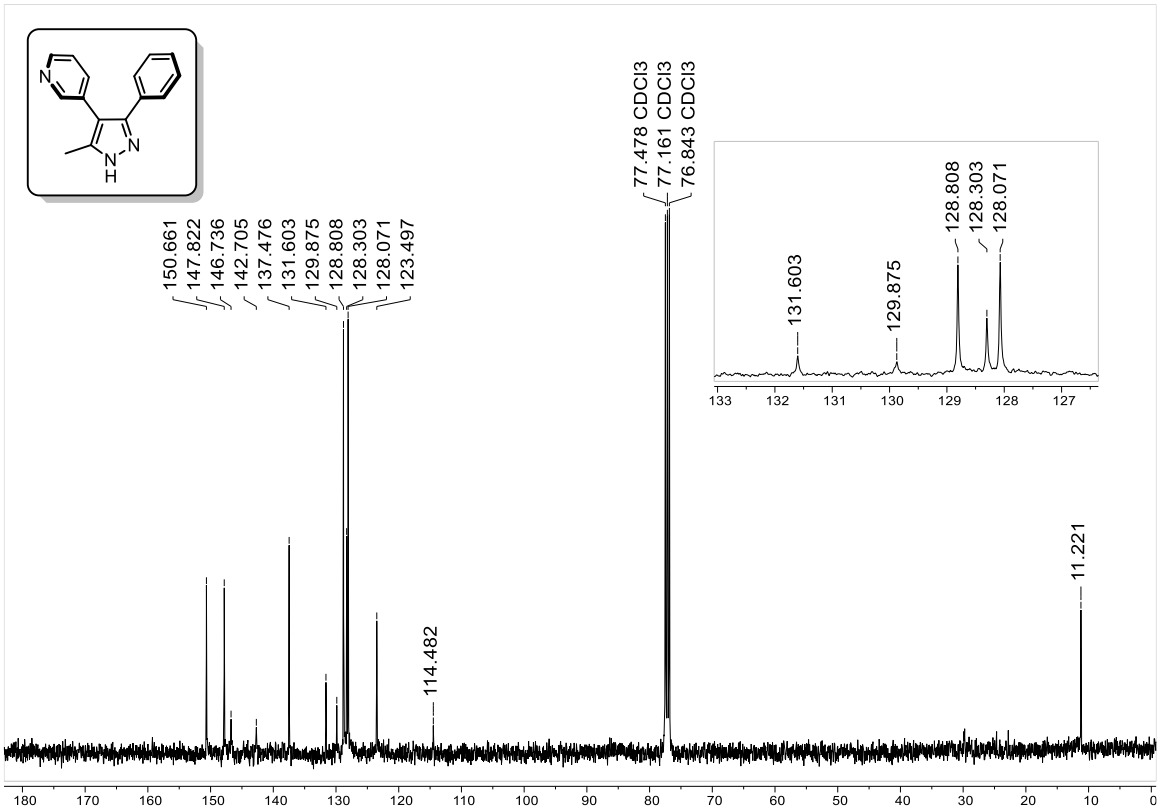


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
288.15009	208716.91	288.15007	0.01	0.05	$^{12}C_{19}{}^{1}H_{18}{}^{14}N_3$	12.5

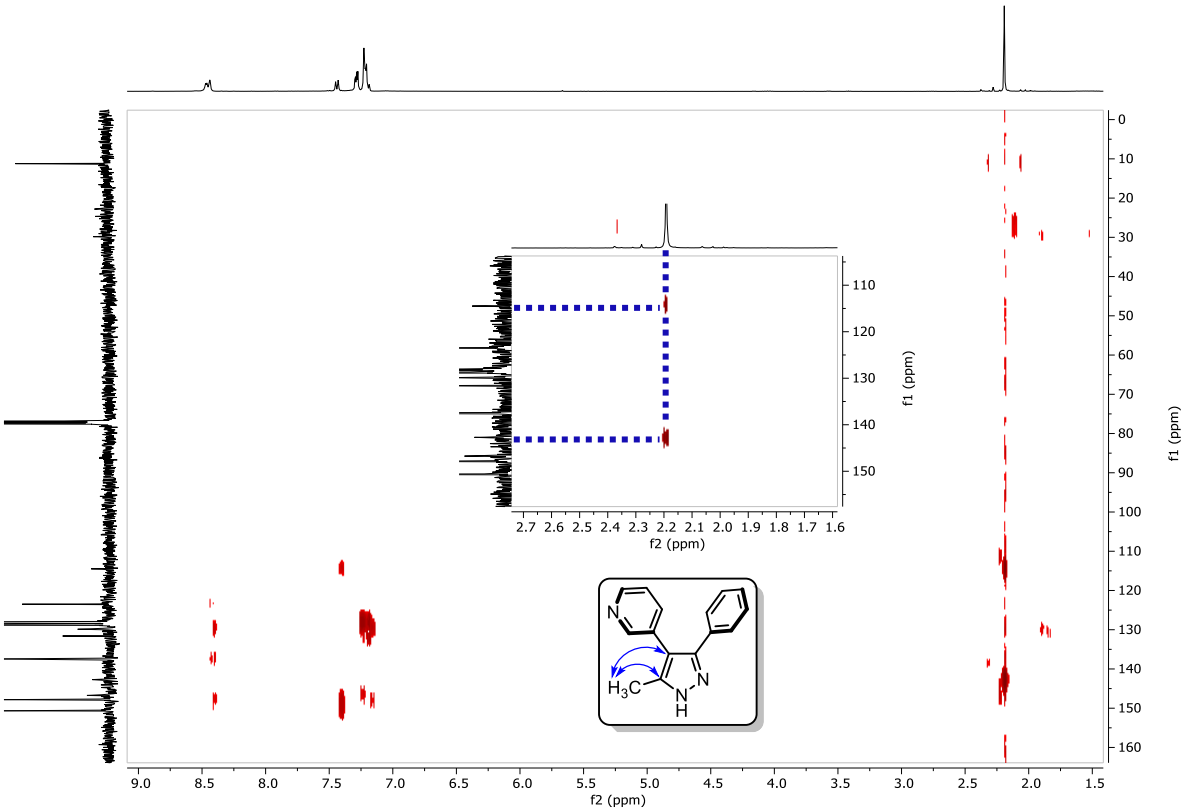
Spectrum 119. HRMS of **8x**.



Spectrum 120. ^{1}H-NMR of **8y**.



Spectrum 121. ^{13}C-NMR of **8y**.



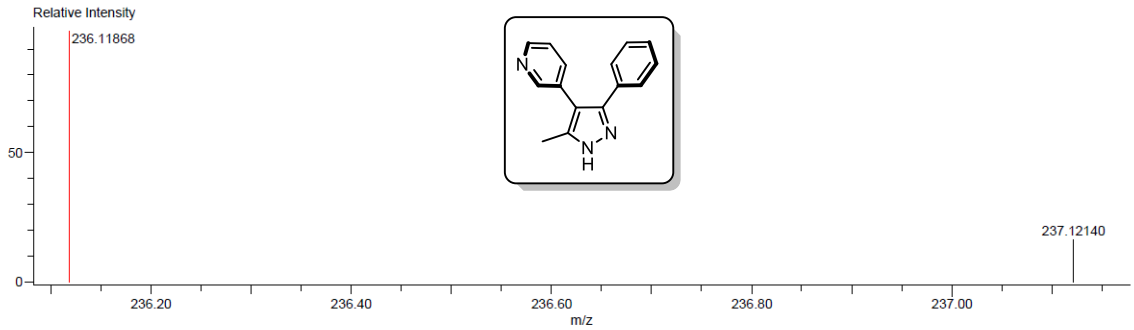
Spectrum 122. ^{13}C-NMR of **8y**.

Description:
Ionization Mode:ESI+
History:Determine m/z[Peak Detect[Centroid,30,Area];Correct Base[];Smooth[5]];Correct Base[5.0%];Average(MS[...

Mass Calibration data:Cal_PEG_600
Created:2/21/2023 10:03:16 AM
Created by:AccuTOF

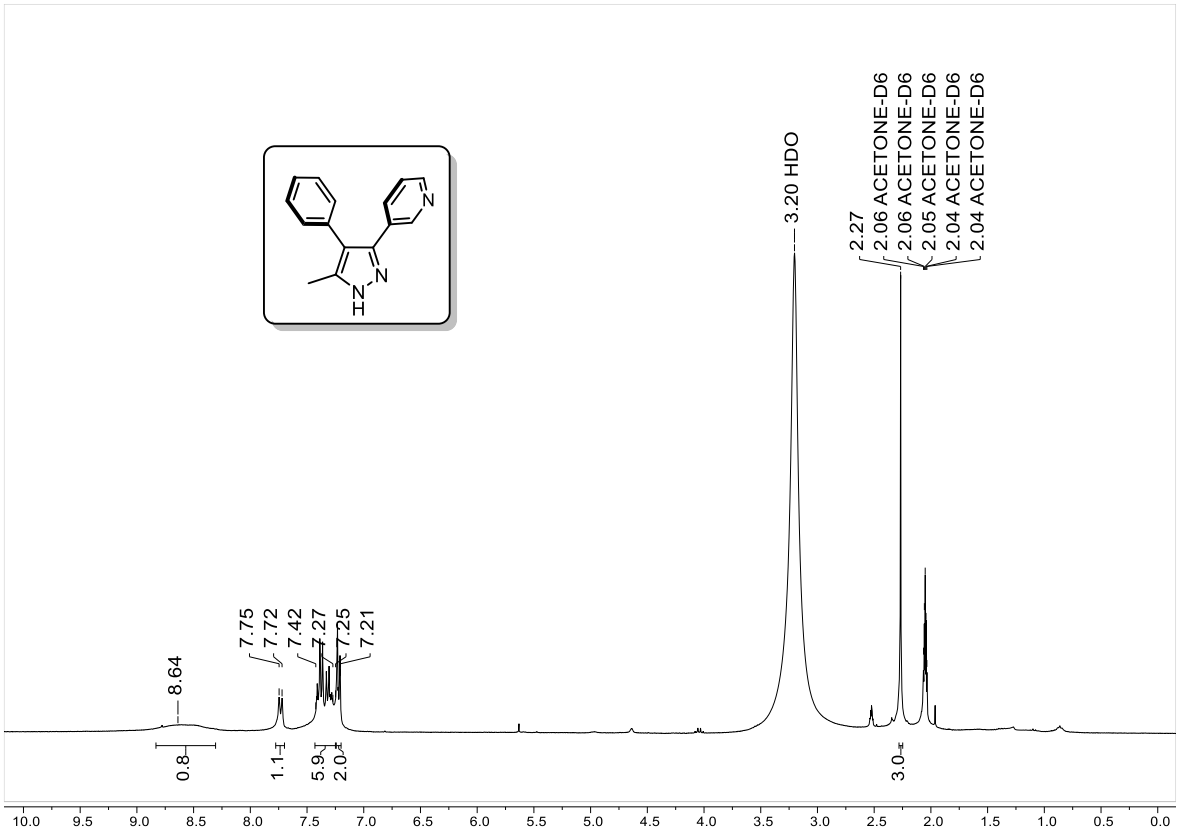
Charge number:1 Tolerance:5.00(mmu)
Element:^{12}C:0 .. 15, ^{1}H:0 .. 22, ^{79}Br:0 .. 0, ^{14}N:0 .. 3, ^{16}O:0 .. 0

