Mild One-Pot Horner-Wadsworth-Emmons Olefination and Intramolecular *N*-arylation for the Syntheses of Indoles, All Regio-isomeric Azaindoles, and Thienopyrroles

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SUPPORTING INFORMATION

Contents:

General Information.

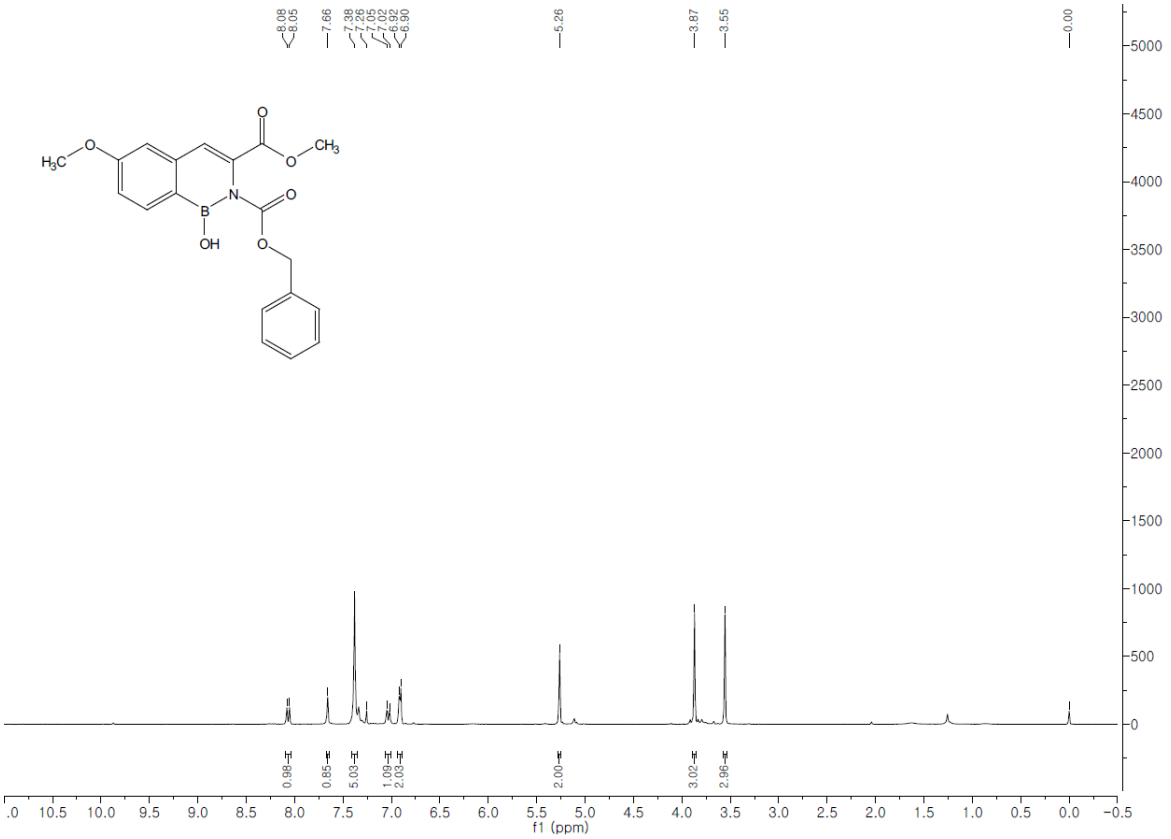
All experiments were performed under an anhydrous atmosphere of nitrogen in oven-dried glassware except as indicated. All solvents were purified using column filter solvent purification system before use unless otherwise indicated. Pyridine was distilled from potassium hydroxide. Reagents were purchased and used without further purification.

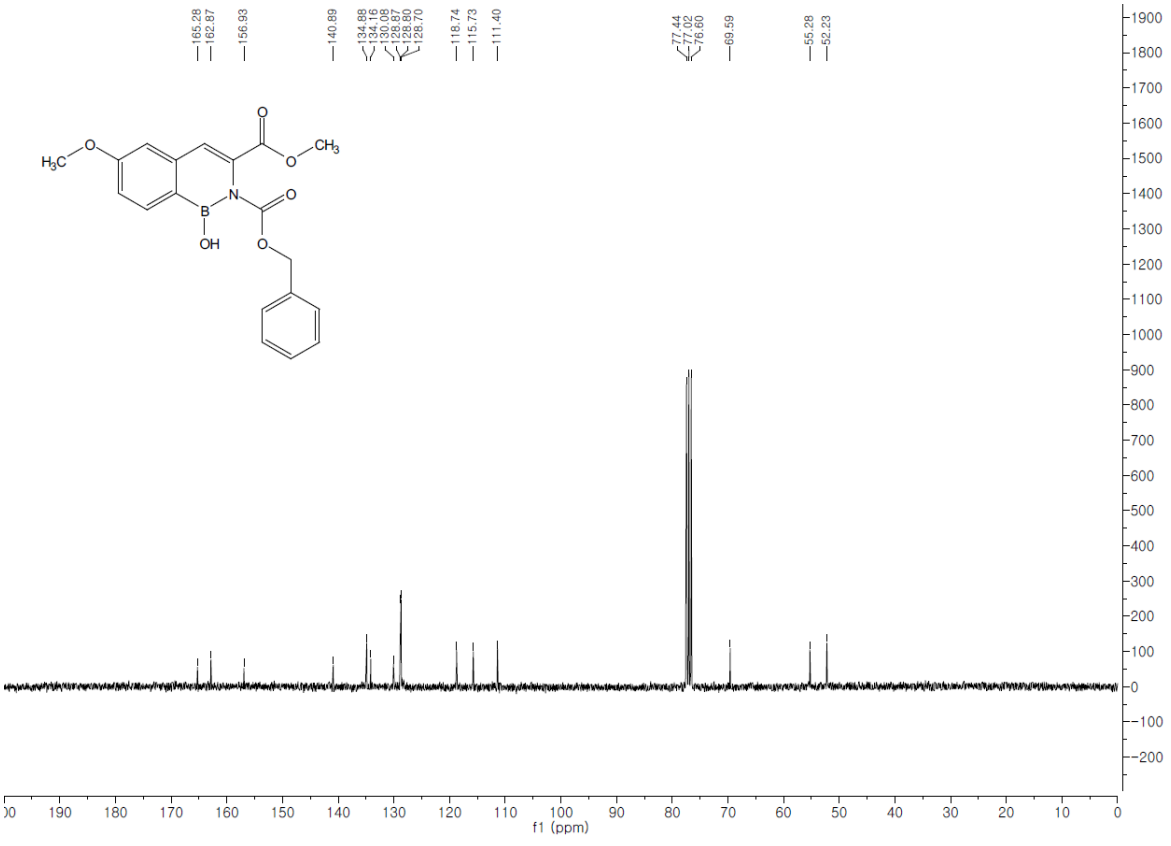
Analytical thin layer chromatography (TLC) was performed on Kieselgel 60 F_{254} glass plates precoated with a 0.2 mm thickness of silica gel. The TLC plates were visualized by shortwave (254 nm), potassium permanganate or ceric ammonium molybdate stain. Flash chromatography on Kieselgel 60 (230−400 mesh) silica gel was performed.

Melting points were determined on a capillary melting point apparatus and are uncorrected. ^{1}H NMR and spectra were obtained at 300 MHz or 500 MHz using $CDCl_3$, DMSO-d_6, or acetone-d_6 as solvent. ^{1}H NMR assignment abbreviations are the following; singlet (s), doublet (d), triplet (t), quartet (q), broad singlet (bs), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). ^{13}C NMR spectra were measured at 75.5 MHz or 125 MHz using $CDCl_3$, DMSO-d_6, or acetone-d_6 as an internal reference. High-resolution mass spectra (HRMS) were recorded with an electron ionization (EI) using a sector field mass analyzer.

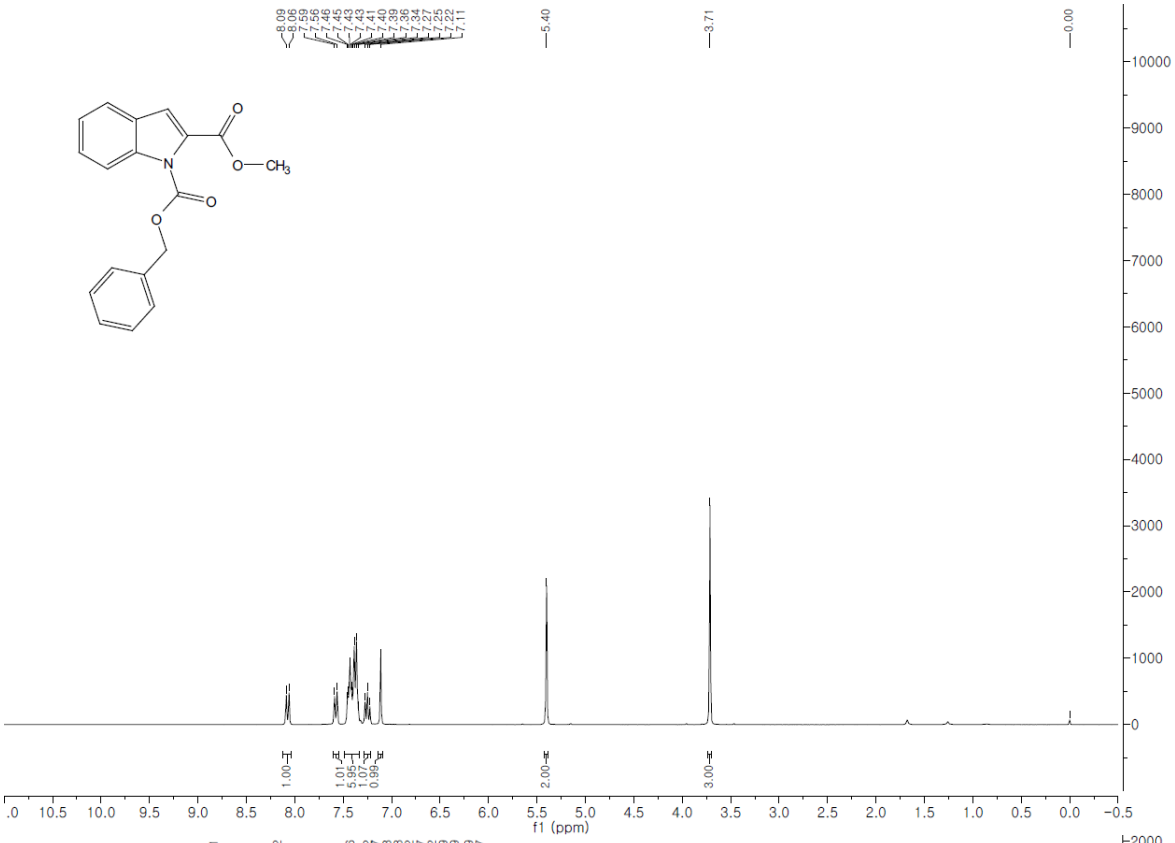
2,4-Dibromo-5-methoxybenzaldehyde (Koo, B.-S. *Synth. Commun.* **2002**, *32*, 2275.), 2-bromo-6-fluoro-4-methoxy-benzaldehyde (Jarnagin, K.; Akama, T. *PCT. Int. Appl.,* 2011094450, **2011)**, and 2-bromo-4,6-difluoro-4-methoxy-benzaldehyde(Jarnagin, K.; Akama, T. *PCT. Int. Appl.,* 2011094450, **2011)** were prepared using the reported procedures.

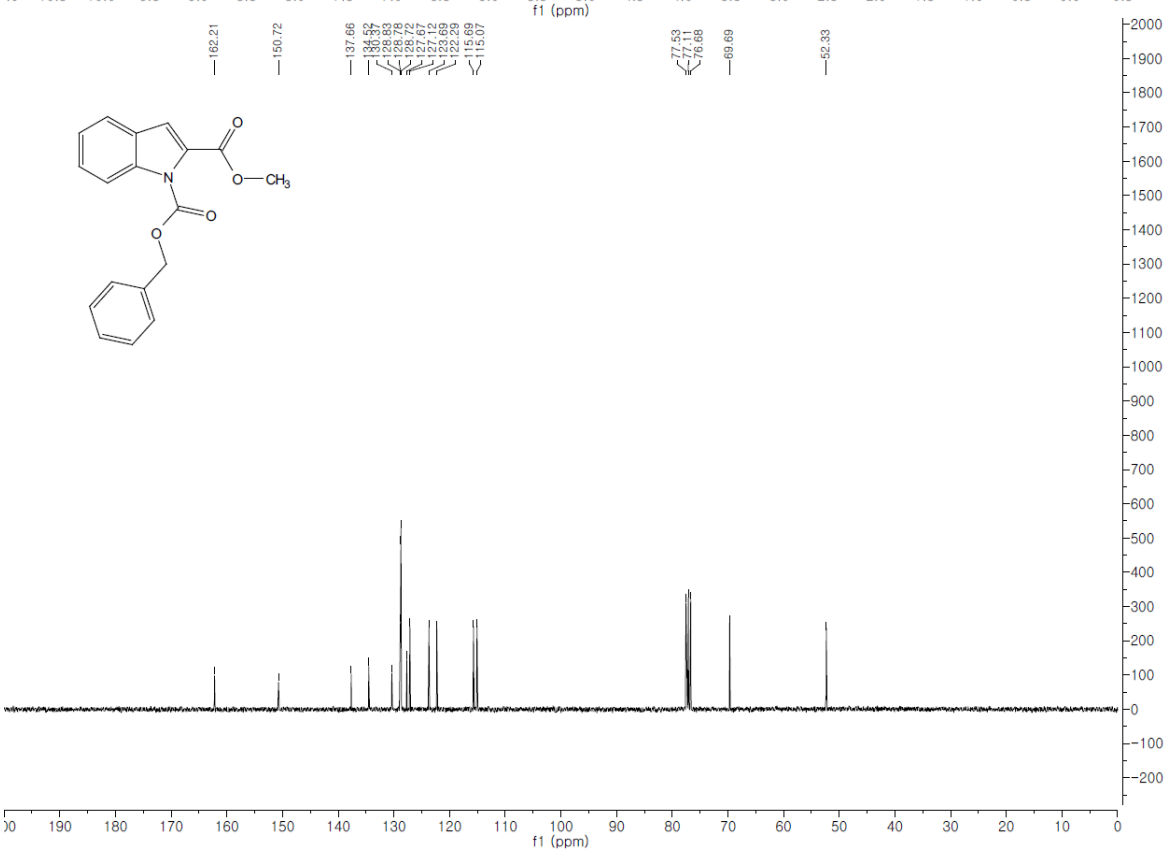
^{1}H and ^{13}C NMR data of **borazaaromatic compound 2**



