Supporting Information

2,6-Di(thiophenyl)-1,5-Dihydrodipyrrolopyrazine (DT-DPP) structural isomers as Donor-Acceptor-Donor molecules for optoelectronic application

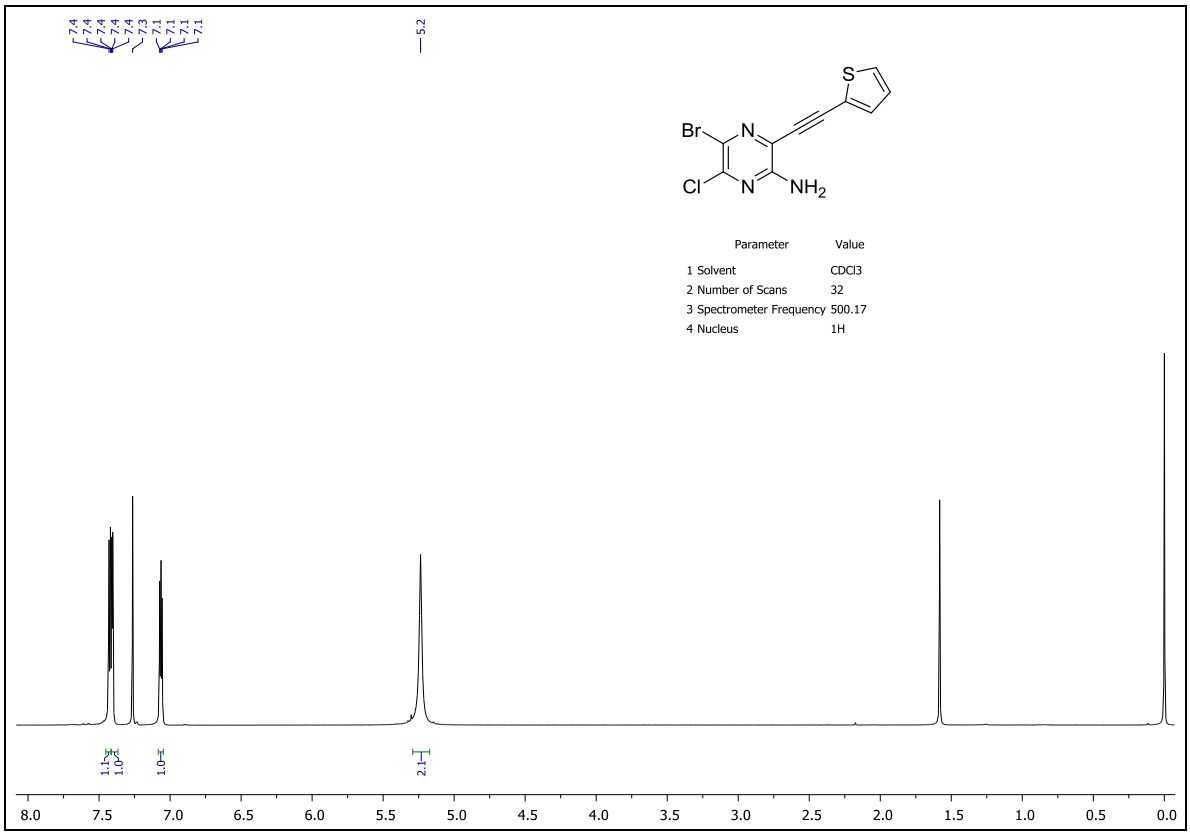
*Puttavva Meti and Young-Dae Gong**

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

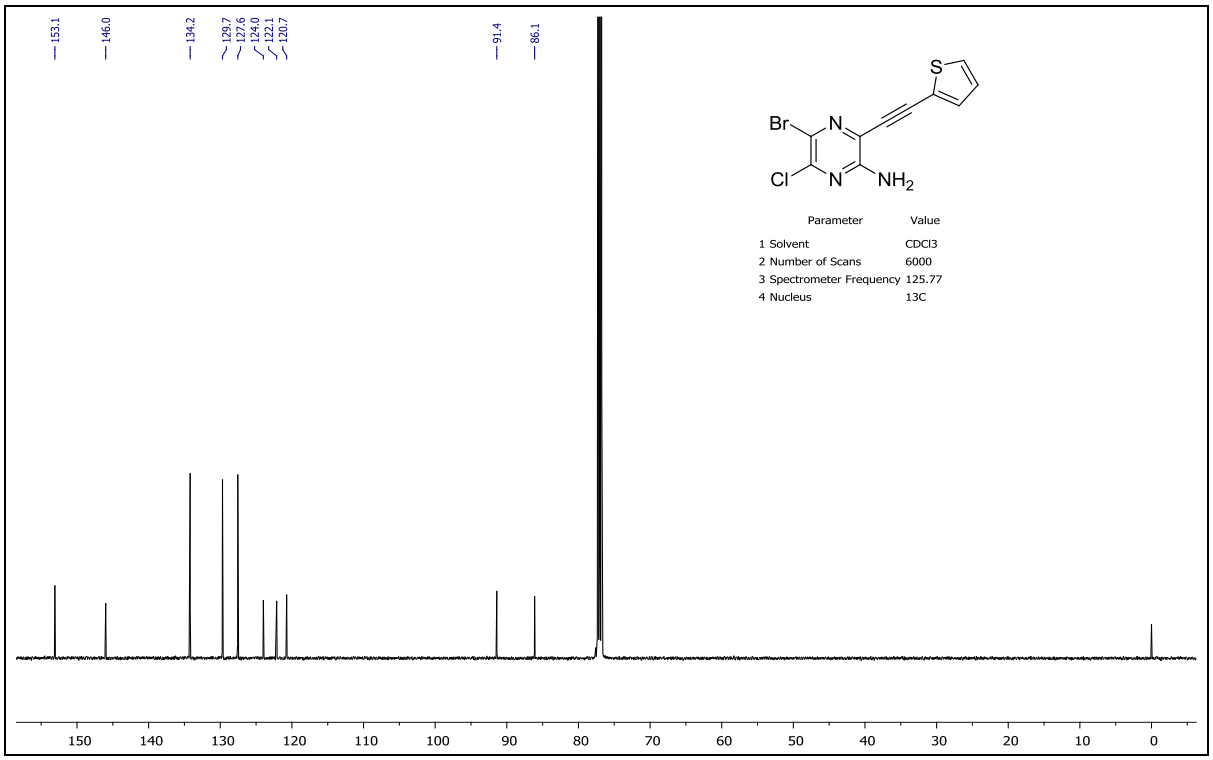
Co-corresponding author's E-Mail: ydgong@dongguk.edu

Contents

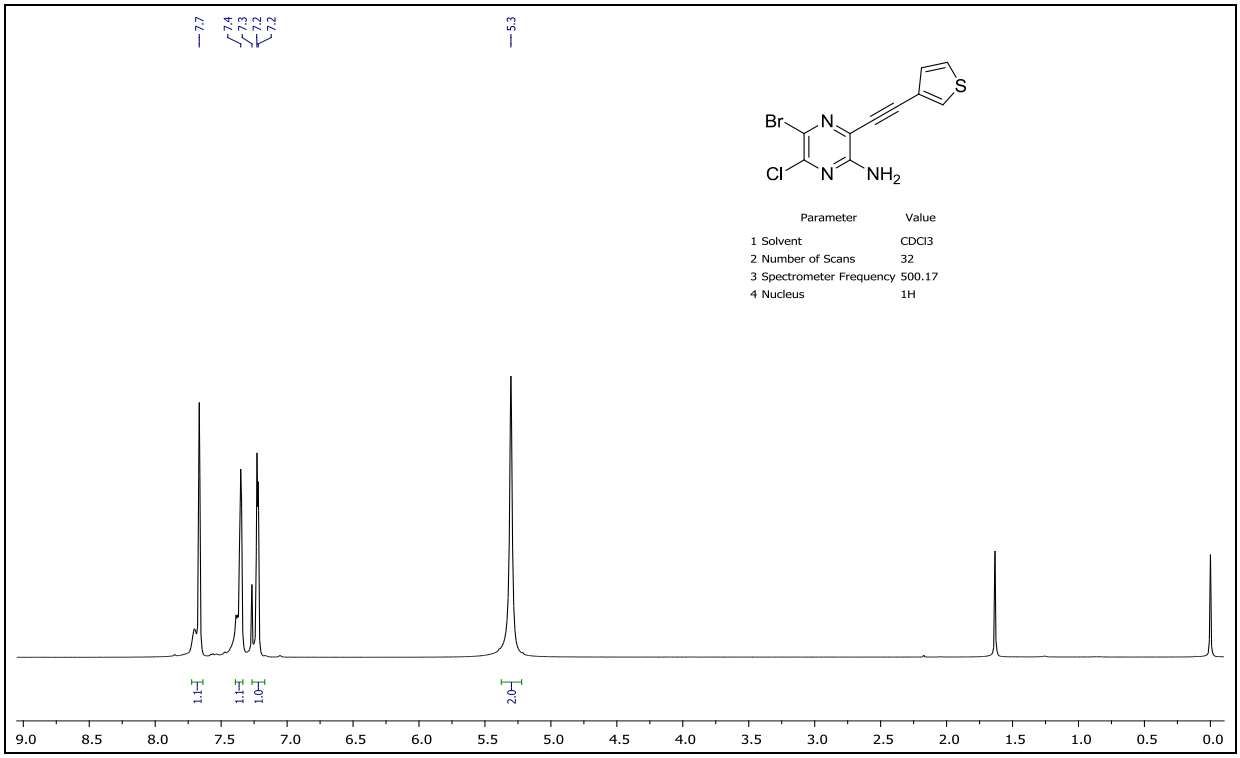
^{1}H NMR ^{13}C NMR of compounds 1(a-b) to 8 (a-b)



