Supporting Information

Palladium-catalyzed Electrooxidative C–H Amination towards the Synthesis of Pyrido[1,2-*a*]benzimidazoles with Hydrogen Evolution

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General Information

All glassware was oven dried at 110 °C for hours and cooled down under vacuum. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. The instrument for electrolysis is dual display potentiostat (DJS-292B) (made in China). Cyclic voltammograms were obtained on a CHI 605E potentiostat. The anodic electrode was carbon cloth (1 cm × 0.5 cm × 0.036 cm) and cathodic electrode was iron plate (1 cm × 0.5 cm × 0.1 cm). These electrodes are commercially available from GaossUnion, China. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 ℃). GC-MS spectra were recorded on a Varian GC-MS 3900-2100T.

The known compounds were characterized by ^{1}H NMR, ^{13}C NMR and ^{19}F NMR. ^{1}H, ^{19}F and ^{13}C NMR data were recorded with ADVANCE III 400 MHz with tetramethylsilane as an internal standard. High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument. All chemical shifts (δ) were reported in ppm and coupling constants (*J*) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for ^{1}H), Chloroform-*d* (77.00 ppm for ^{13}C), respectively.

General Procedures for the Synthesis of *N*-phenylpyridin-2-amines

In an oven-dried Schlenk tube equipped with a stir bar, 30 mmol of *p*-methylaniline and 27 mmol of 2-bromopyridine were added. Under the protection of N_2, the mixture was stirred at 160 °C for 10 hours. After completion of the reaction, the products were determined by TLC. The mixture was then purified by flash chromatography on silica gel with petroleum

ether, triethylamine and ethyl acetate.

General Procedures for the Synthesis of Pyrido[1,2-*a*]benzimidazoles

In an oven-dried undivided three-necked cell (5 mL) equipped with a stir bar, $Pd(PPh_3)_2(OAc)_2$ (0.01 mmol, 7.5 mg), *N*-(*p*-tolyl)pyridin-2-amine **1a** (0.2 mmol, 36.8 mg) and $LiClO_4$ (0.4 mmol, 42.4 mg) were combined and added. The cell was equipped with carbon cloth (10 mm×5 mm×0.36 mm) as the anode and iron plate (10 mm×5 mm×1 mm) as the cathode and was then charged with nitrogen. Under the protection of N_2, MeCN (2.5 mL) and HCOOH (2.5 mL) were injected respectively into the tubes via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 2.0 mA at room temperature for 6.5 h. When the reaction finished, the pure product was obtained by flash column chromatography on silica gel.

General Procedures for the Gram-Scale Synthesis

In an oven-dried undivided four-necked cell (100 mL) equipped with a stir bar, $Pd(PPh_3)_2(OAc)_2$ (0.5 mmol, 375 mg), *N*-(*p*-tolyl)pyridin-2-amine **1a** (10.0 mmol, 1.85 g) and $LiClO_4$ (2.0 mmol, 210 mg) were combined and added. The cell was equipped with carbon cloth (10 mm×5 mm×0.36 mm) as the anode and iron plate (10 mm×5 mm×1 mm) as the cathode and was then charged with nitrogen. Under the protection of N_2, MeCN (30 mL) and HCOOH (30 mL) were injected respectively into the tubes via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 20.0 mA at room temperature for 48 h. When the reaction finished, the pure product was obtained by flash column chromatography on silica gel.

General Procedures for the Competition Experiment

In an oven-dried undivided three-necked cell (5 mL) equipped with a stir bar, $Pd(PPh_3)_2(OAc)_2$ (0.01 mmol, 7.5 mg), *N*-(*p*-tolyl)pyridin-2-amine (0.1 mmol, 36.8 mg), 8-trifluoromethoxybenzo[4,5]imidazo[1,2-*a*]pyridine (0.1 mmol, 36.8 mg) and $LiClO_4$ (0.4 mmol, 42.4 mg) were combined and added. The cell was equipped with carbon cloth (10 mm×5 mm×0.36 mm) as the anode and iron plate (10 mm×5 mm×1 mm) as the cathode and was then charged with nitrogen. Under the protection of N_2, MeCN (2.5 mL) and HCOOH (2.5 mL) were injected respectively into the tubes via syringes. The reaction

mixture was stirred and electrolyzed at a constant current of 2.0 mA at room temperature for 9 h. When the reaction finished, the pure product was obtained by flash column chromatography on silica gel.

Procedure for Cyclic Voltammetry (CV)

Cyclic voltammetry was performed in a three-necked cell under air at room temperature. The working electrode was a steady glassy carbon disk electrode. The counter electrode was a platinum wire and the reference electrode was an Ag/AgCl electrode. 7 mL of MeCN and 7 mL of HCOOH were poured into the electrochemical cell in all experiments. The CV of substrates (**1a**) were measured at the concentration of 0.71 mM. The scan rate of 1a is 0.05 V/s, ranging from 0 V to 2.0 V.

Investigation of the Role of Electrodes

We did several contrast experiments to explain the role of electrode in the catalysis (can be also found in page 4 in supporting information). It indicated that Fe cathode is only responsible for the hydrogen evolution when carbon cloth anode can only oxidize Pd(0) but not substrate. As shown as follows, pictures (a), (b) and (c) (figure S1) are reaction devices of entry 1, 2 and 3 respectively (table S1). The devices of reaction (b) and (c) are absolutely same as standard device (a), equipping with electrode carbon cloth and Fe plate. It proved that catalyst and electricity were all indispensable. And two experiments were conducted to investigate the influence of Fe plate (entry 5 and 6 in table S1). For the entry 5 in table S1, Pt plate was applied as cathode and 0.2 mmol $Fe(OAc)_2$ were added, with no desired products detected. However, for the entry 6 in table S1, 78% yield was detected with Fe cathode replaced by Pt cathode. It illustrated that the Fe salt, which may exist from the etching of Fe cathode, could not promote the reaction. With these results in hand, we could conclude that the Fe cathode was not involved in the catalysis and only played vital role in hydrogen evolution. The different effects of Fe, Pt, and Ni cathodes on the reaction may result from the different hydrogen evolution efficiency of them.

The role of anode was also studied. The result of entry 3 in table S1 indicated anode

could only oxidize catalyst $Pd(PPh_3)_2(OAc)_2$ but not substrate **1a**. And carbon cloth anode could give better yield than Pt anode. The reason why carbon cloth performed better than Pt plate may be because of π–π stacking or π -H interaction between substrate **1a** and the the sp^2-structure of carbon cloth[1, 2]. indicating Pd^{2+} could meet substrate **1a** more easily on the surface of carbon cloth.

(a)  (b)  (c) 

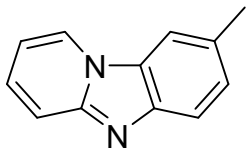
Figure S1. (a) standard reaction device of entry 1 (table S1); (b) reaction device of entry 2 (table S1); reaction device of entry 3 (table S1).

Entry 1	Variation from standard conditions	Yield[a]
1	none	92
2	no electric current	trace
3	no catalyst	n. d.
4	Pt anode instead of C cloth anode	n. d.
5	Pt cathode instead of Fe cathode[b]	trace
6	Pt cathode instead of Fe cathode	78

Table S1. Optimization of reaction conditions. [a]Standard reaction conditions: carbon

cloth plate (10 mm×5 mm×0.36 mm) anode, Fe plate (10 mm×5 mm×1 mm) cathode, constant current=2 mA, 1a (0.20 mmol), $Pd(PPh_3)_2(OAc)_2$ (0.01 mmol), $LiClO_4$ (0.40 mmol), CH_3CN (2.5 mL), HCOOH (2.5 mL), N_2, room temperature, 6.5 hours, undivided cell. Yields were detected by GC. [b]0.2 mmol $Fe(OAc)_2$ was added.

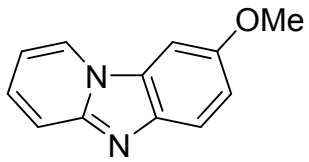
Detail Descriptions for Products.



2a

8-methylbenzo[4,5]imidazo[1,2-*a*]pyridine[3]

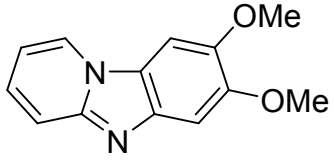
Yield: 92% (33.4 mg) white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.99 (dt, *J* = 6.9, 1.4 Hz, 1H), 8.10 (s, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.62 (dt, *J* = 9.3, 1.2 Hz, 1H), 7.50 (ddd, *J* = 9.3, 6.5, 1.4 Hz, 1H), 7.33 (dd, *J* = 8.3, 1.8 Hz, 1H), 6.95 (td, *J* = 6.7, 1.3 Hz, 1H), 2.53 (s, 3H). ^{13}C{1H} NMR (101 MHz, DMSO-d_6) δ 147.5, 142.1, 130.1, 129.6, 128.7, 127.1, 126.8, 118.6, 117.0, 111.4, 110.2, 21.5.



2b

8-methoxybenzo[4,5]imidazo[1,2-*a*]pyridine[4]

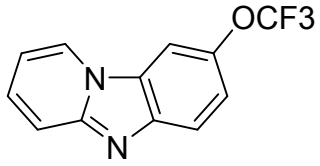
Yield: 99% (39.5 mg) white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35 (dt, *J* = 6.9, 1.3 Hz, 1H), 7.84 (d, *J* = 8.9 Hz, 1H), 7.65 (dt, *J* = 9.4, 1.2 Hz, 1H), 7.35 (ddd, *J* = 9.3, 6.7, 1.4 Hz, 1H), 7.31 (d, *J* = 2.4 Hz, 1H), 7.20 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.81 (td, *J* = 6.7, 1.2 Hz, 1H), 3.95 (s, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 155.3, 148.0, 139.1, 132.1, 128.1, 124.7, 120.6, 118.2, 115.9, 110.1, 93.2, 56.0.



2c

7,8-dimethoxybenzo[4,5]imidazo[1,2-*a*]pyridine

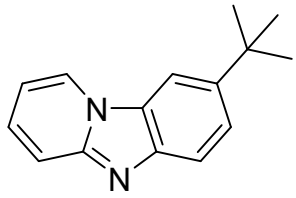
Yield: 99% (46.0 mg) white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 (dt, *J* = 6.9, 1.2 Hz, 1H), 7.66 (dt, *J* = 9.2, 1.1 Hz, 1H), 7.38 (s, 1H), 7.34 (ddd, *J* = 9.2, 6.7, 1.3 Hz, 1H), 7.31 (s, 1H), 6.84 (td, *J* = 6.8, 1.2 Hz, 1H), 4.04 (s, 3H), 4.04 (s, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 149.5, 147.7, 146.3, 138.8, 127.0, 124.2, 121.8, 117.5, 110.2, 100.7, 92.6, 56.5, 56.2. ESI HRMS *m/z* $(M+H)^{+}$ calcd 229.0972, obsd 229.0963.



2d

8-trifluoromethoxybenzo[4,5]imidazo[1,2-*a*]pyridine

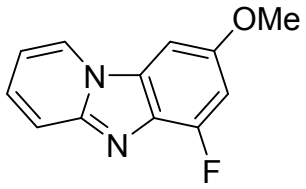
Yield: 62% (23.4 mg) white solid. Yield: 46 % (23.1 mg) white solid. ^{1}H NMR (Chloroform-*d*) δ 8.40 (dt, *J* = 6.9, 1.1 Hz, 1H), 7.92 (d, *J* = 8.9 Hz, 1H), 7.77 (d, *J* = 0.9 Hz, 1H), 7.69 (d, *J* = 9.3 Hz, 1H), 7.47 – 7.45 (m, 1H), 7.43 – 7.40 (m, 1H), 6.88 (td, J = 6.8, 1.0 Hz, 1H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 149.6, 143.2 (q, *J* = 2.0 Hz, 1C), 142.8, 129.8, 128.1, 125.1, 120.5, 119.8, 120.6 (q, *J* = 257.6 Hz, 1C), 118.1, 110.8, 103.9. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -58.16. ESI HRMS m/z (M+H)+ calcd 253.0583, obsd 253.0574.



2e

8-(tert-butyl)benzo[4,5]imidazo[1,2-*a*]pyridine[4]

Yield: 54% (24.0 mg) white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (dt, *J* = 6.9, 1.3 Hz, 1H), 7.88 – 7.86 (m, 2H), 7.67 (dt, *J* = 9.3, 1.1 Hz, 1H), 7.62 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.38 (ddd, *J* = 9.3, 6.6, 1.3 Hz, 1H), 6.82 (td, *J* = 6.7, 1.2 Hz, 1H), 1.45 (s, 9H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 148.5, 144.7, 142. 5, 128.7, 128.4, 125.0, 124.1, 119.2, 118.0, 110.0, 106.3, 35.1, 31.9.

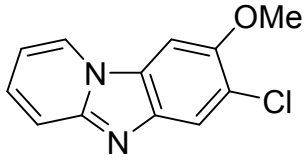


2f

6-fluoro-8-methoxybenzo[4,5]imidazo[1,2-*a*]pyridine

Yield: 99% (43.4 mg) white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (dt, *J* = 7.0, 1.3 Hz, 1H), 7.66 (dt, *J* = 9.3, 1.2 Hz, 1H), 7.36 (ddd, *J* = 9.4, 6.7, 1.4 Hz, 1H), 7.07 (d, *J* = 2.1 Hz, 1H), 6.90 (dd, *J* = 11.8, 2.1 Hz, 1H), 6.83 (td, *J* = 6.8, 1.3 Hz, 1H), 3.91 (s, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 155.5 (d, *J* = 11.1 Hz, 1C), 155.1, 152.6, 148.0, 128.7, 124.7, 118.5,

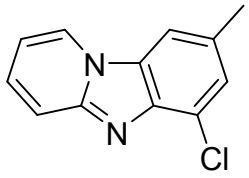
110.7, 101.7, 101.5, 89.3 (d, *J* = 5.1 Hz, 1C), 56.2. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -125.61 (d, *J* = 7.5 Hz). ESI HRMS *m/z* $(M+H)^+$ calcd 217.0772, obsd 217.0765.



2g

7-chloro-8-methoxybenzo[4,5]imidazo[1,2-*a*]pyridine

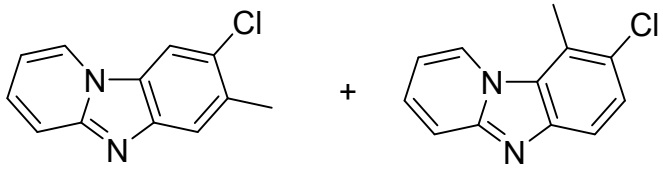
Yield: 70% (32.1 mg) white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 6.9 Hz, 1H), 7.92 (s, 1H), 7.61 (d, *J* = 9.4 Hz, 1H), 7.35 (ddd, *J* = 9.3, 6.6, 1.3 Hz, 1H), 6.82 (td, *J* = 6.8, 1.1 Hz, 1H), 3.99 (s, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 150.6, 148.4, 138.5, 128.5, 127.1, 124.5, 122.2, 120.7, 118.0, 110.5, 93.1, 56.7. ESI HRMS *m/z* $(M+H)^+$ calcd 233.0476, obsd 233.0468.



2h

6-chloro-8-methylbenzo[4,5]imidazo[1,2-*a*]pyridine

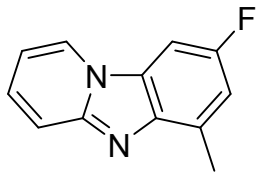
Yield: 71% (32.4 mg) white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (dt, *J* = 6.9, 1.3 Hz, 1H), 7.72 (dt, *J* = 9.3, 1.2 Hz, 1H), 7.52 (s, 1H), 7.40 (ddd, *J* = 9.3, 6.7, 1.4 Hz, 1H), 7.36 (d, *J* = 1.8 Hz, 1H), 6.83 (td, *J* = 6.8, 1.3 Hz, 1H), 2.53 (s, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 148.4, 139.8, 131.8, 129.5, 129.4, 126.8, 125.1, 123.7, 118.3, 110.8, 108.9, 21.6. ESI HRMS *m/z* $(M+H)^+$ calcd 217.0527, obsd 217.0519.



2i

8-chloro-7-methylbenzo[4,5]imidazo[1,2-*a*]pyridine + 8-chloro-9-methylbenzo[4,5] imidazo[1,2-*a*]pyridine

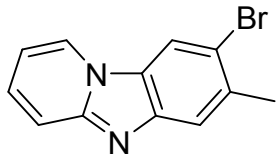
Yield: 40% (16.1 mg) white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.81 (d, *J* = 7.2 Hz, 1H), 8.34 (d, *J* = 6.9 Hz, 1H), 7.88 (s, 1H), 7.77 (s, 1H), 7.73 – 7.66 (m, 3H), 7.53 (d, *J* = 8.7 Hz, 1H), 7.45 – 7.40 (m, 2H), 6.87 – 6.82 (m, 2H), 2.98 (s, 3H), 2.58 (s, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 149.1, 148.9, 143.3, 143.3, 133.8, 129.9, 129.4, 128.8, 128.3, 127.5, 127.3, 127.0, 126.9, 125.0, 121.1, 120.8, 118.2, 118.1, 118.0, 110.6, 110.6, 110.5, 21.0, 15.9. ESI HRMS m/z (M+H)+ calcd 217.0527, obsd 217.0519.



2j

8-fluoro-6-methylbenzo[4,5]imidazo[1,2-*a*]pyridine

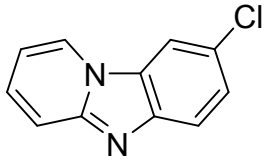
Yield: 64% (25.6 mg) white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (dt, *J* = 6.9, 1.3 Hz, 1H), 7.70 (dt, *J* = 9.4, 1.1 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.11 (ddd, *J* = 10.2, 2.4, 1.0 Hz, 1H), 6.82 (td, *J* = 6.8, 1.2 Hz, 1H), 2.77 (s, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 159.3, 156.9, 148.3, 140.2, 131.5 (d, *J* = 9.1 Hz, 1C), 128.8, 125.0, 118.3, 114.4 (d, *J* = 25.3 Hz, 1C), 110.5, 94.2 (d, *J* = 28.3 Hz, 1C), 17.1, 17.1. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -119.82. ESI HRMS *m/z* $(M+H)^+$ calcd 201.0823, obsd 201.0815.