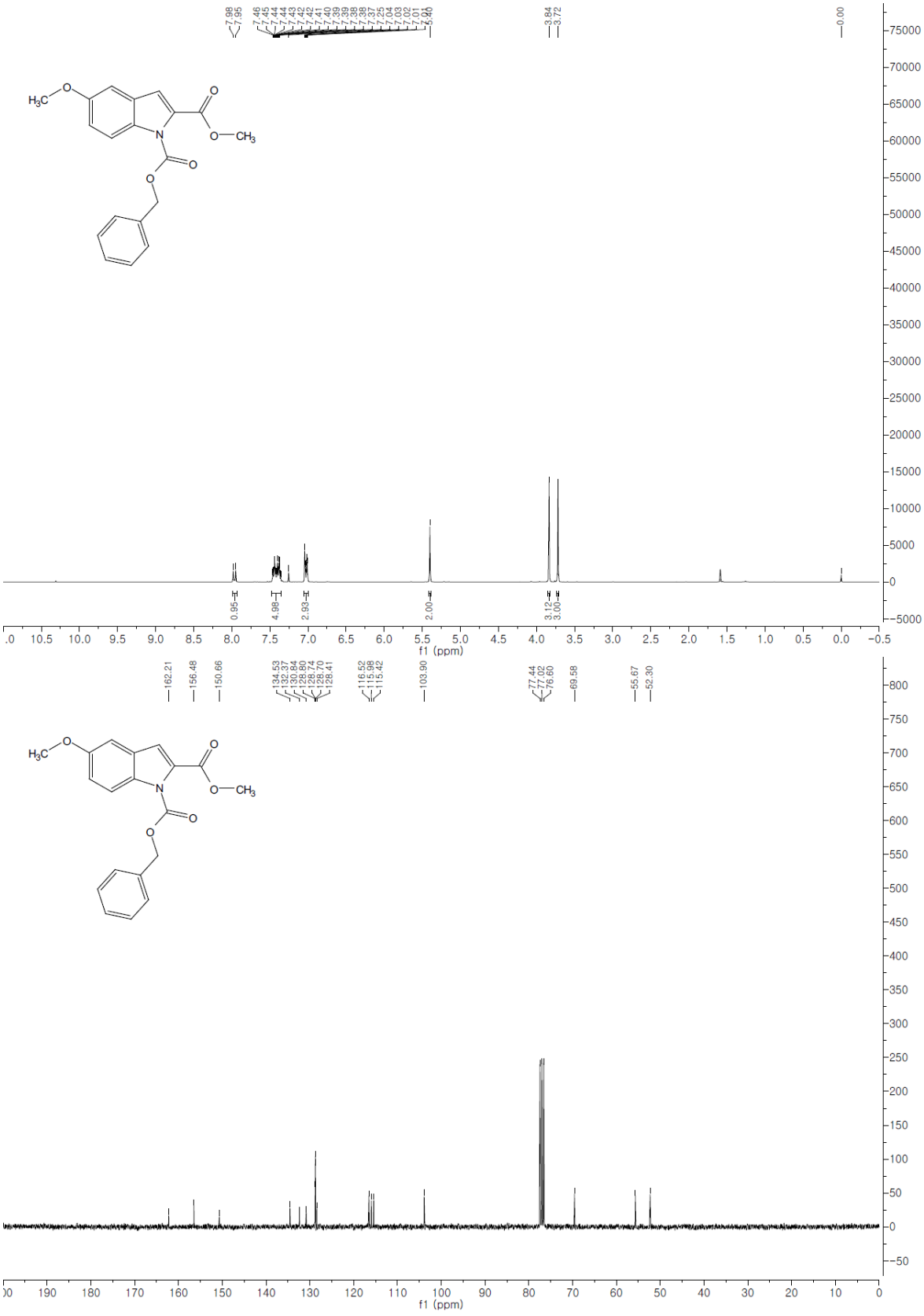


^{1}H and ^{13}C NMR data of **3**

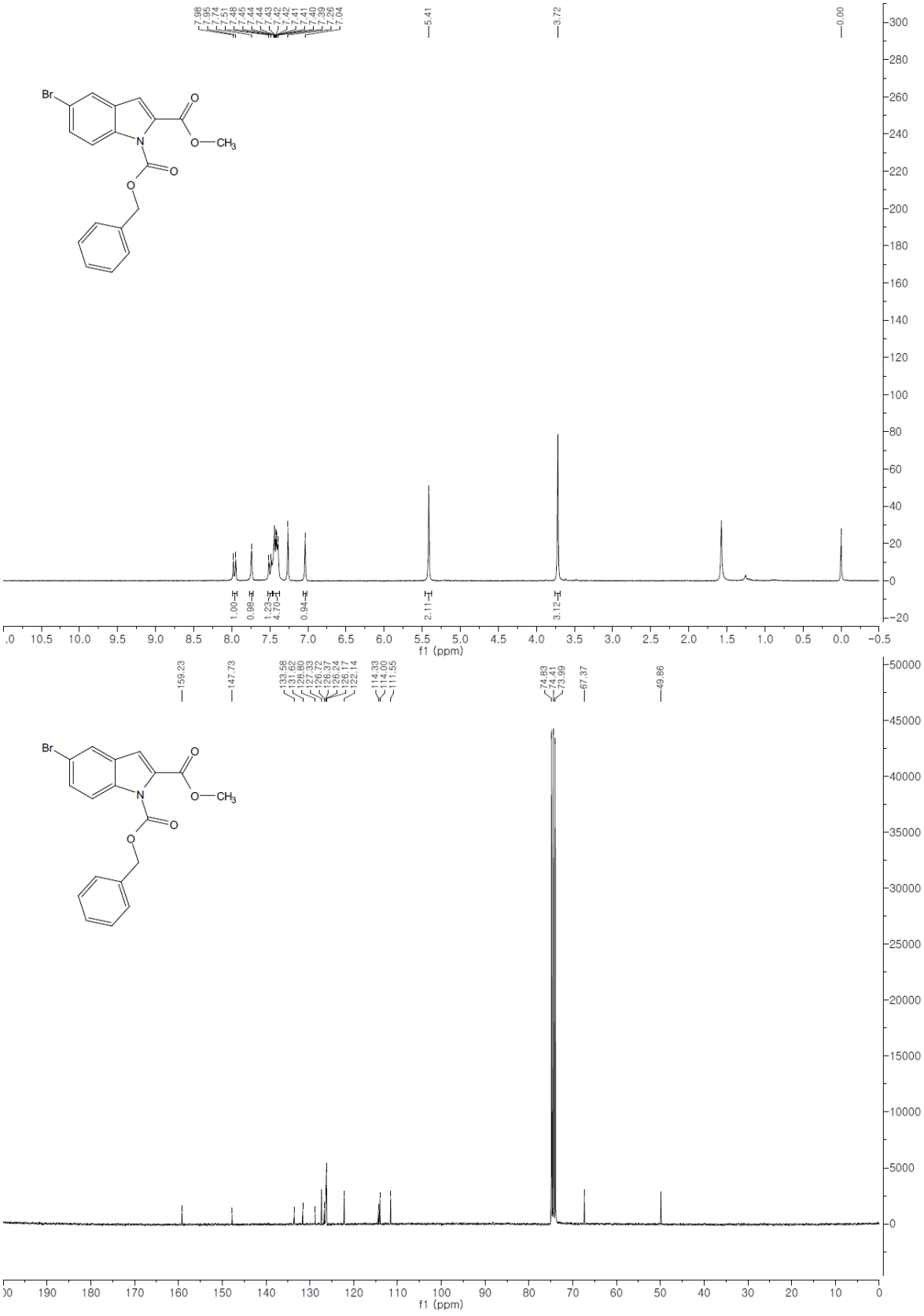




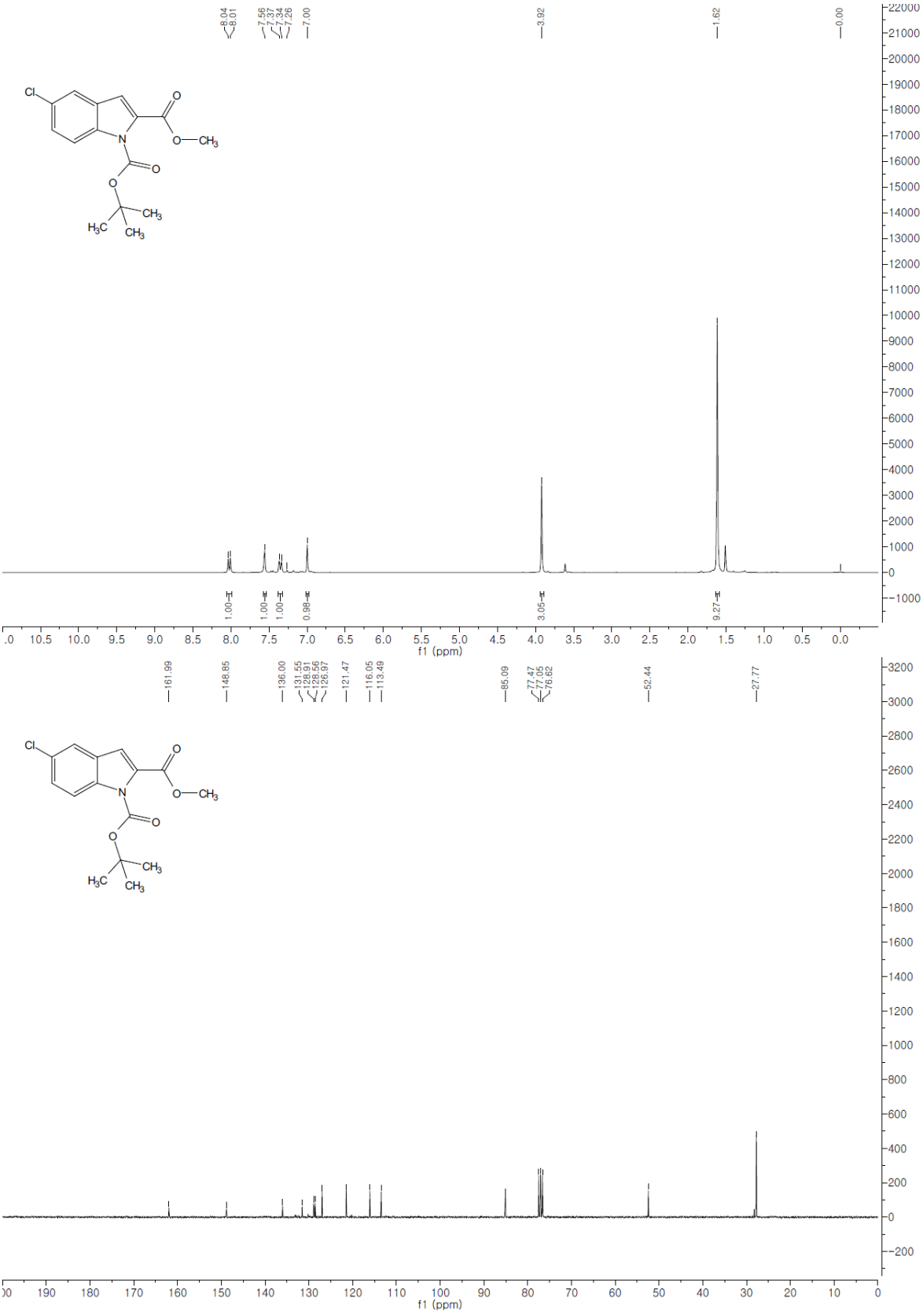
^{1}H and ^{13}C NMR data of **4**



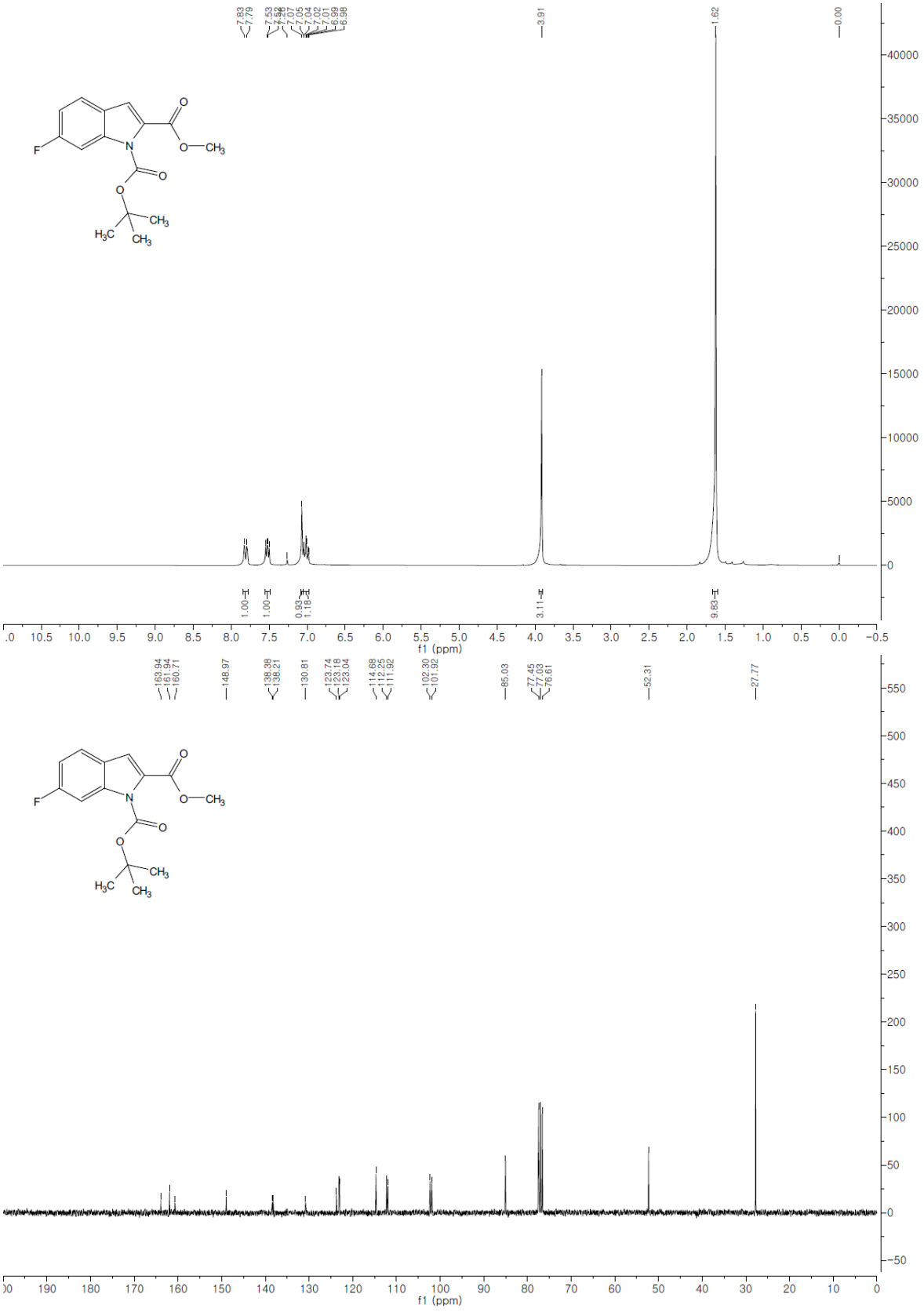
^{1}H and ^{13}C NMR data of **5**



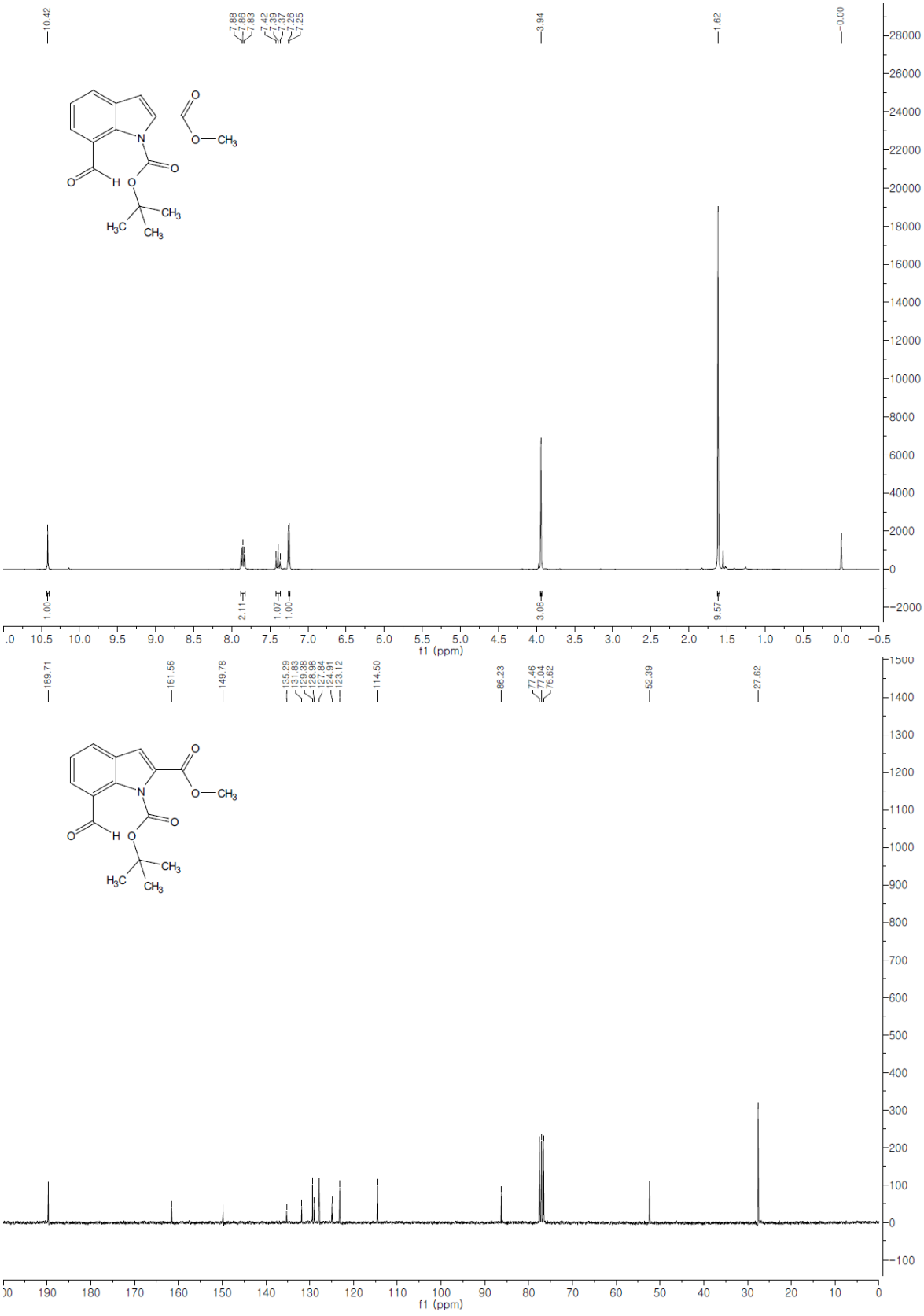
^{1}H and ^{13}C NMR data of **6**



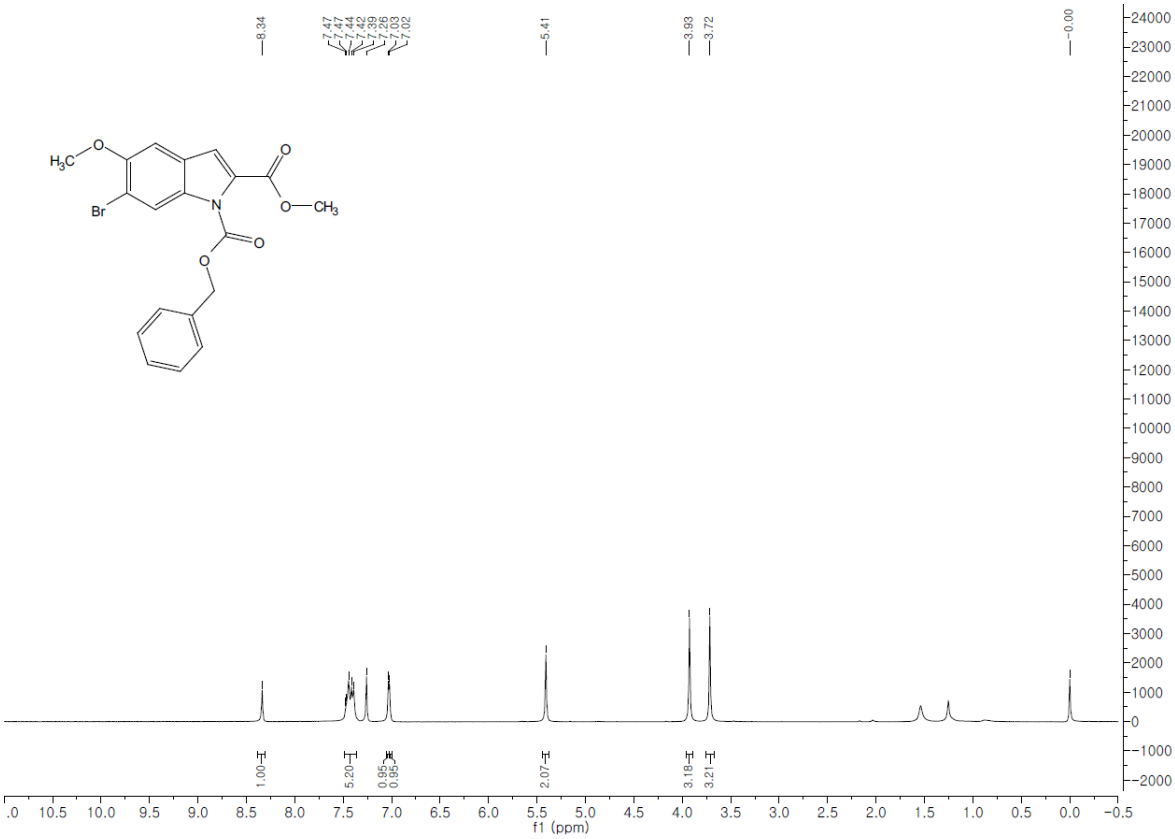
^{1}H and ^{13}C NMR data of **7**

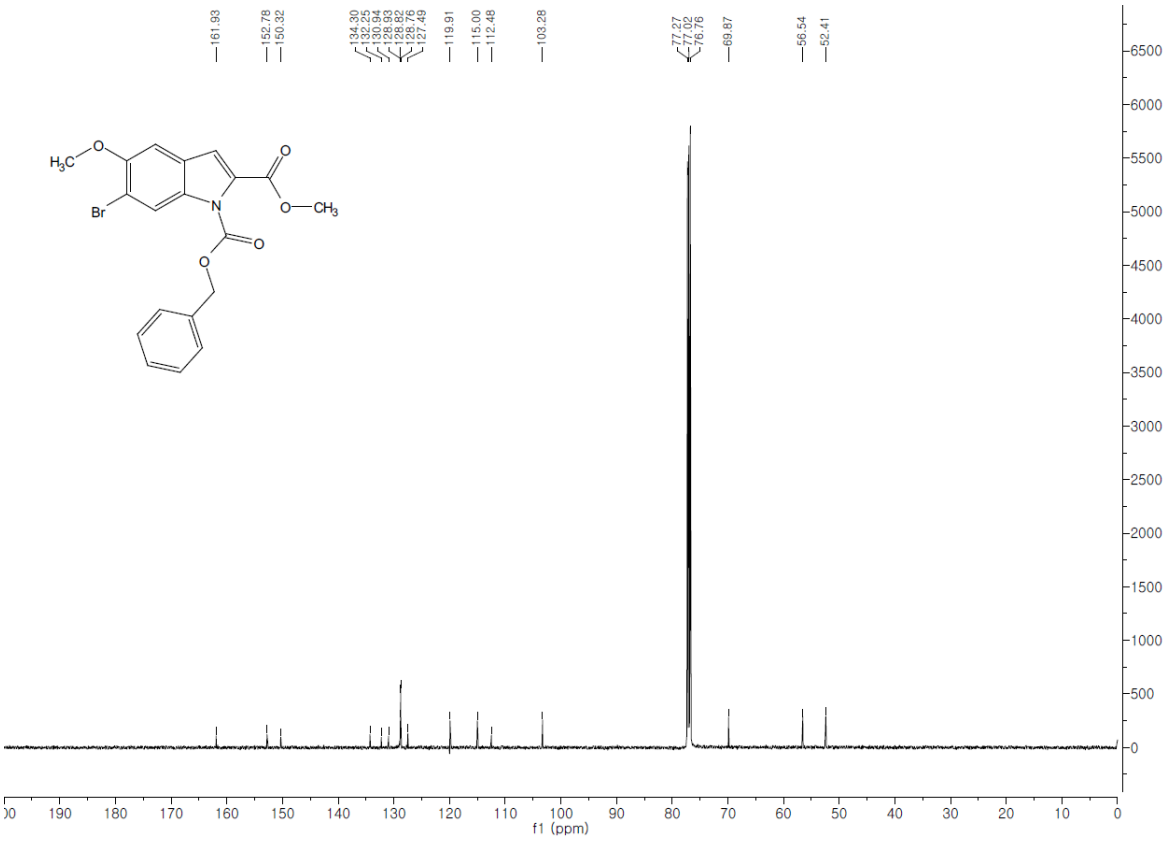


^{1}H and ^{13}C NMR data of **8**

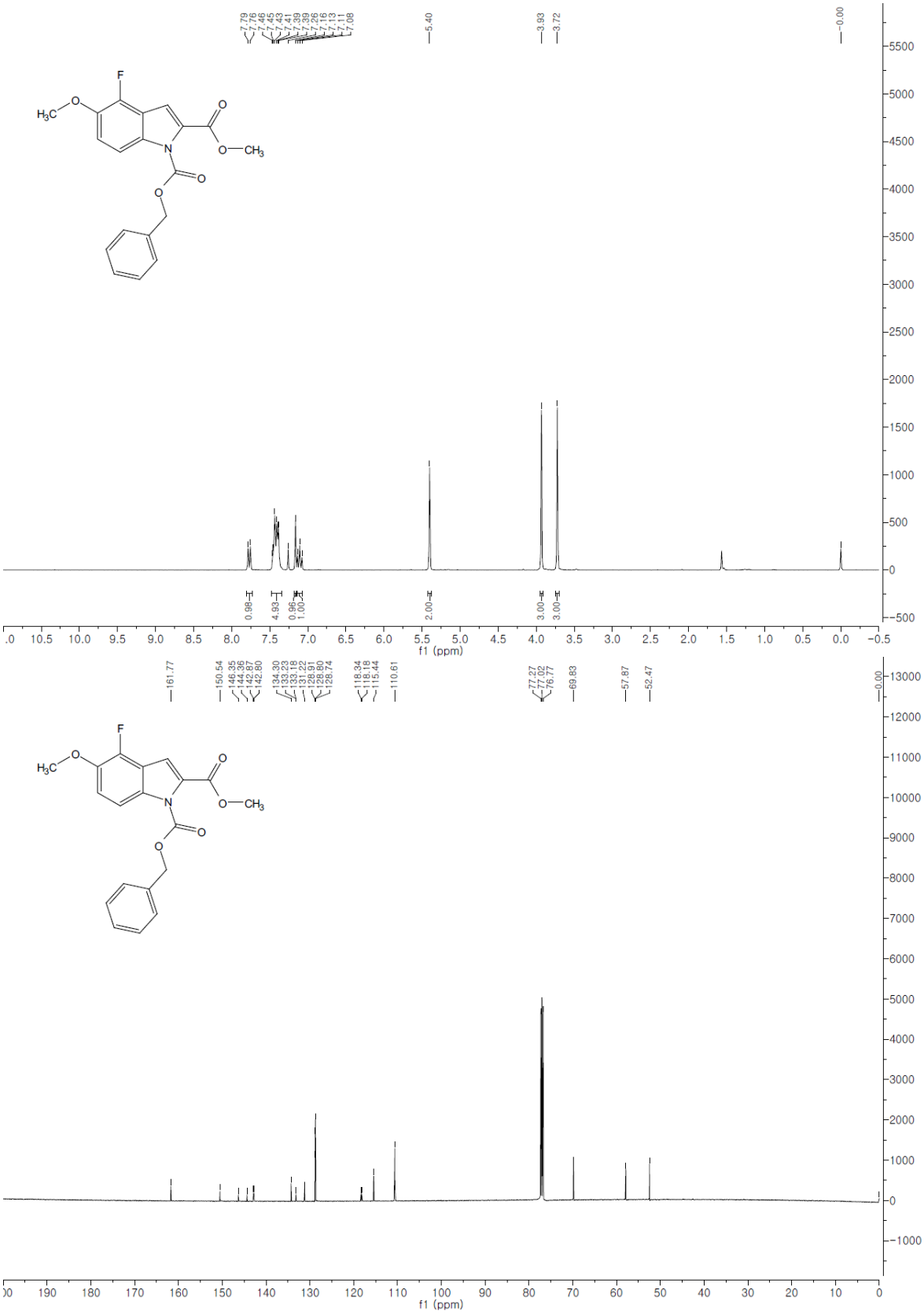


^{1}H and ^{13}C NMR data of **9**

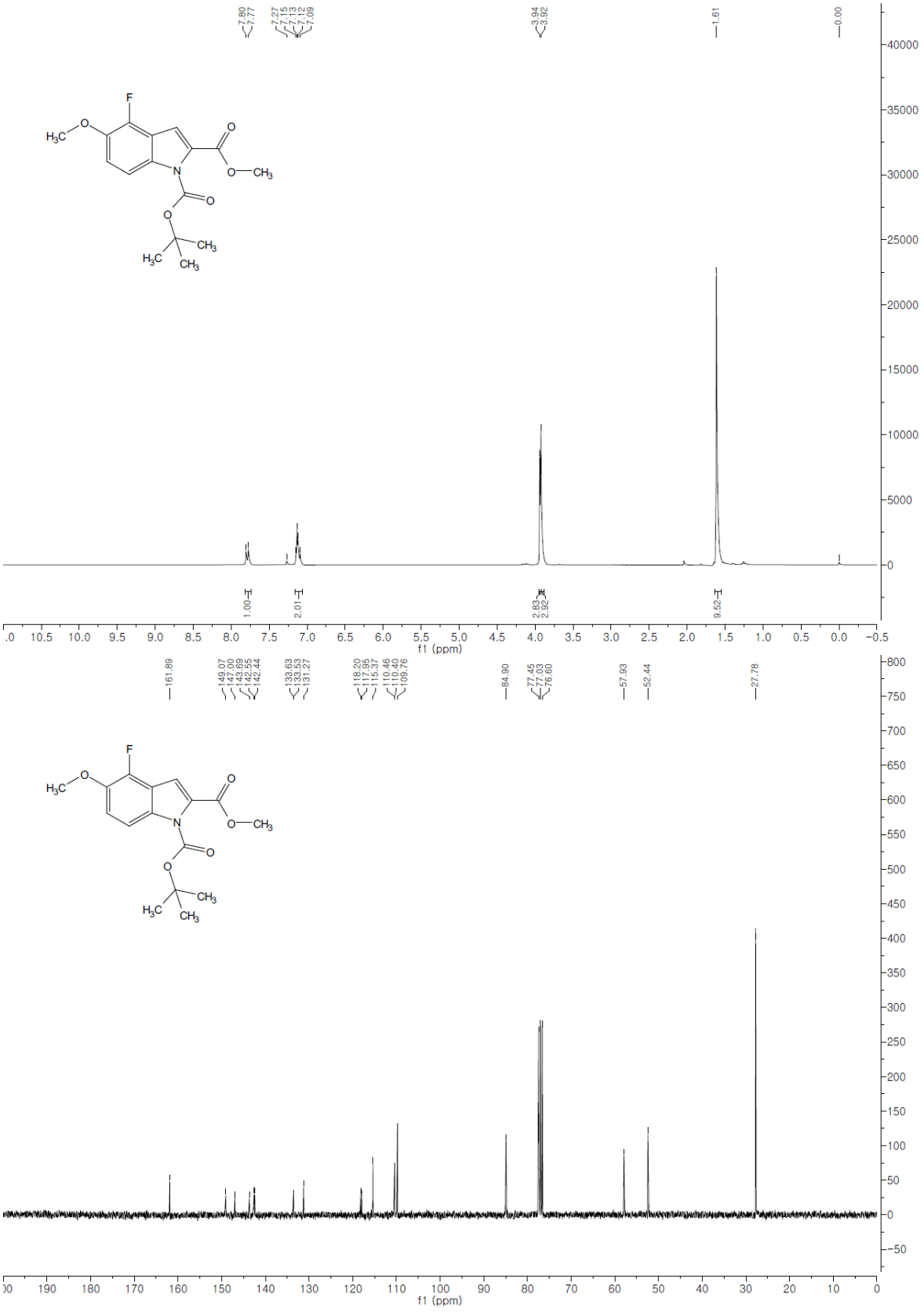




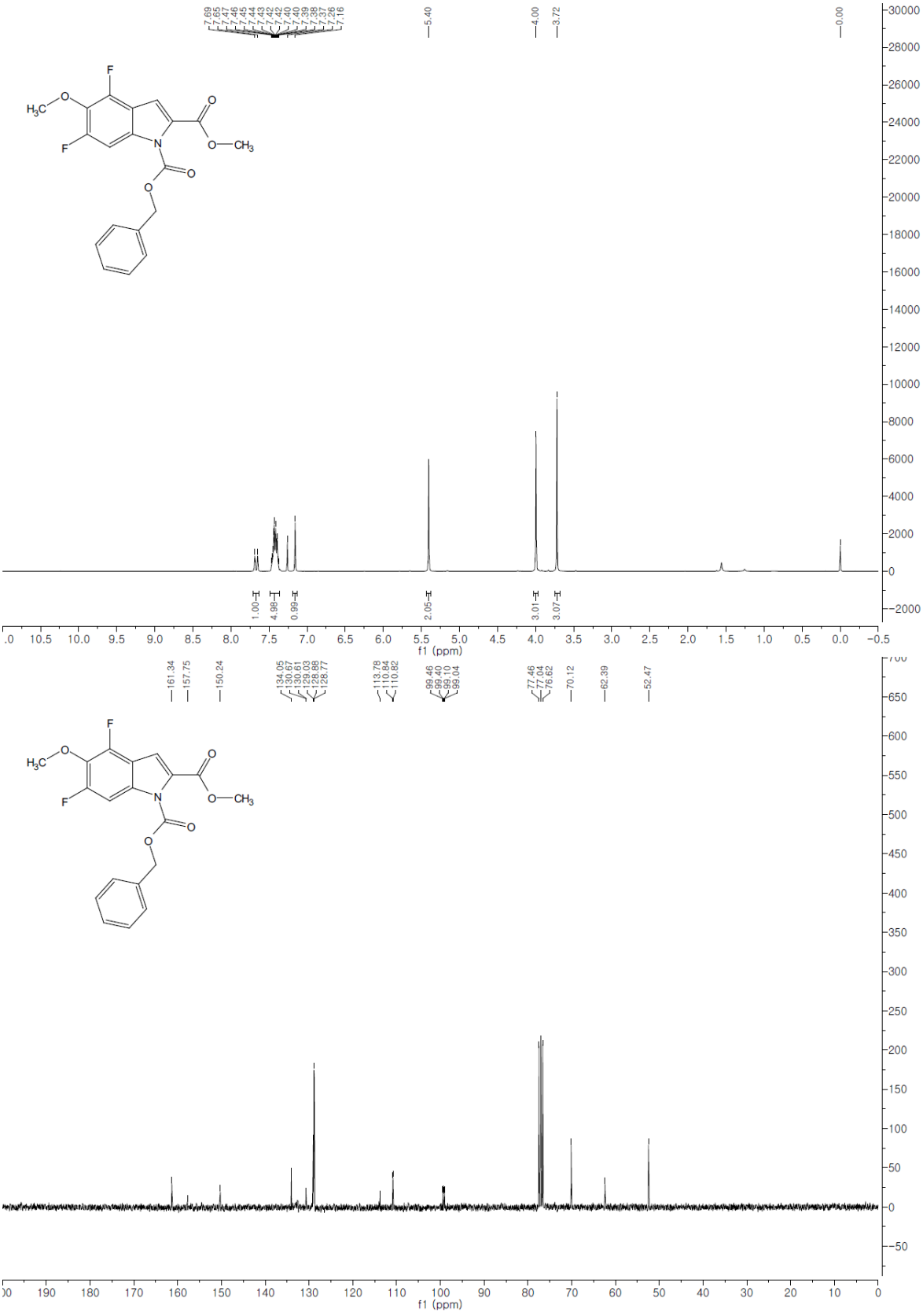
^{1}H and ^{13}C NMR data of **10a**



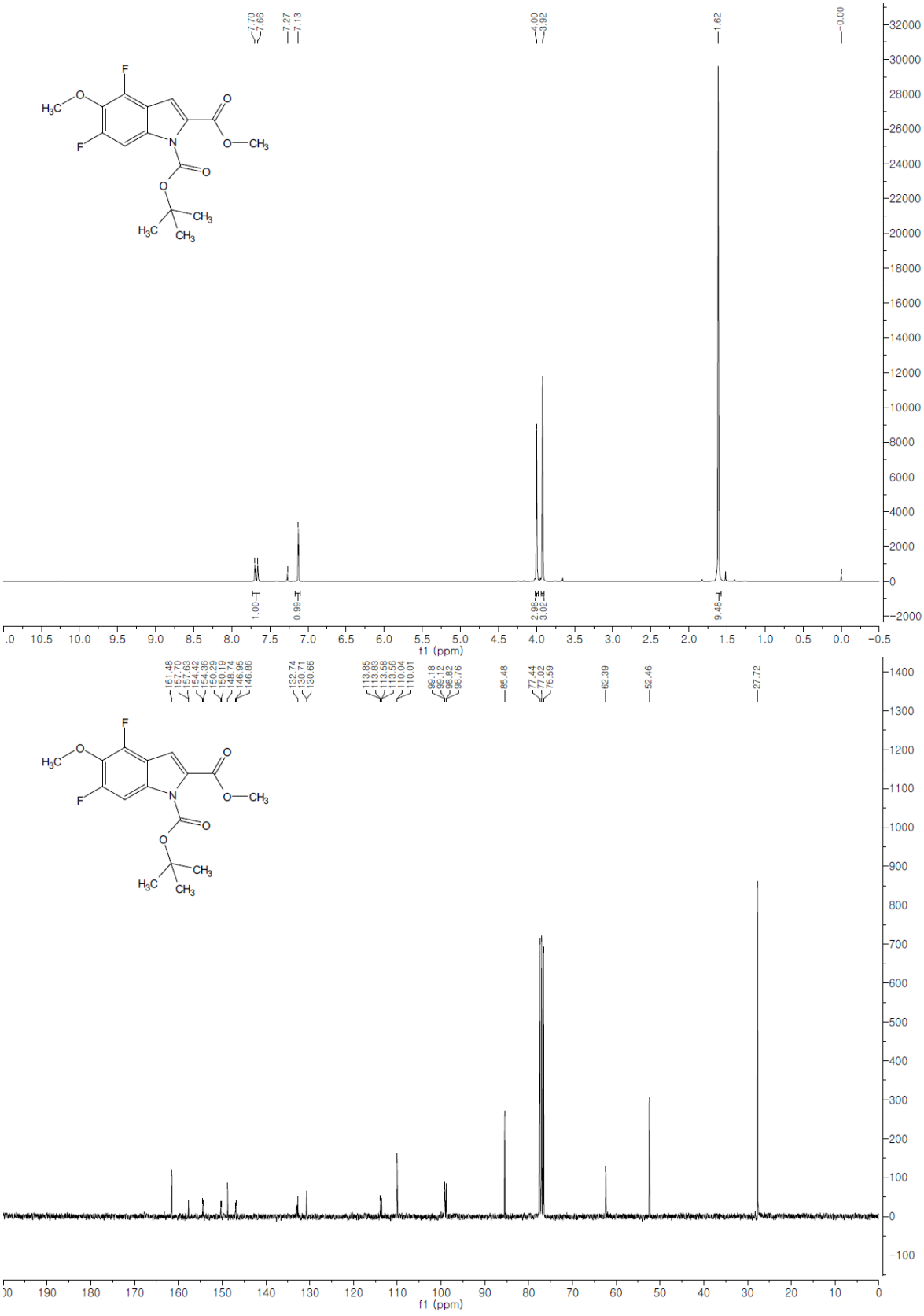
^{1}H and ^{13}C NMR of **10b**



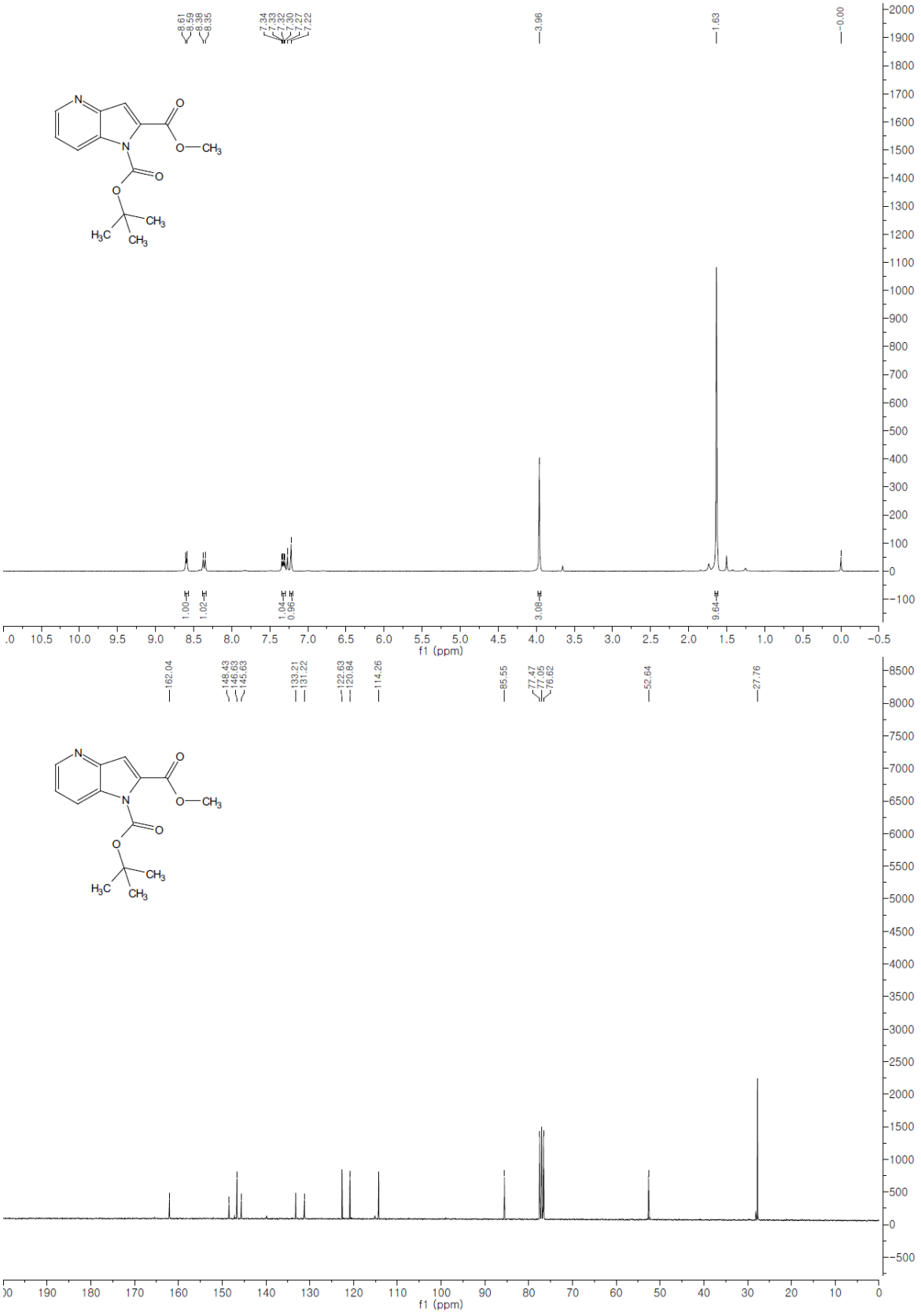
^{1}H and ^{13}C NMR data of **11a**



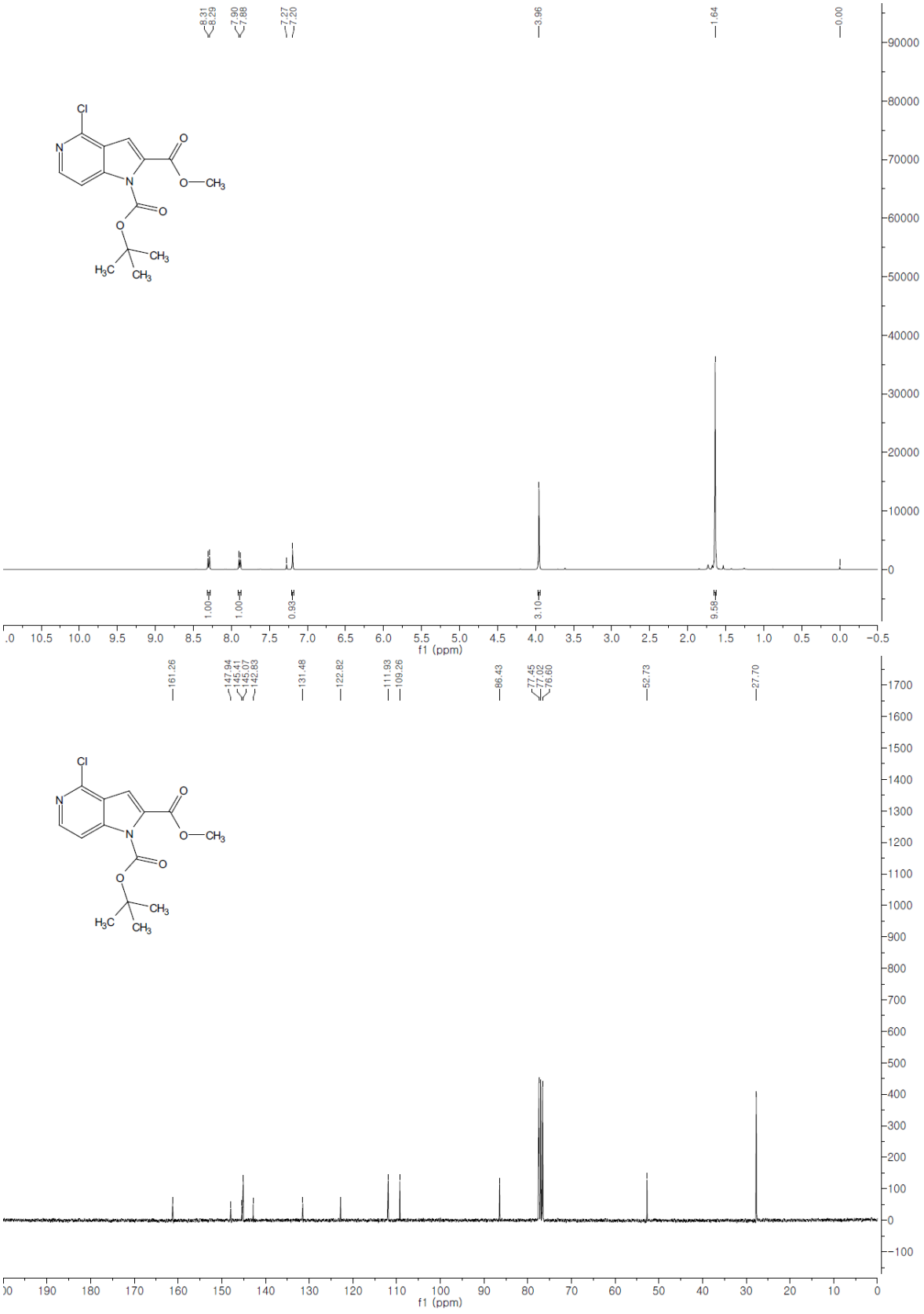
^{1}H and ^{13}C NMR data of **11b**



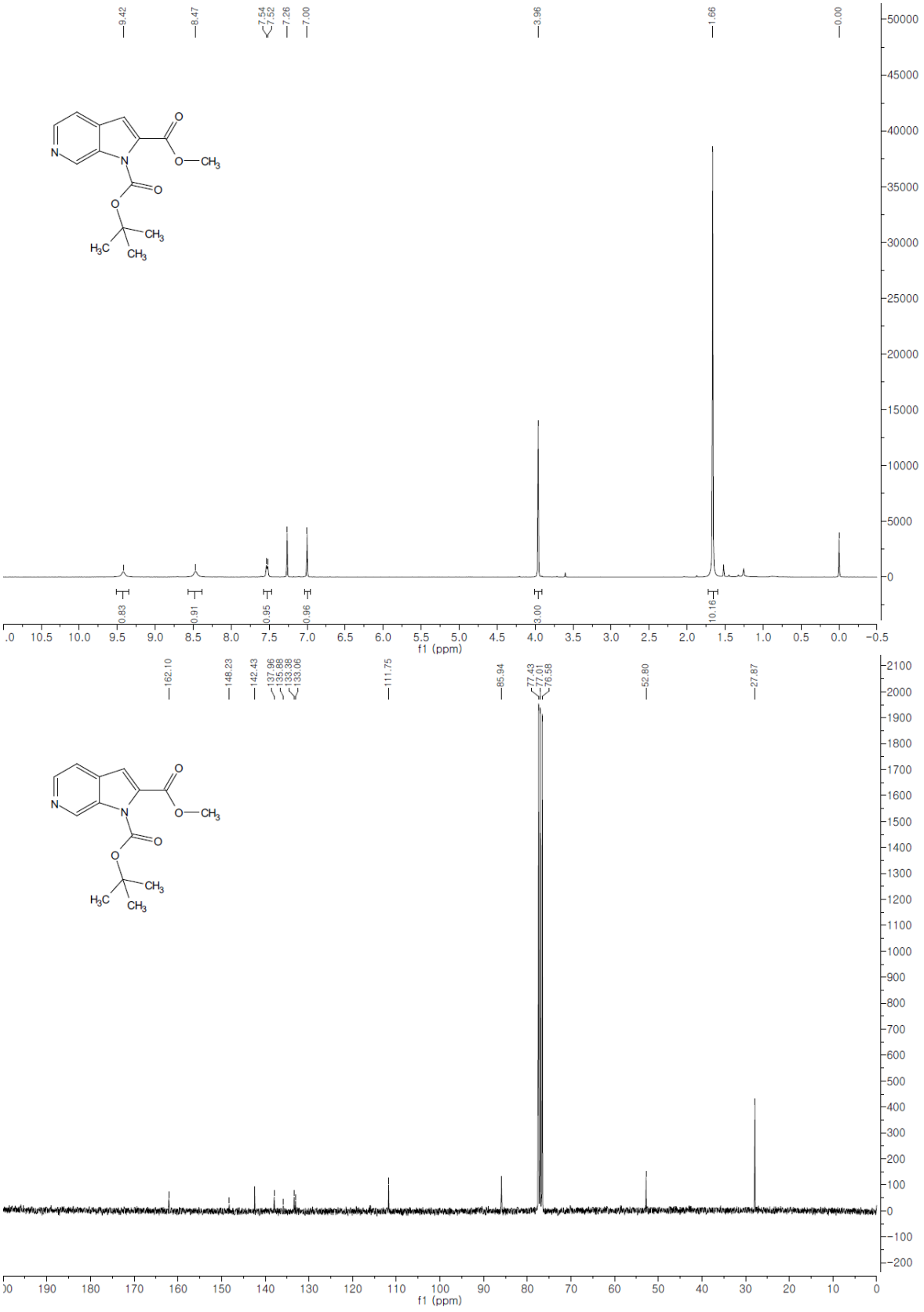
^{1}H and ^{13}C NMR of **12**



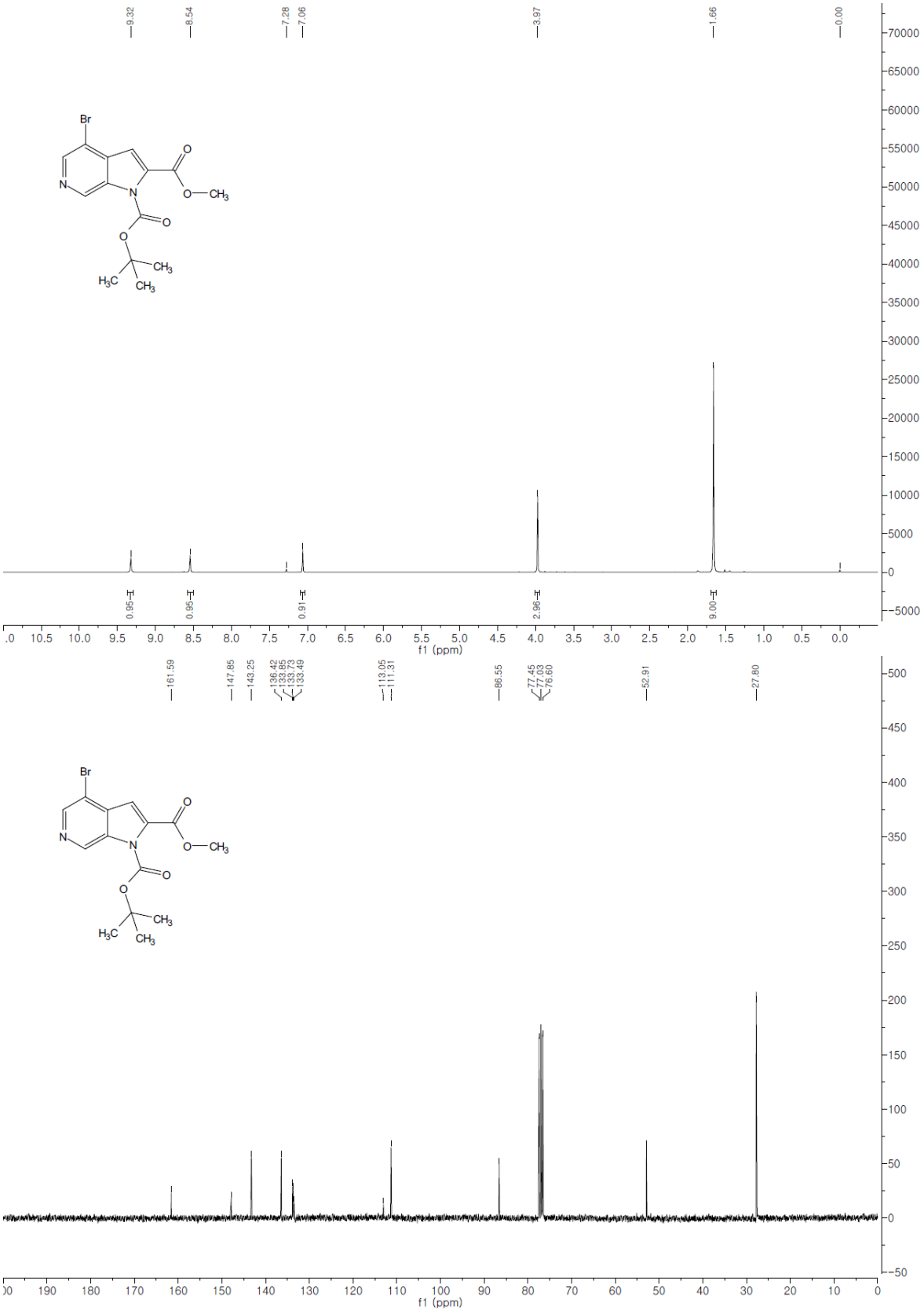
^{1}H and ^{13}C NMR data of **13**



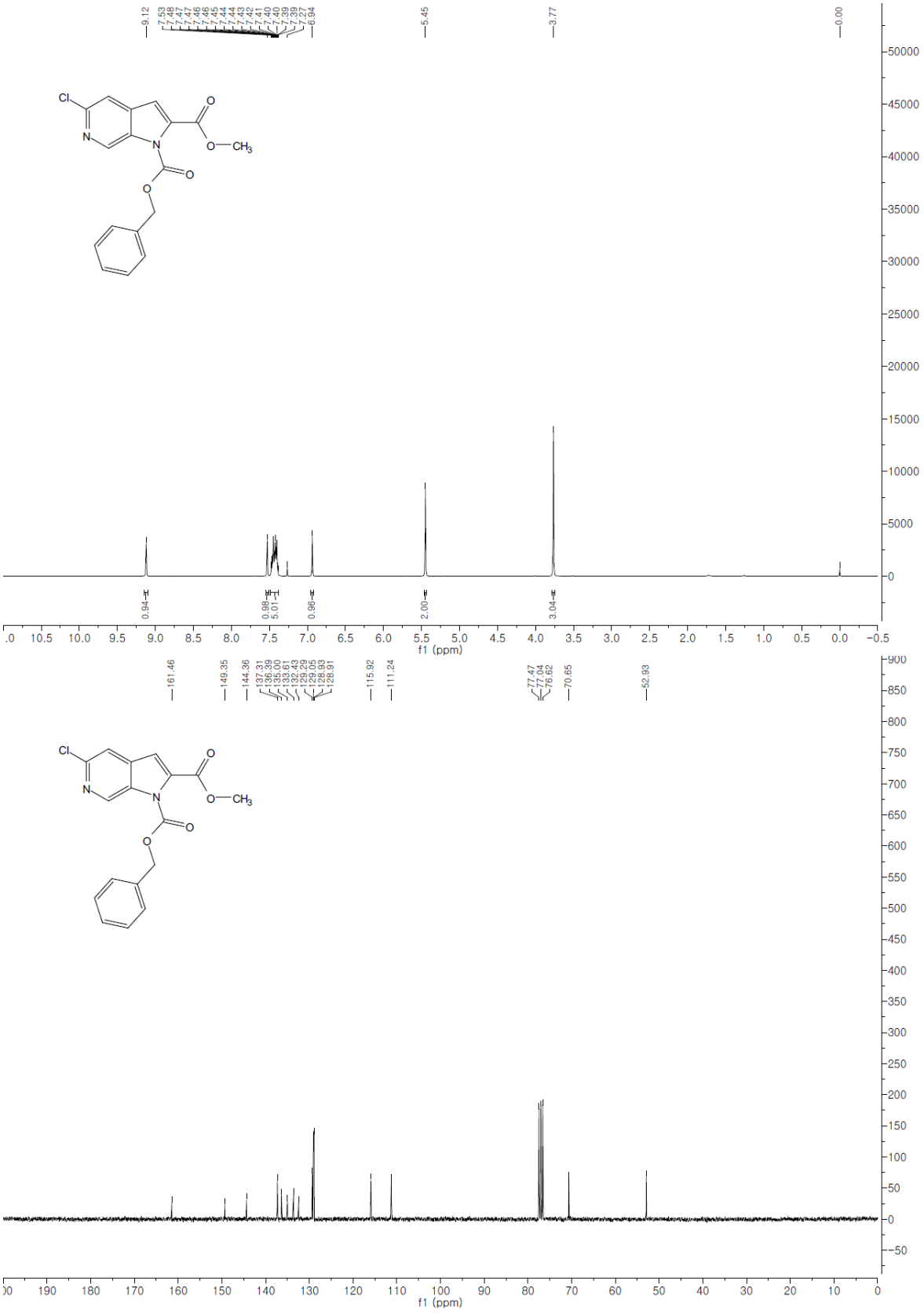
^{1}H and ^{13}C NMR data of **14**



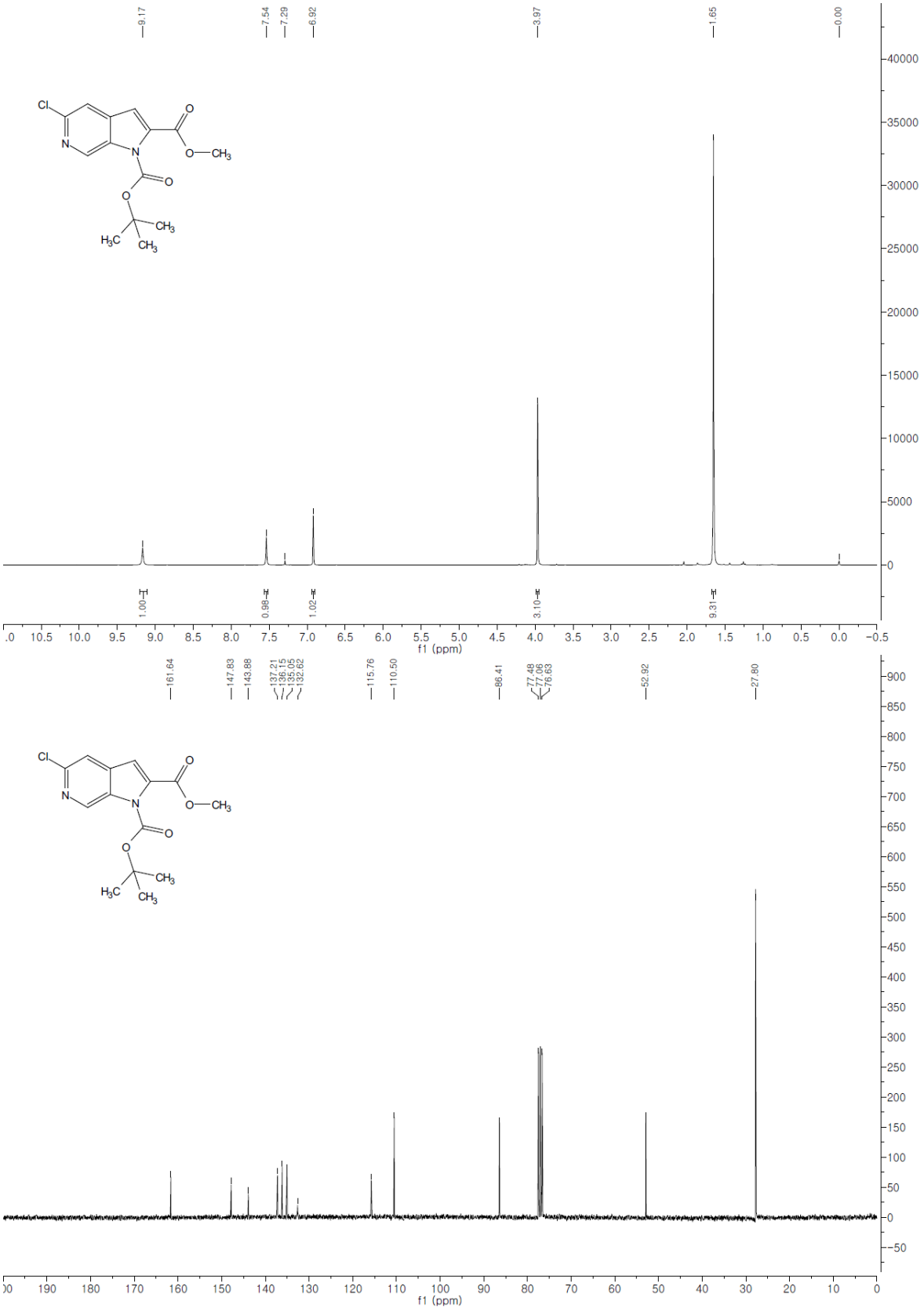
^{1}H and ^{13}C NMR data of **15**



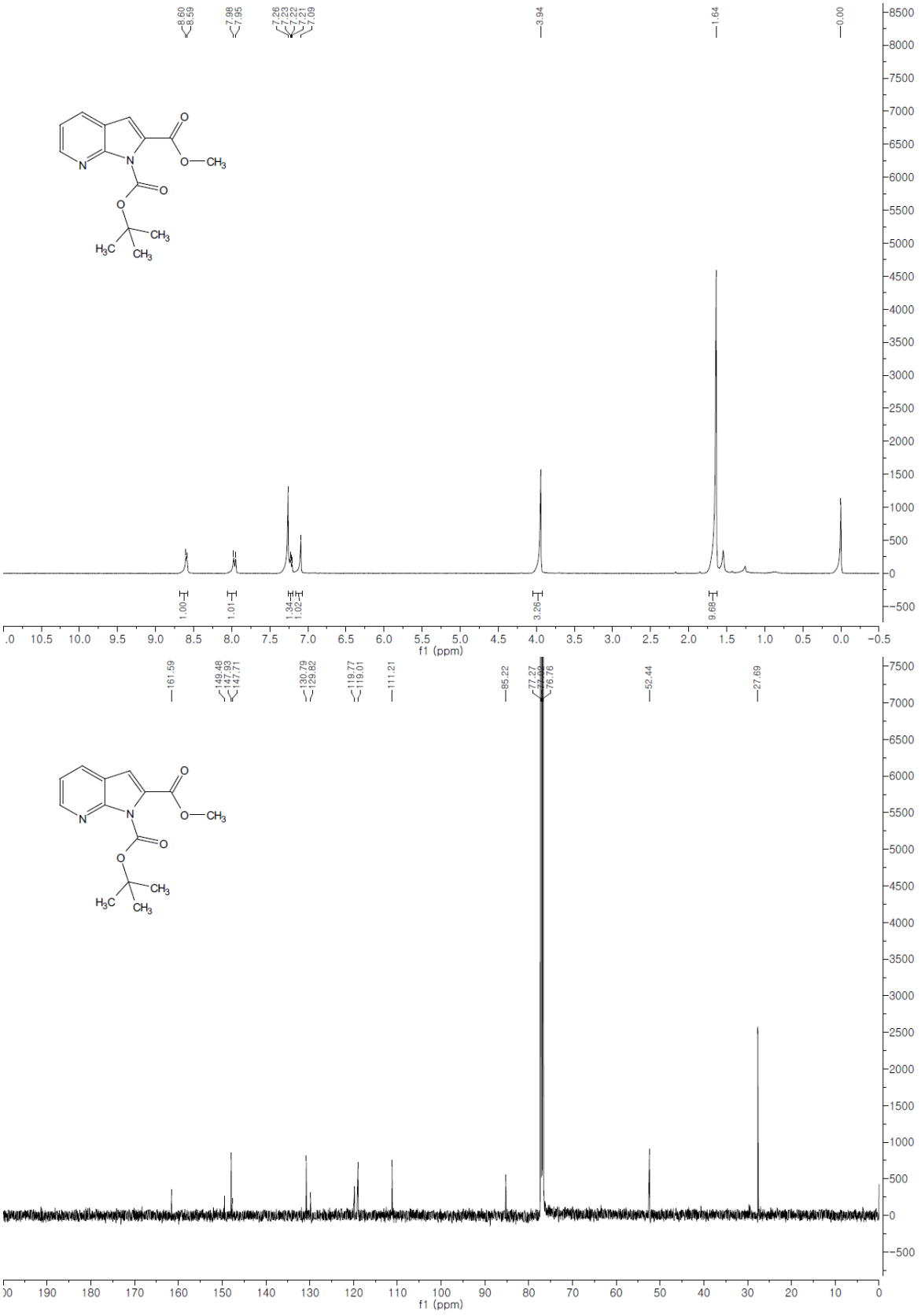
^{1}H and ^{13}C NMR data of **16a**



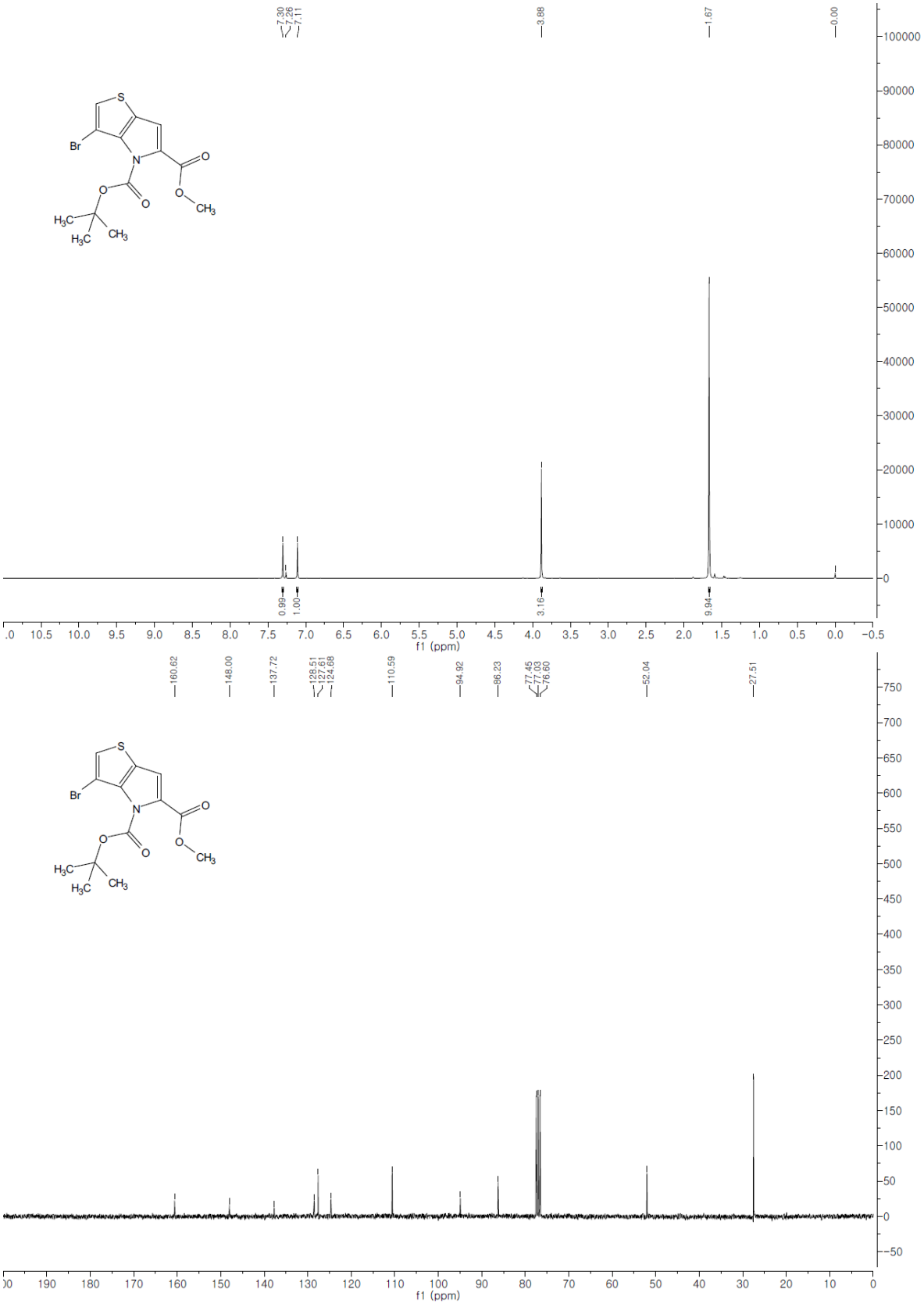
^{1}H and ^{13}C NMR data of **16b**



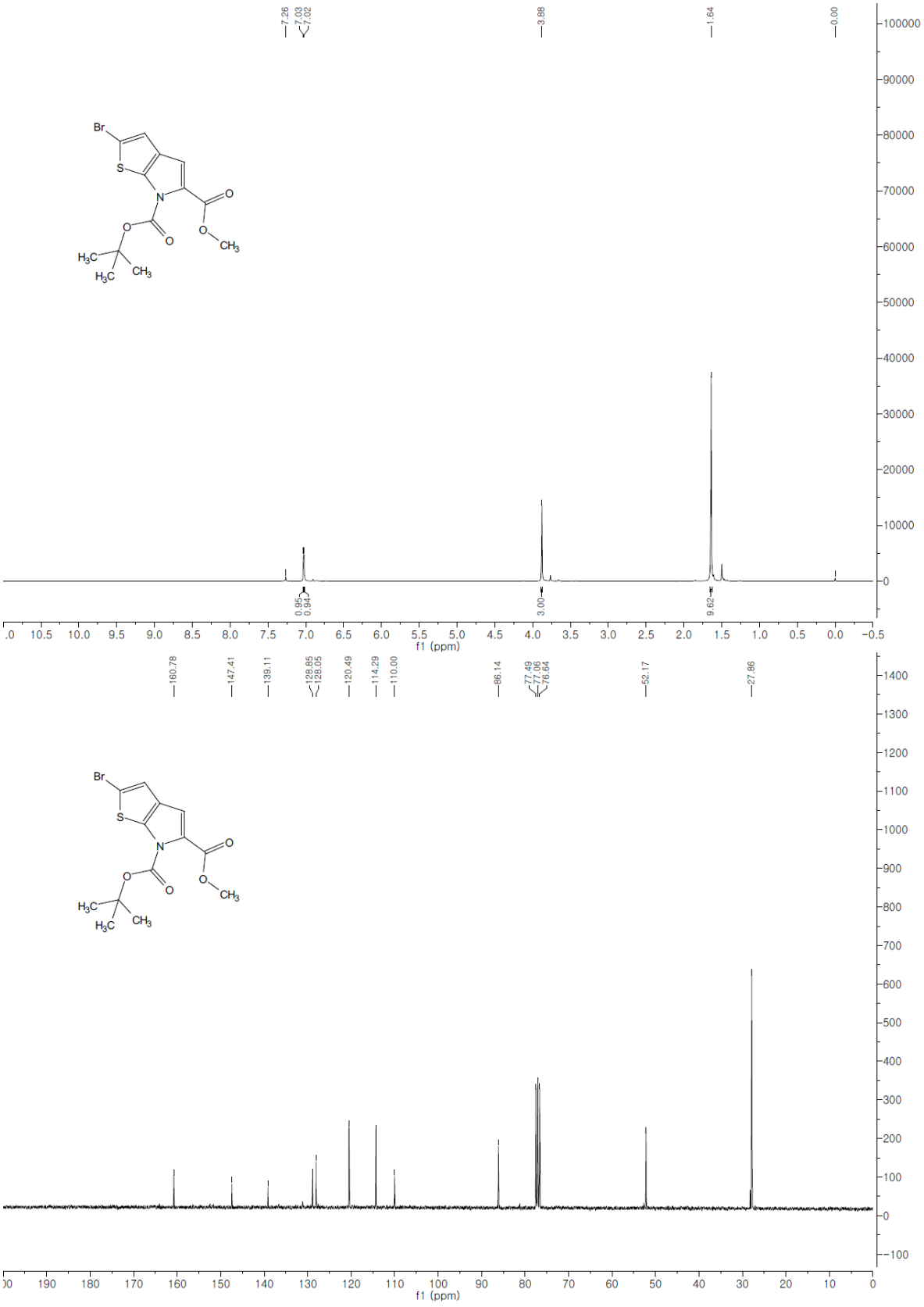
^{1}H and ^{13}C NMR data of **17**



