Supporting Information

Palladium(II) catalyzed site-selective C-H olefination of imidazo[1,2-*a*]pyridines

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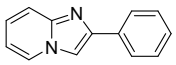
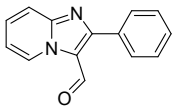
1.General information.

All reactions were carried out using pre-dried reaction tube. Commercially available chemicals were purchased from Sigma-Aldrich and Alfa Aesar Pvt. Ltd., India. These chemicals were used without further purification. IR spectra were measured using a FT-IR spectrometer. Progress of the reactions was monitored by thin-layer chromatography (TLC) plates visualized by UV light, I_2 and by treating the plates with dragendorff reagent followed by heating. Silica-gel column chromatography (100–200 mesh) was used for purification. ^1H and ^{13}C NMR spectra were recorded on Brucker-Avance DPX FT-NMR 500 and 400 MHz instruments. Chemical data for protons are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvent ($CDCl_3$: 7.26 ppm). Carbon nuclear magnetic resonance spectra (^{13}C NMR solvent $CDCl_3$:77.0ppm) were recorded at 125 MHz or 100 MHz. Signal multiplicity is expressed as follows: s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet), m (multiplet). J values are given in hertz (Hz). Mass spectra were obtained using Q-TOF-HR/MS spectrometer using electron spray ionization.

2.General experimental procedure for the synthesis of starting compounds.



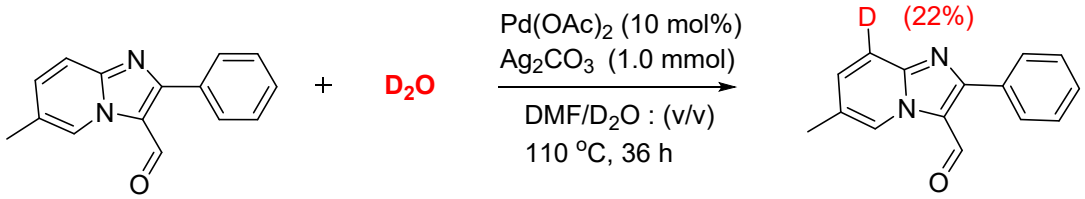
2-Phenylimidazo[1,2-a]pyridine:[1] In a 50 mL round bottom flask, 2-aminopyridine (10 mmol) and phenacyl bromide (10 mmol) were dissolved in 20 mL ethanol after that sodium bicarbonate (12 mmol) was added to the above solution with stirring. The reaction mixture was continued stirred at room temperature for 8-10 h, and the progress of reaction was monitored by TLC. After completion of the reaction, ethanol was evaporated by rotavapor. The resulting mixture was quenched by adding 10 mL water and extracted with CH_2Cl_2 (3 × 20 mL) and combined organic layers were washed with brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography [silica gel, 5% methanol in methylene chloride] to yield desired product (1.746 g, 90% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 6.7 Hz, 1H), 7.96 (d, *J* = 7.3 Hz, 2H), 7.86 (s, 1H), 7.64 (d, *J* = 9.1 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.19 – 7.13 (m, 1H), 6.79-6.77 (m, *J* = 6.6 Hz, 1H).



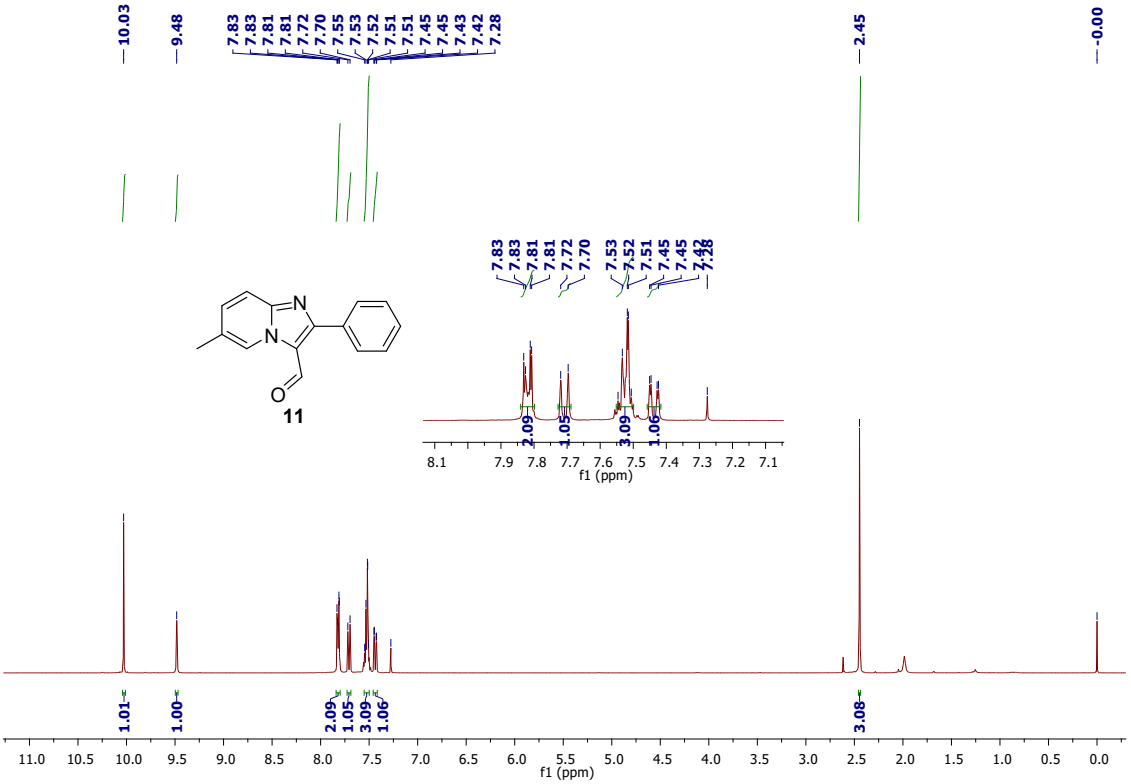
2-Phenylimidazo[1,2-a]pyridine-3-carbaldehyde:[2] In a stirred solution of 2-phenylimidazo [1, 2-a]pyridine (5 mmol) in 5 mL DMF at 0 °C, $POCl_3$ (0.92 mL, 10 mmol) was added dropwise. The reaction mixture was kept at 0 °C for half an hour and then the reaction mixture heated at 60 °C for 3 h. Completion of the reaction was monitored by TLC. After completion, the reaction mixture was cooled and quenched with ice. The reaction mixture was extracted with EtOAc (3 x 20 mL), combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, EtOAc in hexane) to obtain the pure product (0.984g, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 9.67 (d, J = 6.8 Hz, 1H), 7.85 (d, J = 2.5 Hz, 1H), 7.82 (d, J = 8.5 Hz, 2H), 7.62 – 7.56 (m, 1H), 7.54 (d, J = 6.9 Hz, 3H), 7.14 (t, J = 6.7 Hz, 1H).

Deuterium incorporation studies

Mechanistic studies (H/D exchange reaction)



The starting material **1a** (0.3 mmol) dissolved in 2 mL of DMF in a sealed tube and stirred at room temperature. Thereafter, the additon of $Pd(OAc)_2$ (0.04 mmol), D_2O (3mmol, 10 equiv), and Ag_2CO_3 (0.75 mmol) has been done at the same temperature with continous stirring. Finally, the reaction mixture in sealed tube was subjected to 110 °C for 36 h with gentle stirring. The consumption of the starting material was monitored by TLC. After, completation of reaction, the reaction mixture was cooled to room temperatue, passed through celite to expel out metal catalysts under vacuum, further washed with dichloromethane (3 times) and the filtrate collected was concentrated on rotavapour. The desired product **3a** has been purified by column chromatography (silica gel 100-200 using 5% EtOAc in petroleum ether eluent).\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9.48
7.83
7.83
7.81
7.81
7.72
7.70
7.55
7.53
7.52
7.51
7.51
7.45
7.45
7.43
7.42
7.28
2.45
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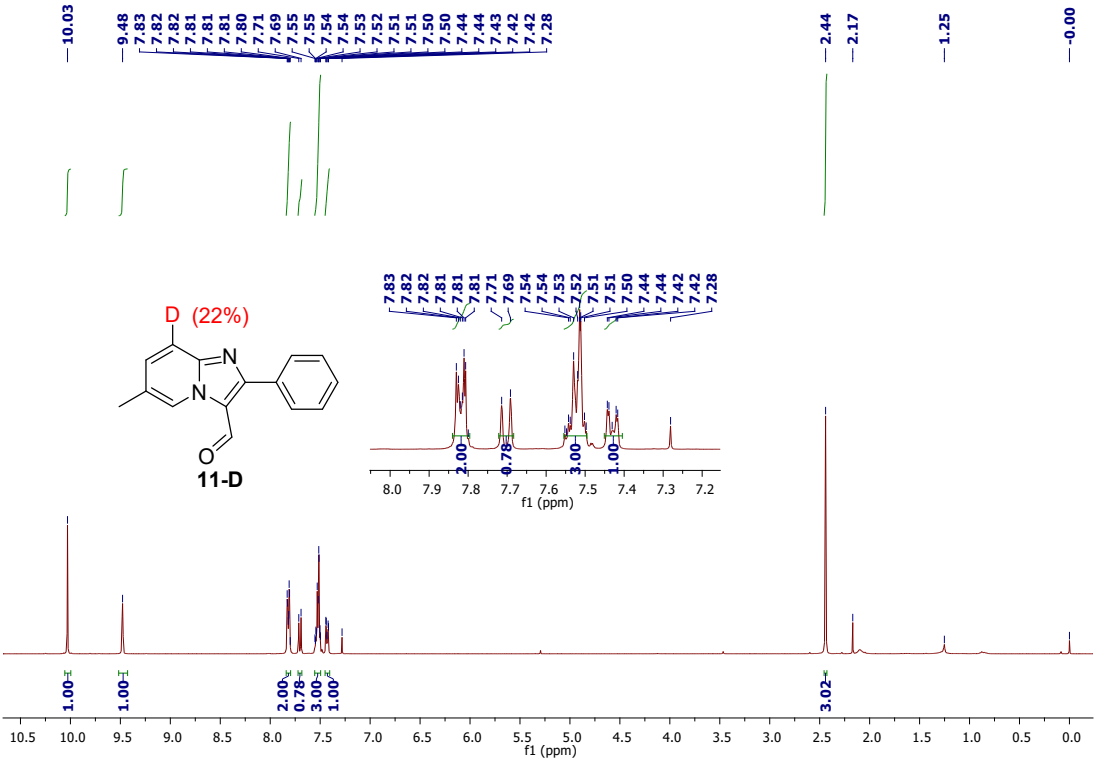
N
N
O
11
f1 (ppm)
1.01
1.00
2.09
1.05
3.09
1.06
3.08


10.03
9.48
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7.82
7.82
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2.17
1.25
-0.00
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N
O
11-D
f1 (ppm)
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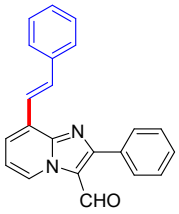
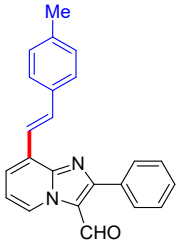
1.00
2.00
0.78
3.00
1.00
3.02

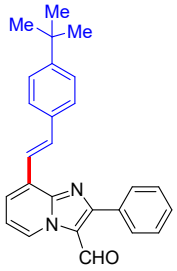


2-Phenyl-8-styrylimidazo[1,2-a]pyridine-3-carbaldehyde (3a); The starting material **1a** (0.3 mmol) dissolved in 2 mL of DMF in a sealed tube and stirred at room temperature. Thereafter, the additon of $Pd(OAc)_2$ (0.04 mmol), styrene (0.6 mmol), and Ag_2CO_3 (0.75 mmol) has been done at the same temperature with continous stirring. Finally, the reaction mixture in sealed tube was subjected to 110 ^oC for 36 h with gentle stirring. The consumption of the starting material was monitored by TLC. After, completation of reaction, the reaction mixture was cooled to room temperatue, passed through celite to expel out metal catalysts under vacuum, further washed with dichloromethane (3 times) and the filtrate collected was concentrated on rotavapour. The desired product **3a** has been purified by column chromatography (silica gel 100-200 using 5% EtOAc in petroleum ether eluent). Yield (101mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 9.56 (dd, J = 6.7, 1.1 Hz, 1H), 7.94 (d, J = 16.4 Hz, 1H), 7.91 (dd, J = 2.3, 1.7 Hz, 1H), 7.89 (dd, J = 2.7, 1.2 Hz, 1H), 7.72 – 7.68 (m, 2H), 7.64 (d, J = 8.5 Hz, 2H), 7.54 (td, J = 5.6, 2.2 Hz, 3H), 7.39 (t, J = 7.4 Hz, 2H), 7.30 (t, J = 7.3 Hz, 1H), 7.12 (t, J = 7.0 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 179.69 (s), 157.77 (s), 146.18 (s), 137.05 (s), 134.22 (s), 132.63 (s), 130.06 (s), 129.82 (s), 128.82 (d, *J* = 15.6 Hz), 128.41 (s), 127.16 (s), 126.95 (s), 126.37 (s), 122.43 (s), 120.93 (s), 115.42 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{22}H_{16}N_2O$, 325.1335; found, 325.1338.

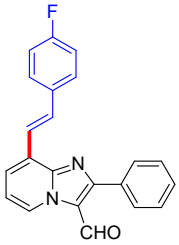


8-(4-Methylstyryl)-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3b); Yield (108mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 9.54 (d, J = 6.7 Hz, 1H), 7.90 (d, J = 1.7 Hz, 1H), 7.89 – 7.85 (m, 2H), 7.68 (d, J = 7.3 Hz, 1H), 7.62 (d, J = 16.4f Hz, 1H), 7.57 – 7.50 (m, 5H), 7.19 (d, J = 8.0 Hz, 2H), 7.10 (t, J = 7.1 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.67 (s), 157.77 (s), 146.18 (s), 138.43 (s), 134.13 (d, *J* = 19.9 Hz), 132.61 (s), 130.03 (s), 129.78 (s), 129.45 (s), 128.88 (s), 127.08 (s), 126.72 (s), 126.05 (s), 121.28 (s), 120.88 (s),

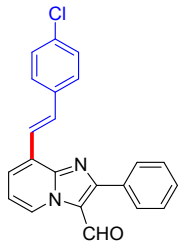
115.46 (s), 77.35 (s), 77.09 (s), 76.84 (s), 21.38 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{23}H_{18}N_2O$, 339.1497; found, 339.1496.



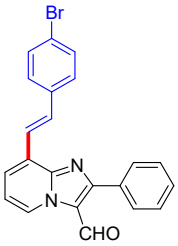
8-(4-(Tert-butyl)styryl)-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3c); Yield (129mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 9.55 (d, J = 6.7 Hz, 1H), 7.92 – 7.90 (m, 1H), 7.90 – 7.87 (m, 2H), 7.71 (d, J = 7.3 Hz, 1H), 7.65 (d, J = 16.4 Hz, 1H), 7.55 (dt, J = 7.6, 7.0 Hz, 5H), 7.41 (d, J = 8.4 Hz, 2H), 7.12 (t, J = 7.0 Hz, 1H), 1.34 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 179.63 (s), 157.76 (s), 151.68 (s), 146.23 (s), 134.27 (s), 133.99 (s), 132.67 (s), 130.02 (s), 129.74 (s), 128.84 (s), 127.17 (s), 126.92 (s), 126.73 (s), 126.01 (s), 125.65 (s), 121.56 (s), 120.92 (s), 115.42 (s), 34.72 (s), 31.29 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{26}H_{24}N_2O$, 381.1967; found, 381.1967.



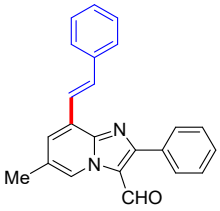
8-(4-Fluorostyryl)-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3d); Yield (100mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 9.55 (d, J = 6.6 Hz, 1H), 7.93 (d, J = 16.7 Hz, 1H), 7.89 (d, J = 7.6 Hz, 2H), 7.65 (d, J = 7.2 Hz, 1H), 7.62 – 7.48 (m, 6H), 7.14 – 7.01 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.68 (s), 162.82 (d, *J* = 248.5 Hz), 157.79 (s), 146.10 (s), 133.26 (d, *J* = 3.2 Hz), 133.01 (s), 132.56 (s), 129.99 (s), 129.80 (s), 128.86 (s), 128.73 (s), 128.65 (s), 126.97 (s), 126.75 (s), 126.37 (s), 122.23 (s), 120.90 (s), 115.69 (d, *J* = 21.8 Hz), 115.37 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{22}H_{15}FN_2O$, 343.1247; found, 343.1248. ^{19}F NMR (377 MHz, $CDCl_3$) δ -112.80 – -112.90 (m).



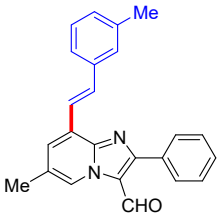
8-(4-Chlorostyryl)-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3e); Yield (108mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 9.53 (d, J = 7.8 Hz, 1H), 7.89 (d, J = 16.5 Hz, 1H), 7.86 (dd, J = 7.8, 1.9 Hz, 2H), 7.64 (d, J = 7.1 Hz, 1H), 7.56 (d, J = 16.3 Hz, 1H), 7.51 (dd, J = 5.2, 2.9 Hz, 5H), 7.31 (d, J = 8.5 Hz, 2H), 7.08 (t, J = 7.0 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 179.76 (s), 157.86 (s), 146.08 (s), 135.52 (s), 134.02 (s), 132.90 (s), 132.50 (s), 130.01 (s), 129.86 (s), 128.91 (s), 128.27 (s), 127.16 (s), 126.68 (s), 126.54 (s), 123.05 (s), 120.88 (s), 115.41 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{22}H_{15}ClN_2O$, 359.0951; found, 359.0954.



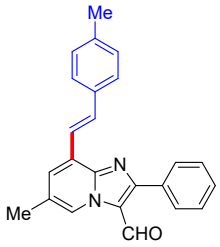
8-(4-Bromostyryl)-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3f); Yield (123mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 9.56 (d, *J* = 6.7 Hz, 1H), 7.92 – 7.87 (m, 3H), 7.66 (d, *J* = 7.1 Hz, 1H), 7.60 (d, *J* = 16.4 Hz, 1H), 7.54 (dd, *J* = 4.7, 2.5 Hz, 3H), 7.48 (d, *J* = 1.6 Hz, 4H), 7.11 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.76 (s), 157.83 (s), 146.03 (s), 135.93 (s), 132.92 (s), 132.47 (s), 131.85 (s), 130.01 (s), 129.87 (s), 128.91 (s), 128.55 (s), 127.17 (s), 126.71 (s), 126.48 (s), 123.12 (s), 122.25 (s), 120.86 (s), 115.41 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{22}H_{15}BrN_2O$, 403.0446; found, 403.0452.



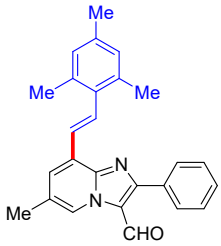
6-Methyl-2-phenyl-8-styrylimidazo[1,2-a]pyridine-3-carbaldehyde (3g); Yield (104mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (d, J = 2.7 Hz, 1H), 9.38 (s, 1H), 7.91 (d, J = 17.7 Hz, 1H), 7.87 (dd, J = 3.3, 1.8 Hz, 2H), 7.66 – 7.58 (m, 3H), 7.53 (dd, J = 9.6, 4.3 Hz, 4H), 7.38 (t, J = 6.9 Hz, 2H), 7.32 – 7.23 (m, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.59 (s), 157.74 (s), 145.23 (s), 137.05 (s), 134.03 (s), 132.75 (s), 129.97 (s), 129.67 (s), 129.16 (s), 128.76 (d, J = 11.8 Hz), 128.33 (s), 127.10 (s), 125.98 (s), 125.34 (d, J = 18.1 Hz), 122.36 (s), 120.71 (s), 18.44 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{23}H_{18}N_2O$, 339.1497; found, 339.1497.



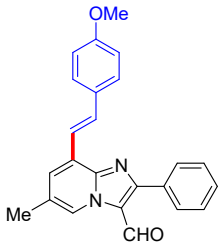
6-Methyl-8-(3-methylstyryl)-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3h); Yield (110mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 9.34 (s, 1H), 7.89 – 7.86 (m, 2H), 7.84 (d, J = 16.2 Hz, 1H), 7.59 (d, J = 16.4 Hz, 1H), 7.52 (d, J = 6.4 Hz, 4H), 7.43 (s, 1H), 7.39 (d, J = 7.7 Hz, 1H), 7.26 (d, J = 7.6 Hz, 1H), 7.10 (d, J = 7.4 Hz, 1H), 2.42 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.56 (s), 157.70 (s), 145.20 (s), 138.27 (s), 136.91 (s), 134.00 (s), 132.75 (s), 129.98 (s), 129.66 (s), 129.20 (s), 128.77 (dd, *J* = 29.1, 14.3 Hz), 127.69 (s), 126.00 (s), 125.44 (s), 125.14 (s), 124.40 (s), 121.99 (s), 120.69 (s), 21.44 (s), 18.47 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{24}H_{20}N_2O$, 353.1654; found, 353.1655.



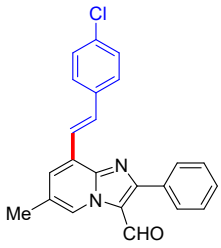
6-Methyl-8-(4-methylstyryl)-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3i); Yield (113mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 9.36 (s, 1H), 7.89 (d, J = 2.5 Hz, 1H), 7.87 – 7.84 (m, 2H), 7.59 (d, J = 16.4 Hz, 1H), 7.55 – 7.50 (m, 6H), 7.19 (d, J = 7.9 Hz, 2H), 2.44 (s, 3H), 2.37 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 180.88 (s), 159.01 (s), 146.59 (s), 139.74 (s), 135.71 (s), 135.32 (s), 134.24 (s), 131.38 (s), 130.83 (s), 130.20 (s), 128.44 (s), 127.54 (s), 126.79 (s), 126.40 (s), 122.72 (s), 122.11 (s), 22.75 (s), 19.84 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{24}H_{20}N_2O$, 353.1654; found, 353.1666.



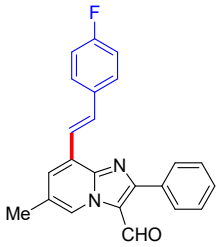
6-Methyl-2-phenyl-8-(2,4,6-trimethylstyryl)imidazo[1,2-a]pyridine-3-carbaldehyde (3j); Yield (130mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 9.42 (s, 1H), 8.13 (d, *J* = 16.6 Hz, 1H), 7.87 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.52 (d, *J* = 7.1 Hz, 2H), 7.26 (s, 3H), 7.09 (d, *J* = 16.6 Hz, 1H), 7.02 – 7.01 (m, 1H), 6.92 (s, 2H), 2.47 (s, 3H), 2.42 (s, 6H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.65 (s), 157.76 (s), 145.19 (s), 136.78 (s), 136.27 (s), 133.78 (s), 133.40 (s), 132.82 (s), 129.92 (s), 129.64 (s), 129.50 (s), 128.88 (s), 128.81 (s), 127.56 (s), 126.34 (s), 125.46 (s), 125.12 (s), 120.60 (s), 21.23 (s), 21.04 (s), 18.47 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{26}H_{24}N_2O$, 381.1967; found, 381.1970.



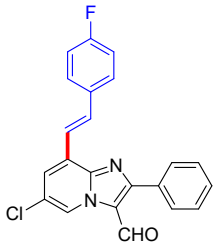
8-(4-Methoxystyryl)-6-methyl-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3k); Yield (111mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 9.36 (s, 1H), 7.87 (dd, J = 9.8, 3.6 Hz, 3H), 7.58 (d, J = 16.5 Hz, 1H), 7.52 (d, J = 5.2 Hz, 4H), 7.28 (t, J = 7.9 Hz, 1H), 7.19 (d, J = 7.6 Hz, 1H), 7.14 (s, 1H), 6.85 (d, J = 7.9 Hz, 1H), 3.85 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.95 (s), 161.38 (s), 159.09 (s), 146.59 (s), 139.93 (s), 135.42 (s), 134.18 (s), 131.39 (s), 131.04 (s), 130.69 (s), 130.22 (s), 127.31 (s), 126.79 (s), 126.69 (s), 124.11 (s), 122.12 (s), 121.29 (s), 115.57 (s), 113.64 (s), 56.76 (s), 19.82 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{24}H_{20}N_2O_2$, 369.1603; found, 369.1609.



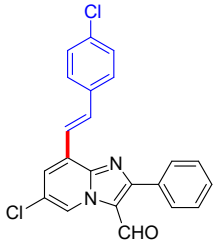
8-(4-Chlorostyryl)-6-methyl-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3l); Yield (111mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (d, J = 1.1 Hz, 1H), 9.39 (s, 1H), 7.90 (d, J = 13.3 Hz, 1H), 7.88 – 7.86 (m, 2H), 7.60 – 7.48 (m, 7H), 7.34 (d, J = 8.4 Hz, 2H), 2.45 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 179.64 (s), 157.75 (s), 145.09 (s), 135.55 (s), 133.96 (s), 132.72 (s), 132.64 (s), 129.95 (s), 129.73 (s), 129.47 (s), 128.90 (s), 128.86 (s), 128.23 (s), 125.59 (s), 125.43 (s), 123.01 (s), 120.68 (s), 18.44 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{23}H_{17}ClN_2O$, 373.1108; found, 373.1107.



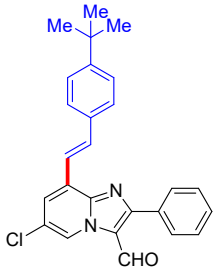
6-Chloro-8-(4-fluorostyryl)-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3m); Yield (104mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 9.35 (s, 1H), 7.88 (d, J = 16.7 Hz, 2H), 7.56 (dd, J = 8.3, 5.6 Hz, 3H), 7.54 – 7.45 (m, 5H), 7.05 (t, J = 8.6 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.55 (s), 162.81 (d, *J* = 248.3 Hz), 157.67 (s), 145.13 (s), 133.33 (d, *J* = 3.2 Hz), 132.82 (d, *J* = 11.1 Hz), 129.96 (s), 129.68 (s), 129.19 (s), 128.82 (s), 128.71 (s), 128.63 (s), 125.82 (s), 125.32 (d, *J* = 12.6 Hz), 122.26 (d, *J* = 2.1 Hz), 120.73 (s), 115.70 (d, *J* = 21.7 Hz), 18.41 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{23}H_{17}FN_2O$, 357.1403; found, 357.1405. ^{19}F NMR (377 MHz, $CDCl_3$) δ -112.93 (dd, J = 7.9, 3.7 Hz).



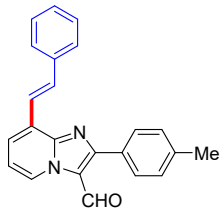
6-Chloro-8-(4-fluorostyryl)-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3n); Yield (94mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 9.63 (s, 1H), 7.92 (d, J = 16.4 Hz, 1H), 7.89 – 7.85 (m, 2H), 7.65 (s, 1H), 7.60 (dd, J = 8.5, 5.5 Hz, 2H), 7.55 (dd, J = 5.2, 1.9 Hz, 3H), 7.50 (d, J = 16.3 Hz, 1H), 7.09 (t, J = 8.6 Hz, 2H) ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.84 (s), 163.05 (d, J = 249.2 Hz), 157.77 (s), 144.52 (s), 134.40 (s), 132.76 (d, J = 3.4 Hz), 132.15 (s), 130.04 (s), 129.91 (s), 128.98 (s), 128.89 (s), 127.07 (s), 126.93 (s), 124.67 (s), 123.63 (s), 121.01 (d, J = 2.1 Hz), 120.88 (s), 115.85 (d, J = 21.7 Hz). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{22}H_{14}ClFN_2O$, 377.0857; found, 377.0857. ^{19}F NMR (377 MHz, $CDCl_3$) δ -111.91 – -112.21 (m).



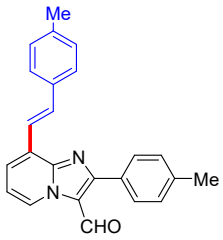
6-Chloro-8-(4-chlorostyryl)-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3o); Yield (101mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 9.62 (d, J = 1.9 Hz, 1H), 7.91 (d, J = 16.4 Hz, 1H), 7.86 (dd, J = 6.5, 3.1 Hz, 2H), 7.62 (d, J = 1.7 Hz, 1H), 7.54 (dt, J = 5.1, 2.6 Hz, 4H), 7.50 (d, J = 11.3 Hz, 2H), 7.34 (d, J = 8.5 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 179.80 (s), 157.73 (s), 144.46 (s), 135.06 (s), 134.54 (s), 134.33 (s), 132.14 (s), 129.97 (d, J = 13.1 Hz), 129.00 (s), 128.97 (s), 128.40 (s), 127.17 (s), 126.86 (s), 124.81 (s), 123.57 (s), 121.88 (s), 120.88 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{22}H_{14}Cl_2N_2O$, 393.0561; found, 393.0590.



