

Electronic Supporting Information

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

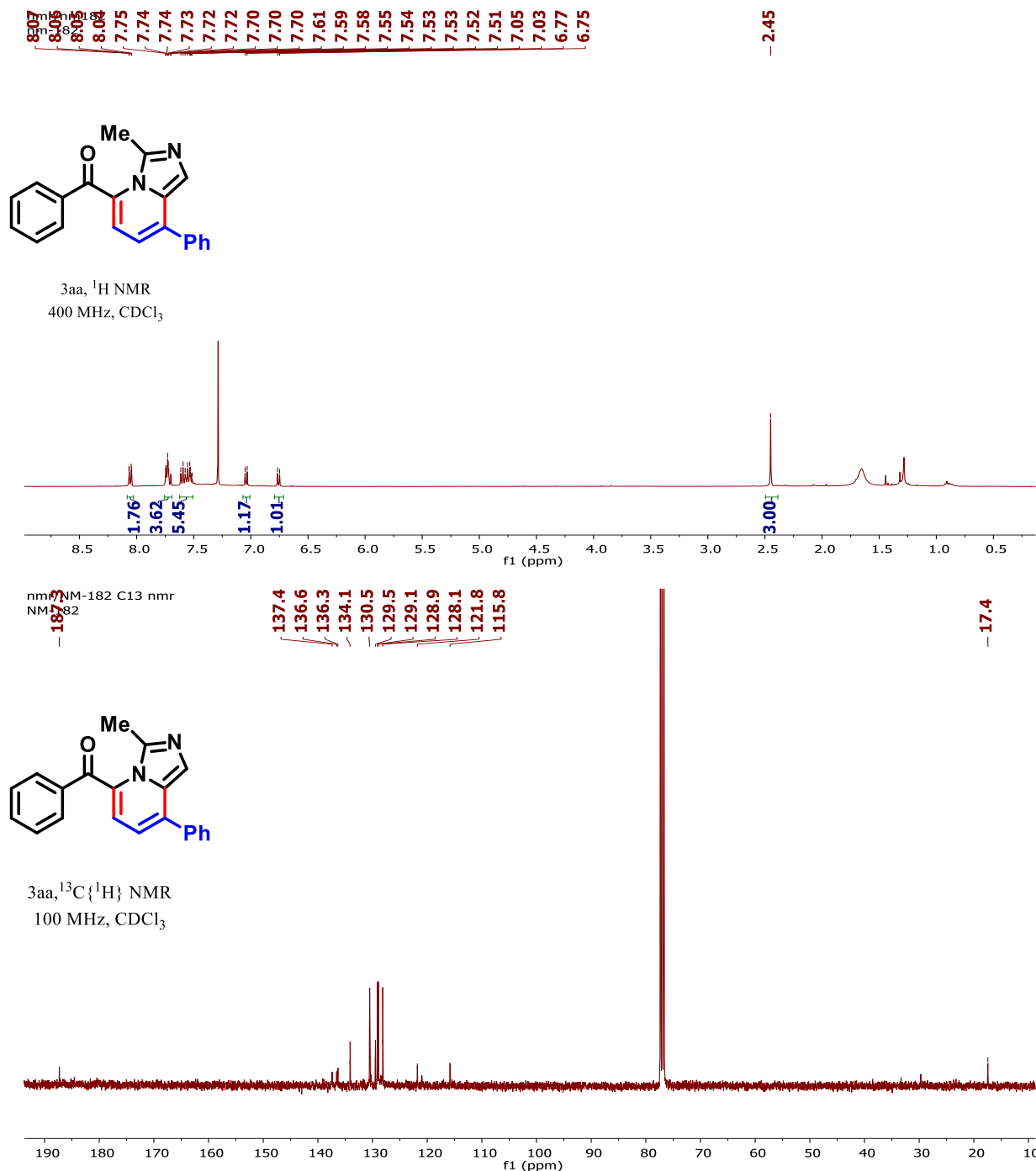
Neha Meena,^{a,†} Shiv Dhiman,^{a,†} Krishnan Rangan,^b and Anil Kumar^{*,a}

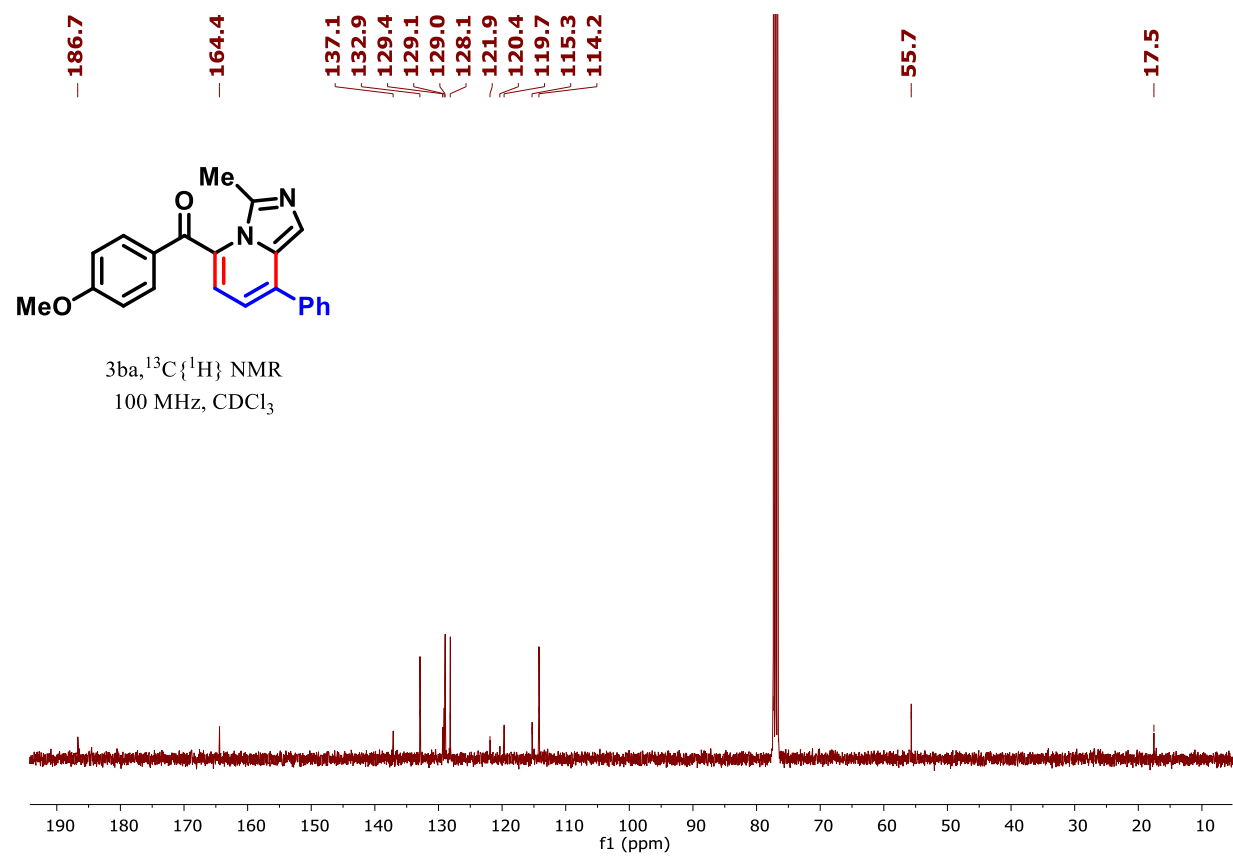
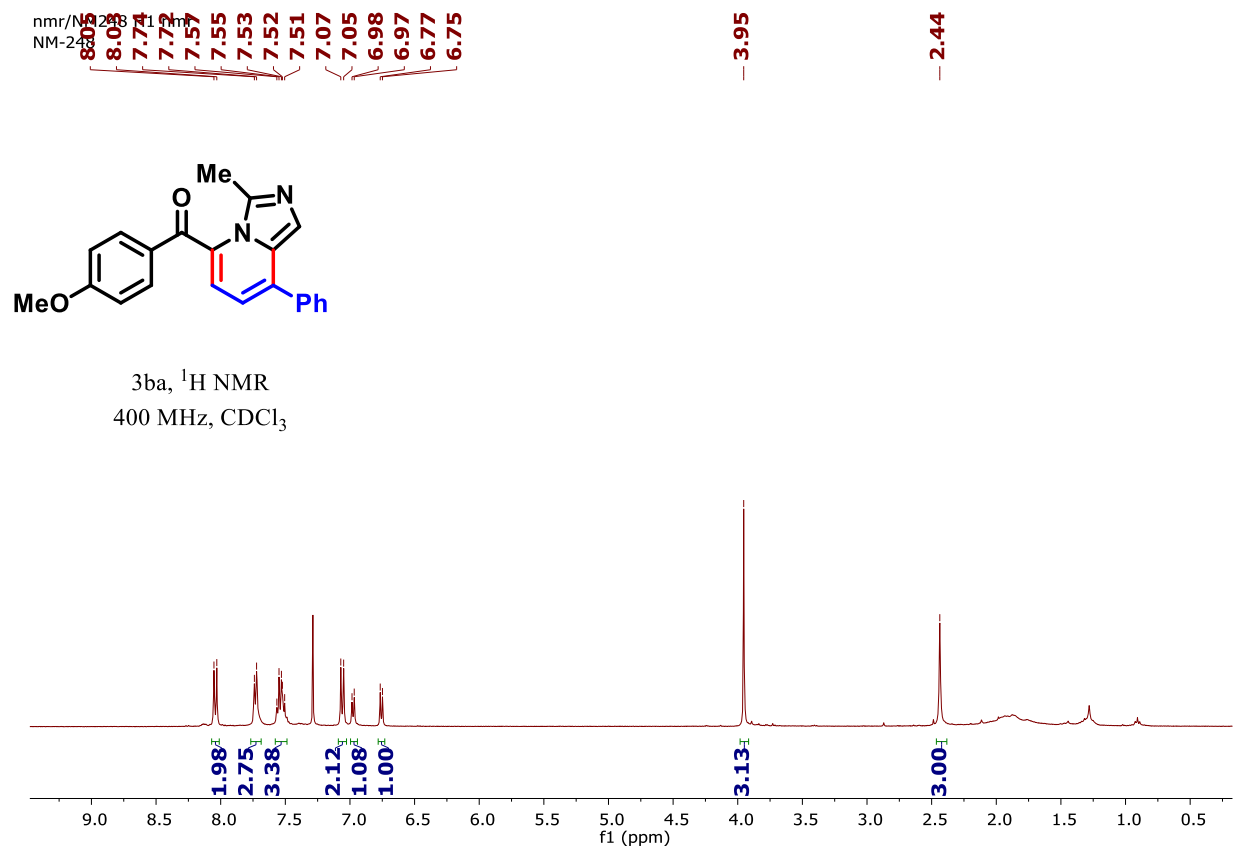
^aDepartment of Chemistry, Birla Institute of Technology and Science Pilani, Pilani Campus, Rajasthan, 333031, India

^bDepartment of Chemistry, Birla Institute of Technology and Science Pilani, Hyderabad Campus, Telangana, 500078, India

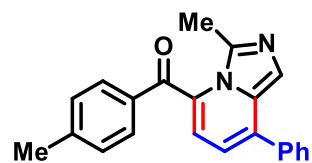
E-mail: anilkumar@pilani.bits-pilani.ac.in

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

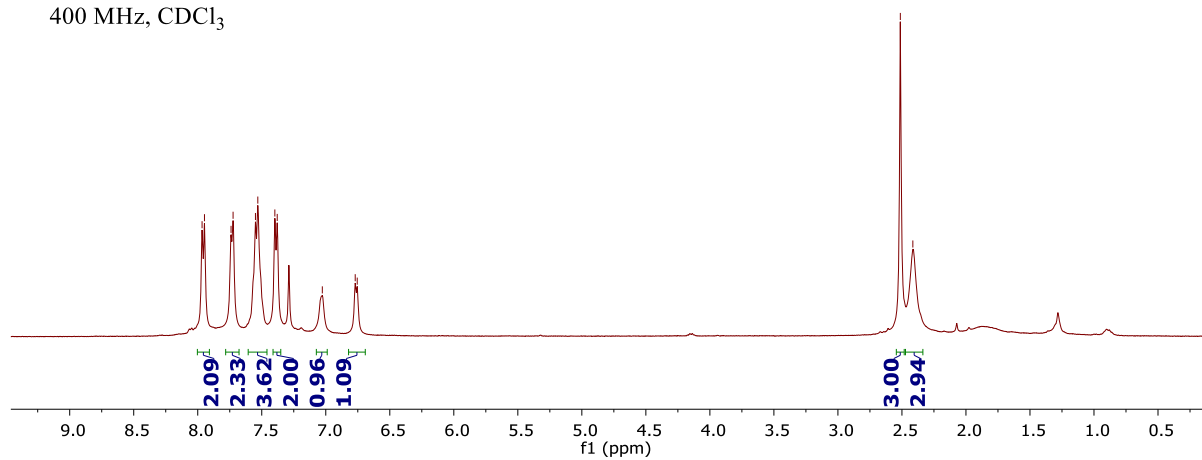




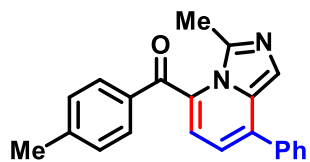
Sep30-2020.8.fid
SD-1104



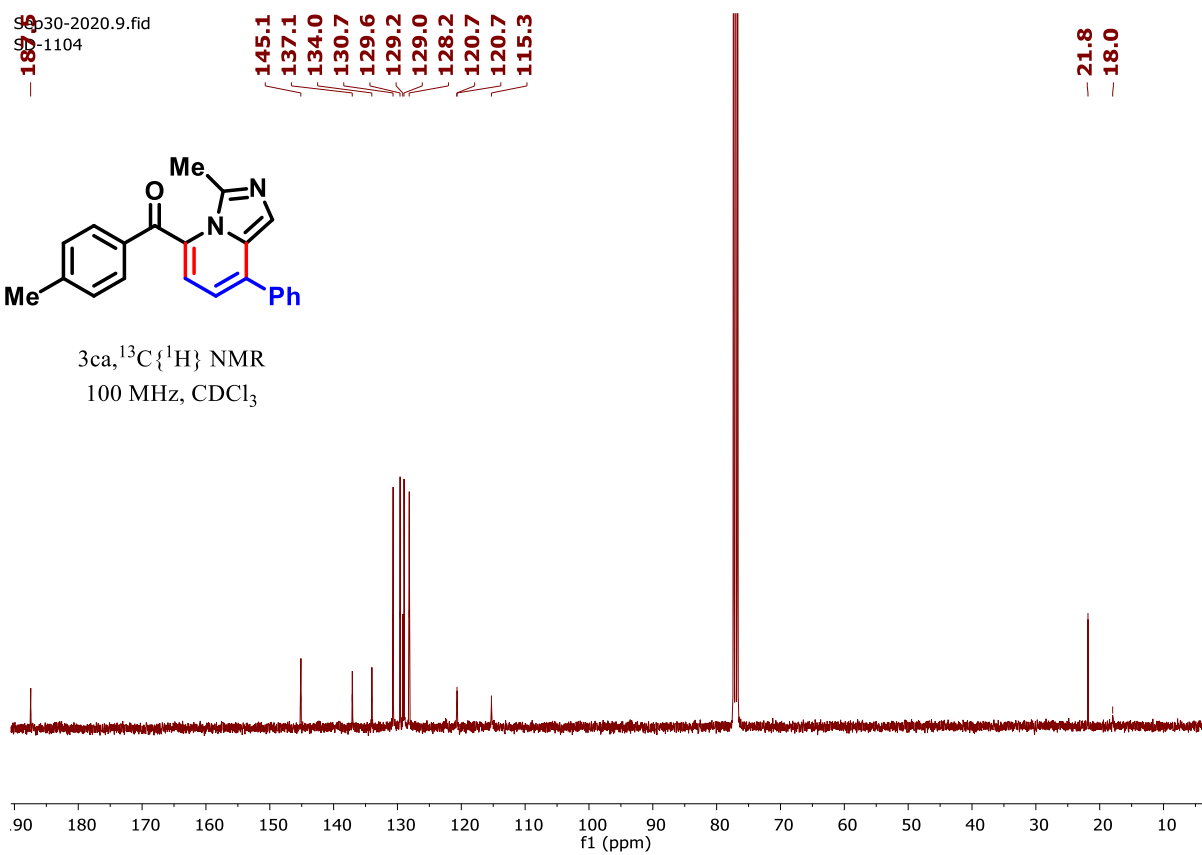
3ca, ^1H NMR
400 MHz, CDCl_3

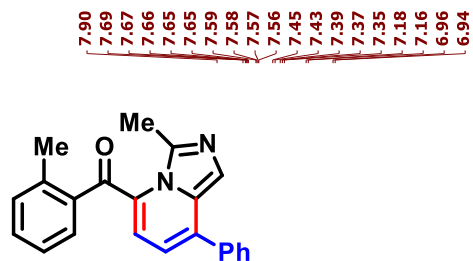


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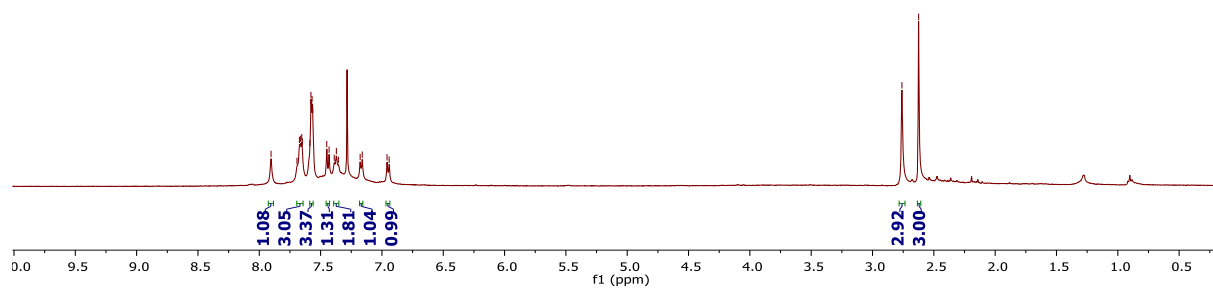


3ca, $^{13}\text{C}\{^1\text{H}\}$ NMR
100 MHz, CDCl_3





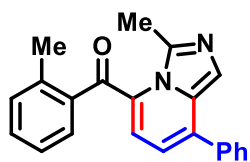
3da, ^1H NMR
400 MHz, CDCl_3



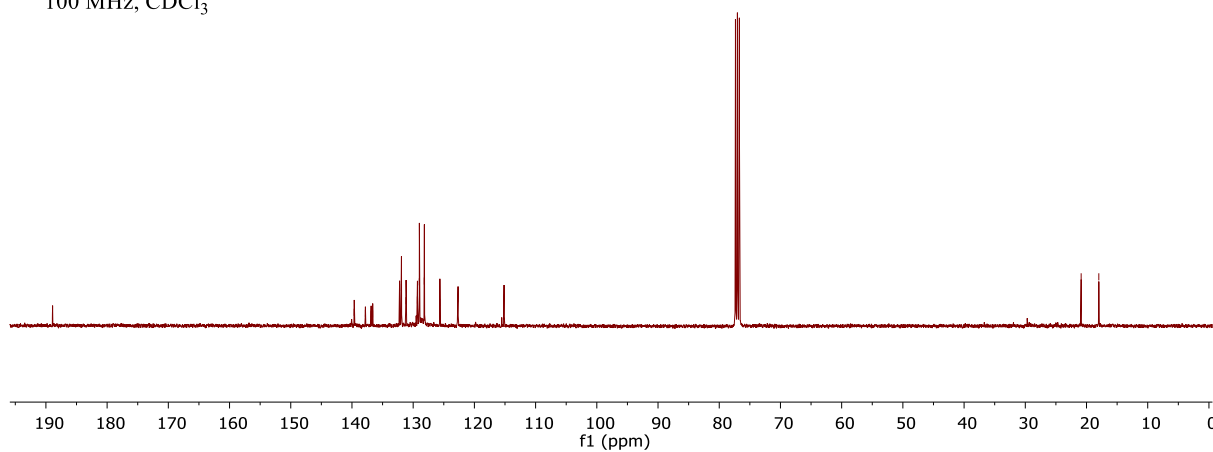
Dec-05-2020.3.fid
NM 188

139.6, 137.8, 136.9, 136.6, 132.2, 131.9, 131.2, 129.3, 129.0, 128.2, 125.6, 122.8, 122.7, 115.2.

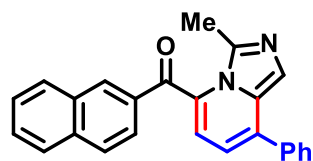
20.9, 18.0.