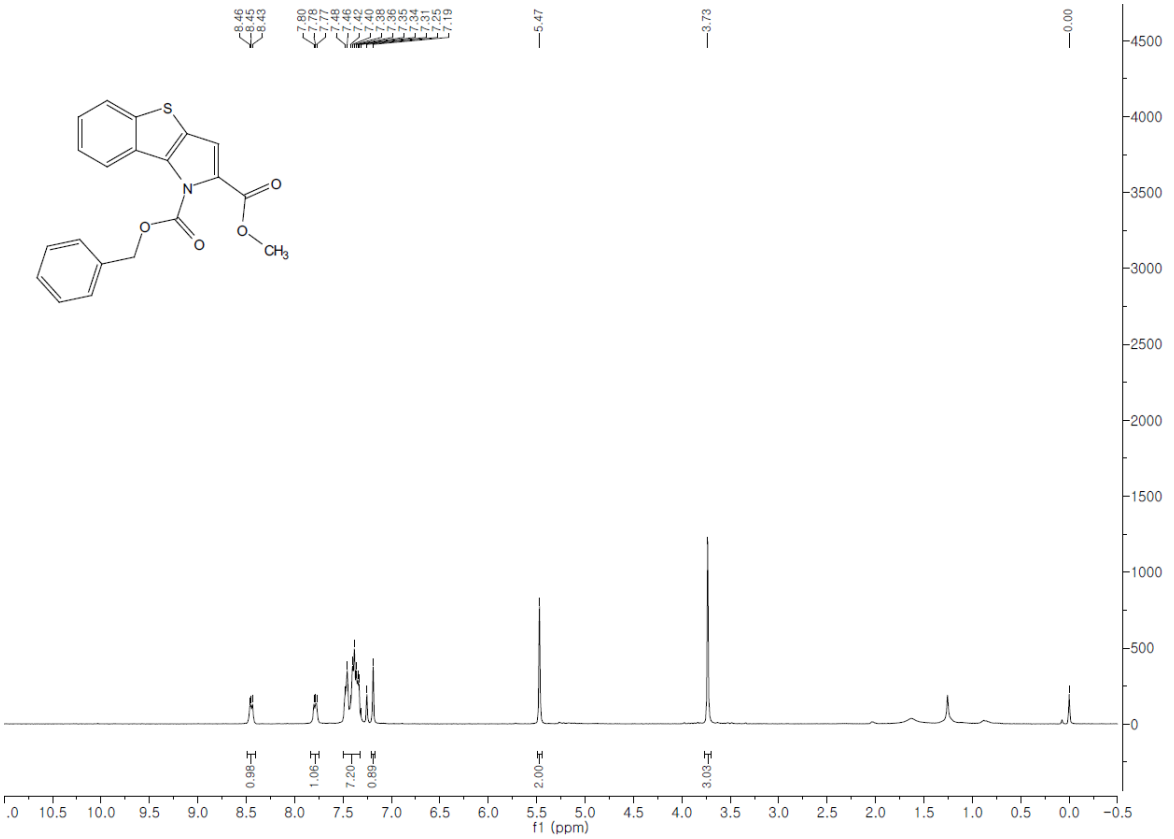
^{1}H and ^{13}C NMR data of **18**

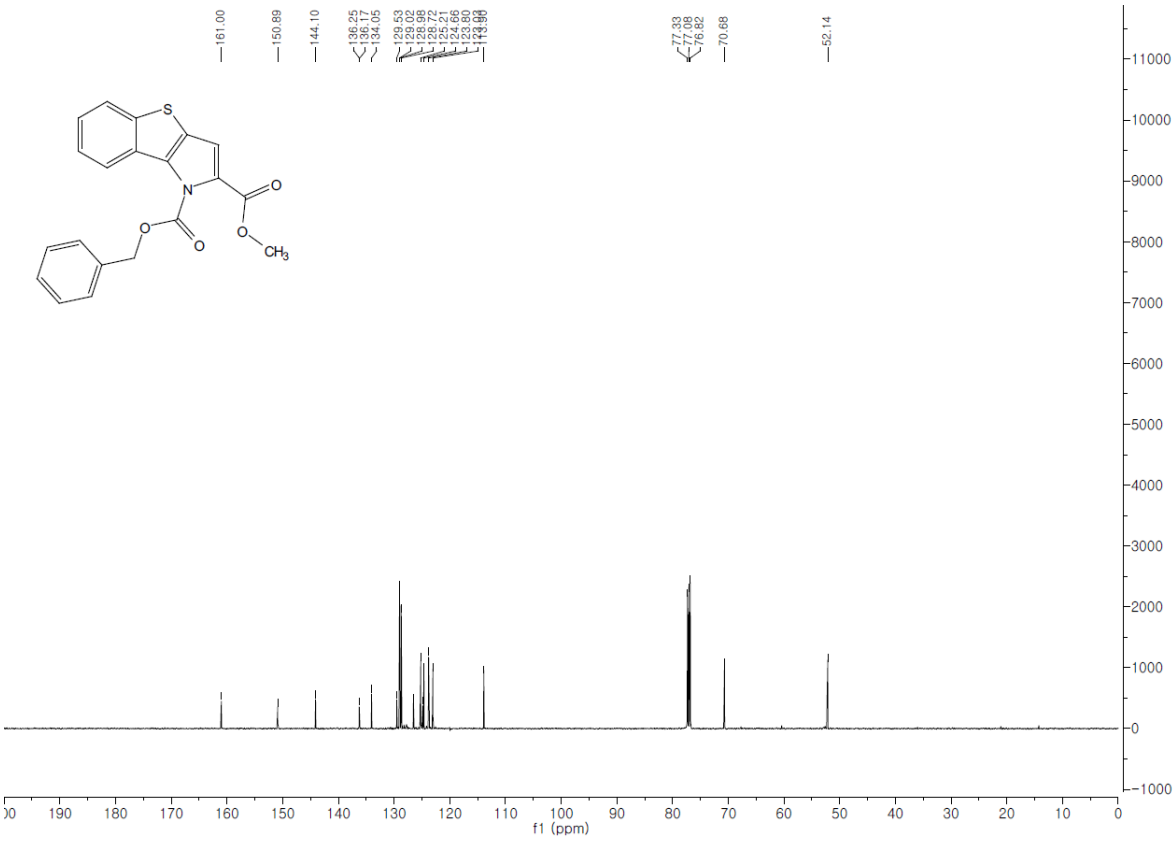


^{1}H and ^{13}C NMR data of **19**



^{1}H and ^{13}C NMR data of **20**





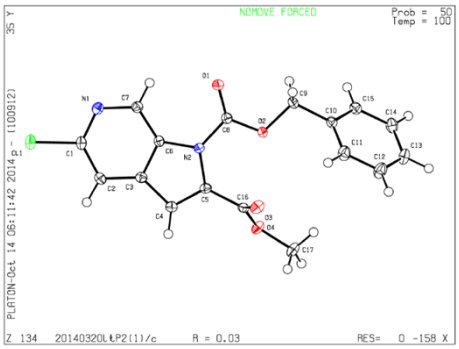


Table 1. Crystal data and structure refinement for **16a**

Identification code	20140320lt	
Empirical formula	C17 H13 Cl N2 O4	
Formula weight	344.74	
Temperature	100(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 8.70220(10) Å	□= 90°.
	b = 21.4243(3) Å	□= 103.4880(10)°.
	c = 8.40400(10) Å	□ = 90°.
Volume	1523.61(3) $Å^3$	
Z	4	
Density (calculated)	1.503 Mg/m^3	
Absorption coefficient	0.276 mm^{-1}	
F(000)	712	
Crystal size	0.22 x 0.16 x 0.04 mm^3	
Theta range for data collection	1.90 to 28.25°	
Index ranges	-11<=h<=11, -28<=k<=28, -11<=l<=11	
Reflections collected	41898	
Independent reflections	3772 [R(int) = 0.0331]	
Completeness to theta = 28.25°	100.0 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9890 and 0.9418	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3772 / 0 / 217	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0303, wR2 = 0.0745	
R indices (all data)	R1 = 0.0361, wR2 = 0.0782	
Largest diff. peak and hole	0.351 and -0.249 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **16a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	9016(1)	10807(1)	11820(1)	21(1)
O(1)	2799(1)	10152(1)	5505(1)	19(1)
O(2)	2502(1)	9124(1)	4901(1)	15(1)
O(3)	5059(1)	8398(1)	4213(1)	19(1)
O(4)	4574(1)	7830(1)	6295(1)	18(1)
N(1)	6476(1)	10740(1)	9456(1)	16(1)
