# Electronic Supplementary Information

# Propargyl Alcohol as Acrolein Equivalent: Synthesis of β-(3-Indolyl)acroleins and β-(Imidazo[1,2-*a*]pyridin-3-yl)acroleins

Bhawani,[a] Sonam,[a] Vikki N. Shinde,[a] Prakash N. Swami,[a] Krishnan Rangan[b] and Anil Kumar[a,*]

[a]Department of Chemistry, Birla Institute of Technology and Science, Pilani, Pilani Campus, Rajasthan, 333031, India

[b]Department of Chemistry, Birla Institute of Technology and Science, Pilani, Hyderabad Campus, Telangana, 500078, India

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

**Contents**

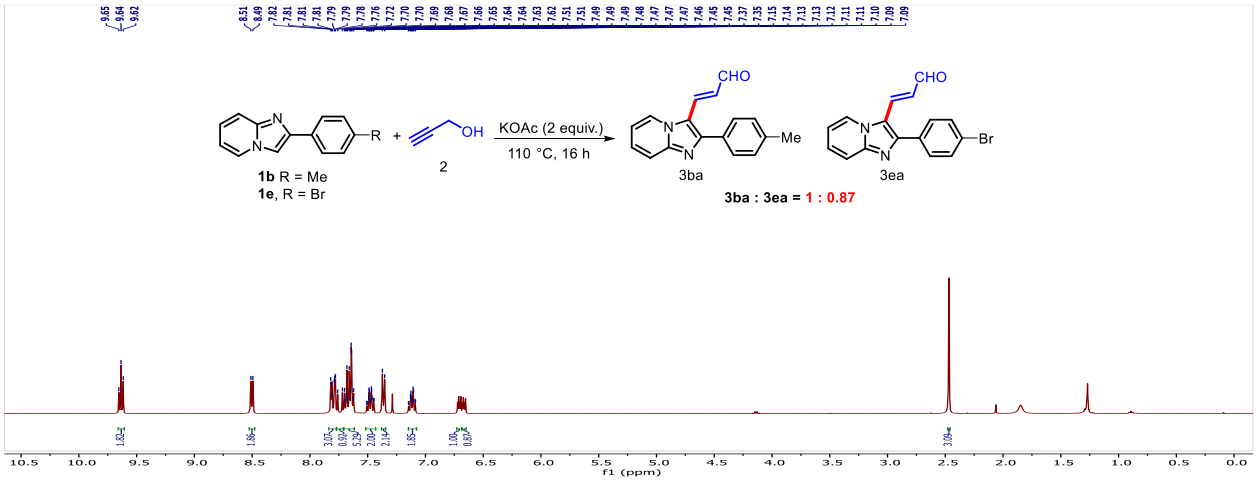
## 1. General information

2-Arylimidazo[1,2-*a*]pyridines and 2-arylindoles were prepared using reported procedures. All the other reagents were commercially available and used as received. The reactions were performed in a 10 mL seal tube at 120 °C, at a stirrer for 16 h. Thin layer chromatography (TLC) was performed on Merck precoated TLC (silica gel 60 F254) plates. Melting points were determined in open capillary tubes on an EZ-Melt automated melting point apparatus and were uncorrected. The $^{1}$H NMR (400 MHz) and $^{13}$C{$^{1}$H} NMR (100 MHz) spectra were recorded on a Bruker Advance 400 spectrometer using $CDCl_3$ (TMS as an internal standard) as solvent. Chemical shifts ($\delta$) and coupling constants ($J$) are reported in parts per million (ppm) and hertz, respectively. The chemical multiplicities were reported as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), and multiplet (m), and combinations of them as well. HRMS data were recorded on an Agilent 6545 Q-TOF spectrometer in positive mode using electrospray ionization (ESI) as the source. X-ray crystal structures were obtained with a Rigaku Oxford XtaLAB AFC12 (RINC): Kappa dual home/near diffractometer.

## 2. General procedure for the synthesis of 3 or 5

A 10 mL oven-dried pressure tube was charged with imidazo[1,2-*a*]pyridine/indole derivative (0.52 mmol) and propargyl alcohol (1.0 mL). Thereafter, anhydrous KOAc (1.04 mmol, 2 equiv.) was added rapidly and tube was capped. The reaction mixture was heated with stirring at 120 °C. After heating for 16 h the sealed tube was cooled and reaction mixture was transferred to a separating funnel using ethyl acetate (2 mL) and water (2 mL). The combined organic layer was washed with brine and dried over anhydrous $Na_2SO_4$. The solvent was evaporated under reduced pressure, and the resulting residue was purified by column chromatography on silica gel (100−200 mesh) using hexanes/ethyl acetate as eluent to afford desired product.

## 3. Intermolecular competition experiment $^{1}$H NMR analysis



**4. General procedure for synthesis of 6**

Solution of **3b** (0.095 mmole) in MeOH: DCM (4: 1) (1 mL) was cooled down up to 0 °C. Then, $NaBH_4$ (0.190 mmole) was added portion-wise over 10 min and the resultant reaction mixture was allowed to blend at RT for 2 h. After completion of the reaction, the solvent was evaporated on reduced pressure, diluted with ethyl acetate (2 mL), and washed with water (2 mL×2). The organic layer was collected separately, dried over the $Na_2SO_4$ layer, and evaporated at reduced pressure. Obtained crude was further passed through column chromatography to get pure product.

**5. General procedure for synthesis of 8**

Initially, compound **3a** (0.160 mmole) and ethyl 2-(diethoxyphosphoryl)acetate (7) (0.133 mmole) were added to dry THF and the solution was stirred in an ice bath, to attain 0 °C temperature. Then, at this temperature, NaH (0.199 mmole, 1.5 equiv.) was added gradually. The obtained reaction mixture was stirred for 10 min at 0 °C and then, at RT for 5 h. After completion of the reaction, the reaction mixture was transferred to a separating funnel and diluted with ethyl acetate (5 mL), which was washed with water (5 mL×2). Separated the organic layer, dried over the $Na_2SO_4$ layer, and used for further purification after evaporating solvent at reduced pressure.

**6. Physical and spectral data for 3a-3v, 5a-5o, 6 and 8**

**(*E*)-3-(2-Phenylimidazo[1,2-*a*]pyridin-3-yl)acrylaldehyde (3a)**: Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 3: 2 v/v); yellow solid; 98 mg (77%); mp = 101-103 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.63 (d, *J* = 7.6 Hz, 1H), 8.51 (d, *J* = 7.2 Hz, 1H), 7.82 – 7.74 (m, 4H), 7.58 – 7.45 (m, 4H), 7.13 – 7.10 (m, 1H), 6.69 (dd, *J* = 16.4, 7.2 Hz, 1H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 193.5, 153.4, 148.2, 138.0, 133.2, 129.6, 129.3, 128.9, 127.8, 125.9, 122.8, 118.4, 117.3, 114.7; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{13}N_2O^+$ 249.1022; Found 249.1026.

**(*E*)-3-(2-(Imidazo[1,2-*a*]pyridin-2-yl)phenyl)prop-2-en-1-ol (3a')**: Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 2: 3 v/v); off-white solid; 48 mg (36%); mp = 85-88 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 6.8 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.69 (s, 1H), 7.67 – 7.56 (m, 2H), 7.36 (t, *J* = 4.2 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 16.0 Hz, 1H), 6.82 (t, *J* = 6.8 Hz, 1H), 6.39 – 6.34 (m, 1H), 4.34 (d, *J* = 4.8 Hz, 2H).; $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 145.01, 144.79, 135.58, 132.41, 130.41, 130.22, 130.03,

128.09, 127.64, 126.77, 125.62, 124.78, 117.54, 112.46, 111.52, 63.74; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{13}N_2O^+$ 251.1179; Found 251.1168.

**(*E*)-3-(2-(*p*-Tolyl)imidazo[1,2-*a*]pyridin-3-yl)acrylaldehyde (3b):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 4: 1 v/v); yellow solid; 110 mg (81%); mp = 92 – 94 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.63 (d, *J* = 7.6 Hz, 1H), 8.50 (d, *J* = 7.2 Hz, 1H), 7.82 (d, *J* = 4.8 Hz, 1H), 7.78 (s, 1H), 7.66 (d, *J* = 8 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 7.0 Hz, 1H), 6.69 (dd, *J* = 16.4, 7.2 Hz, 1H), 2.47 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 193.5, 153.7, 148.2, 139.5, 138.2, 130.3, 129.6, 129.5, 127.7, 125.9, 122.6, 118.4, 117.2, 114.6, 21.4; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{15}N_2O^+$ 263.1179; Found 263.1187.

**(*E*)-3-(2-(4-Methoxyphenyl)imidazo[1,2-*a*]pyridin-3-yl)acrylaldehyde (3c):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 4: 1 v/v) ; yellow solid; 118 mg (83%); mp = 73-75.0 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.64 (d, *J* = 7.6 Hz, 1H), 8.51 – 8.49 (m, 2H), 7.81 – 7.77 (m, 2H), 7.72 – 7.70 (m, 2H), 7.49 – 7.45 (m, 1H), 7.13 – 7.08 (m, 3H), 6.69 (dd, *J* = 16.4, 7.6 Hz, 1H), 3.92(s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 193.5, 160.6, 153.5, 148.2, 138.3, 130.9, 127.8, 125.9, 125.6, 122.4, 118.3, 117.0, 114.5, 114.4, 55.4; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{15}N_2O_2^+$ 279.1128; Found 279.1121.

**(*E*)-3-(2-(4-Fluorophenyl)imidazo[1,2-a]pyridin-3-yl)acrylaldehyde (3d):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 3: 7 v/v); yellow solid; 100 mg (73%); mp = 212-214 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.65 (d, *J* = 7.2 Hz, 1H), 8.52 – 8.50 (m, 1H), 7.81 – 7.78 (m, 1H), 7.77 – 7.73 (m, 3H), 7.51 – 7.47 (m, 1H), 7.27 – 7.23 (m, 2H), 7.15 – 7.11 (m, 1H), 6.69 (dd, *J* = 16.2, 7.4 Hz, 1H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 193.3, 163.5 (d, $J_{C\text{-}F}$ = 249.0 Hz), 152.3, 148.1, 137.5, 131.4 (d, $J_{C\text{-}F}$ = 8.0 Hz), 129.4 (d, $J_{C\text{-}F}$ = 3.0 Hz), 127.9, 125.9, 123.1, 118.4, 117.3, 116.1 (d, $J_{C\text{-}F}$ = 22.0 Hz), 114.7; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -111.52; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{12}FN_2O^+$ 267.0928; Found 267.0920.

**(*E*)-3-(2-(4-Chlorophenyl)imidazo[1,2-*a*]pyridin-3-yl)acrylaldehyde (3e):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 3: 2 v/v); yellow solid; 95 mg (74%); mp = 177-179 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.65 (d, *J* = 7.6 Hz, 1H), 8.51 (d, *J* = 7.2 Hz, 1H), 7.81 (d, *J* = 9.2 Hz, 1H), 7.75 (d, *J* = 16.4 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 6.8 Hz, 1H), 6.70 (dd, *J* = 16.2, 7.4 Hz, 1H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 193.3, 151.9, 148.2, 137.4, 135.6, 131.8, 130.8,

129.2, 127.9, 125.9, 123.3, 118.5, 117.4, 114.8; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{12}ClN_2O^+$ 283.0633; Found 283.0639.

**(*E*)-3-(2-(4-Bromophenyl)imidazo[1,2-*a*]pyridin-3-yl)acrylaldehyde (3f):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 2: 3 v/v); yellow solid; 119 mg (71%); mp = 185-187 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.65 (d, *J* = 7.2 Hz, 1H), 8.51 (d, *J* = 6.8 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.75 (d, *J* = 16.4 Hz, 1H), 7.71 – 7.69 (m, 2H), 7.66 – 7.63 (m, 2H), 7.52 – 7.47 (m, 1H), 7.16 – 7.12 (m, 1H), 6.70 (dd, *J* = 16.2, 7.4 Hz, 1H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 193.3, 151.9, 148.2, 137.4, 132.2, 132.1, 131.0, 127.9, 125.8, 123.9, 123.3, 118.5, 117.3, 114.81; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{12}BrN_2O^+$ 327.0128; Found 327.0134.

**(*E*)-4-(3-(3-Oxoprop-1-en-1-yl)imidazo[1,2-*a*]pyridin-2-yl)benzonitrile (3g):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 2: 3 v/v); yellow solid; 56 mg (41%); mp = 268-270 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.68 (d, *J* = 6.0 Hz, 1H), 8.52 (d, *J* = 6.8 Hz, 1H), 7.91 – 7.82 (m, 5H), 7.74 (d, *J* = 16.4 Hz,, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.0 Hz, 1H), 6.73 (dd, *J* = 16.0, 7.2 Hz, 1H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 193.0, 150.4, 148.2, 137.9, 136.6, 132.7, 130.1, 128.2, 125.8, 124.3, 118.7, 118.5, 117.8, 115.1, 112.9; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{12}N_3O^+$ 274.0975; Found 274.0971.

**(*E*)-3-(2-(*o*-Tolyl)imidazo[1,2-*a*]pyridin-3-yl)acrylaldehyde (3h):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 3:2 v/v); yellow solid; 102 mg (75%); mp = 121-123 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.54 (d, *J* = 7.2 Hz, 1H), 8.49 (d, *J* = 6.8 Hz, 1H), 7.80 (d, *J* = 9.2 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.42 – 7.33 (m, 4H), 7.15 (t, *J* = 7.0 Hz, 1H), 6.43 (dd, *J* = 16.2, 7.4 Hz, 1H), 2.31 (s, 3H).; $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 193.3, 153.3, 151.3, 147.9, 137.3, 136.9, 132.7, 130.7, 130.4, 129.4, 127.5, 125.9, 125.3, 122.7, 118.5, 114.6, 19.9; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{15}N_2O^+$ 263.1179; Found 263.1170.

**(*E*)-3-(2-(2-Methoxyphenyl)imidazo[1,2-*a*]pyridin-3-yl)acrylaldehyde (3i):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 3: 2 v/v); yellow solid; 101 mg (71%); mp = 152-154 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.56 (d, *J* = 7.2 Hz, 1H), 8.46 (d, *J* = 6.8 Hz, 1H), 7.80 (d, *J* = 9.2 Hz, 1H), 7.60 (d, *J* = 16.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.48 – 7.42 (m, 1H), 7.15 – 7.07 (m, 3H), 6.49 (dd, *J* = 16.2, 7.4 Hz, 1H), 3.84 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 193.5, 156.9, 150.3, 148.1, 138.0, 132.0, 131.0, 127.2, 125.3, 122.5, 122.4, 121.1, 118.7, 118.5, 114.5, 111.4, 55.6; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{15}N_2O_2^+$ 279.1128; Found 279.1136.

**(*E*)-3-(2-(3-Methoxyphenyl)imidazo[1,2-*a*]pyridin-3-yl)acrylaldehyde (3j):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 3: 2 v/v); yellow solid; 99 mg (70%); mp = 174-176 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.64 (d, *J* = 7.2 Hz, 1H), 8.51 (d, *J* = 6.8 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.80 (s, 1H), 7.50 – 7.44 (m, 2H), 7.32 – 7.28 (m, 2H), 7.14 – 7.10 (m, 1H), 7.07 – 7.05 (m, 1H), 6.69 (dd, *J* = 16.4, 7.6 Hz, 1H), 3.91 (s, 3H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) δ 193.5, 160.0, 153.2, 148.1, 138.0, 134.5, 129.9, 127.8, 125.9, 122.9, 122.1, 118.5, 117.4, 115.4, 114.68, 114.66, 55.5; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{15}N_2O_2^+$ 279.1128; Found 279.1132.

**(*E*)-3-(2-(3-Nitrophenyl)imidazo[1,2-*a*]pyridin-3-yl)acrylaldehyde (3k):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 3: 7 v/v); yellow solid; 100 mg (66%); mp = 210-212 °C; $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 9.67 (d, *J* = 7.6 Hz, 1H), 8.98 (d, *J* = 6.8 Hz, 1H), 8.56 (t, *J* = 2 Hz, 1H), 8.38 – 8.35 (m, 1H), 8.25 – 8.22 (m, 1H), 8.08 (d, *J* = 16.4 Hz, 1H), 7.89 – 7.85 (m, 2H), 7.63 (dd, *J* = 9.0, 6.6 Hz, 1H), 7.28 – 7.24 (m, 1H), 6.76 (dd, *J* = 16.2, 7.4 Hz, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 194.9, 148.64, 148.60, 147.7, 137.8, 136.0, 135.6, 131.0, 129.2, 127.8, 125.0, 124.2, 124.0, 118.13, 118.06, 115.6; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{12}N_3O_3^+$ 294.0873; Found 294.0877.

**(*E*)-3-(2-(Naphthalen-2-yl)imidazo[1,2-*a*]pyridin-3-yl)acrylaldehyde (3l):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 3: 2 v/v); yellow solid; 121 mg (78%); mp = 130-132 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.64 (d, *J* = 7.2 Hz, 1H), 8.55 (d, *J* = 6.8, 1H), 8.22 (s, 1H), 8.04 – 7.84 (m, 7H), 7.59 (s, 1H), 7.50 (d, *J* = 15.6 Hz, 1H), 7.14 (s, 1H), 6.73 (dd, *J* = 15.8, 7.4 Hz, 1H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) δ 193.4, 157.0, 153.3, 148.3, 138.0, 133.5, 133.3, 130.6, 129.4, 128.7, 128.5, 127.8, 127.0, 126.71, 126.68, 125.9, 123.1, 118.5, 117.6, 114.7; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{20}H_{15}N_2O^+$ 299.1179; Found 299.1177.

**(*E*)-3-(2-(Thiophen-3-yl)imidazo[1,2-*a*]pyridin-3-yl)acrylaldehyde (3m):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 2: 3 v/v); yellow solid; 78 mg (60%); mp = 130-132 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.67 (d, *J* = 7.2 Hz, 1H), 8.48 (d, *J* = 6.8 Hz, 1H), 7.87 (d, *J* = 16.4 Hz, 1H), 7.77 (d, *J* = 9.2 Hz, 1H), 7.73 (s, 1H), 7.54 (dd, *J* = 13.4, 4.6 Hz, 2H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 7.0 Hz, 1H), 6.70 (dd, *J* = 16.4, 7.2 Hz, 1H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) δ 193.4, 148.7, 148.2, 137.5, 134.3, 128.1, 127.9, 126.8, 126.0, 125.9, 122.8, 118.3, 117.3, 114.6; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{11}N_2OS^+$ 255.0587; Found 255.0584.

**(*E*)-3-(8-Methyl-2-phenylimidazo[1,2-*a*]pyridin-3-yl)acrylaldehyde (3n):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 3: 2 v/v); yellow solid; 99 mg (73%); mp = 136-138 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.62 (d, *J* = 7.2 Hz, 1H), 8.38 (d, *J* = 6.8 Hz, 1H), 7.80 – 7.74 (m, 3H), 7.58 – 7.50 (m, 3H), 7.28 (d, *J* = 6.8 Hz, 1H), 7.03 (t, *J* = 7.0 Hz, 1H), 6.66 (dd, *J* = 16.4, 7.6 Hz, 1H), 2.73 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 193.6, 153.0, 148.5, 138.3, 133.5, 129.7, 129.2, 128.9, 128.6, 126.8, 123.7, 122.5, 117.8, 114.6, 17.1; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{15}N_2O^+$ 263.1179; Found 263.1173.

**(*E*)-3-(8-Methyl-2-(*p*-tolyl)imidazo[1,2-*a*]pyridin-3-yl)acrylaldehyde (3o):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 2: 3 v/v); yellow solid; 110 mg (77%); mp = 165-167 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.59 (d, *J* = 7.6 Hz, 1H), 8.37 (d, *J* = 6.8 Hz, 1H), 7.76 (d, *J* = 16.0 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.54 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.62 (dd, *J* = 16.4, 7.6 Hz, 1H), 2.50 (s, 3H), 2.46 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 193.5, 154.0, 148.7, 139.4, 139.3, 138.3, 130.4, 129.6, 129.5, 125.3, 121.7, 117.0, 116.93, 116.89, 21.44, 21.39; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{17}N_2O^+$ 277.1335; Found 277.1339.

**(*E*)-3-(2-(4-Chlorophenyl)-8-methylimidazo[1,2-*a*]pyridin-3-yl)acrylaldehyde (3p):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 2: 3 v/v); yellow solid; 114 mg (75%); mp = 216-218 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.62 (d, *J* = 7.6 Hz, 1H), 8.36 (d, *J* = 6.8 Hz, 1H), 7.74 – 7.69 (m, 3H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 6.0 Hz, 1H), 7.03 (t, *J* = 6.8 Hz, 1H), 6.66 (dd, *J* = 16.2, 7.4 Hz, 1H), 2.71 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 193.3, 151.5, 148.5, 137.7, 135.4, 132.0, 130.9, 129.1, 128.7, 126.9, 123.6, 122.9, 117.8, 114.7, 17.1; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{14}ClN_2O^+$ 297.0789; Found 297.0798.

**(*E*)-3-(7-Methyl-2-phenylimidazo[1,2-*a*]pyridin-3-yl)acrylaldehyde (3q):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 3: 2 v/v); yellow solid; 107 mg (79%); mp = 177-179 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.61 (d, *J* = 7.6 Hz, 1H), 8.39 (d, *J* = 7.2 Hz, 1H), 7.79 – 7.73 (m, 3H), 7.57 – 7.53 (m, 3H), 7.52 – 7.48 (m, 1H), 6.95 (dd, *J* = 7.0, 1.8 Hz, 1H), 6.64 (dd, *J* = 16.4, 7.6 Hz, 1H), 2.52 (s 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 193.5, 153.8, 148.7, 139.5, 138.2, 133.3, 129.6, 129.2, 128.9, 125.3, 121.9, 117.2, 117.0, 21.5; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{15}N_2O^+$ 263.1179; Found 263.1171.

**(*E*)-3-(2-(4-Methoxyphenyl)-7-methylimidazo[1,2-*a*]pyridin-3-yl)acrylaldehyde (3r):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 3: 2 v/v); yellow

solid; 128 mg (85%); mp = 96-98 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.60 (d, *J* = 7.6 Hz, 1H), 8.37 (d, *J* = 7.2 Hz, 1H), 7.77 – 7.67 (m, 1H), 7.53 (s, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 7.2 Hz, 1H), 6.62 (dd, *J* = 16.2, 7.4 Hz, 1H), 3.90 (s, 3H), 2.51 (s, 3H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) δ 193.5, 160.6, 153.8, 148.8, 139.4, 138.4, 130.9, 125.7, 125.3, 121.5, 117.0, 116.9, 116.7, 114.4, 55.4, 21.5; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{17}N_2O_2^+$ 293.1285; Found 293.1280.

**(*E*)-3-(7-Methyl-2-(4-nitrophenyl)imidazo[1,2-*a*]pyridin-3-yl)acrylaldehyde (3s):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 1: 3 v/v); yellow solid; 120 mg (76%); mp = 239-241 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.67 (d, *J* = 7.2 Hz, 1H), 8.43 – 8.40 (m, 3H), 7.98 – 7.94 (m, 2H), 7.73 (d, *J* = 16.4 Hz, 1H), 7.59 (s, 1H), 7.01 (dd, *J* = 7.2, 2.0 Hz, 1H), 6.69 (dd, *J* = 16.4, 7.2 Hz, 1H), 2.55 (s, 3H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) δ 193.0, 150.2, 148.7, 148.1, 140.1, 139.9, 136.7, 130.3, 125.1, 124.1, 123.6, 117.8, 117.7, 117.3, 21.5; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{14}N_3O_3^+$ 308.1030; Found 308.1033.

**(*E*)-3-(7-Chloro-2-phenylimidazo[1,2-*a*]pyridin-3-yl)acrylaldehyde (3t):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 3: 7 v/v); yellow solid; 94 mg (65 %); mp = 194-196 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.67 (d, *J* = 7.6 Hz, 1H), 8.54 (dd, *J* = 2.0, 0.8 Hz, 1H), 7.80 – 7.74 (m, 4H), 7.59 – 7.51 (m, 3H), 7.44 (dd, *J* = 9.4, 1.8 Hz, 1H), 6.71 (dd, *J* = 16.4, 7.2 Hz, 1H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) δ 193.3, 153.6, 146.4, 137.3, 132.9, 129.5, 129.0, 128.9, 123.8, 122.9, 118.7, 117.6, 113.6; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{12}ClN_2O^+$ 283.0633; Found 283.0638.

**(*E*)-3-(7-Bromo-2-phenylimidazo[1,2-*a*]pyridin-3-yl)acrylaldehyde (3u):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 2: 3 v/v); yellow solid; 114 mg (68%); mp = 168-170 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.67 (d, *J* = 7.2 Hz, 1H), 8.63 (s, 1H), 7.79 – 7.69 (m, 4H), 7.59 – 7.52 (m, 4H), 6.71 (dd, *J* = 16.6, 7.4 Hz, 1H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) δ 193.3, 153.4, 146.5, 140.0, 137.3, 132.8, 131.0, 129.5, 129.0, 125.9, 123.9, 118.9, 117.5, 109.4; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{12}BrN_2O^+$ 327.0128; Found 327.0126.

**(*E*)-3-(7-Bromo-2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridin-3-yl)acrylaldehyde (3v):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 3: 2 v/v); yellow solid; 127 mg (69%); mp = 134-136 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.66 (d, *J* = 7.6 Hz, 1H), 8.61 (s, 1H), 7.76 (d, *J* = 16.4 Hz, 1H), 7.68 (dd, *J* = 9.0, 6.6 Hz, 3H), 7.52 (dd, *J* = 9.4,

1.8 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.70 (dd, *J* = 16.4, 7.6 Hz, 1H), 3.92 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 193.3, 160.8, 153.4, 146.5, 137.6, 130.91, 130.87, 125.9, 125.2, 123.4, 118.7, 117.1, 114.5, 109.1, 55.4; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{14}BrN_2O_2^+$ 357.0233; Found 357.0239.

**(*E*)-4-(2-(4-Methoxyphenyl)-7-methylimidazo[1,2-*a*]pyridin-3-yl)but-3-en-2-one (3w)**: Purification by column chromatography on silica gel (eluent: EtOAc/hexanes: 3:7 v/v); Orange-yellow solid; 26 mg (21%); mp = 148-150 °C; $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 6.8 Hz, 1H), 7.89 (d, *J* = 16.4 Hz, 1H), 7.71 – 7.68 (m, 2H), 7.50 (s, 1H), 7.08 – 7.04 (m, 2H), 6.87 (dd, *J* = 7.0, 1.8 Hz, 1H), 6.65 (d, *J* = 16.4 Hz, 1H), 3.91 (s, 3H), 2.49 (s, 3H), 2.36 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 197.9, 160.3, 152.5, 148.2, 138.5, 130.8, 129.9, 126.2, 125.0, 120.7, 116.7, 116.5, 116.4, 114.3, 55.4, 27.7, 21.4; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{13}N_2O^+$ 307.1441; Found 307.1421.

**(*E*)-3-(2-Phenyl-1*H*-indol-3-yl)acrylaldehyde (5a):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 1: 4 v/v); yellow solid; 90 mg (72%); mp = 170-172 °C; $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 9.59 (d, *J* = 8 Hz, 1H), 8.75 (s, 1H), 8.00 (d, *J* = 7.2 Hz, 1H), 7.77 (d, *J* = 16.0 Hz, 1H), 7.61 – 7.54 (m, 5H), 7.49 (dd, *J* = 6.6, 2.2 Hz, 1H), 7.39-7.32 (m, 2H), 6.93 (dd, *J* = 15.8, 7.8 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 194.5, 147.0, 143.6, 136.4, 131.0, 129.6, 129.28, 129.27, 126.3, 125.8, 124.0, 122.4, 121.0, 111.6, 110.4; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{14}NO^+$ 248.1070; Found 248.1078.

**(*E*)-3-(2-(*p*-Tolyl)-1*H*-indol-3-yl)acrylaldehyde (5b):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanse, 1: 4 v/v); yellow solid; 78 mg (73%); mp = 160-162 °C; $^{1}H$ NMR (400 MHz, DMSO-$d_6$) δ 12.25 (s, 1H), 9.51 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 15.6 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 10.8 Hz, 2H), 6.75 (dd, *J* = 16.2, 8.2 Hz, 1H), 2.43 (s, 3H); $^{13}C$ NMR (100 MHz, DMSO-$d_6$) δ 194.5, 147.7, 145.1, 139.5, 137.3, 130.1, 130.0, 128.2, 126.2, 124.2, 123.6, 122.2, 120.9, 112.7, 108.9, 21.4; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{16}NO^+$ 262.1226; Found 262.1219.

**(*E*)-3-(2-(4-Methoxyphenyl)-1*H*-indol-3-yl)acrylaldehyde (5c):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 1: 3 v/v); yellow solid; 110 mg (77%); mp = 156-158 °C;$^{1}H$ NMR (400 MHz, $CDCl_3$) δ 9.57 (d, *J* = 7.6 Hz, 1H), 8.78 (s, 1H), 7.97 – 7.95 (m, 1H), 7.74 (d, *J* = 16.0 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.48 – 7.46 (m, 1H), 7.35 – 7.32 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.91 (dd, *J* = 15.6, 8.0 Hz, 1H), 3.92 (s, 3H); $^{13}C$ NMR

(100 MHz, $CDCl_3$) δ 194.5, 160.8, 147.4, 144.0, 136.3, 130.6, 126.4, 125.2, 123.8, 123.2, 122.3, 120.8, 114.8, 111.5, 110.0, 55.5; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{16}NO_2^+$ 278.1176; Found 278.1181.

**(*E*)-3-(2-(4-Hydroxyphenyl)-1*H*-indol-3-yl)acrylaldehyde (5d):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 1: 3 v/v); yellow solid; 102 mg (75%); mp = 128-130 °C; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 12.15 (s, 1H), 10.01 (s, 1H), 9.50 (d, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 15.6 Hz, 1H), 7.49 (dd, *J* = 13.2, 7.6 Hz, 3H), 7.26 – 7.21 (m, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.72 (dd, *J* = 15.6, 7.6 Hz, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 194.4, 159.1, 148.0, 145.8, 137.2, 131.5, 126.3, 123.7, 123.4, 122.1, 121.7, 120.7, 116.4, 112.5, 108.4; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{14}NO_2^+$ 264.1019; Found 264.1026.

**(*E*)-3-(2-(4-Fluorophenyl)-1*H*-indol-3-yl)acrylaldehyde (5e):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 2: 3 v/v); yellow solid; 93 mg (68%); mp = 232-234 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.59 (d, *J* = 8.0 Hz, 1H), 8.68 (s, 1H), 8.00 – 7.98 (m, 1H), 7.69 (d, *J* = 15.6 Hz, 1H), 7.61 – 7.58 (m, 2H), 7.50 – 7.47 (m, 1H), 7.39-7.34 (m, 2H), 7.32 (t, *J* = 2.8 Hz, 1H), 7.30 (s, 1H), 6.93 (dd, *J* = 15.8, 7.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 194.3, 146.5, 142.4, 136.3, 131.2 (d, *J* = 8.3 Hz), 127.1 (d, *J* = 3.4 Hz), 126.2, 125.9, 123.3 (d, *J* = 159.1 Hz), 120.9, 120.1, 117.6, 116.5 (d, *J* = 21.7 Hz), 111.6, 110.6; $^{19}$F NMR (376 MHz, $CDCl_3$ ) δ -110.44; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{13}FNO^+$ 266.0976; Found 266.0969.

**(*E*)-3-(2-(4-Chlorophenyl)-1*H*-indol-3-yl)acrylaldehyde (5f):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 1: 3 v/v); yellow solid; 96 mg, (66%); mp = 153-155 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.60 (d, *J* = 7.6 Hz, 1H), 8.71 (s, 1H), 7.99 (d, *J* = 7.2 Hz, 1H), 7.69 (d, *J* = 16.0 Hz, 1H), 7.57 (q, *J* = 7.5 Hz, 3H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.39 – 7.32 (m, 2H), 6.93 (dd, *J* = 15.6, 8.0 Hz, 1H), 3.52 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 194.3, 146.3, 135.9, 134.2, 131.9, 130.5, 129.6, 129.4, 126.2, 124.2, 122.5, 121.0, 112.2, 111.6, 111.2; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{13}ClNO^+$ 282.0680; Found 282.0666.

**(*E*)-3-(2-(4-Bromophenyl)-1*H*-indol-3-yl)acrylaldehyde (5g):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 1: 3 v/v); yellow solid; 118 mg (70%); mp = 210-212 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.60 (d, *J* = 7.6 Hz, 1H), 8.70 (s, 1H), 8.00 – 7.98 (m, 1H), 7.74 – 7.67 (m, 3H), 7.50-7.46 (m, 3H), 7.40 – 7.32 (m, 2H), 6.93 (dd, *J* = 15.8,

7.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 194.3, 146.2, 142.0, 136.4, 132.5, 130.7, 129.8, 126.2, 126.2, 124.2, 124.2, 122.6, 121.0, 111.6, 110.7; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{13}BrNO^+$ 326.0175; Found 326.0180.

**(*E*)-3-(2-(*o*-Tolyl)-1*H*-indol-3-yl)acrylaldehyde (5h):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 1: 9 v/v); yellow solid; 96 mg (69%); mp = 194-196 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.44 (d, *J* = 8.0 Hz, 1H), 8.72 (s, 1H), 7.99 – 7.97 (m, 1H), 7.49 – 7.44 (m, 2H), 7.42 (d, *J* = 4.4 Hz, 1H), 7.40 – 7.35 (m, 5H), 6.78 (dd, *J* = 15.8, 7.8 Hz, 1H), 2.29 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 194.5, 146.9, 143.6, 137.7, 136.3, 130.9, 130.8, 130.3, 130.0, 126.1, 125.8, 125.0, 123.7, 122.3, 120.6, 111.6, 111.4, 20.1; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{16}NO^+$ 262.1226; Found 262.1220.

**(*E*)-3-(2-(3-(Trifluoromethyl)phenyl)-1*H*-indol-3-yl)acrylaldehyde (5i):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 2: 3 v/v); yellow solid; 85 mg (52%); mp = 150-152 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.61 (d, *J* = 8.0 Hz, 1H), 8.71 (s, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.87 (s, 1H), 7.83 – 7.80 (m, 2H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 16.0 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.40 – 7.36 (m, 2H), 6.96 (dd, *J* = 15.8, 7.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 194.1, 159.0, 155.8, 145.7, 144.4, 130.3 (q, $^2J_{C\text{-}F}$ = 34.3 Hz) , 129.9, 129.2, 126.8, 126.1, 124.5, 123.0, 122.3 (q, $^1J_{C\text{-}F}$ = 257 Hz), 121.6, 121.1, 118.2, 111.7, 90.3; $^{19}$F NMR (376 MHz, $CDCl_3$ ) δ -62.74; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{13}F_3NO^+$ 316.0944; Found 316.0948.

**(*E*)-3-(2-(Thiophen-2-yl)-1*H*-indol-3-yl)acrylaldehyde (5j):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 1: 3 v/v); yellow solid; 91 mg (69%); mp = 93-95 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.67 (d, *J* = 7.6 Hz, 1H), 8.64 (s, 1H), 7.98 – 7.93 (m, 2H), 7.59 (d, *J* = 5.2 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 3.6 Hz, 1H), 7.38 – 7.31 (m, *J* = 7.4 Hz, 3H), 6.96 (dd, *J* = 15.8, 7.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 194.4, 146.1, 136.4, 136.3, 131.8, 128.6, 128.4, 128.3, 126.3, 124.3, 122.5, 121.0, 112.1, 111.5, 111.1; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{12}NOS^+$ 254.0634; Found 254.0636.

**(*E*)-3-(5-Bromo-2-phenyl-1*H*-indol-3-yl)acrylaldehyde (5k):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 1: 3 v/v); yellow solid; 103 mg (61%); mp = 258-260 °C; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 12.50 (s, 1H), 9.53 (d, *J* = 7.6 Hz, 1H), 8.11 (d, *J* = 1.6 Hz, 1H), 7.78 (d, *J* = 16.0 Hz, 1H), 7.70 – 7.58 (m, 5H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.43 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.74 (dd, *J* = 16.0, 7.6 Hz, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 194.6, 146.6, 145.5, 136.0, 130.7, 130.1, 130.0, 129.6, 127.9, 126.4, 125.0, 122.9,

114.8, 114.7, 108.6; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{13}BrNO^+$ 326.0175; Found 326.0178.

**(*E*)-3-(6-Chloro-5-methyl-2-phenyl-1H-indol-3-yl)acrylaldehyde (5l):** Purification by column chromatography on silica gel (eluent: EtOAc/hexane, 1: 3 v/v); yellow solid; 96 mg (63%); mp = 104-106 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.59 (d, *J* = 7.6 Hz, 1H), 8.55 (s, 1H), 7.84 (,1H), 7.72 (d, *J* = 15.6 Hz, 1H), 7.60 – 7.54 (m, 5H), 7.49 (s, 1H), 6.90 (dd, *J* = 15.8, 7.8 Hz, 1H), 2.54 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 194.3, 146.4, 135.3, 130.1, 129.7, 129.3, 129.2, 126.0, 125.3, 122.2, 111.7, 20.6; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{15}ClNO^+$ 296.0837; Found 296.0841.

**(*E*)-3-(1-Methyl-1*H*-indol-3-yl)acrylaldehyde (5m):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 3: 7 v/v); semisolid; 40 mg (44%); $^1$H NMR (400 MHz, $CDCl_3$) δ 9.64 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 16.0 Hz, 1H), 7.48 (s, 1H), 7.42 – 7.33 (m, 3H), 6.77 (dd, *J* = 15.8, 7.8 Hz, 1H), 3.88 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 194.0, 146.3, 133.9, 125.9, 124.3, 123.4, 121.9, 120.5, 112.4, 110.2, 100.0, 33.4; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{12}H_{12}NO^+$ 186.0913; Found 186.0910.

**(*E*)-3-(1-methyl-2-phenyl-1*H*-indol-3-yl)acrylaldehyde (5n):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 1: 4 v/v); yellow solid; 95 mg (70%); mp = 128-130 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.46 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.62 – 7.60 (m, 3H), 7.49 – 7.44 (m, 4H), 7.42 – 7.36 (m, 2H), 6.82 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.69 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 194.4, 147.4, 146.6, 138.1, 130.9, 129.7, 128.9, 125.4, 124.5, 123.6, 122.4, 120.8, 118.0, 110.9, 110.3, 31.3; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{16}NO^+$ 262.1226; Found 262.1230.

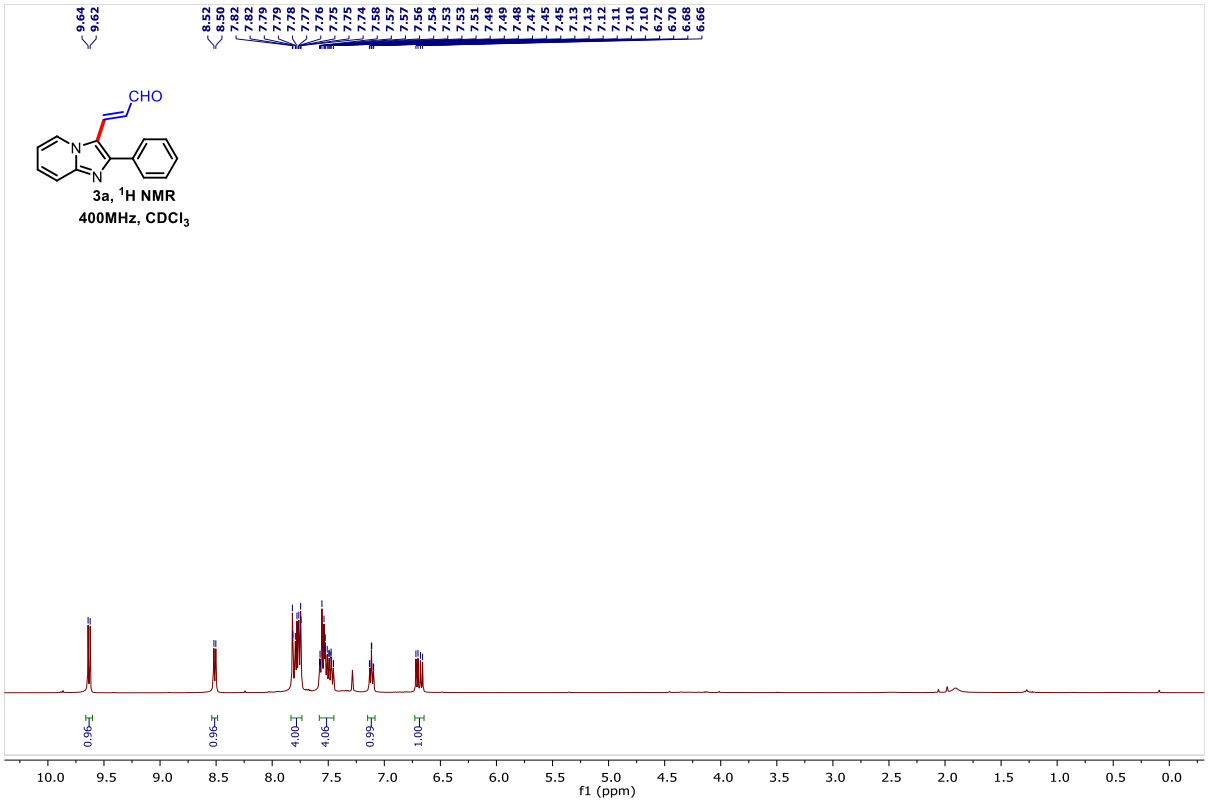
**(*E*)-3-(1-Methyl-2-(*p*-tolyl)-1*H*-indol-3-yl)acrylaldehyde (5o):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 1: 4 v/v); yellow solid, 102 mg, (72%); mp = 144-146 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.46 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 6.8 Hz, 1H), 7.48 (d, *J* = 16.0 Hz, 1H), 7.45 – 7.35 (m, 6H), 7.30 (d, *J* = 16.4 Hz, 1H), 6.81 (dd, *J* = 15.8, 7.8 Hz, 1H), 3.69 (s, 3H), 2.52 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 194.4, 147.5, 146.8, 139.8, 138.1, 130.7, 129.6, 126.6, 125.4, 124.3, 123.4, 122.3, 120.7, 110.8, 110.2, 31.3, 21.5; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{16}NO^+$ 276.1383; Found 276.1388.