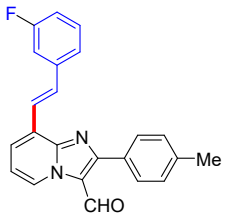
8-(4-(Tert-butyl)styryl)-6-chloro-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3p); Yield (112mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 9.61 (s, 1H), 7.89 (d, J = 16.3 Hz, 2H), 7.65 (d, J = 1.3 Hz, 1H), 7.56 (dd, J = 14.2, 5.7 Hz, 7H), 7.41 (d, J = 8.3 Hz, 2H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.14 (s), 159.09 (s), 153.63 (s), 146.05 (s), 136.86 (s), 135.21 (s), 133.71 (s), 131.34 (s), 130.34 (s), 128.93 (s), 128.51 (s), 127.96 (s), 127.15 (s), 125.81 (s), 125.06 (s), 122.33 (s), 121.80 (s), 36.19 (s), 32.67 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{26}H_{23}ClN_2O$, 415.1577; found, 415.1579.



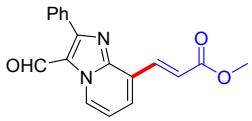
8-Styryl-2-(p-tolyl)imidazo[1,2-a]pyridine-3-carbaldehyde (3q); Yield (100mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 9.56 (d, J = 7.7 Hz, 1H), 7.96 (d, J = 16.4 Hz, 1H), 7.82 – 7.78 (m, 2H), 7.69 (d, J = 8.1 Hz, 1H), 7.64 (dd, J = 5.5, 3.0 Hz, 2H), 7.38 (dd, J = 15.7, 7.8 Hz, 4H), 7.30 (t, J = 7.3 Hz, 1H), 7.10 (t, J = 7.0 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, CDC_{l3}) δ 179.09 (s), 157.38 (s), 145.58 (s), 139.38 (s), 136.41 (s), 133.50 (s), 129.27 (s), 129.09 (s), 128.97 (s), 128.07 (s), 127.71 (s), 126.49 (s), 126.34 (s), 126.18 (s), 125.71 (s), 121.83 (s), 120.15 (s), 114.66 (s), 20.78 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{23}H_{18}N_2O$, 339.1497; found, 339.1501.



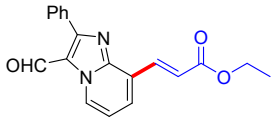
8-(4-Methylstyryl)-2-(p-tolyl)imidazo[1,2-a]pyridine-3-carbaldehyde (3r); Yield (107mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 9.55 (d, J = 6.7 Hz, 1H), 7.91 (d, J = 16.4 Hz, 1H), 7.80 (d, J = 8.1 Hz, 2H), 7.69 (d, J = 7.2 Hz, 1H), 7.63 (d, J = 16.4 Hz, 1H), 7.54 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 7.8 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.11 (t, J = 7.0 Hz, 1H), 2.46 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.72 (s), 158.02 (s), 146.26 (s), 139.99 (s), 138.41 (s), 134.29 (s), 134.05 (s), 129.91 (s), 129.77 (s), 129.60 (s), 129.44 (s), 127.08 (s), 126.78 (s), 126.05 (s), 121.41 (s), 120.80 (s), 115.34 (s), 21.42 (s), 21.34 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{24}H_{20}N_2O$, 353.1654; found, 353.1661.



8-(3-Fluorostyryl)-2-(p-tolyl)imidazo[1,2-a]pyridine-3-carbaldehyde (3s); Yield (103mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 9.56 (d, J = 6.7 Hz, 1H), 7.98 (d, J = 16.3 Hz, 1H), 7.79 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 7.3 Hz, 1H), 7.60 (d, J = 16.3 Hz, 1H), 7.40 – 7.29 (m, 5H), 7.10 (t, J = 7.0 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.77 (s), 163.19 (d, J = 245.5 Hz), 158.01 (s), 146.07 (s), 140.10 (s), 139.45 (d, J = 7.9 Hz), 133.02 (d, J = 2.6 Hz), 130.12 (d, J = 8.4 Hz), 129.89 (s), 129.63 (s), 127.29 (s), 126.92 (s), 126.27 (s), 123.94 (s), 123.04 (d, J = 2.6 Hz), 120.75 (s), 115.21 (s), 114.98 (s), 113.35 (d, J = 21.9 Hz), 21.42 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{23}H_{17}FN_2O$, 357.1403; found, 357.1416. ^{19}F NMR (377 MHz, $CDCl_3$) δ -113.24 – -113.34 (m).

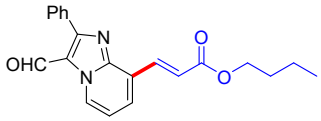


Methyl-3-(3-formyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5a); Yield (94mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.13 (d, *J* = 21.2 Hz, 1H), 9.67 (dd, *J* = 6.8, 1.1 Hz, 1H), 8.00 (d, *J* = 15.9 Hz, 1H), 7.89 (dd, *J* = 7.5, 2.2 Hz, 2H), 7.69 (d, *J* = 7.1 Hz, 1H), 7.65 (d, *J* = 15.9 Hz, 1H), 7.58 – 7.51 (m, 3H), 7.16 (t, *J* = 7.0 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.02 (s), 167.48 (s), 158.10 (s), 145.74 (s), 138.71 (s), 132.20 (s), 131.33 (s), 130.05 (s), 129.29 (s), 128.94 (s), 124.13 (s), 123.93 (s), 120.67 (s), 115.05 (s), 51.89 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{18}H_{14}N_2O_3$, 307.1083; found, 307.1090.

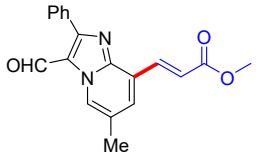


Ethyl-3-(3-formyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5b); Yield (93mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 9.67 (dd, J = 6.8, 1.1 Hz, 1H), 7.99 (d, J = 15.9 Hz, 1H), 7.90 (dd, J = 7.6, 2.0 Hz, 2H), 7.69 (d, J = 6.9 Hz, 1H), 7.62 (d, J = 15.9 Hz, 1H), 7.58 – 7.51 (m, 3H), 7.16 (t, J = 7.0 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C

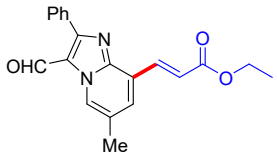
NMR (101 MHz, $CDCl_3$) δ 179.99 (s), 167.02 (s), 158.12 (s), 145.77 (s), 138.39 (s), 132.23 (s), 131.20 (s), 130.07 (s), 130.01 (s), 129.22 (s), 128.93 (s), 124.65 (s), 124.08 (s), 120.70 (s), 115.04 (s), 60.74 (s), 14.35 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{19}H_{16}N_2O_3$, 321.1239; found, 321.1244.



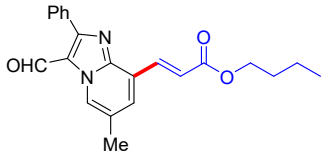
Butyl-3-(3-formyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5c); Yield (98mg, 63%). ^1H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 9.66 (dd, J = 6.8, 1.1 Hz, 1H), 7.98 (d, J = 15.9 Hz, 1H), 7.90 (dd, J = 7.6, 2.0 Hz, 2H), 7.68 (d, J = 7.1 Hz, 1H), 7.63 (s, 1H), 7.57 – 7.52 (m, 3H), 7.15 (t, J = 7.0 Hz, 1H), 4.26 (t, J = 6.7 Hz, 2H), 1.78 – 1.63 (m, 2H), 1.46 (dq, J = 14.7, 7.4 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.98 (s), 167.12 (s), 158.10 (s), 145.76 (s), 138.38 (s), 132.22 (s), 131.23 (s), 130.07 (s), 130.01 (s), 129.21 (s), 128.92 (s), 124.63 (s), 124.07 (s), 120.69 (s), 115.03 (s), 64.68 (s), 30.79 (s), 19.20 (s), 13.75 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{21}H_{20}N_2O_3$, 349.1552; found, 349.1557.



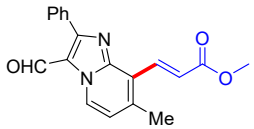
Methyl-3-(3-formyl-6-methyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5d); Yield (96mg, 71%). ^1H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 9.50 (s, 1H), 7.97 (d, J = 15.9 Hz, 1H), 7.90 – 7.85 (m, 2H), 7.63 (d, J = 15.9 Hz, 1H), 7.56 – 7.52 (m, 3H), 7.26 (s, 1H), 3.85 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.91 (s), 167.48 (s), 144.81 (s), 138.75 (s), 134.03 (s), 132.39 (s), 130.00 (s), 129.89 (s), 128.88 (s), 127.50 (s), 125.13 (s), 124.08 (s), 123.11 (s), 120.51 (s), 51.83 (s), 18.26 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{19}H_{16}N_2O_3$, 321.1239; found, 321.1244.



Ethyl-3-(3-formyl-6-methyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5e); Yield (96mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 9.48 (s, 1H), 7.94 (d, J = 15.9 Hz, 1H), 7.90 – 7.85 (m, 2H), 7.60 (d, J = 16.0 Hz, 1H), 7.57 – 7.51 (m, 4H), 4.31 (q, J = 7.1 Hz, 2H), 2.46 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.89 (s), 167.05 (s), 158.00 (s), 144.78 (s), 138.45 (s), 134.01 (s), 132.37 (s), 130.01 (s), 129.89 (s), 128.88 (s), 127.41 (s), 125.15 (s), 124.53 (s), 123.15 (s), 120.47 (s), 60.72 (s), 18.27 (s), 14.36 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{20}H_{18}N_2O_3$, 335.1396; found, 335.1404.

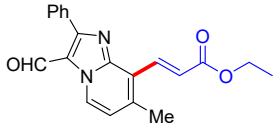


Butyl-3-(3-formyl-6-methyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5f); Yield (101mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 9.49 (s, 1H), 7.94 (d, J = 15.9 Hz, 1H), 7.90 – 7.85 (m, 2H), 7.59 (d, J = 15.9 Hz, 1H), 7.56 – 7.52 (m, 4H), 4.25 (t, J = 6.7 Hz, 2H), 2.46 (d, J = 0.6 Hz, 3H), 1.71 (dd, J = 15.2, 7.4 Hz, 2H), 1.45 (dd, J = 15.1, 7.5 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.89 (s), 167.15 (s), 157.99 (s), 144.78 (s), 138.45 (s), 134.03 (s), 132.38 (s), 130.02 (s), 129.89 (s), 128.88 (s), 127.41 (s), 125.14 (s), 124.53 (s), 123.17 (s), 120.47 (s), 64.65 (s), 30.79 (s), 19.21 (s), 18.26 (s), 13.77 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{22}H_{22}N_2O_3$, 363.1709; found, 363.1703.

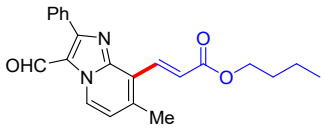


Methyl-3-(3-formyl-7-methyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5g); Yield (94mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 9.52 (d, J = 6.9 Hz, 1H), 8.08 (d, J = 15.8 Hz, 1H), 7.96 (d, J = 15.8 Hz, 1H), 7.90 (d, J = 2.5 Hz, 1H), 7.88 (d, J = 1.7 Hz, 1H), 7.58 – 7.50 (m, 3H), 7.00 (d, J = 7.0 Hz, 1H), 3.86 (s, 3H), 2.65 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.74 (s), 168.10 (s), 158.22 (s), 146.30 (s), 142.14 (s), 135.52 (s), 132.36 (s), 130.02 (s),

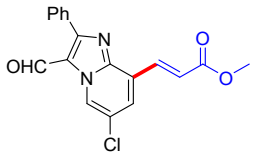
129.94 (s), 128.89 (s), 128.19 (s), 125.59 (s), 121.11 (s), 120.24 (s), 118.81 (s), 51.84 (s), 20.00 (s).HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{19}H_{16}N_2O_3$, 321.1239; found, 321.1242.



Ethyl-3-(3-formyl-7-methyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5h); Yield (94mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 9.52 (d, J = 6.9 Hz, 1H), 8.07 (d, J = 15.8 Hz, 1H), 7.92 (d, J = 15.6 Hz, 1H), 7.90 – 7.87 (m, 2H), 7.60 – 7.50 (m, 3H), 7.00 (d, J = 7.0 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 2.65 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.73 (s), 167.69 (s), 158.24 (s), 146.32 (s), 142.06 (s), 135.27 (s), 132.39 (s), 129.93 (s), 128.89 (s), 128.11 (s), 126.05 (s), 121.20 (s), 120.25 (s), 118.82 (s), 60.70 (s), 20.00 (s), 14.38 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{20}H_{18}N_2O_3$, 335.1396; found, 335.1396.

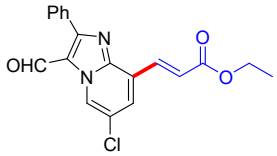


Butyl-3-(3-formyl-7-methyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5i); Yield (98mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 9.52 (d, J = 6.9 Hz, 1H), 8.07 (d, J = 15.8 Hz, 1H), 7.90 (dd, J = 12.6, 6.1 Hz, 3H), 7.55 (d, J = 6.0 Hz, 3H), 7.01 (d, J = 6.9 Hz, 1H), 4.26 (t, J = 6.7 Hz, 2H), 2.65 (s, 3H), 1.77 – 1.68 (m, 2H), 1.46 (dd, J = 15.0, 7.5 Hz, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.80 (s), 159.00 (s), 158.47 (s), 158.25 (s), 135.28 (s), 132.36 (s), 130.04 (s), 129.94 (s), 128.89 (s), 128.11 (s), 126.01 (s), 121.19 (s), 118.84 (s), 64.65 (s), 30.78 (s), 20.01 (s), 19.22 (s), 13.79 (s), 0.00 (s). HRMS (ESI-TOF): m/z: [M+H]+ calctd for $C_{22}H_{22}N_2O_3$, 363.1709; found, 363.1712.

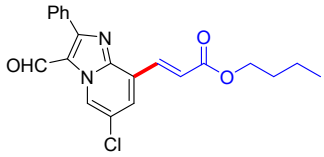


Ethyl-3-(6-chloro-3-formyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5j); Yield (87mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 9.75 (d, J = 2.0 Hz, 1H), 7.93 (d, J = 15.5 Hz, 1H), 7.90 – 7.85 (m, 2H), 7.66 (s, 1H), 7.64 (d, J = 13.1 Hz, 1H), 7.56 (dd, J = 5.0, 1.9 Hz,

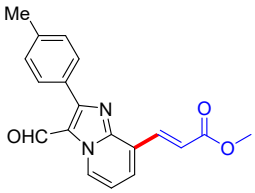
3H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.08 (s), 167.03 (s), 158.09 (s), 144.13 (s), 137.41 (s), 131.82 (s), 131.63 (s), 130.25 (s), 129.97 (s), 129.03 (s), 126.97 (s), 125.60 (s), 124.18 (s), 123.13 (s), 120.67 (s), 52.01 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{18}H_{13}ClN_2O_3$, 341.0693; found, 341.0702.



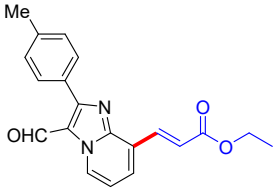
Ethyl-3-(6-chloro-3-formyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5k); Yield (88mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 9.75 (d, J = 2.0 Hz, 1H), 7.92 (d, J = 15.9 Hz, 1H), 7.90 – 7.86 (m, 2H), 7.66 (d, J = 1.8 Hz, 1H), 7.61 (d, J = 15.9 Hz, 1H), 7.56 (dd, J = 5.1, 1.9 Hz, 3H), 4.32 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.06 (s), 166.57 (s), 158.10 (s), 144.16 (s), 137.10 (s), 131.85 (s), 131.53 (s), 130.23 (s), 129.99 (s), 129.02 (s), 126.90 (s), 126.09 (s), 124.31 (s), 123.14 (s), 120.69 (s), 60.91 (s), 14.31 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{19}H_{15}ClN_2O_3$, 355.0849; found, 355.0549.



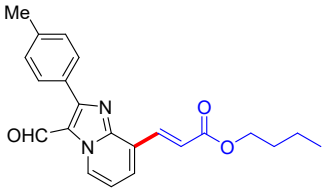
Butyl-3-(6-chloro-3-formyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5l); Yield (92mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 9.75 (d, J = 2.0 Hz, 1H), 7.92 (d, J = 15.9 Hz, 1H), 7.90 – 7.87 (m, 2H), 7.67 (d, J = 1.9 Hz, 1H), 7.61 (d, J = 15.9 Hz, 1H), 7.57 (dd, J = 5.1, 1.9 Hz, 3H), 7.26 (s, 1H), 4.26 (t, J = 6.7 Hz, 2H), 1.82 – 1.65 (m, 2H), 1.46 (dq, J = 14.7, 7.4 Hz, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.07 (s), 166.68 (s), 158.11 (s), 144.16 (s), 137.10 (s), 131.85 (s), 131.55 (s), 130.23 (s), 129.99 (s), 129.03 (s), 126.90 (s), 126.08 (s), 124.32 (s), 123.15 (s), 120.69 (s), 64.85 (s), 30.75 (s), 19.19 (s), 13.75 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{21}H_{19}ClN_2O_3$, 383.1162; found, 383.1155.



Methyl-3-(3-formyl-2-(p-tolyl)imidazo[1,2-a]pyridin-8-yl)acrylate (5m); Yield (91mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 9.67 (dd, J = 6.8, 1.1 Hz, 1H), 8.00 (d, J = 15.9 Hz, 1H), 7.79 (d, J = 8.1 Hz, 2H), 7.66 (t, J = 11.1 Hz, 2H), 7.36 (d, J = 7.8 Hz, 2H), 7.14 (t, J = 7.0 Hz, 1H), 3.85 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.02 (s), 167.50 (s), 158.27 (s), 145.78 (s), 140.32 (s), 138.77 (s), 131.25 (s), 129.95 (s), 129.67 (s), 129.37 (s), 129.30 (s), 124.09 (s), 123.86 (s), 120.57 (s), 114.88 (s), 51.85 (s), 21.43 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{19}H_{16}N_2O_3$, 321.1239; found, 321.1250.

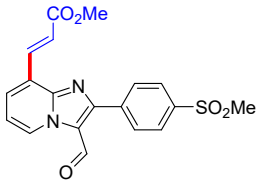


Ethyl-3-(3-formyl-2-(p-tolyl)imidazo[1,2-a]pyridin-8-yl)acrylate (5n); Yield (93mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 9.66 (d, J = 6.7 Hz, 1H), 7.99 (d, J = 15.6 Hz, 1H), 7.80 (d, J = 7.5 Hz, 2H), 7.68 (d, J = 7.2 Hz, 1H), 7.62 (d, J = 15.9 Hz, 1H), 7.37 (d, J = 7.7 Hz, 2H), 7.14 (t, J = 6.8 Hz, 1H), 4.31 (q, J = 7.0 Hz, 2H), 2.46 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.00 (s), 167.06 (s), 158.29 (s), 145.80 (s), 140.30 (s), 138.45 (s), 131.14 (s), 130.18 (s), 129.96 (s), 129.65 (s), 129.39 (s), 129.22 (s), 129.17 (s), 124.58 (s), 123.97 (s), 120.58 (s), 114.88 (s), 60.71 (s), 21.41 (s), 14.34 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{20}H_{18}N_2O_3$, 335.1396; found, 335.1408.

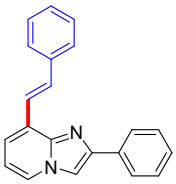


Butyl-3-(3-formyl-2-(p-tolyl)imidazo[1,2-a]pyridin-8-yl)acrylate (5o); Yield (98mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.11 (s, 1H), 9.65 (d, J = 6.8 Hz, 1H), 7.97 (d, J = 15.9 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.67 (d, J = 6.9 Hz, 1H), 7.61 (d, J = 15.9 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.13 (t, J = 7.0 Hz, 1H), 4.25 (t, J = 6.7 Hz, 2H), 2.46 (s, 3H), 1.78 – 1.67 (m, 2H), 1.51 – 1.40

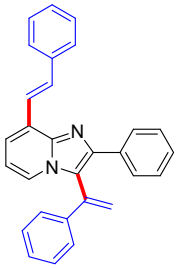
(m, 2H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.97 (s), 167.14 (s), 158.24 (s), 145.78 (s), 140.29 (s), 138.43 (s), 131.15 (s), 129.95 (s), 129.65 (s), 129.40 (s), 129.20 (s), 124.58 (s), 123.98 (s), 120.58 (s), 114.86 (s), 64.64 (s), 30.80 (s), 21.41 (s), 19.20 (s), 13.74 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{22}H_{22}N_2O_3$, 363.1709; found, 363.1718.



Methyl-3-(3-formyl-2-(4-(methylsulfonyl)phenyl)imidazo[1,2-a]pyridin-8-yl)acrylate (8); Yield (82mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 9.67 (d, J = 5.8 Hz, 1H), 8.12 (q, J = 8.6 Hz, 4H), 8.00 (d, J = 16.0 Hz, 1H), 7.74 (d, J = 7.1 Hz, 1H), 7.62 (d, J = 15.9 Hz, 1H), 7.22 (t, J = 7.1 Hz, 1H), 3.86 (s, 3H), 3.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.10 (s), 167.26 (s), 155.30 (s), 145.79 (s), 141.68 (s), 138.31 (s), 137.59 (s), 131.59 (s), 130.86 (s), 129.25 (s), 127.97 (s), 124.38 (d, J = 14.6 Hz), 121.17 (s), 115.71 (s), 51.92 (s), 44.55 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{19}H_{16}N_2O_5S$, 385.0858; found, 385.0859.

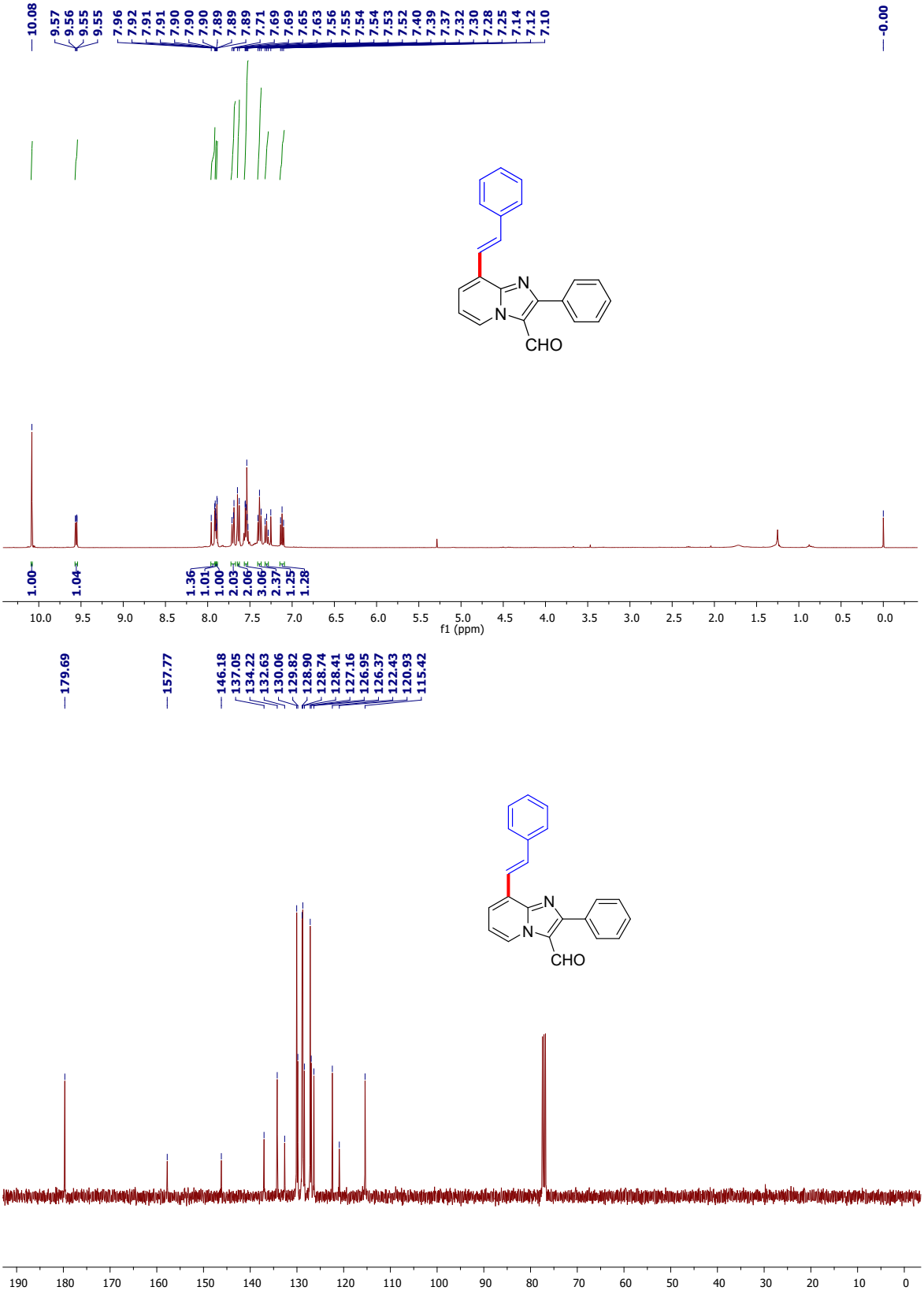


2-Phenyl-8-styrylimidazo[1,2-a]pyridine (9); Yield (49mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 16.3 Hz, 1H), 8.07 – 8.03 (m, 2H), 8.01 (dd, J = 6.7, 1.0 Hz, 1H), 7.87 (s, 1H), 7.68 (dd, J = 8.1, 0.9 Hz, 2H), 7.54 (d, J = 16.3 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.37 – 7.32 (m, 1H), 7.29 (ddd, J = 17.2, 6.3, 2.3 Hz, 2H), 6.78 (t, J = 6.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.40 (s), 144.11 (s), 137.68 (s), 133.92 (s), 133.78 (s), 128.74 (s), 128.68 (s), 127.95 (s), 127.05 (s), 126.76 (s), 126.17 (s), 124.05 (s), 123.93 (s), 122.31 (s), 112.54 (s), 108.43 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for $C_{21}H_{16}N_2$, 297.1392; found, 297.1399.