N(2)	4710(1)	9448(1)	6665(1)	14(1)
C(1)	7674(1)	10400(1)	10295(1)	15(1)
C(2)	7945(1)	9775(1)	10058(1)	16(1)
C(3)	6857(1)	9484(1)	8793(1)	14(1)
C(4)	6703(1)	8861(1)	8138(2)	16(1)
C(5)	5419(1)	8855(1)	6860(1)	14(1)
C(6)	5602(1)	9839(1)	7870(1)	13(1)
C(7)	5422(1)	10464(1)	8240(1)	15(1)
C(8)	3258(1)	9621(1)	5644(1)	14(1)
C(9)	996(1)	9270(1)	3770(2)	18(1)
C(10)	251(1)	8668(1)	3083(1)	16(1)
C(11)	1003(2)	8280(1)	2169(2)	22(1)
C(12)	290(2)	7730(1)	1505(2)	26(1)
C(13)	-1187(2)	7565(1)	1746(2)	22(1)
C(14)	-1944(2)	7951(1)	2647(2)	20(1)
C(15)	-1228(1)	8502(1)	3320(2)	17(1)
C(16)	4968(1)	8347(1)	5614(1)	14(1)
C(17)	4238(2)	7293(1)	5203(2)	22(1)

Table 3. Bond lengths [Å] and angles [°] for **16a**.

Cl(1)-C(1)	1.7511(12)
O(1)-C(8)	1.2024(14)
O(2)-C(8)	1.3274(14)
O(2)-C(9)	1.4623(14)
O(3)-C(16)	1.2031(14)
O(4)-C(16)	1.3283(14)
O(4)-C(17)	1.4578(14)
N(1)-C(1)	1.3307(16)
N(1)-C(7)	1.3402(16)
N(2)-C(6)	1.4015(14)
N(2)-C(8)	1.4015(15)
N(2)-C(5)	1.4043(14)
C(1)-C(2)	1.3823(17)
C(2)-C(3)	1.3956(16)
C(2)-H(2A)	0.9500
C(3)-C(6)	1.4072(16)
C(3)-C(4)	1.4375(16)
C(4)-C(5)	1.3579(16)
C(4)-H(4A)	0.9500
C(5)-C(16)	1.4979(16)
C(6)-C(7)	1.3917(15)
C(7)-H(7A)	0.9500
C(9)-C(10)	1.4977(16)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-C(15)	1.3935(17)
C(10)-C(11)	1.3946(17)
C(11)-C(12)	1.3859(18)
C(11)-H(11A)	0.9500
C(12)-C(13)	1.3923(18)
C(12)-H(12A)	0.9500
C(13)-C(14)	1.3872(18)
C(13)-H(13A)	0.9500
C(14)-C(15)	1.3907(17)
C(14)-H(14A)	0.9500

C(15)-H(15A)	0.9500
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800

