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Supporting Information

Regioselective Synthesis of Dipyrrolopyrazine (DPP) Derivatives via Metal Free and Metal Catalyzed Amination and Investigation of Their Optical Thermal Properties

Puttavva Meti, Eun-Sil Lee, Jung-Won Yang and Young-Dae Gong*

Innovative Drug Library Research Center, Department of Chemistry, College of Science, Dongguk University, 26, 3-ga, Pil-dong, Jung-gu, Seoul 04620, Korea

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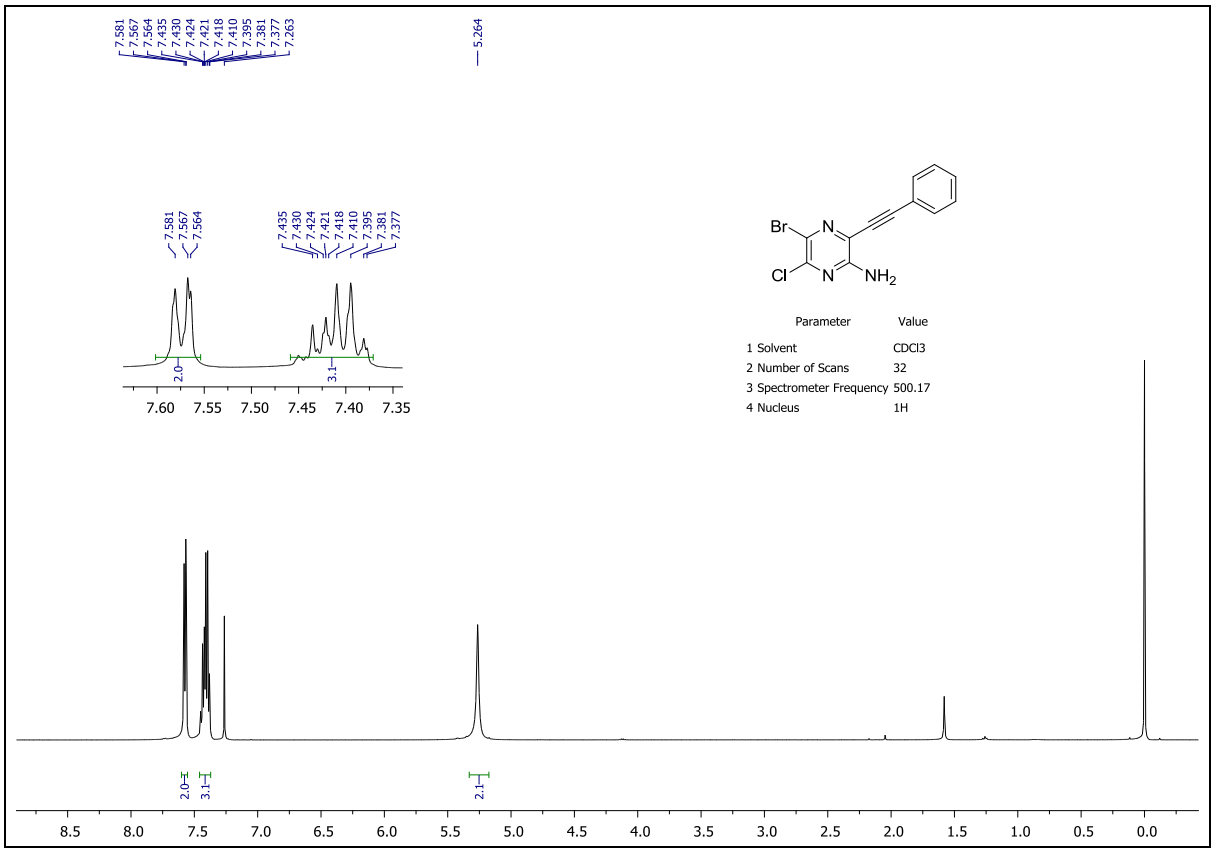
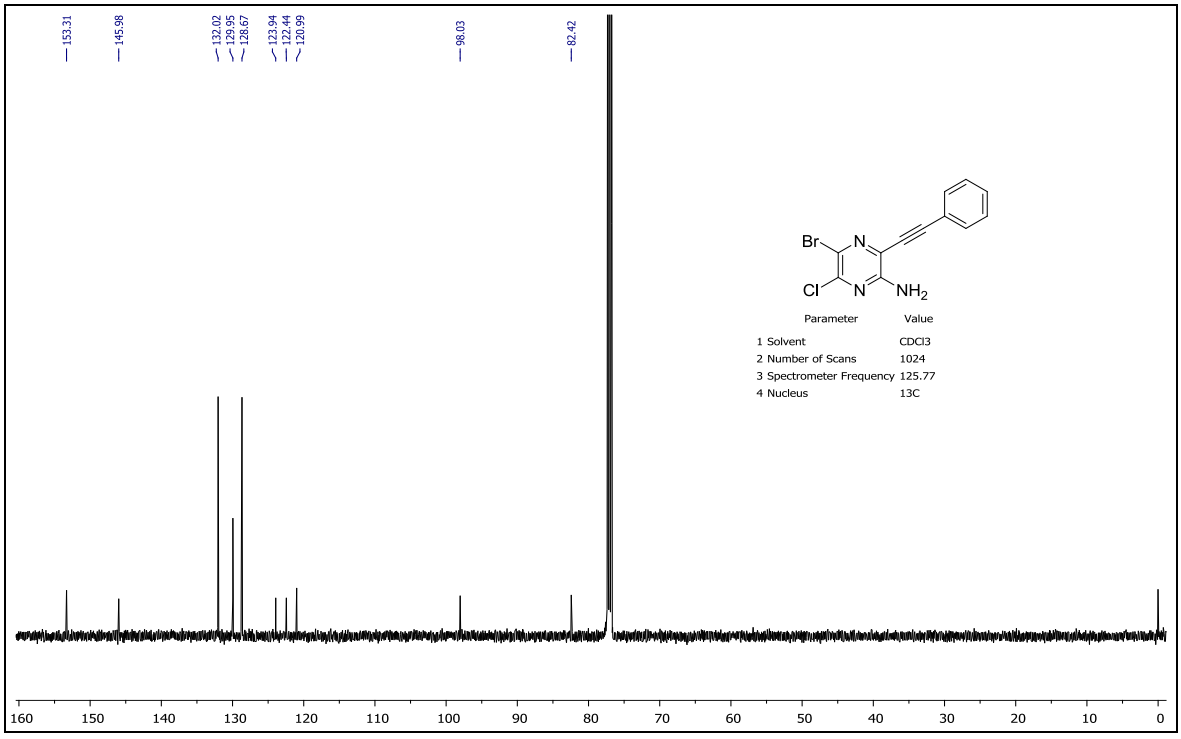
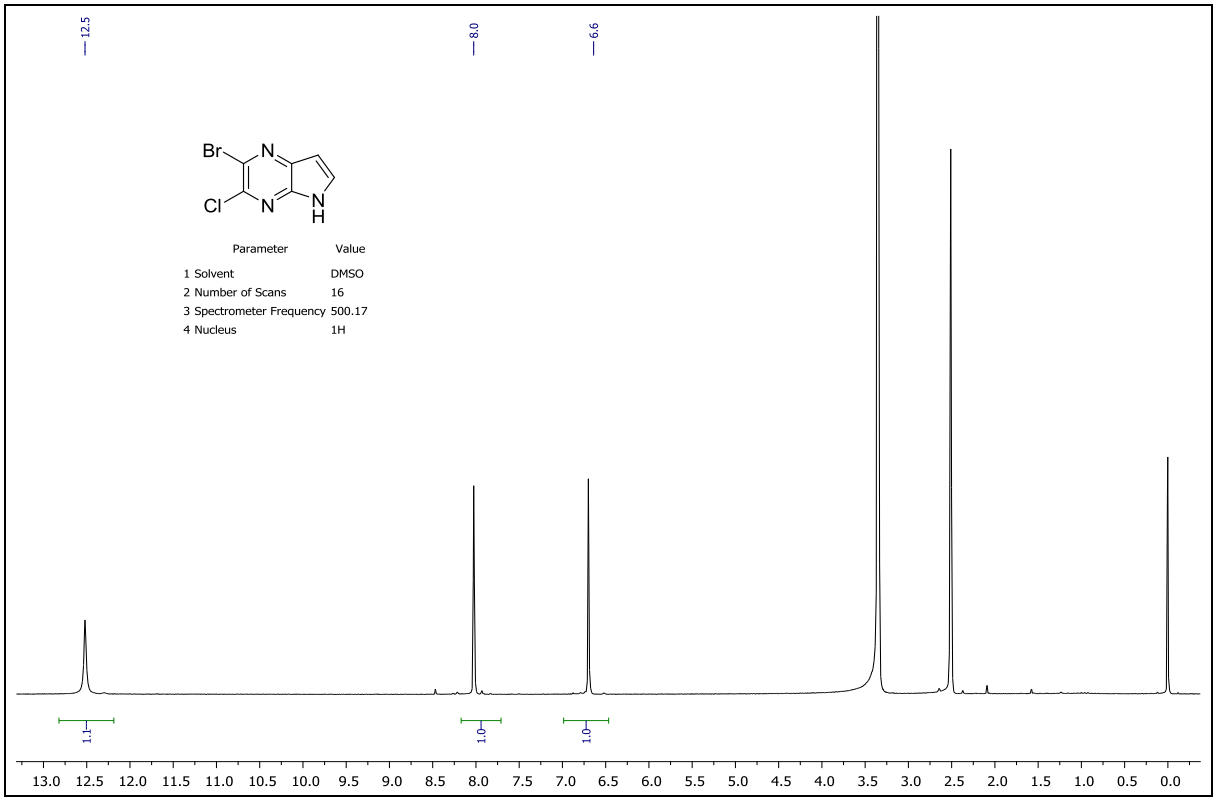
^{1}H NMR and ^{13}C NMR Spectra of Compounds



^{1}H NMR – 1b



^{13}C NMR – 1b



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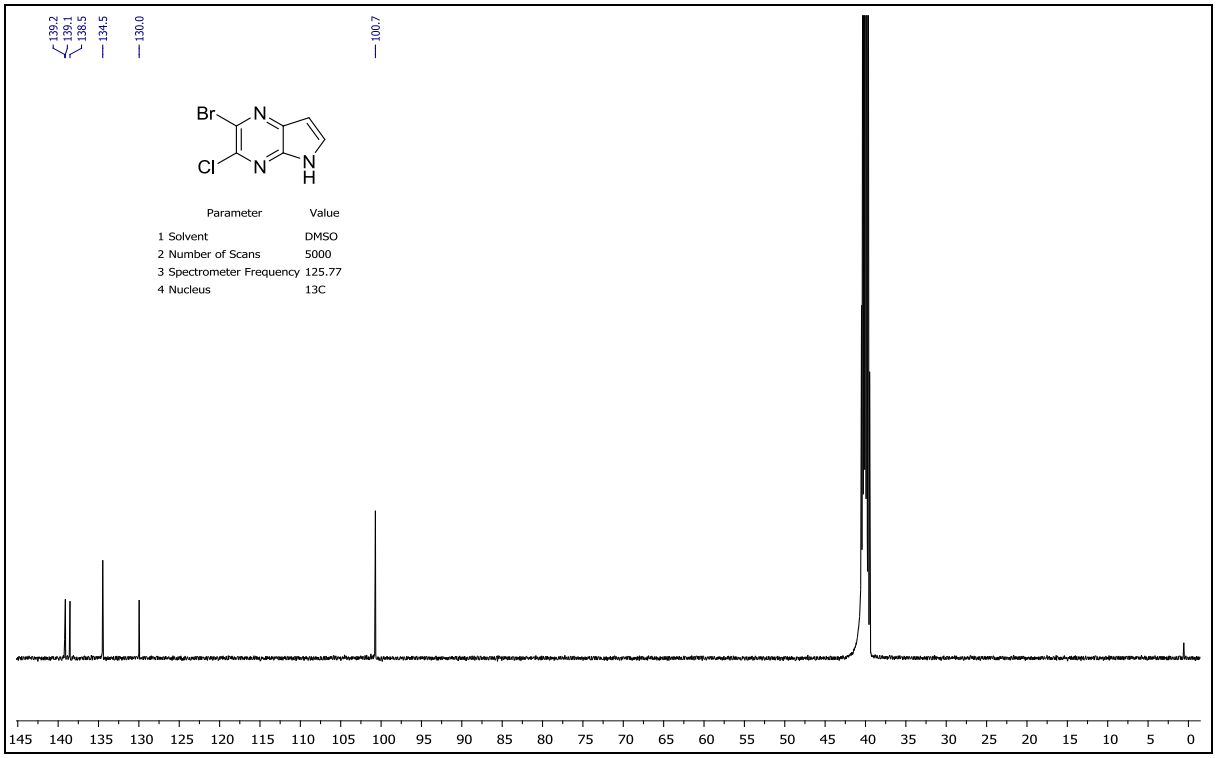

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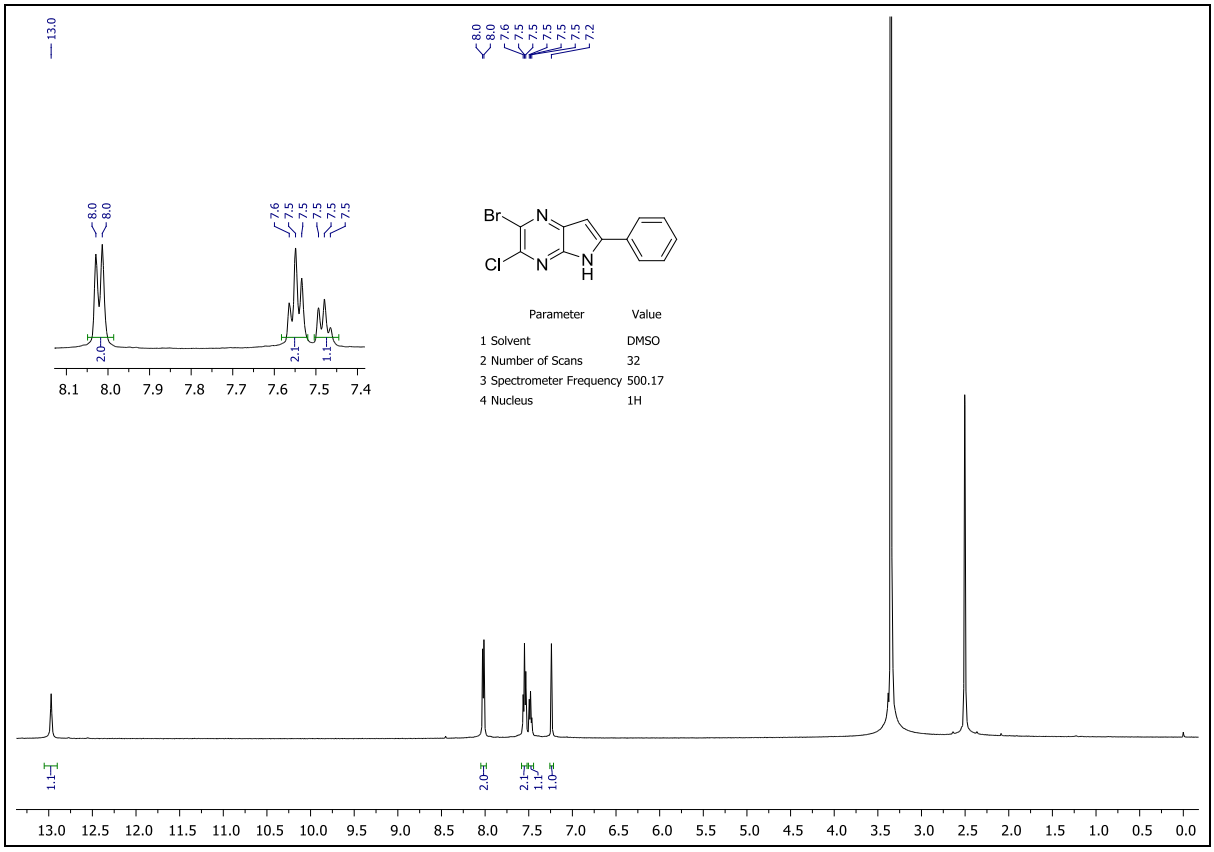

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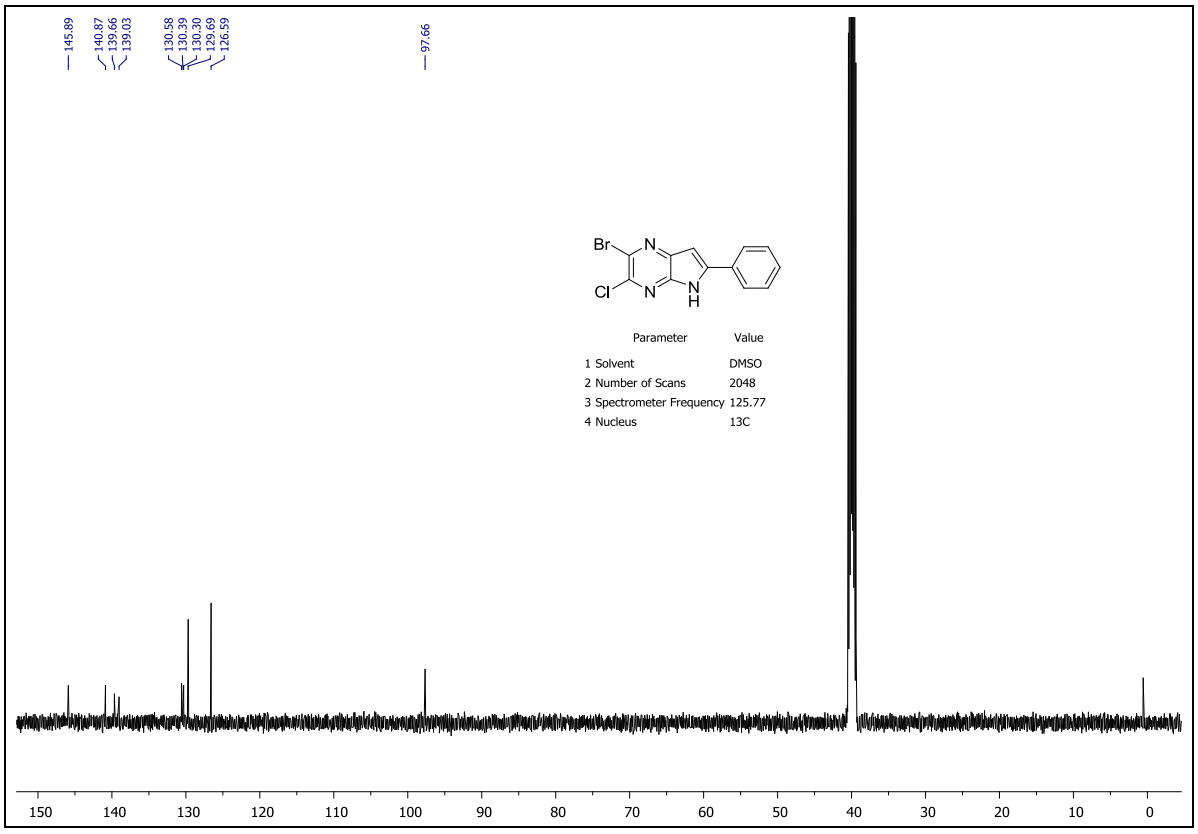

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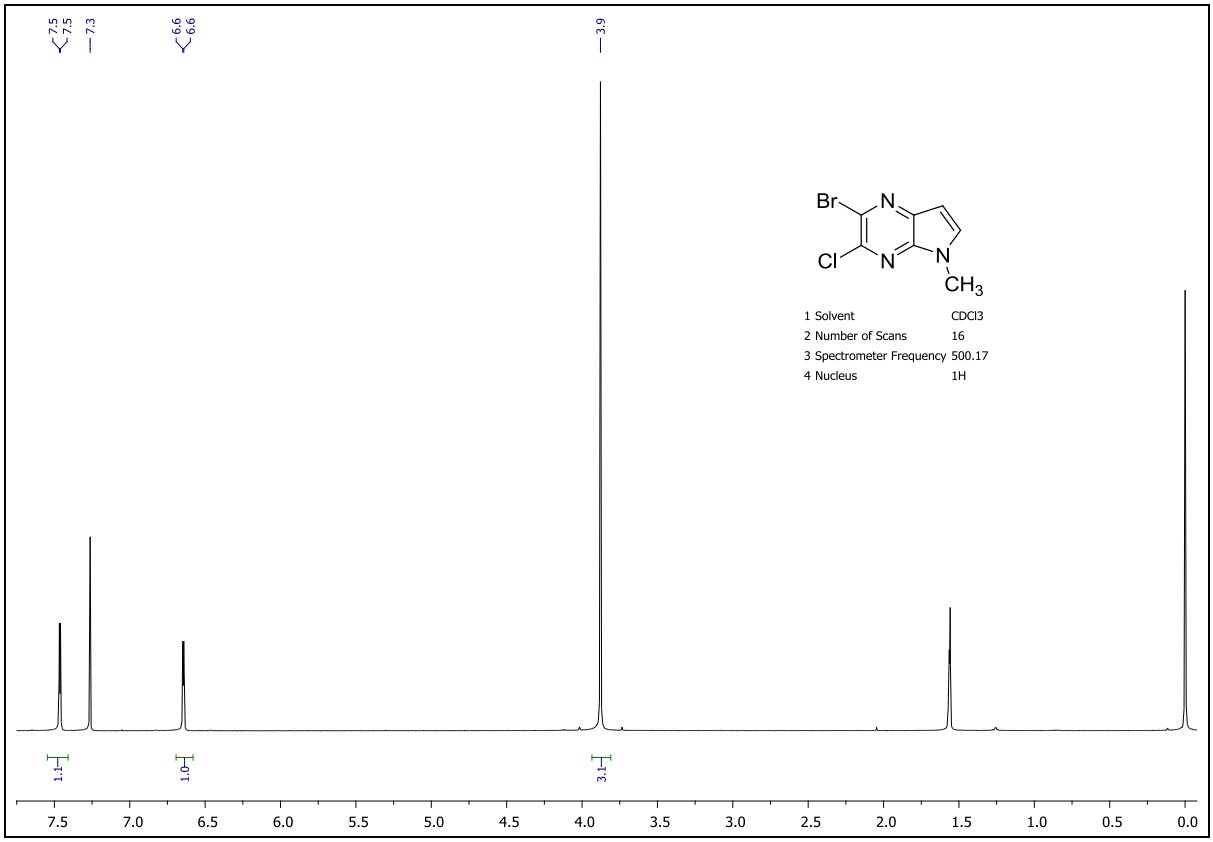

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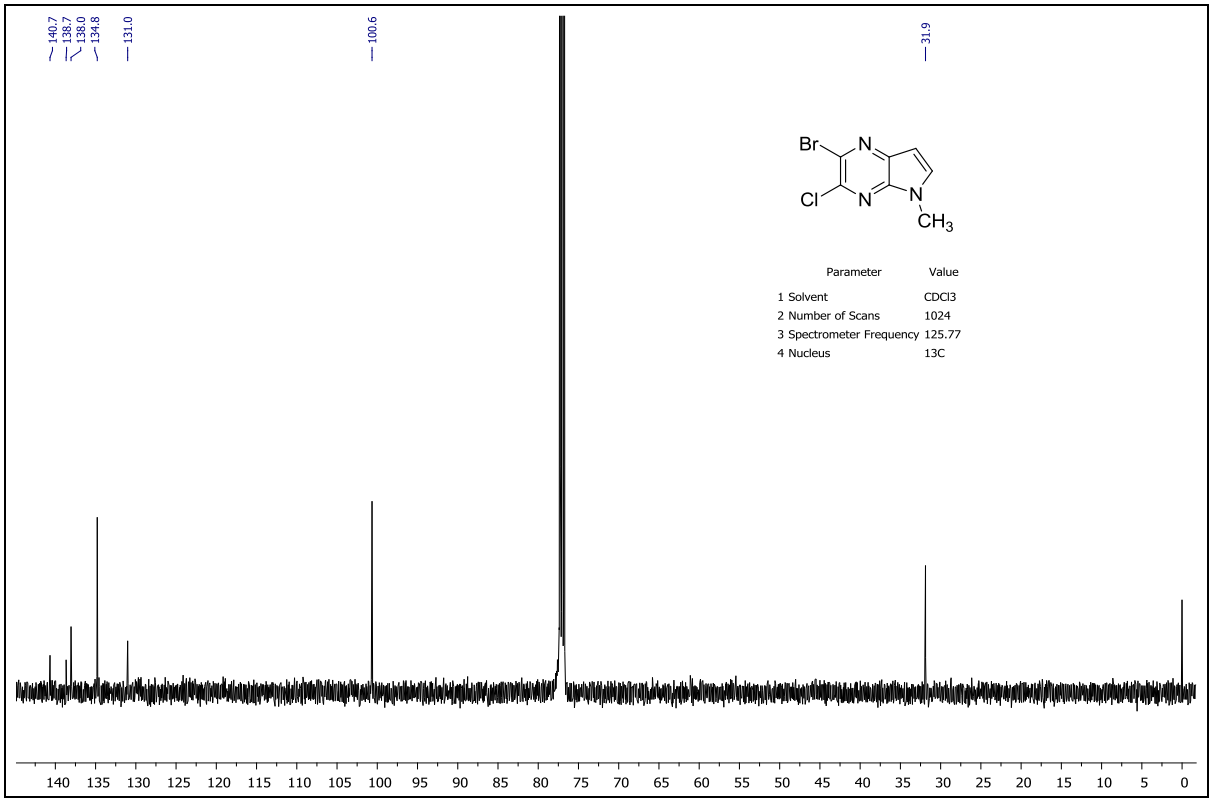

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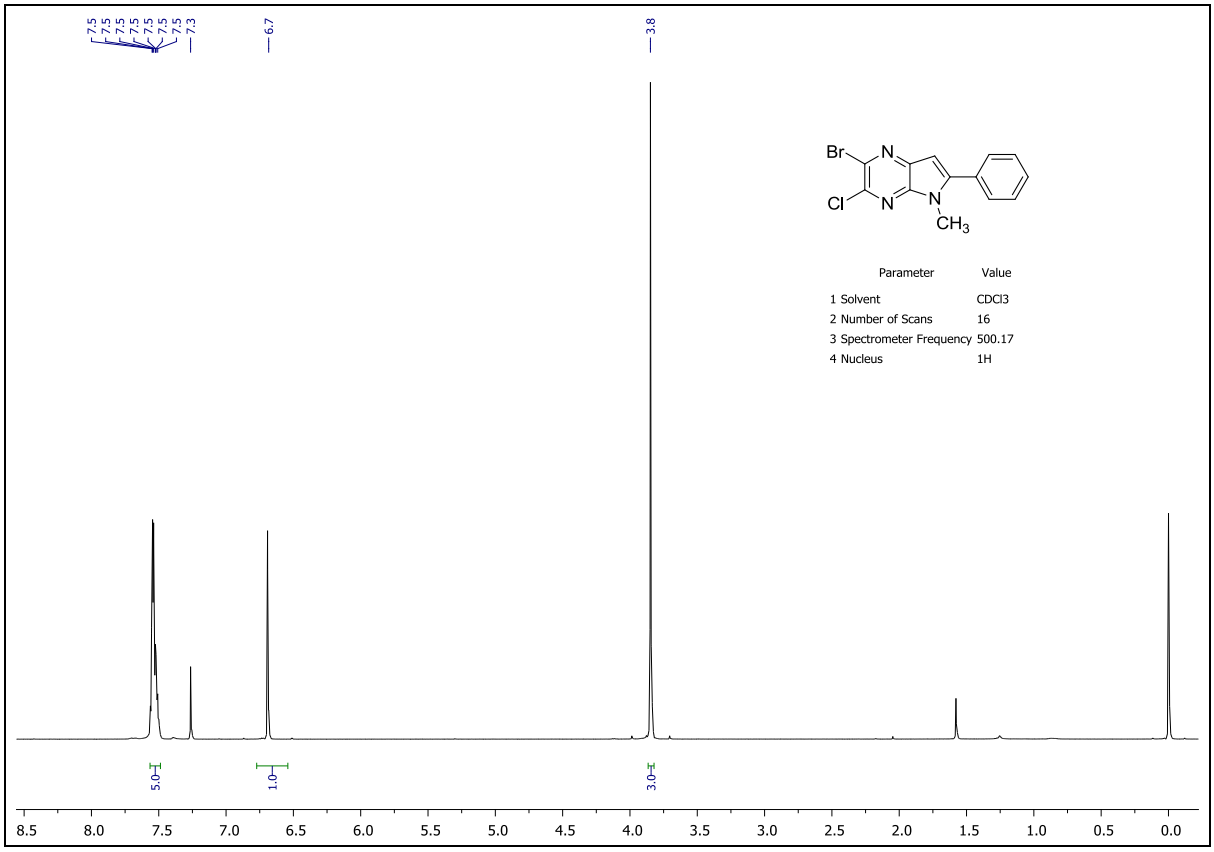

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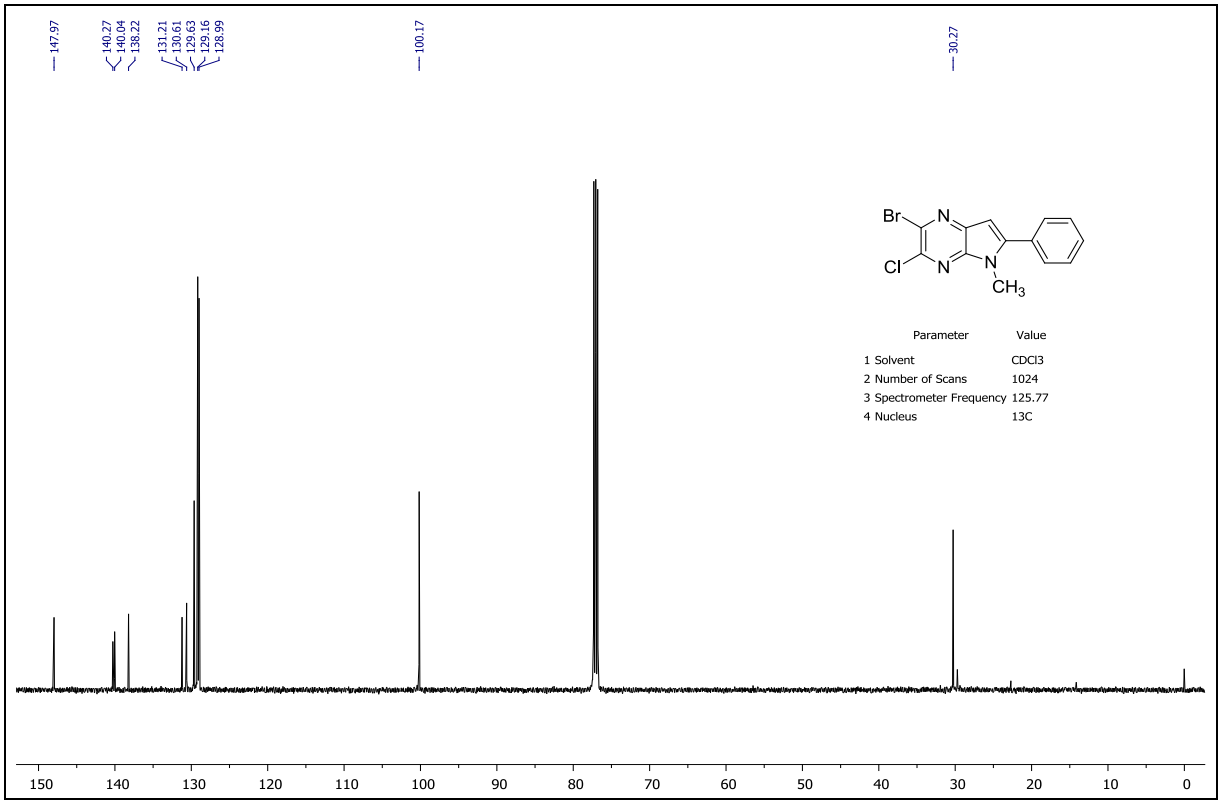

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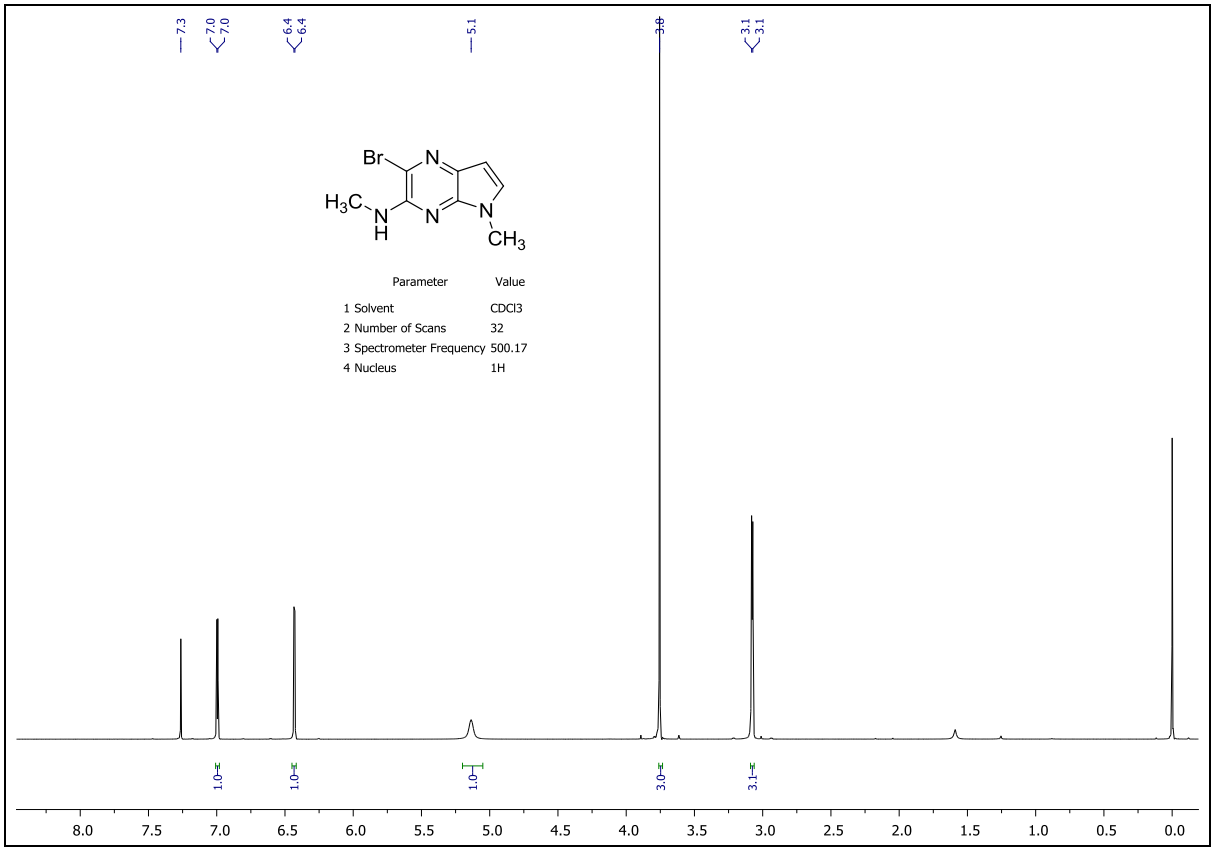

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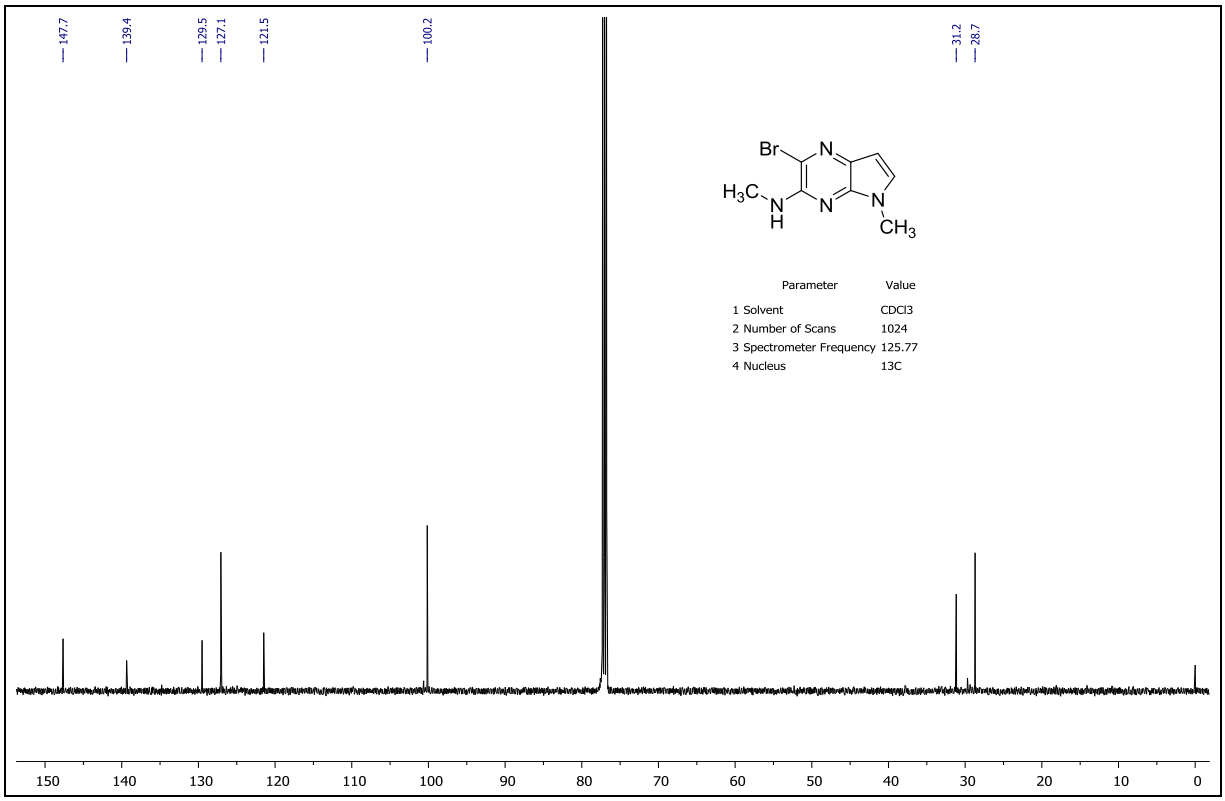

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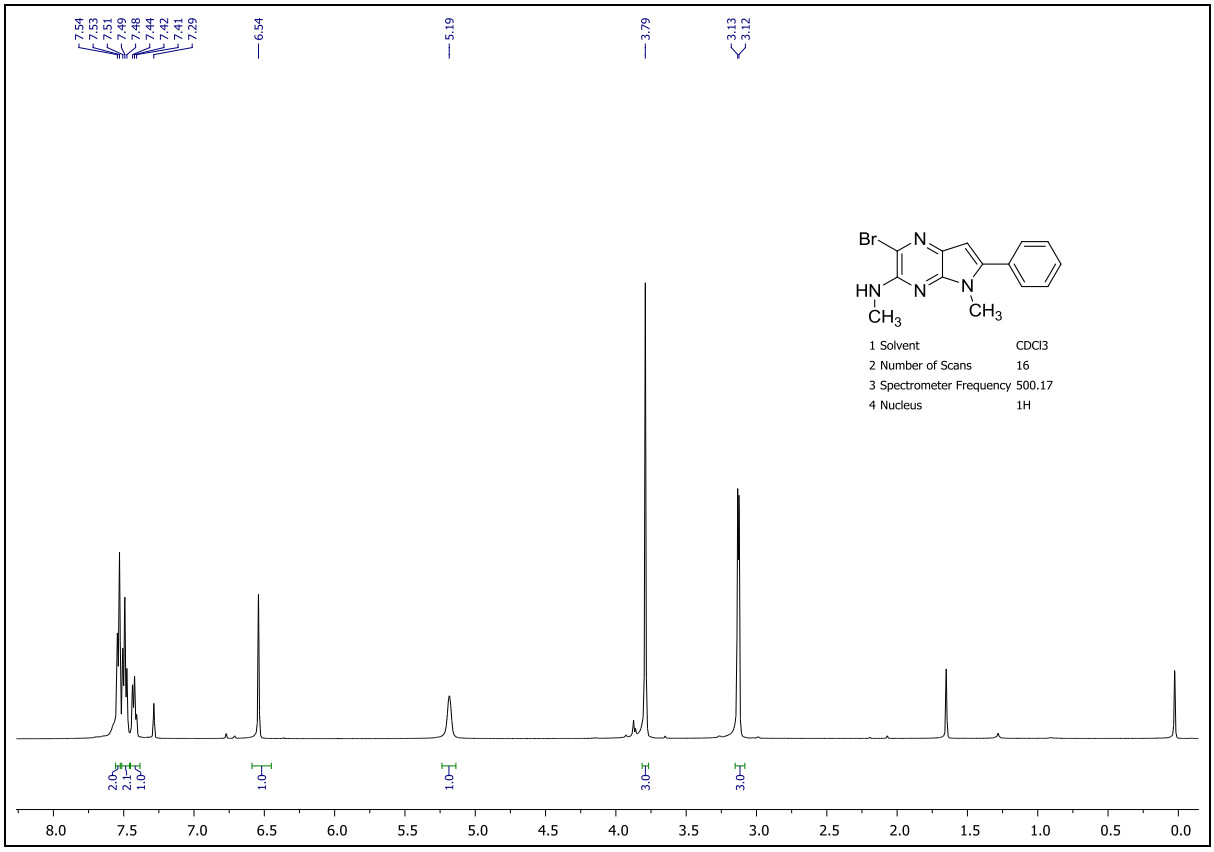

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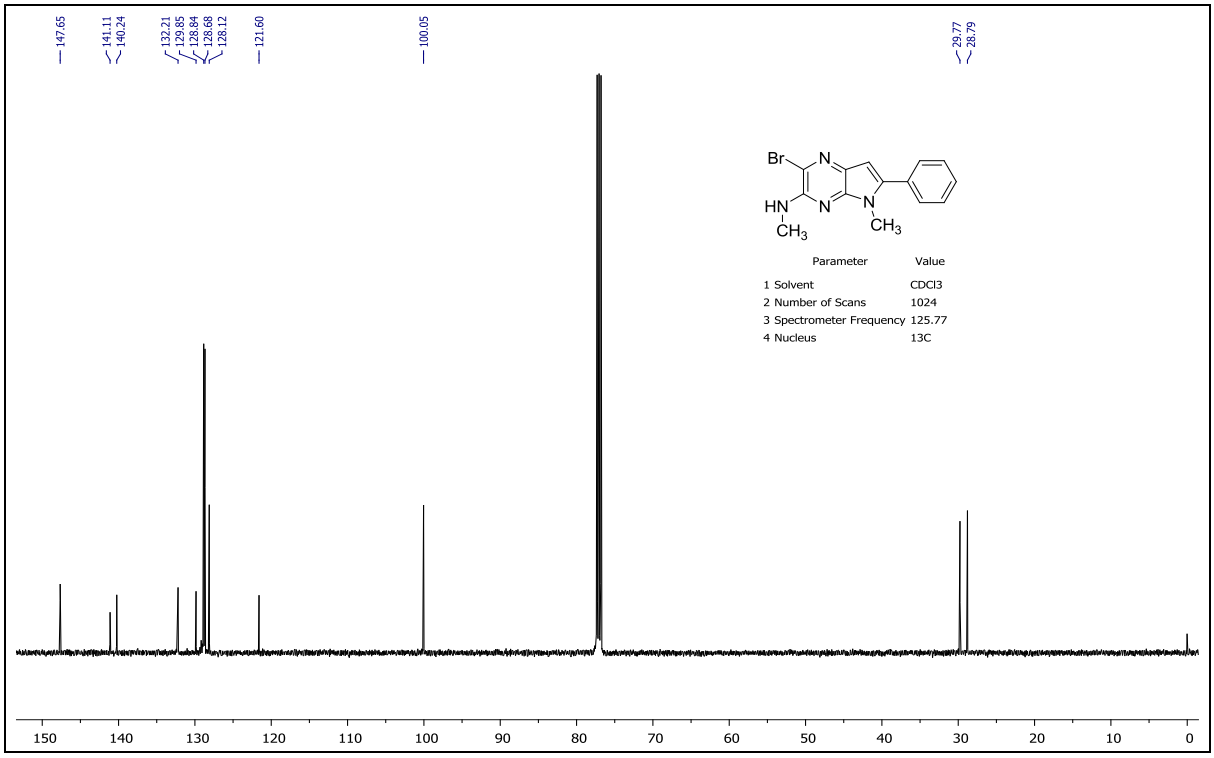
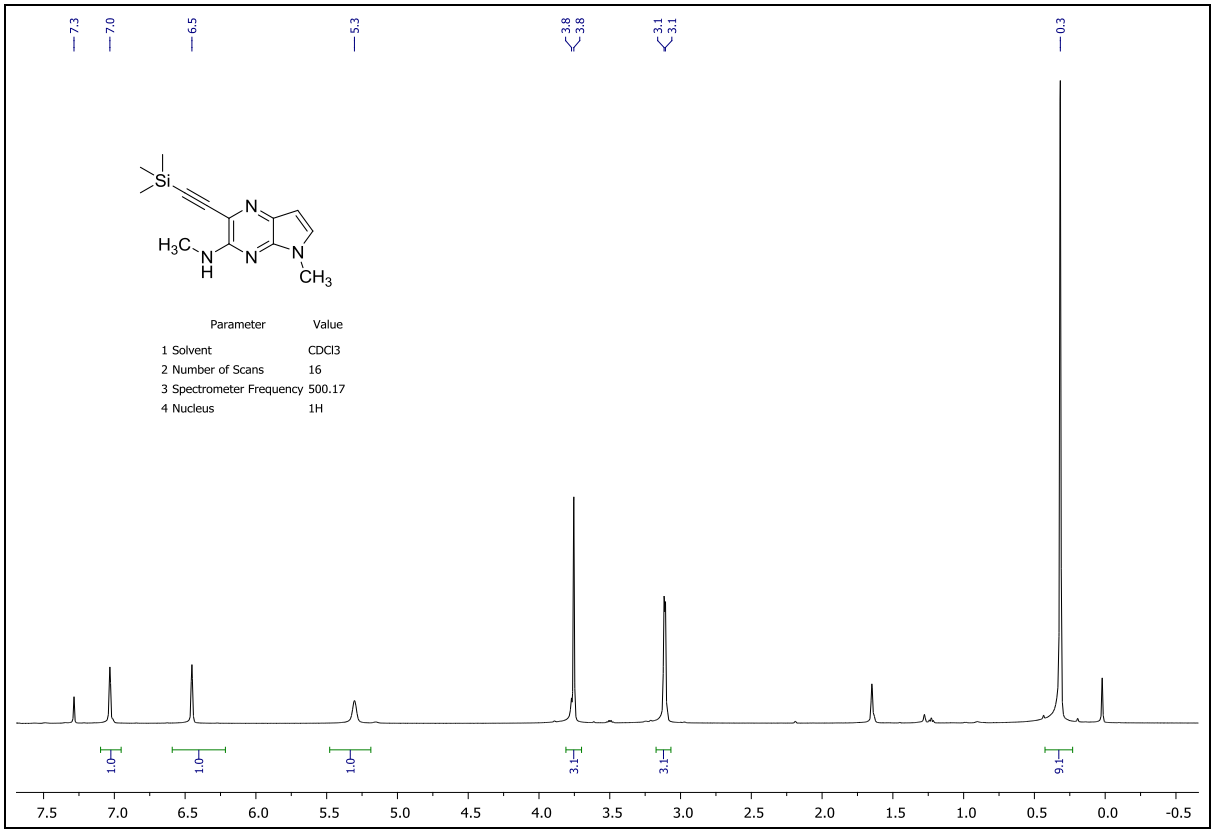


^{13}C NMR – 4b



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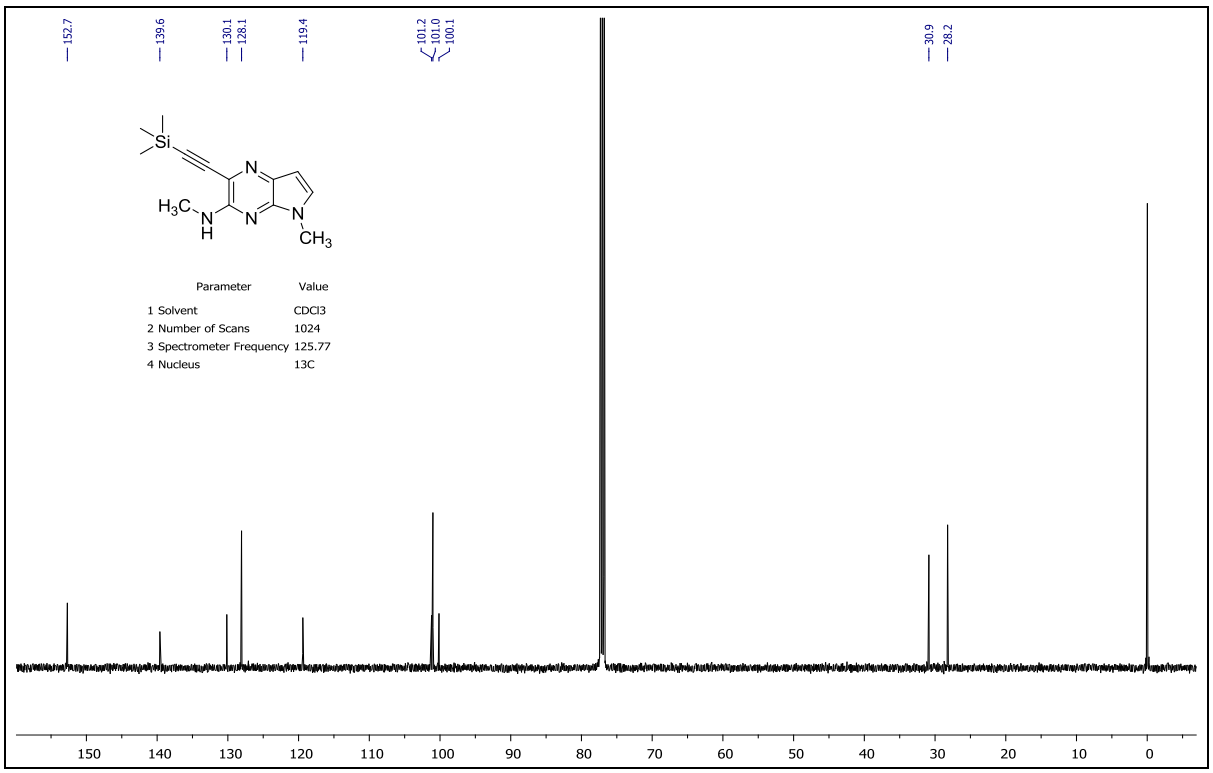

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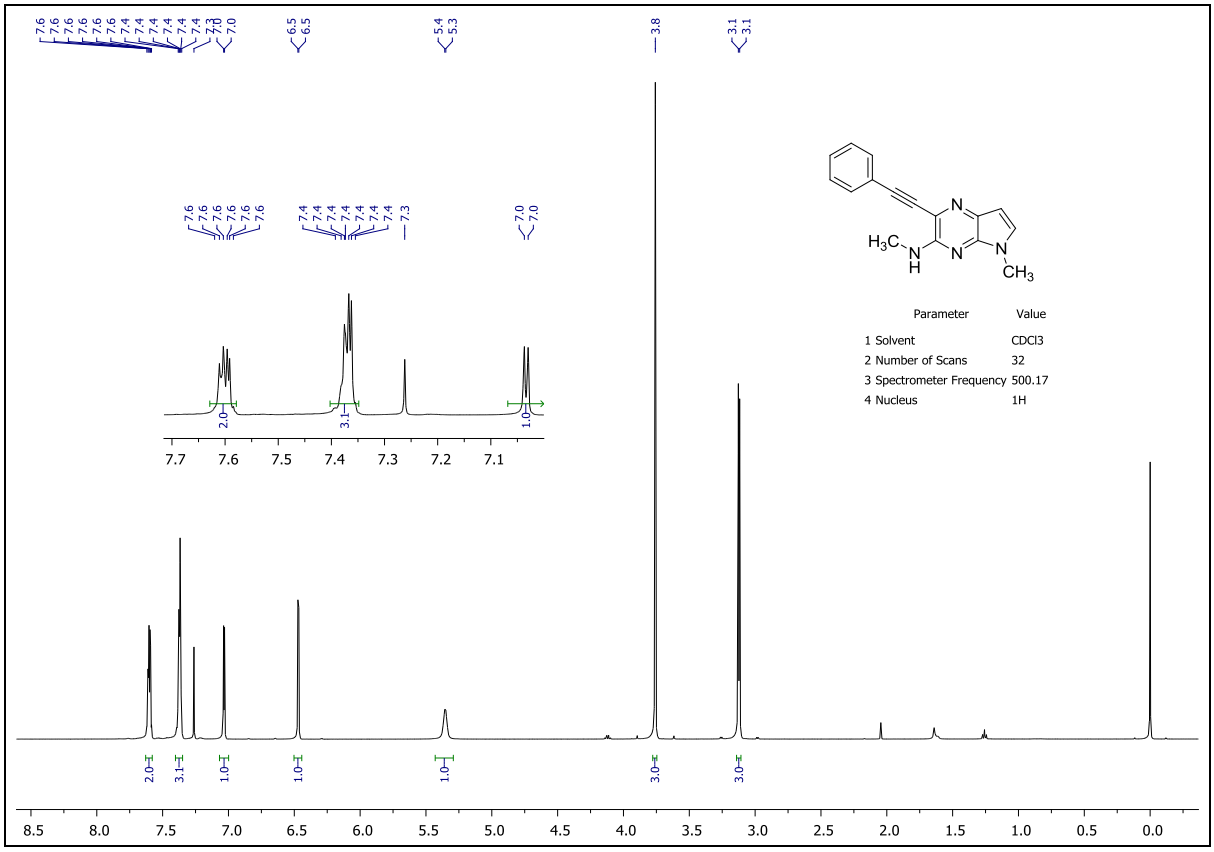

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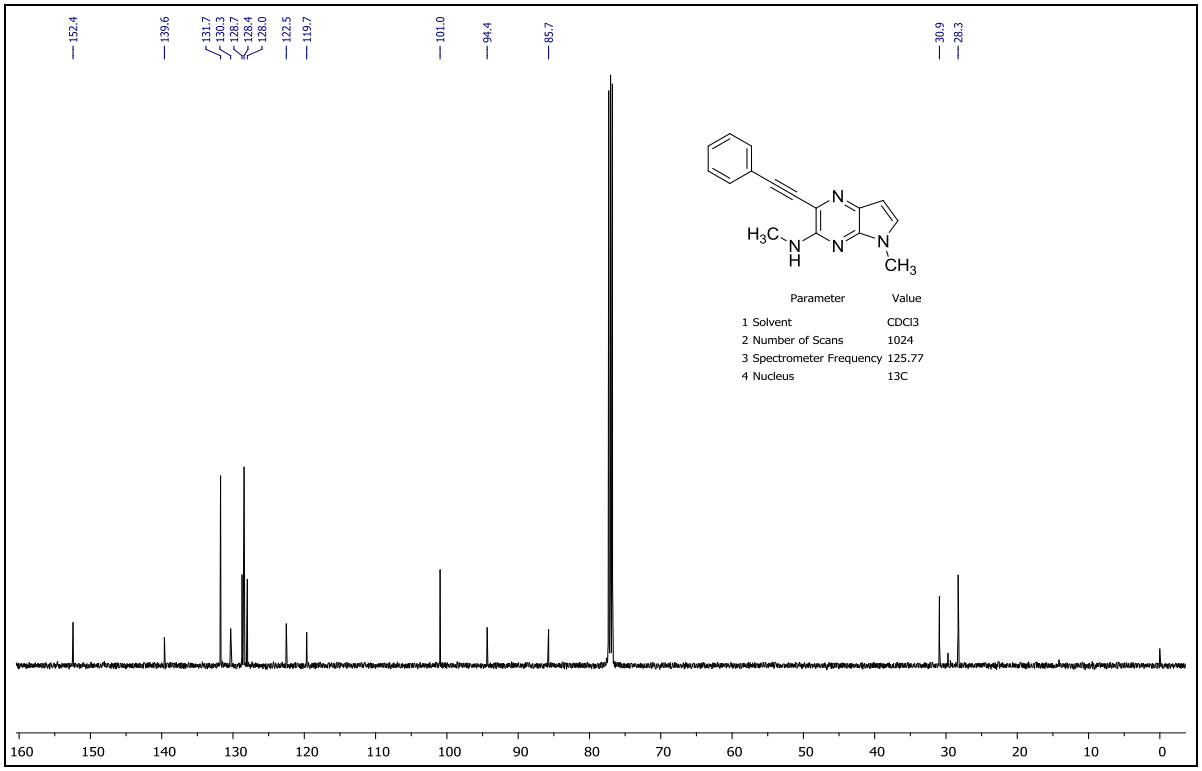

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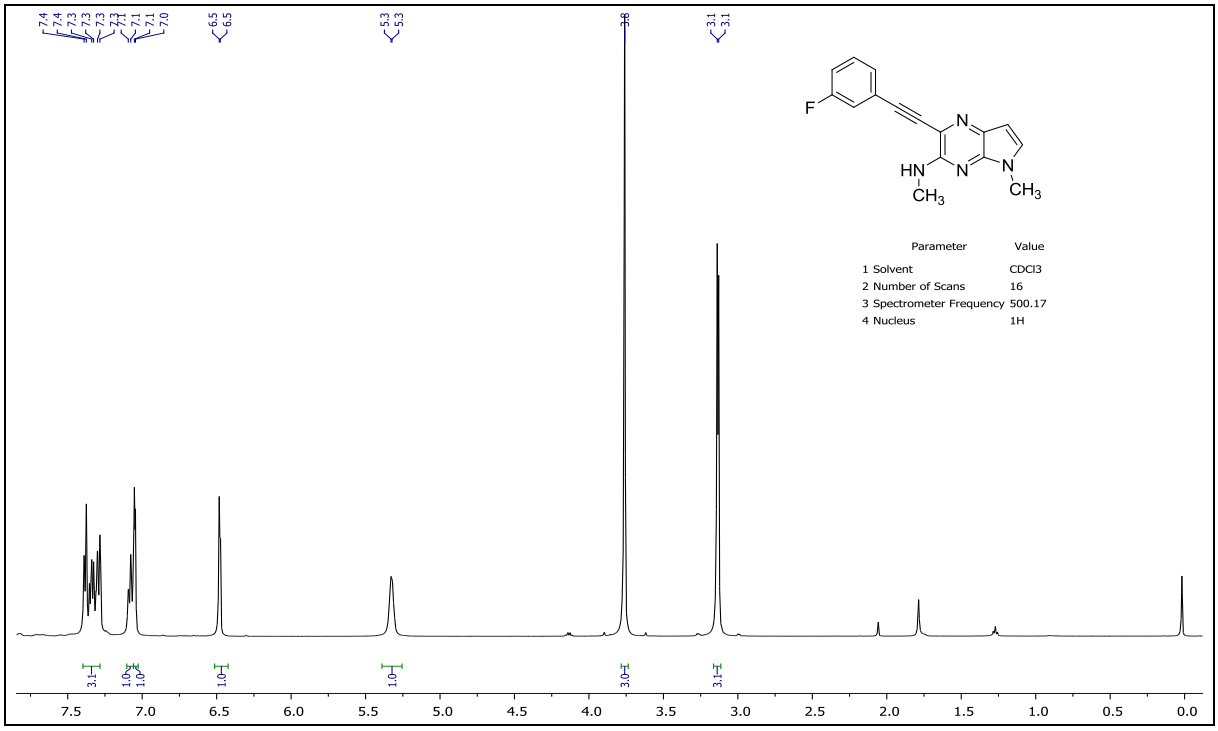

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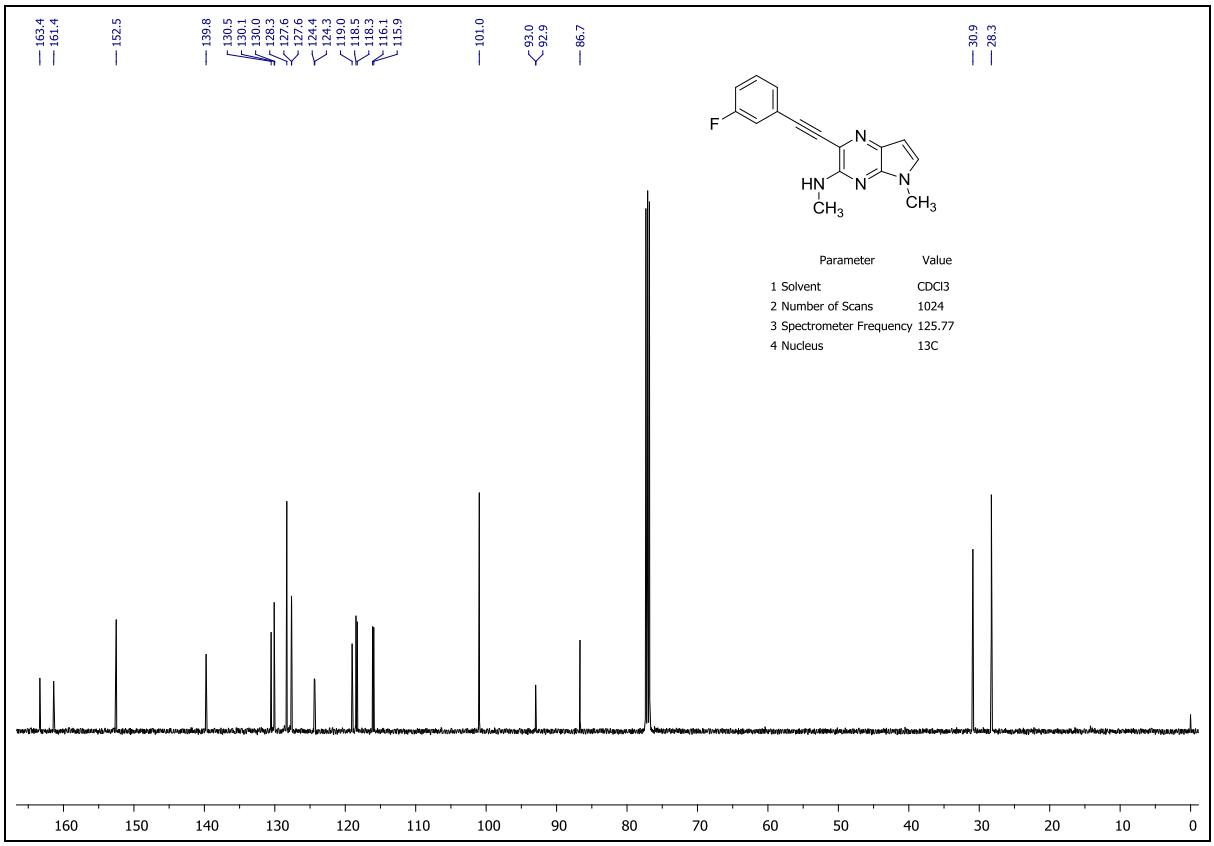

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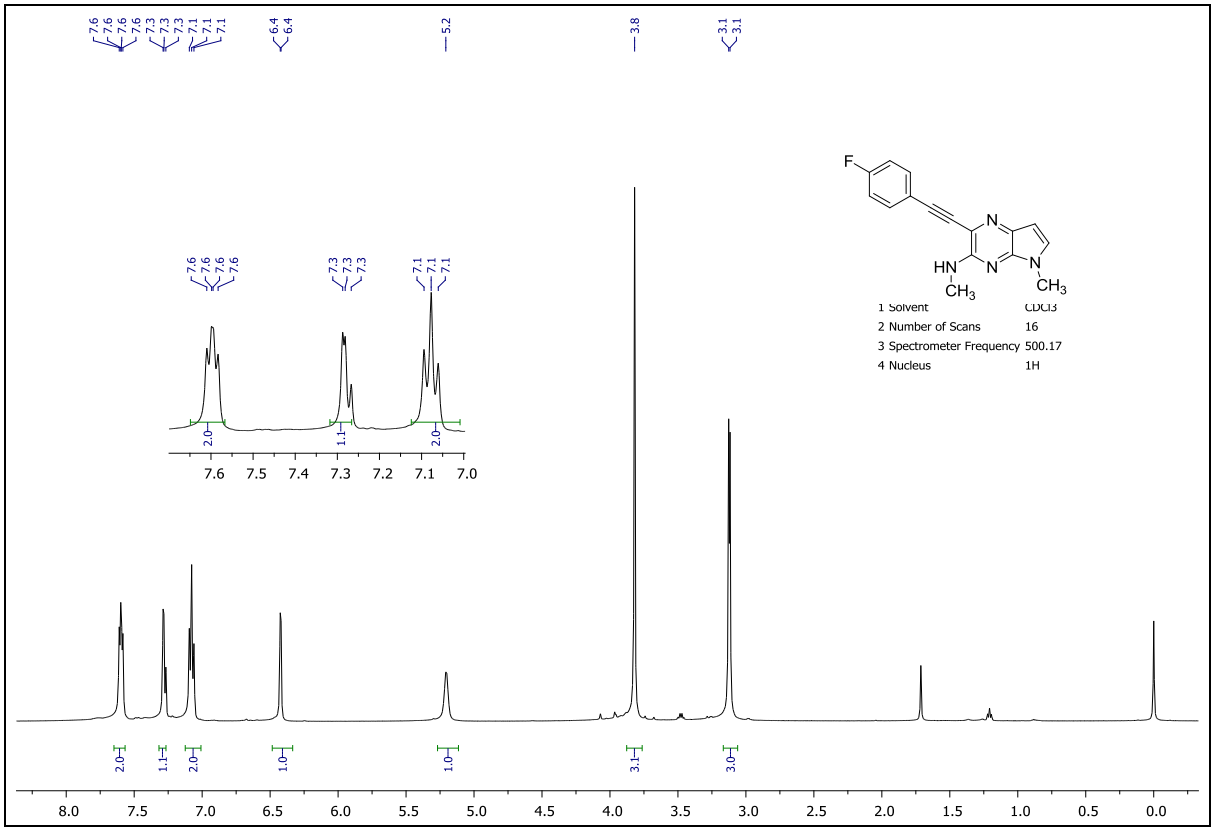

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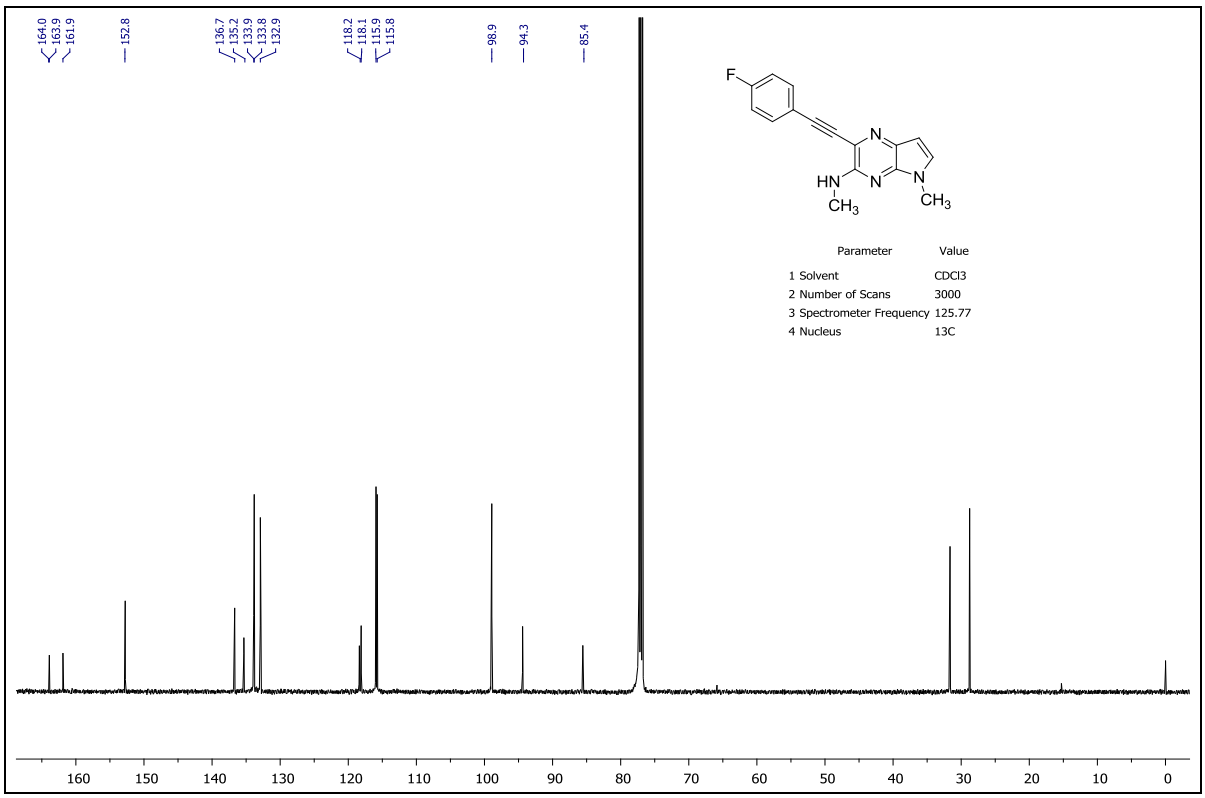

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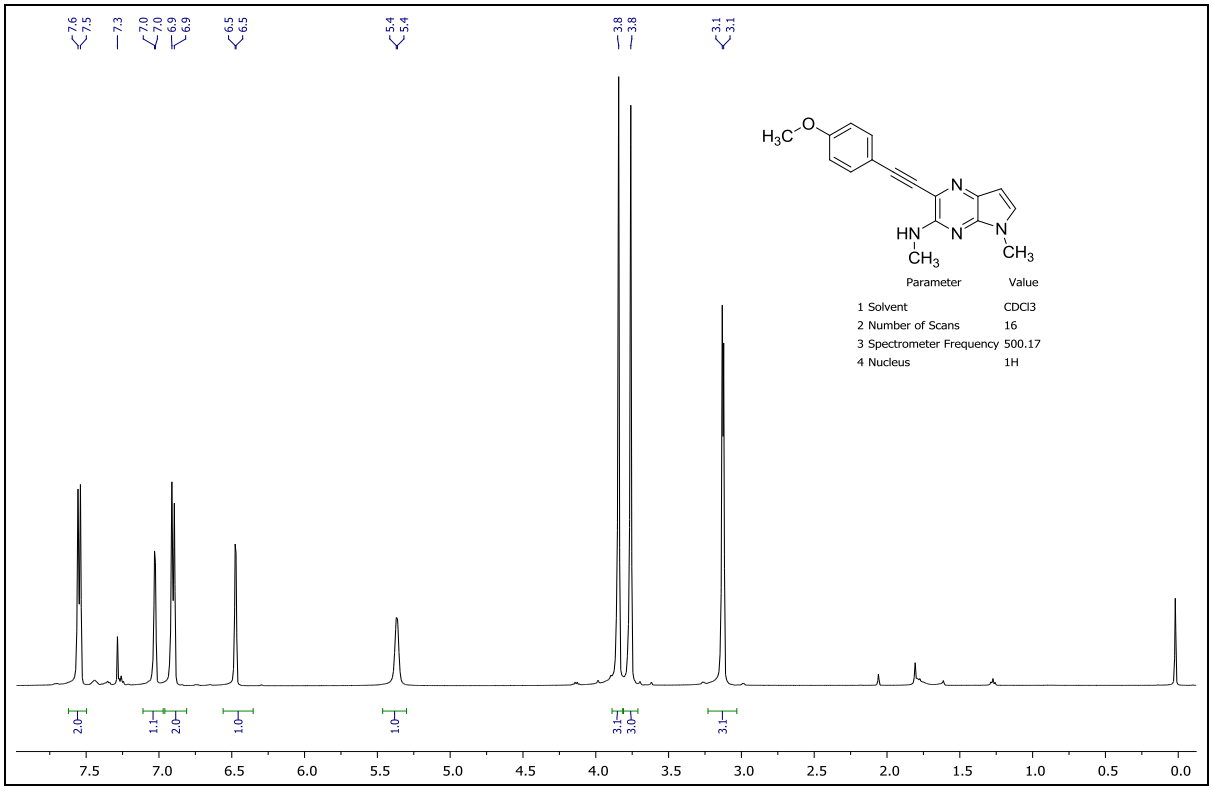

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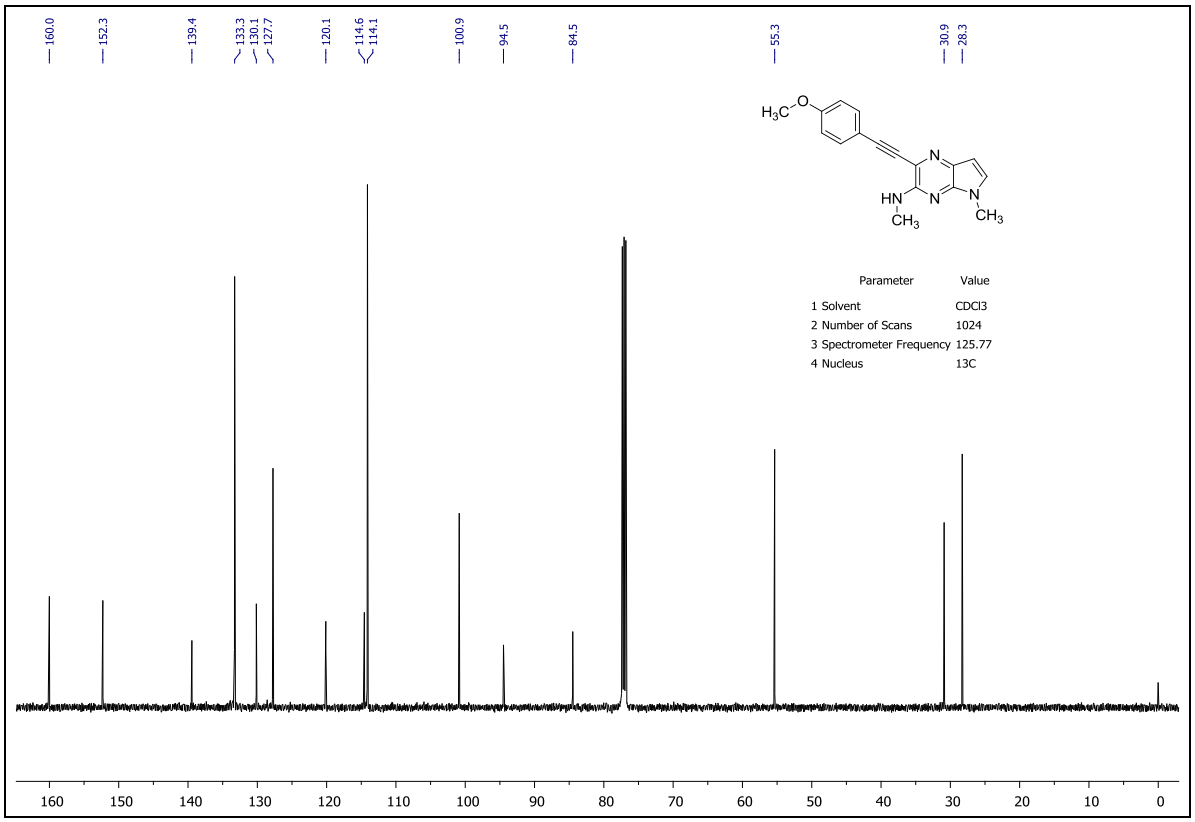