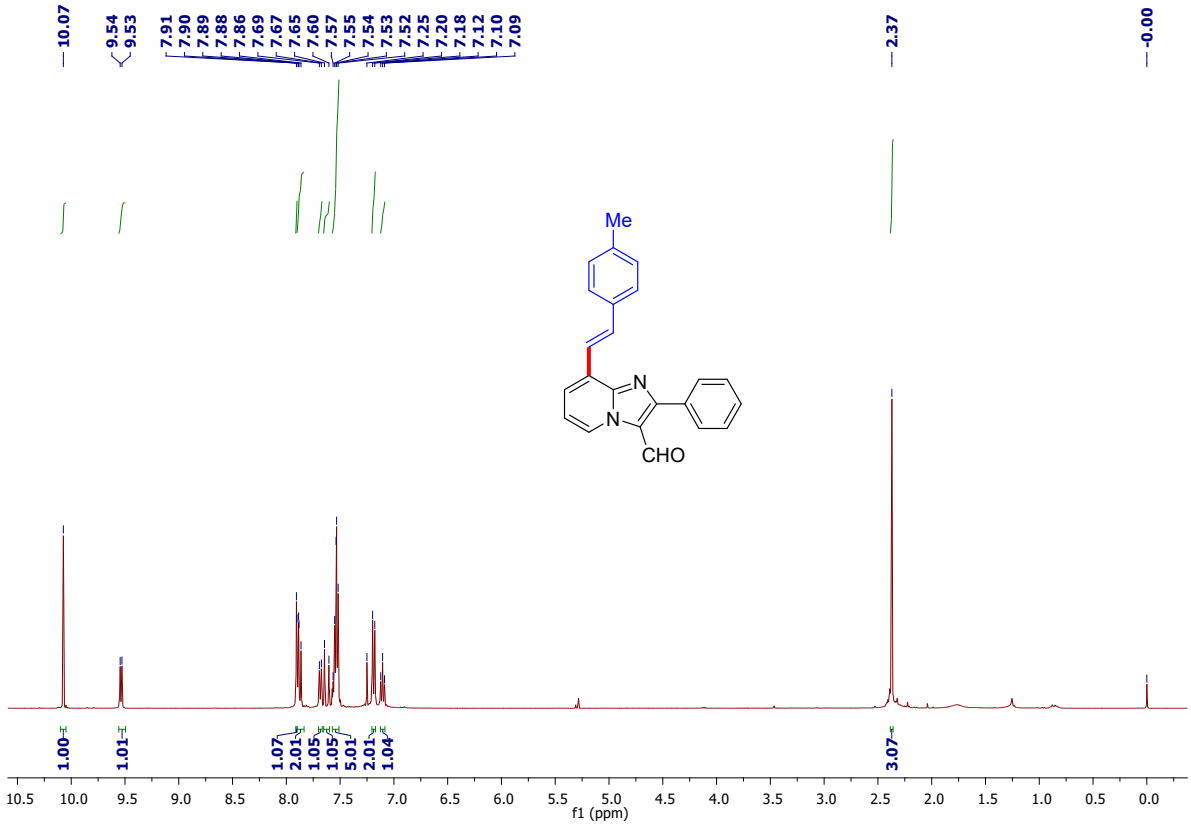


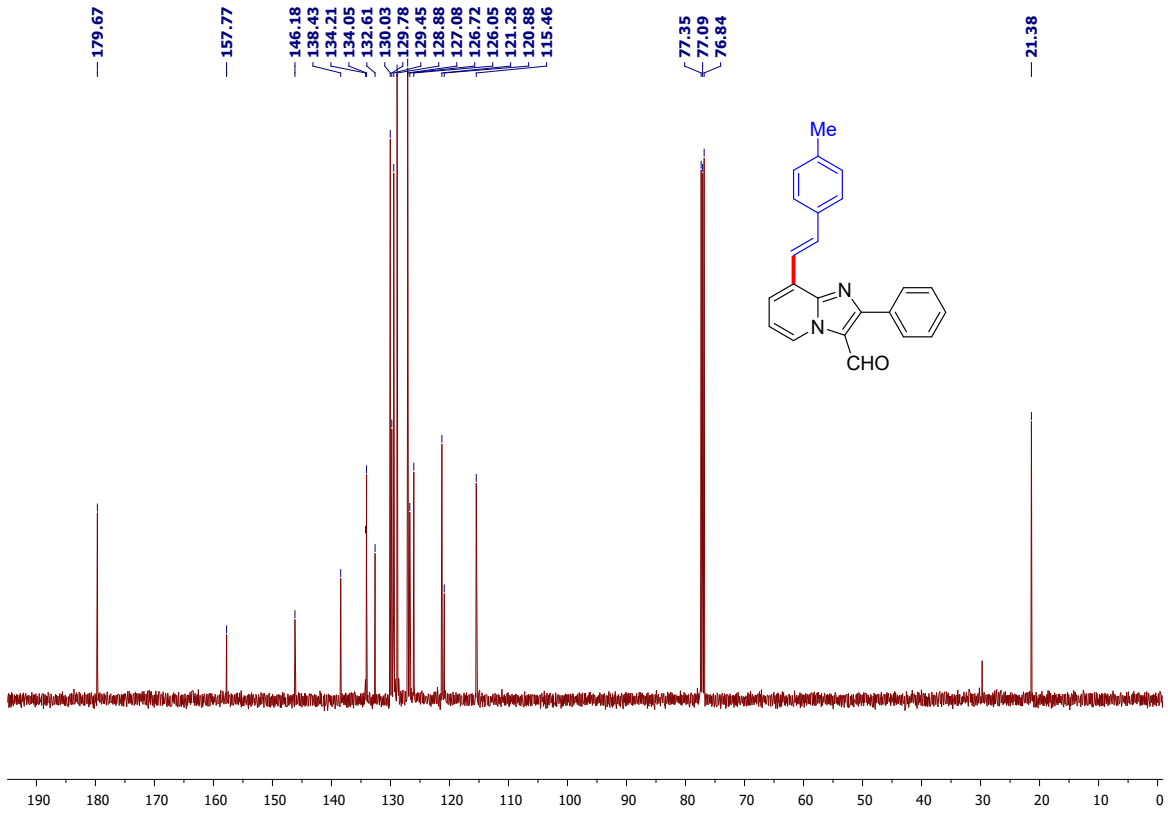
2-Phenyl-3-(1-phenylvinyl)-8-styrylimidazo[1,2-a]pyridine (10); Yield (78mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 16.3 Hz, 1H), 8.12 – 7.93 (m, 2H), 7.69 (d, J = 7.3 Hz, 2H), 7.59 (t, J = 11.3 Hz, 2H), 7.44 – 7.38 (m, 4H), 7.36 (s, 1H), 7.35 – 7.27 (m, 6H), 7.26 (s, 1H), 6.82 – 6.47 (m, 1H), 6.21 (s, 1H), 5.61 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.28 (s), 143.01 (s), 137.90 (s), 137.71 (s), 134.23 (s), 133.70 (s), 129.05 (s), 128.76 (s), 128.66 (s), 128.32 (s), 127.94 (s), 127.56 (s), 127.04 (s), 126.57 (s), 126.22 (s), 123.95 (s), 122.76 (s), 122.23 (s), 121.44 (s), 120.36 (s), 112.31 (s). HRMS (ESI-TOF): m/z: $[M+H]^+$ calctd for : $C_{29}H_{22}N_2$, 399.1861; found, 399.1861.

2-Phenyl-8-styrylimidazo[1,2-a]pyridine-3-carbaldehyde (3a);

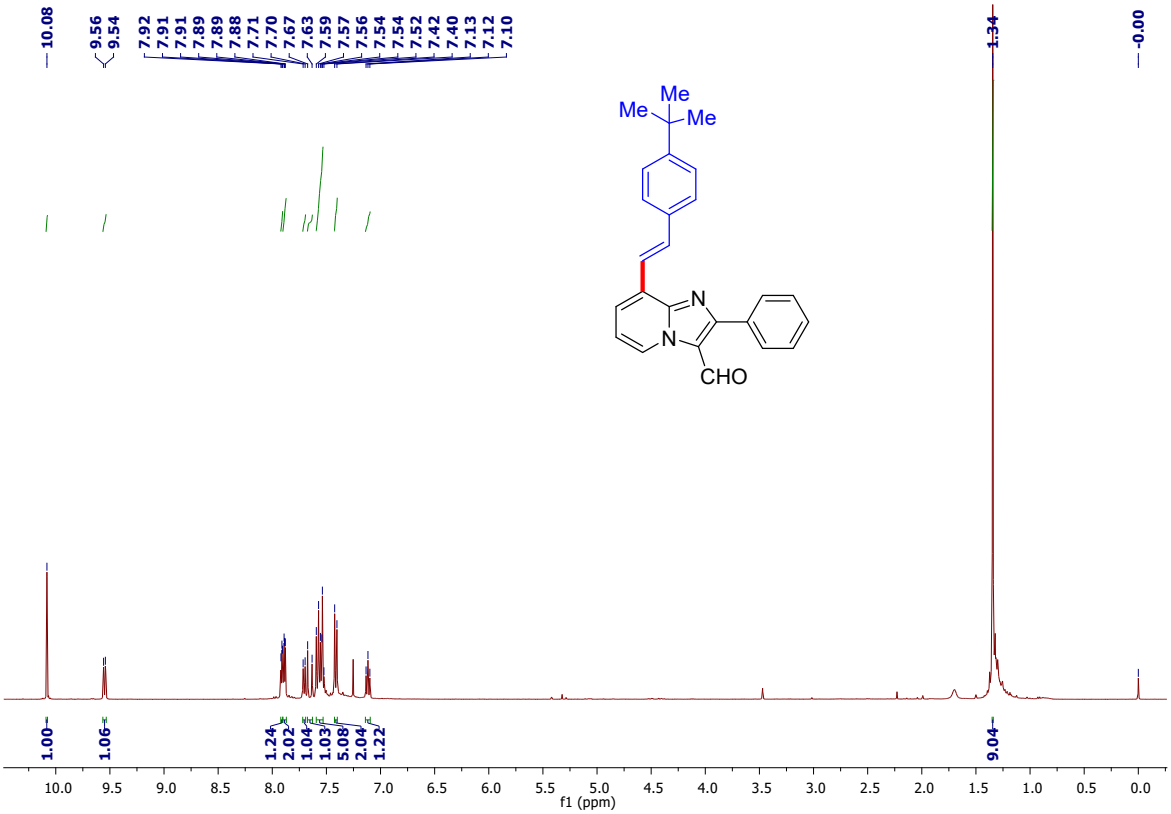


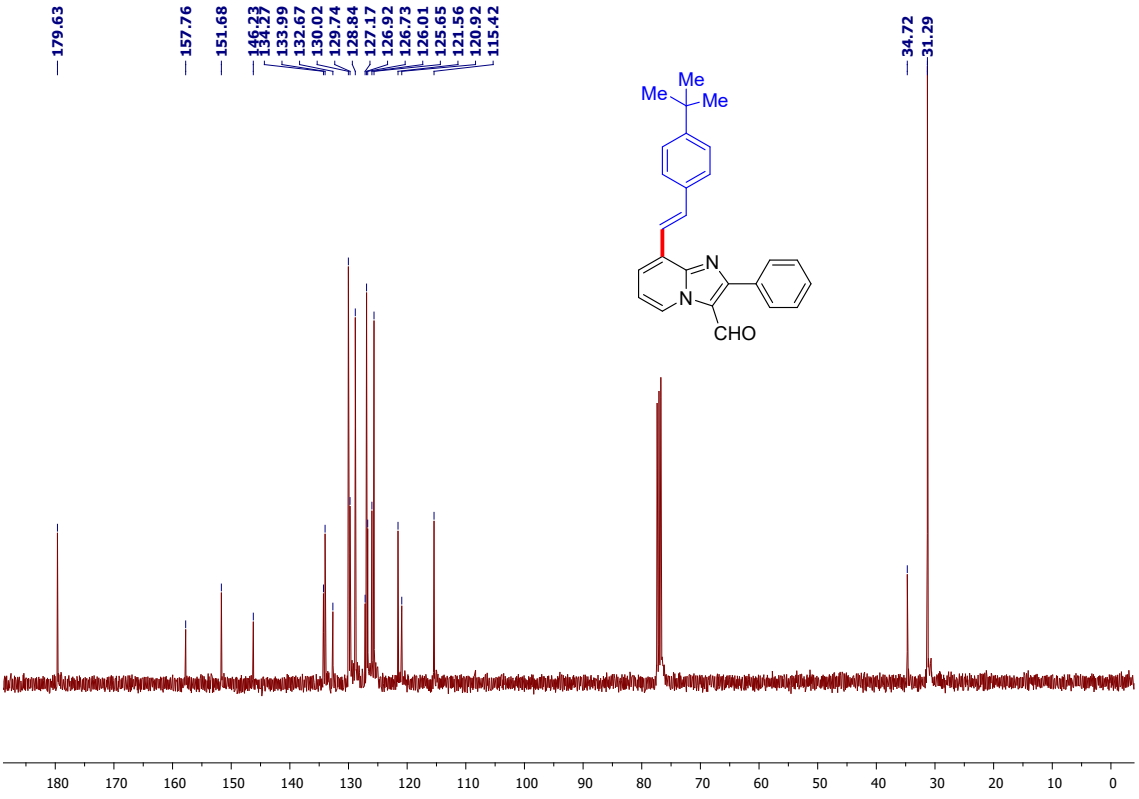
8-(4-Methylstyryl)-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3b);



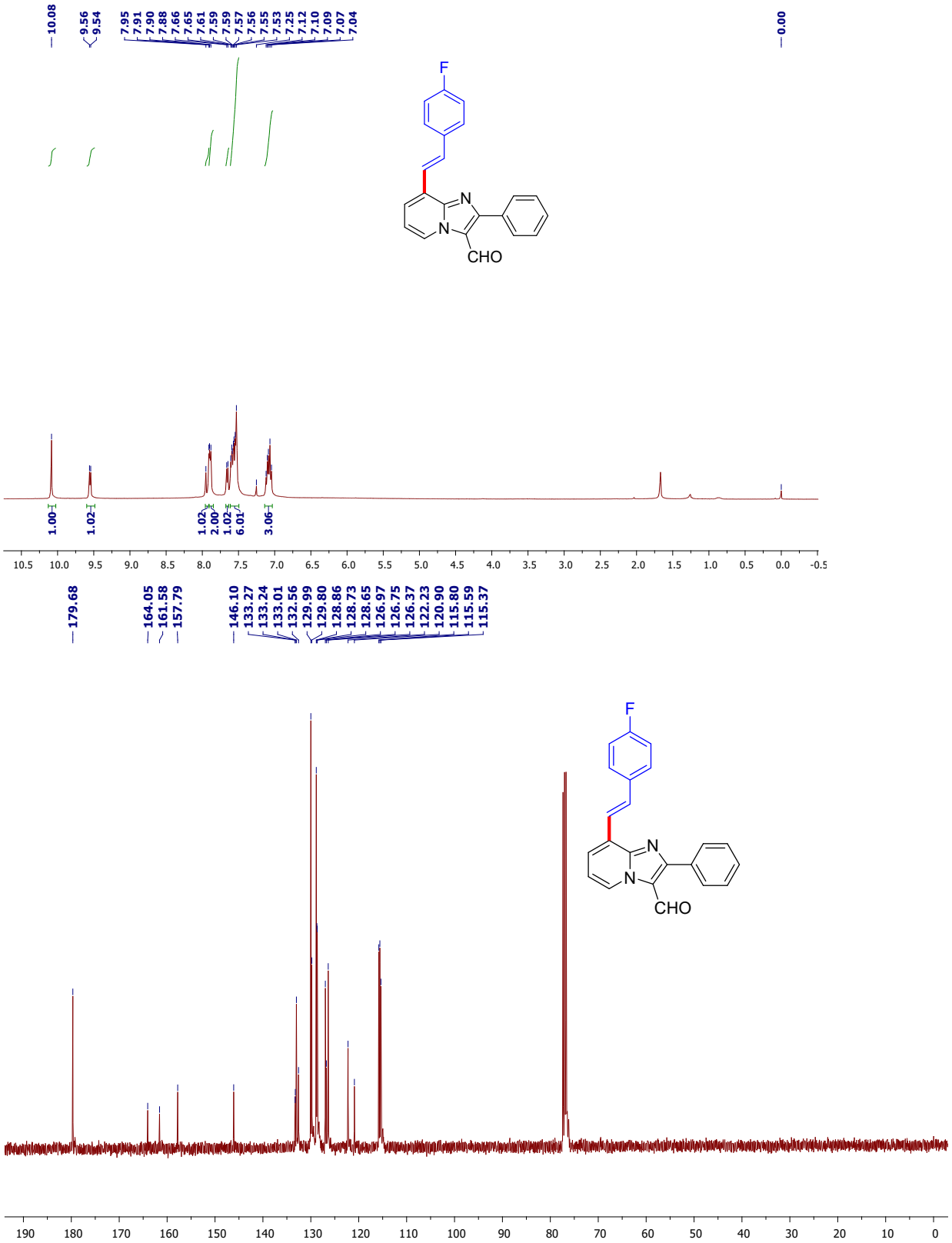


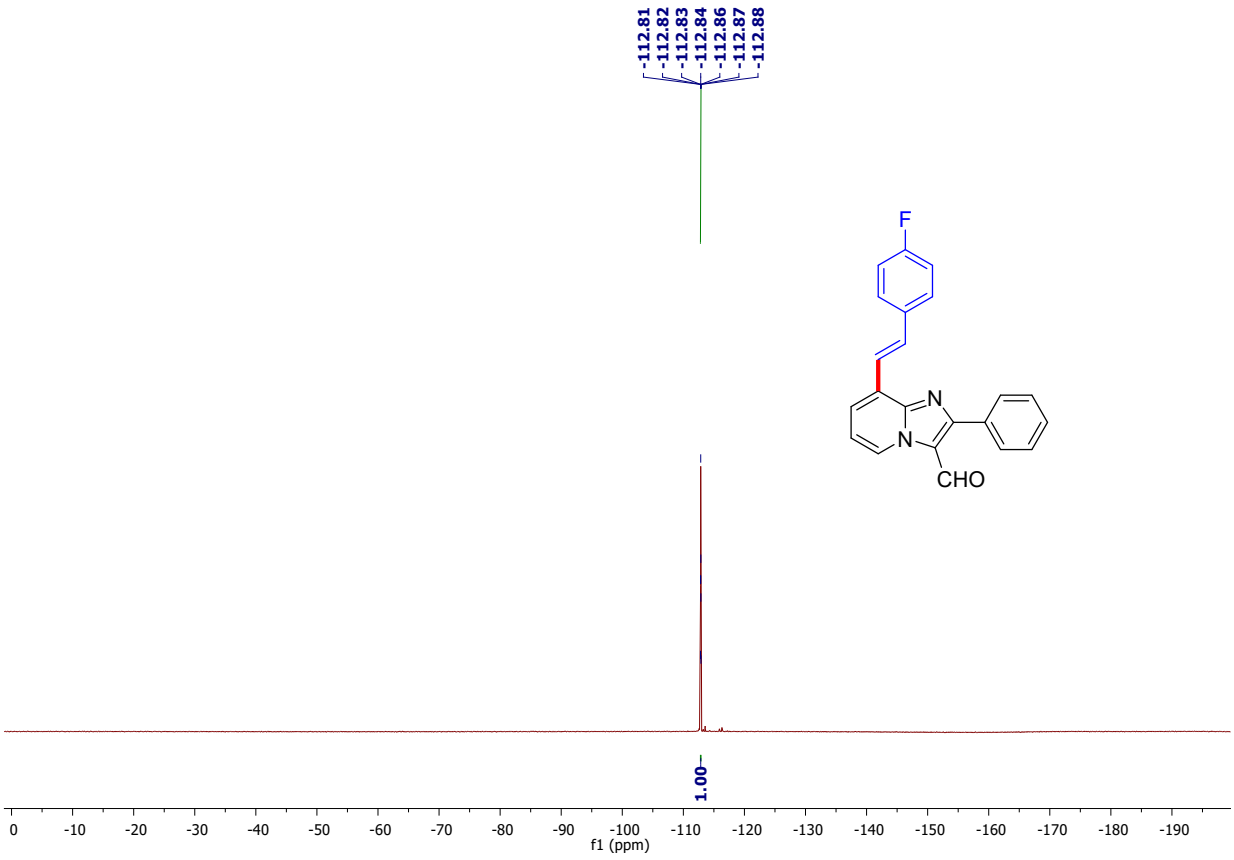
8-(4-(Tert-butyl)styryl)-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3c);



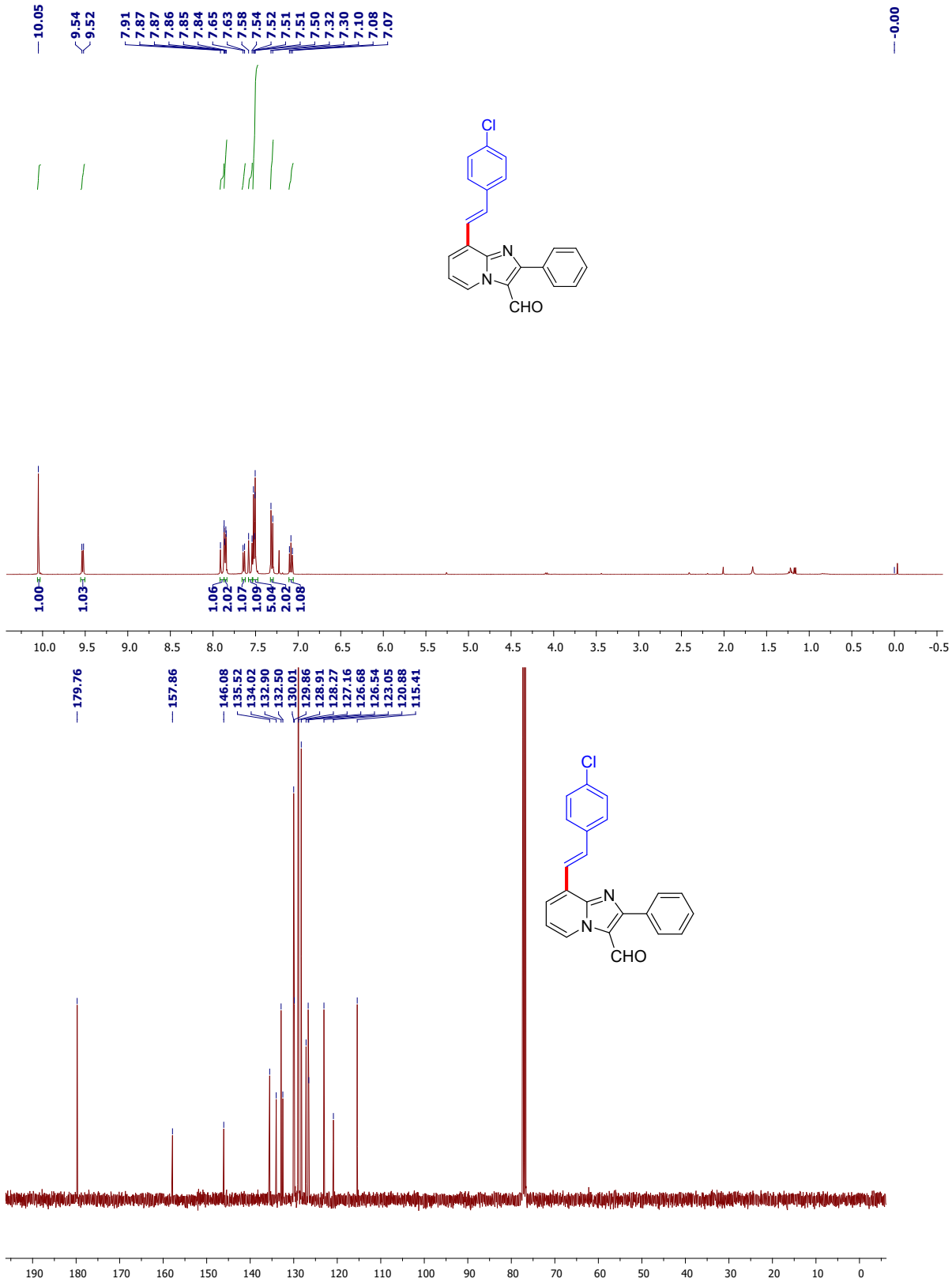


8-(4-Fluorostyryl)-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3d);

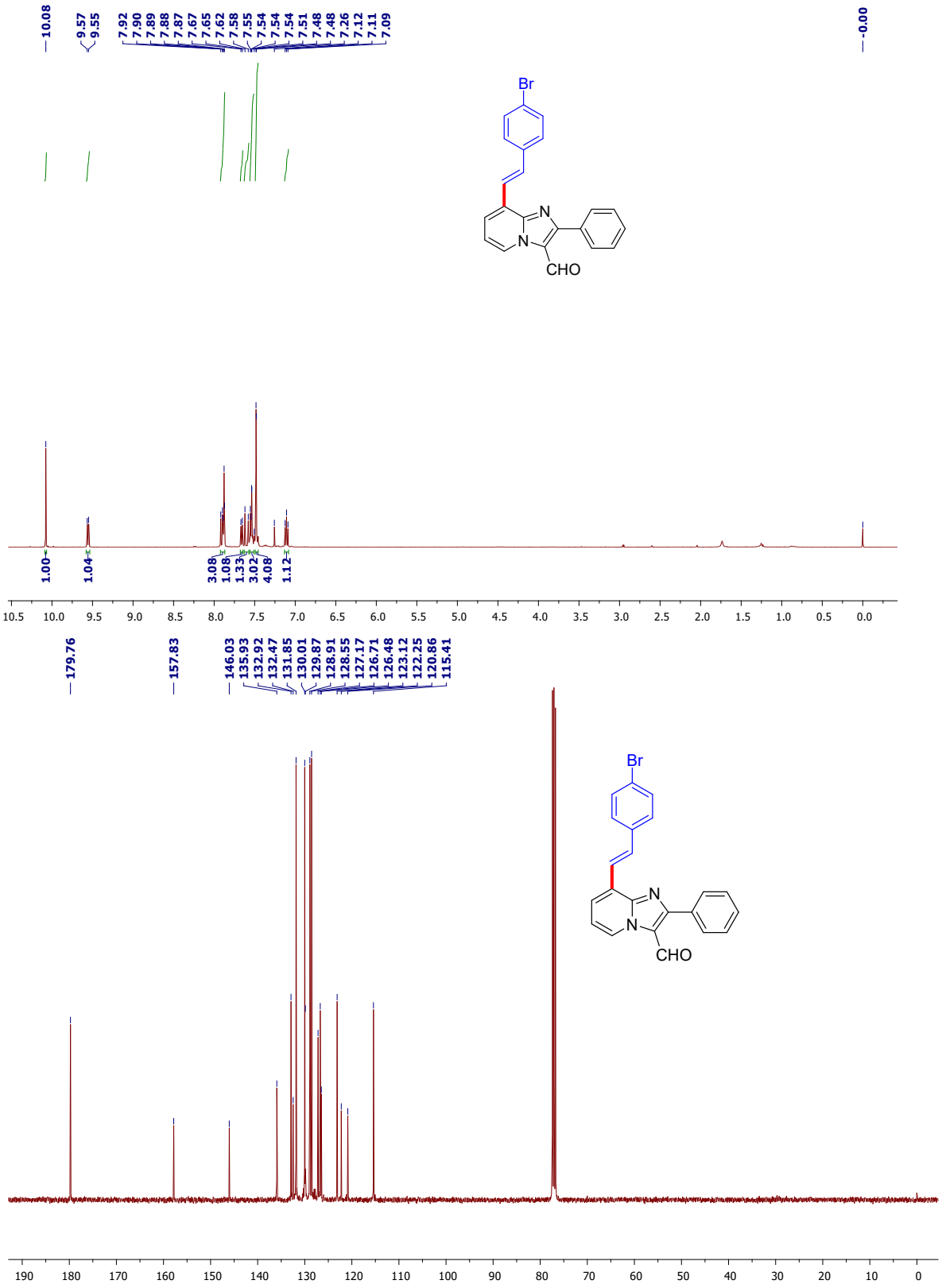



-112.81
-112.82
-112.83
-112.84
-112.86
-112.87
-112.88
F
N
N
CHO
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

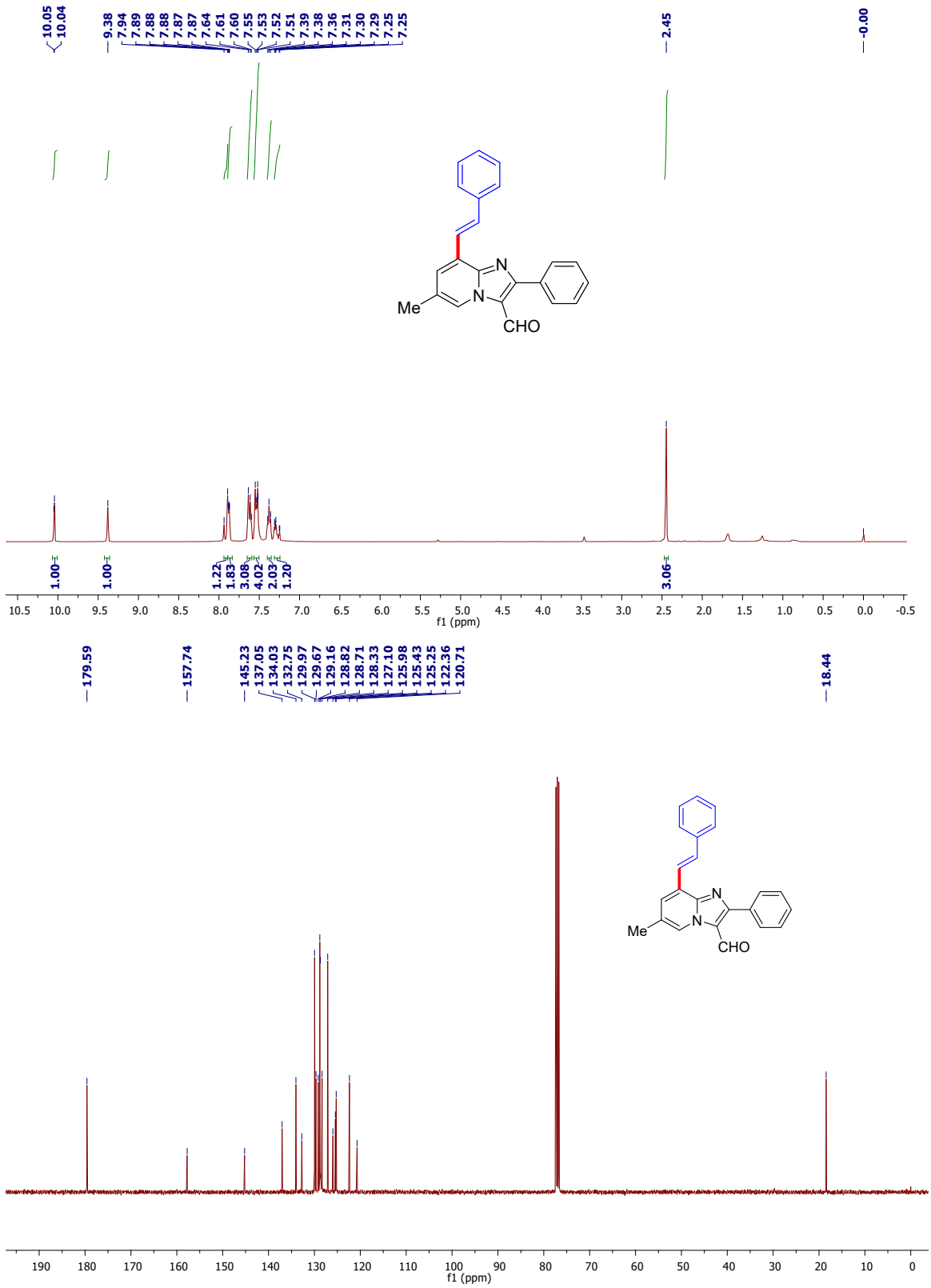
8-(4-Chlorostyryl)-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3e);



