Supplementary Information

Metal-Free Electrochemical [3+2] Heteroannulation of Anilines with Pyridines Enabled by Dual C-H Radical Aminations

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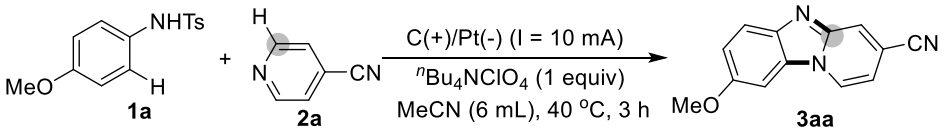
(A) Typical Experimental Procedure

(a) General

The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solvent on a NMR spectrometer using TMS as internal standard. HRMS was measured on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Melting points are uncorrected. The instrument for electrolysis is DC power source (PM3005B) (made in China). Cyclic voltammograms were obtained on a CHI 605E potentiostat. The anode electrode is graphite rod (Φ6 mm×80 mm) and cathode electrode is platinum electrodes (1.0×1.0 cm^2).

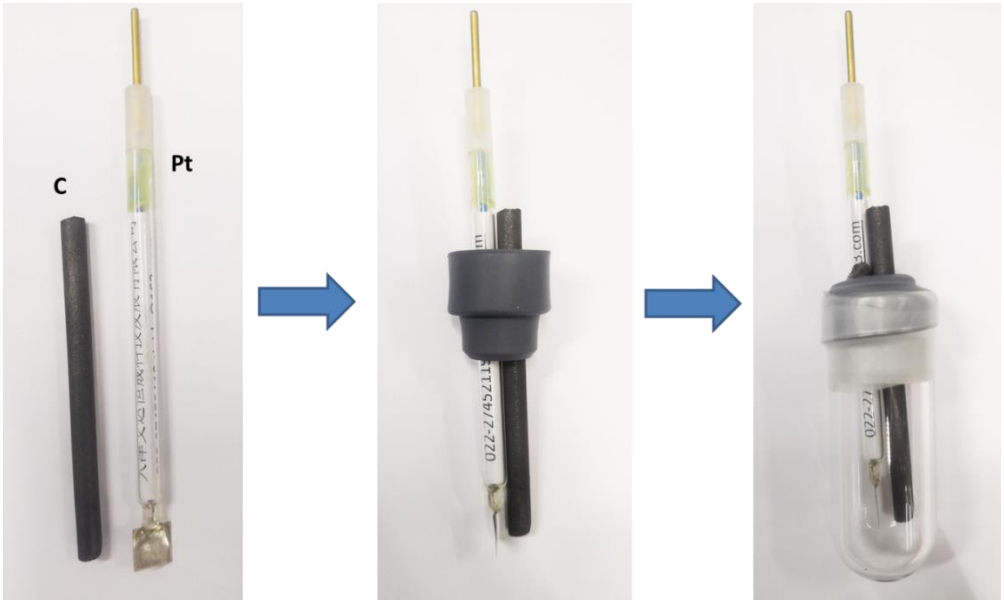
(b) General procedures for electrochemical [3+2] heteroannulation of anilines (1) with pyridines (2)



