Supplementary Information (SI) for Organic & Biomolecular Chemistry.
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Directed Regioselective Arylation of Imidazo[1,2-*a*]pyridine-3-carboxamides using Rh(III) catalysis.

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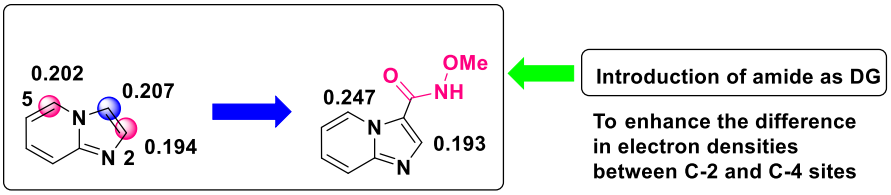
1. General Information

The reagents and chemicals required were commercially obtained from sigma aldrich and used as such without further purification unless otherwise mentioned. 2-methyl-imidazo[1,2-*a*]pyridine-3-carboxylic acid derivatives were synthesized according to previously reported methods. The progress of the reaction was monitored by thin layer chromatography (TLC) performed on silica gel aluminium plates and visualization was done by UV light. High resolution mass spectra were recorded using ESI-TOF method. ^{1}H NMR and ^{13}C NMR spectra were recorded on Brucker-Avance DPX FT-NMR and Jeol at 600 and 500 MHz respectively, with TMS as an internal standard. The ^{1}H NMR and ^{13}C NMR spectra were recorded for $CDCl_3$ at 7.26 ppm and 77.1 ppm respectively. Chemical shifts (δ) are reported in parts per million (ppm). Coupling constants (J) were reported in hertz (Hz). The chemical shifts characterize the signals are as follows: s = singlet, m = multiplet, d = doublet, br. s. = broad singlet, dd = doublet of doublet, t = triplet.

2. Experimental Section

2.1 NBO analysis

The imidazo[1,2-*a*]pyridine moiety exhibits variations in electron density across different hydrogens based on their electronic characteristics. The NBO anayalysis indicate that the C-3 position is the most electron rich site, thereby it is easy to activate the C-3 position of imidazo[1,2-*a*]pyridine by innate or inherent C-H activation. C-5 position can be made elctron-rich by the introduction of any carbonyl containing directing group. The NBO analysis of imidazo[1,2-*a*]pyridine-3-carboxamides showed that adding a carbonyl group at the C-3 position reduces the electron density at C-2 and makes C-5 the most electron-rich site by blocking the highly reactive C-3 site. This change causes a difference in electron densities between the C-2 and C-5 positions. Additionally, various substitutions at the C-2 position, such as methyl, chloro, or no substitution, resulted in minimal changes in the charge density at the nitrogen in the amide group. Therefore, both electron-donating and electron-withdrawing groups at C-2 have little effect on this charge density. The reactivity of the proton at the C-5 position remains nearly the same across all cases.



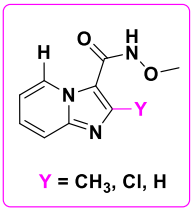


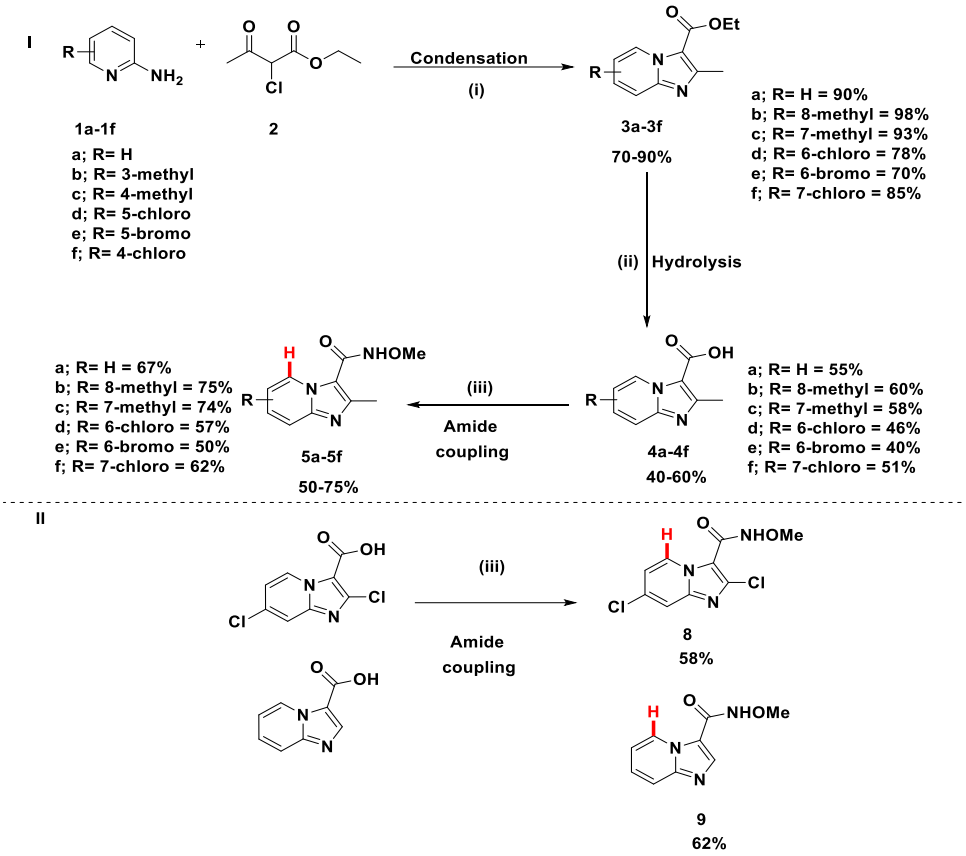
Table S1. NBO analysis of 2-substituted imidazo[1,2-*a*]carboxamides.

Substituent at C-2 position	Charge density at C-5(H)	Charge density at C5	Charge density at amide N
CH_3	0.258	0.058	-0.344
Cl	0.254	0.058	-0.338
H	0.247	0.056	-0.341

2.2 General Procedure Synthesis of imidazo[1,2-*a*]pyridine-3-carboxamides.

A new *N*-methoxy-2-methylimidazo[1,2-*a*]pyridine-3-carboxamides can be procure in three steps (**5a**-**5f**). First step involves cyclocondensation of 2-amino pyridine (**1a**, 10 mmol, 1 equiv.) with 2-chloroethylacetoacetate (**2**, 12.75 mmol, 1 equiv.) in DCE (5 mL) at reflux for overnight. The reaction mixture was diluted with DCM and transferred into separating funnel consisting of water. The organic layer was separated and concentrated under reduced pressure to obtained crude product. The crude product subjected to column chromatography on 60-120 grade silica and the product was eluted with at 1:9 ratios of acetate and hexane with 90% yield. The product was obtained as a white solid on drying under vacuum. The structure of 2-methylimidazo[1,2-*a*]pyridine-3-carboxalate (**3a**) was confirmed by ^{1}H NMR, ^{13}C NMR, and mass spectrometry.

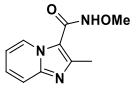
The second step involves hydrolysis of synthesized ester in basic condition using LiOH and ethanol as solvent and the reaction kept was at reflux for 24 h. The reaction mixture was subjected for neutralization by using 1N HCl to get white precipitate and filteration was performed using Buchner funnel to afford imidazo[1,2-*a*]pyridine-3-carboxylic acid derivative (**4a**) with 55% yield. The structure of imidazo[1,2-*a*]pyridine-3-carboxylic acid (**4a**) was confirmed by ^{1}H NMR, ^{13}C NMR, and mass spectrometry. Finally the imidazo[1,2-*a*]pyridine-3-carboxylic acid (**4a**, 1 mmol, 1 equiv.) was reacted with *N*-methoxy amine hydrochloride (2 mmol, 2 equiv) via amide coupling using EDC.HCl (1 mmol, 1 equiv.), Triethylamine (5 mmol, 5 equiv.) and HOBt (1 mmol, 1 equiv.) in DCM at RT for 24 h to get the desired *N*-methoxy-2-methylimidazo[1,2-*a*]pyridine-3-carboxamide derivative (**5a**) with 67% yield. A new 2,7-dichloro-N-methoxyimidazo[1,2-*a*]pyridine-3-carboxamide (**8**) and *N*-methoxy-imidazo[1,2-*a*]pyridine-3-carboxamide (**9**) were synthesized using commercially available 2,7 dichloro imidazo[1,2-*a*]pyridine-3-carboxylic acid and imidazo[1,2-*a*]pyridine-3-carboxylic acid respectively using same procedure for amide coupling.



Scheme S1. Synthetic scheme for the synthesis of starting materials. (i) Dimethoxy ethane, reflux 12 h, (ii) LiOH, ethanol reflux, 12 h. (iii) $NH_2OME.HCl$, EDC.HCl, TEA, HOBt, RT.

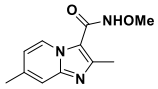
2.3 Spectral data of synthesized compounds from 5a-5f, 8 and 9 (starting materials).

5a) *N*-methoxy-2-methylimidazo[1,2-*a*]pyridine-3-carboxamide



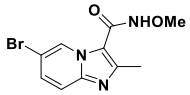
White solid (154 mg, 75%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.25 (d, J = 6.9 Hz, 1H), 8.76 (s, 1H), 7.53 (d, J = 9.1 Hz, 1H), 7.35 – 7.30 (m, 1H), 6.92 (t, J = 7.1 Hz, 1H), 3.90 (s, 3H), 2.64 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.0, 146.7, 146.6, 128.0, 122.6, 116.5, 113.1, 65.1, 16.7; HRMS (EI-TOF) calcd for $C_{10}H_{11}N_3O_2$ $[M+H]^+$: 206.0924, found 206.0924.

5b) *N*-methoxy-2,7-dimethylimidazo[1,2-*a*]pyridine-3-carboxamide



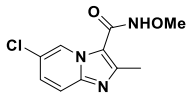
Off white solid (158 mg, 72%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.25 (d, J = 6.9 Hz, 1H), 7.30 (s, 1H), 6.87 (d, J = 9.1 Hz, 1H), 3.91 (s, 3H), 2.61 (s, 3H) 2.61 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.8., 145.1, 126.0, 115.2, 113.8, 113.8, 111.6, 63.9, 20.3, 15.4; HRMS (EI-TOF) calcd for $C_{11}H_{13}N_3O_2$ $[M+H]^+$: 220.1086, found 220.1086.

5c) 6-bromo-*N*-methoxy-2-methylimidazo[1,2-*a*]pyridine-3-carboxamide



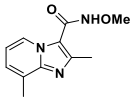
Brown solid (142 mg, 50%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.46 (s, 1H), 8.66 (s, 1H), 7.43 (d, J = 8.9 Hz, 1H), 7.41 (d, J = 9.1 Hz, 1H), 3.91 (s, 3H), 2.64 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.8., 145.1, 126.0, 115.2, 113.8, 113.8, 111.6, 63.9, 20.3, 15.4; HRMS (EI-TOF) calcd for $C_{10}H_{10}BrN_3O_2$ $[M+H]^+$: 284.0034, found 284.0034.

5d) 6-chloro-*N*-methoxy-2-methylimidazo[1,2-*a*]pyridine-3-carboxamide



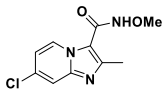
Light brown solid (148 mg, 62%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.42 (s, 1H), 7.39 (d, J = 8.7 Hz, 1H), 7.21 (d, J = 9.1 Hz, 1H), 3.91 (s, 3H), 2.64 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.1., 141.8, 124.0, 113.2, 111.8, 111.8, 111.6, 63.9, 20.3, 15.4; Mass (EI-LTQ) calcd for $C_{10}H_{10}ClN_3O_2$ $[M+H]^+$: 240.05, found. 239.94.

5e) *N*-methoxy-2,8-dimethylimidazo[1,2-*a*]pyridine-3-carboxamide



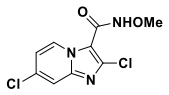
White solid (126 mg, 57%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.10 (d, J = 6.9 Hz, 1H), 7.11 (d, J = 7.0 Hz, 1H), 6.82 (t, J = 6.9 Hz, 1H), 3.90 (s, 3H), 2.67 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.0, 152.3, 147.2, 126.8, 126.5, 125.8, 113.7, 112.9, 51.3, 17.0, 16.6; Mass (LTQ) calcd for $C_{11}H_{13}N_3O_2$ $[M+H]^+$: 220.1085 , found 220.1085.

5f) 7-chloro-*N*-methoxy-2-methylimidazo[1,2-*a*]pyridine-3-carboxamide



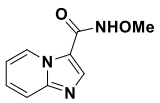
Yellowish-white solid (138 mg, 53%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.25 (1H, d, J= 7.4 Hz), 8.43 (1H, s), 7.55 (1H, d, J=1.8 Hz), 6.93 (1H, dd, J=7.4 Hz, 1.9 Hz), 3.99 (3H, s), 2.66 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.7, 147.3, 146.7, 134.4, 128.3, 115.7, 115.6, 115.2, 65.2, 16.9; HRMS (EI-TOF) calcd for $C_{10}H_{10}ClN_3O_2$ $[M+Na]^+$:262.0397, found 262.0359.

8) 2,7-dichloro-*N*-methoxyimidazo[1,2-a]pyridine-3-carboxamide



White solid (161 mg, 62%)NMR (600 MHz, $CDCl_3$) δ 9.44 (d, J = 7.4 Hz, 1H), 9.28 (s, 2H), 7.56 (d, J = 1.6 Hz, 1H), 6.99 (dd, J = 7.5, 2.0 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.1, 145.5, 137.8, 135.8, 128.9, 116.4, 116.00, 111.24, 65.4.

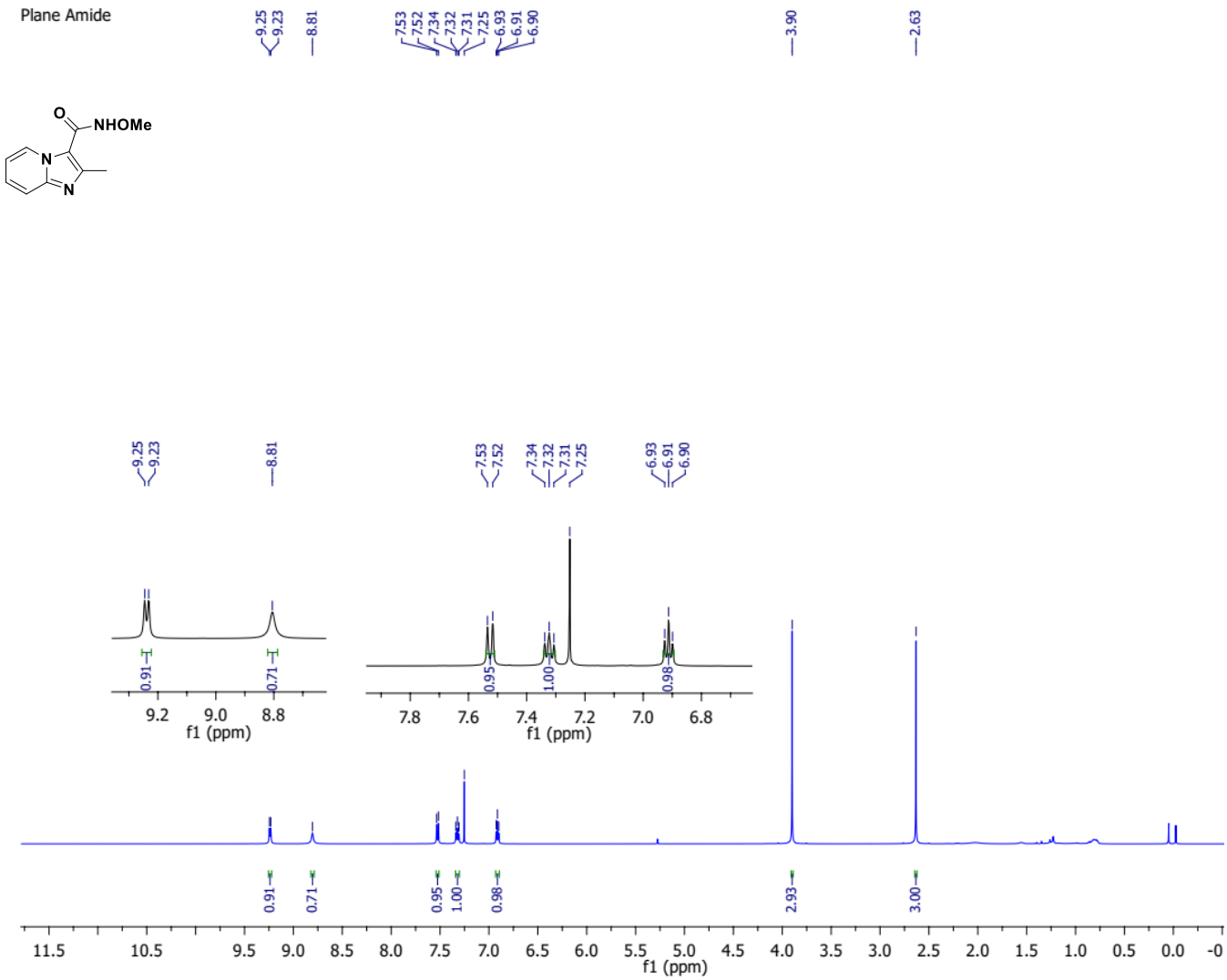
9) *N*-methoxyimidazo[1,2-*a*]pyridine-3-carboxamide

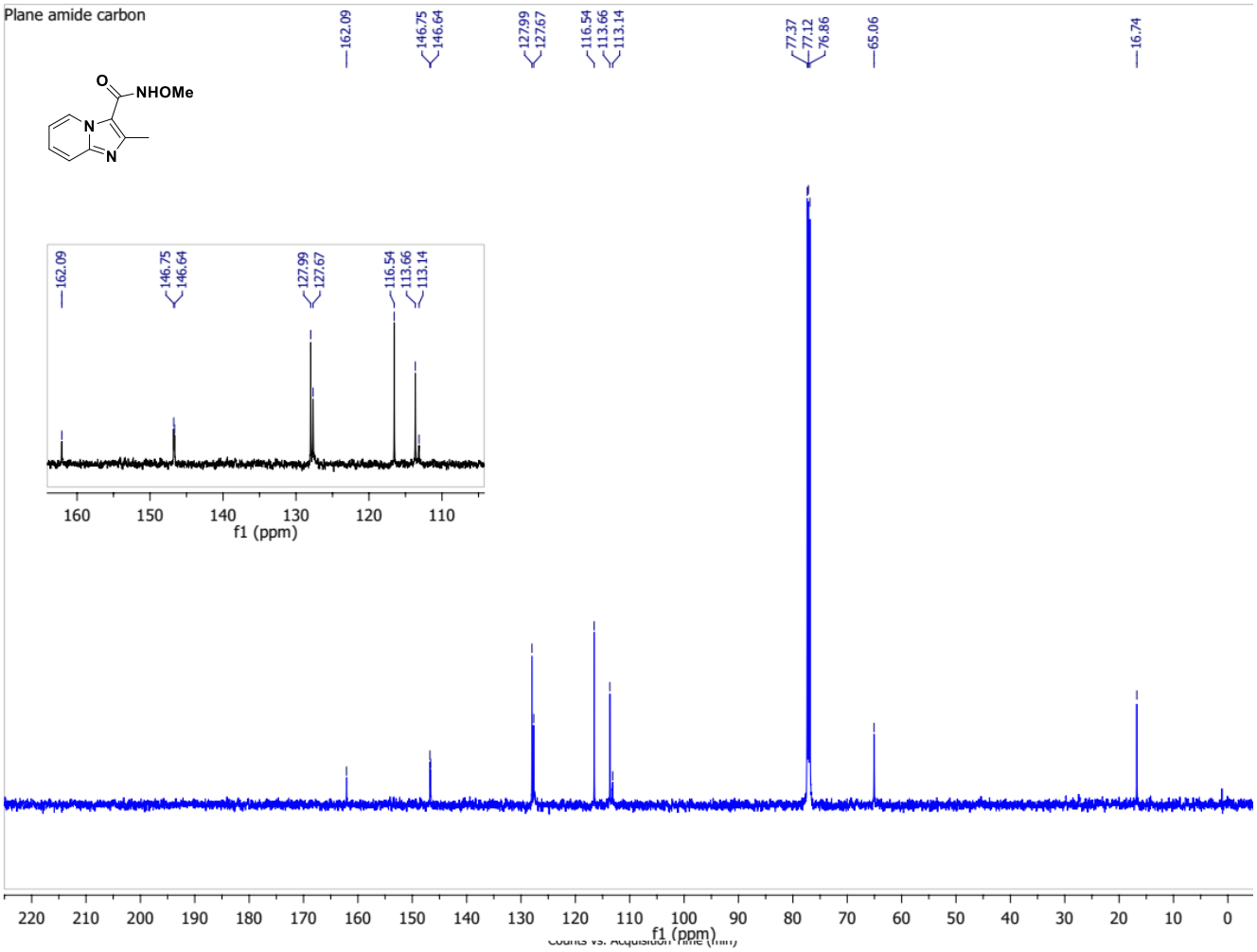


Yellowish white solid (165 mg, 86%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.49 (d, J = 7.4 Hz, 1H), 8.30 (s, 1H), 7.74 (d, J = 9.3 Hz, 1H), 7.42 (ddd, J = 9.1 Hz, 8.5 Hz, 5.1 Hz, 1H), 6.99-7.08 (m, 1H), 3.90 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.0, 147.8, 136.8, 136.8, 128.3, 128.0, 117.4, 115.8, 114.4, 64.9; HRMS (EI-TOF) calcd for $C_9H_9N_3O_2$ $[M+H]^+$:192.0779, found 192.0776.

2.4 Scanned copies of ^{1}H NMR, ^{13}C NMR and HRMS for starting materials.

5a) *N*-methoxy-2-methylimidazo[1,2-*a*]pyridine-3-carboxamide





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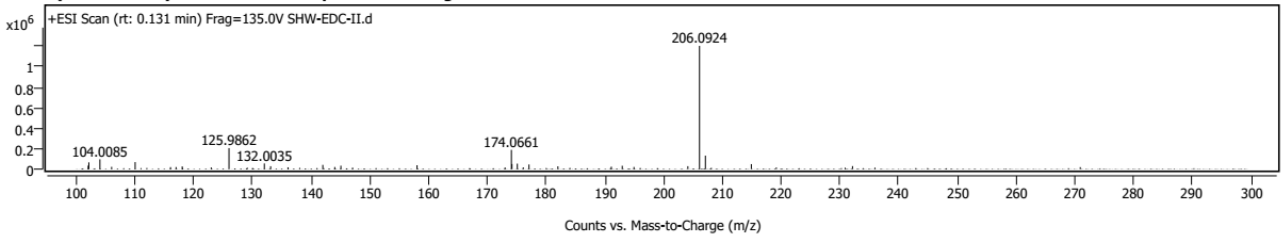

Spectrum Peaks

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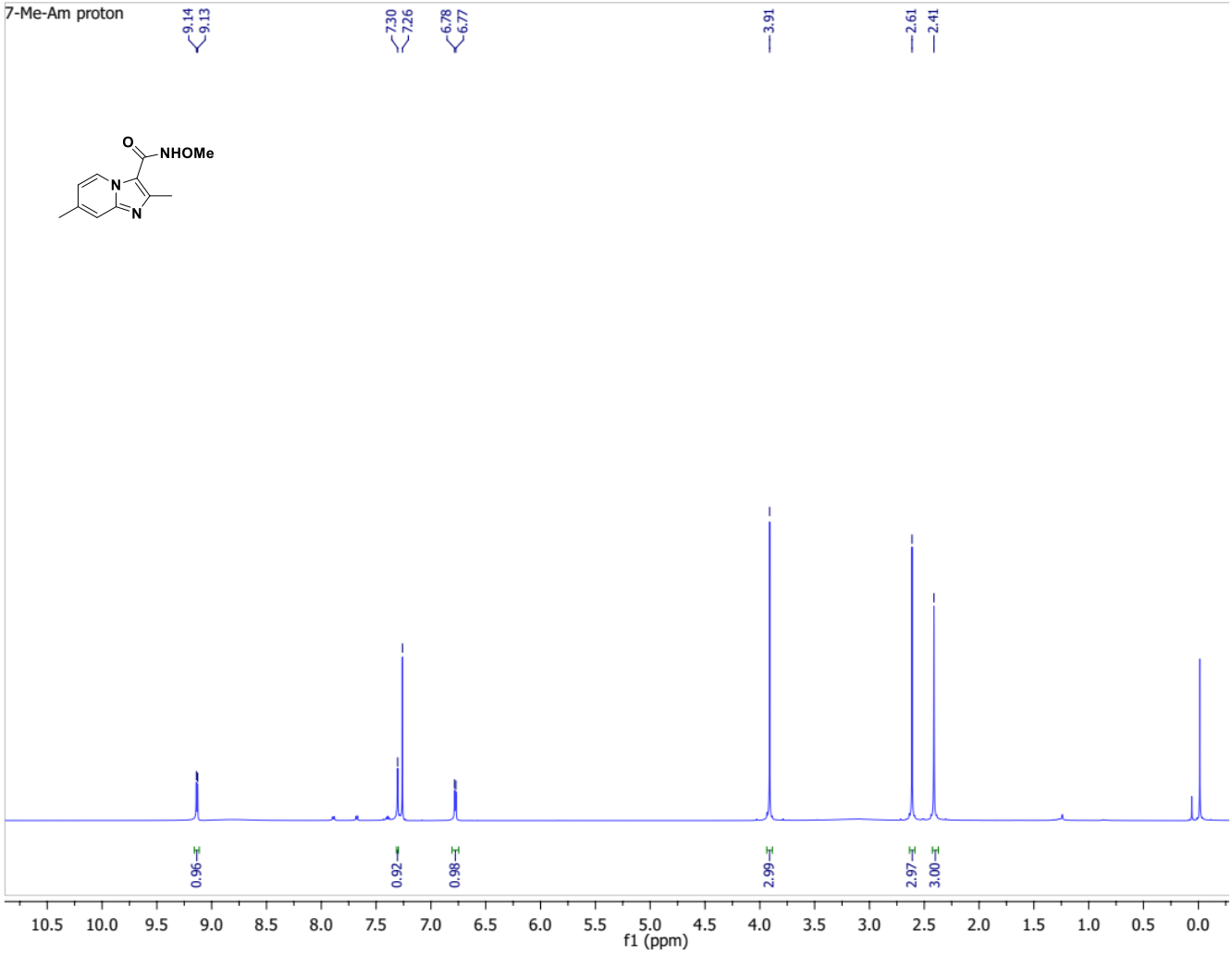
104.0085		95947	7.97					
110.0085		68328	5.68					
125.9862		205118	17.05					
132.0035		55292	4.59					
174.0661		187820	15.61					
174.1601		49569	4.12					
175.0735		53215	4.42					
206.0924	1	1203307	100.00					
207.0956	1	131407	10.92					

5b) *N*-methoxy-2,7-dimethylimidazo[1,2-*a*]pyridine-3-carboxamide



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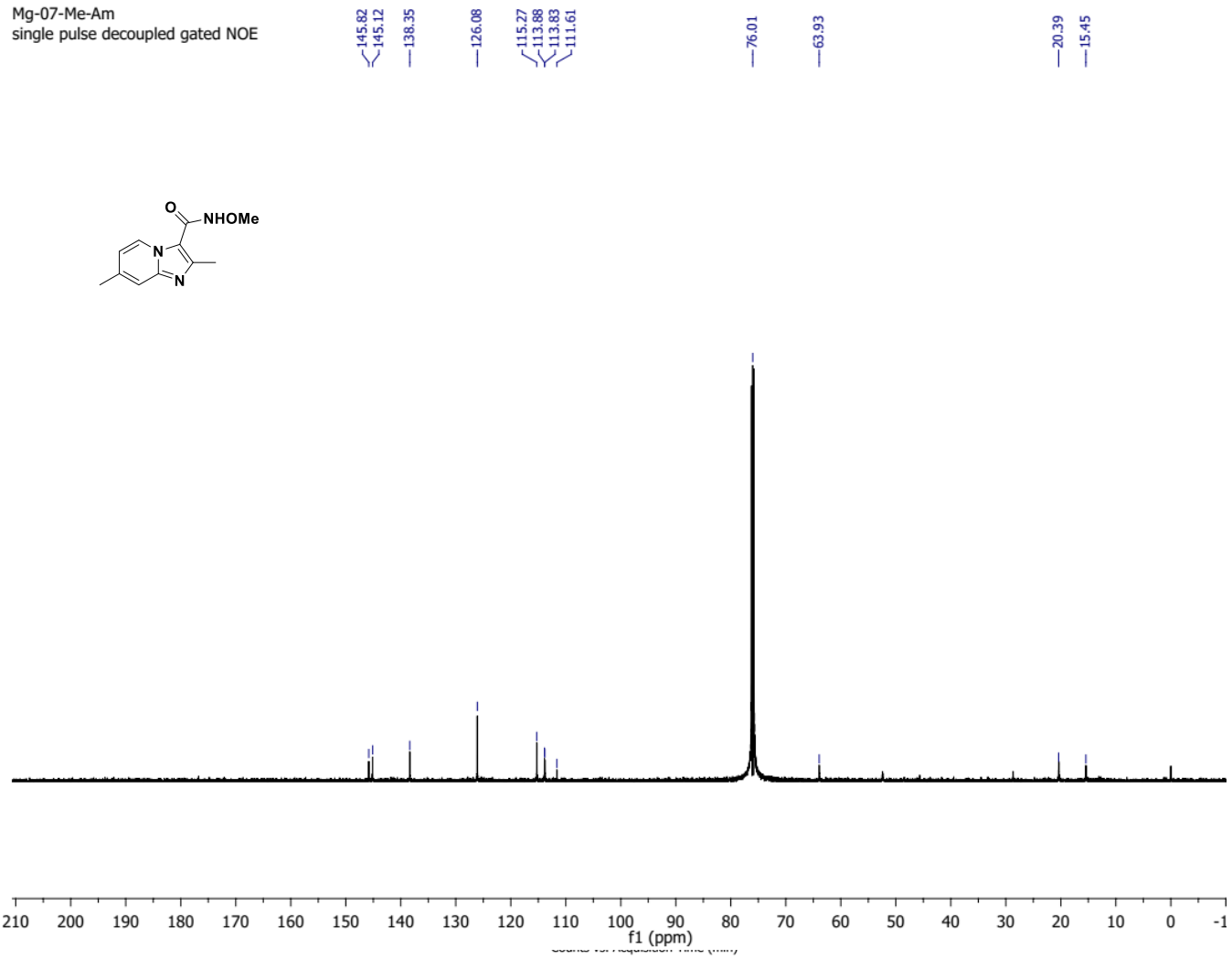

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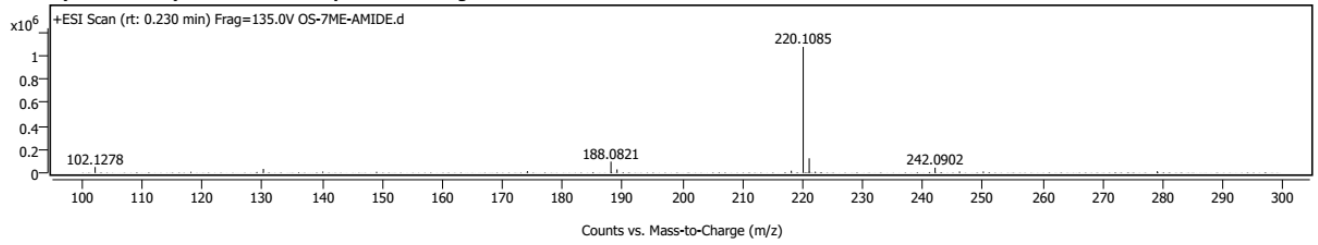

Spectrum Peaks

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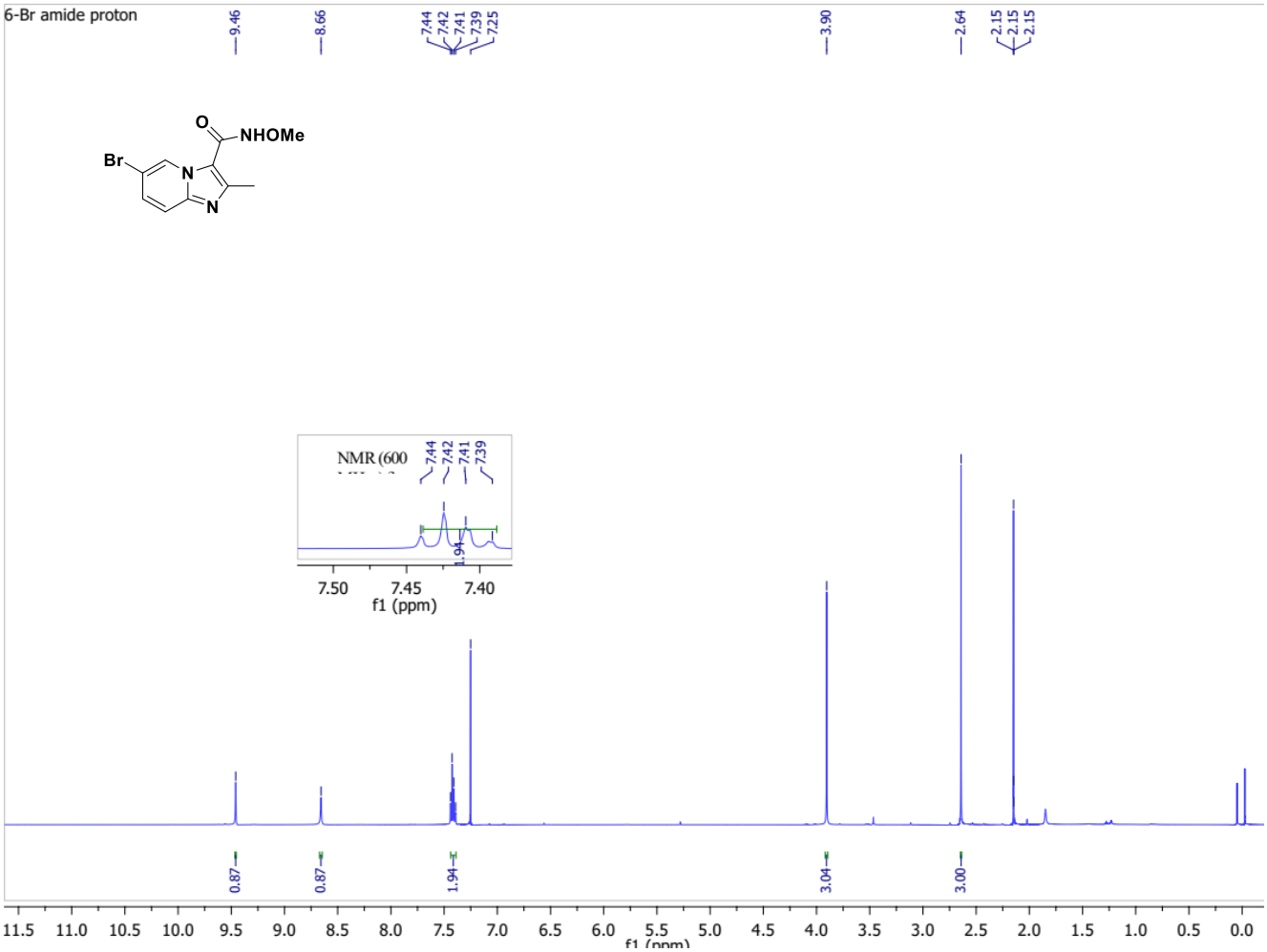
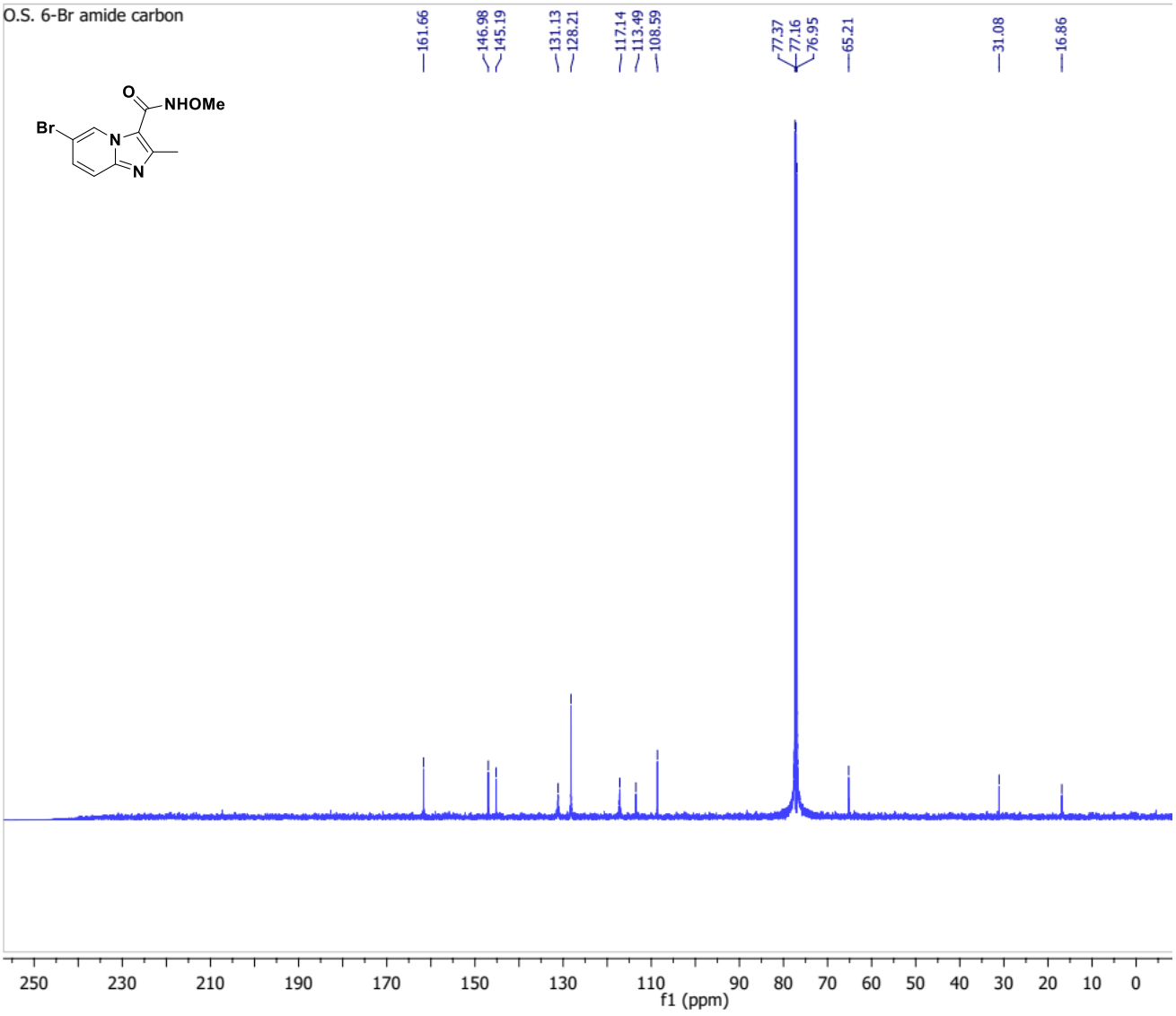
188.0821		95772	8.92					
220.1085	1	1074053	100.00					
221.1115	1	124028	11.55					
242.0902		43962	4.09					

5c) 6-Bromo-*N*-methoxy-2-methylimidazo[1,2-*a*]pyridine-3-carboxamide

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Br
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Peak Spec

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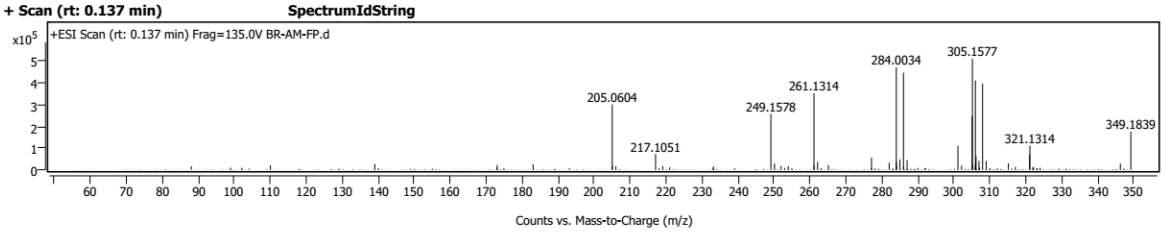

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261.1314		352846	68.95					
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284.0034	1	472490	92.33					
285.0066	1	47571	9.30					
286.0014	1	447436	87.43					
287.0046	1	44478	8.69					
301.1414		110513	21.60					
305.0762	1	246666	48.20					
305.1577	1	511740	100.00					
305.9854	1	411548	80.42					
306.0787	1	42252	8.26					
306.1611	1	64550	12.61					
306.9884	1	40984	8.01					
307.9834	1	397673	77.71					
321.0500		69291	13.54					
321.1314		110851	21.66					
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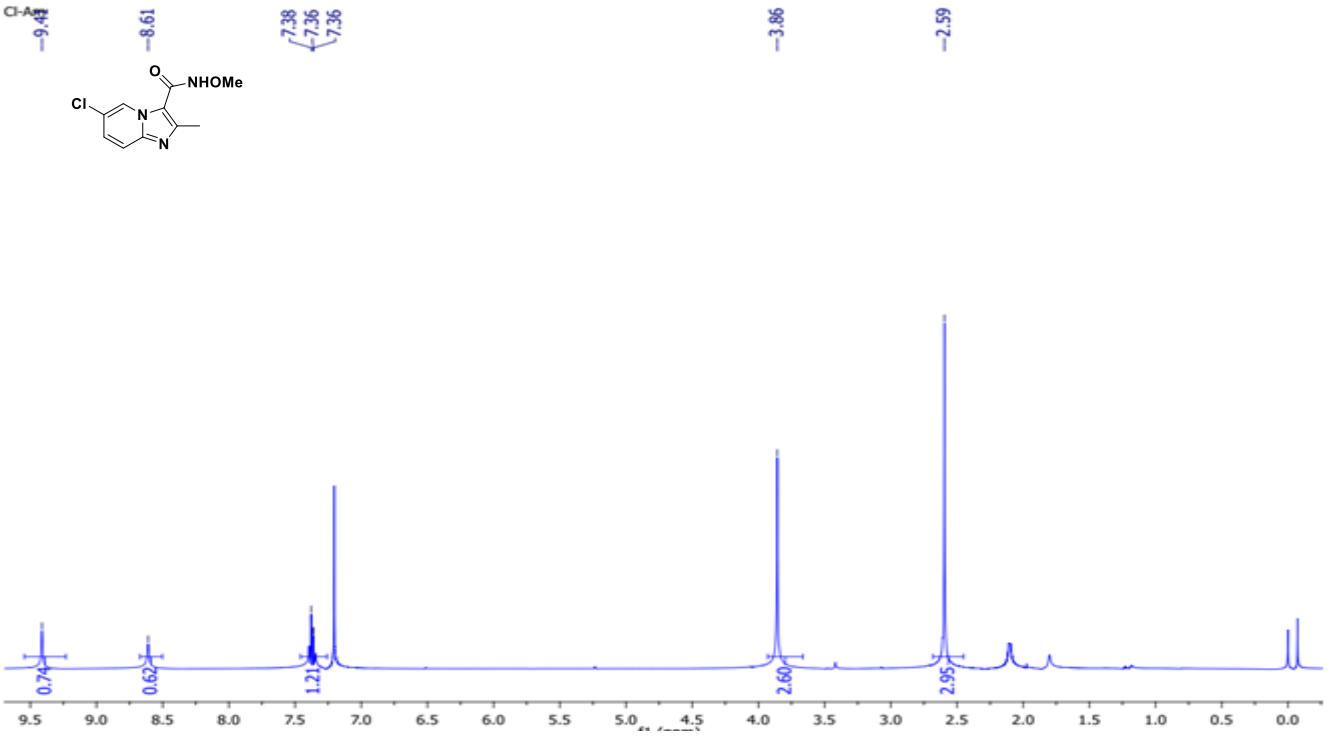
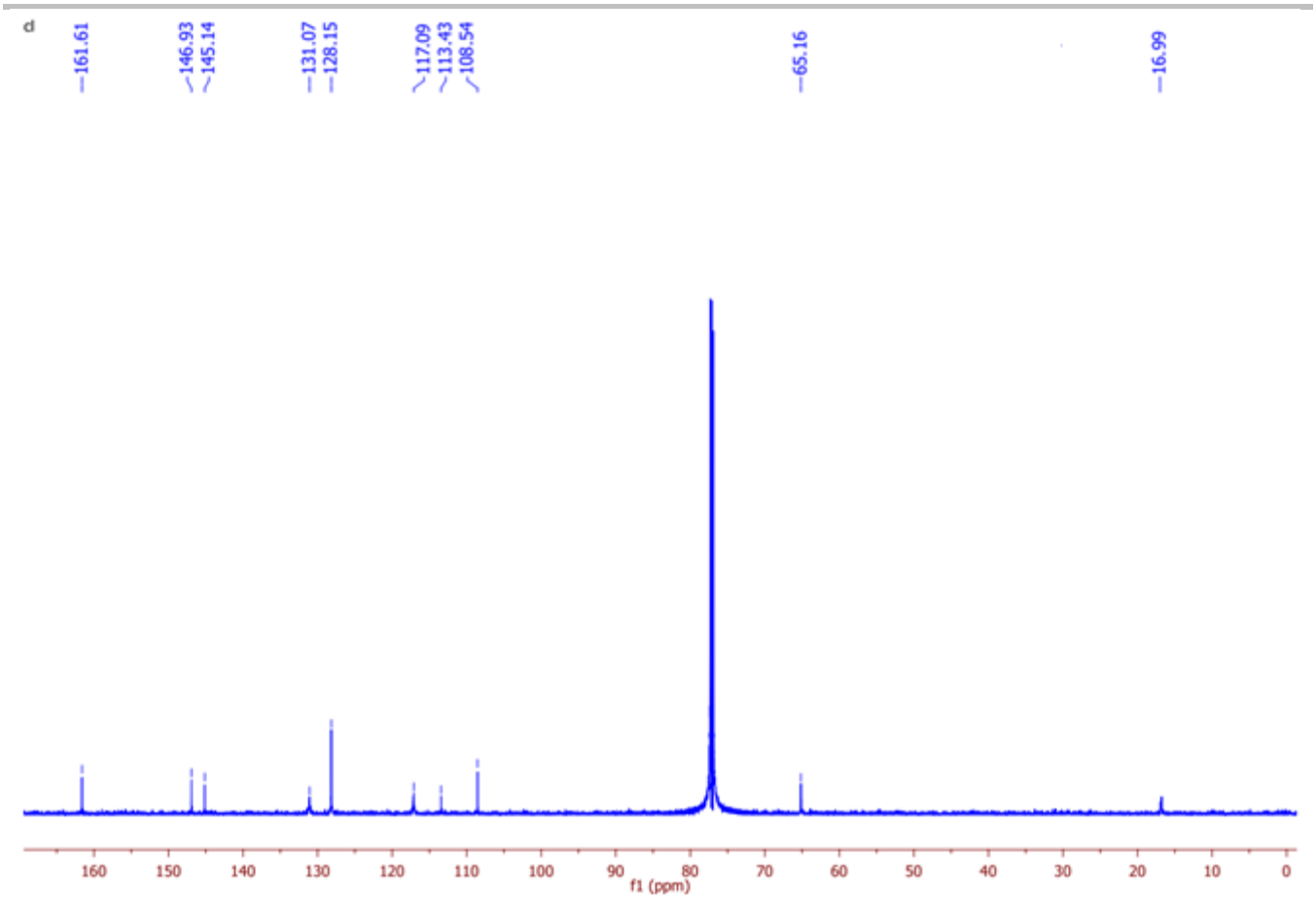
5d) 6-Chloro-*N*-methoxy-2-methylimidazo[1,2-*a*]pyridine-3-carboxamide

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90
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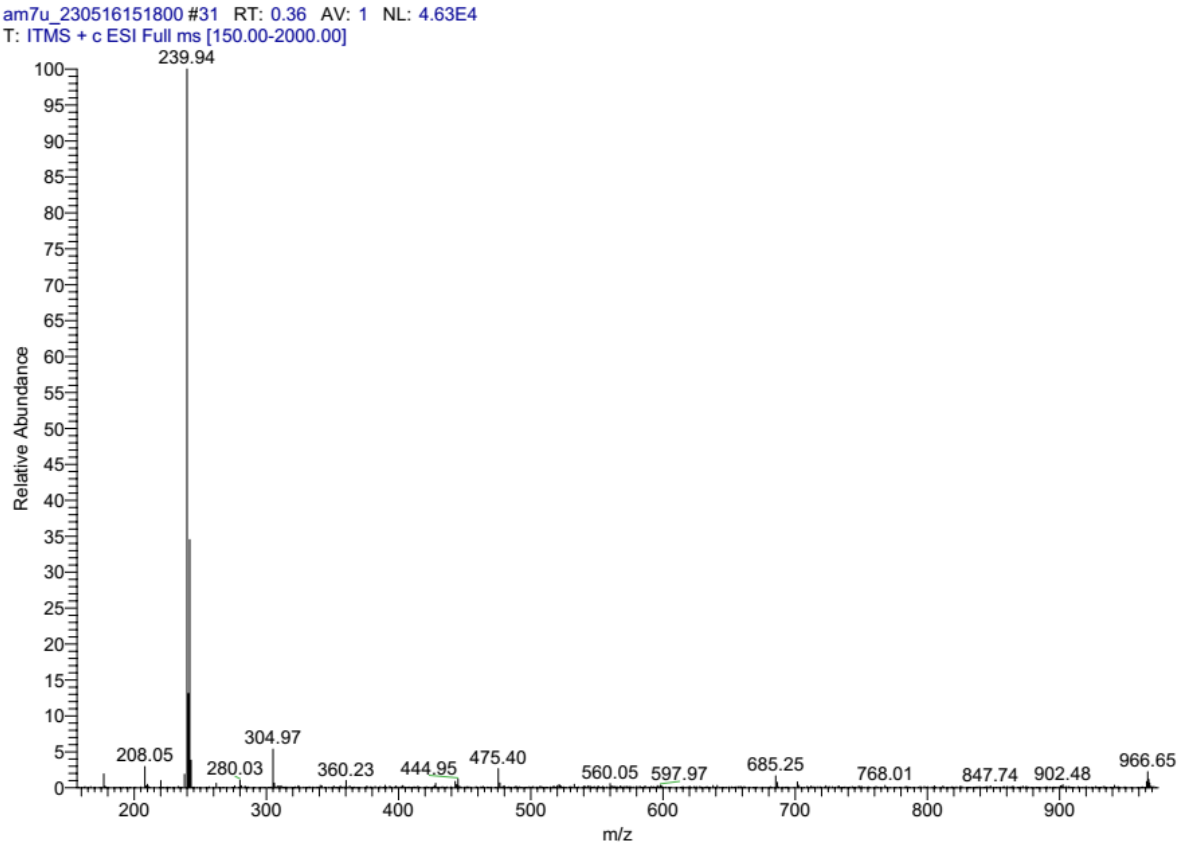
f1 (ppm)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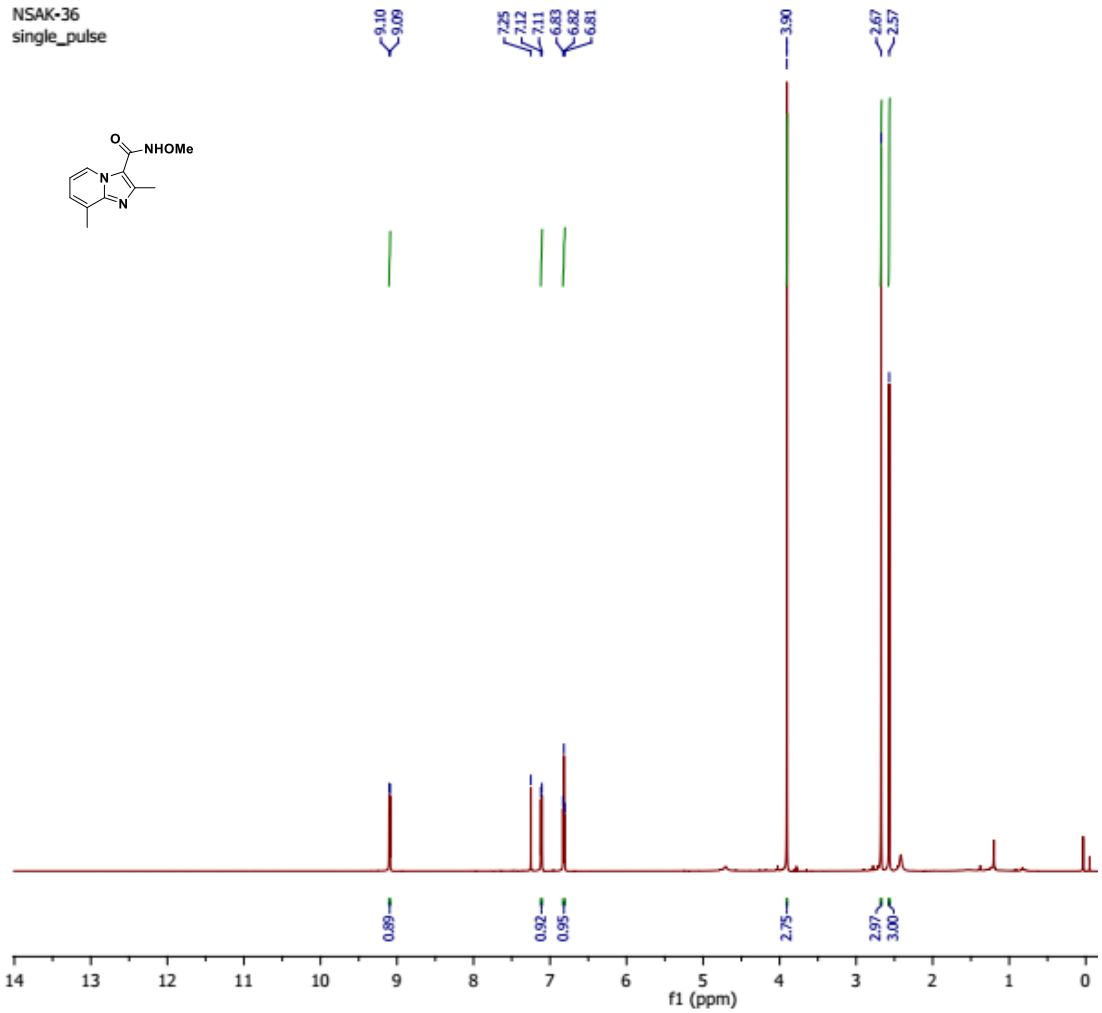
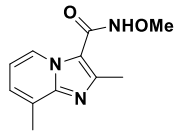
360.23
444.95
475.40
560.05
597.97
685.25
768.01
847.74
902.48
966.65
Relative Abundance
m/z