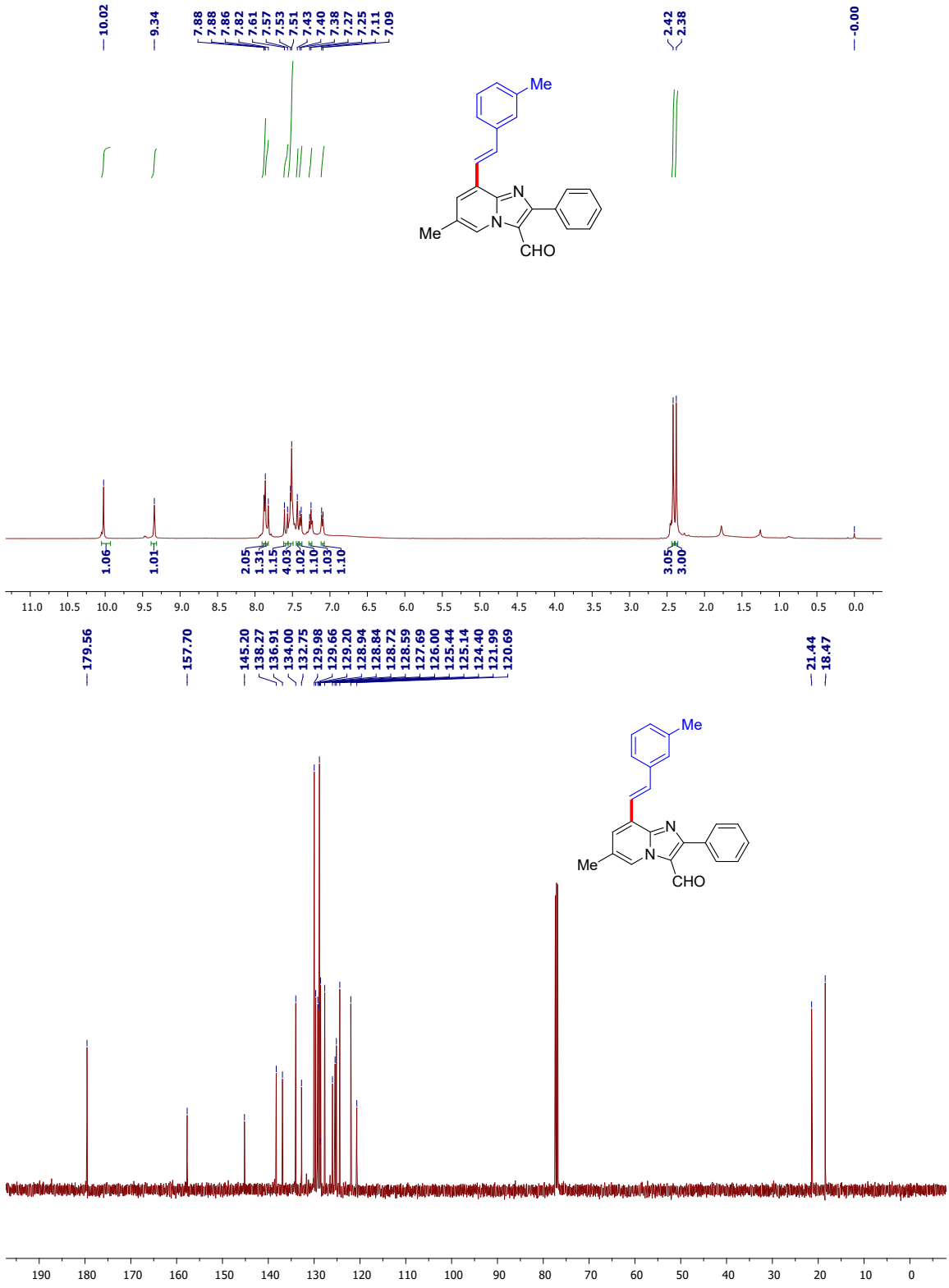
8-(4-Bromostyryl)-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3f);



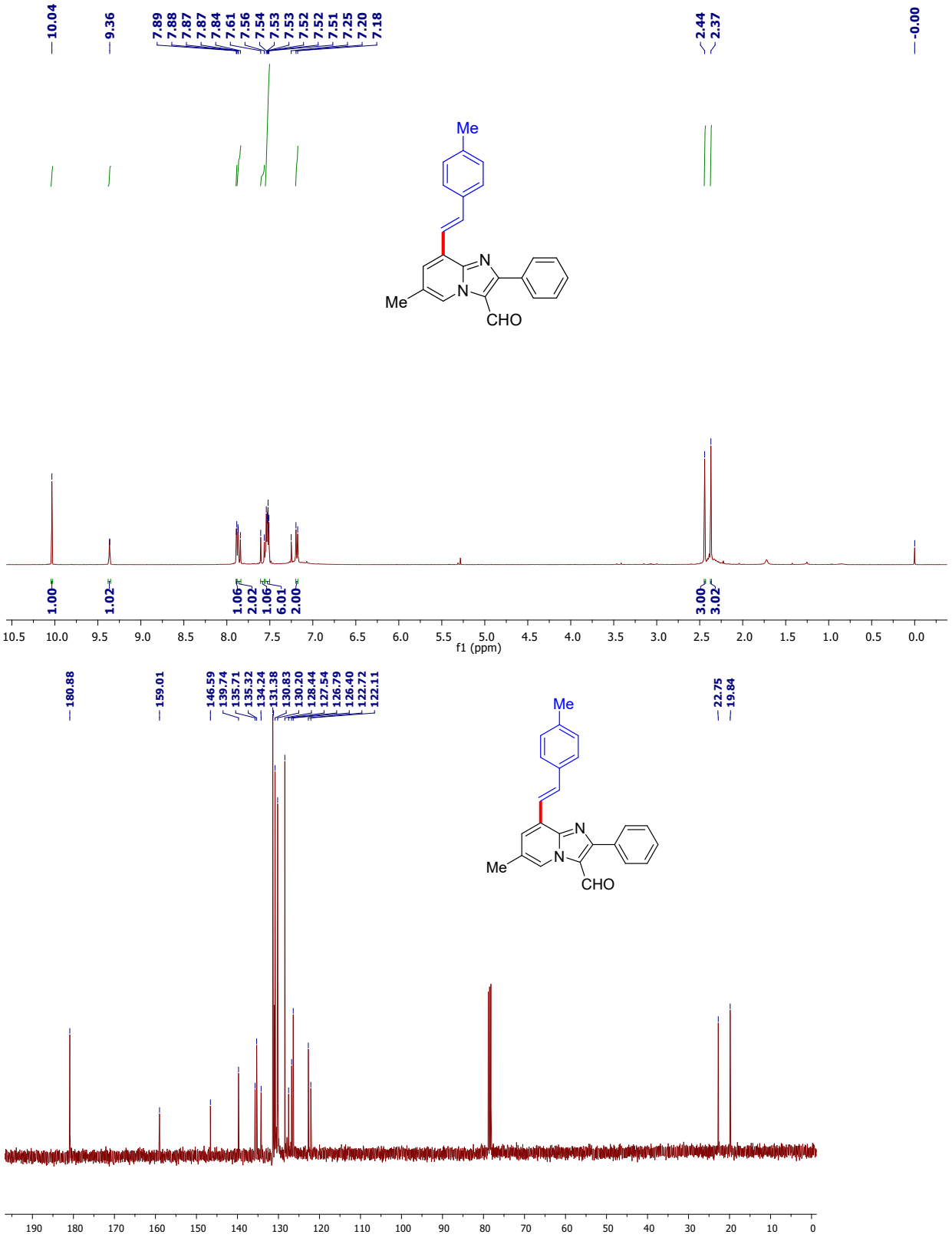
6-Methyl-2-phenyl-8-styrylimidazo[1,2-a]pyridine-3-carbaldehyde (3g);



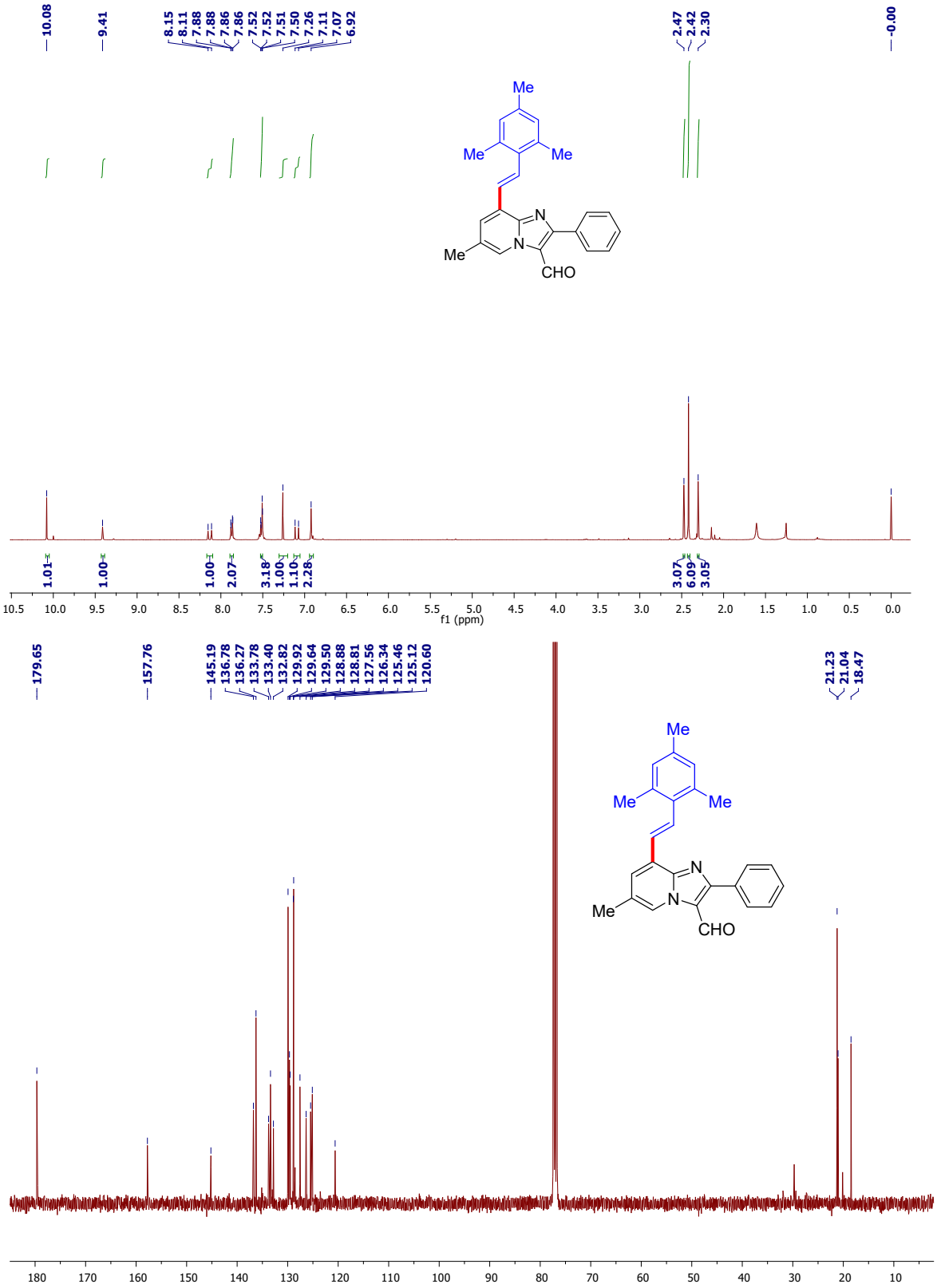
6-Methyl-8-(3-methylstyryl)-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3h);



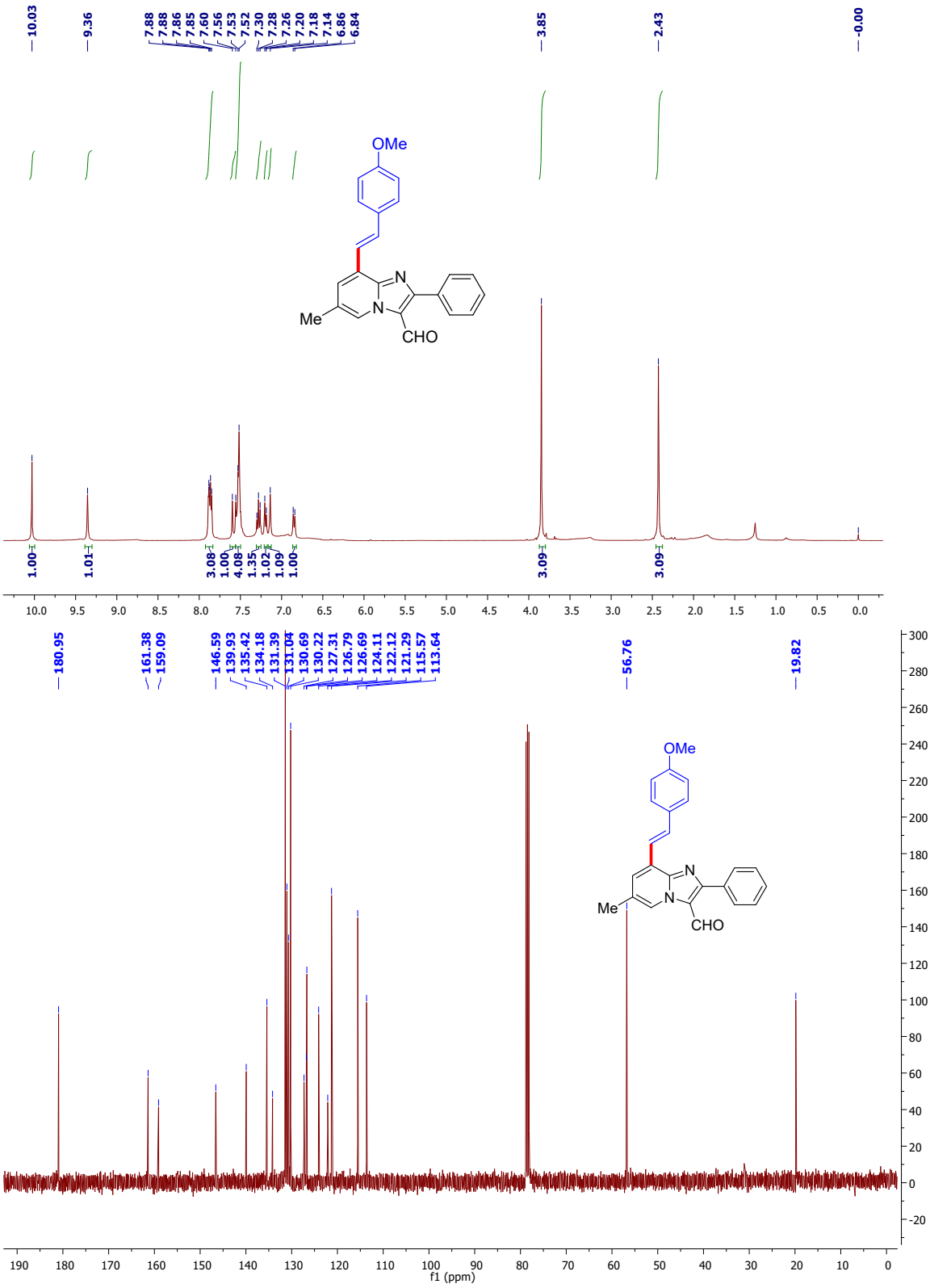
6-Methyl-8-(4-methylstyryl)-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3i);



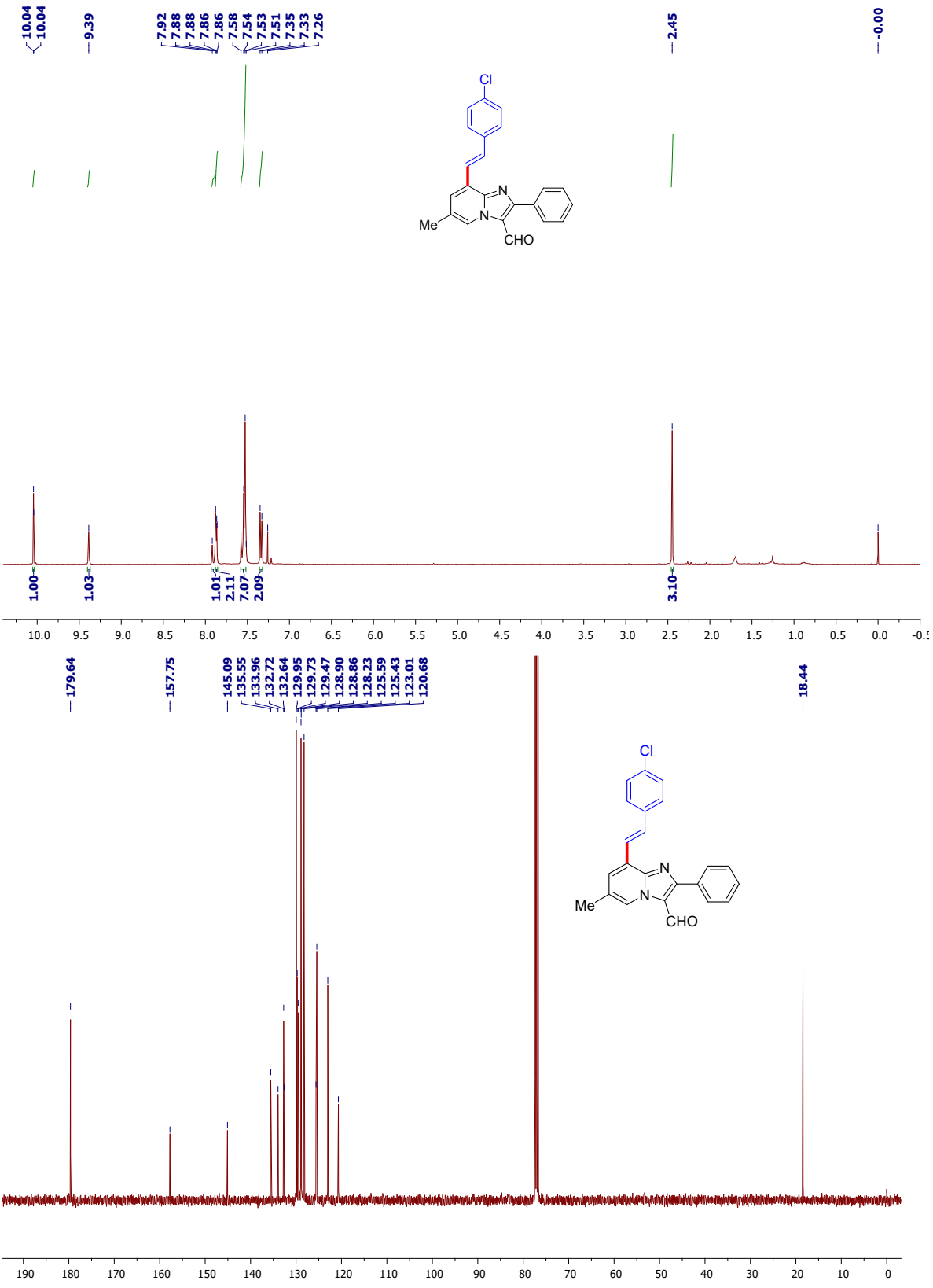
6-Methyl-2-phenyl-8-(2,4,6-trimethylstyryl)imidazo[1,2-a]pyridine-3-carbaldehyde (3j);



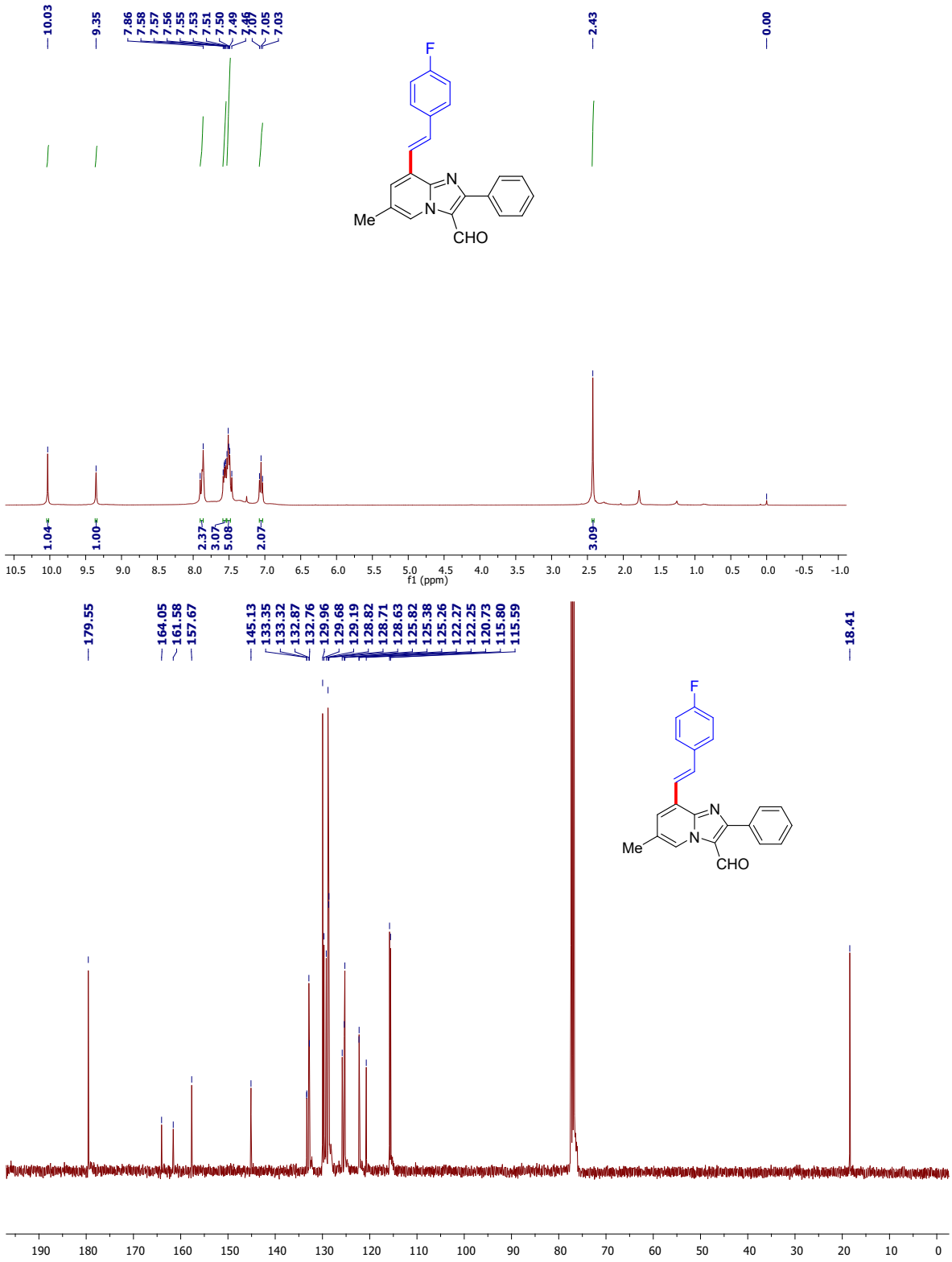
8-(4-Methoxystyryl)-6-methyl-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3k);

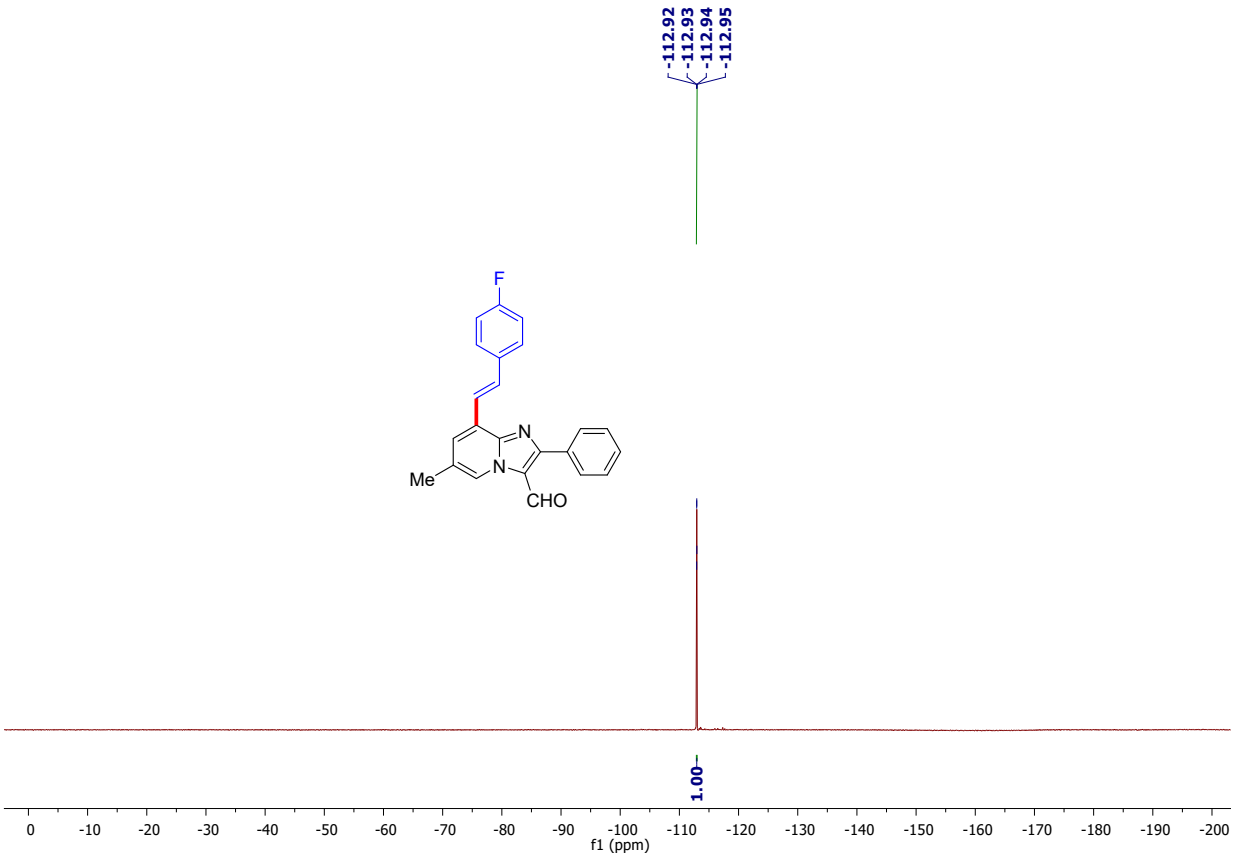


8-(4-Chlorostyryl)-6-methyl-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3l);