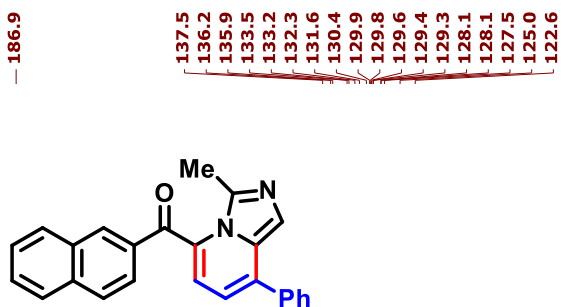
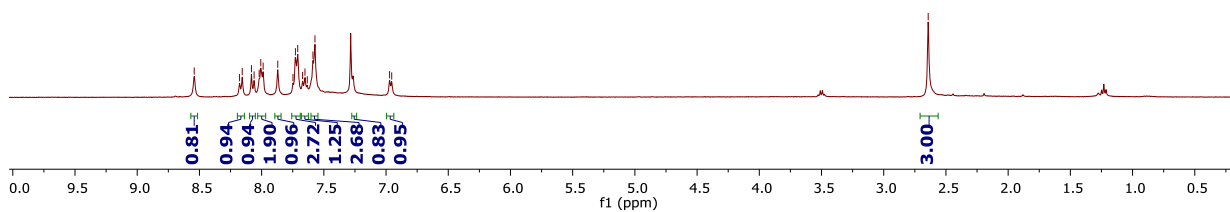
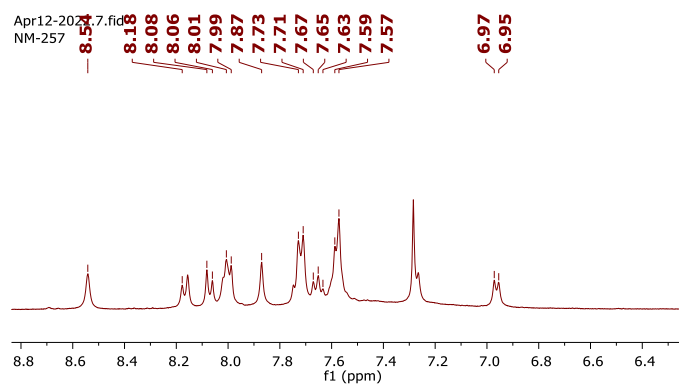
3da $^{13}\text{C}\{^1\text{H}\}$ NMR
100 MHz, CDCl_3



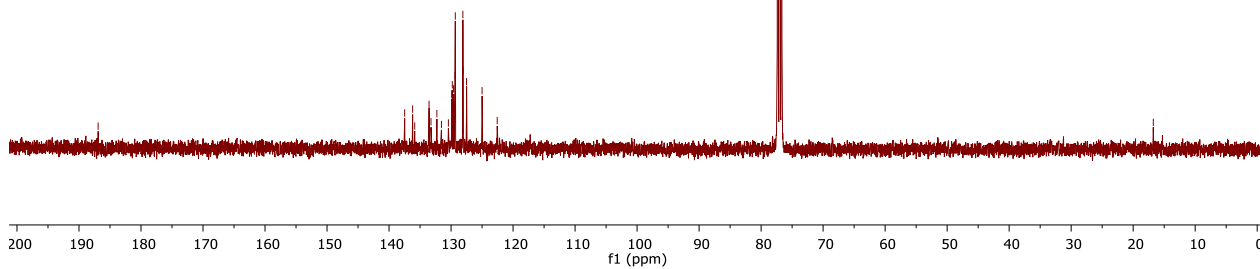
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NM-257



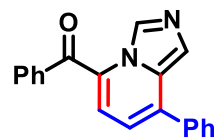
3fa, ^1H NMR
400 MHz, CDCl_3



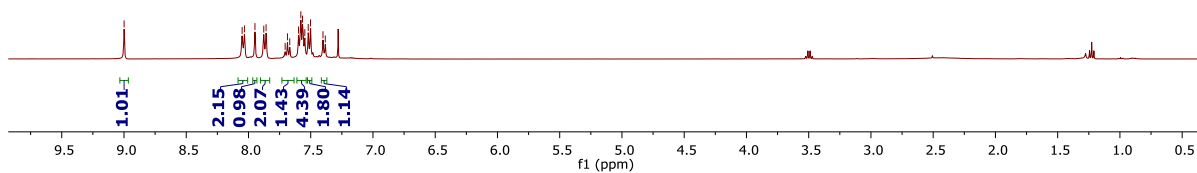
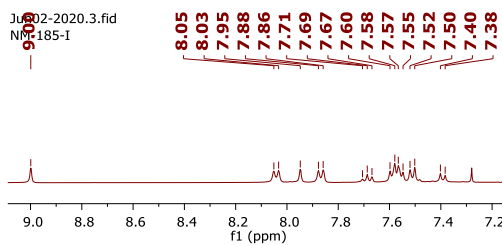
3fa, $^{13}\text{C}\{^1\text{H}\}$ NMR
100 MHz, CDCl_3



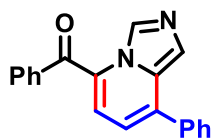
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NM-185-I



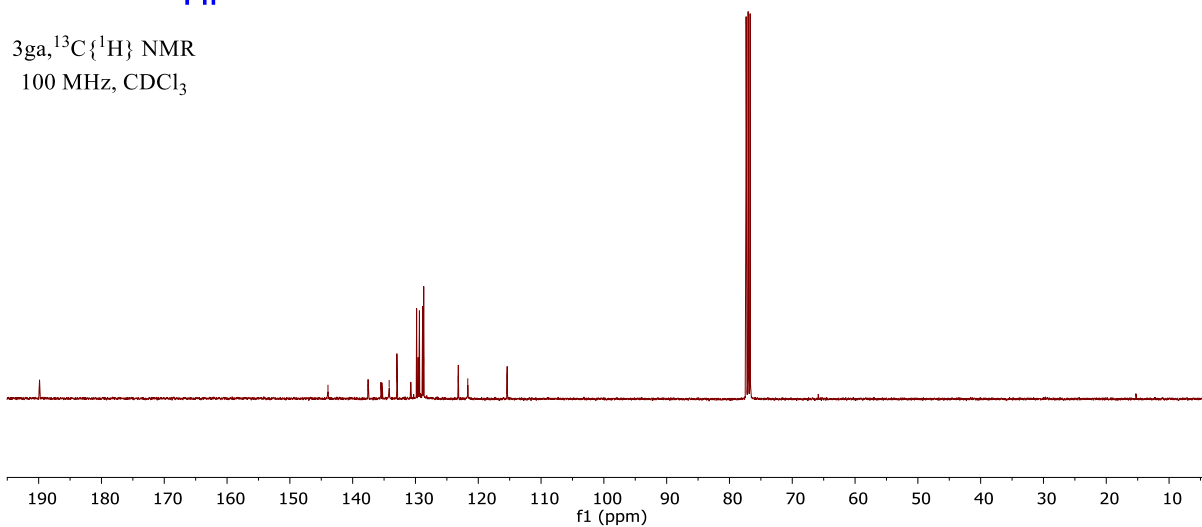
3ga, ^1H NMR
400 MHz, CDCl_3



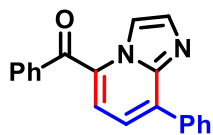
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NM-185-I



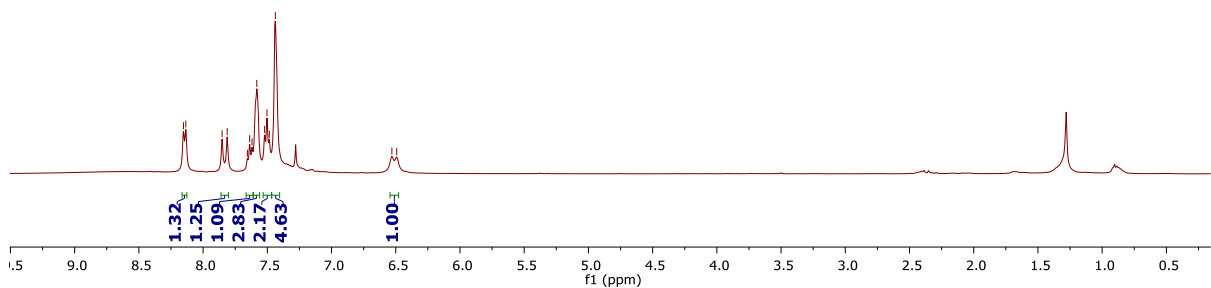
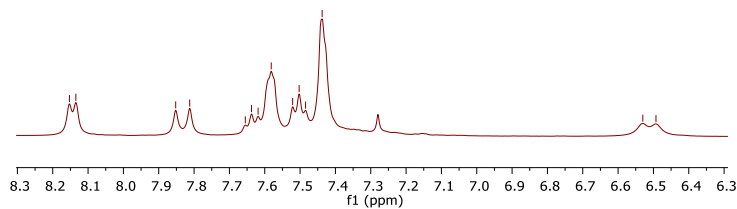
3ga, $^{13}\text{C}\{^1\text{H}\}$ NMR
100 MHz, CDCl_3



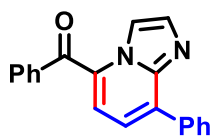
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7.58
7.52
7.50
7.48
7.44
6.53
6.49



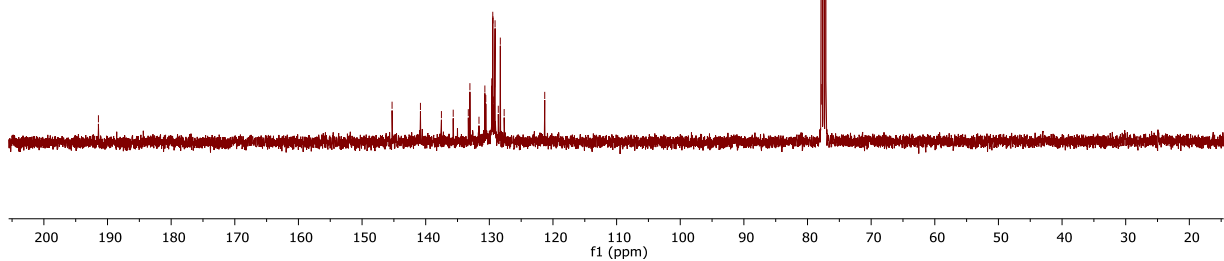
4ga, ^1H NMR
400 MHz, CDCl_3



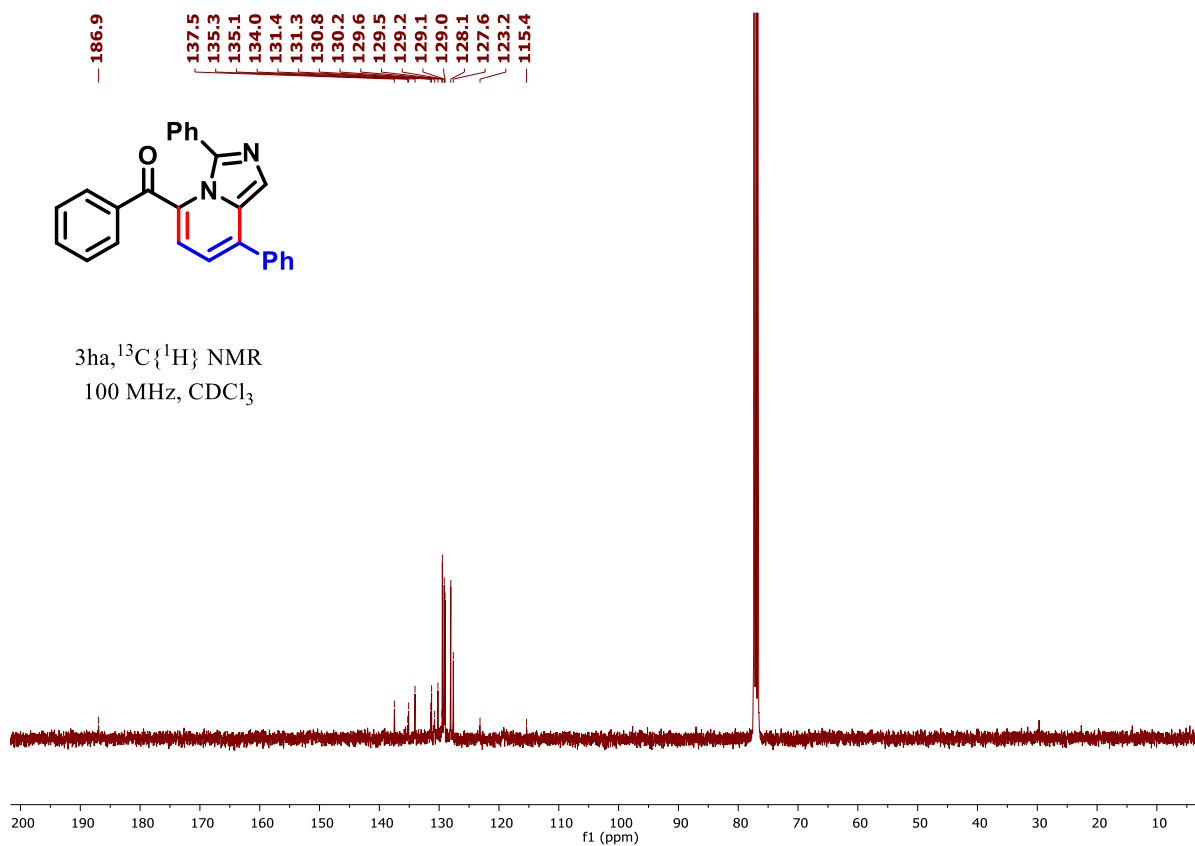
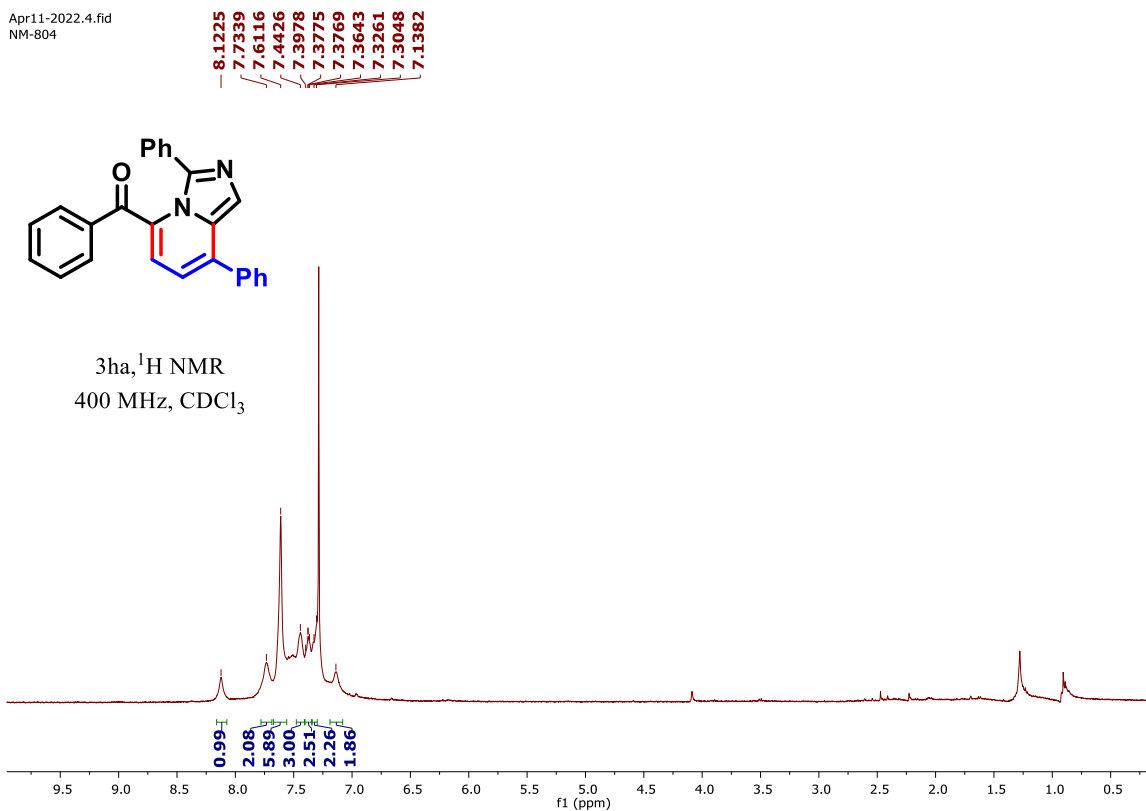
191.4
145.3
140.8
137.5
135.7
133.3
133.1
131.6
130.7
130.6
129.6
129.5
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129.3
129.1
129.1
128.6
128.3
127.7
121.3



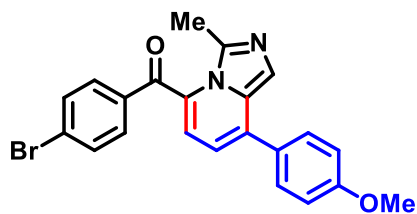
4ga, $^{13}\text{C}\{^1\text{H}\}$ NMR
100 MHz, CDCl_3



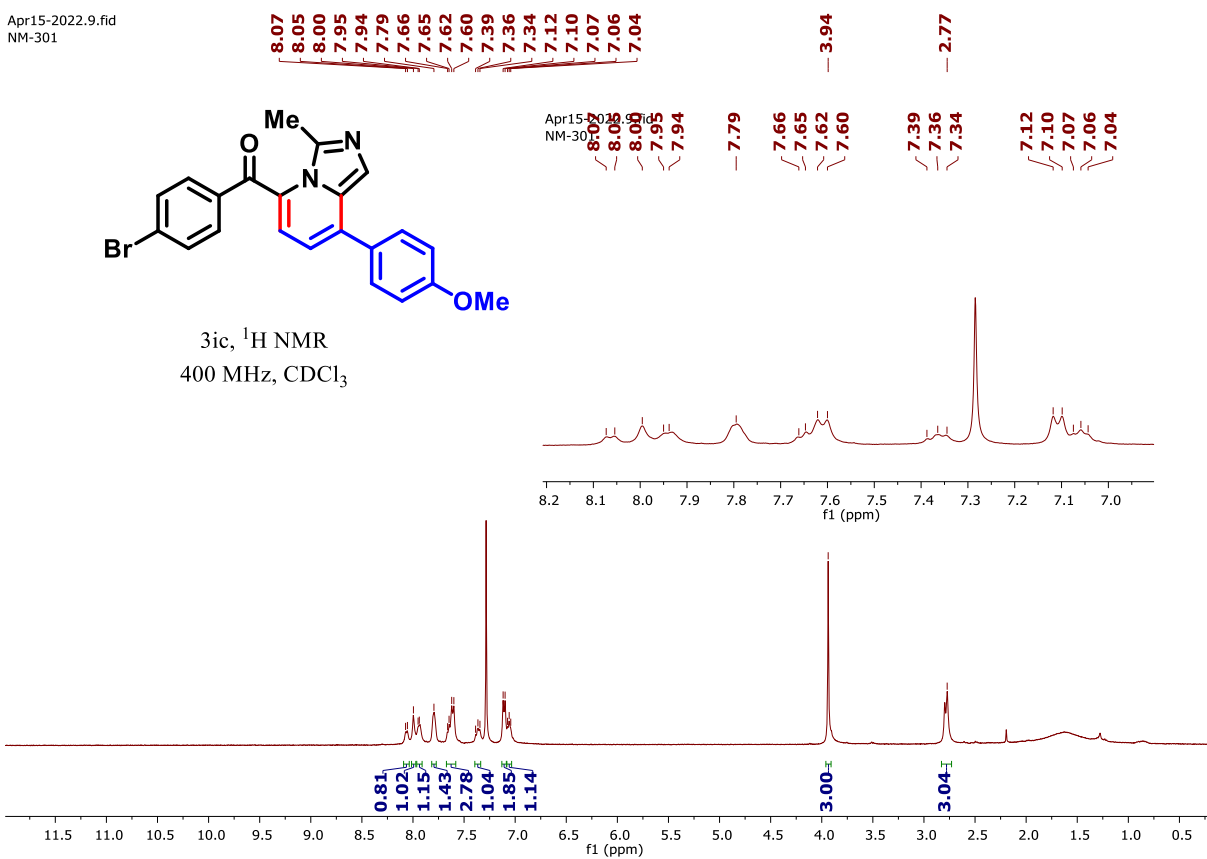
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NM-804



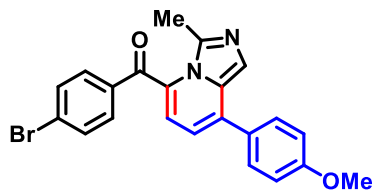
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NM-301