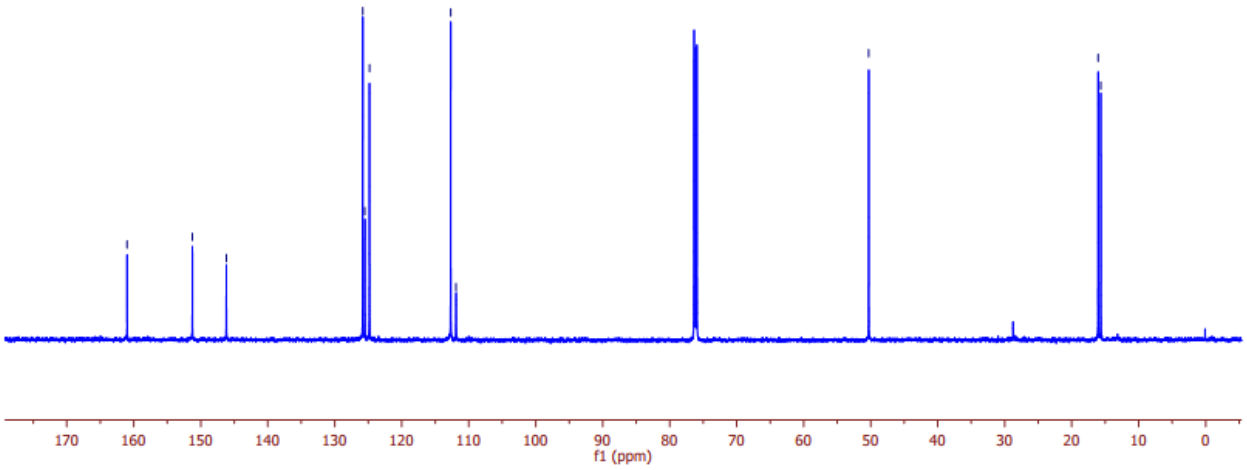
5e) *N*-methoxy-2,8-dimethylimidazo[1,2-*a*]pyridine-3-carboxamide



8-methyl amide

161.00 151.26 146.19 125.82 125.51 124.81 112.70 111.89 50.30 16.05 15.65





SpectrumIdString

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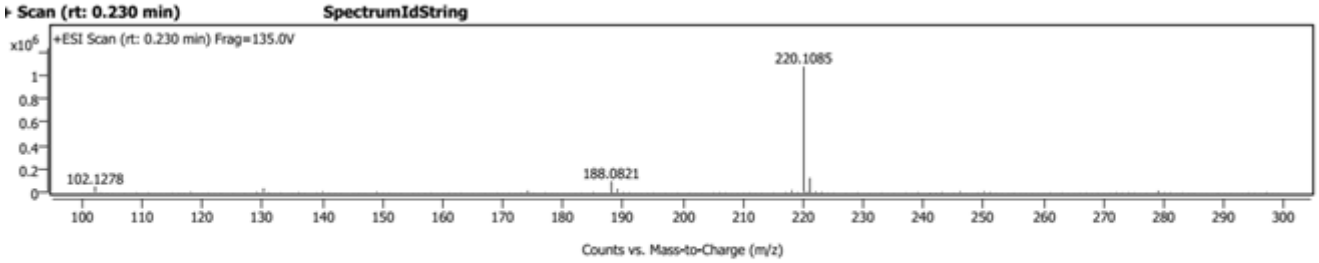
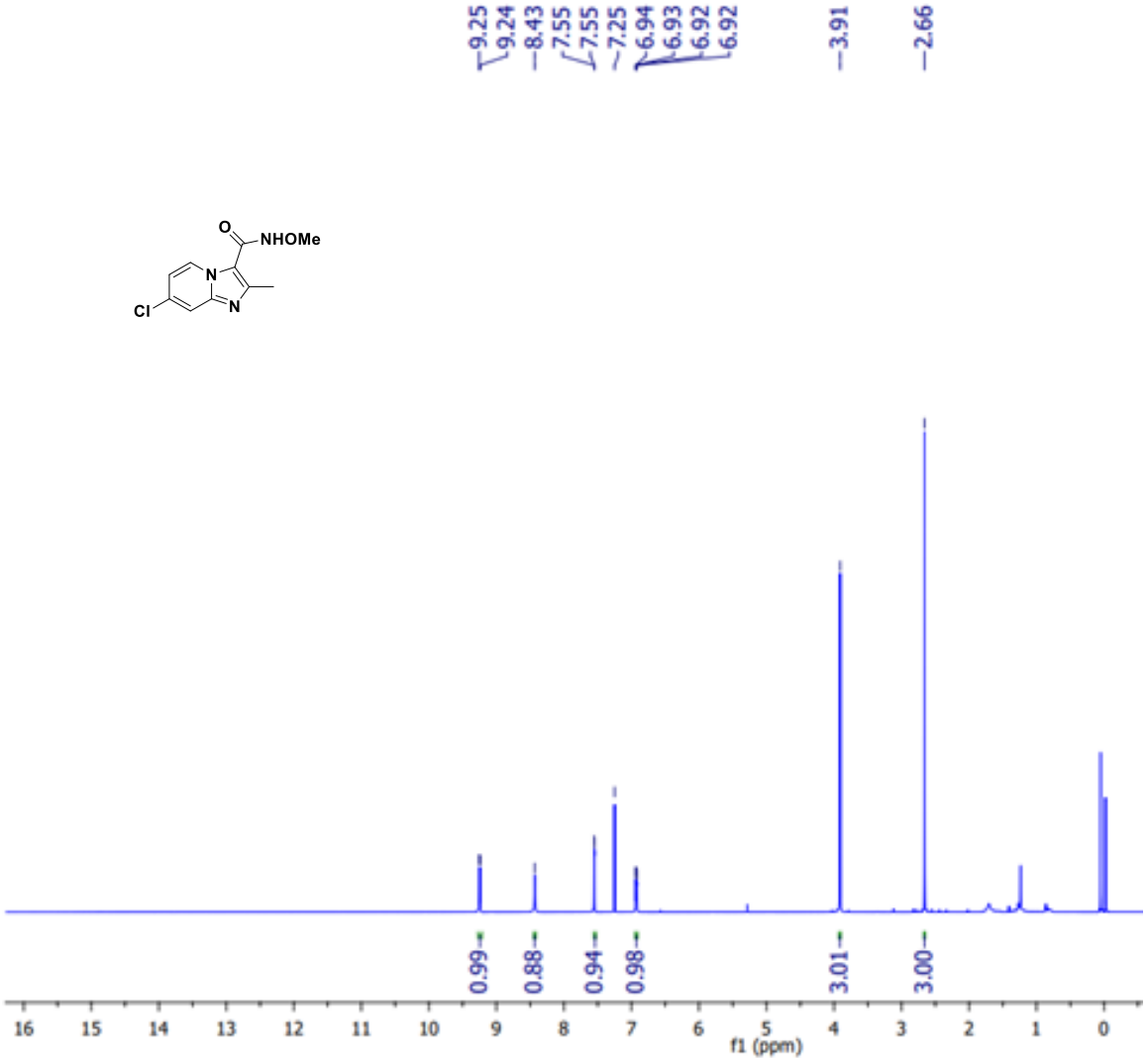
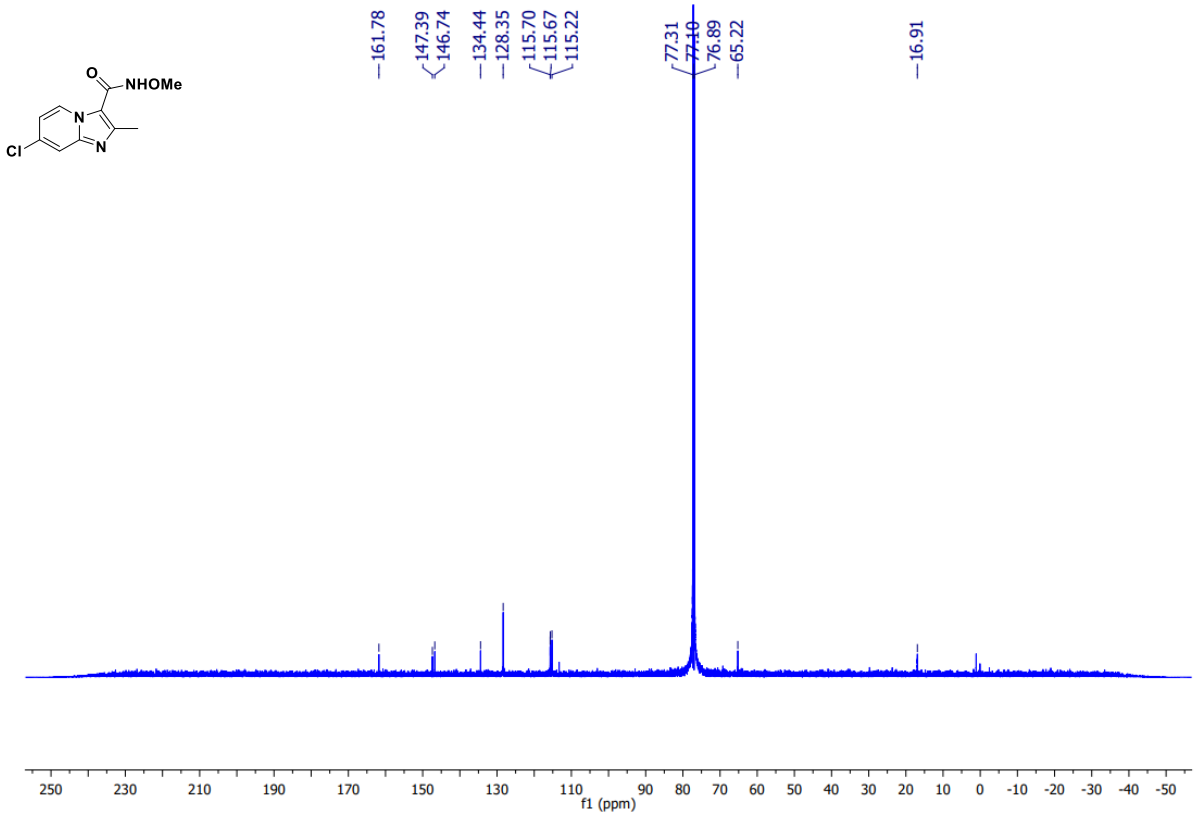


Spectrum Peaks

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
102.1278		49640	4.62					
188.0821		95772	8.92					
220.1085	1	1074053	100.00					
221.1115	1	124028	11.55					

5f) 7-chloro-N-methoxy-2-methylimidazo[1,2-*a*]pyridine-3-carboxamide





Peak Spec

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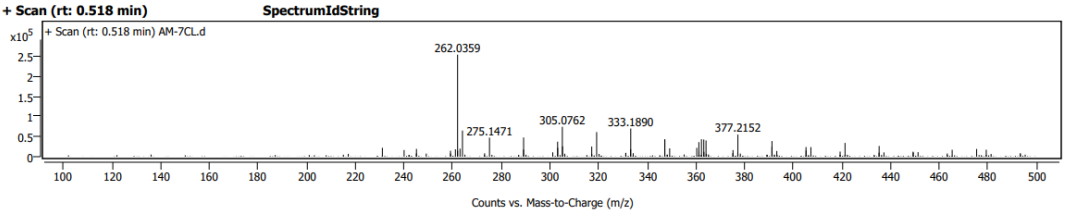
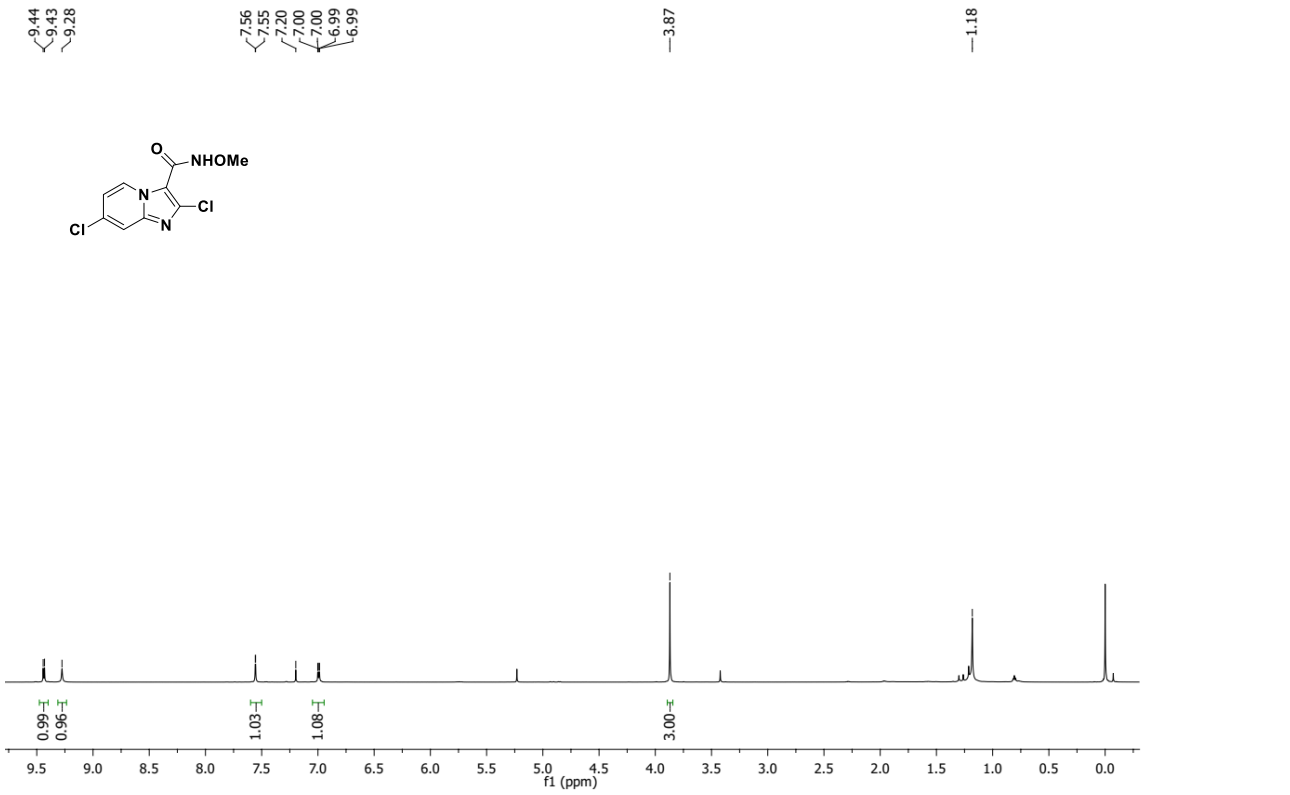


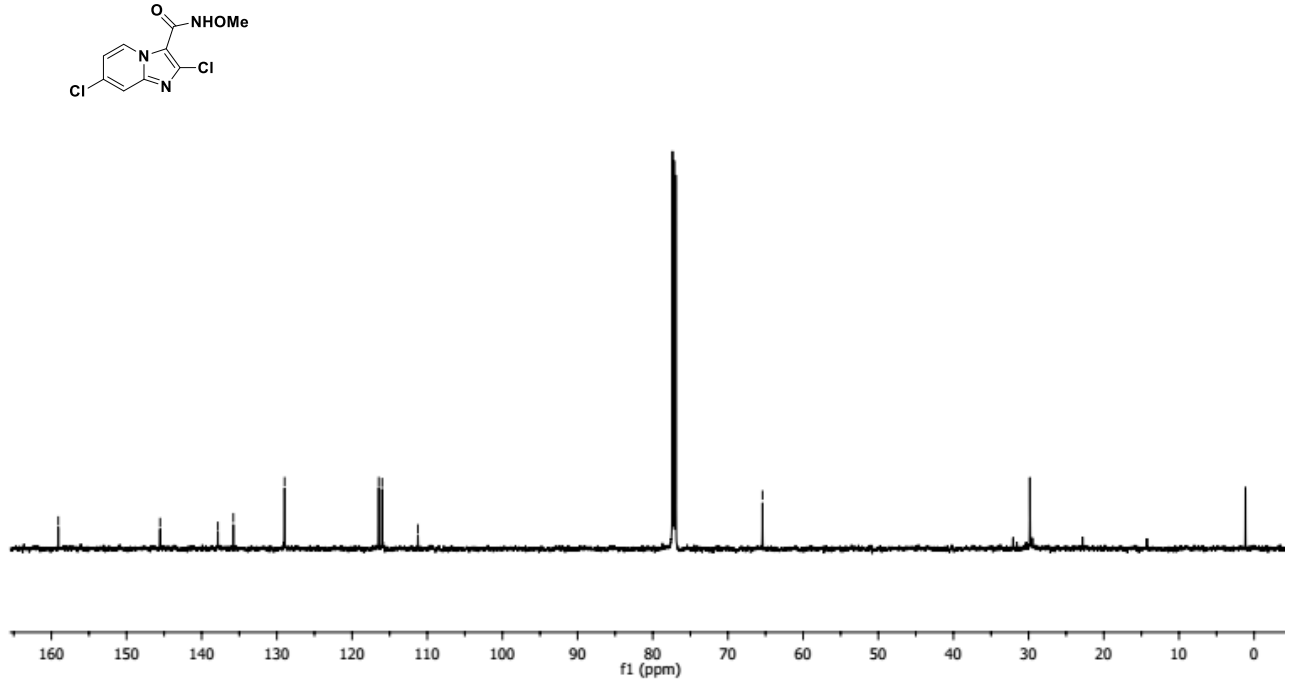
SpectrumIdString

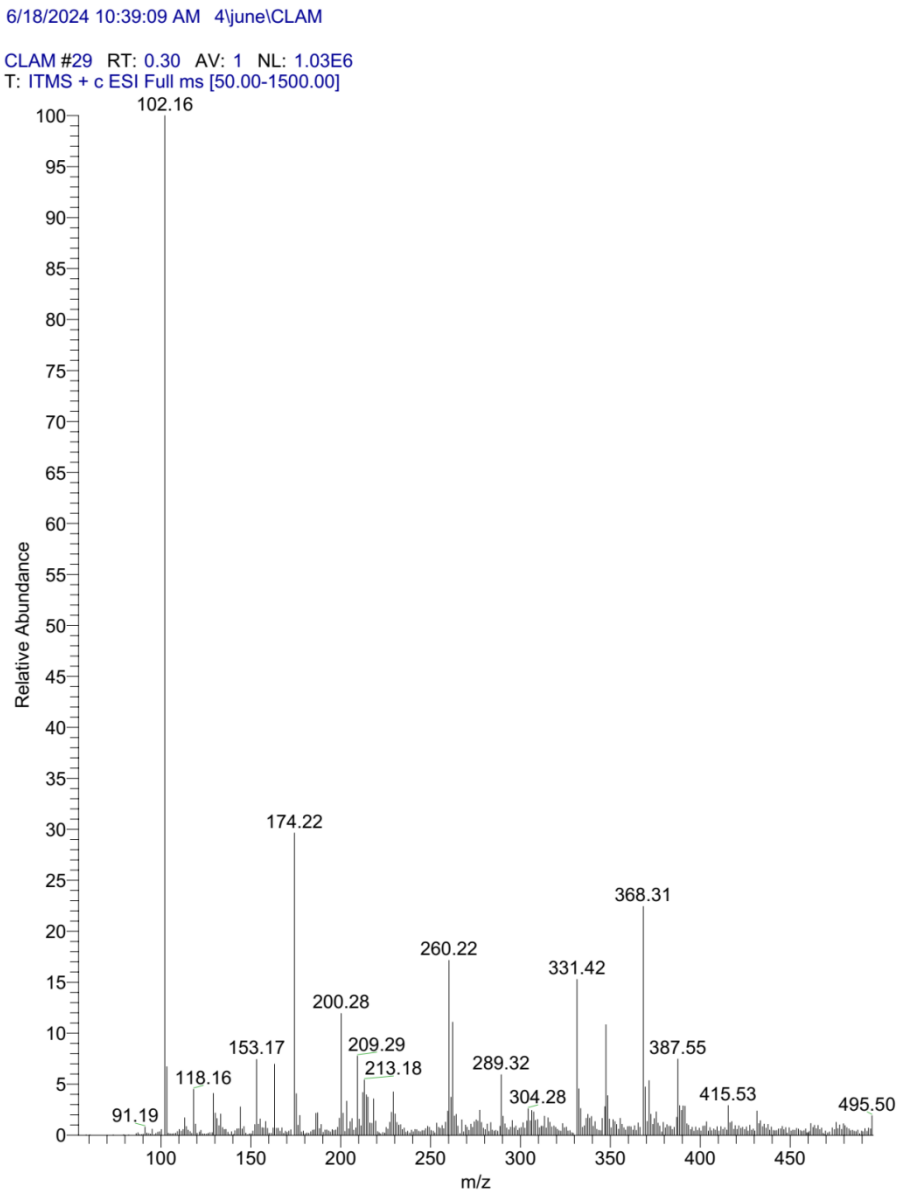
m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
262.0359		253368	100.00					
264.0330		64042	25.28					
275.1471		47523	18.76					
289.1628		47892	18.90					
305.0762		73421	28.98					
319.1732		60243	23.78					
333.1890		69084	27.27					
347.1683		43393	17.13					
362.2421		43581	17.20					
377.2152		55204	21.79					

MassHunter Qual 10.0
(End of Report)

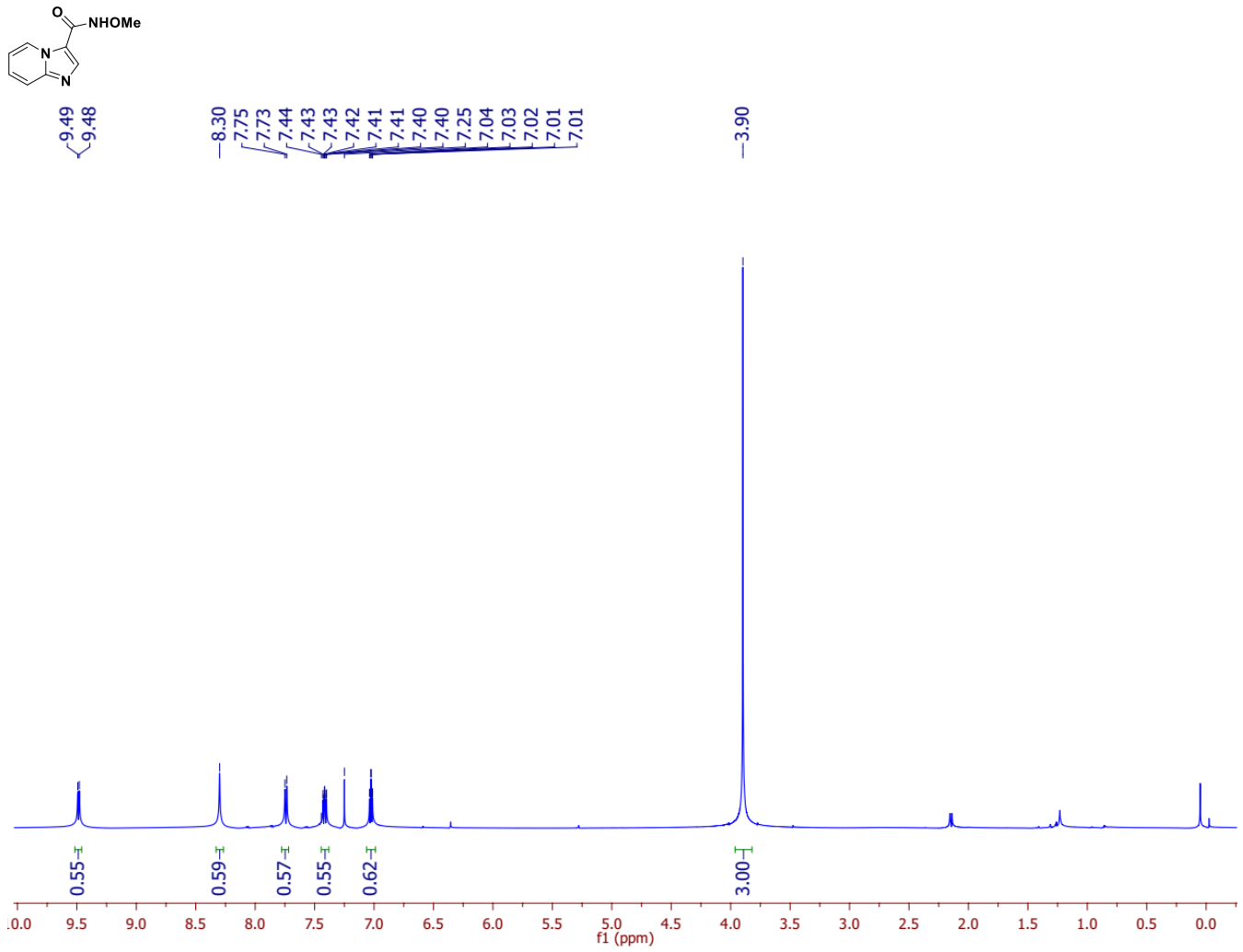
8) 2, 7-dichloro-*N*-methoxyimidazo[1,2-*a*]pyridine-3-carboxamide

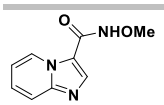


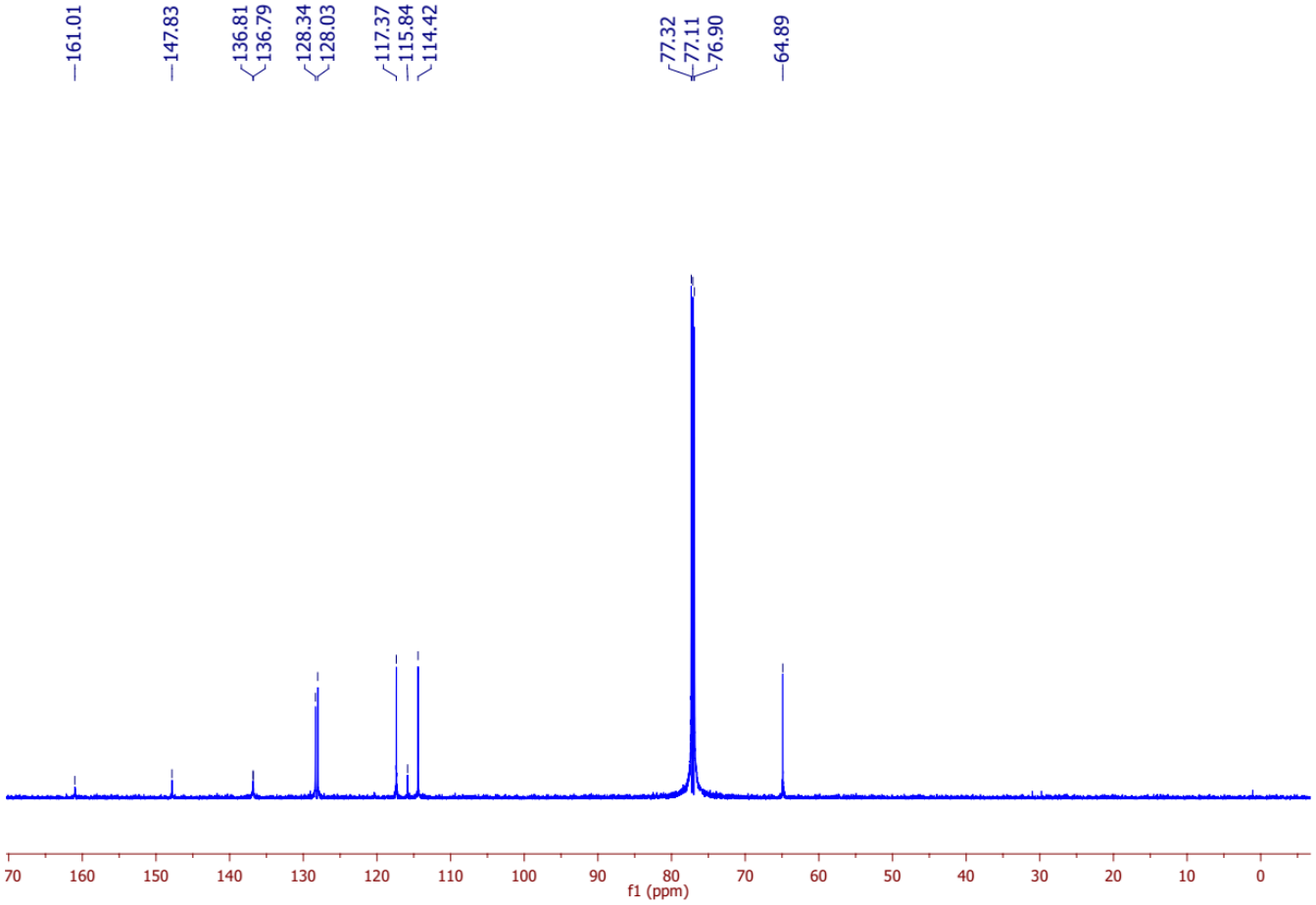



6/18/2024 10:39:09 AM 4\june\CLAM
CLAM #29 RT: 0.30 AV: 1 NL: 1.03E6
T: ITMS + c ESI Full ms [50.00-1500.00]
Relative Abundance
m/z
102.16
174.22
368.31
260.22
331.42
200.28
153.17
209.29
213.18
289.32
387.55
118.16
304.28
415.53
91.19
495.50

9) *N*-methoxyimidazo[1,2-*a*]pyridine-3-carboxamide

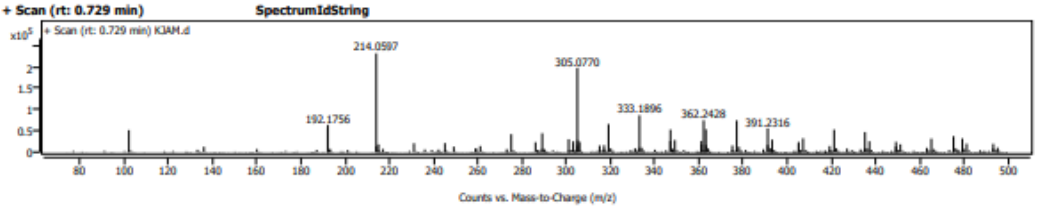






Peak Spec

+ Scan (rt: 0.729 min) **SpectrumIdString**



SpectrumIdString

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
192.0776		57953	25.05					
192.1756		64062	27.69					
214.0597		231390	100.00					
305.0770		197297	85.27					
319.1741		65760	28.42					
333.1896		86472	37.37					
362.2428		74475	32.19					
363.2003		53493	23.12					
377.2162		74341	32.13					
391.2316		55869	24.15					

MassHunter Qual 10.0
(End of Report)

2.5 Additional information (Trial reactions)

This compound is not a part of this work. This is shown only to exhibit that C-5 arylation does not occurs in 2-arylimidazo[1,2-*a*]pyridine -3-carboxamide.

Figure S1. Scanned copies of ^{1}H NMR for C-2′ arylated products.

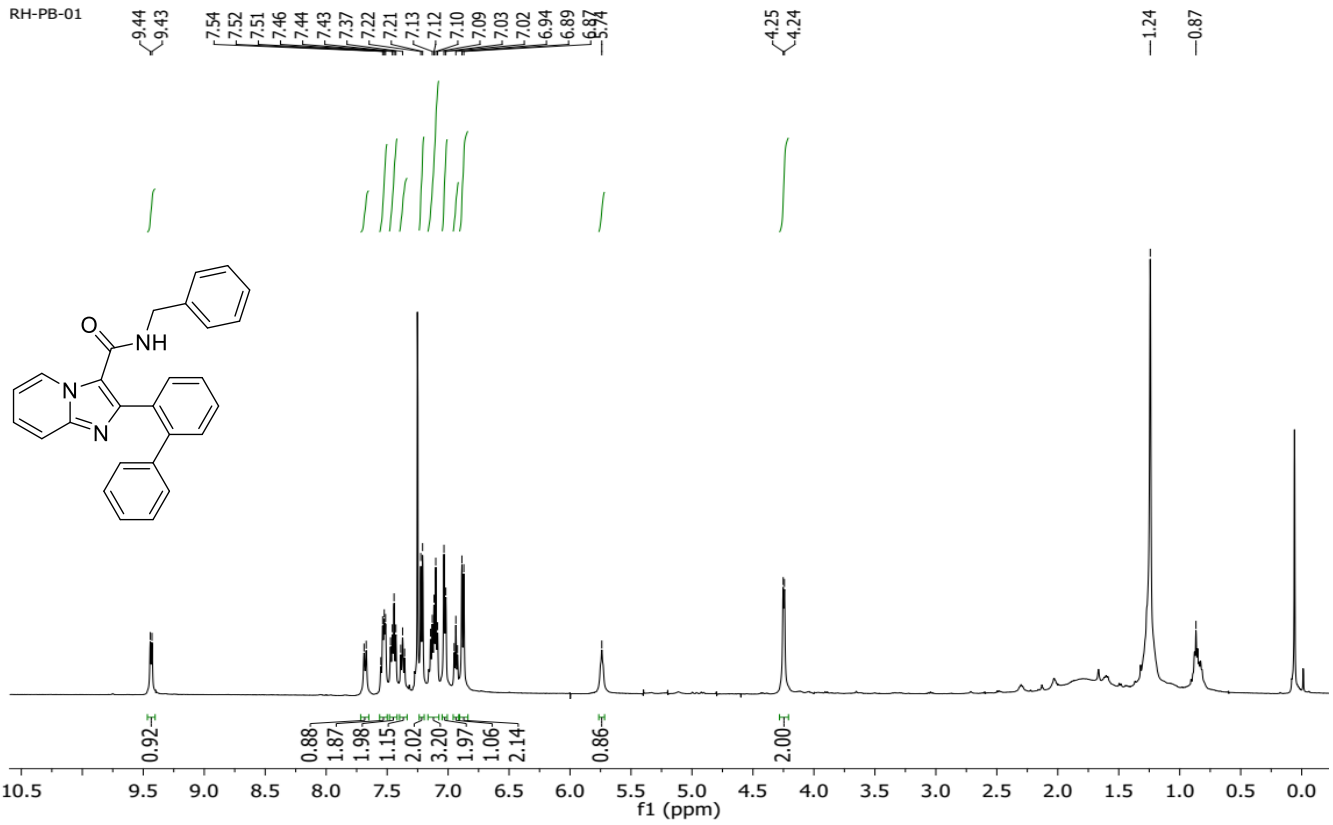
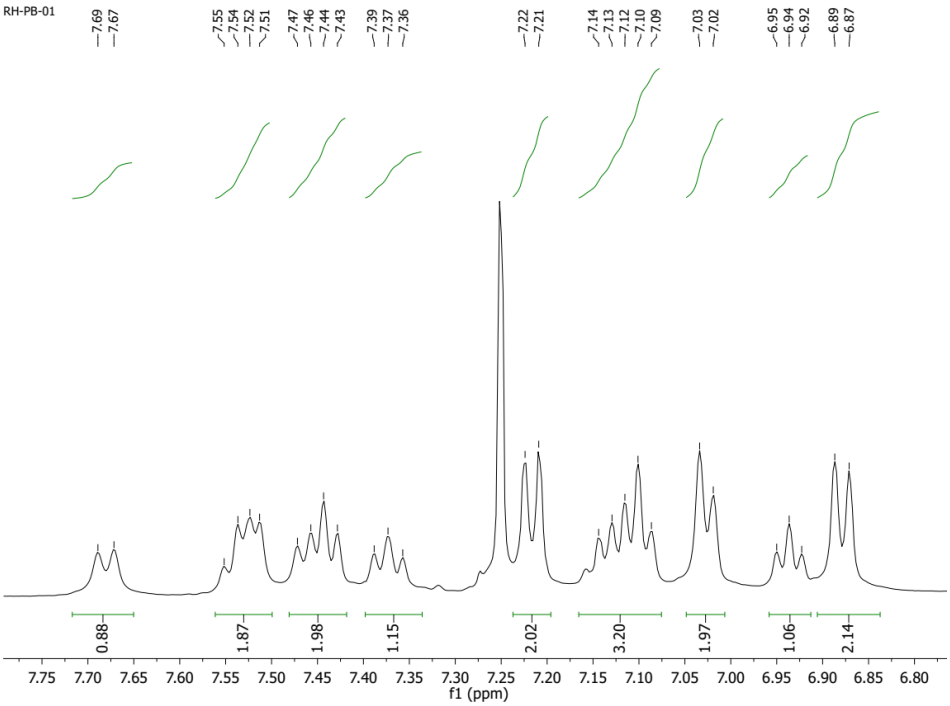


Figure S2. Expanded aromatic region.



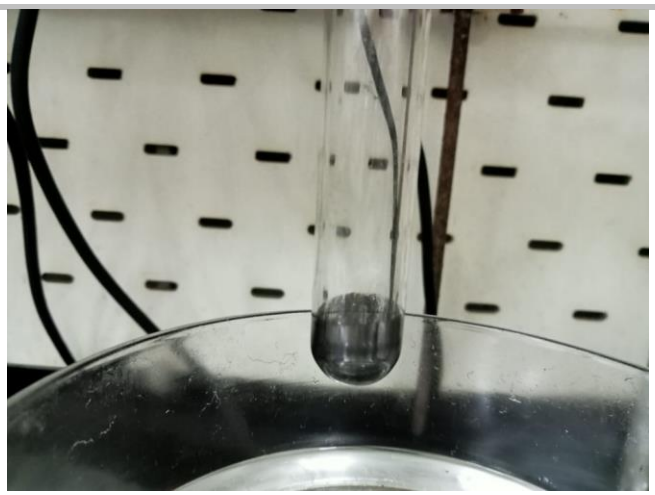
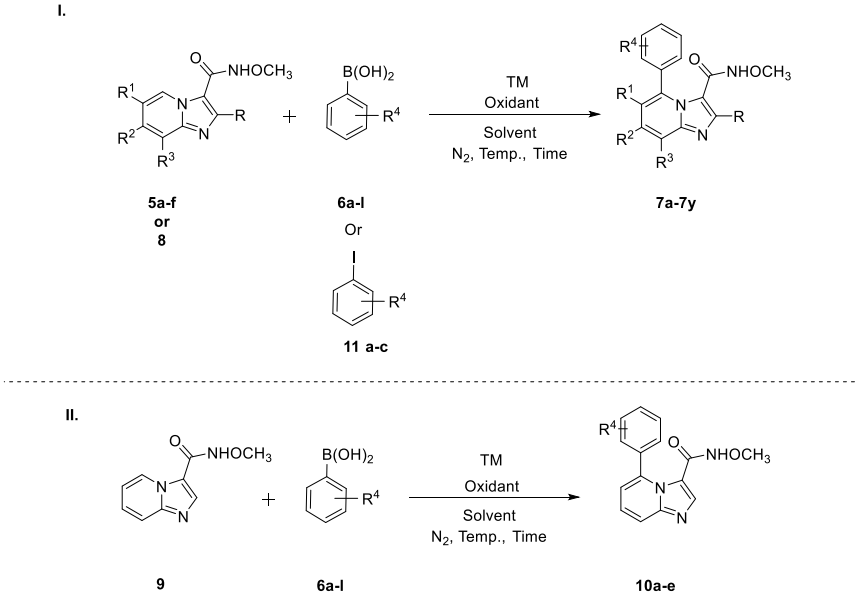


Figure S3. Image of reaction tube oncompletion of reaction with the formation of Ag deposit on the tube.

2.6 Screening for reaction conditions for the synthesis of C-5 arylated 2-methylimidazo[1,2-*a*]pyridine-3-carboxamide:



Scheme S2. Optimization for reaction conditions.

Table S2. Optimization table for screening of catalysts .

Entry	Catalyst (3 mol%)	Temperature	Time	Yield*
1.	$[RhCp^*Cl_2]_2$	80 ˚ C	12 h	74
2.	Pd $(OAc)_2$	80 ˚C	12 h	NR
3.	$[Ru(p\text{-cyemene})Cl_2]_2$	80 ˚C	12 h	NR
4.	$[Rh(cod)Cl]_2$	80 ˚C	12 h	NR
5.	$[IrCp^*Cl_2]_2$	80 ˚C	12 h	46

Reagents and conditions: 2-methylimidazo[1,2-*a*]pyridine-3-carboxamide **5a** (1 equiv.), phenylboronic acid **6a** (1.2 equiv.) in the presence of silver oxide (4 equiv.) anhydrous MeOH (2 mL) at 80 ˚C (oil bath) for 12 h, nitrogen atmosphere. NR = No reaction.*Isolated yeids.

Table S3. Optimization table for screening oxidants.

Entry	Catalyst (3 mol %)	Oxidant (4 equiv.)	Temperature	Time	Yield*
1	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2$	80 ° C	12 h	10
2	$[RhCp^*Cl_2]_2$	$AgSbF_6$	80 °C	12 h	Traces
3	$[RhCp^*Cl_2]_2$	Ag_2O	80 °C	12 h	74
4	$[RhCp^*Cl_2]_2$	AgOAc	80 ° C	12 h	Traces
5	$[RhCp^*Cl_2]_2$	$K_2S_2O_8$	80 °C	12 h	NR
6	$[RhCp^*Cl_2]_2$	-	80 °C	12 h	NR

Reagents and conditions: 2-methylimidazo[1,2-*a*]pyridine-3-carboxamide **5a** (1 equiv.), phenylboronic acid **6a** (1.2 equiv.) $[RhCp^*Cl_2]_2$ (3 mol%) in anhydrous MeOH (2 mL) at 80 °C (oil bath) for 12 h nitrogen atmosphere. NR = No reaction, *Isolated yeids.

Table S4. Optimization table for screening bases.

Entry	Catalyst (3 mol%)	Oxidant (4 equiv.)	Temperature	Time	Base (2 equiv.)	Yield*
1	$[RhCp^*Cl_2]_2$	Ag_2O	80 ° C	12 h	AgOAc	74
2	$[RhCp^*Cl_2]_2$	Ag_2O	80 °C	12 h	CsOAc	NR
3	$[RhCp^*Cl_2]_2$	Ag_2O (2 equiv.)	80 °C	12 h	AgOAc	53%
4	$[RhCp^*Cl_2]_2$	Ag_2O (3 equiv.)	80 °C	12 h	AgOAc (1 equiv.)	49%

Reagents and conditions: 2-methylimidazo[1,2-*a*]pyridine-3-carboxamide **5a** (1 equiv.), phenylboronic acid **6a** (1.2 equiv.) $[RhCp^*Cl_2]_2$ (3 mol%) in anhydrous MeOH (2 mL) at 80 °C (oil bath) for 12 h nitrogen atmosphere. NR = No reaction. *Isolated yeids.

Table S5: Optimization table for screening of solvents.

Entry	Catalyst (3 mol%)	Oxidant (4 equiv.)	Temperature	Time	Solvent	Yield*
1	$[RhCp^*Cl_2]_2$	Ag_2O	80 ° C	12 h	MeOH	74
2	$[RhCp^*Cl_2]_2$	Ag_2O	80 °C	12 h	ACN	Traces
3	$[RhCp^*Cl_2]_2$	Ag_2O	80 ° C	12 h	DCE	NR
4	$[RhCp^*Cl_2]_2$	Ag_2O	80 °C	12 h	t-BuOH	Traces

Reagents and conditions: 2-methylimidazo[1,2-*a*]pyridine-3-carboxamide **5a** (1 equiv.), phenylboronic acid **6a** (1.2 equiv.) $[RhCp^*Cl_2]_2$ (3 mol%), Ag_2O (4 equiv.) at 80 °C (oil bath) for 12 h nitrogen atmosphere. NR = No reaction. *Isolated yeids.

Table S6: Screening of reaction at different temperatur.

Entry	Catalyst (3 mol%)	Oxidant (4 equiv.)	Time	Solvent	Temperature in °C	Yield*

1	$[RhCp^*Cl_2]_2$	Ag_2O	12 h	MeOH	RT	5%
2	$[RhCp^*Cl_2]_2$	Ag_2O	12 h	MeOH	60	58%
3	$[RhCp^*Cl_2]_2$	Ag_2O	12 h	MeOH	80	74%
4	$[RhCp^*Cl_2]_2$	Ag_2O	12 h	MeOH	100	69%

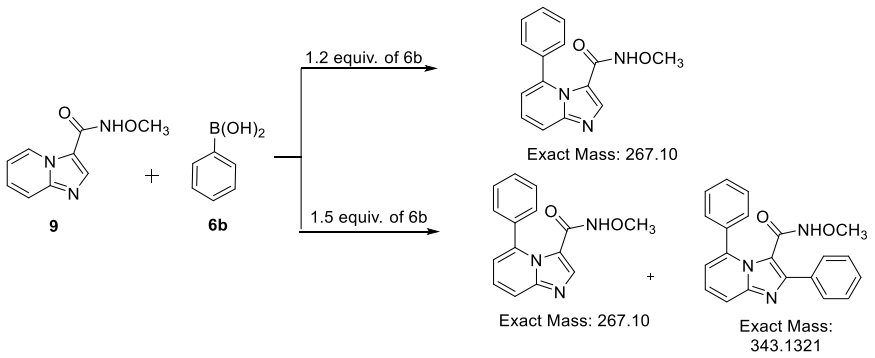
Reagents and conditions: 2-methylimidazo[1,2-*a*]pyridine-3-carboxamide **5a** (1 equiv.), phenylboronic acid **6a** (1.2 equiv.) $[RhCp^*Cl_2]_2$ (3 mol%), Ag_2O (4 equiv.) in anhydrous MeOH (2 mL) at 80 °C (oil bath) for 12 h nitrogen atmosphere. NR = No reaction. *Isolated yeids.

Table S7: Screening of reaction at different catalytic load.

Entry	Catalyst	Oxidant (4 equiv.)	Time	Temperature in ˚C	Solvent	Amount of Rhodium catalyst (mol%)	Yield*
1	$[RhCp^*Cl_2]_2$	Ag_2O	12 h	80	MeOH	2	68%
2	$[RhCp^*Cl_2]_2$	Ag_2O	12 h	80	MeOH	3	74%
3	$[RhCp^*Cl_2]_2$	Ag_2O	12 h	80	MeOH	5	63%

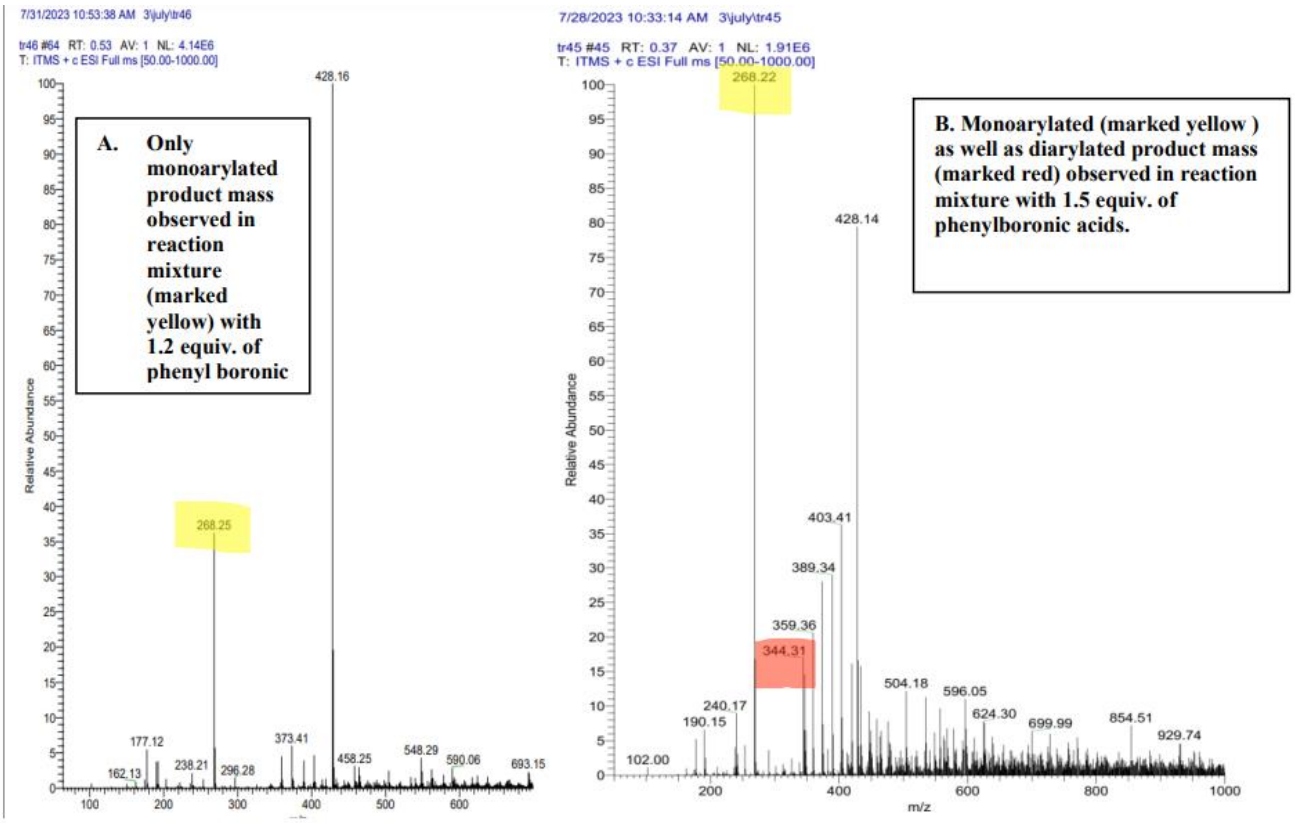
Reagents and conditions: 2-methylimidazo[1,2-*a*]pyridine-3-carboxamide **5a** (1 equiv.), phenylboronic acid **6a** (1.2 equiv.) $[RhCp^*Cl_2]_2$, Ag_2O (4 equiv.) in anhydrous MeOH (2 mL) at 80 ˚C (oil bath) for 12 h nitrogen atmosphere. NR = No reaction. *Isolated yeids.

The regioselective C-5 arylation was achieved using the same reaction conditions even when the C-2 position is free i.e. unsubstituted. But if the equivalents of phenylboronic acid was increased from 1.2 equiv. to 1.5 equiv., diarylated product was also obtained as shown in Scheme S3 and Figure S5.

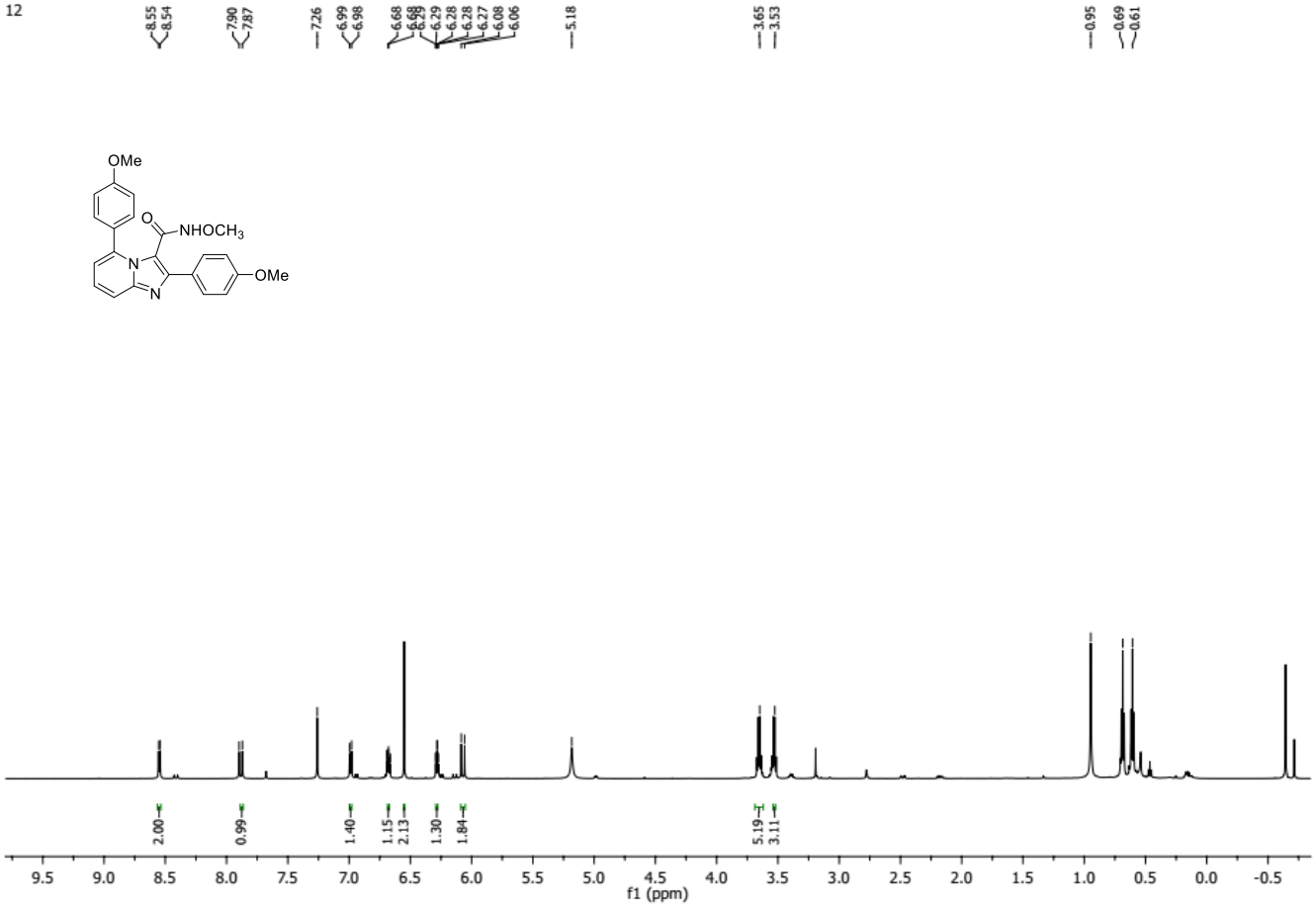


Scheme S3. Optimising euivalents of phenylboronic acids to get the monoarylated product exclusively. The optimised reaction conditions for C-2 free IMPC are imidazo[1,2-*a*]pyridine-3-carboxamide **9** (1

equiv.), phenylboronic acid **6a** (1.2 equiv.) [RhCp*Cl_2]$_2$, Ag_2O (4 equiv.) in anhydrous MeOH (2 mL) at 80 ˚C (oil bath) for 12 h nitrogen atmosphere.