2k

8-bromo-7-methylbenzo[4,5]imidazo[1,2-*a*]pyridine

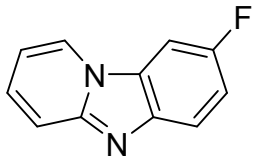
Yield: 35% (18.2 mg) white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (dt, *J* = 6.9, 1.3 Hz, 1H), 8.04 (s, 1H), 7.76 (s, 1H), 7.64 (dt, *J* = 9.3, 1.1 Hz, 1H), 7.40 (ddd, *J* = 9.3, 6.7, 1.4 Hz, 1H), 6.82 (td, *J* = 6.8, 1.3 Hz, 1H), 2.58 (s, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 148.8, 143.8, 135.1, 129.5, 127.8, 125.0, 120.6, 117.9, 116.9, 113.8, 110.5, 23.8. ESI HRMS m/z (M+H)+ calcd 261.0022, obsd 261.0015.



2l

8-chlorobenzo[4,5]imidazo[1,2-*a*]pyridine[4]

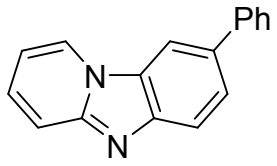
Yield: 45% (18.5 mg) white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.07 (d, *J* = 6.9 Hz, 1H), 8.51 (s, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.67 (d, *J* = 9.2 Hz, 1H), 7.58 (d, *J* = 6.4 Hz, 1H), 7.49 (d, *J* = 8.8 Hz, 1H), 7.02 (t, *J* = 6.8 Hz, 1H). ^{13}C{1H} NMR (101 MHz, DMSO-d_6) δ 149.0, 143.1, 131.2, 129.7, 127.7, 126.2, 125.2, 120.7, 117.6, 112.7, 111.3.



2m

8-fluorobenzo[4,5]imidazo[1,2-*a*]pyridine[4]

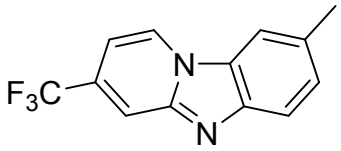
Yield: 60% (22.1 mg) white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (d, J = 6.9 Hz, 1H), 8.52 (d, J = 2.1 Hz, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.68 (d, J = 9.3 Hz, 1H), 7.58 (ddd, J = 9.2, 6.5, 1.4 Hz, 1H), 7.51 (dd, J = 8.7, 2.1 Hz, 1H), 7.03 (td, J = 6.7, 1.3 Hz, 1H). ^{13}C{1H} NMR (101 MHz, DMSO-d_6) δ 149.0, 143.1, 131.2, 129.7, 127.7, 126.2, 125.2, 120.7, 117.6, 112.7, 111.3. ^{19}F NMR (377 MHz, Chloroform-d) δ -58.12.



2n

8-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine

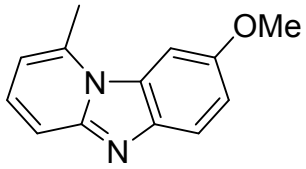
Yield: 40% (19.1 mg) white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.51 (d, J = 6.9 Hz, 1H), 8.09 (d, J = 1.9 Hz, 1H), 8.01 (d, J = 8.5 Hz, 1H), 7.82 (dd, J = 8.6, 1.7 Hz, 1H), 7.74 – 7.71 (m, 3H), 7.52 (t, J = 7.7 Hz, 2H), 7.46 (ddd, J = 9.3, 6.7, 1.4 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 6.89 (td, J = 6.8, 1.3 Hz, 1H). ^{13}C{1H} NMR (101 MHz, Chloroform-d) δ 149.0, 143.9, 141.4, 134.7, 129.4, 129.2, 128.9, 127.4, 127.0, 125.6, 125.2, 119.9, 118.1, 110.5, 108.7. ESI HRMS *m/z* $(M+H)^+$ calcd 245.1073, obsd 245.1065.



2o

8-methyl-3-(trifluoromethyl)benzo[4,5]imidazo[1,2-*a*]pyridine

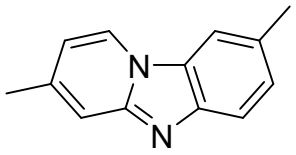
Yield: 14% (6.7 mg) white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.77 (s, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.78 - 7.75 (m, 2H), 7.51 (dd, J = 9.7, 2.0 Hz, 1H), 7.44 (dd, J = 8.4, 1.8 Hz, 1H), 2.63 (s, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-d) δ 147.3, 143.2, 132.7, 130.0, 128.8, 128.5, 124.3 (d, J = 3.0 Hz, 1C), 122.3, 120.0, 118.7, 114.3 (q, J = 34.0 Hz, 1C), 110.2, 21.9. ^{19}F NMR (377 MHz, Chloroform-d) δ -62.02. ESI HRMS *m/z* (M+H)+ calcd 251.0791, obsd 251.0781.



2p

8-methoxy-1-methylbenzo[4,5]imidazo[1,2-*a*]pyridine

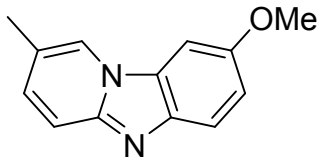
Yield: 85% (36.1 mg) white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.85 (d, J = 9.0 Hz, 1H), 7.62 (s, 1H), 7.52 (d, J = 9.2 Hz, 1H), 7.29 – 7.16 (m, 2H), 6.51 (d, J = 6.7 Hz, 1H), 3.92 (s, 3H), 3.00 (s, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-d) δ 154.6, 149.4, 139.7, 138.4, 130.1, 128.4, 119.9, 115.5, 114.3, 110.6, 98.8, 56.1, 21.2. ESI HRMS *m/z* $(M+H)^+$ calcd 213.1022, obsd 213.1014.



2q

3,8-dimethylbenzo[4,5]imidazo[1,2-*a*]pyridine

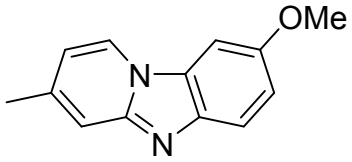
Yield: 95% (37.1 mg) white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.63 (s, 1H), 7.57 (d, *J* = 9.4 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.23 (dd, *J* = 9.4, 1.9 Hz, 1H), 2.57 (s, 3H), 2.38 (s, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 147.4, 142.7, 132.1, 130.8, 128.6, 127.1, 122.4, 119.6, 119.3, 117.3, 110.0, 21.8, 18.2. ESI HRMS *m/z* $(M+H)^+$ calcd 197.1073, obsd 197.1067.



2r

8-methoxy-2-methylbenzo[4,5]imidazo[1,2-*a*]pyridine[3]

Yield: 95% (40.6 mg) white solid. Yield: 74 % (34.0 mg) white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (s, 1H), 7.80 (d, *J* = 8.9 Hz, 1H), 7.54 (d, *J* = 9.4 Hz, 1H), 7.22 (d, *J* = 2.4 Hz, 1H), 7.20 – 7.11 (m, 2H), 3.91 (s, 3H), 2.37 (d, *J* = 1.4 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 155.1, 147.2, 139.1, 131.4, 128.6, 122.0, 120.4, 119.6, 117.3, 115.6, 92.9, 55.9, 18.1. ESI HRMS m/z (M+H)+ calcd 213.1022, obsd 213.1015.



2s

8-methoxy-3-methylbenzo[4,5]imidazo[1,2-*a*]pyridine

Yield: 80 % (34.7 mg) white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 7.0 Hz, 1H), 7.77 (d, *J* = 8.9 Hz, 1H), 7.34 (d, *J* = 1.4 Hz, 1H), 7.20 (d, *J* = 2.4 Hz, 1H), 7.13 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.56 (dd, *J* = 7.1, 1.7 Hz, 1H), 3.89 (s, 3H), 2.41 (d, *J* = 1.3 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 154.9, 148.5, 139.3, 139.1, 128.6, 123.6, 120.1, 115.9, 115.2, 112.8, 93.1, 55.9, 21.7. ESI HRMS *m/z* $(M+H)^+$ calcd 213.1022, obsd 213.1014.

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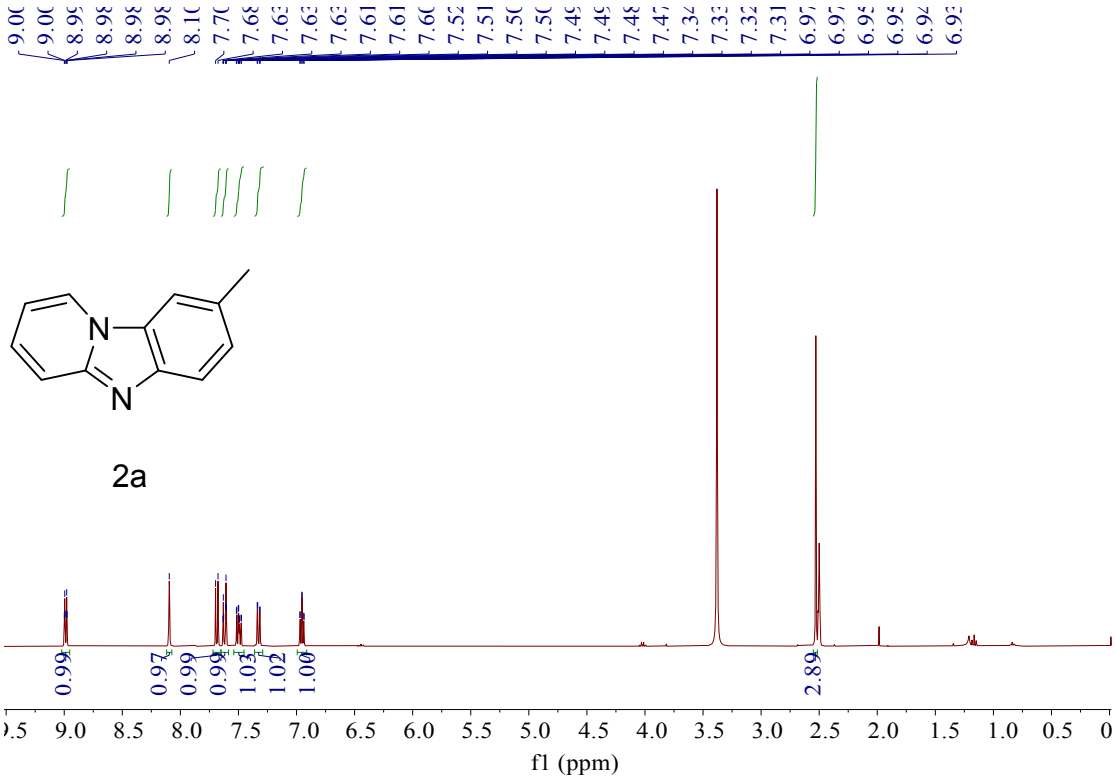
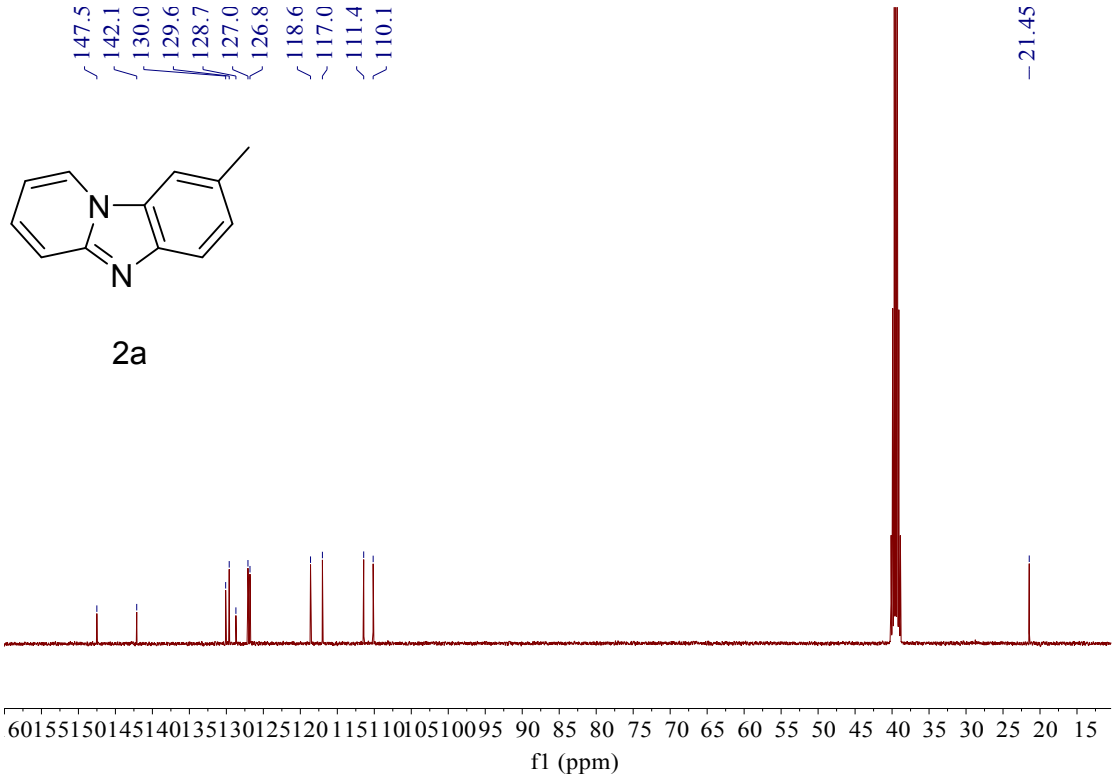
Copies of Product NMR Spectra