Unsaturation Number:0.0 .. 30.0 (Fraction:.5)

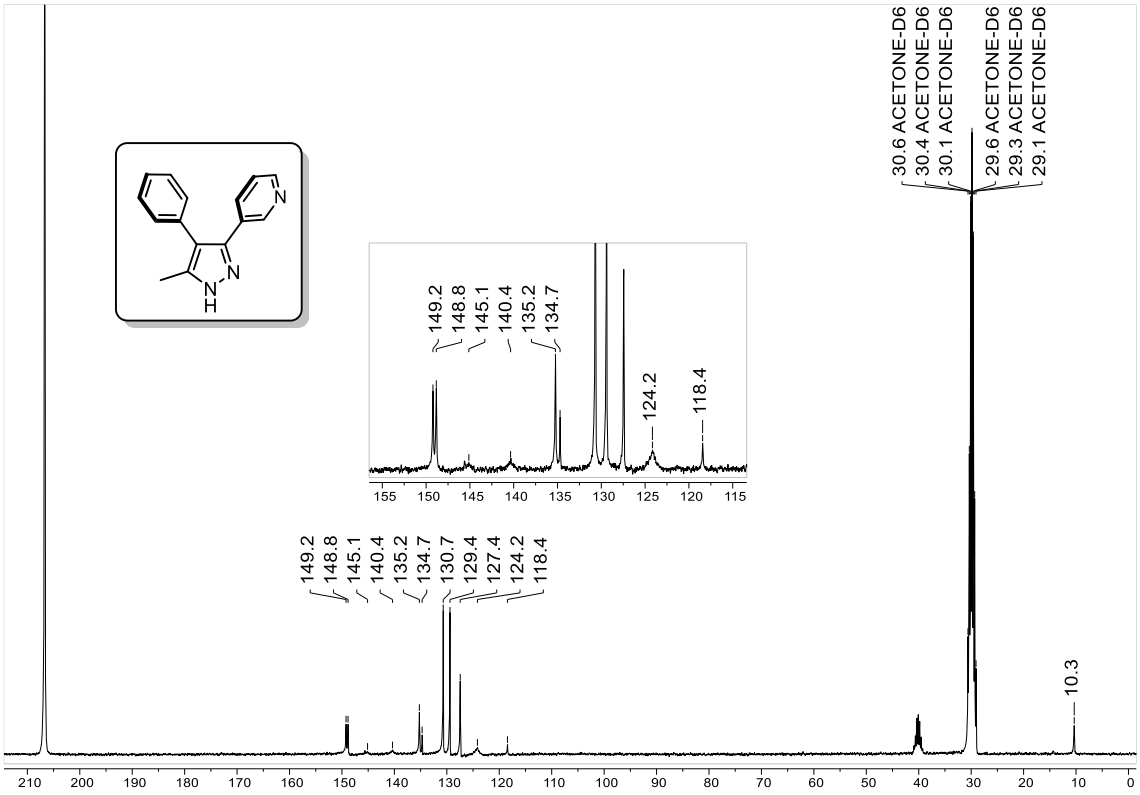


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
236.11868	41968.84	236.11877	-0.10	-0.41	$^{12}C_{15}{}^{1}H_{14}{}^{14}N_3$	10.5

Spectrum 123. HRMS of **8y**.



Spectrum 124. ^{1}H-NMR of **8z**.

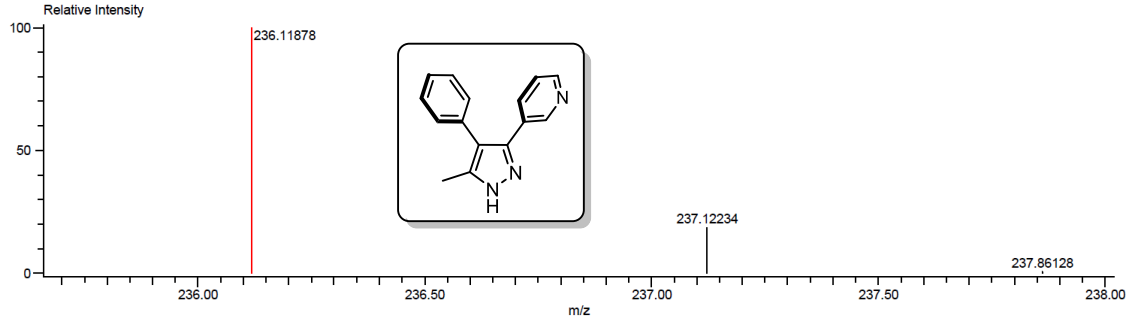


Spectrum 125. ^{13}C-NMR of **8z**.

Description:
Ionization Mode:ESI+
History:Determine m/z[Peak Detect[Centroid,30,Area];Correct Base[];Smooth[5]];Correct Base[5.0%];Average(MS[...

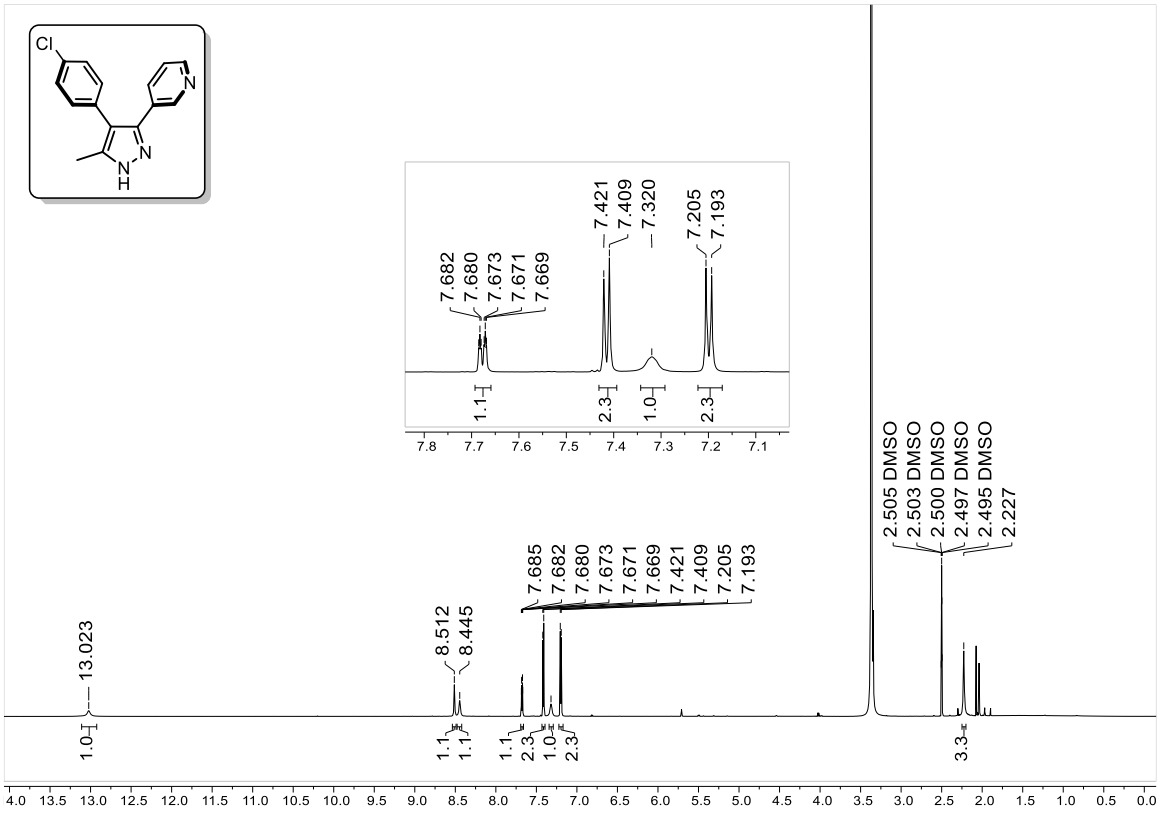
Mass Calibration data:Cal_PEG_600
Created:1/27/2023 10:29:43 AM
Created by:AccuTOF

Charge number:1
Tolerance:5.00(ppm), 5.00 .. 15.00(mmu)
Unsaturation Number:0.0 .. 45.0 (Fraction:Both)
Element:^{12}C:0 .. 15, ^{1}H:0 .. 22, ^{35}Cl:0 .. 0, ^{14}N:3 .. 3, ^{16}O:0 .. 0