12


8.55
8.54
7.90
7.87
7.26
6.99
6.98
6.68
6.29
6.28
6.27
6.08
6.06
5.18
3.65
3.53
0.95
0.69
0.61
OMe
O
NHOCH3
N
N
OMe
2.00
0.99
1.40
1.15
2.13
1.30
1.84
5.19
3.11
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
0.0
-0.5
f1 (ppm)

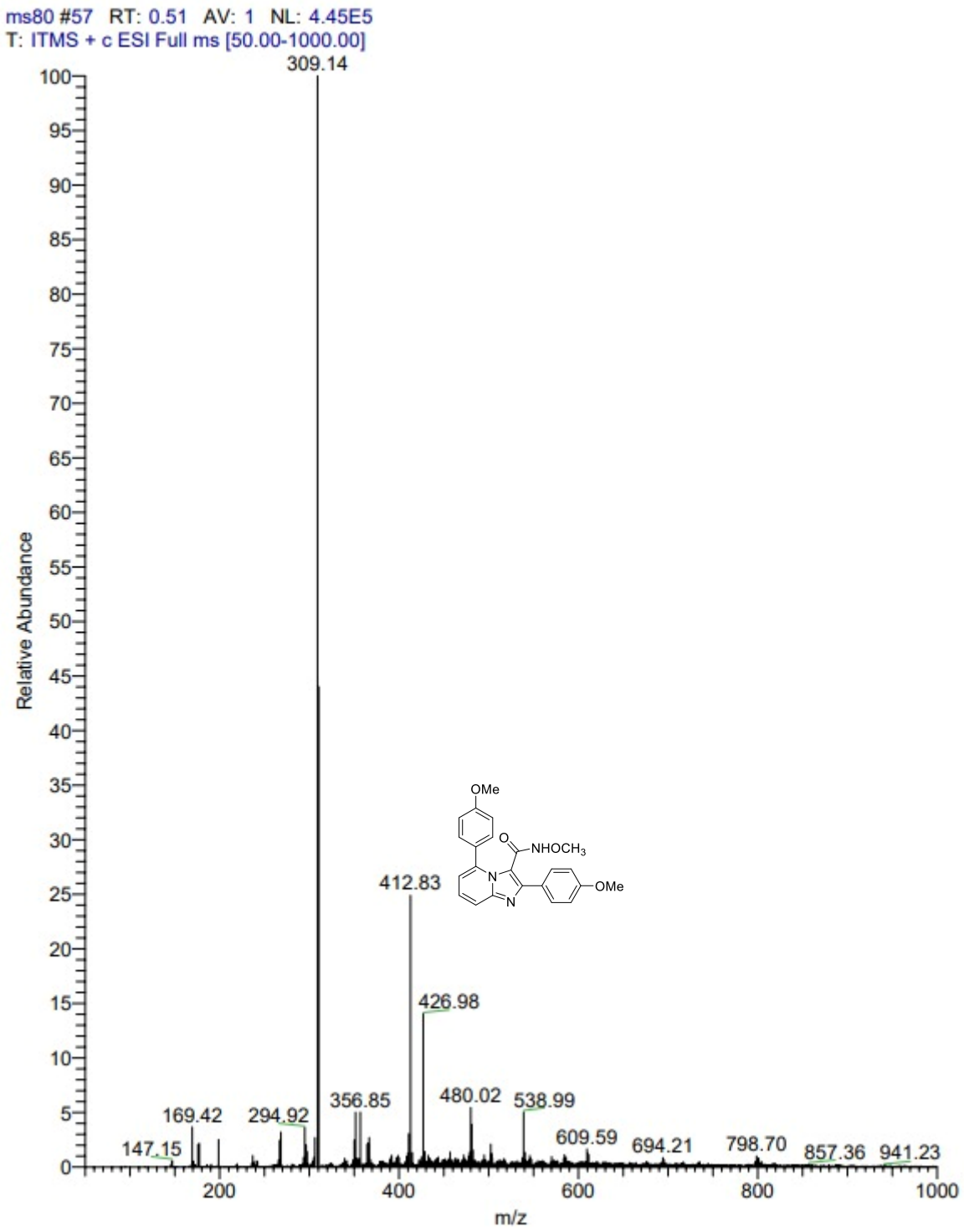
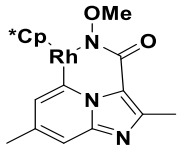
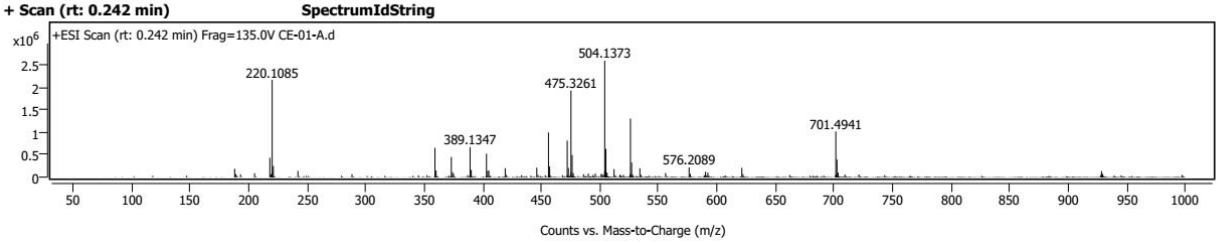


Figure S4 : Comparitive observation in the reaction mixture : **A.** 1.2 equiv. of phenylboronic acid – only monoarylated mass observed. **B.** 1.5 equiv. of phenylboronic acid and 4-methoxyphenylboronic acid – mono- as- well- as diarylated product mass observed (Mass highlighted yellow/red = [M=H]+ peak), 428.16 is the mass of rhodacycle formed. Also shown the HNMR of one of the diarylated derivative isolated.



Peak Spec

+ Scan (rt: 0.242 min) SpectrumIdString



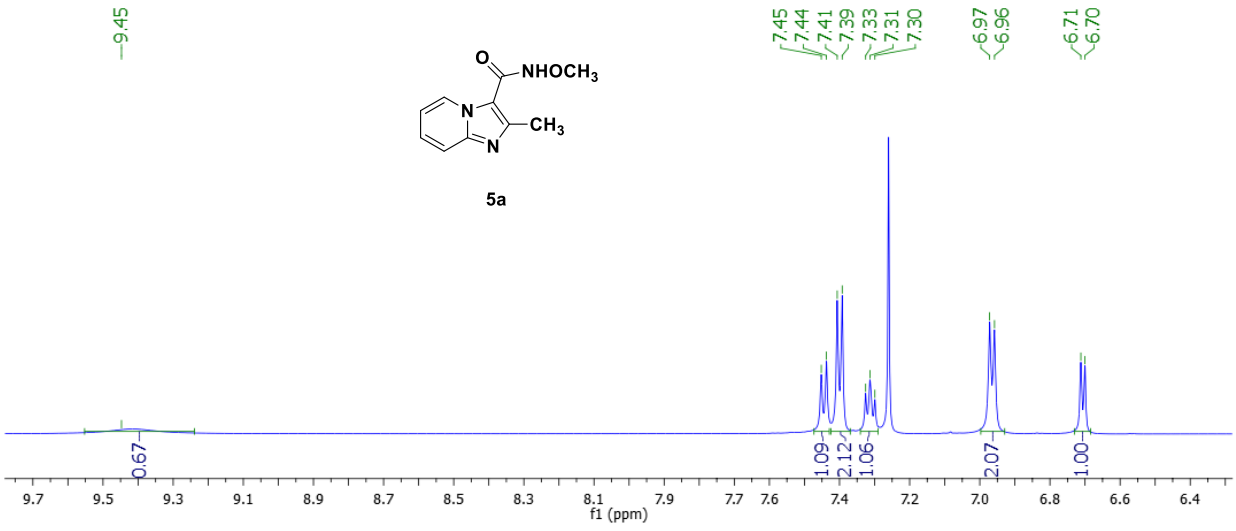
SpectrumIdString

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
218.1288		436322	16.71					
220.1085	1	2180233	83.49					
221.1114	1	249996	9.57					
359.1241		657067	25.16					
373.1397		452668	17.34					
389.1347		670984	25.70					
403.1503		526541	20.16					
446.1310		211129	8.09					
456.1155	1	1001348	38.35					
457.1184	1	239073	9.16					
472.1104		817800	31.32					
475.3261	1	1942537	74.39					
476.3288	1	495456	18.97					
504.1373	1	2611267	100.00					

Figure S5. Mass of the *in situ* generated 6-membered rhodacycle with substrate (**5b**) was observed in mass spectrometry

2.7 Characterization of C-5 arylated compound 7d by ^{1}H NMR and XRD.

The expanded aromatic region revealed that C-5 proton which is found to have high deshielded (9.25 ppm) value disappeared and corresponding aromatic protons of 4-methoxy phenyl ring appeared in the spectrum in the product. This clearly supported the C-5 functionalization in **5a**.Compound **7q** was subjected to crystallization using vapour diffusion in DCM and diethyl ether. The colourless needle crystal of **7q** could be obtained within 12 h of crystallization. The crystals were subjected to X-ray diffraction analysis. These orthorhombic crystal data analysed for the structure, which confirmed the expected C-5 functionalised product.



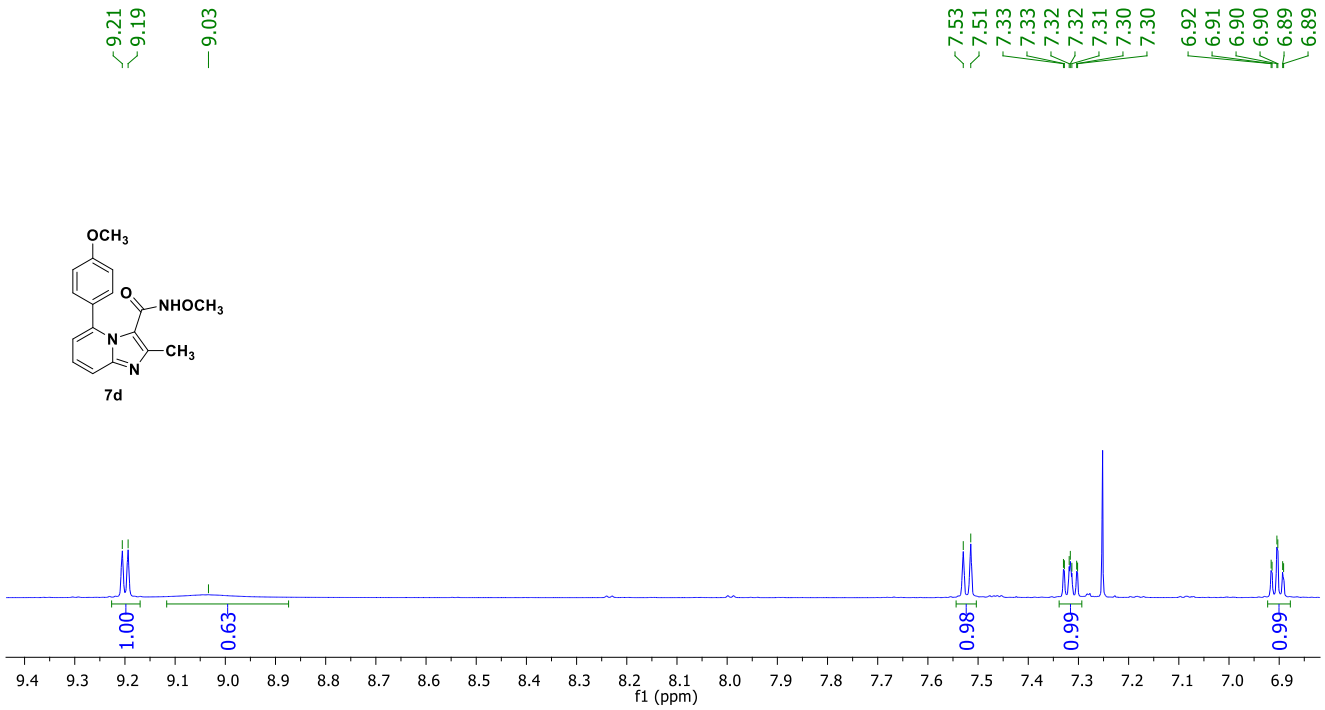


Figure S6. Comparative analysis of ^{1}HNMR of the starting substrate (**5a**) and product (**7d**) in the expanded aromatic region.

XRD structure of compound **7q**

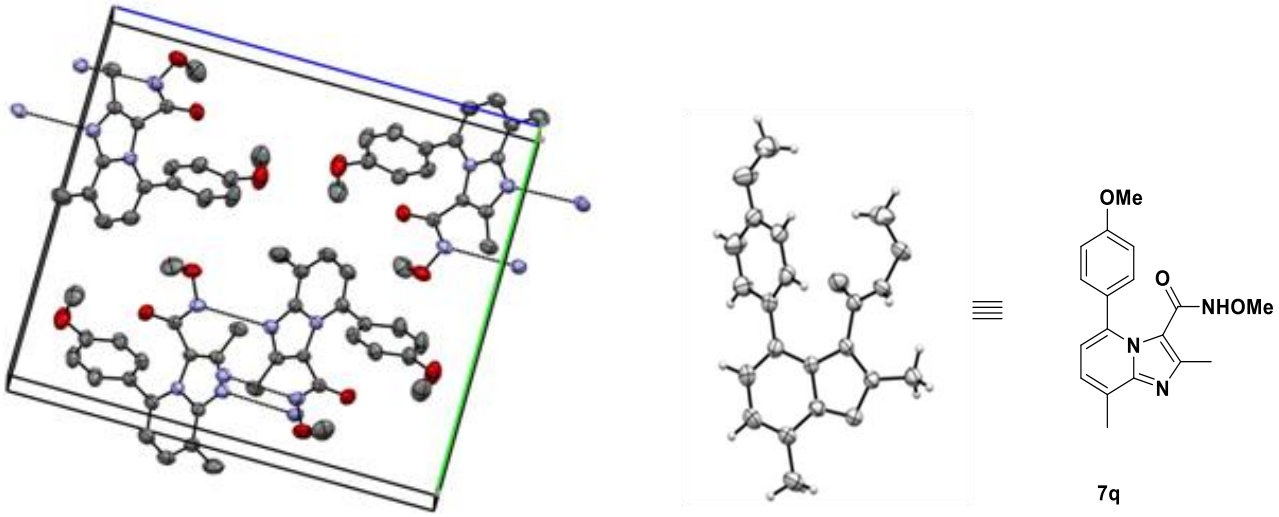


Figure S7. Unit Cell arrangement and XRD structure for the compound **7q**.

2.8 Parameters for crystallization

SCS-Ksl-niper

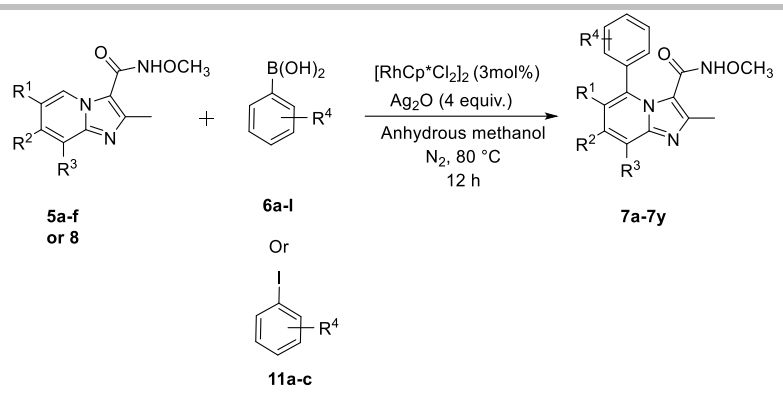
Table S7. Crystal data and structure refinement for 7b

Identification code	SCS-Ksl-niper
Empirical formula	$C_{18}H_{19}N_3O_3$
Formula weight	325.36
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.4420(2)
b/Å	14.9737(5)
c/Å	17.2226(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1661.31(11)
Z	4
ρ_{calc}g/cm^3	1.301
μ/mm^{-1}	0.090
F(000)	688.0
Crystal size/mm^3	0.03 × 0.025 × 0.018
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.752 to 52.744
Index ranges	-8 ≤ h ≤ 7, -18 ≤ k ≤ 18, -18 ≤ l ≤
Reflections collected	16477
Independent reflections	3362 [R_{int} = 0.0616, R_{sigma} = 0.05
Data/restraints/parameters	3362/0/221
Goodness-of-fit on F^2	1.007
Final R indexes [I>=2σ (I)]	R_1 = 0.0504, wR_2 = 0.1070
Final R indexes [all data]	R_1 = 0.0801, wR_2 = 0.1213
Largest diff. peak/hole / e Å^{-3}	0.14/-0.20
Flack parameter	0.5(10)

Table S8 : Crystal data and structure refinement of **7q**.

2.9 Procedure for C-5 arylation of imidazo[1,2-*a*]pyridine-3-carboxamides (7a, Optimized conditions)

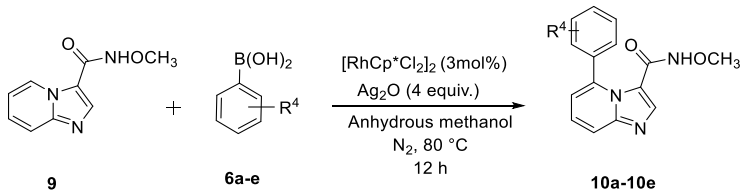
The direct C-5 arylation of imidazo[1,2-*a*]pyridine-3-carboxamides (**Ia**) has been carried out to facilitate the direct C-H activation of 5th position of imidazo[1,2-*a*]pyridine-3-carboxamides followed by C-5 functionalization. Initially, we explored the feasibility of C-5 arylation on 2-methylimidazo[1,2-*a*]pyridine-3-carboxamides by treating between **5a or 8** (0.5 mmol, 1 equiv.) and phenylboronic acid (**6a,** 0.6 mmol, 1.2 equiv.) using $[RhCp^*Cl_2]_2$(3 mol%) as transition metal catalyst, in the presence of Ag_2O (2 mmol, 4 equiv.) in anhydrous MeOH at 80 ˚C for 12 h. The crude product subjected to column chromatography on 100-200 grade silica and the product was eluted with at 6:4 ratios of ethyl acetate and hexane. Delightfully, the desired product *N*-methoxy-2-methyl-5-phenylimidazo[1,2-*a*]pyridine-3-carboxamide (**7a**) was formed with a yield of 75%. The product was confirmed through ^{1}HNMR and ^{13}CNMR spectroscopy and mass spectrometry. Same procedure was used to obtain all C-5 arylated products (**7a-7y**). Instead of phenylboronic acids three derivatives were synthesized (**11a-11c**) using substituted iodobenzene via same procedure as mentioned above.



Scheme S4. Synthesis of C-5 functionalized imidazo[1,2-*a*]pyridine-3-carboxamides.

Procedure for C-5 arylation of imidazo[1,2-*a*]pyridine-3-carboxamides (**10a-10e, Optimized conditions**)

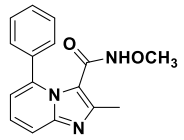
The direct C-5 arylation of C-2 unsubstituted imidazo[1,2-*a*]pyridine-3-carboxamides has been carried out to facilitate the direct C-H activation of 5th position of imidazo[1,2-*a*]pyridine-3-carboxamides followed by C-5 functionalization. Initially, we explored the feasibility of C-5 arylation on C-2 unsubstituted imidazo[1,2-*a*]pyridine-3-carboxamides by treating between **9** (0.5 mmol, 1 equiv.) and 4-methoxy phenylboronic acid (**6a**, 0.60 mmol, 1.2 equiv.) using $[RhCp^*Cl_2]_2$ (3mol%) as transition metal catalyst, in the presence of Ag_2O (2 mmol, 4 equiv.) in anhydrous MeOH at 80 °C for 12 h. The crude product subjected to column chromatography on 100-200 grade silica and the product was eluted with at 6:4 ratios of ethyl acetate and hexane. Delightfully, the desired product *N*-methoxy-5-(4-phenyl)imidazo[1,2-*a*]pyridine-3-carboxamide (**10a**) was formed with a yield of 78%. The product was confirmed through ^{1}HNMR and ^{13}CNMR spectroscopy and mass spectrometry. Same procedure was used to obtain all C-5 arylated products (**10a-10e**).



Scheme S5. Synthesis of C-5 functionalized imidazo[1,2-*a*]pyridine-3-carboxamides.

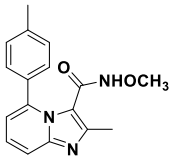
2.10 Spectral data of synthesized compounds from 7a-7y and 10a-10e

7a) ^{1}H NMR, ^{13}C NMR and HRMS of *N*-methoxy-2-methyl-5-phenylimidazo[1,2-*a*]pyridine-3-carboxamide.



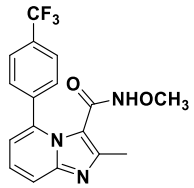
Yellow solid (104 mg, 74%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (m, 6H), 7.36 – 7.30 (m, 1H), 6.76 (d, J = 6.8 Hz, 1H), 3.44 (s, 3H), 2.36 (s, H).; ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.2, 146.2, 139.9, 135.6, 129.7, 129.2, 127.6, 127.2, 116.0, 115.3, 77.5, 77.3, 77.1, 64.3, 14.4.; HRMS calcd for $C_{16}H_{15}N_3O_2$: 282.1242, found 282.1251.

7b) ^{1}H NMR, ^{13}C NMR and HRMS of *N*-methoxy-2-methyl-5-(*p*-tolyl)imidazo[1,2-*a*]pyridine-3-carboxamide.



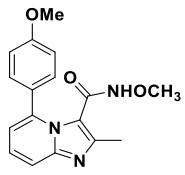
White solid (101 mg, 70%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, J = 8.8 Hz, 1H), 7.26 (dt, J = 12.7, 8.1 Hz, 2H), 7.20 (d, J = 5.2 Hz, 2H), 7.17 (d, J = 7.5 Hz, 2H), 6.68 (d, J = 6.9 Hz, 1H), 3.38 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.2, 146.2, 139.9, 135.4, 130.4, 128.9, 124.0, 115.5, 114.9, 64.0, 21.6, 21.5; HRMS calcd for $C_{17}H_{17}N_3O_2$: 296.1399, found 296.1401.

7c) *N*-methoxy-2-methyl-5-(4-(trifluoromethyl)phenyl)imidazo[1,2-*a*]pyridine-3-carboxamide.



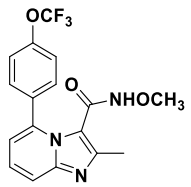
Pale yellow solid (91 mg, 52%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 7.8 Hz, 2H), 7.38 (d, J = 7.5 Hz, 1H), 6.93 (t, J = 6.9 Hz, 1H), 6.77 (d, J = 6.8 Hz, 1H), 3.44 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.0, 149.0, 147.3, 146.4, 139.6, 128.1, 127.3, 120.0, 115.5, 115.1, 111.4, 110.0, 77.3, 77.1, 76.9, 56.0, 14.3.

7d) *N*-methoxy-5-(4-methoxyphenyl)-2-methylimidazo[1,2-*a*]pyridine-3-carboxamide.



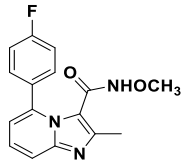
Yellow solid (110 mg, 71%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.35 (s,1H), 7.38 (d, J = 8.8 Hz, 1H), 7.34 (d, J = 8.5 Hz, 2H), 7.29 – 7.22 (m, 1H), 6.90 (d, J = 8.4 Hz, 2H), 6.64 (d, J = 6.8 Hz, 1H), 3.77 (s, 3H), 3.43 (s), 2.32 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.4, 147.5, 139.6, 128.4, 127.2, 115.4, 114.9, 64.3, 55.4, 14.5.; HRMS calcd for $C_{17}H_{17}N_3O_3$: 312.1348, found 312.1335.

7e) *N*-methoxy-2-methyl-5-(4-(trifluoromethoxy)phenyl)imidazo-[1,2-*a*]pyridine-3-carboxamide.



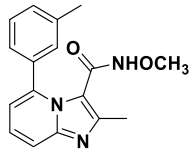
Yellow solid (102 mg, 56%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 7.8 Hz, 2H), 7.40 (d, J = 7.5 Hz,1 H), 6.95 (t, J = 6.9 Hz, 3H), 6.79 (d, J = 6.8 Hz, 1H), 3.46 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.0, 149.0, 147.3, 146.4, 139.6, 128.1, 127.3, 120.0, 115.5, 115.1, 111.4, 110.0, 56.1, 14.3; HRMS calcd for $C_{17}H_{14}F_3N_3O_3$: 366.1065, found 366.1067.

7f) 5-(4-Fluorophenyl)-*N*-methoxy-2-methylimidazo[1,2-*a*]pyridine-3-carboxamide.



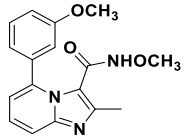
Yellow solid (87 mg, 58%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.38 (s, 1H), 7.43 – 7.37 (m, 2H), 7.33 – 7.28 (m, 1H), 7.09 (t, J = 8.5 Hz, 2H), 6.69 (d, J = 6.8 Hz, 1H), 3.47 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.0, 162.3, 147.3, 146.3, 138.7, 131.6, 129.2, 127.1, 116.1, 115.9, 115.7, 115.4, 64.1, 14.3; HRMS calcd for $C_{16}H_{14}FN_3O_2$: 300.1148, found 300.1146.

7g) *N*-methoxy-2-methyl-5-(*m*-tolyl)imidazo[1,2-*a*]pyridine-3-carboxamide.



White solid (91 mg, 62%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.43 (m, 5H), 7.21 (s, H), 6.59 (s, 1H), 3.43 (s, 3H), 2.38 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.7, 146.1, 138.9, 138.6, 135.5, 129.4, 129.0, 127.0, 118.3, 113.9, 64.1, 21.2, 14.3; HRMS calcd for $C_{17}H_{17}N_3O_2$: 296.1399, found 296.1405.

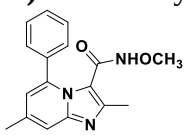
7h) *N*-methoxy-5-(3-methoxyphenyl)-2-methylimidazo[1,2-*a*]pyridine-3-carboxamide.



Off-white solid (113 mg, 73%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.53 (s, 1H), 7.49 (m, 4H), 7.44 (d, J = 9.3 Hz, 1H), 7.37 (d, J = 5.5 Hz, 1H), 3.47 (s,3H), 3.44 (s,3H), 2.38 (s,3H); ^{13}C NMR (151

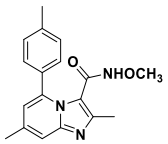
MHz, $CDCl_3$) δ 143.3, 143.3, 134.7, 129.8, 127.8, 127.9, 126.9, 126.8, 113.9, 113.7, 107.9, 62.0, 48.3, 27.2; HRMS calcd for $C_{17}H_{17}N_3O_3$: 312.1348, found 312.1355.

7i) *N*-methoxy-2,7-dimethyl-5-phenylimidazo[1,2-*a*]pyridine-3-carboxamide.



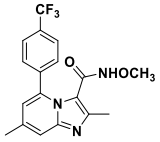
Yellow solid (112 mg, 76%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.43 (m, 5H), 7.21 (s, 1H), 6.59 (s, 1H), 3.43 (s, 3H), 2.38 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.7, 146.2, 138.9, 138.6, 135.6, 129.5, 129.0, 127.0, 118.3, 113.9, 64.2, 21.9, 14.3; HRMS calcd for $C_{17}H_{17}N_3O_2$: 296.1399, found 296.1401.

7j) *N*-methoxy-2,7-dimethyl-5-(*p*-tolyl)imidazo[1,2-*a*]pyridine-3-carboxamide.



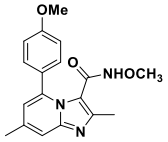
White solid (116 mg, 75%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, J = 7.9 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 7.13 (s, 1H), 6.50 (s, 1H), 3.39 (s, 3H), 2.31 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.7, 146.2, 139.5, 139.1, 138.5, 132.7, 129.7, 126.9, 118.1, 114.4, 113.7, 64.0, 21.5, 21.2, 14.3; HRMS calcd for $C_{18}H_{19}N_3O_2$: 310.1555, found 310.1550.

7k) *N*-methoxy-2,7-dimethyl-5-(4-(trifluoromethyl)phenyl)imidazo[1,2-*a*]pyridine-3-carboxamide.



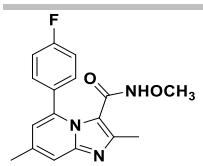
Yellow oil (99 mg,55%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.43 (m, 4H), 7.21 (s, 1H), 6.59 (s, 1H), 3.43 (s, 3H), 2.38 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.70, 146.18 (s), 138.95 (s), 138.60 (s), 135.6 (s), 129.5 (s), 129.0 (s), 127.0 (s), 118.3 (s), 113.9 (s), 64.2 (s), 21.3 (s), 14.3 (s); HRMS calcd for $C_{18}H_{16}F_3N_3O_2$: 364.1273, found 364.1268.

7l) *N*-methoxy-5-(4-methoxyphenyl)-2,7-dimethylimidazo[1,2-*a*]pyridine-3-carboxamide.



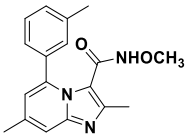
Yellow solid (123 mg, 76%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, J = 8.9 Hz, 2H), 6.96 (d, J = 9.1 Hz, 2H), 6.56 (d, J = 1.8 Hz, 1H), 3.83 (s, 3H), 3.48(m, 3H), 2.45 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.6, 146.9, 139.2, 138.2, 128.5, 127.4, 125.9, 116.4, 116.0, 113.6, 64.1, 53.5, 29.8, 16.7; HRMS calcd for $C_{18}H_{19}N_3O_3$: 326.1504, found 326.1507.

7m) 5-(4-fluorophenyl)-*N*-methoxy-2,7-dimethylimidazo[1,2-*a*]pyridine-3-carboxamide.



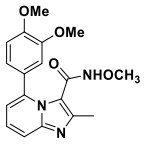
White solid (97 mg, 62%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (dd, J = 8.3, 5.3 Hz, 2H), 7.07 (t, J = 8.4 Hz, 2H), 6.51 (s, 1H), 3.46 (s, 3H), 2.34 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.03, 162.3, 148.1, 146.8, 137.9, 129.1, 118.3, 116.0, 114.5, 65.2, 30.2, 21.3; HRMS calcd for $C_{17}H_{16}FN_3O_2$: 314.1305, found 314.1298.

7n) *N*-methoxy-2,7-dimethyl-5-(*m*-tolyl)imidazo[1,2-*a*]pyridine-3-carboxamide.



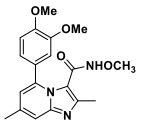
White solid (101 mg, 67%); ^{1}H NMR (600 MHz, $CDCl_3$) δ .28 (d, J = 7.9 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 7.13 (s, 1H), 6.50 (s, 1H), 3.39 (s, 3H), 2.31 (s, 6H), 2.28 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.71, 146.16, 139.48, 139.11, 138.6, 132.7, 129.7, 126.9, 118.1, 114.4, 113.6, 64.0, 21.5, 21.3, 14.29; HRMS calcd for $C_{18}H_{19}N_3O_2$: 310.15555, found 310.1560.

7o) 5-(3,4-Dimethoxyphenyl)-*N*-methoxy-2-methylimidazo[1,2-*a*]pyridine-3-carboxamide.



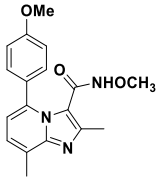
Yellow solid (109 mg, 64%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, J = 8.1 Hz, 1H), 7.32 (t, J = 7.8 Hz, 1H), 7.06 (m, 1H), 6.97 (s,1H), 6.93 (d, J = 8.2 Hz, 1H), 6.75 (d, J = 6.8 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.47 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.0, 149.0, 147.3, 146.4, 139.6, 128.1, 127.3, 120.0 115.5, 115.1, 111.4, 110.0, 64.2, 56.0 (2C), 14.3; HRMS calcd for $C_{18}H_{19}N_3O_4$: 342.1454, found 342.1454.

7p) 5-(3,4-Dimethoxyphenyl)-*N*-methoxy-2,7-dimethylimidazo[1,2-*a*]pyridine-3-carboxamide.



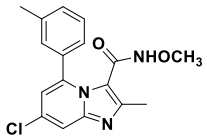
White solid (121 mg, 68%); ^{1}H NMR (600 MHz, $CDCl_3$) δ .06 (d, J = 1.6 Hz, 1H), 6.97 (d, J = 1.7 Hz, 1H), 6.95 (d, J = 8.2 Hz, 1H), 6.61 (s, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 3.48 (s, 3H), 2.46 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.2, 147.1, 138.6, 137.5, 119.9, 114.1, 111.5, 109.9, 107.8, 64.5, 56.1, 53.6, 21.4, 14.7; HRMS calcd for $C_{19}H_{21}N_3O_4$: 356.1610, found 356.1611.

7q) *N*-methoxy-5-(4-methoxyphenyl)-2,8-dimethylimidazo[1,2-*a*]pyridine-3-carboxamide.



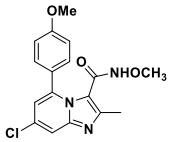
White solid (122 mg, 76%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (dd, J = 9.4, 2.4 Hz, 2H), 7.14 – 7.04 (m, 1H), 6.96 – 6.86 (m, 2H), 6.59 (d, J = 7.3 Hz, 1H), 3.80 (s, 3H), 3.43 (s, 3H), 2.57 (d, J = 0.7 Hz, 3H), 2.42 (s, 3H); ^{13}C NMR (151 MHz,$CDCl_3$) δ 160.2, 147.6, 146.0, 137.3, 128.4, 128.2, 126.1, 124.9, 115.2, 115.2, 114.3, 64.2, 55.4, 17.1, 14.5; HRMS calcd for $C_{18}H_{19}N_3O_3$: 326.1504, found 326.1498.

7r) 7-Chloro-*N*-methoxy-2-methyl-5-(*m*-tolyl)imidazo[1,2-*a*]pyridine-3-carboxamide.



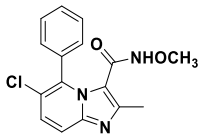
Yellow solid (85 mg, 52%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.36 (d, J = 7.5 Hz, 1H), 7.30 (s, 1H), 7.29 (s, 1H), 7.28 (s, 1H), 7.06 (d, J = 2.3 Hz, 1H), 7.04 (d, J = 2.3 Hz, 1H), 6.92 (d, J = 6.8 Hz, 1H), 3.60 (s), 2.39 (s).; ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.1, 142.7, 139.3, 138.8, 135.2, 124.1, 123.7, 123.4, 115.9, 115.9, 114.5, 114.1, 114.1, 113.8, 55.9, 34.8, 22.9; LTQ calcd for $C_{17}H_{16}ClN_3O_3$ $[M+H]^+$: 330.09, found 330.88.

7s) 7-Chloro-*N*-methoxy-5-(4-methoxyphenyl)-2-methylimidazo[1,2-*a*]pyridine-3-carboxamide.



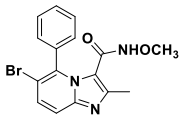
Yellow solid (96 mg, 56%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, J = 3.3 Hz, 2H), 7.66 (s, 1H), 7.49 (d, J = 3.0 Hz, 2H), 6.97 (s, 1H), 4.27 (s, 3H), 4.06 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.6, 160.1, 151.8, 140.1, 139.2, 139.2, 128.4, 123.6, 123.2, 123.2, 114.0, 62.3, 55.3, 14.1; LTQ calcd for $C_{17}H_{16}ClN_3O_3$ $[M+H]^+$: 346.09, found 346.77.

7t) 6-Chloro-*N*-methoxy-2-methyl-5-phenylimidazo[1,2-*a*]pyridine-3-carboxamide.



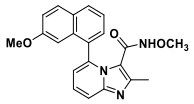
Brown semi-solid (71 mg, 45%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (dd, J = 14.8, 8.0 Hz, 3H), 7.45 – 7.37 (m, 2H), 7.23 (s, 1H), 3.62 – 3.27 (m, 3H), 2.57 – 2.26 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.9, 130.0, 129.3, 128.9, 128.7, 116.3, 64.5, 14.3; HRMS calcd for $C_{16}H_{14}ClN_3O_2$: 316.0853, found 316.0840.

7u) 6-Bromo-*N*-methoxy-2-methyl-5-phenylimidazo[1,2-*a*]pyridine-3-carboxamide.



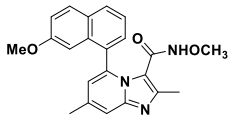
Brown semi-solid (36 mg, 20%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (dd, J = 6.9, 2.7 Hz, 2H), 7.36 (d, J = 9.6 Hz, 1H), 7.08 (s, 2H), 7.00 (m, 1H), 3.52 – 3.38 (m, 3H), 2.41 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.5, 136.2, 131.6, 129.4, 129.0, 128.7, 126.9, 126.8, 126.8, 116.1, 115.6, 64.2, 21.4; HRMS calcd for $C_{16}H_{14}BrN_3O_2$: 360.3221, found 360.3227.

7v) *N*-methoxy-5-(7-methoxynaphthalen-1-yl)-2-methylimidazo[1,2-*a*]pyridine-3-carboxamide.



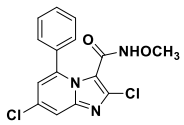
Yellow solid (106 mg, 59%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.80 (d, J = 8.9 Hz, 1H), 7.72 (d, J = 9.3 Hz, 1H), 7.52 (dd, J = 8.7, 1.8 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.26 (d, J = 10.2 Hz, 1H), 7.17 – 7.12 (m, 1H), 6.83 (d, J = 8.2 Hz, 1H), 3.92 (s, 3H), 3.08 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 147.5, 146.7, 139.9, 134.9, 130.7, 129.9, 128.5, 127.8, 127.7, 127.3, 126.0, 126.0, 125.0, 124.8, 119.7, 115.8, 115.4, 115.3, 105.9, 105.5, 63.9, 55.4, 22.7; HRMS calcd for $C_{21}H_{19}N_3O_3$: 362.1493, found 362.1504.

7w) *N*-methoxy-5-(7-methoxynaphthalen-1-yl)-2,7-dimethylimidazo[1,2-*a*]pyridine-3-carboxamide.



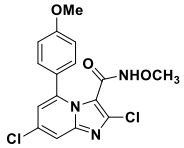
Yellow solid (122 mg, 65%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.80 (d, J = 8.5 Hz, 1H), 7.73 (d, J = 8.9 Hz, 1H), 7.55 – 7.47 (m, 1H), 7.29 (s, 1H), 7.19 – 7.12 (m, 2H), 6.69 (s, 1H), 3.92 (s, 4H), 3.10 (s, 3H), 2.46 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.5, 146.8, 139.0, 134.9, 129.8, 128.5, 127.6, 125.8, 124.9, 119.7, 118.4, 114.1, 105.8, 64.1, 55.5, 21.3, 14.7; HRMS calcd for $C_{22}H_{21}N_3O_3$: 376.1661 found 376.1664.

7x) 2,7-dichloro-N-methoxy-5-phenylimidazo[1,2-a]pyridine-3-carboxamide.



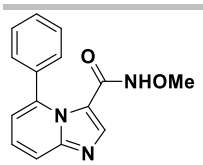
White solid (99 mg, 59%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.88 (bs, 1H), 7.57 (s, 1H), 7.49-7.25 (m, 5H), 6.89 (s, 1H), 3.55(s, 1H)**;** ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.8, 138.8, 135.5, 134.1, 130.2, 129.2, 126.7, 117.9, 114.6, 113.6, 64.6.

7y) 2,7-dichloro-N-methoxy-5-(4-methoxyphenyl)imidazo[1,2-a]pyridine-3-carboxamide.



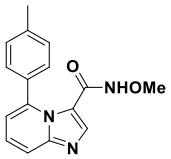
White solid (117 mg, 64%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.53 (s, 1H), 7.38 (d, J = 8.6 Hz, 2H), 6.98 (d, J = 8.5 Hz, 2H), 6.84 (s, 1H), 3.84 (s, 3H), 3.59 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.9, 146.7, 140.8, 139.4, 138.7, 135.5, 128.2, 126.5, 117.5, 114.4, 114.2, 113.6, 64.6, 55.5.

10a) *N*-methoxy-5-phenylimidazo[1,2-*a*]pyridine-3-carboxamide.



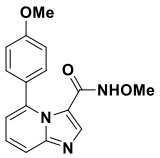
Brown semi-solid (104 mg, 72%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.70 (d, J = 9.0 Hz, 1H), 7.48 (m, 1H), 7.48 (m, 2H), 7.28 (d, J = 2.4 Hz, 1H), 7.05 (dd, J = 8.2, 2.4 Hz, 1H), 6.89 (d, J = 6.7 Hz, 1H), 3.59 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.27, 155.57, 153.2, 139.3, 138.6, 130.8, 130.2, 129.0, 128.7, 124.1, 116.0, 114.1, 77.3, 77.0, 76.8, 55.8; HRMS (EI-TOF) calcd for $C_{16}H_{15}N_3O_2$ $[M+Na]^+$: 290.0897, found 290.0902.

10b) *N*-methoxy-5-(*p*-tolyl)imidazo[1,2-*a*]pyridine-3-carboxamide.



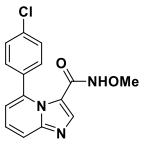
Yellow sticky solid (143 mg, 85%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (s,1H), 7.52 (d, J = 3.2 Hz, 1H), 7.38 (d, J = 7.7 Hz, 2H), 7.28 (d, J = 7.7 Hz, 2H), 7.06 (d, J = 8.5 Hz, 1H), 6.90 (d, J = 6.8 Hz, 1H), 3.60 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.6, 154.3, 142.6, 139.7, 138.5, 137.9, 136.6, 136.5, 135.6, 129.0, 126.0, 124.0, 119.6, 55.9, 19.2; HRMS (EI-TOF) calcd for $C_{16}H_{15}N_3O_2$ $[M+H+Na+MeOH]^+$: 337.1577, found 337.1625. LTQ found

10c) *N*-methoxy-5-(4-methoxyphenyl)imidazo[1,2-*a*]pyridine-3-carboxamide.



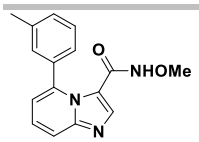
Brownish liquid (124 mg, 78%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.51 (d, J = 3.3 Hz, 1H), 7.41 (d, J = 6.6 Hz, 2H), 7.10 (dd, J = 8.6, 2.5 Hz, 1H), 6.96 (d, J = 5.0 Hz, 2H), 6.89 (d, J = 24.1 Hz, 1H), 3.81 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.0, 147.8, 136.8, 128.3, 128.0, 117.3, 115.8, 114.4, 64.8, 62.7; HRMS (EI-TOF) calcd for $C_{16}H_{15}N_3O_3$ $[M+H]^+$: 298.1172, found 298.1190 $[M+Na]^+$: 320.0997, found 320.1010

10d) 5-(4-Chlorophenyl)-*N*-methoxyimidazo[1,2-*a*]pyridine-3-carboxamide.



Brown liquid (75 mg, 50%); ^{1}H NMR (600 MHz, $CDCl_3$) 7.44 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 7.28 (s, 1H), 7.05 (dd, J = 8.2, 2.3 Hz, 1H), 6.87 (d, J = 6.9 Hz, 1H), 6.60 (d, J = 8.2 Hz, 1H), 3.63 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.5, 152.0, 142.8, 139.4, 135.5, 135.3, 129.3, 127.9, 124.1, 123.6, 116.6, 114.1, 77.3, 77.1, 76.8, 57.4; LTQ for $C_{15}H_{12}ClN_3O_2$ $[M+1+H]^+$: 303.06, found 303.04.

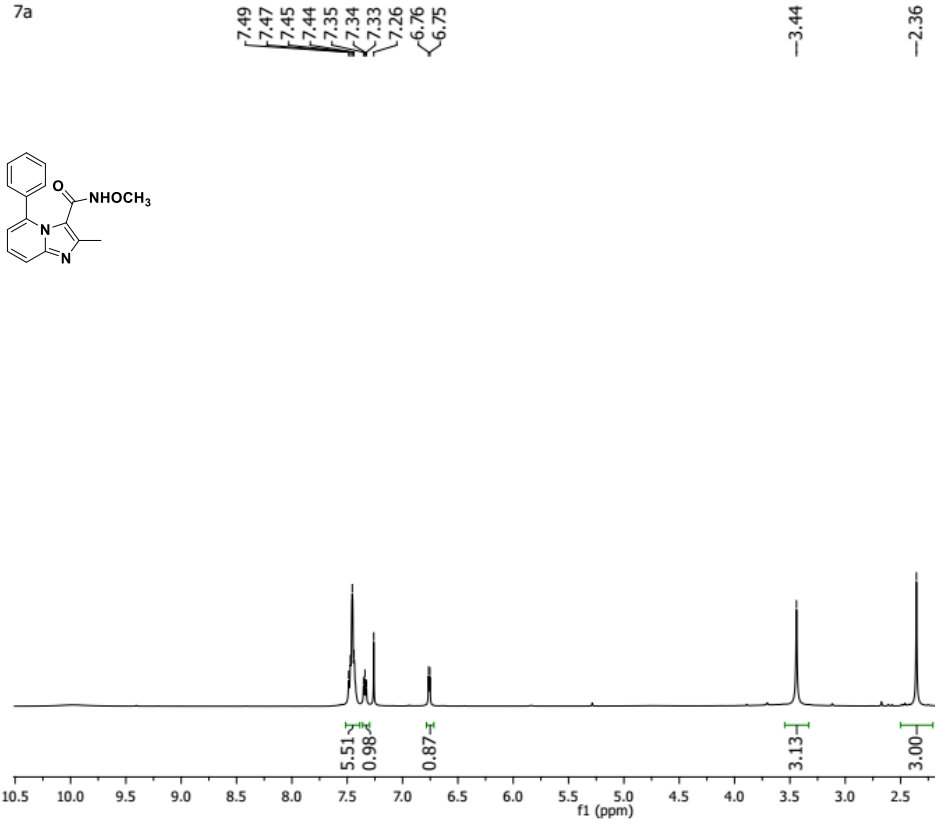
10e) *N*-methoxy-5-(*m*-tolyl)imidazo[1,2-*a*]pyridine-3-carboxamide.



Brown liquid (118 mg, 84%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.36 (d, J = 7.5 Hz, 1H), 7.30 (s, 1H), 7.29 (s, 1H), 7.28 (s, 1H), 7.06 (d, J = 2.3 Hz, 1H), 7.04 (d, J = 2.3 Hz, 1H), 6.92 (d, J = 6.8 Hz, 1H), 3.60 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.5, 152.1, 142.7, 139.36, 138.8, 135.2, 124.1, 123.7, 123.3, 116.0, 115.9, 115.9, 114.2, 114.1, 67.4, 22.8; LTQ for $C_{16}H_{15}N_3O_2$ $[M+H]^+$: 282.12, found 282.45

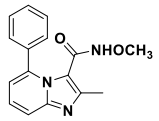
2.11 Scanned copies of ^{1}H NMR, ^{13}C NMR and HRMS for C-5 arylated products.

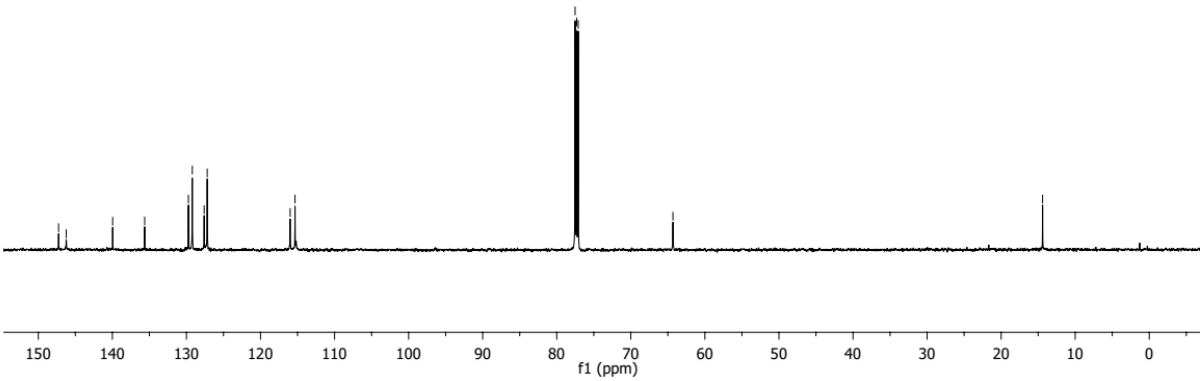
7a) ^{1}H NMR, ^{13}C NMR and HRMS of *N*-methoxy-2-methyl-5-phenylimidazo[1,2-*a*]pyridine-3-carboxamide.



7a

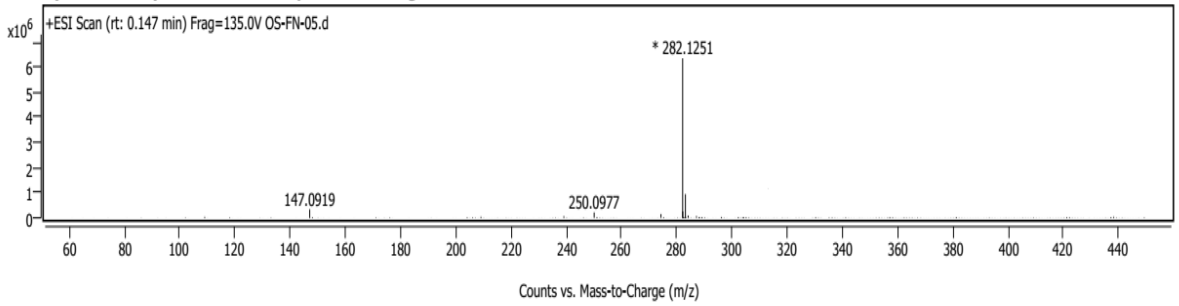
147.26
146.23
139.96
135.64
129.73
129.21
127.61
127.19
116.00
115.34
77.52
77.31
77.10
64.31
14.40





Peak Spec

+ Scan (rt: 0.147 min) **SpectrumIdString**



SpectrumIdString

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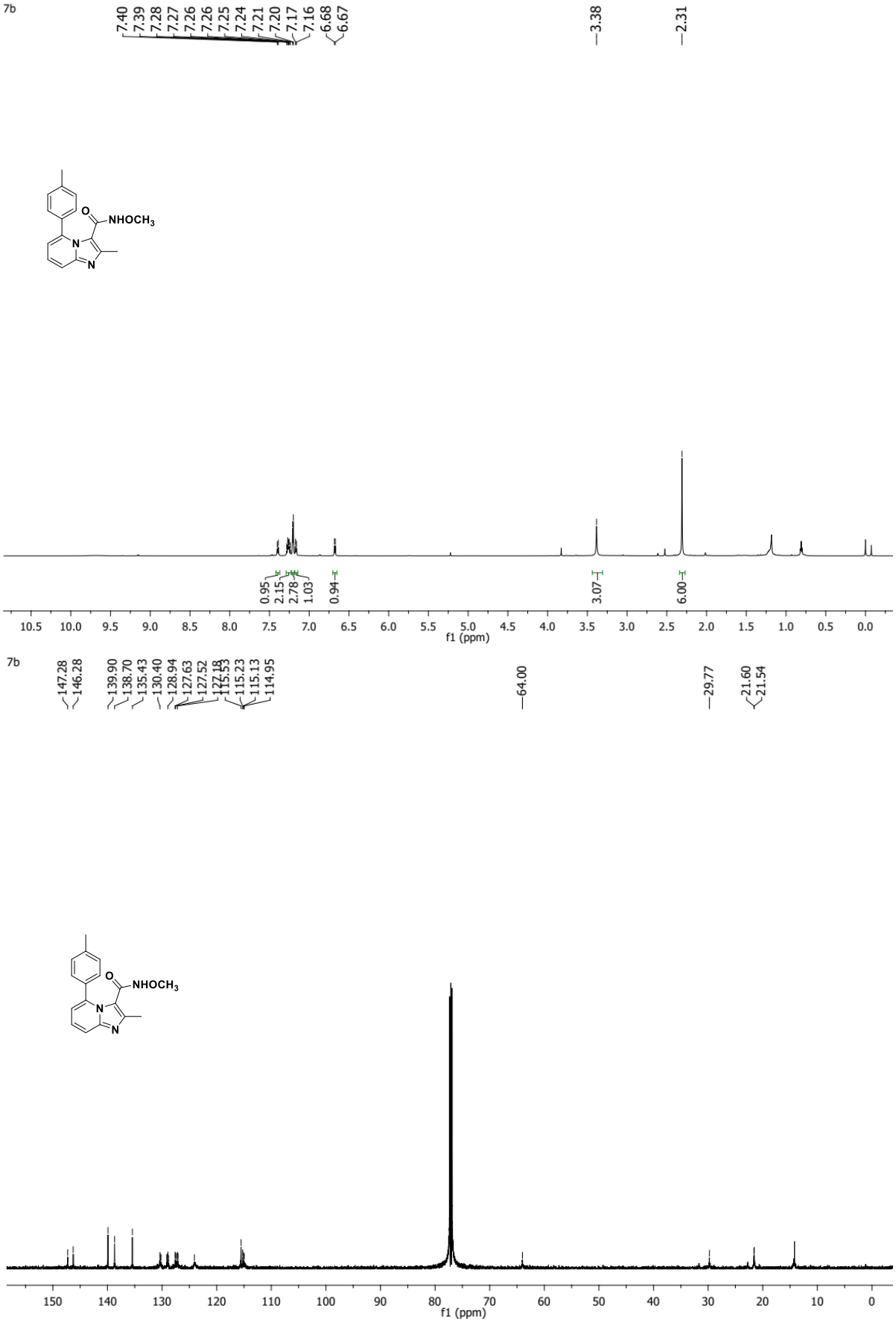
250.0977		216972	3.42					
274.2743		155706	2.45					
282.1251	1	6352103	100.00					
282.1620		256548	4.04					
283.1274	1	944009	14.86					
284.1301	1	93945	1.48					

7b) ^{1}H NMR, ^{13}C NMR and HRMS of *N*-methoxy-2-methyl-5-(*p*-tolyl)imidazo[1,2-*a*]pyridine-3-carboxamide.