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118.6
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111.4
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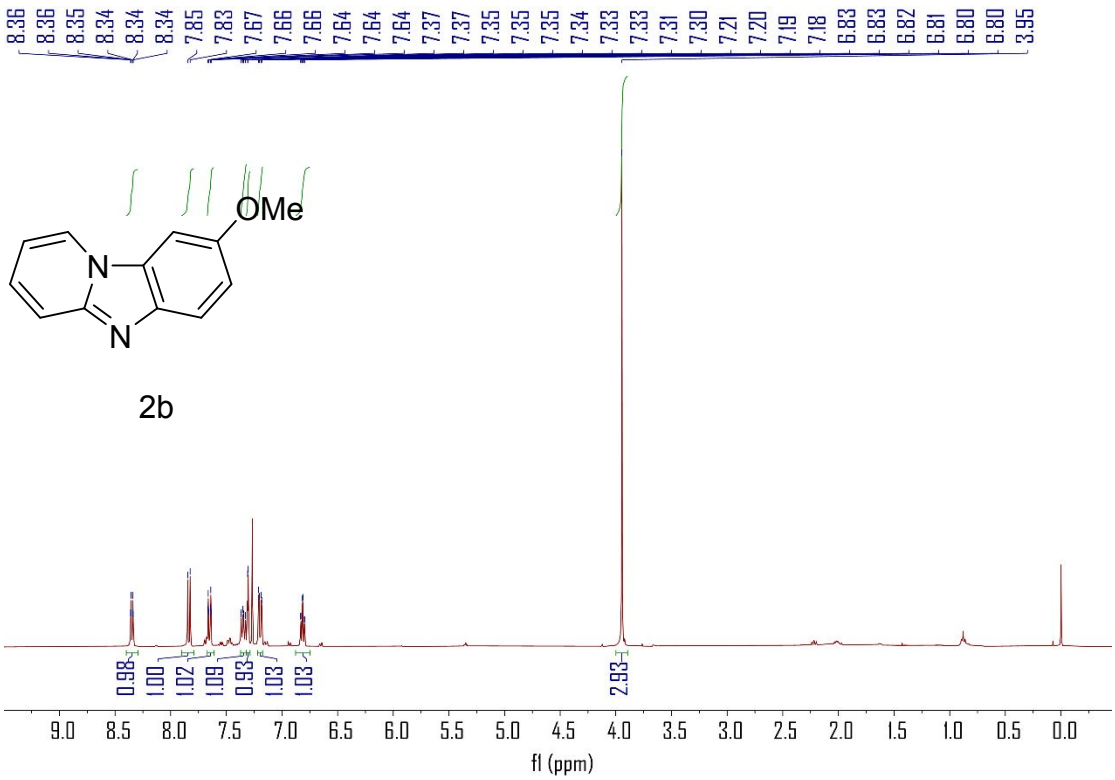
N
N
2a
f1 (ppm)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7.83
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7.66
7.66
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7.37
7.37
7.35
7.35
7.35
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7.33
7.31
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7.21
7.20
7.19
7.18
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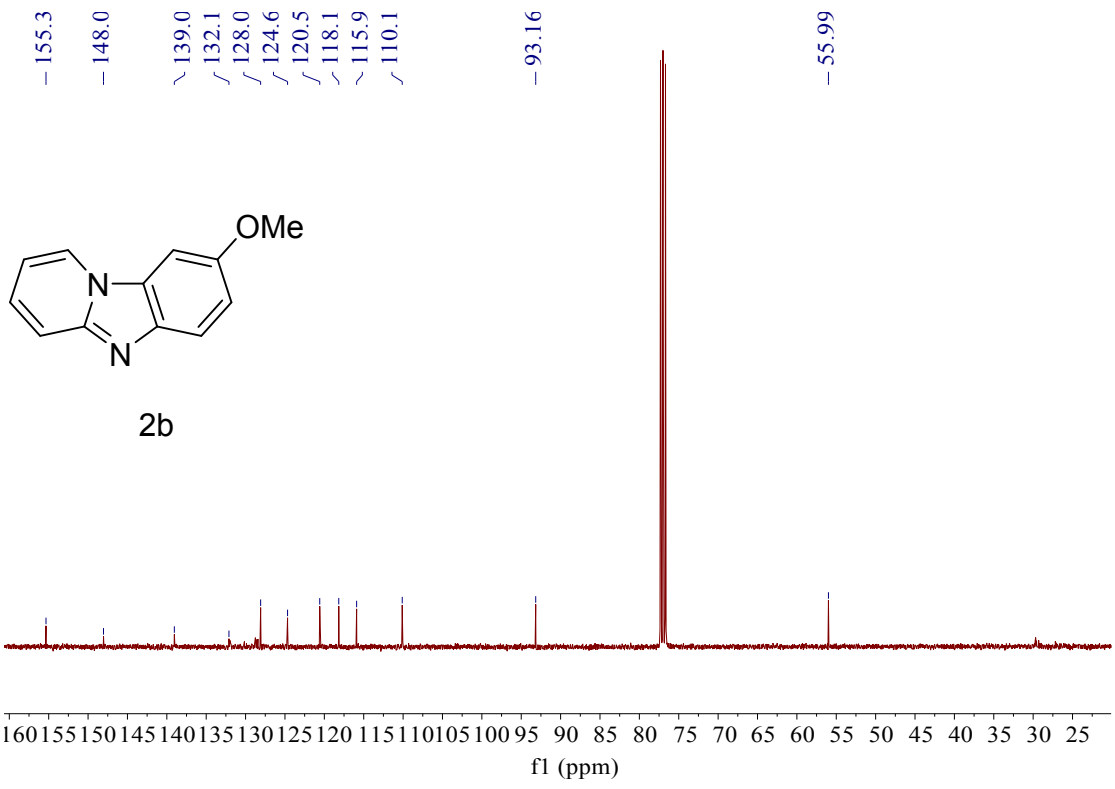
6.82
6.81
6.80
6.80
3.95
OMe
N
N
2b
0.98
1.00
1.02
1.09
0.93
1.03
1.03
2.93
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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118.1
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110.1
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N
N
2b
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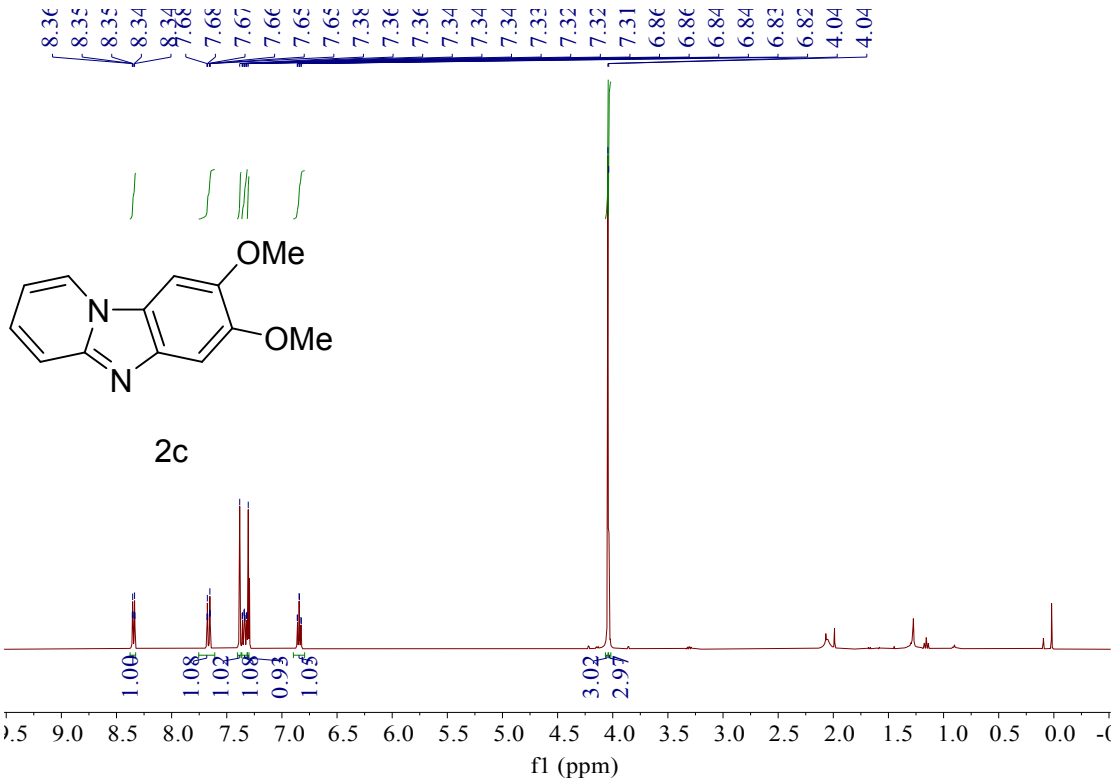
f1 (ppm)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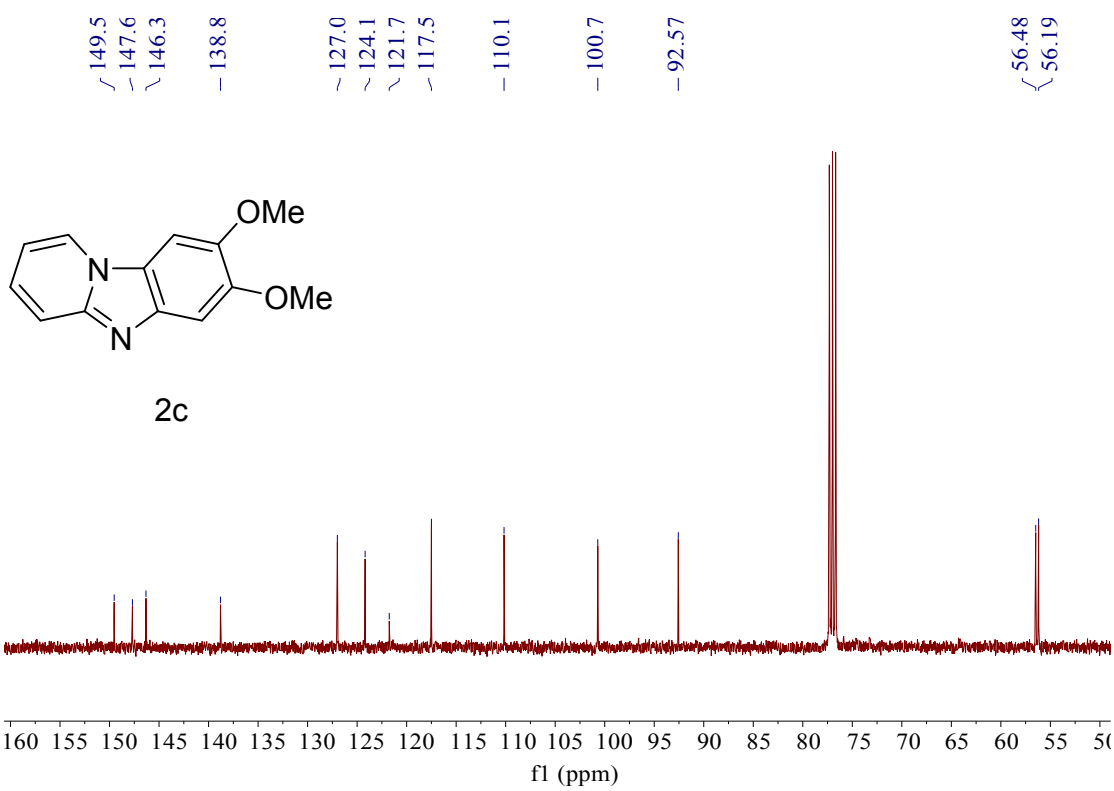
OMe
N
N
2c
f1 (ppm)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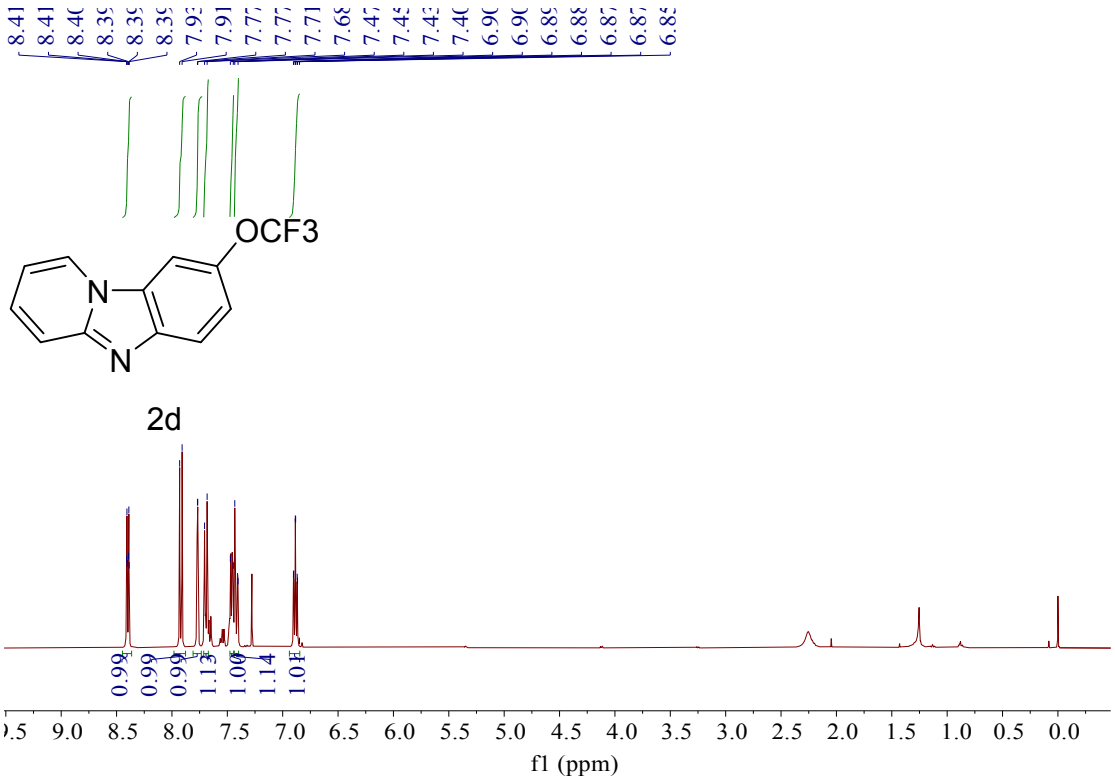
N
N
2c
f1 (ppm)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1.00
1.14
1.01
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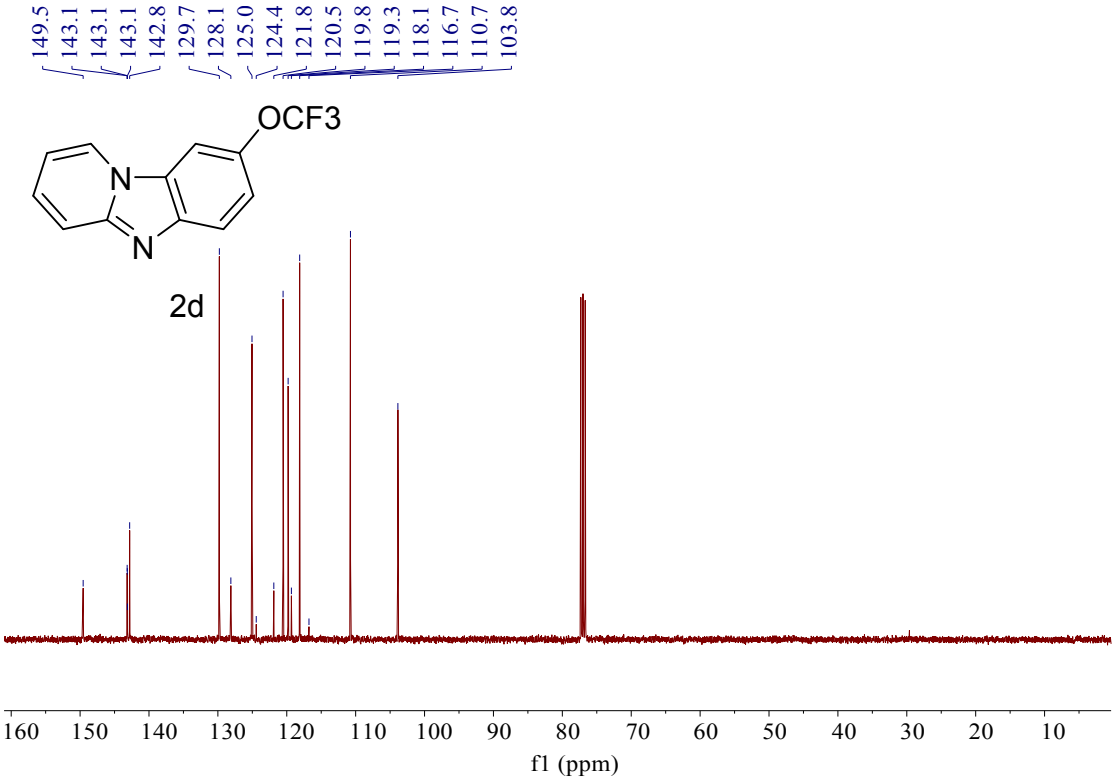
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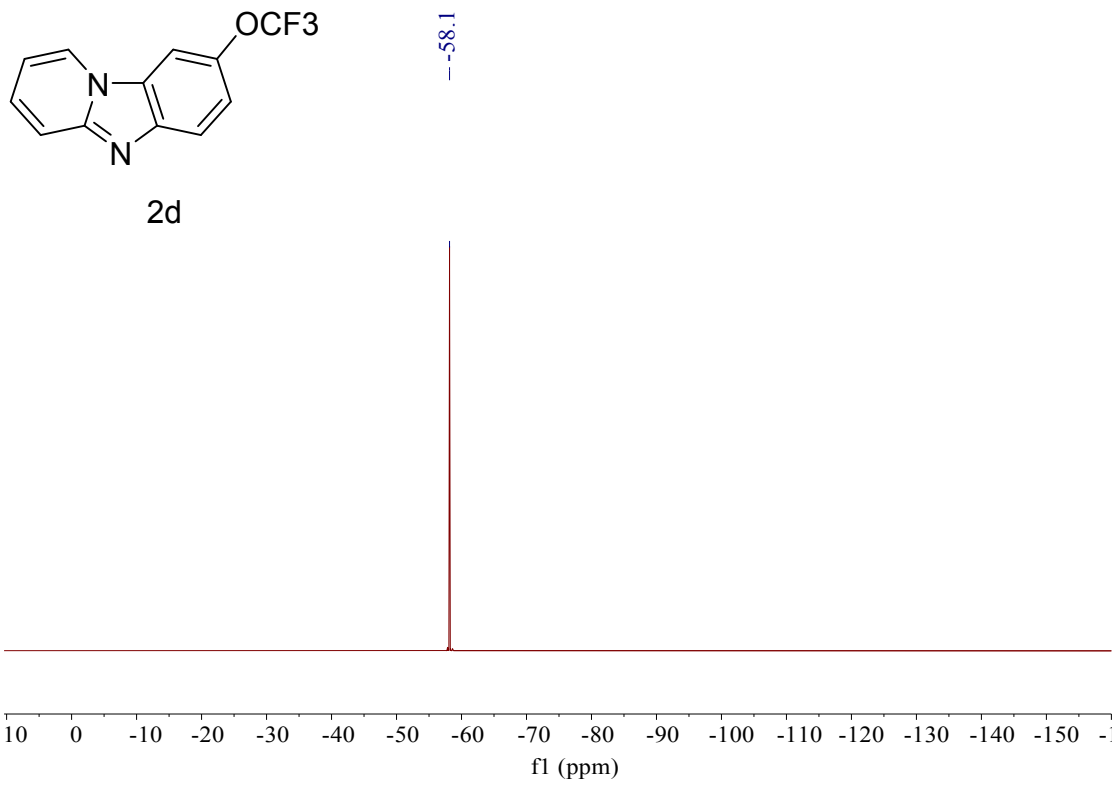
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2d
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-30
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-110
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-130
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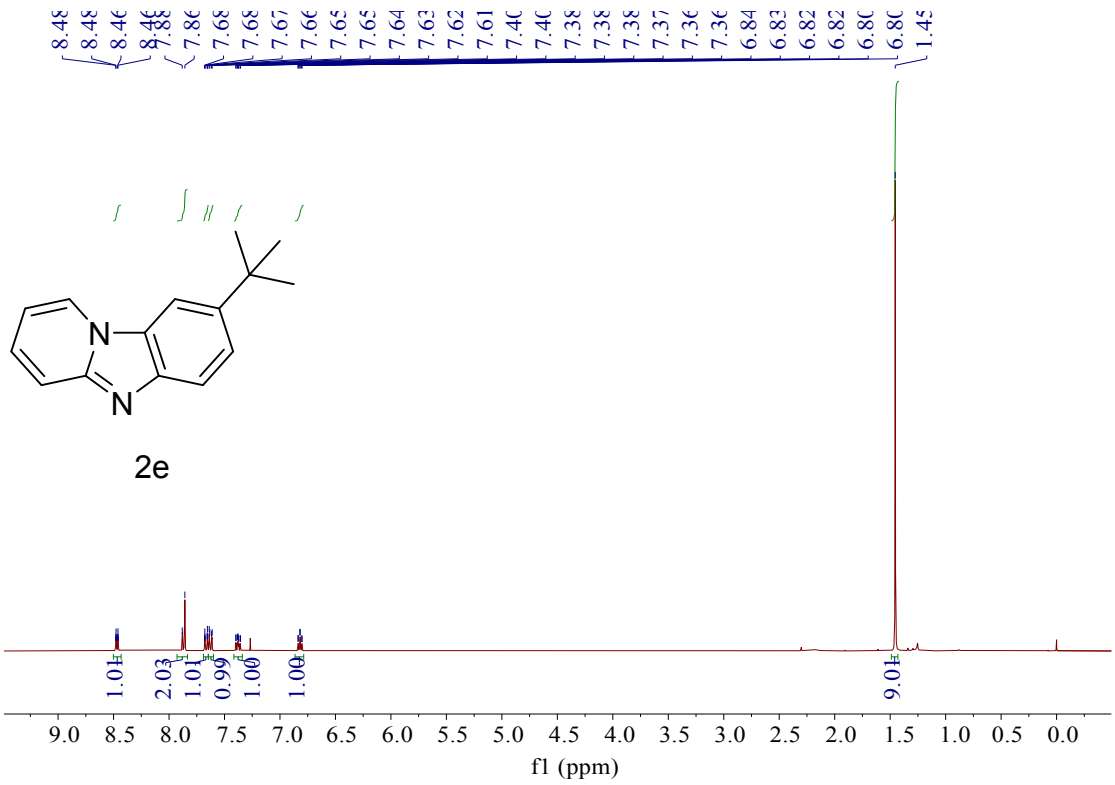
-150
f1 (ppm)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7.61
7.40
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7.38
7.37
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6.84
6.83
6.82
6.82
6.80
6.80
1.45
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N
2e
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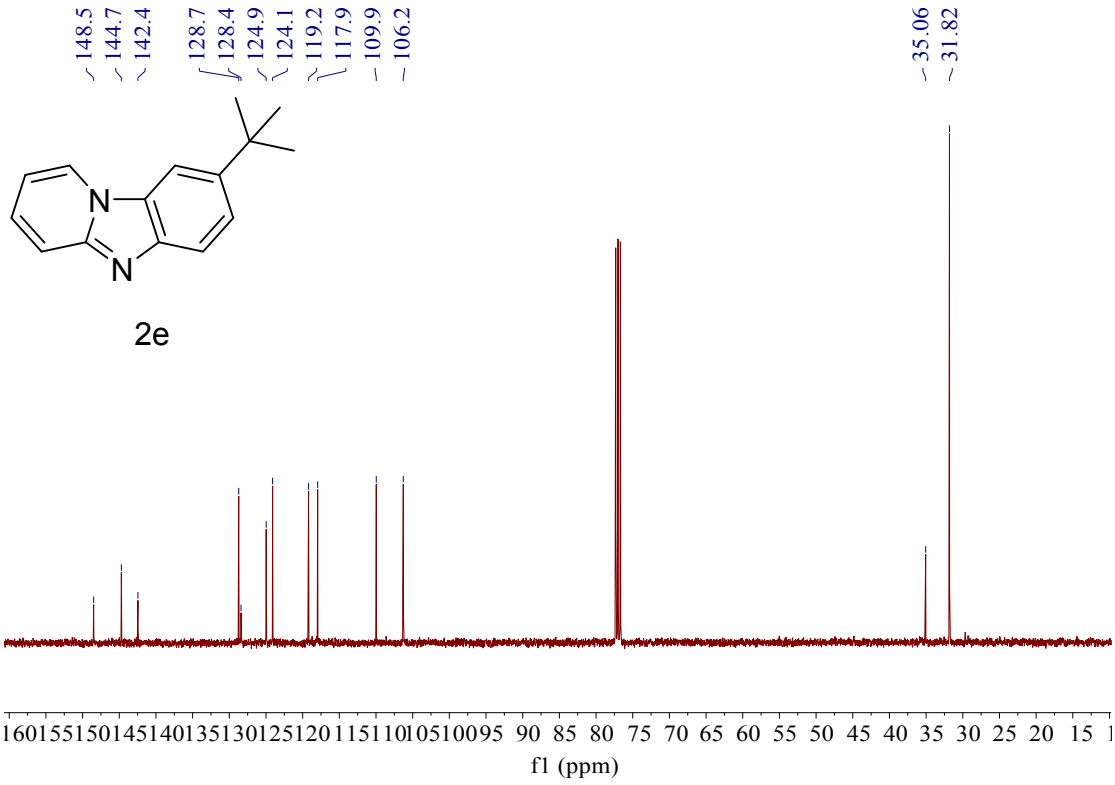
2.03
1.01
0.99
1.00
1.00
9.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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2e
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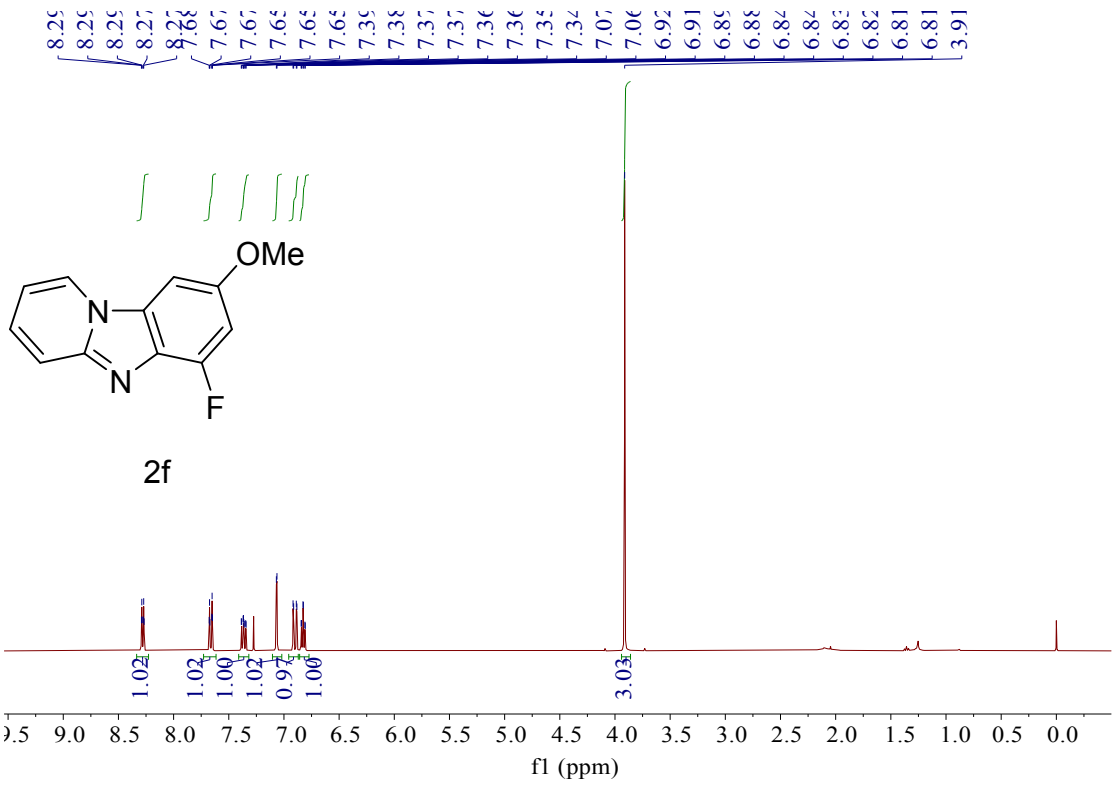
f1 (ppm)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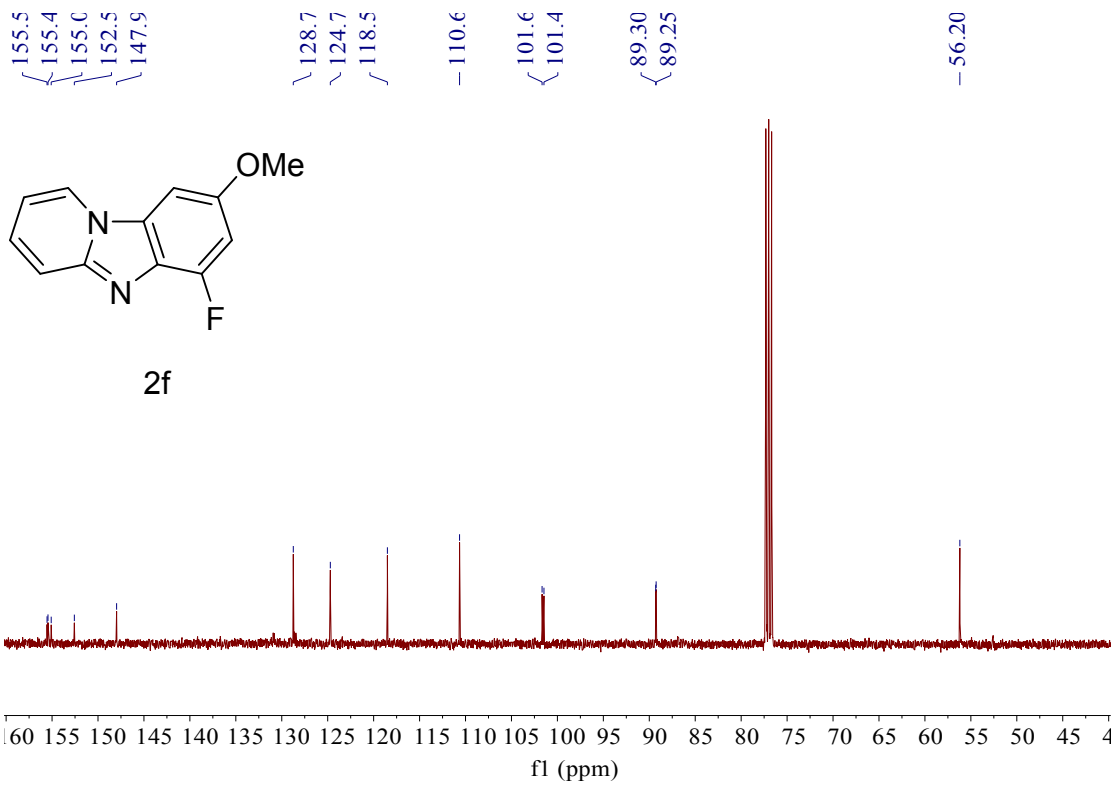
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2f
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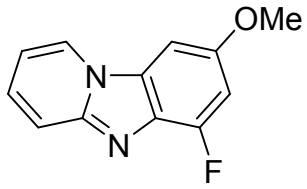
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F