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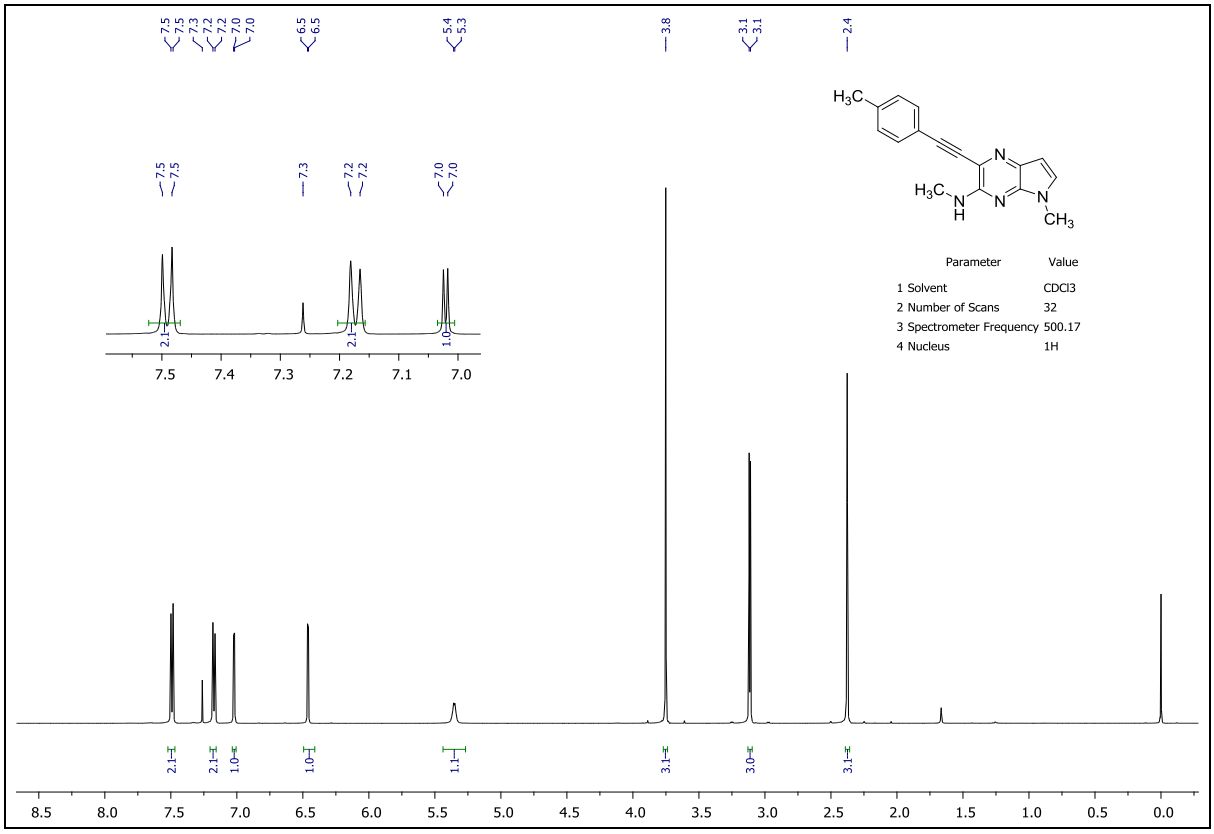
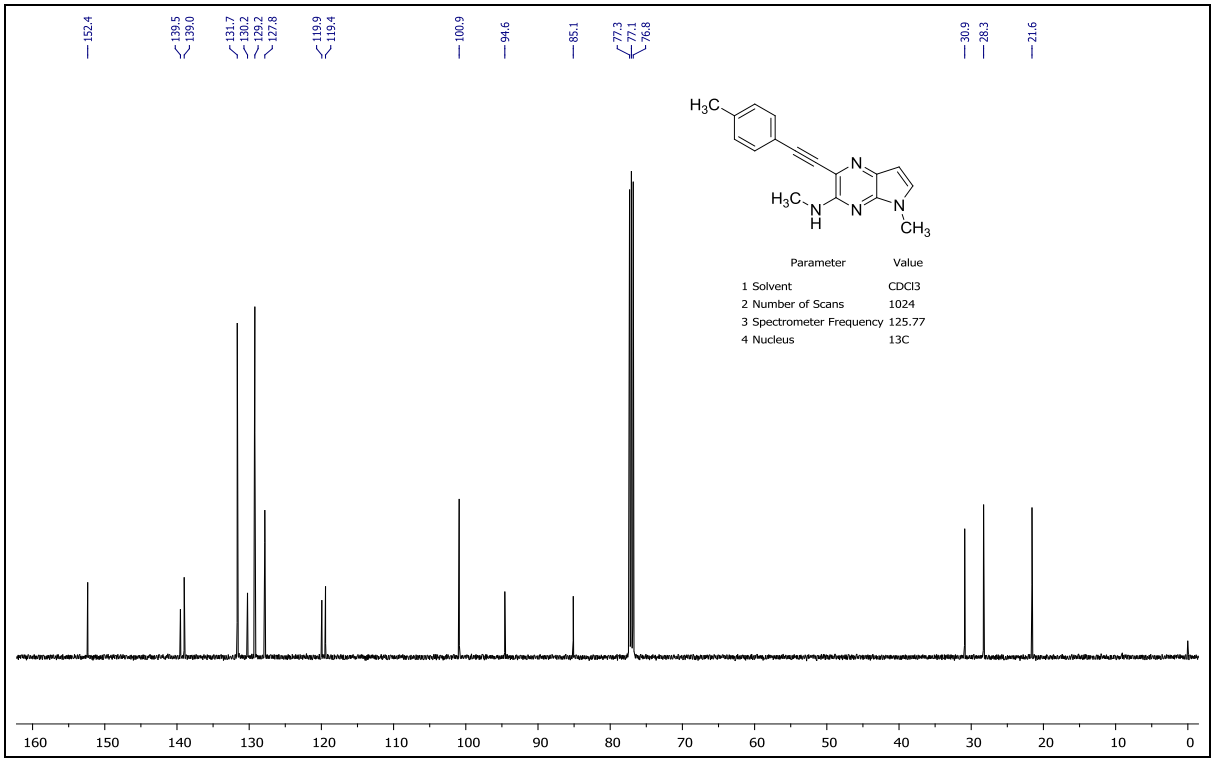
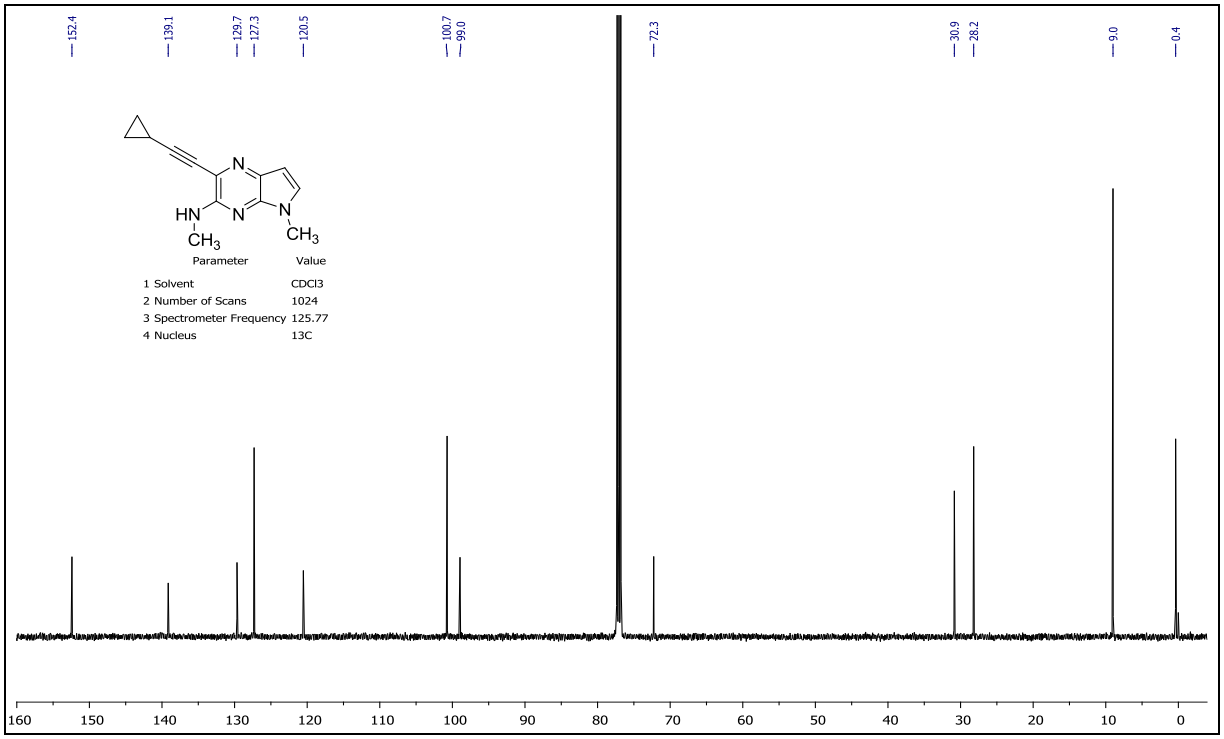


^{1}H NMR – 5f

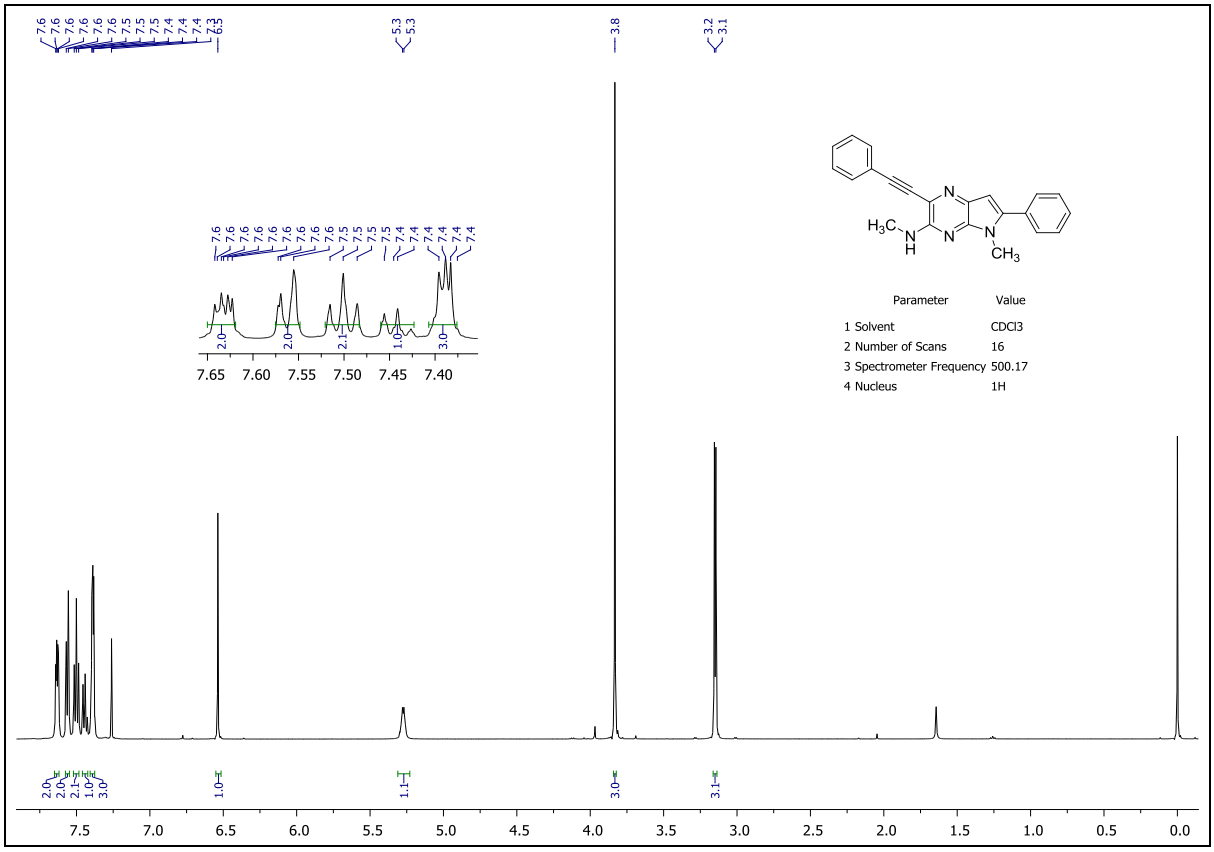


^{13}C NMR – 5f

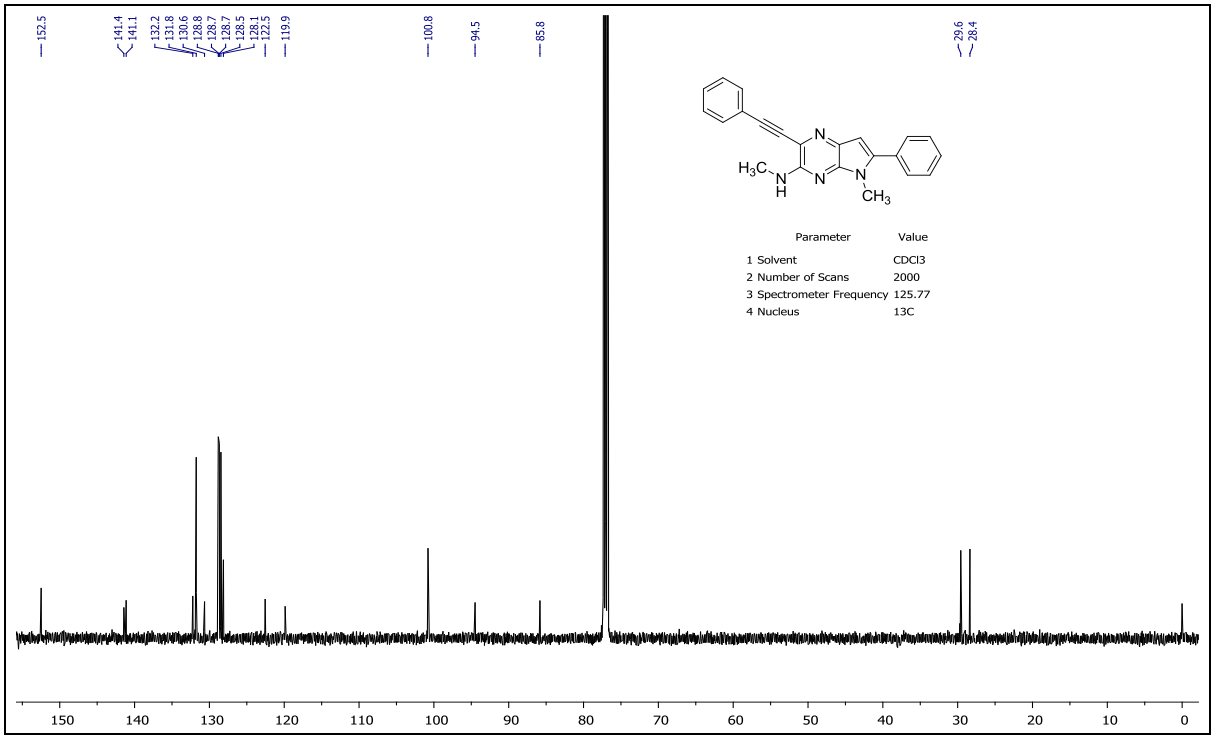
^{1}H NMR – 5g



^{13}C NMR – 5g



^{1}H NMR – 5i



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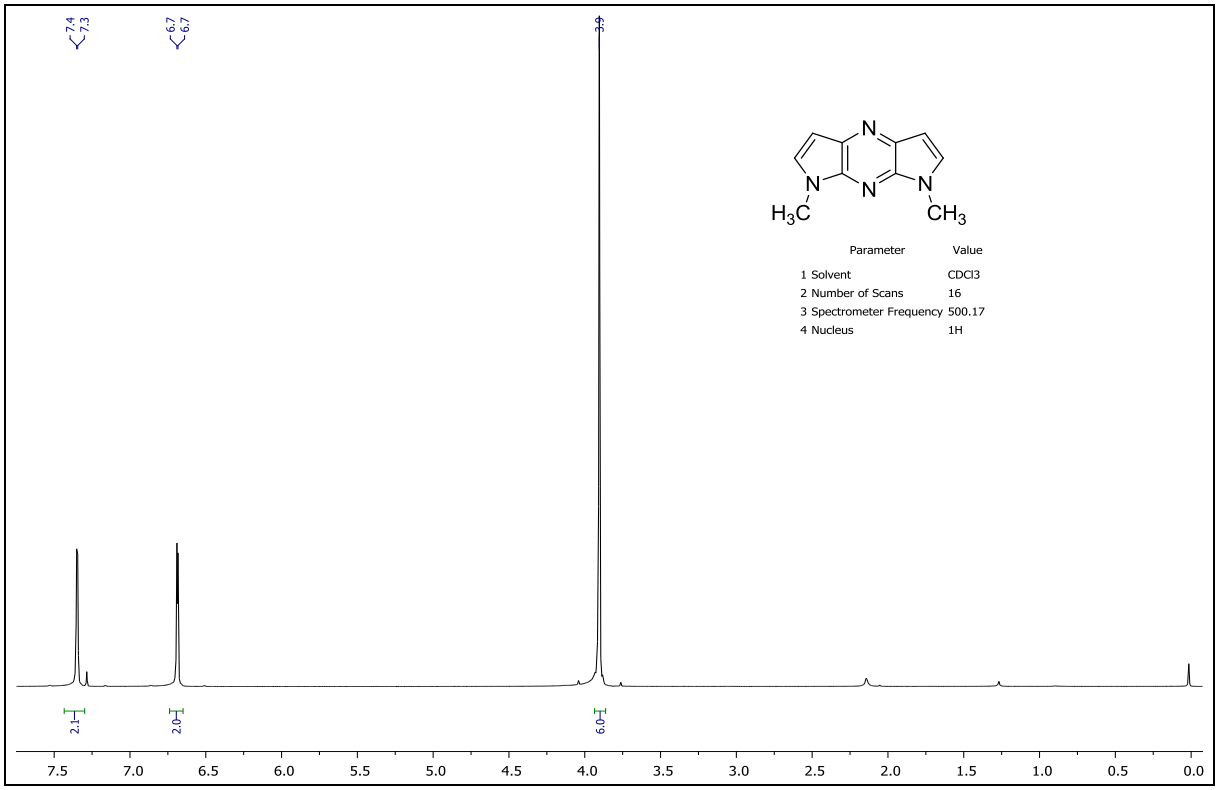
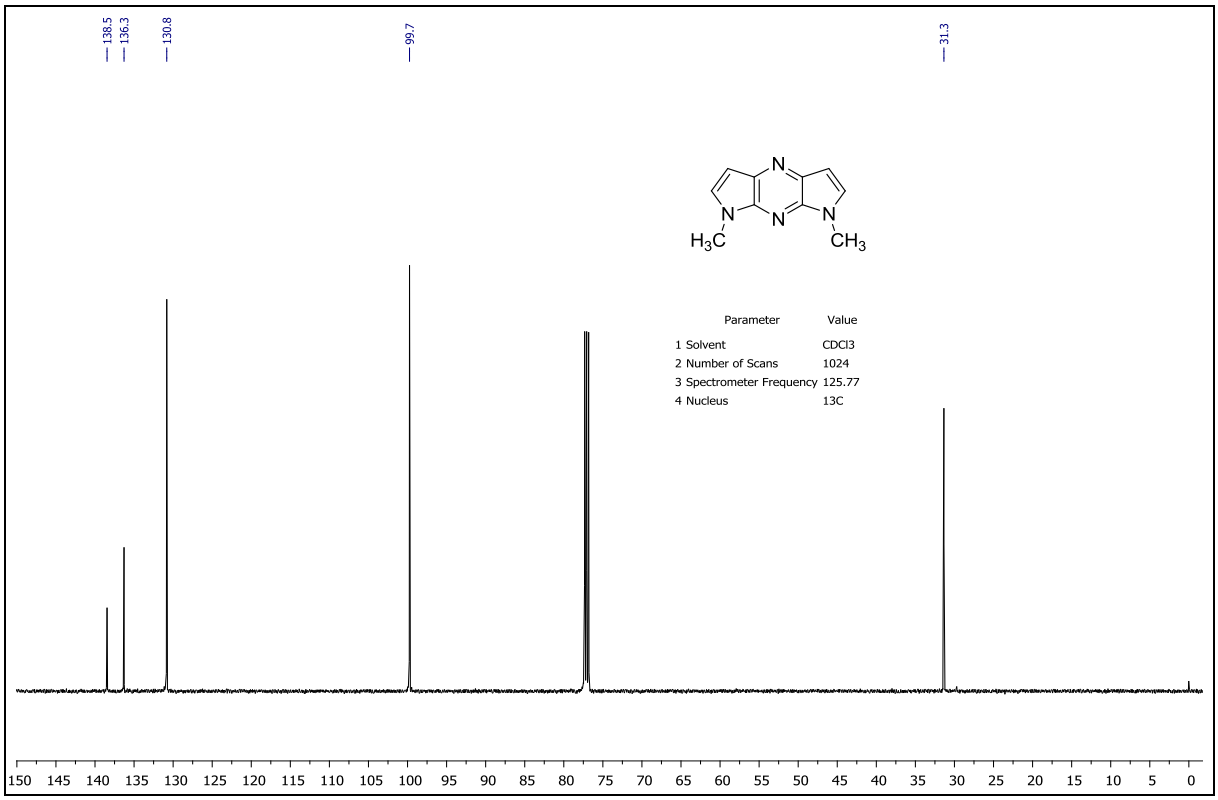
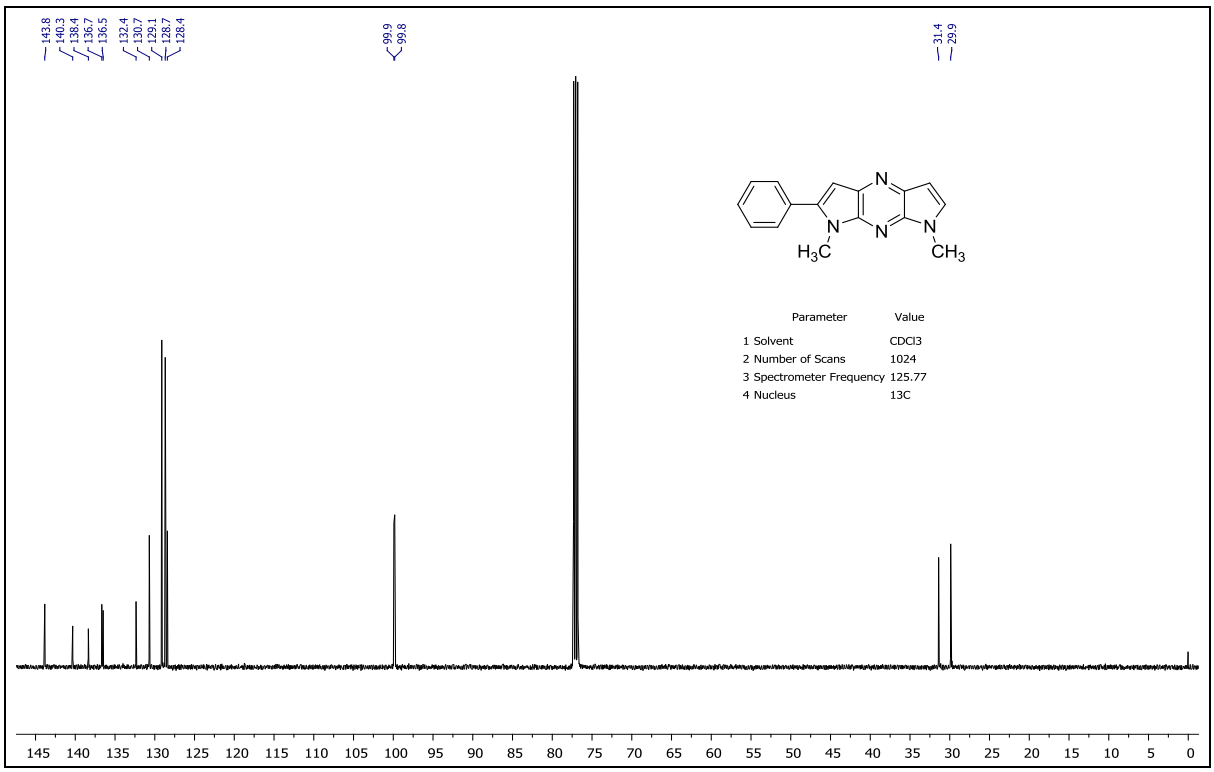


^{1}H NMR – 6a



^{13}C NMR – 6a

^{1}H NMR – 6b



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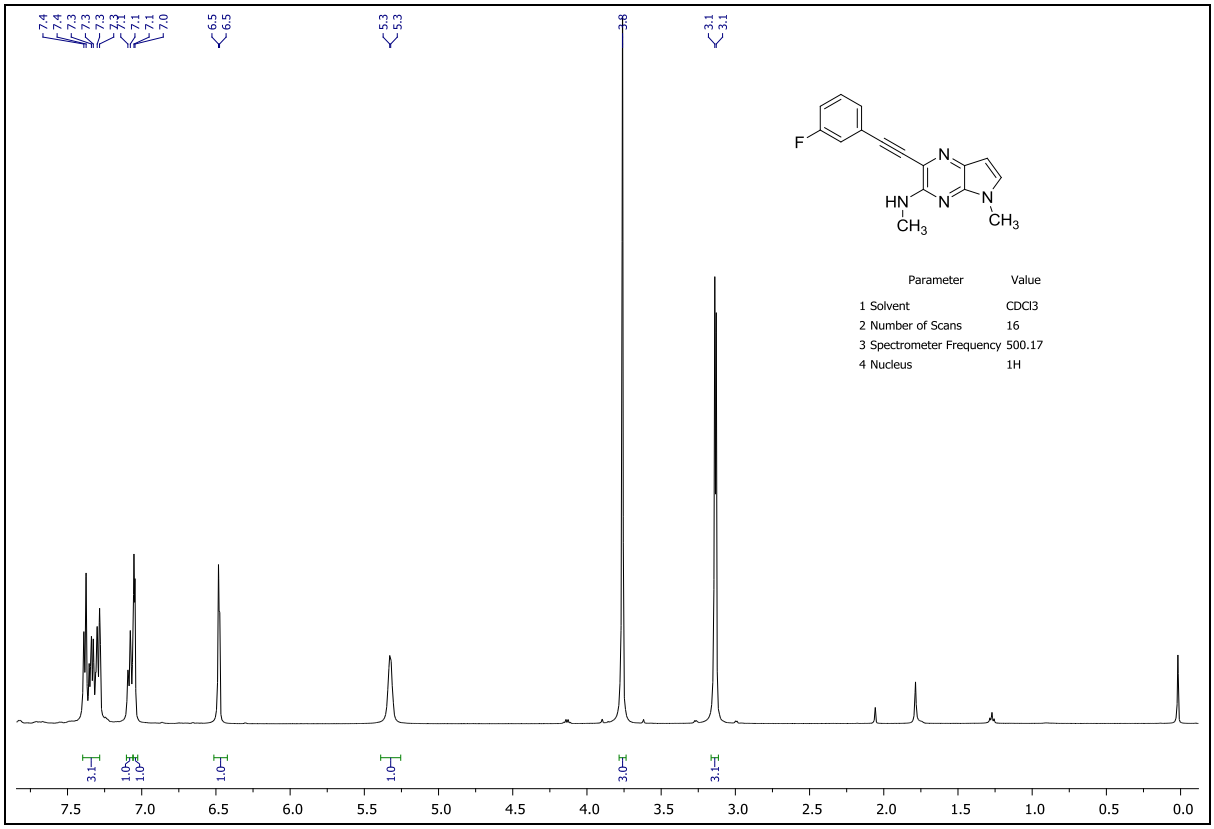

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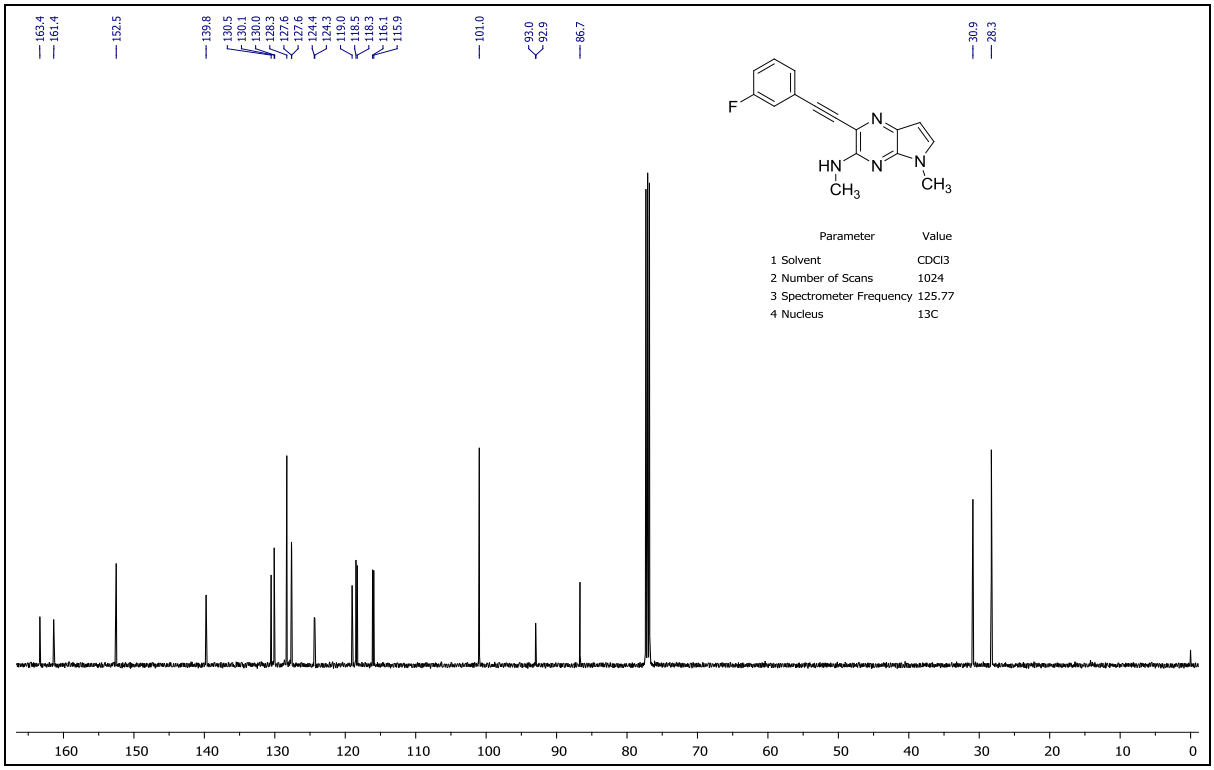

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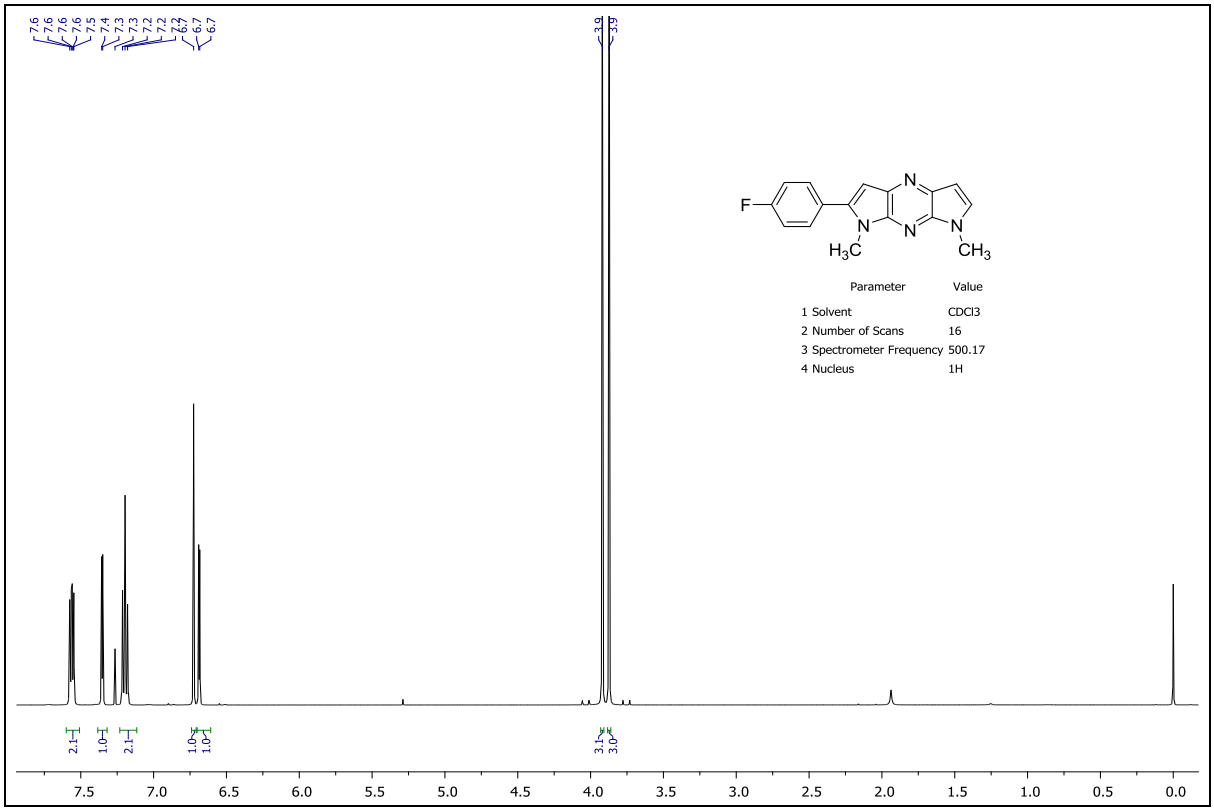

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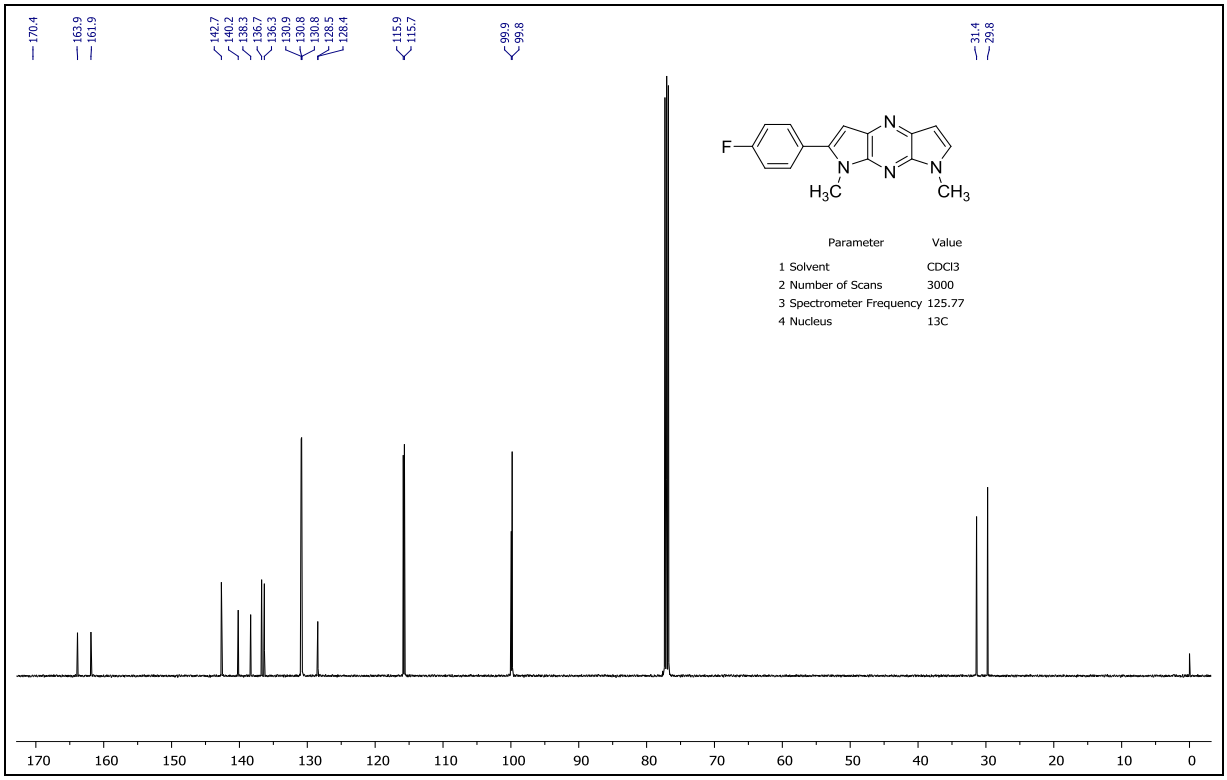

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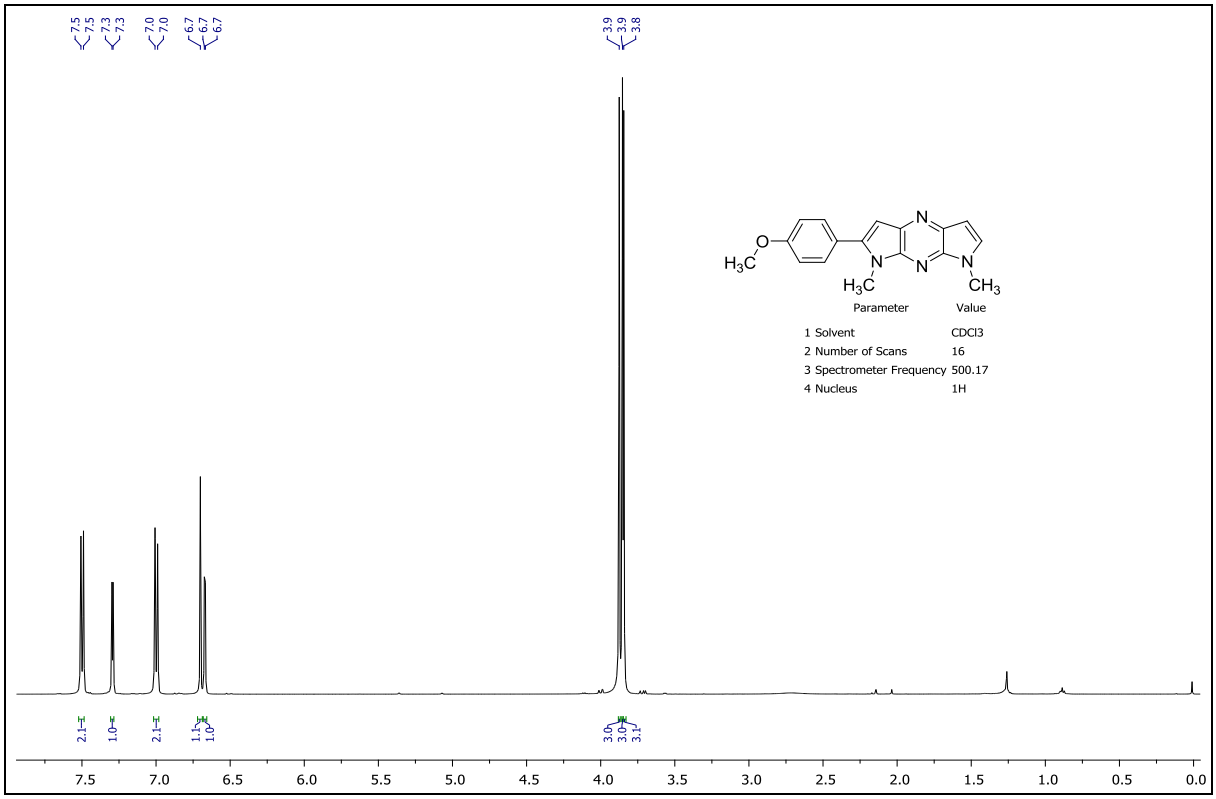

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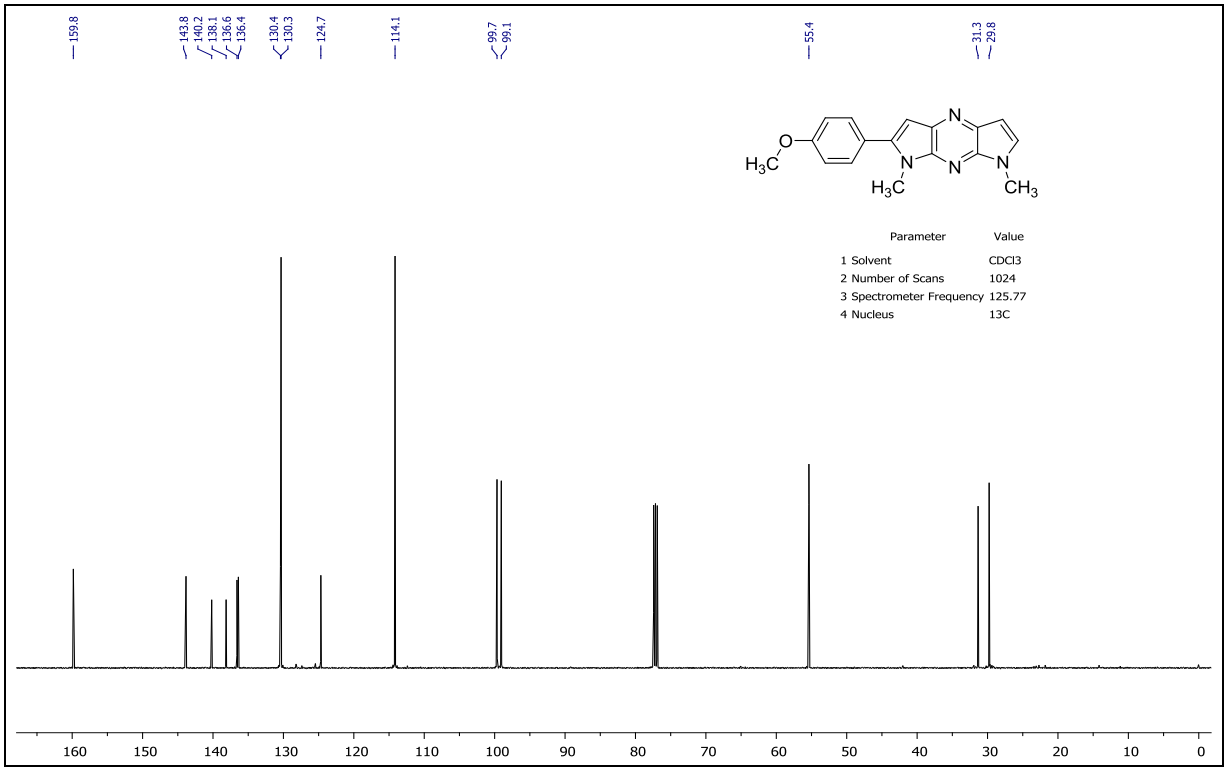
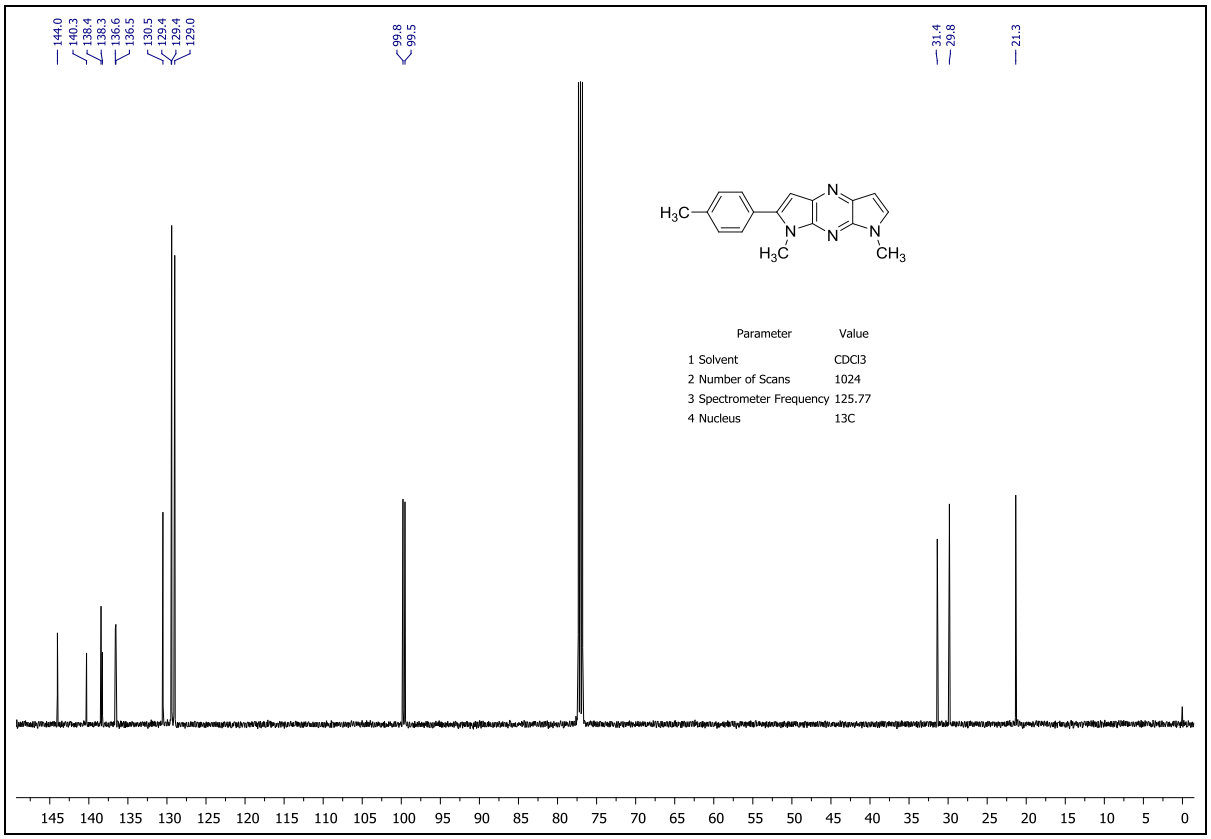


^{13}C NMR – 6e

^{1}H NMR – 6f



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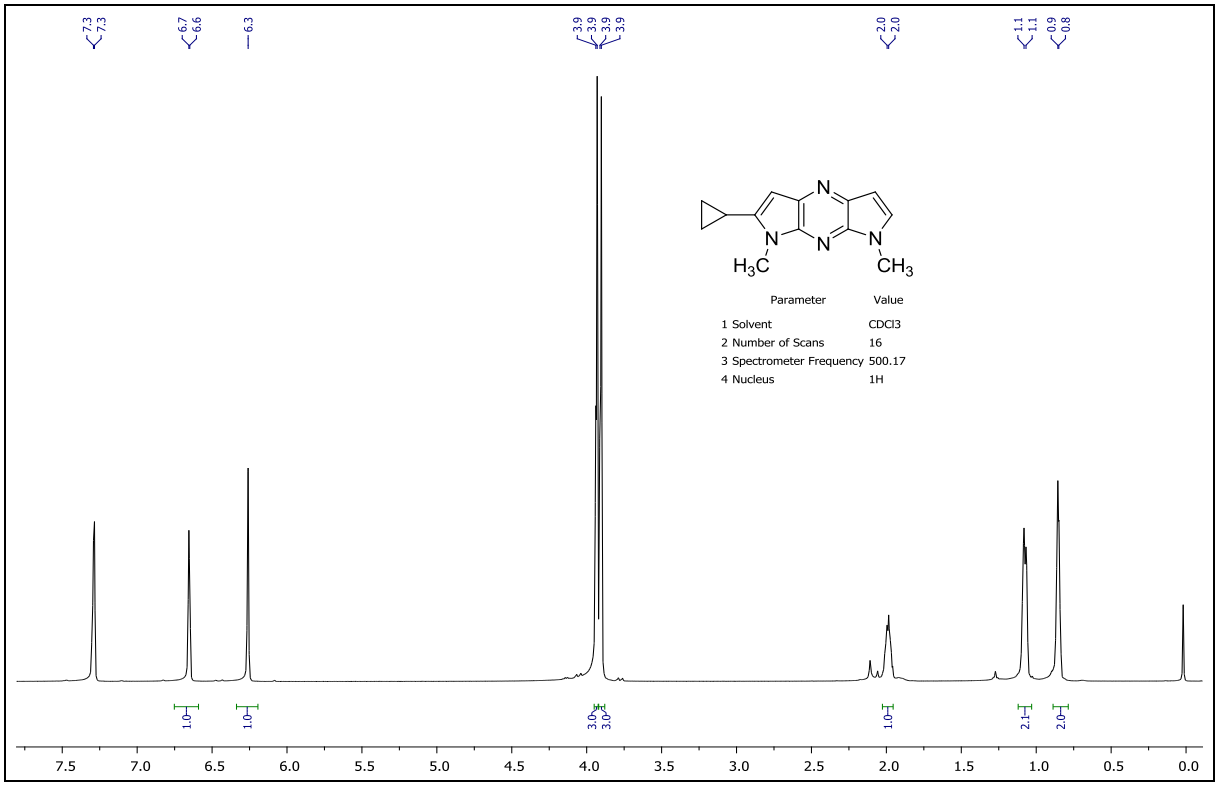

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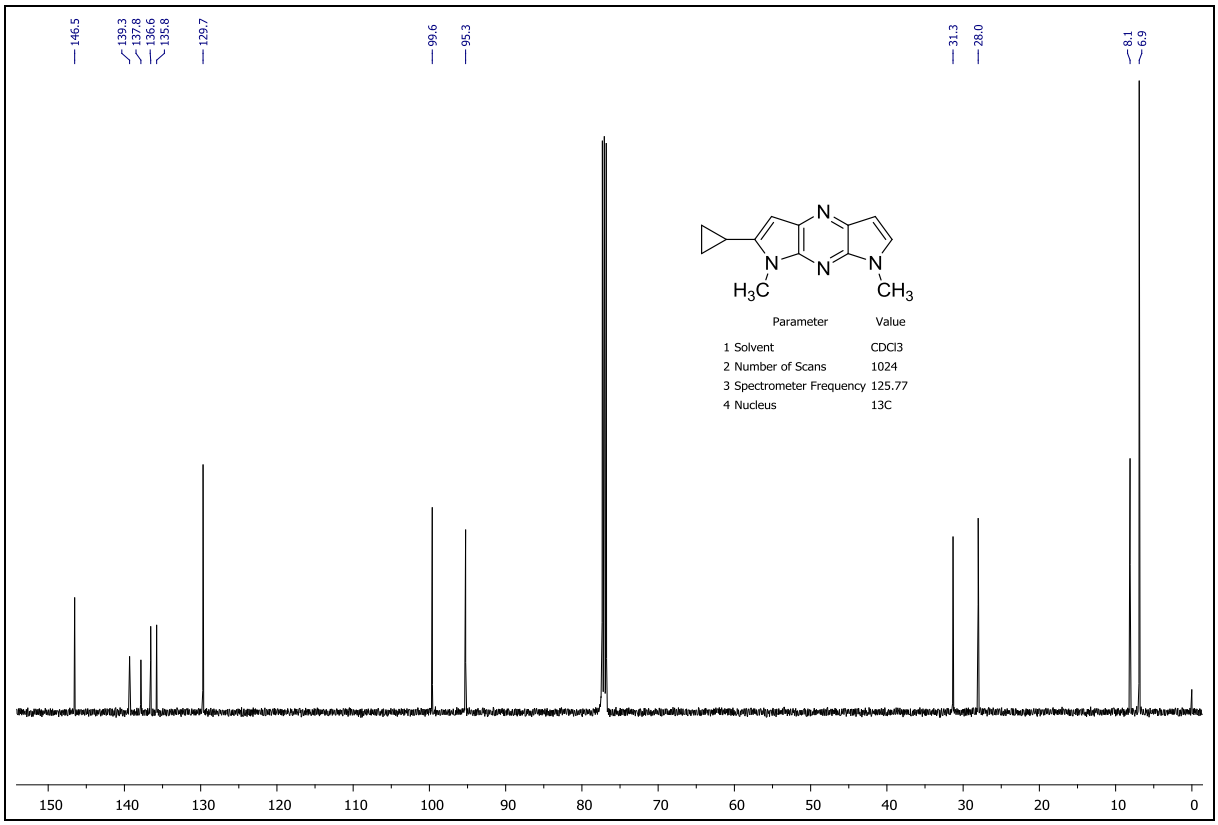
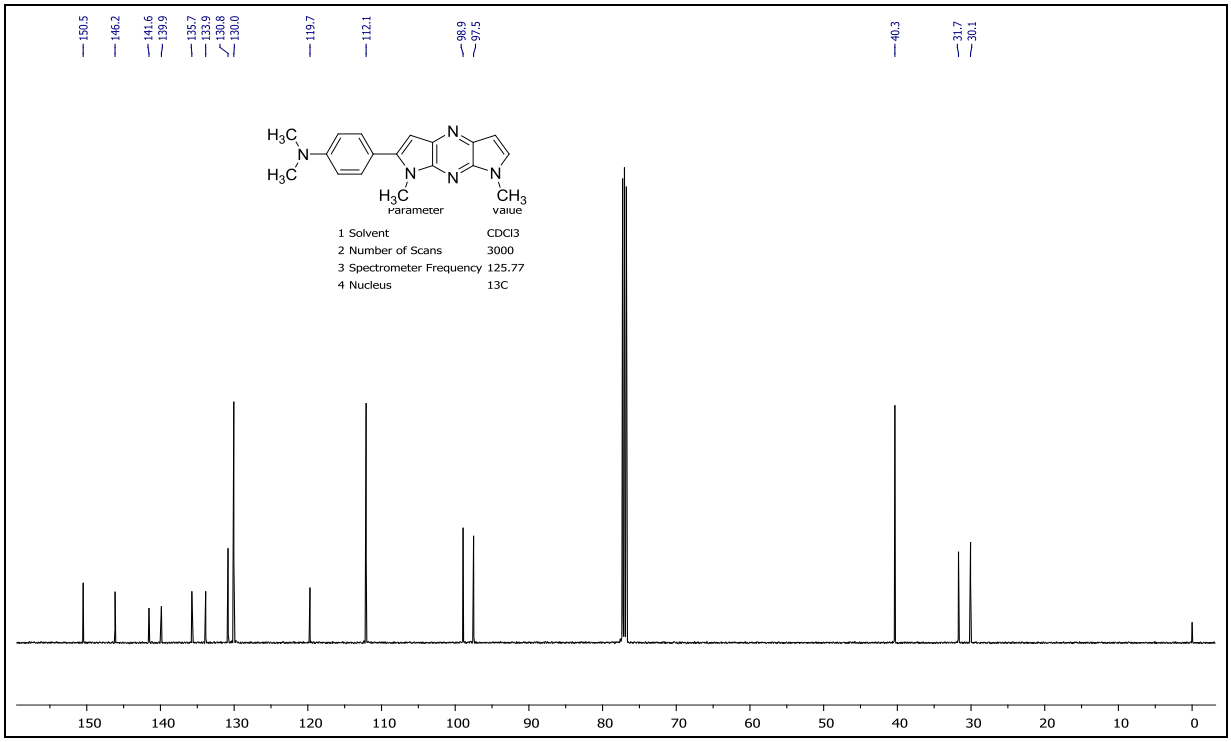


^{13}C NMR – 6g

^{1}H NMR – 6h



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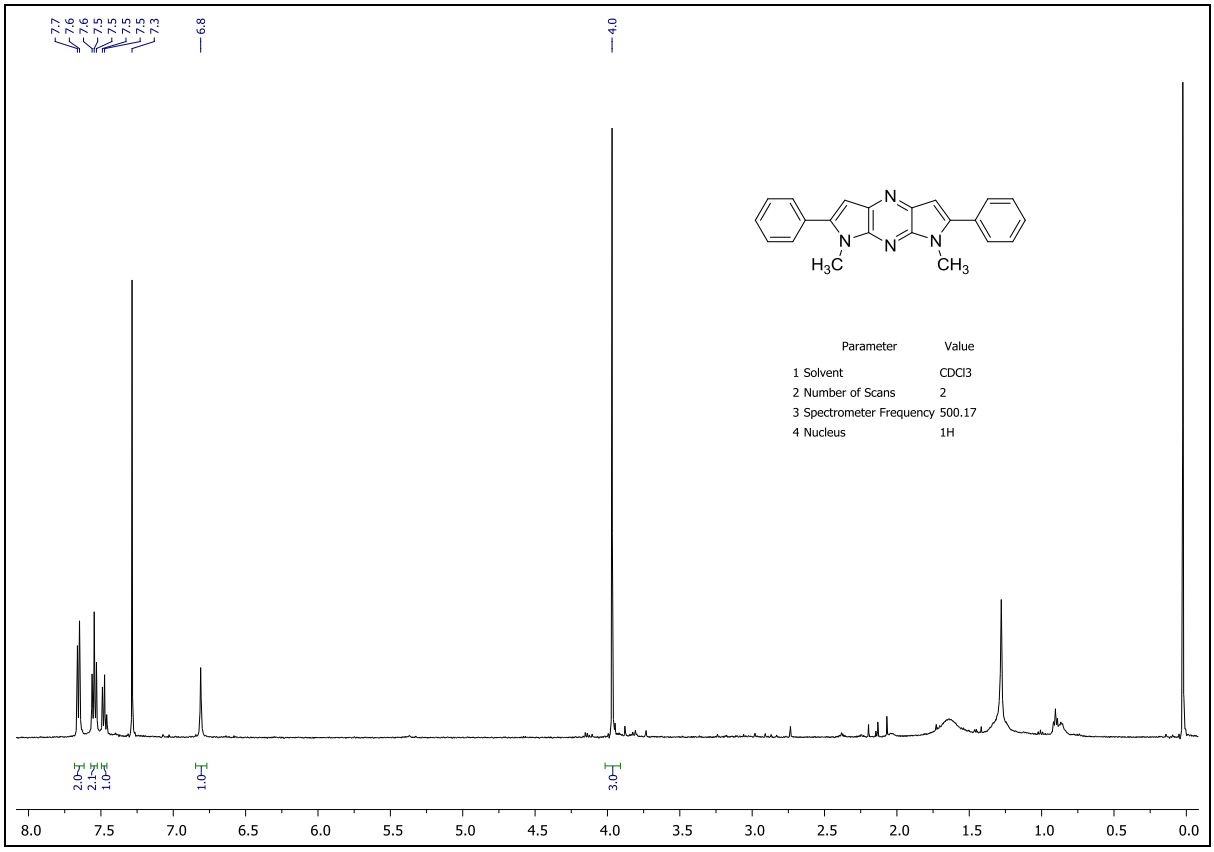
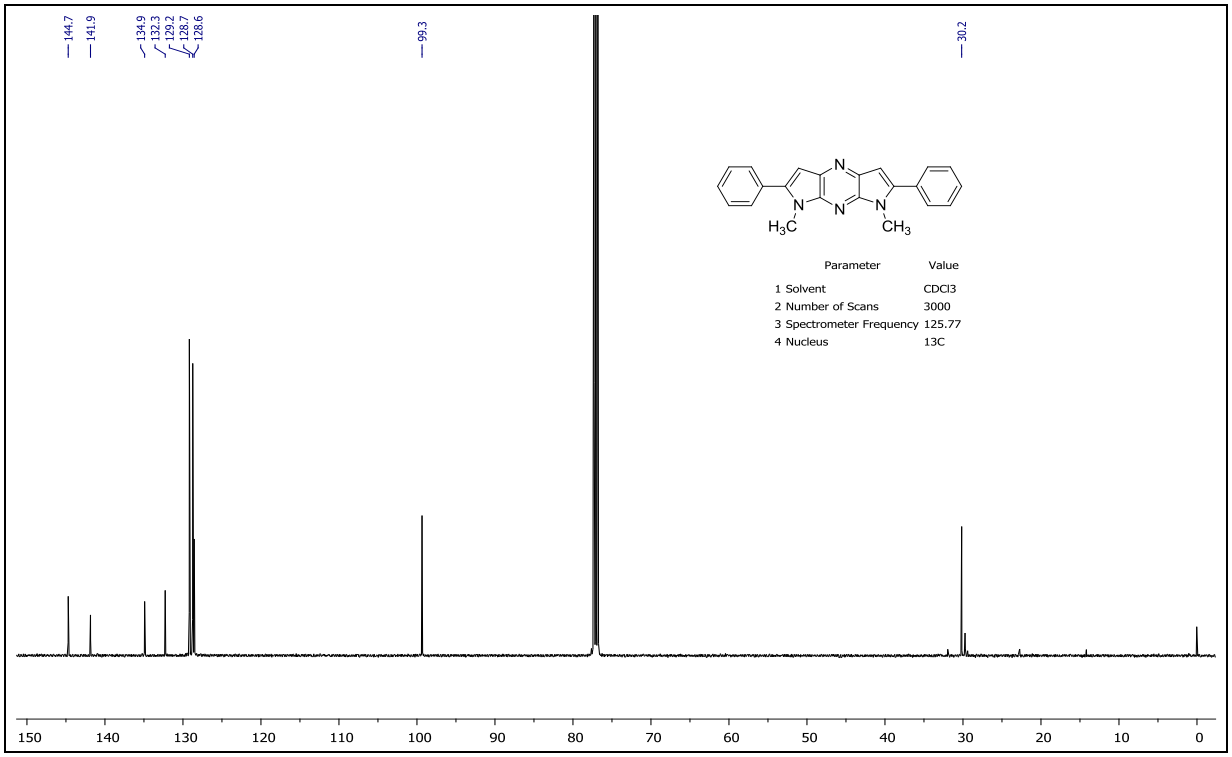


^{1}H NMR – 6i



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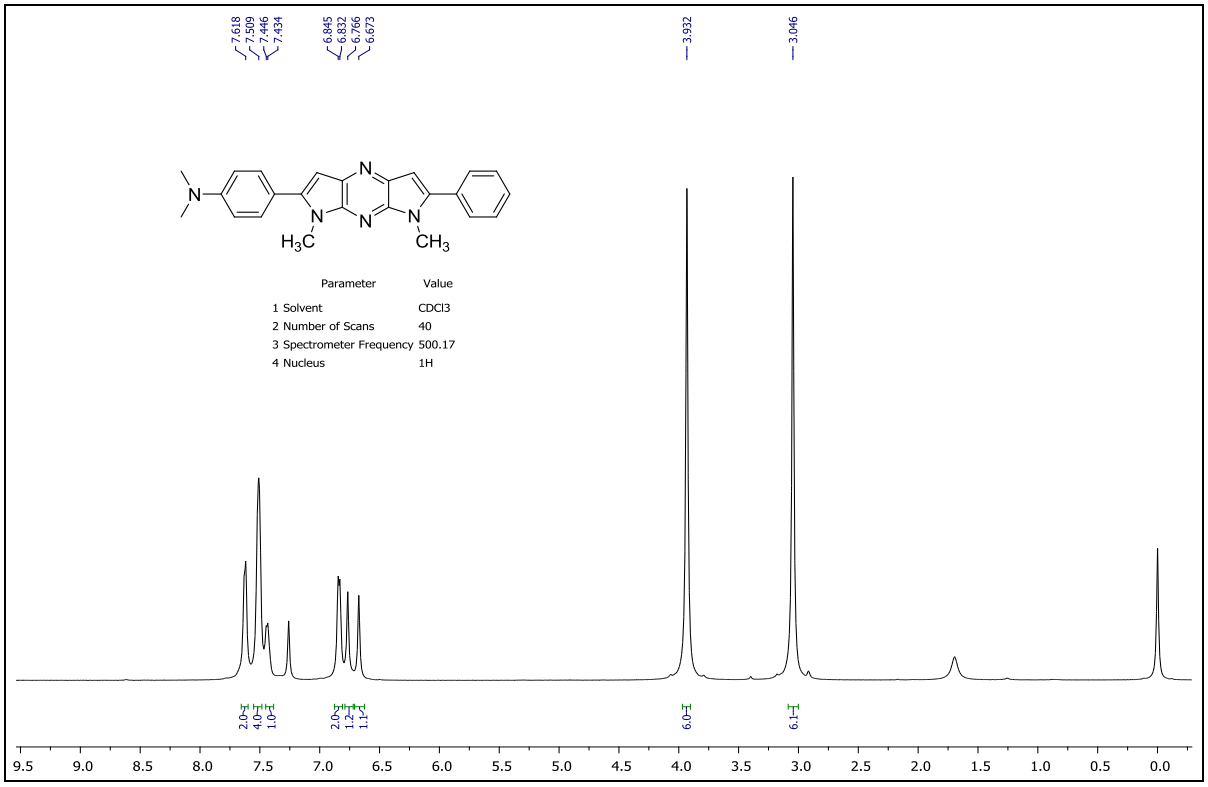
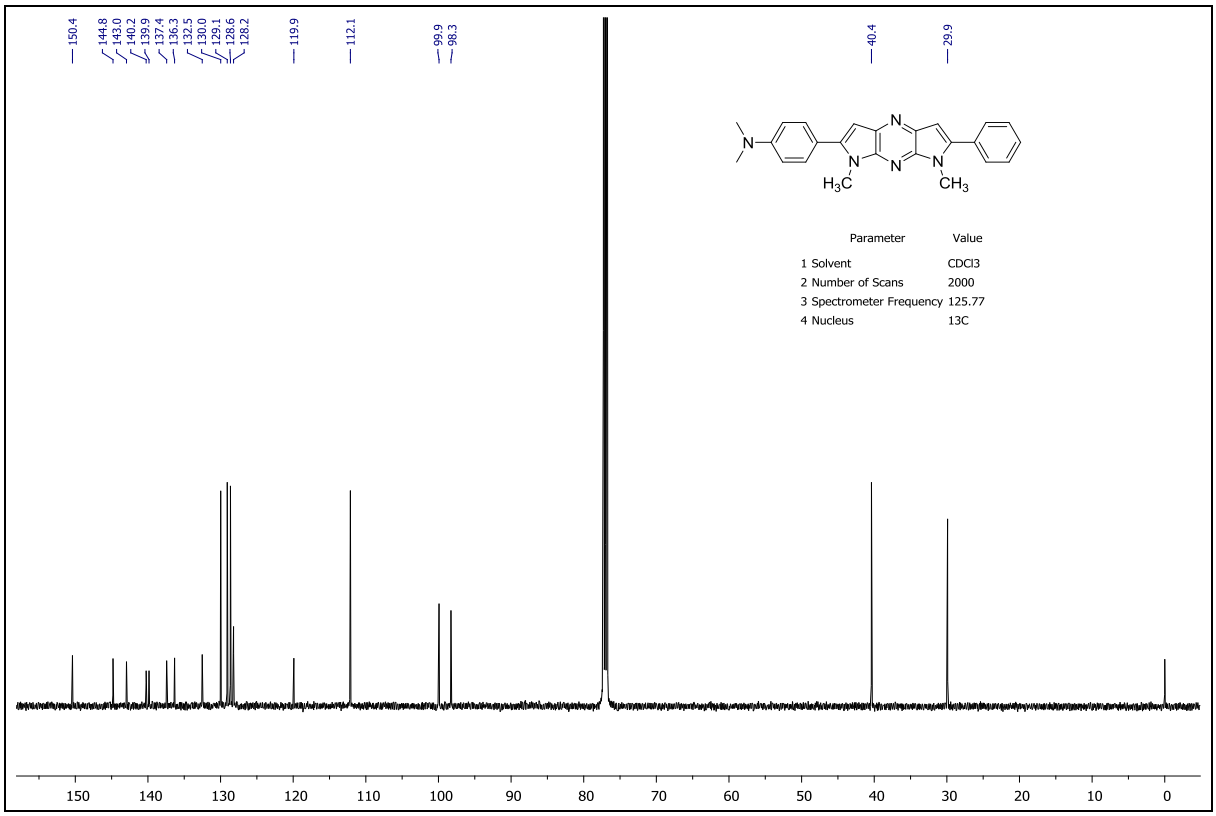
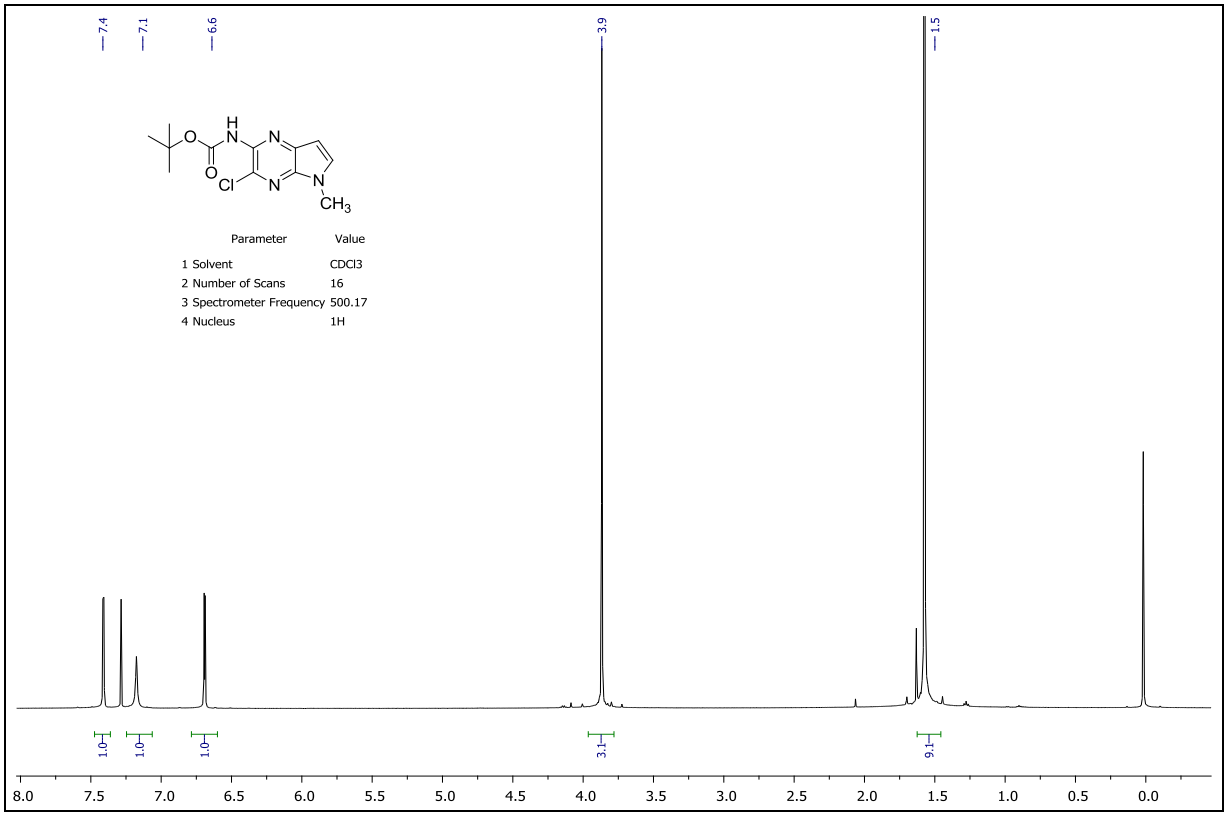


