

**Selective access to 3-cyano-1*H*-indoles, 9*H*-pyrimido[4,5-*b*]indoles or 9*H*-pyrido[2,3-*b*]indoles
through copper-catalyzed one-pot multi-component cascade reactions**

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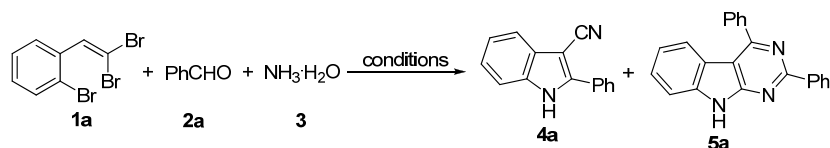
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I. Optimization Studies^[a]



Entry	3 (mL)	Catalyst	Additives (equiv)	Solvent (mL)	Yield of 4a [%] ^[b]	Yield of 5a [%] ^[b]
1	1.5	CuI	-	DMF(3)	15	21
2	1.5	CuI	1,10-phen(0.2)	DMF(3)	19	24
3	1.5	CuI	TMEDA(0.2)	DMF(3)	11	13
4	1.5	CuI	DMEDA(0.2)	DMF(3)	14	18
5	1.5	CuI	DMAP(0.2)	DMF(3)	17	19
6	1.5	CuI	L-Proline(0.2)	DMF(3)	15	24
7	1.5	CuI	DABCO(A) (0.2)	DMF(3)	22	30
8	1.5	CuI	PivOH(B) (1)	DMF(3)	26	24
9	1.5	CuI	TBAB(1)	DMF(3)	20	23
10	1.5	CuI	DABCO(0.5)	DMF(3)	23	31
11	1.5	CuI	DABCO(1)	DMF(3)	21	31
12	1.5	CuI	B(1)+TBAB(1)	DMF(3)	27	23
13	1.5	CuI	A(0.2)+ DMAP(0.2)	DMF(3)	19	22
14	1.5	CuI	A(0.2) + B(1)	DMF(3)	32	30
15	1.5	CuI	A(0.2) + B(1)	DMF(2)	56	13
16	1.5	CuI	A(0.2) + B(1)	DMF(1.5)	62	trace
17	0.75	CuI	A(0.2) + B(1)	DMF(0.75)	25	13
18	3	CuI	A(0.2) + B(1)	DMF(3)	52	trace
19	1.5	CuI	A(0.2) + B(1)	DMF(1)	49	trace
20	1.5	CuI	A(0.2) + B(0.5)	DMF(1.5)	54	trace
21	1.5	CuI	A(0.2) + B(2)	DMF(1.5)	62	trace
22	1.5	CuI	A(0.2) + B(1)	DMSO(1.5)	60	trace
23	1.5	CuI	A(0.2) + B(1)	NMP(1.5)	53	trace
24	1.5	CuI	A(0.2) + B(1)	<i>i</i> -PrOH(1.5)	44	trace
25	1.5	CuI	A(0.2) + B(1)	dioxane(1.5)	35	trace
26	1.5	CuCl	A(0.2) + B(1)	DMF(1.5)	52	trace

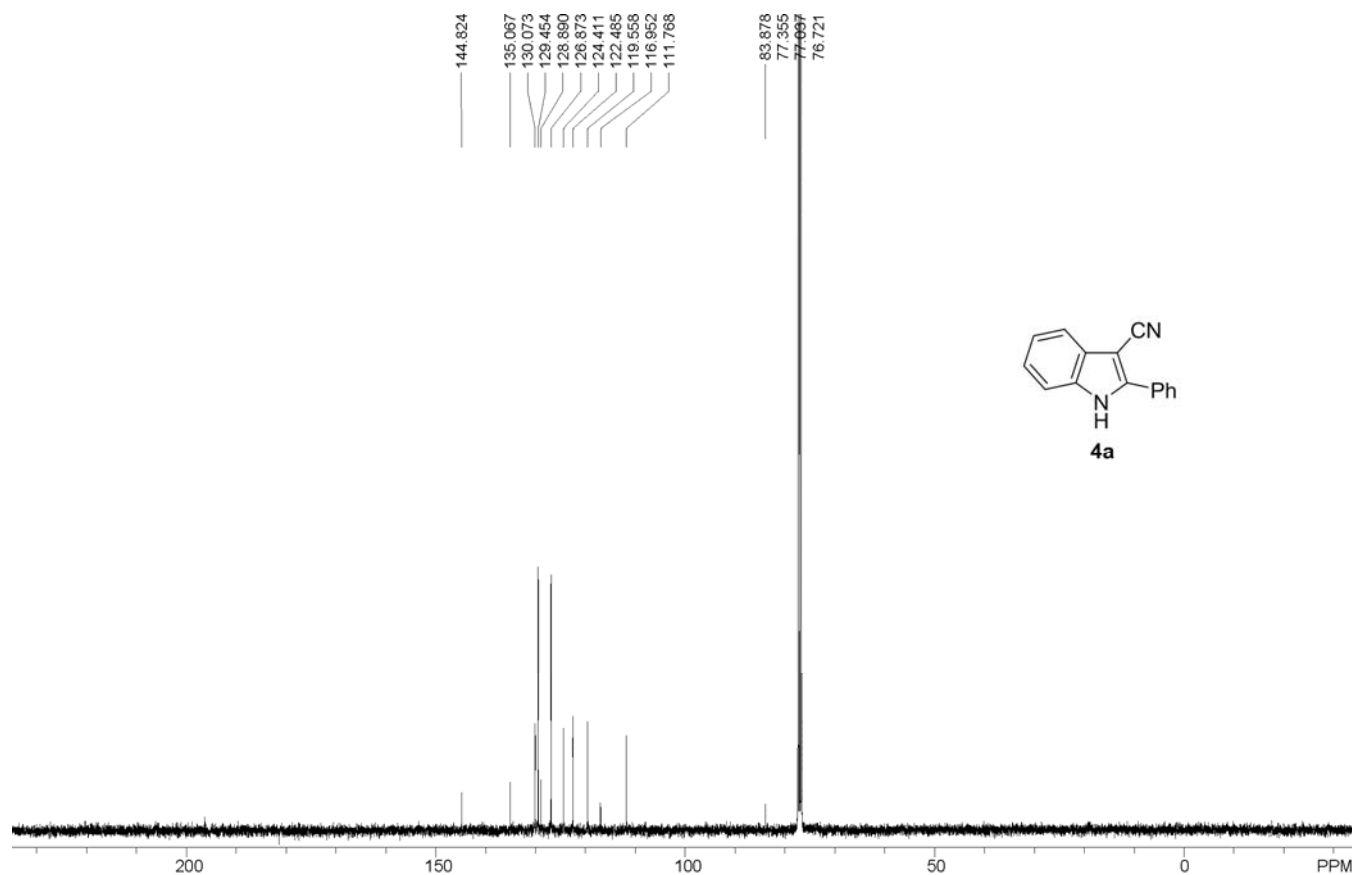
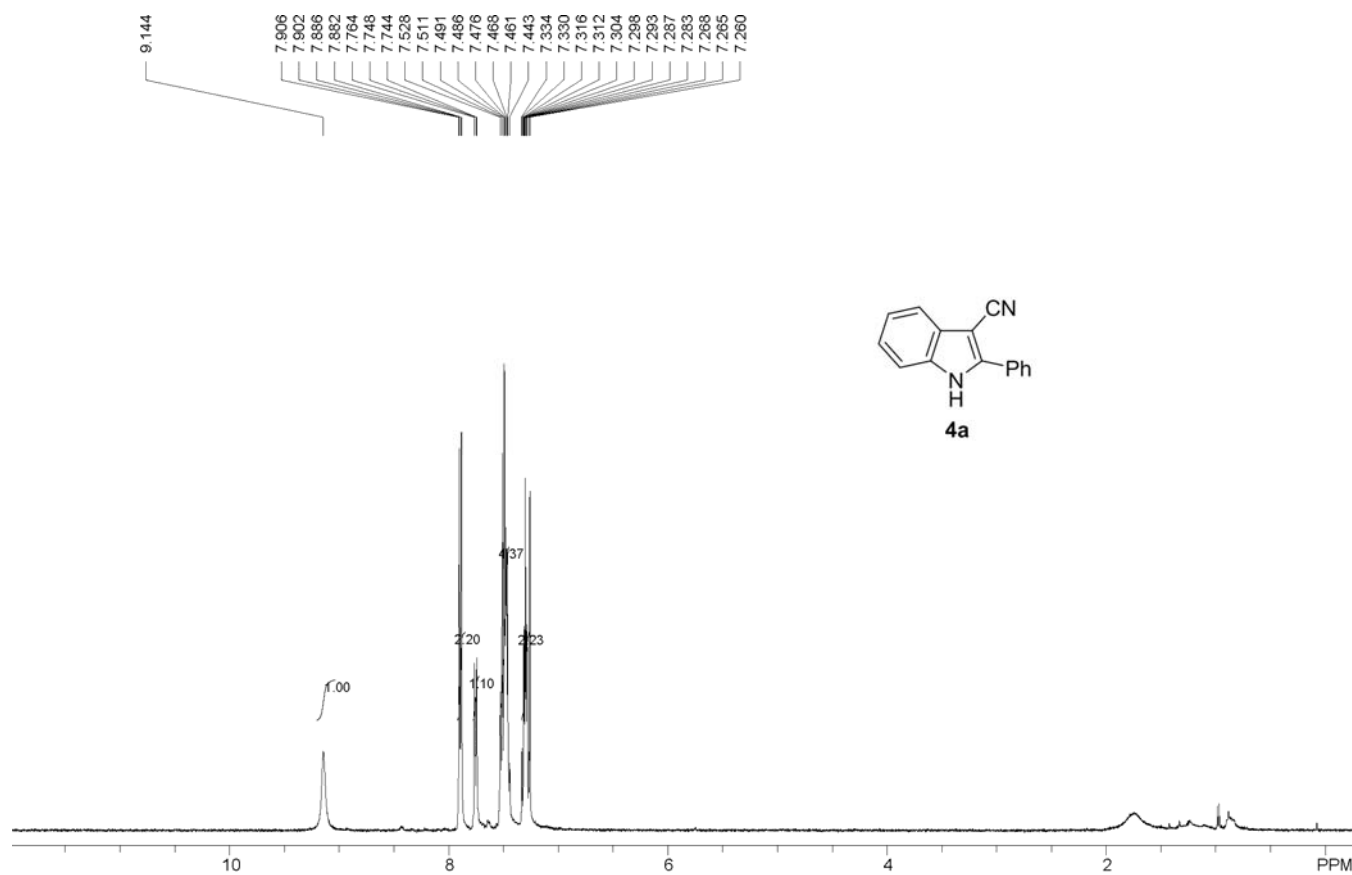
27	1.5	CuBr	A(0.2) + B(1)	DMF(1.5)	58	trace
28	1.5	Cu(OAc) ₂	A(0.2) + B(1)	DMF(1.5)	32	trace
29	1.5	-	A(0.2) + B(1)	DMF(1.5)	-	-
30	1	CuI	A(0.2) + B(1)	DMF(3)	22	35
31 ^[c]	1	CuI	A(0.2) + B(1)	DMF(3)	16	42
32 ^[c]	0.5	CuI	A(0.2) + B(1)	DMF(3)	trace	55
33 ^[c]	0.25	CuI	A(0.2) + B(1)	DMF(1.5)	trace	35
34 ^[c]	1	CuI	A(0.2) + B(1)	DMF(6)	5	47
35 ^[c]	0.5	CuI	A(0.2) + B(1)	DMF(4)	trace	41
36 ^[c]	0.5	CuI	A(0.2) + B(1)	DMSO(3)	trace	50
37 ^[c]	0.5	CuI	A(0.2) + B(1)	NMP(3)	trace	52
38 ^[c]	0.5	CuI	A(0.2) + B(1)	<i>i</i> -PrOH(3)	trace	37
39 ^[c]	0.5	CuI	A(0.2) + B(1)	dioxane(3)	trace	17
40 ^[c]	0.5	CuCl	A(0.2) + B(1)	DMF(3)	trace	43
41 ^[c]	0.5	CuBr	A(0.2) + B(1)	DMF(3)	trace	48
42 ^[c]	0.5	CuCl ₂	A(0.2) + B(1)	DMF(3)	trace	32
43 ^[c]	0.5	Cu(OAc) ₂	A(0.2) + B(1)	DMF(3)	trace	31

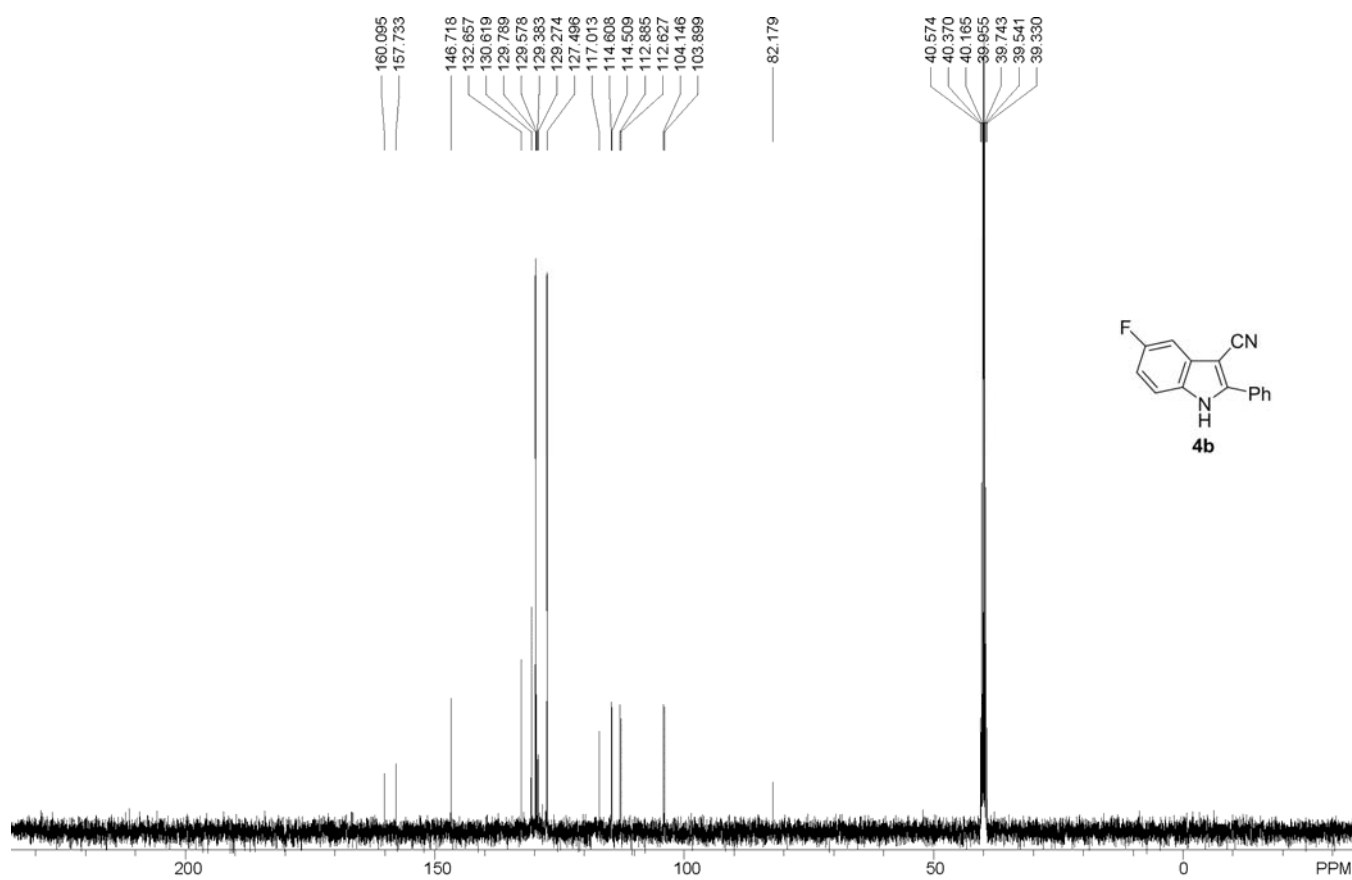
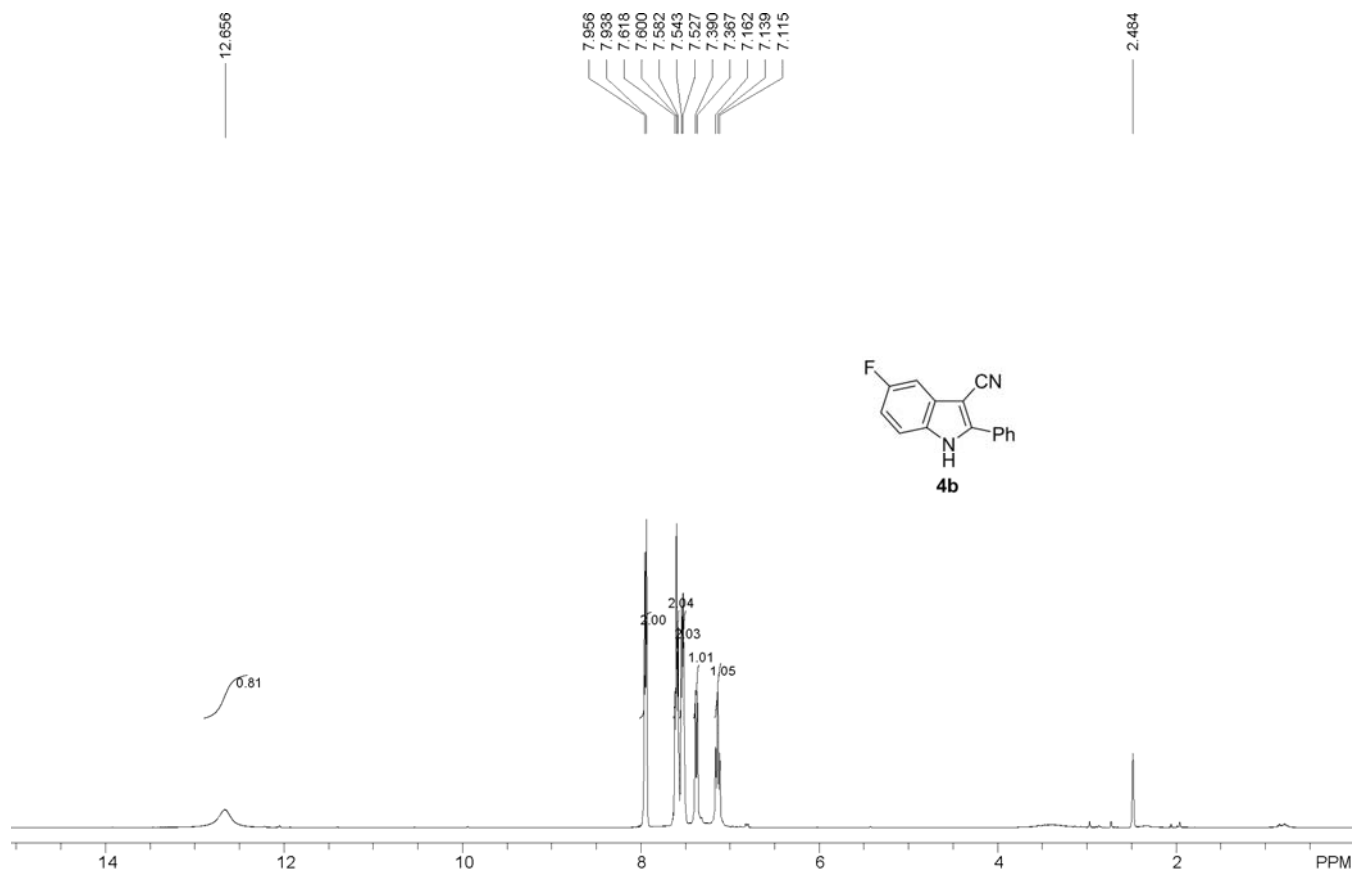
[a] Unless otherwise noted, reactions were carried out with 0.5 mmol of **1a**, 1 mmol of **2a**, 0.05 mmol of catalyst, at 80 °C in a sealed tube under air atmosphere for 24 h, 1,10-phen = 1,10-phenanthroline, TMEDA = N,N,N',N'-tetramethylethylene diamine, DMEDA = N,N'-dimethylethylene diamine, DMAP = 4-dimethylaminopyridine, DABCO = 1,4-diazabicyclo[2.2.2]octane, PivOH = 2,2-dimethylpropanoic acid, TBAB = tetrabutyl ammonium bromide.

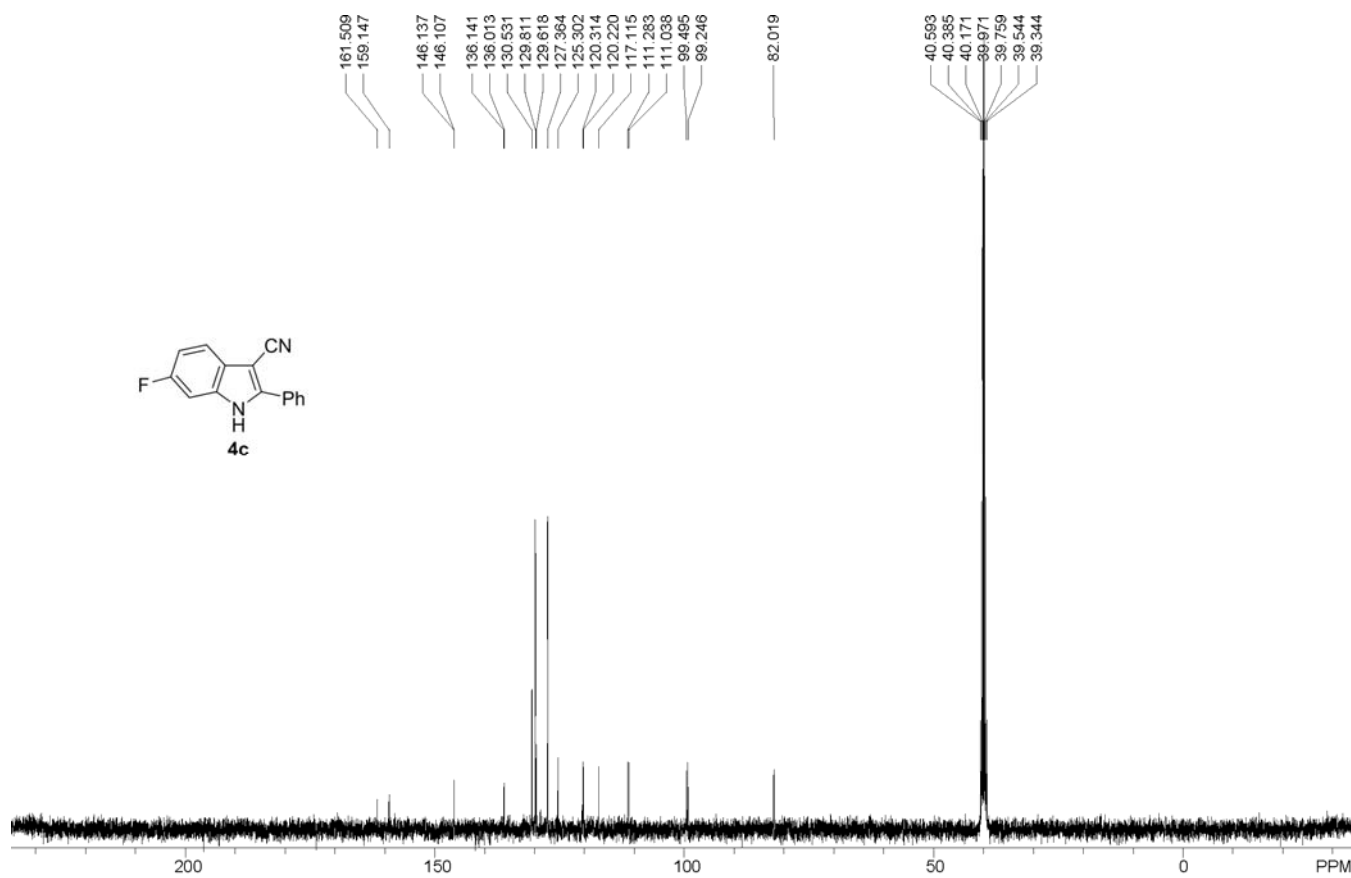
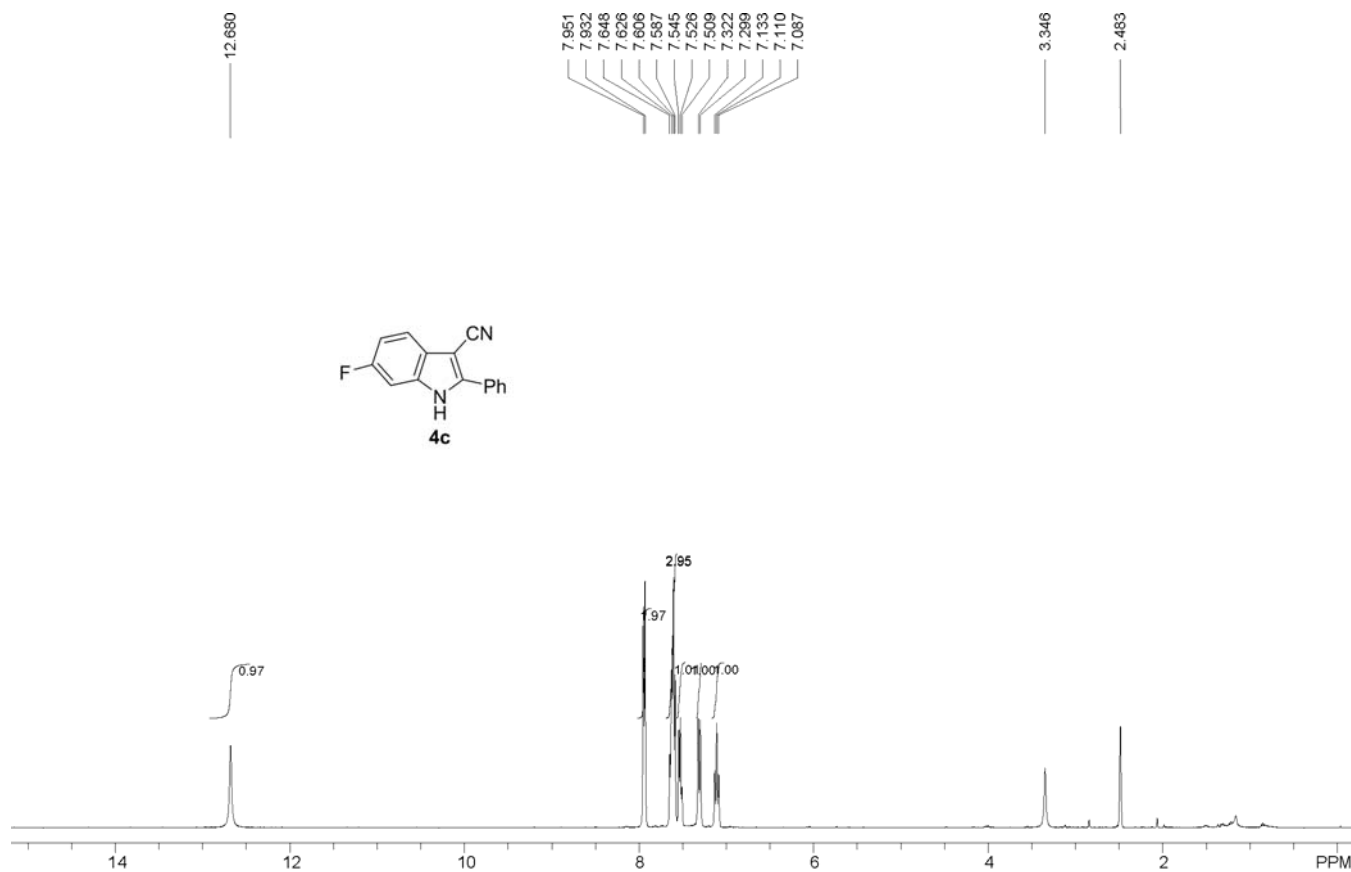
[b] Isolated yield.

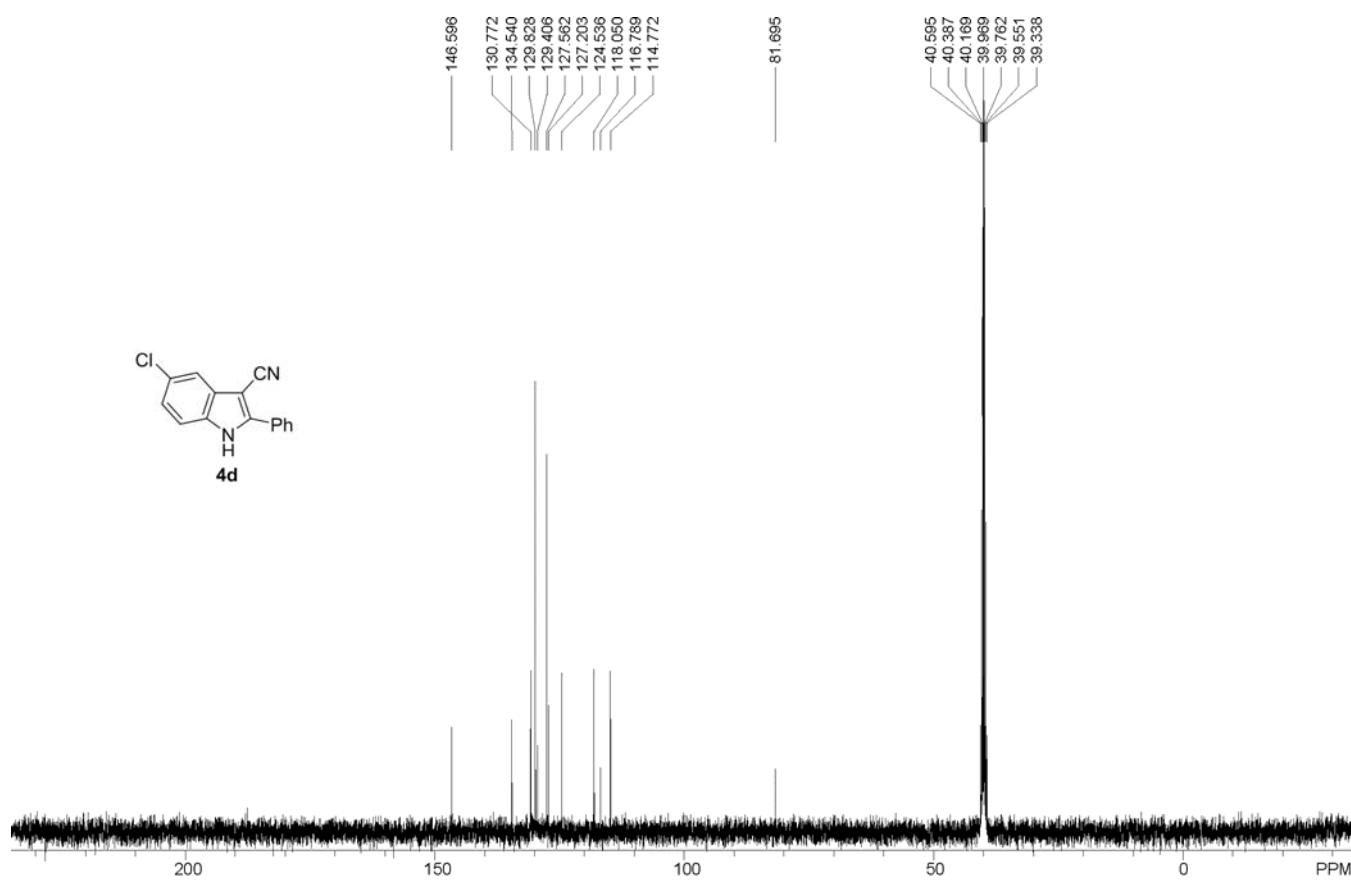
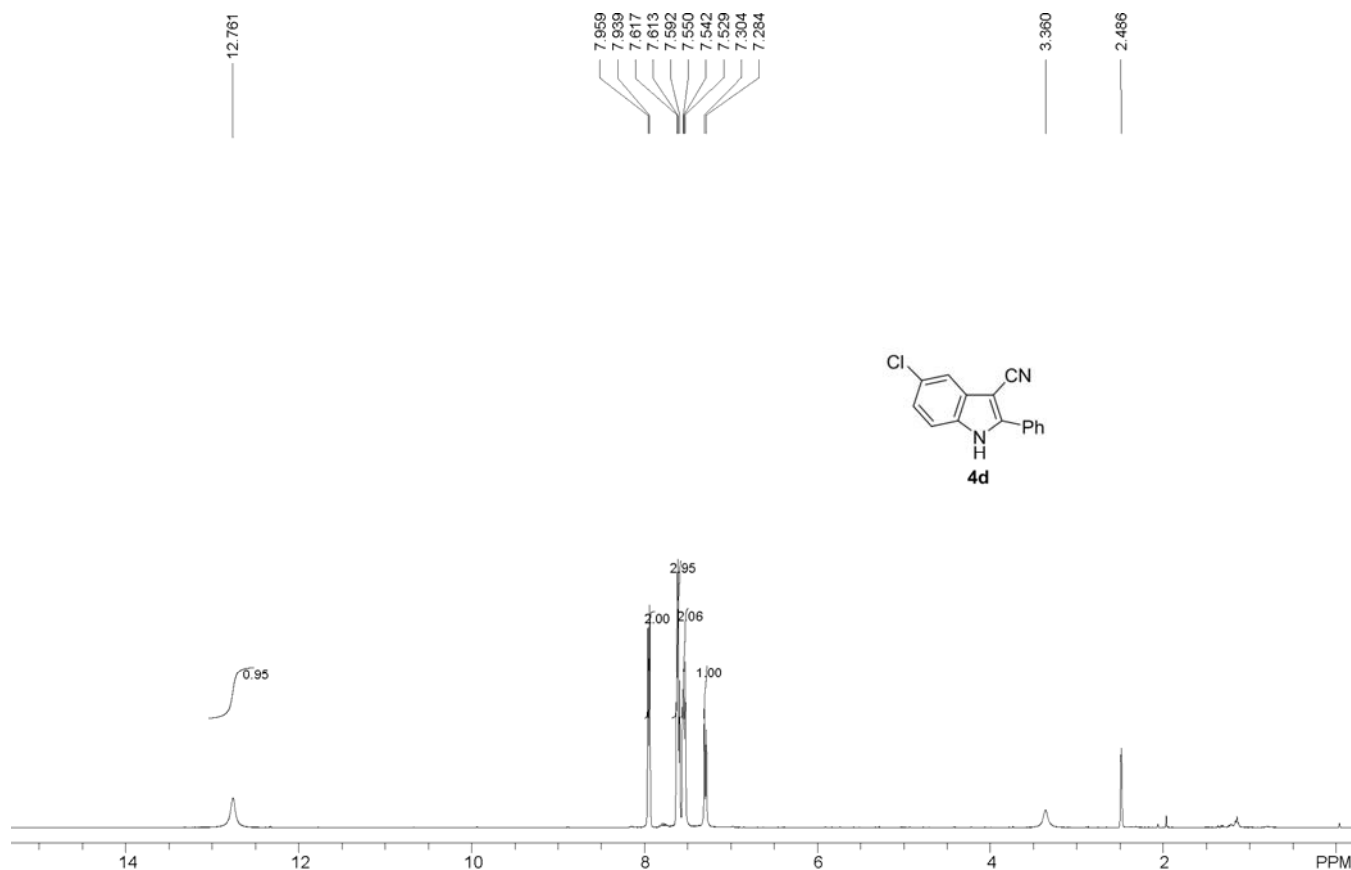
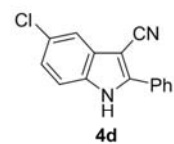
[c] With 1.5 mmol of **2a**, 30 h.

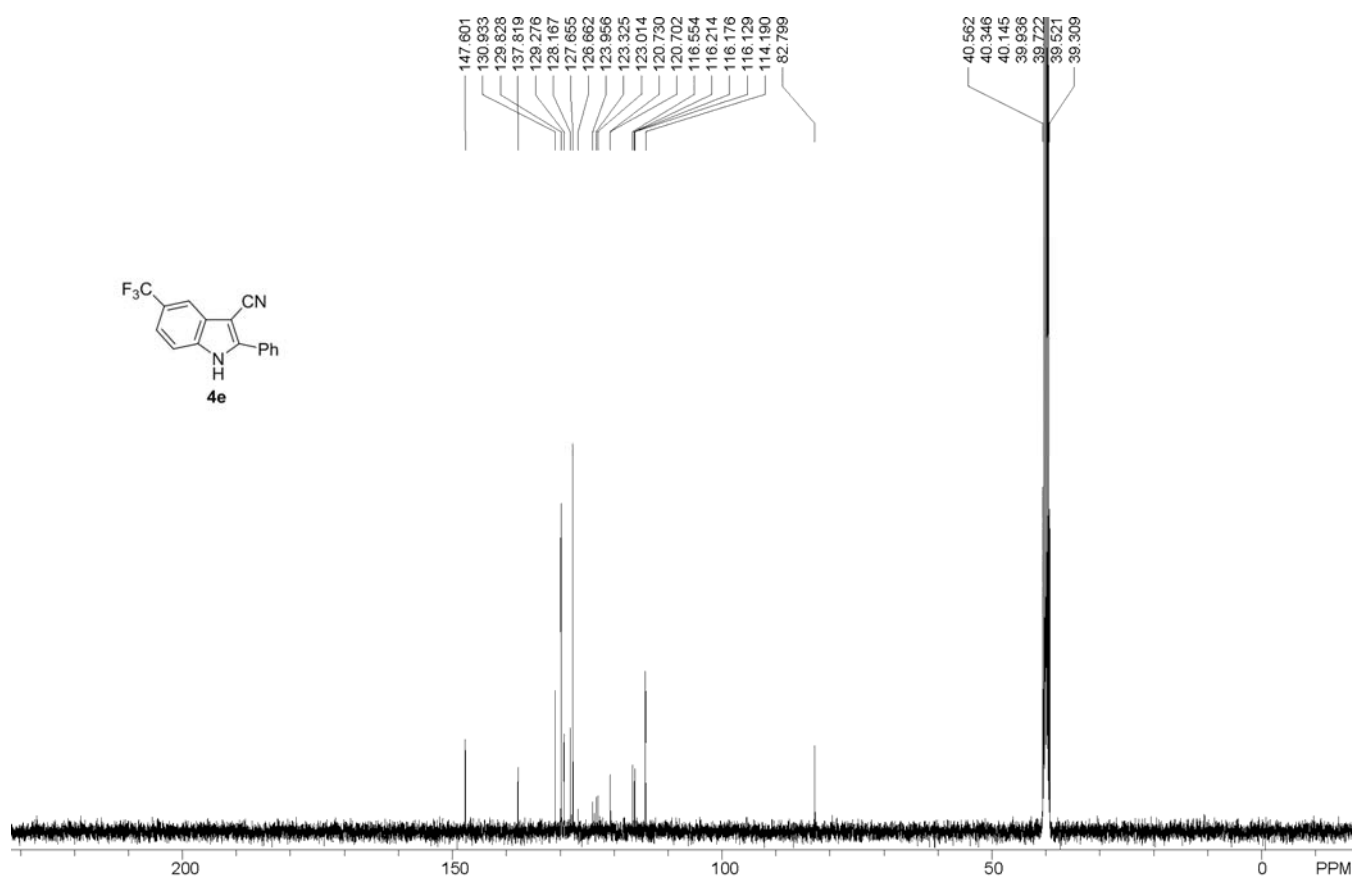
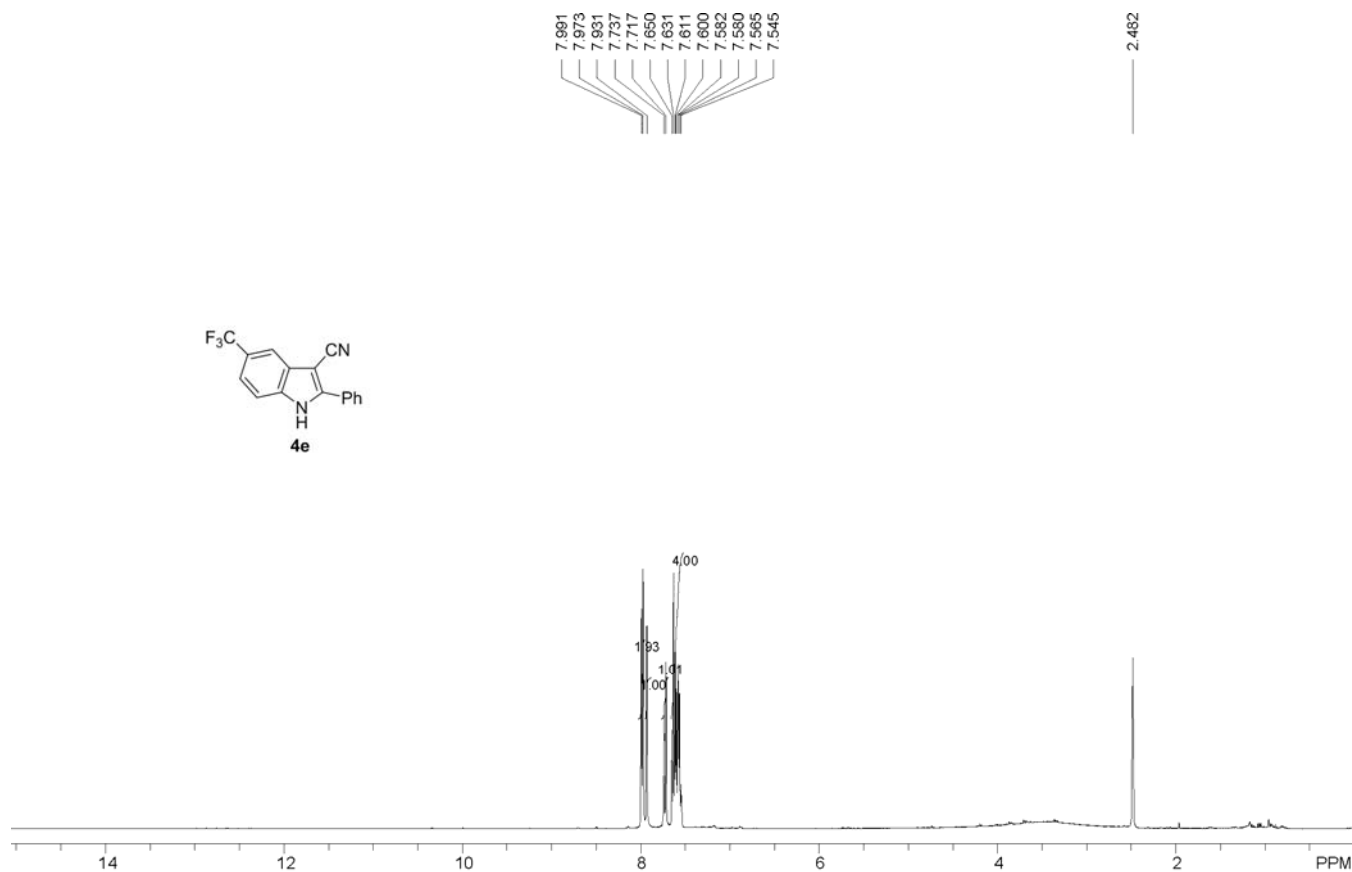
II. Copies of ^1H and ^{13}C NMR spectra of 4a-4ii

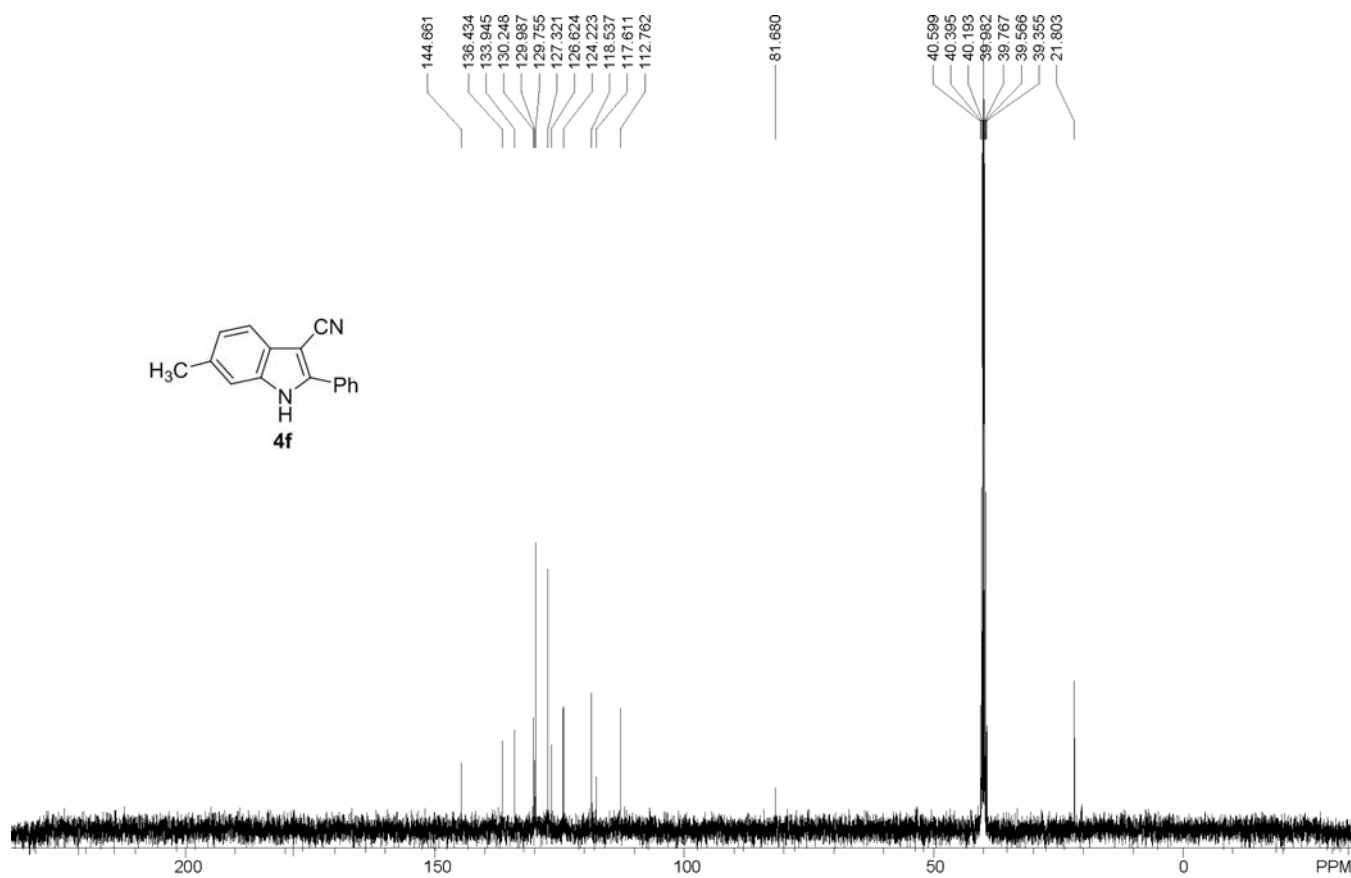
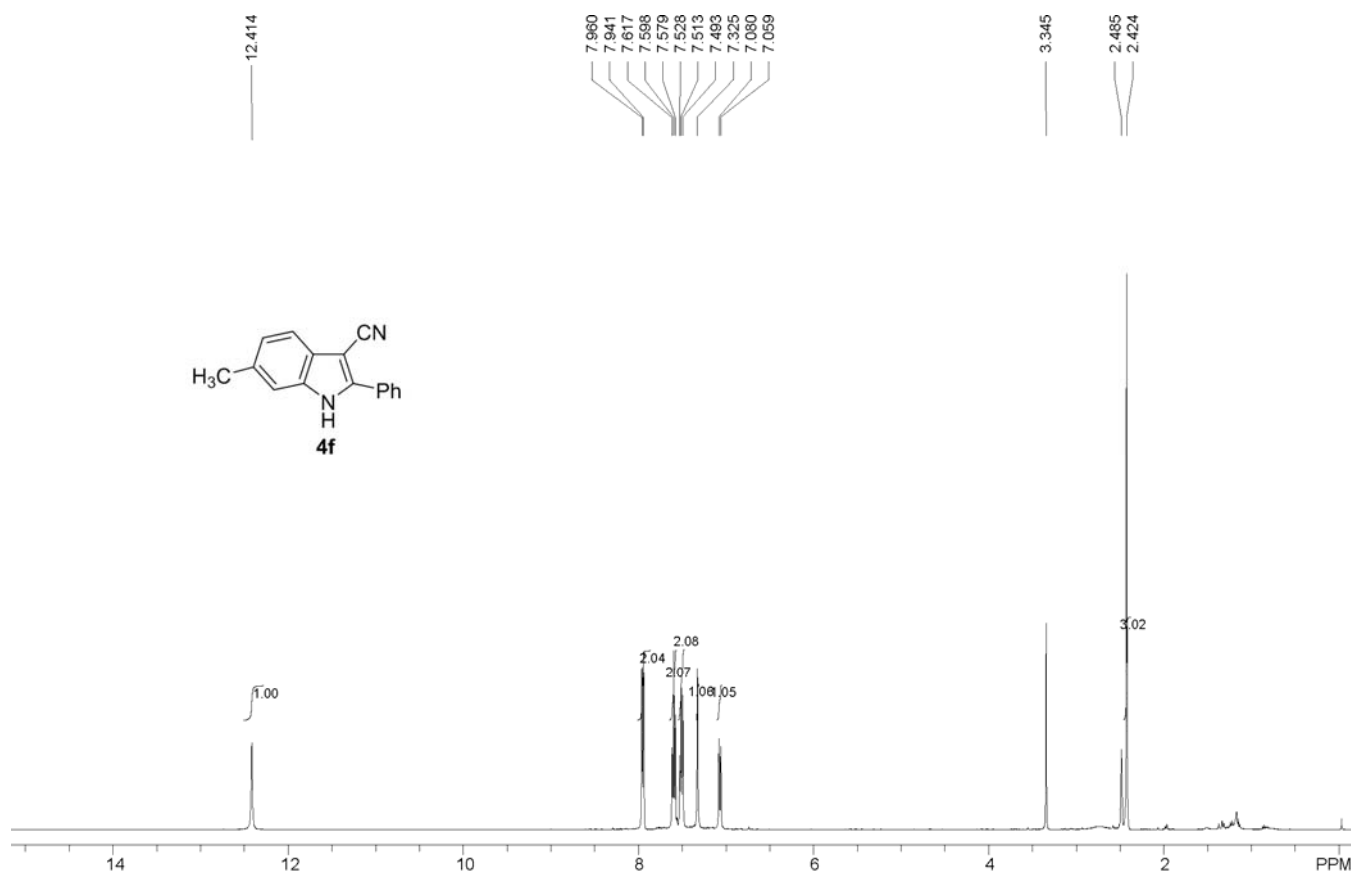


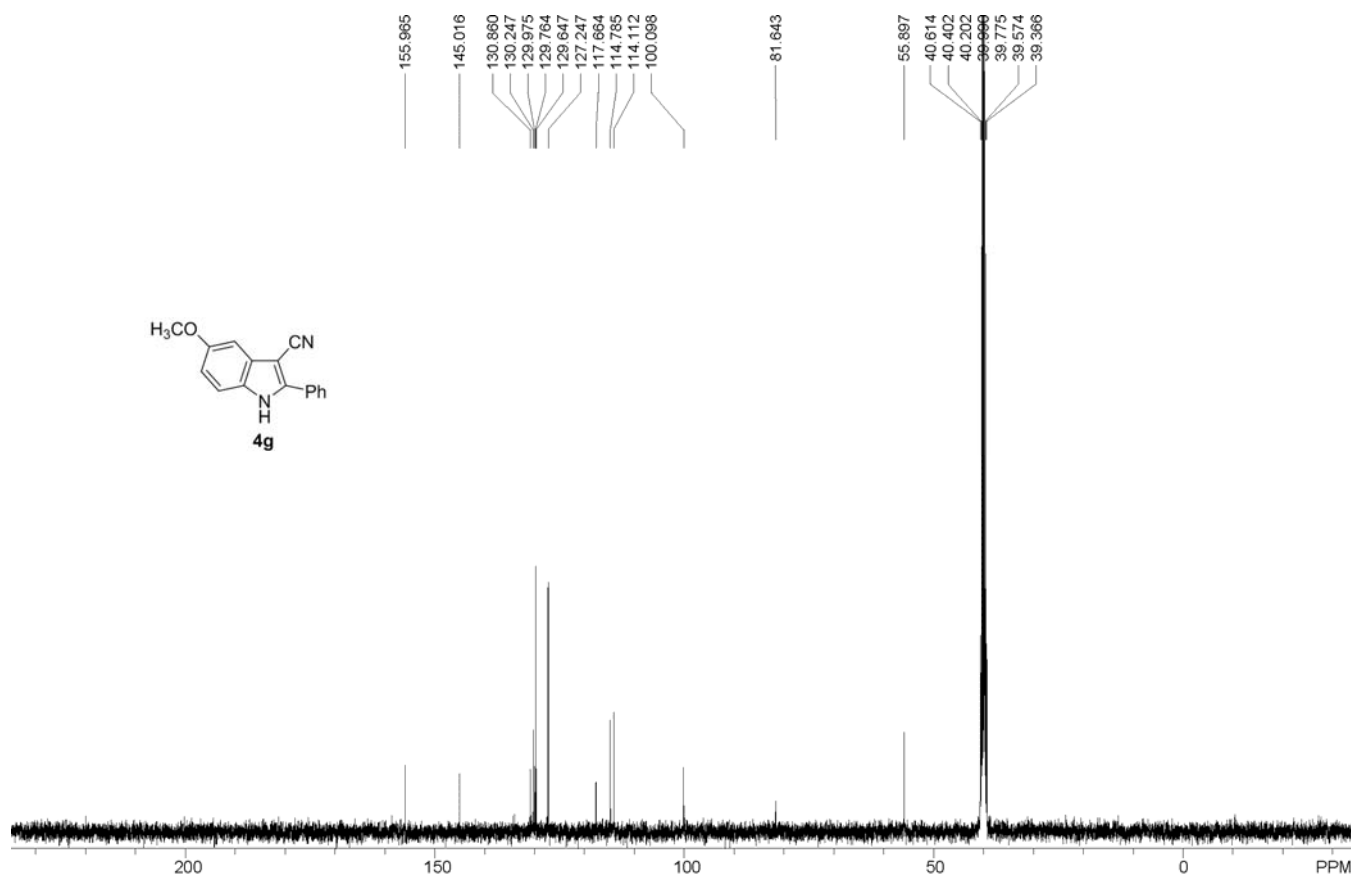
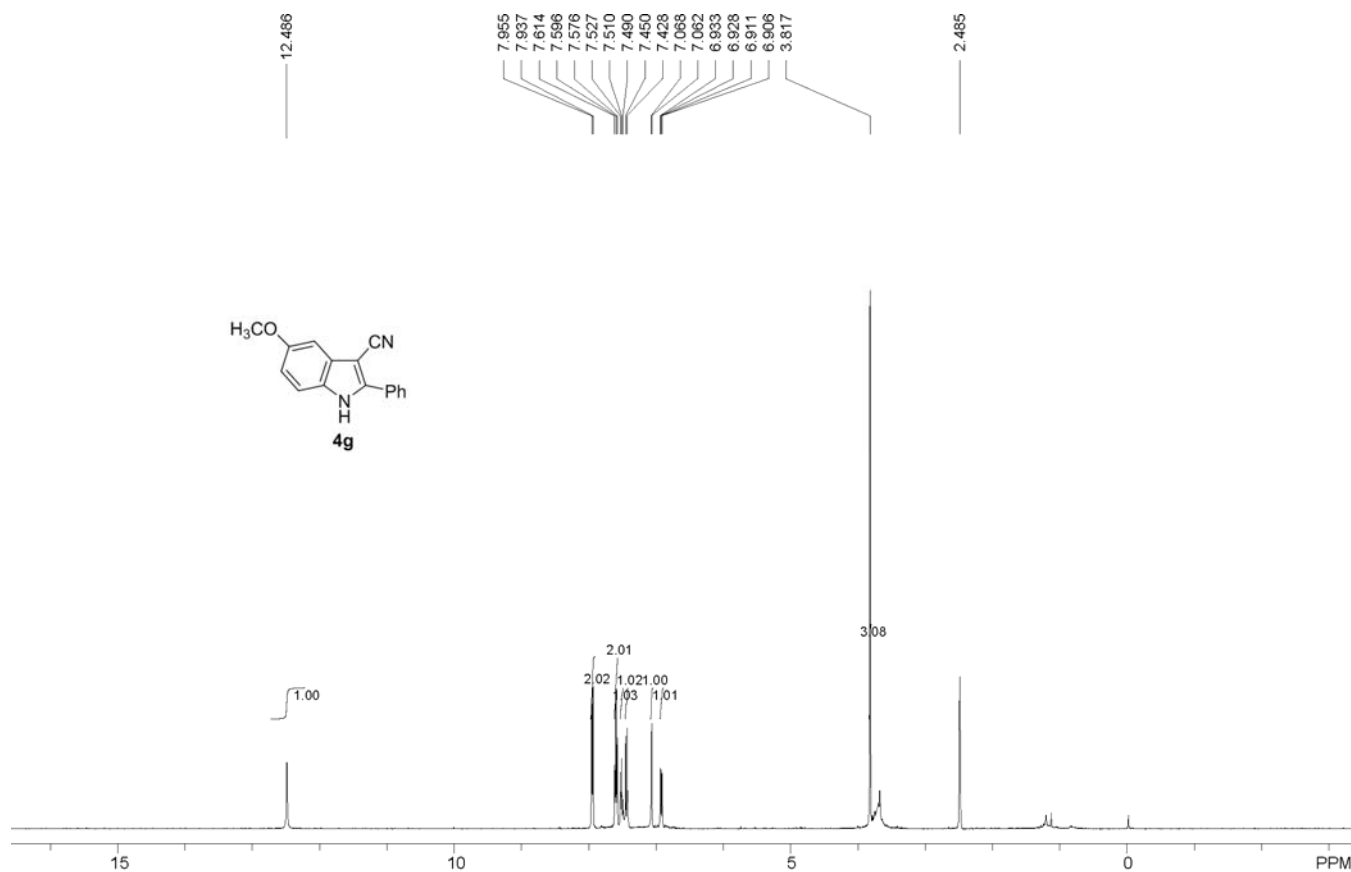


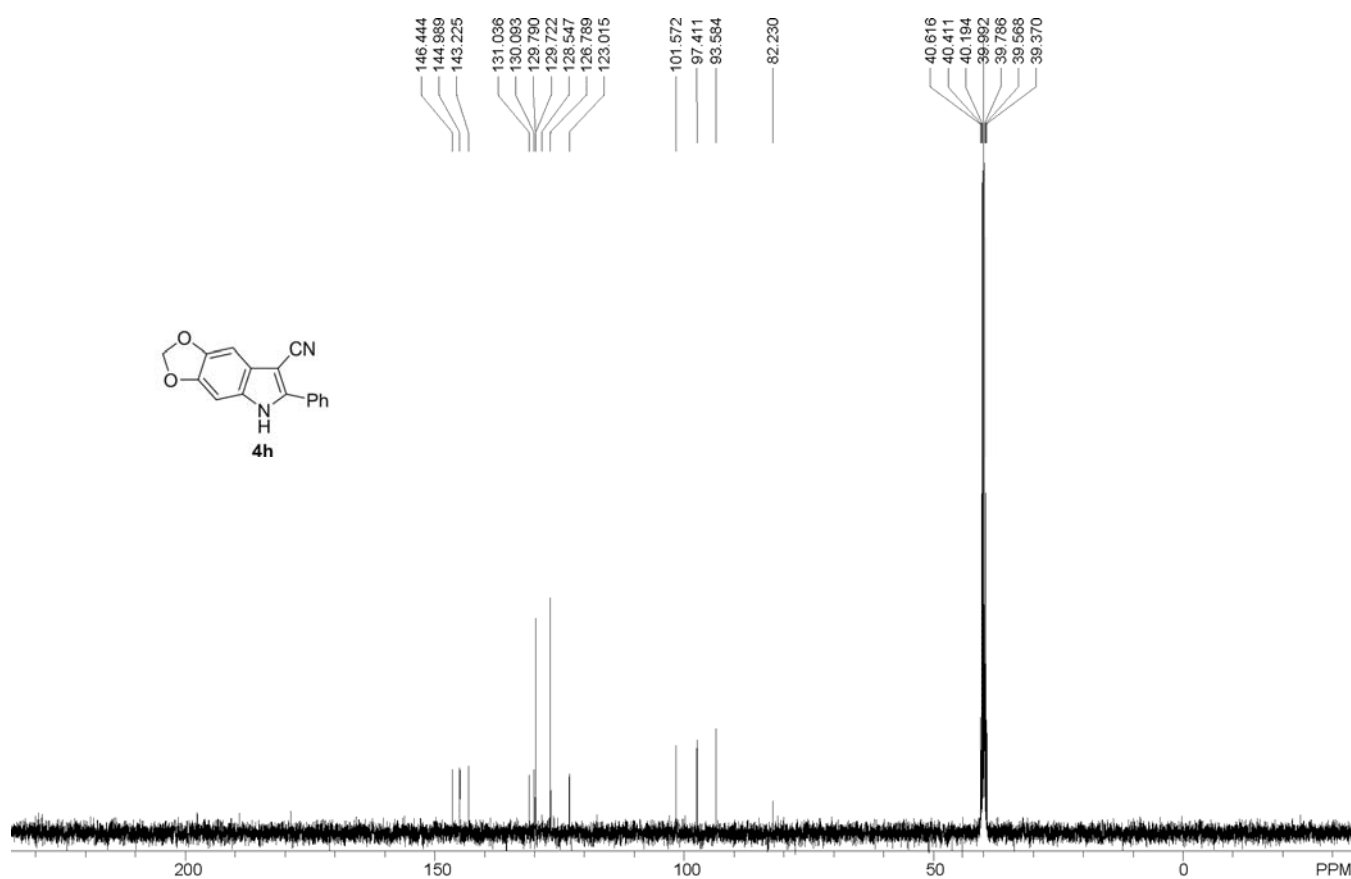
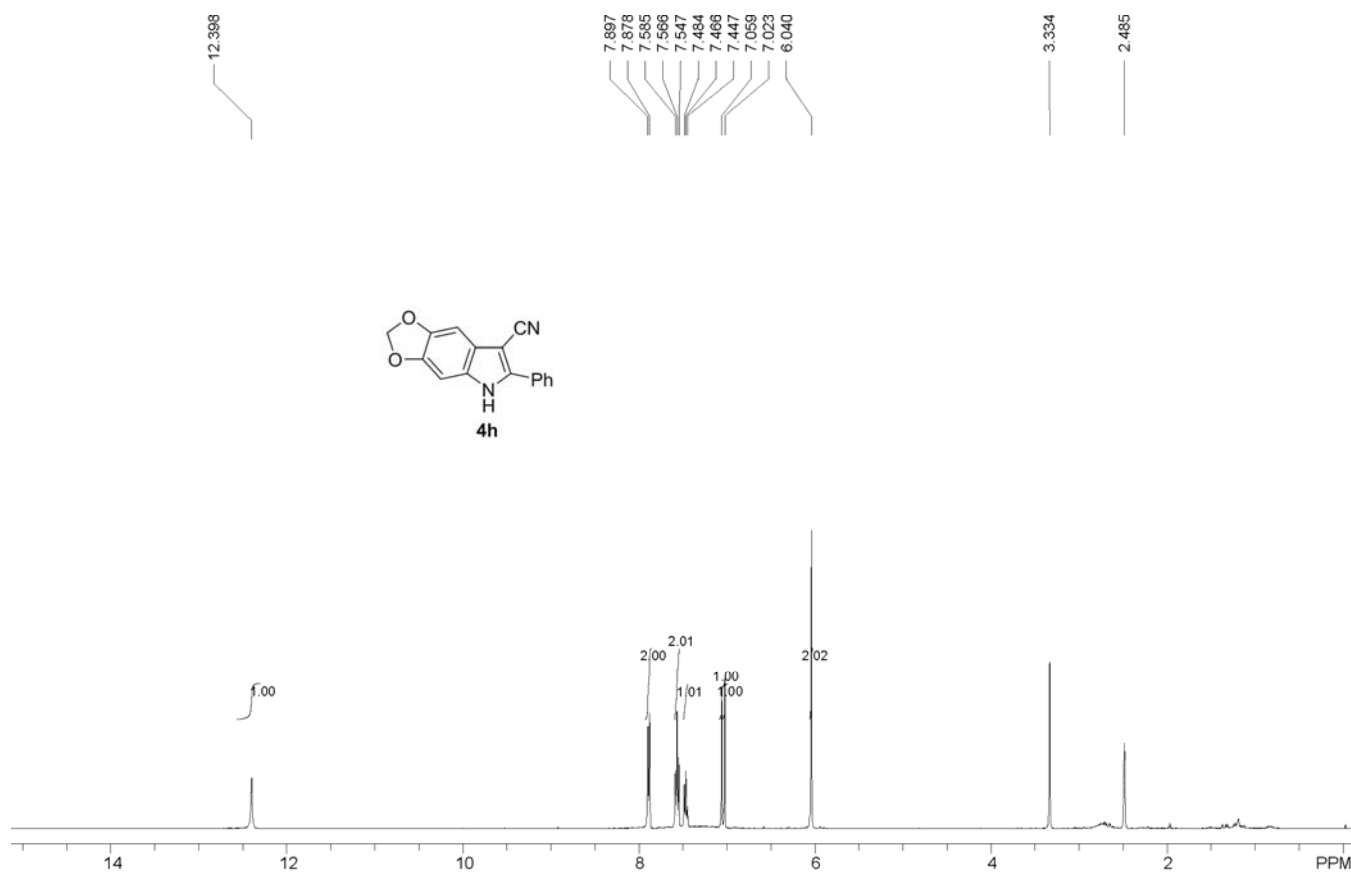