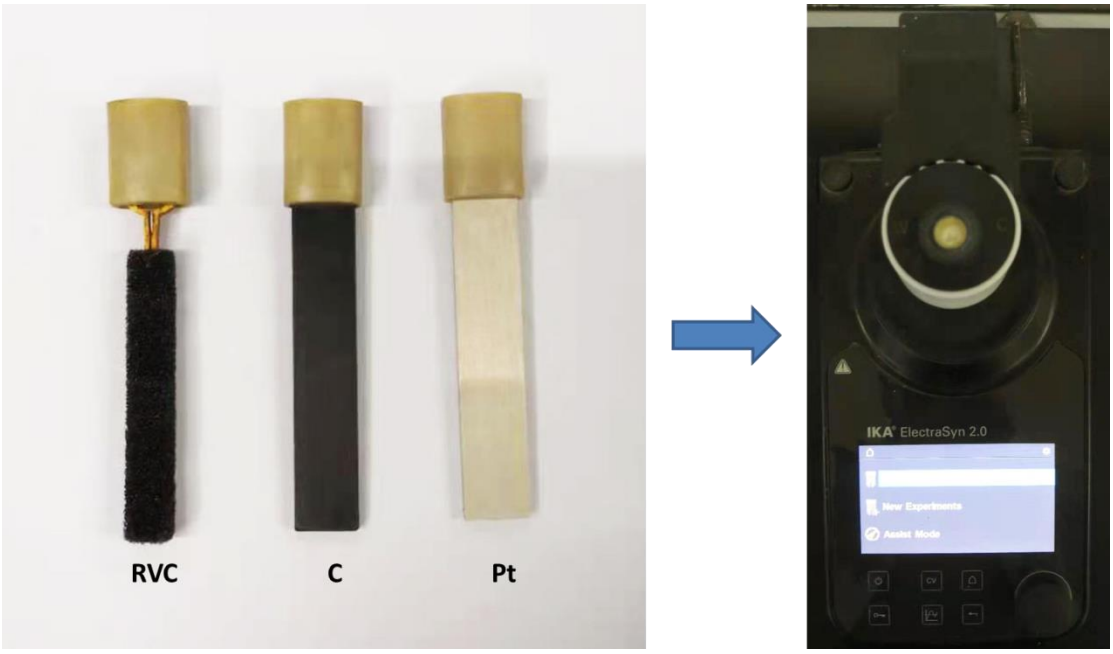
To an undivided single-necked bottle (10 mL) were added **1a** (0.3 mmol), **2a** (0.6 mmol), $^{n}Bu_4NClO_4$ (1.0 equiv) and MeCN (6 mL). The bottle was equipped with platinum electrodes (1.0×1.0 cm^2) as cathode and graphite rod electrode as anode under air or argon. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA at 40 ºC for 3 h until complete consumption of **1a** as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the solution was extracted with EtOAc (3×10 mL). The combined organic layer was dried with Na_2SO_4, filtered and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired products **3aa**.

(c) Experimental devices

The electrochemical effectiveness is equivalent with our prepared electrochemical reaction device or the IKA ElectroSyn 2.0 electrochemical reaction device.



(a) Self-prepared electrochemical reaction devices



(b) IKA ElectroSyn 2.0 electrochemical reaction devices

(d) Cyclic voltammogram analysis

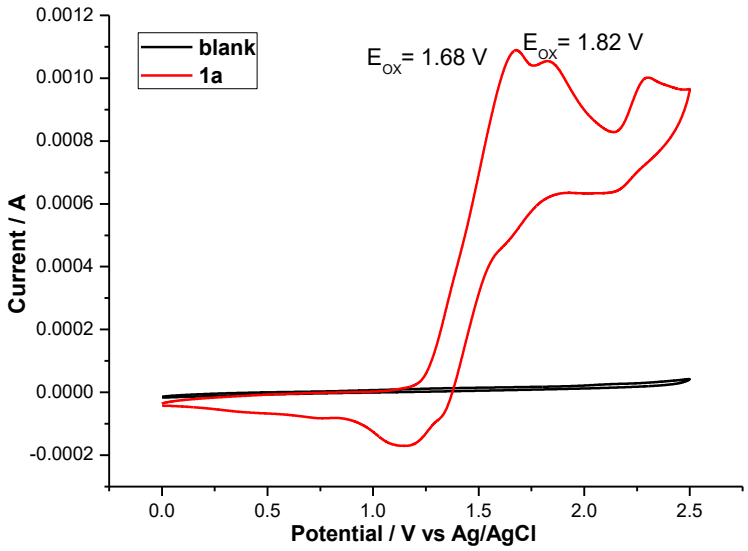


Figure S1. Cyclic voltammogram curves (0-2.5 V). Using GC disk as working electrode, Pt slice, and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate. **1a** (0.05 M), $^{n}Bu_4NClO_4$ (0.1 M) and MeCN (6 mL).