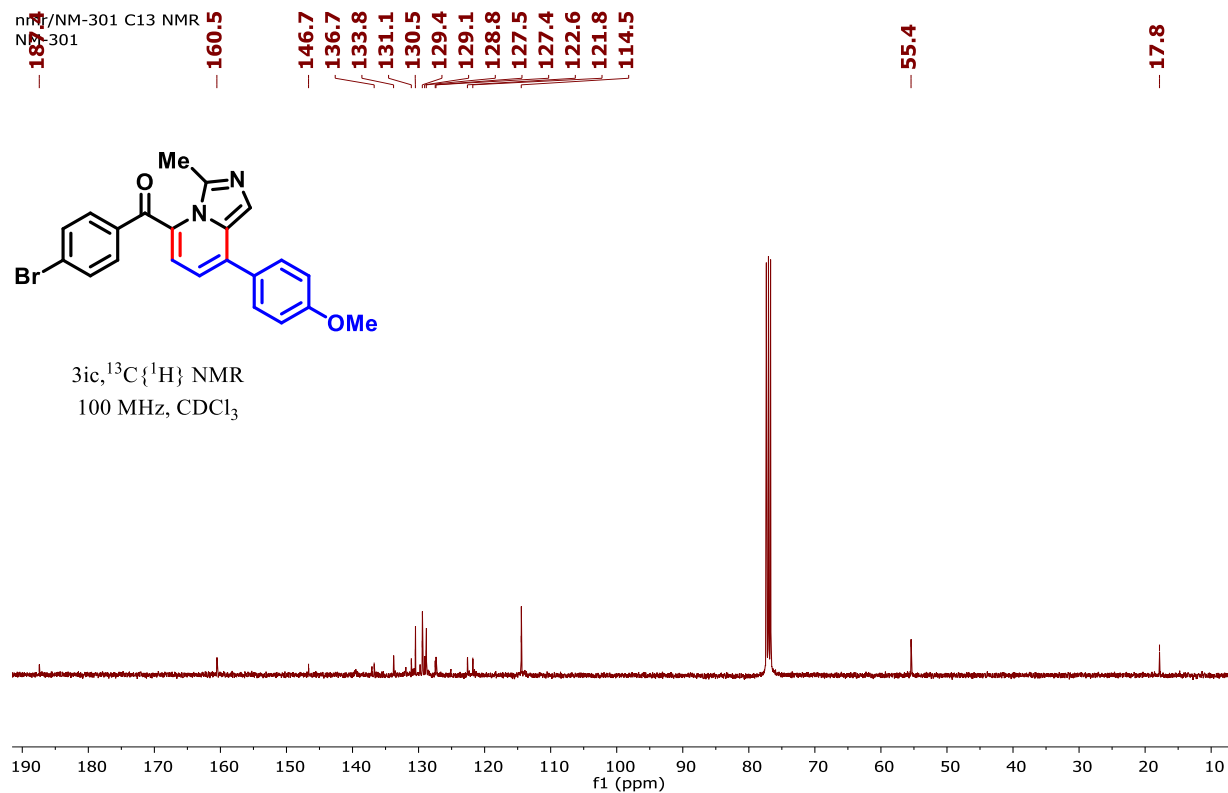
3ic, ^1H NMR
400 MHz, CDCl_3



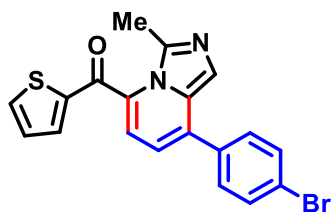
nmr1/NM-301 C13 NMR
NM-301



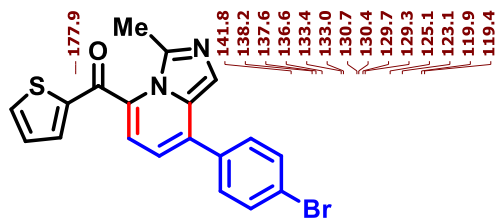
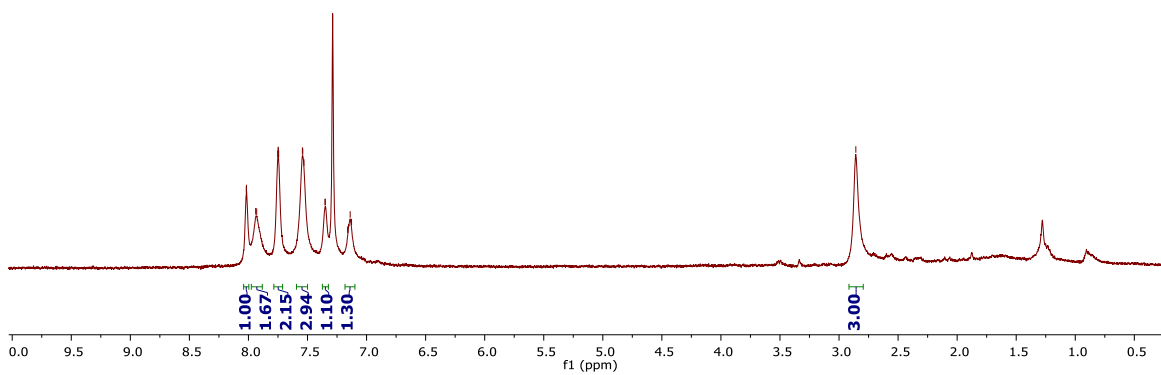
3ic, $^{13}\text{C}\{^1\text{H}\}$ NMR
100 MHz, CDCl_3



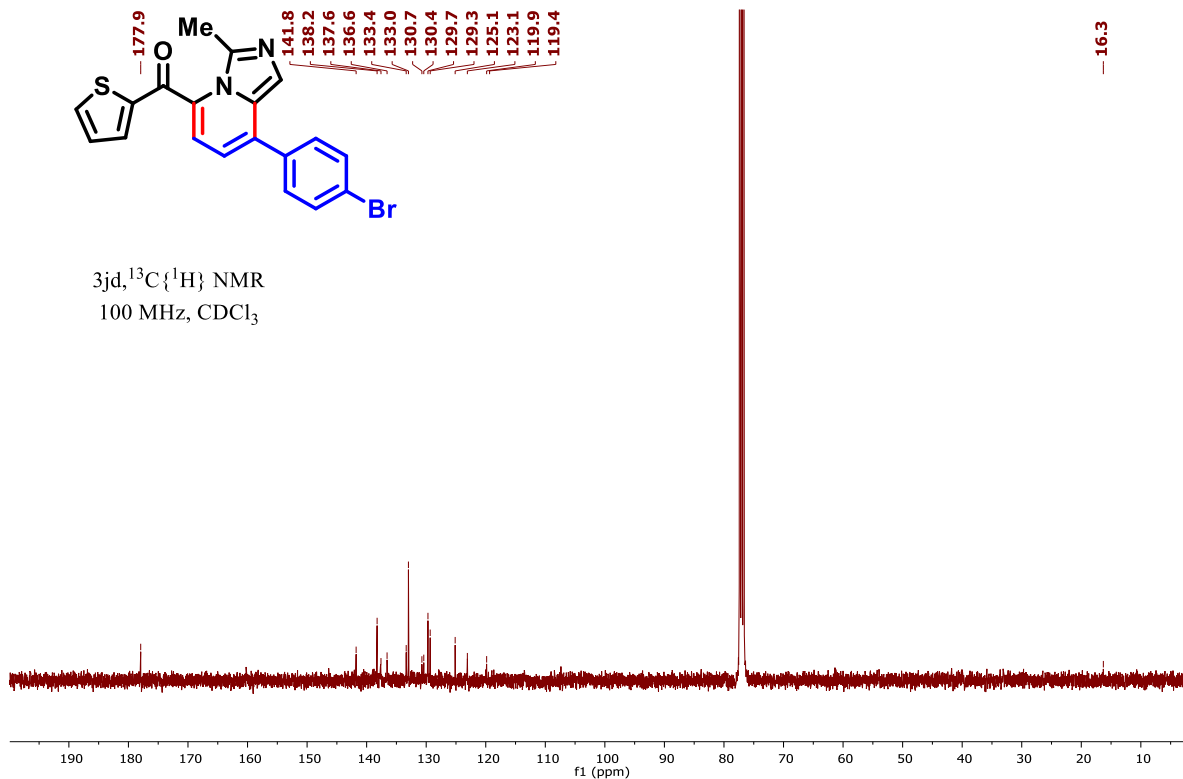
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NM-311

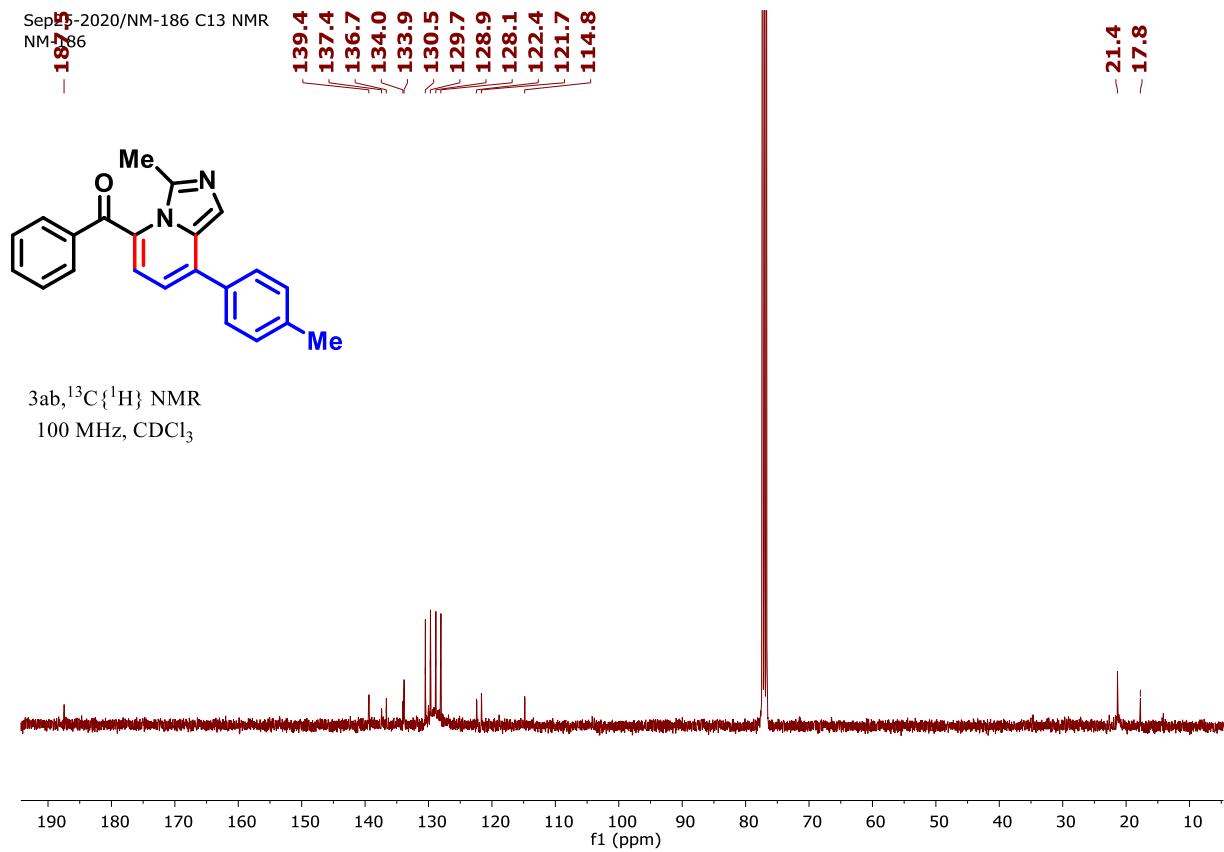
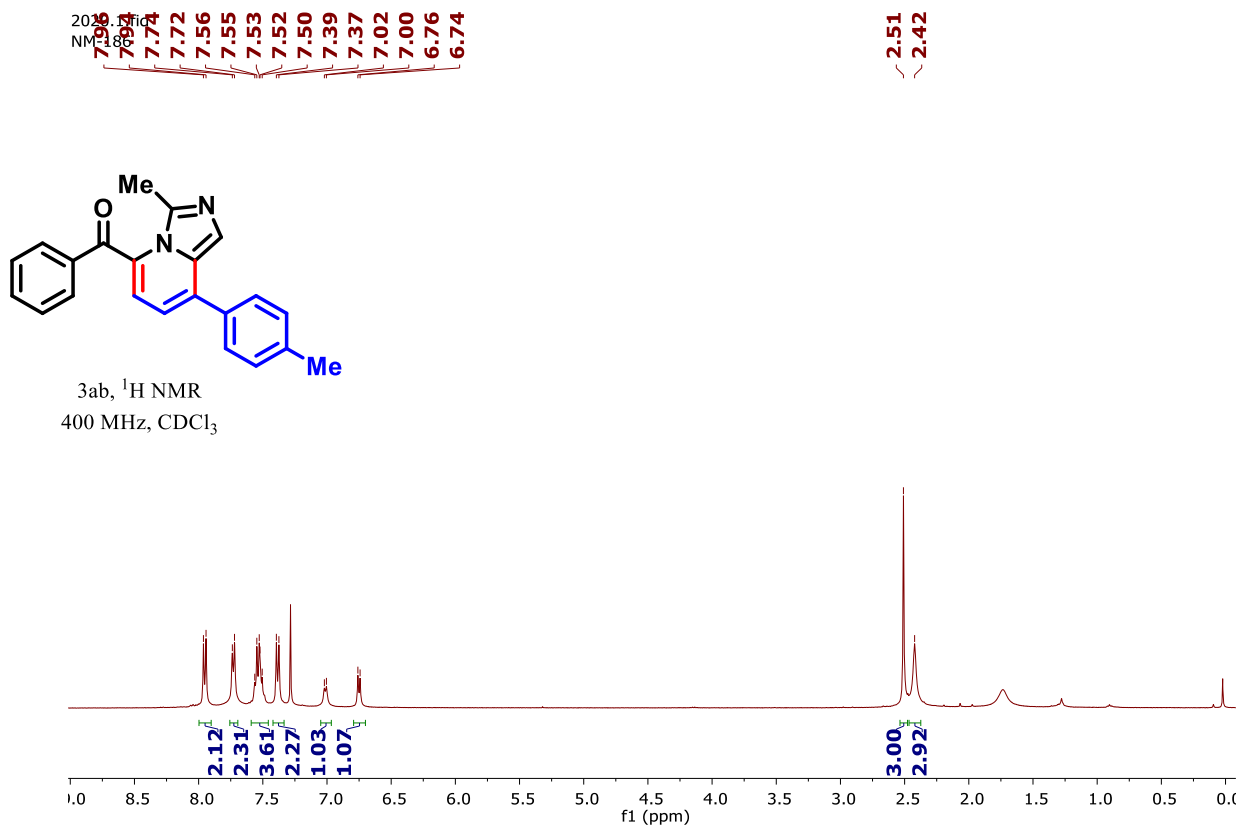


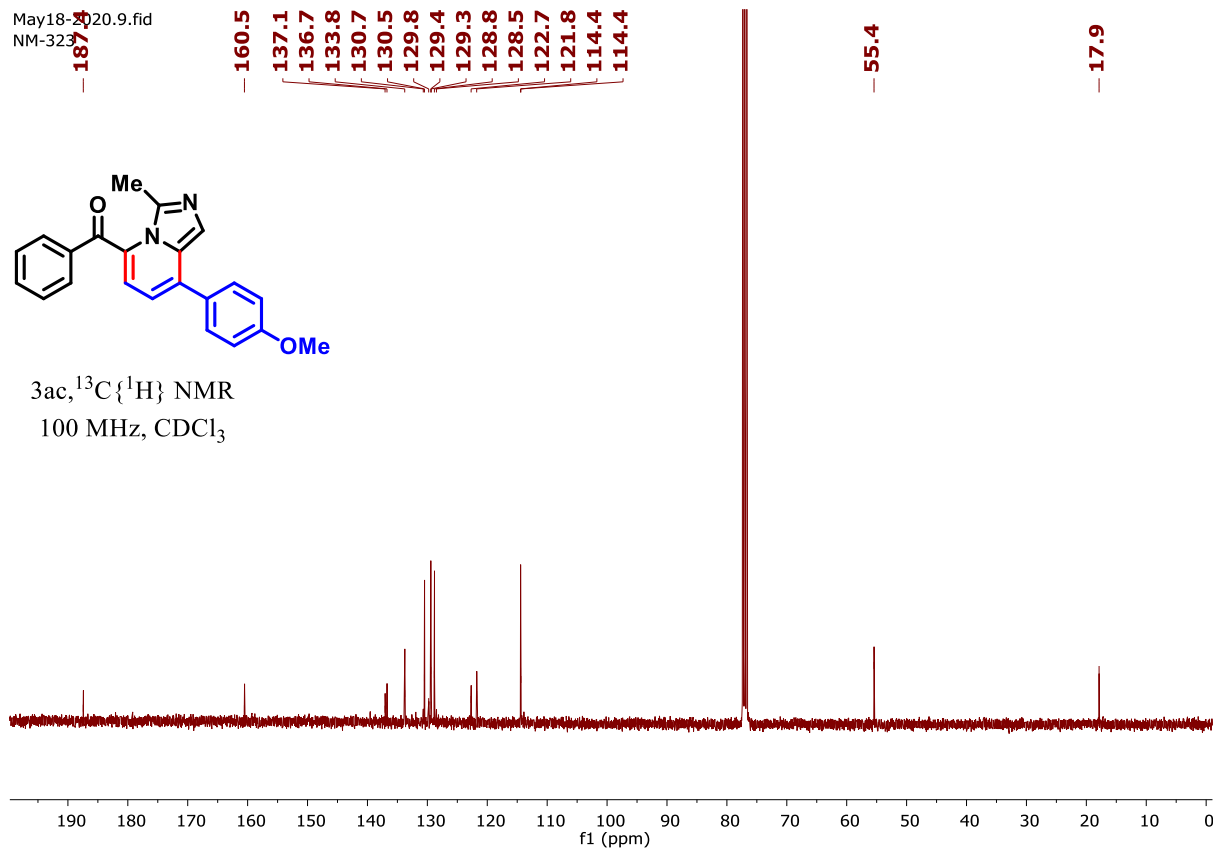
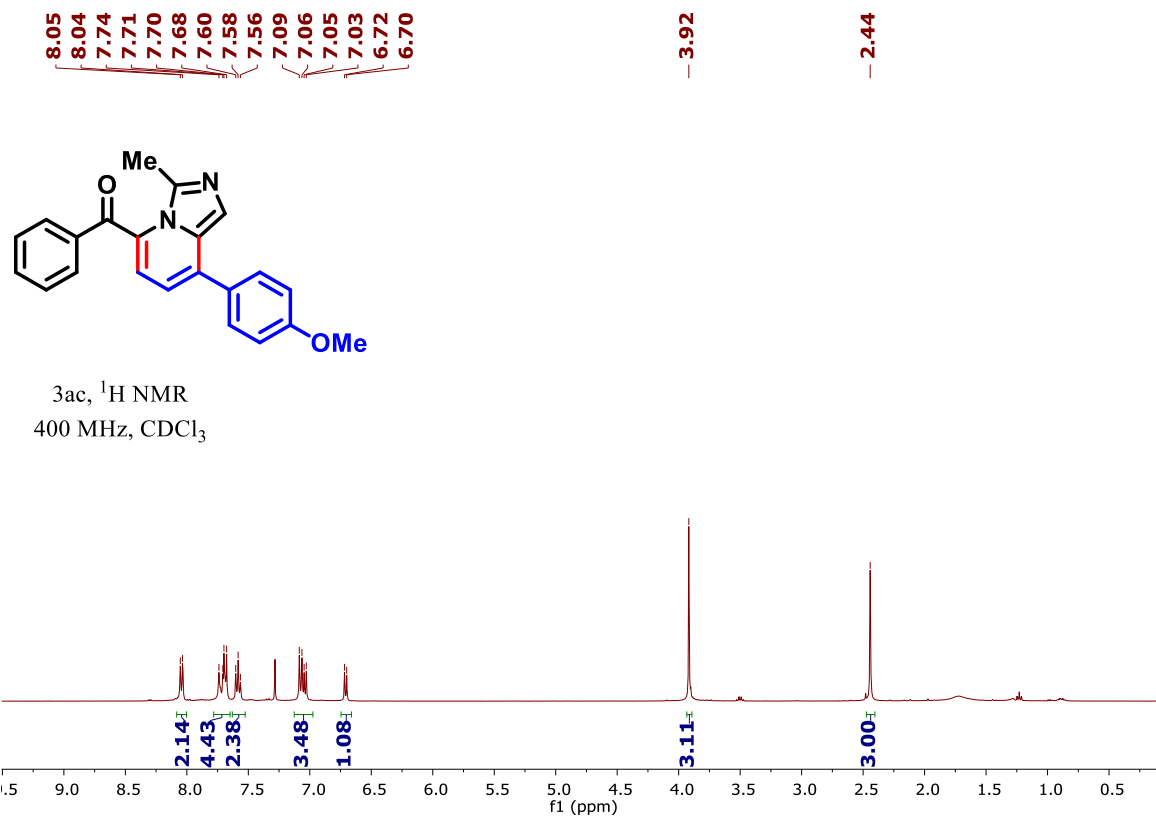
3jd, ^1H NMR
400 MHz, CDCl_3

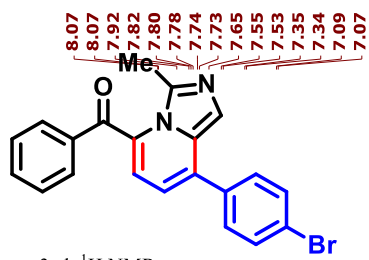


3jd, $^{13}\text{C}\{^1\text{H}\}$ NMR
100 MHz, CDCl_3

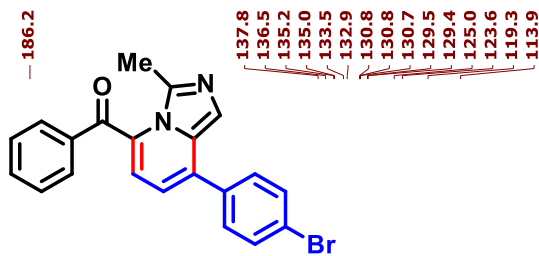
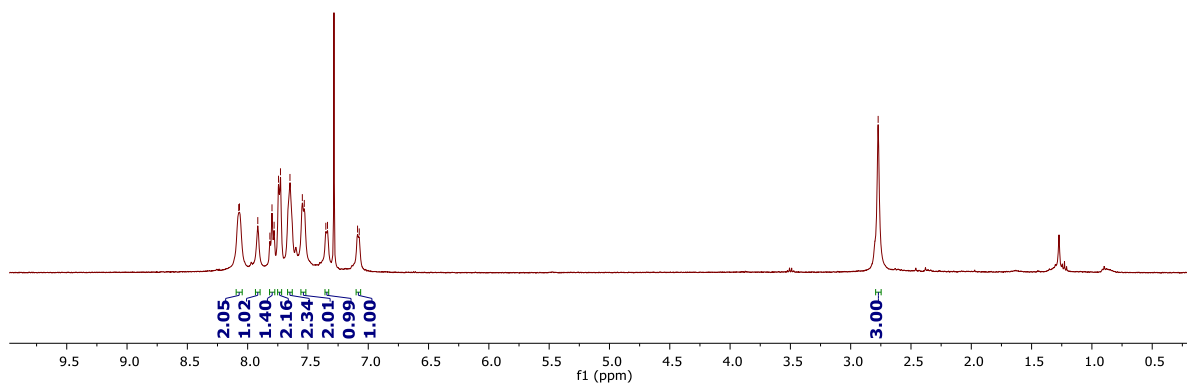