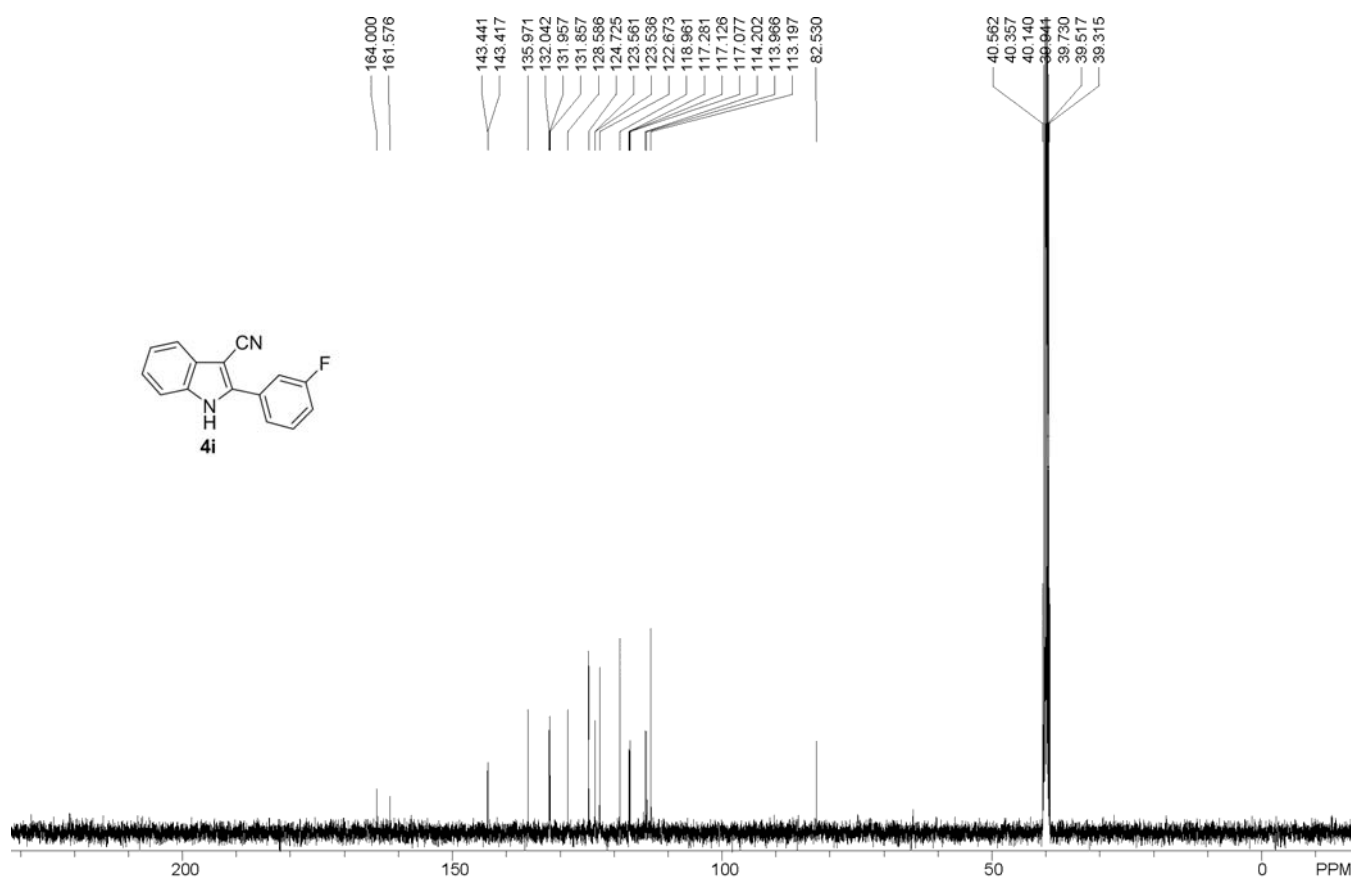
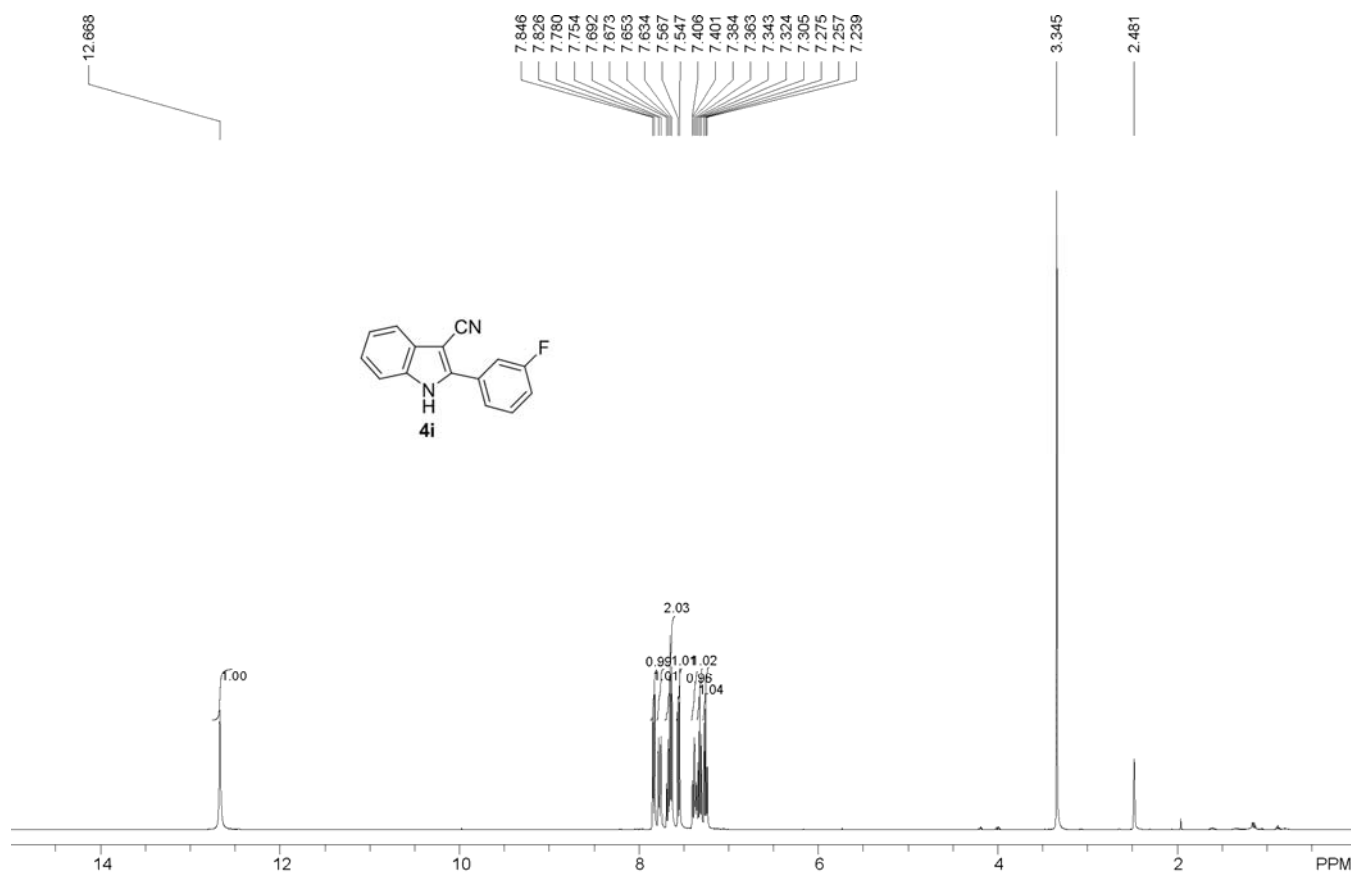


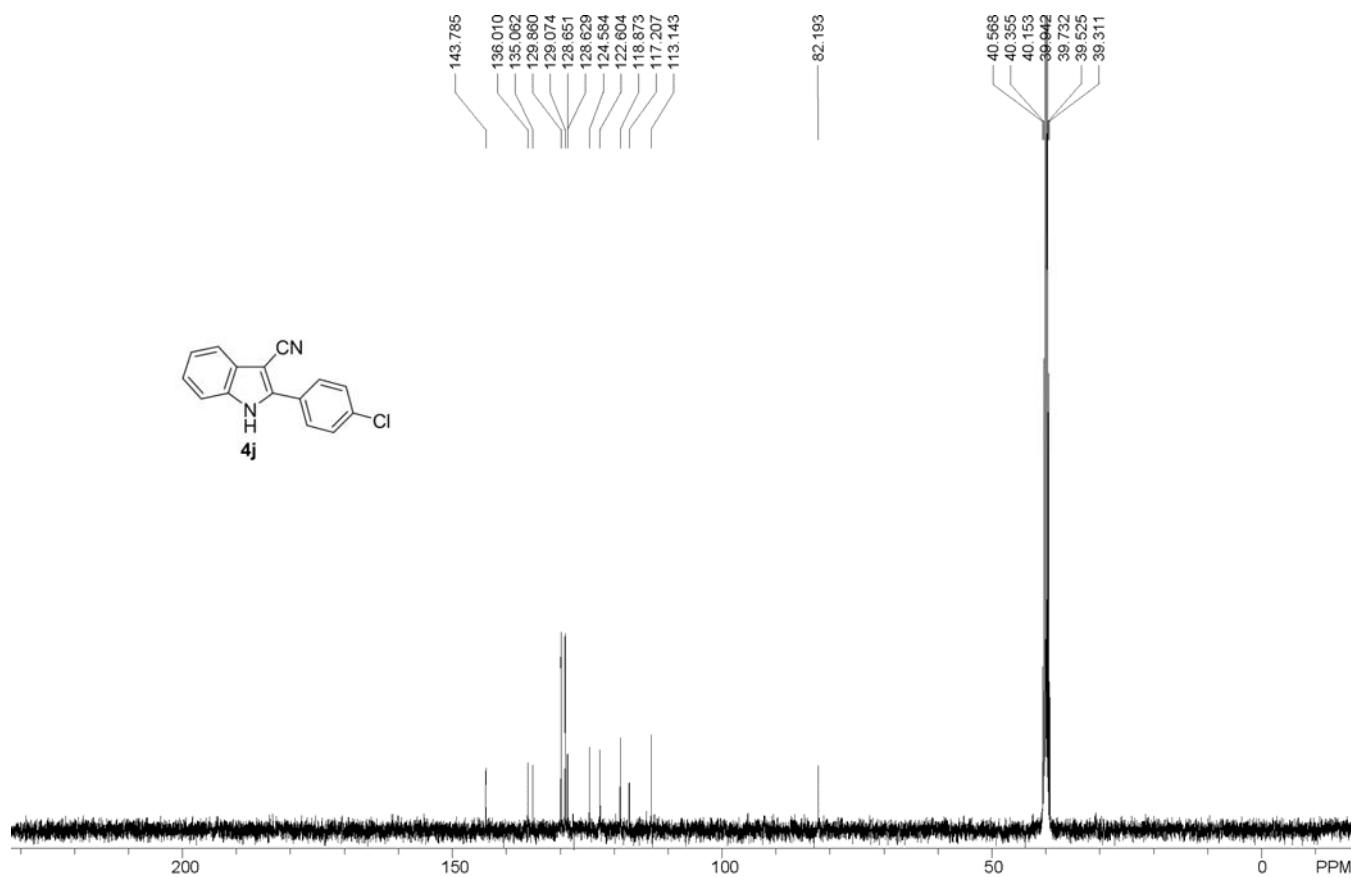
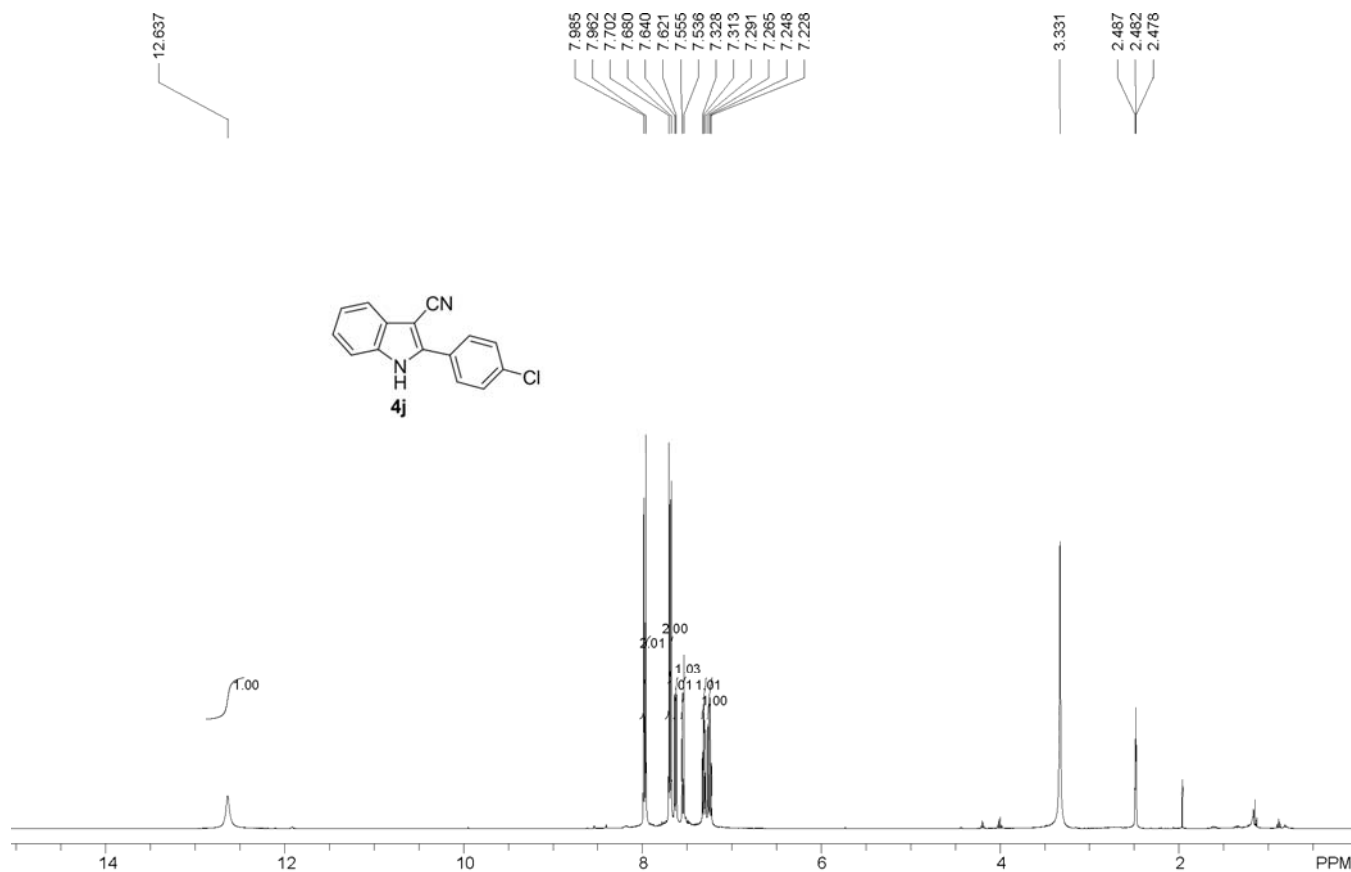


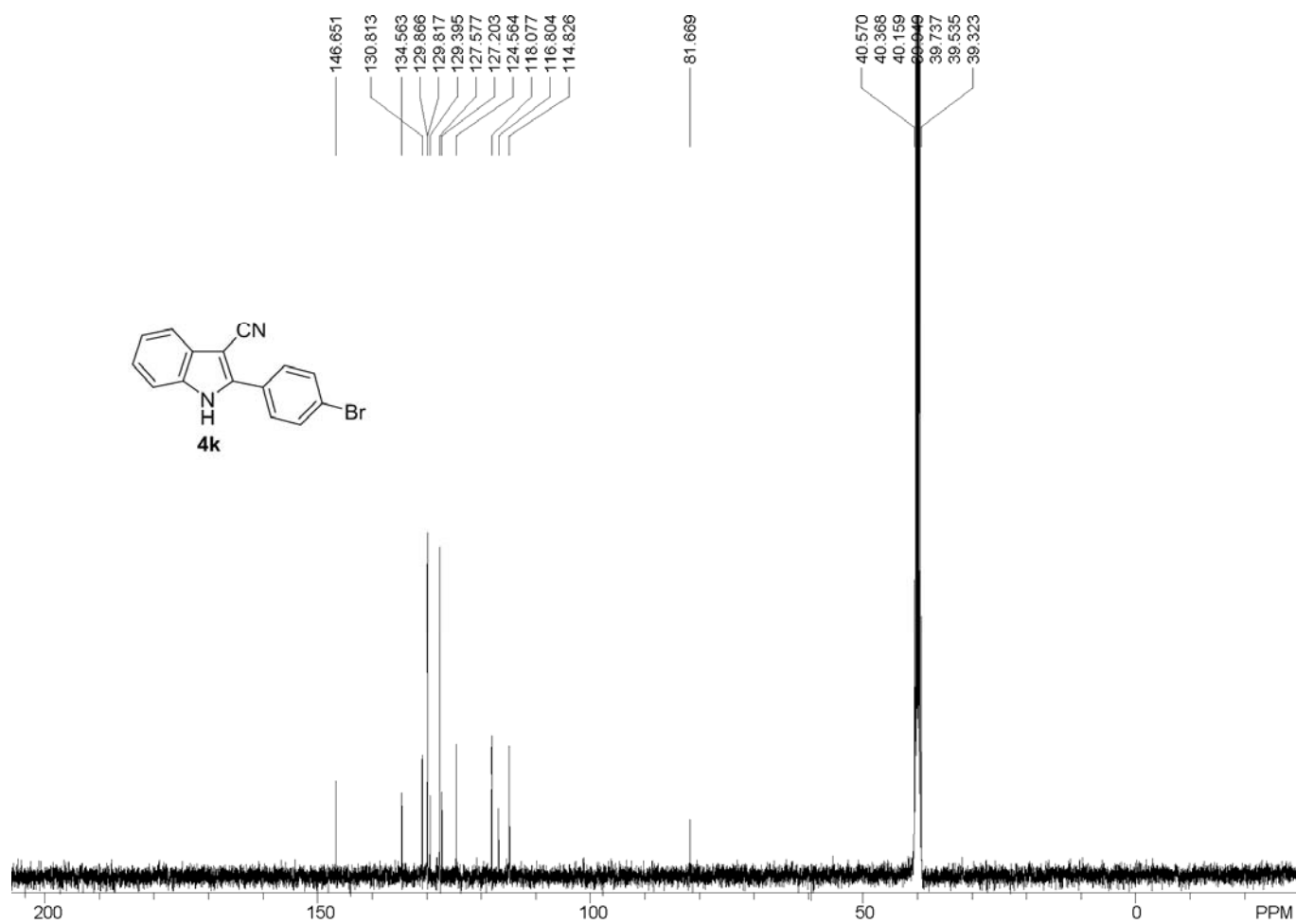
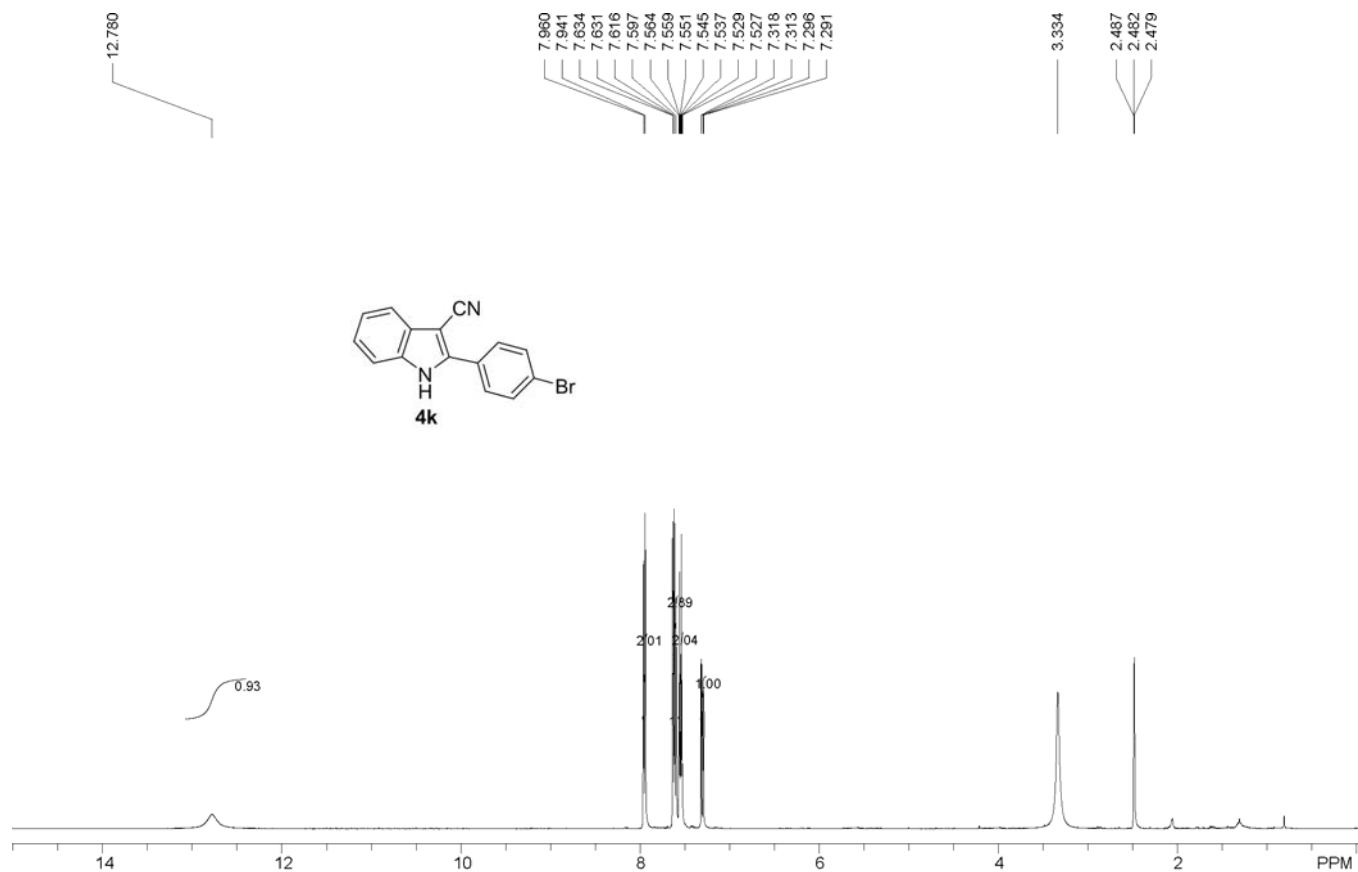


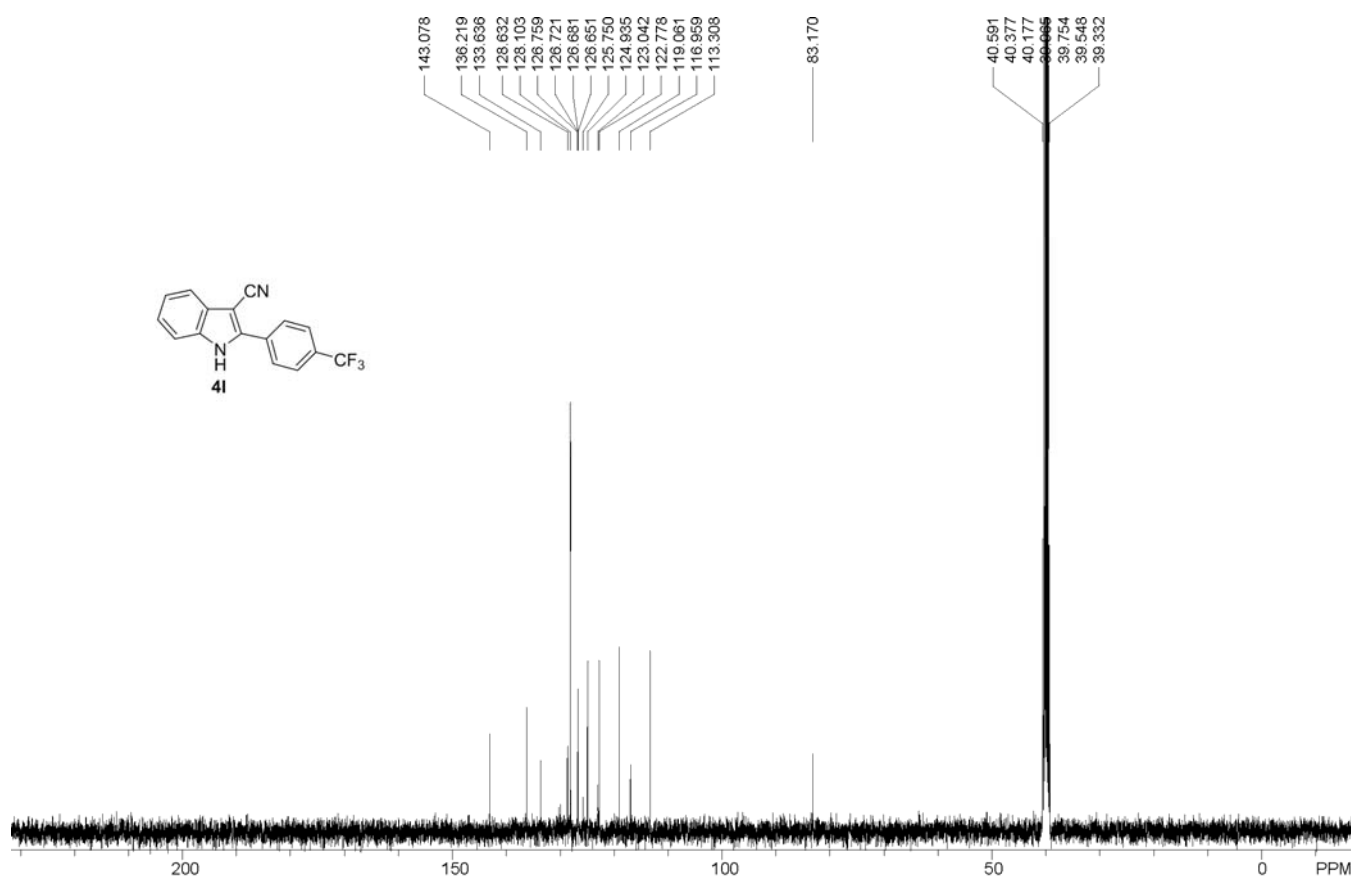
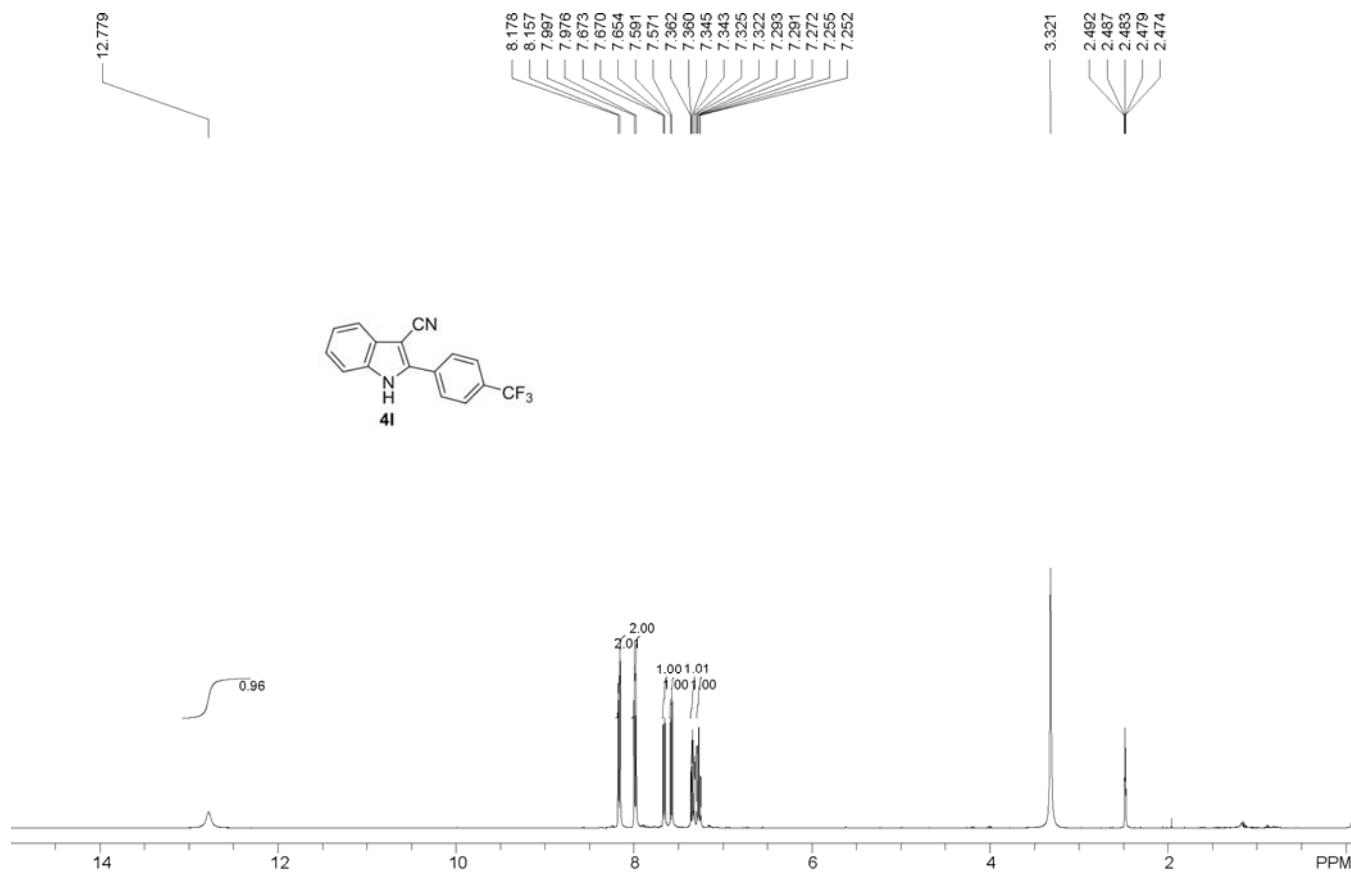


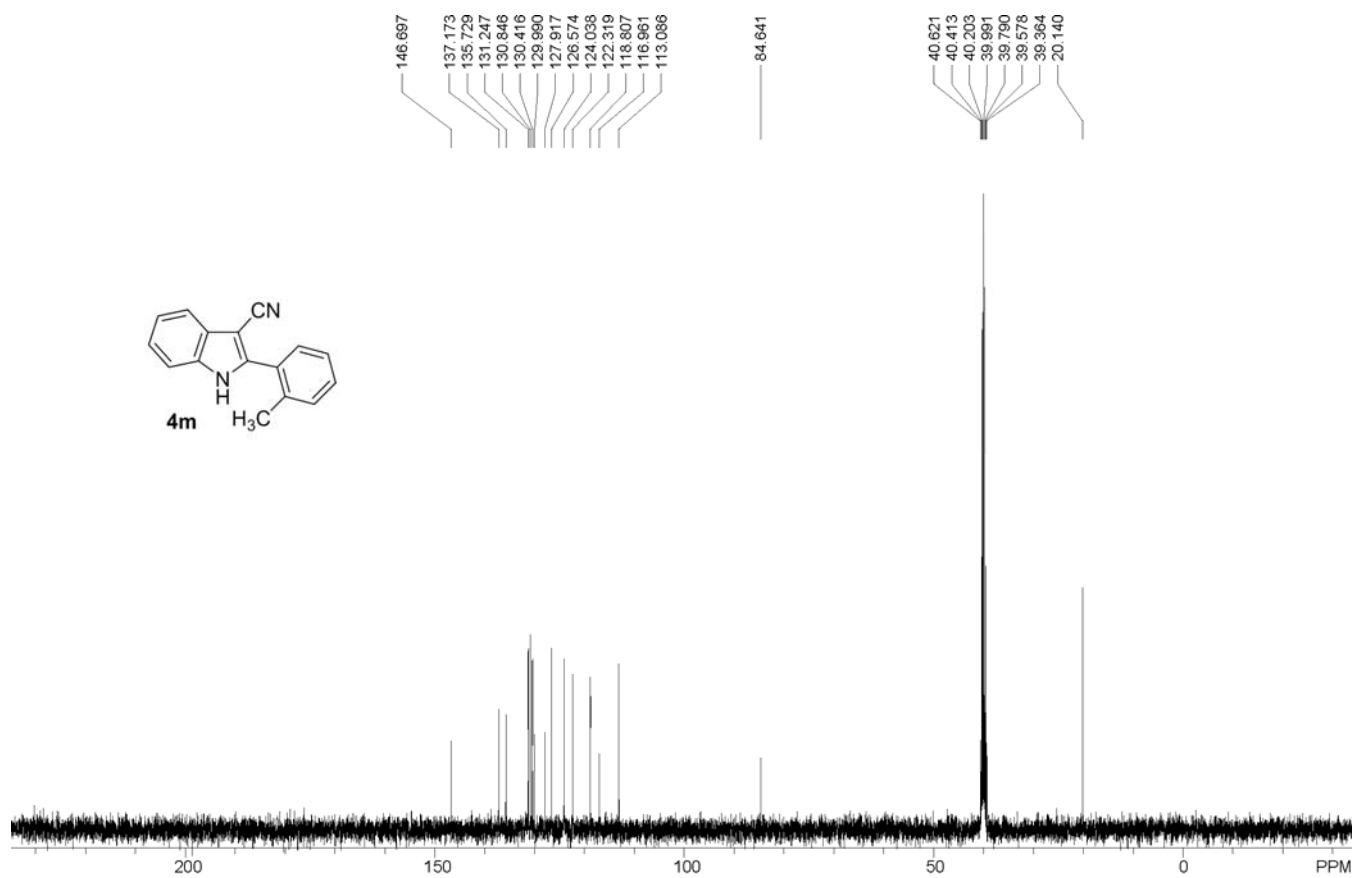
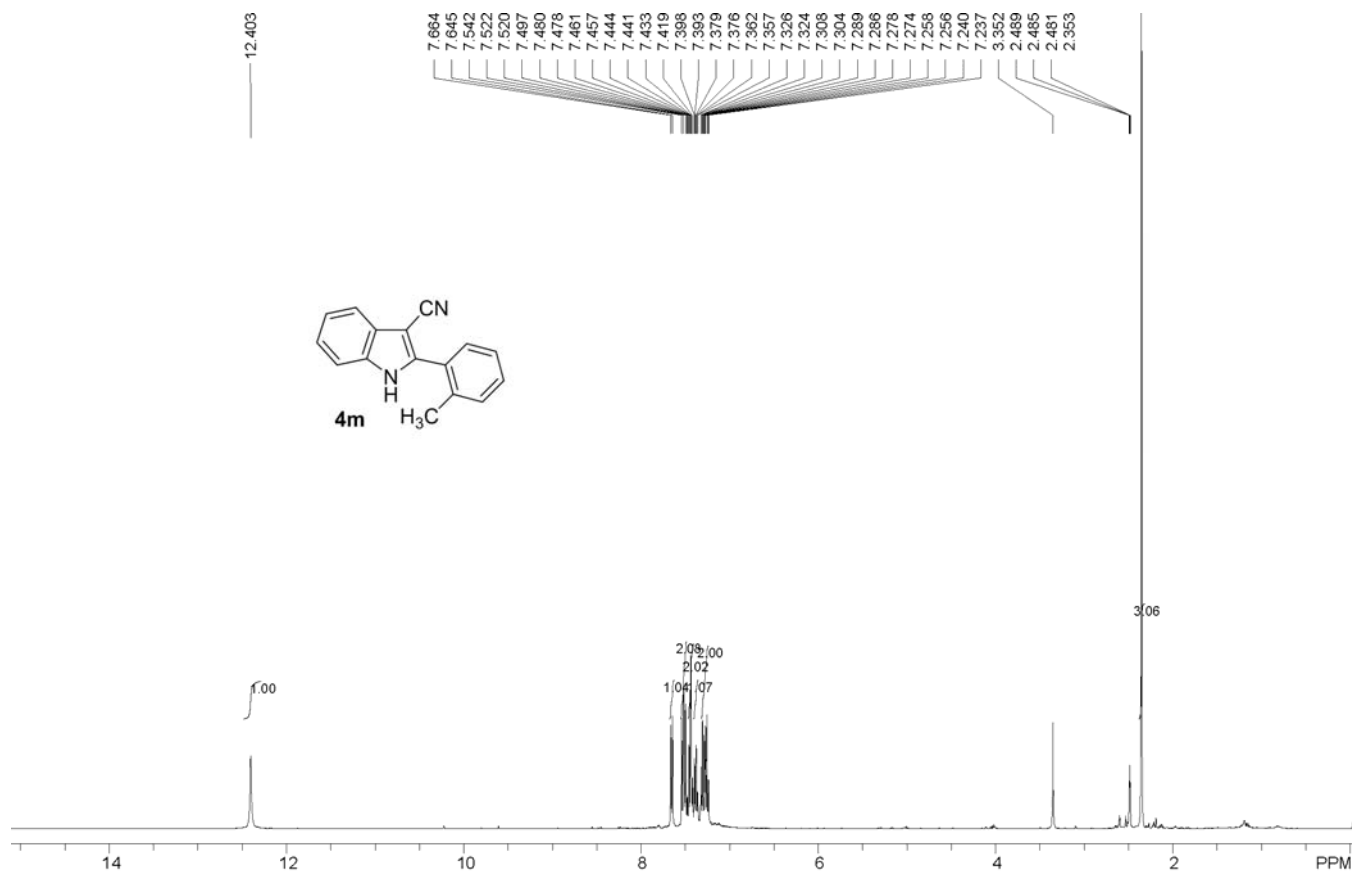


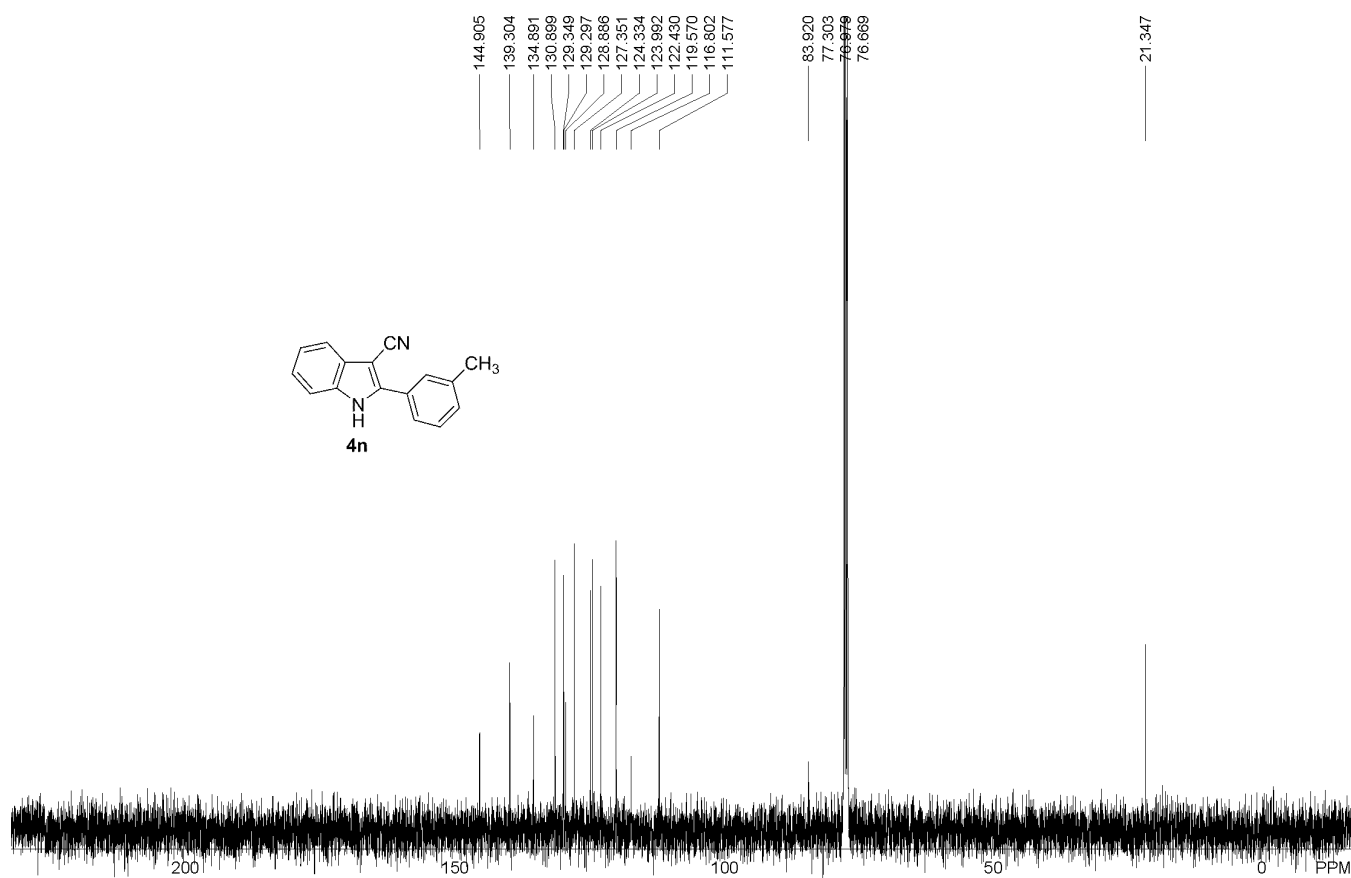
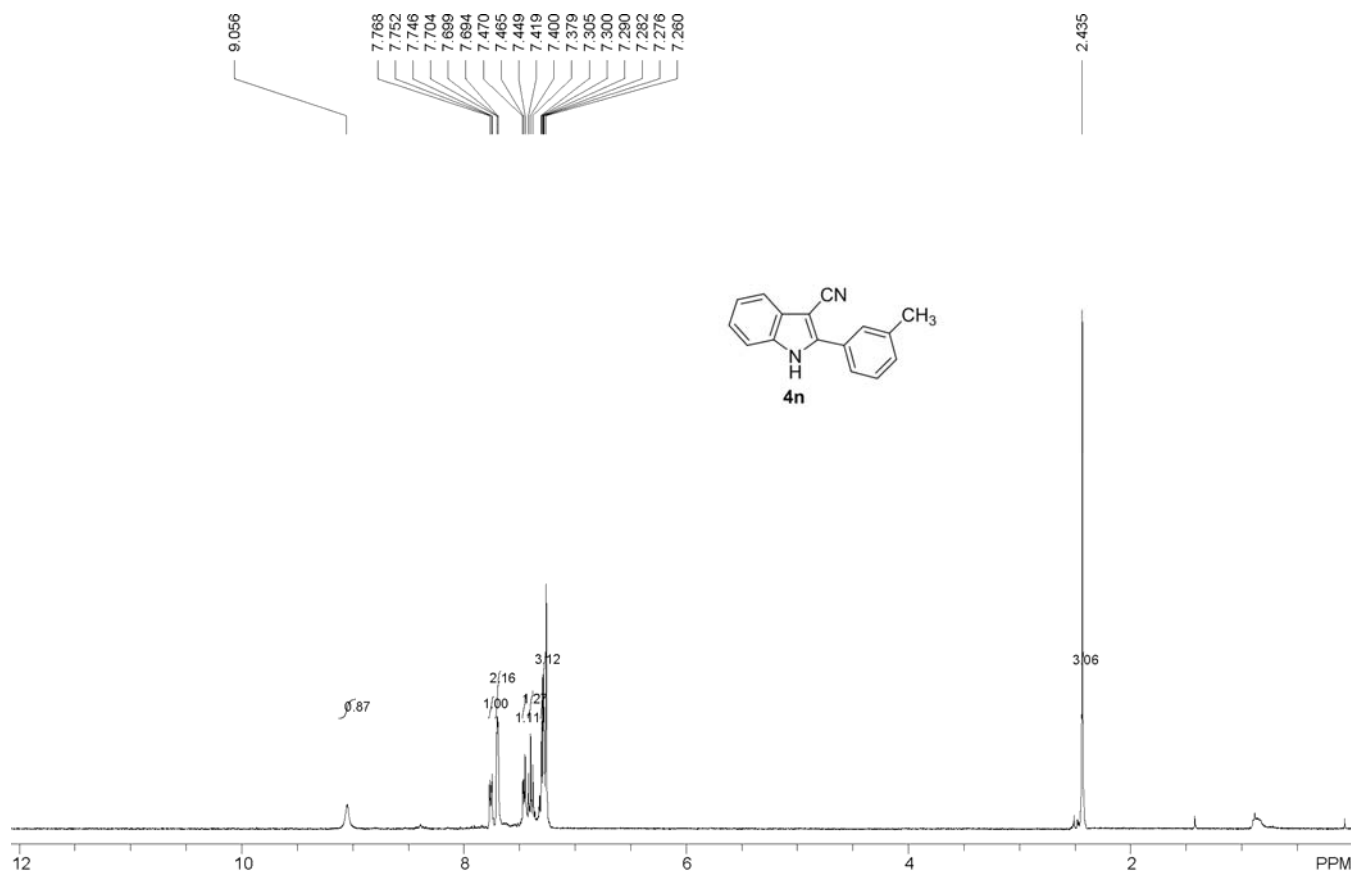


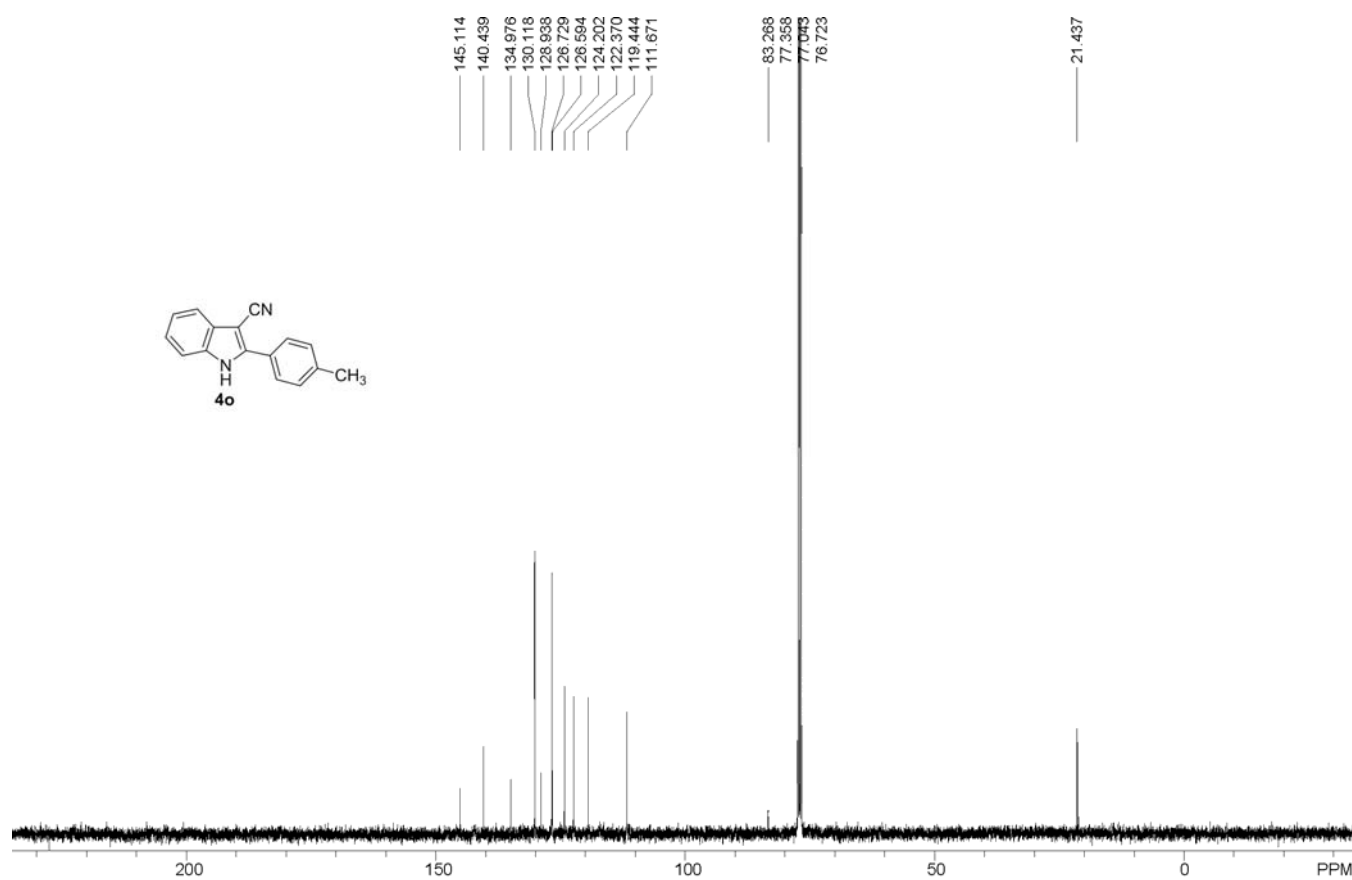
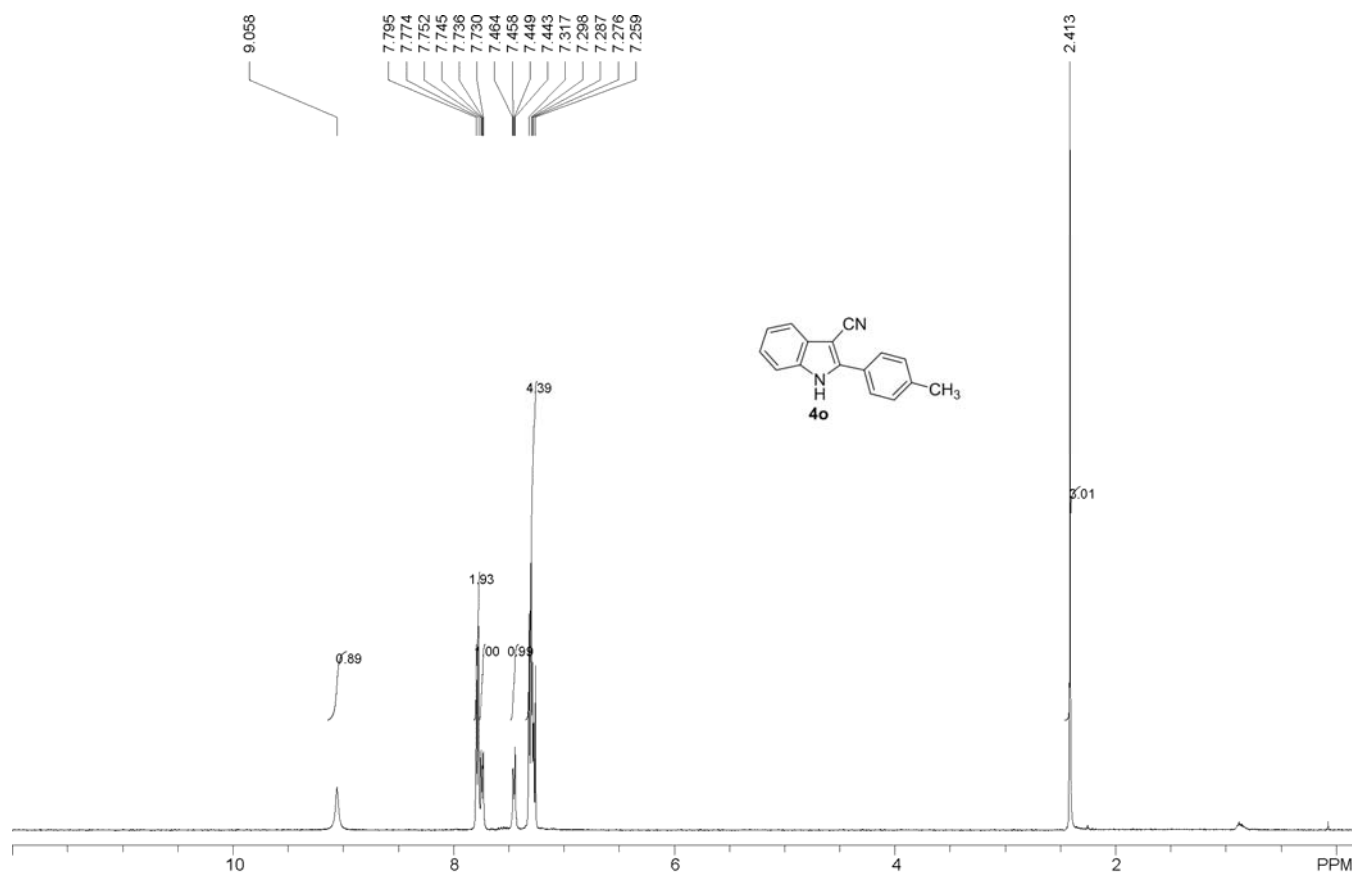


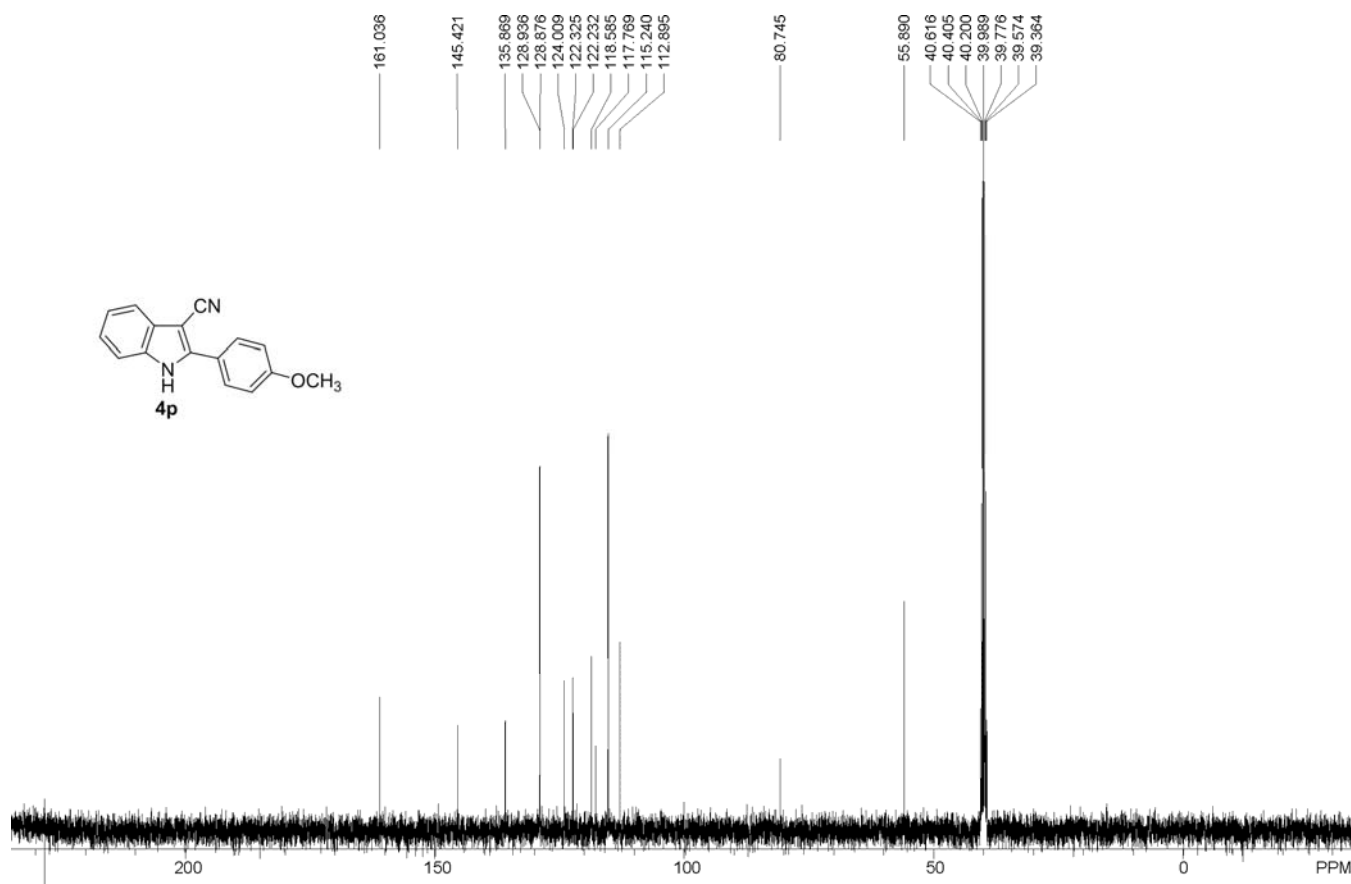
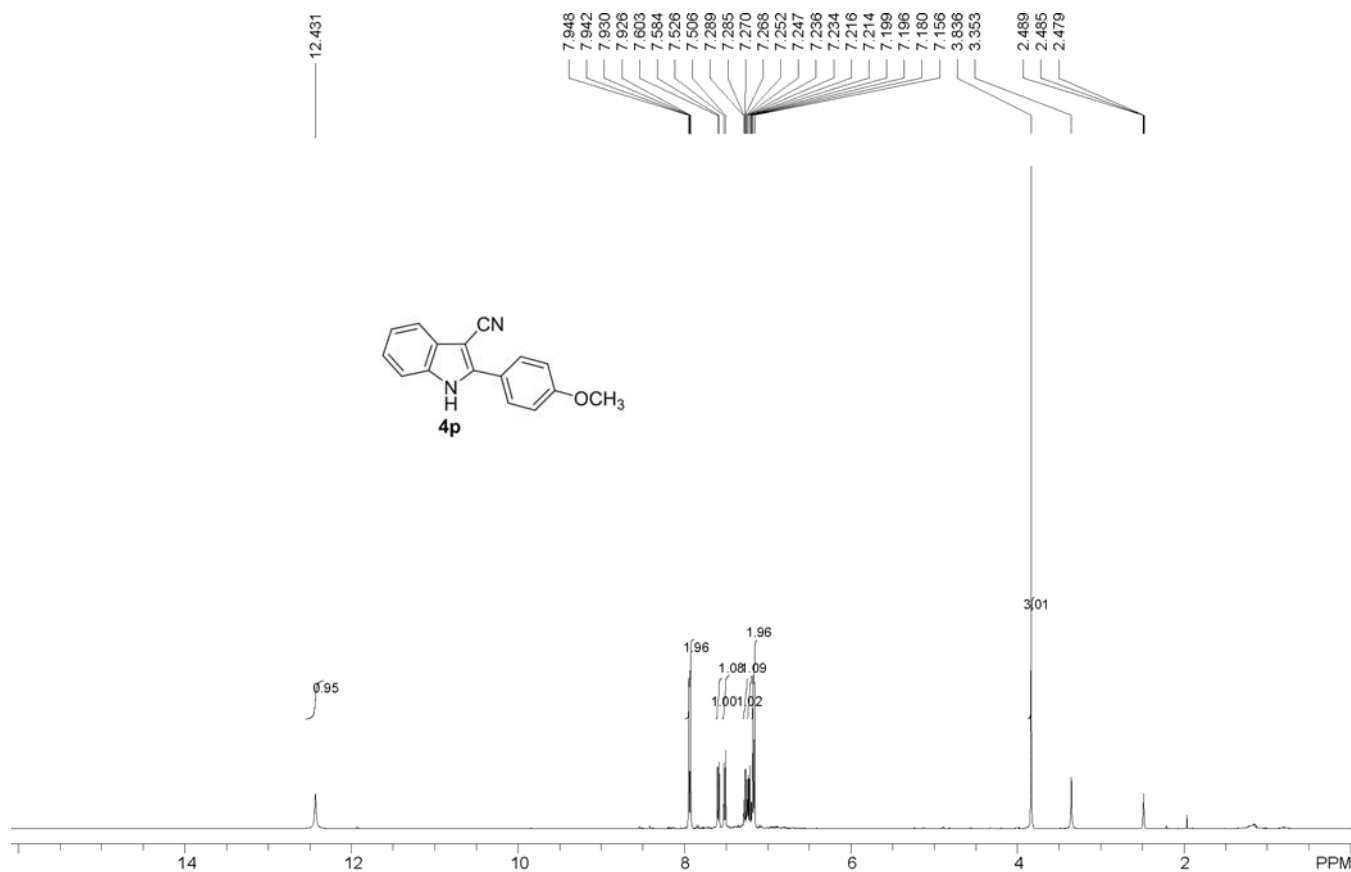


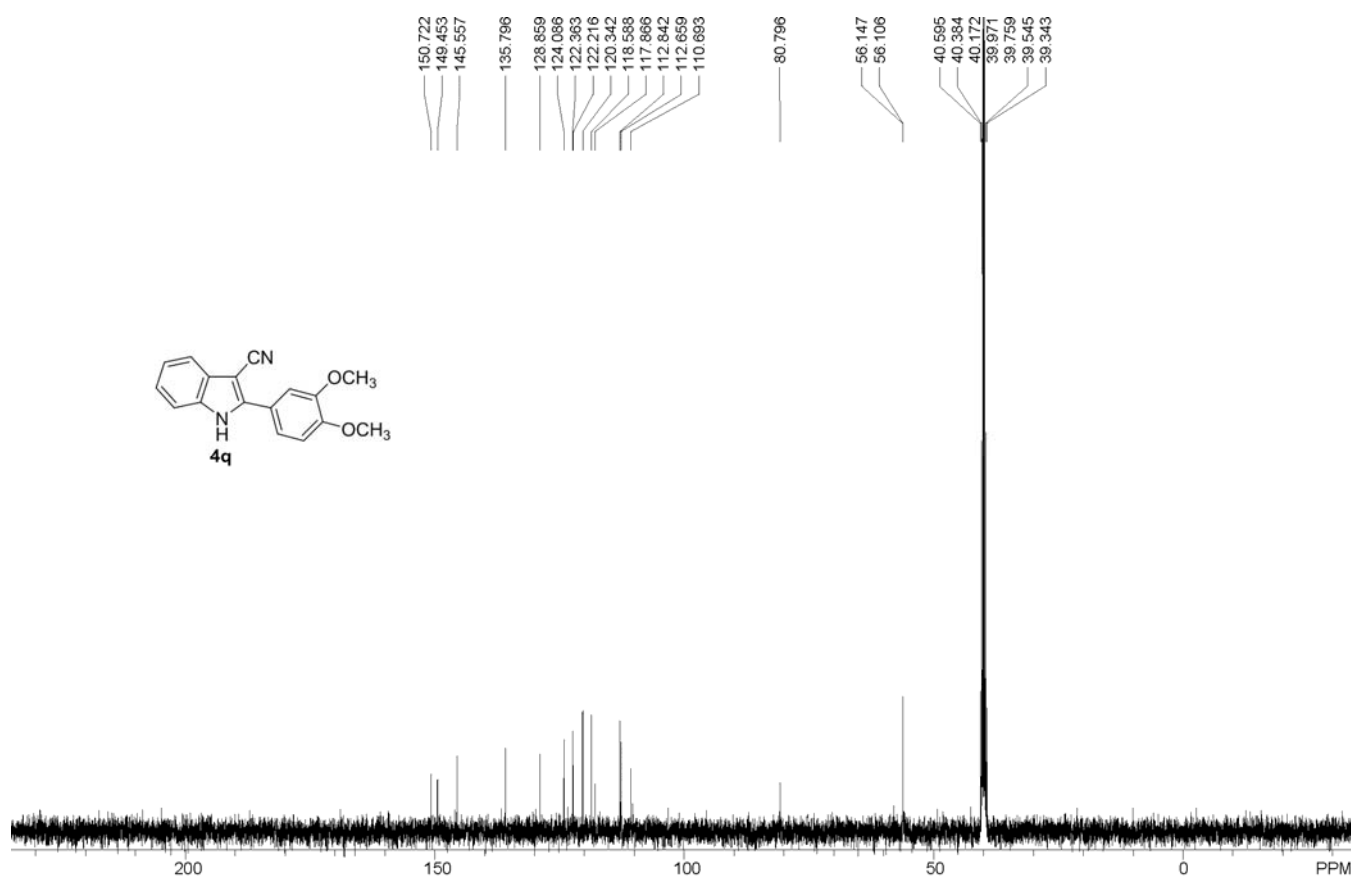
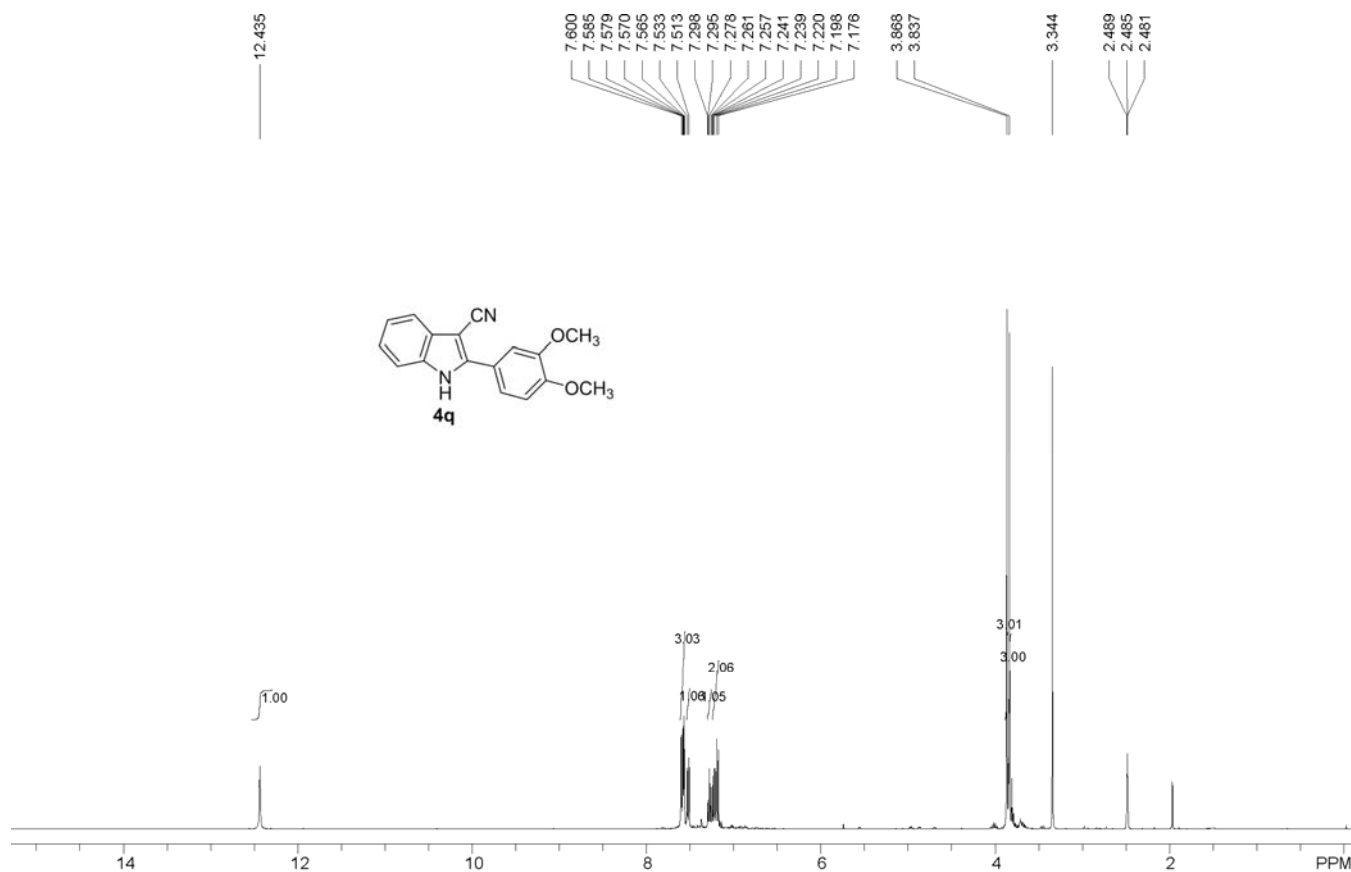


