**Electronic Supporting Information**

# Metal-Free Benzoylation of Imidazoheterocycles by Oxidative Decarboxylation of Arylglyoxylic Acids

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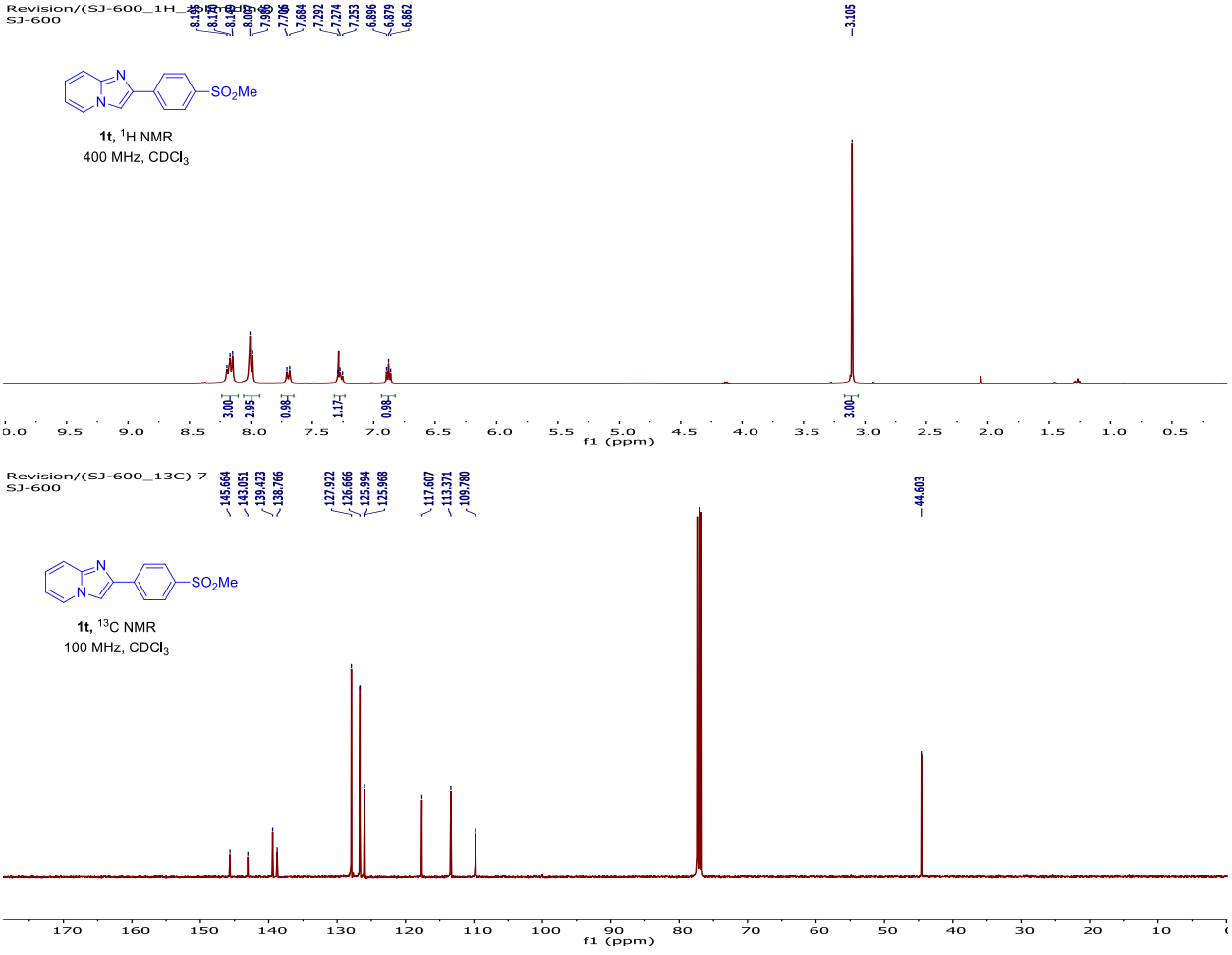
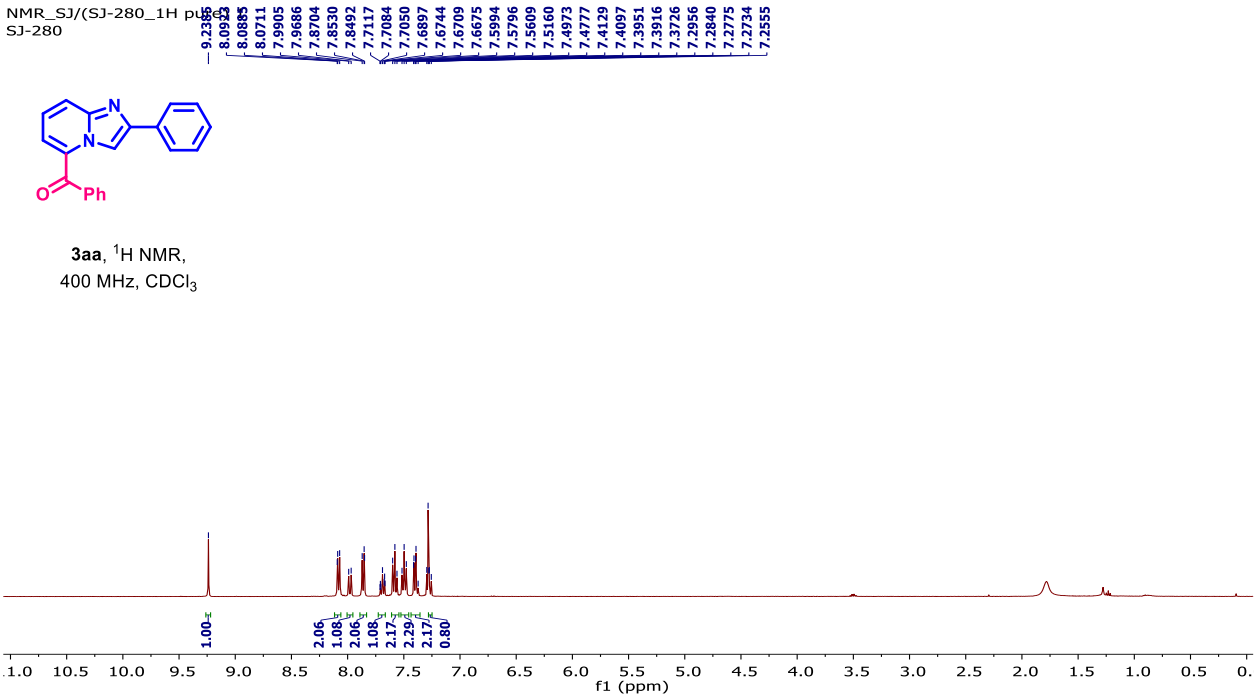
1. Copy of $^{1}H$ and $^{13}C$ NMR for compound **1t**, **3**, **4**, **5** and **8**

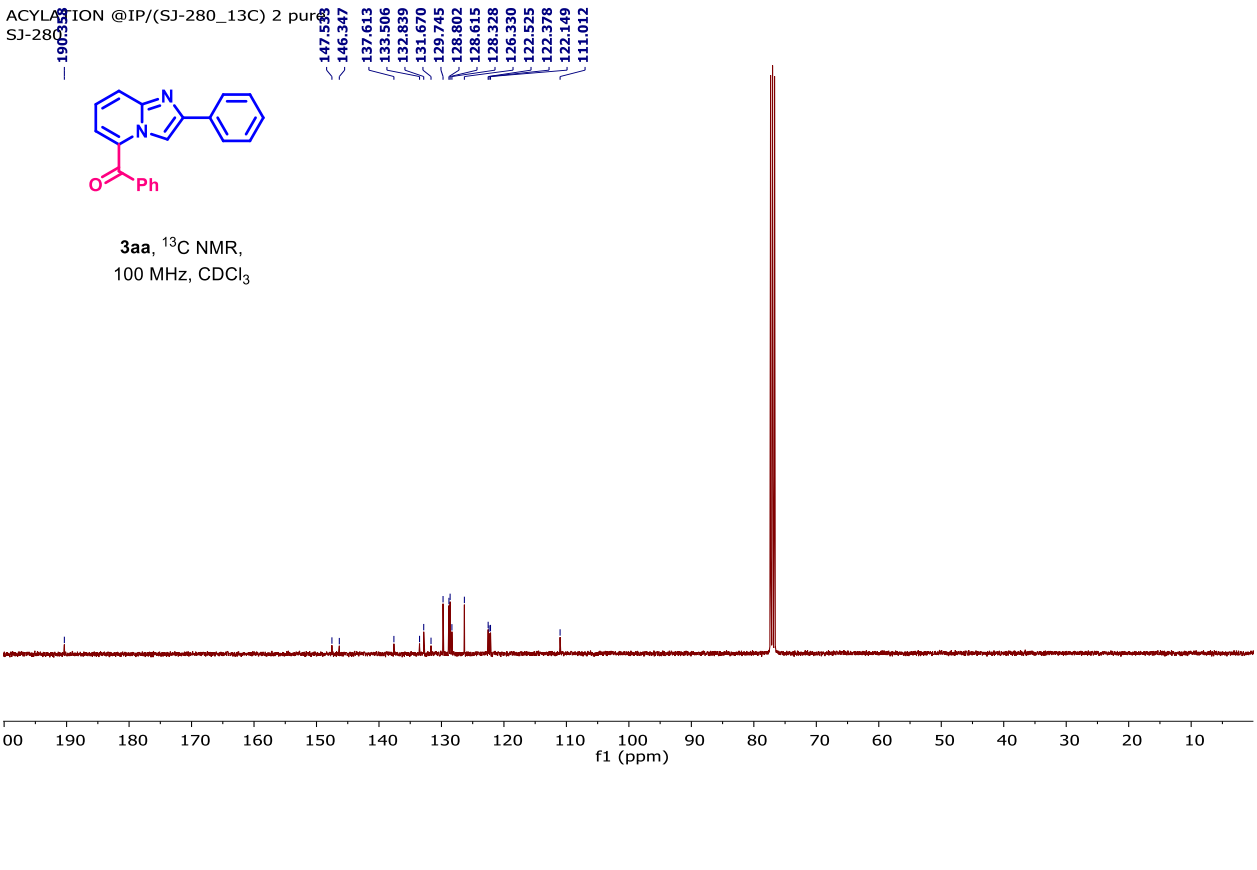
## (2-(4-(Methylsulfonyl)phenyl)imidazo[1,2-a]pyridin-5-yl)(phenyl)methanone (Zolimidine, 1t)

Eluent: *n*-Hexane; brown solid; yield: 200 mg (74 %); M. P. = 225-227 °C; FT-IR (neat) 2848, 2254, 1720, 1641, 1521, 1284, 727 $cm^{-1}$; $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.15 (m, 3H), 8.00 (d, *J* = 8.4 Hz, 3H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.29 – 7.25 (m, 1H) (with merged $CDCl_3$ peak), 6.88 (t, *J* = 6.8 Hz, 1H), 3.10 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 145.7, 143.0 , 139.4, 138.8, 127.9, 126.7, 126.0, 126.0, 117.6, 113.4, 109.8, 44.6; HRMS (ESI) calcd for $C_{14}H_{13}N_2O_2S^+$ $[M + H]^+$ 273.0692, found 273. 0690.