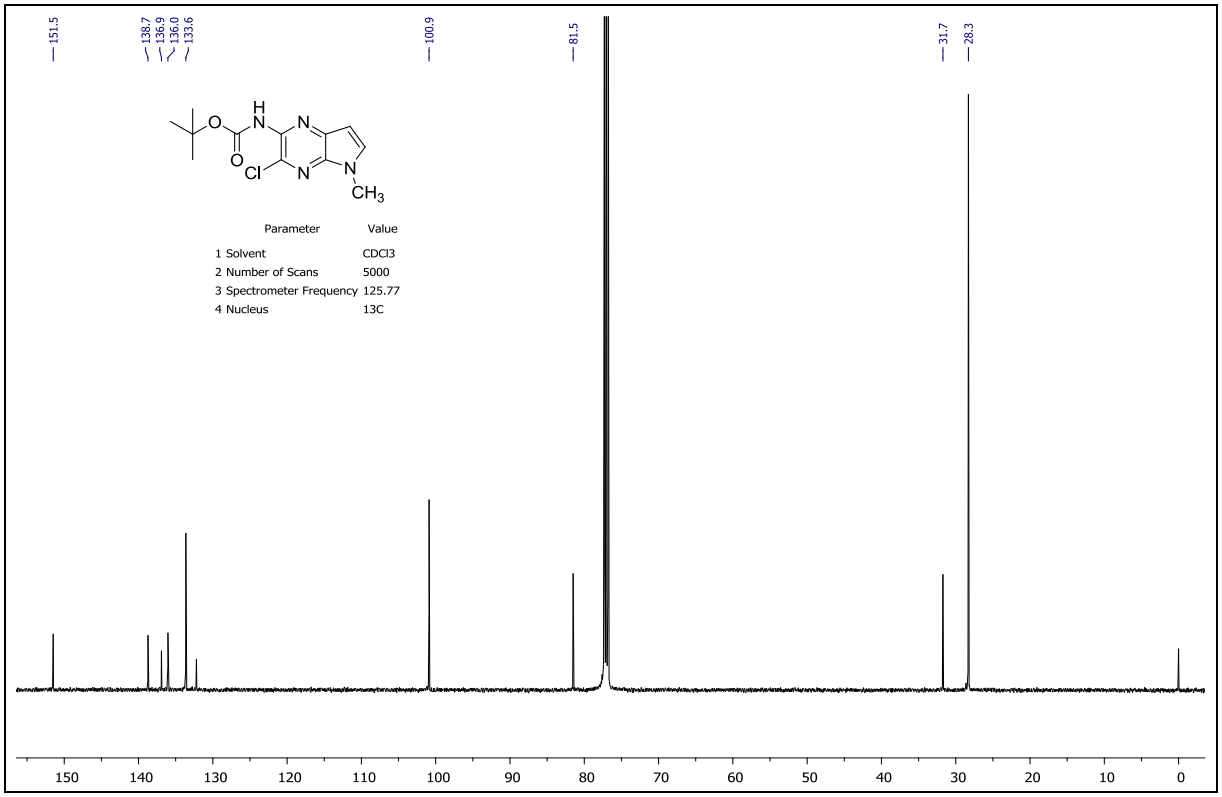
^{1}H NMR – 6j



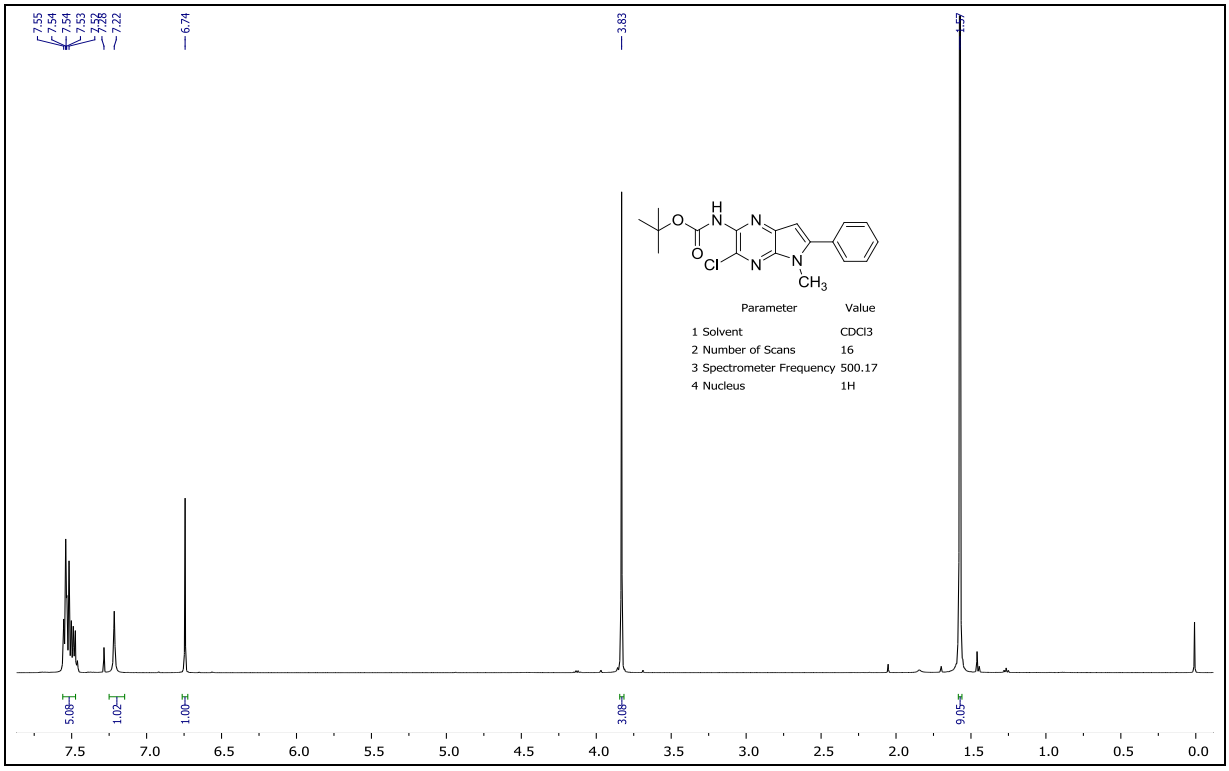
^{13}C NMR – 6j



^{1}H NMR – 7a



^{13}C NMR – 7a



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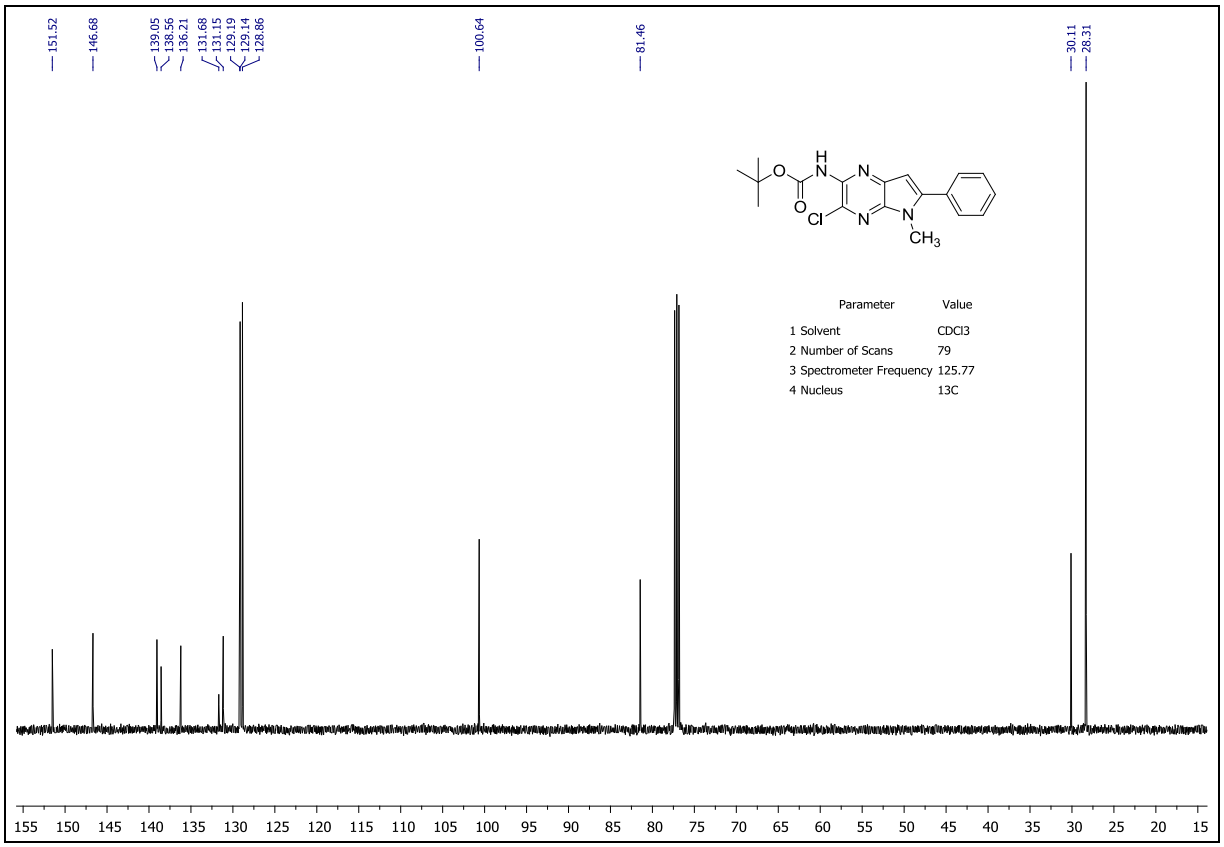

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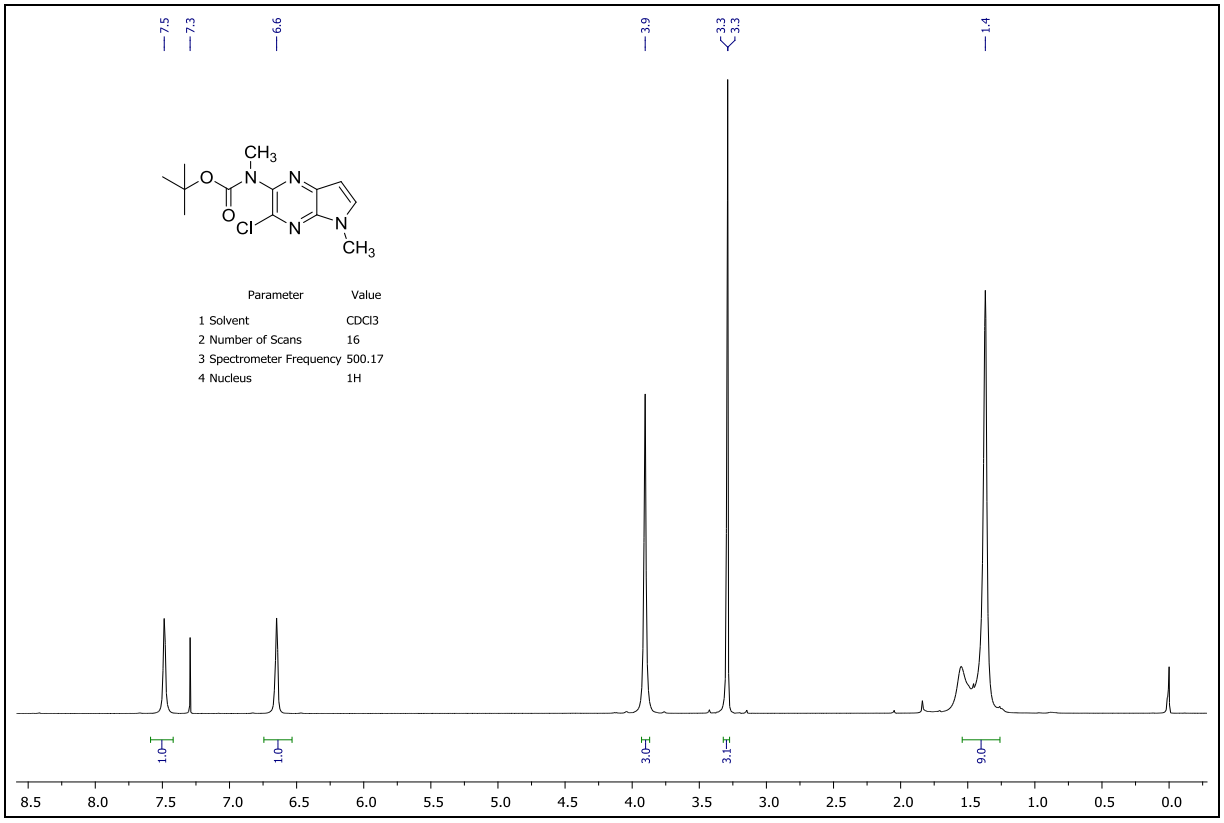
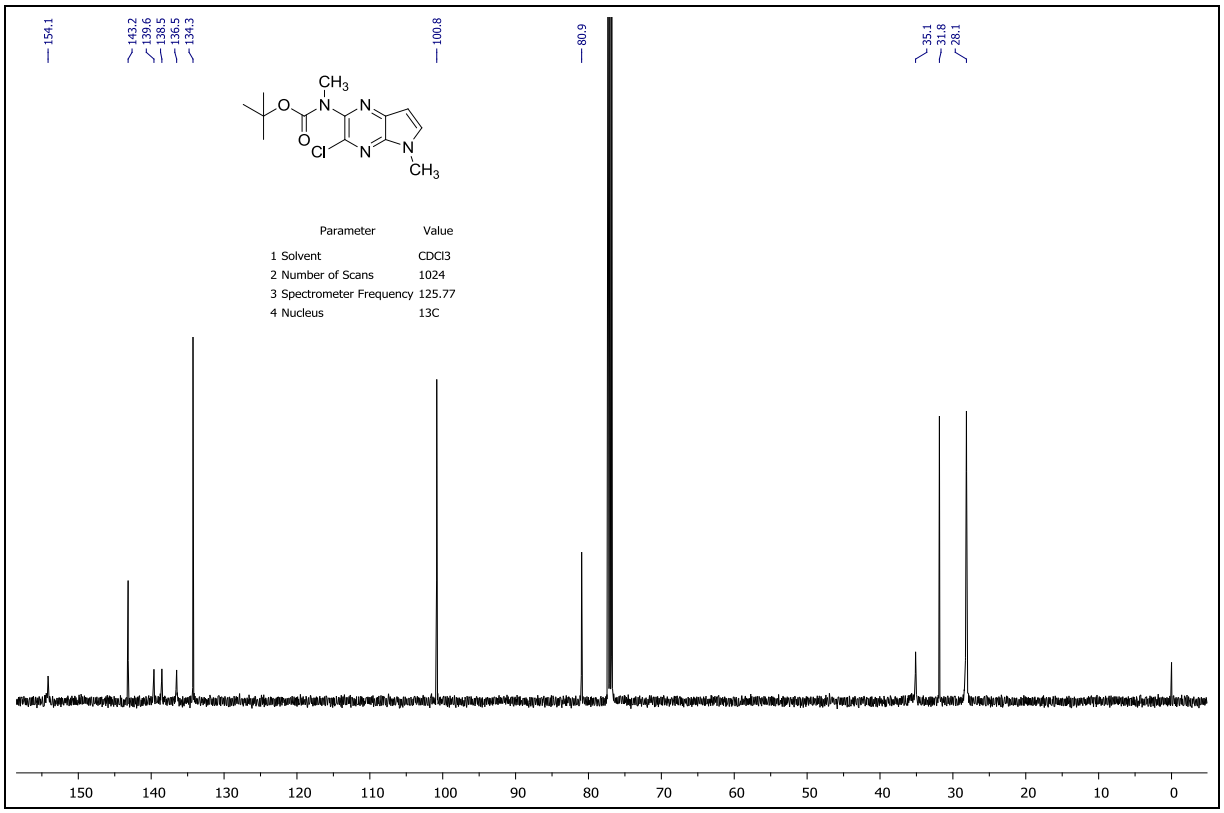
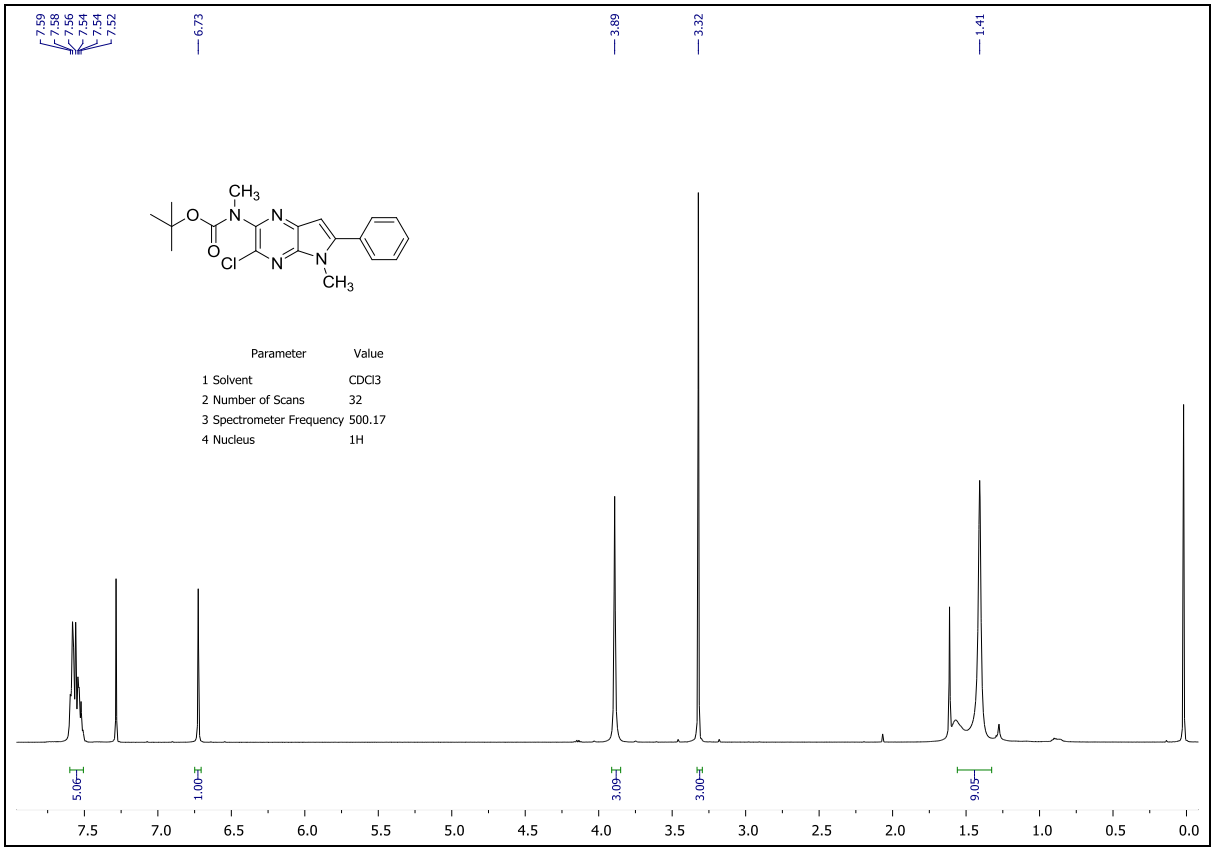


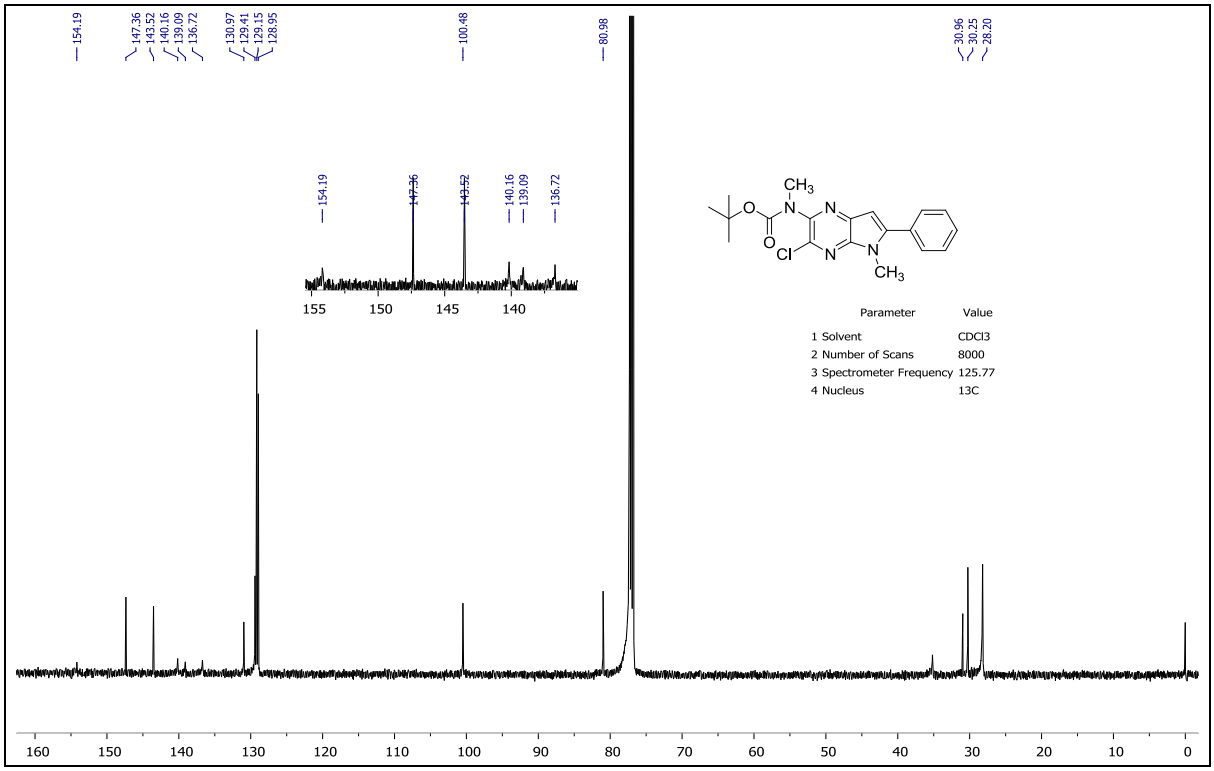
^{1}H NMR – 8a



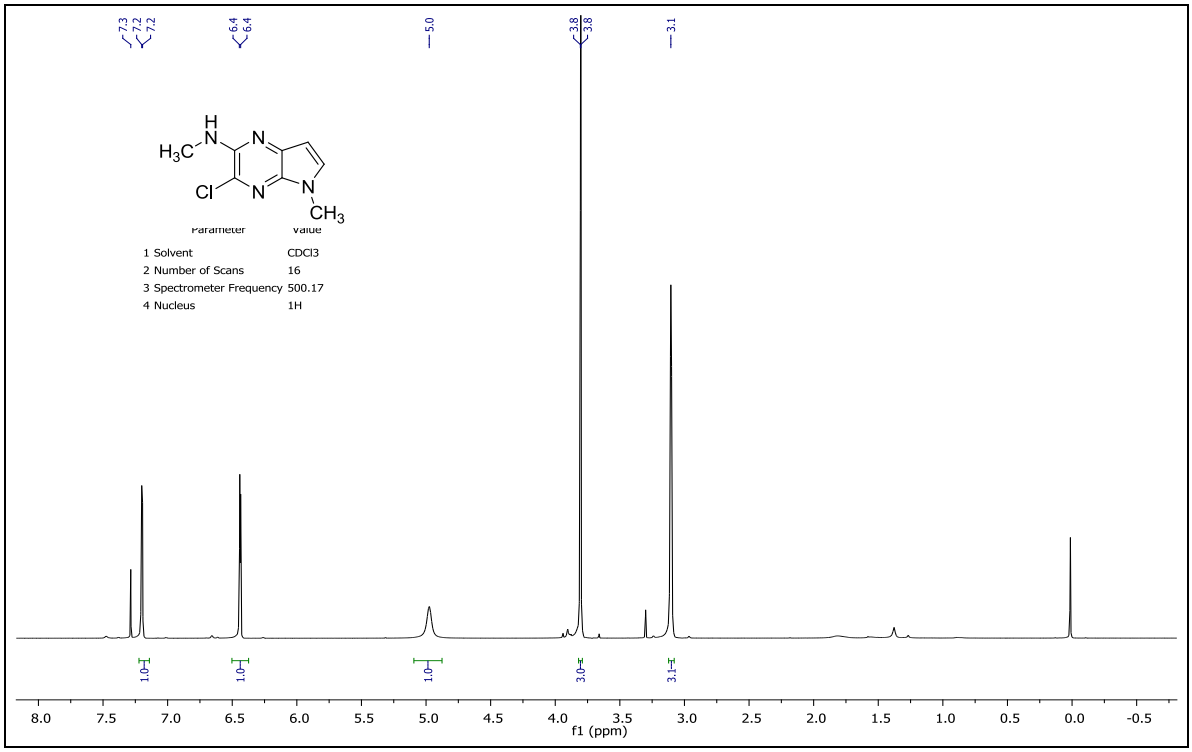
^{13}C NMR – 8a



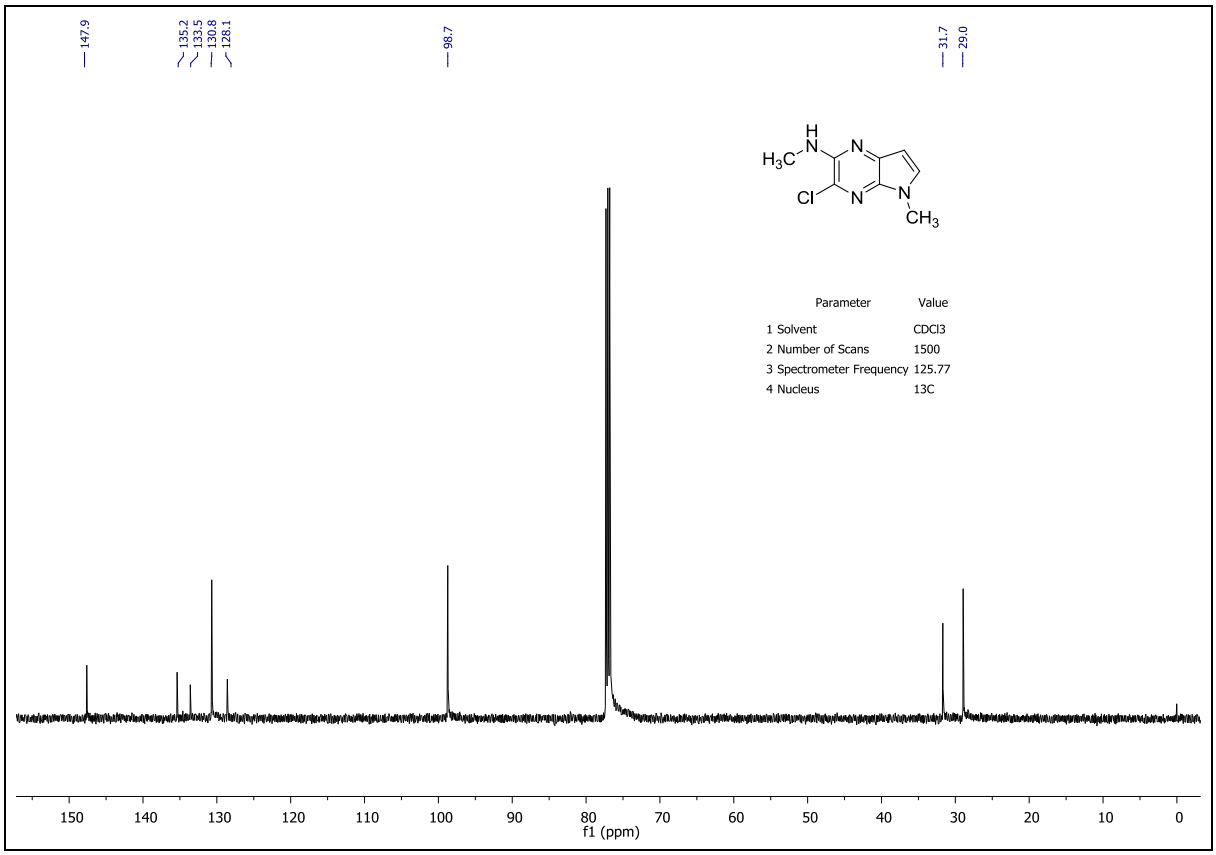
^{1}H NMR – 8b



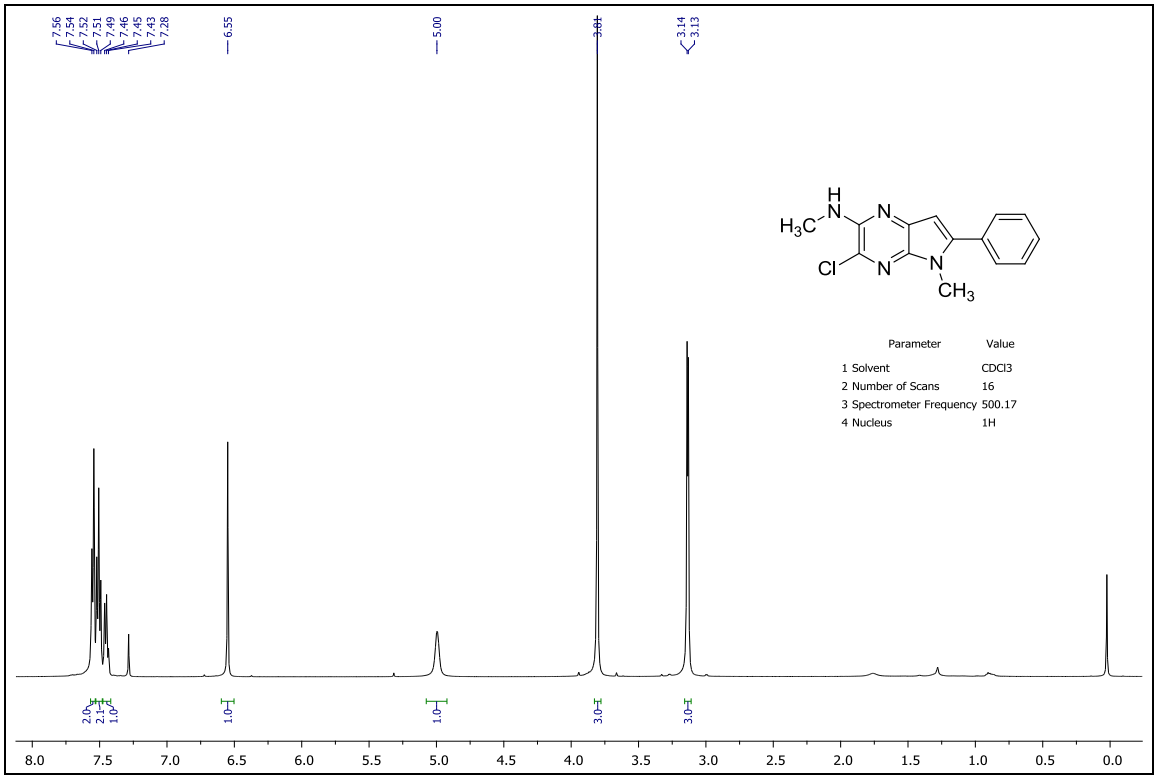
^{13}C NMR – 8b



^{1}H NMR – 9a



^{13}C NMR – 9a



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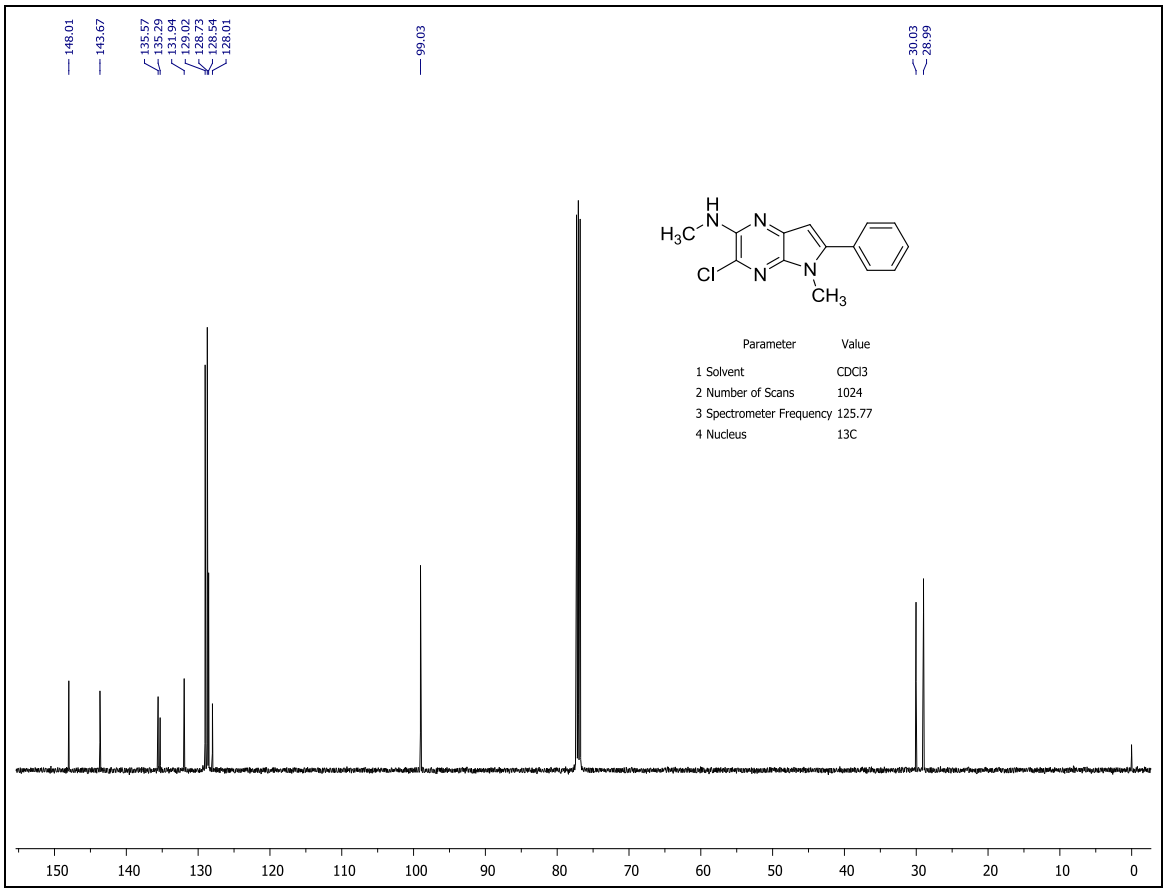
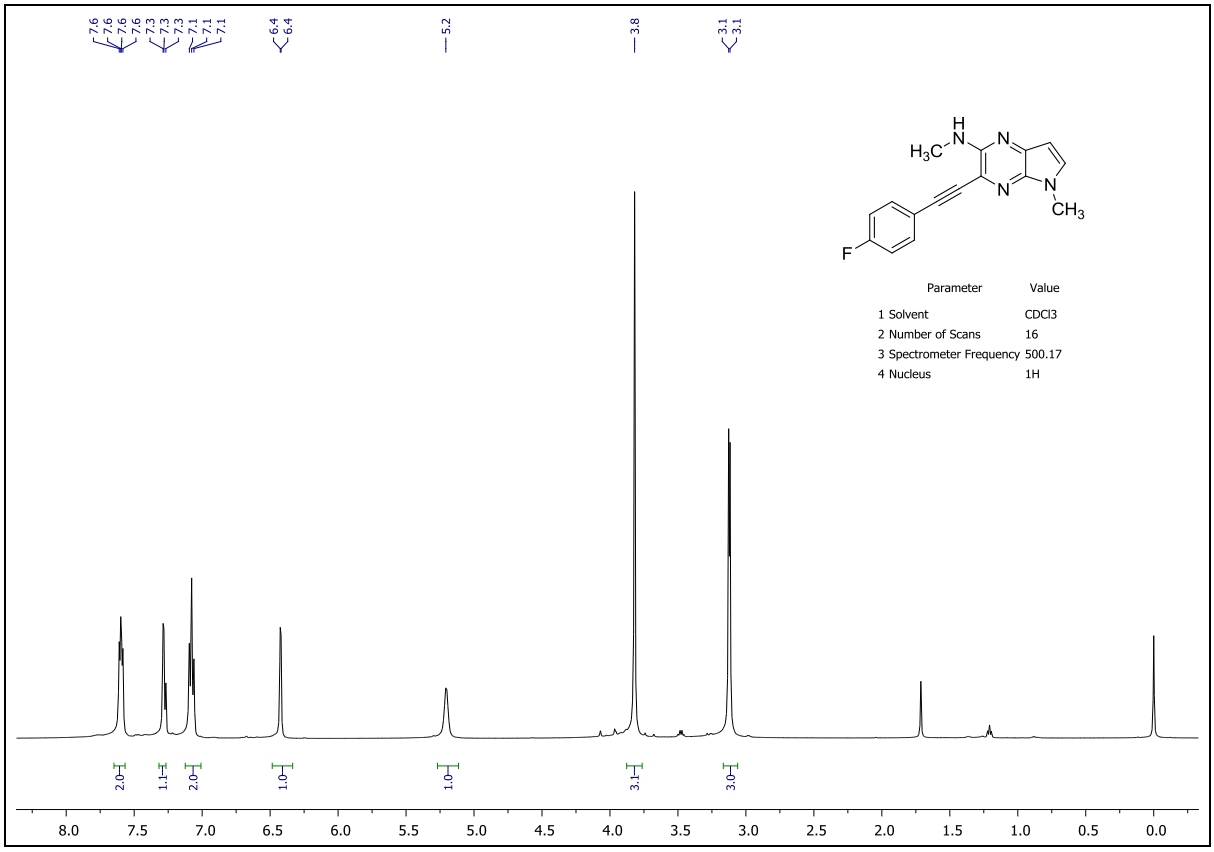
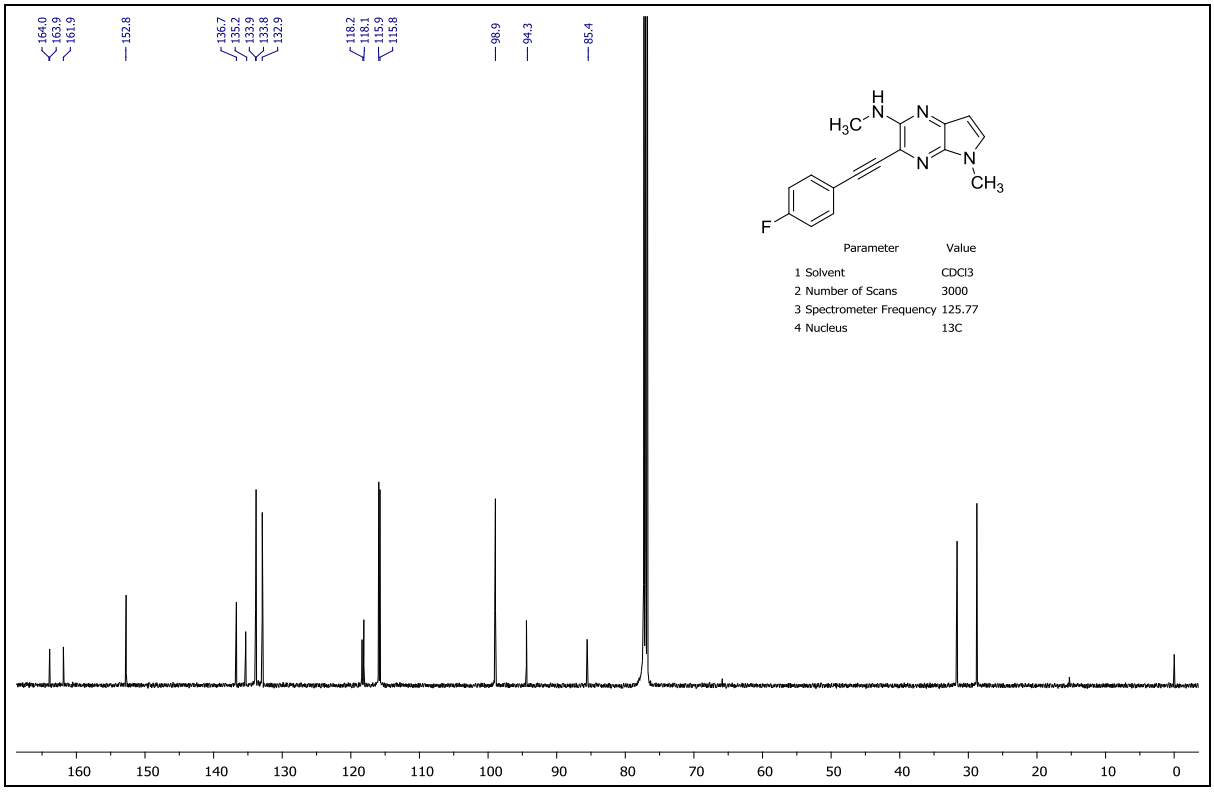


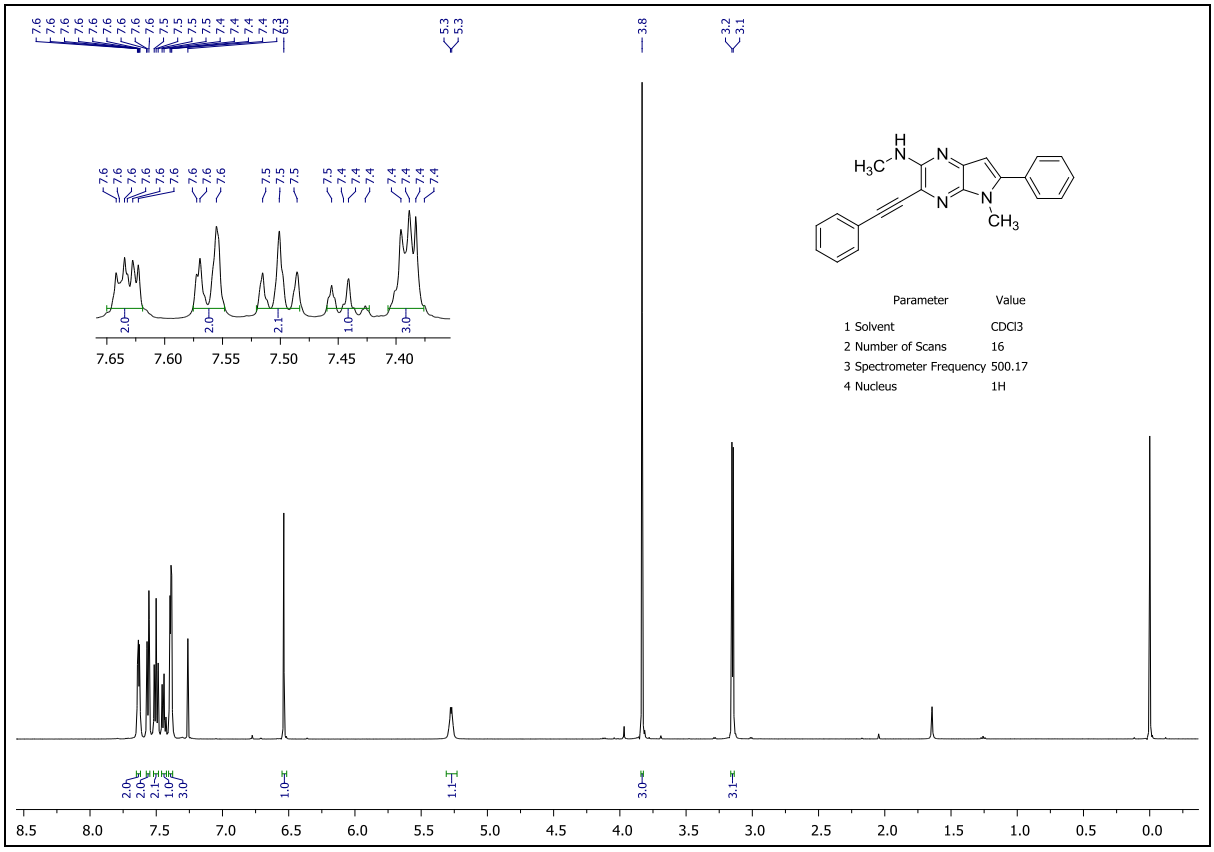
^{13}C NMR – 9b



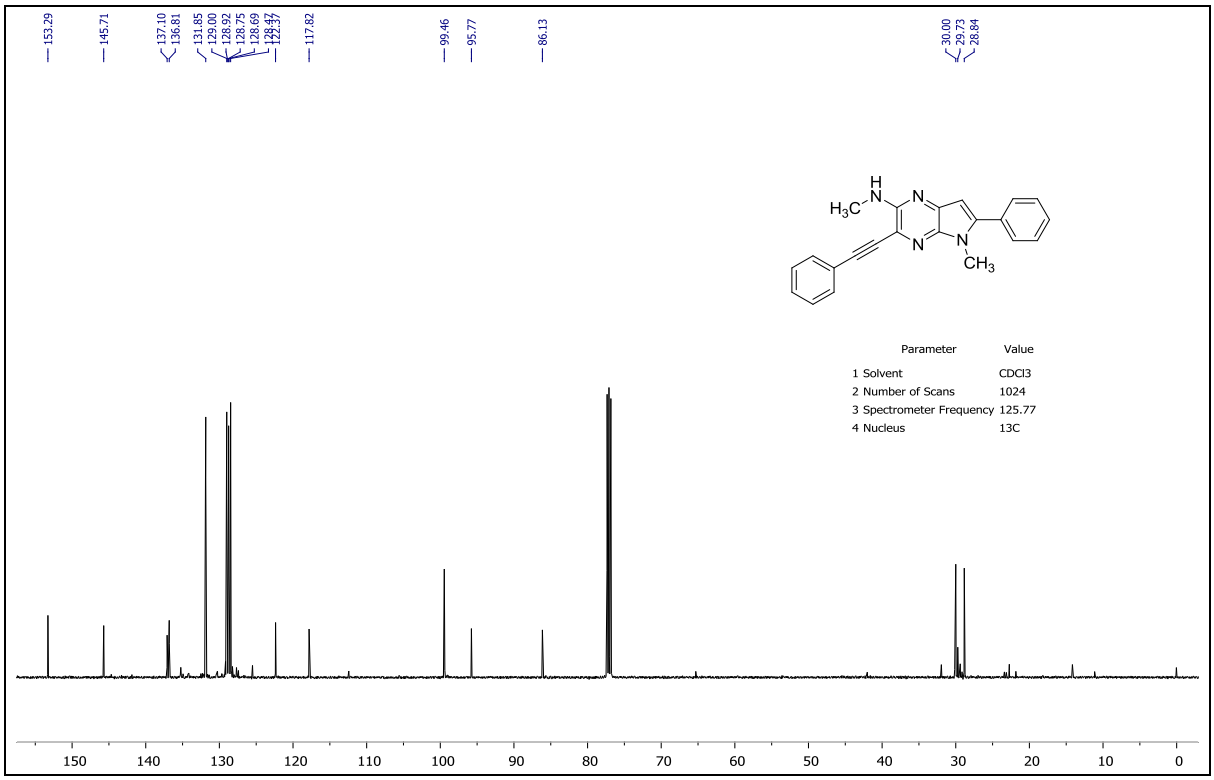
^{1}H NMR – 10c



^{13}C NMR – 10c



^{1}H NMR – 10f



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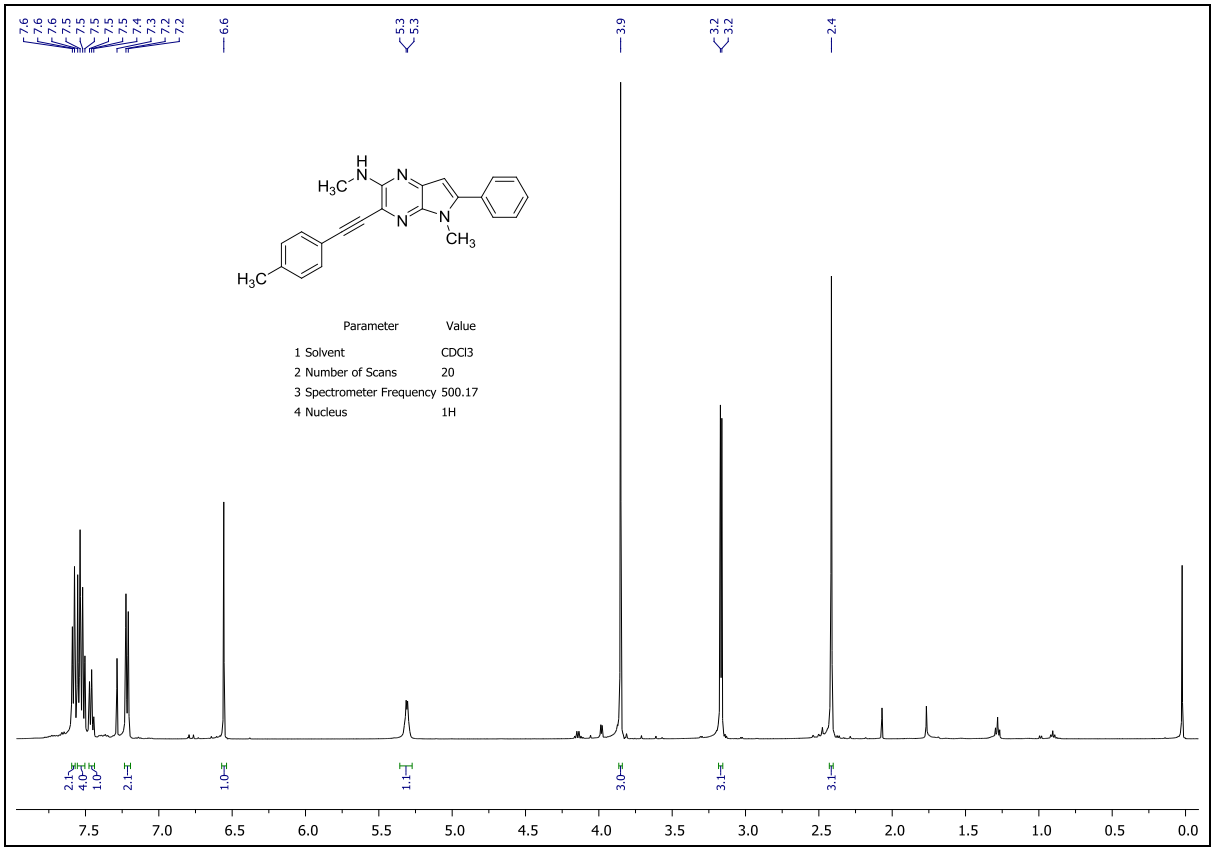

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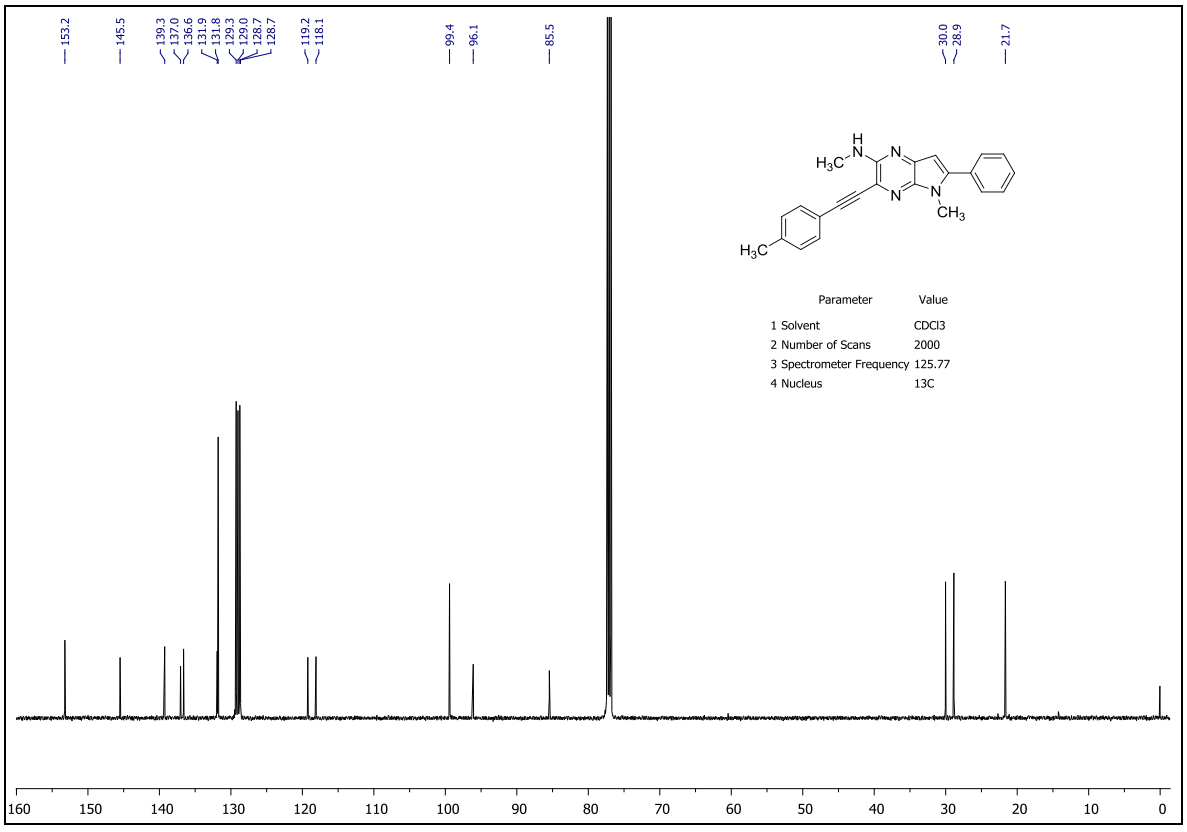
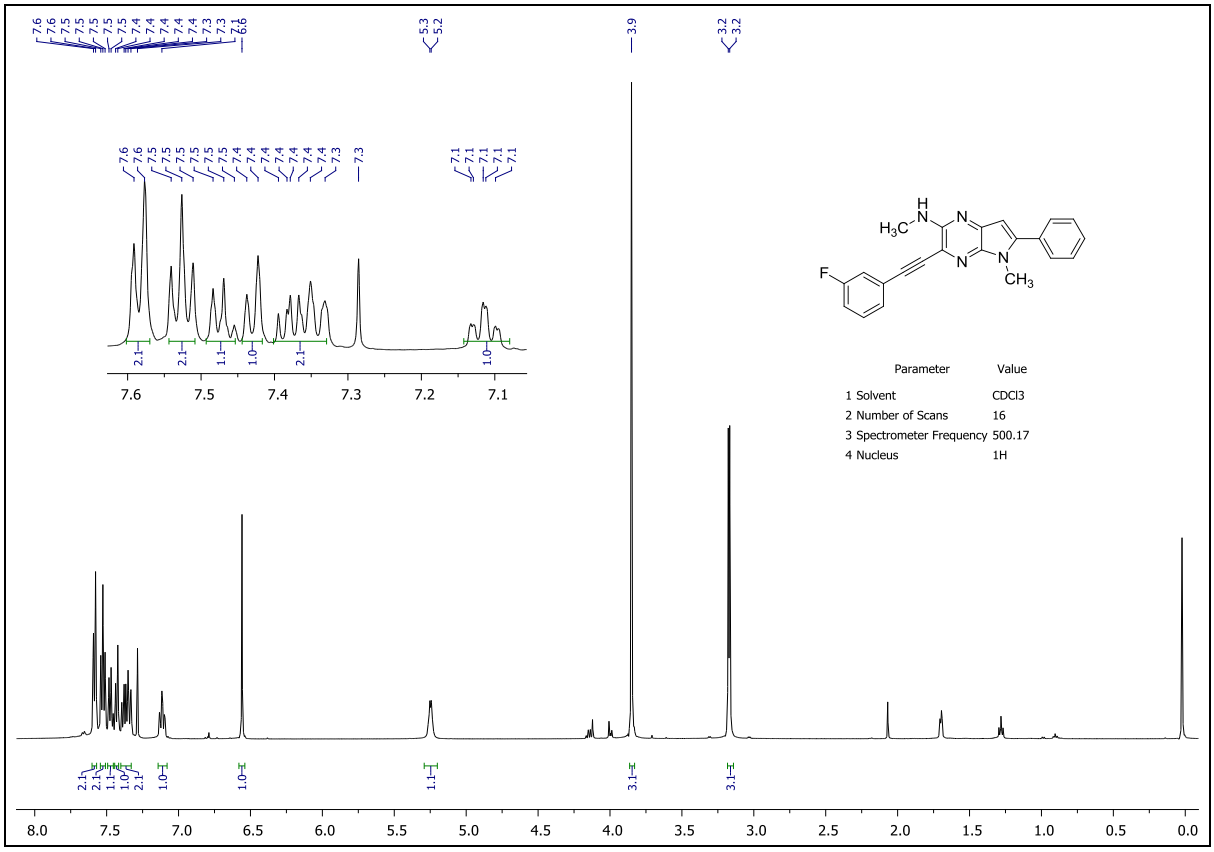
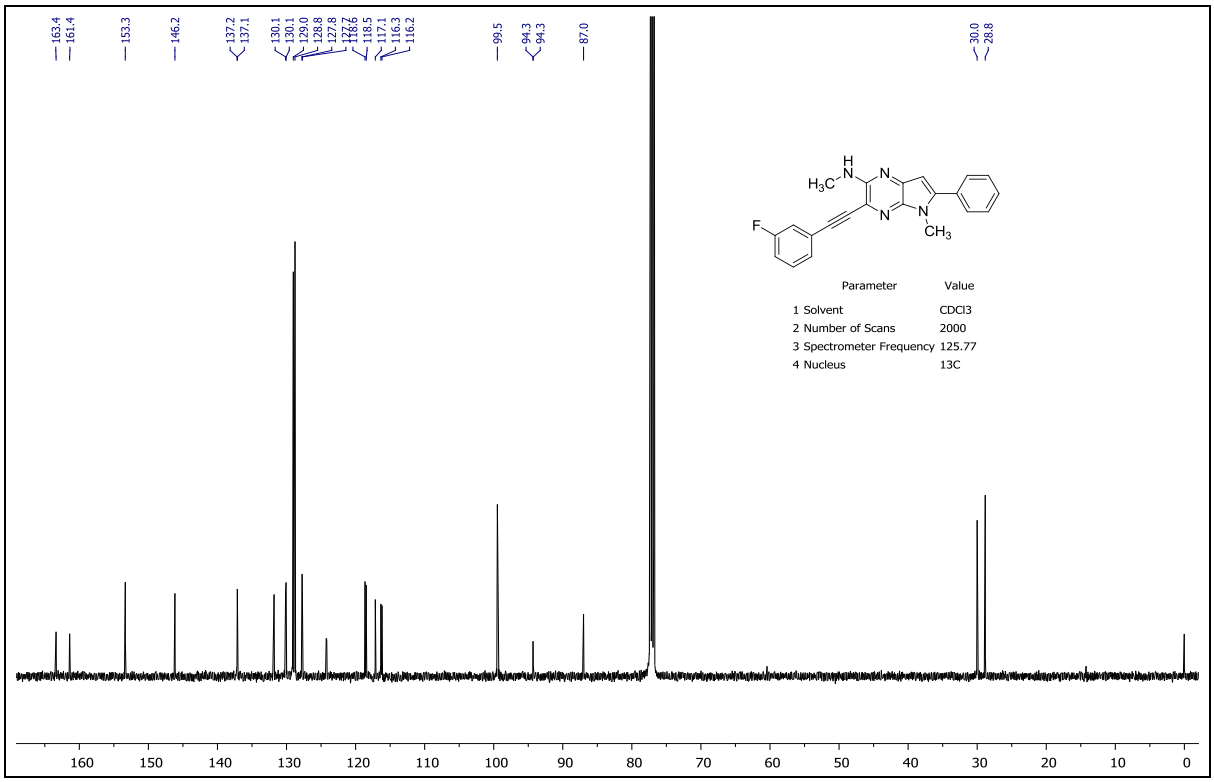


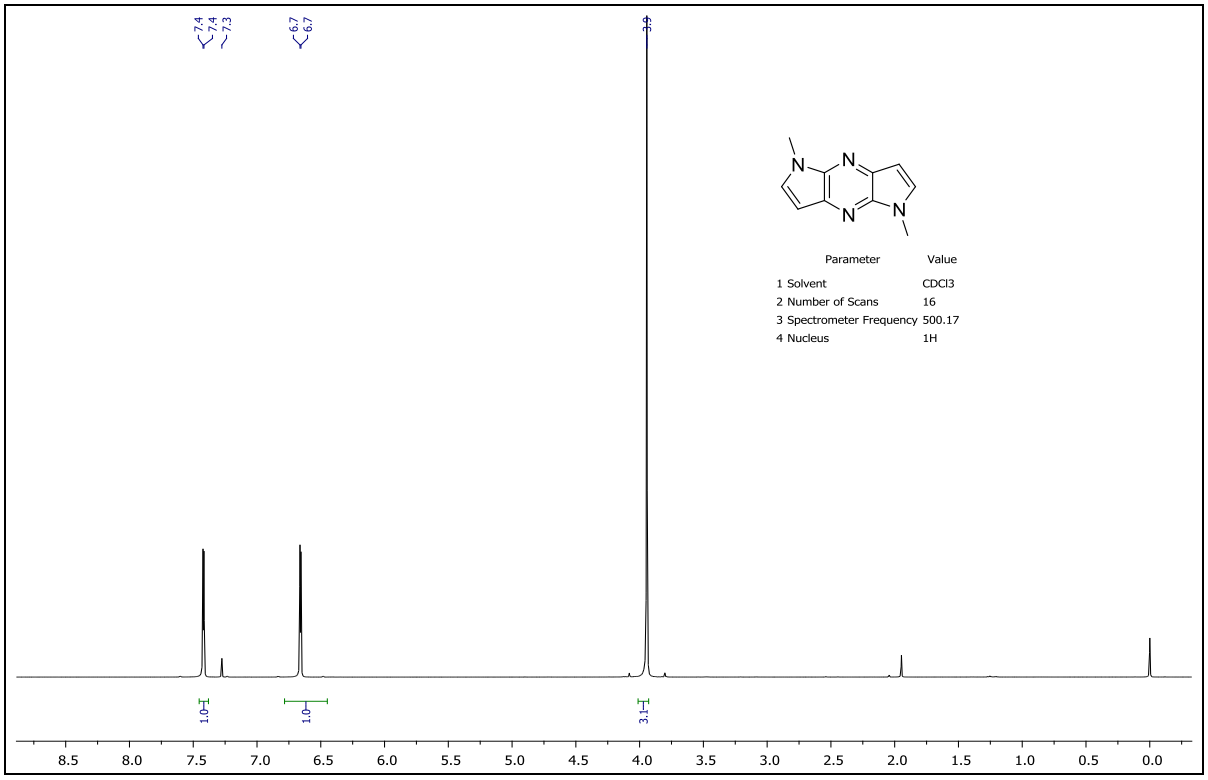
^{13}C NMR – 10h



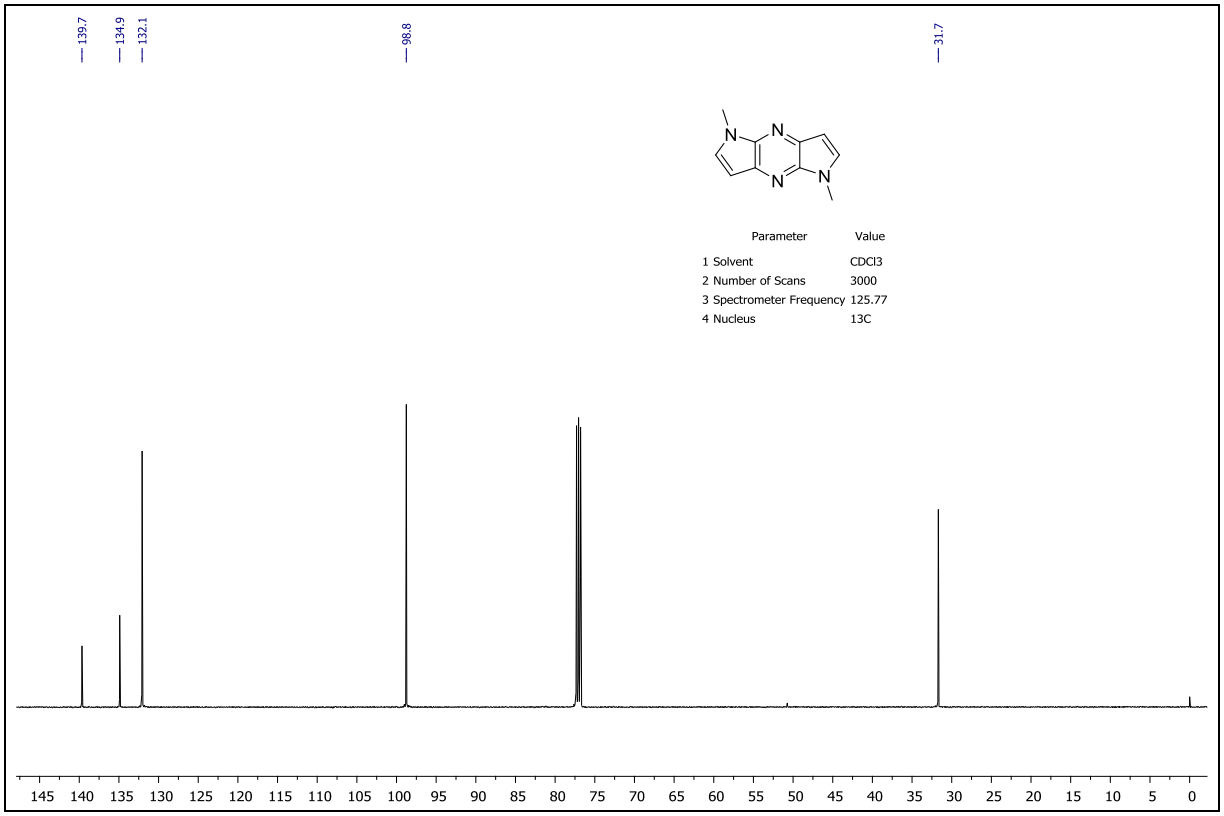
^{1}H NMR – 10j



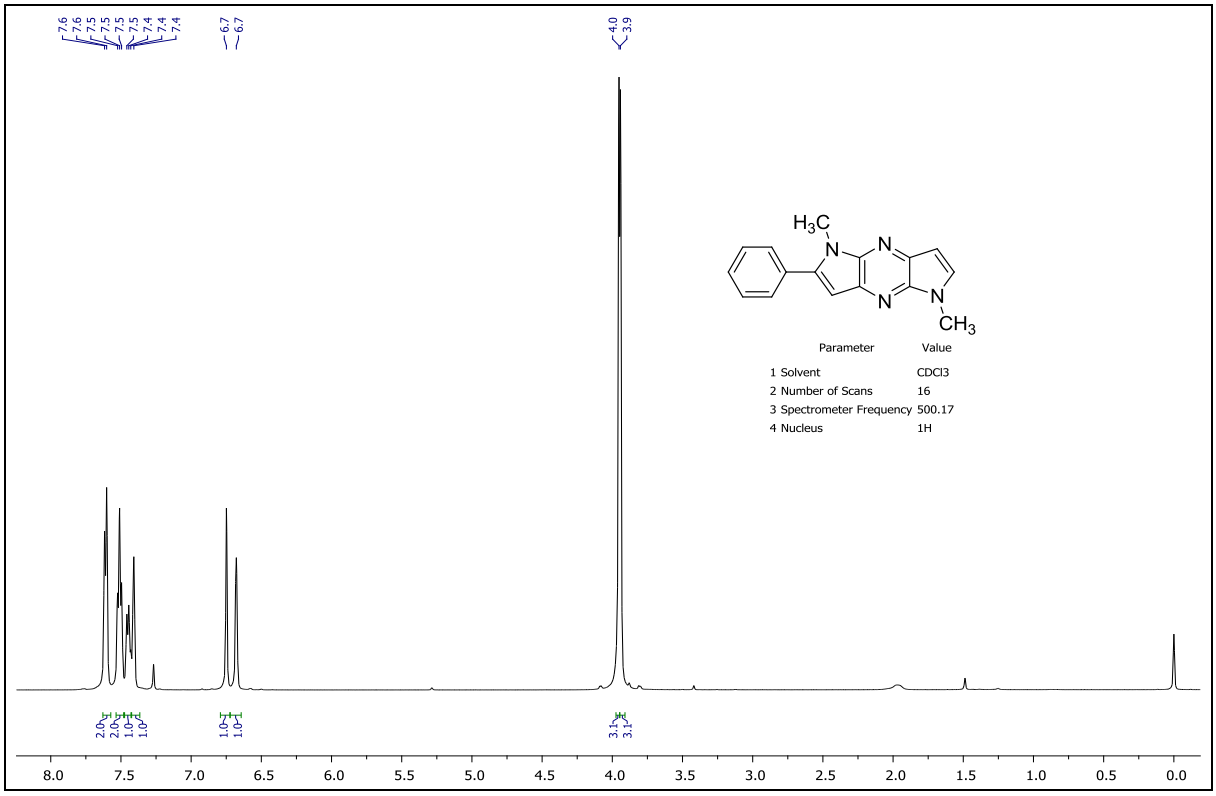
^{13}C NMR – 10j



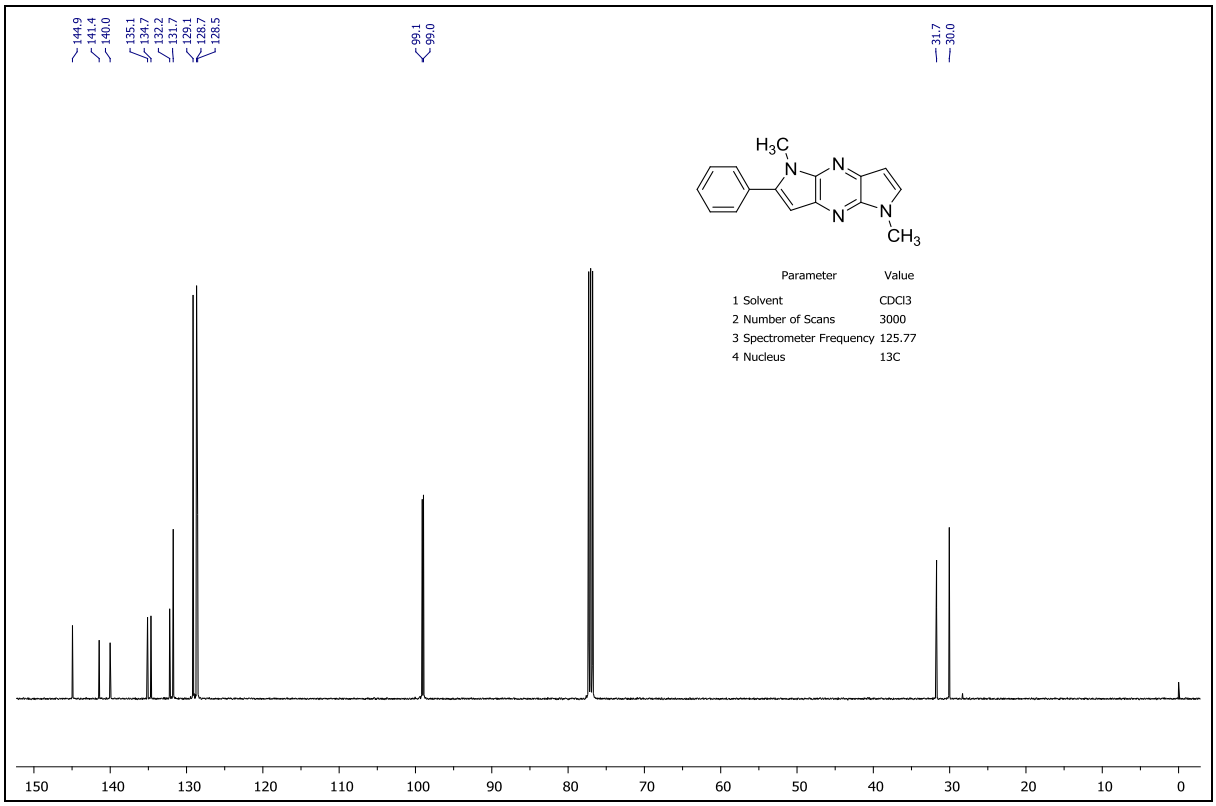
^{1}H NMR – 11a



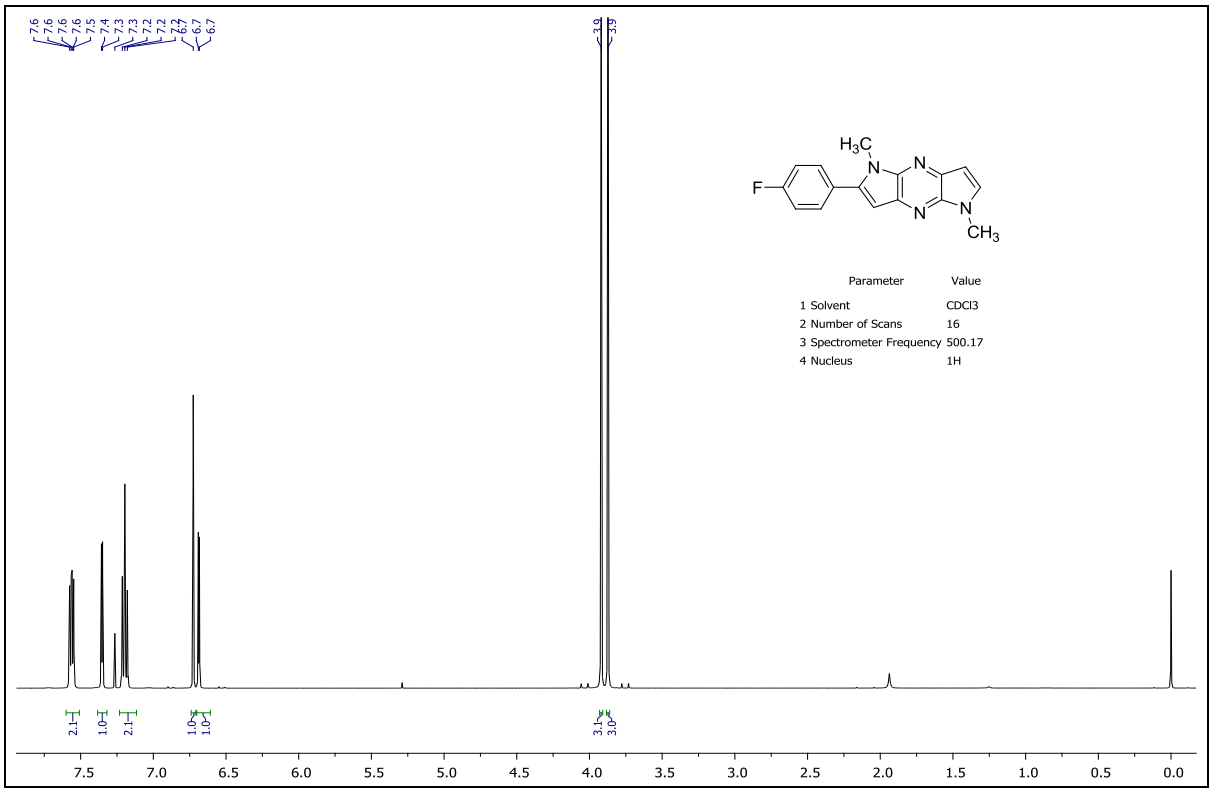
^{13}C NMR – 11a



^{1}H NMR – 11b



^{13}C NMR – 11b



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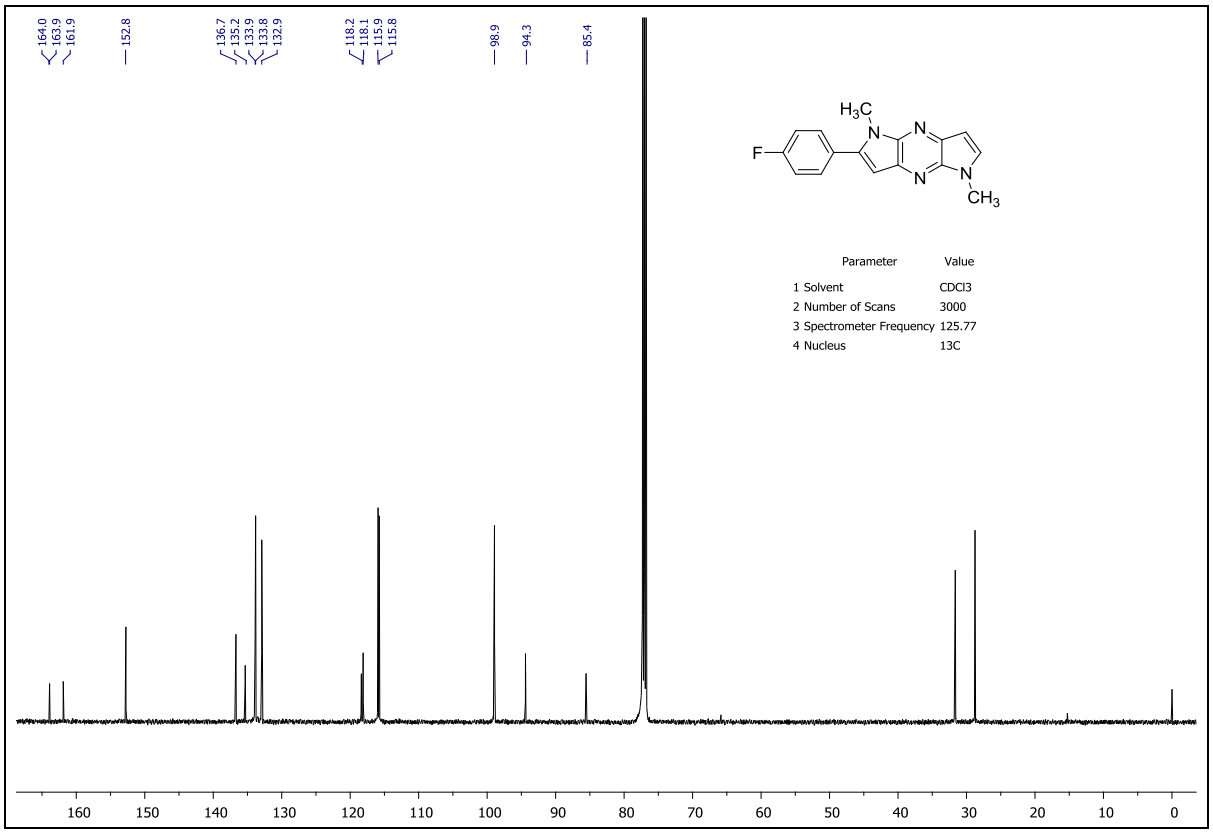