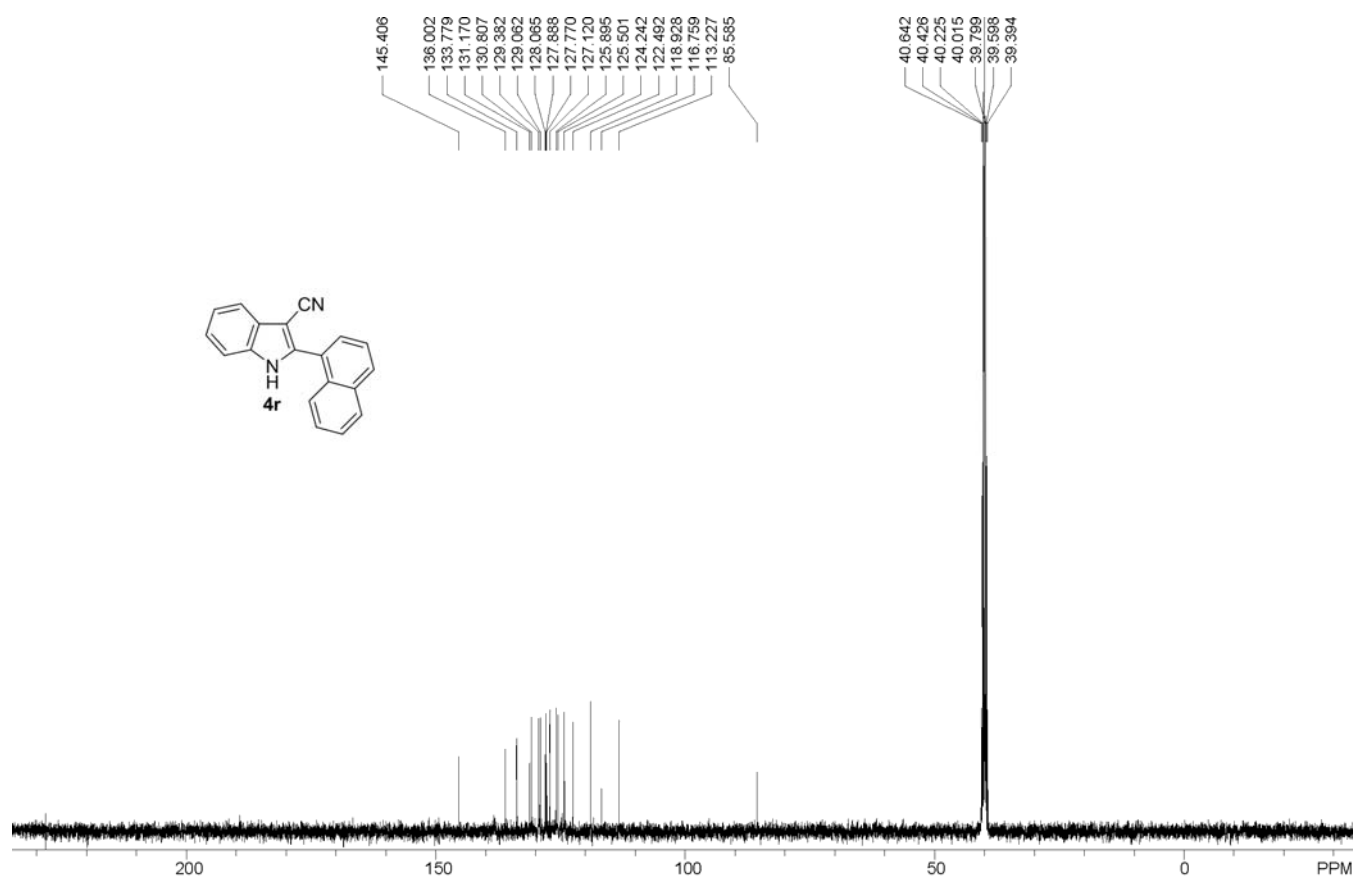
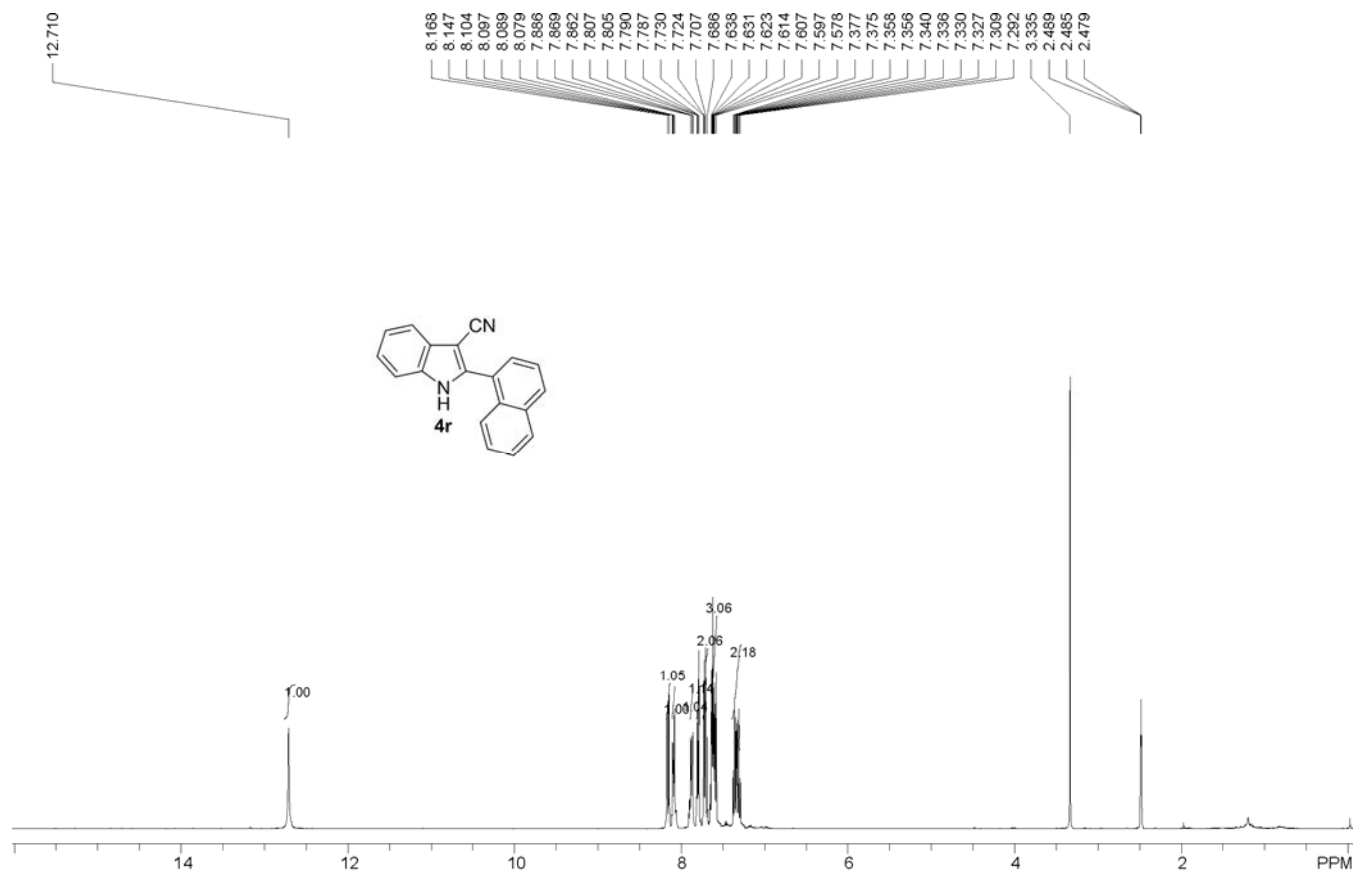


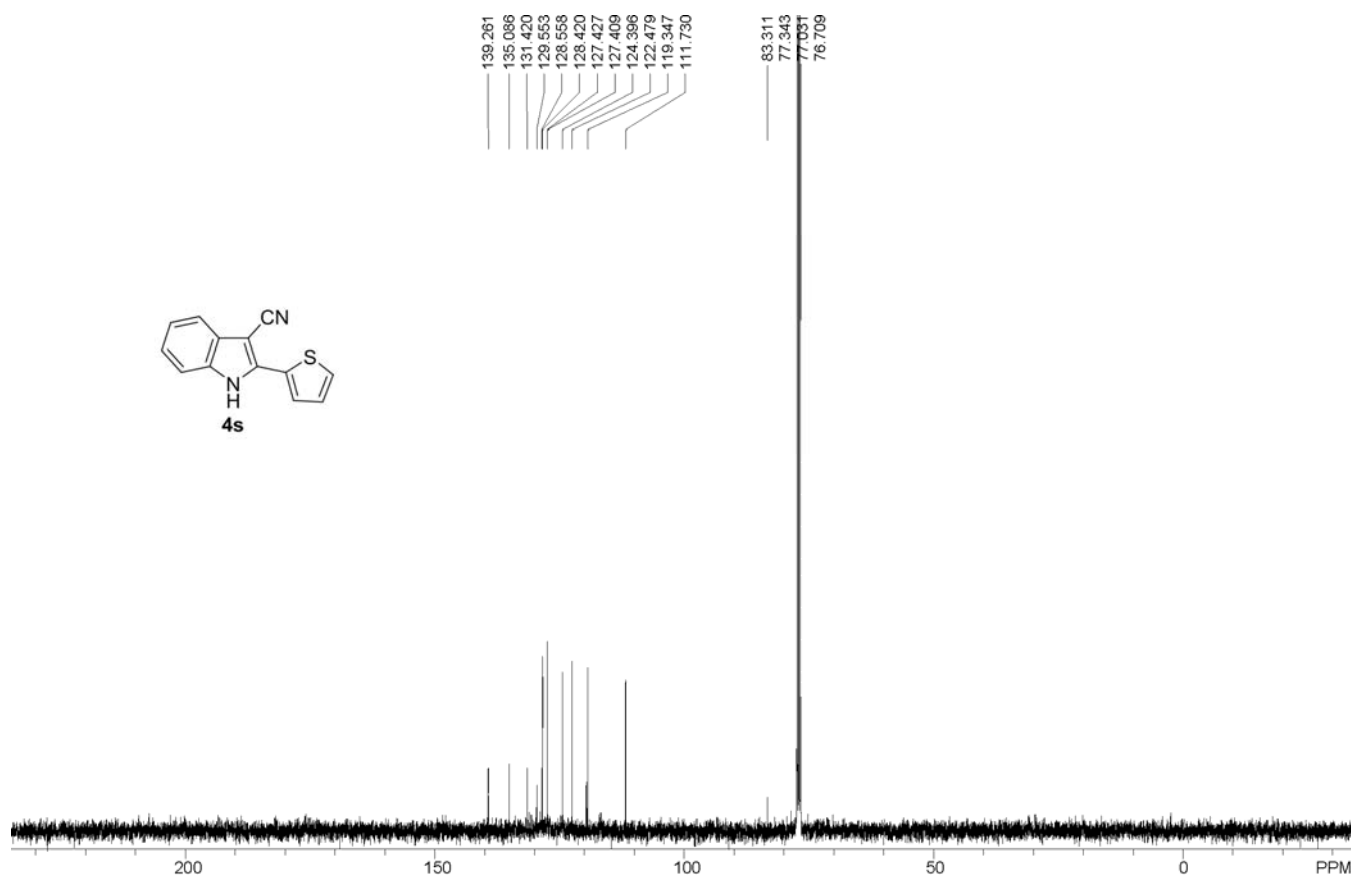
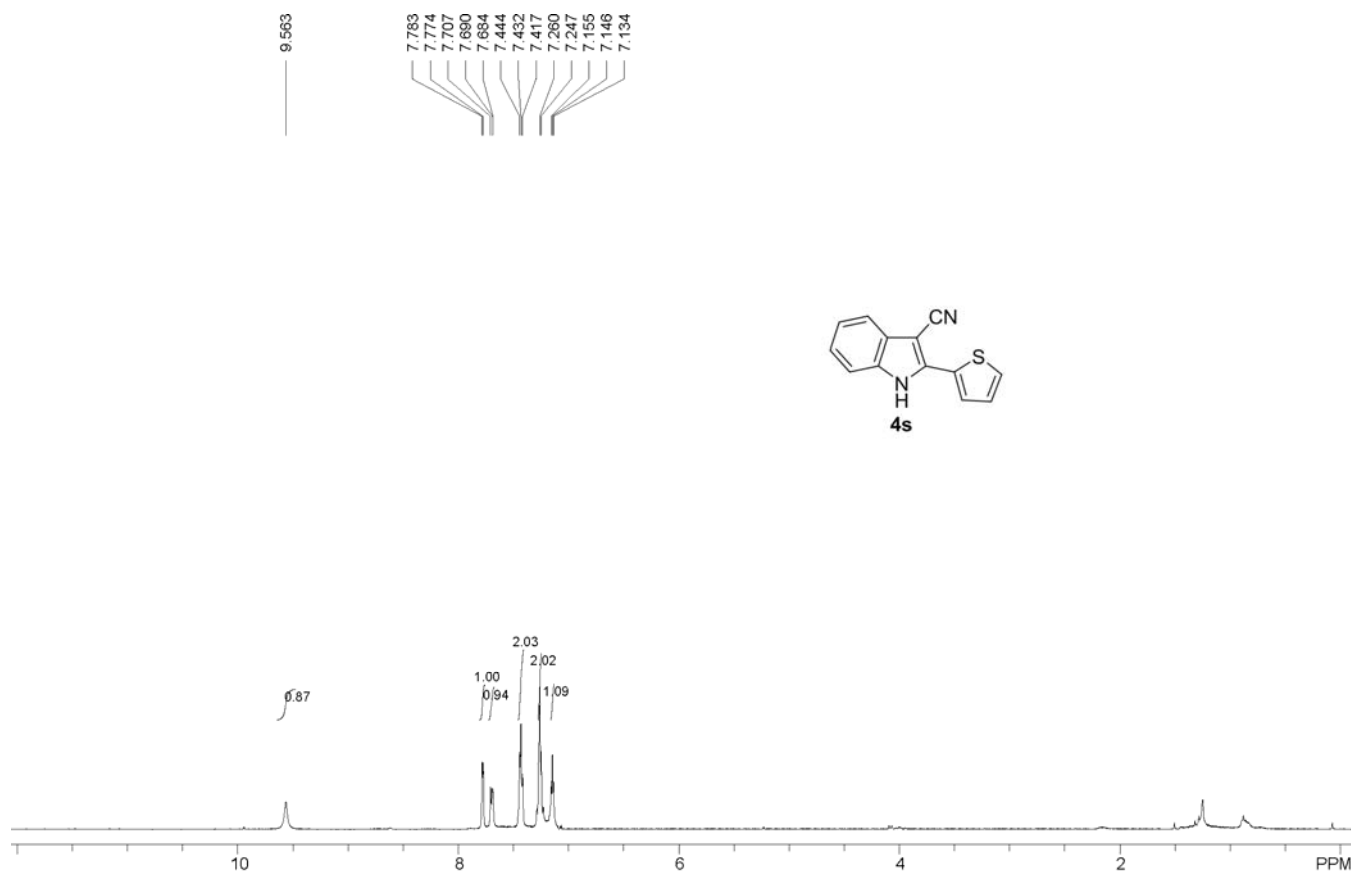


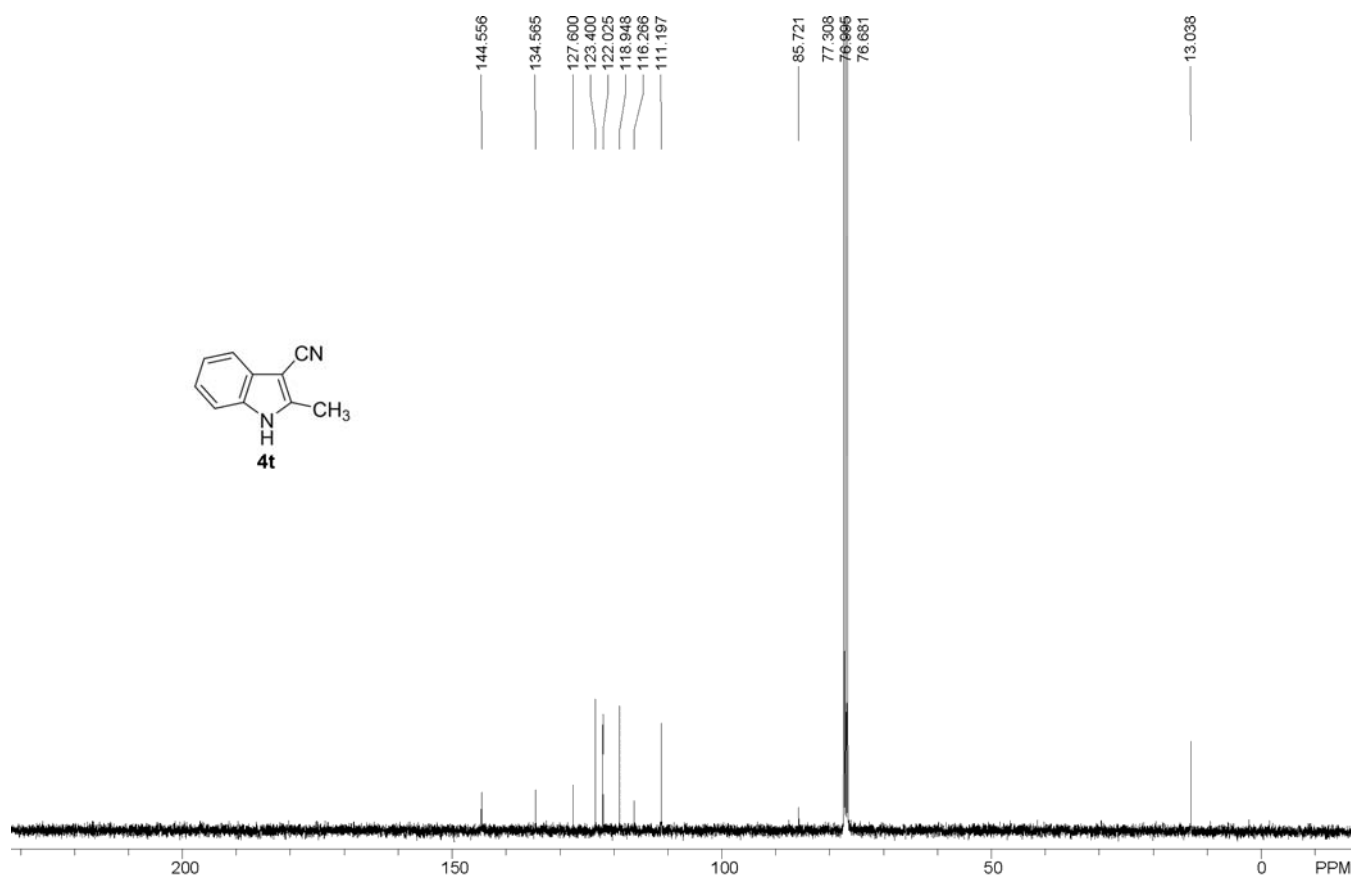
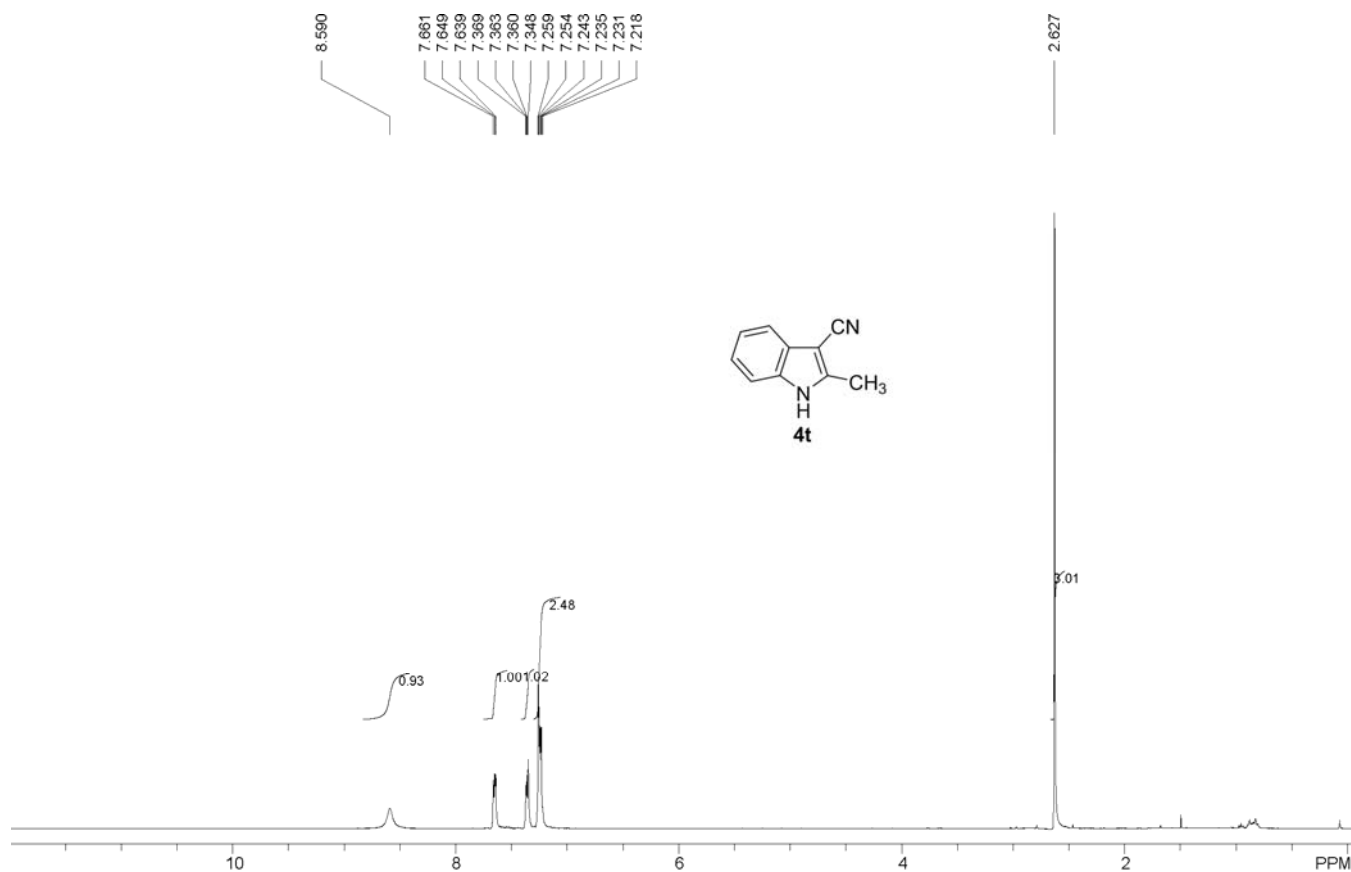


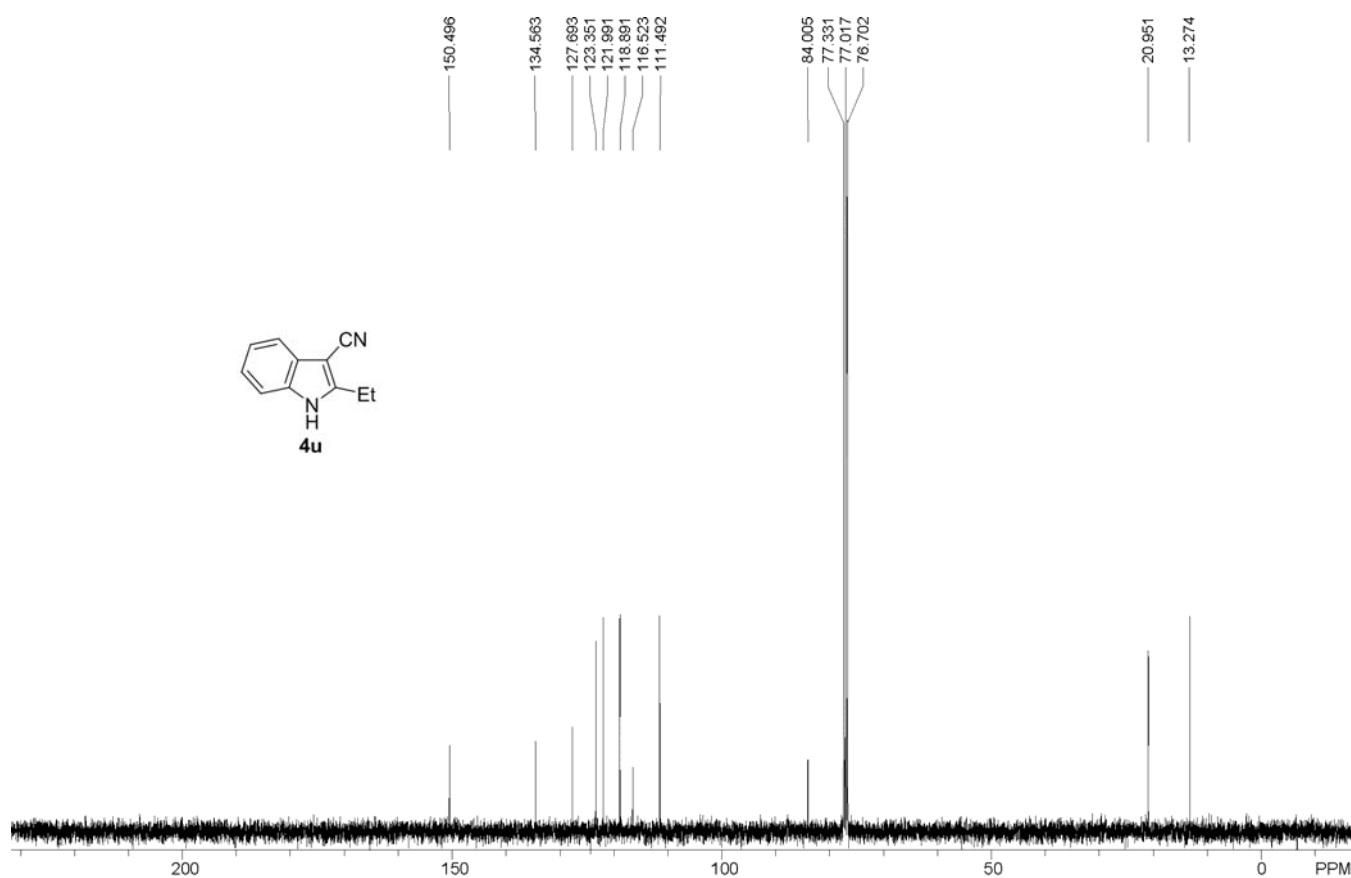
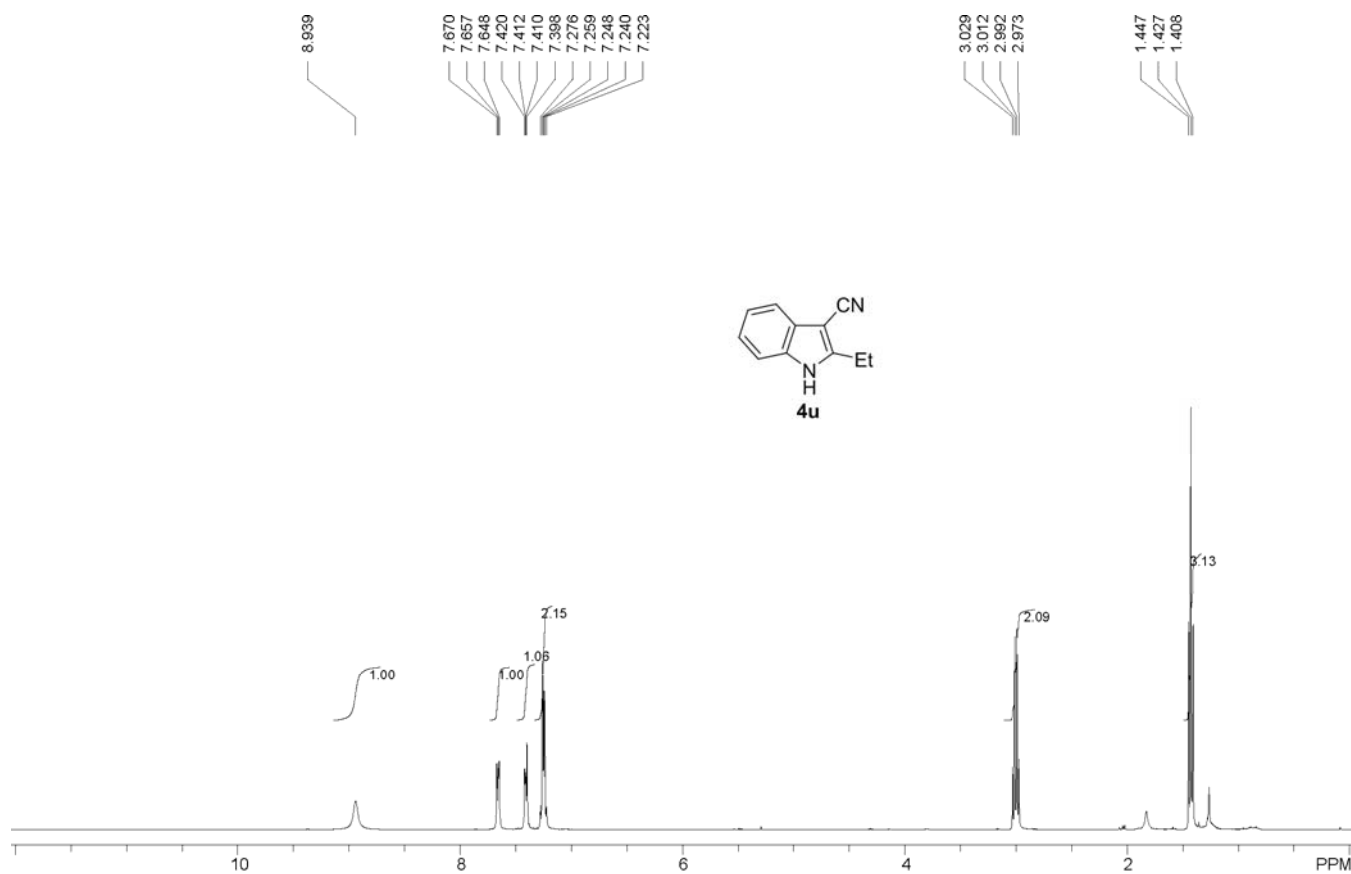


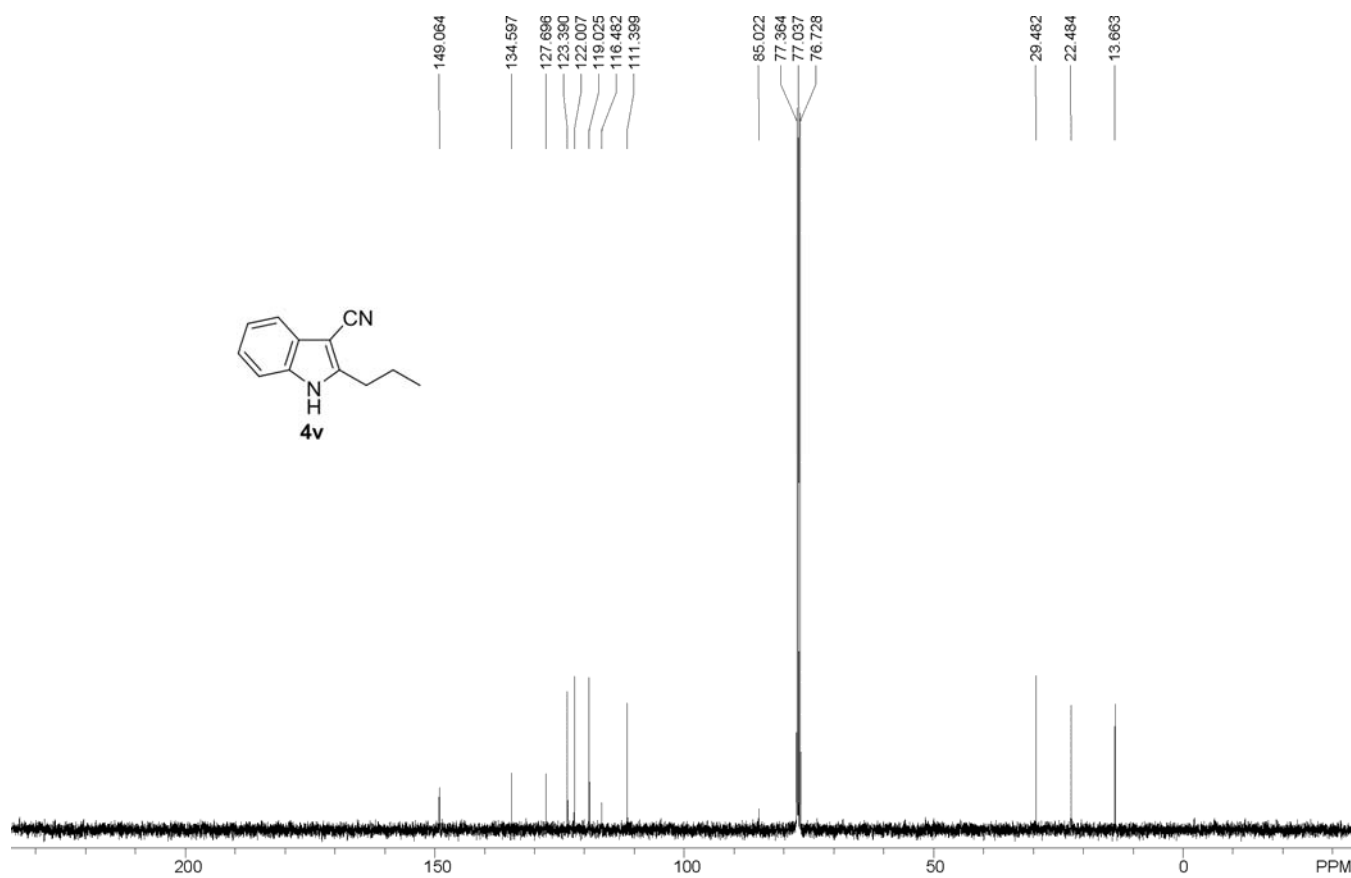
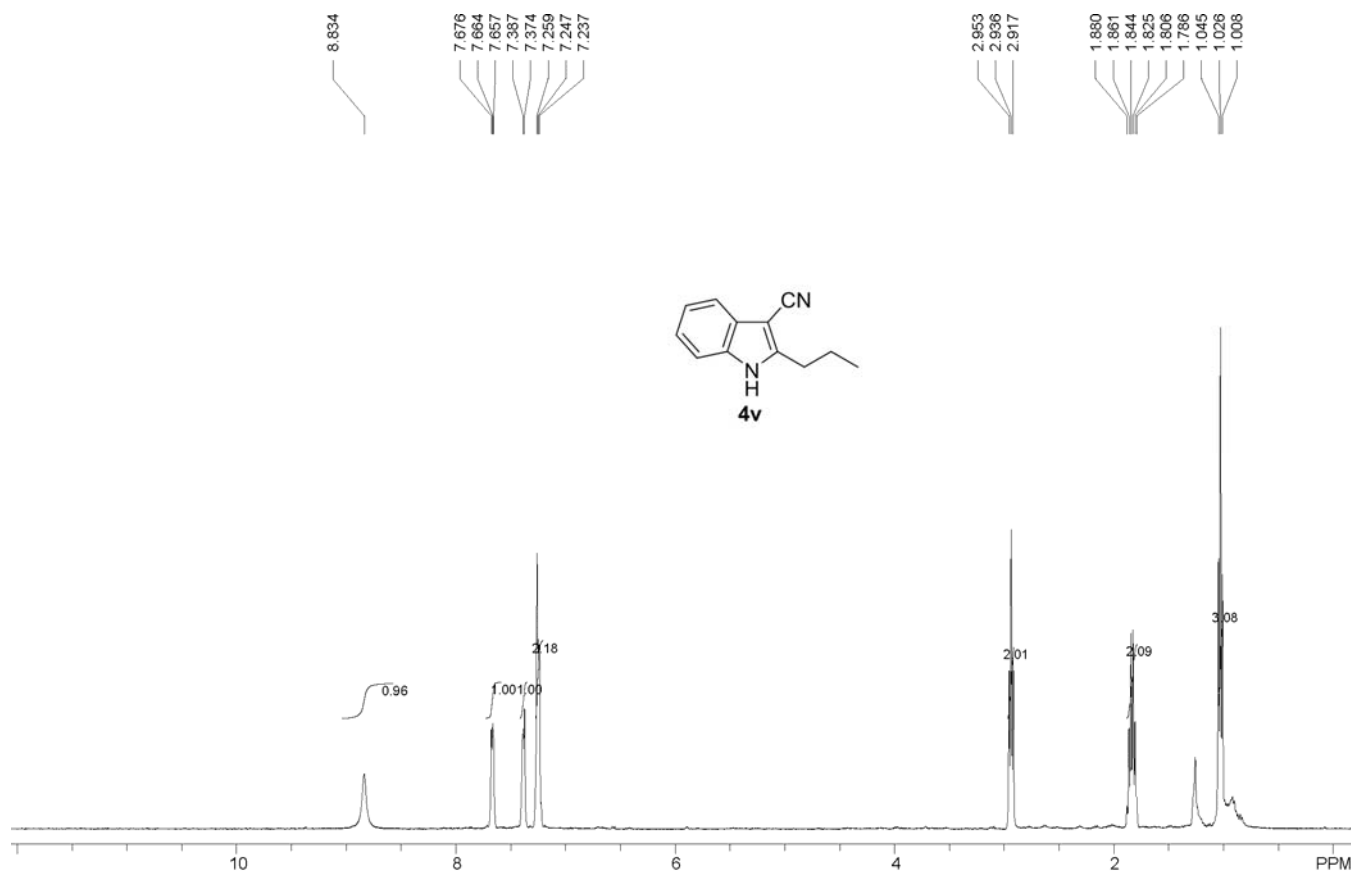


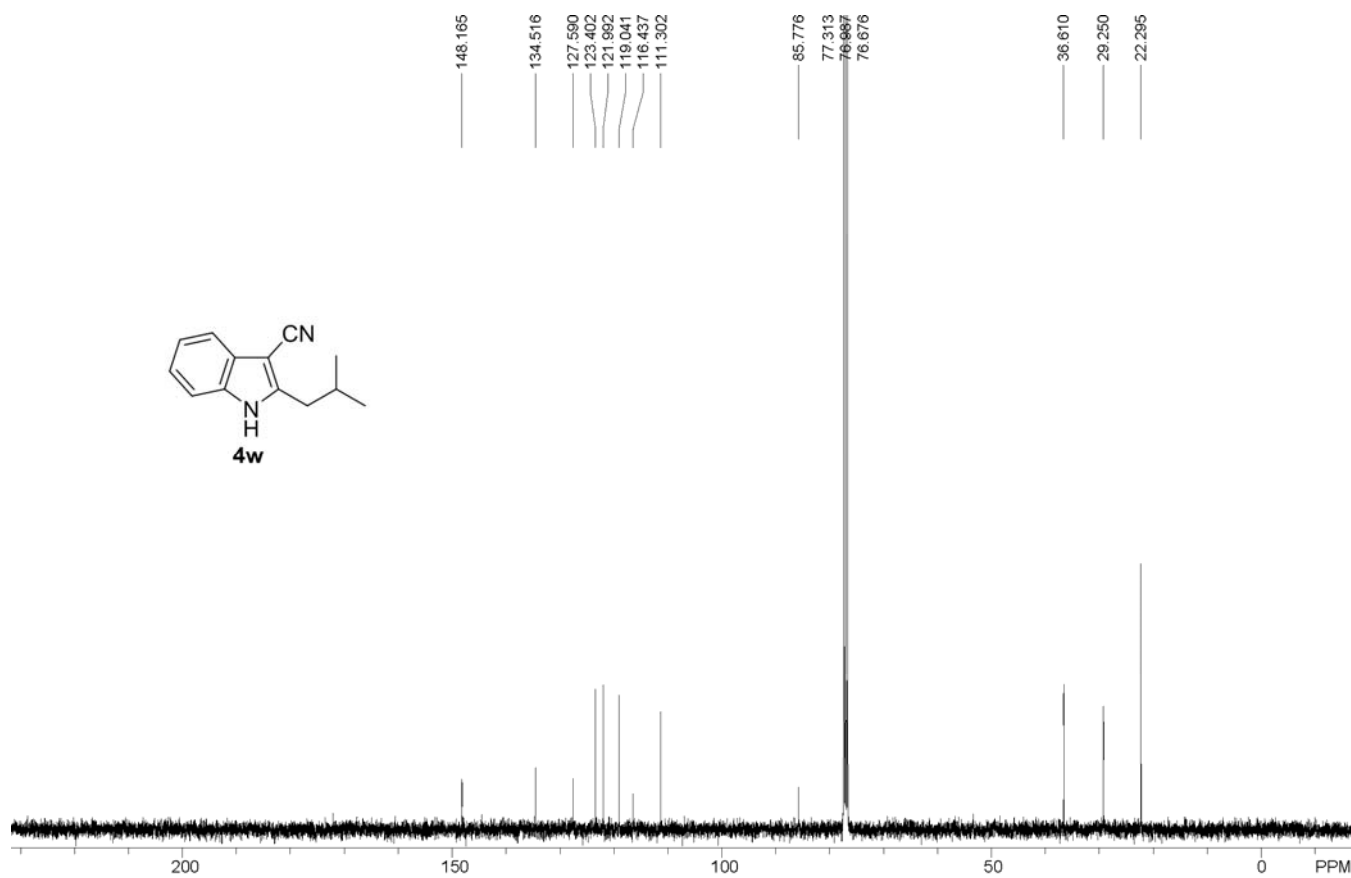
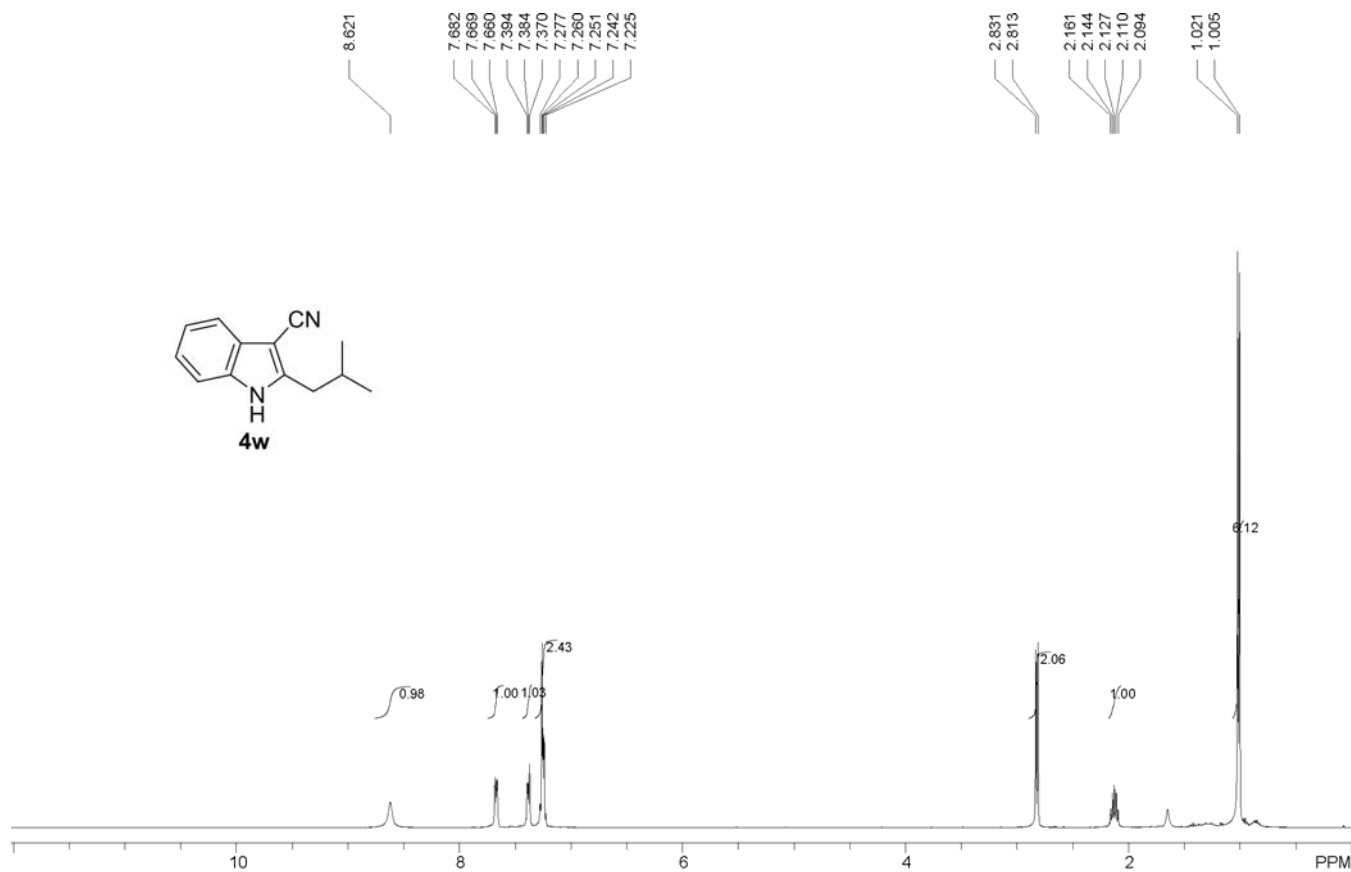


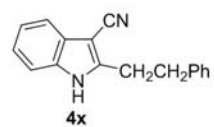
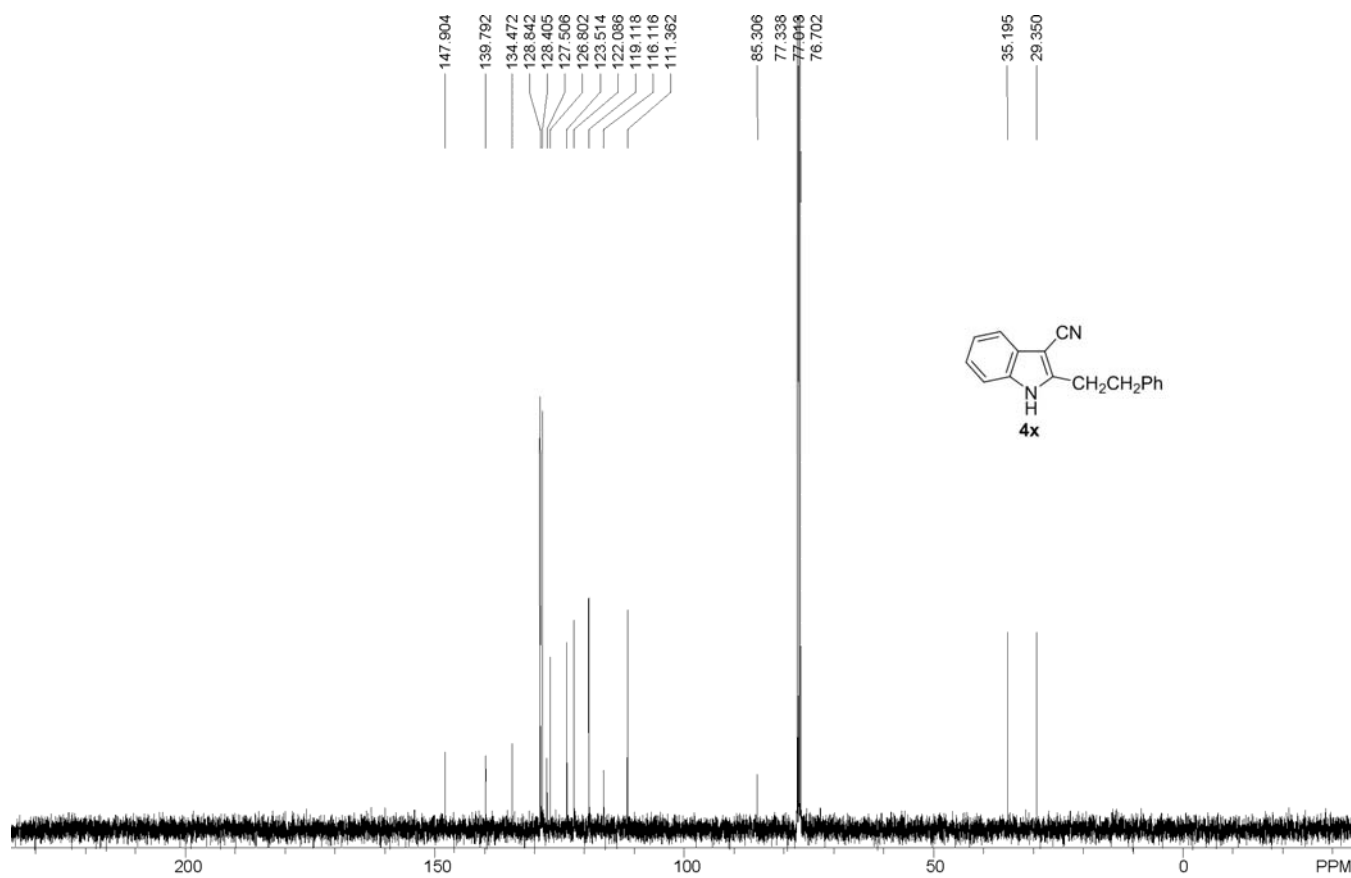
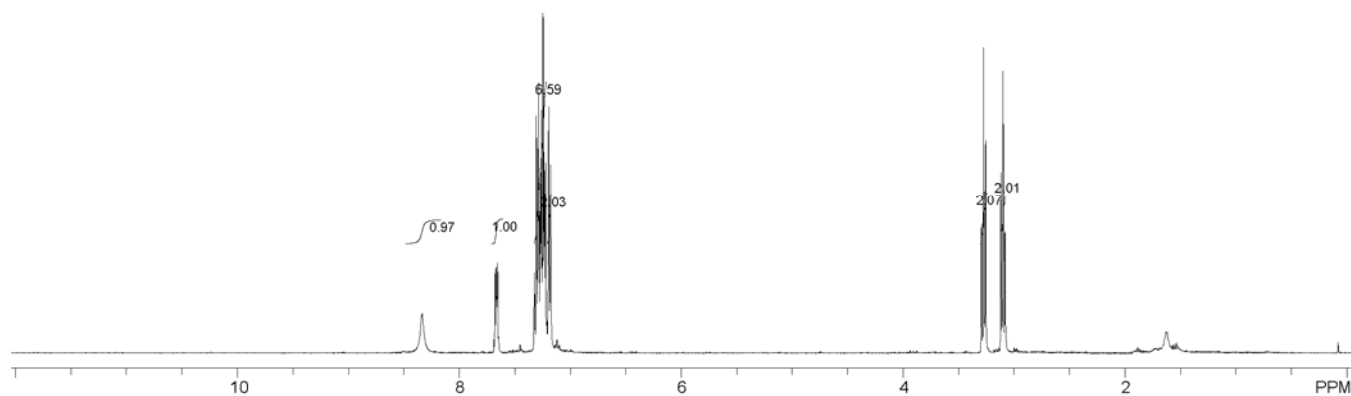
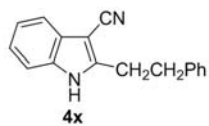
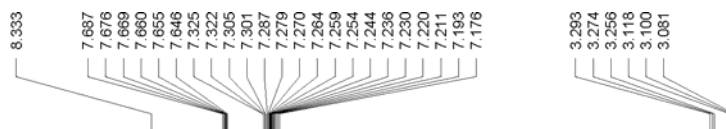


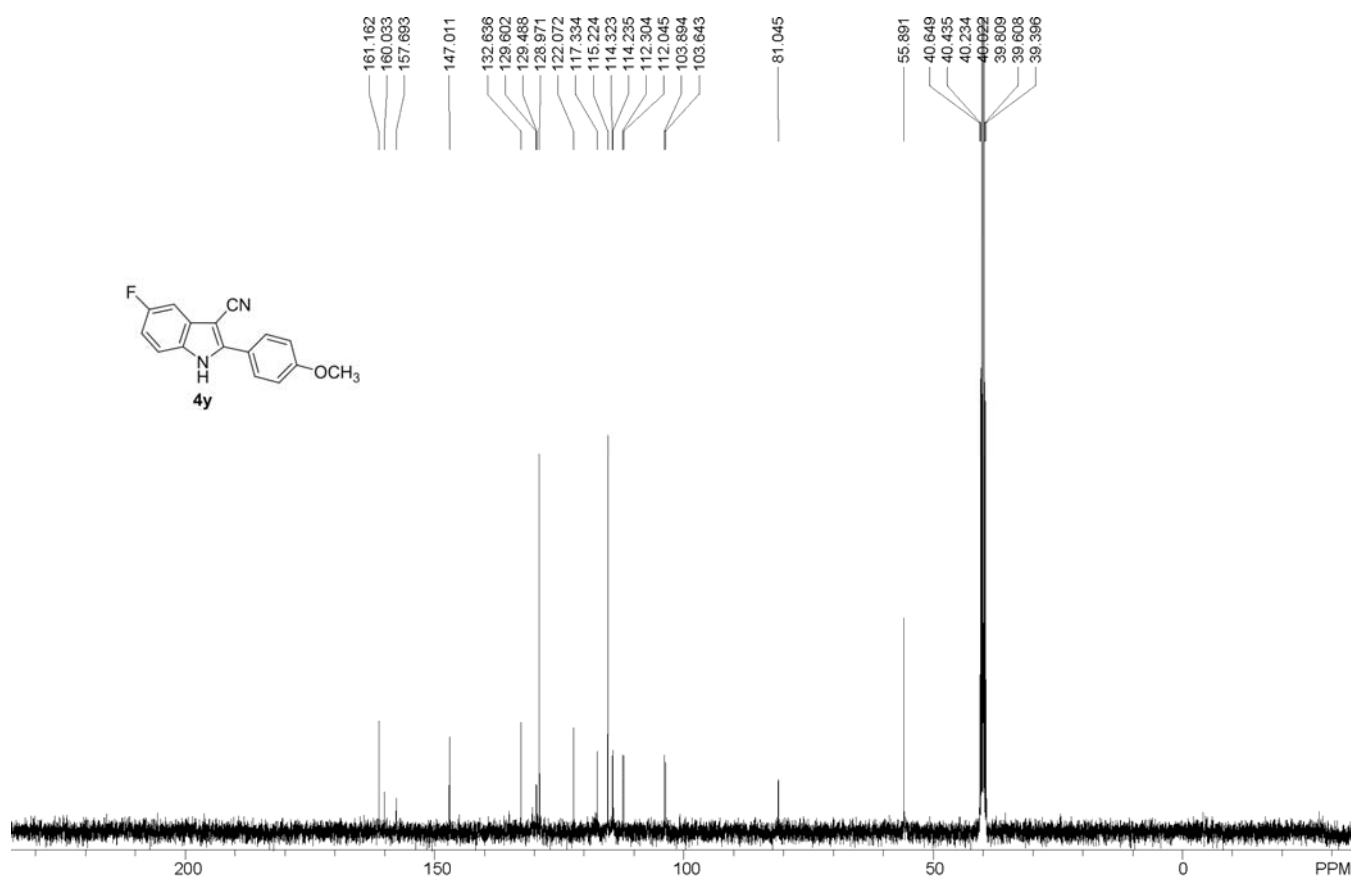
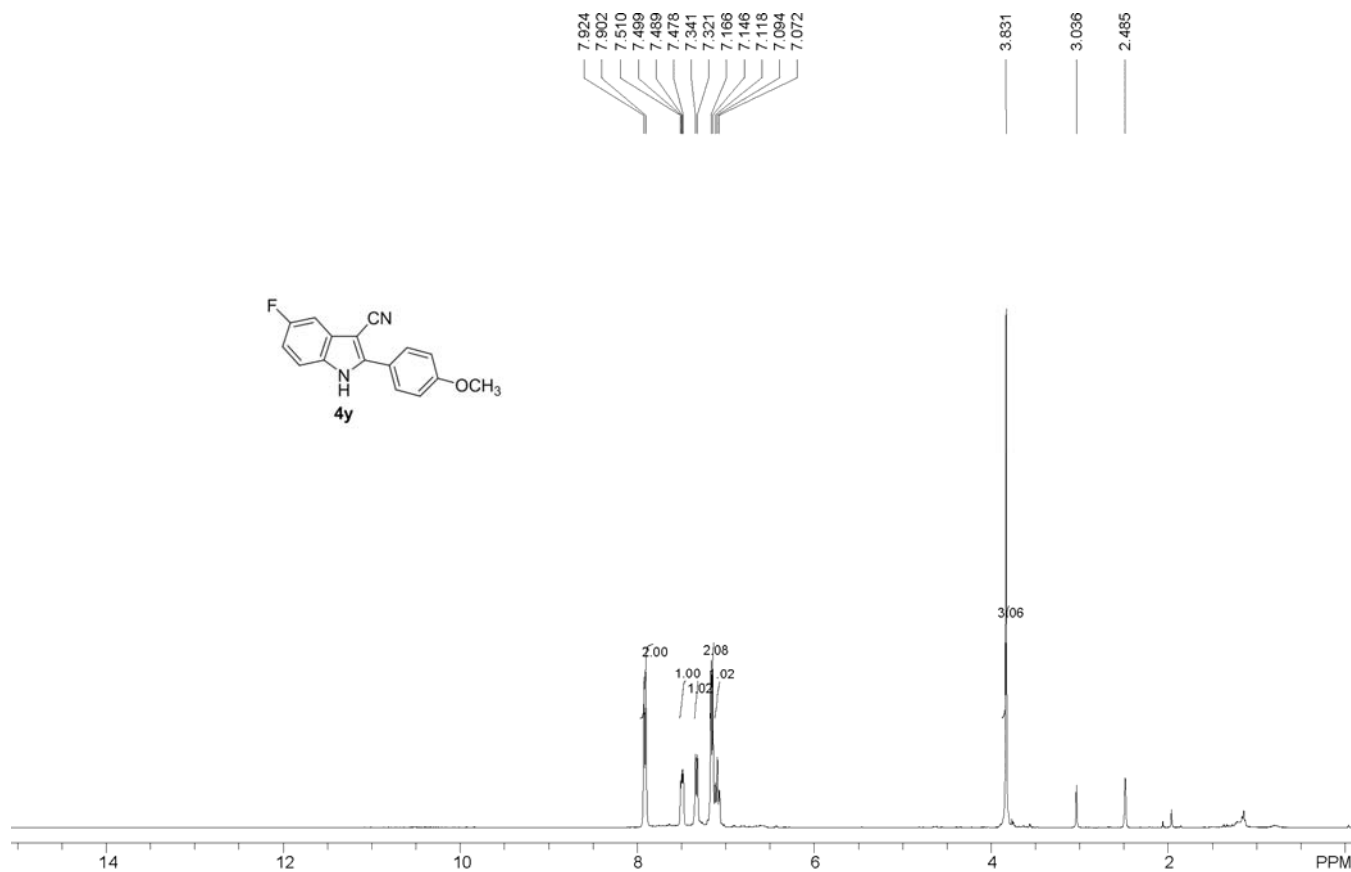


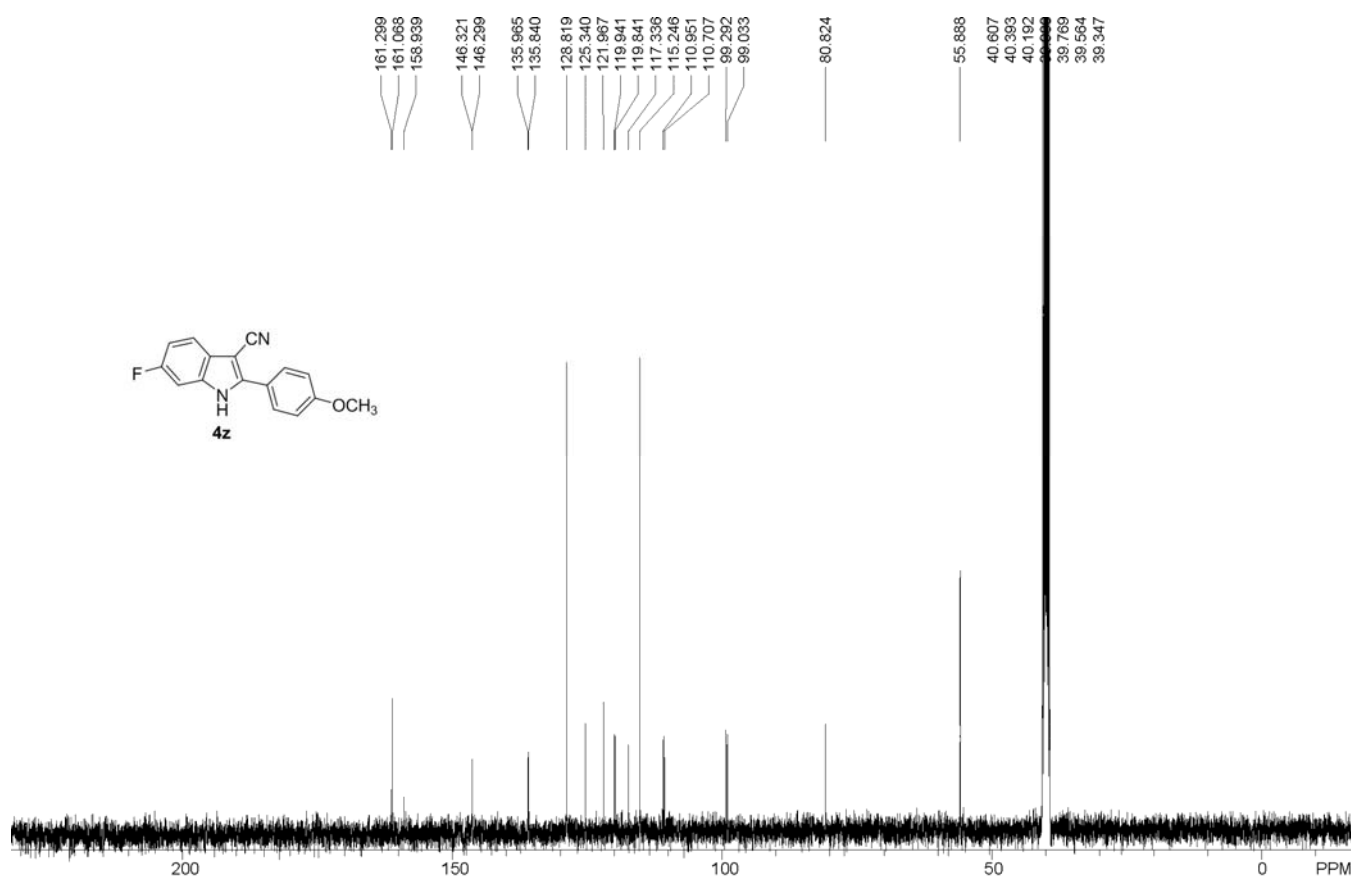
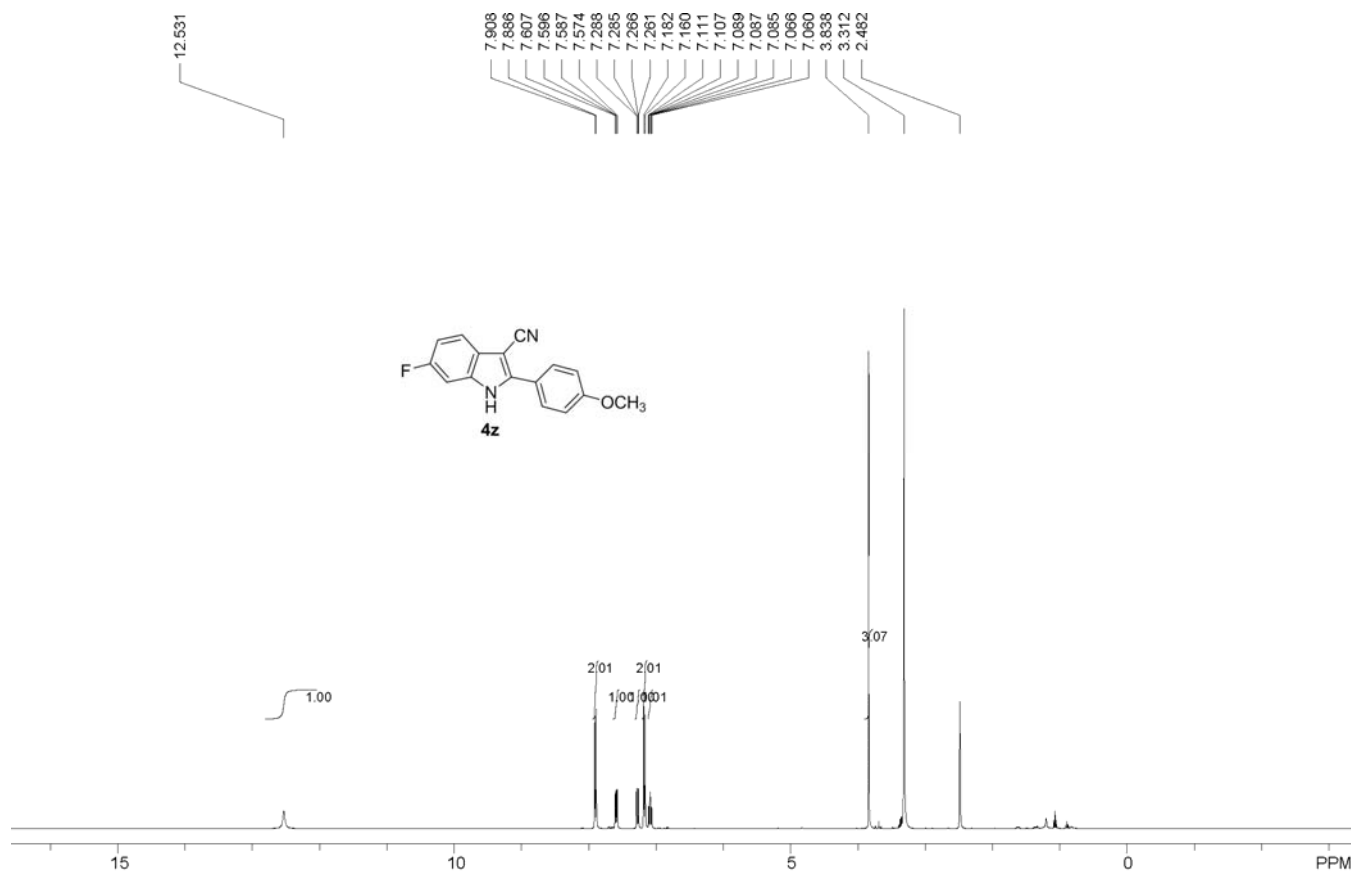