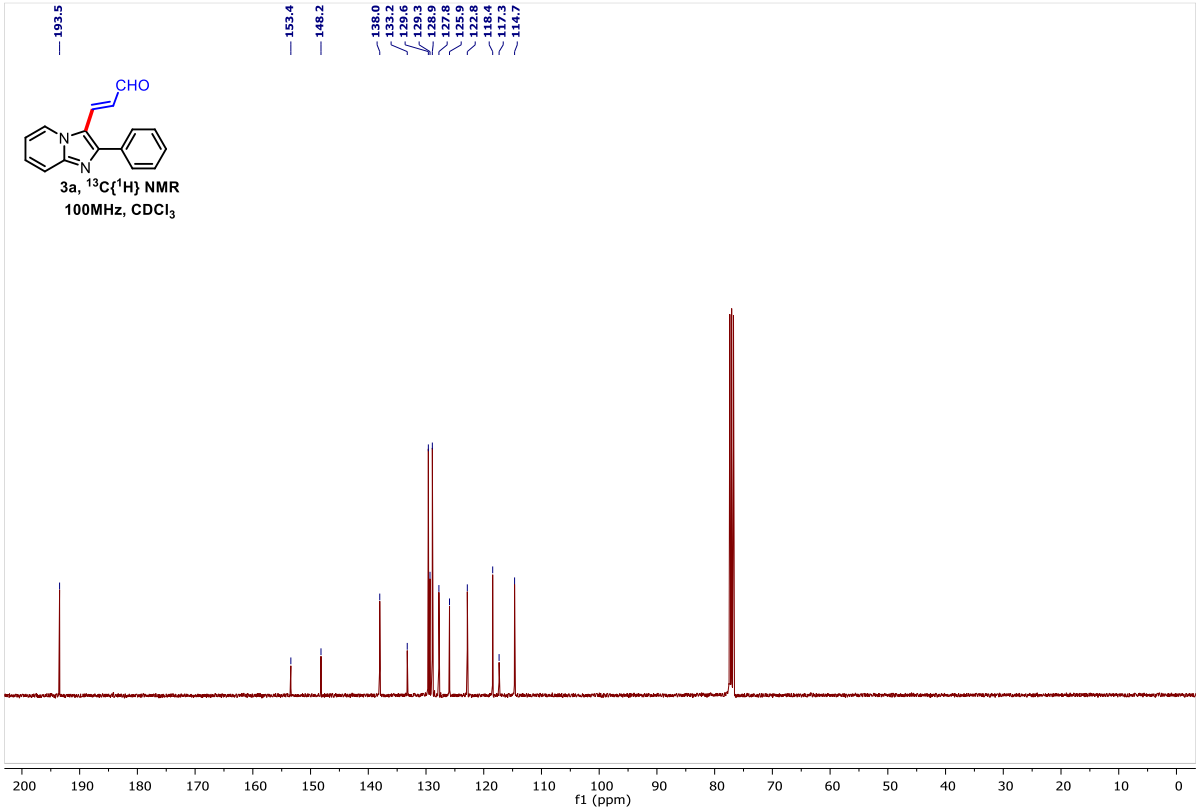
**(*E*)-3-(2-(*p*-Tolyl)imidazo[1,2-*a*]pyridin-3-yl)prop-2-en-1-ol (6):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 4: 1 v/v); yellow solid; 23 mg (92%); mp = 104-106 °C $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.60 – 8.58 (m, 1H), 7.70 (d, *J* = 8.0 Hz,

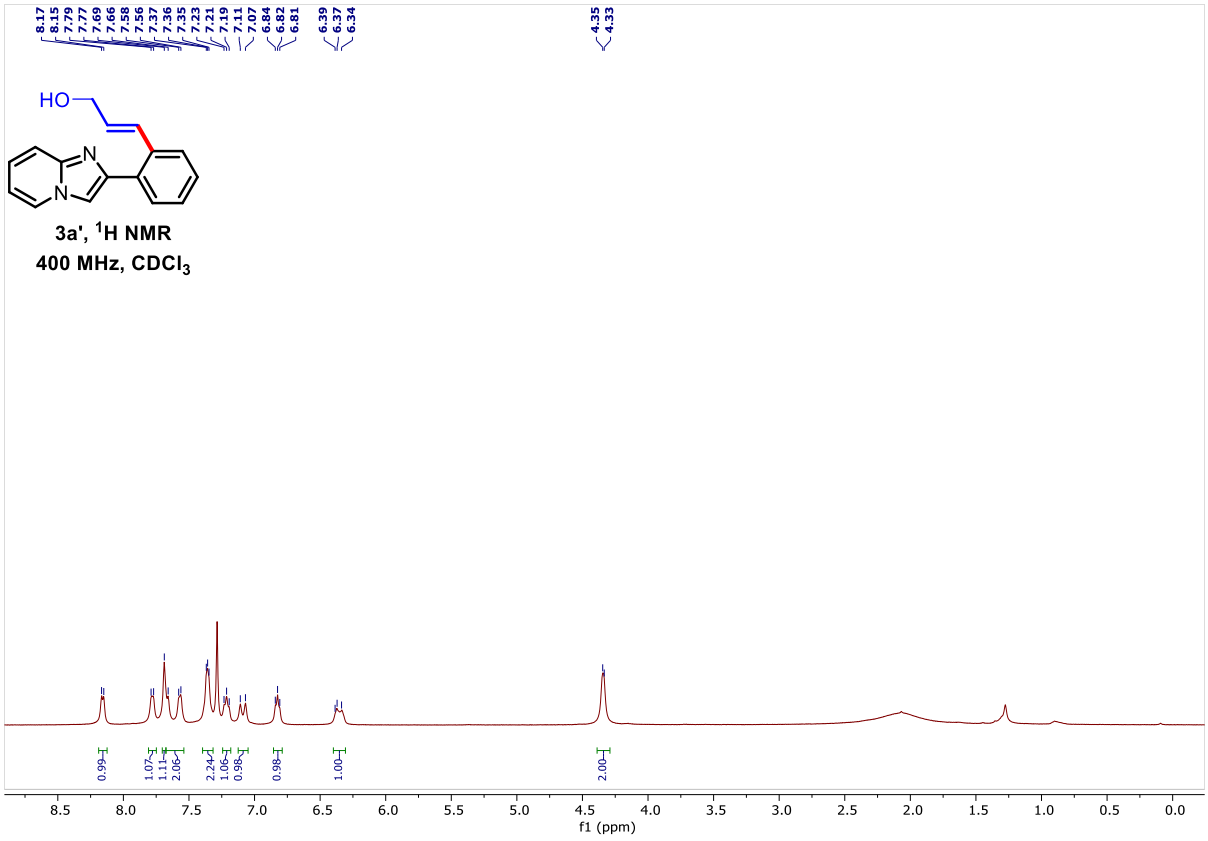
2H), 7.63 – 7.60 (m, 1H), 7.32 – 7.27 (m, 3H), 7.00 – 6.97 (m, 1H), 6.89 – 6.84 (m, 1H), 6.40 – 6.34 (m, 1H), 5.01 (t, $J$ = 5.4 Hz, 1H), 4.24 – 4.21 (m, 1H), 2.36 (s, 3H);$^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 144.8, 143.4, 137.4, 133.7, 132.2, 129.5, 128.7, 125.3, 125.3, 118.6, 117.4, 115.8, 113.2, 62.1, 21.3; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{17}N_2O^+$ 265.1335; Found 265.1331.

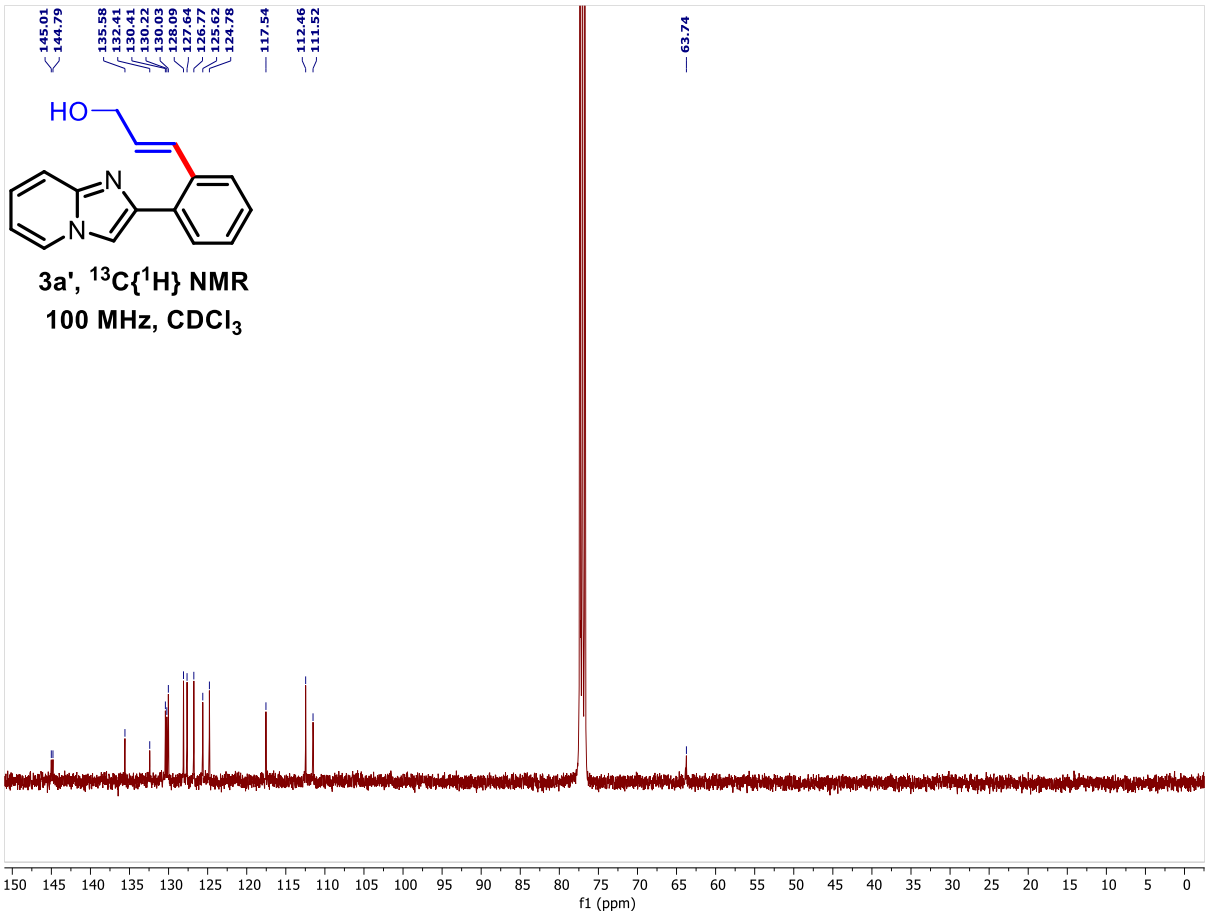
**Ethyl-(2*E*,4*E*)-5-(2-(*p*-tolyl)imidazo[1,2-*a*]pyridin-3-yl)penta-2,4-dienoate (8):** Purification by column chromatography on silica gel (eluent: EtOAc/hexanes, 2: 3 v/v); yellow solid; 30 mg (68%); mp = 102-104 °C $^1$H NMR (400 MHz, $CDCl_3$) δ 8.45 – 8.43 (m, 1H), 7.79 – 7.76 (m, 2H), 7.75 – 7.72 (m, 1H), 7.54 – 7.49 (m, 2H), 7.48 – 7.45 (m, 1H), 7.36 – 7.32 (m, 1H), 7.21 (d, $J$ = 16.0 Hz, 1H), 7.02 – 6.99 (m, 1H), 6.89 – 6.82 (m, 1H), 5.96 (d, $J$ = 15.2 Hz, 1H), 4.26 (q, $J$ = 7.1 Hz, 2H), 1.34 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.1, 148.5, 146.6, 145.1, 134.1, 129.3, 128.7, 128.6, 126.6, 125.9, 124.8, 124.4, 120.4, 118.3, 118.2, 113.6, 60.4, 14.4; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{20}H_{19}N_2O_2^+$ 319.1441; Found 319.1446.

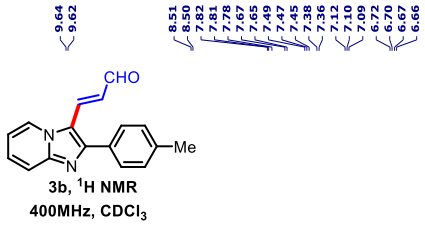
## 7. Copies of $^{1}H$ and $^{13}C$ NMR for 3a-3v, 5a-5o, 6 and 8



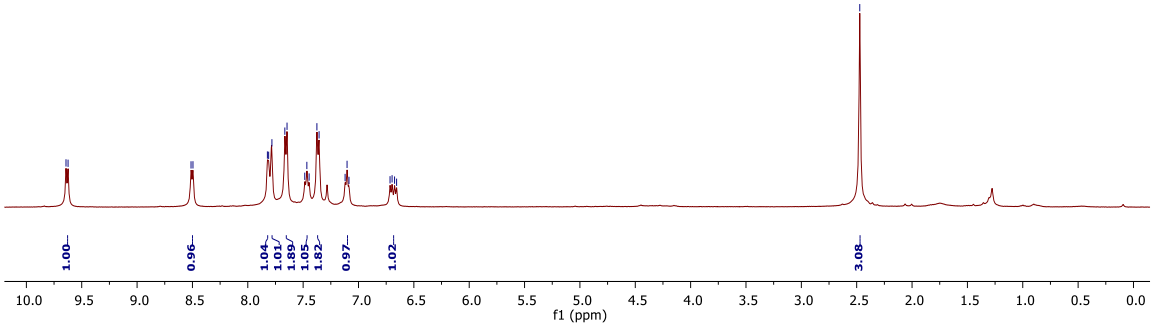



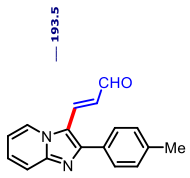

8.17
8.15
7.79
7.77
7.69
7.66
7.58
7.56
7.37
7.36
7.35
7.23
7.21
7.19
7.11
7.07
6.84
6.82
6.81
6.39
6.37
6.34
4.35
4.33
HO
N
N
3a', 1H NMR
400 MHz, CDCl3
0.99
1.07
1.11
2.06
2.24
1.06
0.98
0.98
1.00
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


145.01
144.79
135.58
132.41
130.41
130.22
130.03
128.09
127.64
126.77
125.62
124.78
117.54
112.46
111.52
63.74
HO
N
N
3a', 13C{1H} NMR
100 MHz, CDCl3
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

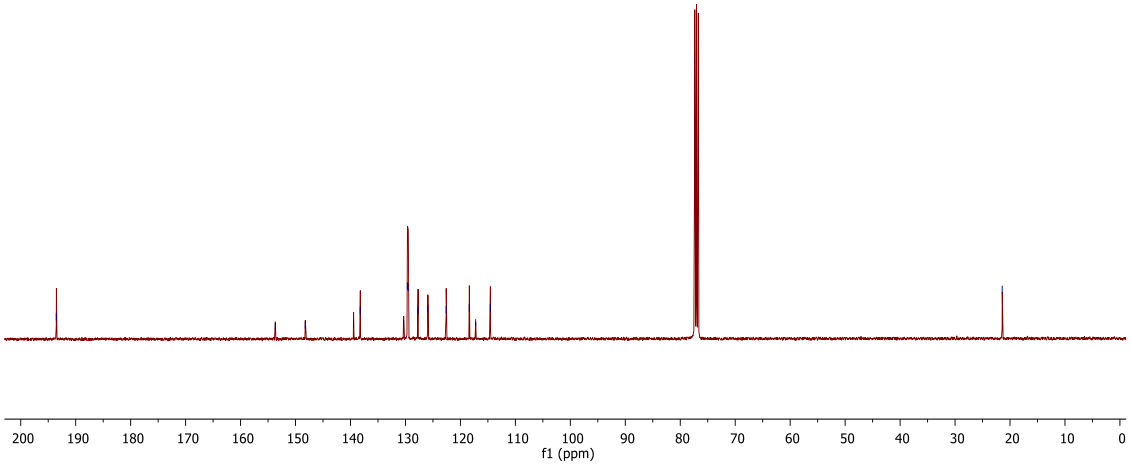


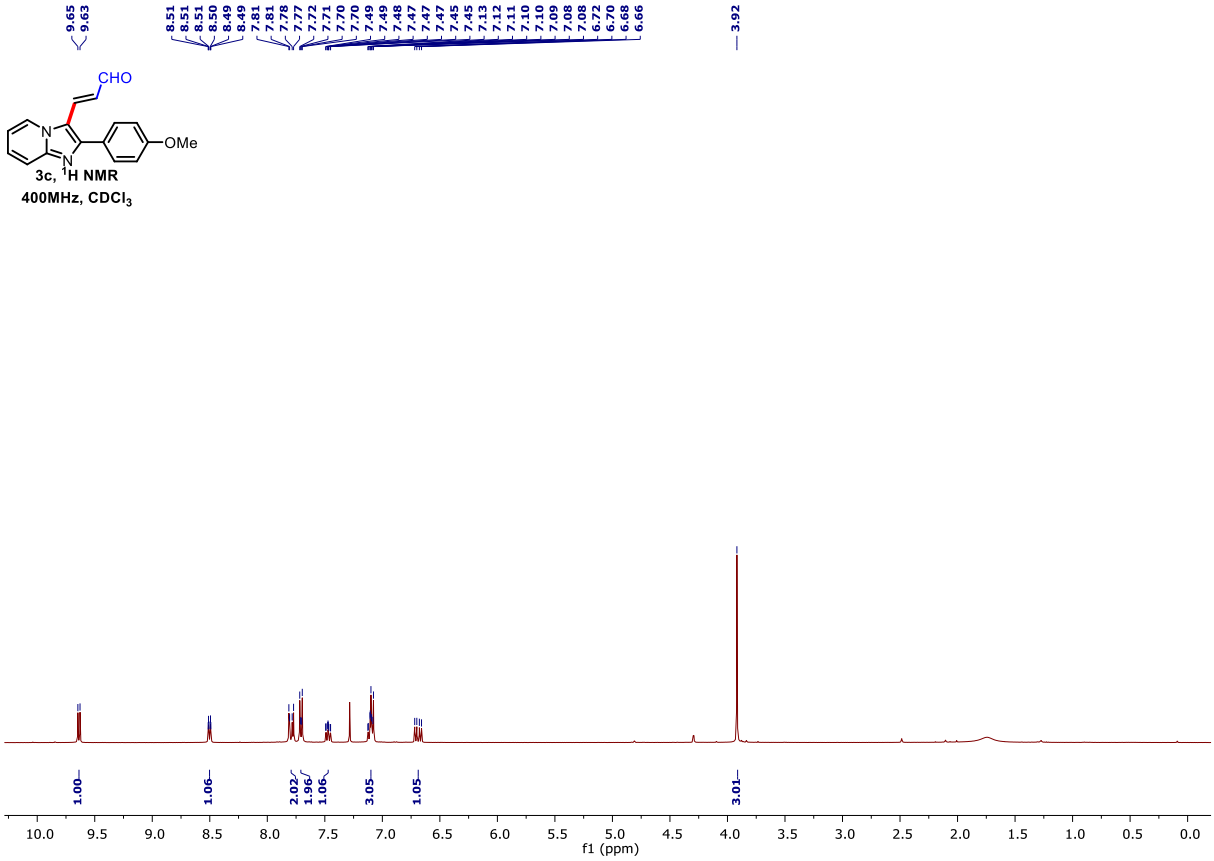

**3b, $^{1}$H NMR**
**400MHz, $CDCl_3$**

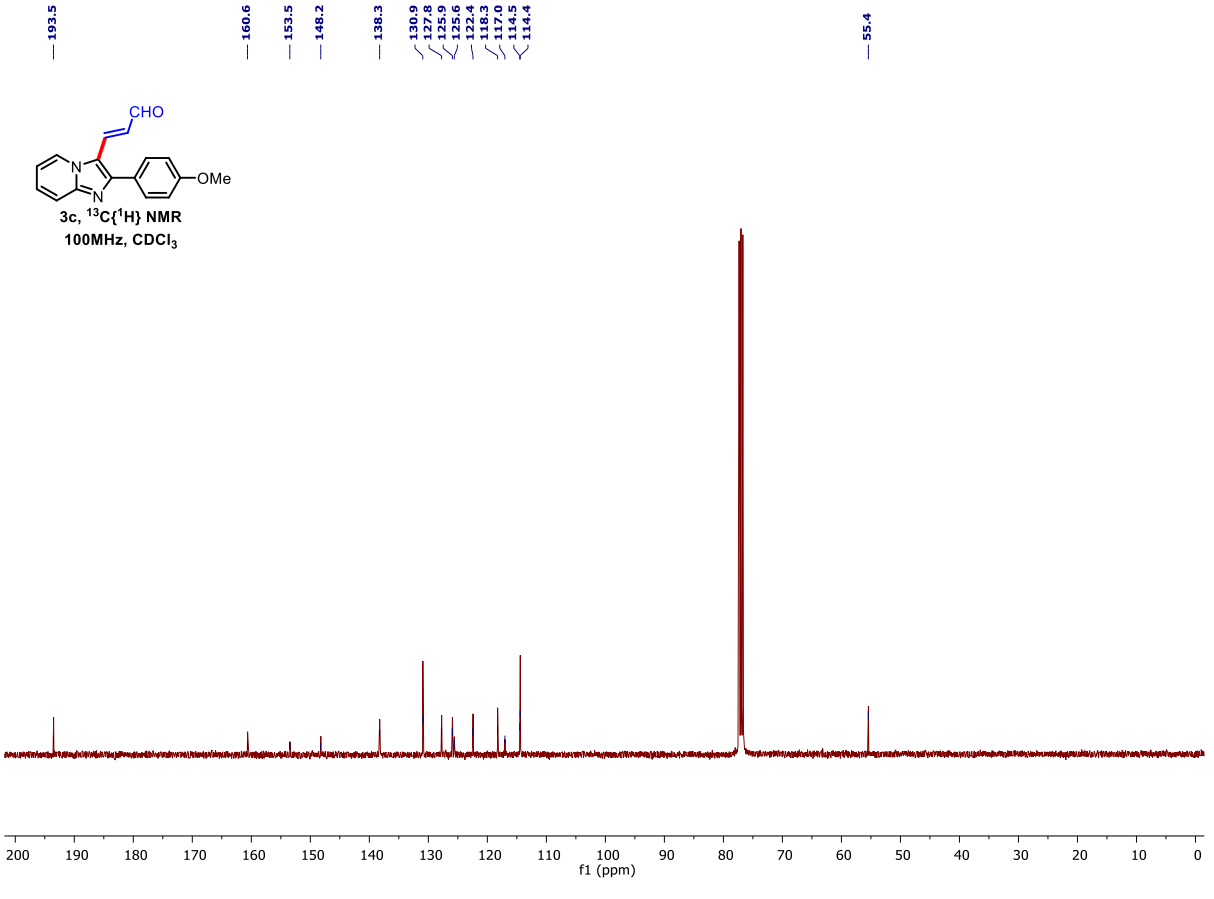


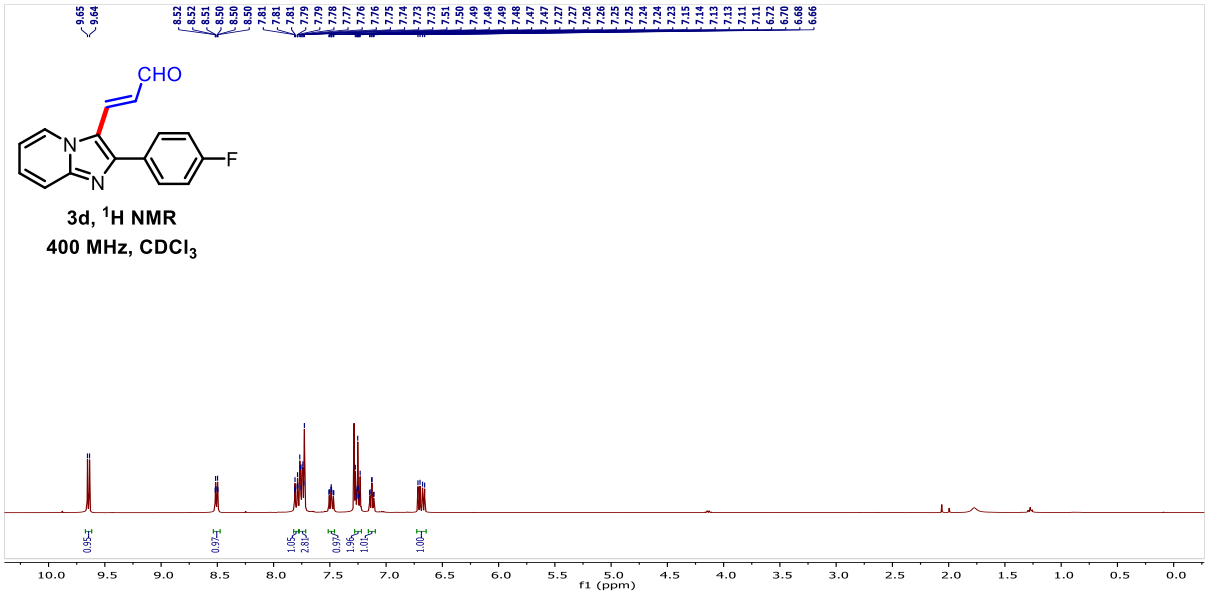



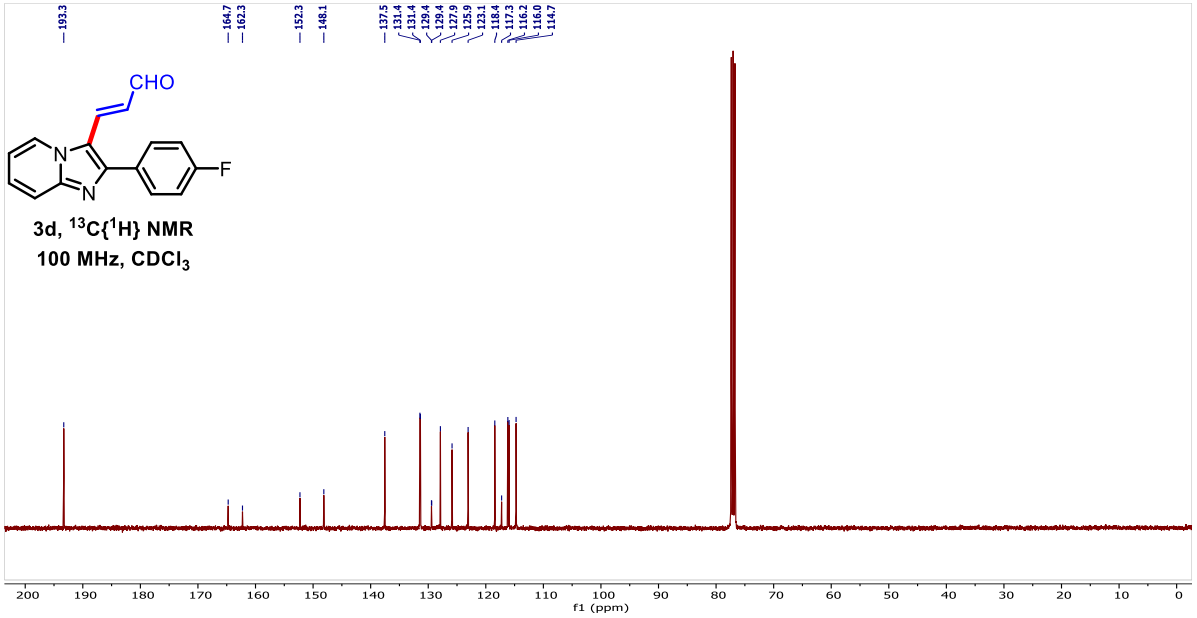

**3b, $^{13}C\{^{1}H\}$ NMR**
**100MHz, $CDCl_3$**

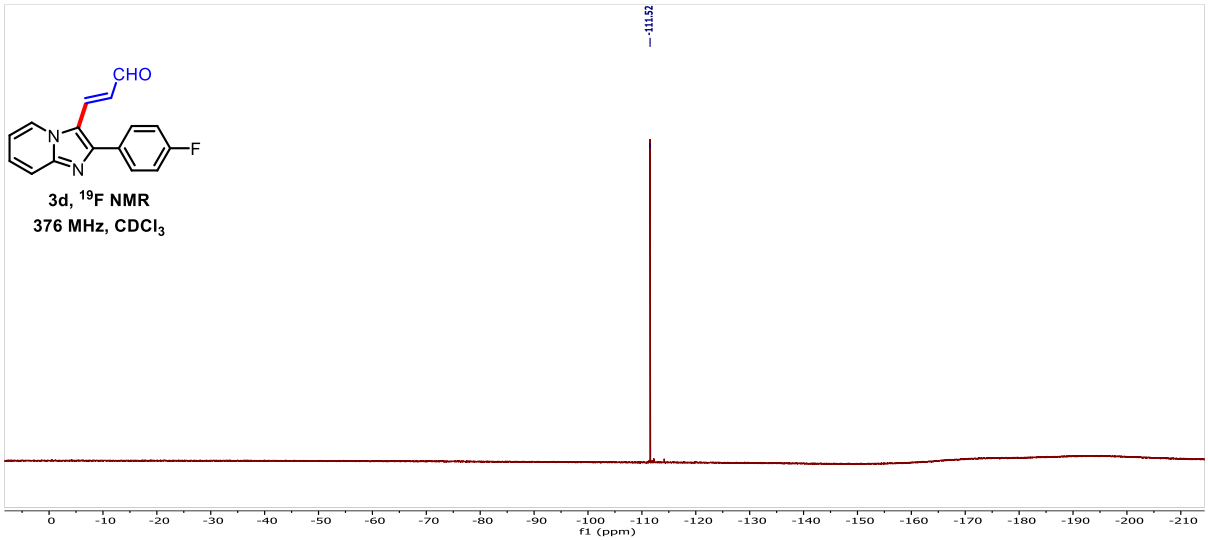


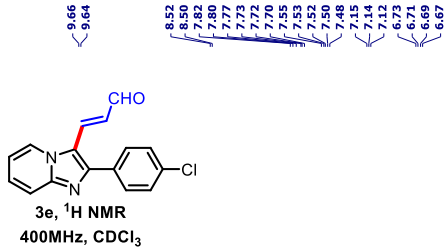

9.65
9.63
8.51
8.51
8.51
8.50
8.49
8.49
7.81
7.81
7.78
7.77
7.72
7.71
7.70
7.70
7.49
7.49
7.48
7.47
7.47
7.47
7.45
7.45
7.13
7.12
7.11
7.10
7.10
7.09
7.08
7.08
6.72
6.70
6.68
6.66
3.92
CHO
OMe
N
N
3c, $^{1}$H NMR
400MHz, CDCl$_3$
1.00
1.06
2.02
1.96
1.06
3.05
1.05
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


193.5
160.6
153.5
148.2
138.3
130.9
127.8
125.9
125.6
122.4
118.3
117.0
114.5
114.4
55.4
CHO
OMe
N
N
3c, $^{13}$C{$^{1}$H} NMR
100MHz, CDCl$_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

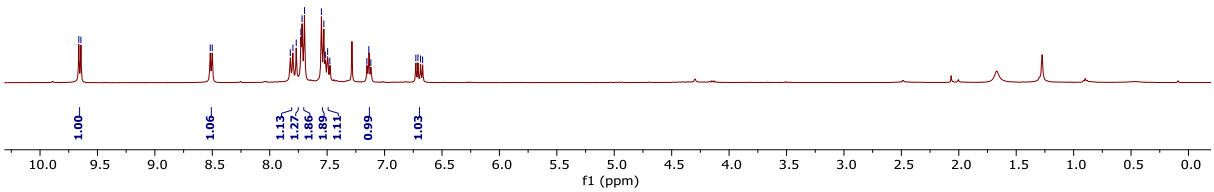

CHO
N
N
F
3d, $^{1}$H NMR
400 MHz, $CDCl_3$
f1 (ppm)

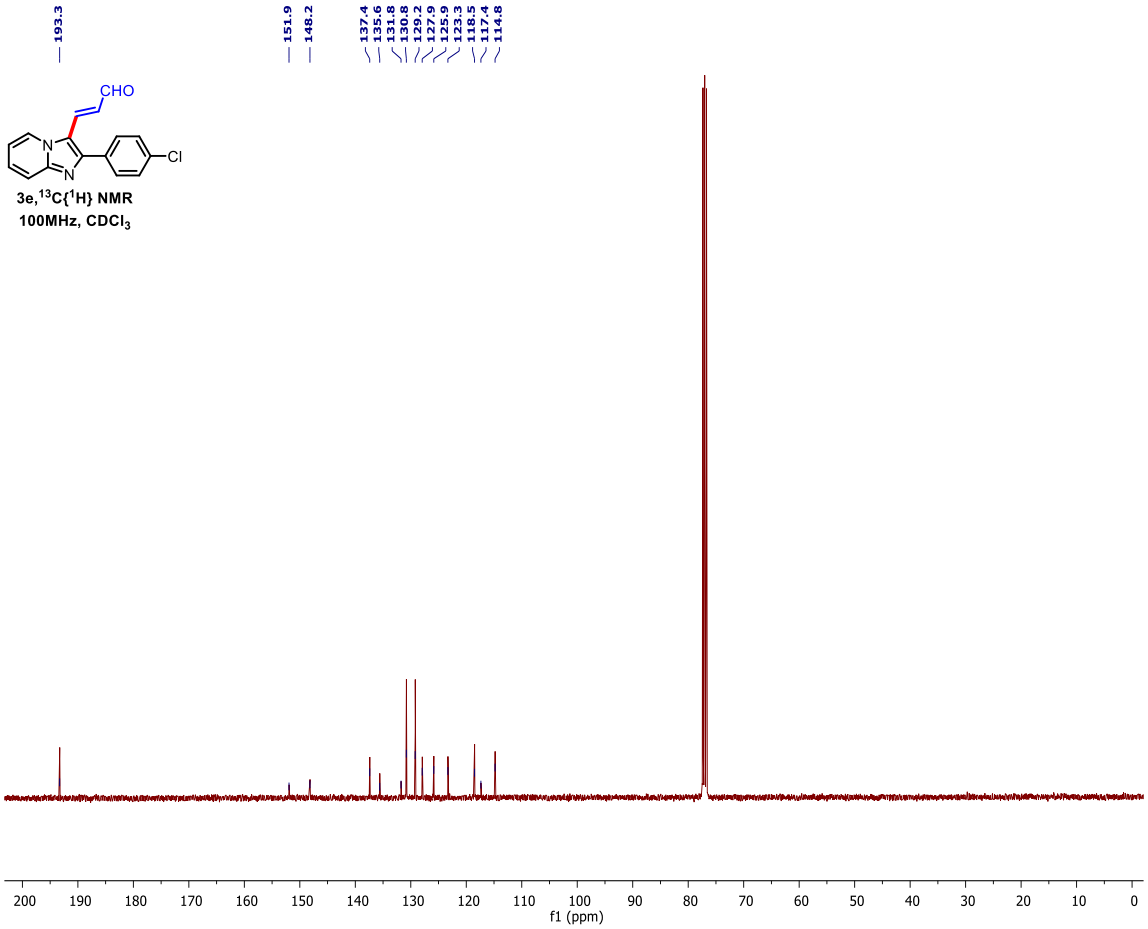

CHO
N
N
F
3d, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$
f1 (ppm)


CHO
N
N
F
3d, $^{19}$F NMR
376 MHz, $CDCl_3$
f1 (ppm)