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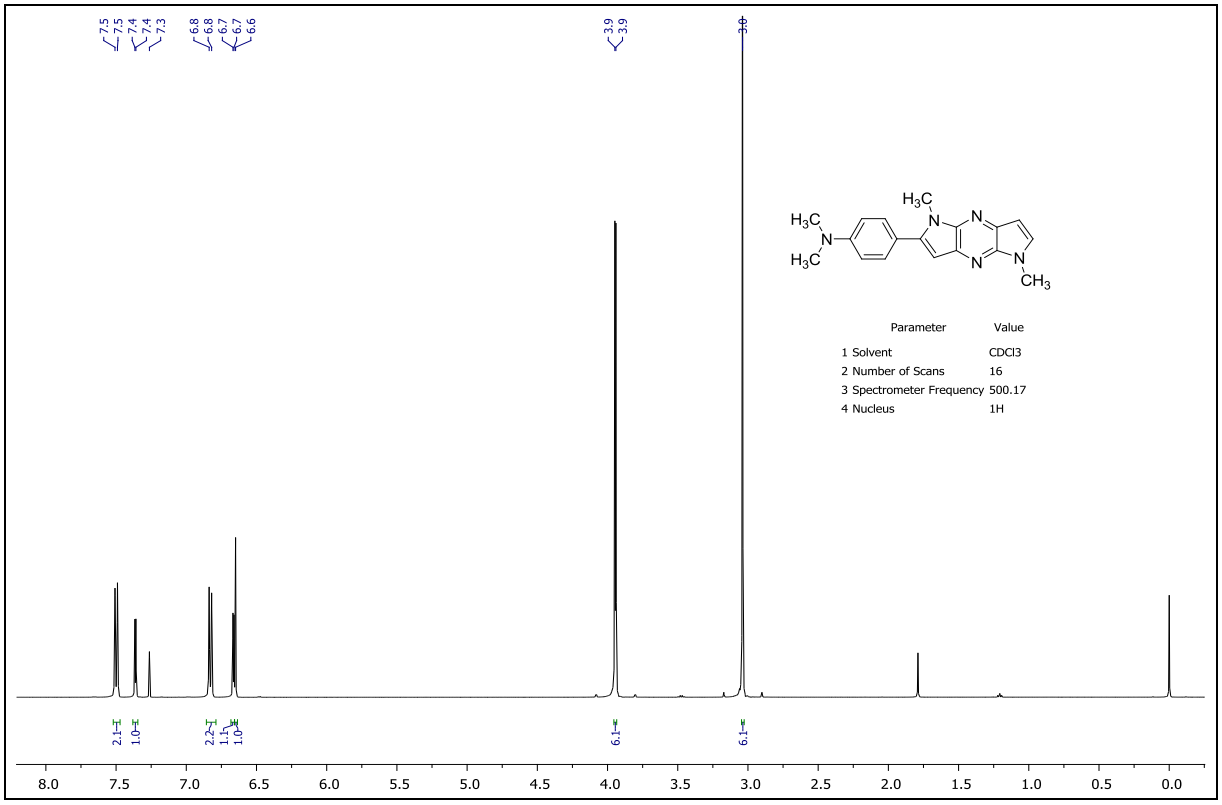

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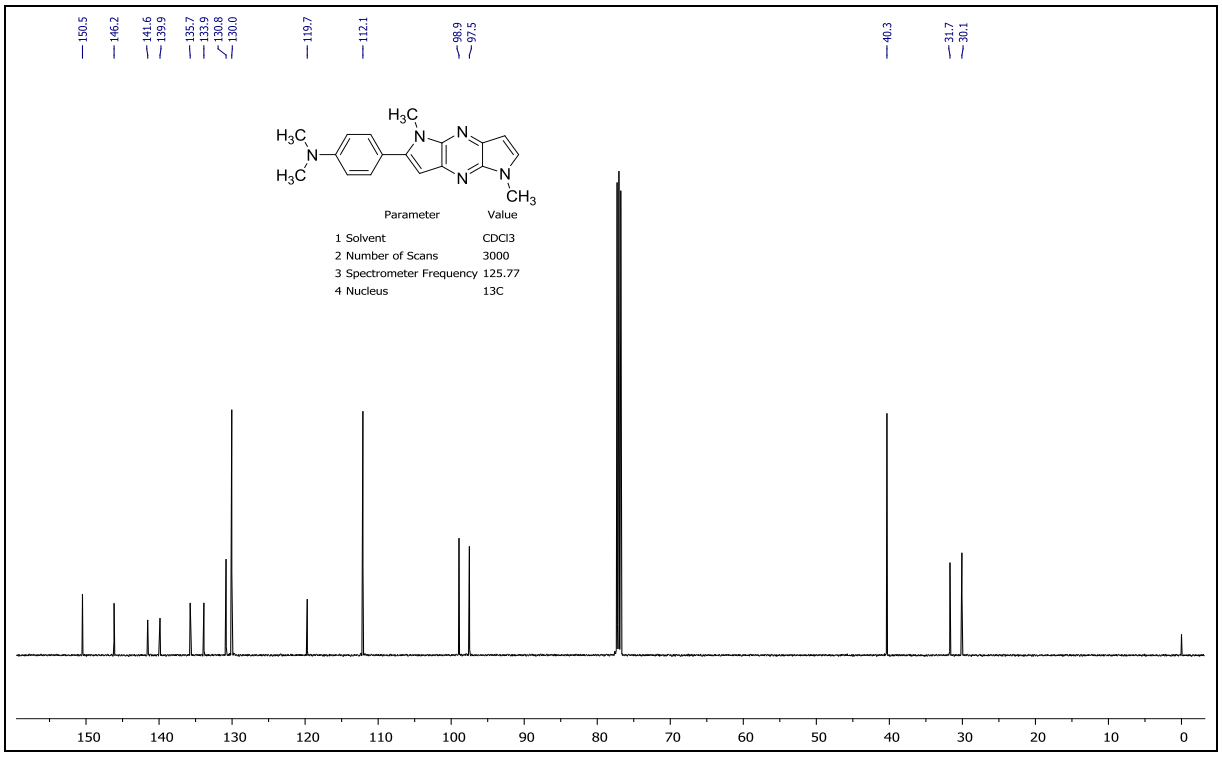

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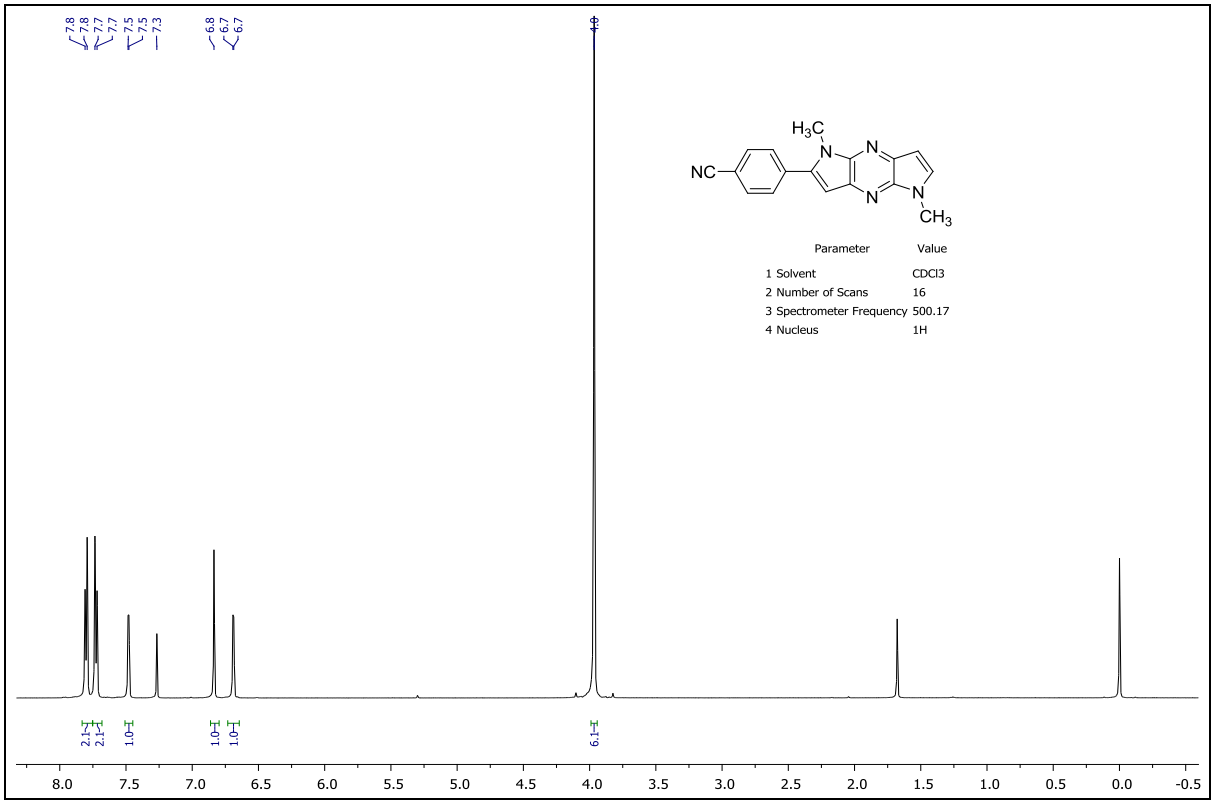

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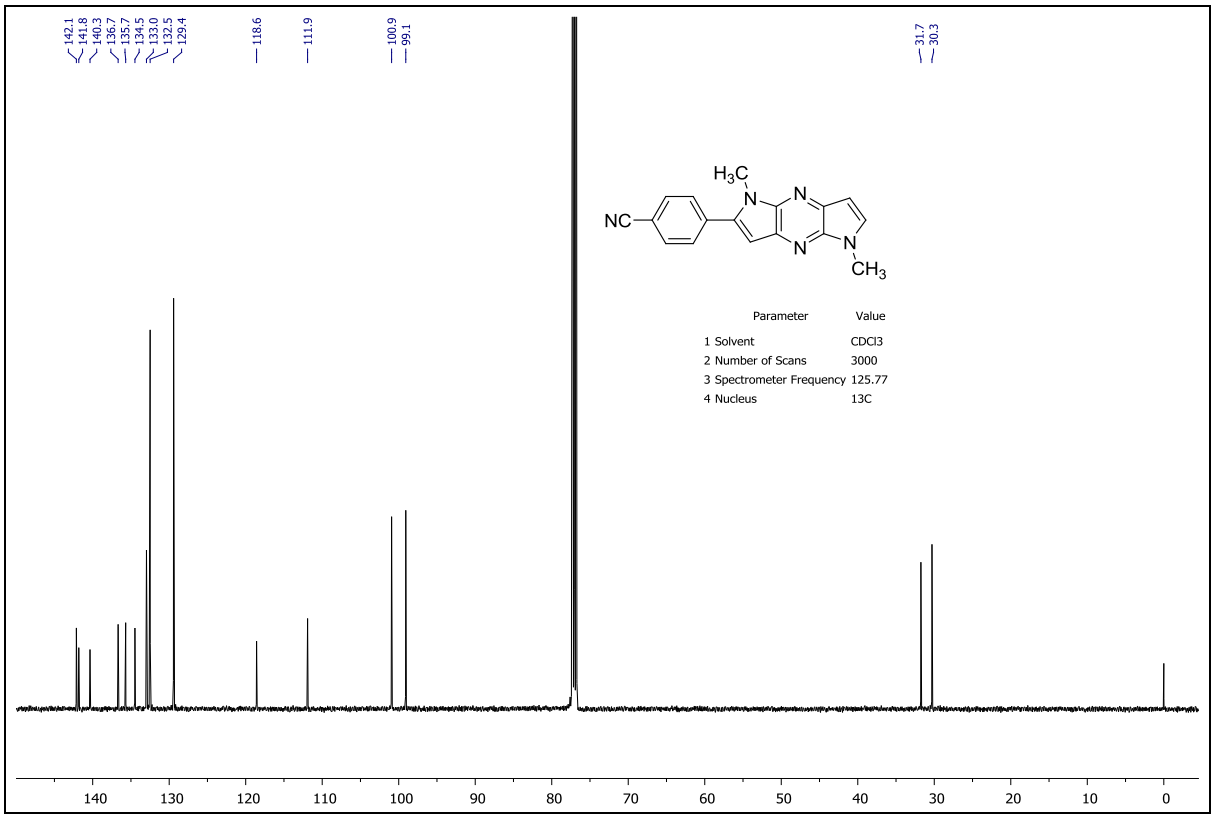

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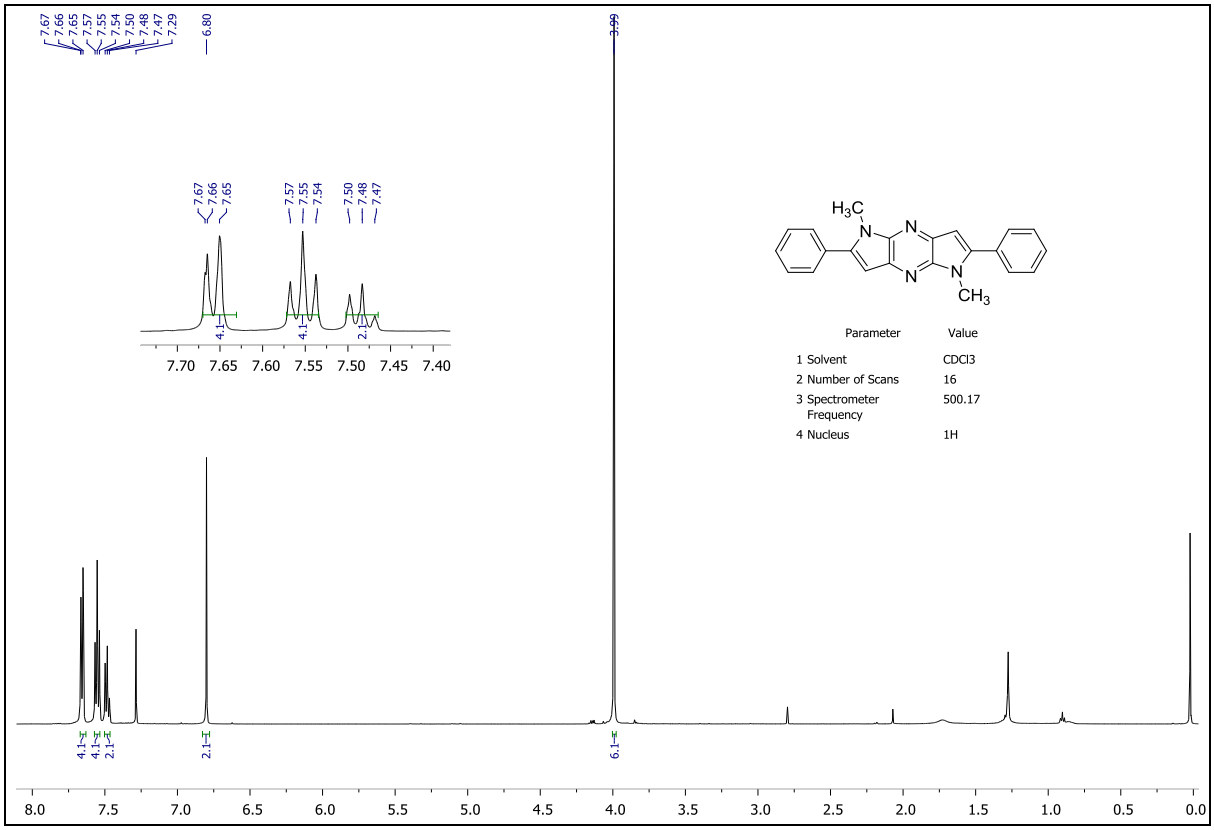
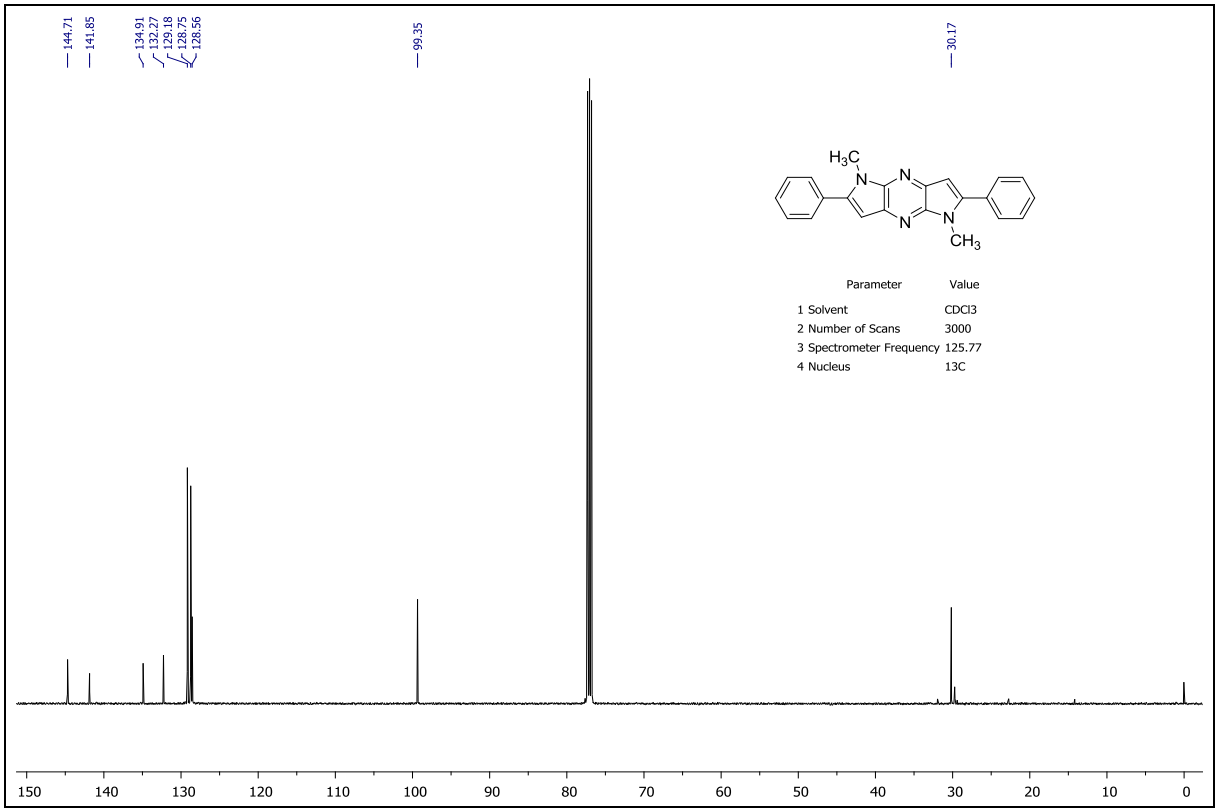
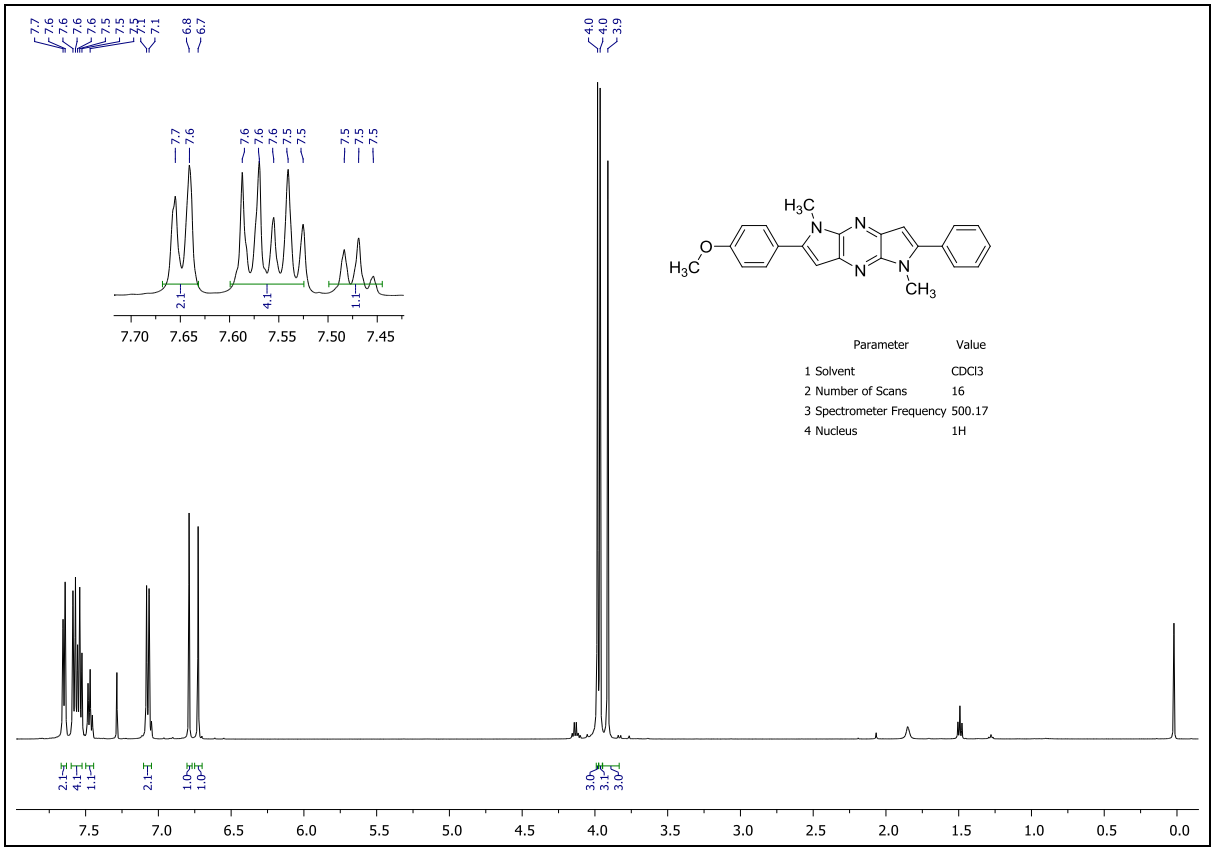


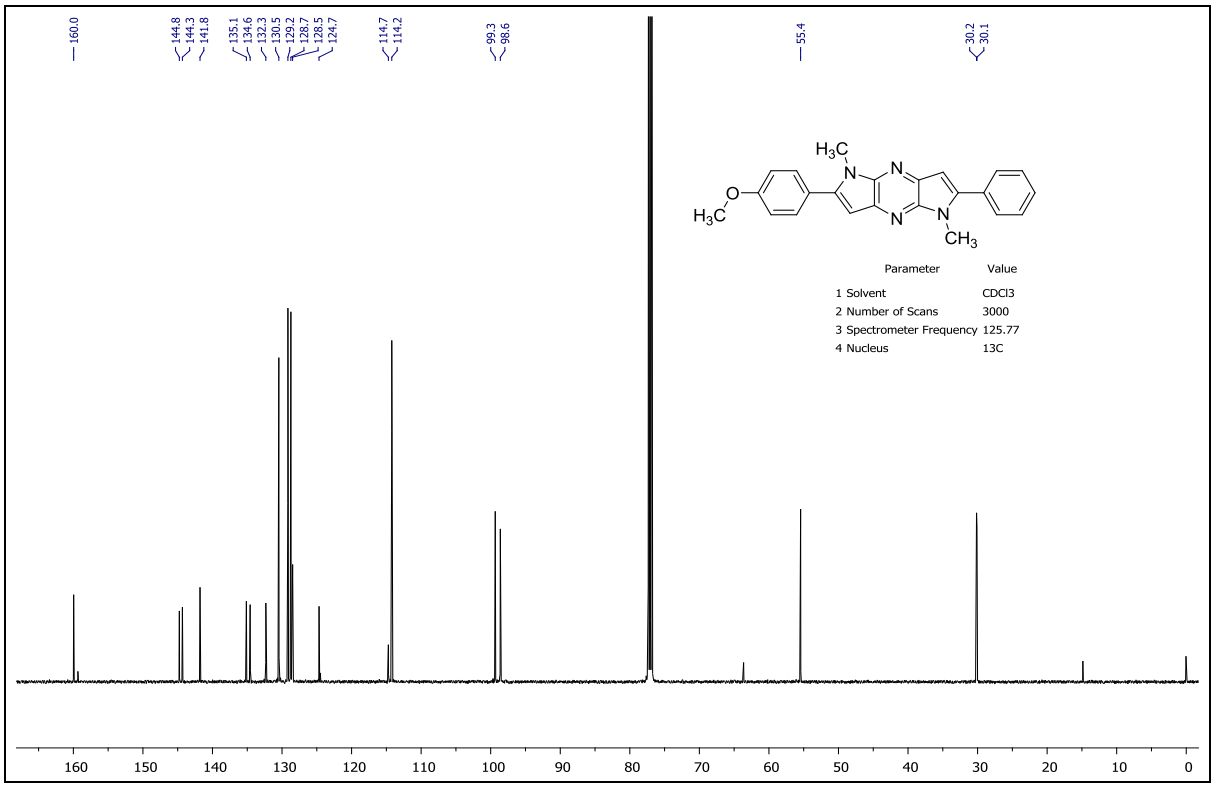
^{1}H NMR – 11f



^{13}C NMR – 11f



^{1}H NMR – 11g



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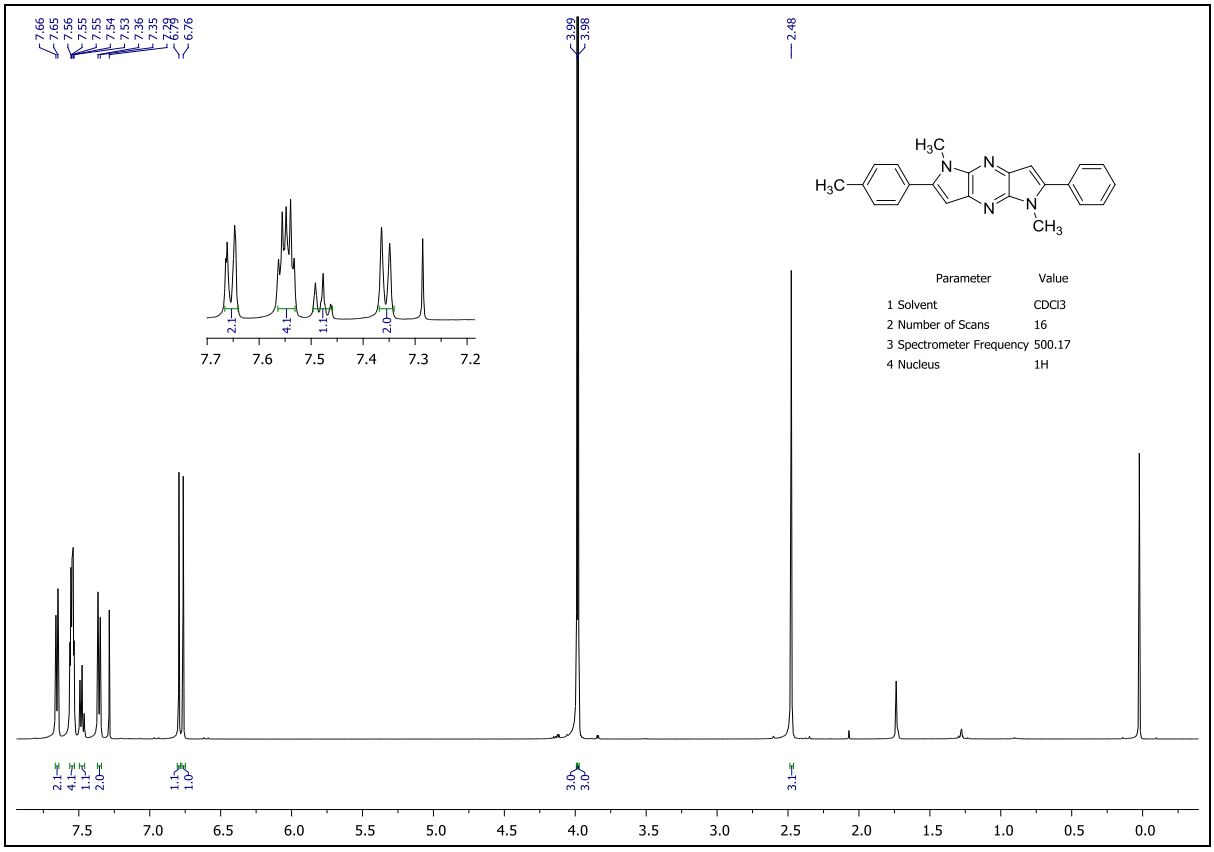

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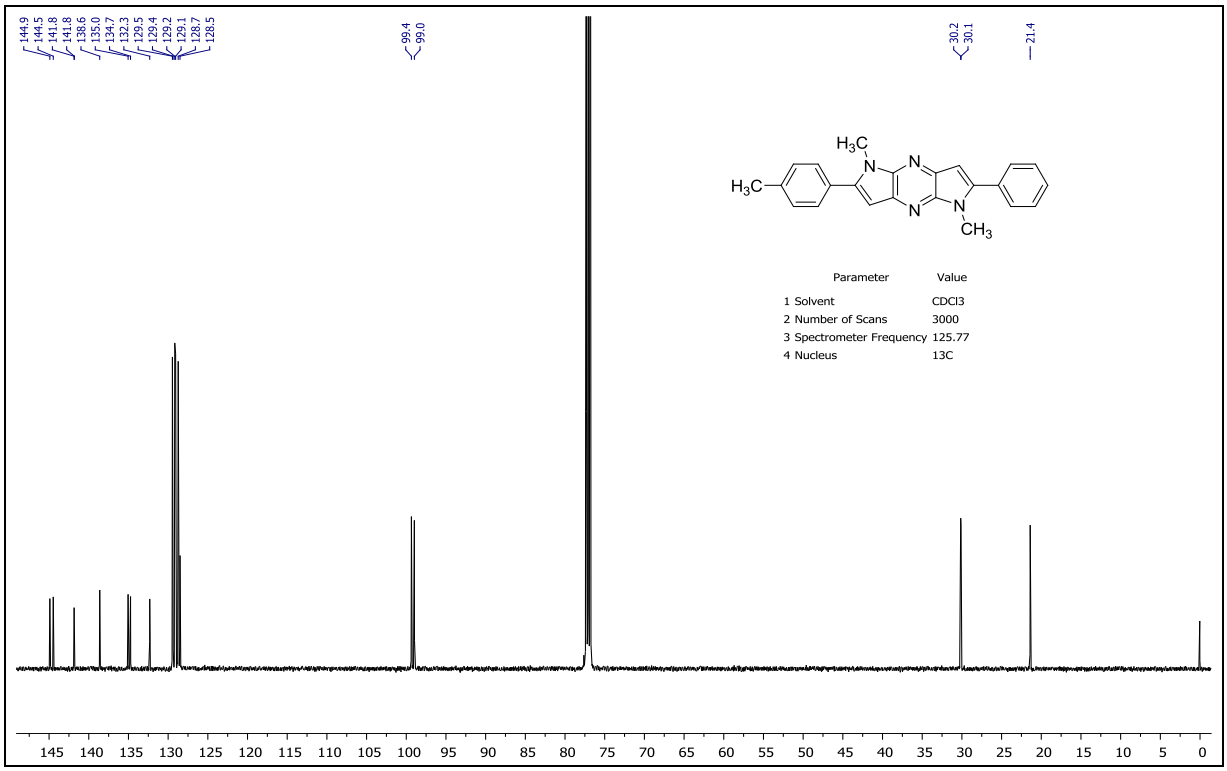
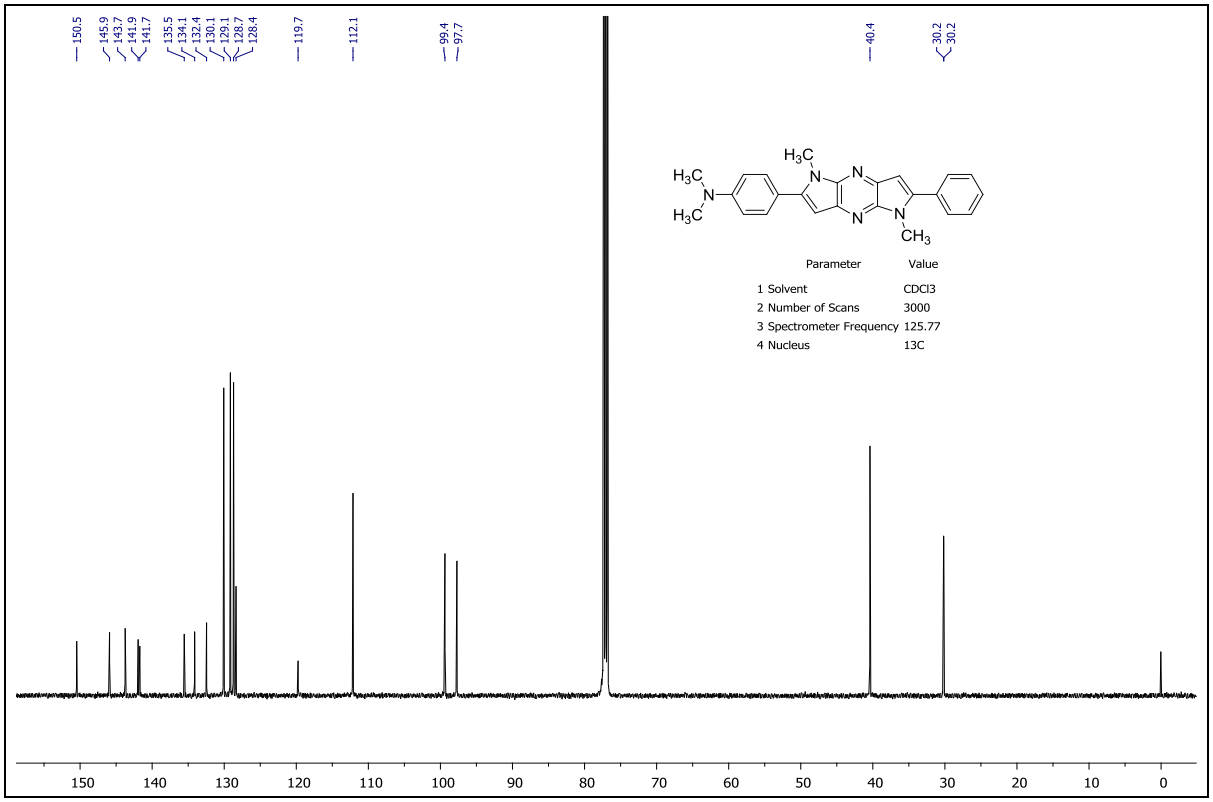
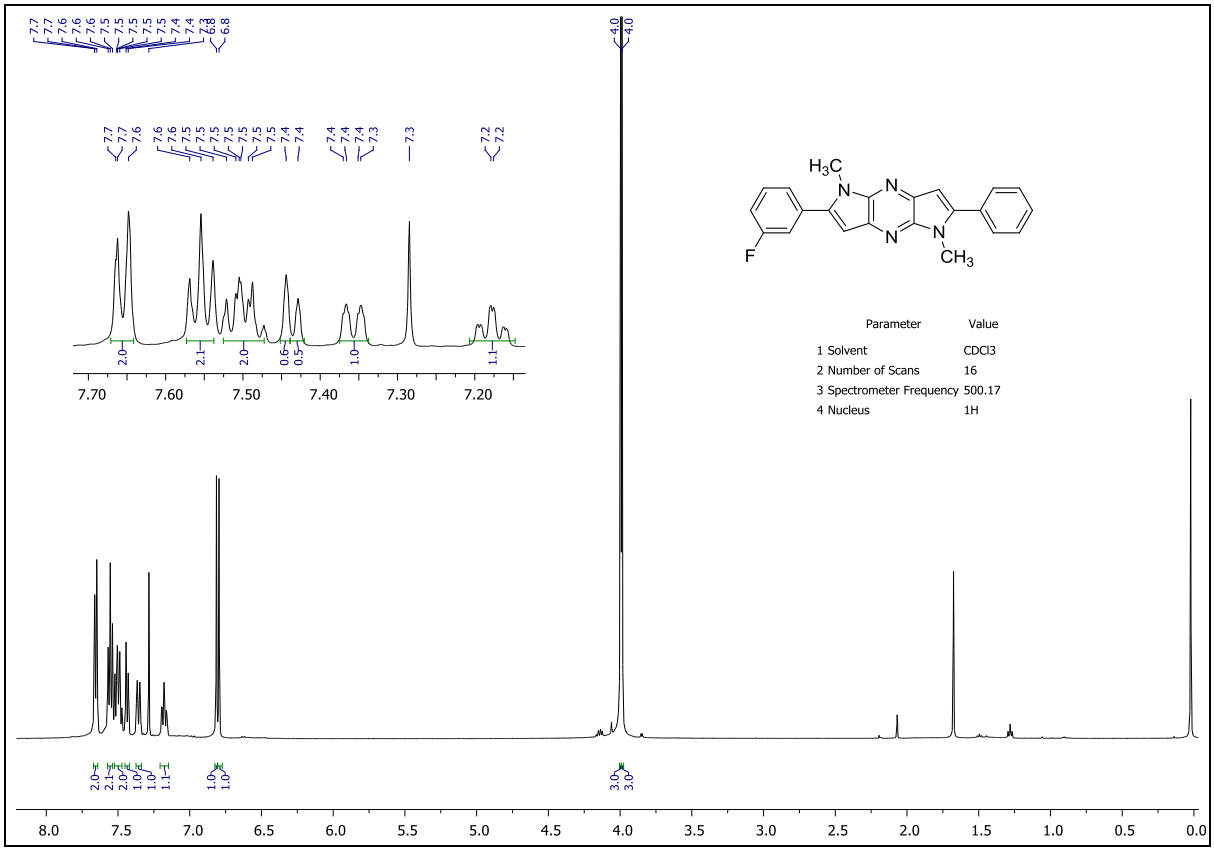


^{13}C NMR – 11h

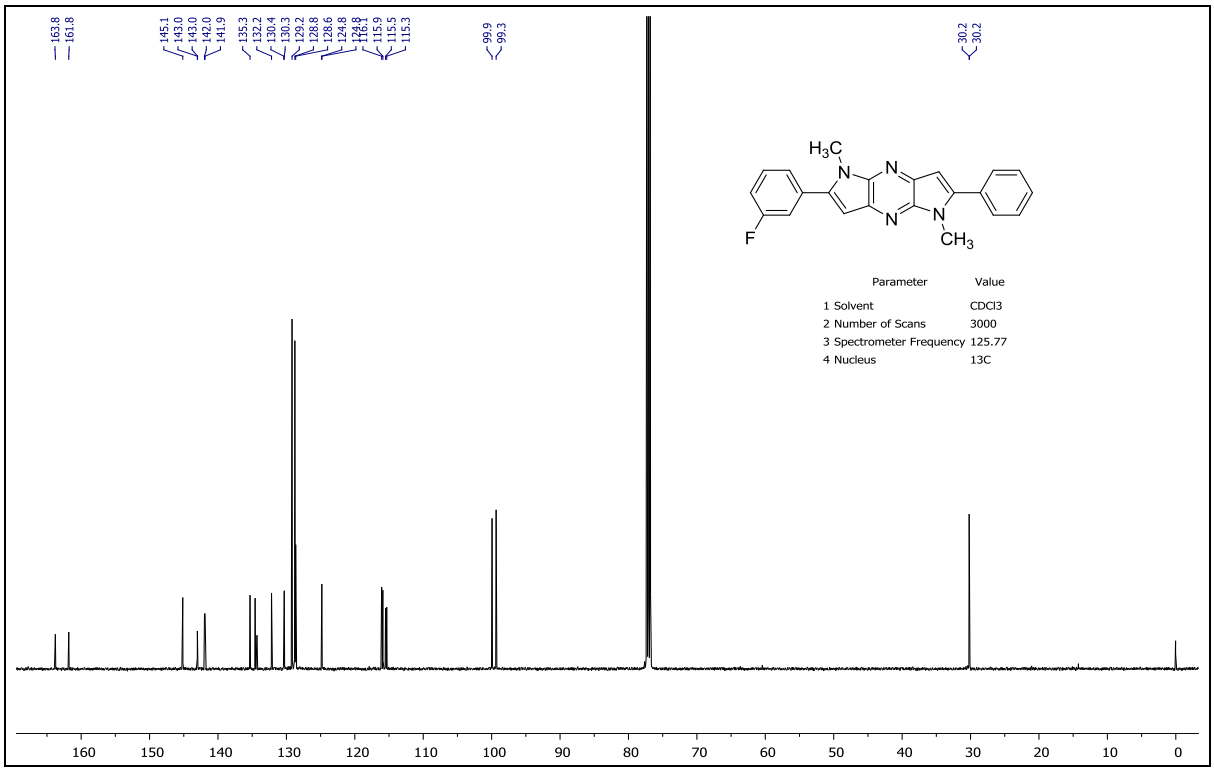
^{1}H NMR – 11i



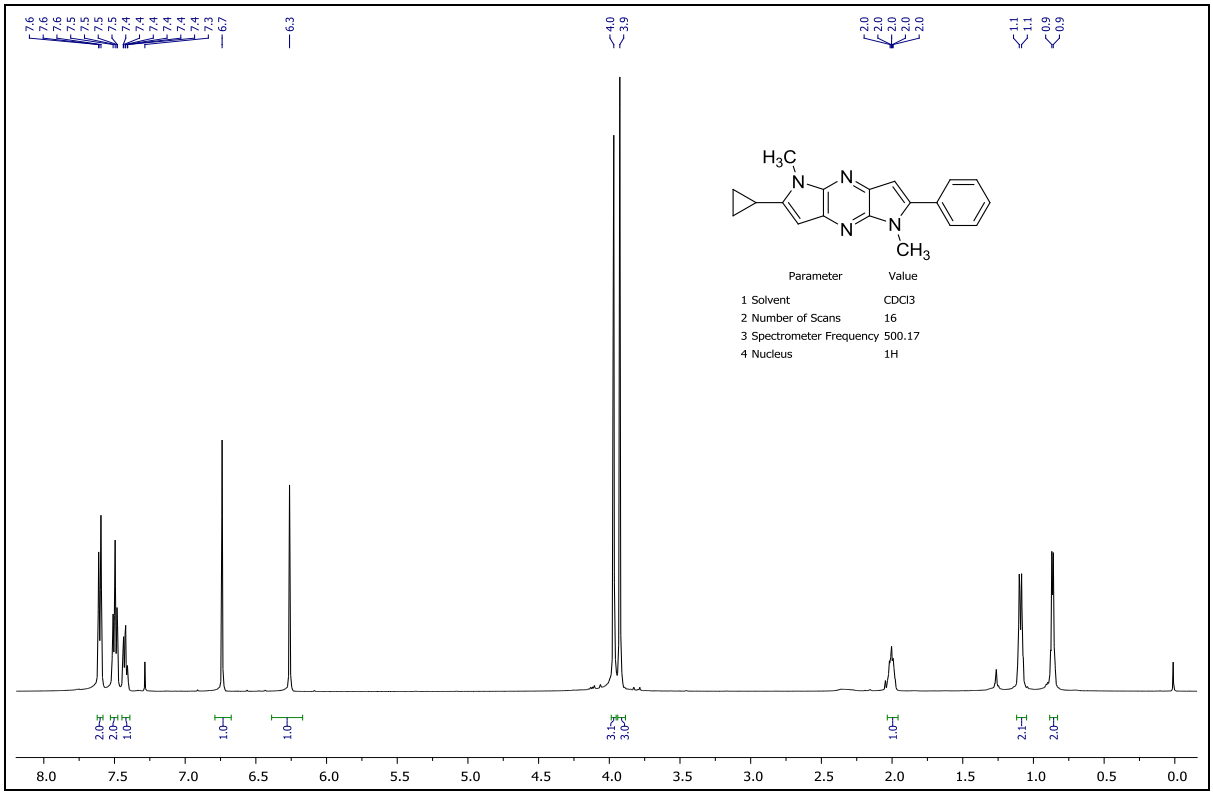
^{13}C NMR – 11i



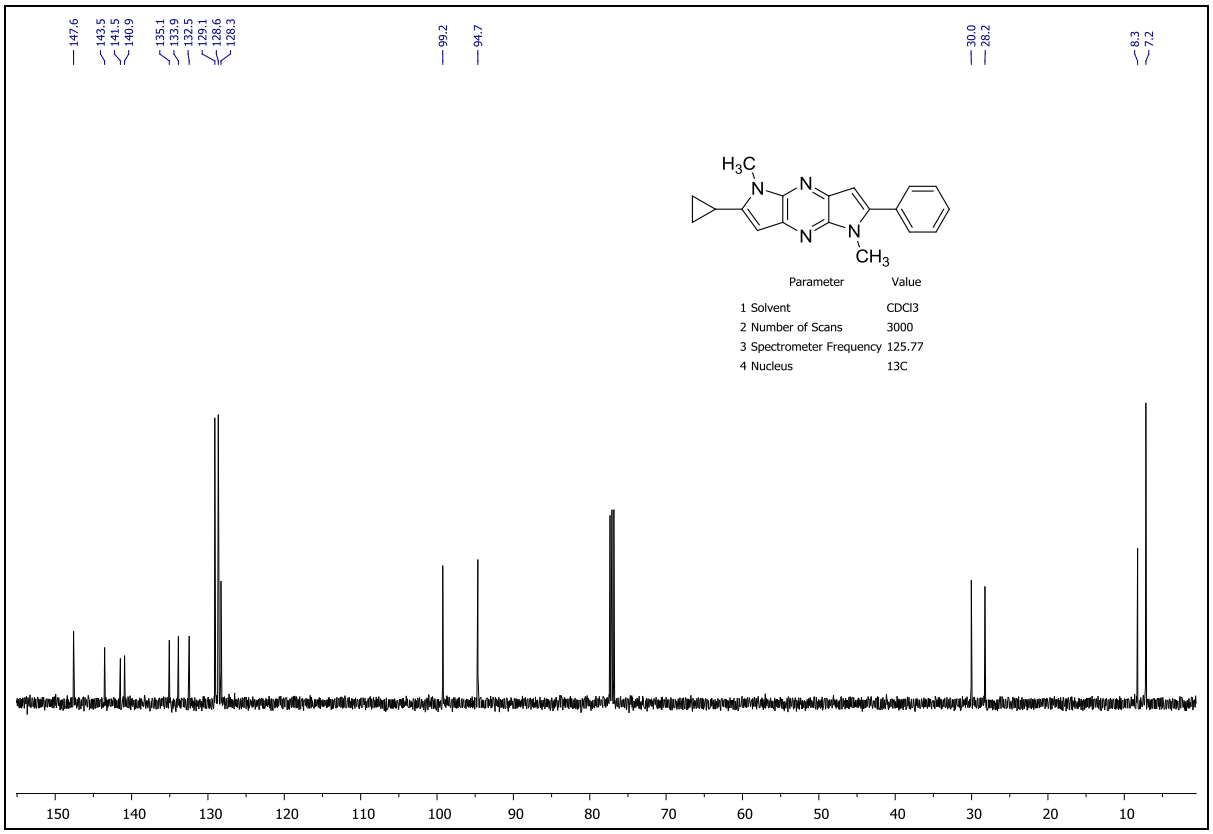
^{1}H NMR – 11j



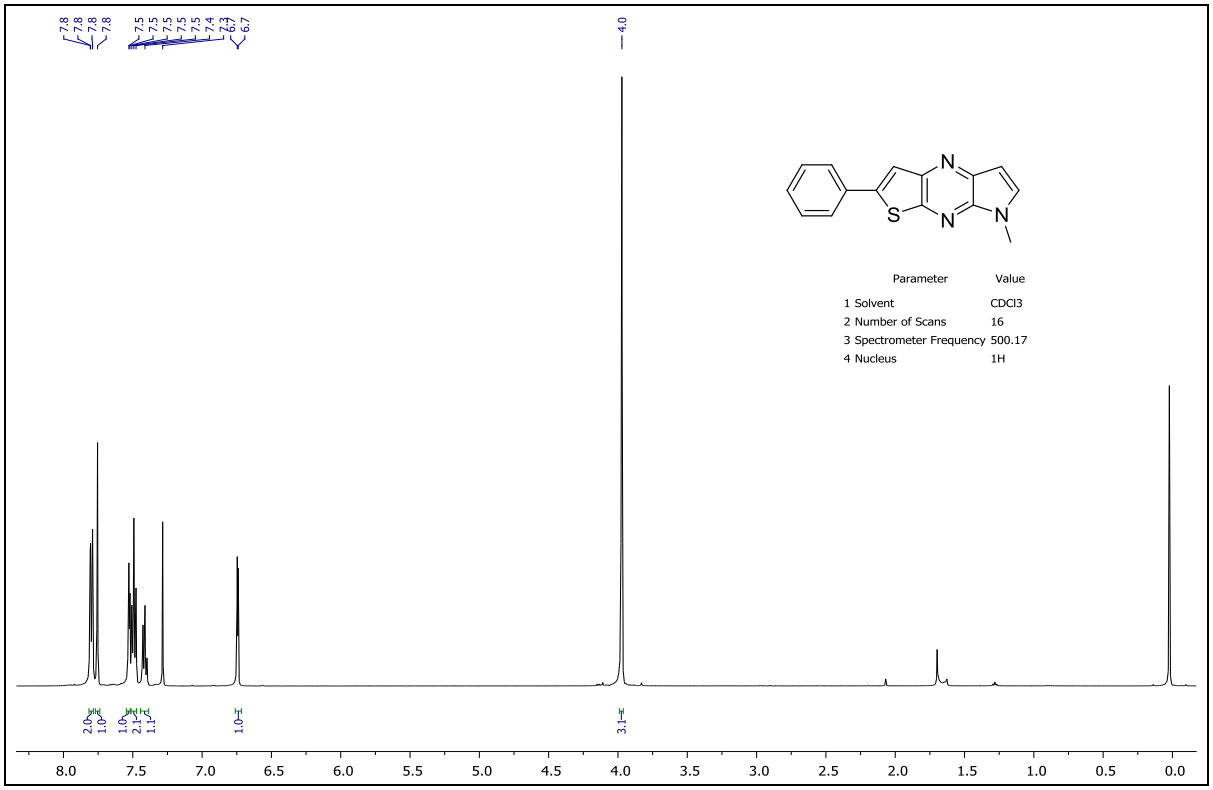
^{13}C NMR – 11j



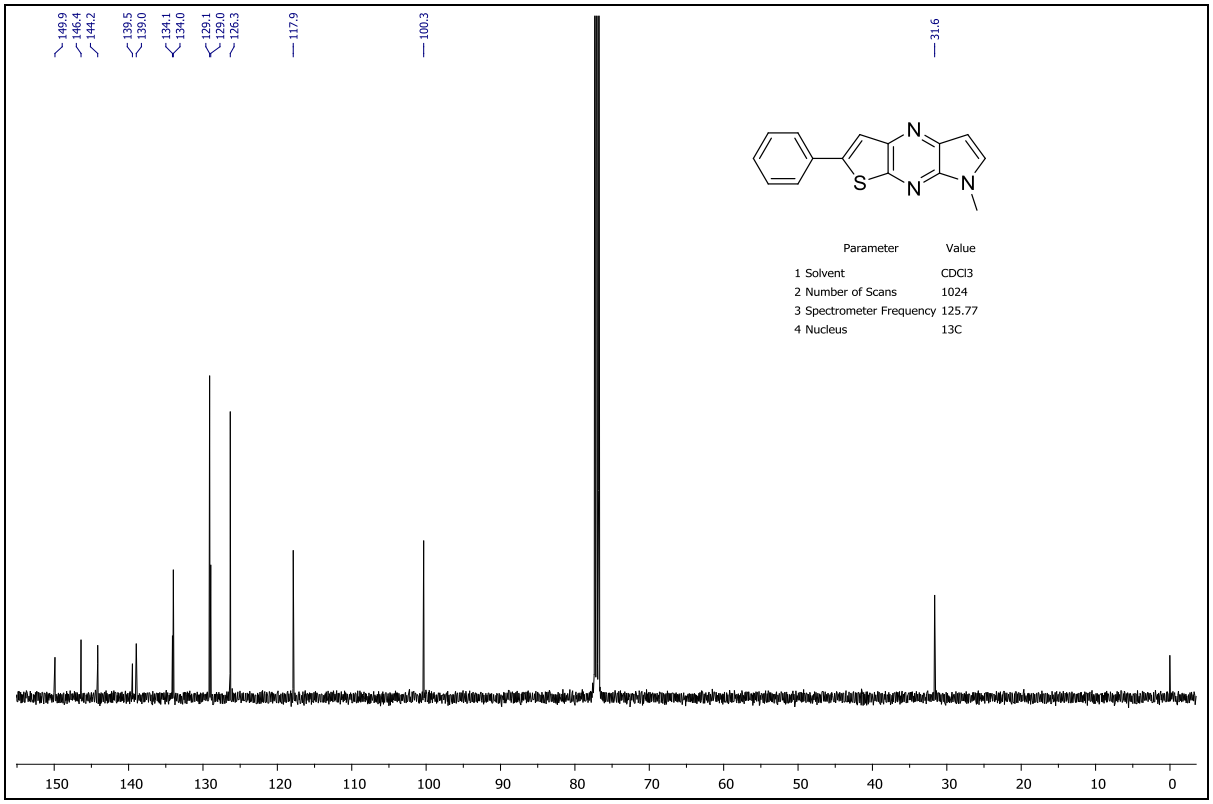
^{1}H NMR – 11k



^{13}C NMR – 11k



^{1}H NMR – 13a



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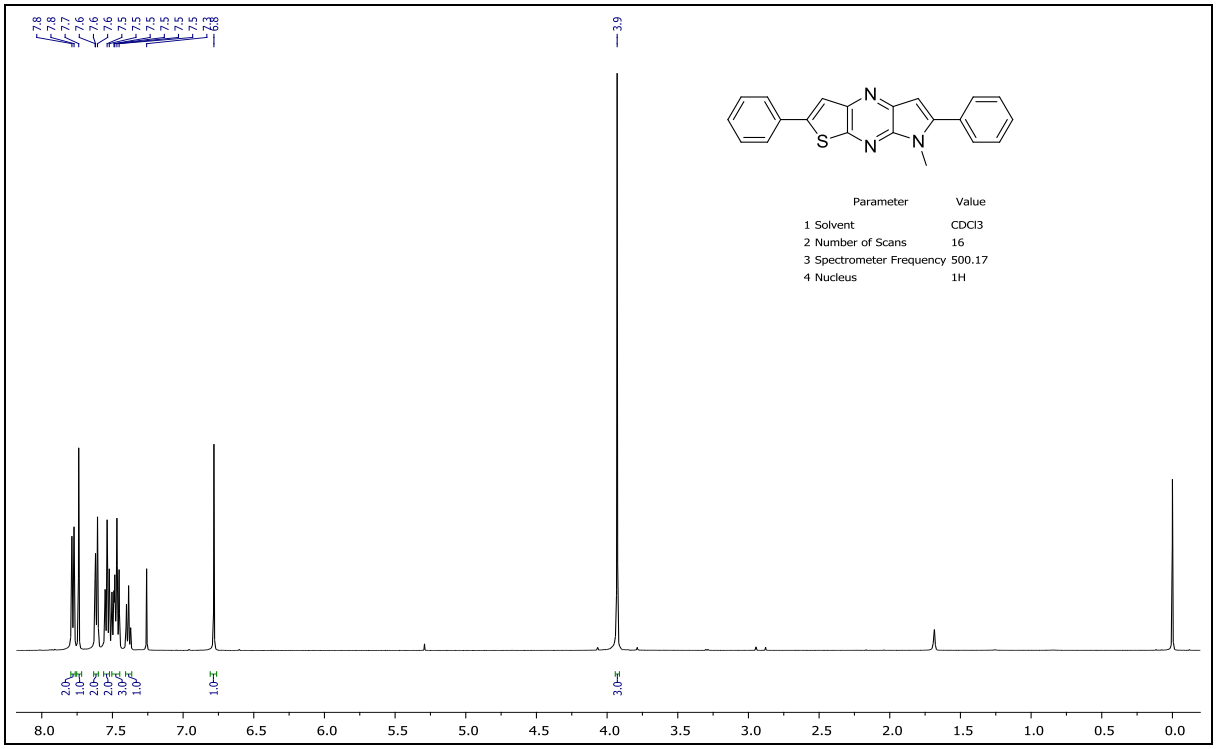

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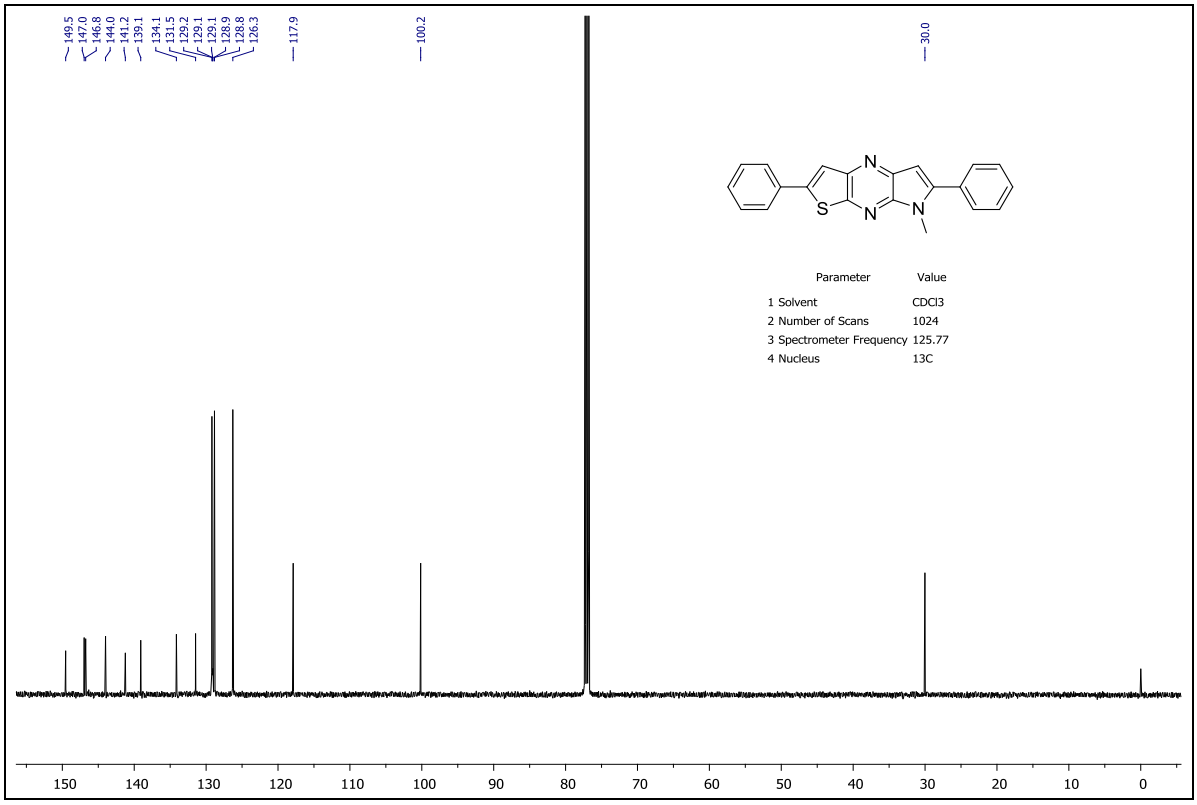

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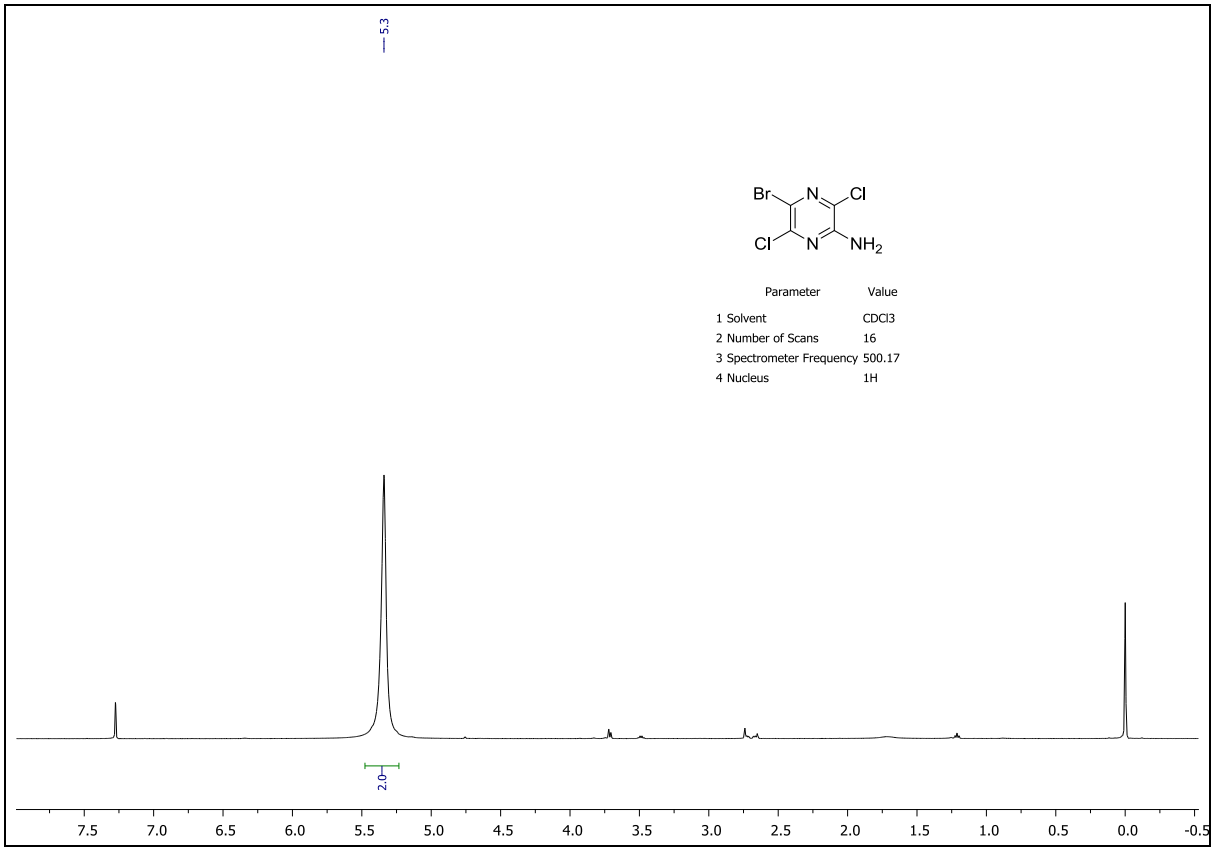
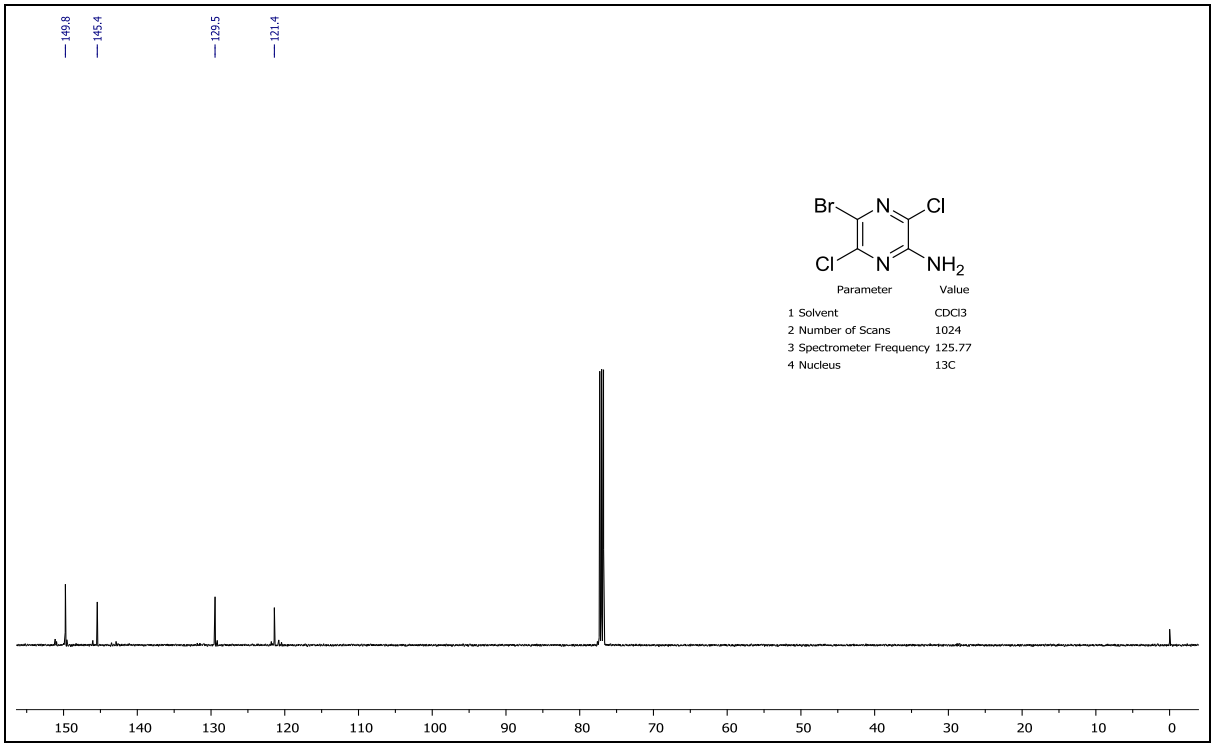
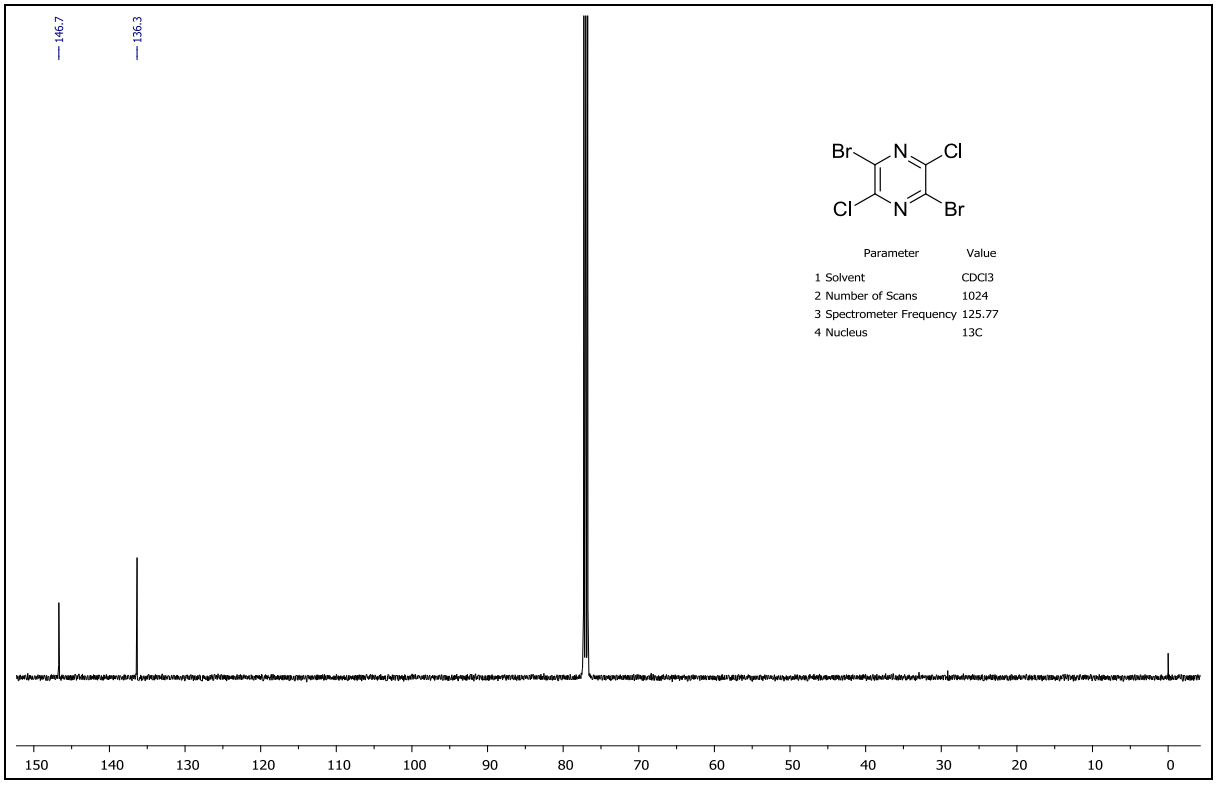