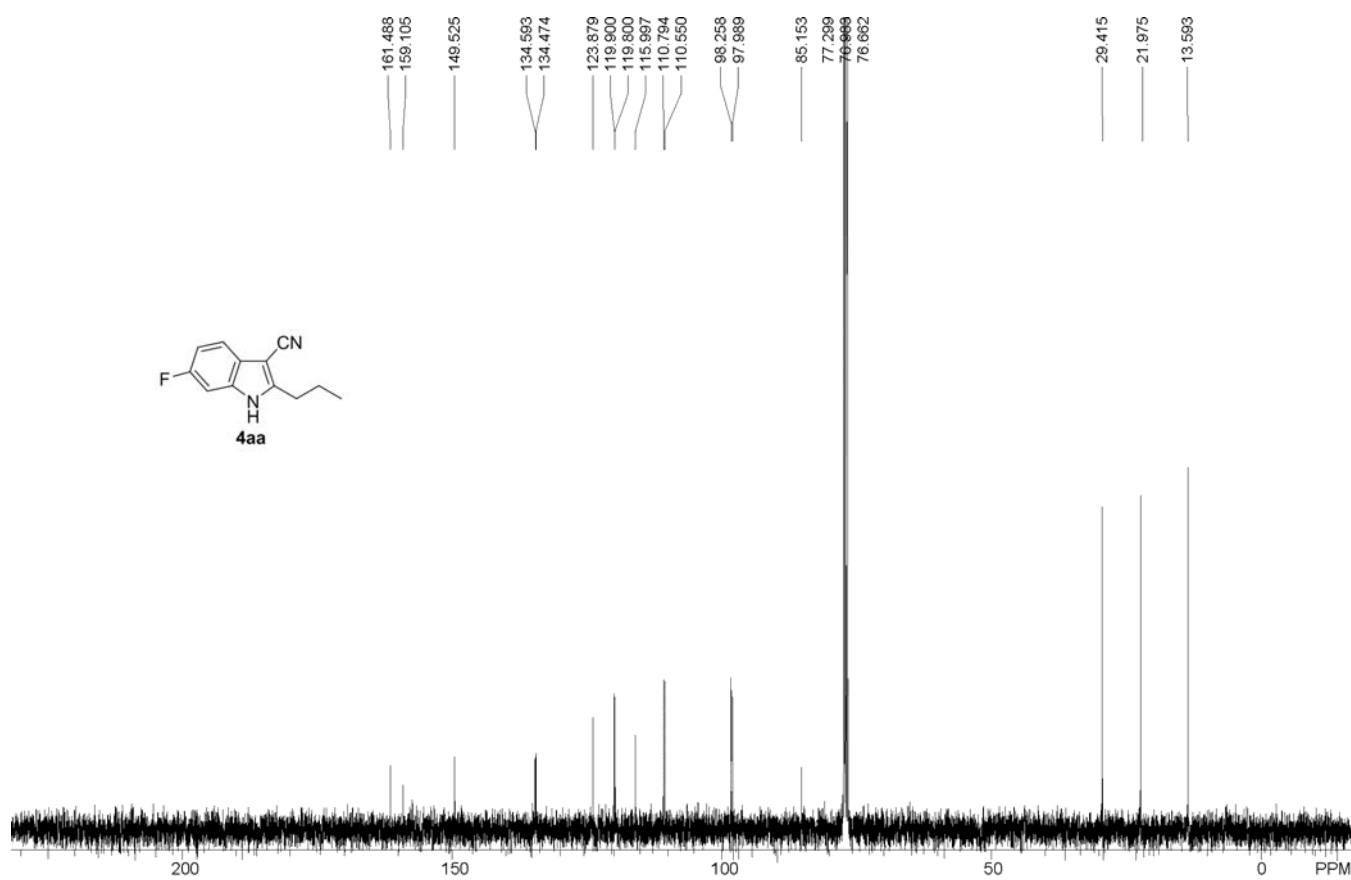
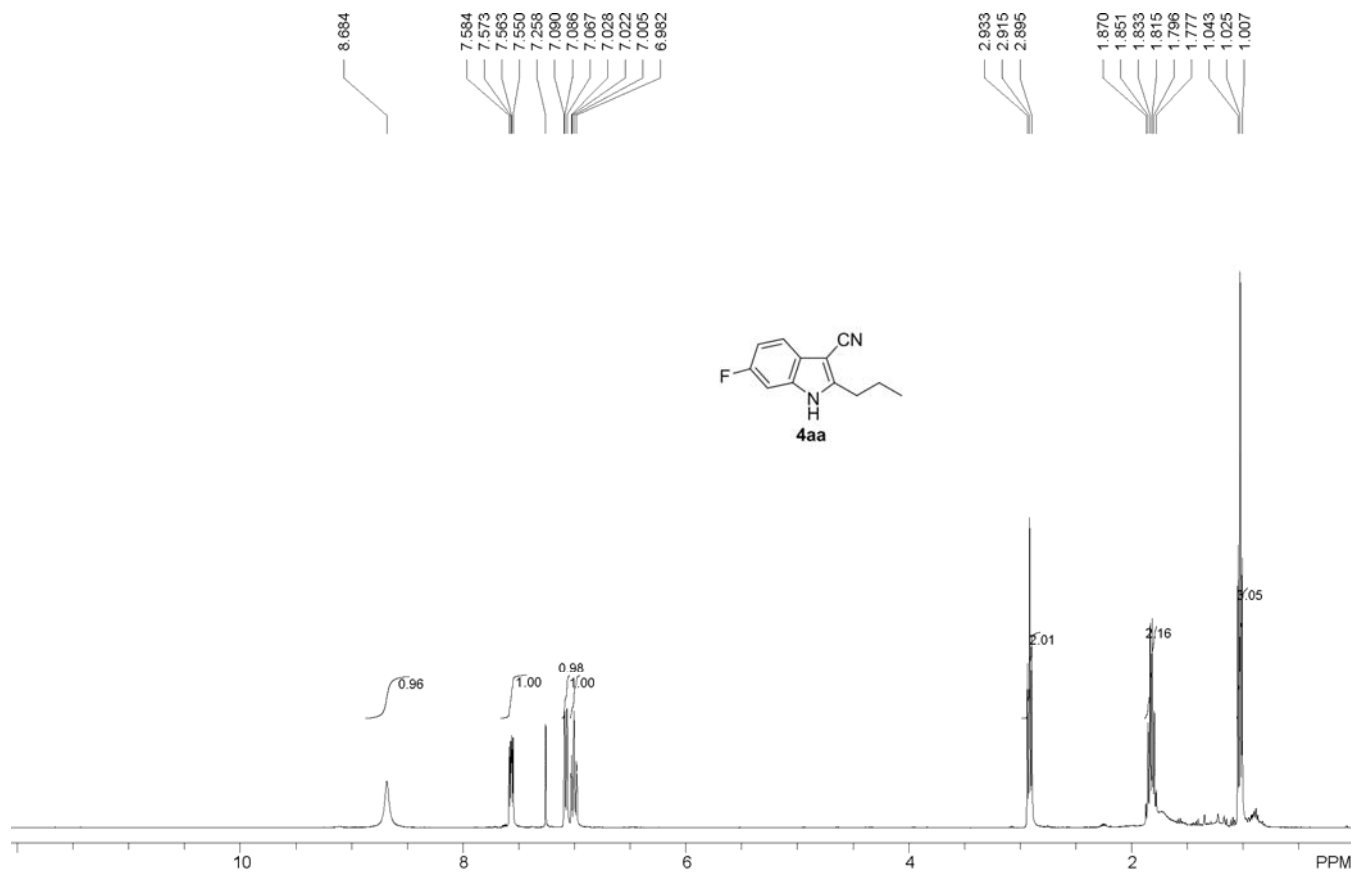


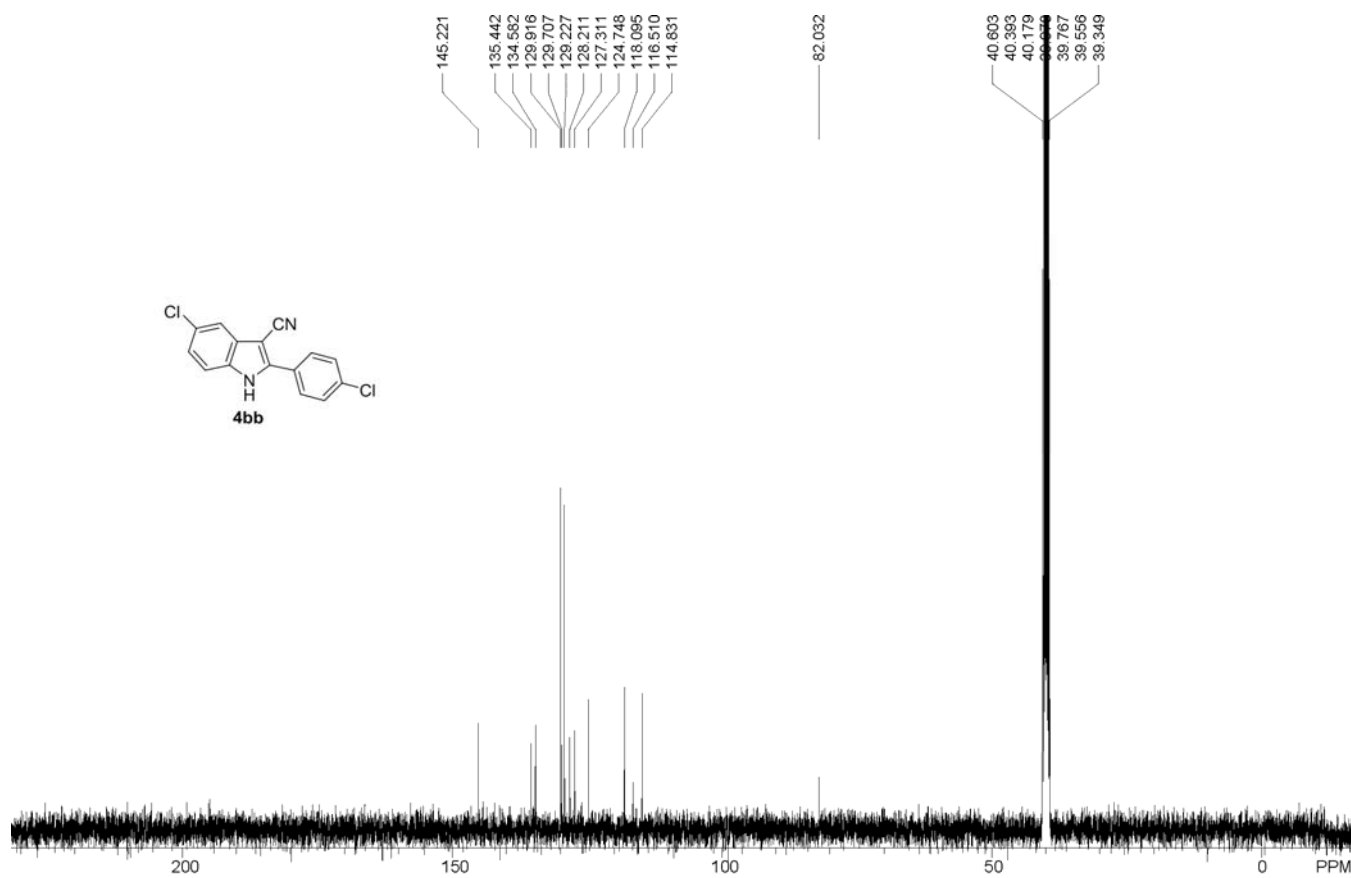
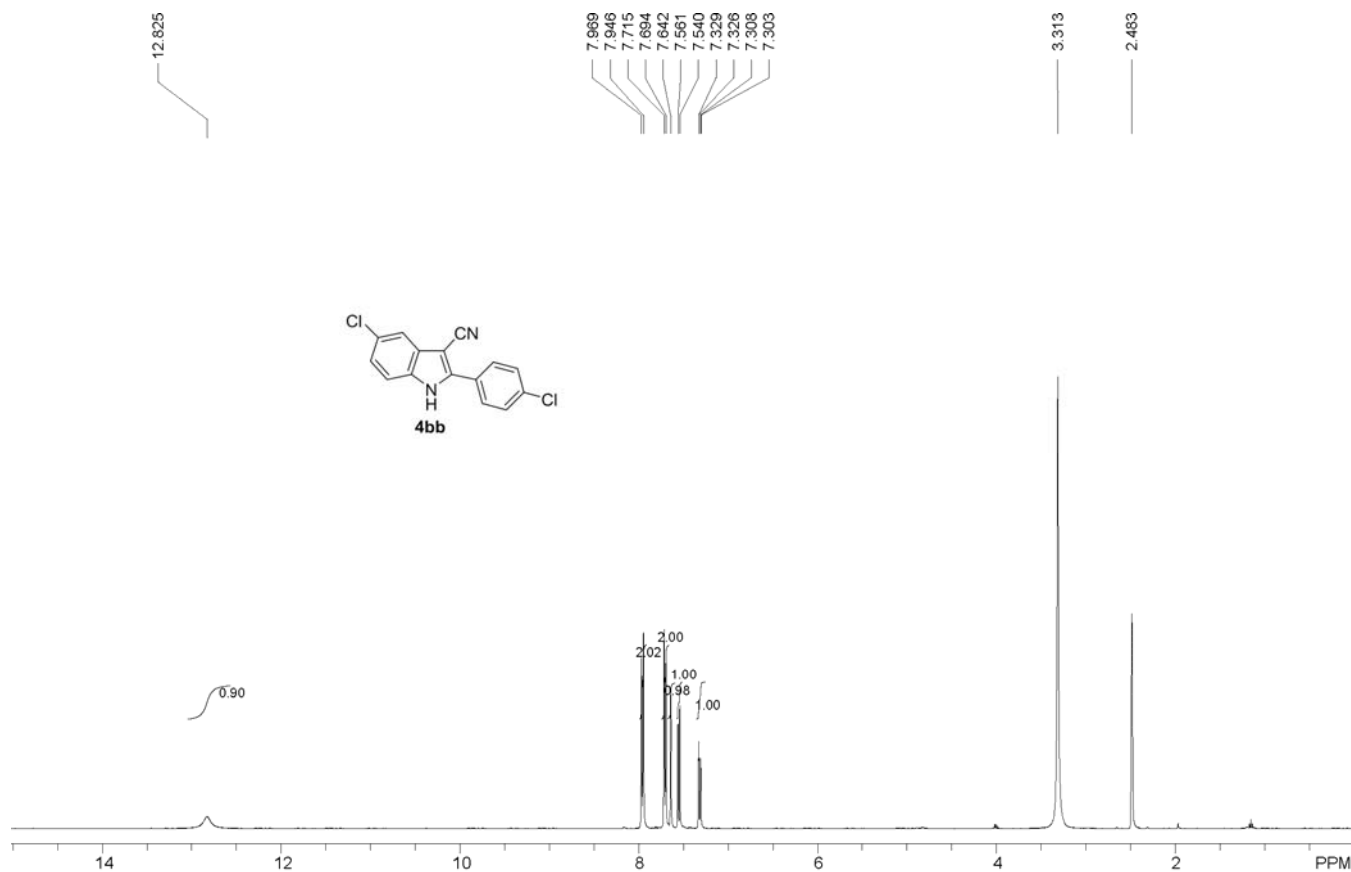


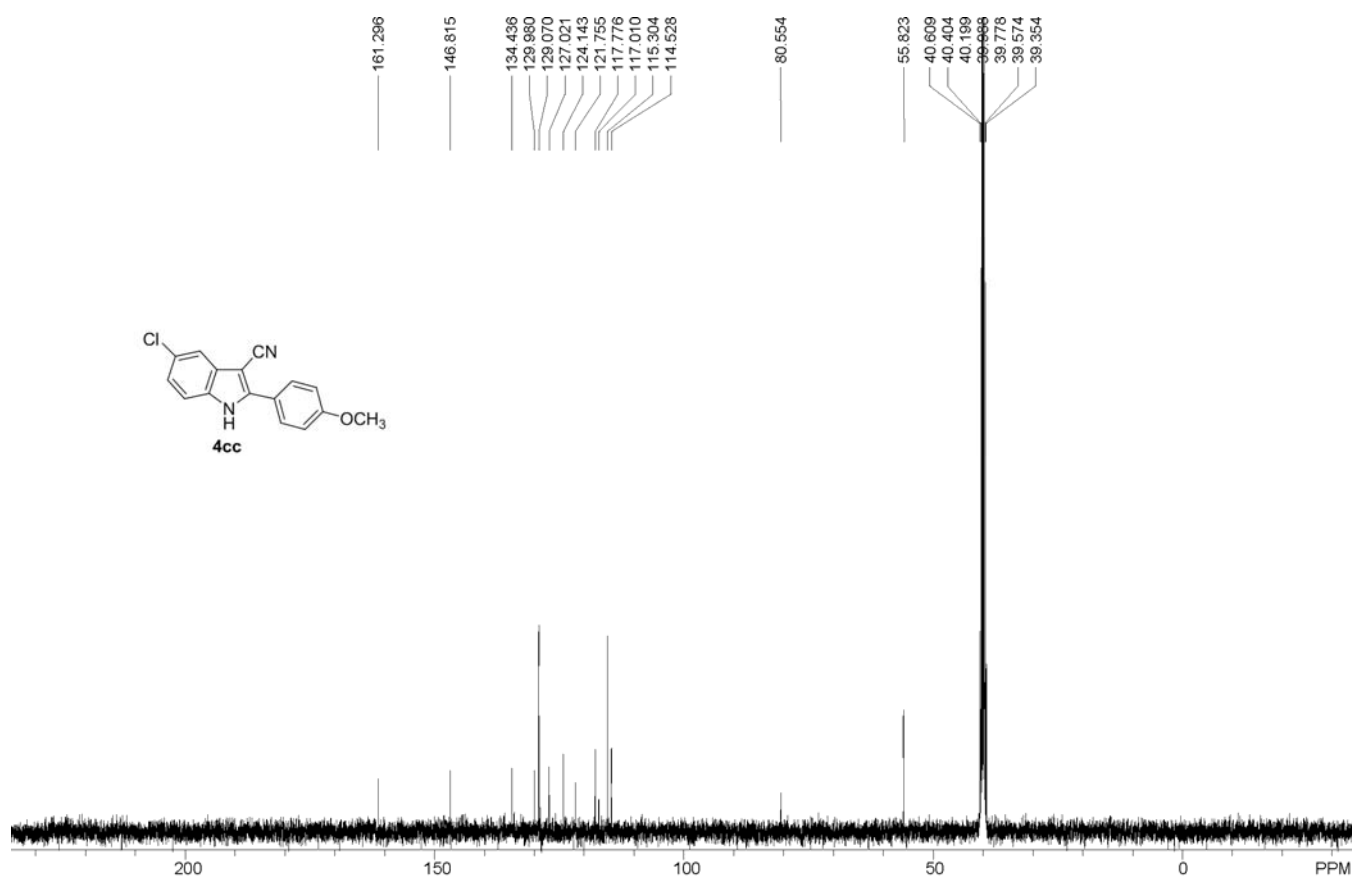
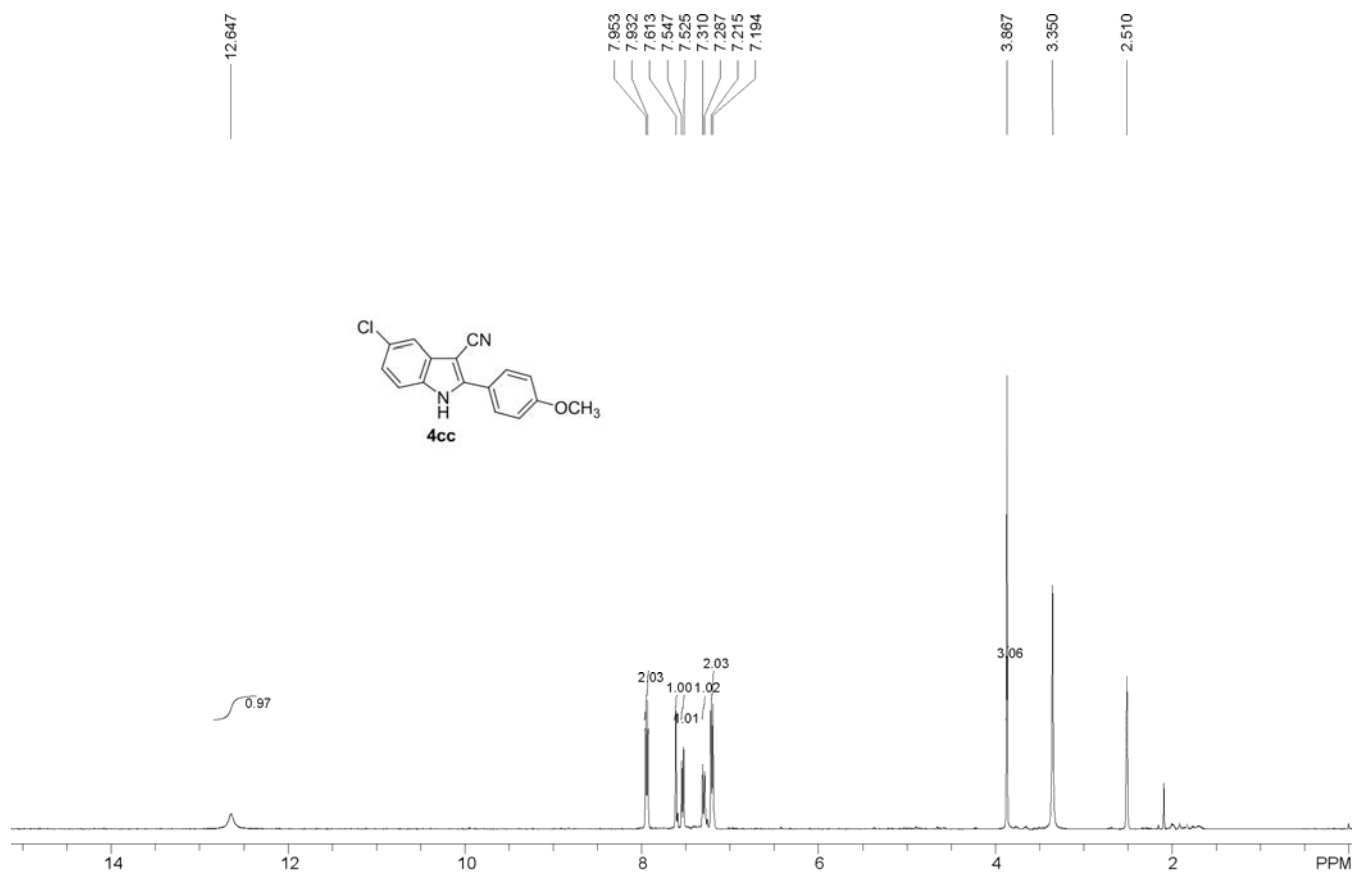


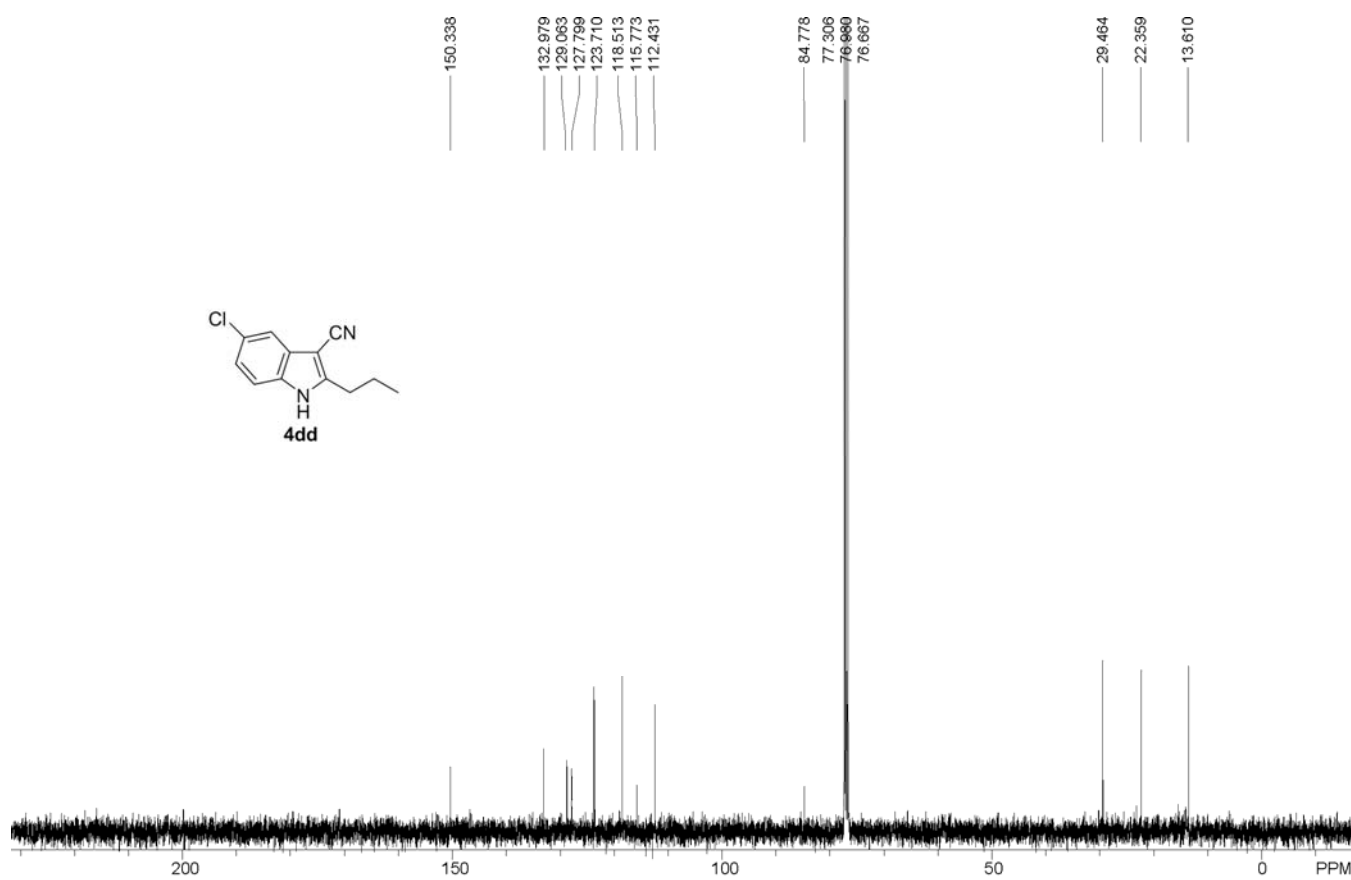
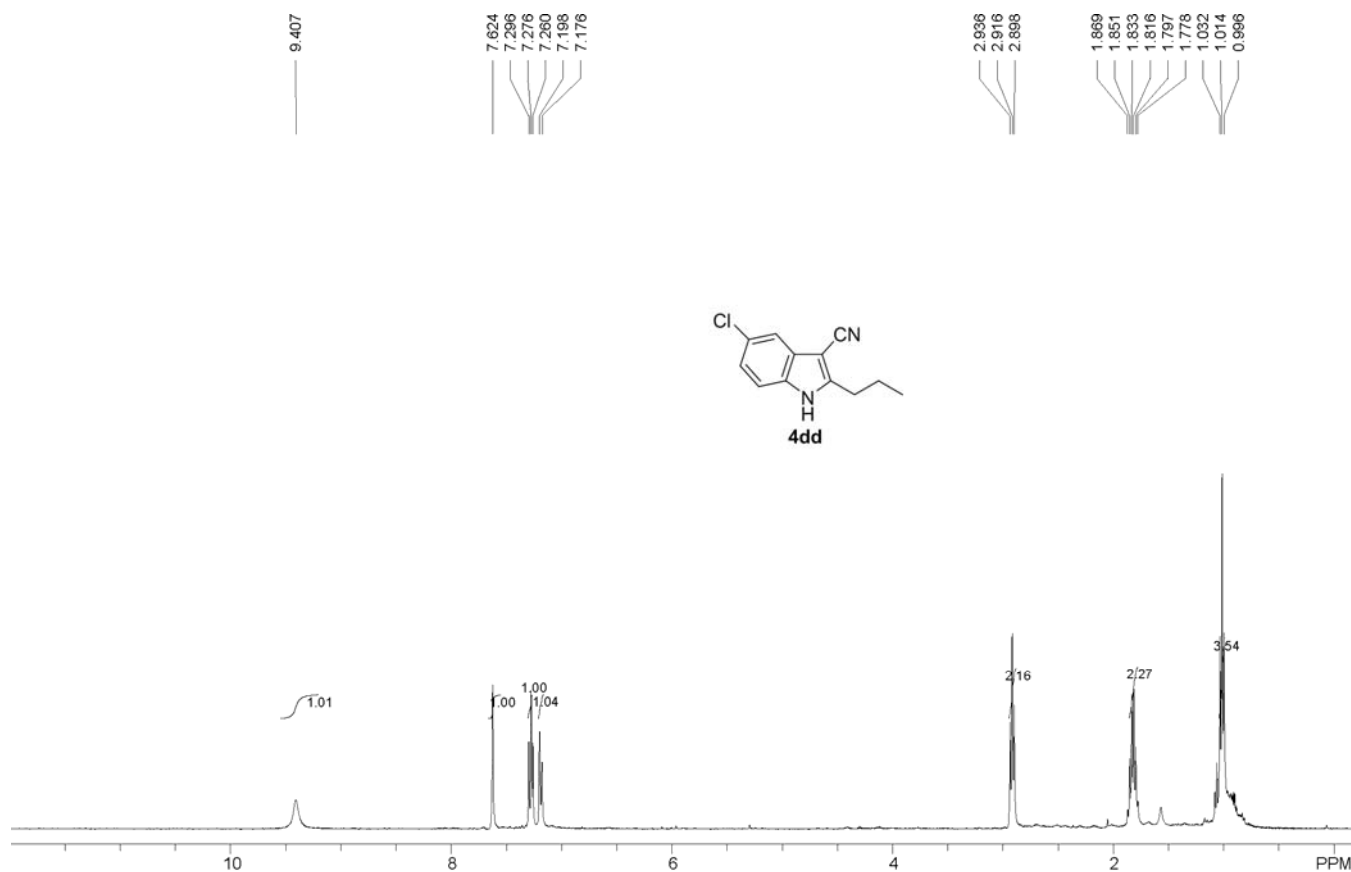


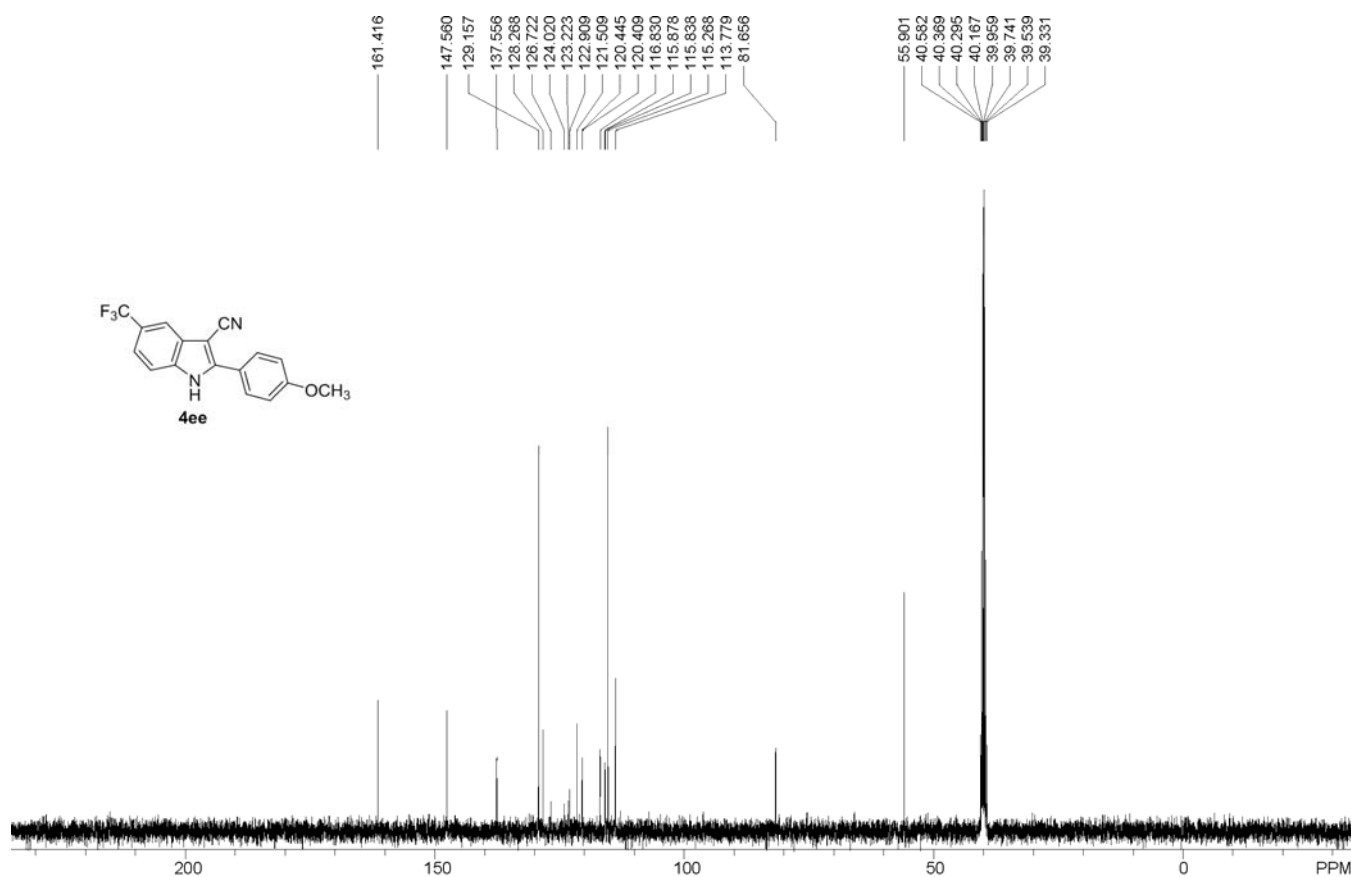
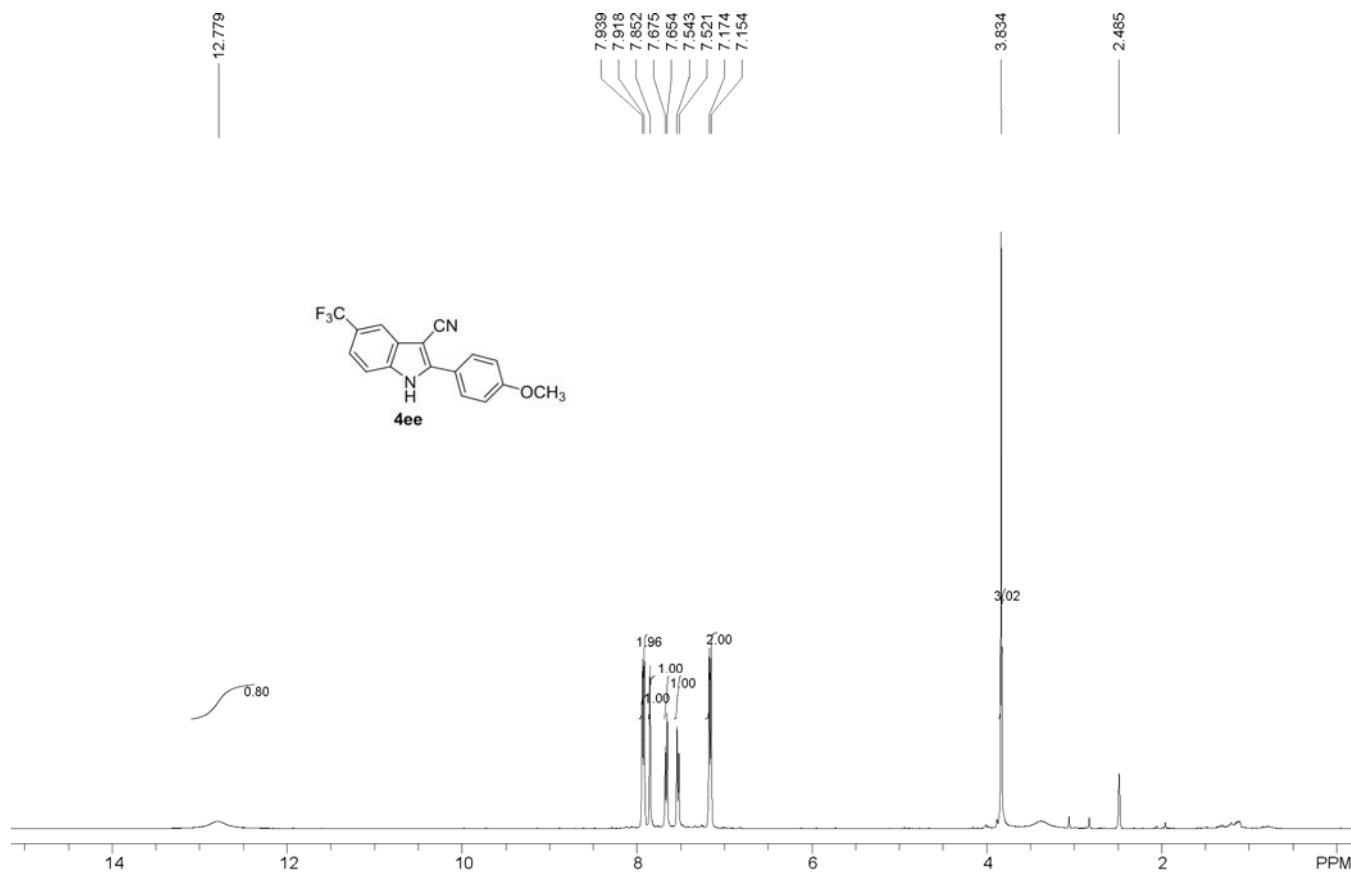


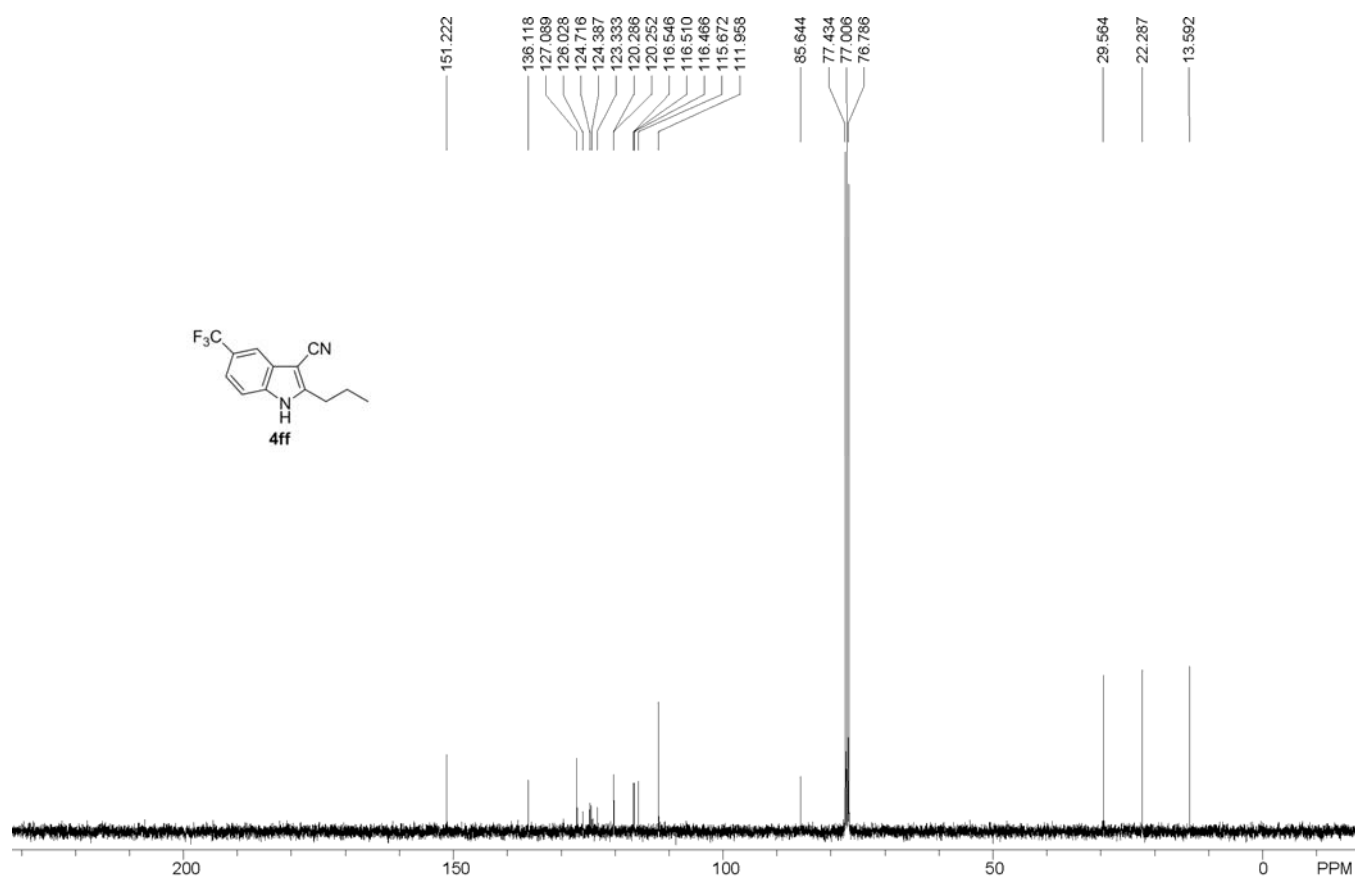
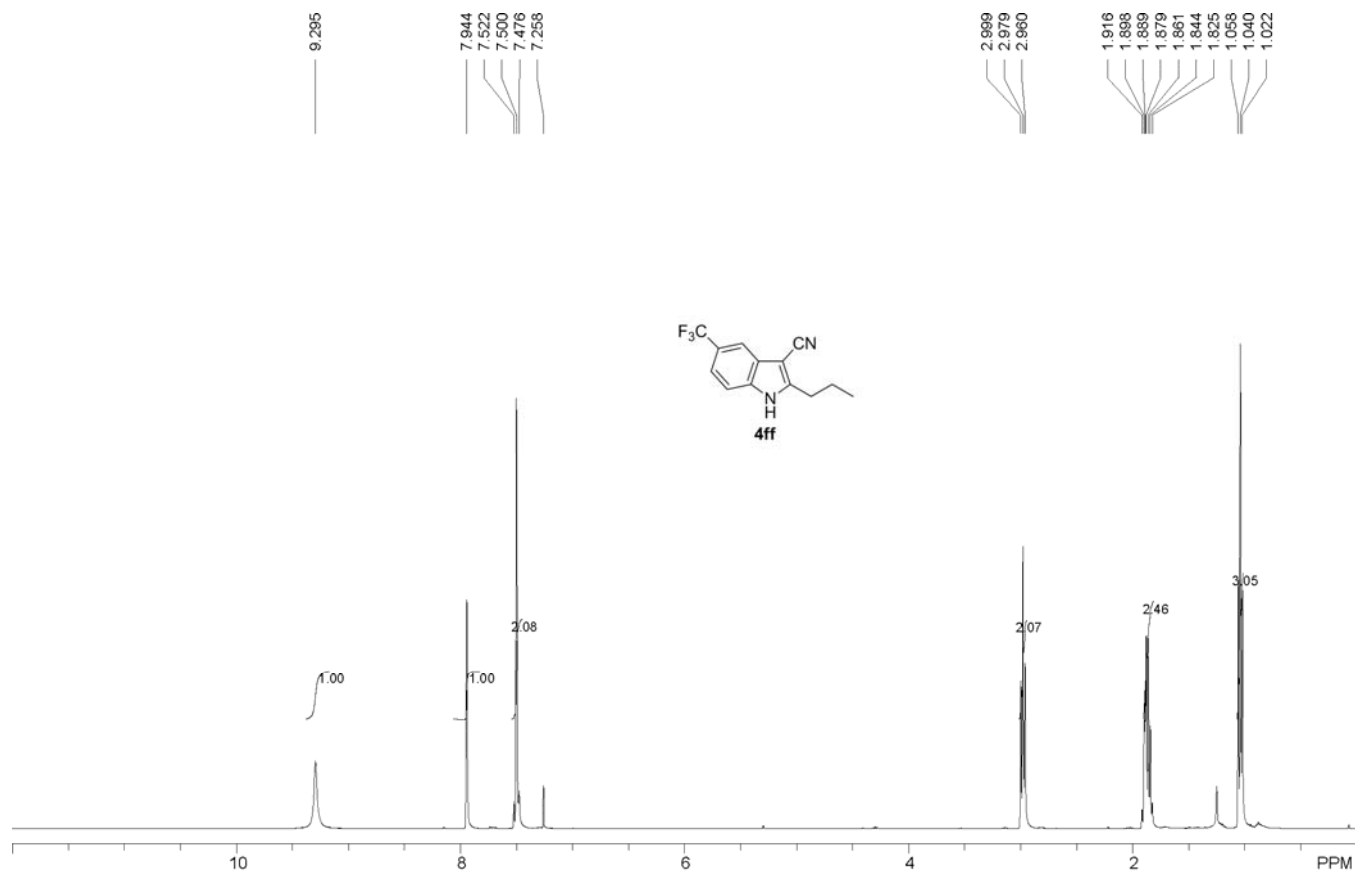


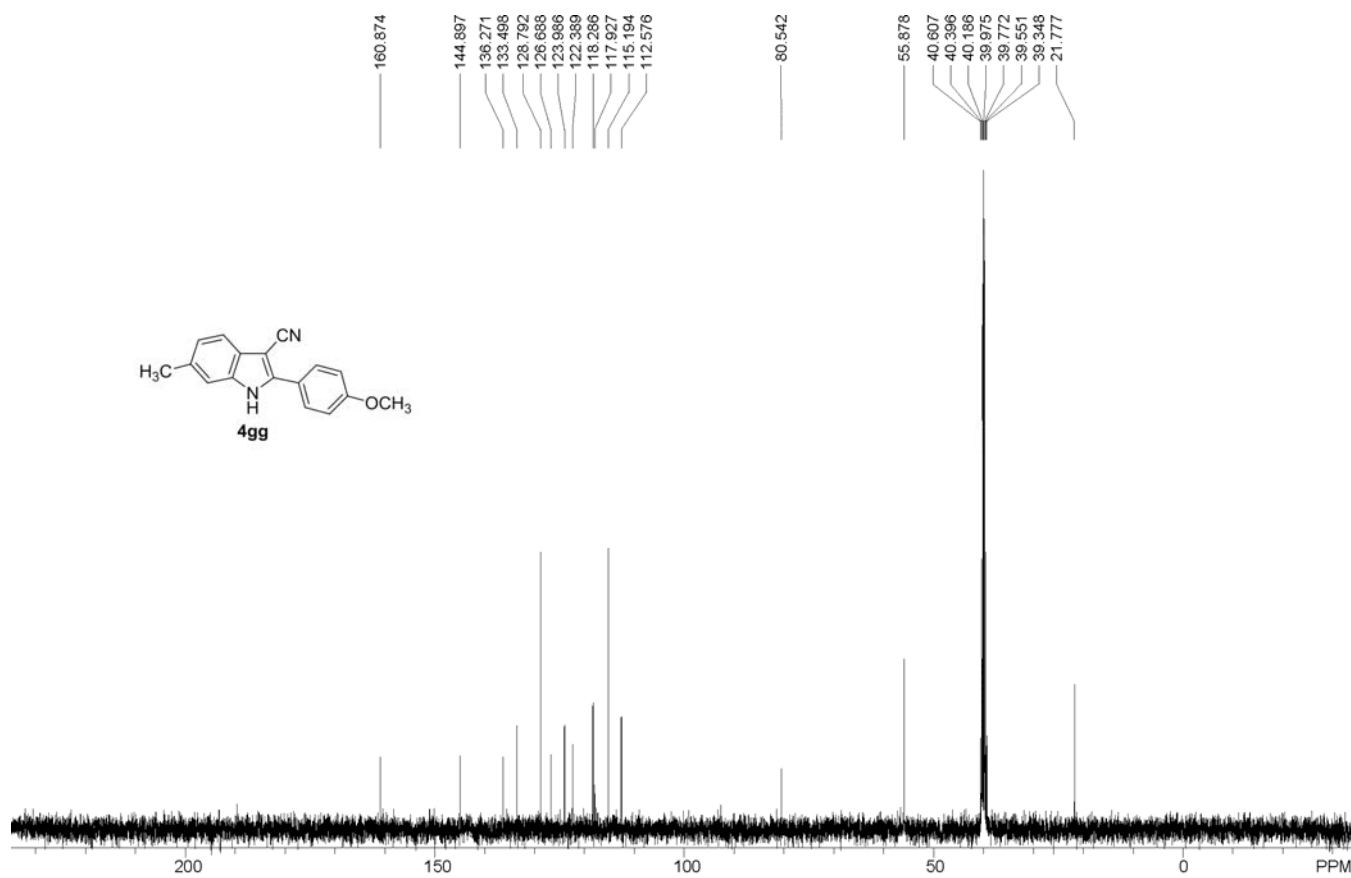
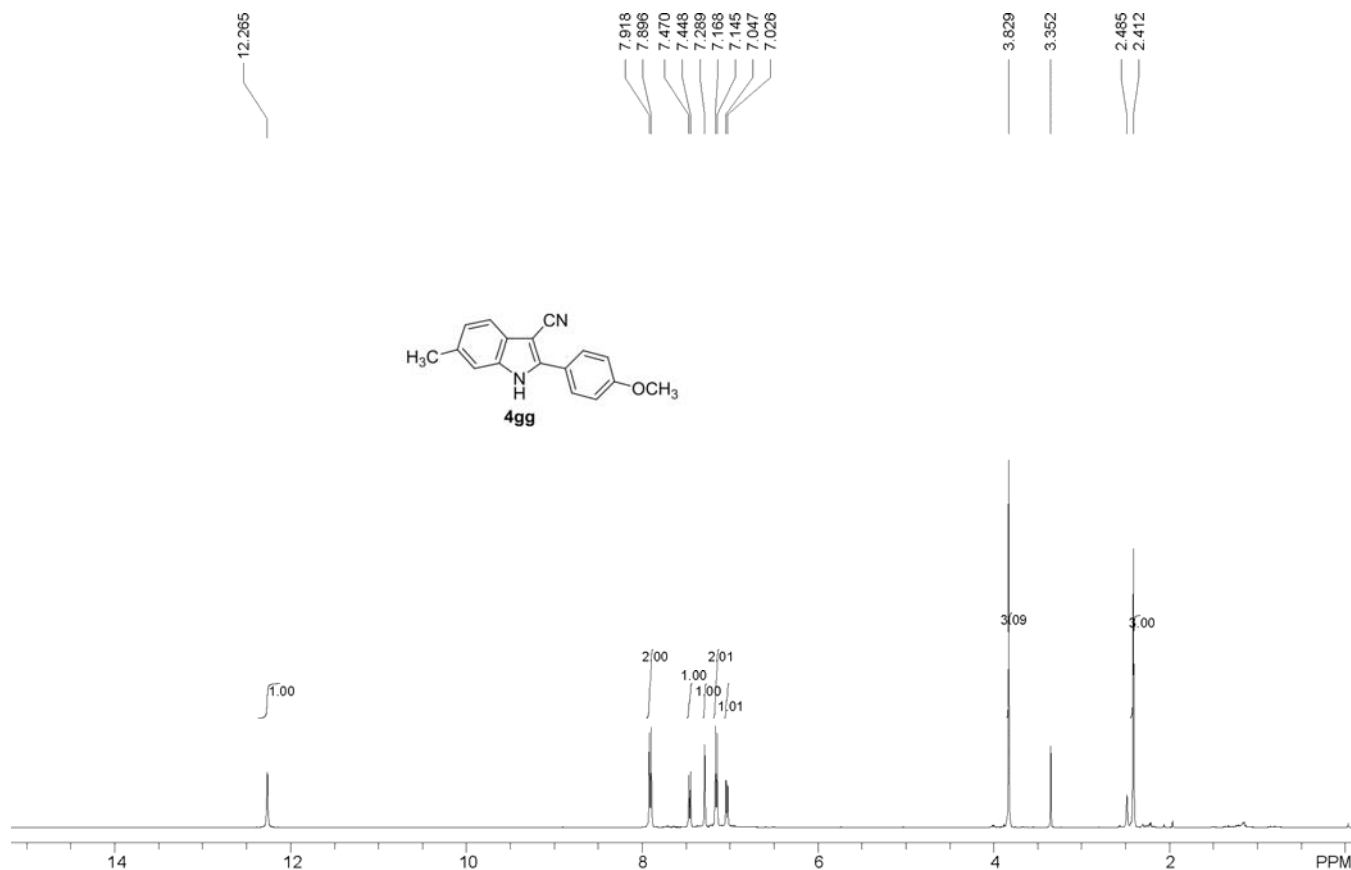


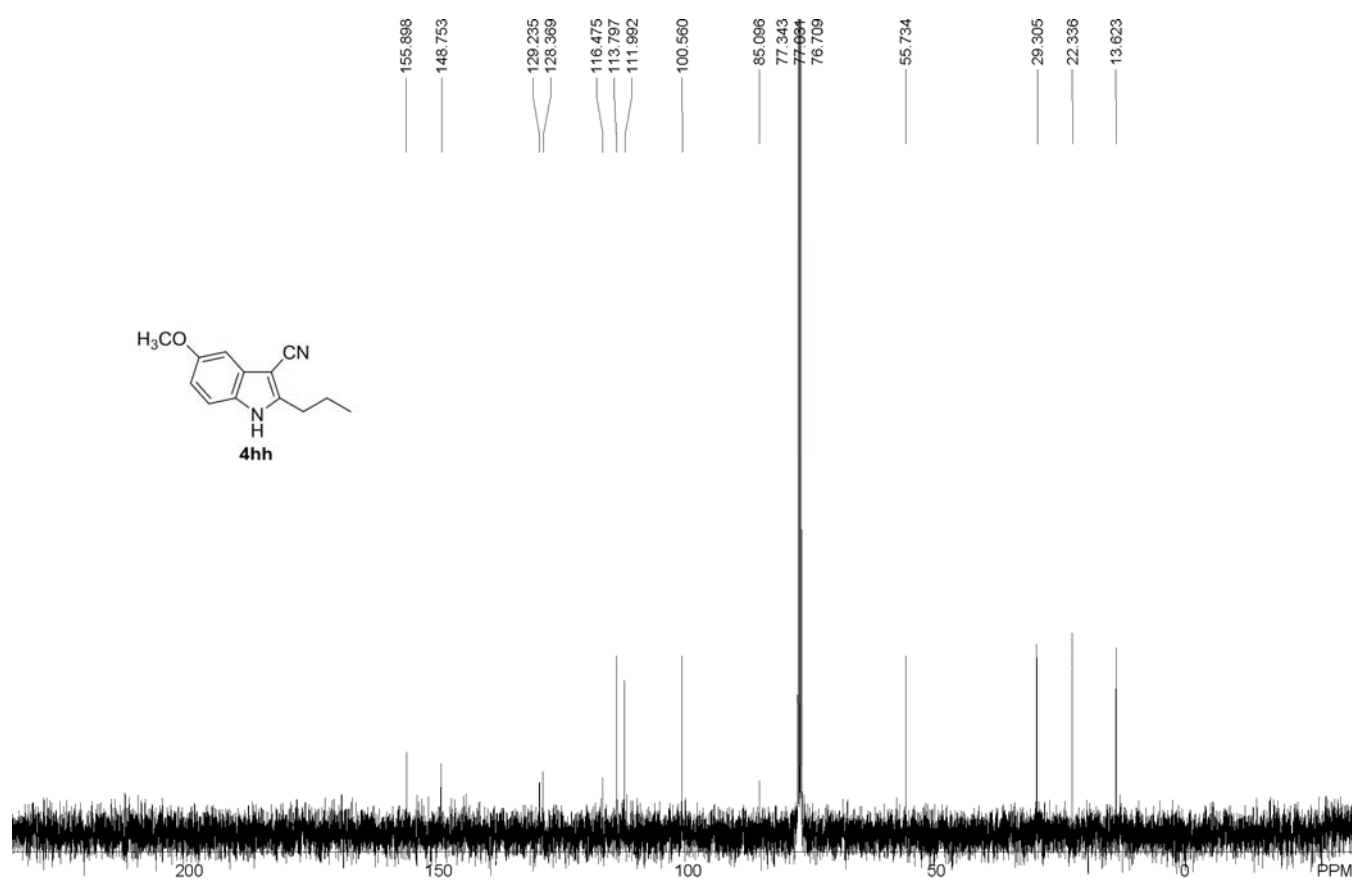
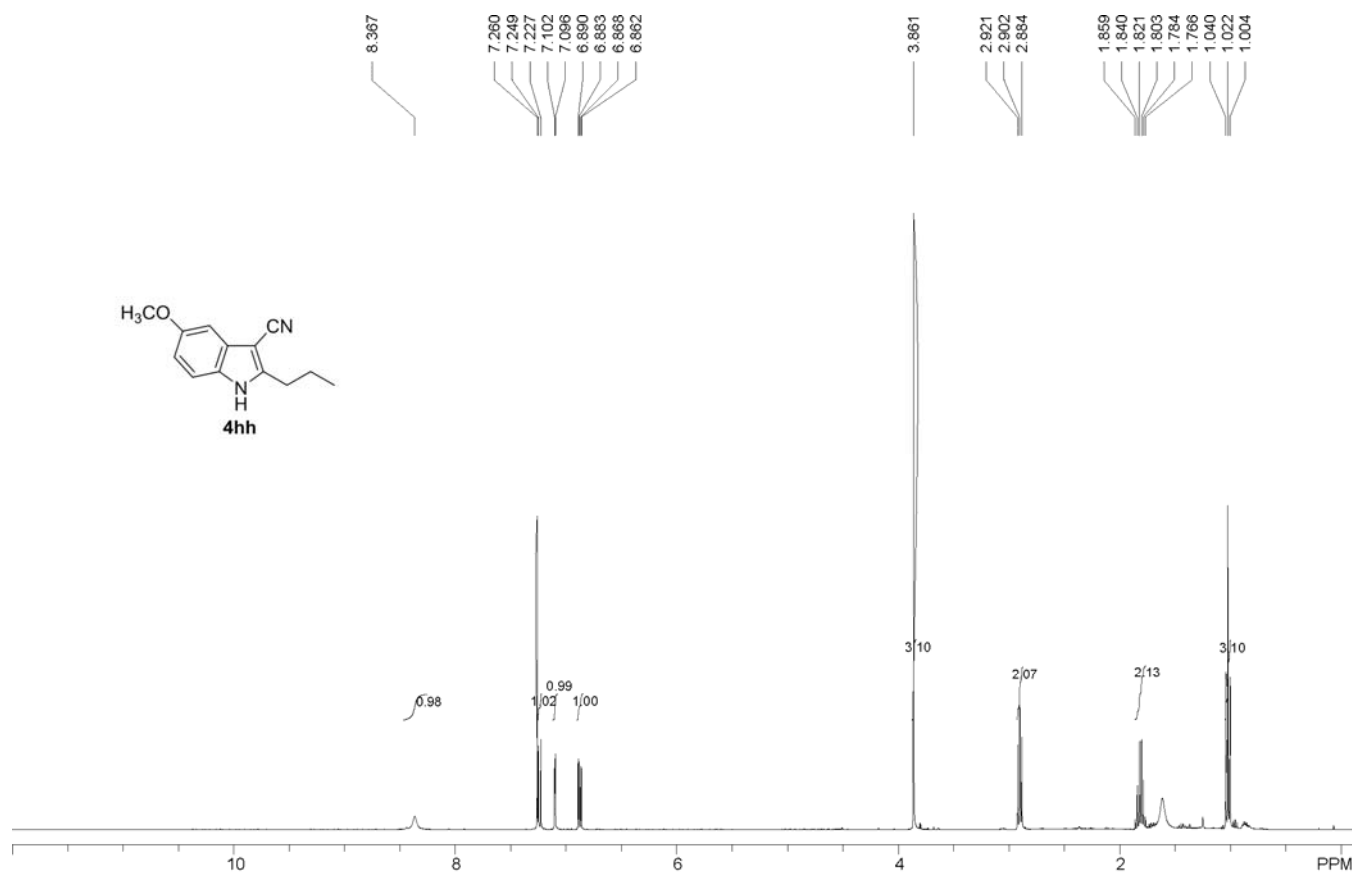