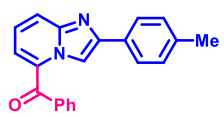



**3aa**, $^{1}$H NMR,
400 MHz, $CDCl_3$

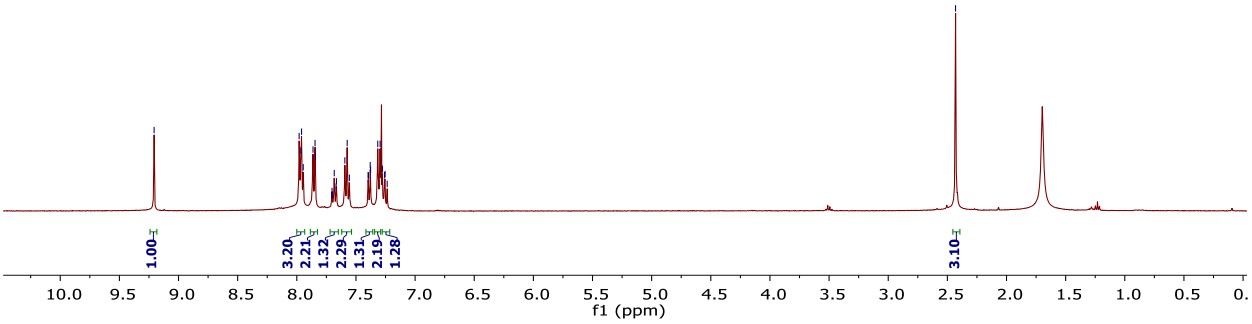



**3aa**, $^{13}$C NMR,
100 MHz, $CDCl_3$

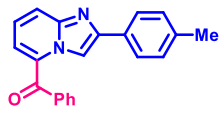
Jun03-2020/4
SJ-432

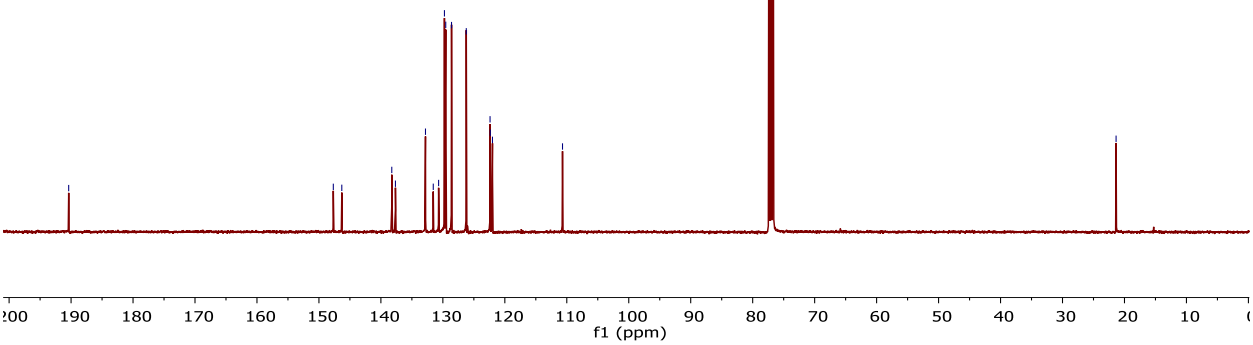

**3ba,** $^{1}$H NMR
400 MHz, $CDCl_3$

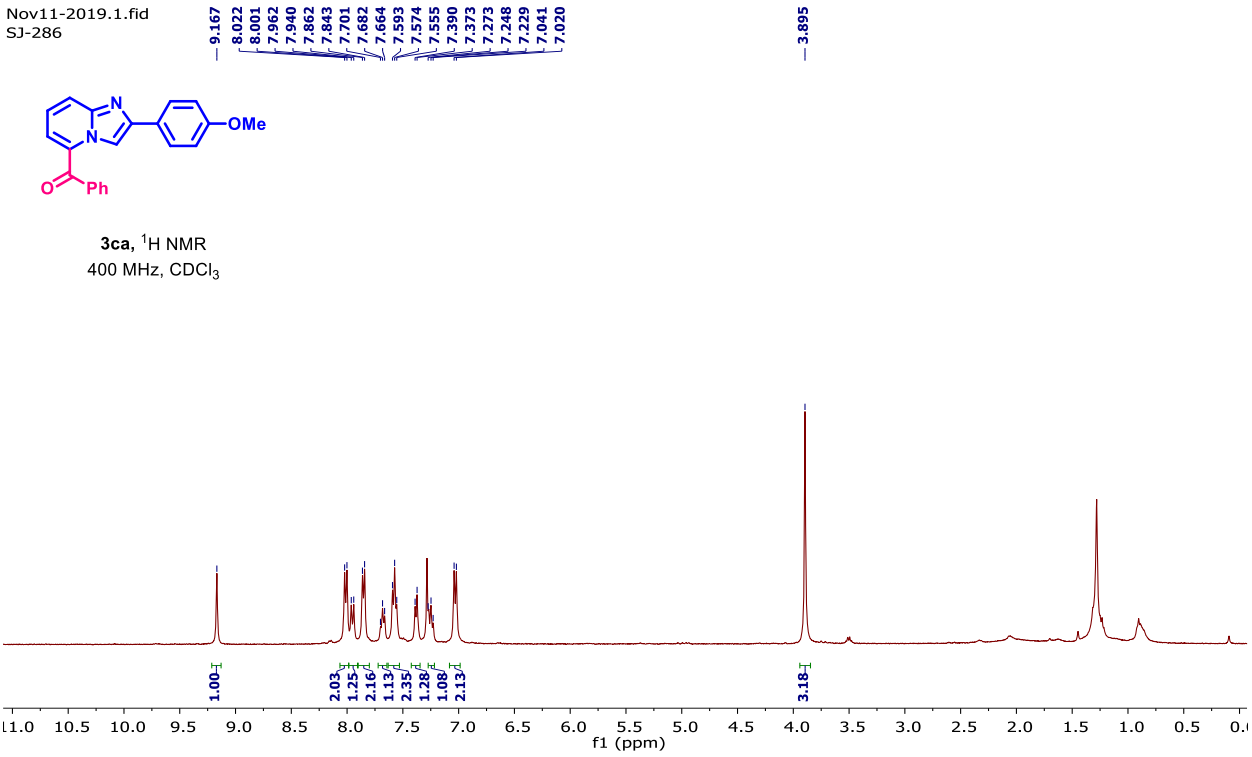




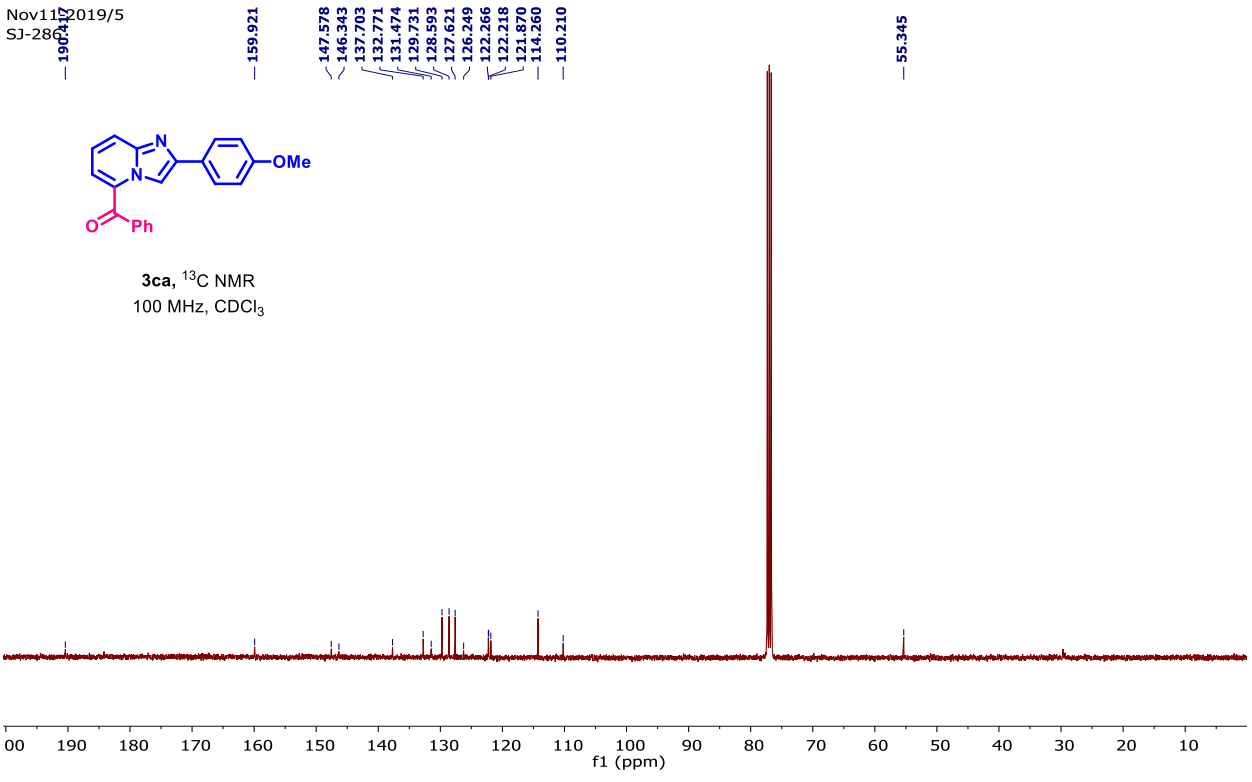



**3ba,** $^{13}$C NMR
100 MHz, $CDCl_3$

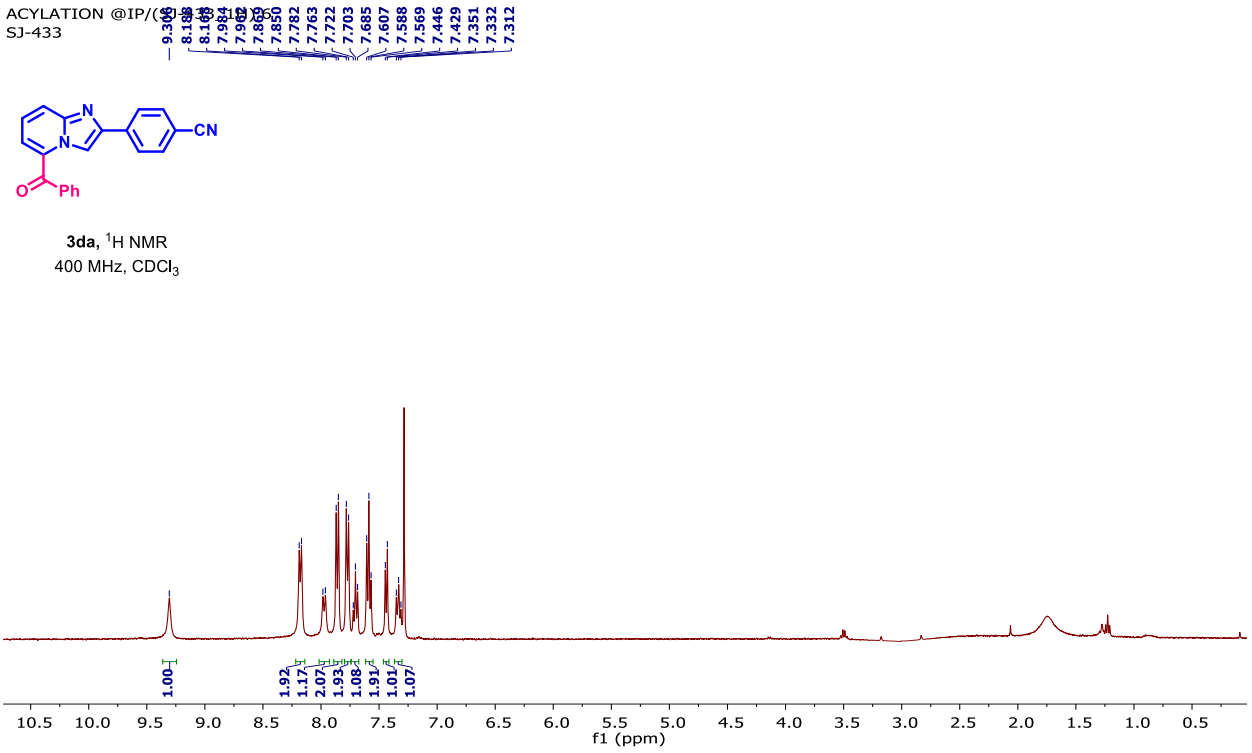




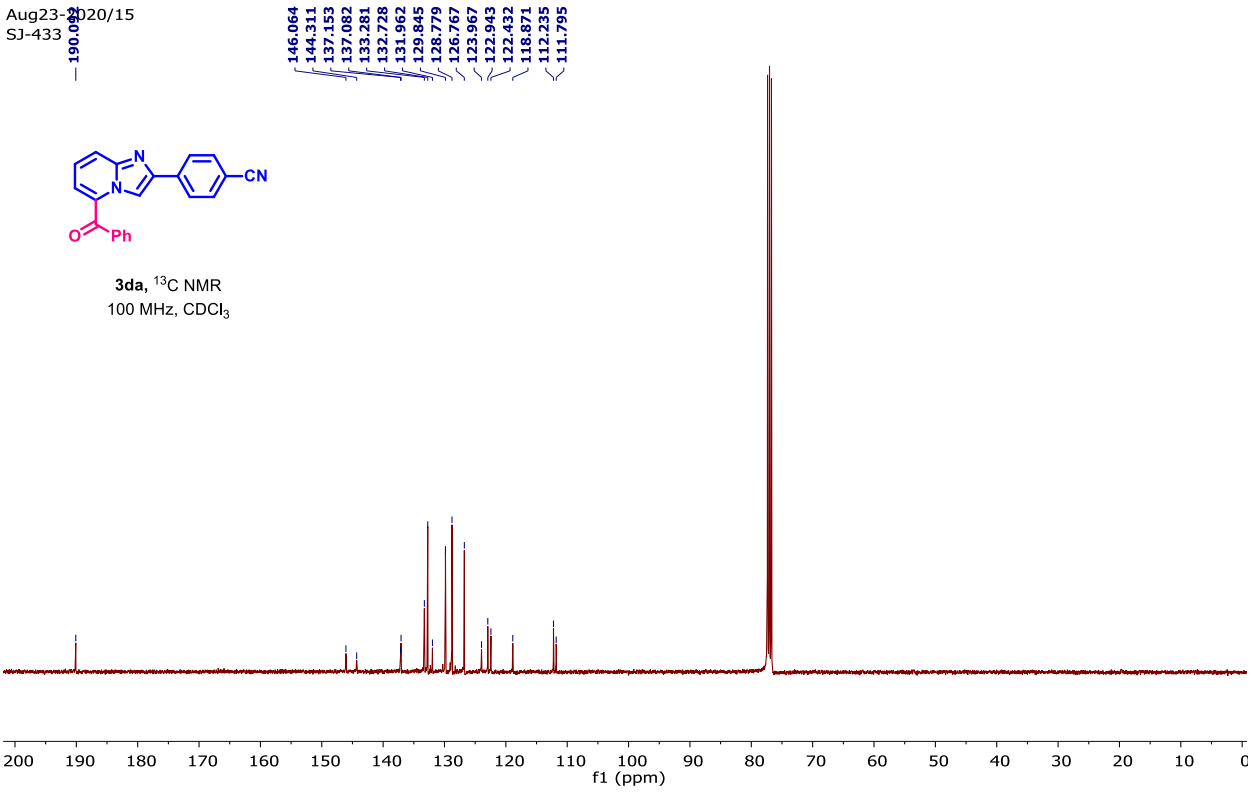

**3ca,** $^{1}$H NMR
400 MHz, $CDCl_3$




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

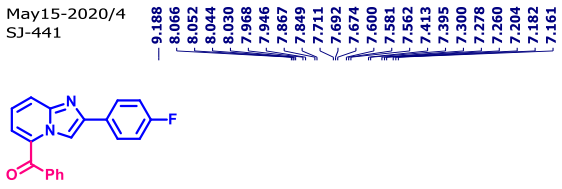



**3da,** $^{1}$H NMR
400 MHz, $CDCl_3$

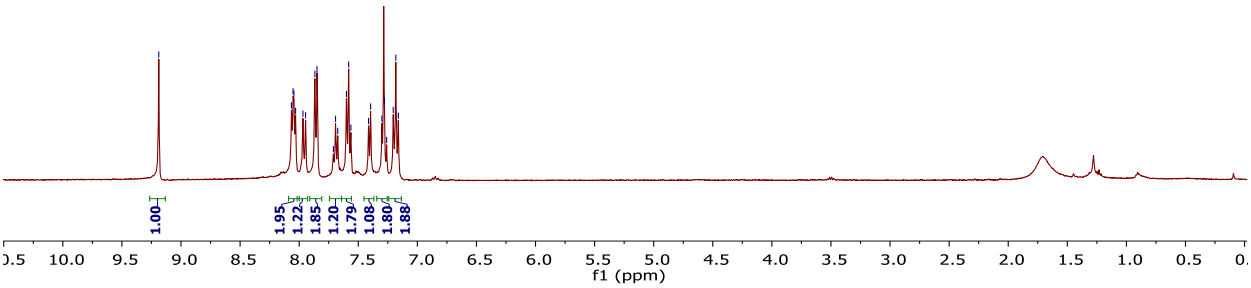



**3da,** $^{13}$C NMR
100 MHz, $CDCl_3$

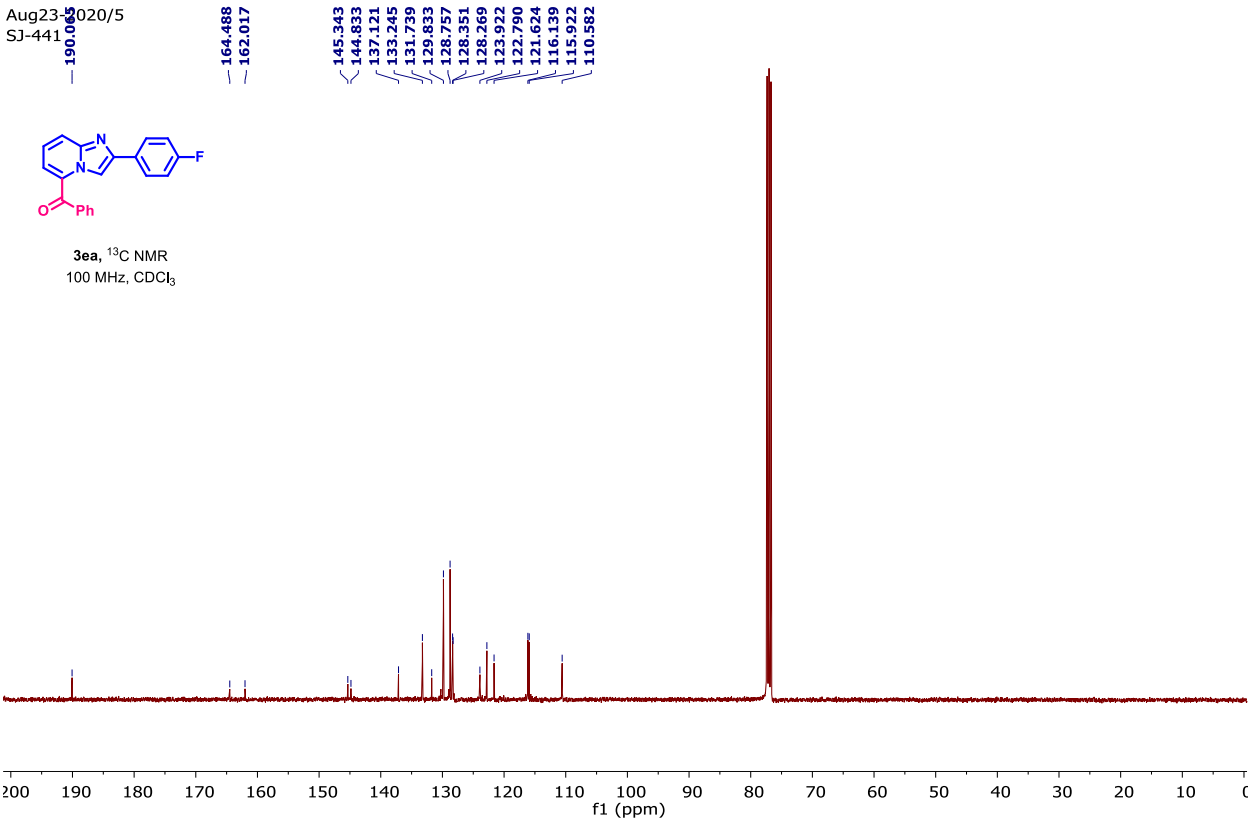
May15-2020/4
SJ-441



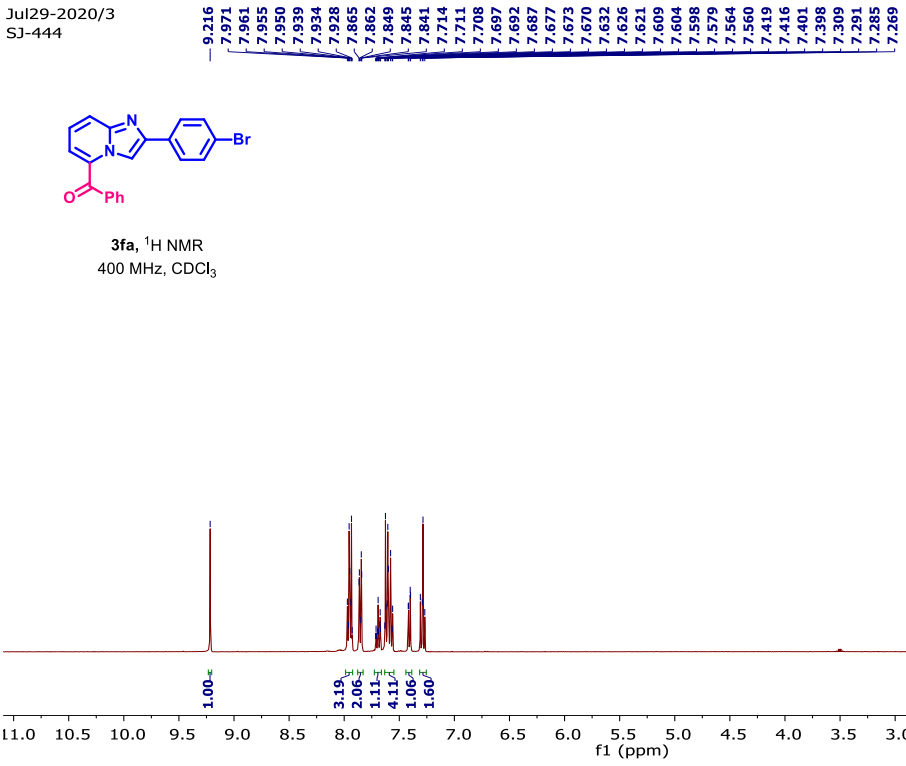

**3ea,** $^{1}$H NMR
400 MHz, $CDCl_3$



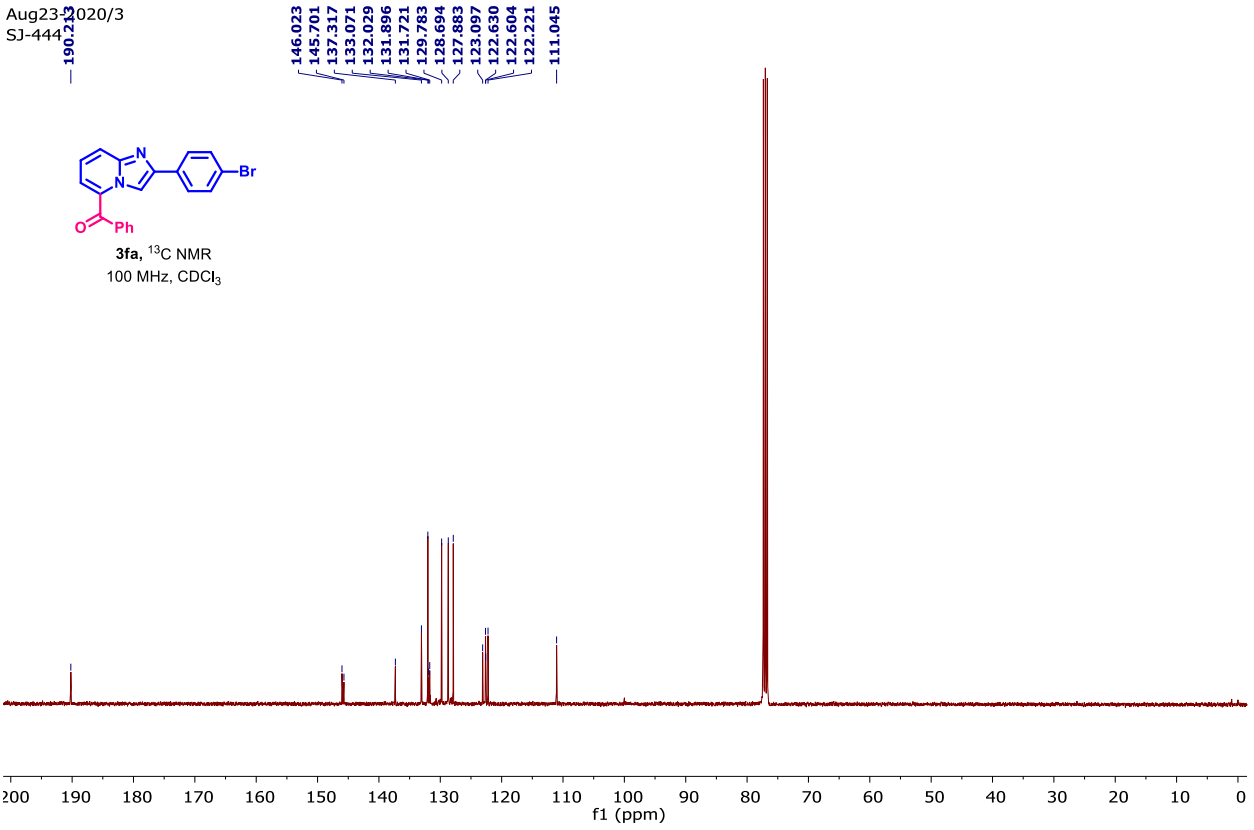

Aug23-2020/5
SJ-441



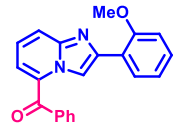

**3ea,** $^{13}$C NMR
100 MHz, $CDCl_3$



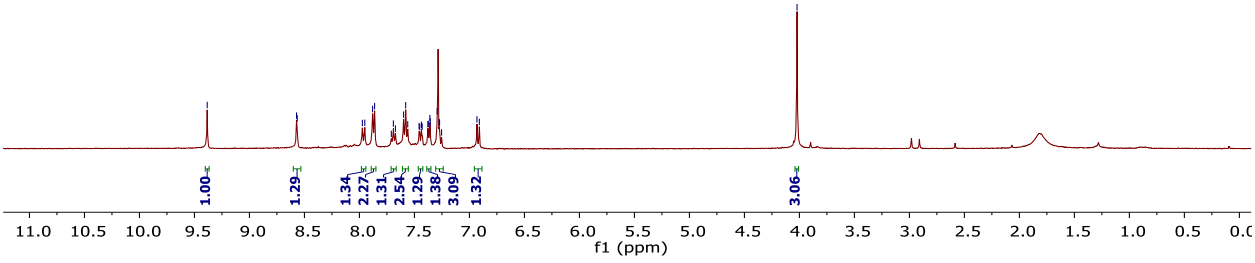

**3fa,** $^{1}$H NMR
400 MHz, $CDCl_3$

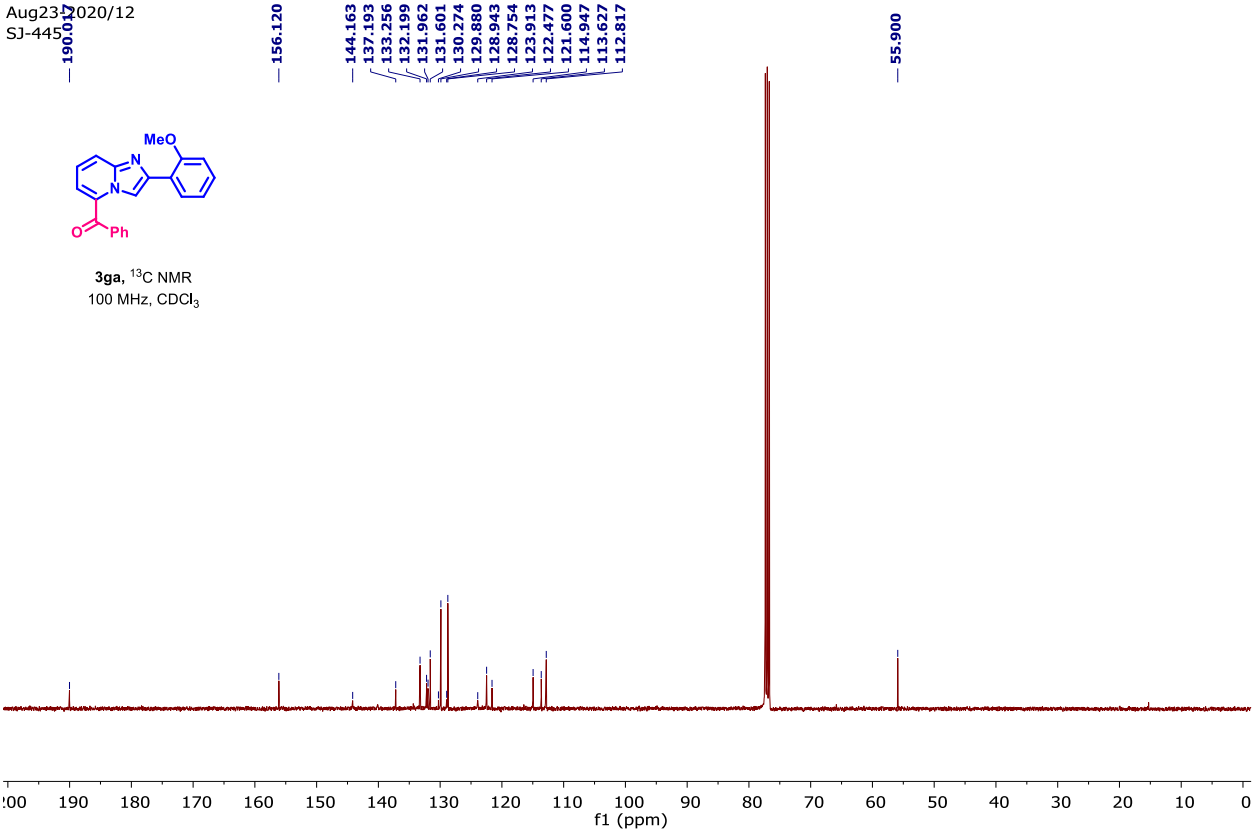



**3fa,** $^{13}$C NMR
100 MHz, $CDCl_3$

