

Synthesis of 3-Hydroxy-9*H*-fluorene-2-carboxylates via Michael reaction, Robinson annulation and Aromatization

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Supplementary Materials

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Table S1 Crystal data of **2a**

Empirical formula	C ₂₂ H ₂₀ O ₃		
Formula weight	332.38		
Crystal system	Monoclinic		
Space group	P2 ₁ /c		
Unit cell dimensions	a = 14.0692(15) Å	α= 90°.	
	b = 7.0376(6) Å	β= 91.234(8)°	
	c = 17.1586(13) Å	γ = 90°.	
Volume	1698.5(3) Å ³		
Z	4		
F(000)	704		
Density (calculated)	1.300 Mg/m ³		
Wavelength	0.71073 Å		
Cell parameters reflections used	4483		
Theta range for Cell parameters	4.3740 to 29.4510°.		
Absorption coefficient	0.085 mm ⁻¹		
Temperature	100(2) K		
Crystal size	0.25 x 0.20 x 0.15 mm ³		
Data collection			
Diffractometer	Xcalibur, Atlas, Gemini		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	1.00000 and 0.85961		
No. of measured reflections	12742		
No. of independent reflections	3887 [R(int) = 0.0395]		
No. of observed [I>2_igma(I)]	2995		
Completeness to theta = 25.242°	99.8 %		
Theta range for data collection	3.129 to 27.494°.		
Refinement			
Final R indices [I>2sigma(I)]	R1 = 0.0470, wR2 = 0.1341		
R indices (all data)	R1 = 0.0636, wR2 = 0.1551		
Goodness-of-fit on F ²	1.022		
No. of reflections	3887		
No. of parameters	226		
No. of restraints	0		
Largest diff. peak and hole	0.228 and -0.259 e.Å ⁻³		

Table S2 Summary of Oxidation study of **2a** and **3a**¹

entry	Substrate/oxidant	conditions	Yield of 4a
1	2a / H ₂ O ₂ (2 eq)	THF/refluxing/24 h	trace
2	2a / MnO ₂ (2 eq)	THF/refluxing/rt	mixture
3	2a / O ₂ (1 atm)	<i>t</i> -BuOK(1 eq)/dioxane/80 °C/24 h	36%
4	3a / O ₂ (1 atm)	<i>t</i> -BuOK(1 eq)/dioxane/80 °C/24 h	8%
5	3a /DDQ (1.1 eq)	dioxane/100 °C/3 h	13%
6	3a /DDQ (1.1 eq)	H ₂ SO ₄ (0.3 eq)/ dioxane/100 °C/3 h	100%
7	2a /DDQ (1.1 eq)	H ₂ SO ₄ (0.3 eq)/ dioxane/100 °C/3 h	50%

¹ Substrate **2a** or **3a** (20 mg, 0.06 mmol)

