

Supporting Information
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Supporting Information

Pd-Catalyzed C–H Benzannulation of Functionalized Furans and Pyrroles with Alkynes

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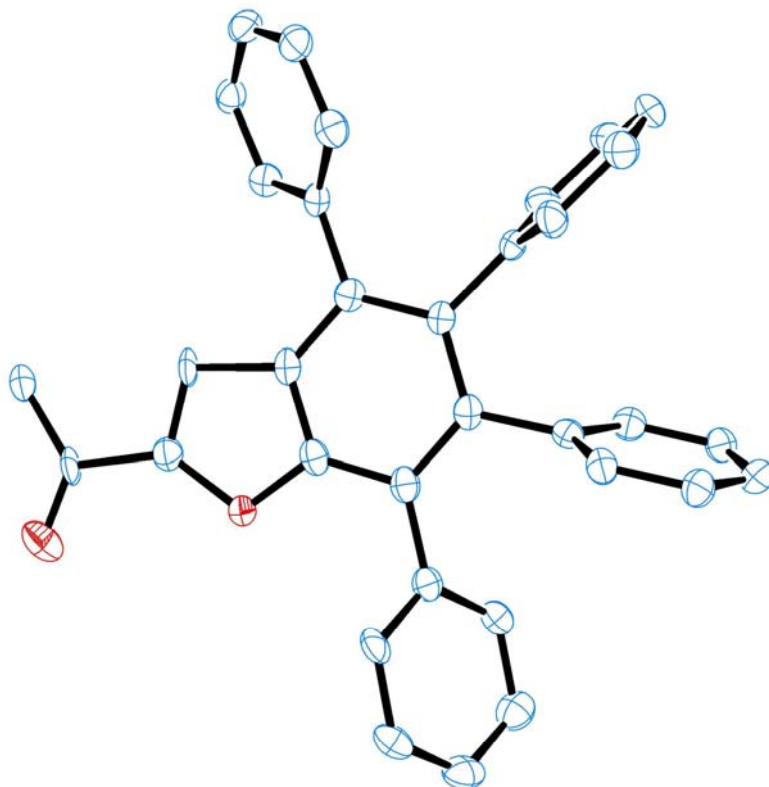
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I. X-ray Crystal Data for Compound **8**

Figure S1. ORTEP diagram of **8** with anisotropic displacement parameters at 50% probability



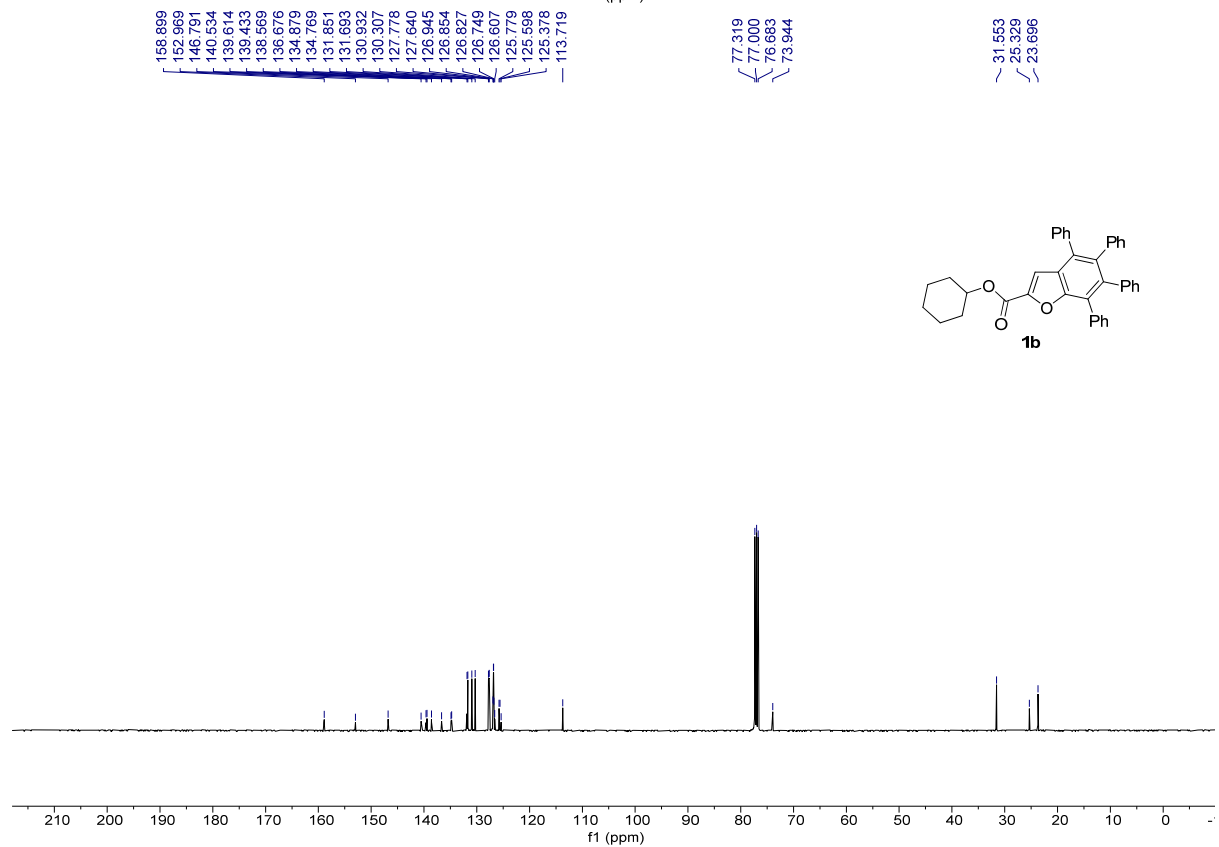
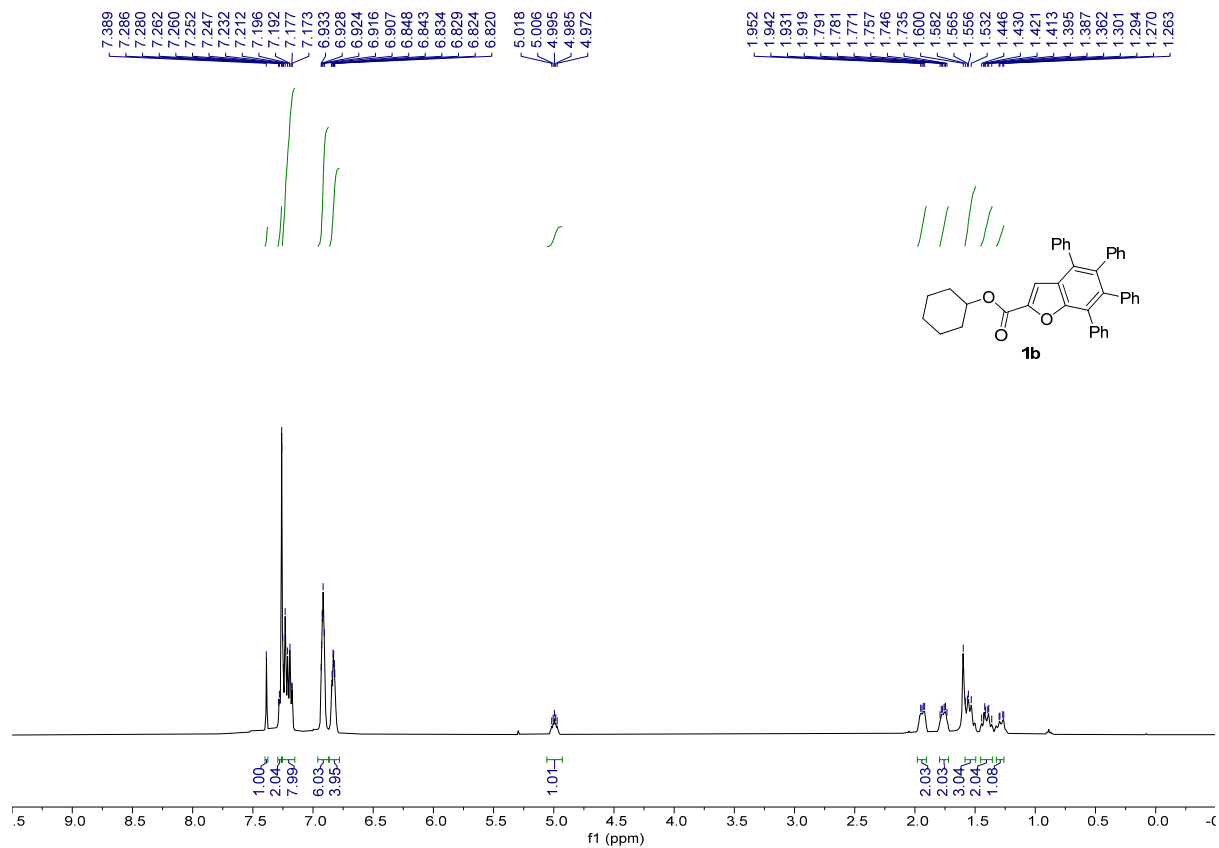
X-ray Structural Analyses. The diffraction data of **8** were collected on a Bruker X8 APEX instrument. The data were collected with graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). Cell parameters were determined and refined by the APEX2 program. CCDC No. 2065316 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

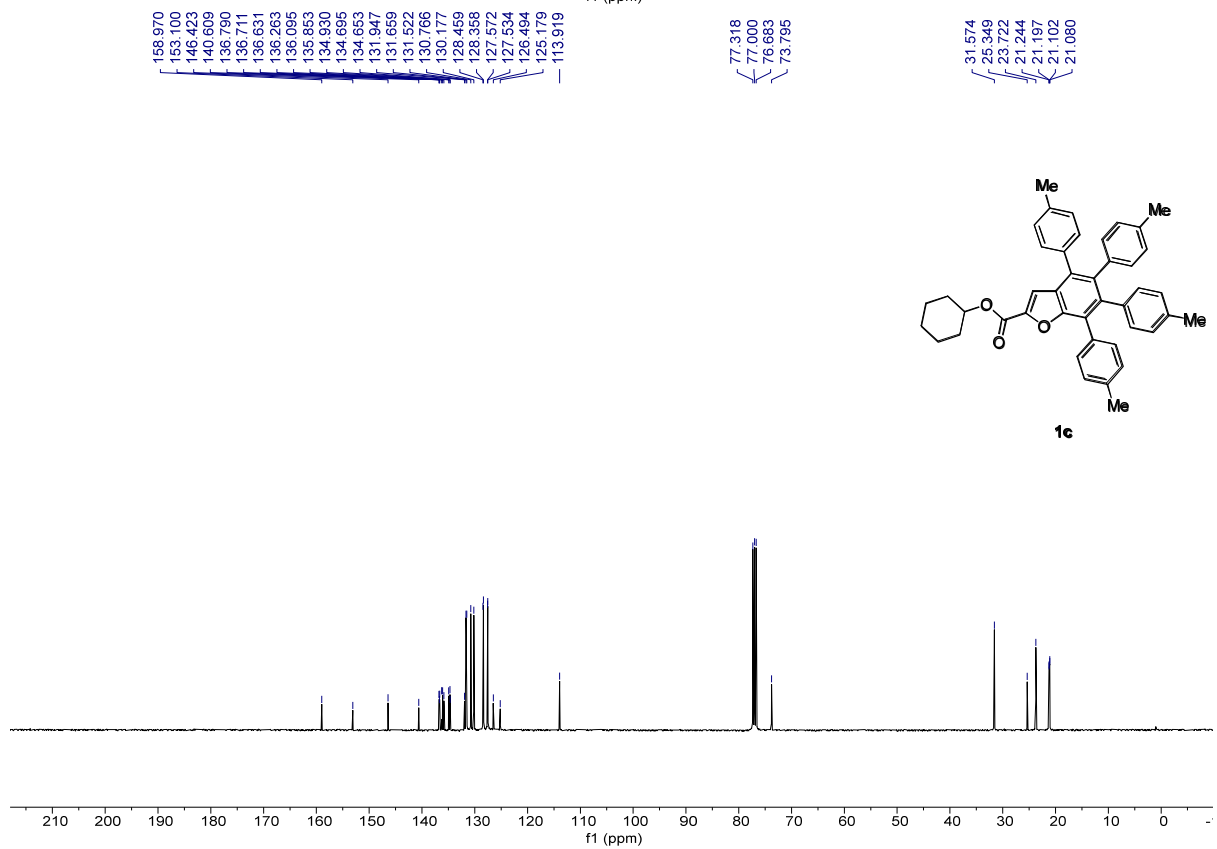
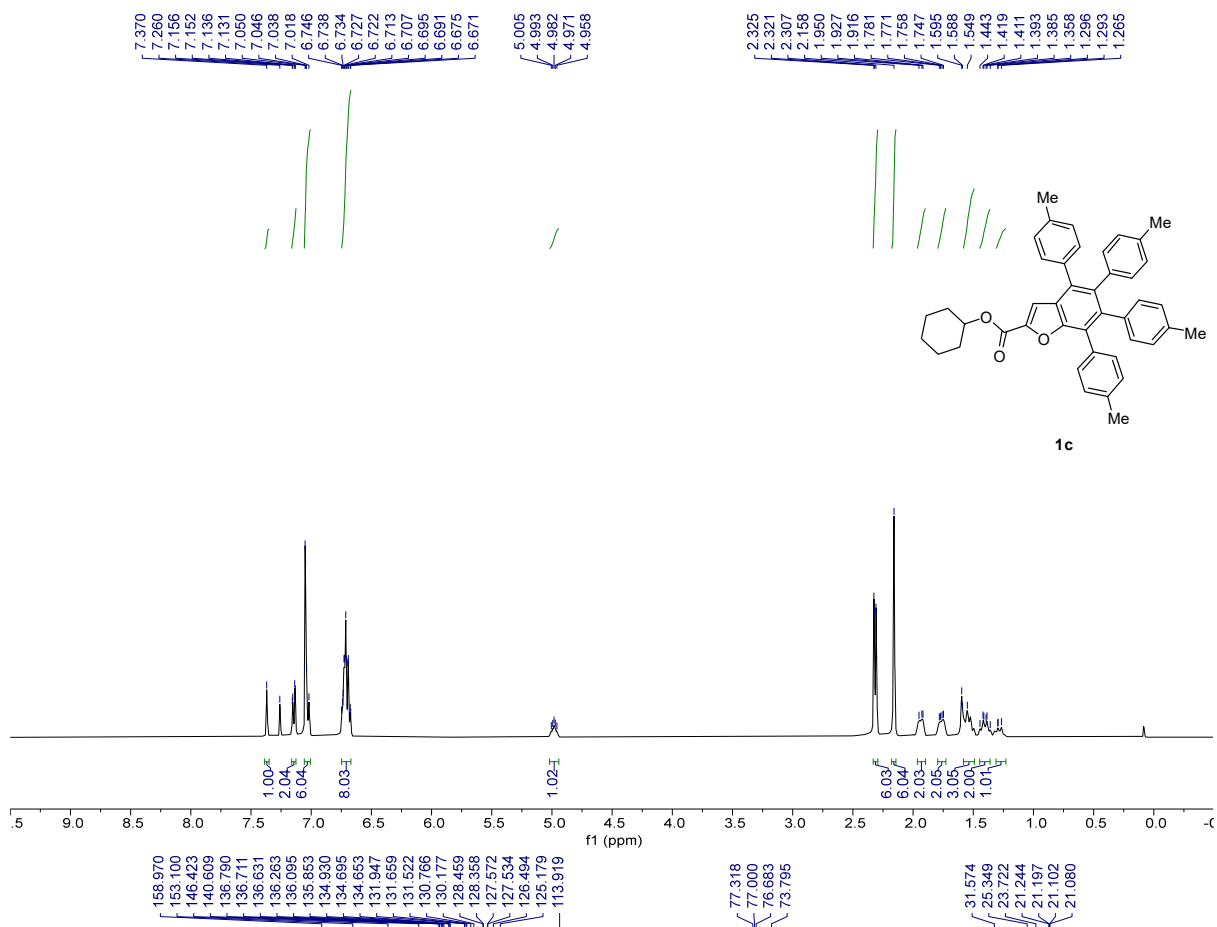
Table S1. Crystal data and experimental details for compound **8**.

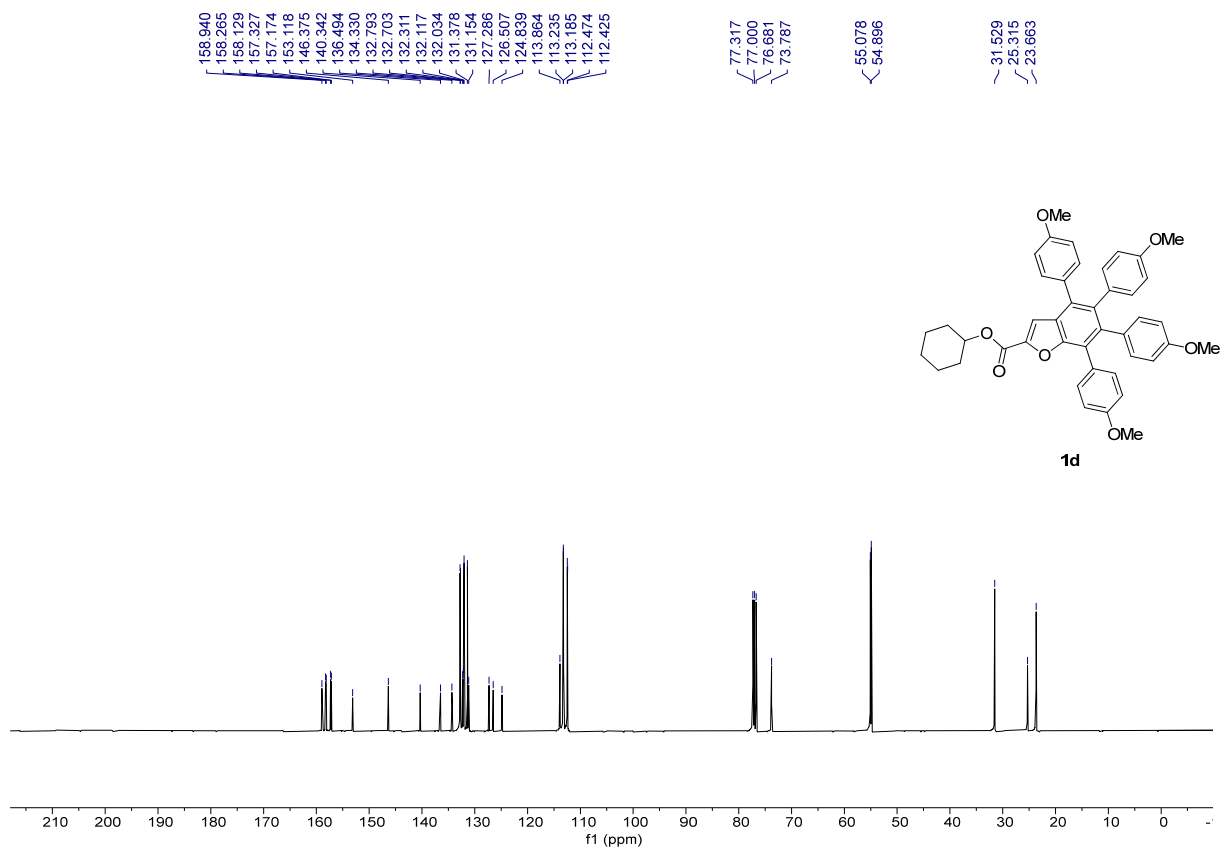
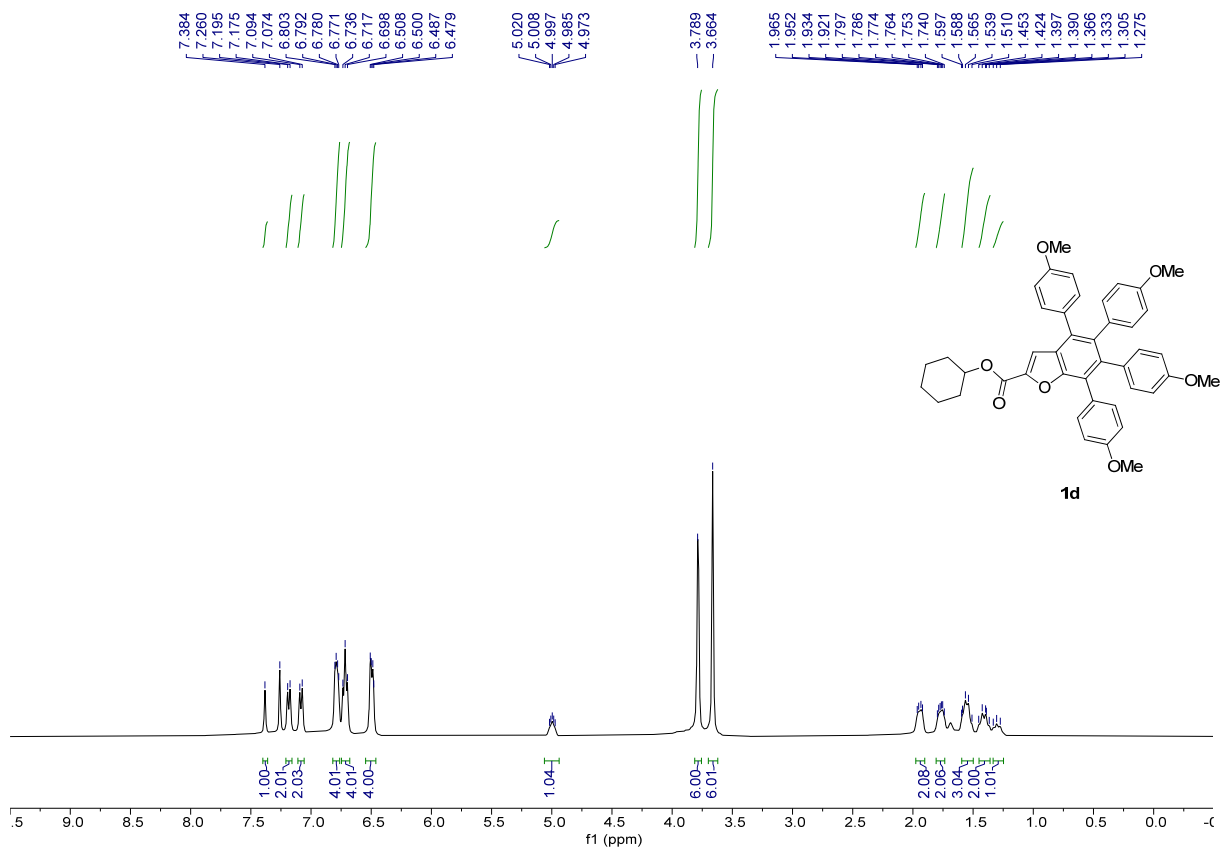
Identification code	CCDC 2065316	
Empirical formula	C ₃₄ H ₂₄ O ₂	
Formula weight	464.53	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 15.2843(8) Å	$\alpha = 90^\circ$.
	b = 18.7694(10) Å	$\beta = 124.143(2)^\circ$.

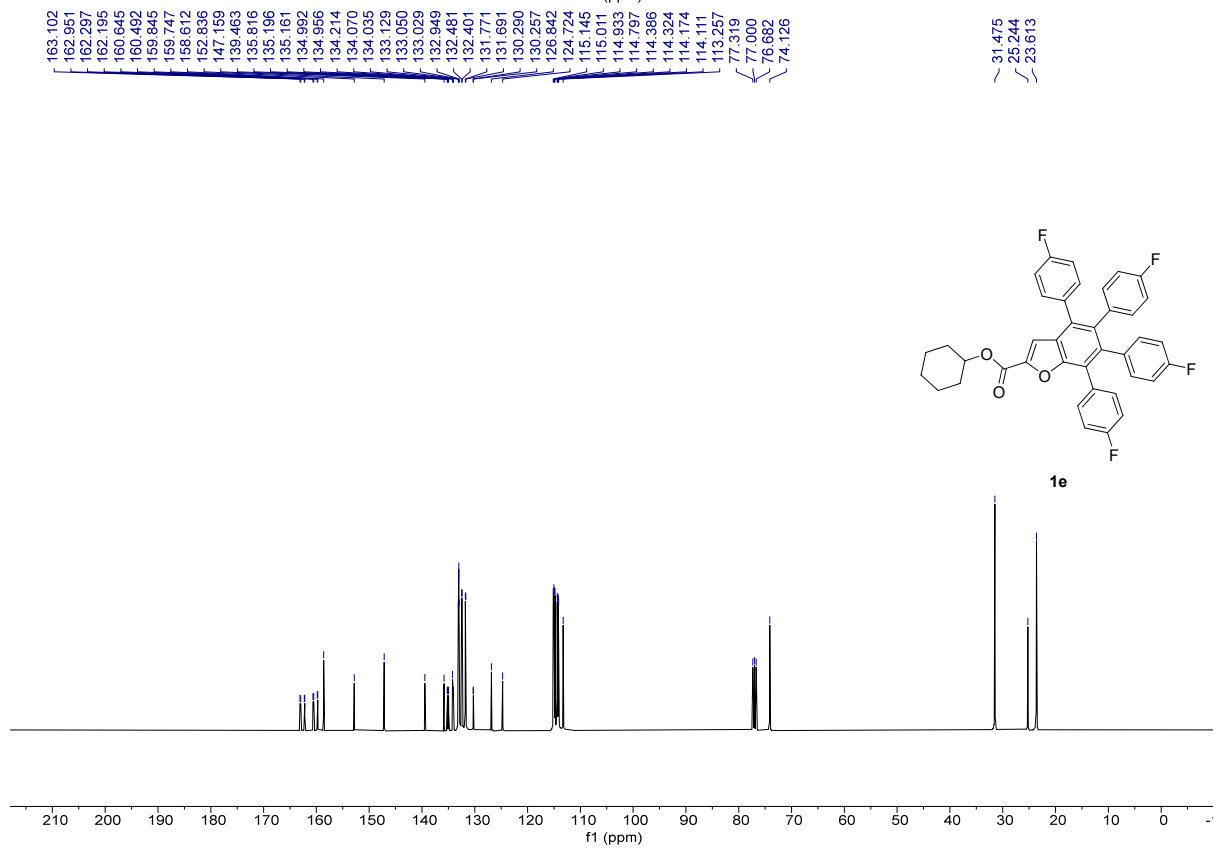
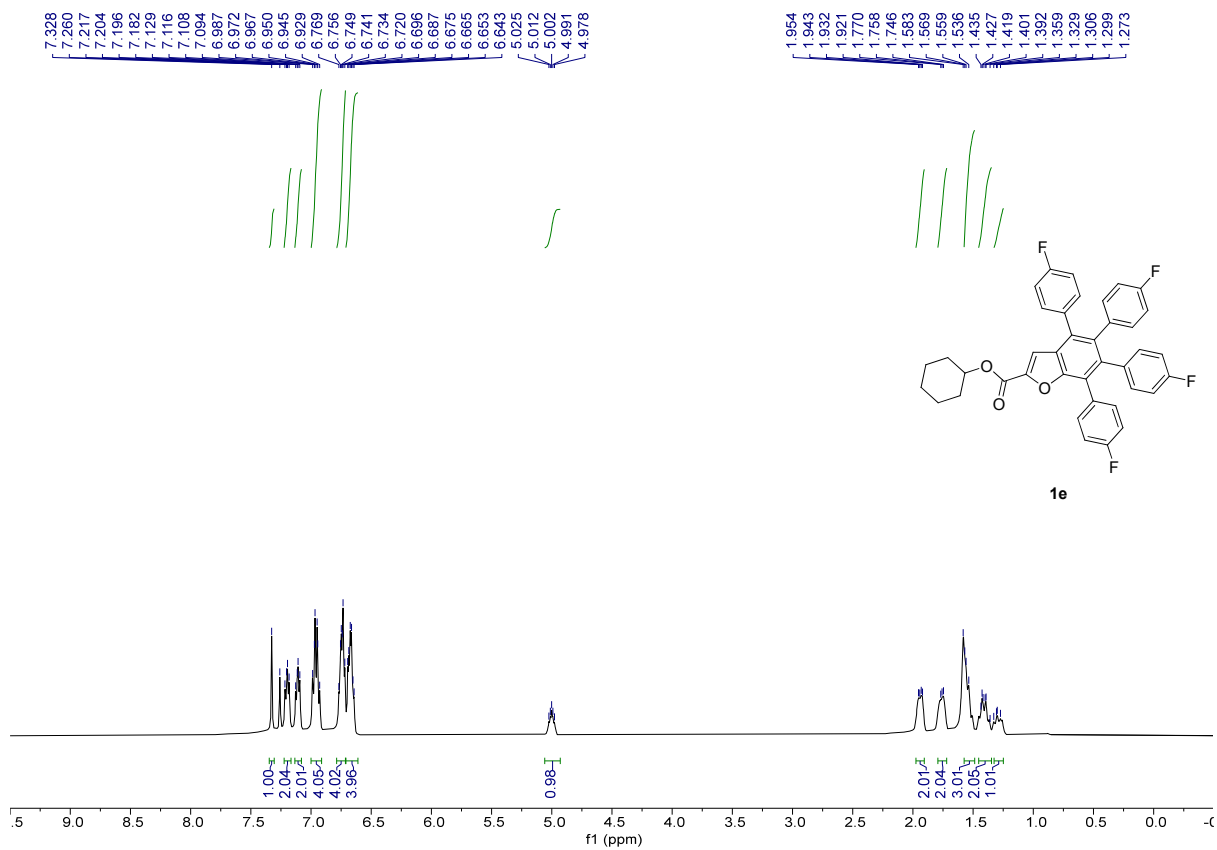
	$c = 10.0802(5) \text{ \AA}$	$\gamma = 90^\circ$.
Volume	$2393.4(2) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.289 Mg/m^3	
Absorption coefficient	0.079 mm^{-1}	
F(000)	976	
Crystal size	$0.15 \times 0.06 \times 0.05 \text{ mm}^3$	
Theta range for data collection	1.941 to 26.399°.	
Index ranges	$-16 \leq h \leq 19, -17 \leq k \leq 23, -12 \leq l \leq 12$	
Reflections collected	10688	
Independent reflections	4553 [R(int) = 0.0210]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7454 and 0.7109	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4553 / 498 / 375	
Goodness-of-fit on F ²	1.044	
Final R indices [I > 2σ(I)]	R1 = 0.0341, wR2 = 0.0824	
R indices (all data)	R1 = 0.0399, wR2 = 0.0864	
Absolute structure parameter	0(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.186 and -0.200 e.Å ⁻³	

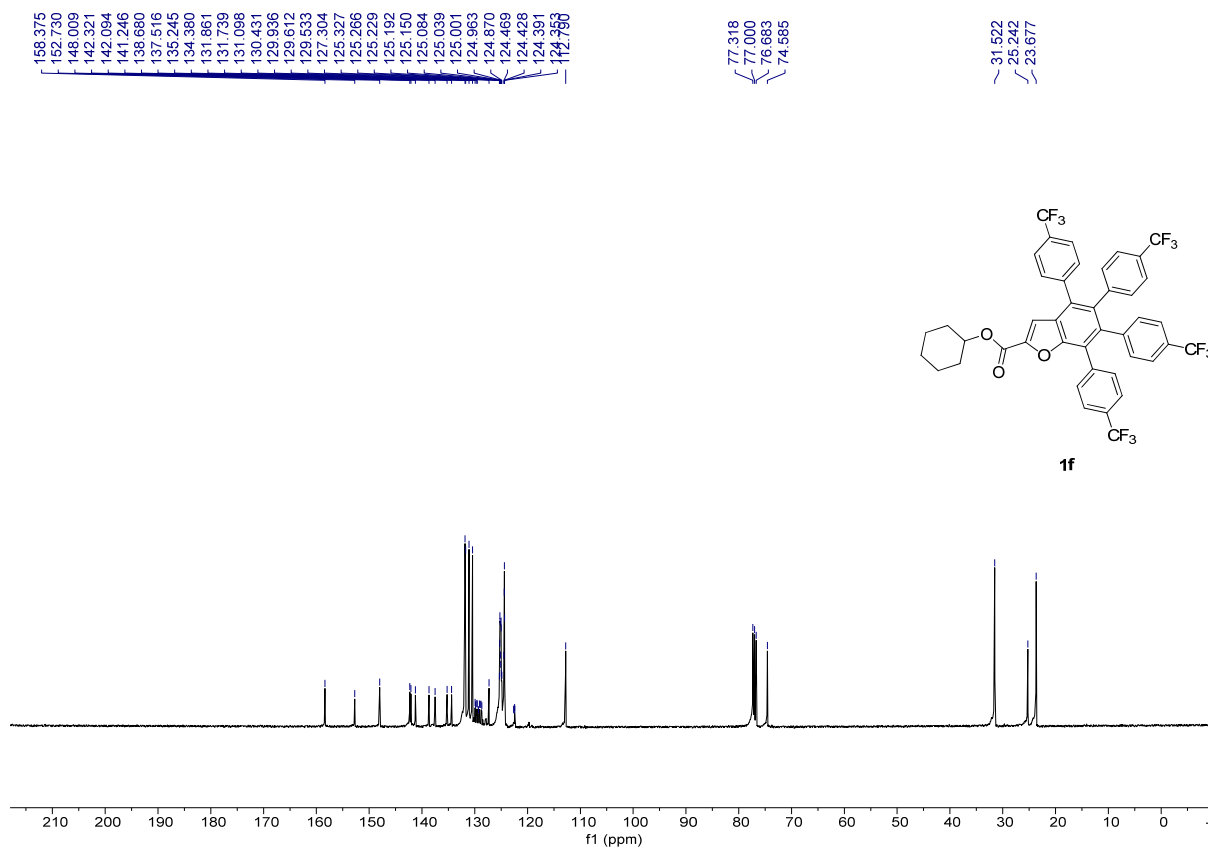
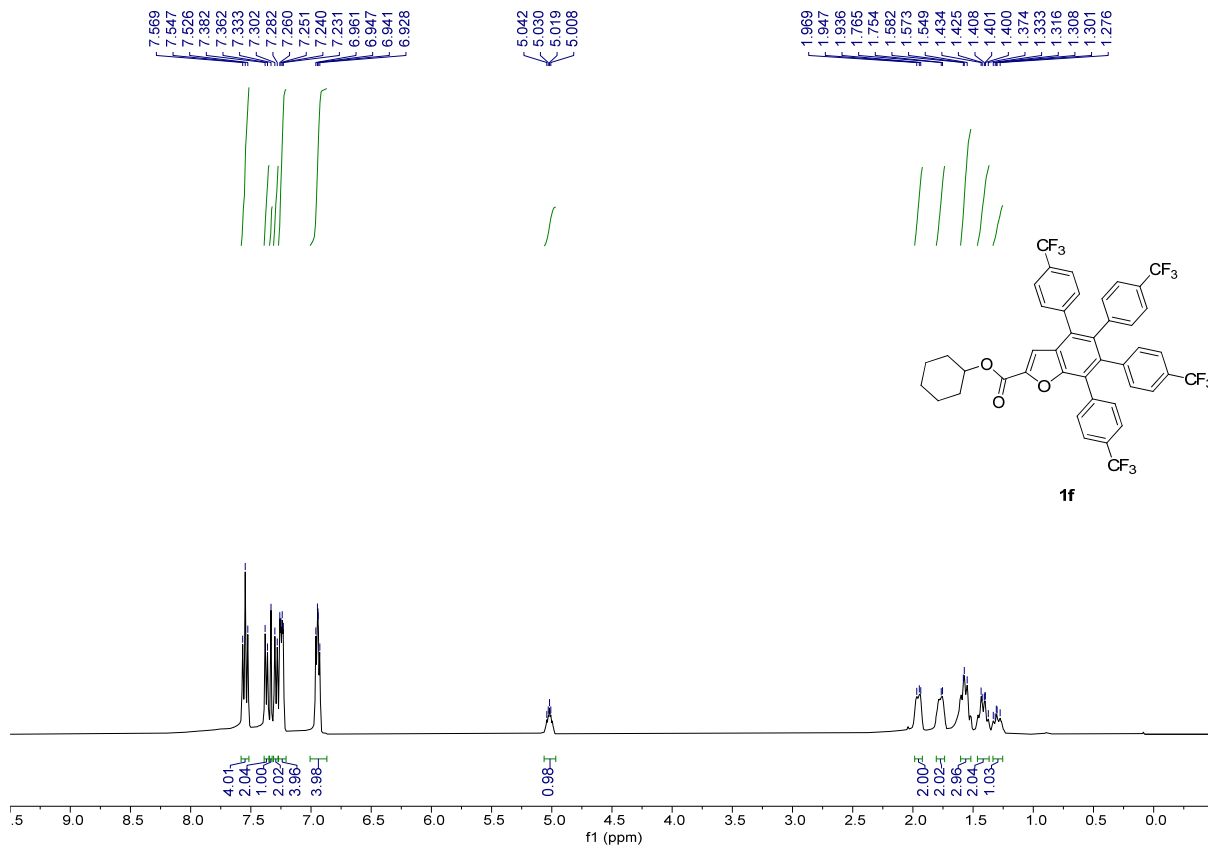
II. ¹H and ¹³C NMR Spectra

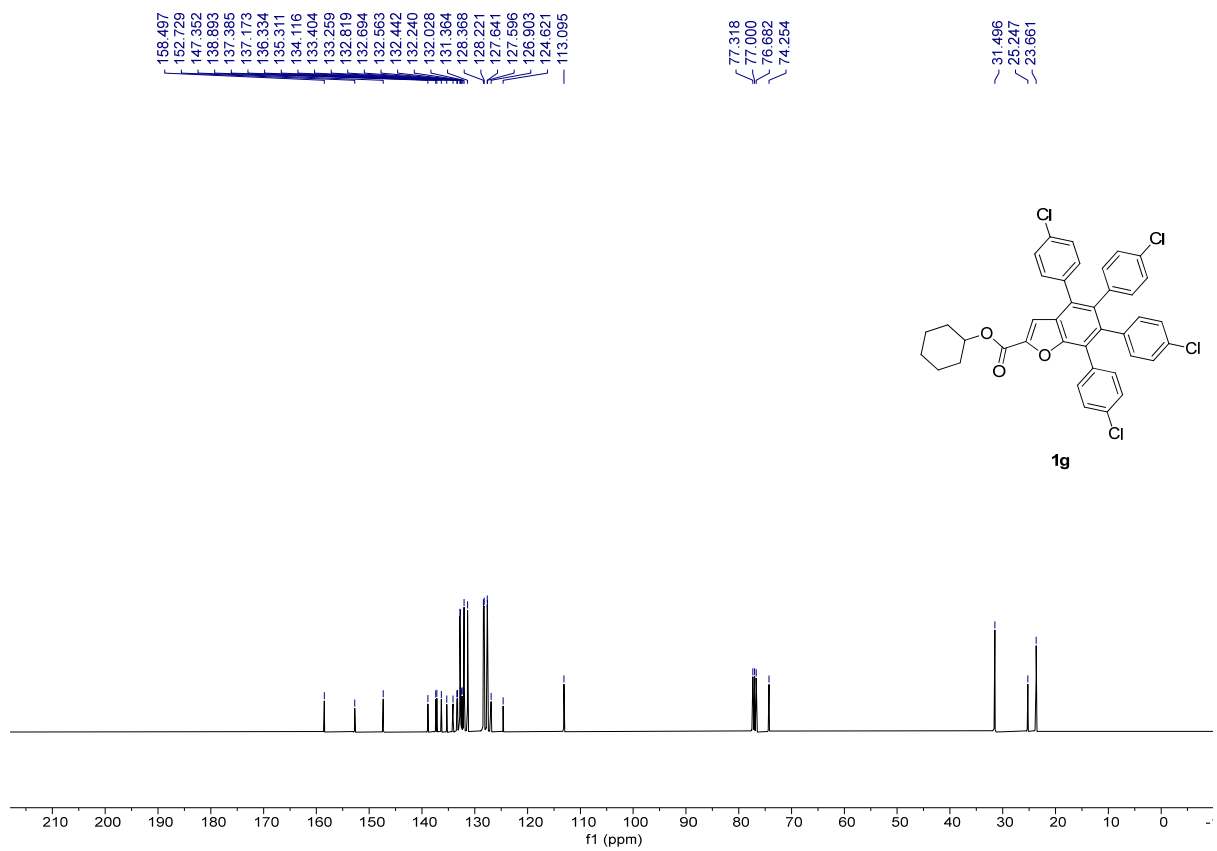
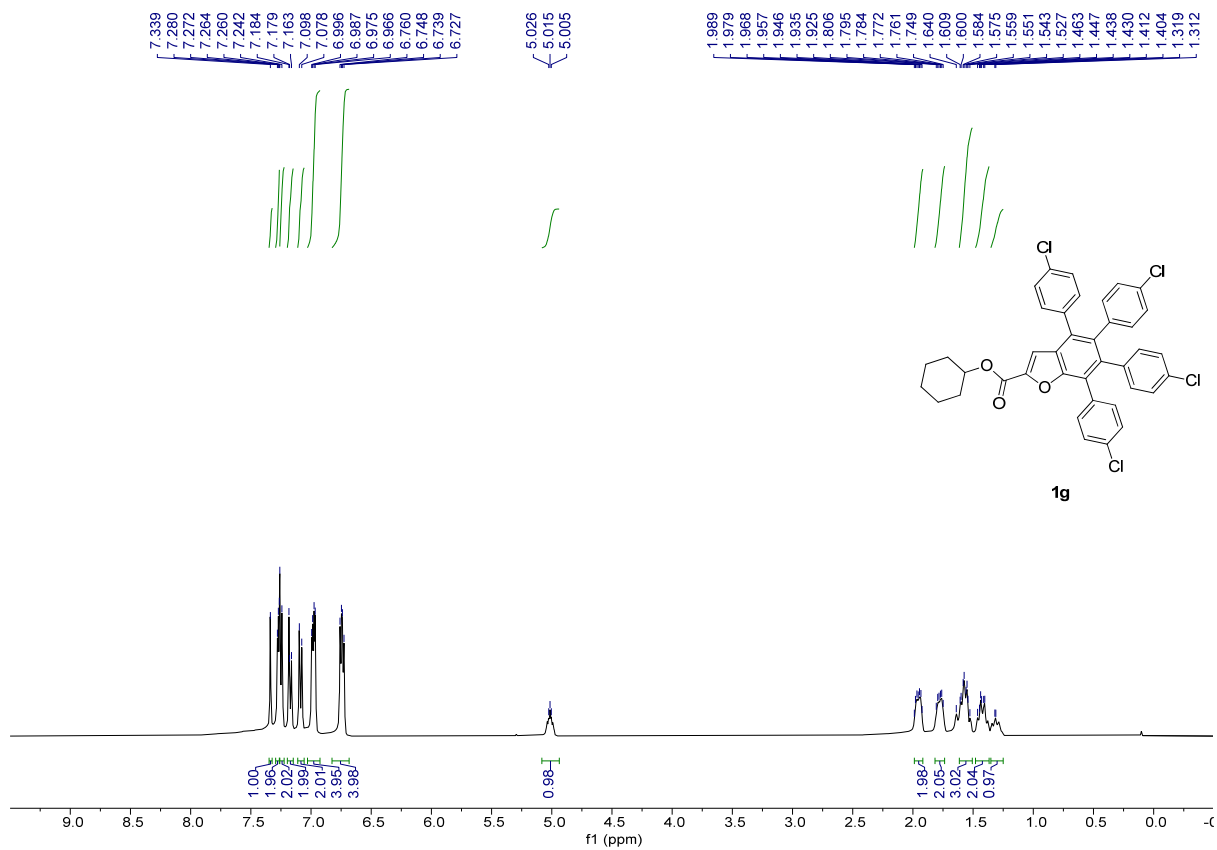


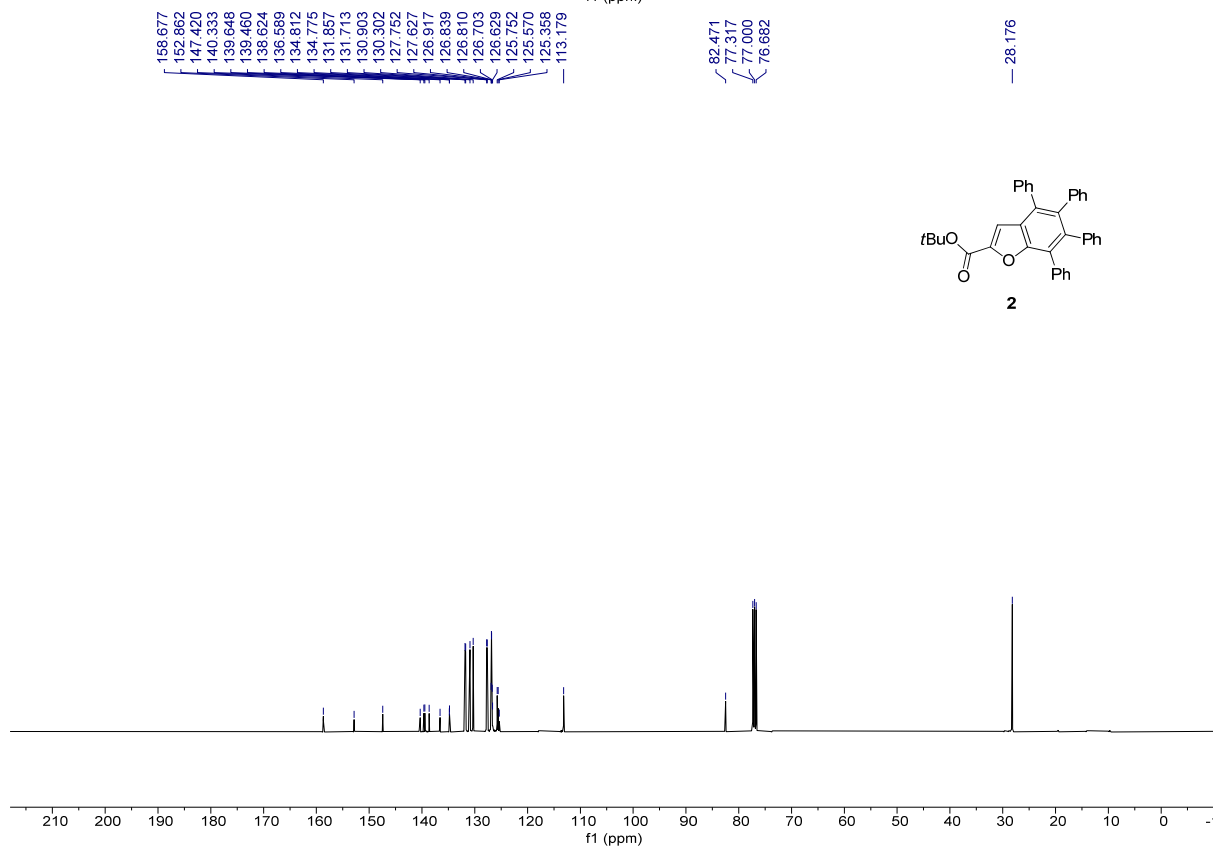
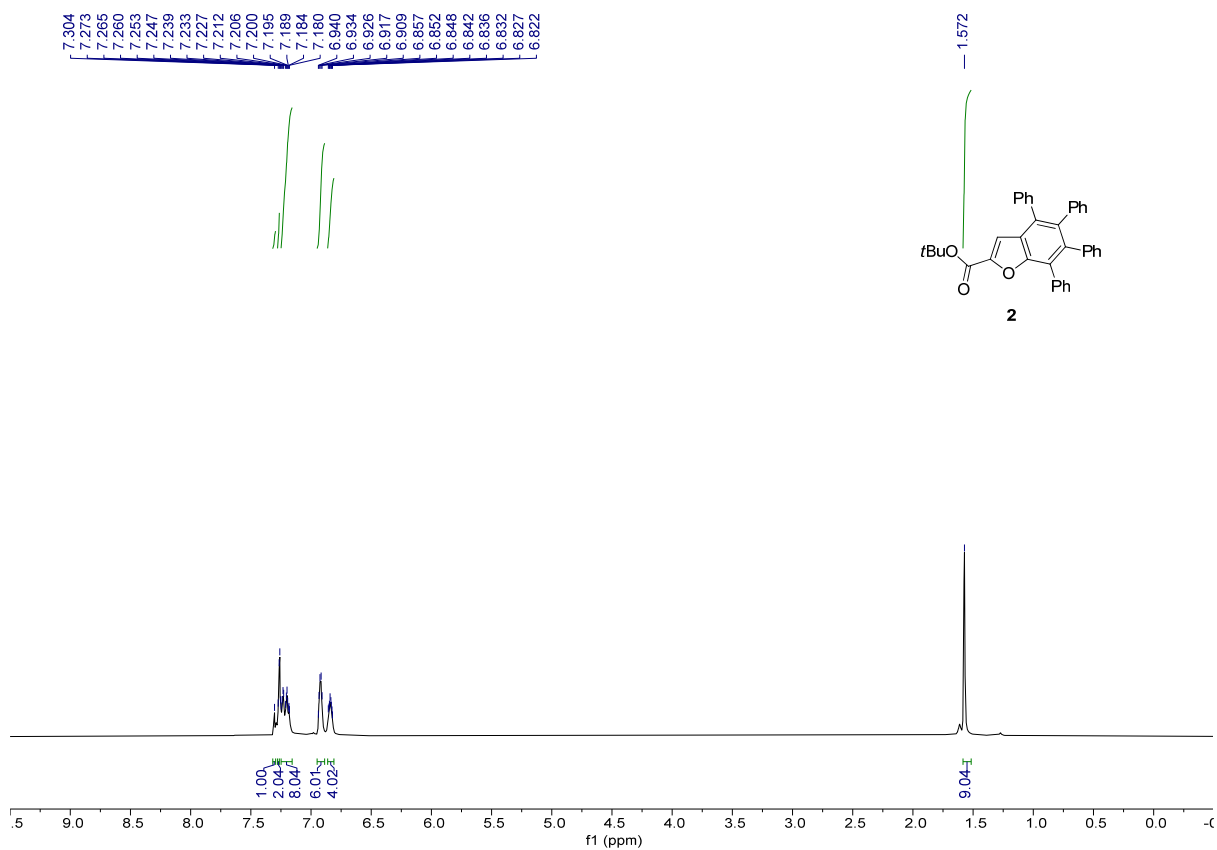


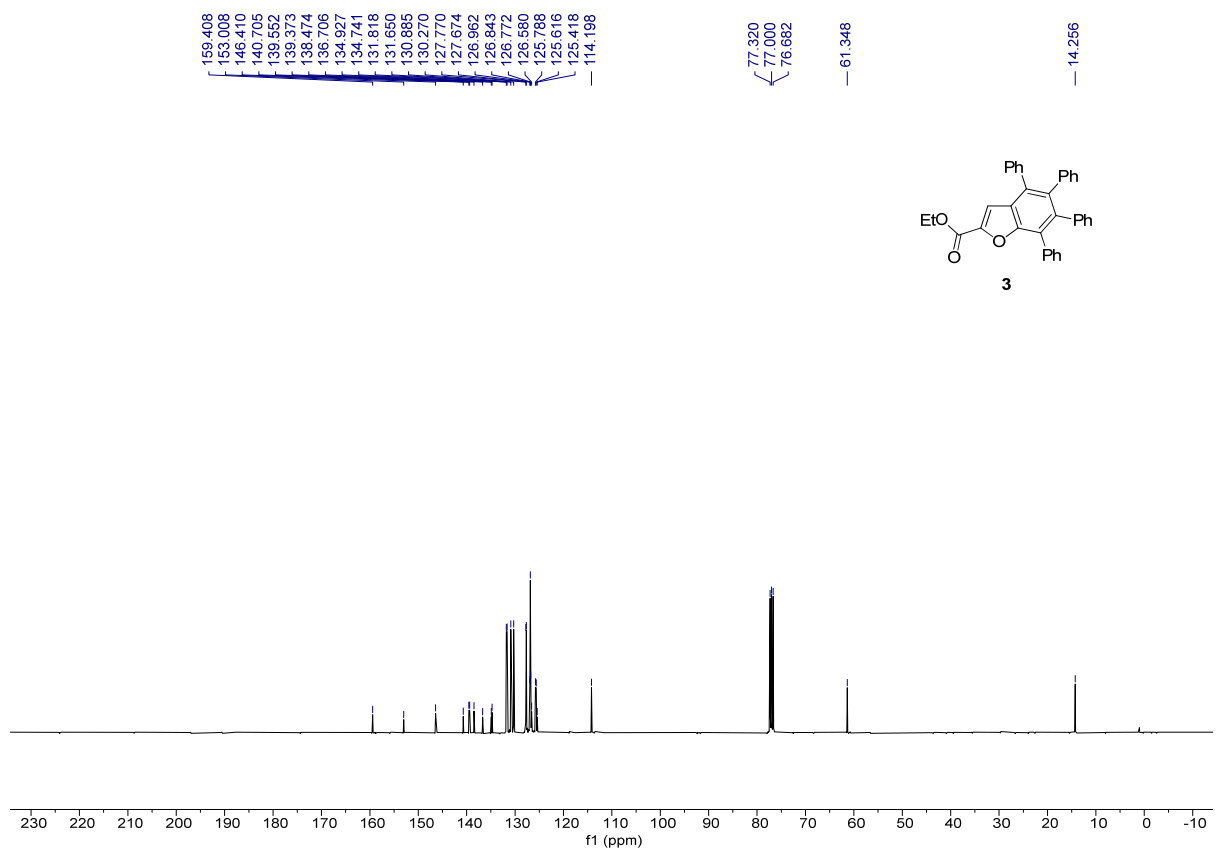
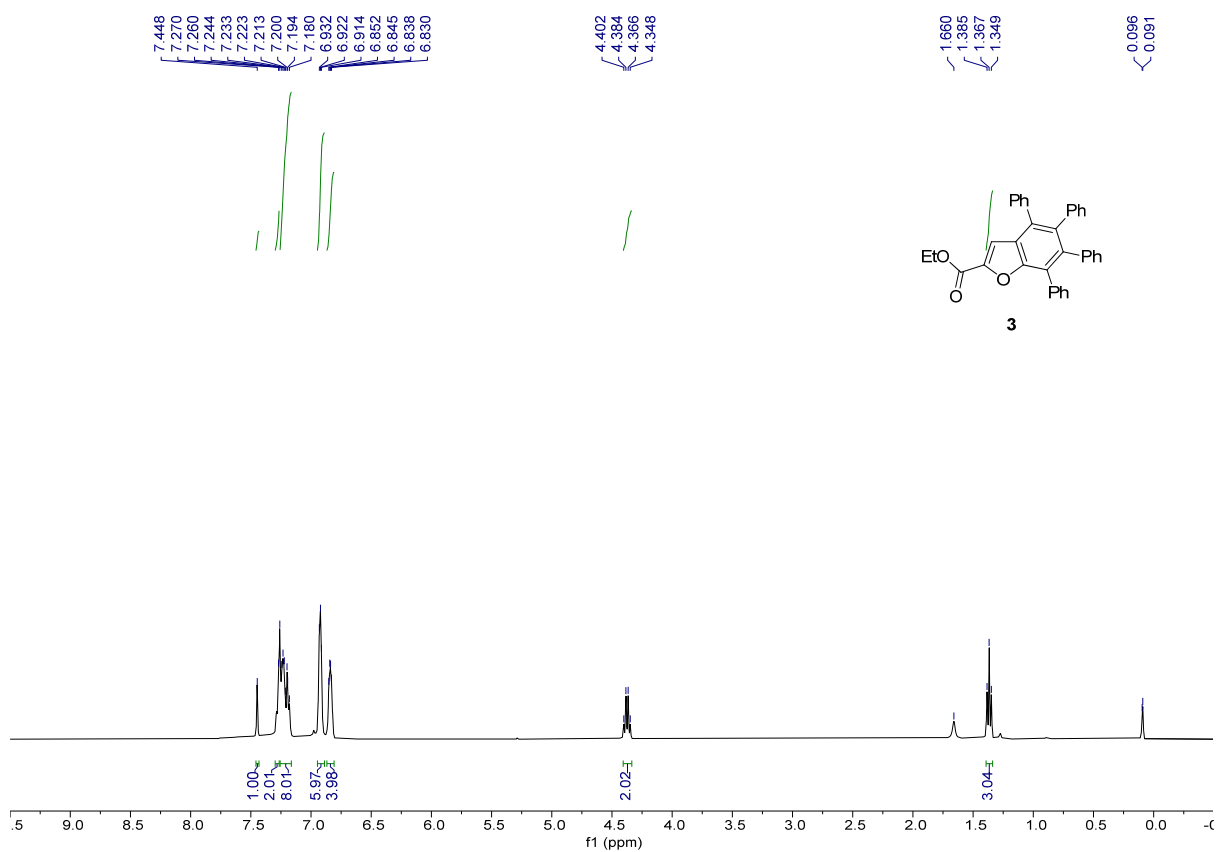


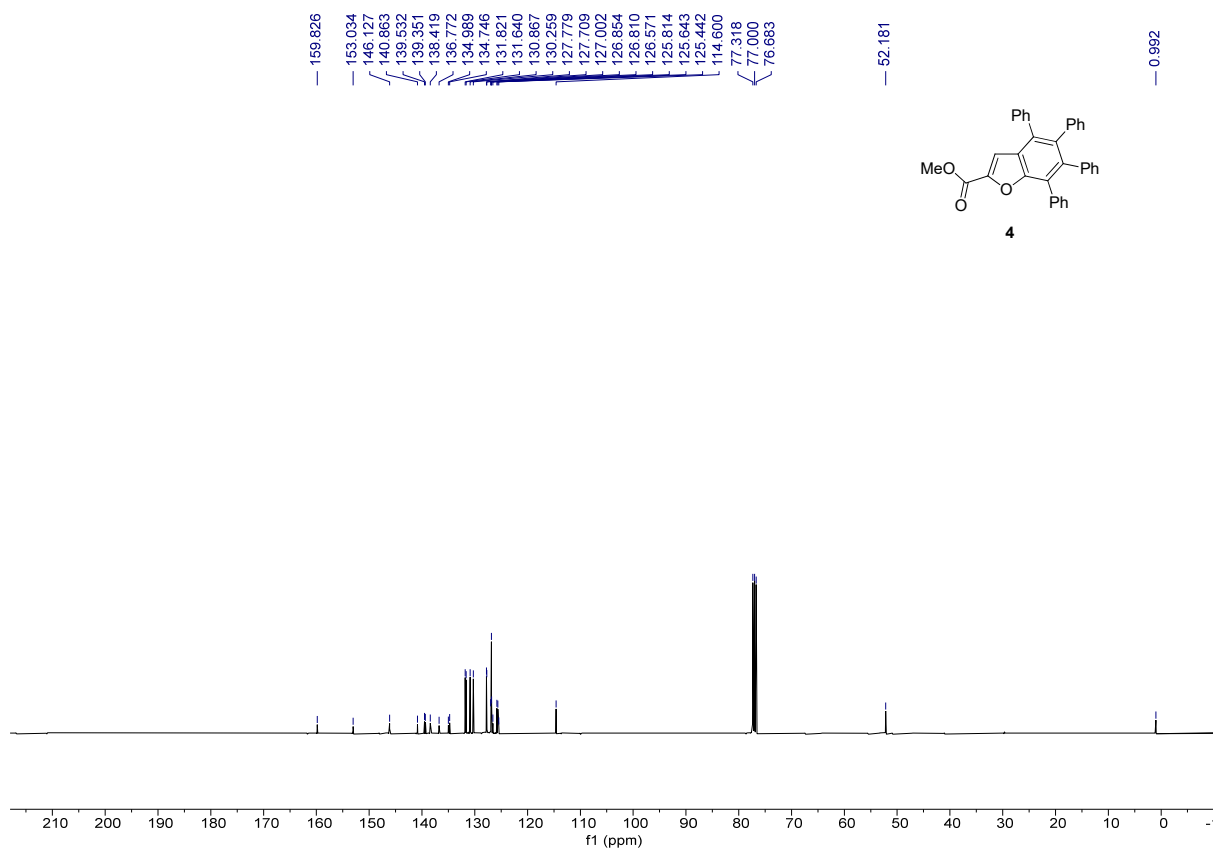
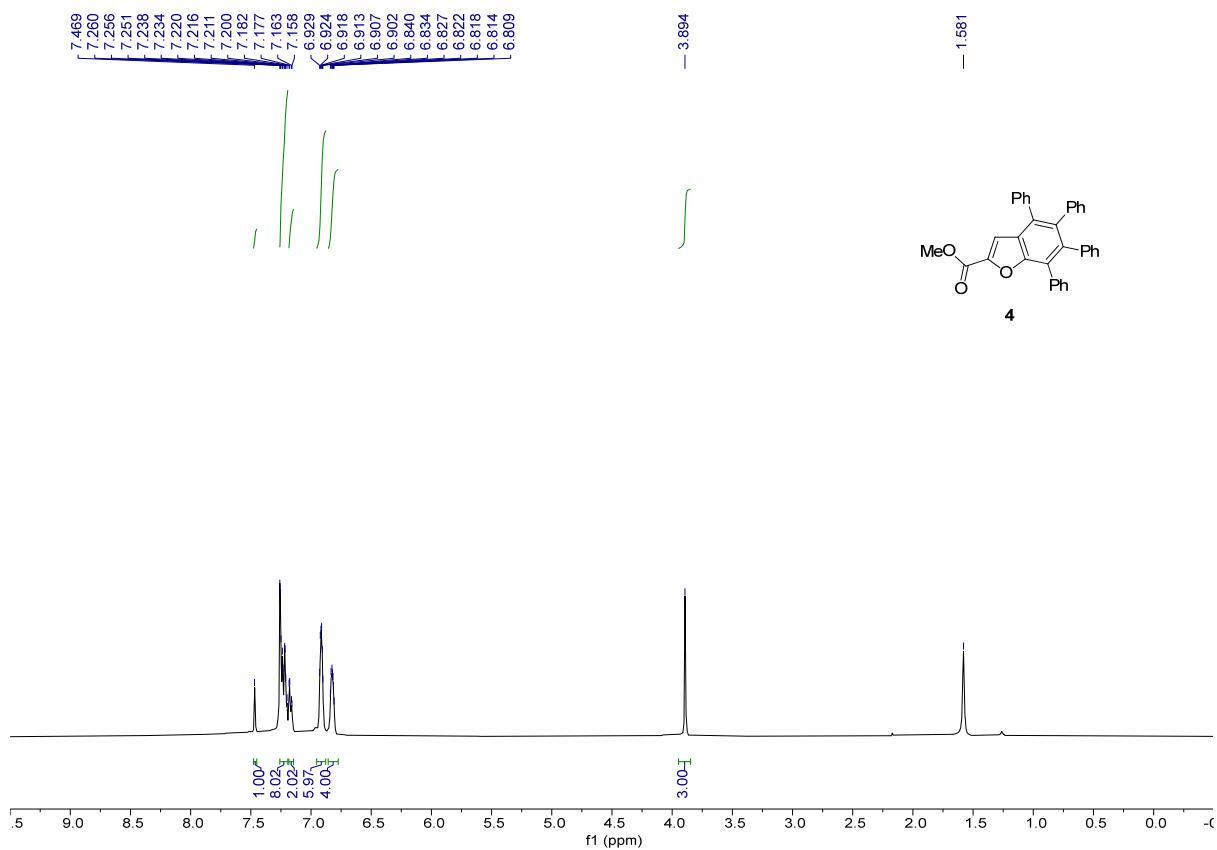


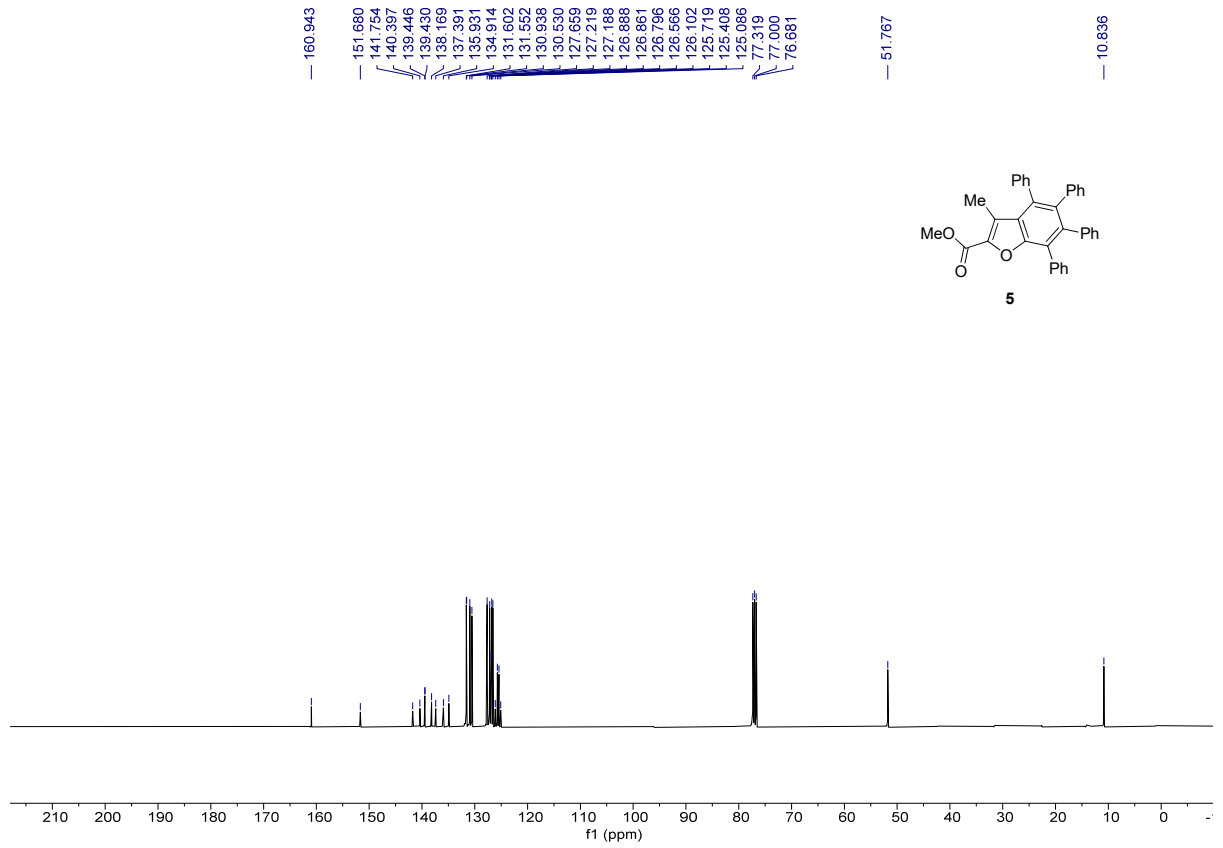
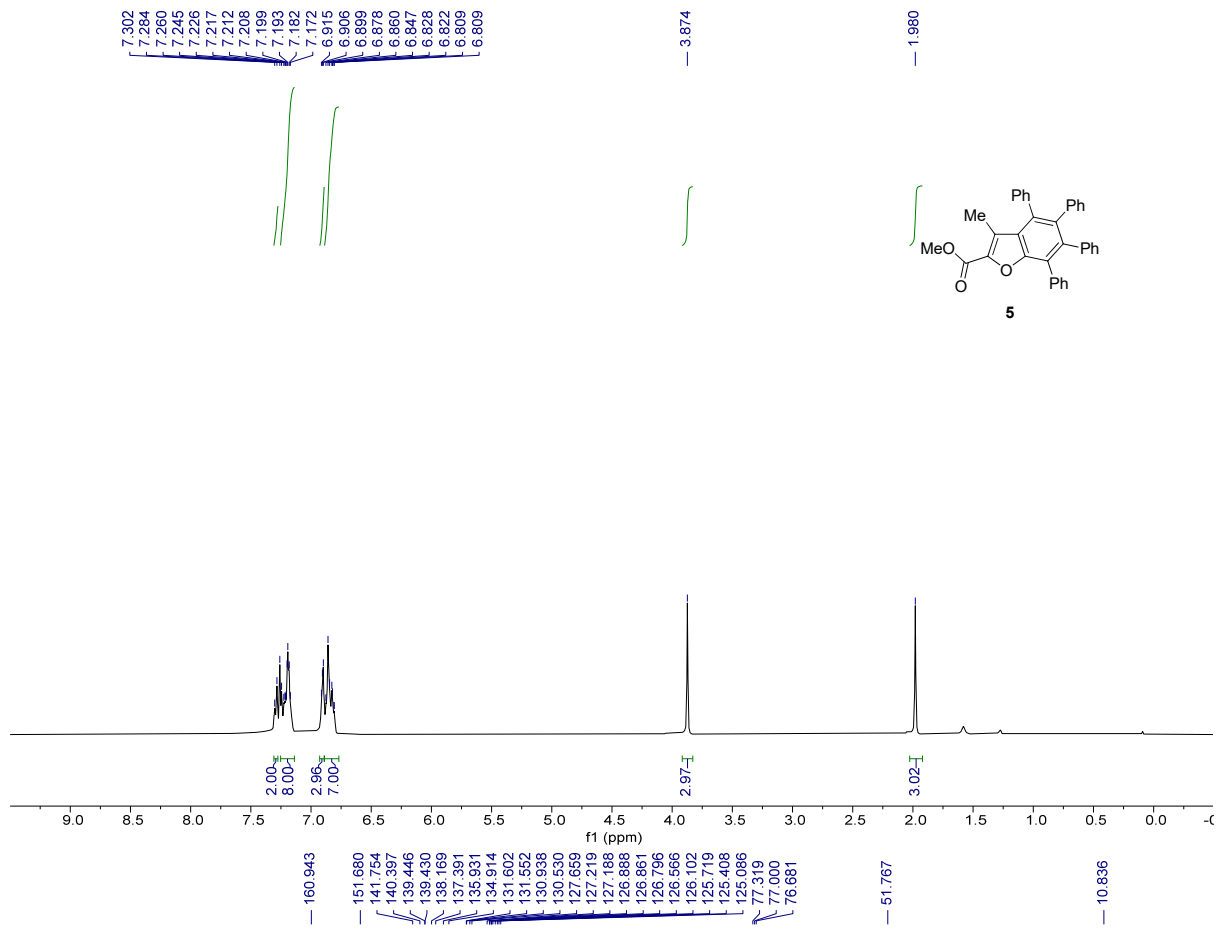


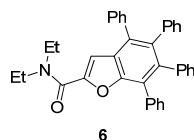
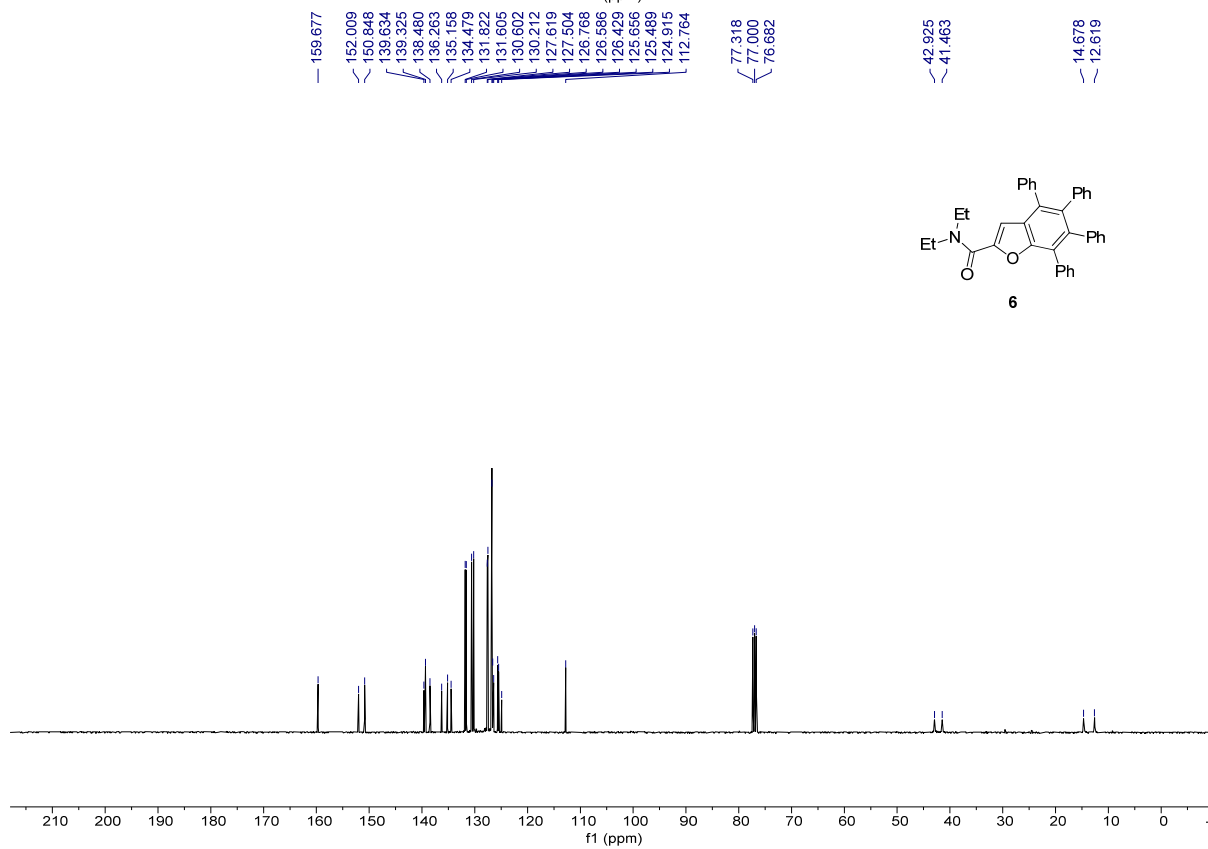
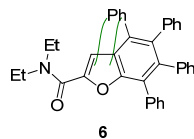
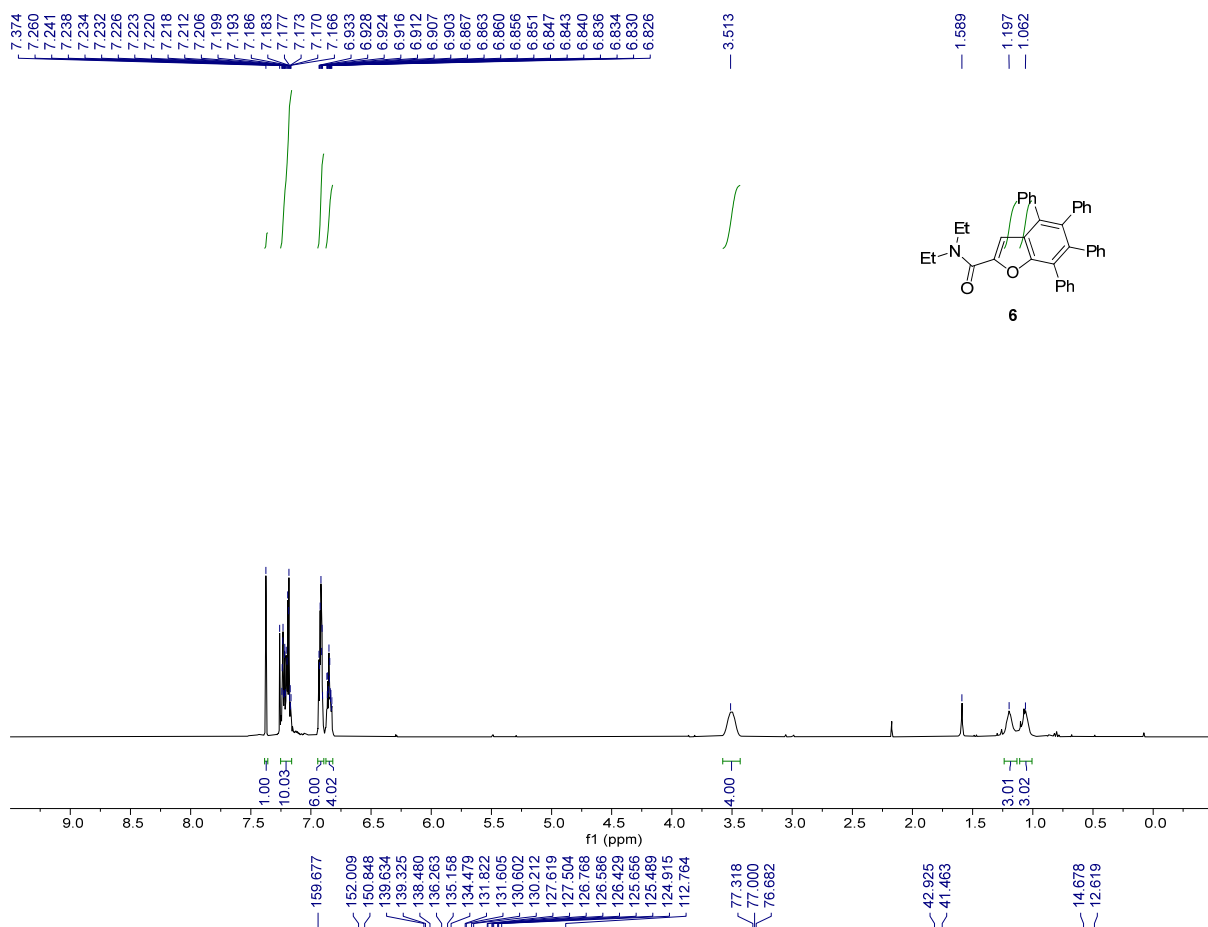


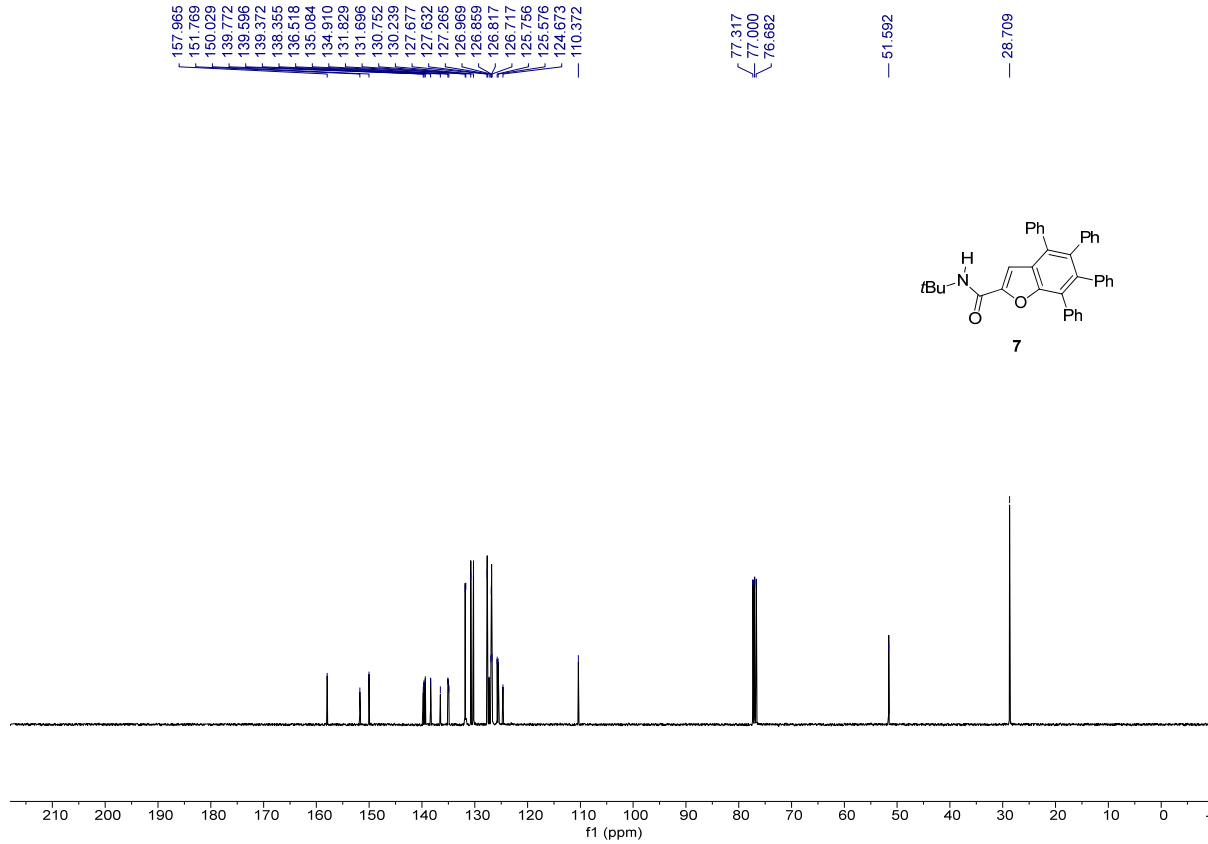
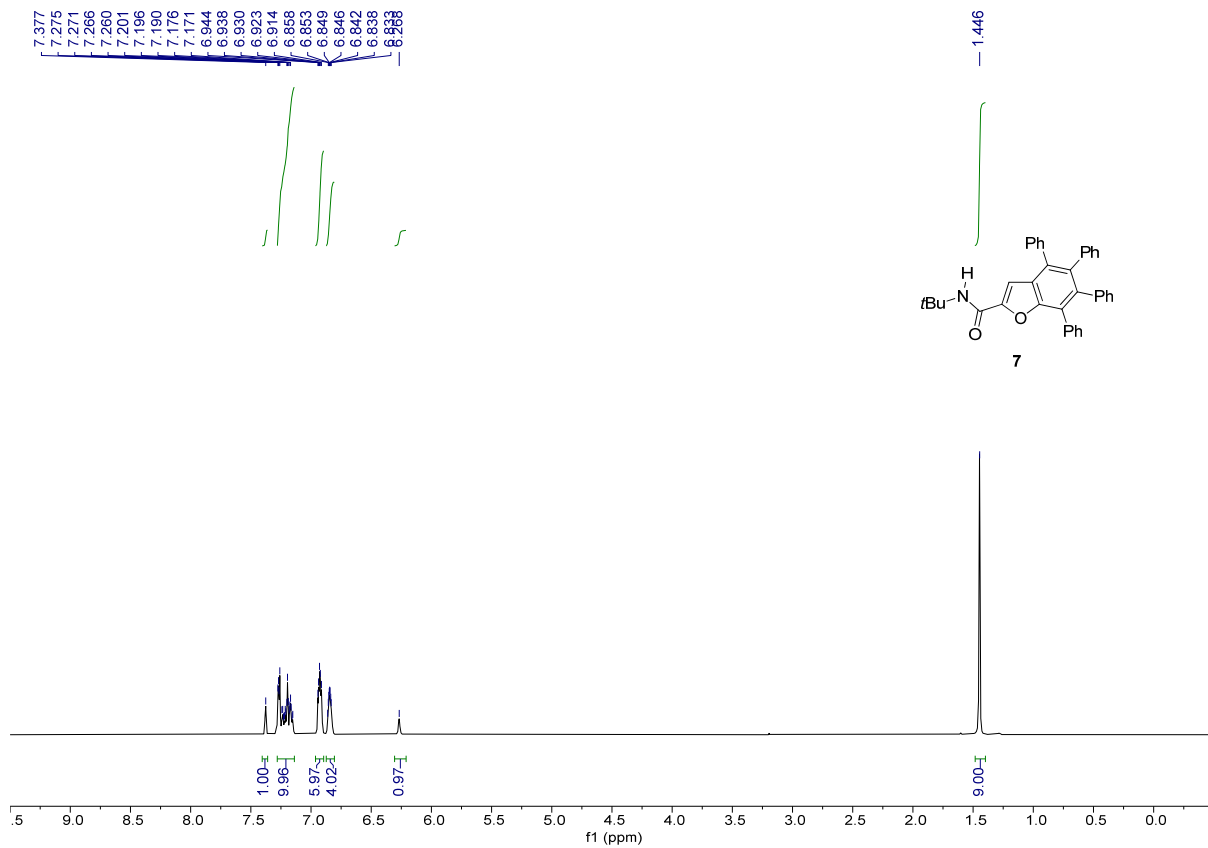


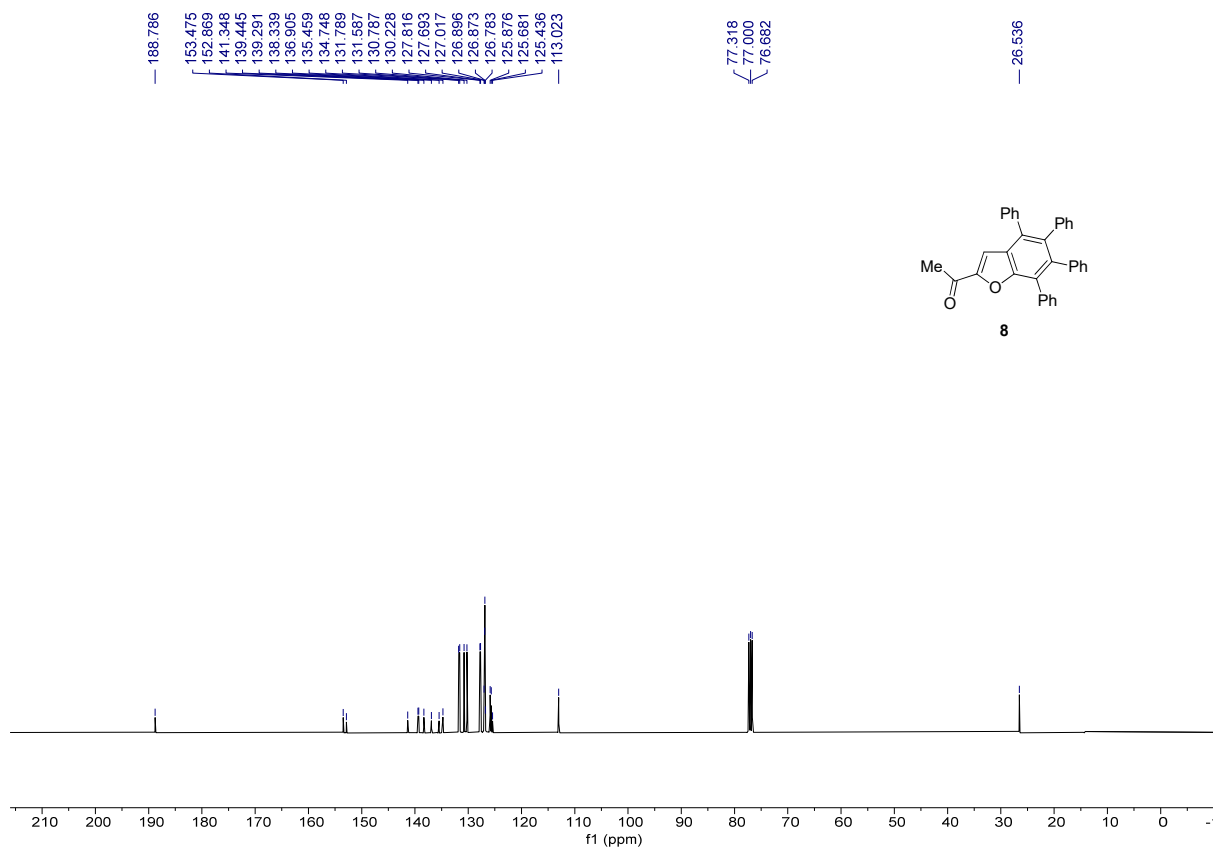
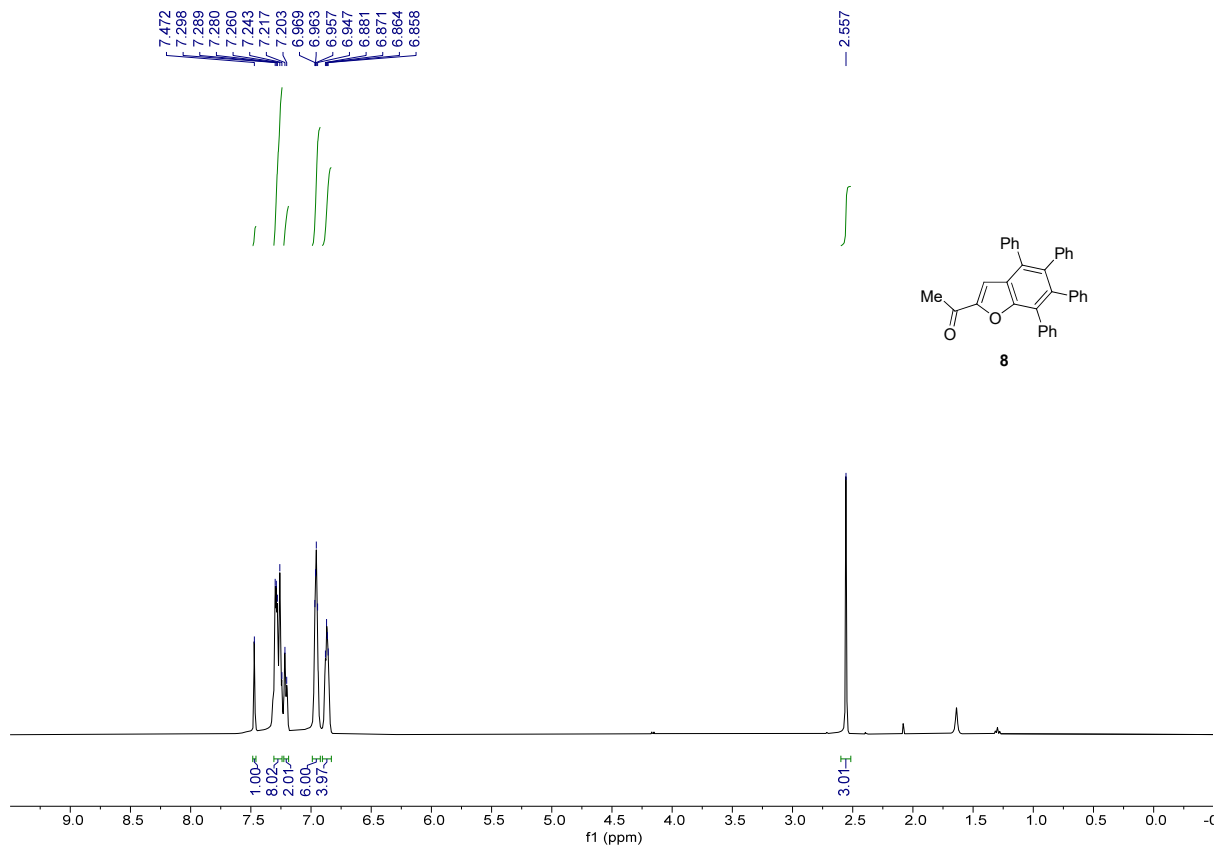


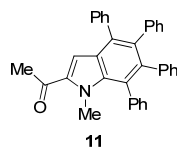
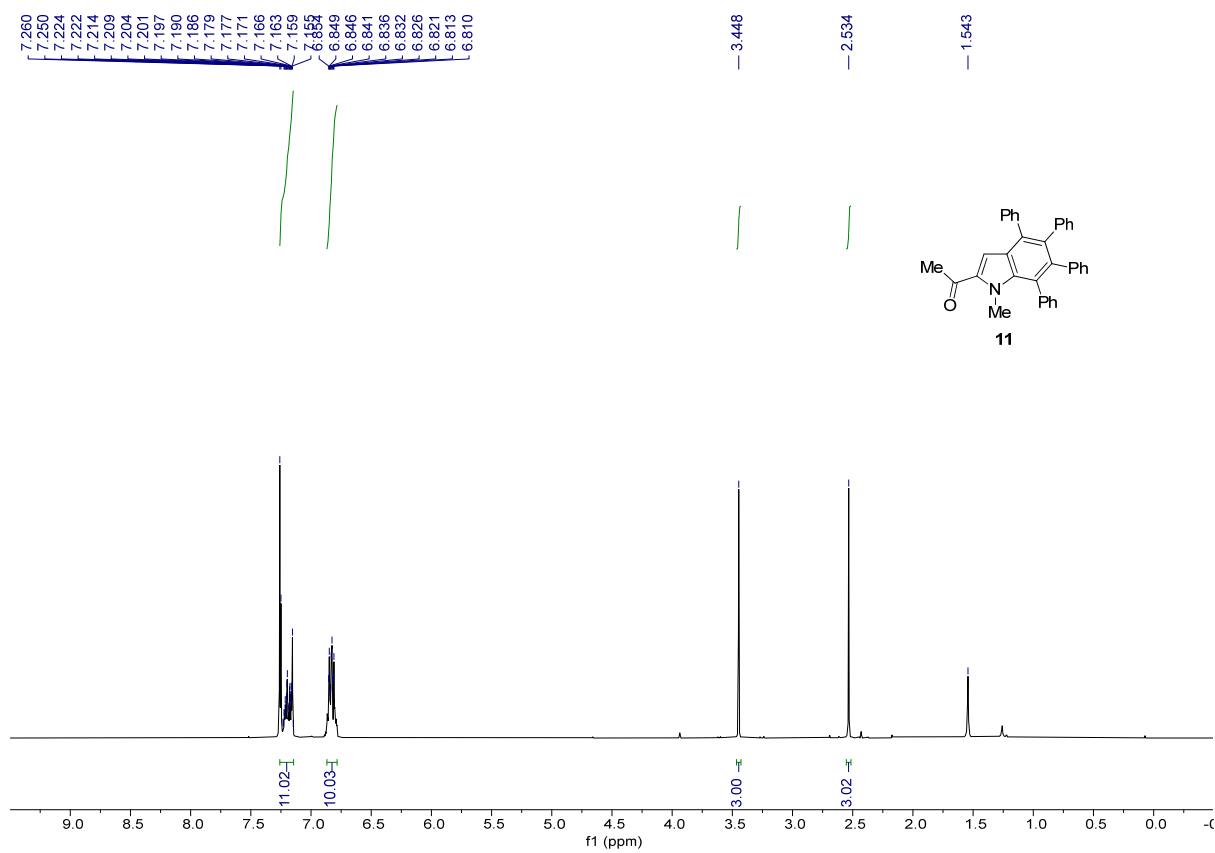
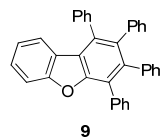
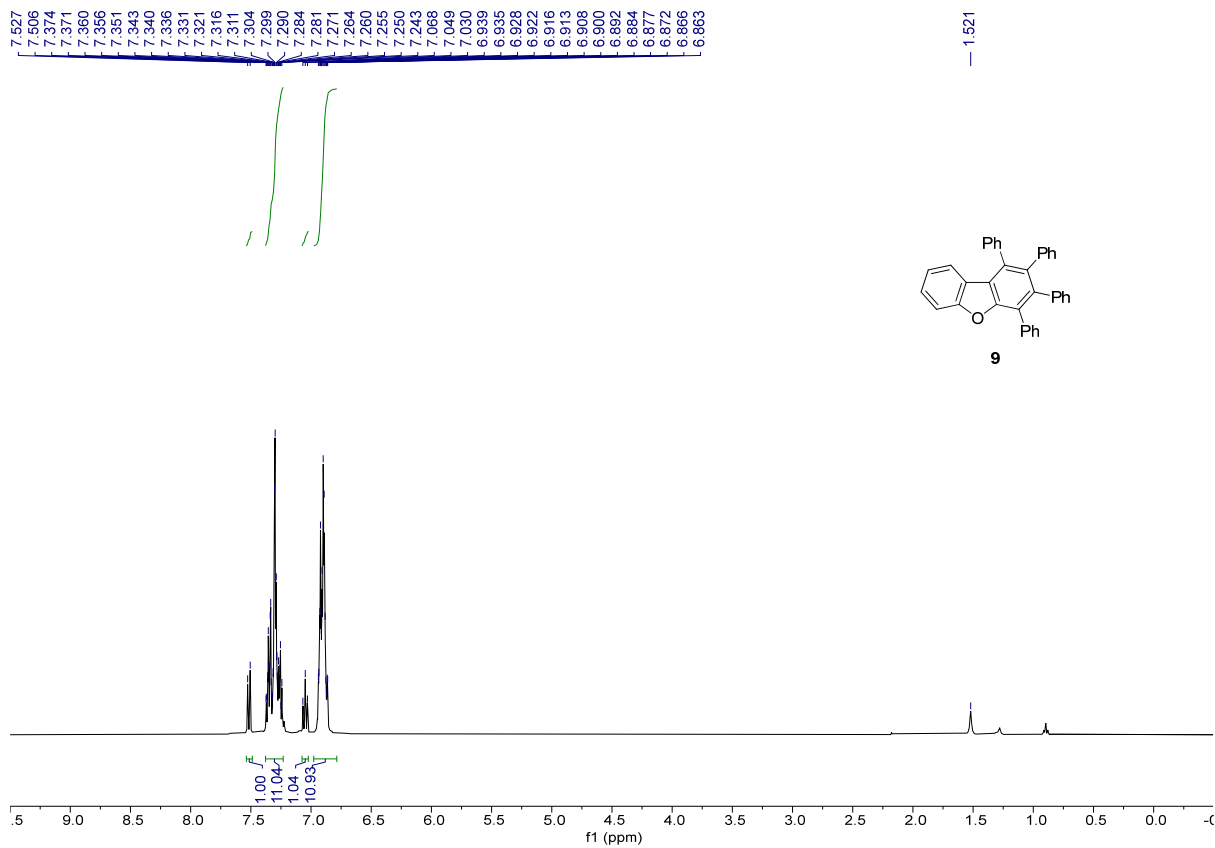


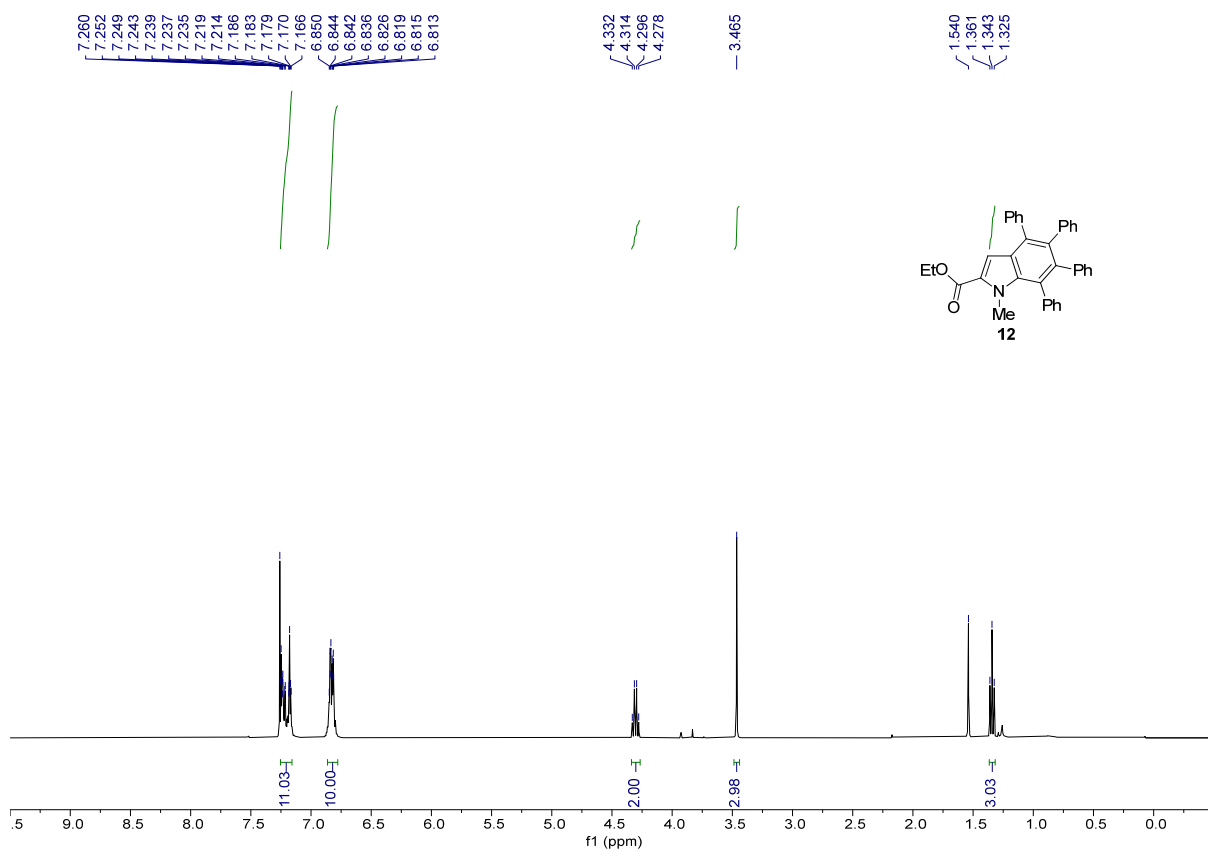
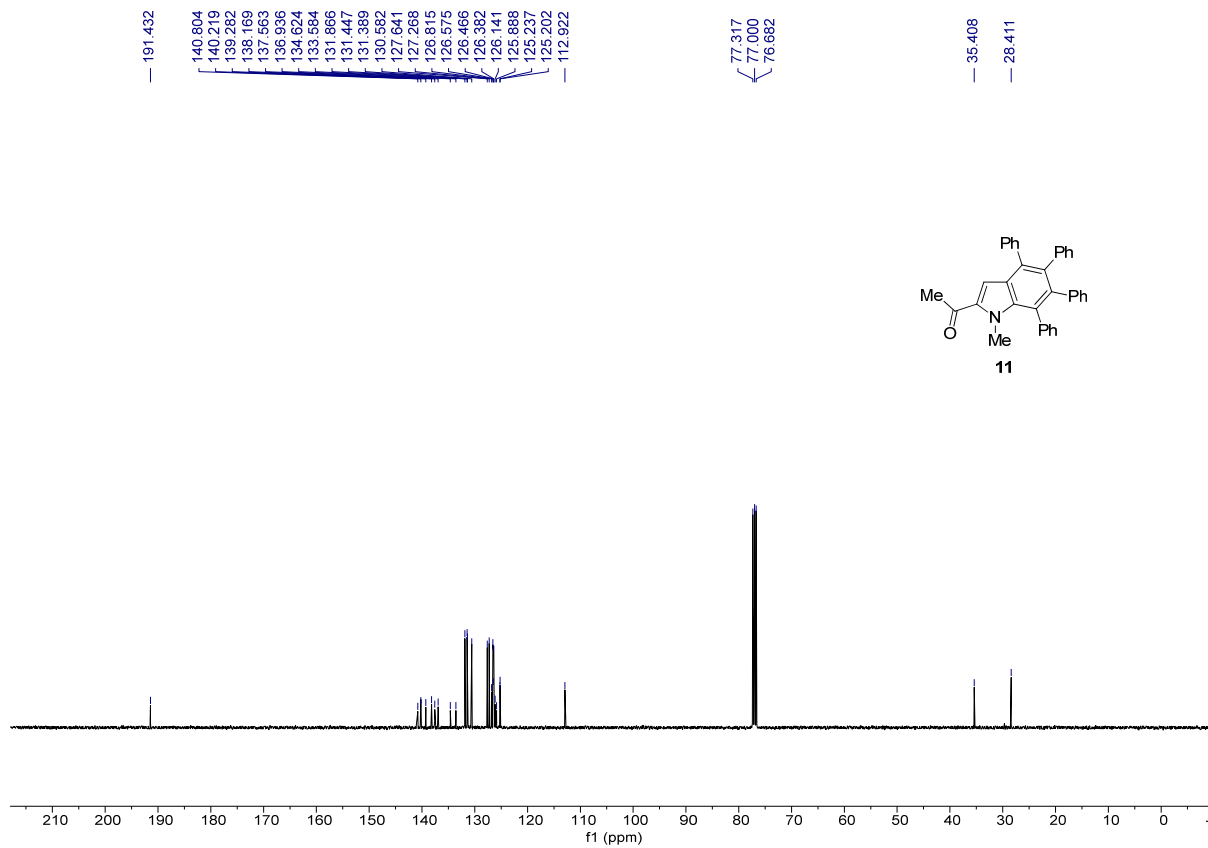


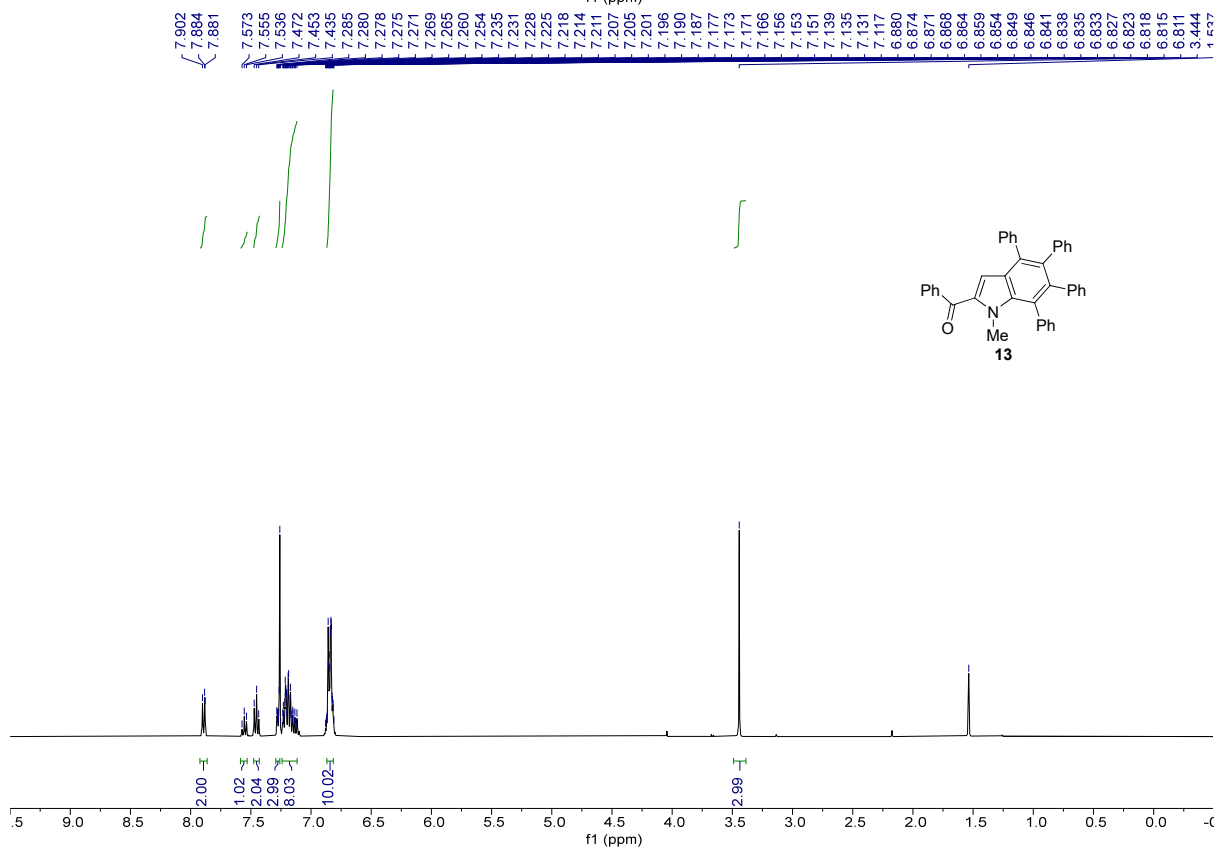
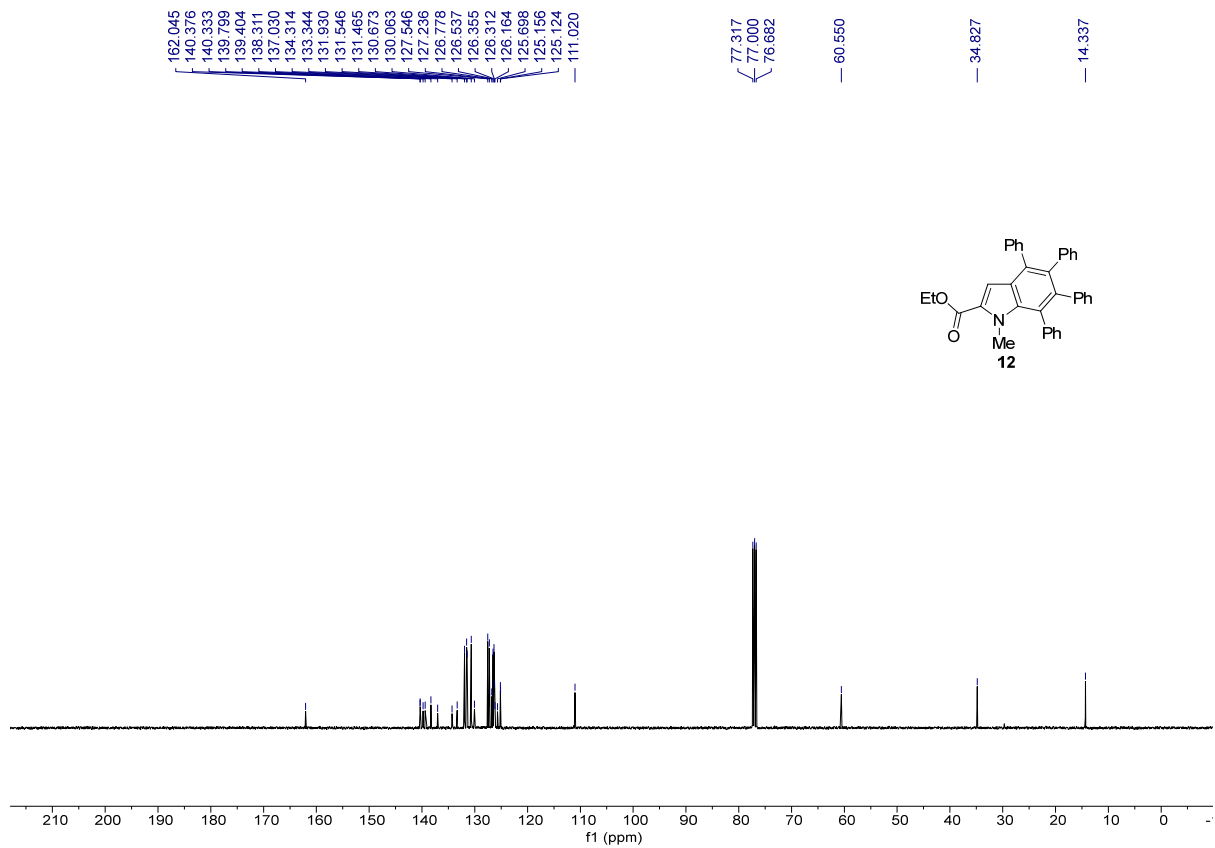


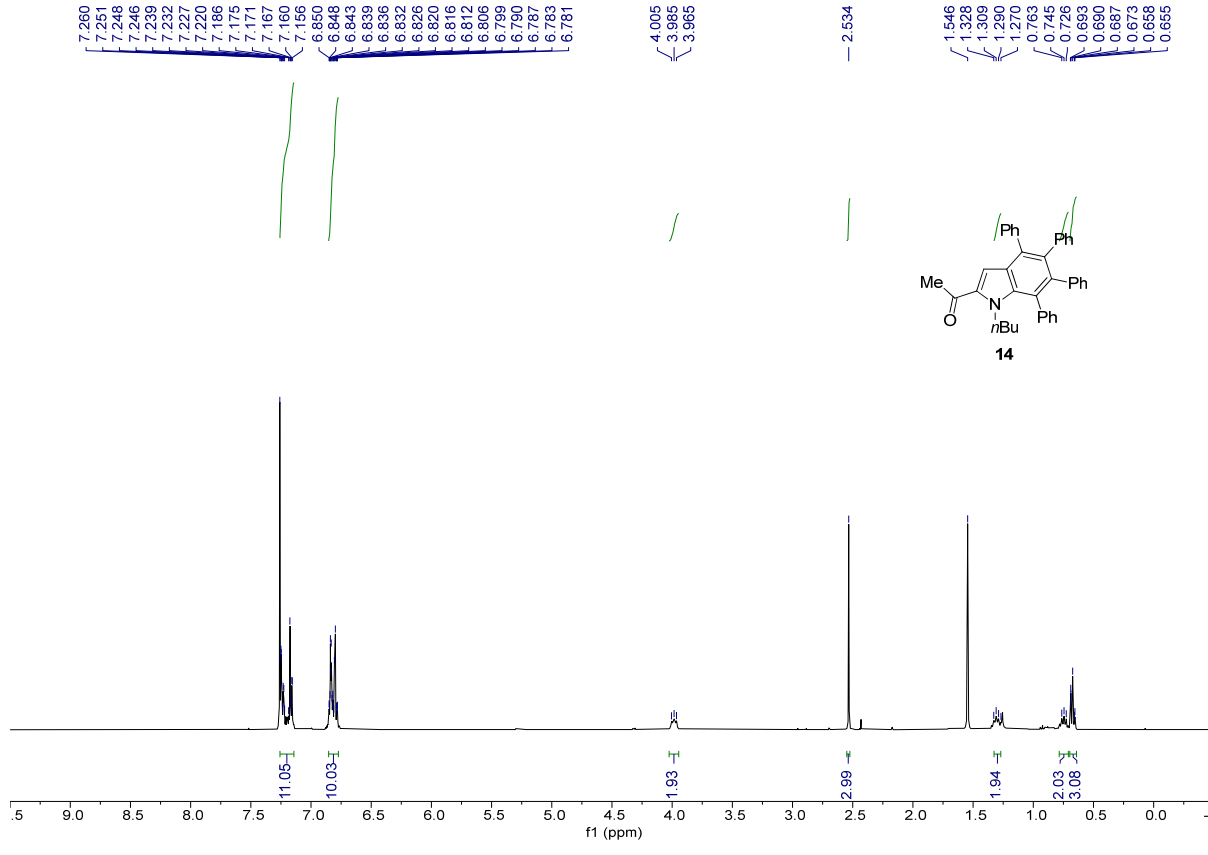
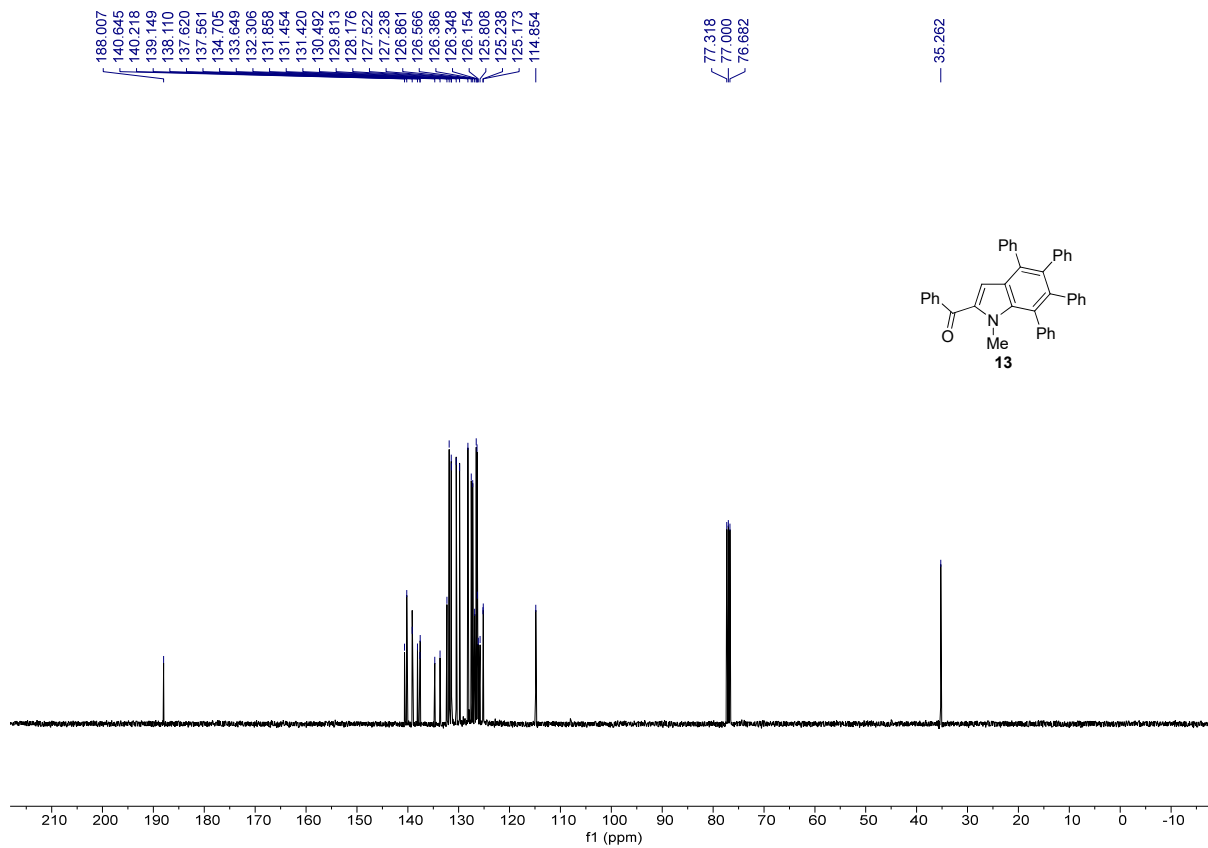


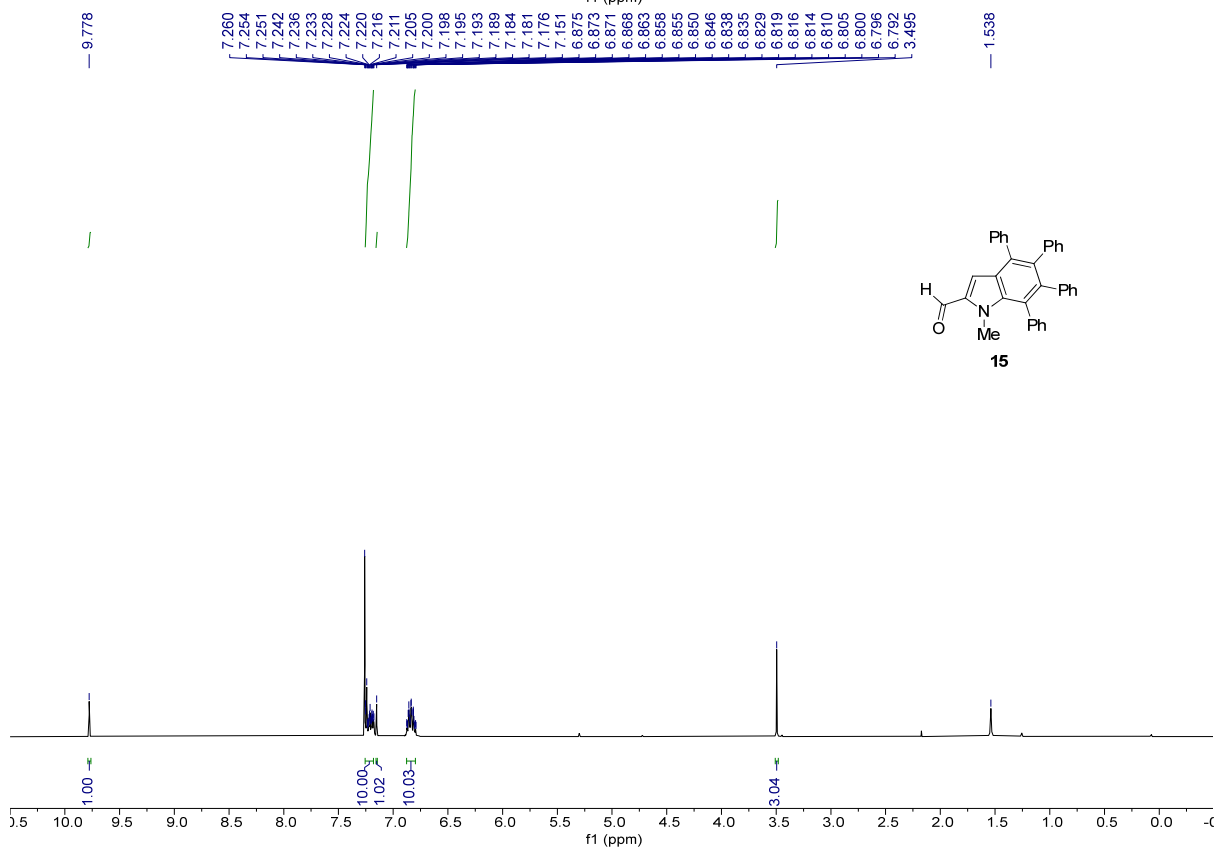
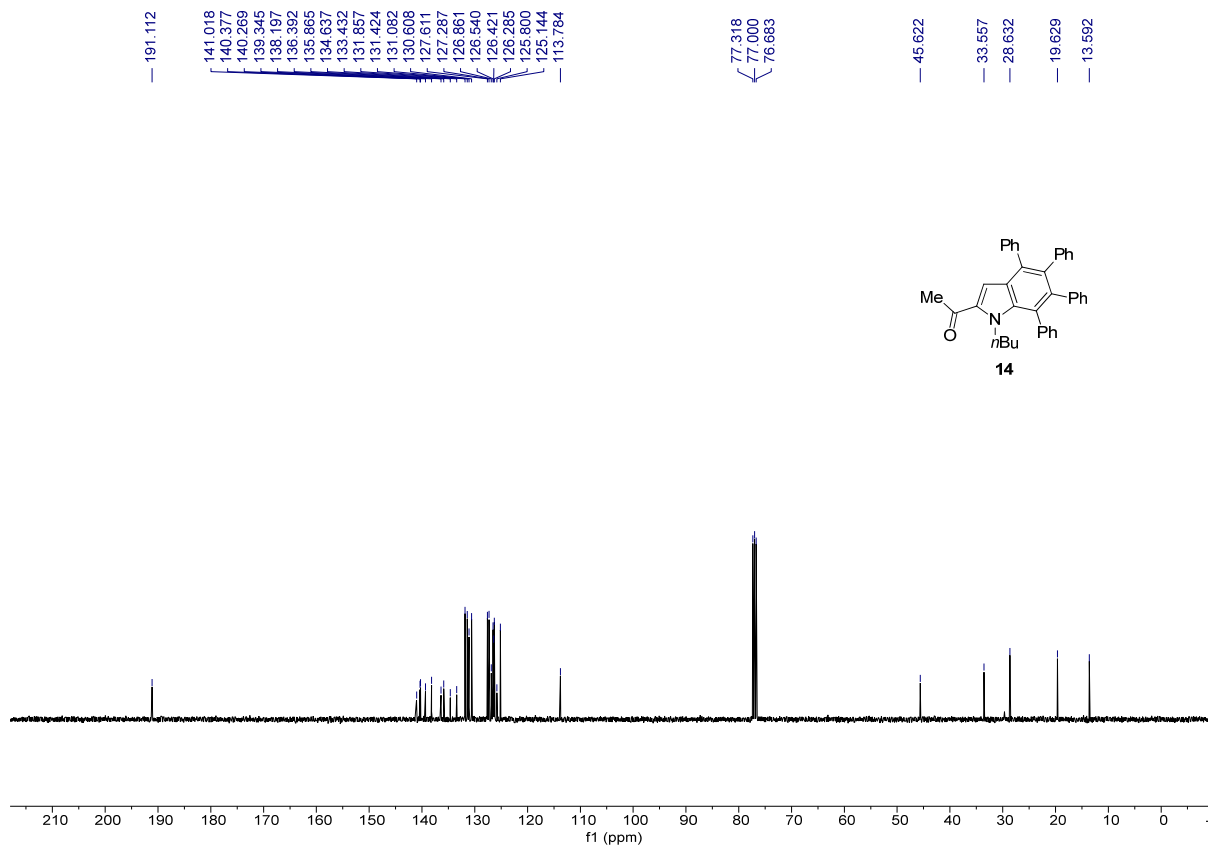


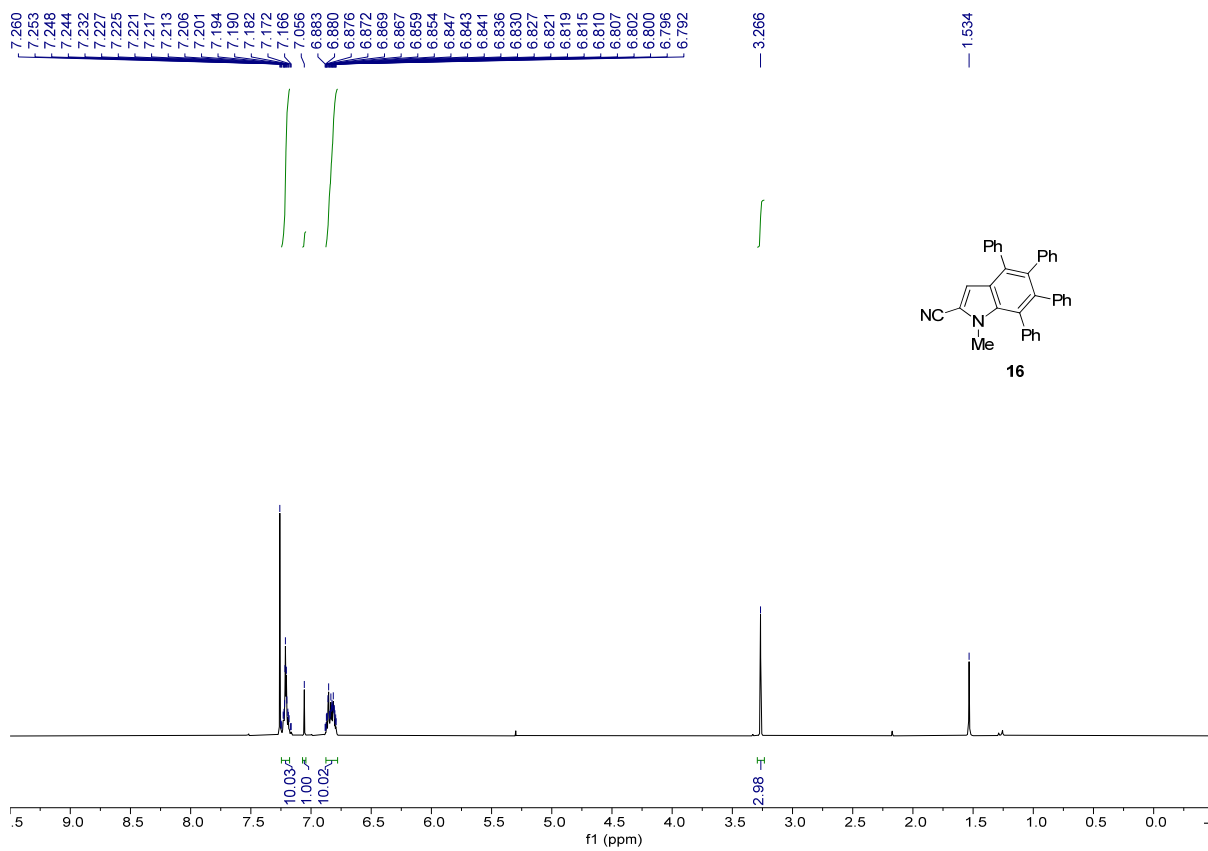
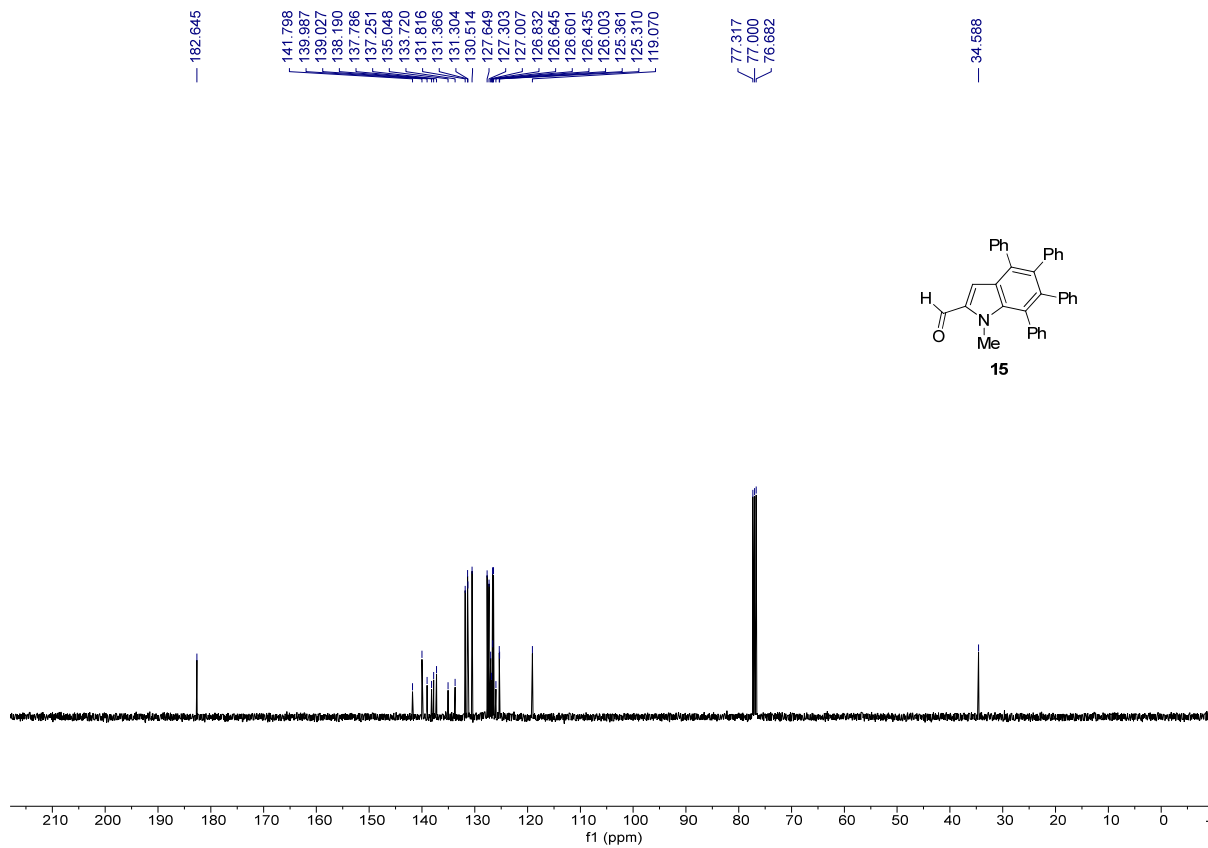


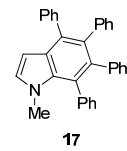
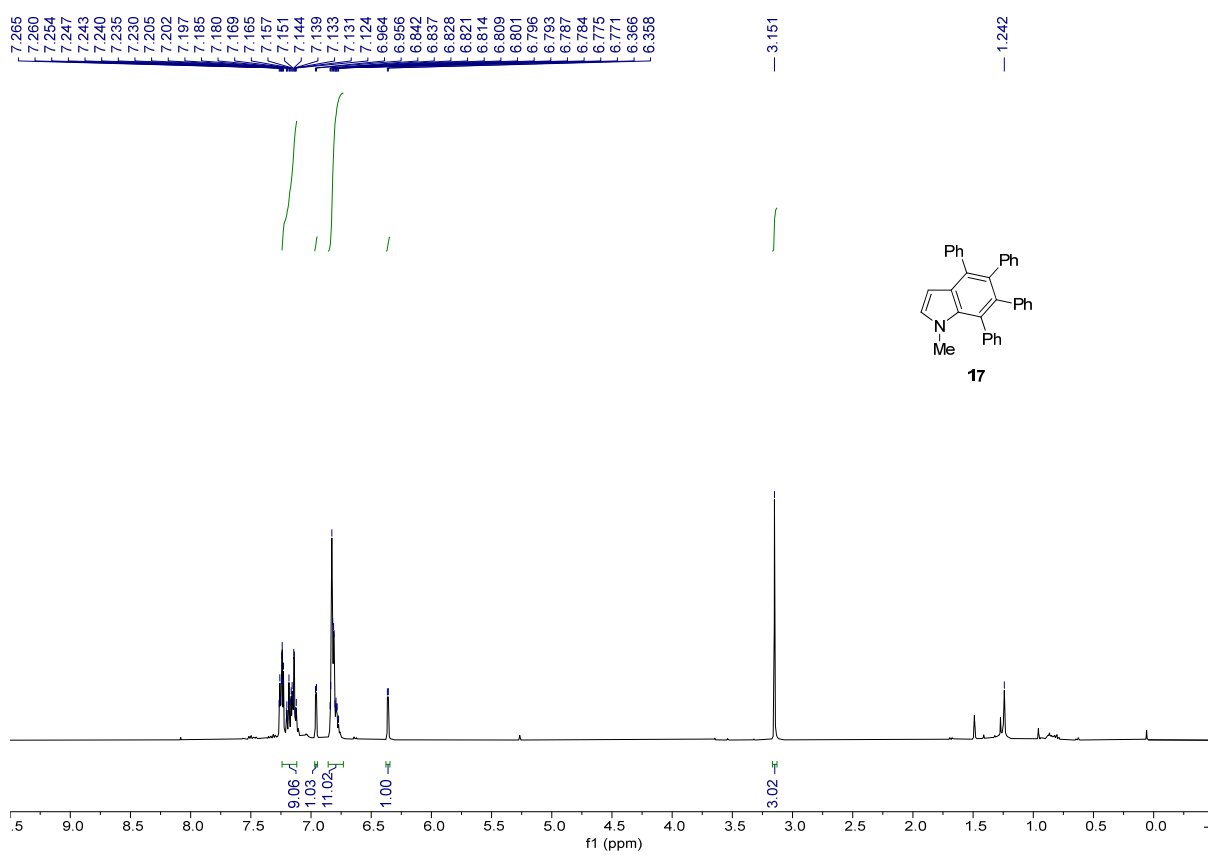
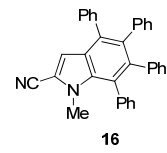
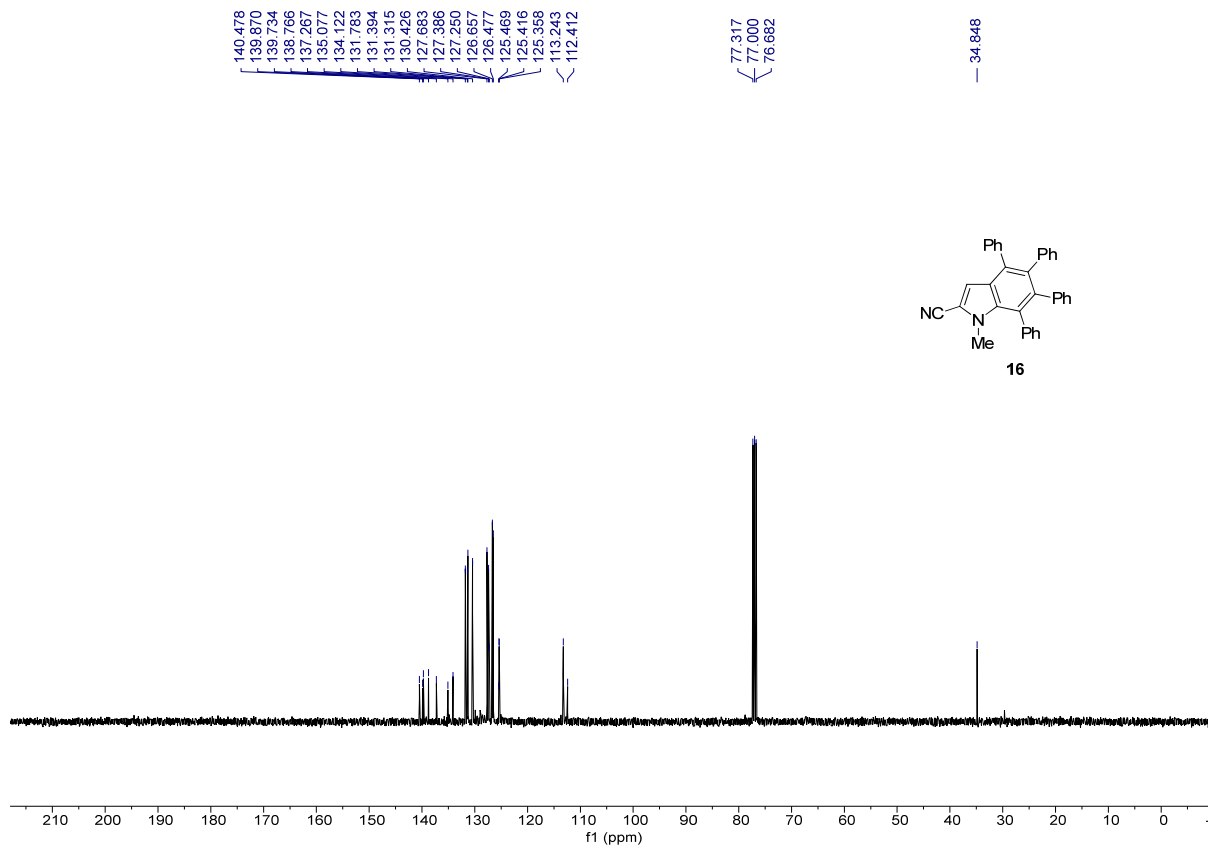


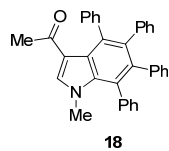
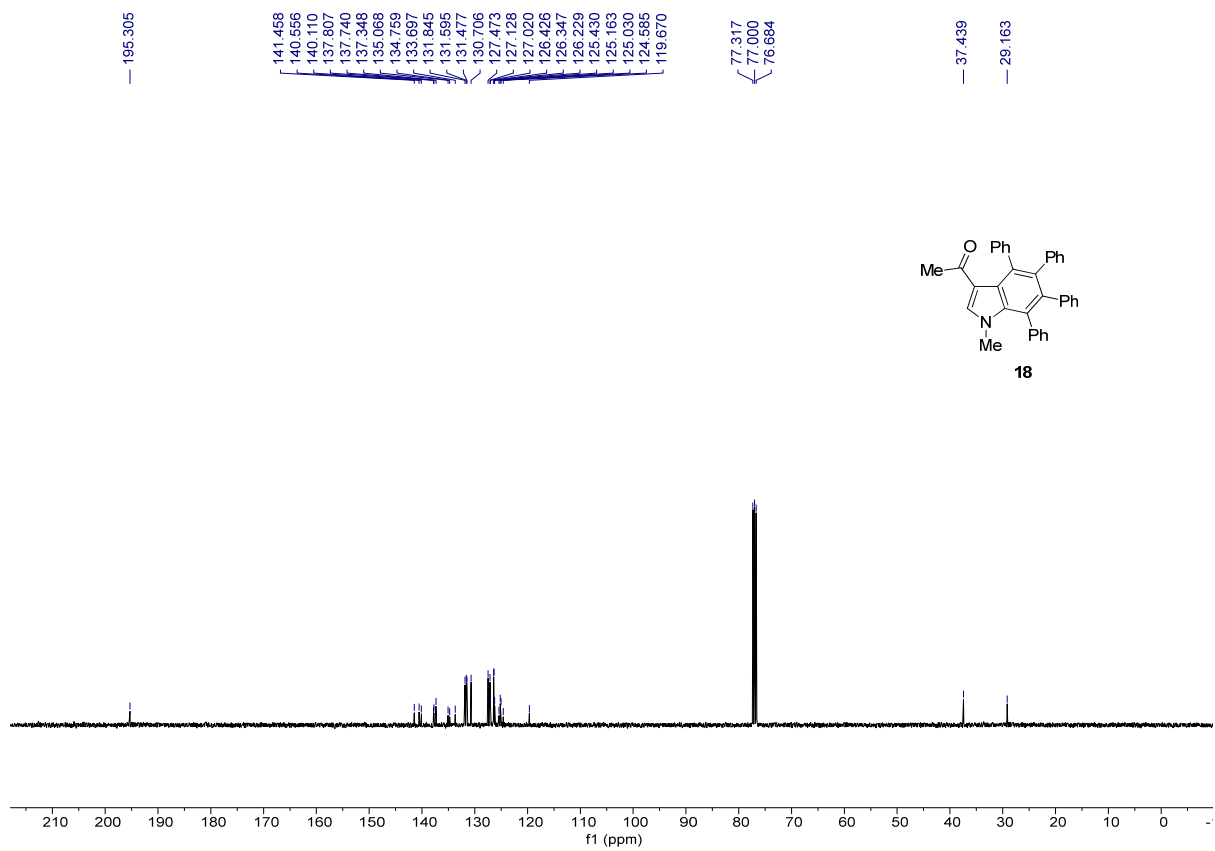
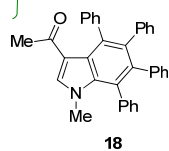
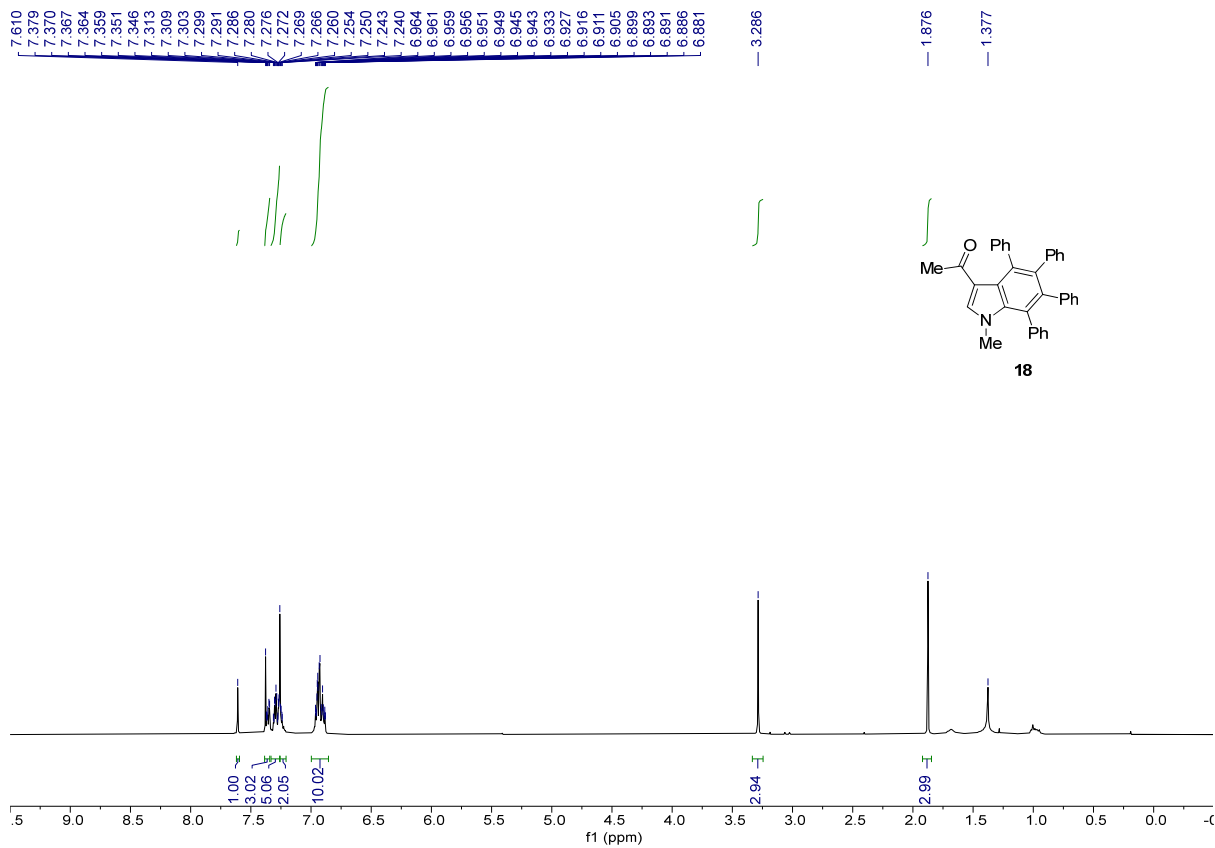






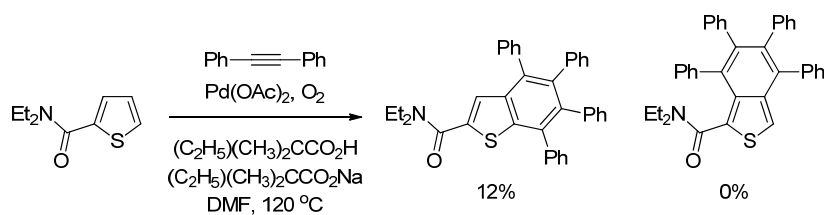






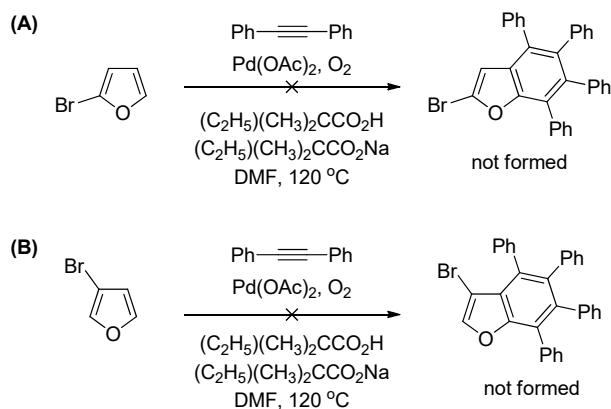
III. C-H Benzannulation of Heterocycles

Scheme S1. C-H Benzannulation of *N,N*-diethylthiophene-2-carboxamide



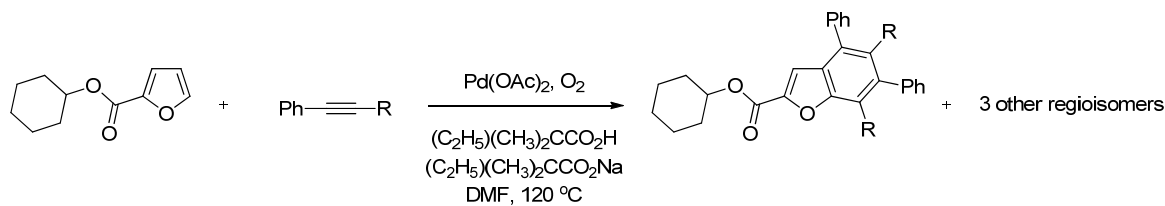
To compare with the Rh-catalyzed annulation,¹ the Pd-catalyzed reaction of *N,N*-diethylthiophene-2-carboxamide was performed to give the corresponding benzo[*b*]thiophene in 12% yield. In this reaction, the benzo[*c*]thiophene derivative formed by the Rh-catalyzed annulation was not obtained.

Scheme S2. C-H Benzannulation of bromofurans



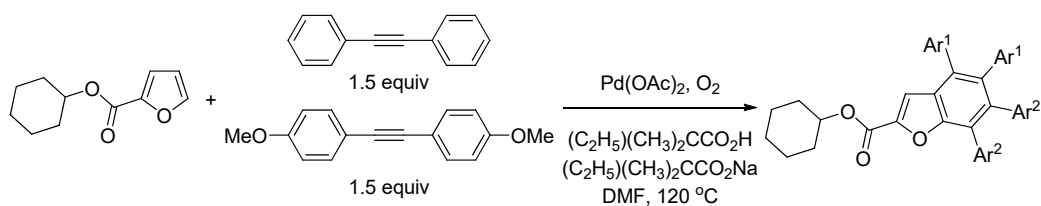
IV. C-H Benzannulation with Different Alkynes

Table S2. Reactions with unsymmetrical alkynes



R	Yield (%)
H	0
Me	0
CO ₂ Et	0
(<i>p</i> -MeO)C ₆ H ₄	64% (1:1:1:1)

Table S3. Reaction with two different alkynes



Ar ¹	Ar ²	Yield (%)
C ₆ H ₅	C ₆ H ₅	15
(<i>p</i> -MeO)C ₆ H ₄	(<i>p</i> -MeO)C ₆ H ₄	19
C ₆ H ₅	(<i>p</i> -MeO)C ₆ H ₄	21 (1:1)
(<i>p</i> -MeO)C ₆ H ₄	C ₆ H ₅	

(1) Fukuzumi, K.; Unoh, Y.; Nishii, Y.; Satoh, T.; Hirano, K.; Miura, M. *J. Org. Chem.* **2016**, *81*, 2474.