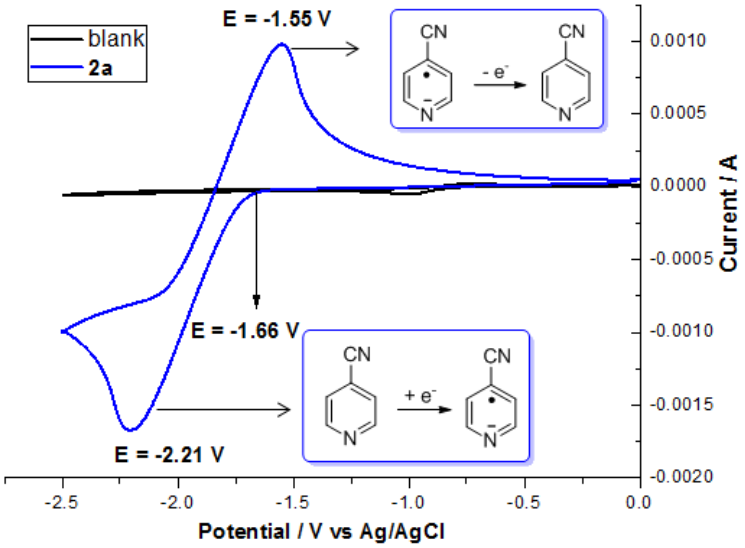


Figure S2. Cyclic voltammogram curves (-2.5-0 V). Using GC disk as working electrode, Pt slice, and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate. **2a** (0.1 M), $^{n}Bu_4NClO_4$ (0.1 M) and MeCN (6 mL).

Scanning range: 0 – 2.5 V (4-Cyanopyridine is electron deficient aromatics, no oxidative peak in 0-2.5 V).

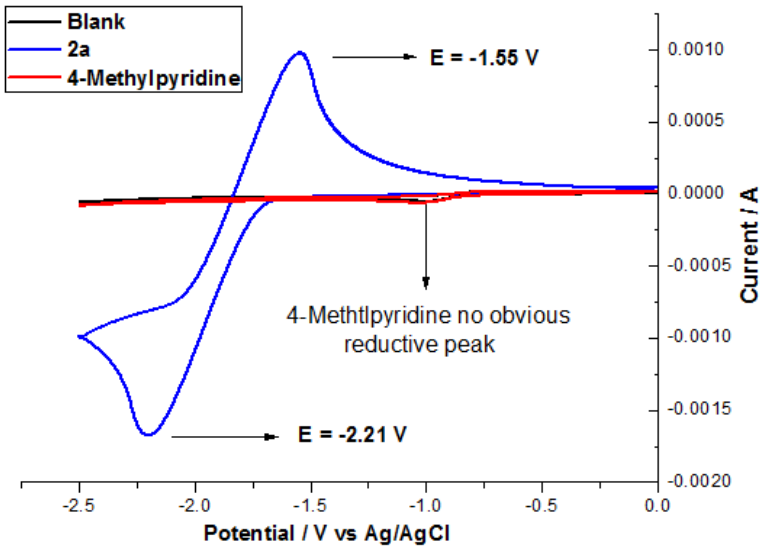


Figure S3. Cyclic voltammogram curves (-2.5-0 V). Using GC disk as working electrode, Pt slice, and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate. **2a / 4-Methylpridine** (0.1 M), $^{n}Bu_4NClO_4$ (0.1 M) and MeCN (6 mL).