Peak Spec

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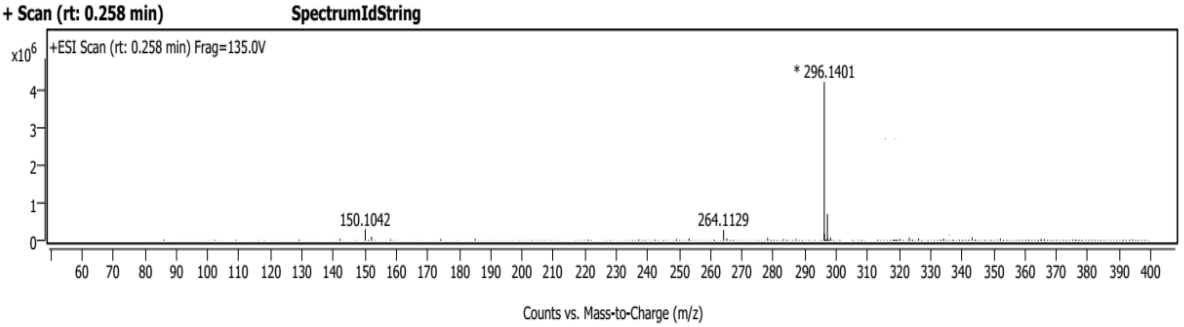

SpectrumIdString

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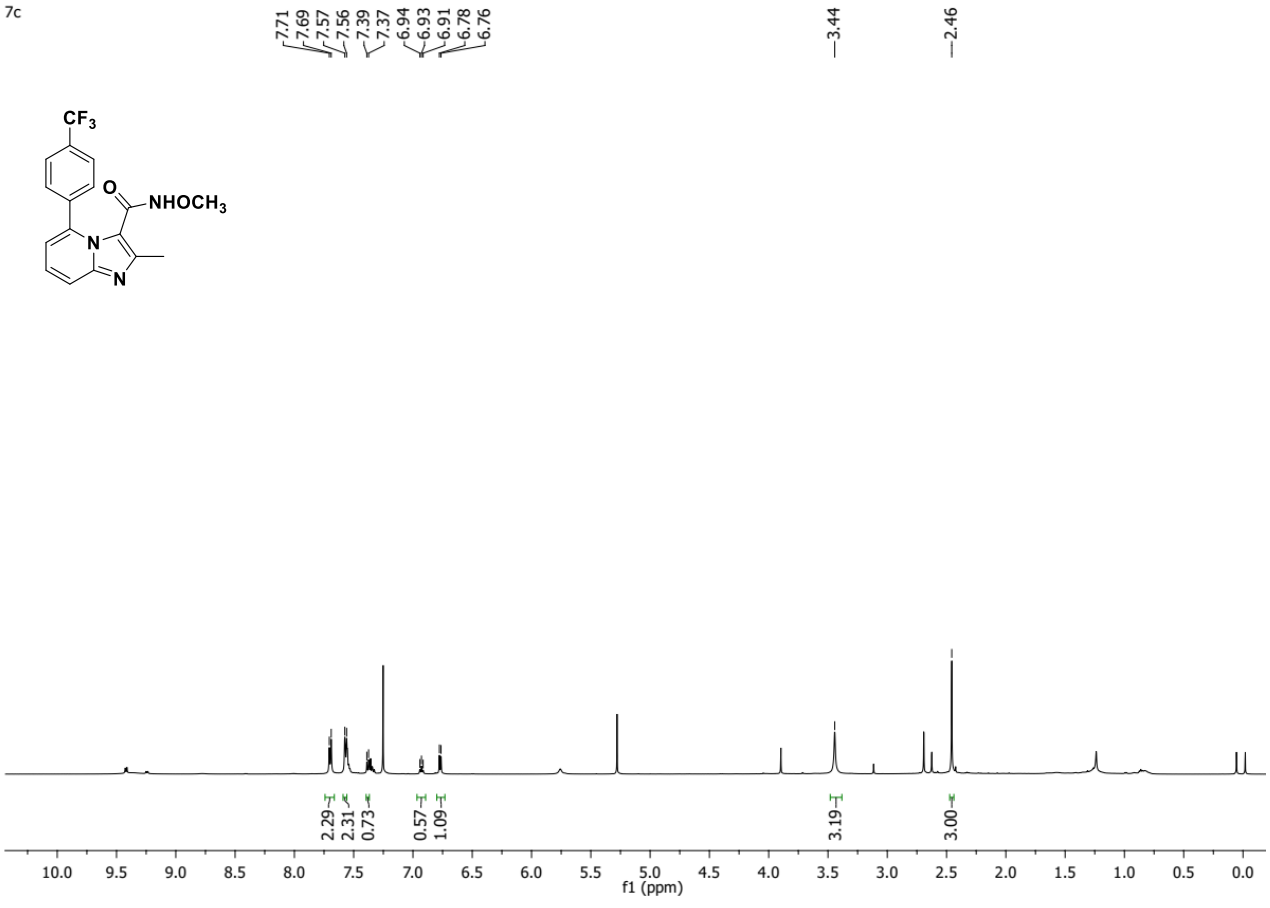
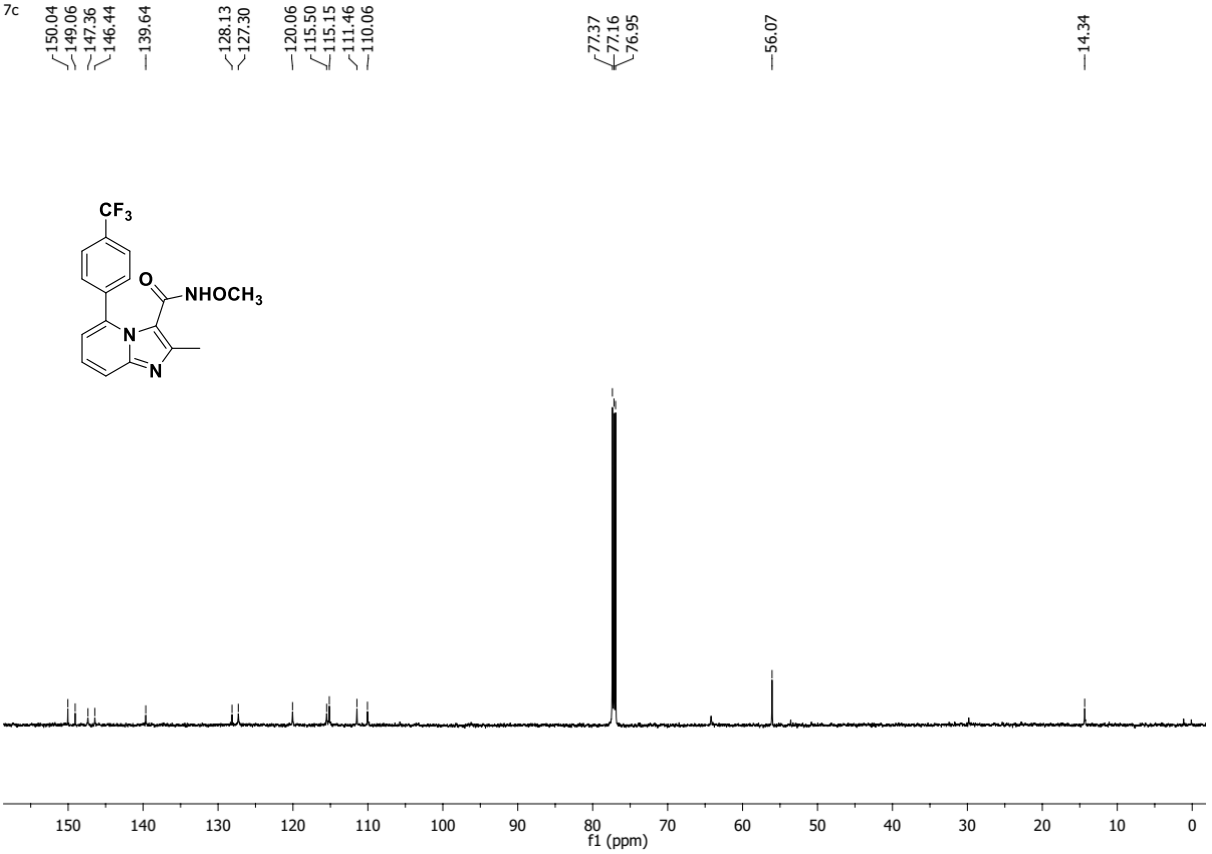
152.1012		97917	2.30					
223.1227		257787	6.06					
253.1332		59356	1.40					
264.1129	1	284609	6.69					
265.1175	1	60749	1.43					
278.1278		73462	1.73					
296.1401	1	4253173	100.00					
296.1763		184901	4.35					
297.1423	1	710782	16.71					

7c) ^{1}H NMR, ^{13}C NMR and HRMS of *N*-methoxy-2-methyl-5-(4-(trifluoromethyl)phenyl)imidazo[1,2-*a*]pyridine-3-carboxamide.

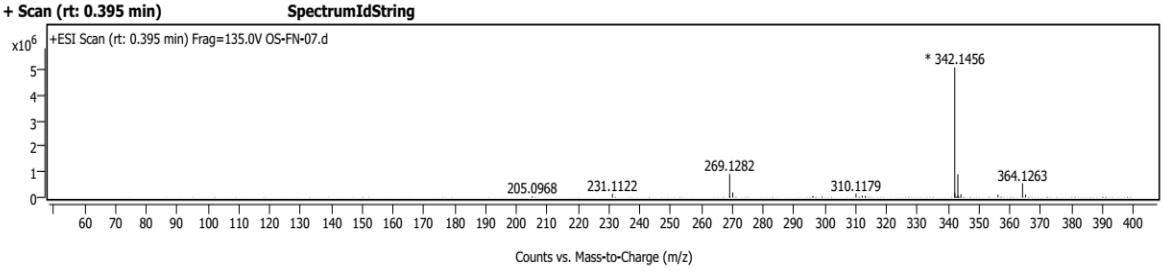


7c



Peak Spec

+ Scan (rt: 0.395 min) **SpectrumIdString**



SpectrumIdString

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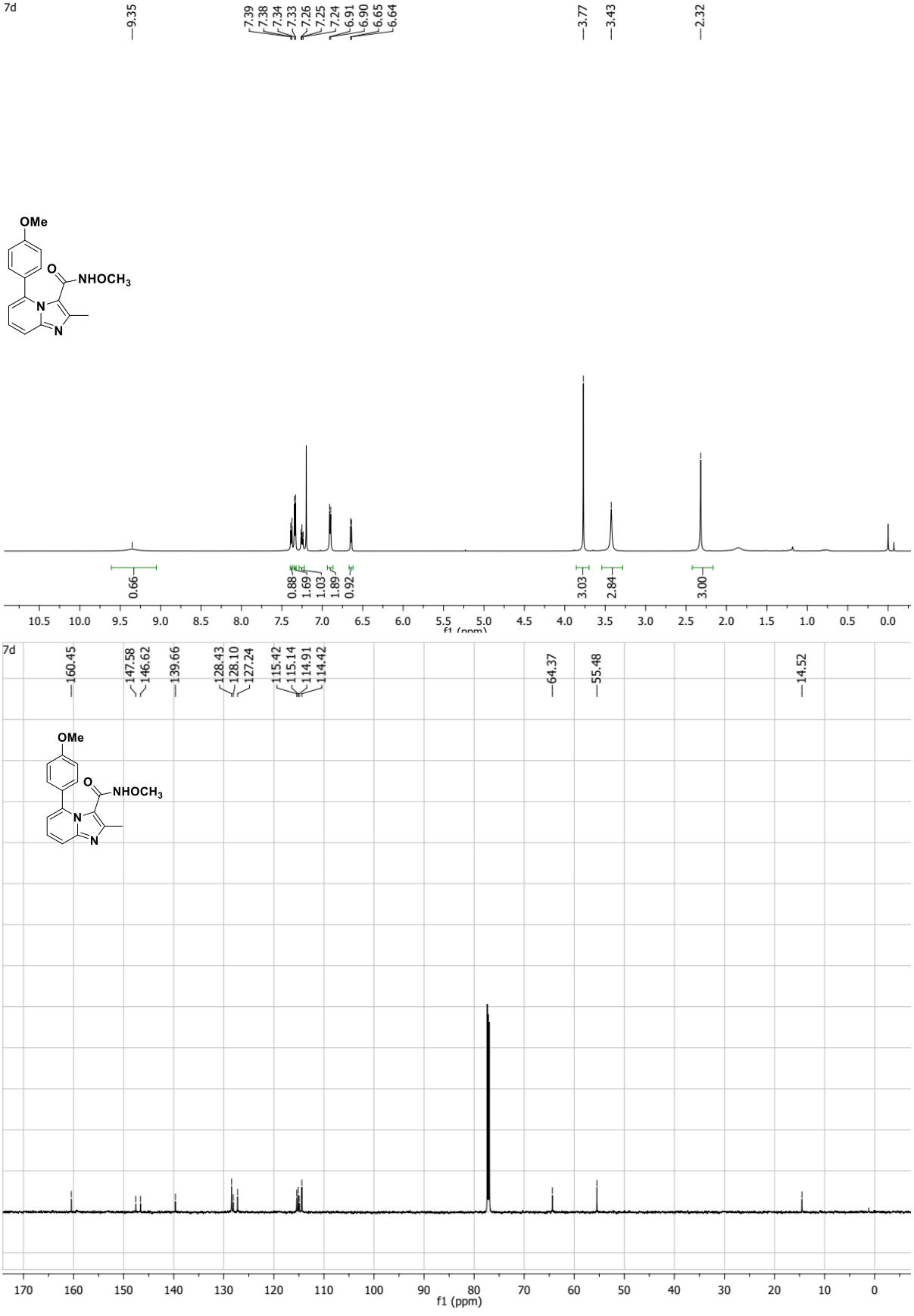
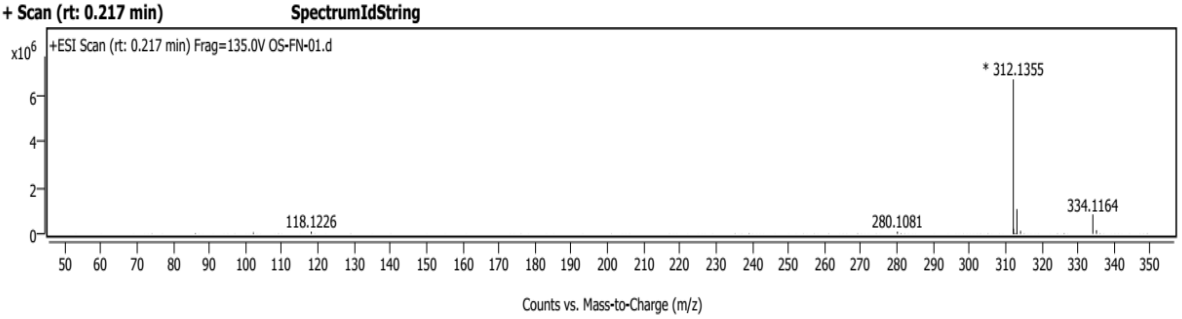
231.1122		144446	2.85					
269.1282	1	920660	18.13					
269.1646		50874	1.00					
270.1312	1	193941	3.82					
296.1388		58797	1.16					
310.1179		151030	2.97					
312.1334		69872	1.38					
313.1538		51987	1.02					
342.1456	1	5077151	100.00					
342.1836	1	172874	3.40					
343.1477	1	904787	17.82					
343.1881	1	54089	1.07					
344.1500	1	124382	2.45					
356.1598		106793	2.10					
364.1263	1	551616	10.86					
365.1293	1	113653	2.24					

7d) ^{1}H NMR, ^{13}C NMR and HRMS of *N*-methoxy-5-(4-methoxyphenyl)-2-methylimidazo[1,2-*a*]pyridine-3-carboxamide.



Peak Spec

+ Scan (rt: 0.217 min) **SpectrumIdString**



SpectrumIdString

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
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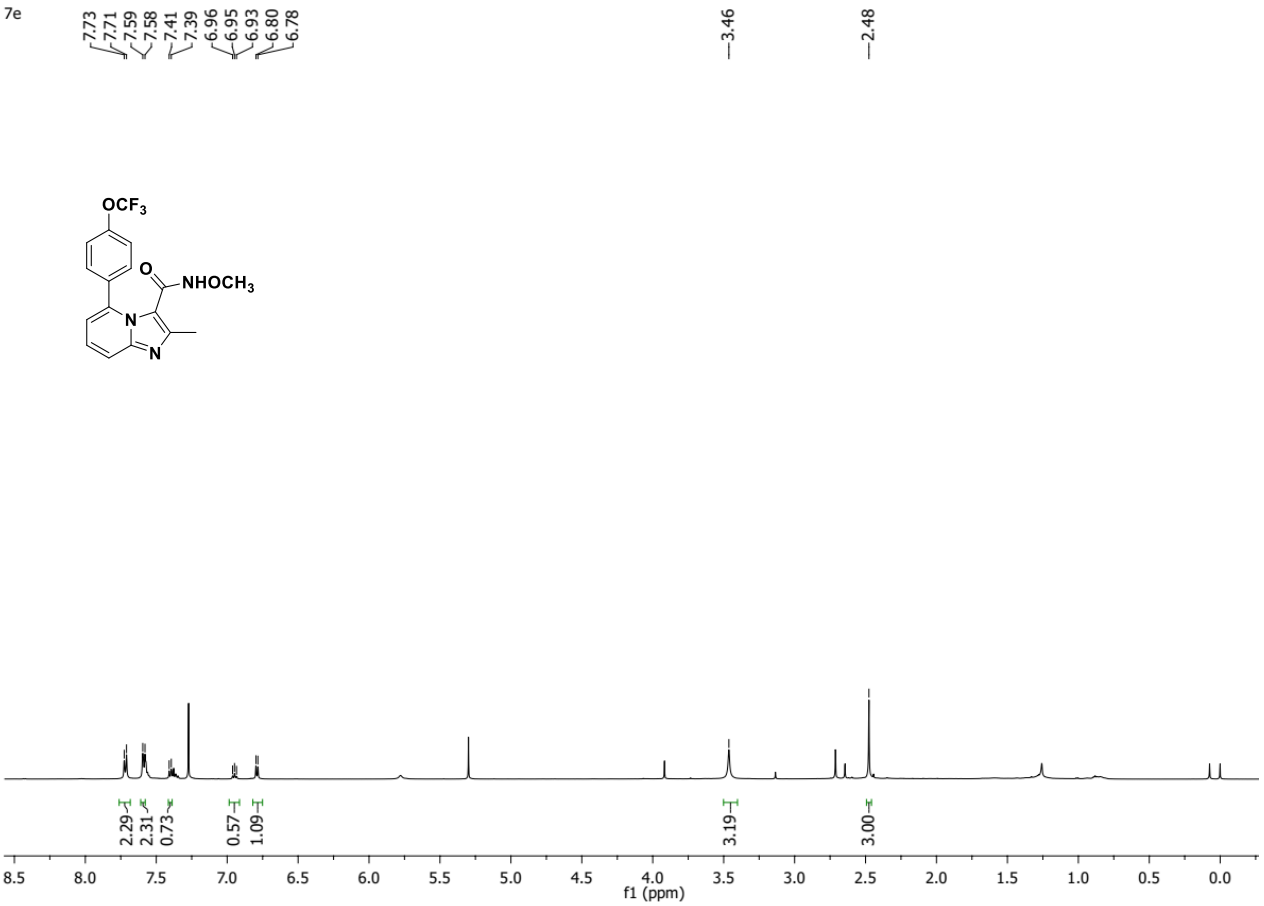
280.1081		95788	1.43					
312.1355	1	6719933	100.00					
312.1746		223536	3.33					
313.1377	1	1071049	15.94					
314.1401	1	126595	1.88					
334.1164	1	843846	12.56					
335.1195	1	160659	2.39					

7e) ^{1}H NMR, ^{13}C NMR and HRMS of *N*-methoxy-2-methyl-5-(4-(trifluoromethoxy)phenyl)imidazo-[1,2-*a*]pyridine-3-carboxamide.



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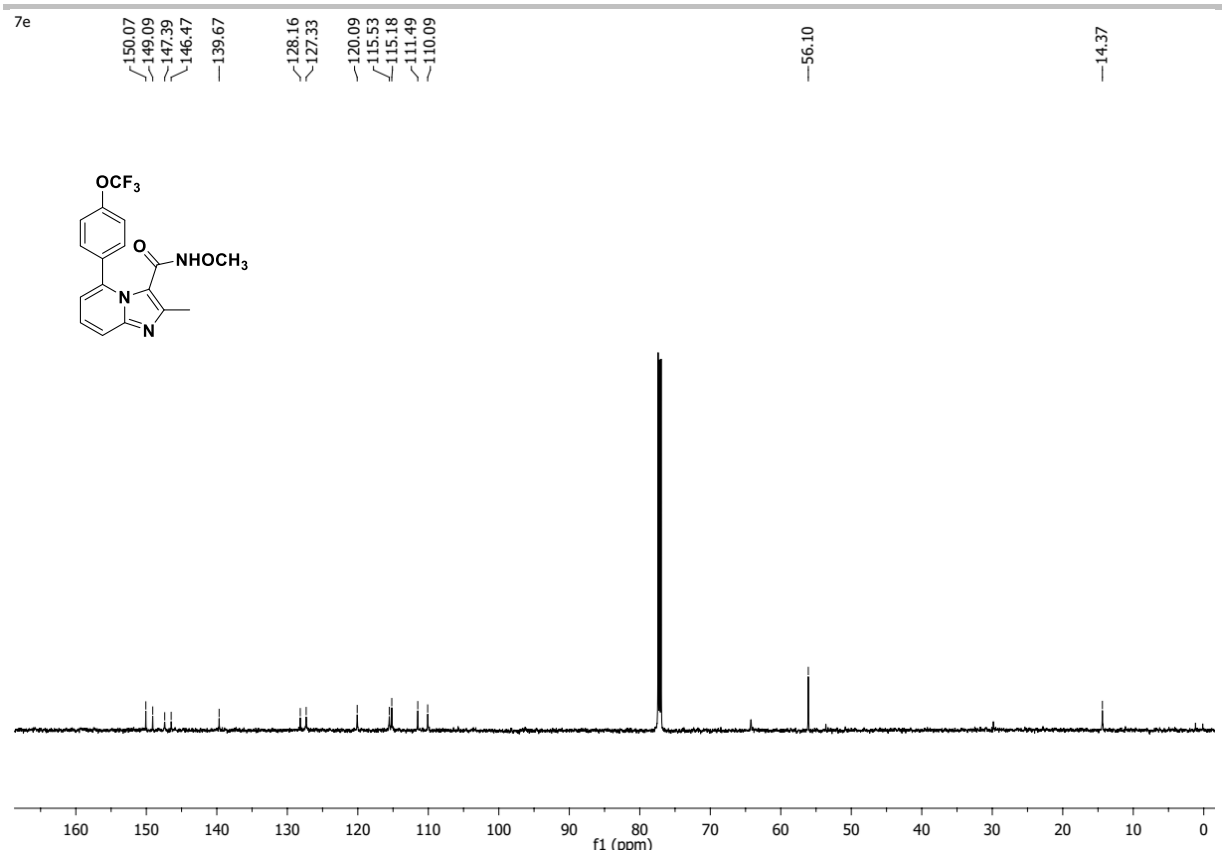
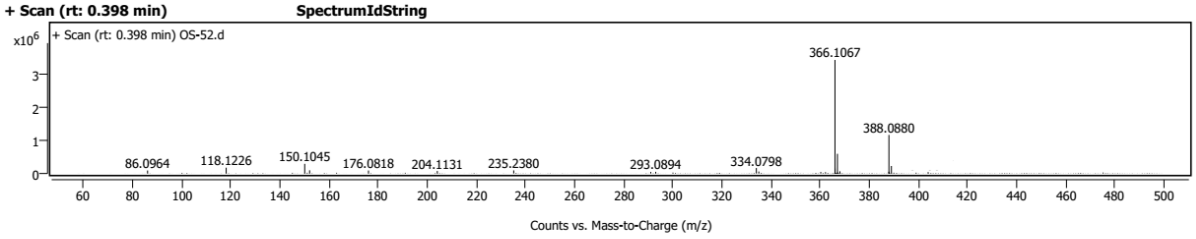


Peak Spec

+ Scan (rt: 0.398 min) **SpectrumIdString**



SpectrumIdString

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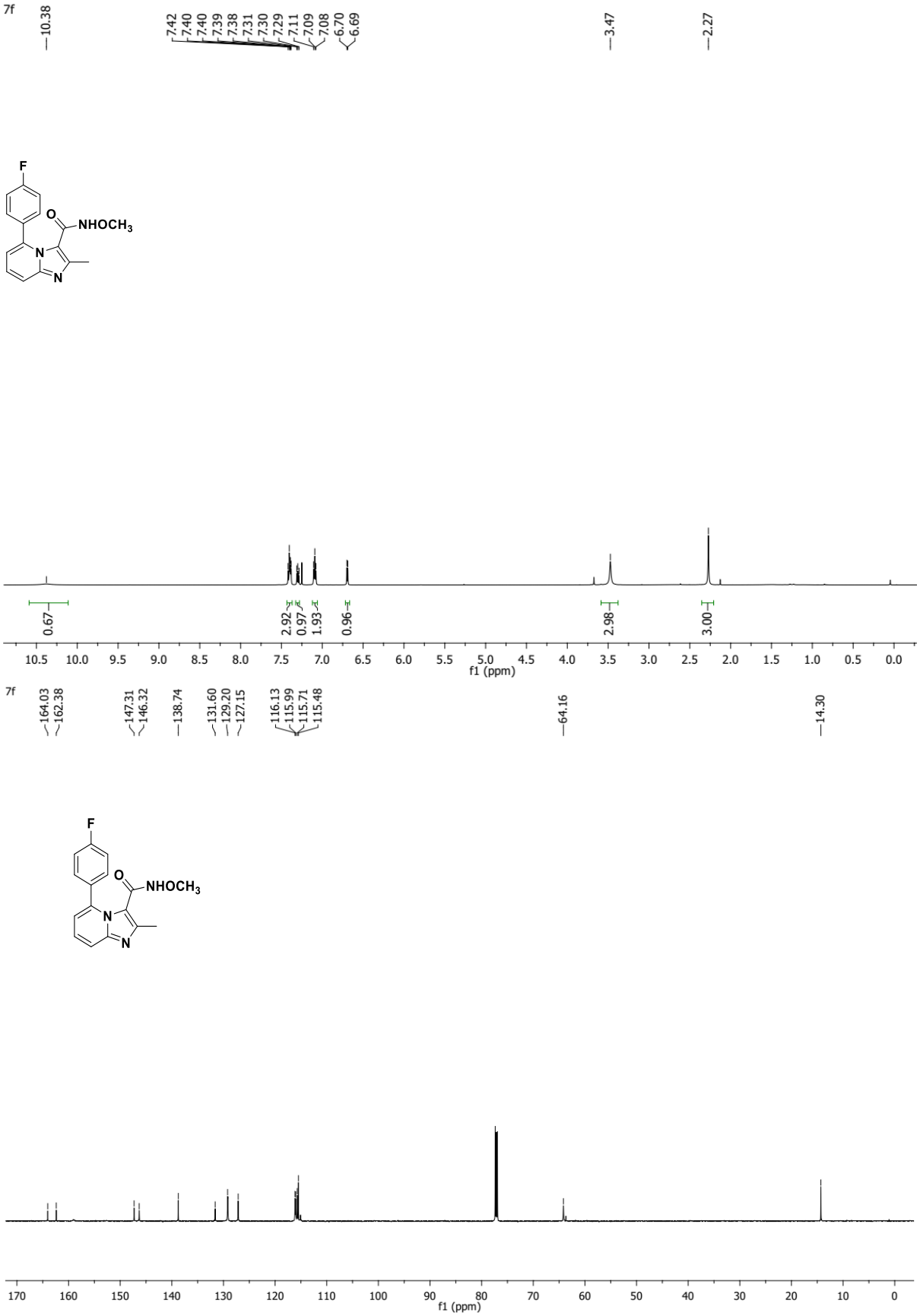
118.1226		176612	5.10					
150.1045		294503	8.50					
152.1015		97752	2.82					
176.0818		90843	2.62					
204.1131		76120	2.20					
235.2380		94184	2.72					
291.0739		48282	1.39					
293.0894		51008	1.47					
334.0798	1	167365	4.83					
335.0860	1	60112	1.73					
360.3234		45351	1.31					
362.2412		40262	1.16					
366.1067	1	3464791	100.00					
366.1481		150610	4.35					
367.1092	1	599648	17.31					
368.1119	1	66172	1.91					
388.0880	1	1176682	33.96					
388.1123		49077	1.42					
388.1317		55624	1.61					
389.0910	1	228724	6.60					

7f) ^{1}H NMR, ^{13}C NMR and HRMS of 5-(4-Fluorophenyl)-*N*-methoxy-2-methylimidazo[1,2-*a*]pyridine-3-carboxamide.



Peak Spec

Peak Spec

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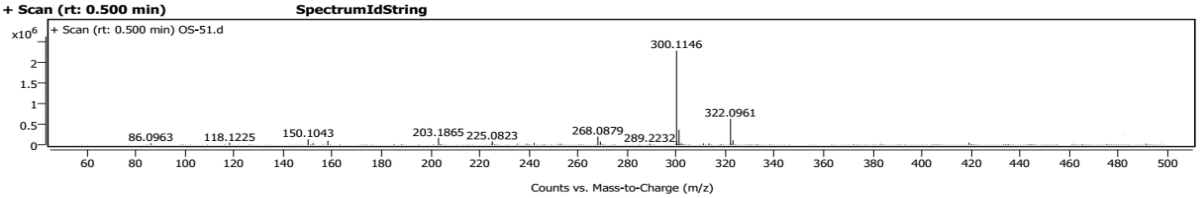

SpectrumIdString

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
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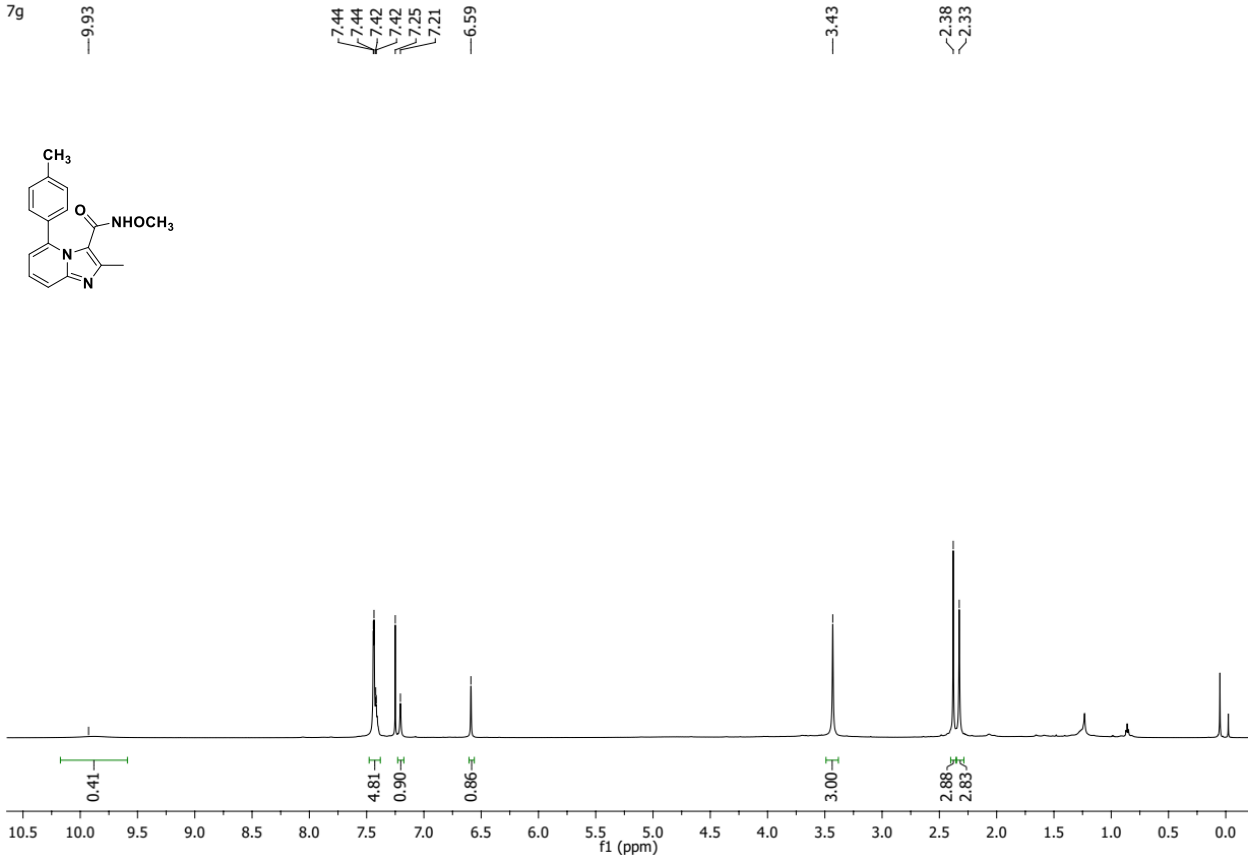
118.1225		49469	2.15					
150.1043		133959	5.83					
152.1013		41055	1.79					
158.1288		98519	4.29					
203.1865		168989	7.36					
225.0823		84978	3.70					
239.0526		25988	1.13					
242.1399		44432	1.94					
268.0879		199330	8.68					
269.0948		77071	3.36					
289.2232		25691	1.12					
300.1146	1	2295859	100.00					
300.1529		101780	4.43					
301.1173	1	365390	15.92					
302.1197	1	36716	1.60					
311.0735		31228	1.36					
313.2708		30931	1.35					
322.0961	1	628420	27.37					
322.1340		27190	1.18					

7g) ^{1}H NMR, ^{13}C NMR and HRMS of *N*-methoxy-2-methyl-5-(*p*-tolyl)imidazo[1,2-*a*]pyridine-3-carboxamide.



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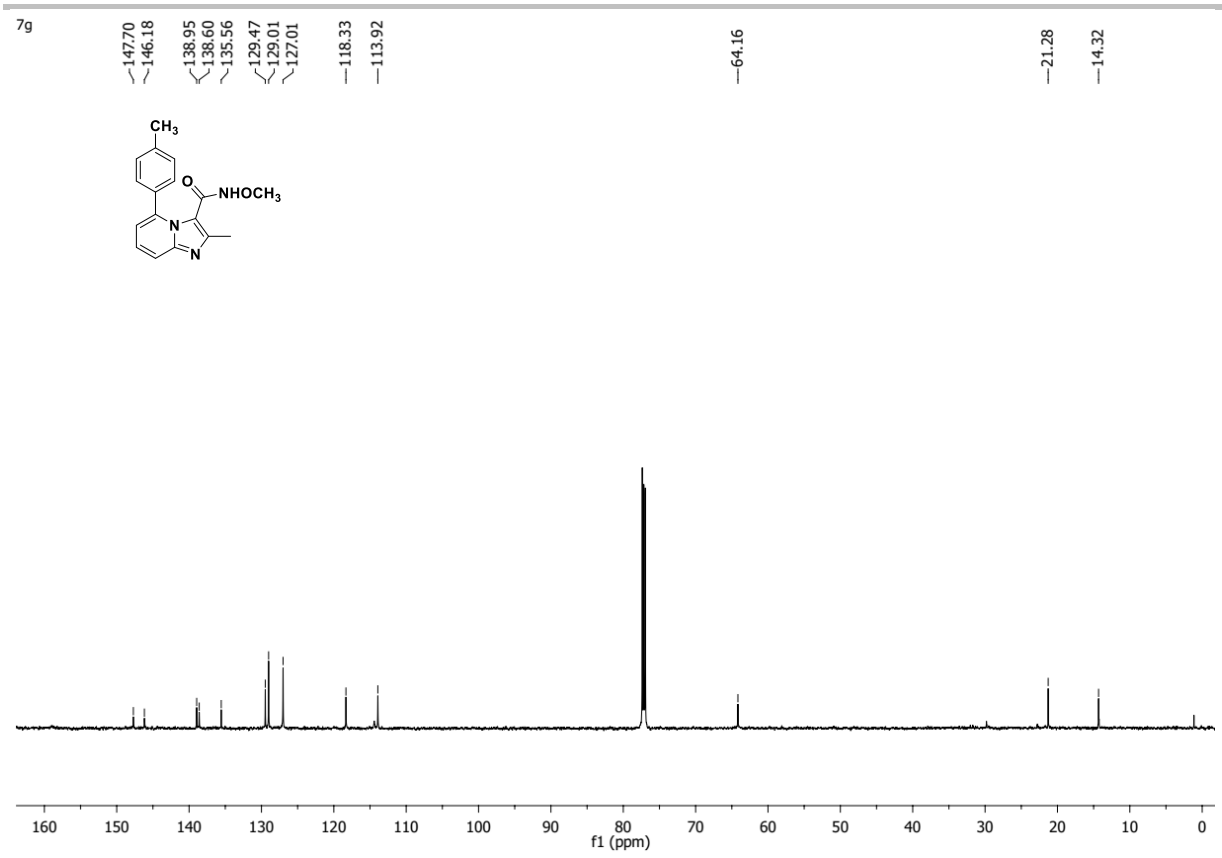

Peak Spec

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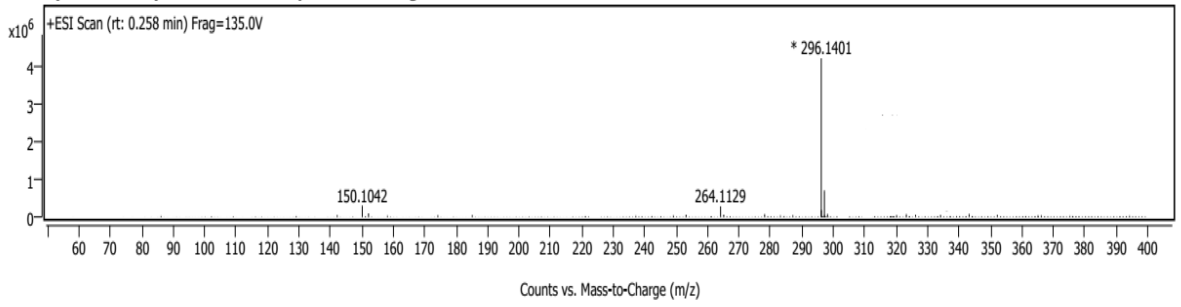
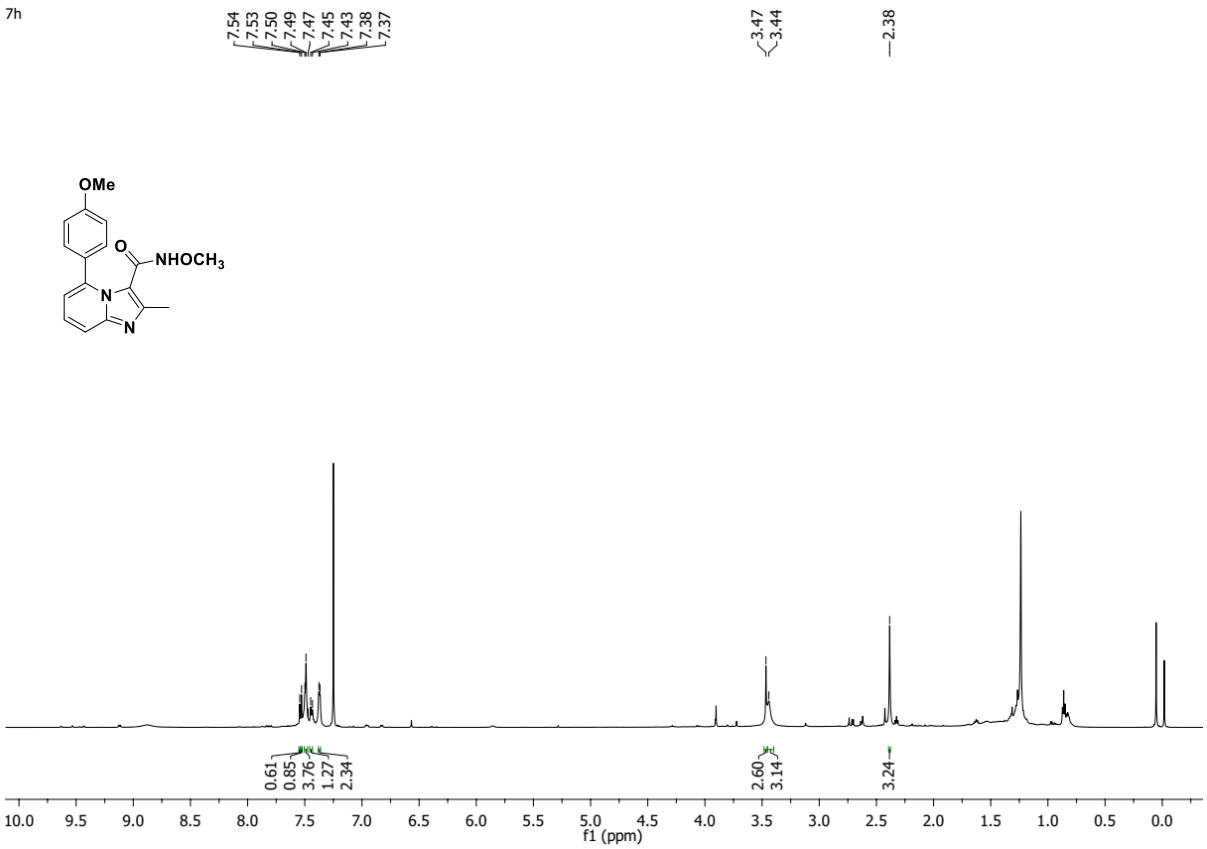
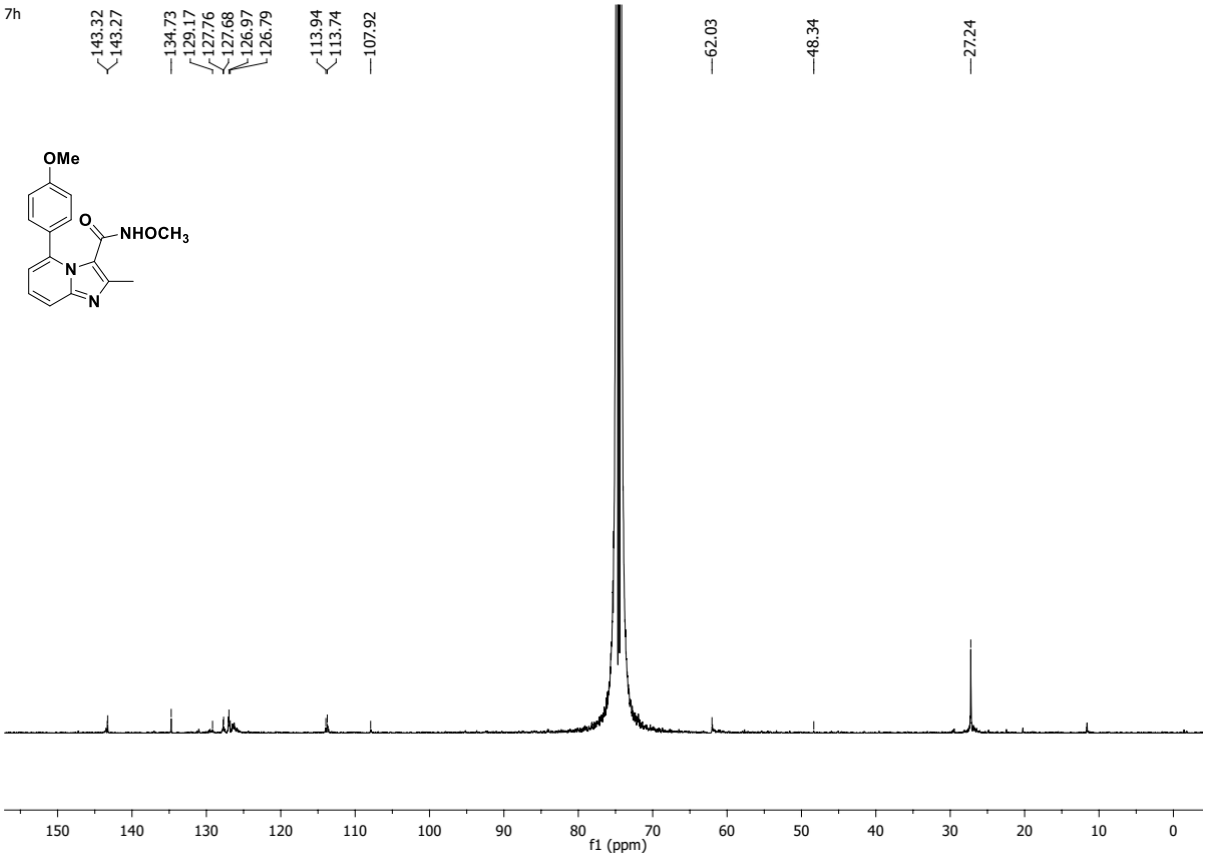


SpectrumIdString

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
150.1042		304406	7.16					
152.1012		97917	2.30					
223.1227		257787	6.06					
253.1332		59356	1.40					
264.1129	1	284609	6.69					
265.1175	1	60749	1.43					
278.1278		73462	1.73					
296.1401	1	4253173	100.00					
296.1763		184901	4.35					
297.1423	1	710782	16.71					

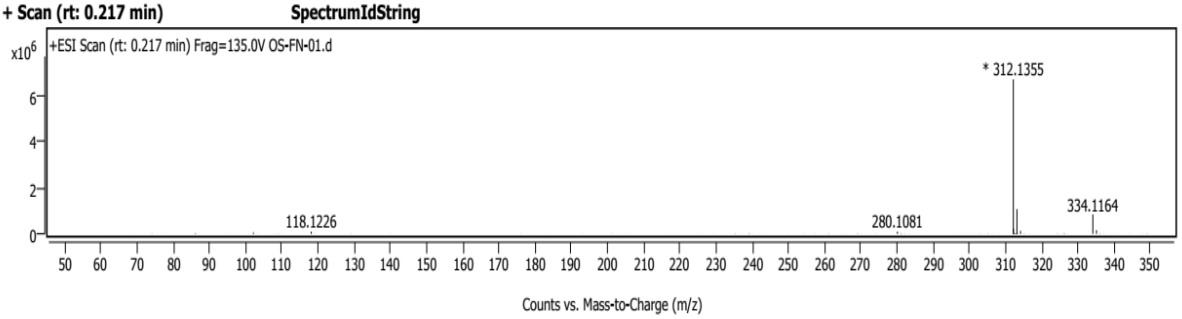
7h) ^{1}H NMR, ^{13}C NMR and HRMS of *N*-methoxy-5-(4-methoxyphenyl)-2-methylimidazo[1,2-*a*]pyridine-3-carboxamide.





Peak Spec

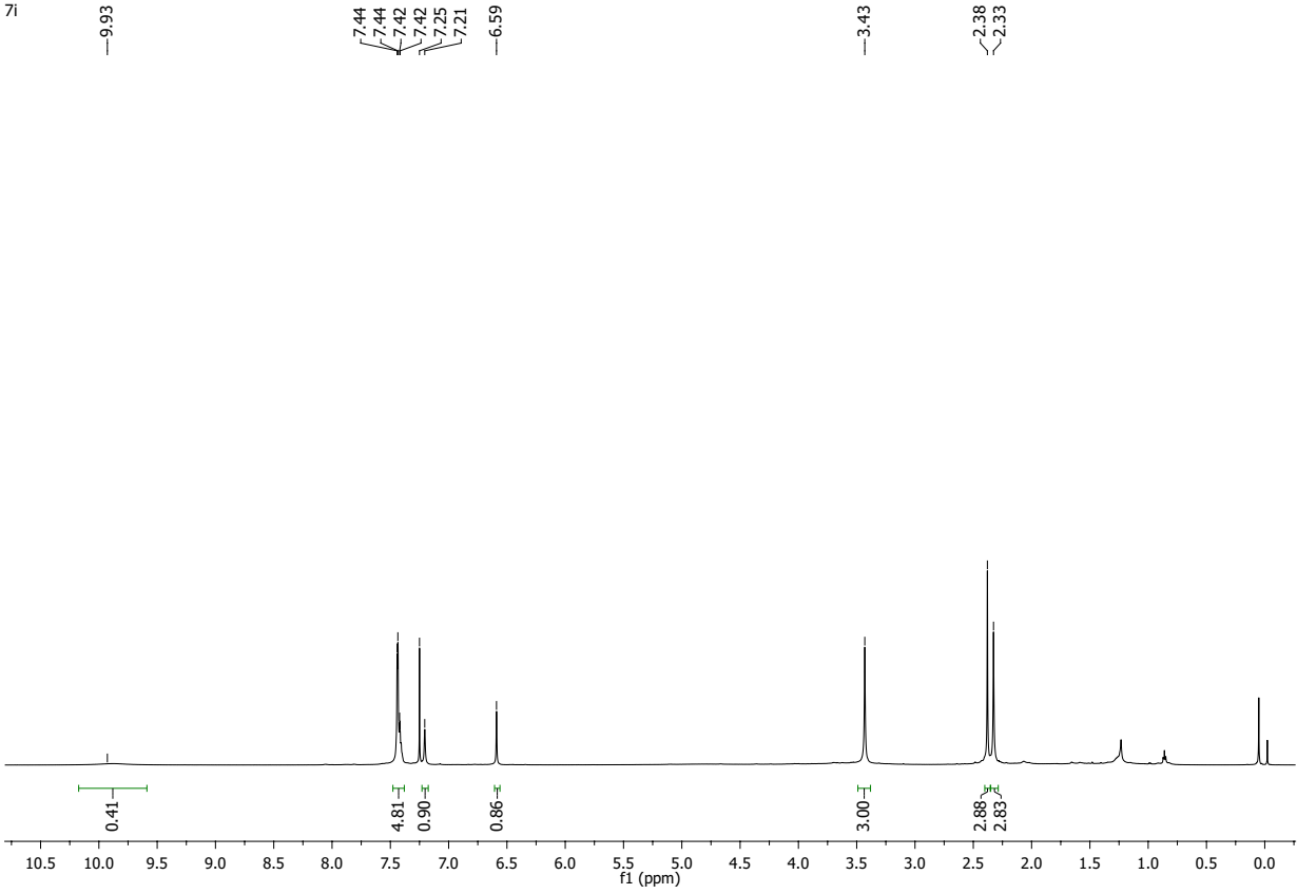
+ Scan (rt: 0.217 min) **SpectrumIdString**



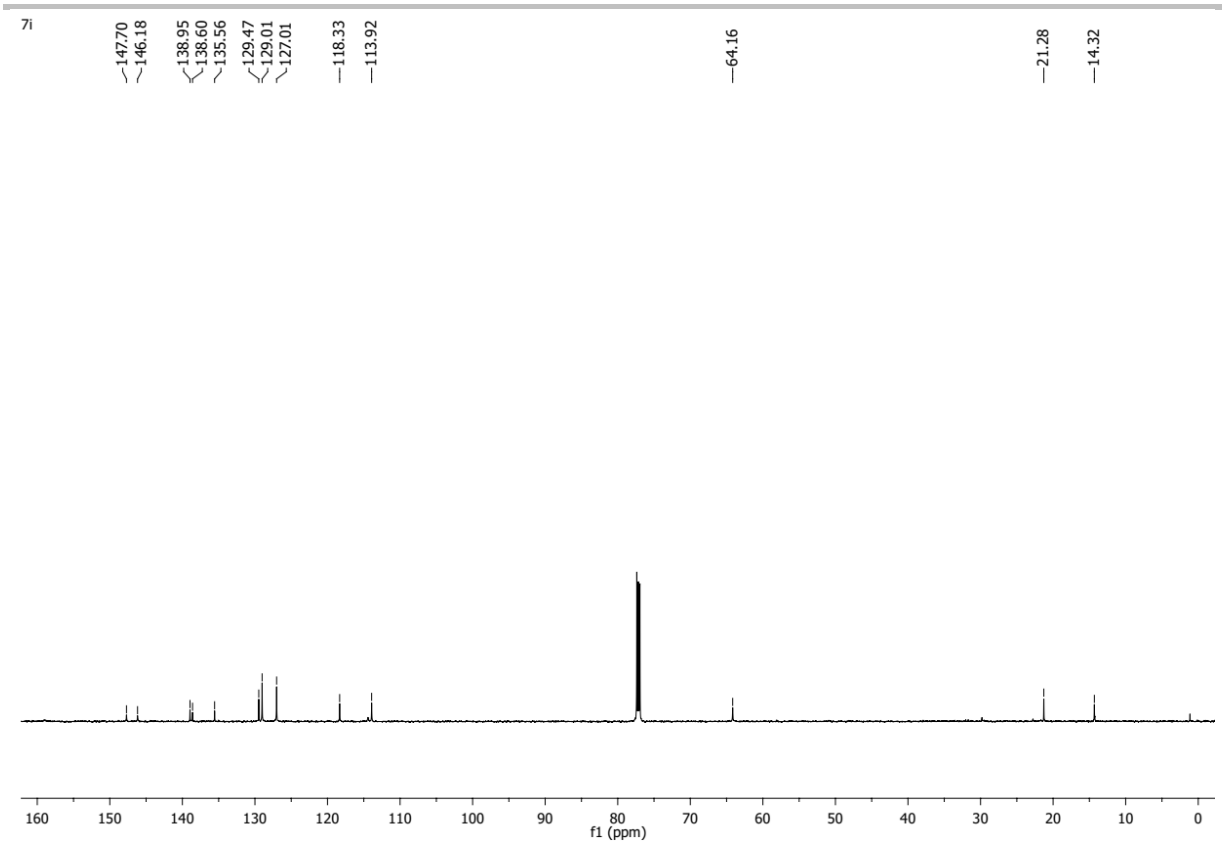
SpectrumIdString

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
118.1226		95235	1.42					
280.1081		95788	1.43					
312.1355	1	6719933	100.00					
312.1746		223536	3.33					
313.1377	1	1071049	15.94					
314.1401	1	126595	1.88					
334.1164	1	843846	12.56					
335.1195	1	160659	2.39					

7i) ^{1}H NMR, ^{13}C NMR and HRMS of *N*-methoxy-2,7-dimethyl-5-phenylimidazo[1,2-*a*]pyridine-3-carboxamide.