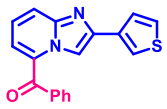

**3ga**, $^{1}$H NMR
400 MHz, $CDCl_3$



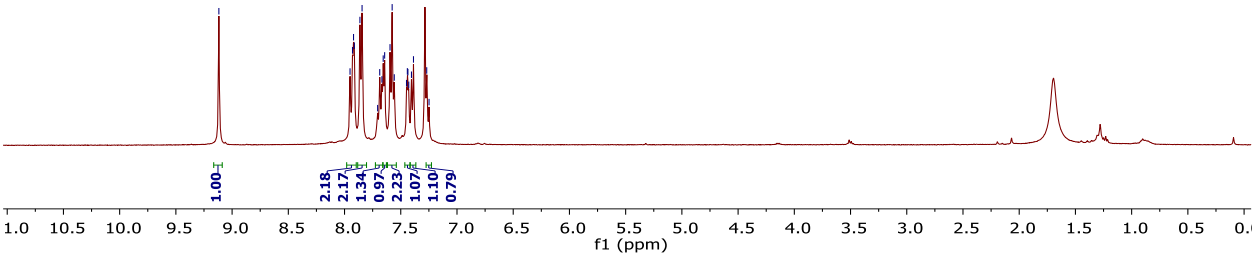




**3ga**, $^{13}$C NMR
100 MHz, $CDCl_3$

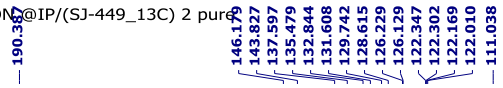
Jun08-2020/(SJ-449_1H) 1
sj-449

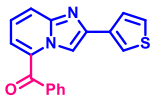




**3ha,** $^{1}$H NMR
400 MHz, $CDCl_3$



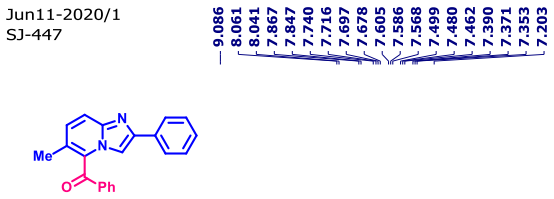

ACYLATION@IP/(SJ-449_13C) 2 pure
sj-449



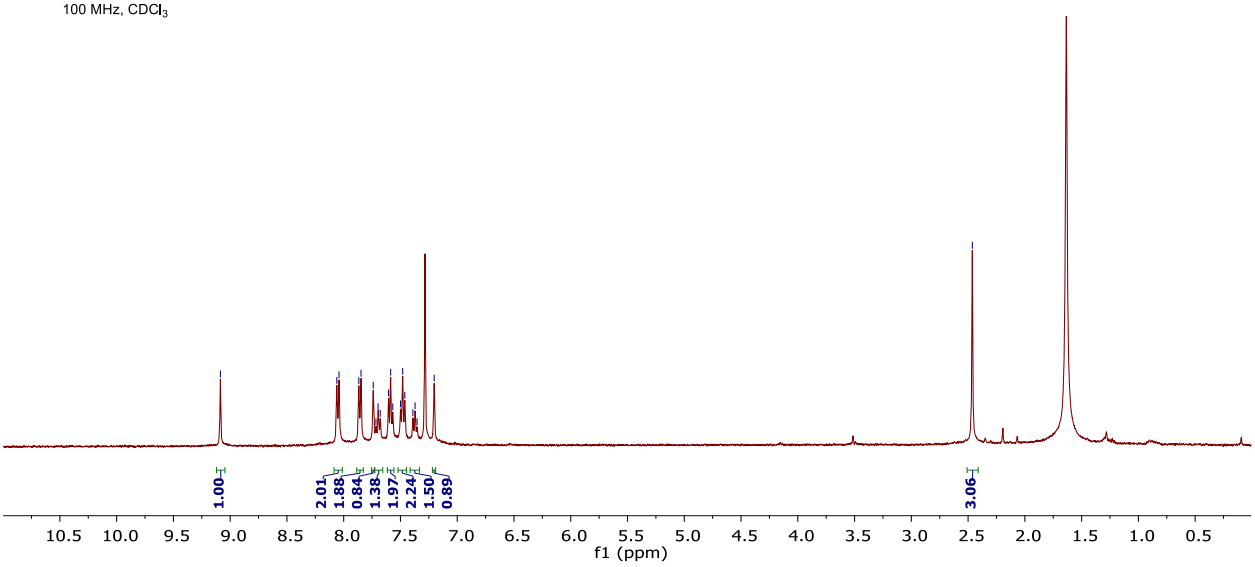



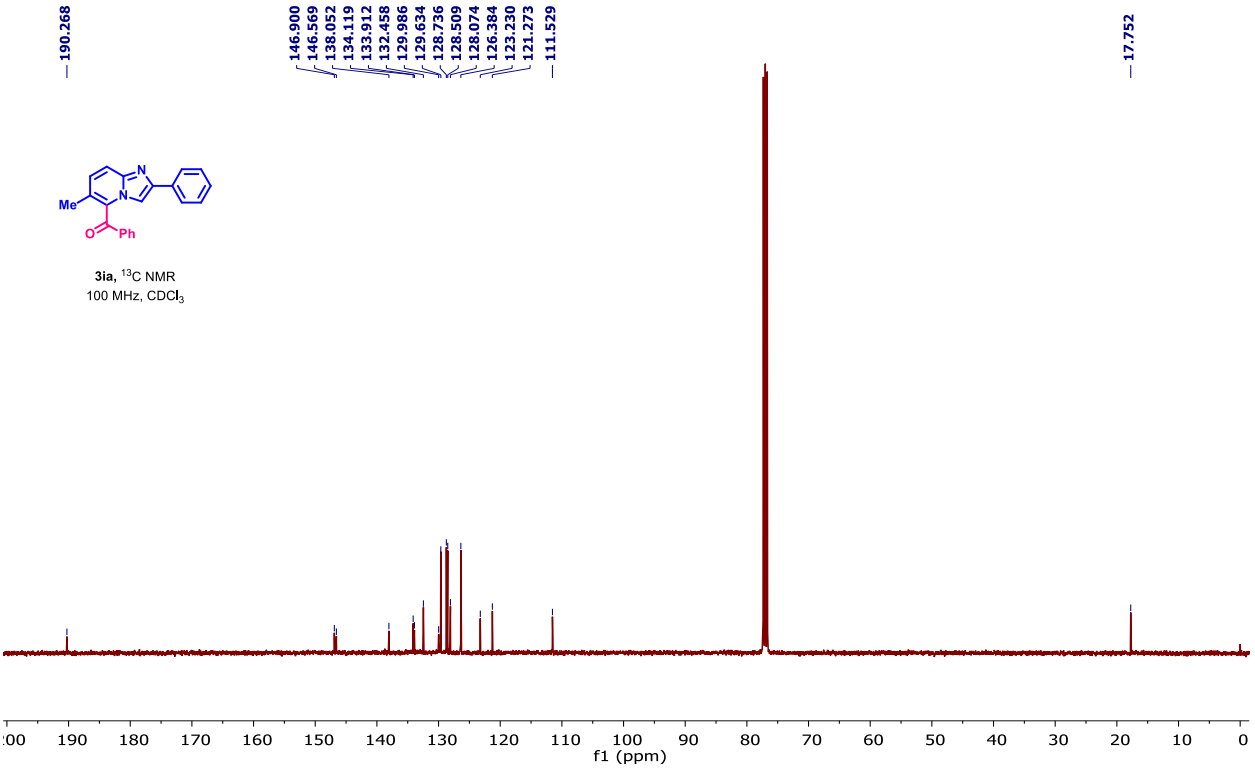

**3ha,** $^{13}$C NMR
100 MHz, $CDCl_3$

Jun11-2020/1
SJ-447

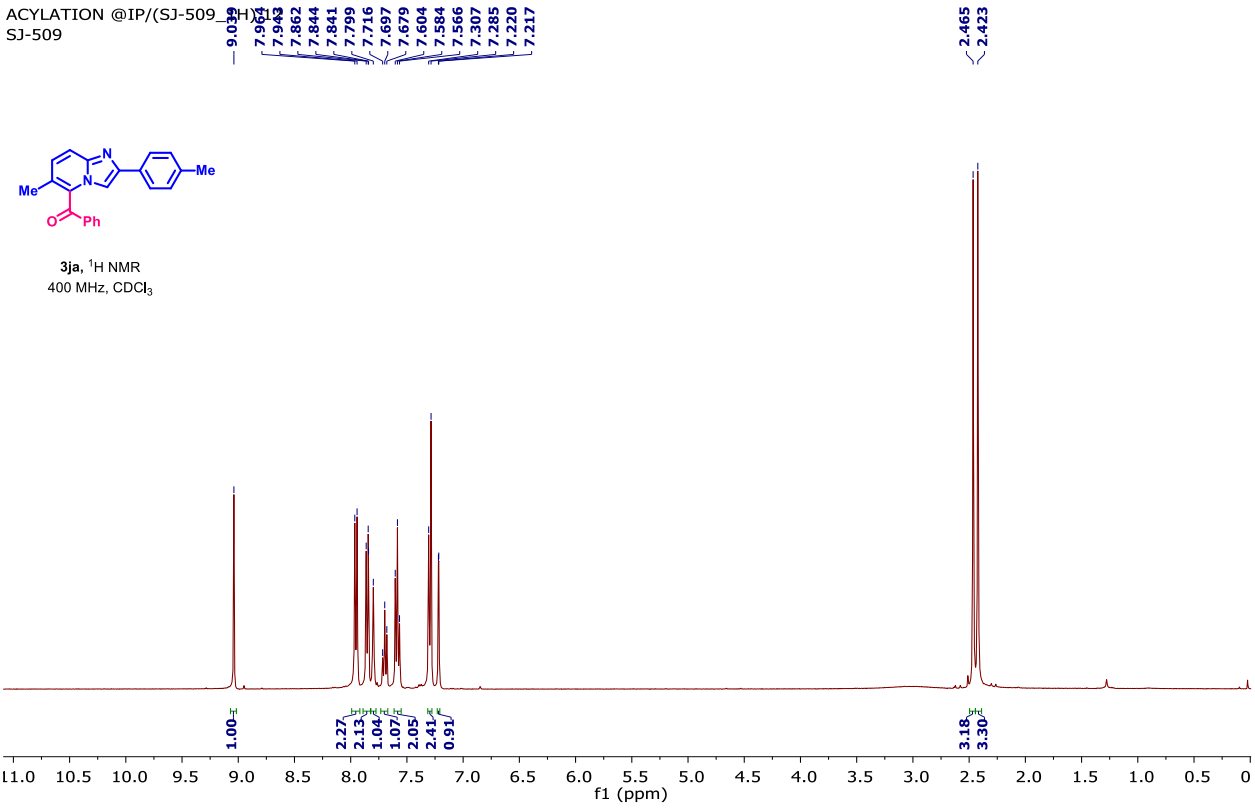



**3ia**, $^{1}$H NMR
100 MHz, $CDCl_3$




**3ia**, $^{13}$C NMR
100 MHz, $CDCl_3$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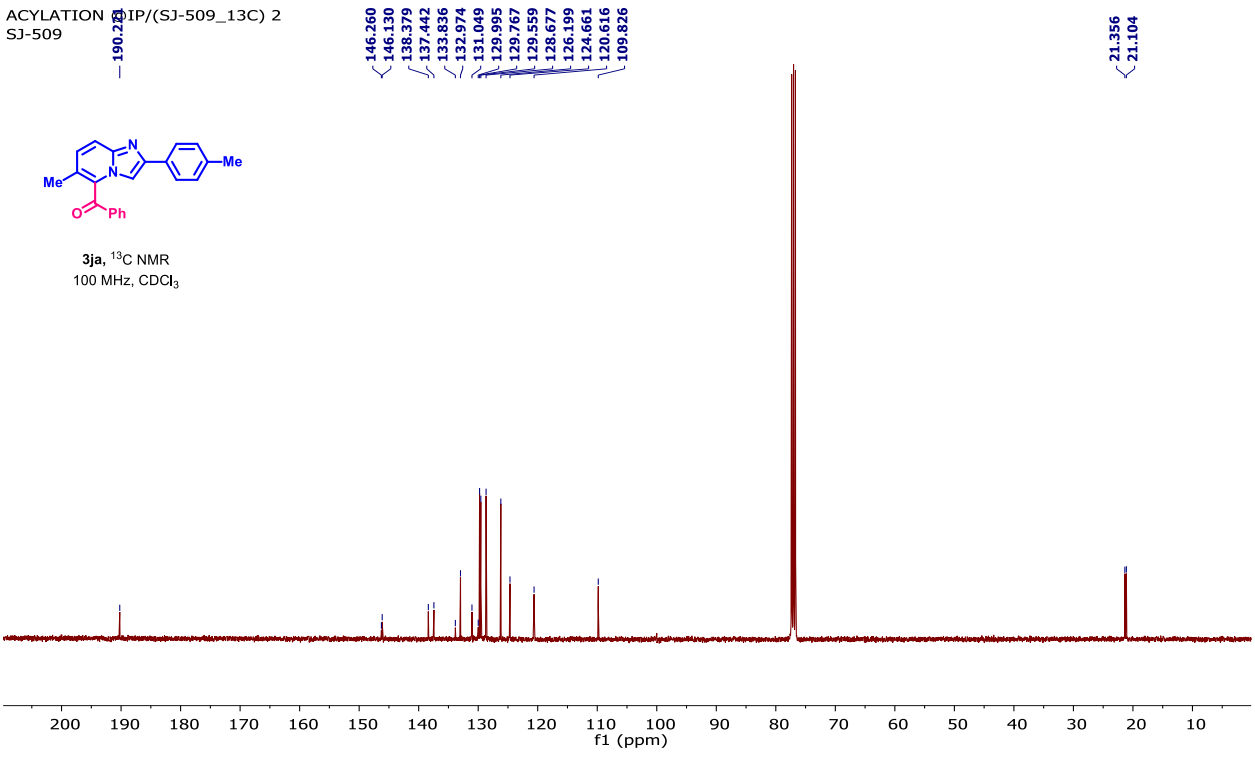
SJ-509
9.034
7.964
7.943
7.862
7.844
7.841
7.799
7.716
7.697
7.679
7.604
7.584
7.566
7.307
7.285
7.220
7.217
2.465
2.423
Me
Me
N
N
O
Ph
3ja, 1H NMR
400 MHz, CDCl3
1.00
2.27
2.13
1.04
1.07
2.05
2.41
0.91
3.18
3.30
f1 (ppm)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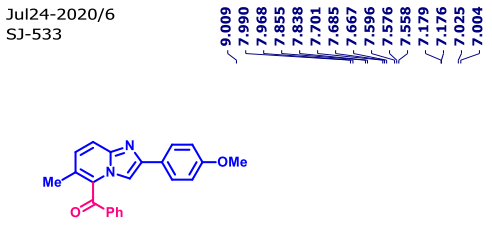
SJ-509
190.221
146.260
146.130
138.379
137.442
133.836
132.974
131.049
129.995
129.767
129.559
128.677
126.199
124.661
120.616
109.826
21.356
21.104
Me
Me
N
N
O
Ph
3ja, 13C NMR
100 MHz, CDCl3
f1 (ppm)