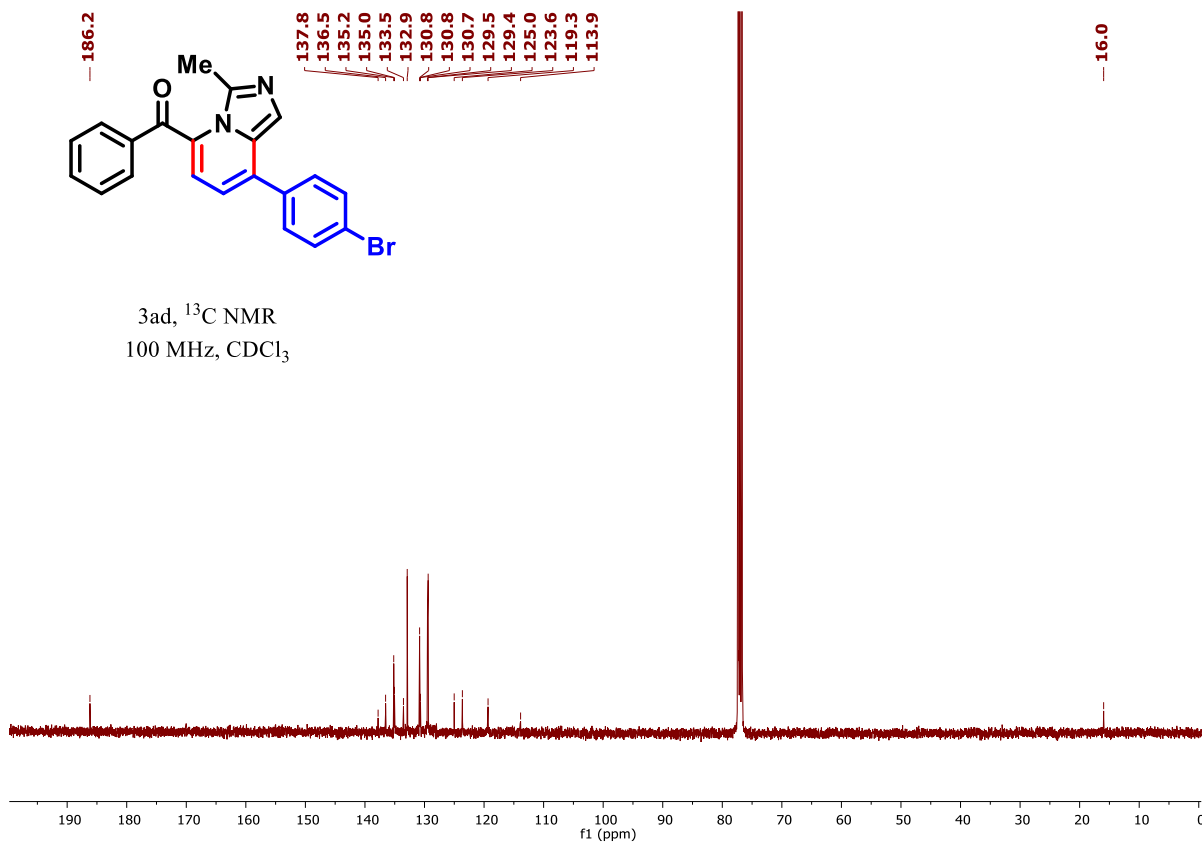




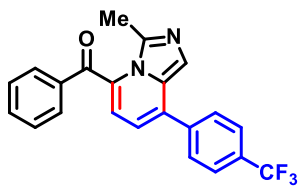
3ad, ^1H NMR
400 MHz, CDCl_3



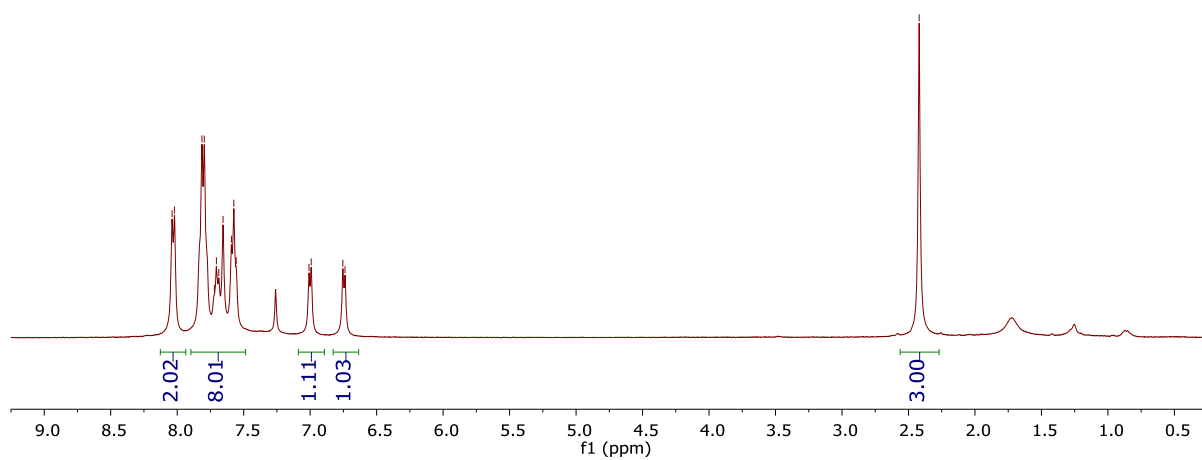
3ad, ^{13}C NMR
100 MHz, CDCl_3



¹H NMR
 400 MHz, CDCl₃
 7.80, 7.78, 7.76, 7.69, 7.66, 7.59, 7.57, 7.56, 7.51, 6.99, 6.75, 6.74, 2.42



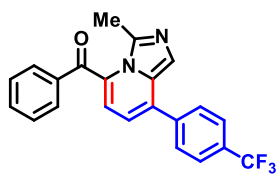
3ae, ¹H NMR
 400 MHz, CDCl₃



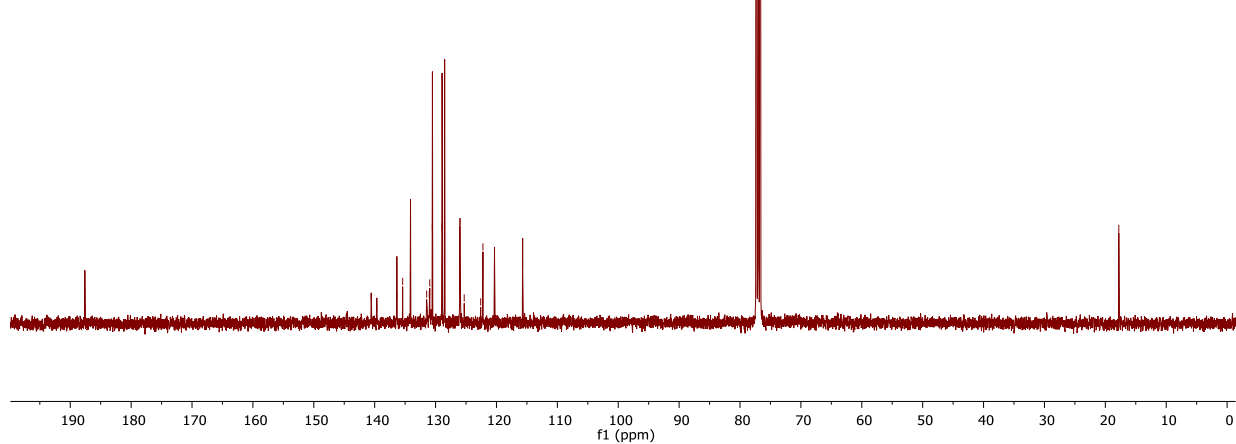
187.6

140.6, 139.7, 136.4, 135.4, 134.1, 131.5, 131.0, 131.0, 130.5, 128.9, 128.5, 126.0, 126.0, 125.9, 125.3, 122.6, 122.2, 120.3, 115.7

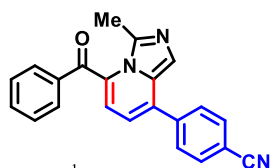
17.8



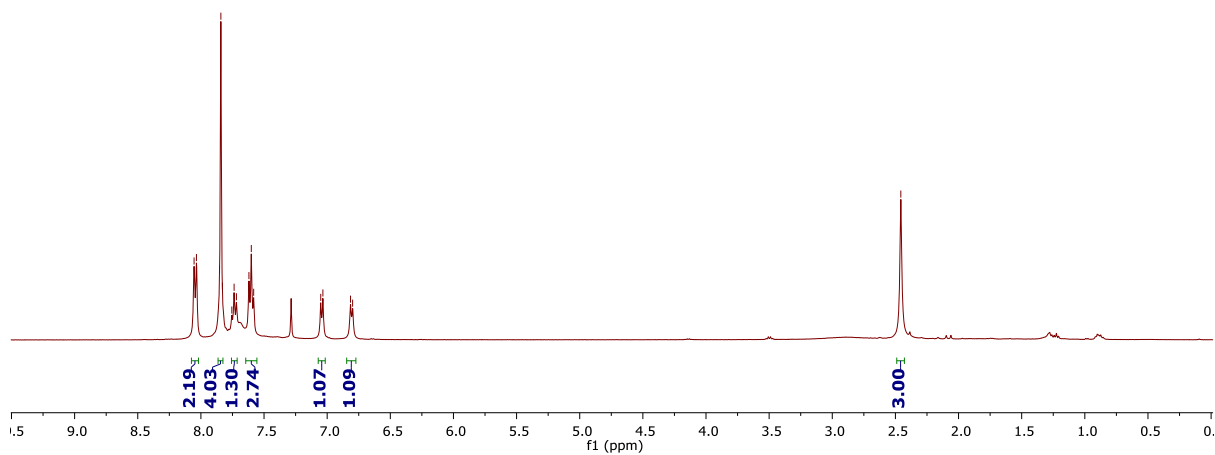
3ae, ¹³C{¹H} NMR
 100 MHz, CDCl₃



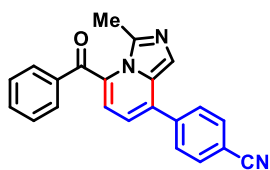
nmr/NM-348
NM-348



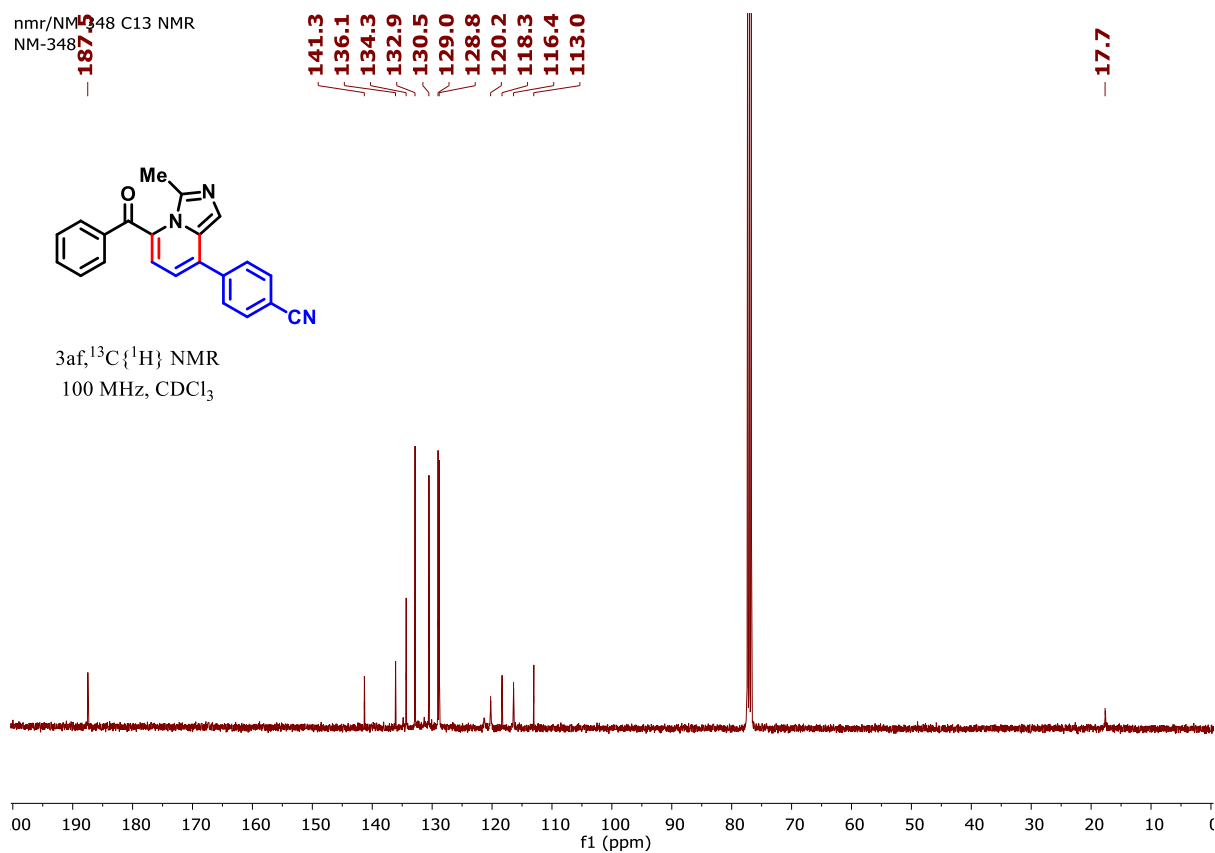
3af, ^1H NMR
400 MHz, CDCl_3

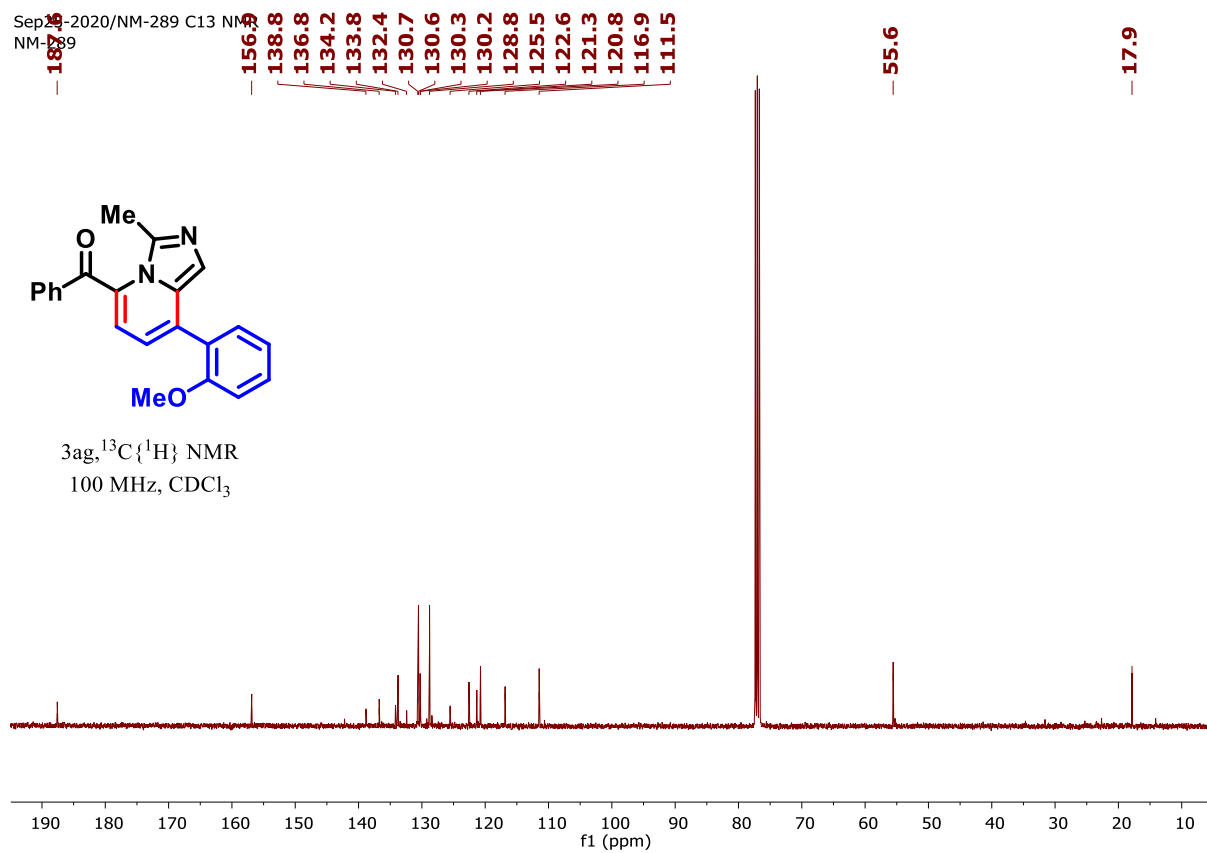
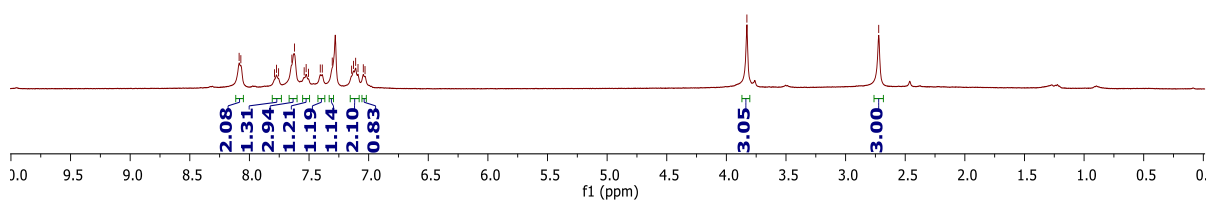
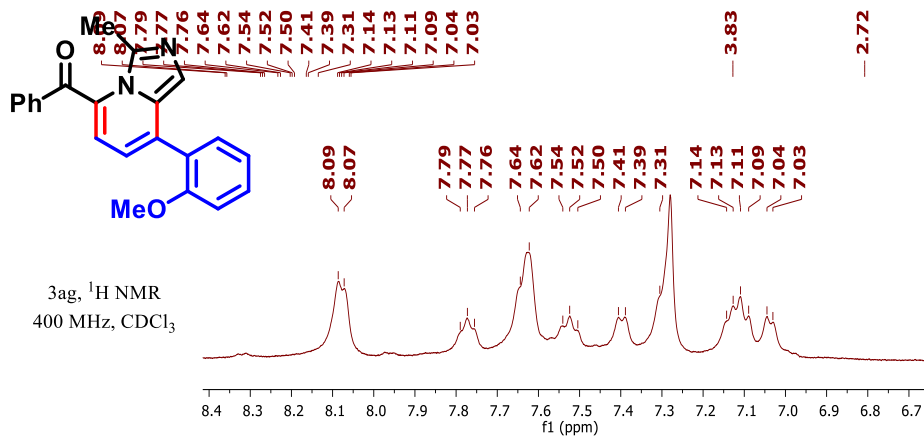


nmr/NM-348 C13 NMR
NM-348



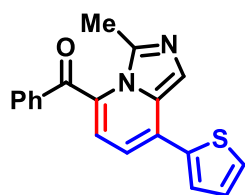
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100 MHz, CDCl_3



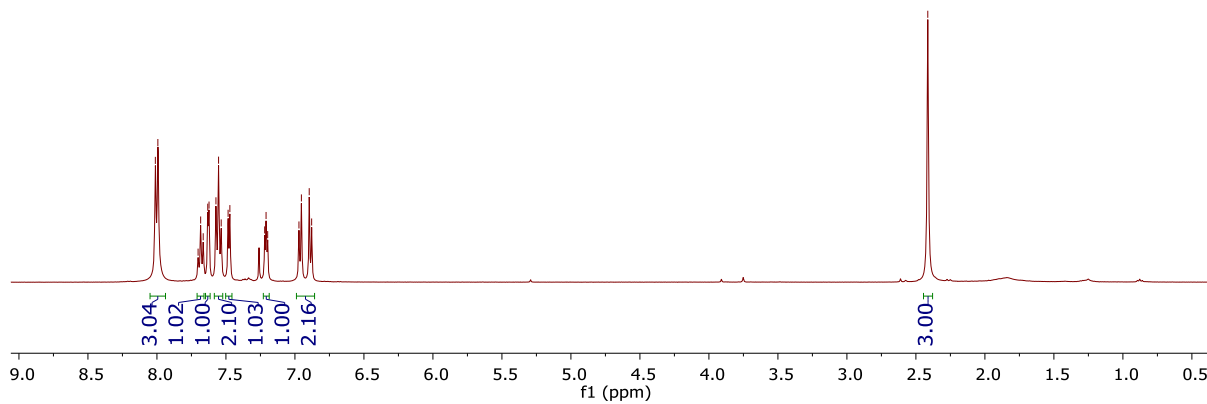


8.01
7.99
7.70
7.68
7.66
7.63
7.62
7.57
7.55
7.53
7.48
7.47
7.22
7.21
7.20
6.97
6.95
6.90
6.88

— 2.41



3ah, ^1H NMR
400 MHz, CDCl_3

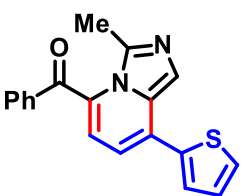


nmr/NM-288c13 nmr
nm-288

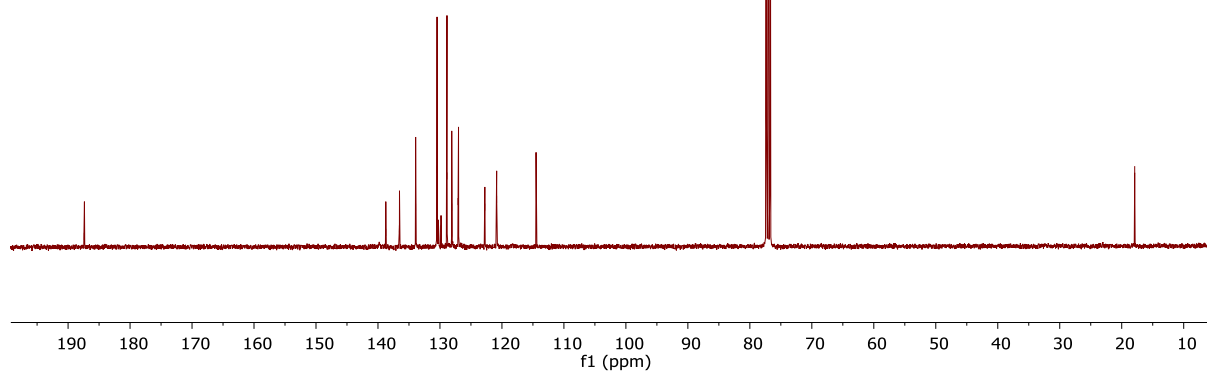
— 187.2

138.8
136.5
133.9
130.5
130.3
129.8
128.9
128.1
127.1
127.0
122.8
120.9

— 17.9



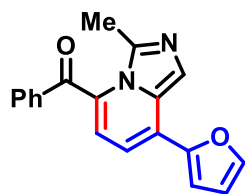
3ah, $^{13}\text{C}\{^1\text{H}\}$ NMR
100 MHz, CDCl_3