Figure S1 ^1H NMR and ^{13}C NMR spectra of **4a**

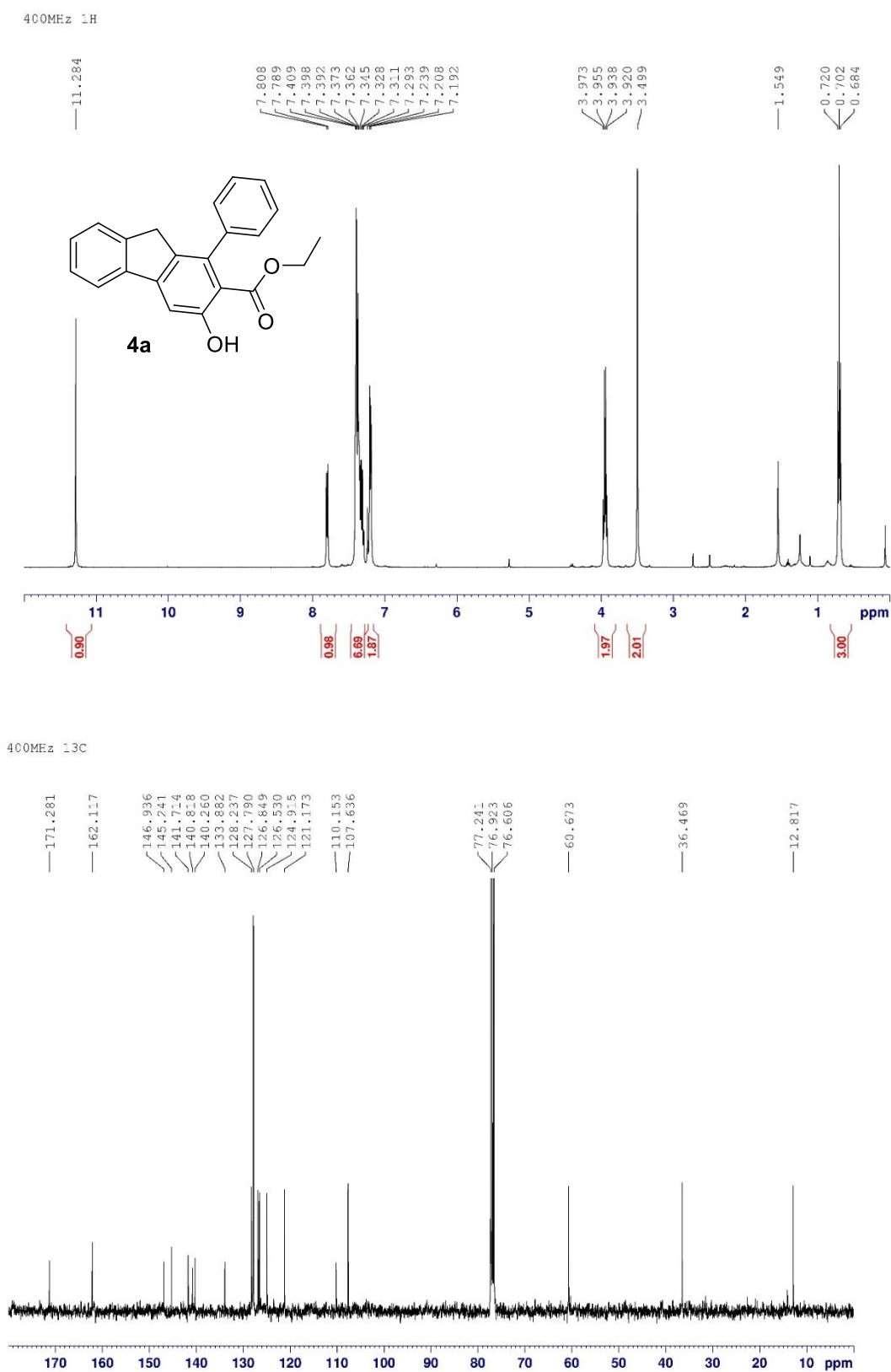


Figure S2 ^1H NMR and ^{13}C NMR spectra of **4b**