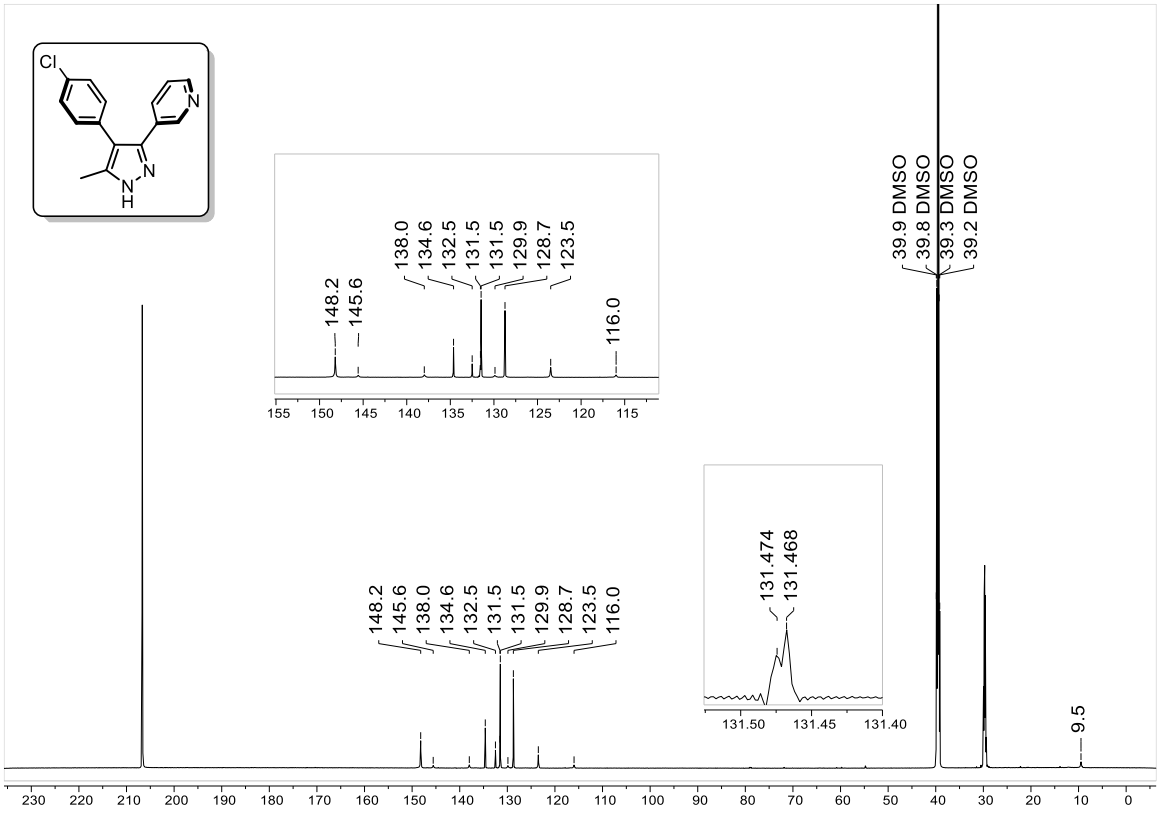


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
236.11878	11340.26	236.11877	0.01	0.04	$^{12}C_{15}{}^{1}H_{14}{}^{14}N_3$	10.5

Spectrum 126. HRMS of **8z**.



Spectrum 127. ^{1}H-NMR of **8aa**.

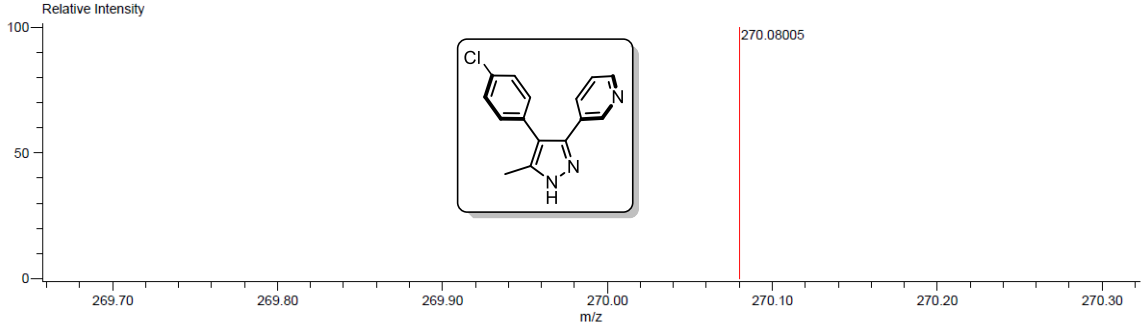


Spectrum 128. ^{13}C-NMR of **8aa**.

Description:
Ionization Mode:ESI+
History:Determine m/z[Peak Detect[Centroid,30,Area];Correct Base[];Smooth[5]];Correct Base[5.0%];Average(MS[...

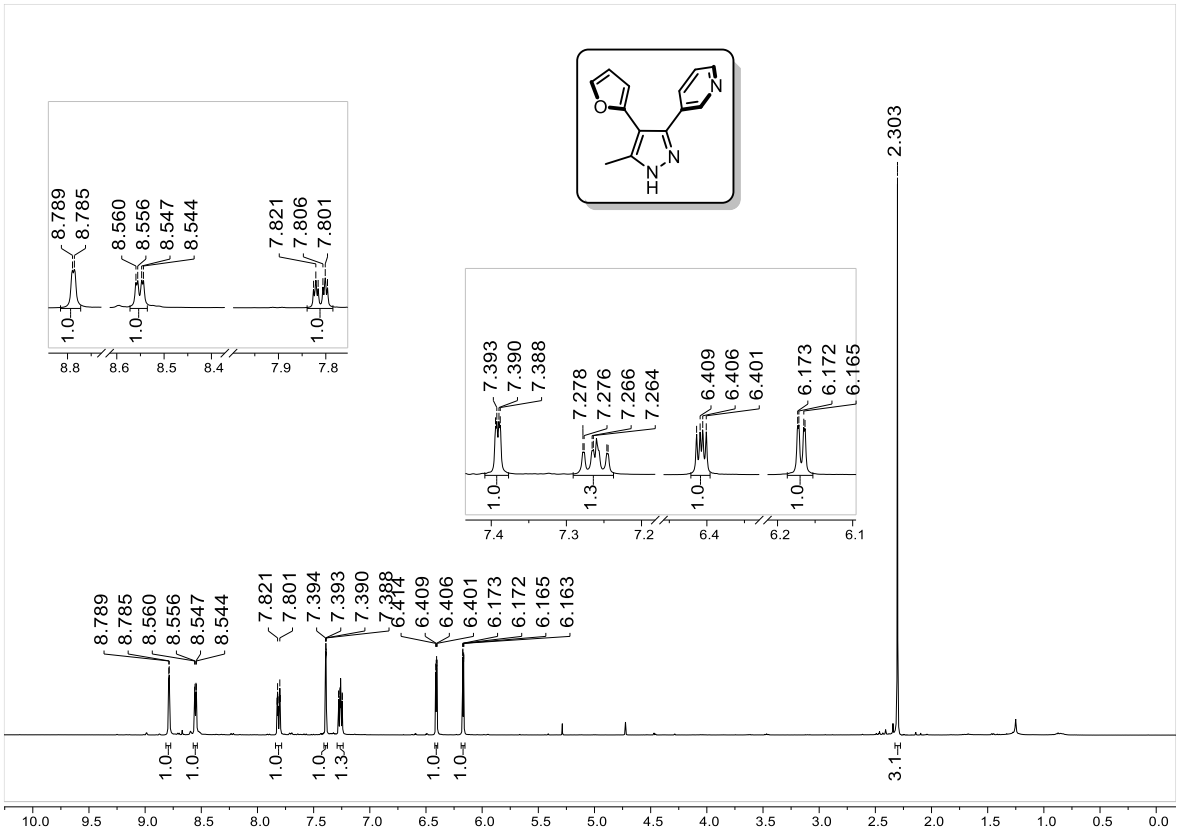
Mass Calibration data:Cal_PEG_600
Created:2/2/2023 11:17:31 AM
Created by:AccuTOF

Charge number:1
Tolerance:50.00(ppm), 5.00 .. 15.00(mmu)
Unsaturation Number:0.0 .. 50.0 (Fraction:.5)
Element:^{12}C:0 .. 15, ^{1}H:0 .. 50, ^{35}Cl:0 .. 1, ^{19}F:0 .. 0, ^{14}N:0 .. 3, ^{16}O:0 .. 0