7i



Peak Spec

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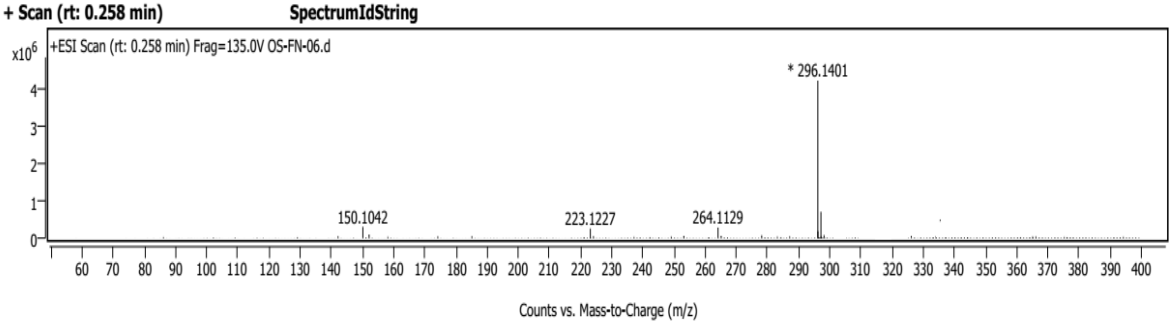
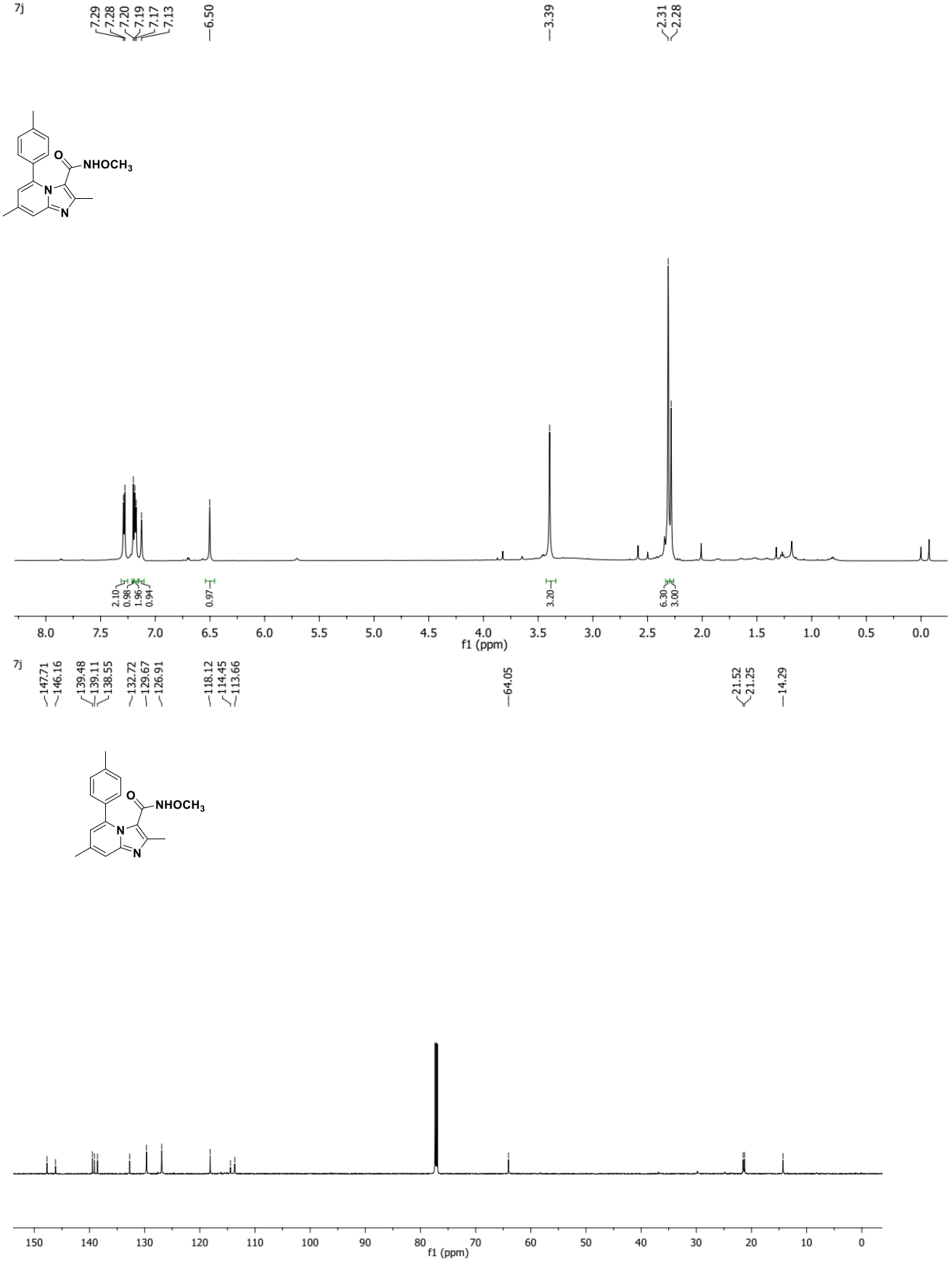
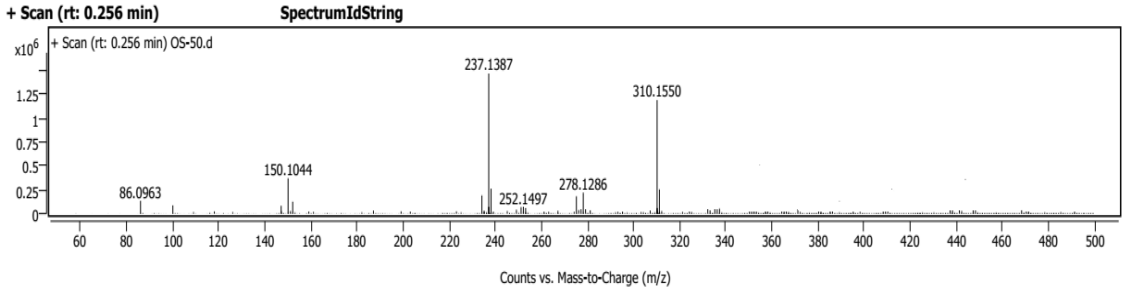


SpectrumIdString

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
150.1042		304406	7.16					
152.1012		97917	2.30					
223.1227		257787	6.06					
253.1332		59356	1.40					
264.1129	1	284609	6.69					
265.1175	1	60749	1.43					
278.1278		73462	1.73					
296.1401	1	4253173	100.00					
296.1763		184901	4.35					
297.1423	1	710782	16.71					
298.1449	1	79051	1.86					

7j) ^{1}H NMR, ^{13}C NMR and HRMS of *N*-methoxy-2,7-dimethyl-5-phenylimidazo[1,2-*a*]pyridine-3-carboxamide.

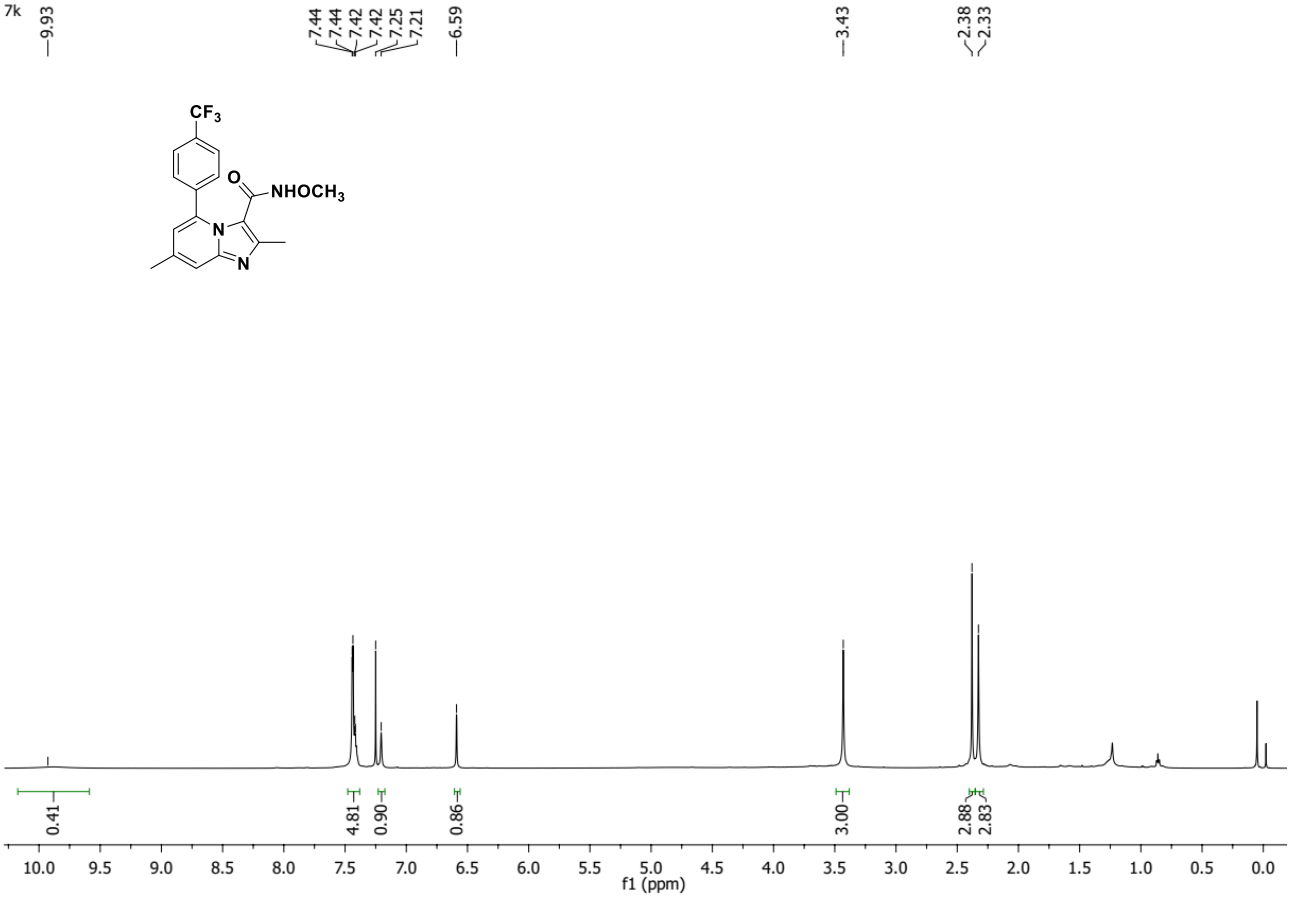




SpectrumIdString

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
86.0963		133518	9.09					
100.1119		85963	5.86					
147.0916		81349	5.54					
150.1044		369773	25.19					
152.1015		124309	8.47					
234.1600		189986	12.94					
237.1387	1	1468094	100.00					
237.1576		67760	4.62					
237.1733		69608	4.74					
238.1418	1	260792	17.76					
252.1497		70962	4.83					
275.1540		180519	12.30					
278.1286		219392	14.94					
310.1550	1	1190519	81.09					

7k) ^{1}H NMR, ^{13}C NMR and HRMS of *N*-methoxy-2,7-dimethyl-5-(4(trifluoromethyl)phenyl)imidazo-[1,2-*a*]pyridine-3-carboxamide.



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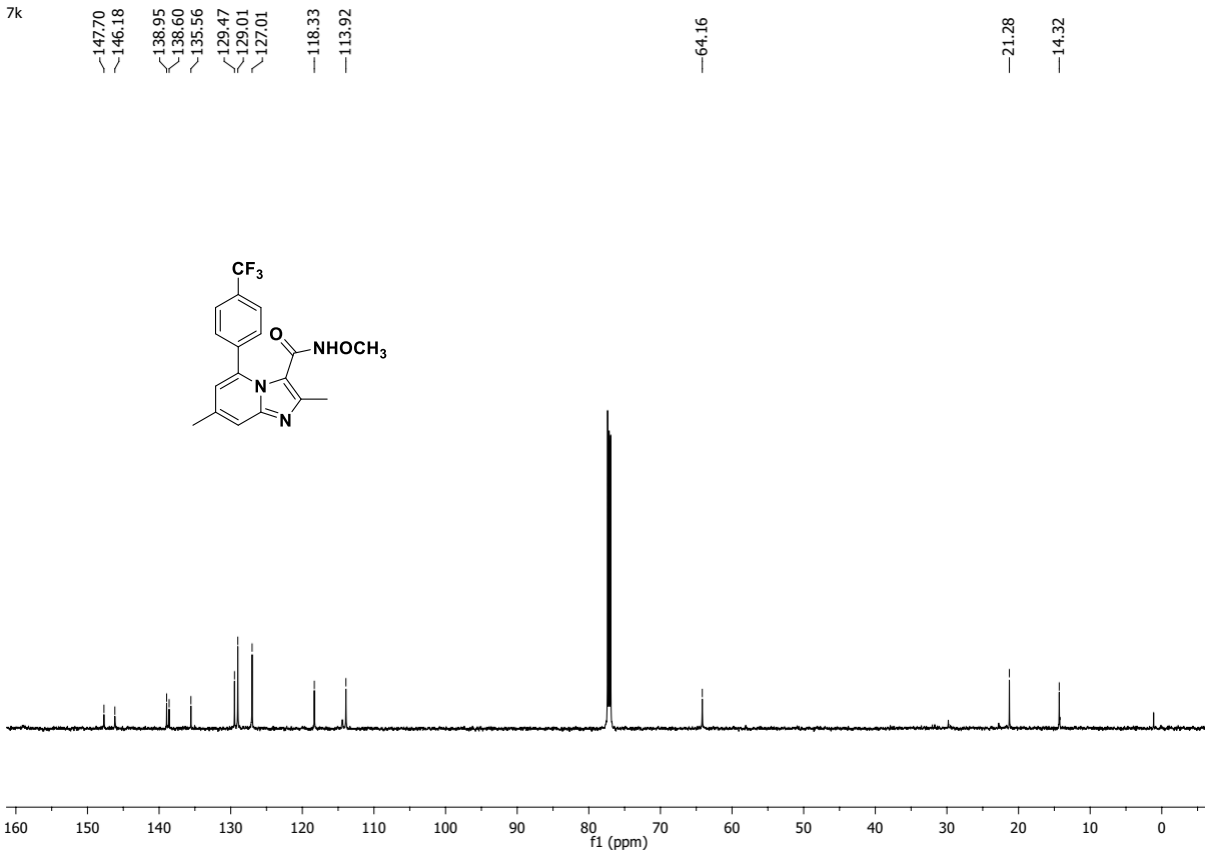

Peak Spec

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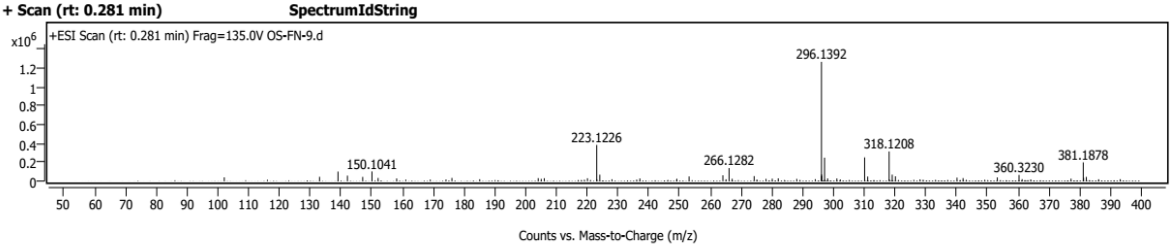

SpectrumIdString

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
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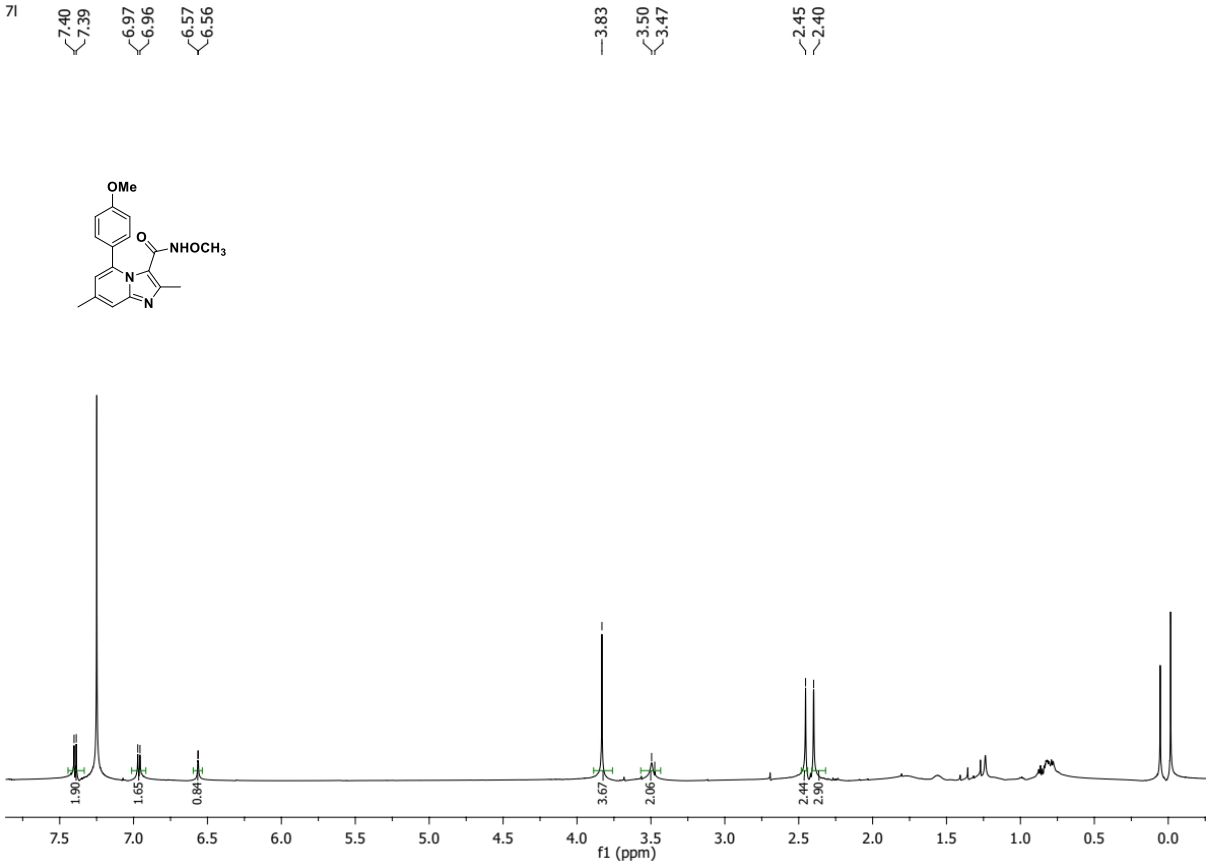
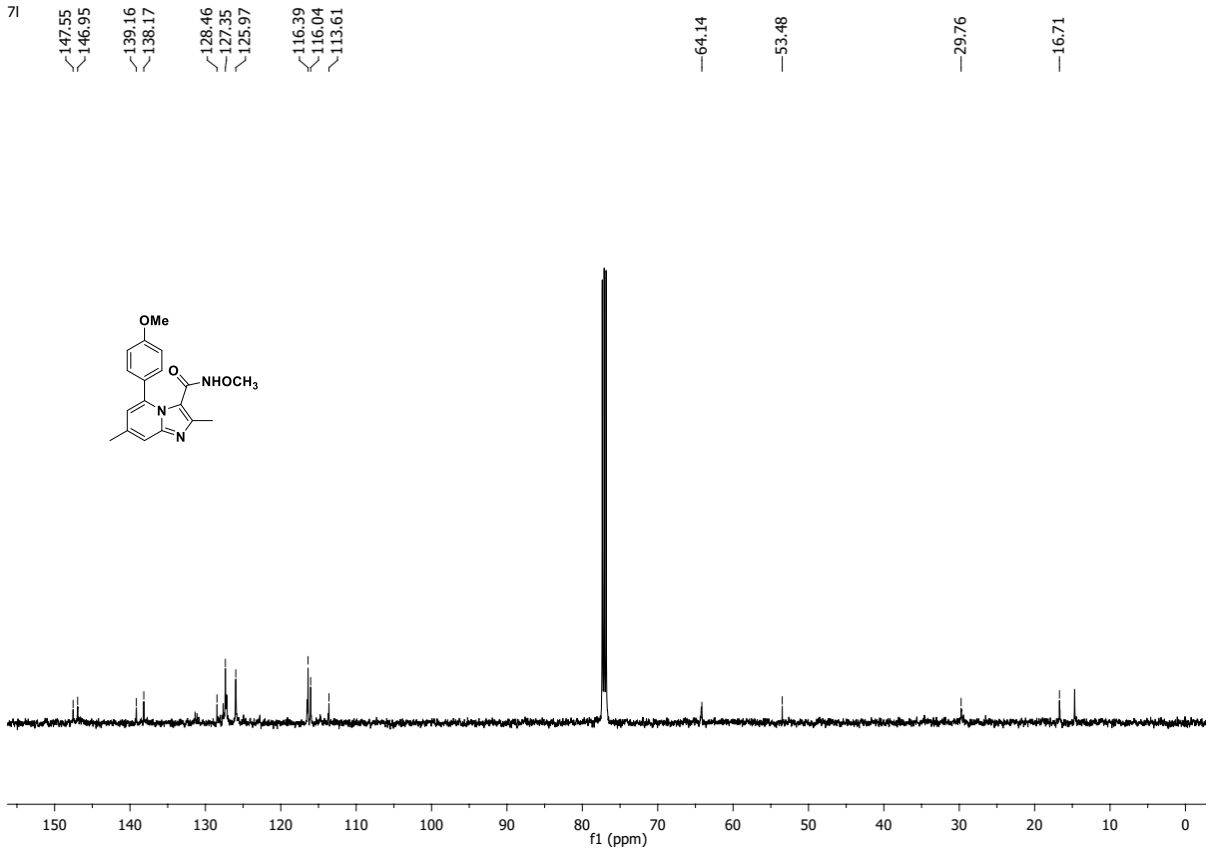
142.1336		57581	4.55					
150.1041		101802	8.04					
223.1226	1	383661	30.29					
224.1258	1	67732	5.35					
253.1331		49013	3.87					
264.1127		61481	4.85					
266.1282		138136	10.91					
274.2732		52630	4.16					
296.1392	1	1266455	100.00					
296.1603		51356	4.06					
296.1772		69121	5.46					
297.1423	1	248391	19.61					
310.1545	1	251393	19.85					
311.1574	1	47708	3.77					
318.1208	1	314493	24.83					
319.1240	1	68138	5.38					
320.1596		50502	3.99					
360.3230		65148	5.14					
381.1878		198670	15.69					

7l) ^{1}H NMR, ^{13}C NMR and HRMS of *N*-methoxy-5-(4-methoxyphenyl)-2,7-dimethylimidazo[1,2-*a*]pyridine-3-carboxamide.





Peak Spec

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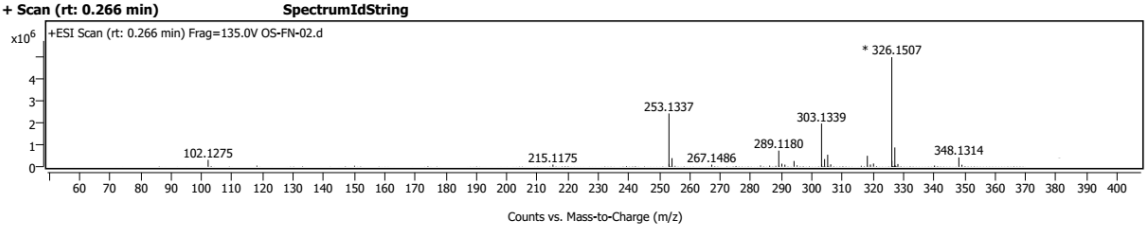

SpectrumIdString

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
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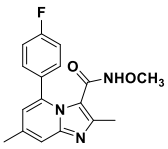
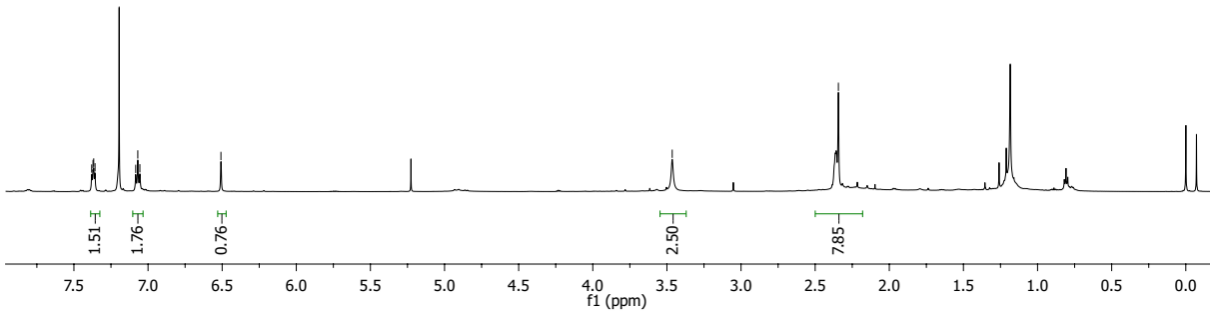
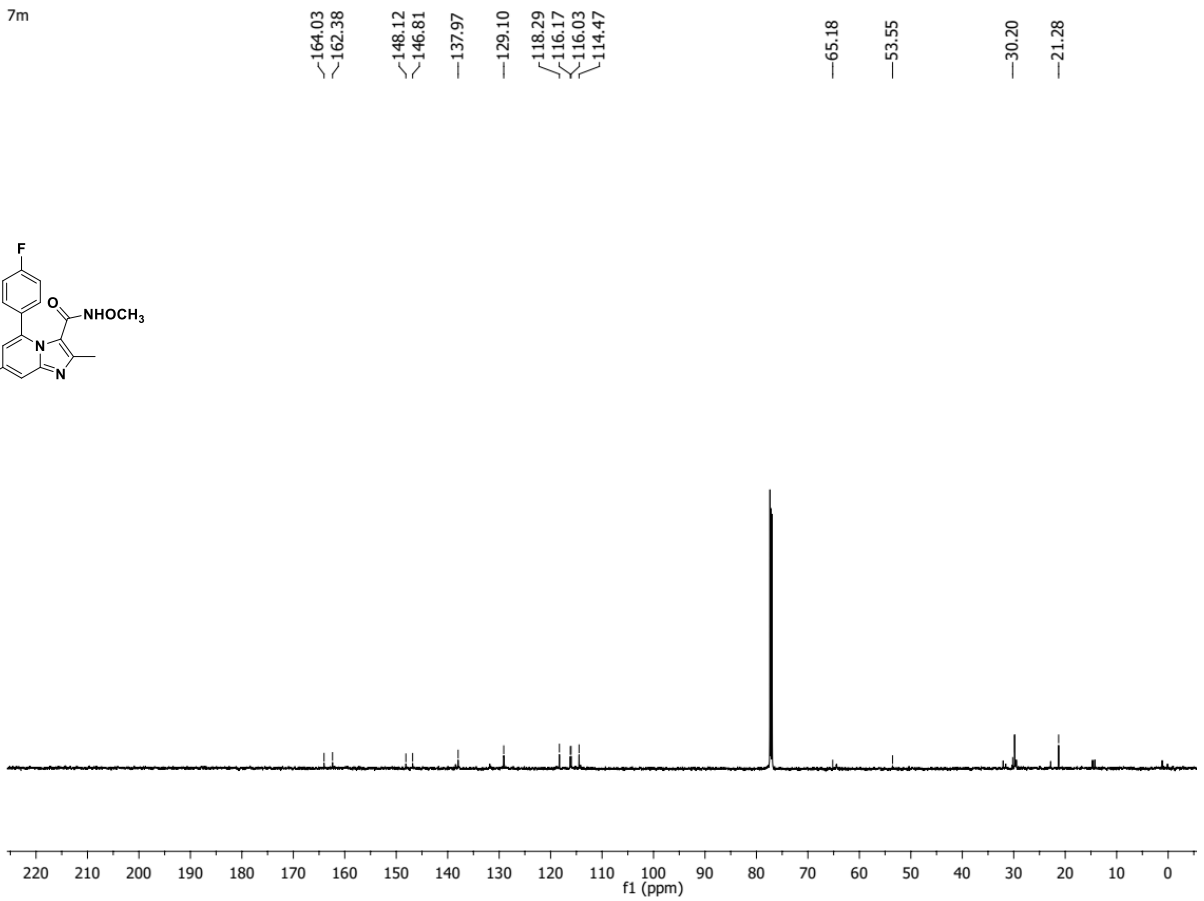
215.1175		93635	1.88					
253.1337	1	2414891	48.57					
253.1684		121183	2.44					
254.1365	1	384981	7.74					
267.1486		89711	1.80					
289.1180	1	726932	14.62					
290.1213	1	134292	2.70					
291.1332		90680	1.82					
294.1232	1	255960	5.15					
295.1274	1	55043	1.11					
303.1339	1	1957077	39.36					
303.1721		97305	1.96					
304.1361	1	343116	6.90					
305.1490	1	541147	10.88					
306.1521	1	102143	2.05					
318.1444	1	492039	9.90					
319.1475	1	94746	1.91					
320.1597		141631	2.85					
326.1507	1	4971873	100.00					
326.1896	1	262595	5.28					
327.1529	1	871952	17.54					
327.1927	1	54644	1.10					
328.1549	1	118484	2.38					
348.1314	1	418407	8.42					
349.1346	1	85100	1.71					

7m) ^{1}H NMR, ^{13}C NMR and HRMS of 5-(4-Fluorophenyl)-*N*-methoxy-2,7-dimethylimidazo[1,2-*a*]pyridine-3-carboxamide.





7m



Peak Spec

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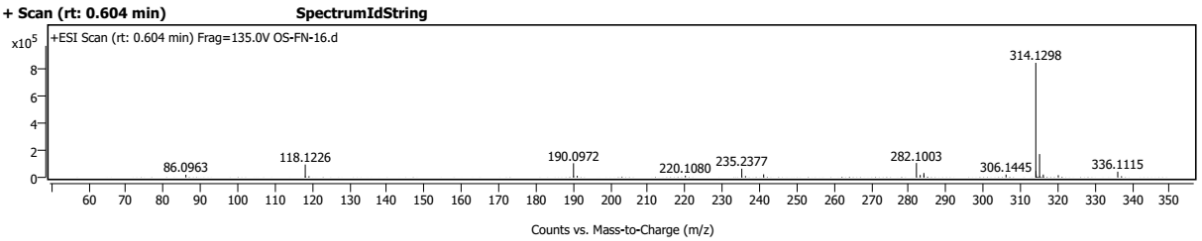
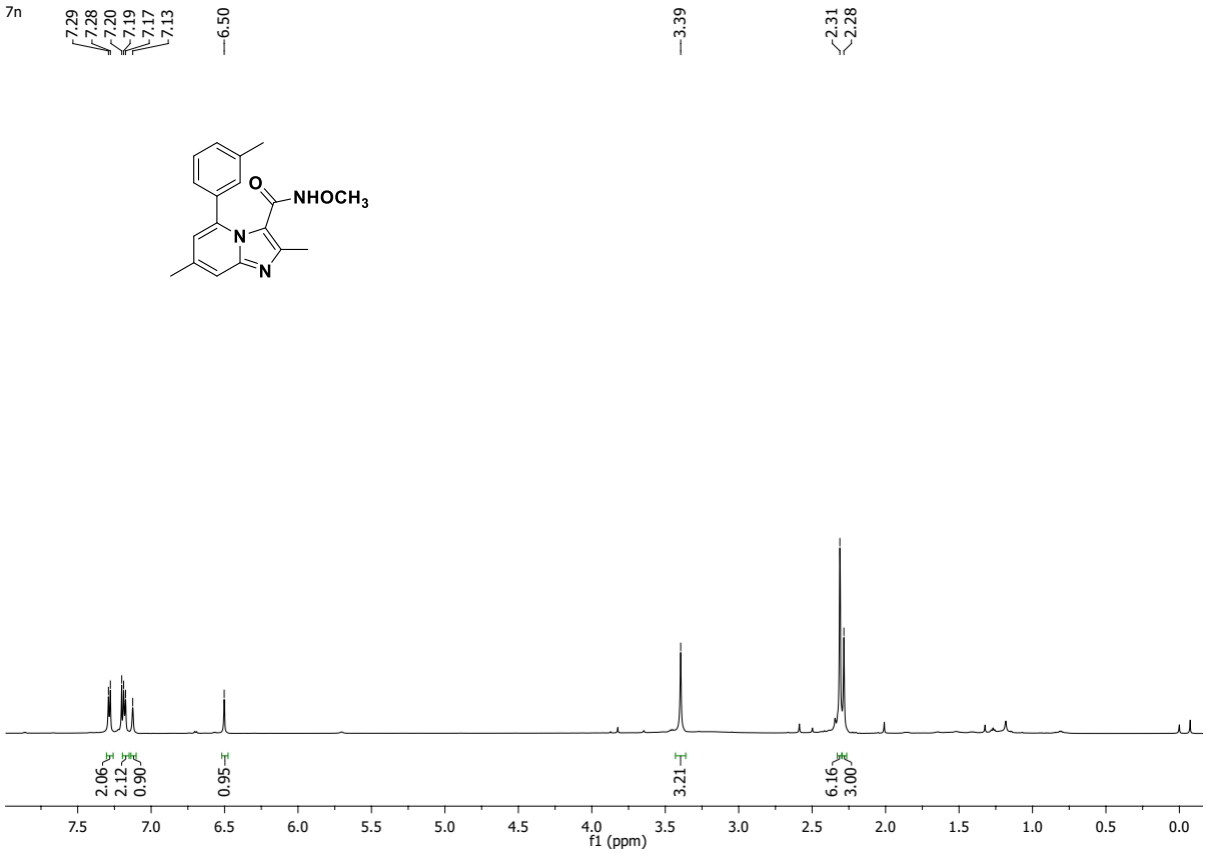
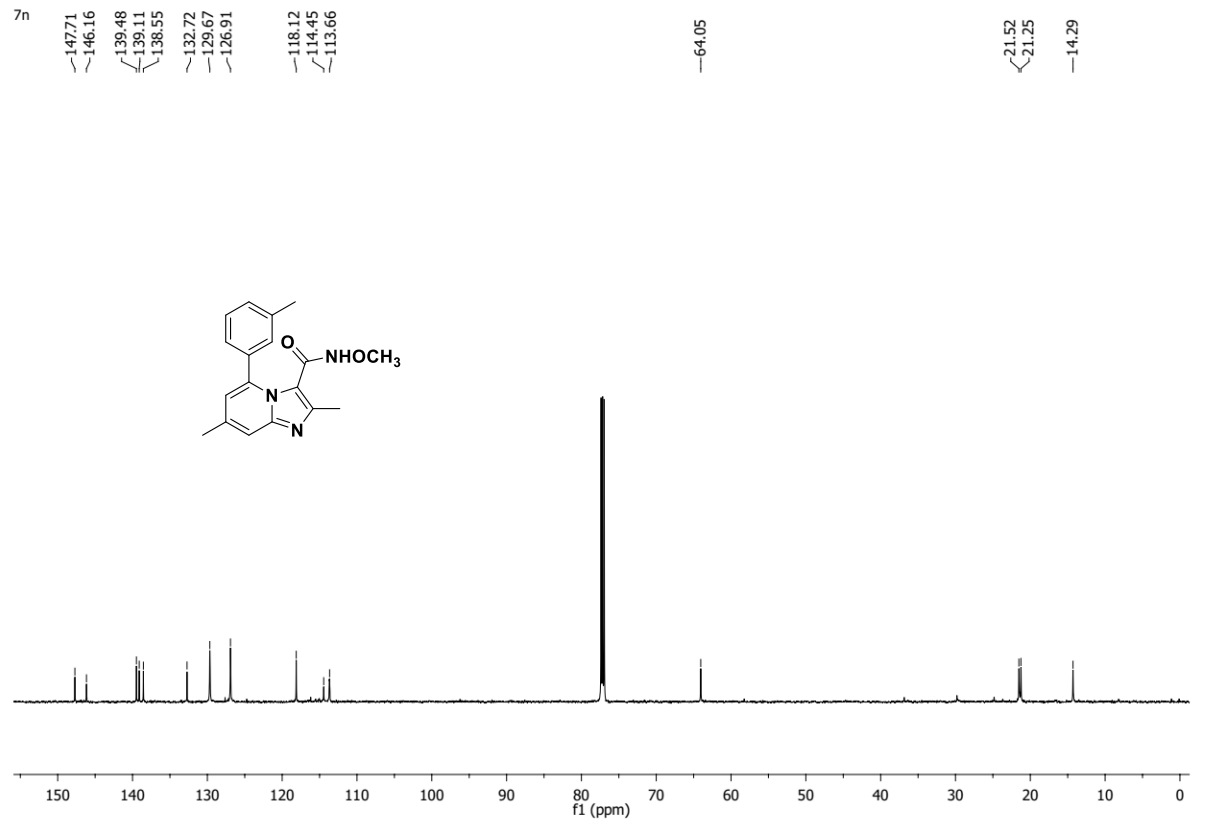


SpectrumIdString

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
86.0963		19513	2.31					
118.1226	1	94752	11.21					
119.1261	1	8534	1.01					
190.0972	1	104401	12.35					
191.1006	1	11350	1.34					
220.1080		12533	1.48					
235.2377	1	63984	7.57					
236.2411	1	9833	1.16					
241.1131		22422	2.65					
282.1003	1	106135	12.55					
283.1045	1	17595	2.08					
284.0969	1	32244	3.81					
284.1191		15409	1.82					
306.1445		20603	2.44					
314.1298	1	845420	100.00					
314.1689		47995	5.68					
314.2212		21632	2.56					
315.1328	1	172125	20.36					
316.1356	1	20741	2.45					
320.1597		16101	1.90					
336.1115	1	42052	4.97					
337.1150	1	8524	1.01					

7n) ^{1}H NMR, ^{13}C NMR and HRMS of *N*-methoxy-2,7-dimethyl-5-(*m*-tolyl)imidazo[1,2-*a*]pyridine-3-carboxamide.





Peak Spec

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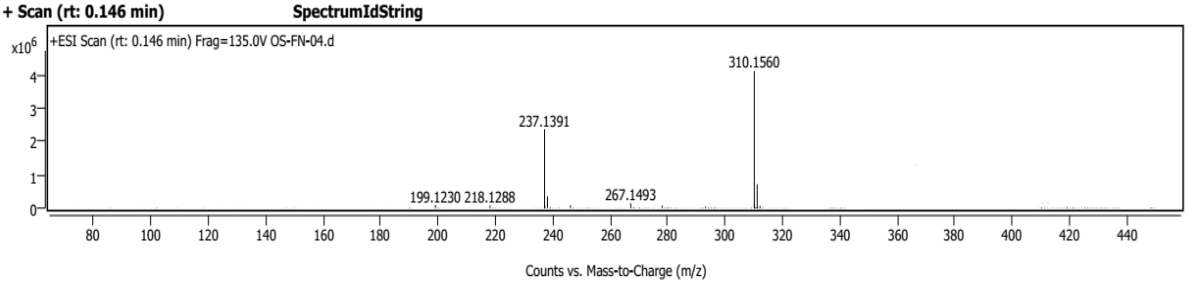
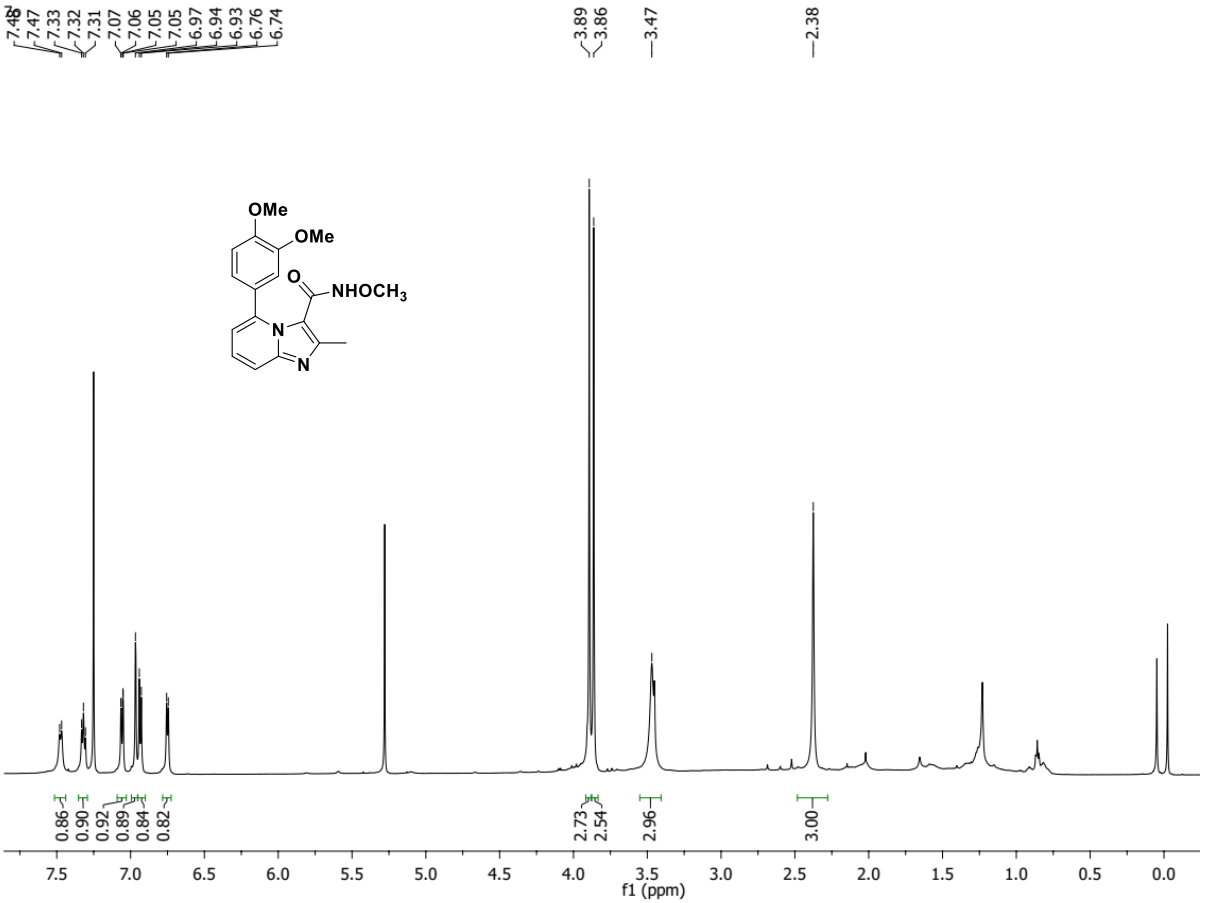


SpectrumIdString

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
199.1230		90902	2.21					
218.1288		79721	1.93					
237.1391	1	2370771	57.54					
237.1578		104713	2.54					
237.1736		92115	2.24					
238.1423	1	354015	8.59					
246.1602		83913	2.04					
267.1493		147024	3.57					
310.1560	1	4120033	100.00					
310.1944		179840	4.37					

7o) ^{1}H NMR, ^{13}C NMR and HRMS of 5-(3,4-dimethoxyphenyl)-*N*-methoxy-2-methylimidazo[1,2-*a*]pyridine-3-carboxamide.



7o

150.04
149.06
147.36
146.44
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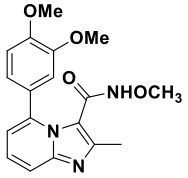
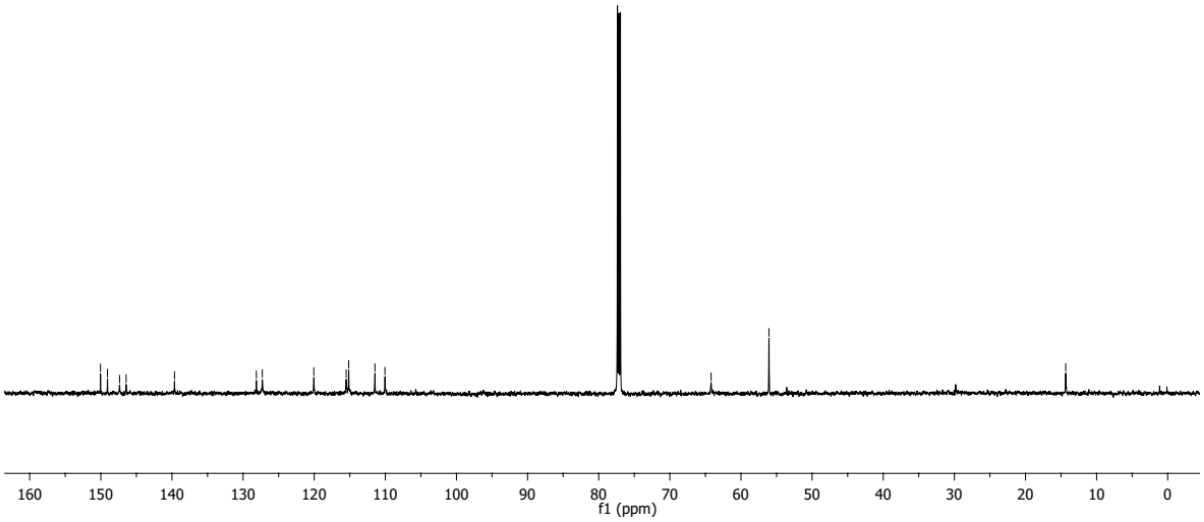
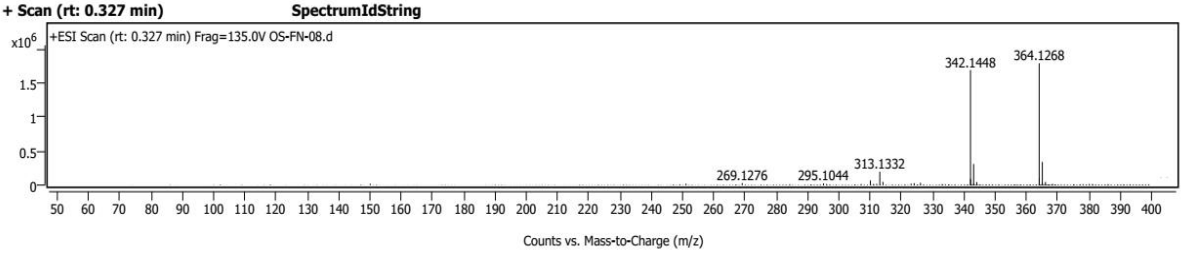




Peak Spec

+ Scan (rt: 0.327 min) **SpectrumIdString**



SpectrumIdString

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
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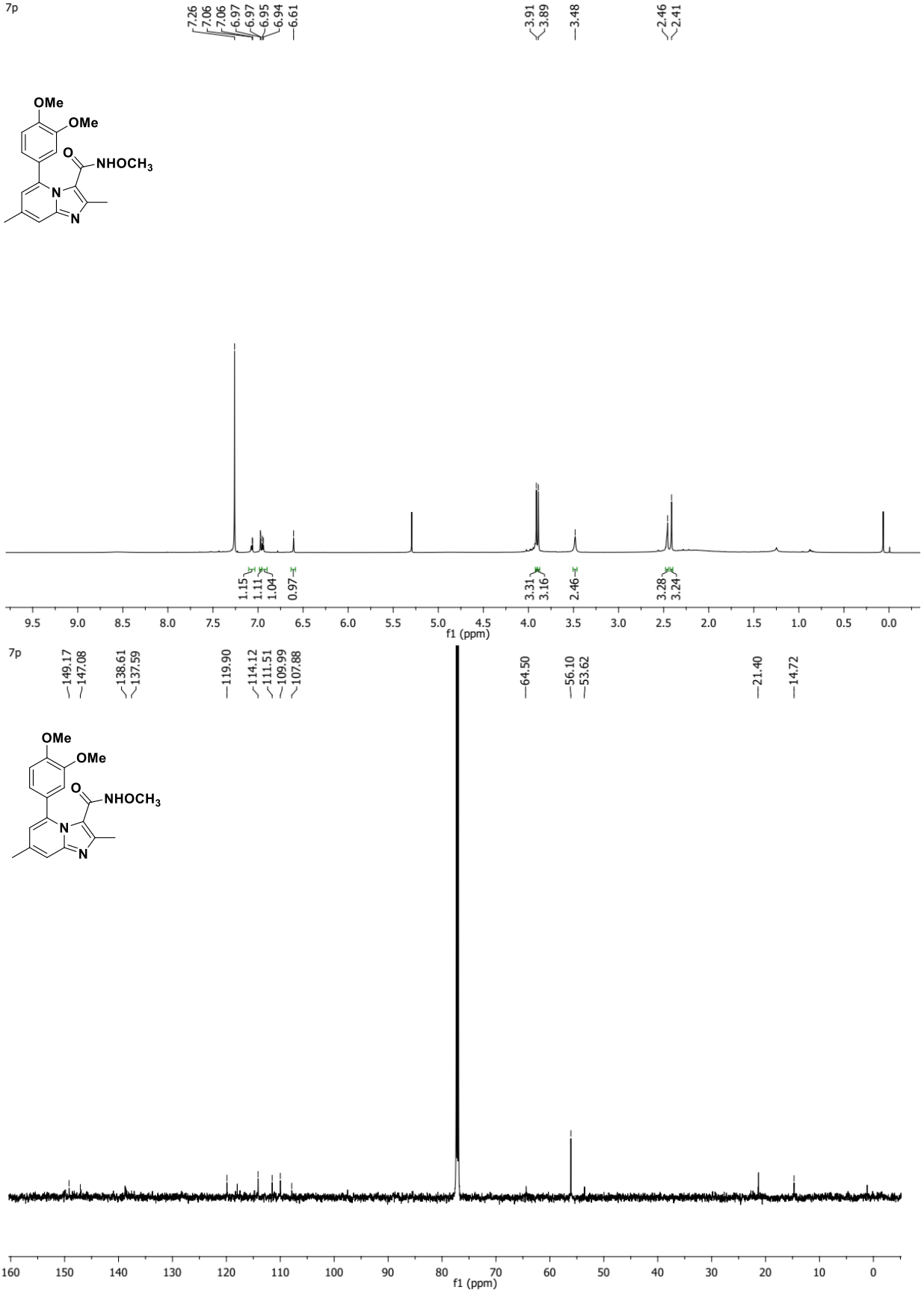
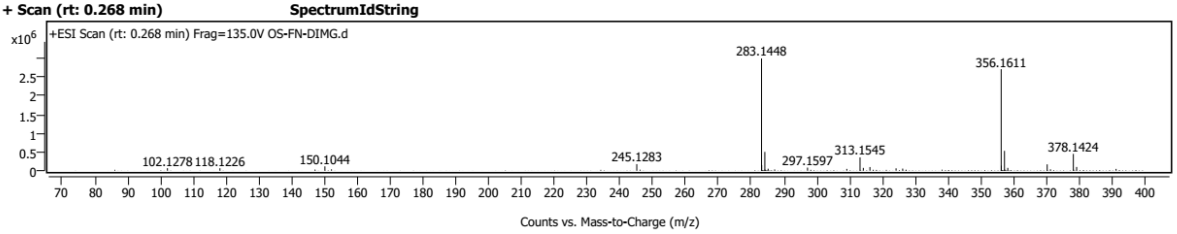
295.1044		24966	1.39					
310.1180		67933	3.79					
313.1332	1	198279	11.07					
314.1362	1	47415	2.65					
324.1336		27689	1.55					
326.1491		33047	1.85					
342.1448	1	1692531	94.51					
342.1852		90876	5.07					
343.1477	1	310169	17.32					
344.1504	1	44574	2.49					
356.1600	1	391998	21.89					
356.1984		22768	1.27					
357.1631	1	83379	4.66					
364.1268	1	1790915	100.00					
364.1684	1	98392	5.49					
365.1296	1	341765	19.08					
365.1678	1	21562	1.20					
366.1321	1	45738	2.55					

7p) ^{1}H NMR, ^{13}C NMR and HRMS of 5-(3,4-Dimethoxyphenyl)-*N*-methoxy-2,7-dimethylimidazo[1,2-*a*]pyridine-3-carboxamide.



Peak Spec

+ Scan (rt: 0.268 min) **SpectrumIdString**

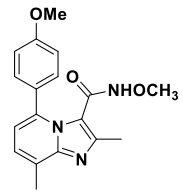


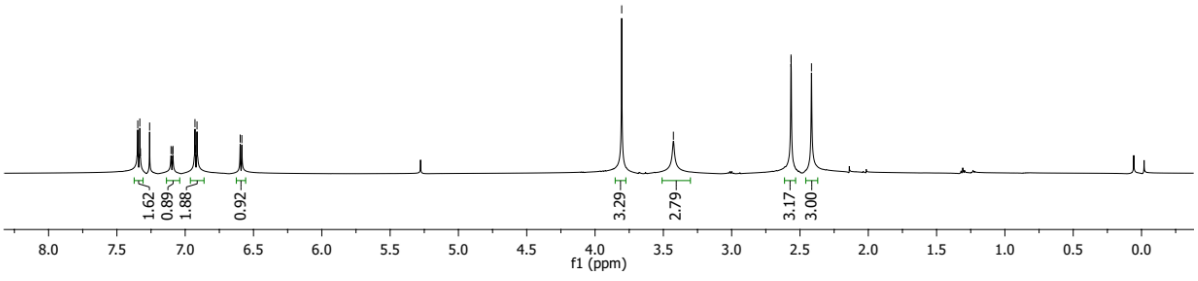
SpectrumIdString

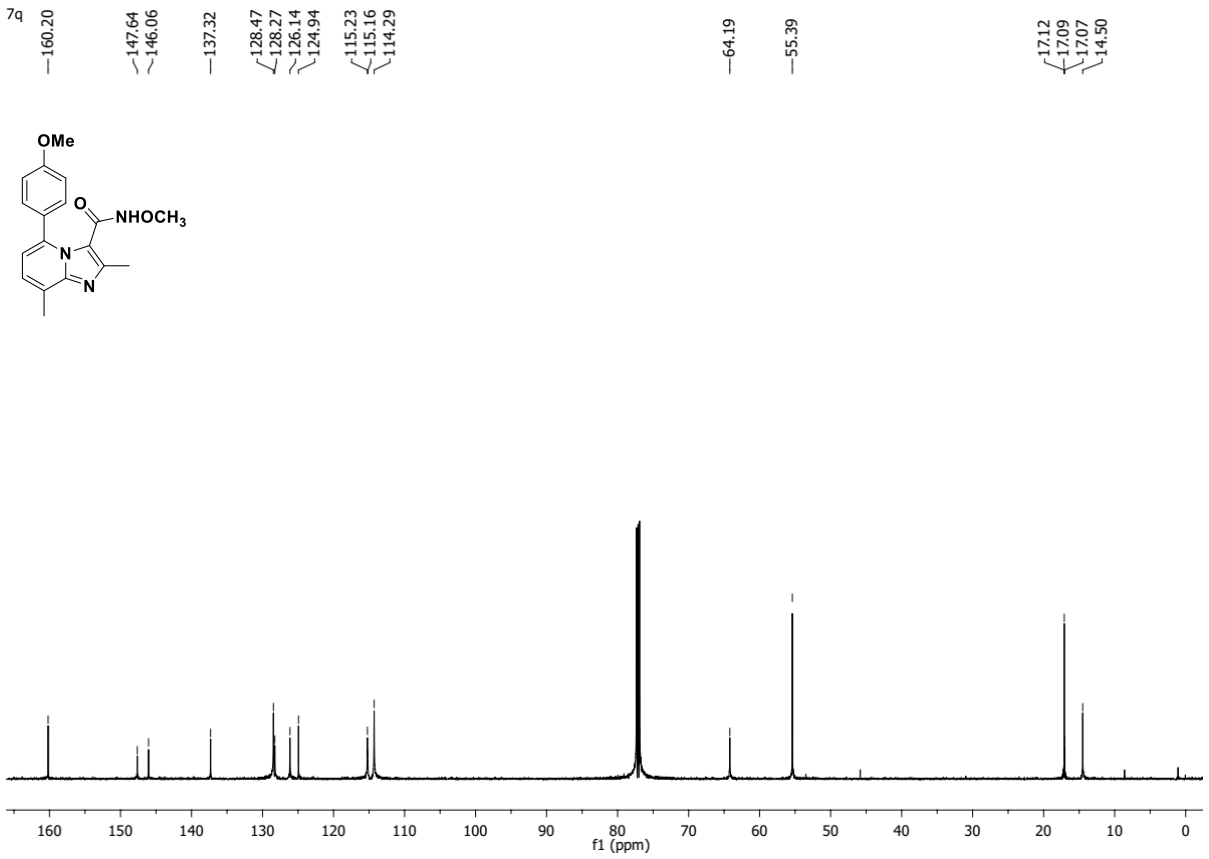
m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
102.1278		65474	2.18					
118.1226		64116	2.14					
150.1044		113693	3.79					
245.1283		173904	5.80					
283.1448	1	2998619	100.00					
283.1811		147216	4.91					
284.1474	1	500883	16.70					
297.1597		80731	2.69					
313.1545	1	354265	11.81					
314.1577	1	73392	2.45					
316.1654		95422	3.18					
324.1337		61088	2.04					
326.1496		54239	1.81					
356.1611	1	2712335	90.45					
356.2019		133553	4.45					
357.1638	1	528738	17.63					
358.1660	1	73531	2.45					
370.1760		167849	5.60					
378.1424	1	446842	14.90					
379.1455	1	97780	3.26					

MassHunter Qual 10.0

7q) ^{1}H NMR, ^{13}C NMR and HRMS of *N*-methoxy-5-(4-methoxyphenyl)-2,8-dimethylimidazo[1,2-*a*]pyridine-3-carboxamide.