2f

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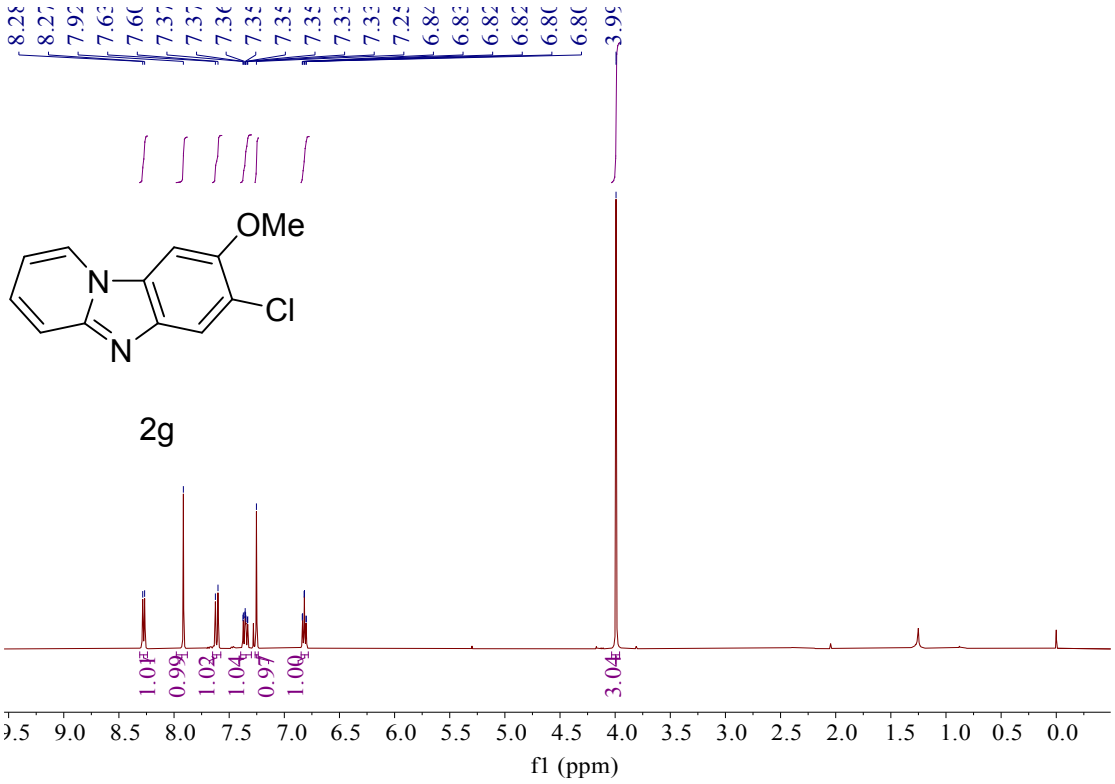
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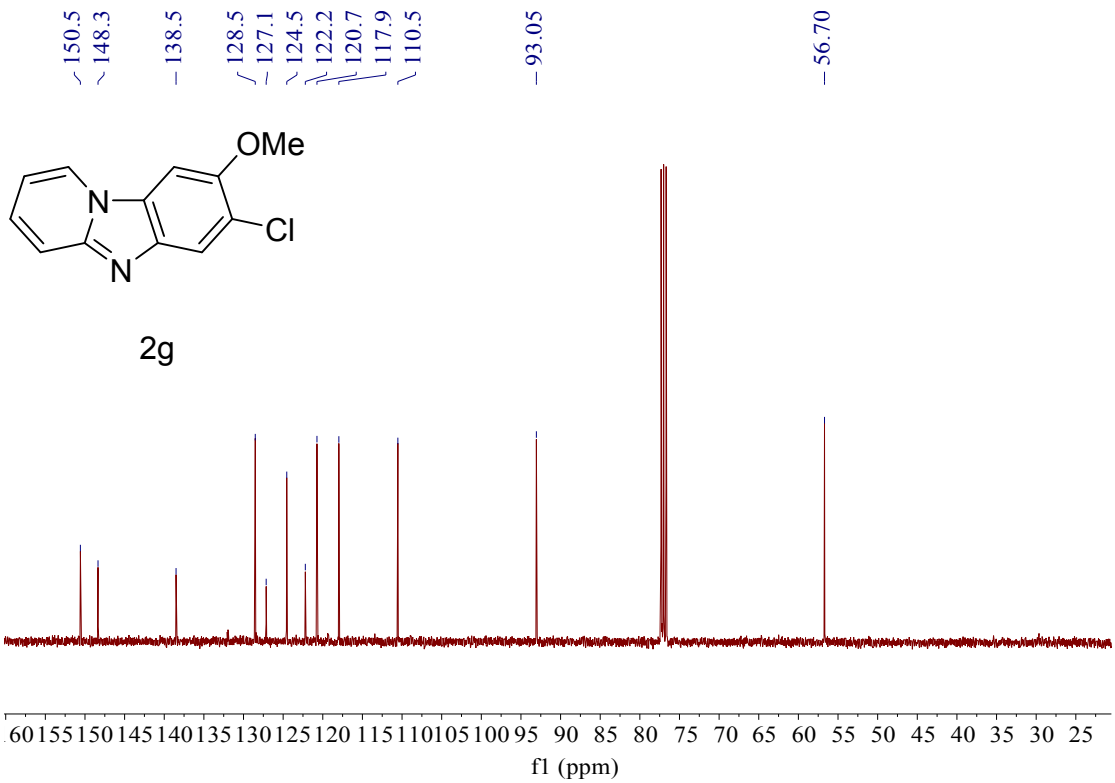
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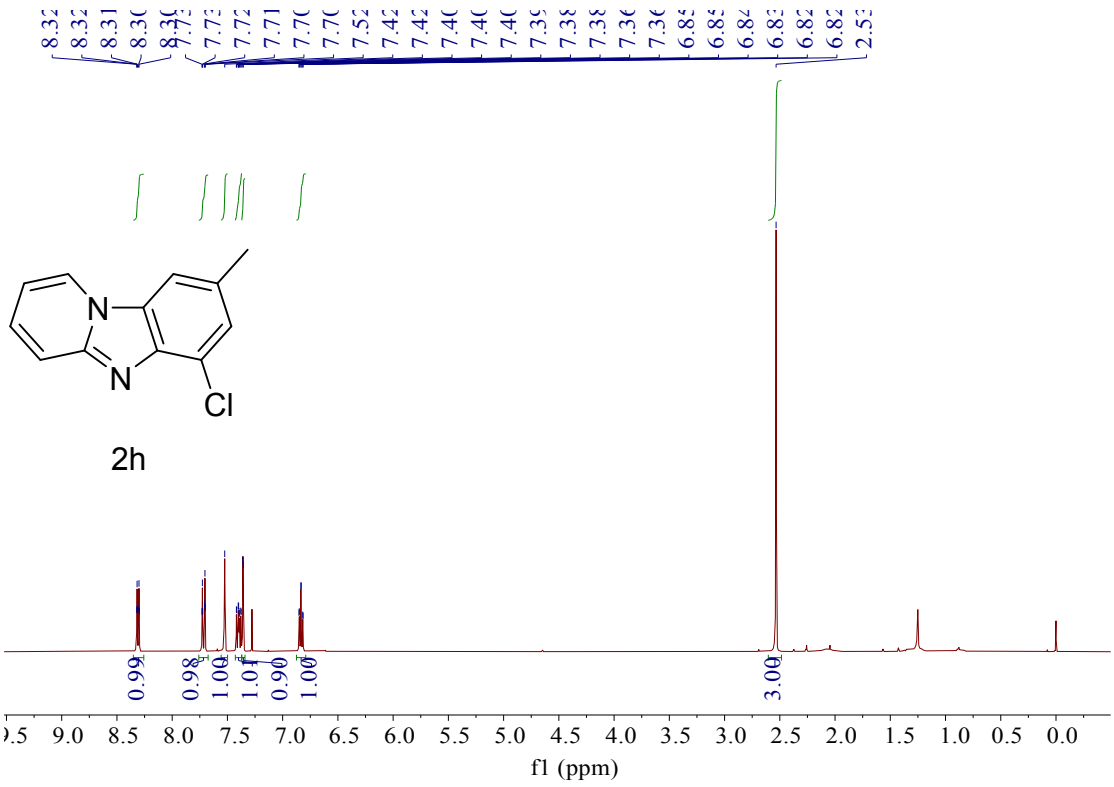
N
N
2g
f1 (ppm)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3.00
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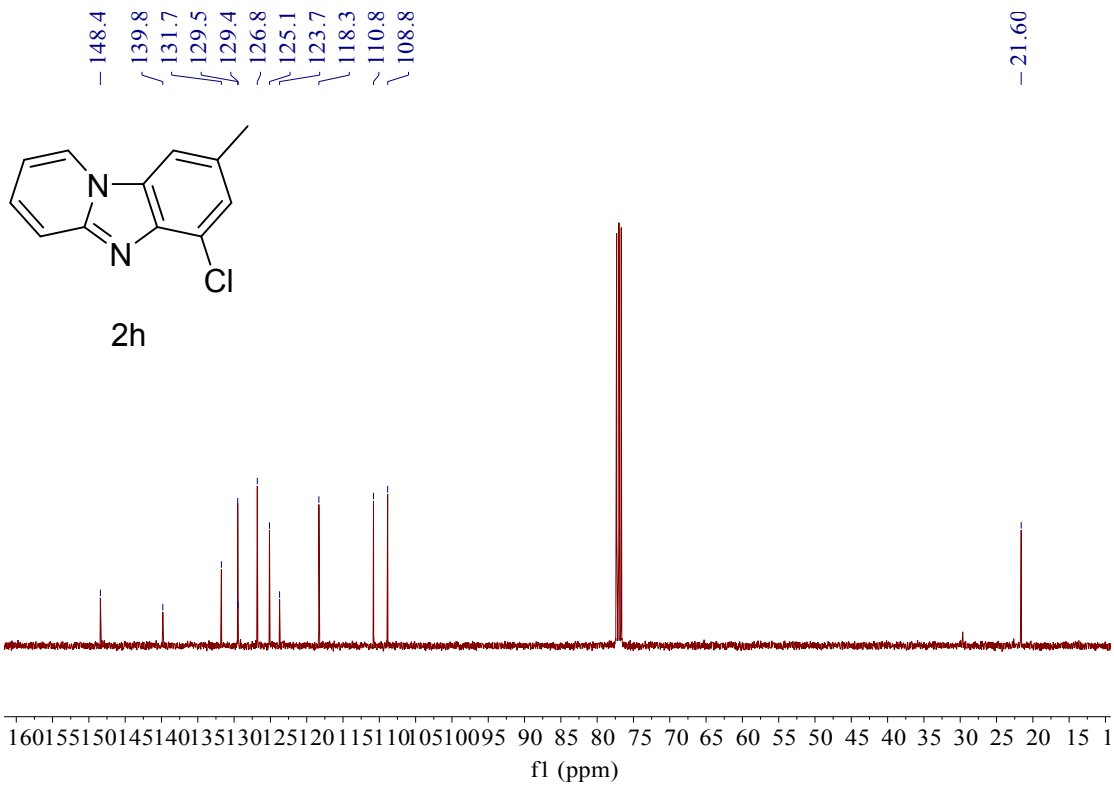
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110.8
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2h
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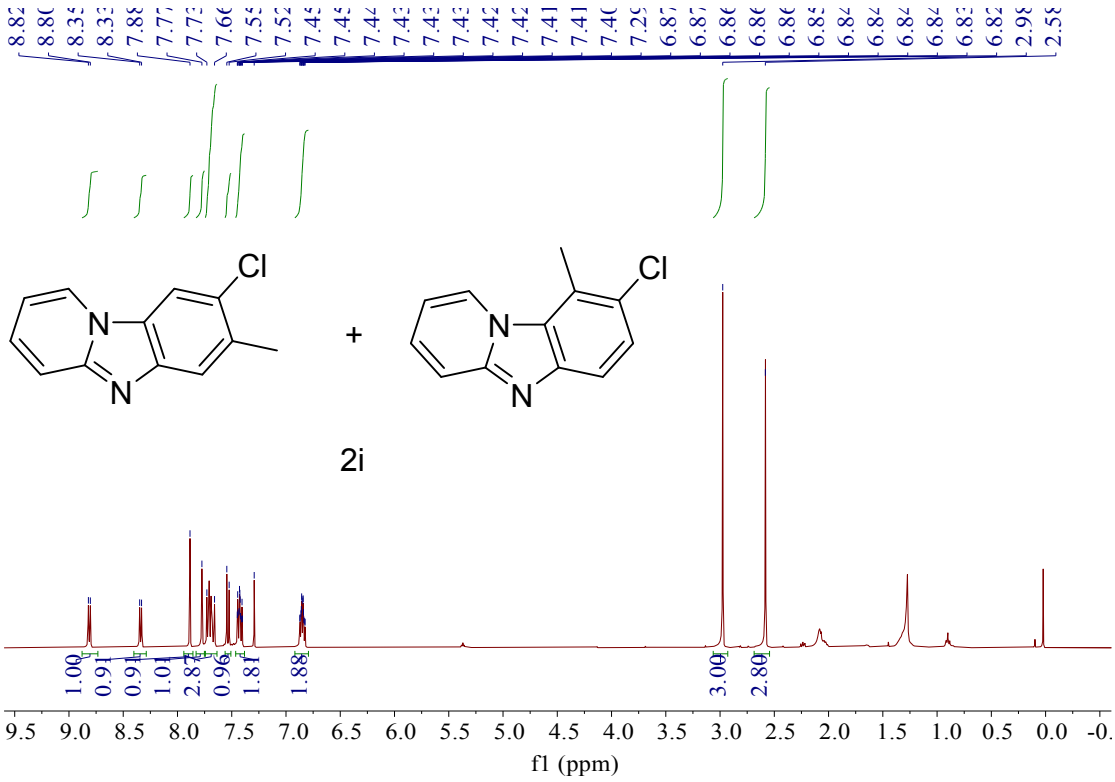
f1 (ppm)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N
+
Cl
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N
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2.87
0.96
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1.88
3.00
2.80
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