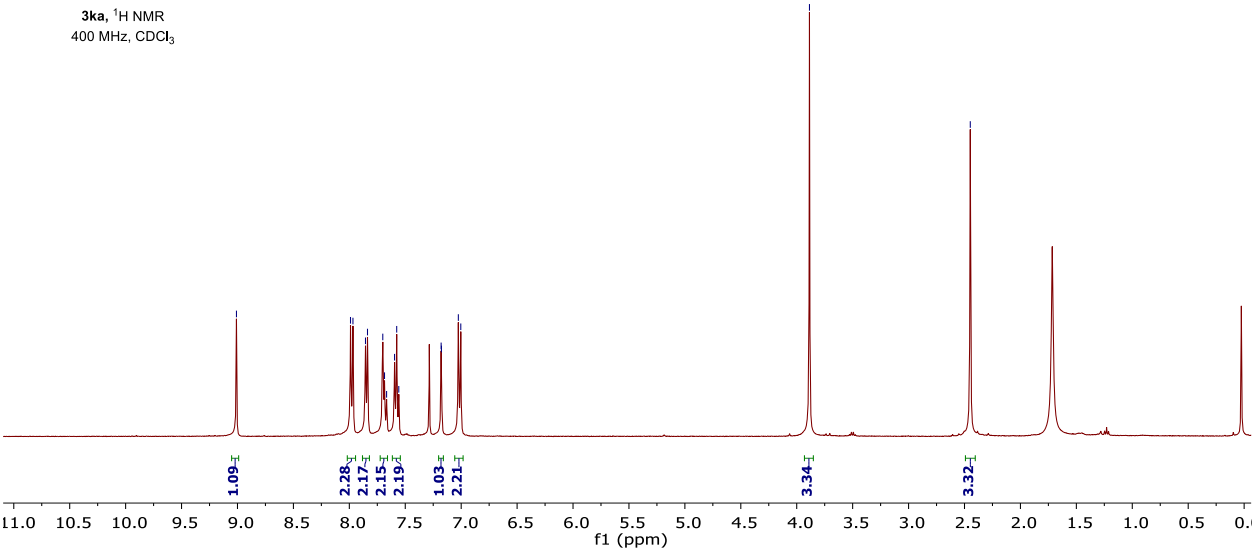
Jul24-2020/6
SJ-533



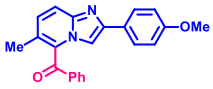




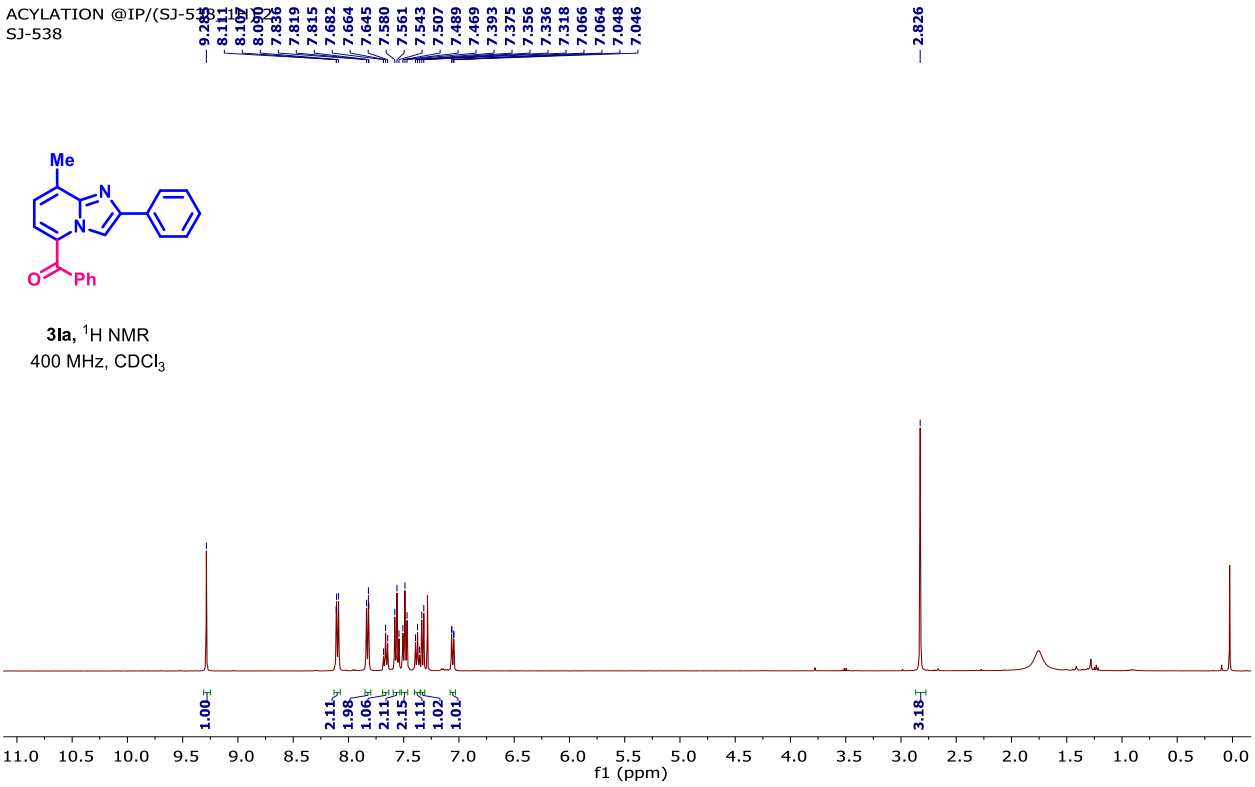
**3ka**, $^{1}$H NMR
400 MHz, $CDCl_3$



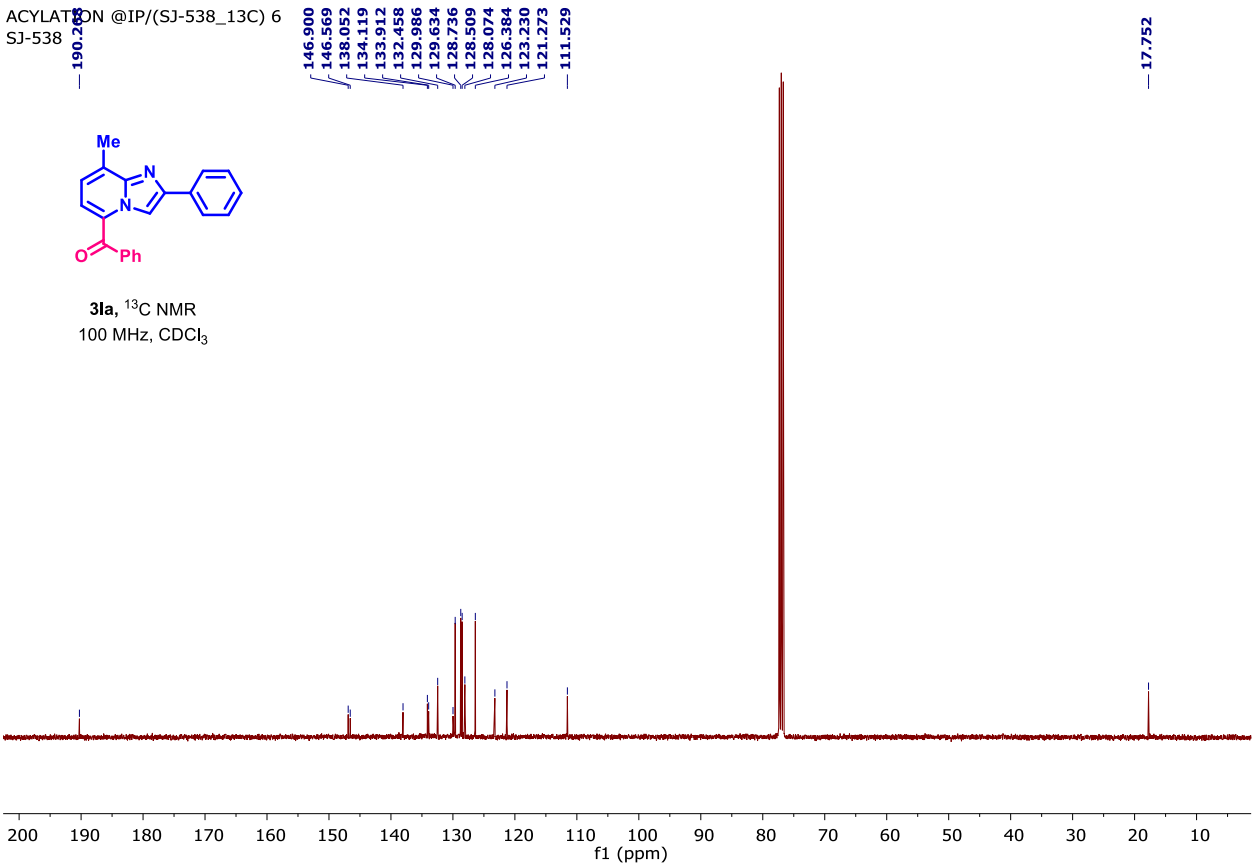

ACYLATION @IP/(SJ-533_13C) 7
SJ-533

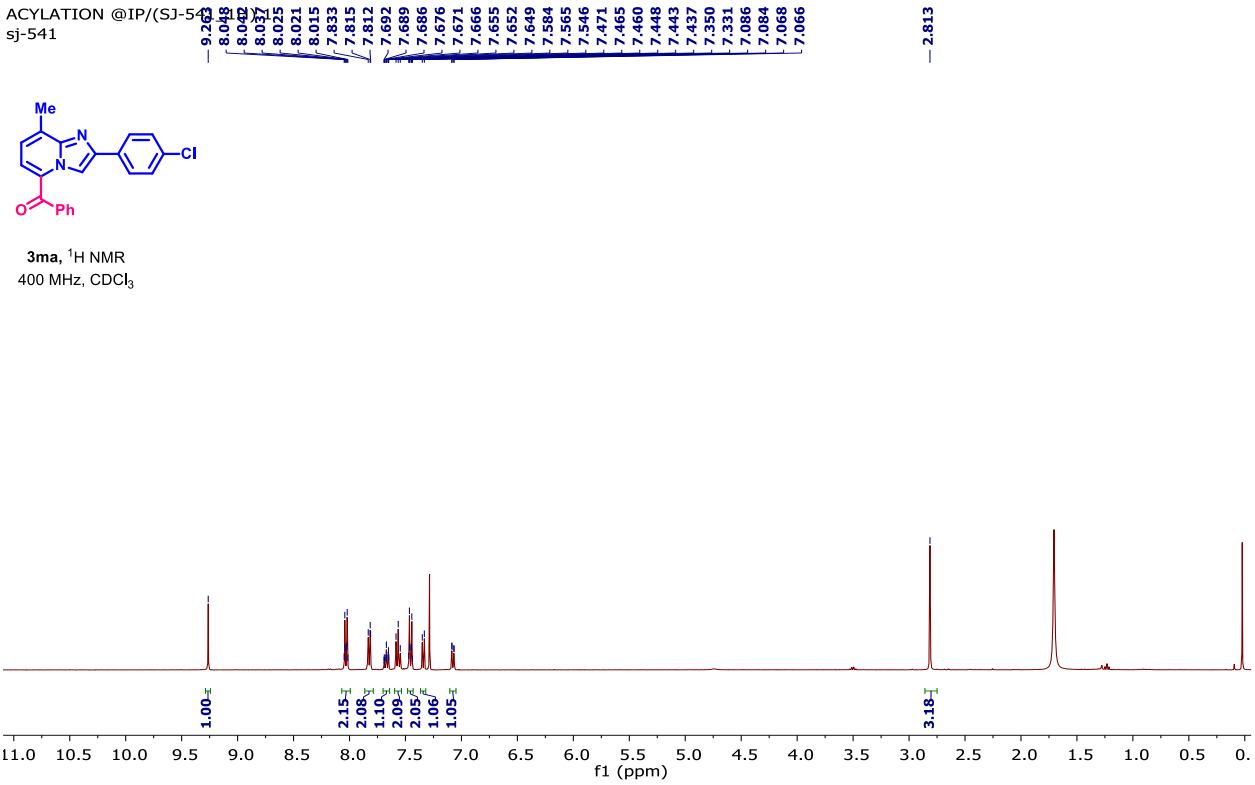

**3ka**, $^{13}$C NMR
100 MHz, $CDCl_3$



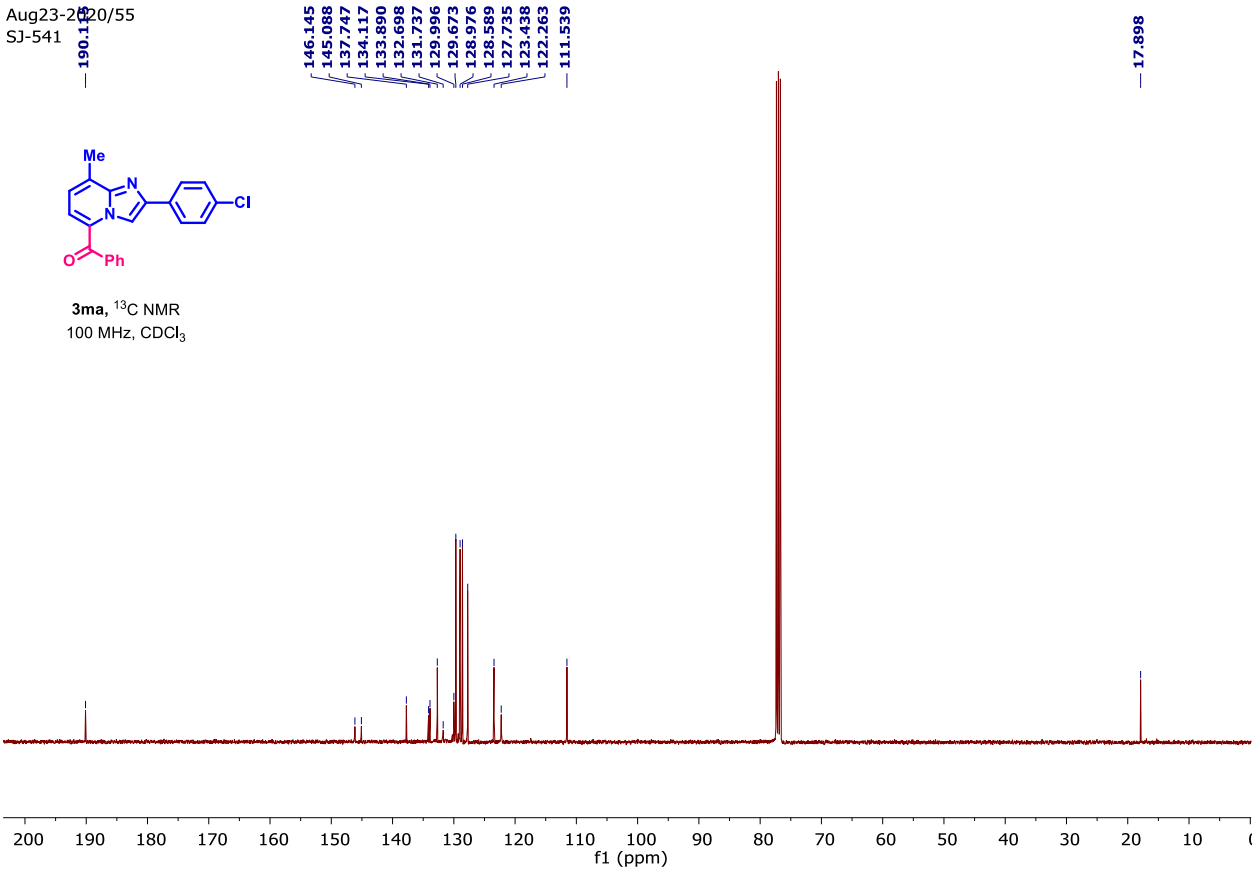

**3la,** $^{1}$H NMR
400 MHz, $CDCl_3$



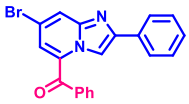

**3la,** $^{13}$C NMR
100 MHz, $CDCl_3$



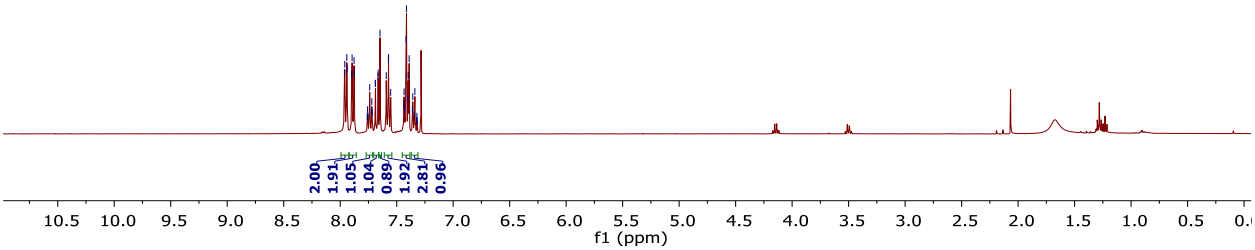

**3ma,** $^{1}$H NMR
400 MHz, $CDCl_3$




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



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





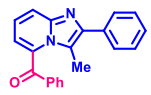


**3na,** $^{13}$C NMR
100 MHz, $CDCl_3$

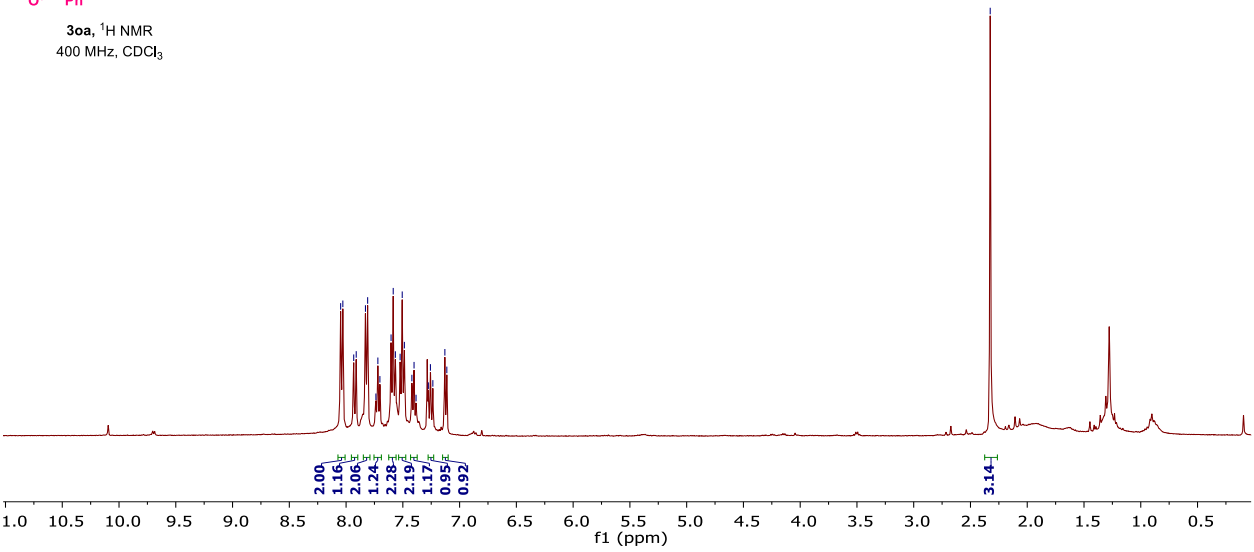
Jun11-2020/6
SJ-479

8.048
8.029
7.933
7.911
7.829
7.810
7.737
7.720
7.702
7.604
7.585
7.566
7.524
7.505
7.486
7.420
7.401
7.384
7.275
7.257
7.236
7.130
7.113

2.326

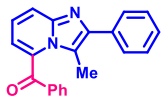



**3oa,** $^{1}$H NMR
400 MHz, $CDCl_3$

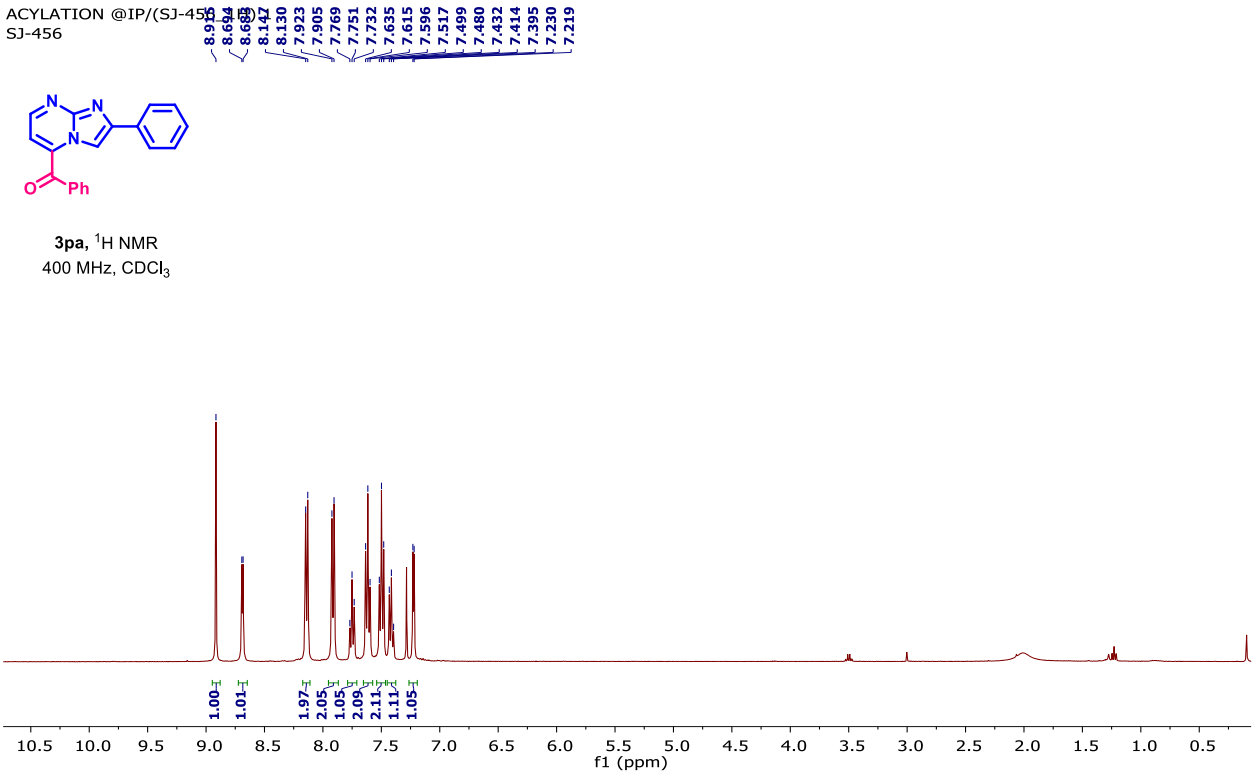



Jun17-2020/(SJ-479_13C) 6
SJ-479

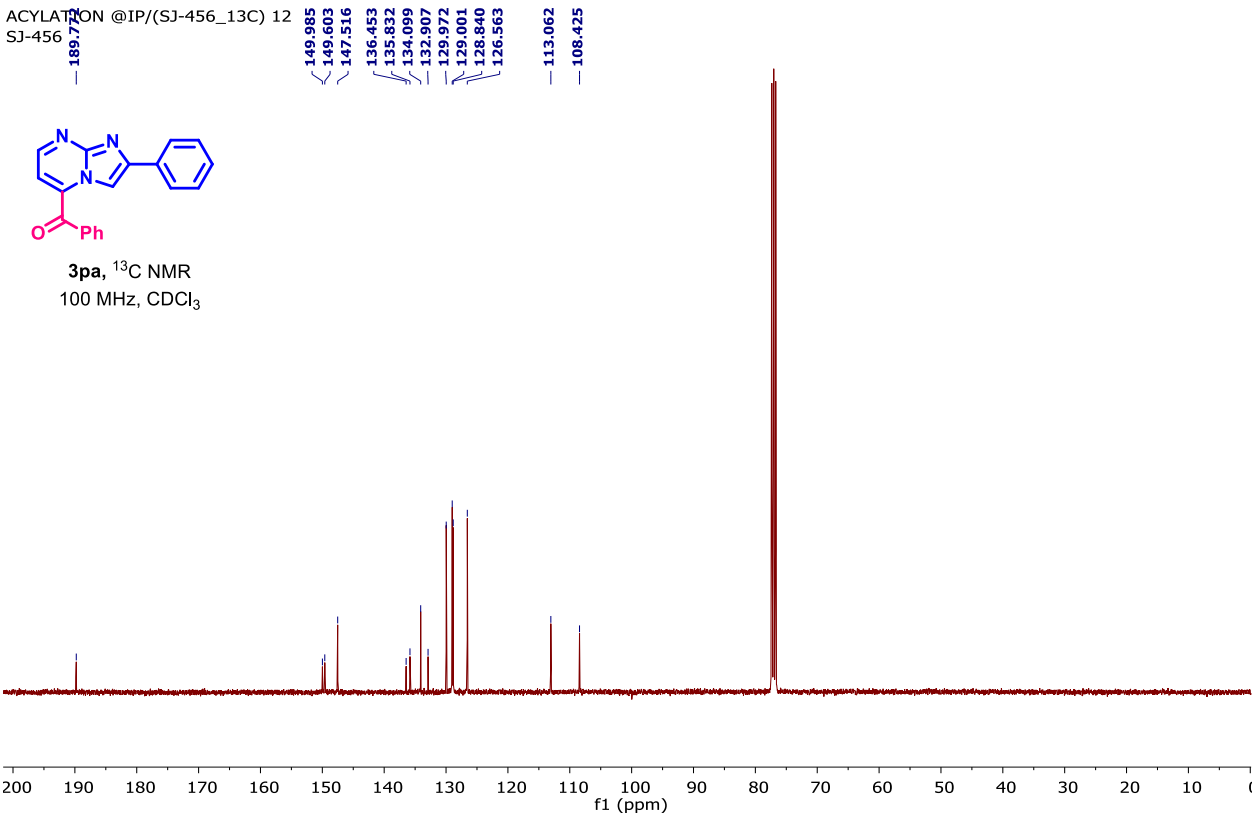
188.024
145.267
145.214
136.423
134.268
134.156
130.612
129.856
128.986
128.903
128.489
127.764
121.561
120.702
119.425
117.986
14.411