C(8)-O(2)-C(9)	113.84(9)
C(16)-O(4)-C(17)	114.86(9)
C(1)-N(1)-C(7)	118.40(10)
C(6)-N(2)-C(8)	123.57(9)
C(6)-N(2)-C(5)	107.60(9)
C(8)-N(2)-C(5)	128.22(10)
N(1)-C(1)-C(2)	126.33(11)
N(1)-C(1)-Cl(1)	114.98(9)
C(2)-C(1)-Cl(1)	118.68(9)
C(1)-C(2)-C(3)	115.76(11)
C(1)-C(2)-H(2A)	122.1
C(3)-C(2)-H(2A)	122.1
C(2)-C(3)-C(6)	118.65(10)
C(2)-C(3)-C(4)	133.85(11)
C(6)-C(3)-C(4)	107.50(10)
C(5)-C(4)-C(3)	107.27(10)
C(5)-C(4)-H(4A)	126.4
C(3)-C(4)-H(4A)	126.4
C(4)-C(5)-N(2)	110.03(10)
C(4)-C(5)-C(16)	126.32(10)
N(2)-C(5)-C(16)	122.65(10)
C(7)-C(6)-N(2)	131.68(11)
C(7)-C(6)-C(3)	120.72(11)
N(2)-C(6)-C(3)	107.59(10)
N(1)-C(7)-C(6)	120.10(11)
N(1)-C(7)-H(7A)	120.0
C(6)-C(7)-H(7A)	120.0
O(1)-C(8)-O(2)	126.58(11)
O(1)-C(8)-N(2)	122.72(10)
O(2)-C(8)-N(2)	110.70(9)
O(2)-C(9)-C(10)	107.90(9)
O(2)-C(9)-H(9A)	110.1

C(10)-C(9)-H(9A)	110.1
O(2)-C(9)-H(9B)	110.1
C(10)-C(9)-H(9B)	110.1
H(9A)-C(9)-H(9B)	108.4
C(15)-C(10)-C(11)	119.53(11)
C(15)-C(10)-C(9)	119.80(11)
C(11)-C(10)-C(9)	120.64(11)
C(12)-C(11)-C(10)	120.34(12)
C(12)-C(11)-H(11A)	119.8
C(10)-C(11)-H(11A)	119.8
C(11)-C(12)-C(13)	119.94(12)
C(11)-C(12)-H(12A)	120.0
C(13)-C(12)-H(12A)	120.0
C(14)-C(13)-C(12)	119.99(12)
C(14)-C(13)-H(13A)	120.0
C(12)-C(13)-H(13A)	120.0
C(13)-C(14)-C(15)	120.15(11)
C(13)-C(14)-H(14A)	119.9
C(15)-C(14)-H(14A)	119.9
C(14)-C(15)-C(10)	120.05(11)
C(14)-C(15)-H(15A)	120.0
C(10)-C(15)-H(15A)	120.0
O(3)-C(16)-O(4)	125.46(11)
O(3)-C(16)-C(5)	123.47(10)
O(4)-C(16)-C(5)	110.90(10)
O(4)-C(17)-H(17A)	109.5