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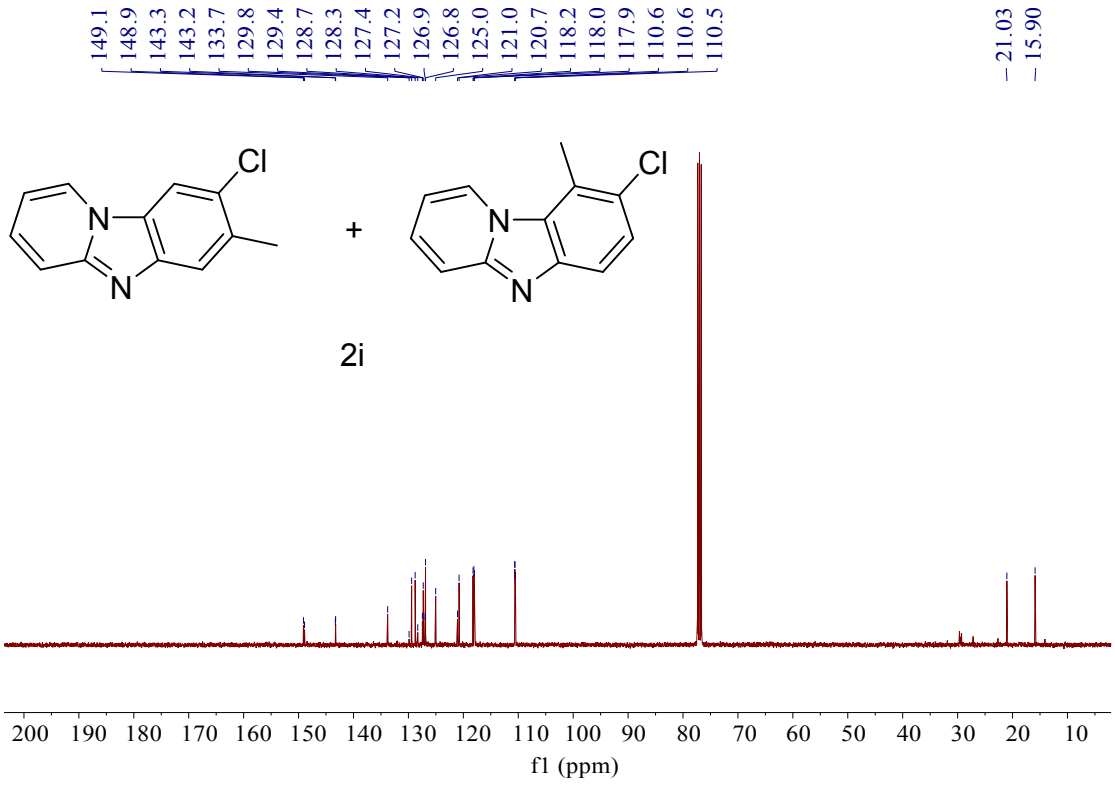
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120.7
118.2
118.0
117.9
110.6
110.6
110.5
21.03
15.90
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N
+
Cl
N
N
2i
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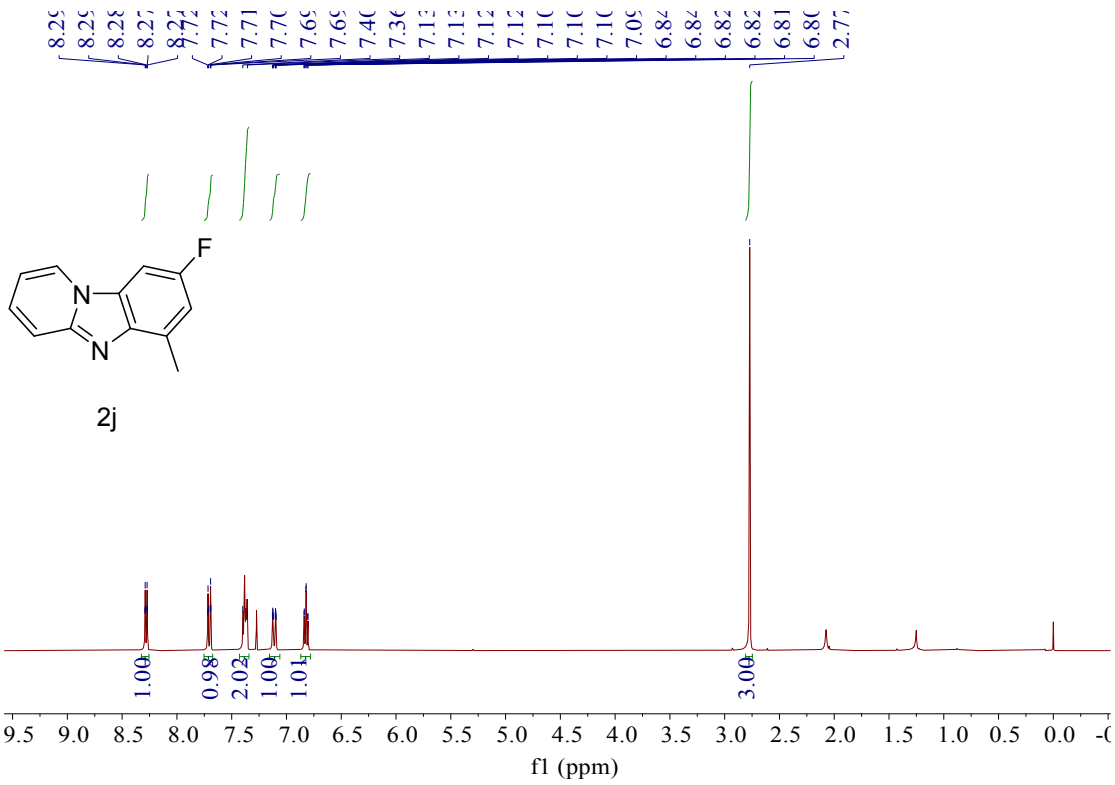
f1 (ppm)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1.01
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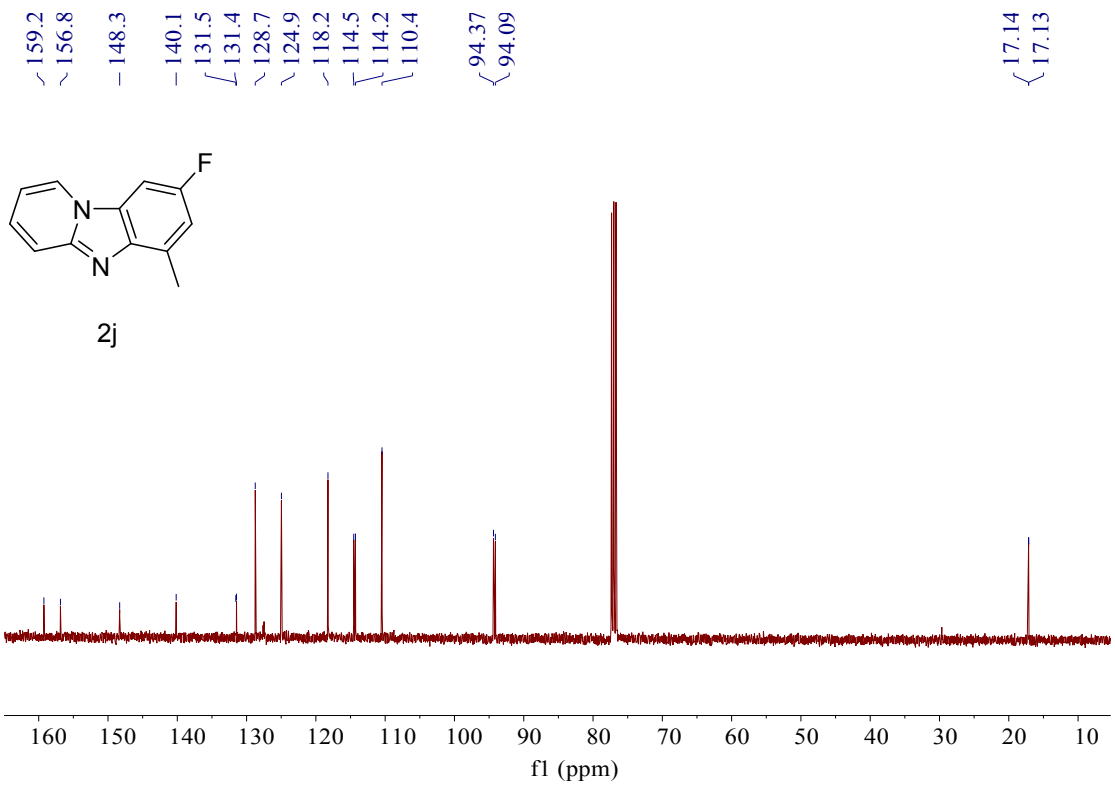
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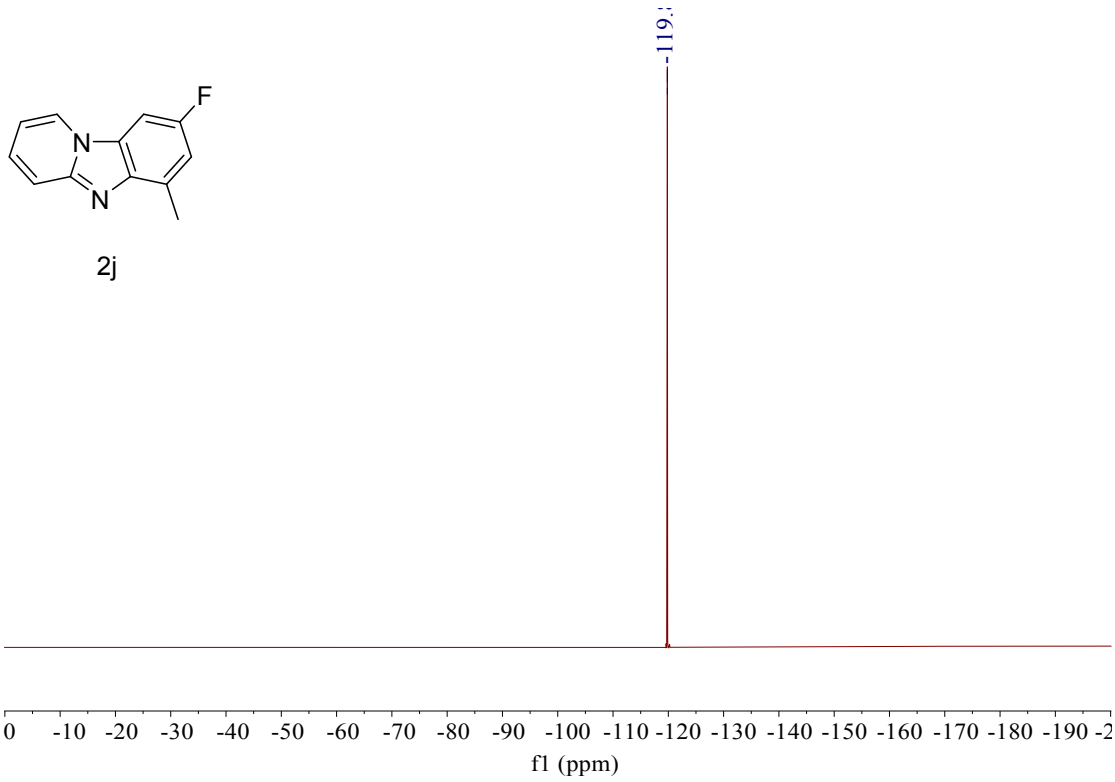
N
2j
f1 (ppm)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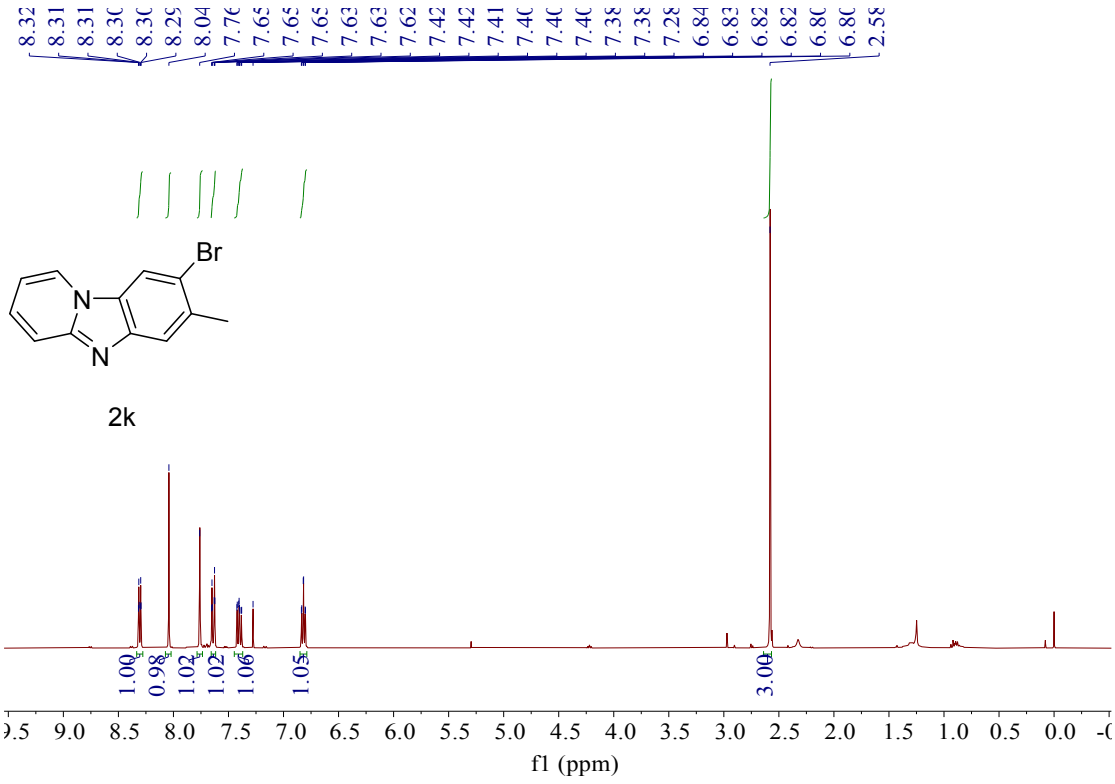
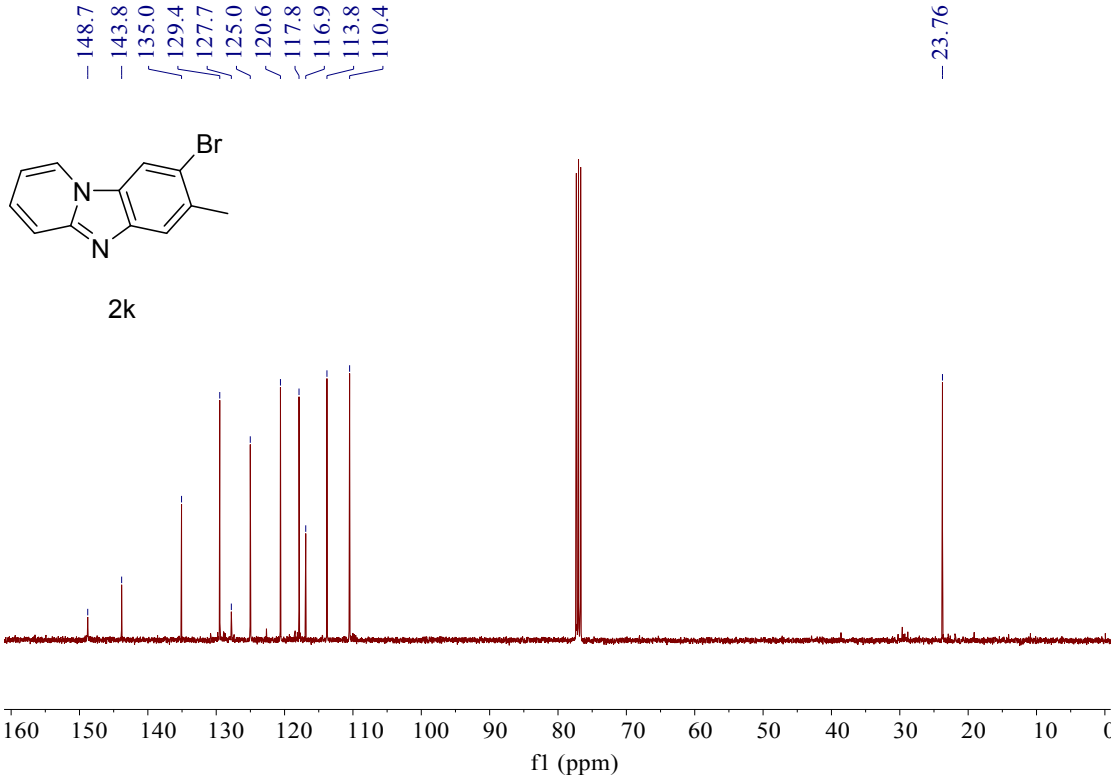
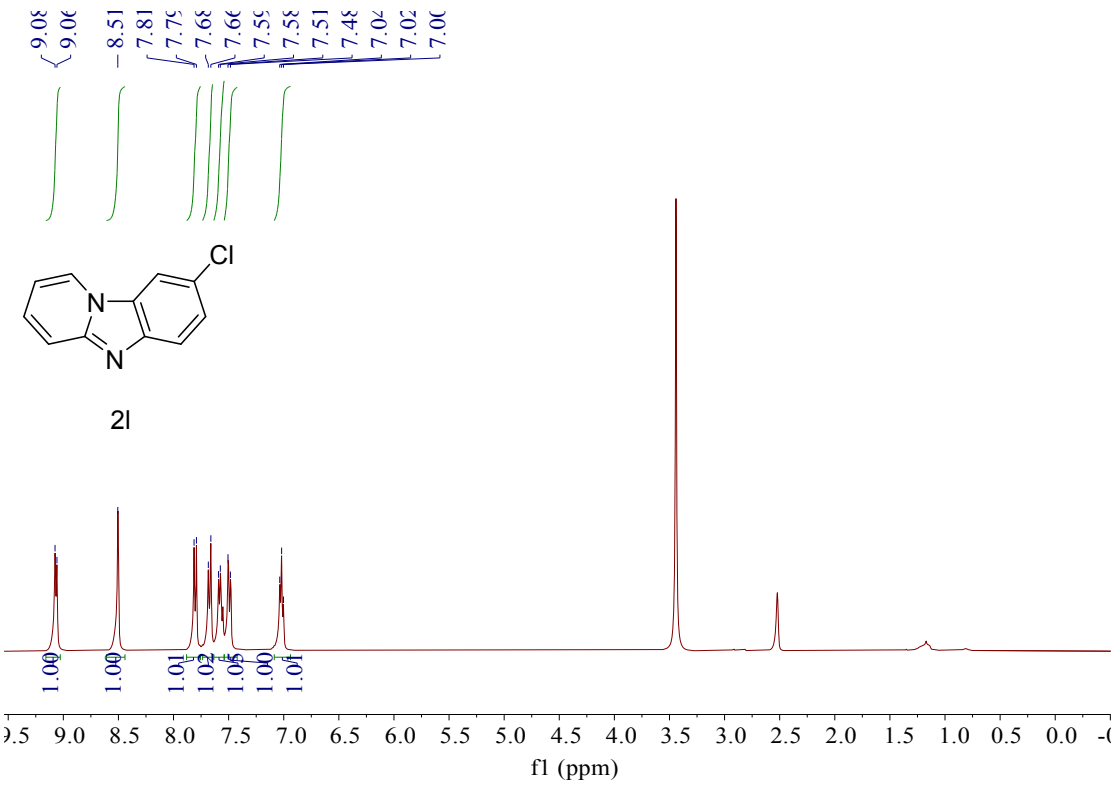
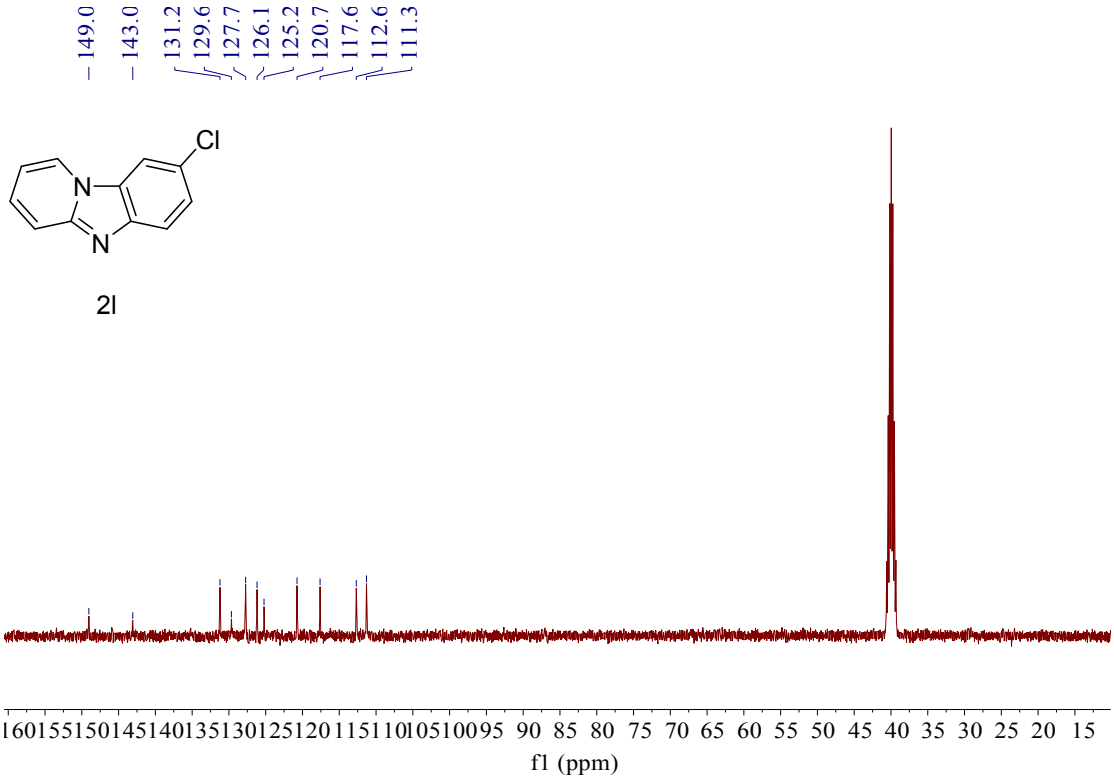
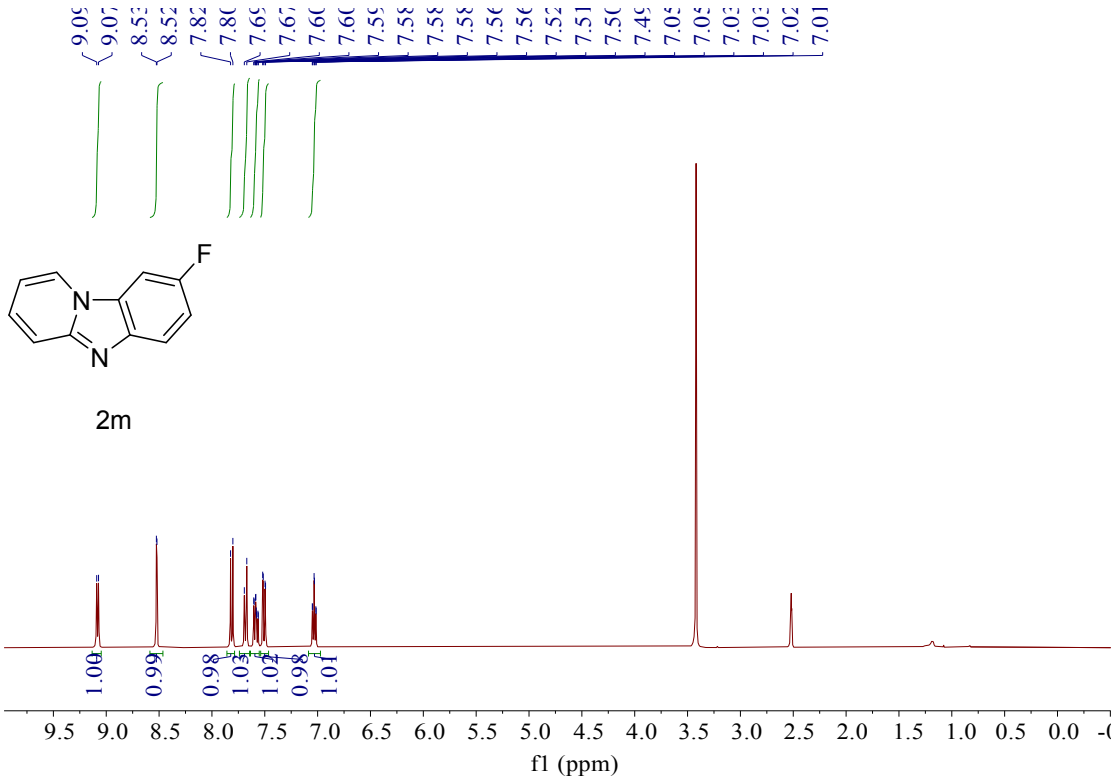
-119.
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