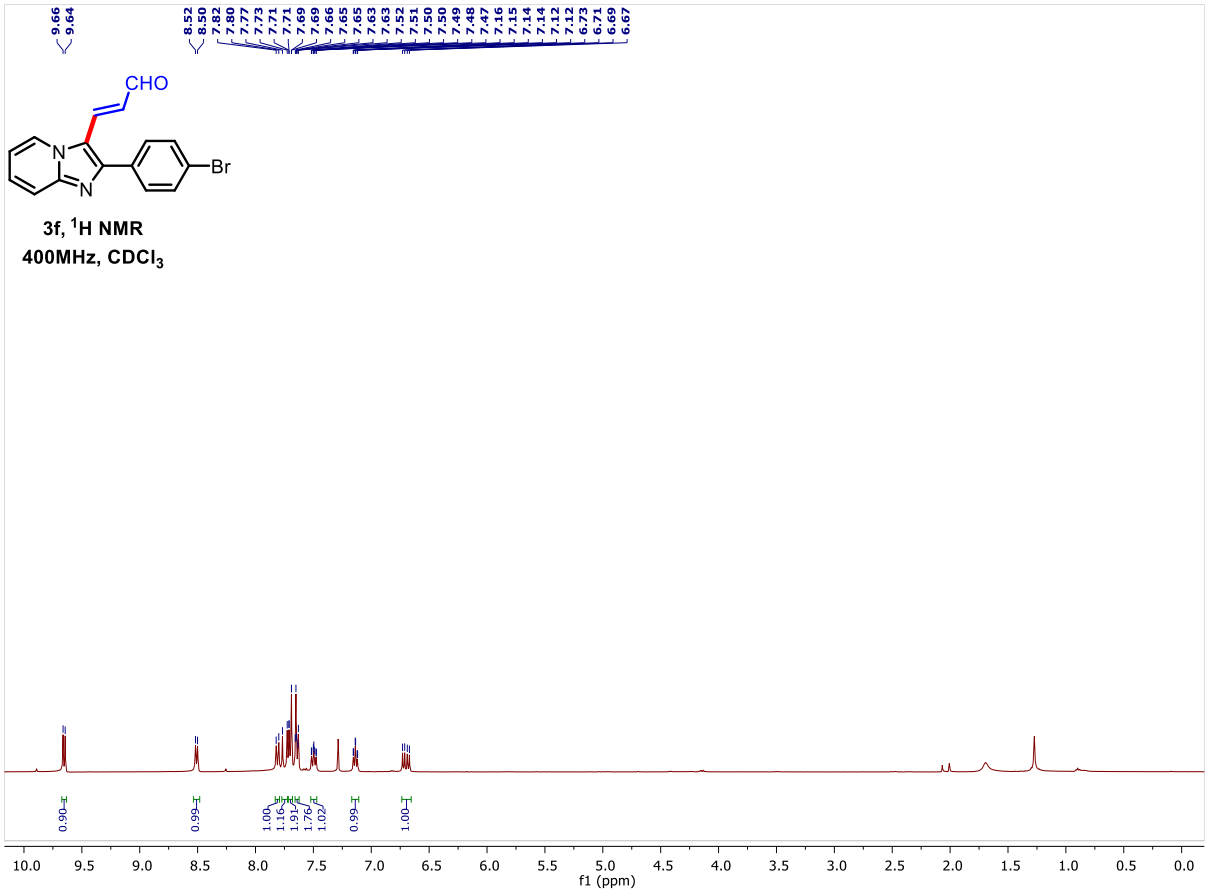



**3e, $^{1}$H NMR**
**400MHz, $CDCl_3$**

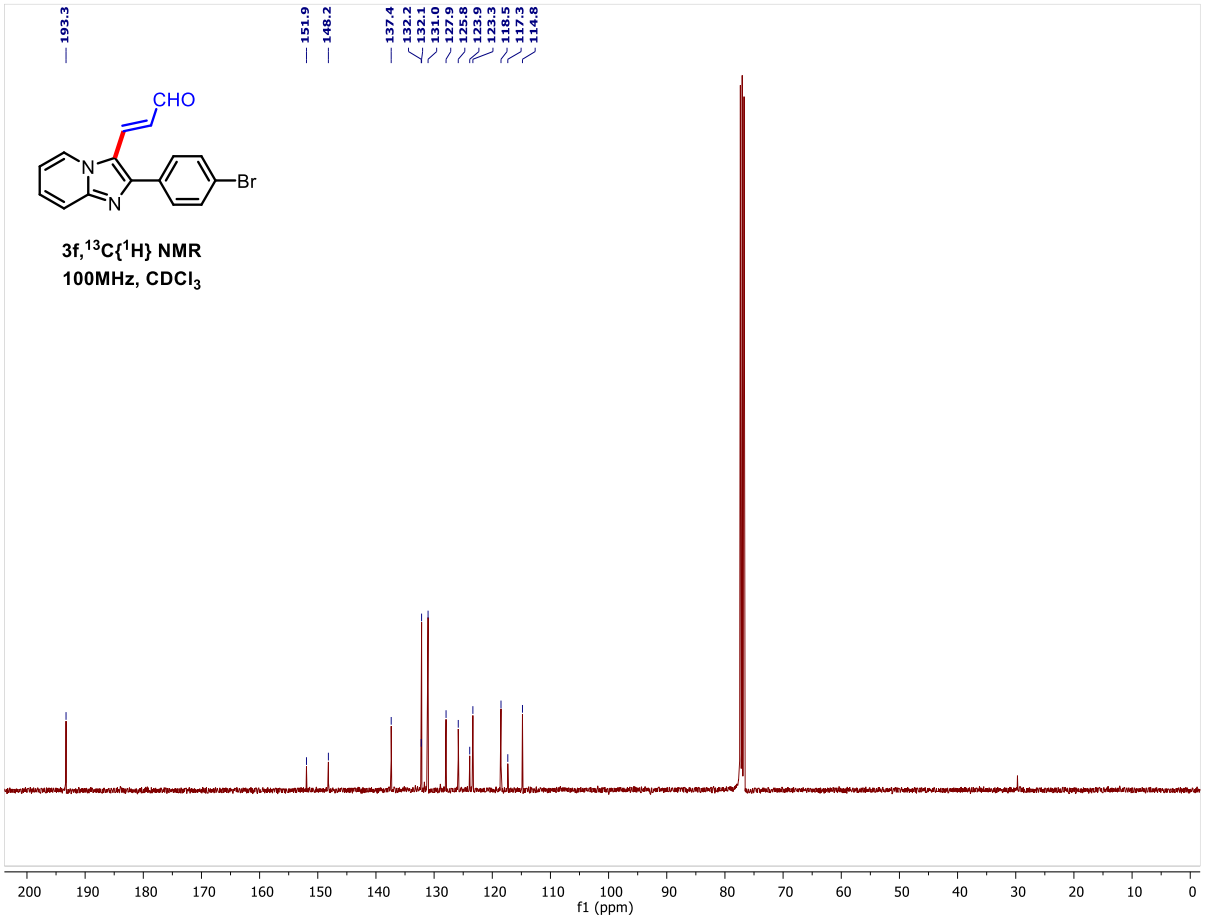


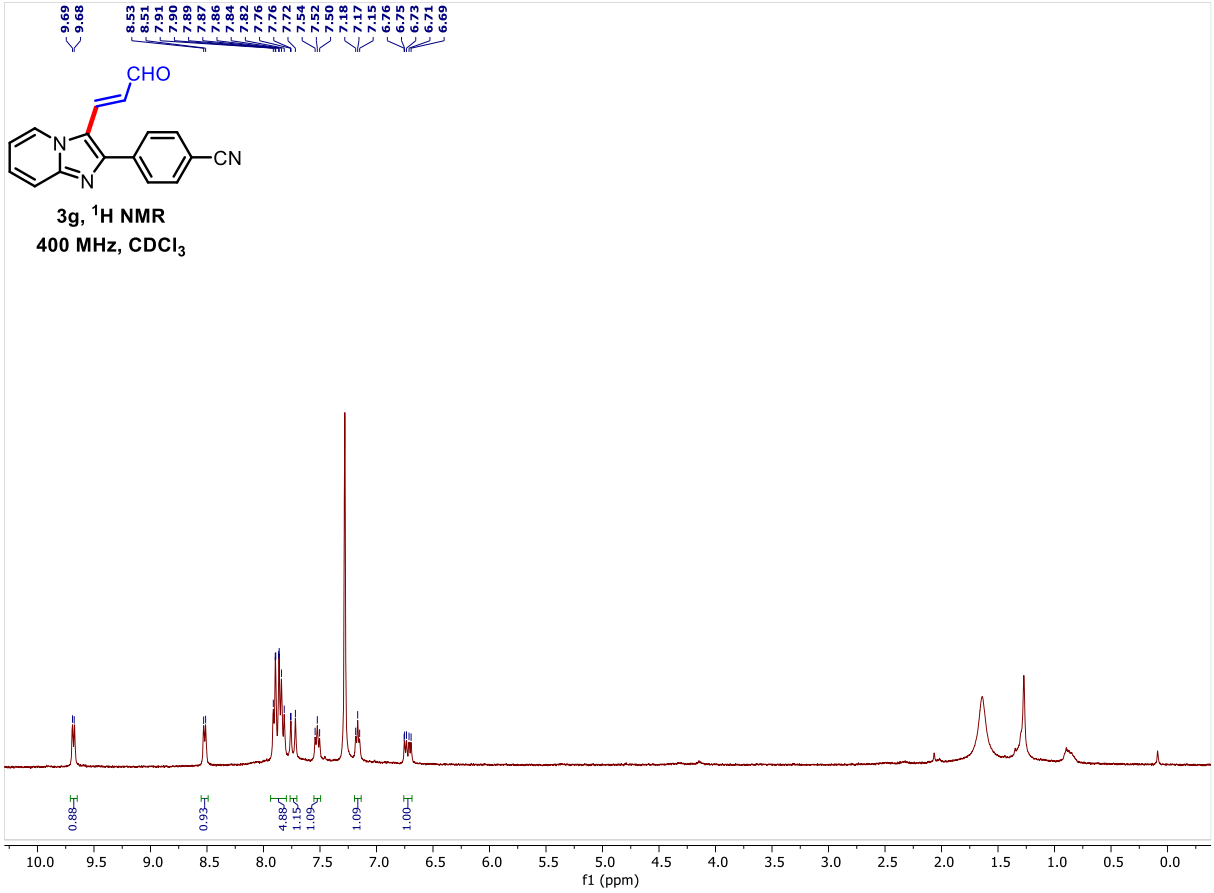

**3e,$^{13}$C{$^{1}$H} NMR**
**100MHz, $CDCl_3$**



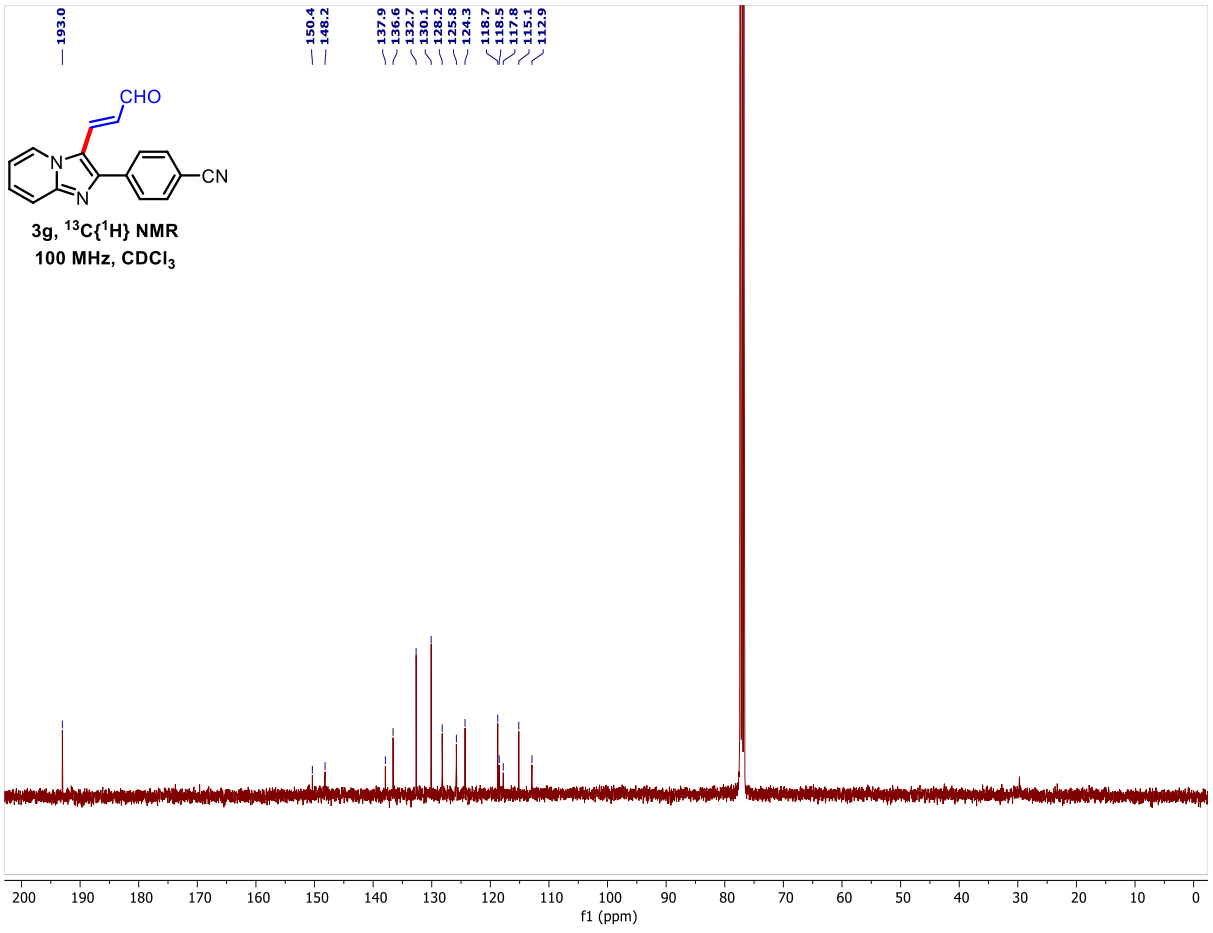

**3f, $^{1}$H NMR**
**400MHz, $CDCl_3$**



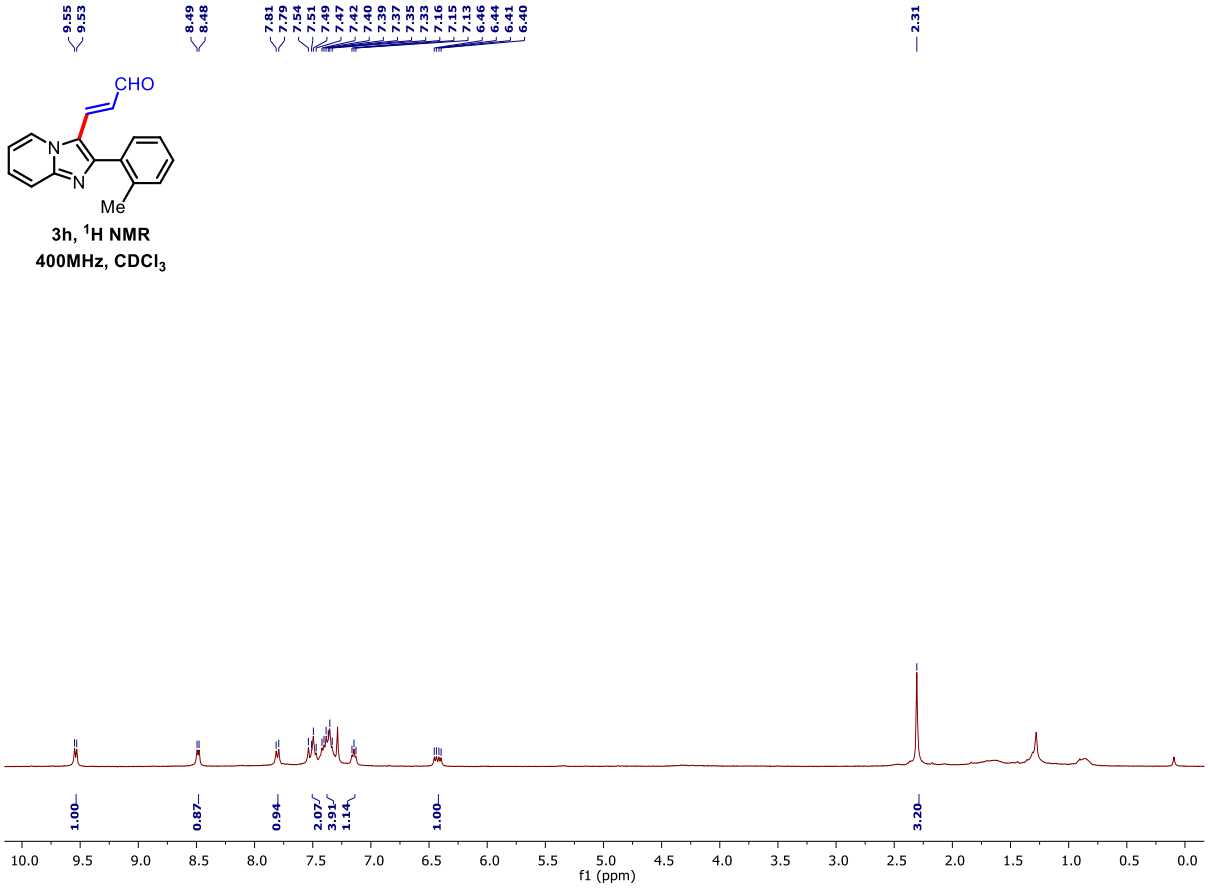

**3f, $^{13}C\{^{1}H\}$ NMR**
**100MHz, $CDCl_3$**



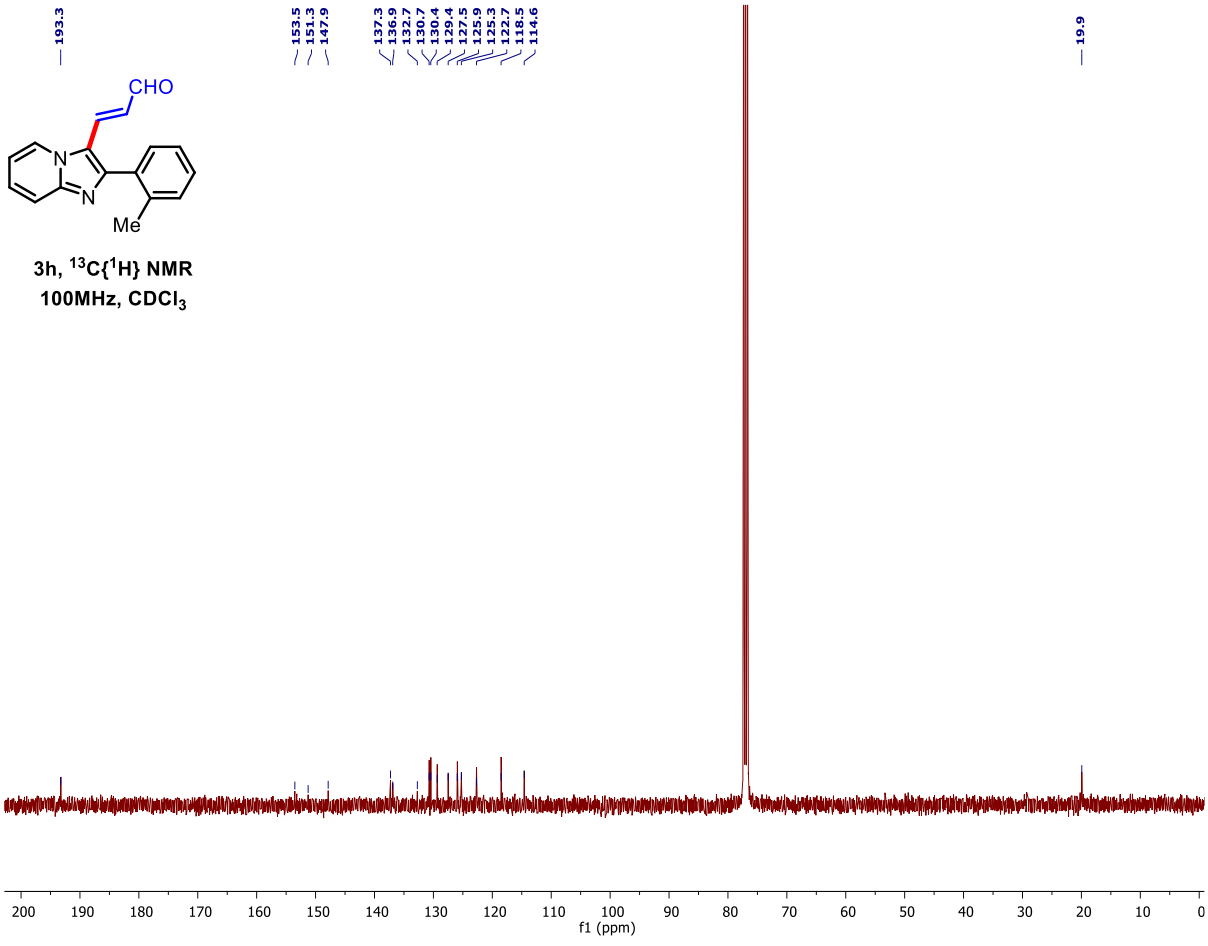

**3g, $^{1}$H NMR**
**400 MHz, $CDCl_3$**



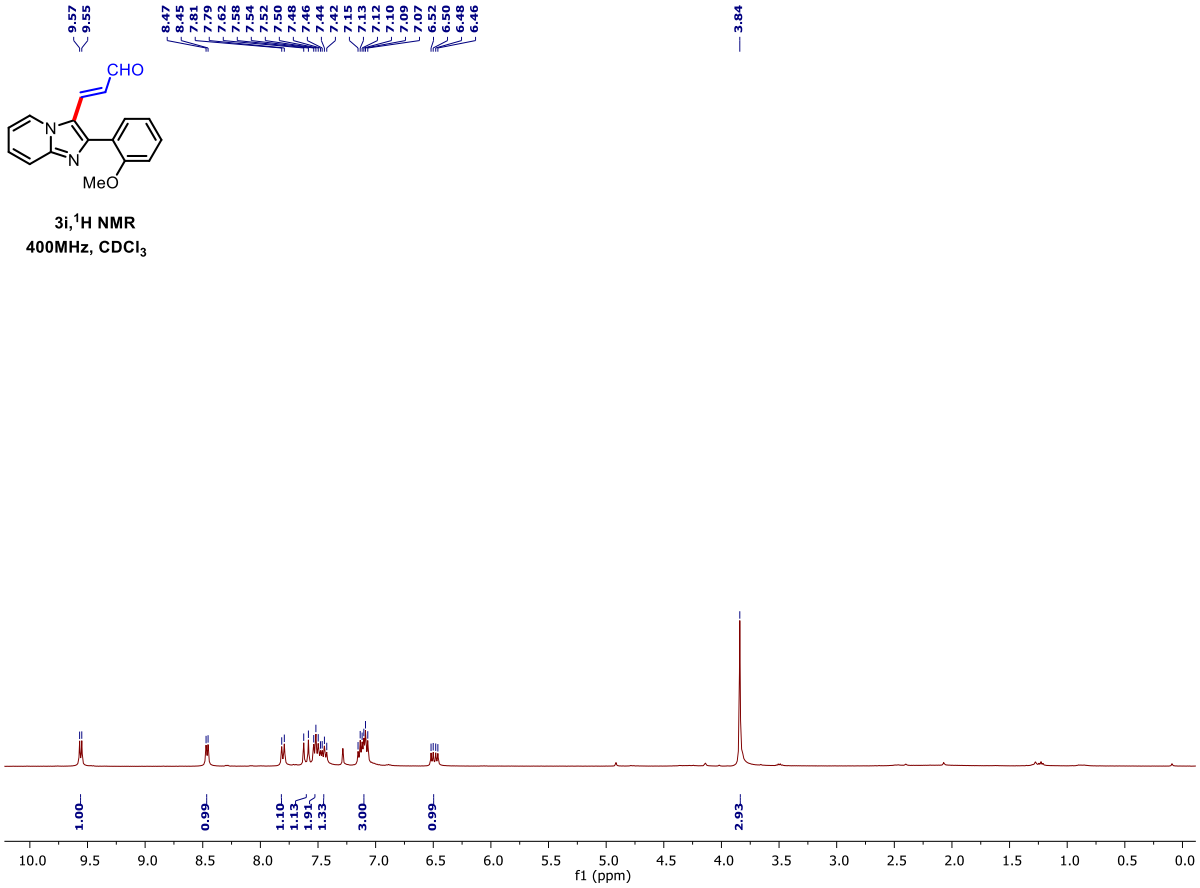

**3g, $^{13}$C{$^{1}$H} NMR**
**100 MHz, $CDCl_3$**



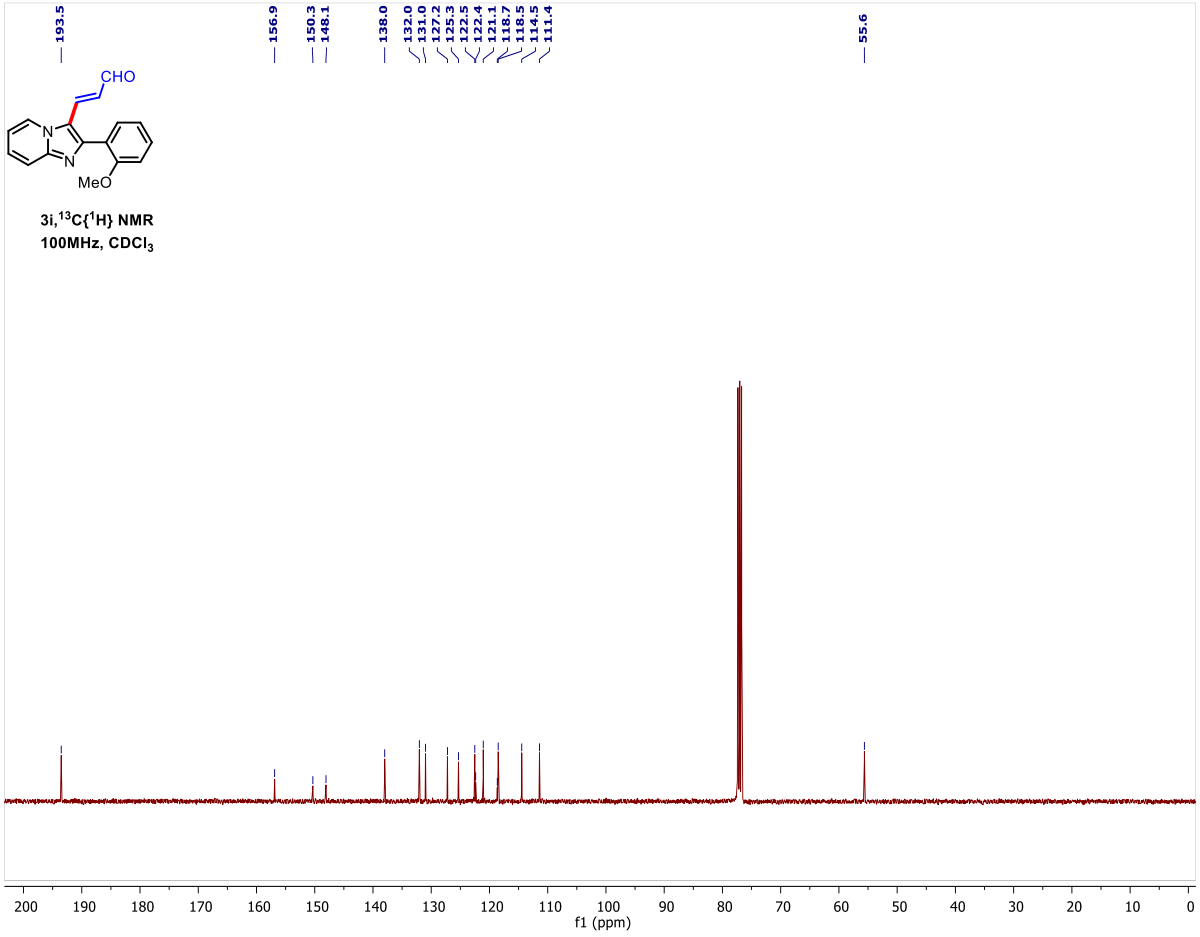

**3h, $^{1}$H NMR**
**400MHz, $CDCl_3$**



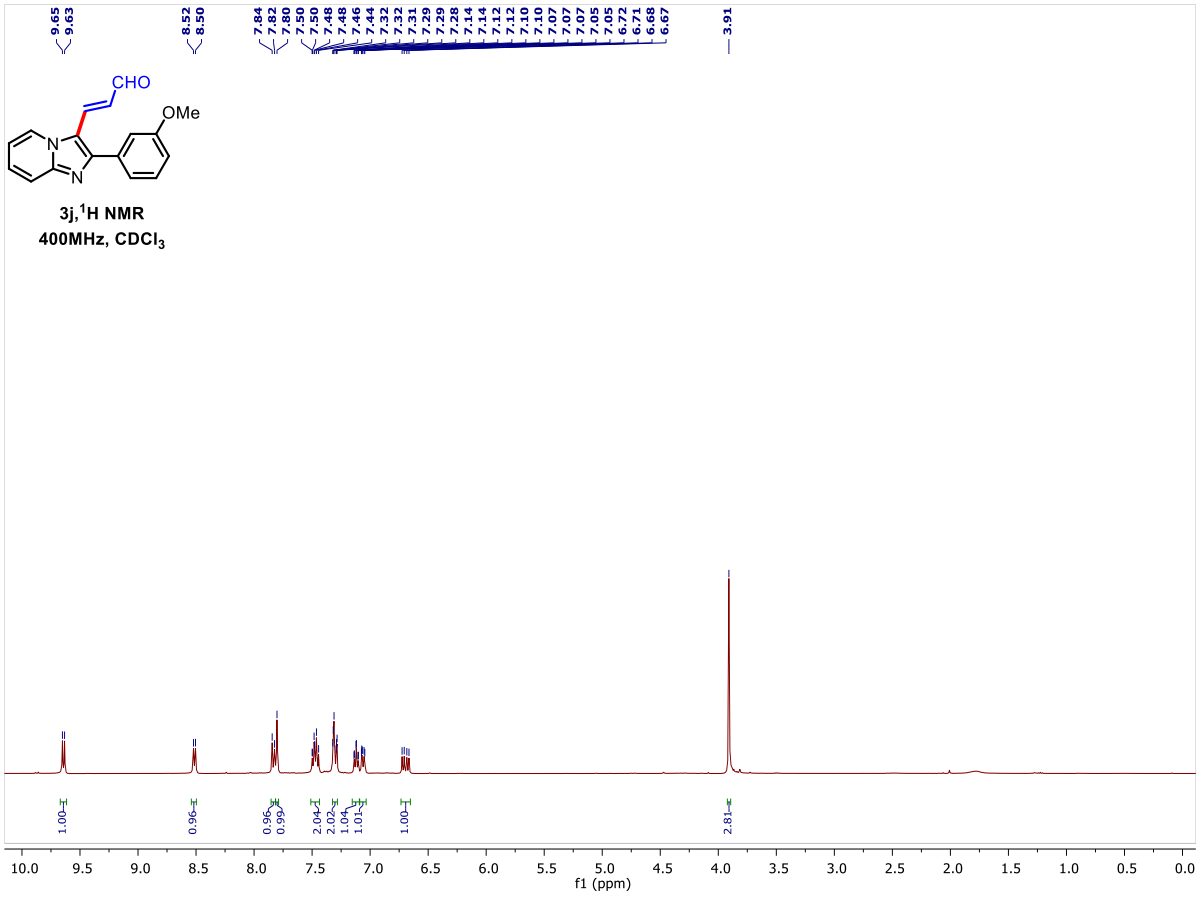

**3h, $^{13}$C{$^{1}$H} NMR**
**100MHz, $CDCl_3$**

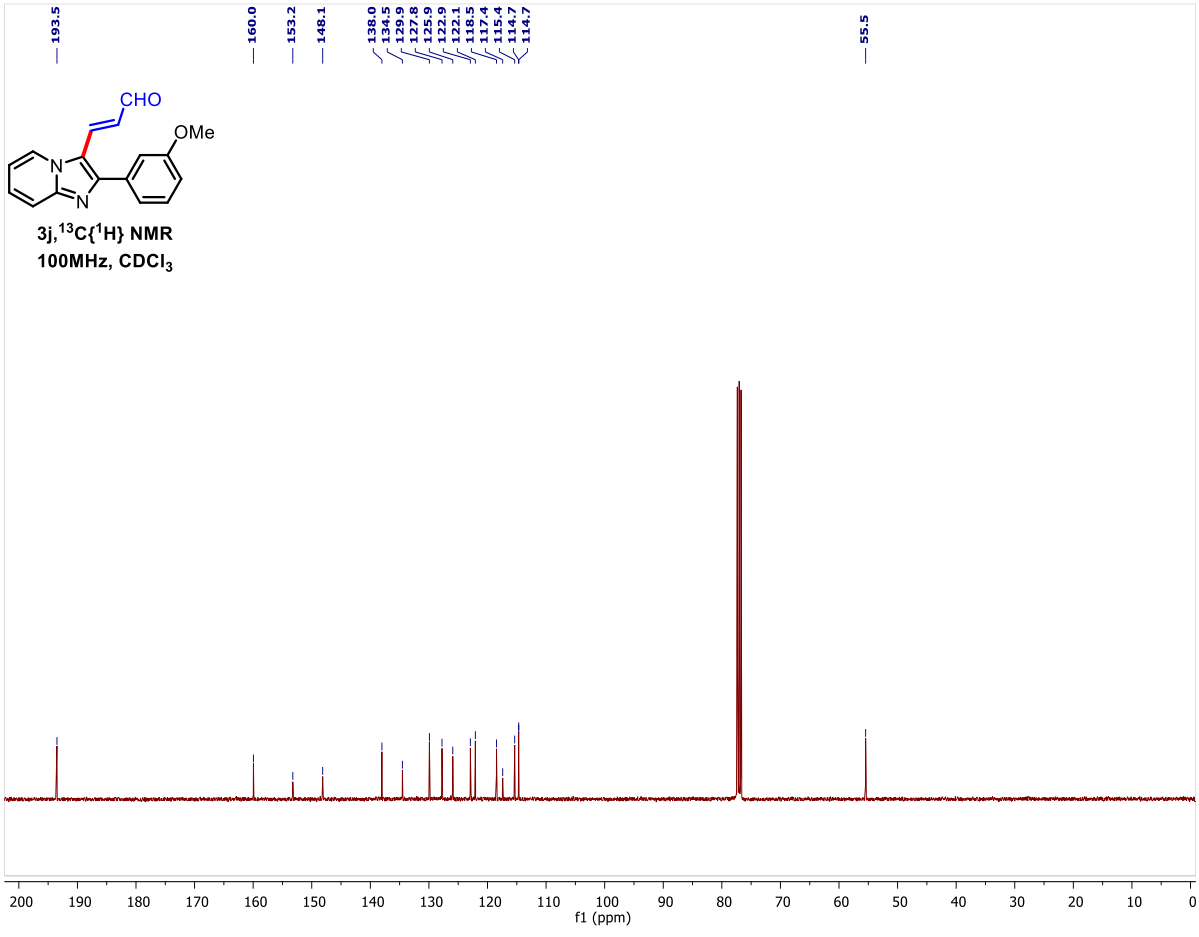


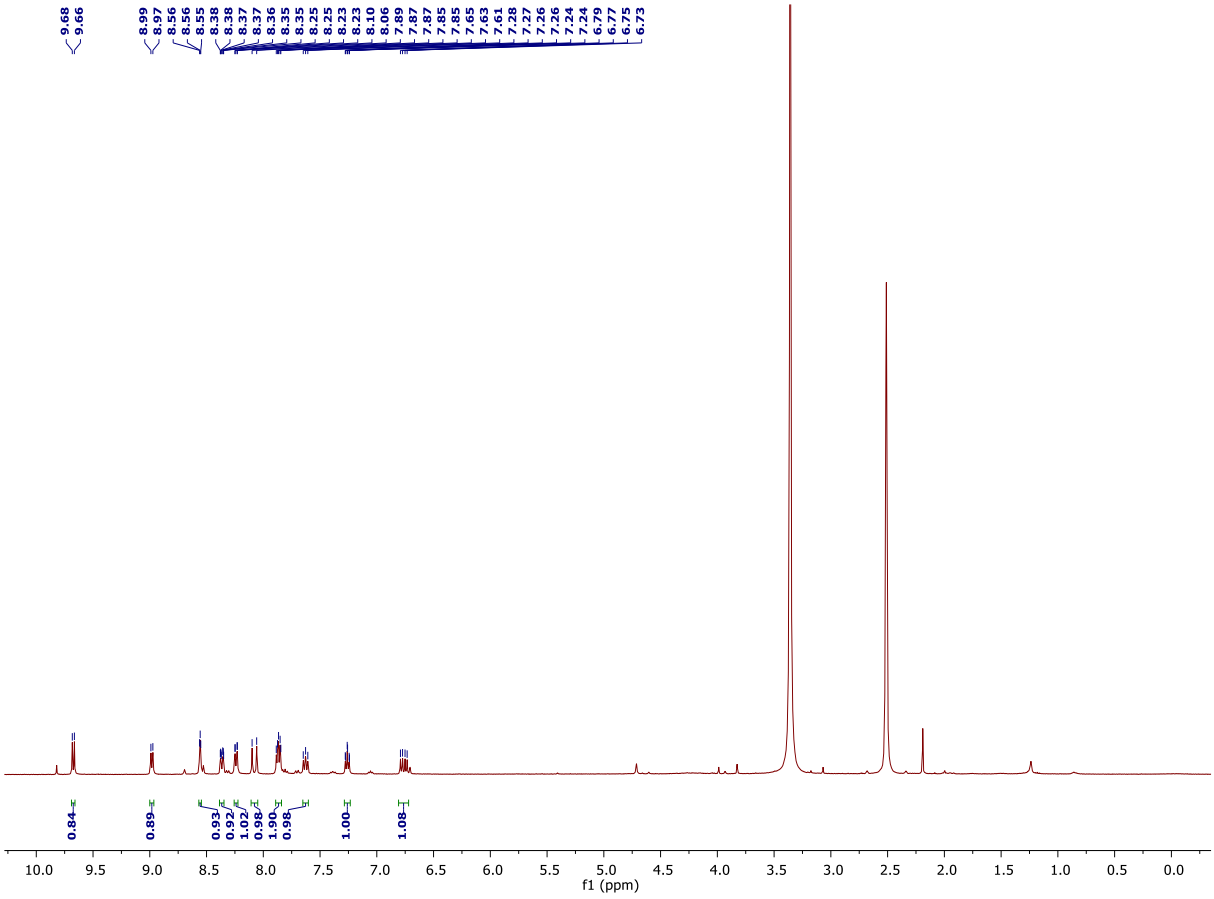

**3i,$^{1}$H NMR**
**400MHz, $CDCl_3$**

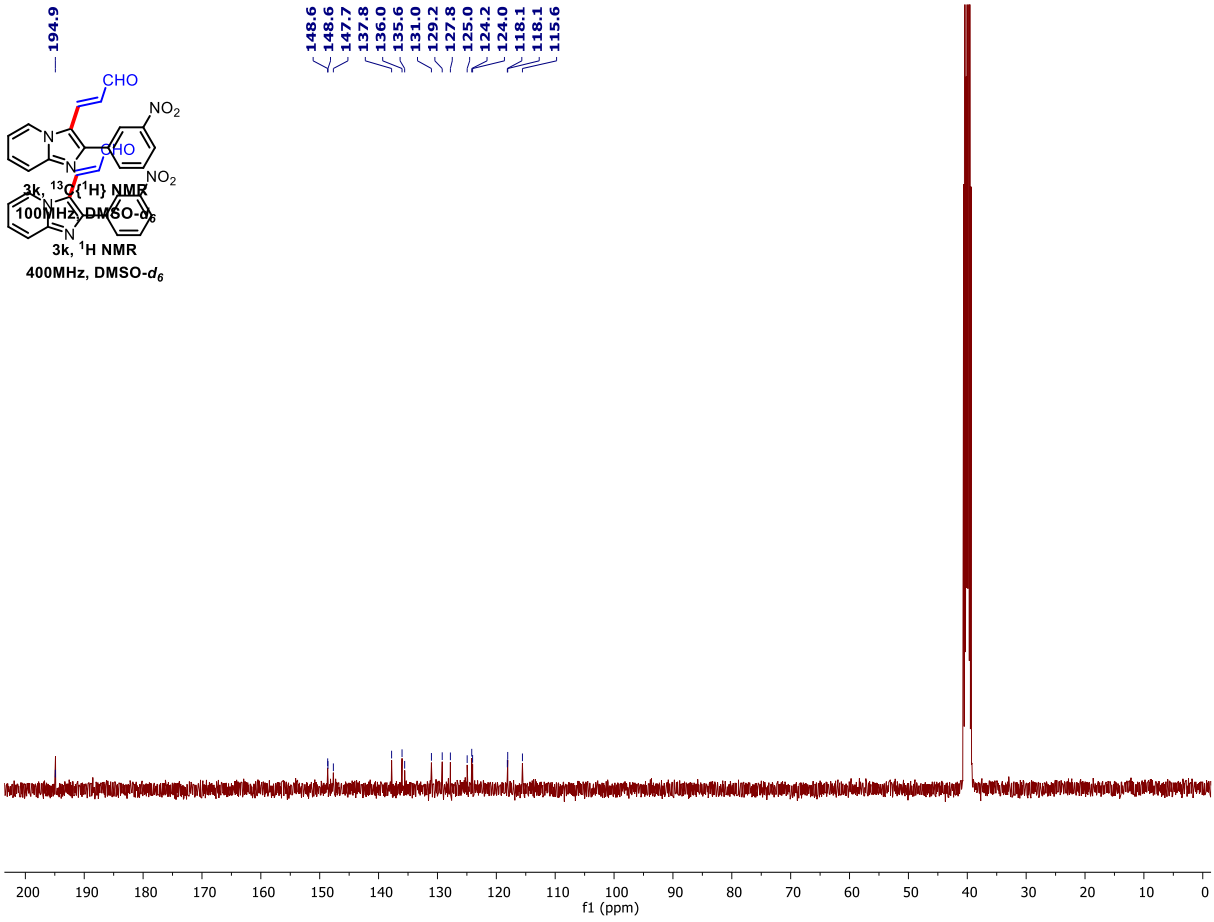


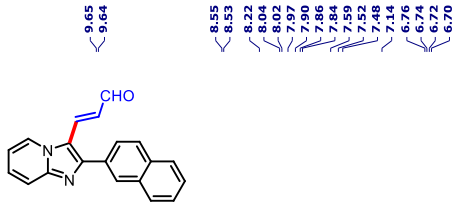

**3i,$^{13}$C{$^{1}$H} NMR**
**100MHz, $CDCl_3$**


9.65
9.63
8.52
8.50
7.84
7.82
7.80
7.50
7.48
7.46
7.44
7.32
7.31
7.29
7.28
7.14
7.12
7.10
7.07
7.07
7.05
7.05
6.72
6.71
6.68
6.67
3.91
CHO
OMe
N
N
3j,1H NMR
400MHz, CDCl3
1.00
0.96
0.96
0.99
2.04
2.02
1.04
1.01
1.00
2.81
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