O(4)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
O(4)-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 **16a**. 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}
Cl(1)	20(1)	24(1)	17(1)	-5(1)	1(1)	-5(1)
O(1)	17(1)	13(1)	24(1)	0(1)	-1(1)	2(1)
O(2)	14(1)	13(1)	16(1)	-1(1)	-1(1)	0(1)
O(3)	26(1)	17(1)	17(1)	0(1)	8(1)	0(1)
O(4)	26(1)	12(1)	17(1)	-1(1)	7(1)	-3(1)
N(1)	17(1)	15(1)	17(1)	0(1)	4(1)	-2(1)
N(2)	14(1)	11(1)	15(1)	0(1)	2(1)	0(1)
C(1)	15(1)	18(1)	12(1)	-1(1)	4(1)	-4(1)
C(2)	14(1)	19(1)	15(1)	2(1)	1(1)	1(1)
C(3)	14(1)	14(1)	15(1)	2(1)	4(1)	0(1)
C(4)	16(1)	14(1)	18(1)	1(1)	2(1)	2(1)
C(5)	15(1)	12(1)	16(1)	1(1)	5(1)	1(1)
C(6)	12(1)	14(1)	13(1)	0(1)	3(1)	-1(1)
C(7)	15(1)	14(1)	16(1)	1(1)	3(1)	0(1)
C(8)	13(1)	14(1)	14(1)	0(1)	4(1)	0(1)
C(9)	14(1)	16(1)	19(1)	0(1)	-3(1)	0(1)
C(10)	15(1)	15(1)	14(1)	1(1)	0(1)	0(1)
C(11)	17(1)	24(1)	26(1)	-5(1)	9(1)	-5(1)
C(12)	25(1)	26(1)	28(1)	-10(1)	12(1)	-5(1)
C(13)	24(1)	21(1)	20(1)	-6(1)	5(1)	-8(1)
C(14)	17(1)	24(1)	20(1)	0(1)	5(1)	-6(1)
C(15)	16(1)	19(1)	16(1)	0(1)	3(1)	1(1)
C(16)	12(1)	13(1)	17(1)	1(1)	3(1)	2(1)
C(17)	30(1)	14(1)	23(1)	-4(1)	7(1)	-4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **16a**.

	x	y	z	U(eq)
H(2A)	8818	9558	10715	20
H(4A)	7376	8517	8527	20
H(7A)	4552	10696	7629	18
H(9A)	1175	9542	2876	21
H(9B)	295	9493	4353	21
H(11A)	2008	8393	2000	26
H(12A)	808	7466	887	31
H(13A)	-1677	7189	1292	26
H(14A)	-2955	7840	2805	24
H(15A)	-1746	8764	3941	21
H(17A)	3960	6934	5801	33
H(17B)	5175	7193	4793	33
H(17C)	3353	7392	4280	33

Table 6. Torsion angles [°] for **16a**.