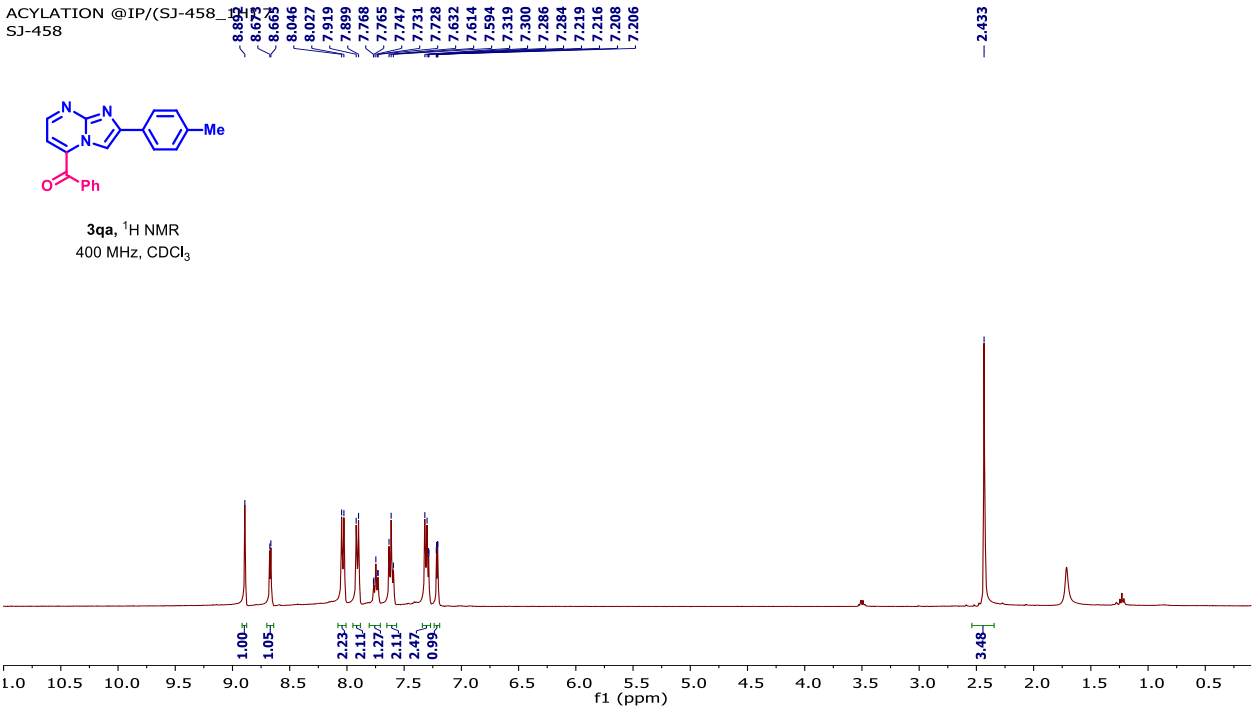

**3oa,** $^{13}$C NMR
100 MHz, $CDCl_3$



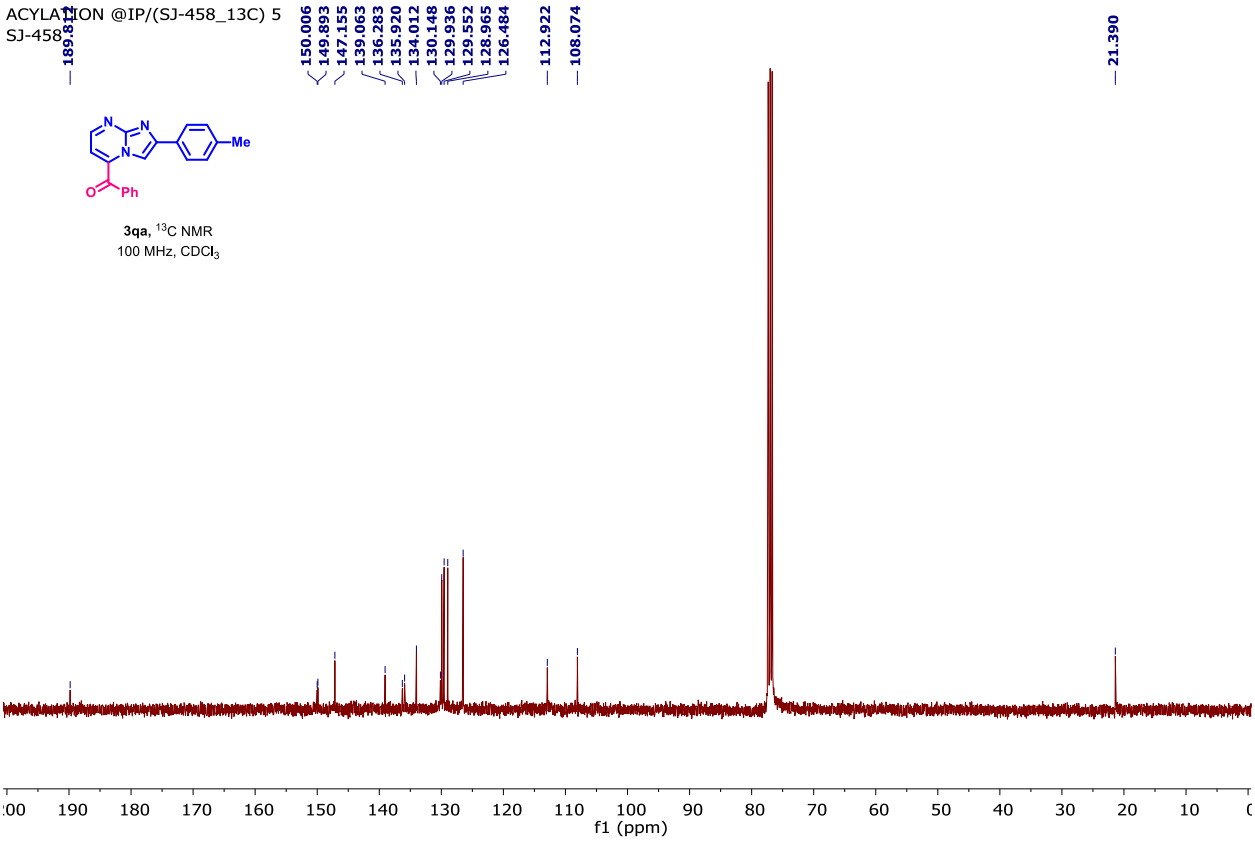

**3pa,** $^{1}$H NMR
400 MHz, $CDCl_3$



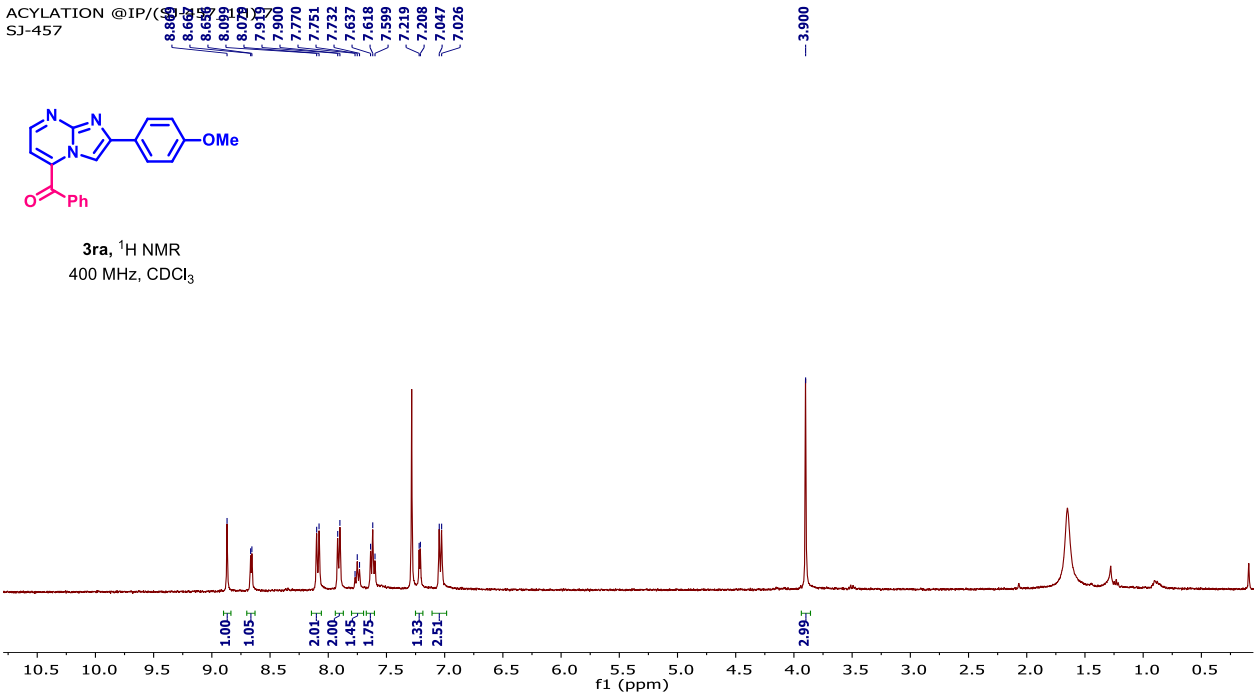

**3pa,** $^{13}$C NMR
100 MHz, $CDCl_3$



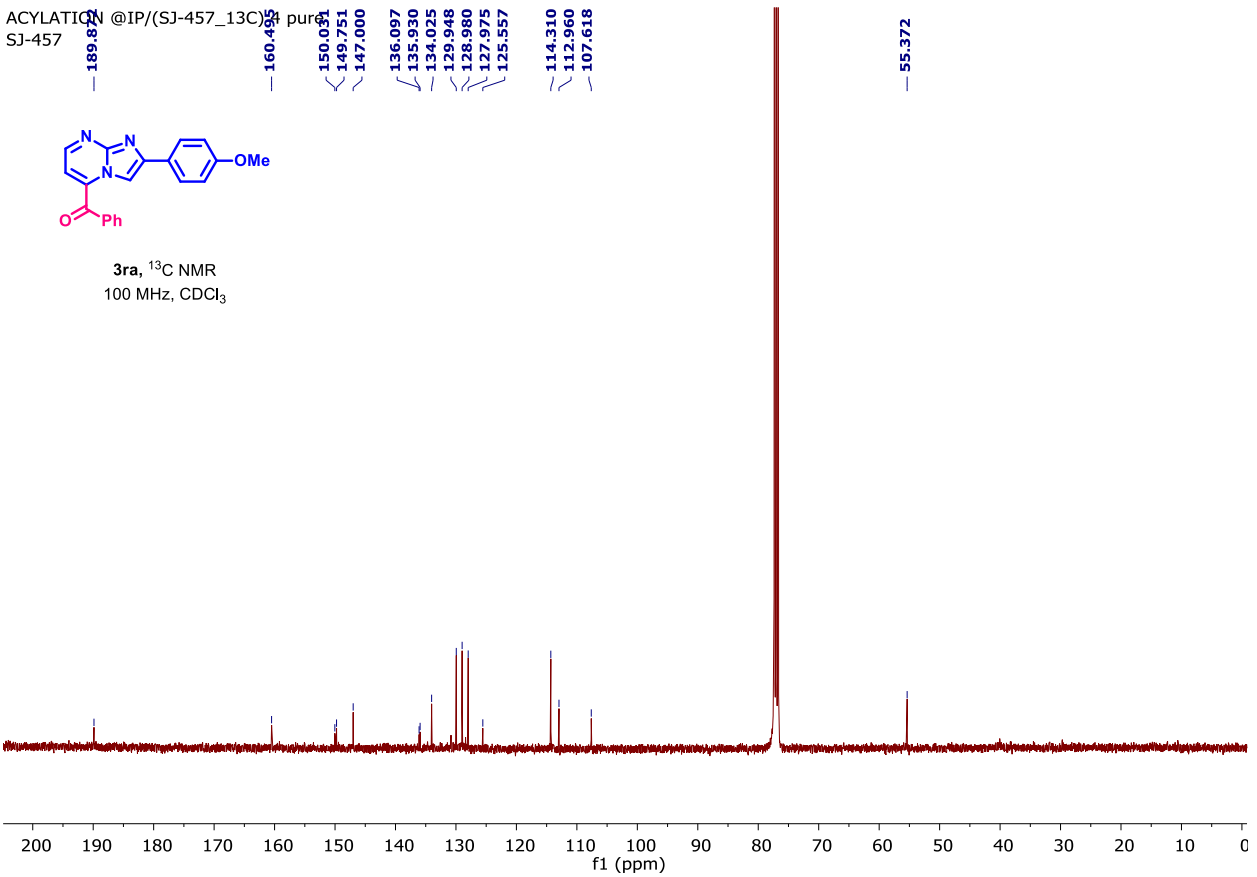

**3qa,** $^{1}$H NMR
400 MHz, $CDCl_3$



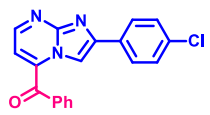

**3qa,** $^{13}$C NMR
100 MHz, $CDCl_3$



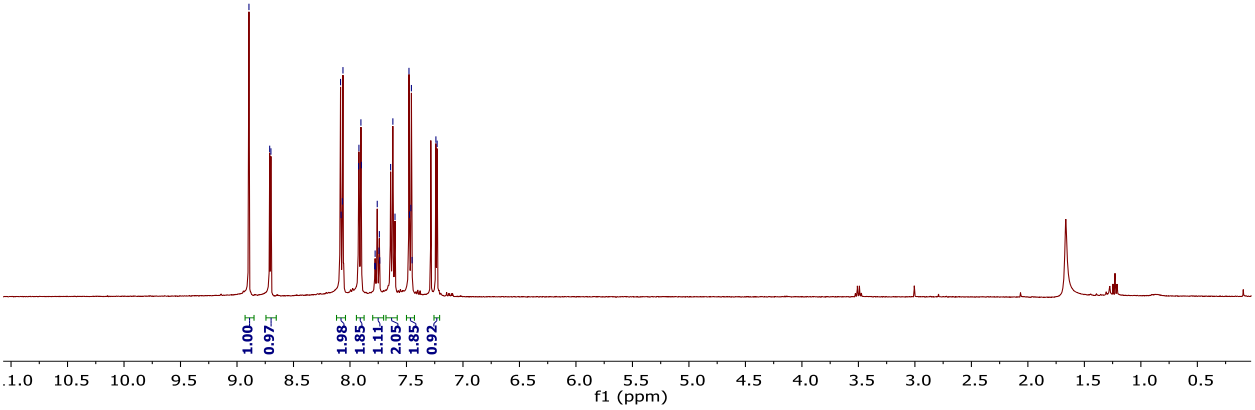

**3ra,** $^{1}$H NMR
400 MHz, $CDCl_3$

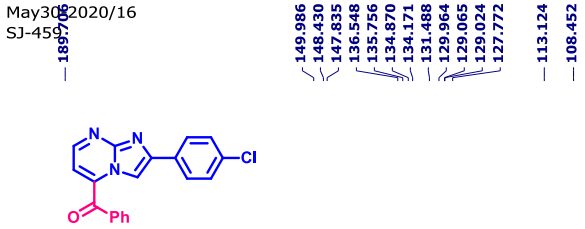



**3ra,** $^{13}$C NMR
100 MHz, $CDCl_3$


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

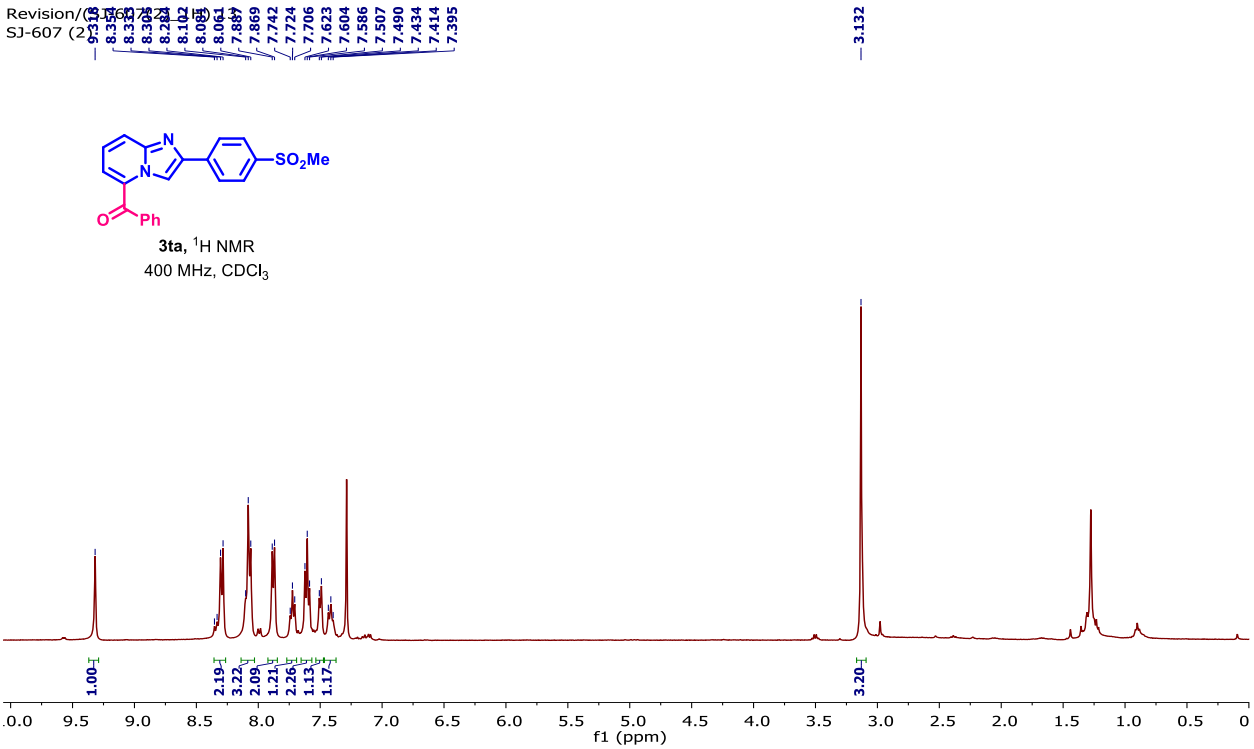


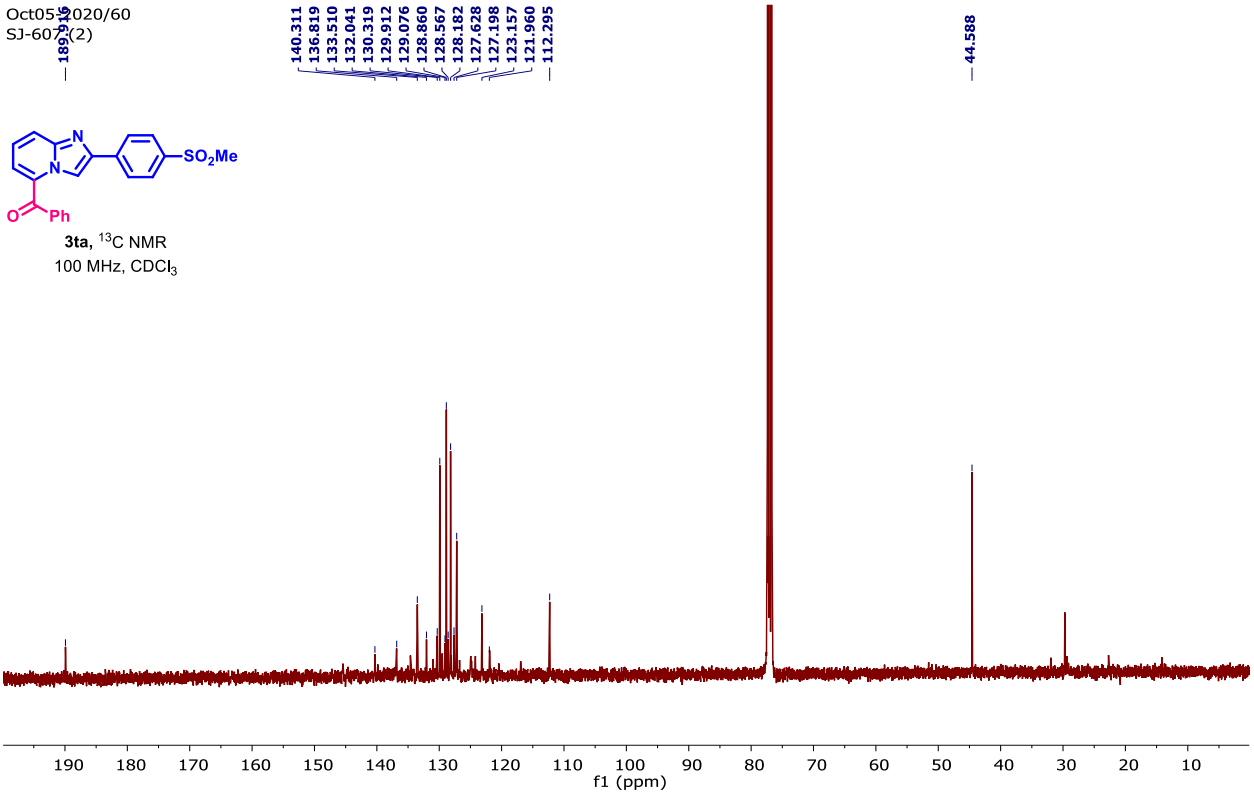




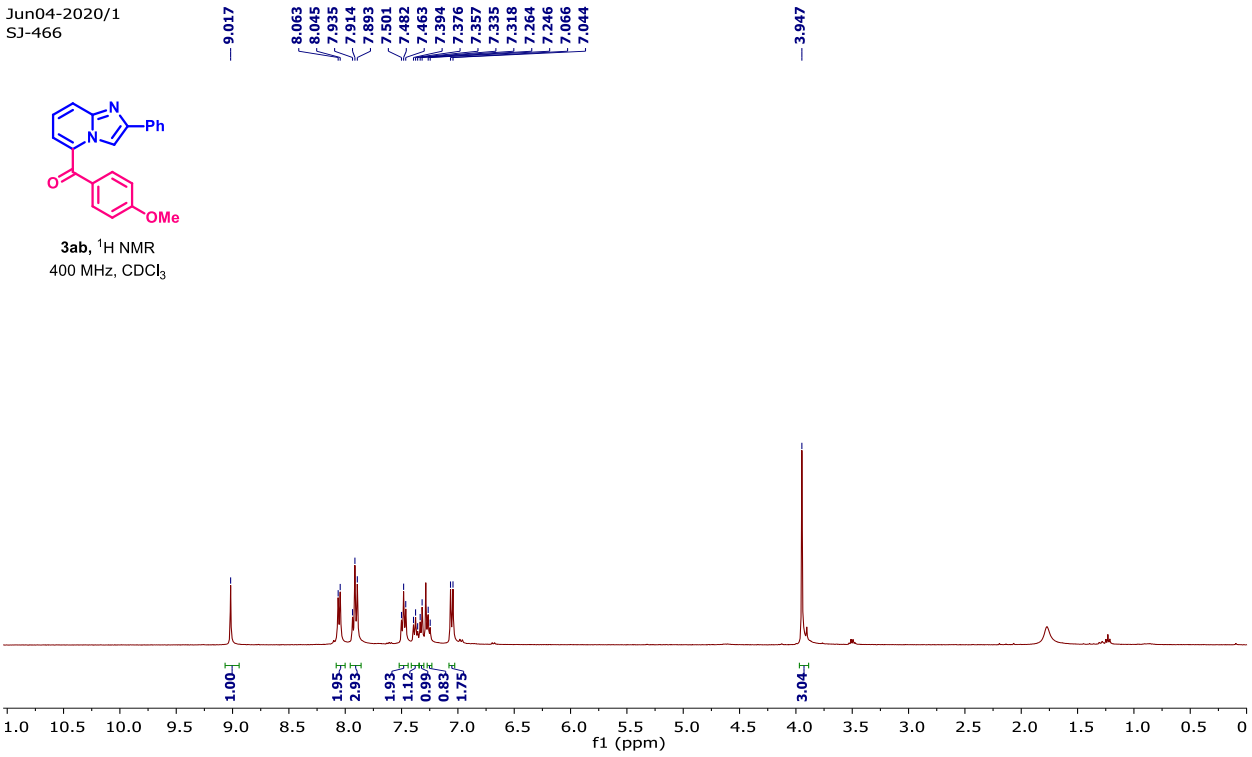