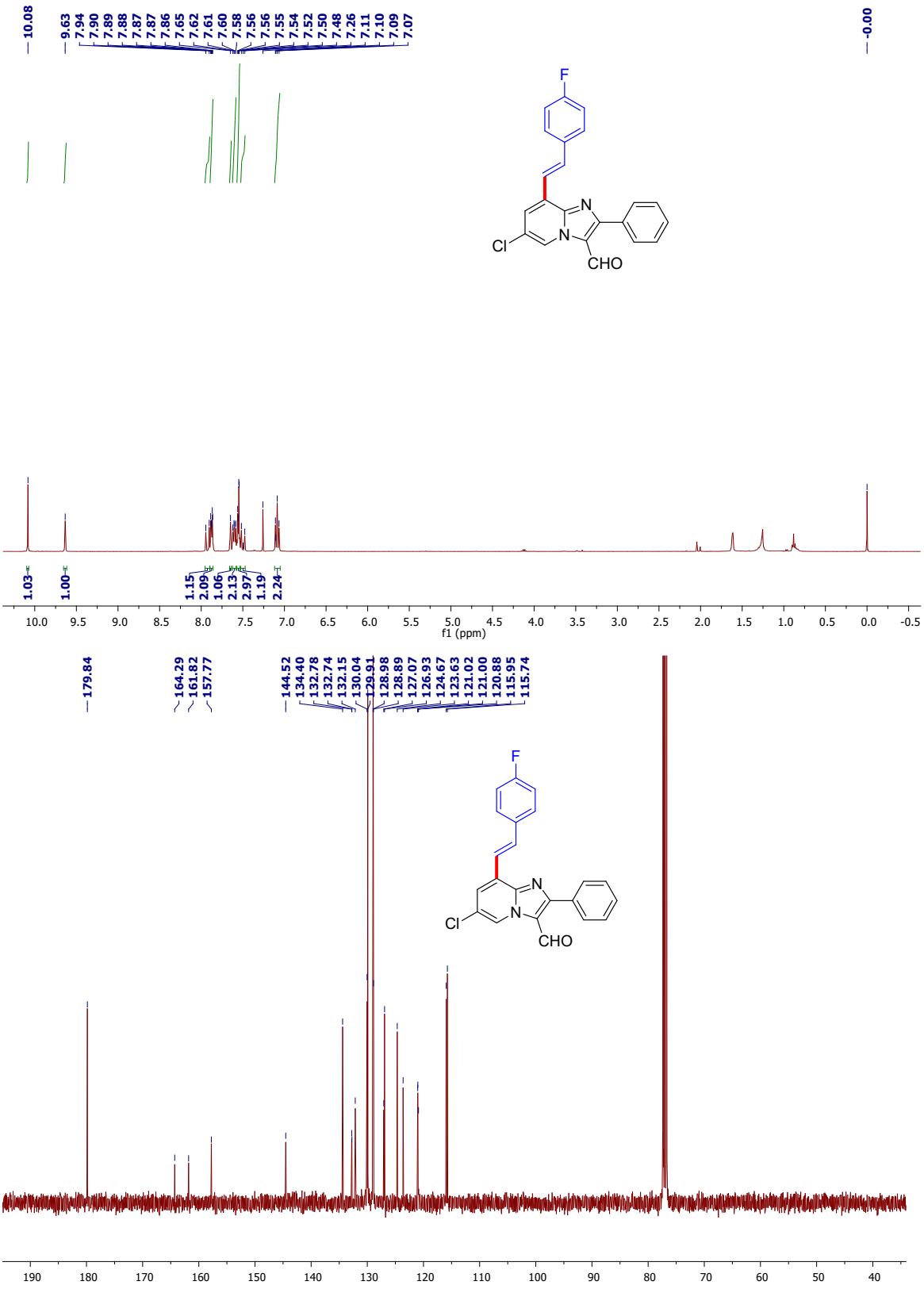


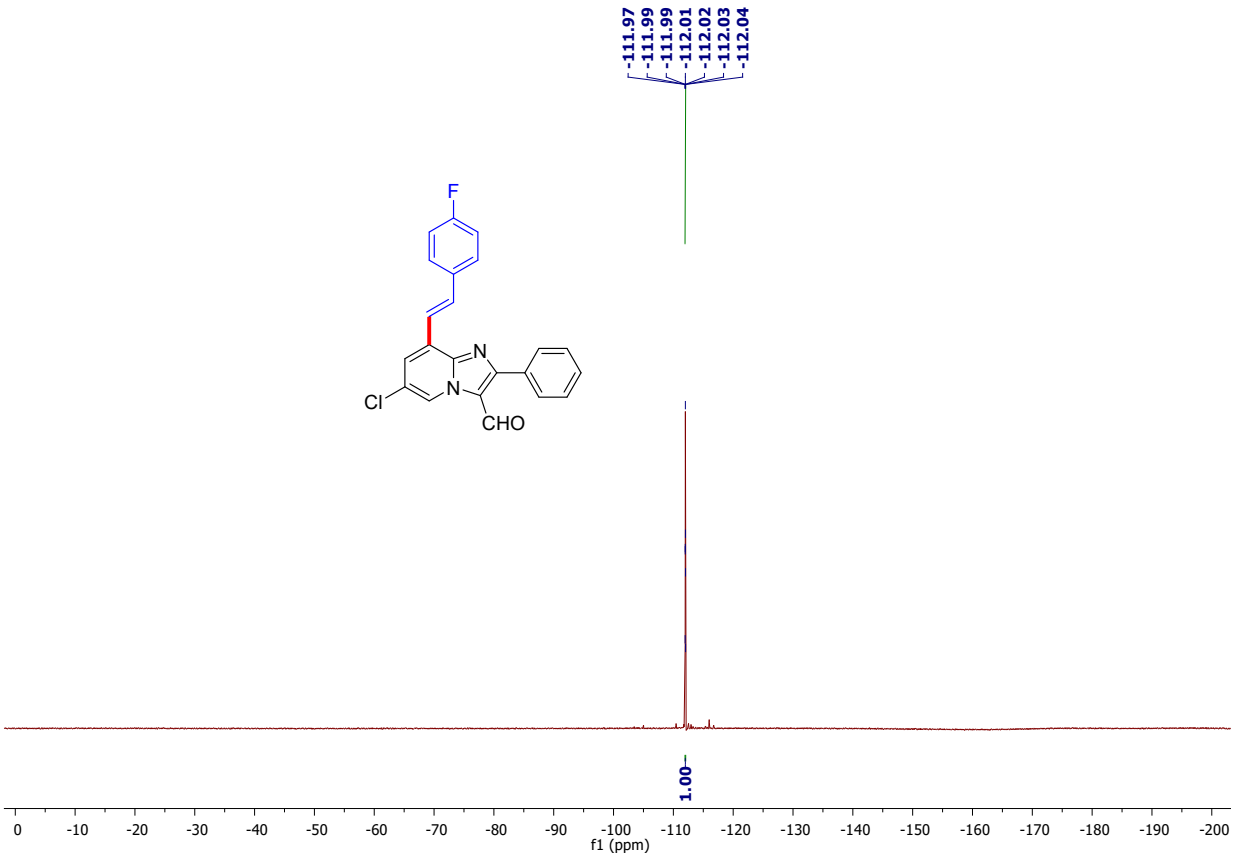
6-Chloro-8-(4-fluorostyryl)-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3m);




-112.92
-112.93
-112.94
-112.95
F
N
N
Me
CHO
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

6-Chloro-8-(4-fluorostyryl)-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3n);

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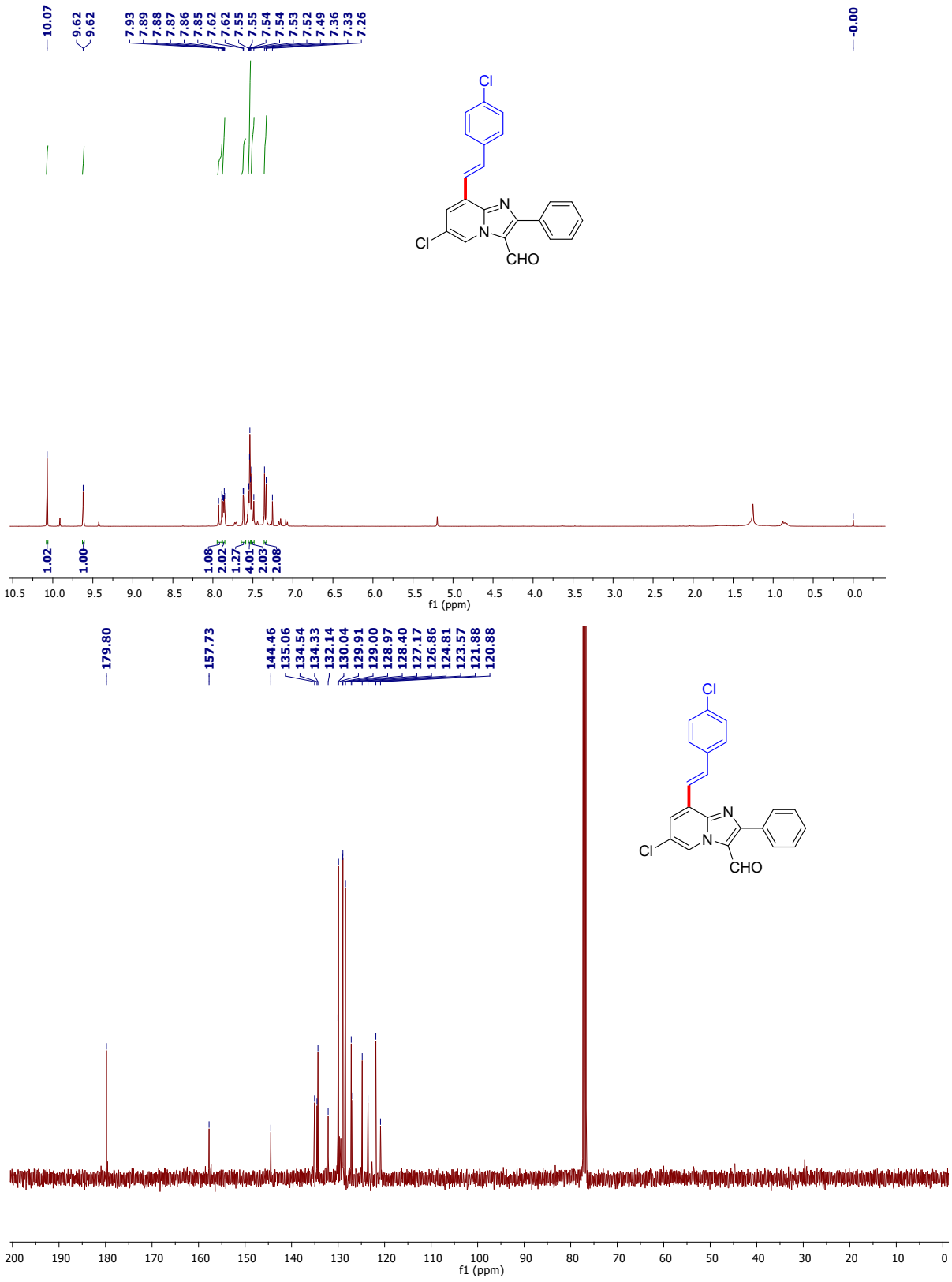
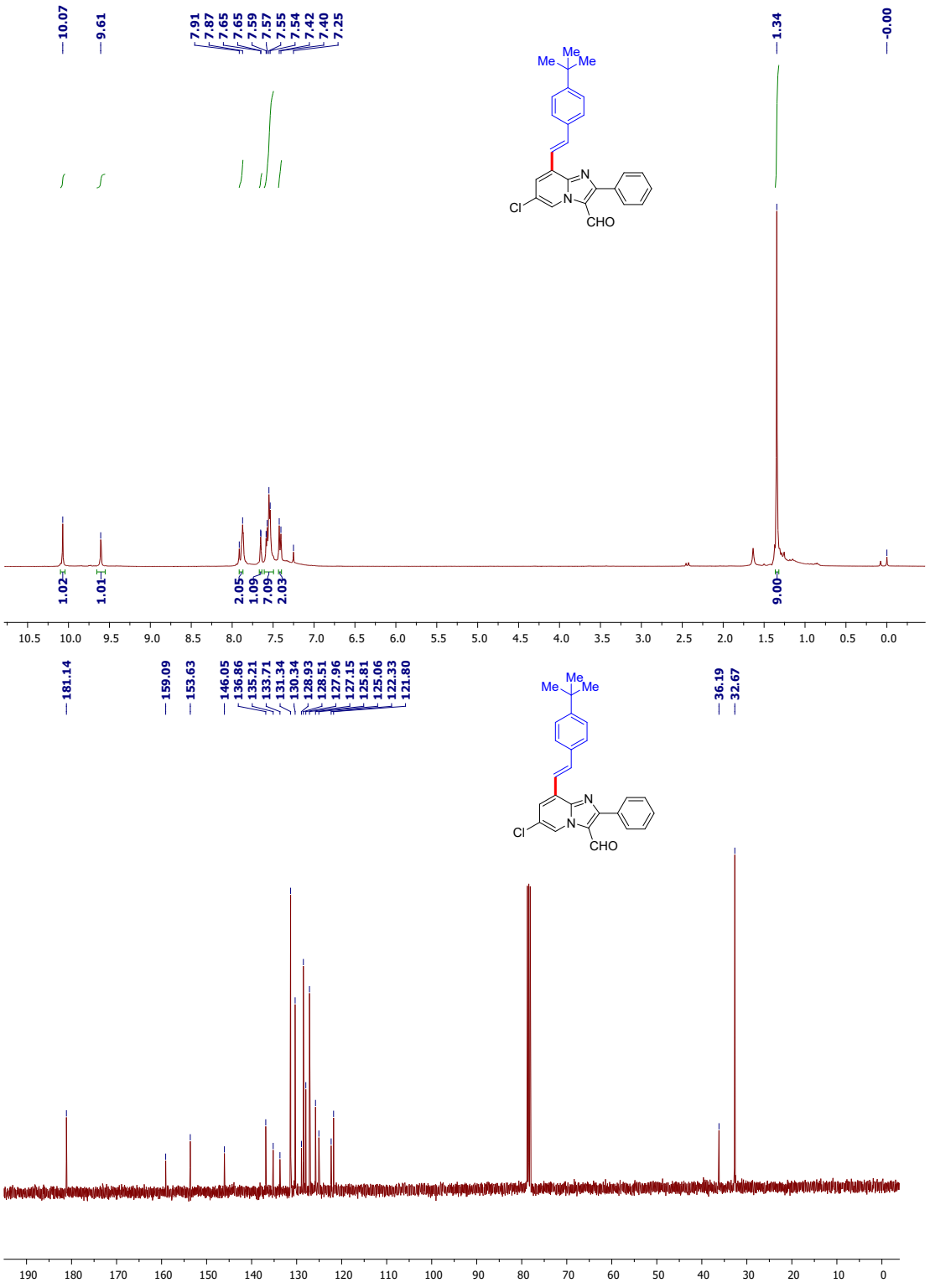
-111.99
-111.99
-112.01
-112.02
-112.03
-112.04
F
N
N
Cl
CHO
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

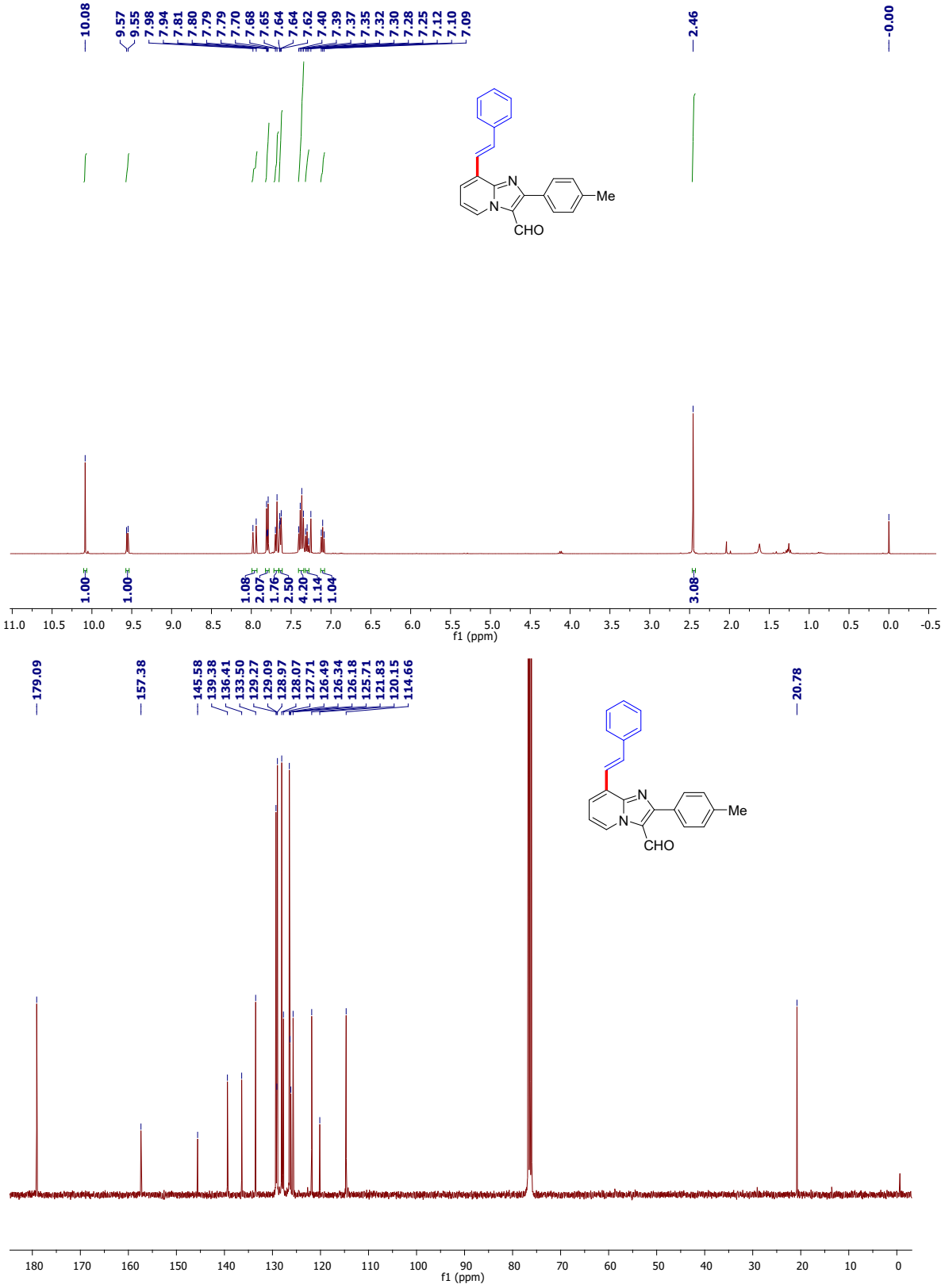
6-Chloro-8-(4-chlorostyryl)-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3o);



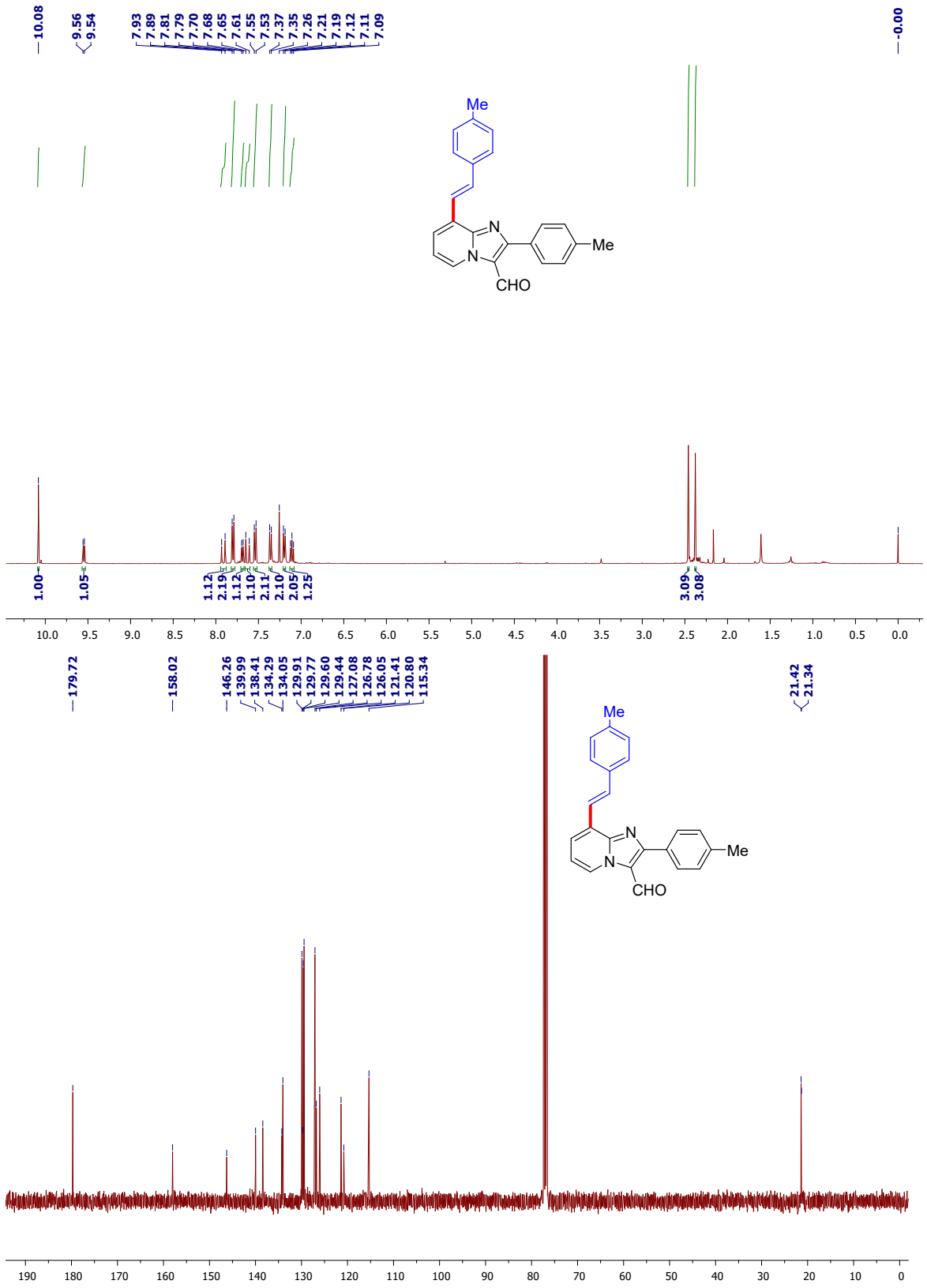
8-(4-(Tert-butyl)styryl)-6-chloro-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3p);



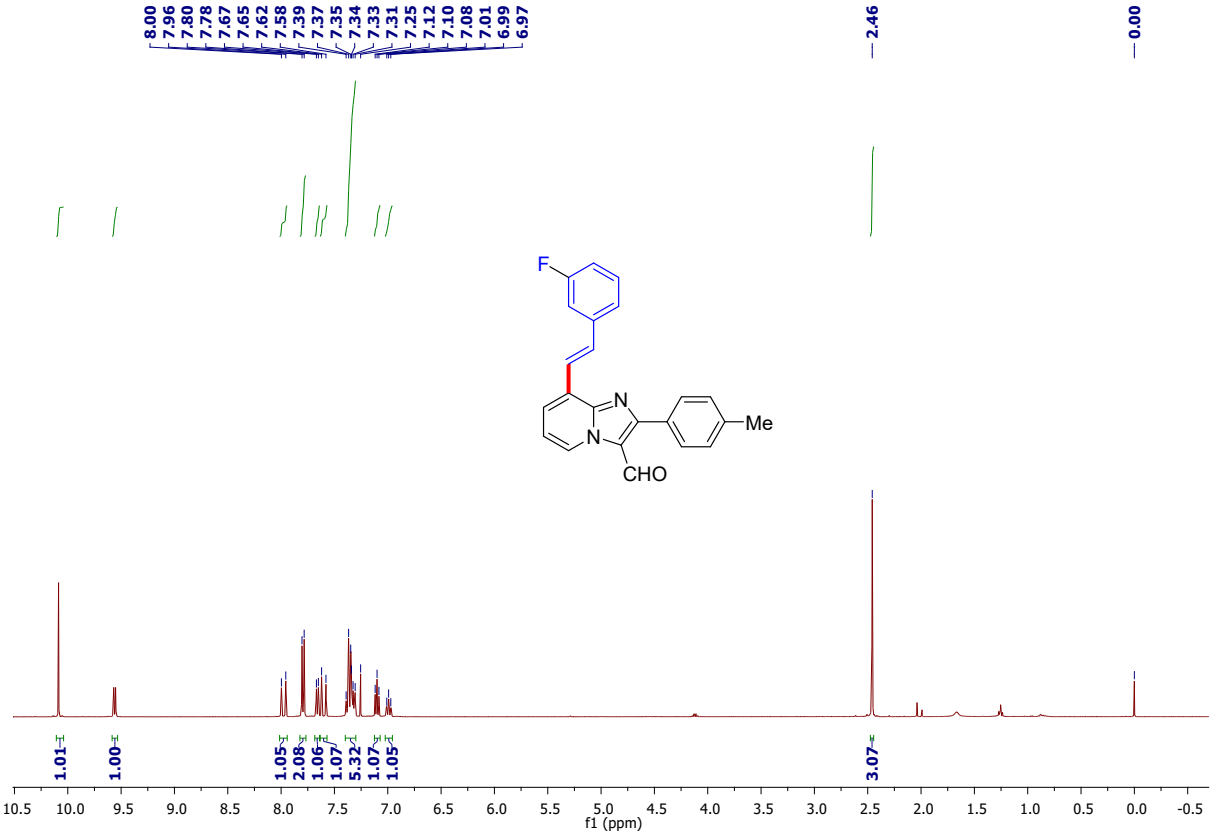
8-Styryl-2-(p-tolyl)imidazo[1,2-a]pyridine-3-carbaldehyde (3q);

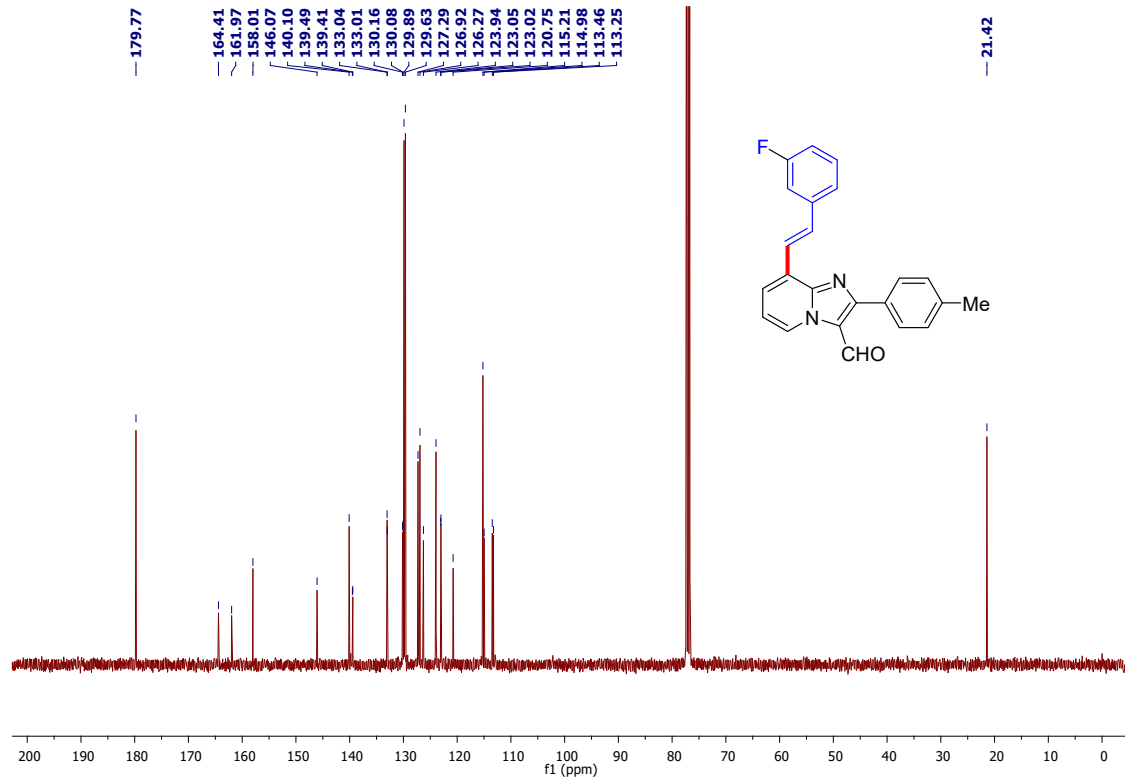


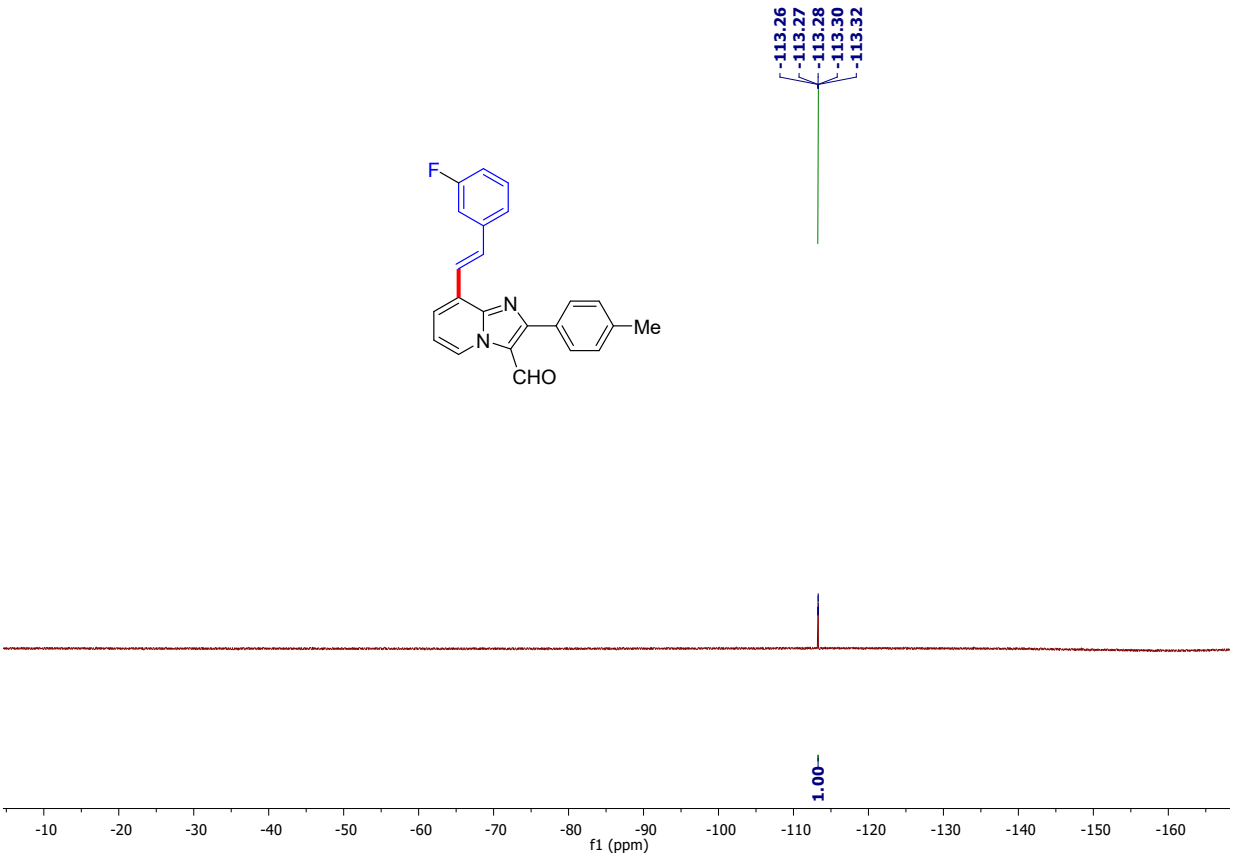
8-(4-Methylstyryl)-2-(p-tolyl)imidazo[1,2-a]pyridine-3-carbaldehyde (3r);