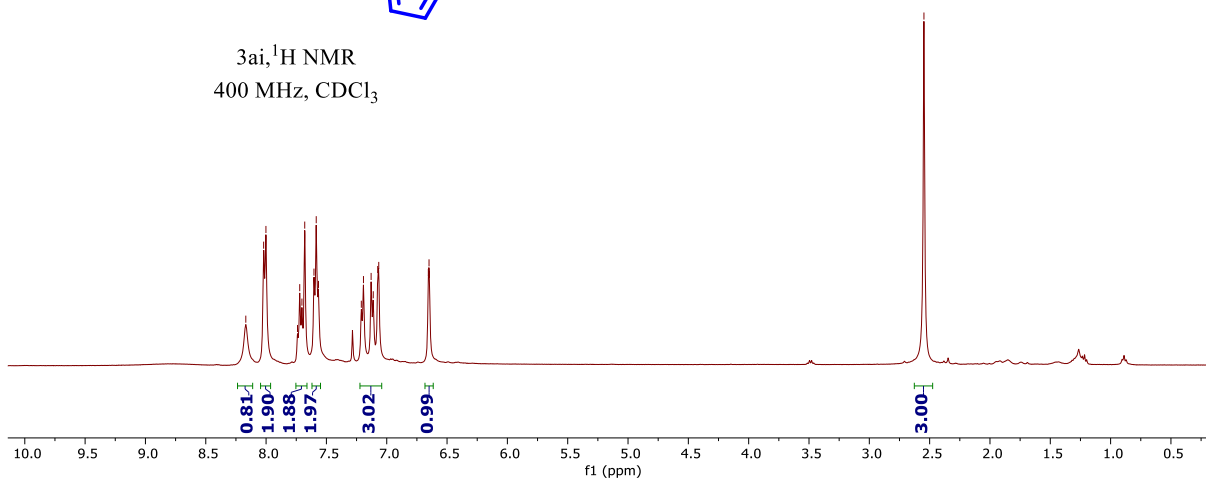
Revision work
NM-808

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6.65

2.55



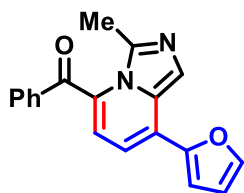
3ai, ^1H NMR
400 MHz, CDCl_3



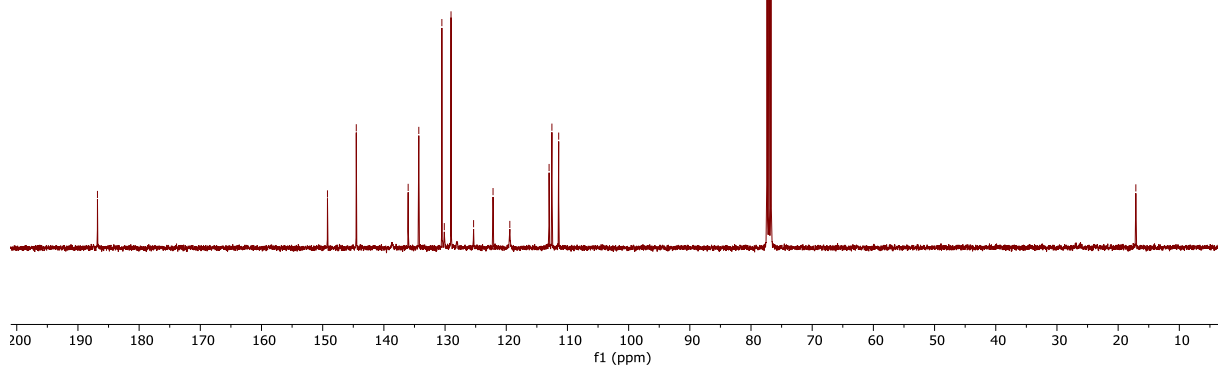
Revision work
NM-808 C13 NMR

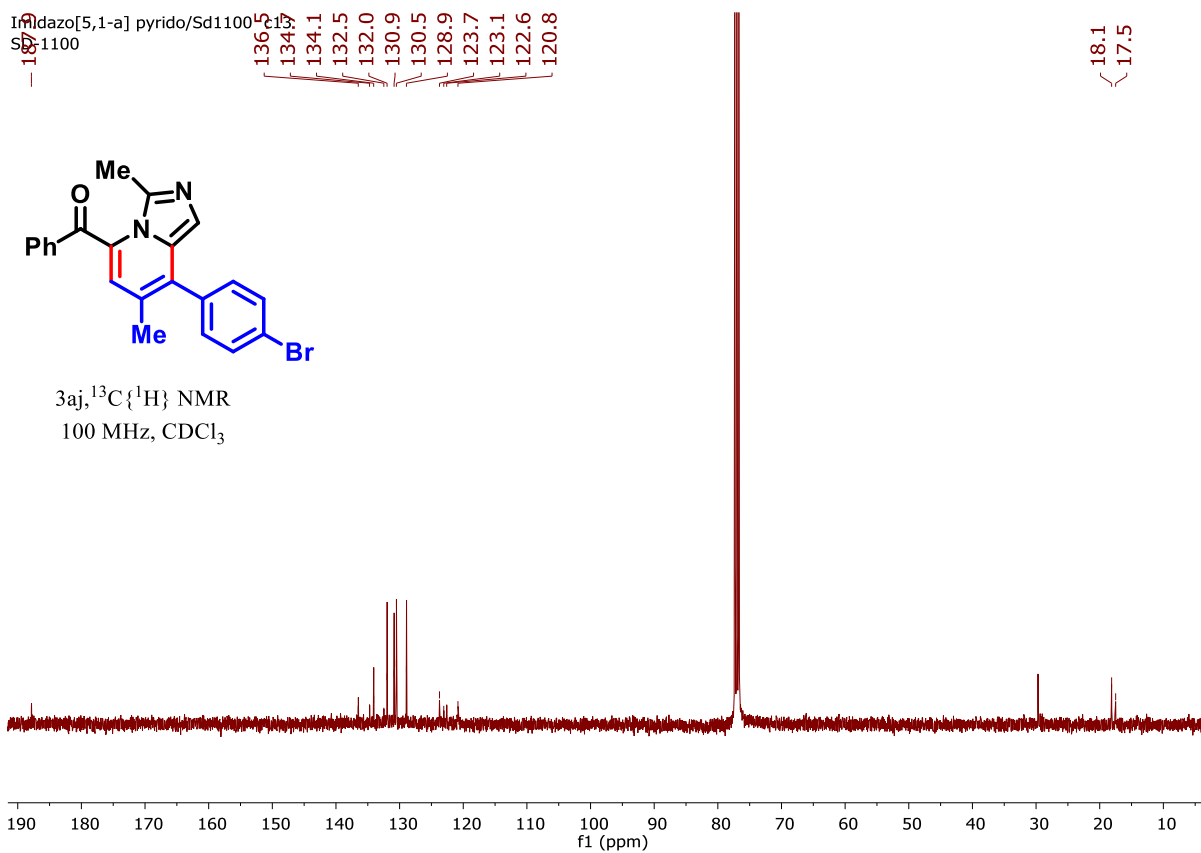
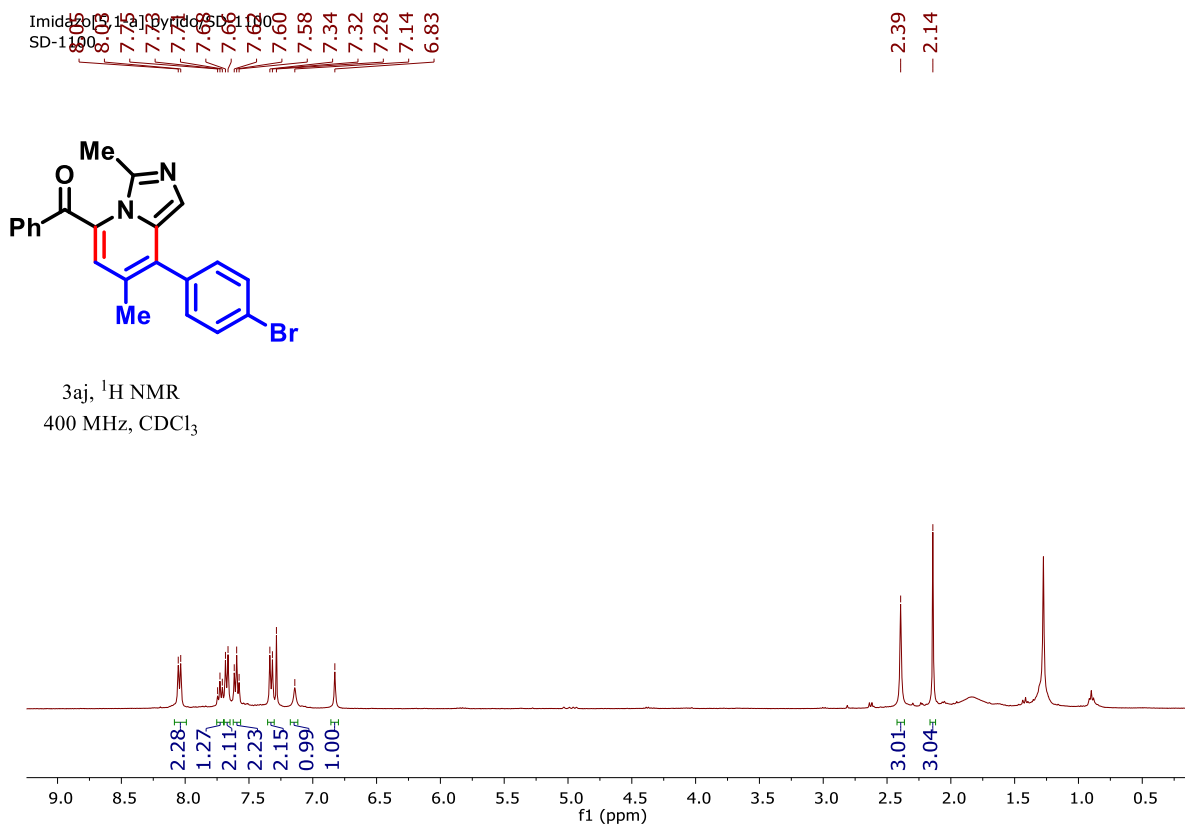
186.6
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119.4
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111.4

17.1

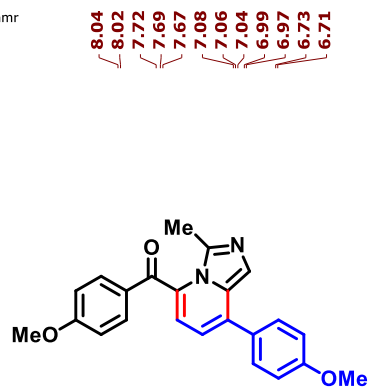


3ai, $^{13}\text{C}\{^1\text{H}\}$ NMR
100 MHz, CDCl_3

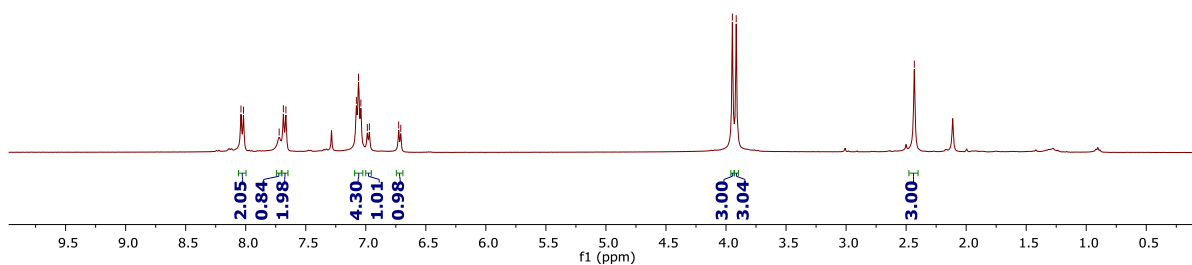
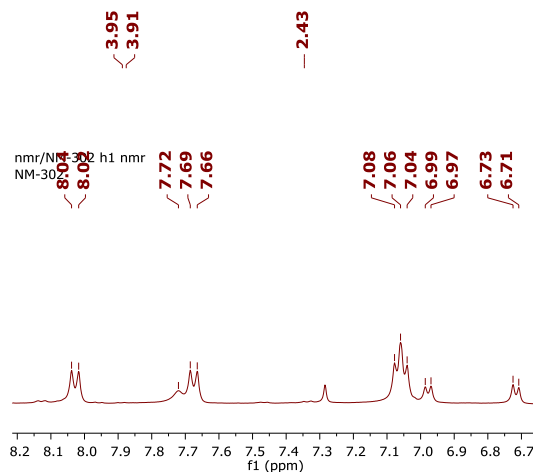




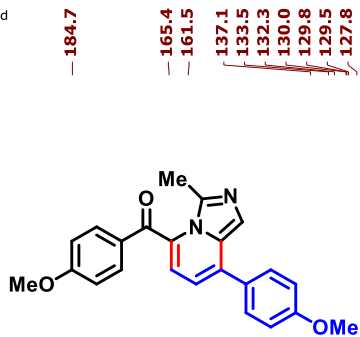
nmr/NM-302 h1 nmr
NM-302



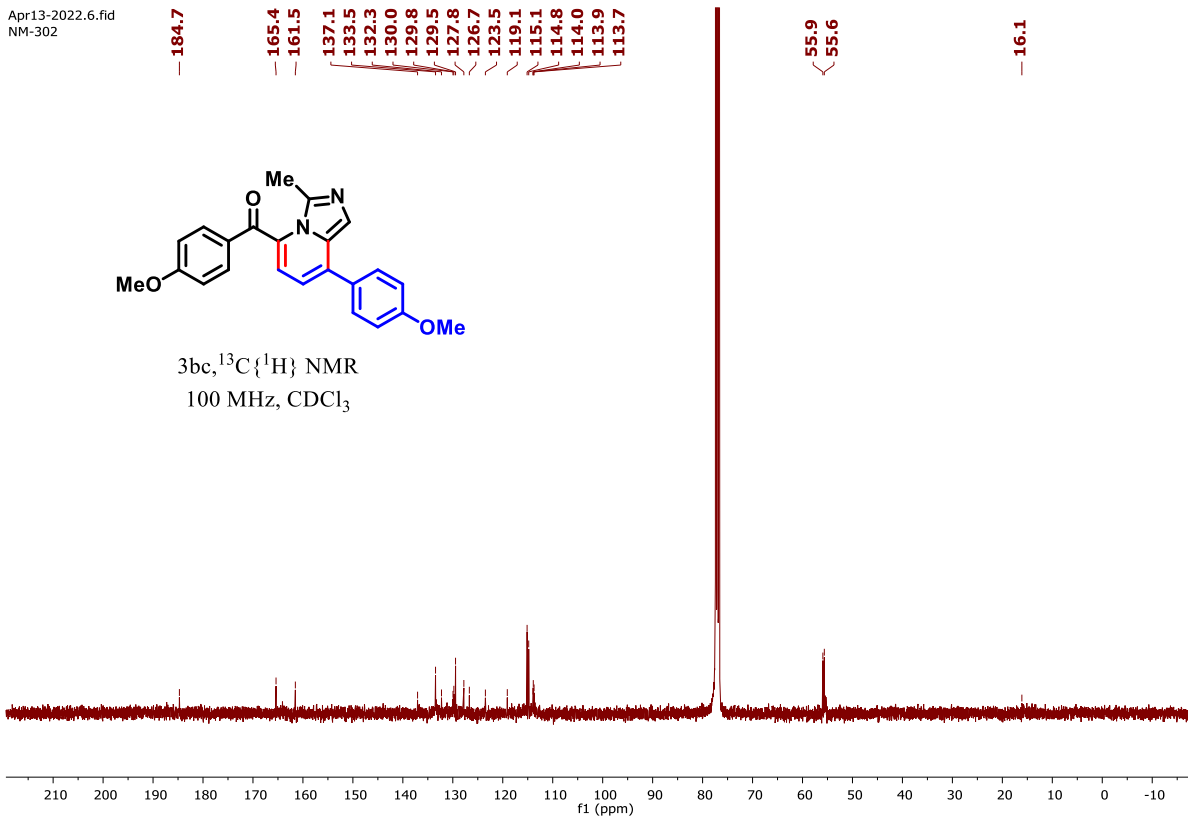
3bc, ^1H NMR
400 MHz, CDCl_3

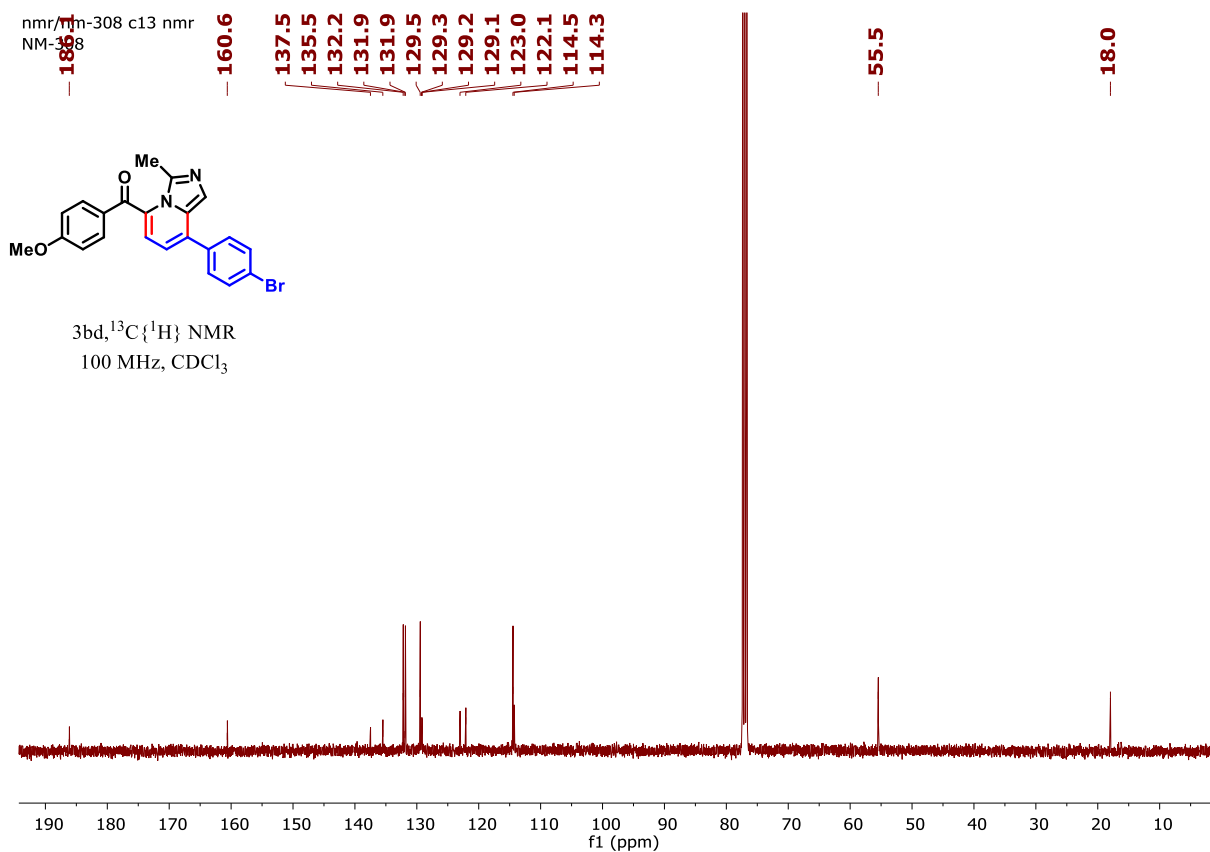
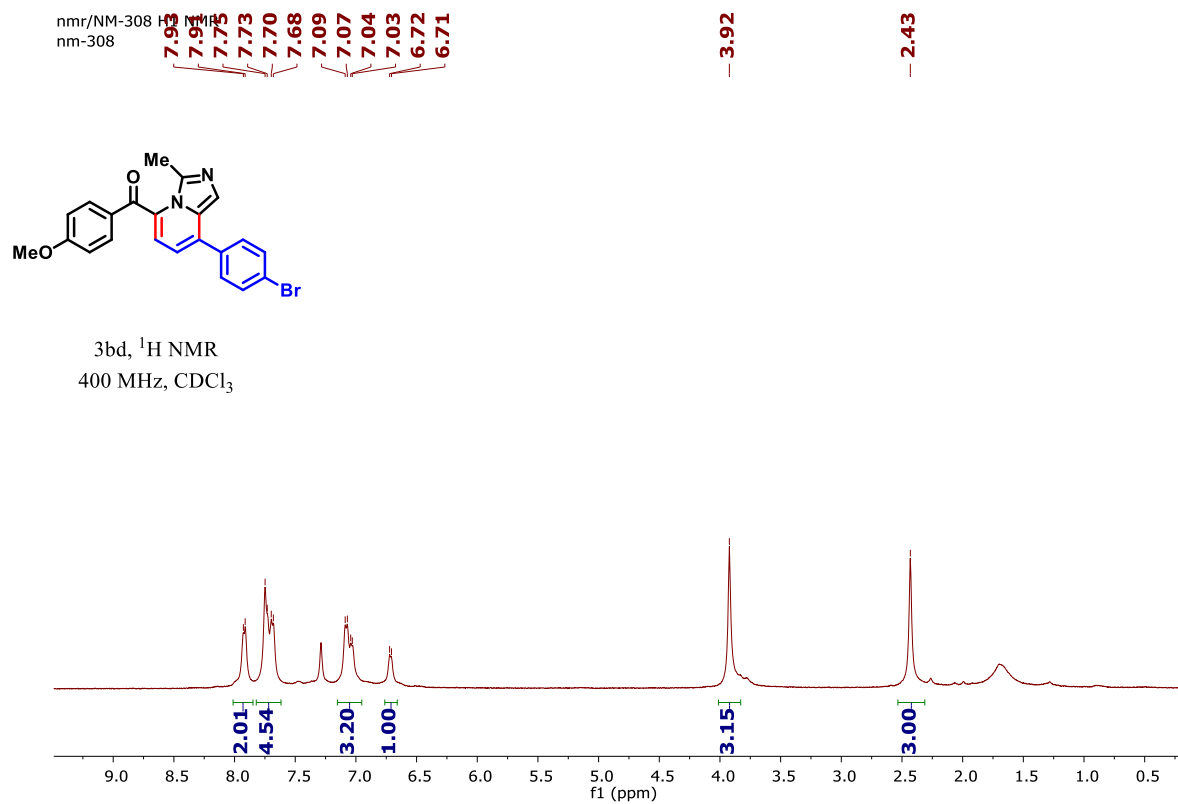