Peak Spec

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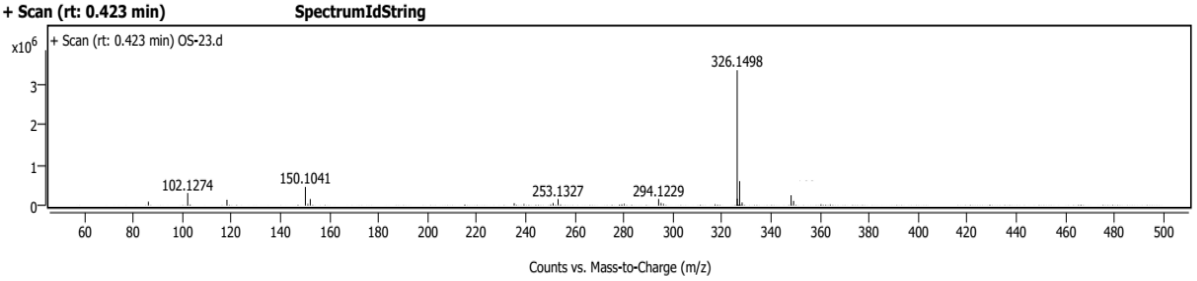

SpectrumIdString

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
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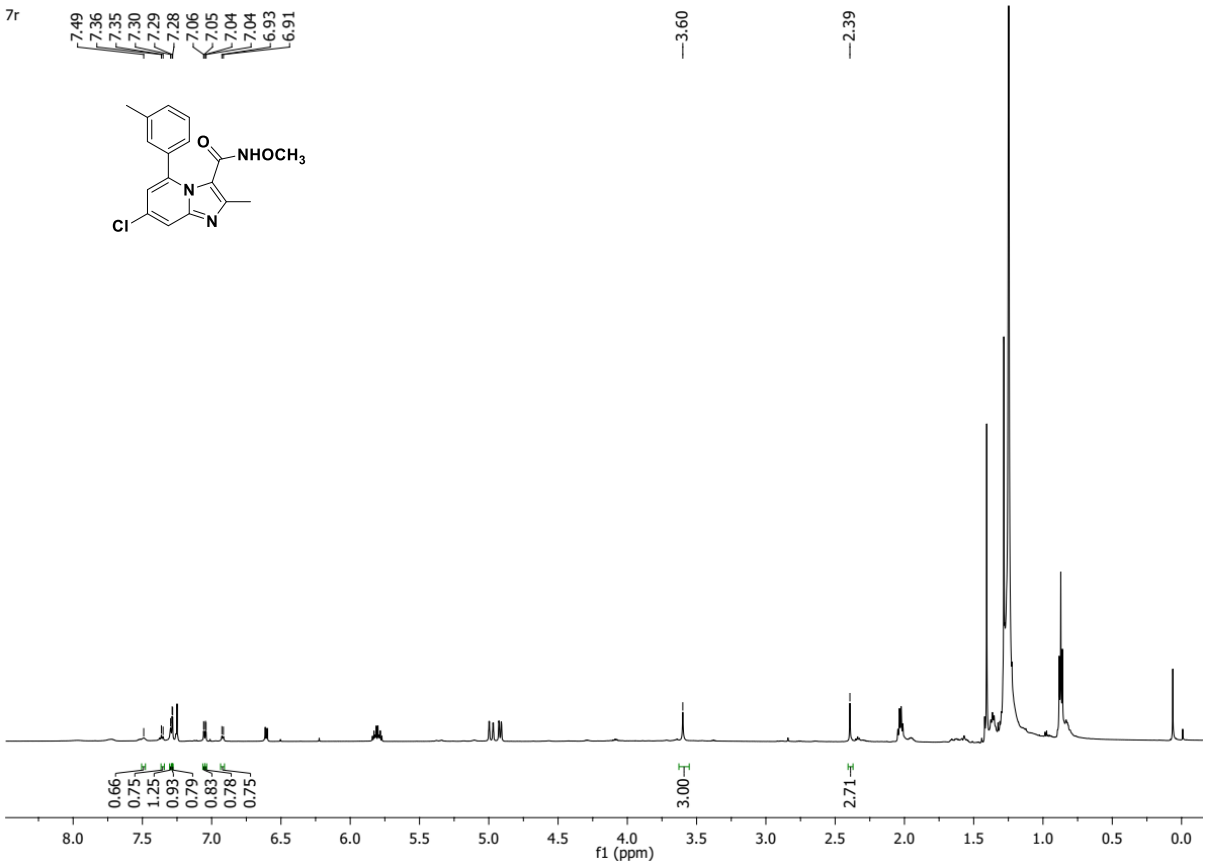
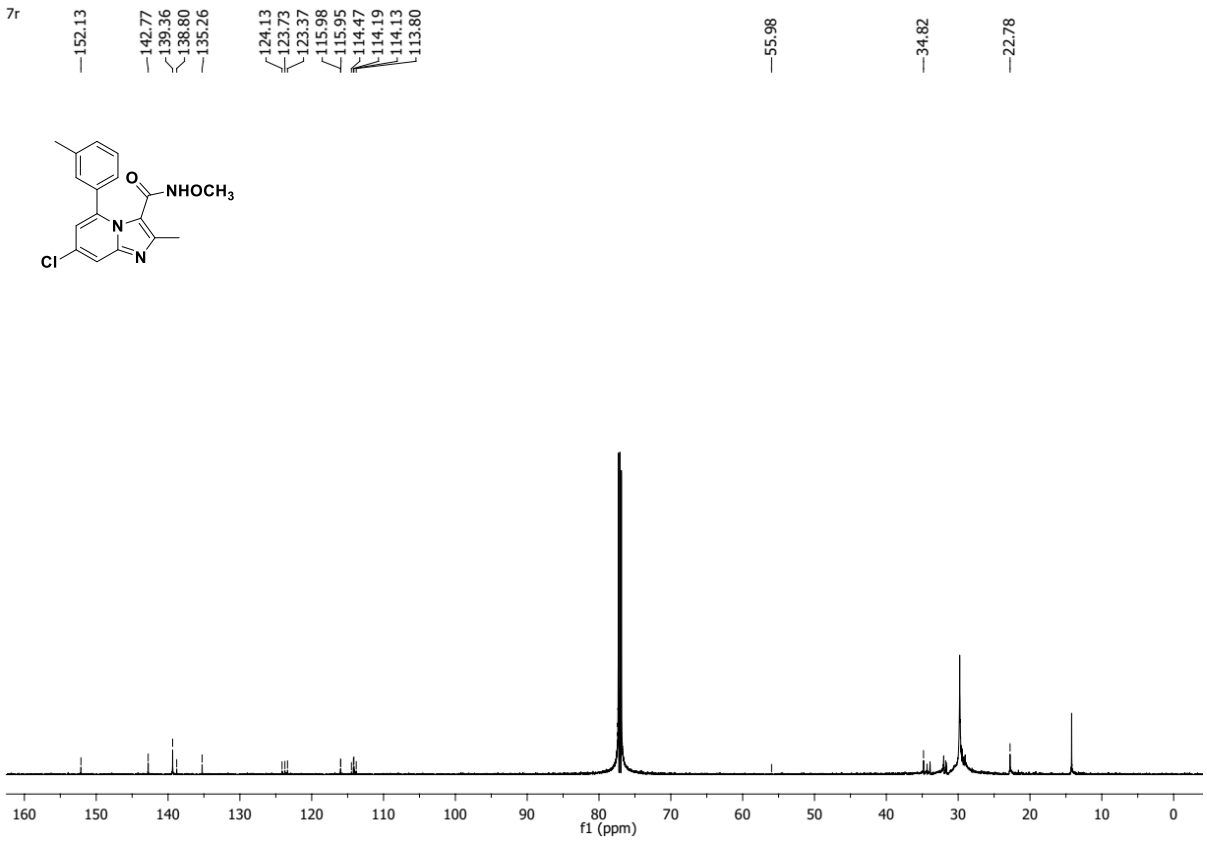
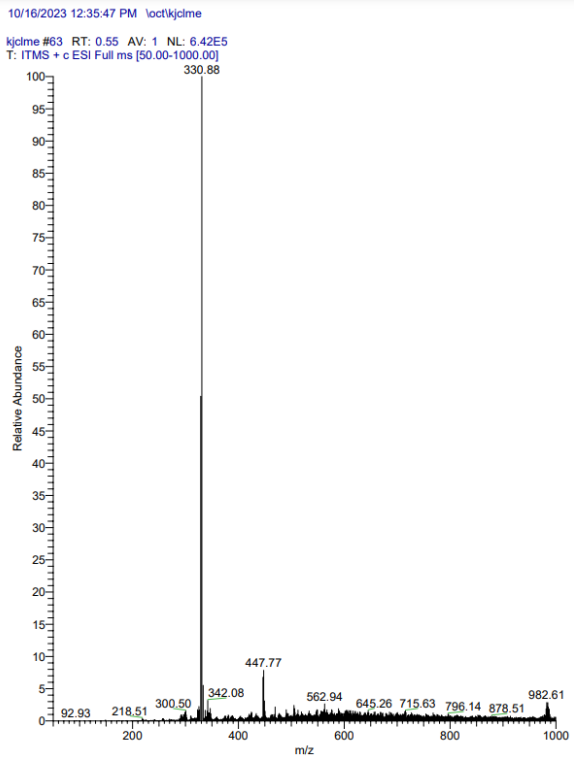
102.1274		303774	9.06					
118.1223		137177	4.09					
150.1041		457571	13.65					
152.1011		154327	4.60					
235.2375		51561	1.54					
251.1174		55361	1.65					
253.1327		155229	4.63					
280.1074		34716	1.04					
294.1229	1	156053	4.66					
295.1293	1	57678	1.72					
296.1378		34785	1.04					
326.1498	1	3351315	100.00					
326.1890		165218	4.93					
327.1523	1	601325	17.94					
328.1549	1	68217	2.04					

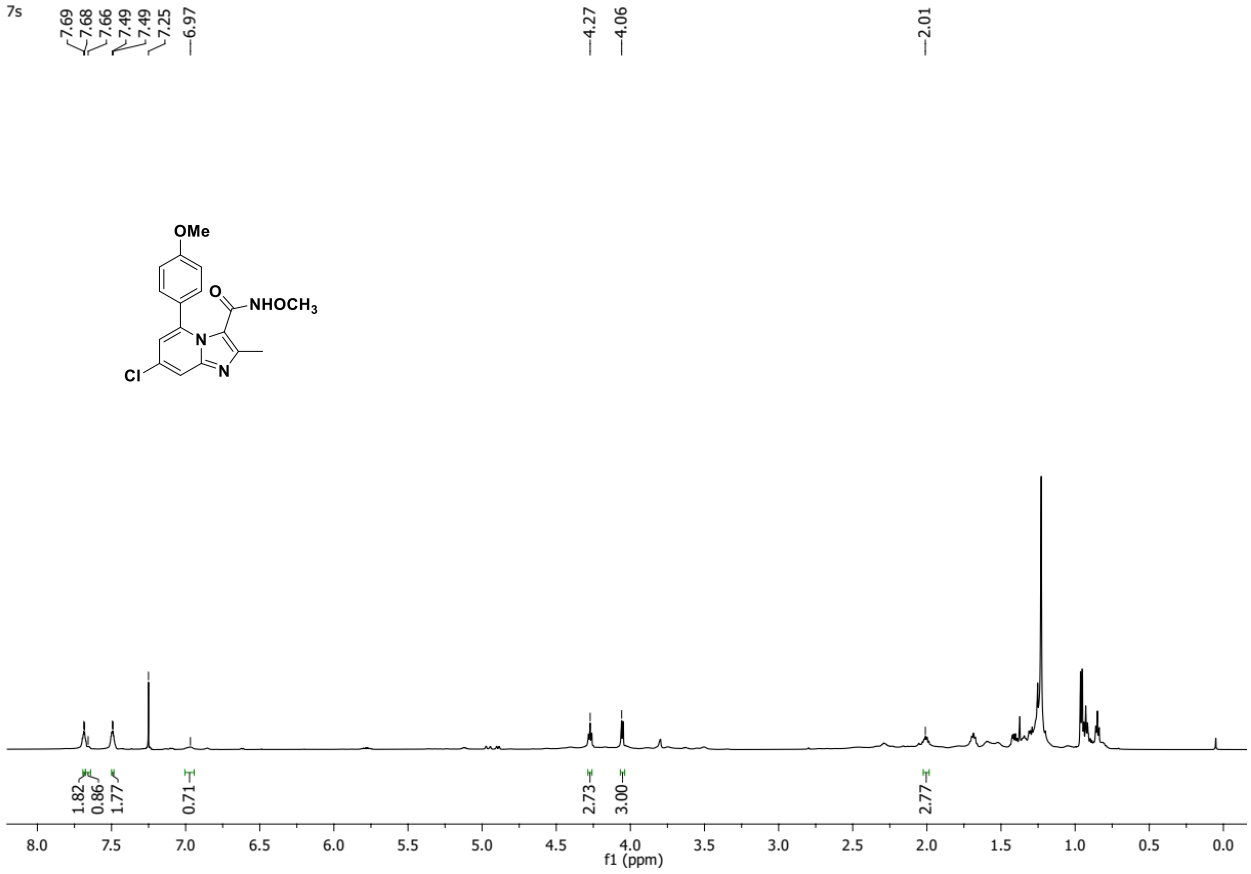
7r) ^{1}H NMR, ^{13}C NMR and LTQ of 7-Chloro-*N*-methoxy-2-methyl-5-(*m*-tolyl)imidazo[1,2-*a*]pyridine-3-carboxamide.





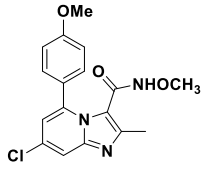


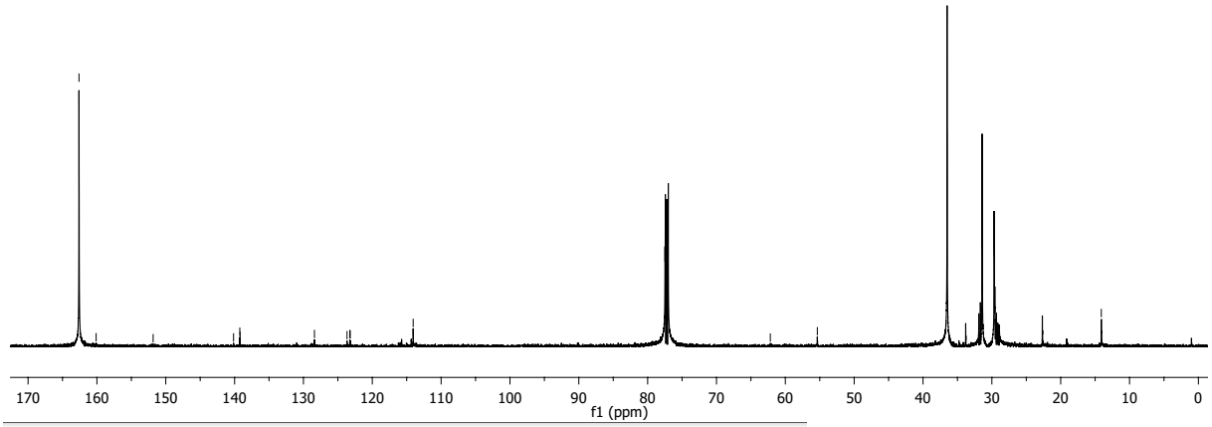
7s) ^{1}H NMR, ^{13}C NMR and HRMS of 7-Chloro-*N*-methoxy-5-(4-methoxyphenyl)-2-methylimidazo-[1,2-*a*]pyridine-3-carboxamide.

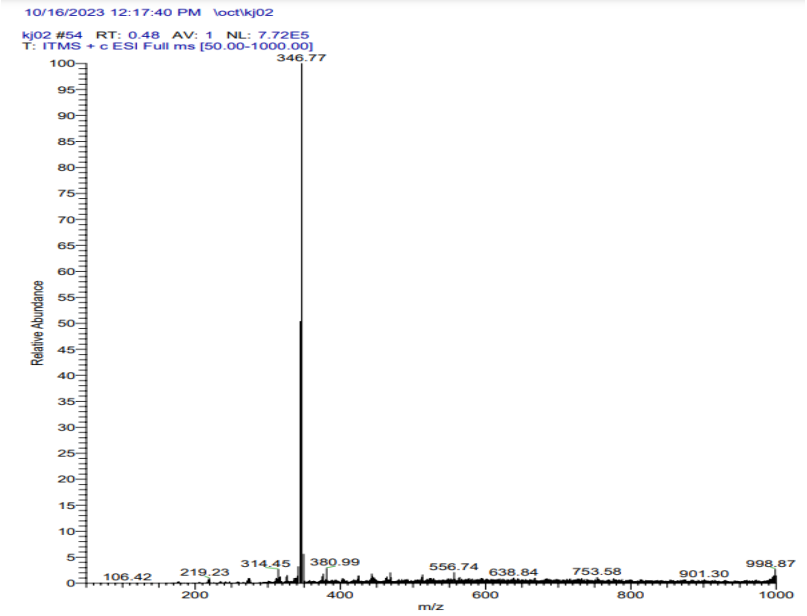


7s

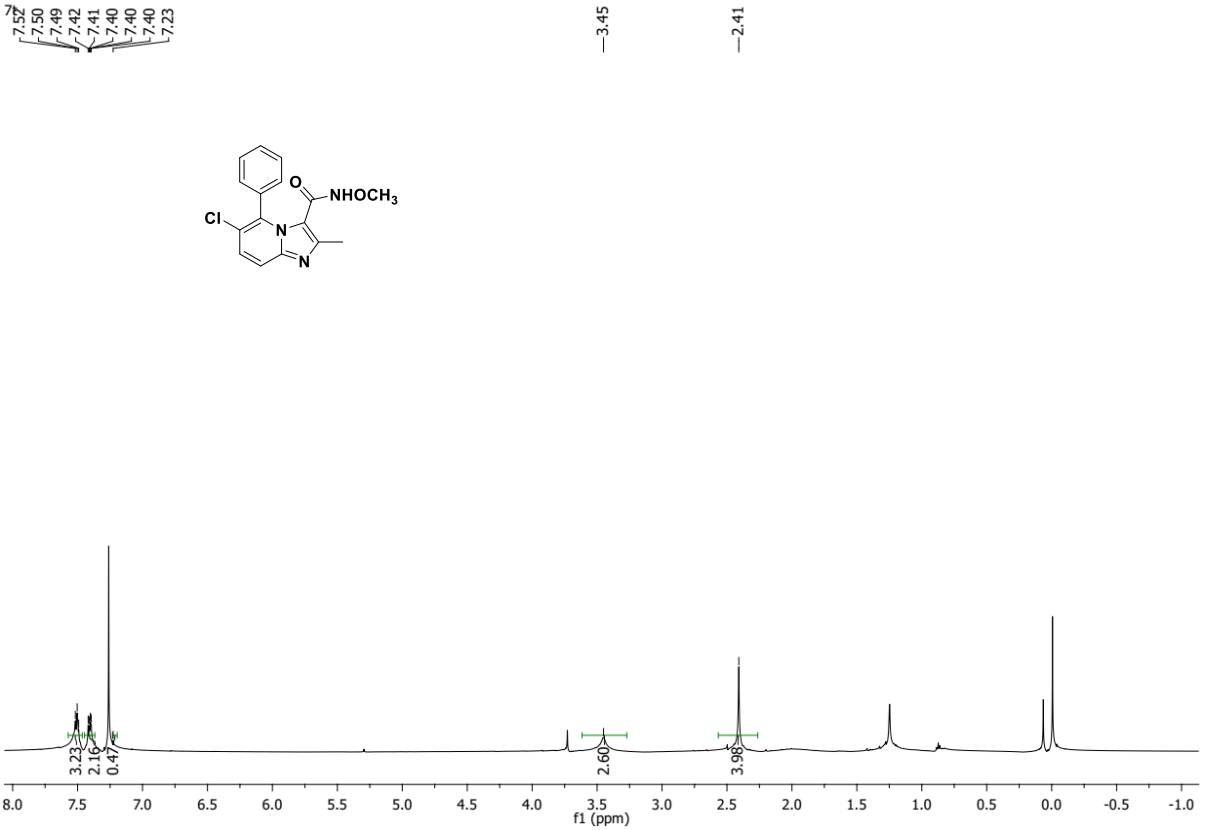
162.60
160.11
151.83
140.15
139.24
139.20
128.40
123.67
123.26
123.21
114.06
62.18
55.35
14.10

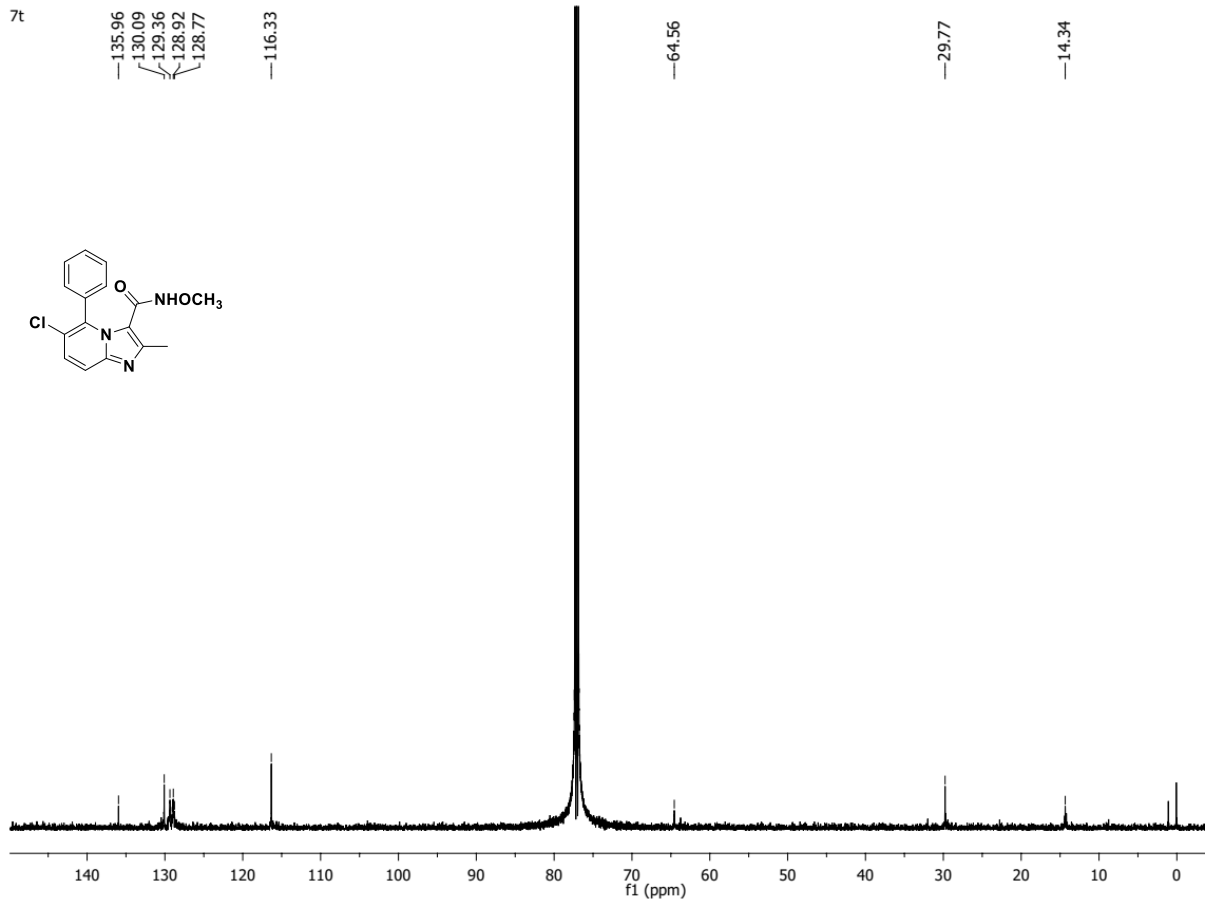






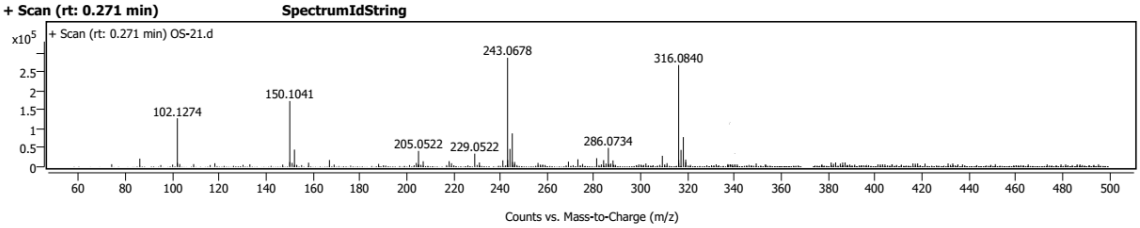
7t) ^{1}H NMR, ^{13}C NMR and HRMS of 6-Chloro-*N*-methoxy-2-methyl-5-phenylimidazo[1,2-*a*]pyridine-3-carboxamide.





Peak Spec

+ Scan (rt: 0.271 min) **SpectrumIdString**



SpectrumIdString

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
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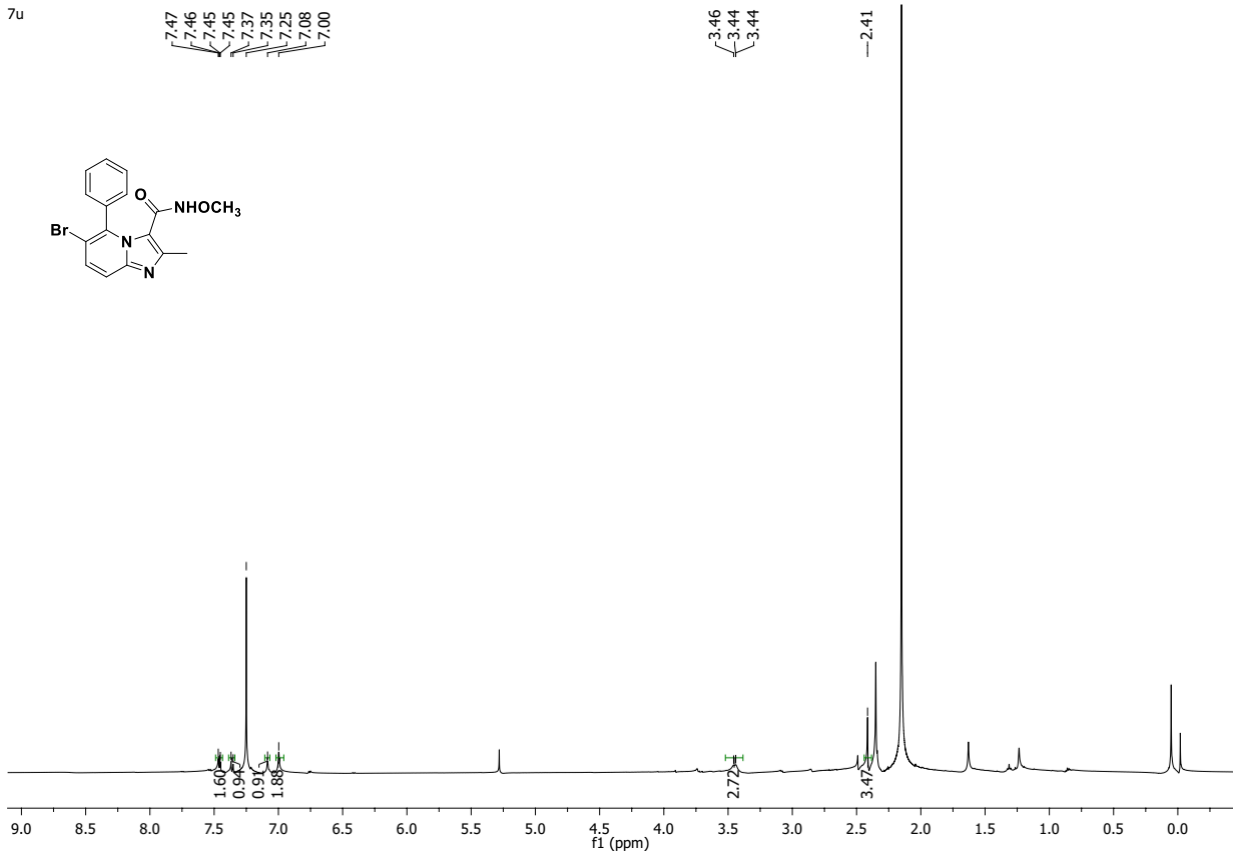
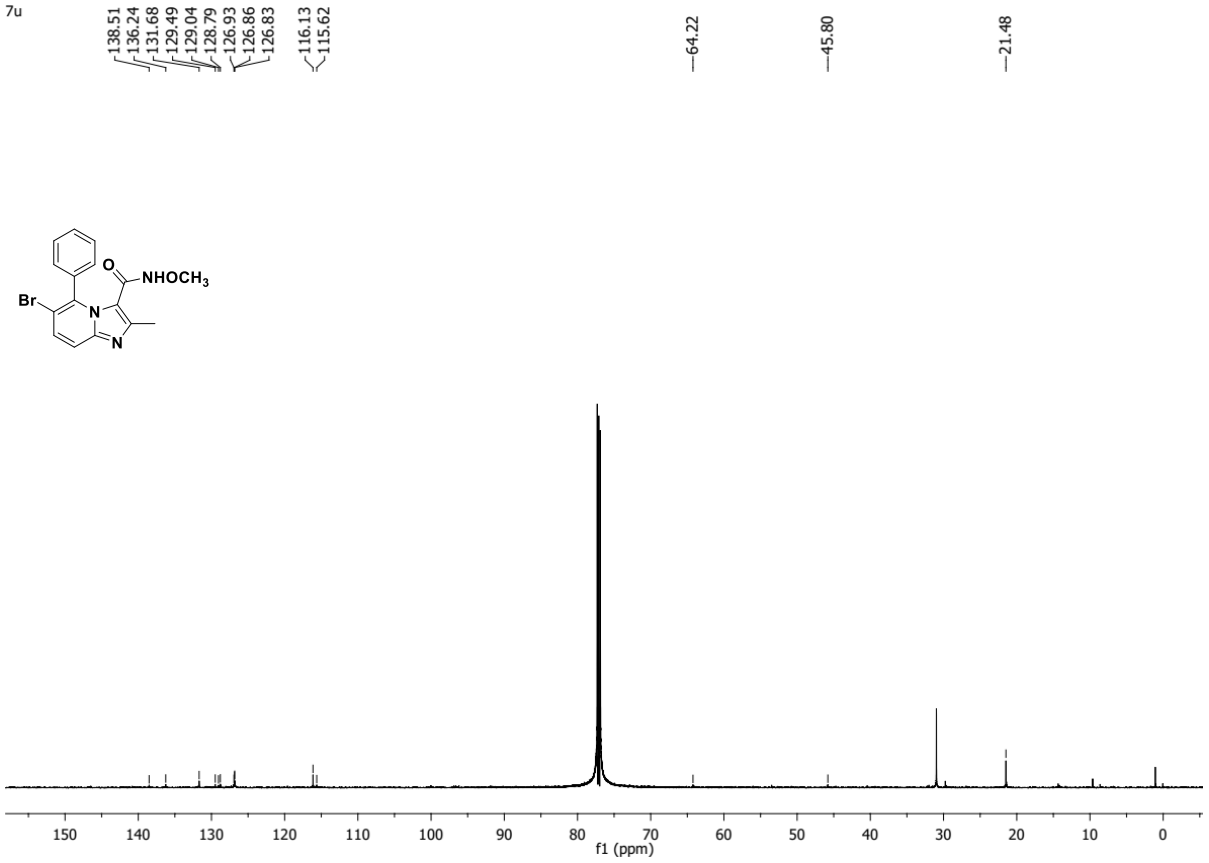
150.1041		172745	60.33					
152.1012		45316	15.83					
205.0522		41787	14.59					
229.0522		34670	12.11					
243.0678	1	286338	100.00					
244.0705	1	46971	16.40					
245.0649	1	87864	30.69					
286.0734		49784	17.39					
309.1145		28953	10.11					
316.0840	1	267419	93.39					
317.0872	1	44354	15.49					
318.0811	1	78060	27.26					

7u) ^{1}H NMR, ^{13}C NMR and HRMS of 6-Bromo-*N*-methoxy-2-methyl-5-phenylimidazo[1,2-*a*]pyridine-3-carboxamide.

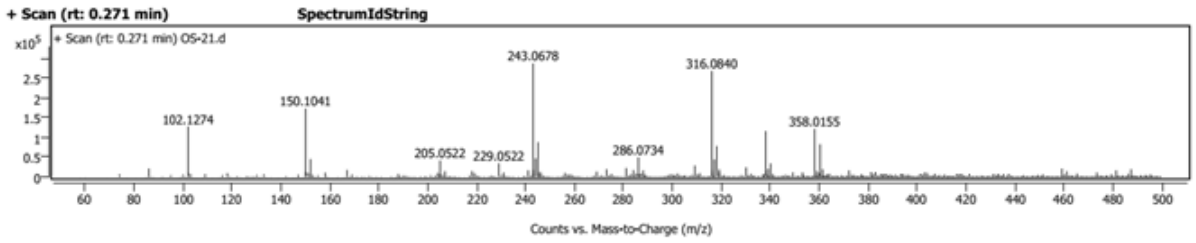


7u



Peak Spec

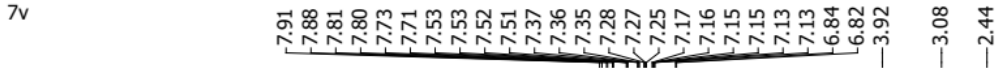
+ Scan (rt: 0.271 min) **SpectrumIdString**

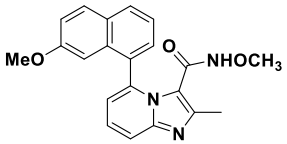


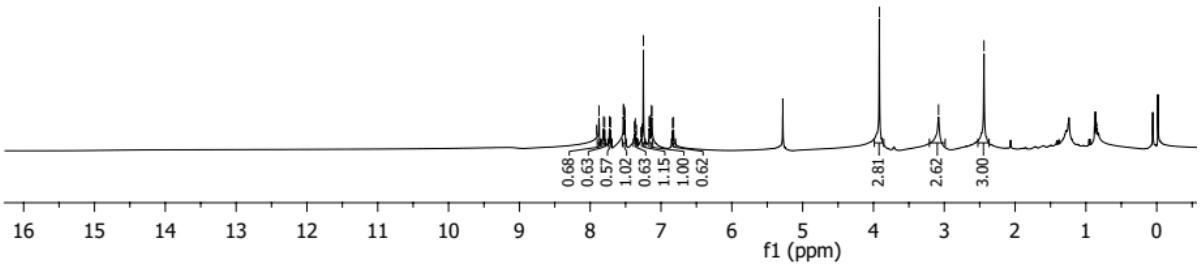
SpectrumIdString

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
102.1274		127627	44.57					
150.1041		172745	60.33					
152.1012		45316	15.83					
205.0522		41787	14.59					
229.0522		34670	12.11					
243.0678	1	286338	100.00					
244.0705	1	46971	16.40					
245.0649	1	87864	30.69					
286.0734		49784	17.39					
309.1145		28953	10.11					
316.0840	1	267419	93.39					
317.0872	1	44354	15.49					
318.0811	1	78060	27.26					
338.0657		115922	40.48					
340.0631		34414	12.02					
358.0155		121389	42.39					
360.3227		82555	28.83					

7v) ^{1}H NMR, ^{13}C NMR and HRMS of *N*-methoxy-5-(7-methoxynaphthalen-1-yl)-2-methylimidazo[1,2-*a*]pyridine-3-carboxamide.







7v

158.61
147.53
146.71
139.93
134.95
129.91
128.53
127.80
127.68
127.30
126.04
126.01
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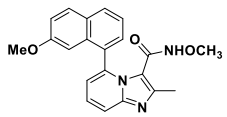
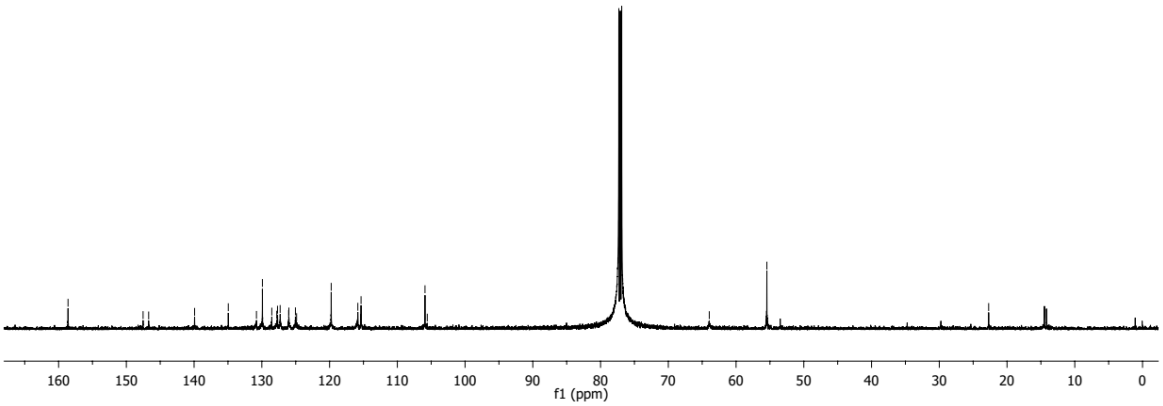
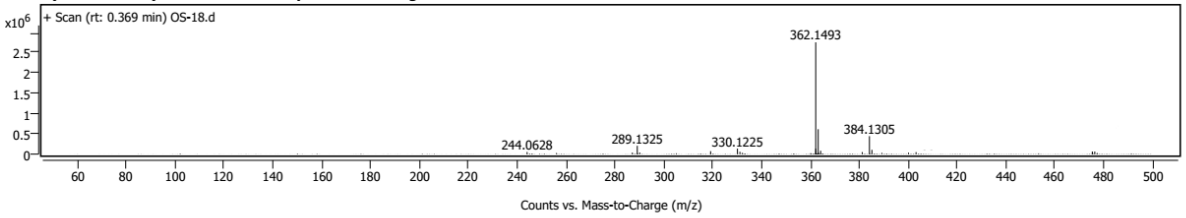
115.35
105.92
105.58
63.95
55.45
22.71





eak Spec

Scan (rt: 0.369 min) **SpectrumIdString**



SpectrumIdString

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
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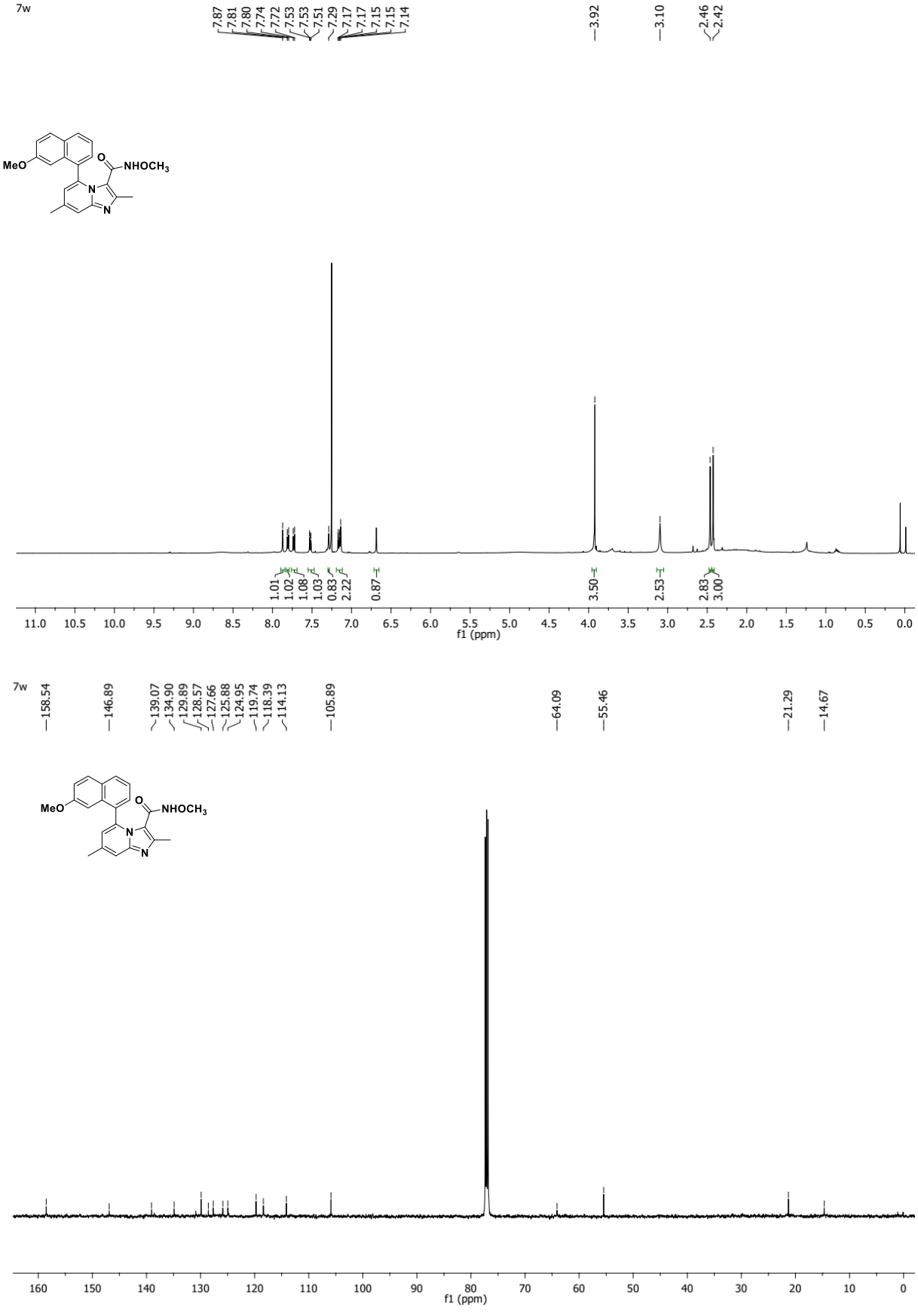
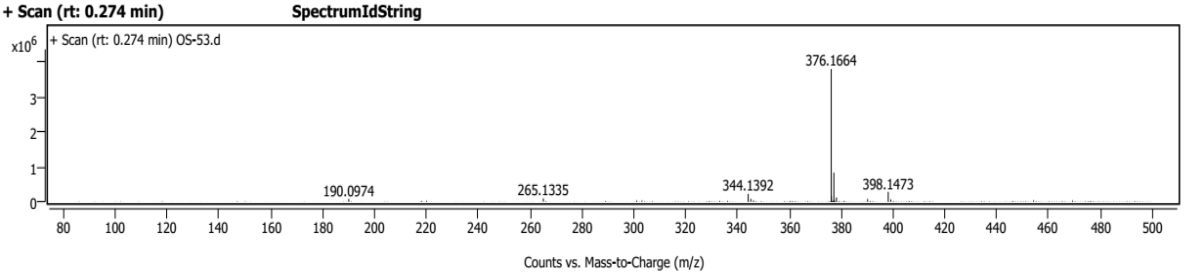
287.1169		36221	1.31					
289.1325	1	201322	7.27					
290.1358	1	38706	1.40					
319.1430		71007	2.56					
330.1225	1	133816	4.83					
331.1288	1	56193	2.03					
362.1493	1	2770335	100.00					
362.1909	1	133577	4.82					
362.2462		78093	2.82					
363.1520	1	606152	21.88					
363.1941	1	36074	1.30					
364.1546	1	80794	2.92					
381.1870		48577	1.75					
384.1305	1	436795	15.77					

7w) ^{1}H NMR, ^{13}C NMR and HRMS of *N*-methoxy-5-(7-methoxynaphthalen-1-yl)-2,7-dimethylimidazo-[1,2-*a*]pyridine-3-carboxamide.



Peak Spec

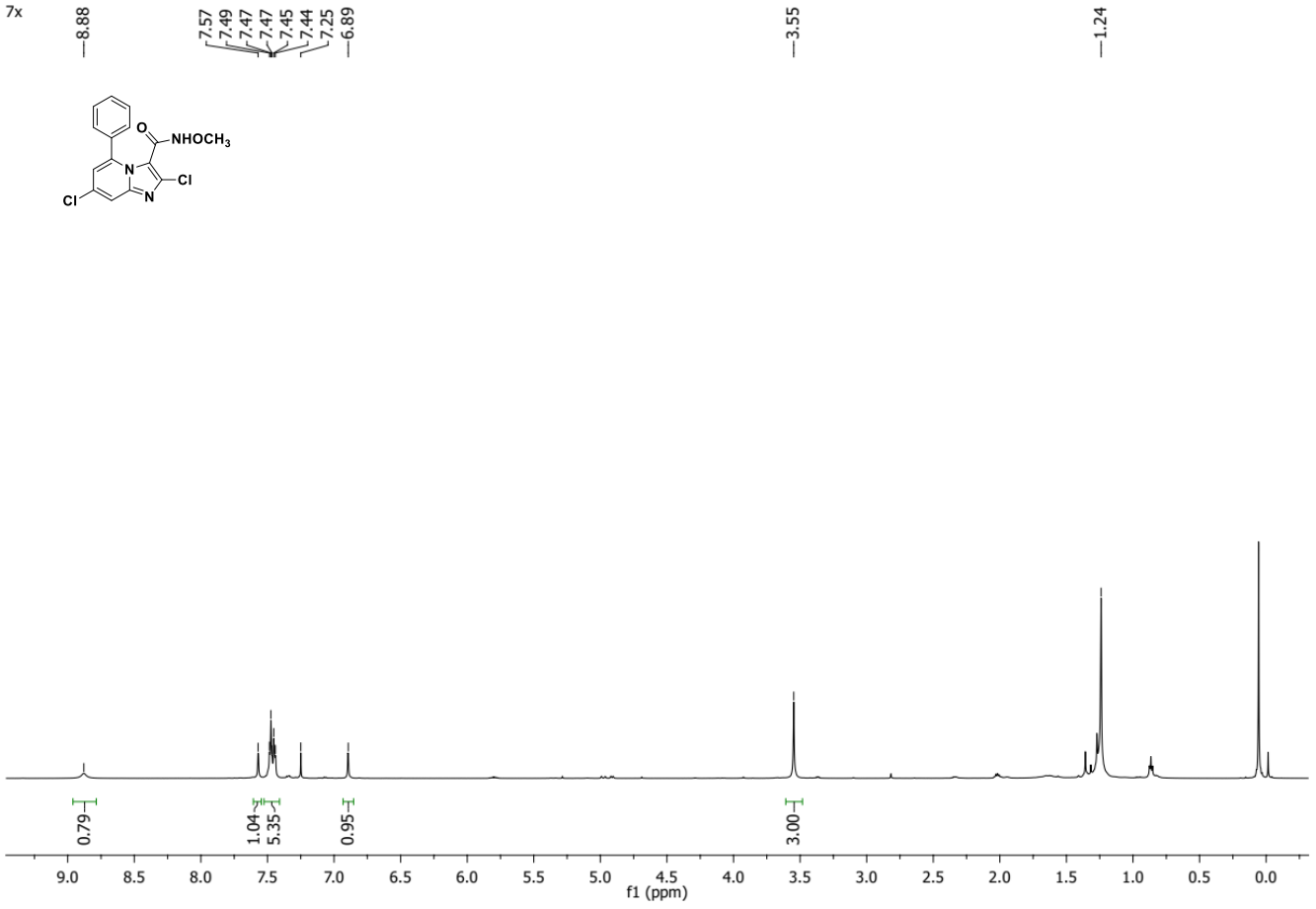
+ Scan (rt: 0.274 min) **SpectrumIdString**

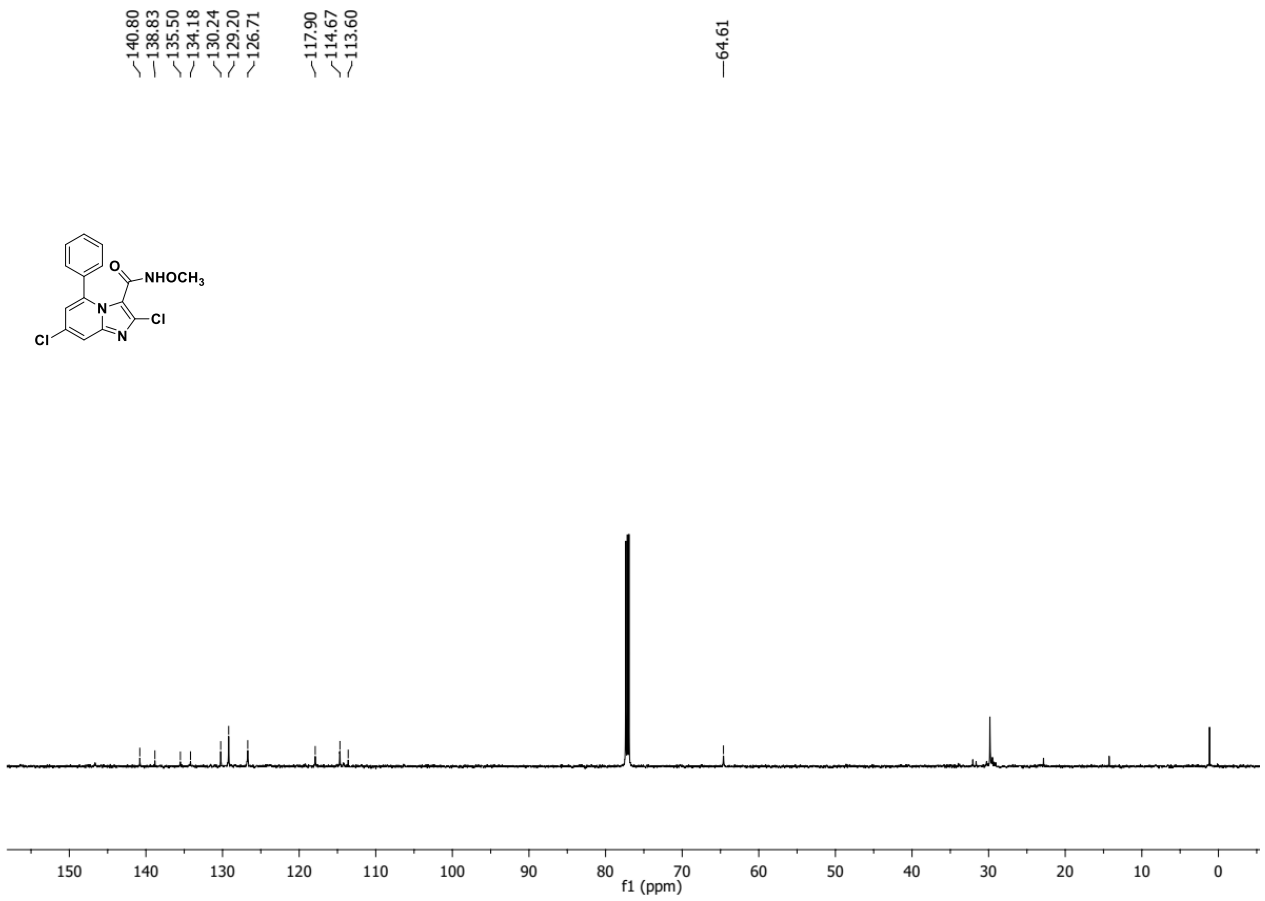


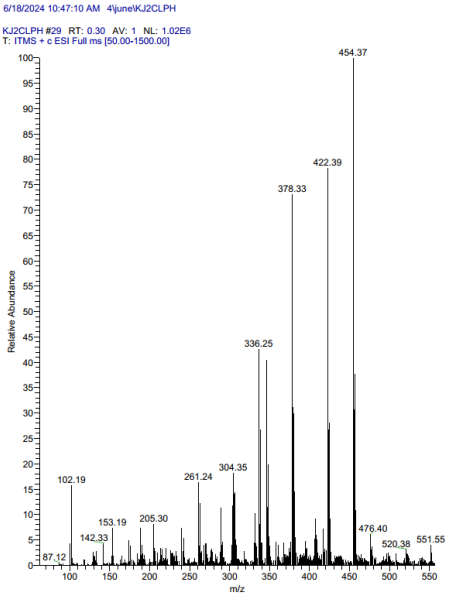
SpectrumIdString

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
190.0974		77100	2.02					
265.1335		92076	2.41					
344.1392	1	223560	5.86					
345.1450	1	79468	2.08					
376.1664	1	3816329	100.00					
376.2081	1	159605	4.18					
377.1689	1	834032	21.85					
377.2118	1	50905	1.33					
378.1713	1	120209	3.15					
390.1808		72823	1.91					
398.1473	1	280007	7.34					
399.1504	1	62610	1.64					
424.1864		72156	1.89					

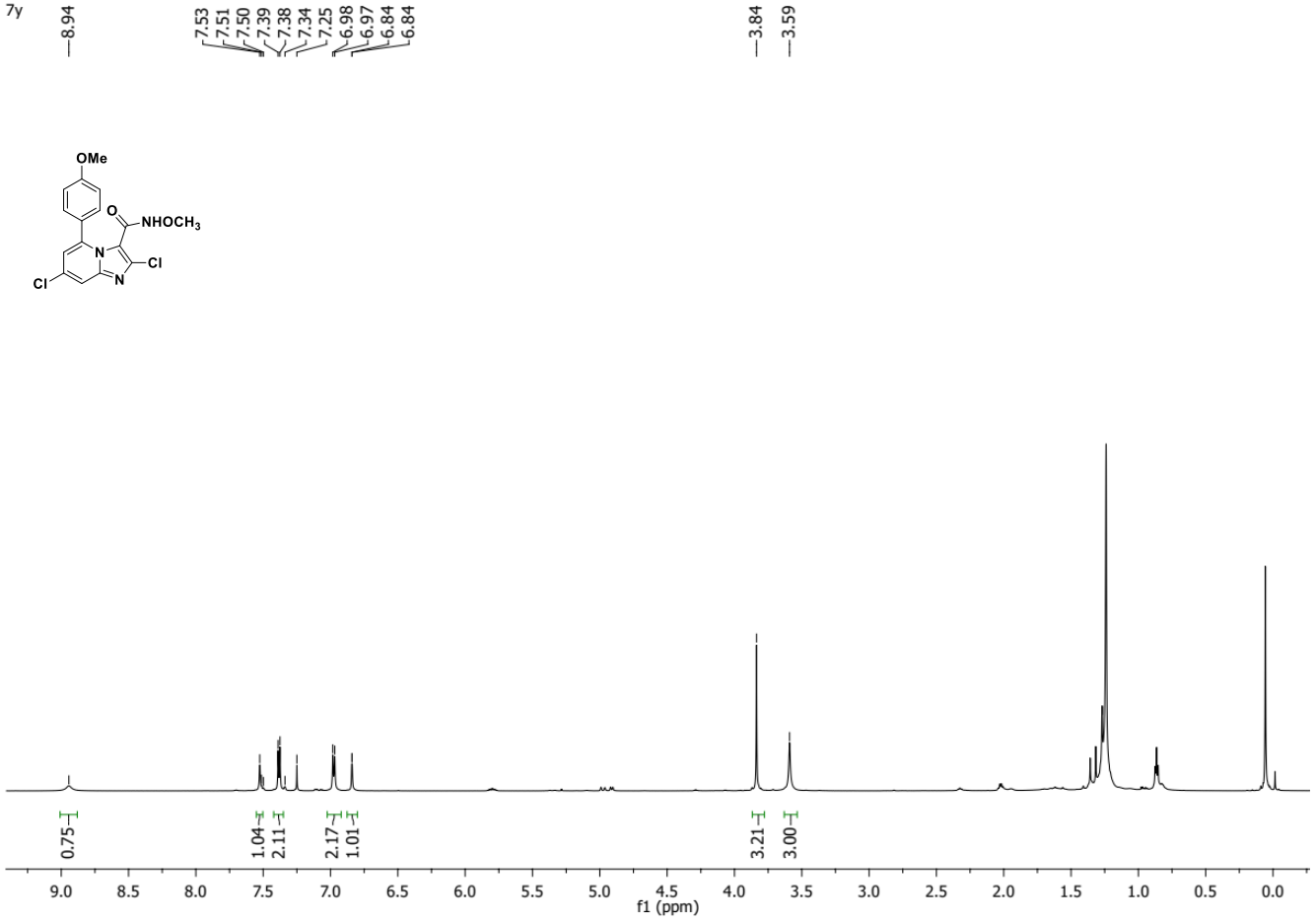
7x) ^{1}H NMR, ^{13}C NMR and HRMS of 2,7-dichloro-*N*-methoxy-5-phenylimidazo[1,2-a]pyridine-3-carboxamide.