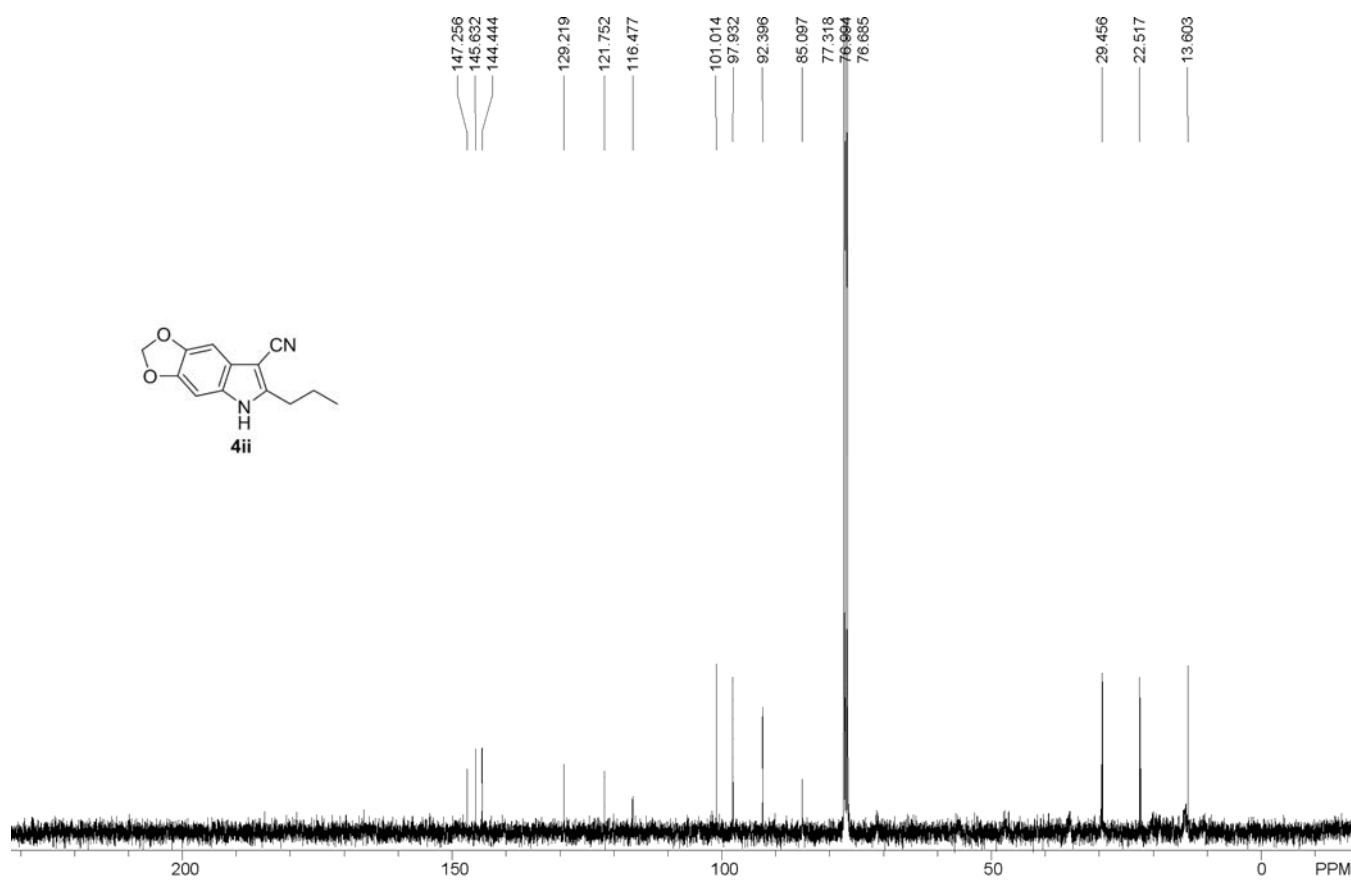
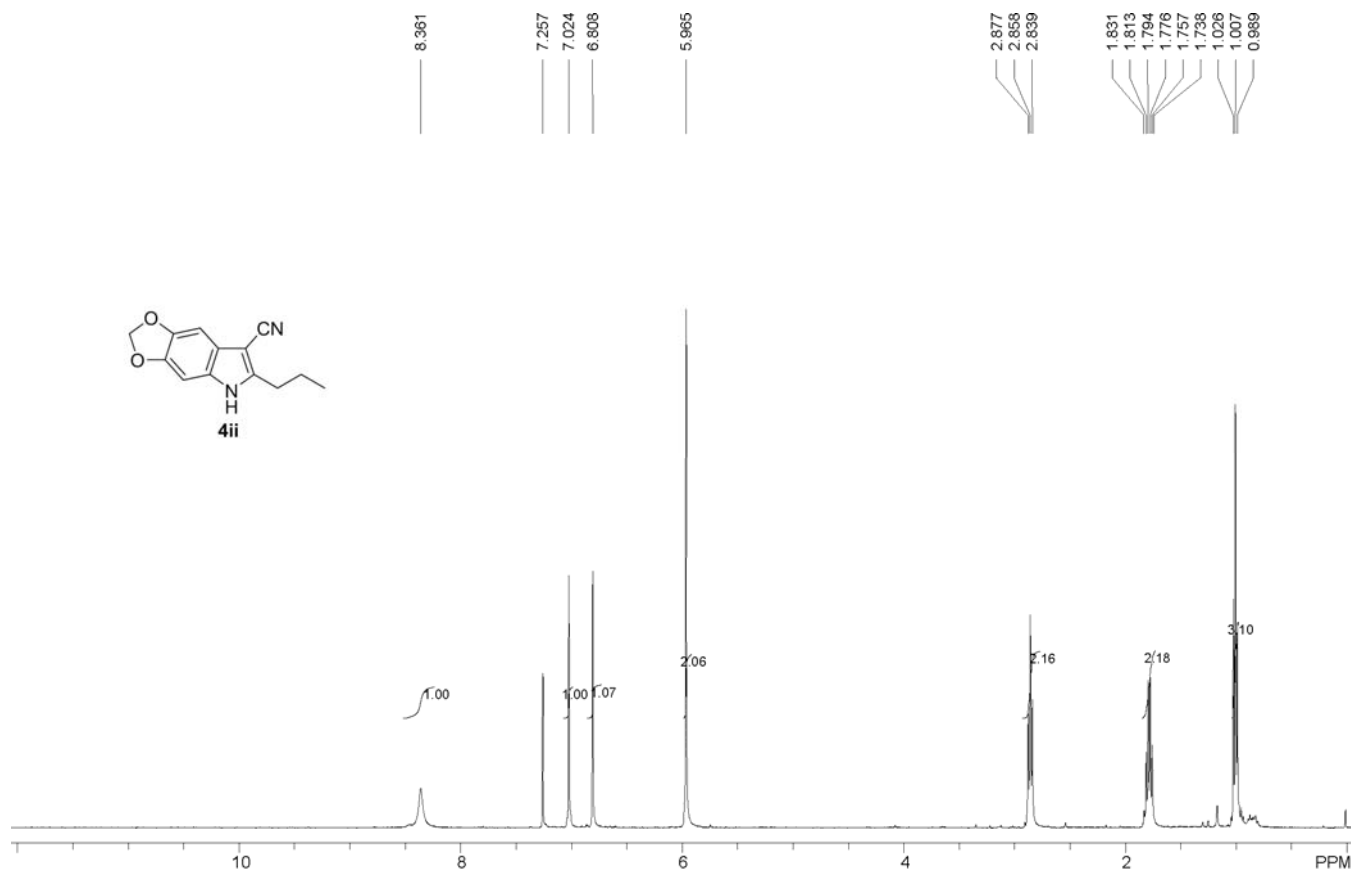




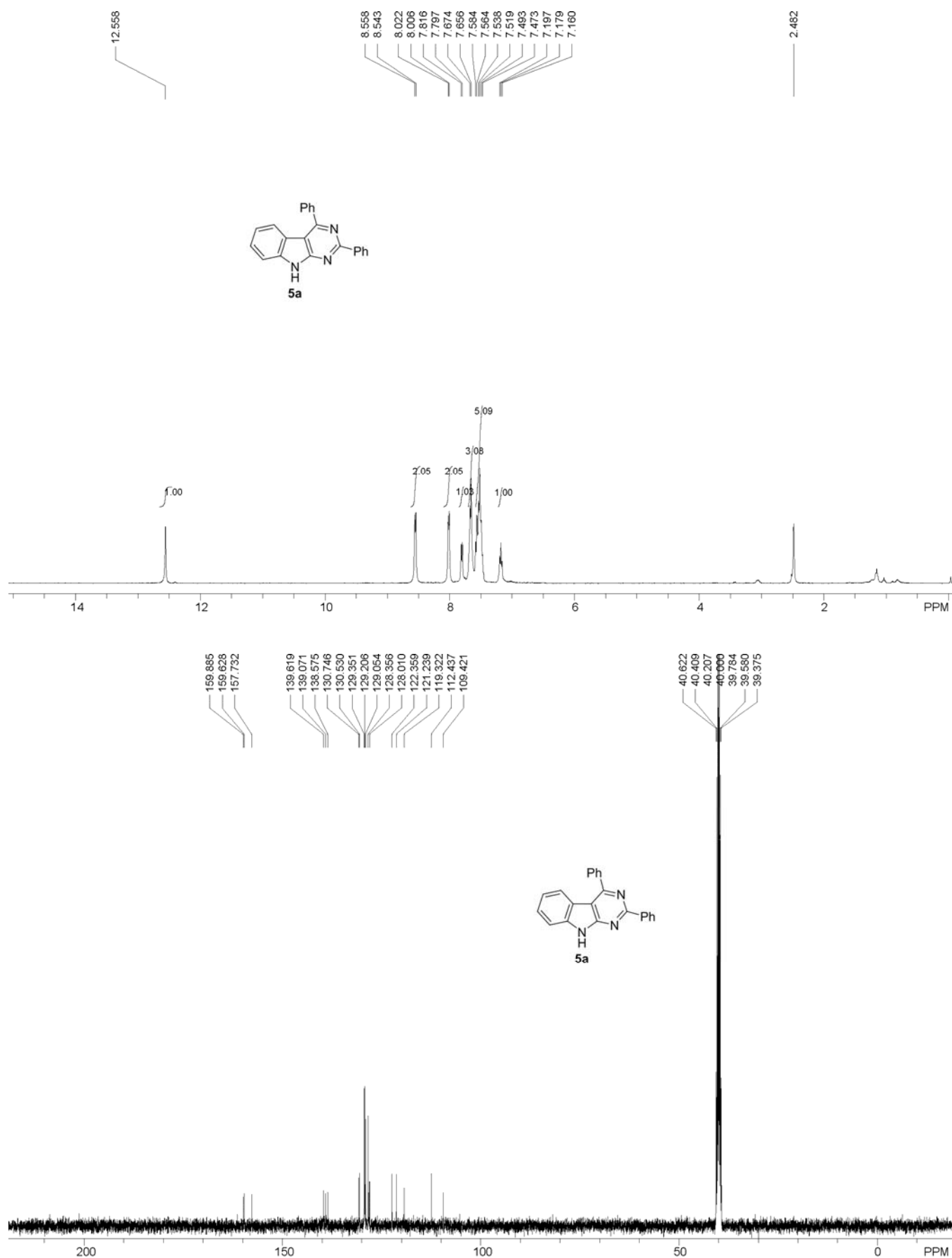


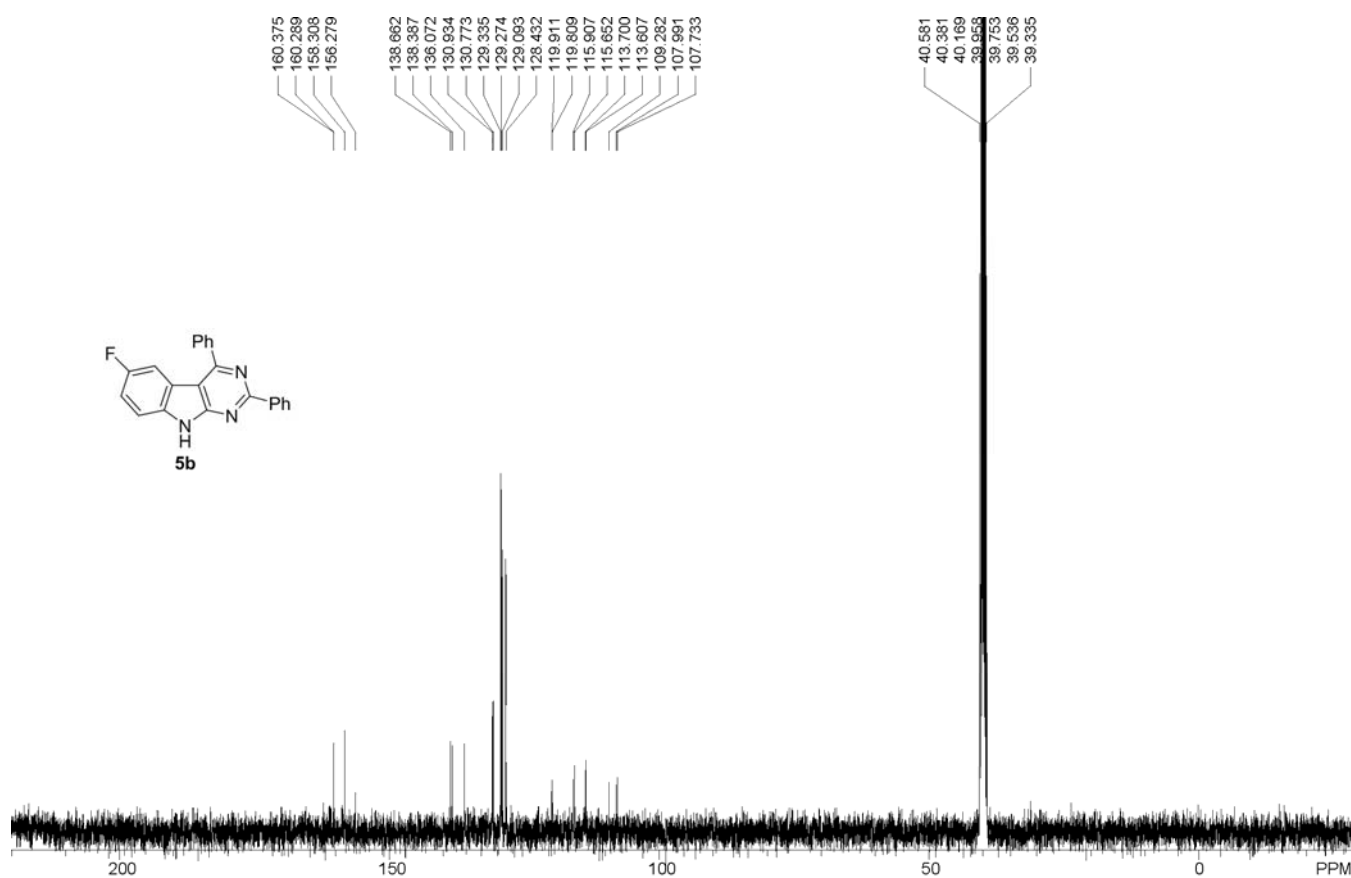
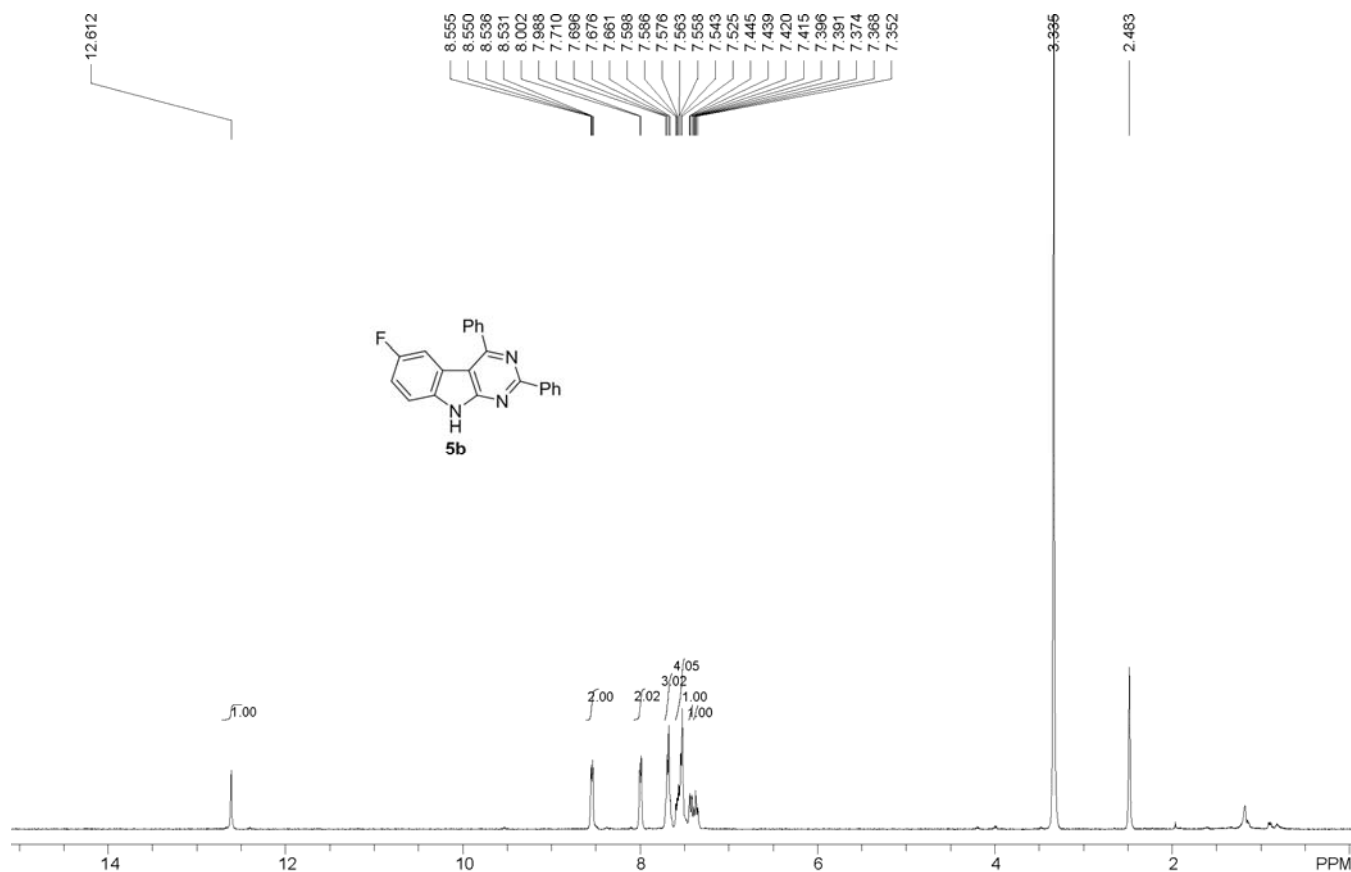


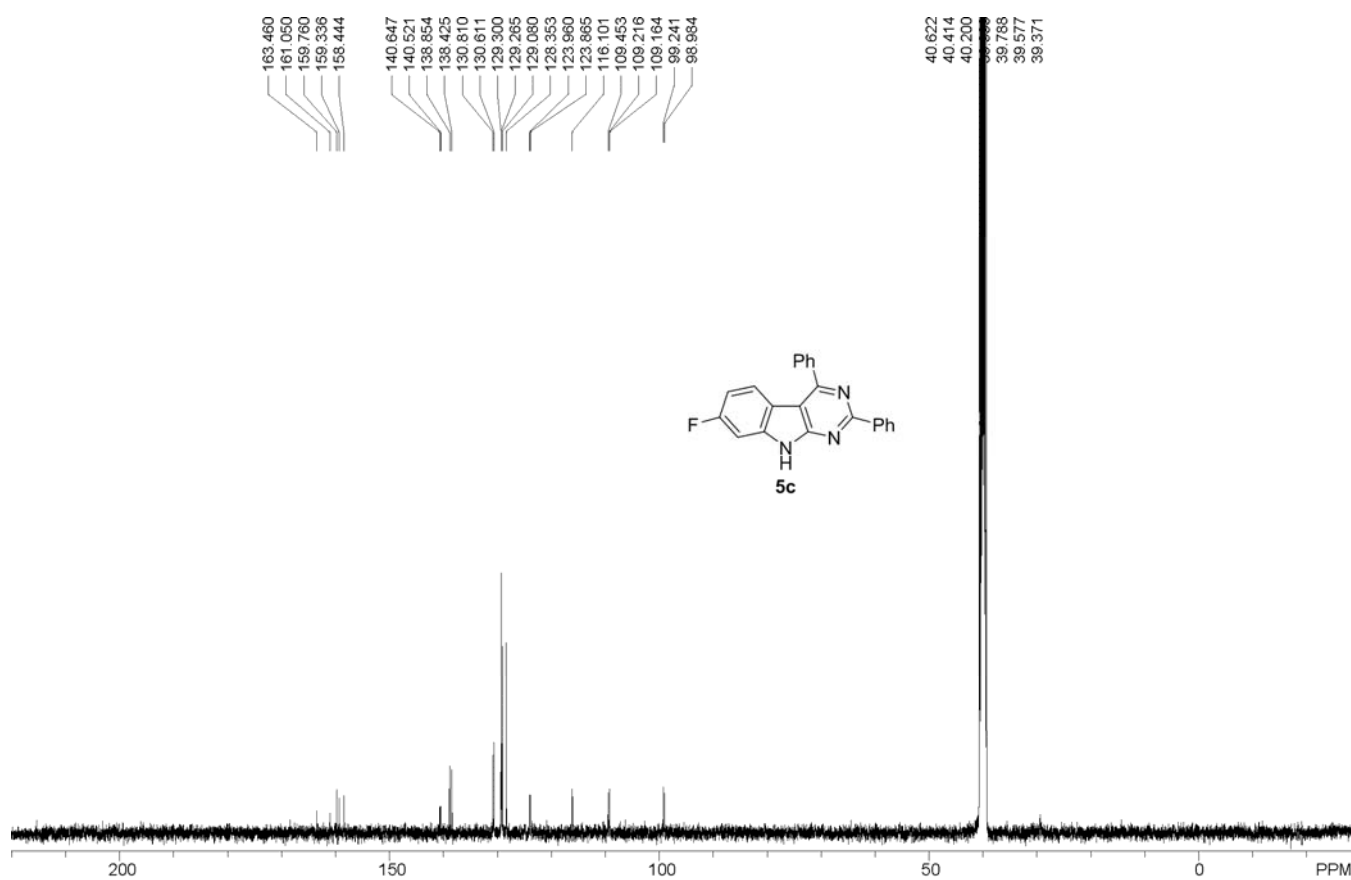
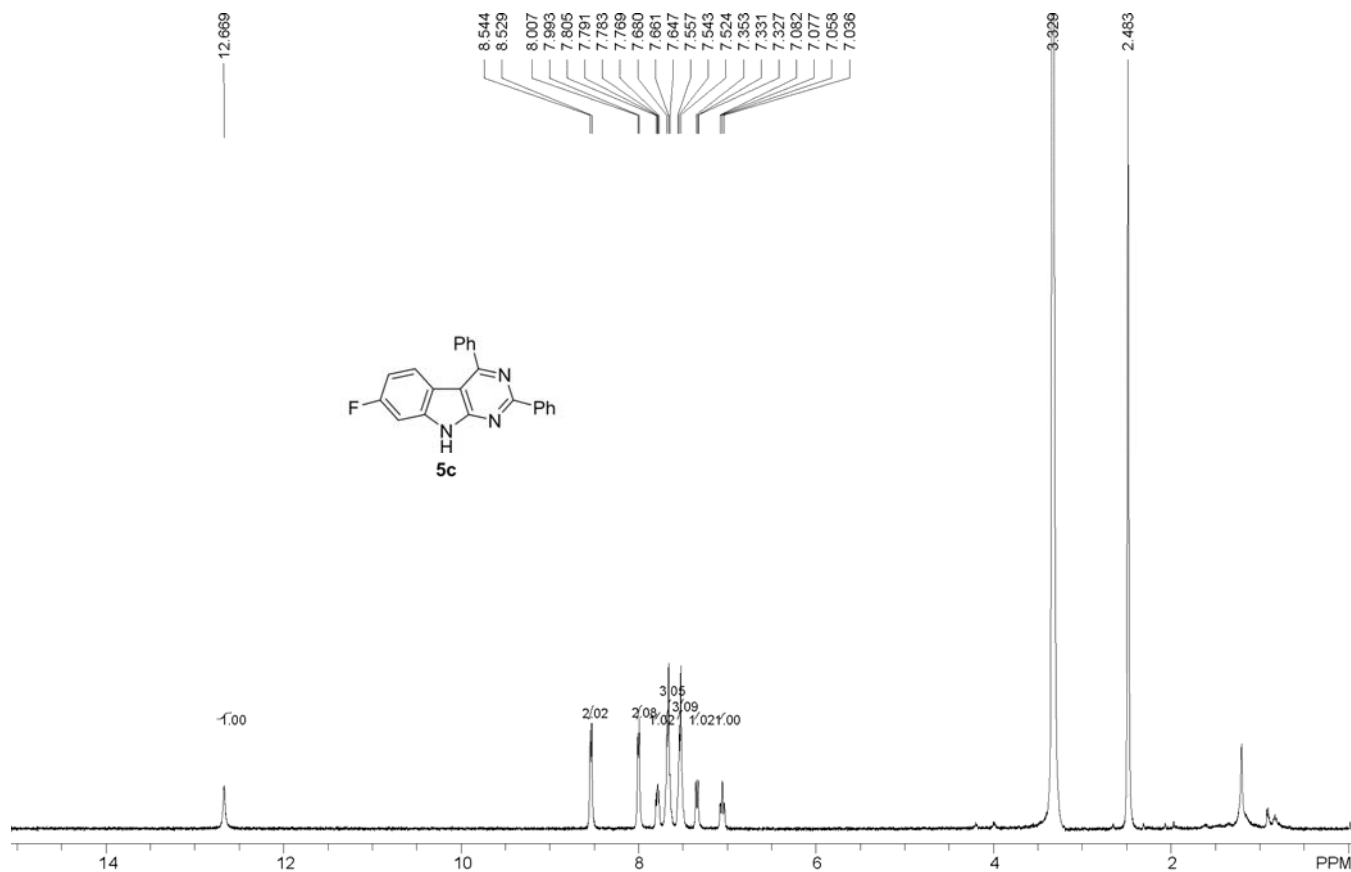


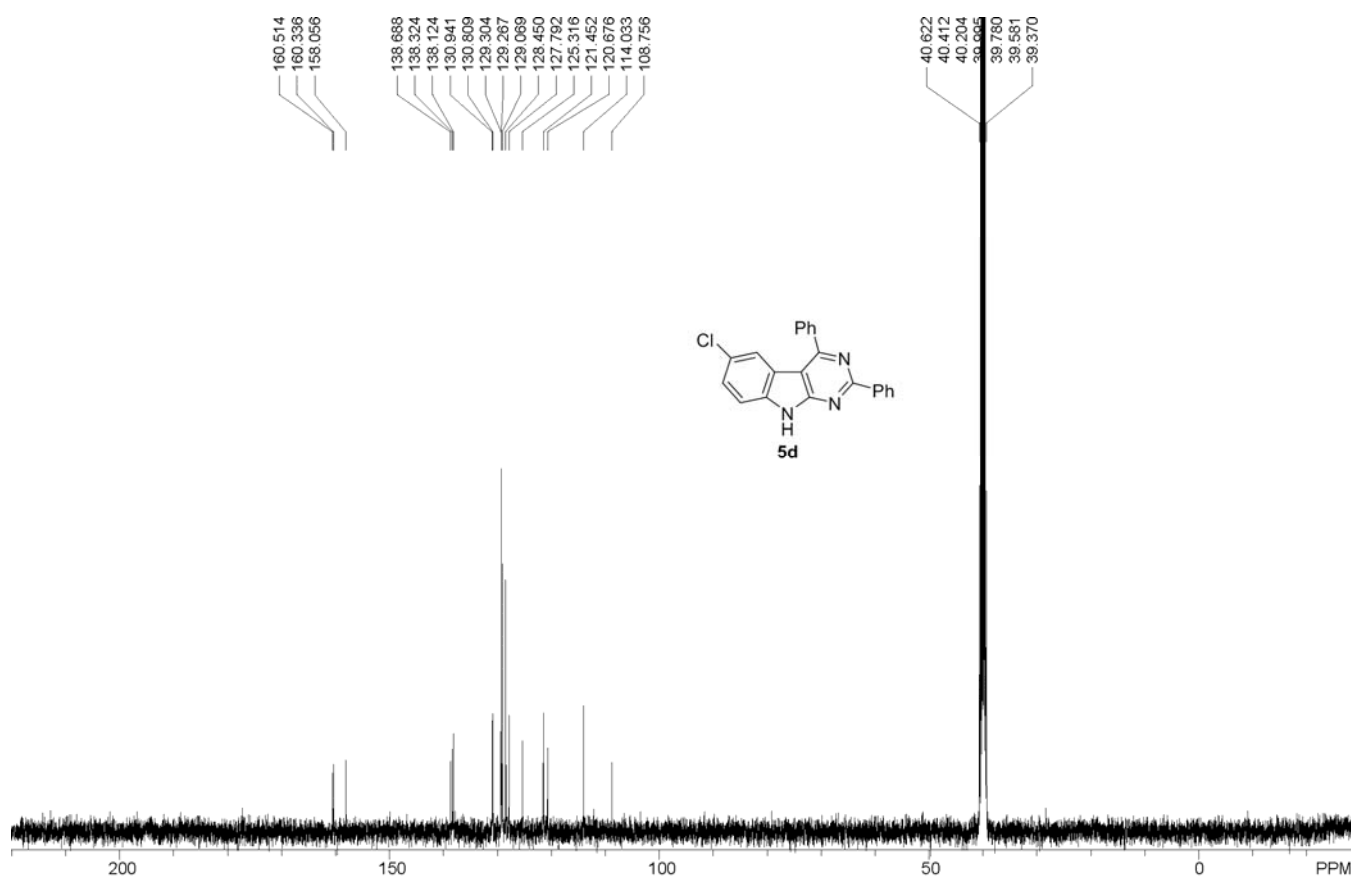
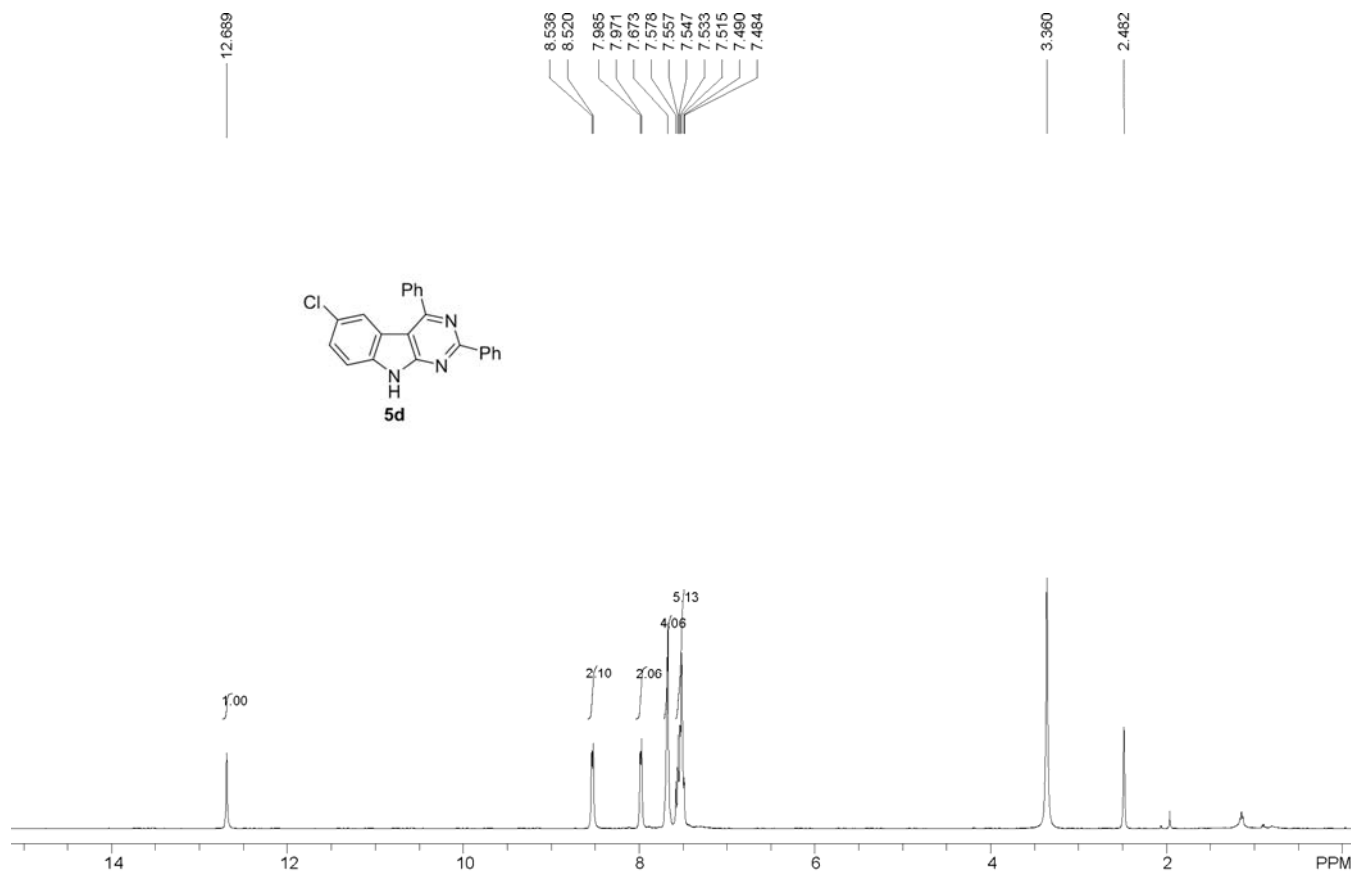


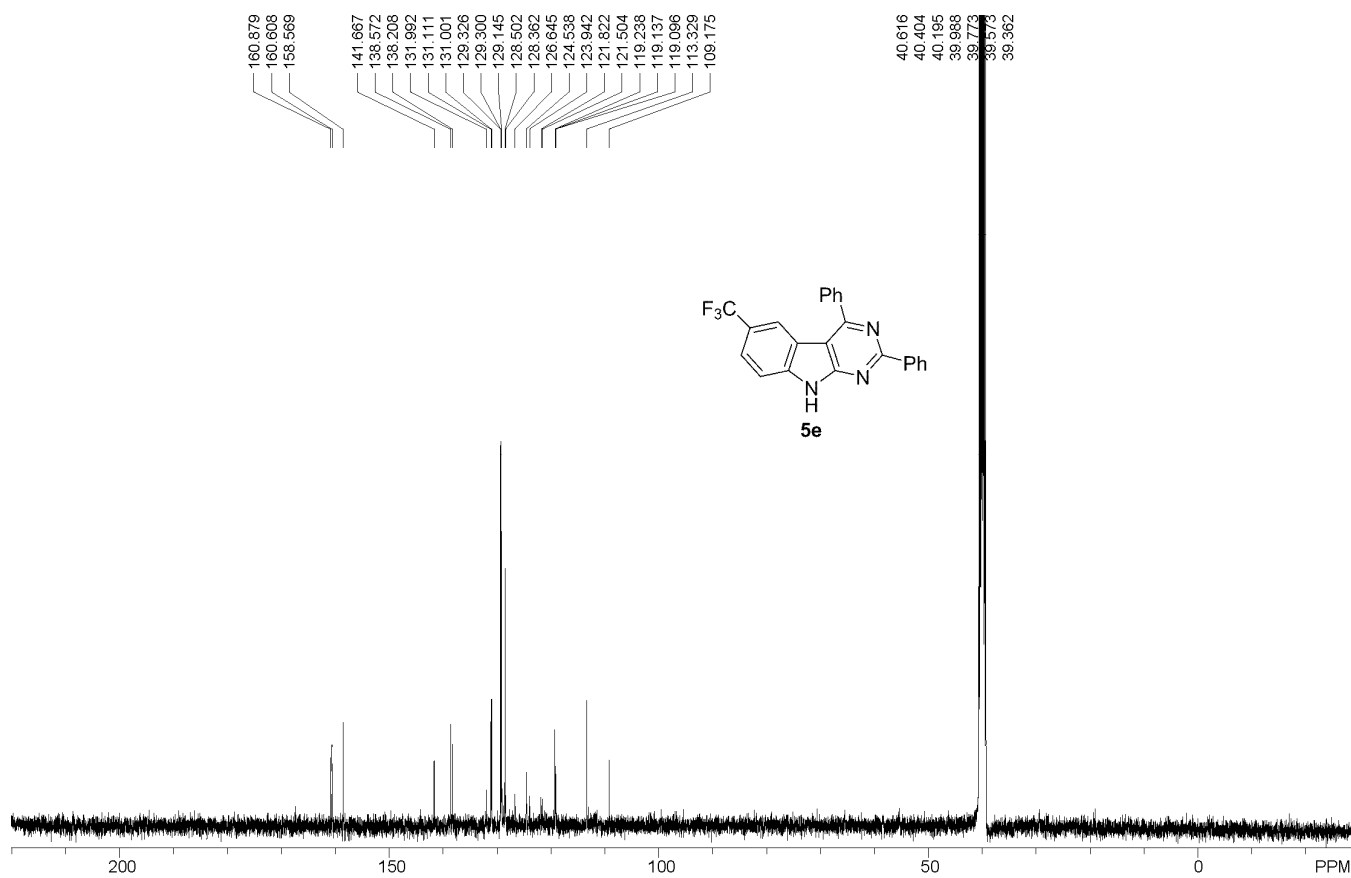
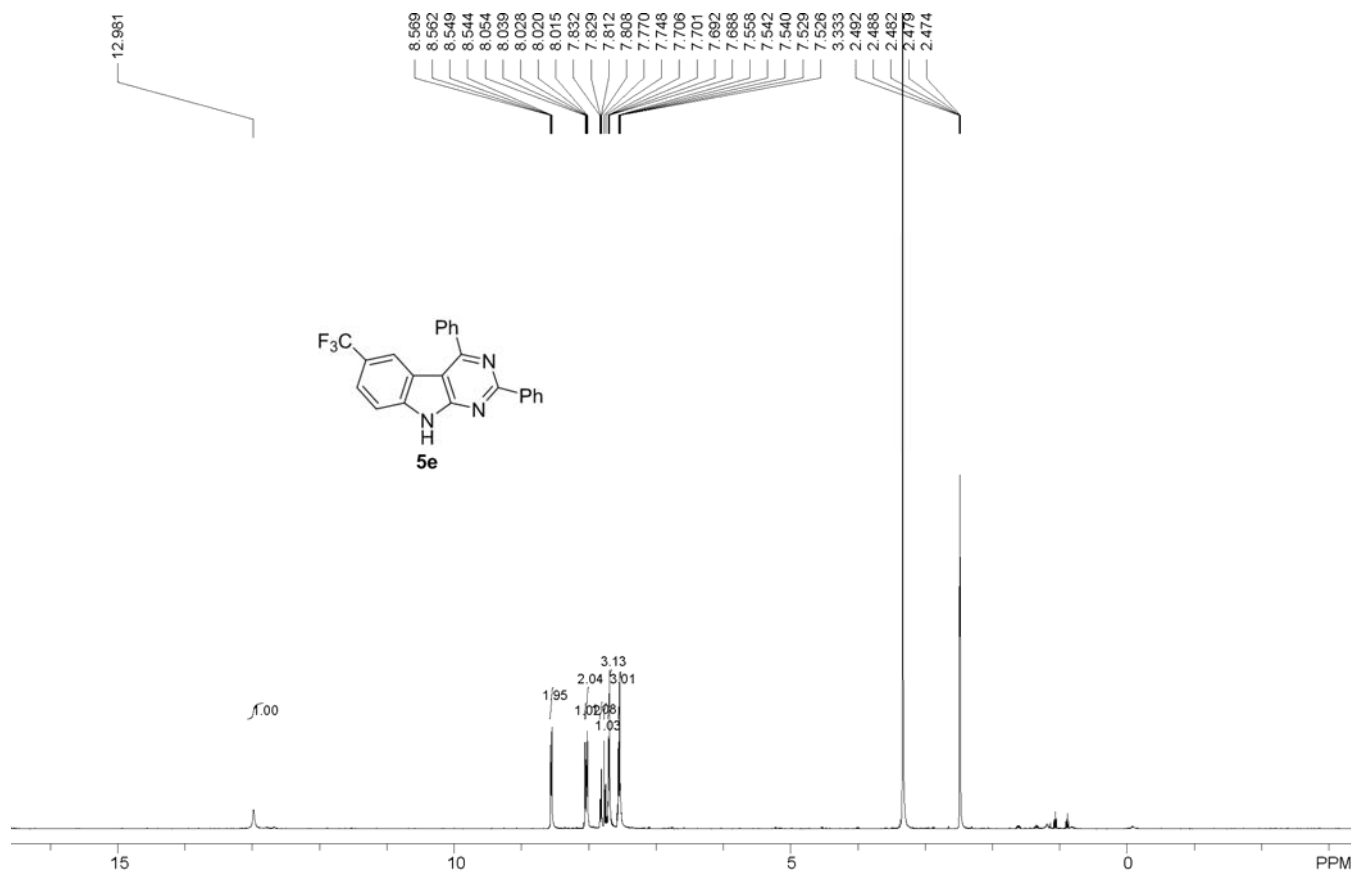
III. Copies of ^1H and ^{13}C NMR spectra of 5a-5u

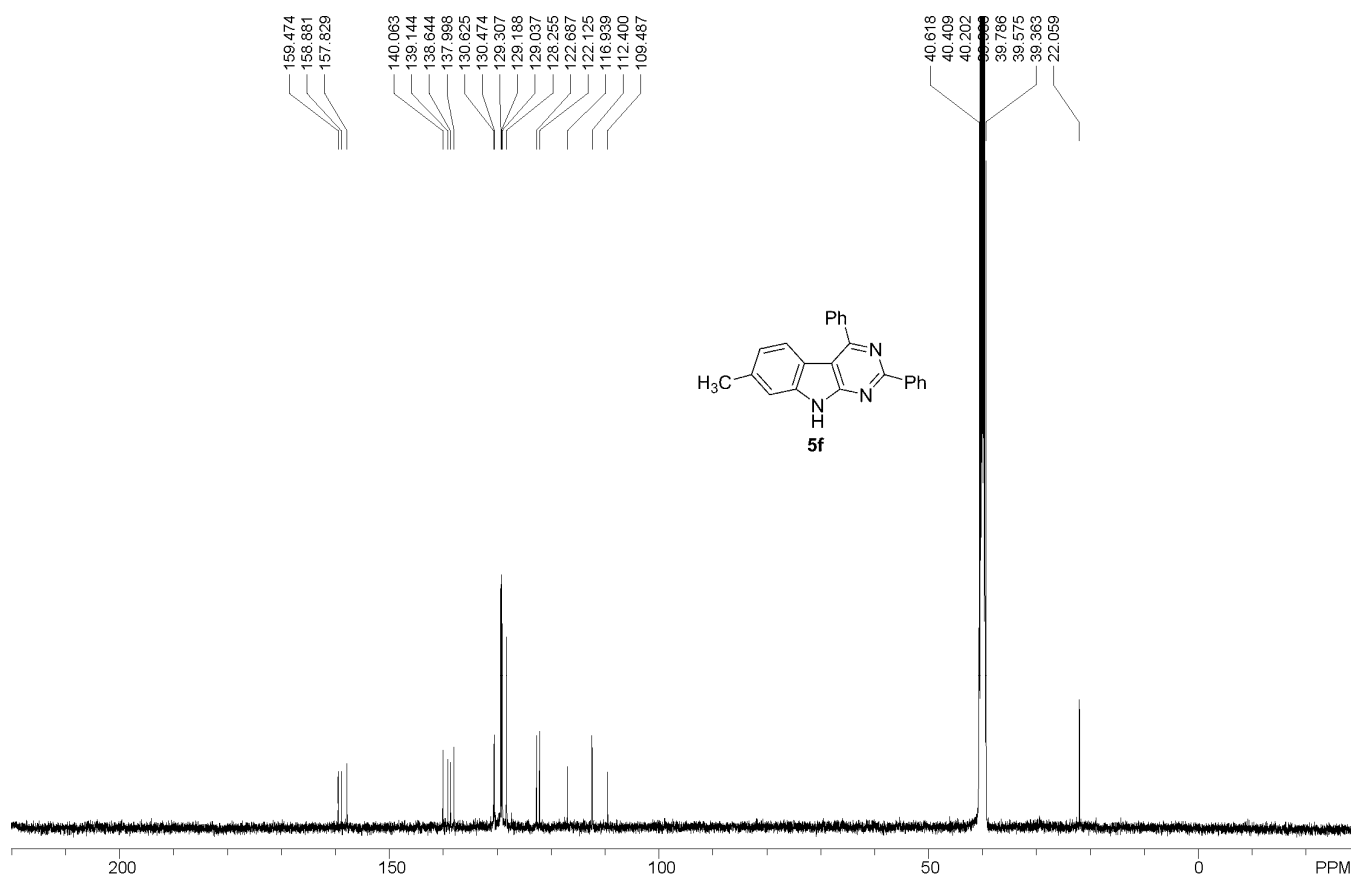
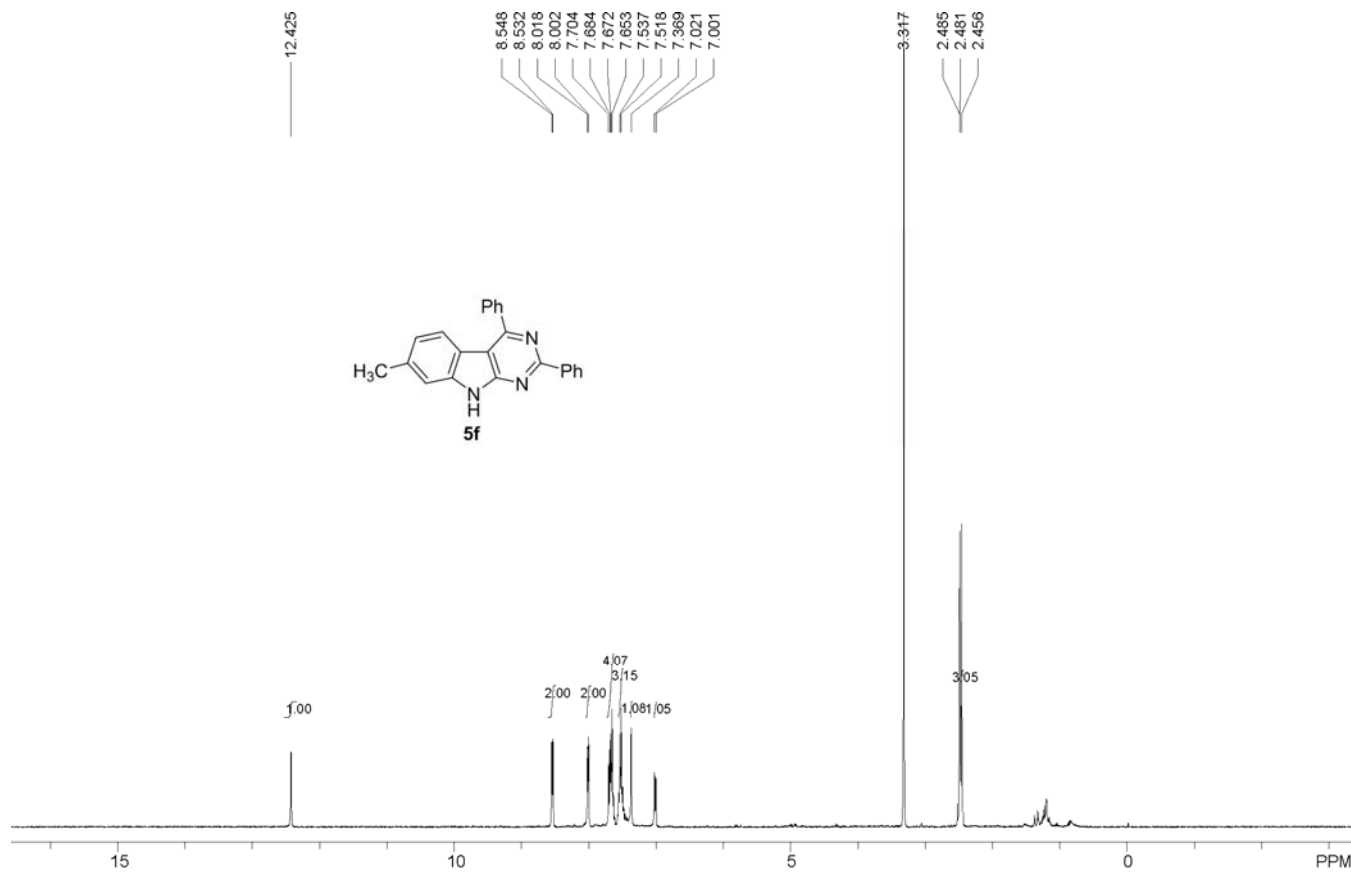


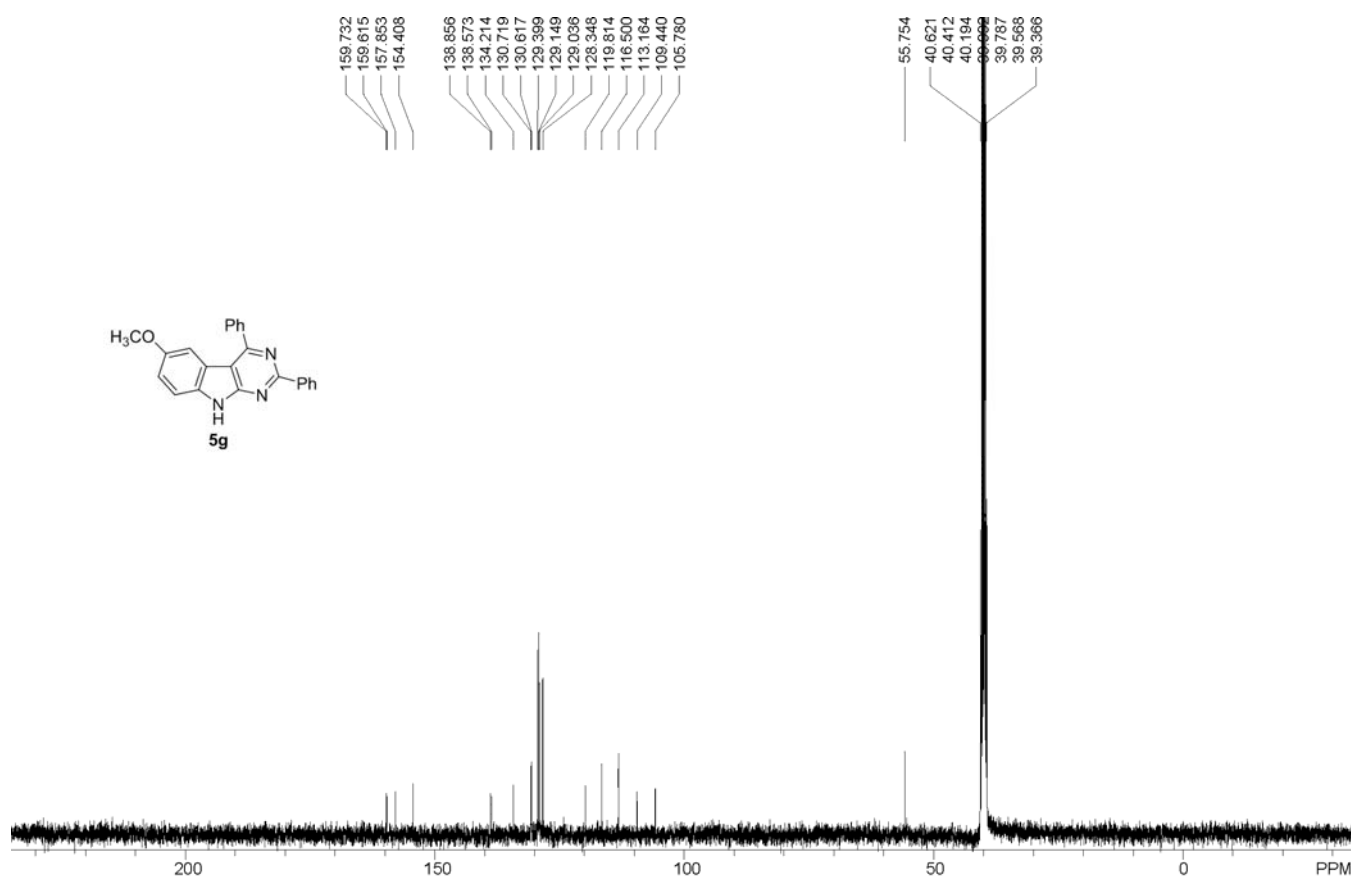
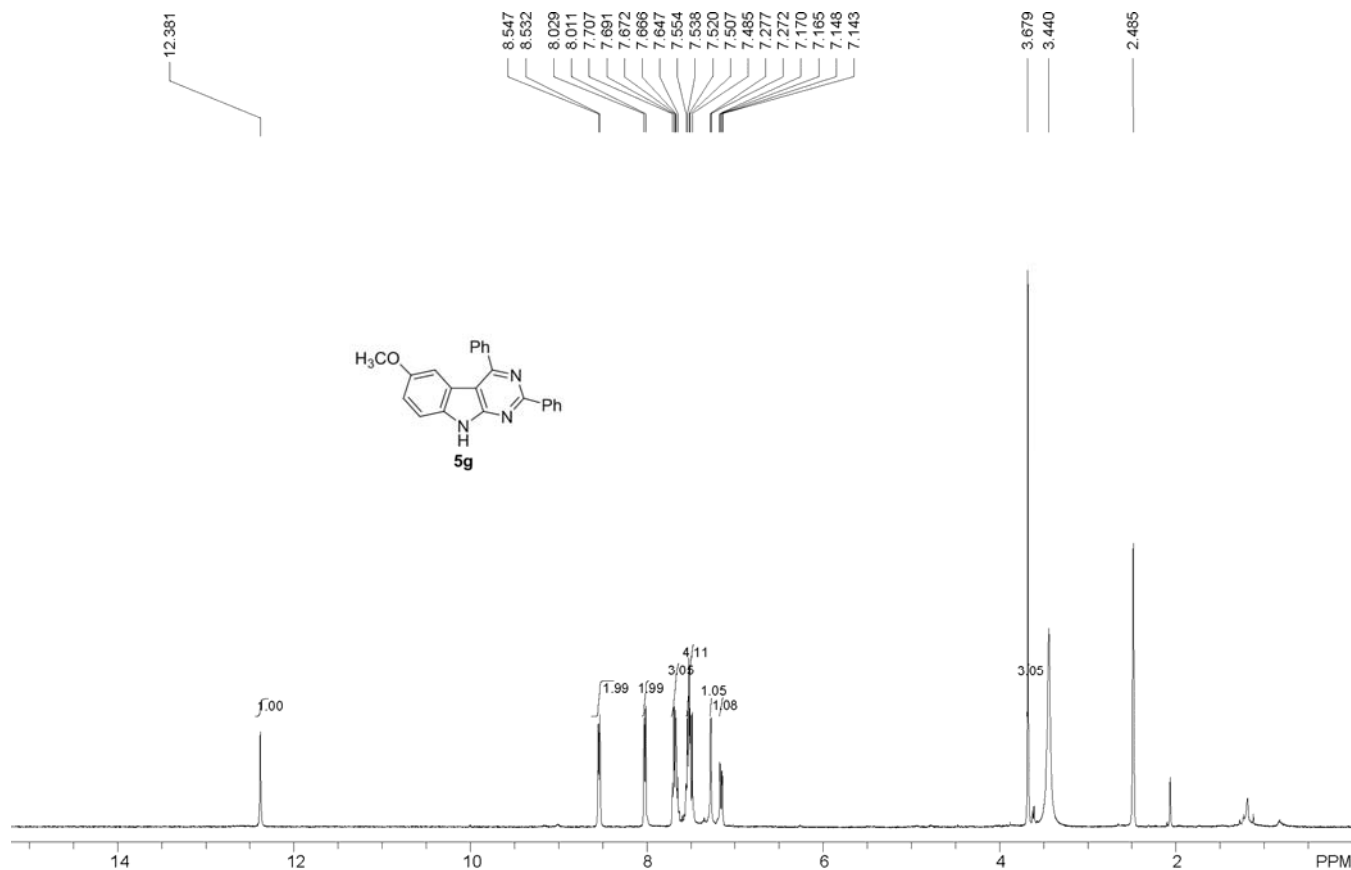


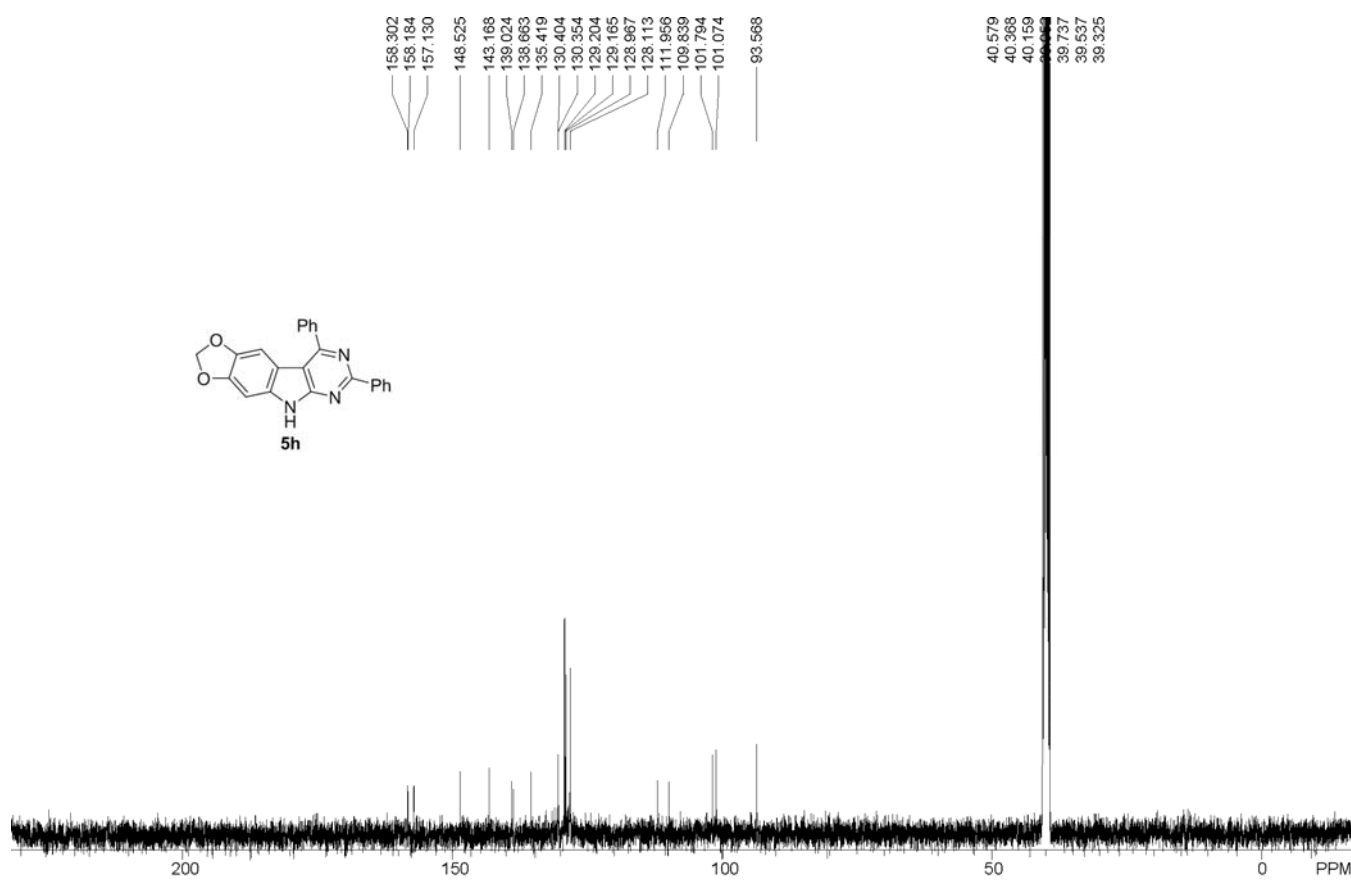
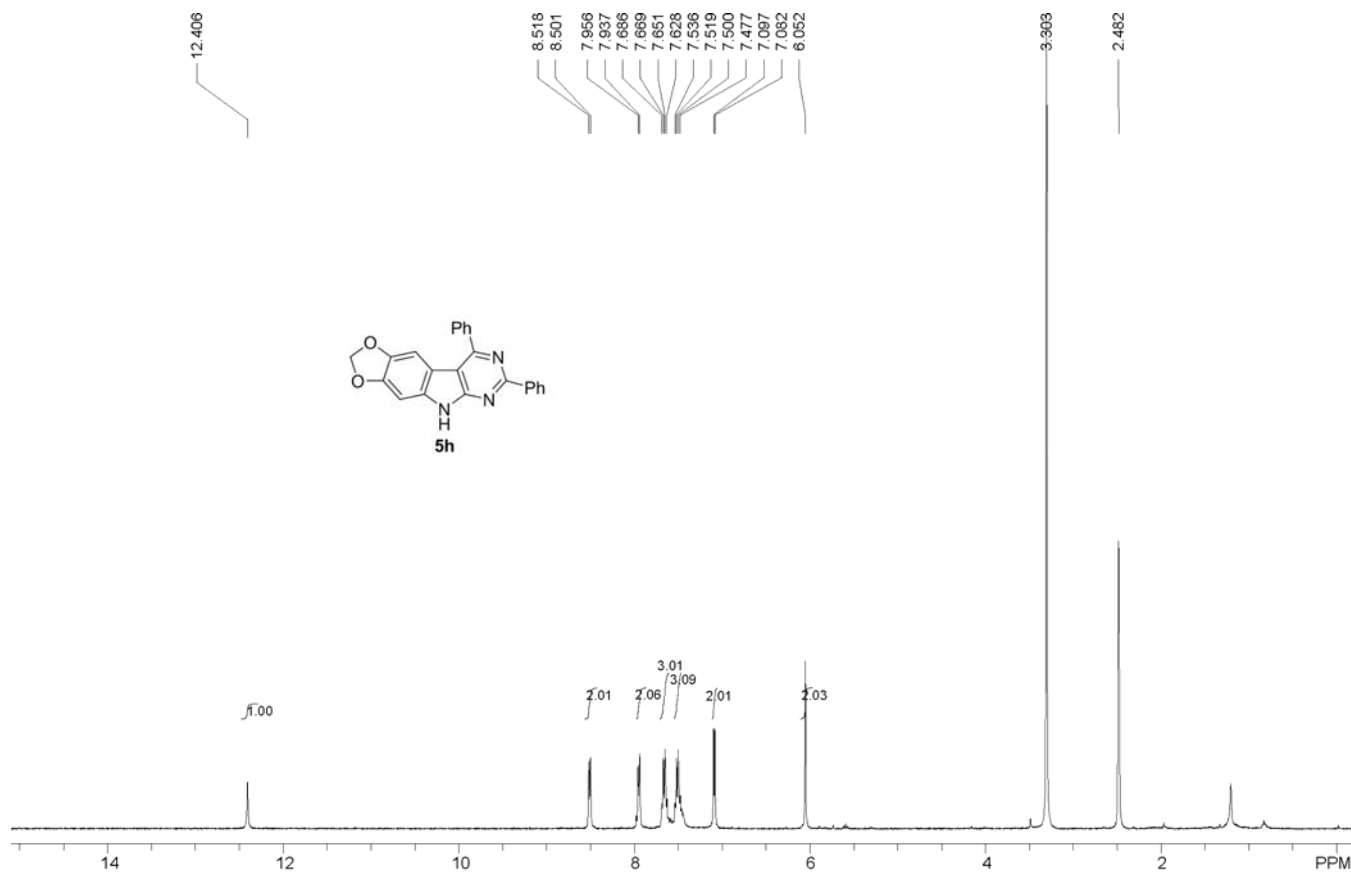


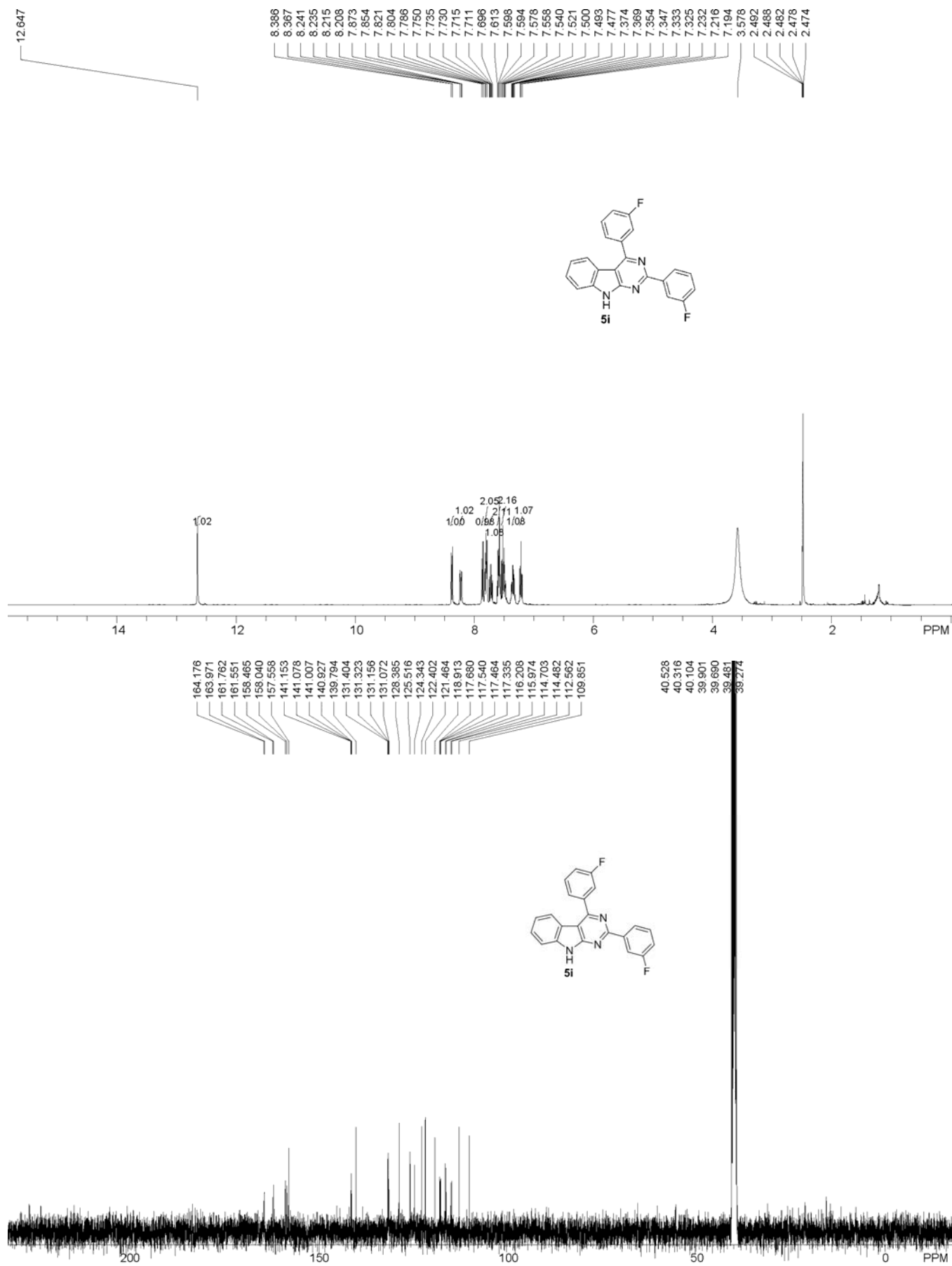


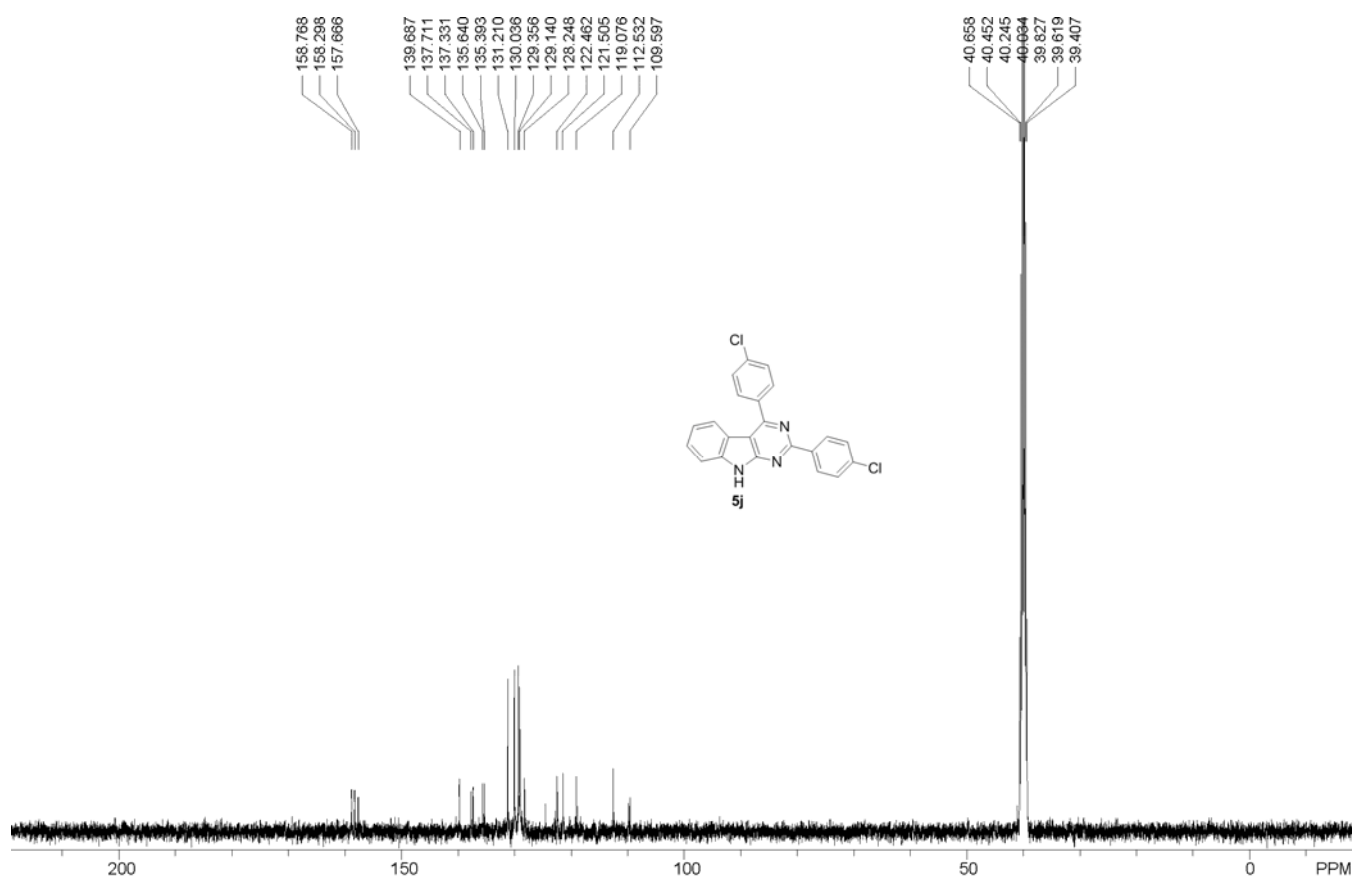
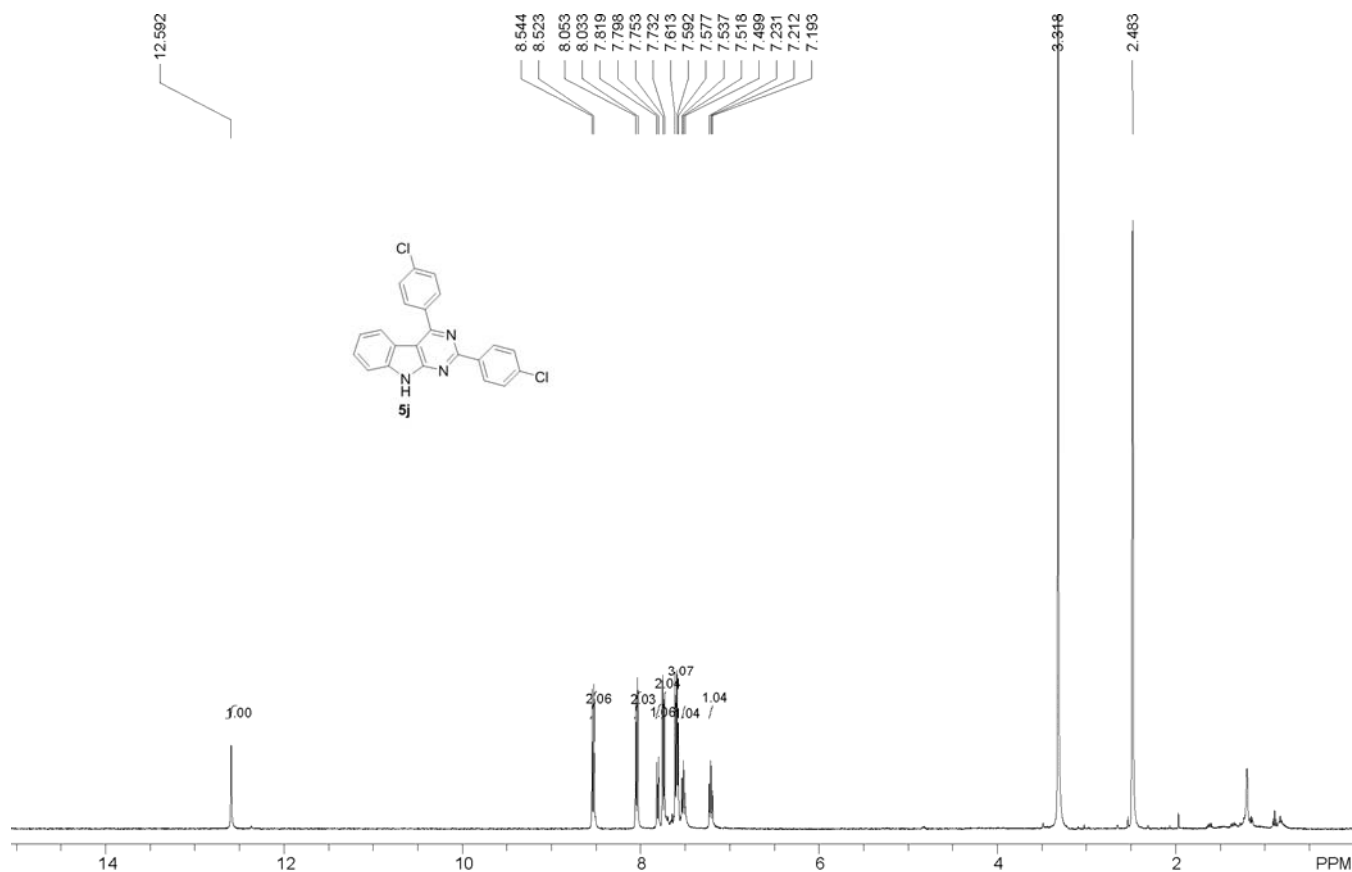


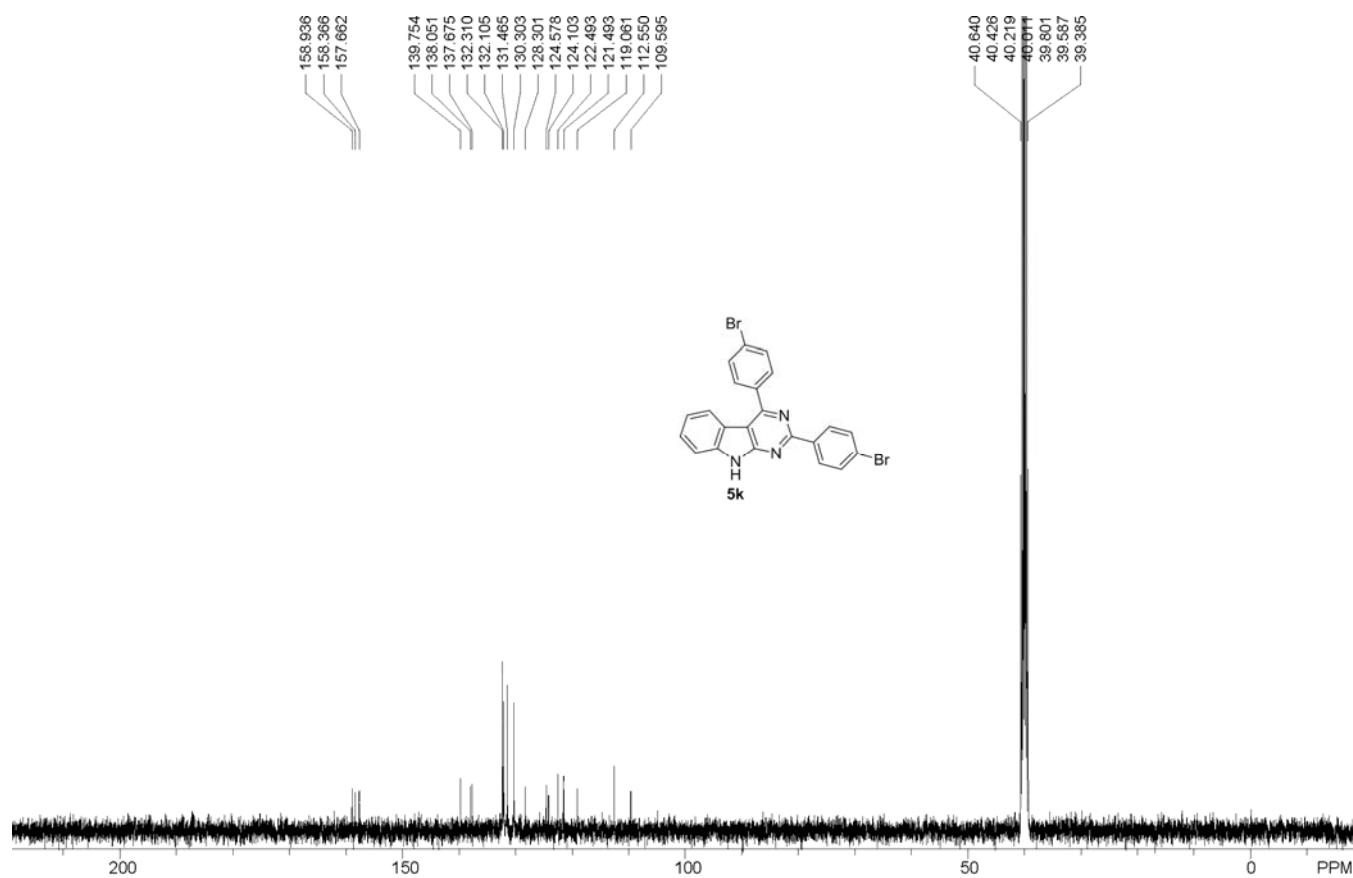
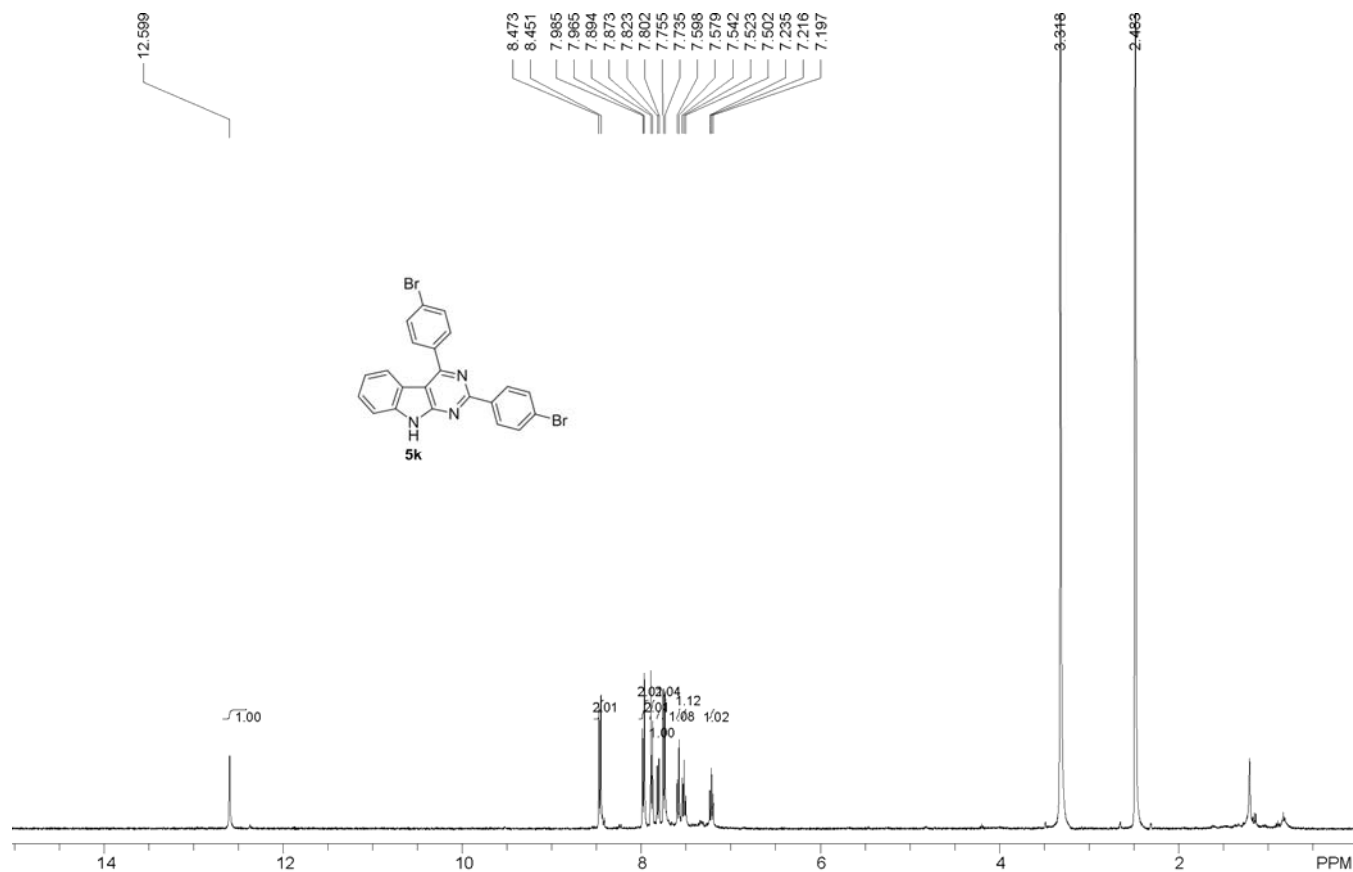


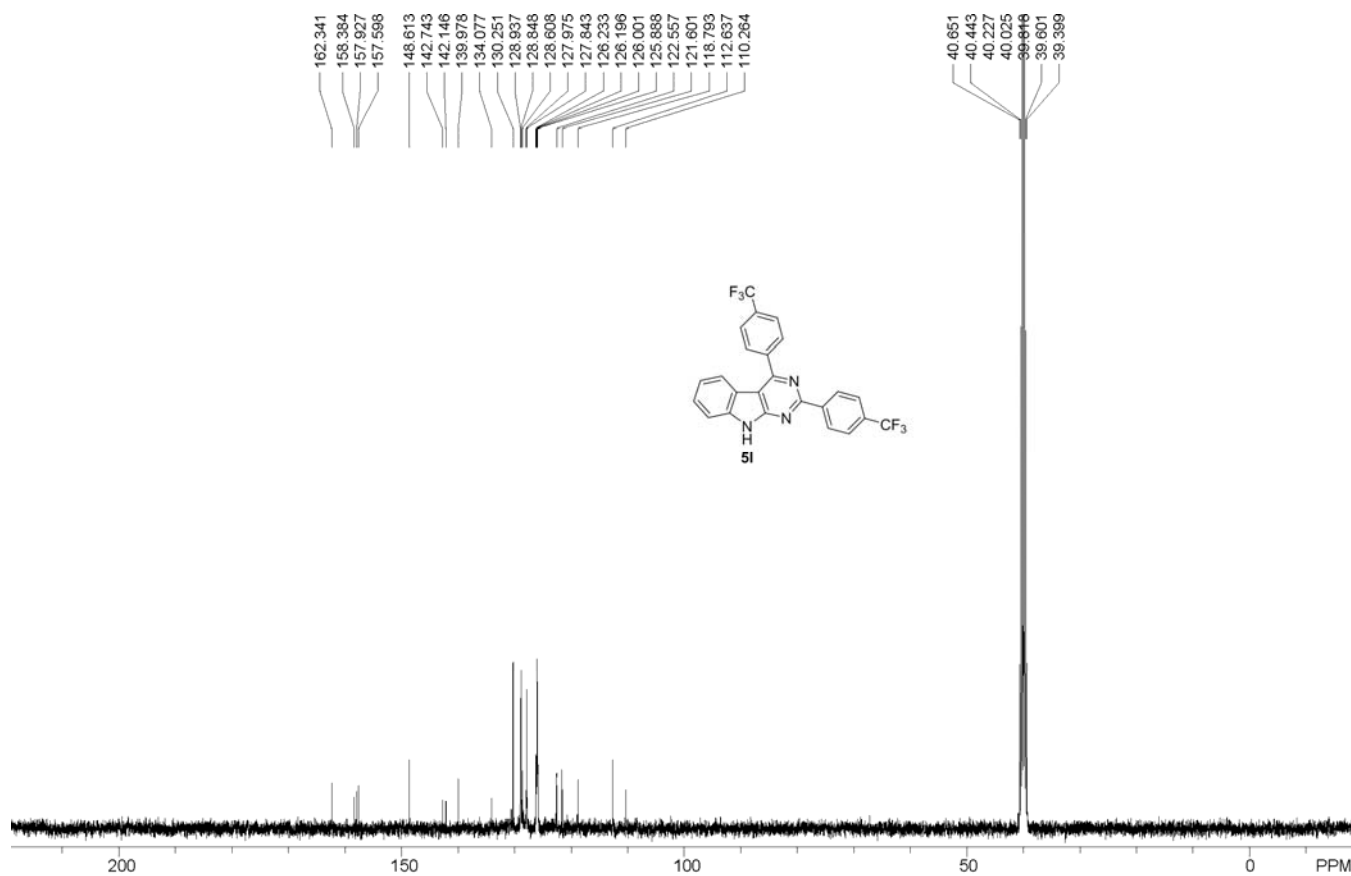
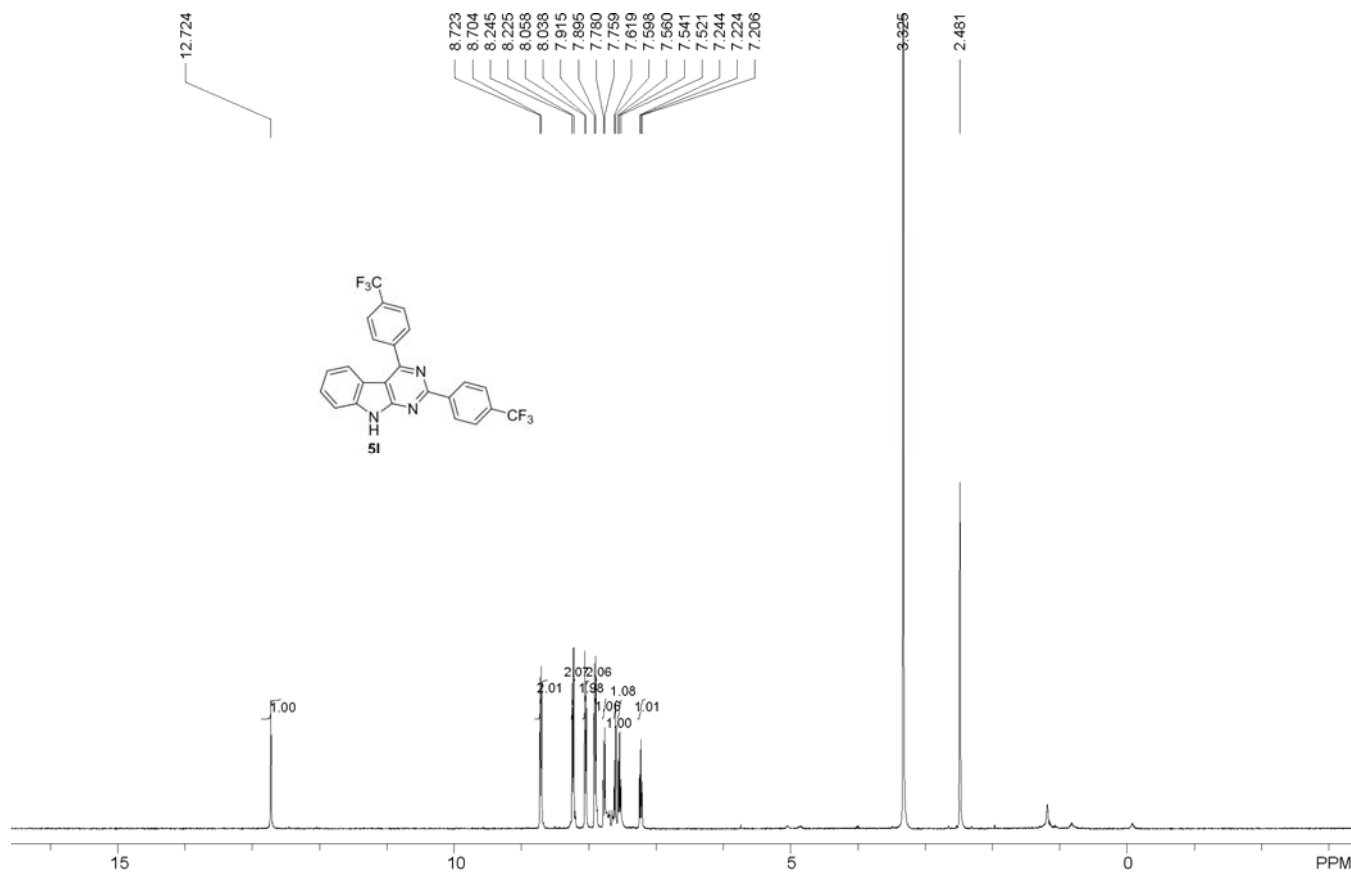


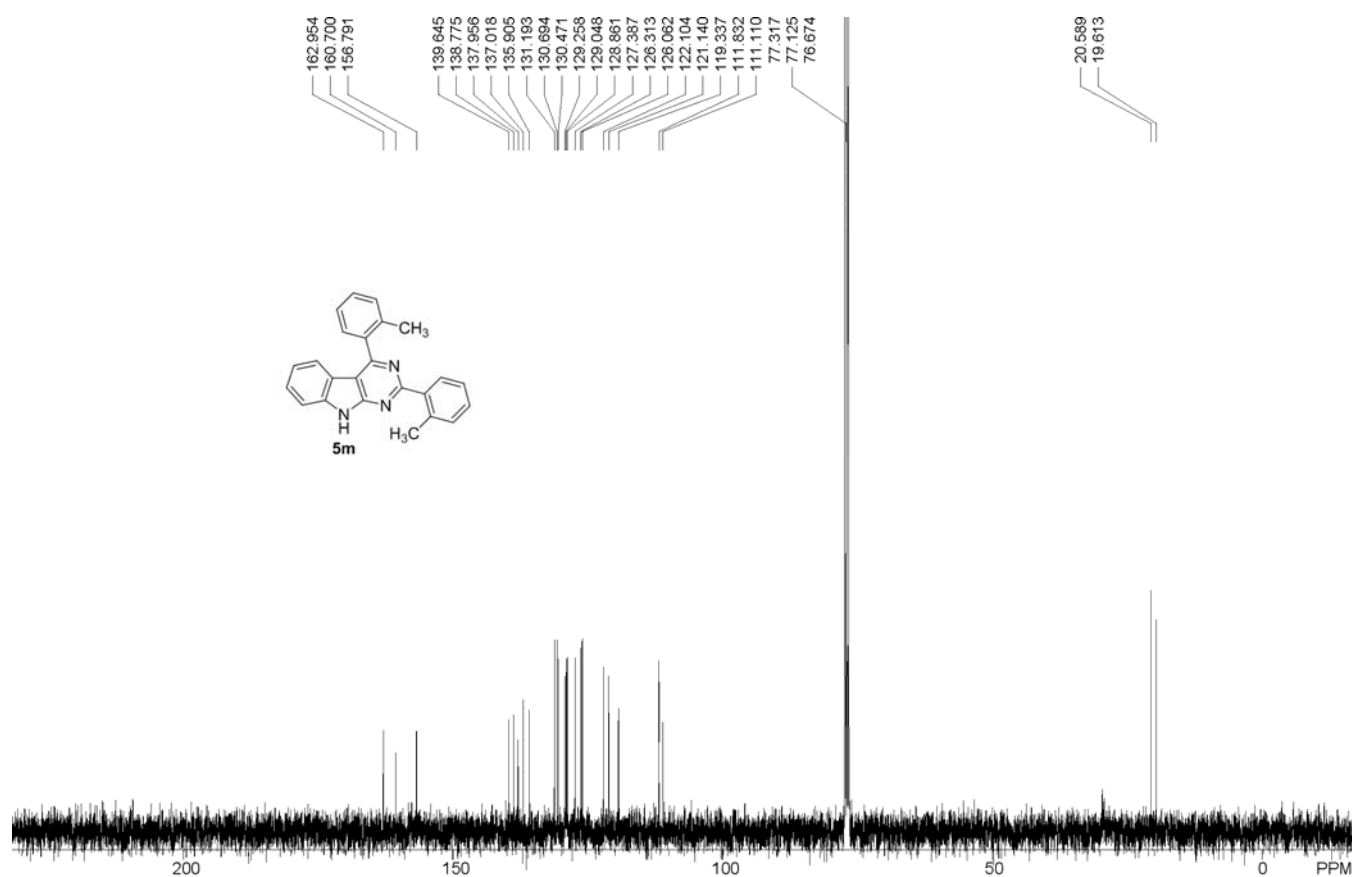
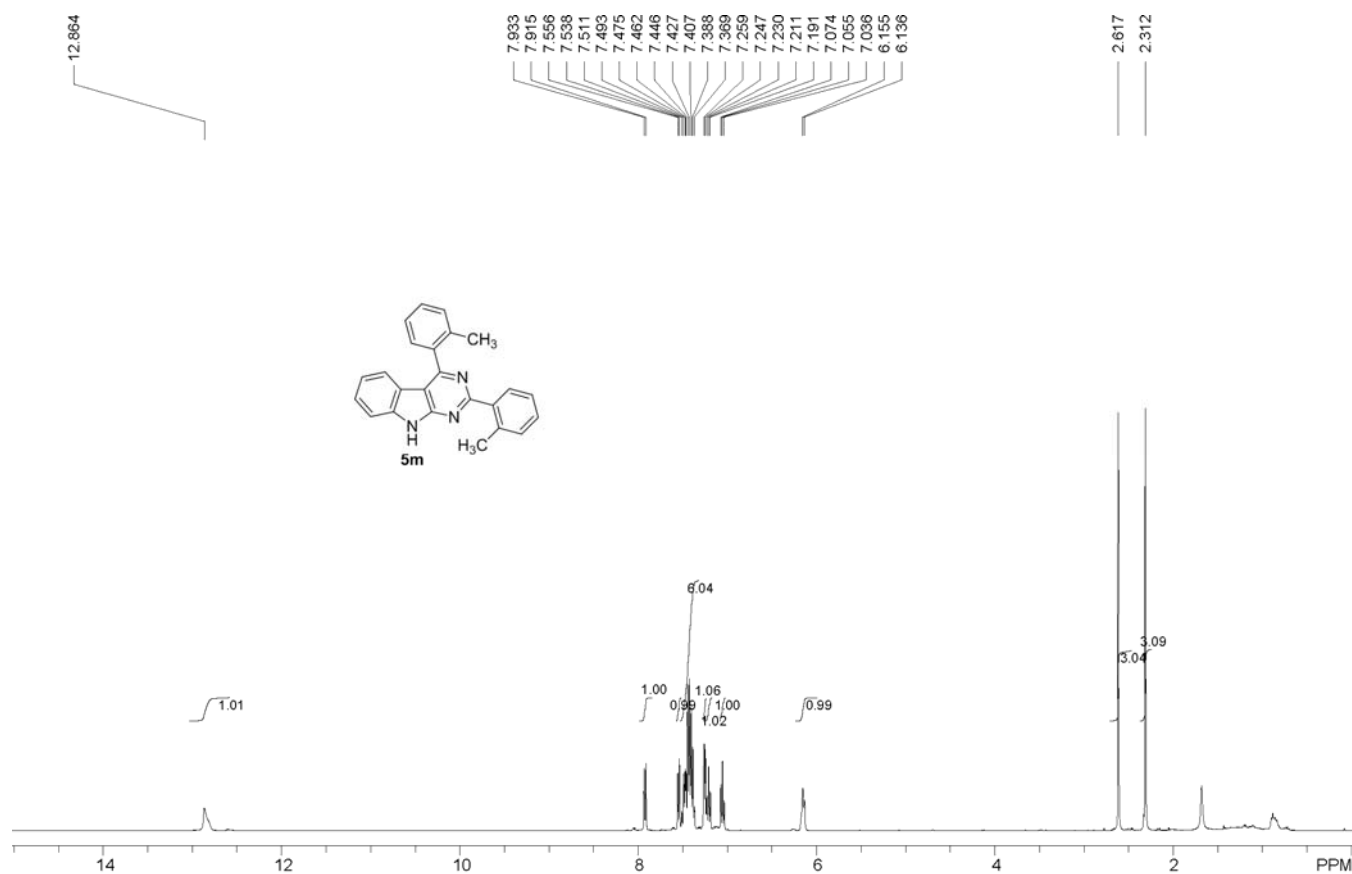


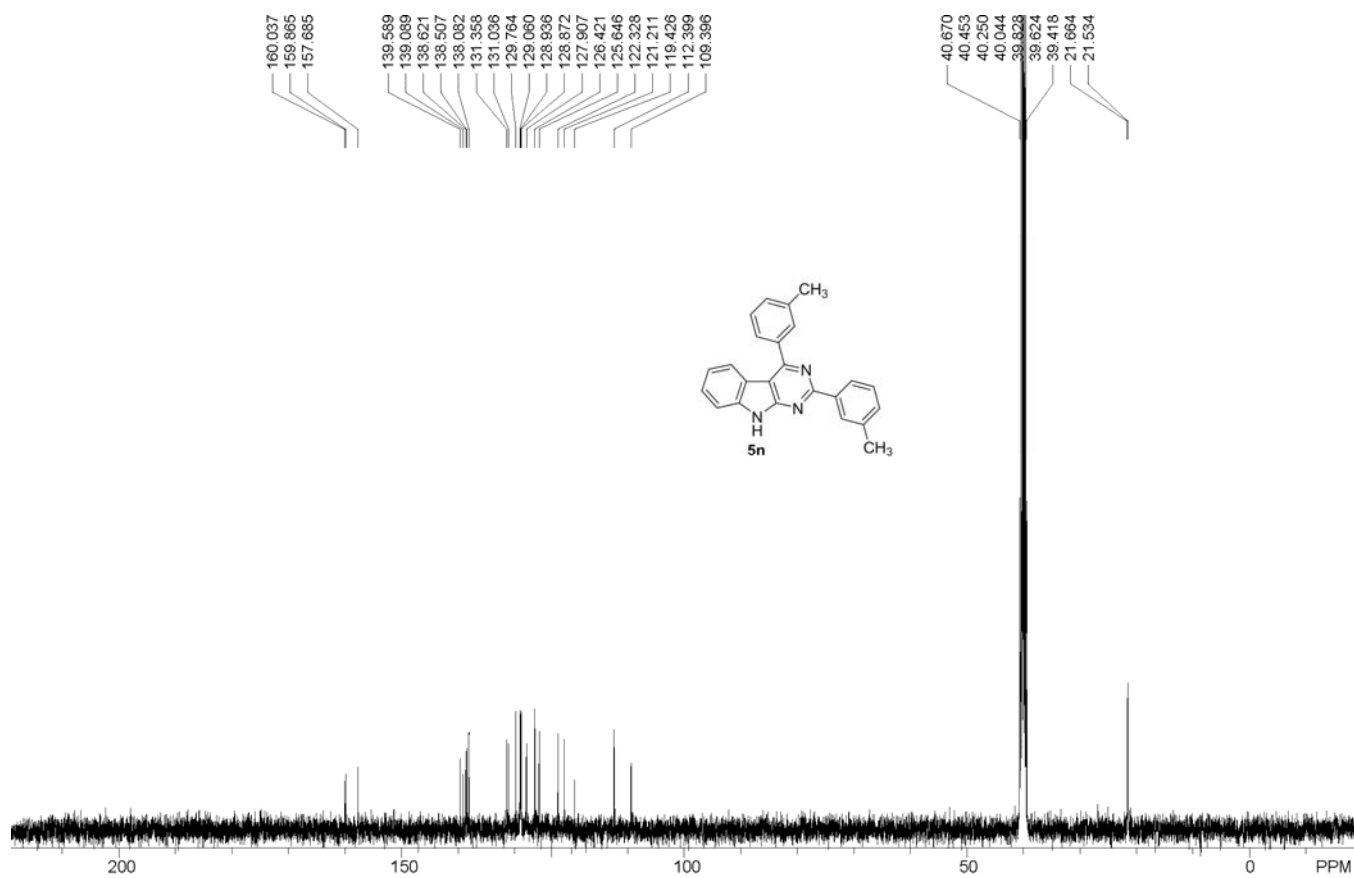
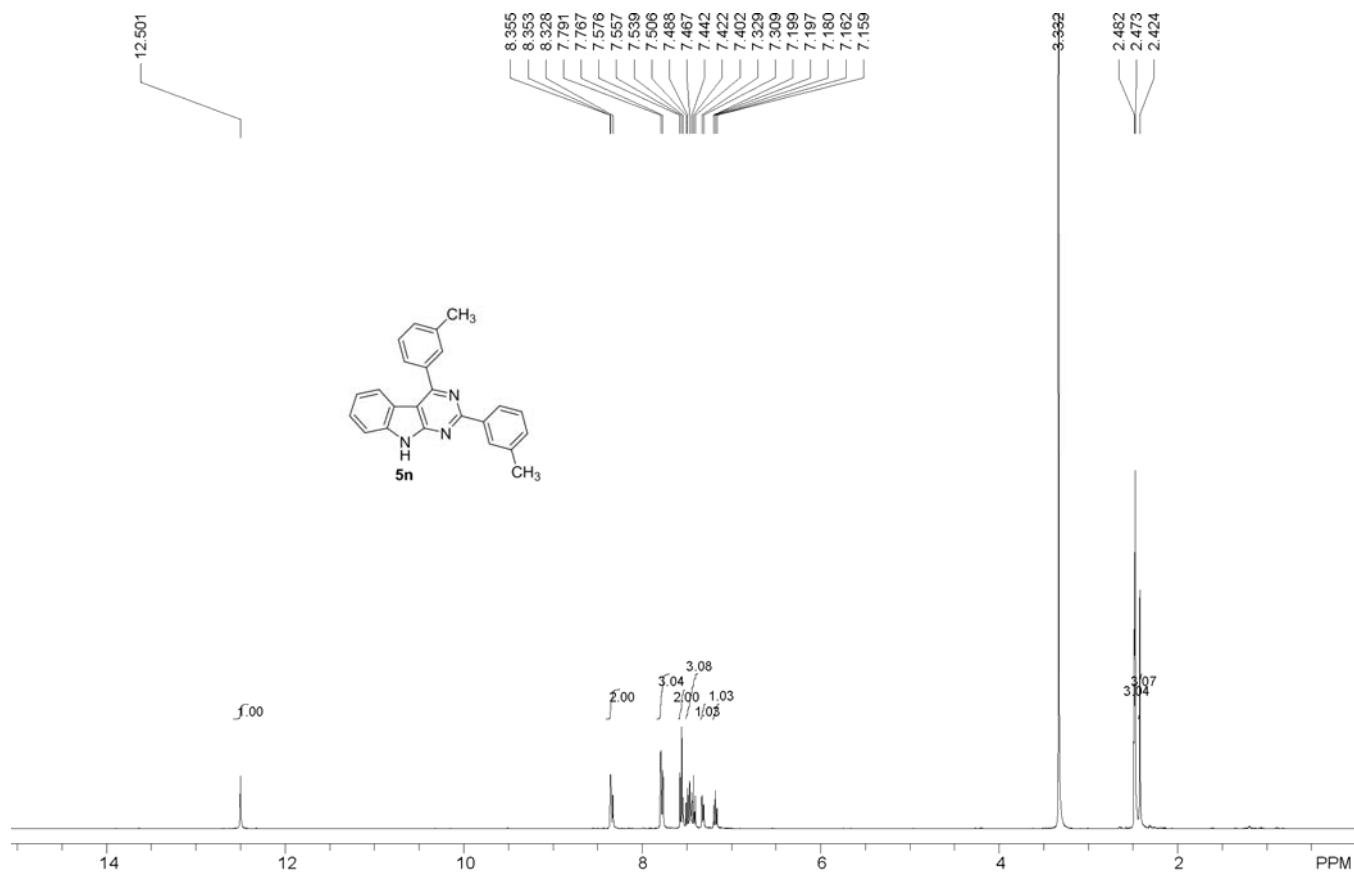


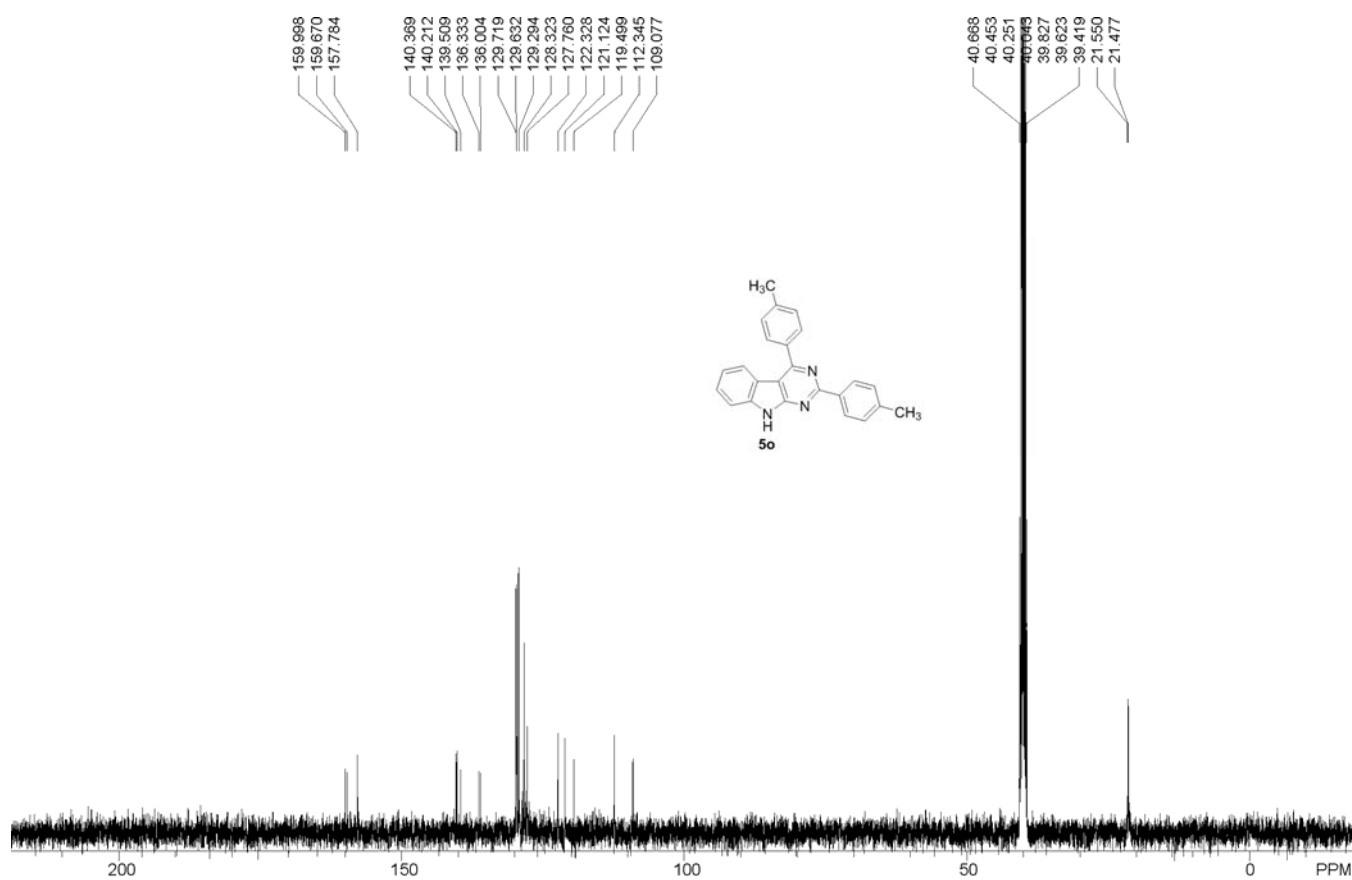
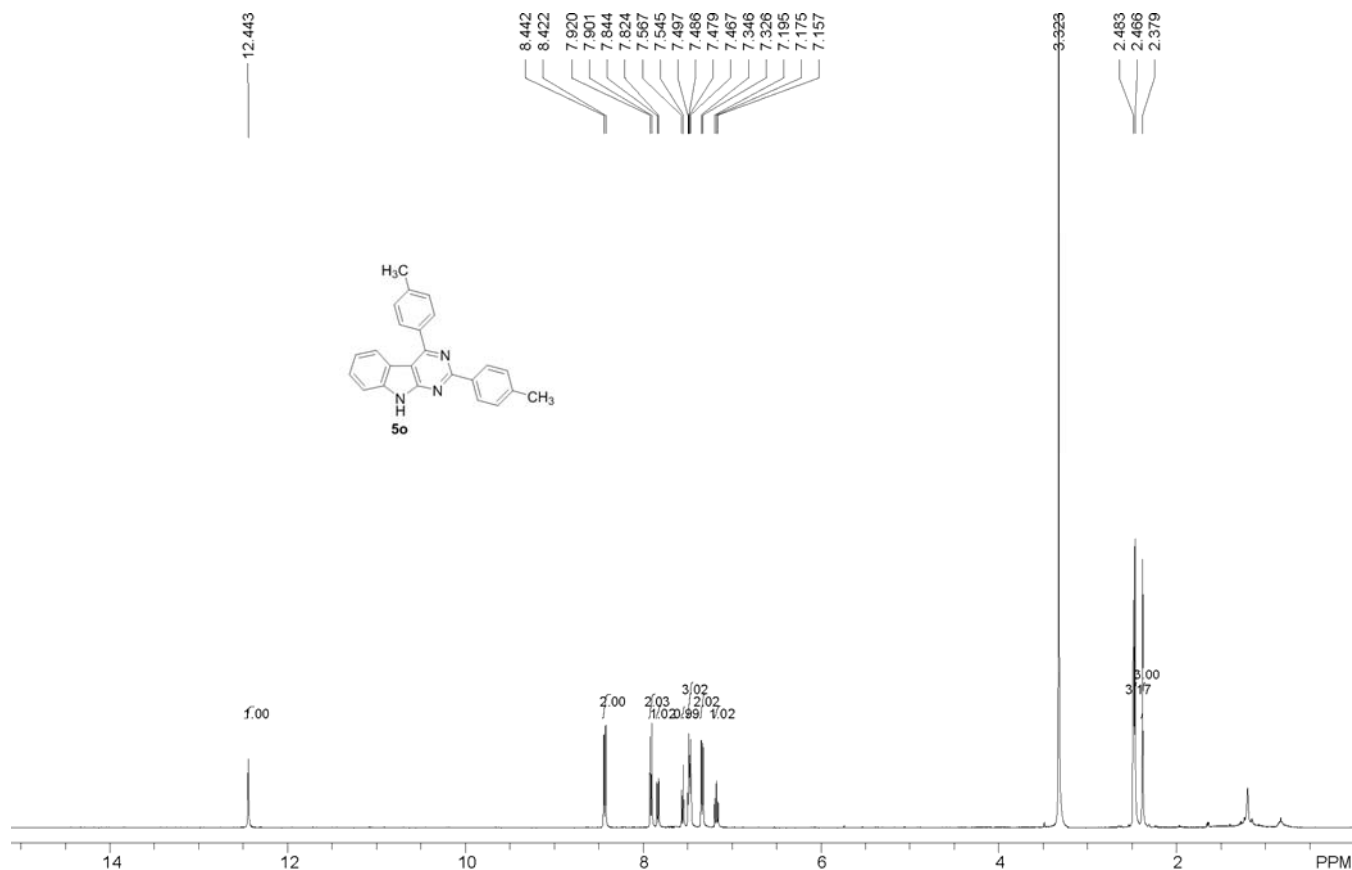


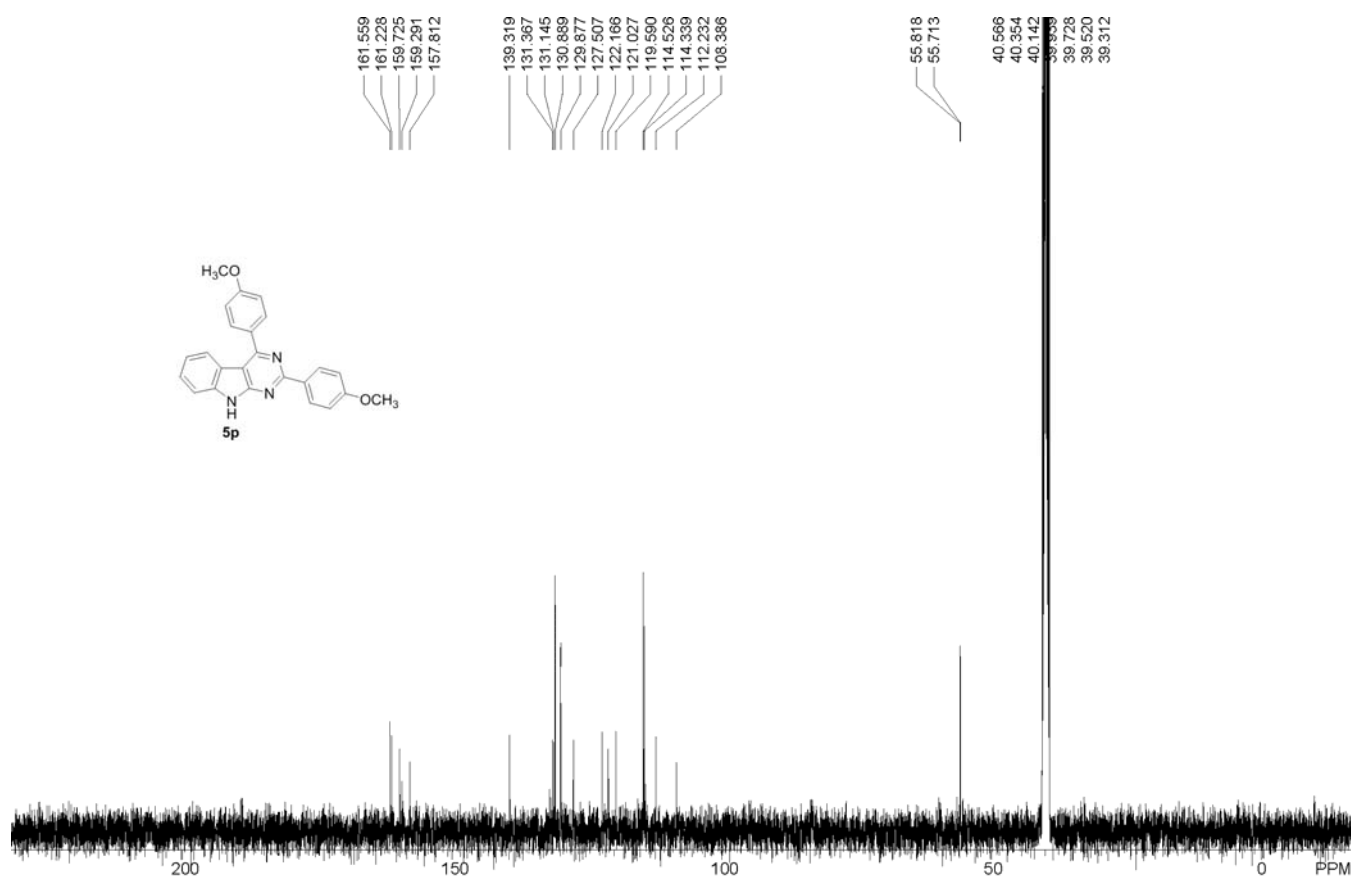
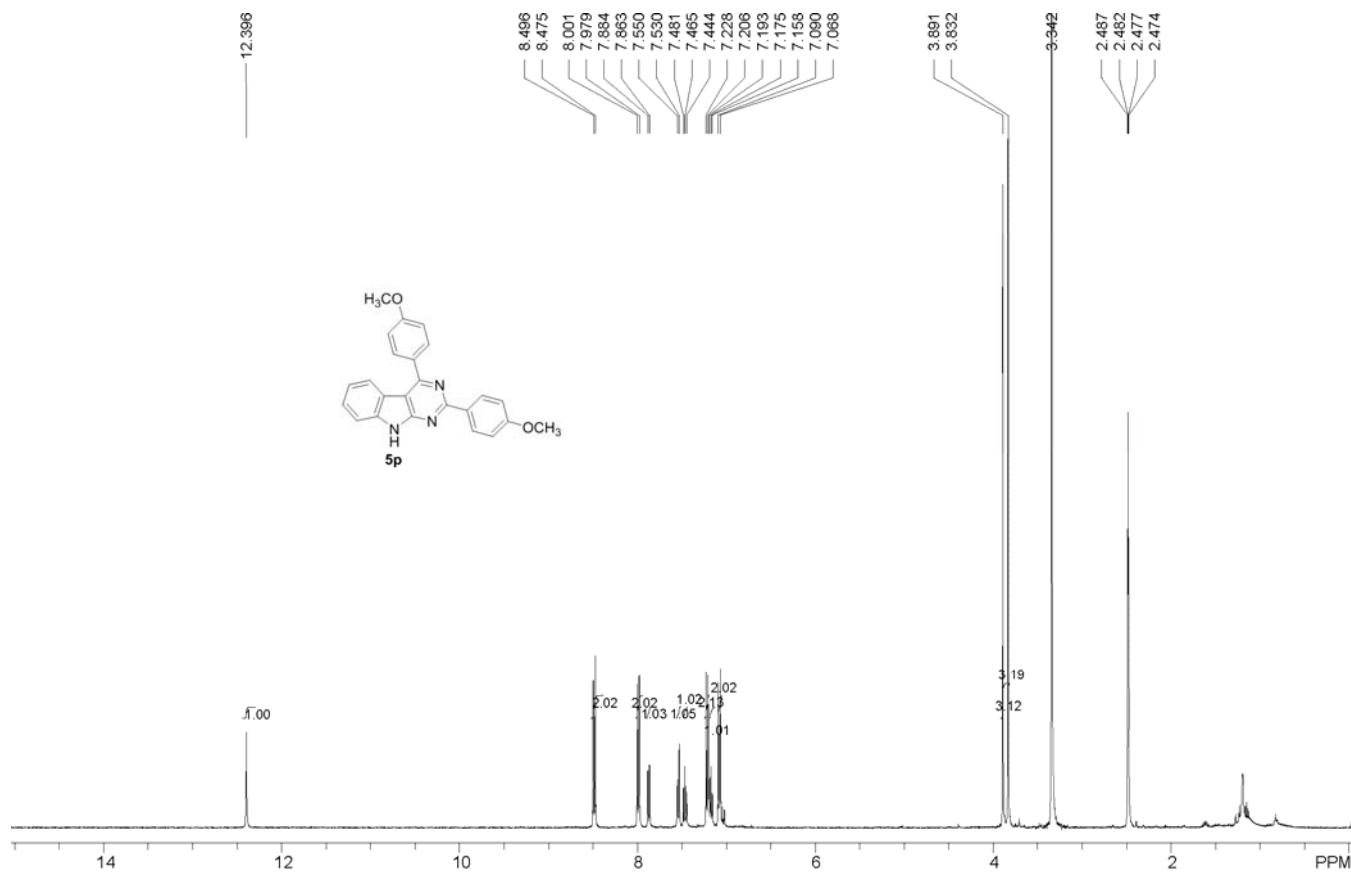


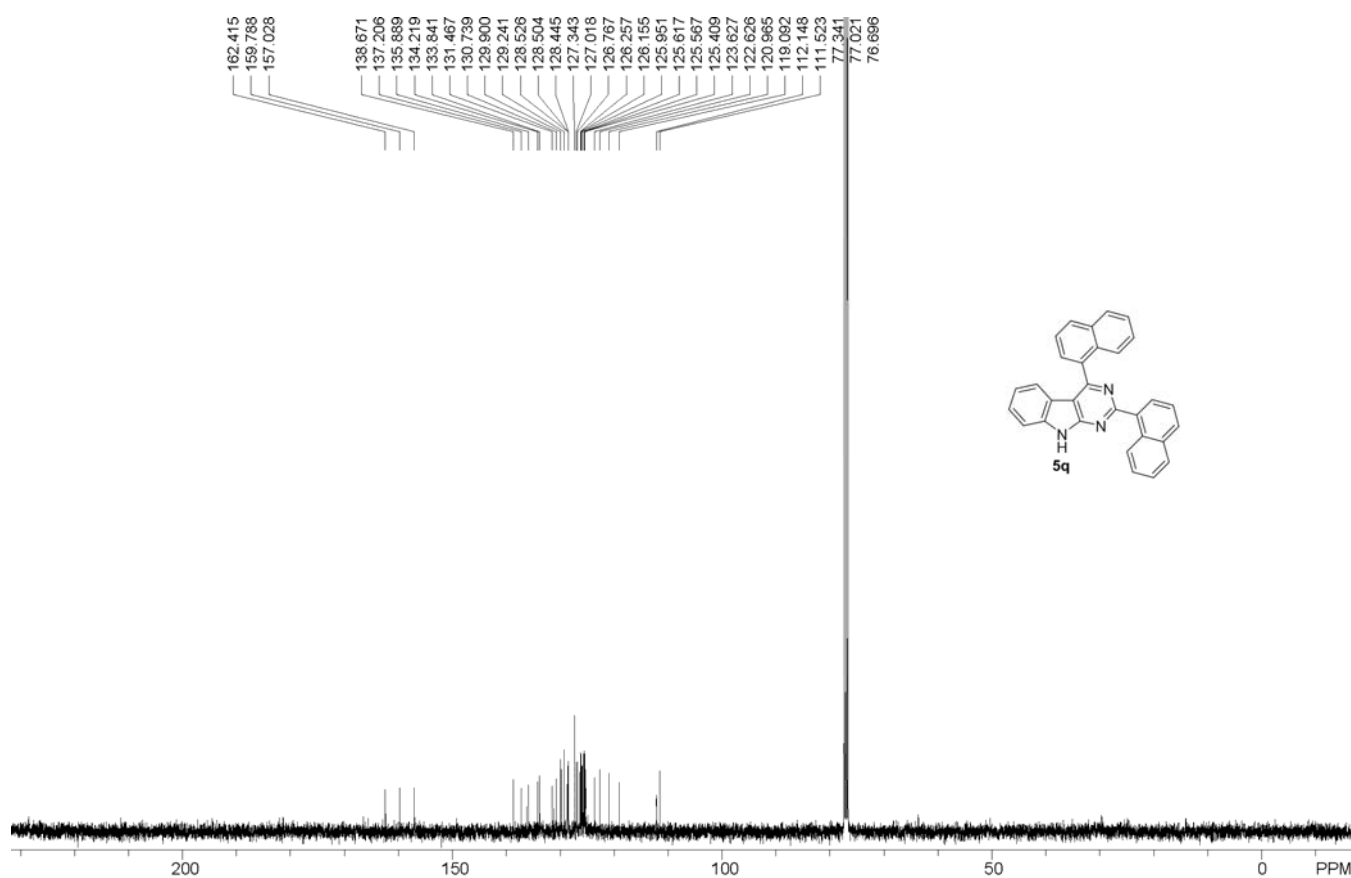
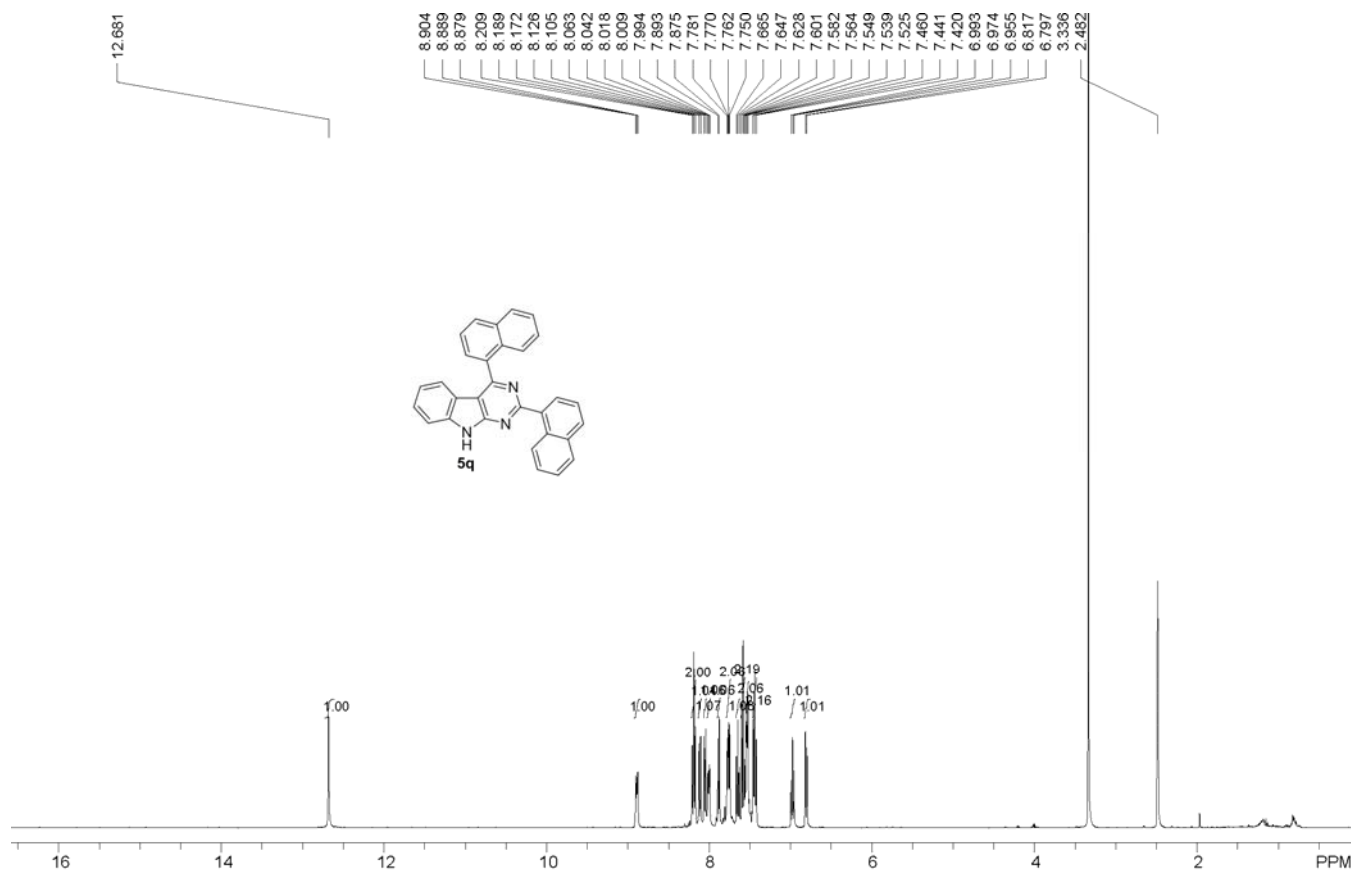


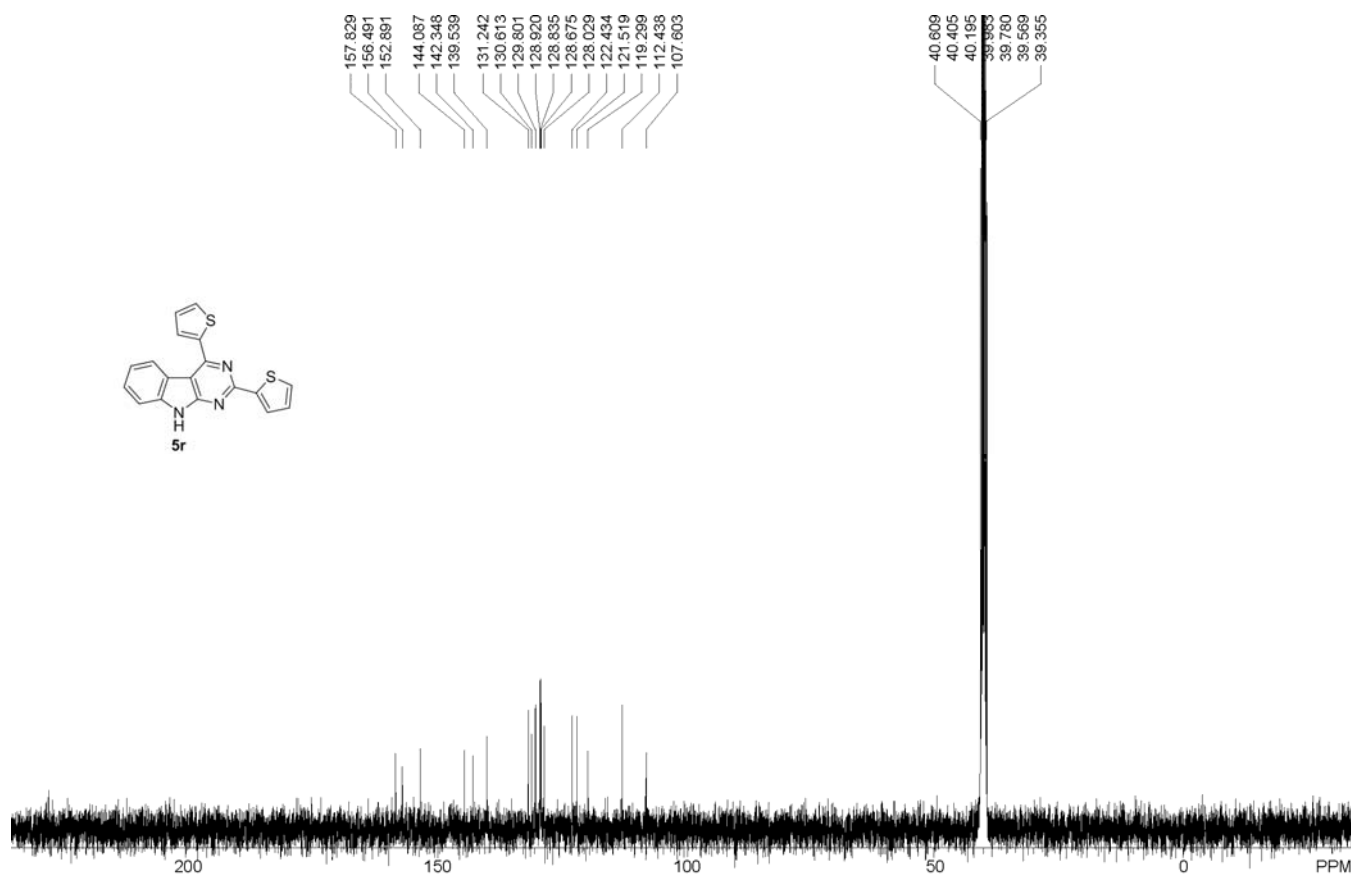
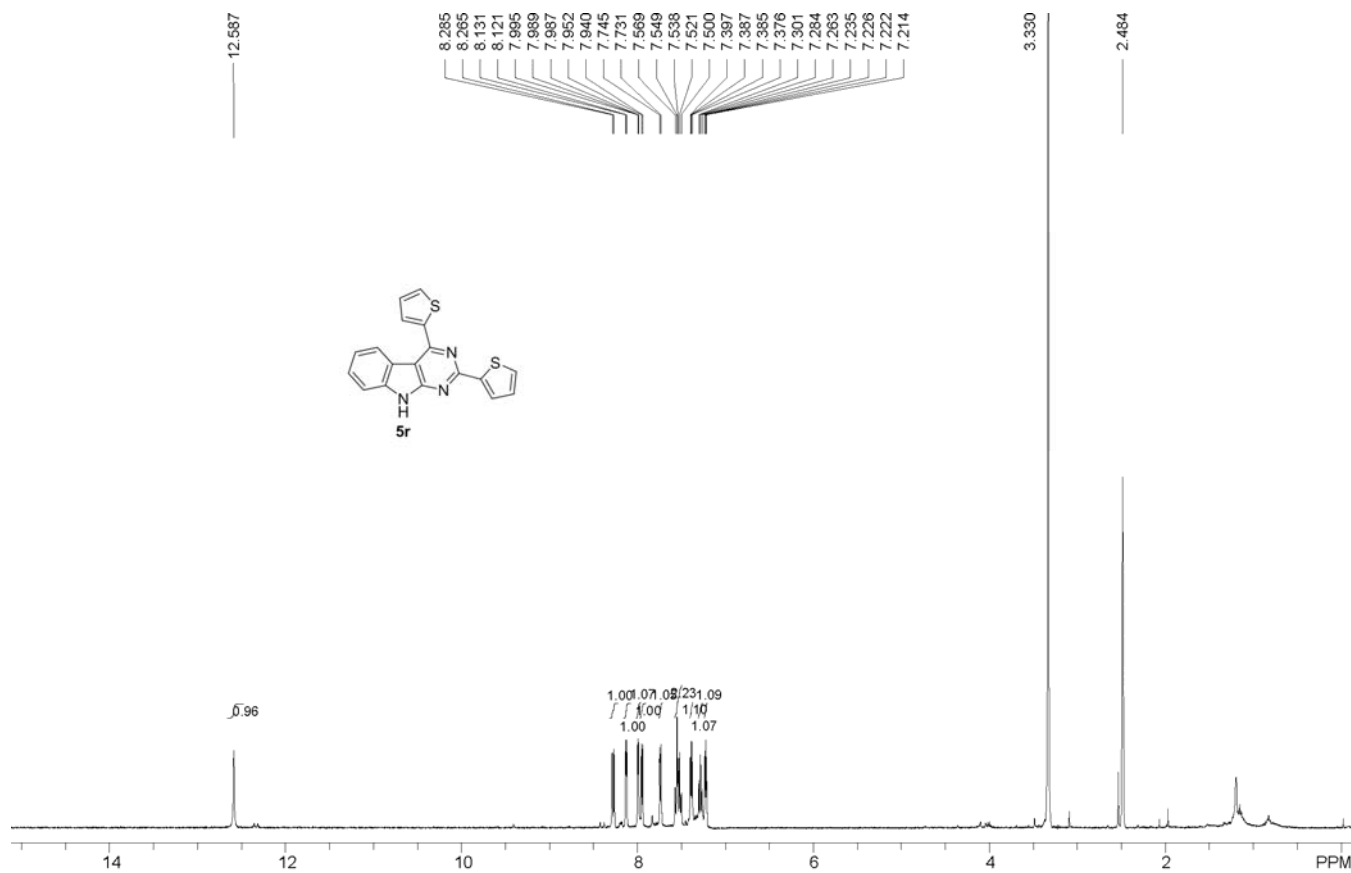


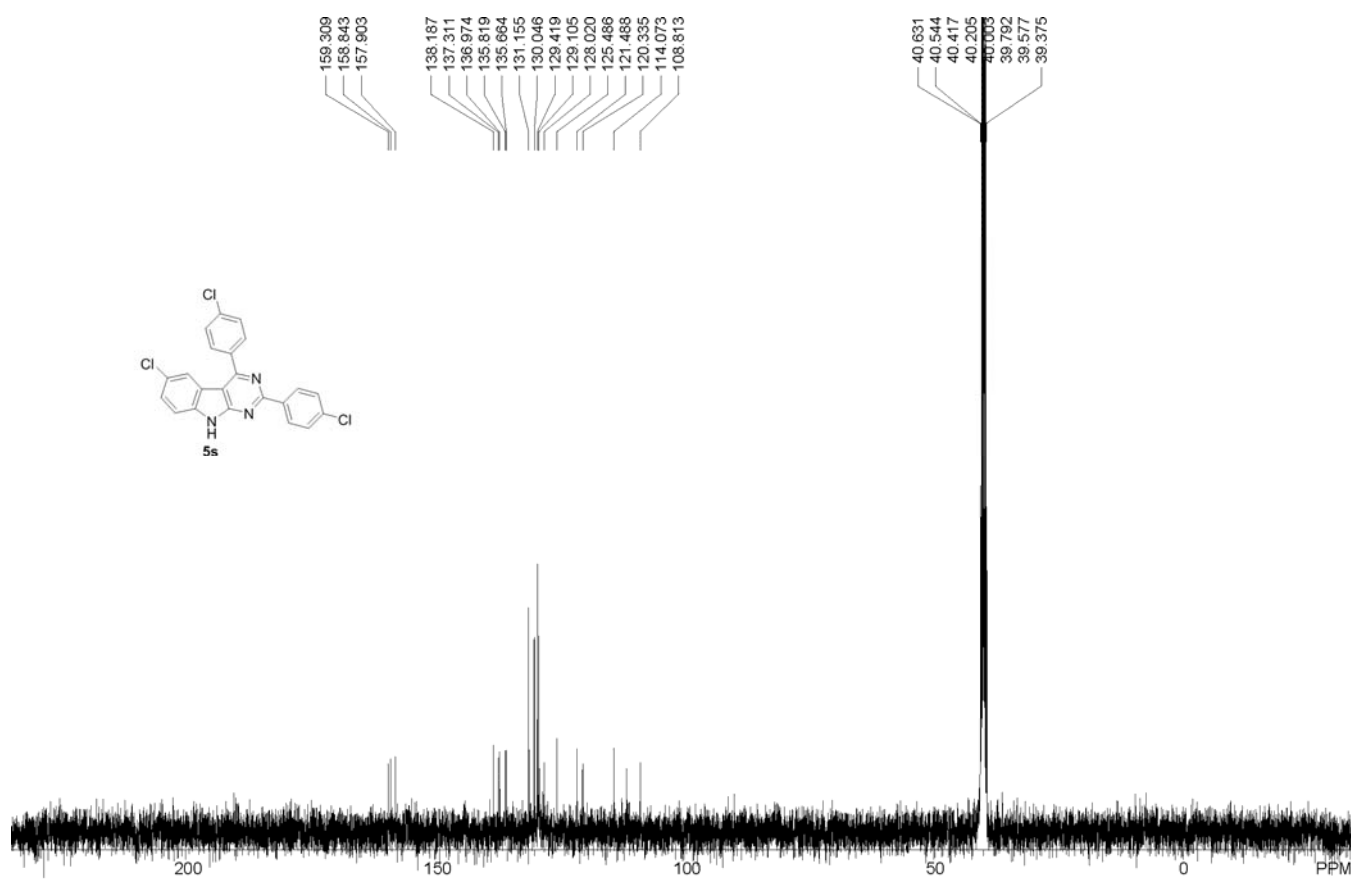
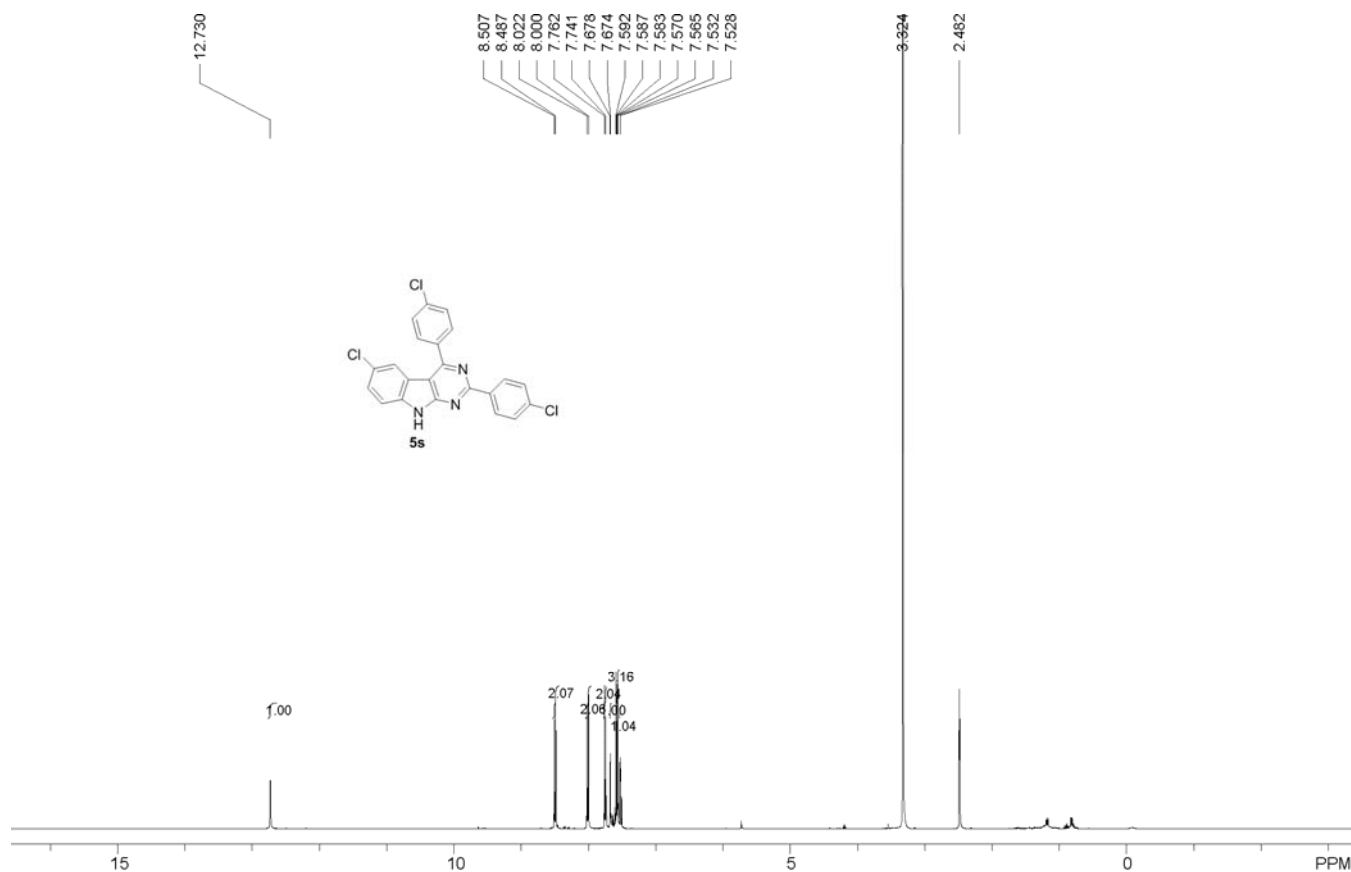


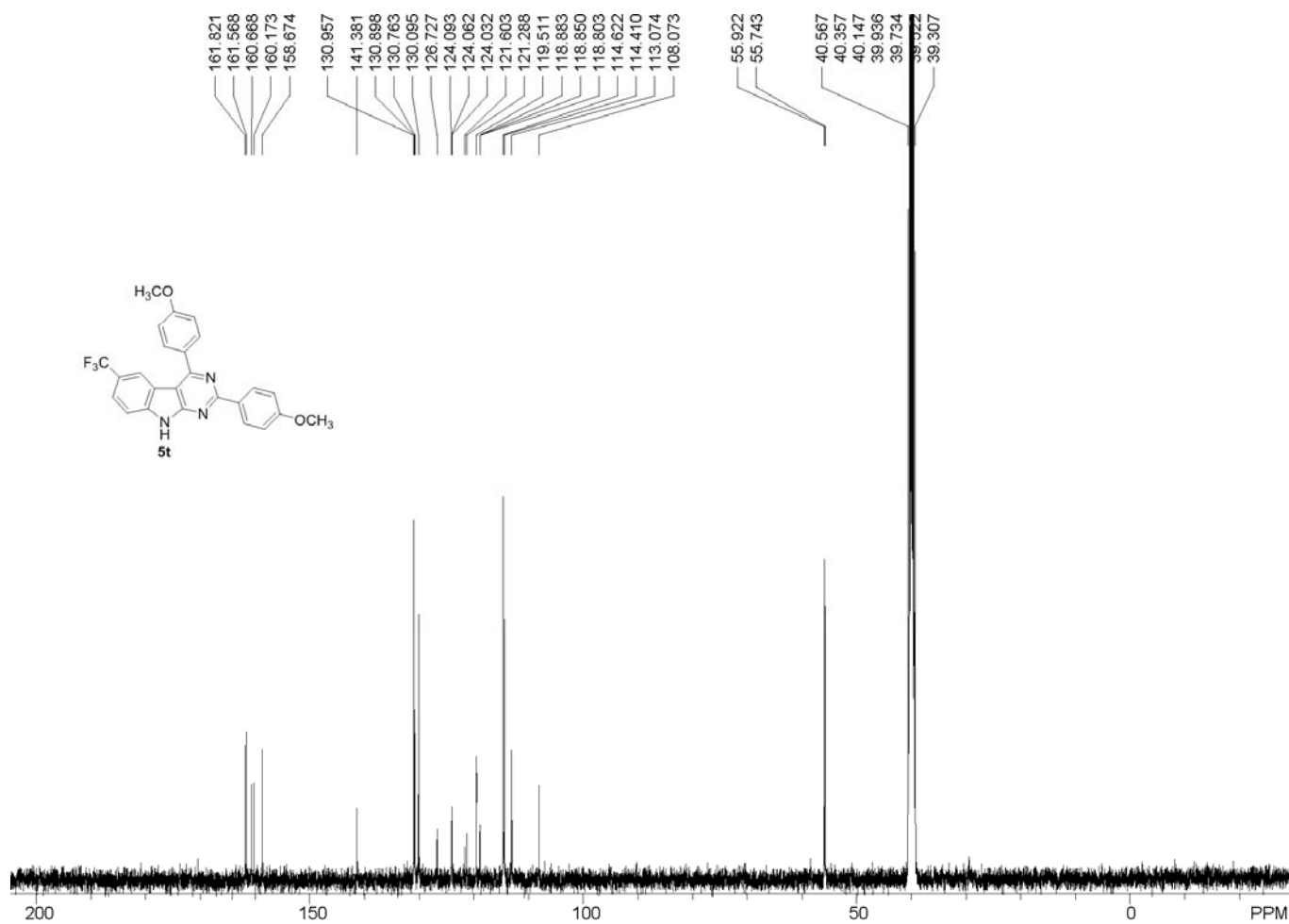
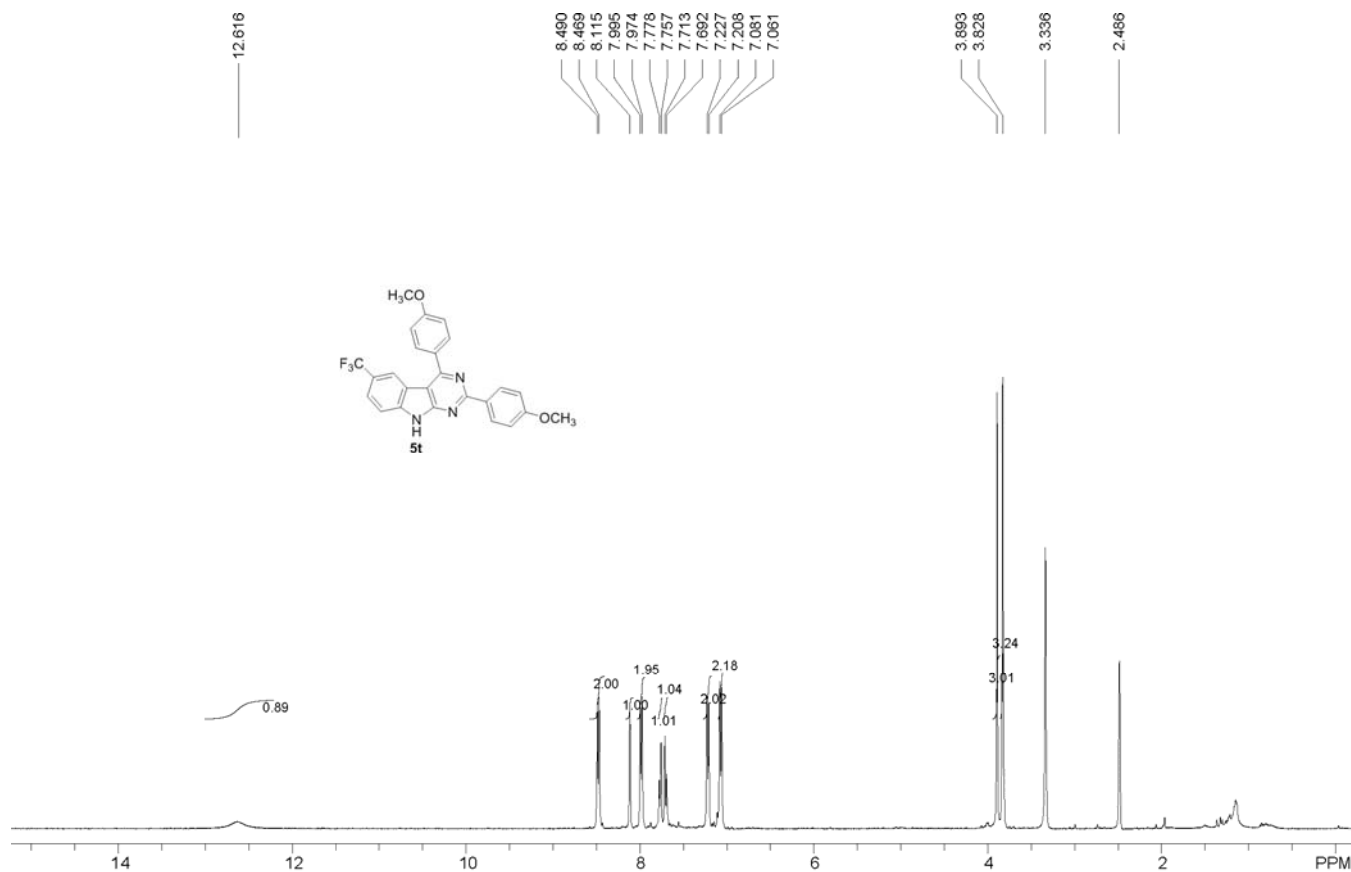


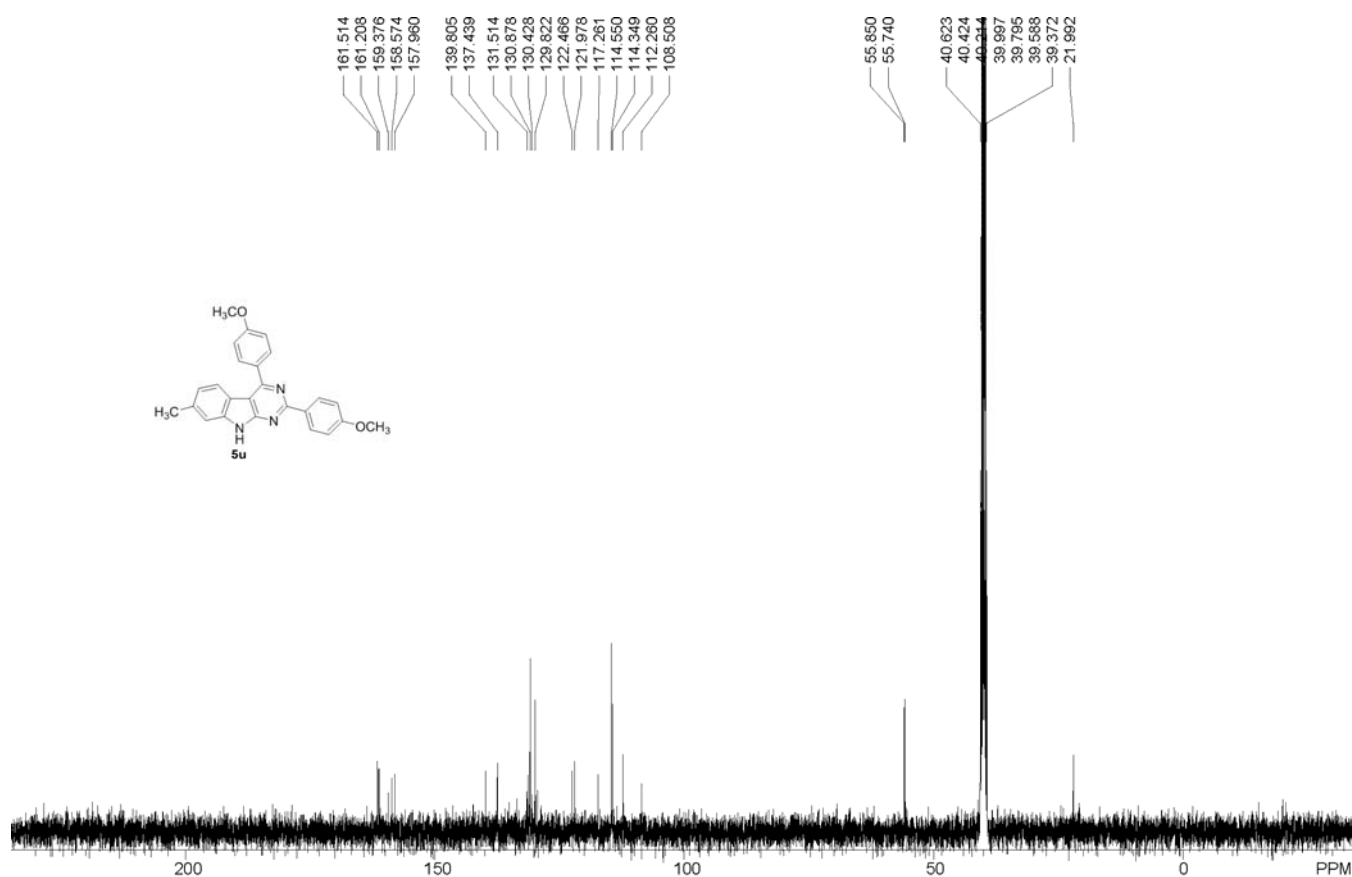
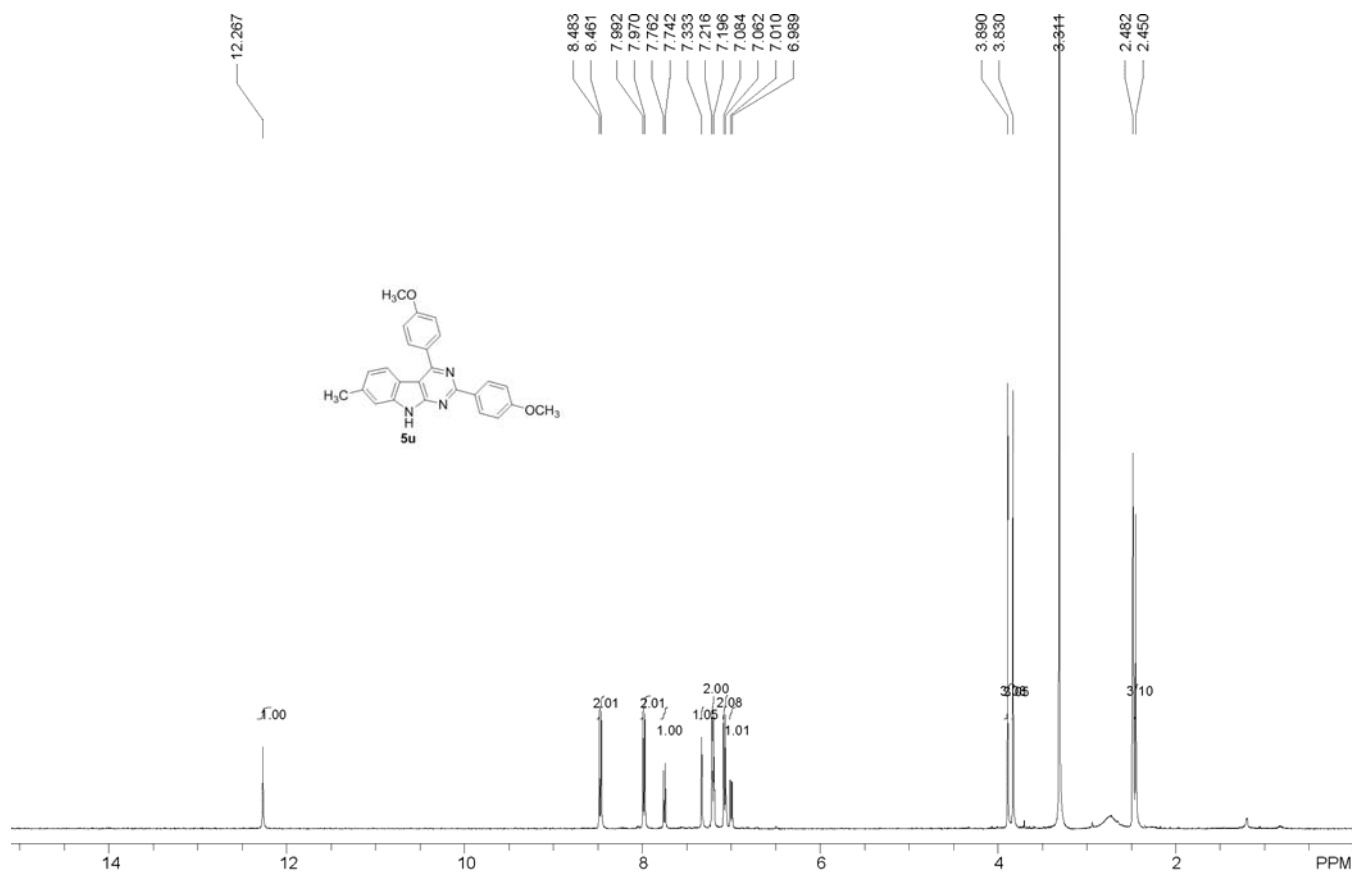




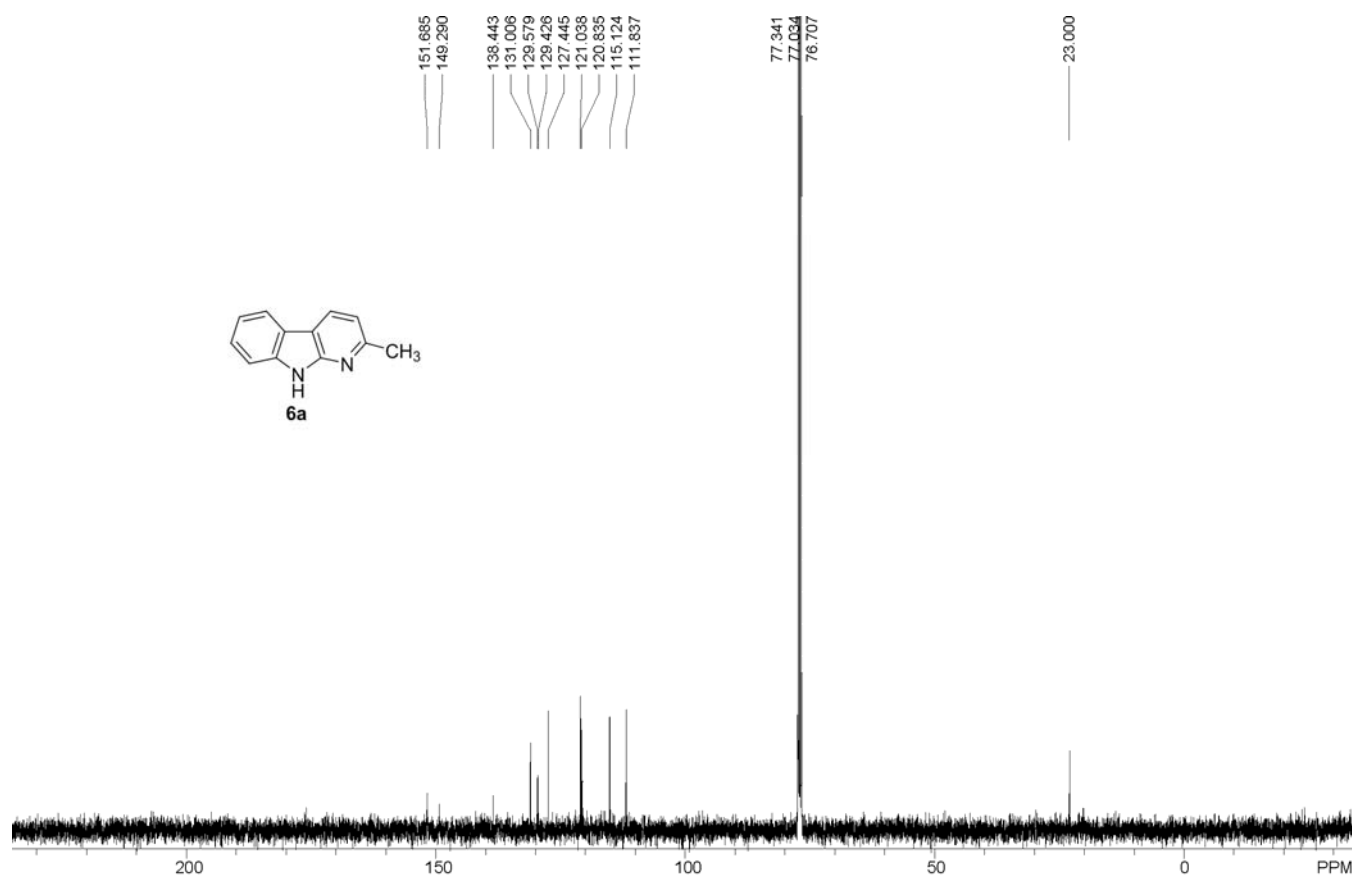
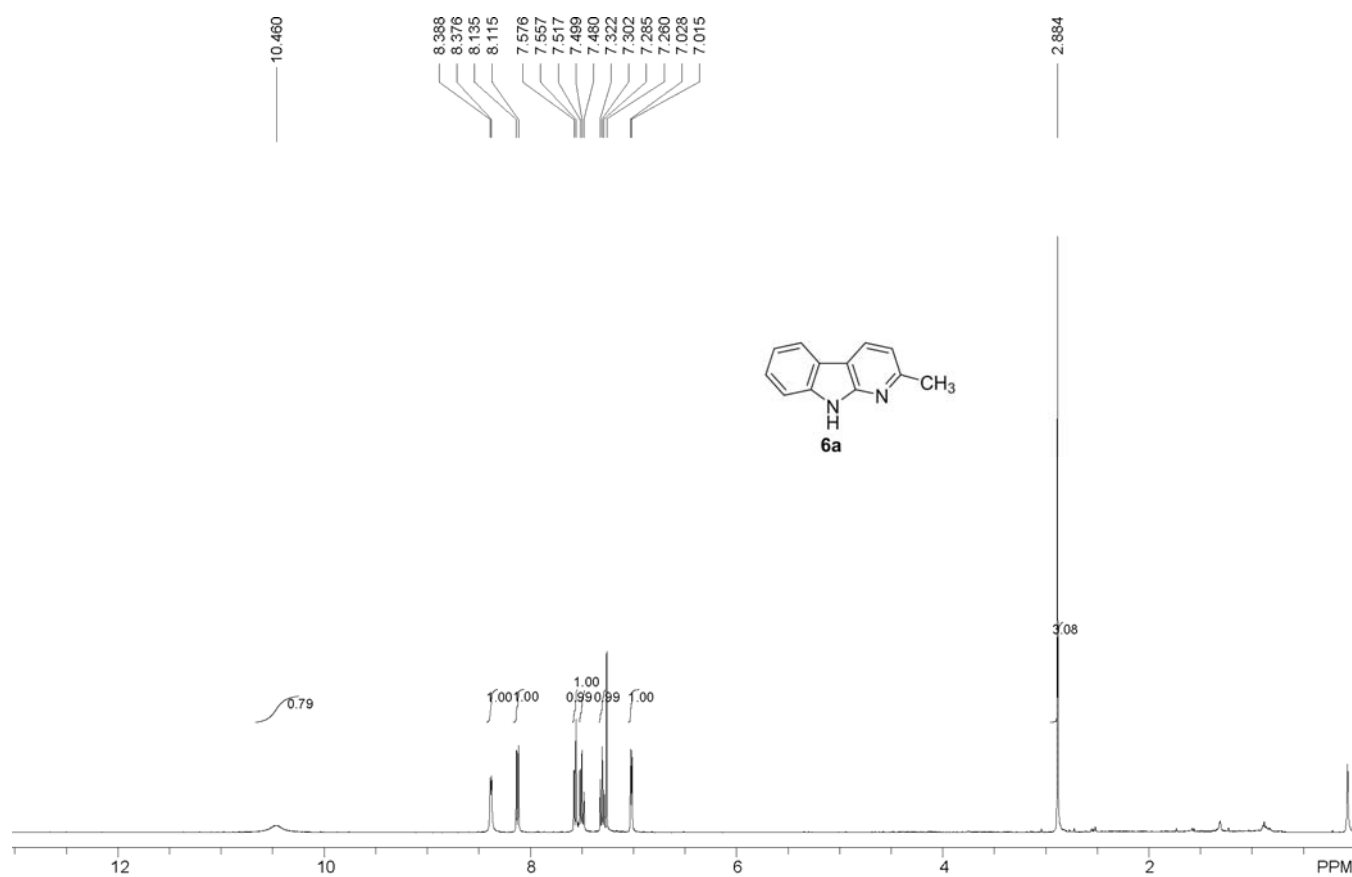


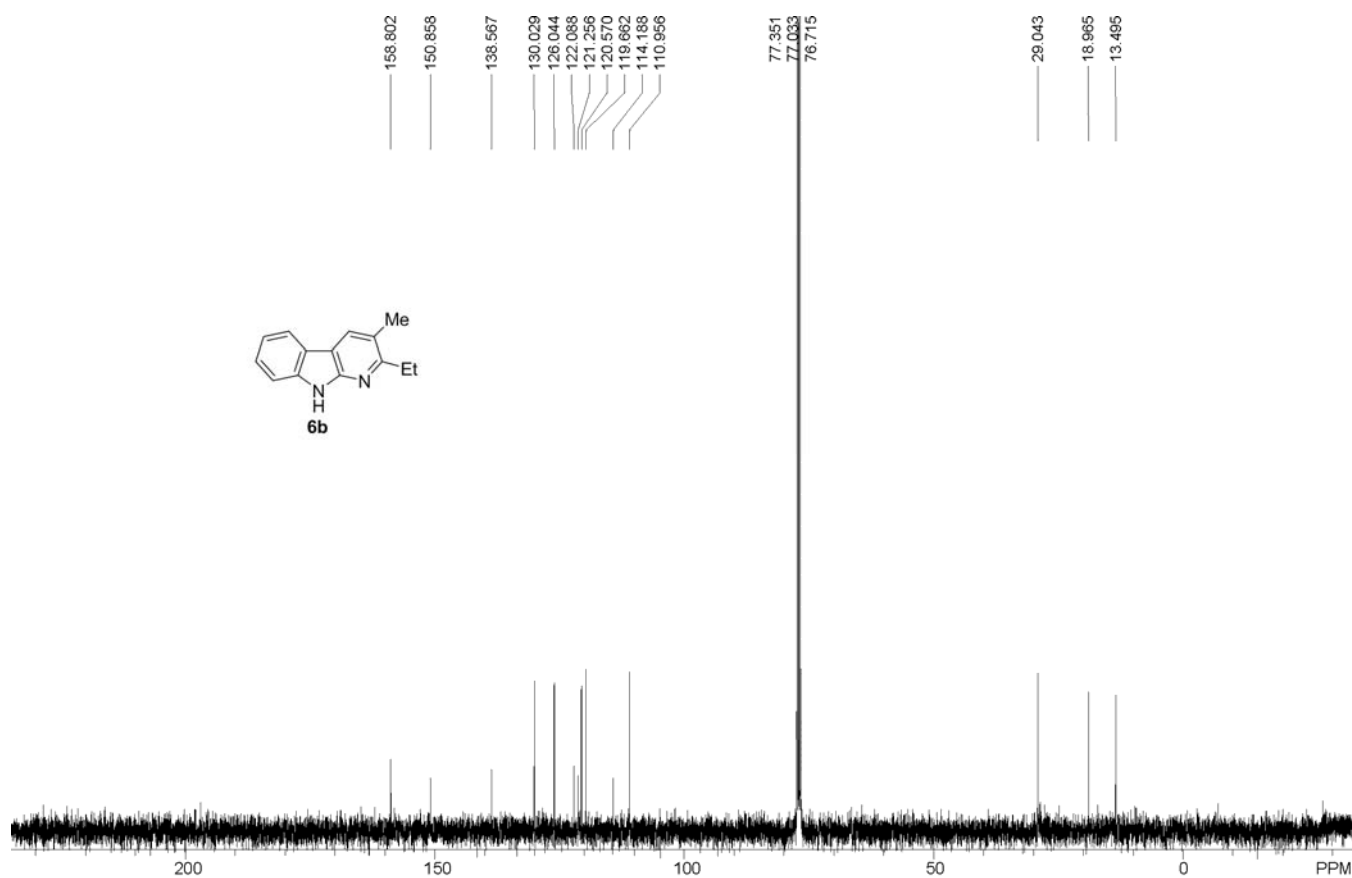
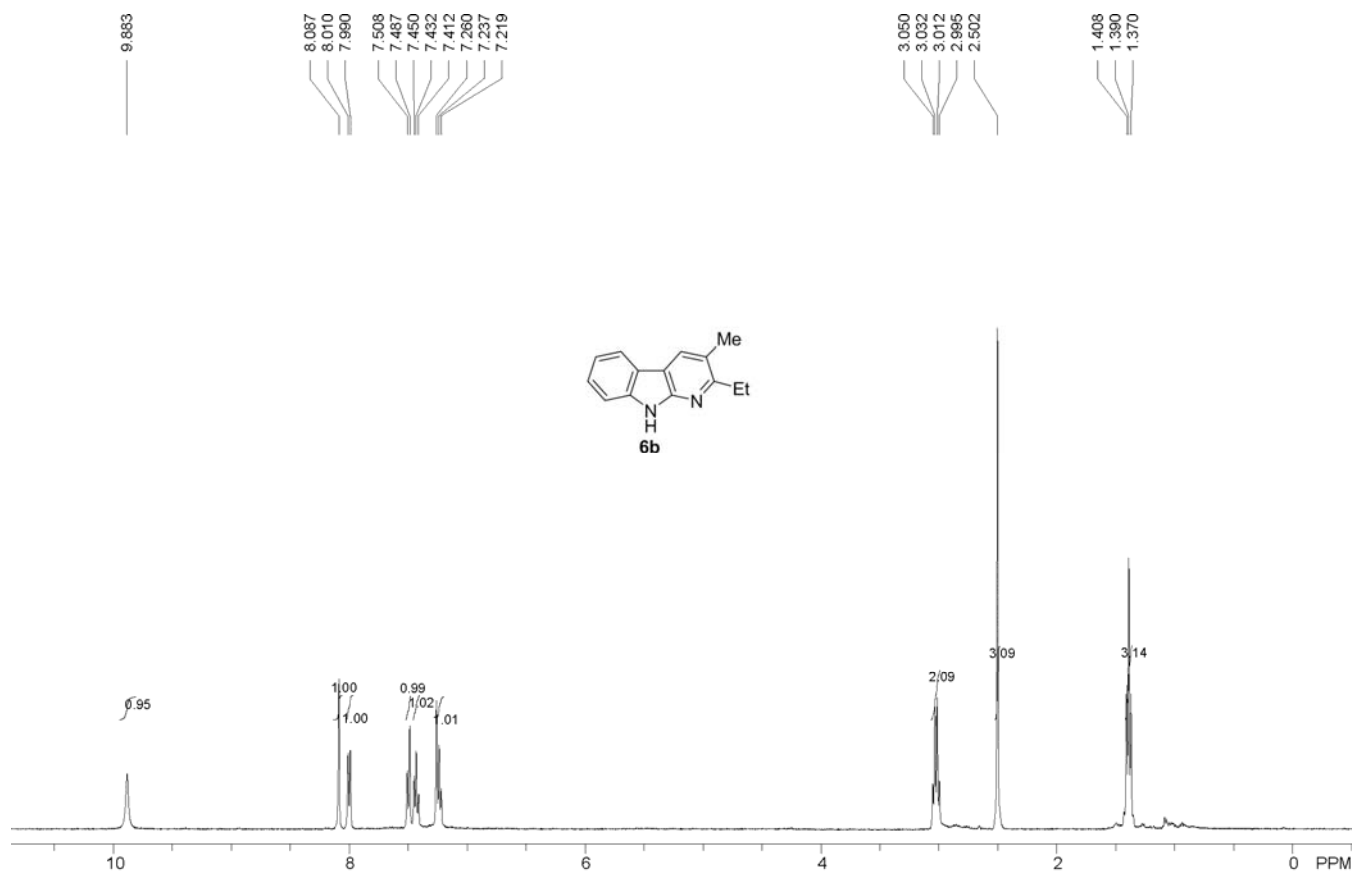


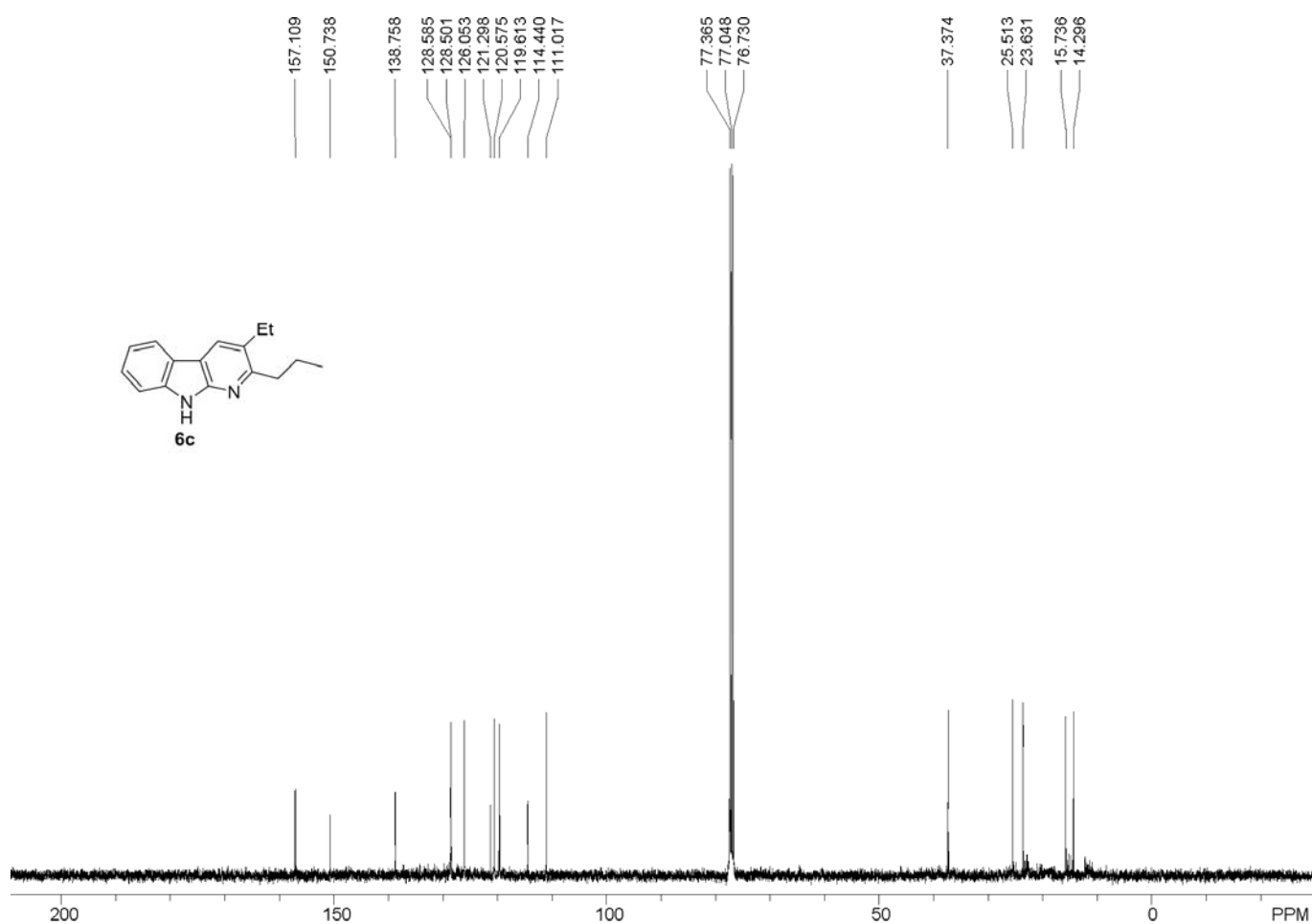
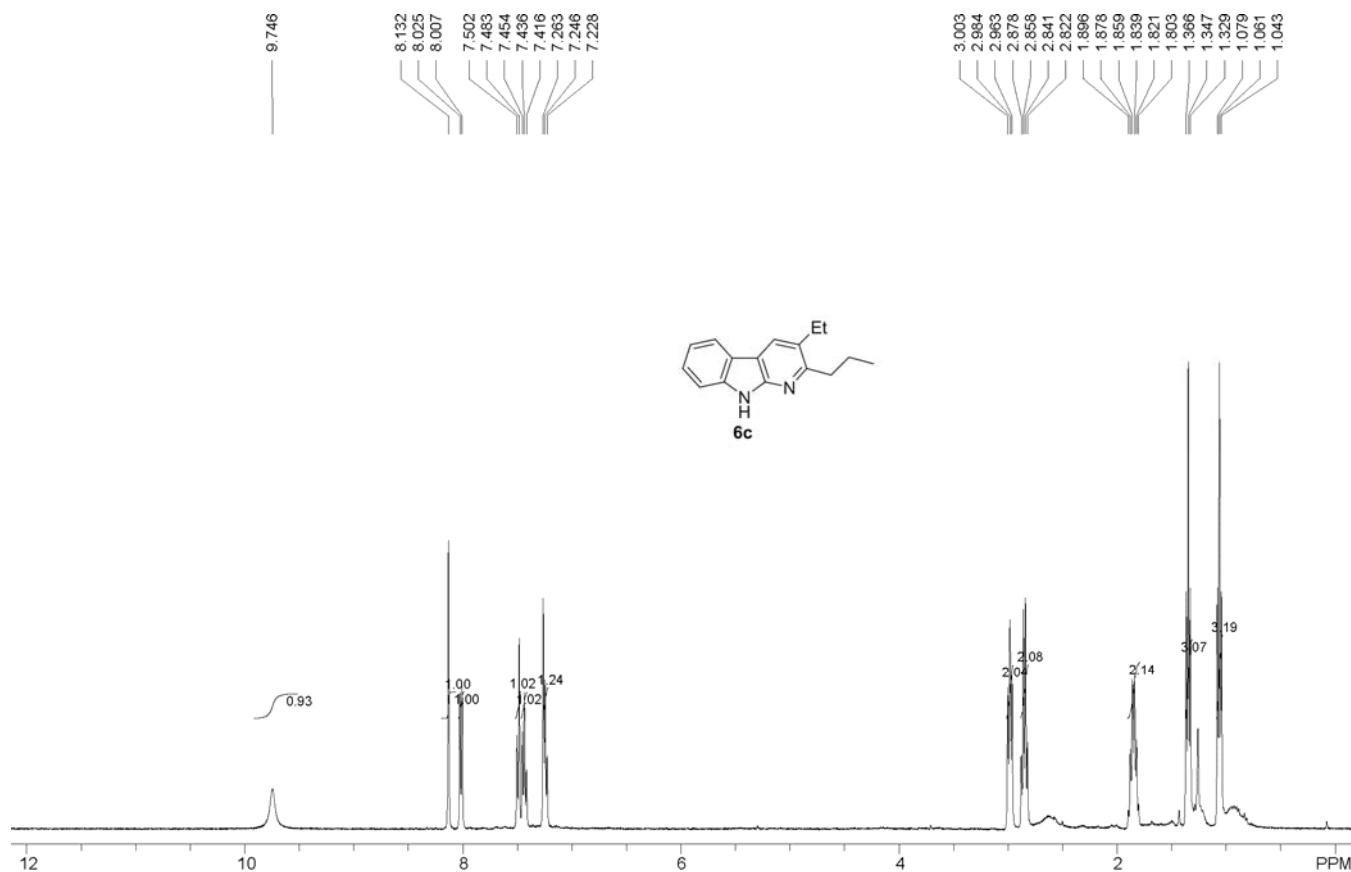


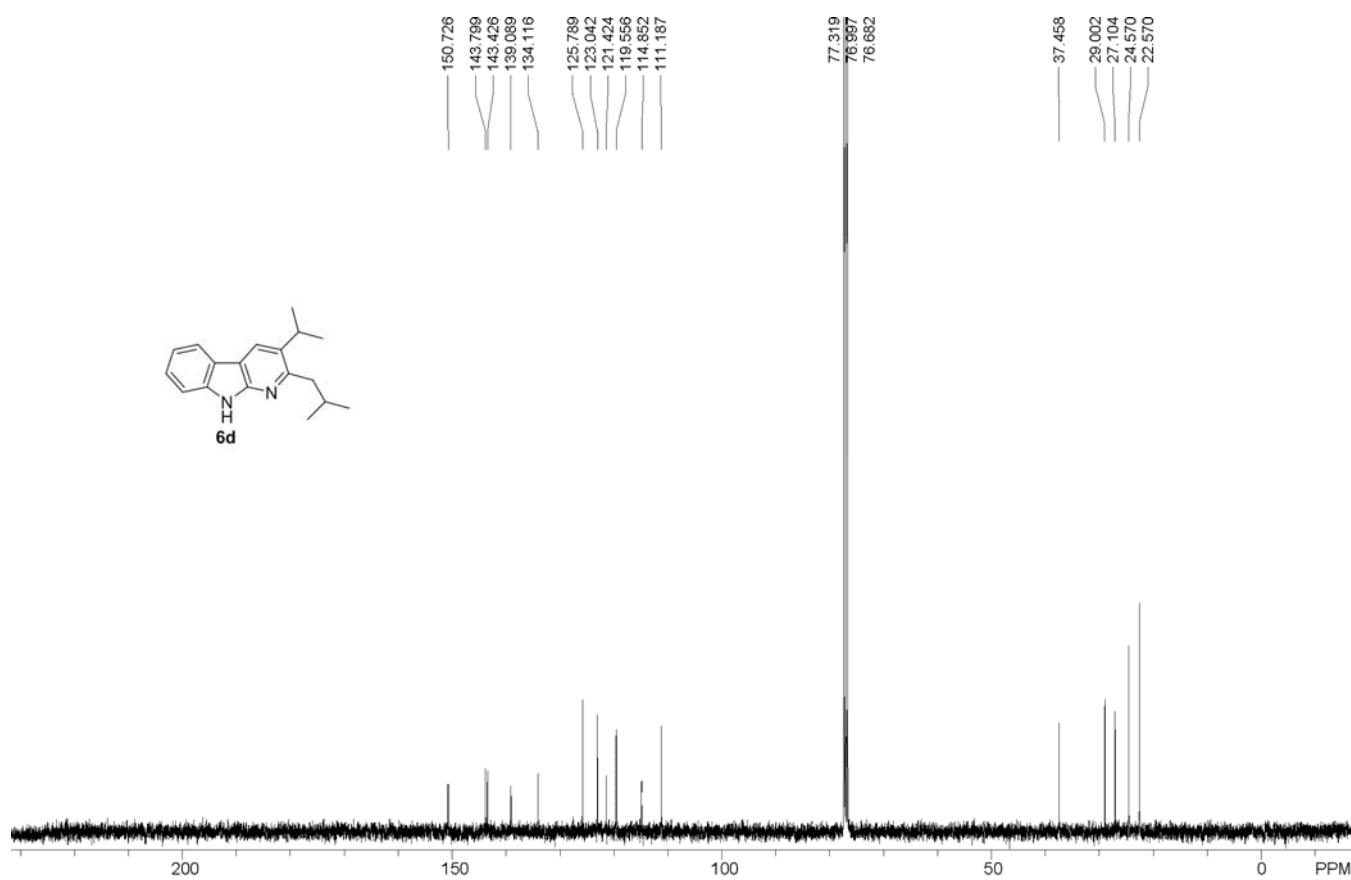
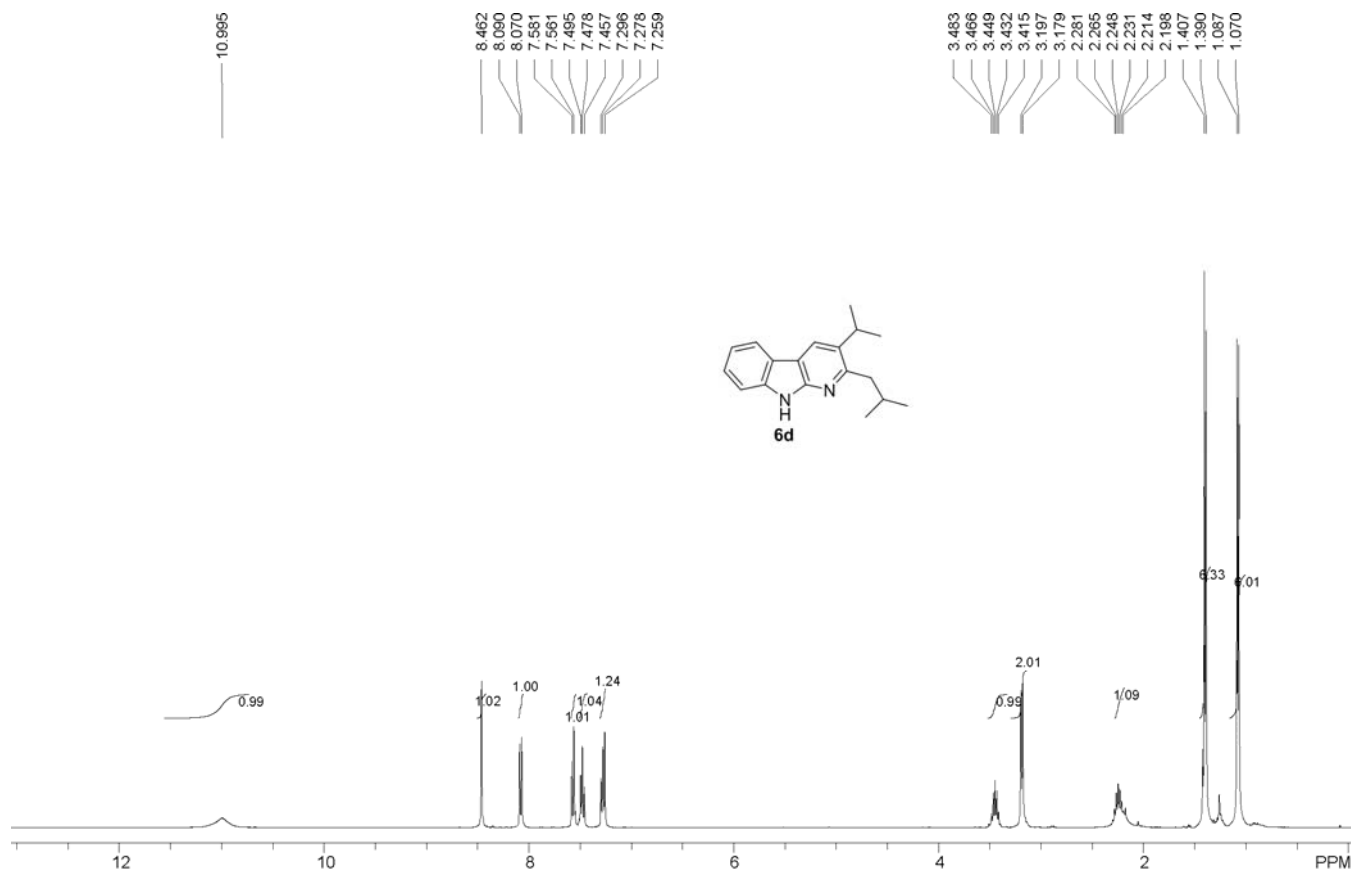


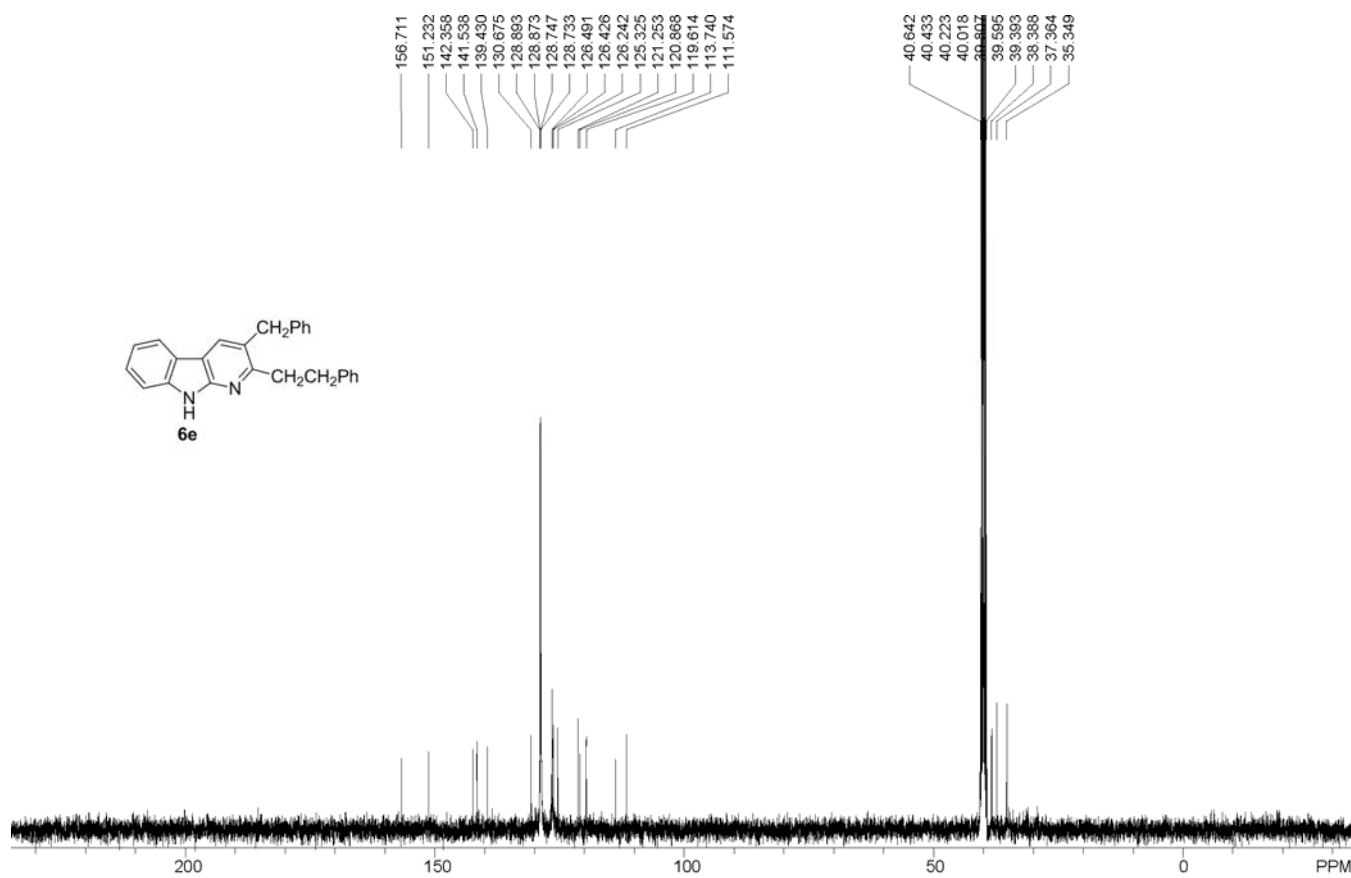
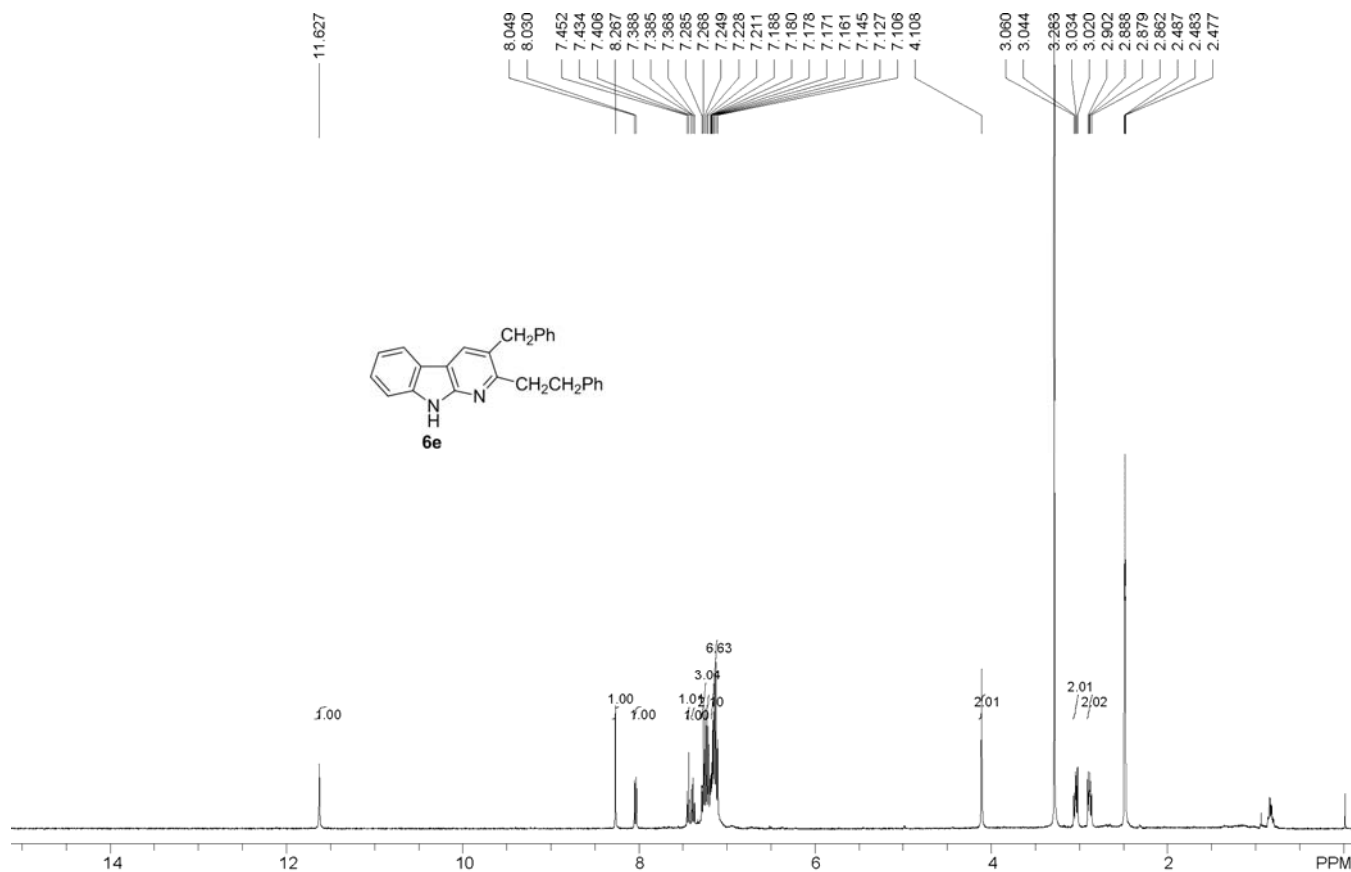
IV. Copies of ^1H and ^{13}C NMR spectra of 6a-6k

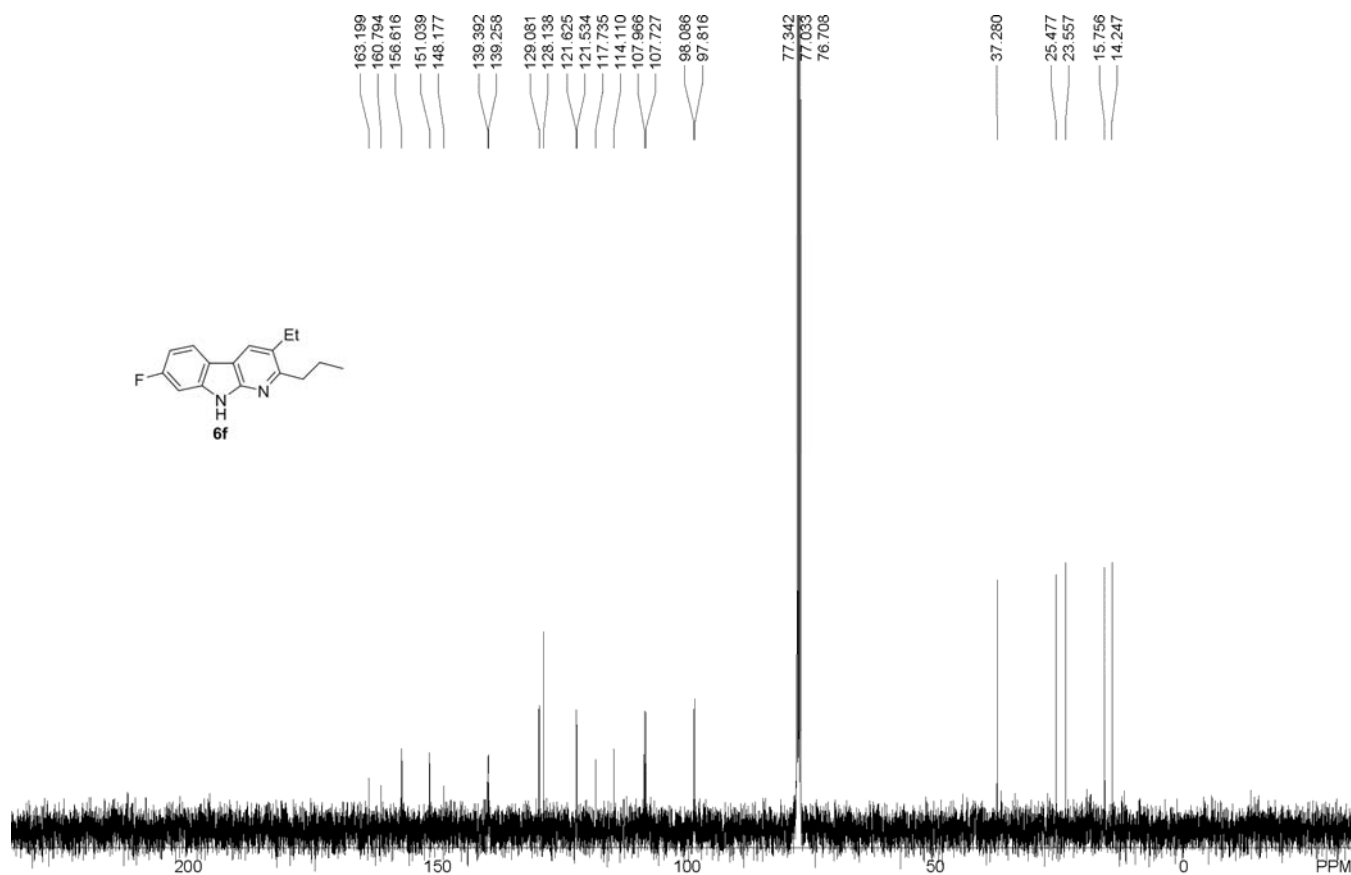
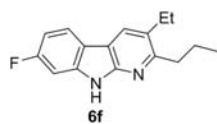
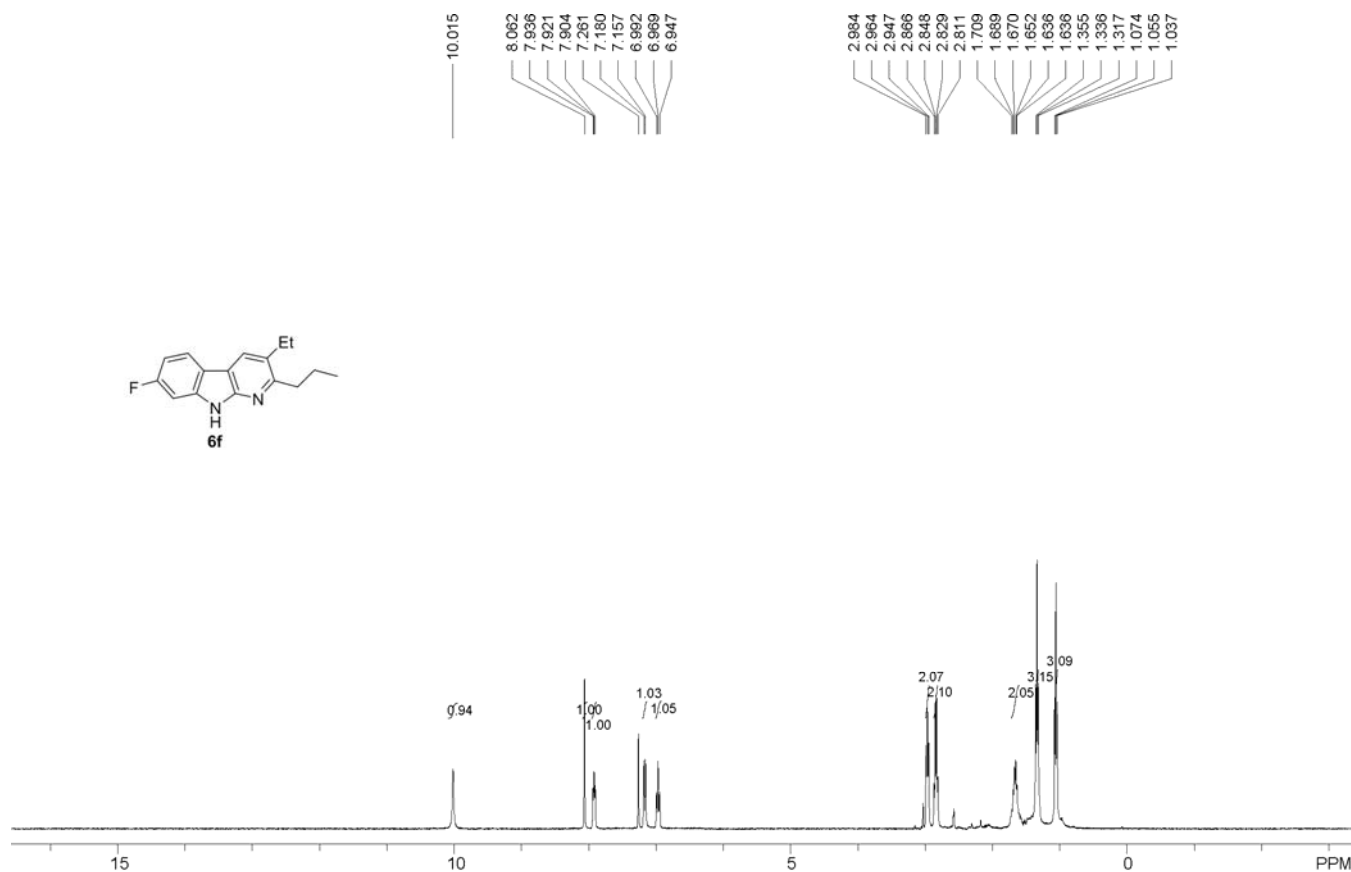
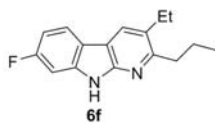


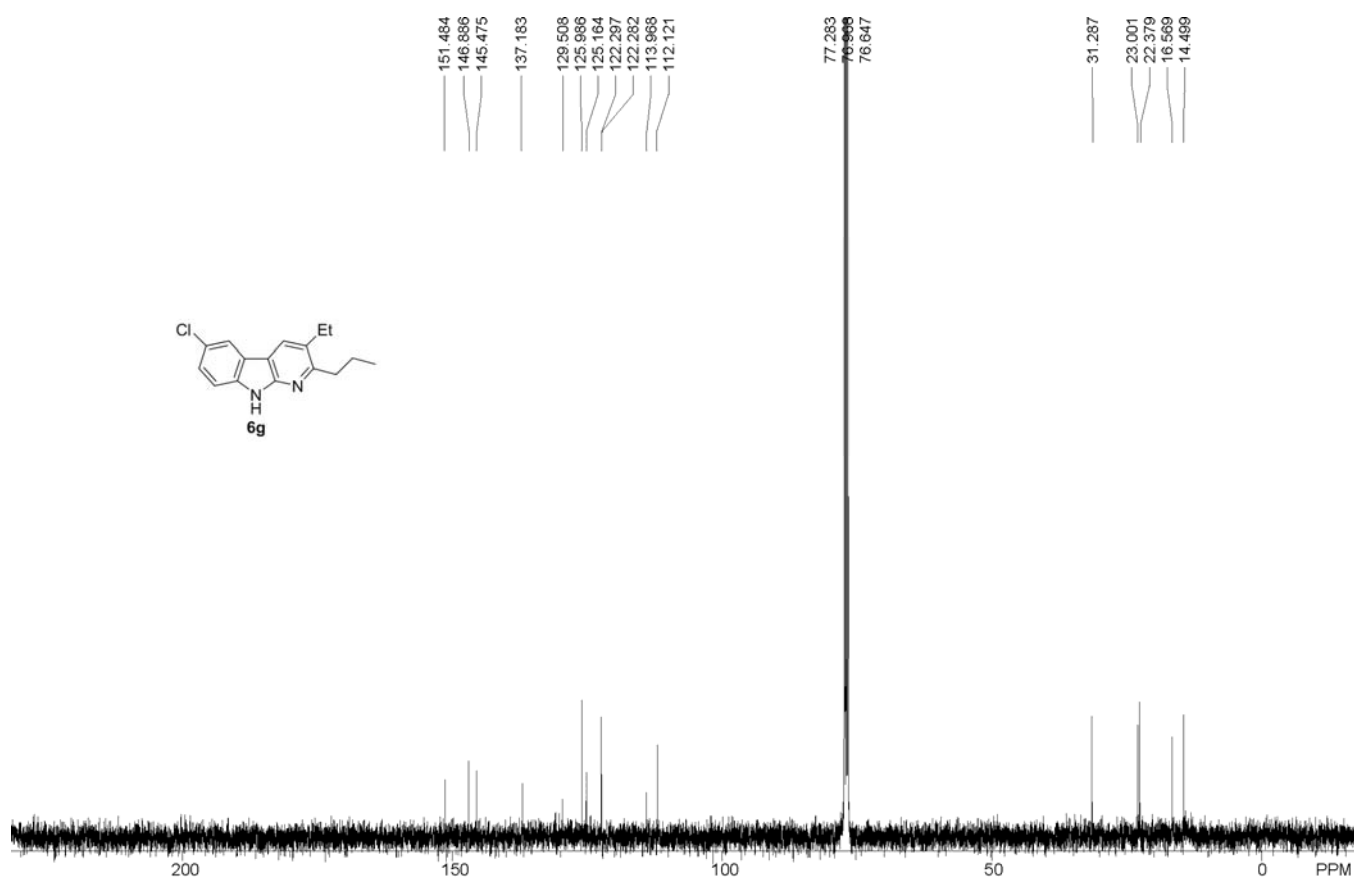
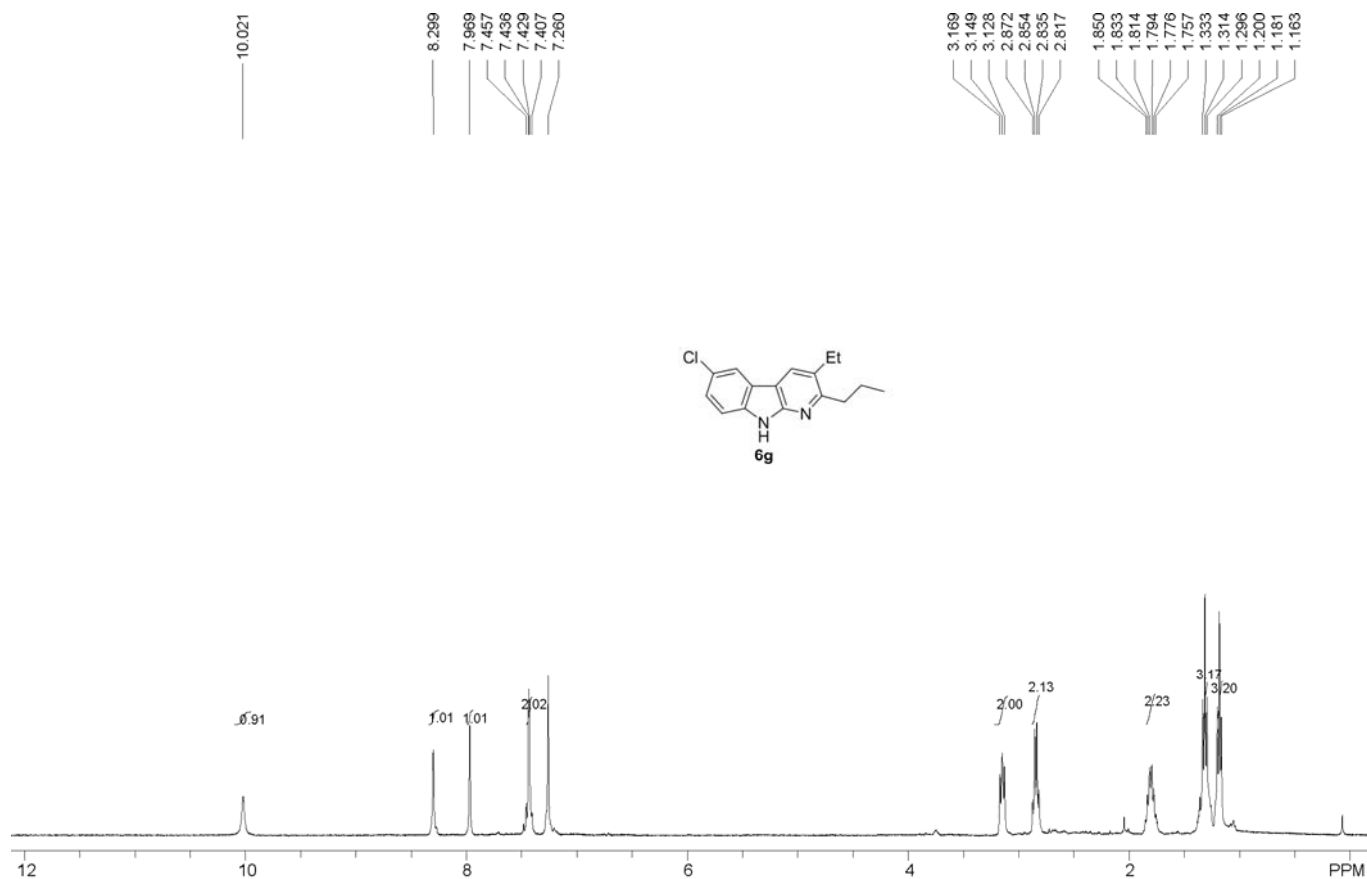


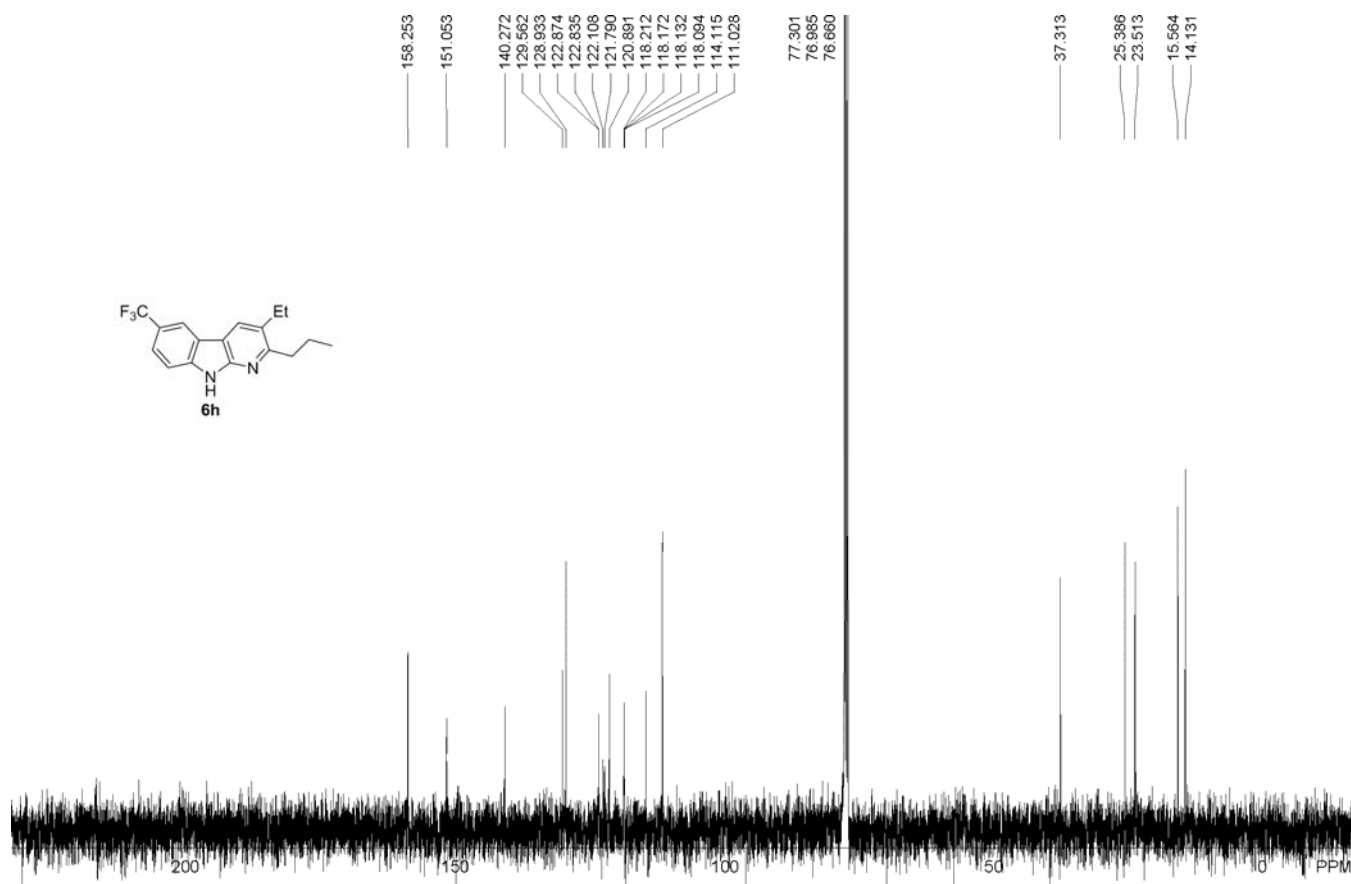
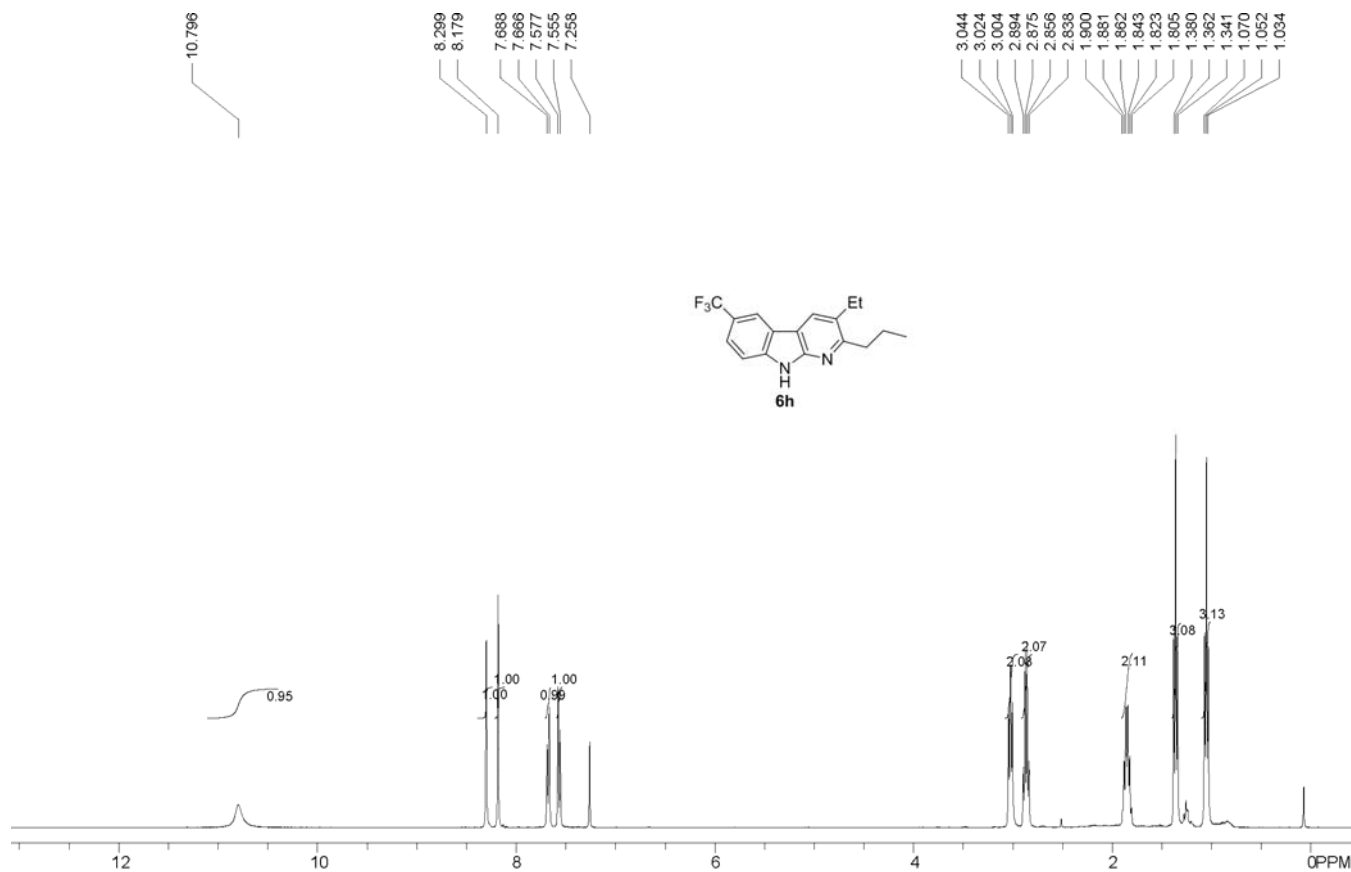


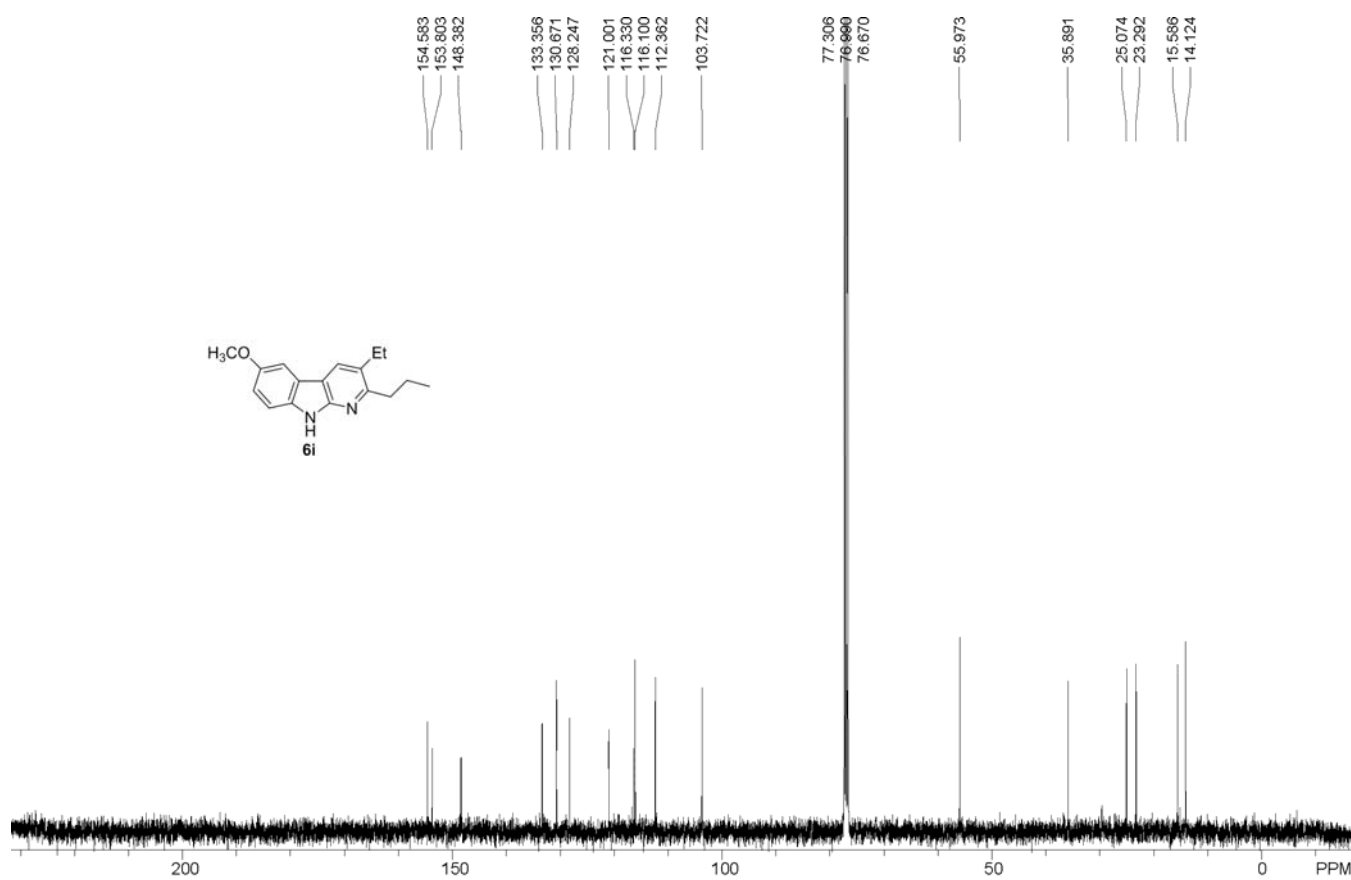
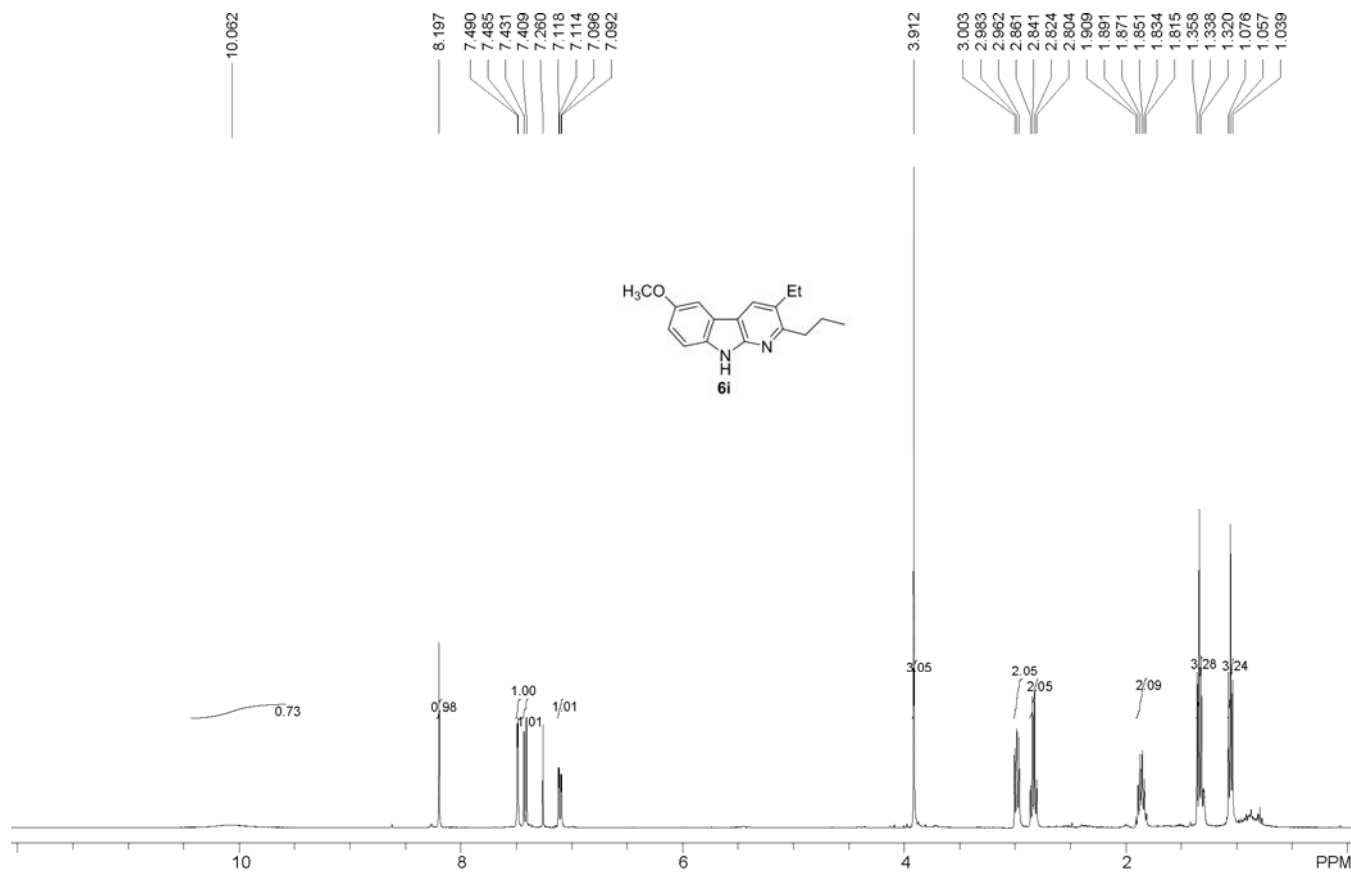


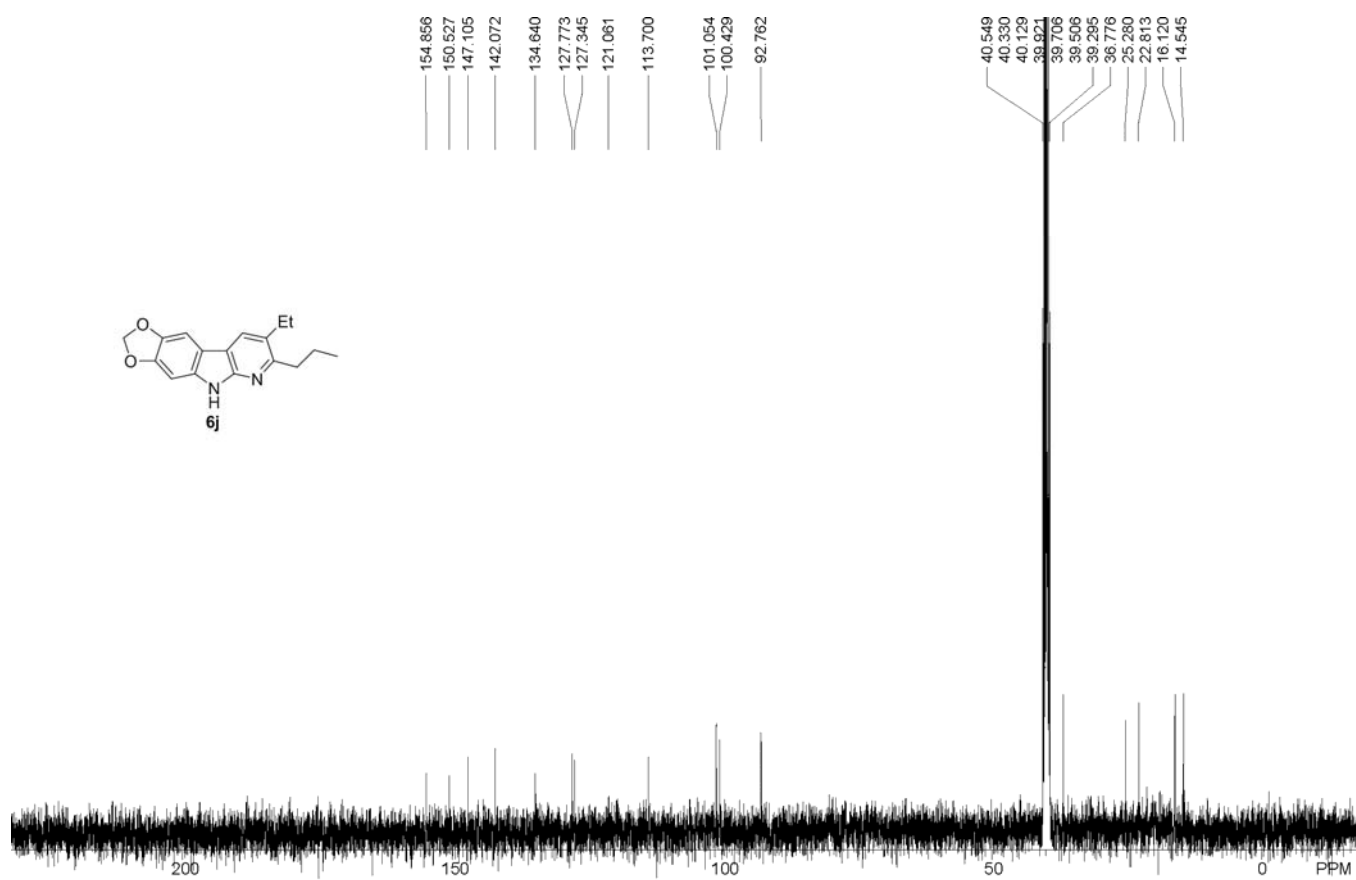
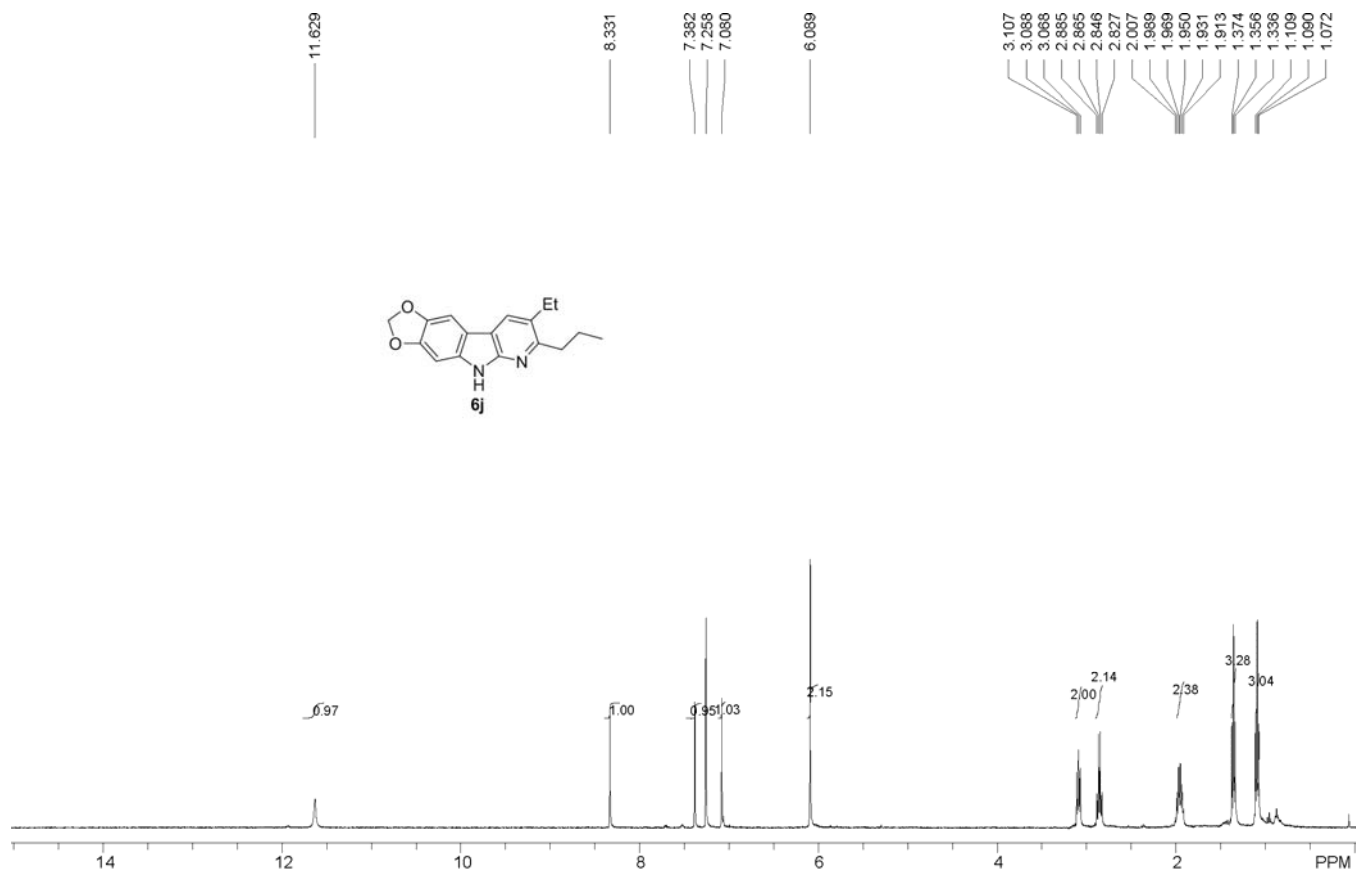


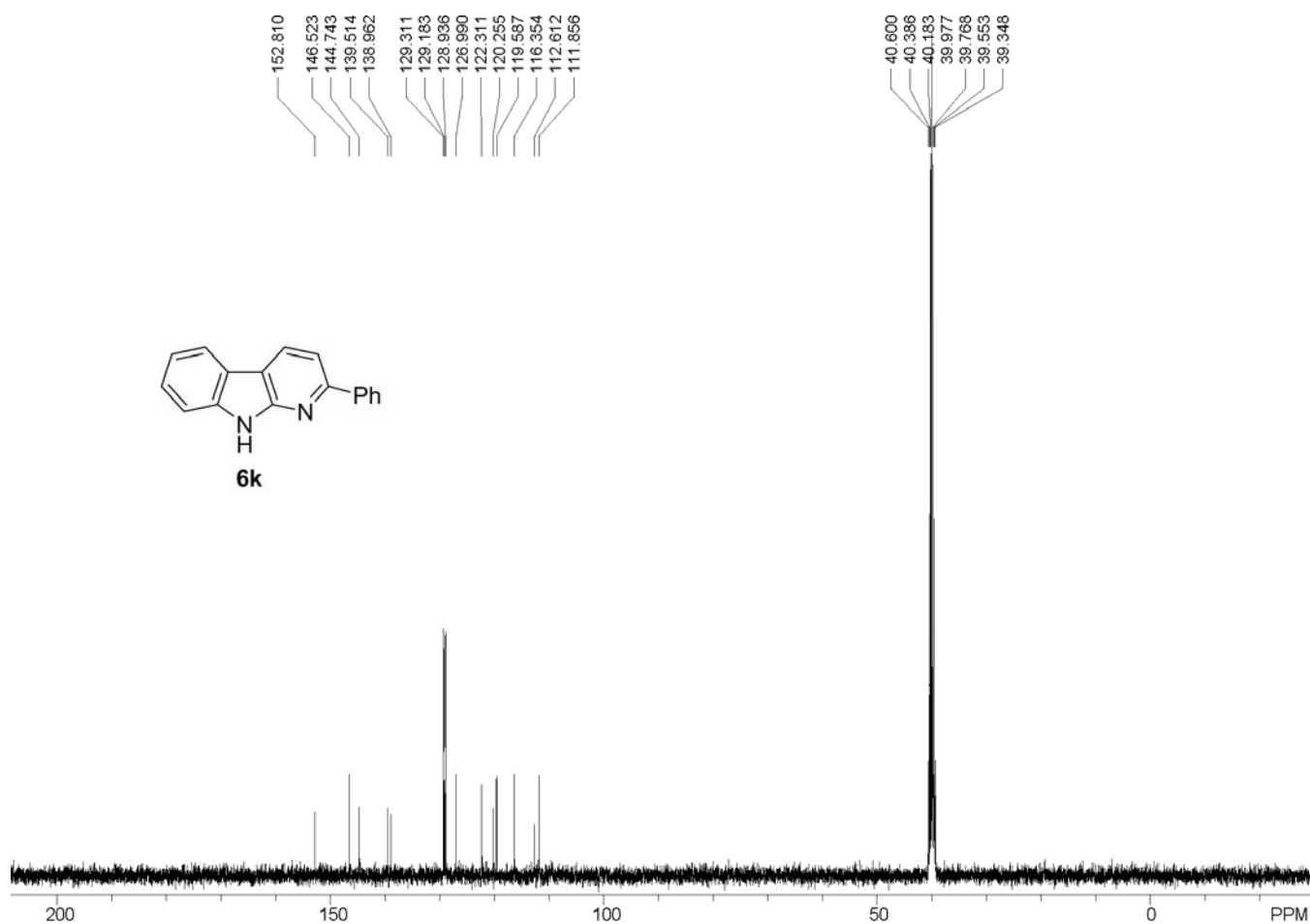
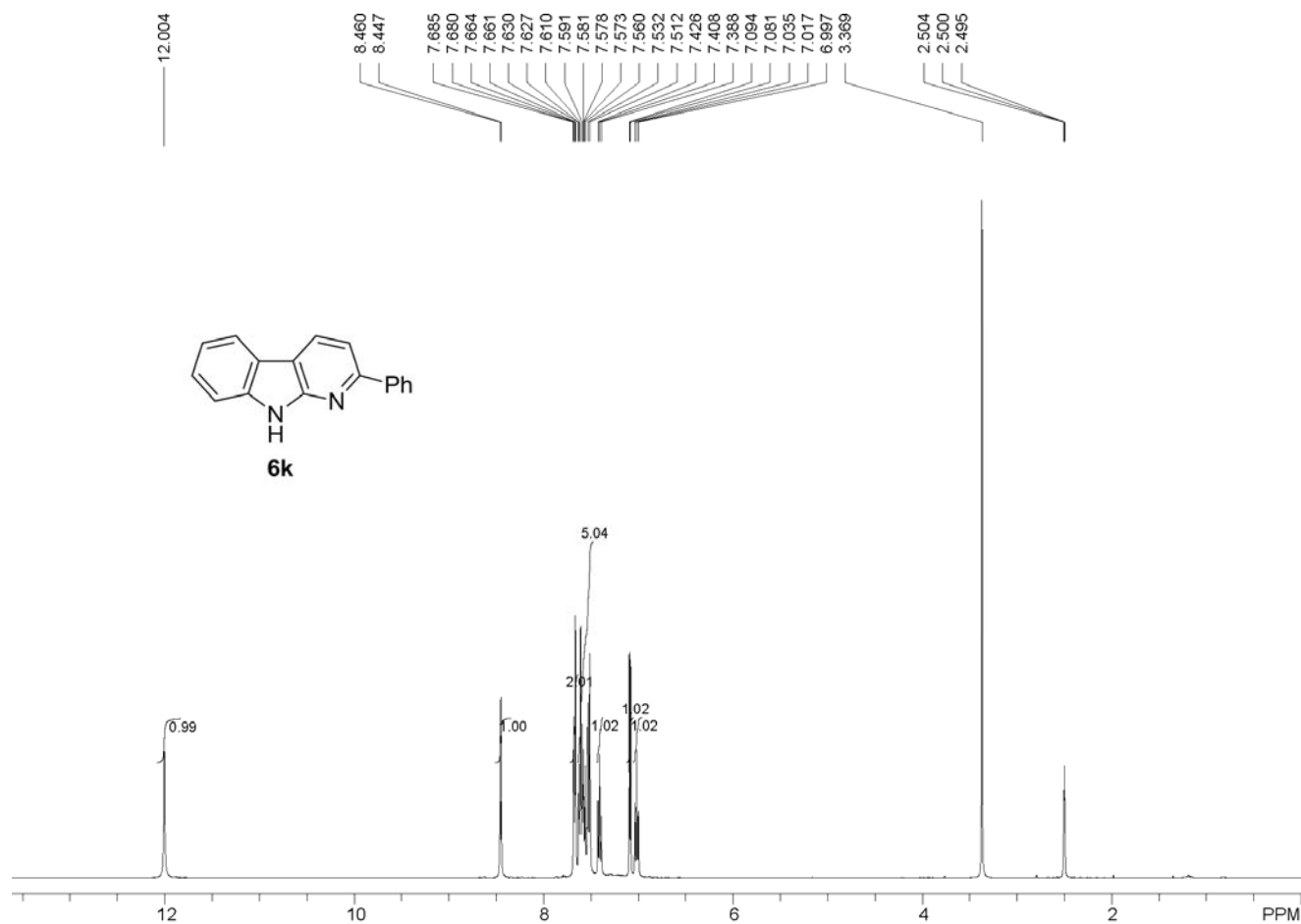




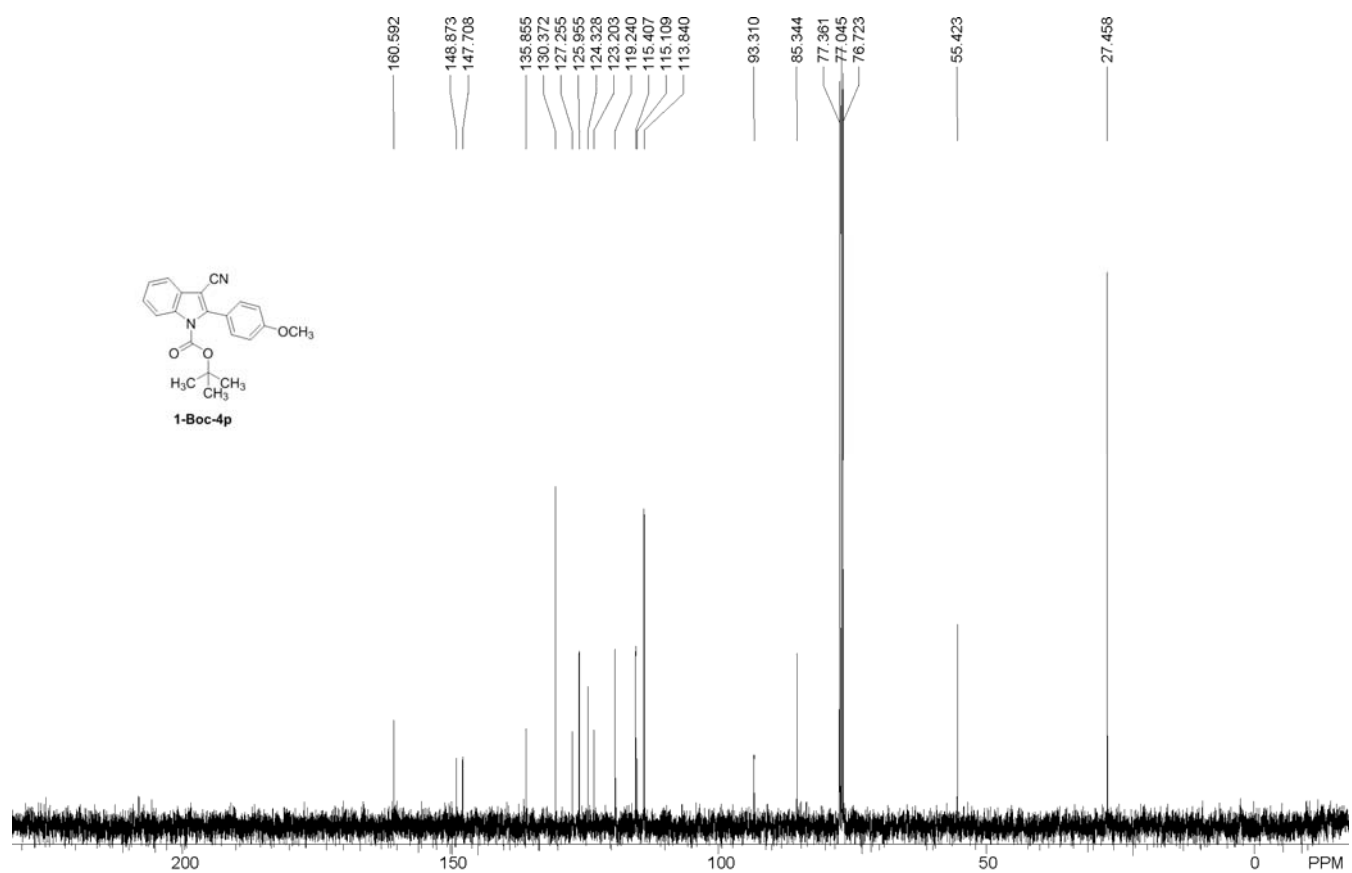
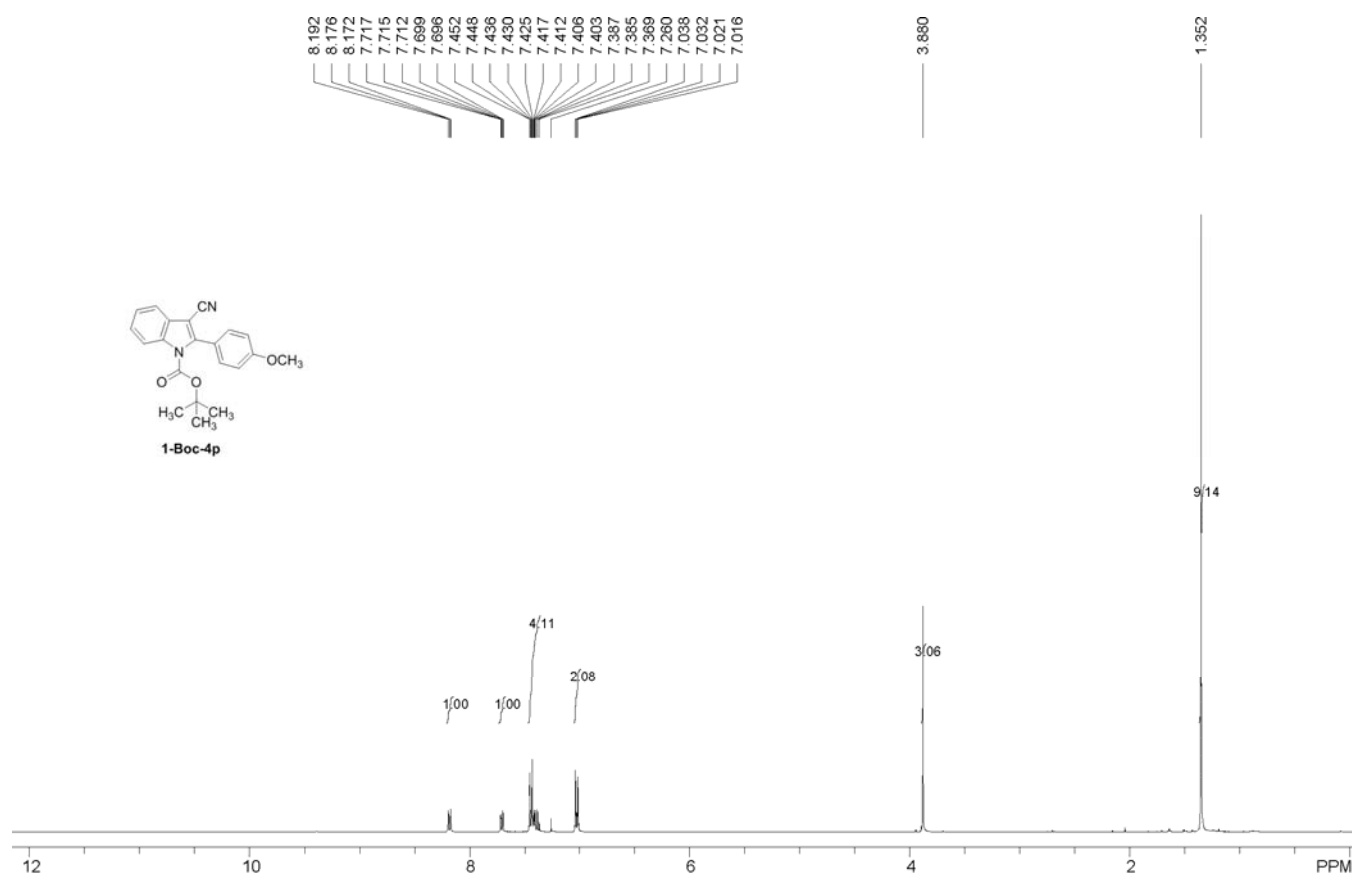




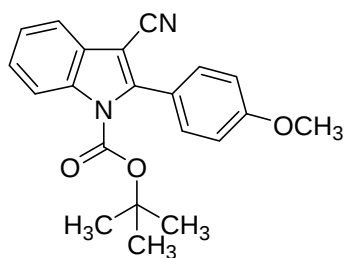




V. Copies of ^1H and ^{13}C NMR spectra of 1-Boc-4p



VI. X-ray Crystal Structure and data of 1-Boc-4p



1-Boc-4p

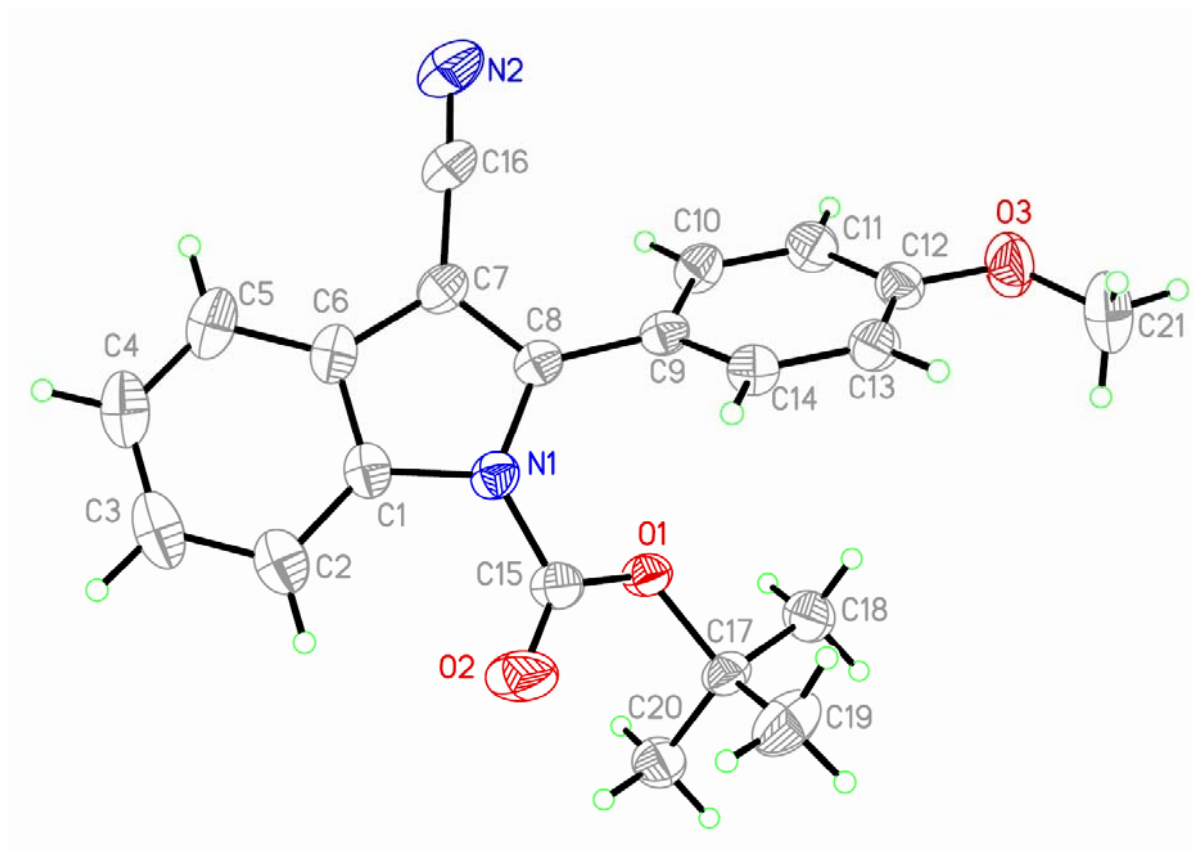
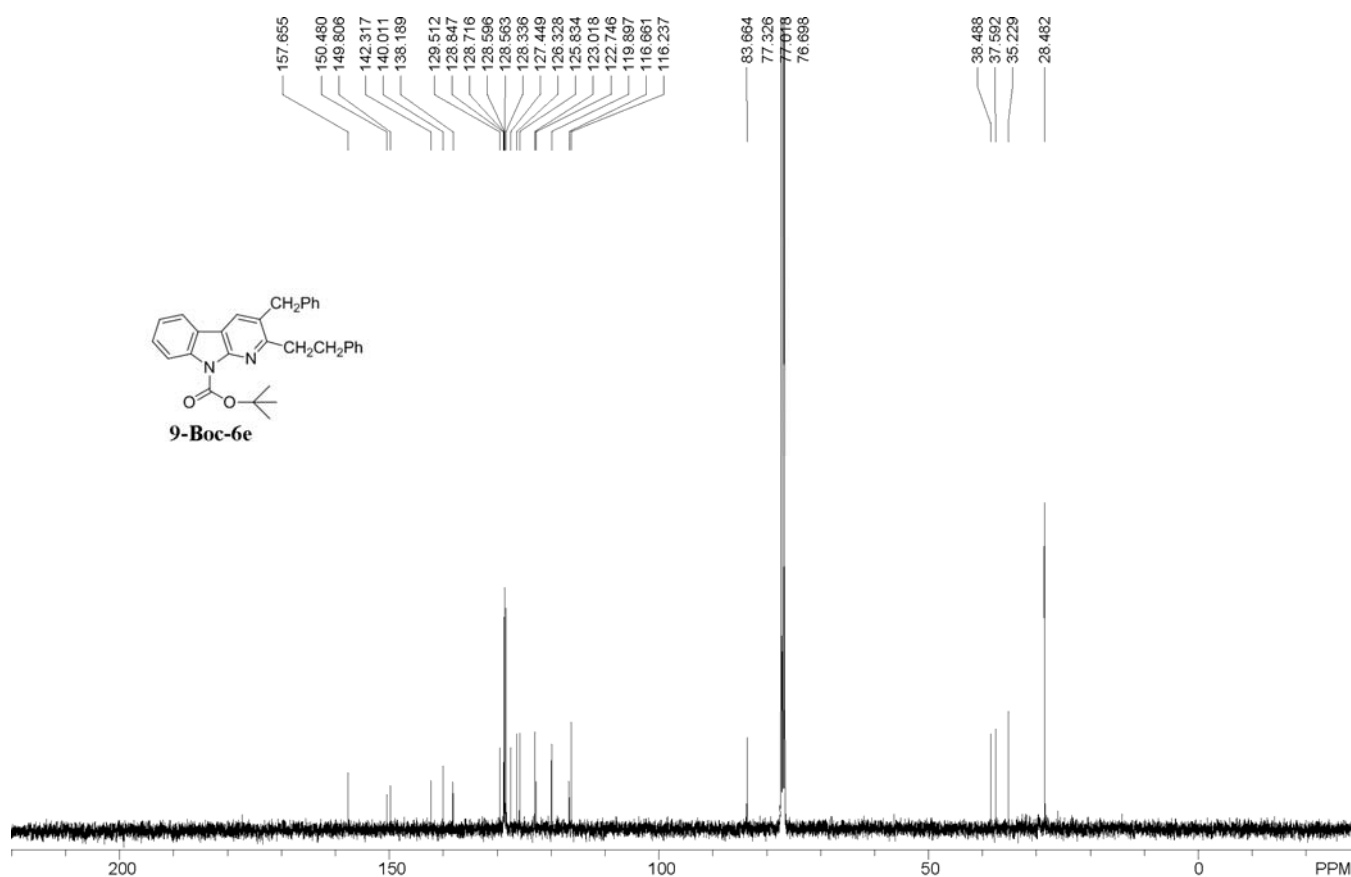
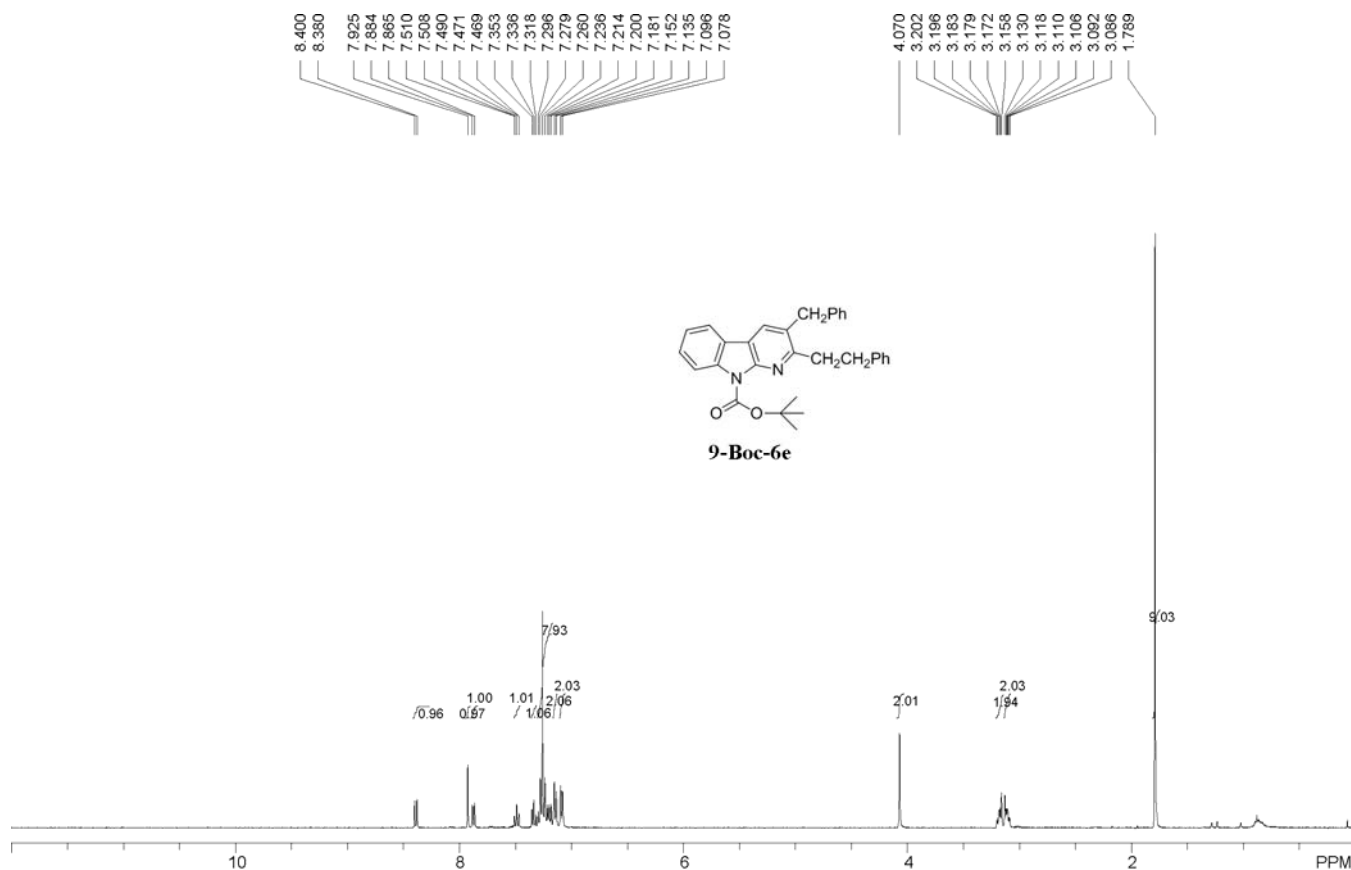


Figure 1. Molecular structure of **1-Boc-4p**, with displacement ellipsoids drawn at the 30% probability level.

Table 1 Crystallographic data and structure refinement of **1-Boc-4p**

Chemical formula	C ₂₁ H ₂₀ N ₂ O ₃
Formula weight	348.39
Temperature	293(2) K
Radiation type, wavelength	Mo K α , 0.71073 Å
Crystal system, space group	Triclinic, <i>P</i> -1
Unit cell dimensions	$a = 9.982(2)$ Å $\alpha = 64.99(3)^\circ$ $b = 10.135(2)$ Å $\beta = 67.67(3)^\circ$ $c = 11.350(2)$ Å $\gamma = 88.86(3)^\circ$
Volume	948.9(3) Å ³
Z	2
Calculated density	1.219 g/cm ³
Absorption coefficient	0.082 mm ⁻¹
F(000)	368
Crystal size	0.4 × 0.3 × 0.3 mm
Theta range for data collection	2.24° to 24.99°
Limiting indices	$-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-13 \leq l \leq 13$
Reflections collected	9093
Independent reflections	3277 [R(int) = 0.032]
Reflections observed (>2 σ)	2701
Data completeness	0.982
Theta (max)	25.0
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	3277/0/239
Goodness-of-fit on F ²	1.144
Final R indices [$I > 2\sigma(I)$]	R ₁ = 0.0667, wR ₂ = 0.2331
R indices (all data)	R ₁ = 0.0828, wR ₂ = 0.2777
Largest diff. peak and hole	0.24 and -0.26 e/Å ³

VII. Copies of ^1H and ^{13}C NMR spectra of 9-Boc-6e



VIII. X-ray Crystal Structure and data of 9-Boc-6e

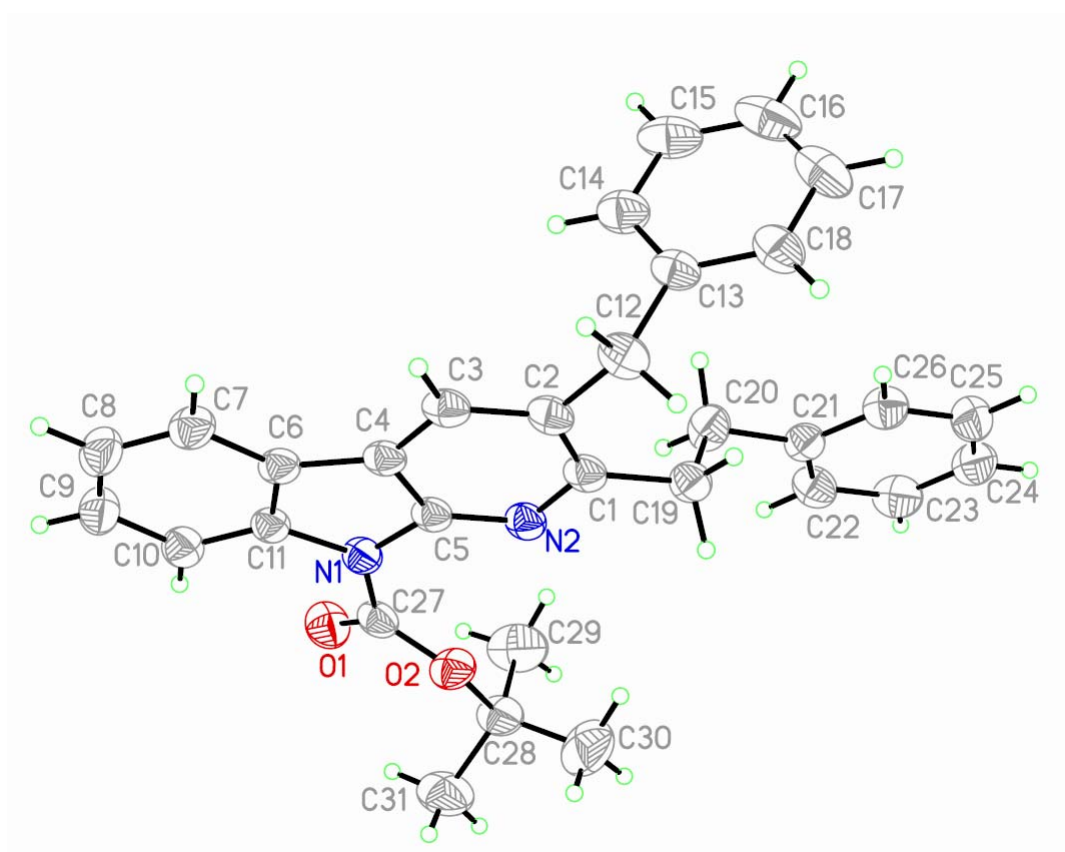
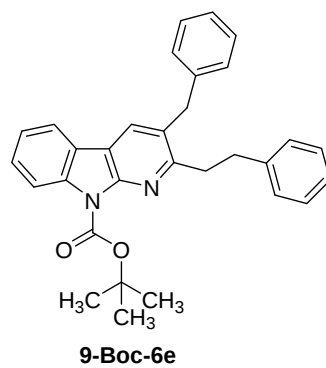


Figure 2. Molecular structure of **9-Boc-6e**, with displacement ellipsoids drawn at the 30% probability level.

Table 2 Crystallographic data and structure refinement of **9-Boc-6e**

Chemical formula	$C_{31}H_{30}N_2O_2$	
Formula weight	462.57	
Temperature	296(2) K	
Radiation type, wavelength	Mo $K\alpha$, 0.71073 Å	
Crystal system, space group	Monoclinic, $C2/c$	
Unit cell dimensions	$a = 24.847(3)$ Å	$\alpha = 90.00^\circ$
	$b = 8.6971(10)$ Å	$\beta = 111.133(2)^\circ$
	$c = 25.520(3)$ Å	$\gamma = 90.00^\circ$
Volume	$5143.9(10)$ Å ³	
Z	8	
Calculated density	1.195 g/cm ³	
Absorption coefficient	0.08 mm ⁻¹	
F(000)	1968	
Crystal size	$0.31 \times 0.25 \times 0.17$ mm	
Theta range for data collection	1.71° to 25.99°	
Limiting indices	$-30 \leq h \leq 27$, $-10 \leq k \leq 10$, $-31 \leq l \leq 29$	
Reflections collected	14529	
Independent reflections	5048 [$R(\text{int}) = 0.028$]	
Reflections observed ($>2\sigma$)	3408	
Data completeness	0.998	
Theta (max)	25.99	
Absorption correction	Multi-scan	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	5048/30/320	
Goodness-of-fit on F^2	1.009	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0405$, $wR_2 = 0.0981$	
R indices (all data)	$R_1 = 0.0693$, $wR_2 = 0.1132$	
Largest diff. peak and hole	0.16 and -0.11 e/Å ³	