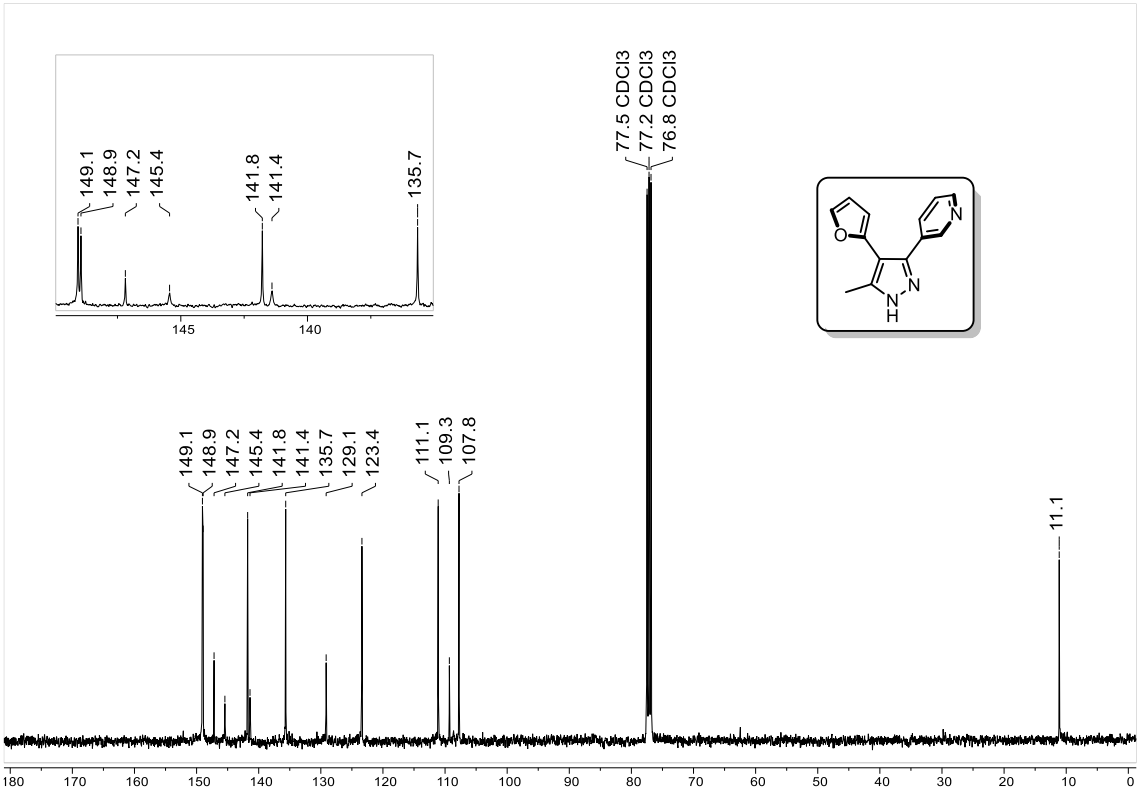


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
270.08005	4805.12	270.07980	0.25	0.92	$^{12}C_{15}{}^{1}H_{13}{}^{35}Cl_{1}{}^{14}N_{3}$	10.5

Spectrum 129. HRMS of **8aa**.



Spectrum 130. ^{1}H-NMR of **8ab**.

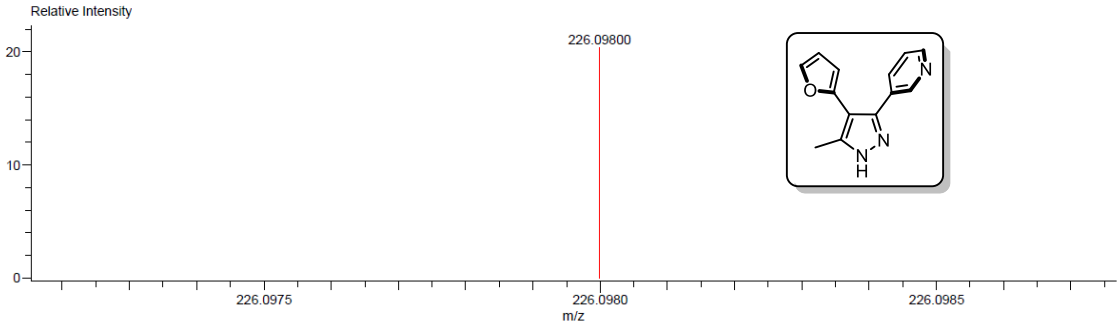


Spectrum 131. ^{13}C-NMR of **8ab**.

Description:
Ionization Mode:ESI+
History:Determine m/z[Peak Detect[Centroid,30,Area];Correct Base[];Smooth[5]];Correct Base[5.0%];Average(MS[...

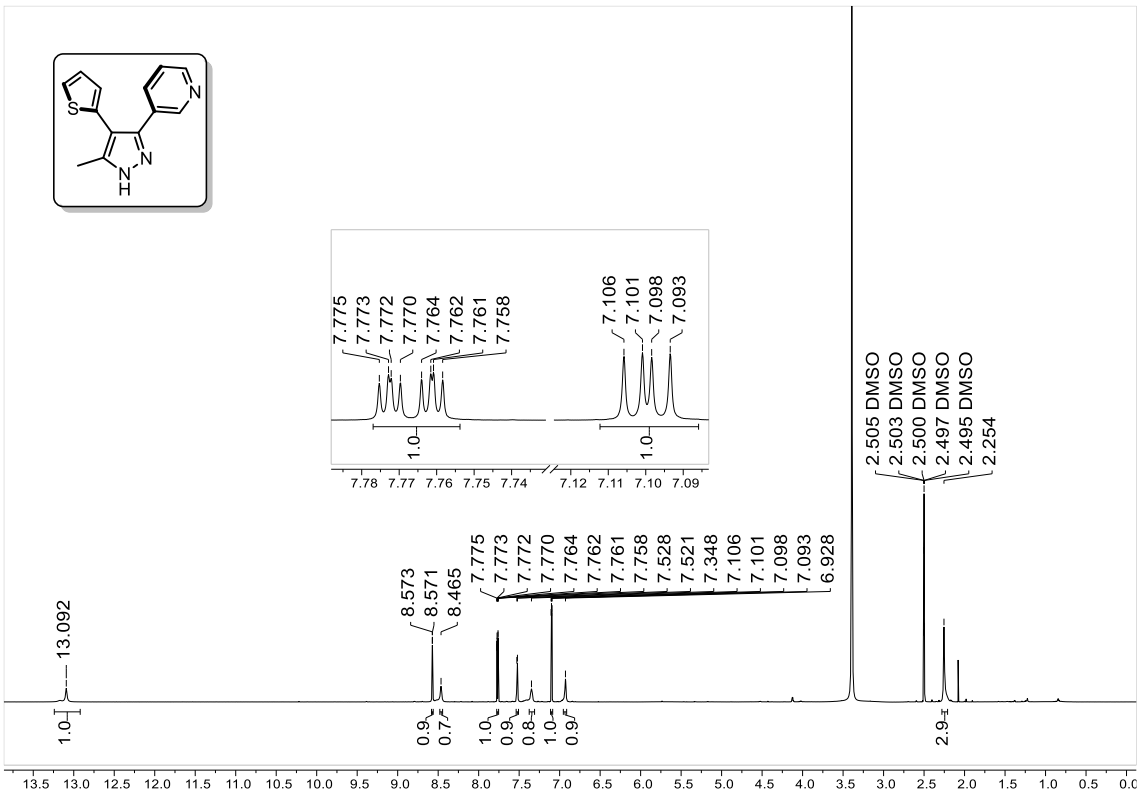
Mass Calibration data:Cal_PEG_600
Created:2/27/2023 2:22:47 PM
Created by:AccuTOF

Charge number:1
Tolerance:200.00(ppm), 5.00 .. 15.00(mmu)
Unsaturation Number:0.0 .. 30.0 (Fraction:Both)
Element:^{12}C:0 .. 13, ^{1}H:0 .. 20, ^{35}Cl:0 .. 0, ^{19}F:0 .. 0, ^{14}N:2 .. 3, ^{16}O:0 .. 1

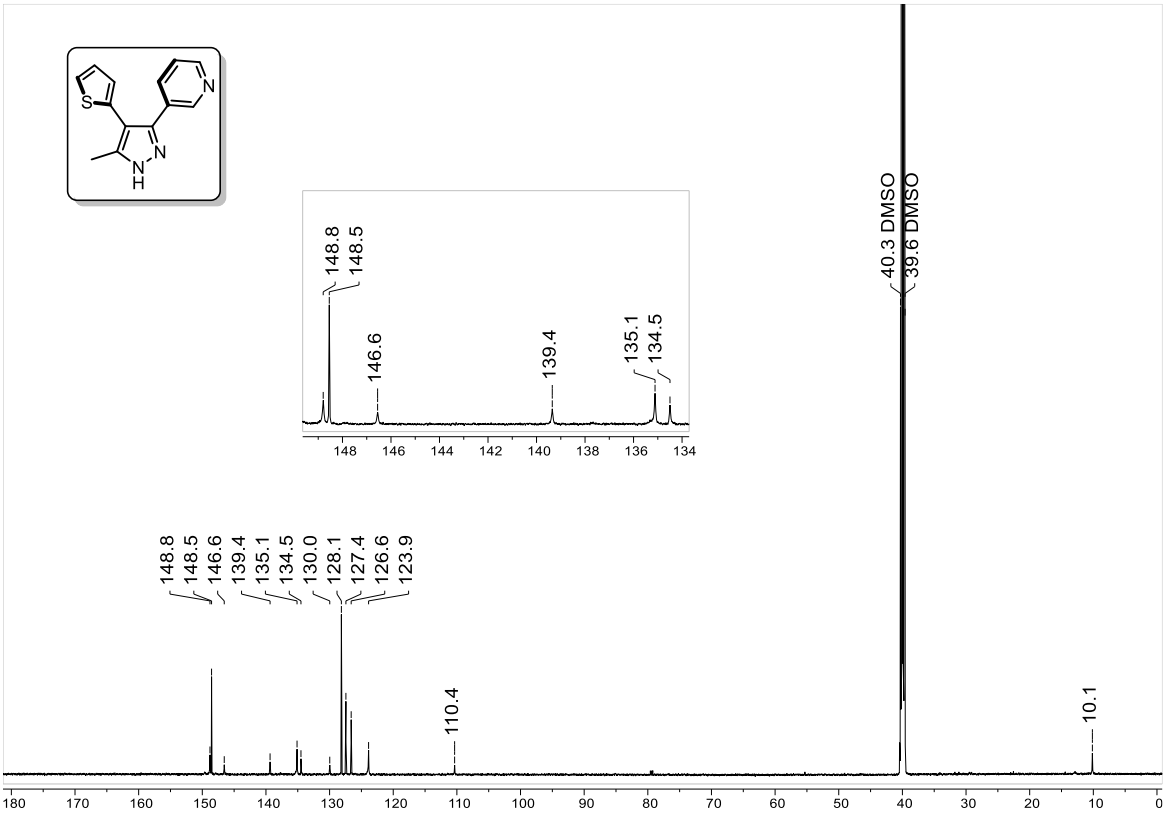


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
226.09800	18117.10	226.09804	-0.04	-0.17	$^{12}C_{13}{}^{1}H_{12}{}^{14}N_{3}{}^{16}O_{1}$	9.5