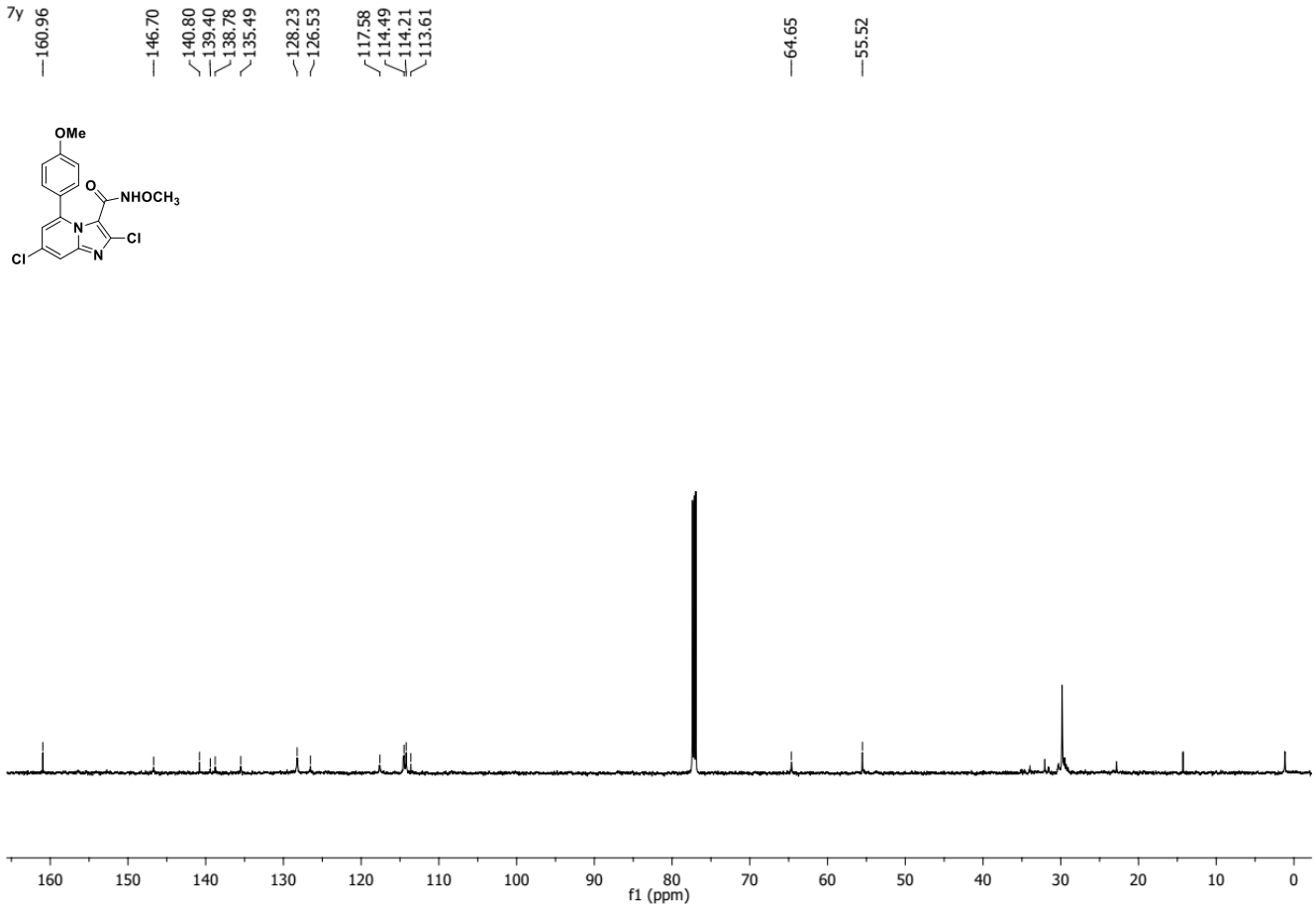


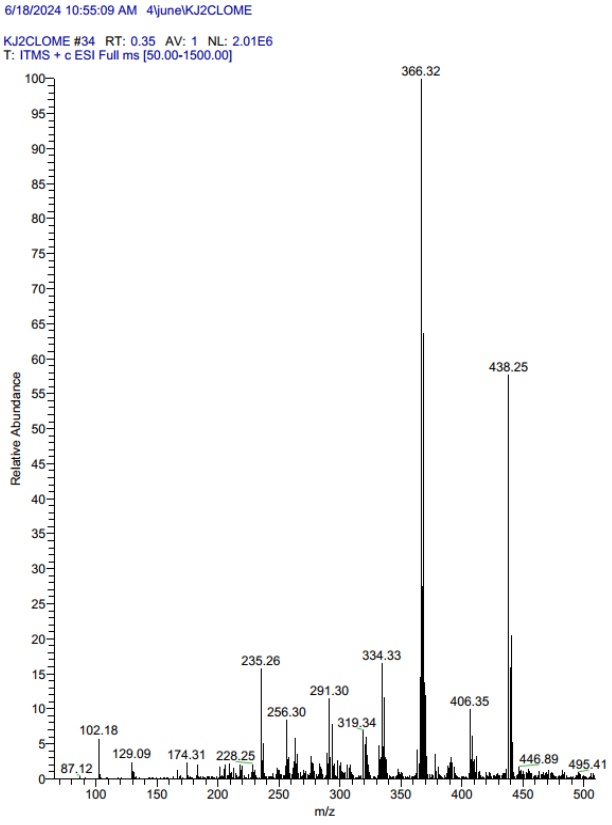

140.80
138.83
135.50
134.18
130.24
129.20
126.71
117.90
114.67
113.60
64.61
O
NHOCH3
N
Cl
Cl
N
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


6/18/2024 10:47:10 AM 4\june\KJ2CLPH
KJ2CLPH #29 RT: 0.30 AV: 1 NL: 1.02E6
T: ITMS + c ESI Full ms [50.00-1500.00]
Relative Abundance
m/z
454.37
422.39
378.33
336.25
304.35
261.24
205.30
153.19
142.33
102.19
87.12
476.40
520.38
551.55

7y) ^{1}H NMR, ^{13}C NMR and HRMS of 2,7-dichloro-*N*-methoxy-5-(4-methoxyphenyl)imidazo[1,2-a]pyridine-3-carboxamide.




7y
160.96
146.70
140.80
139.40
138.78
135.49
128.23
126.53
117.58
114.49
114.21
113.61
64.65
55.52
OMe
O
NHOCH3
N
Cl
Cl
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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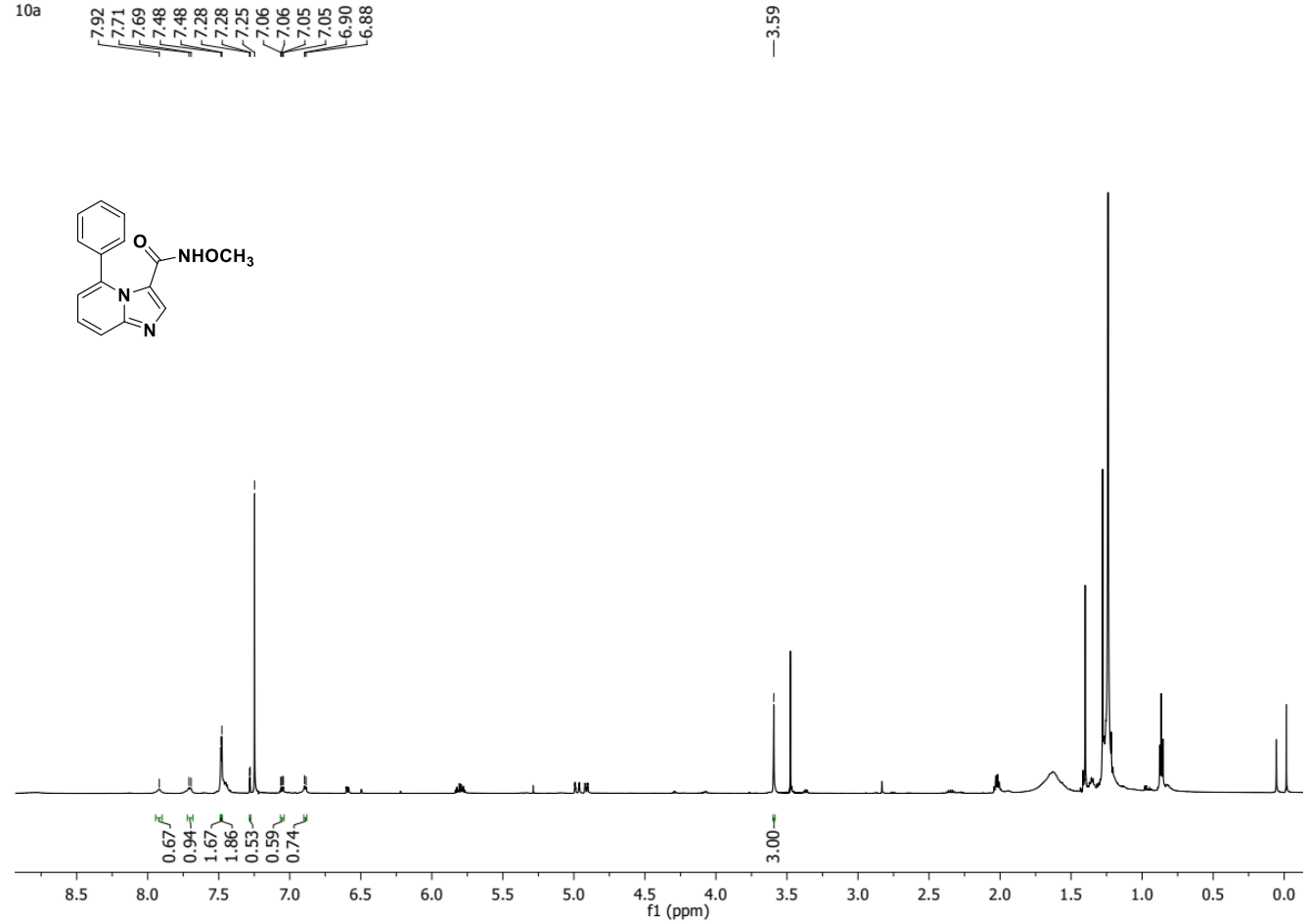
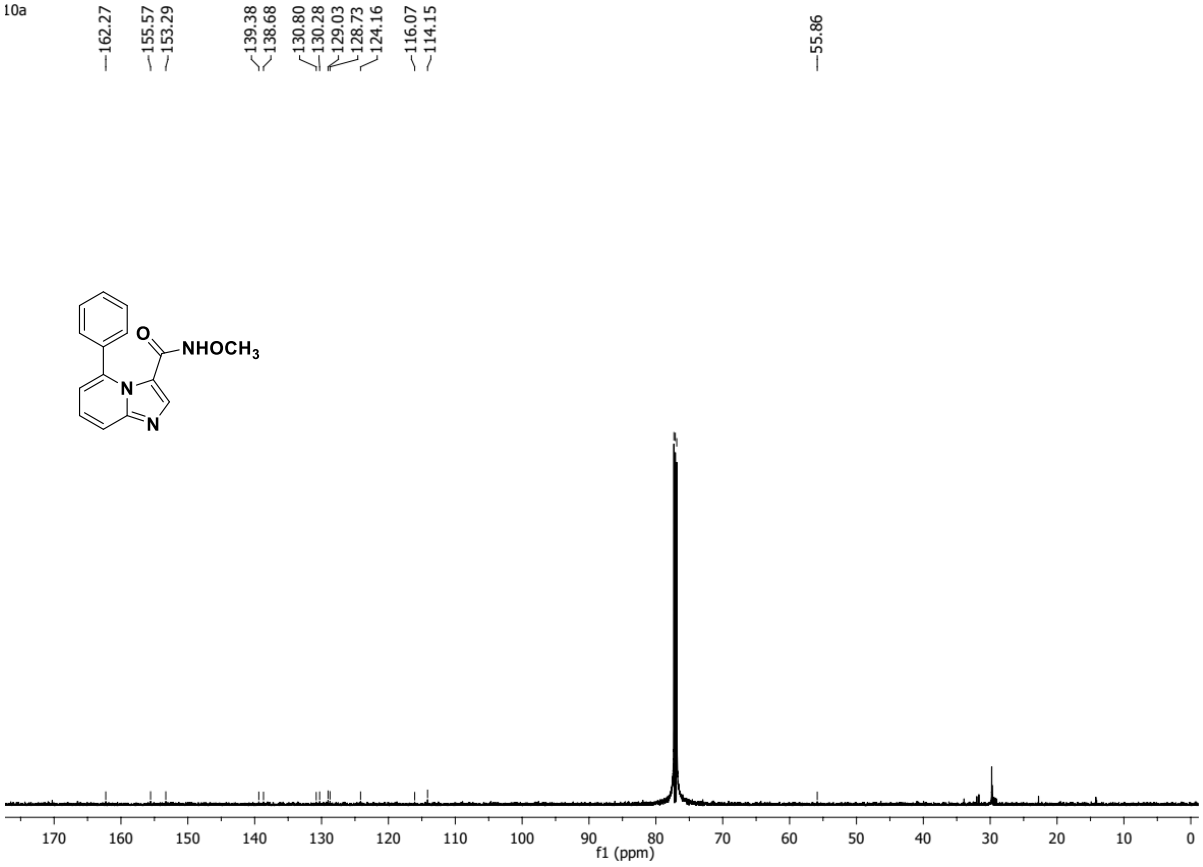
KJ2CLOME #34 RT: 0.35 AV: 1 NL: 2.01E6
T: ITMS + c ESI Full ms [50.00-1500.00]
Relative Abundance
m/z
366.32
438.25
334.33
235.26
291.30
406.35
256.30
319.34
102.18
129.09
174.31
228.25
87.12
446.89
495.41

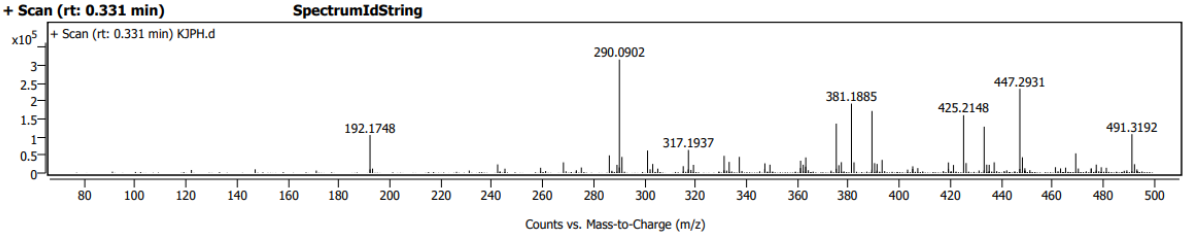
10a) ^{1}H NMR, ^{13}C NMR and HRMS of *N*-methoxy-5-phenylimidazo[1,2-*a*]pyridine-3-carboxamide.





Peak Spec

+ Scan (rt: 0.331 min) **SpectrumIdString**



SpectrumIdString

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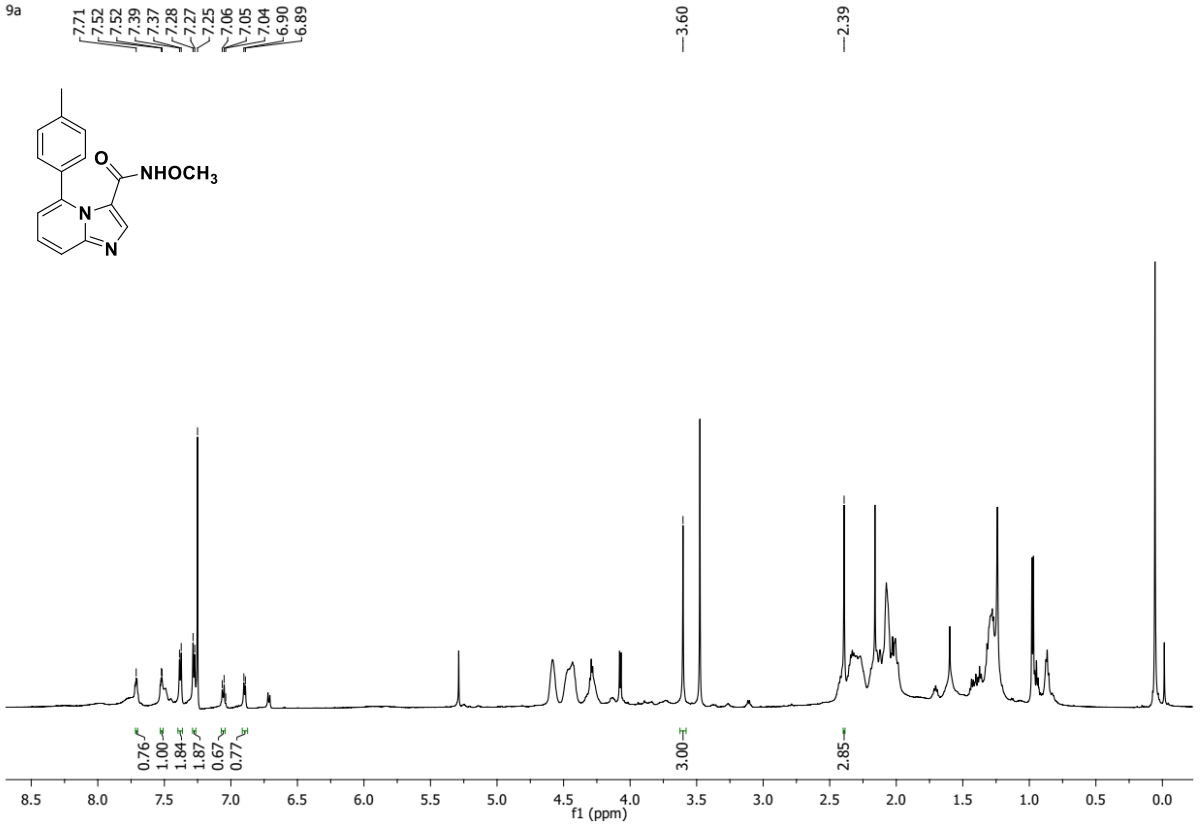
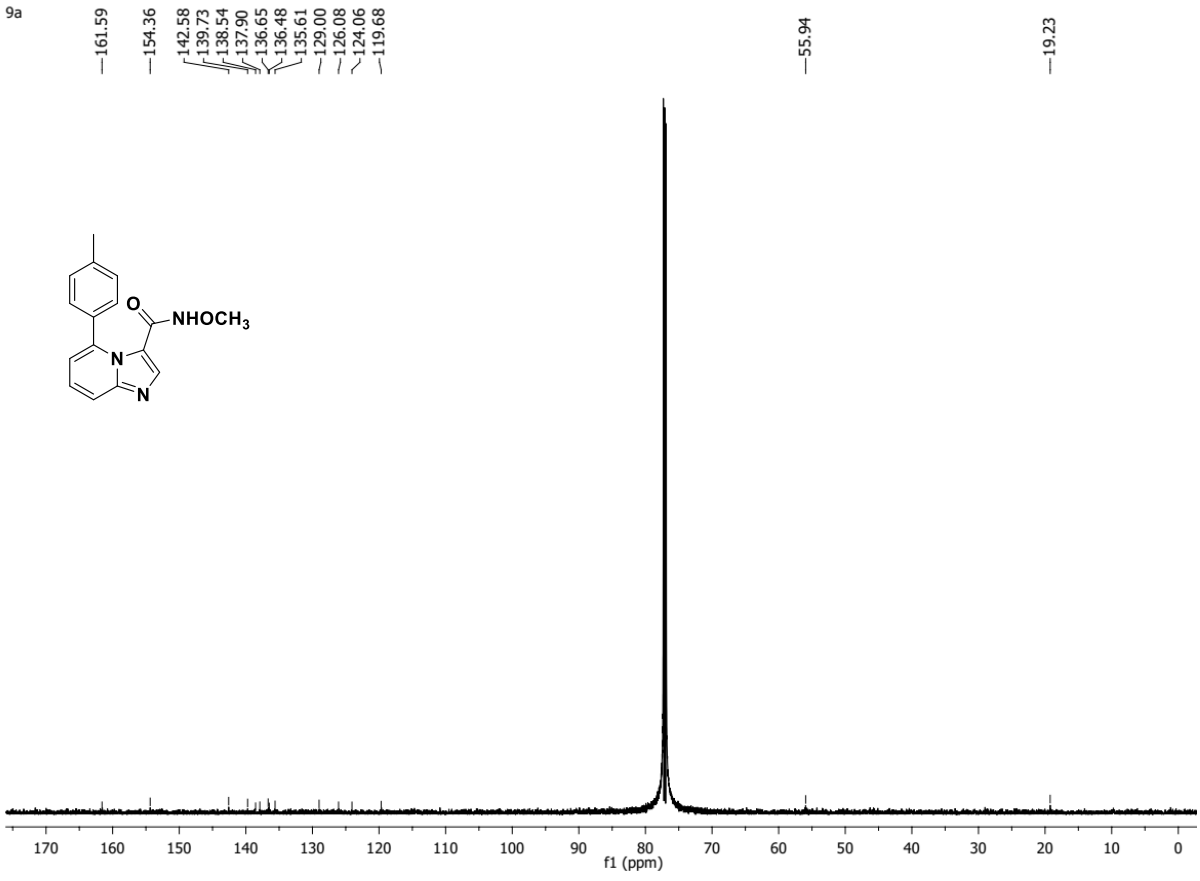
290.0902		315307	100.00					
317.1937		64409	20.43					
375.2355		136510	43.29					
381.1885		192289	60.98					
389.2512		171686	54.45					
425.2148		159924	50.72					
433.2773		127995	40.59					
447.2931		233628	74.10					
491.3192		107206	34.00					

MassHunter Qual 10.0
(End of Report)

10b) ^{1}H NMR, ^{13}C NMR and HRMS of *N*-methoxy-5-(*p*-tolyl)imidazo[1,2-*a*]pyridine-3-carboxamide.





Peak Spec

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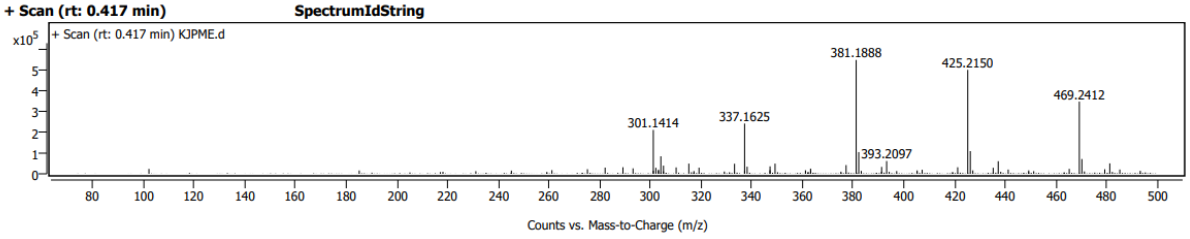

SpectrumIdString

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
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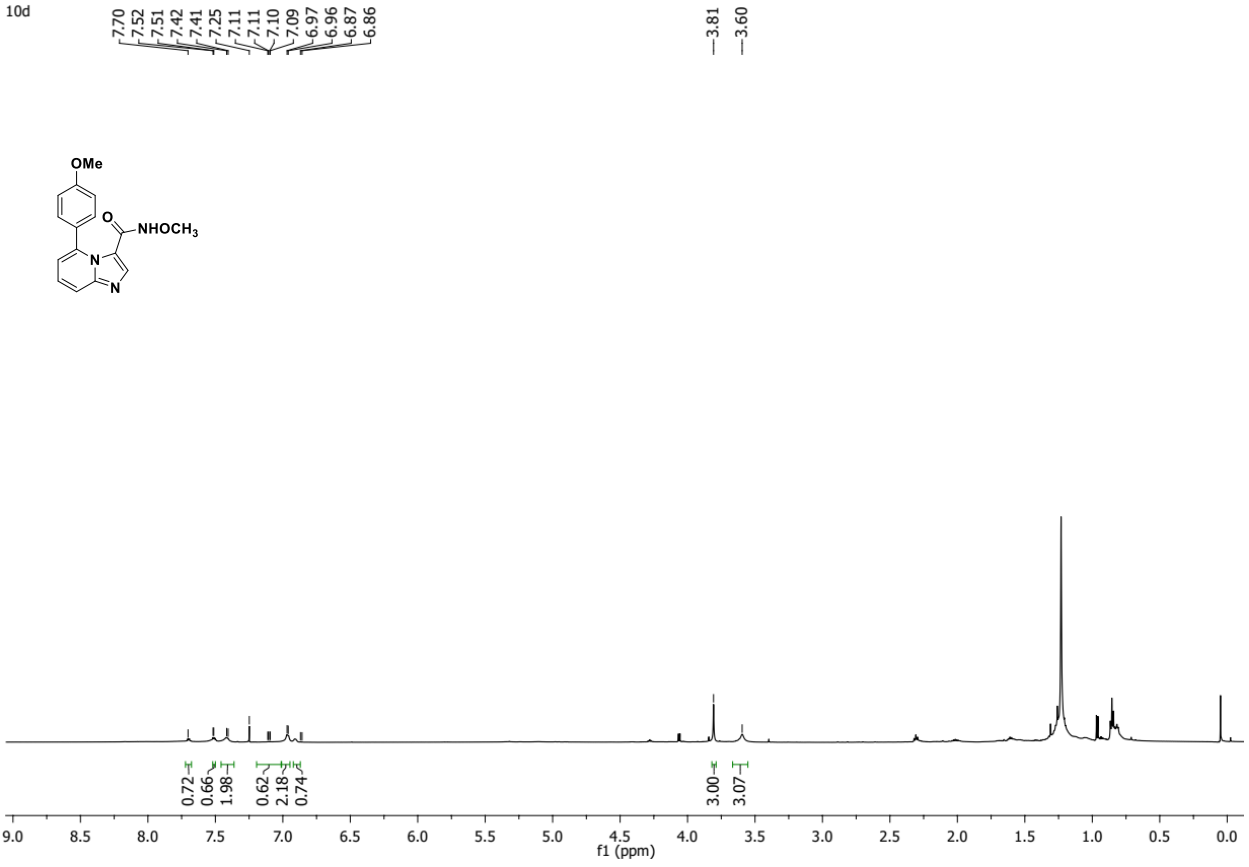
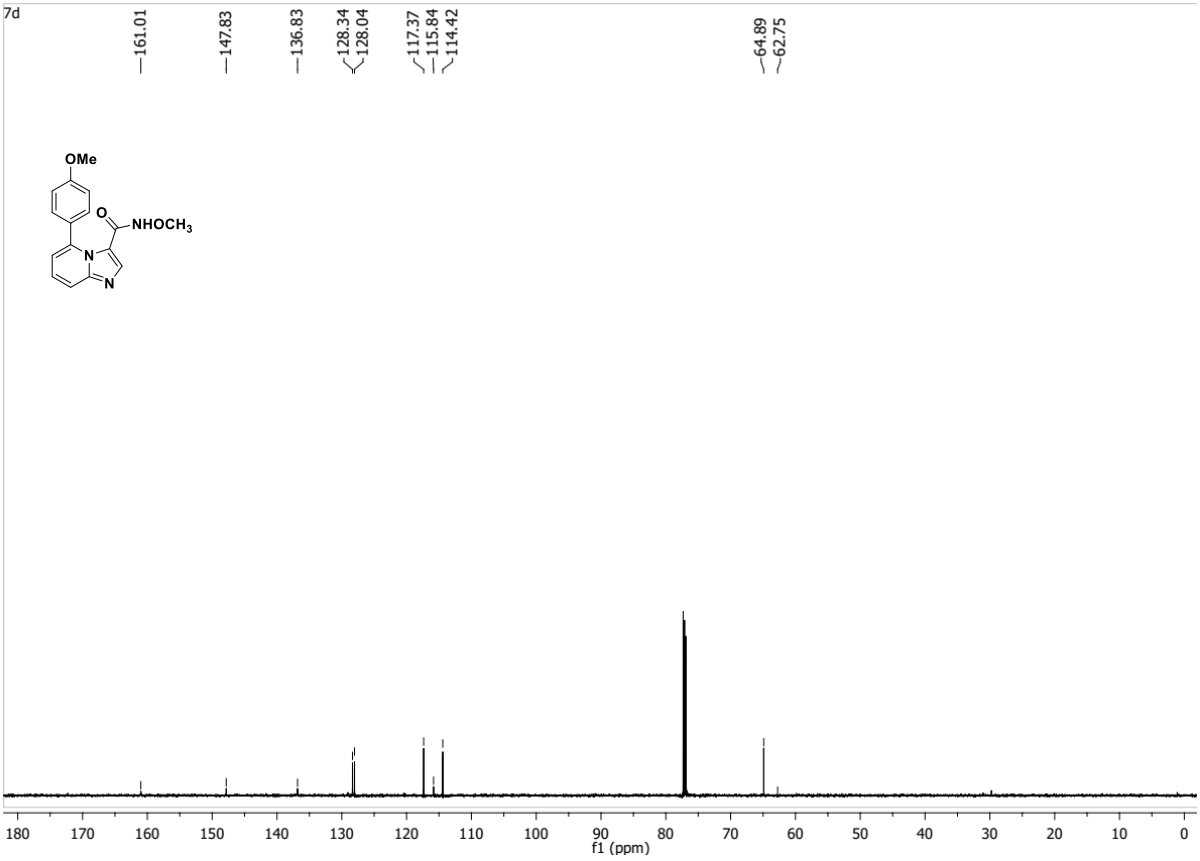
304.1059		85491	15.48					
337.1625		242452	43.90					
381.1888	1	552304	100.00					
382.1922	1	105871	19.17					
393.2097		62198	11.26					
425.2150	1	504127	91.28					
426.2184	1	110628	20.03					
469.2412	1	349460	63.27					
470.2445	1	72067	13.05					

MassHunter Qual 10.0
(End of Report)

10c) ^{1}H NMR, ^{13}C NMR and HRMS of *N*-methoxy-5-(4-methoxyphenyl)imidazo[1,2-*a*]pyridine-3-carboxamide.





Peak Spec

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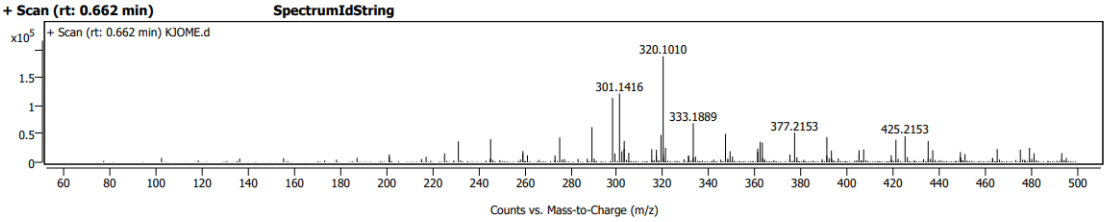

SpectrumIdString

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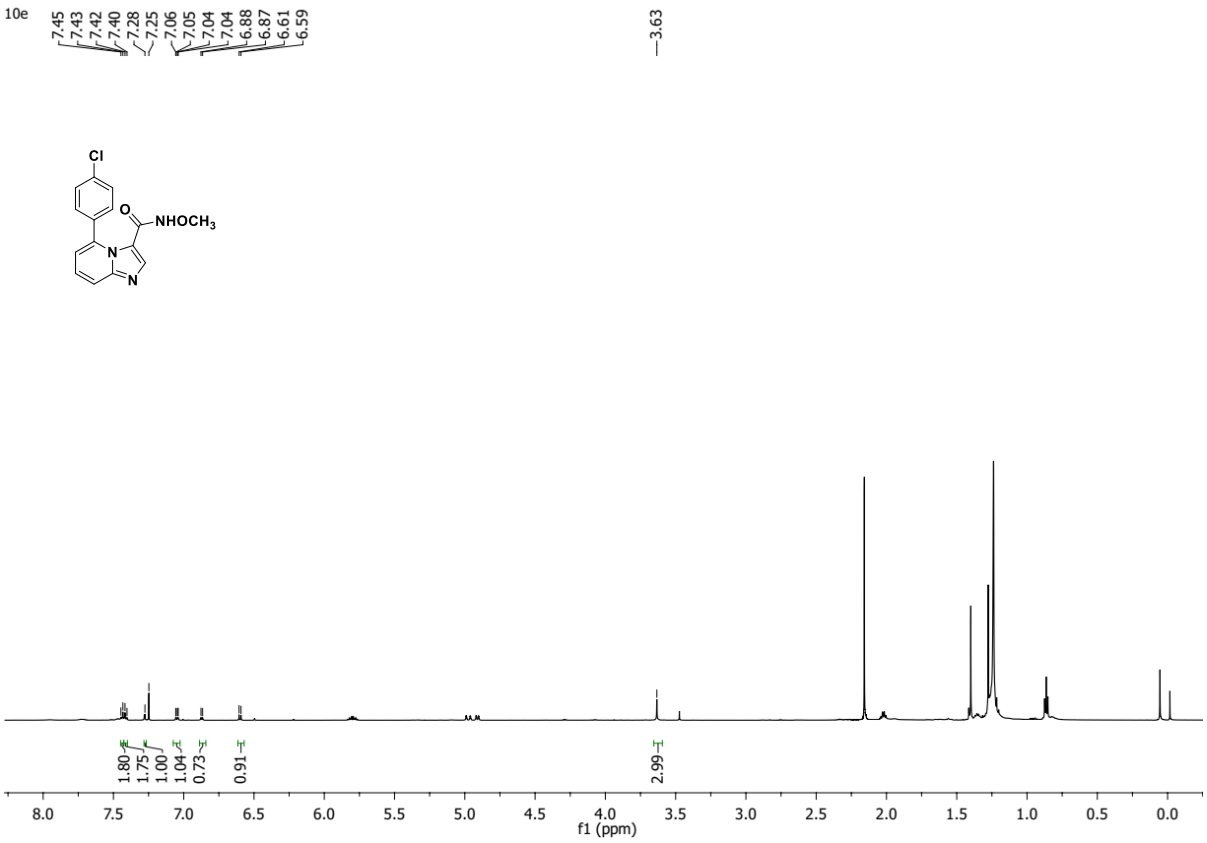
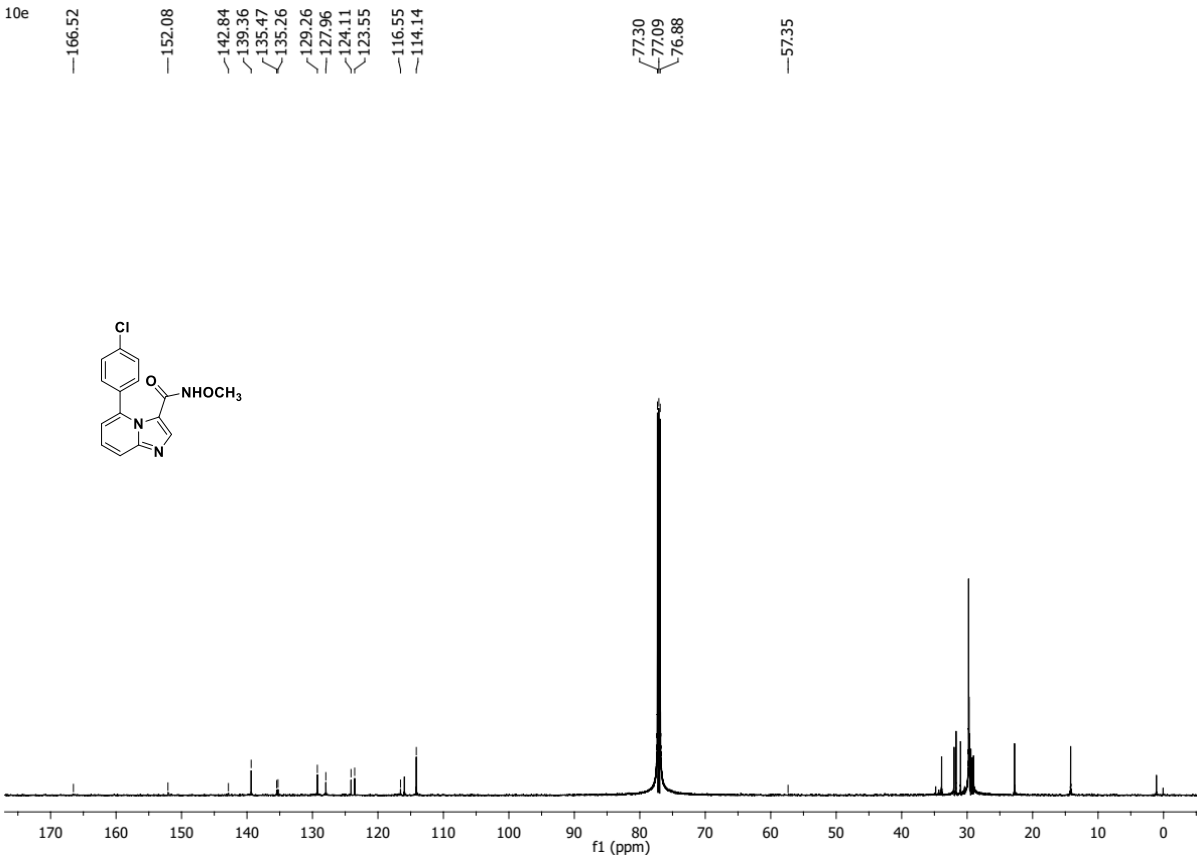
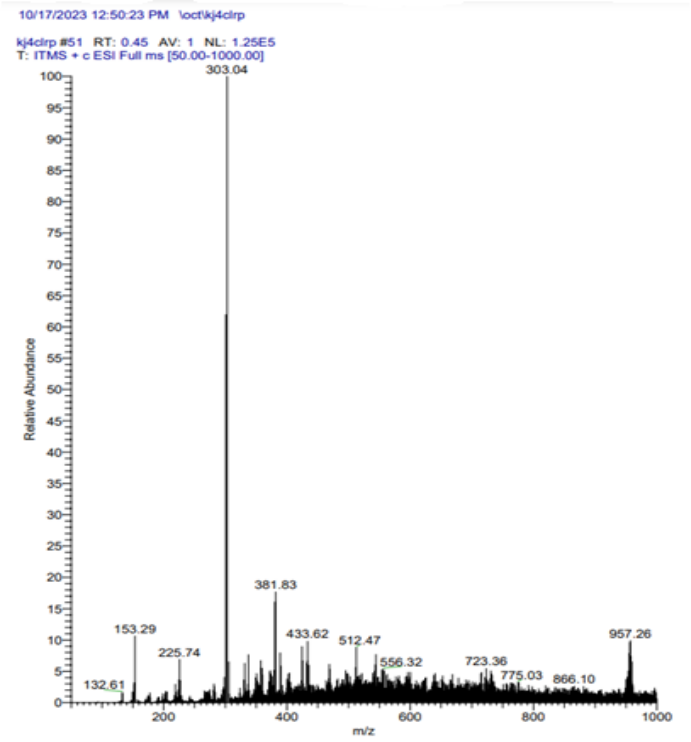
298.1190		113521	60.52					
301.1416		121416	64.73					
319.1732		47710	25.43					
320.1010		187579	100.00					
333.1889		68674	36.61					
347.2047		49812	26.56					
377.2153		52020	27.73					
391.2307		44221	23.57					
425.2153		45548	24.28					

MassHunter Qual 10.0
(End of Report)

10d) ^{1}H NMR, ^{13}C NMR and LTQ-mass of 5-(4-Chlorophenyl)-*N*-methoxyimidazo[1,2-*a*]pyridine-3-carboxamide.




10e
166.52
152.08
142.84
139.36
135.47
135.26
129.26
127.96
124.11
123.55
116.55
114.14
77.30
77.09
76.88
57.35
Cl
O
NHOCH3
N
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


10/17/2023 12:50:23 PM \oct\kj4clrp
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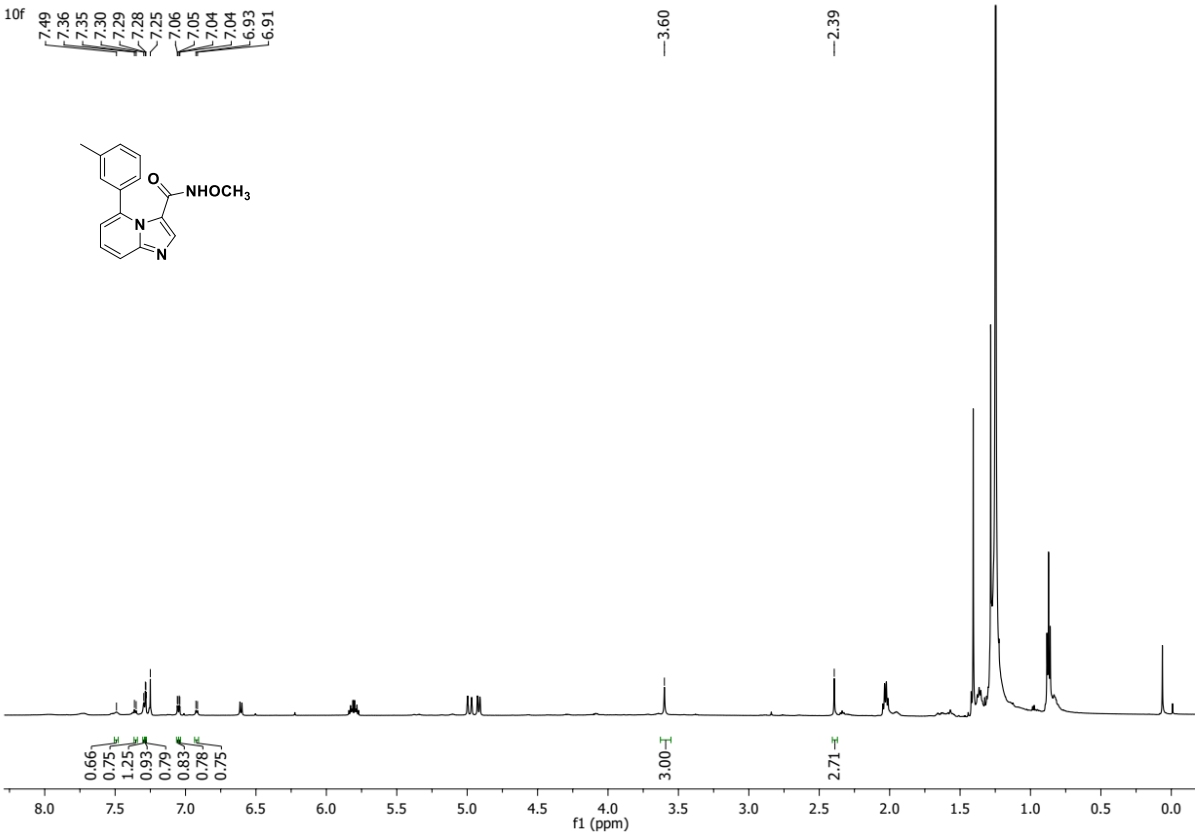
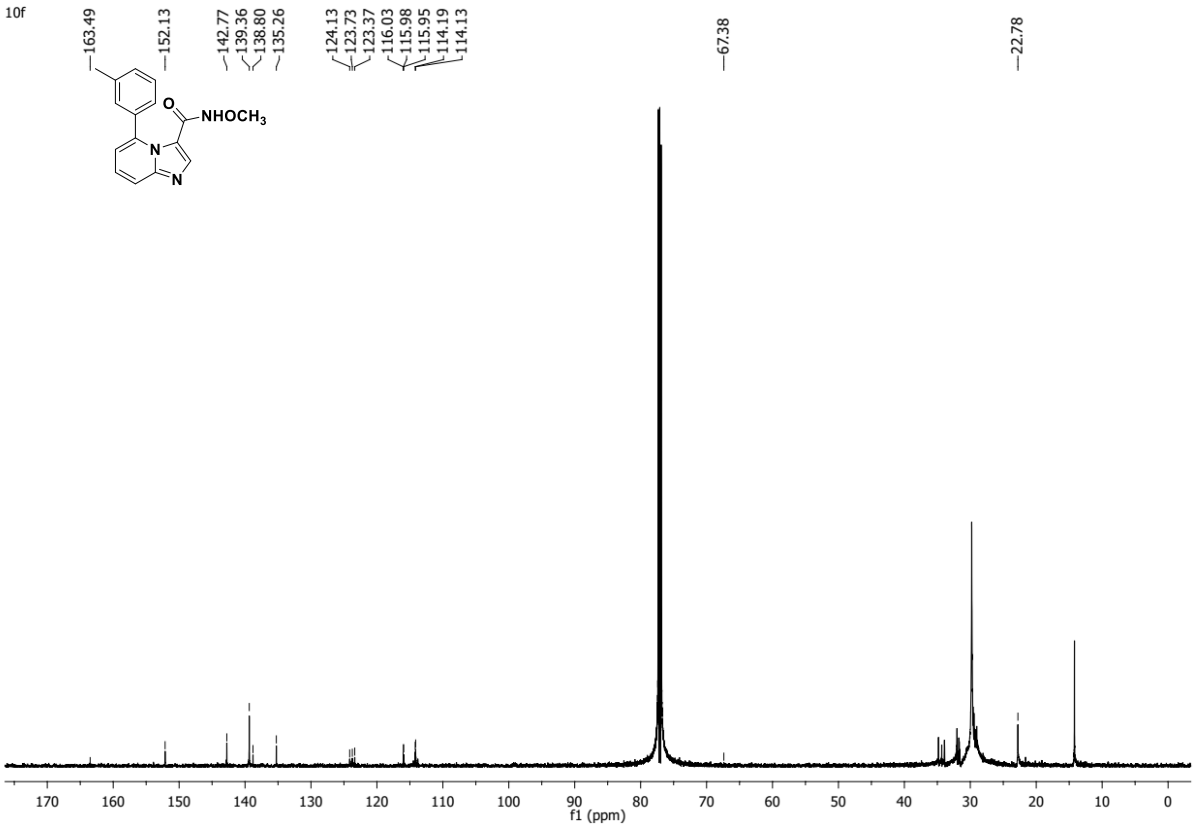
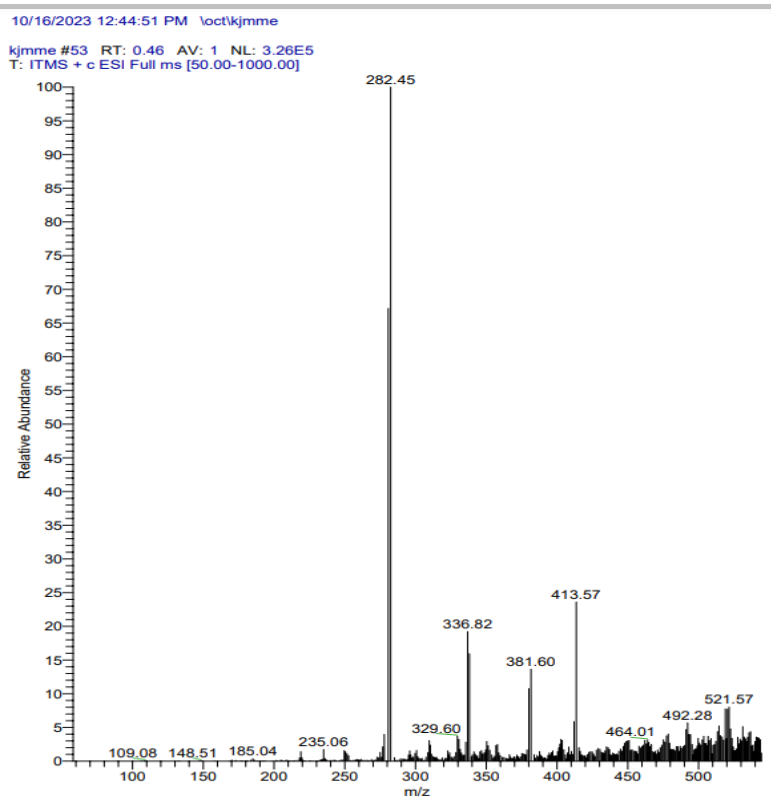
T: ITMS + c ESI Full ms [50.00-1000.00]
303.04
381.83
153.29
225.74
433.62
512.47
556.32
723.36
775.03
866.10
957.26
132.61
Relative Abundance
m/z
200
400
600
800
1000

10e) ^{1}H NMR, ^{13}C NMR and LTQ-mass of *N*-methoxy-5-(*m*-tolyl)imidazo[1,2-*a*]pyridine-3-carboxamide






10/16/2023 12:44:51 PM \oct\kjmme
kjmme #53 RT: 0.46 AV: 1 NL: 3.26E5
T: ITMS + c ESI Full ms [50.00-1000.00]
Relative Abundance
m/z
282.45
413.57
336.82
381.60
521.57
492.28
464.01
329.60
235.06
109.08
148.51
185.04

2.12 Deuterium Exchange

The starting material (**9**, 1 equiv.) $[RhCp^*Cl_2]_2$ as transition metal catalyst, in the presence of Ag_2O (4 equiv.) in anhydrous MeOH at 80 °C for 12 h in a reaction tube. After, completation of reaction, the reaction mixture passed through celite to expel out metal catalysts under vacuum, further washed with dichloromethane (3 times) and the filtrate collected was concentrated on rotatory evaporator.The crude product subjected to column chromatography on 100-200 grade silica and the product was eluted with at 6:4 ratios of ethyl acetate and hexane. The desired product **9** has been purified by silica gel 100-200 using *n*-hexane /EtOAc as solvents afforded 65% yield.

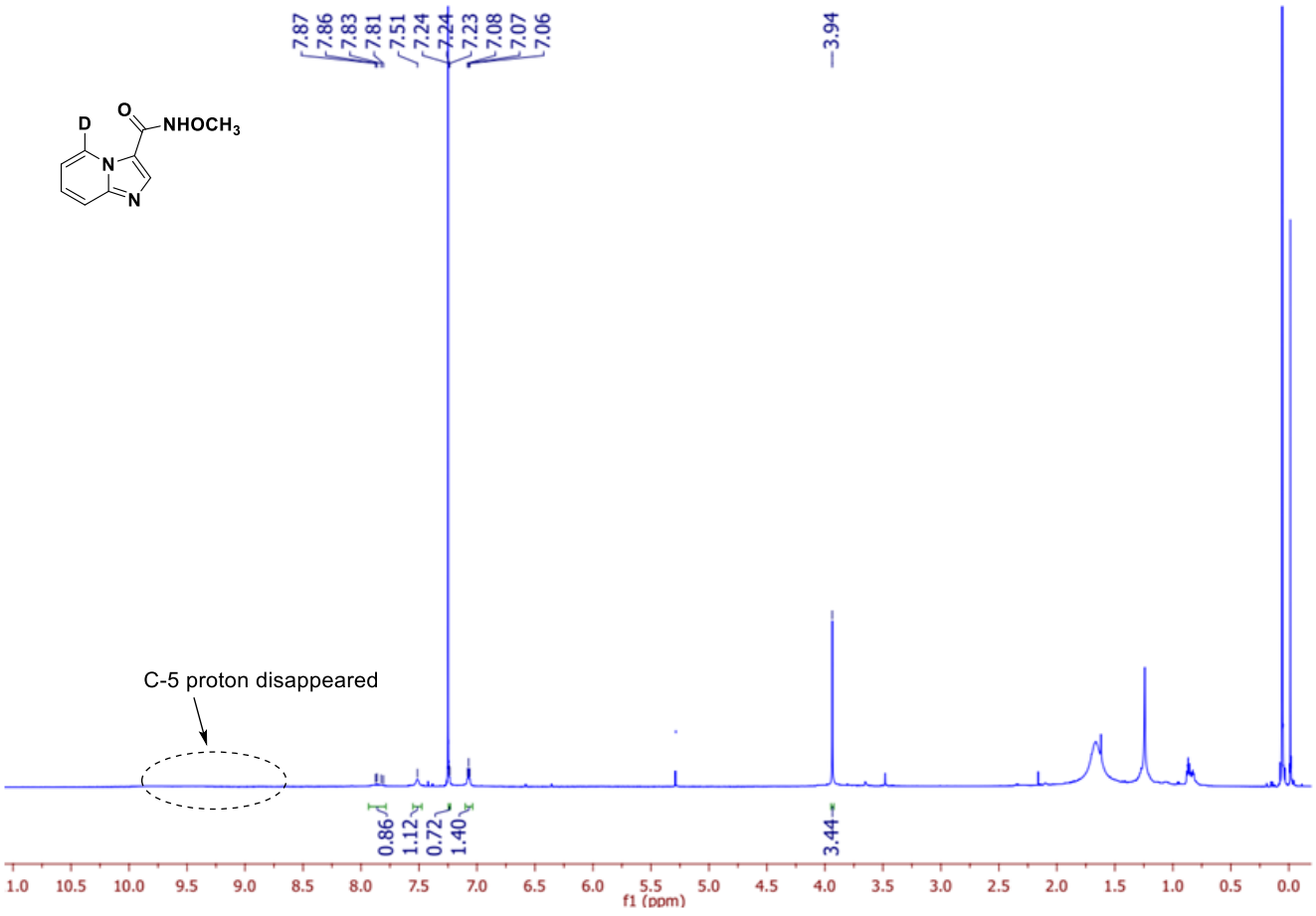


Figure S8 : Diappearance of C-5 Proton from starting material **9**.