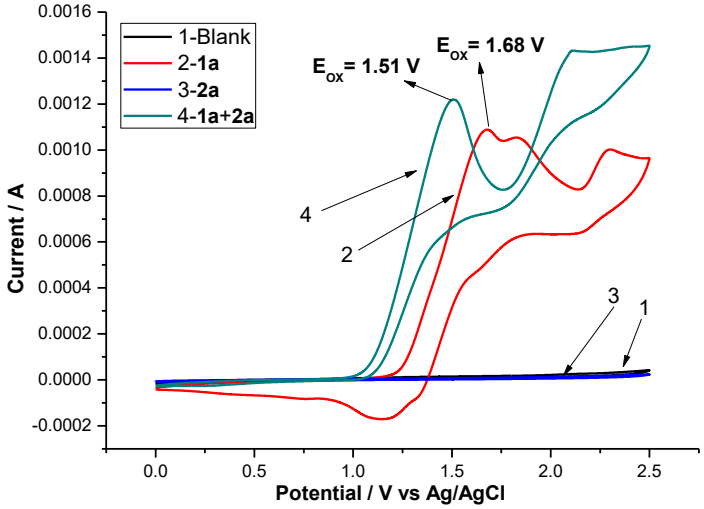


Figure S4. Cyclic voltammogram curves (0 – 2.5 V). Using GC disk as working electrode, Pt slice, and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate. (1) $^{n}Bu_4NClO_4$ (0.1 M) and MeCN (6 mL); (2) **1a** (0.05 M), $^{n}Bu_4NClO_4$ (0.1 M) and MeCN (6 mL); (3) **2a** (0.1 M), $^{n}Bu_4NClO_4$ (0.1 M) and MeCN (6 mL); (4) **1a** (0.05 M), **2a** (0.1 M), $^{n}Bu_4NClO_4$ (0.1 M) and MeCN (6 mL).

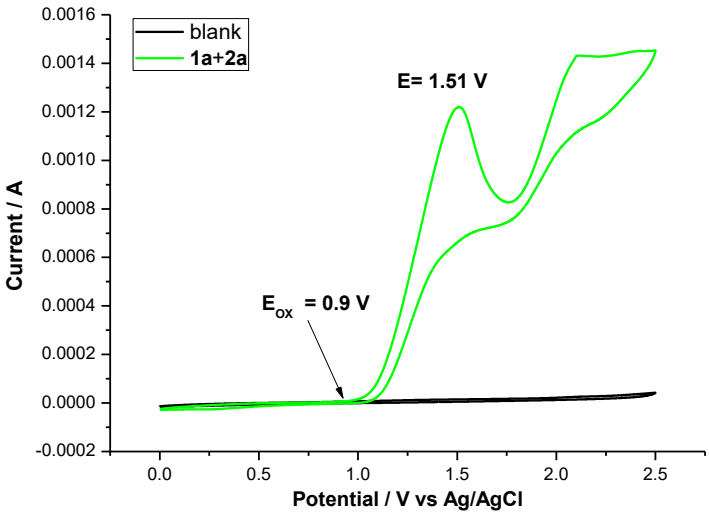


Figure S5. Cyclic voltammogram curves (0 – 2.5 V). Using GC disk as working electrode, Pt slice, and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate. **1a** (0.05 M), **2a** (0.1 M), $^{n}Bu_4NClO_4$ (0.1 M) and MeCN (6 mL).