**3sa**, $^{13}$C NMR
100 MHz, $CDCl_3$



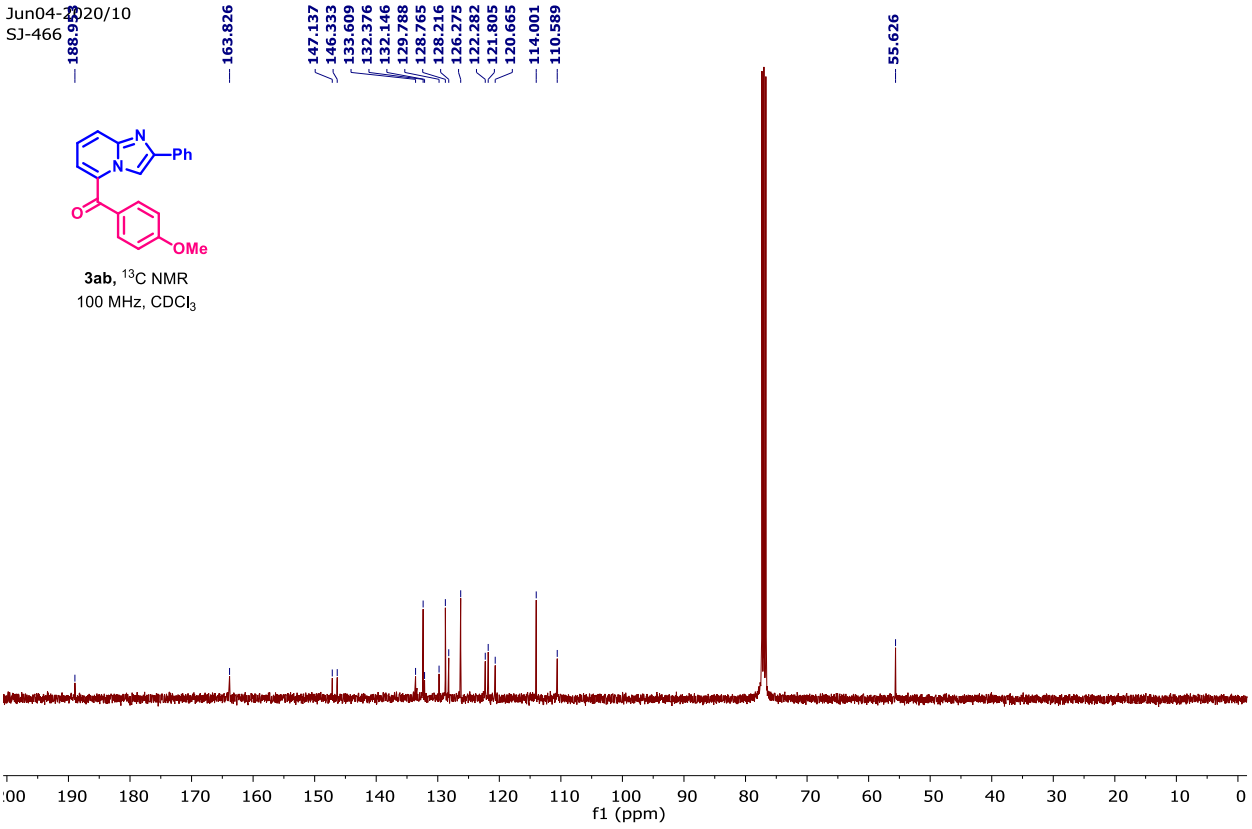

**3ta,** $^{1}$H NMR
400 MHz, $CDCl_3$



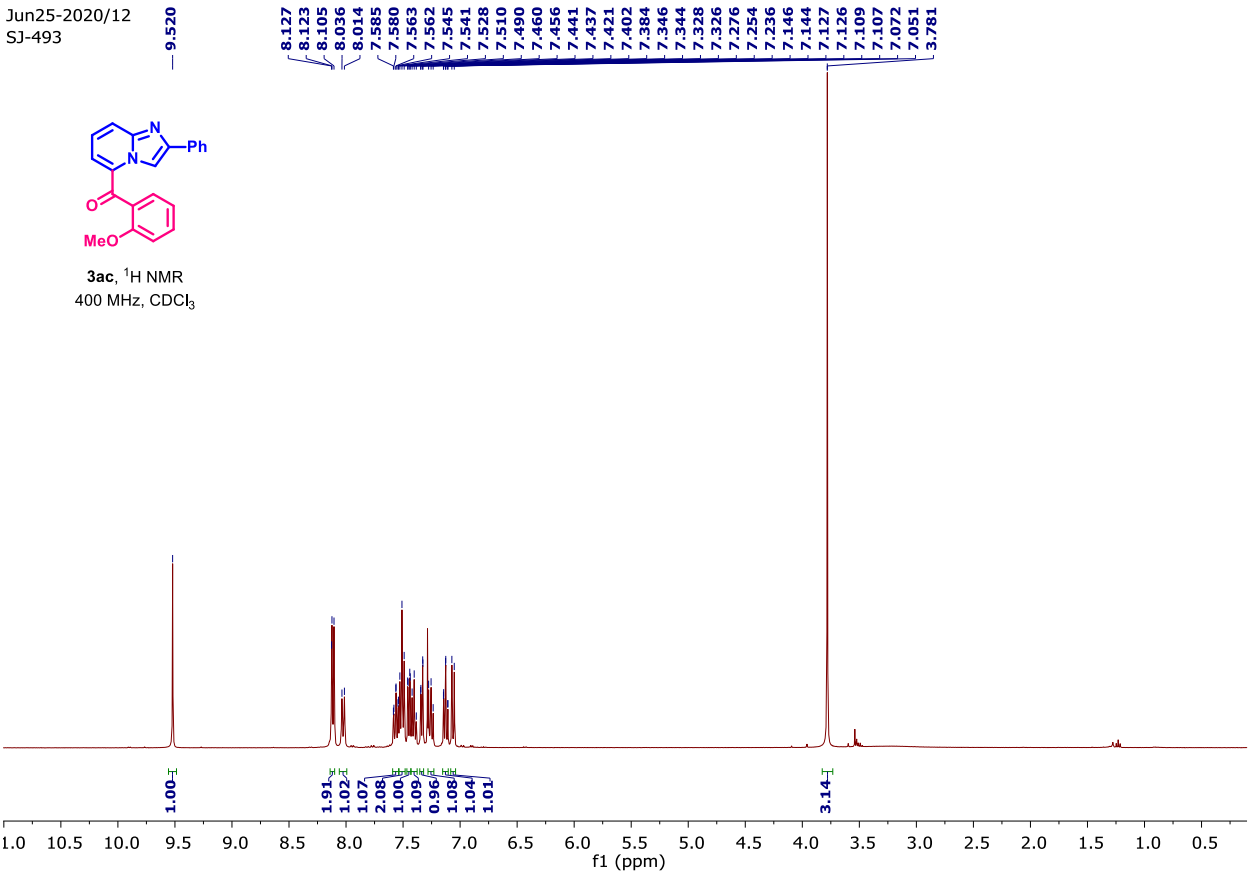

**3ta,** $^{13}$C NMR
100 MHz, $CDCl_3$

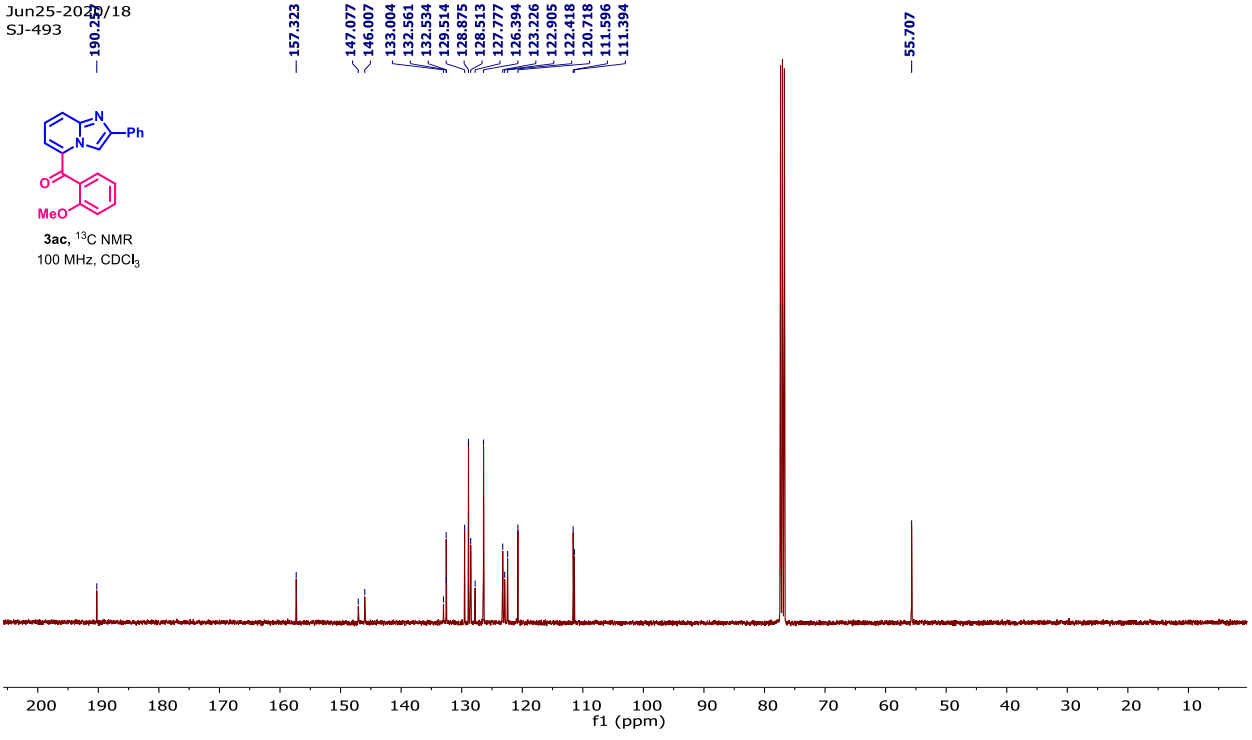


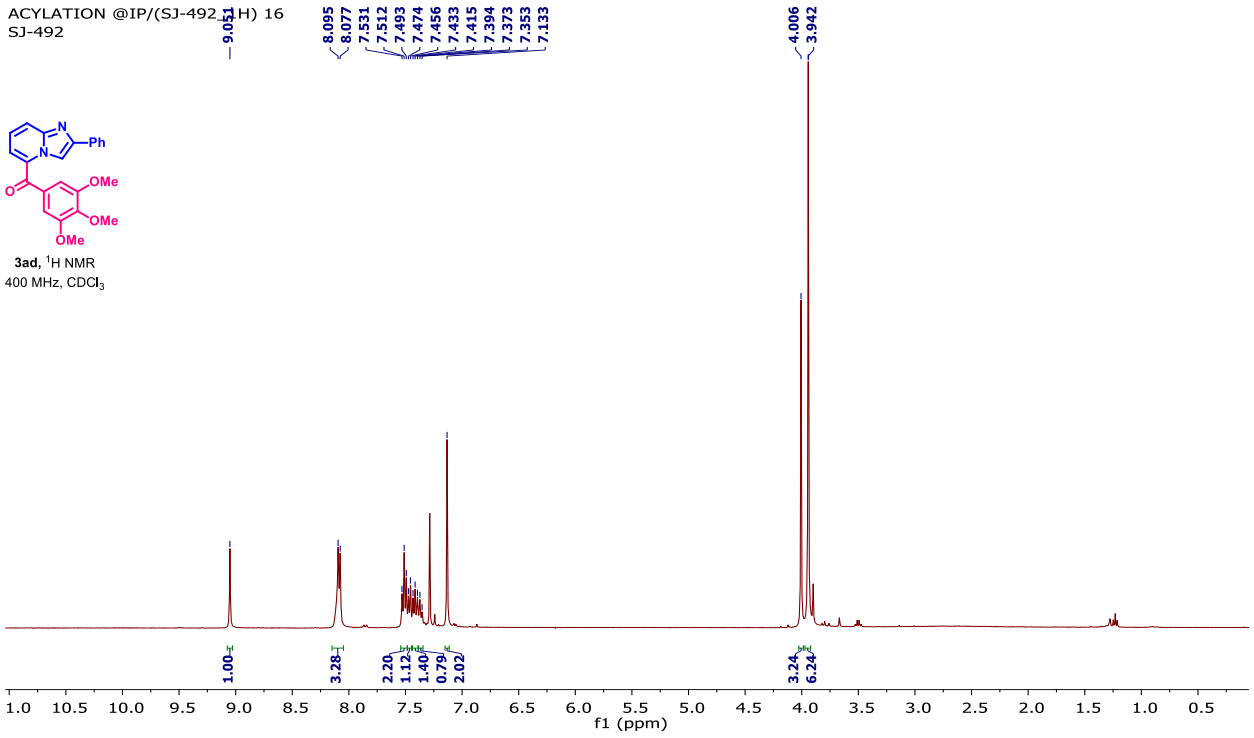

**3ab,** $^{1}$H NMR
400 MHz, $CDCl_3$

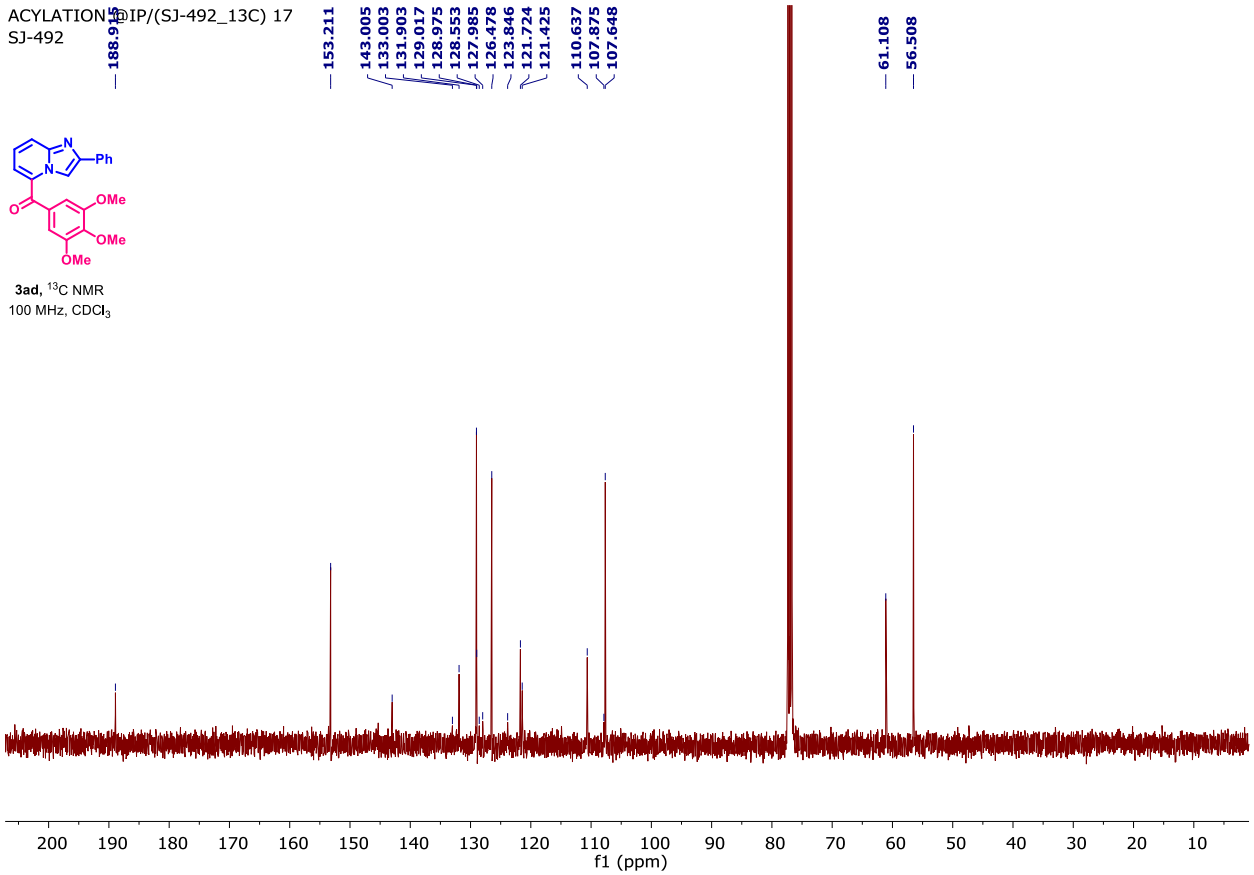



**3ab,** $^{13}$C NMR
100 MHz, $CDCl_3$


Jun25-2020/12
SJ-493
9.520
8.127
8.123
8.105
8.036
8.014
7.585
7.580
7.563
7.562
7.545
7.541
7.528
7.510
7.490
7.460
7.456
7.441
7.437
7.421
7.402
7.384
7.346
7.344
7.328
7.326
7.276
7.254
7.236
7.146
7.144
7.127
7.126
7.109
7.107
7.072
7.051
3.781
Ph
N
O
MeO
3ac, 1H NMR
400 MHz, CDCl3
1.00
1.91
1.02
1.07
2.08
1.00
1.09
0.96
1.08
1.04
1.01
3.14
f1 (ppm)