Apr13-2022.6.fid
NM-302



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



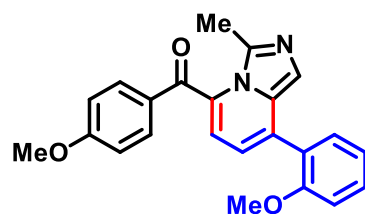


nmr repeated (SHIV sir)/NM-434
NM-434

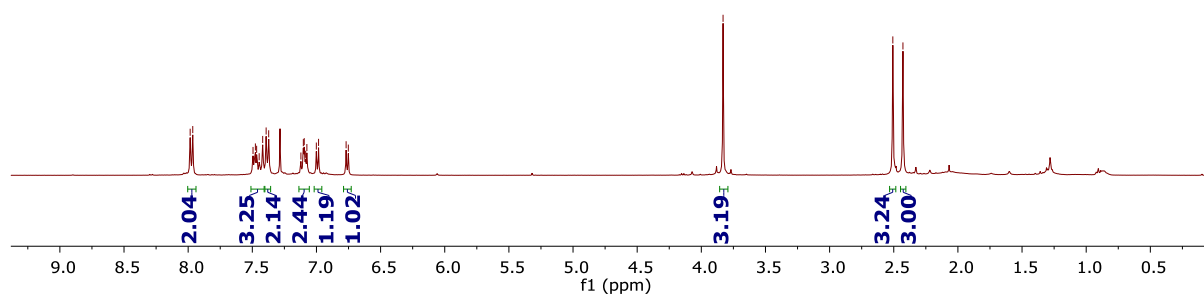
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6.77
6.75

3.83

2.51
2.43



3bg, ^1H NMR
400 MHz, CDCl_3

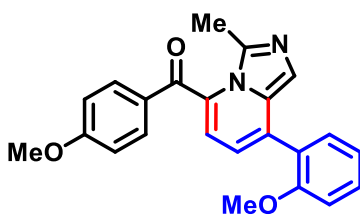


nmr repeated (SHIV sir)/NM-434
NM-434

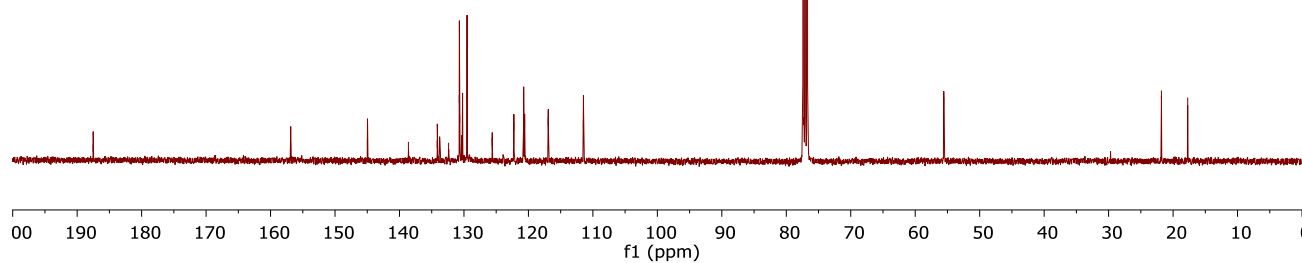
187.5
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138.5
134.1
133.8
132.4
130.7
130.7
130.4
130.2
129.5
125.6
122.3
120.7
120.6
116.9
111.5

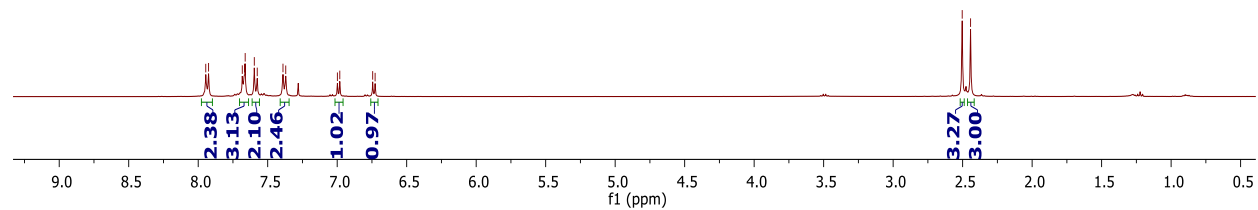
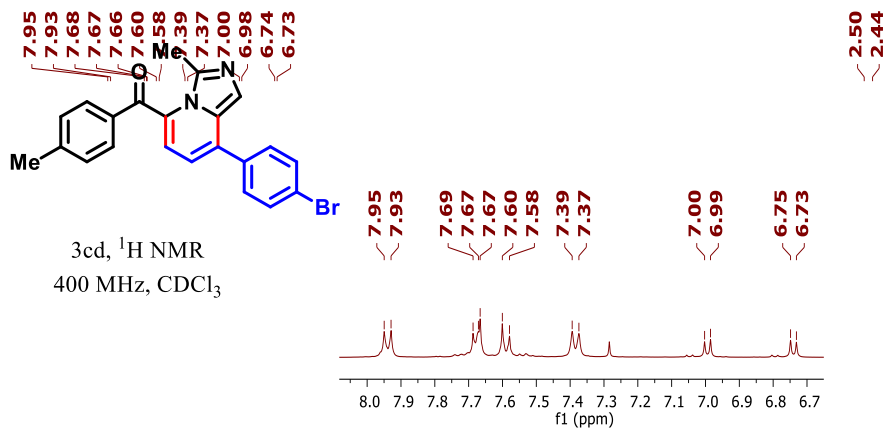
55.6

21.8
17.7

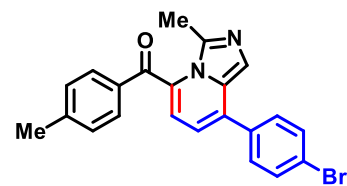


3bg, $^{13}\text{C}\{^1\text{H}\}$ NMR
100 MHz, CDCl_3

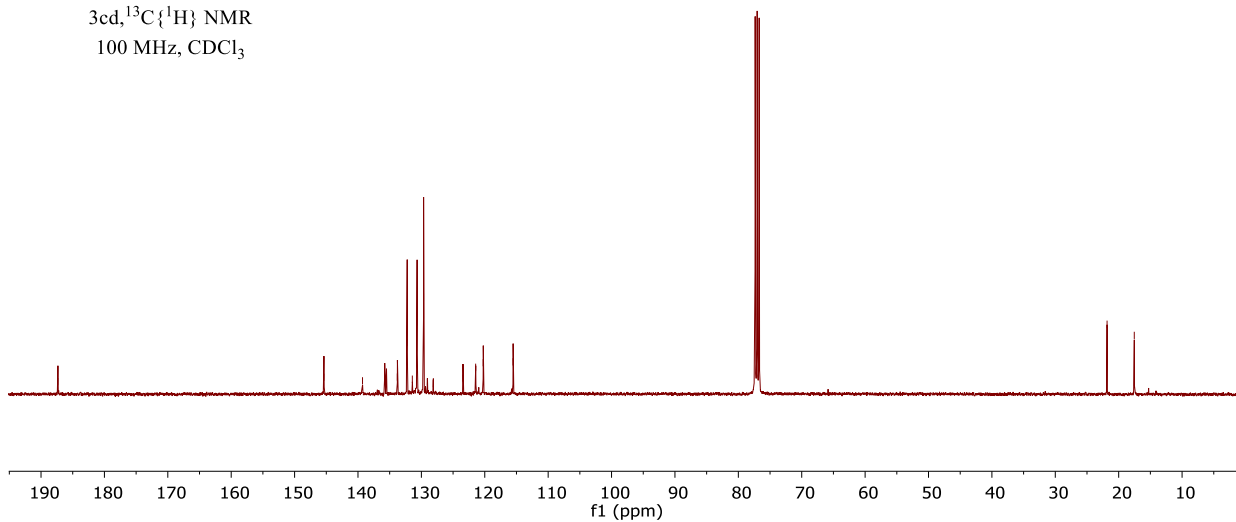


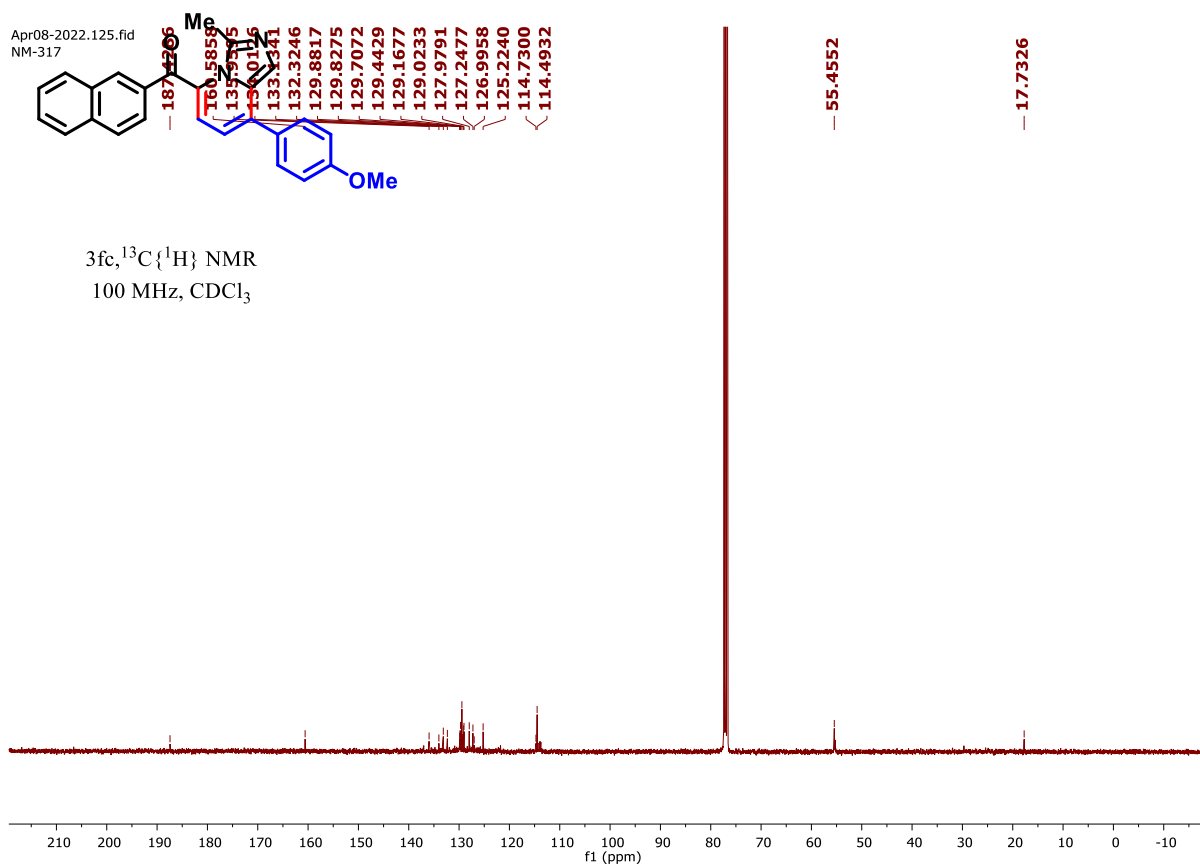
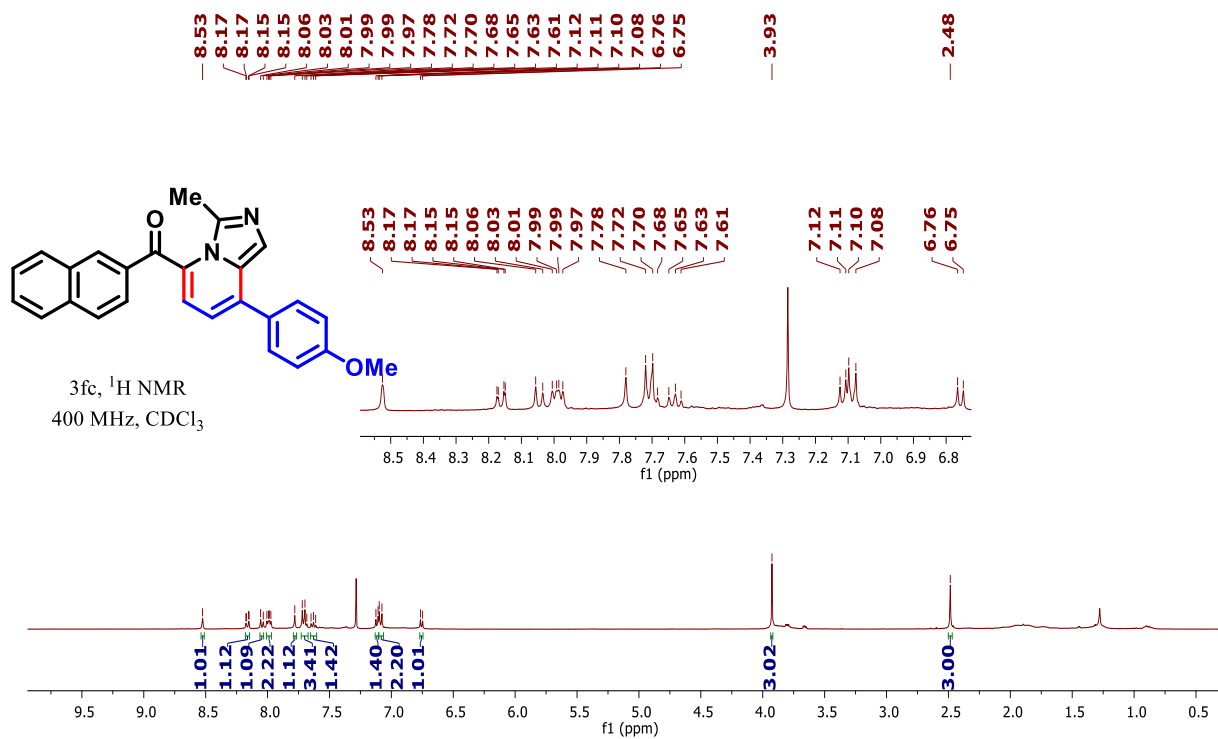