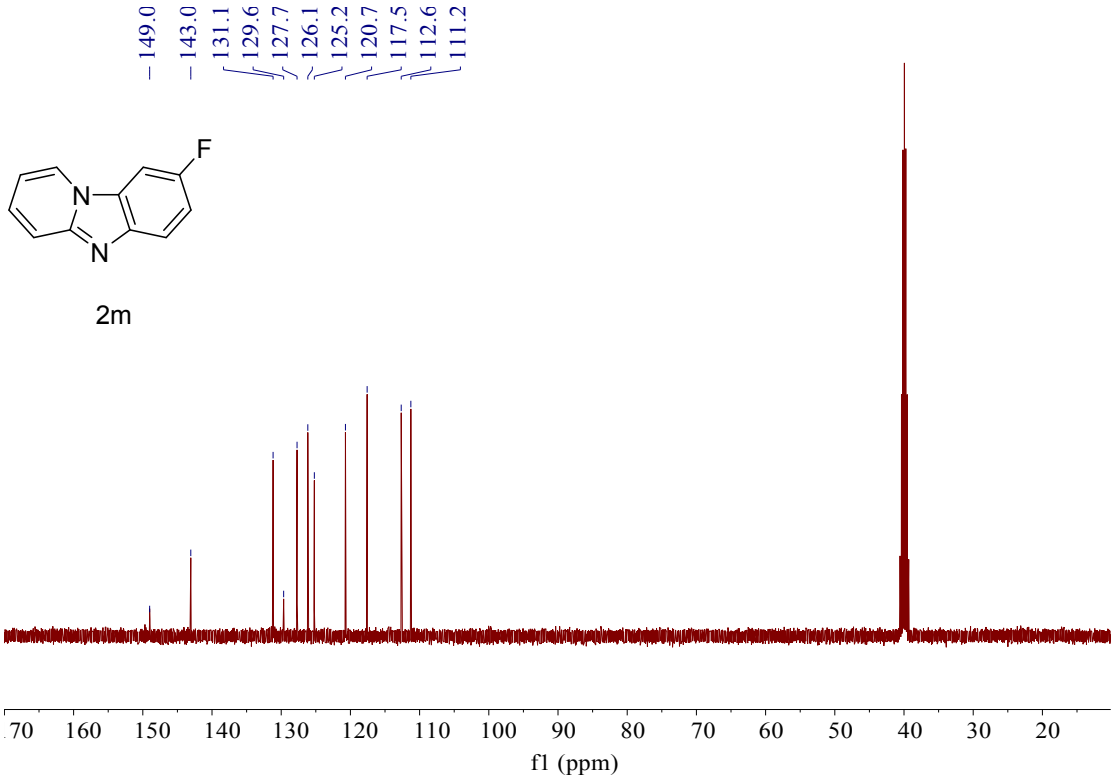

8.32
8.31
8.31
8.30
8.30
8.25
8.04
7.76
7.65
7.65
7.65
7.63
7.63
7.62
7.42
7.42
7.41
7.40
7.40
7.40
7.38
7.38
7.28
6.84
6.83
6.82
6.82
6.80
6.80
2.58
Br
N
N
2k
1.00
0.98
1.02
1.02
1.06
1.05
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

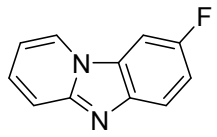

148.7
143.8
135.0
129.4
127.7
125.0
120.6
117.8
116.9
113.8
110.4
23.76
Br
N
N
2k
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Cl
N
N
2l
1.00
1.00
1.01
1.02
1.05
1.00
1.01
f1 (ppm)

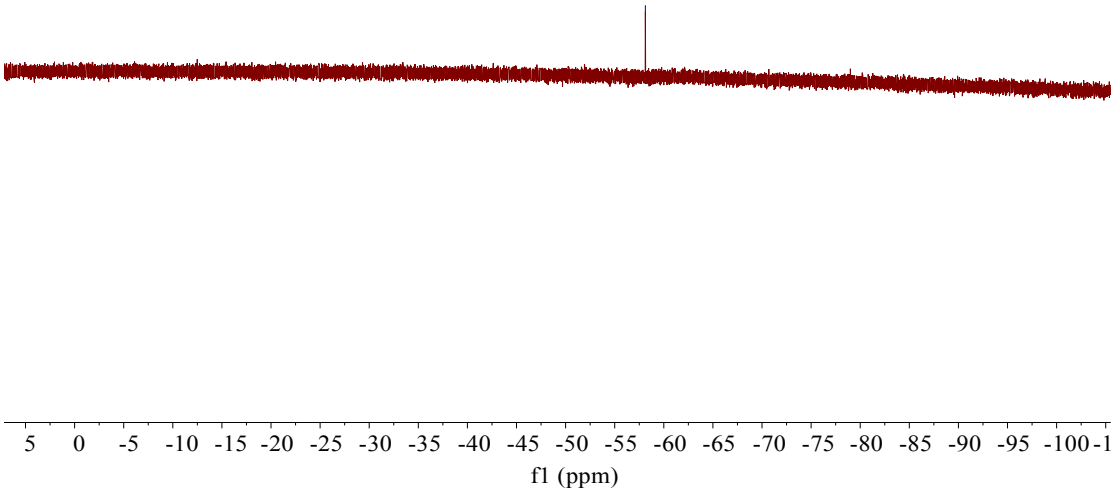

Cl
N
N
2l
f1 (ppm)

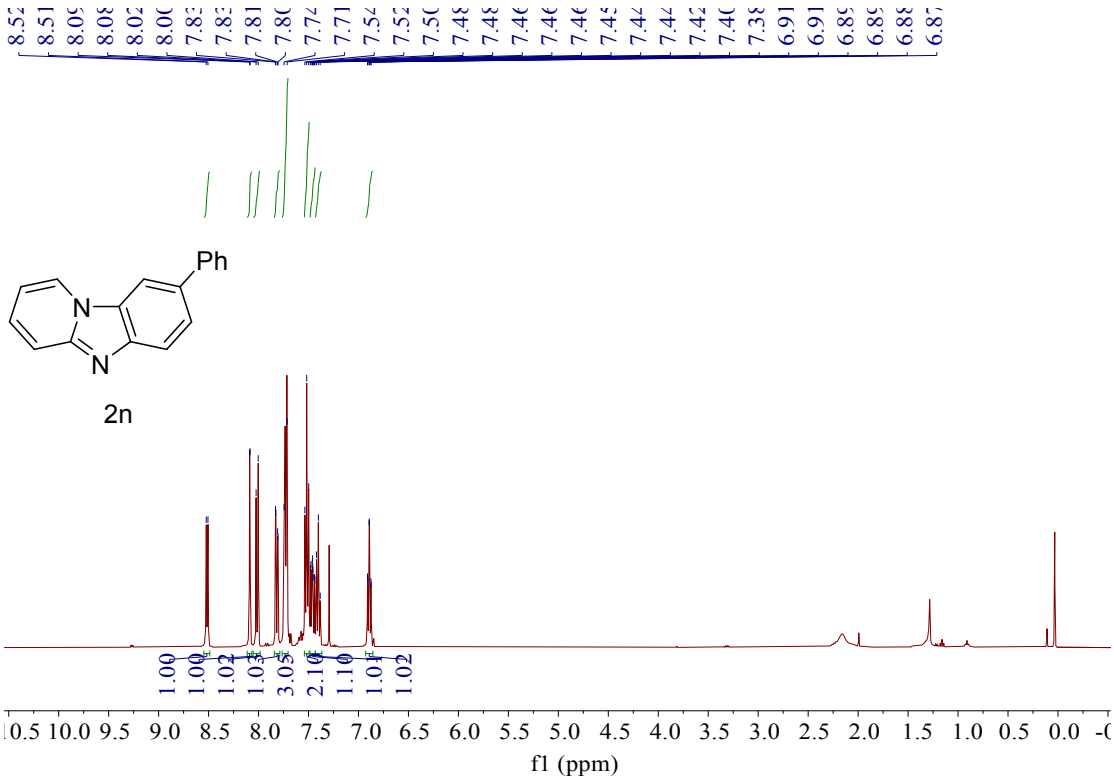

F
N
N
2m
1.00
0.99
0.98
1.03
1.02
0.98
1.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