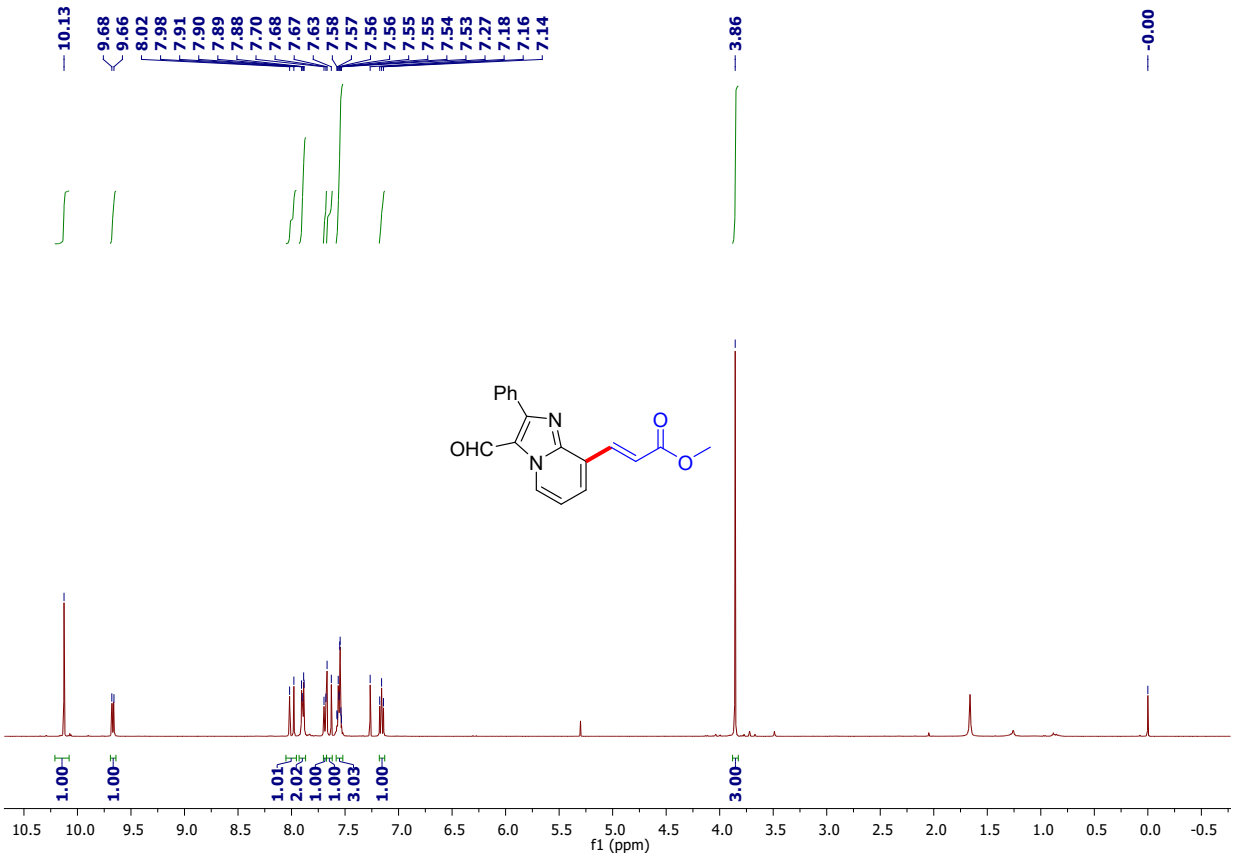
8-(3-Fluorostyryl)-2-(p-tolyl)imidazo[1,2-a]pyridine-3-carbaldehyde (3s);

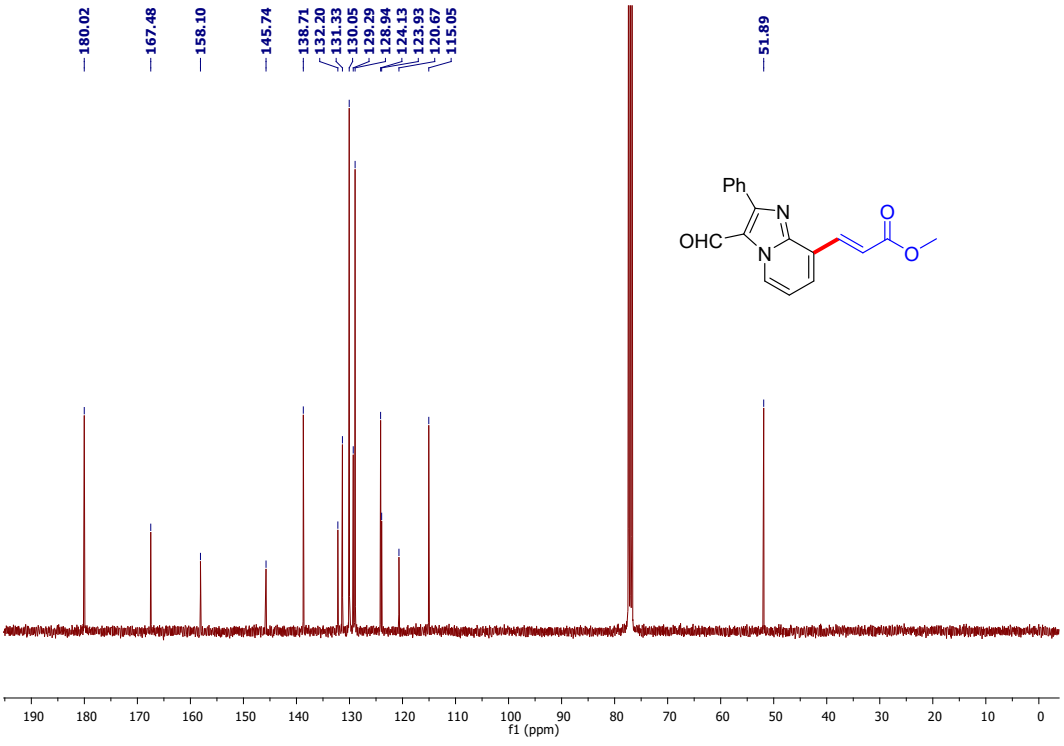




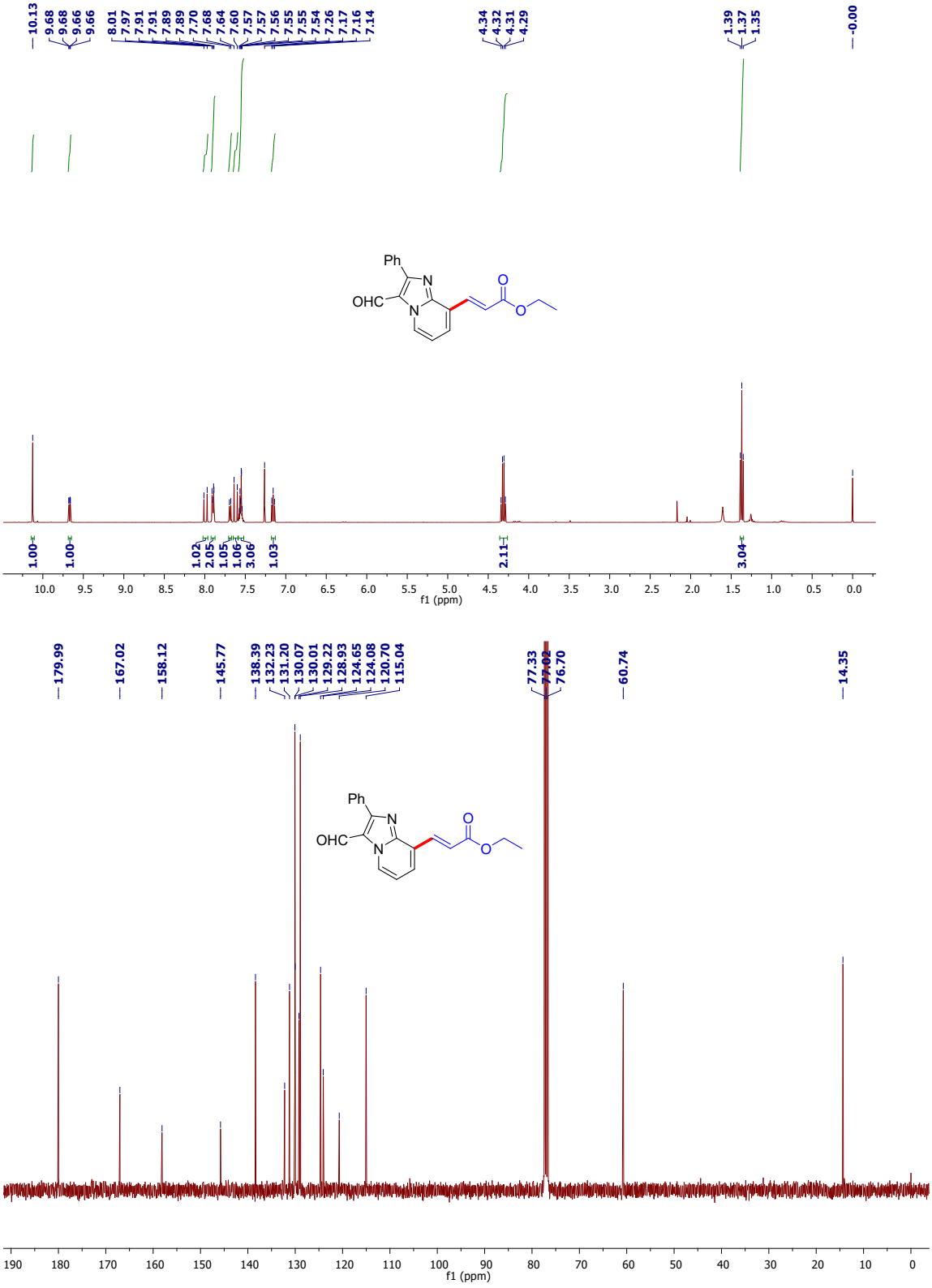

-113.26
-113.27
-113.28
-113.30
-113.32
F
N
N
Me
CHO
1.00
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

Methyl-3-(3-formyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5a);

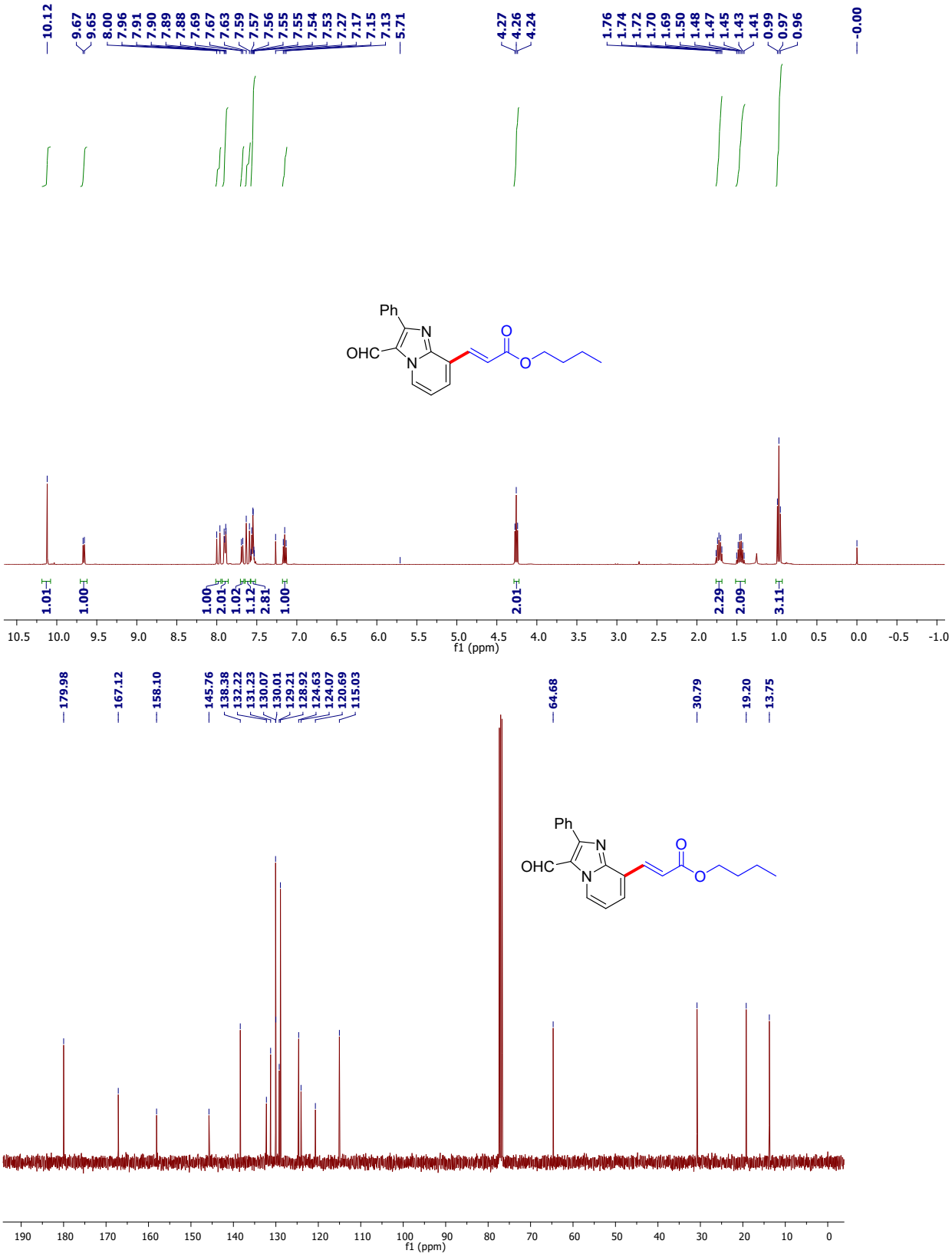




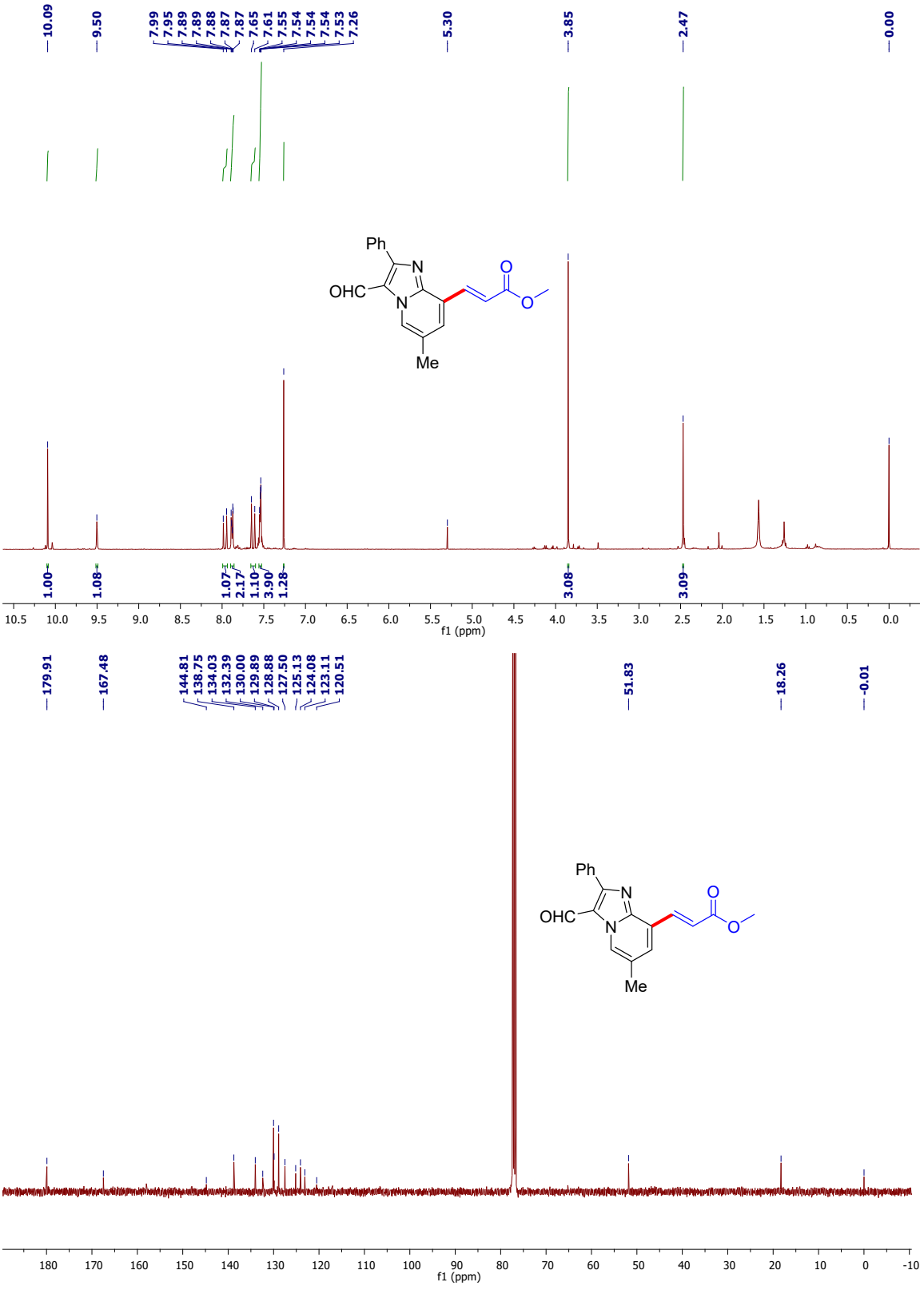
Ethyl-3-(3-formyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5b);



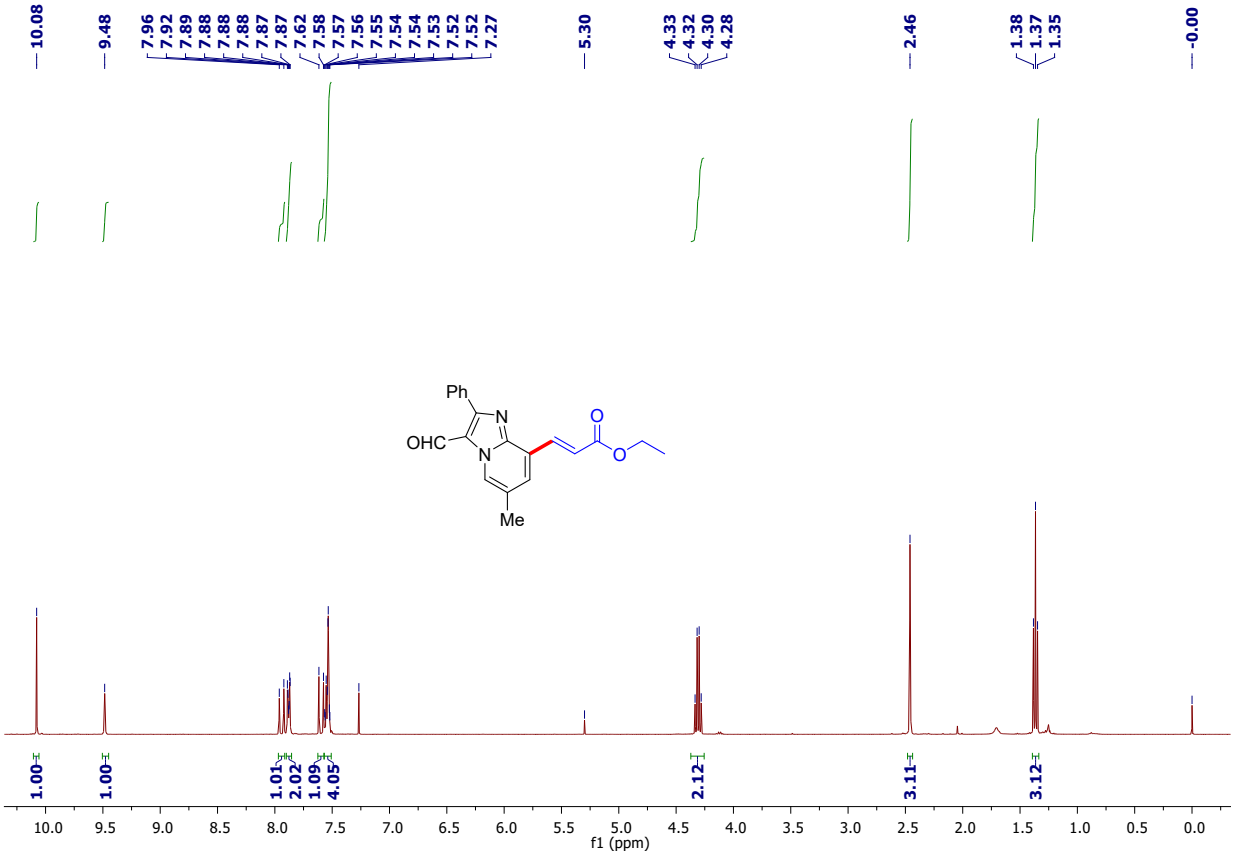
Butyl -3-(3-formyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5c);

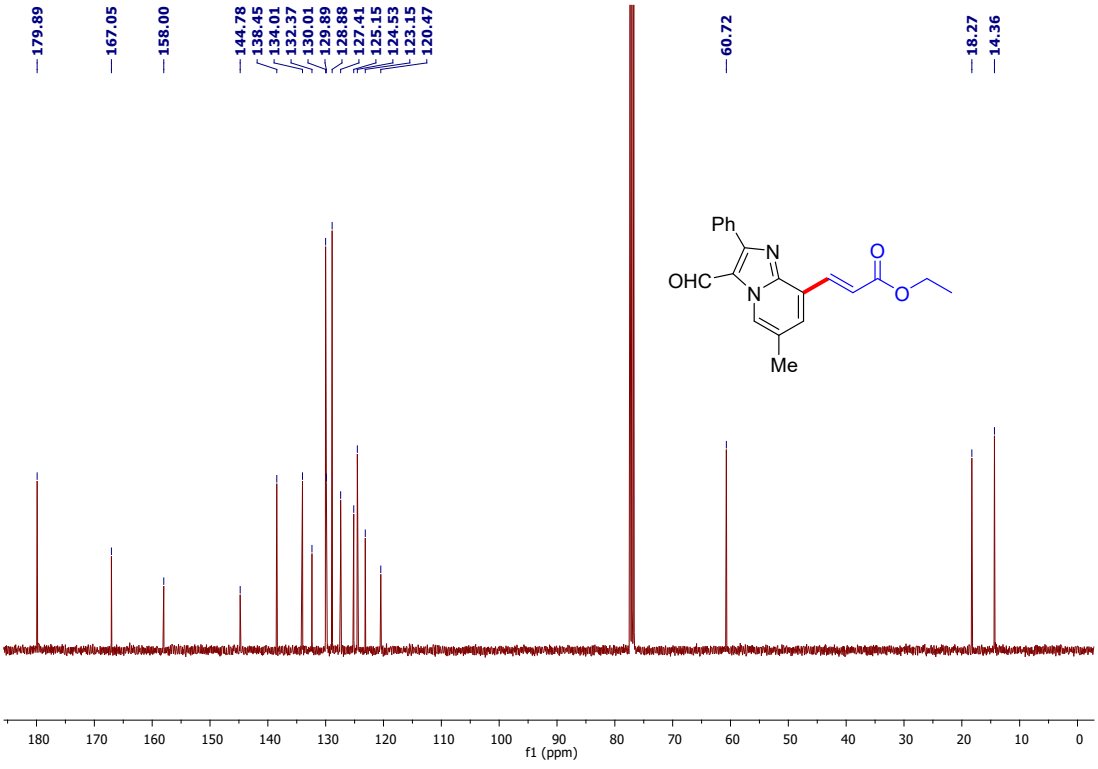


Methyl-3-(3-formyl-6-methyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5d);

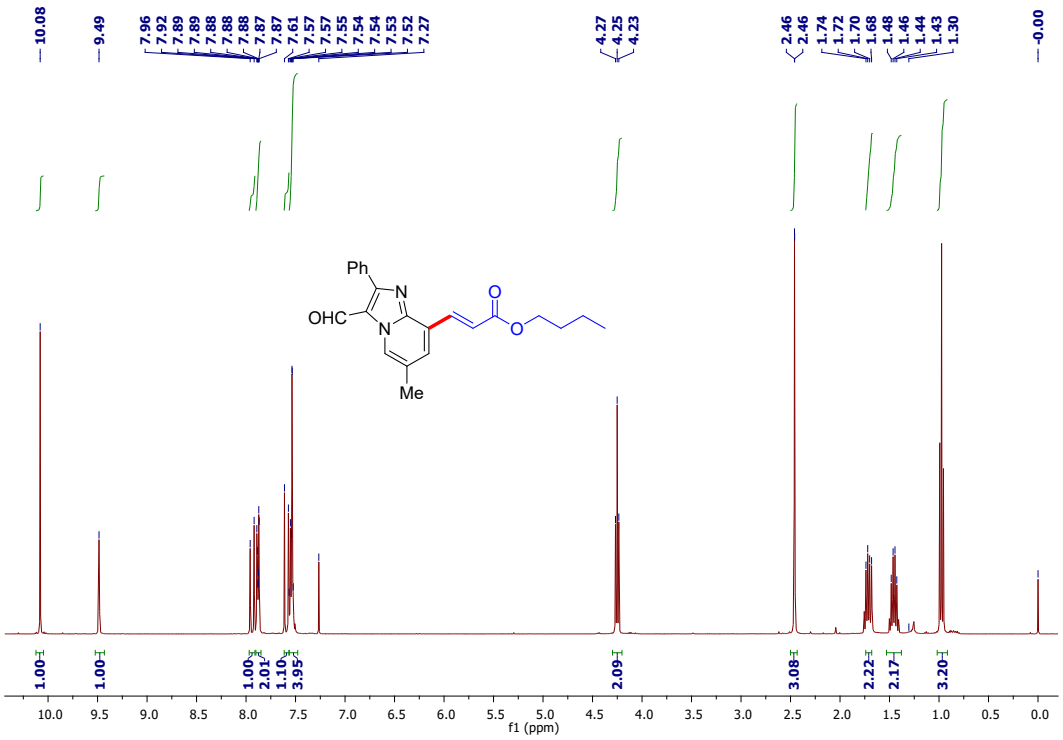


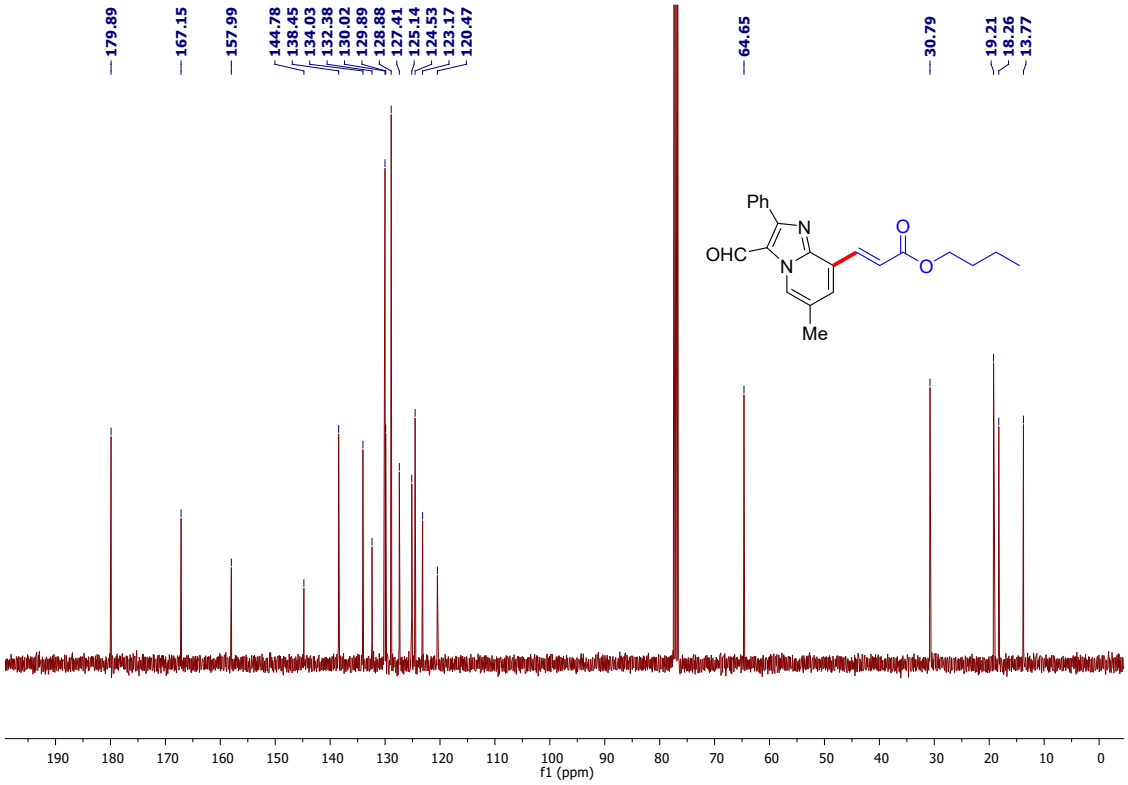
Ethyl -3-(3-formyl-6-methyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5e);