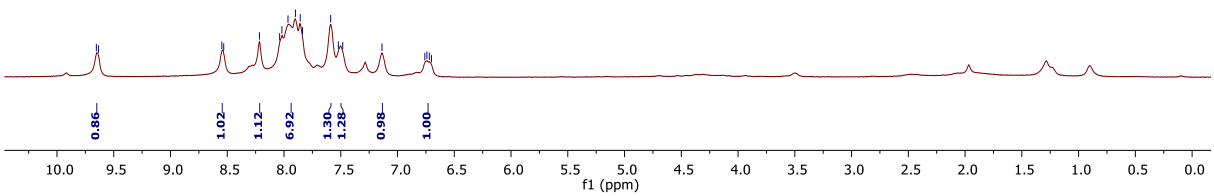

193.5
160.0
153.2
148.1
138.0
134.5
129.9
127.8
125.9
122.9
122.1
118.5
117.4
115.4
114.7
114.7
55.5
CHO
OMe
N
N
3j,13C{1H} NMR
100MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

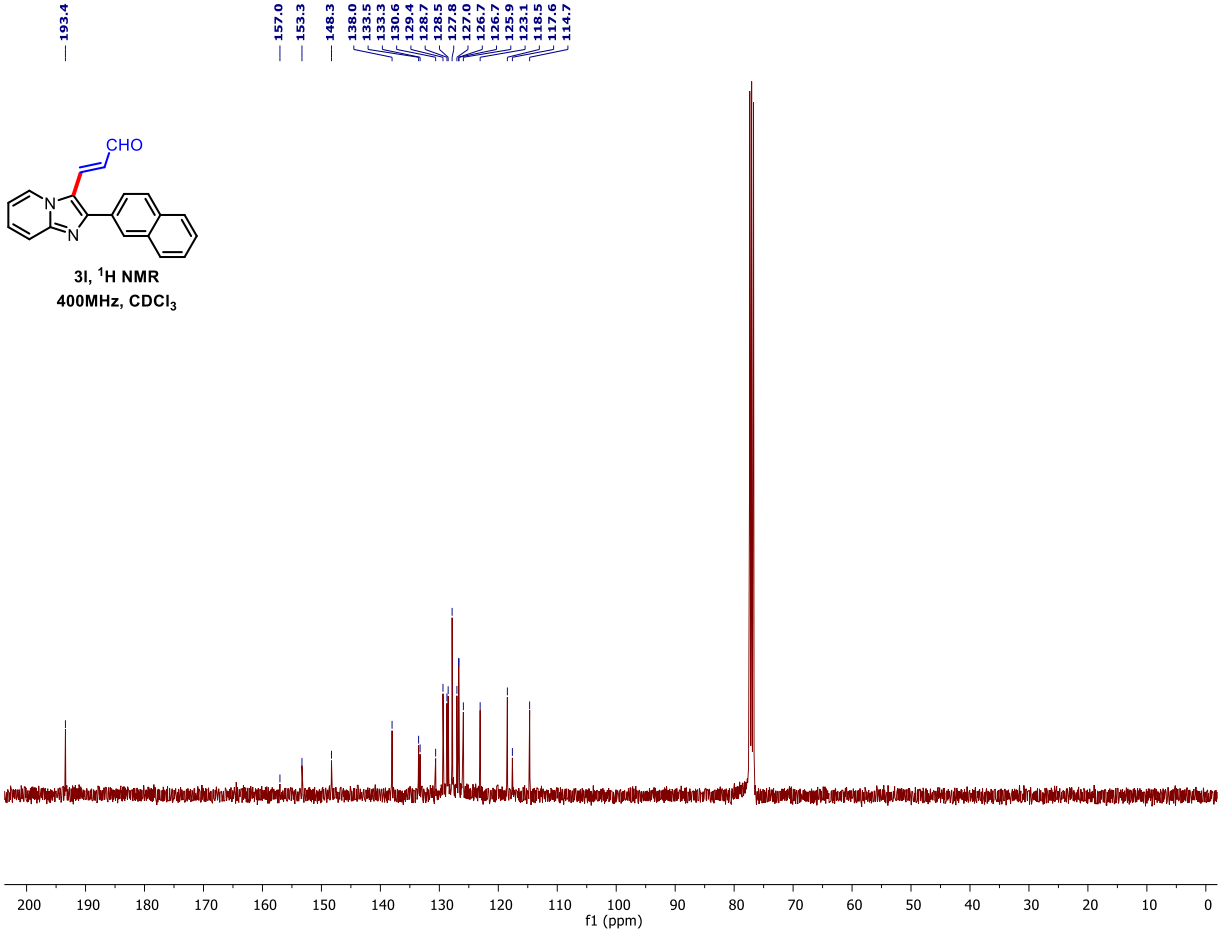

9.68
9.66
8.99
8.97
8.56
8.56
8.55
8.38
8.38
8.37
8.37
8.36
8.35
8.35
8.25
8.25
8.23
8.23
8.10
8.06
7.89
7.87
7.87
7.85
7.85
7.65
7.63
7.61
7.28
7.27
7.26
7.26
7.24
7.24
7.19
6.77
6.75
6.73
0.84
0.89
0.93
0.92
1.02
0.98
1.90
0.98
1.00
1.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


194.9
148.6
148.6
147.7
137.8
136.0
135.6
131.0
129.2
127.8
125.0
124.2
124.0
118.1
118.1
115.6
CHO
NO2
CHO
NO2
3k, 13C{1H} NMR
100MHz, DMSO-d6
3k, 1H NMR
400MHz, DMSO-d6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

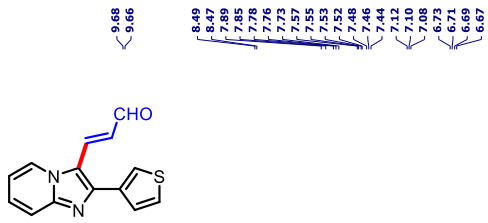



**3l, $^{13}C\{^{1}H\}$ NMR**
**100MHz, $CDCl_3$**

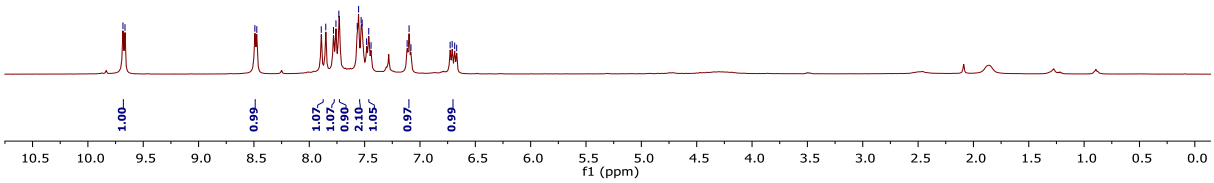


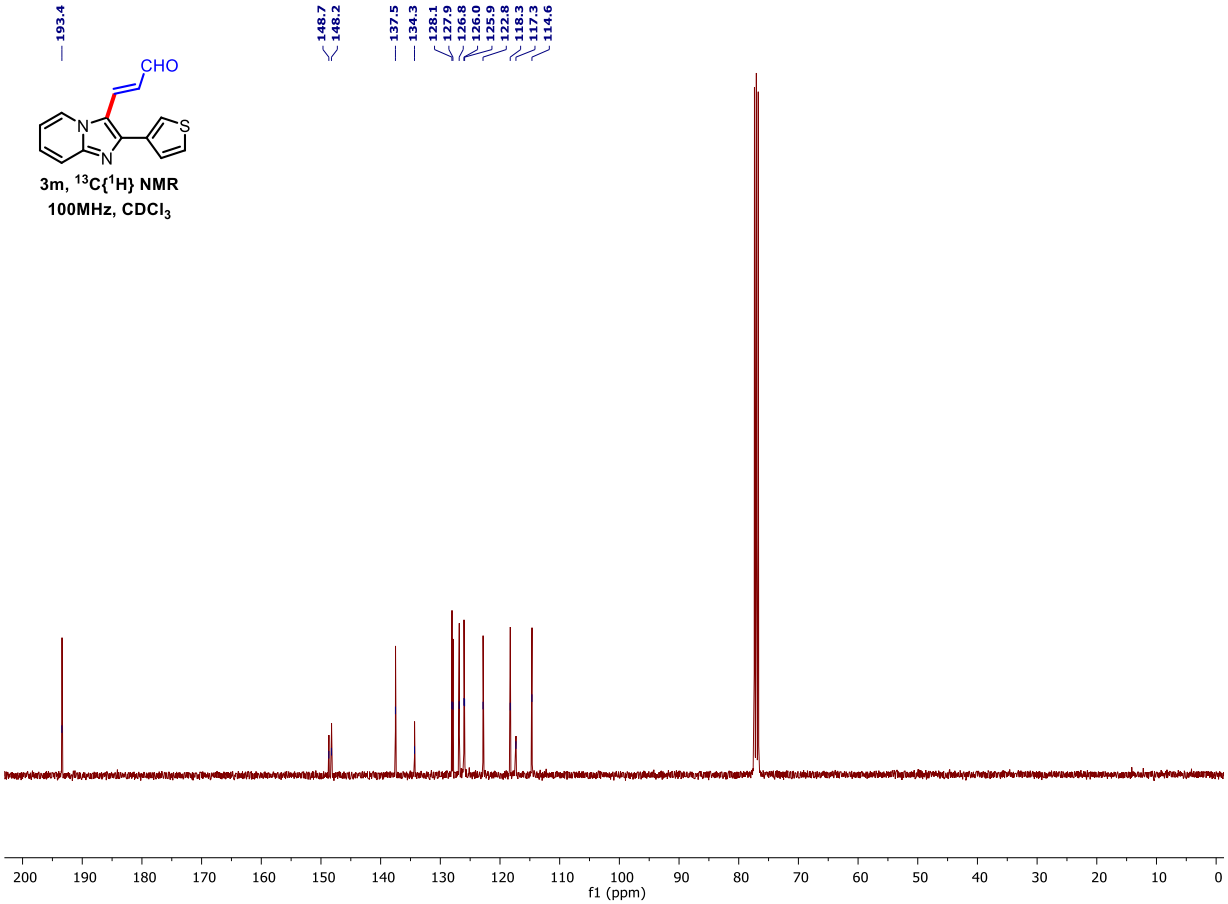




**3l, $^{1}H$ NMR**
**400MHz, $CDCl_3$**

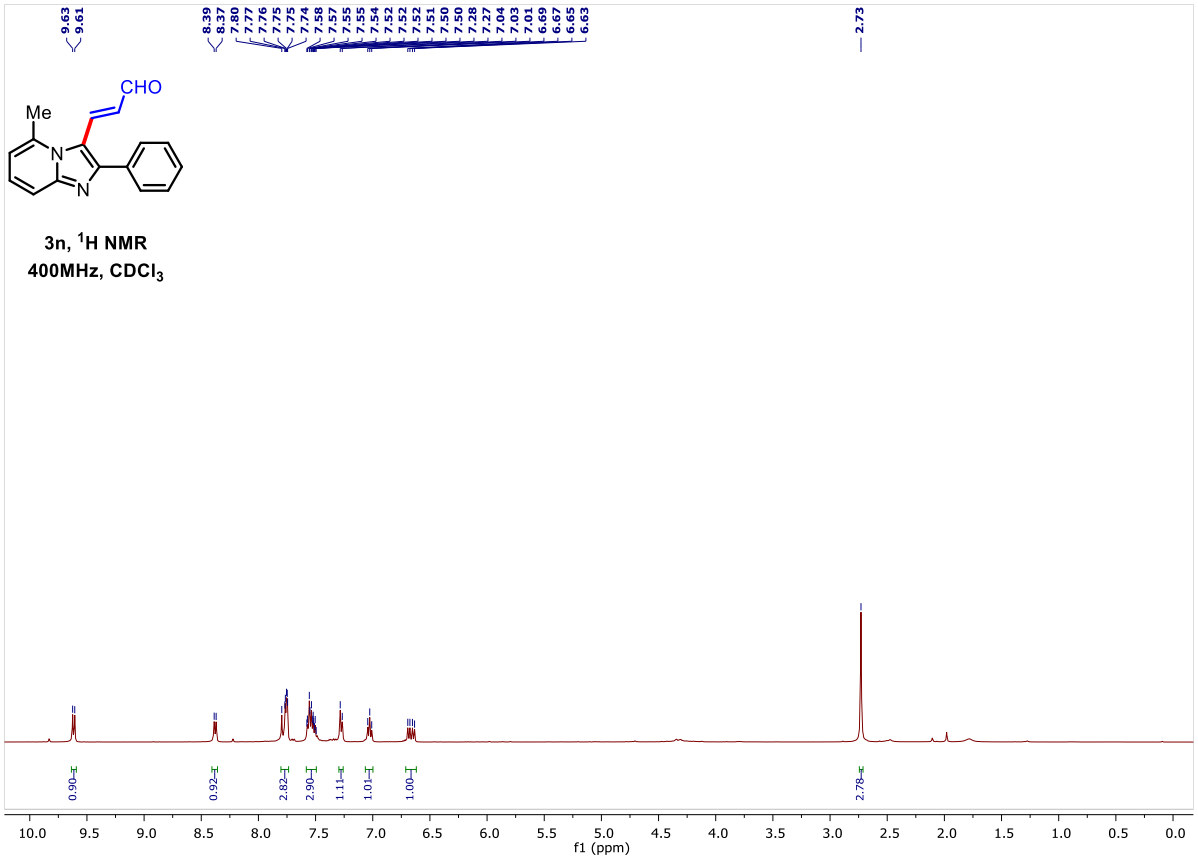



**3m, $^{1}$H NMR**
**400MHz, $CDCl_3$**

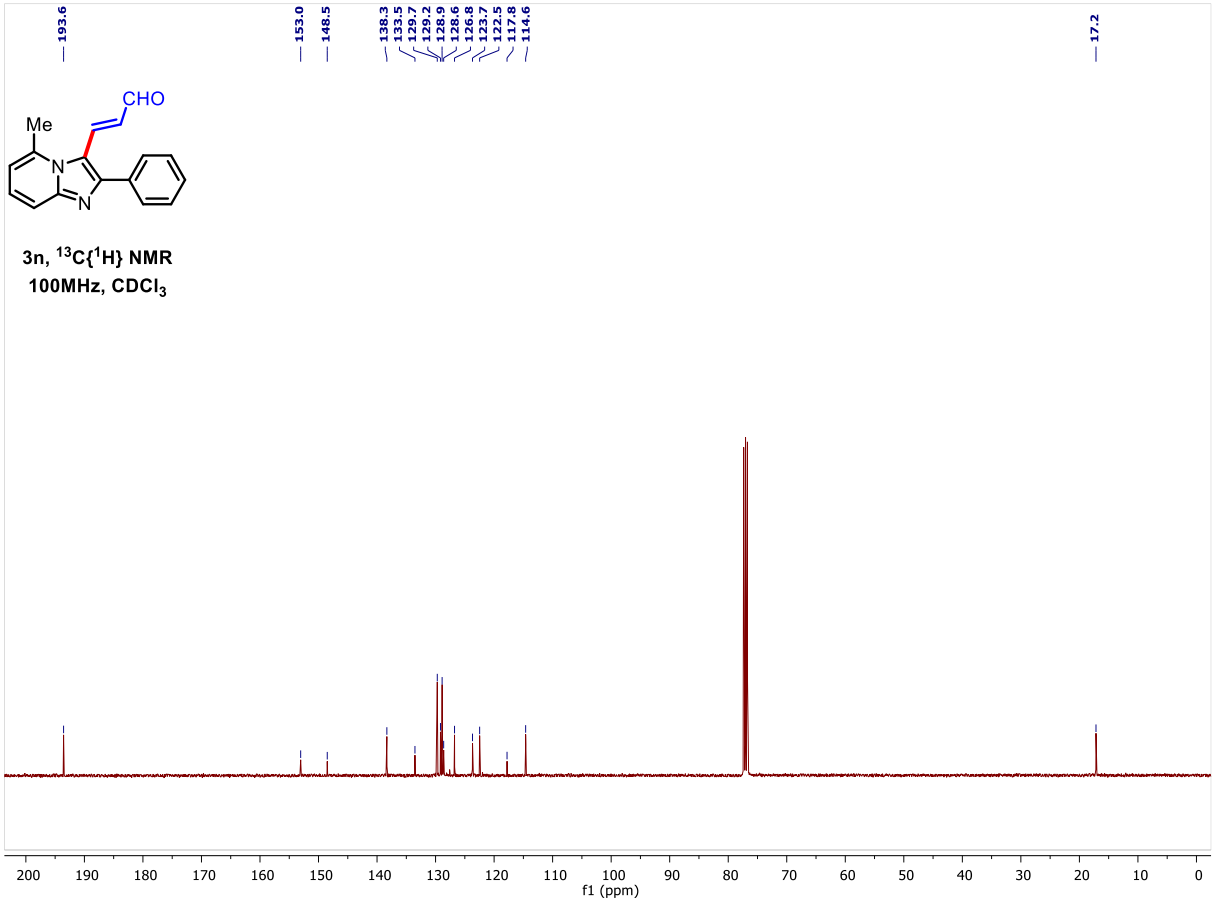


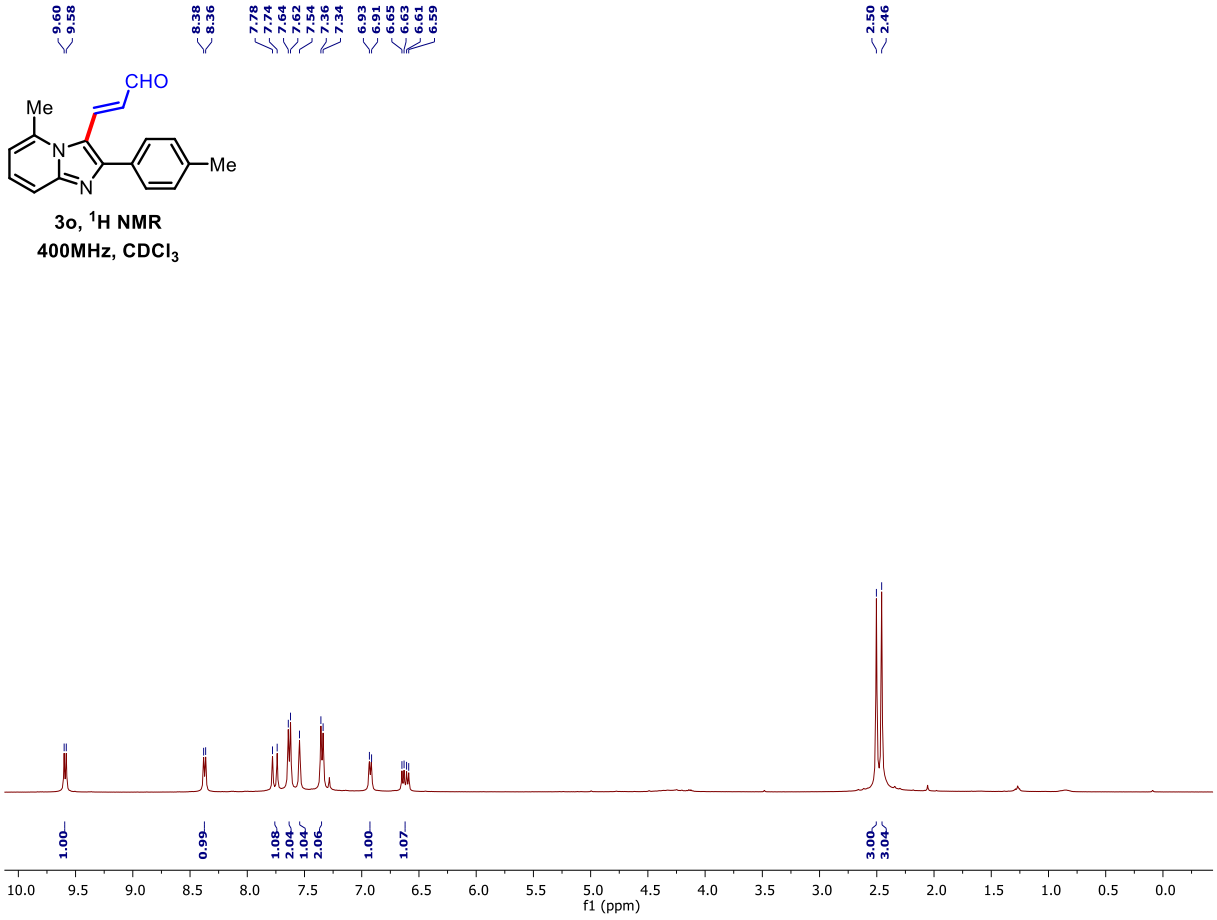

**3m, $^{13}C\{^{1}H\}$ NMR**
**100MHz, $CDCl_3$**

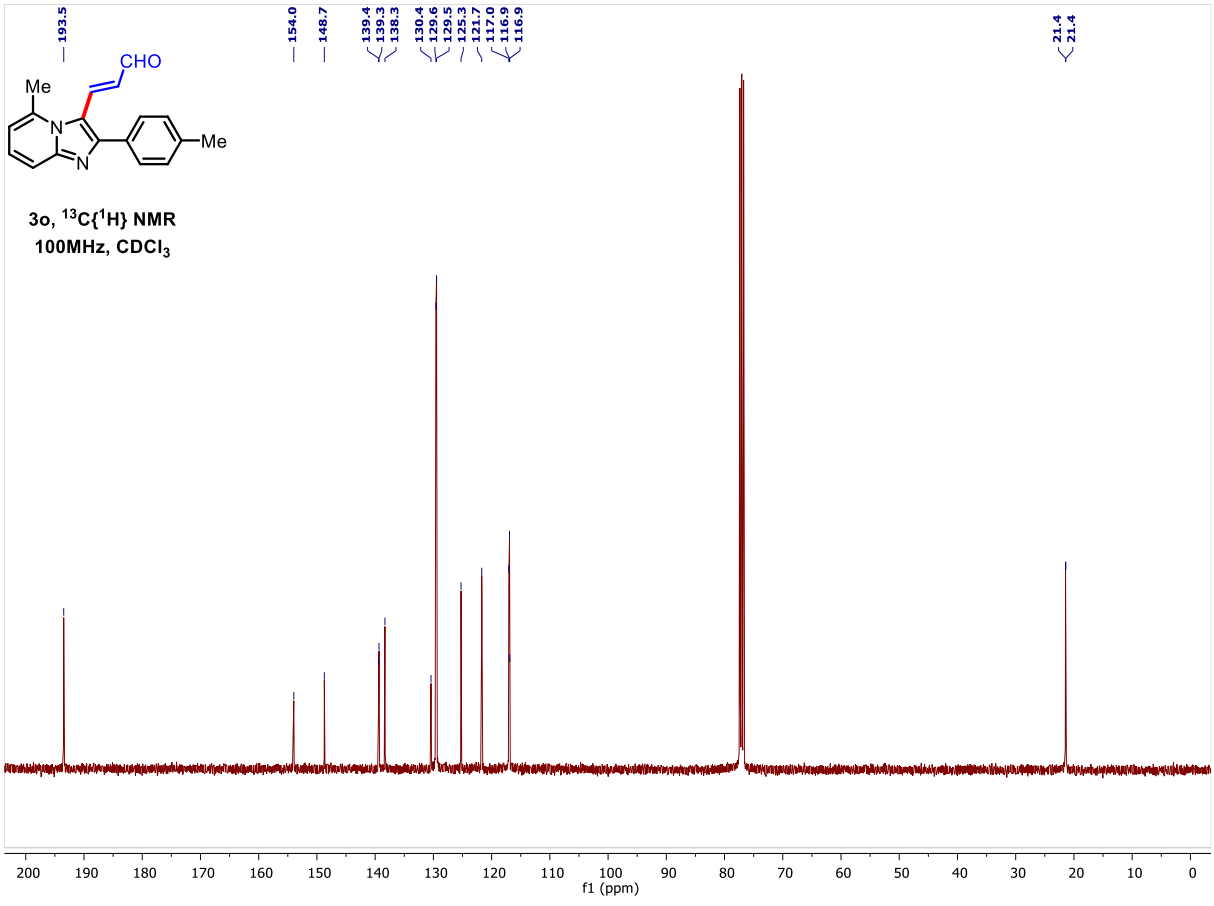


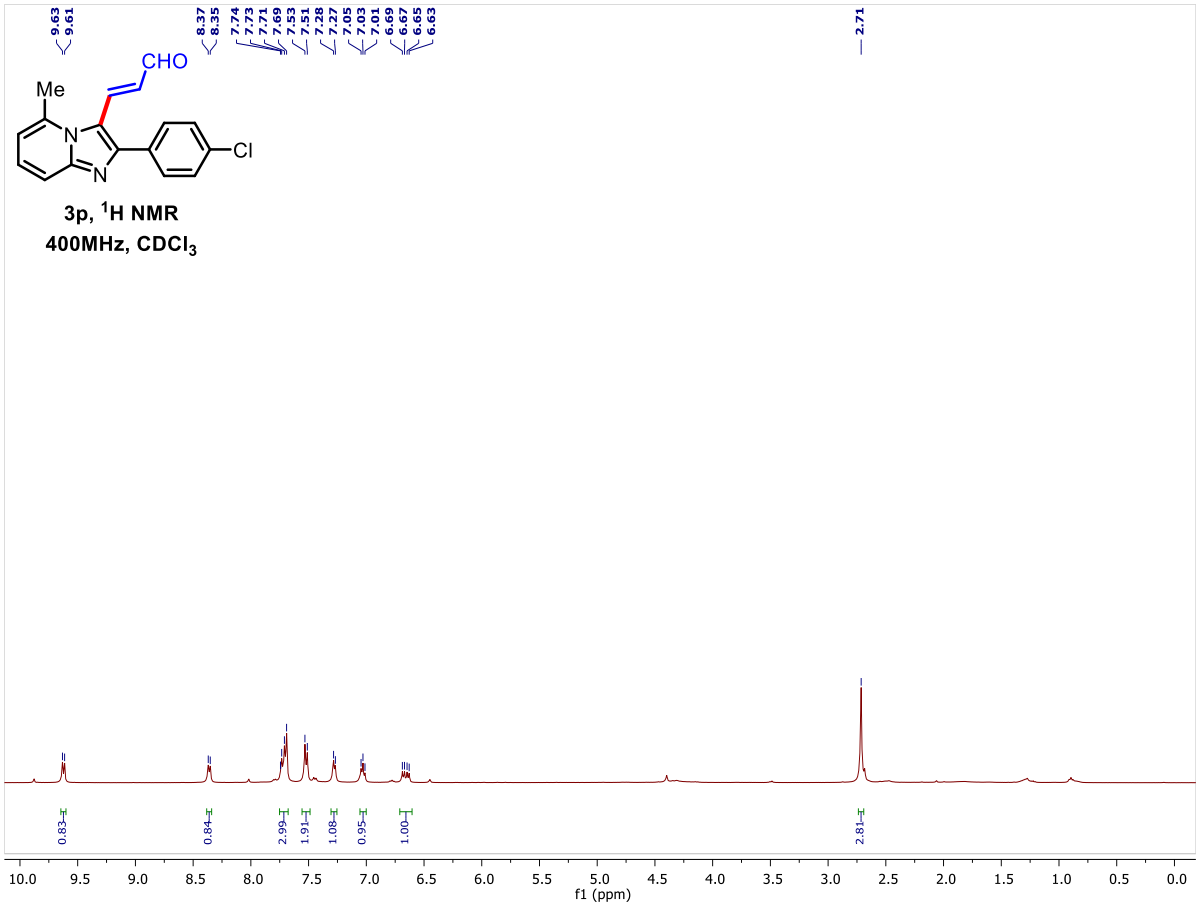

**3n, $^{1}$H NMR**
**400MHz, $CDCl_3$**



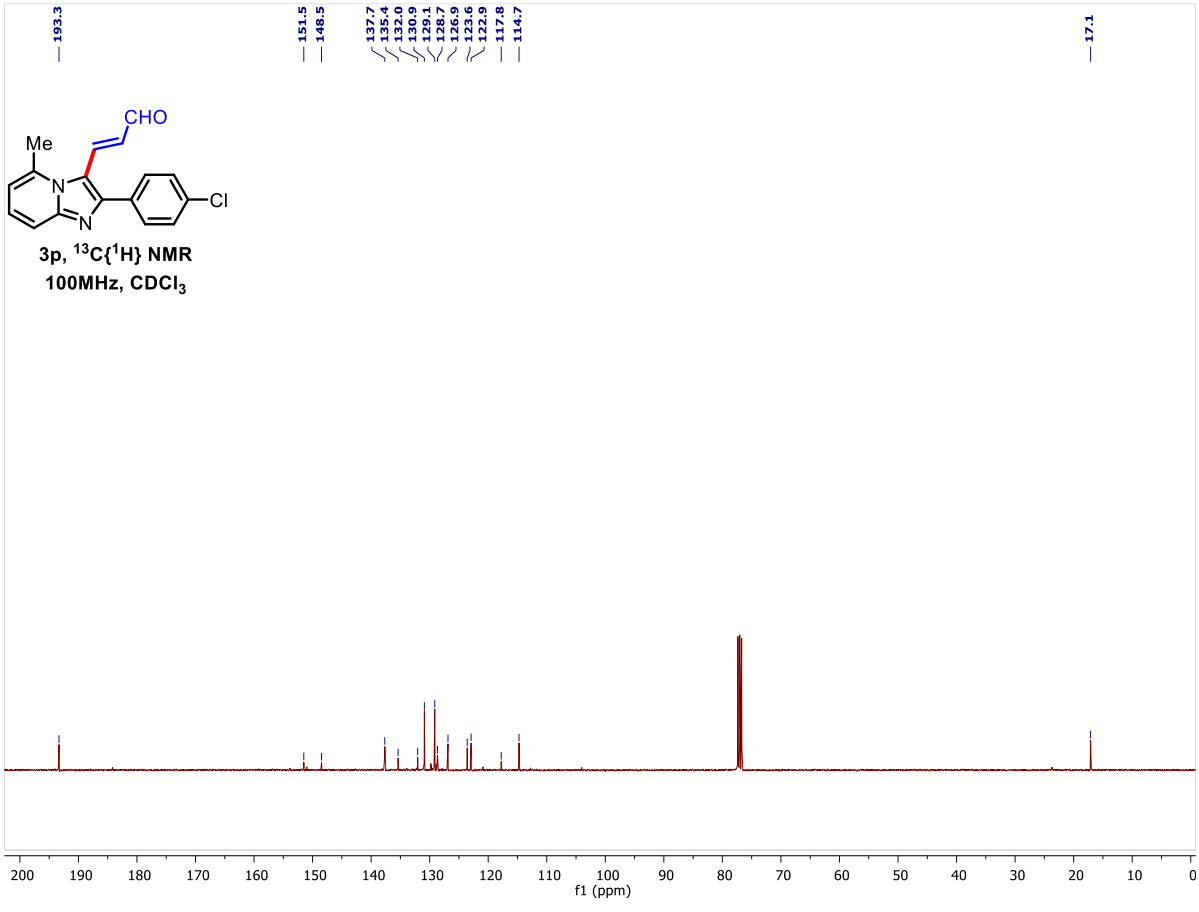

**3n, $^{13}$C{$^{1}$H} NMR**
**100MHz, $CDCl_3$**


9.60
9.58
8.38
8.36
7.78
7.74
7.64
7.62
7.54
7.36
7.34
6.93
6.91
6.65
6.63
6.61
6.59
2.50
2.46
CHO
Me
N
N
Me
3o, $^{1}$H NMR
400MHz, CDCl$_3$
1.00
0.99
1.08
2.04
1.04
2.06
1.00
1.07
3.00
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

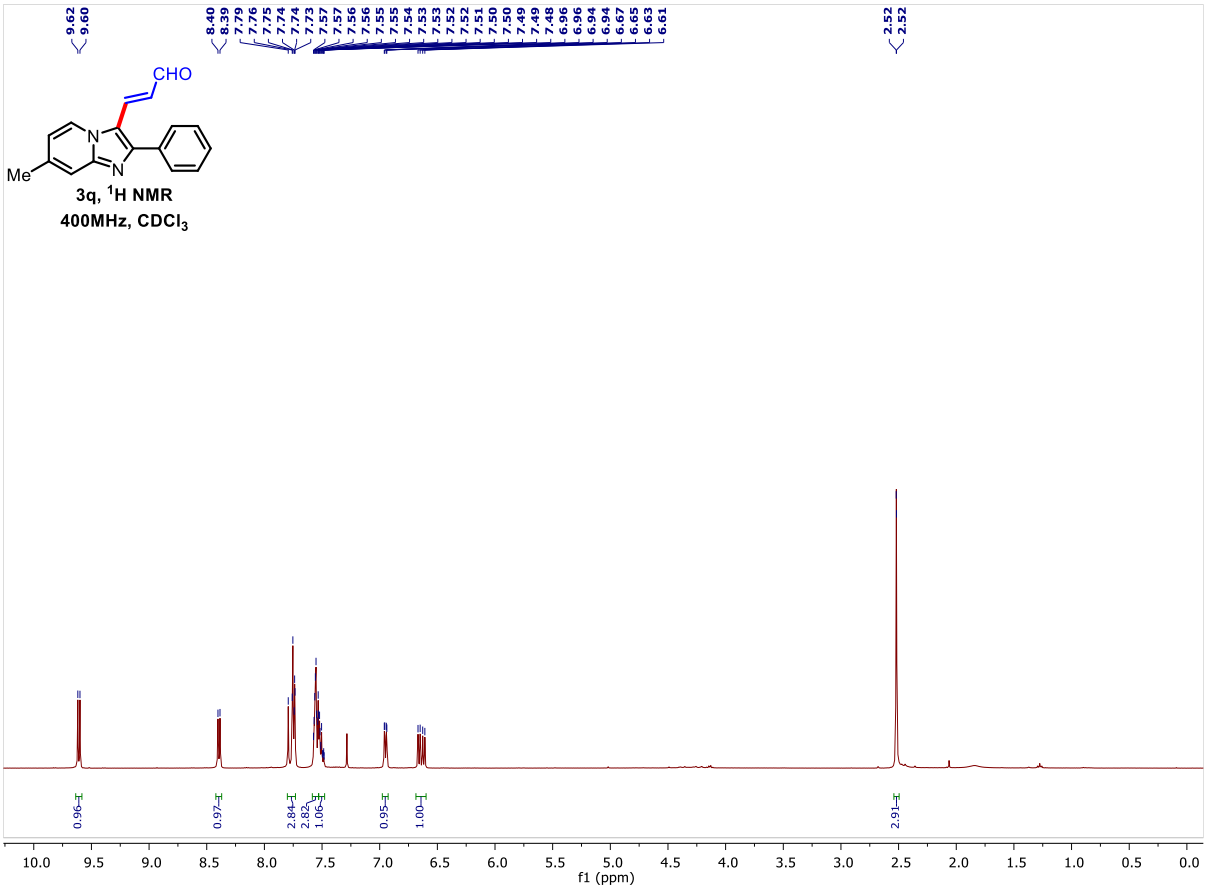

193.5
154.0
148.7
139.4
139.3
138.3
130.4
129.6
129.5
125.3
121.7
117.0
116.9
116.9
21.4
21.4
CHO
Me
N
N
Me
3o, $^{13}$C{$^{1}$H} NMR
100MHz, CDCl$_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

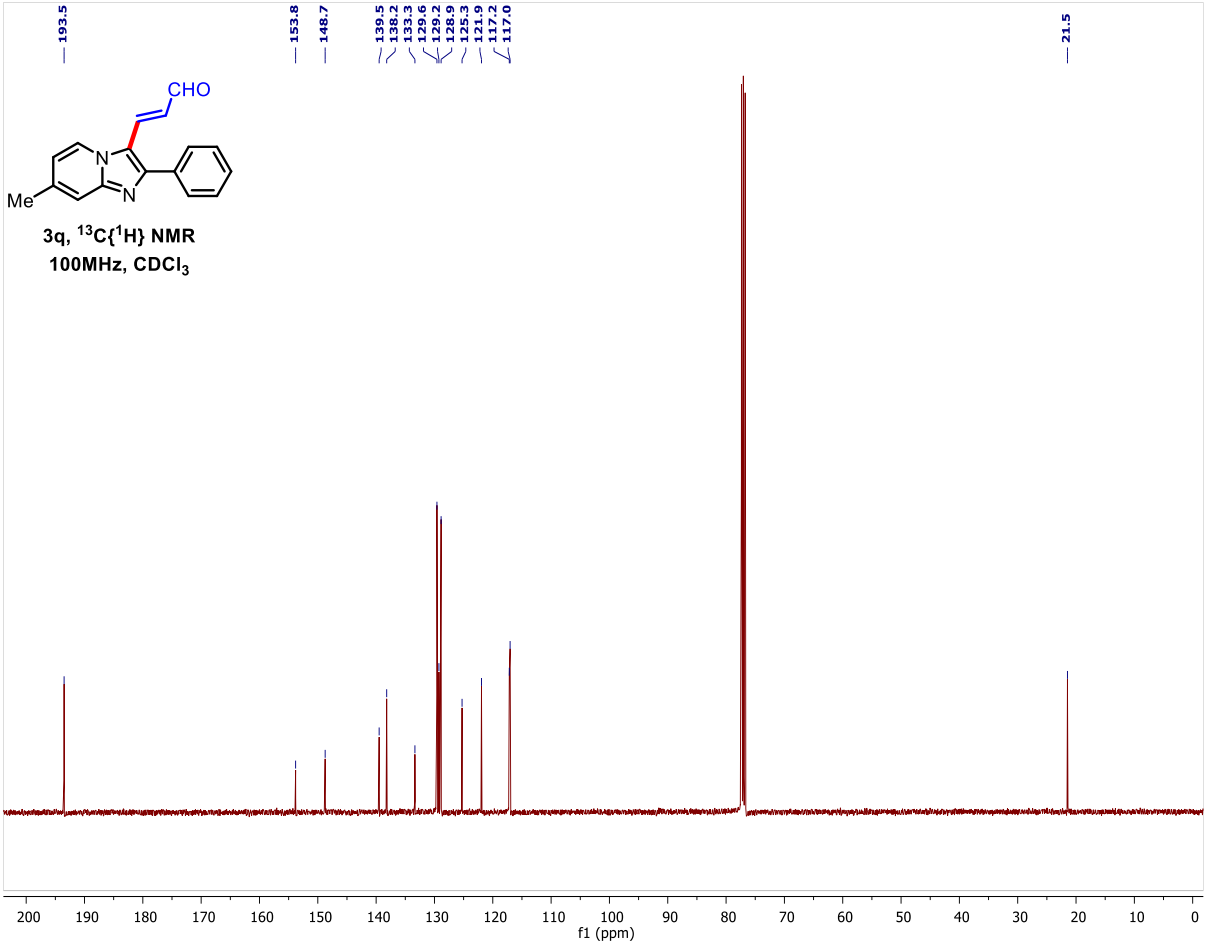


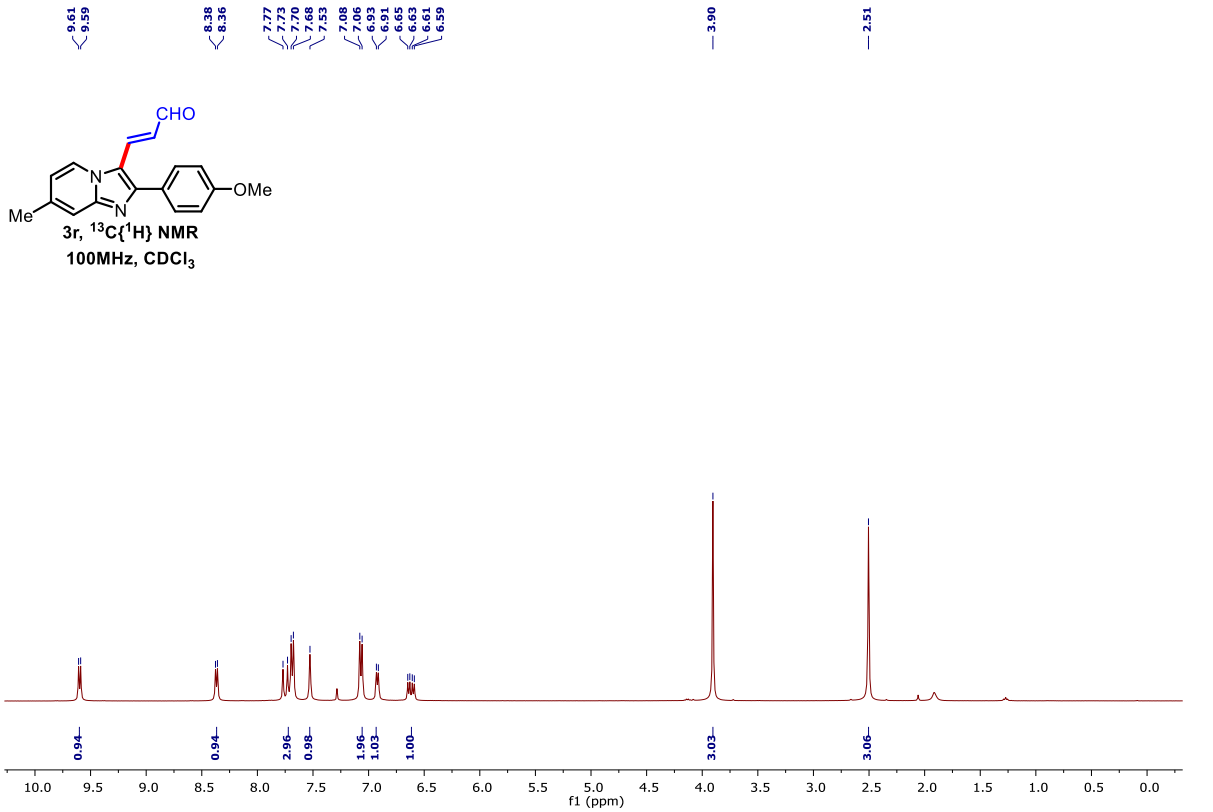

**3p, $^{1}$H NMR**
**400MHz, $CDCl_3$**



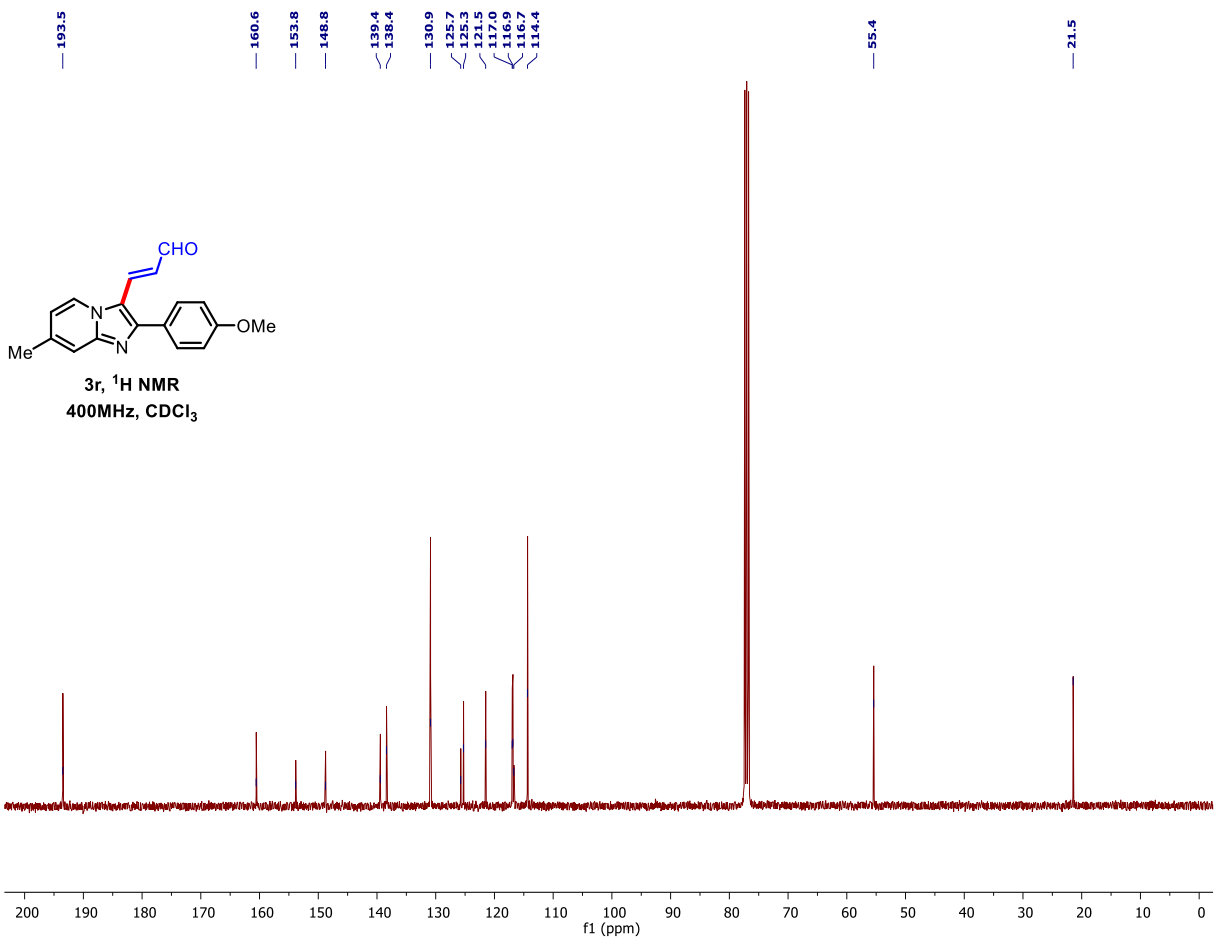

**3p, $^{13}C\{^{1}H\}$ NMR**
**100MHz, $CDCl_3$**


9.62
9.60
8.40
8.39
7.79
7.76
7.75
7.74
7.74
7.73
7.57
7.57
7.56
7.56
7.55
7.55
7.54
7.53
7.53
7.52
7.52
7.51
7.50
7.50
7.49
7.49
7.48
6.96
6.96
6.94
6.94
6.67
6.65
6.63
6.61
2.52
2.52
CHO
N
N
Me
3q, $^{1}$H NMR
400MHz, CDCl$_3$
0.96
0.97
2.84
2.82
1.06
0.95
1.00
2.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