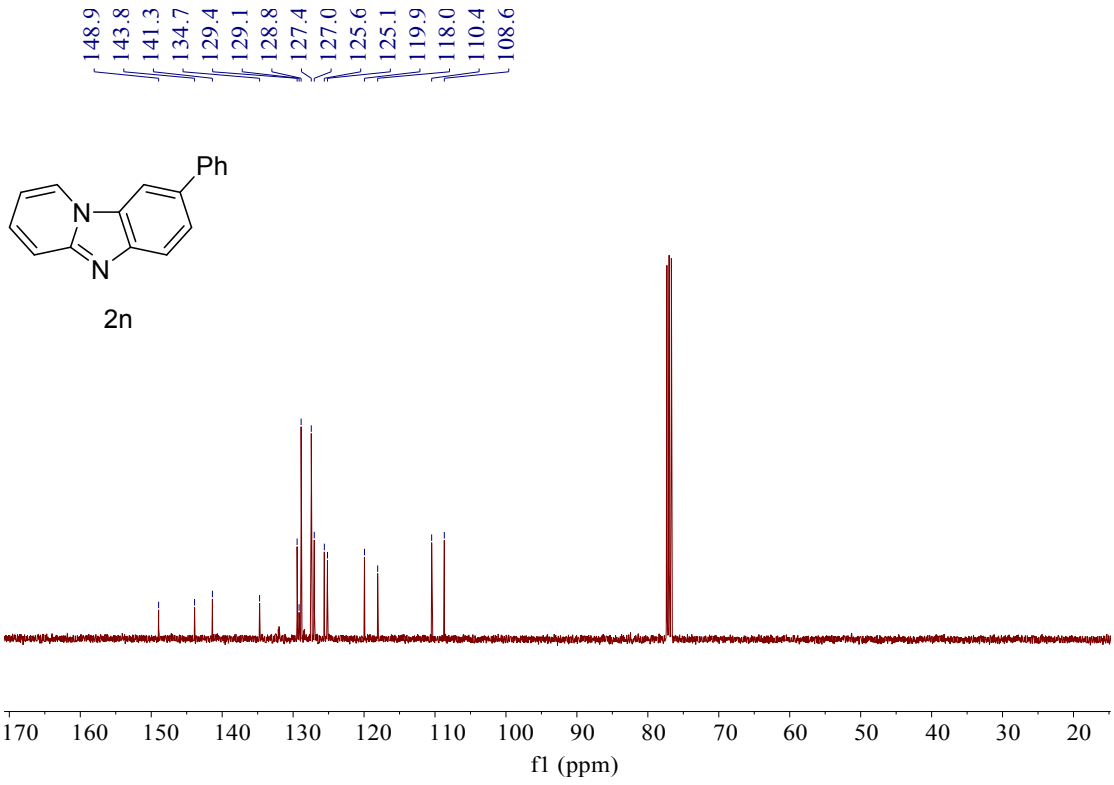

149.0
143.0
131.1
129.6
127.7
126.1
125.2
120.7
117.5
112.6
111.2
F
N
N
2m
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

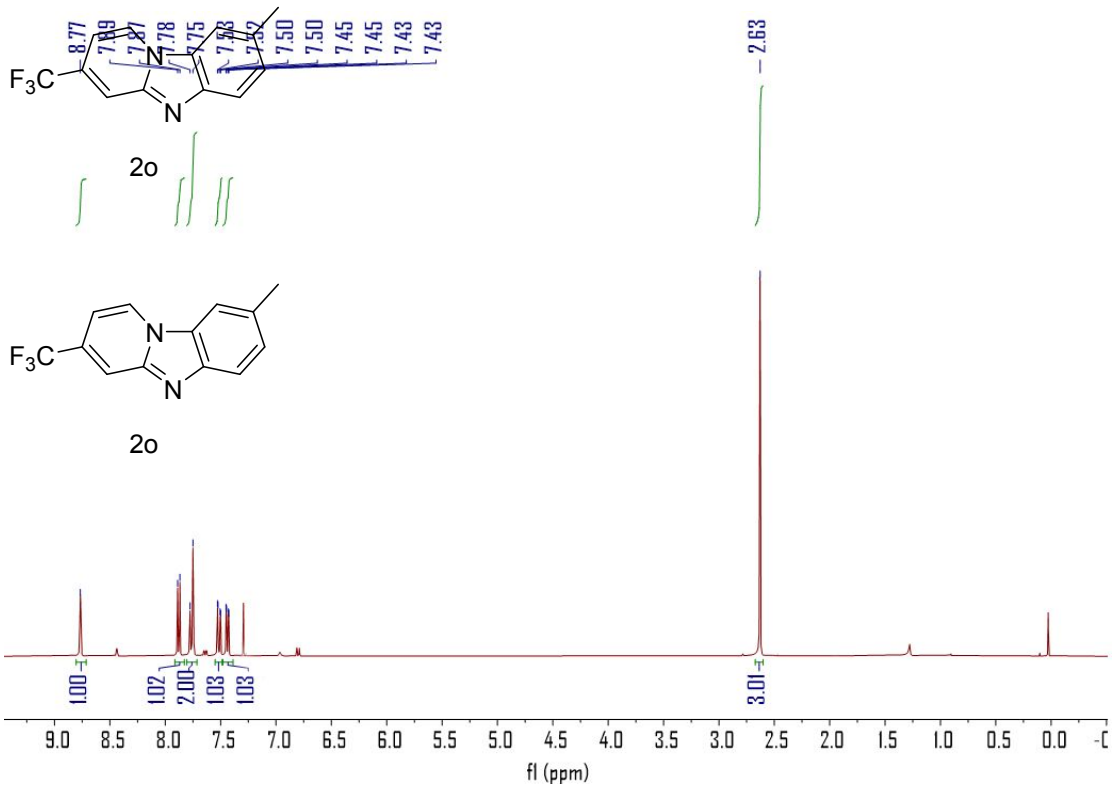

F
N
N

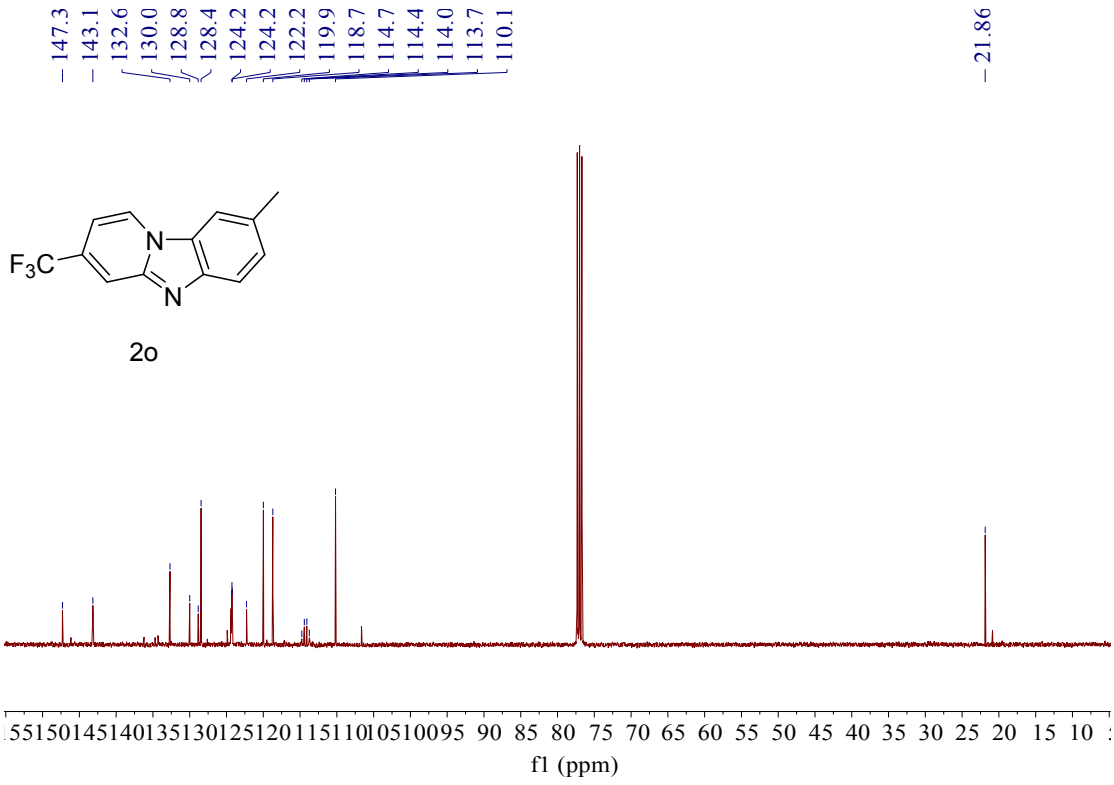
2m

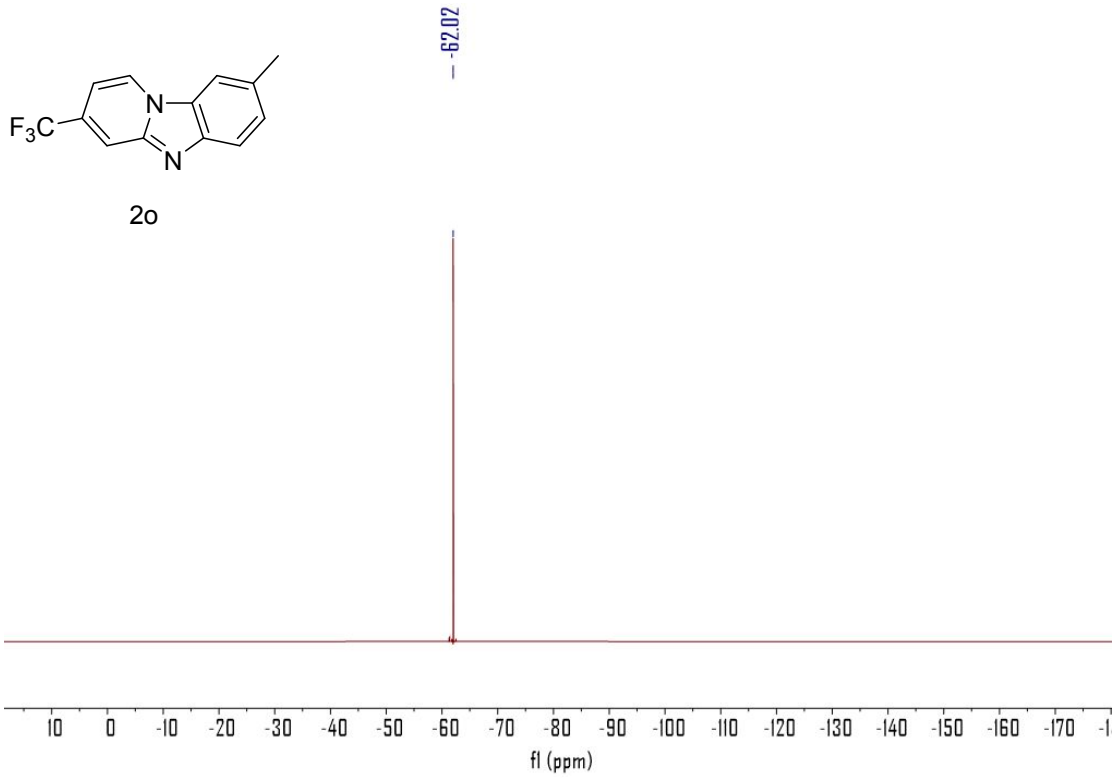

-58.1
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -1
f1 (ppm)


Ph
N
N
2n
1.00
1.00
1.02
1.03
3.05
2.10
1.10
1.01
1.02
f1 (ppm)

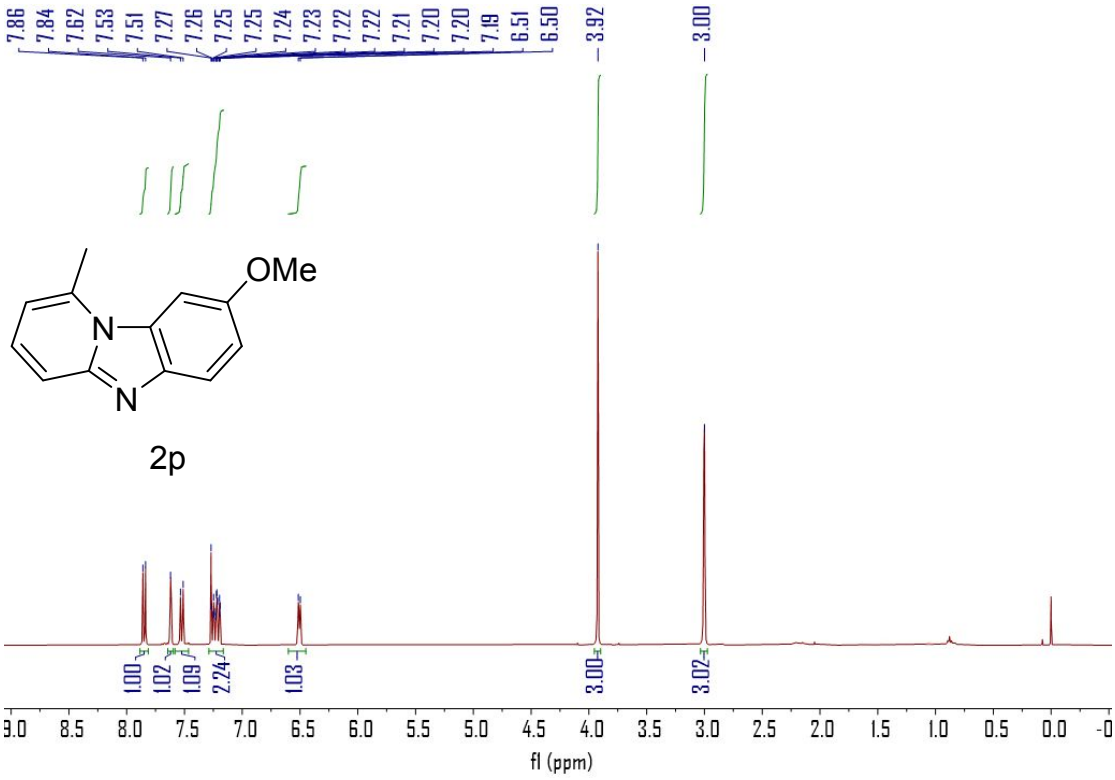

148.9
143.8
141.3
134.7
129.4
129.1
128.8
127.4
127.0
125.6
125.1
119.9
118.0
110.4
108.6
Ph
N
N
2n
f1 (ppm)

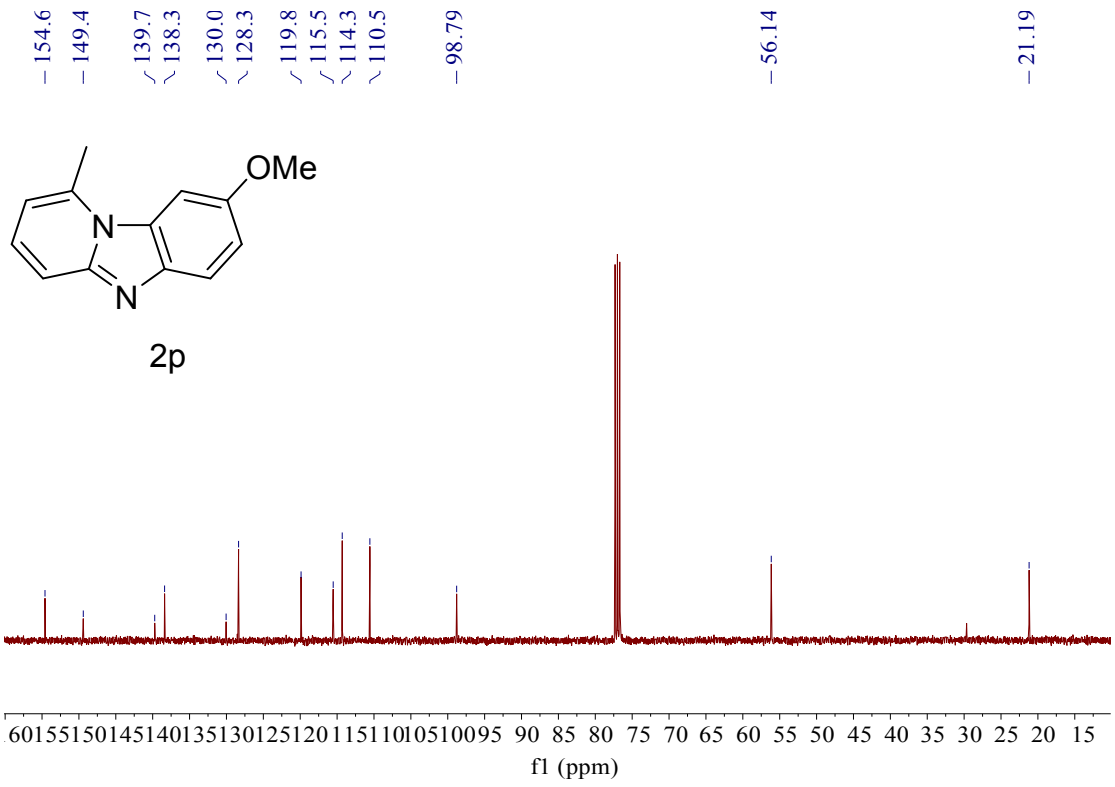

8.77
7.87
7.78
7.75
7.50
7.50
7.45
7.45
7.43
7.43
2.63
F3C
N
N
2o
1.00
1.02
2.00
1.03
1.03
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