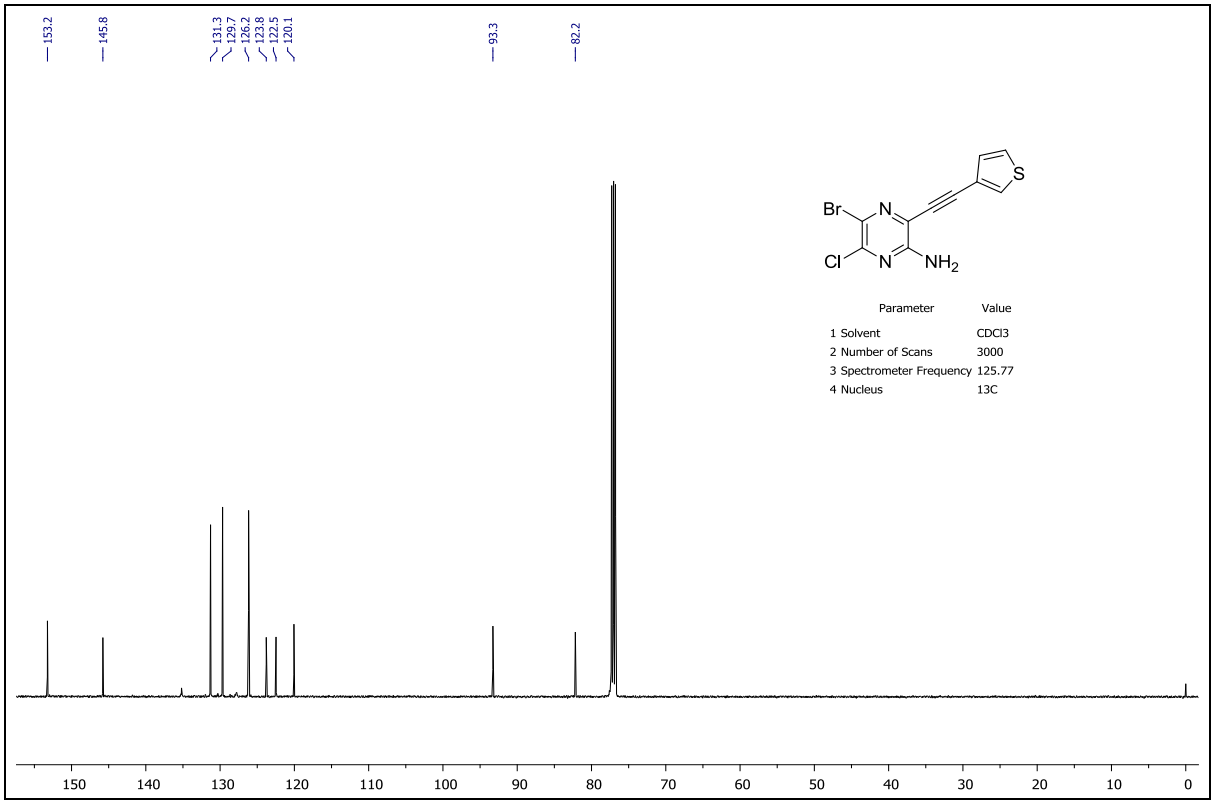
^{1}H NMR - 1a



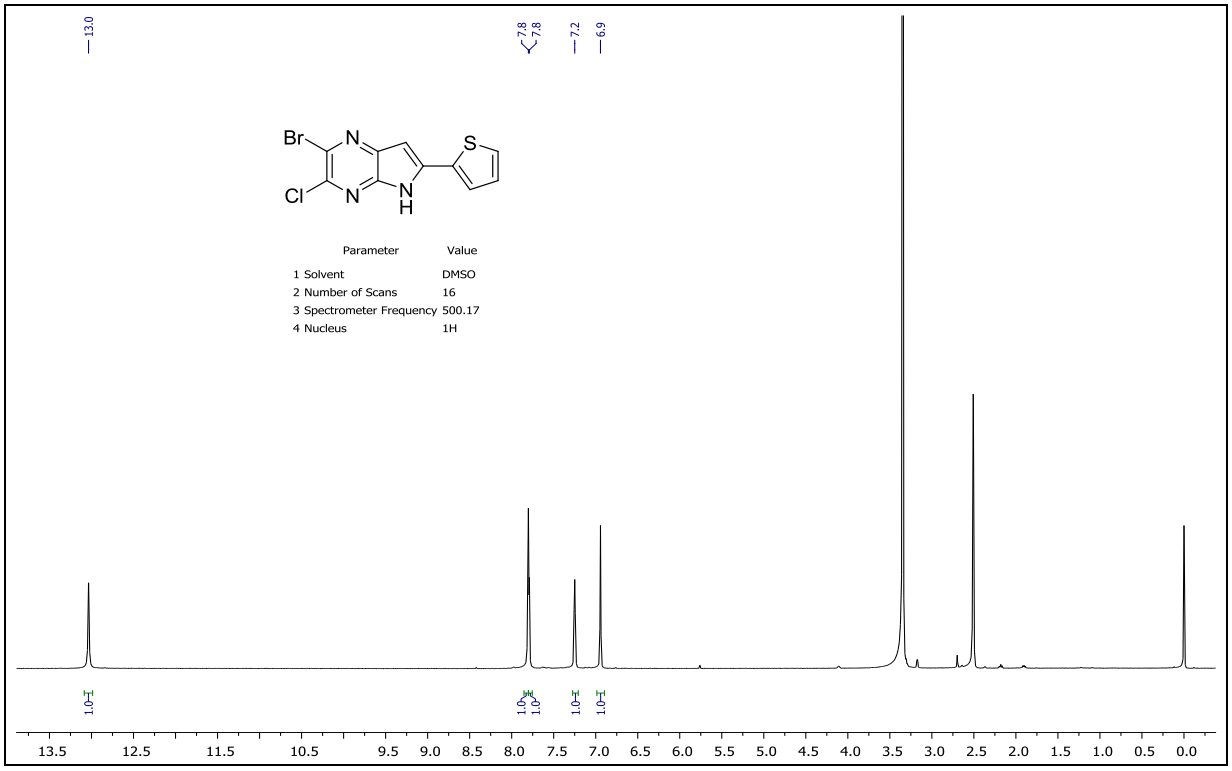
^{13}C NMR - 1a



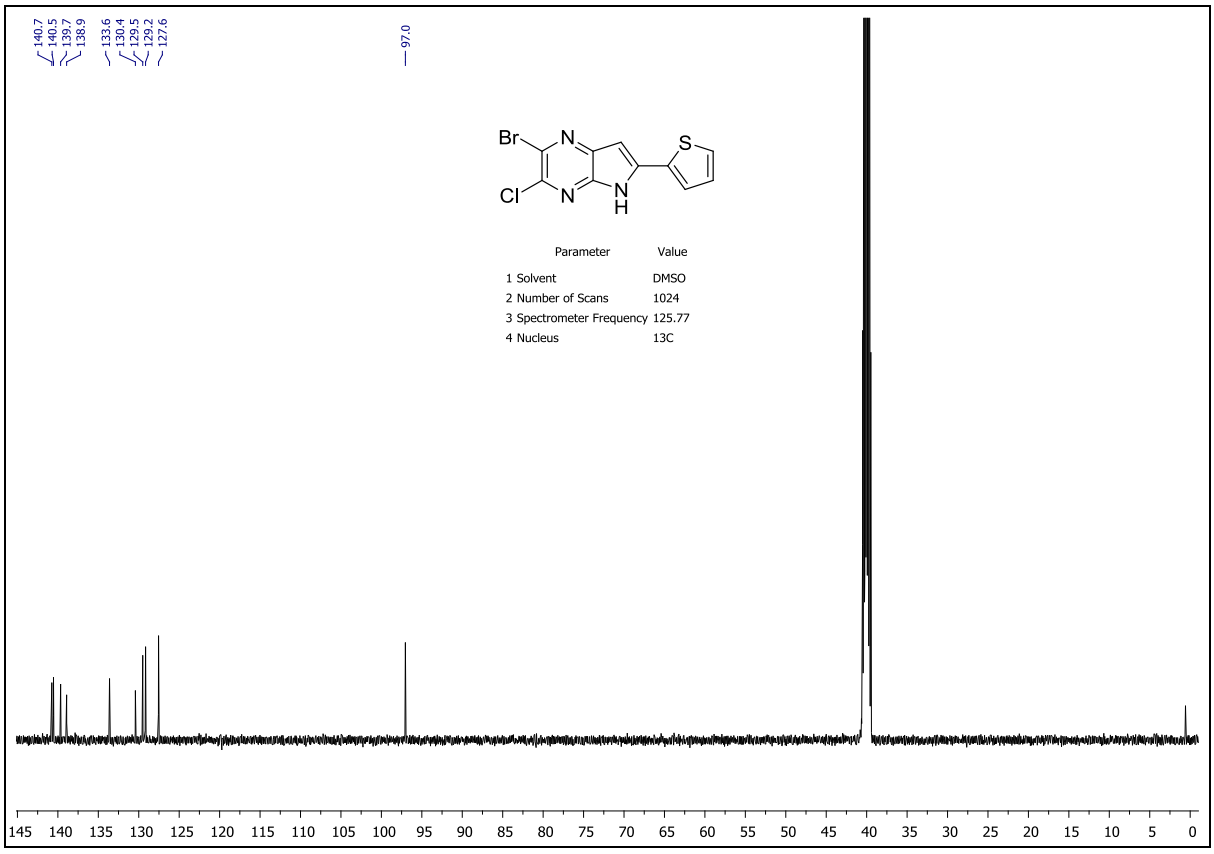
^{1}H NMR – 1b



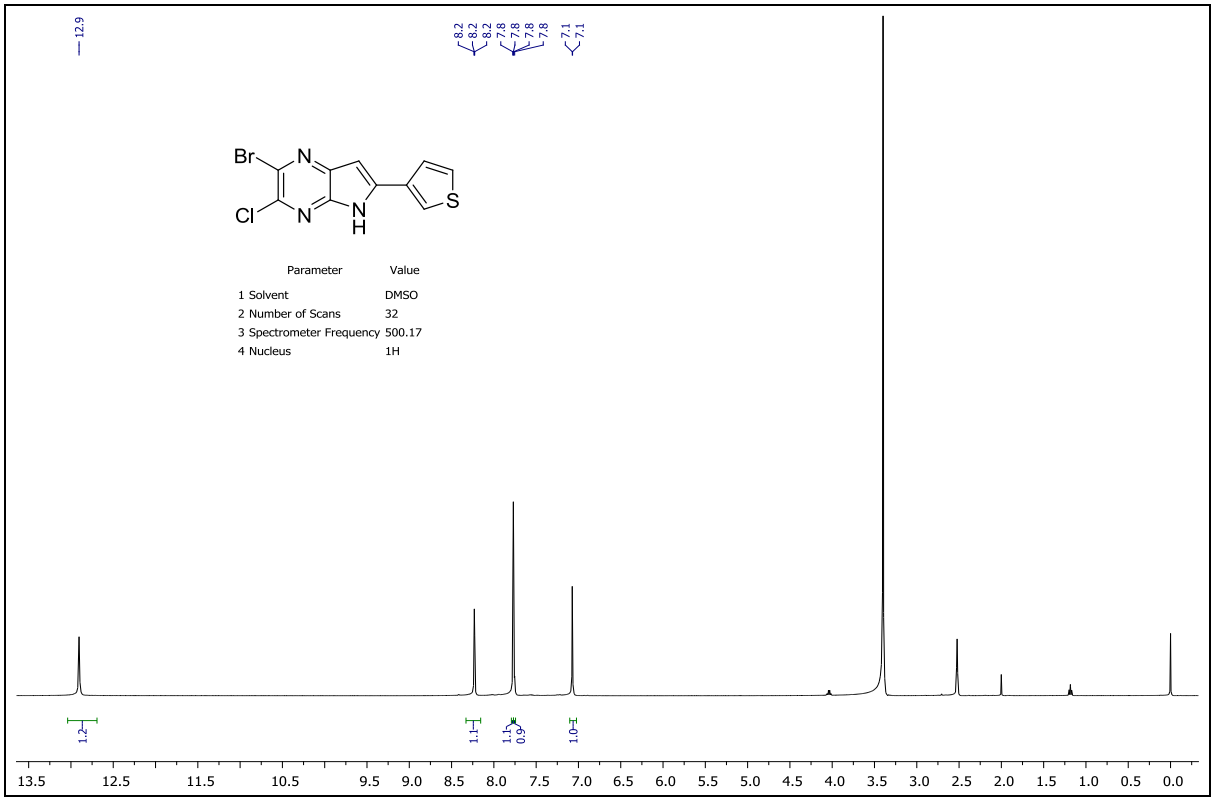
^{13}C NMR – 1b



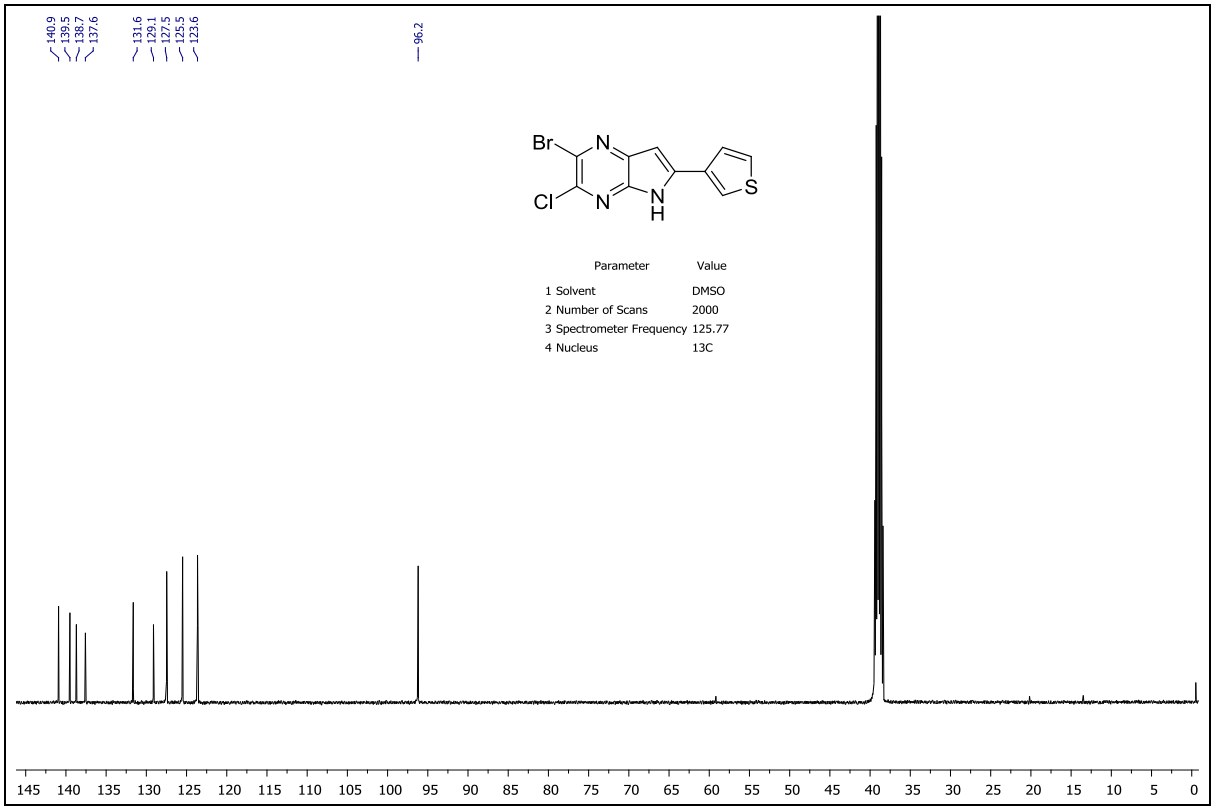
^{1}H NMR – 2a



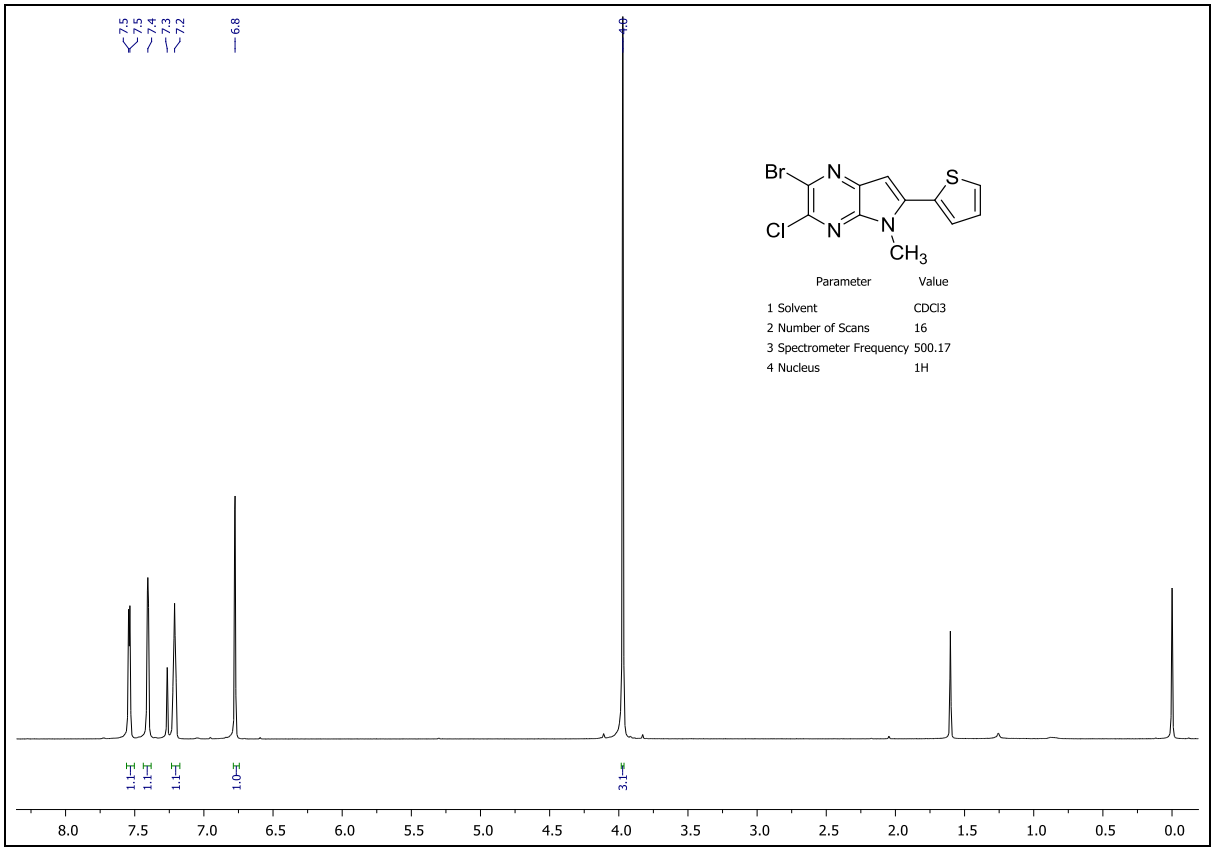
^{13}C NMR – 2a



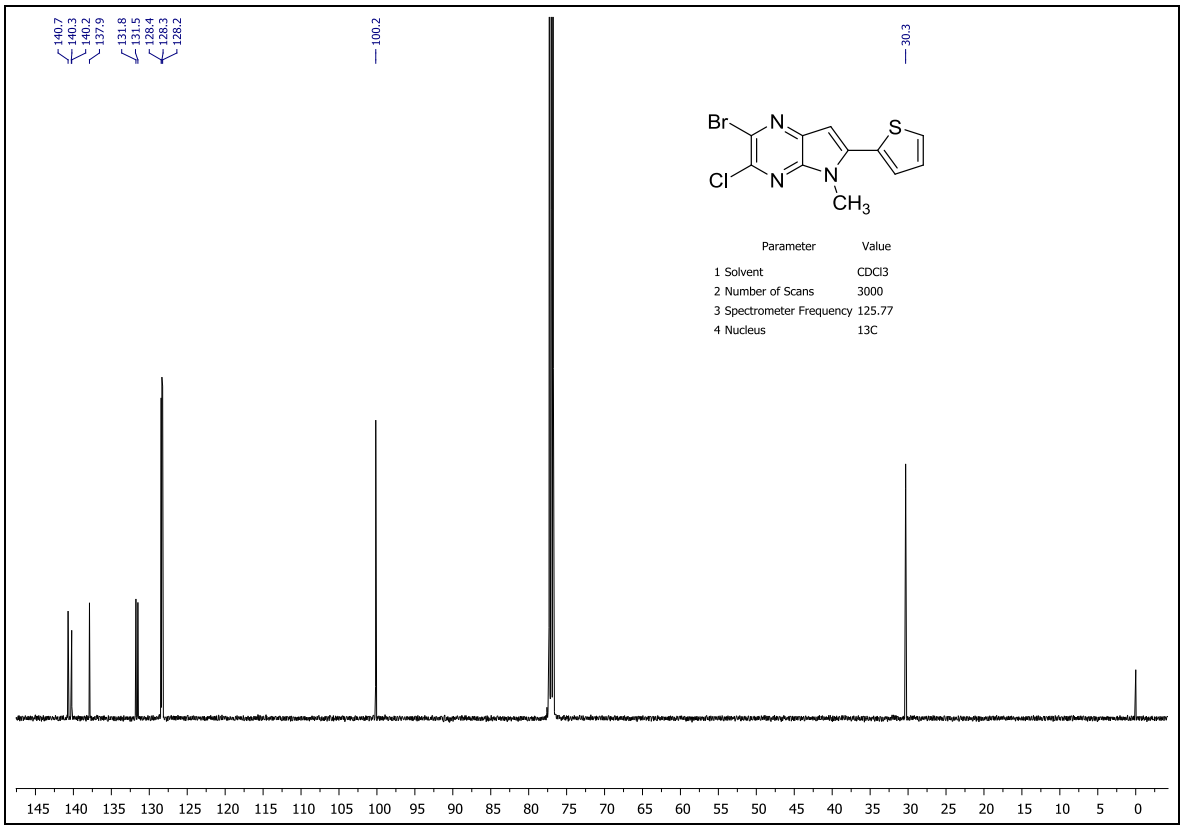
^{1}H NMR – 2b



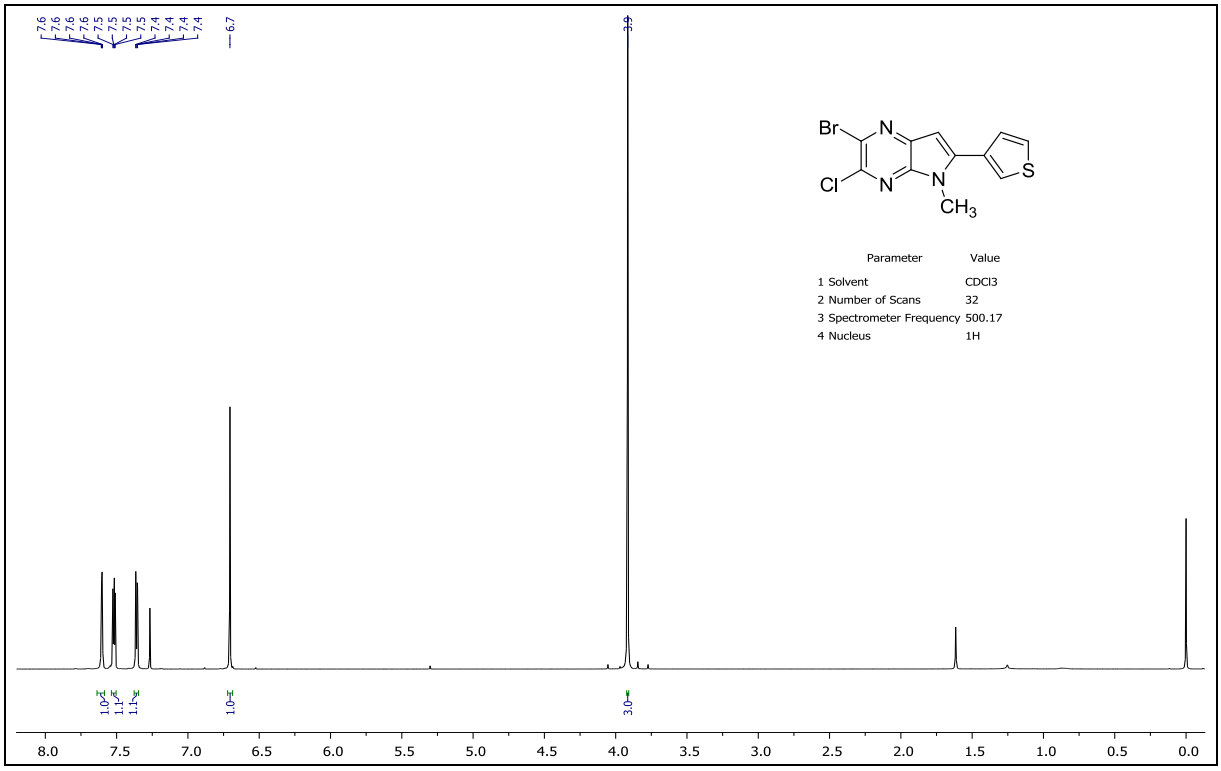
^{13}C NMR – 2b



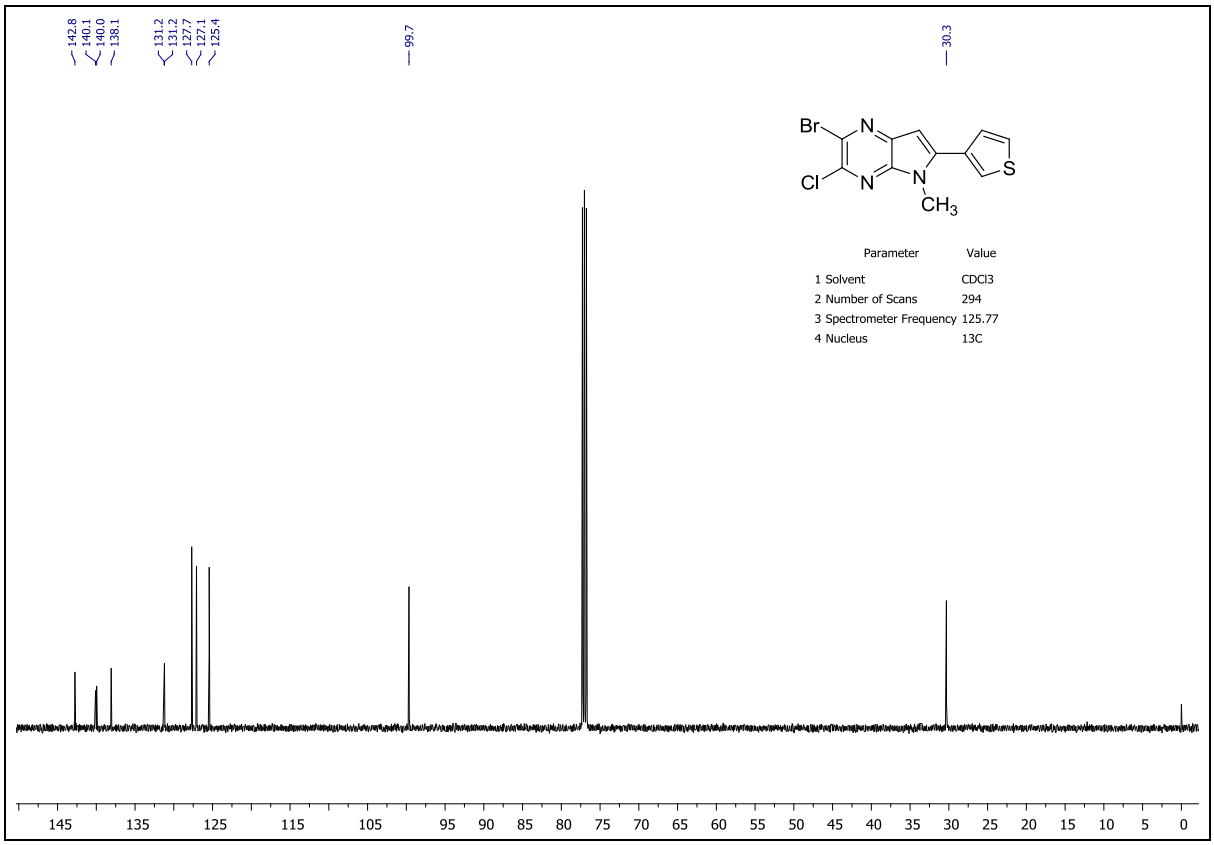
^{1}H NMR – 3a



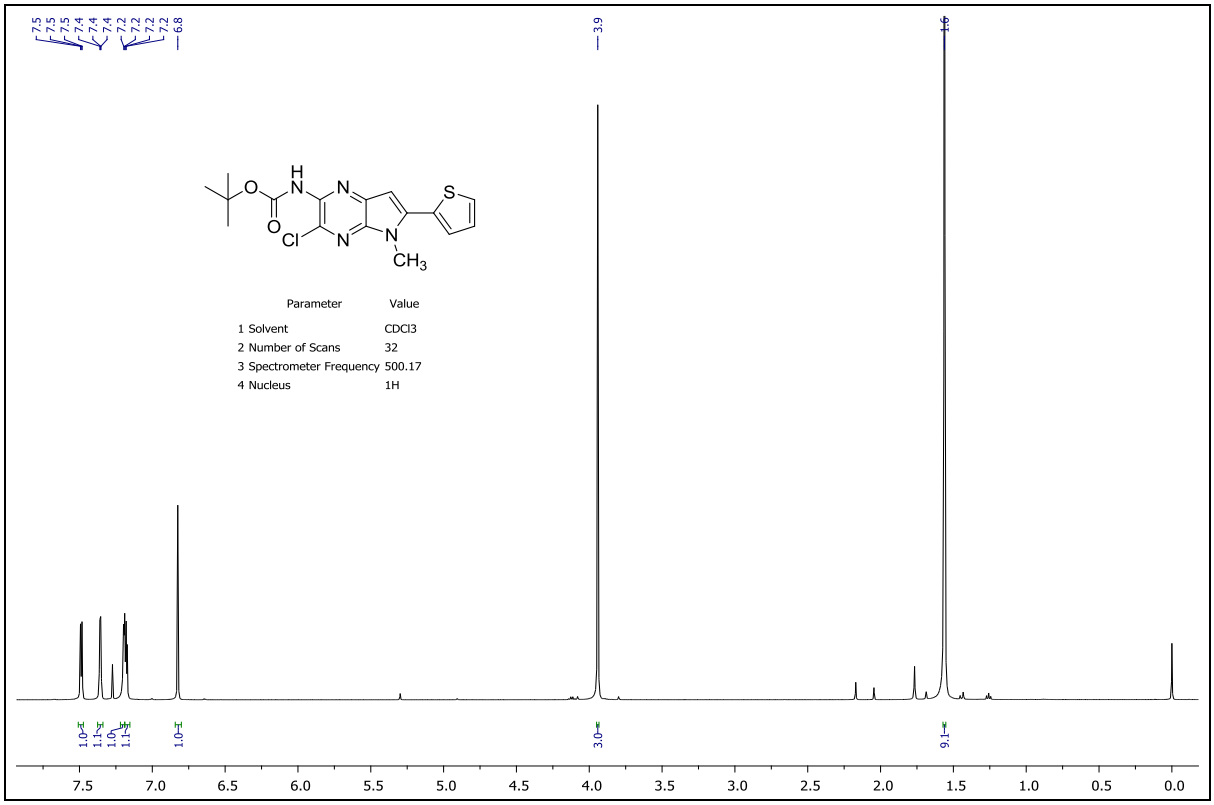
^{13}C NMR – 3a



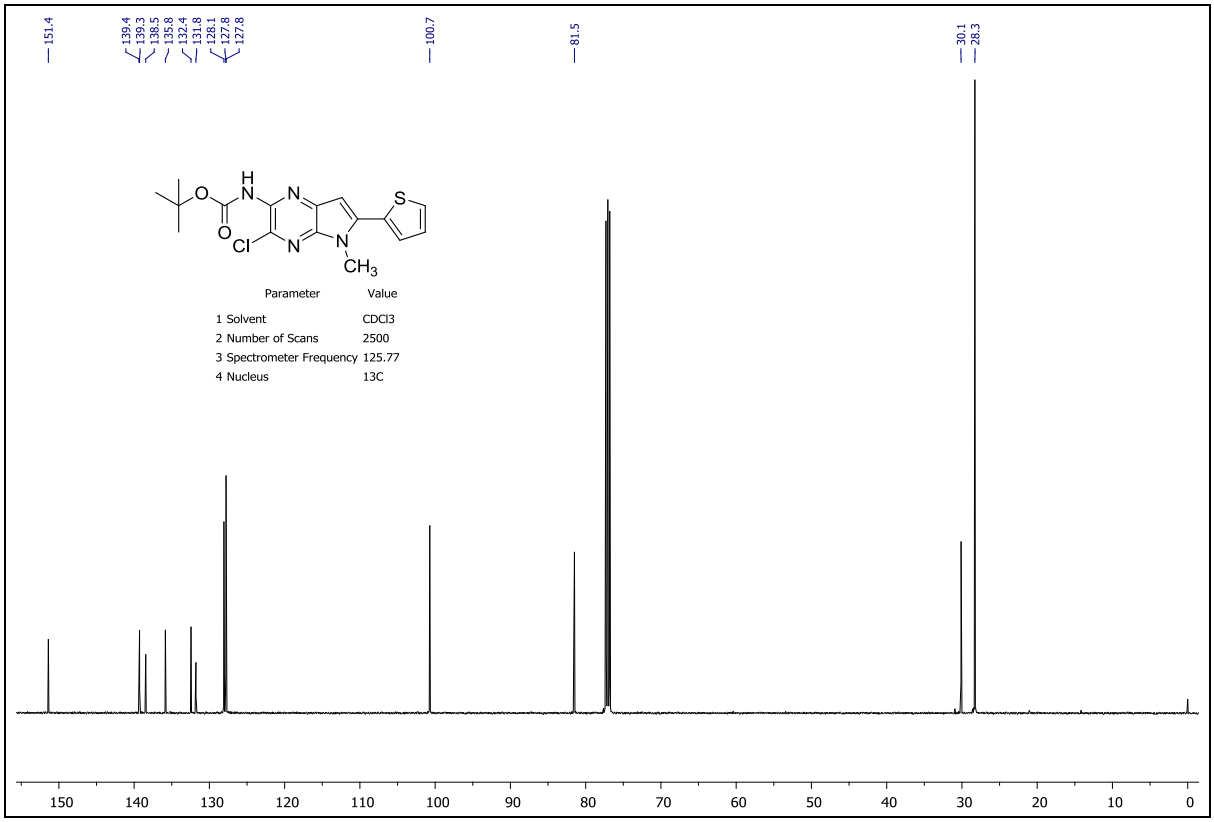
^{1}H NMR – 3b



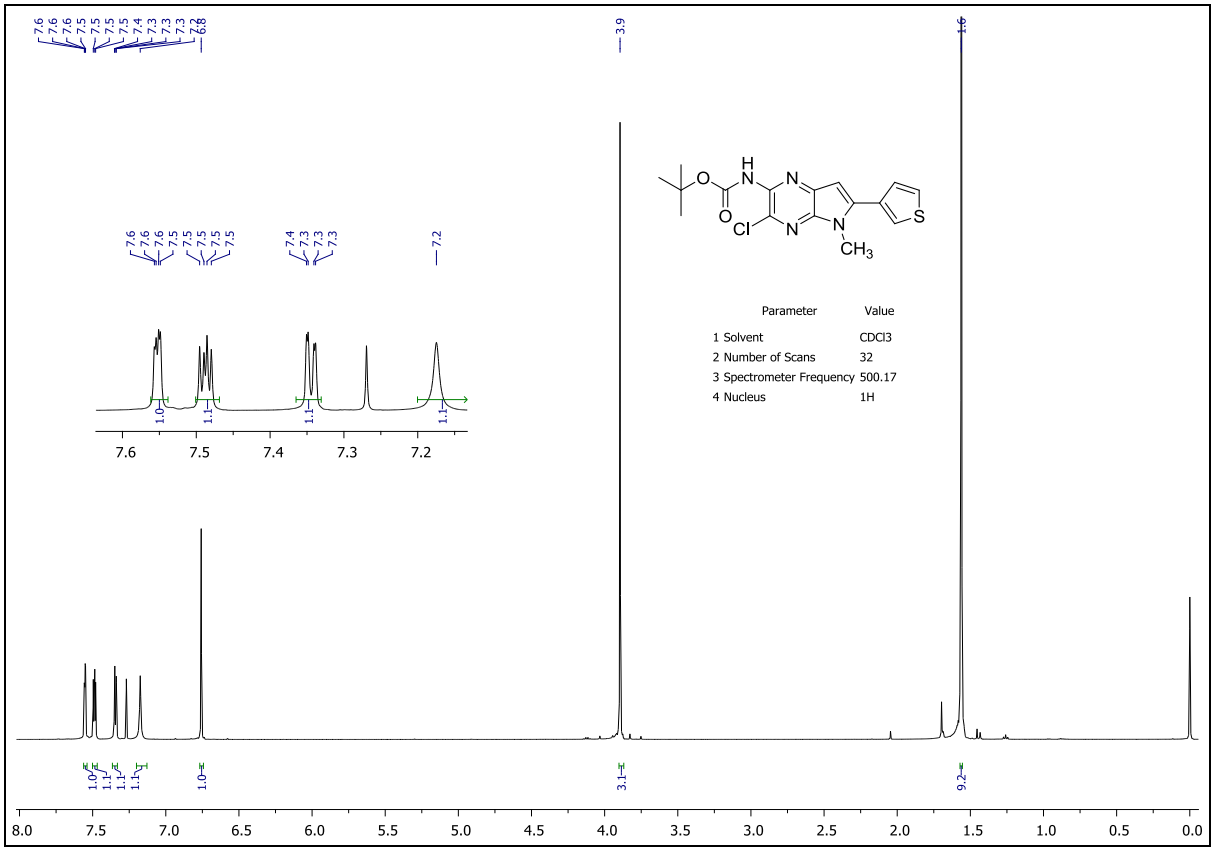
^{13}C NMR – 3b



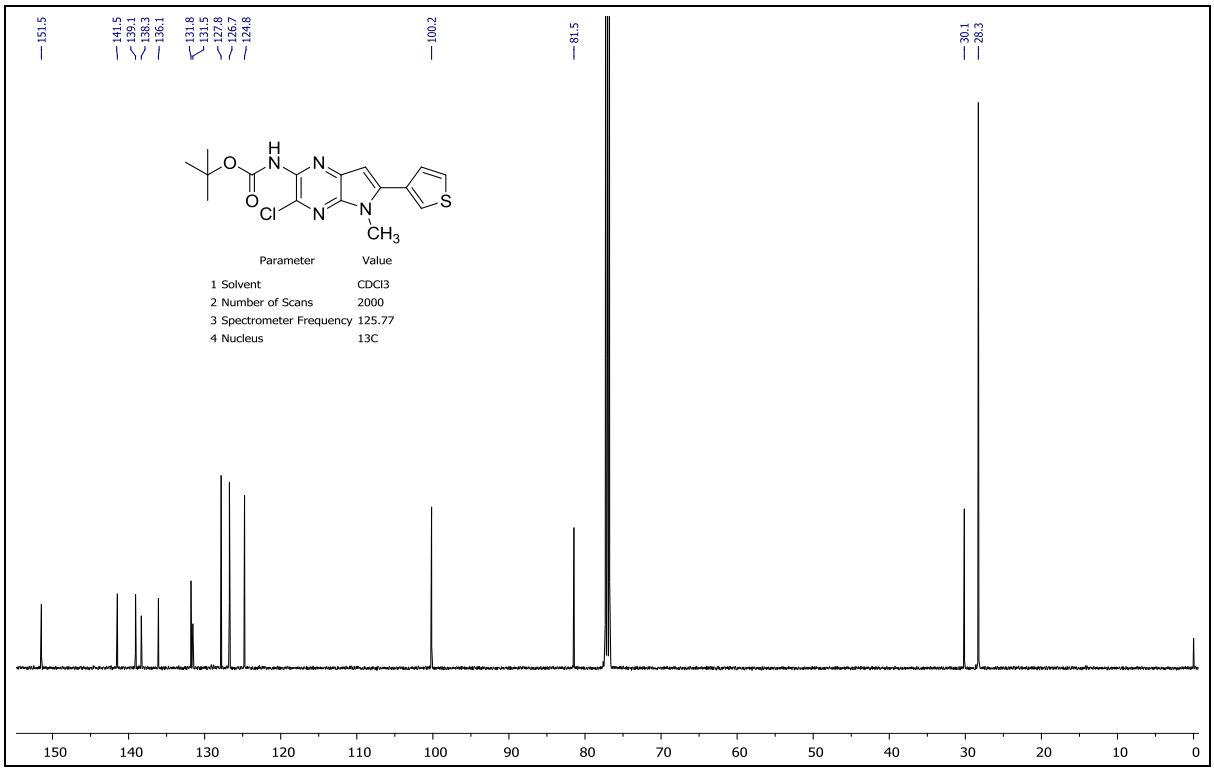
^{1}H NMR – 4a



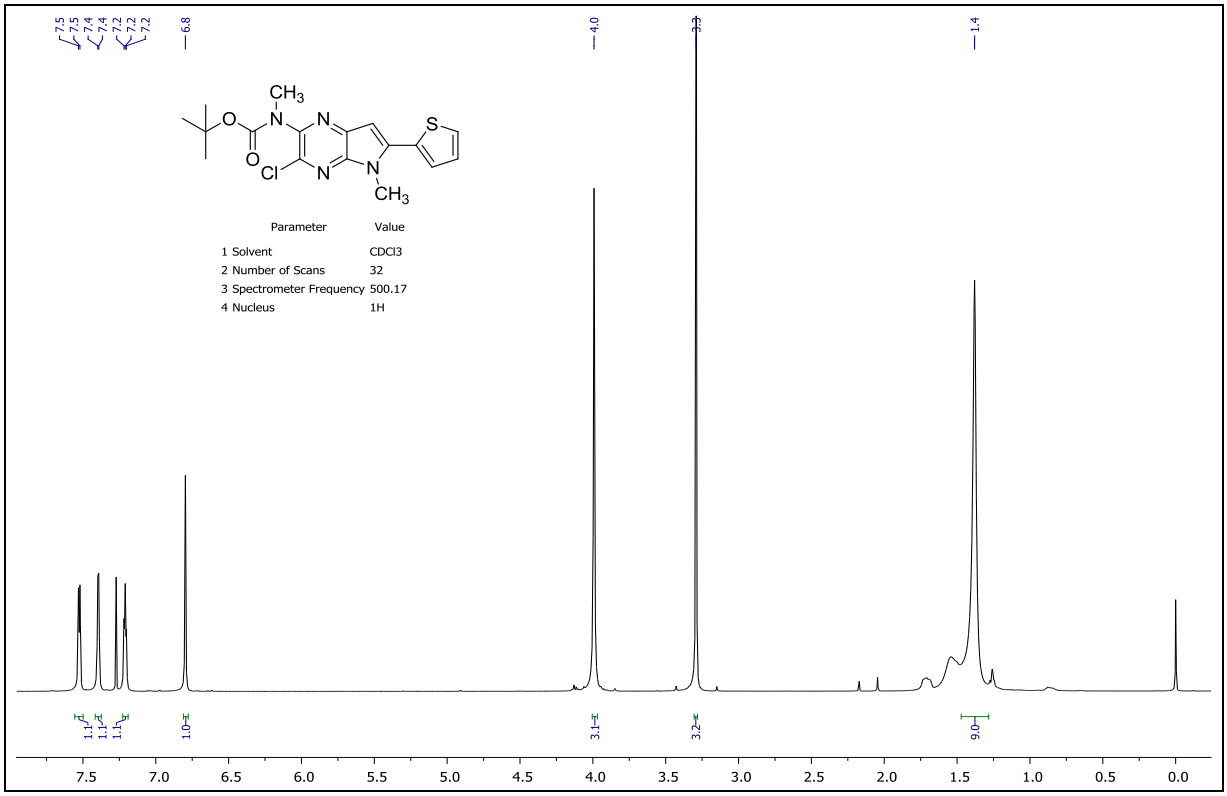
^{13}C NMR – 4a



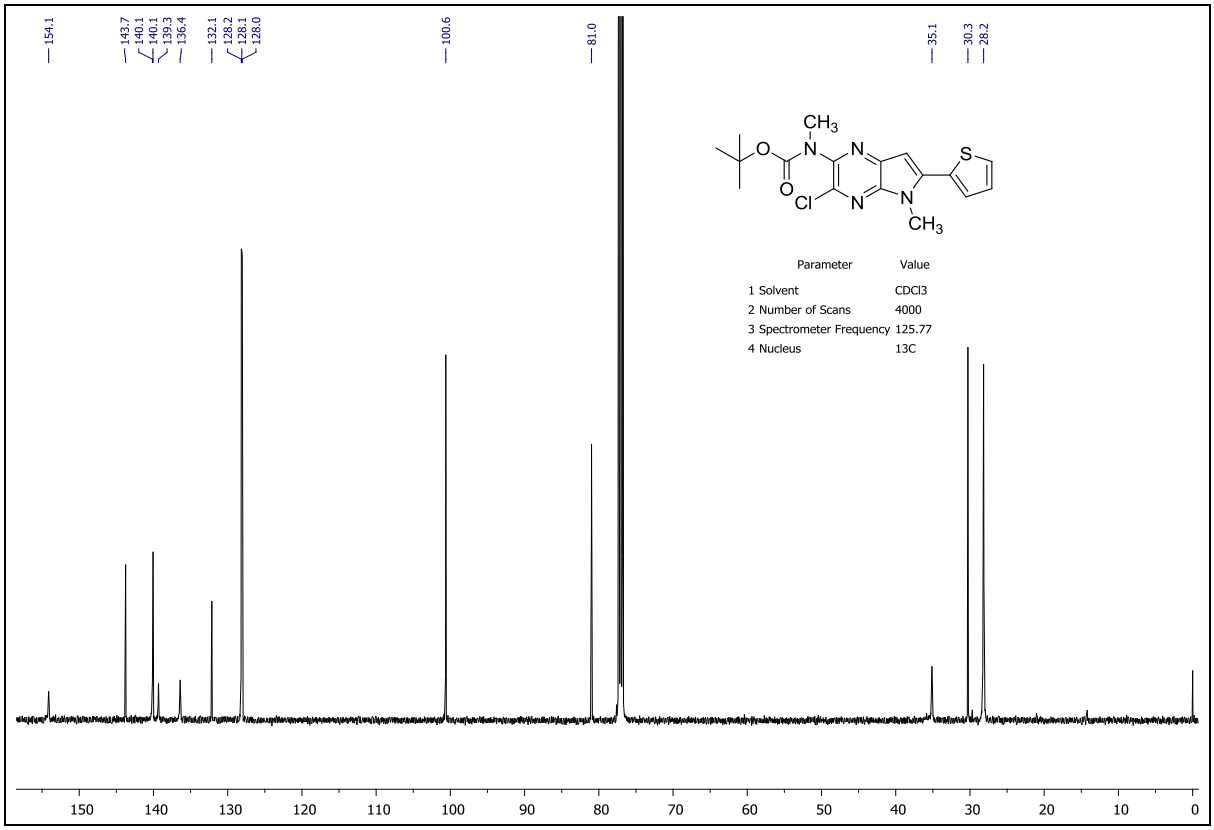
^{1}H NMR – 4b



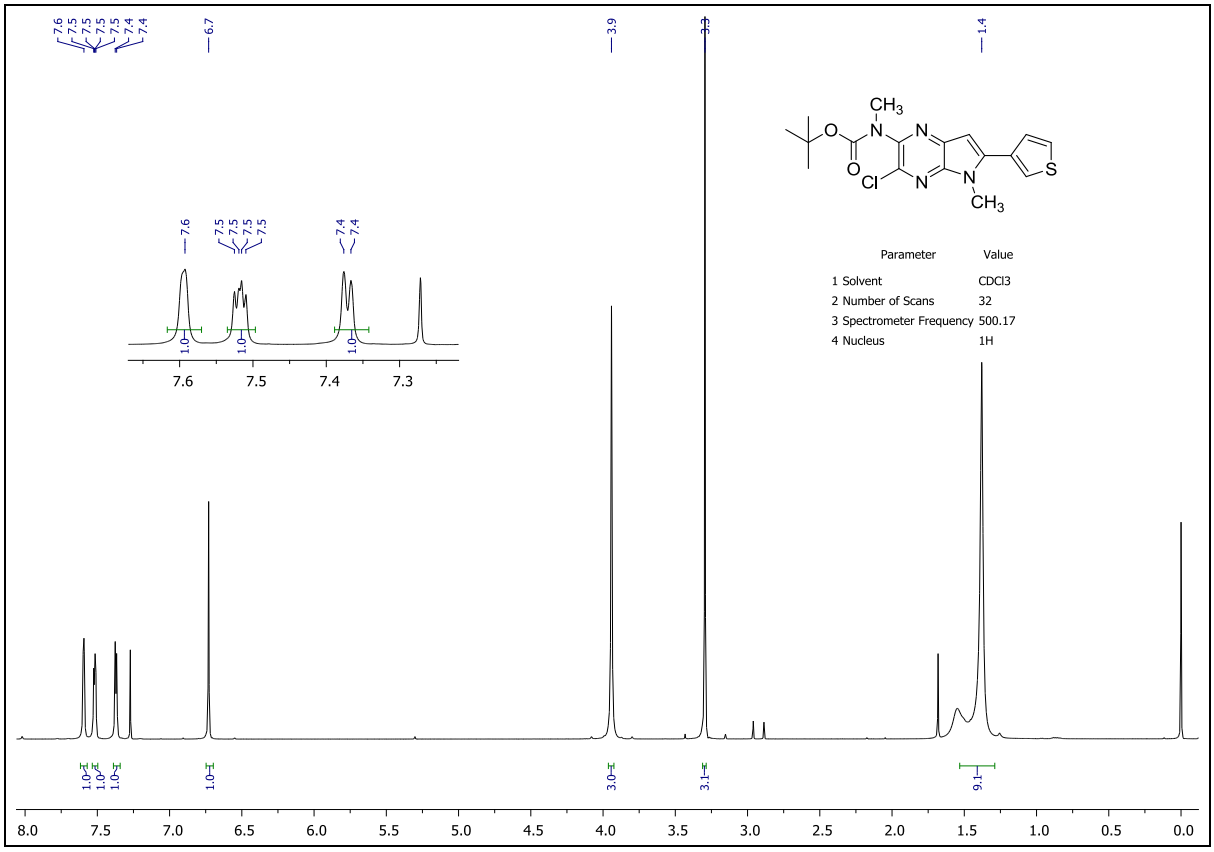
^{13}C NMR – 4b



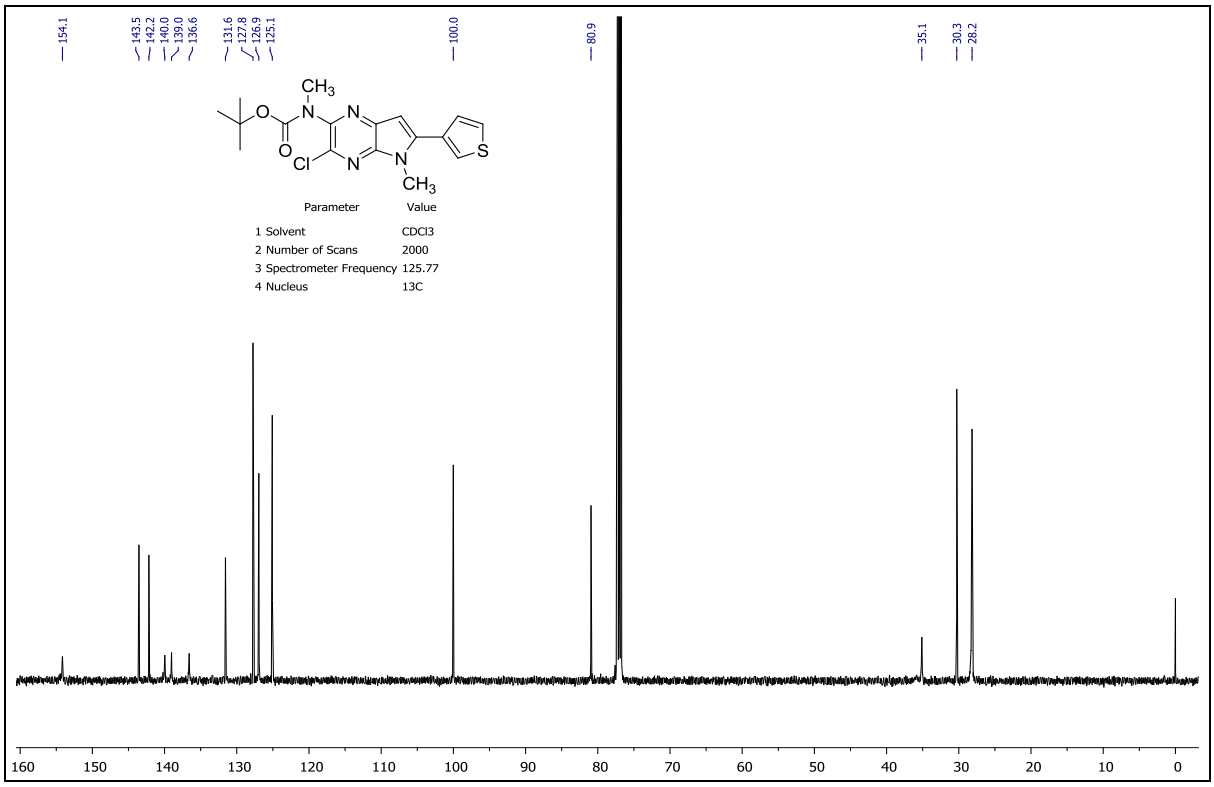
^{1}H NMR – 5a



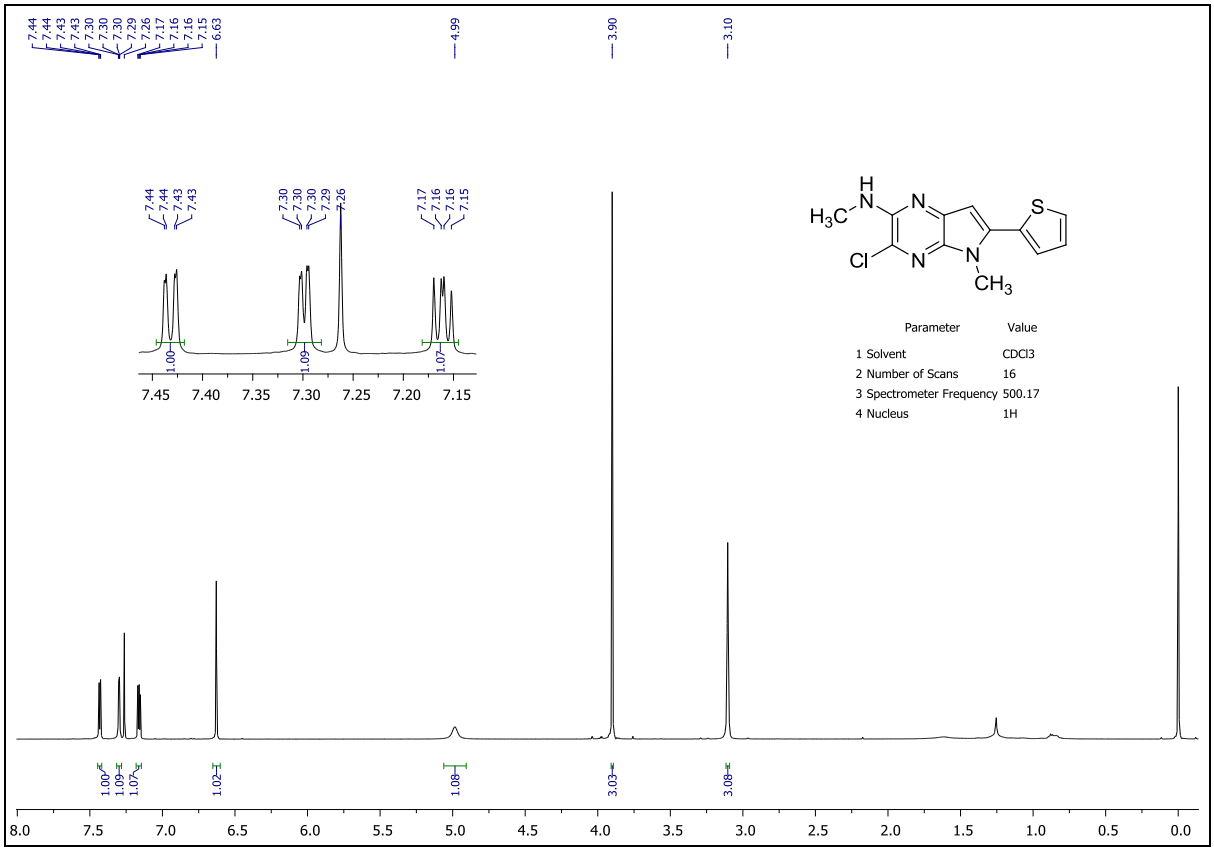
^{13}C NMR – 5a



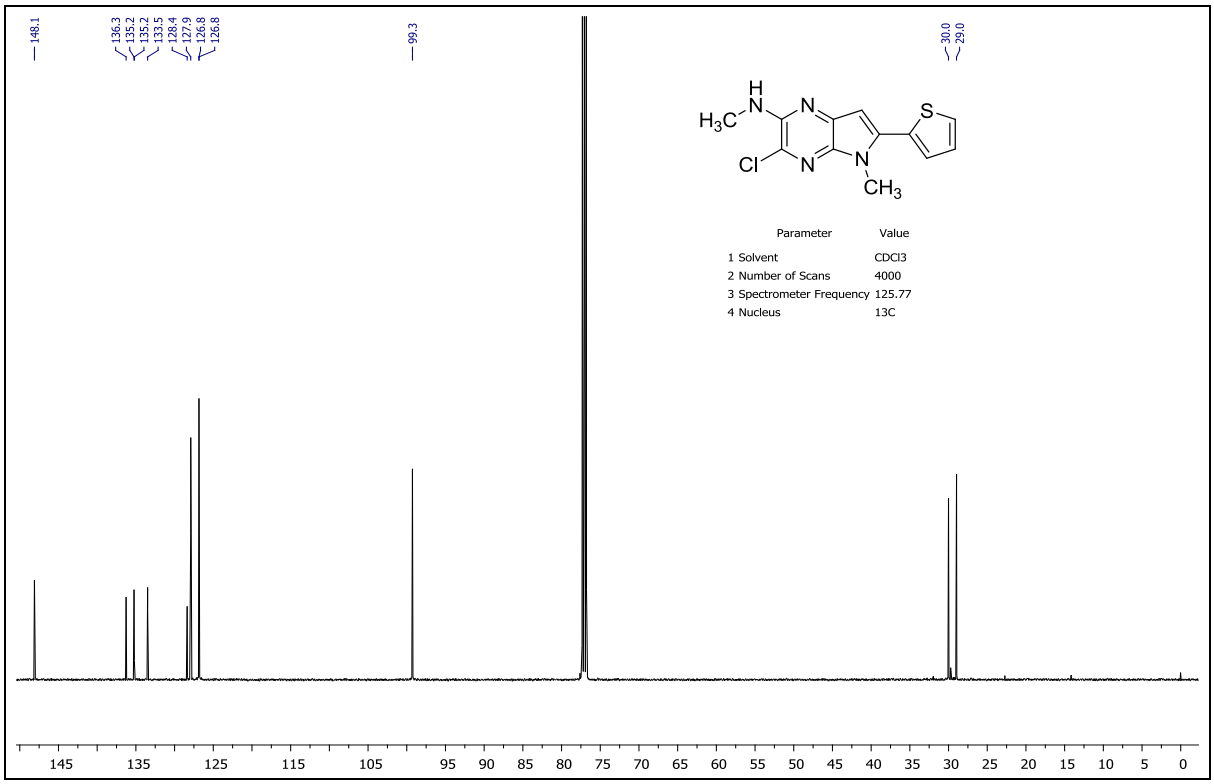
^{1}H NMR – 5b



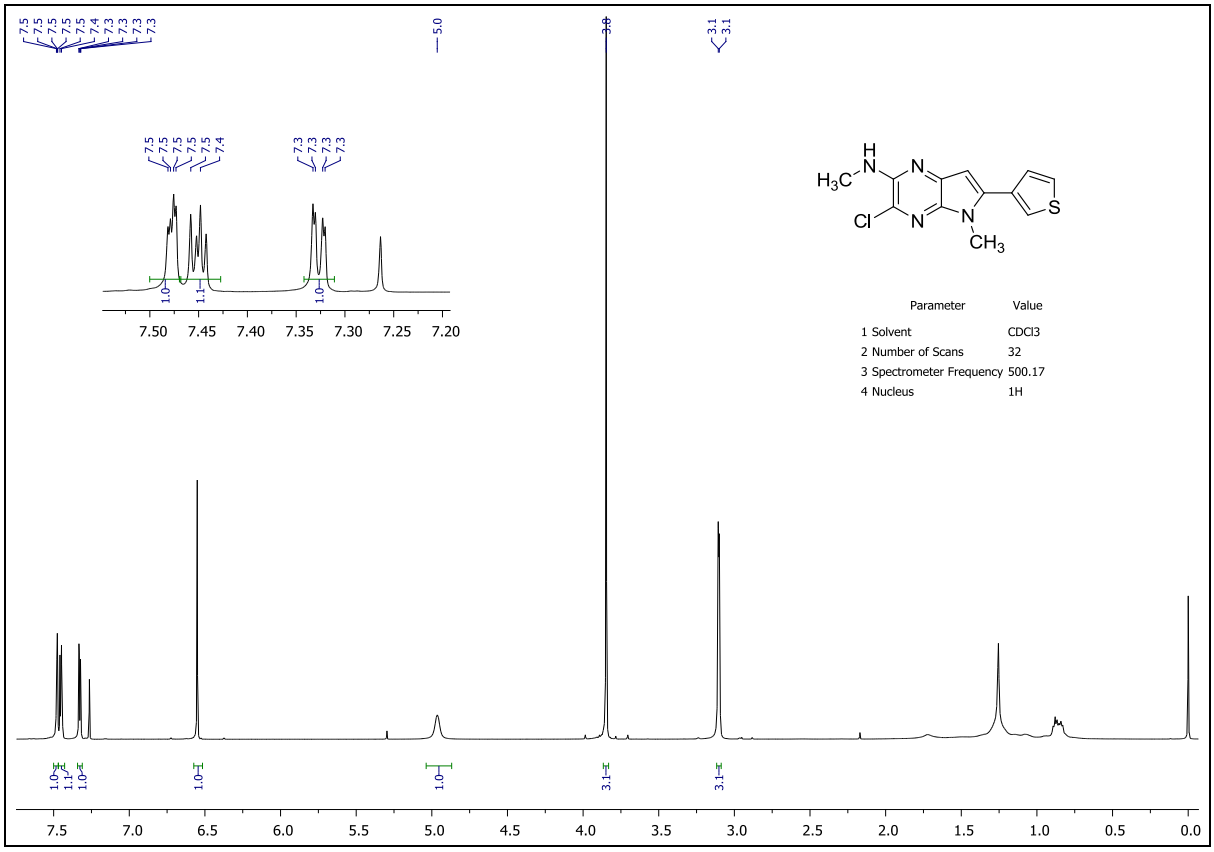
^{13}C NMR – 5b



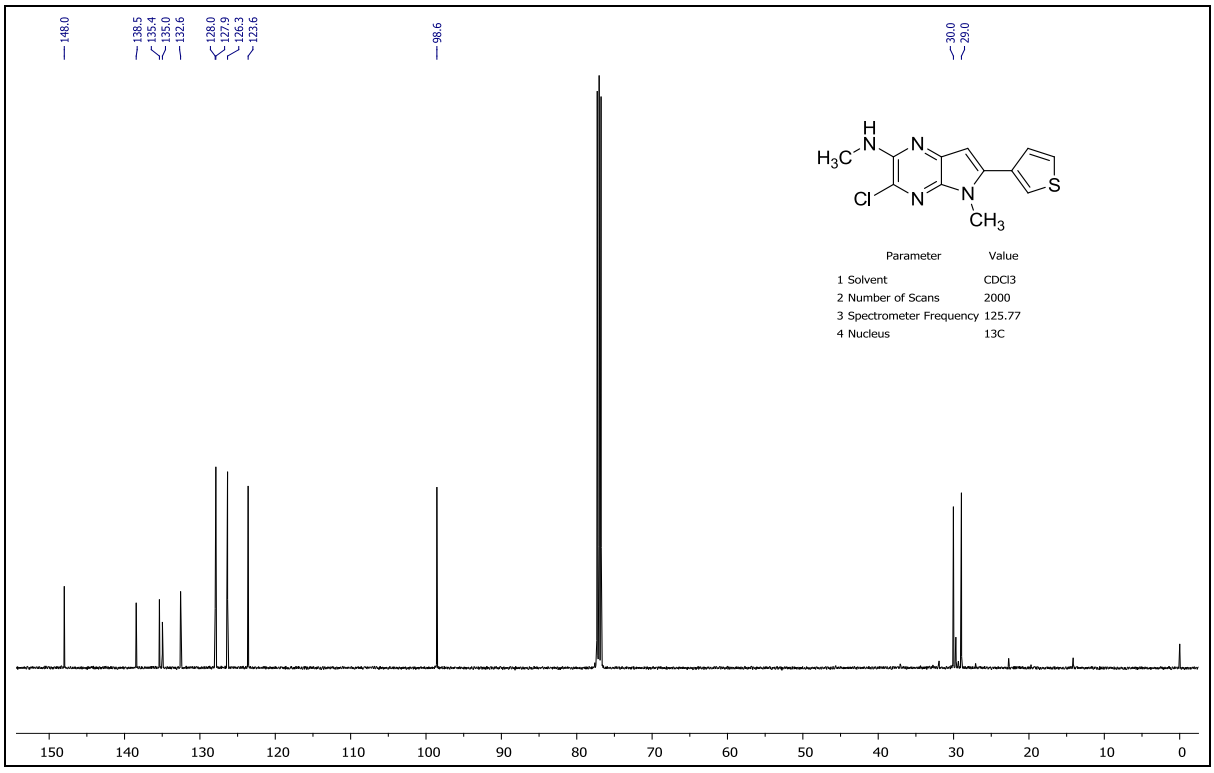
^{1}H NMR – 6a



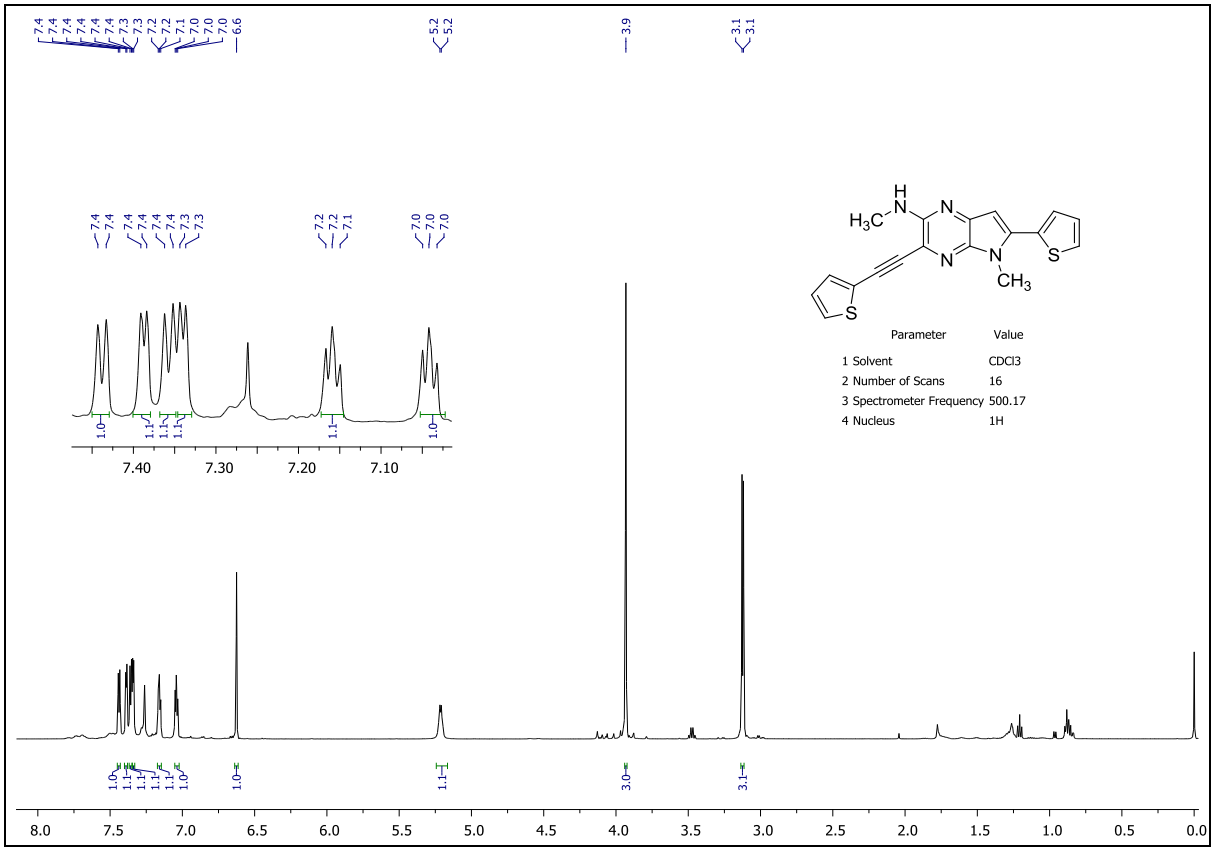
^{13}C NMR – 6a



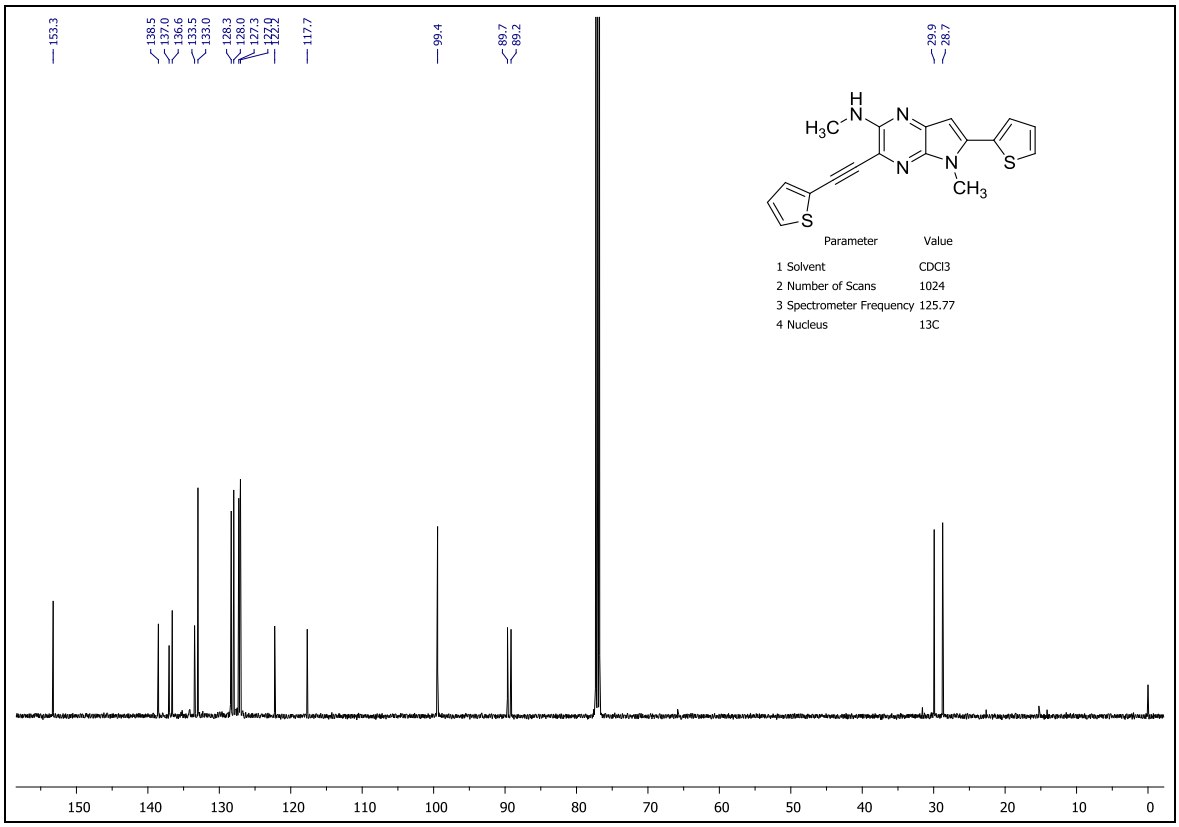
^{1}H NMR – 6b



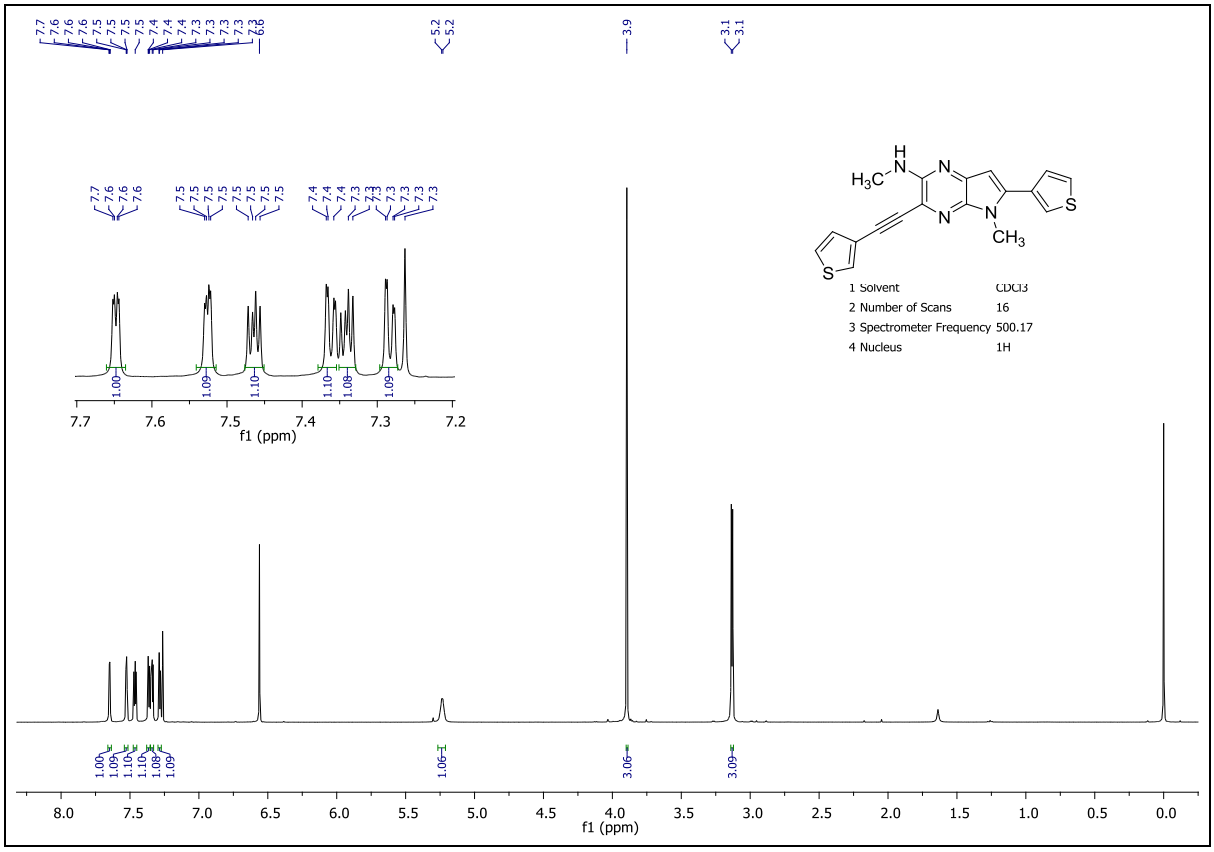
^{13}C NMR – 6b



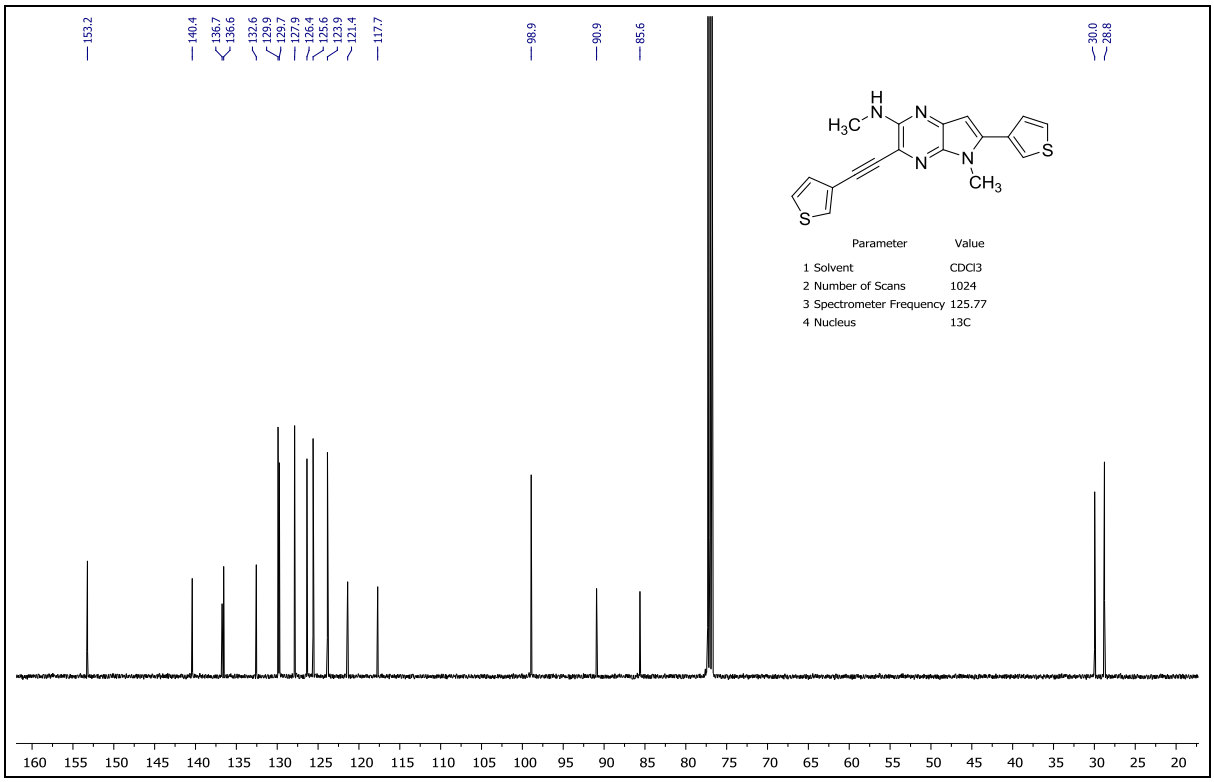
^{1}H NMR – 7a