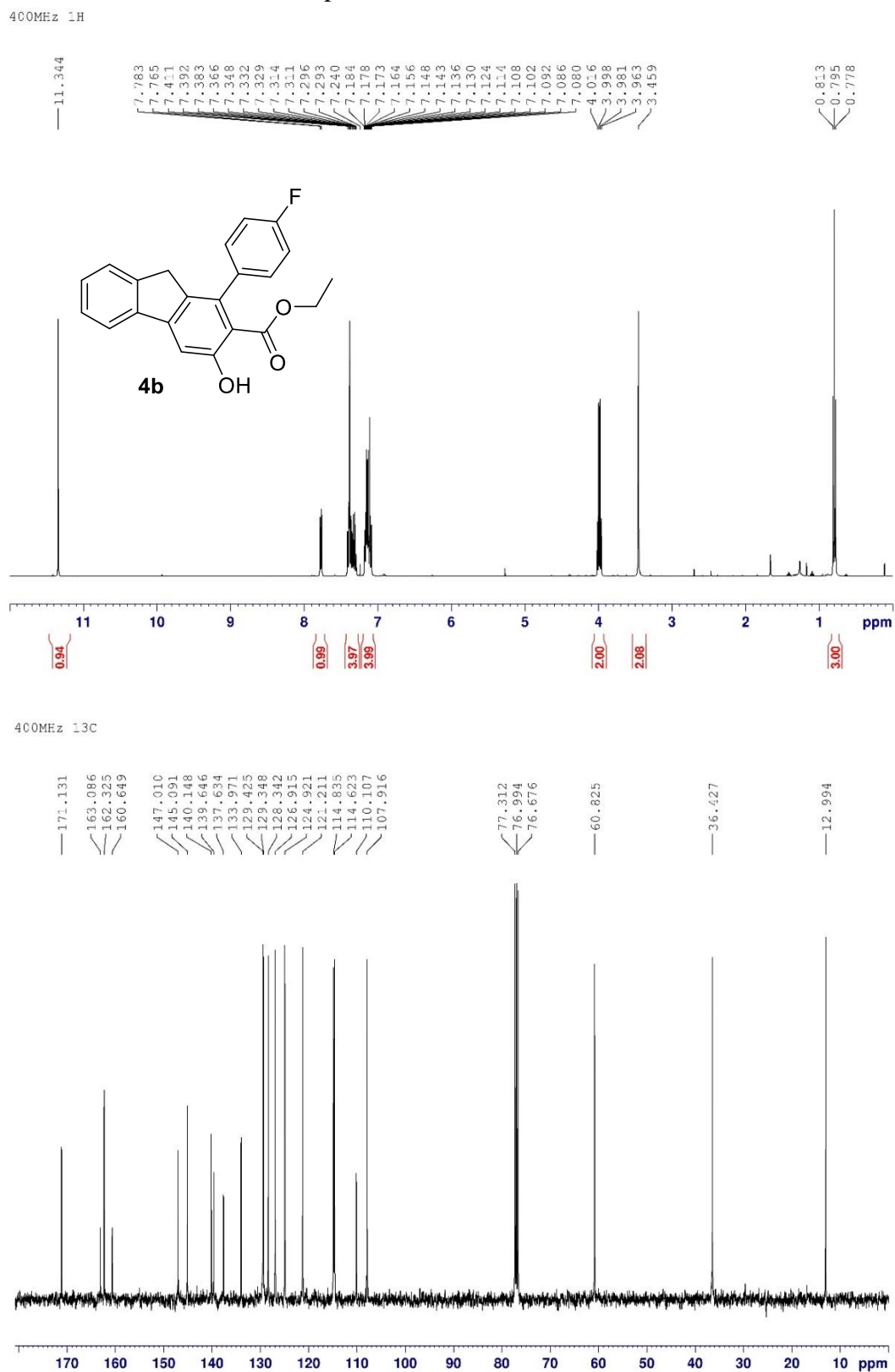


Figure S3 ^1H NMR and ^{13}C NMR spectra of **4c**

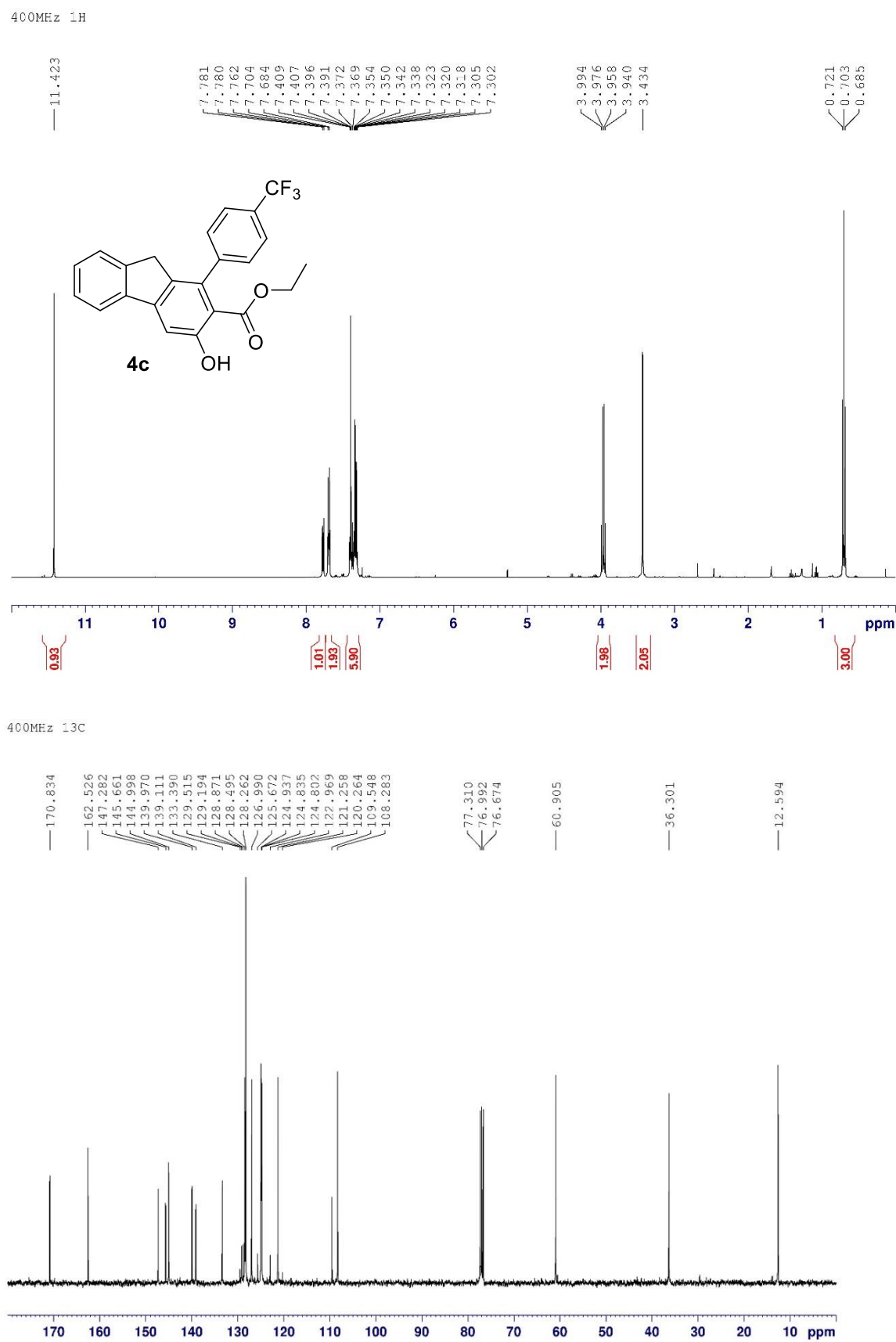