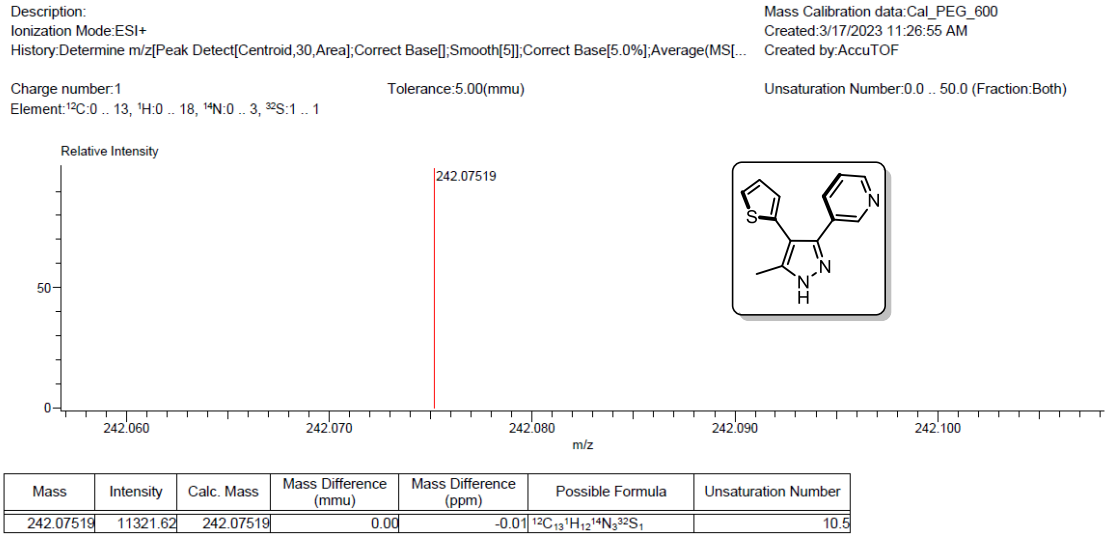
Spectrum 132. HRMS of **8ab**.



Spectrum 133. ^{1}H-NMR of **8ac**.

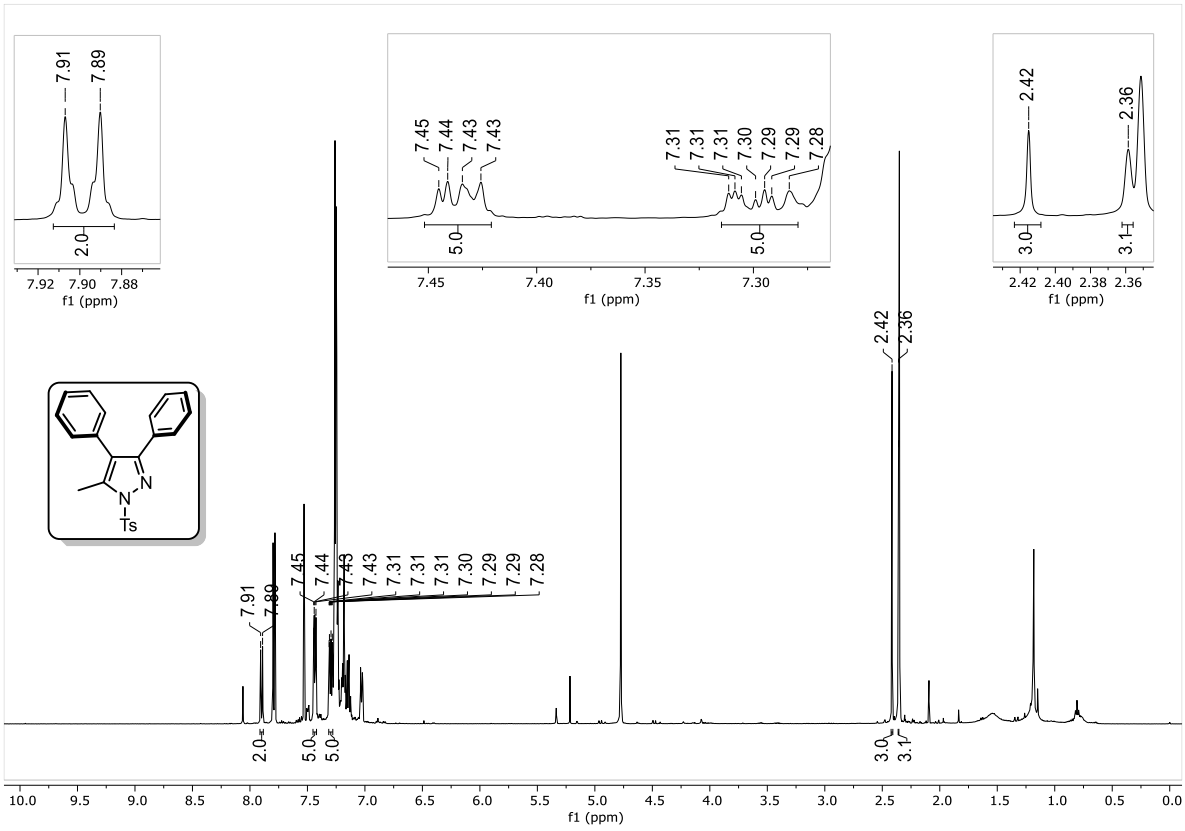


Spectrum 134. ^{13}C-NMR of **8ac**.



Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
242.07519	11321.62	242.07519	0.00	-0.01	$^{12}C_{13}{}^{1}H_{12}{}^{14}N_{3}{}^{32}S_{1}$	10.5

Spectrum 135. HRMS of **8ac**.



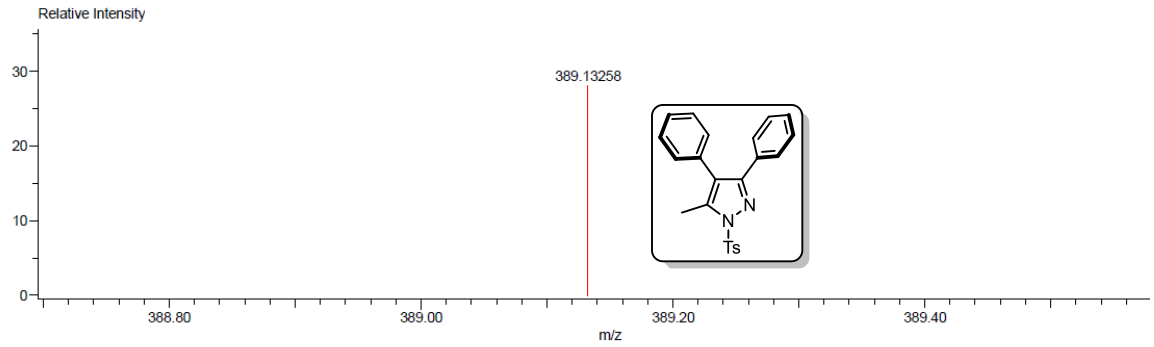
Spectrum 136. ^{1}H-NMR of **9**.

Description:
Ionization Mode:ESI+
History:Determine m/z[Peak Detect[Centroid,30,Area];Correct Base[];Smooth[5]];Correct Base[5.0%];Average(MS[...

Mass Calibration data:Cal_PEG_600
Created:6/14/2023 9:50:50 AM
Created by:AccuTOF

Charge number:1 Tolerance:4.00(mmu)
Element:^{12}C:0 .. 23, ^{1}H:0 .. 25, ^{14}N:0 .. 2, ^{16}O:2 .. 2, ^{32}S:0 .. 1

Unsaturation Number:-1.0 .. 60.0 (Fraction:Both)



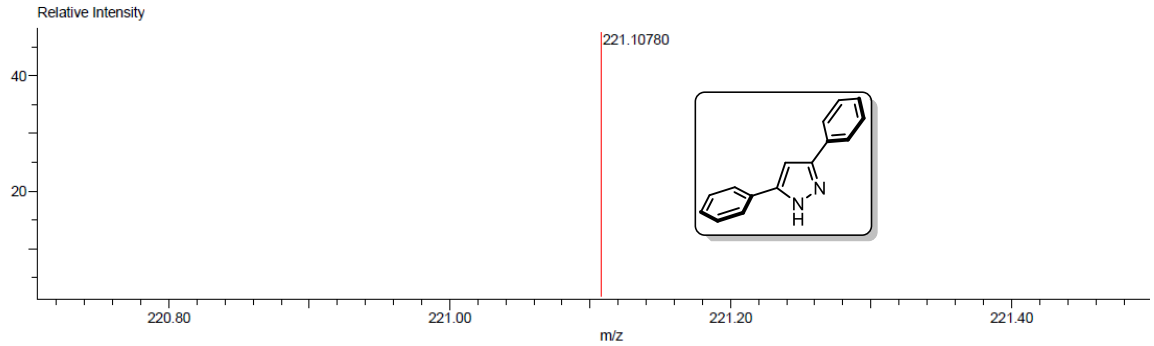
Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
389.13258	246534.04	389.13237	0.20	0.52	$^{12}C_{23}{}^{1}H_{21}{}^{14}N_{2}{}^{16}O_{2}{}^{32}S_{1}$	15.5

Spectrum 137. HRMS of **9**.

Description:
Ionization Mode:ESI+
History:Determine m/z[Peak Detect[Centroid,30,Area];Correct Base[];Smooth[5]];Correct Base[5.0%];Average(MS[...