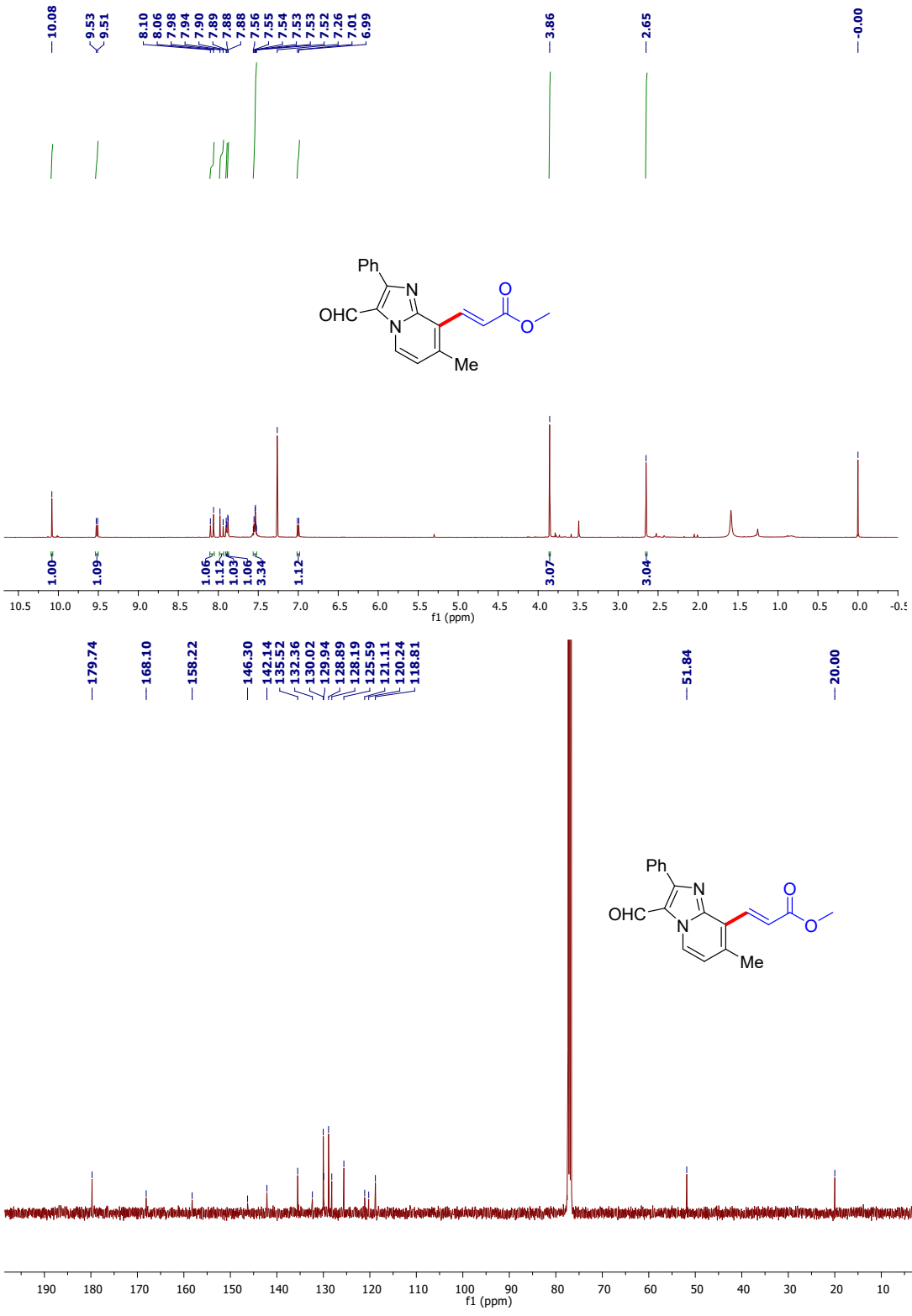


Butyl -3-(3-formyl-6-methyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5f);

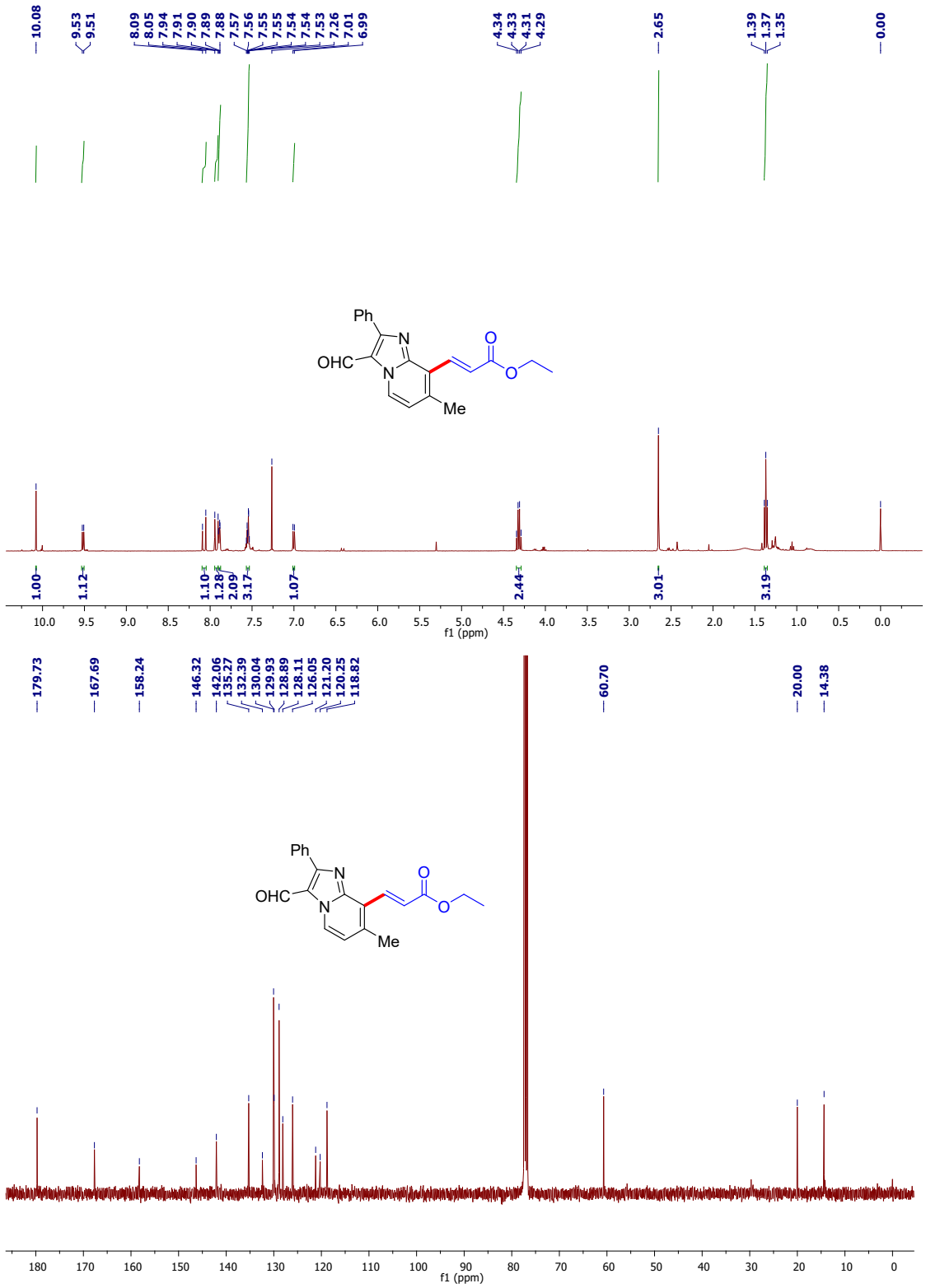




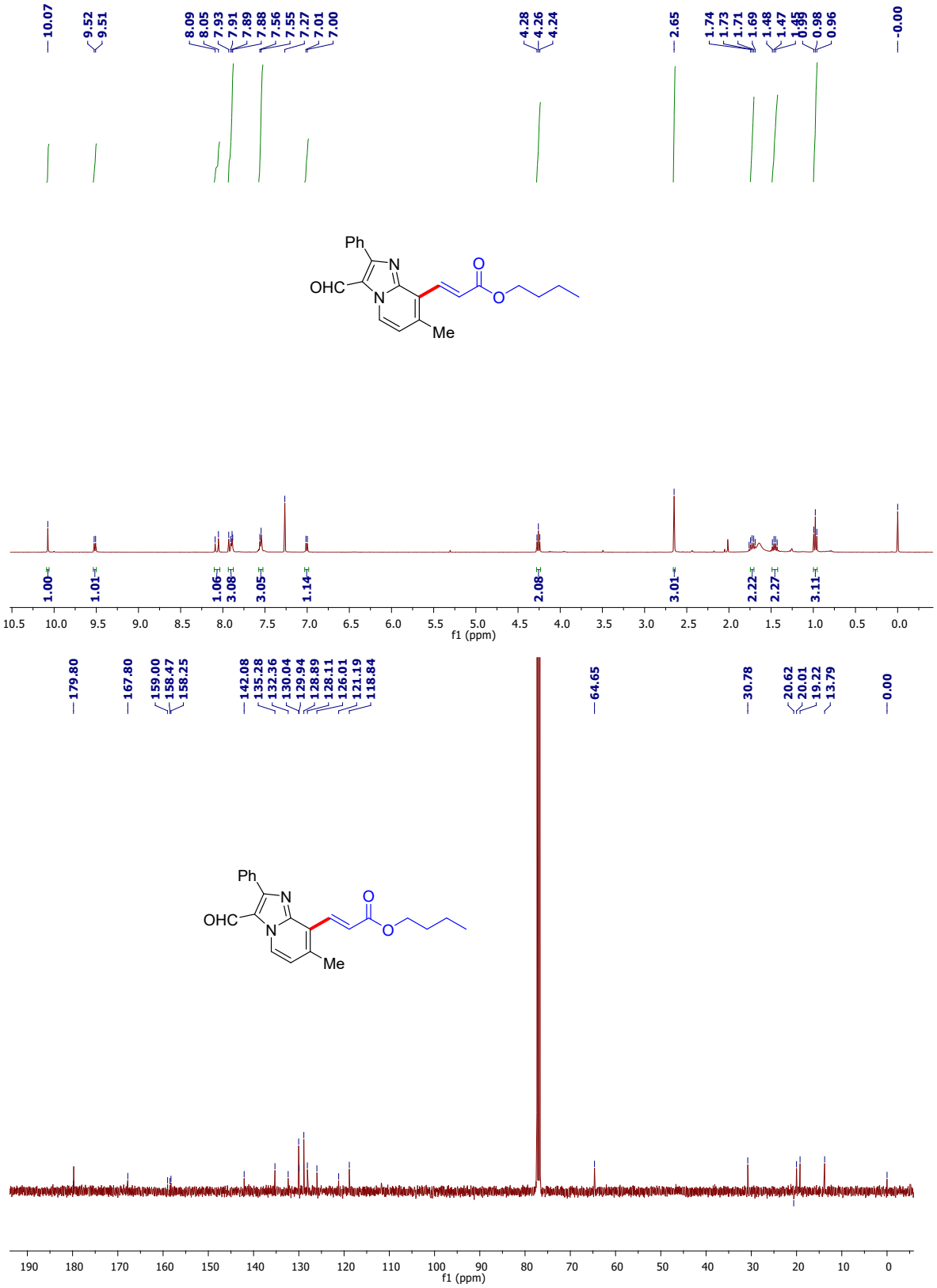
Methyl-3-(3-formyl-7-methyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5g);



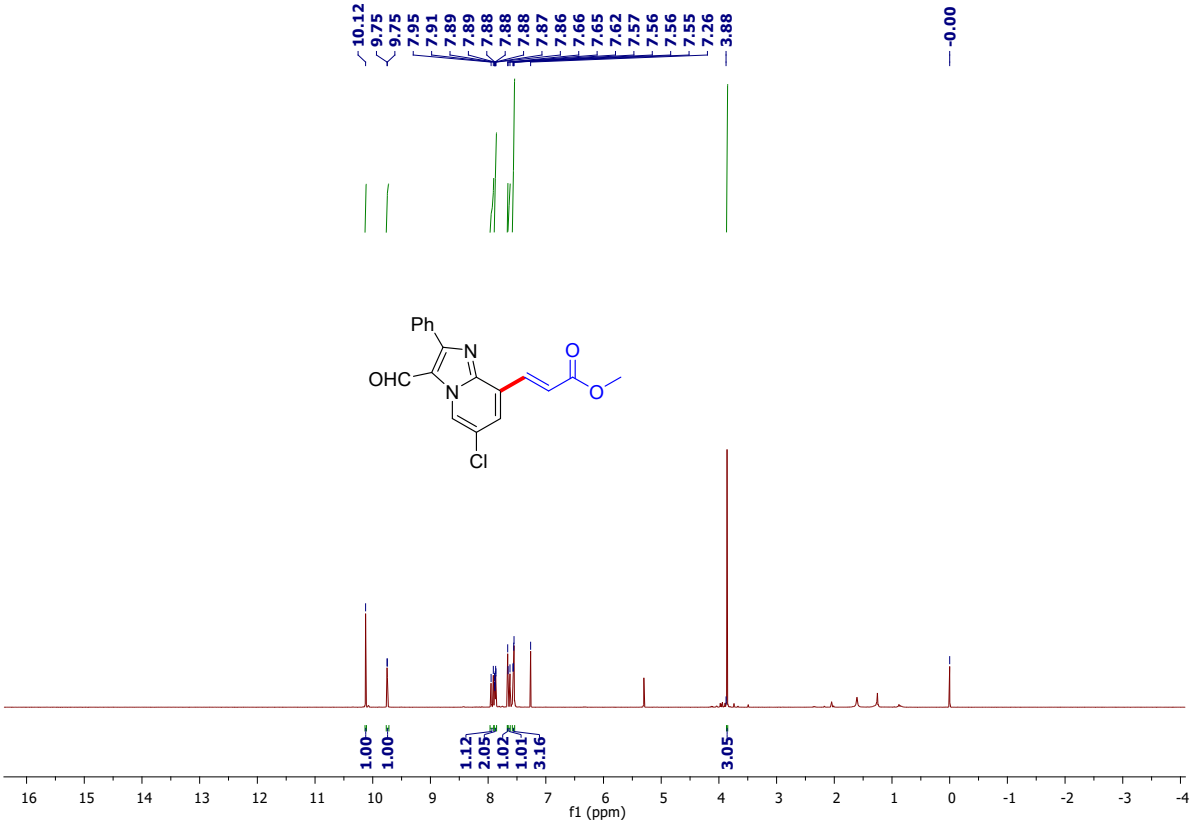
Ethyl -3-(3-formyl-7-methyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5h);

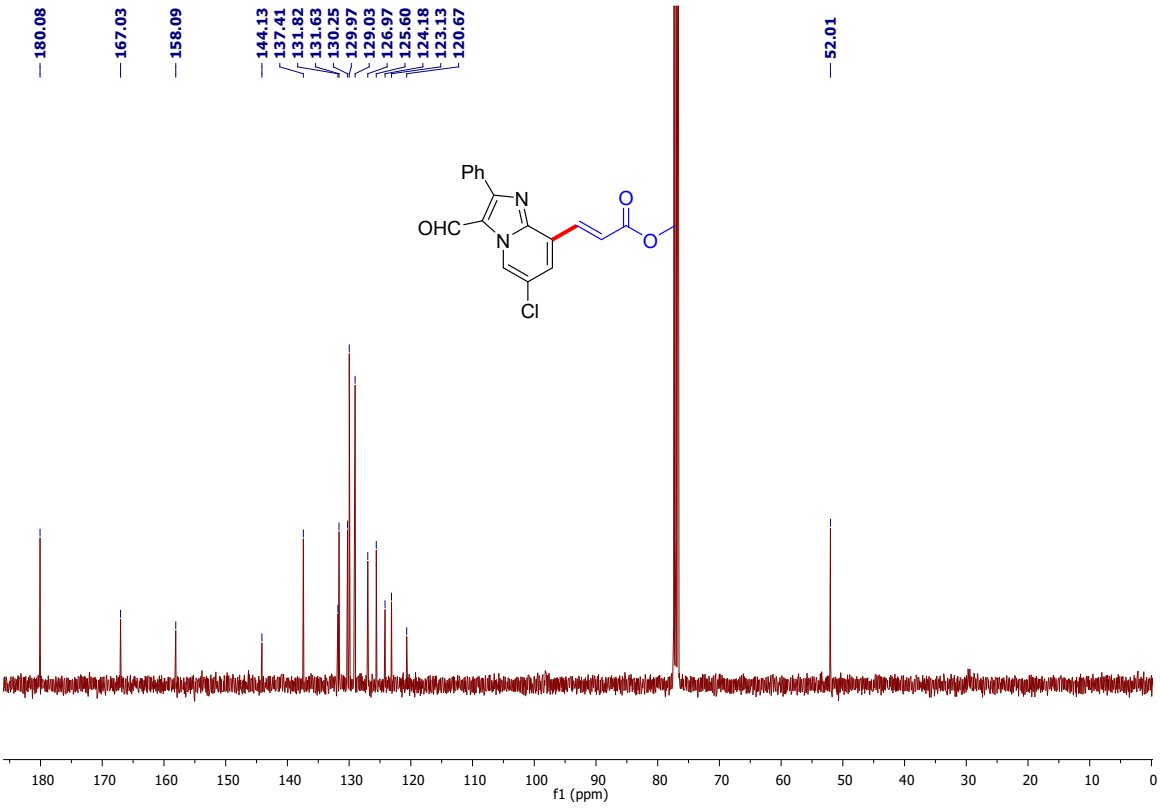


Butyl -3-(3-formyl-7-methyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5i);

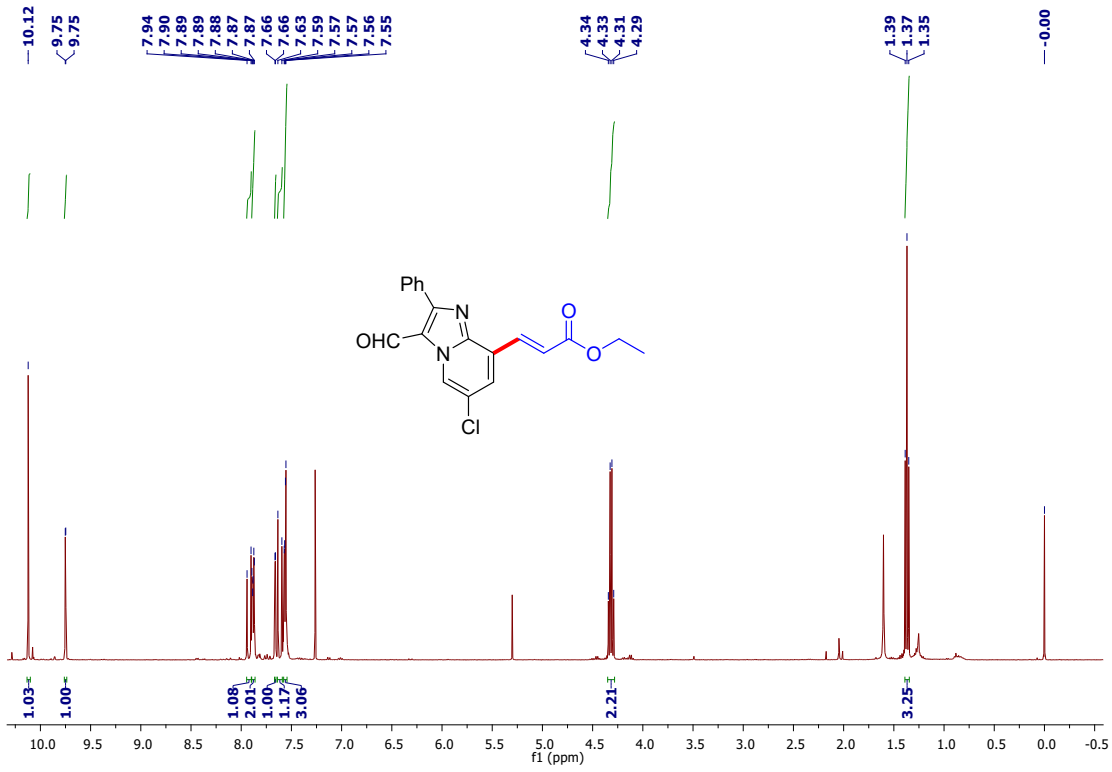


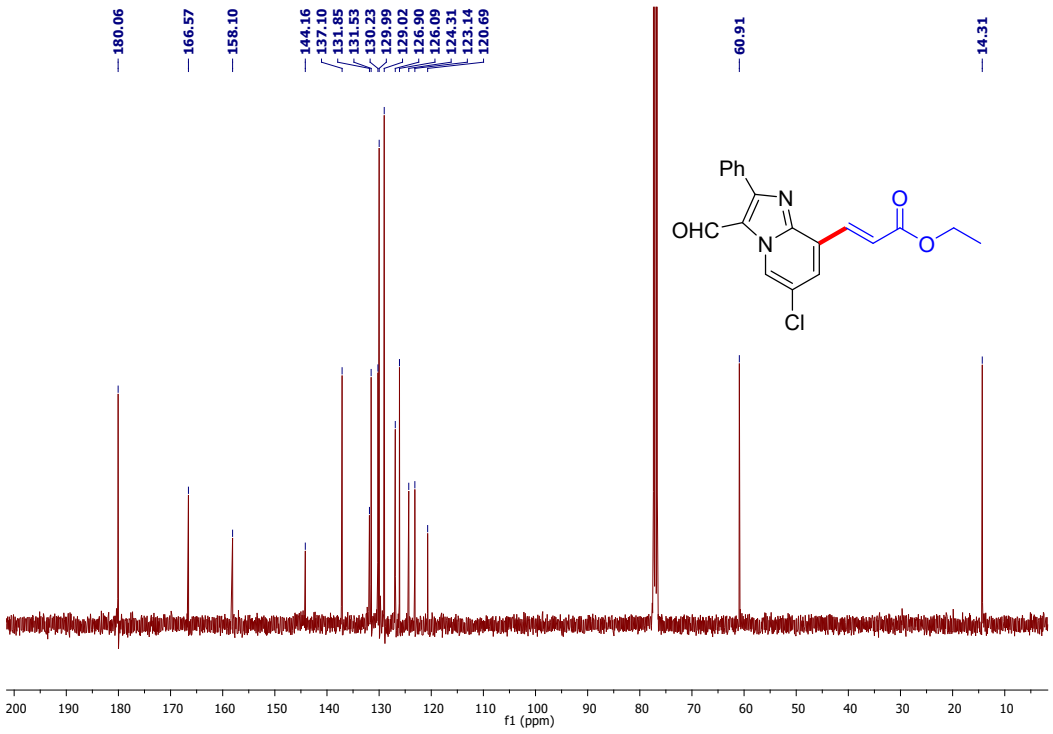
Methyl -3-(6-chloro-3-formyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5j);



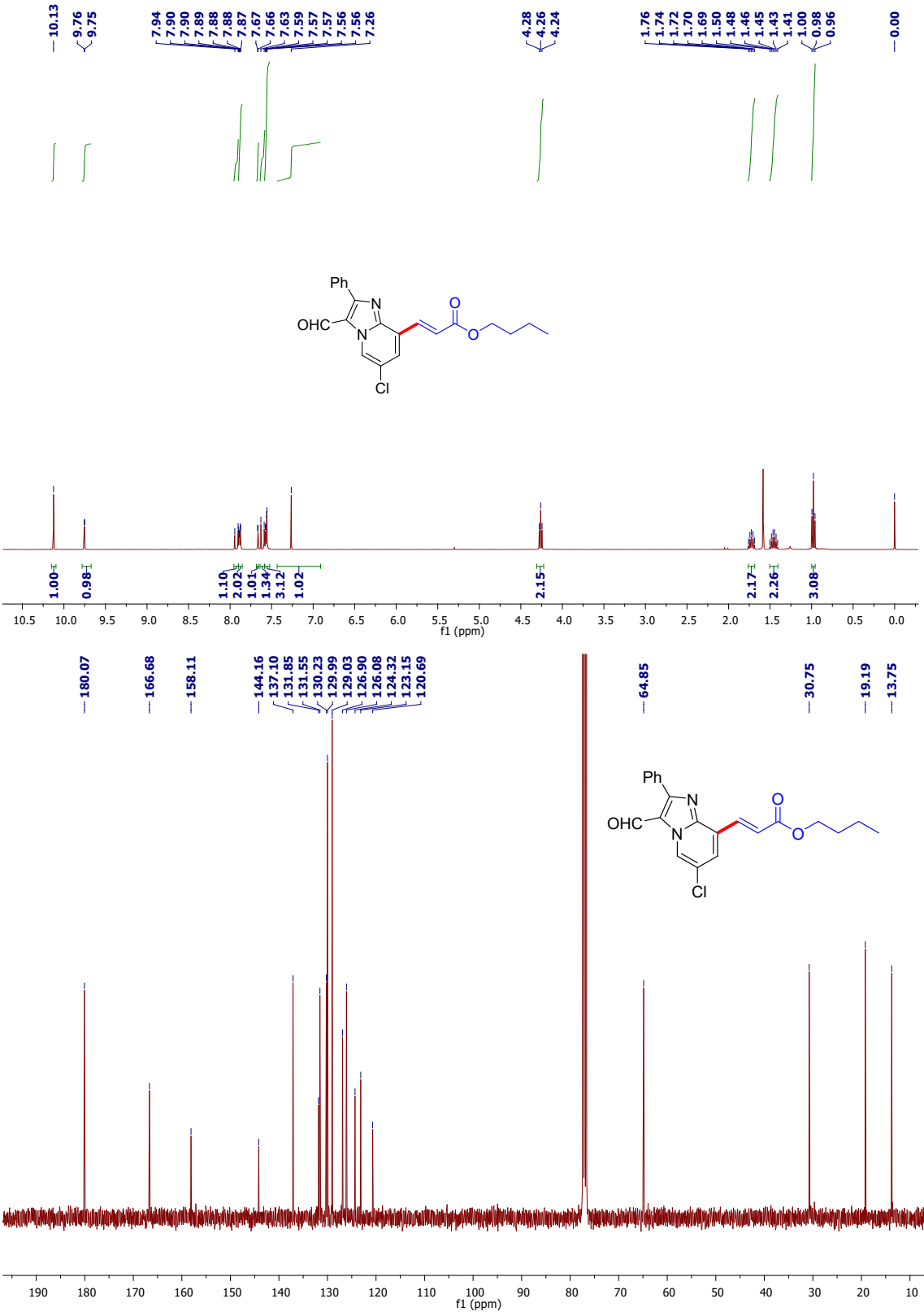


Ethyl -3-(6-chloro-3-formyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5k);