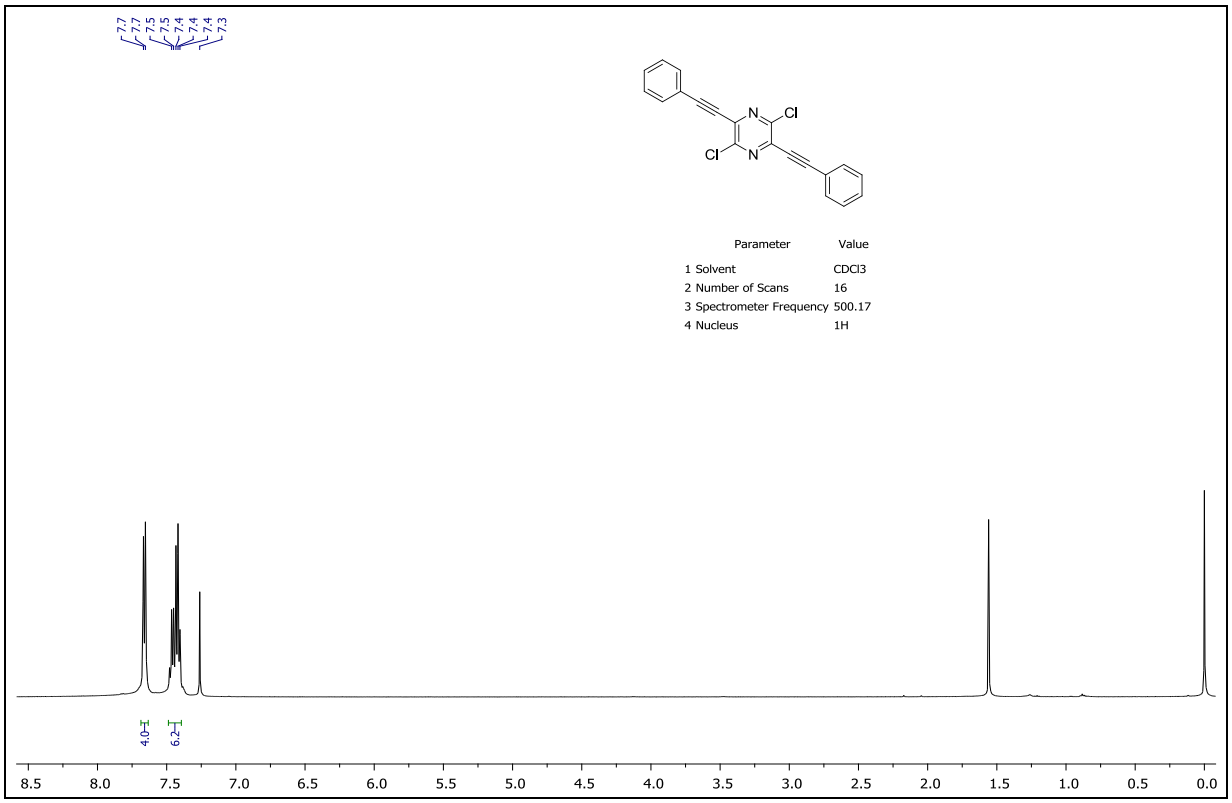
^{1}H NMR – 15



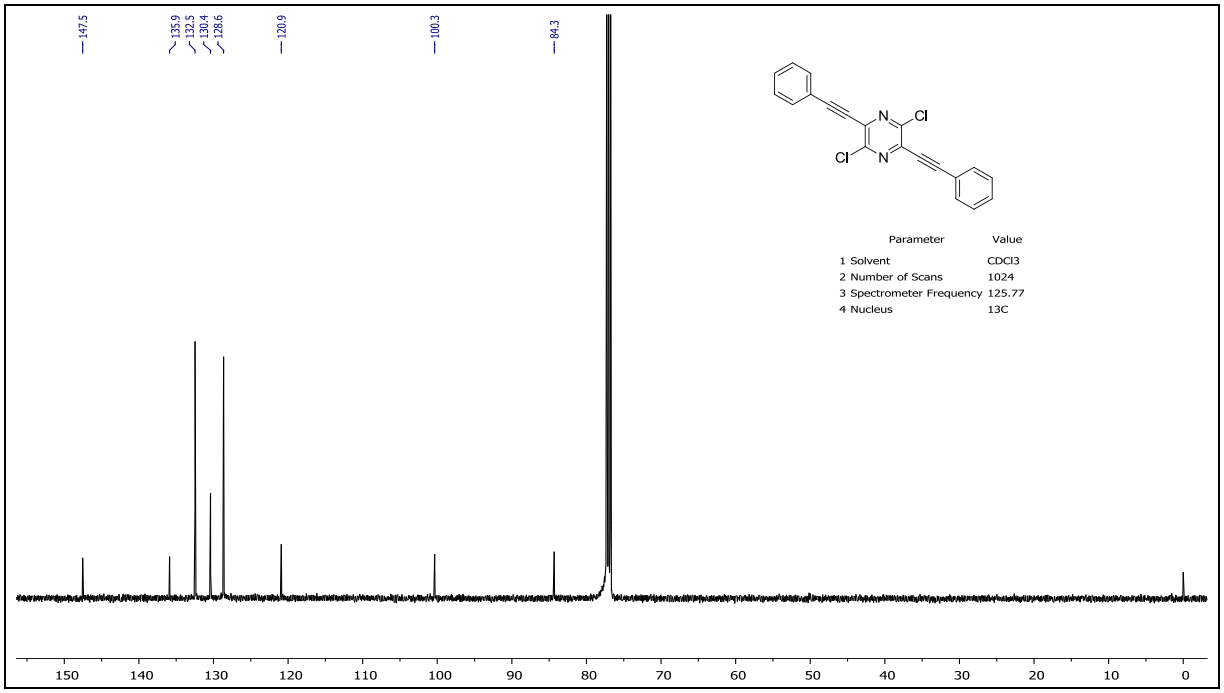
^{13}C NMR – 15



^{1}H NMR – 16

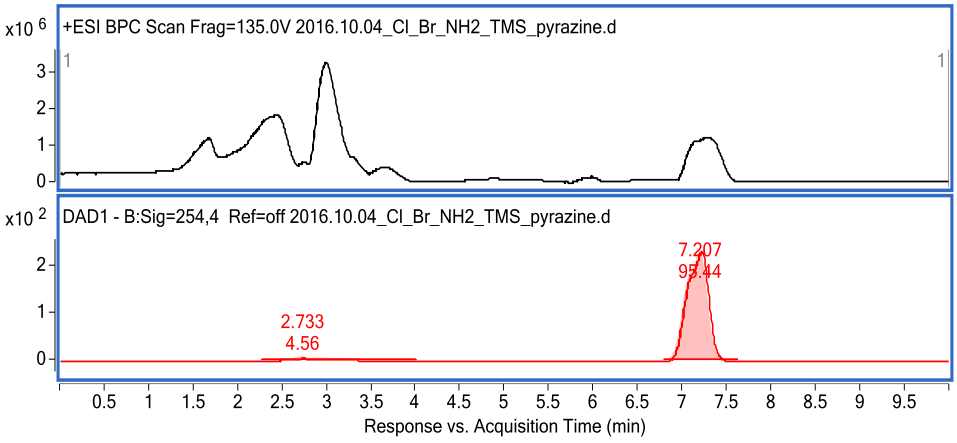


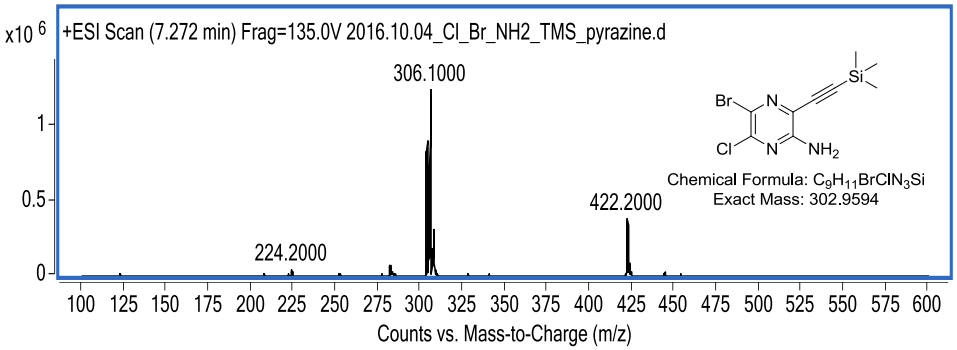
^{1}H NMR – 17



^{13}C NMR – 17

LC-MS and HRMS spectra of compounds





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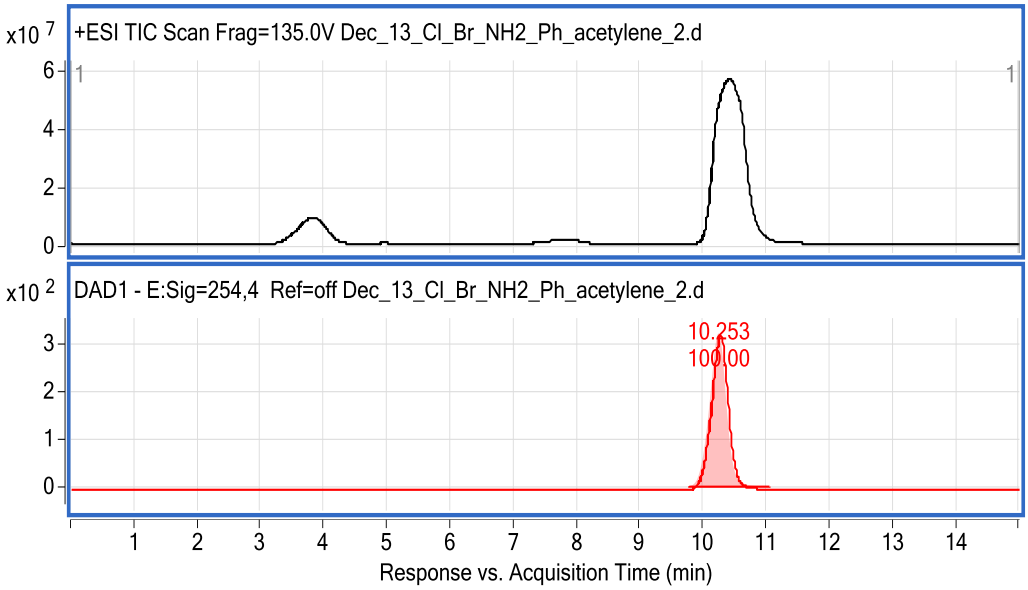

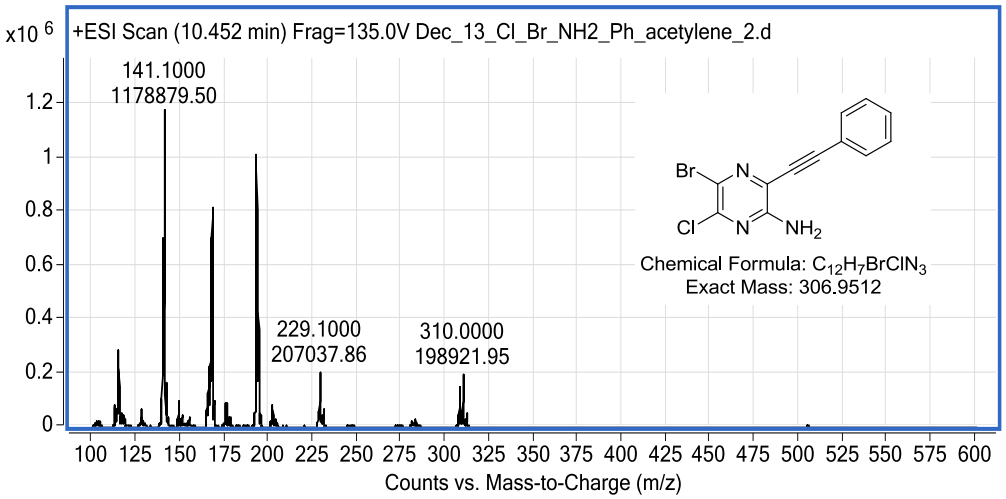

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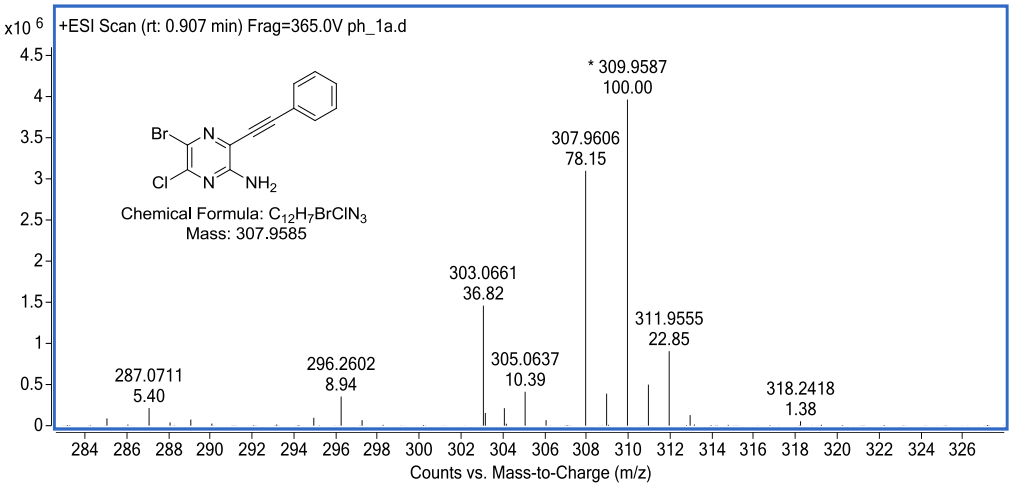

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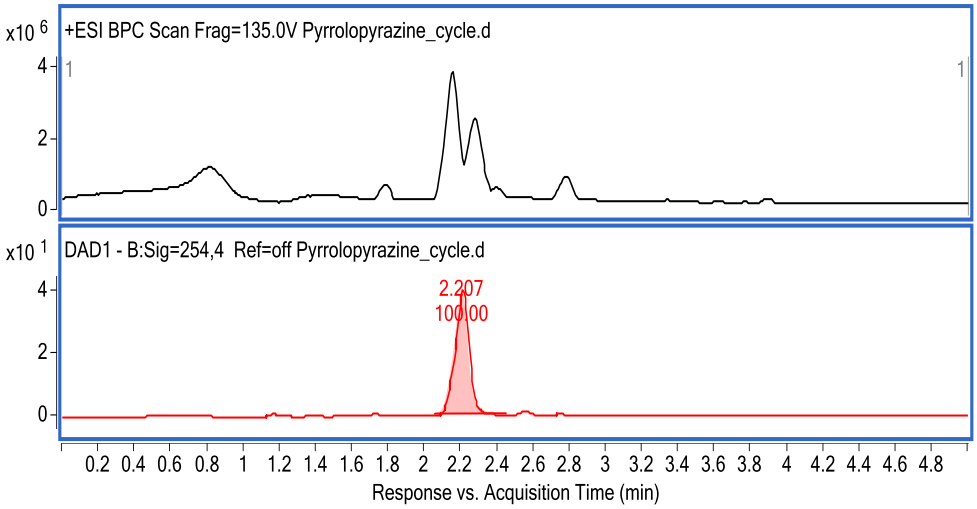
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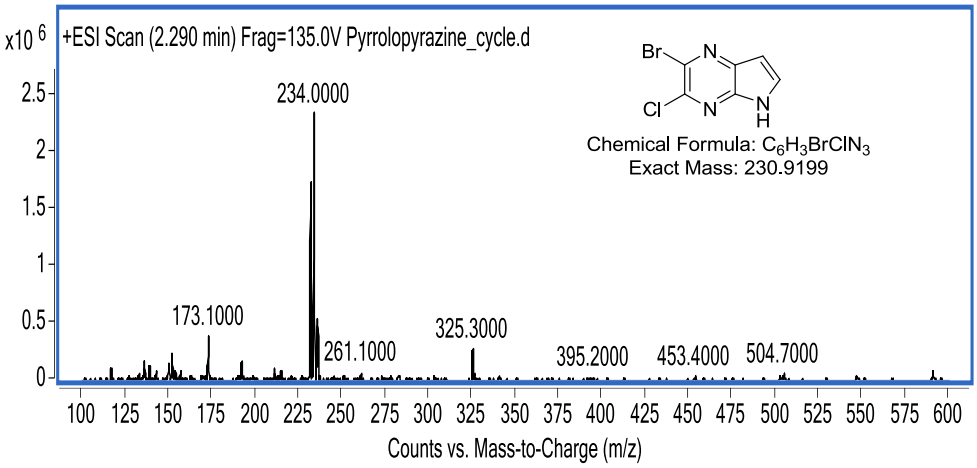
2.207
100100
Response vs. Acquisition Time (min)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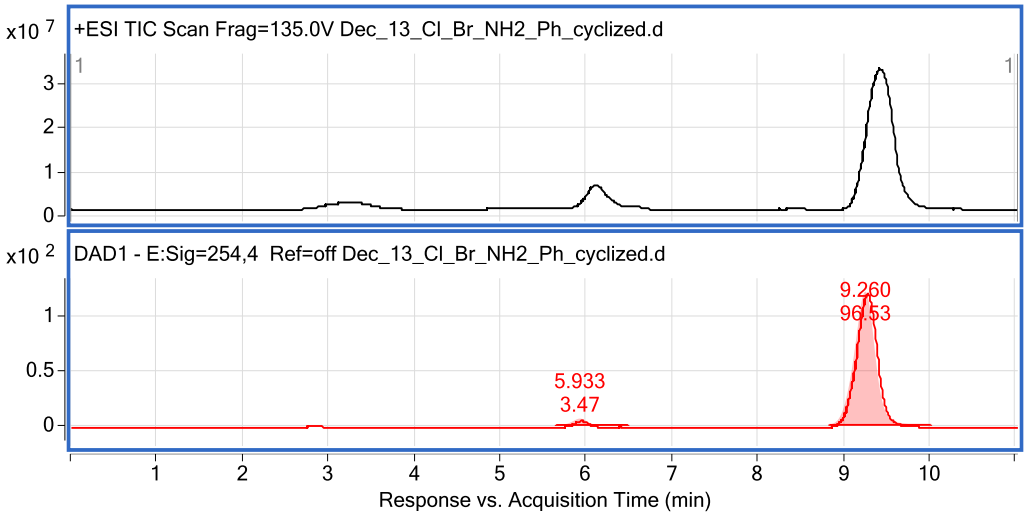
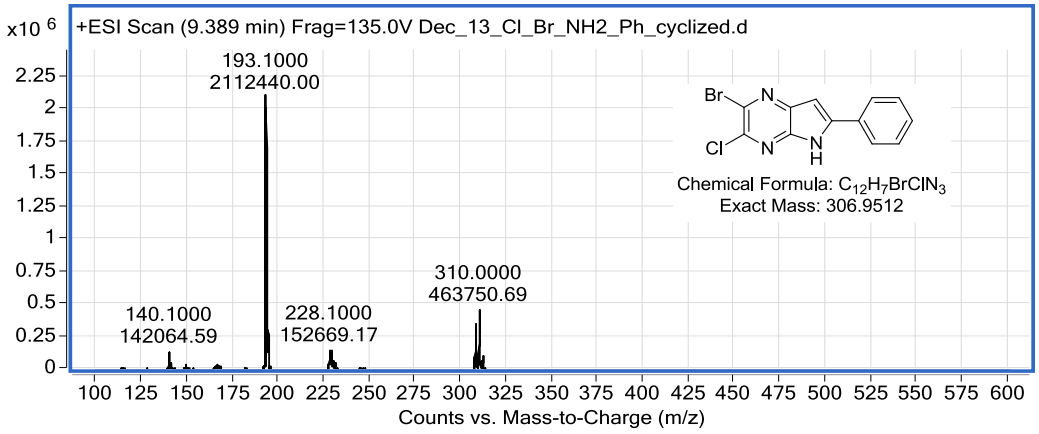
Exact Mass: 230.9199
Counts vs. Mass-to-Charge (m/z)

LC/MS – 2a





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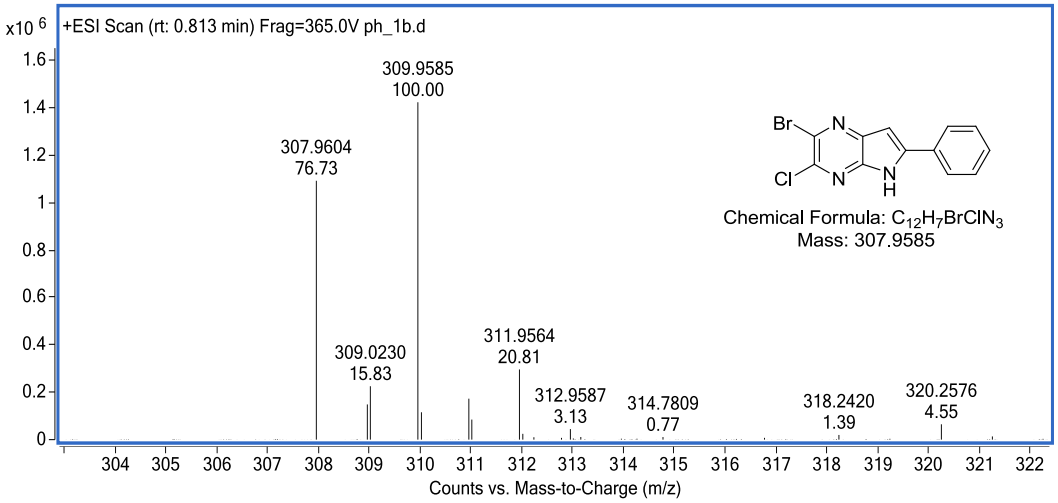
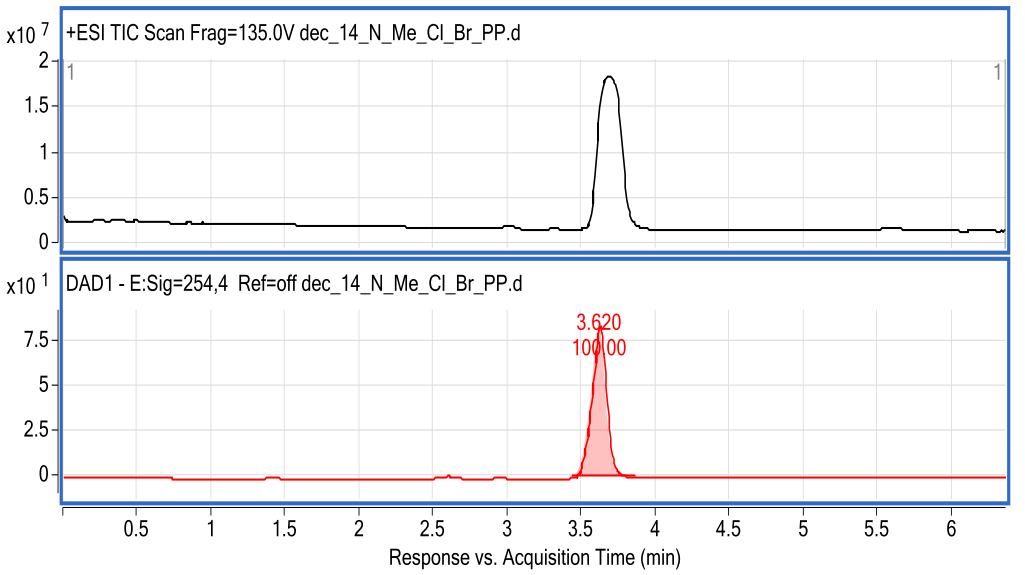
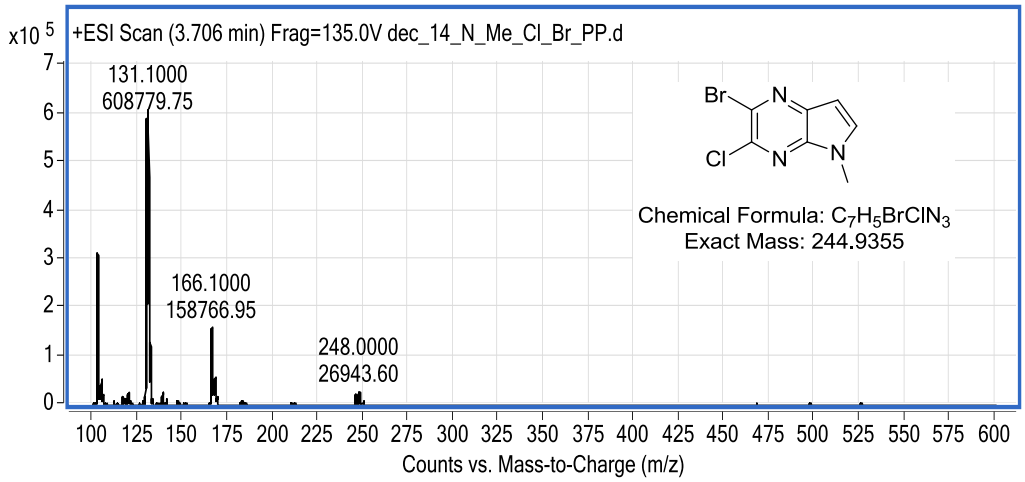


HR/MS – 2b





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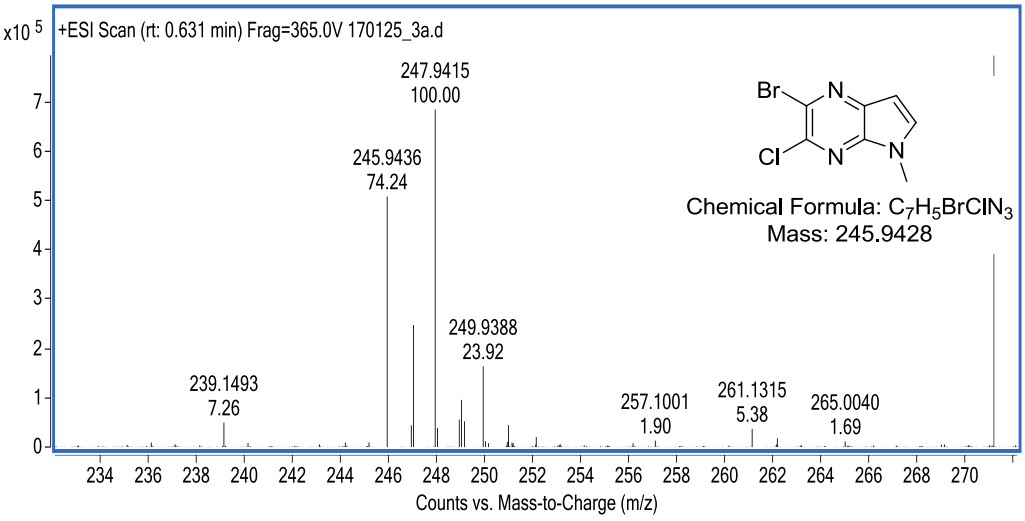

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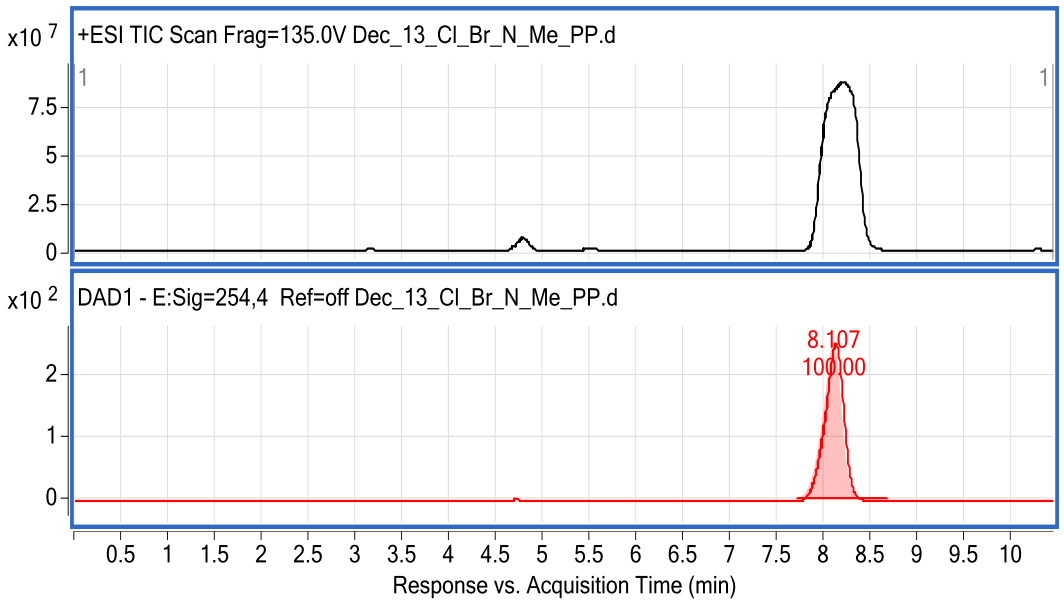

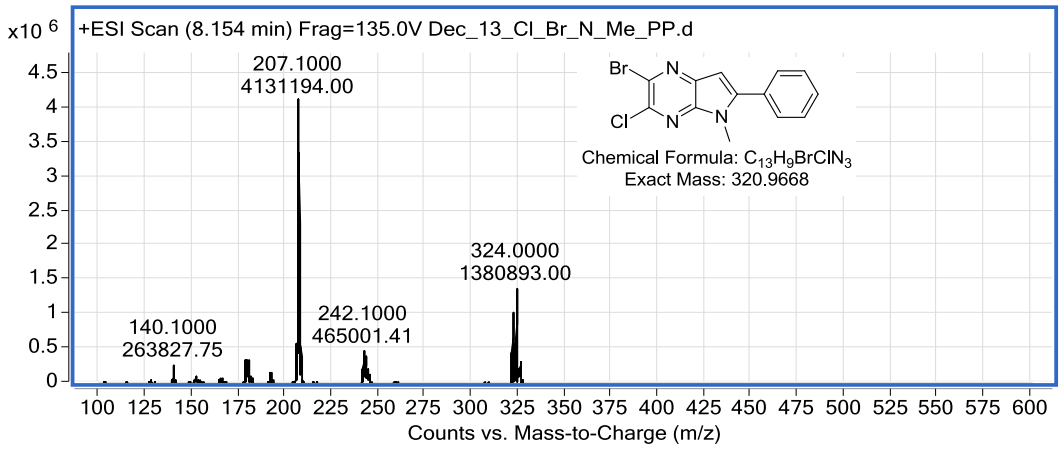

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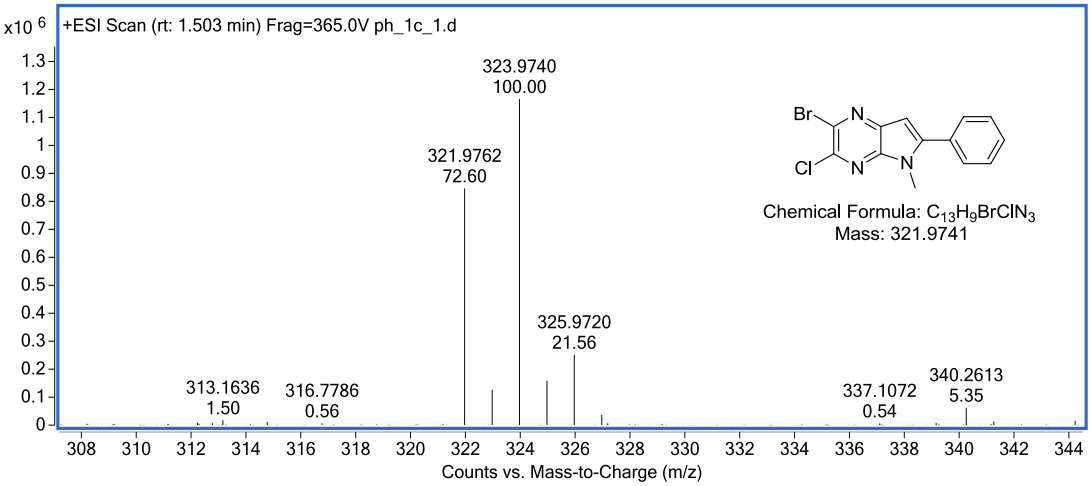

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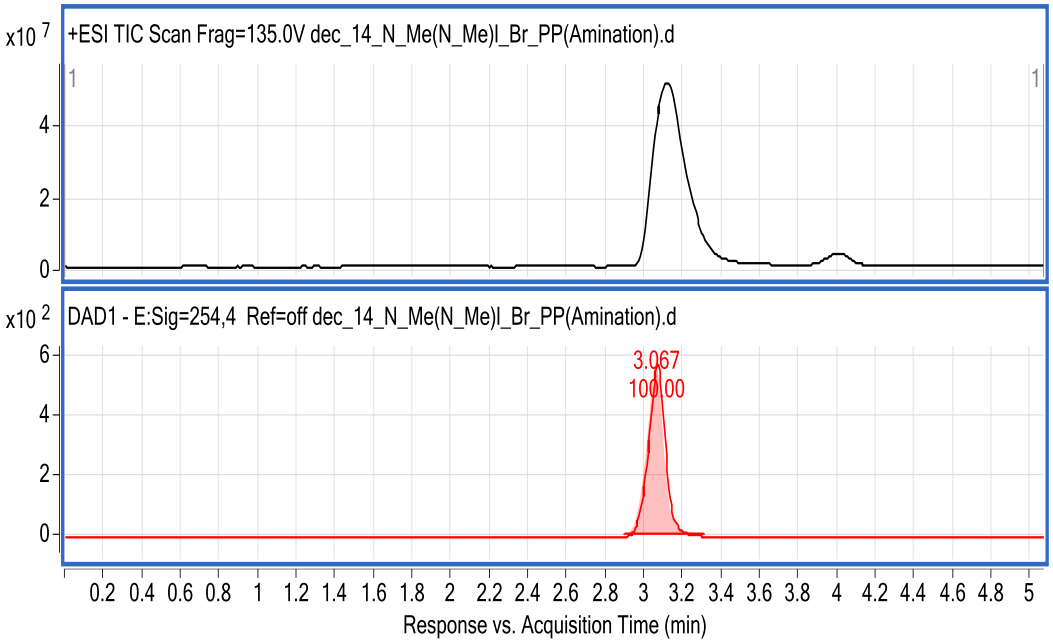

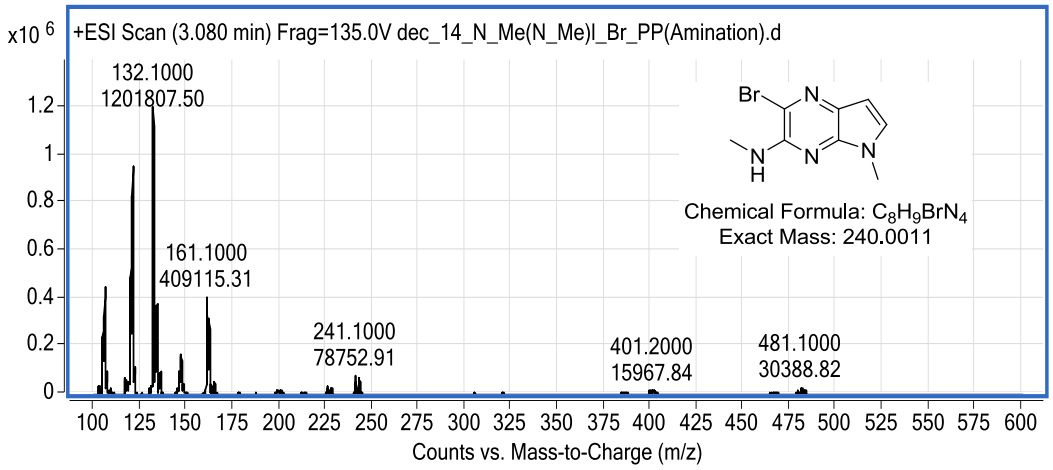

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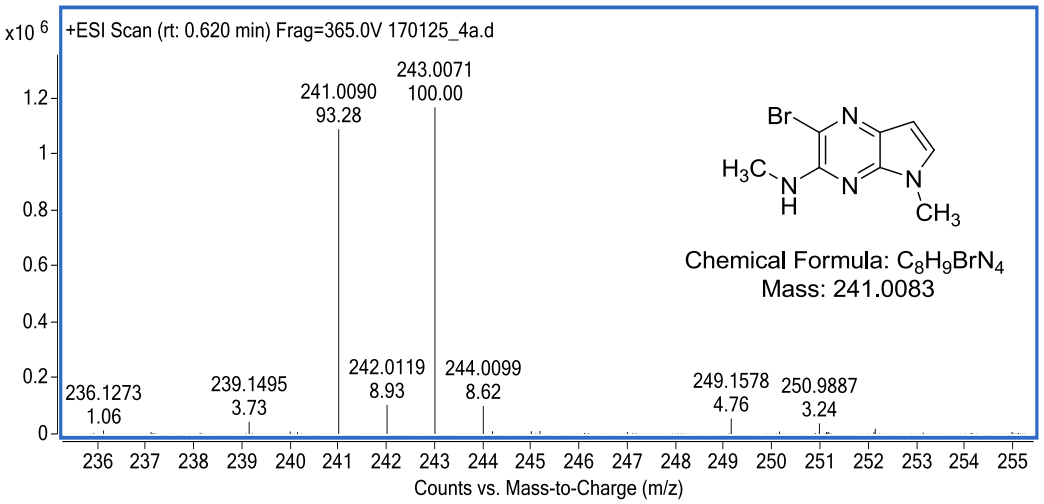

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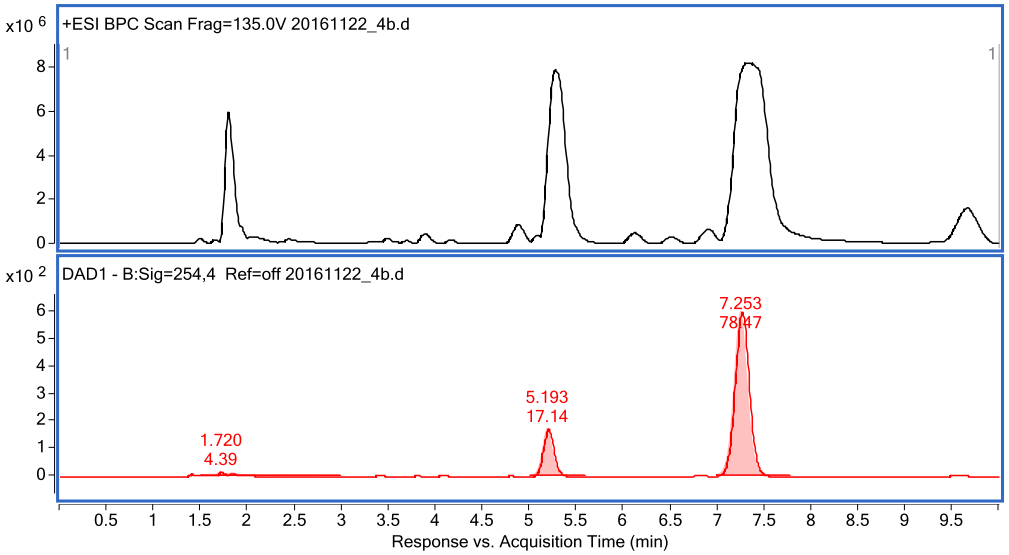

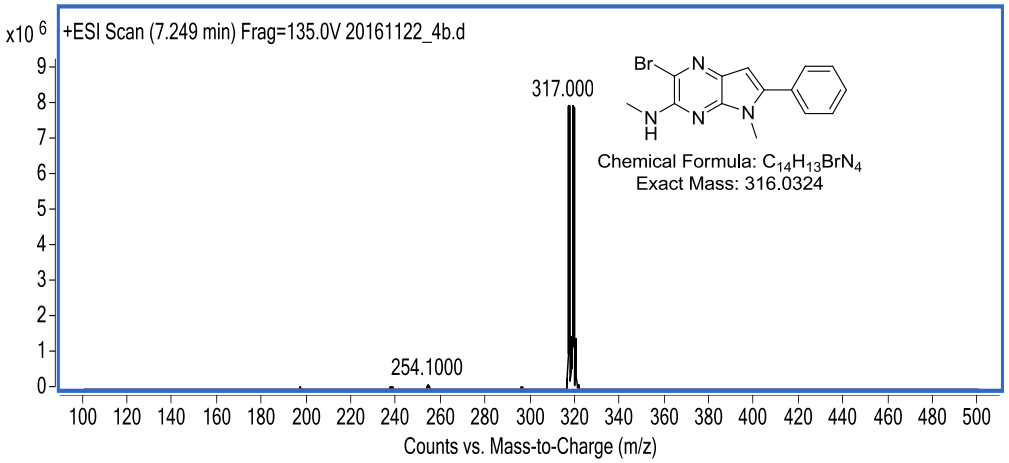

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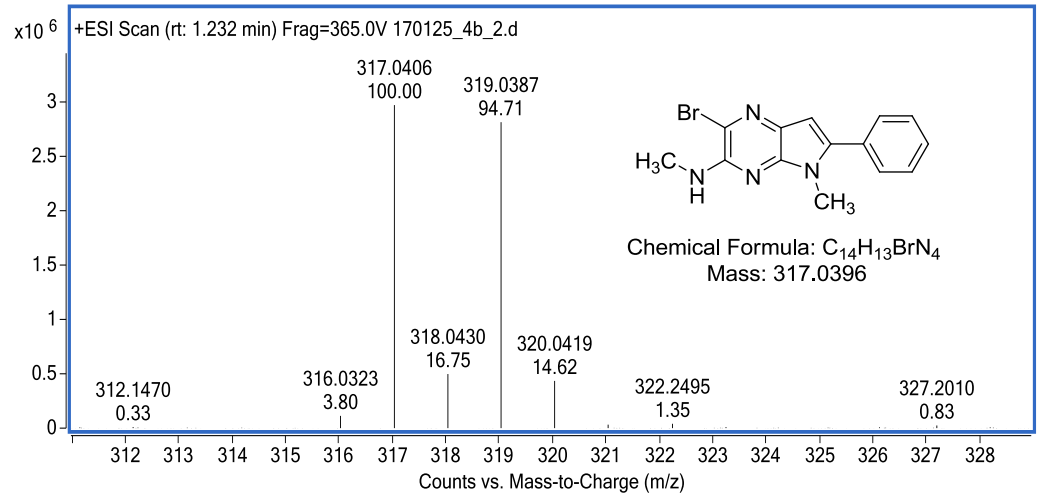

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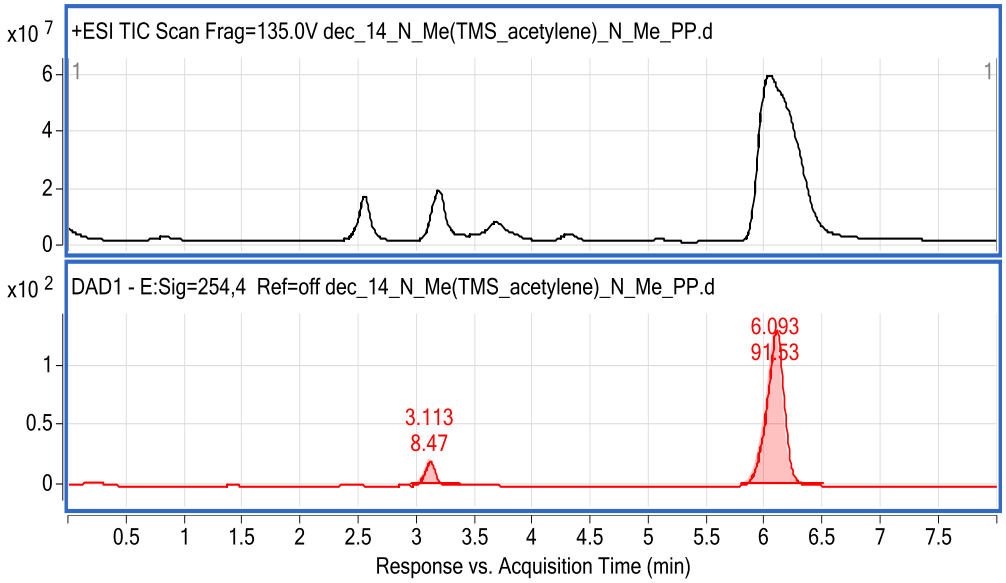
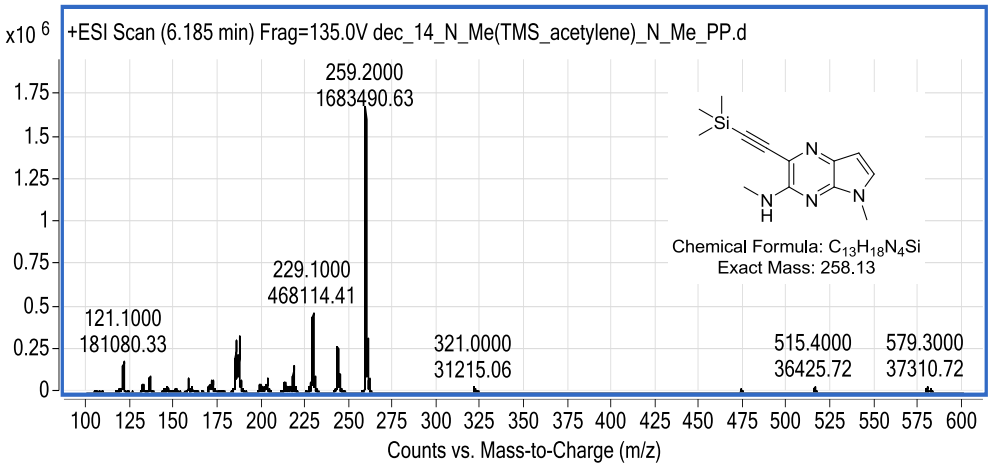
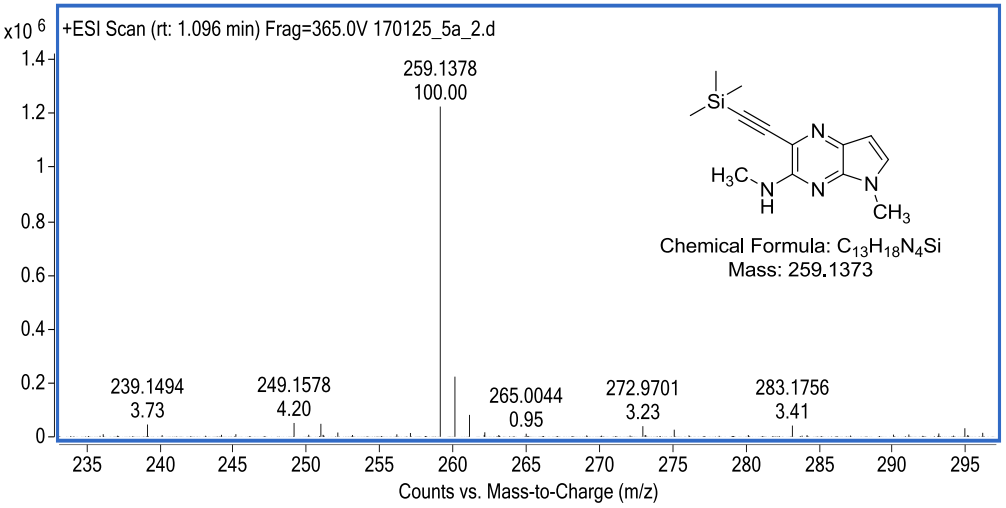




LC/MS – 5a



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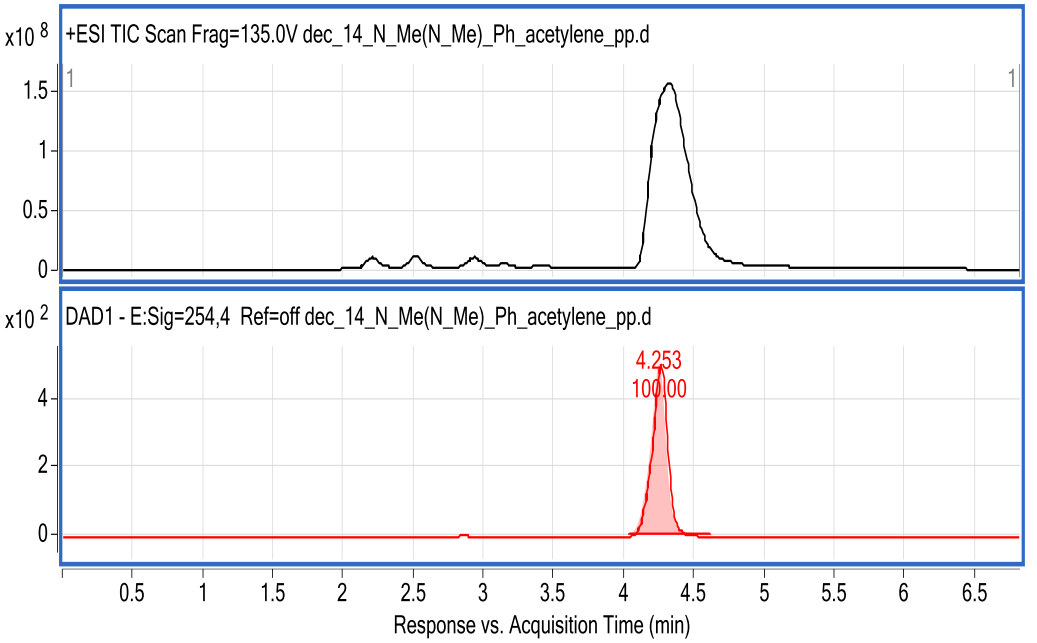

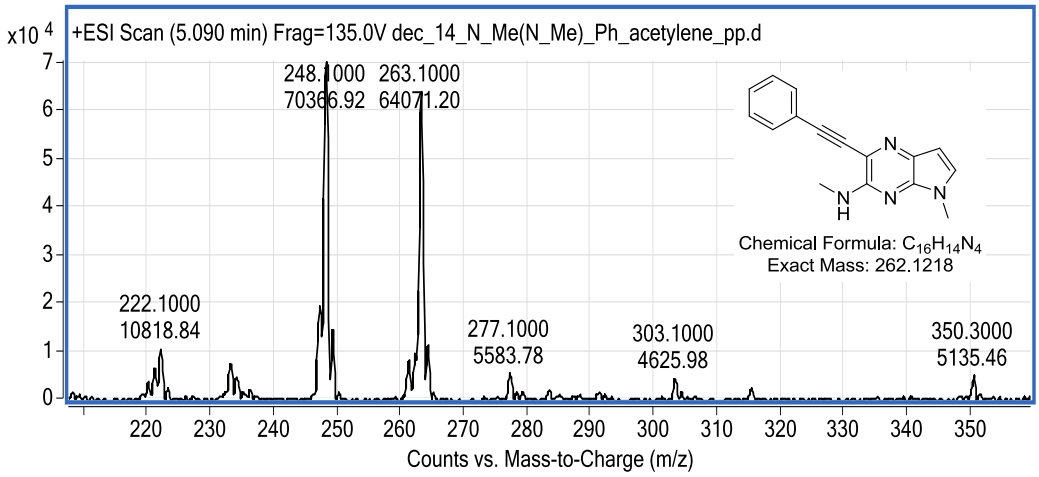

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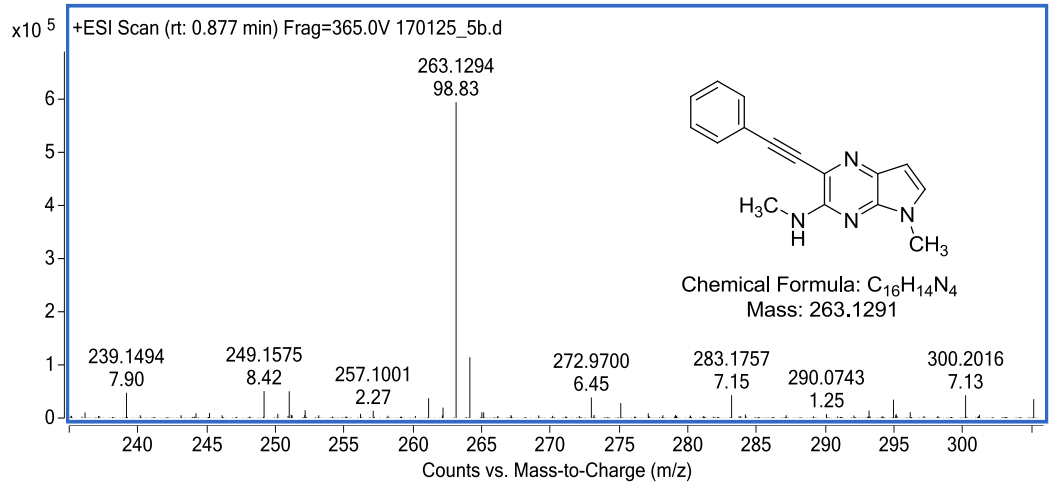

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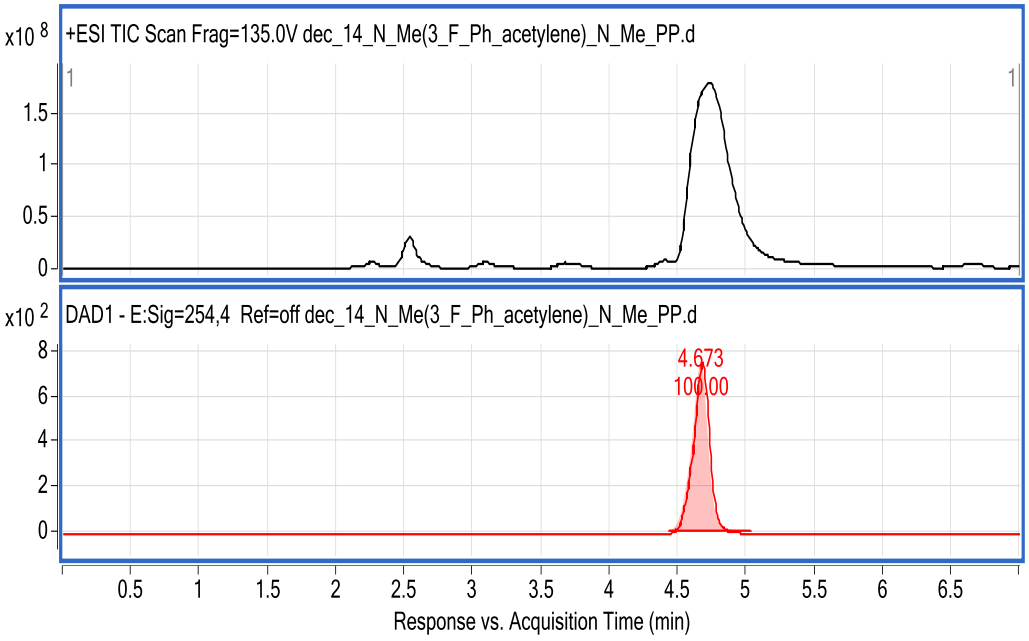

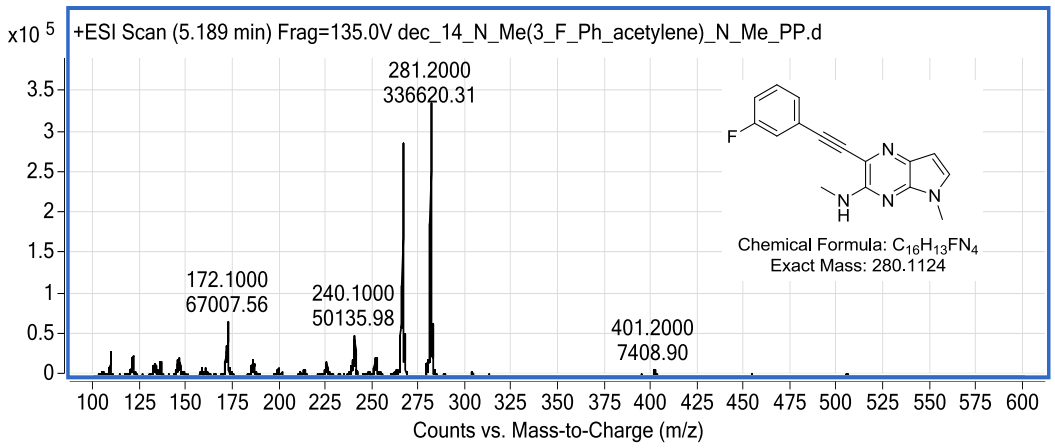

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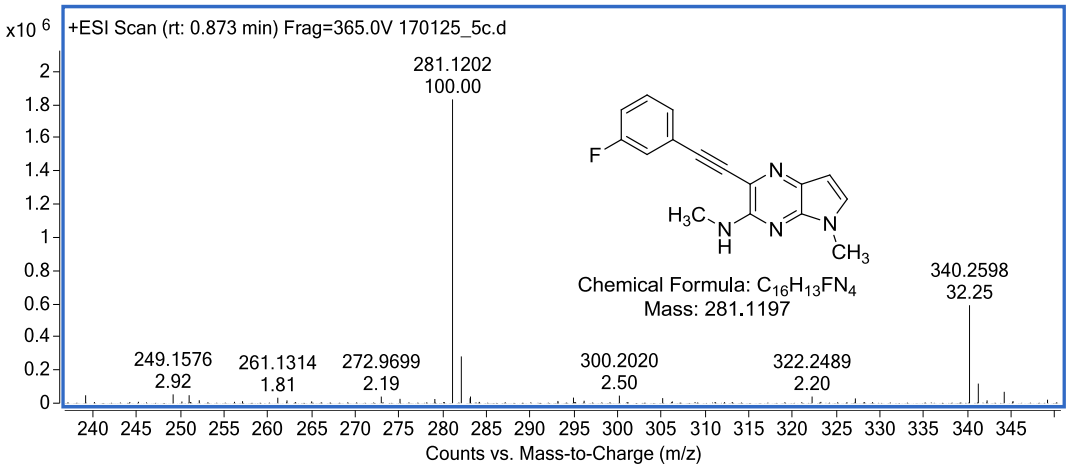

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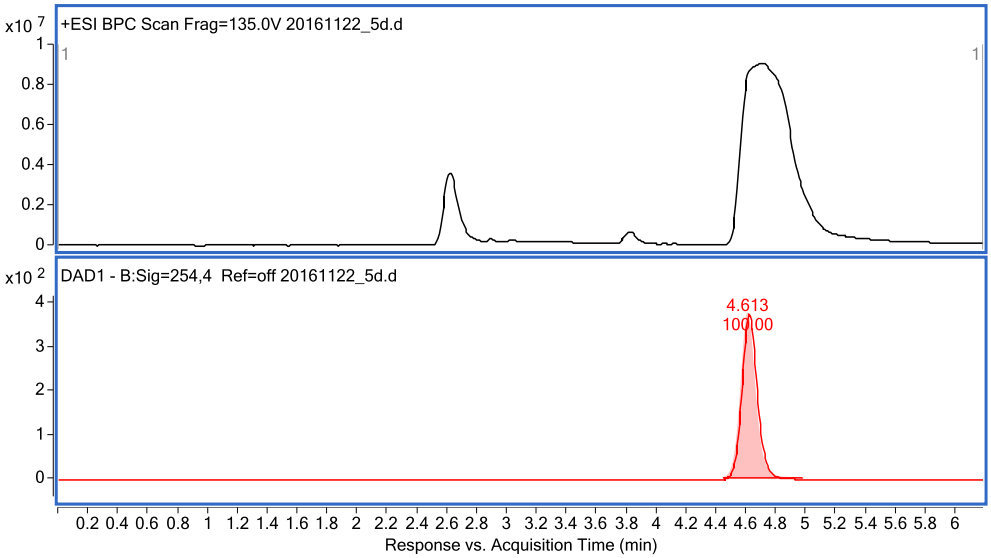

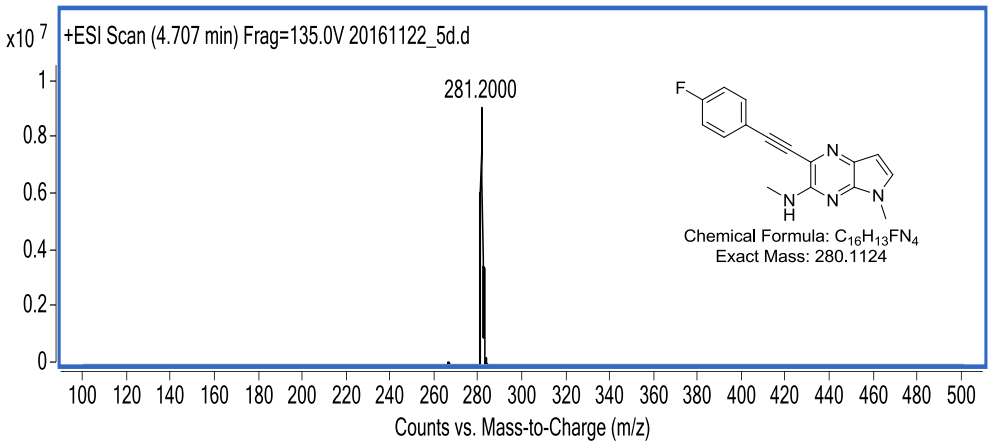

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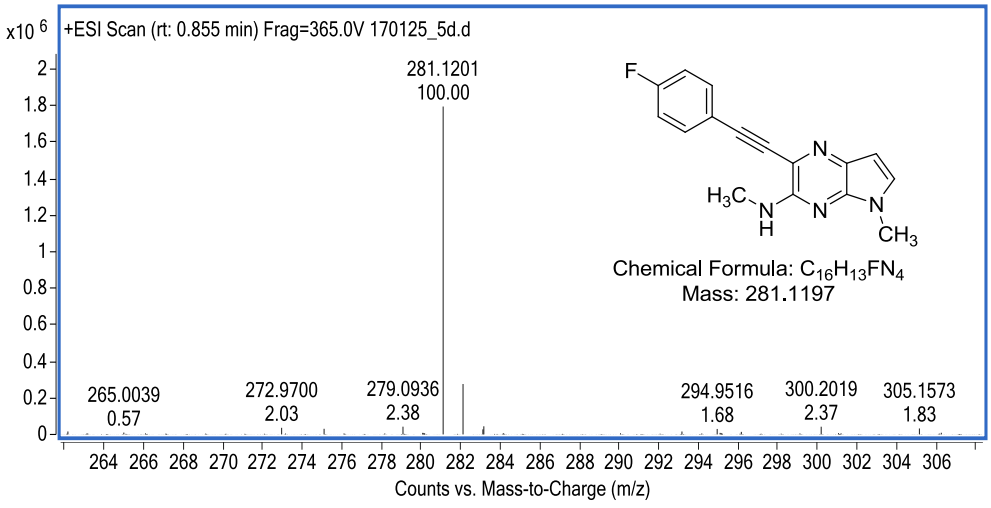

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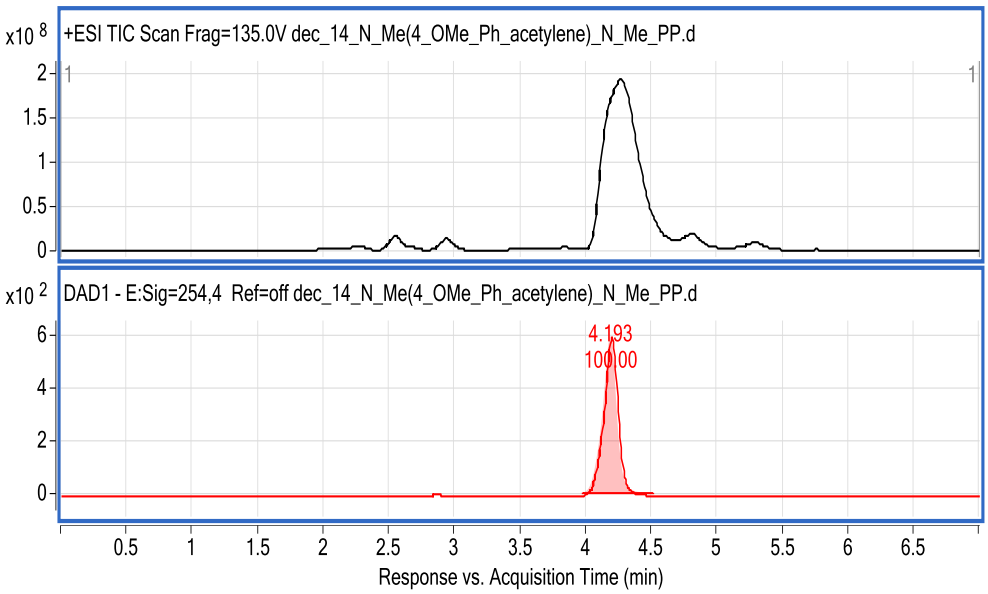

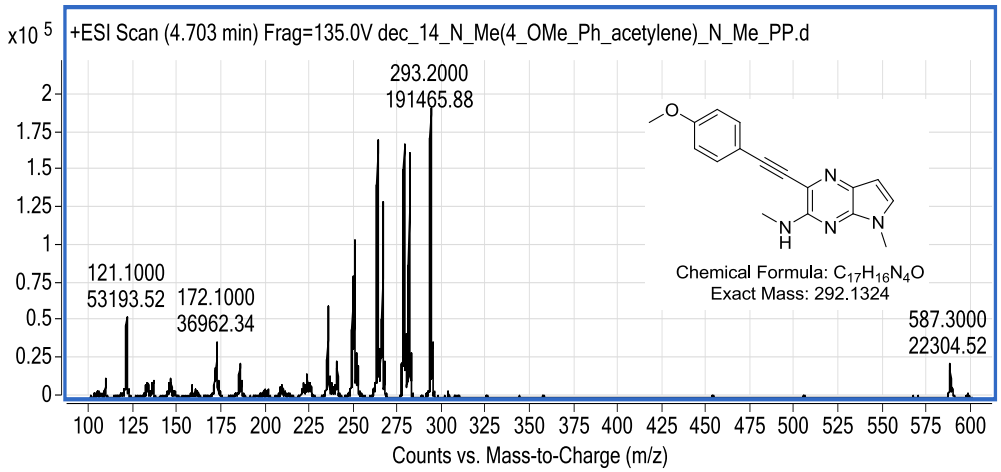

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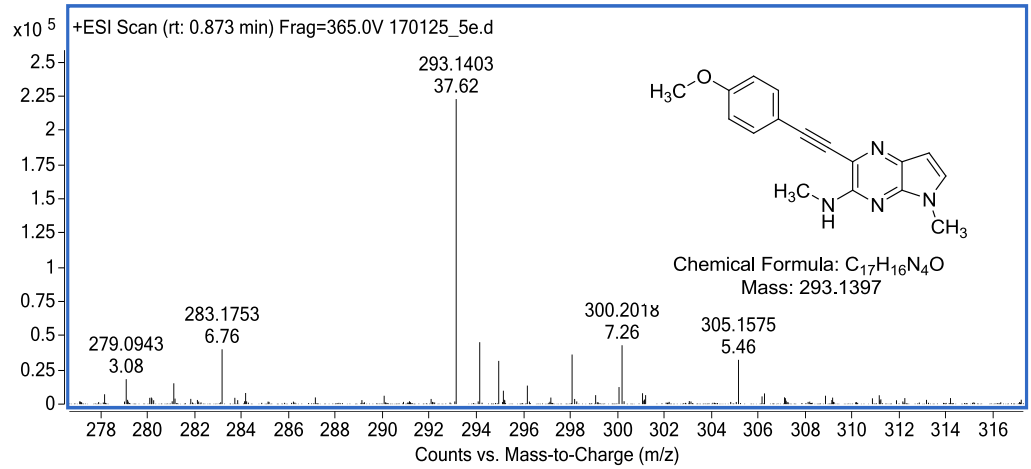

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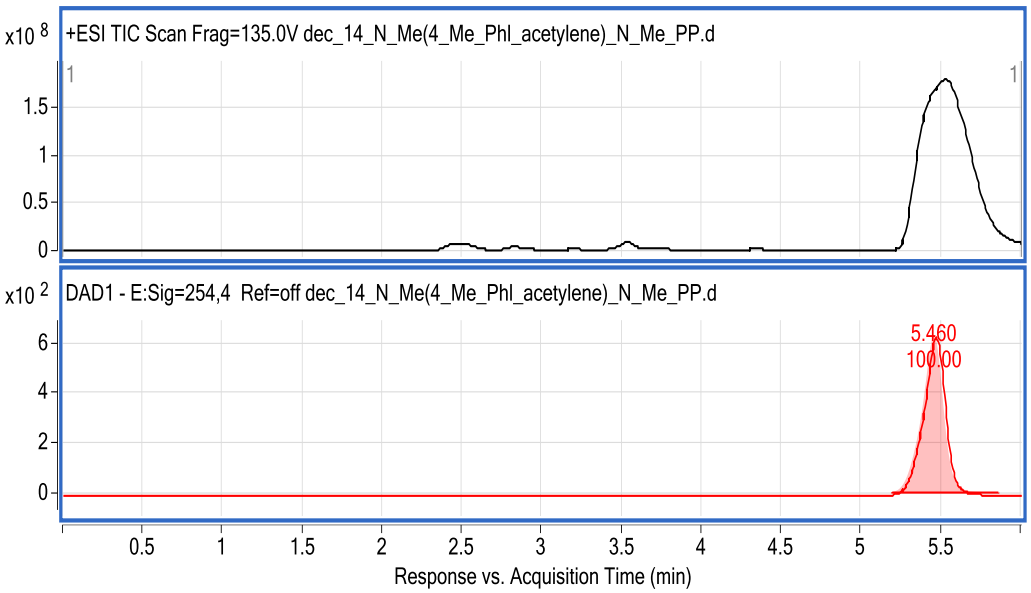

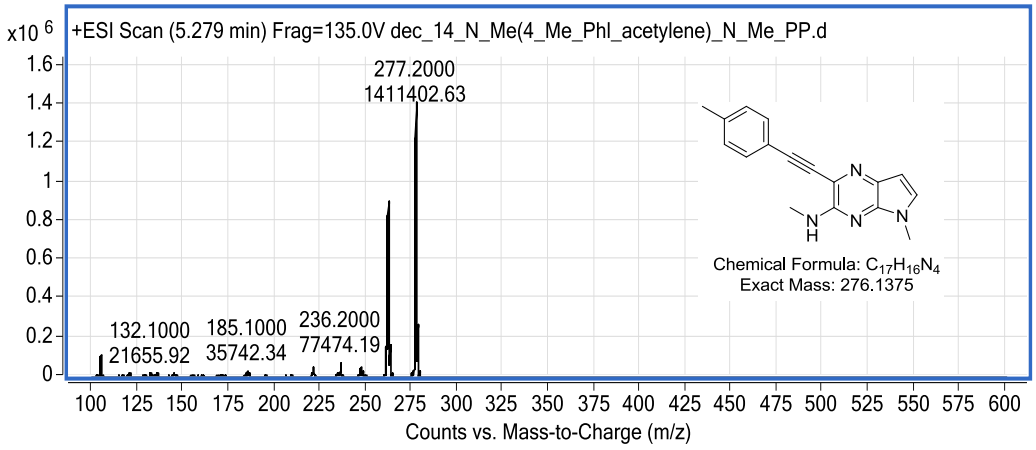

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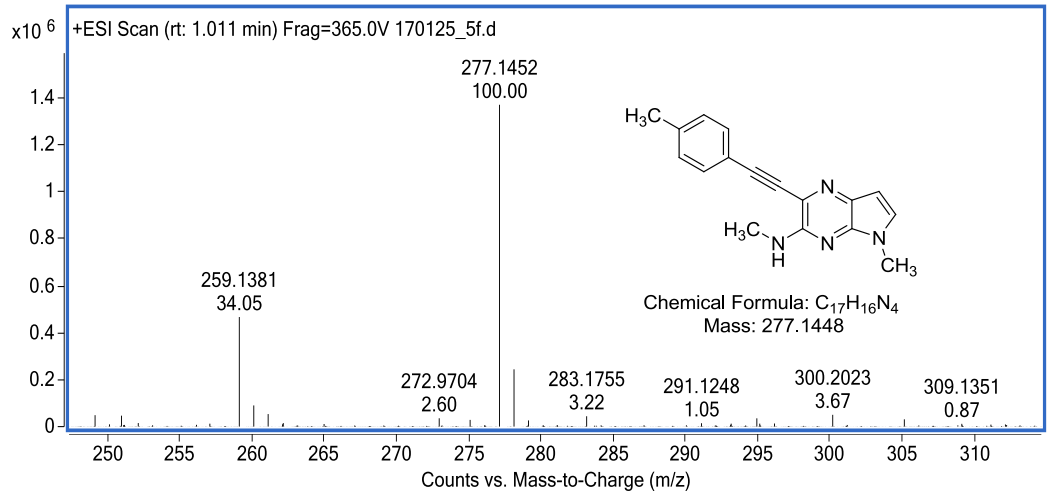

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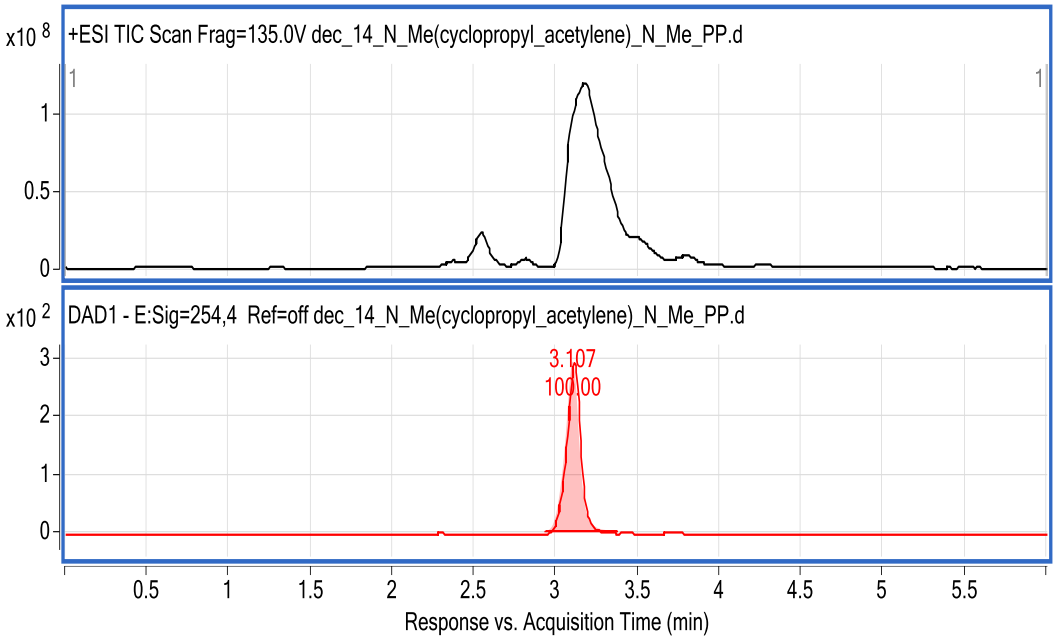

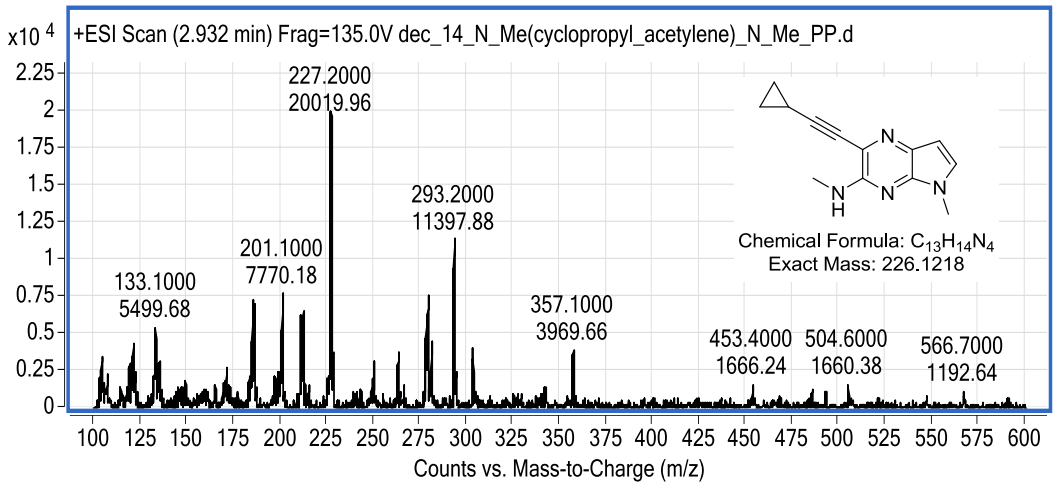

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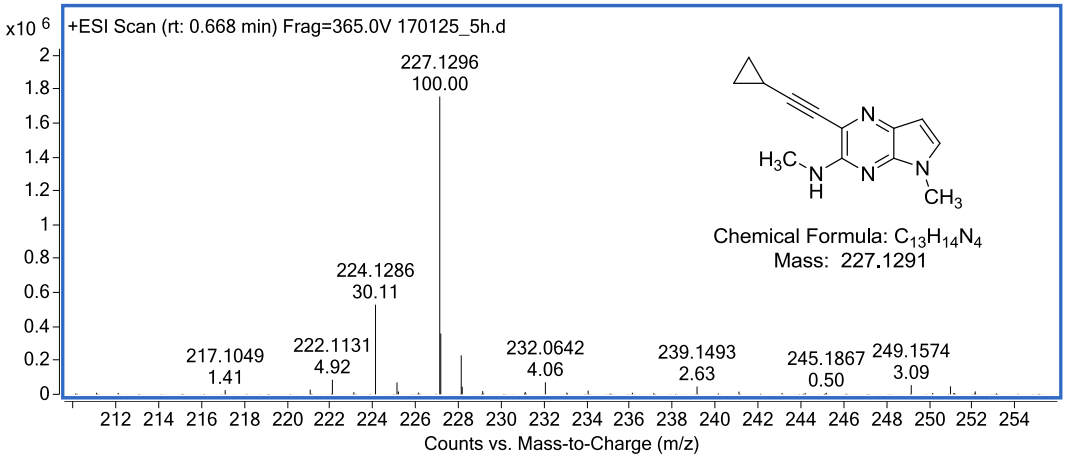