Mass Calibration data:Cal_PEG_600
Created:6/14/2023 3:22:25 PM
Created by:AccuTOF

Charge number:1
Tolerance:3.00(mmu)
Unsaturation Number:-1.0 .. 60.0 (Fraction:Both)
Element:^{12}C:0 .. 15, ^{1}H:0 .. 13, ^{14}N:0 .. 2, ^{16}O:0 .. 0



Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
221.10780	11449.31	221.10787	-0.07	-0.34	$^{12}C_{15}{}^{1}H_{13}{}^{14}N_2$	10.5

Spectrum 138. HRMS of **11**.

Comparative TLC of the methodologies.

Although Tang's and our conditions are similar, TLC outcomes reveal a different pattern. In our methodology, the 3,4-diaryl-1*H*-pyrazole (Rf = 0.06; Hex-AcOEt 8:2) is more polar than the 3,5-isomer (Rf = 0.48), which was obtained only traces (< 5%). It is noteworthy to mention that the yield of 3,4-regioisomer decreases when our protocol is carried out at 80 °C, while 3,5-regiosomer increases (Figure S1).

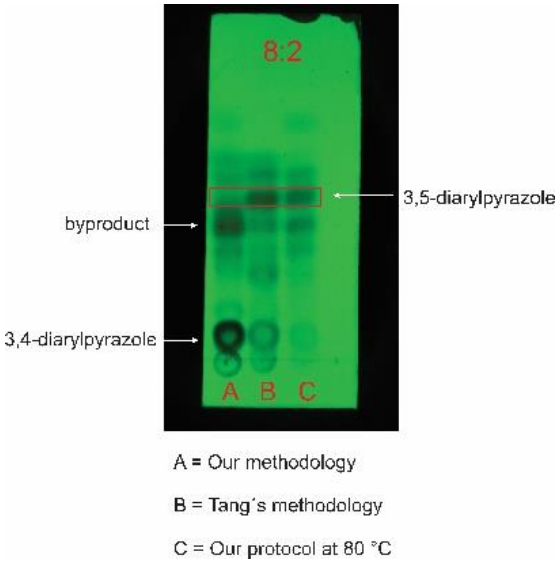


Figure S1. Comparative TLC of the methodologies (Eluent: Hex-AcOEt 8:2).

To bring a proof about the mechanism of 3,4-aza-heterocyclic synthesis, we tested our conditions without base (K_2CO_3). The result indicated the importance of the base for converting the *N*-tosylhydrazones to the corresponding diazo compounds; thus, the reaction proceeds *via* a [3+2] cycloaddition. Moreover, we identified that the most abundant byproduct as the tosylated pyrazole.

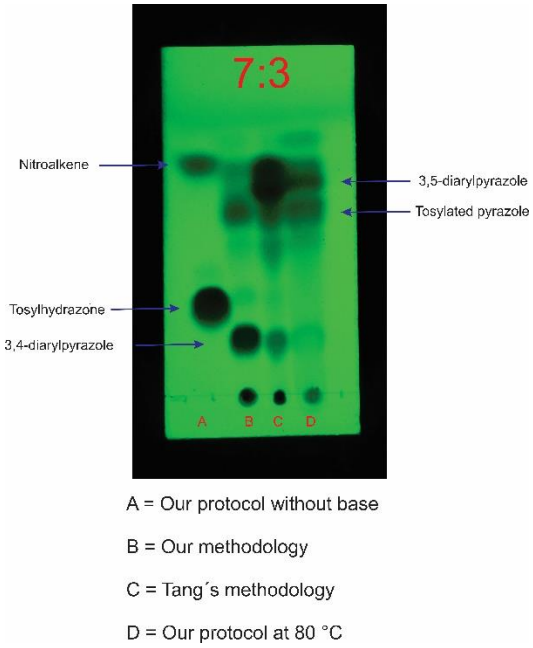


Figure S2. Comparative TLC of the methodologies (Eluent: Hex-AcOEt 7:3).

X-Ray Data.

Table S1. X-ray data.

Identification code	089HVE23	
Empirical formula	C_{15} H_{12} Cl N_3	
Formula weight	269.73	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 14.1324(5) Å	α= 90°.
	b = 8.3919(3) Å	β= 103.5870(10)°.
	c = 11.1269(4) Å	γ = 90°.
Volume	1282.69(8) Å^3	
Z	4	
Density (calculated)	1.397 Mg/m^3	
Absorption coefficient	0.286 mm^{-1}	
F(000)	560	
Crystal size	0.360 x 0.261 x 0.208 mm^3	
Theta range for data collection	2.844 to 27.948°.	
Index ranges	-18<=h<=18, -11<=k<=11, -14<=l<=14	
Reflections collected	18891	
Independent reflections	3087 [R(int) = 0.0187]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.7186	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3087 / 1 / 176	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0304, wR2 = 0.0845	
R indices (all data)	R1 = 0.0323, wR2 = 0.0861	
Largest diff. peak and hole	0.407 and -0.222 e.Å^{-3}	

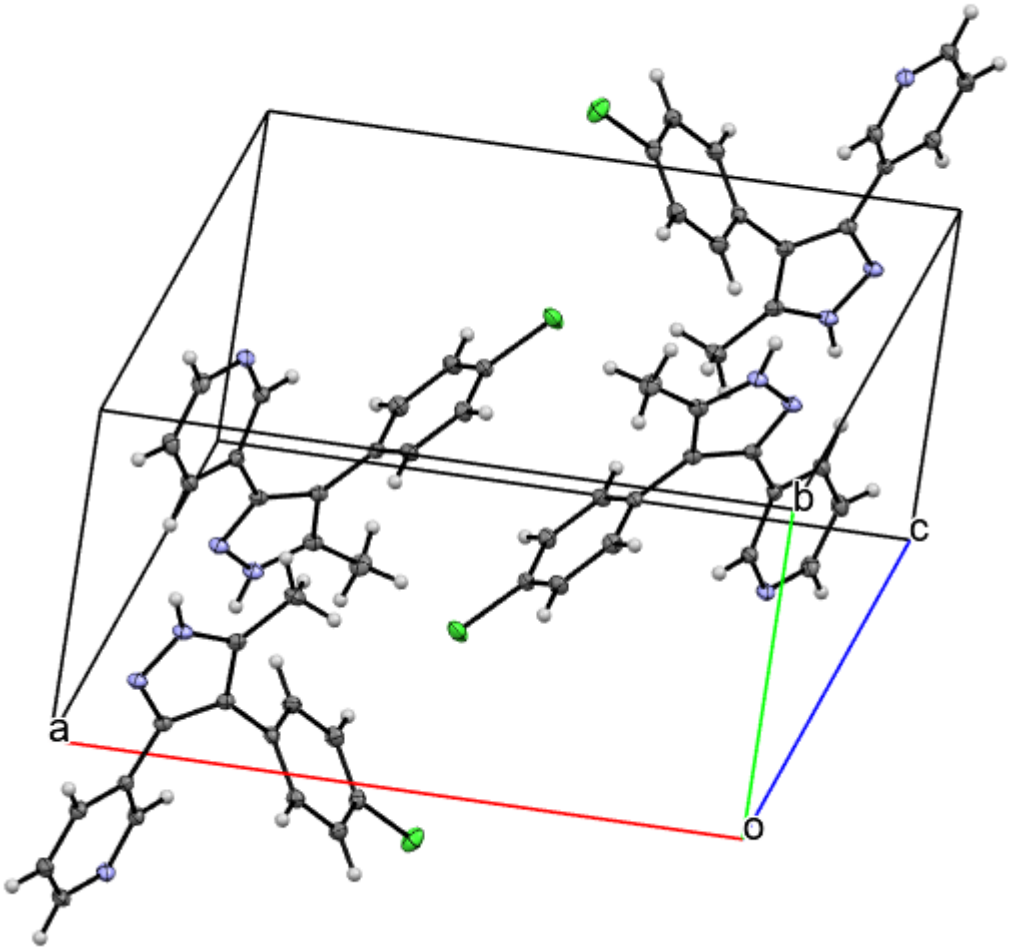


Figure S3. X-Ray of **8aa.**

Coordinates of optimized geometries.

Nitroalkene (6a).

@<TRIPOS>MOLECULE
21 21
SMALL
NO_CHARGES

@<TRIPOS>ATOM
1 C1 -3.7717 0.1353 0.0155 C
2 C2 -3.2296 -1.1239 0.2943 C
3 C3 -1.8505 -1.3157 0.2381 C
4 C4 -0.9791 -0.2471 -0.0677 C
5 C5 -1.5427 1.0120 -0.3651 C
6 C6 -2.9247 1.1958 -0.3245 C
7 H7 -4.8468 0.2864 0.0482 H
8 H8 -3.8805 -1.9565 0.5448 H
9 H9 -1.4323 -2.2979 0.4415 H
10 H10 -0.9097 1.8387 -0.6648 H
11 H11 -3.3425 2.1686 -0.5673 H
12 C12 0.4528 -0.5442 -0.0989 C
13 C13 1.5067 0.2822 0.0863 C
14 H14 0.6963 -1.5879 -0.2748 H
15 N15 2.8346 -0.3380 -0.0696 N
16 O16 2.9358 -1.5514 -0.3012 O
17 O17 3.8190 0.4075 0.0335 O
18 C18 1.5375 1.7302 0.4586 C
19 H19 1.7567 2.3724 -0.4024 H
20 H20 0.5749 2.0279 0.8762 H
21 H21 2.3106 1.9171 1.2075 H
@<TRIPOS>BOND
1 1 2 Ar
2 1 6 Ar
3 1 7 1
4 2 3 Ar
5 2 8 1
6 3 4 Ar
7 3 9 1
8 4 5 Ar
9 4 12 1
10 5 6 Ar
11 5 10 1
12 6 11 1
13 12 13 2
14 12 14 1
15 13 15 1
16 13 18 1
17 15 16 Ar
18 15 17 Ar
19 18 19 1
20 18 20 1
21 18 21 1

Diazo compound.