193.5
153.8
148.7
139.5
138.2
133.3
129.6
129.2
128.9
125.3
121.9
117.2
117.0
21.5
CHO
N
N
Me
3q, $^{13}$C{$^{1}$H} NMR
100MHz, CDCl$_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

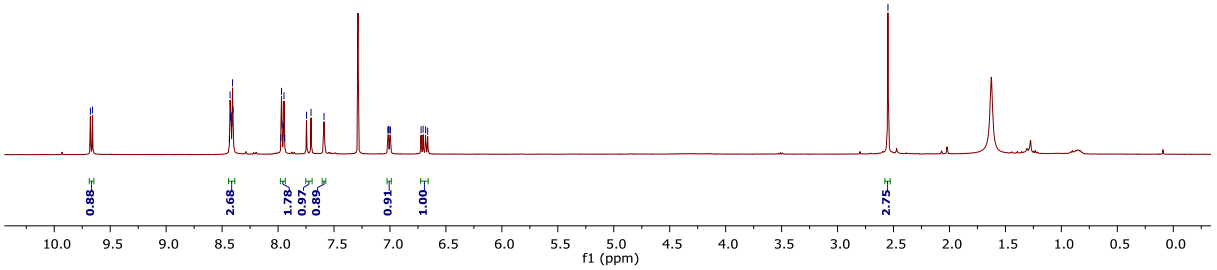


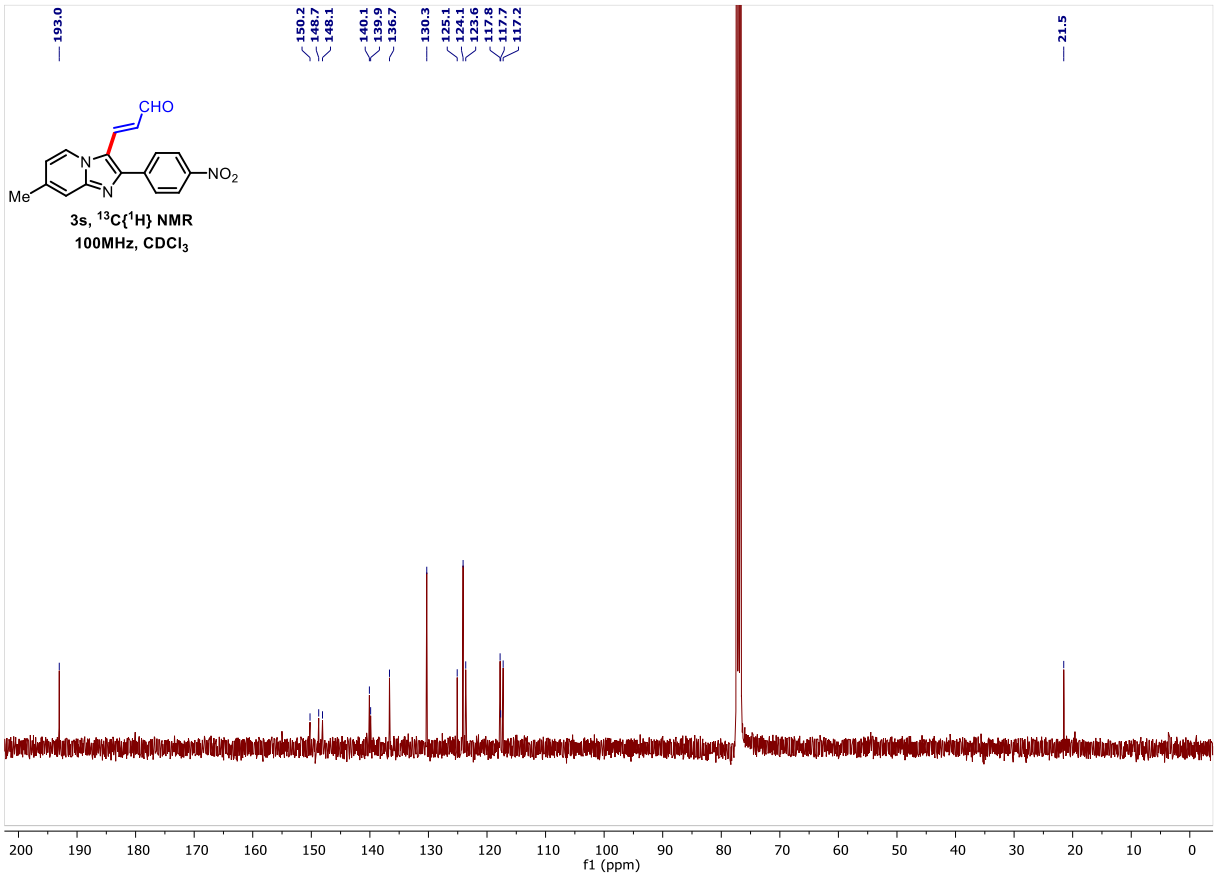

3r, $^{13}C\{^{1}H\}$ NMR
100MHz, $CDCl_3$

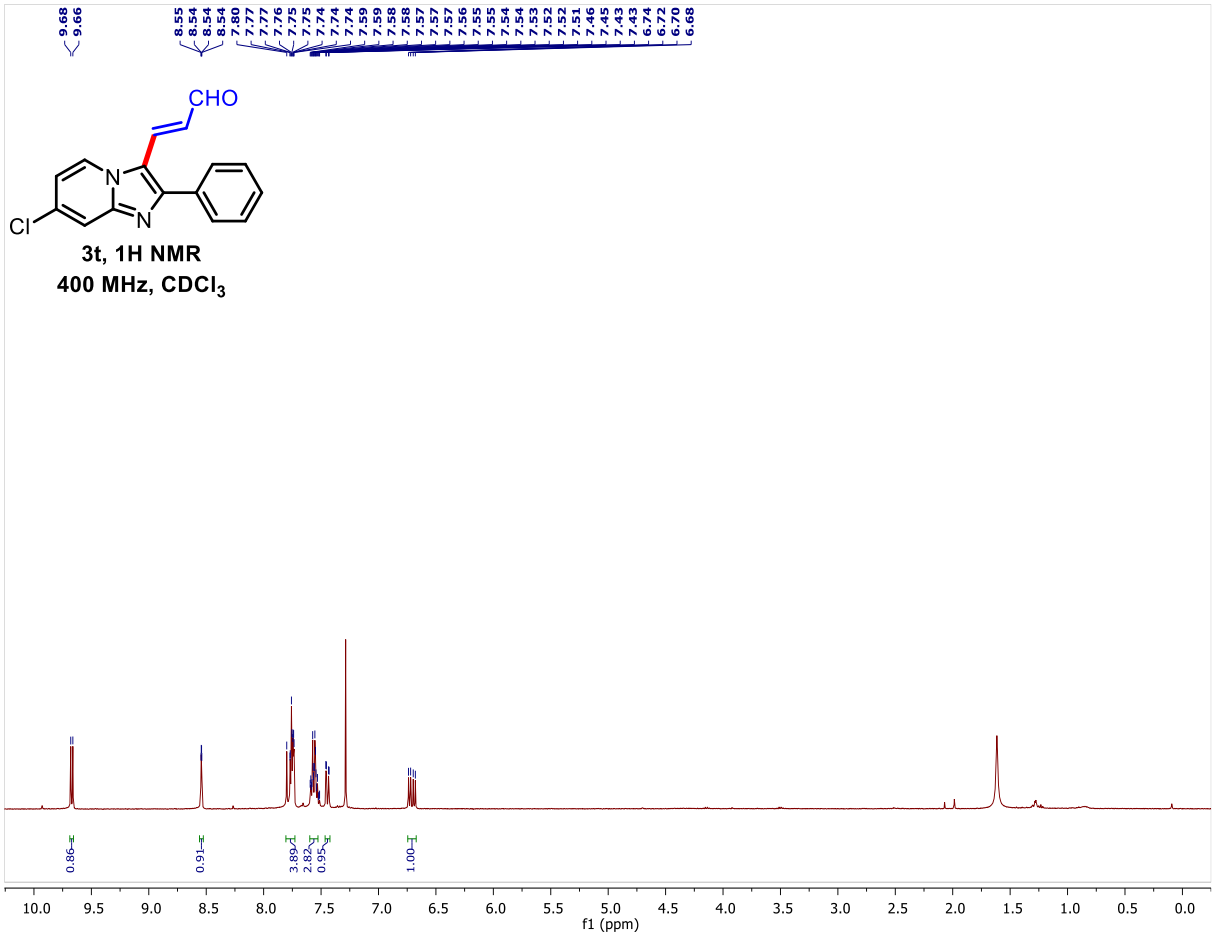



3r, $^{1}H$ NMR
400MHz, $CDCl_3$

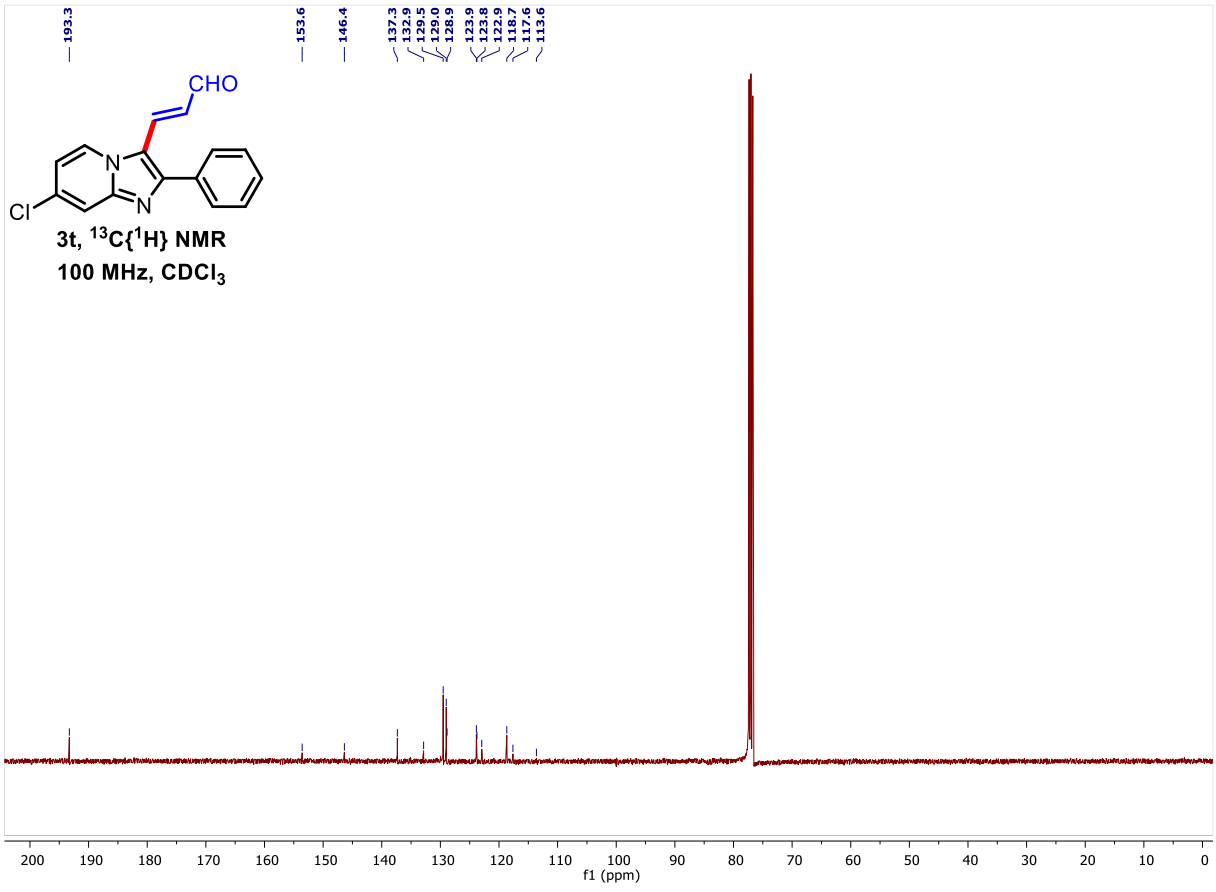

9.68
9.66
8.43
8.43
8.42
8.42
8.41
8.41
8.40
7.98
7.97
7.96
7.95
7.95
7.94
7.75
7.71
7.59
7.02
7.01
7.00
7.00
6.72
6.70
6.68
6.66
2.55
CHO
N
N
NO2
Me
3s, 1H NMR
100MHz, CDCl3


0.88
2.68
1.78
0.97
0.89
0.91
1.00
2.75
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

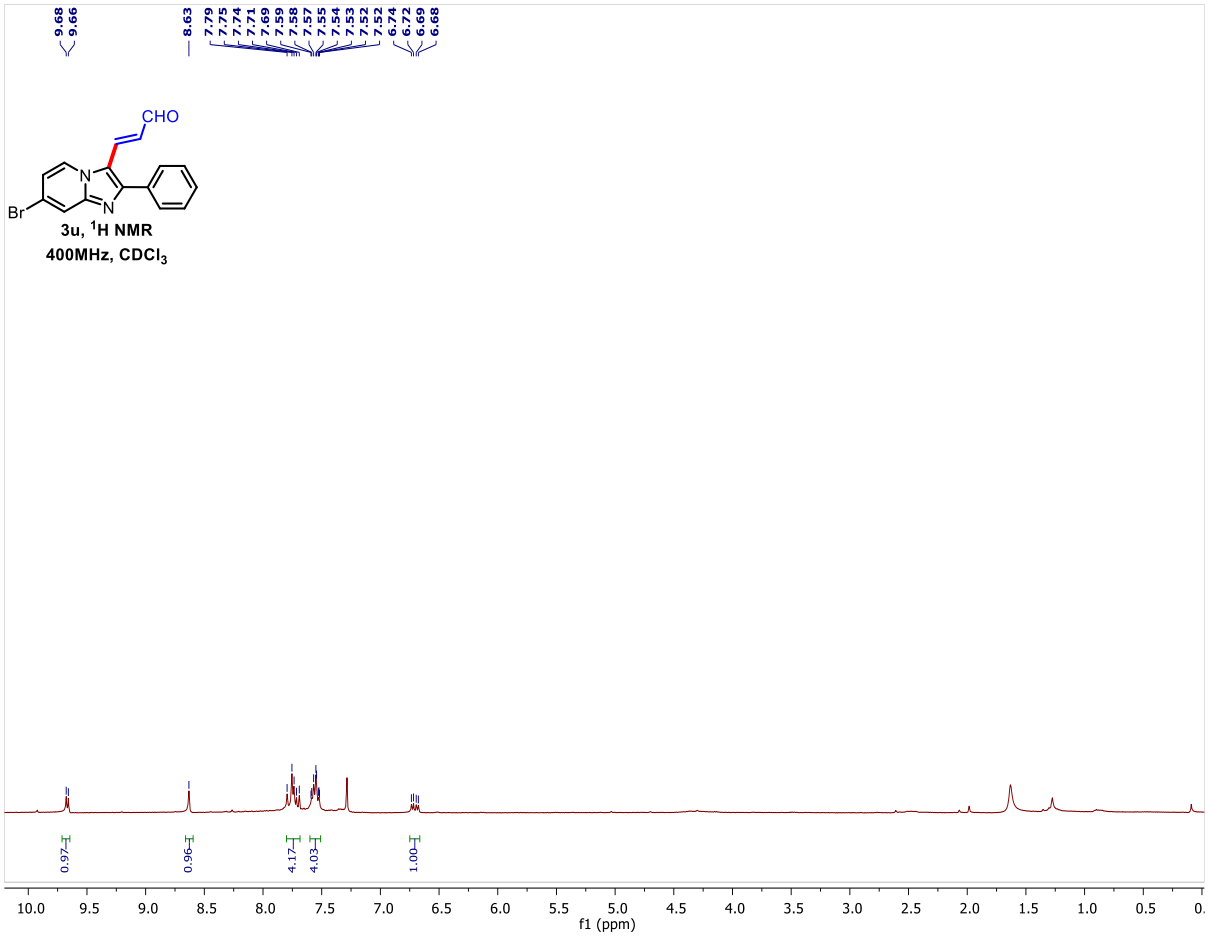

193.0
150.2
148.7
148.1
140.1
139.9
136.7
130.3
125.1
124.1
123.6
117.8
117.7
117.2
21.5
CHO
N
N
NO2
Me
3s, 13C{1H} NMR
100MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

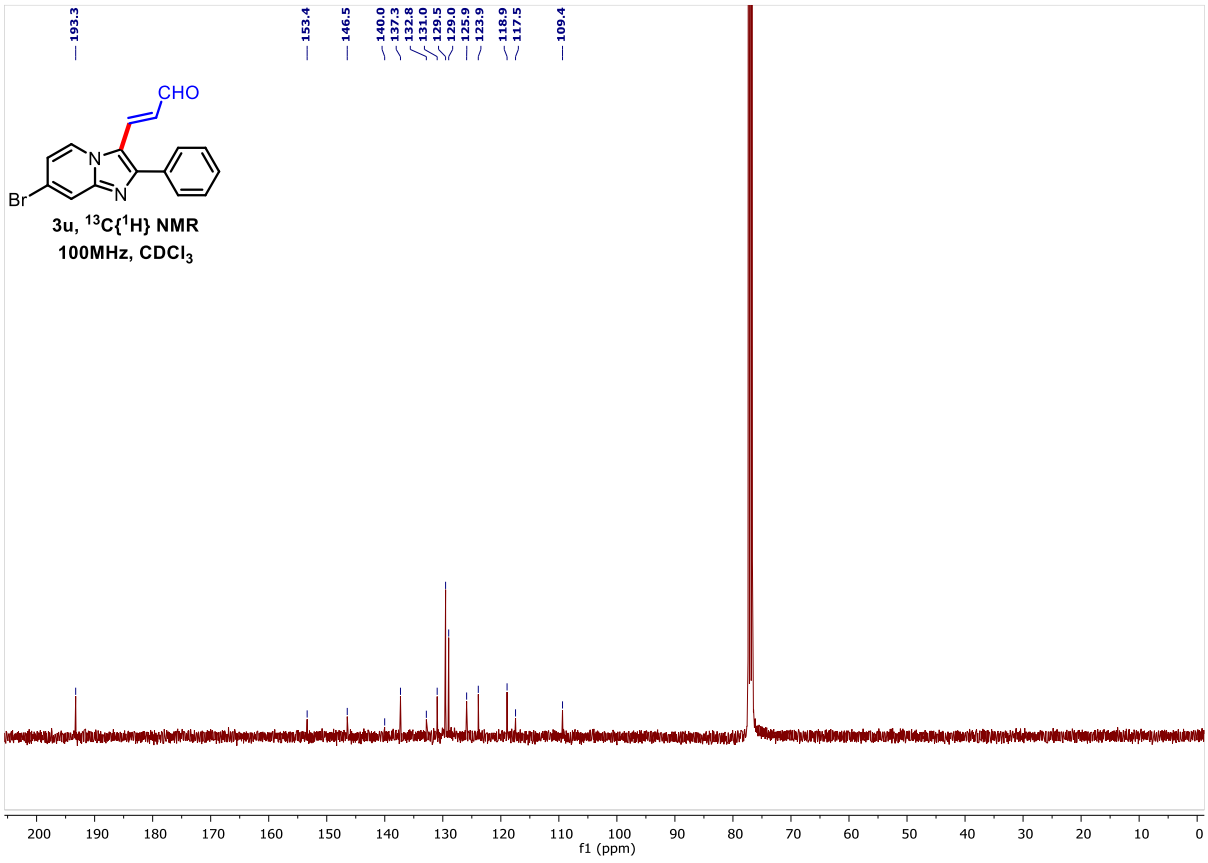


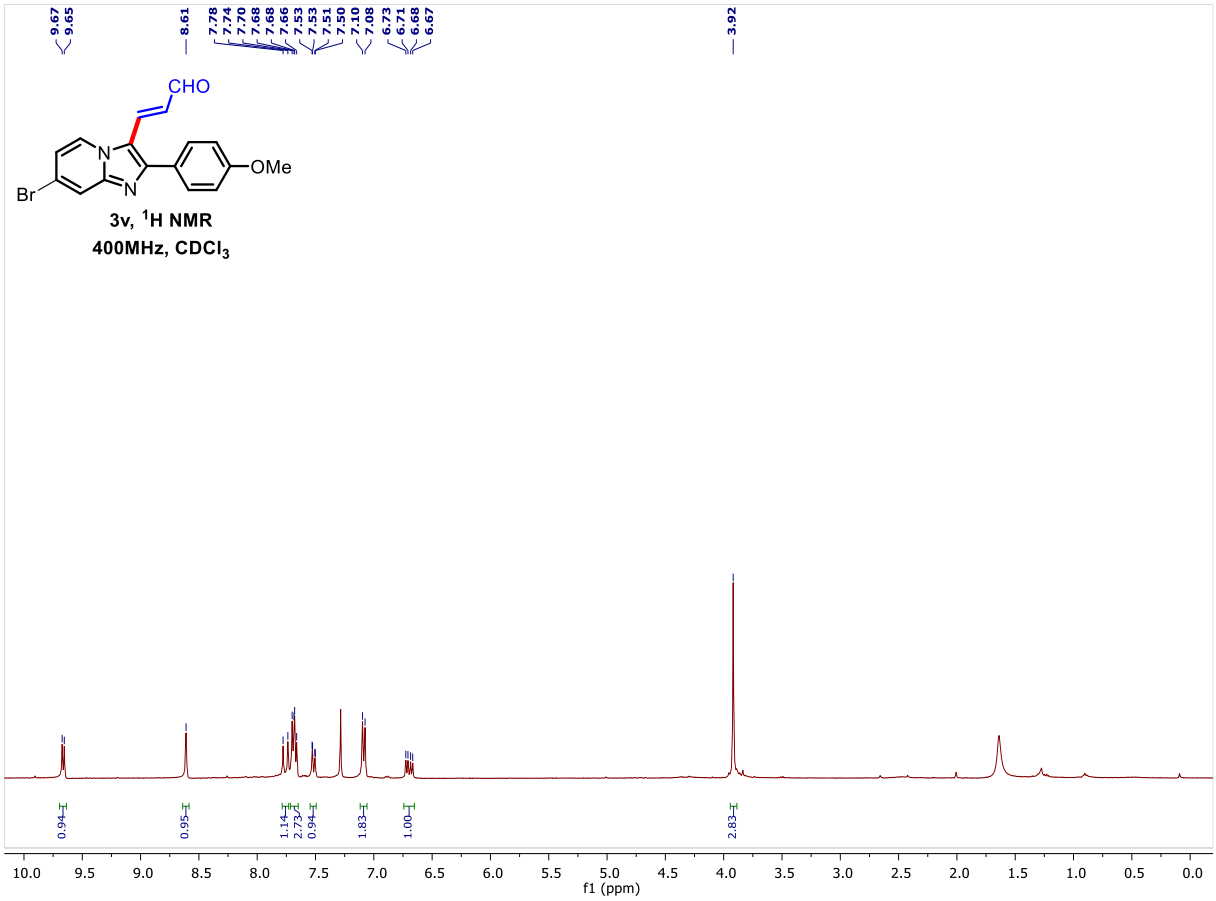

**3t, 1H NMR**
**400 MHz, $CDCl_3$**



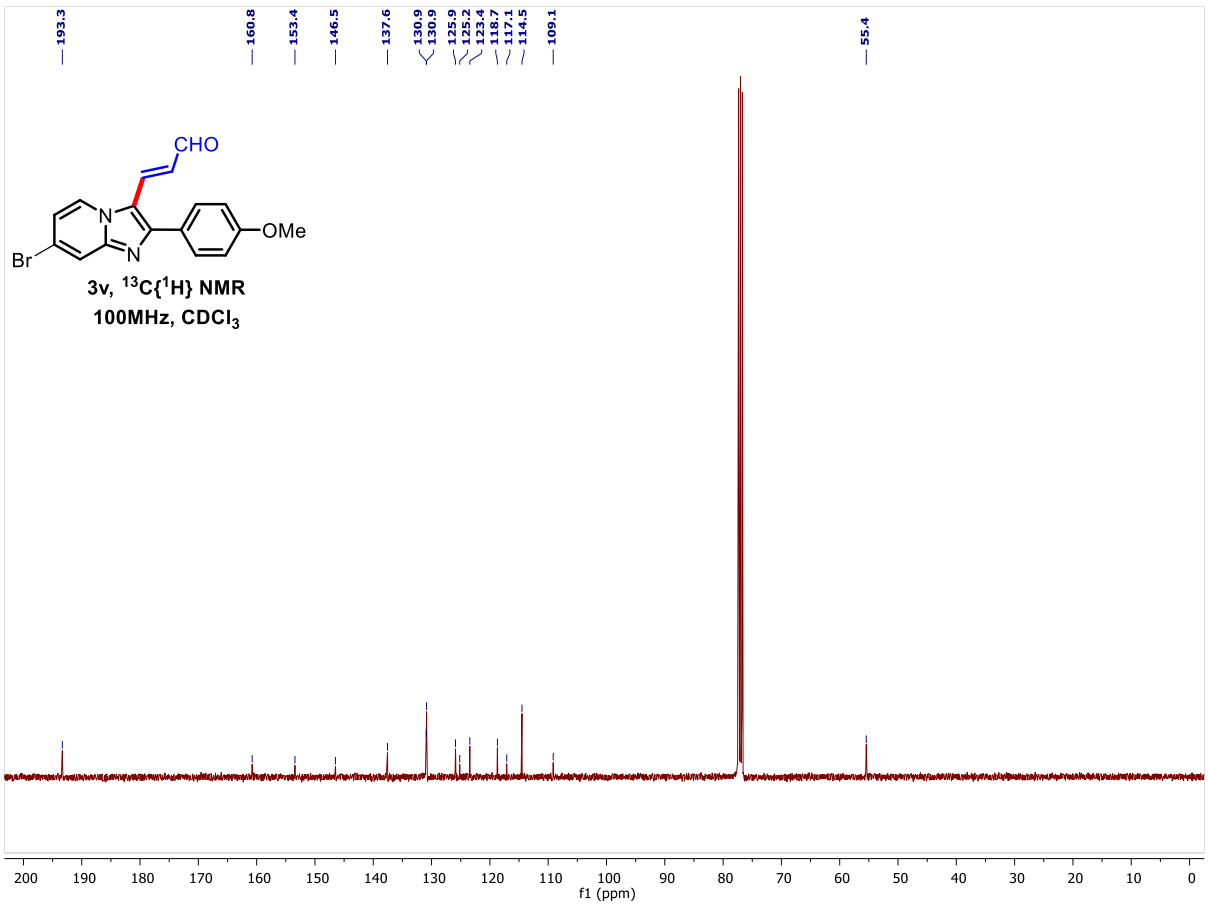

**3t, $^{13}C\{^1H\}$ NMR**
**100 MHz, $CDCl_3$**


9.68
9.66
8.63
7.79
7.75
7.74
7.71
7.69
7.59
7.58
7.57
7.55
7.54
7.53
7.52
7.52
6.74
6.72
6.69
6.68
CHO
N
N
Br
3u, $^{1}$H NMR
400MHz, CDCl$_3$
0.97
0.96
4.17
4.03
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

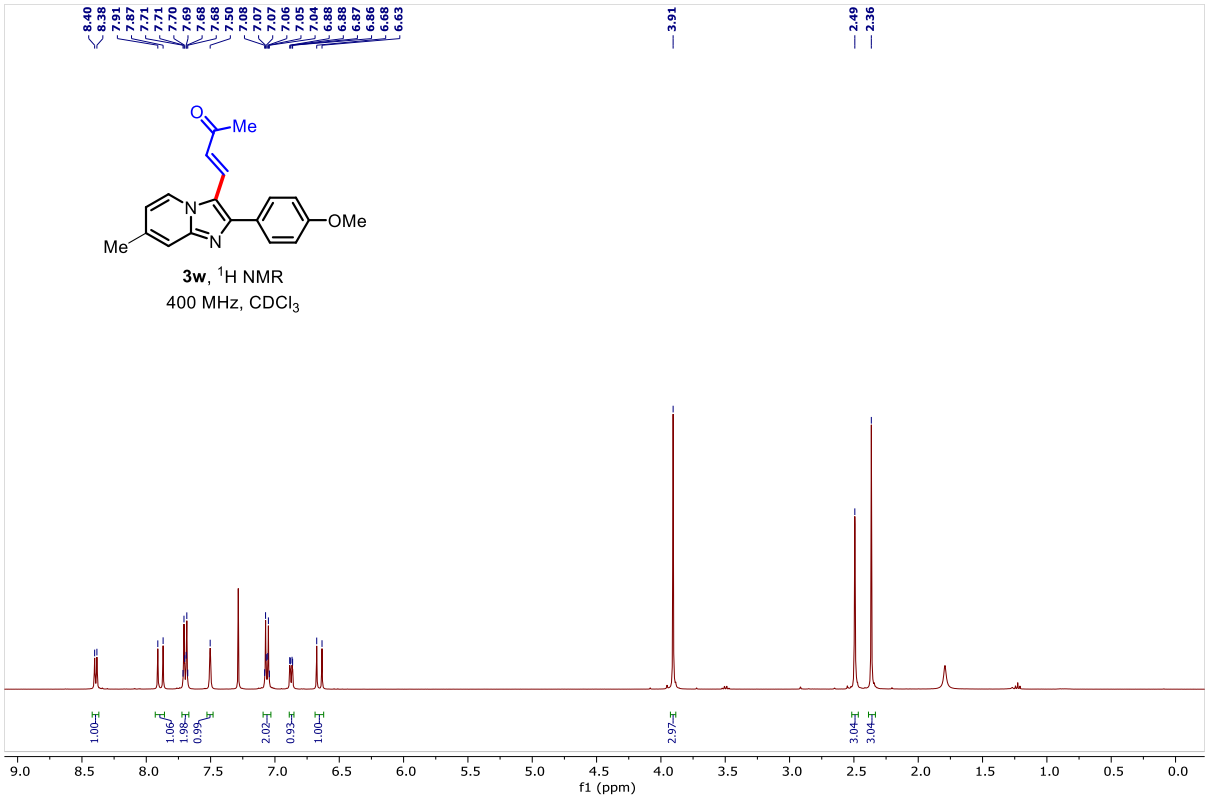

193.3
153.4
146.5
140.0
137.3
132.8
131.0
129.5
129.0
125.9
123.9
118.9
117.5
109.4
CHO
N
N
Br
3u, $^{13}$C{$^{1}$H} NMR
100MHz, CDCl$_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