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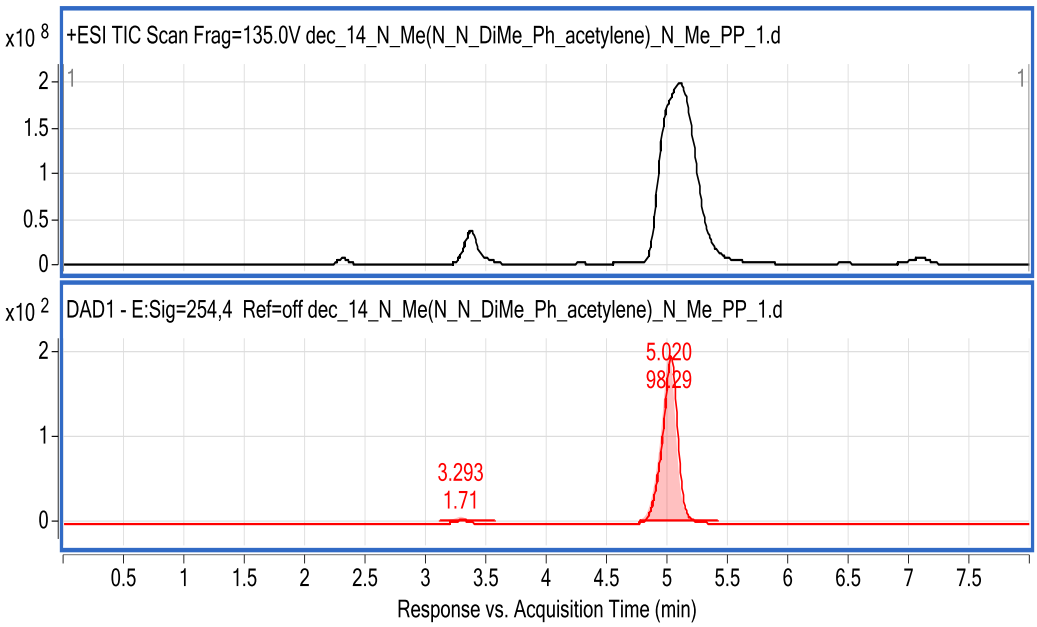
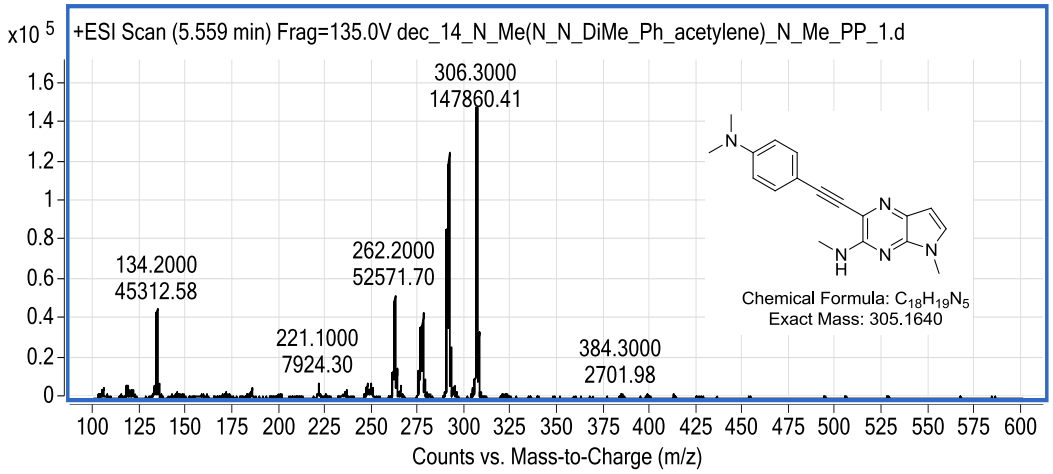
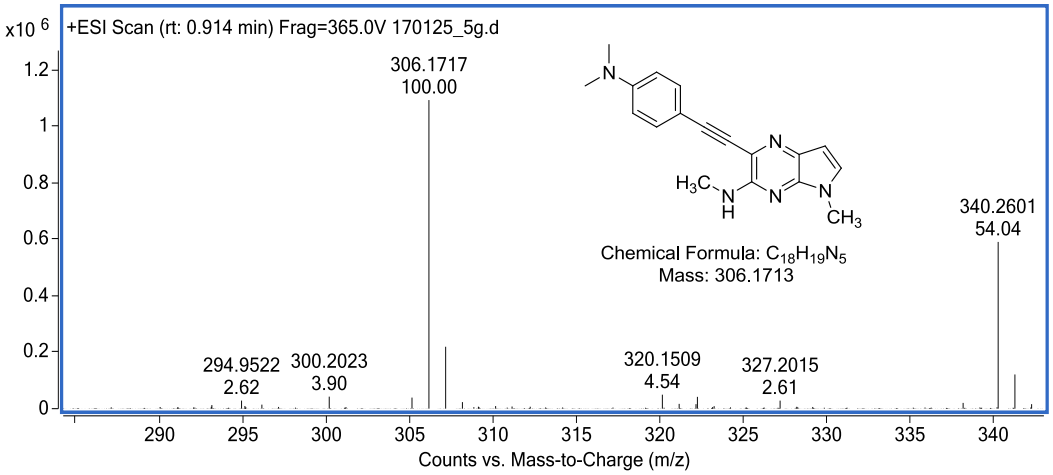
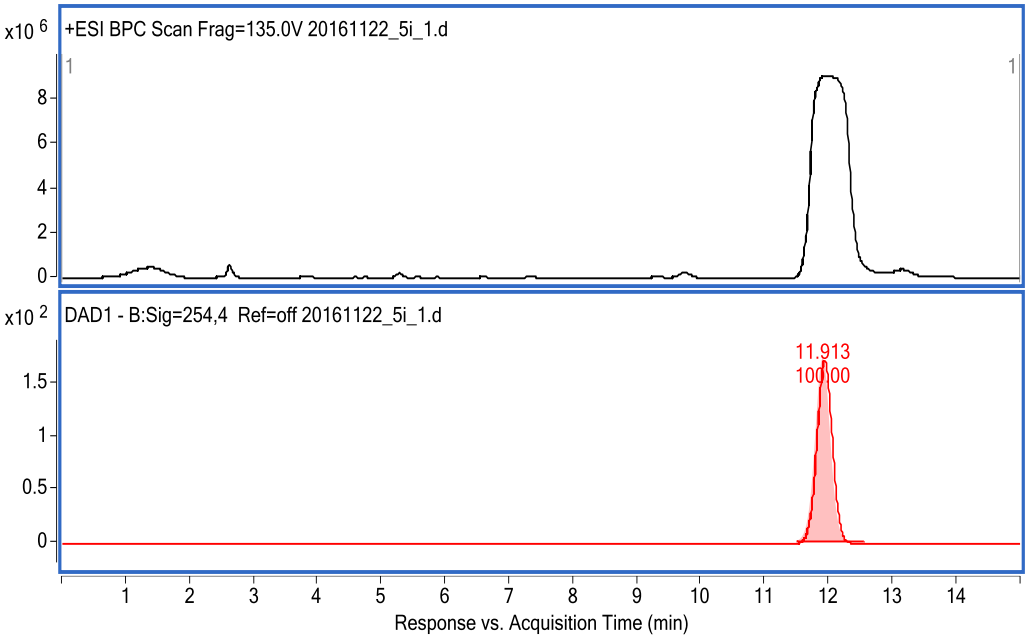


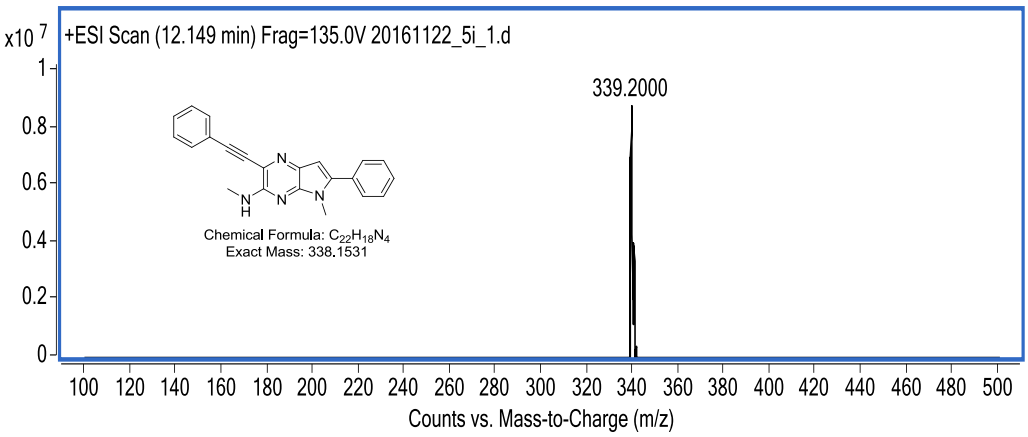


LC/MS – 5h

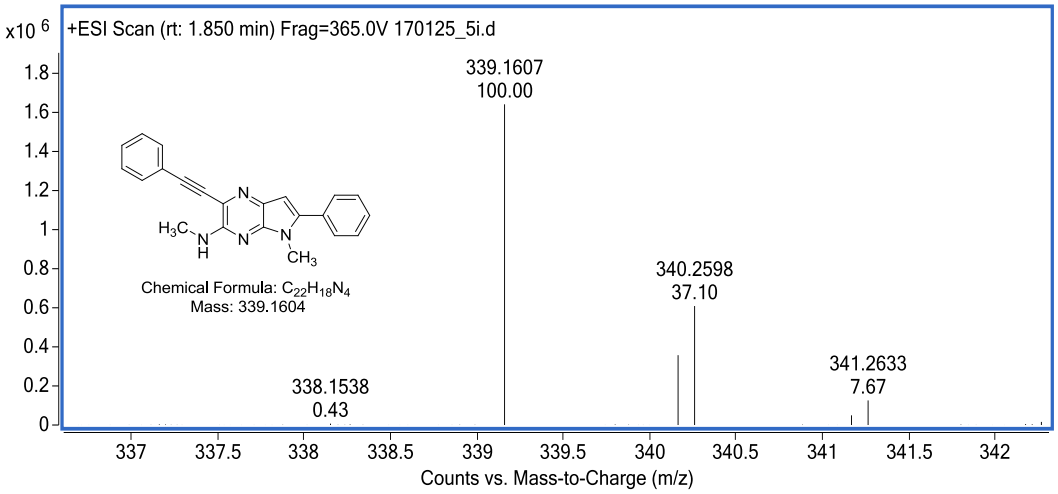


HR/MS – 5h





LC/MS – 5i



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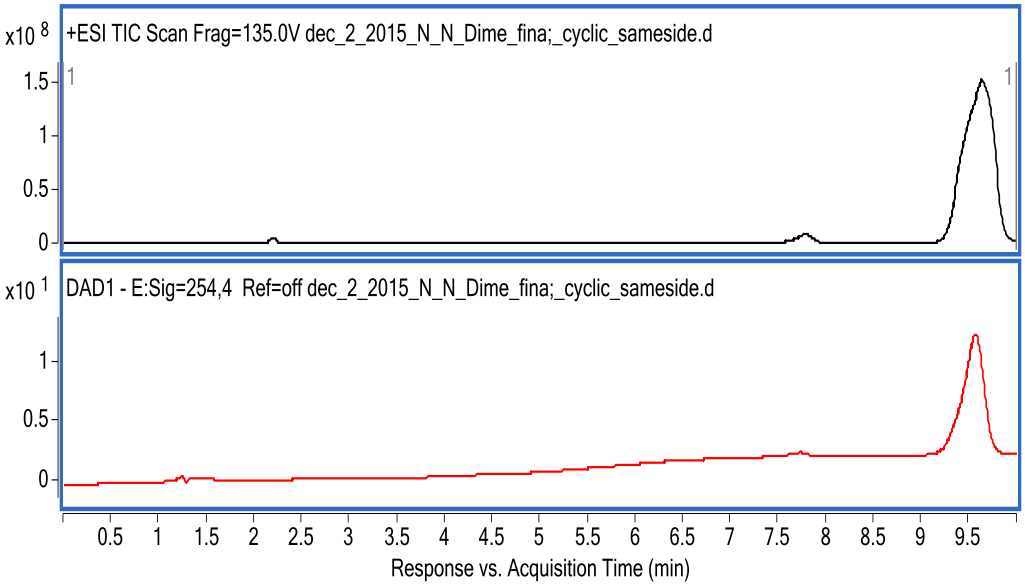
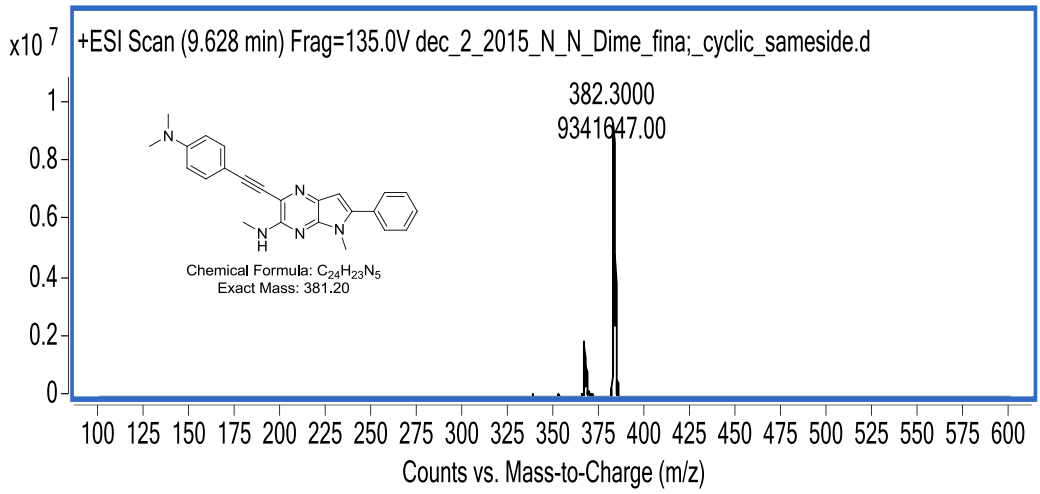
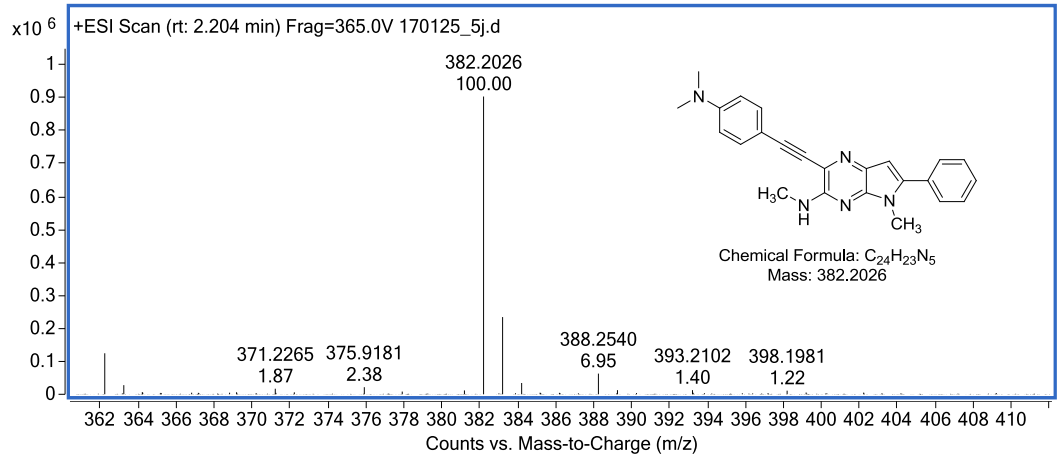




LC/MS – 5j



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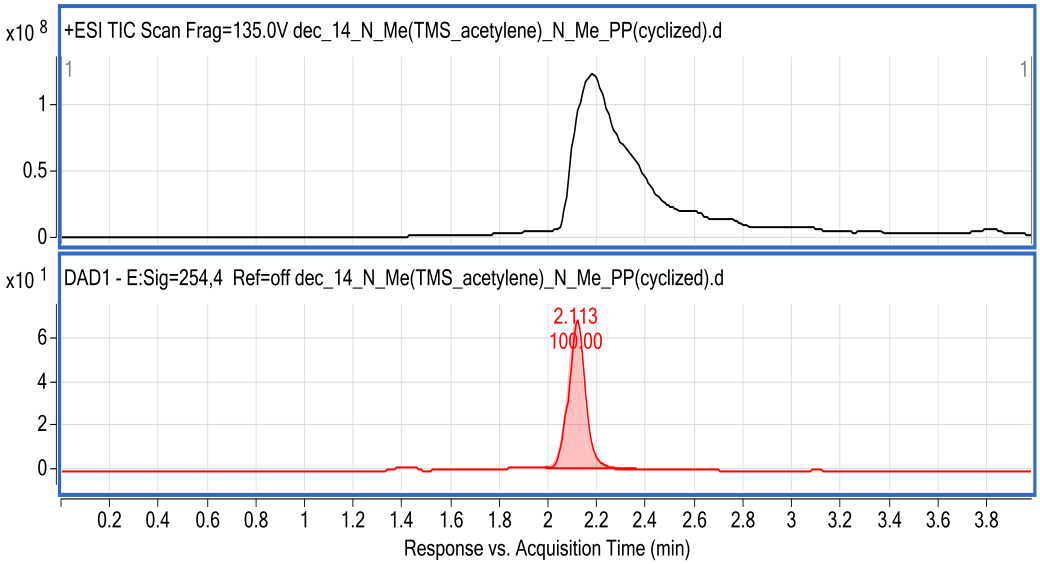
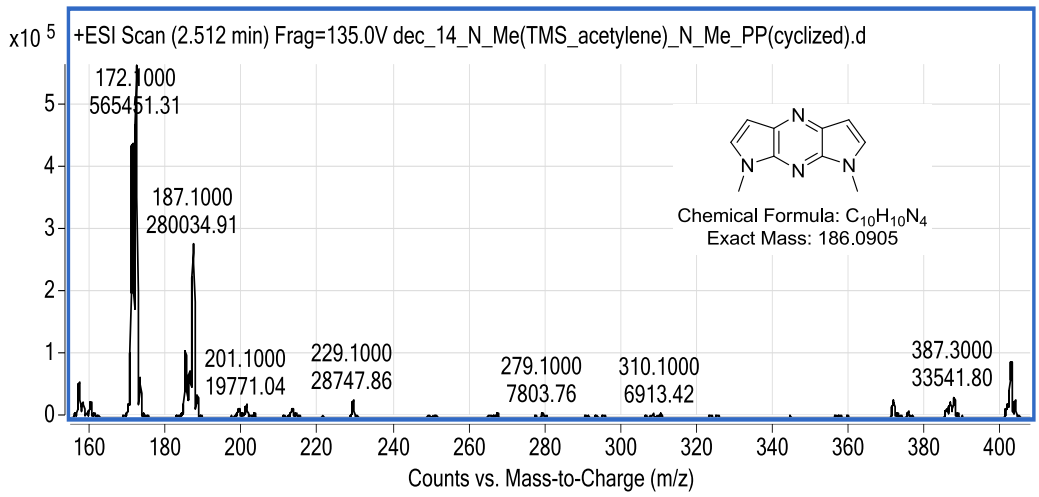
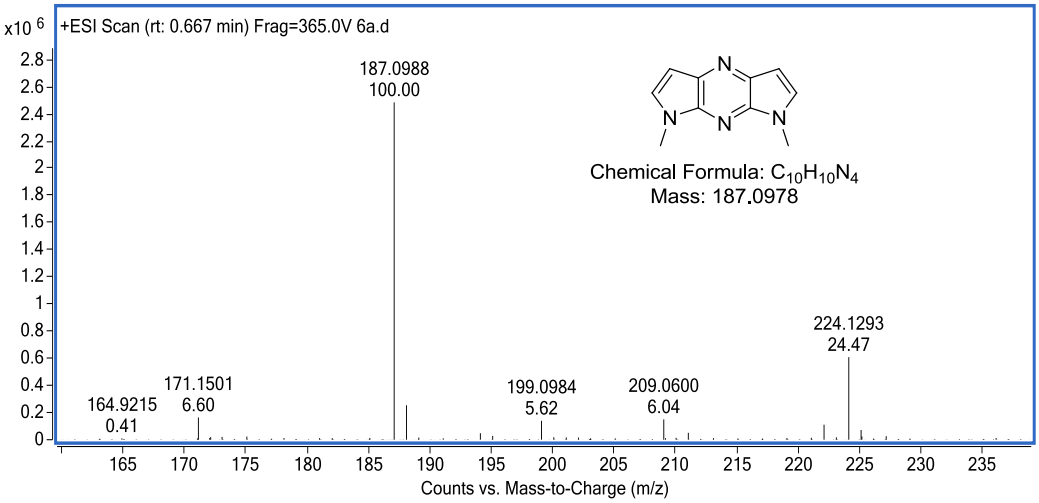
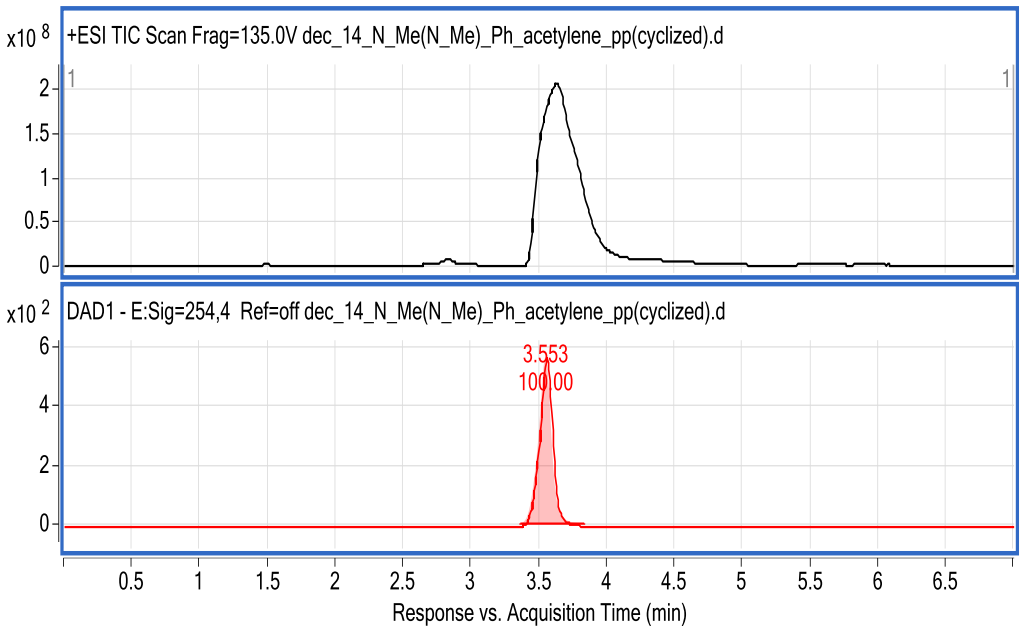


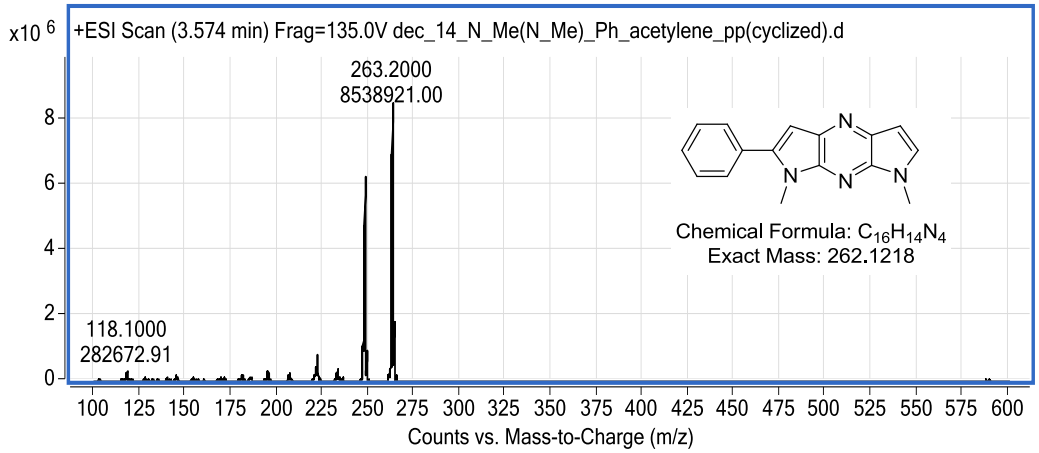


LC/MS – 6a



HR/MS – 6a





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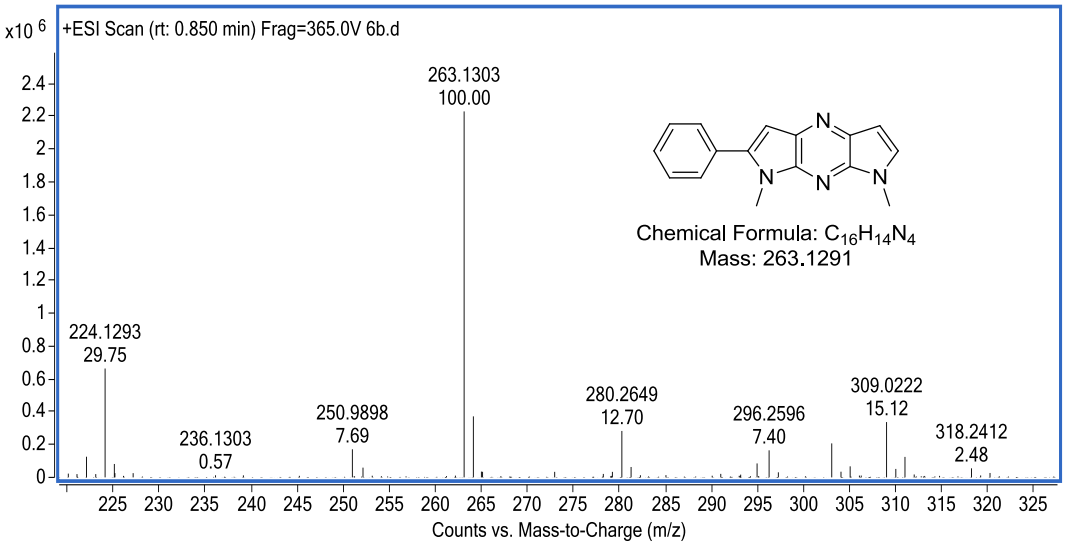

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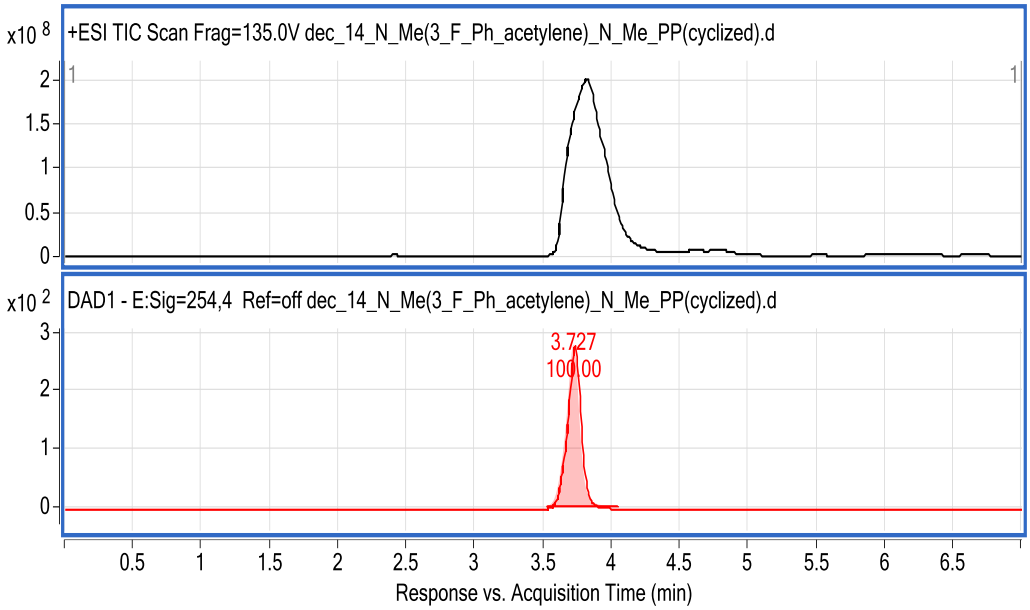

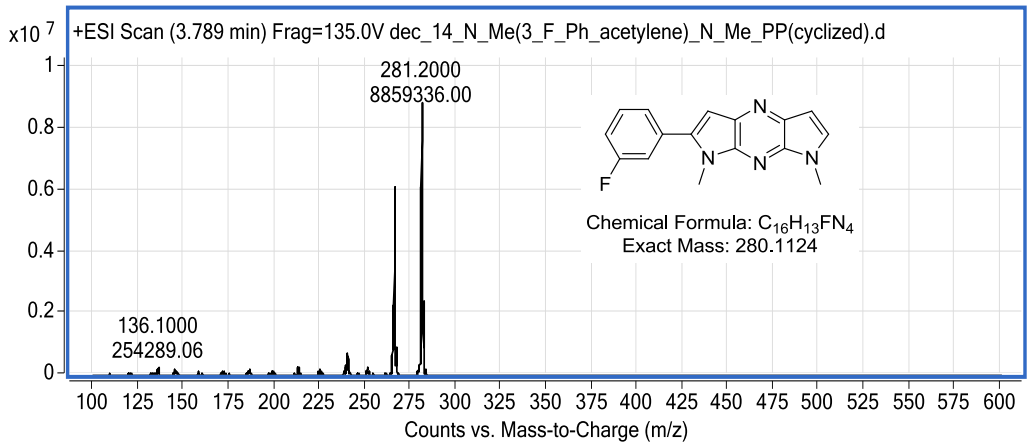

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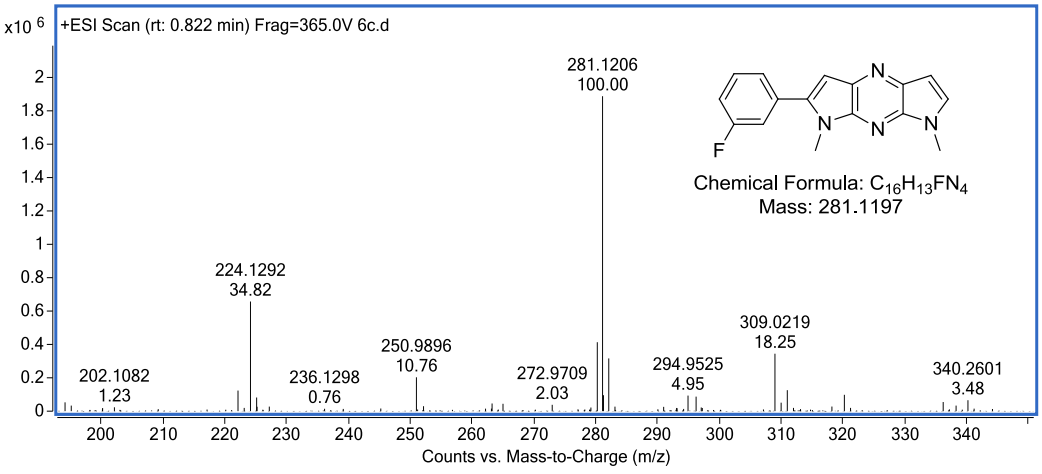
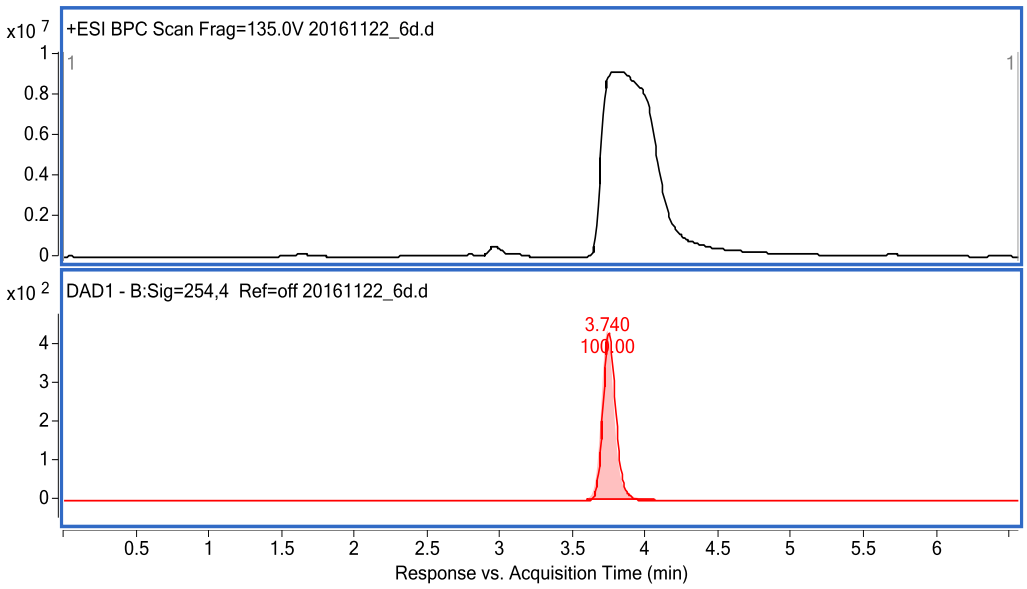
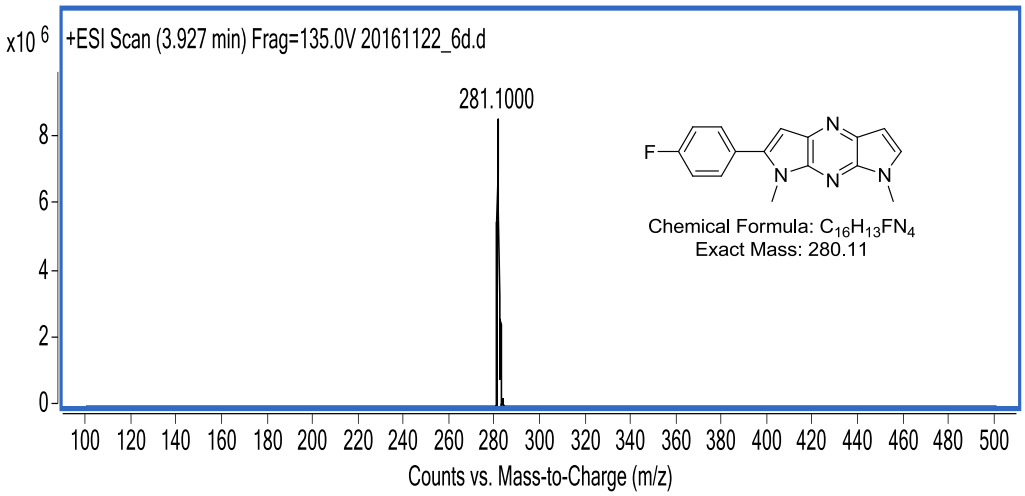
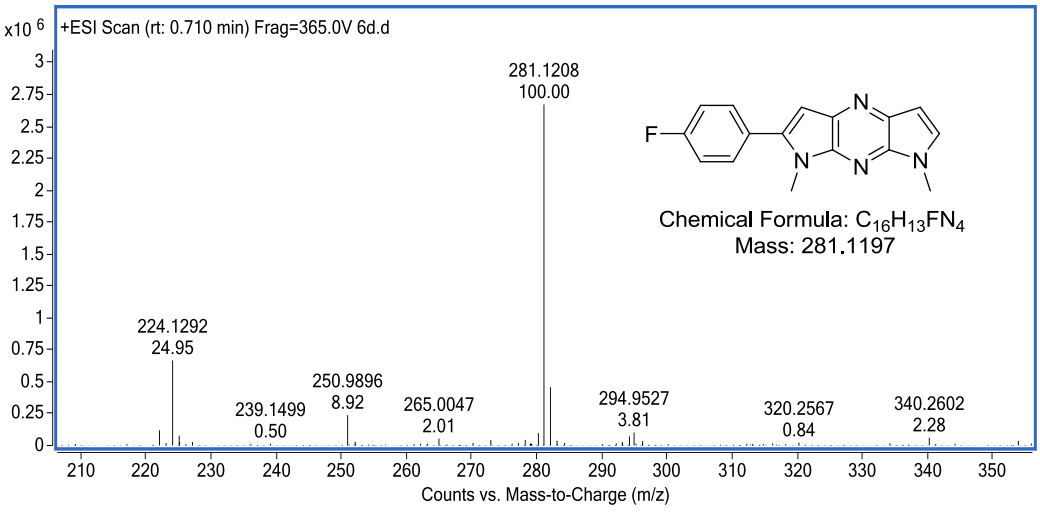


HR/MS – 6c

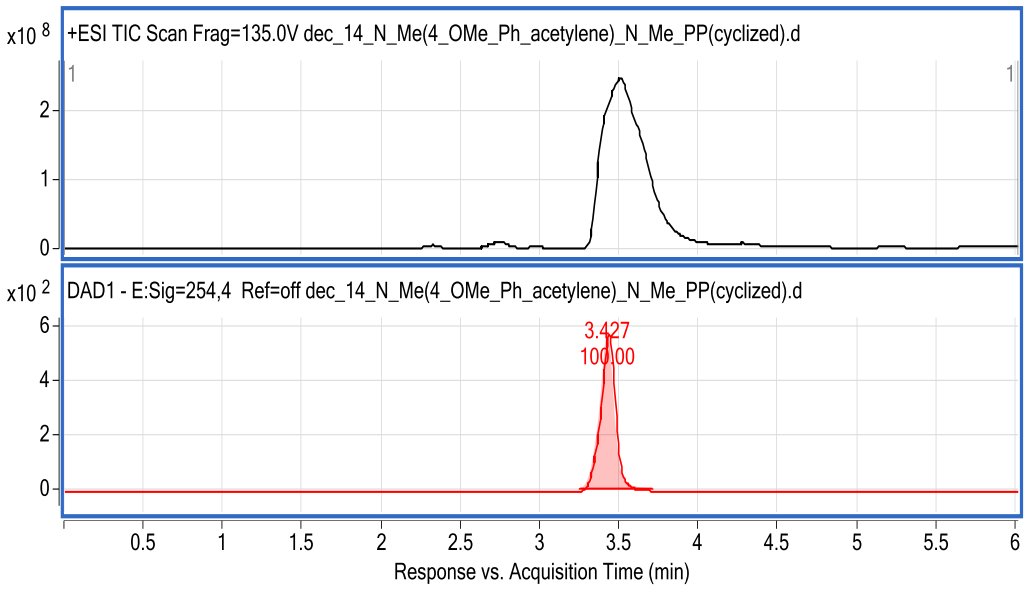


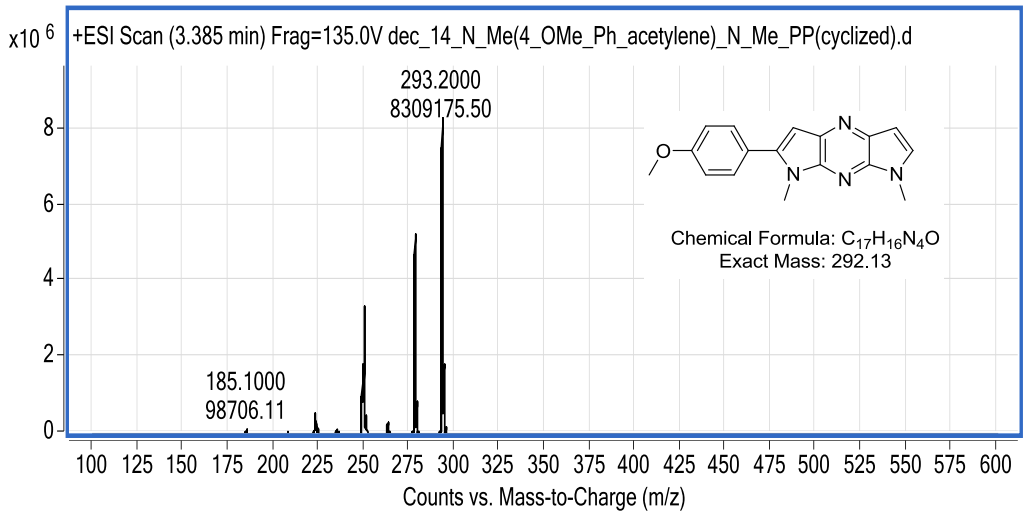


LC/MS – 6d

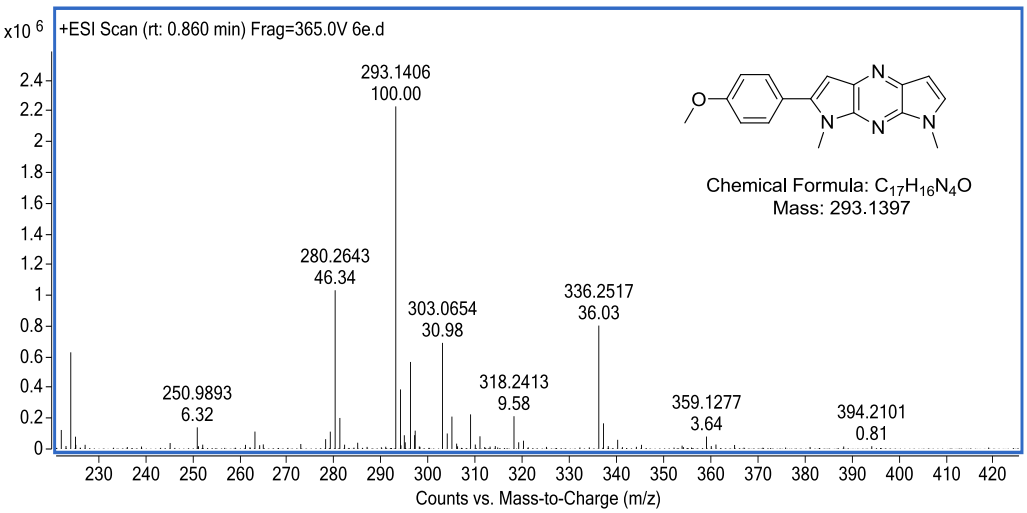


HR/MS – 6d

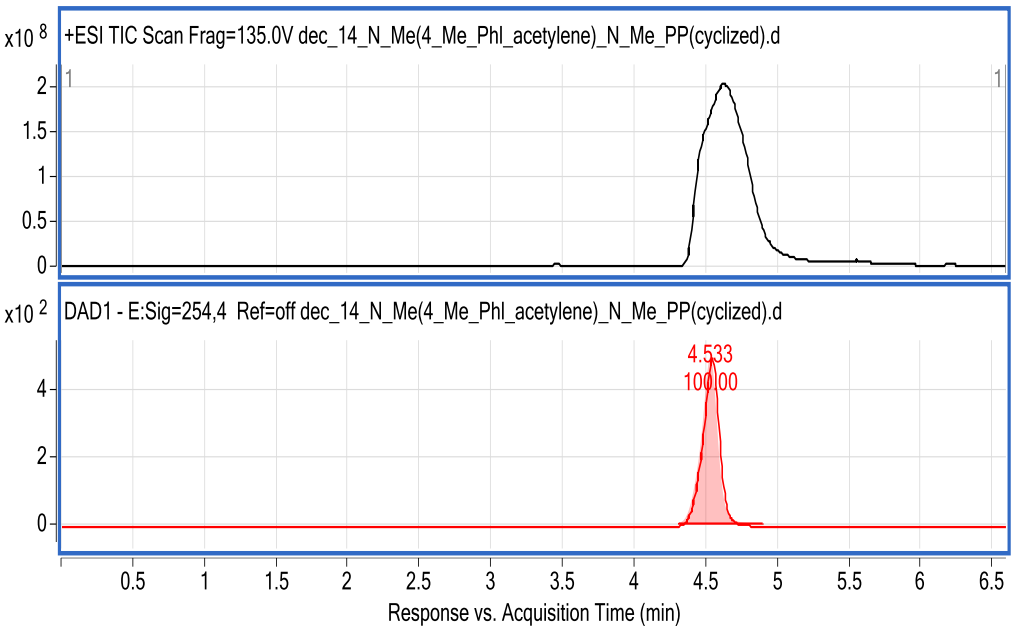


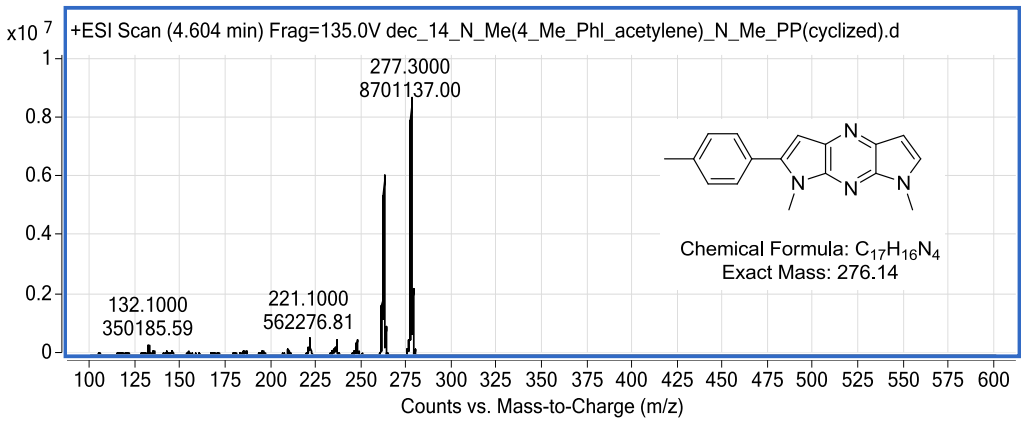


LC/MS – 6e

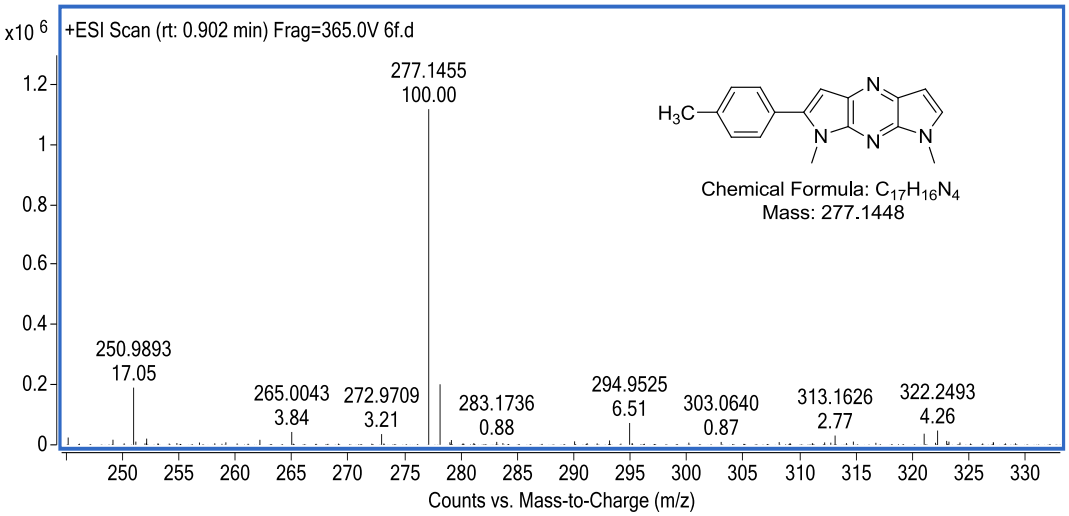


HR/MS – 6e

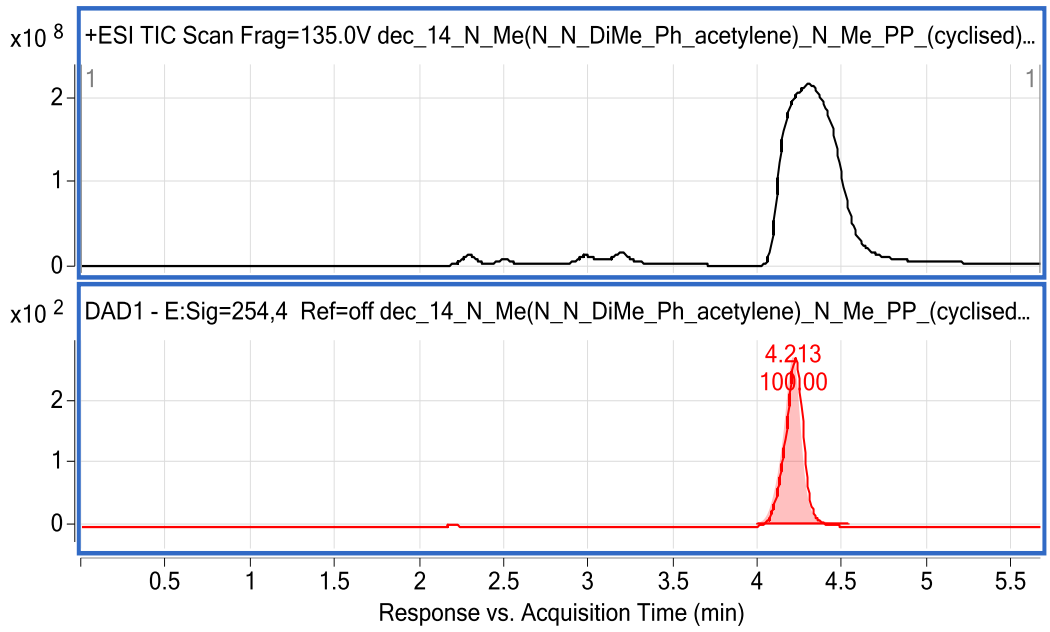


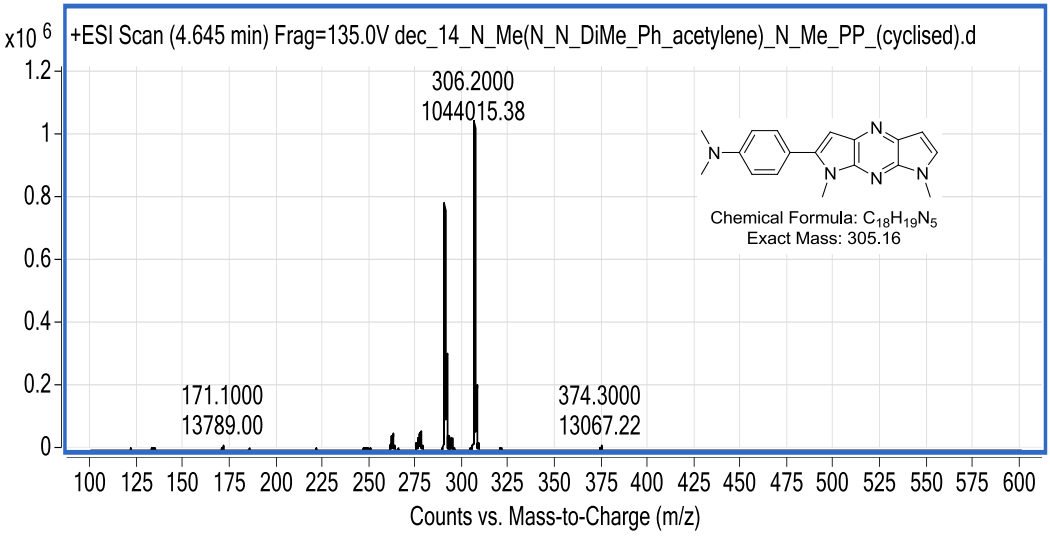


LC/MS – 6f

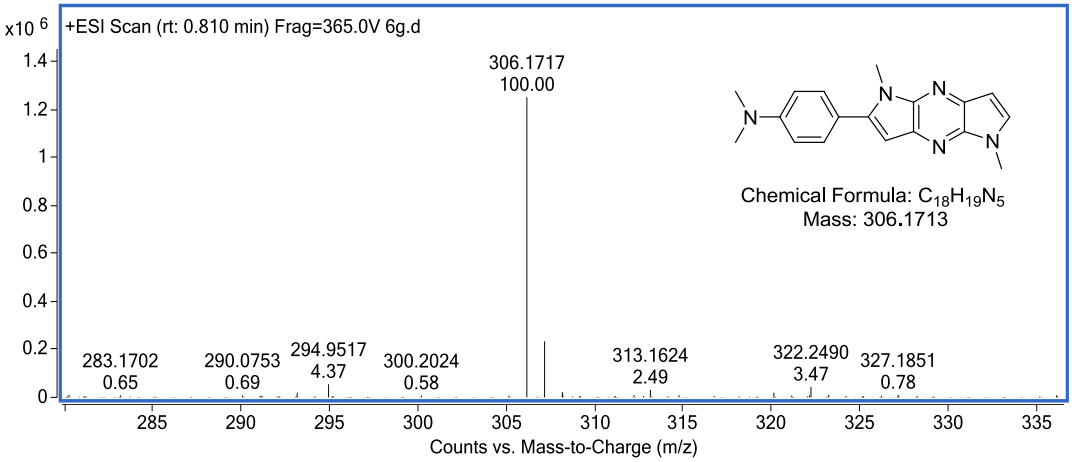


HR/MS – 6f

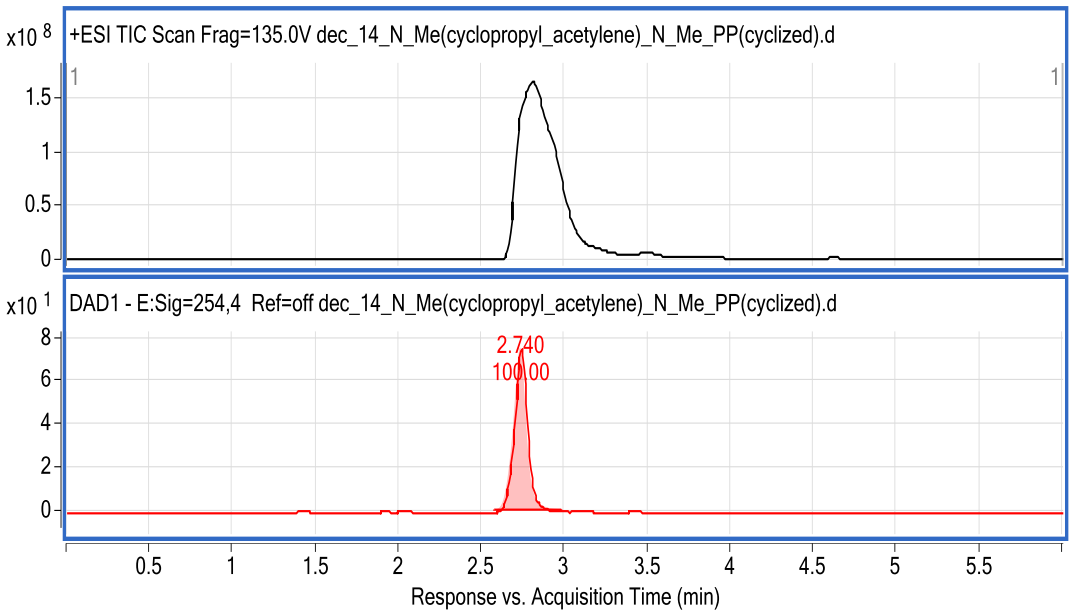


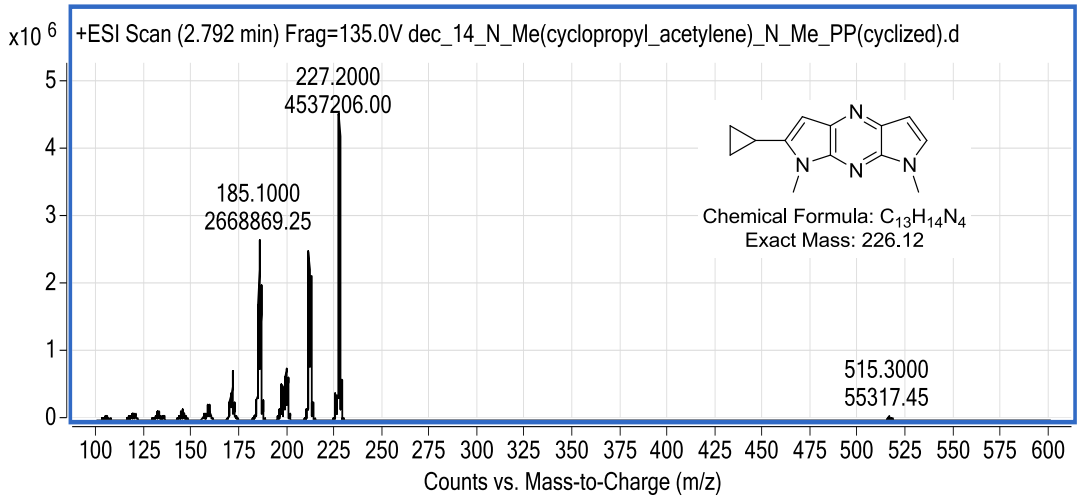


LC/MS – 6g

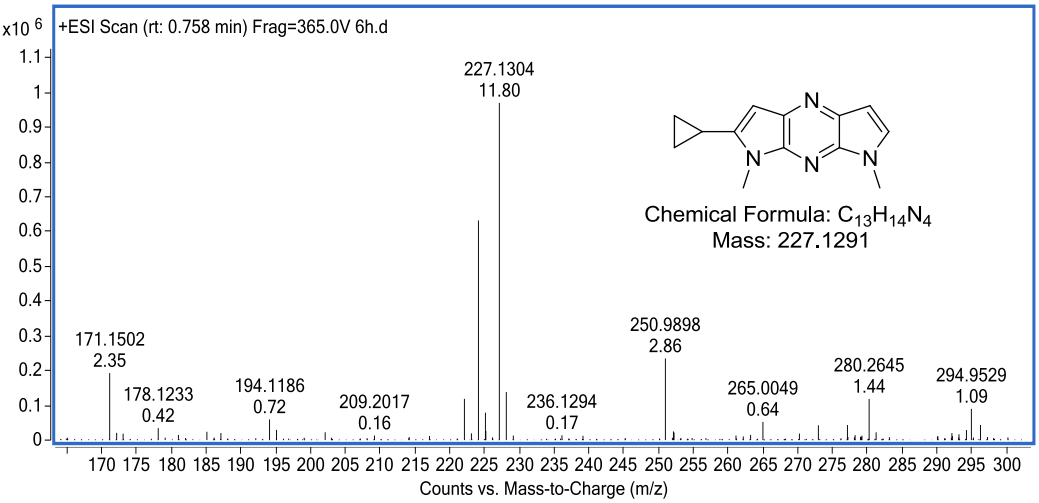


HR/MS – 6g

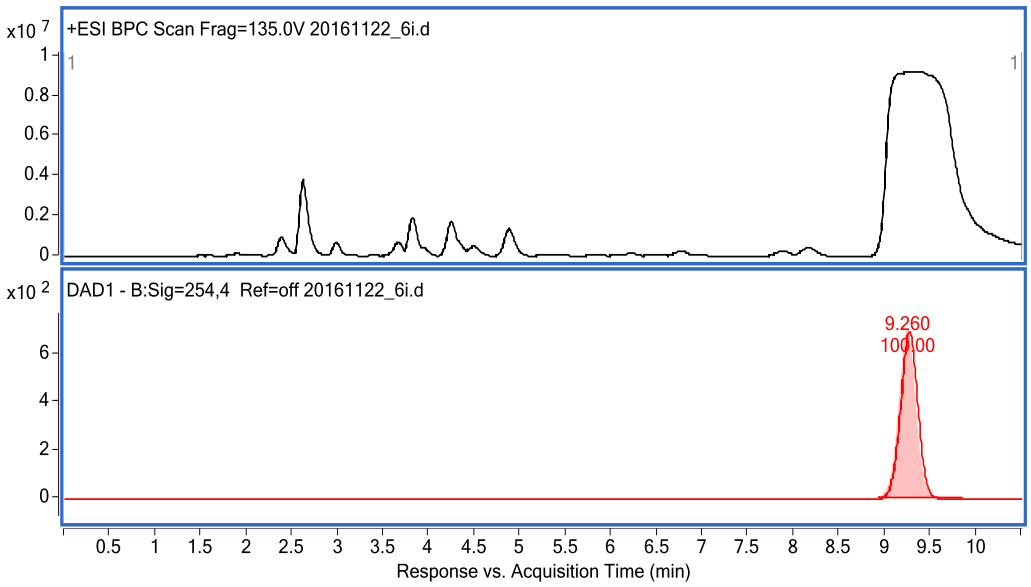


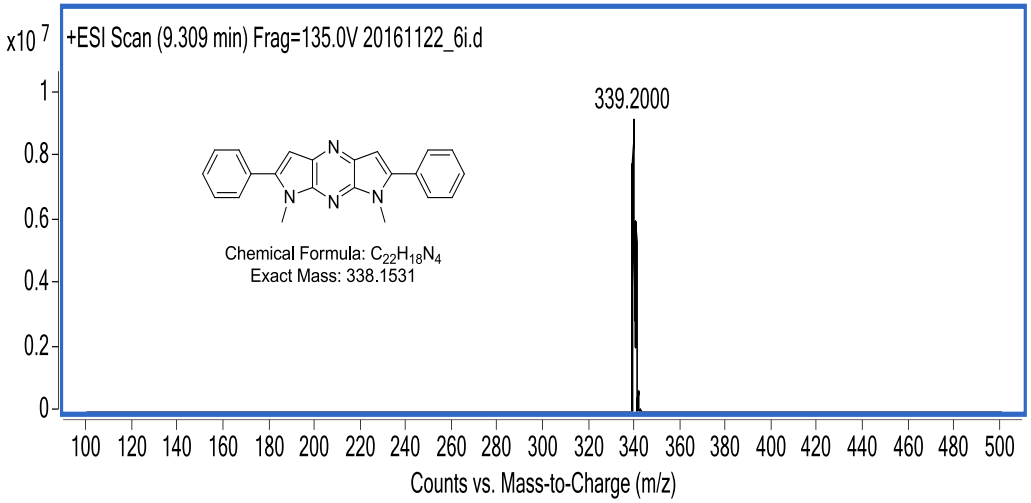


LC/MS – 6h

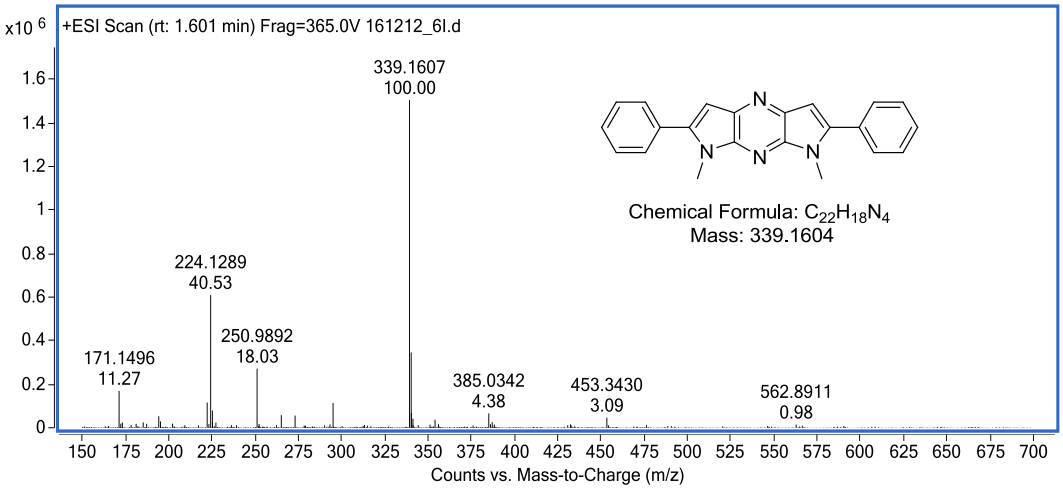


HR/MS – 6h

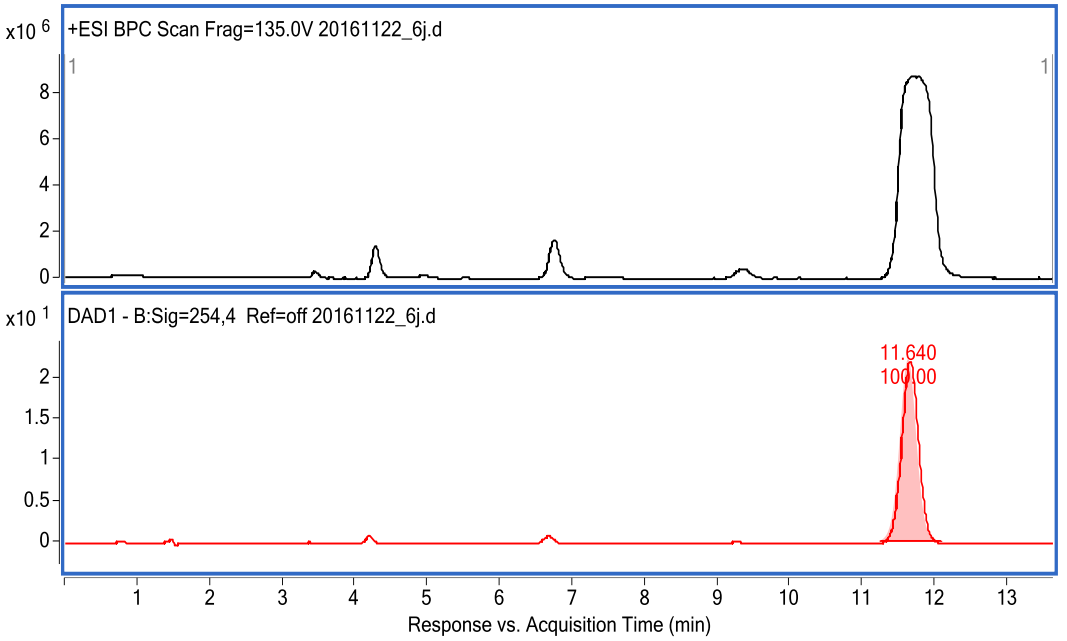


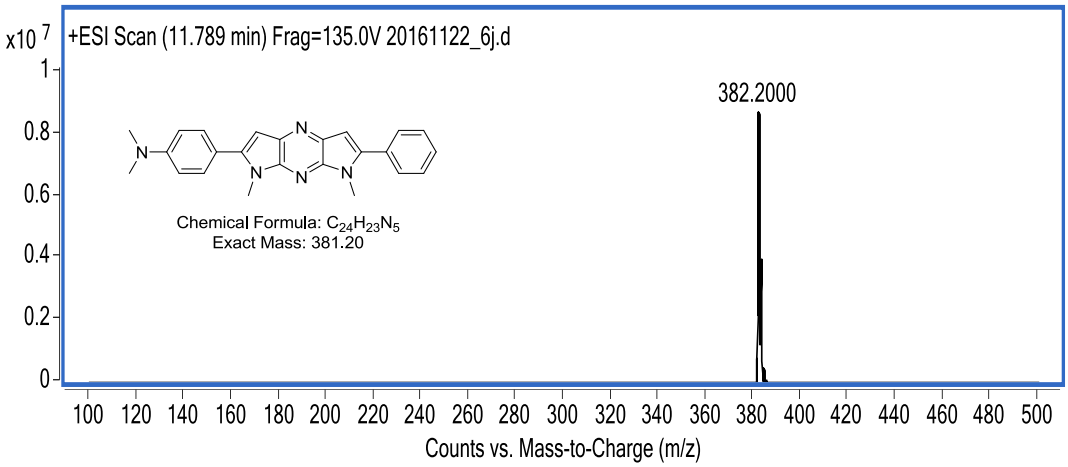


LC/MS – 6i



HR/MS – 6i





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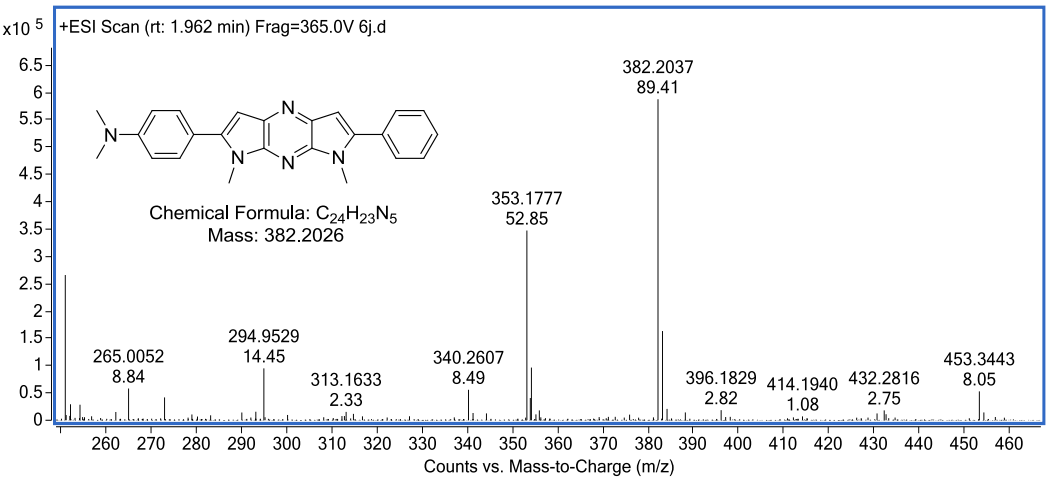
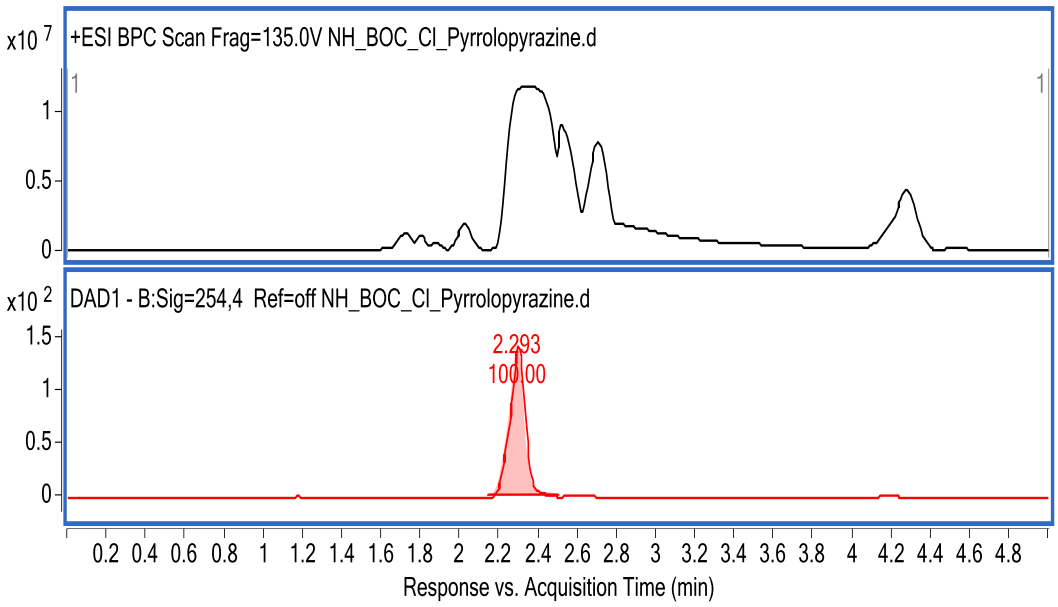
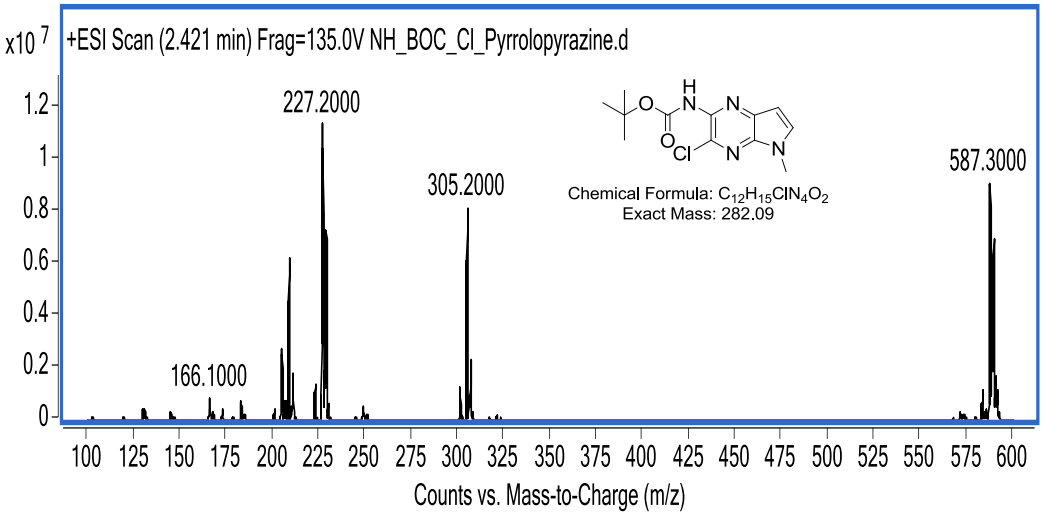
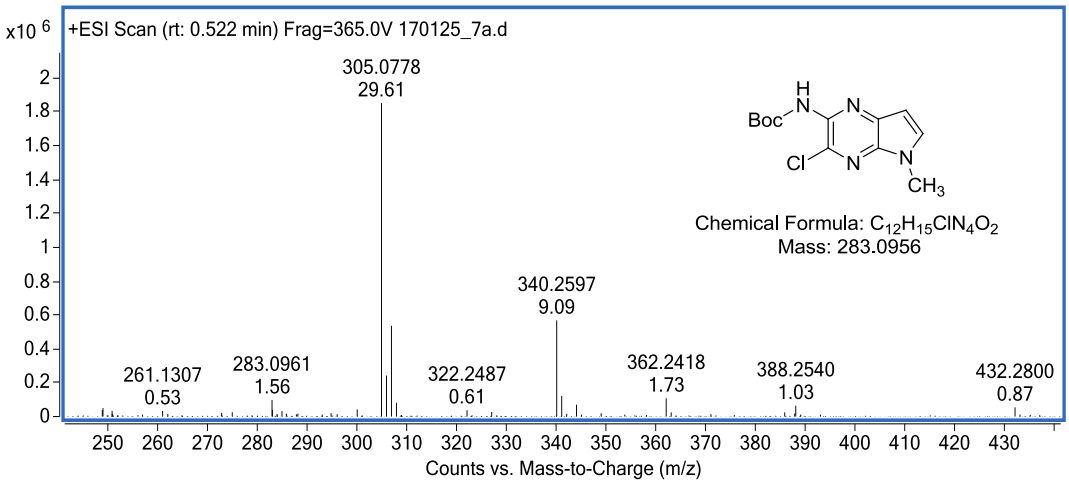