@<TRIPOS>MOLECULE
15 15
SMALL
NO_CHARGES

@<TRIPOS>ATOM
1 C1 -0.1288 -0.3729 0.0000 C
2 C2 0.9303 -1.3039 -0.0000 C
3 C3 0.1822 1.0026 0.0000 C
4 C4 2.2563 -0.8713 -0.0000 C
5 H5 0.7062 -2.3674 -0.0000 H
6 C6 -1.4979 -0.8781 0.0000 C
7 C7 1.5116 1.4258 0.0000 C
8 H8 -0.6138 1.7427 0.0000 H
9 C9 2.5572 0.4954 -0.0000 C

10 H10 3.0570 -1.6061 -0.0000 H
11 H11 -1.7300 -1.9370 0.0001 H
12 H12 1.7308 2.4902 0.0000 H
13 H13 3.5903 0.8304 -0.0000 H
14 N14 -2.5235 -0.0826 0.0000 N
15 N15 -3.4202 0.6342 -0.0000 N
@<TRIPOS>BOND
1 1 2 Ar
2 1 3 Ar
3 1 6 1
4 2 4 Ar
5 2 5 1
6 3 7 Ar
7 3 8 1
8 4 9 Ar
9 4 10 1
10 6 11 1
11 6 14 2
12 7 9 Ar
13 7 12 1
14 9 13 1
15 14 15 2

TS-1.

@<TRIPOS>MOLECULE
36 38
SMALL
NO_CHARGES

@<TRIPOS>ATOM
1 C1 3.3870 -2.9826 -0.2050 C
2 C2 2.6110 -2.7105 -1.3351 C
3 C3 1.7508 -1.6096 -1.3472 C
4 C4 1.6600 -0.7477 -0.2389 C
5 C5 2.4339 -1.0442 0.8981 C
6 C6 3.2900 -2.1471 0.9129 C
7 H7 4.0542 -3.8397 -0.1910 H
8 H8 2.6690 -3.3563 -2.2069 H
9 H9 2.3594 -0.4236 1.7859 H
10 H10 3.8774 -2.3570 1.8025 H
11 C11 0.7212 0.4088 -0.3366 C
12 C12 1.1231 1.7488 -0.1544 C
13 H13 -0.0274 0.2867 -1.1130 H
14 N14 0.3317 2.7315 -0.8427 N
15 O15 -0.8003 2.4248 -1.2798 O
16 O16 0.8047 3.8781 -0.9774 O
17 C17 2.4492 2.2454 0.3440 C
18 H18 2.3387 3.1620 0.9276 H
19 H19 2.9307 1.4941 0.9681 H
20 H20 3.1240 2.4702 -0.4922 H
21 C21 -1.9681 -0.5788 0.6024 C
22 C22 -2.1461 -1.9724 0.5604 C
23 C23 -2.9578 0.2590 0.0579 C
24 C24 -3.2925 -2.5196 -0.0193 C
25 H25 -1.3865 -2.6243 0.9834 H
26 C26 -0.7074 -0.0513 1.1693 C
27 C27 -4.1078 -0.2928 -0.5048 C
28 H28 -2.8236 1.3362 0.0685 H
29 C29 -4.2781 -1.6821 -0.5494 C
30 H30 -3.4185 -3.5981 -0.0472 H
31 H31 -0.1504 -0.7555 1.7869 H
32 H32 -4.8701 0.3627 -0.9159 H
33 H33 -5.1738 -2.1070 -0.9932 H
34 N34 -0.7189 1.1786 1.7702 N
35 N35 -0.2550 2.2317 1.7577 N
36 H36 1.1469 -1.4079 -2.2280 H
@<TRIPOS>BOND
1 1 2 Ar
2 1 6 Ar

3 1 7 1
4 2 3 Ar
5 2 8 1
6 3 4 Ar
7 3 36 1
8 4 5 Ar
9 4 11 1
10 5 6 Ar
11 5 9 1
12 6 10 1
13 11 12 Ar
14 11 13 1
15 11 26 Wk
16 12 14 1
17 12 17 1
18 12 35 Wk
19 14 15 Ar
20 14 16 Ar
21 17 18 1
22 17 19 1
23 17 20 1
24 21 22 Ar
25 21 23 Ar
26 21 26 1
27 22 24 Ar
28 22 25 1
29 23 27 Ar
30 23 28 1
31 24 29 Ar
32 24 30 1
33 26 31 1
34 26 34 Ar
35 27 29 Ar
36 27 32 1
37 29 33 1
38 34 35 2

TS-1´.

@<TRIPOS>MOLECULE
36 38
SMALL
NO_CHARGES

@<TRIPOS>ATOM
1 C1 0.1519 0.5779 0.7236 C
2 C2 -1.2716 -0.3034 -0.9733 C
3 C3 2.5856 -0.3659 0.3146 C
4 C4 3.5608 -0.5269 1.3189 C
5 C5 3.0194 -0.2448 -1.0178 C
6 C6 4.9223 -0.5244 1.0106 C
7 H7 3.2458 -0.6475 2.3524 H
8 C8 1.1598 -0.4199 0.7509 C
9 C9 4.3815 -0.2567 -1.3273 C
10 H10 2.2951 -0.1461 -1.8161 H
11 C11 5.3389 -0.3877 -0.3171 C
12 H12 5.6544 -0.6364 1.8057 H
13 H13 1.0480 -1.0452 1.6344 H
14 H14 4.6932 -0.1644 -2.3642 H
15 H15 6.3972 -0.3923 -0.5627 H
16 N16 0.4749 -1.8574 -0.5281 N
17 N17 -0.4972 -1.4090 -1.0049 N
18 H18 -1.0192 0.3954 -1.7702 H
19 C19 -2.6711 -0.3864 -0.5591 C
20 C20 -3.5182 0.6981 -0.8595 C
21 C21 -3.1829 -1.4741 0.1765 C
22 C22 -4.8429 0.7002 -0.4227 C
23 H23 -3.1324 1.5362 -1.4337 H
24 C24 -4.5107 -1.4706 0.5985 C

25 H25 -2.5485 -2.3264 0.4034 H
26 C26 -5.3441 -0.3835 0.3056 C
27 H27 -5.4848 1.5441 -0.6582 H
28 H28 -4.8987 -2.3183 1.1559 H
29 H29 -6.3782 -0.3859 0.6374 H
30 N30 0.3632 1.8068 -0.0033 N
31 O31 1.0202 1.7917 -1.0602 O
32 O32 -0.1471 2.8481 0.4505 O
33 C33 -0.7998 0.6926 1.8880 C
34 H34 -1.7339 1.1863 1.6159 H
35 H35 -1.0329 -0.3089 2.2599 H
36 H36 -0.3492 1.2613 2.7106 H
@<TRIPOS>BOND
1 1 8 Ar
2 1 30 1
3 1 33 1
4 1 2 Wk
5 2 17 Ar
6 2 18 1
7 2 19 1
8 3 4 Ar
9 3 5 Ar
10 3 8 1
11 4 6 Ar
12 4 7 1
13 5 9 Ar
14 5 10 1
15 6 11 Ar
16 6 12 1
17 8 13 1
18 8 16 Wk
19 9 11 Ar
20 9 14 1
21 11 15 1
22 16 17 2
23 19 20 Ar
24 19 21 Ar
25 20 22 Ar
26 20 23 1
27 21 24 Ar
28 21 25 1
29 22 26 Ar
30 22 27 1
31 24 26 Ar
32 24 28 1
33 26 29 1
34 30 31 Ar
35 30 32 Ar
36 33 34 1
37 33 35 1
38 33 36 1

PS-1 (8a).

@<TRIPOS>MOLECULE
32 34
SMALL
NO_CHARGES

@<TRIPOS>ATOM
1 C1 2.7777 -2.8764 0.2604 C
2 C2 3.1791 -1.9363 -0.6932 C
3 C3 2.5221 -0.7059 -0.7893 C
4 C4 1.4543 -0.3865 0.0698 C
5 C5 1.0645 -1.3416 1.0281 C
6 C6 1.7162 -2.5731 1.1200 C
7 H7 3.2864 -3.8335 0.3346 H
8 H8 4.0004 -2.1611 -1.3685 H
9 H9 0.2500 -1.1131 1.7090 H
10 H10 1.3982 -3.2938 1.8687 H

11 C11 0.7764 0.9263 -0.0133 C
12 C12 1.4020 2.1755 0.0048 C
13 C13 2.8402 2.5786 0.0689 C
14 H14 3.2680 2.7152 -0.9315 H
15 H15 2.9547 3.5225 0.6119 H
16 H16 3.4311 1.8153 0.5818 H
17 C17 -1.7877 0.3093 -0.1043 C
18 C18 -2.9657 0.6265 0.5966 C
19 C19 -1.7571 -0.8717 -0.8667 C
20 C20 -4.0792 -0.2143 0.5382 C
21 H21 -3.0009 1.5340 1.1916 H
22 C22 -0.6249 1.2229 -0.0508 C
23 C23 -2.8709 -1.7129 -0.9222 C
24 H24 -0.8650 -1.1275 -1.4289 H
25 C25 -4.0357 -1.3898 -0.2188 C
26 H26 -4.9787 0.0461 1.0896 H
27 H27 -2.8290 -2.6191 -1.5204 H
28 H28 -4.9005 -2.0462 -0.2613 H
29 N29 -0.8328 2.5471 -0.0535 N
30 N30 0.4020 3.0915 -0.0162 N
31 H31 2.8311 0.0082 -1.5474 H
32 H32 0.5014 4.0987 -0.0094 H
@<TRIPOS>BOND
1 1 2 Ar
2 1 6 Ar
3 1 7 1
4 2 3 Ar
5 2 8 1
6 3 4 Ar
7 3 31 1
8 4 5 Ar
9 4 11 1
10 5 6 Ar
11 5 9 1
12 6 10 1
13 11 12 Ar
14 11 22 1
15 12 13 1
16 12 30 Ar
17 13 14 1
18 13 15 1
19 13 16 1
20 17 18 Ar
21 17 19 Ar
22 17 22 1
23 18 20 Ar
24 18 21 1
25 19 23 Ar
26 19 24 1
27 20 25 Ar
28 20 26 1
29 22 29 Ar
30 23 25 Ar
31 23 27 1
32 25 28 1
33 29 30 Ar
34 30 32 1

PS-1´.