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NM-R

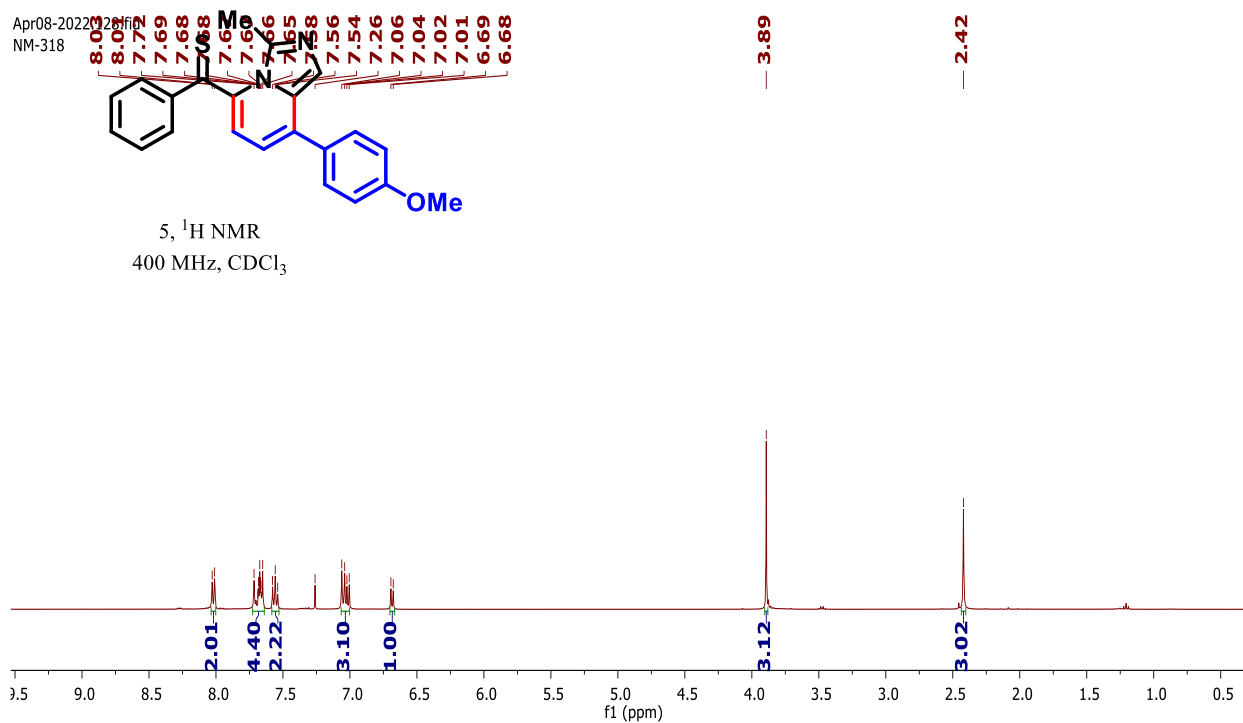


3cd, $^{13}\text{C}\{^1\text{H}\}$ NMR
100 MHz, CDCl_3

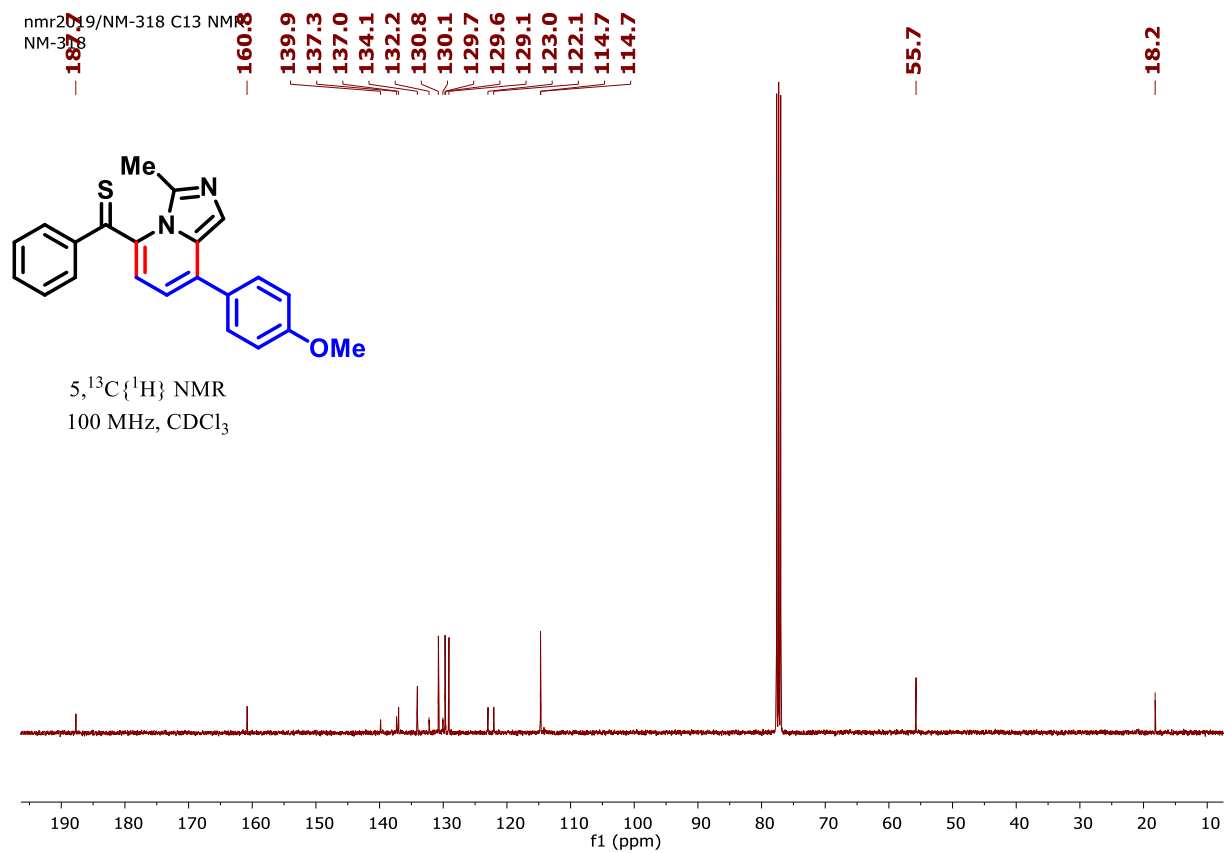


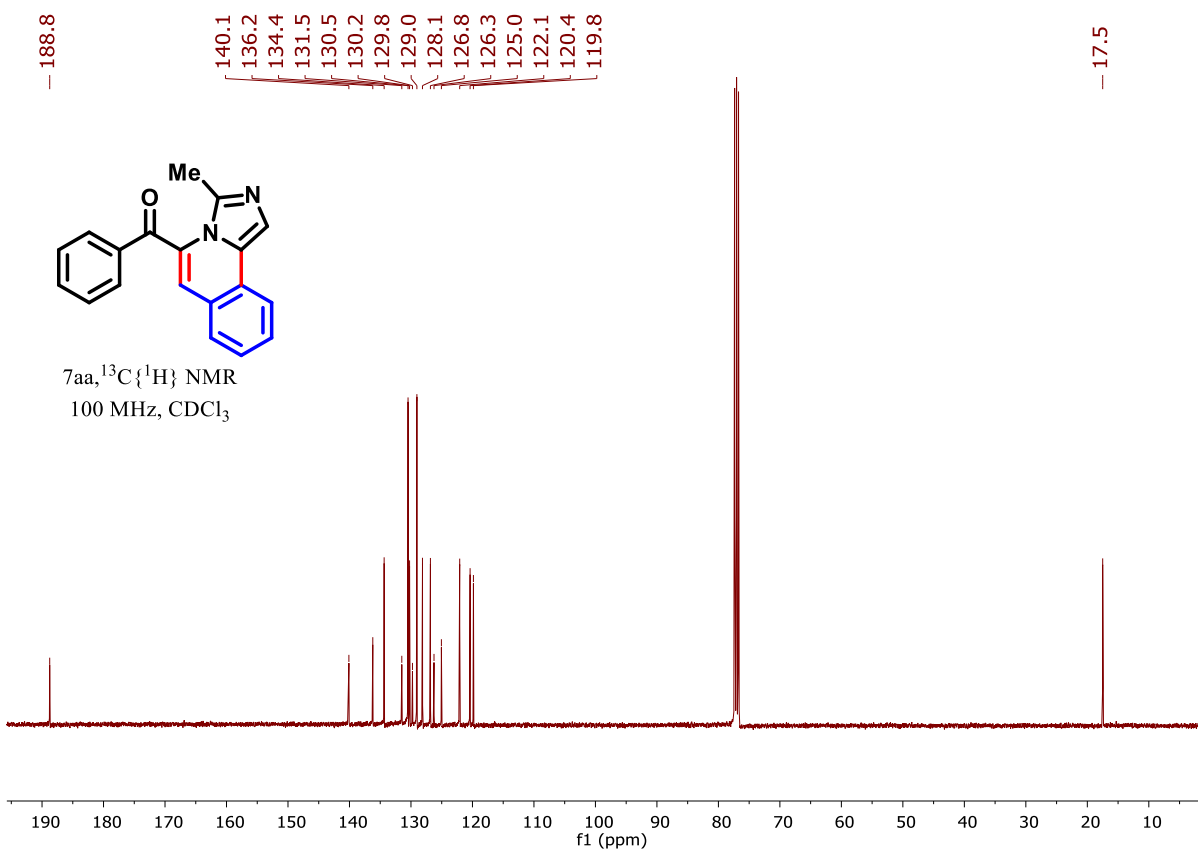
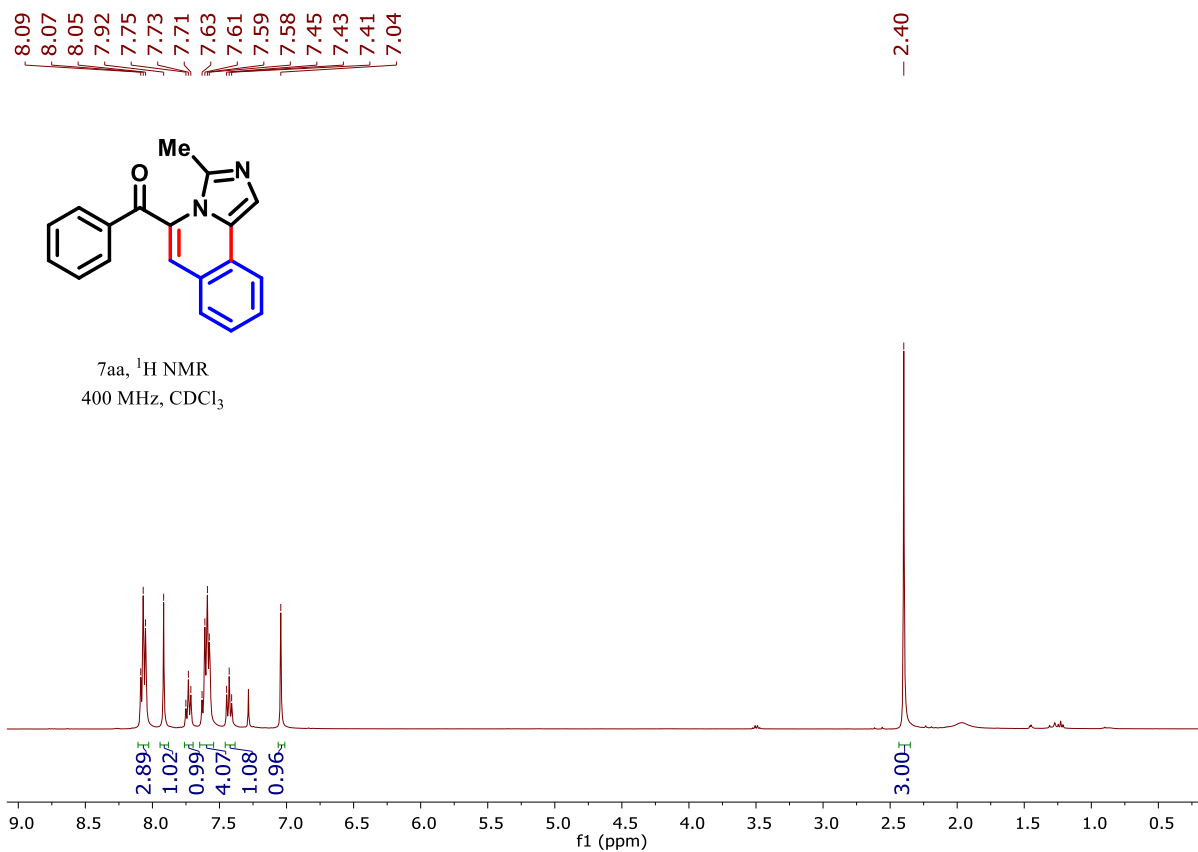


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NM-318



nmr2019/NM-318 C13 NMR
NM-318

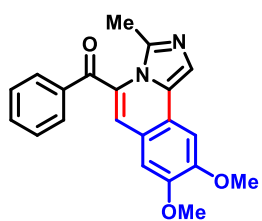




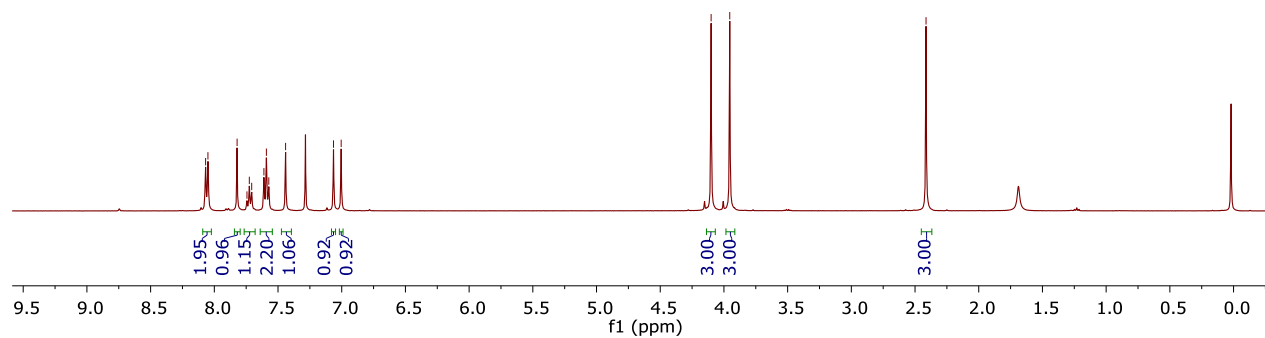
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7.82
7.74
7.73
7.71
7.61
7.59
7.57
7.44
7.06
7.00

4.10
3.95

2.41



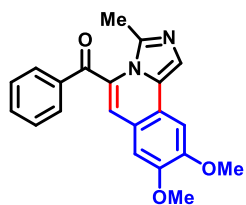
7ab, ^1H NMR
400 MHz, CDCl_3



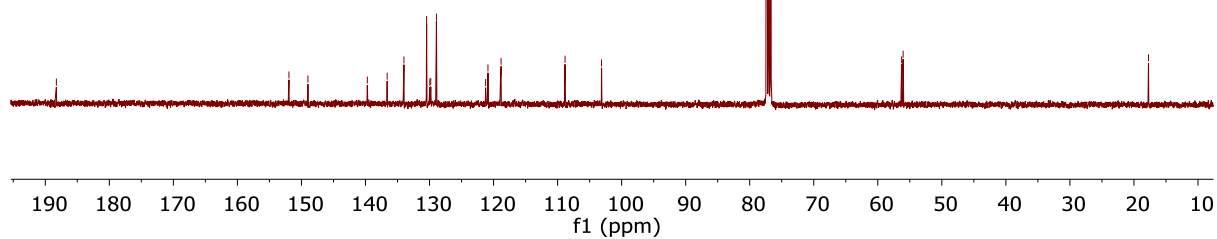
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130.0
129.8
128.9
121.2
120.9
118.9
118.8
108.8
103.1

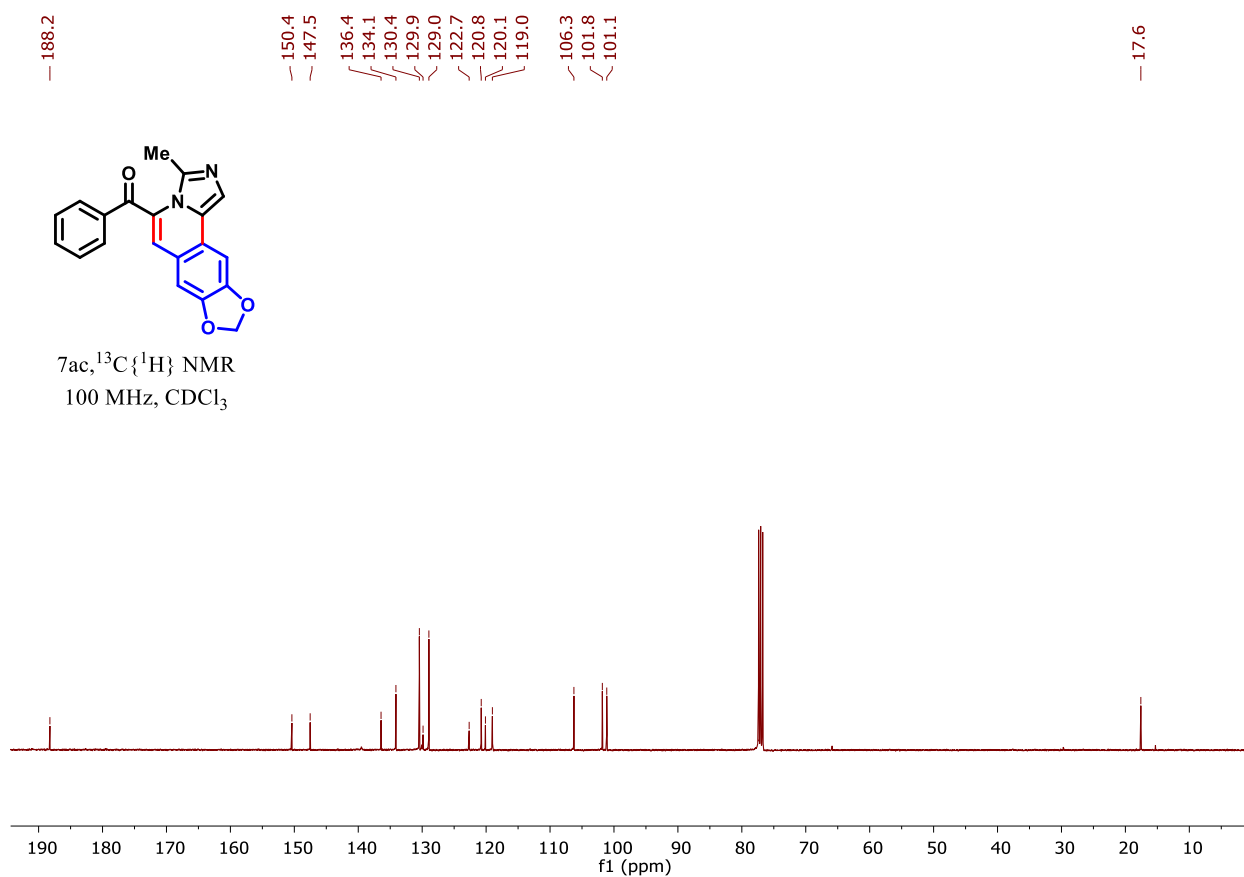
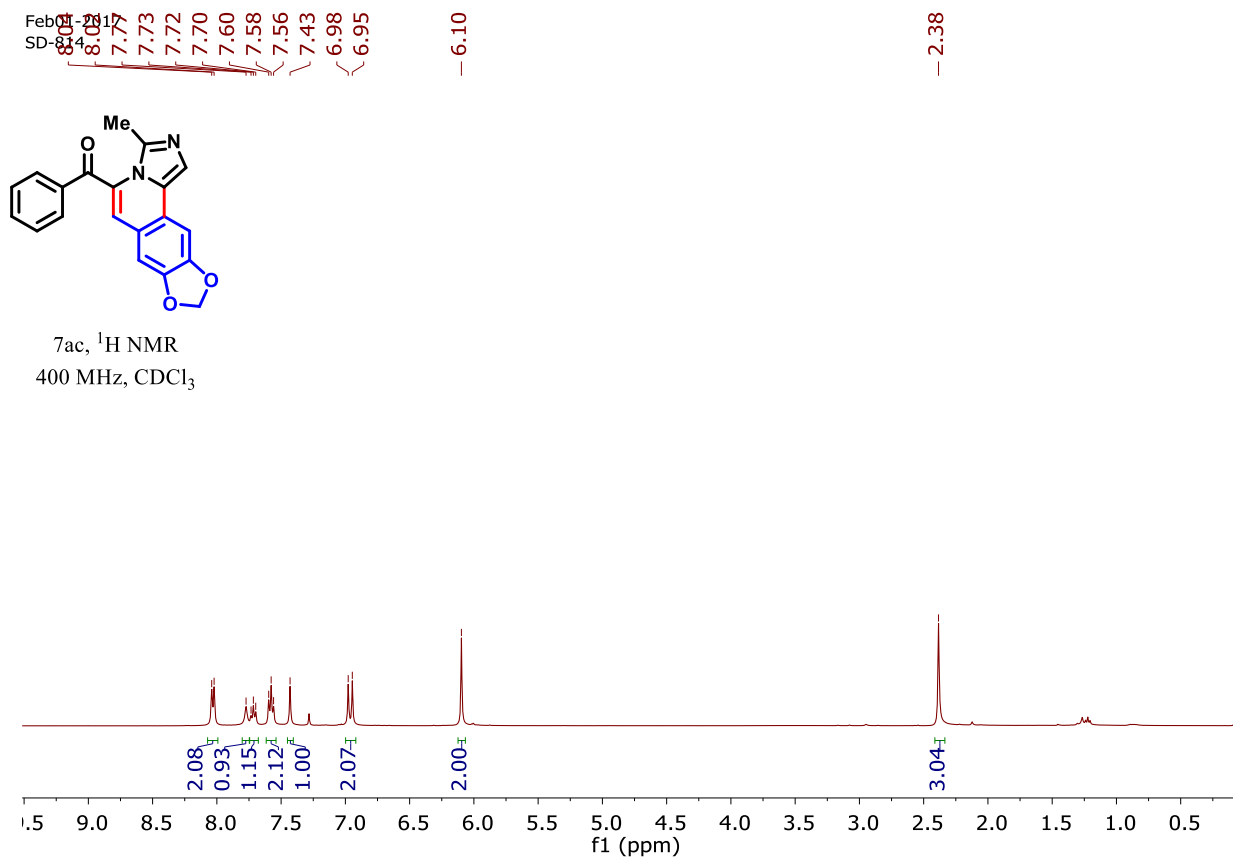
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56.0

17.7



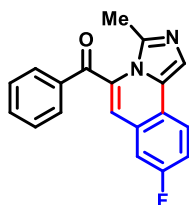
7ab, $^{13}\text{C}\{^1\text{H}\}$ NMR
100 MHz, CDCl_3



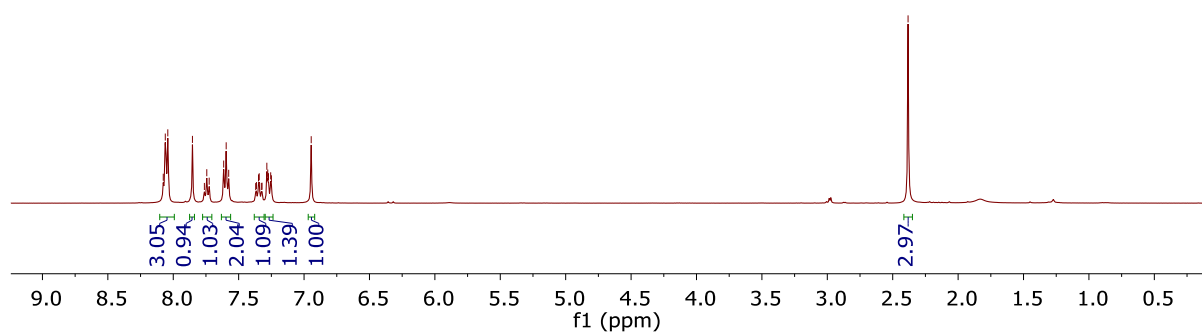


8.08
8.06
8.04
7.85
7.76
7.74
7.73
7.61
7.60
7.58
7.37
7.36
7.35
7.34
7.33
7.32
7.28
7.28
7.27
7.26
7.25
6.95

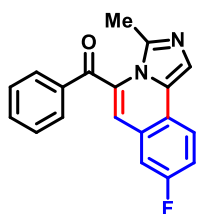
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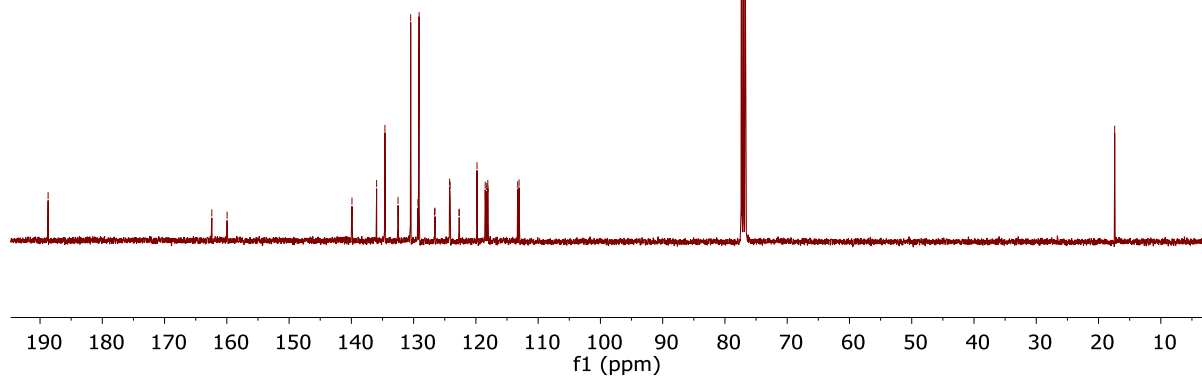
7ad, ^1H NMR
400 MHz, CDCl_3



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160.0
139.9
135.9
134.6
132.5
130.5
129.3
129.1
126.7
126.6
124.2
124.1
122.7
122.7
119.8
118.5
118.3
118.1
118.1
113.3
113.1
17.4

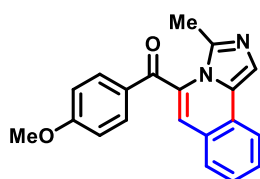


7ad, $^{13}\text{C}\{^1\text{H}\}$ NMR
100 MHz, CDCl_3

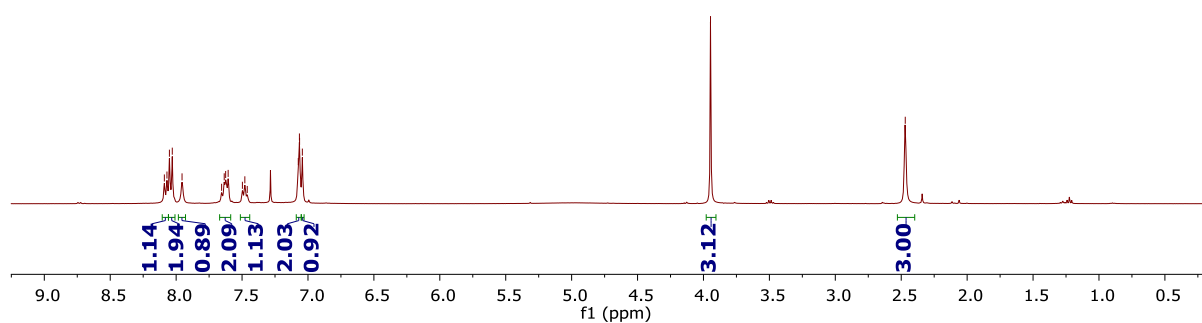


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8.06
8.07
8.08
8.03
7.99
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7.50
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7.46
7.07
7.06
7.06
7.04