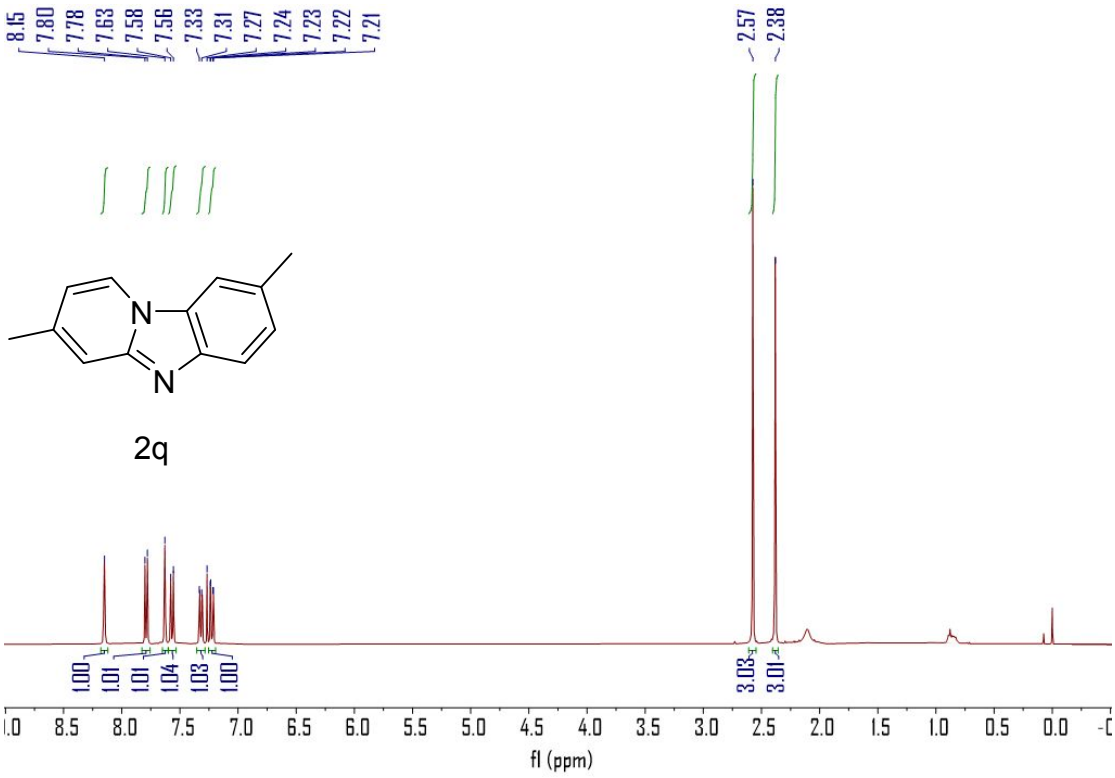

147.3
143.1
132.6
130.0
128.8
128.4
124.2
124.2
122.2
119.9
118.7
114.7
114.4
114.0
113.7
110.1
21.86
F3C
N
N
2o
f1 (ppm)

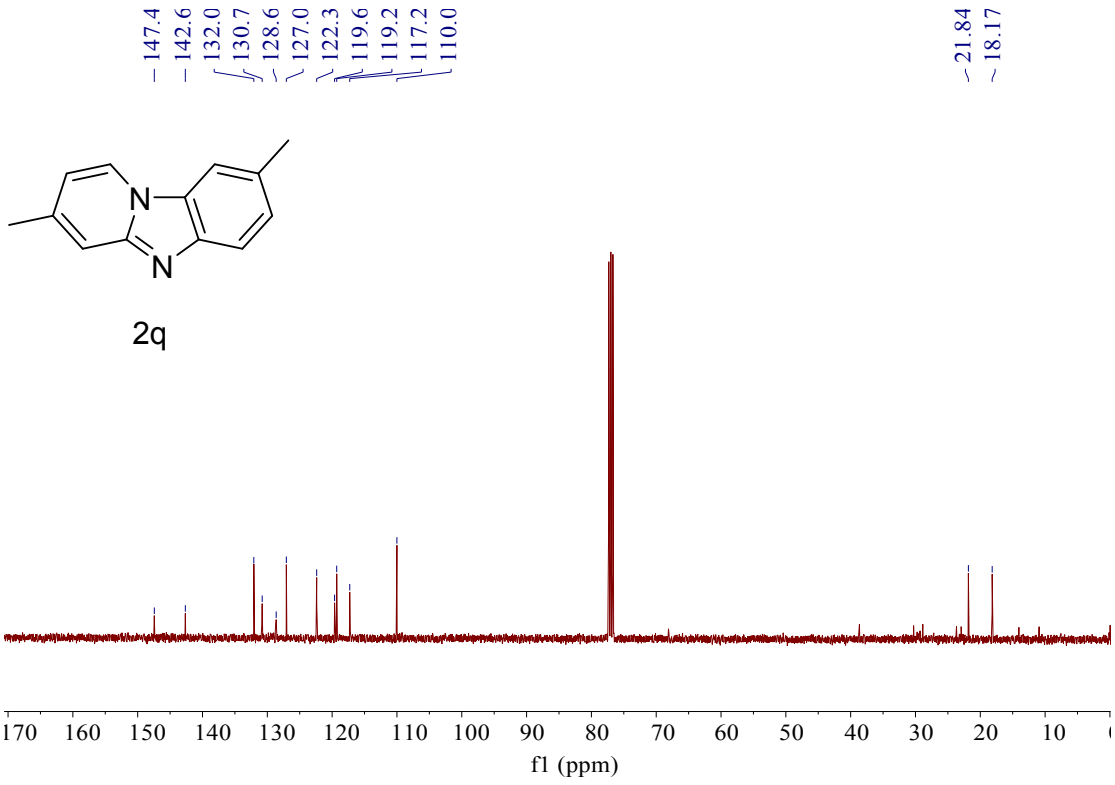

-62.02
F3C
N
N
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

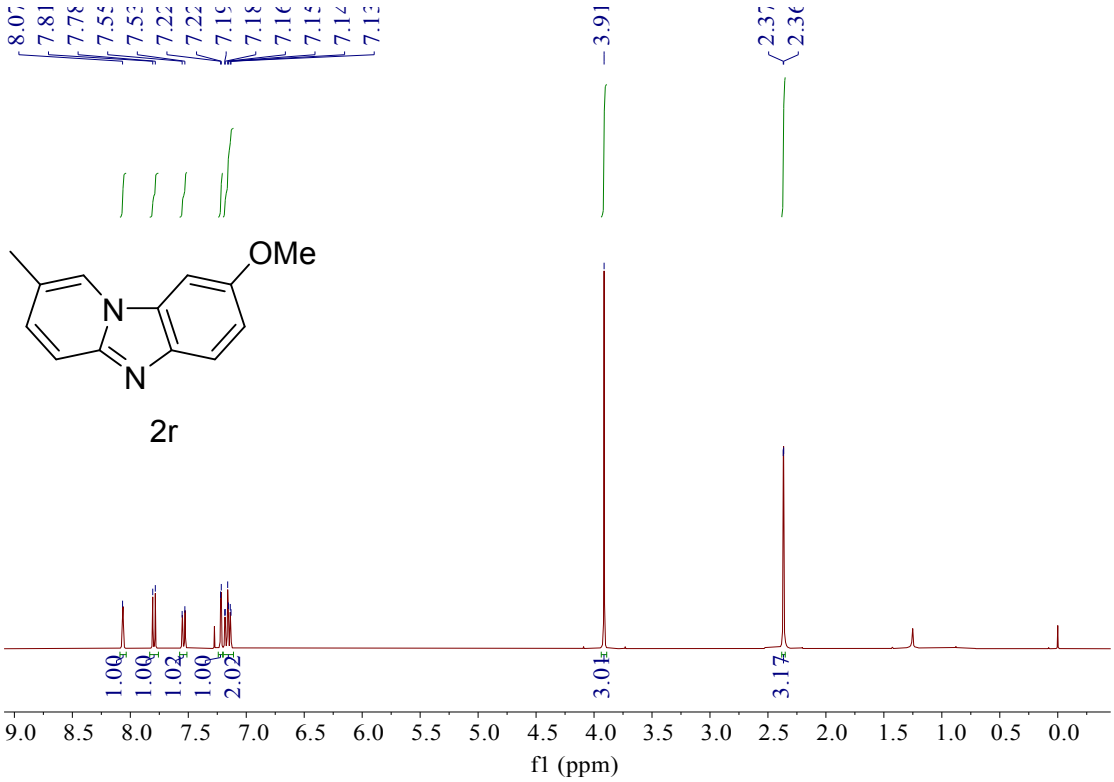
2o

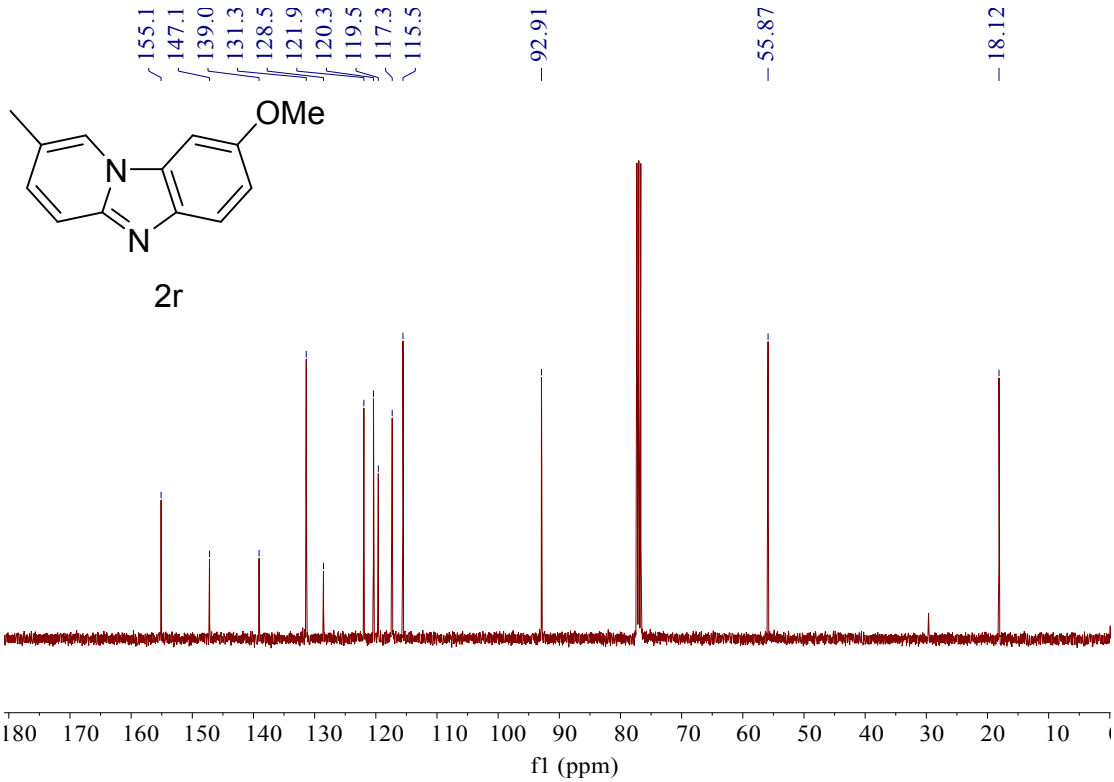

7.86
7.84
7.62
7.53
7.51
7.27
7.26
7.25
7.25
7.24
7.23
7.22
7.22
7.21
7.20
7.20
7.19
6.51
6.50
3.92
3.00
OMe
N
N
2p
1.00
1.02
1.09
2.24
1.03
3.00
3.02
f1 (ppm)

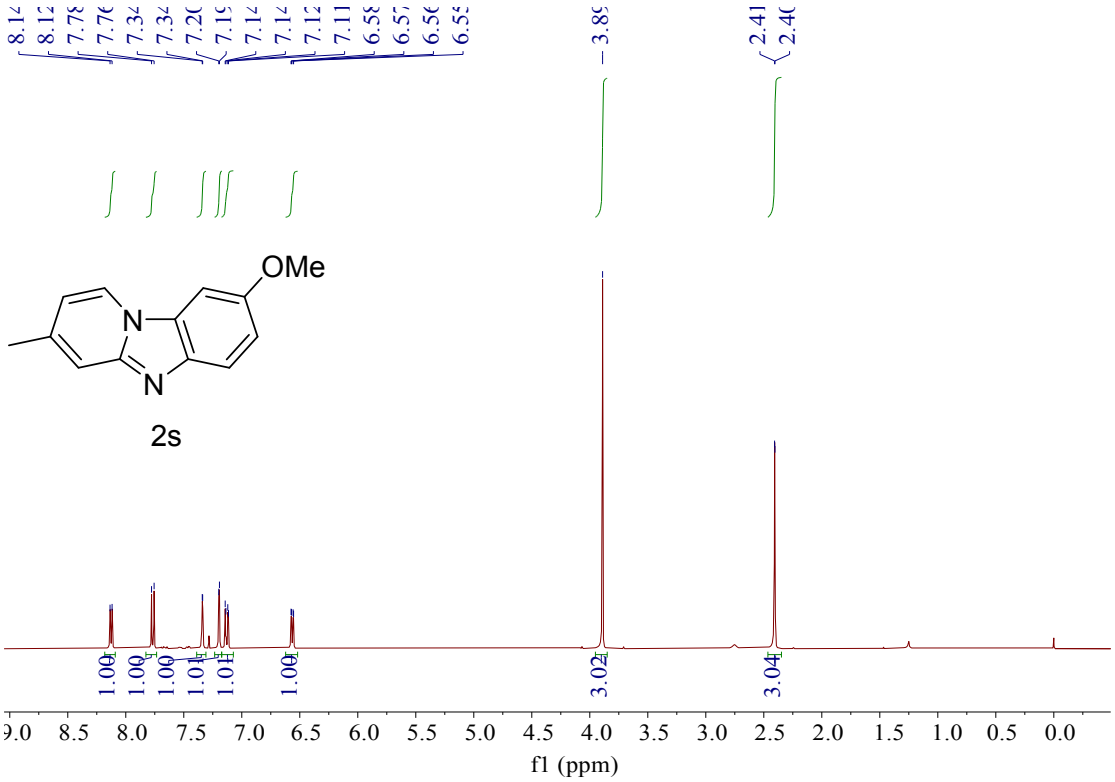

154.6
149.4
139.7
138.3
130.0
128.3
119.8
115.5
114.3
110.5
98.79
56.14
21.19
OMe
N
N
2p
f1 (ppm)

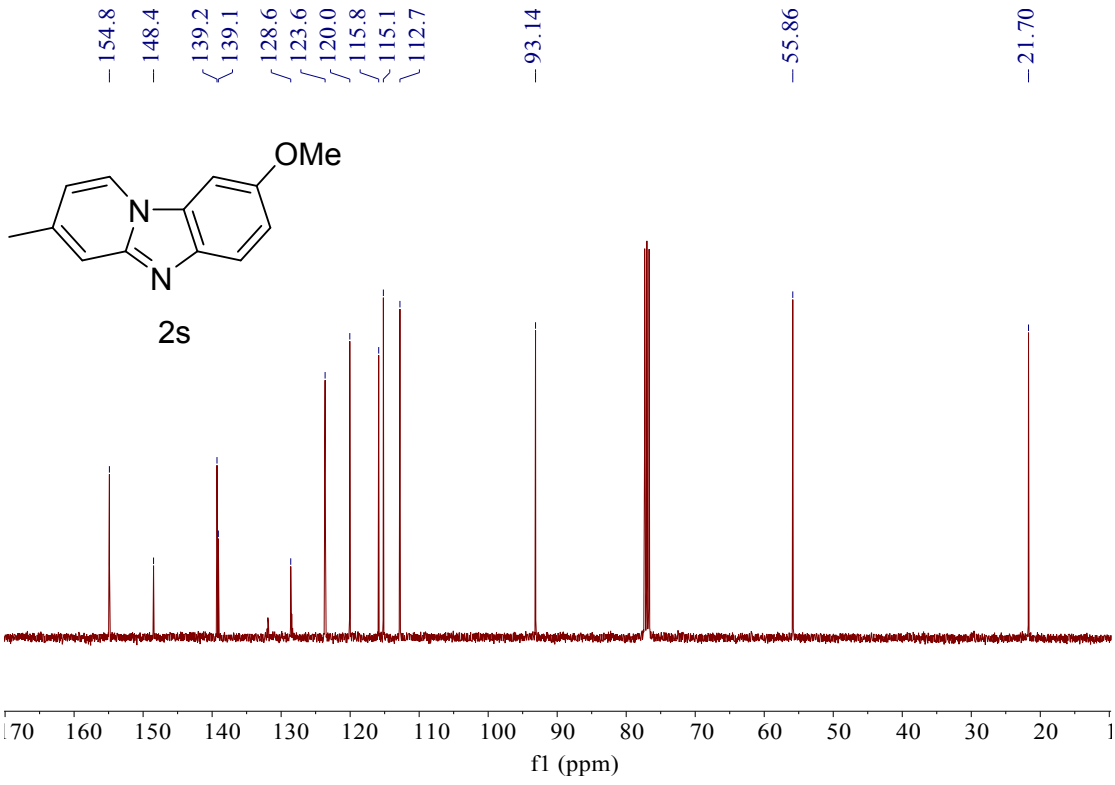

8.15
7.80
7.78
7.63
7.58
7.56
7.33
7.31
7.27
7.24
7.23
7.22
7.21
2.57
2.38
N
N
2q
1.00
1.01
1.01
1.04
1.03
1.00
3.03
3.01
f1 (ppm)


147.4
142.6
132.0
130.7
128.6
127.0
122.3
119.6
119.2
117.2
110.0
21.84
18.17
N
N
2q
f1 (ppm)


OMe
N
N
2r
f1 (ppm)


OMe
N
N
2r
f1 (ppm)


OMe
N
N
2s
f1 (ppm)


OMe
N
N
2s
f1 (ppm)