@<TRIPOS>MOLECULE
32 34
SMALL
NO_CHARGES

@<TRIPOS>ATOM
1 C1 0.0092 0.4407 -0.0319 C
2 C2 1.1186 -0.4539 0.0026 C
3 C3 -2.5600 -0.1225 -0.0204 C
4 C4 -3.0969 0.9930 -0.6902 C

5 C5 -3.4429 -0.9869 0.6574 C
6 C6 -4.4720 1.2361 -0.6787 C
7 H7 -2.4427 1.6620 -1.2380 H
8 C8 -1.1140 -0.3946 -0.0293 C
9 C9 -4.8173 -0.7444 0.6603 C
10 H10 -3.0529 -1.8426 1.2019 H
11 C11 -5.3385 0.3697 -0.0055 C
12 H12 -4.8664 2.1013 -1.2044 H
13 H13 -5.4799 -1.4214 1.1924 H
14 H14 -6.4078 0.5610 0.0013 H
15 N15 -0.6308 -1.6698 0.0028 N
16 N16 0.7121 -1.7346 0.0119 N
17 C17 2.5691 -0.1550 0.0192 C
18 C18 3.1125 0.7847 0.9129 C
19 C19 3.4393 -0.8383 -0.8491 C
20 C20 4.4859 1.0420 0.9292 C
21 H21 2.4618 1.2994 1.6135 H
22 C22 4.8126 -0.5843 -0.8285 C
23 H23 3.0320 -1.5671 -1.5434 H
24 C24 5.3409 0.3602 0.0576 C
25 H25 4.8882 1.7681 1.6304 H
26 H26 5.4690 -1.1209 -1.5083 H
27 H27 6.4087 0.5604 0.0714 H
28 C28 0.0320 1.9416 -0.0969 C
29 H29 1.0127 2.3347 0.1771 H
30 H30 -0.1889 2.3081 -1.1071 H
31 H31 -0.7063 2.3863 0.5792 H
32 H32 -1.1676 -2.5270 -0.0203 H
@<TRIPOS>BOND
1 1 2 Ar
2 1 8 Ar
3 1 28 1
4 2 16 Ar
5 2 17 1
6 3 4 Ar
7 3 5 Ar
8 3 8 1
9 4 6 Ar
10 4 7 1
11 5 9 Ar
12 5 10 1
13 6 11 Ar
14 6 12 1
15 8 15 Ar
16 9 11 Ar
17 9 13 1
18 11 14 1
19 15 16 1
20 15 32 1
21 17 18 Ar
22 17 19 Ar
23 18 20 Ar
24 18 21 1
25 19 22 Ar
26 19 23 1
27 20 24 Ar
28 20 25 1
29 22 24 Ar
30 22 26 1
31 24 27 1
32 28 29 1
33 28 30 1
34 28 31 1

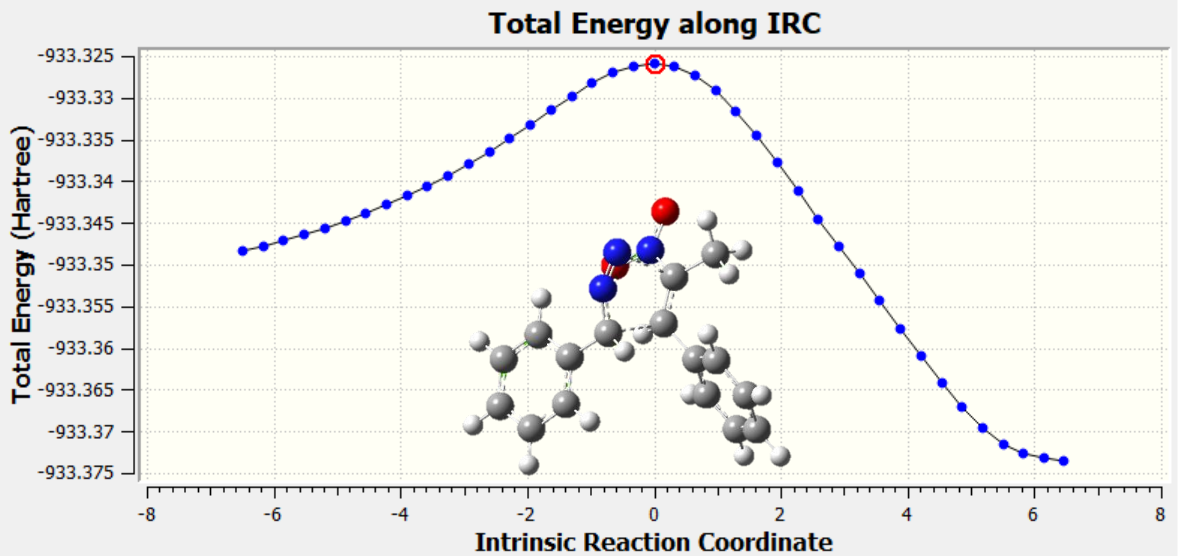
Table S2. Calculated energy values.

Molecules	G	H	E-opt
Diazo Compound	-379.751428	-379.710897	-379.833602
Nitroalkene (**6a**)	-553.394375	-553.345723	-553.521571
TS-1	-933.093703	-933.026443	-933.325866
TS-1´	-933.082648	-933.015308	-933.314513
PS-1 (**8a**)	-727.488152	-727.430168	-727.706292
PS-1´	-727.486576	-727.428357	-727.704591

Values shown at Hartree at 298.15 K

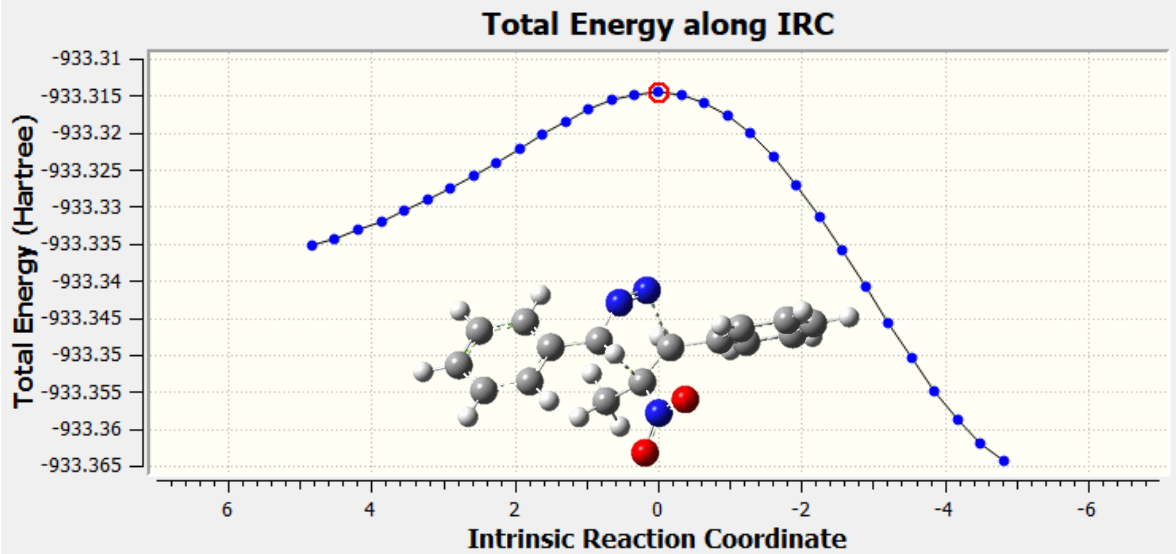
Intrinsic Reaction Coordinate (IRC) of Transition States.

IRC TS-1.



Negative frequency magnitude: -409.46

IRC TS-1´.



Negative frequency magnitude: -405.71

Results of Cytotoxicity screening.

Table S3. Cytotoxicity activity of pyrazoles in different cell lines.

Compound	% growth inhibition by cell line[a]			
	PC-3[b]	HCT-15[c]	MCF-7[d]	COS-7[e]
8a	12.29	0.13	4.35	NC[f]
8b	13.71	5.66	11.78	8.50
8c	18.22	10.92	9.90	16.20
8d	NC	0.14	20.68	12.37
8e	24.21	29.69	30.23	32.80
8f	25.08	NC	6.09	2.55
8g	11.94	1.86	NC	1.17
8h	11.72	8.22	45.56	28.46
8i	36.34	27.27	26.38	18.50
8j	4.04	8.08	35.47	31.39
8k	28.59	12.91	15.52	30.07
8l	7.06	NC	21.93	15.80
8m	14.41	2.50	2.90	4.40
8n	6.57	NC	NC	NC
8o	27.07	21.88	36.78	42.52
8p	8.98	7.29	34.90	34.33
8q	11.54	9.97	35.82	23.37
8r	4.84	5.12	27.68	12.92
8s	23.37	10.74	NC	16.83
8t	5.29	16.03	1.45	NC
8u	8.83	3.61	NC	NC
8v	18.91	21.14	20.14	7.42
8w	5.88	NC	9.81	4.85
8x	17.74	1.14	22.28	6.94
8y	6.82	0.40	NC	NC
8aa	10.68	2.73	5.90	7.26
8ab	6.42	NC	0.32	3.19
8ac	15.69	10.09	10.63	10.61

a) Concentration: 25 μM; Vehicle: DMSO. b) Prostate cancer. c) Colon cancer. d) Breast cancer. e) Monkey's kidney cell line (not cancerous). f) Non-cytotoxic.