Jun25-2020/18
SJ-493
190.252
157.323
147.077
146.007
133.004
132.561
132.534
129.514
128.875
128.513
127.777
126.394
123.226
122.905
122.418
120.718
111.596
111.394
55.707
Ph
N
O
MeO
3ac, 13C NMR
100 MHz, CDCl3
f1 (ppm)

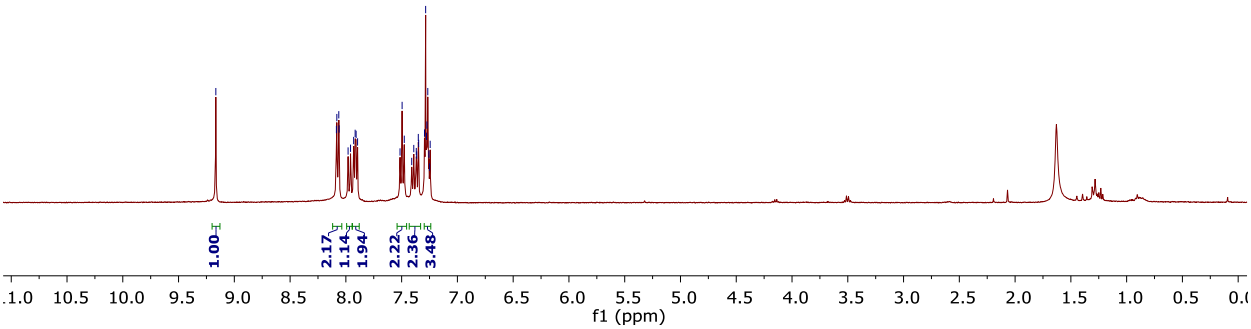

ACYLATION @IP/(SJ-492_1H) 16
SJ-492
9.051
8.095
8.077
7.531
7.512
7.493
7.474
7.456
7.433
7.415
7.394
7.373
7.353
7.133
4.006
3.942
Ph
OMe
OMe
OMe
3ad, 1H NMR
400 MHz, CDCl3
1.00
3.28
2.20
1.12
1.40
0.79
2.02
3.24
6.24
f1 (ppm)


ACYLATION @IP/(SJ-492_13C) 17
SJ-492
188.915
153.211
143.005
133.003
131.903
129.017
128.975
128.553
127.985
126.478
123.846
121.724
121.425
110.637
107.875
107.648
61.108
56.508
Ph
OMe
OMe
OMe
3ad, 13C NMR
100 MHz, CDCl3
f1 (ppm)

Jun09-2020/8
SJ-476

9.166
8.085
8.081
8.063
8.061
7.980
7.958
7.930
7.917
7.908
7.895
7.514
7.496
7.476
7.410
7.391
7.369
7.365
7.351
7.347
7.295
7.285
7.277
7.273
7.266
7.256
7.249
7.244


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



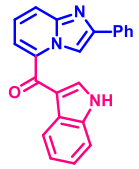

Jun17-2020/7
SJ-476

188.837

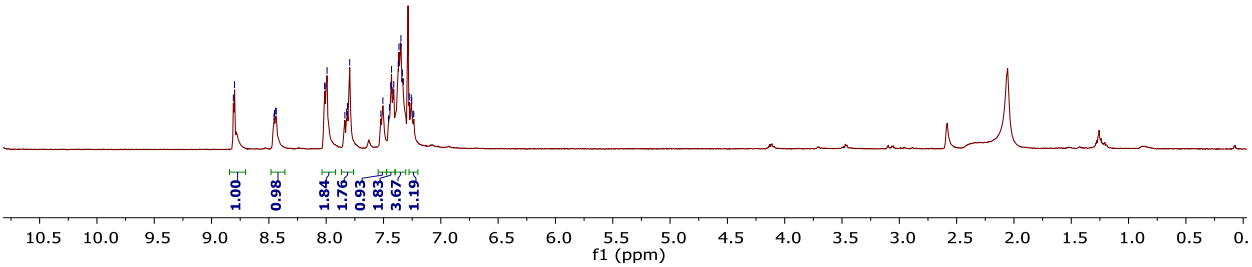
147.480
146.262
133.706
133.673
133.332
132.459
132.368
131.503
128.838
128.424
126.338
122.560
122.229
121.986
116.051
115.832
110.907