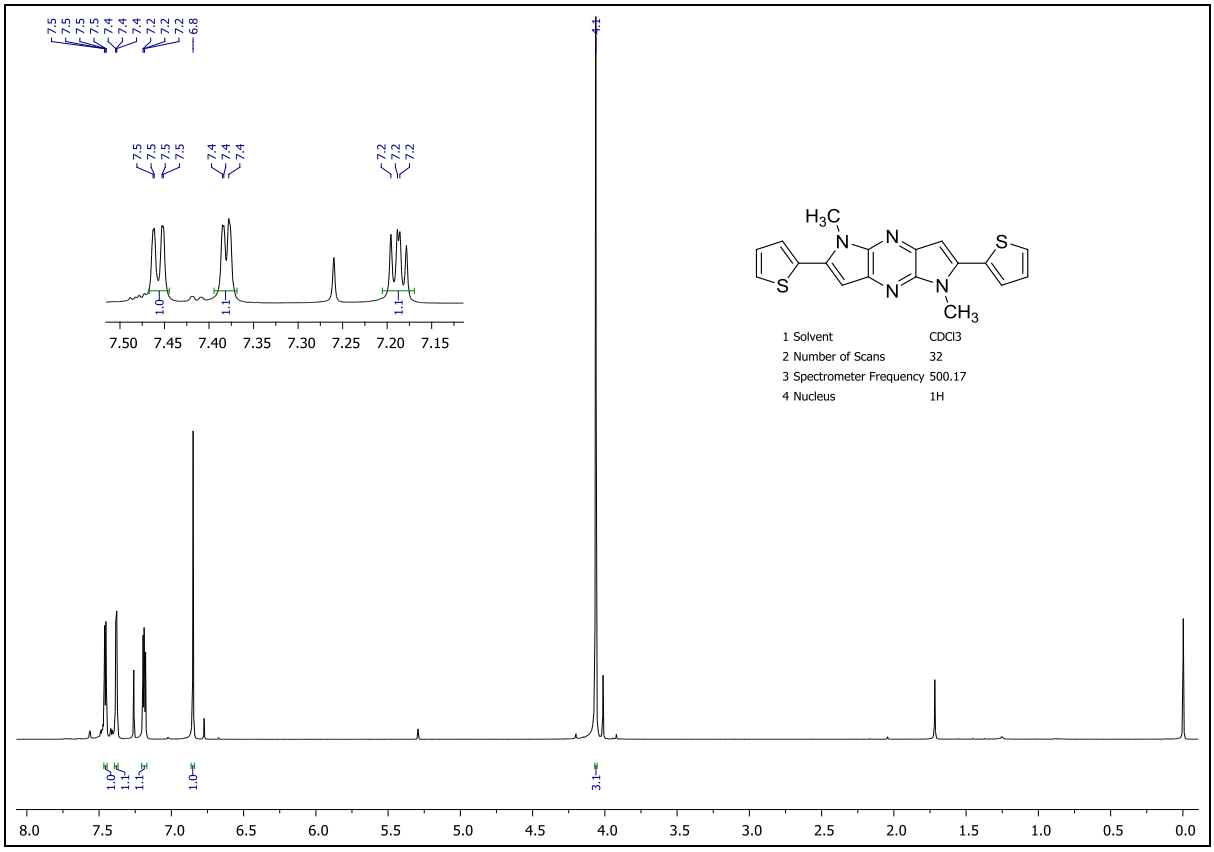
^{13}C NMR – 7a



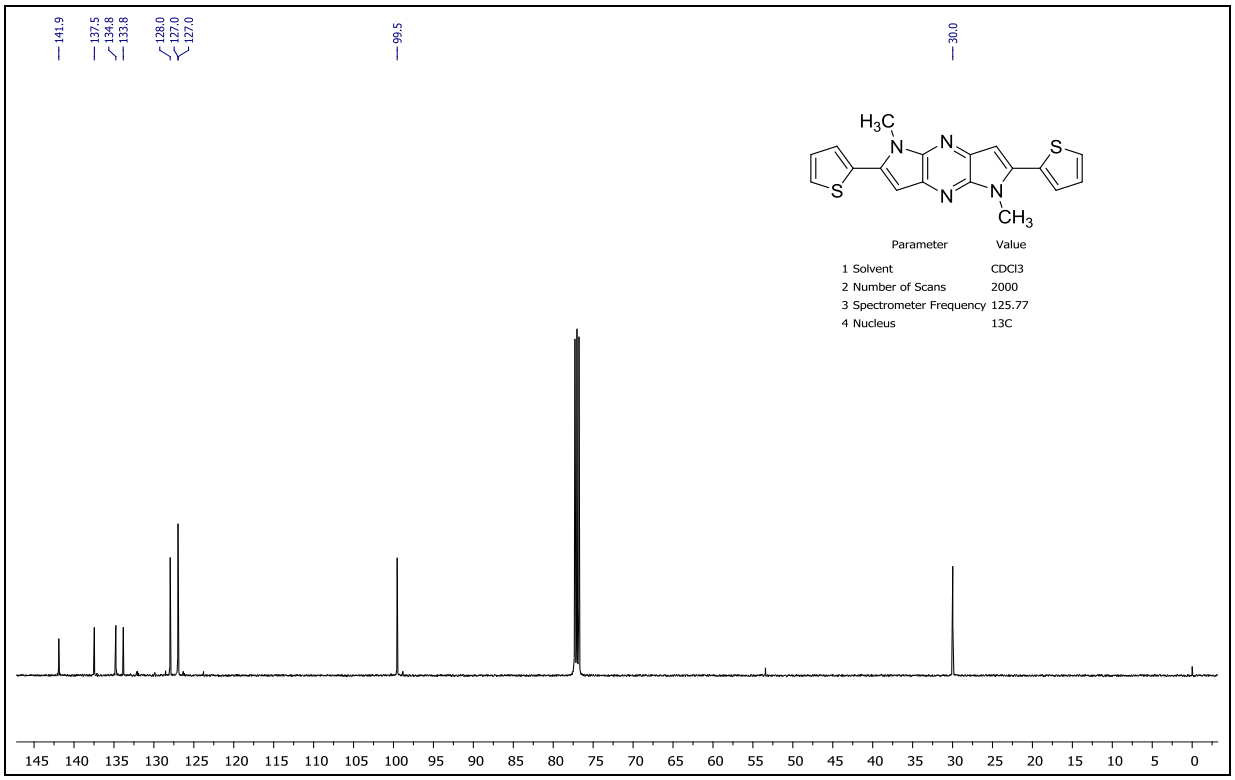
^{1}H NMR – 7b



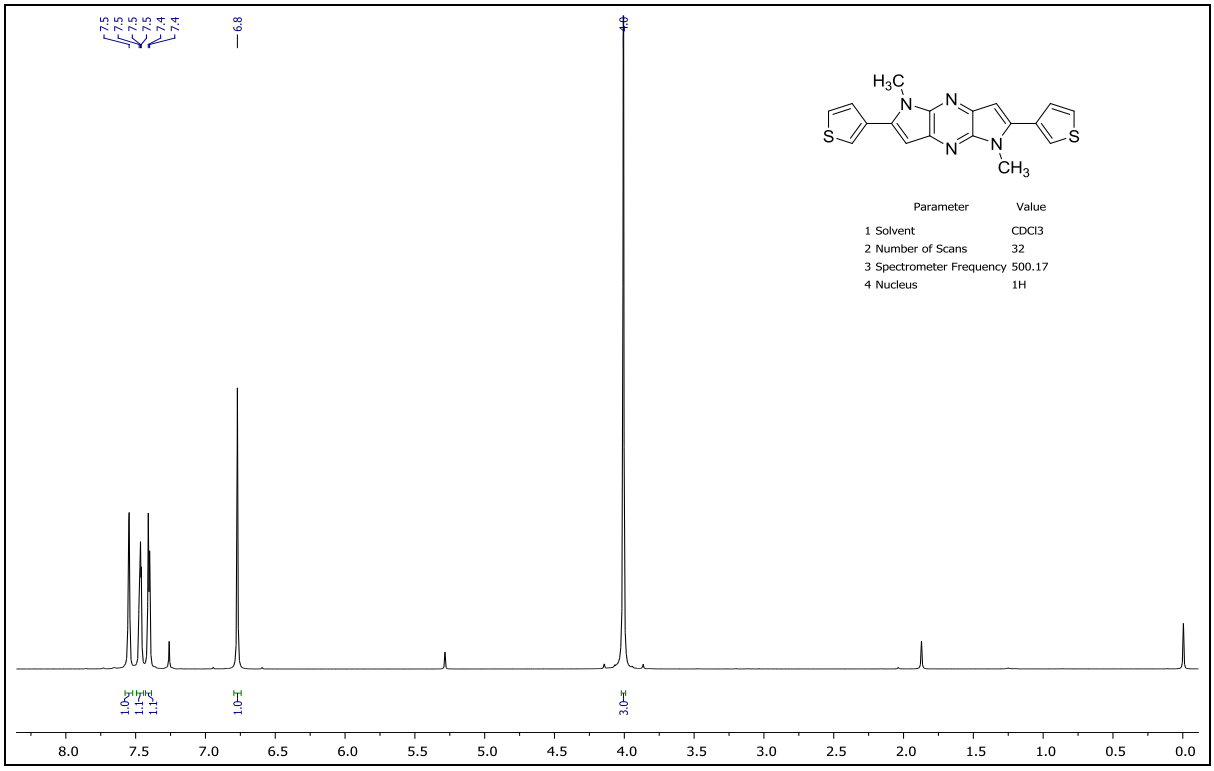
^{13}C NMR – 7b



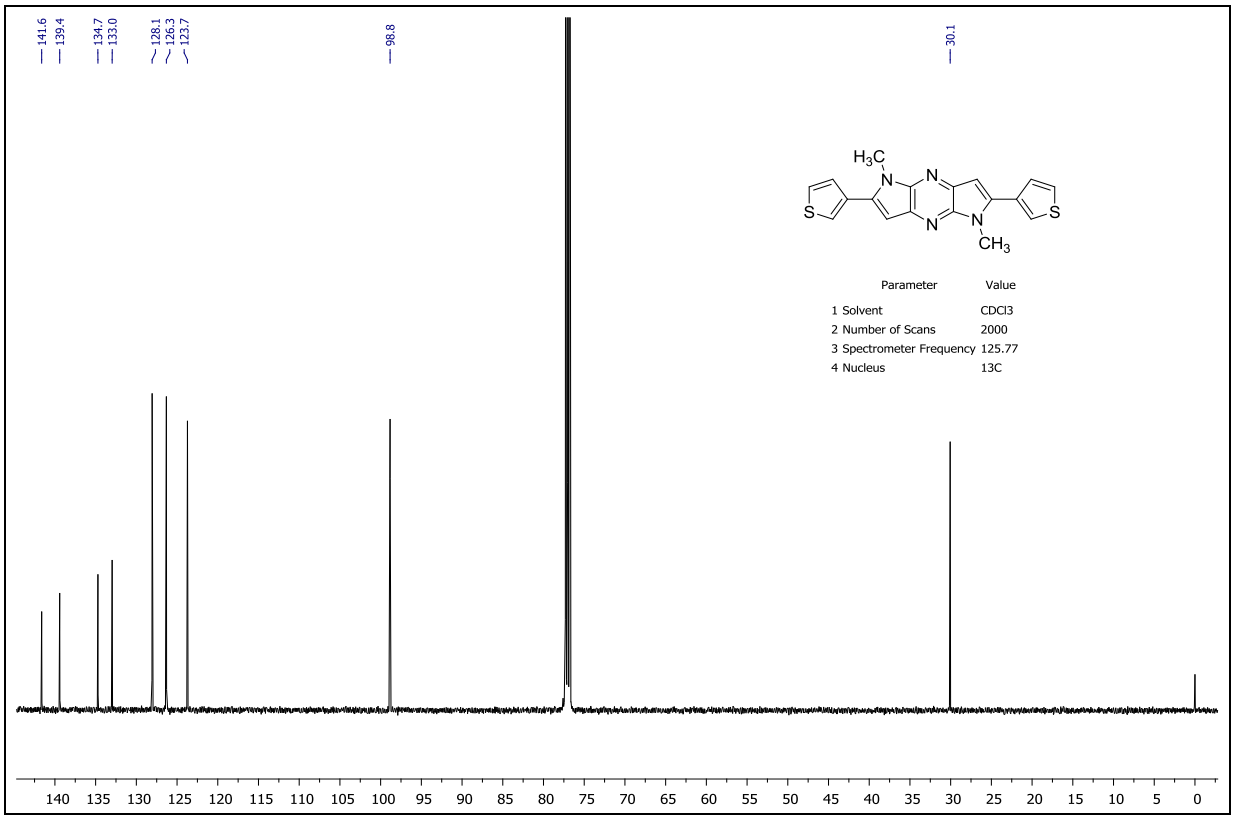
^{1}H NMR – 8a



^{13}C NMR – 8a

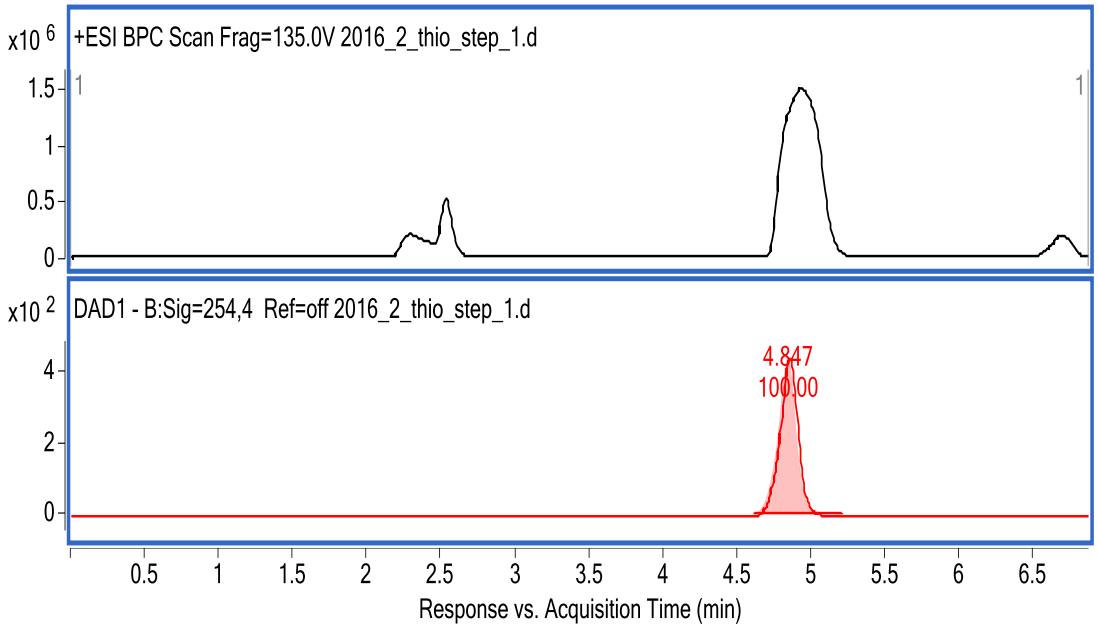


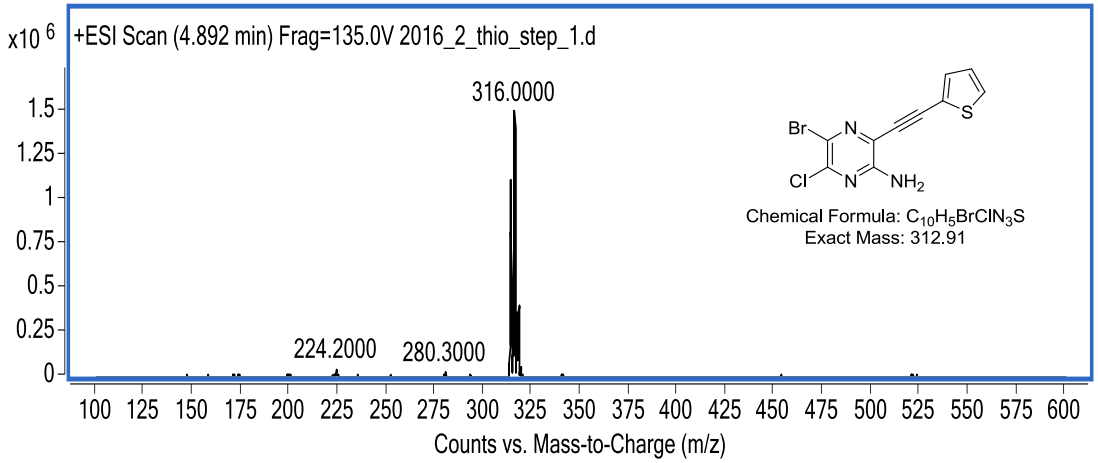
^{1}H NMR – 8b



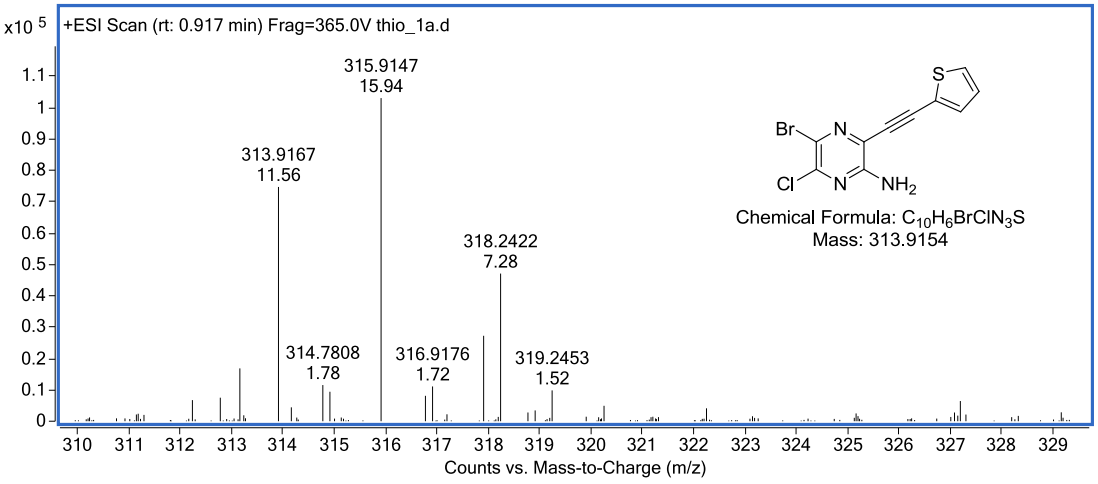
^{13}C NMR – 8b

LC/MS and HRMS spectra of compounds 1a to 8a

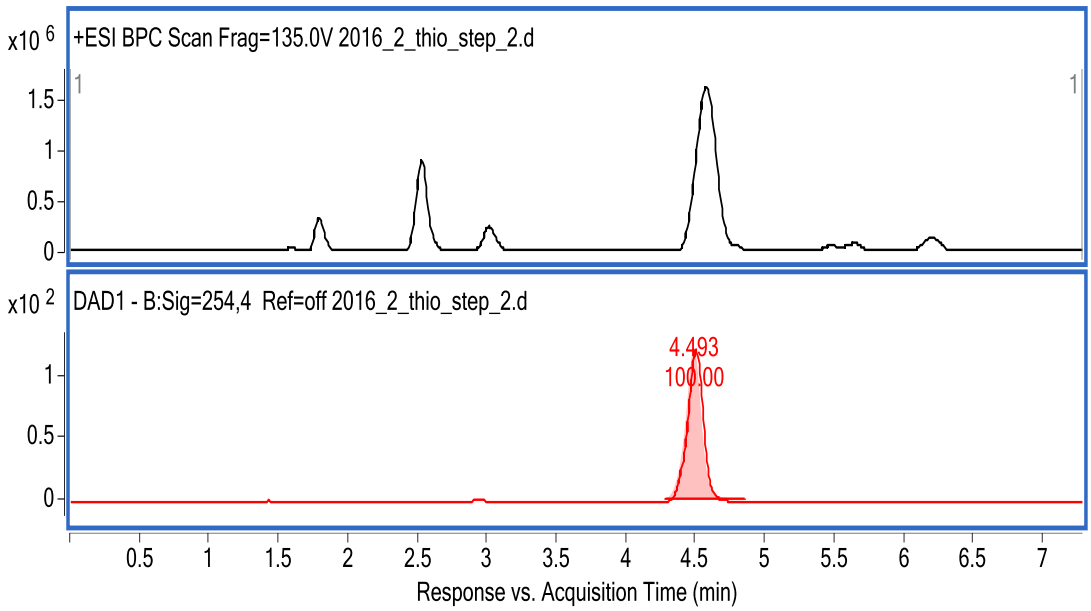


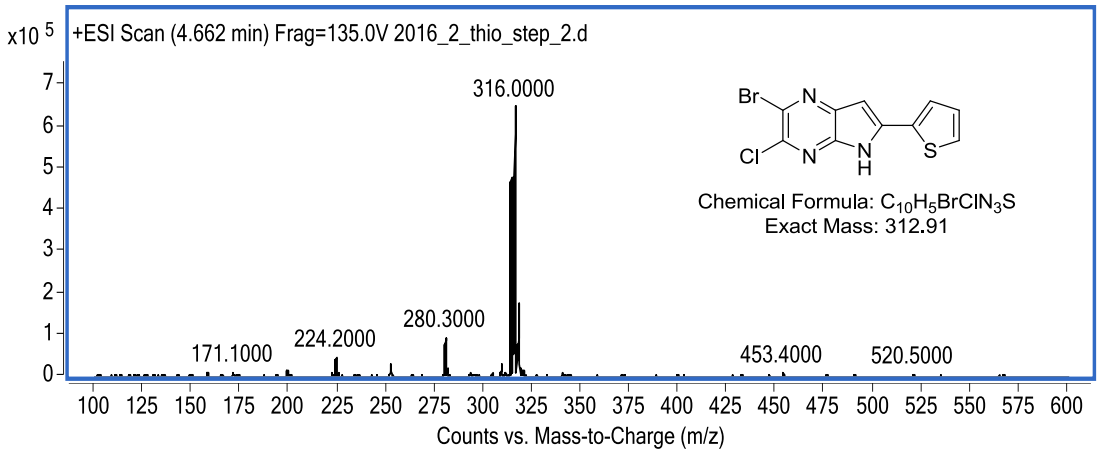


LC/MS – 1a

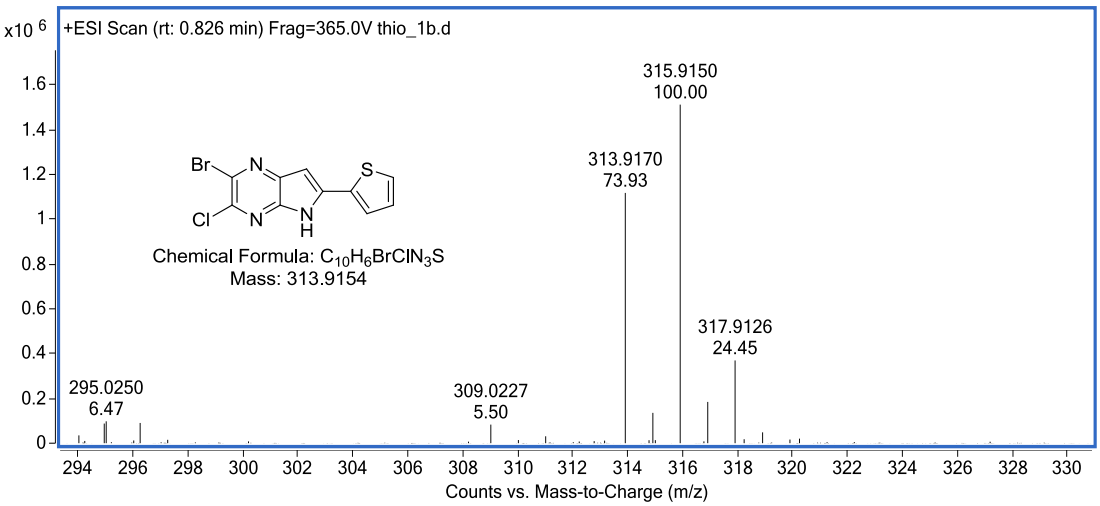


HRMS – 1a

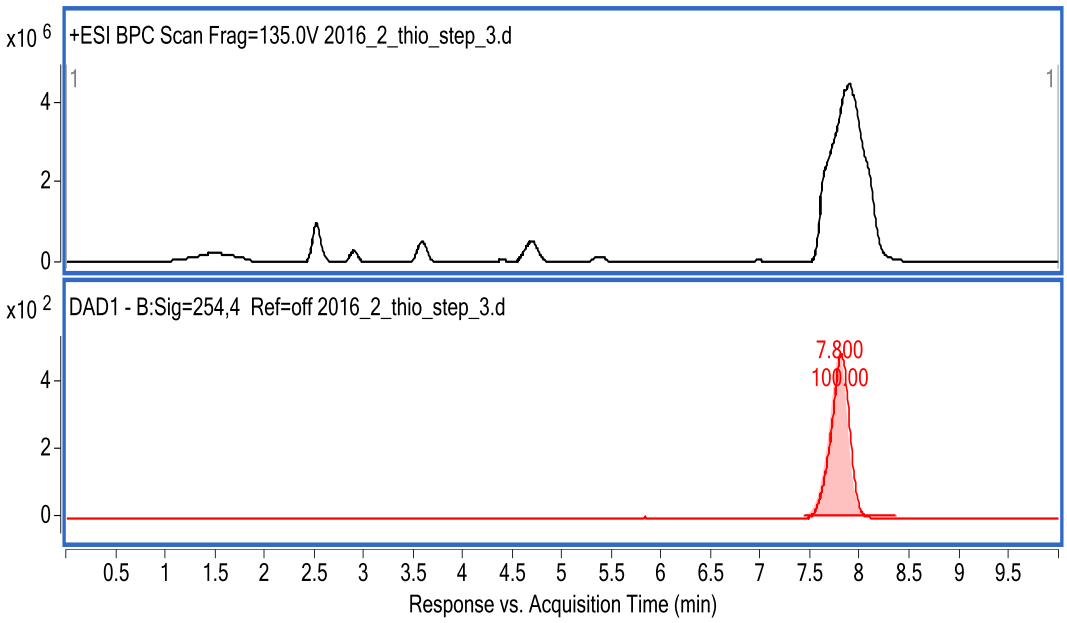


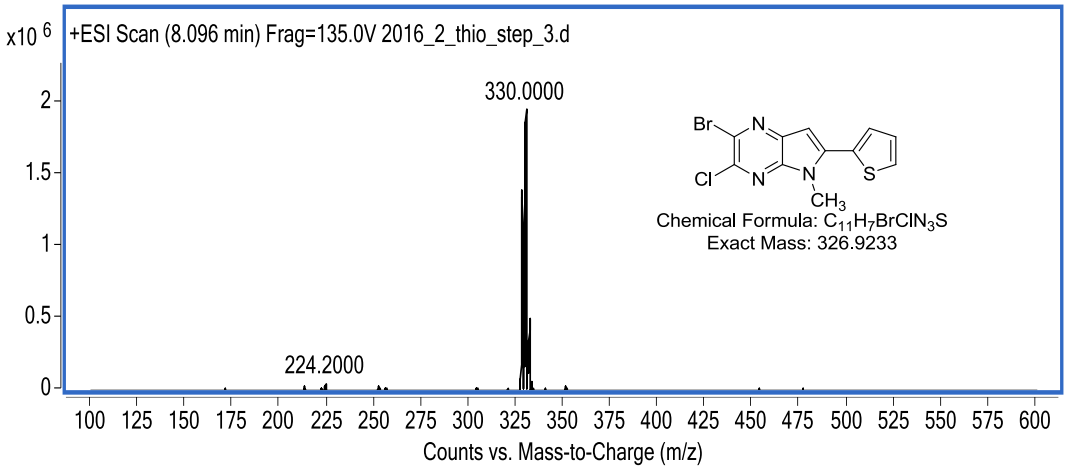


LC/MS – 2a

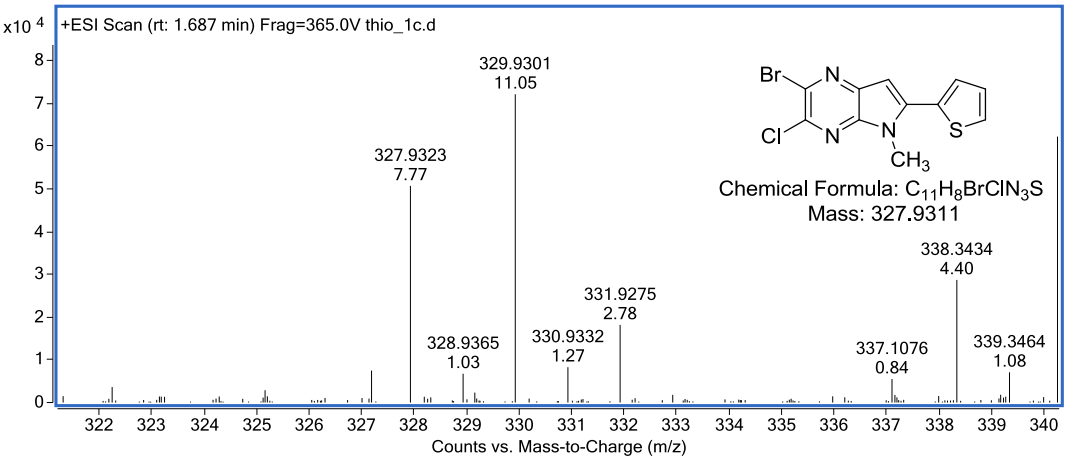


HRMS – 2a

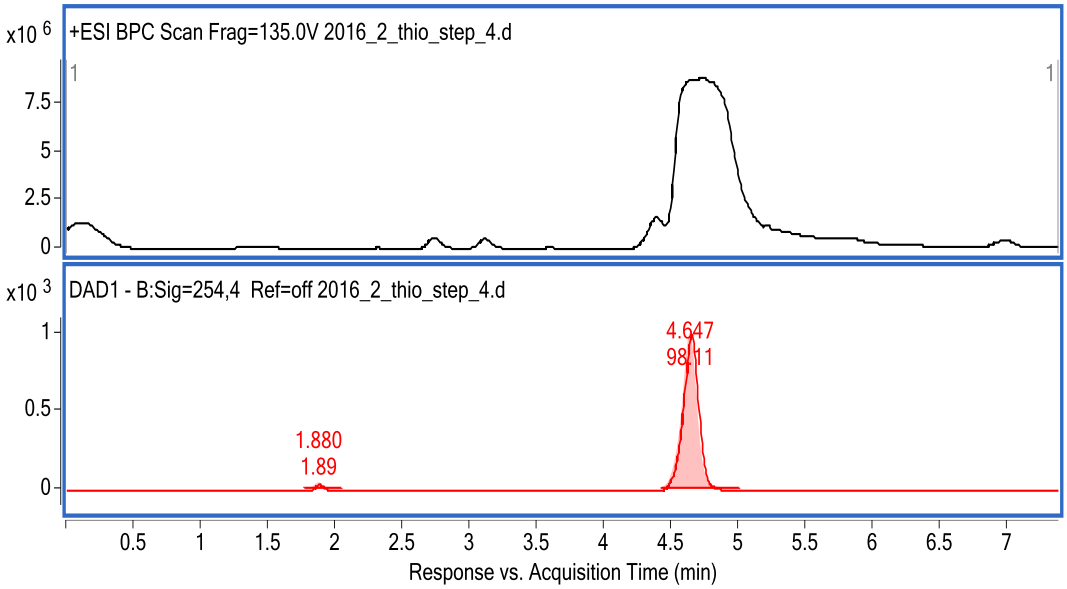


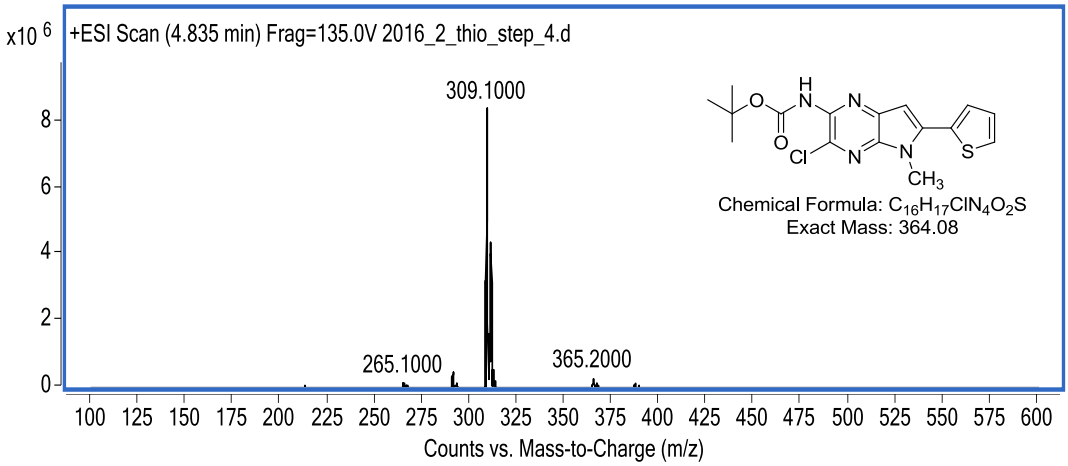


LC/MS – 3a

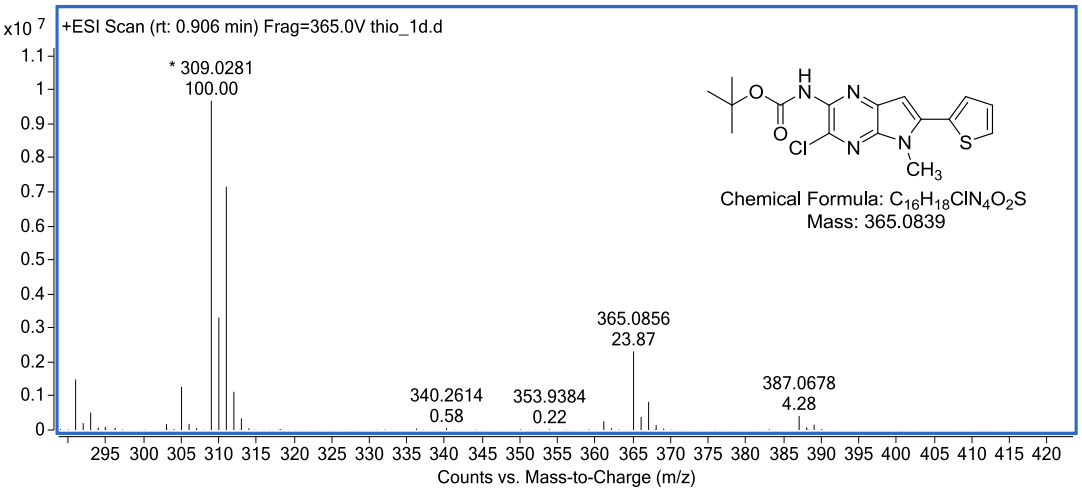


HRMS – 3a

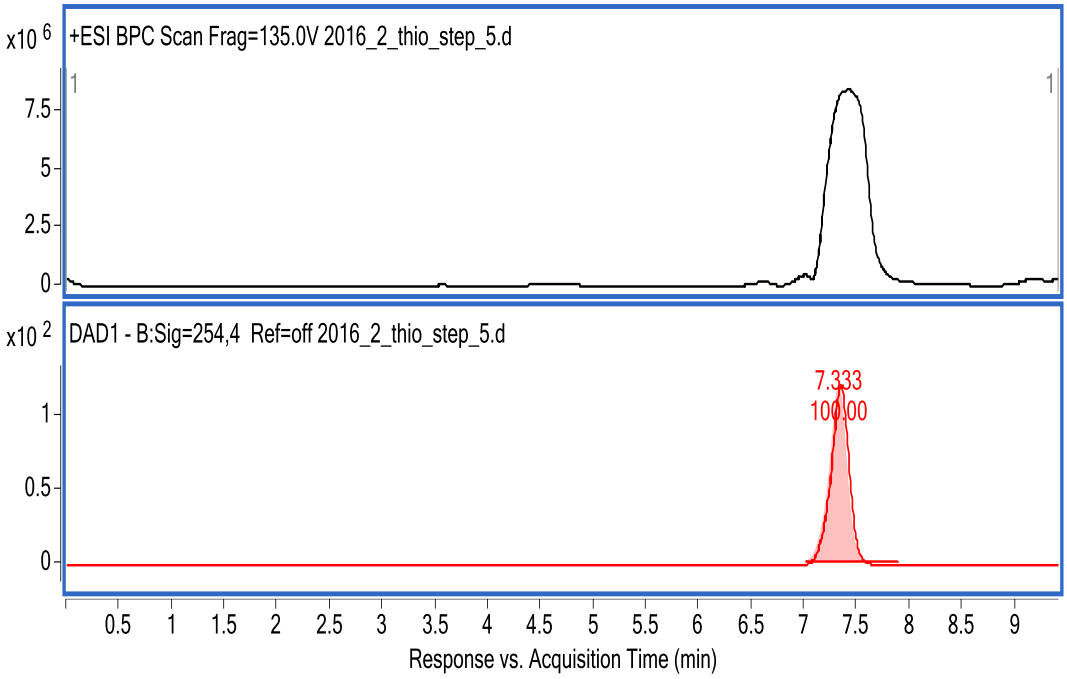


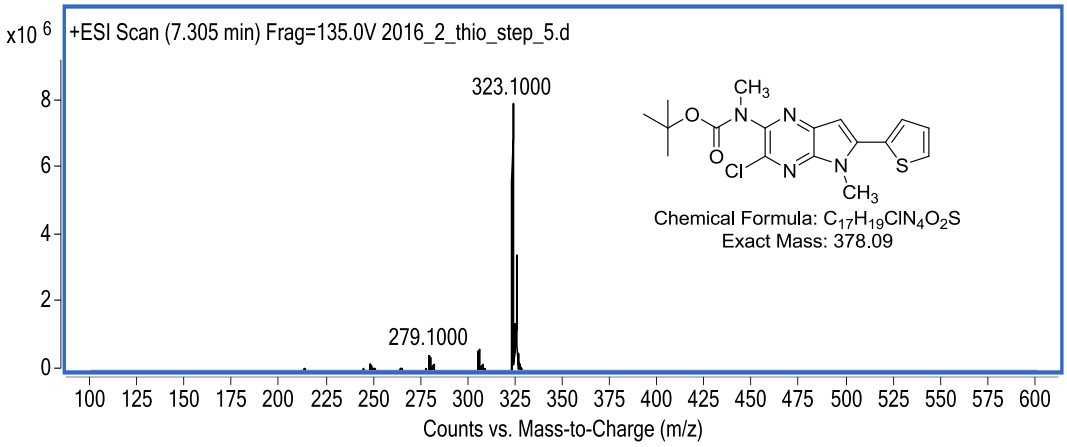


LC/MS – 4a

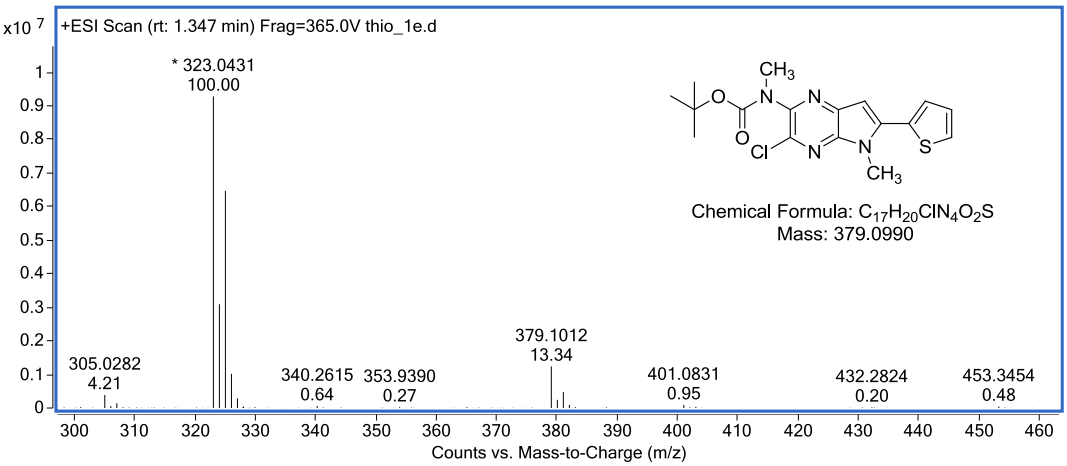


HRMS – 4a

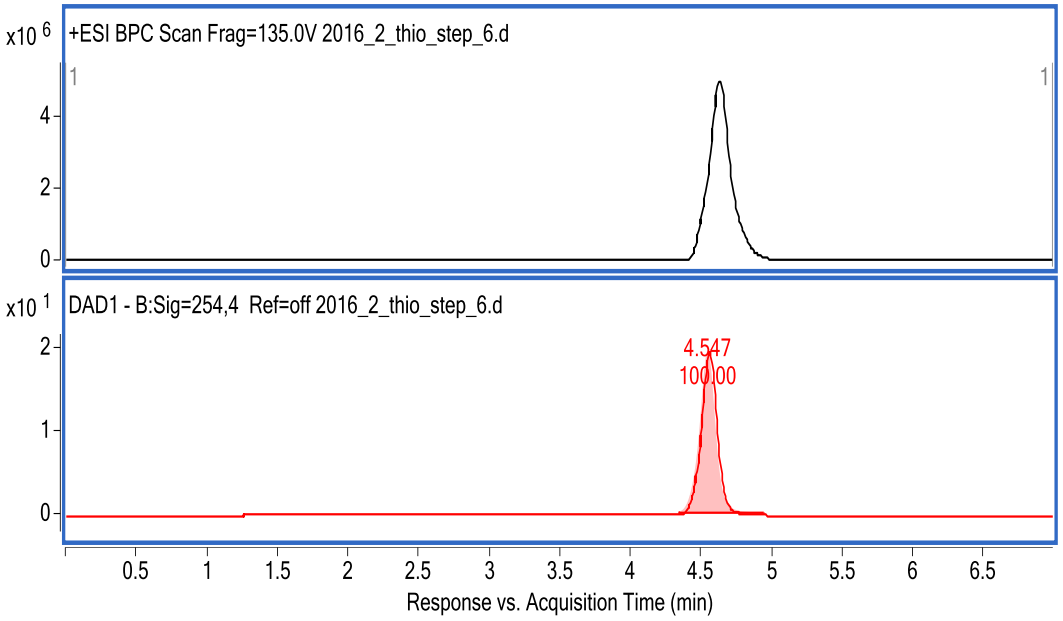


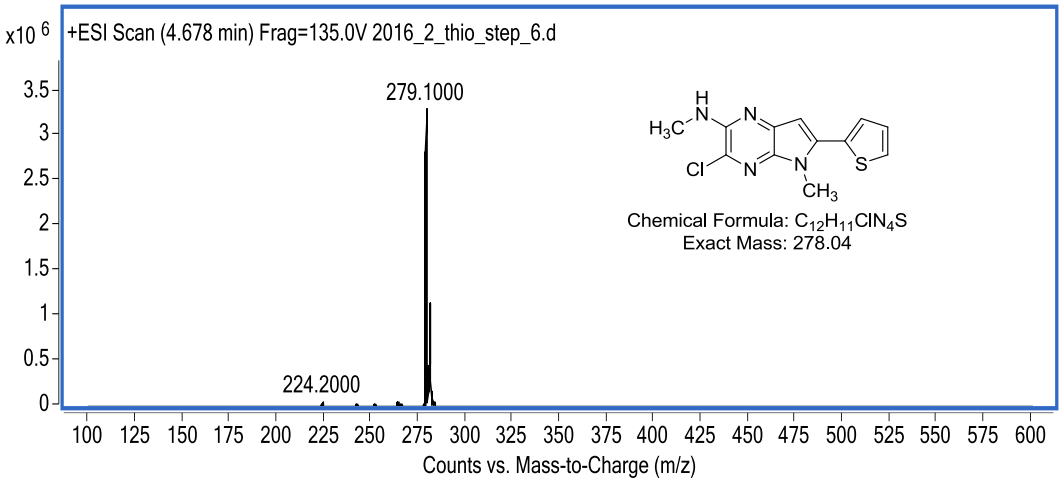


LC/MS – 5a

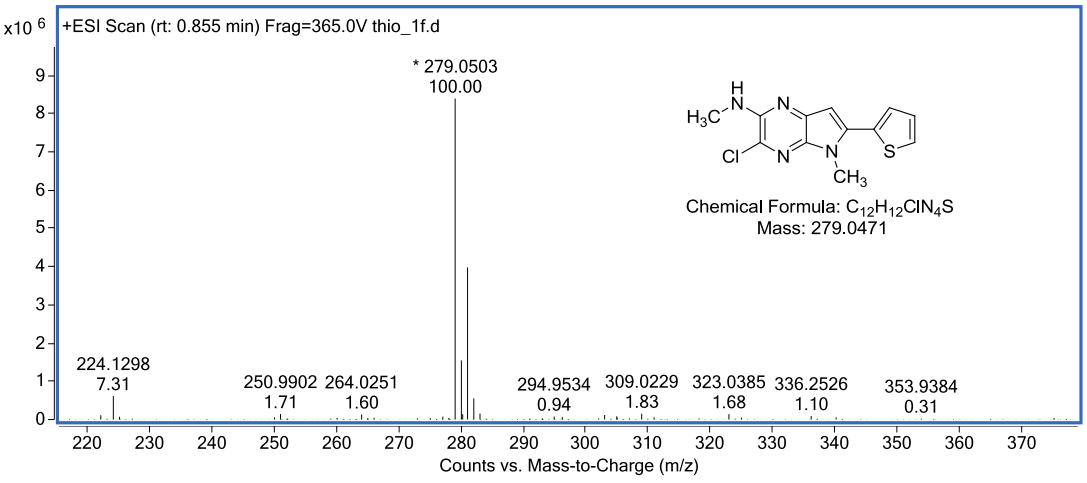


HRMS – 5a

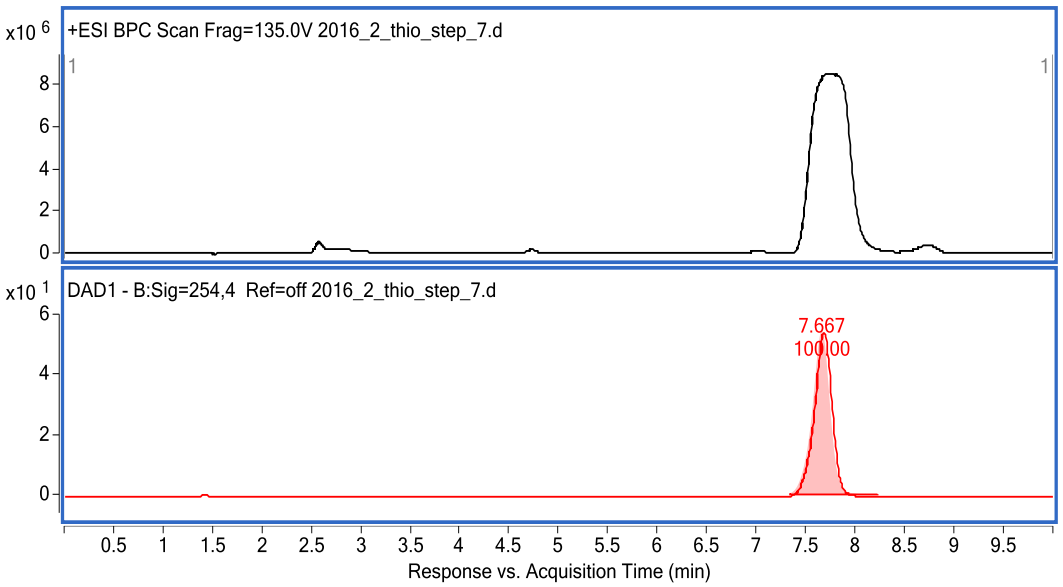


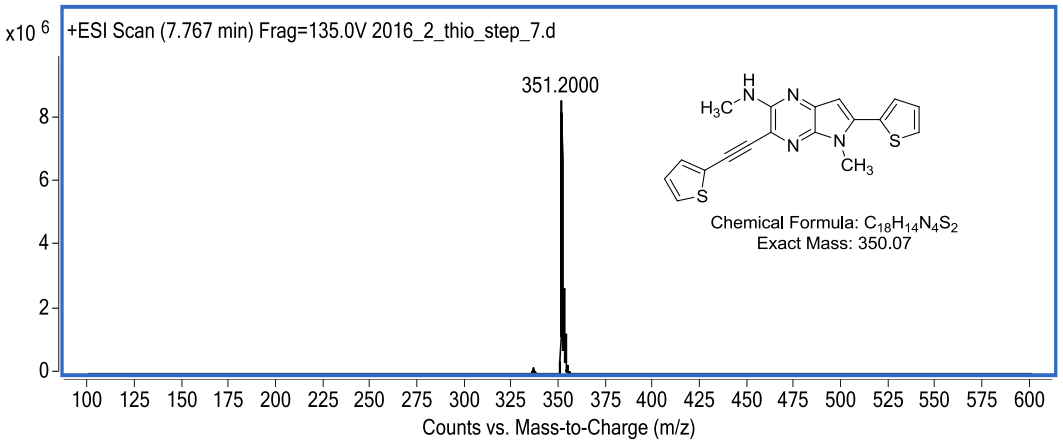


LC/MS – 6a

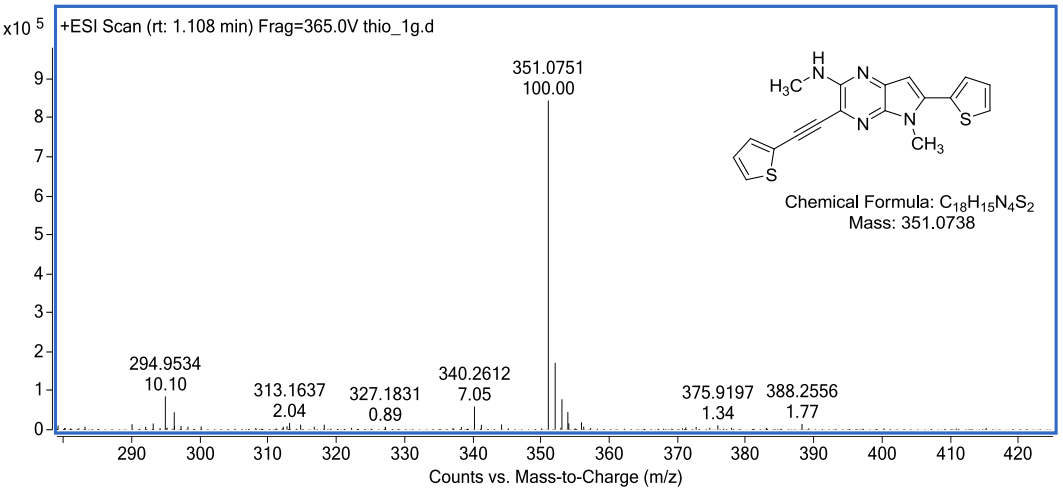


HRMS – 6a

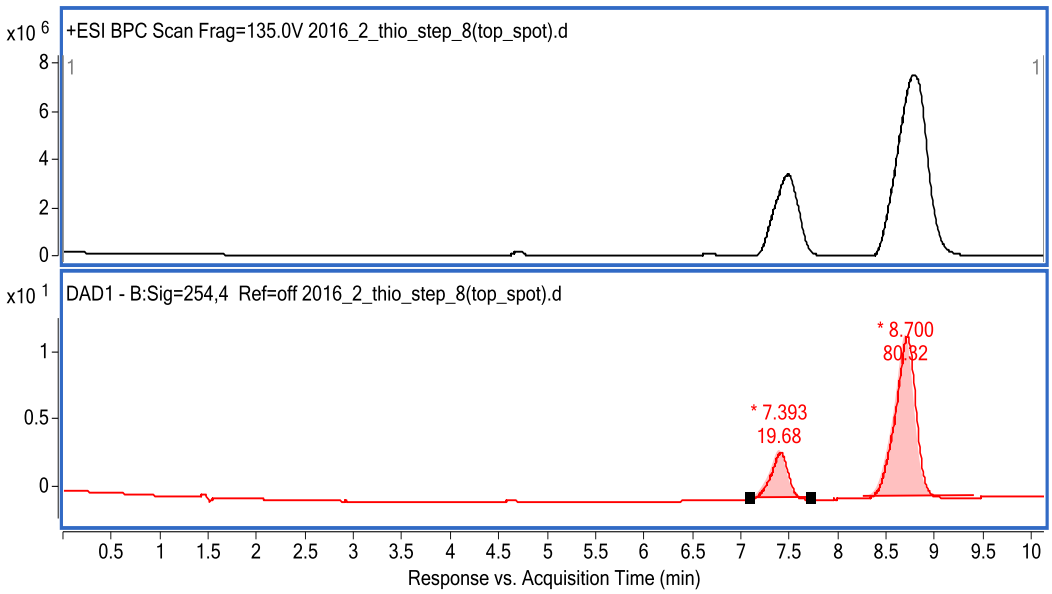


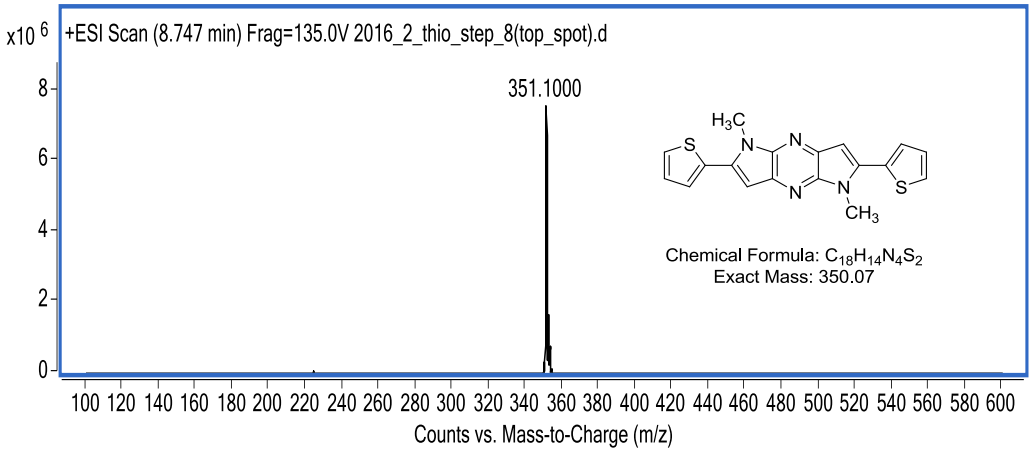


LC/MS – 7a