C(7)-N(1)-C(1)-C(2)	-1.02(18)
C(7)-N(1)-C(1)-Cl(1)	178.26(9)
N(1)-C(1)-C(2)-C(3)	1.07(18)
Cl(1)-C(1)-C(2)-C(3)	-178.19(8)
C(1)-C(2)-C(3)-C(6)	0.39(16)
C(1)-C(2)-C(3)-C(4)	179.39(12)
C(2)-C(3)-C(4)-C(5)	-178.13(13)
C(6)-C(3)-C(4)-C(5)	0.94(13)
C(3)-C(4)-C(5)-N(2)	-0.86(13)
C(3)-C(4)-C(5)-C(16)	167.87(11)
C(6)-N(2)-C(5)-C(4)	0.45(13)
C(8)-N(2)-C(5)-C(4)	-170.82(11)
C(6)-N(2)-C(5)-C(16)	-168.77(10)
C(8)-N(2)-C(5)-C(16)	19.96(17)
C(8)-N(2)-C(6)-C(7)	-7.61(19)
C(5)-N(2)-C(6)-C(7)	-179.38(12)
C(8)-N(2)-C(6)-C(3)	171.93(10)
C(5)-N(2)-C(6)-C(3)	0.16(12)
C(2)-C(3)-C(6)-C(7)	-1.83(17)
C(4)-C(3)-C(6)-C(7)	178.93(10)
C(2)-C(3)-C(6)-N(2)	178.57(10)
C(4)-C(3)-C(6)-N(2)	-0.67(13)
C(1)-N(1)-C(7)-C(6)	-0.52(17)
N(2)-C(6)-C(7)-N(1)	-178.59(11)
C(3)-C(6)-C(7)-N(1)	1.93(17)
C(9)-O(2)-C(8)-O(1)	2.51(17)
C(9)-O(2)-C(8)-N(2)	-178.06(9)
C(6)-N(2)-C(8)-O(1)	14.18(17)
C(5)-N(2)-C(8)-O(1)	-175.81(11)
C(6)-N(2)-C(8)-O(2)	-165.27(10)
C(5)-N(2)-C(8)-O(2)	4.74(16)
C(8)-O(2)-C(9)-C(10)	-177.63(10)
O(2)-C(9)-C(10)-C(15)	120.31(12)
O(2)-C(9)-C(10)-C(11)	-61.51(15)
C(15)-C(10)-C(11)-C(12)	-0.31(19)

C(9)-C(10)-C(11)-C(12)	-178.50(12)
C(10)-C(11)-C(12)-C(13)	0.3(2)
C(11)-C(12)-C(13)-C(14)	0.1(2)
C(12)-C(13)-C(14)-C(15)	-0.3(2)
C(13)-C(14)-C(15)-C(10)	0.29(19)
C(11)-C(10)-C(15)-C(14)	0.04(18)
C(9)-C(10)-C(15)-C(14)	178.24(11)
C(17)-O(4)-C(16)-O(3)	0.14(17)
C(17)-O(4)-C(16)-C(5)	-175.33(10)
C(4)-C(5)-C(16)-O(3)	-108.82(15)
N(2)-C(5)-C(16)-O(3)	58.58(16)
C(4)-C(5)-C(16)-O(4)	66.76(15)
N(2)-C(5)-C(16)-O(4)	-125.84(11)