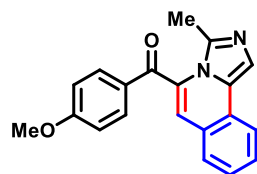


7ba, ^1H NMR
400 MHz, CDCl_3

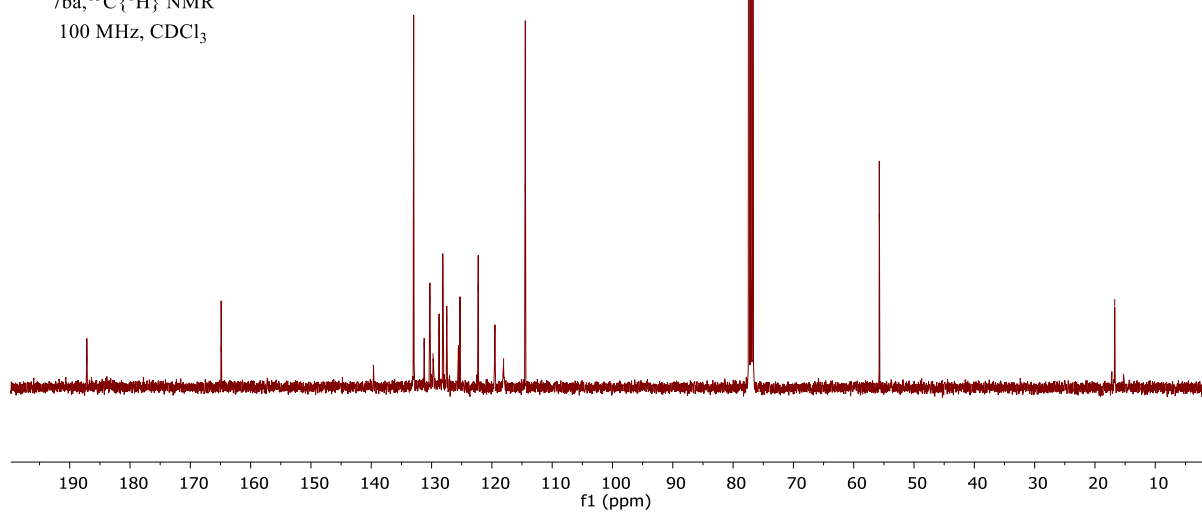


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NM-529

187.8
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125.3
122.3
119.5
118.1
114.5
55.8
16.7



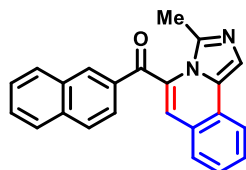
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100 MHz, CDCl_3



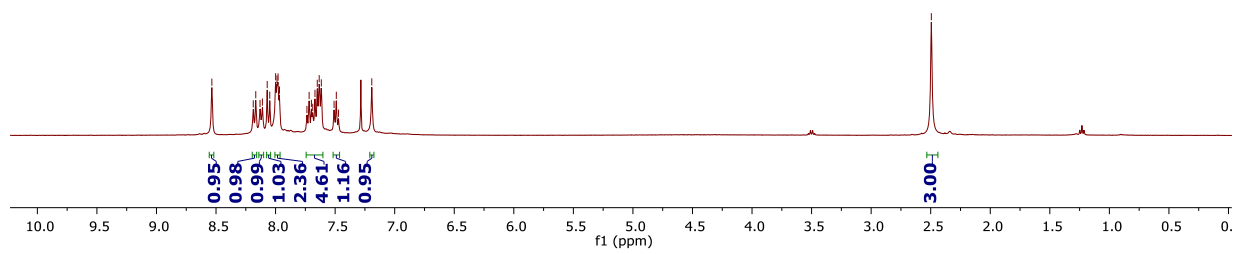
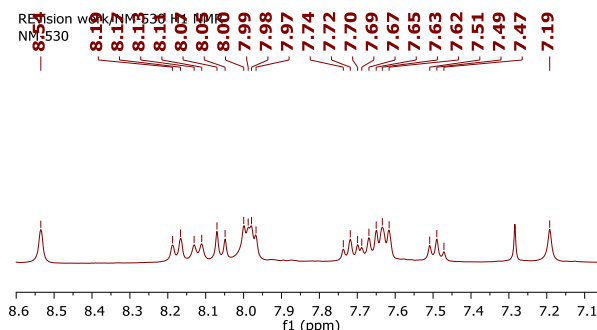
REVISION WORK
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8.19
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8.13
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8.05
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7.97
7.74
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7.51
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7.47
7.19

2.49



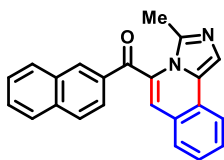
7fa, ^1H NMR
400 MHz, CDCl_3



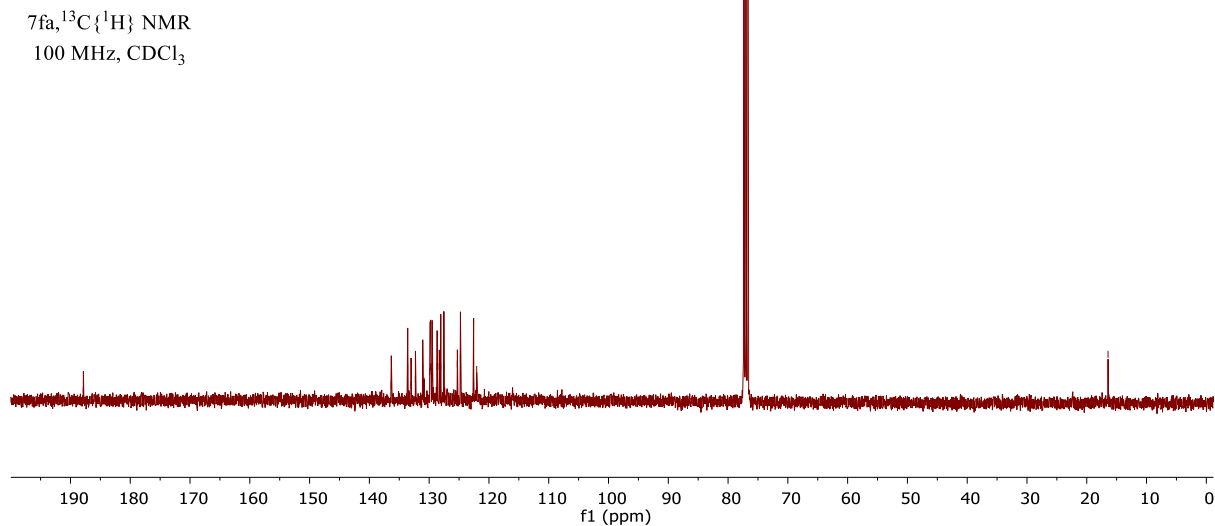
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NM-530

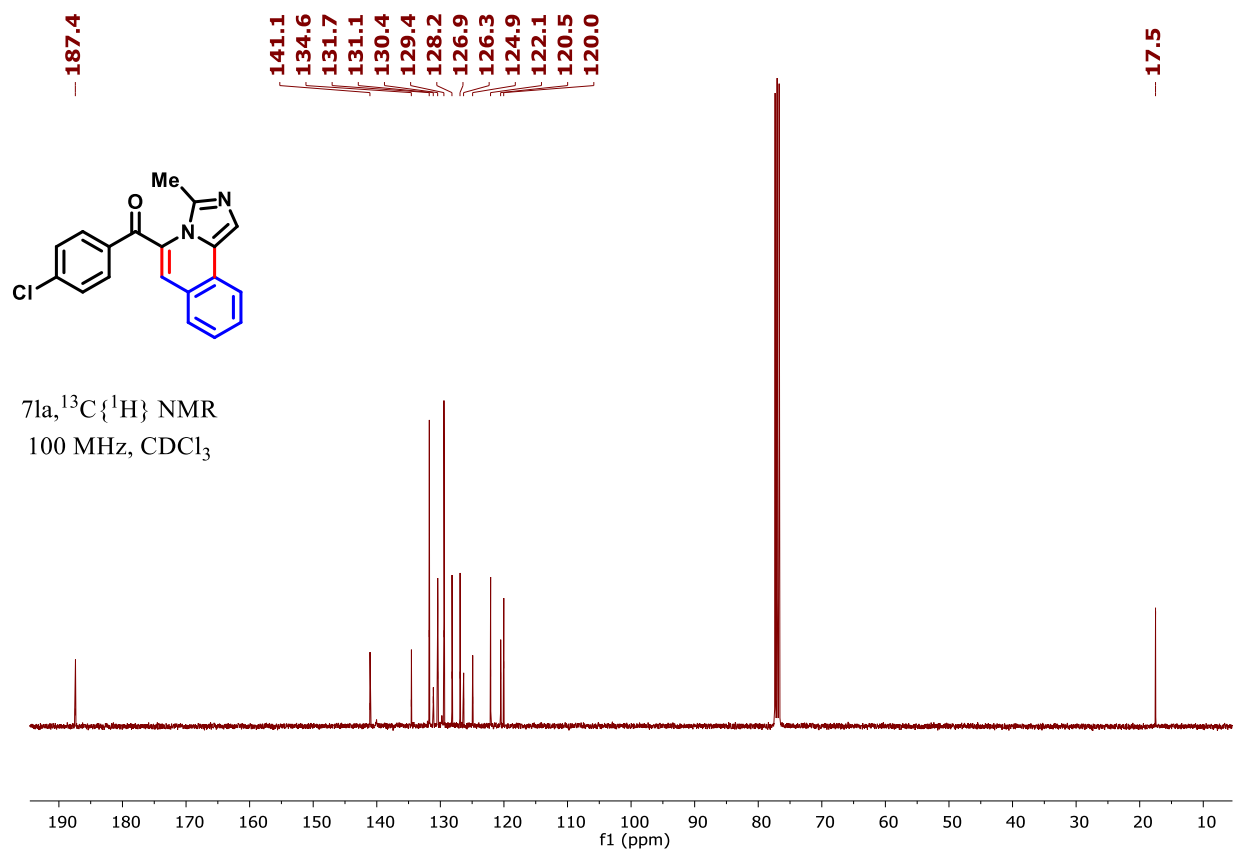
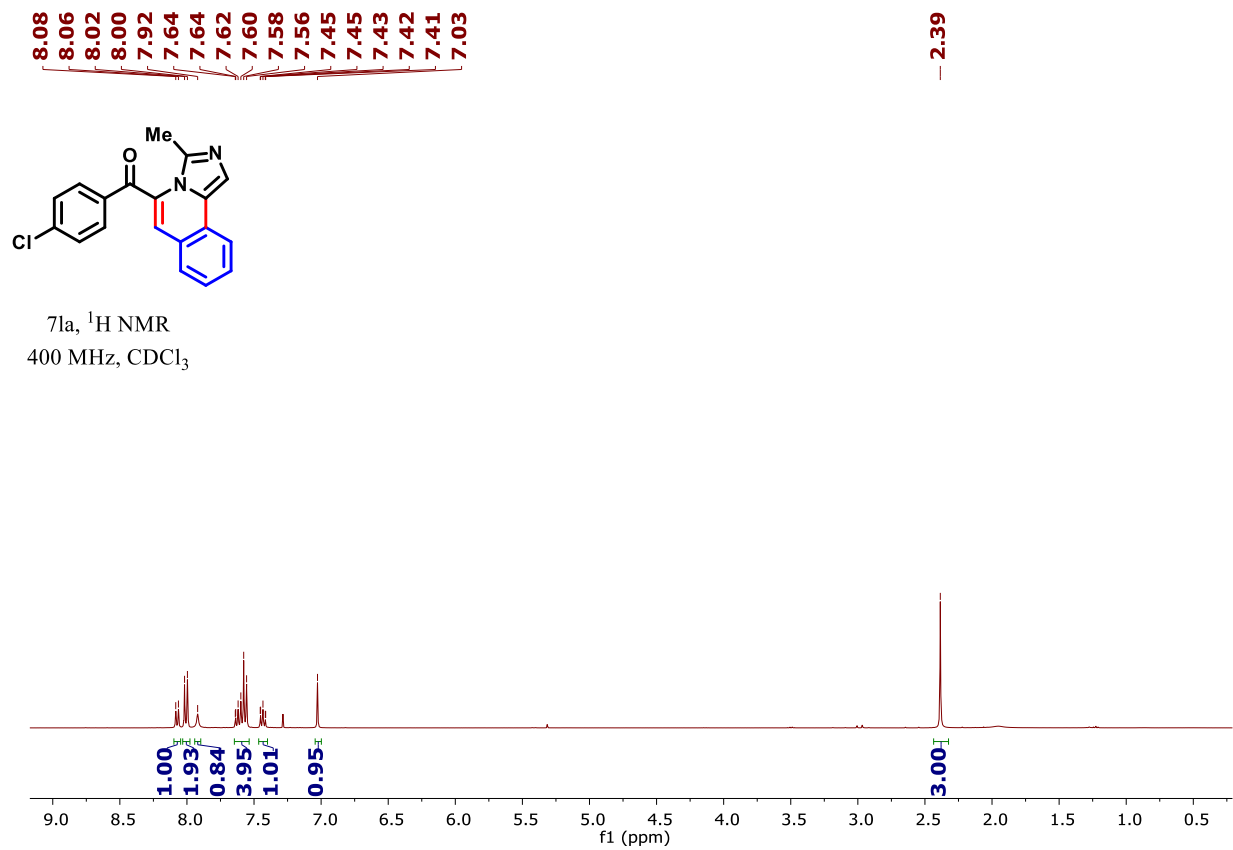
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125.3
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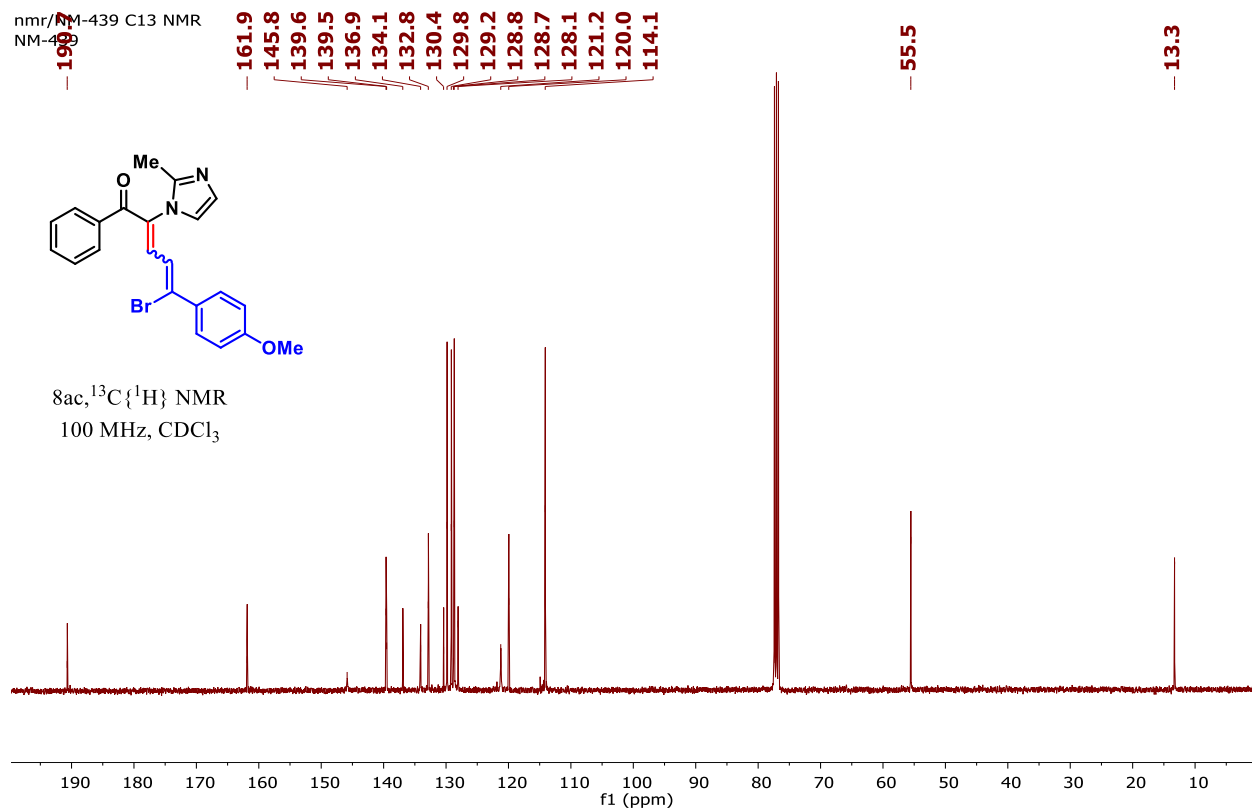
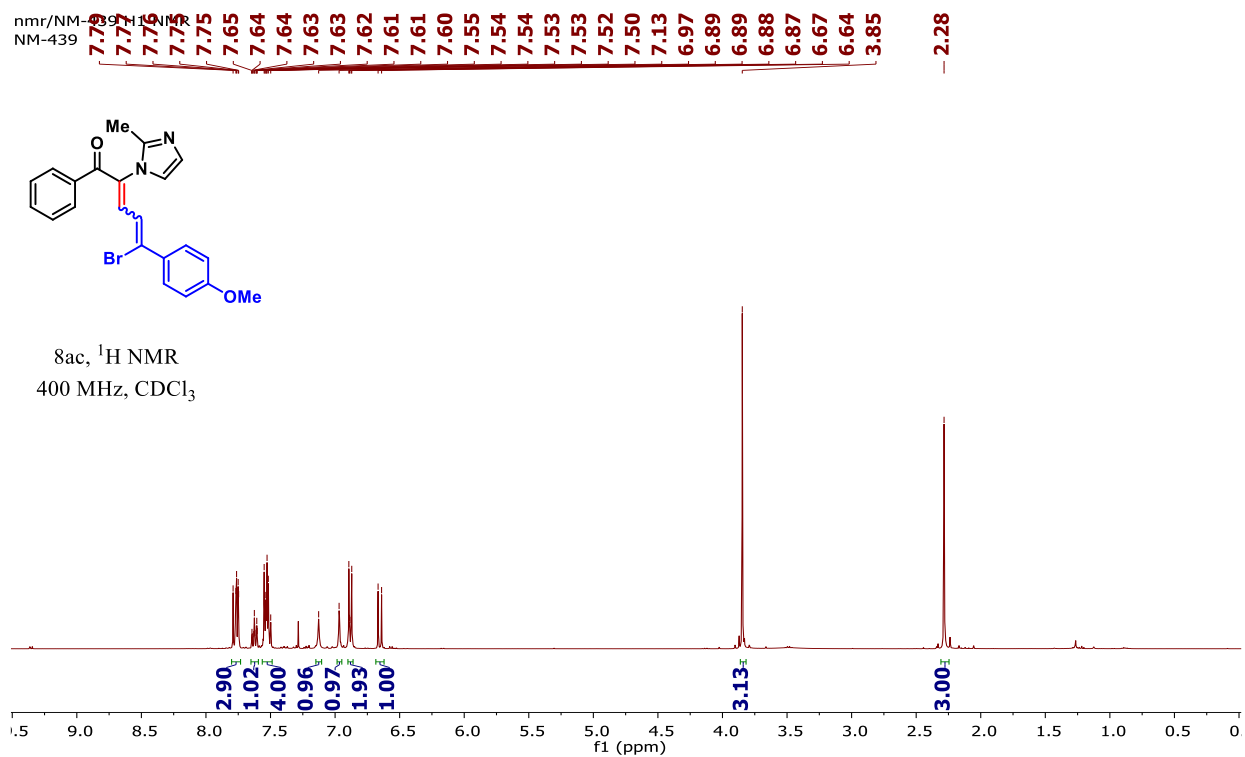
16.4



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







2. Single Crystal X-ray Crystallographic Analysis

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

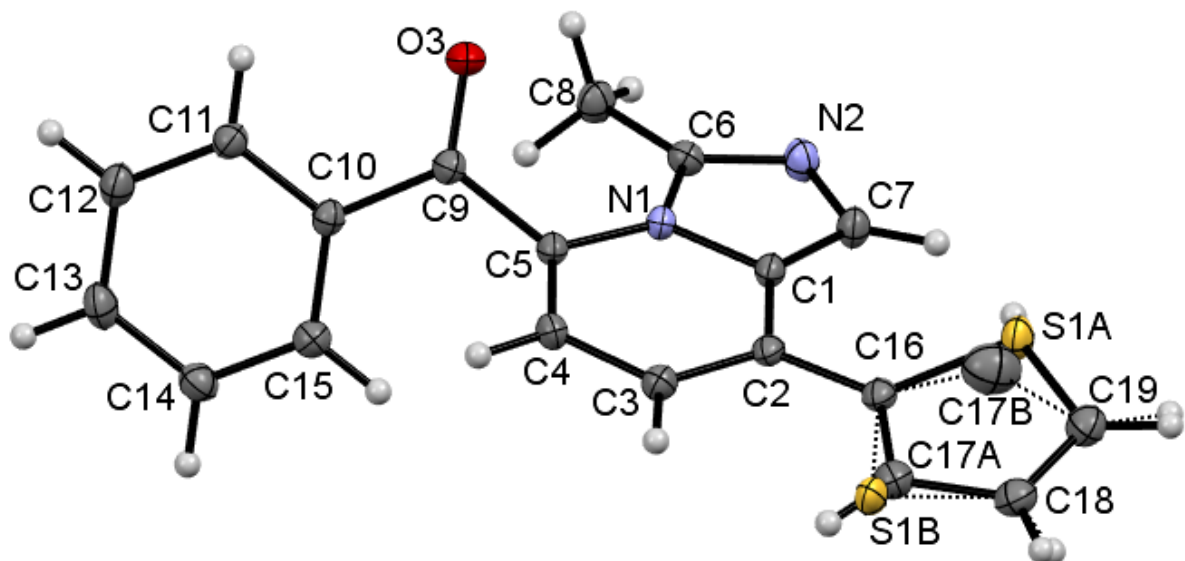


Figure S1. Single crystal ORTEP diagram of compound **3ah**, due to the rotation of the thiophen ring along C2-C16 bond the occupancies of S1A and S1B are fixed to 70 % and 30 % respectively, and similarly C17A and C17B occupancies are fixed to 70 % and 30 % respectively. The thermal ellipsoids are drawn 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 CuK α ($\lambda = 1.54184$) radiation. Using Olex2,¹ the structure was solved with the ShelXT² structure solution program using Intrinsic Phasing and refined with the ShelXL³ 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 ₂ OS
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} /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 K α (λ = 1.54184)
2 θ range for data collection/°	12.522 to 160.416
Index ranges	-7 ≤ h ≤ 9, -9 ≤ k ≤ 9, -17 ≤ l ≤ 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 [$I \geq 2\sigma(I)$]	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.