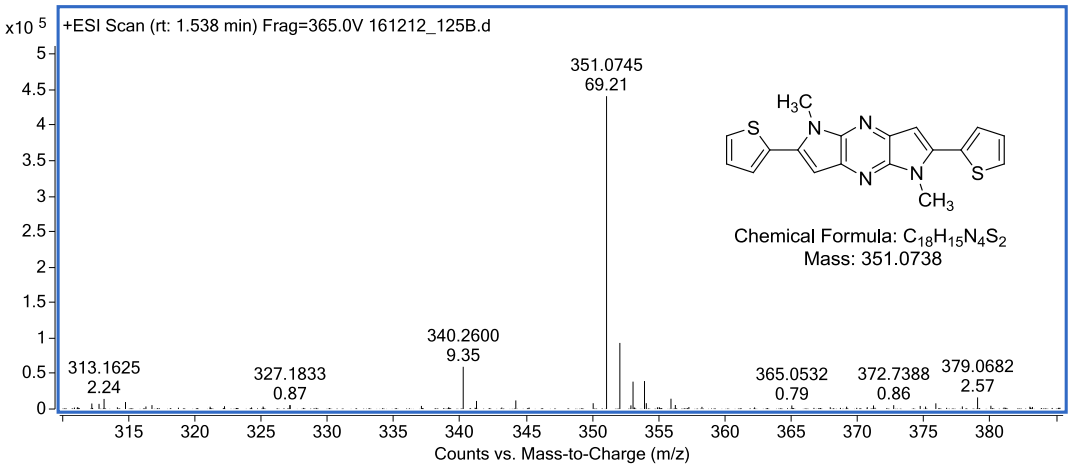


HRMS – 7a



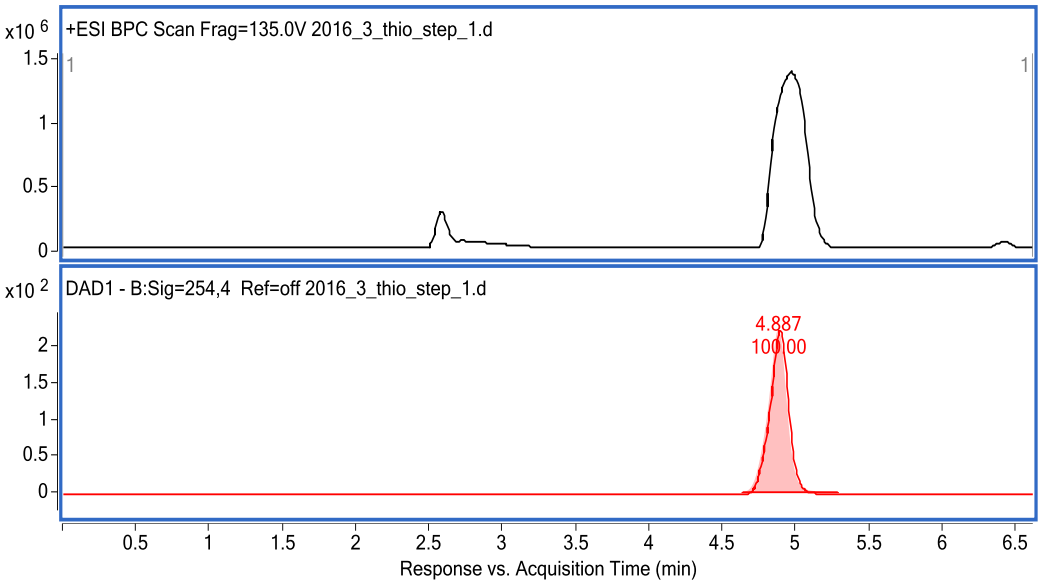


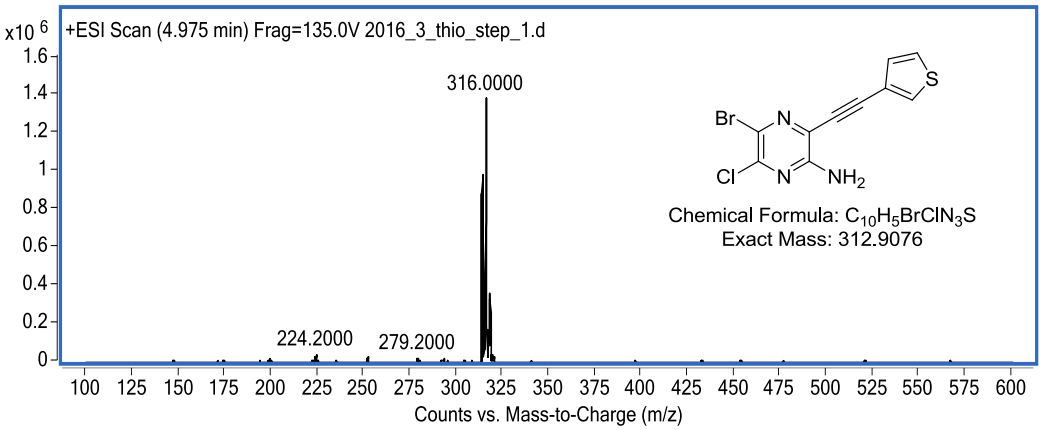
Top spot LC/MS – 8a



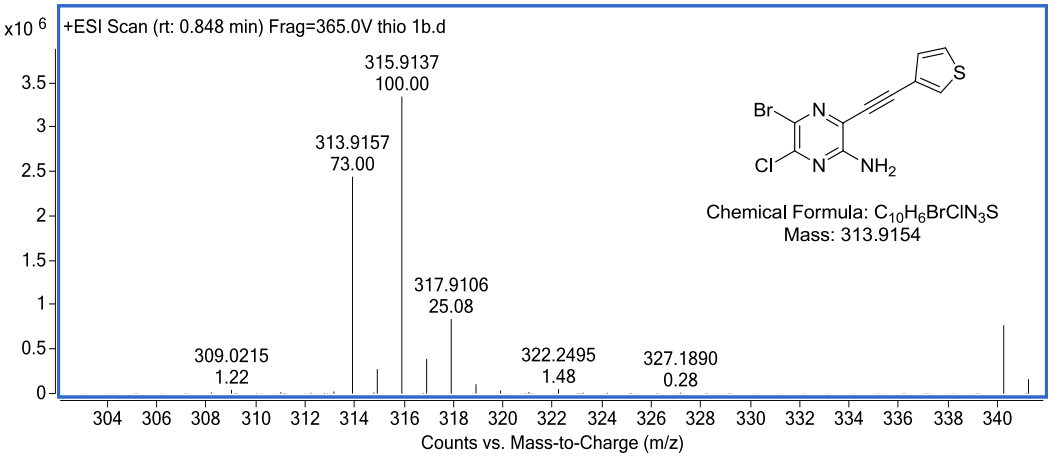
HRMS – 8a

LC/MS and HRMS spectra of compounds 1b to 8b

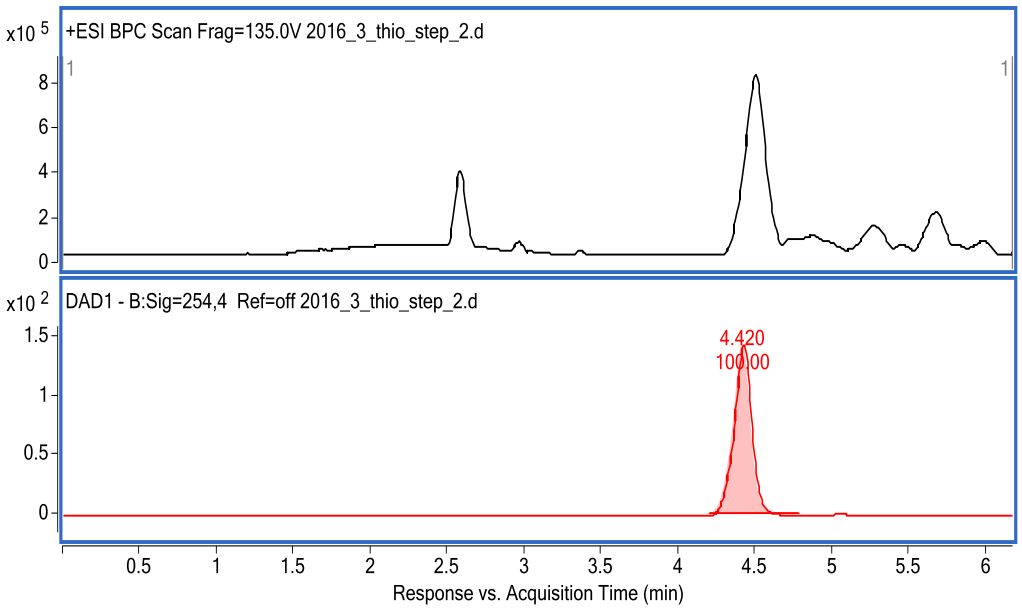


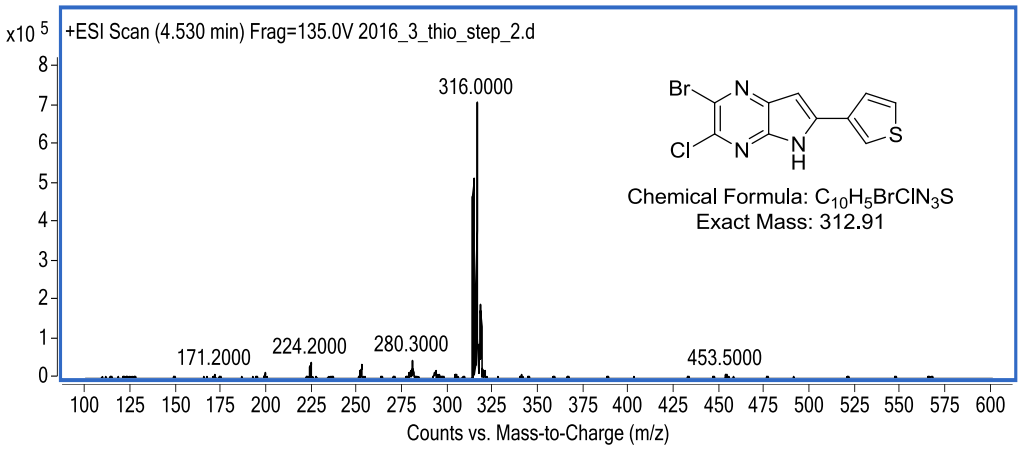


LC/MS – 1b

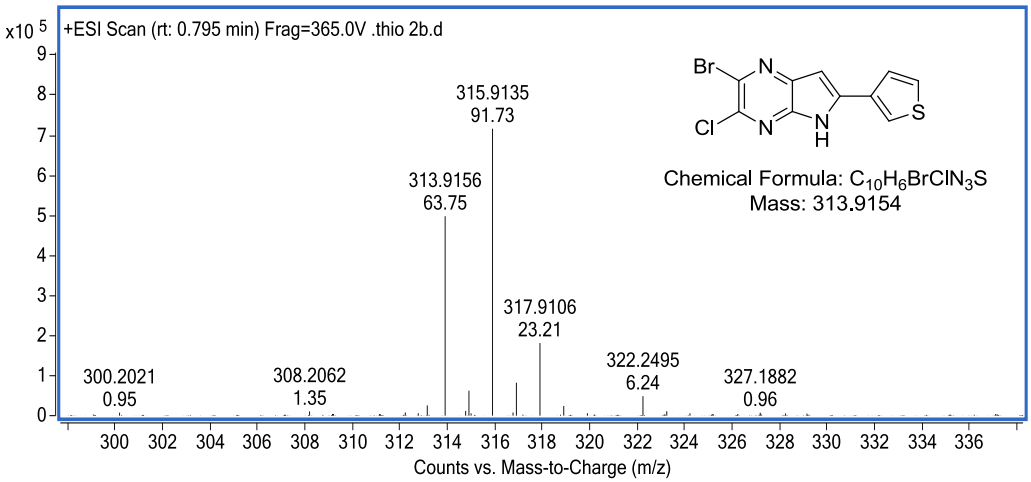


HRMS – 1b

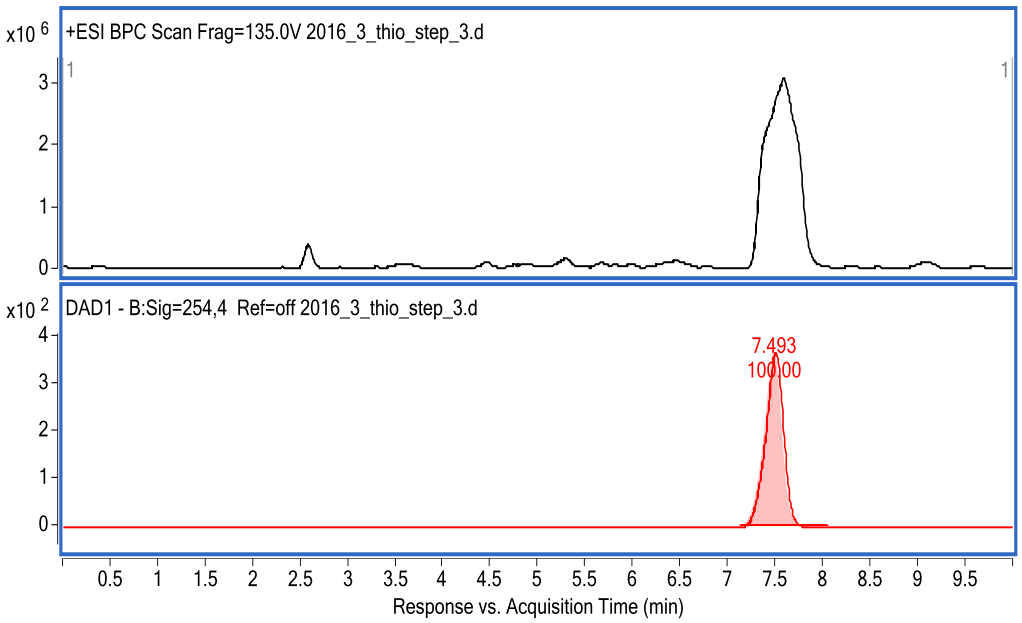


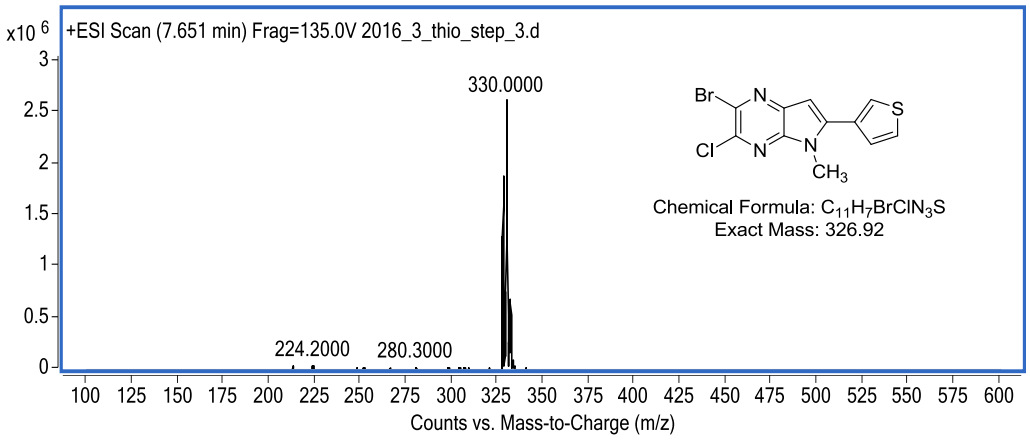


LC/MS – 2b

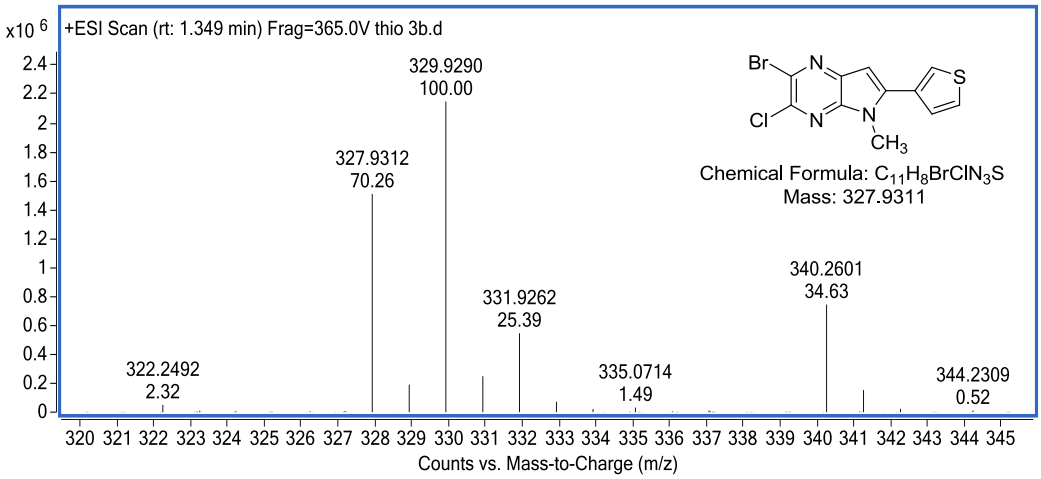


HRMS – 2b

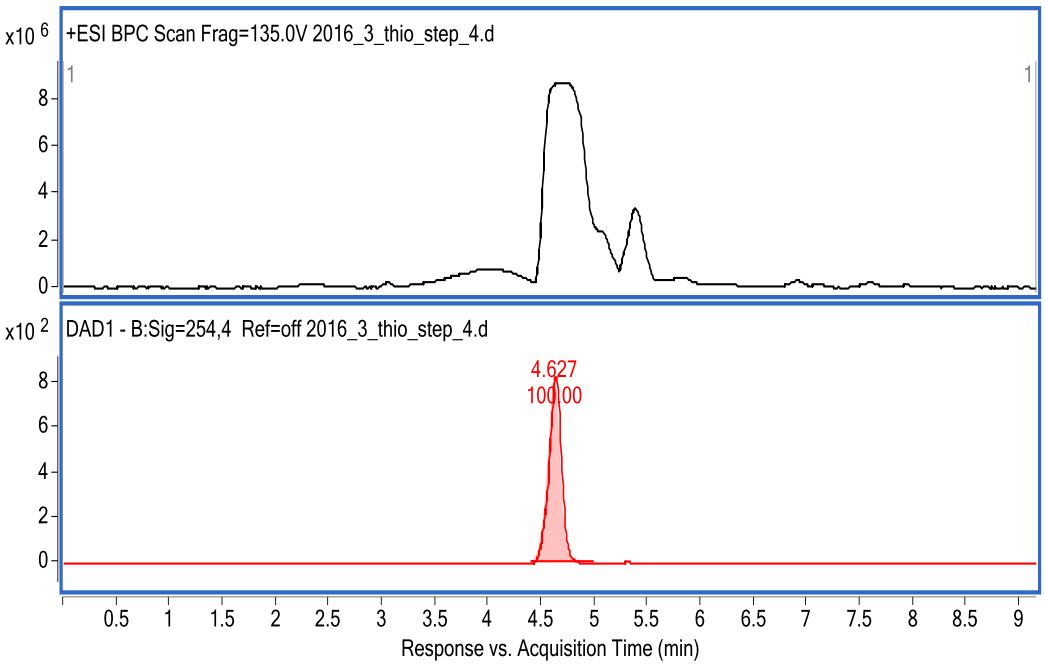


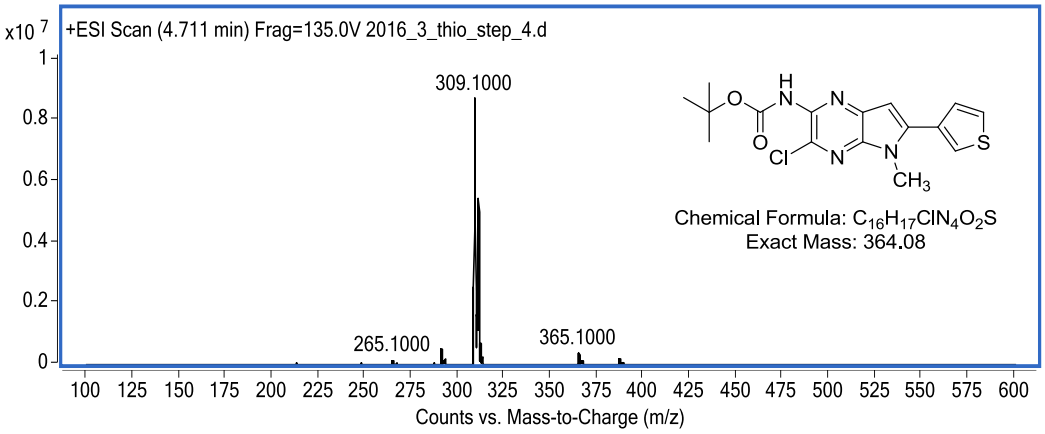


LC/MS – 3b

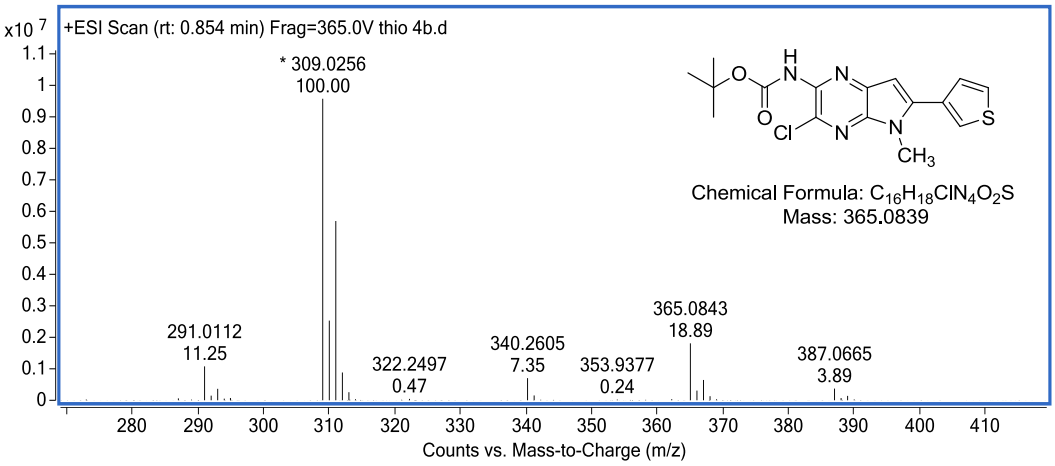


HRMS – 3b

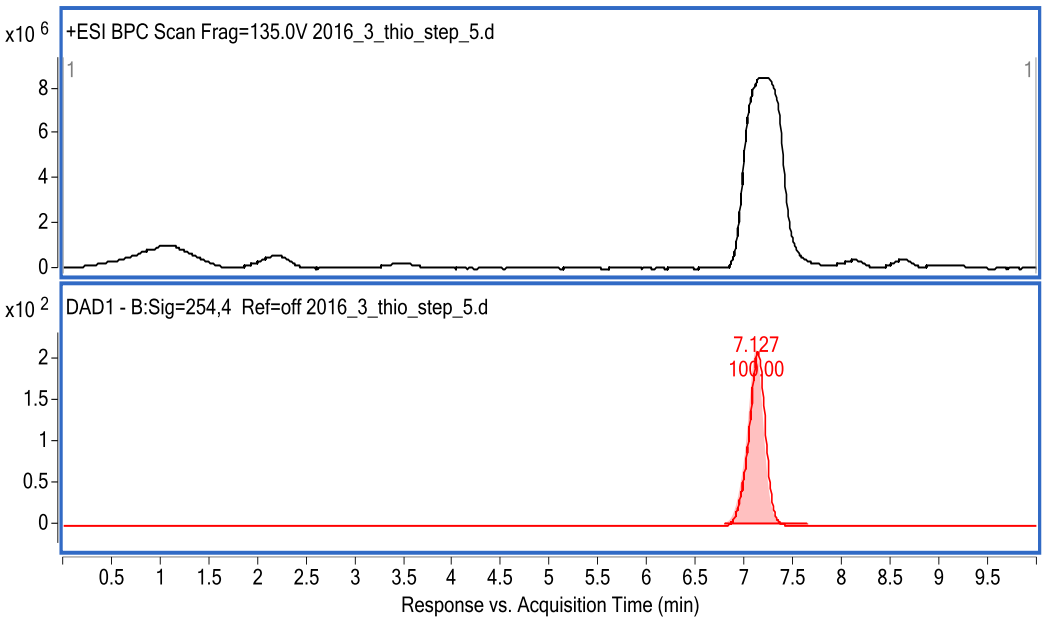


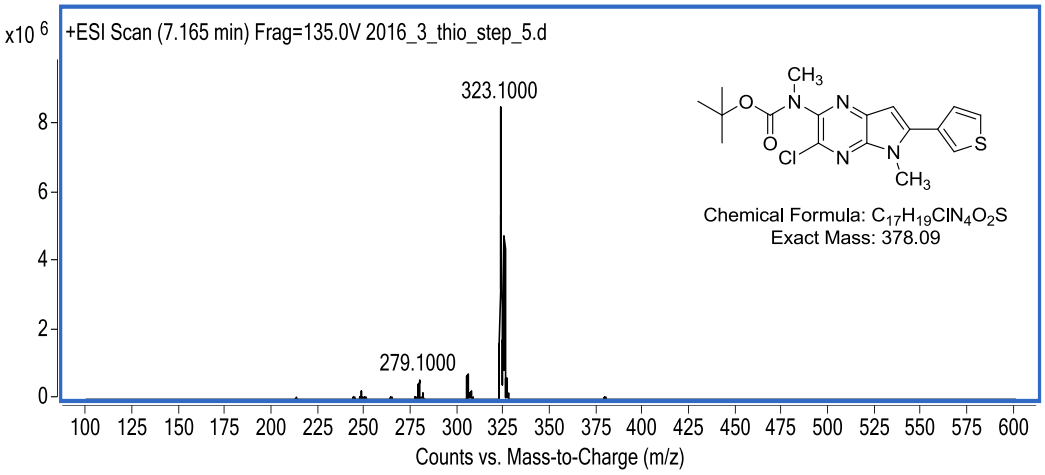


LC/MS – 4b

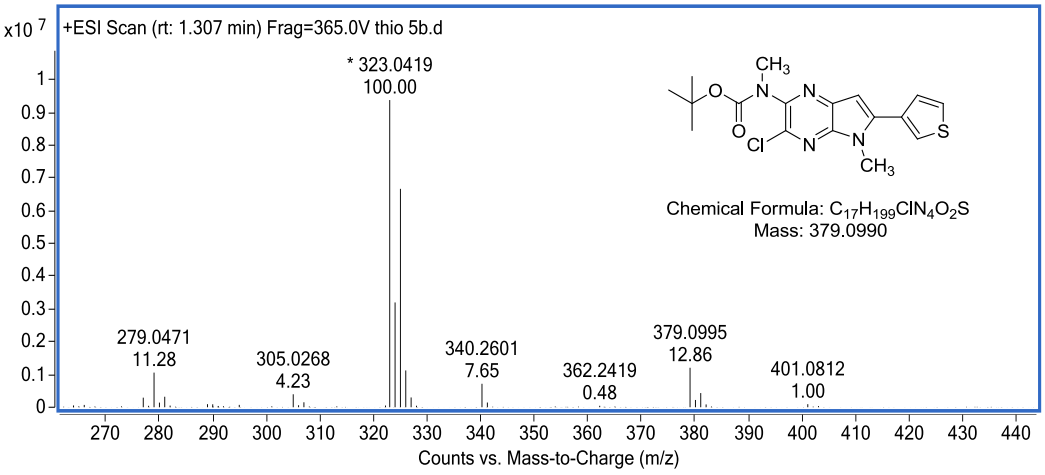


HRMS – 4b

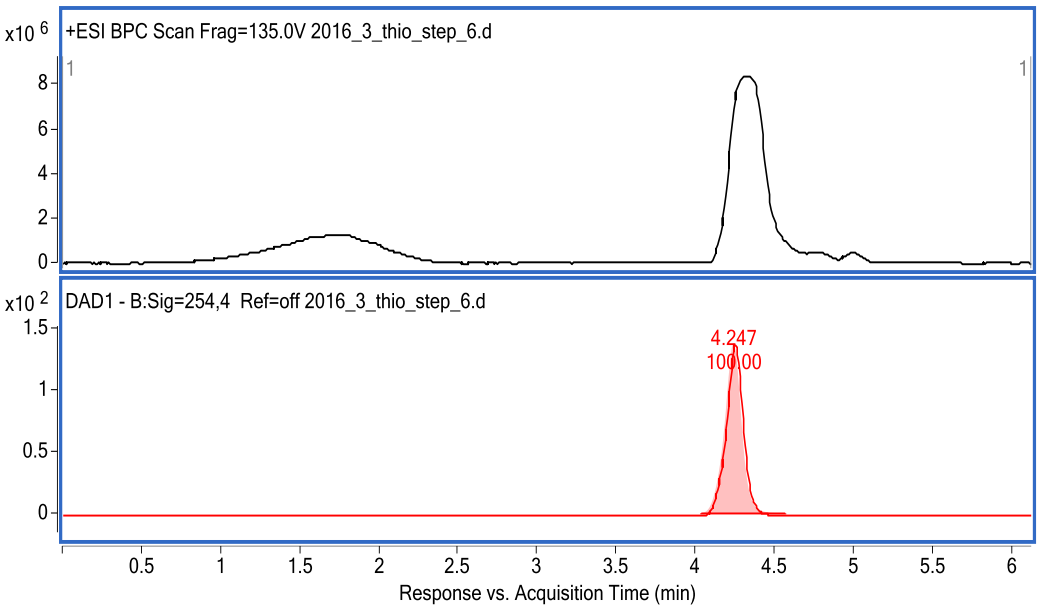


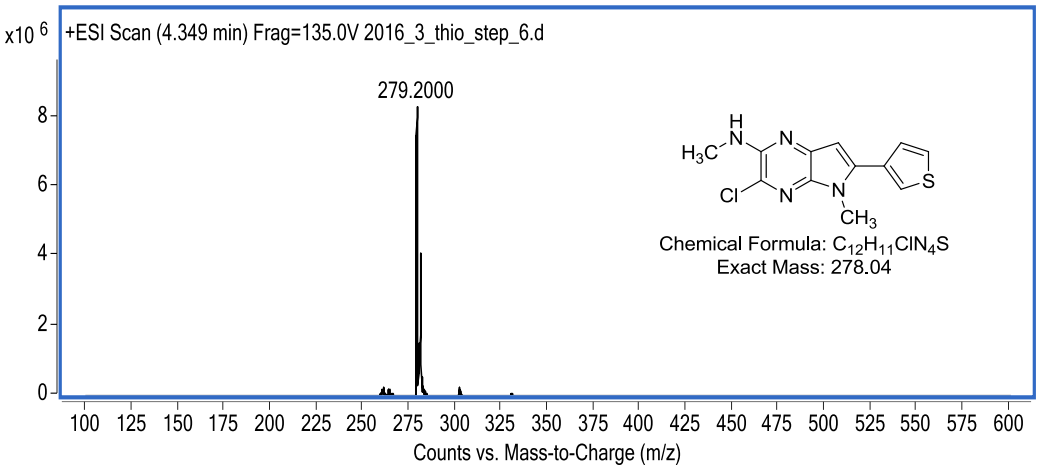


LC/MS – 5b

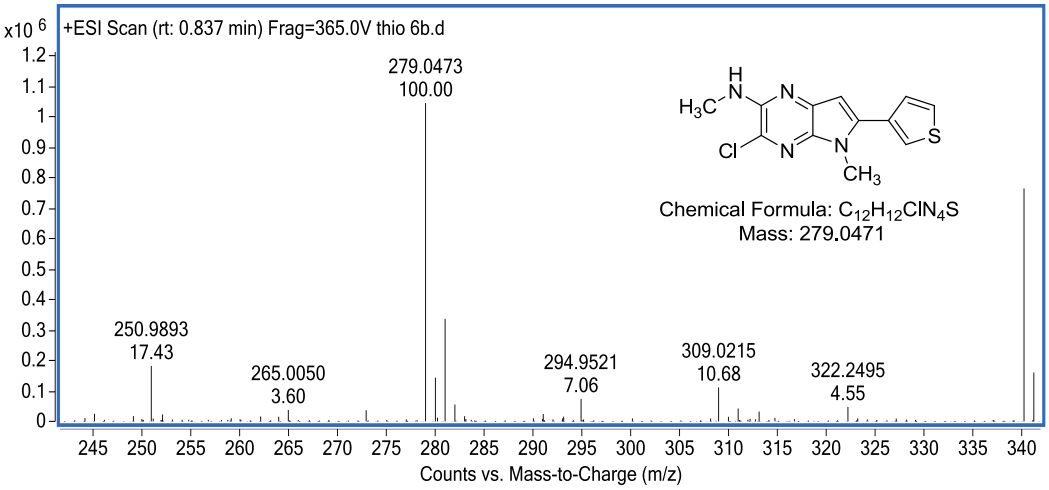


HRMS – 5b

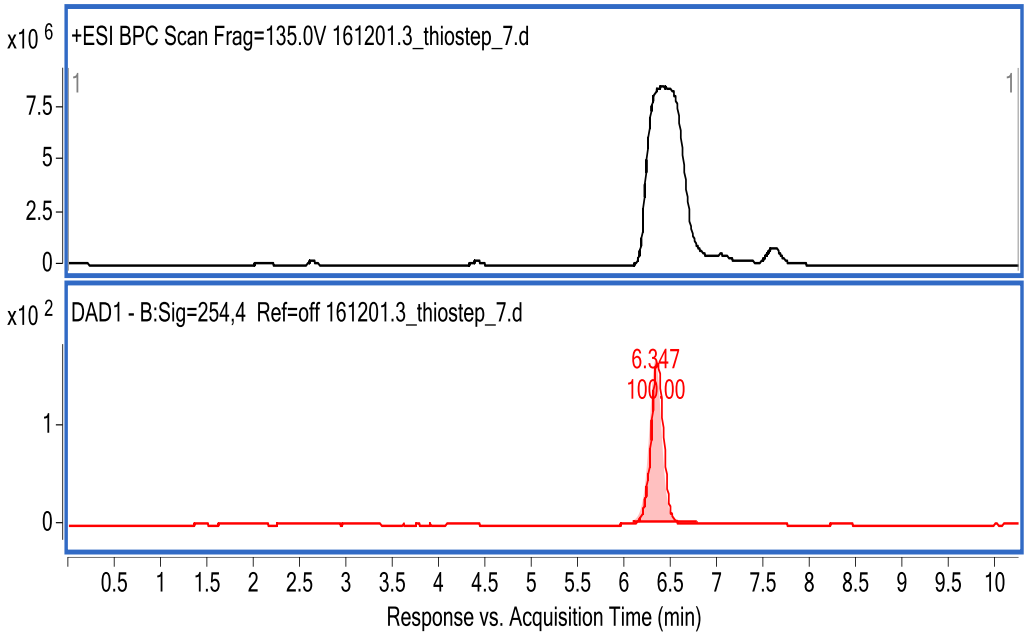


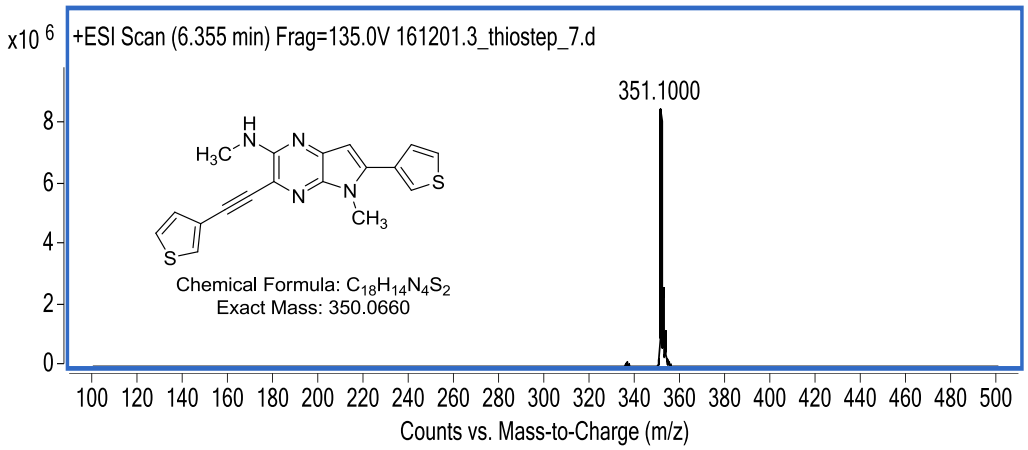


LC/MS – 6b

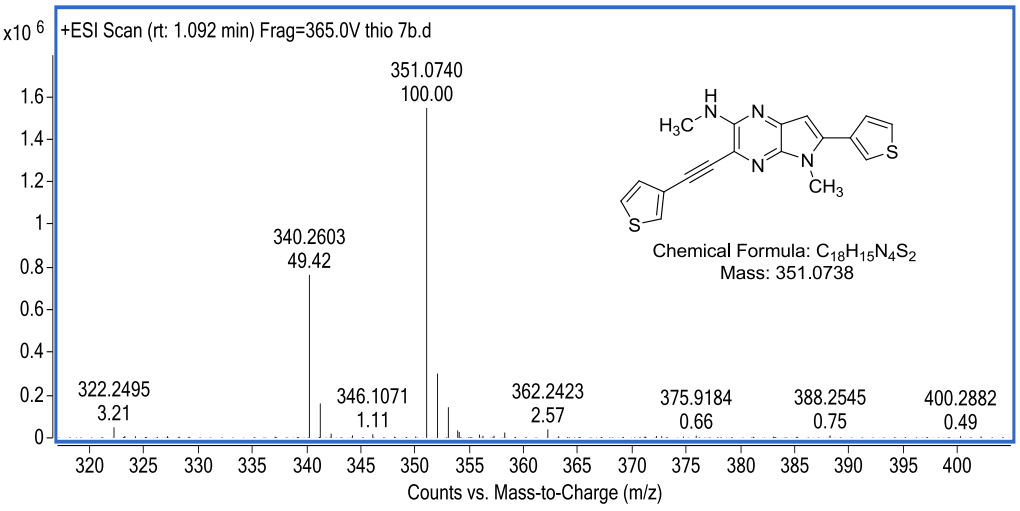


HRMS – 6b

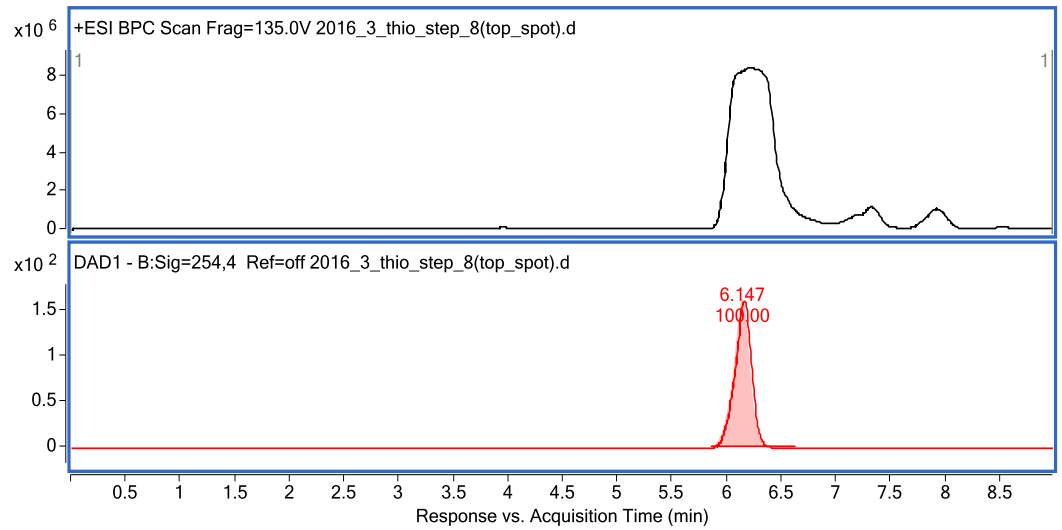


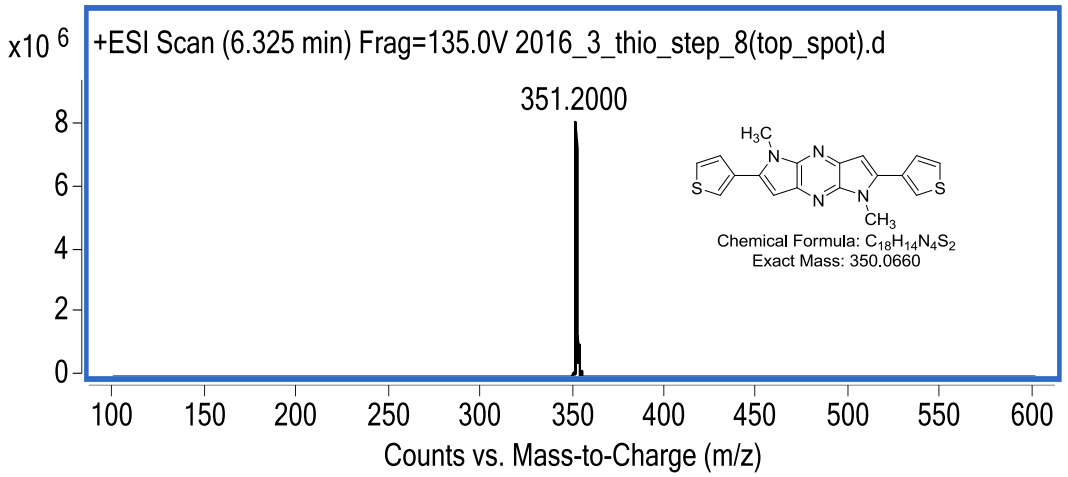


LC/MS – 7b

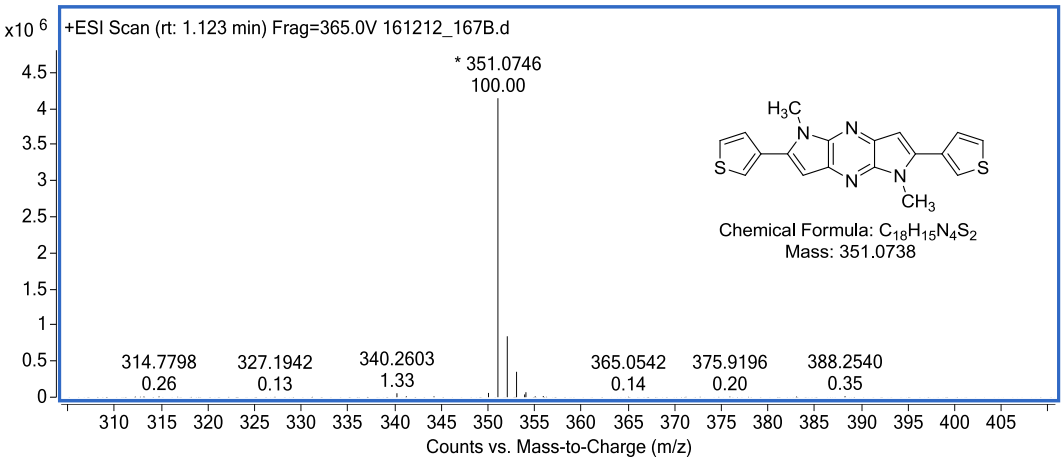


HRMS – 7b





LC/MS – 8b



HRMS – 8b

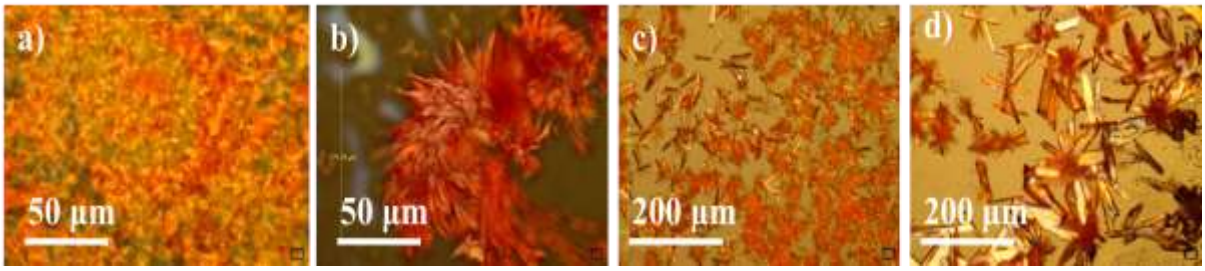


Figure 1. Reflection polarized light micrographs of thin films of **2DT-DPP** on silica substrate.