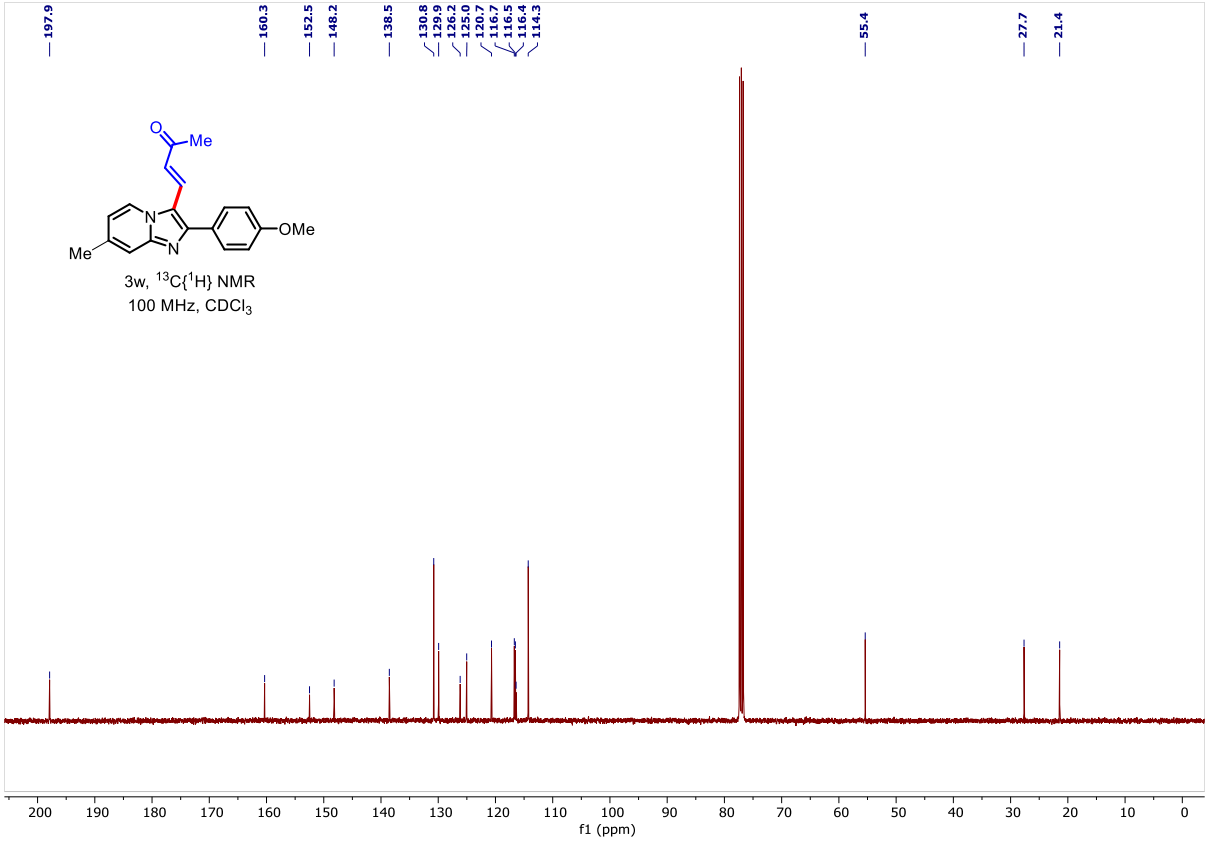

3v, $^{1}$H NMR
400MHz, $CDCl_3$



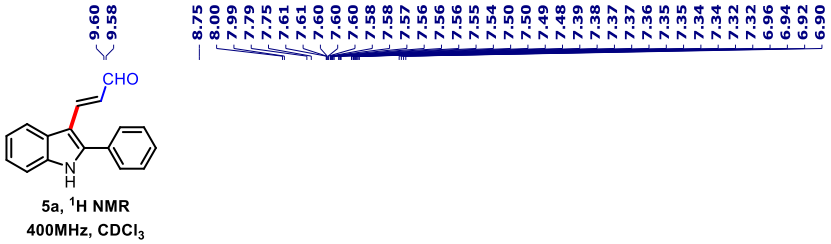

3v, $^{13}C\{^{1}H\}$ NMR
100MHz, $CDCl_3$



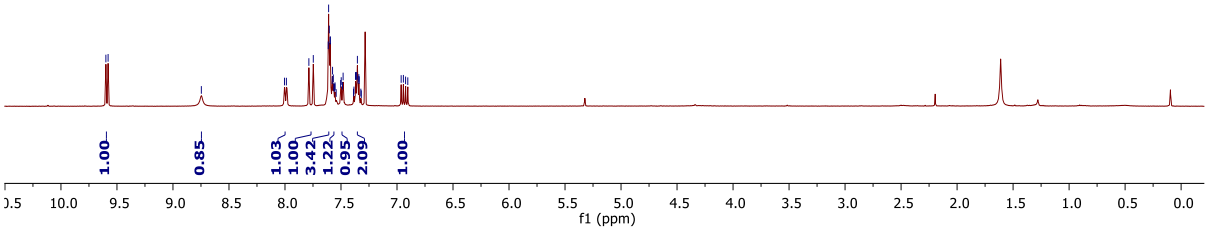

**3w**, $^{1}$H NMR
400 MHz, $CDCl_3$

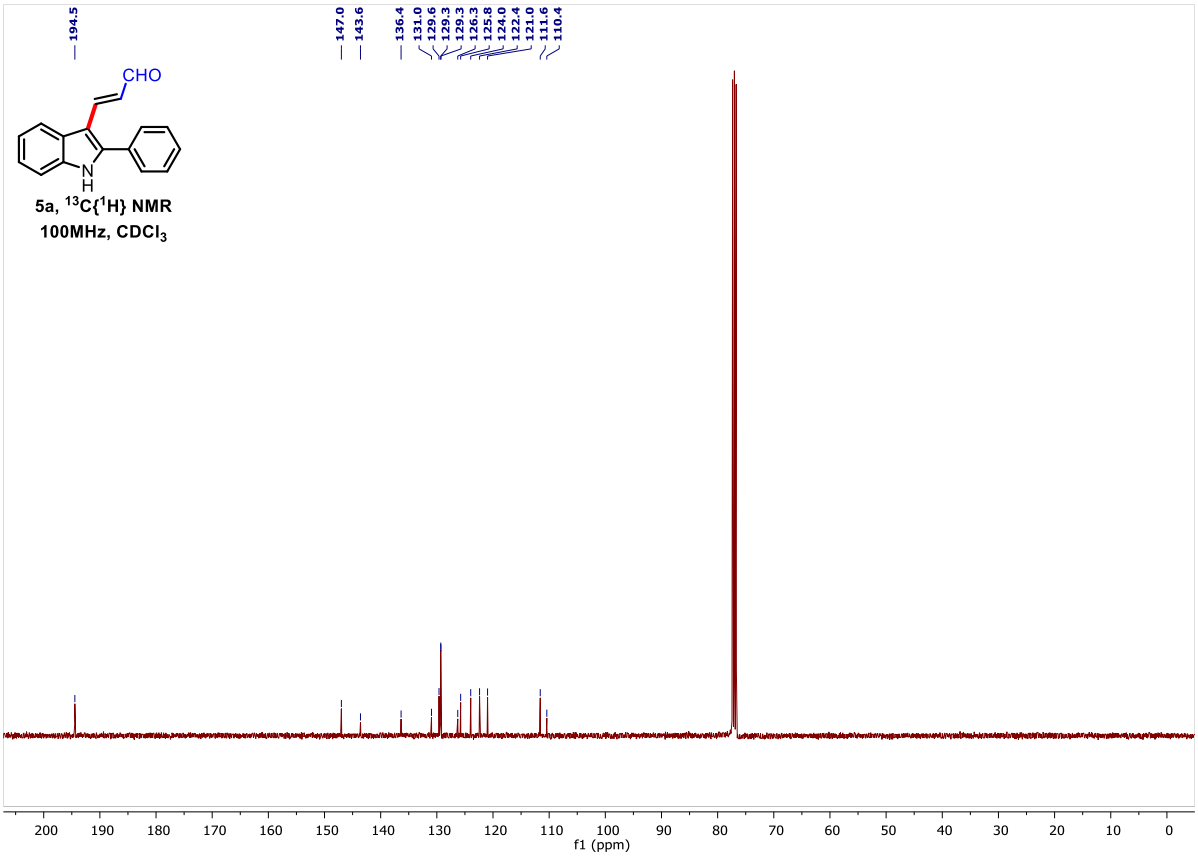



3w, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$

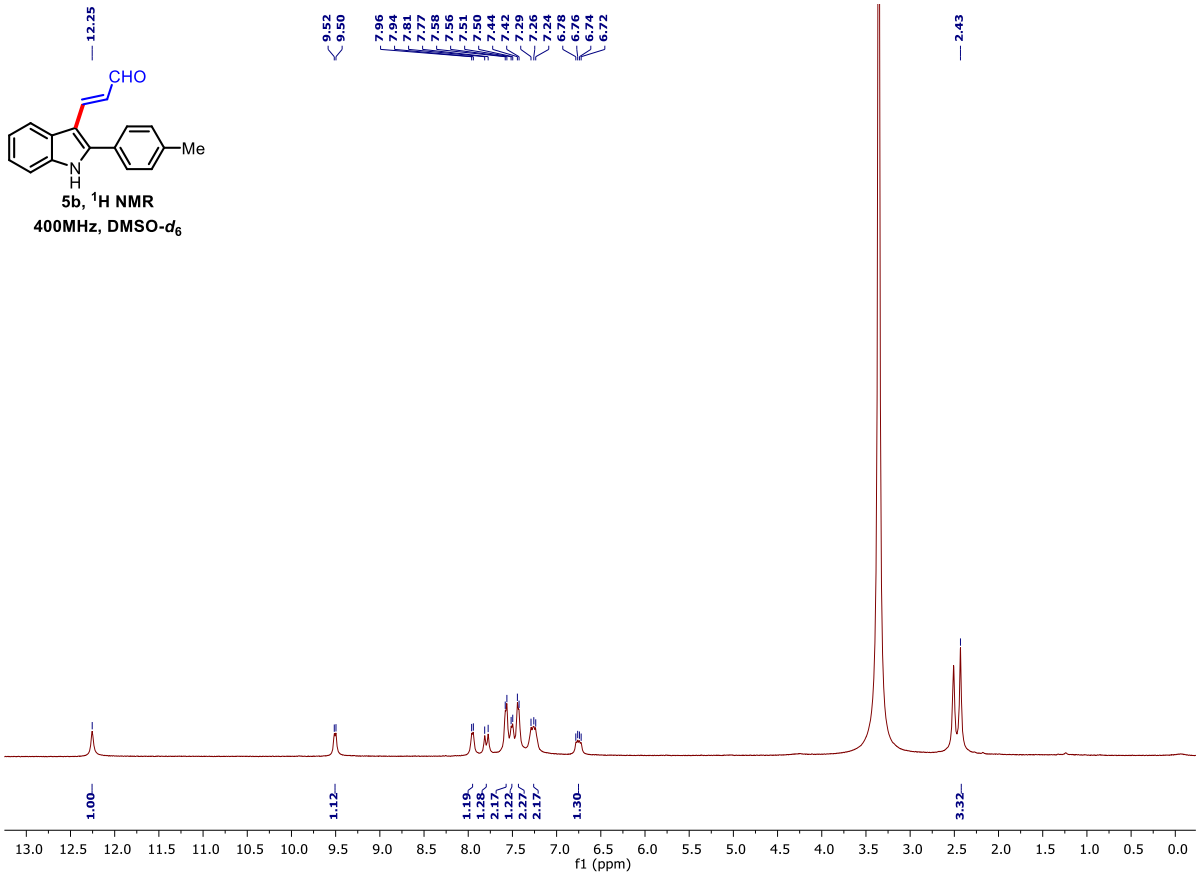



**5a, $^{1}$H NMR**
**400MHz, $CDCl_3$**

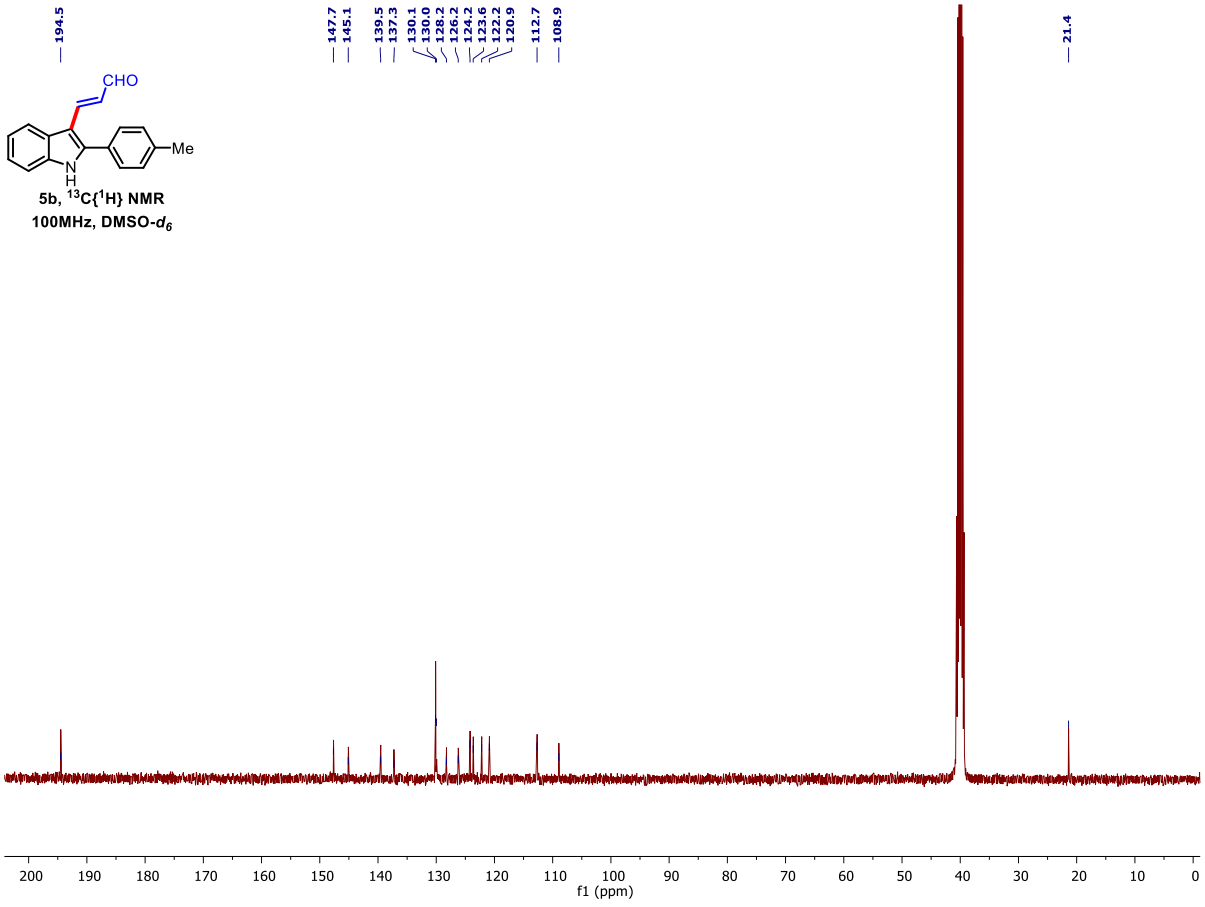


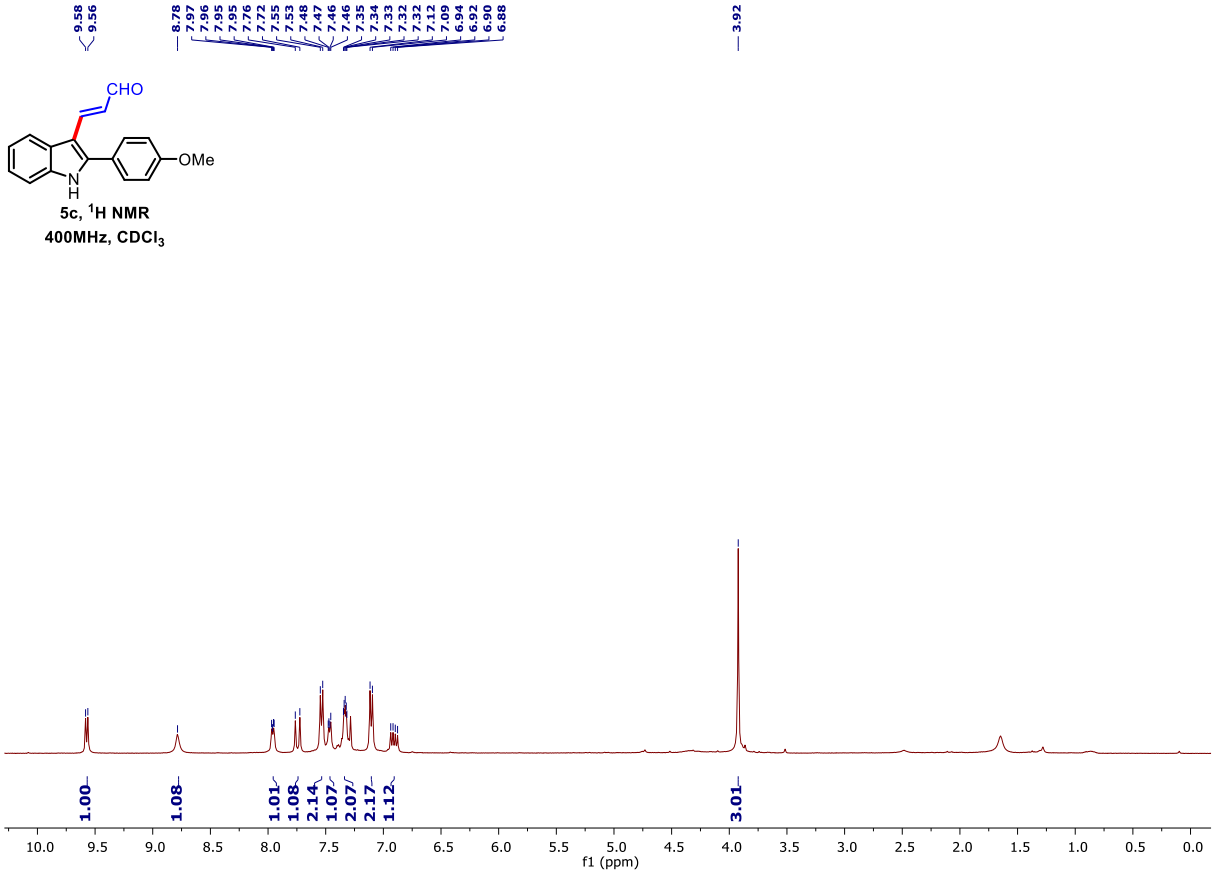

**5a, $^{13}C\{^{1}H\}$ NMR**
**100MHz, $CDCl_3$**



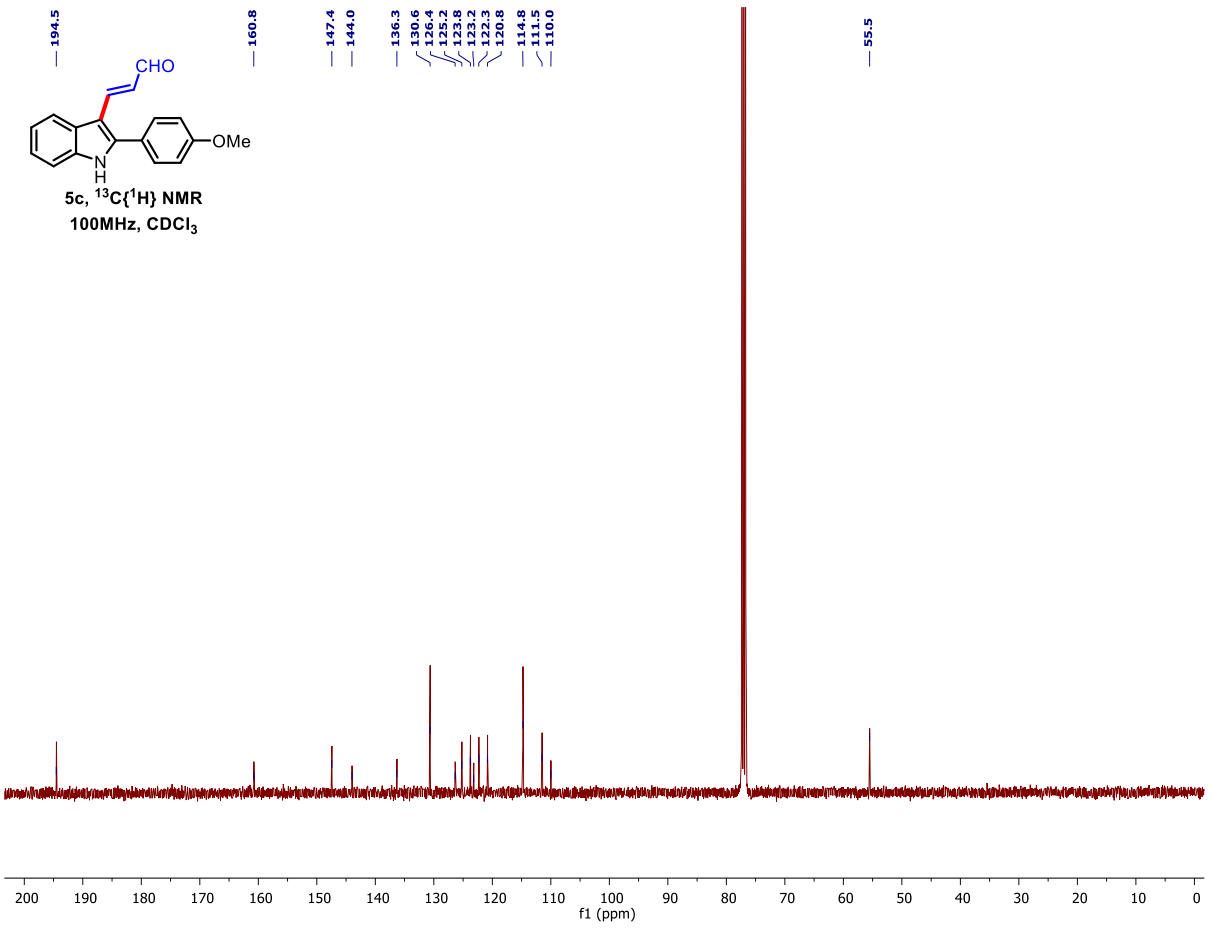

5b, $^{1}$H NMR
400MHz, DMSO-$d_6$



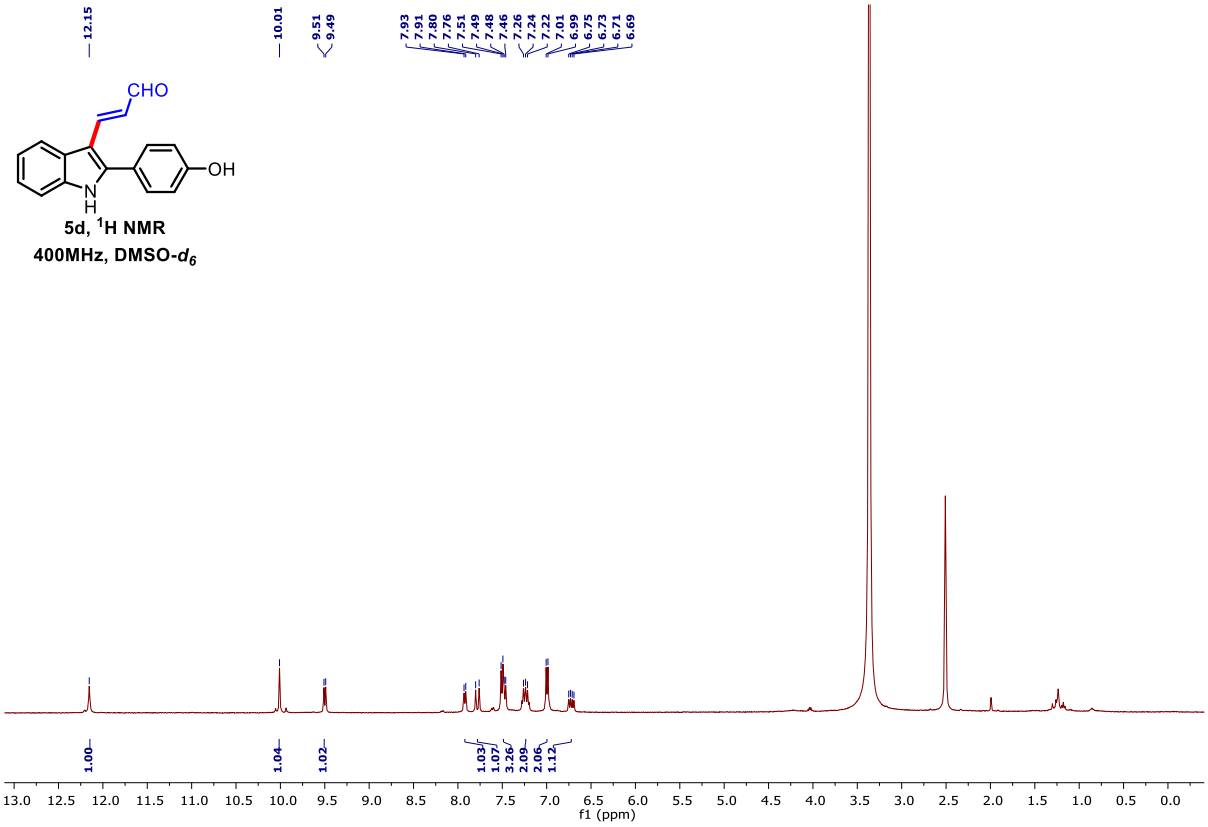

5b, $^{13}$C{$^{1}$H} NMR
100MHz, DMSO-$d_6$



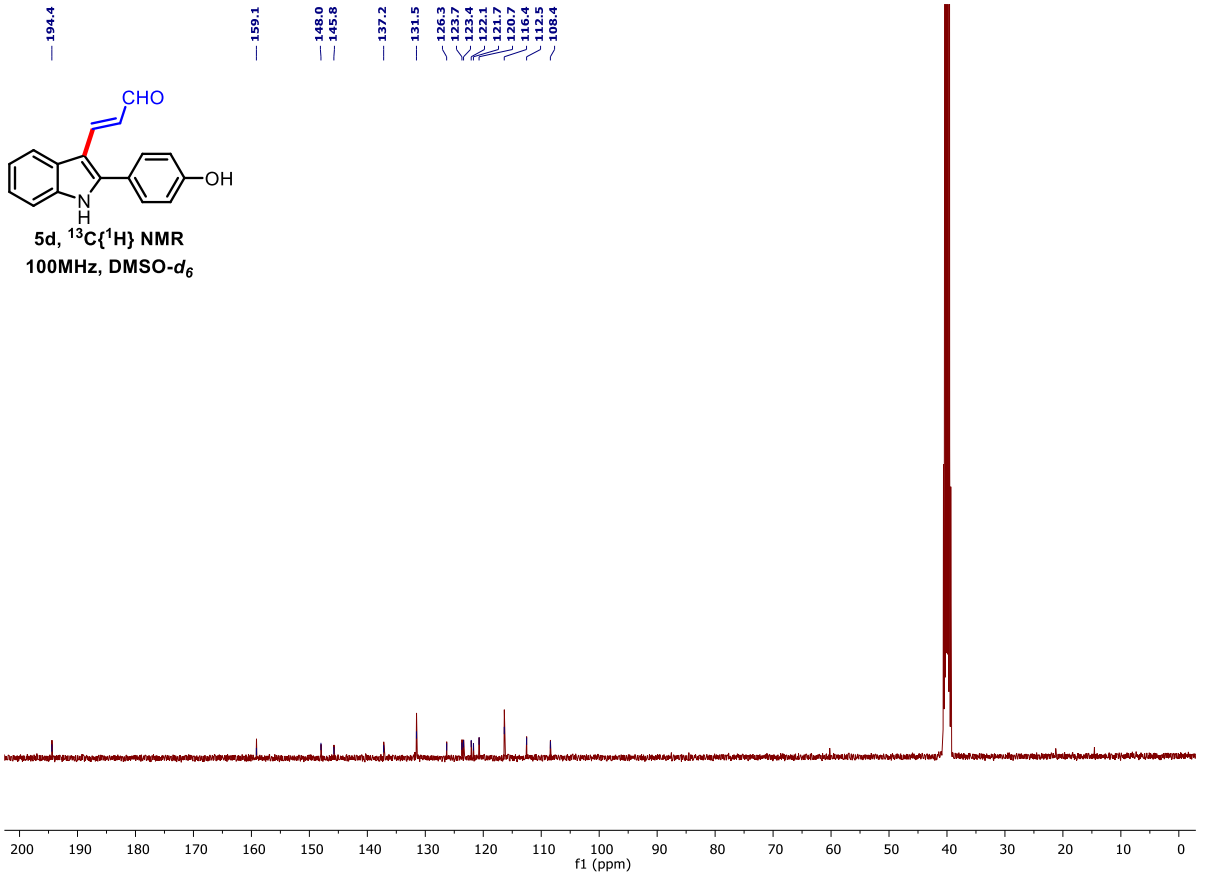

**5c, $^{1}$H NMR**
**400MHz, $CDCl_3$**



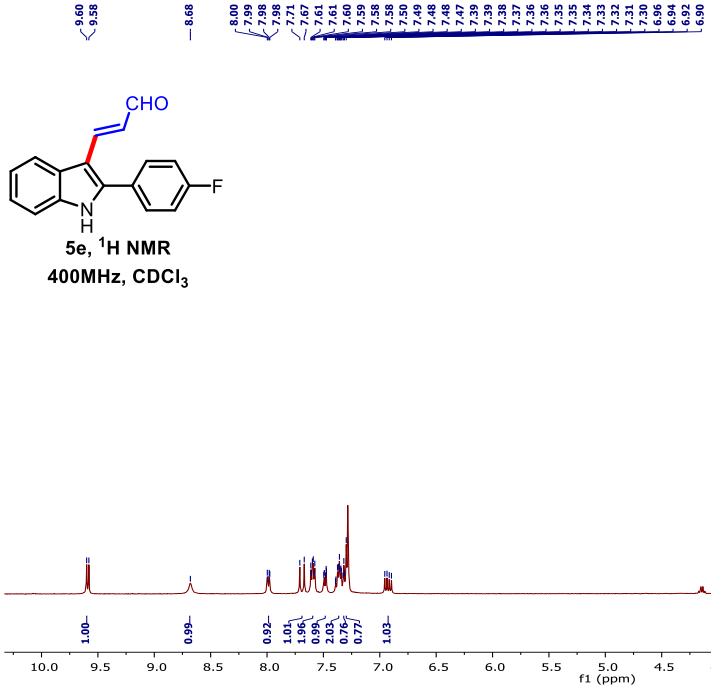

**5c, $^{13}C\{^{1}H\}$ NMR**
**100MHz, $CDCl_3$**

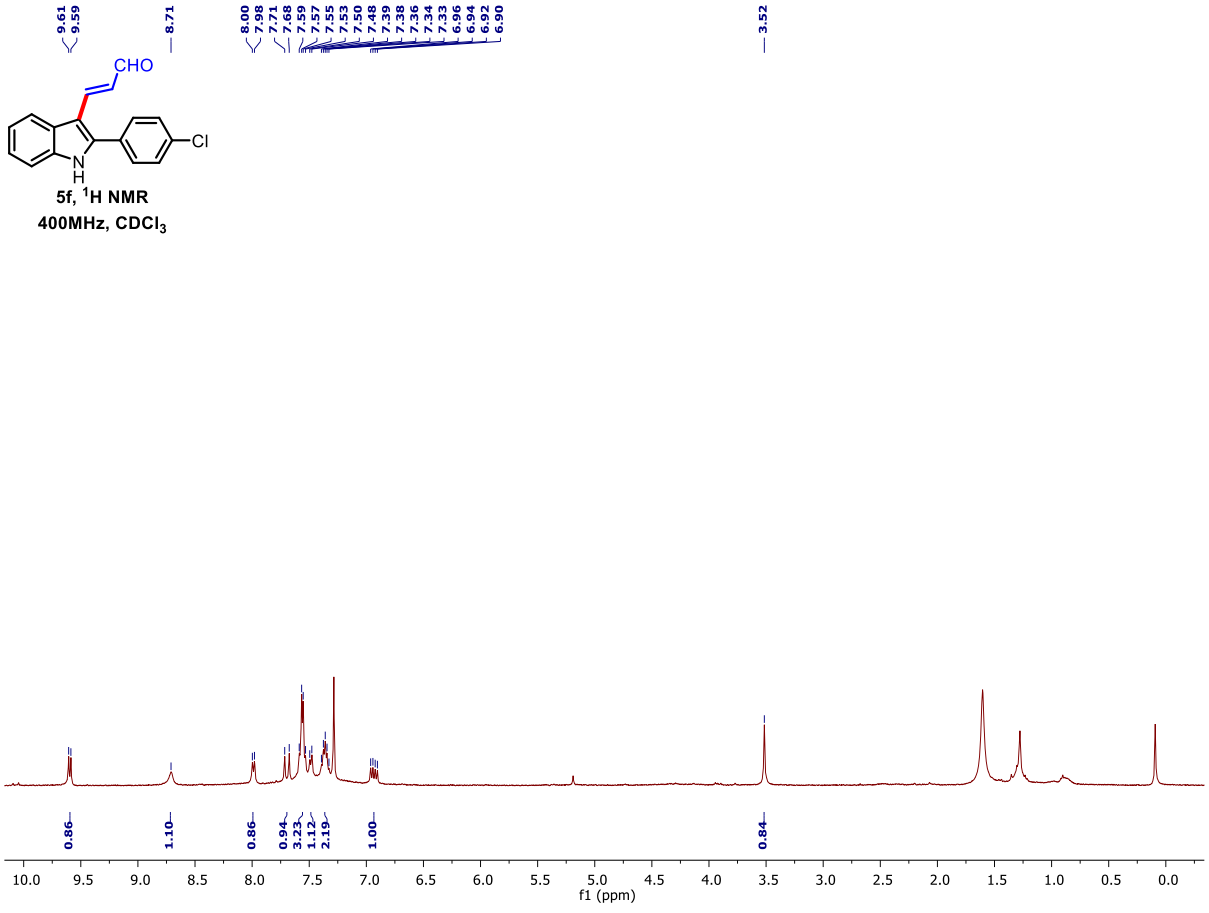



5d, $^{1}$H NMR
400MHz, DMSO-$d_6$

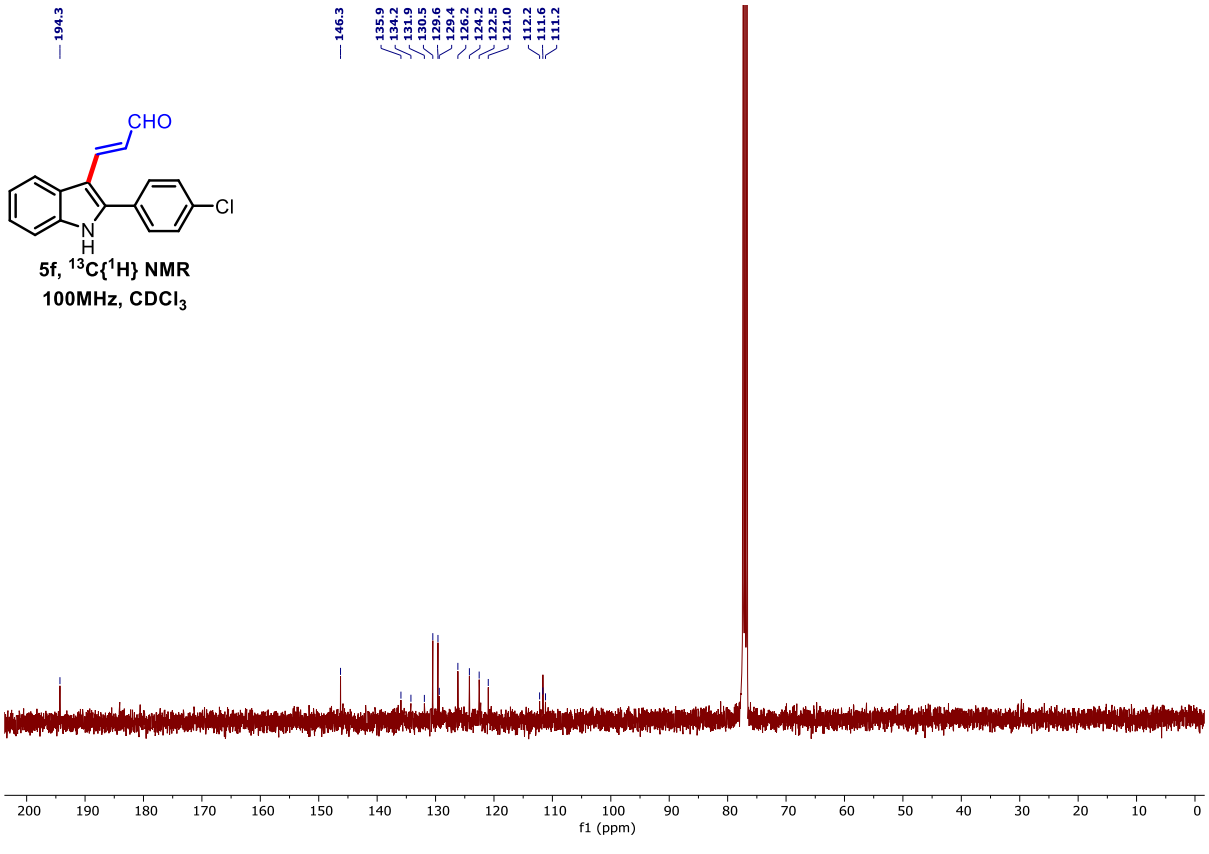



5d, $^{13}$C{$^{1}$H} NMR
100MHz, DMSO-$d_6$

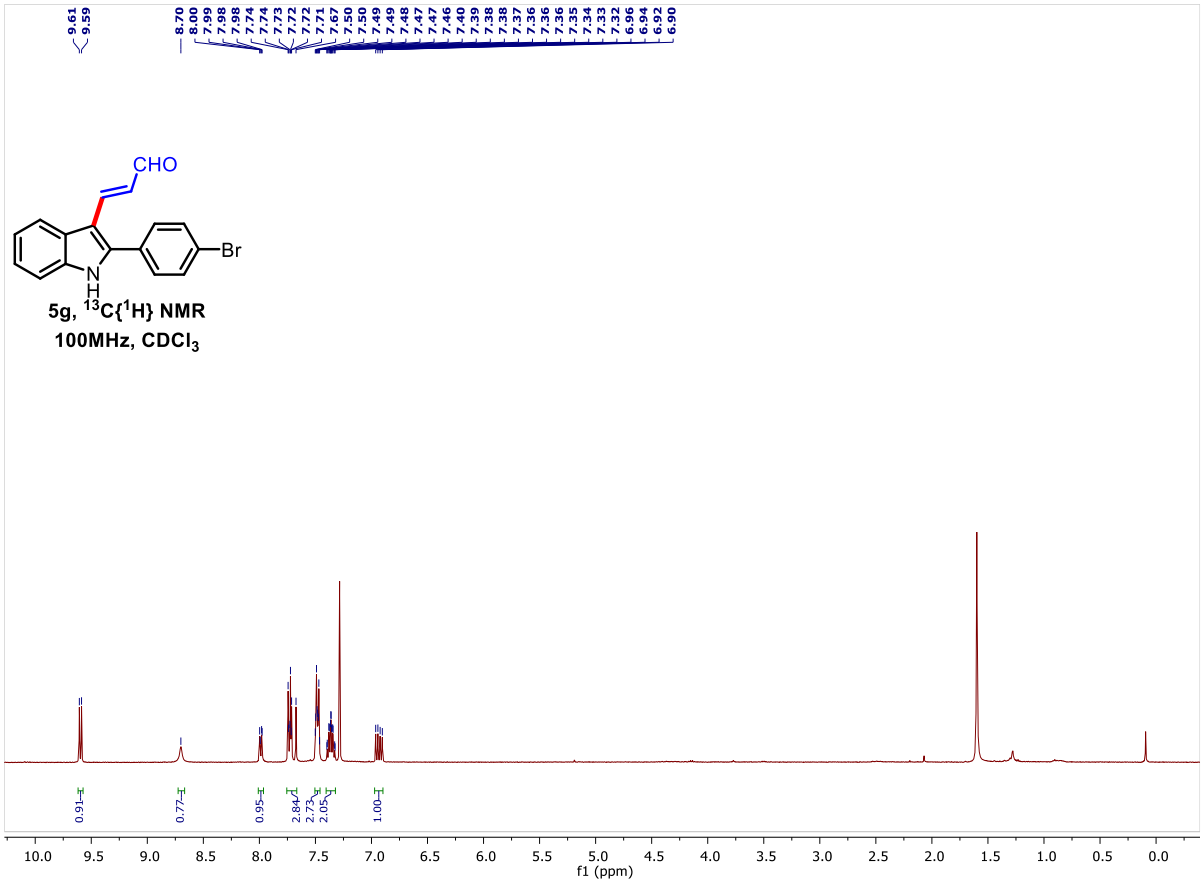

CHO
F
N
H
5e, $^{1}$H NMR
400MHz, $CDCl_3$
f1 (ppm)
CHO
F
N
H
5e, $^{13}C\{^{1}H\}$ NMR
100MHz, $CDCl_3$
f1 (ppm)
CHO
F
N
H
5e, $^{19}$F NMR
376 MHz, $CDCl_3$
f1 (ppm)