Figure S4 ^1H NMR and ^{13}C NMR spectra of **4d**

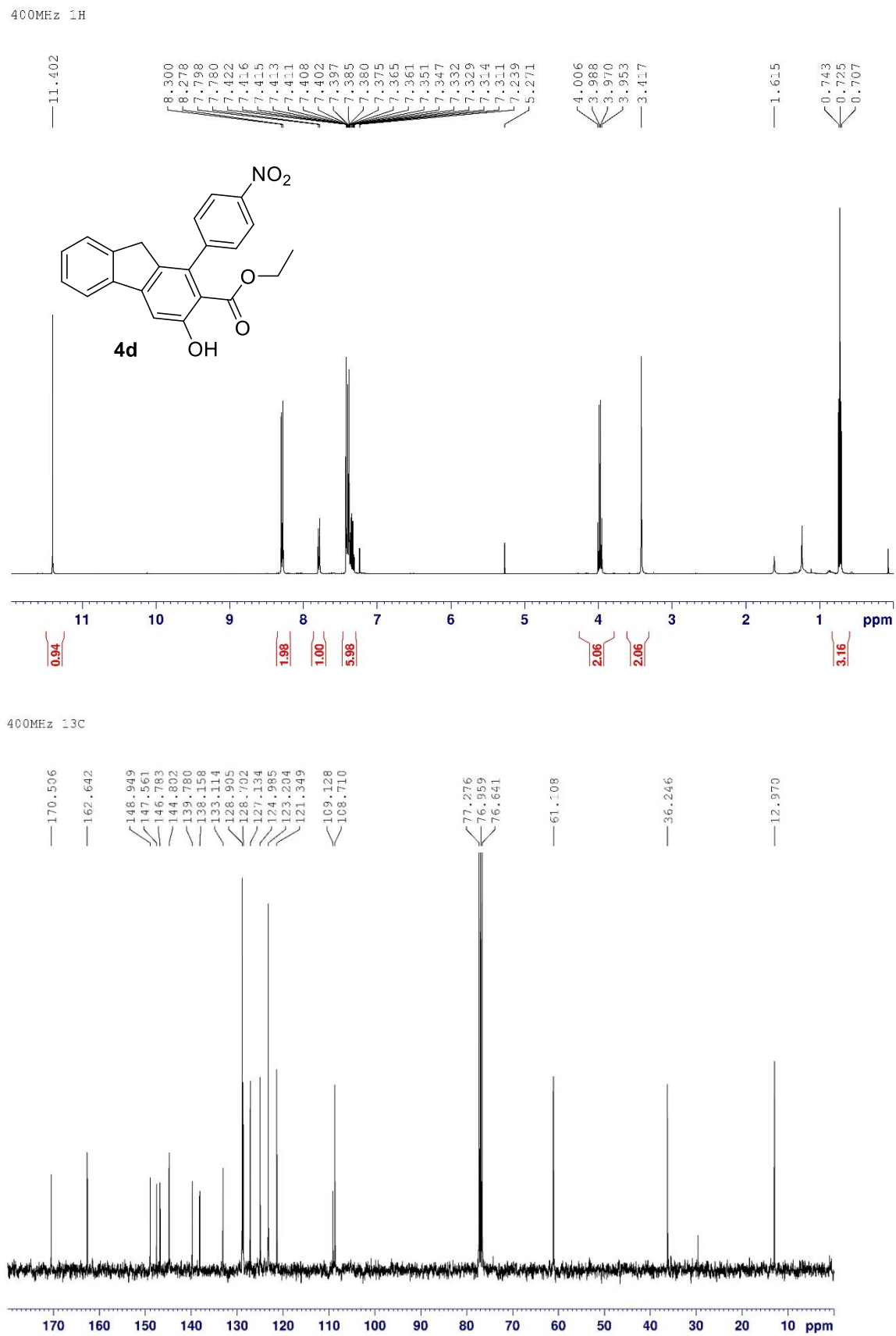


Figure S5 ^1H NMR and ^{13}C NMR spectra of **4e**

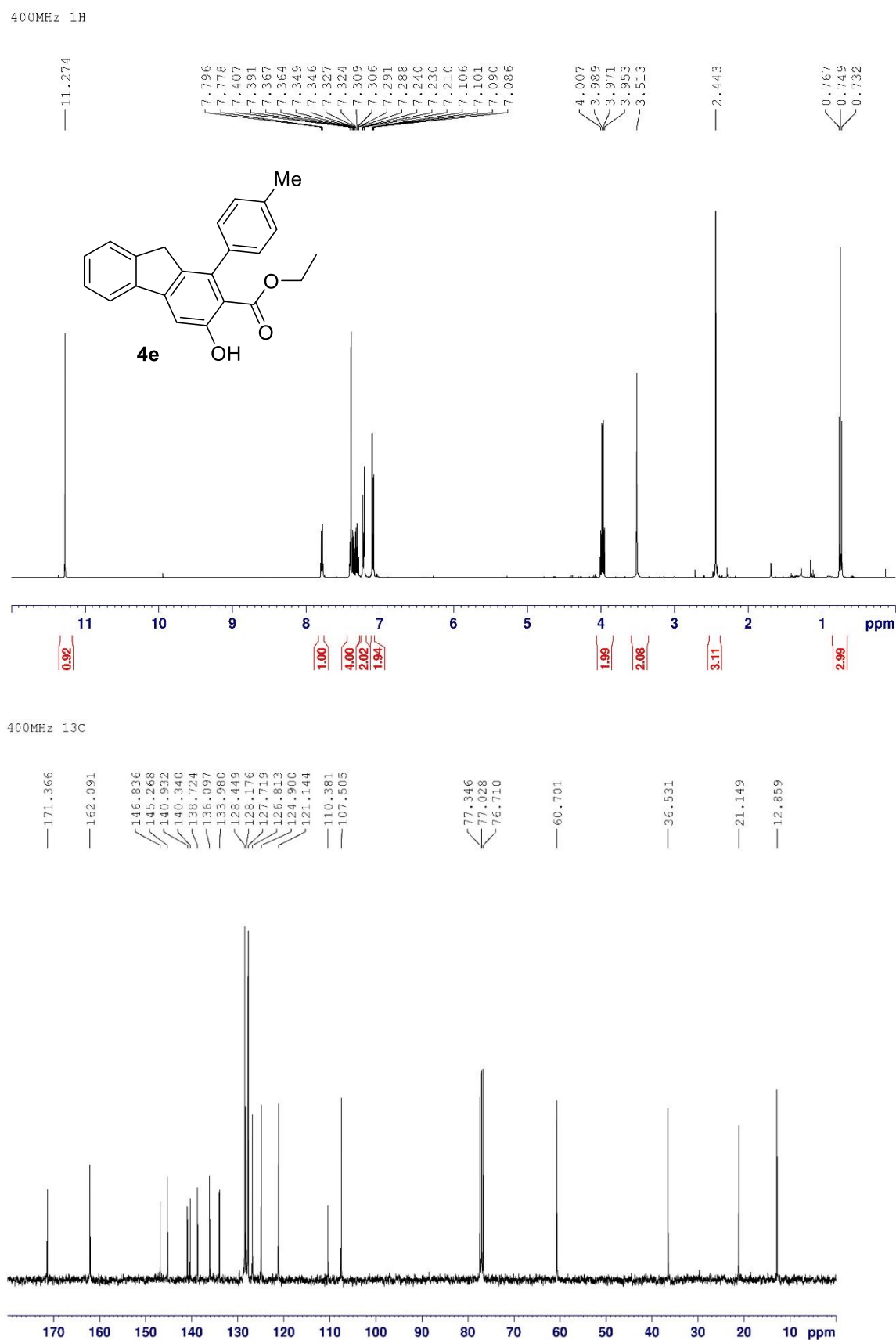


Figure S6 ^1H NMR and ^{13}C NMR spectra of **4f**

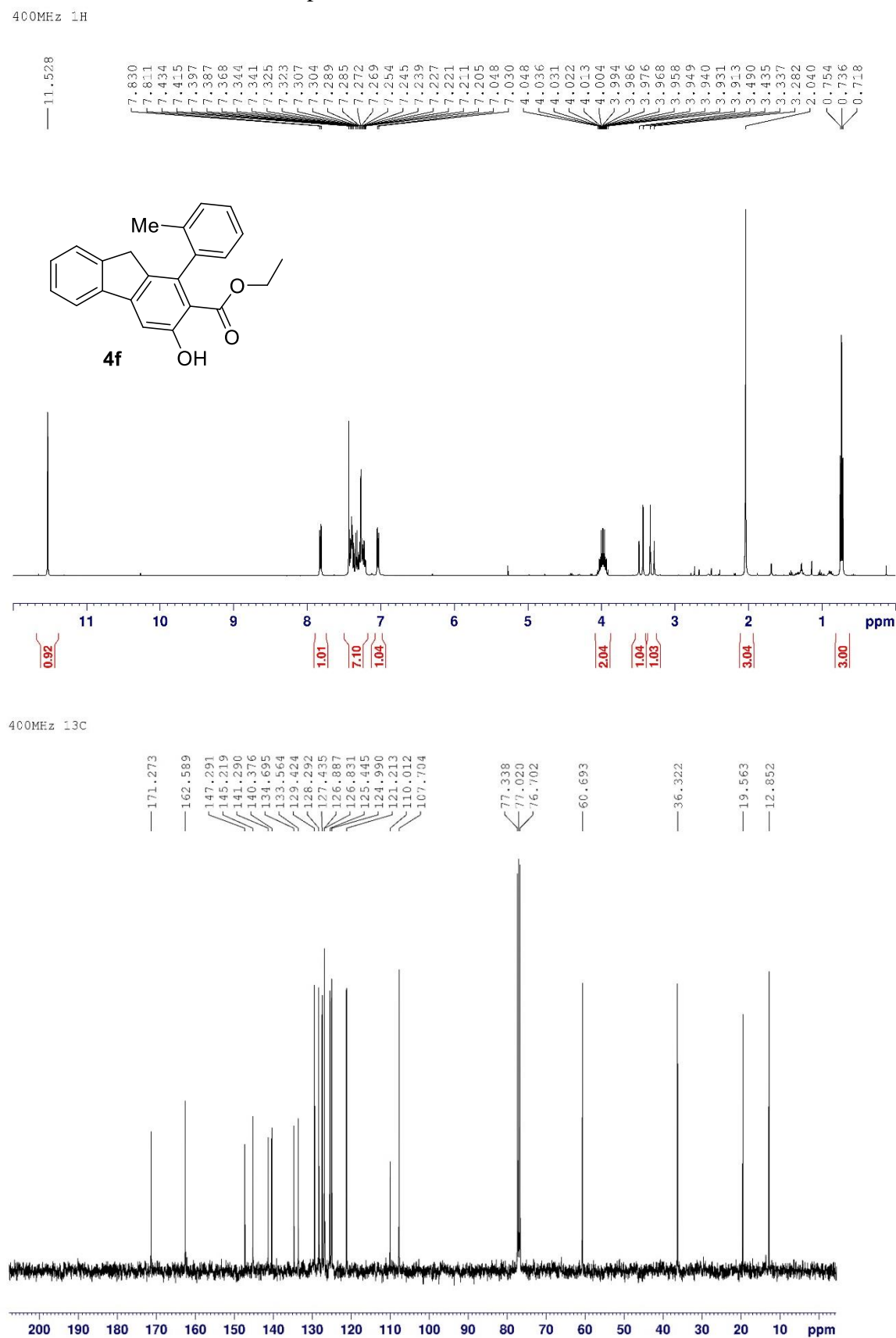


Figure S7 ^1H NMR and ^{13}C NMR spectra of **4g**

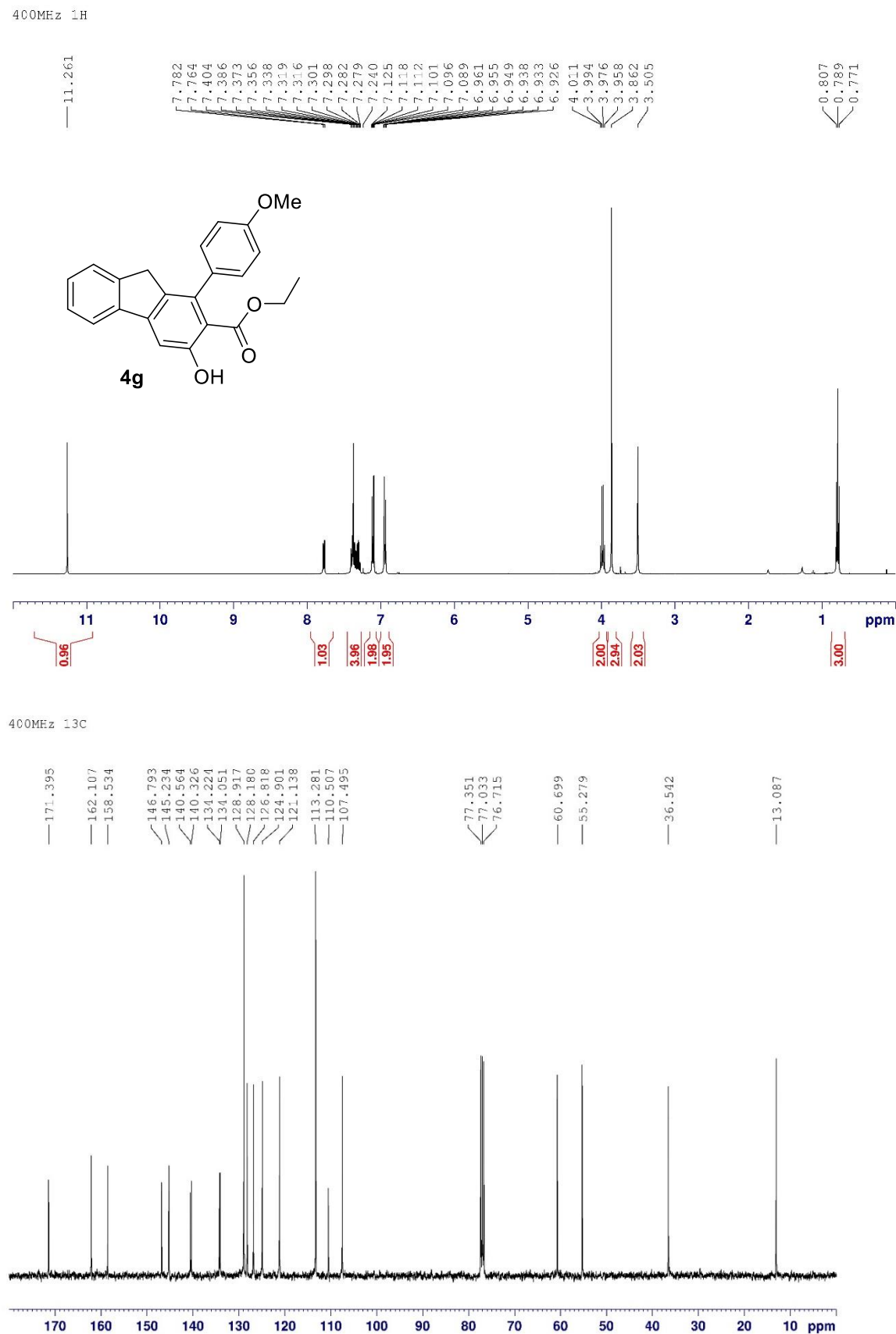
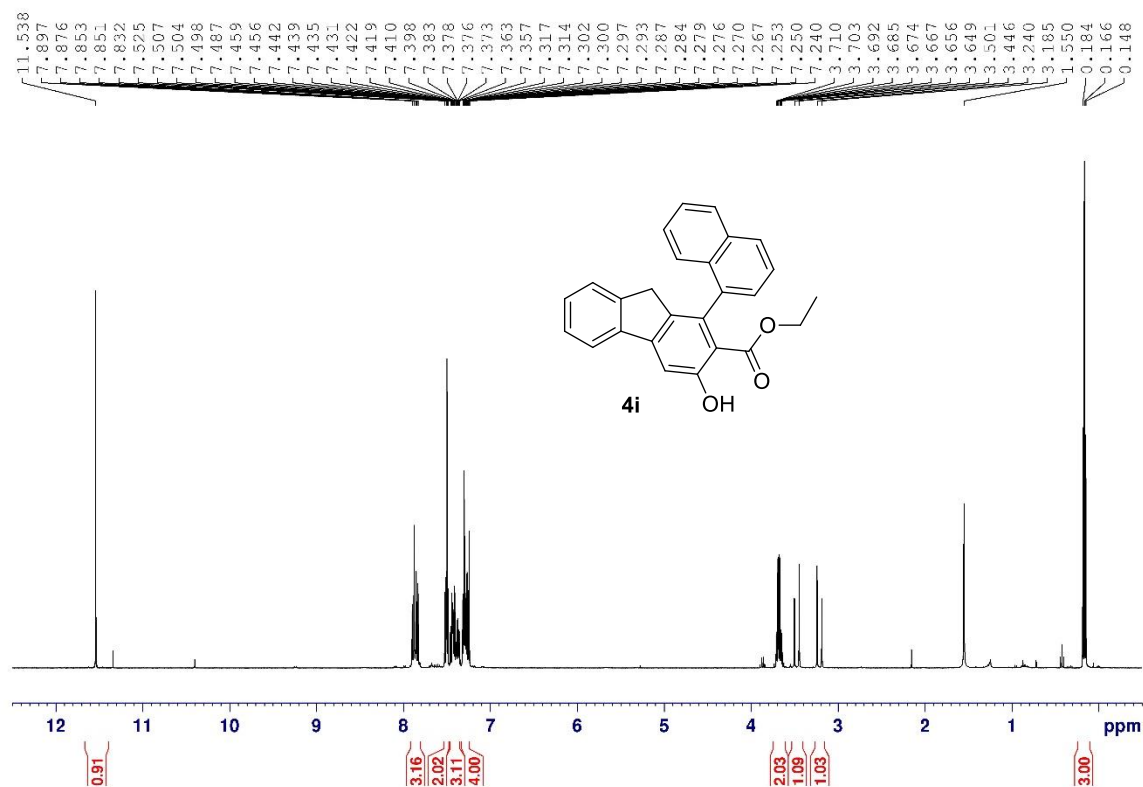


Figure S8 ^1H NMR and ^{13}C NMR spectra of **4i**

400MHz ^1H



400MHz ^{13}C

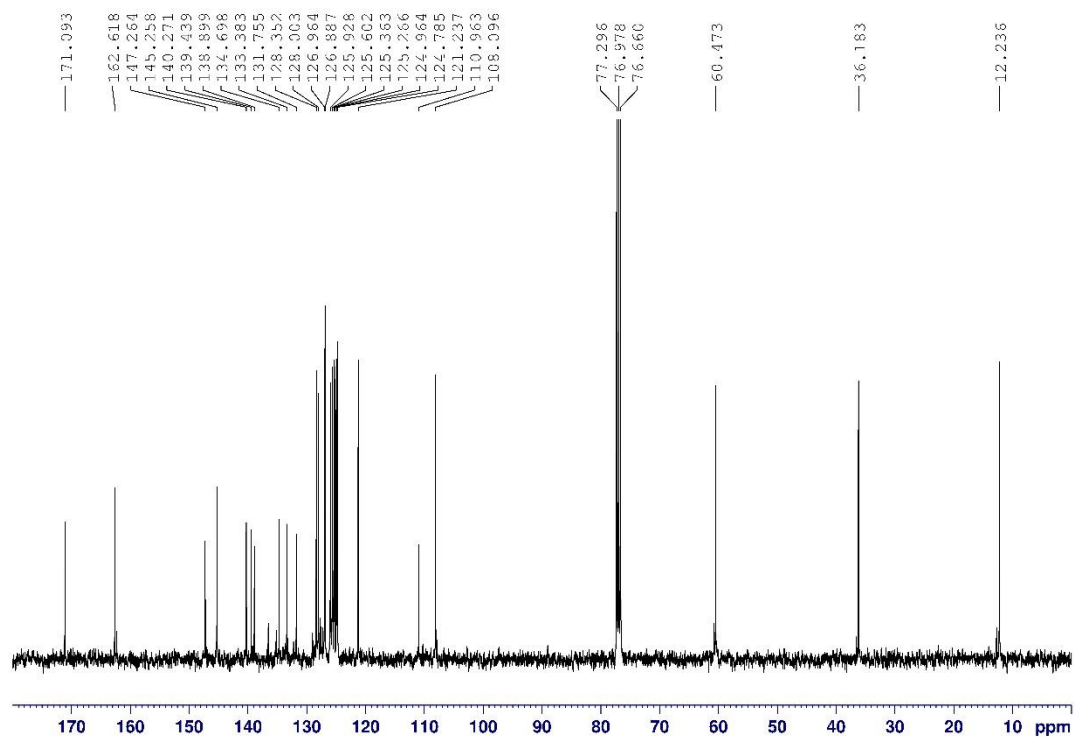


Figure S9 ^1H NMR and ^{13}C NMR spectra of **4j**

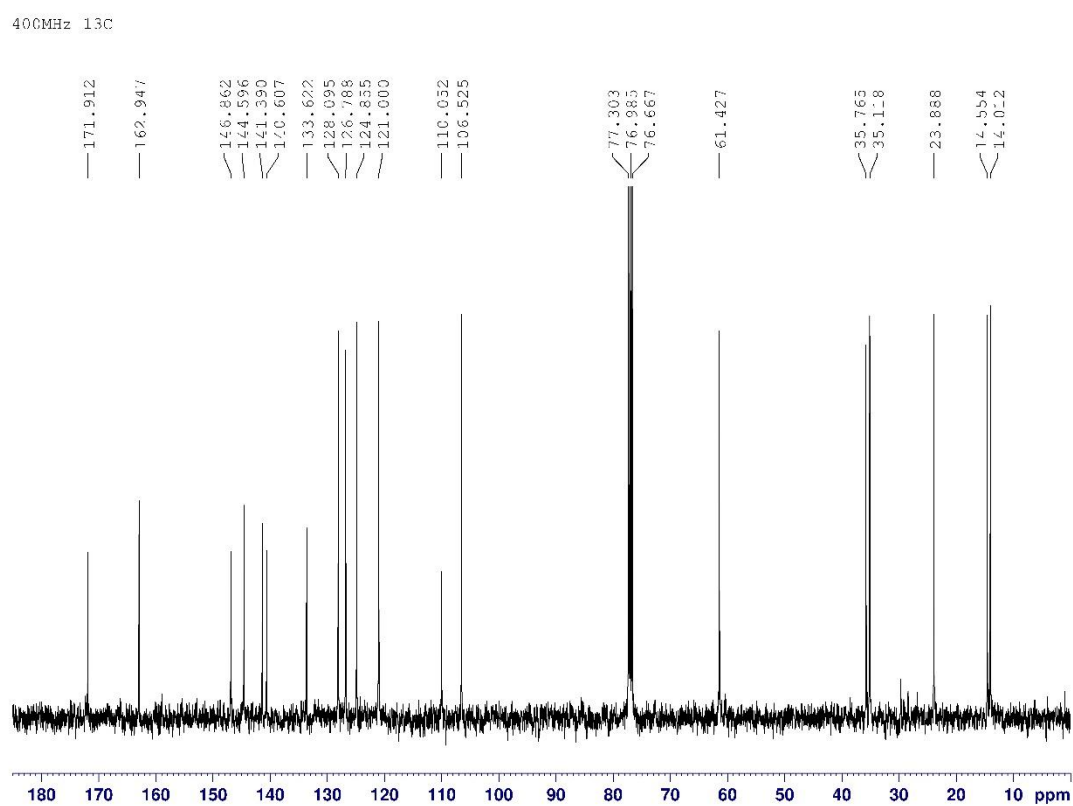
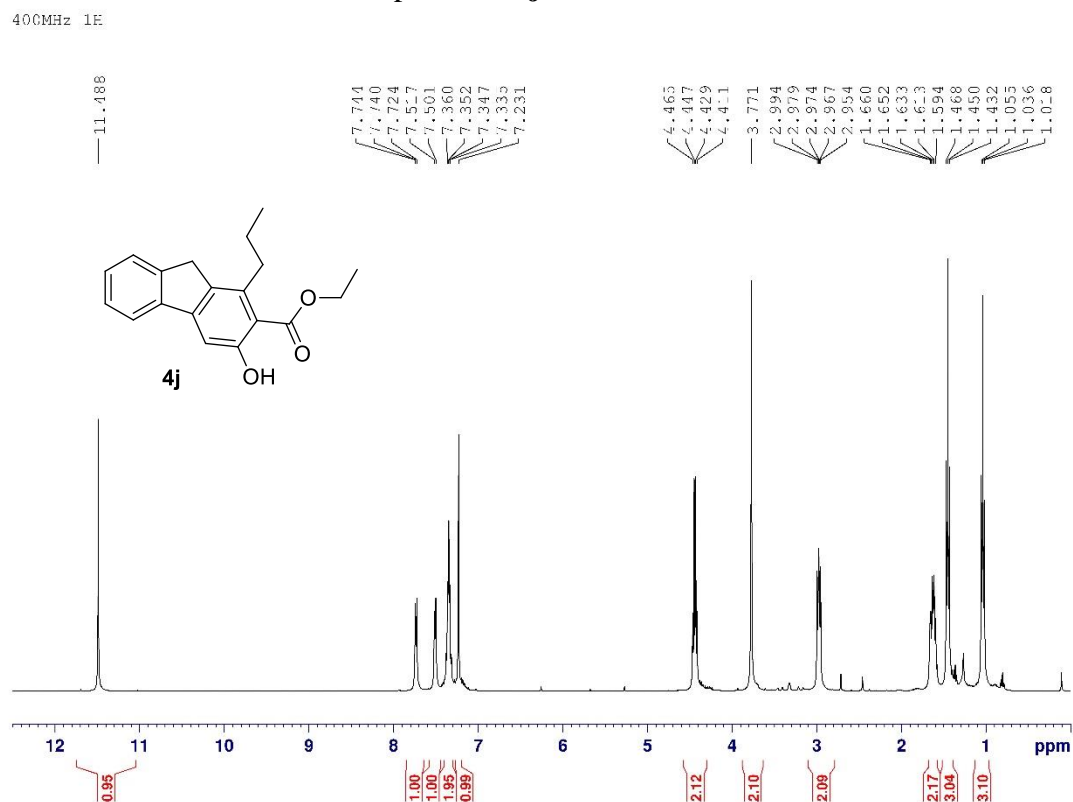


Figure S10 ^1H NMR and ^{13}C NMR spectra of **4k**

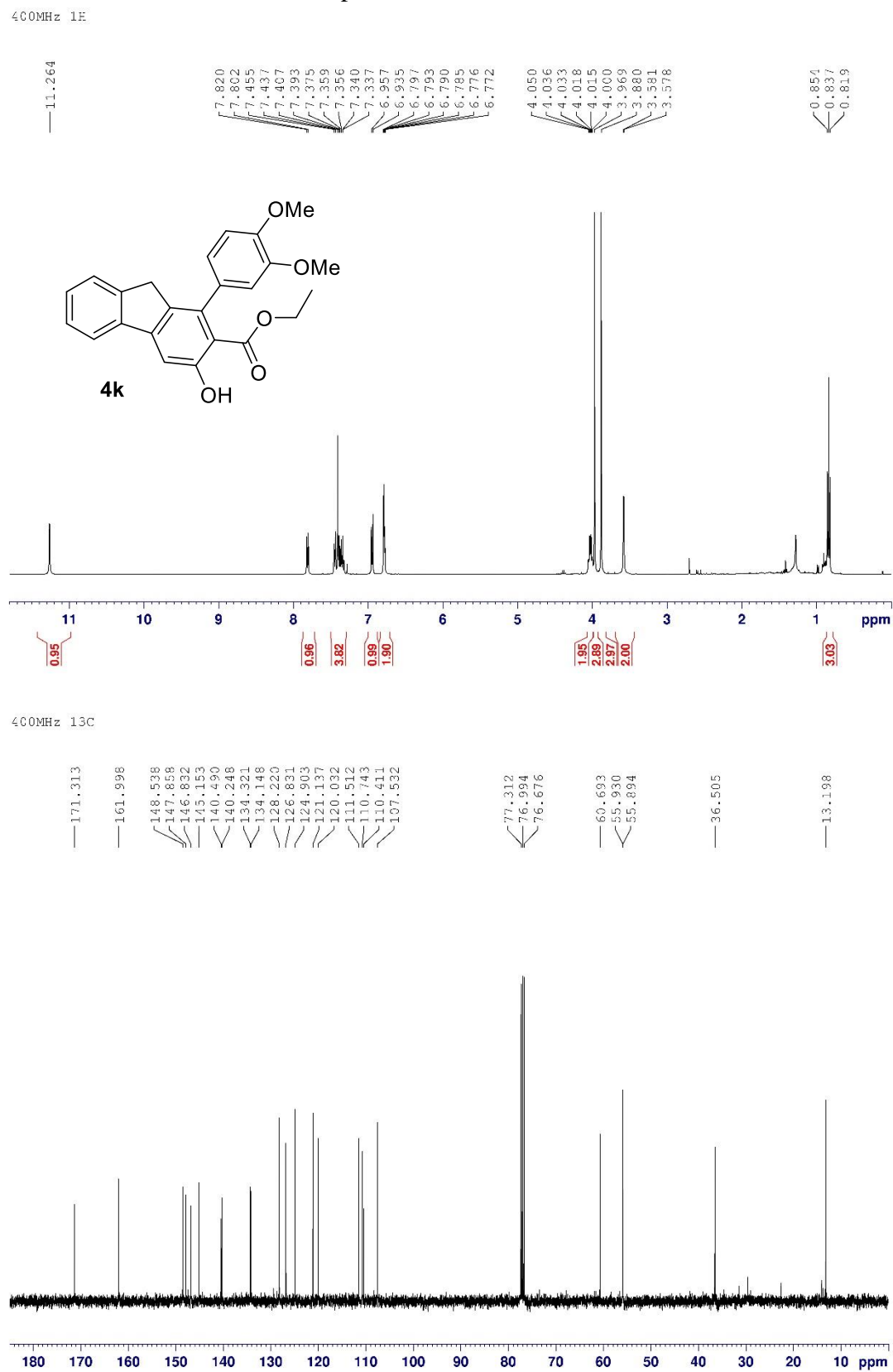


Figure S11 ^1H NMR and ^{13}C NMR spectra of **4I**