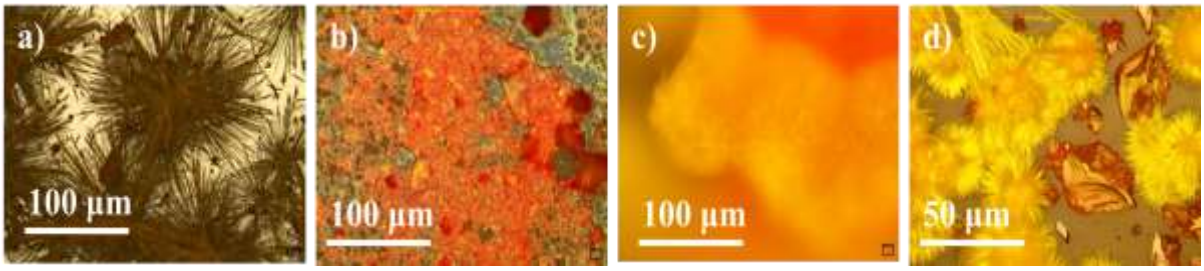


Figure 2. Reflection polarized light micrographs of thin films of **3DT-DPP** on silica substrate.

Single crystal XRD data of compound 3DT-DPP

Table 1. Crystal data and structure refinement for **3DT-DPP**

Identification code	20170120_0m	
Empirical formula	$C_{18}H_{14}N_4S_2$	
Formula weight	350.45	
Temperature	296(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.1901(2) Å	α= 90°.
	b = 9.9832(2) Å	β= 115.4630(10)°.
	c = 9.6509(2) Å	γ = 90°.
Volume	799.43(3) $Å^3$	
Z	2	
Density (calculated)	1.456 Mg/m^3	
Absorption coefficient	0.340 mm^{-1}	
F(000)	364	
Crystal size	0.40 x 0.18 x 0.10 mm^3	
Theta range for data collection	2.56 to 28.33°	
Index ranges	-10<=h<=12, -13<=k<=12, -12<=l<=12	
Reflections collected	7593	

Independent reflections	1986 [R(int) = 0.0221]
Completeness to theta = 28.33°	99.8 %
Absorption correction	Multi-scan
Max. and min. transmission	0.9668 and 0.8761
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1986 / 0 / 140
Goodness-of-fit on F^2	1.054
Final R indices [I>2sigma(I)]	R1 = 0.0500, wR2 = 0.1389
R indices (all data)	R1 = 0.0601, wR2 = 0.1486
Largest diff. peak and hole	0.337 and -0.320 e.$Å^{-3}$

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

	x	y	z	U(eq)
S(1)	501(3)	4091(2)	-3071(2)	68(1)
C(4)	1878(8)	5017(7)	-3209(6)	37(1)
S(1A)	1938(8)	5091(6)	-3042(5)	95(2)
C(4A)	540(30)	3980(20)	-2786(16)	94(6)
N(1)	5523(2)	6363(1)	4870(1)	43(1)
N(2)	4056(2)	5936(1)	2170(1)	41(1)