HR/MS – 6j

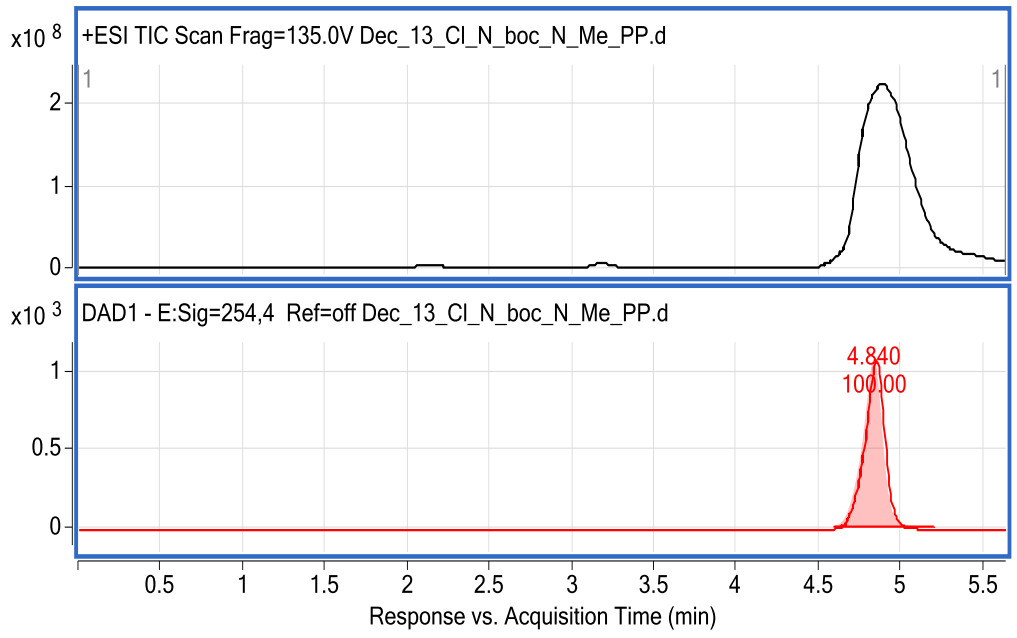


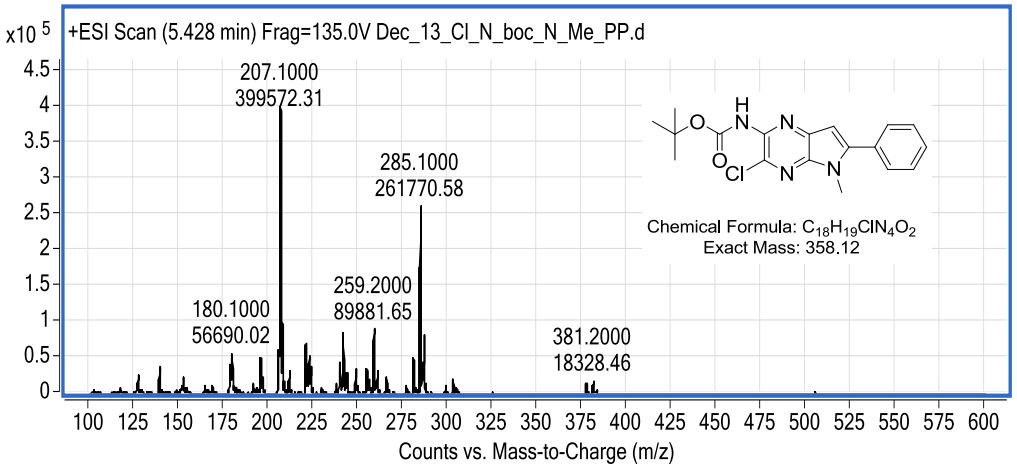


LC/MS – 7a

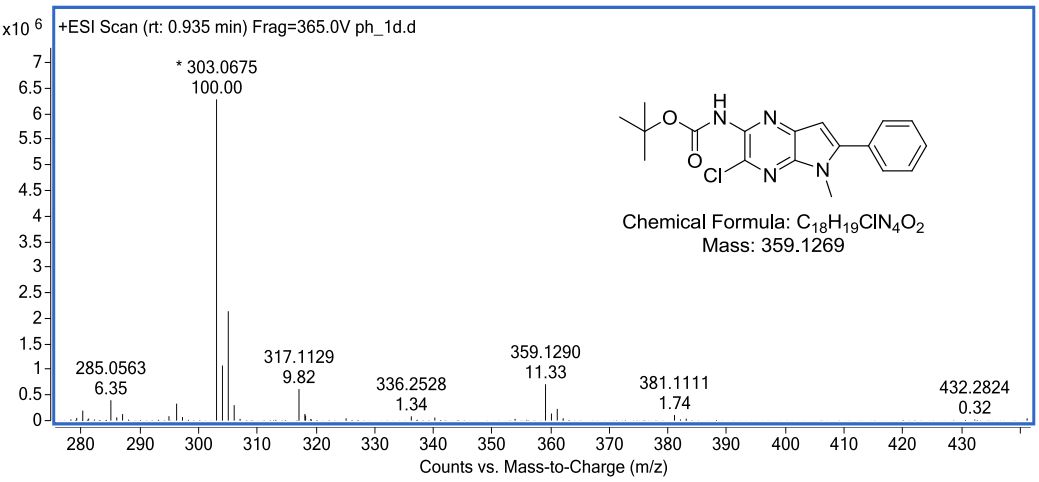


HR/MS – 7a

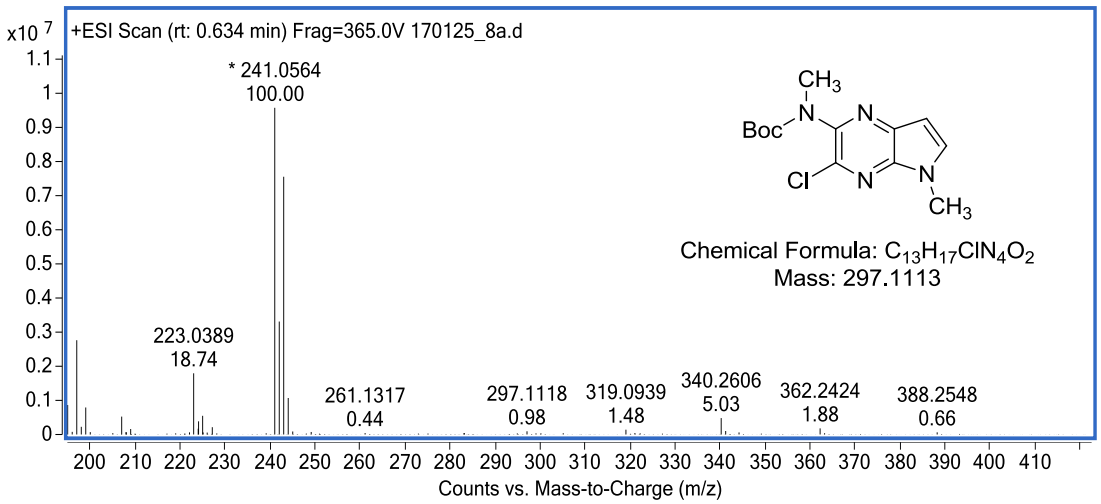




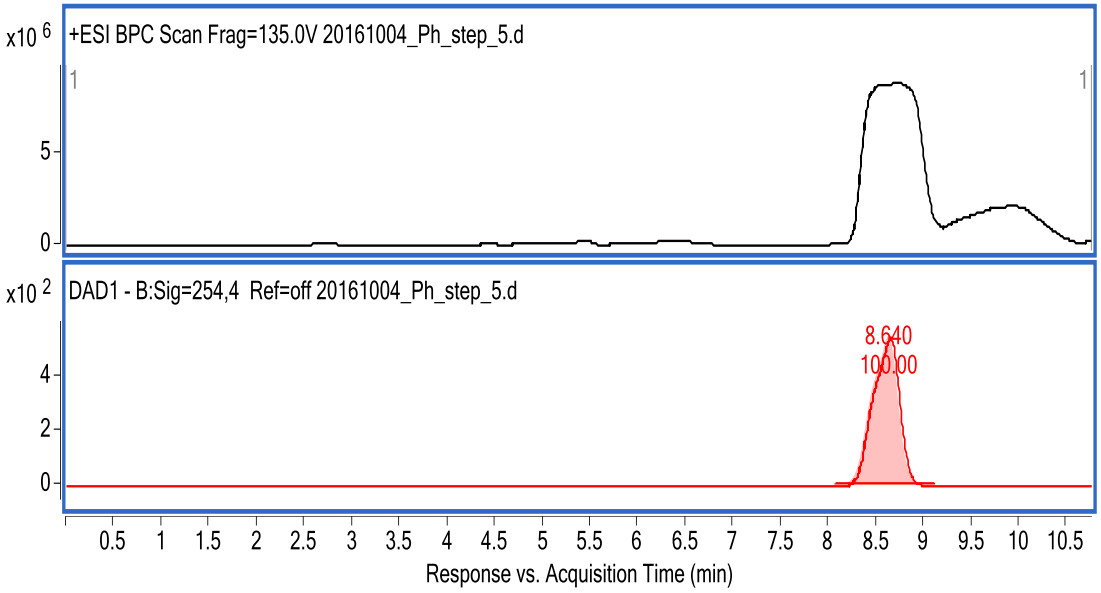
LC/MS – 7b

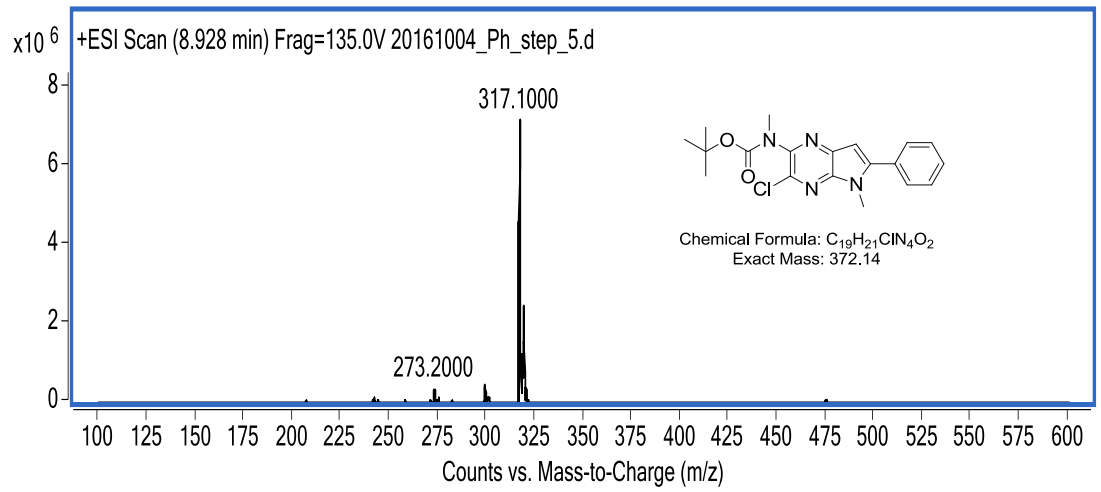


HR/MS – 7b

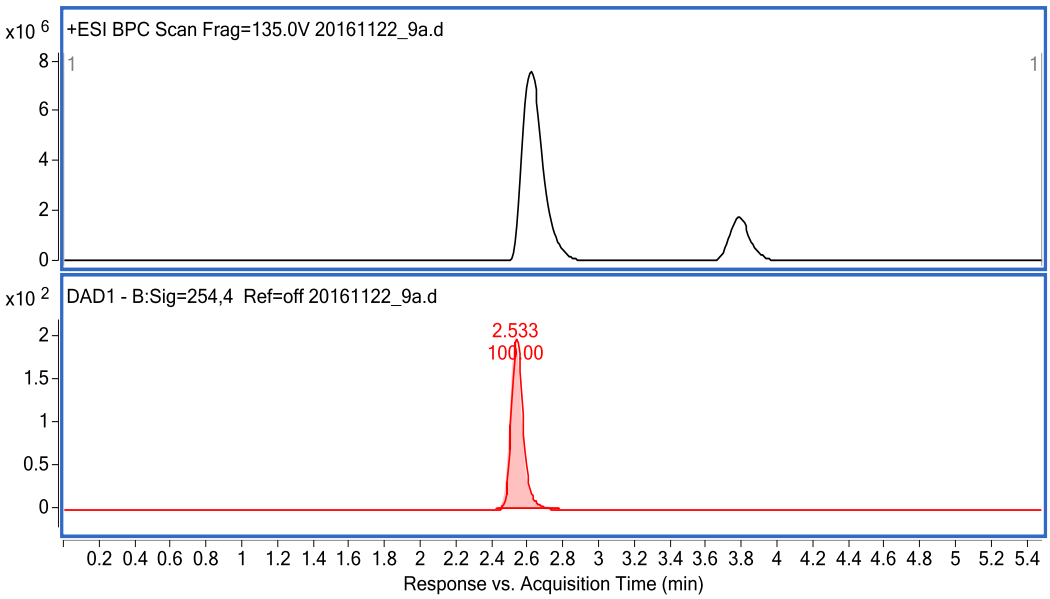


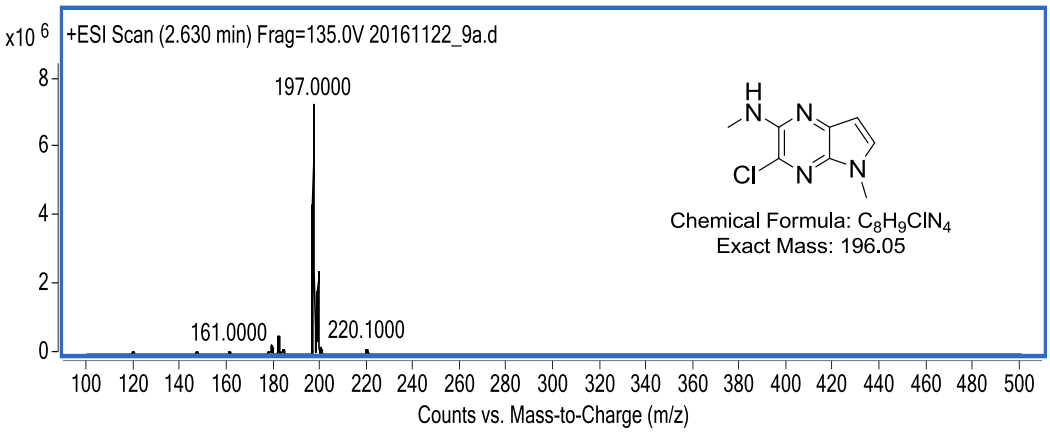
HR/MS – 8a



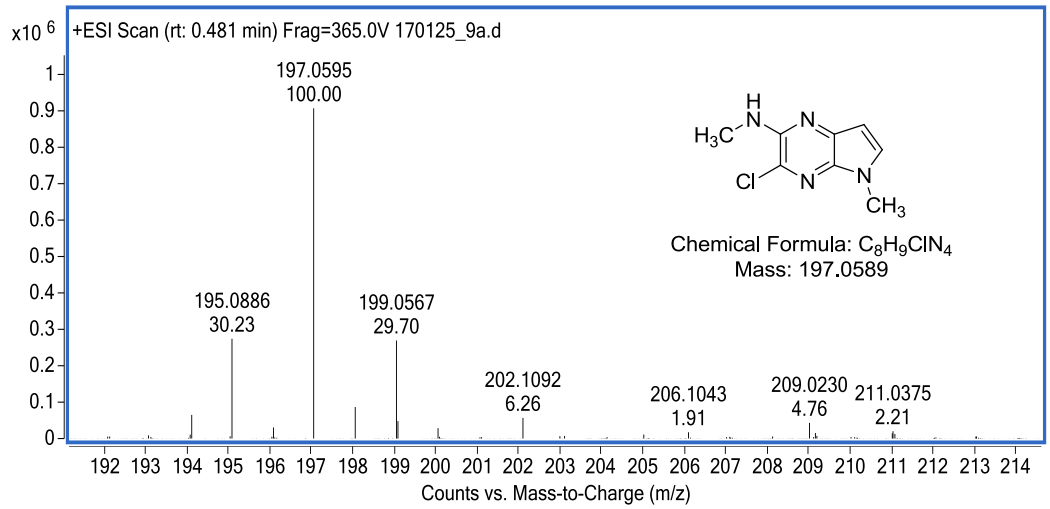


LC/MS – 8b

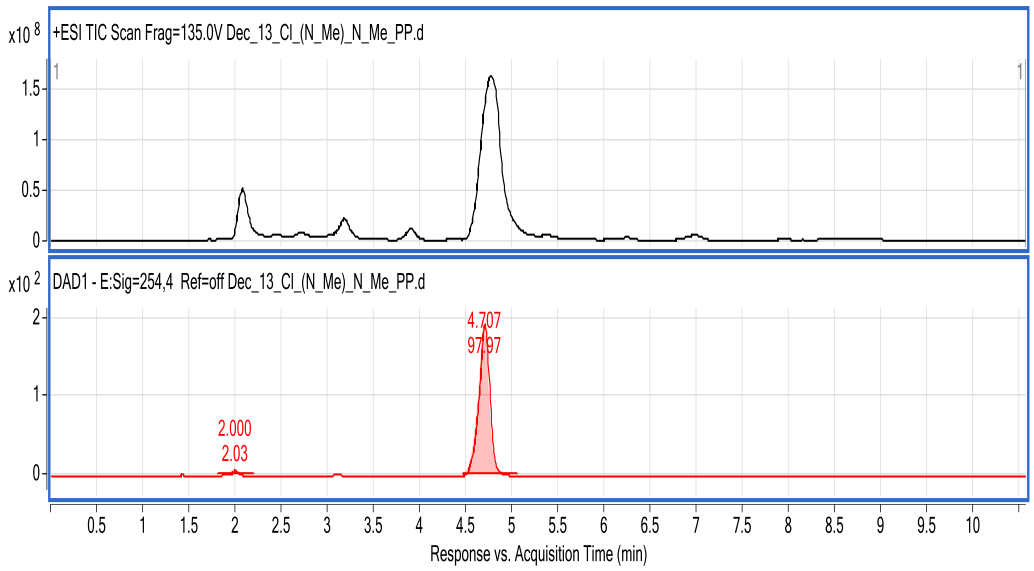


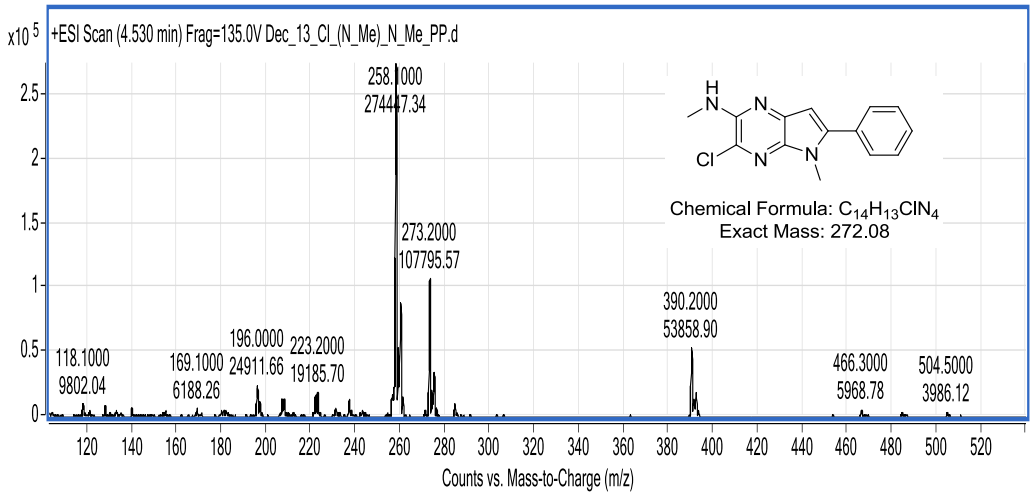


LC/MS – 9a

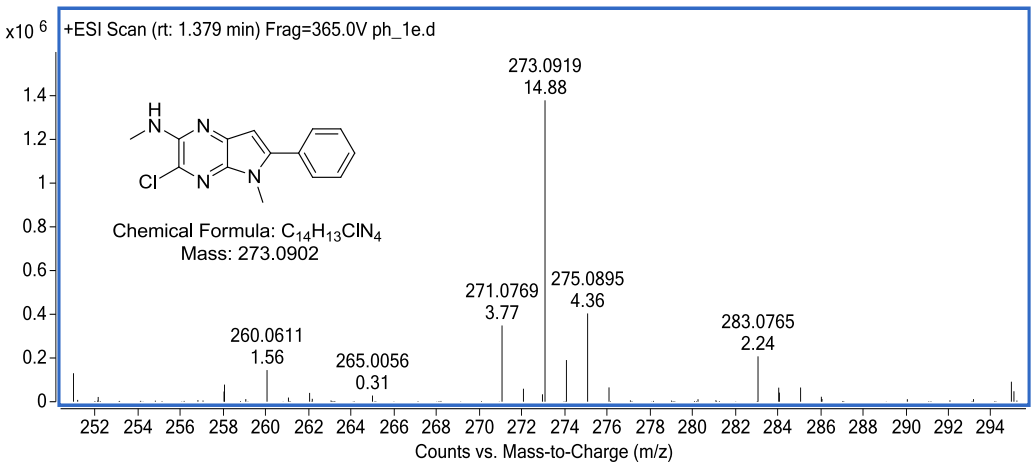


HR/MS – 9a

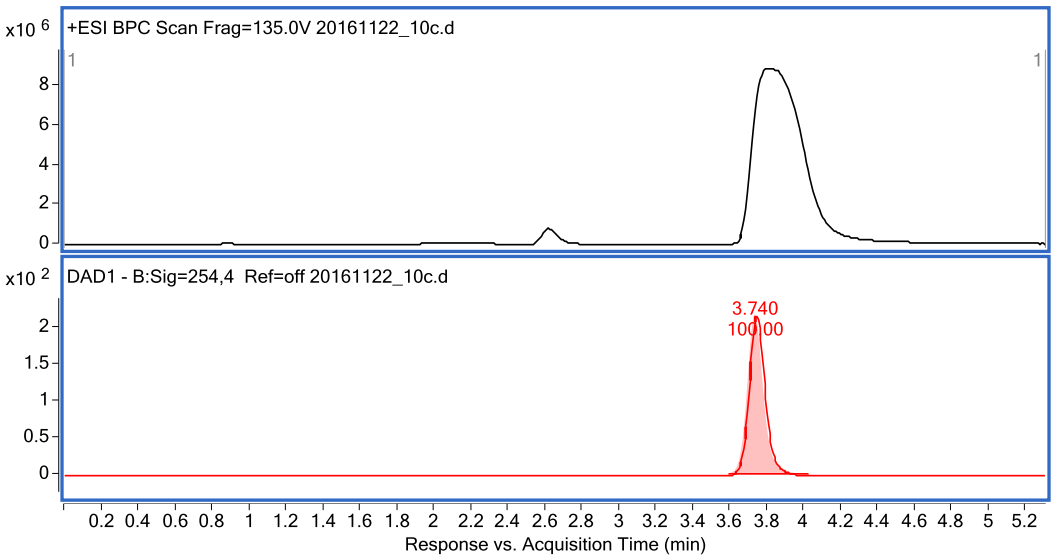


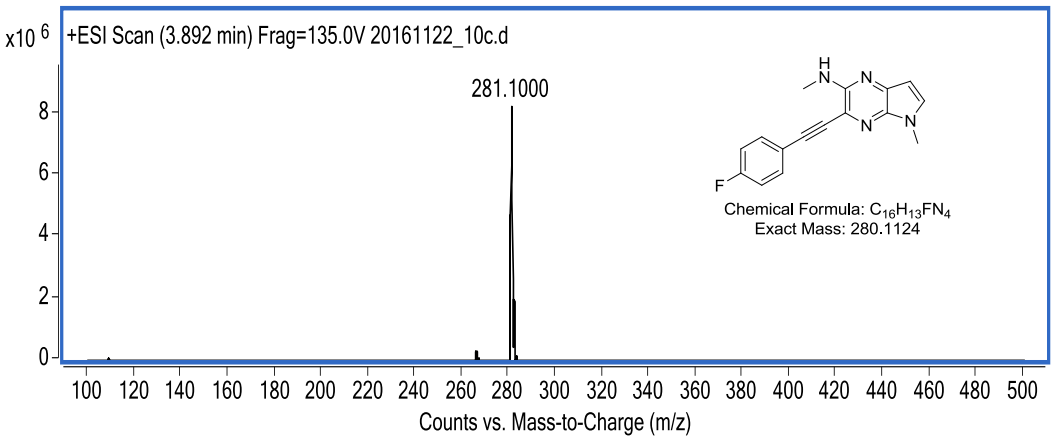


LC/MS – 9b

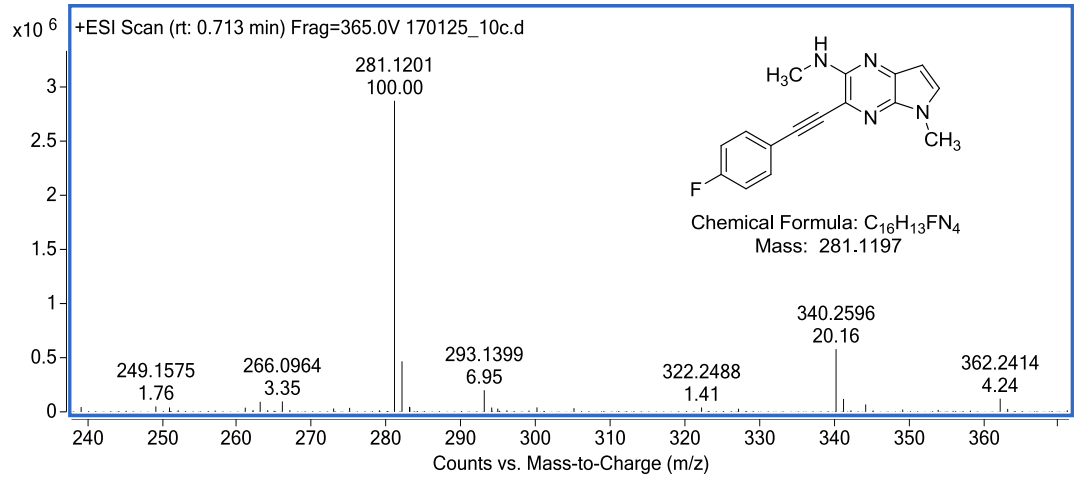


HR/MS – 9b

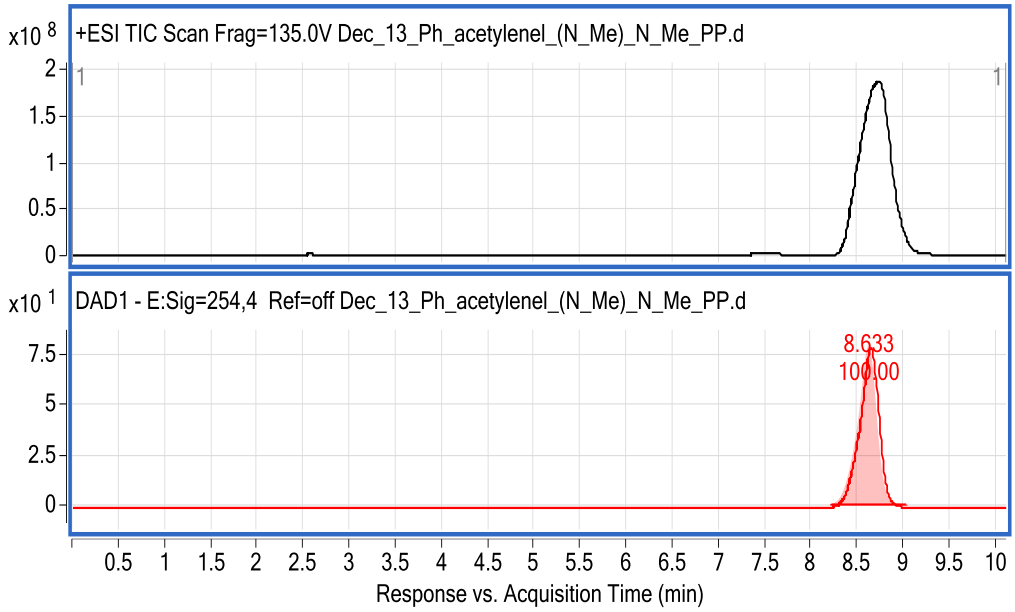


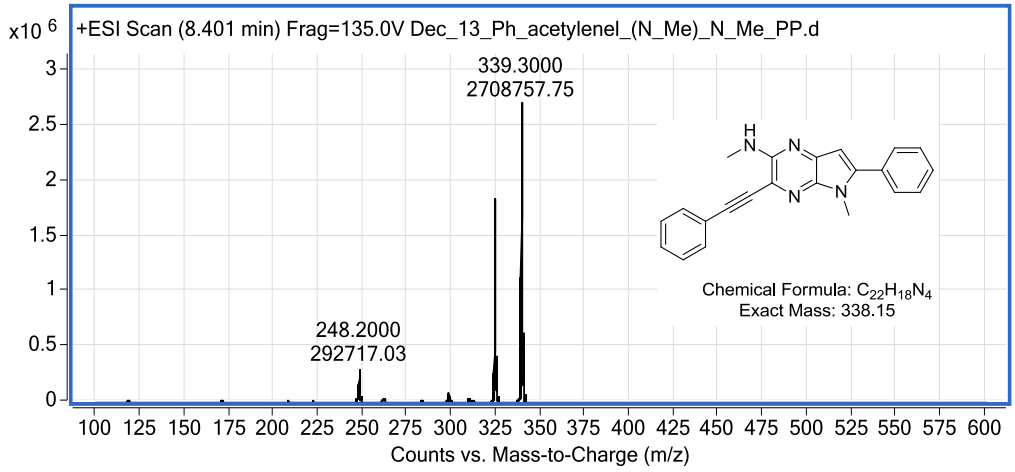


LC/MS – 10c

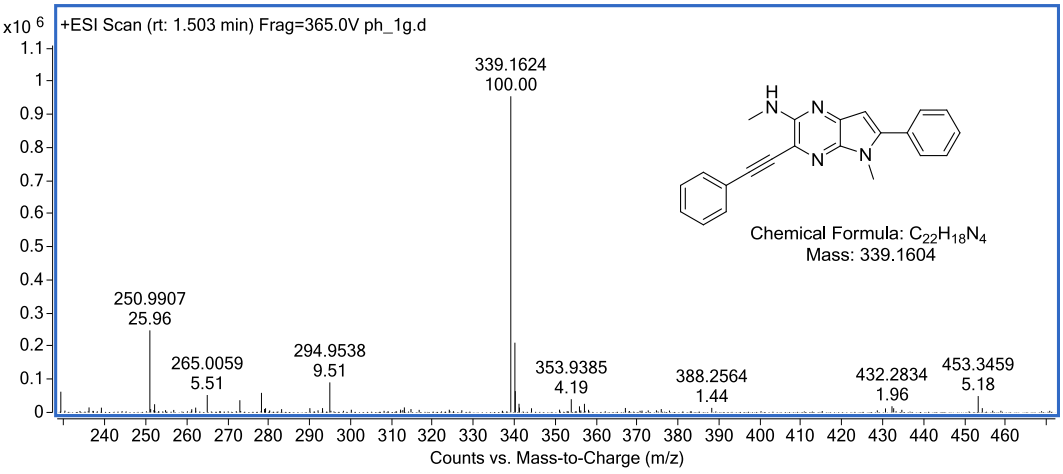


HR/MS – 10c

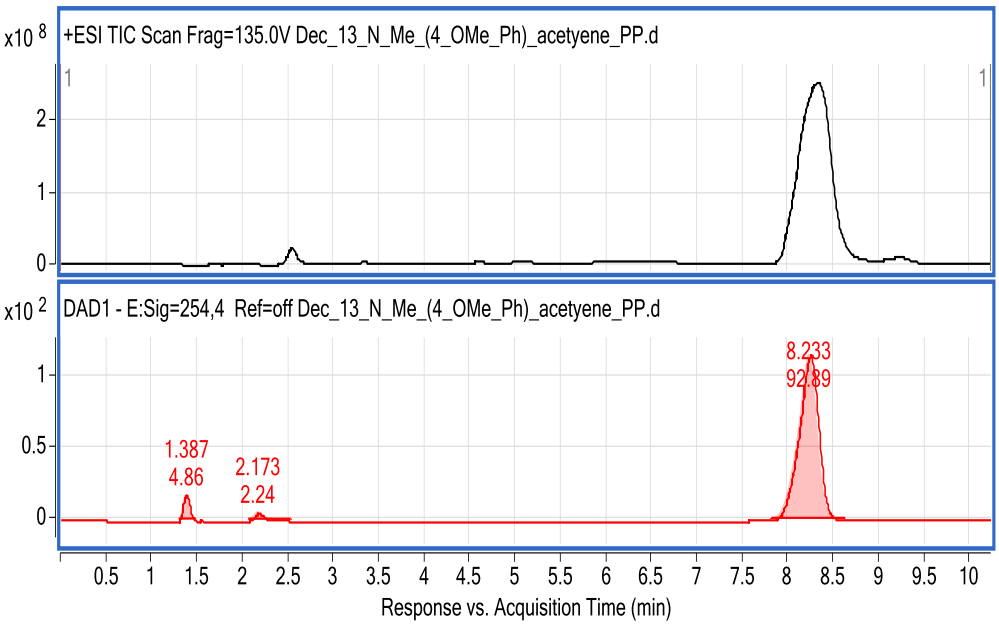


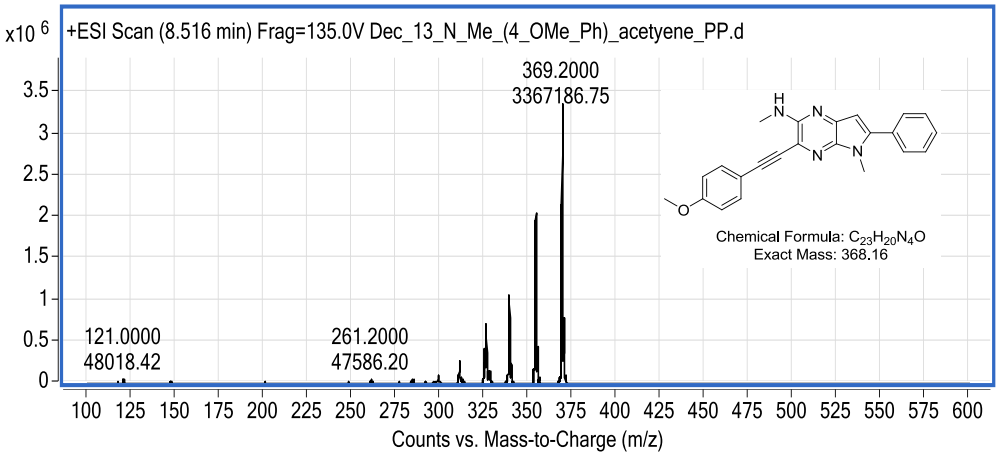


LC/MS – 10f

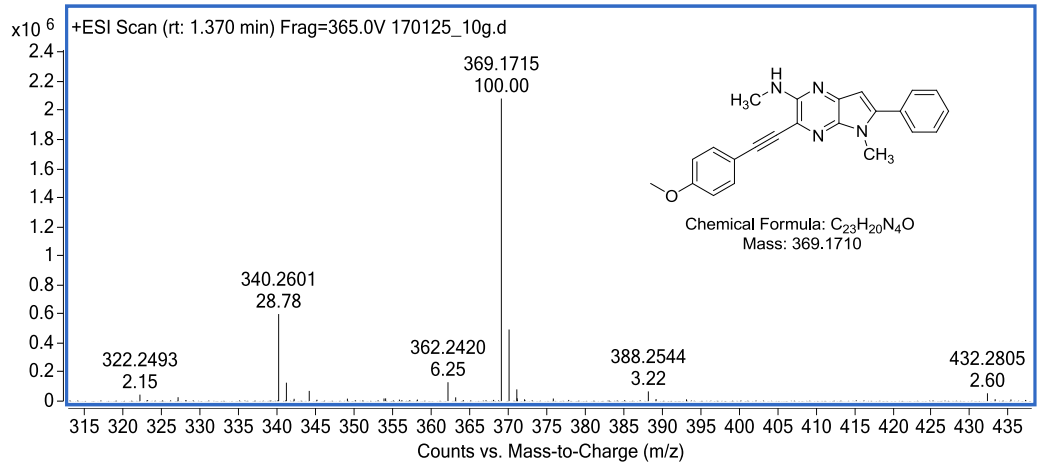


HR/MS – 10f

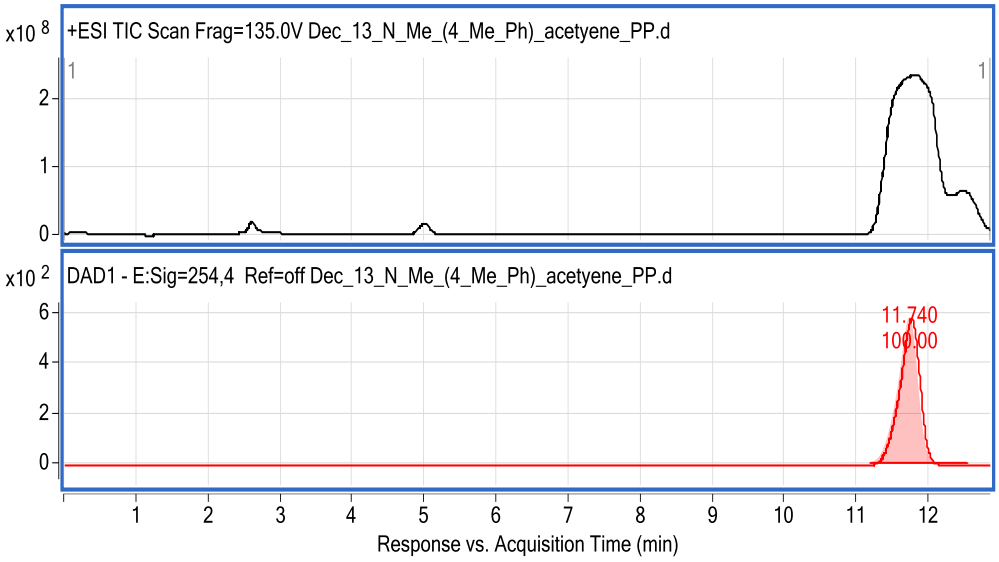


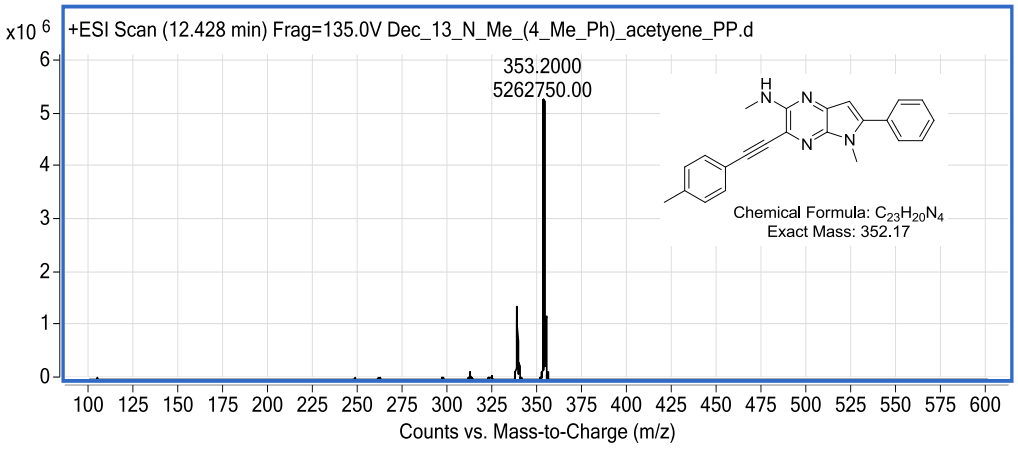


LC/MS – 10g

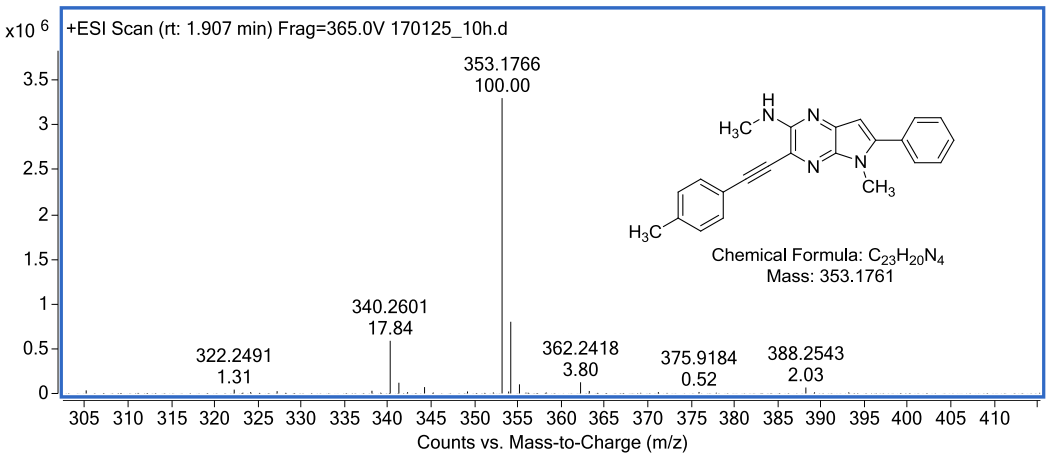


HR/MS – 10g

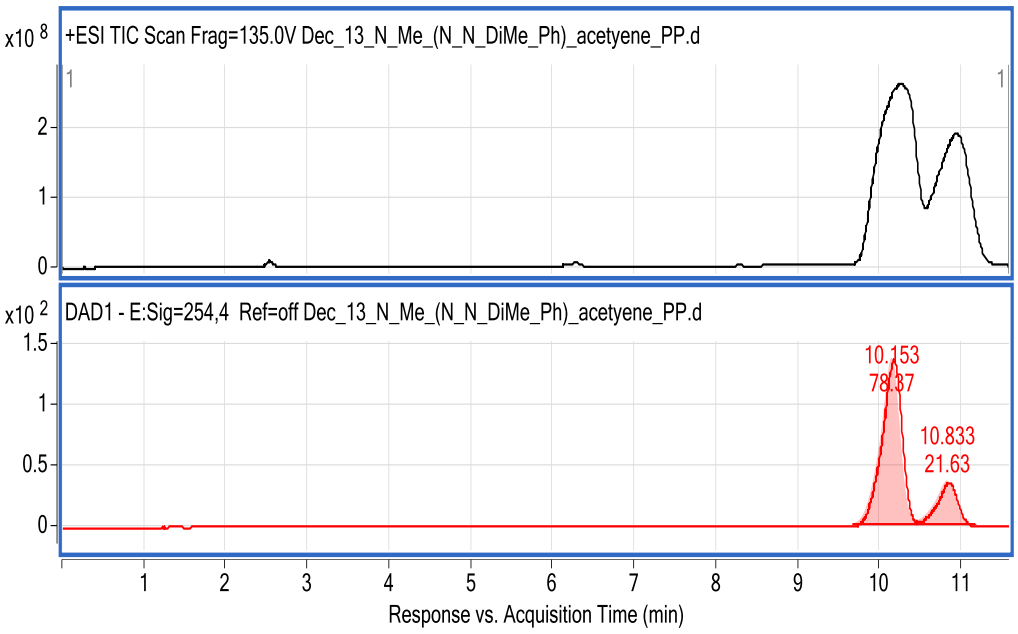


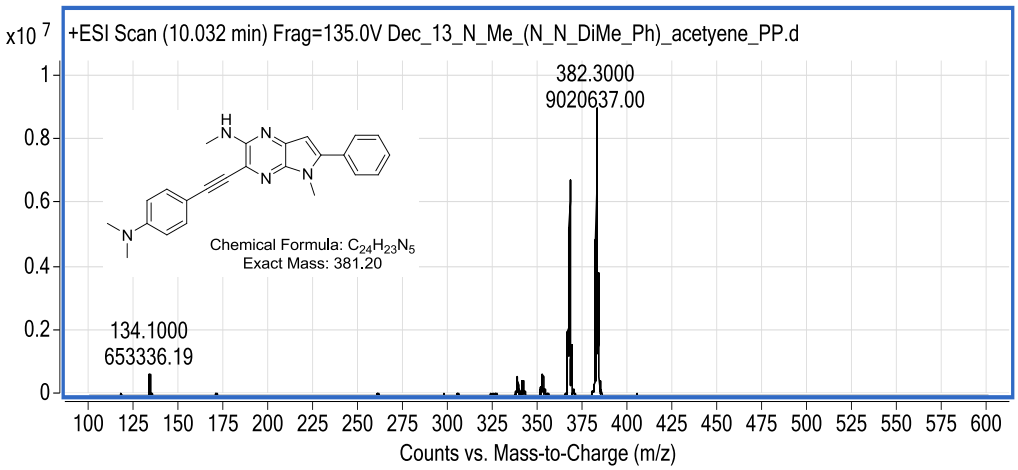


LC/MS – 10h

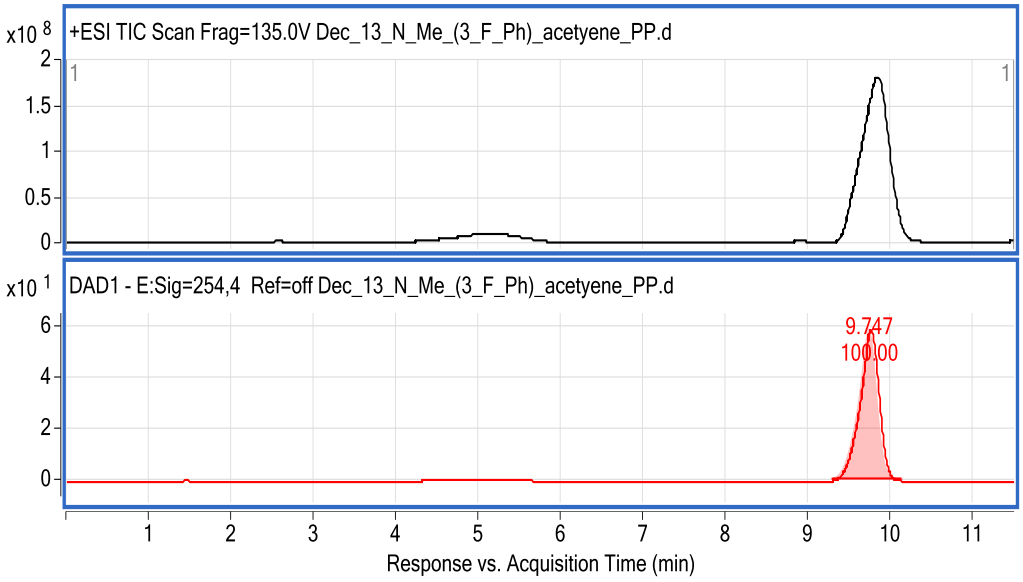


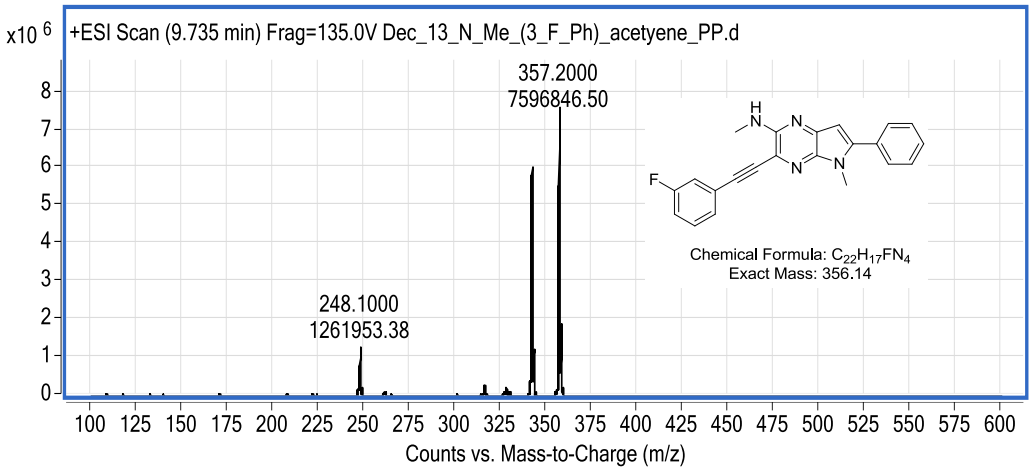
HR/MS – 10h


x10 8
+ESI TIC Scan Frag=135.0V Dec_13_N_Me_(N_N_DiMe_Ph)_acetyene_PP.d
x10 2
DAD1 - E:Sig=254,4 Ref=off Dec_13_N_Me_(N_N_DiMe_Ph)_acetyene_PP.d
10.153
78.37
10.833
21.63
Response vs. Acquisition Time (min)

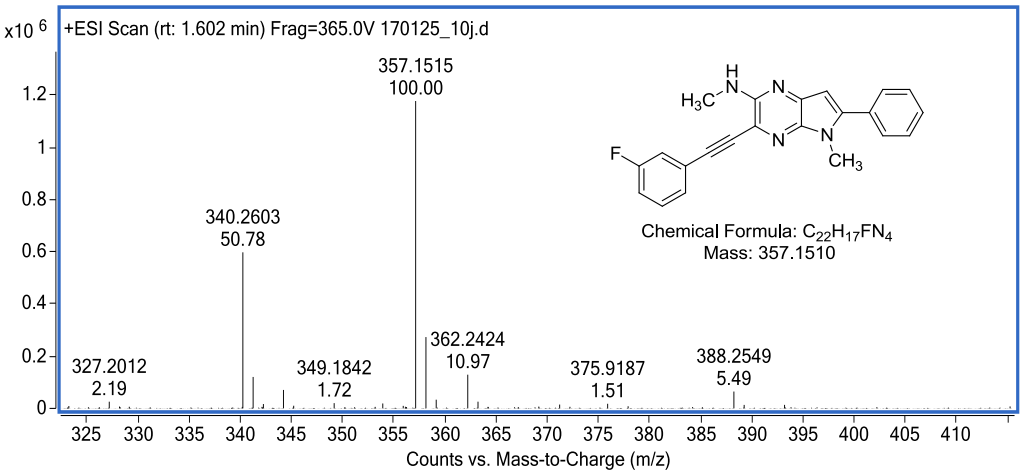

x10 7
+ESI Scan (10.032 min) Frag=135.0V Dec_13_N_Me_(N_N_DiMe_Ph)_acetyene_PP.d
382.3000
9020637.00
Chemical Formula: C24H23N5
Exact Mass: 381.20
134.1000
653336.19
Counts vs. Mass-to-Charge (m/z)

LC/MS – 10i

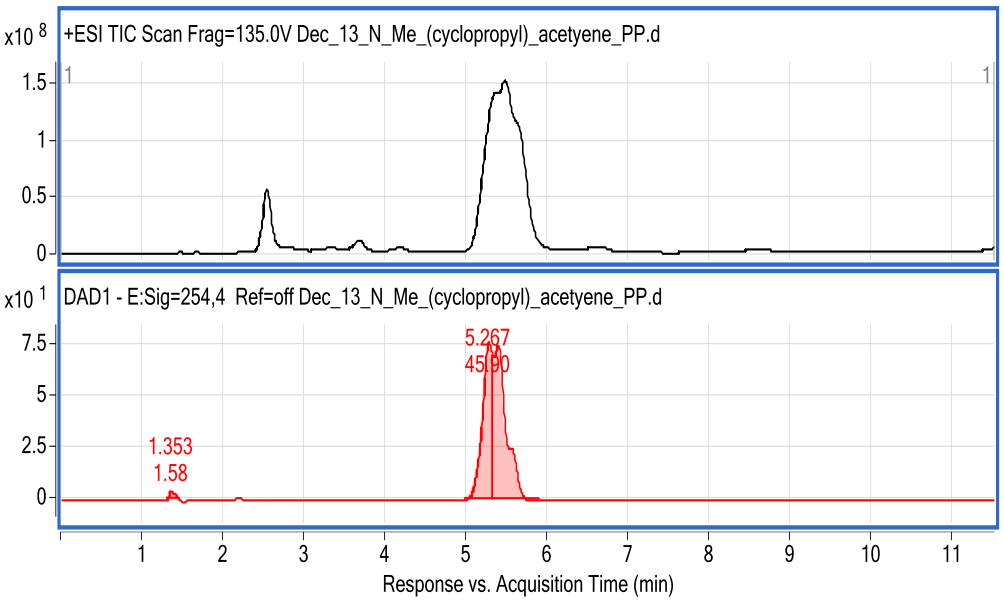


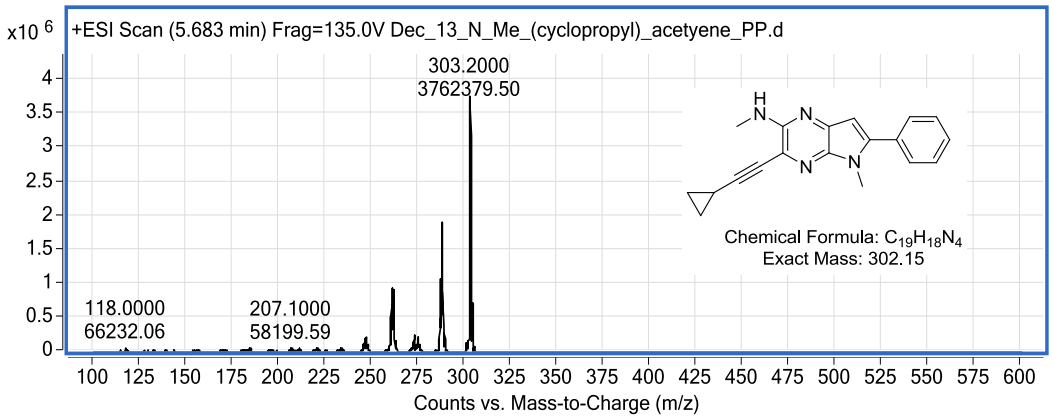


LC/MS – 10j

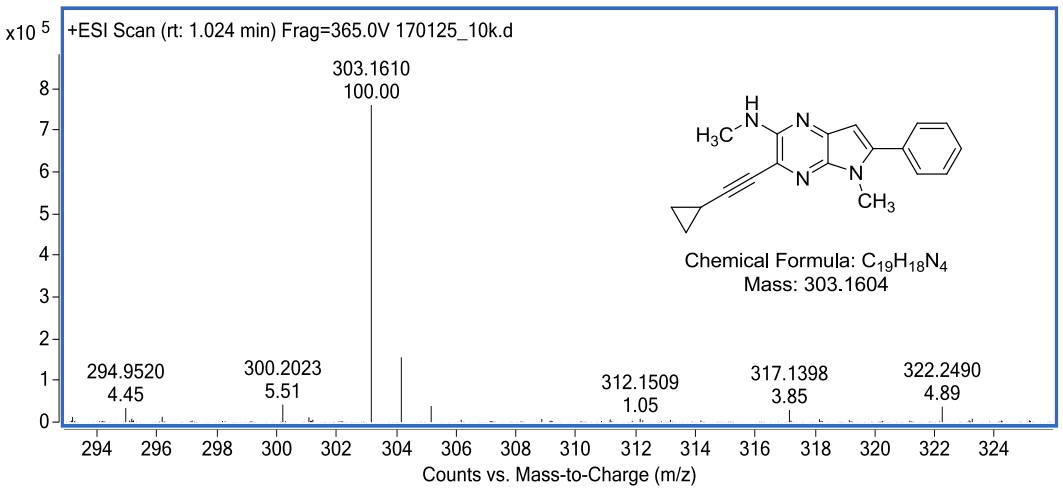


HR/MS – 10j





LC/MS – 10k



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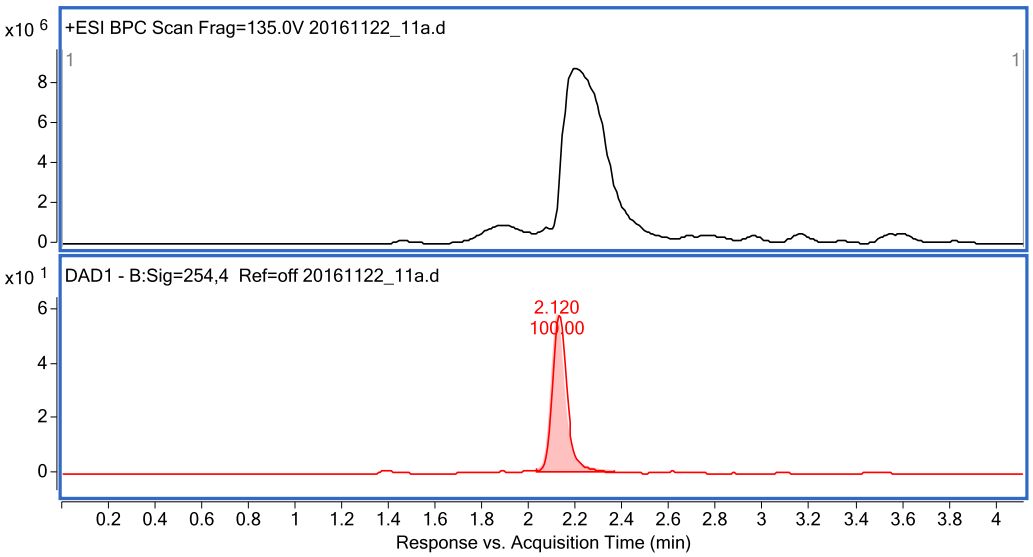
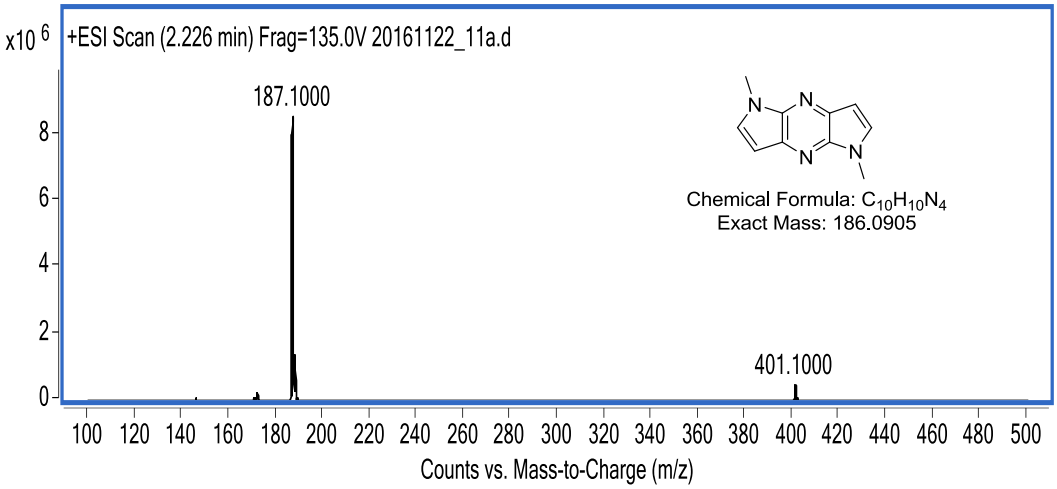
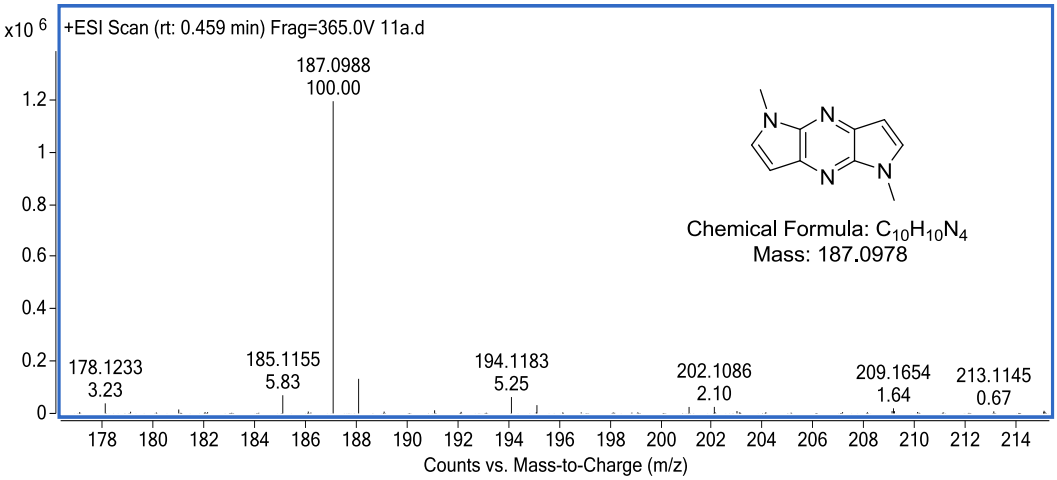




LC/MS – 11a



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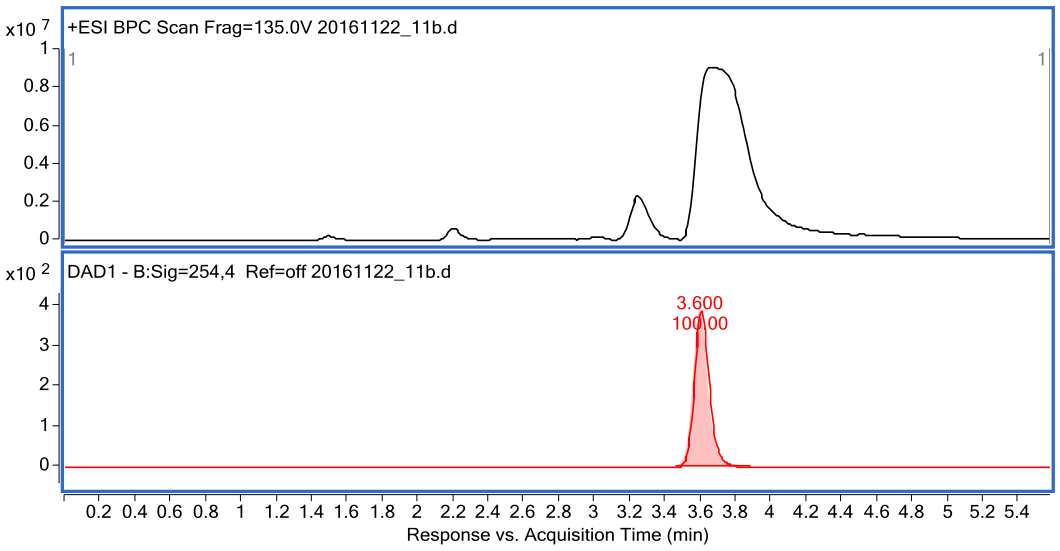
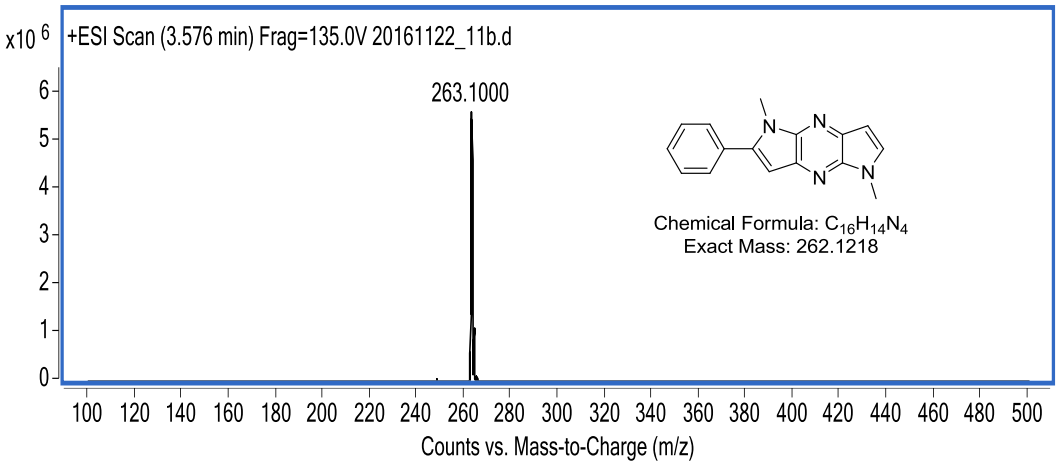
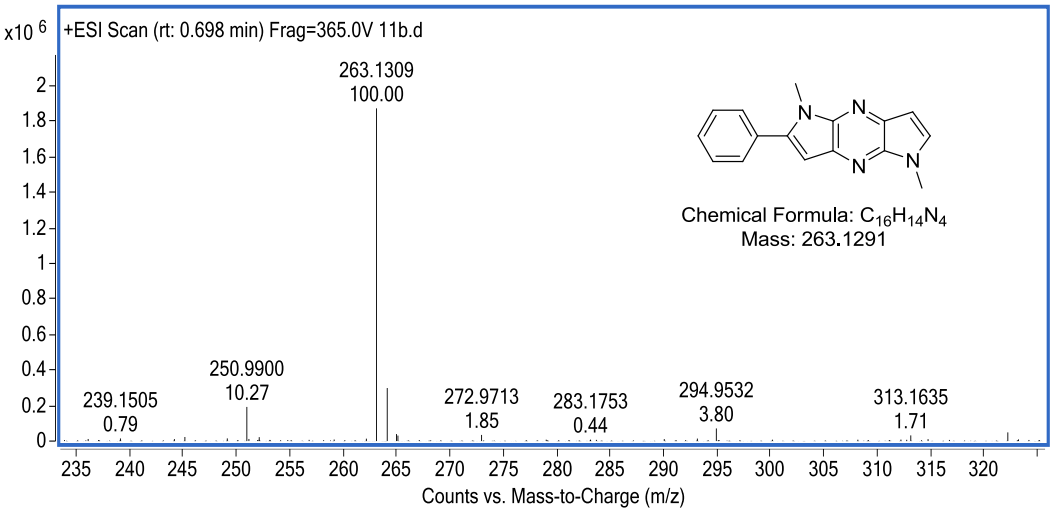
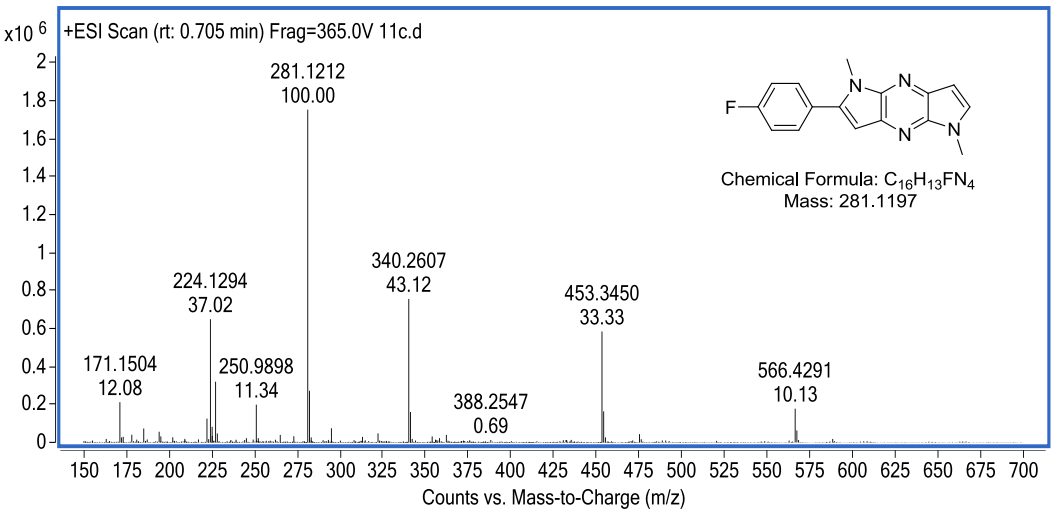




LC/MS – 11b



HRMS – 11b



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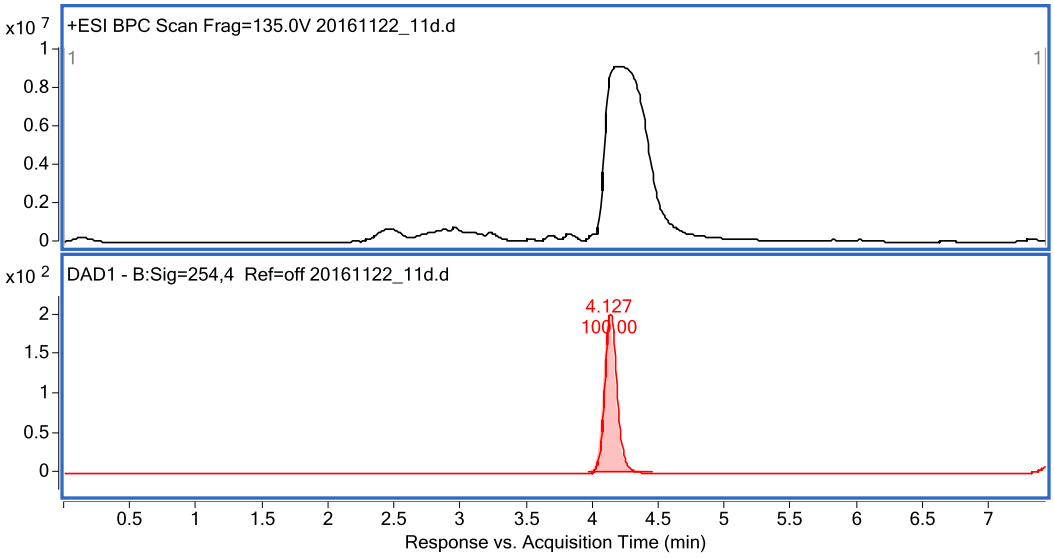
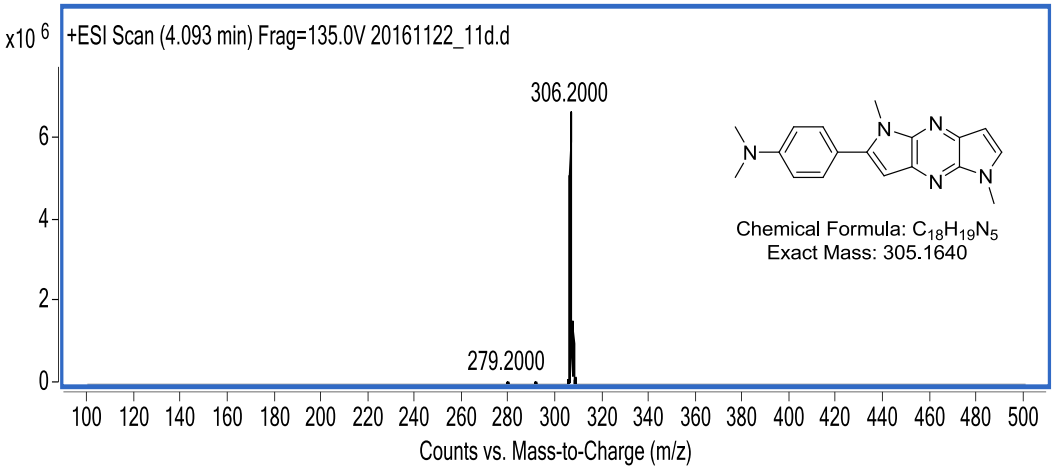
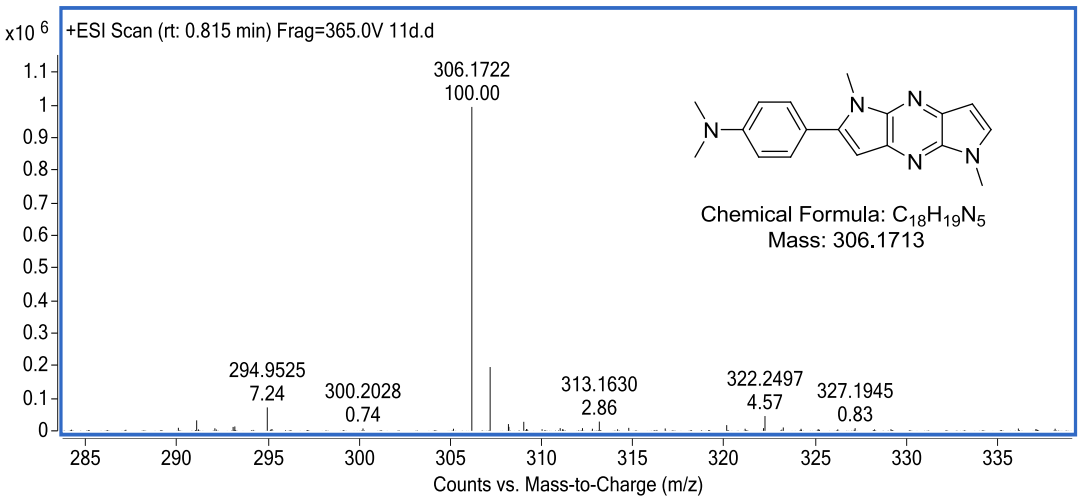
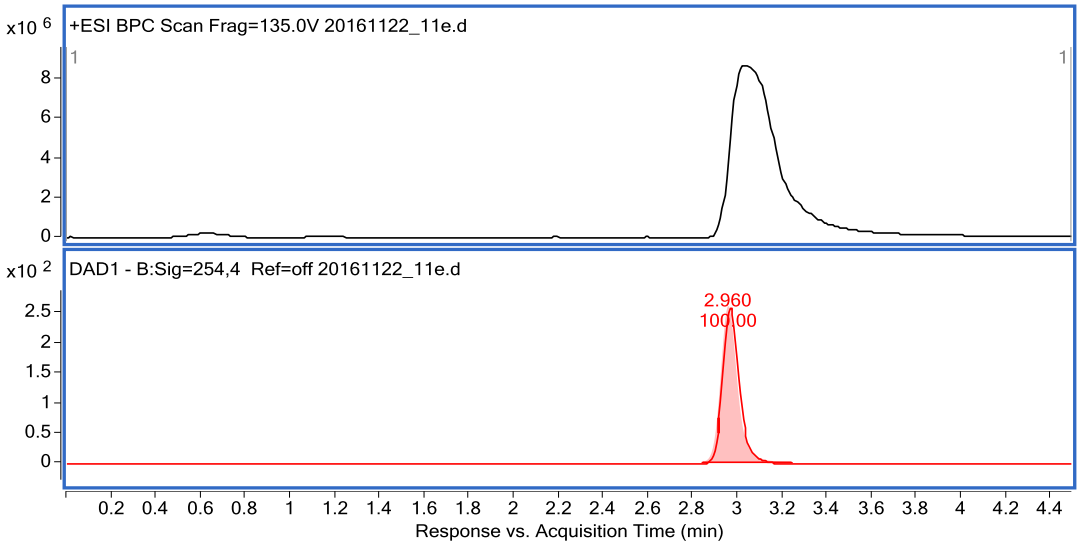