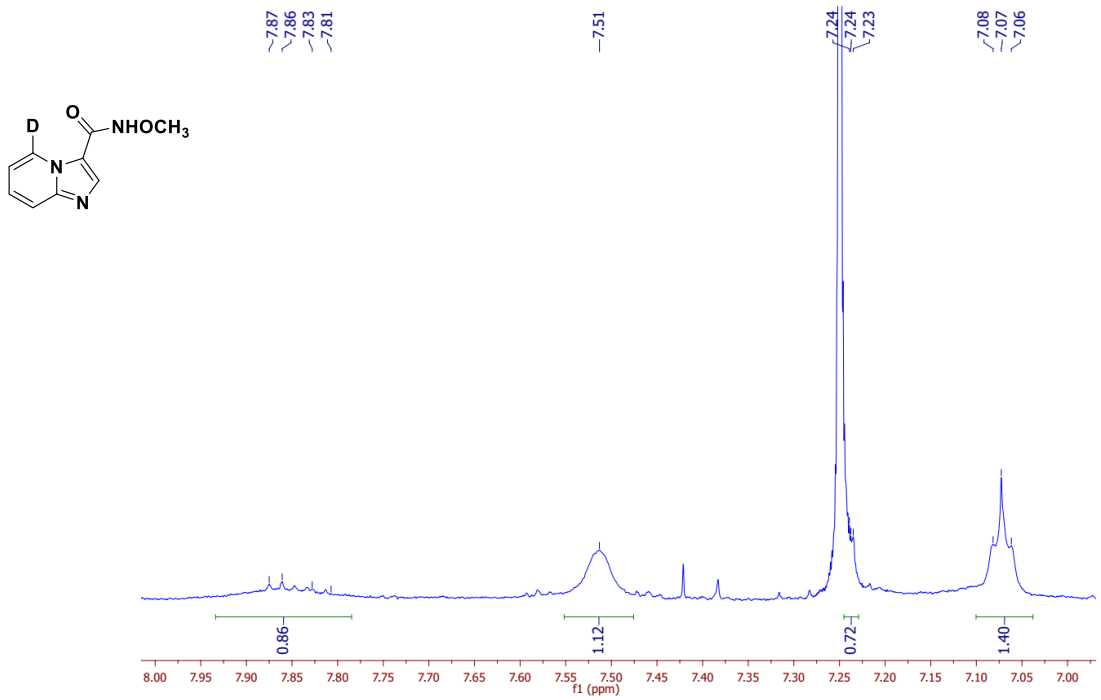
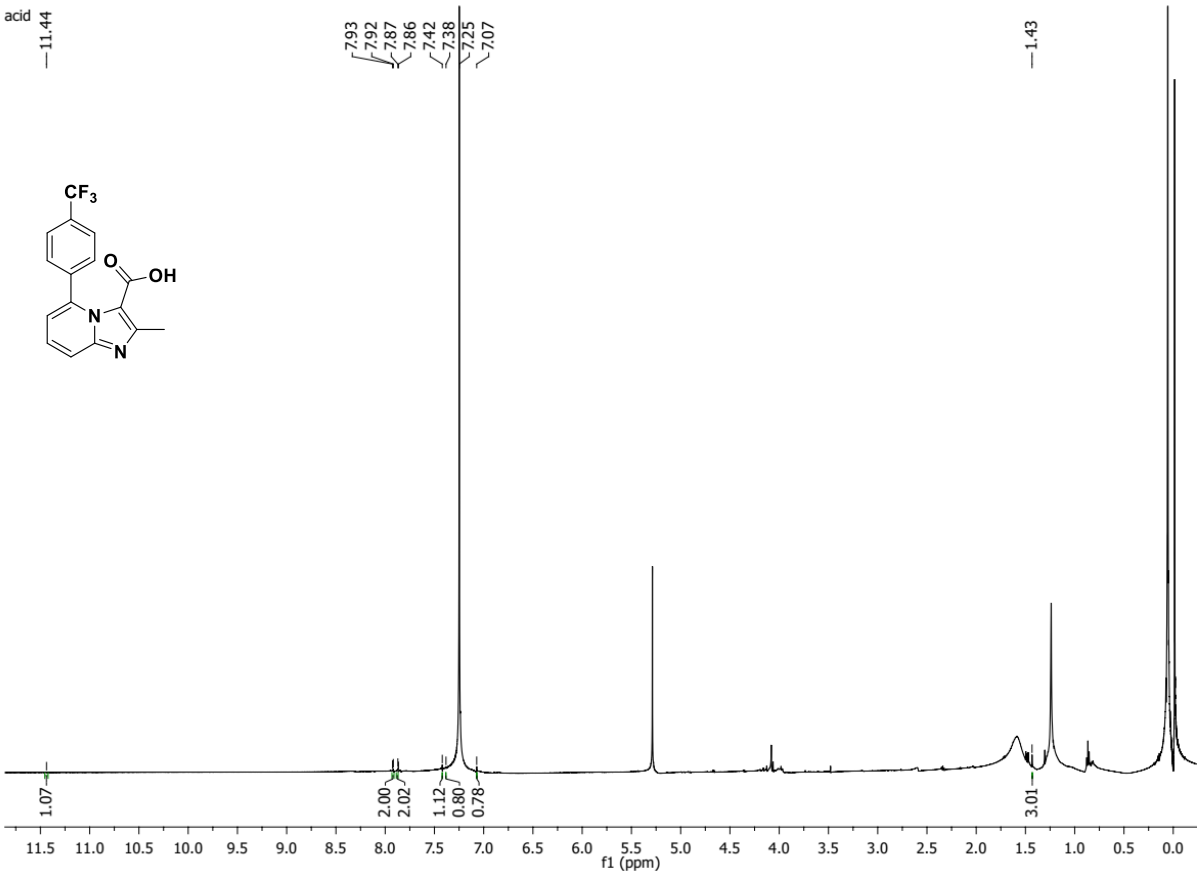


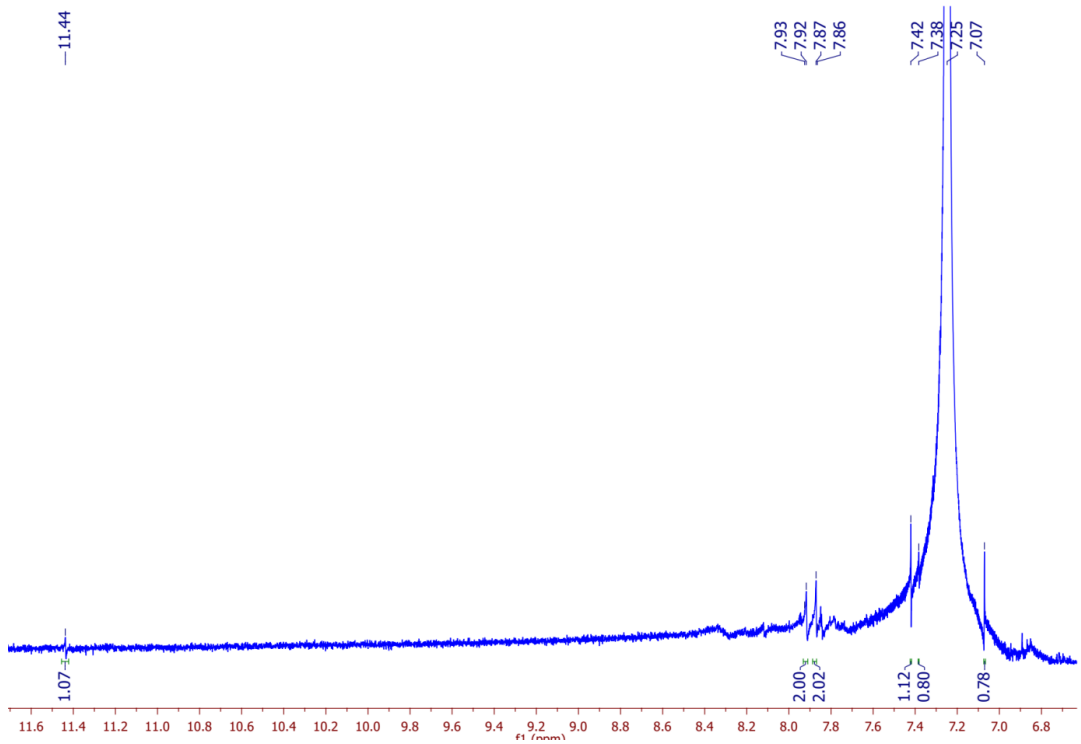
Figure S9 : Magnified view of the ^{1}HNMR spectra; indicating complete disappearance of C-5 proton.

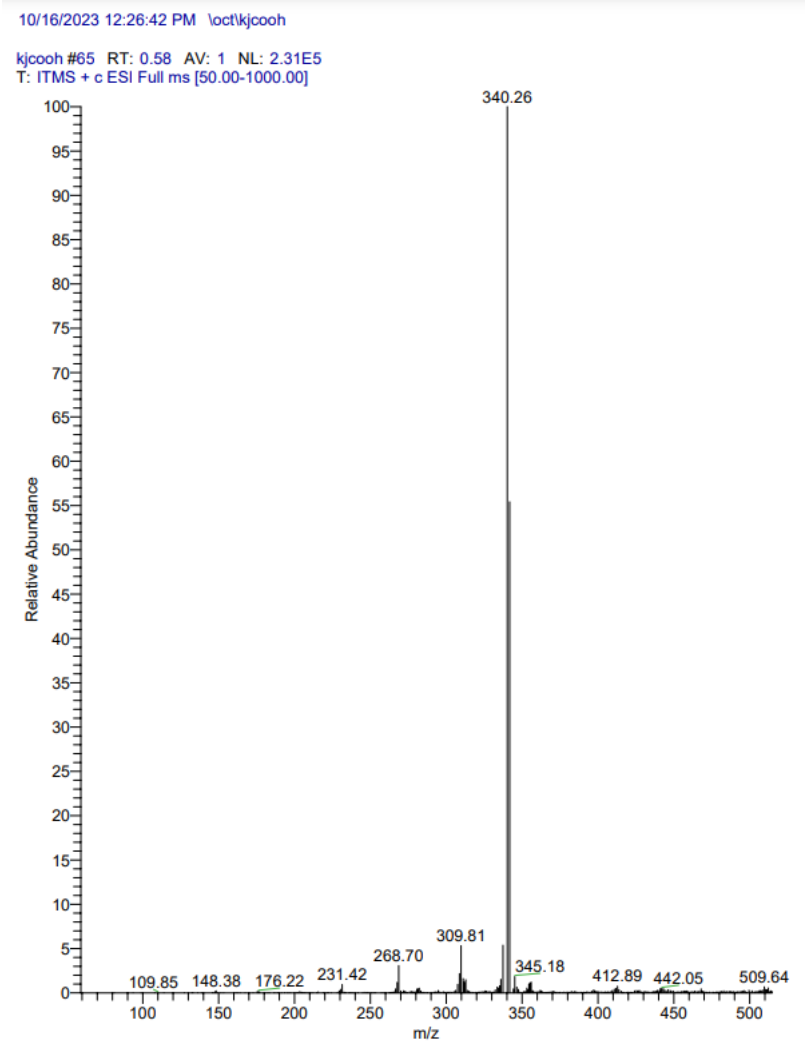
2.13 Post-functionalization

Post-functionalization was also performed for the replacement of the amide with acid, this reaction was subjected in the presence of *tert*-butyl nitrite (TBN) and water as solvent at room tempertaure using earlier reported method. (shown in Scheme 4 in manuscript).[21]

Brown semi-solid (80 mg, 58%); ^{1}H NMR (600 MHz, $CDCl_3$) δ δ 11.44 (s, 1H), 7.92 (d, J = 4.8 Hz, 2H), 7.87 (bs, 2H), 7.42 (s,1H), 7.38 (s, 1H), 7.07 (s, 1H), 1.43 (s, 3H).







LTQ calculated for $C_{16}H_{11}F_3N_2O_2$ $[M+H+H_2O]+$ found : 340.26.

2.14 Quantum Chemical Analysis

2.14.1 Gussian 9.0 software[1] was employed to perform quantum chemical analysis. All the 3D structures (given in Figure 4 in manuscript) were optimised using density functional [M06/6-311++G(d,p)][2] level of theory. The analytical frequencies for all the species were obtained to established the character of the saddle points along the reaction path (0 to negative frequencies for all minima and one negative frequecncy for the TS). Free energy corrected absolute values are employed in the calculation of ΔG values for all indiviual reaction along the reaction path. The activation (E_a) for the C-C bond formation from the intermediate to give final product **7a** has been estimated using Berny optimization procedures (OPT=TS option). 3D structure of TS is provided in Figure S11.

2.14.2 Absolute energies of all the reactants, intermediates and products.

Table S10. Absolute energies of all the reactants, intermediates and products in atomic unit (HF). Quantum chemical analysis has been carried out using density functional [M06/6-311++G(d,p)][2]

S.No.	Code	Absolute energies in (Hartrees)
1.	DIMER	-838.770585
2.	MONOMER	-1419.696646
3.	Substrate (**5a**)	-701.897996
4.	Ag_2O	-366.733162
5.	Phenyl boronic	-408.021571
6.	IN-I	-1660.765738
7.	IN-II	-1199.939173
8.	IN-III	-1431.344368
9.	Boronic acid	-252.440675
10.	AgCl	-606.023867
11.	AgOH	-221.576139
12.	HCl	-460.804154
13.	TS	-1431.918329
14.	Product (**7a**)	-1476.652729

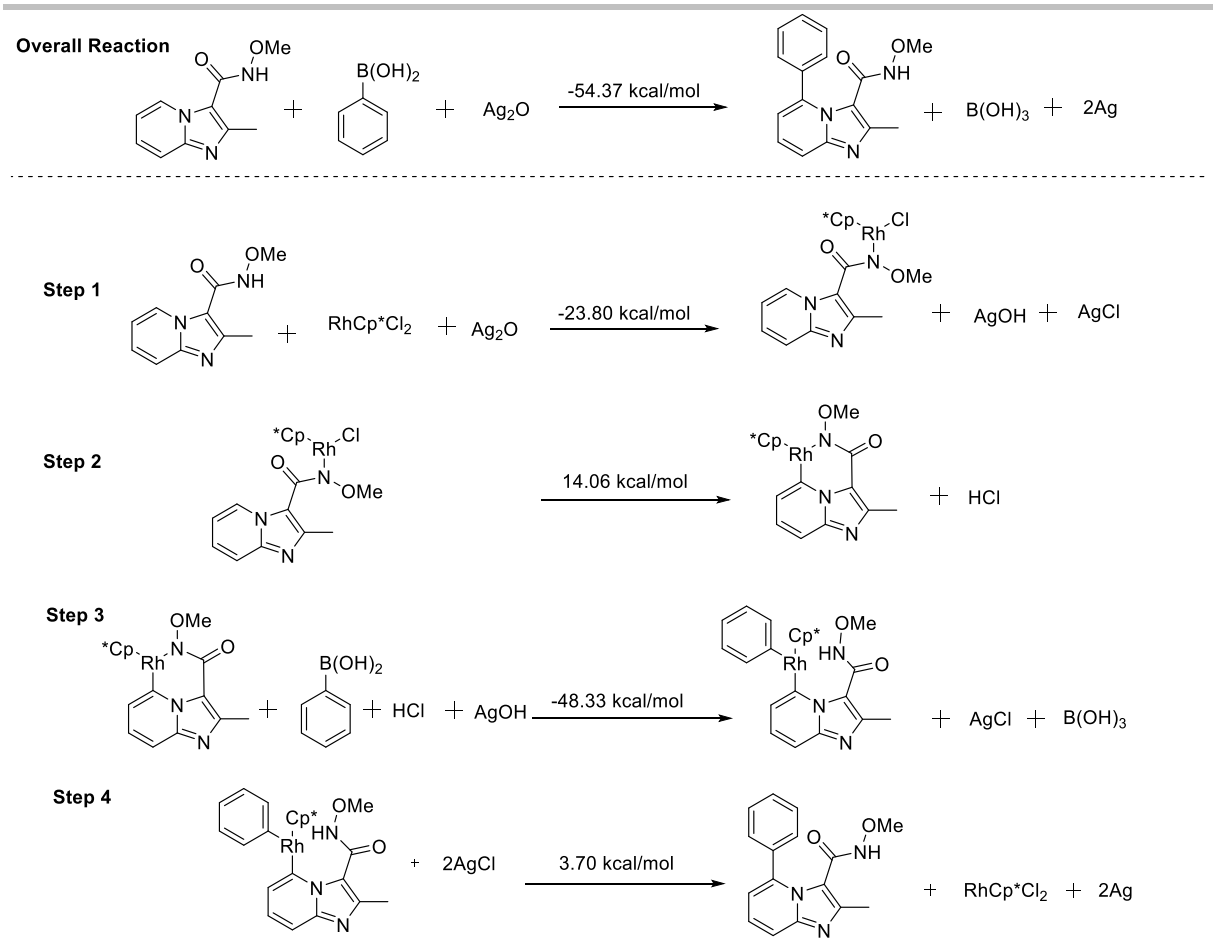


Figure S10 : Details of Reaction mechanism for C-5 arylation assisted by *N*-methoxyamide group.

2.14.3 Structure of Transition state between intermediate **III** and product **7a** (Figure 4 in manuscript)

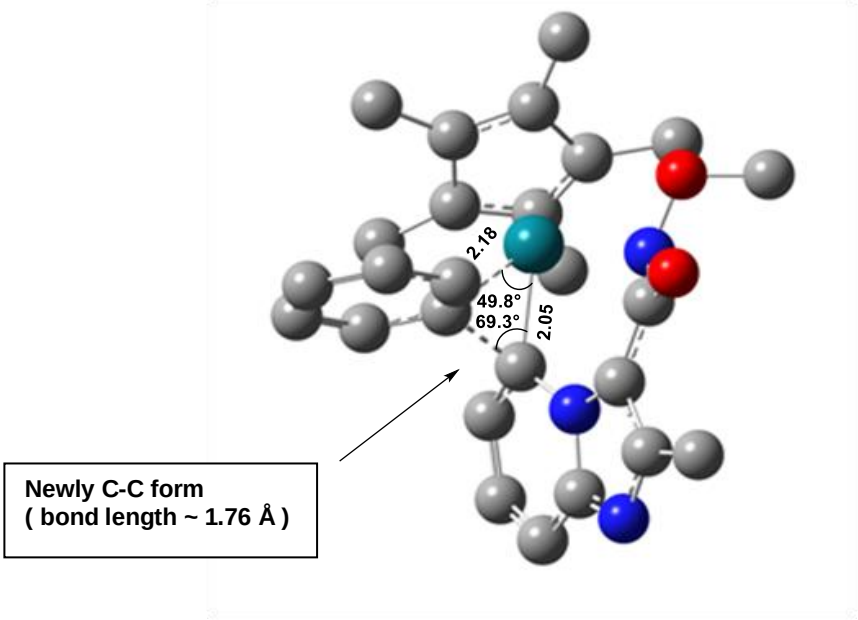
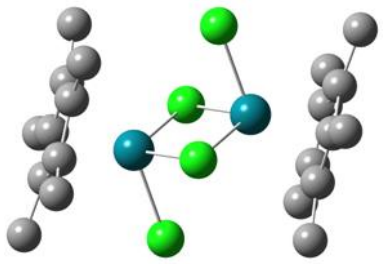


Figure S11. The TS for the C-C bond formation between the phenyl ring of boronic acid and C-5 carbon of IMP. The estimated activation energy (E_a) for the C-C bond formation is 22.10 kcal/mol. All hydrogen atoms are removed to increase visibility. Unit for bond length in Å.

2.14.4 Archeive entries of the species optimized using Quantum chemical method. In some of the structures hydrogen atoms are remove to increase visibility.

Dimer



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862,-0.086724158\C,3.4839647145,-0.1785413245,-1.1775462686\C,2.909422
0113,-1.3874869563,-0.6172278344\Rh,1.7588993196,0.3637301073,-0.04418
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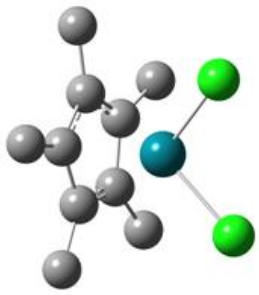
983432\PG=C01 [X(C20H30Cl4Rh2)]\\@

Monomer



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056251,-1.5010468303,-0.0045583155\\Version=ES64L-G16RevC.01\State=1-A
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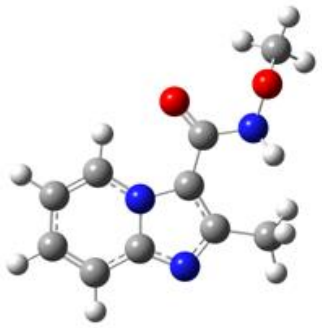
164441,0.0232563\Quadrupole=-8.750854,0.1434461,8.607408,-0.7519387,0.

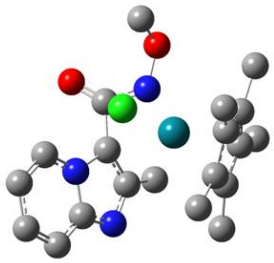
0936007,0.0387895\PG=C01 [X(C10H15Cl2Rh1)]\\@

Substrate (5a)



1\1\GINC-USER\FOpt\RM06\6-311++G(d,p)\C10H11N3O2\USER\22-Jul-2022\0\\#
opt freq m06/6-311++g(d,p)\\PVBa\\0,1\C,-1.9979148885,-2.3224981158,-0.1105427256\C,-0.8481174938,-1.595587103,-0.0711849751\C,-2.1515331606,0.4342963041,-0.0066185271\C,-3.3352483537,-0.3191548572,-0.0471309048\C,-3.2569066489,-1.6824685081,-0.0987684304\H,-1.9272306536,-3.4028206943,-0.1491622001\H,0.1524221043,-2.0050427847,-0.0713314478\H,-4.277472405,0.2157774285,-0.0358978515\H,-4.1621952385,-2.2793916023,-0.1303415735\N,-1.9890330517,1.7532364576,0.0463781429\N,-0.9308339279,-0.2292320628,-0.0219812606\C,0.0486042907,0.7602611013,0.0145820427\C,-0.6601293854,1.9617002112,0.0595059715\C,1.4660285767,0.4189268316,0.0201758972\C,-0.1322469297,3.3507285886,0.1292320277\H,0.3247468041,3.662261142,-0.8190085043\H,-0.9615992444,4.0313583947,0.3282967577\H,0.6155649128,3.4654331962,0.9201848496\N,2.3209325397,1.5161546855,0.0071927181\H,2.0178054113,2.3550226496,-0.4736187787\O,1.8901692637,-0.7178595574,0.0933464389\C,4.3902672187,1.0370255869,0.8804997226\H,4.0395014813,0.1454776316,1.4095802278\H,5.419024026,0.884485532,0.5500167488\H,4.3365980492,1.9123751795,1.5383201164\O,3.6392349532,1.2482514145,-0.3040763724\\Version=ES64L-G16RevC.01\State=1-A\HF=-702.0607932\RMSD=3.689e-09\RMSF=6.390e-06\Dipole=-0.2325416,0.104332,0.1955356\Quadrupole=0.8222262,3.3906961,-4.2129223,9.6134546,3.4287254,0.0160428\PG=C01 [X(C10H11N3O2)]\\@

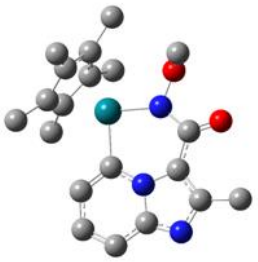
Intermediate I



1\1\GINC-USER\FOpt\RM06\Gen\C20H25Cl1N3O2Rh1\USER\31-Aug-2022\0\\# opt
freq gen m06 pseudo=read\\PVBkf\\0,1\C,-4.1157918769,-1.7914099293,0.
7245354239\C,-3.3395941127,-0.6928996531,0.9574981183\C,-2.6430607026,
-0.7049718605,-1.3508811453\C,-3.4064478187,-1.8522600633,-1.586966367
9\C,-4.1348057461,-2.3834306035,-0.551265566\H,-4.7104323175,-2.195767
2337,1.5338173606\H,-3.4166482587,-2.2708162996,-2.5861442931\H,-4.746
4340924,-3.2638774952,-0.7204438961\N,-1.8996588342,0.0248947633,-2.19
65799082\N,-2.6100602808,-0.1857206019,-0.0701505004\C,-1.6910281476,0
.8697176332,-0.0848272786\C,-1.3697300772,1.0097685076,-1.4557327915\C
,-1.5837420122,1.8704424849,1.0365380929\C,-0.7044847822,2.1707549201,
-2.0934888965\H,-0.0820546362,1.8494663619,-2.9324469693\H,-1.48119025
34,2.8240883079,-2.5078525163\N,-0.2526799744,2.0659783169,1.150467733
9\O,-2.5310315909,2.3192460148,1.6546442756\C,0.0171710886,2.358072540
4,3.4458307827\H,0.5115622048,1.3823982509,3.5406301375\H,0.4642479232
,3.0787756532,4.1340294361\H,-1.049430114,2.2424560777,3.6615157345\O,
0.2190133393,2.8965614974,2.1441313829\Rh,0.5642137715,0.2306545758,0.
5176611818\C,2.6999341632,0.4675272223,0.762058573\C,2.3613962985,-0.9
143579363,0.9545301092\C,1.7945233561,-1.410370479,-0.268901101\C,1.83
68998143,-0.3504278176,-1.2271066477\C,2.3660126236,0.8220684282,-0.58
89490154\C,3.3020958988,1.3951491504,1.7539117769\H,3.3917238897,0.928
9558281,2.7376572794\H,4.3047035816,1.7052286351,1.4341343518\H,2.6876
332715,2.2970576237,1.8627763715\C,1.2919706214,-2.7845834709,-0.52866
60537\H,2.0763498686,-3.432160448,-0.9412210717\H,0.9156399126,-3.2449
469787,0.3883340124\H,0.4637064295,-2.7630487084,-1.2449623866\C,1.440
3949902,-0.5005695367,-2.6501764159\H,1.9896570796,-1.3374306148,-3.09
67581976\H,0.3685006082,-0.7131723292,-2.7606903879\H,1.6676600353,0.3
955515564,-3.2317632236\H,-0.1214678934,2.7491092656,-1.3757500736\C,2
.6072472259,-1.699823657,2.1874033449\H,1.9157793395,-2.5395779949,2.2
728856954\H,3.6327889539,-2.0908672082,2.17456641\H,2.483872955,-1.087
4192015,3.0841785306\H,-3.2727978339,-0.1664038273,1.8993947567\Cl,-0.
6013598931,-0.9649190048,2.2969519455\C,2.6626611352,2.1459053699,-1.1
941520858\H,3.7433501387,2.268603877,-1.3393211725\H,2.1787389413,2.27
41326905,-2.1643879352\H,2.3231277899,2.9553004001,-0.5388679205\\Vers
ion=ES64L-G16RevC.01\State=1-A\HF=-1661.1227173\RMSD=2.441e-09\RMSF=7.
332e-06\Dipole=2.003994,-1.5041669,-1.3950127\Quadrupole=8.7378443,-4.

5490249,-4.1888194,10.4591397,2.1181235,-1.3301609\PG=C01 [X(C20H25Cl1
N3O2Rh1)]\\@

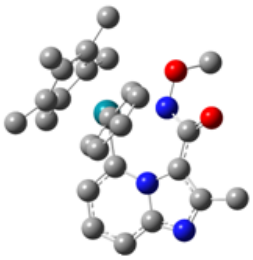
Intermediate II



1\1\GINC-USER\FOpt\RM06\Gen\C20H24N3O2Rh1\USER\01-Sep-2022\0\\# opt fr
eq gen m06 pseudo=read\\IN2KJ\\0,1\C,0.7613772454,2.5437868642,-0.4431
156478\C,0.9336610064,1.1891568391,-0.2094923349\C,3.3231085862,1.5669
483524,-0.639703683\C,3.1023892351,2.9224685688,-0.8705139234\C,1.8194
949019,3.4033780092,-0.770761757\H,-0.2356684731,2.9593276646,-0.37434
94895\H,3.9521568398,3.5472033006,-1.1191986724\H,1.6178708433,4.45592
99266,-0.9464384749\N,4.462853066,0.8760554931,-0.6730257965\N,2.23353
73888,0.7468851257,-0.3195631911\C,2.7619123437,-0.5191308685,-0.15066
47883\C,4.1362612156,-0.3910754827,-0.3762359753\C,2.0407079268,-1.719
5647852,0.1979048933\C,5.1604186384,-1.4609895915,-0.3155332392\H,4.92
7135489,-2.2702034032,-1.0135922915\H,6.1375520876,-1.0365459197,-0.55
50771139\N,0.6610848722,-1.5674199747,0.328980556\O,2.6062681131,-2.79
27074255,0.3498097124\C,-0.1102887489,-3.6432550708,-0.3513889224\H,0.
8555844737,-3.9788339764,-0.7394433004\H,-0.6654394942,-4.4984392486,0
.0429664948\H,-0.6921216088,-3.1609166595,-1.1519927644\O,0.0574849002
,-2.7533783628,0.7359007044\Rh,-0.6074887378,-0.058818071,0.2684942011
\C,-2.1975851521,-0.062365137,1.7784024683\C,-2.1159006249,1.261466251
6,1.182450267\C,-2.4317517778,1.1268360378,-0.1875588741\C,-2.70639589
95,-0.2740333562,-0.4362912773\C,-2.6376547377,-0.9853425391,0.7920966
603\C,-1.9292288154,-0.3890353595,3.1996194406\H,-1.262470265,0.343495
013,3.6610428803\H,-2.8643270207,-0.4024012947,3.7752905307\H,-1.46618
73251,-1.3761299209,3.2916807521\C,-2.5991095785,2.1948684686,-1.21081
81425\H,-3.6381962781,2.226047501,-1.5607873495\H,-2.3630460323,3.1839

239011,-0.8116411786\H,-1.959835835,2.0271701461,-2.0836669342\C,-3.08
78735952,-0.817905278,-1.7627725954\H,-4.1435349792,-0.6011717149,-1.9
742368129\H,-2.4942537274,-0.3621752749,-2.560605078\H,-2.9510859763,-
1.9004860144,-1.8148920358\H,5.1899876448,-1.9211219921,0.6764094634\C
,-1.8453408892,2.5068155861,1.9489543927\H,-1.7078763177,3.3694003528,
1.2934749946\H,-2.6817996493,2.7308601073,2.6223210066\H,-0.9419992569
,2.4138397007,2.5593929826\C,-2.9548731313,-2.4169398769,1.0328006008\
H,-3.9165828134,-2.5146972691,1.5510962241\H,-3.026380319,-2.978043985
7,0.0975354535\H,-2.184289758,-2.8939793569,1.6434089646\\Version=ES64
L-G16RevC.01\State=1-A\HF=-1200.2850437\RMSD=2.737e-09\RMSF=2.937e-06\
Dipole=-3.9496508,1.1407844,0.0880841\Quadrupole=-5.290343,1.7249137,3
.5654293,3.0709397,0.5768351,3.2096517\PG=C01 [X(C20H24N3O2Rh1)]\\@

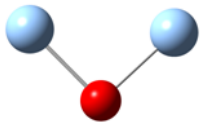
Intermediate III



1\1\GINC-USER\FOpt\RM06\Gen\C26H30N3O2Rh1(2+)\USER\25-Jul-2022\0\\# op
t freq gen m06 pseudo=read\\INIIK\\2,1\C,0.6205997726,2.6696192802,0.0
89302694\C,0.8018897173,1.2958242137,-0.1394279994\C,3.119432521,1.840
6231147,-0.7257752407\C,2.8951891839,3.1904037901,-0.4874781955\C,1.63
79254955,3.5993632031,-0.0605516561\H,-0.3618513553,3.0121993189,0.389
5778567\H,3.7139141695,3.8831619772,-0.6496640177\H,1.4480218086,4.649
1288273,0.1349128732\N,4.2215575372,1.2459669019,-1.1810437713\N,2.088
2088824,0.9236486441,-0.4968390378\C,2.6304312099,-0.3048948766,-0.845
0968425\C,3.9500493563,-0.0574380774,-1.2760780969\C,1.9963427028,-1.5
878055054,-0.680780119\C,4.9388598465,-1.0462589428,-1.7511598874\H,4.
6619049265,-1.4200294901,-2.7423246656\H,5.921105991,-0.5776286336,-1.
8133422523\N,0.8558580412,-1.5347011469,0.2788468868\O,2.3223306112,-2
.6169304219,-1.183574054\C,1.006466918,-3.661198511,1.285600274\H,1.22
24824439,-3.1962296486,2.2567078712\H,0.3540340968,-4.5221583675,1.434
3750526\H,1.9235002752,-3.9720796714,0.7838108878\O,0.2396092572,-2.75
74417129,0.4685445984\Rh,-0.6851720441,-0.0183865922,-0.0800381977\C,-
2.2674433618,-0.464299701,1.4538831288\C,-2.3290297681,0.9504239665,1.
1095464964\C,-2.6806173805,1.0323059103,-0.2602330818\C,-2.9742790229,
-0.3265203217,-0.7203622682\C,-2.7035133269,-1.2303324851,0.3246922832
\C,-1.9377712107,-1.0008393241,2.7901779979\H,-1.2628922215,-0.3448653

009,3.3469455003\H,-2.8572681692,-1.0907126415,3.3871683251\H,-1.50411
53816,-2.0030808613,2.729207289\C,-3.0003338457,2.2520127541,-1.038887
4742\H,-4.0850477784,2.4209640257,-1.0248093139\H,-2.5293351253,3.1482
949806,-0.6304214655\H,-2.7105612272,2.1537009297,-2.0885892777\C,-3.5
60292725,-0.6410518581,-2.0343239769\H,-4.6155162725,-0.3300534089,-2.
021367003\H,-3.0832943624,-0.0873924952,-2.8493252929\H,-3.5325169257,
-1.7069073597,-2.2644067926\H,4.9862615252,-1.9172782403,-1.0918420193
\C,-2.1962192854,2.0584535337,2.0847008331\H,-2.1808832125,3.038791049
5,1.6052435199\H,-3.0688771046,2.046272911,2.7514622688\H,-1.311831626
9,1.9612414562,2.721043281\C,-2.9121292988,-2.6988921765,0.3056430231\
H,-3.9268977188,-2.9341511787,0.6487488254\H,-2.8030720034,-3.11789008
65,-0.6971807687\H,-2.212082302,-3.2144917125,0.965561205\C,-0.5007813
848,-0.379735961,-2.1251143184\C,-0.4821238498,-1.7063808069,-2.513235
434\C,-0.3759458089,0.6755422759,-3.0174070076\C,-0.2209086095,-1.9899
168316,-3.853084798\H,-0.6354370987,-2.5207922778,-1.8103625756\C,-0.1
202914221,0.3645867638,-4.3500864341\H,-0.4383328914,1.7128709947,-2.7
064122102\C,-0.0477356903,-0.9595776804,-4.7655407498\H,-0.1703189642,
-3.0259672155,-4.1728847291\H,0.0221681604,1.1725269045,-5.0615006137\
H,0.1315213794,-1.1879914837,-5.810992275\H,1.2185147975,-1.19822625,1
.1870913424\\Version=ES64L-G16RevC.01\State=1-A\HF=-1431.7815584\RMSD=
5.548e-09\RMSF=5.579e-06\Dipole=-1.8856315,0.8748523,1.4731956\Quadrup
ole=4.156317,0.0534152,-4.2097322,1.6266411,-5.9720467,-1.5487842\PG=C
01 [X(C26H30N3O2Rh1)]\\@

Ag_2O

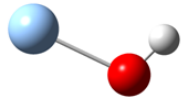


1\1\GINC-USER\Freq\RM06\Gen\Ag2O1\USER\22-Jul-2022\0\\#N Geom=AllCheck
Guess=TCheck SCRF=Check GenChk RM06/ChkBas Freq\\Ag2o\\0,1\Ag,-0.6843
578623,-1.2126511407,0.1489249951\O,1.3487200446,-1.2226674742,-0.1379
052673\Ag,1.7562730574,-1.152436395,1.873250082\\Version=ES64L-G16RevC
.01\State=1-A1\HF=-366.7053975\RMSD=1.115e-09\RMSF=4.843e-06\ZeroPoint
=0.0022317\Thermal=0.006379\ETot=-366.6990185\HTot=-366.6980743\GTot=-
366.7331617\Dipole=-1.1201949,0.0553007,1.5836065\DipoleDeriv=0.640036
2,0.0064416,0.1844623,-0.0000066,0.3647249,-0.0028485,-0.0001889,-0.00
28485,0.2832543,-1.0208739,-0.0096355,-0.2759235,-0.0096355,-0.7297654
,-0.0033434,-0.2759235,-0.0033434,-0.8253915,0.3808376,0.0031939,0.091
4612,0.0096421,0.3650406,0.0061919,0.2761124,0.0061919,0.5421372\Polar
=93.1345761,0.7196794,54.9361869,20.6089271,0.824353,78.5137873\Quadru
pole=3.7982886,-2.8242056,-0.974083,0.2352626,6.73704,0.0646866\PG=C02
V [C2(O1),SGV(Ag2)]\NImag=0\\0.11944702,-0.00031066,-0.00042264,-0.008
89621,0.00018537,0.00487923,-0.10799314,0.00049241,0.01410084,0.108572
03,0.00080710,0.00045966,-0.00002678,0.00002680,-0.00078850,0.02311226
,-0.00002678,-0.00030623,0.00076753,0.00379998,0.10789588,-0.01145388,
-0.00018175,-0.00520463,-0.00057889,-0.00083390,-0.02387979,0.01203277
,-0.00049644,-0.00003703,-0.00015859,-0.00051921,0.00032883,-0.0037732
0,0.00101565,-0.00029181,-0.01421605,-0.00015859,-0.00457300,-0.014868
36,-0.00377320,-0.10758965,0.02908442,0.00393179,0.11216266\\-0.000006
75,-0.00000025,-0.00000721,-0.00000231,0.00000011,0.00000326,0.0000090
5,0.00000014,0.00000395\\\@

AgCl

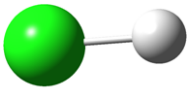
1\1\GINC-USER\FOpt\RM06\Gen\Ag1Cl1\USER\22-Jul-2022\0\\# opt freq m06/
gen pseudo=read\\Agcl\\0,1\Ag,-0.7567643284,-1.21785172,0.\Cl,1.589033
6884,-1.21785172,0.\\Version=ES64L-G16RevC.01\State=1-SG\HF=-606.00029
06\RMSD=3.395e-09\RMSF=1.662e-07\Dipole=-2.5018091,0.,0.\Quadrupole=-0
.8682923,0.4341461,0.4341461,0.,0.,0.\PG=C*V [C*(Cl1Ag1)]\\@

AgOH



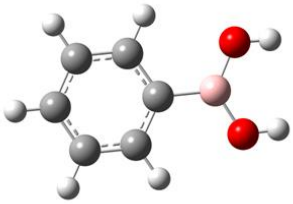
1\1\GINC-USER\FOpt\RM06\Gen\Ag1H1O1\USER\22-Jul-2022\0\\# opt freq m06
/gen pseudo=read\\AgOH\\0,1\Ag,-0.7821318538,-1.2179549882,-0.00295735
32\O,1.2763357405,-1.2179187038,-0.001918252\H,1.5796547333,-1.1860996
58,0.9092601751\\Version=ES64L-G16RevC.01\State=1-A'\HF=-221.5630939\R
MSD=5.743e-09\RMSF=4.558e-05\Dipole=-1.9867879,0.014502,0.415284\Quadr
upole=-1.7556106,0.0002561,1.7553545,0.092695,2.6544386,0.0613642\PG=C
S [SG(Ag1H1O1)]\\@

HCl



1\1\GINC-USER\FOpt\RM06\6-311++G(d,p)\Cl1H1\USER\25-Jul-2022\0\\# opt
freq m06/6-311++g(d,p)\\Hcl\\0,1\Cl,-2.2903630993,-1.80505412,0.\H,-3.
5758103407,-1.80505412,0.\\Version=ES64L-G16RevC.01\State=1-SG\HF=-460
.7929985\RMSD=4.190e-09\RMSF=5.418e-05\Dipole=-0.5422275,0.,0.\Quadrup
ole=1.8033288,-0.9016644,-0.9016644,0.,0.,0.\PG=C*V [C*(H1Cl1)]\\@

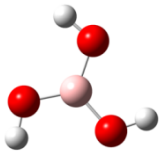
Phenyl boronic acid



1\1\GINC-USER\FOpt\RM06\6-311++G(d,p)\C6H7B1O2\USER\23-Jul-2022\0\\# o
pt freq m06/6-311++g(d,p)\\Phenylboronic acid\\0,1\C,-1.8034794367,-1.
1375934885,-0.3573142511\C,-0.4164856306,-1.1369304243,-0.363727296\C,
0.2765891467,0.0138539304,-0.0103374184\C,-0.419894741,1.1608704566,0.
3485240092\C,-1.8068867324,1.1539924598,0.3531138357\C,-2.5225229529,0
.0062607538,0.0007350464\H,-2.3461272859,-2.0376174479,-0.6337583855\H
,0.127752094,-2.0339495985,-0.6443694208\H,1.3628805661,0.0167593589,-
0.0146116199\H,0.1216477412,2.0608550706,0.6248506814\H,-2.352216054,2
.051068549,0.6338413153\B,-4.0783727249,0.001993417,0.0070870441\O,-4.

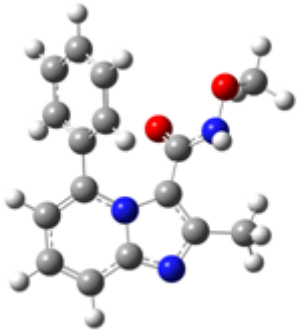
7223785653,-1.1514575742,-0.3471102002\H,-5.6797090811,-1.1262100239,-0.3343058272\O,-4.7259040859,1.1518797094,0.3665465548\H,-5.6831510672,1.1211765118,0.3618600085\\Version=ES64L-G16RevC.01\State=1-A\HF=-408.1131066\RMSD=6.187e-09\RMSF=5.130e-06\Dipole=-0.9589659,-0.0028104,0.0041347\Quadrupole=10.7100955,-4.2406003,-6.4694951,0.0450926,-0.0728145,0.764438\PG=C01 [X(C6H7B1O2)]\\@

Boronic acid



1\1\GINC-USER\FOpt\RM06\6-311++G(d,p)\B1H3O3\USER\23-Jul-2022\0\\# opt freq m06/6-311++g(d,p)\\Boronic acid\\0,1\B,0.393682516,-2.3106087429,0.0080530717\O,-0.5069195111,-1.3136851726,-0.2224891213\H,-0.0972154012,-0.5203315401,-0.5716967033\O,1.7150832762,-2.1102134922,-0.2601173423\H,2.2524580773,-2.878372931,-0.0592321479\O,-0.0266259918,-3.5075963398,0.506432085\H,-0.9732165254,-3.5338321814,0.6559890481\\Version=ES64L-G16RevC.01\State=1-A\HF=-252.4638564\RMSD=5.398e-09\RMSF=4.292e-05\Dipole=-0.0002502,-0.0010662,0.0011171\Quadrupole=0.5903774,0.4142149,-1.0045923,-0.0831958,-0.2428614,-0.5963831\PG=C01 [X(B1H3O3)]\\@

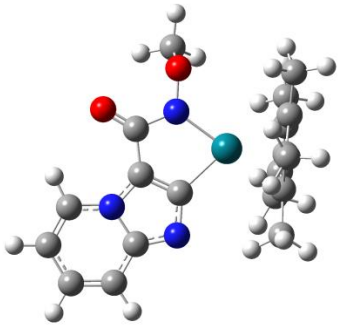
7a (Product)



1\1\GINC-USER\FOpt\RM06\6-311++G(d,p)\C16H15N3O2\USER\23-Jul-2022\0\\# opt freq m06/6-311++g(d,p)\\Product\\0,1\C,0.9076823005,-2.7346896699,-0.5305977952\C,0.4242959285,-1.4993648967,-0.1957656379\C,2.7198029112,-0.7079516656,-0.0661221846\C,3.1893579589,-1.9923347989,-0.3913416478\C,2.2912283741,-2.9835331707,-0.6566857555\H,0.1964438958,-3.5483023119,-0.6172478723\H,4.2619160223,-2.1439132603,-0.4169576979\H,2.6326053384,-3.9800523899,-0.9154144784\N,3.4078131733,0.3804638155,0.2293

52142\N,1.3372191228,-0.466452427,-0.0629617605\C,1.2037430101,0.88847
28608,0.2397248161\C,2.4937675802,1.3568058314,0.4292073229\C,0.006254
2513,1.74220255,0.091750263\C,2.9099199855,2.7413688479,0.7596409344\H
,3.367861307,2.7633036065,1.7537994829\H,3.6670597239,3.0851384928,0.0
489493793\H,2.0636570443,3.4299714189,0.7622294534\N,-0.6958154438,1.4
965685469,-1.0690852496\H,-0.2164938165,1.0973775362,-1.8677253573\O,-
0.3143437994,2.5915643514,0.8916733598\C,-2.9102799009,2.0845000567,-0
.8819675518\H,-2.8741503157,2.1714422688,0.2089371974\H,-3.6093072919,
2.8187250669,-1.2857612319\H,-3.2205470331,1.0718396157,-1.1663262448\
O,-1.6505114138,2.4091818386,-1.4538269289\C,-0.9976070416,-1.30089244
41,0.13696143\C,-1.9900001946,-1.8074310111,-0.701128639\C,-1.36776360
83,-0.6994068528,1.3407875286\C,-3.3271758489,-1.7114940915,-0.3457888
814\H,-1.7074266862,-2.2679578636,-1.6441299902\C,-2.7040549003,-0.605
6583732,1.6935533607\H,-0.6052497486,-0.3083954426,2.009123367\C,-3.68
78681244,-1.1096620703,0.8521165057\H,-4.0907836973,-2.1055010842,-1.0
095803488\H,-2.9779231761,-0.1388222696,2.6345285444\H,-4.7343218869,-
1.034702611,1.1312211662\\Version=ES64L-G16RevC.01\State=1-A\HF=-932.9
798812\RMSD=5.507e-09\RMSF=2.218e-05\Dipole=-1.0376867,-1.5578713,-0.6
601668\Quadrupole=2.7202526,-2.6237474,-0.0965052,-0.554533,-1.0988174
,1.5664565\PG=C01 [X(C16H15N3O2)]\\@

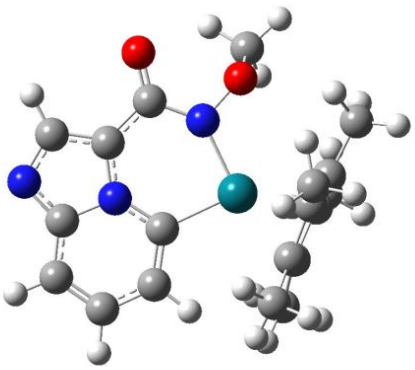
5 membered rodacycle



1\1\GINC-USER\FOpt\RM06\Gen\C19H22N3O2Rh1\USER\27-Sep-2023\0\\# opt fr
eq gen m06 pseudo=read\\INT 5mem\\0,1\C,-0.884579672,-4.951795006,-0.5
84493036\C,-0.80807957,-3.5997516214,-0.4413268786\C,-3.1231843639,-3.
402025764,-1.1674475265\C,-3.1856760288,-4.7960985757,-1.3124996798\C,
-2.083738258,-5.5573638279,-1.0249280296\H,-0.0127726996,-5.5537754436
,-0.3574675407\H,-4.1184711609,-5.2316194175,-1.6521787228\H,-2.126950
8759,-6.6358608732,-1.1351168346\N,-4.045610685,-2.4583075418,-1.37920
94689\N,-1.9089811653,-2.8453553952,-0.727863126\C,-2.1325827989,-1.49
37483382,-0.6842448257\C,-3.4318179191,-1.2922838136,-1.0811846795\C,-

5.5007208659,2.2227447396,-0.399446943\C,-6.0999695892,0.9199482328,-0
.7020288169\C,-5.8772656571,0.6297569666,-2.0683882325\C,-5.0210084844
,1.666866057,-2.5729797967\C,-4.8573596349,2.6906605224,-1.5496547065\
C,-5.5822186198,2.8755424525,0.9312837955\H,-5.322589269,2.1744100643,
1.7313767376\H,-4.9114403974,3.734402954,1.0057009654\H,-6.6039534102,
3.2254718013,1.125984175\C,-6.3835007271,-0.5619760417,-2.8033152554\H
,-6.0516612134,-0.5548155005,-3.8445526337\H,-6.0230213449,-1.49454721
58,-2.3520011629\H,-7.4797292398,-0.5728082604,-2.8056019636\C,-4.4770
578024,1.7567564681,-3.9491010021\H,-3.5015392864,2.250333601,-3.95685
33964\H,-4.3576775106,0.7666510712,-4.3952641109\H,-5.1513376658,2.340
5124281,-4.5898257788\C,-6.8981509716,0.0947588285,0.2389946468\H,-6.8
428338544,-0.9631008213,-0.0328037157\H,-6.5367482246,0.1959619049,1.2
662469086\H,-7.9542477504,0.395724603,0.2264274305\C,-4.0660979337,3.9
382549612,-1.7150470817\H,-3.1214879817,3.738687182,-2.2302309752\H,-4
.6144114486,4.6883058715,-2.2982647074\H,-3.8119970644,4.3798309253,-0
.7481484303\C,-1.2872352109,-0.3811226278,-0.2683261776\O,-0.133092793
5,-0.4392590321,0.1079809235\N,-2.0716446224,0.7706869346,-0.367966171
\O,-1.3953209781,1.9521144771,-0.1227101119\C,-1.469179645,2.285256221
6,1.2460348289\H,-0.9598789951,3.245384782,1.3587891923\H,-2.519176714
2,2.3842440357,1.5628701415\H,-0.9702314144,1.5315462982,1.8664100534\
H,0.0665748816,-3.0497961566,-0.1133053611\Rh,-3.9655154431,0.67795682
01,-0.9903956492\\Version=ES64L-G16RevC.01\State=1-A\HF=-1160.9731405\
RMSD=9.171e-09\RMSF=2.530e-05\Dipole=-2.2641314,0.9601339,-0.220429\Qu
adrupole=-9.5890761,9.7627146,-0.1736385,-8.9394238,-1.1907208,0.33304
1\PG=C01 [X(C19H22N3O2Rh1)]\\@

6 membered rodacycle



1\1\GINC-USER\FOpt\RM06\Gen\C19H22N3O2Rh1\USER\28-Sep-2023\0\\# opt fr
eq gen m06 pseudo=read\\INT 6 mem\\0,1\C,-0.8702739161,-2.6048080963,-

0.1664617156\C,-0.9290517837,-1.2258072251,-0.0755208257\C,-3.3787235584,-1.4769647778,-0.0731387541\C,-3.2681196966,-2.8639407843,-0.1686079719\C,-2.0140283513,-3.4187351417,-0.2154738482\H,0.1006316756,-3.0818837116,-0.2060293662\H,-4.1779804797,-3.4516097562,-0.2017380429\H,-1.8987091343,-4.4958697149,-0.2912902003\N,-4.4689778848,-0.7119266003,-0.0111457331\N,-2.2054958765,-0.7079064781,-0.0326040479\C,-2.6269624004,0.6023930767,0.0589838519\C,-4.0120812805,0.5438891287,0.0697865675\C,-1.804023905,1.7906758035,0.1357171625\N,-0.4330780705,1.5609907511,0.0676416727\O,-2.2937273543,2.9035467783,0.2359563369\C,0.3225368365,3.4792858913,-0.9867106743\H,-0.6759028056,3.8286590338,-1.2646899851\H,0.9723657436,4.337269347,-0.7956016103\H,0.7471708229,2.8655520894,-1.7961119597\O,0.2875851404,2.7410131645,0.2200165785\Rh,0.7293487688,-0.0354119686,-0.0008867793\C,2.5370182872,0.0212168786,1.2344846191\C,2.2956662561,-1.3502586484,0.8158695979\C,2.3920576937,-1.3830665493,-0.5924634153\C,2.6954525337,-0.0377295535,-1.0408748442\C,2.8612871745,0.8027042107,0.0923442258\C,2.5186033363,0.5127658949,2.6329870302\H,1.8852491682,-0.1104185204,3.2691025768\H,3.5318671108,0.5045627826,3.0565529252\H,2.1447123209,1.5398549256,2.68101765\C,2.3380265714,-2.5617518859,-1.4995447611\H,3.3125429176,-2.7175199331,-1.9784503938\H,2.0909818866,-3.480535792,-0.9629513676\H,1.5957450384,-2.4309319557,-2.2935064172\C,2.8837324311,0.3322981597,-2.4649962342\H,3.8699580135,0.0016145164,-2.8170643364\H,2.1326731573,-0.1486393373,-3.0985855113\H,2.8163804537,1.4113719513,-2.6194526842\C,2.0899751134,-2.484612706,1.7552833088\H,1.8203800622,-3.4051862688,1.2334524206\H,3.0075660629,-2.6814385361,2.3231410765\H,1.2927795778,-2.2705631427,2.4735825114\C,3.2819201098,2.2280484073,0.117680575\H,4.3008552628,2.3195220025,0.5129074818\H,3.2759472577,2.6692146616,-0.8822814683\H,2.613169234,2.8251427455,0.7432801544\H,-4.6680995515,1.4020279231,0.1351053049\\Version=ES64L-G16RevC.01\State=1-A\HF=-1160.985348\RMSD=3.094e-09\RMSF=1.209e-05\Dipole=4.1385876,-1.583366,-0.407738\Quadrupole=-8.1539033,1.9572286,6.1966748,5.613771,0.7247823,-3.4668822\PG=C01 [X(C19H22N3O2Rh1)]\\@

References

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2. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb , J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.