C(1)	1063(3)	4055(2)	-1181(2)	59(1)
C(2)	2418(2)	4831(2)	-382(2)	45(1)
C(3)	2955(2)	5440(2)	-1395(2)	52(1)
C(5)	3188(2)	4855(2)	1293(2)	41(1)
C(6)	3194(2)	3826(2)	2245(2)	44(1)
C(7)	5904(2)	5737(2)	6224(2)	40(1)
C(8)	4628(2)	5594(2)	3692(2)	39(1)
C(9)	4440(2)	7196(2)	1643(2)	49(1)

Table 3. Bond lengths [Å] and angles [°] for **3DT-DPP.**

S(1)-C(4)	1.618(8)
S(1)-C(1)	1.669(3)
C(4)-C(3)	1.653(6)
C(4)-H(4)	0.9300
S(1A)-C(3)	1.498(6)
S(1A)-C(4A)	1.79(2)
C(4A)-C(1)	1.412(14)
C(4A)-H(4A)	0.9300
N(1)-C(8)	1.3241(19)
N(1)-C(7)	1.3513(18)
N(2)-C(8)	1.3736(18)
N(2)-C(5)	1.3917(19)
N(2)-C(9)	1.4566(19)
C(1)-C(2)	1.386(3)
C(1)-H(3A)	0.99(3)
C(2)-C(3)	1.409(2)
C(2)-C(5)	1.460(2)
C(3)-H(1A)	0.99(2)
C(5)-C(6)	1.376(2)
C(6)-C(7)#1	1.417(2)
C(6)-H(6A)	0.967(18)
C(7)-C(6)#1	1.417(2)
C(7)-C(8)#1	1.431(2)
C(8)-C(7)#1	1.431(2)
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(4)-S(1)-C(1)	102.5(2)
S(1)-C(4)-C(3)	101.1(3)
S(1)-C(4)-H(4)	129.4
C(3)-C(4)-H(4)	129.4
C(3)-S(1A)-C(4A)	98.9(5)
C(1)-C(4A)-S(1A)	101.2(11)
C(1)-C(4A)-H(4A)	129.4
S(1A)-C(4A)-H(4A)	129.4
C(8)-N(1)-C(7)	111.67(13)

C(8)-N(2)-C(5)	108.28(12)
C(8)-N(2)-C(9)	123.29(13)
C(5)-N(2)-C(9)	128.28(12)
C(2)-C(1)-C(4A)	116.1(9)
C(2)-C(1)-S(1)	112.20(18)
C(4A)-C(1)-S(1)	4.5(9)
C(2)-C(1)-H(3A)	127.3(16)
C(4A)-C(1)-H(3A)	116.6(18)
S(1)-C(1)-H(3A)	120.4(16)
C(1)-C(2)-C(3)	110.75(15)
C(1)-C(2)-C(5)	121.14(15)
C(3)-C(2)-C(5)	127.87(16)
C(2)-C(3)-S(1A)	113.0(3)
C(2)-C(3)-C(4)	113.3(3)
S(1A)-C(3)-C(4)	1.9(5)