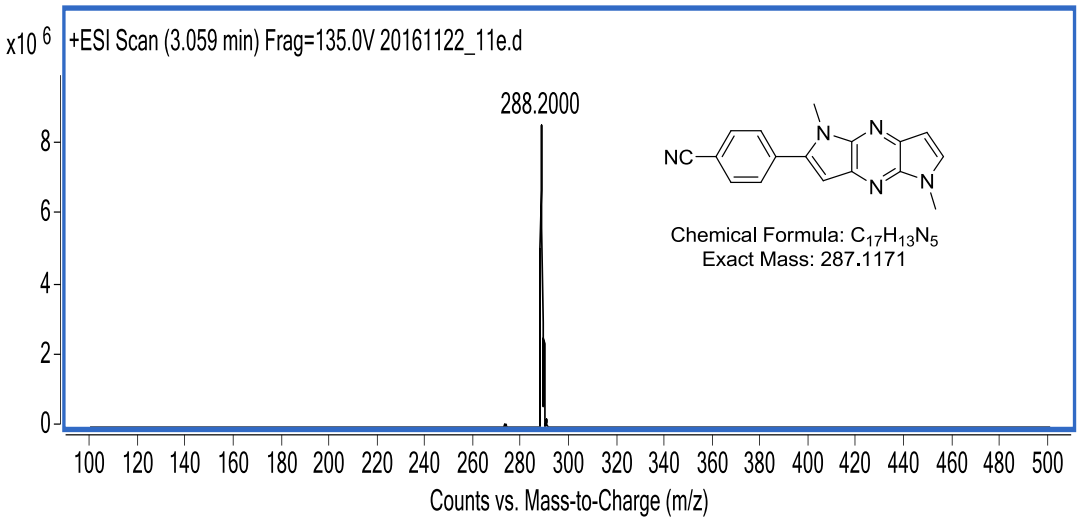


LC/MS – 11d

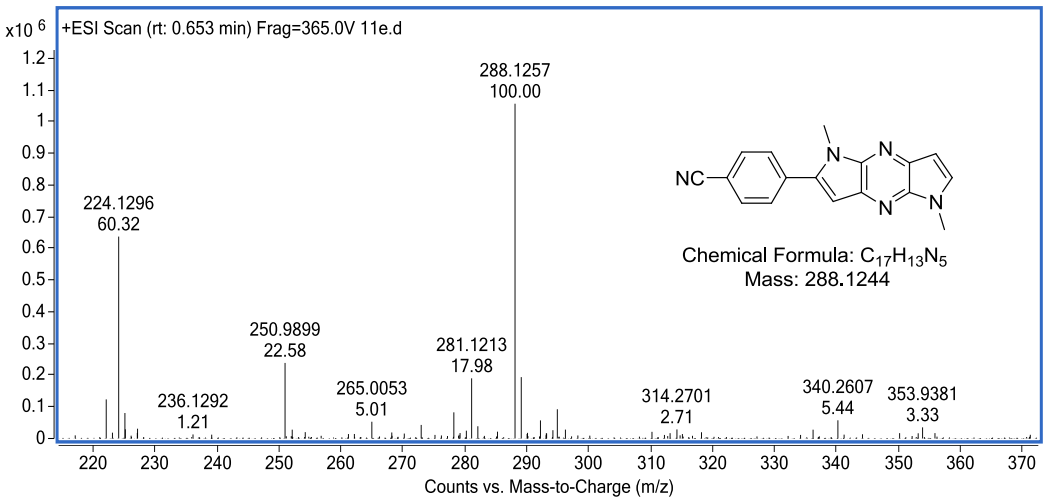


HRMS – 11d

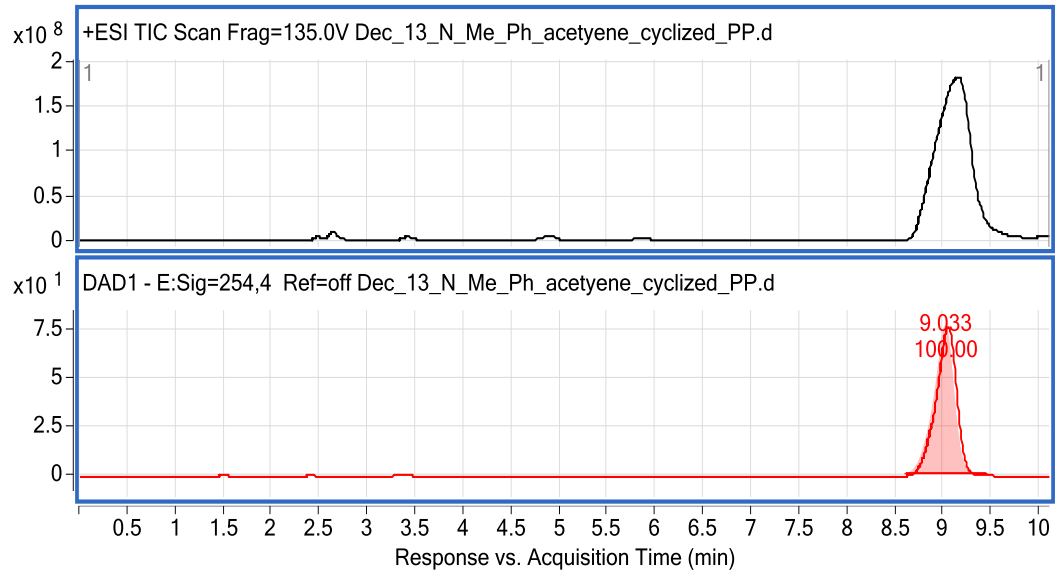


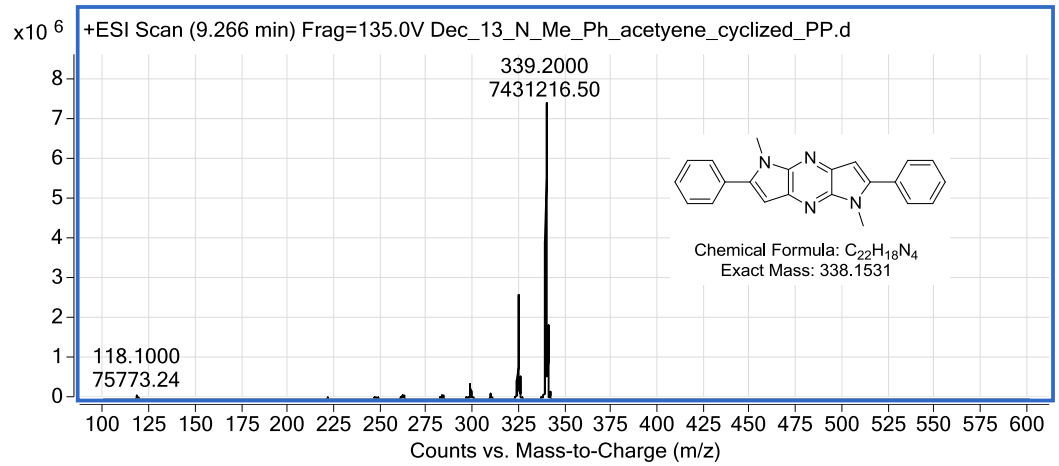


LC/MS – 11e

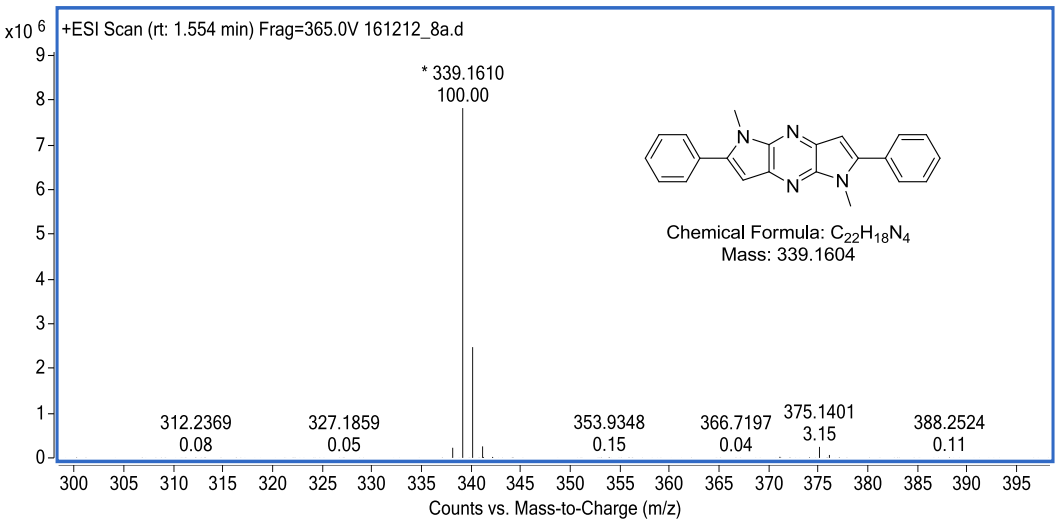


HRMS – 11e

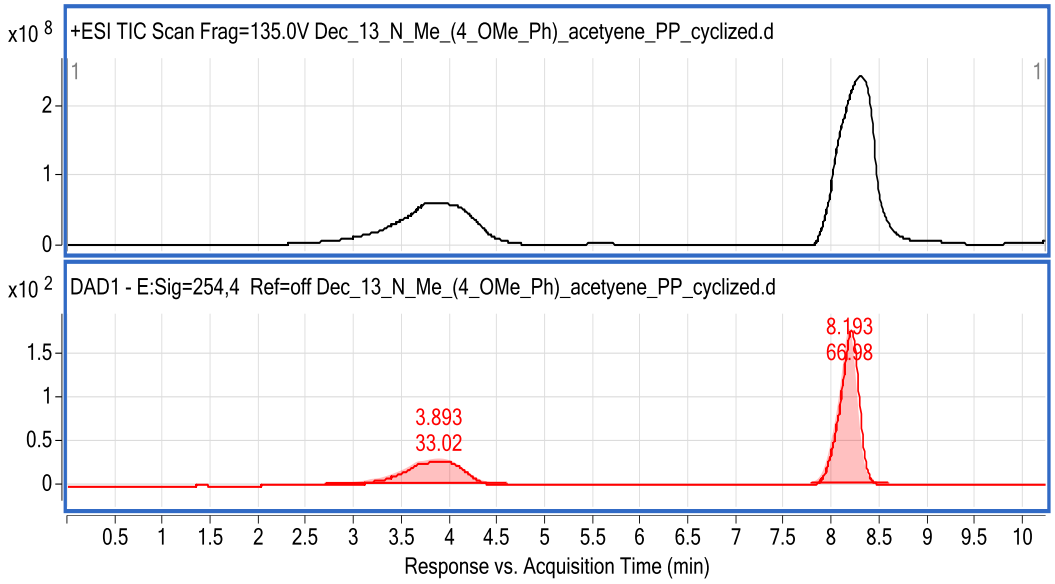


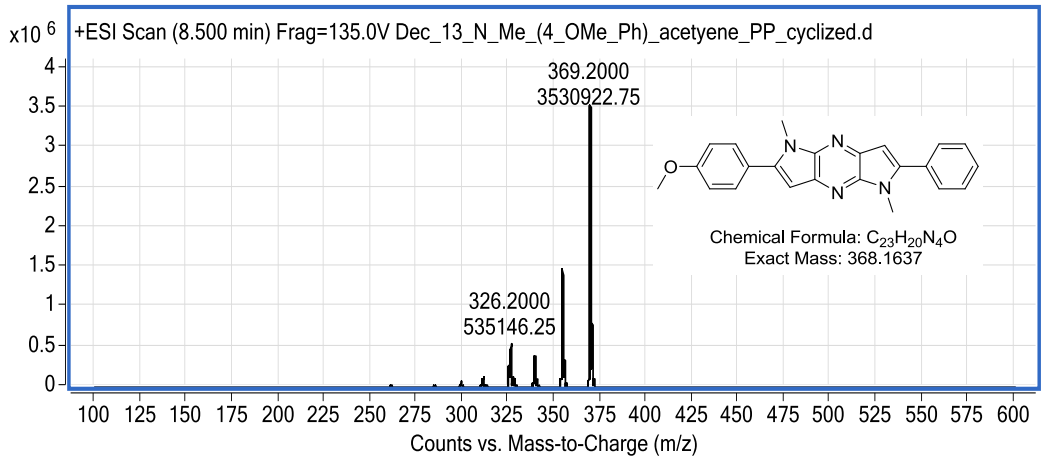


LC/MS – 11f

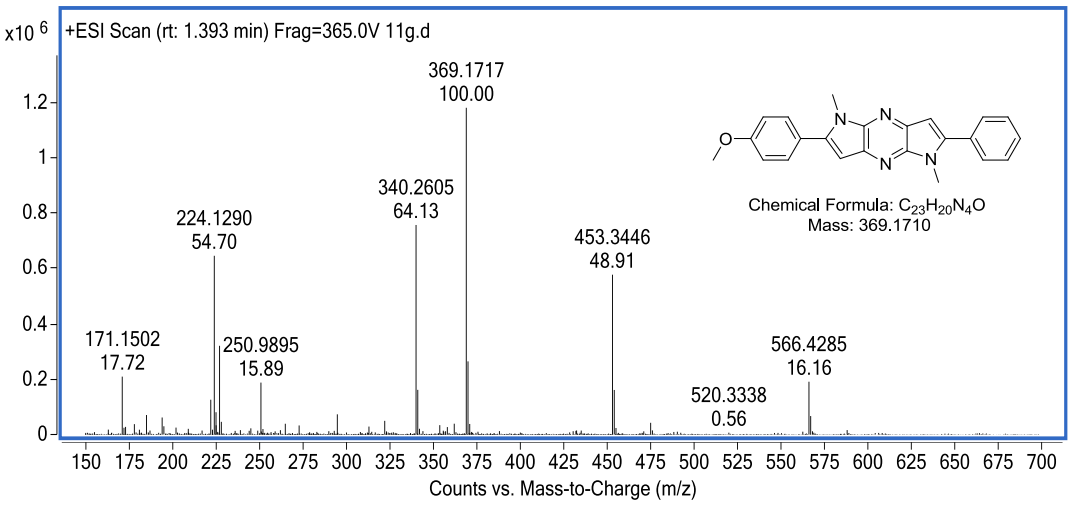


HR//MS – 11f

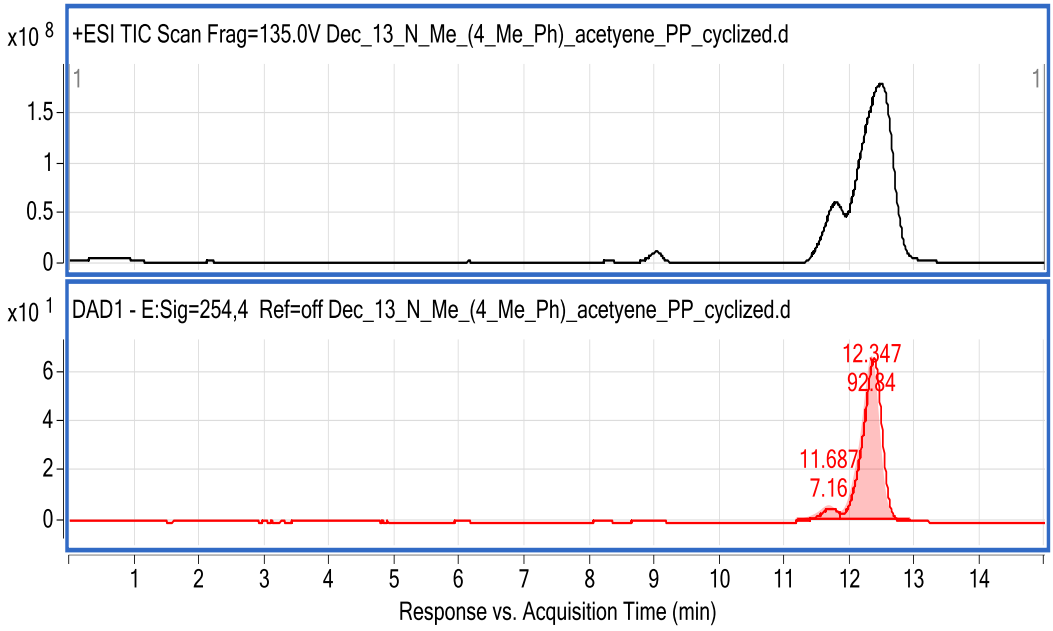


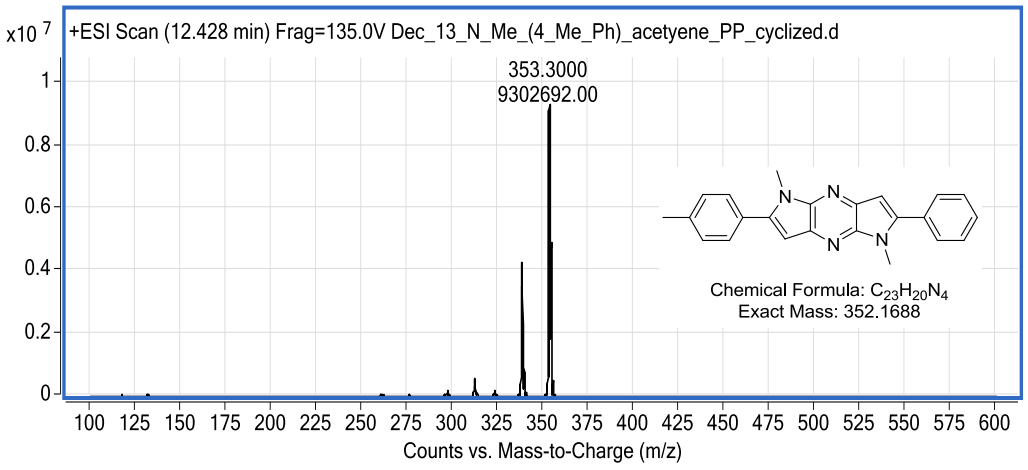


LC/MS – 11g

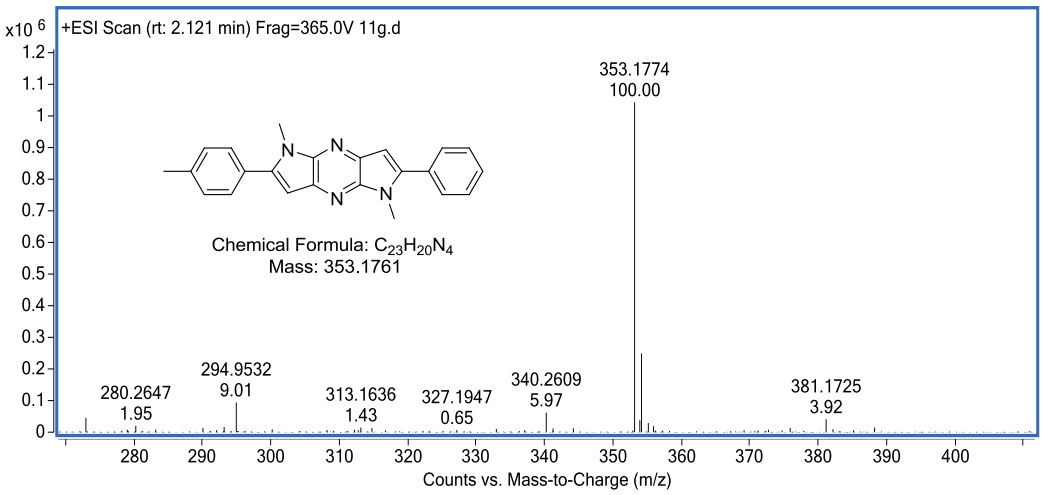


HRMS – 11g

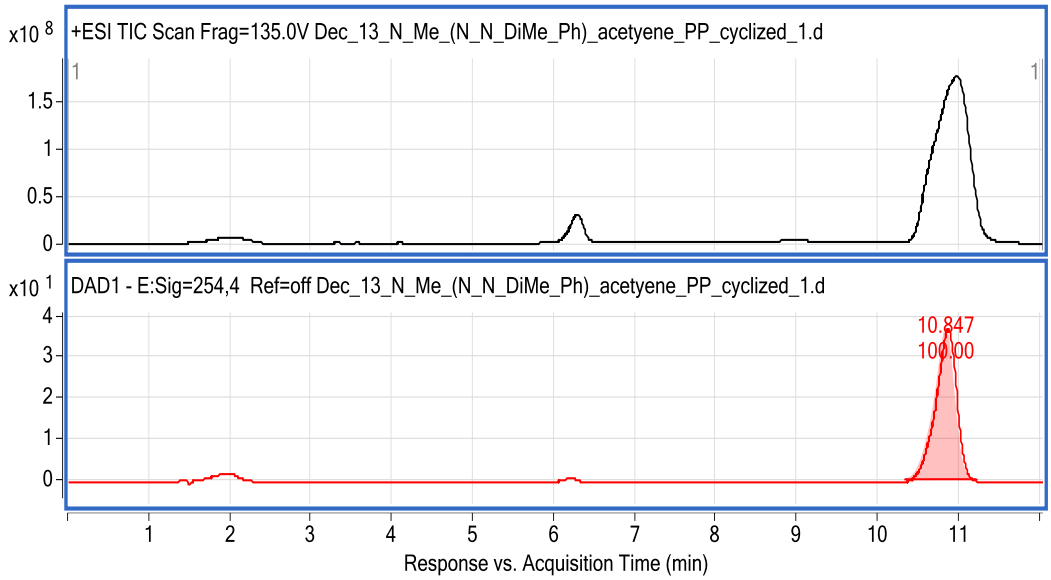


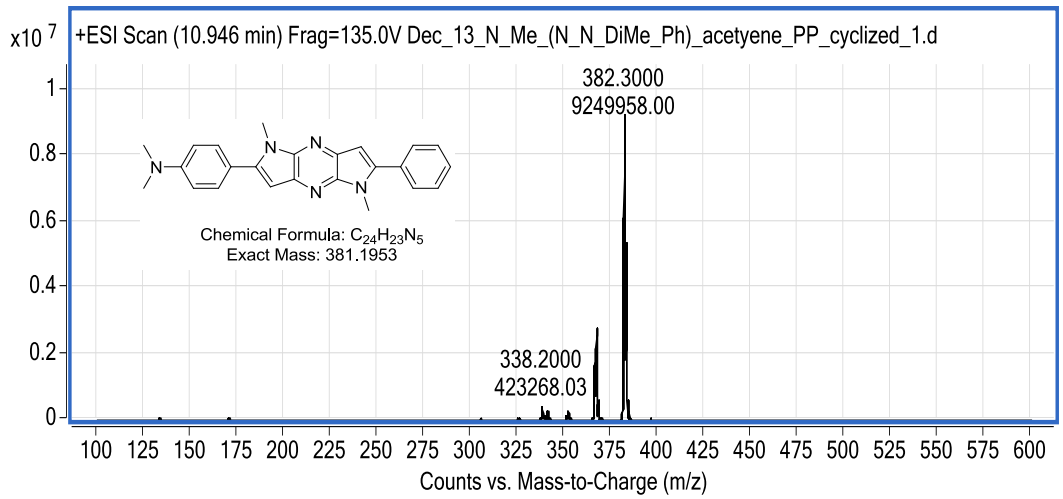


LC/MS – 11h

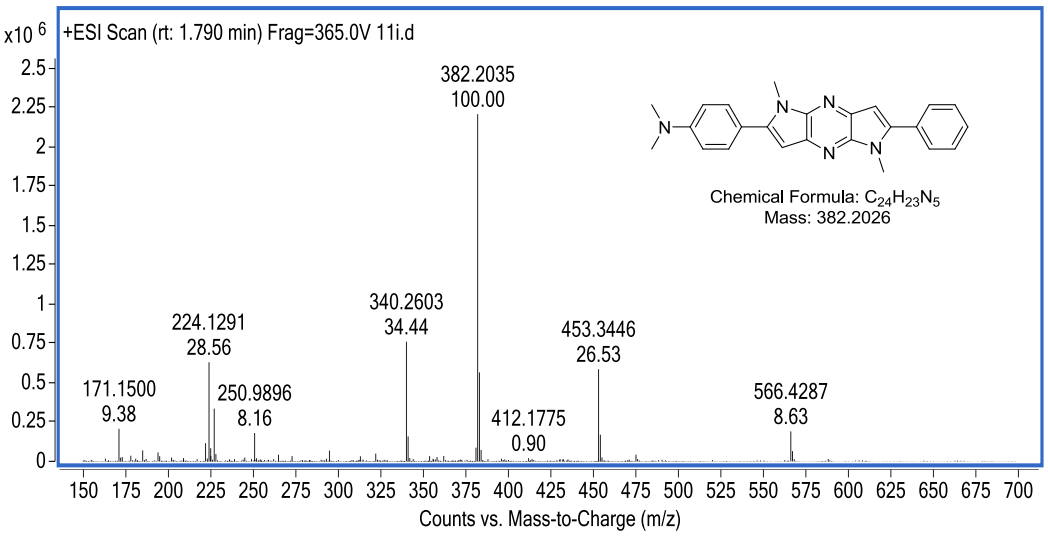


HRMS – 11h

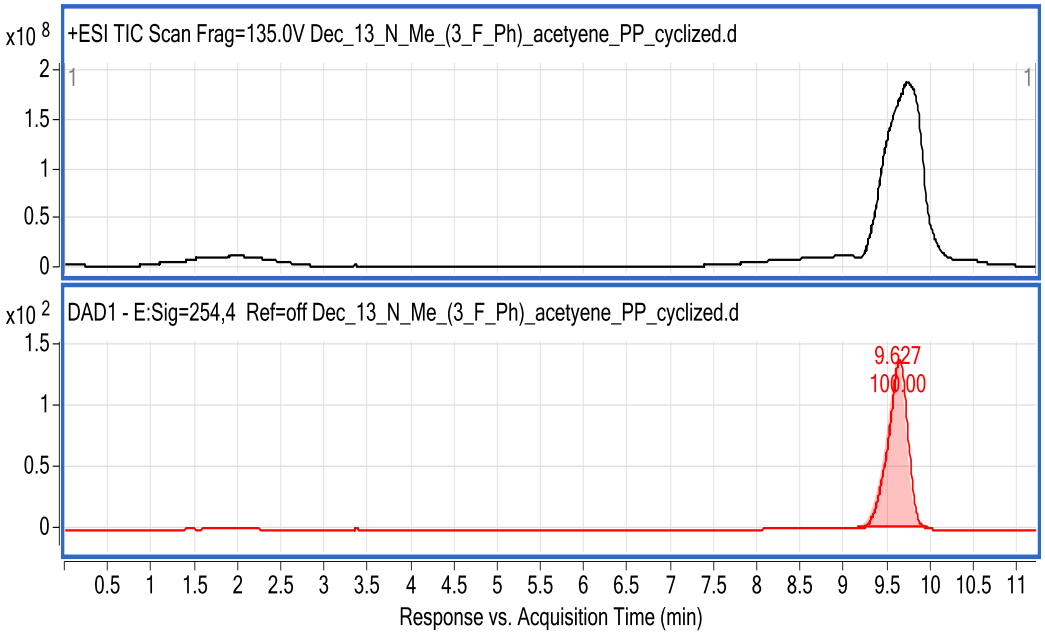


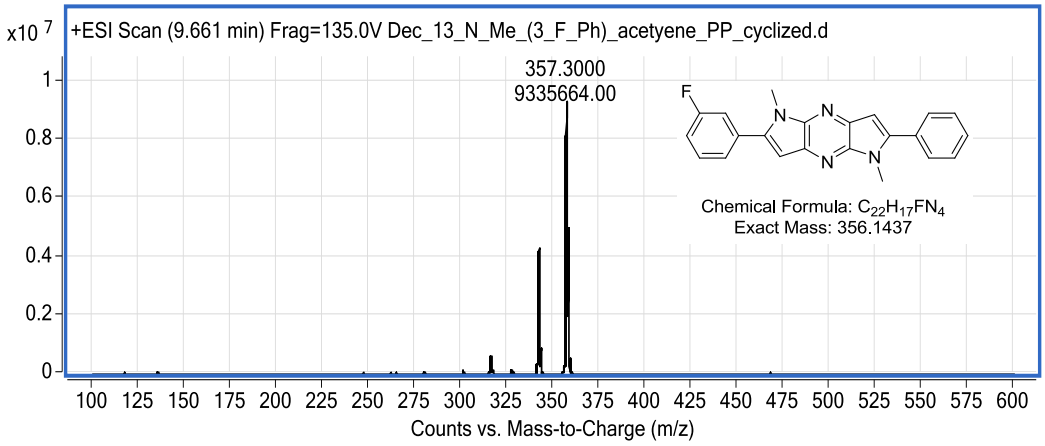


LC/MS – 11i

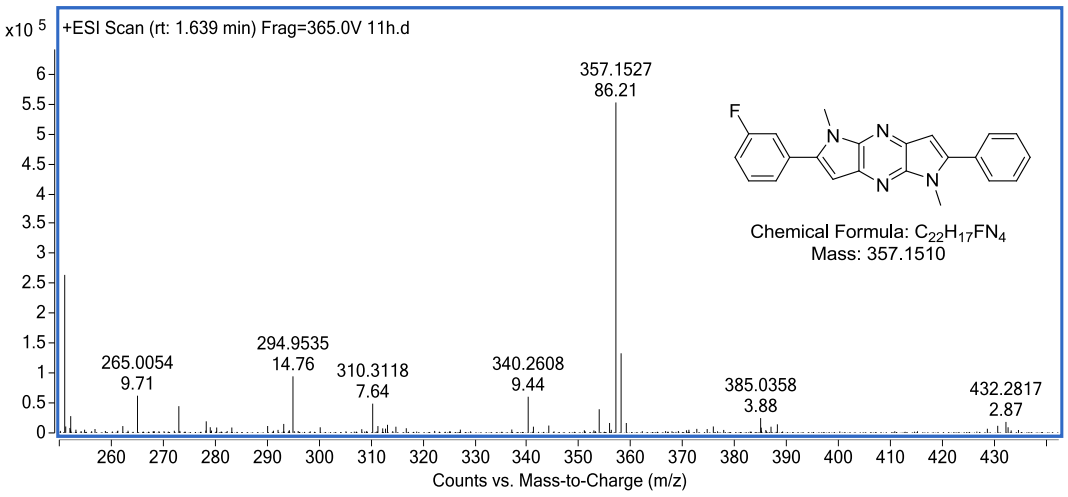


HR/MS – 11i

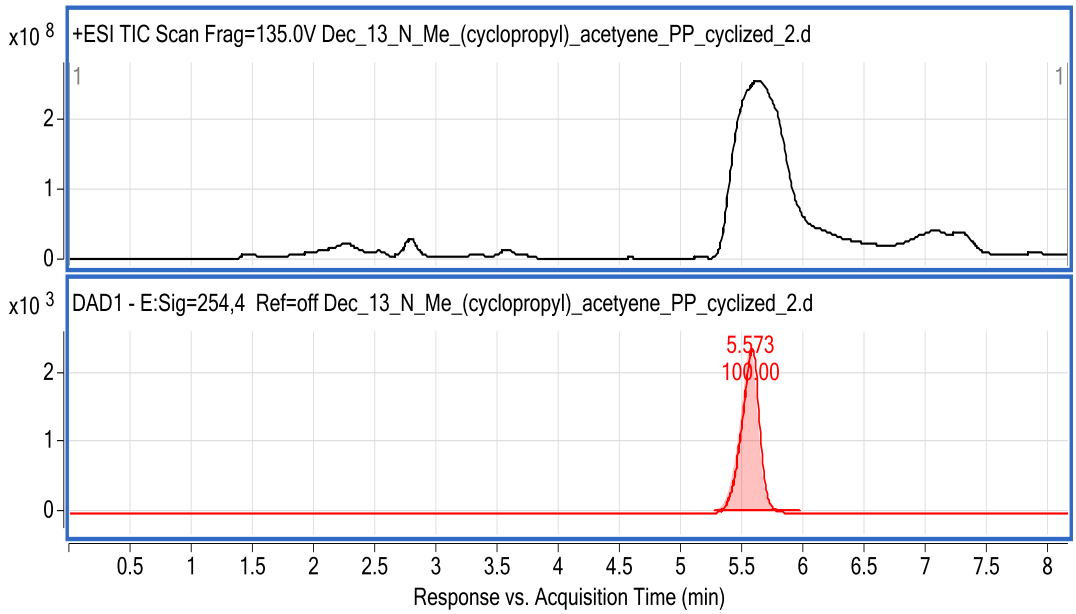


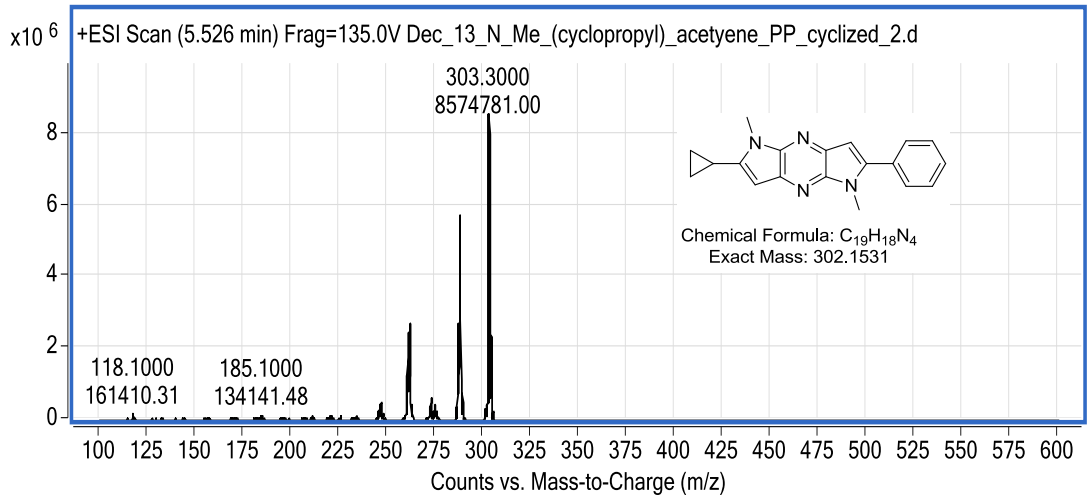


LC/MS – 11j

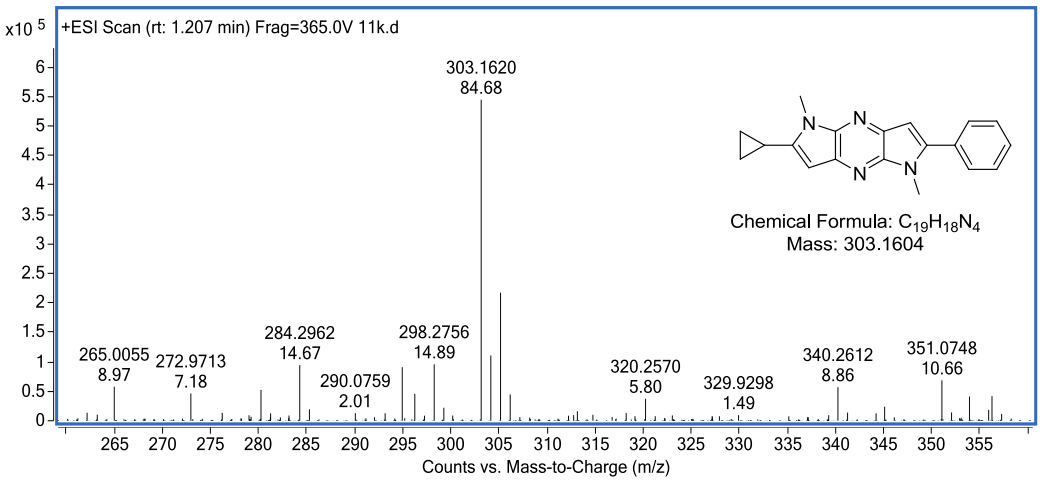


HR/MS – 11j

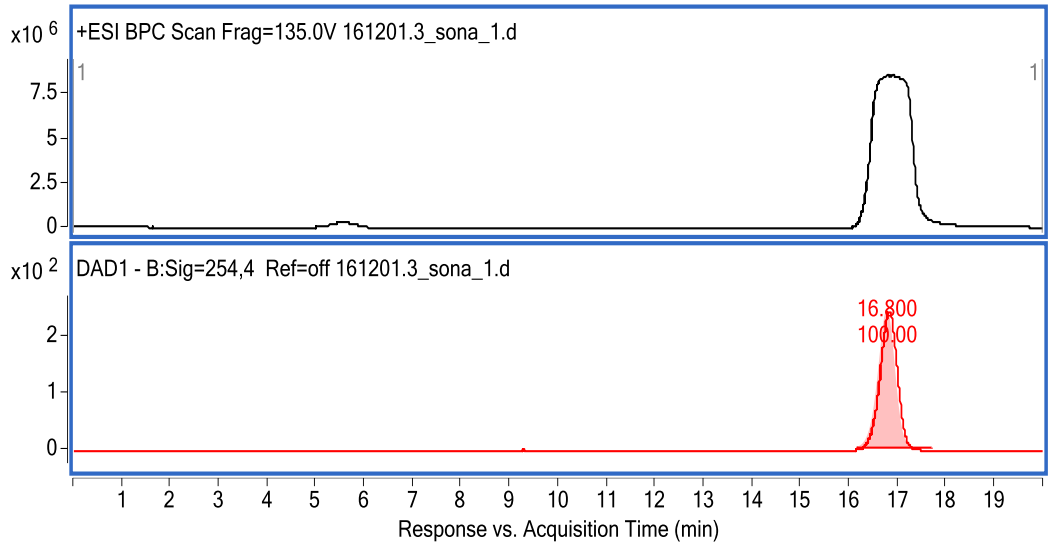


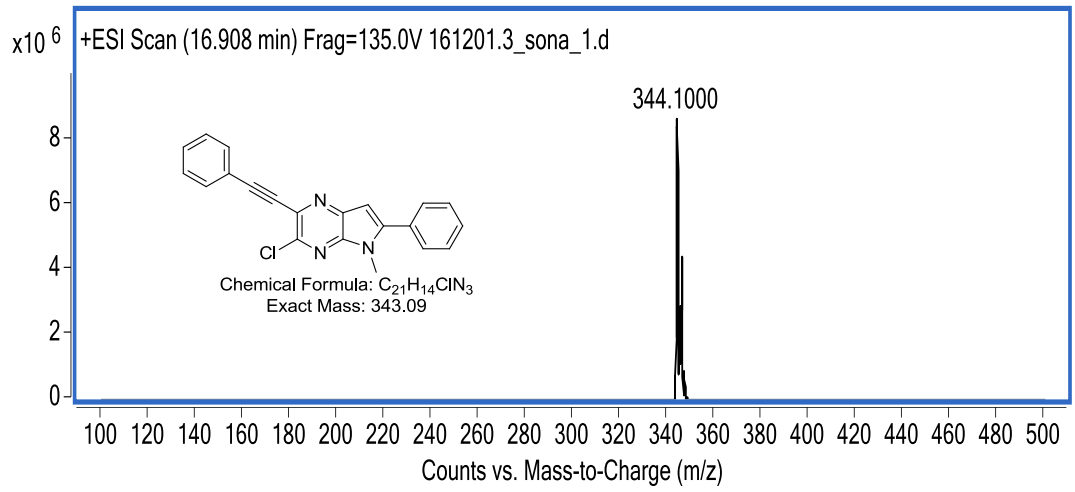


LC/MS – 11k

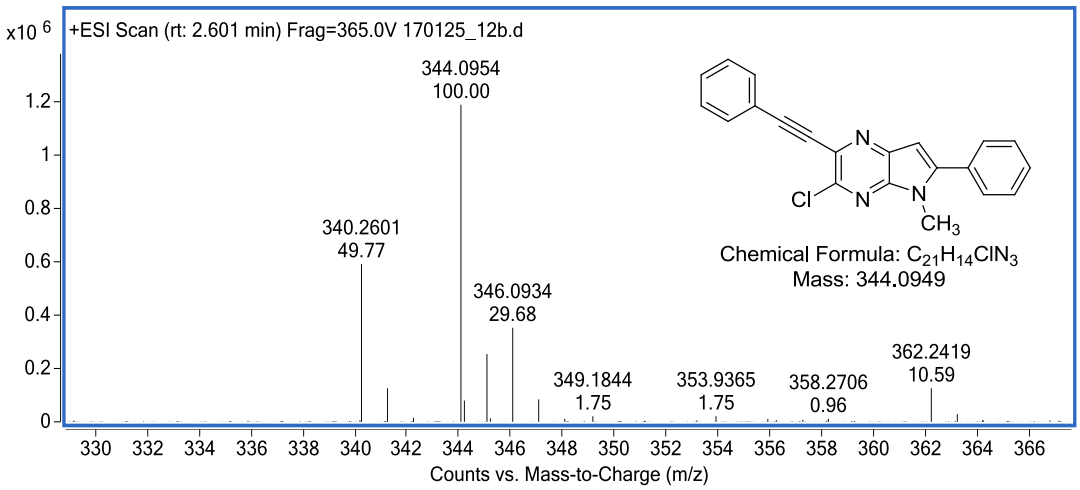


HR/MS – 11k

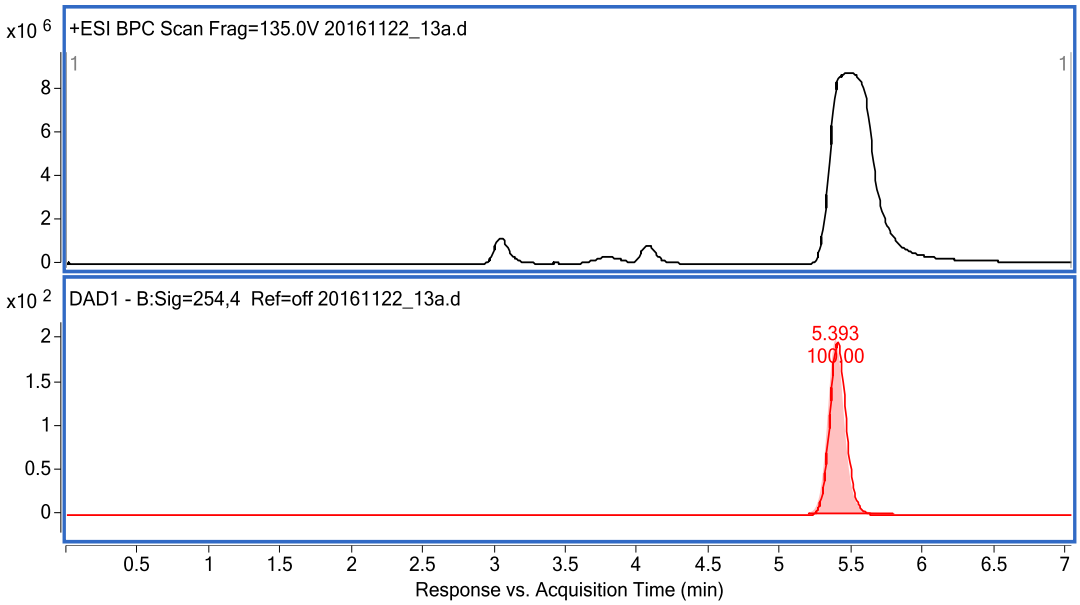


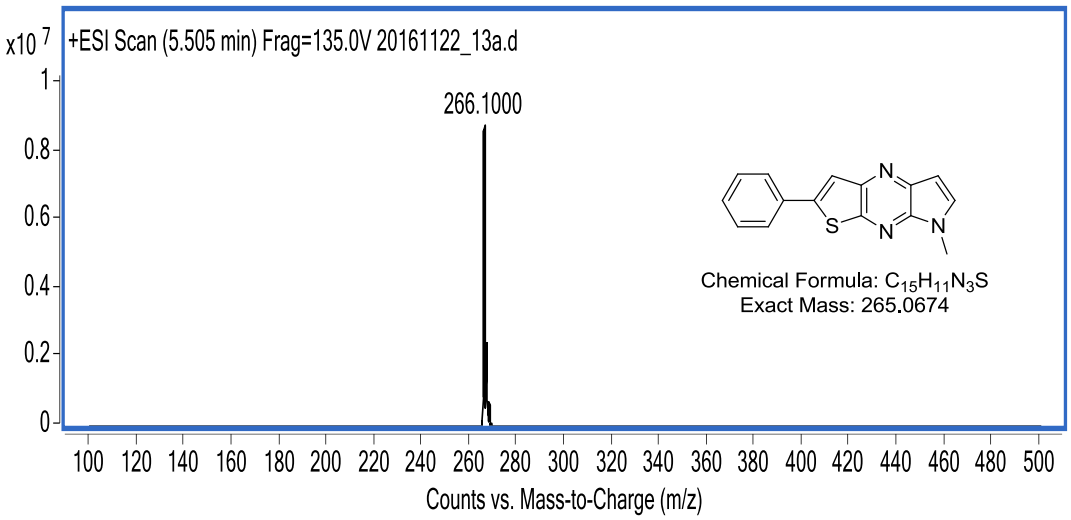


LC/MS – 12b

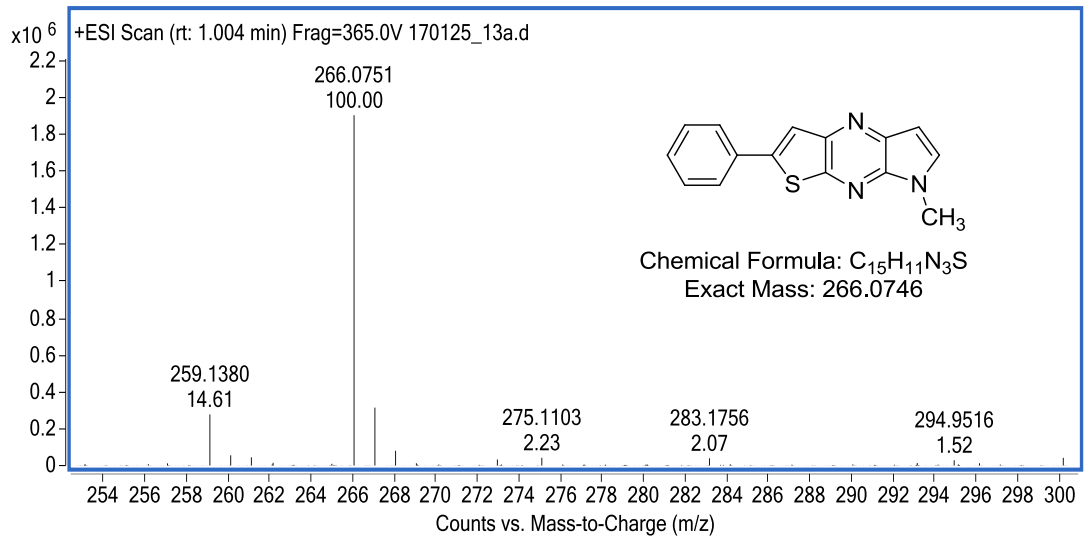


HR/MS – 12b

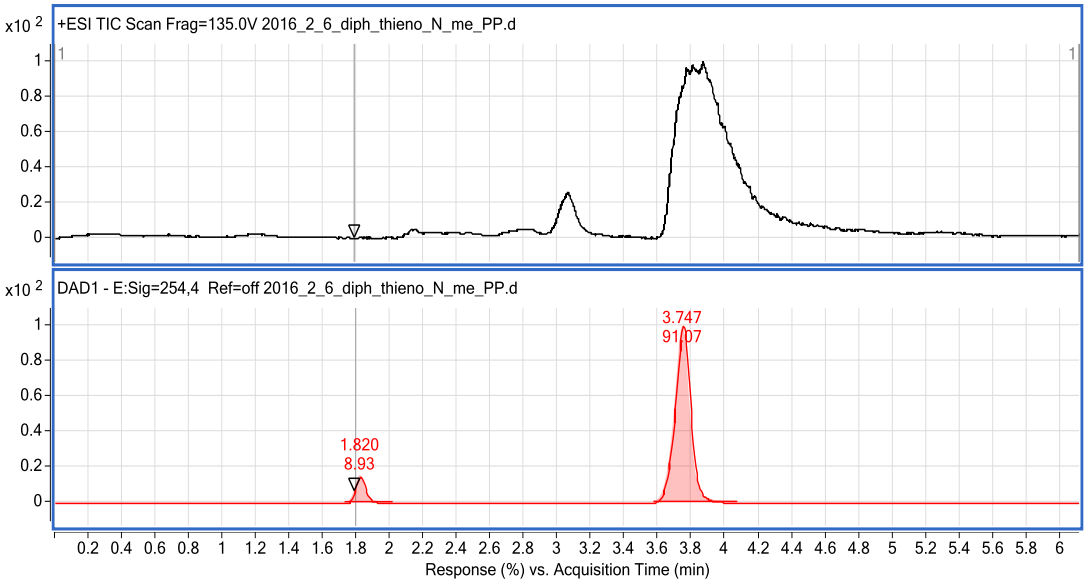


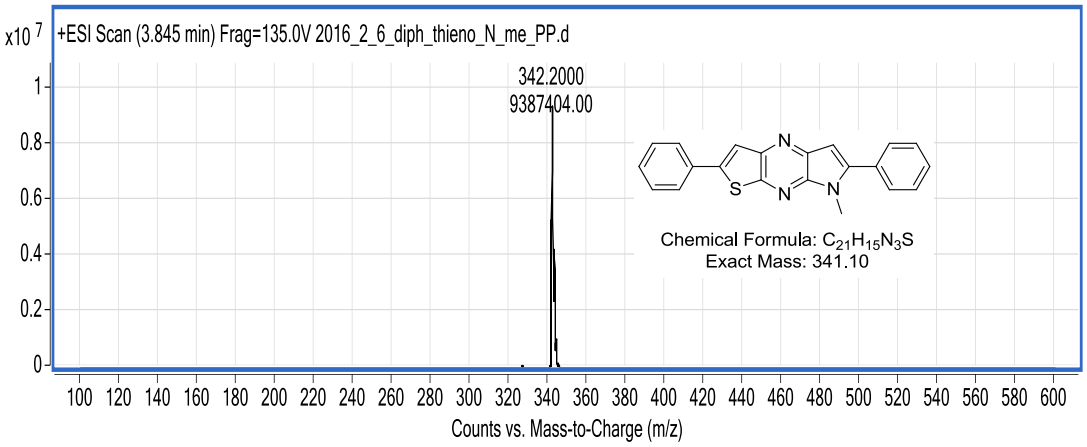


LC/MS – 13a

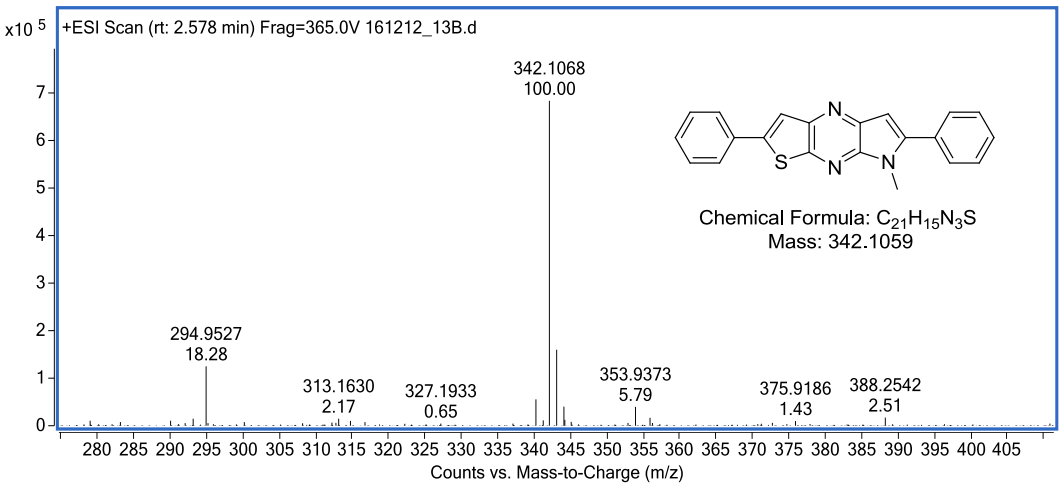


HRMS – 13a

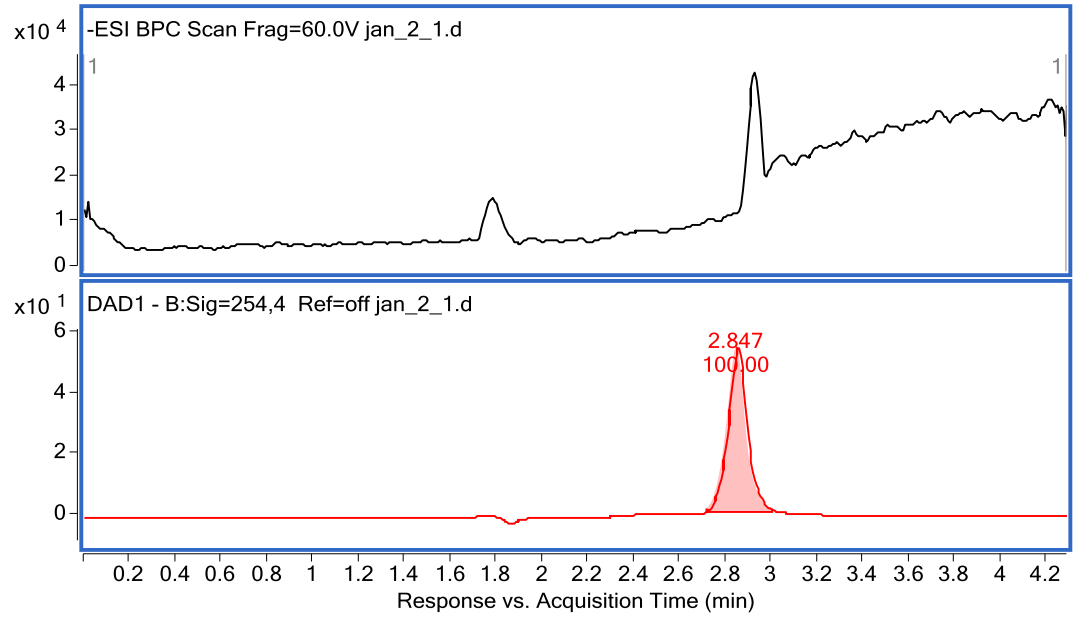


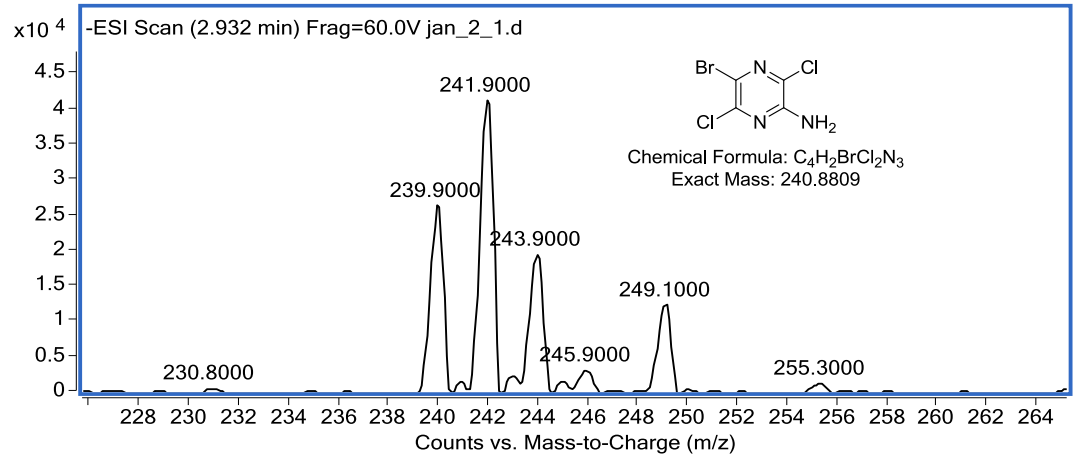


LC/MS – 13b

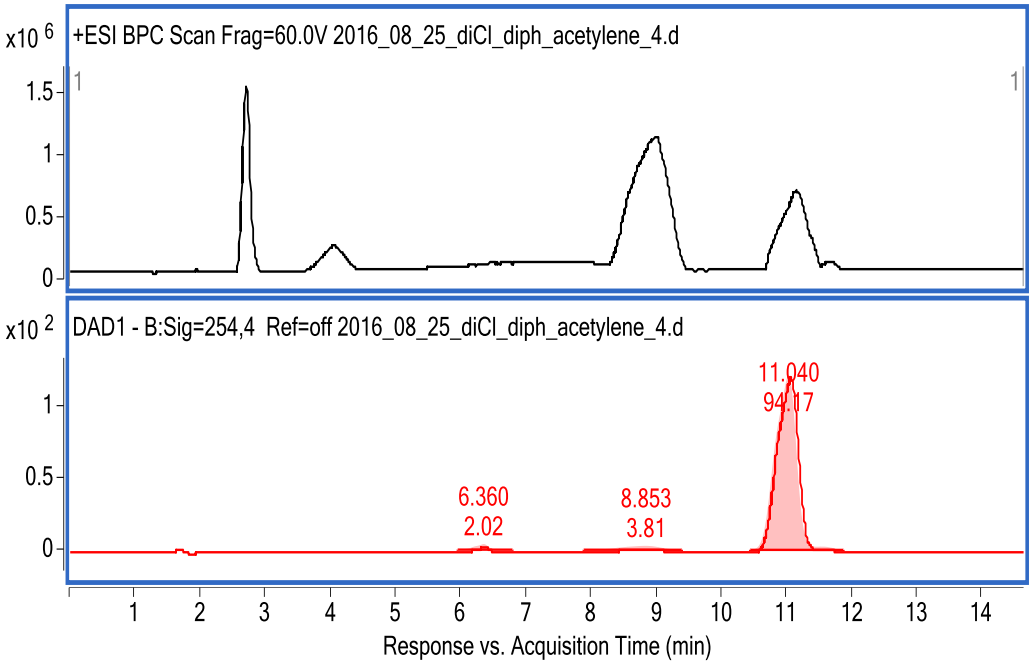


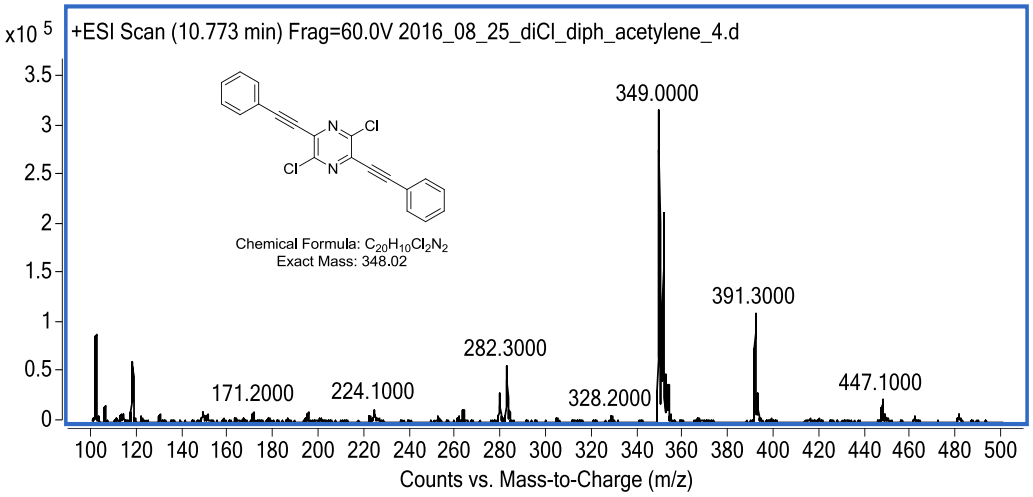
HR/MS – 13b





LC/MS – 15


x10 6
+ESI BPC Scan Frag=60.0V 2016_08_25_diCl_diph_acetylene_4.d
x10 2
DAD1 - B:Sig=254,4 Ref=off 2016_08_25_diCl_diph_acetylene_4.d
11.040
94.17
6.360
2.02
8.853
3.81
Response vs. Acquisition Time (min)


x10 5
+ESI Scan (10.773 min) Frag=60.0V 2016_08_25_diCl_diph_acetylene_4.d
Chemical Formula: C20H10Cl2N2
Exact Mass: 348.02
349.0000
391.3000
282.3000
171.2000
224.1000
328.2000
447.1000
Counts vs. Mass-to-Charge (m/z)

LC/MS – 17

Single crystal XRD data

Table 1. Crystal data and structure refinement for compound 6f

Identification code	20161123_0m	
Empirical formula	$C_{17}H_{16}N_4$	
Formula weight	276.34	
Temperature	296(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.6046(4) Å	α= 90°.
	b = 10.6651(5) Å	β= 100.530(3)°.
	c = 14.3071(6) Å	γ = 90°.
Volume	1440.85(11) $Å^3$	
Z	4	
Density (calculated)	1.274 Mg/m^3	
Absorption coefficient	0.079 mm^{-1}	
F(000)	584	
Crystal size	0.40 x 0.30 x 0.16 mm^3	
Theta range for data collection	2.37 to 28.33°	
Index ranges	-12<=h<=12, 0<=k<=14, 0<=l<=19	
Reflections collected	3579	
Independent reflections	3579 [R(int) = 0.0000]	
Completeness to theta = 28.33°	99.6 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9875 and 0.9692	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3579 / 0 / 208	
Goodness-of-fit on F^2	1.123	
Final R indices [I>2sigma(I)]	R1 = 0.0597, wR2 = 0.1485	
R indices (all data)	R1 = 0.0793, wR2 = 0.1617	
Largest diff. peak and hole	0.283 and -0.264 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound 6f. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	2022(2)	4912(1)	-452(1)	52(1)
N(2)	3250(1)	6650(1)	398(1)	47(1)
N(3)	3945(1)	8684(1)	1042(1)	47(1)
N(4)	650(2)	7984(1)	-433(1)	53(1)
C(1)	2136(2)	6134(2)	-162(1)	45(1)
C(2)	3012(2)	7864(2)	518(1)	43(1)
C(3)	3301(2)	9863(2)	1001(1)	46(1)
C(4)	1974(2)	9791(2)	458(1)	52(1)
C(5)	1760(2)	8536(2)	130(1)	47(1)
C(6)	860(2)	6763(2)	-579(1)	48(1)
C(7)	-12(2)	5845(2)	-1125(1)	56(1)
C(8)	720(2)	4760(2)	-1028(1)	57(1)
C(9)	3064(3)	3948(2)	-153(2)	74(1)
C(10)	5328(2)	8326(2)	1556(2)	65(1)
C(11)	3989(2)	10976(2)	1486(1)	46(1)
C(12)	5364(2)	11335(2)	1424(1)	54(1)
C(13)	5937(2)	12433(2)	1840(1)	58(1)
C(14)	5169(2)	13219(2)	2331(1)	55(1)
C(15)	3810(2)	12848(2)	2404(1)	56(1)
C(16)	3227(2)	11755(2)	1991(1)	52(1)
C(17)	5772(3)	14444(2)	2751(2)	84(1)

Table 3. Bond lengths [Å] and angles [°] for compound 6f.

N(1)-C(1)	1.365(2)
N(1)-C(8)	1.376(2)
N(1)-C(9)	1.445(3)
N(2)-C(2)	1.332(2)
N(2)-C(1)	1.332(2)
N(3)-C(2)	1.372(2)
N(3)-C(3)	1.398(2)
N(3)-C(10)	1.447(2)
N(4)-C(6)	1.340(2)
N(4)-C(5)	1.348(2)
C(1)-C(6)	1.428(2)
C(2)-C(5)	1.422(2)
C(3)-C(4)	1.368(2)
C(3)-C(11)	1.470(2)
C(4)-C(5)	1.422(2)
C(4)-H(4B)	0.9300
C(6)-C(7)	1.425(2)
C(7)-C(8)	1.347(3)
C(7)-H(7A)	0.9300
C(8)-H(8A)	0.9300
C(9)-H(9A)	1.00(3)
C(9)-H(9B)	0.96(3)
C(9)-H(9C)	0.94(3)
C(10)-H(10A)	1.02(3)
C(10)-H(10B)	1.05(3)
C(10)-H(10C)	0.92(3)
C(11)-C(12)	1.393(2)
C(11)-C(16)	1.393(2)
C(12)-C(13)	1.381(3)
C(12)-H(12A)	0.9300
C(13)-C(14)	1.389(3)
C(13)-H(13A)	0.9300
C(14)-C(15)	1.386(3)
C(14)-C(17)	1.509(3)
C(15)-C(16)	1.379(3)
C(15)-H(15A)	0.9300

C(16)-H(16A)	0.9300
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600

C(1)-N(1)-C(8)	107.92(15)
C(1)-N(1)-C(9)	125.25(16)
C(8)-N(1)-C(9)	126.74(17)
C(2)-N(2)-C(1)	110.00(13)
C(2)-N(3)-C(3)	108.06(13)
C(2)-N(3)-C(10)	123.86(15)
C(3)-N(3)-C(10)	128.07(15)
C(6)-N(4)-C(5)	113.07(14)
N(2)-C(1)-N(1)	125.99(15)
N(2)-C(1)-C(6)	126.14(15)
N(1)-C(1)-C(6)	107.86(15)
N(2)-C(2)-N(3)	125.44(14)
N(2)-C(2)-C(5)	126.27(15)
N(3)-C(2)-C(5)	108.29(14)
C(4)-C(3)-N(3)	109.47(14)
C(4)-C(3)-C(11)	127.24(15)
N(3)-C(3)-C(11)	123.30(14)
C(3)-C(4)-C(5)	107.65(15)
C(3)-C(4)-H(4B)	126.2
C(5)-C(4)-H(4B)	126.2
N(4)-C(5)-C(4)	131.25(15)
N(4)-C(5)-C(2)	122.23(15)
C(4)-C(5)-C(2)	106.52(14)
N(4)-C(6)-C(7)	131.50(16)
N(4)-C(6)-C(1)	122.28(15)
C(7)-C(6)-C(1)	106.22(15)
C(8)-C(7)-C(6)	106.88(16)
C(8)-C(7)-H(7A)	126.6
C(6)-C(7)-H(7A)	126.6
C(7)-C(8)-N(1)	111.12(16)
C(7)-C(8)-H(8A)	124.4
N(1)-C(8)-H(8A)	124.4
N(1)-C(9)-H(9A)	108.2(18)

N(1)-C(9)-H(9B)	113.0(18)
H(9A)-C(9)-H(9B)	106(2)
N(1)-C(9)-H(9C)	111.7(18)
H(9A)-C(9)-H(9C)	108(2)
H(9B)-C(9)-H(9C)	110(2)
N(3)-C(10)-H(10A)	111.0(14)
N(3)-C(10)-H(10B)	109.1(14)
H(10A)-C(10)-H(10B)	105(2)
N(3)-C(10)-H(10C)	107.1(18)
H(10A)-C(10)-H(10C)	116(2)
H(10B)-C(10)-H(10C)	109(2)
C(12)-C(11)-C(16)	117.56(16)
C(12)-C(11)-C(3)	122.82(15)
C(16)-C(11)-C(3)	119.51(15)
C(13)-C(12)-C(11)	120.89(17)
C(13)-C(12)-H(12A)	119.6
C(11)-C(12)-H(12A)	119.6
C(12)-C(13)-C(14)	121.54(17)
C(12)-C(13)-H(13A)	119.2
C(14)-C(13)-H(13A)	119.2
C(15)-C(14)-C(13)	117.42(17)
C(15)-C(14)-C(17)	121.03(19)
C(13)-C(14)-C(17)	121.54(19)
C(16)-C(15)-C(14)	121.53(17)
C(16)-C(15)-H(15A)	119.2
C(14)-C(15)-H(15A)	119.2
C(15)-C(16)-C(11)	121.05(16)
C(15)-C(16)-H(16A)	119.5
C(11)-C(16)-H(16A)	119.5
C(14)-C(17)-H(17A)	109.5
C(14)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(14)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for compound 6f. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	59(1)	45(1)	54(1)	-8(1)	13(1)	3(1)
N(2)	46(1)	45(1)	49(1)	-4(1)	9(1)	8(1)
N(3)	43(1)	45(1)	51(1)	-4(1)	5(1)	8(1)
N(4)	49(1)	46(1)	60(1)	3(1)	2(1)	4(1)
C(1)	50(1)	43(1)	44(1)	0(1)	15(1)	5(1)
C(2)	43(1)	43(1)	45(1)	0(1)	10(1)	5(1)
C(3)	47(1)	43(1)	50(1)	0(1)	11(1)	6(1)
C(4)	48(1)	42(1)	63(1)	3(1)	4(1)	8(1)
C(5)	45(1)	44(1)	51(1)	4(1)	7(1)	6(1)
C(6)	49(1)	48(1)	47(1)	2(1)	9(1)	2(1)
C(7)	57(1)	58(1)	51(1)	-2(1)	3(1)	-3(1)
C(8)	64(1)	56(1)	50(1)	-9(1)	12(1)	-6(1)
C(9)	79(2)	52(1)	90(2)	-13(1)	12(1)	18(1)
C(10)	52(1)	60(1)	75(1)	-18(1)	-8(1)	16(1)
C(11)	50(1)	43(1)	46(1)	2(1)	8(1)	4(1)
C(12)	54(1)	56(1)	54(1)	-2(1)	16(1)	2(1)
C(13)	53(1)	62(1)	60(1)	3(1)	11(1)	-8(1)
C(14)	59(1)	51(1)	51(1)	0(1)	-2(1)	0(1)
C(15)	59(1)	51(1)	56(1)	-6(1)	8(1)	8(1)
C(16)	48(1)	48(1)	60(1)	-3(1)	12(1)	3(1)
C(17)	82(2)	64(1)	100(2)	-21(1)	2(1)	-13(1)

Table 5. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^{\ 3}$) for compound 6f.

	x	y	z	U(eq)
H(4B)	1328	10446	328	62
H(7A)	-913	5970	-1480	67
H(8A)	388	4007	-1313	68
H(9A)	2610(30)	3120(30)	-330(20)	111
H(9B)	3390(30)	3930(30)	520(20)	111
H(9C)	3850(30)	4020(30)	-460(20)	111

H(10A)	5660(30)	8920(30)	2112(19)	97
H(10B)	6070(30)	8440(20)	1112(18)	97
H(10C)	5280(30)	7490(30)	1710(20)	97
H(12A)	5902	10830	1097	64
H(13A)	6858	12650	1791	70
H(15A)	3279	13348	2740	67
H(16A)	2310	11534	2049	63
H(17A)	5090	14855	3060	126
H(17B)	5990	14972	2253	126
H(17C)	6620	14286	3206	126

Table 6. Torsion angles [°] for compound 6f.

C(2)-N(2)-C(1)-N(1)	178.68(15)
C(2)-N(2)-C(1)-C(6)	-0.3(2)
C(8)-N(1)-C(1)-N(2)	-179.43(15)
C(9)-N(1)-C(1)-N(2)	3.8(3)
C(8)-N(1)-C(1)-C(6)	-0.33(18)
C(9)-N(1)-C(1)-C(6)	-177.12(19)
C(1)-N(2)-C(2)-N(3)	-179.00(14)
C(1)-N(2)-C(2)-C(5)	1.0(2)
C(3)-N(3)-C(2)-N(2)	-179.51(15)
C(10)-N(3)-C(2)-N(2)	-1.0(3)
C(3)-N(3)-C(2)-C(5)	0.53(18)
C(10)-N(3)-C(2)-C(5)	179.01(18)
C(2)-N(3)-C(3)-C(4)	0.15(19)
C(10)-N(3)-C(3)-C(4)	-178.25(19)
C(2)-N(3)-C(3)-C(11)	179.69(14)
C(10)-N(3)-C(3)-C(11)	1.3(3)
N(3)-C(3)-C(4)-C(5)	-0.8(2)
C(11)-C(3)-C(4)-C(5)	179.72(16)
C(6)-N(4)-C(5)-C(4)	-179.96(18)
C(6)-N(4)-C(5)-C(2)	0.0(2)
C(3)-C(4)-C(5)-N(4)	-178.97(17)
C(3)-C(4)-C(5)-C(2)	1.06(19)
N(2)-C(2)-C(5)-N(4)	-0.9(3)
N(3)-C(2)-C(5)-N(4)	179.05(15)
N(2)-C(2)-C(5)-C(4)	179.06(16)

N(3)-C(2)-C(5)-C(4)	-0.98(18)
C(5)-N(4)-C(6)-C(7)	-179.27(17)
C(5)-N(4)-C(6)-C(1)	0.6(2)
N(2)-C(1)-C(6)-N(4)	-0.6(3)
N(1)-C(1)-C(6)-N(4)	-179.66(15)
N(2)-C(1)-C(6)-C(7)	179.37(15)
N(1)-C(1)-C(6)-C(7)	0.27(18)
N(4)-C(6)-C(7)-C(8)	179.81(18)
C(1)-C(6)-C(7)-C(8)	-0.11(19)
C(6)-C(7)-C(8)-N(1)	-0.1(2)
C(1)-N(1)-C(8)-C(7)	0.3(2)
C(9)-N(1)-C(8)-C(7)	177.0(2)
C(4)-C(3)-C(11)-C(12)	-131.89(19)
N(3)-C(3)-C(11)-C(12)	48.6(2)
C(4)-C(3)-C(11)-C(16)	44.5(2)
N(3)-C(3)-C(11)-C(16)	-135.01(17)
C(16)-C(11)-C(12)-C(13)	-0.7(3)
C(3)-C(11)-C(12)-C(13)	175.74(16)
C(11)-C(12)-C(13)-C(14)	-0.3(3)
C(12)-C(13)-C(14)-C(15)	1.2(3)
C(12)-C(13)-C(14)-C(17)	-177.34(19)
C(13)-C(14)-C(15)-C(16)	-1.3(3)
C(17)-C(14)-C(15)-C(16)	177.31(19)
C(14)-C(15)-C(16)-C(11)	0.4(3)
C(12)-C(11)-C(16)-C(15)	0.6(3)
C(3)-C(11)-C(16)-C(15)	-175.91(16)

Symmetry transformations used to generate equivalent atoms: