Electronic Supporting Information

Cobalt-catalyzed tandem one-pot synthesis of polysubstituted imidazo[1,5-*a*]pyridines and imidazo[1,5-*a*]isoquinolines

Neha Meena,[a,†] Shiv Dhiman,[a,†] Krishnan Rangan,[b] and Anil Kumar*[,a]

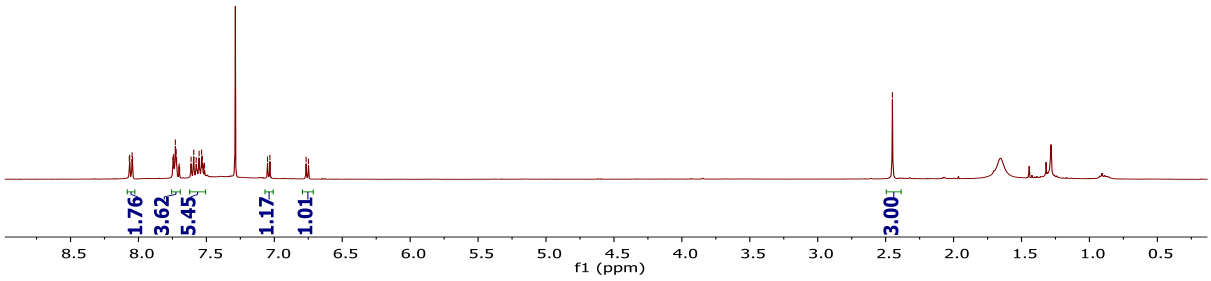
[a]Department of Chemistry, Birla Institute of Technology and Science Pilani, Pilani Campus, Rajasthan, 333031, India

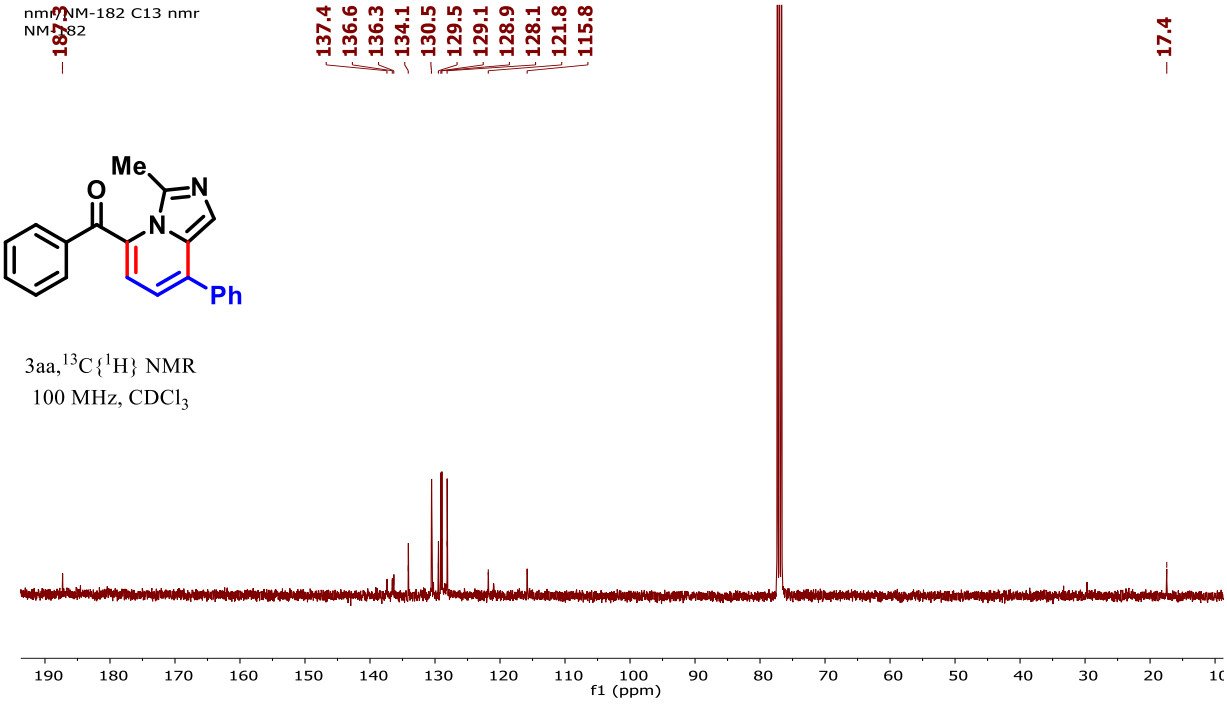
[b]Department of Chemistry, Birla Institute of Technology and Science Pilani, Hyderabad Campus, Telangana, 500078, India

E-mail: anilkumar@pilani.bits-pilani.ac.in

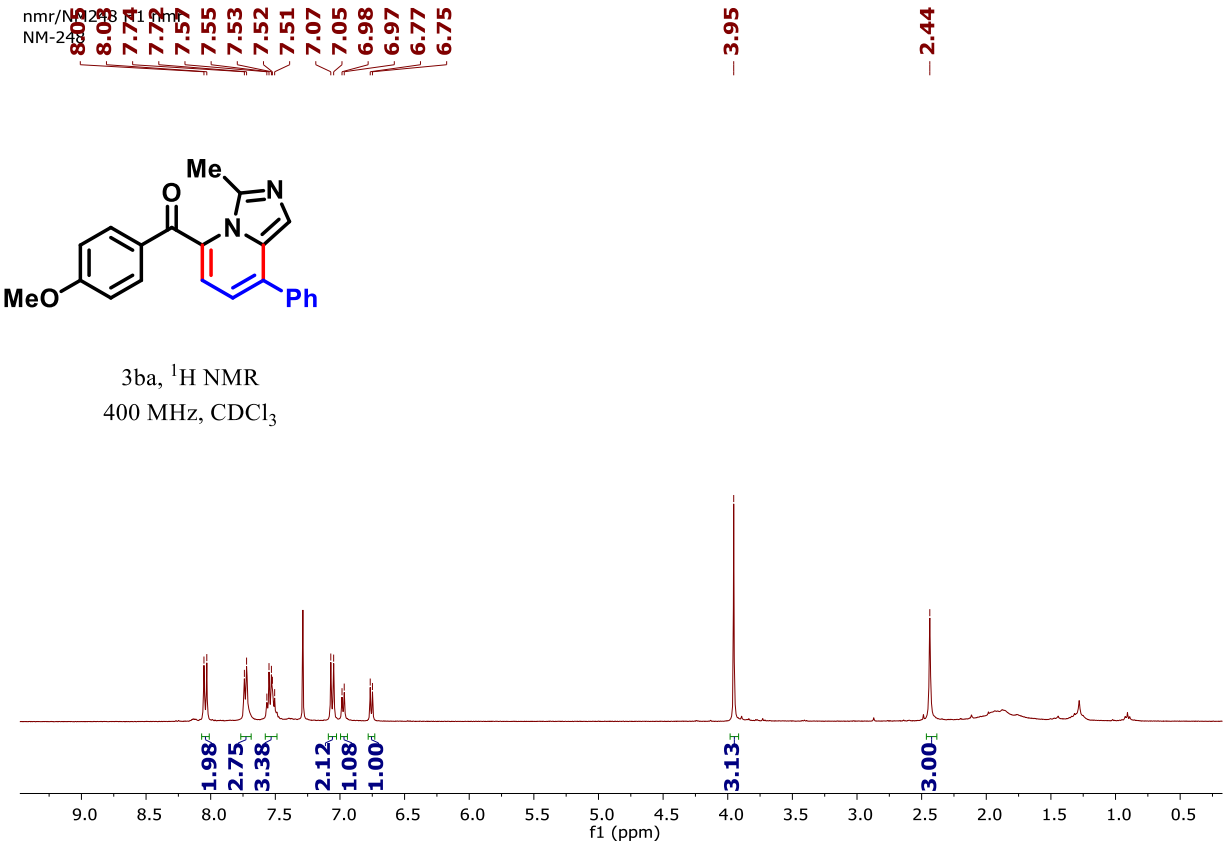
1. Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **3aa-fc**, **5**, **7aa-la** and **8ac**.

3aa, ^{1}H NMR
400 MHz, $CDCl_3$

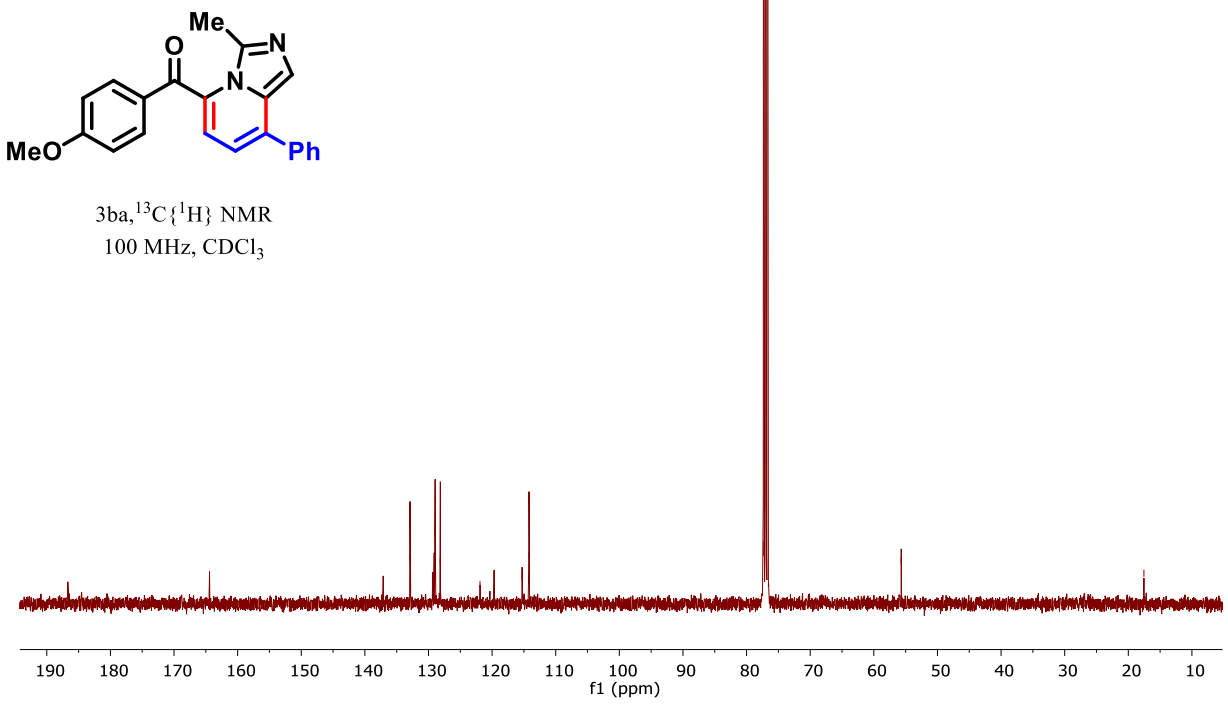




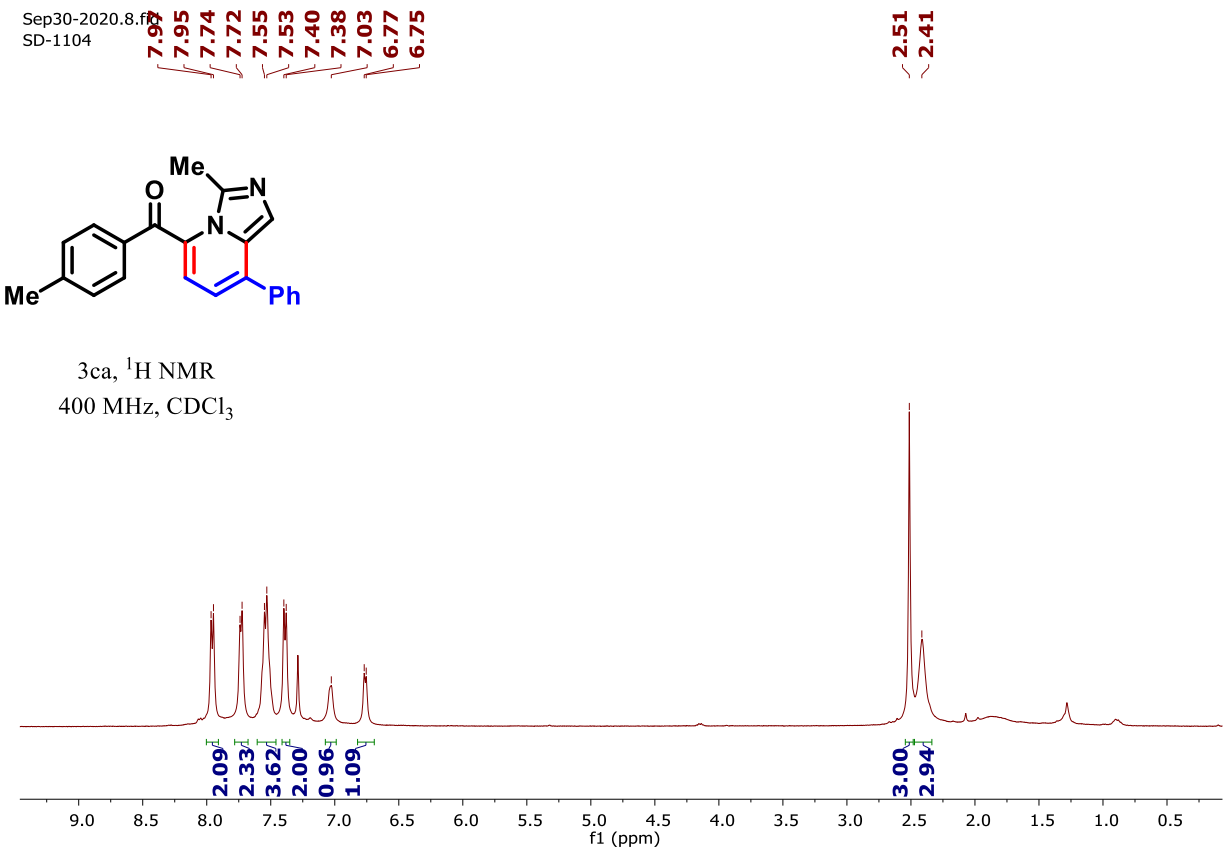
3aa, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



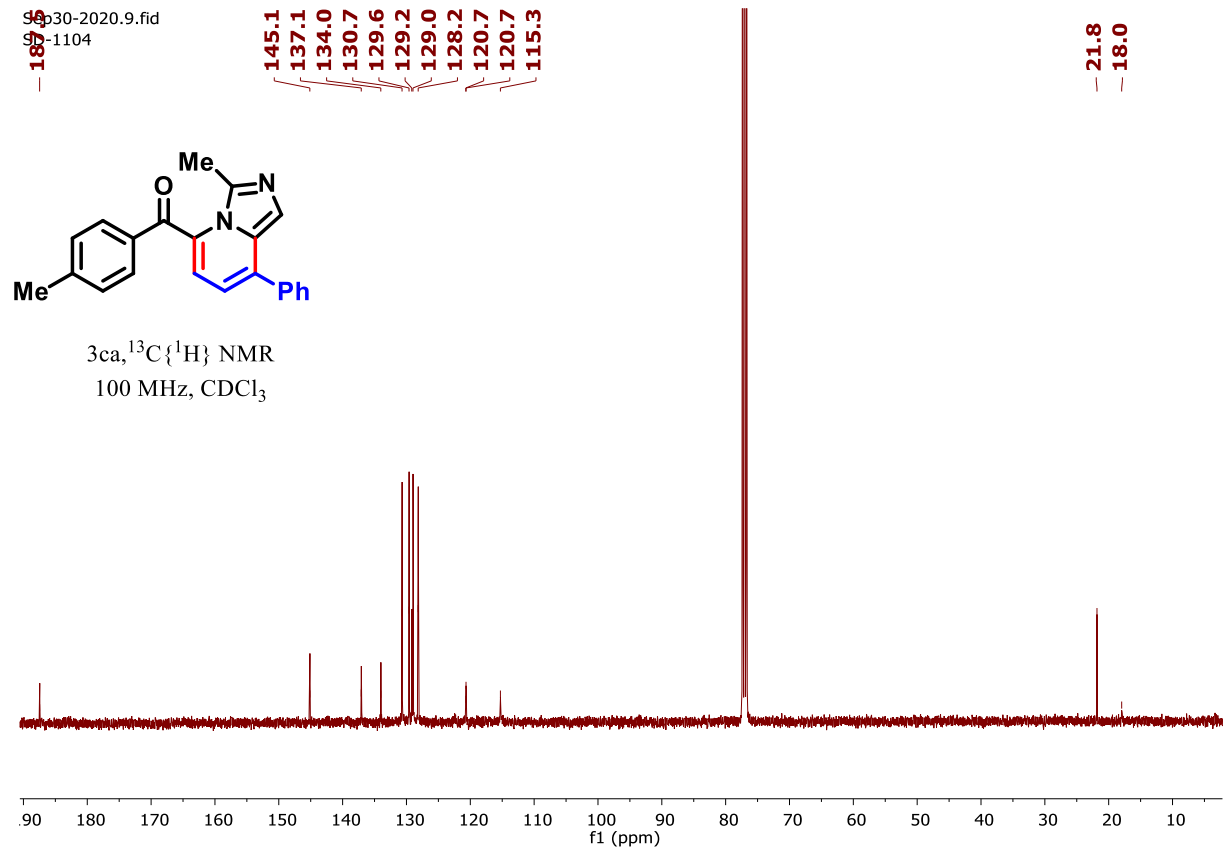
3ba, ^{1}H NMR
400 MHz, $CDCl_3$



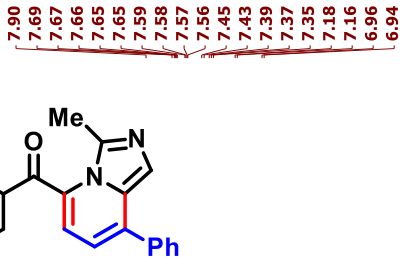
3ba, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



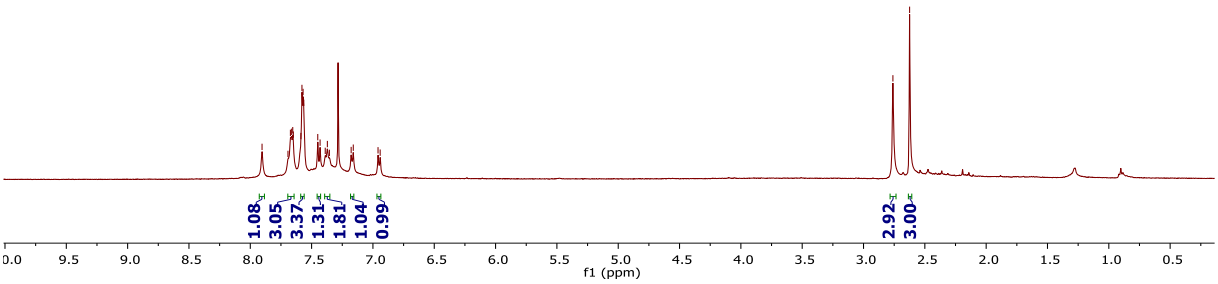
3ca, ^{1}H NMR
400 MHz, $CDCl_3$

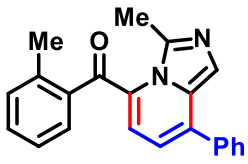


3ca, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$

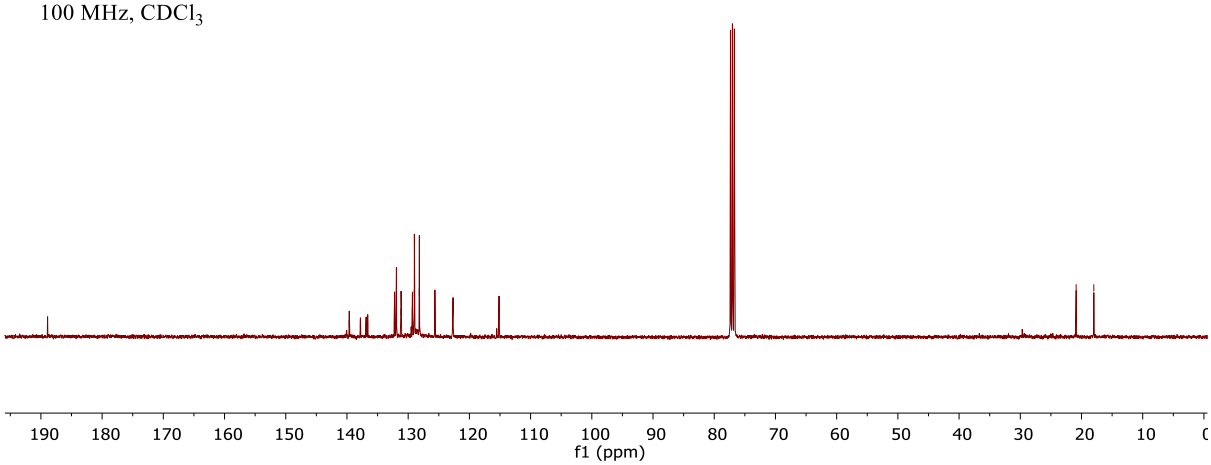


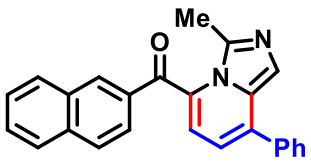
3da, ^{1}H NMR
400 MHz, $CDCl_3$



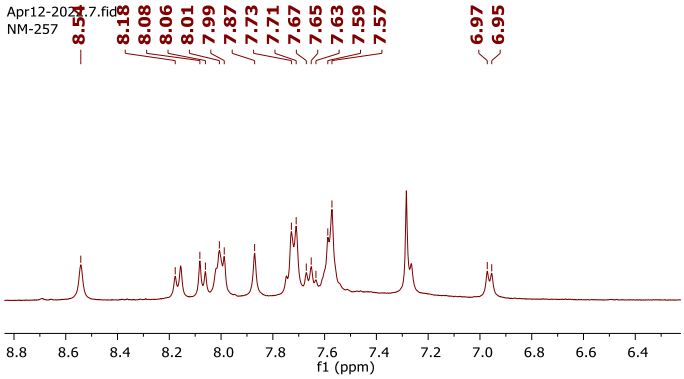


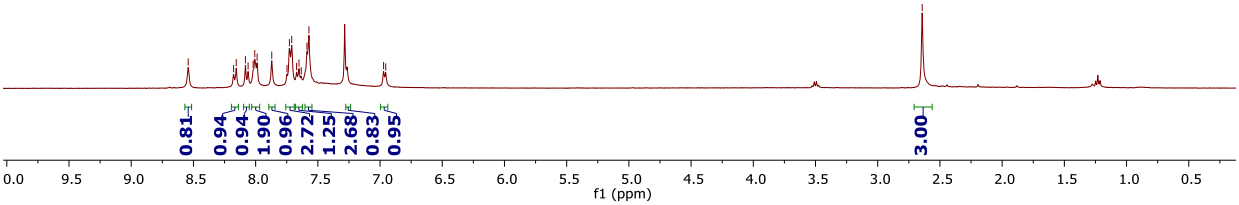
3da $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$

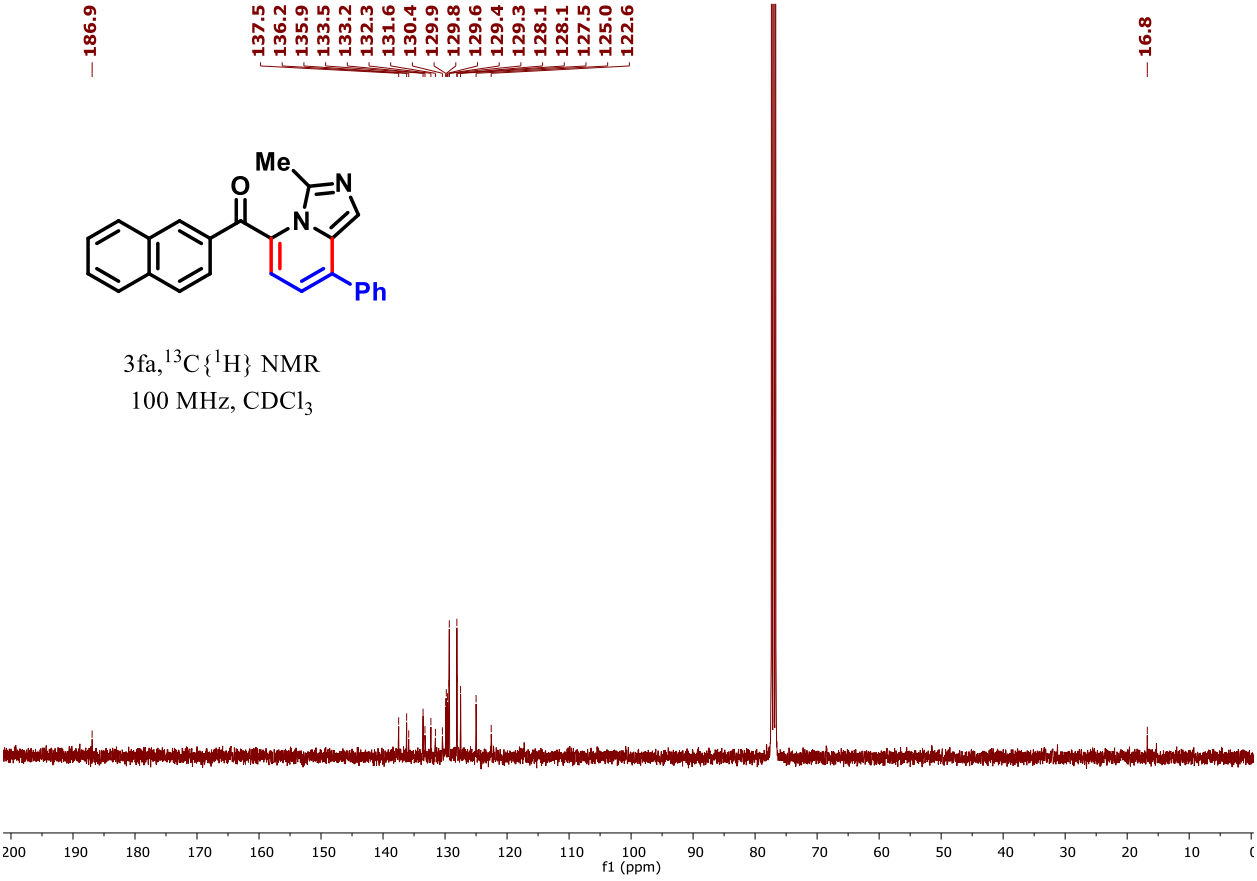




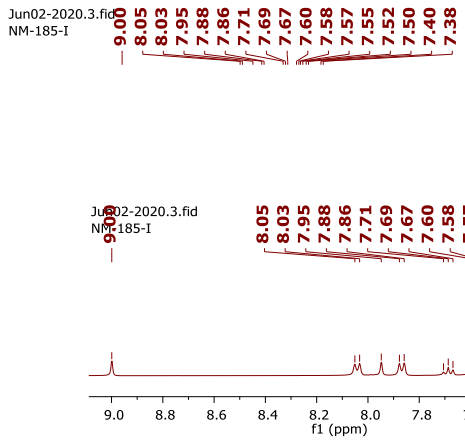
3fa, ^{1}H NMR
400 MHz, $CDCl_3$

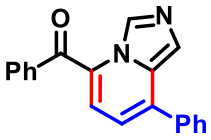




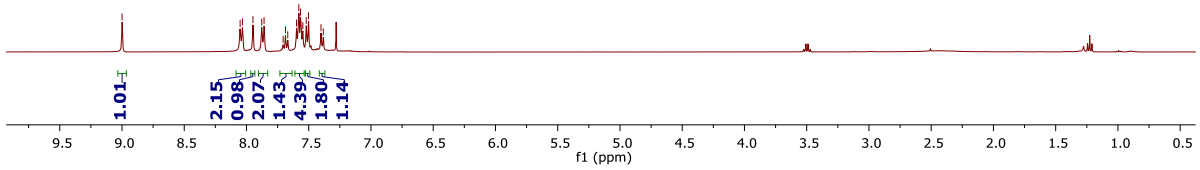


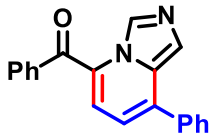
3fa, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



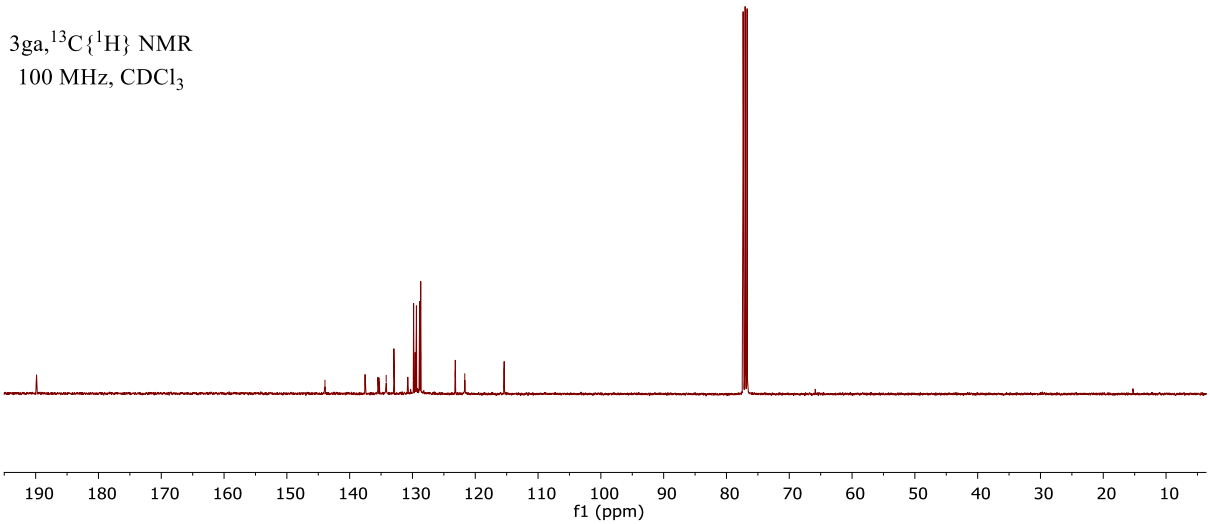


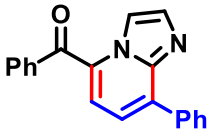
3ga, ^{1}H NMR
400 MHz, $CDCl_3$



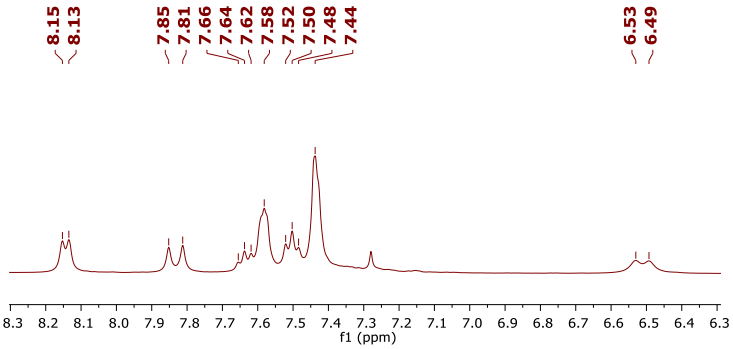


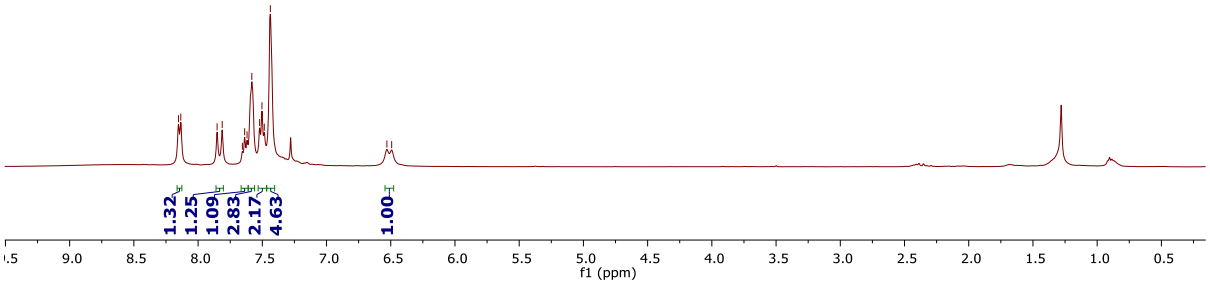
3ga,^{13}C{^{1}H} NMR
100 MHz, $CDCl_3$

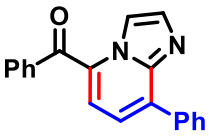




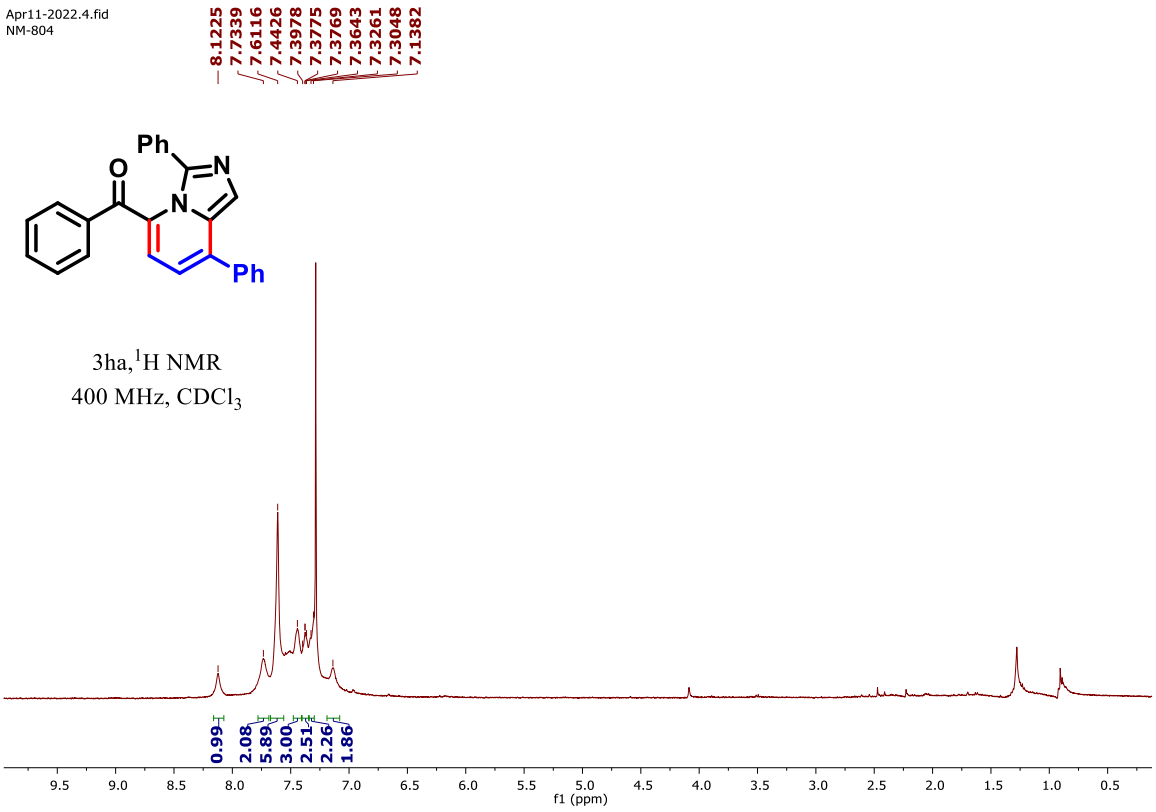
4ga, ^{1}H NMR
400 MHz, $CDCl_3$



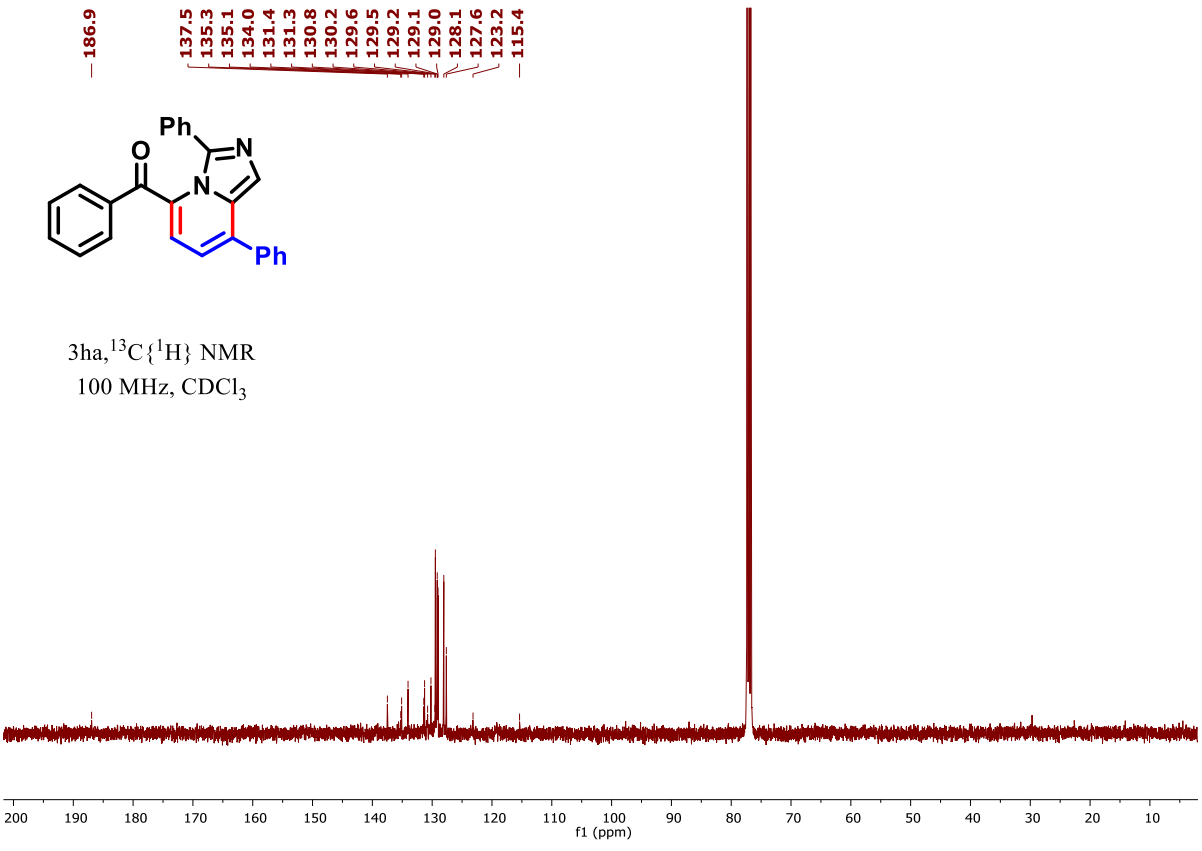




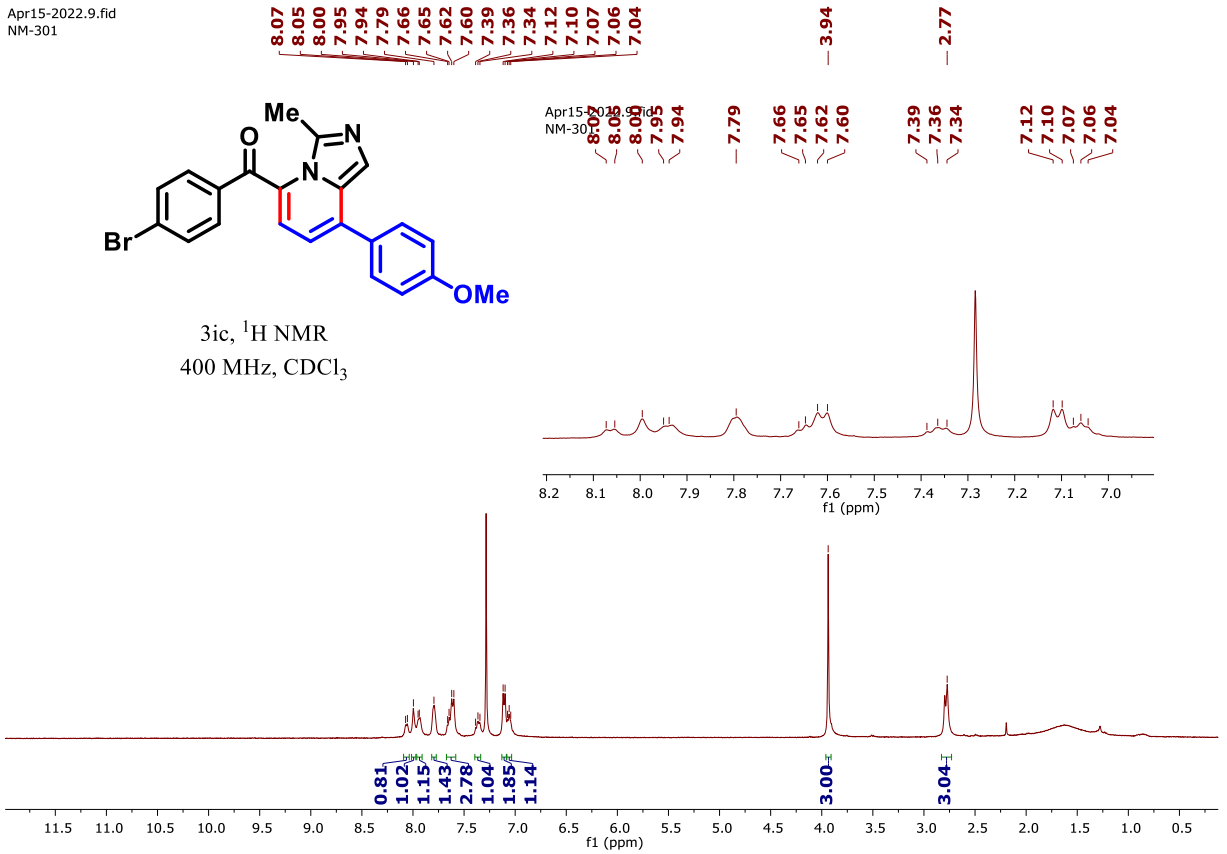
4ga, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



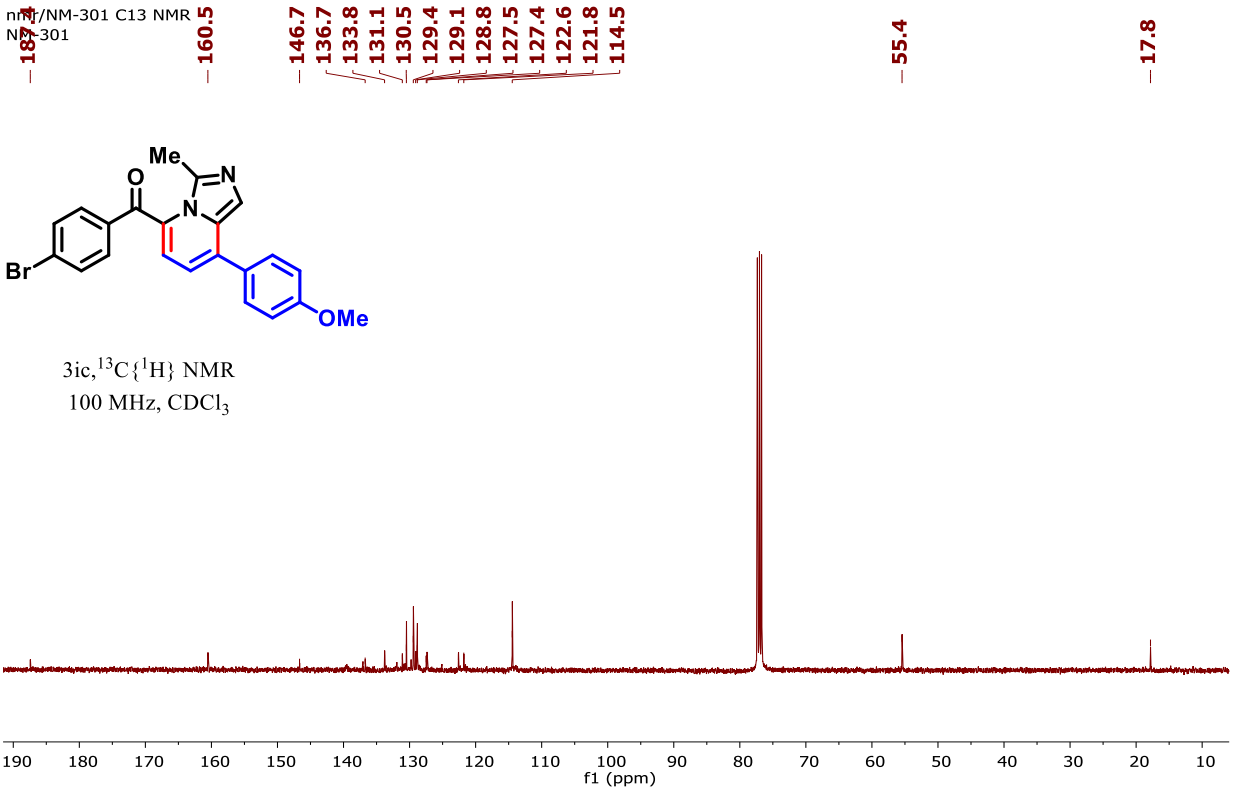
3ha, ^{1}H NMR
400 MHz, $CDCl_3$



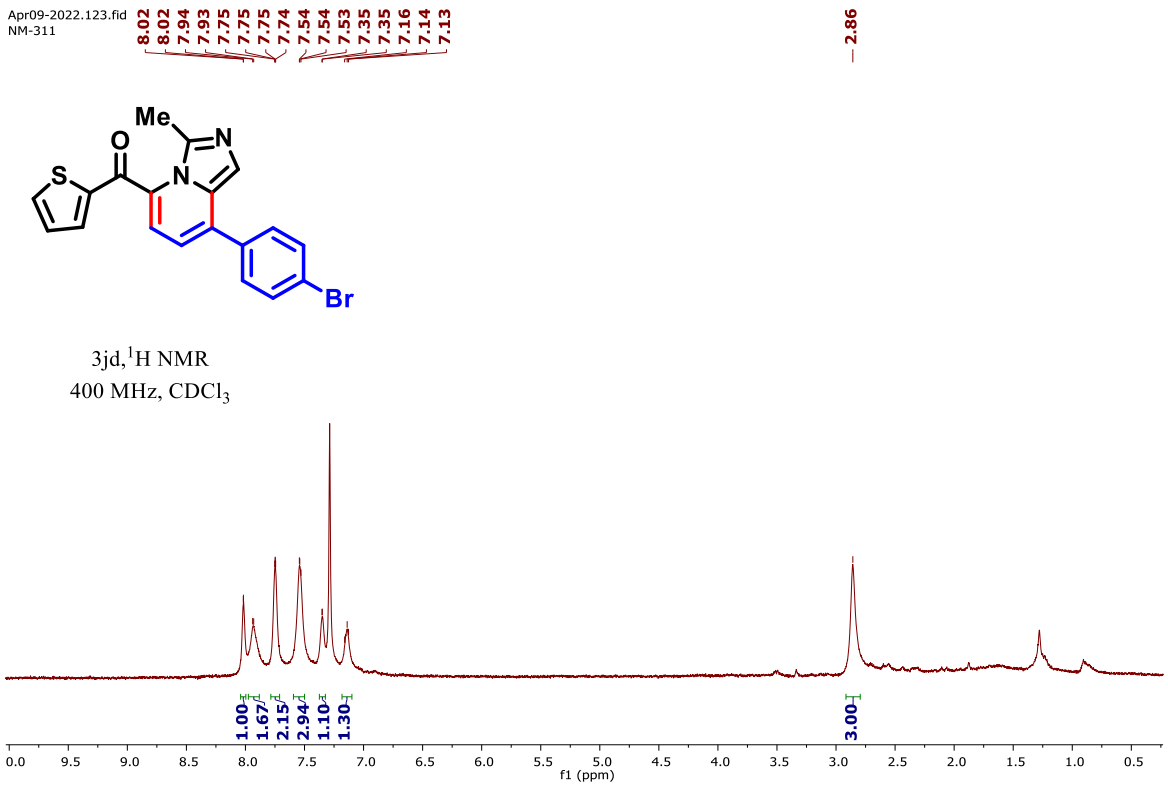
3ha, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



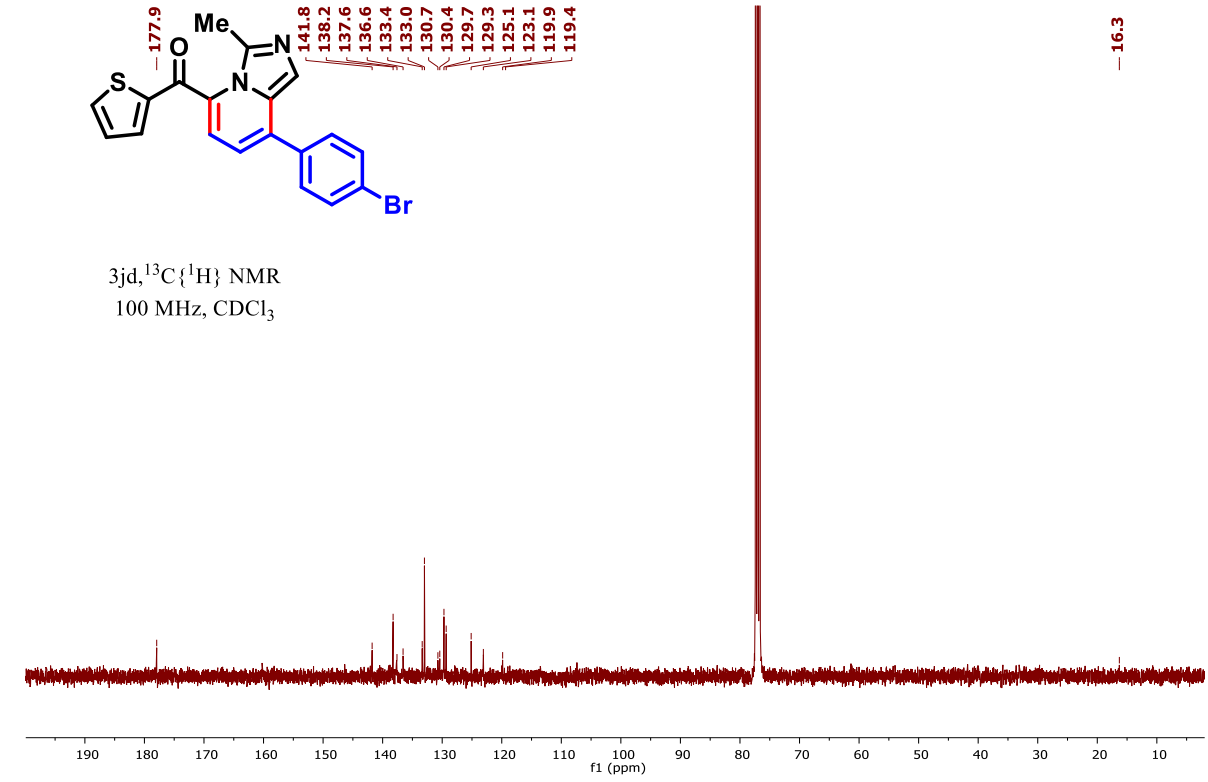
3ic, ^{1}H NMR
400 MHz, $CDCl_3$



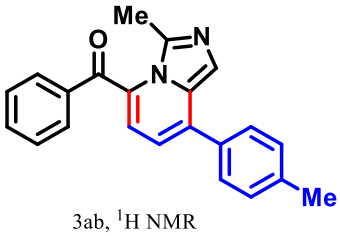
3ic,$^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



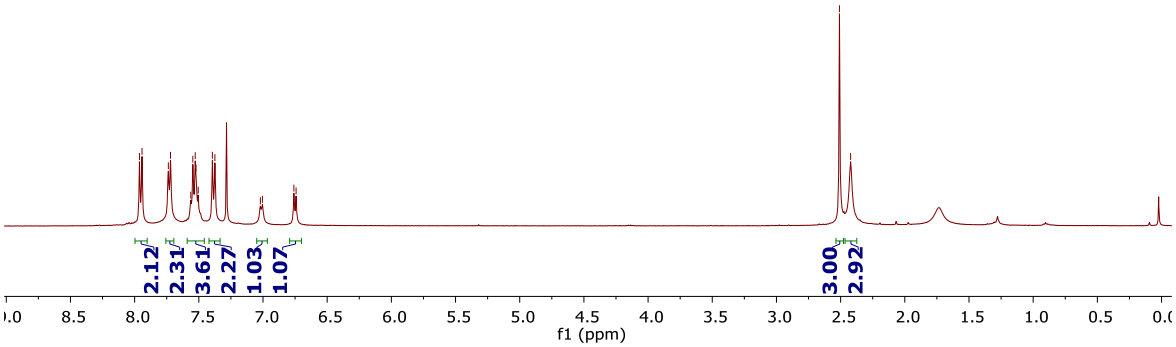
3jd,^{1}H NMR
400 MHz, $CDCl_3$

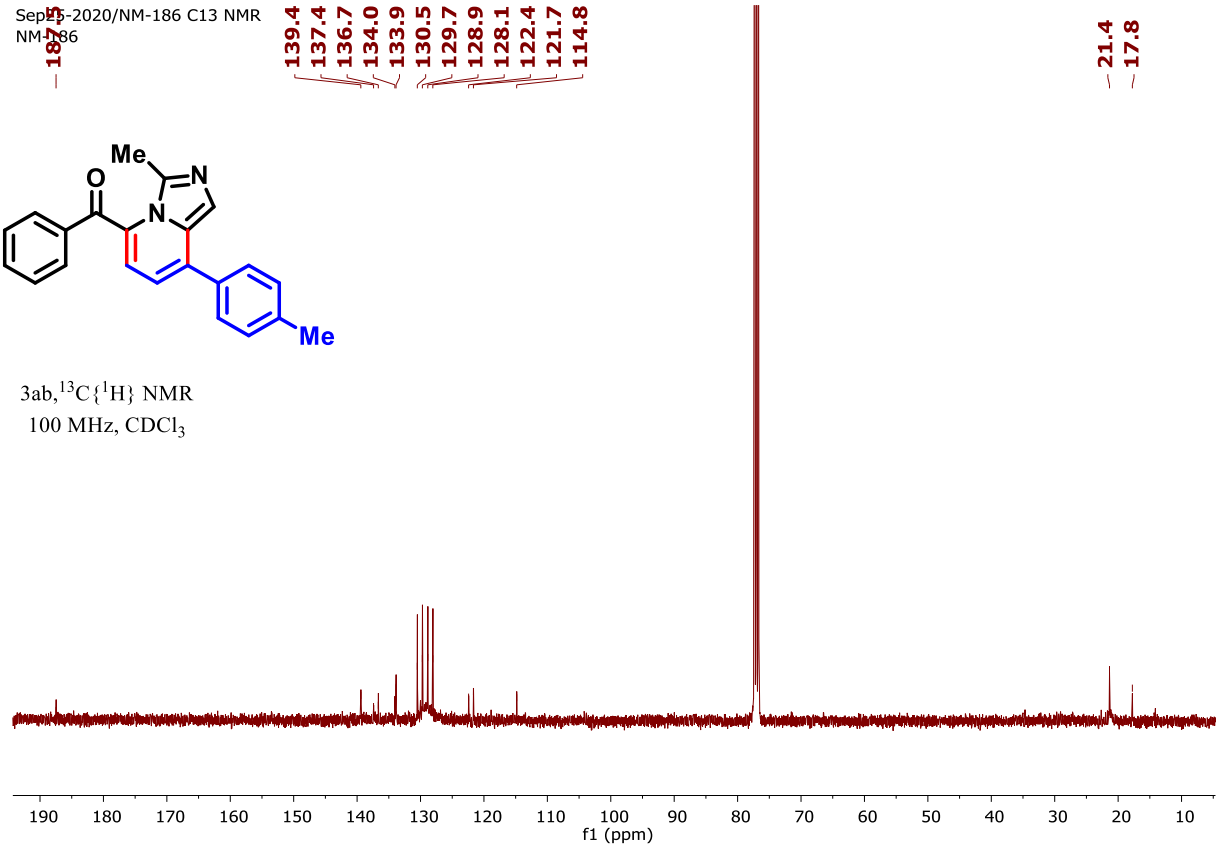


3jd,^{13}C{^{1}H} NMR
100 MHz, $CDCl_3$

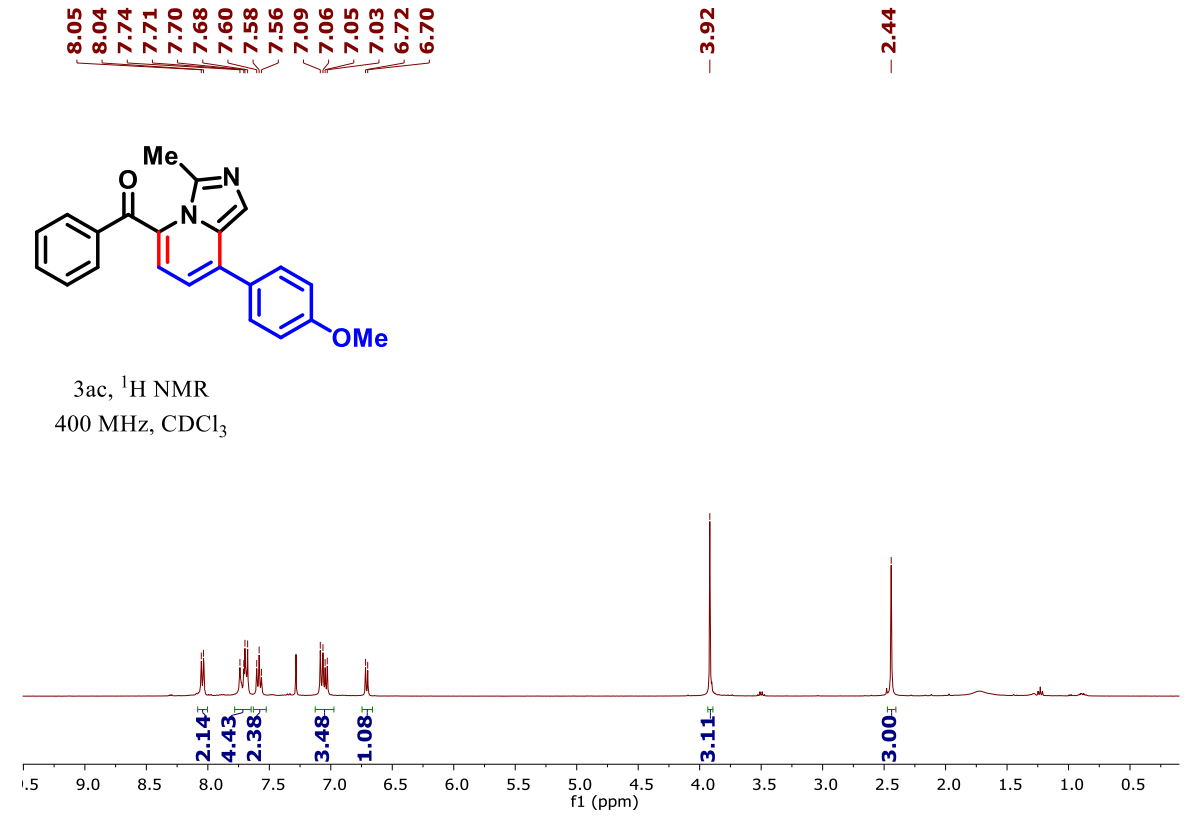


3ab, ^{1}H NMR
400 MHz, $CDCl_3$

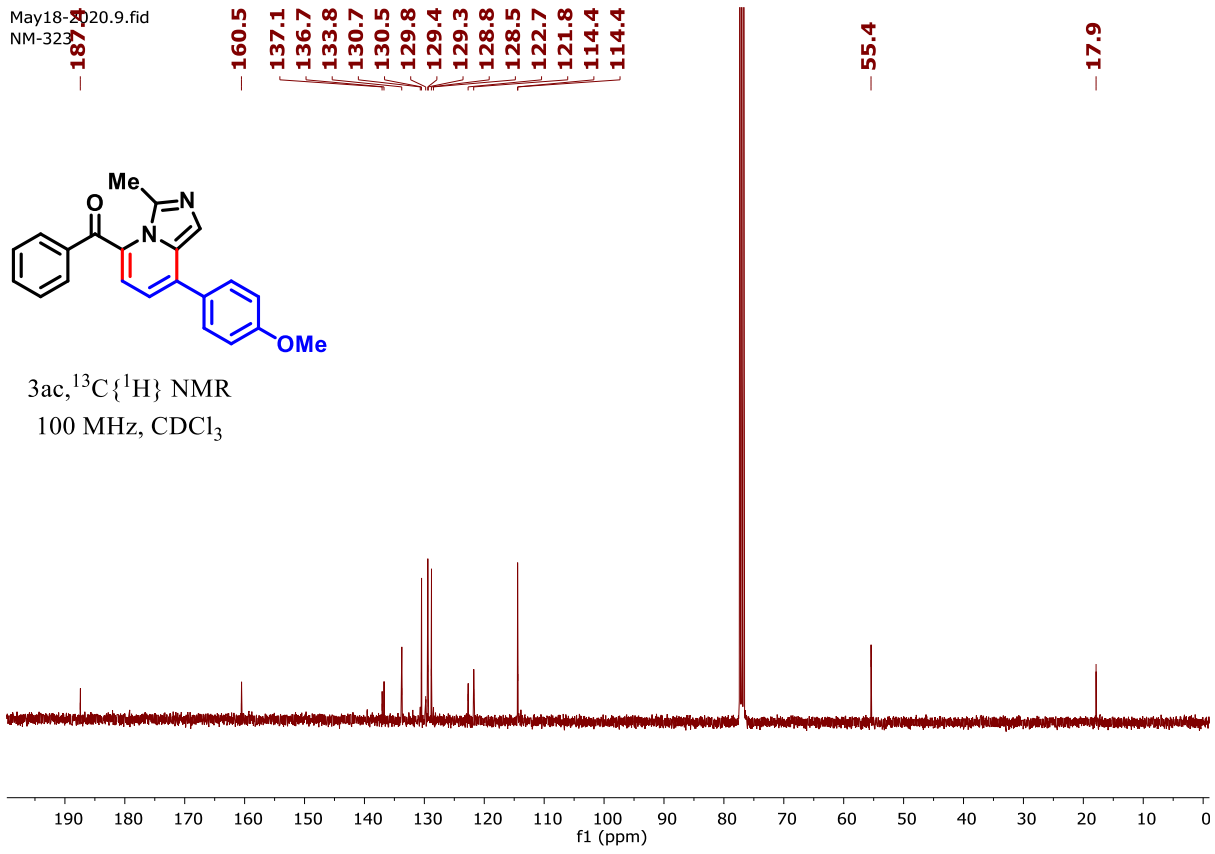




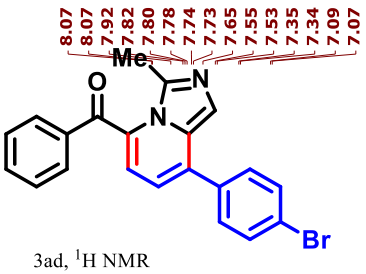
3ab, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



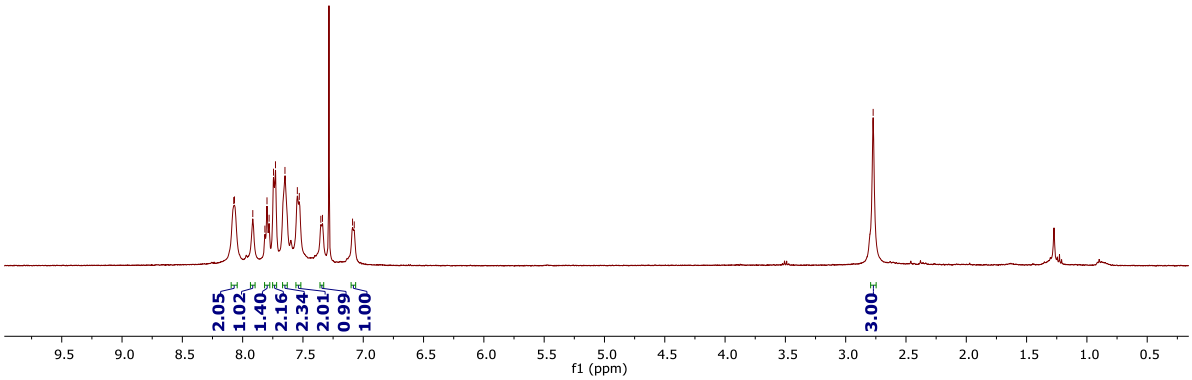
3ac, ^{1}H NMR
400 MHz, $CDCl_3$

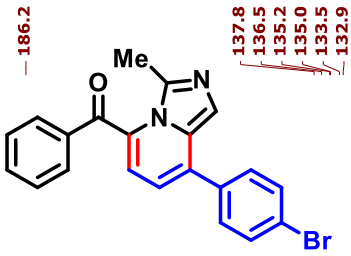


3ac,^{13}C{^{1}H} NMR
100 MHz, $CDCl_3$

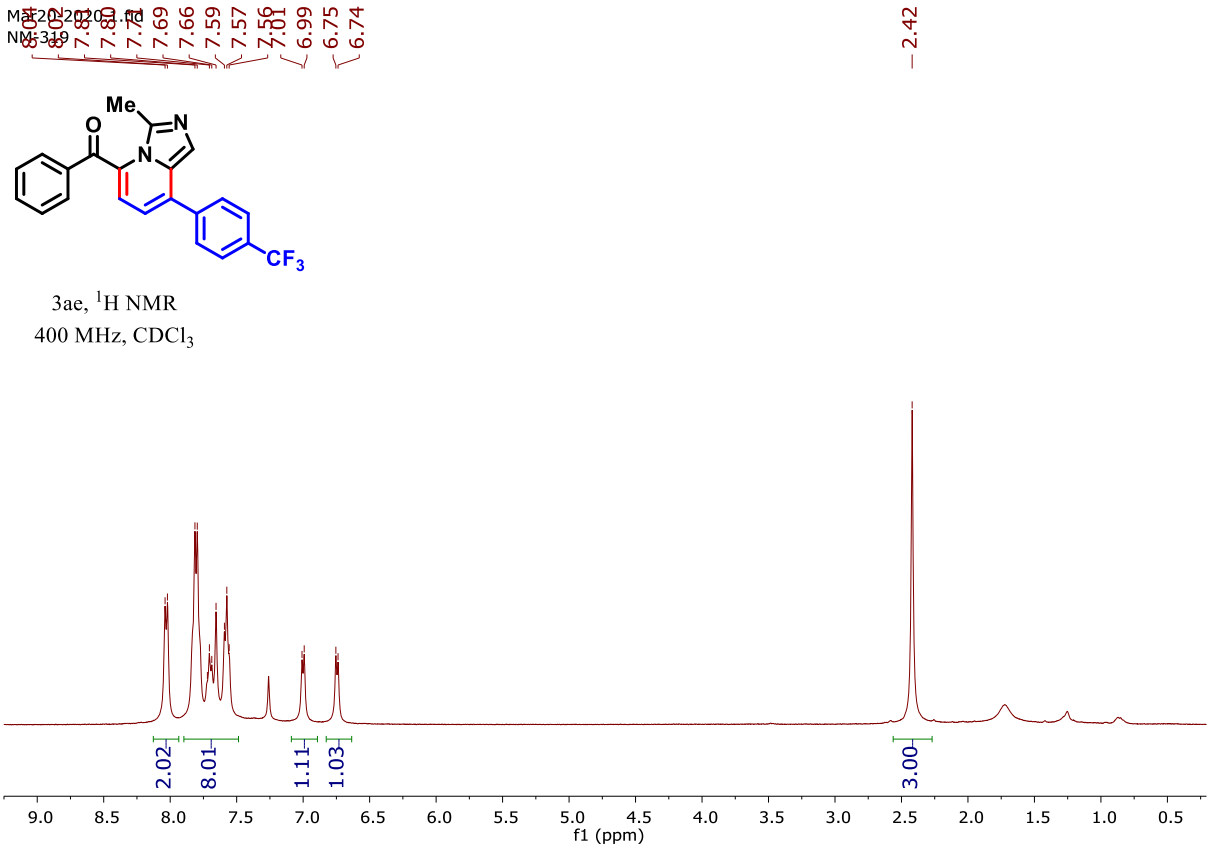


3ad, ^{1}H NMR
400 MHz, $CDCl_3$

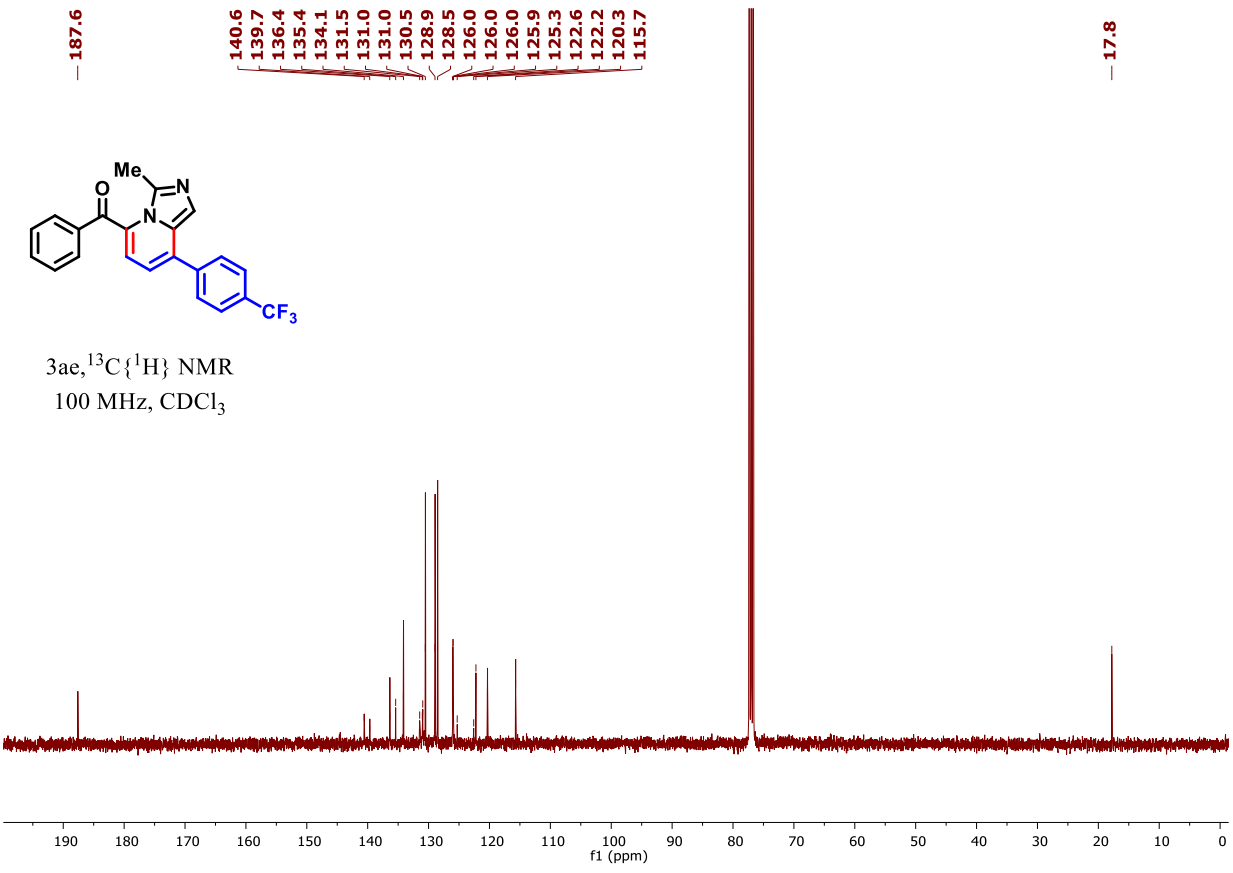




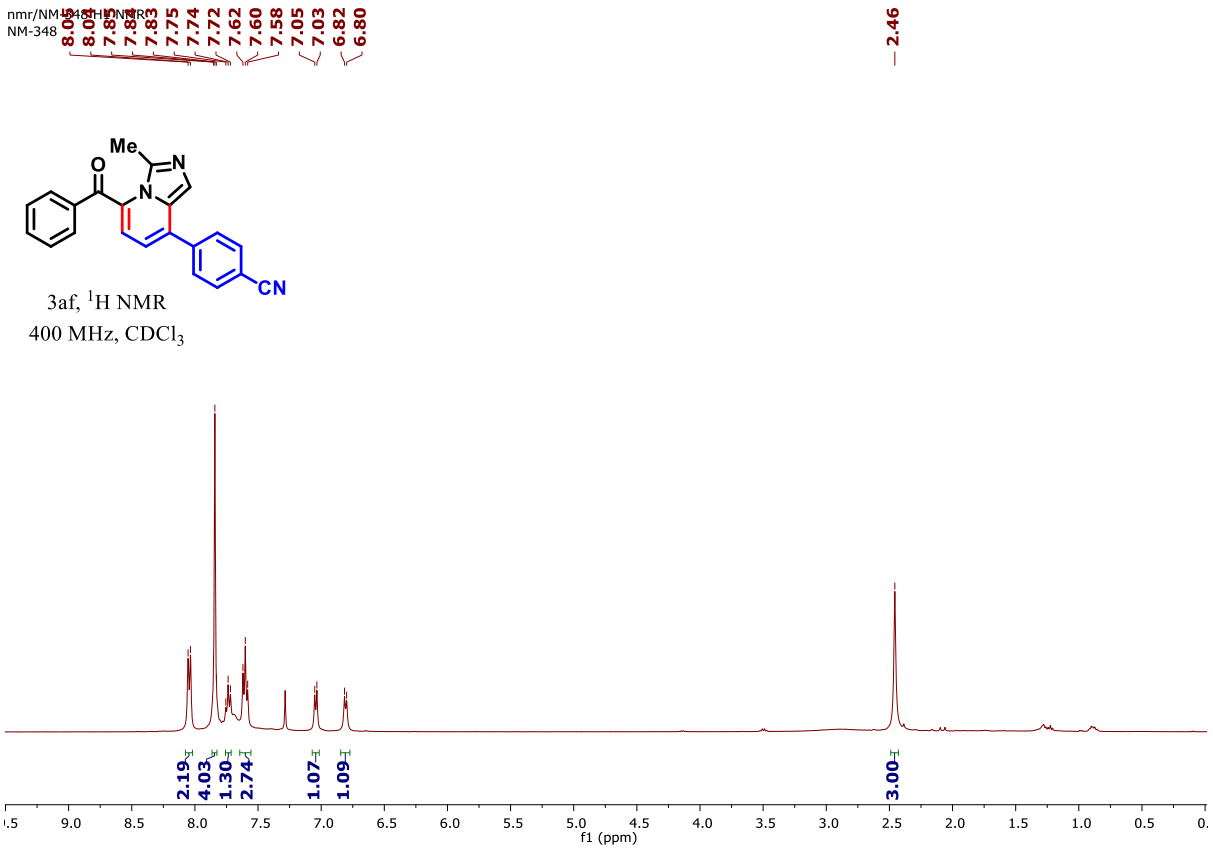
3ad, ^{13}C NMR
100 MHz, $CDCl_3$



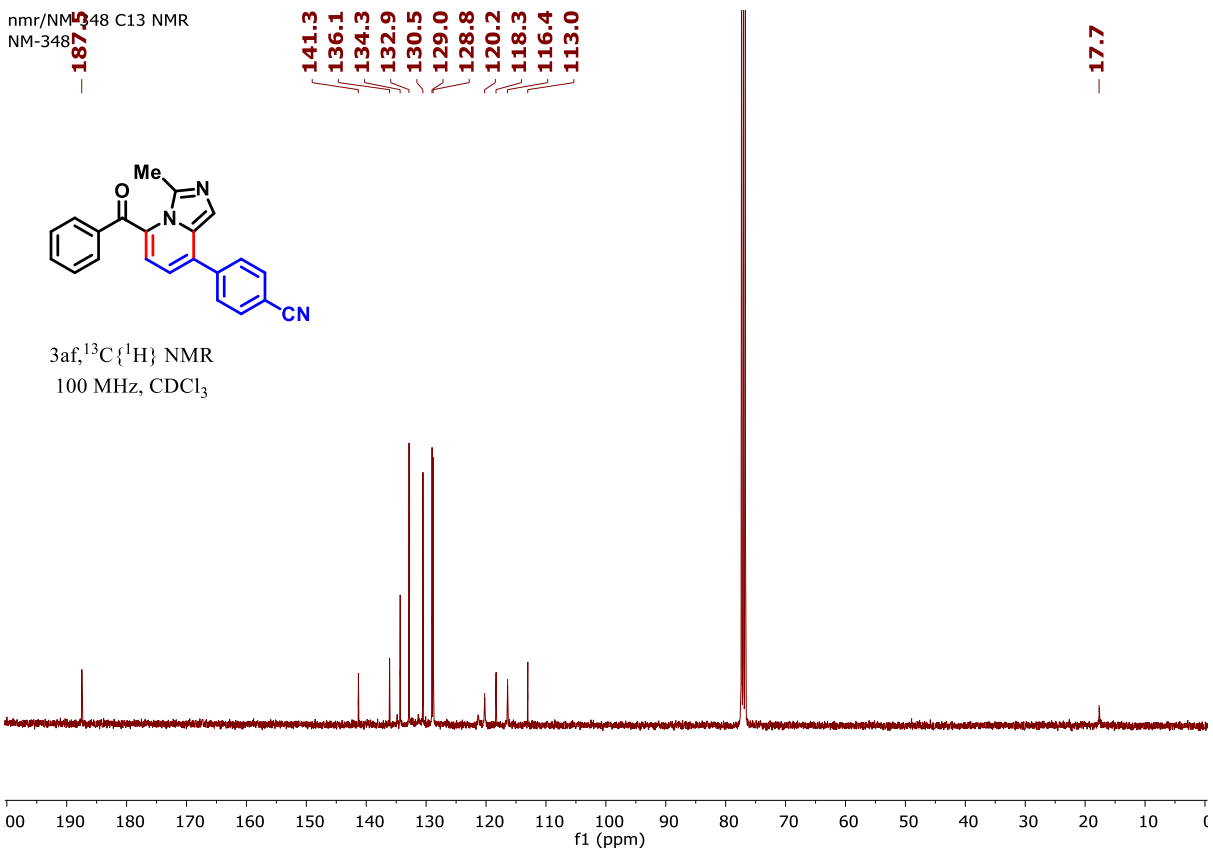
3ae, ^{1}H NMR
400 MHz, $CDCl_3$



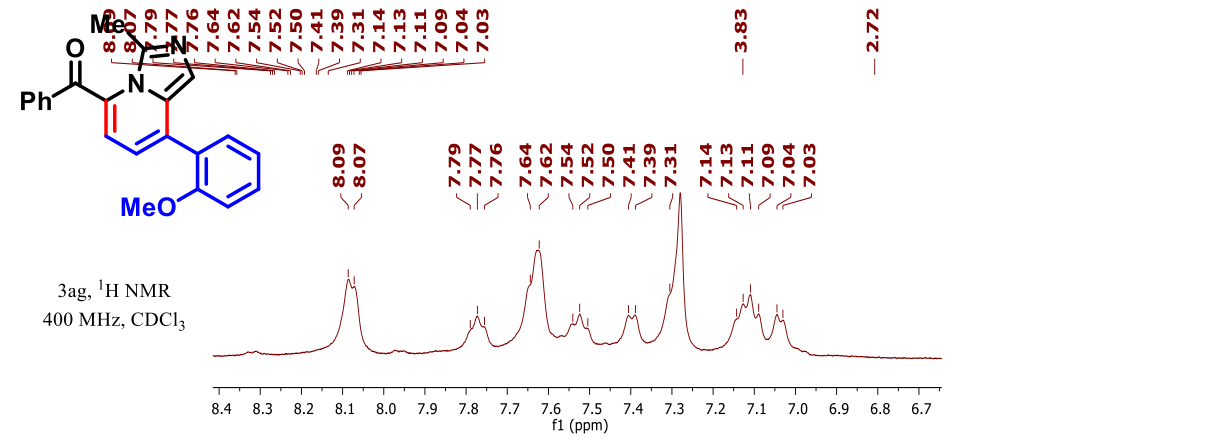
3ae, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



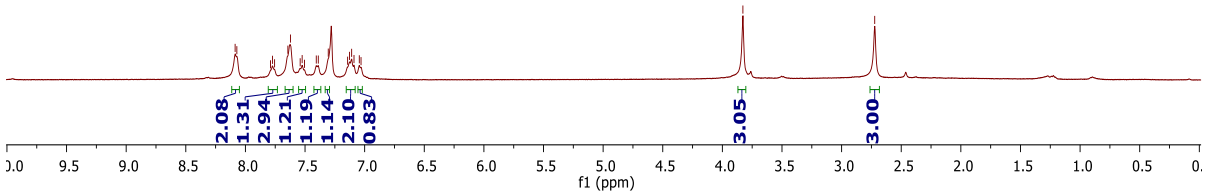
3af, ^{1}H NMR
400 MHz, $CDCl_3$

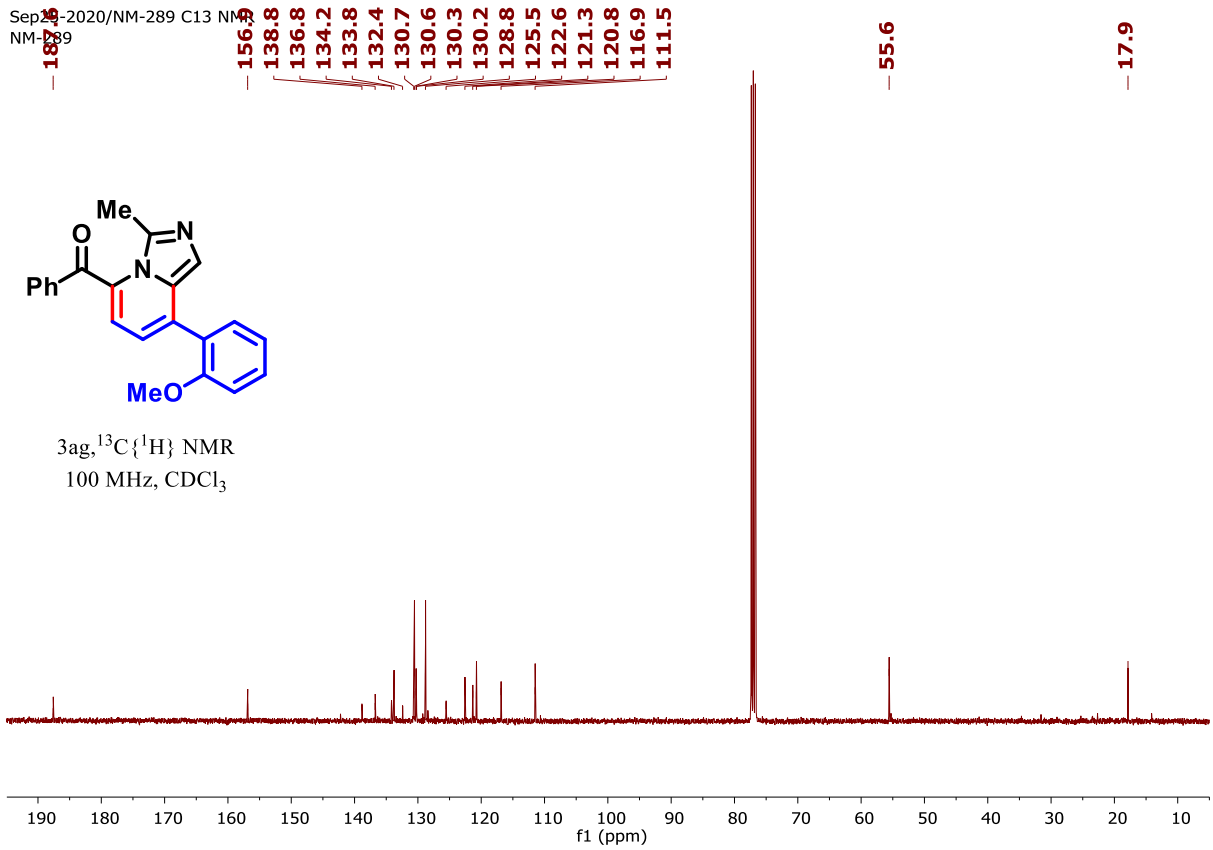


3af, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$

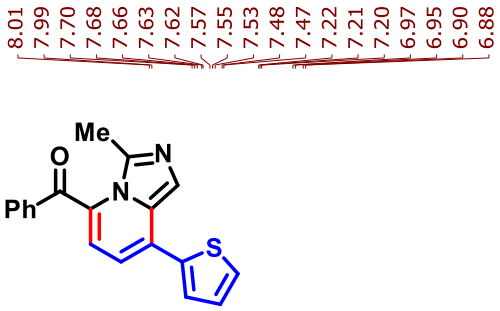


3ag, ^{1}H NMR
400 MHz, $CDCl_3$

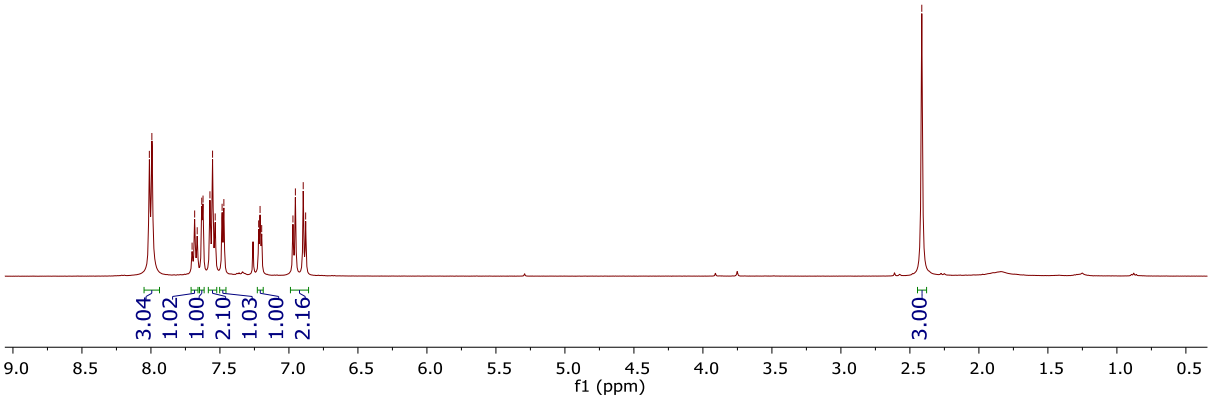


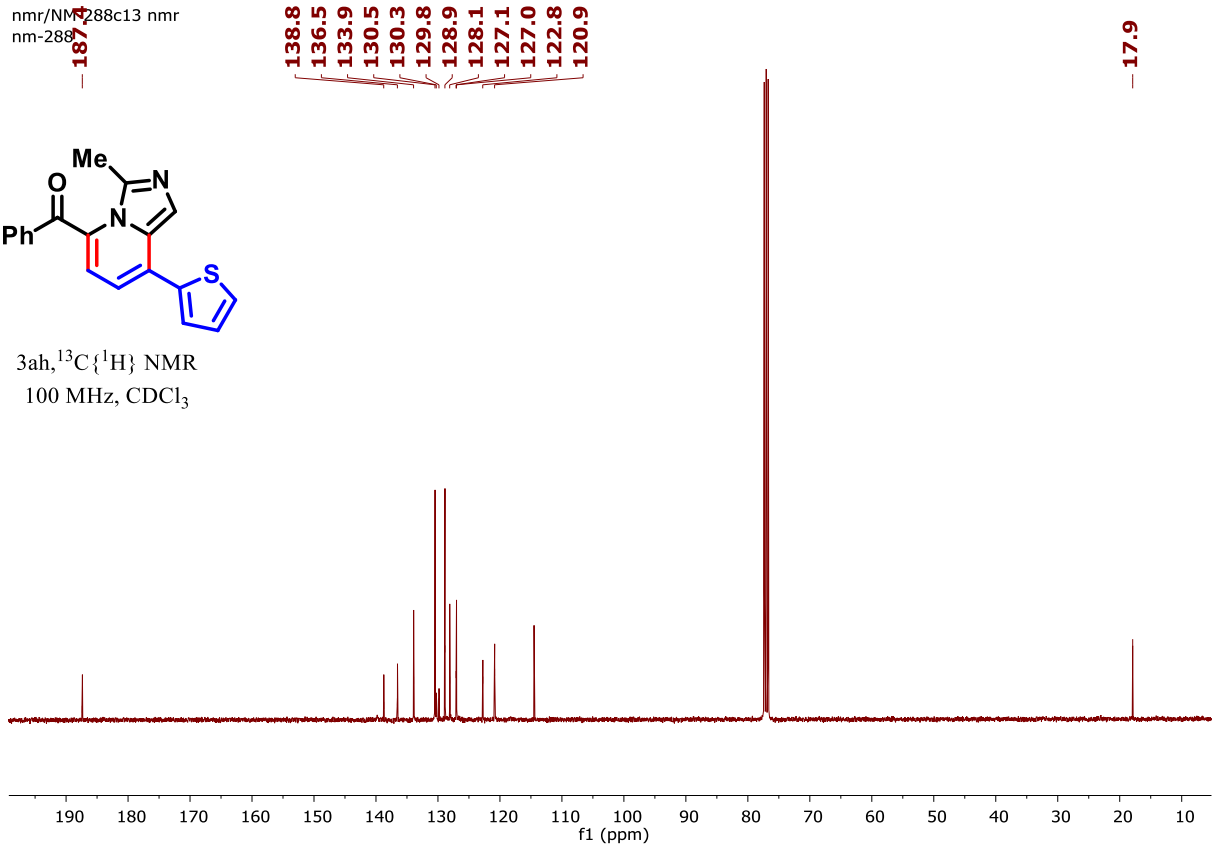


3ag, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$

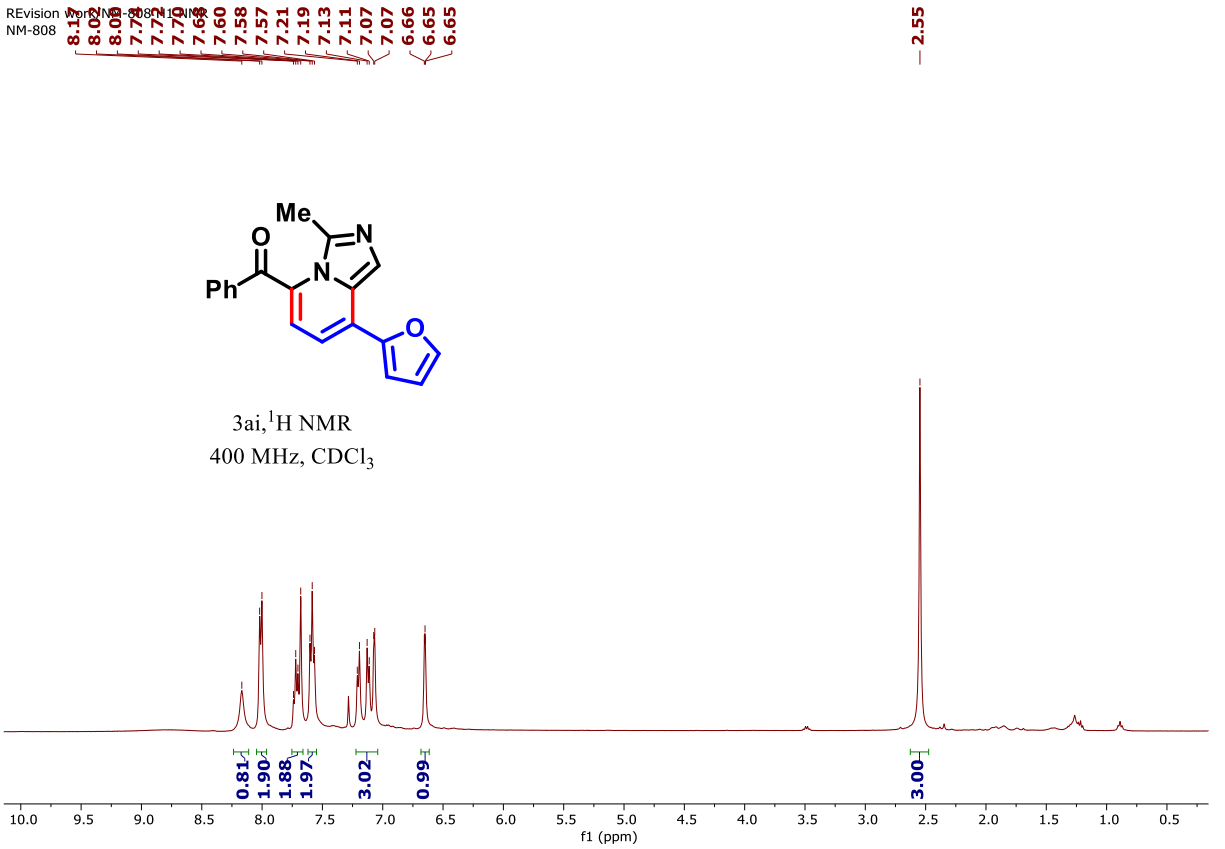


3ah, ^{1}H NMR
400 MHz, $CDCl_3$

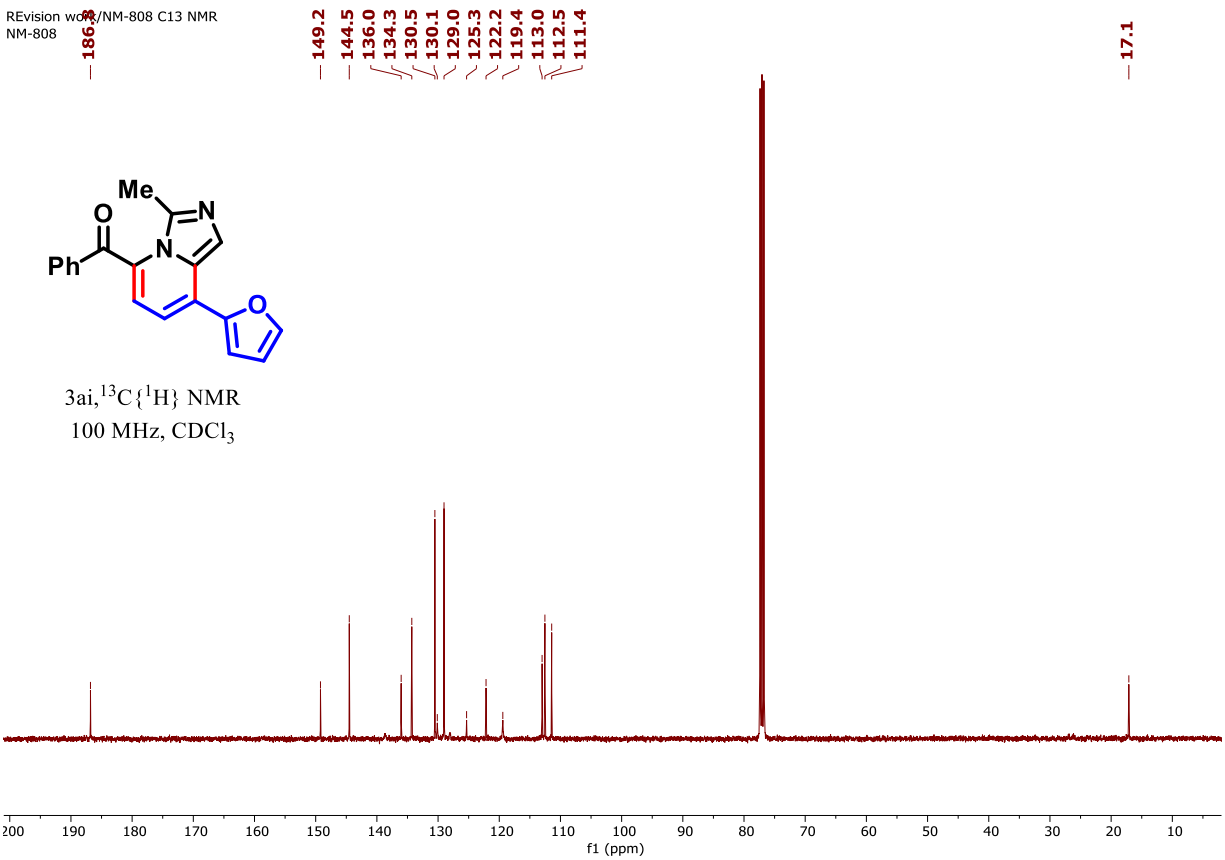




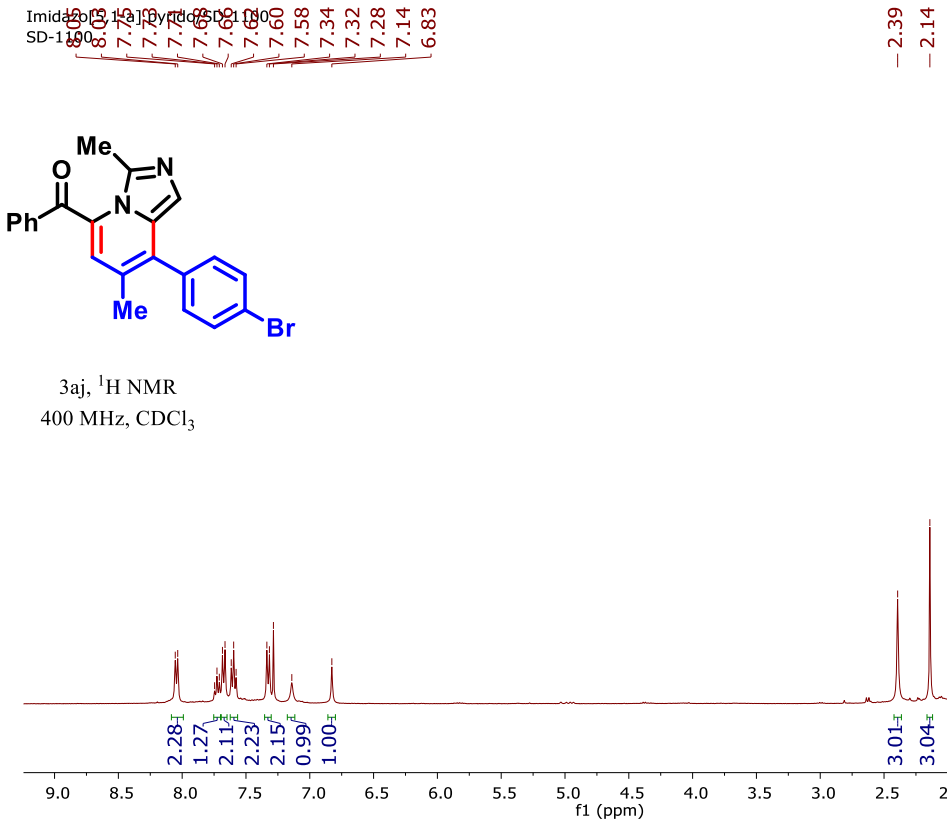
3ah, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



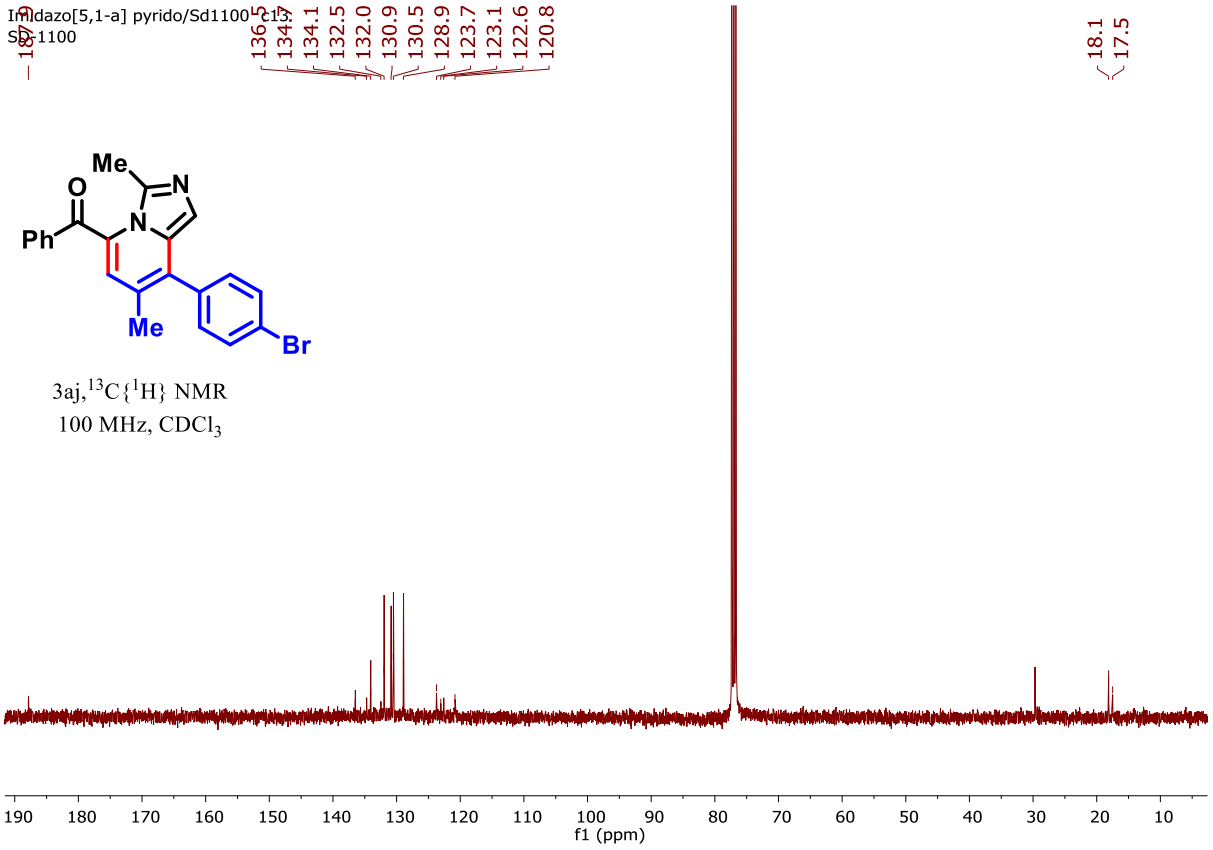
3ai, ^{1}H NMR
400 MHz, $CDCl_3$



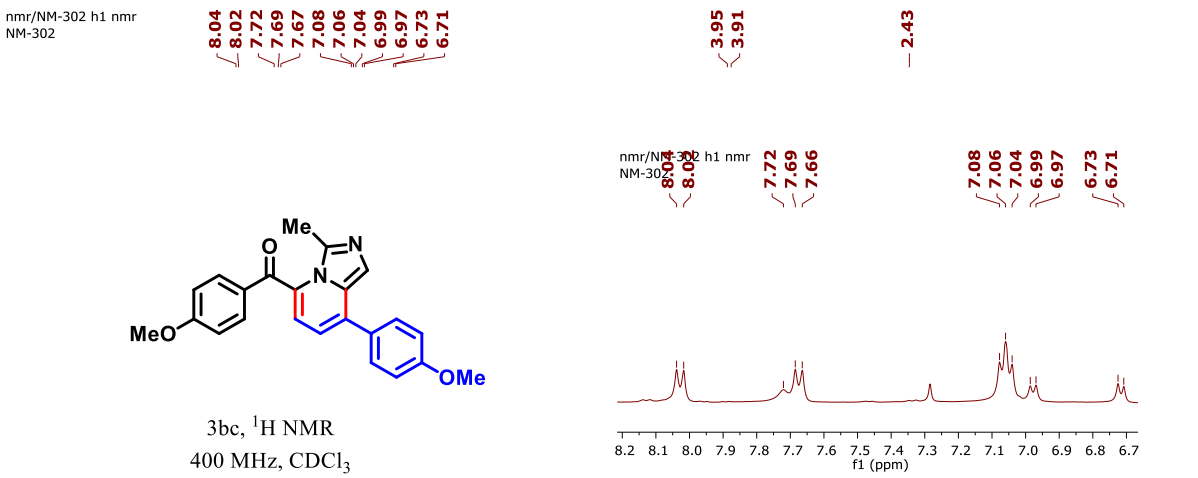
3ai, ^{13}C{^{1}H} NMR
100 MHz, $CDCl_3$



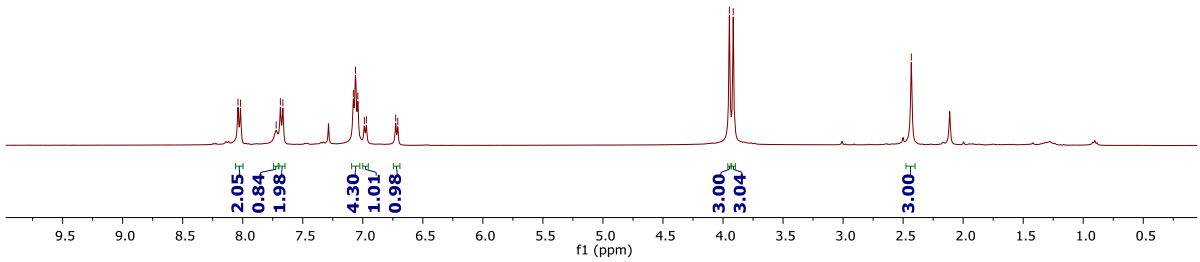
3aj, ^{1}H NMR
400 MHz, $CDCl_3$

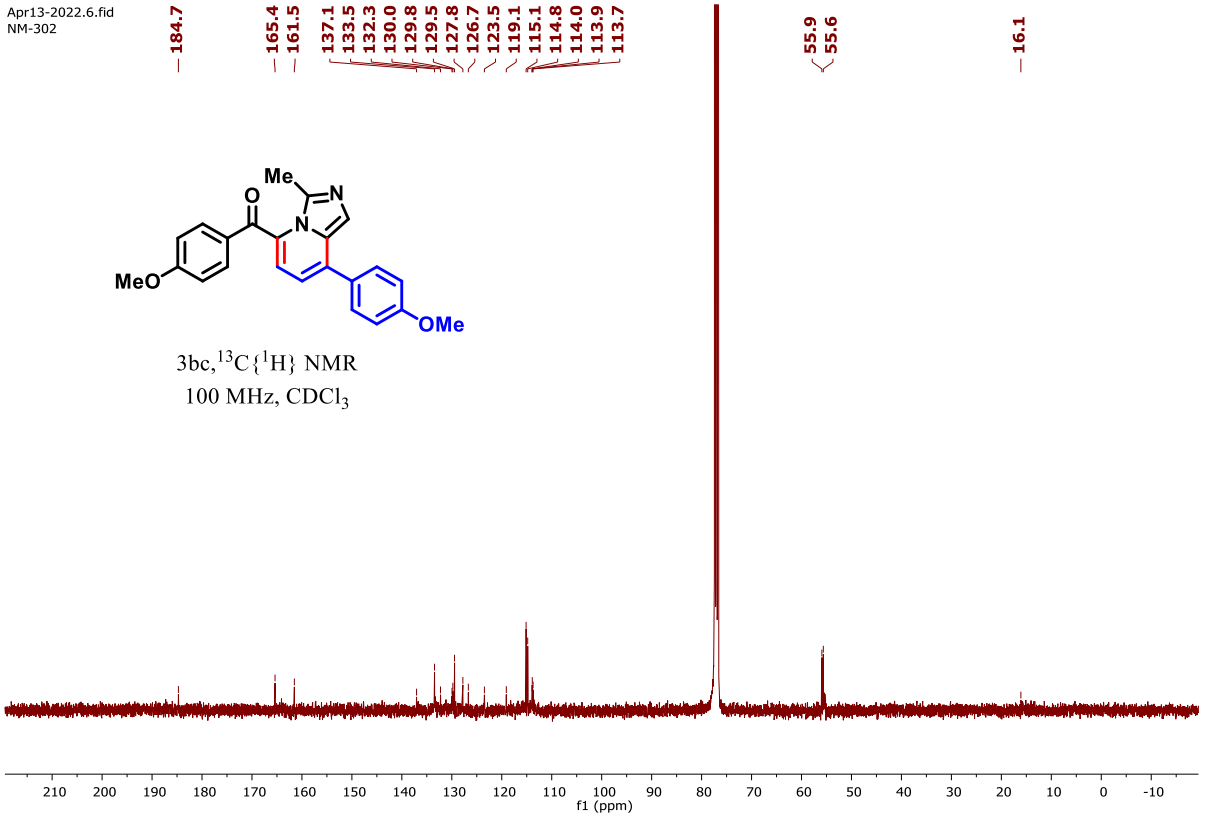


3aj, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$

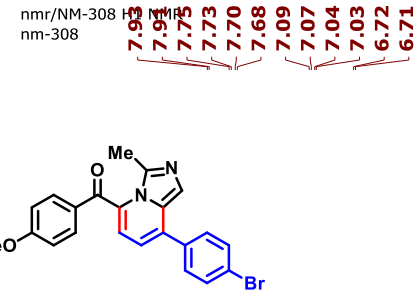


3bc, ^{1}H NMR
400 MHz, $CDCl_3$

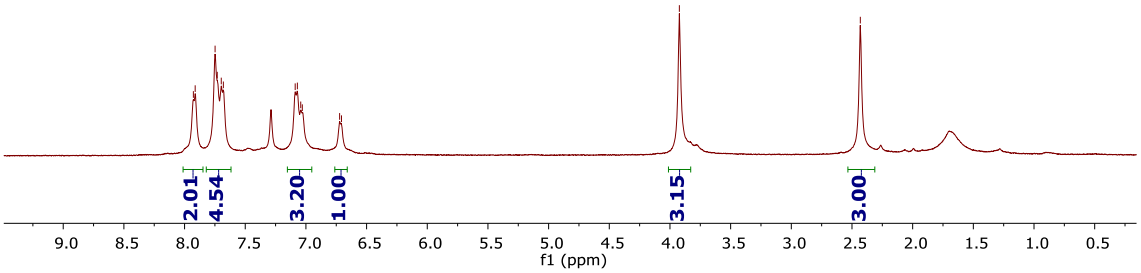


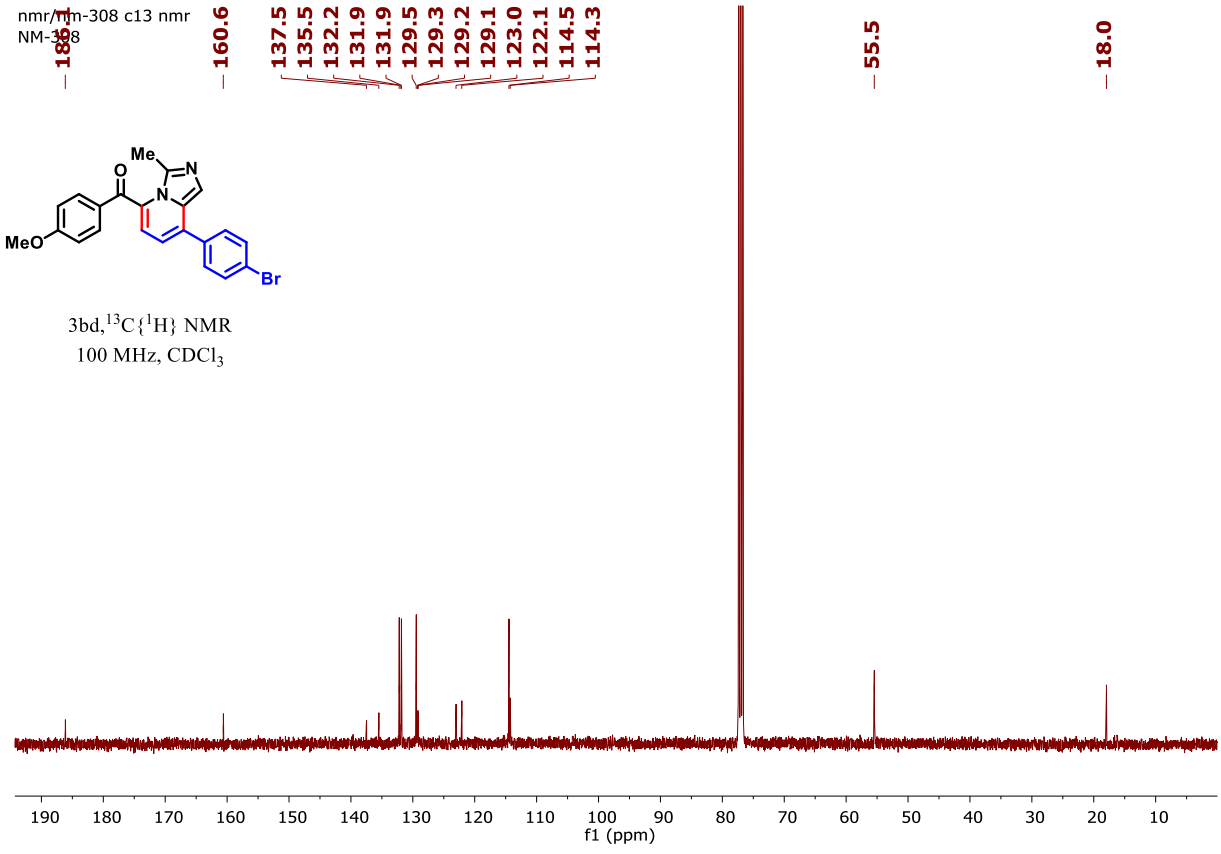


3bc, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$

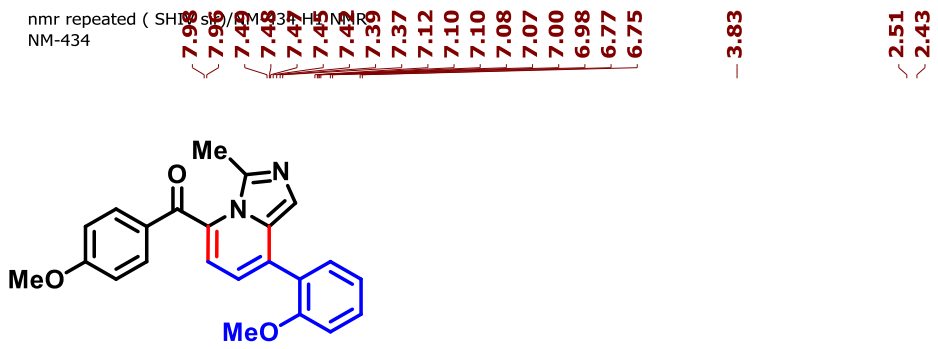


3bd, ^{1}H NMR
400 MHz, $CDCl_3$

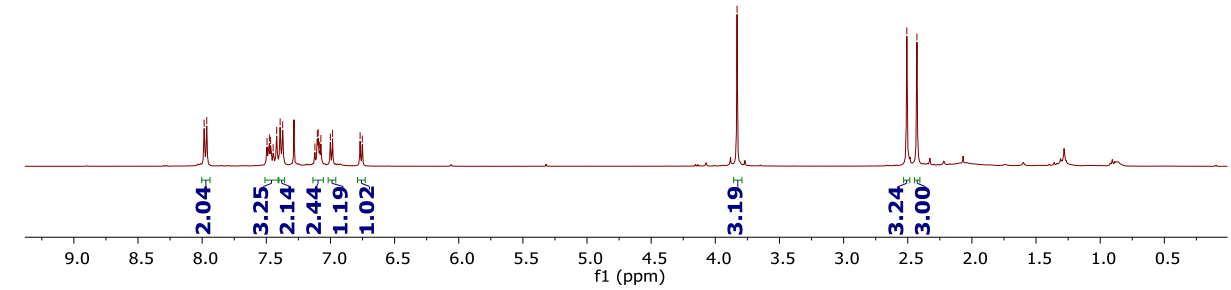


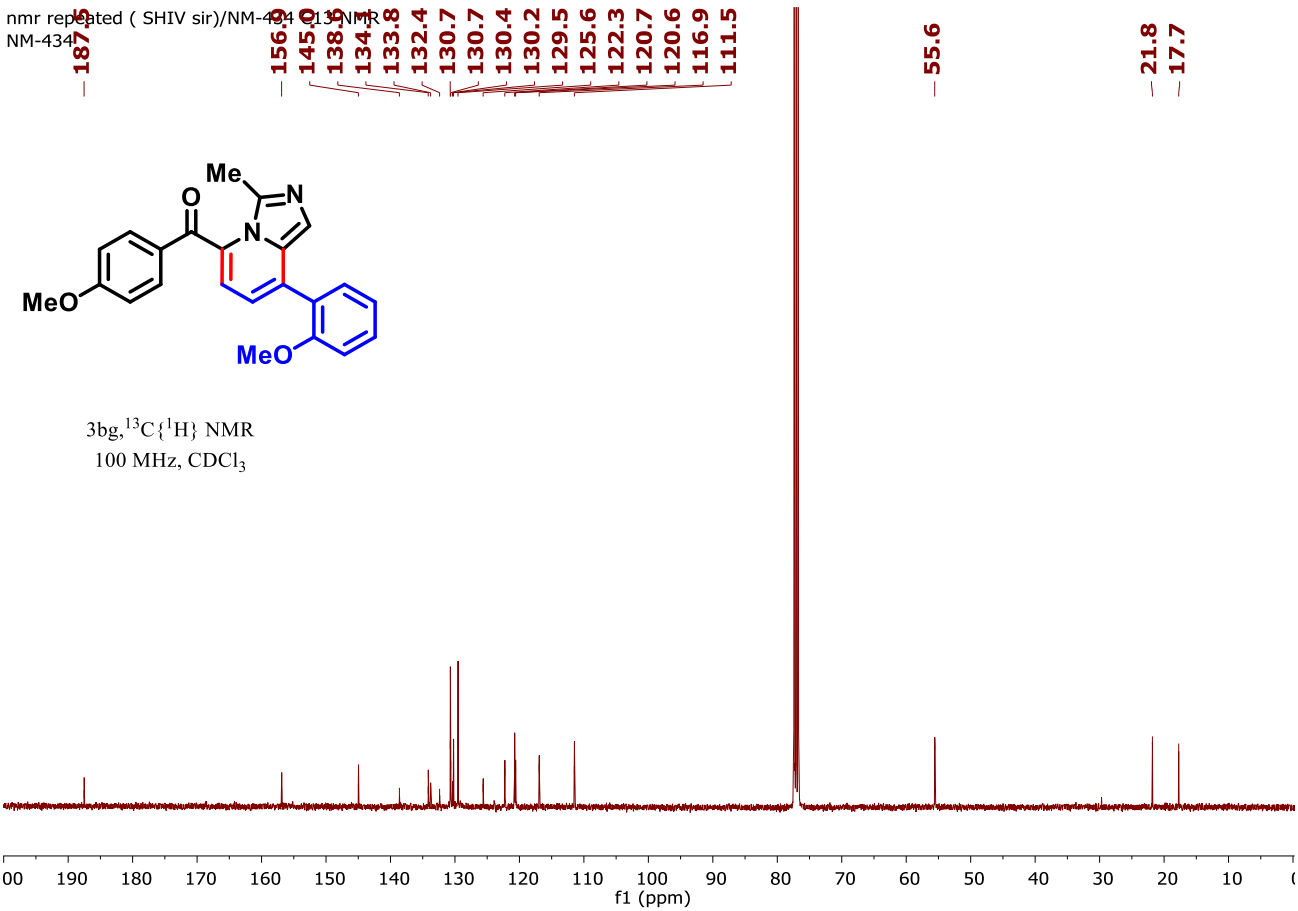


3bd, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$

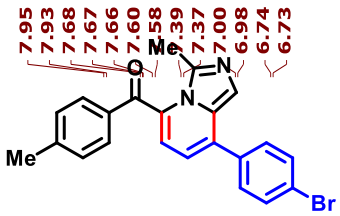


3bg, ^{1}H NMR
400 MHz, $CDCl_3$

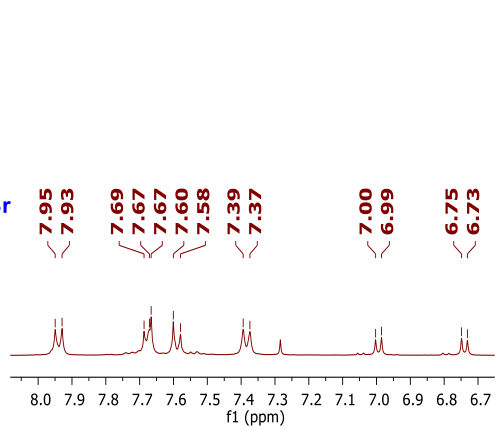


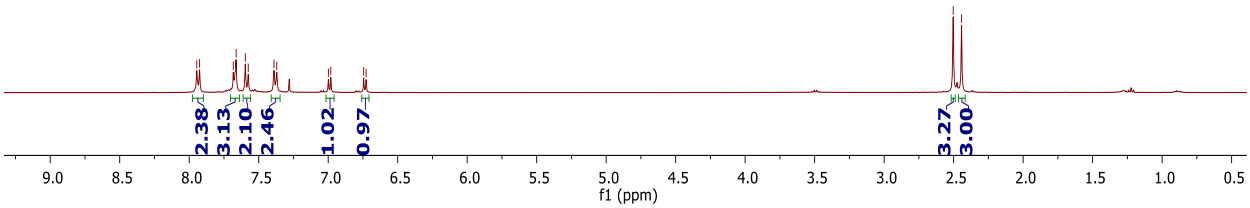


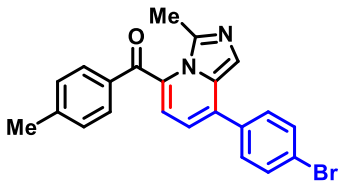
3bg, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



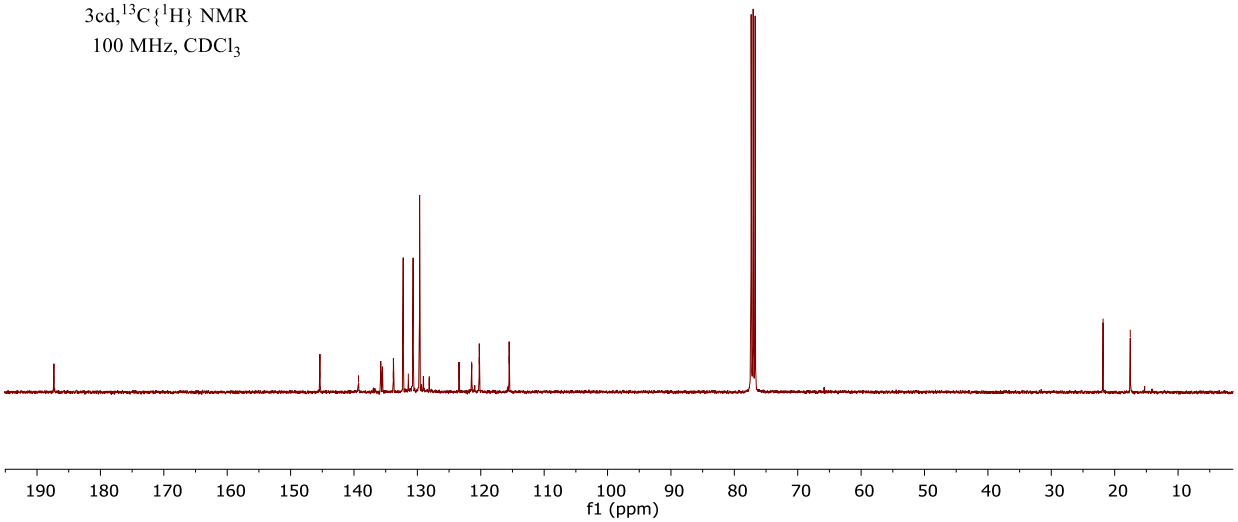
3cd, ^{1}H NMR
400 MHz, $CDCl_3$

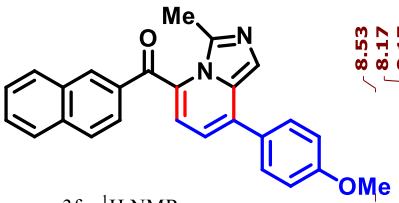




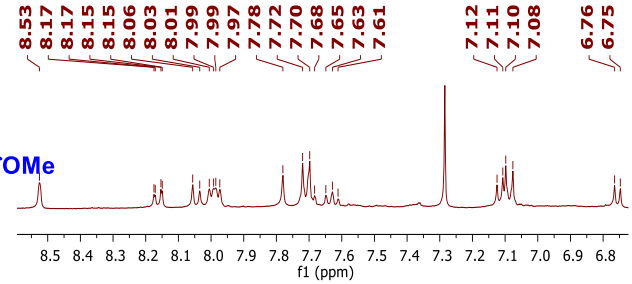


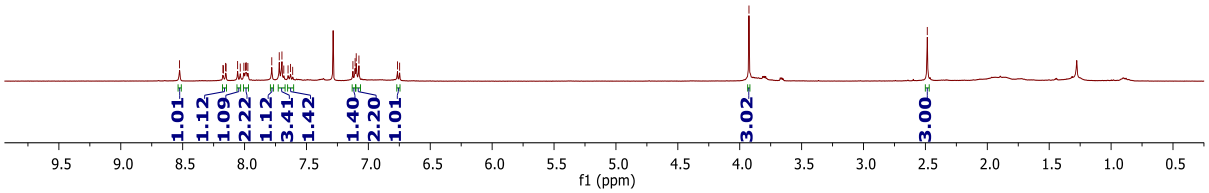
3cd, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$

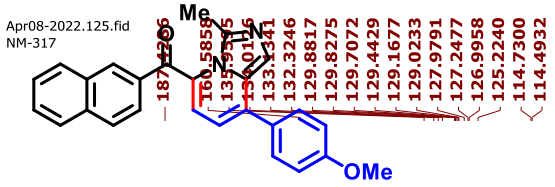




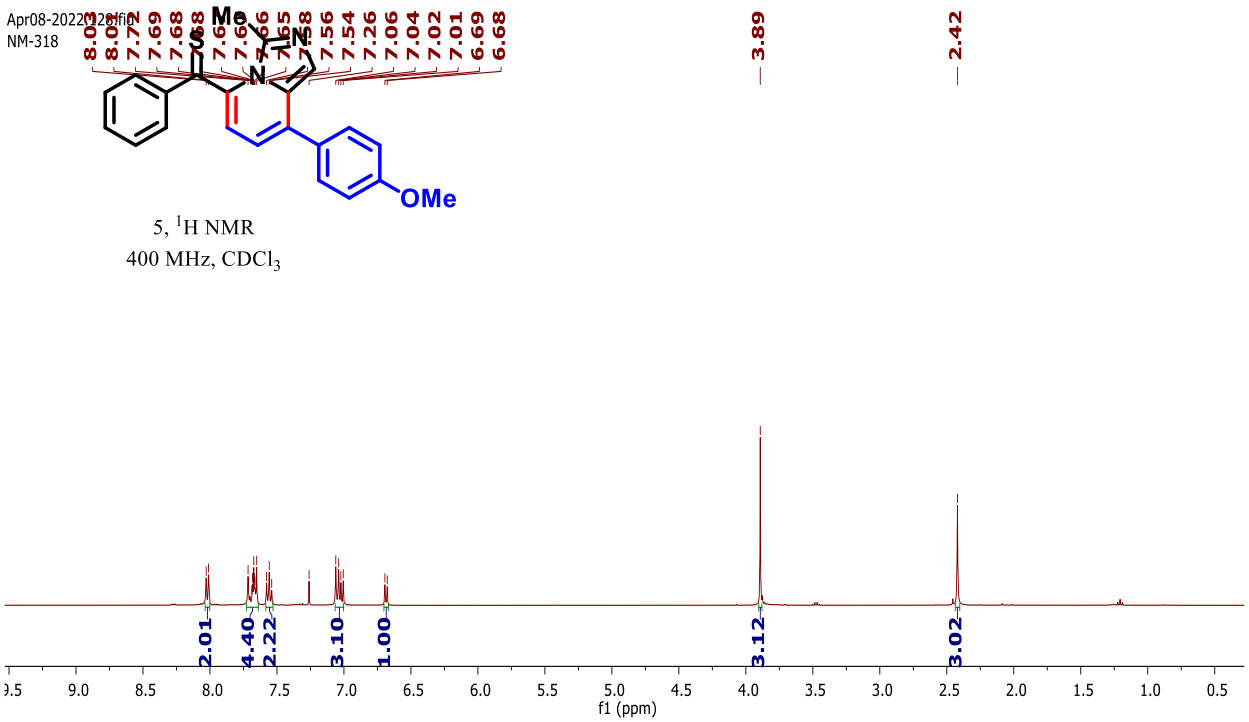
3fc, ^{1}H NMR
400 MHz, $CDCl_3$



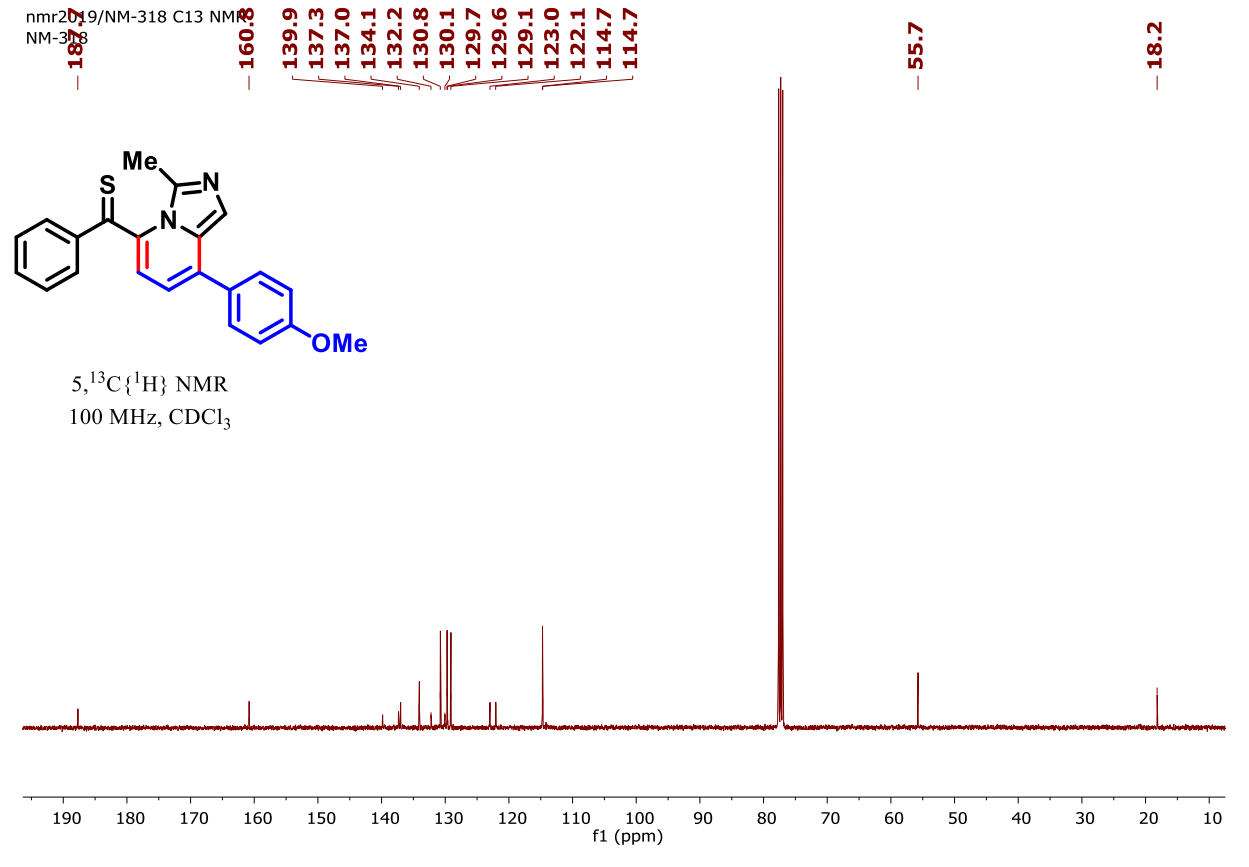




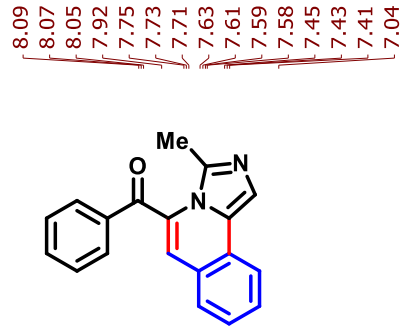
3fc,^{13}C{^{1}H} NMR
100 MHz, $CDCl_3$



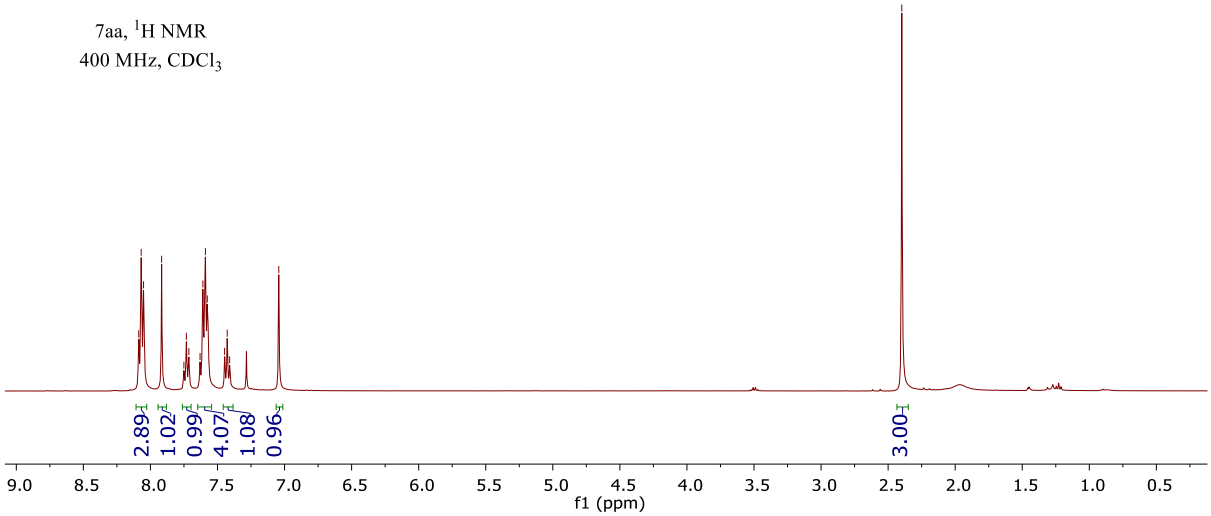
5, ^{1}H NMR
400 MHz, $CDCl_3$

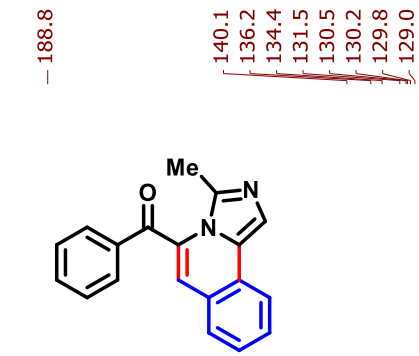


5, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$

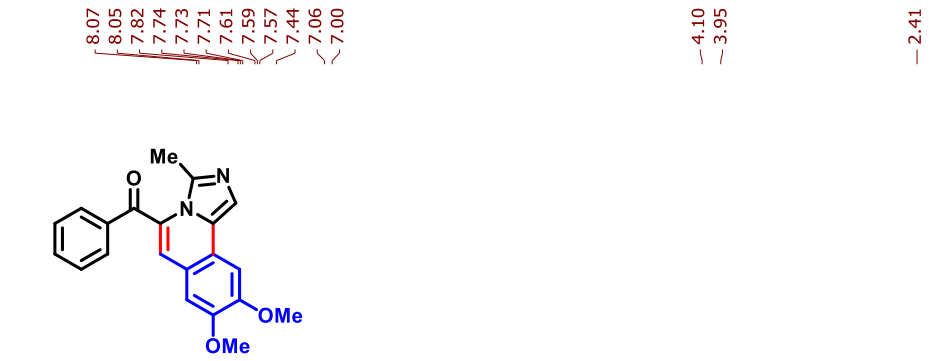


7aa, ^{1}H NMR
400 MHz, $CDCl_3$

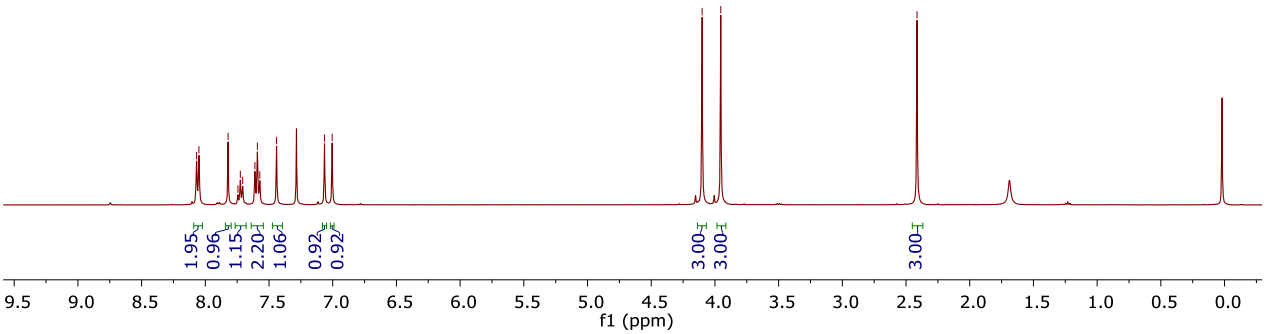


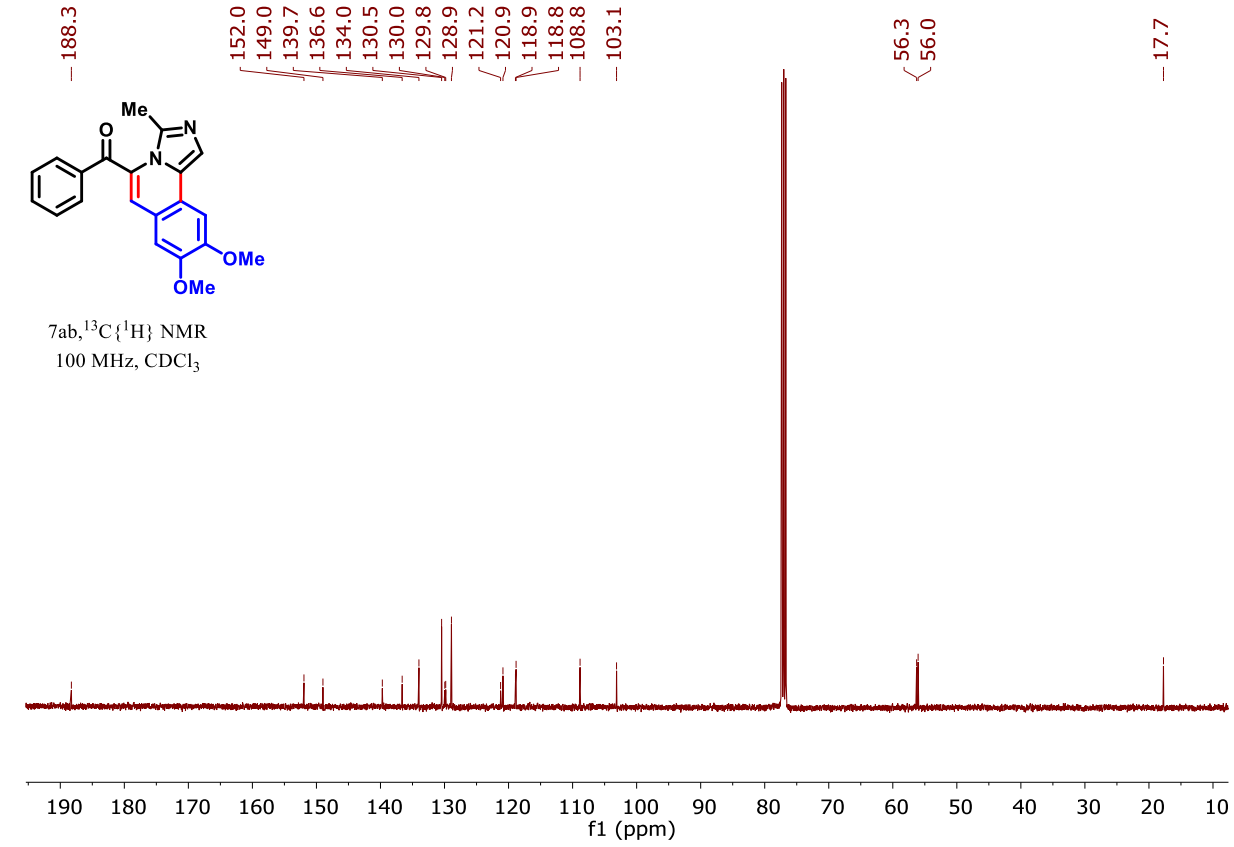


7aa,$^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$

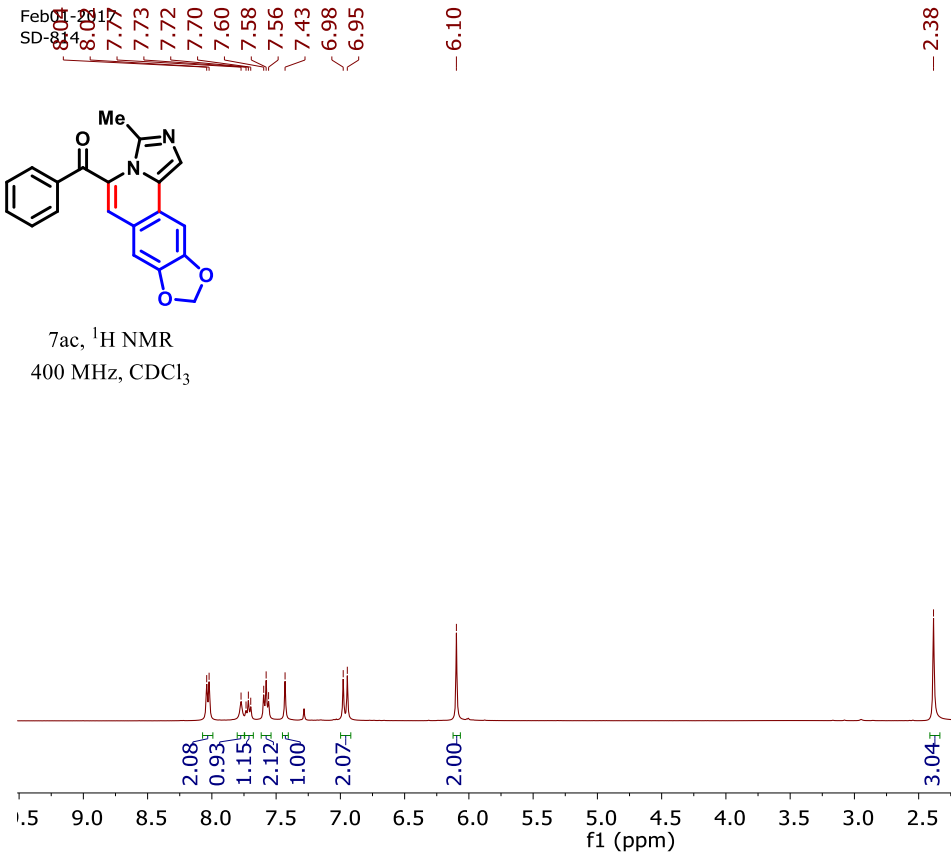


7ab, ^{1}H NMR
400 MHz, $CDCl_3$

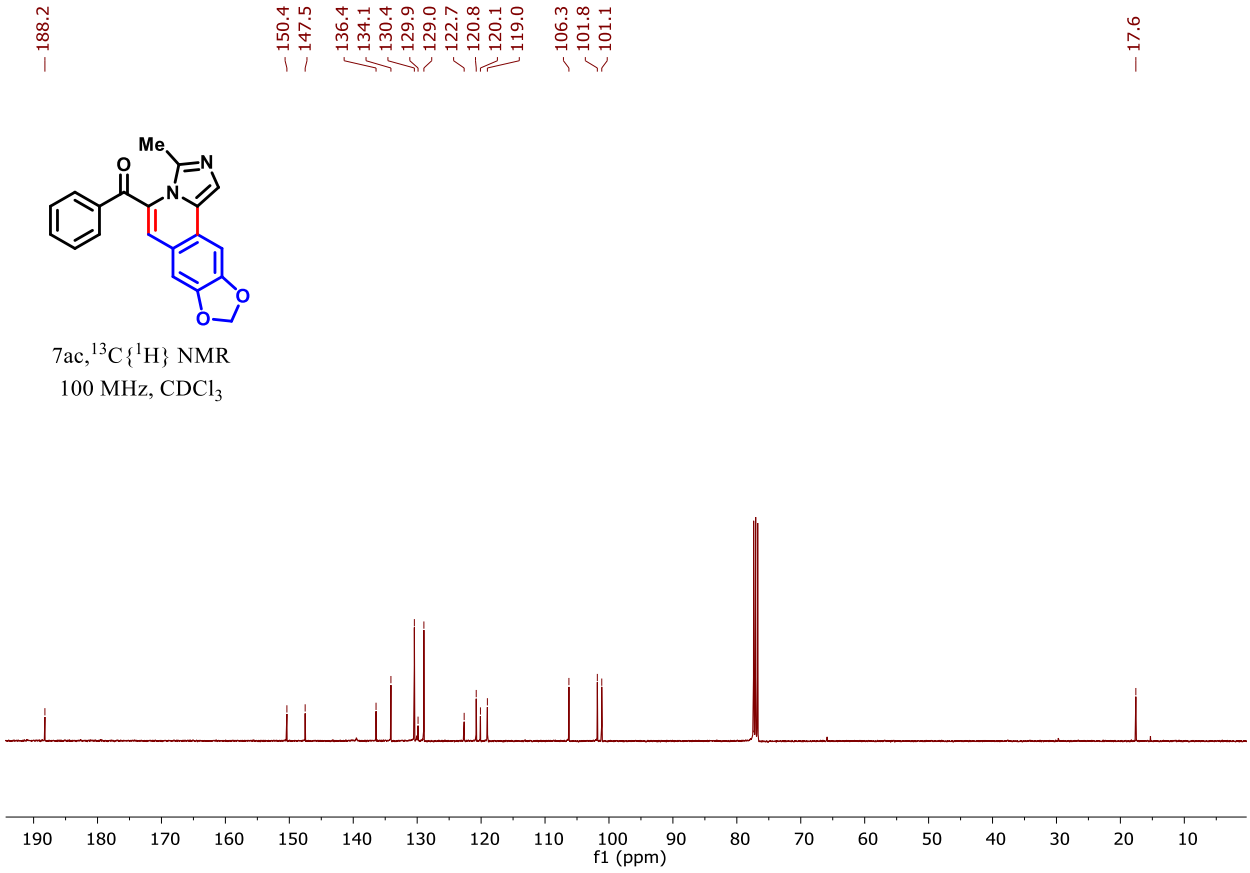




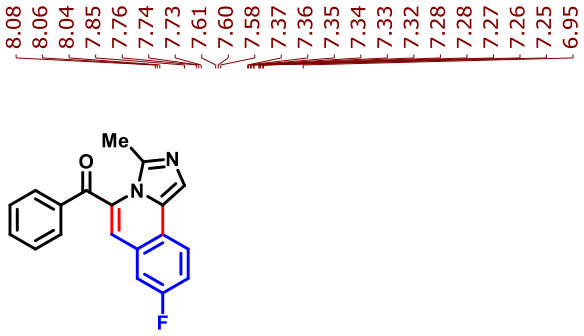
7ab, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



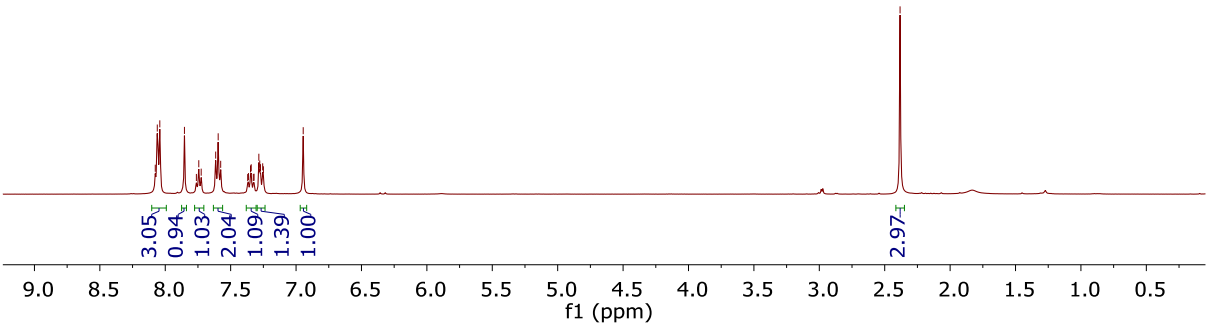
7ac, ^{1}H NMR
400 MHz, $CDCl_3$

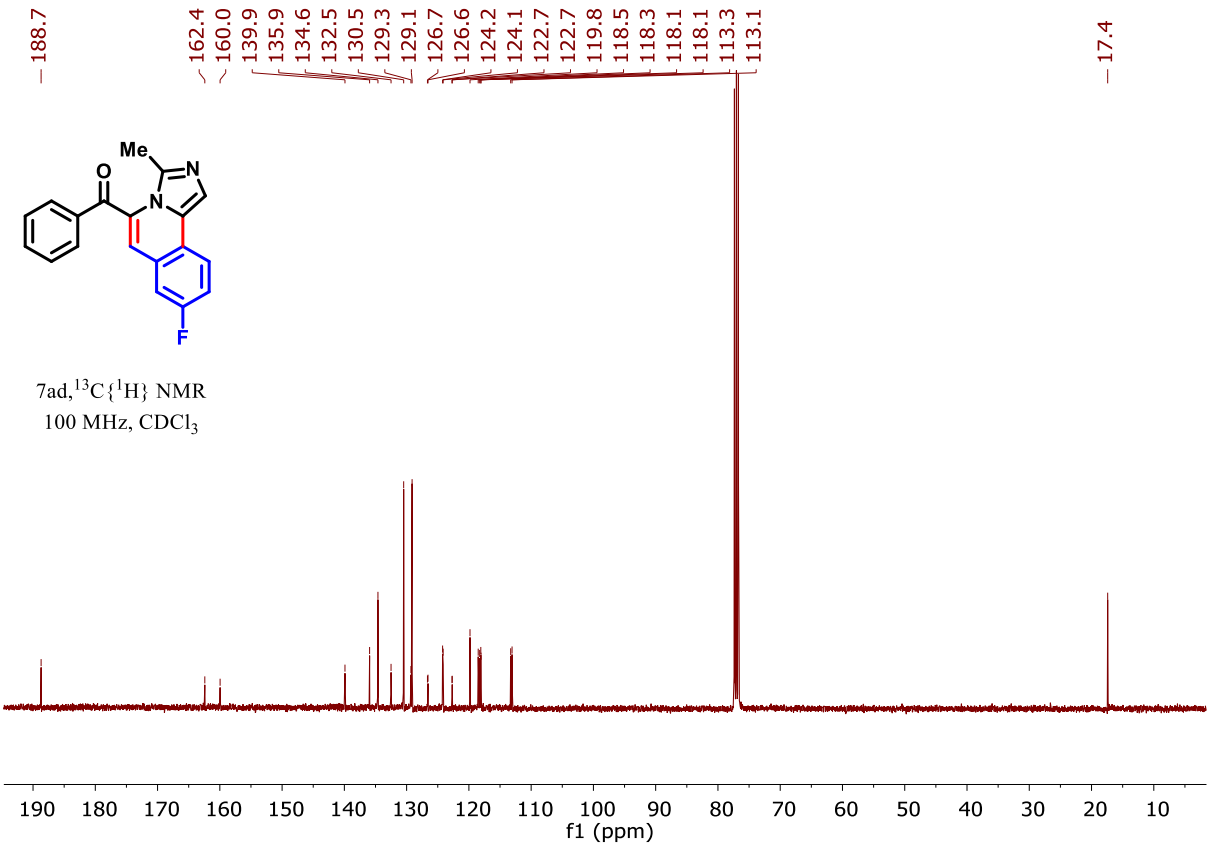


7ac, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$

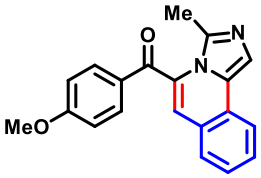


7ad, ^{1}H NMR
400 MHz, $CDCl_3$

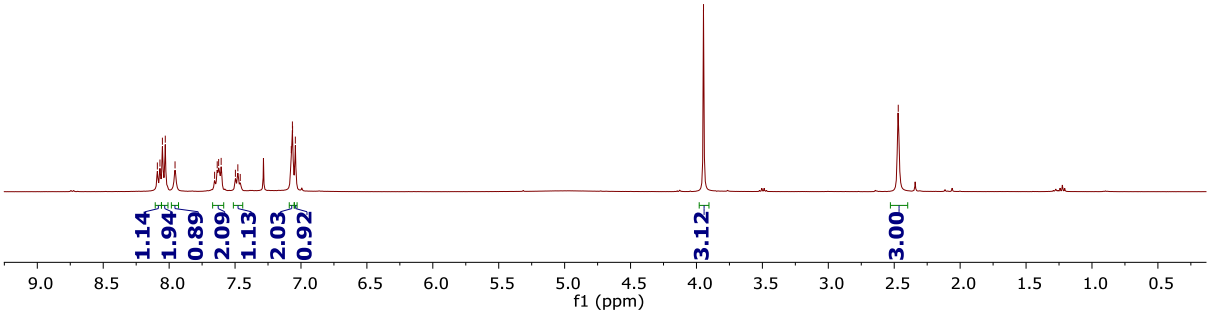


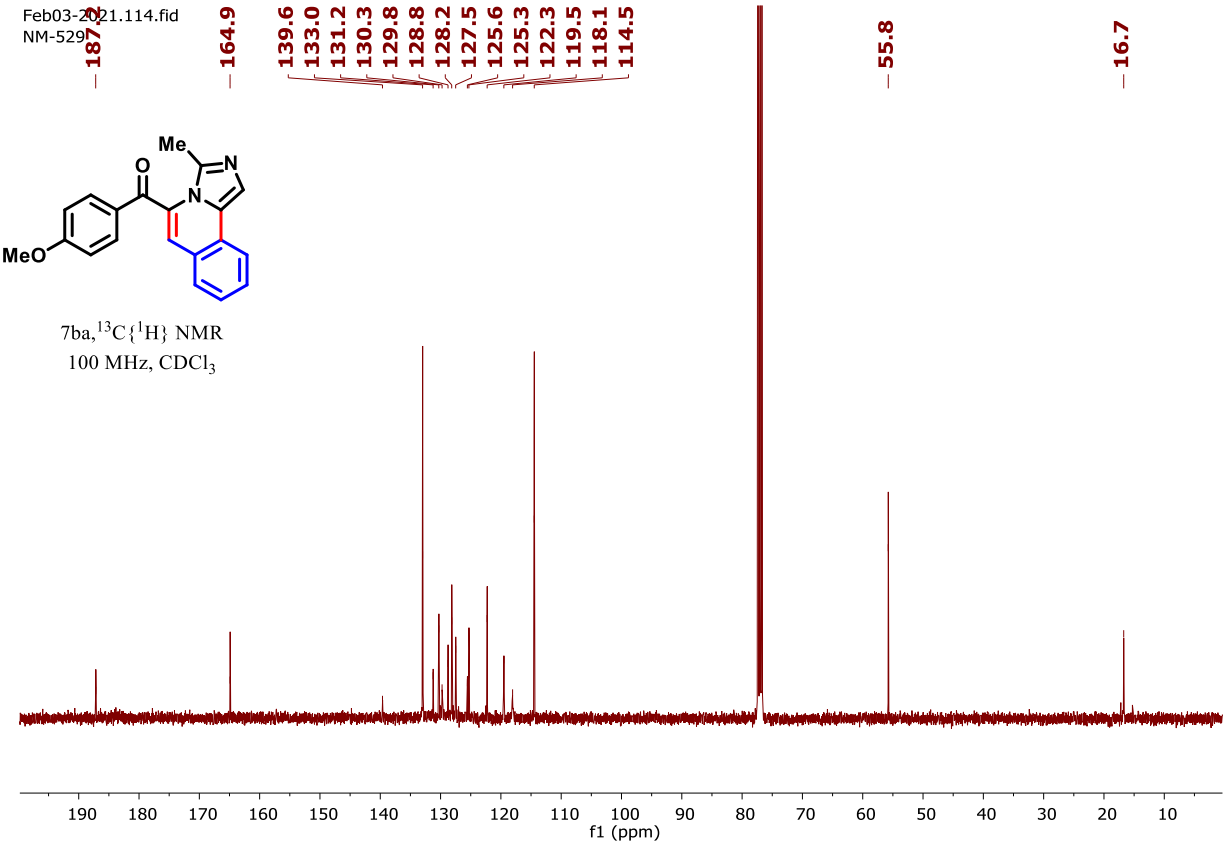


7ad, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$

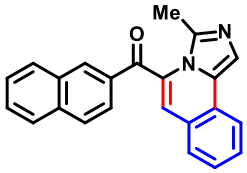


7ba, ^{1}H NMR
400 MHz, $CDCl_3$

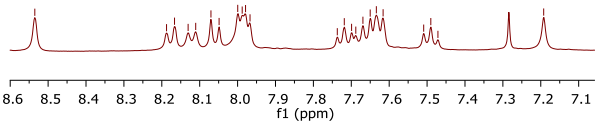


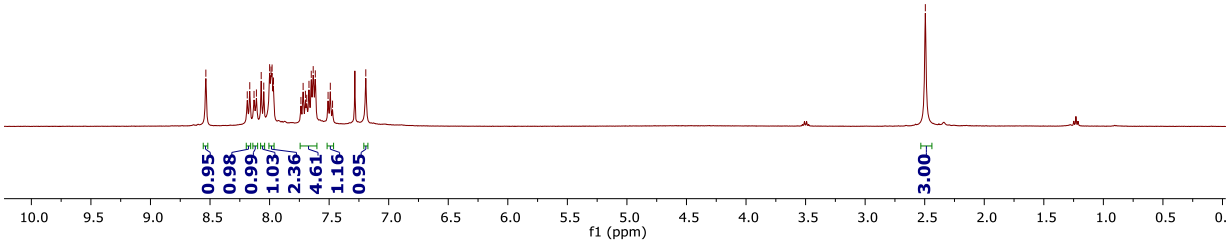


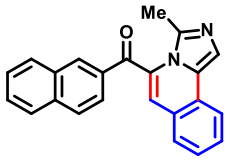
7ba, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



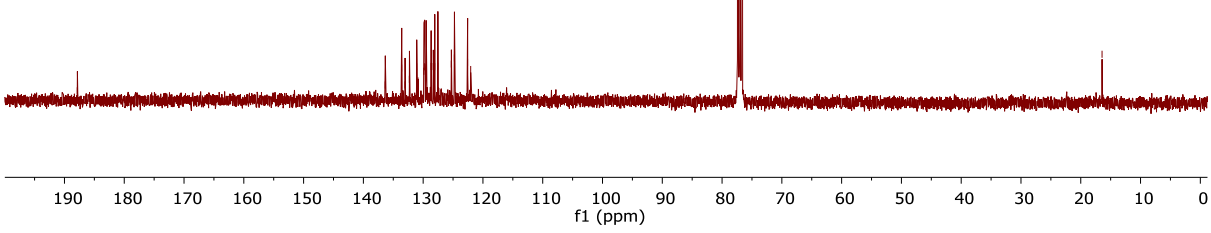
7fa, ^{1}H NMR
400 MHz, $CDCl_3$

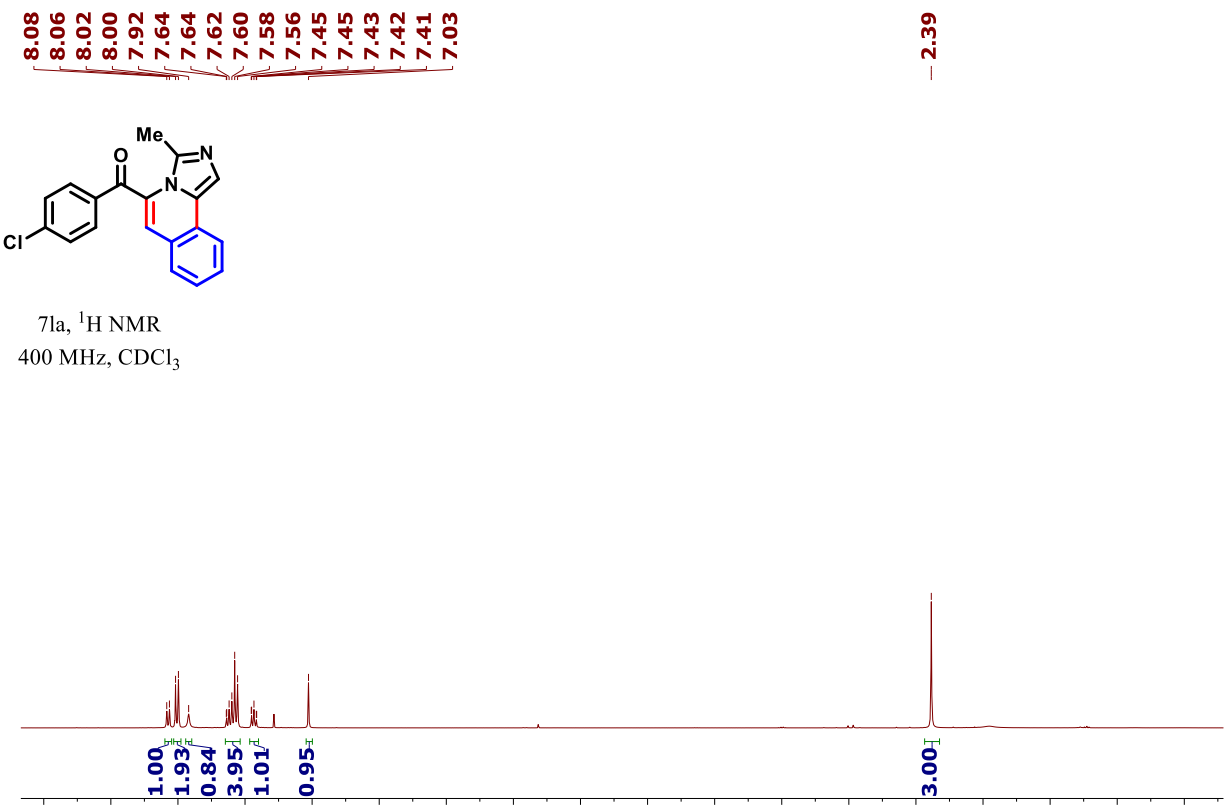




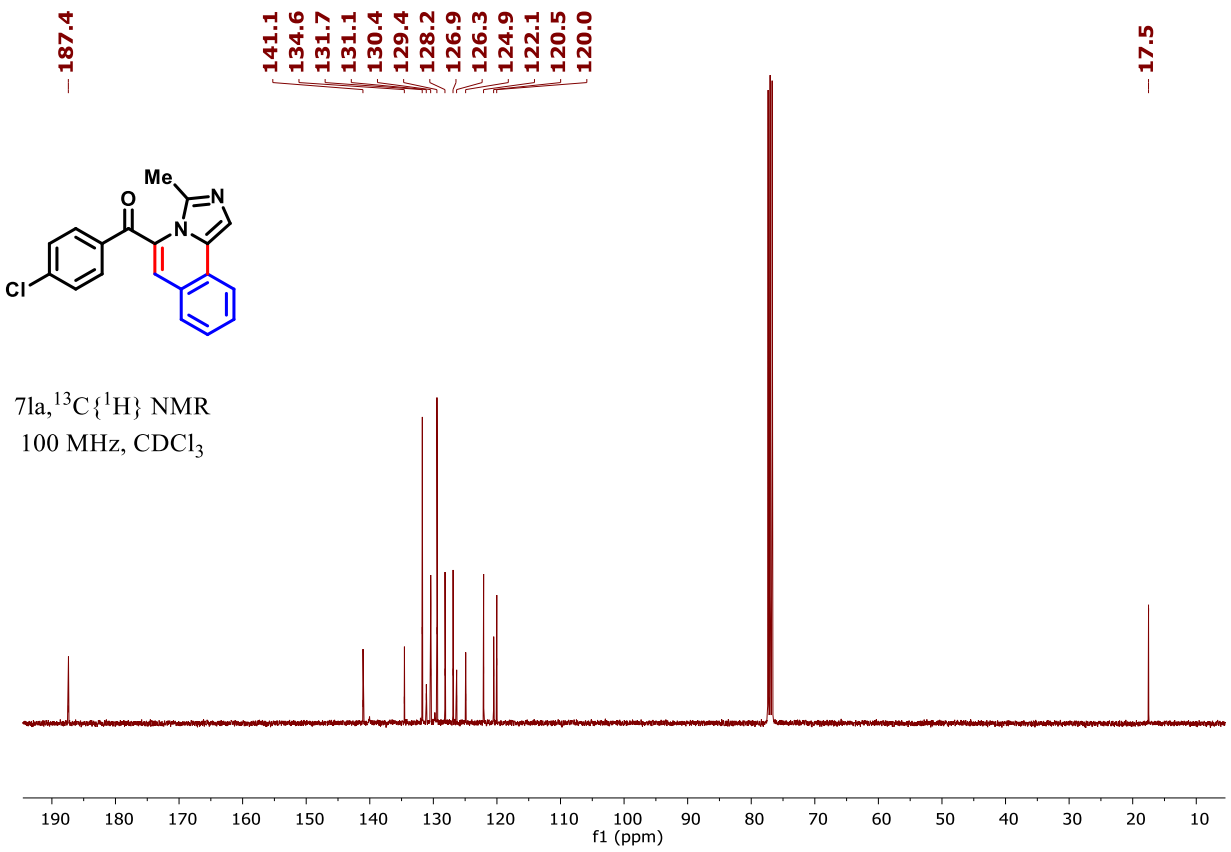


7fa,^{13}C{^{1}H} NMR
100 MHz, $CDCl_3$

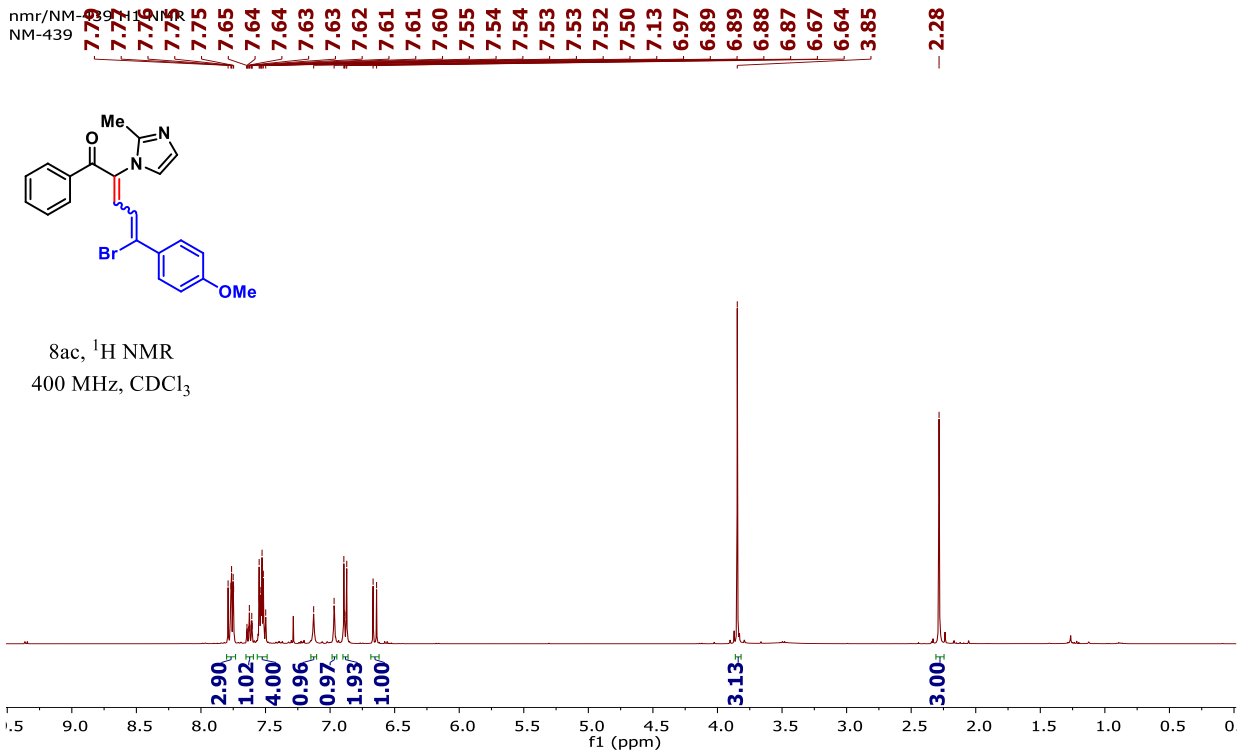




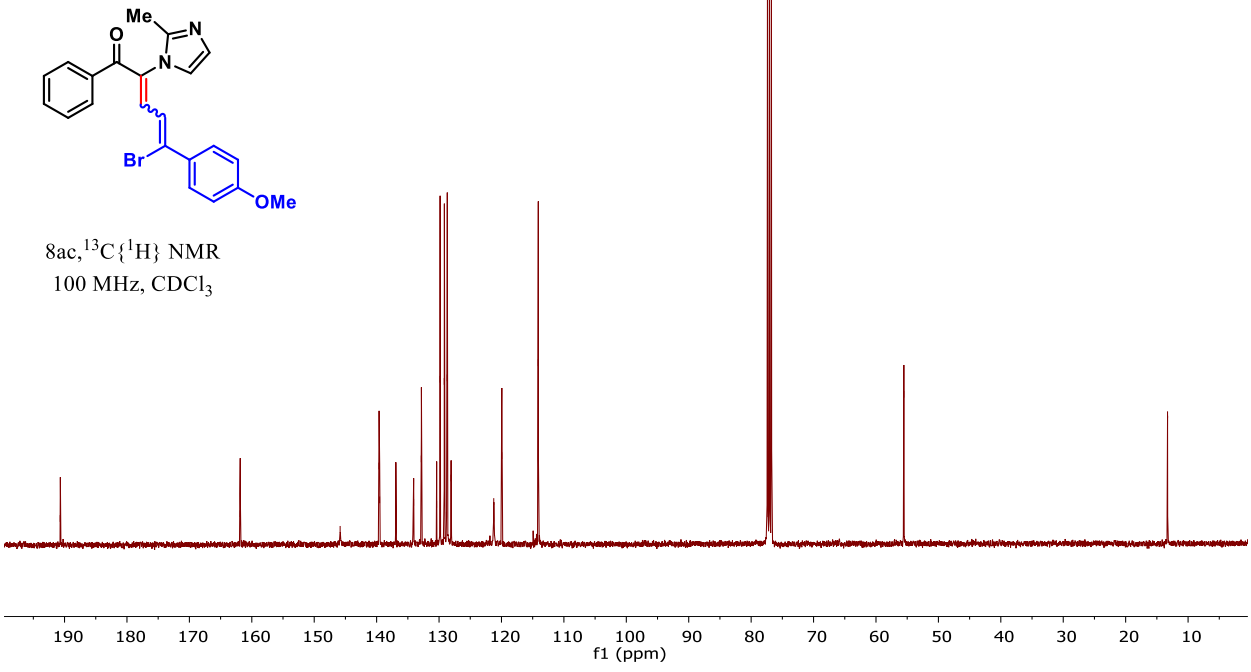
7la, ^{1}H NMR
400 MHz, $CDCl_3$



7la, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$



8ac, ^{1}H NMR
400 MHz, $CDCl_3$



8ac, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$

2. Single Crystal X-ray Crystallographic Analysis

Single crystal X-ray data of compound **3ah** (CCDC 2159571)

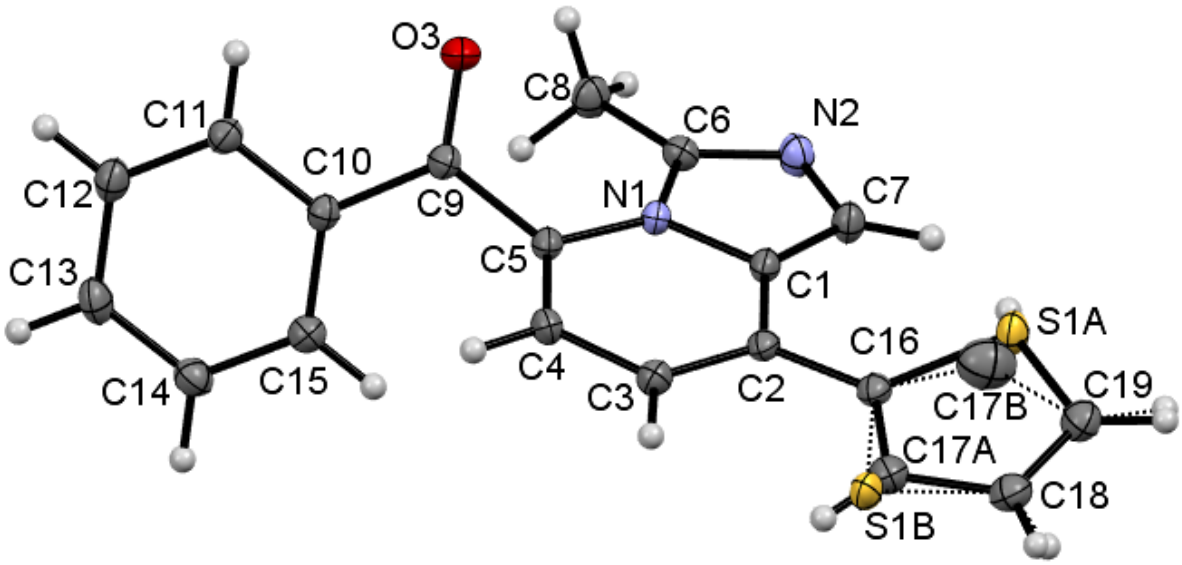


Figure S1. Single crystal ORTEP diagram of compound **3ah**, due to the rotation of the thiophen ring along C2-C16 bond the occupancies of S1A and S1B are fixed to 70 % and 30 % respectively, and similarly C17A and C17B occupancies are fixed to 70 % and 30 % respectively. The thermal ellipsoids are drawn to a 50 % probability level.

Sample Preparation and Crystal Measurement: The single crystals of the compound **3ah** were obtained as needles. The crystal data collection and data reduction were performed using CrysAlis PRO on a single crystal Rigaku Oxford XtaLab Pro diffractometer. The crystals were kept at 93(2) K during data collection using CuKα (λ = 1.54184) radiation. Using Olex2,[1] the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimization.

Table S1 Crystal data and structure refinement for 3ah (exp_665_AK_NM-288).

Identification code	**3ah** (exp_665_AK_NM-288)
Empirical formula	$C_{19}H_{14}N_2OS$
Formula weight	318.38
Temperature/K	93(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.6918(2)
b/Å	7.7847(2)
c/Å	13.7184(3)
α/°	90.026(2)
β/°	97.054(2)
γ/°	114.557(3)
Volume/Å^3	740.27(4)
Z	2
ρ_{calc}g/cm^3	1.428
μ/mm^{-1}	1.982
F(000)	332.0
Crystal size/mm^3	0.1 × 0.08 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	12.522 to 160.416
Index ranges	$-7 \leq h \leq 9$, $-9 \leq k \leq 9$, $-17 \leq l \leq 17$
Reflections collected	7457
Independent reflections	3095 [R_{int} = 0.0340, R_{sigma} = 0.0402]
Data/restraints/parameters	3095/2/227
Goodness-of-fit on F^2	1.113
Final R indexes [I>=2σ (I)]	R_1 = 0.0487, wR_2 = 0.1375
Final R indexes [all data]	R_1 = 0.0505, wR_2 = 0.1397
Largest diff. peak/hole / e Å^{-3}	0.26/-0.51

3. References

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.
2. G. Sheldrick, *Acta Cryst. A*, 2015, **71**, 3-8.
3. G. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3-8.