C(2)-C(3)-H(1A)	123.1(12)
S(1A)-C(3)-H(1A)	123.8(12)
C(4)-C(3)-H(1A)	123.4(12)
C(6)-C(5)-N(2)	109.64(13)
C(6)-C(5)-C(2)	126.02(14)
N(2)-C(5)-C(2)	124.34(13)
C(5)-C(6)-C(7)#1	107.40(14)
C(5)-C(6)-H(6A)	125.3(10)
C(7)#1-C(6)-H(6A)	127.2(10)
N(1)-C(7)-C(6)#1	131.16(14)
N(1)-C(7)-C(8)#1	122.10(13)
C(6)#1-C(7)-C(8)#1	106.73(13)
N(1)-C(8)-N(2)	125.82(13)
N(1)-C(8)-C(7)#1	126.23(13)
N(2)-C(8)-C(7)#1	107.95(12)
N(2)-C(9)-H(9A)	109.5
N(2)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
N(2)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3DT-DPP**. 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}
S(1)	87(1)	68(1)	31(1)	-7(1)	9(1)	5(1)
C(4)	46(2)	45(2)	16(1)	4(1)	10(1)	12(2)
S(1A)	117(4)	98(3)	82(3)	17(2)	54(2)	36(2)
C(4A)	107(12)	69(6)	110(14)	5(7)	49(10)	-28(7)
N(1)	51(1)	40(1)	33(1)	2(1)	15(1)	-3(1)
N(2)	47(1)	42(1)	30(1)	3(1)	13(1)	-2(1)
C(1)	67(1)	59(1)	39(1)	-2(1)	12(1)	-8(1)
C(2)	50(1)	47(1)	32(1)	2(1)	14(1)	8(1)
C(3)	54(1)	63(1)	39(1)	9(1)	20(1)	11(1)
C(5)	42(1)	45(1)	34(1)	0(1)	15(1)	1(1)
C(6)	52(1)	44(1)	34(1)	-1(1)	14(1)	-5(1)
C(7)	44(1)	40(1)	34(1)	1(1)	14(1)	-2(1)
C(8)	42(1)	41(1)	33(1)	4(1)	15(1)	1(1)
C(9)	62(1)	42(1)	42(1)	8(1)	22(1)	-1(1)

Table 5. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for **3DT-DPP.**

	x	y	z	U(eq)
H(4)	2024	5248	-4075	44
H(4A)	-308	3497	-3513	113
H(1A)	3940(30)	6010(20)	-1040(20)	57(6)
H(3A)	430(30)	3540(30)	-750(30)	85(7)
H(6A)	2710(20)	2956(18)	1910(19)	42(4)
H(9A)	5056	7751	2512	73
H(9B)	3460	7649	996	73