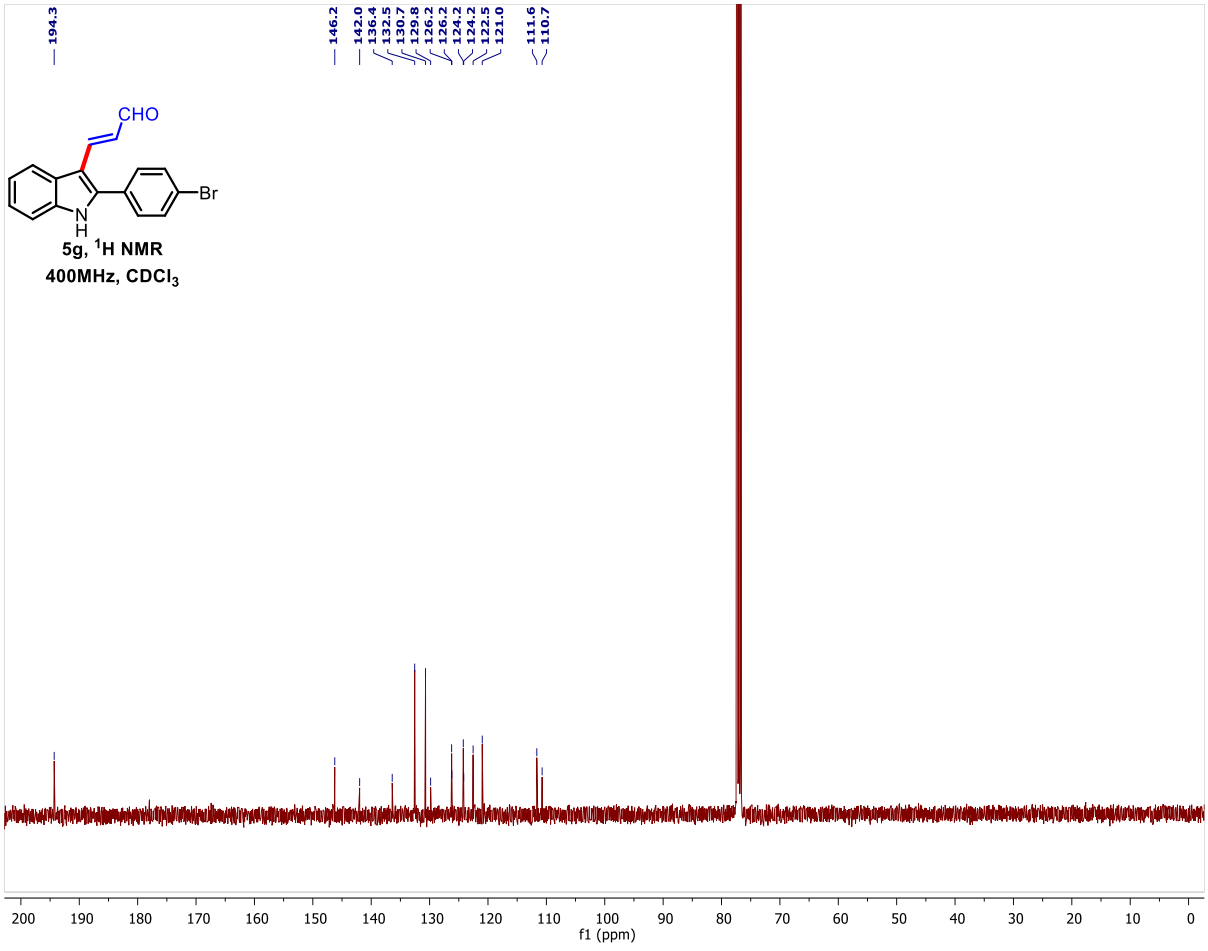

**5f, $^{1}$H NMR**
**400MHz, $CDCl_3$**



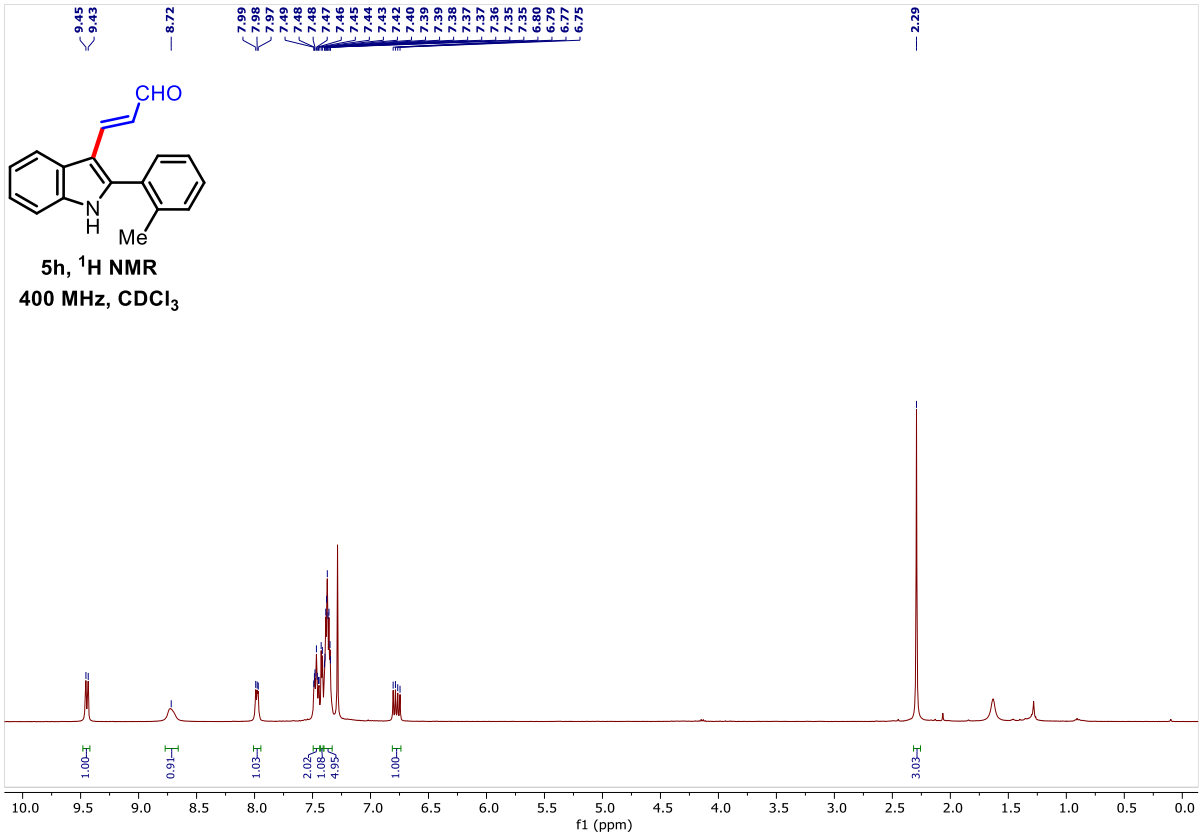

**5f, $^{13}C\{^{1}H\}$ NMR**
**100MHz, $CDCl_3$**

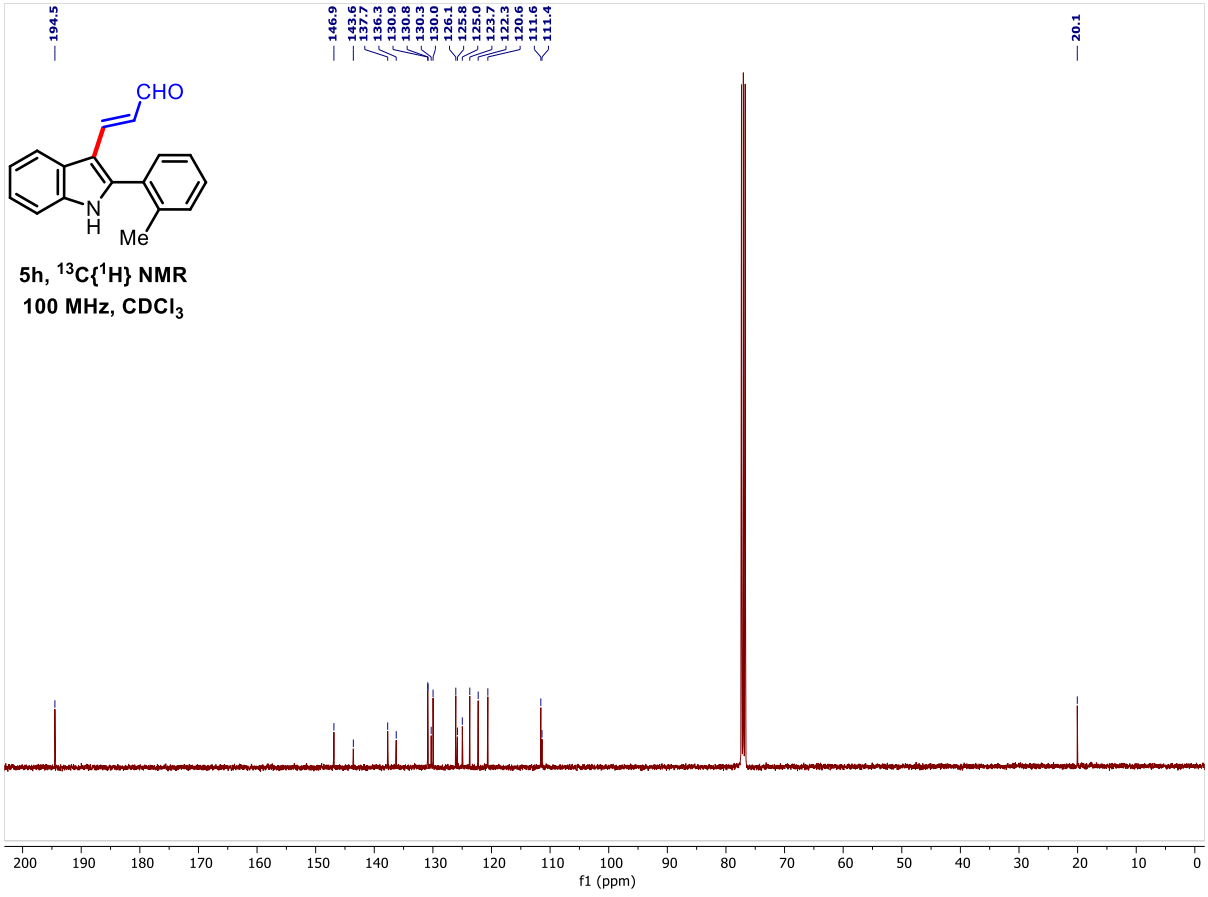


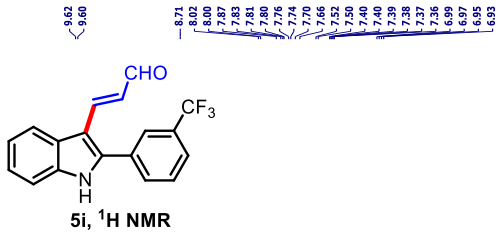

**5g, $^{13}C\{^{1}H\}$ NMR**
**100MHz, $CDCl_3$**



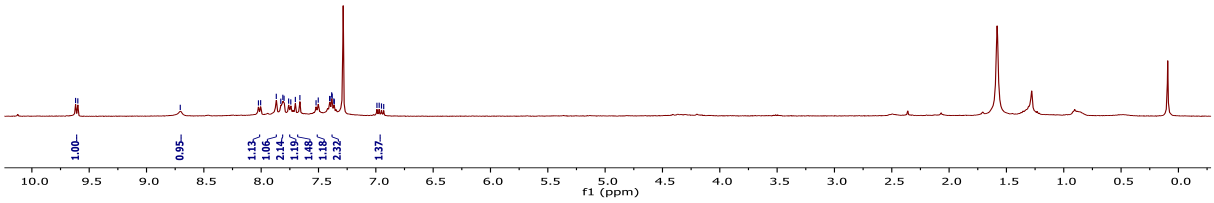

**5g, $^{1}H$ NMR**
**400MHz, $CDCl_3$**

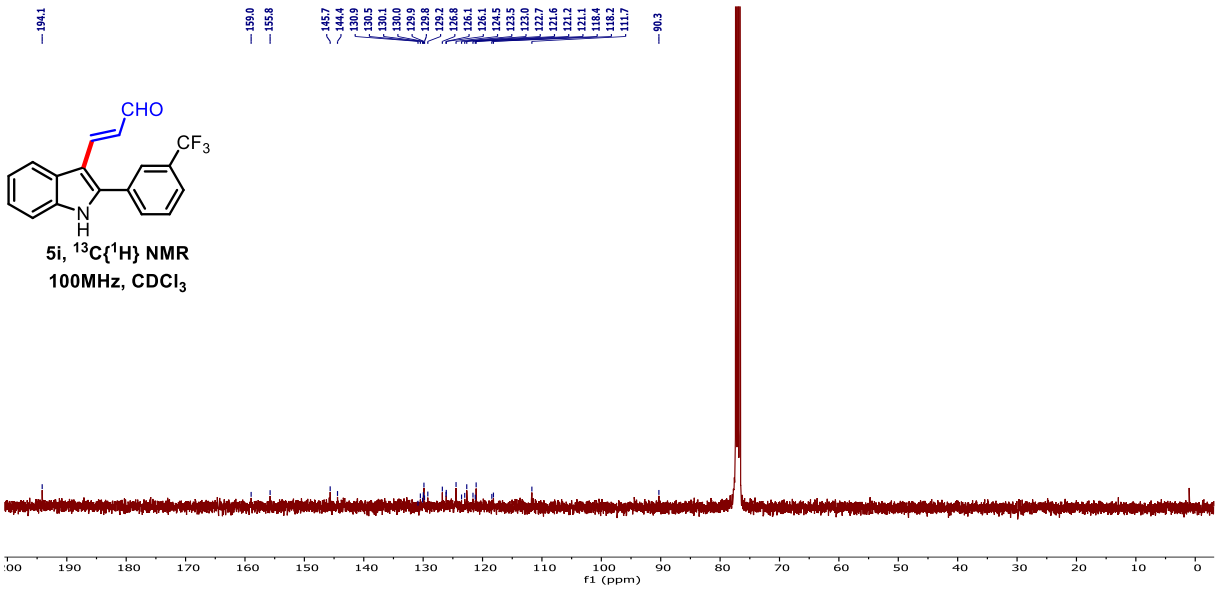

9.45
9.43
8.72
7.99
7.98
7.97
7.49
7.48
7.48
7.47
7.46
7.45
7.44
7.43
7.42
7.40
7.39
7.39
7.38
7.37
7.37
7.36
7.35
6.80
6.79
6.77
6.75
2.29
CHO
N
H
Me
5h, 1H NMR
400 MHz, CDCl3
1.00
0.91
1.03
2.02
1.08
4.95
1.00
3.03
f1 (ppm)


194.5
146.9
143.6
137.7
136.3
130.9
130.8
130.3
130.0
126.1
125.8
125.0
123.7
122.3
120.6
111.6
111.4
20.1
CHO
N
H
Me
5h, 13C{1H} NMR
100 MHz, CDCl3
f1 (ppm)

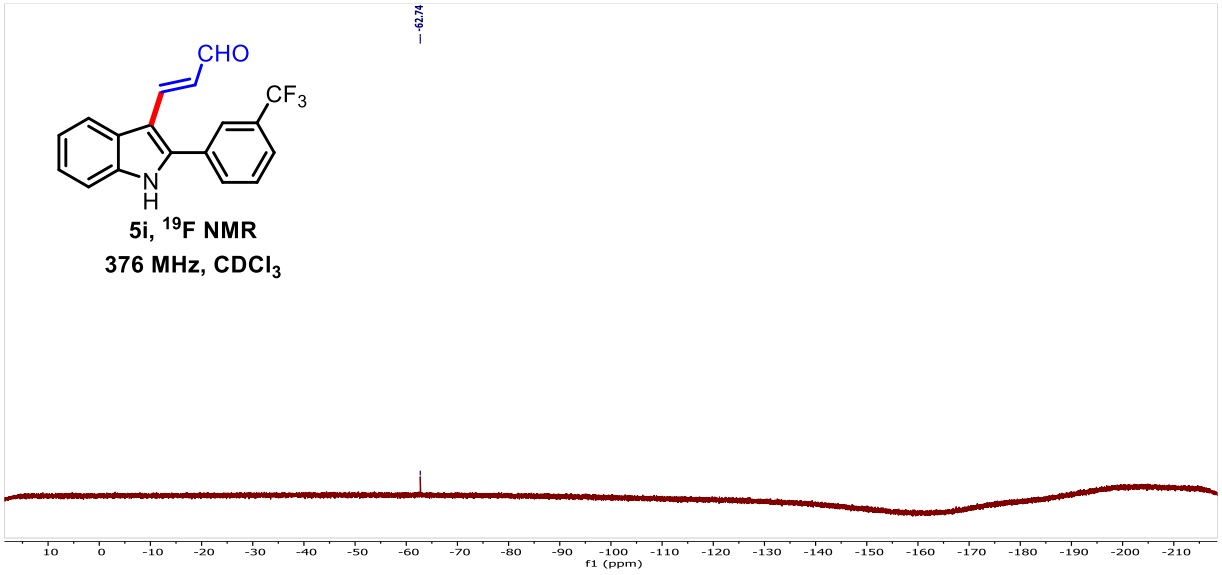



**5i, $^{1}$H NMR**
**400MHz, $CDCl_3$**

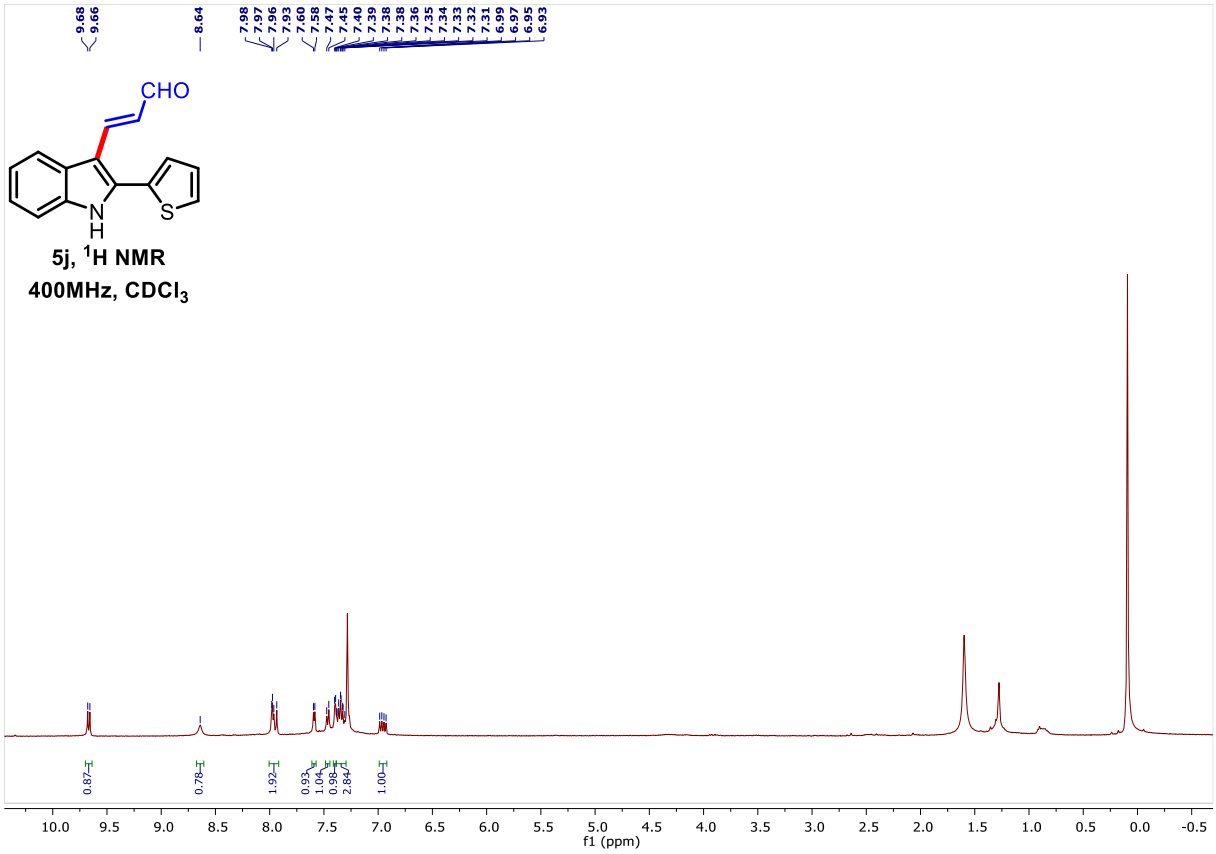


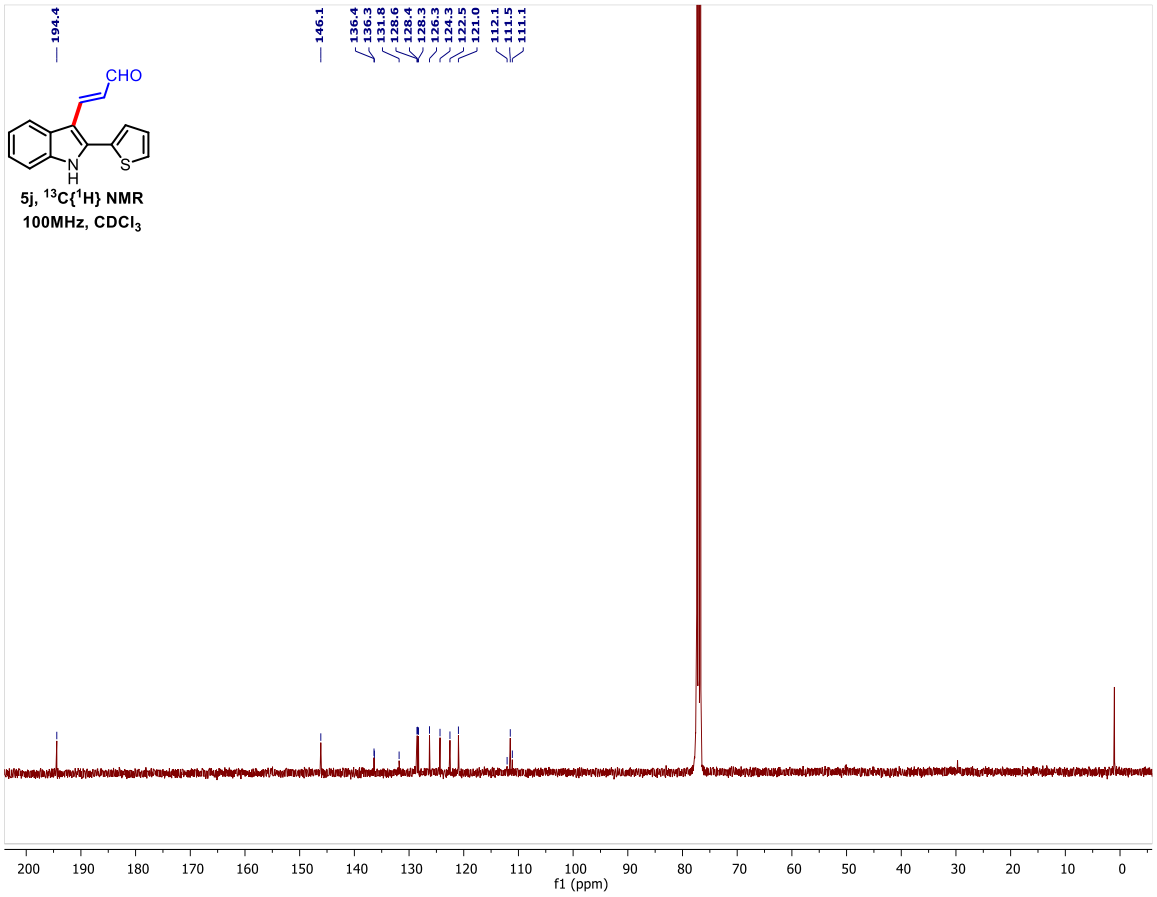


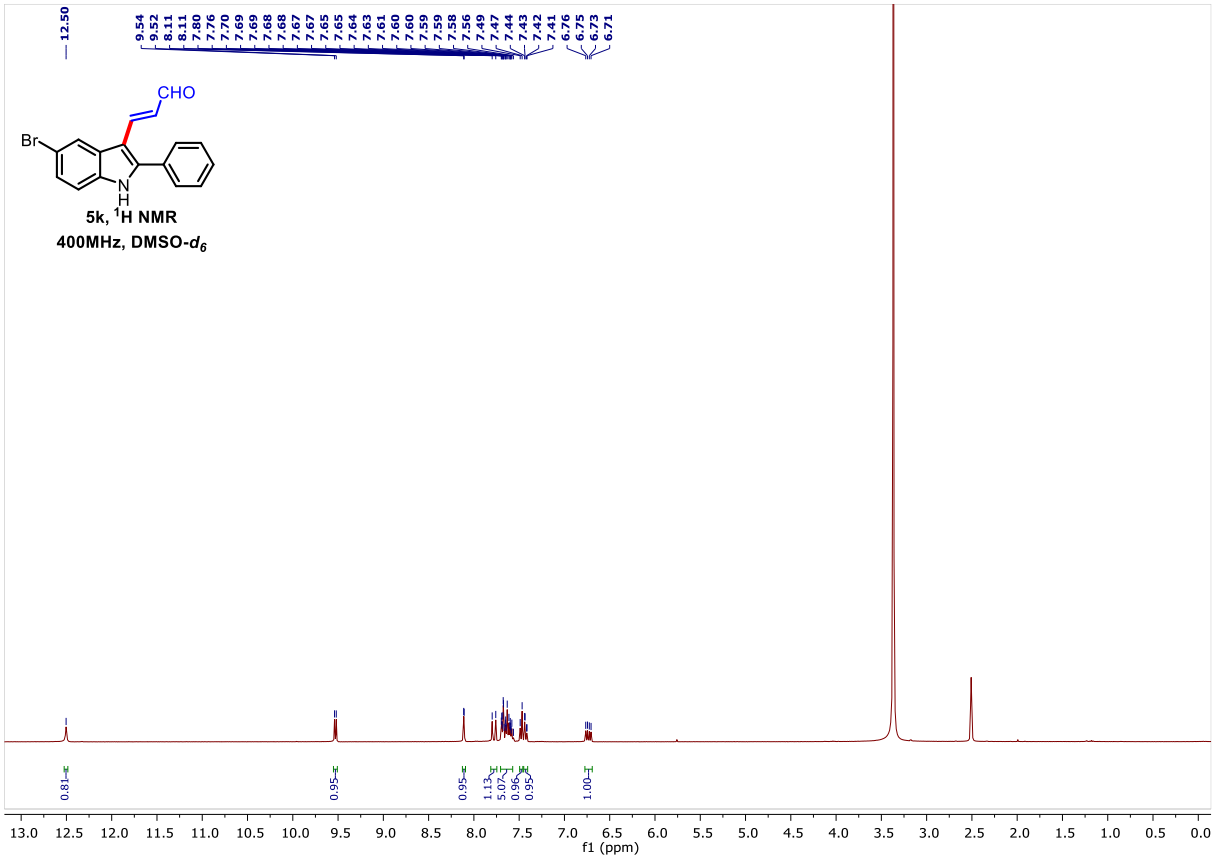

**5i, $^{13}C\{^{1}H\}$ NMR**
**100MHz, $CDCl_3$**



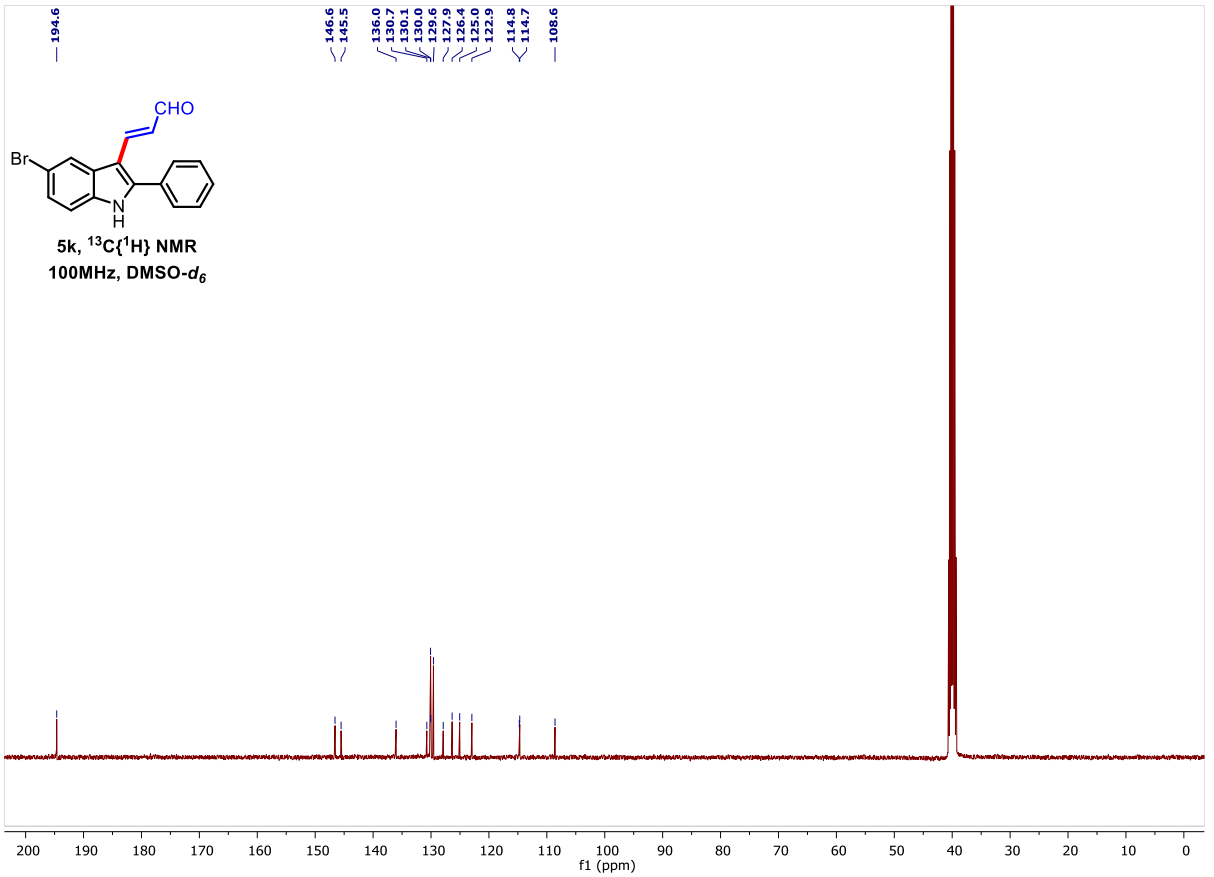

**5i, $^{19}F$ NMR**
**376 MHz, $CDCl_3$**


9.68
9.66
8.64
7.98
7.97
7.96
7.93
7.60
7.58
7.47
7.45
7.40
7.39
7.38
7.38
7.36
7.35
7.34
7.33
7.32
7.31
6.99
6.97
6.95
6.93
CHO
N
H
S
5j, $^{1}$H NMR
400MHz, CDCl$_3$
0.87
0.78
1.92
0.93
1.04
0.98
2.84
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

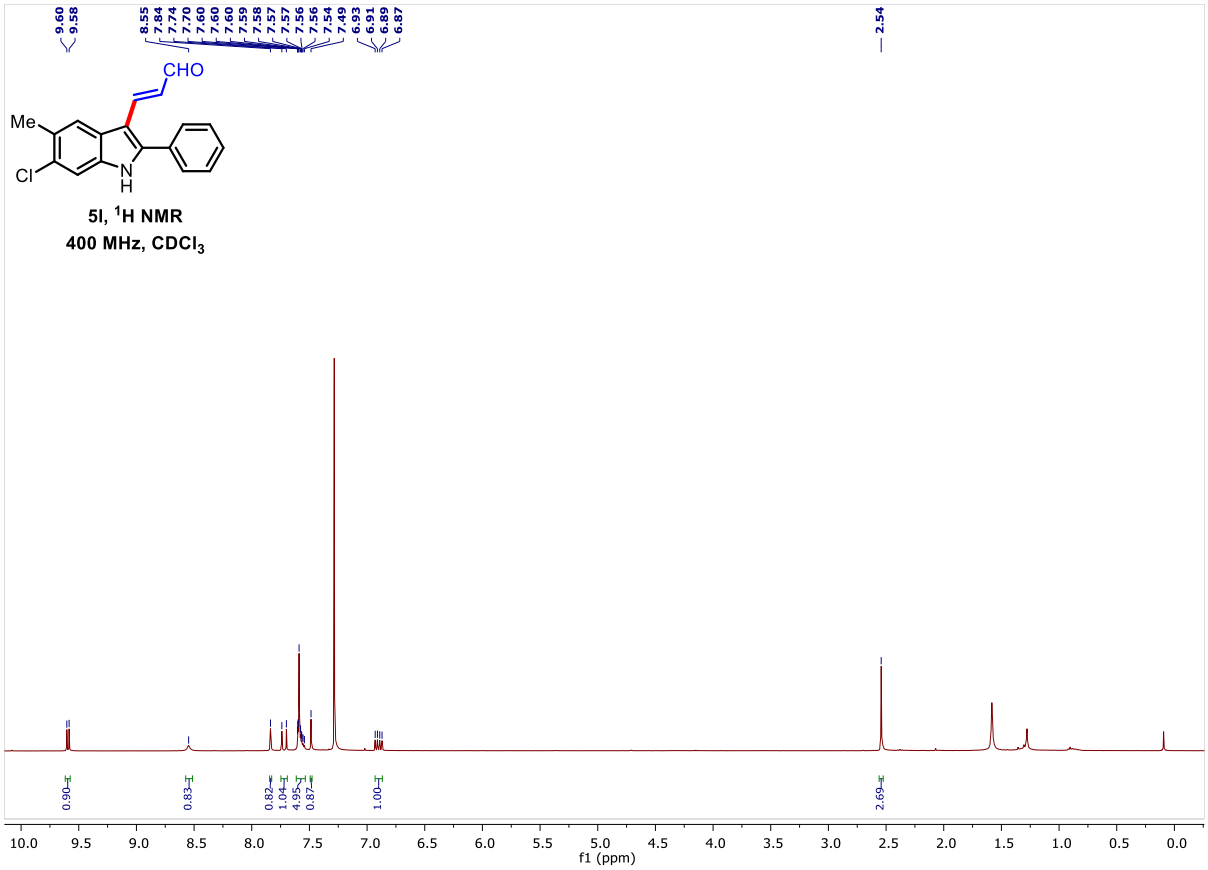

194.4
146.1
136.4
136.3
131.8
128.6
128.4
128.3
126.3
124.3
122.5
121.0
112.1
111.5
111.1
CHO
N
H
S
5j, $^{13}$C{$^{1}$H} NMR
100MHz, CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