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

Jun17-2020/(SJ-483_1H)-5
SJ-483

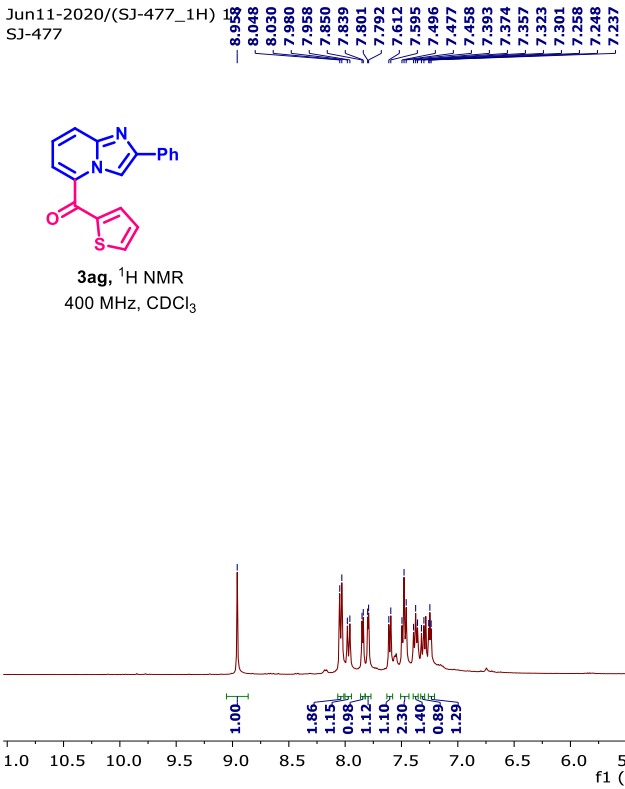




**3af,** $^{1}$H NMR
400 MHz, $CDCl_3$

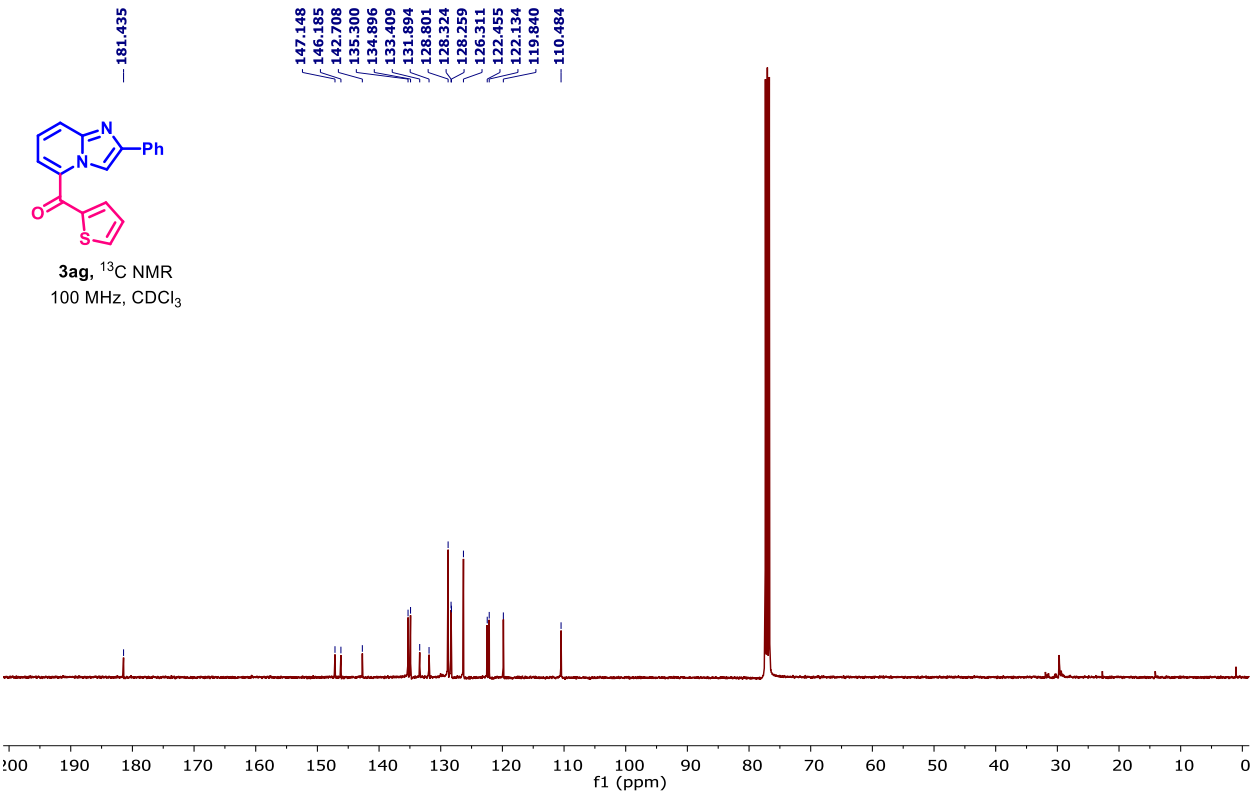




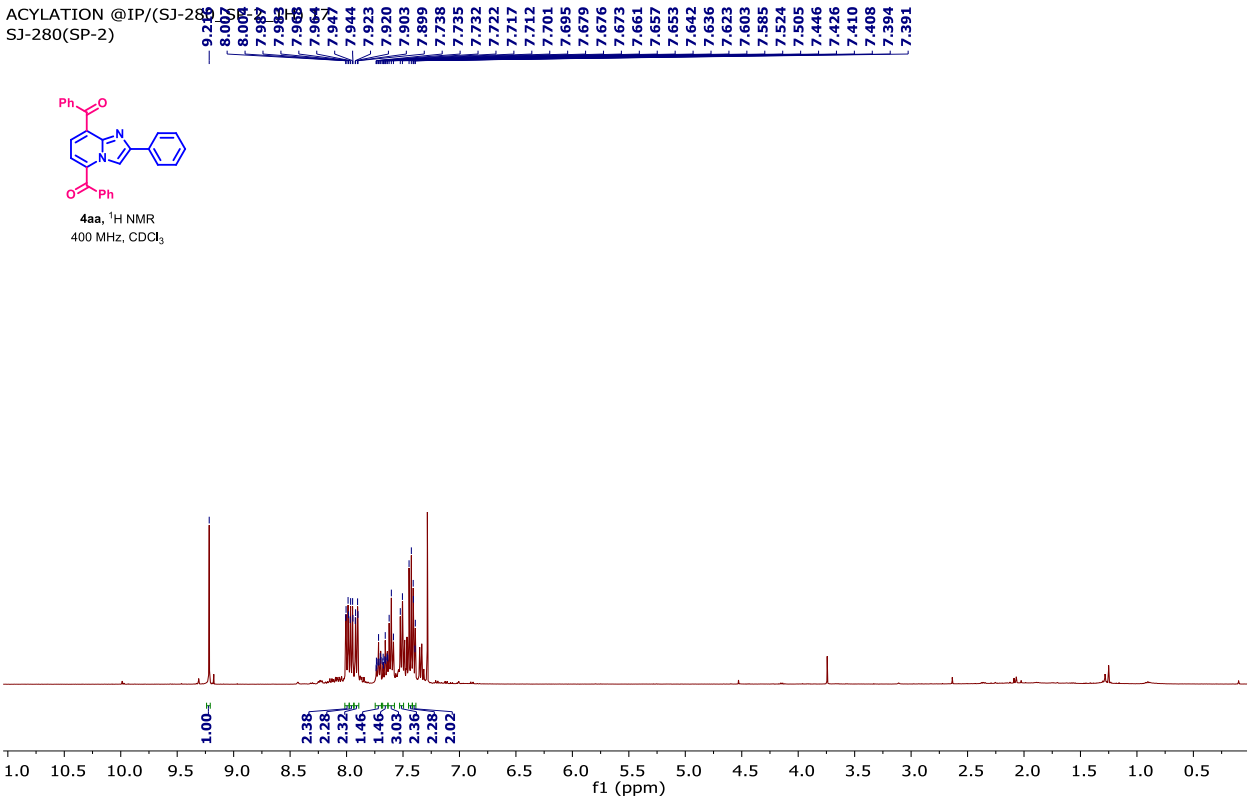
**3af,** $^{13}$C NMR
100 MHz, $CDCl_3$

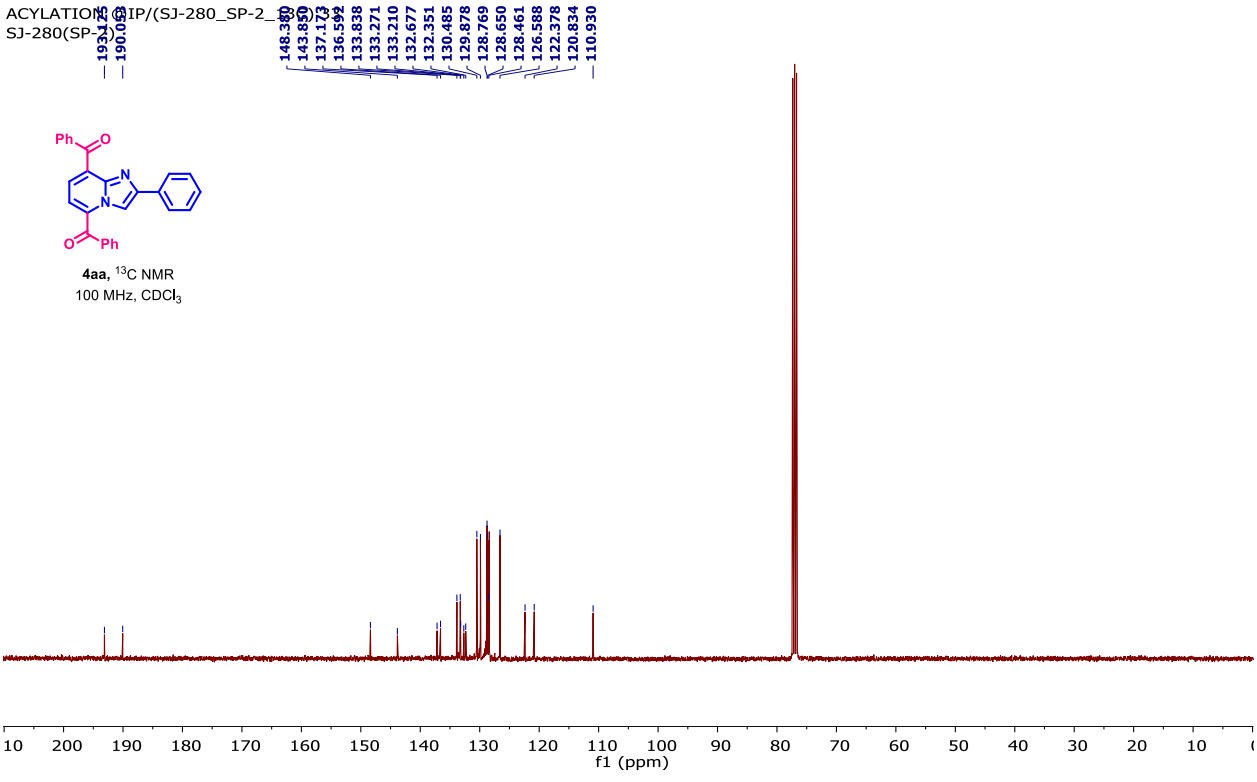


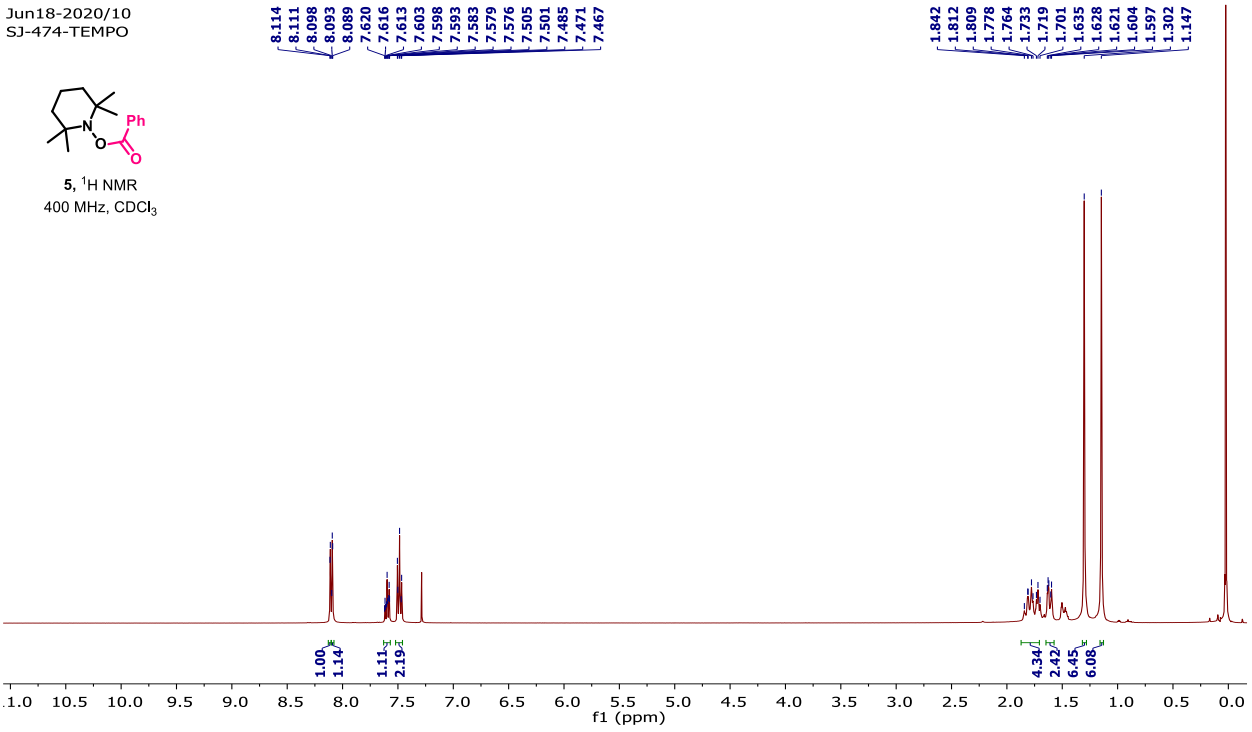

**3ag,** $^{1}$H NMR
400 MHz, $CDCl_3$

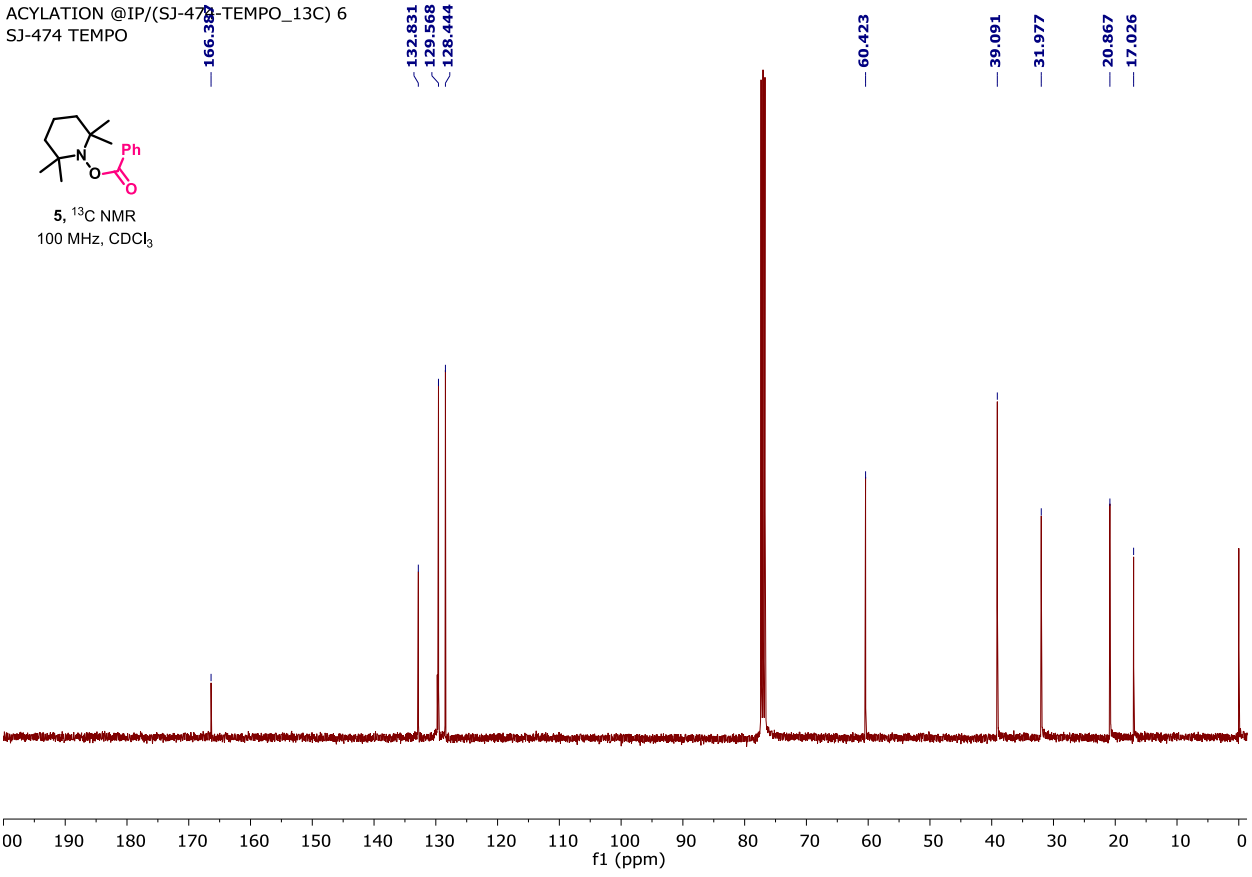



**3ag,** $^{13}$C NMR
100 MHz, $CDCl_3$

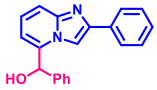

ACYLATION @IP/(SJ-280_SP-2_
SJ-280(SP-2)
9.210
8.007
8.004
7.987
7.983
7.965
7.947
7.944
7.923
7.920
7.903
7.899
7.738
7.735
7.732
7.722
7.717
7.712
7.701
7.695
7.679
7.676
7.673
7.661
7.657
7.653
7.642
7.636
7.623
7.603
7.585
7.524
7.505
7.446
7.426
7.410
7.408
7.394
7.391
Ph
O
N
N
O
Ph
4aa, 1H NMR
400 MHz, CDCl3
1.00
2.38
2.28
2.32
1.46
1.46
3.03
2.36
2.28
2.02
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


ACYLATION @IP/(SJ-280_SP-2_13C)
SJ-280(SP-2)
193.170
190.083
148.380
143.850
137.173
136.592
133.838
133.271
133.210
132.677
132.351
130.485
129.878
128.769
128.650
128.461
126.588
122.378
120.834
110.930
Ph
O
N
N
O
Ph
4aa, 13C NMR
100 MHz, CDCl3
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

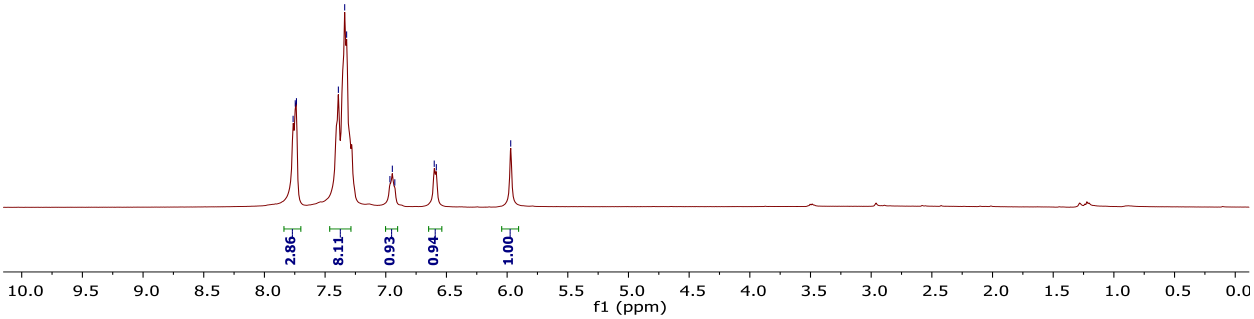

Jun18-2020/10
SJ-474-TEMPO
8.114
8.111
8.098
8.093
8.089
7.620
7.616
7.613
7.603
7.598
7.593
7.583
7.579
7.576
7.505
7.501
7.485
7.471
7.467
1.842
1.812
1.809
1.778
1.764
1.733
1.719
1.701
1.635
1.628
1.621
1.604
1.597
1.302
1.147
Ph
N
O
O
5, 1H NMR
400 MHz, CDCl3
1.00
1.14
1.11
2.19
4.34
2.42
6.45
6.08
f1 (ppm)


ACYLATION @IP/(SJ-474-TEMPO_13C) 6
SJ-474 TEMPO
166.382
132.831
129.568
128.444
60.423
39.091
31.977
20.867
17.026
Ph
N
O
O
5, 13C NMR
100 MHz, CDCl3
f1 (ppm)

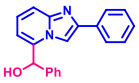
Aug28-2020/3
SJ-542

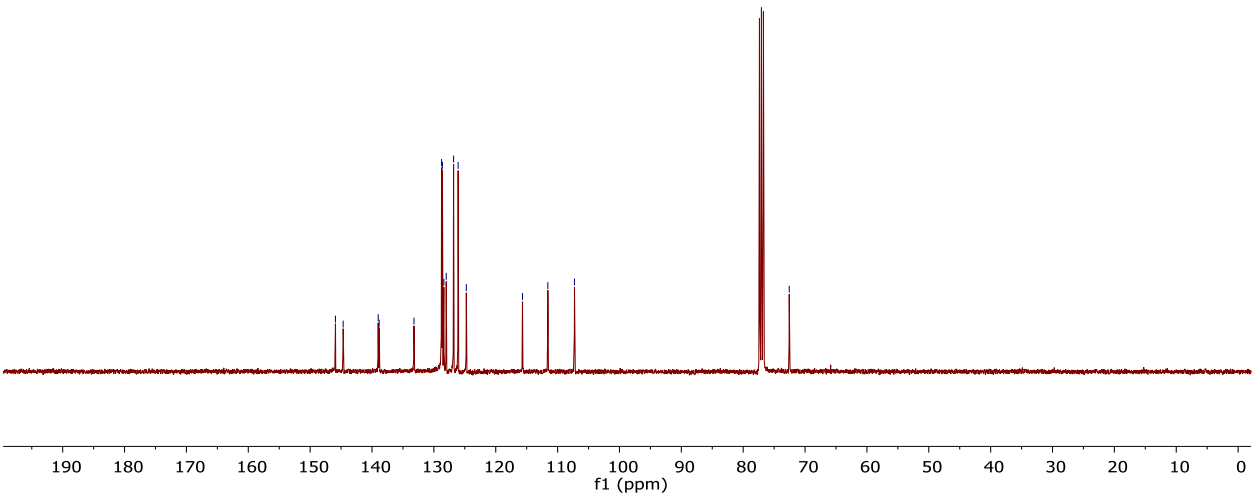

**8**, $^{1}$H NMR
400 MHz, $CDCl_3$



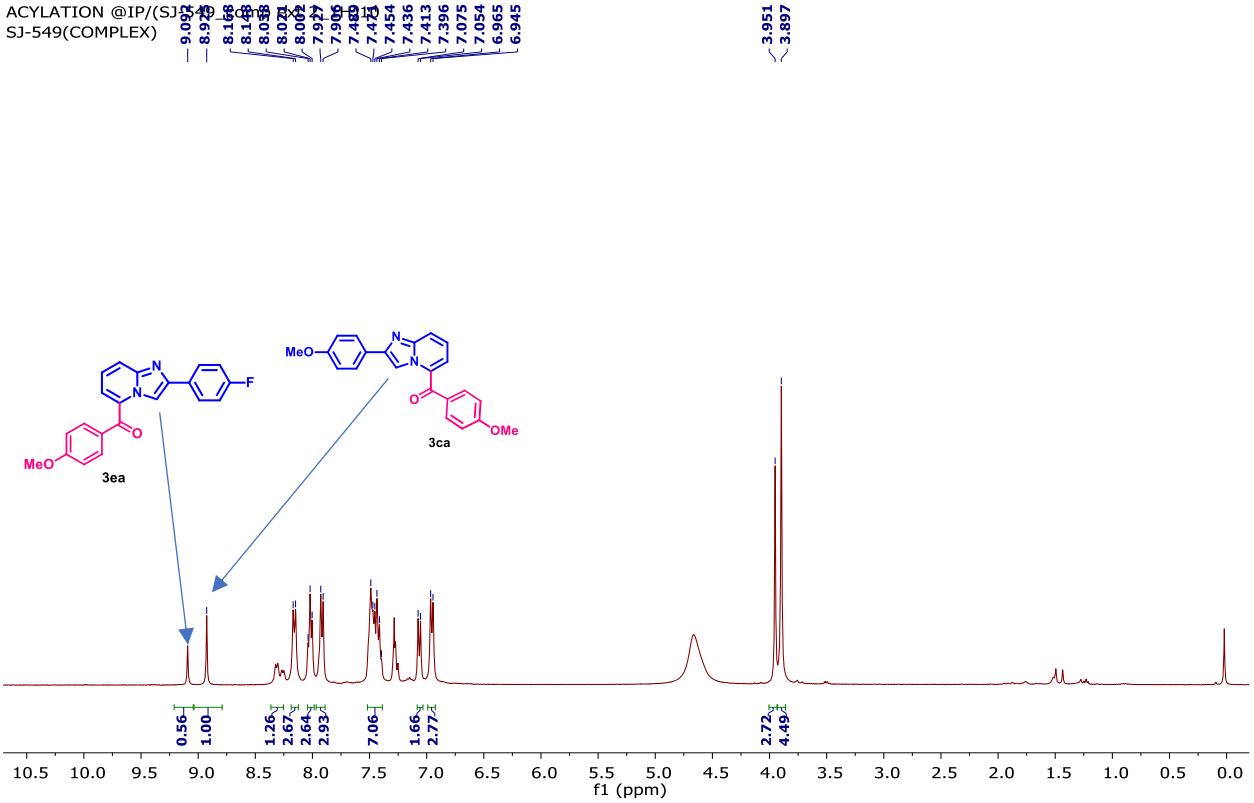

Aug28-2020/25
SJ-542

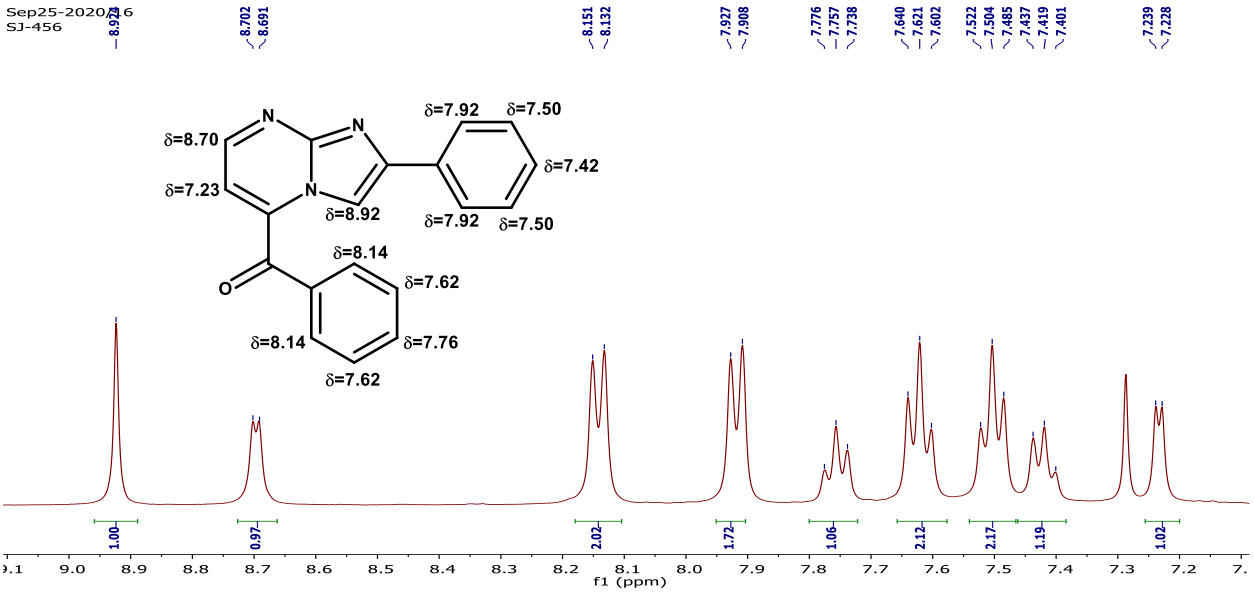

**8**, $^{13}$C NMR
100 MHz, $CDCl_3$

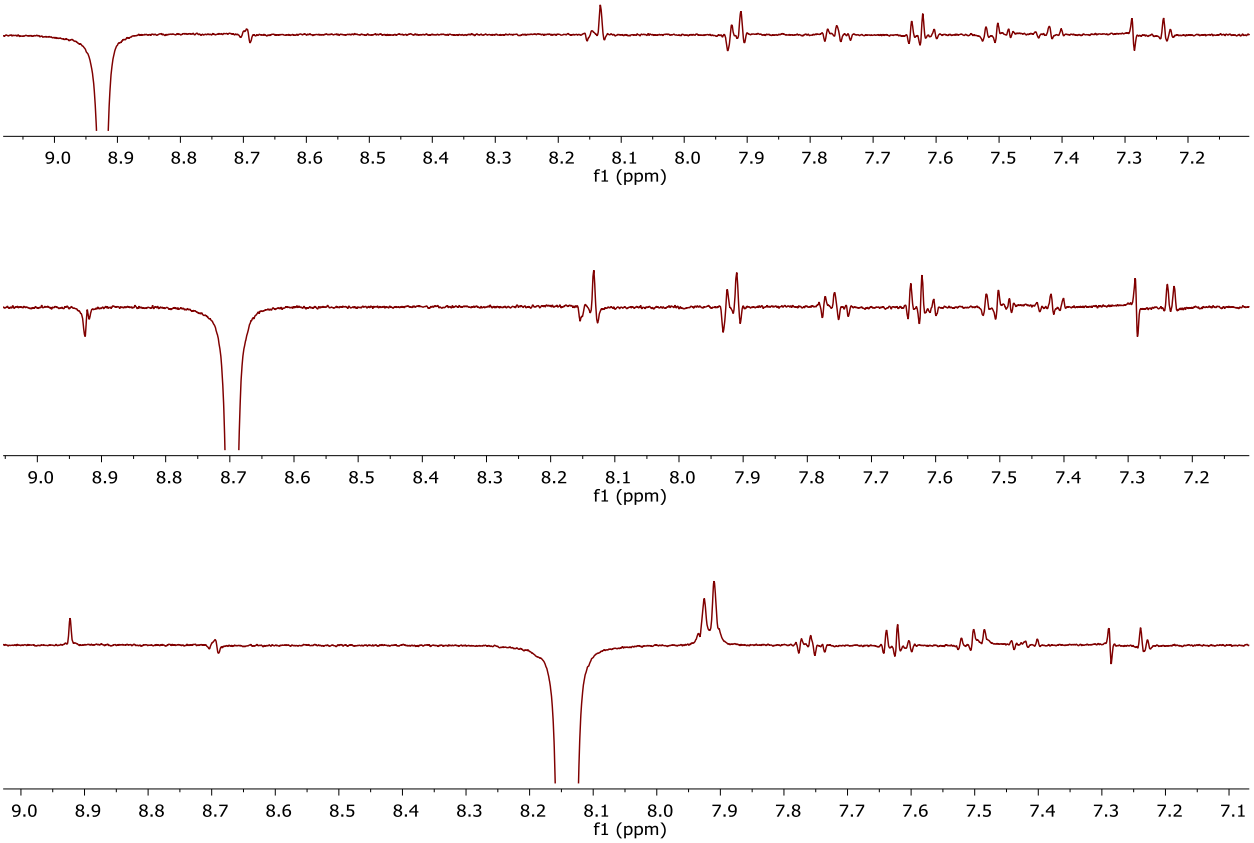


## 2. Competitive experiment




## 1D NOE Experiment of 3pa






### 3. Single crystal X-ray analysis of 3aa

The compound **3aa** (Exp 565_AK-SJ-280) ($C_{20}H_{14}N_2O$) crystallized in orthorhombic Pbca space group. The ORTEP diagram of compound is given in Figure S1, CCDC 1978834. The bond lengths N1-C1, N1-C5, N1-C6, N2-C7 and N2-C1 bond lengths respectively are 1.4016(15), 1.3925(15), 1.3770(16), 1.3693(16) and 1.3271(16) Å, respectively and the corresponding bond angles C1-N1-C5, C1-N1-C6, C5-N1-C6, C1-N2-C7 are 121.55(10), 106.07(10), 132.29(11), and 105.34(10)º, respectively. The torsional angles C6-C7-C8-C9 and C5-C14-C15-C16 are -7.05 and 43.10º, respectively.

## Experimental

Single crystals of **3aa** [$C_{20}H_{14}N_2O$] were grown from slow evaporation of dichloromethane solution. A suitable crystal was selected and mounted on a XtaLAB Pro: Kappa dual home/near diffractometer. The crystal was kept at 93(2) K during data collection. Using Olex2[2], the structure was solved with the ShelXT[3] structure solution program using Intrinsic Phasing and refined with the ShelXL[4] refinement package using Least Squares minimization.

**Table S1 Crystal data and structure refinement for 3aa (Exp 565_AK-SJ-280)**

| | |
|---|---|
| Identification code | Exp 565_AK-SJ-280 |
| Empirical formula | $C_{20}H_{14}N_2O$ |
| Formula weight | 298.33 |
| Temperature/K | 93(2) |
| Crystal system | orthorhombic |
| Space group | Pbca |
| a/Å | 8.3127(2) |
| b/Å | 17.1849(3) |
| c/Å | 20.9916(4) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2998.71(11) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.322 |
| μ/mm$^{-1}$ | 0.656 |
| F(000) | 1248.0 |
| Crystal size/mm$^3$ | 0.1 × 0.1 × 0.1 |
| Radiation | CuKα (λ = 1.54184) |
| 2Θ range for data collection/° | 8.424 to 159.084 |
| Index ranges | $-10 \leq h \leq 8$, $-21 \leq k \leq 17$, $-25 \leq l \leq 26$ |
| Reflections collected | 10545 |
| Independent reflections | 3204 [$R_{int}$ = 0.0331, $R_{sigma}$ = 0.0312] |
| Data/restraints/parameters | 3204/0/208 |
| Goodness-of-fit on F$^2$ | 1.096 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0442, $wR_2$ = 0.1217 |
| Final R indexes [all data] | $R_1$ = 0.0464, $wR_2$ = 0.1239 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.24/-0.27 |

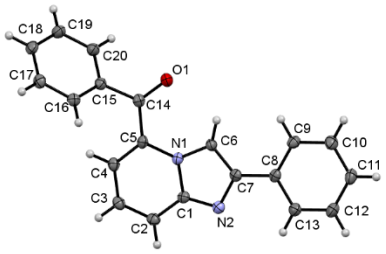



Figure S1. The ORTEP crystal structure diagram of compound **3aa**. The thermal ellipsoids are drawn at the 50% probability level.

## 4. References


(1) Wadhwa, K.; Yang, C; Paul, R. W.; Kris, C. D.; Chemrbukar, S. R.; Reddy, R. E.; Synthesis of arylglyoxylic acids and their collision-induced dissociation. *Synth. Commun.* **2008**, 38, 4434-4444.

(2) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschman, H. Olex2: A complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, 42, 339-341.

(3) Sheldrick, G. Shelxet – intergated space group and crystal-structure determination. *Acta Cryst. A* **2015**, 71, 3-8.

(4) Sheldrick, G. Crystal structure refinement with shelxet *Acta Cryst. C* **2015**, 71, 3-8.