Symmetry transformations used to generate equivalent atoms:

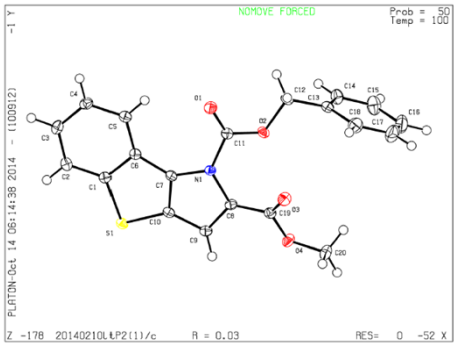


Table 1. Crystal data and structure refinement for **20**

Identification code	20140210lt	
Empirical formula	C20 H15 N O4 S	
Formula weight	365.39	
Temperature	100(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 15.7471(4) Å	□= 90°.
	b = 7.1137(2) Å	□= 94.4920(10)°.
	c = 15.1029(3) Å	□ = 90°.
Volume	1686.63(7) $Å^3$	
Z	4	
Density (calculated)	1.439 Mg/m^3	
Absorption coefficient	0.218 mm^{-1}	
F(000)	760	
Crystal size	0.20 x 0.07 x 0.06 mm^3	
Theta range for data collection	1.30 to 28.31°	
Index ranges	-20<=h<=20, -9<=k<=9, -19<=l<=20	
Reflections collected	44270	
Independent reflections	4181 [R(int) = 0.0477]	
Completeness to theta = 28.31°	99.6 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9870 and 0.9576	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4181 / 0 / 235	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R1 = 0.0349, wR2 = 0.0824	
R indices (all data)	R1 = 0.0486, wR2 = 0.0896	
Largest diff. peak and hole	0.288 and -0.313 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **20**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	5800(1)	7482(1)	-760(1)	15(1)
O(1)	4181(1)	6669(2)	2324(1)	20(1)
O(2)	2958(1)	6135(1)	1476(1)	17(1)
O(3)	2401(1)	9586(1)	848(1)	20(1)
O(4)	2191(1)	8832(2)	-600(1)	19(1)
N(1)	4037(1)	7523(2)	851(1)	13(1)
C(1)	6266(1)	6786(2)	282(1)	14(1)
C(2)	7122(1)	6325(2)	461(1)	18(1)
C(3)	7406(1)	5815(2)	1317(1)	20(1)
C(4)	6842(1)	5733(2)	1988(1)	18(1)
C(5)	5991(1)	6181(2)	1816(1)	16(1)
C(6)	5687(1)	6726(2)	956(1)	14(1)
C(7)	4858(1)	7298(2)	576(1)	14(1)
C(8)	3510(1)	8110(2)	104(1)	15(1)
C(9)	3987(1)	8254(2)	-616(1)	15(1)
C(10)	4826(1)	7728(2)	-315(1)	14(1)
C(11)	3755(1)	6753(2)	1632(1)	15(1)
C(12)	2525(1)	5646(2)	2264(1)	18(1)
C(13)	1620(1)	5230(2)	1931(1)	19(1)
C(14)	1402(1)	3465(2)	1589(1)	23(1)
C(15)	576(1)	3102(3)	1240(1)	31(1)
C(16)	-41(1)	4494(3)	1241(1)	33(1)
C(17)	168(1)	6241(3)	1596(1)	34(1)
C(18)	997(1)	6615(2)	1932(1)	27(1)
C(19)	2658(1)	8898(2)	187(1)	16(1)
C(20)	1367(1)	9713(2)	-596(1)	23(1)

Table 3. Bond lengths [Å] and angles [°] for **20**.

S(1)-C(10)	1.7303(14)
S(1)-C(1)	1.7544(13)
O(1)-C(11)	1.1974(16)
O(2)-C(11)	1.3337(16)
O(2)-C(12)	1.4592(16)
O(3)-C(19)	1.2088(16)
O(4)-C(19)	1.3494(16)
O(4)-C(20)	1.4417(17)
N(1)-C(7)	1.3989(17)
N(1)-C(11)	1.4042(17)
N(1)-C(8)	1.4092(16)
C(1)-C(2)	1.3942(18)
C(1)-C(6)	1.4189(19)
C(2)-C(3)	1.383(2)
C(2)-H(2A)	0.9500
C(3)-C(4)	1.399(2)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.3826(19)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.4026(18)
C(5)-H(5A)	0.9500
C(6)-C(7)	1.4426(18)
C(7)-C(10)	1.3757(18)
C(8)-C(9)	1.3730(19)
C(8)-C(19)	1.4686(19)
C(9)-C(10)	1.4148(18)
C(9)-H(9A)	0.9500
C(12)-C(13)	1.5046(19)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(18)	1.390(2)
C(13)-C(14)	1.391(2)
C(14)-C(15)	1.389(2)
C(14)-H(14A)	0.9500
C(15)-C(16)	1.386(2)

C(15)-H(15A)	0.9500
C(16)-C(17)	1.383(3)
C(16)-H(16A)	0.9500
C(17)-C(18)	1.389(2)
C(17)-H(17A)	0.9500
C(18)-H(18A)	0.9500
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800

C(10)-S(1)-C(1)	90.05(6)
C(11)-O(2)-C(12)	115.29(10)
C(19)-O(4)-C(20)	114.19(11)
C(7)-N(1)-C(11)	124.43(11)
C(7)-N(1)-C(8)	107.24(11)
C(11)-N(1)-C(8)	125.67(11)
C(2)-C(1)-C(6)	121.32(12)
C(2)-C(1)-S(1)	124.79(11)
C(6)-C(1)-S(1)	113.89(10)
C(3)-C(2)-C(1)	118.65(13)
C(3)-C(2)-H(2A)	120.7
C(1)-C(2)-H(2A)	120.7
C(2)-C(3)-C(4)	120.74(13)
C(2)-C(3)-H(3A)	119.6
C(4)-C(3)-H(3A)	119.6
C(5)-C(4)-C(3)	121.00(13)
C(5)-C(4)-H(4A)	119.5
C(3)-C(4)-H(4A)	119.5
C(4)-C(5)-C(6)	119.56(13)
C(4)-C(5)-H(5A)	120.2
C(6)-C(5)-H(5A)	120.2
C(5)-C(6)-C(1)	118.73(12)
C(5)-C(6)-C(7)	132.77(13)
C(1)-C(6)-C(7)	108.50(11)
C(10)-C(7)-N(1)	107.50(11)
C(10)-C(7)-C(6)	114.51(12)
N(1)-C(7)-C(6)	137.97(12)

C(9)-C(8)-N(1)	109.39(12)
C(9)-C(8)-C(19)	126.78(12)
N(1)-C(8)-C(19)	121.95(12)
C(8)-C(9)-C(10)	106.28(12)
C(8)-C(9)-H(9A)	126.9
C(10)-C(9)-H(9A)	126.9
C(7)-C(10)-C(9)	109.58(12)
C(7)-C(10)-S(1)	113.04(10)
C(9)-C(10)-S(1)	137.38(11)
O(1)-C(11)-O(2)	126.34(13)
O(1)-C(11)-N(1)	124.12(12)
O(2)-C(11)-N(1)	109.54(11)
O(2)-C(12)-C(13)	105.36(11)
O(2)-C(12)-H(12A)	110.7
C(13)-C(12)-H(12A)	110.7
O(2)-C(12)-H(12B)	110.7
C(13)-C(12)-H(12B)	110.7
H(12A)-C(12)-H(12B)	108.8
C(18)-C(13)-C(14)	119.16(14)
C(18)-C(13)-C(12)	120.67(14)
C(14)-C(13)-C(12)	120.13(13)
C(15)-C(14)-C(13)	120.36(14)
C(15)-C(14)-H(14A)	119.8
C(13)-C(14)-H(14A)	119.8
C(16)-C(15)-C(14)	120.11(16)
C(16)-C(15)-H(15A)	119.9
C(14)-C(15)-H(15A)	119.9
C(17)-C(16)-C(15)	119.79(15)
C(17)-C(16)-H(16A)	120.1
C(15)-C(16)-H(16A)	120.1
C(16)-C(17)-C(18)	120.15(15)
C(16)-C(17)-H(17A)	119.9
C(18)-C(17)-H(17A)	119.9
C(17)-C(18)-C(13)	120.41(16)
C(17)-C(18)-H(18A)	119.8
C(13)-C(18)-H(18A)	119.8
O(3)-C(19)-O(4)	123.13(12)

O(3)-C(19)-C(8)	126.31(12)
O(4)-C(19)-C(8)	110.51(11)
O(4)-C(20)-H(20A)	109.5
O(4)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
O(4)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **20**. 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)	17(1)	17(1)	13(1)	0(1)	3(1)	-1(1)
O(1)	19(1)	29(1)	12(1)	0(1)	1(1)	1(1)
O(2)	17(1)	22(1)	12(1)	1(1)	3(1)	-2(1)
O(3)	21(1)	22(1)	17(1)	-3(1)	2(1)	3(1)
O(4)	17(1)	25(1)	15(1)	-2(1)	-2(1)	4(1)
N(1)	15(1)	14(1)	11(1)	0(1)	0(1)	0(1)
C(1)	17(1)	12(1)	15(1)	-1(1)	0(1)	-1(1)
C(2)	16(1)	18(1)	20(1)	-2(1)	3(1)	-2(1)
C(3)	16(1)	18(1)	24(1)	-2(1)	-2(1)	1(1)
C(4)	20(1)	16(1)	18(1)	0(1)	-3(1)	-1(1)
C(5)	19(1)	15(1)	15(1)	0(1)	2(1)	-1(1)
C(6)	16(1)	10(1)	15(1)	-1(1)	1(1)	-2(1)
C(7)	16(1)	12(1)	13(1)	0(1)	2(1)	-1(1)
C(8)	18(1)	14(1)	12(1)	-1(1)	-1(1)	0(1)
C(9)	19(1)	13(1)	12(1)	0(1)	0(1)	-1(1)
C(10)	17(1)	13(1)	13(1)	0(1)	3(1)	-2(1)
C(11)	18(1)	14(1)	13(1)	-2(1)	3(1)	1(1)
C(12)	19(1)	22(1)	14(1)	3(1)	4(1)	-2(1)
C(13)	18(1)	24(1)	14(1)	4(1)	4(1)	1(1)
C(14)	19(1)	25(1)	27(1)	-2(1)	5(1)	1(1)
C(15)	24(1)	34(1)	36(1)	-10(1)	4(1)	-5(1)
C(16)	18(1)	48(1)	33(1)	-1(1)	1(1)	-1(1)
C(17)	24(1)	39(1)	38(1)	2(1)	2(1)	11(1)
C(18)	26(1)	25(1)	30(1)	0(1)	4(1)	4(1)
C(19)	17(1)	14(1)	16(1)	1(1)	0(1)	-2(1)
C(20)	16(1)	29(1)	25(1)	-1(1)	-2(1)	3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **20**.

	x	y	z	U(eq)
H(2A)	7504	6360	4	22
H(3A)	7990	5517	1452	23
H(4A)	7048	5365	2570	22
H(5A)	5614	6119	2276	20
H(9A)	3792	8632	-1200	18
H(12A)	2549	6706	2690	22
H(12B)	2793	4531	2562	22
H(14A)	1820	2503	1593	28
H(15A)	432	1898	1001	37
H(16A)	-605	4249	998	39
H(17A)	-256	7187	1610	41
H(18A)	1140	7826	2164	33
H(20A)	1067	9613	-1188	35
H(20B)	1439	11042	-436	35
H(20C)	1034	9083	-161	35

Table 6. Torsion angles [°] for **20**.

C(10)-S(1)-C(1)-C(2)	-179.40(13)
C(10)-S(1)-C(1)-C(6)	0.52(11)
C(6)-C(1)-C(2)-C(3)	-0.5(2)
S(1)-C(1)-C(2)-C(3)	179.41(11)
C(1)-C(2)-C(3)-C(4)	1.0(2)
C(2)-C(3)-C(4)-C(5)	-0.8(2)
C(3)-C(4)-C(5)-C(6)	-0.1(2)
C(4)-C(5)-C(6)-C(1)	0.6(2)
C(4)-C(5)-C(6)-C(7)	-178.76(14)
C(2)-C(1)-C(6)-C(5)	-0.3(2)
S(1)-C(1)-C(6)-C(5)	179.77(10)
C(2)-C(1)-C(6)-C(7)	179.18(12)
S(1)-C(1)-C(6)-C(7)	-0.74(14)
C(11)-N(1)-C(7)-C(10)	162.01(12)
C(8)-N(1)-C(7)-C(10)	-0.36(14)
C(11)-N(1)-C(7)-C(6)	-16.4(2)
C(8)-N(1)-C(7)-C(6)	-178.80(15)
C(5)-C(6)-C(7)-C(10)	-179.96(14)
C(1)-C(6)-C(7)-C(10)	0.65(16)
C(5)-C(6)-C(7)-N(1)	-1.6(3)
C(1)-C(6)-C(7)-N(1)	179.02(15)
C(7)-N(1)-C(8)-C(9)	-0.15(15)
C(11)-N(1)-C(8)-C(9)	-162.25(12)
C(7)-N(1)-C(8)-C(19)	-165.54(12)
C(11)-N(1)-C(8)-C(19)	32.37(19)
N(1)-C(8)-C(9)-C(10)	0.59(15)
C(19)-C(8)-C(9)-C(10)	165.08(13)
N(1)-C(7)-C(10)-C(9)	0.73(15)
C(6)-C(7)-C(10)-C(9)	179.59(11)
N(1)-C(7)-C(10)-S(1)	-179.14(9)
C(6)-C(7)-C(10)-S(1)	-0.28(15)
C(8)-C(9)-C(10)-C(7)	-0.82(15)
C(8)-C(9)-C(10)-S(1)	179.00(12)
C(1)-S(1)-C(10)-C(7)	-0.13(11)
C(1)-S(1)-C(10)-C(9)	-179.95(15)

C(12)-O(2)-C(11)-O(1)	12.2(2)
C(12)-O(2)-C(11)-N(1)	-168.24(11)
C(7)-N(1)-C(11)-O(1)	38.9(2)
C(8)-N(1)-C(11)-O(1)	-161.92(13)
C(7)-N(1)-C(11)-O(2)	-140.60(12)
C(8)-N(1)-C(11)-O(2)	18.55(18)
C(11)-O(2)-C(12)-C(13)	173.18(11)
O(2)-C(12)-C(13)-C(18)	-94.92(15)
O(2)-C(12)-C(13)-C(14)	82.86(15)
C(18)-C(13)-C(14)-C(15)	1.0(2)
C(12)-C(13)-C(14)-C(15)	-176.83(14)
C(13)-C(14)-C(15)-C(16)	-0.7(3)
C(14)-C(15)-C(16)-C(17)	-0.5(3)
C(15)-C(16)-C(17)-C(18)	1.5(3)
C(16)-C(17)-C(18)-C(13)	-1.3(3)
C(14)-C(13)-C(18)-C(17)	0.0(2)
C(12)-C(13)-C(18)-C(17)	177.83(14)
C(20)-O(4)-C(19)-O(3)	2.04(19)
C(20)-O(4)-C(19)-C(8)	-175.40(12)
C(9)-C(8)-C(19)-O(3)	-141.93(15)
N(1)-C(8)-C(19)-O(3)	20.8(2)
C(9)-C(8)-C(19)-O(4)	35.40(19)
N(1)-C(8)-C(19)-O(4)	-161.89(12)

Symmetry transformations used to generate equivalent atoms: