DBU-mediated [4 + 1] Annulations of Donor-Acceptor Cyclopropanes with Carbon disulfide or Thiourea for Synthesis of 2-Aminothiophene-3-carboxylates

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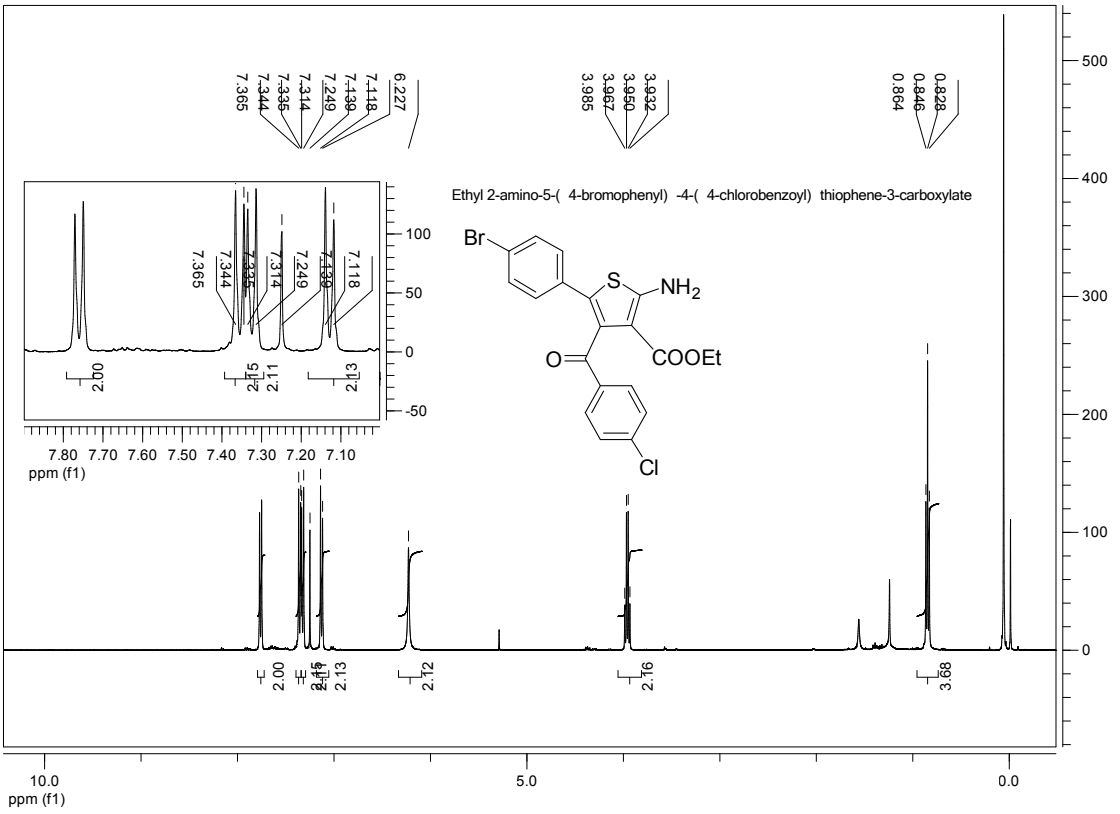

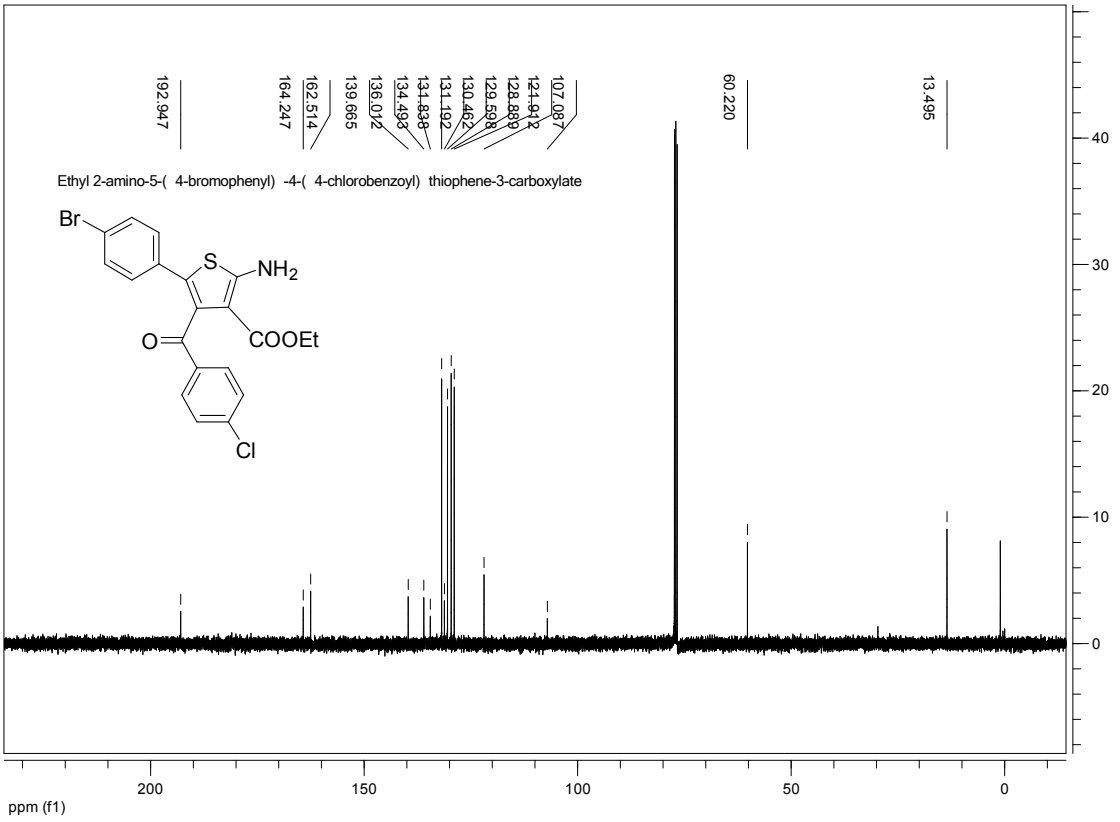

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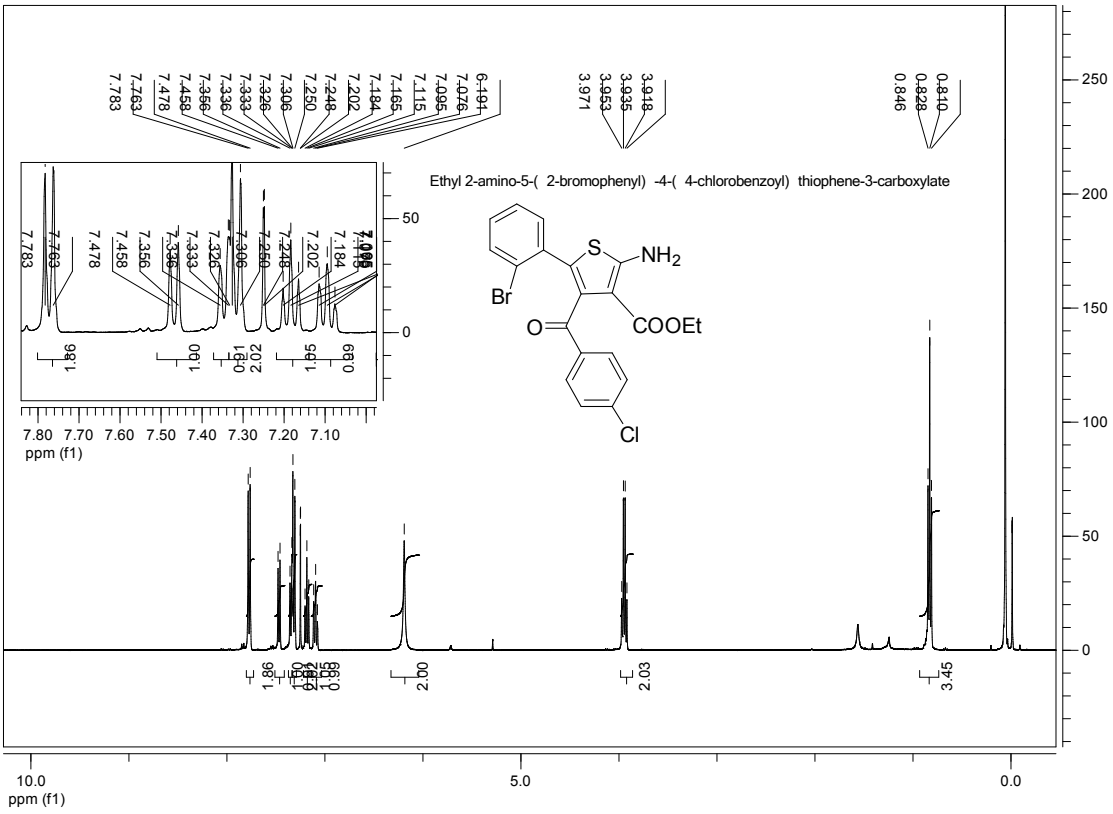

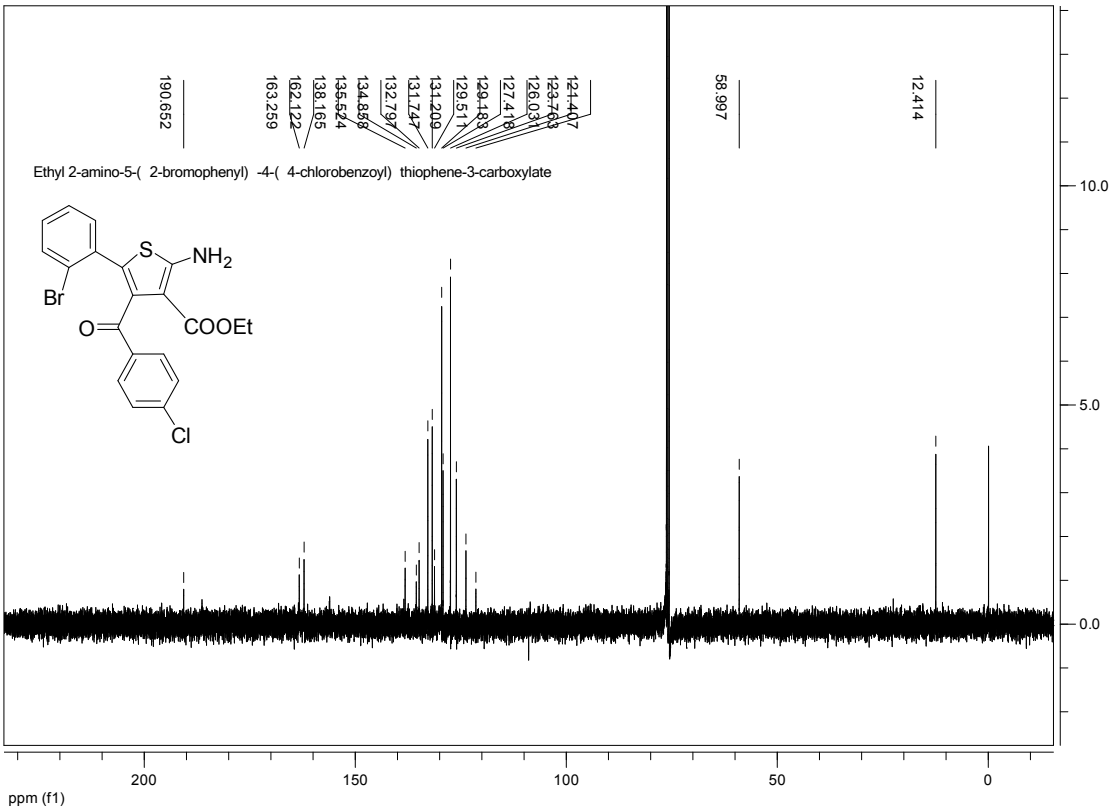

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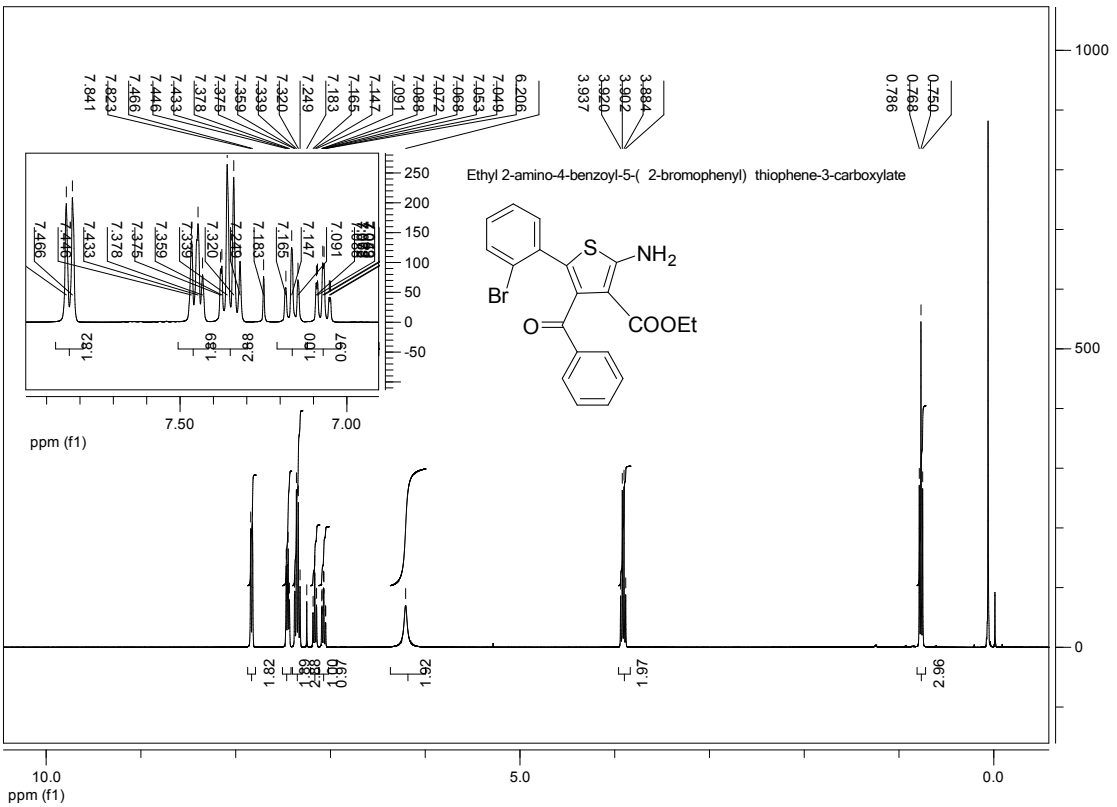

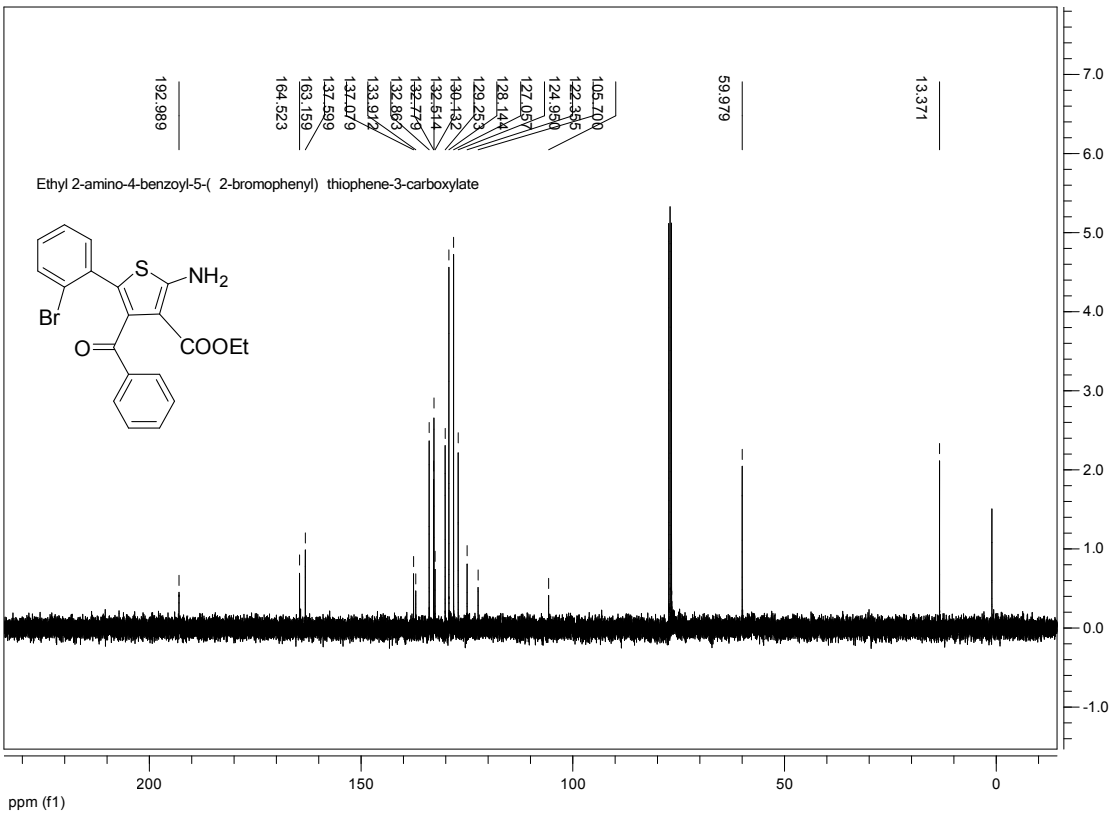

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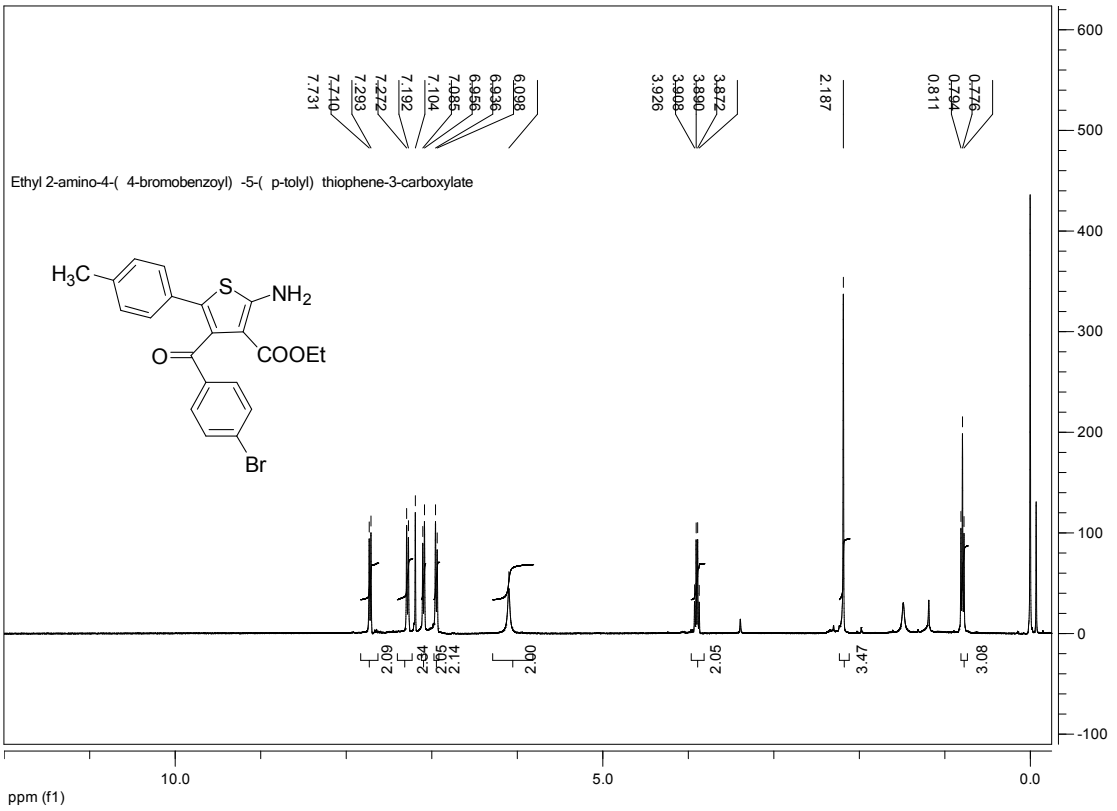

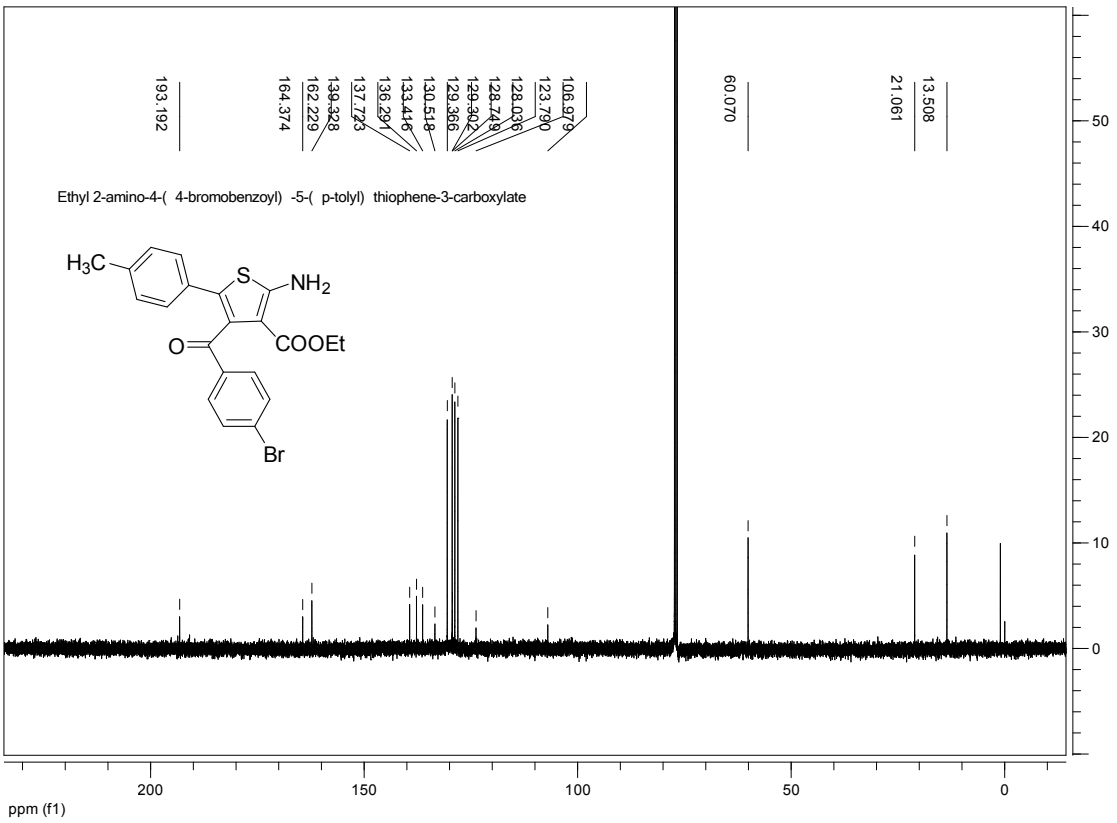

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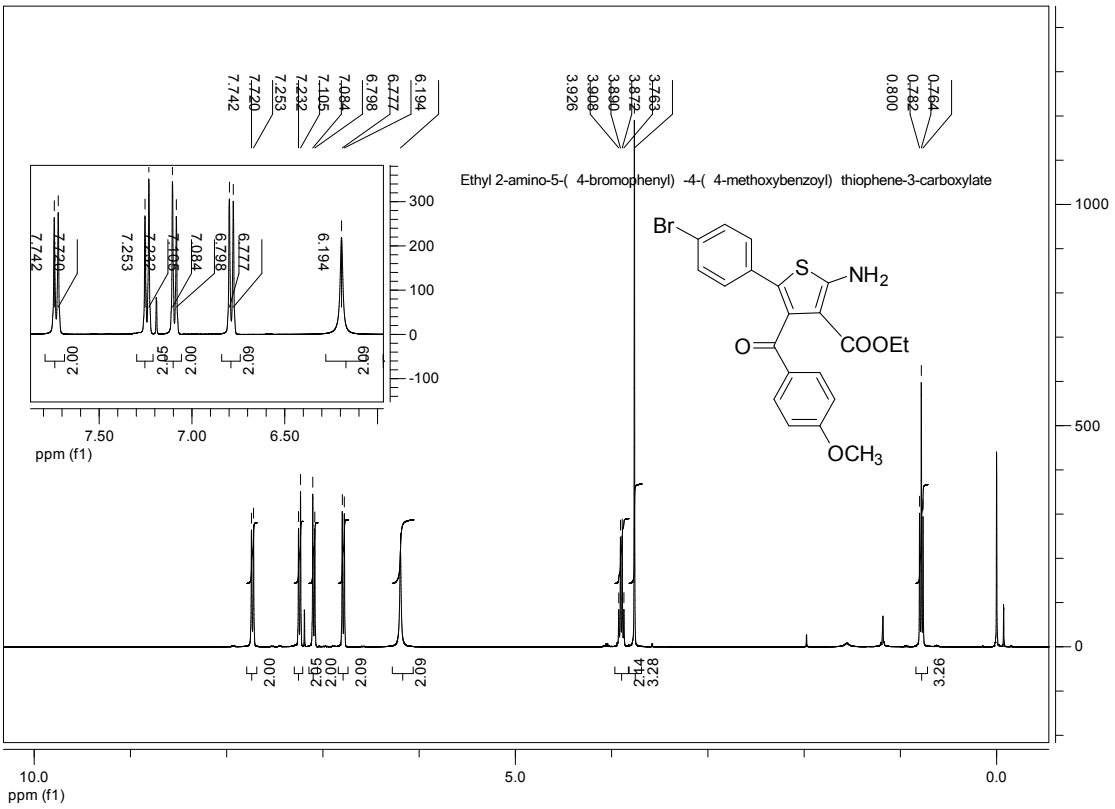

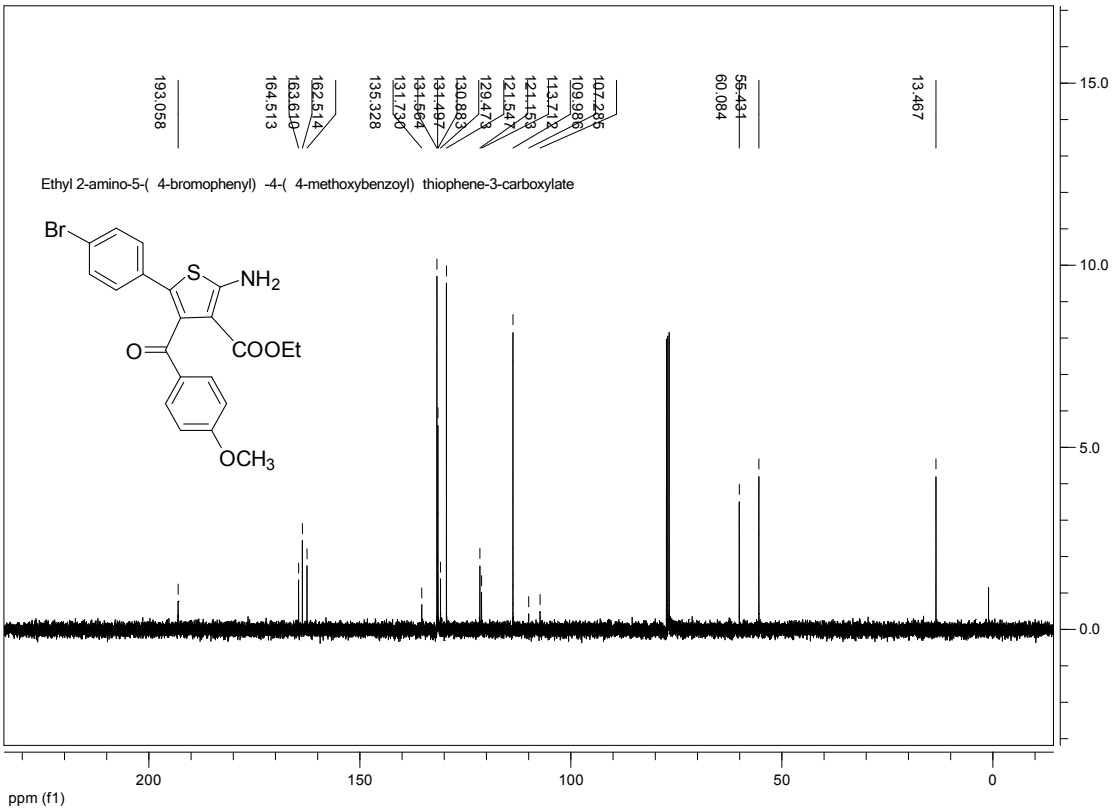

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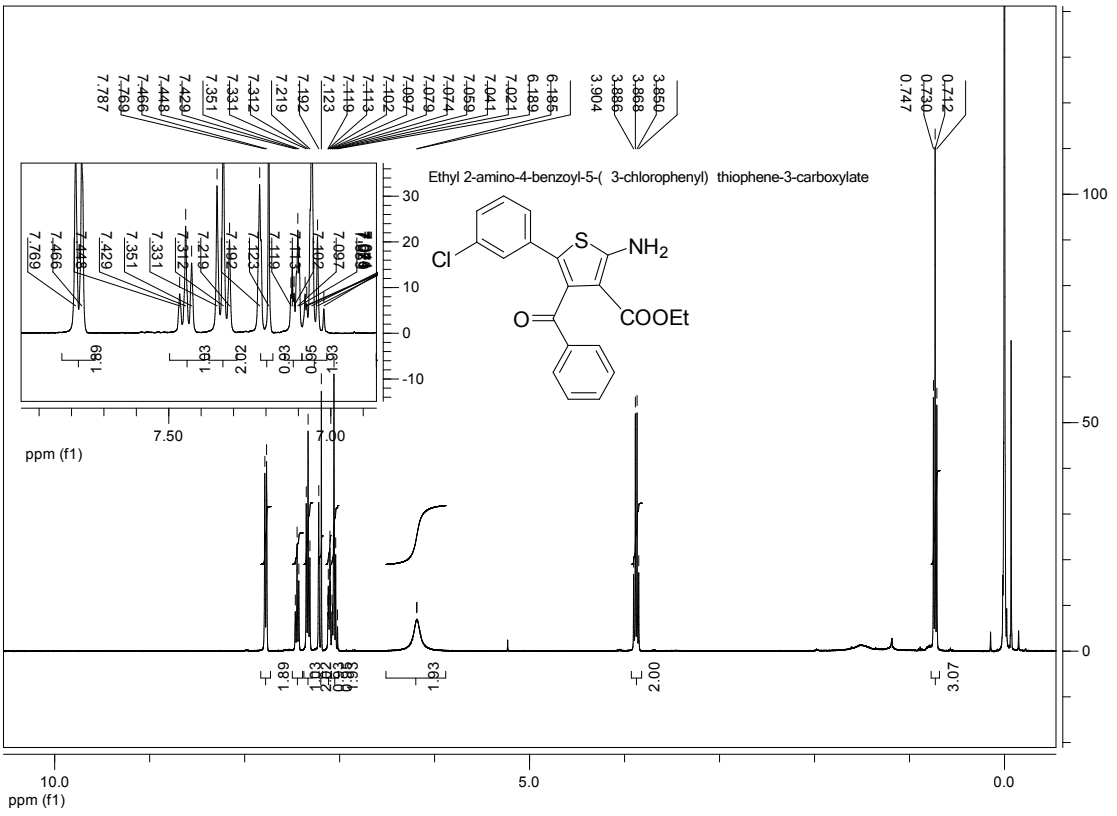

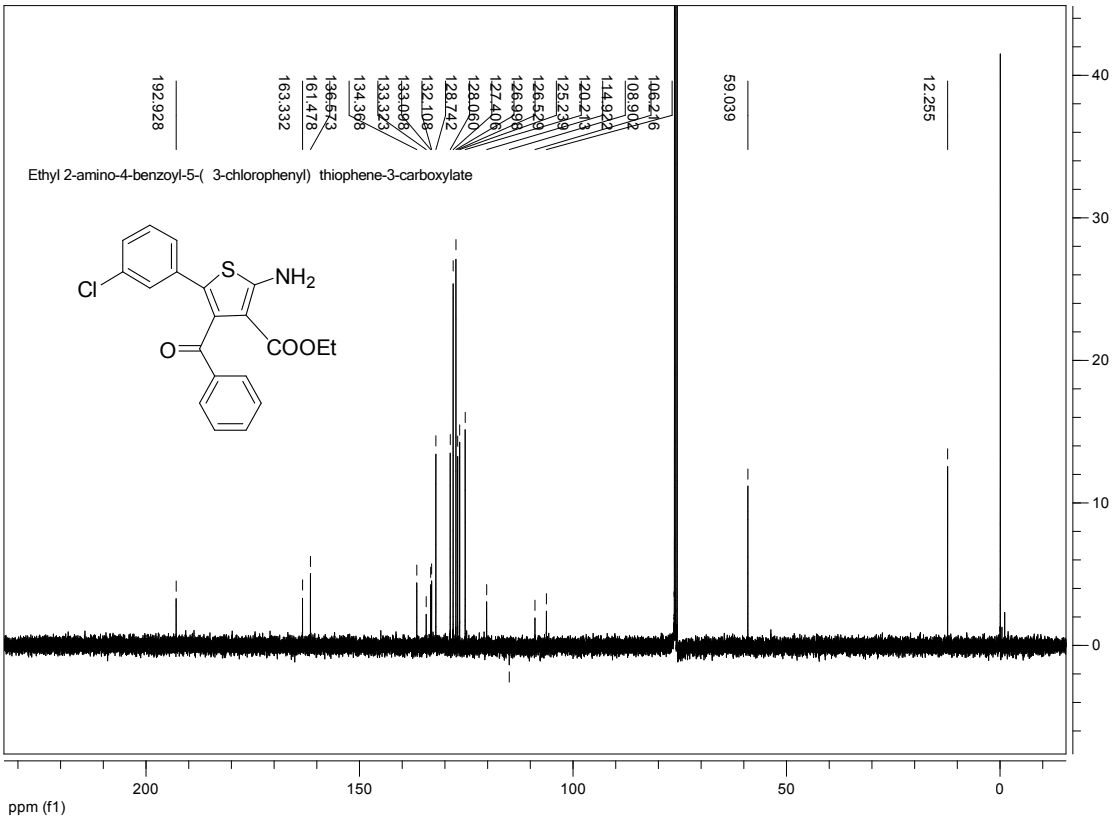

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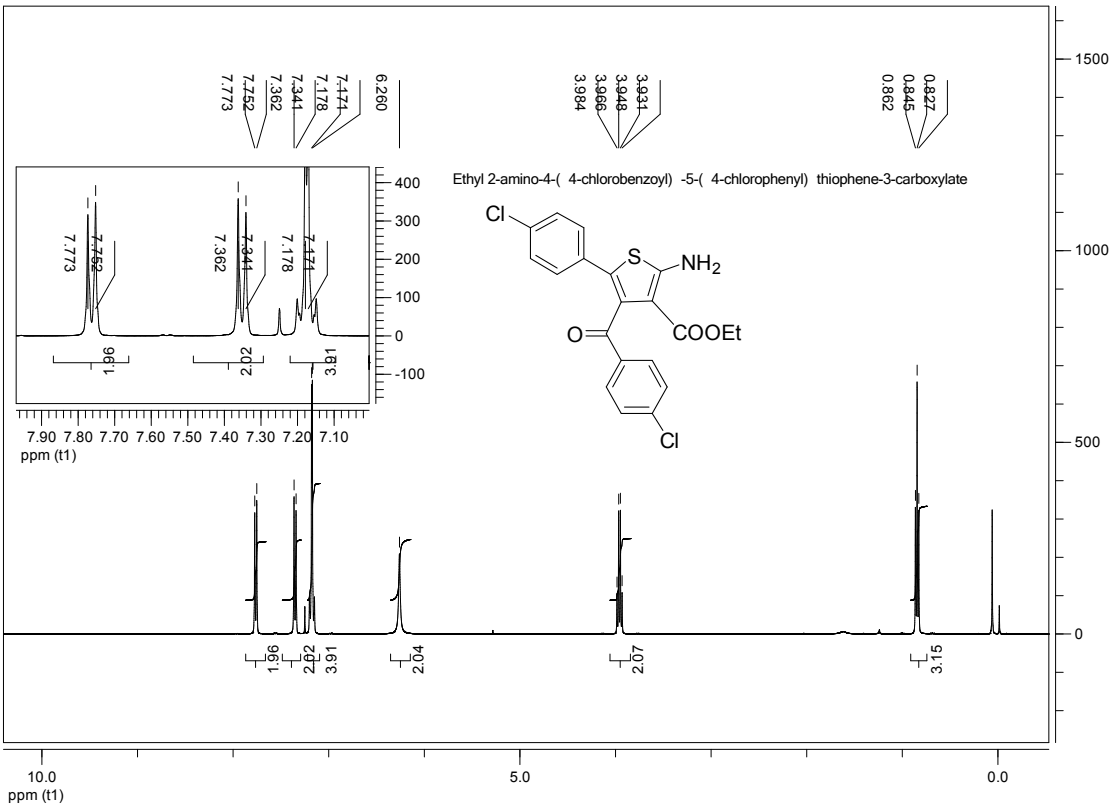

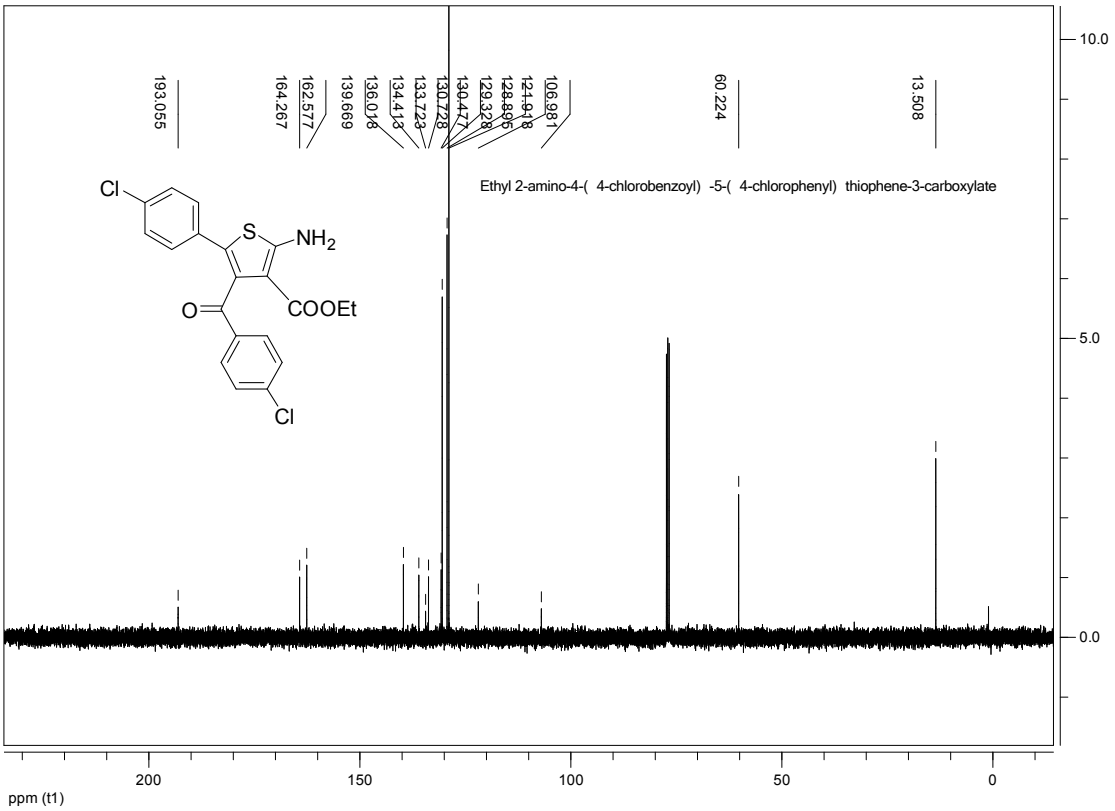

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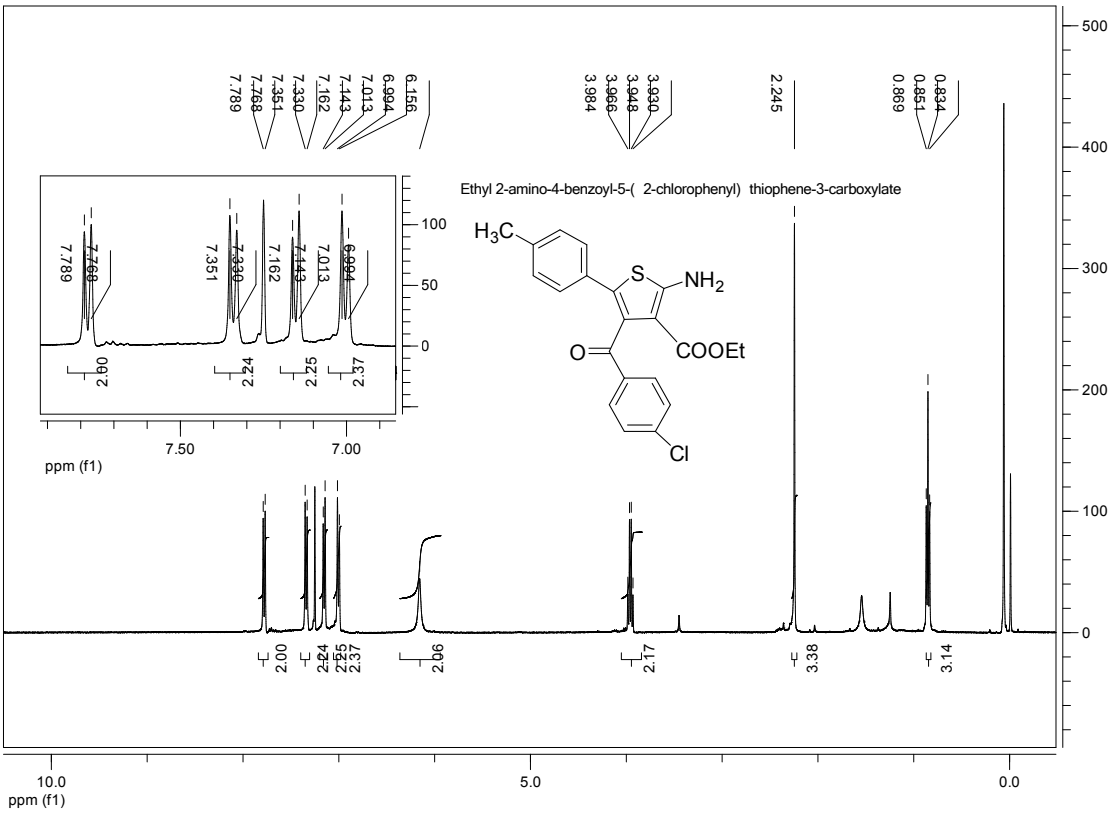

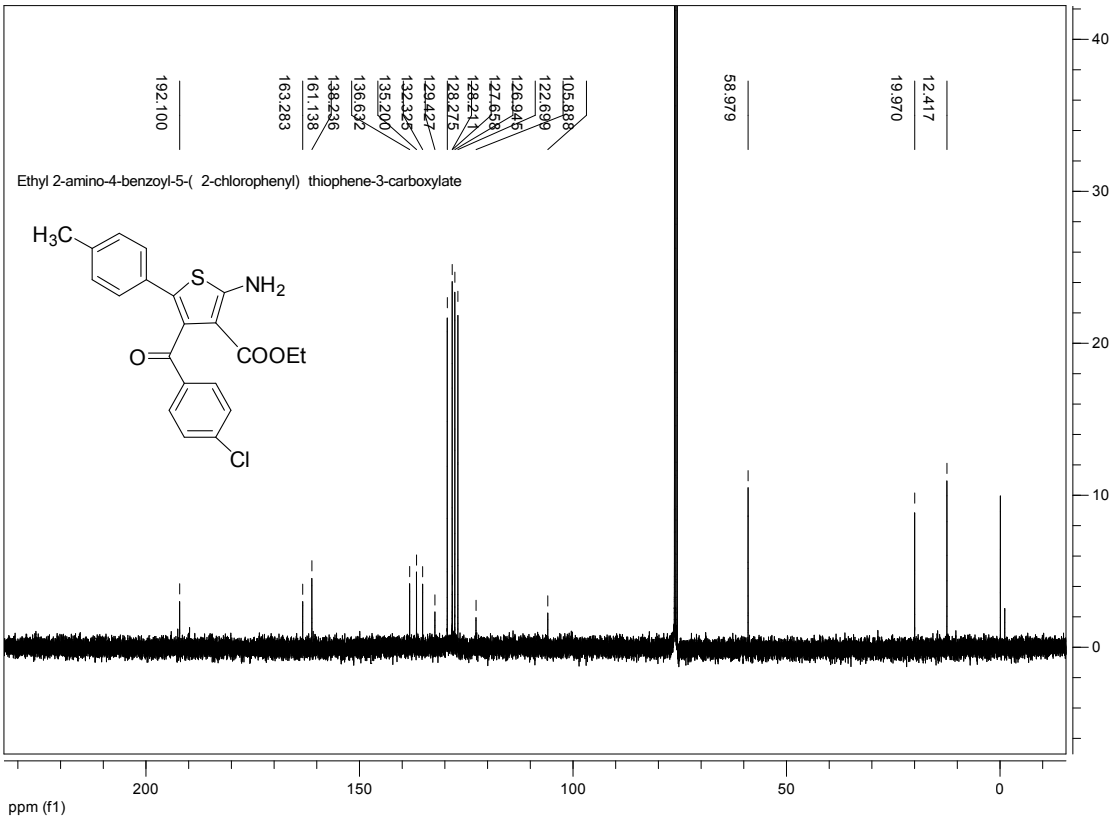

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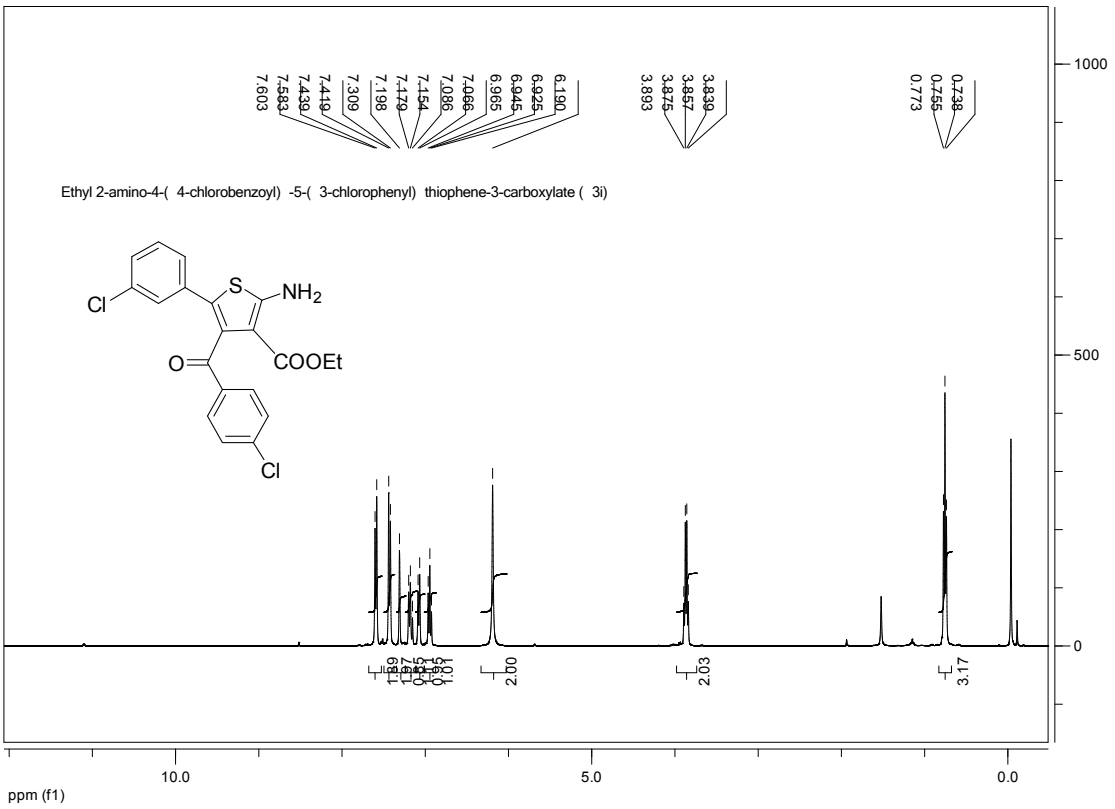

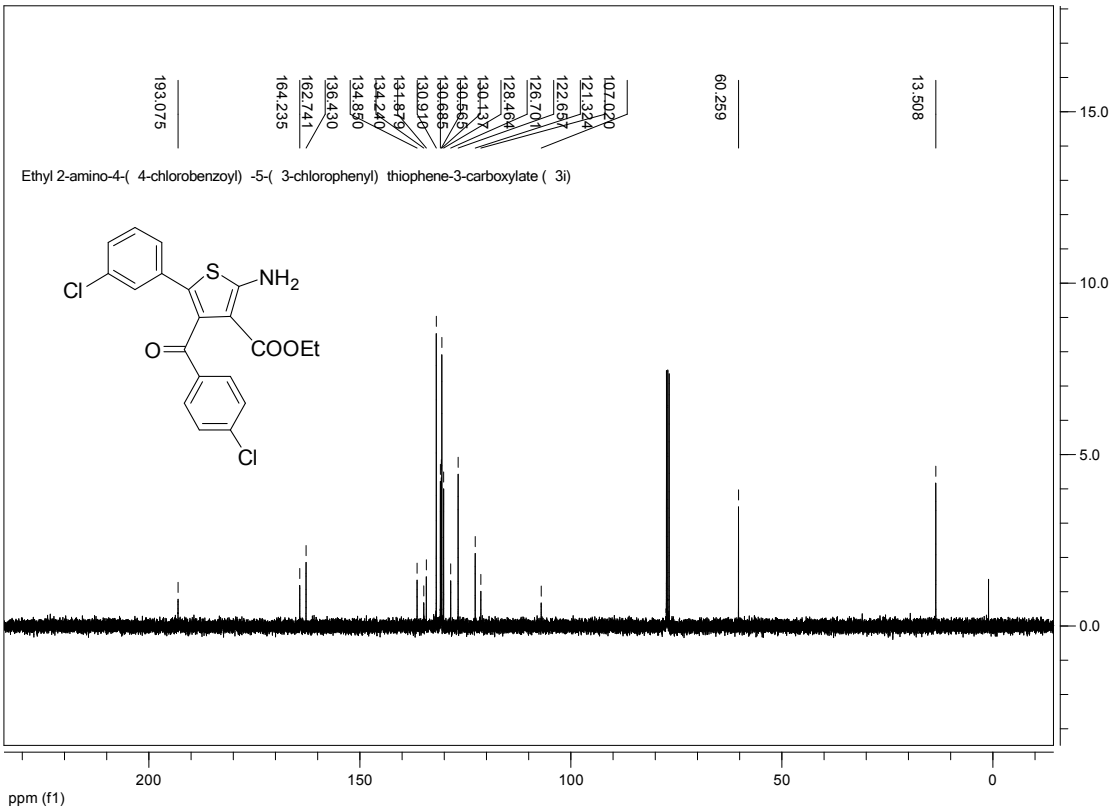

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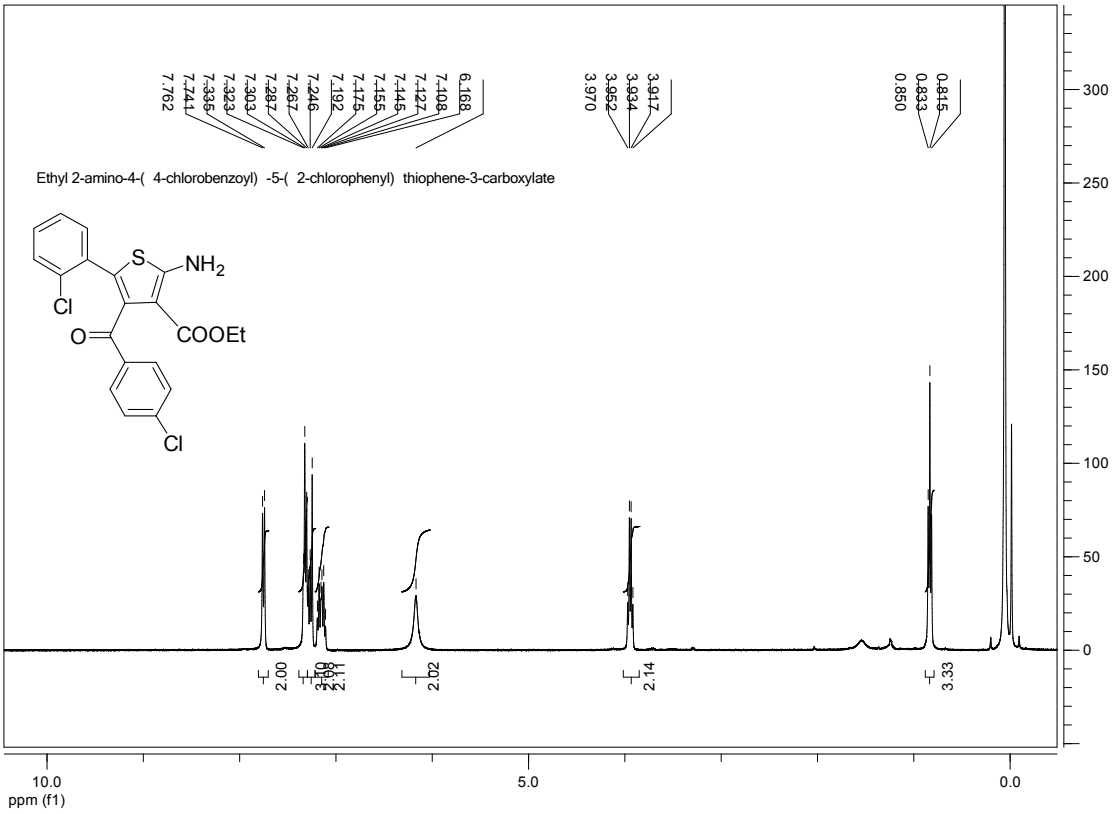

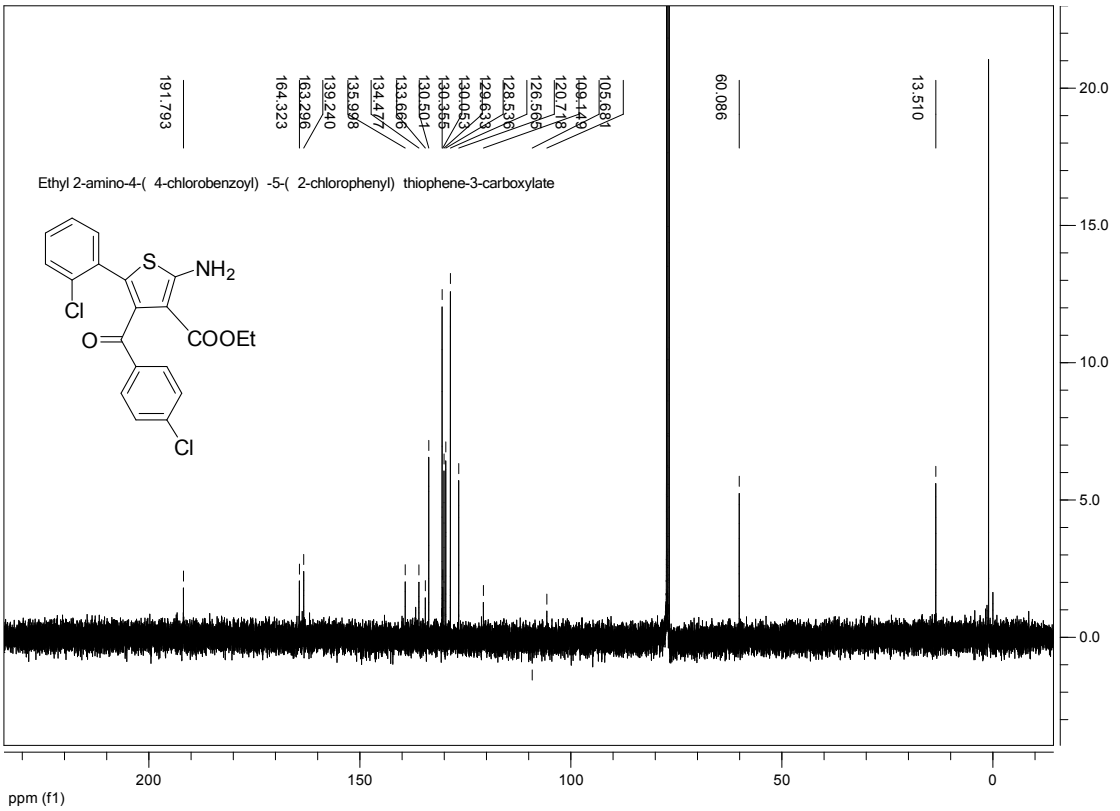

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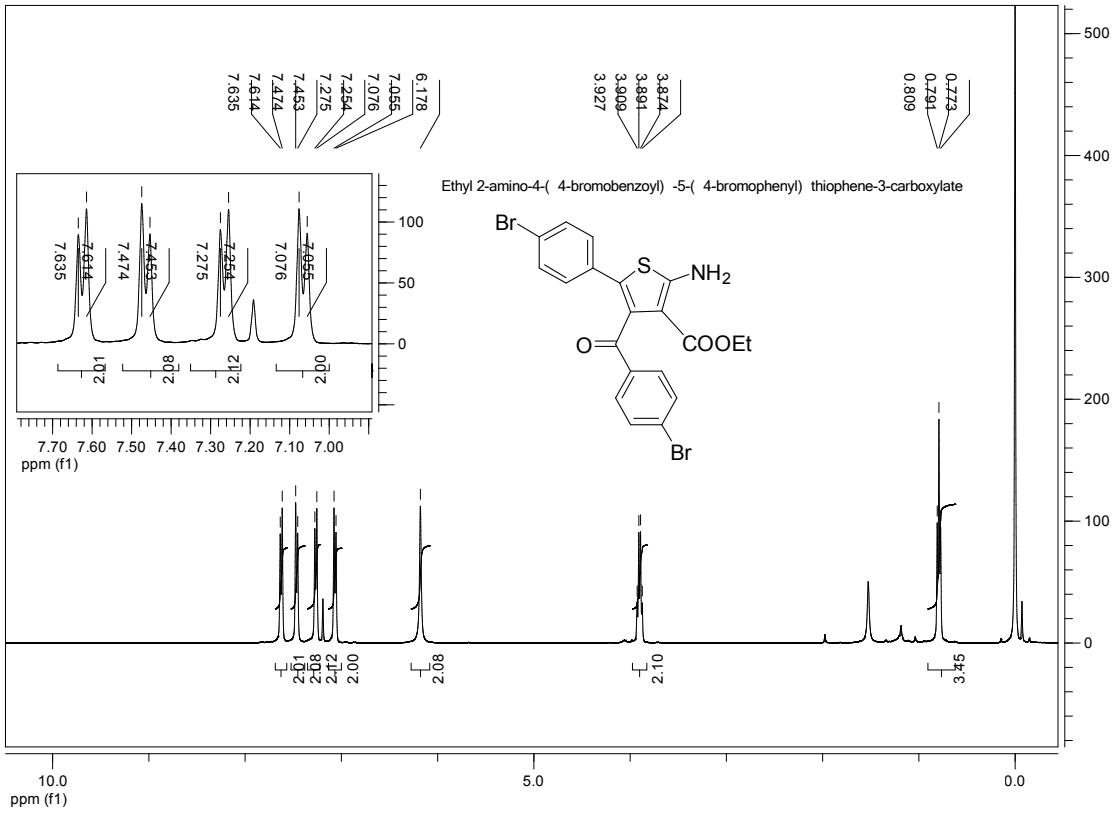

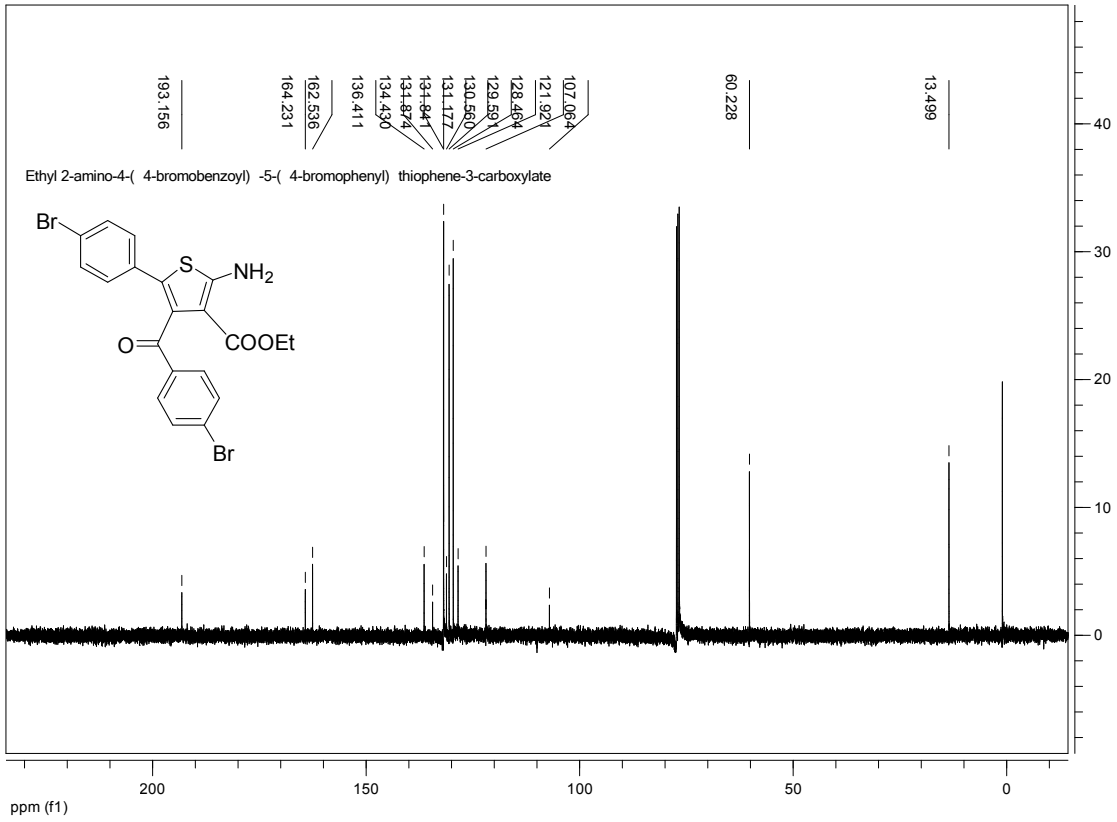

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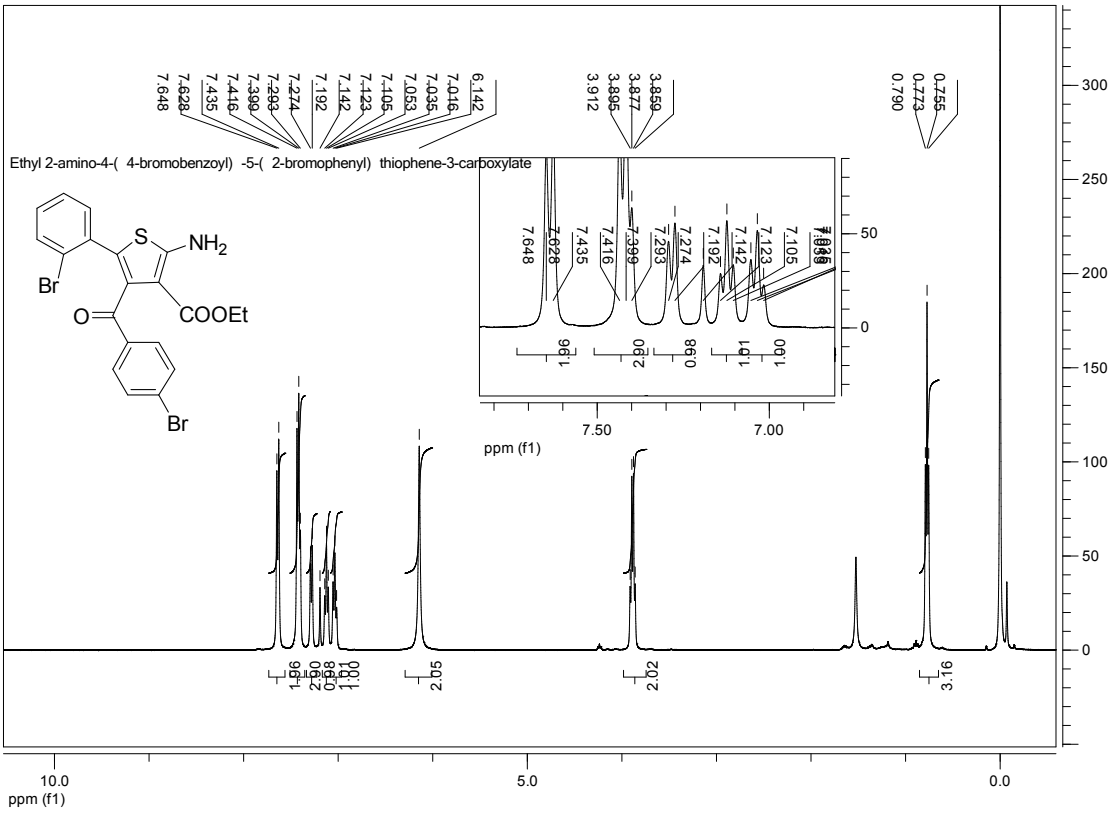

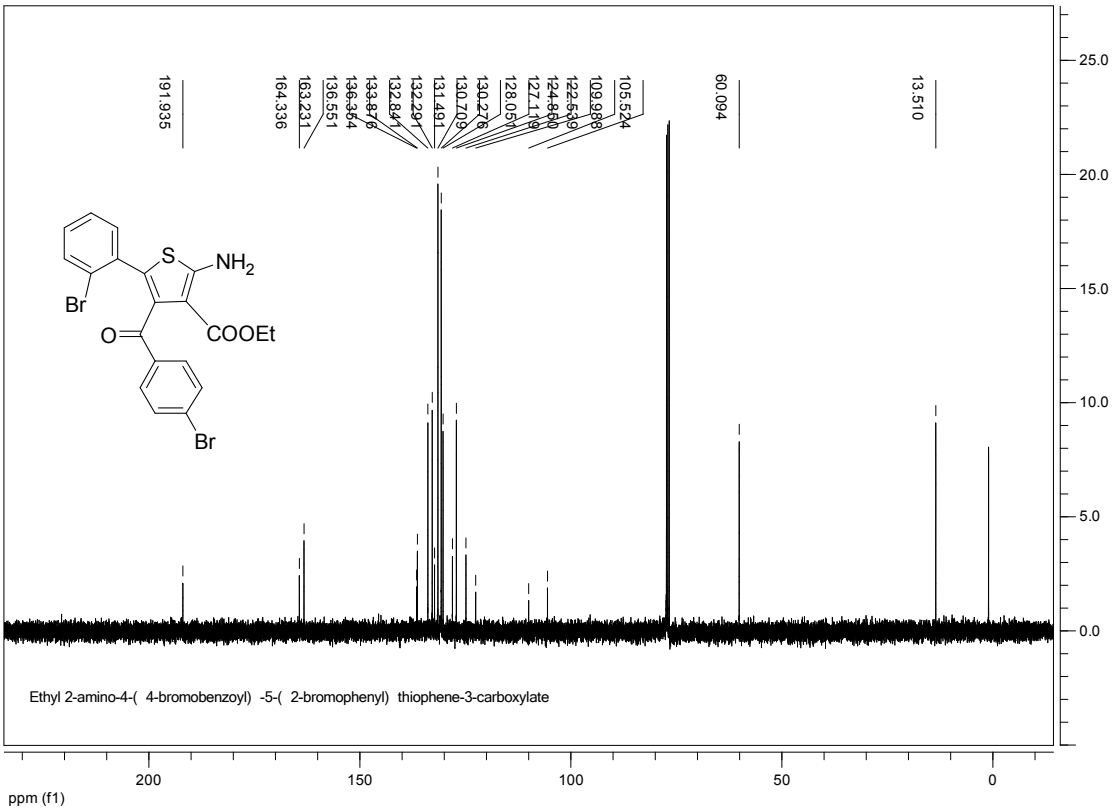

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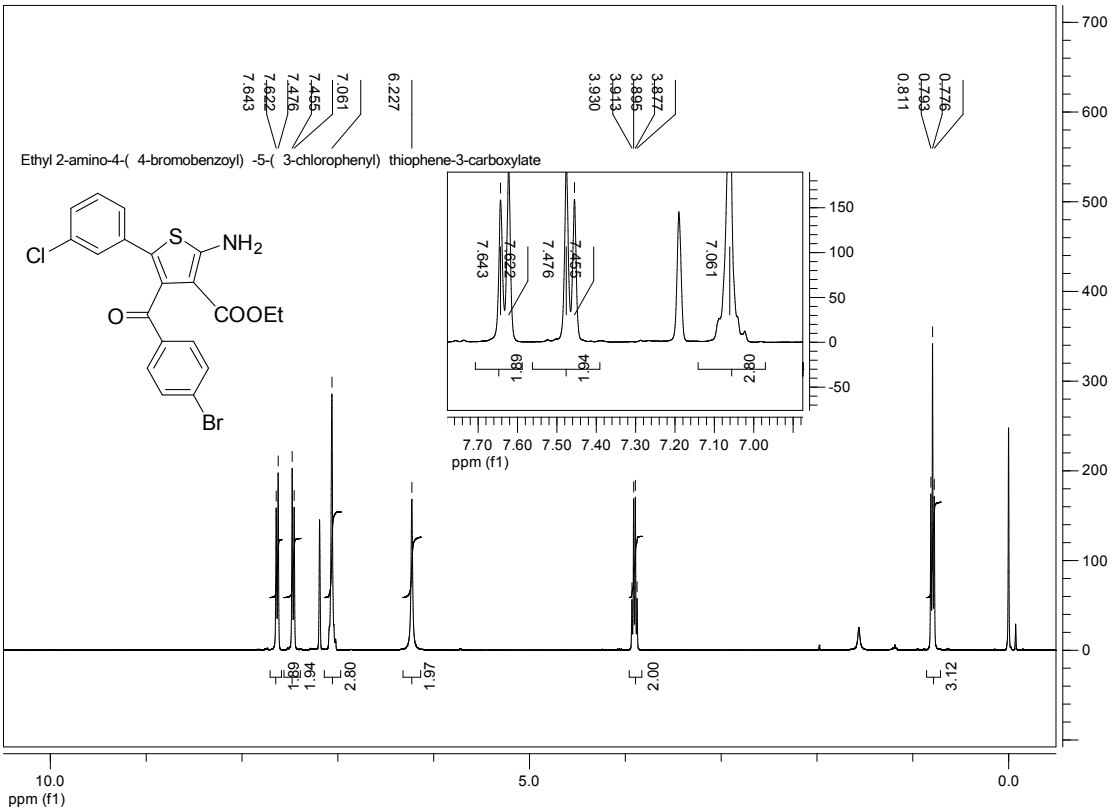

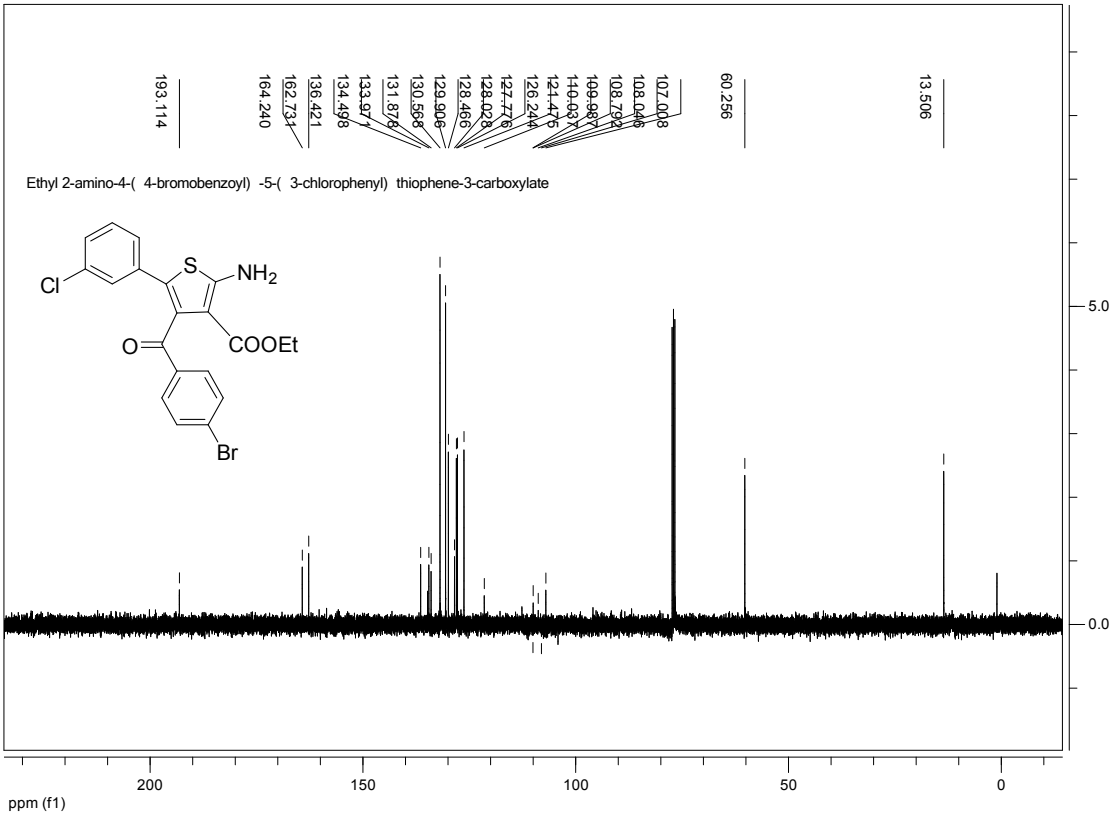

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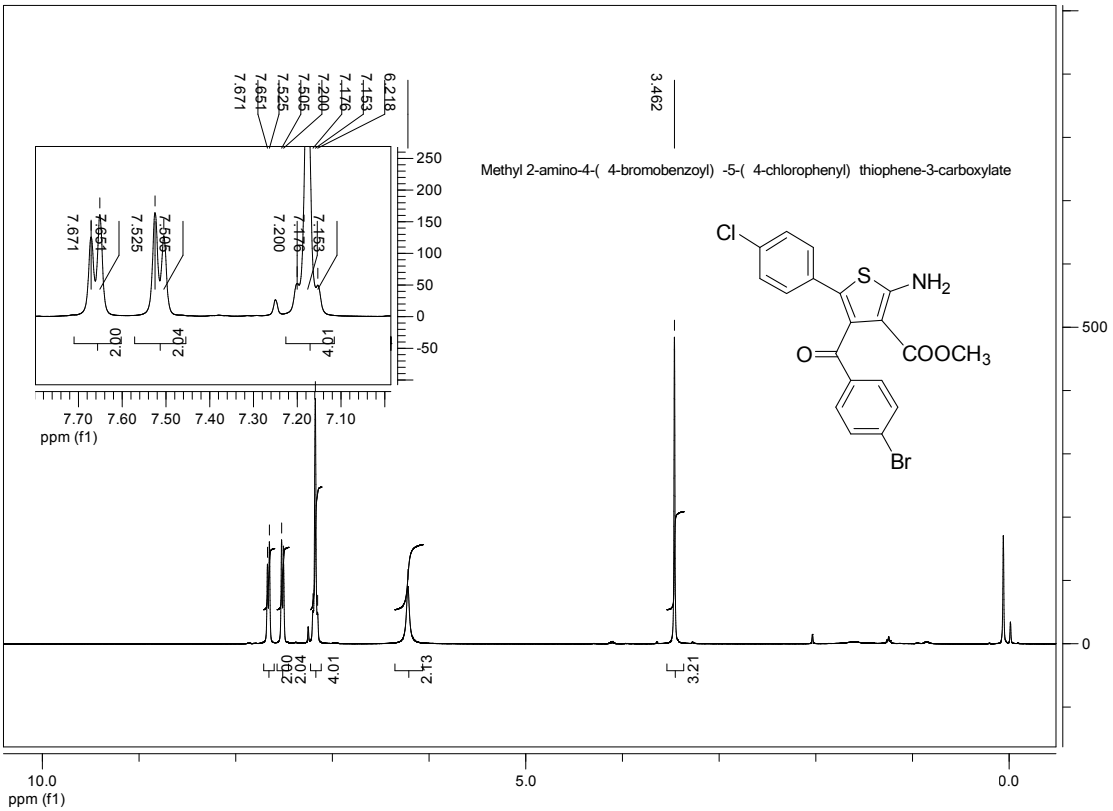

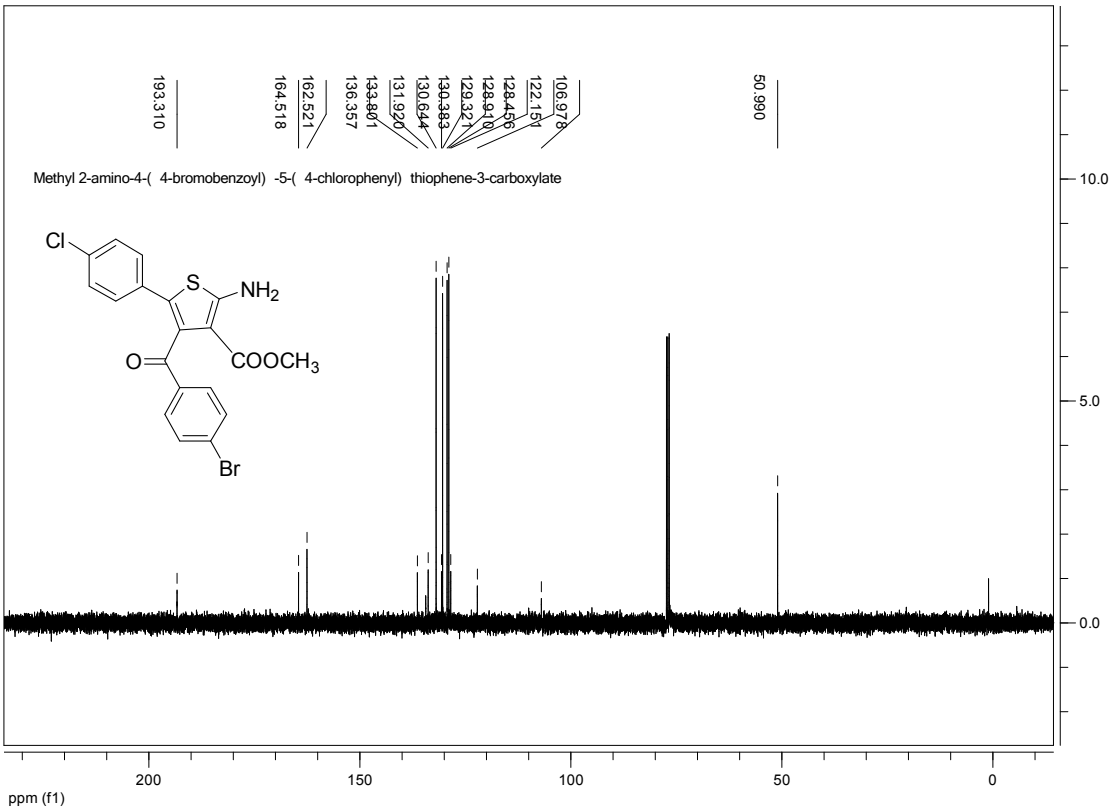

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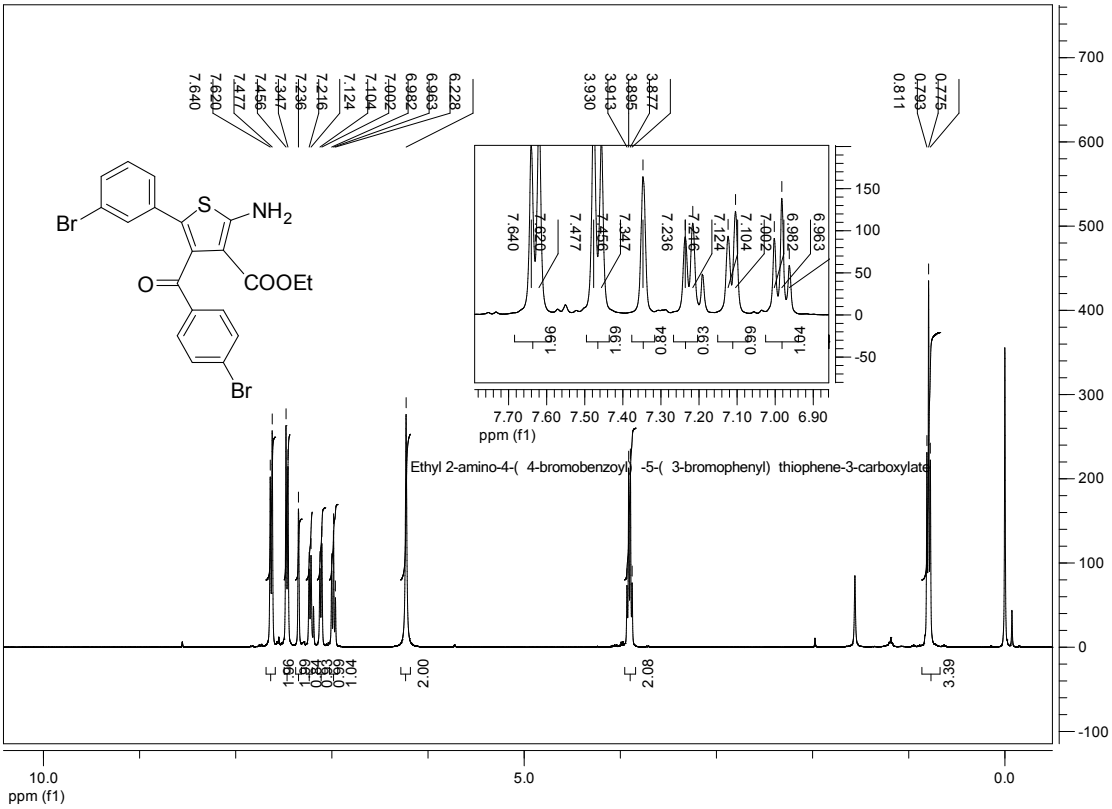
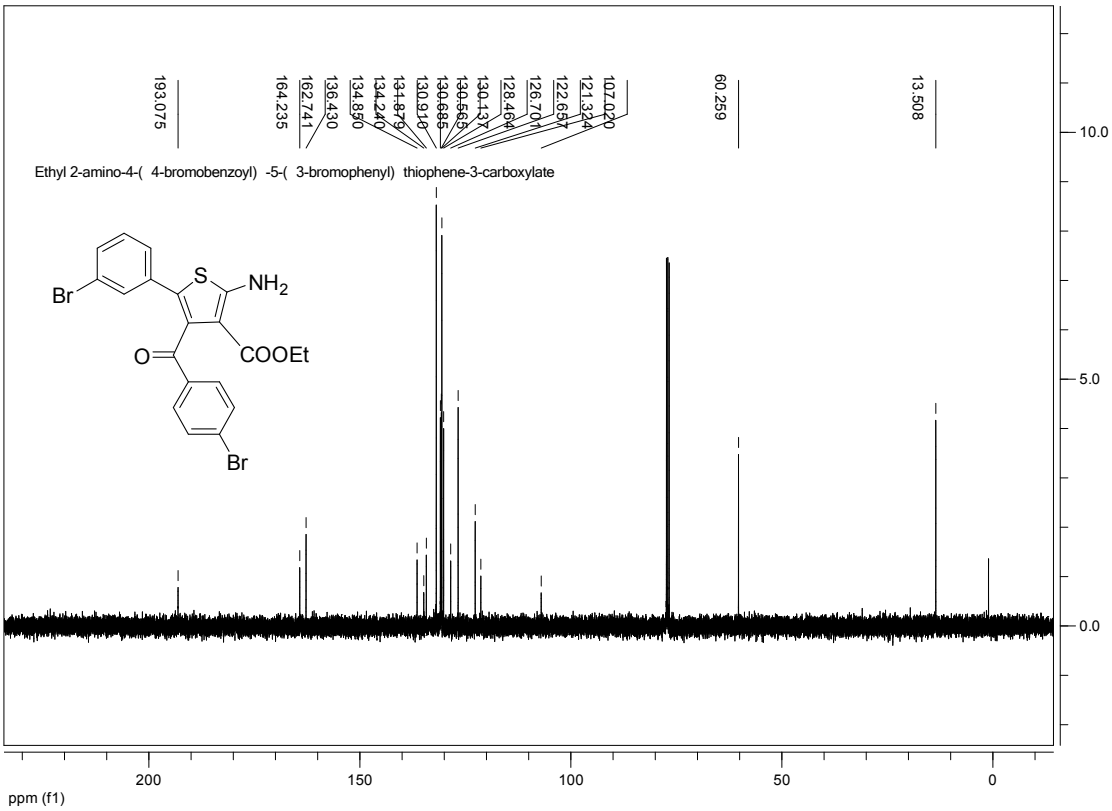
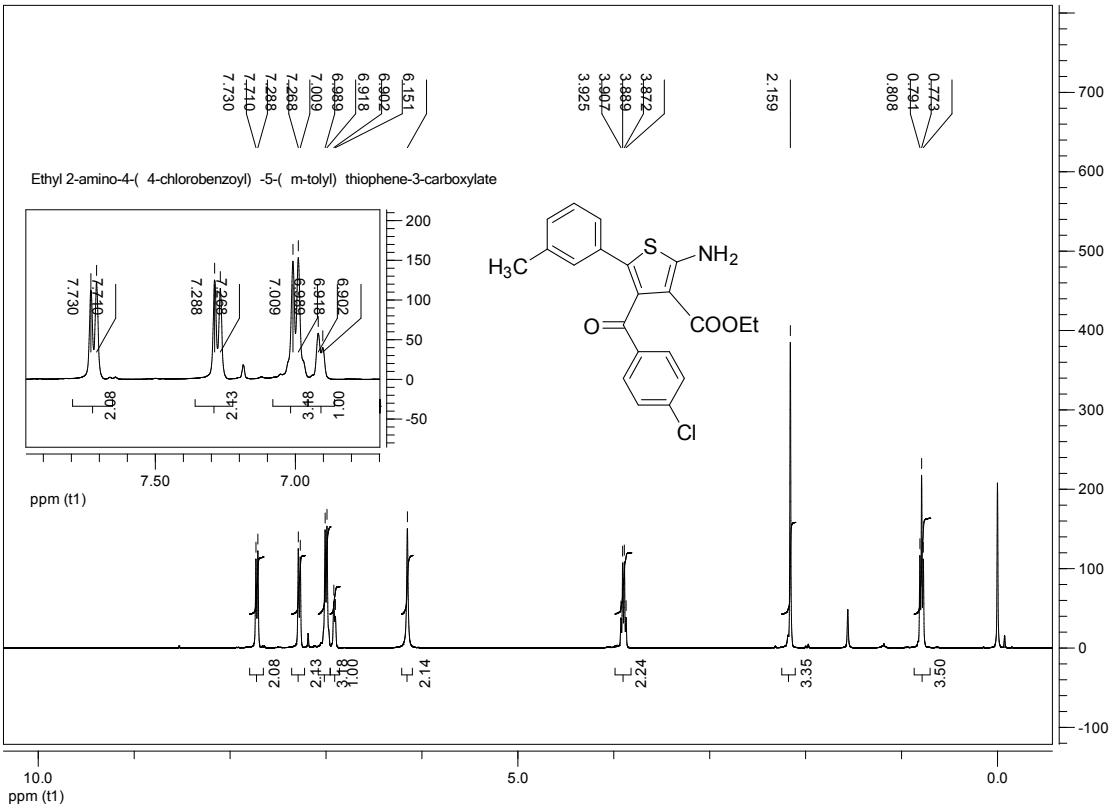
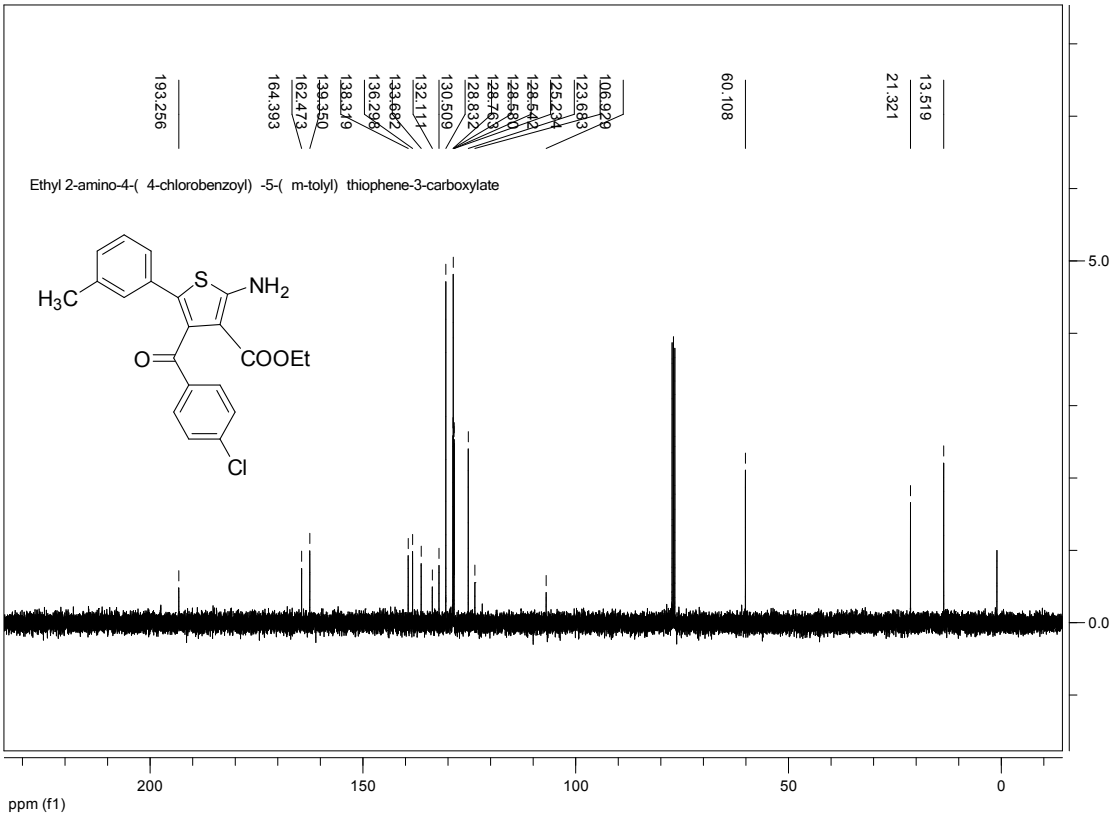




Ethyl 2-amino-4-(4-chlorobenzoyl)-5-(m-tolyl)thiophene-3-carboxylate (3p)





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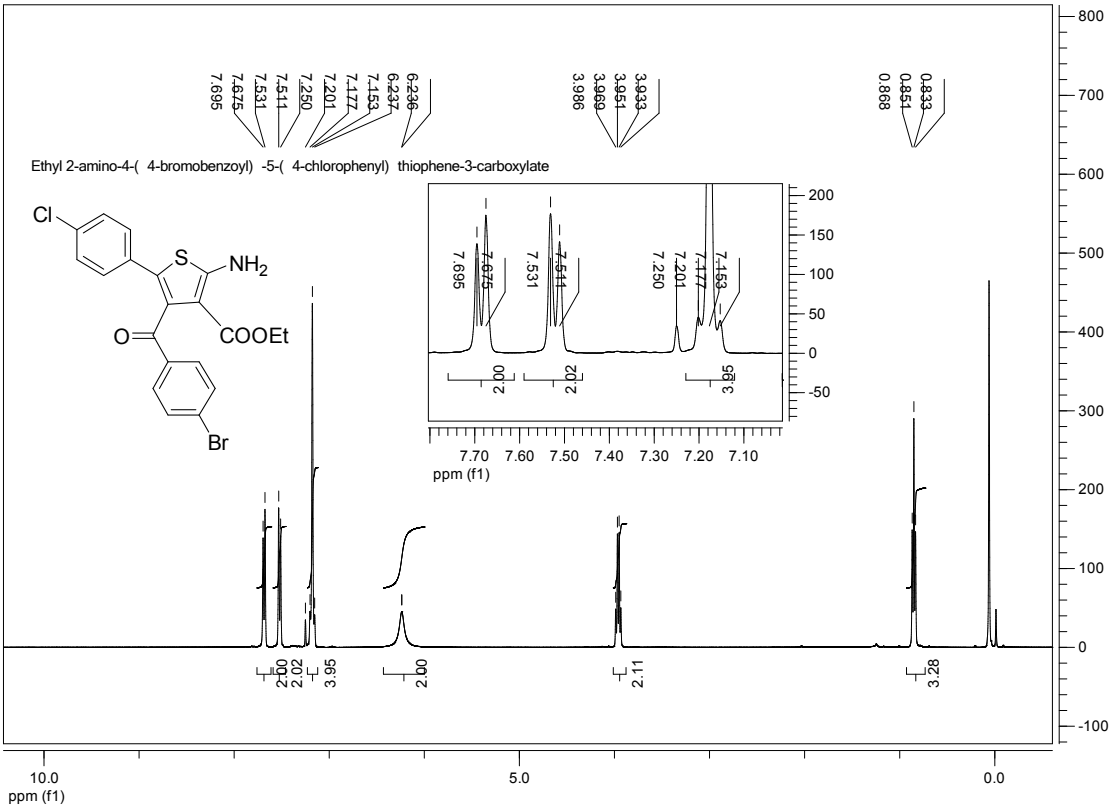

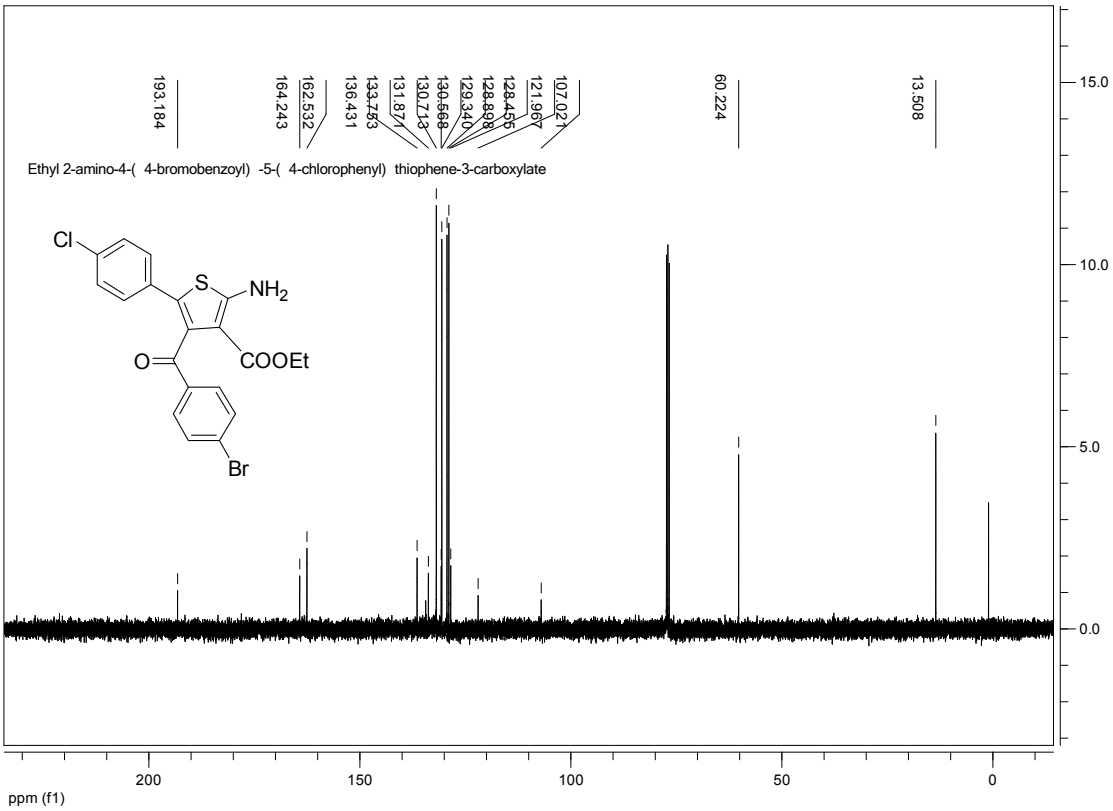

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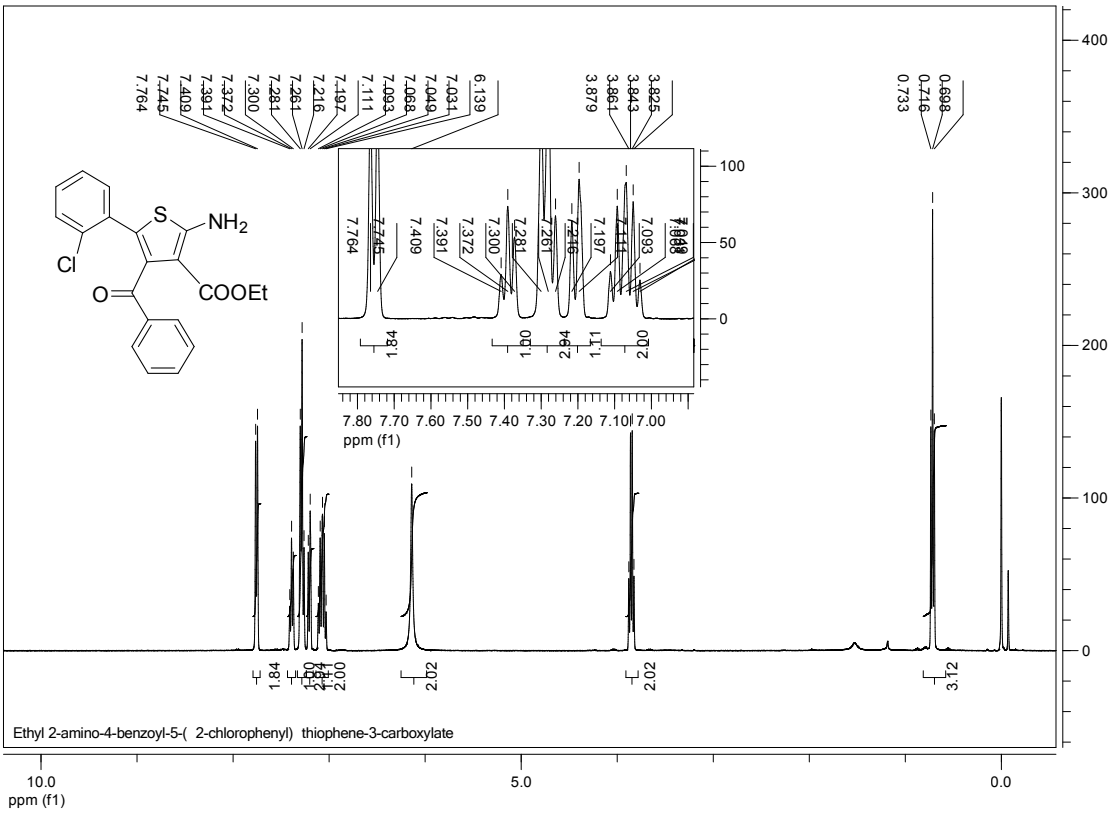
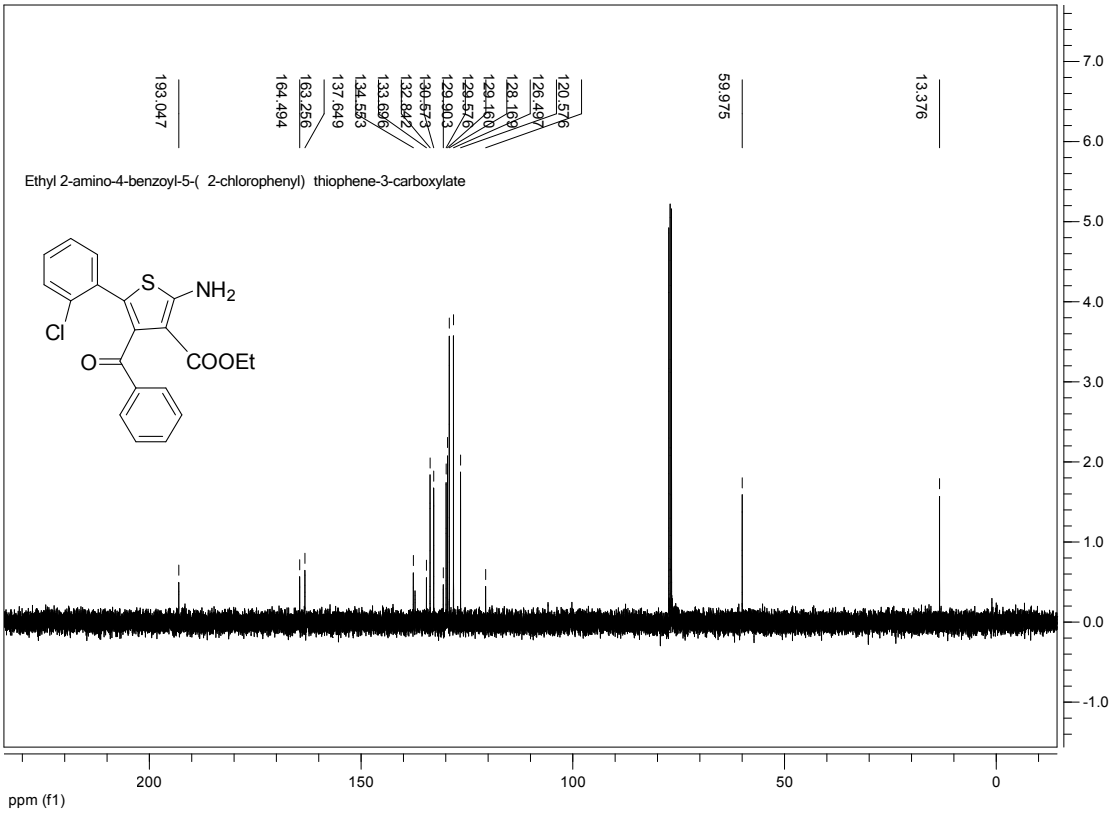
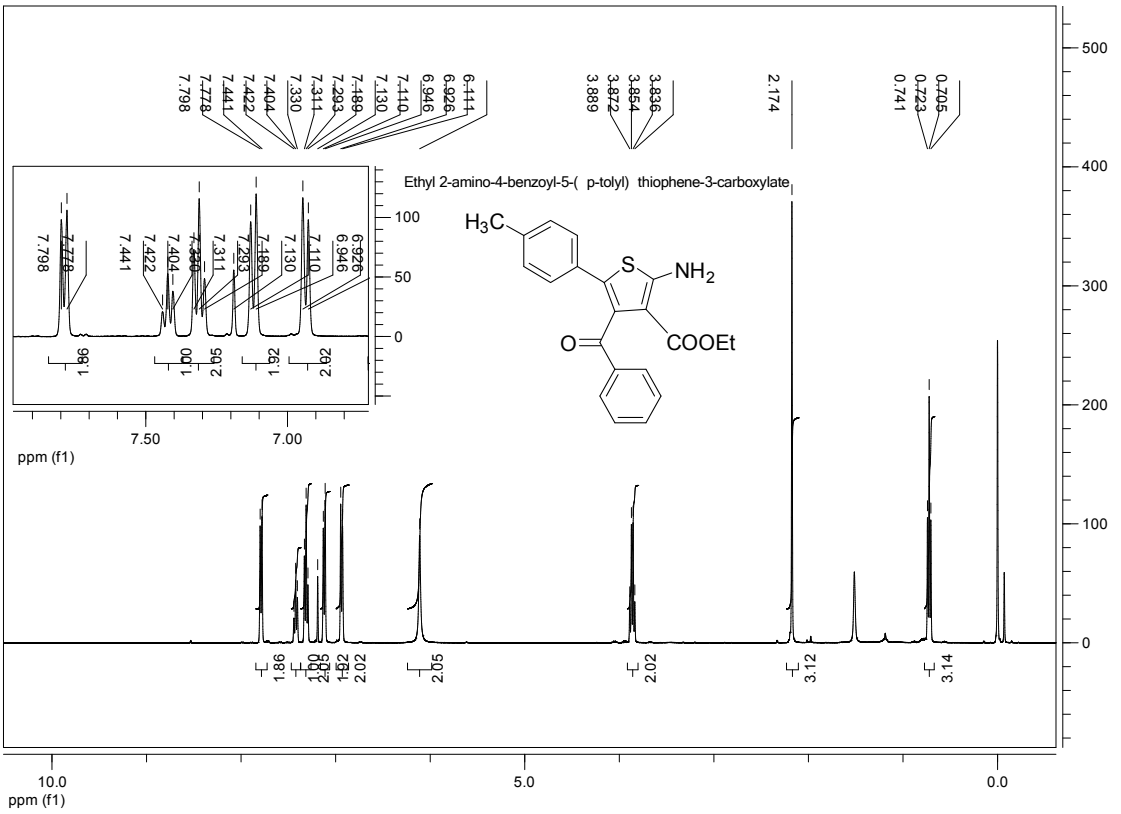
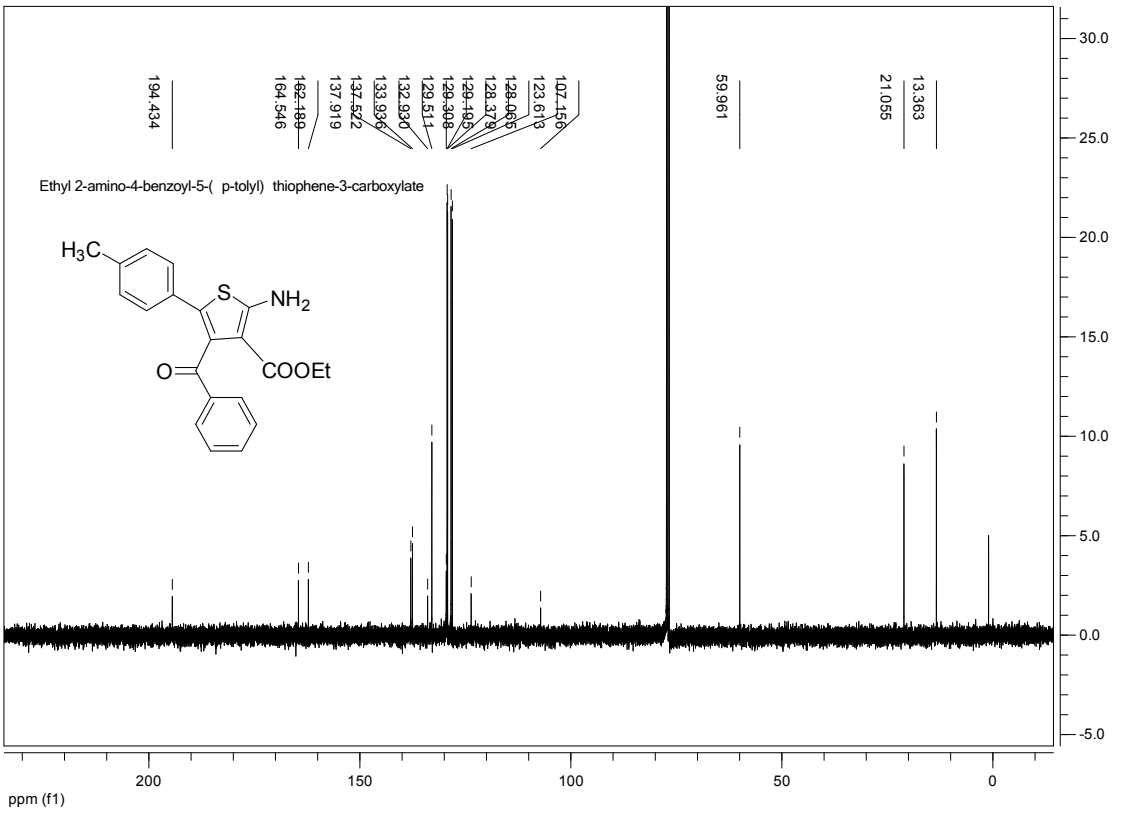




Ethyl 2-amino-4-benzoyl-5-(p-tolyl)thiophene-3-carboxylate (3s)





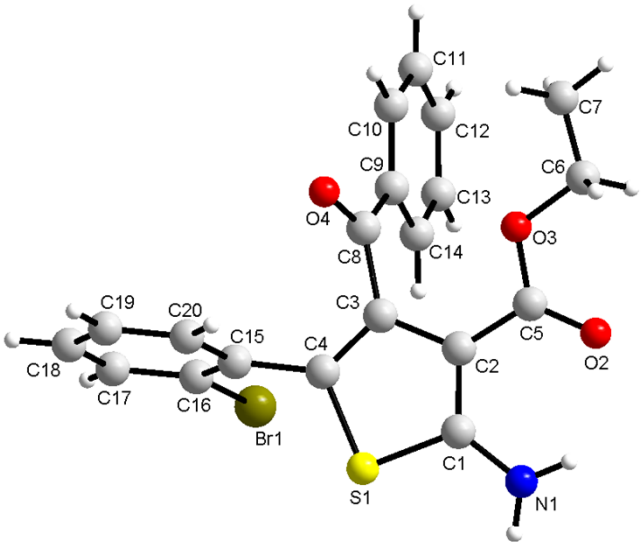


Figure **S1** Structure of 2-aminothiophene-3-carboxylate **3c**

Table S1. Crystal data and structure refinement for **3c**.

Identification code	**3c**
Empirical formula	C20 H16 Br N O3 S
Formula weight	430.30
Temperature	296 K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 31.62(6) A alpha = 90 deg. b = 8.854(17) A beta = 99.52(4) deg. c = 13.34(3) A gamma = 90 deg.
Volume	3682(12) A^3
Z, Calculated density	8, 1.552 Mg/m^3
Absorption coefficient	2.365 mm^-1

F(000)	1744
Crystal size	0.35 x 0.33 x 0.3 mm
Theta range for data collection	1.31 to 25.00 deg.
Limiting indices	-35<=h<=37, -10<=k<=10, -15<=l<=15
Reflections collected / unique	18452 / 3245 [R(int) = 0.0399]
Completeness to theta = 25.00	99.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3240 / 3 / 236
Goodness-of-fit on F^2	1.064
Final R indices [I>2sigma(I)]	R1 = 0.0447, wR2 = 0.1250
R indices (all data)	R1 = 0.0670, wR2 = 0.1489
Largest diff. peak and hole	0.440 and -0.857 e.A^-3

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **3c**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	7286(1)	3010(1)	7490(1)	89(1)
C(1)	5954(1)	555(4)	7247(3)	53(1)
N(1)	5701(1)	164(4)	7906(3)	73(1)
S(1)	6483(1)	84(1)	7438(1)	53(1)
C(2)	5842(1)	1334(4)	6369(3)	50(1)
O(2)	5111(1)	1484(5)	6427(3)	99(1)
C(3)	6198(1)	1545(4)	5859(3)	41(1)
O(3)	5352(1)	2229(4)	5078(3)	78(1)
C(4)	6560(1)	940(4)	6331(2)	43(1)
O(4)	6219(1)	1912(4)	4159(2)	74(1)
C(5)	5406(1)	1686(5)	5984(4)	66(1)
C(6)	4921(2)	2550(9)	4612(6)	114(2)
C(7)	4930(3)	3304(14)	3735(7)	185(5)
C(8)	6186(1)	2476(5)	4947(3)	48(1)
C(9)	6157(1)	4090(5)	5030(3)	58(1)
C(10)	6067(2)	4966(6)	4196(5)	87(2)
C(11)	6059(2)	6508(9)	4299(8)	123(3)
C(12)	6146(2)	7149(8)	5207(12)	140(4)
C(13)	6237(2)	6316(7)	6026(7)	107(2)
C(14)	6244(1)	4802(5)	5987(4)	72(1)
C(15)	6980(1)	855(4)	6019(3)	43(1)
C(16)	7329(1)	1643(4)	6465(3)	55(1)
C(17)	7722(1)	1478(6)	6158(4)	74(1)
C(18)	7758(1)	530(6)	5397(4)	78(1)
C(19)	7419(2)	-247(5)	4930(4)	73(1)
C(20)	7033(1)	-105(5)	5229(3)	56(1)

Table S3. Bond lengths [A] and angles [deg] for **3c**.

Br(1)-C(16)	1.847(5)
C(1)-N(1)	1.330(5)
C(1)-C(2)	1.355(6)
C(1)-S(1)	1.701(5)
N(1)-H(1A)	0.8600
N(1)-H(1B)	0.8600
S(1)-C(4)	1.712(4)
C(2)-C(3)	1.417(5)
C(2)-C(5)	1.426(6)
O(2)-C(5)	1.197(5)
C(3)-C(4)	1.325(5)
C(3)-C(8)	1.465(6)
O(3)-C(5)	1.286(6)
O(3)-C(6)	1.430(6)
C(4)-C(15)	1.460(5)
O(4)-C(8)	1.183(5)
C(6)-C(7)	1.350(10)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
C(8)-C(9)	1.438(6)
C(9)-C(10)	1.346(7)
C(9)-C(14)	1.410(6)
C(10)-C(11)	1.373(10)
C(10)-H(10)	0.9300
C(11)-C(12)	1.325(13)
C(11)-H(11)	0.9300
C(12)-C(13)	1.310(13)
C(12)-H(12)	0.9300
C(13)-C(14)	1.342(8)
C(13)-H(13)	0.9300
C(14)-H(14)	0.9300
C(15)-C(16)	1.356(5)
C(15)-C(20)	1.386(6)
C(16)-C(17)	1.378(7)
C(17)-C(18)	1.337(8)
C(17)-H(17)	0.9300

C(18)-C(19)	1.339(7)
C(18)-H(18)	0.9300
C(19)-C(20)	1.349(6)
C(19)-H(19)	0.9300
C(20)-H(20)	0.9300

N(1)-C(1)-C(2)	127.2(4)
N(1)-C(1)-S(1)	121.5(3)
C(2)-C(1)-S(1)	111.4(3)
C(1)-N(1)-H(1A)	120.0
C(1)-N(1)-H(1B)	120.0
H(1A)-N(1)-H(1B)	120.0
C(1)-S(1)-C(4)	92.14(19)
C(1)-C(2)-C(3)	111.5(3)
C(1)-C(2)-C(5)	121.4(3)
C(3)-C(2)-C(5)	126.6(4)
C(4)-C(3)-C(2)	114.2(3)
C(4)-C(3)-C(8)	121.5(3)
C(2)-C(3)-C(8)	124.0(3)
C(5)-O(3)-C(6)	116.7(4)
C(3)-C(4)-C(15)	130.0(3)
C(3)-C(4)-S(1)	110.7(3)
C(15)-C(4)-S(1)	119.2(3)
O(2)-C(5)-O(3)	121.9(4)
O(2)-C(5)-C(2)	125.3(5)
O(3)-C(5)-C(2)	112.8(3)
C(7)-C(6)-O(3)	108.7(6)
C(7)-C(6)-H(6A)	110.0
O(3)-C(6)-H(6A)	110.0
C(7)-C(6)-H(6B)	110.0
O(3)-C(6)-H(6B)	110.0
H(6A)-C(6)-H(6B)	108.3
C(6)-C(7)-H(7A)	109.5
C(6)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(6)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
O(4)-C(8)-C(9)	120.2(4)
O(4)-C(8)-C(3)	120.5(4)
C(9)-C(8)-C(3)	119.2(3)
C(10)-C(9)-C(14)	118.2(5)
C(10)-C(9)-C(8)	121.1(5)

C(14)-C(9)-C(8)	120.6(4)
C(9)-C(10)-C(11)	119.7(7)
C(9)-C(10)-H(10)	120.1
C(11)-C(10)-H(10)	120.1
C(12)-C(11)-C(10)	120.8(8)
C(12)-C(11)-H(11)	119.6
C(10)-C(11)-H(11)	119.6
C(13)-C(12)-C(11)	120.3(7)
C(13)-C(12)-H(12)	119.8
C(11)-C(12)-H(12)	119.8
C(12)-C(13)-C(14)	122.3(8)
C(12)-C(13)-H(13)	118.9
C(14)-C(13)-H(13)	118.9
C(13)-C(14)-C(9)	118.6(6)
C(13)-C(14)-H(14)	120.7
C(9)-C(14)-H(14)	120.7
C(16)-C(15)-C(20)	117.2(3)
C(16)-C(15)-C(4)	124.2(3)
C(20)-C(15)-C(4)	118.6(3)
C(15)-C(16)-C(17)	121.5(4)
C(15)-C(16)-Br(1)	120.5(3)
C(17)-C(16)-Br(1)	118.0(3)
C(18)-C(17)-C(16)	119.1(4)
C(18)-C(17)-H(17)	120.4
C(16)-C(17)-H(17)	120.4
C(17)-C(18)-C(19)	120.8(4)
C(17)-C(18)-H(18)	119.6
C(19)-C(18)-H(18)	119.6
C(18)-C(19)-C(20)	120.6(5)
C(18)-C(19)-H(19)	119.7
C(20)-C(19)-H(19)	119.7
C(19)-C(20)-C(15)	120.7(4)
C(19)-C(20)-H(20)	119.7
C(15)-C(20)-H(20)	119.7

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for **3c**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	96(1)	83(1)	81(1)	-21(1)	2(1)	-30(1)
C(1)	57(2)	53(2)	57(2)	-4(2)	30(2)	-3(2)
N(1)	69(2)	84(2)	80(2)	14(2)	47(2)	2(2)
S(1)	54(1)	58(1)	52(1)	7(1)	22(1)	1(1)
C(2)	39(2)	52(2)	62(2)	-3(2)	23(2)	-3(2)
O(2)	53(2)	138(3)	118(3)	23(2)	49(2)	6(2)
C(3)	38(2)	41(2)	47(2)	-6(2)	15(2)	-5(2)
O(3)	35(1)	114(3)	86(2)	24(2)	11(1)	3(2)
C(4)	42(2)	43(2)	45(2)	-3(1)	16(2)	-5(2)
O(4)	85(2)	94(2)	47(2)	-5(2)	21(2)	15(2)
C(5)	46(2)	69(3)	90(3)	5(2)	27(2)	-1(2)
C(6)	38(2)	153(5)	144(6)	23(5)	-3(3)	10(3)
C(7)	86(5)	331(15)	130(7)	72(8)	-9(5)	32(6)
C(8)	33(2)	62(2)	52(2)	4(2)	14(2)	0(2)
C(9)	32(2)	60(2)	85(3)	19(2)	23(2)	4(2)
C(10)	61(3)	91(4)	113(4)	41(3)	29(3)	15(3)
C(11)	78(4)	88(5)	213(9)	86(6)	50(5)	19(4)
C(12)	66(4)	59(4)	303(14)	22(6)	55(6)	-2(3)
C(13)	75(4)	54(3)	194(7)	-15(4)	27(4)	-9(3)
C(14)	55(2)	54(3)	110(4)	-5(2)	19(2)	-4(2)
C(15)	37(2)	47(2)	47(2)	6(2)	12(1)	-1(2)
C(16)	44(2)	58(2)	62(2)	11(2)	4(2)	-10(2)
C(17)	39(2)	86(3)	94(4)	29(3)	3(2)	-15(2)
C(18)	41(2)	98(4)	101(4)	23(3)	29(2)	6(3)
C(19)	67(3)	82(3)	79(3)	3(3)	39(2)	10(2)
C(20)	41(2)	68(2)	62(2)	7(2)	21(2)	-1(2)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **3c**.

	x	y	z	U(eq)
H(1A)	5434	408	7794	88
H(1B)	5804	-334	8445	88
H(6A)	4762	1616	4474	136
H(6B)	4781	3158	5065	136
H(7A)	5081	4240	3880	278
H(7B)	4641	3507	3407	278
H(7C)	5073	2701	3295	278
H(10)	6011	4528	3554	104
H(11)	5991	7110	3723	148
H(12)	6142	8196	5264	168
H(13)	6300	6790	6655	128
H(14)	6305	4233	6580	87
H(17)	7959	2019	6477	89
H(18)	8023	408	5189	94
H(19)	7449	-890	4395	88
H(20)	6801	-657	4900	67

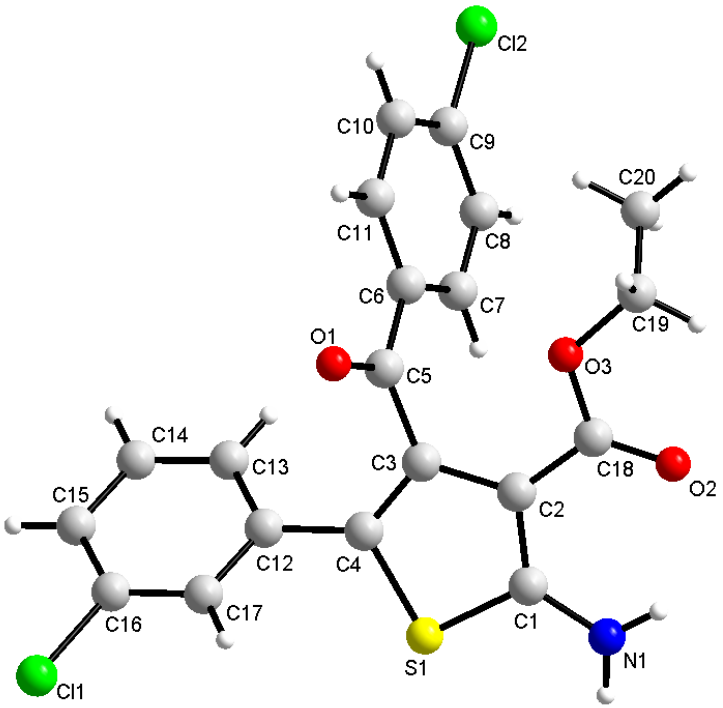


Figure **S2** Structure of 2-aminothiophene-3-carboxylate **3i**

Table S6. Crystal data and structure refinement for **3i**.

Identification code	**3i**
Empirical formula	C20 H15 Cl2 N O3 S
Formula weight	420.29
Temperature	296 K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.1715(6) A alpha = 74.718(2) deg. b = 9.5381(7) A beta = 78.453(2) deg. c = 13.8371(10) A gamma = 70.740(2) deg.
Volume	974.49(12) A^3

Z, Calculated density	2, 1.432 Mg/m^3
Absorption coefficient	0.461 mm^-1
F(000)	432
Crystal size	0.35 x 0.33 x 0.3 mm
Theta range for data collection	1.54 to 25.00 deg.
Limiting indices	-9<=h<=9, -11<=k<=11, -16<=l<=15
Reflections collected / unique	12313 / 3447 [R(int) = 0.0469]
Completeness to theta = 25.00	99.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3414 / 438 / 245
Goodness-of-fit on F^2	1.062
Final R indices [I>2sigma(I)]	R1 = 0.0466, wR2 = 0.1309
R indices (all data)	R1 = 0.0534, wR2 = 0.1437
Largest diff. peak and hole	0.543 and -0.383 e.A^-3

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **3i**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	3958(1)	6991(1)	10864(1)	36(1)
Cl(2)	7940(1)	12883(1)	5233(1)	74(1)
Cl(1)	9135(2)	5679(1)	13400(1)	93(1)
O(1)	9094(2)	6393(2)	8727(1)	46(1)
C(5)	7765(3)	7449(3)	8571(2)	33(1)
C(6)	7793(3)	8822(3)	7763(2)	34(1)
O(2)	3224(3)	6753(2)	7738(2)	52(1)
C(18)	4509(3)	6902(3)	7963(2)	38(1)
C(3)	6103(3)	7344(3)	9246(2)	31(1)
C(12)	7066(3)	7619(3)	10825(2)	31(1)
C(2)	4653(3)	7073(3)	8952(2)	32(1)
N(1)	1888(3)	6541(3)	9769(2)	44(1)
C(13)	7650(3)	8911(3)	10494(2)	38(1)
O(3)	5979(3)	6873(3)	7326(2)	63(1)
C(17)	7539(3)	6625(3)	11726(2)	39(1)
C(1)	3401(3)	6831(3)	9766(2)	34(1)
C(11)	9324(3)	8853(3)	7112(2)	42(1)
C(7)	6316(3)	10069(3)	7631(2)	42(1)
C(14)	8669(4)	9196(3)	11061(2)	45(1)
C(9)	7889(4)	11324(3)	6220(2)	46(1)
C(10)	9372(4)	10107(3)	6340(2)	48(1)
C(4)	5918(3)	7340(3)	10244(2)	33(1)
C(8)	6359(4)	11325(3)	6857(2)	49(1)
C(16)	8564(4)	6939(3)	12273(2)	46(1)
C(15)	9141(4)	8209(3)	11955(2)	50(1)
C(19)	5974(6)	6735(6)	6305(3)	85(1)
C(20)	6322(14)	7924(9)	5598(4)	169(3)

Table S8. Bond lengths [A] and angles [deg] for **3i**.

S(1)-C(1)	1.727(3)
S(1)-C(4)	1.750(2)
Cl(2)-C(9)	1.739(3)
Cl(1)-C(16)	1.740(3)
O(1)-C(5)	1.224(3)
C(5)-C(6)	1.484(3)
C(5)-C(3)	1.502(3)
C(6)-C(7)	1.390(4)
C(6)-C(11)	1.392(3)
O(2)-C(18)	1.213(3)
C(18)-O(3)	1.337(3)
C(18)-C(2)	1.452(3)
C(3)-C(4)	1.358(3)
C(3)-C(2)	1.444(3)
C(12)-C(17)	1.390(3)
C(12)-C(13)	1.399(3)
C(12)-C(4)	1.475(3)
C(2)-C(1)	1.388(3)
N(1)-C(1)	1.352(3)
C(13)-C(14)	1.381(4)
O(3)-C(19)	1.454(4)
C(17)-C(16)	1.379(4)
C(11)-C(10)	1.383(4)
C(7)-C(8)	1.385(4)
C(14)-C(15)	1.379(4)
C(9)-C(10)	1.376(4)
C(9)-C(8)	1.379(4)
C(16)-C(15)	1.377(4)
C(19)-C(20)	1.357(7)
C(1)-S(1)-C(4)	92.18(11)
O(1)-C(5)-C(6)	121.3(2)
O(1)-C(5)-C(3)	118.2(2)
C(6)-C(5)-C(3)	120.5(2)
C(7)-C(6)-C(11)	119.1(2)
C(7)-C(6)-C(5)	121.5(2)
C(11)-C(6)-C(5)	119.3(2)
O(2)-C(18)-O(3)	123.0(2)
O(2)-C(18)-C(2)	124.3(2)

O(3)-C(18)-C(2)	112.6(2)
C(4)-C(3)-C(2)	113.3(2)
C(4)-C(3)-C(5)	121.3(2)
C(2)-C(3)-C(5)	125.1(2)
C(17)-C(12)-C(13)	119.0(2)
C(17)-C(12)-C(4)	120.4(2)
C(13)-C(12)-C(4)	120.6(2)
C(1)-C(2)-C(3)	112.1(2)
C(1)-C(2)-C(18)	120.8(2)
C(3)-C(2)-C(18)	126.8(2)
C(14)-C(13)-C(12)	120.3(2)
C(18)-O(3)-C(19)	117.4(2)
C(16)-C(17)-C(12)	119.3(2)
N(1)-C(1)-C(2)	128.1(2)
N(1)-C(1)-S(1)	120.6(2)
C(2)-C(1)-S(1)	111.25(17)
C(10)-C(11)-C(6)	120.4(2)
C(8)-C(7)-C(6)	120.6(2)
C(15)-C(14)-C(13)	120.7(3)
C(10)-C(9)-C(8)	121.4(3)
C(10)-C(9)-Cl(2)	119.3(2)
C(8)-C(9)-Cl(2)	119.3(2)
C(9)-C(10)-C(11)	119.4(2)
C(3)-C(4)-C(12)	129.9(2)
C(3)-C(4)-S(1)	111.10(17)
C(12)-C(4)-S(1)	119.00(17)
C(9)-C(8)-C(7)	119.1(3)
C(15)-C(16)-C(17)	122.1(3)
C(15)-C(16)-Cl(1)	119.5(2)
C(17)-C(16)-Cl(1)	118.4(2)
C(16)-C(15)-C(14)	118.5(3)
C(20)-C(19)-O(3)	112.3(4)

Symmetry transformations used to generate equivalent atoms:

Table S9. Anisotropic displacement parameters (A^2 x 10^3) for **3i**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S(1)	32(1)	37(1)	38(1)	-5(1)	-1(1)	-12(1)
Cl(2)	100(1)	61(1)	52(1)	9(1)	-3(1)	-33(1)
Cl(1)	132(1)	96(1)	60(1)	16(1)	-57(1)	-43(1)
O(1)	29(1)	49(1)	50(1)	-4(1)	-6(1)	-3(1)
C(5)	29(1)	39(1)	35(1)	-11(1)	-6(1)	-10(1)
C(6)	33(1)	39(1)	31(1)	-10(1)	-5(1)	-12(1)
O(2)	45(1)	64(1)	58(1)	-11(1)	-21(1)	-22(1)
C(18)	37(1)	36(1)	44(1)	-7(1)	-11(1)	-12(1)
C(3)	27(1)	28(1)	36(1)	-4(1)	-7(1)	-7(1)
C(12)	28(1)	30(1)	35(1)	-11(1)	-2(1)	-6(1)
C(2)	29(1)	28(1)	39(1)	-5(1)	-9(1)	-7(1)
N(1)	32(1)	50(1)	54(1)	-8(1)	-6(1)	-18(1)
C(13)	38(1)	34(1)	40(1)	-5(1)	-4(1)	-11(1)
O(3)	56(1)	109(2)	46(1)	-36(1)	3(1)	-44(1)
C(17)	45(1)	34(1)	39(1)	-6(1)	-7(1)	-14(1)
C(1)	28(1)	25(1)	45(1)	-5(1)	-8(1)	-5(1)
C(11)	33(1)	54(2)	38(1)	-9(1)	-4(1)	-13(1)
C(7)	40(1)	43(1)	39(1)	-10(1)	3(1)	-10(1)
C(14)	45(1)	42(1)	55(2)	-16(1)	-1(1)	-20(1)
C(9)	61(2)	47(1)	33(1)	-6(1)	-5(1)	-22(1)
C(10)	45(1)	64(2)	36(1)	-8(1)	2(1)	-23(1)
C(4)	29(1)	30(1)	37(1)	-5(1)	-5(1)	-8(1)
C(8)	52(2)	42(1)	45(1)	-7(1)	-3(1)	-5(1)
C(16)	51(2)	50(2)	38(1)	-8(1)	-15(1)	-12(1)
C(15)	50(2)	57(2)	52(2)	-21(1)	-12(1)	-18(1)
C(19)	93(3)	131(3)	54(2)	-42(2)	-1(2)	-51(2)
C(20)	314(9)	164(6)	57(3)	-9(3)	-41(4)	-107(6)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **3i**.

	x	y	z	U(eq)
H(1A)	1606	6489	9216	53
H(1B)	1207	6409	10324	53
H(13)	7350	9581	9890	45
H(17)	7169	5758	11958	46
H(11)	10321	8026	7196	50
H(7)	5290	10060	8066	51
H(14)	9042	10062	10838	54
H(10)	10396	10127	5907	58
H(8)	5368	12158	6770	59
H(15)	9834	8397	12335	59
H(19A)	6841	5800	6182	101
H(19B)	4840	6673	6242	101
H(20A)	7453	7979	5650	254
H(20B)	5452	8850	5707	254
H(20C)	6308	7785	4938	254

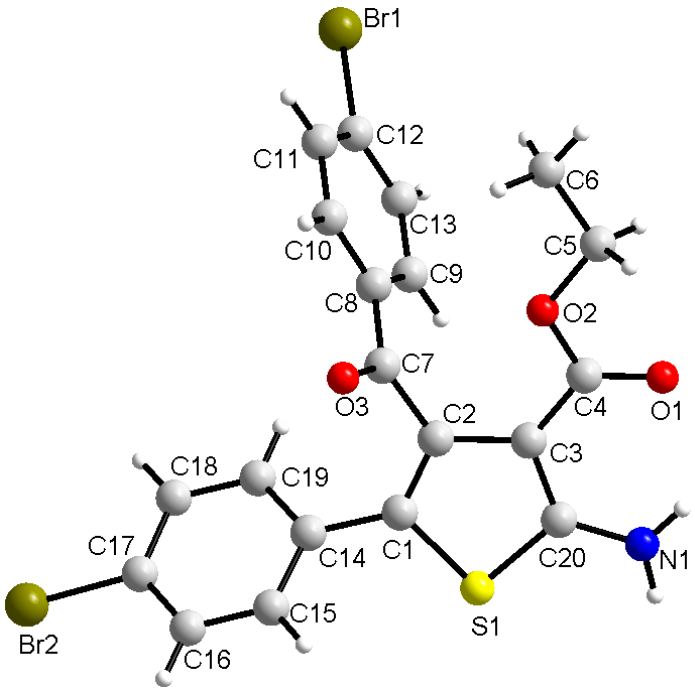


Figure **S2** Structure of 2-aminothiophene-3-carboxylate **3k**

Table S11. Crystal data and structure refinement for **3k**.

Identification code	**3k**
Empirical formula	C20 H15 Br2 N O3 S
Formula weight	509.19
Temperature	296 K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.24(4) A alpha = 103.86(16) deg. b = 10.18(6) A beta = 92.63(11) deg. c = 13.48(7) A gamma = 113.20(12) deg.
Volume	997(9) A^3
Z, Calculated density	2, 1.696 Mg/m^3
Absorption coefficient	4.190 mm^-1
F(000)	504
Crystal size	0.35 x 0.33 x 0.3 mm
Theta range for data collection	1.58 to 25.00 deg.
Limiting indices	-9<=h<=9, -11<=k<=12, -16<=l<=16
Reflections collected / unique	13106 / 3503 [R(int) = 0.0727]
Completeness to theta = 25.00	99.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3494 / 440 / 245
Goodness-of-fit on F^2	1.021

Final R indices [I>2sigma(I)]	R1 = 0.0725, wR2 = 0.2067
R indices (all data)	R1 = 0.1165, wR2 = 0.2440
Largest diff. peak and hole	0.991 and -1.046 e.A^-3

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **3k**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	6005(2)	8444(2)	-213(1)	104(1)
Br(2)	10624(1)	10779(1)	7462(1)	87(1)
C(1)	3002(9)	7324(7)	5085(5)	45(1)
C(2)	2376(8)	6489(7)	4096(5)	44(1)
C(3)	473(9)	6005(8)	3802(6)	46(1)
C(4)	-594(10)	5022(8)	2843(6)	52(1)
C(5)	-767(12)	3412(10)	1236(7)	83(2)
C(6)	373(16)	2994(15)	537(10)	135(4)
C(7)	3532(9)	5994(7)	3413(5)	46(1)
C(8)	4100(9)	6583(7)	2542(5)	46(1)
C(9)	3691(9)	7719(8)	2344(6)	50(1)
C(10)	5058(9)	6025(8)	1888(6)	48(1)
C(11)	5620(9)	6581(8)	1075(6)	51(1)
C(12)	5201(10)	7672(8)	904(6)	53(1)
C(13)	4262(10)	8248(8)	1533(6)	54(1)
C(14)	4858(9)	8081(7)	5640(5)	45(1)
C(15)	5297(9)	7970(8)	6611(6)	50(1)
C(16)	7004(9)	8733(8)	7139(6)	53(1)
C(17)	8301(9)	9618(8)	6705(6)	51(1)
C(18)	7924(9)	9733(7)	5730(6)	51(1)
C(19)	6211(9)	8964(7)	5207(6)	48(1)
C(20)	-267(9)	6493(7)	4630(5)	44(1)
N(1)	-2002(7)	6232(7)	4634(5)	55(2)
O(1)	-2175(6)	4691(6)	2602(4)	64(1)
O(2)	299(7)	4452(6)	2212(5)	77(2)
O(3)	4057(7)	5129(6)	3650(4)	60(1)
S(1)	1306(2)	7545(2)	5712(1)	49(1)

Table S13. Bond lengths [A] and angles [deg] for **3k**.

Br(1)-C(12)	1.891(11)
Br(2)-C(17)	1.887(11)
C(1)-C(2)	1.347(12)
C(1)-C(14)	1.478(12)
C(1)-S(1)	1.727(10)
C(2)-C(3)	1.449(12)
C(2)-C(7)	1.498(10)
C(3)-C(20)	1.379(11)
C(3)-C(4)	1.424(12)
C(4)-O(1)	1.215(11)
C(4)-O(2)	1.327(10)
C(5)-O(2)	1.454(12)
C(5)-C(6)	1.468(10)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(6)-H(6A)	0.9600
C(6)-H(6B)	0.9600
C(6)-H(6C)	0.9600
C(7)-O(3)	1.220(9)
C(7)-C(8)	1.458(11)
C(8)-C(10)	1.379(10)
C(8)-C(9)	1.404(11)
C(9)-C(13)	1.355(12)
C(9)-H(9)	0.9300
C(10)-C(11)	1.369(12)
C(10)-H(10)	0.9300
C(11)-C(12)	1.350(12)
C(11)-H(11)	0.9300
C(12)-C(13)	1.357(11)
C(13)-H(13)	0.9300
C(14)-C(19)	1.384(11)
C(14)-C(15)	1.384(12)
C(15)-C(16)	1.367(12)
C(15)-H(15)	0.9300
C(16)-C(17)	1.359(11)
C(16)-H(16)	0.9300
C(17)-C(18)	1.380(12)
C(18)-C(19)	1.369(12)
C(18)-H(18)	0.9300

C(19)-H(19)	0.9300
C(20)-N(1)	1.347(11)
C(20)-S(1)	1.715(10)
N(1)-H(1A)	0.8600
N(1)-H(1B)	0.8600

C(2)-C(1)-C(14)	129.4(6)
C(2)-C(1)-S(1)	111.2(6)
C(14)-C(1)-S(1)	119.3(6)
C(1)-C(2)-C(3)	113.8(6)
C(1)-C(2)-C(7)	122.0(7)
C(3)-C(2)-C(7)	123.9(7)
C(20)-C(3)-C(4)	122.1(7)
C(20)-C(3)-C(2)	110.6(7)
C(4)-C(3)-C(2)	126.9(7)
O(1)-C(4)-O(2)	121.4(8)
O(1)-C(4)-C(3)	125.3(7)
O(2)-C(4)-C(3)	113.3(7)
O(2)-C(5)-C(6)	110.7(9)
O(2)-C(5)-H(5A)	109.5
C(6)-C(5)-H(5A)	109.5
O(2)-C(5)-H(5B)	109.5
C(6)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	108.1
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
O(3)-C(7)-C(8)	121.0(6)
O(3)-C(7)-C(2)	116.9(7)
C(8)-C(7)-C(2)	121.9(6)
C(10)-C(8)-C(9)	118.3(7)
C(10)-C(8)-C(7)	120.3(7)
C(9)-C(8)-C(7)	121.4(6)
C(13)-C(9)-C(8)	119.6(7)
C(13)-C(9)-H(9)	120.2
C(8)-C(9)-H(9)	120.2
C(11)-C(10)-C(8)	120.9(7)
C(11)-C(10)-H(10)	119.6
C(8)-C(10)-H(10)	119.6
C(12)-C(11)-C(10)	119.4(7)

C(12)-C(11)-H(11)	120.3
C(10)-C(11)-H(11)	120.3
C(11)-C(12)-C(13)	121.3(7)
C(11)-C(12)-Br(1)	119.0(6)
C(13)-C(12)-Br(1)	119.7(6)
C(9)-C(13)-C(12)	120.5(8)
C(9)-C(13)-H(13)	119.7
C(12)-C(13)-H(13)	119.7
C(19)-C(14)-C(15)	117.9(7)
C(19)-C(14)-C(1)	120.2(7)
C(15)-C(14)-C(1)	121.8(6)
C(16)-C(15)-C(14)	121.3(7)
C(16)-C(15)-H(15)	119.4
C(14)-C(15)-H(15)	119.4
C(17)-C(16)-C(15)	119.6(8)
C(17)-C(16)-H(16)	120.2
C(15)-C(16)-H(16)	120.2
C(16)-C(17)-C(18)	120.8(7)
C(16)-C(17)-Br(2)	120.0(7)
C(18)-C(17)-Br(2)	119.2(6)
C(19)-C(18)-C(17)	119.2(7)
C(19)-C(18)-H(18)	120.4
C(17)-C(18)-H(18)	120.4
C(18)-C(19)-C(14)	121.2(8)
C(18)-C(19)-H(19)	119.4
C(14)-C(19)-H(19)	119.4
N(1)-C(20)-C(3)	126.5(7)
N(1)-C(20)-S(1)	121.4(6)
C(3)-C(20)-S(1)	112.1(6)
C(20)-N(1)-H(1A)	120.0
C(20)-N(1)-H(1B)	120.0
H(1A)-N(1)-H(1B)	120.0
C(4)-O(2)-C(5)	114.7(7)
C(20)-S(1)-C(1)	92.2(5)

Symmetry transformations used to generate equivalent atoms:

Table S14. Anisotropic displacement parameters (A^2 x 10^3) for **3k**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	125(1)	148(1)	76(1)	64(1)	51(1)	71(1)
Br(2)	52(1)	92(1)	83(1)	-9(1)	-14(1)	18(1)
C(1)	44(2)	50(2)	48(2)	16(2)	12(2)	23(1)
C(2)	42(2)	49(2)	48(2)	17(2)	12(2)	25(1)
C(3)	43(2)	52(2)	49(2)	15(2)	12(2)	25(2)
C(4)	47(2)	57(2)	53(2)	14(2)	12(2)	23(2)
C(5)	65(3)	85(3)	68(3)	-3(3)	7(3)	14(3)
C(6)	101(6)	140(6)	103(6)	-14(6)	4(5)	17(5)
C(7)	42(2)	51(2)	49(2)	15(2)	11(2)	24(1)
C(8)	42(2)	52(2)	48(2)	14(2)	12(2)	25(1)
C(9)	47(2)	55(2)	50(2)	14(2)	12(2)	25(2)
C(10)	43(2)	54(2)	50(2)	11(2)	11(2)	25(2)
C(11)	44(2)	57(2)	50(2)	10(2)	13(2)	21(2)
C(12)	49(2)	60(2)	48(2)	13(2)	12(2)	20(2)
C(13)	52(2)	60(2)	53(2)	15(2)	10(2)	24(2)
C(14)	44(2)	48(2)	49(2)	14(2)	11(2)	23(2)
C(15)	48(2)	52(2)	51(2)	16(2)	9(2)	20(2)
C(16)	50(2)	55(2)	50(2)	14(2)	5(2)	20(2)
C(17)	47(2)	53(2)	53(2)	9(2)	7(2)	23(2)
C(18)	47(2)	52(2)	52(2)	12(2)	11(2)	20(2)
C(19)	46(2)	51(2)	49(2)	16(2)	10(2)	22(2)
C(20)	42(2)	50(2)	49(2)	18(2)	13(2)	26(2)
N(1)	40(3)	64(4)	68(4)	20(3)	20(3)	27(3)
O(1)	37(3)	82(4)	70(4)	19(3)	1(2)	24(2)
O(2)	43(3)	91(4)	65(4)	-14(3)	6(3)	18(3)
O(3)	70(3)	80(3)	62(4)	33(3)	32(3)	52(3)
S(1)	50(1)	53(1)	51(1)	17(1)	19(1)	27(1)

Table S15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **3k**.

	x	y	z	U(eq)
H(5A)	-1398	3866	912	100
H(5B)	-1647	2527	1366	100
H(6A)	1042	3814	276	203
H(6B)	-361	2149	-29	203
H(6C)	1183	2745	908	203
H(9)	3032	8107	2766	60
H(10)	5326	5261	2000	58
H(11)	6285	6211	645	62
H(13)	4008	9011	1407	65
H(15)	4413	7364	6910	60
H(16)	7275	8647	7791	63
H(18)	8822	10326	5432	61
H(19)	5953	9037	4549	57
H(1A)	-2768	5714	4080	66
H(1B)	-2343	6583	5190	66