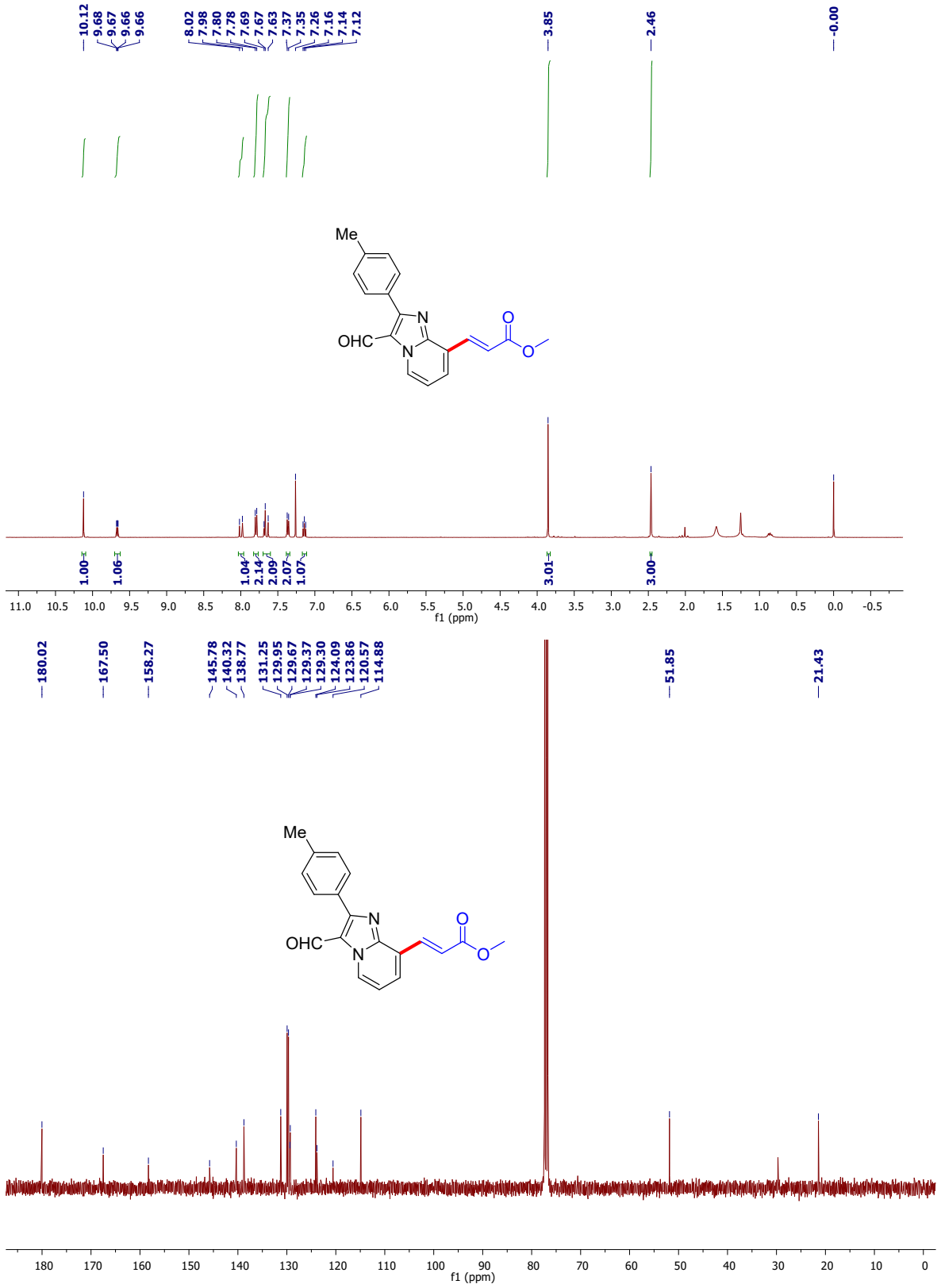




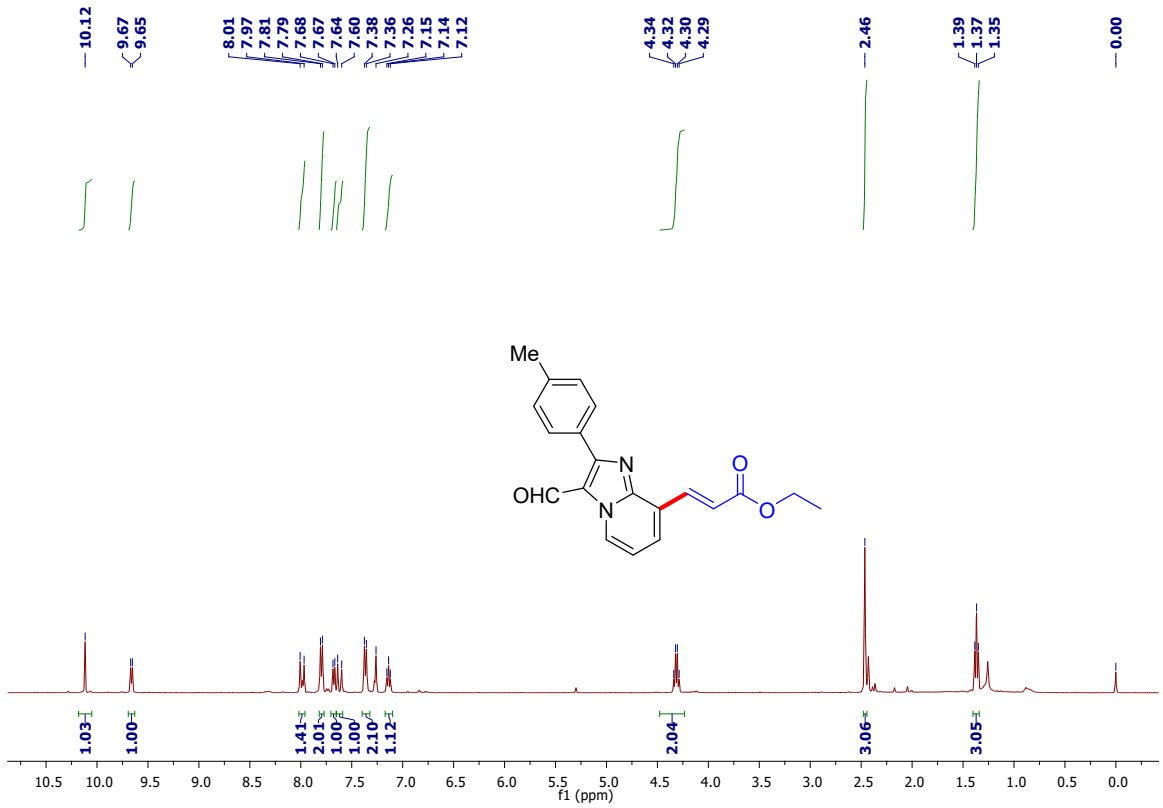
Butyl -3-(6-chloro-3-formyl-2-phenylimidazo[1,2-a]pyridin-8-yl)acrylate (5l);

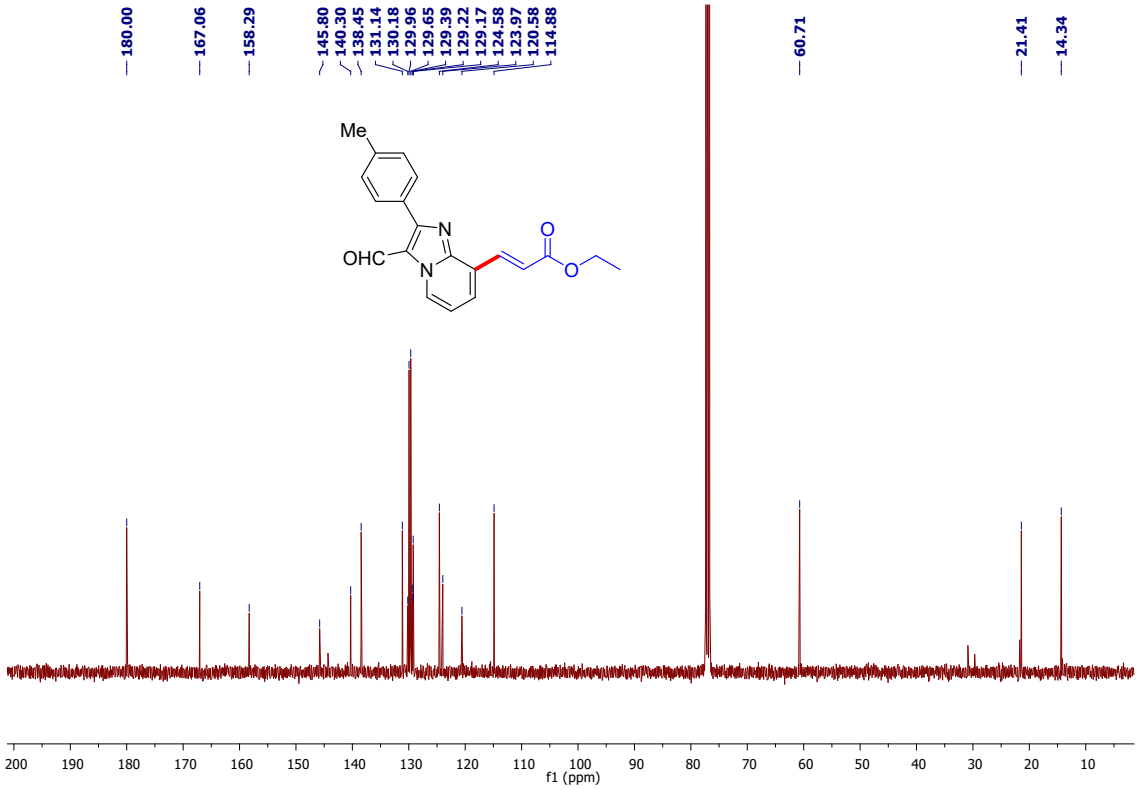


Methyl-3-(3-formyl-2-(p-tolyl)imidazo[1,2-a]pyridin-8-yl)acrylate (5m);

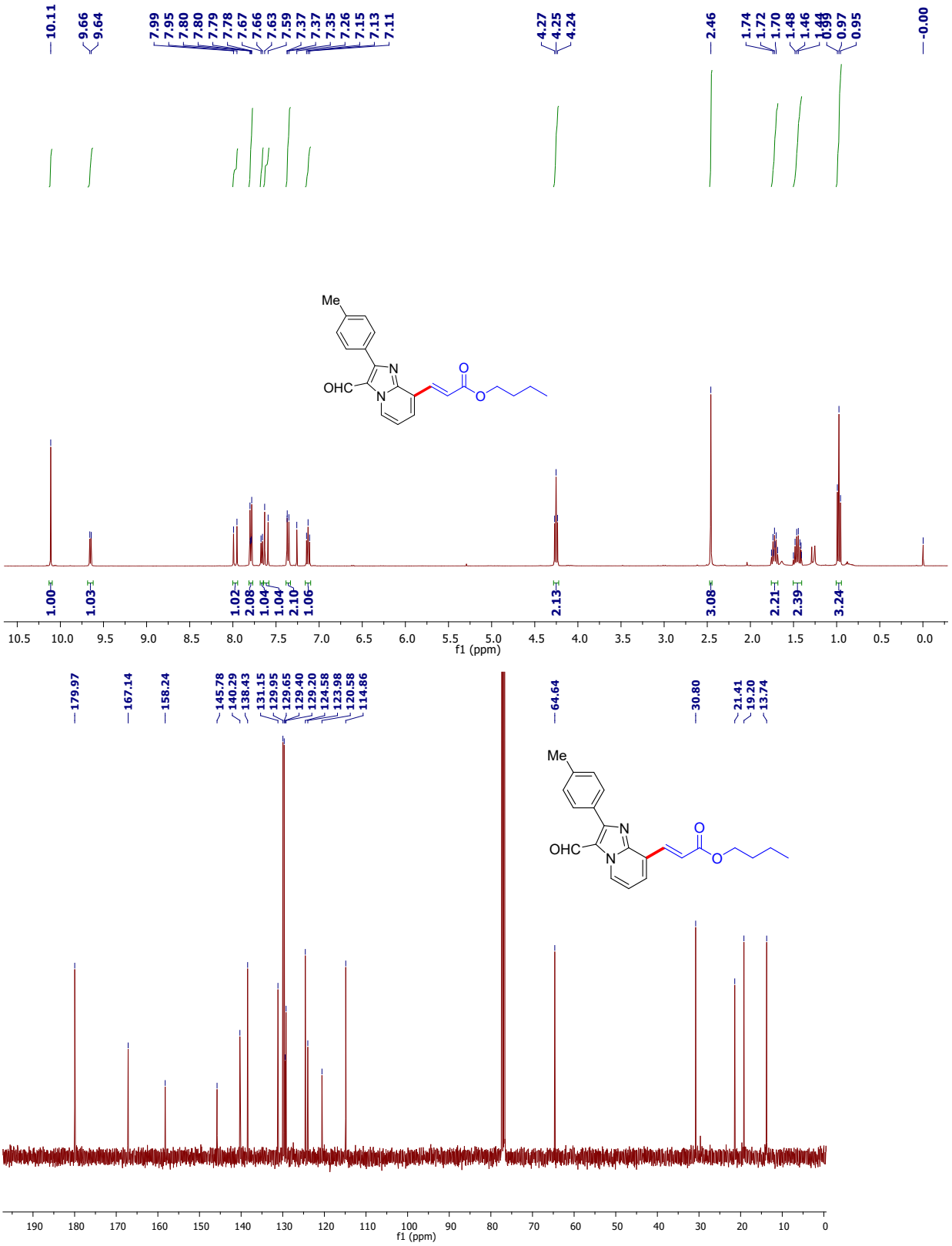


Ethyl-3-(3-formyl-2-(p-tolyl)imidazo[1,2-a]pyridin-8-yl)acrylate (5n);

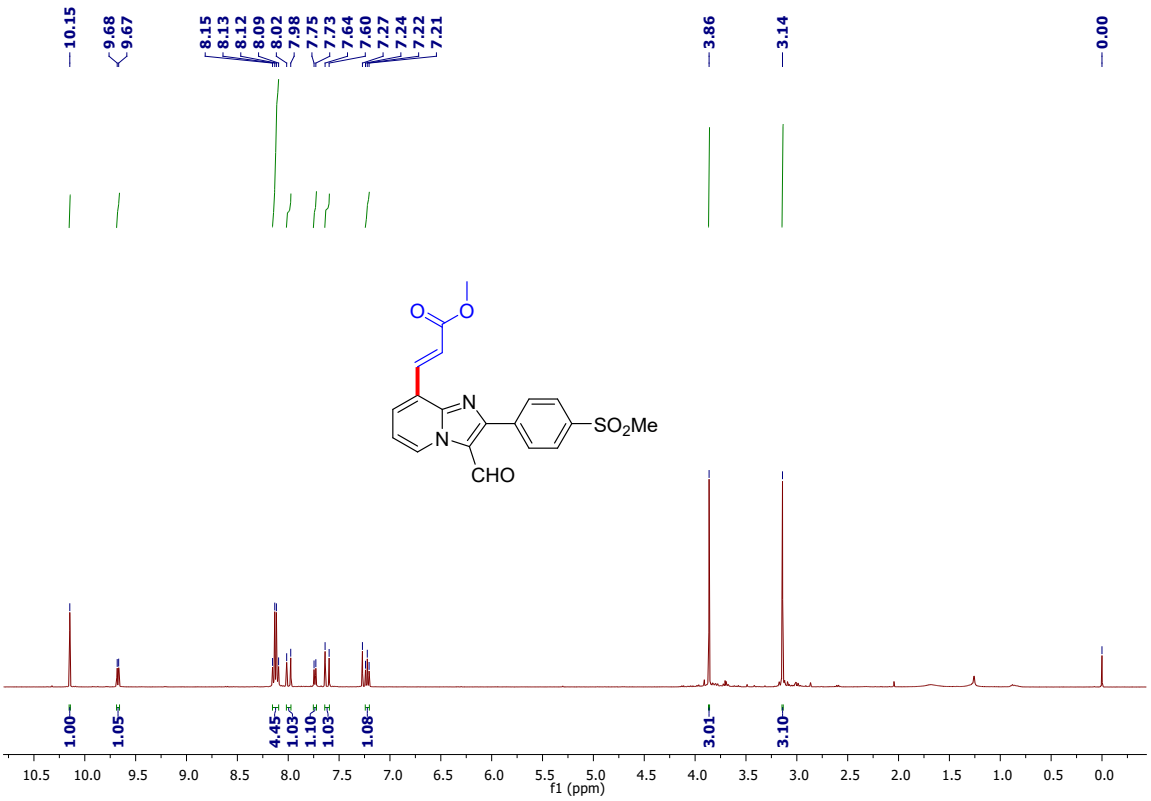


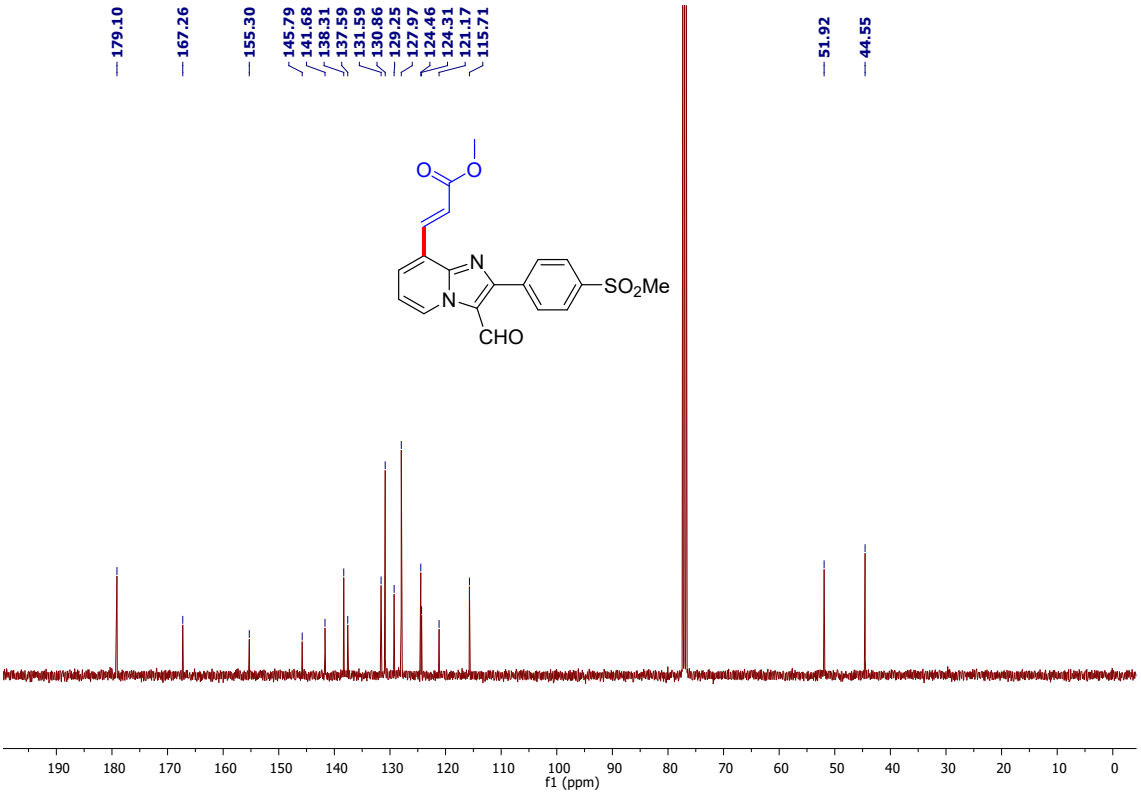


Butyl -3-(3-formyl-2-(p-tolyl)imidazo[1,2-a]pyridin-8-yl)acrylate (5o);

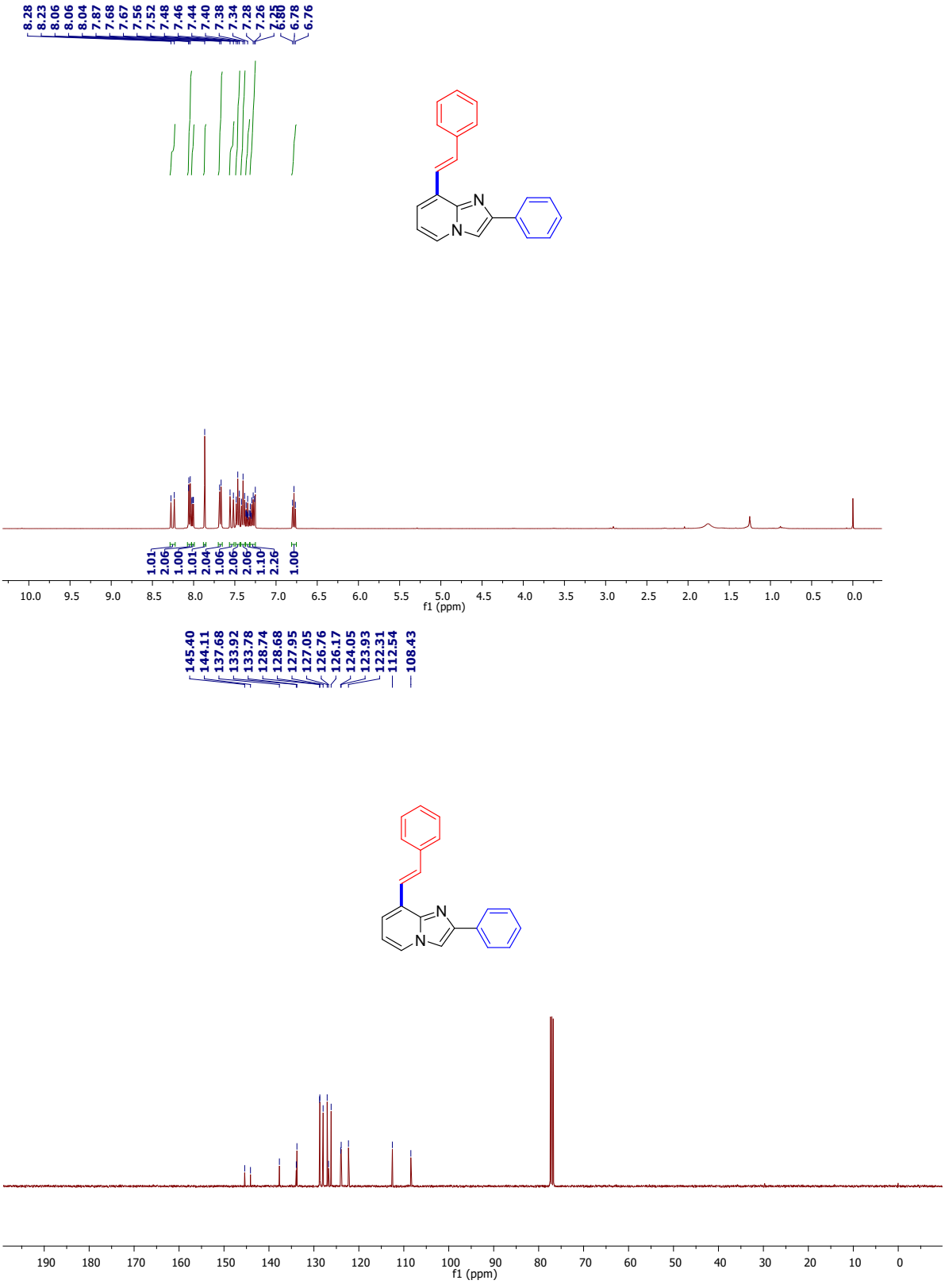


Methyl-3-(3-formyl-2-(4-(methylsulfonyl)phenyl)imidazo[1,2-a]pyridin-8-yl)acrylate (8);

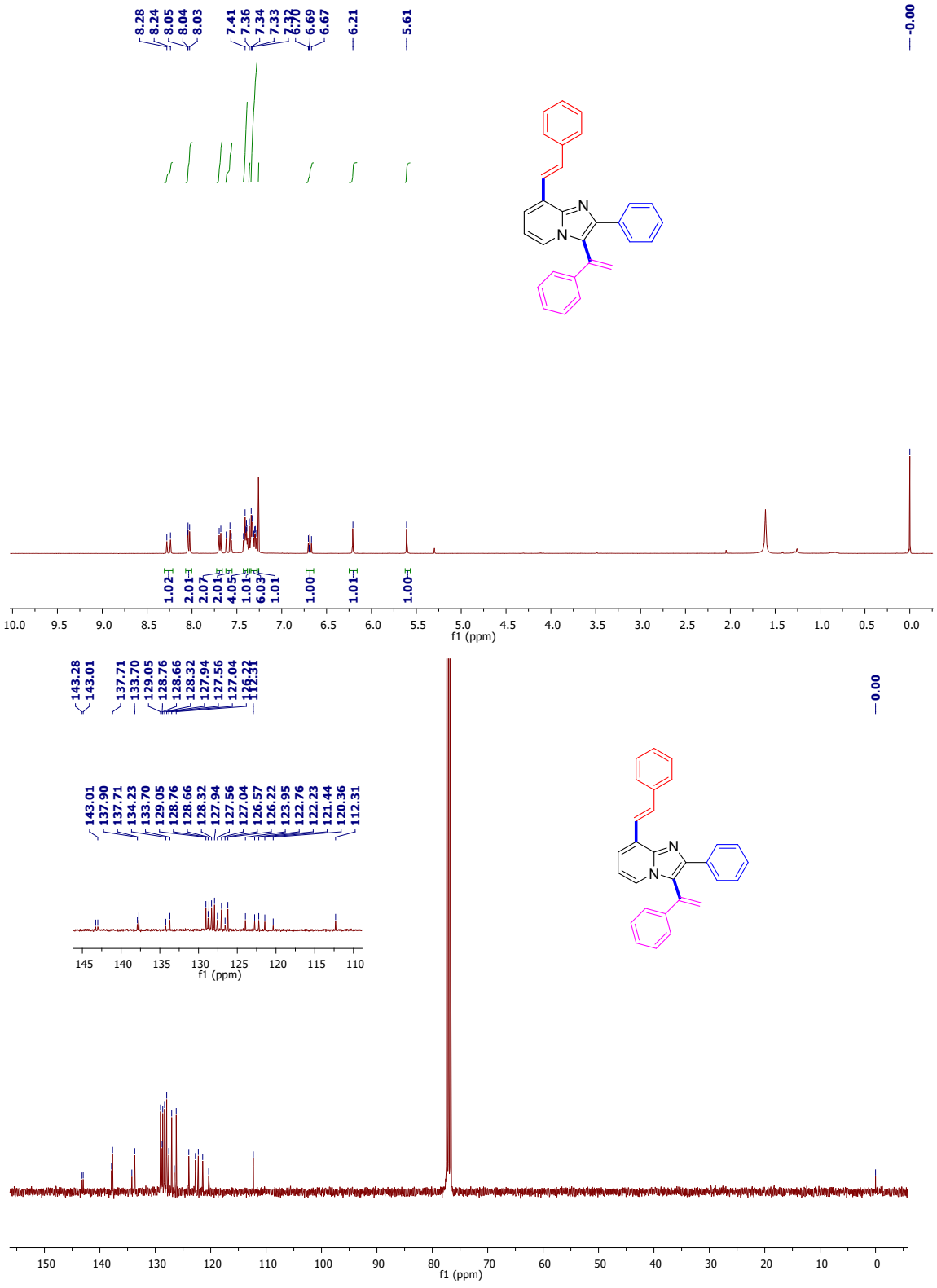




2-Phenyl-8-styrylimidazo[1,2-a]pyridine (9);



2-Phenyl-3-(1-phenylvinyl)-8-styrylimidazo[1,2-a]pyridine (10);



Refrences.

(1) (a) Bhutia, Z. T.; Panjikar, P. C.; Iyer, S.; Chatterjee, A.; Banerjee, M., Iodine Promoted Efficient Synthesis of 2-Arylimidazo[1,2-a]pyridines in Aqueous Media: A Comparative Study between Micellar Catalysis and an "On-Water" Platform. *ACS Omega* **2020,** *5*, 13333-13343; (b) Campos, J. F.; Scherrmann, M.-C.; Berteina-Raboin, S., Eucalyptol: a new solvent for the synthesis of heterocycles containing oxygen, sulfur and nitrogen. *Green Chem.* **2019,** *21*, 1531-1539.
(2)Cao, H.; Lei, S.; Li, N.; Chen, L.; Liu, J.; Cai, H.; Qiu, S.; Tan, J., Cu-Catalyzed selective C3-formylation of imidazo[1,2-a]pyridine C–H bonds with DMSO using molecular oxygen. *Chem. Commun.* **2015,** *51*, 1823-1825.