H(9C)	5057	7021	1074	73

Table 6. Torsion angles [°] for **3DT-DPP**

C(1)-S(1)-C(4)-C(3)	-3.1(4)
C(3)-S(1A)-C(4A)-C(1)	2.5(11)
S(1A)-C(4A)-C(1)-C(2)	-2.9(12)
S(1A)-C(4A)-C(1)-S(1)	26(12)
C(4)-S(1)-C(1)-C(2)	2.3(3)
C(4)-S(1)-C(1)-C(4A)	-149(12)
C(4A)-C(1)-C(2)-C(3)	2.2(9)
S(1)-C(1)-C(2)-C(3)	-0.2(2)
C(4A)-C(1)-C(2)-C(5)	-172.7(9)
S(1)-C(1)-C(2)-C(5)	-175.03(15)
C(1)-C(2)-C(3)-S(1A)	-0.1(3)
C(5)-C(2)-C(3)-S(1A)	174.3(3)
C(1)-C(2)-C(3)-C(4)	-2.2(3)
C(5)-C(2)-C(3)-C(4)	172.3(3)
C(4A)-S(1A)-C(3)-C(2)	-1.5(7)
C(4A)-S(1A)-C(3)-C(4)	97(15)
S(1)-C(4)-C(3)-C(2)	3.5(5)
S(1)-C(4)-C(3)-S(1A)	-79(15)
C(8)-N(2)-C(5)-C(6)	0.32(18)
C(9)-N(2)-C(5)-C(6)	175.96(16)
C(8)-N(2)-C(5)-C(2)	-178.86(14)
C(9)-N(2)-C(5)-C(2)	-3.2(2)
C(1)-C(2)-C(5)-C(6)	29.1(3)
C(3)-C(2)-C(5)-C(6)	-144.85(19)
C(1)-C(2)-C(5)-N(2)	-151.90(17)
C(3)-C(2)-C(5)-N(2)	34.2(3)
N(2)-C(5)-C(6)-C(7)#1	-0.11(18)
C(2)-C(5)-C(6)-C(7)#1	179.06(14)
C(8)-N(1)-C(7)-C(6)#1	-179.10(16)
C(8)-N(1)-C(7)-C(8)#1	-0.1(2)
C(7)-N(1)-C(8)-N(2)	-179.52(15)
C(7)-N(1)-C(8)-C(7)#1	0.1(2)
C(5)-N(2)-C(8)-N(1)	179.25(14)
C(9)-N(2)-C(8)-N(1)	3.4(2)
C(5)-N(2)-C(8)-C(7)#1	-0.40(17)
C(9)-N(2)-C(8)-C(7)#1	-176.30(14)

Symmetry transformations used to generate equivalent atoms:

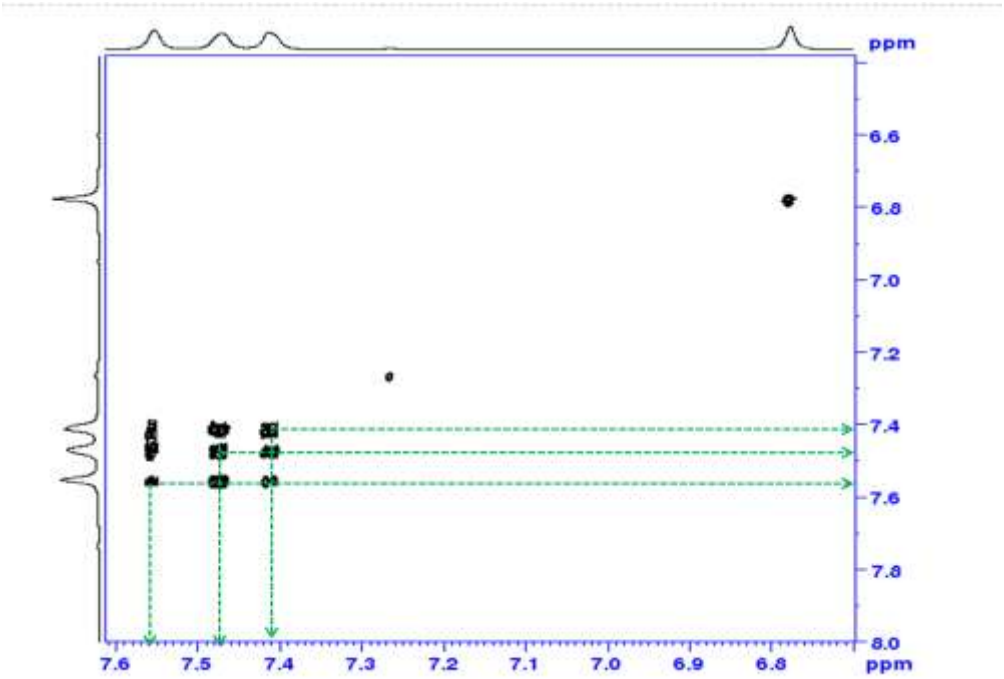


Figure 3. COSY spectrum of **3DT-DPP.**

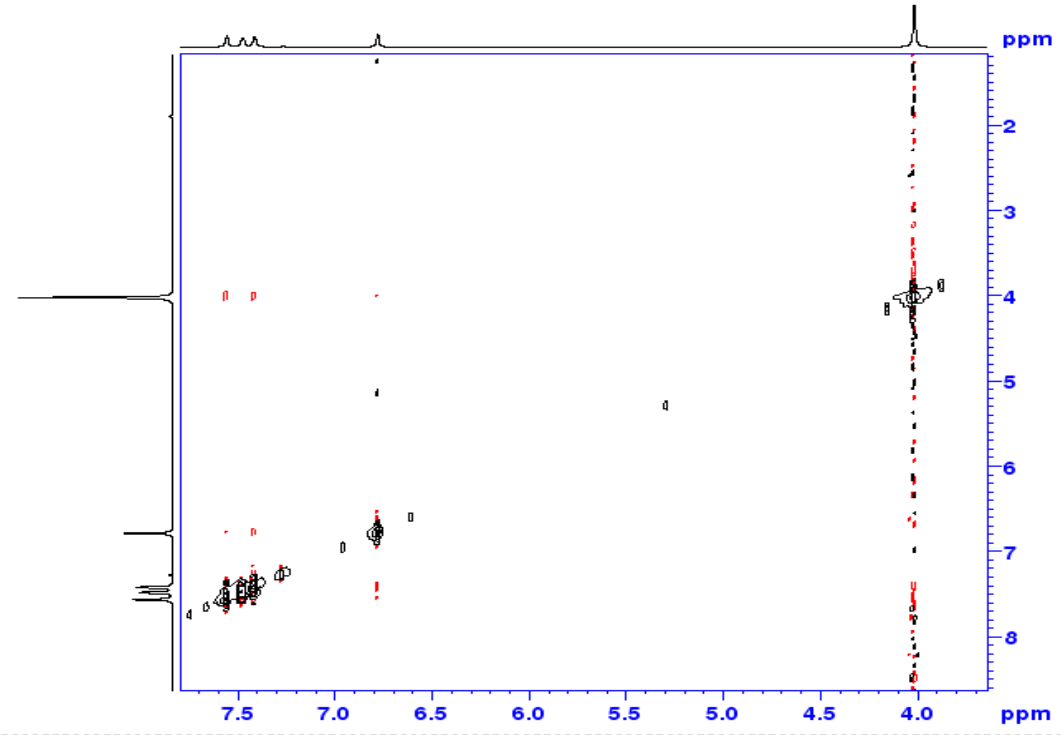


Figure 4. NOESY spectrum of **3DT-DPP**

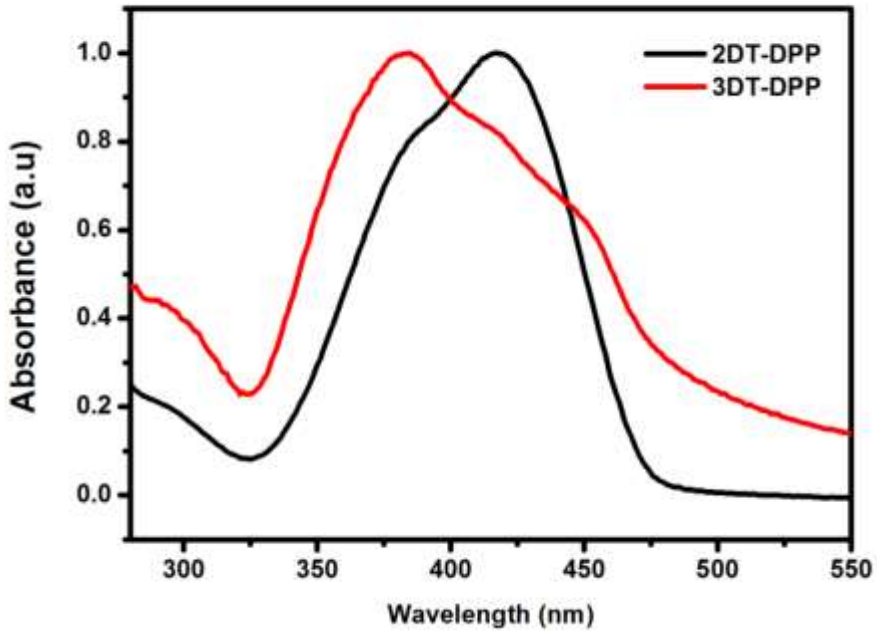


Figure 5. Absorption spectrum of solid films of **DT-DPP** isomers.