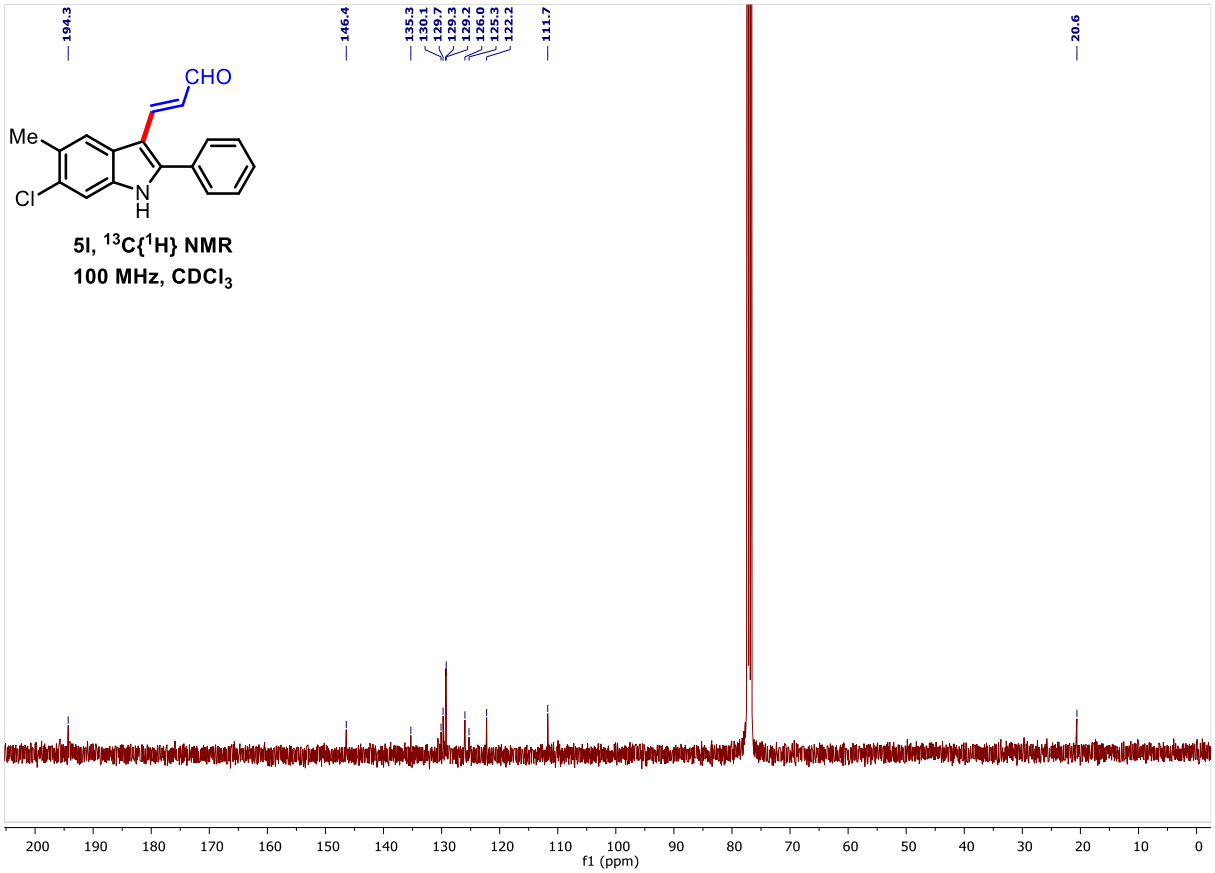

**5k, $^{1}$H NMR**
**400MHz, DMSO-$d_6$**



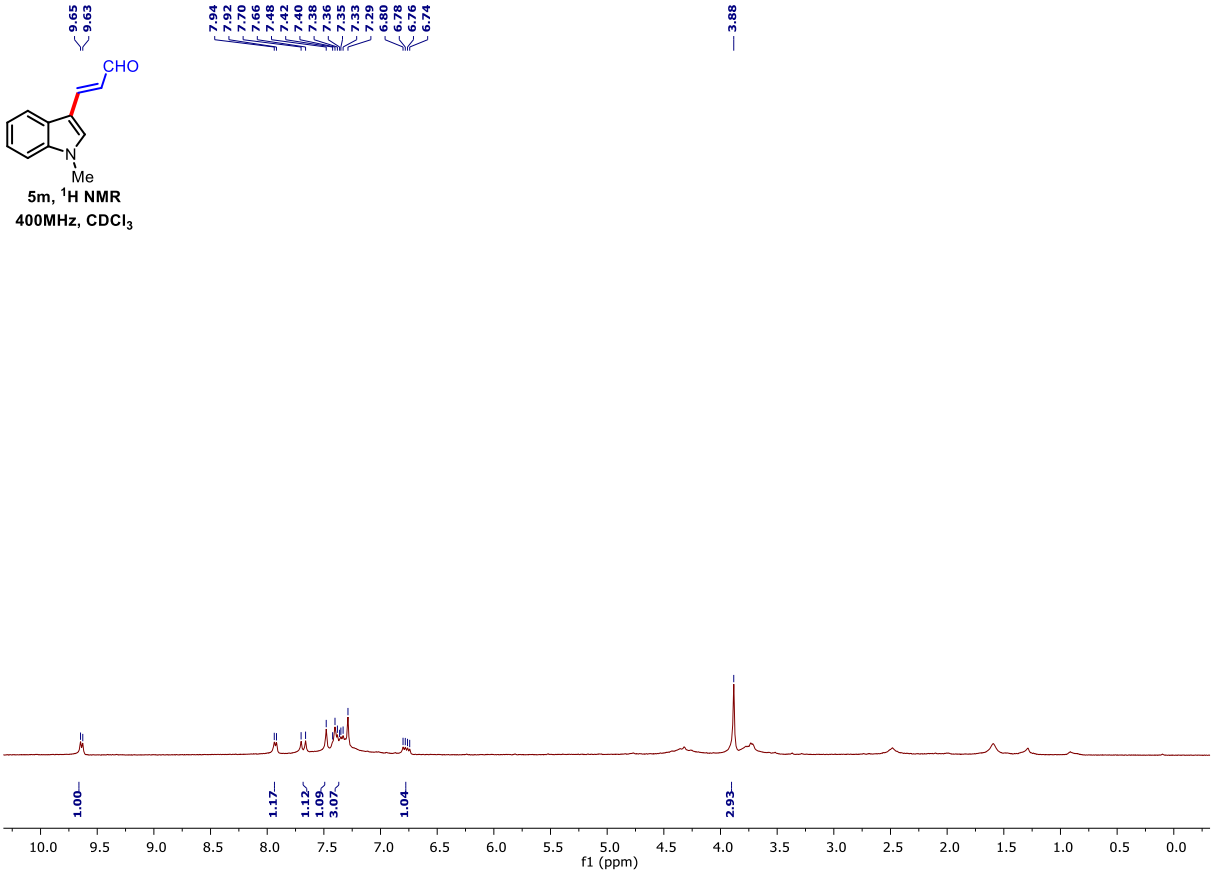

**5k, $^{13}$C{$^{1}$H} NMR**
**100MHz, DMSO-$d_6$**



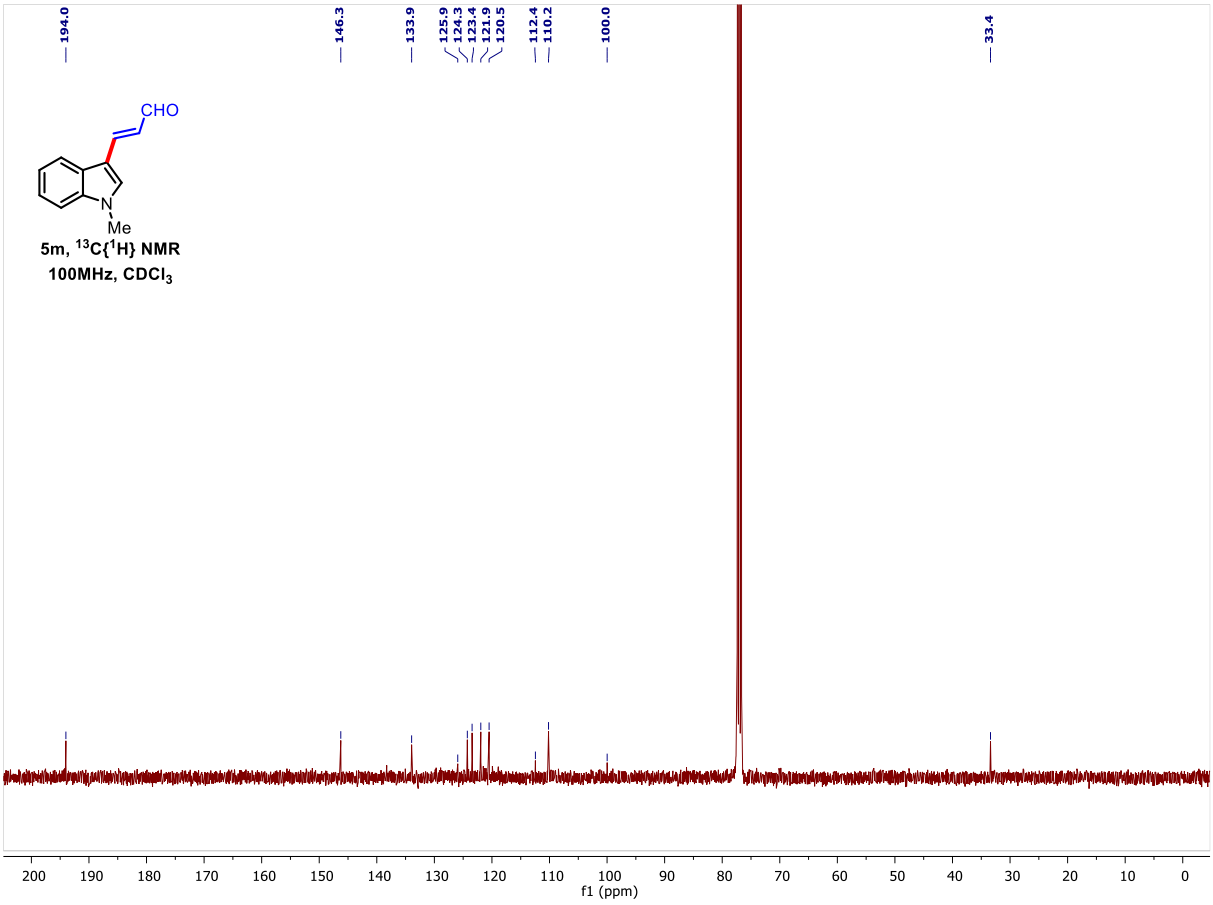

**5l, $^{1}$H NMR**
**400 MHz, $CDCl_3$**



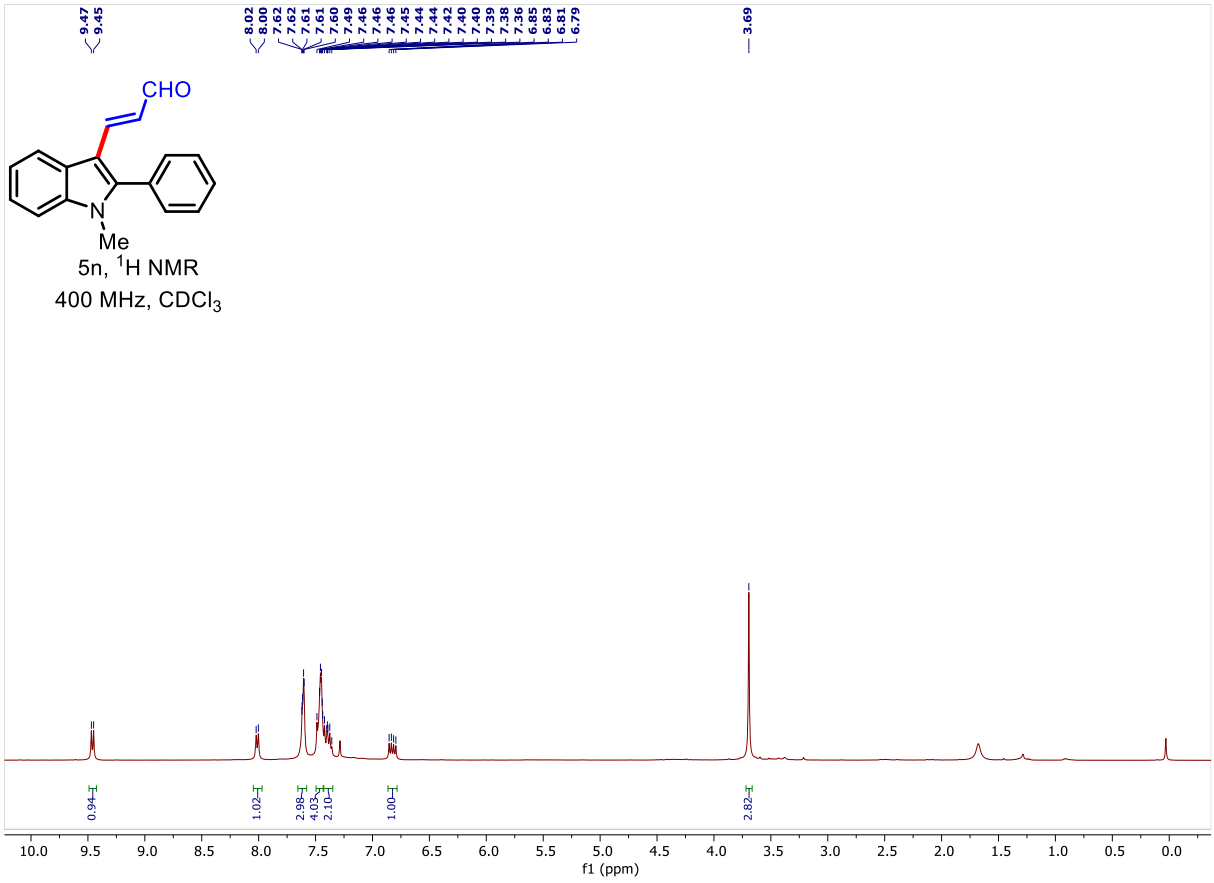

**5l, $^{13}C\{^{1}H\}$ NMR**
**100 MHz, $CDCl_3$**

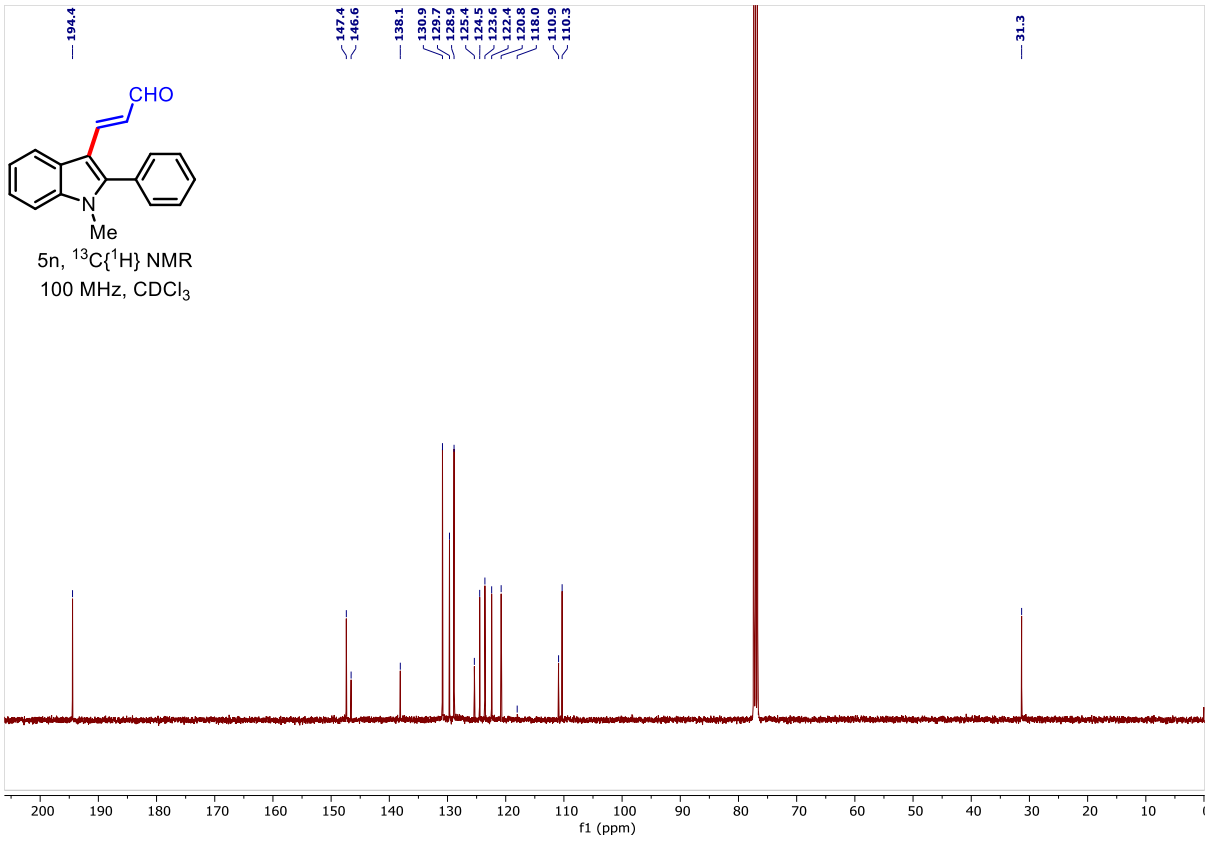


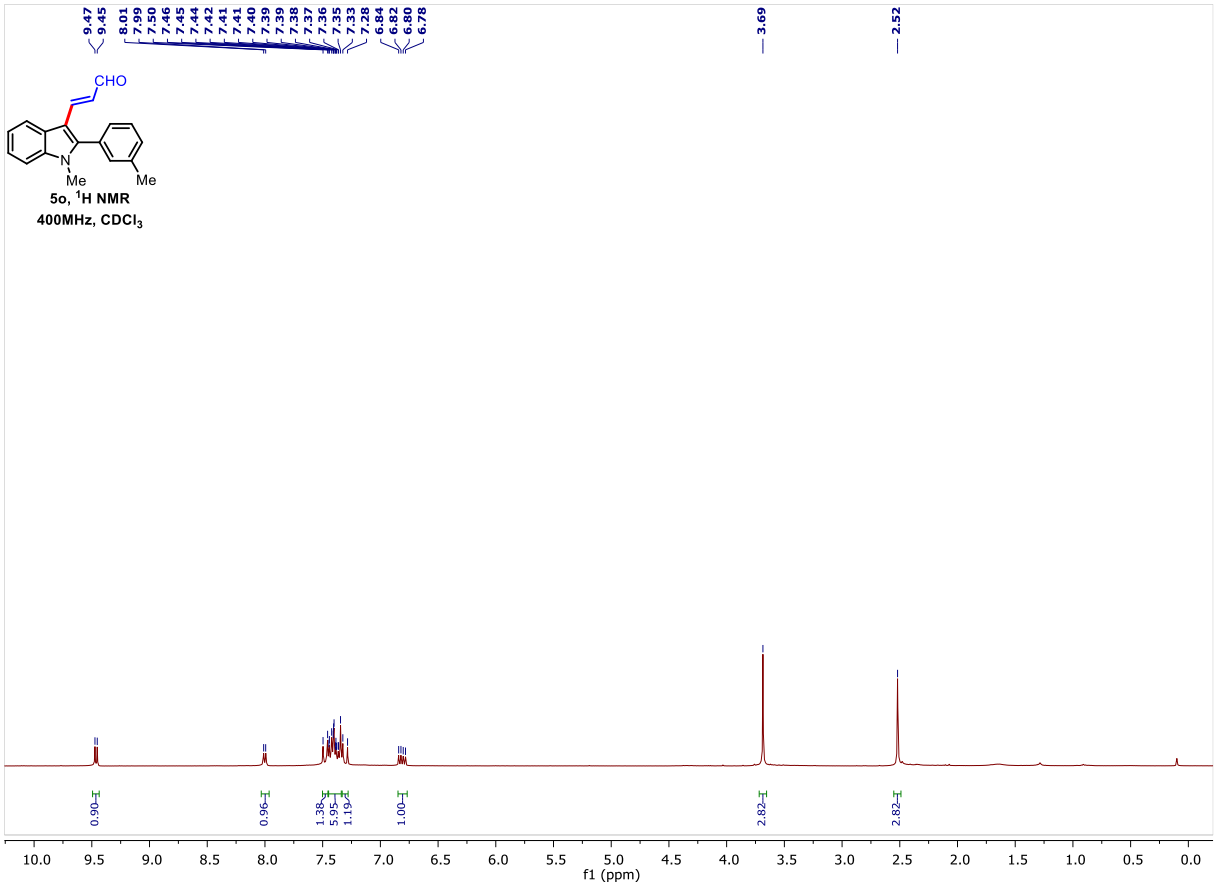

5m, $^{1}$H NMR
400MHz, $CDCl_3$

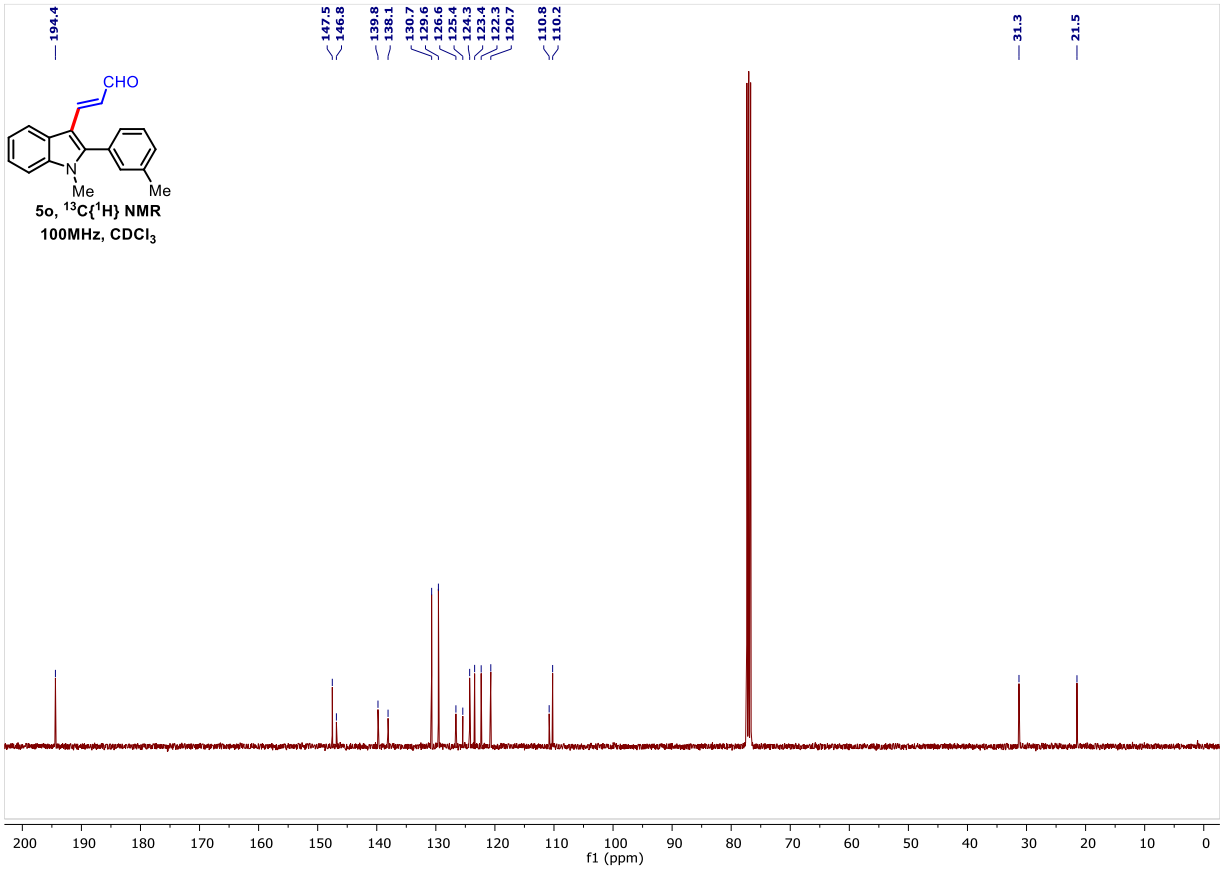


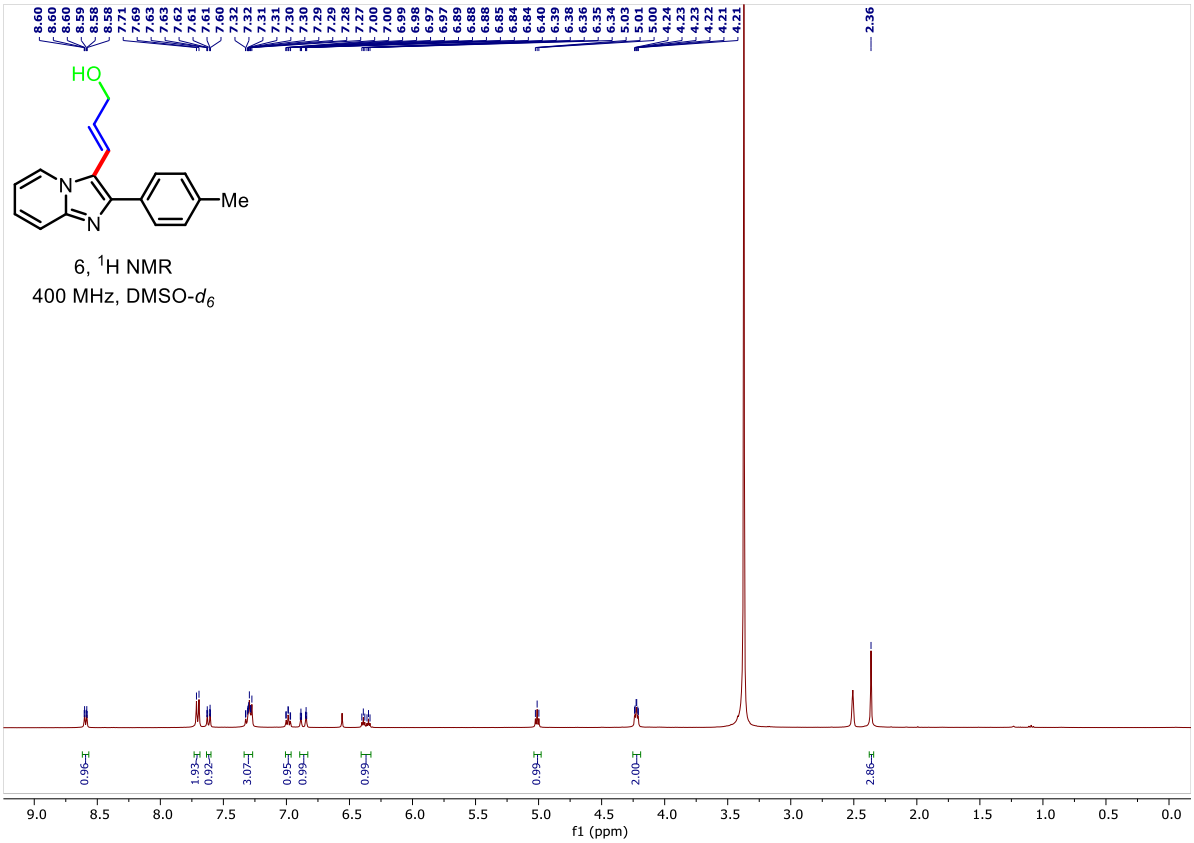

5m, $^{13}C\{^{1}H\}$ NMR
100MHz, $CDCl_3$

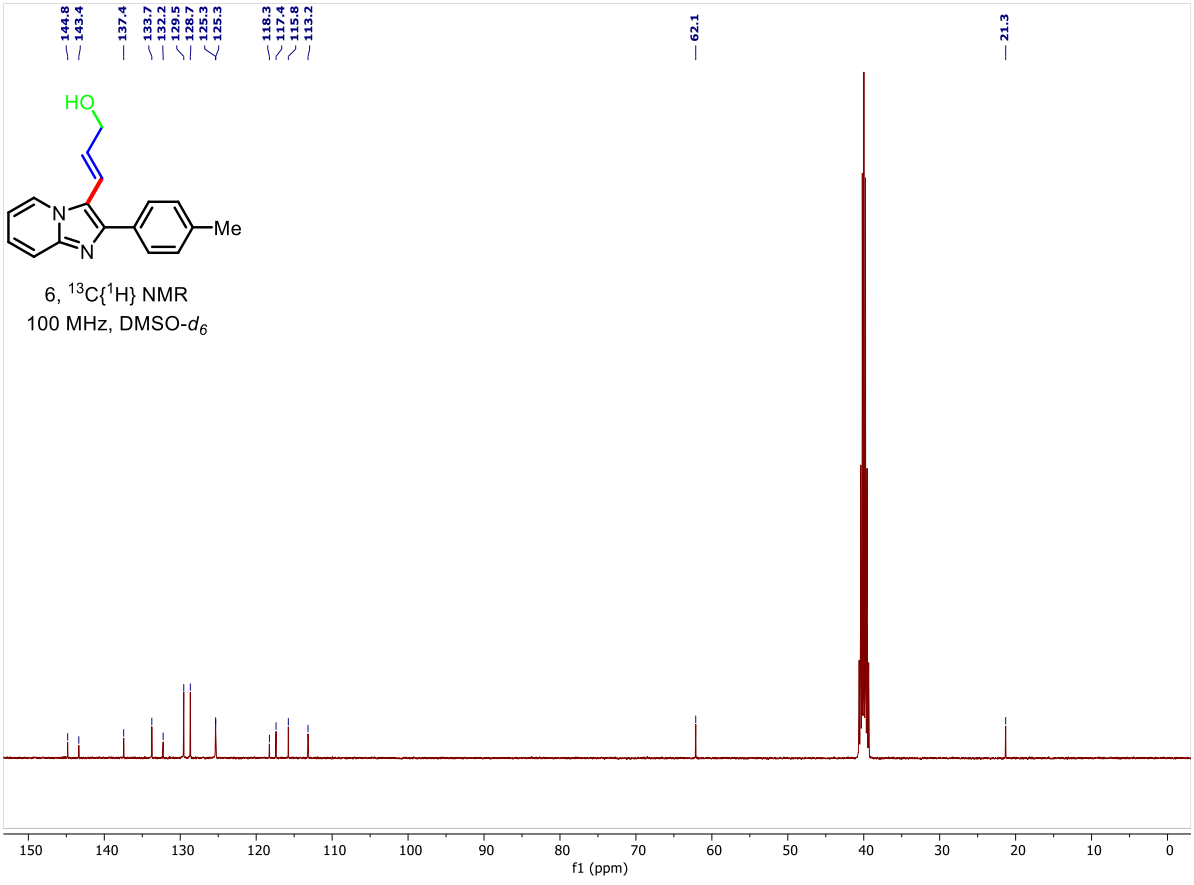

9.47
9.45
8.02
8.00
7.62
7.62
7.61
7.61
7.60
7.49
7.46
7.46
7.46
7.45
7.44
7.44
7.42
7.40
7.40
7.39
7.38
7.36
6.85
6.83
6.81
6.79
3.69
CHO
N
Me
5n, $^{1}$H NMR
400 MHz, $CDCl_3$
0.94
1.02
2.98
4.03
2.10
1.00
2.82
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

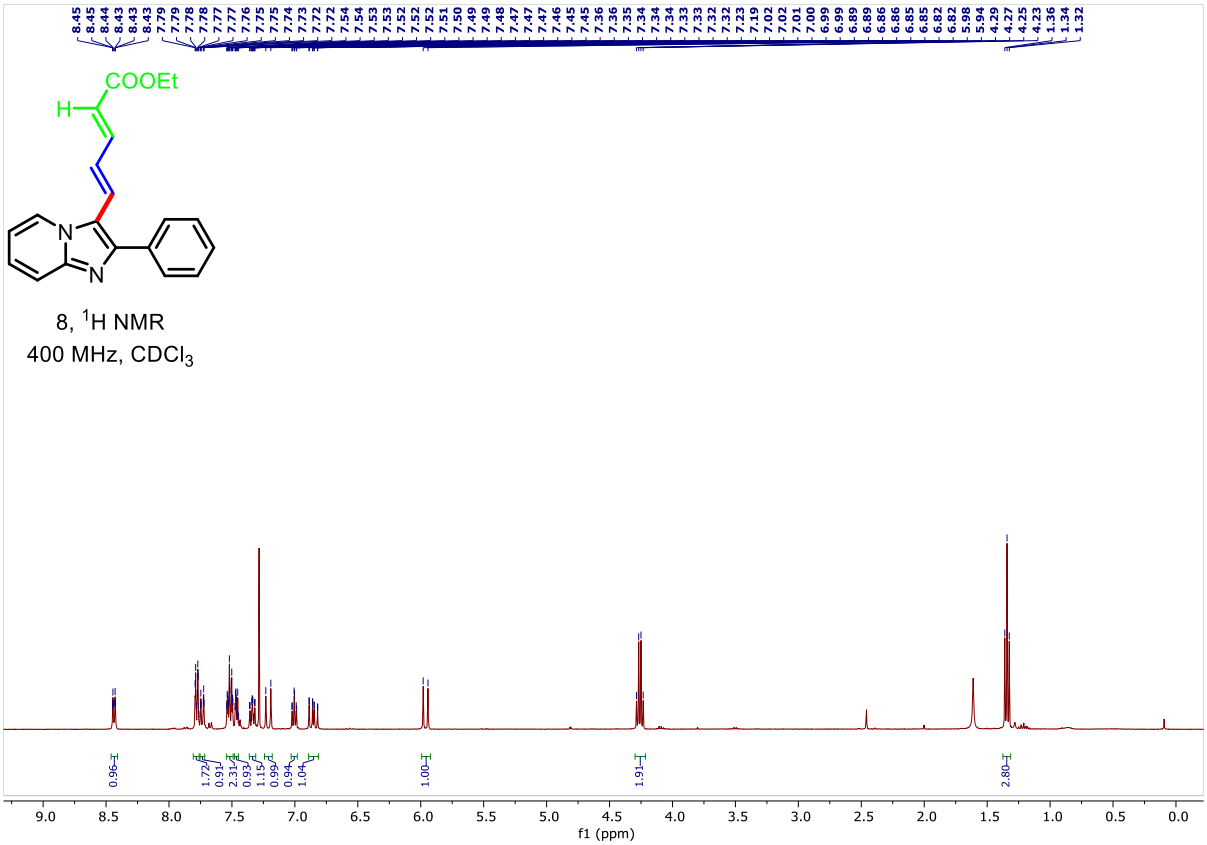

194.4
147.4
146.6
138.1
130.9
129.7
128.9
125.4
124.5
123.6
122.4
120.8
118.0
110.9
110.3
31.3
CHO
N
Me
5n, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


9.47
9.45
8.01
7.99
7.50
7.46
7.45
7.44
7.42
7.41
7.41
7.40
7.39
7.39
7.38
7.37
7.36
7.35
7.33
7.28
6.84
6.82
6.80
6.78
3.69
2.52
CHO
N
Me
Me
5o, $^{1}$H NMR
400MHz, CDCl$_3$
0.90
0.96
1.38
5.95
1.19
1.00
2.82
2.82
f1 (ppm)

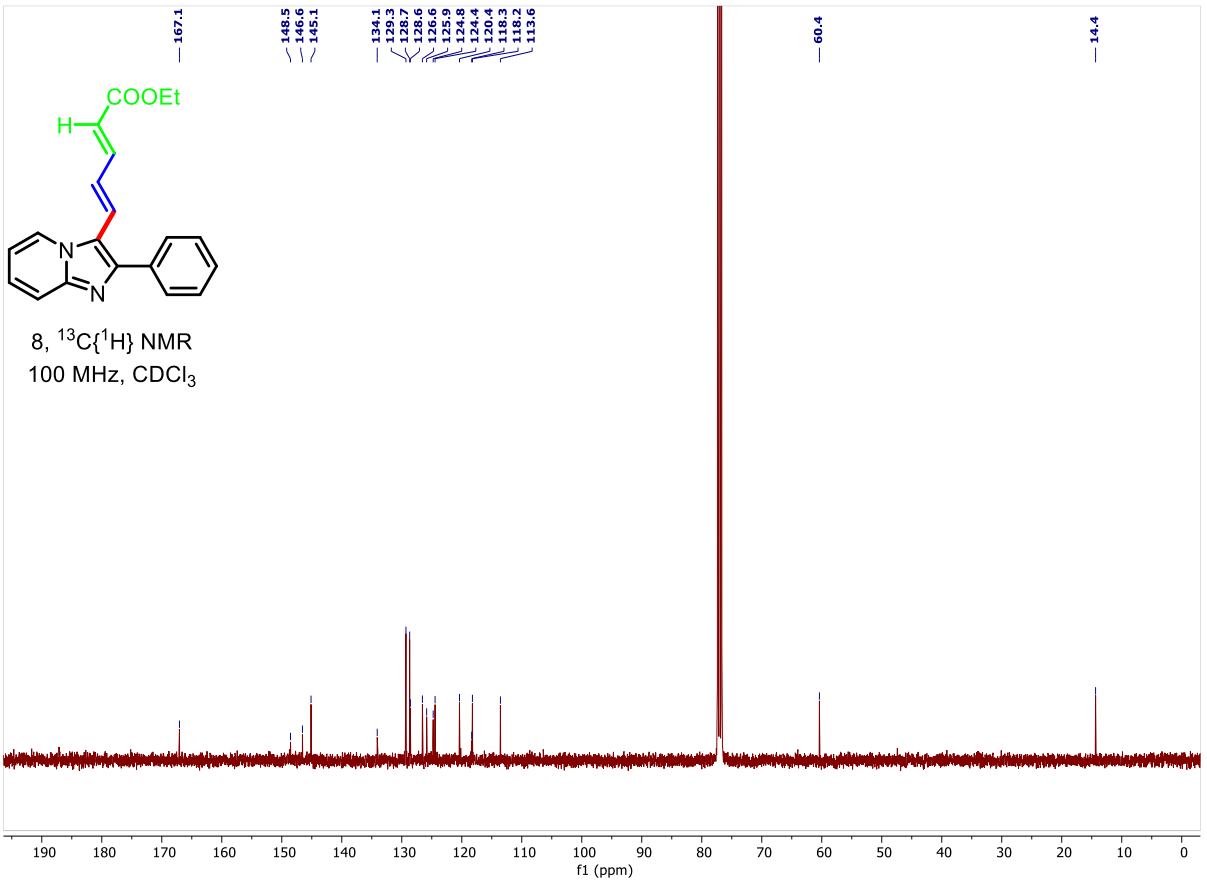

194.4
147.5
146.8
139.8
138.1
130.7
129.6
126.6
125.4
124.3
123.4
122.3
120.7
110.8
110.2
31.3
21.5
CHO
N
Me
Me
5o, $^{13}$C{$^{1}$H} NMR
100MHz, CDCl$_3$
f1 (ppm)


HO
N
N
Me
6, $^{1}$H NMR
400 MHz, DMSO-$d_6$
f1 (ppm)


HO
N
N
Me
6, $^{13}$C{$^{1}$H} NMR
100 MHz, DMSO-$d_6$
f1 (ppm)




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




8, $^{13}C\{^{1}H\}$ NMR
100 MHz, $CDCl_3$

## 8. X-ray crystallographic data of 3a, 3m and 5c

### 8.1 Single crystal X-ray data of 3a

**Experimentation**: Single crystals of **3a** [$C_{16}H_{12}N_2O$] were grown from slow evaporation of $CDCl_3$ solution. A suitable crystal was selected and mounted on an XtaLAB AFC12 (RINC): Kappa dual home/near diffractometer. The crystal was kept at 93(2) K during data collection. Using Olex2,[1] the structure was solved with the ShelXT[2] structure solution program using Intrinsic phasing and refined with the ShelXL[3] refinement package using least squares minimization.

**Table S1: Crystal data and structure refinement for 3a**

| | |
|---|---|
| 100Identification code | **3a** [exp_1006_AK-NS-1491(MF)-1_autored] |
| Empirical formula | $C_{16}H_{12}N_2O$ |
| Formula weight | 248.28 |
| Temperature/K | 93(2) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 10.1660(3) |
| b/Å | 11.6979(5) |
| c/Å | 12.1456(5) |
| α/° | 63.066(4) |
| β/° | 84.657(3) |
| γ/° | 84.039(3) |
| Volume/Å$^3$ | 1279.00(9) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.289 |
| μ/mm$^{-1}$ | 0.656 |
| F(000) | 520.0 |
| Crystal size/mm$^3$ | 0.18 × 0.05 × 0.03 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 8.176 to 159.496 |
| Index ranges | $-10 \leq h \leq 12$, $-14 \leq k \leq 14$, $-15 \leq l \leq 15$ |
| Reflections collected | 11900 |

| | |
|---|---|
| Independent reflections | 5258 [$R_{int}$ = 0.0348, $R_{sigma}$ = 0.0491] |
| Data/restraints/parameters | 5258/0/343 |
| Goodness-of-fit on $F^2$ | 1.068 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0415, $wR_2$ = 0.1111 |
| Final R indexes [all data] | $R_1$ = 0.0514, $wR_2$ = 0.1180 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.16/-0.25 |

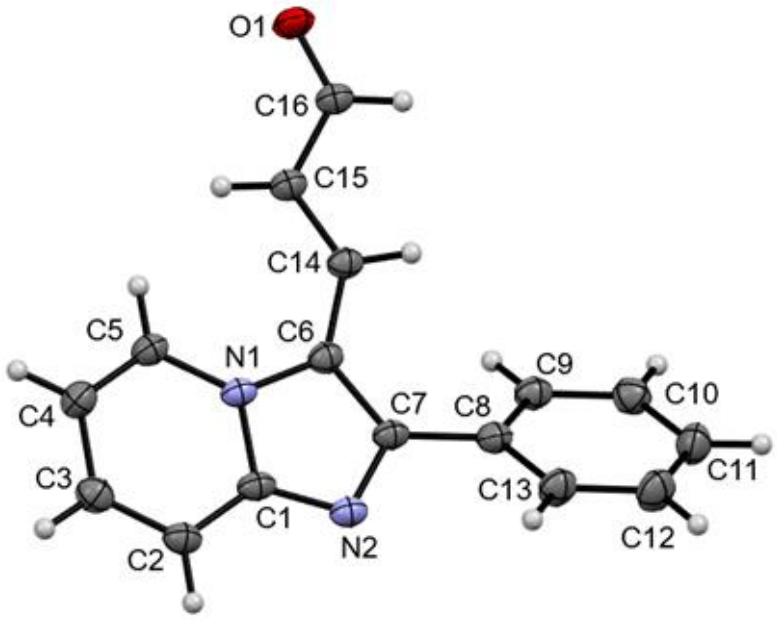



**Figure S1**. The ORTEP diagram of **3a** [CCDC: 2266949]. Thermal ellipsoids are drawn at 50 % probability level.

## 8.2 Single crystal X-ray data of 3m

**Experimentation**: Single crystals of **3m** [$C_{14}H_{10}N_2OS$] were grown from slow evaporation of $CDCl_3$ solution. A suitable crystal was selected and mounted on an XtaLAB AFC12 (RINC): Kappa dual home/near diffractometer. The crystal was kept at 93(2) K during data collection. Using Olex2,[1] the structure was solved with the ShelXT[2] structure solution program using Intrinsic phasing and refined with the ShelXL[3] refinement package using least squares minimization.

**Table S2: Crystal data and structure refinement for 3m.**

| | |
|---|---|
| Identification code | **3m** [exp_1007_AK-VNS-1506_autored] |
| Empirical formula | $C_{14}H_{10}N_2OS$ |
| Formula weight | 254.30 |
| Temperature/K | 93(2) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 10.0711(4) |
| b/Å | 11.4925(5) |
| c/Å | 11.9654(5) |
| α/° | 61.660(4) |
| β/° | 81.255(3) |
| γ/° | 84.932(3) |
| Volume/Å$^3$ | 1204.54(10) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.402 |
| μ/mm$^{-1}$ | 2.286 |
| F(000) | 528.0 |
| Crystal size/mm$^3$ | 0.2 × 0.1 × 0.05 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 8.464 to 159.424 |
| Index ranges | -10 ≤ h ≤ 12, -14 ≤ k ≤ 14, -14 ≤ l ≤ 14 |
| Reflections collected | 13008 |
| Independent reflections | 5049 [$R_{int}$ = 0.0351, $R_{sigma}$ = 0.0376] |
| Data/restraints/parameters | 5049/0/326 |
| Goodness-of-fit on F$^2$ | 1.096 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0664, w$R_2$ = 0.2033 |
| Final R indexes [all data] | $R_1$ = 0.0706, w$R_2$ = 0.2088 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.44/-1.09 |

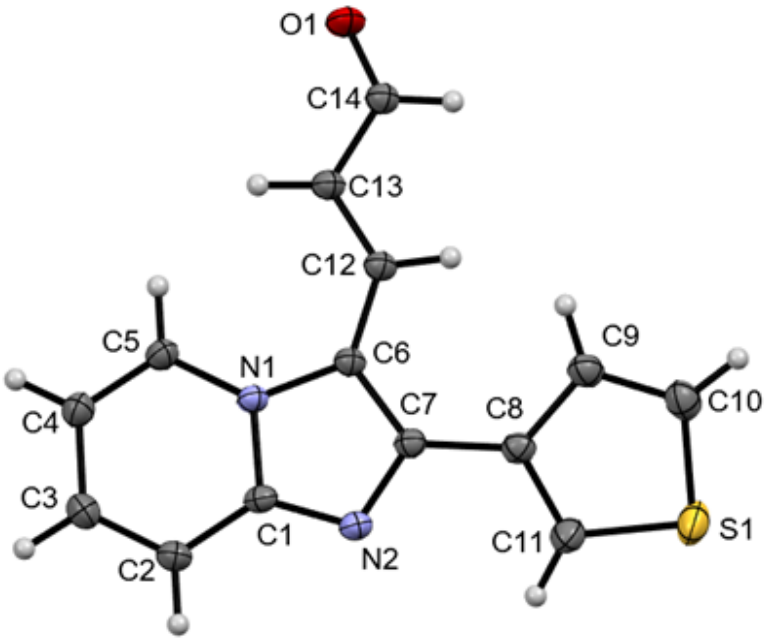



Figure S2. The ORTEP diagram of 3m [CCDC: 2266961]. Thermal ellipsoids are drawn at 50 % probability level.

## 8.3 Single crystal X-ray data of 5c

**Experimentation**: Single crystals of **5c** [$C_{18}H_{15}NO_2$] were grown from slow evaporation of $CDCl_3$ solution. A suitable crystal was selected and mounted on an XtaLAB AFC12 (RINC): Kappa dual home/near diffractometer. The crystal was kept at 93(2) K during data collection. Using Olex2,[1] the structure was solved with the ShelXT[2] structure solution program using Intrinsic phasing and refined with the ShelXL[3] refinement package using least squares minimization.

**Table S3: Crystal data and structure refinement for 5c**

| | |
|---|---|
| Identification code | **5c** [exp_1005_AK_VNS-1499(A)] |
| Empirical formula | $C_{18}H_{15}NO_2$ |
| Formula weight | 277.31 |
| Temperature/K | 93(2) |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 9.8190(2) |
| b/Å | 13.9258(2) |
| c/Å | 10.6950(2) |

| | |
|---|---|
| α/° | 90 |
| β/° | 97.120(2) |
| γ/° | 90 |
| Volume/Å$^3$ | 1451.13(5) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.269 |
| μ/mm$^{-1}$ | 0.664 |
| F(000) | 584.0 |
| Crystal size/mm$^3$ | 0.12 × 0.06 × 0.05 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 9.076 to 158.934 |
| Index ranges | -12 ≤ h ≤ 12, -17 ≤ k ≤ 17, -13 ≤ l ≤ 8 |
| Reflections collected | 8389 |
| Independent reflections | 3060 [$R_{int}$ = 0.0319, $R_{sigma}$ = 0.0369] |
| Data/restraints/parameters | 3060/0/191 |
| Goodness-of-fit on F$^2$ | 1.051 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0401, $wR_2$ = 0.1035 |
| Final R indexes [all data] | $R_1$ = 0.0460, $wR_2$ = 0.1070 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.21/-0.22 |

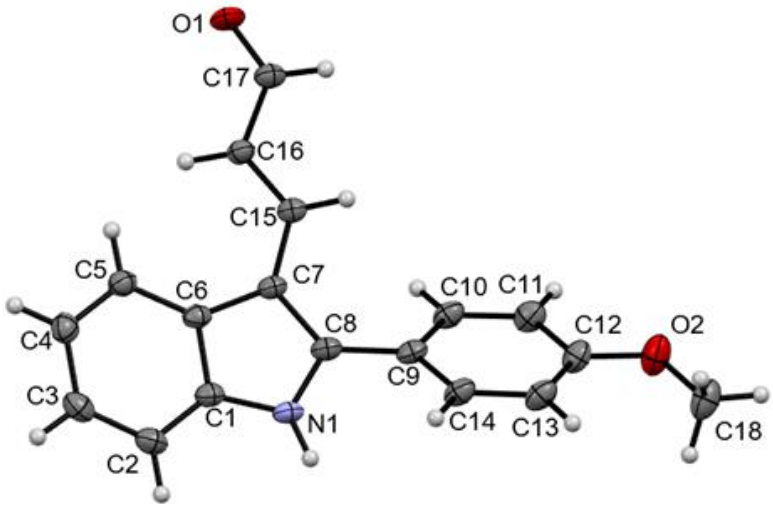



Figure S3. The ORTEP diagram of **5c** [CCDC: 2266943]. Thermal ellipsoids are drawn at 50 % probability level.

## 9. References


[1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339-341.

[2] G. Sheldrick, *Acta Cryst. A* **2015**, *71*, 3-8.

[3] G. Sheldrick, *Acta Cryst. C* **2015**, *71*, 3-8.