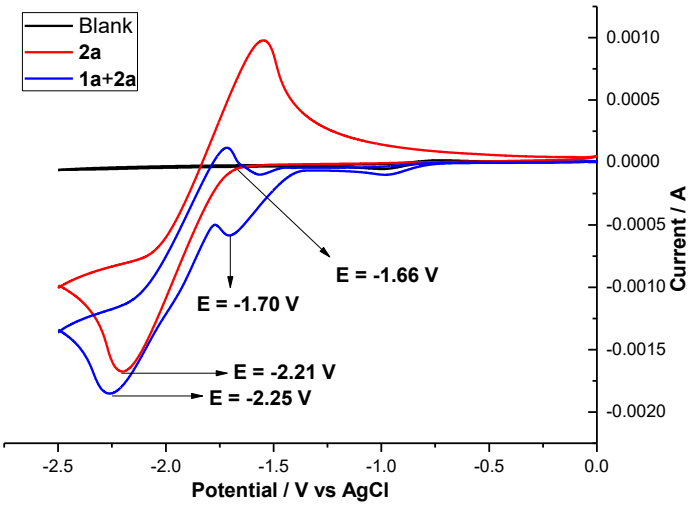


Figure S6. Cyclic voltammogram curves (-2.5 – 0 V). Using GC disk as working electrode, Pt slice, and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate. (black curve) $^{n}Bu_4NClO_4$ (0.1 M) and MeCN (6 mL); (red curve) **2a** (0.1 M), $^{n}Bu_4NClO_4$ (0.1 M) and MeCN (6 mL); (blue curve) **1a** (0.05 M), **2a** (0.1 M), $^{n}Bu_4NClO_4$ (0.1 M) and MeCN (6 mL).

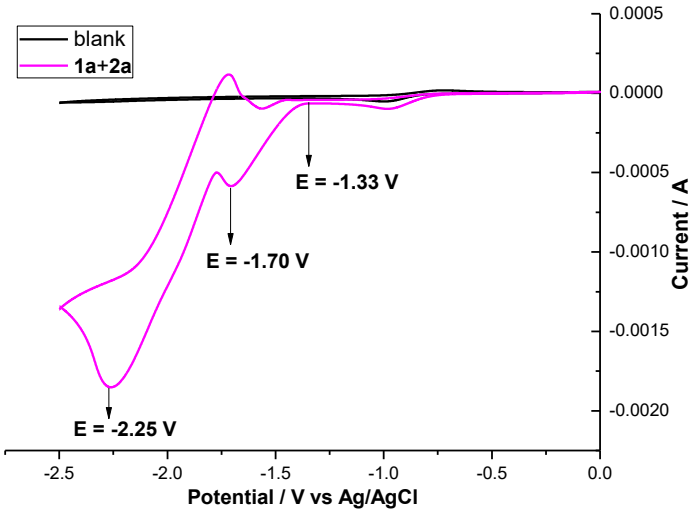


Figure S7. Cyclic voltammogram curves (-2.5 – 0 V). Using GC disk as working electrode, Pt slice, and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate. **1a** (0.05 M), **2a** (0.1 M), $^{n}Bu_4NClO_4$ (0.1 M) and MeCN (6 mL).

(e) UV spectrum and fluorescence spectrum

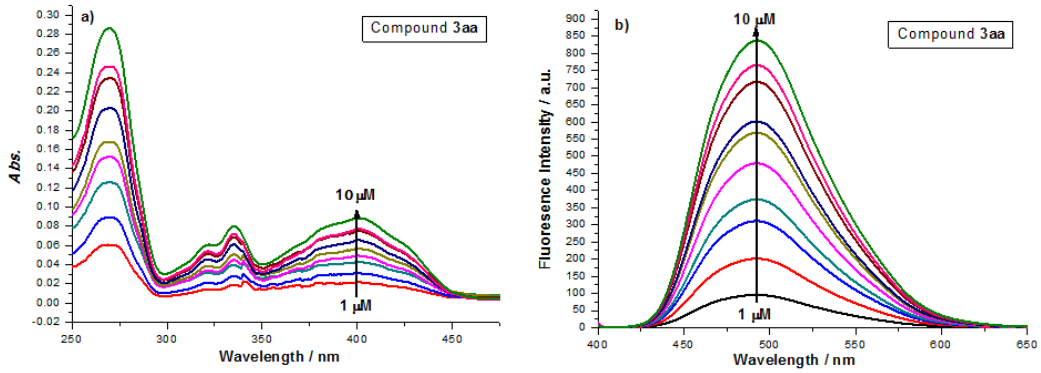


Figure S8. UV-vis absorption spectra and fluorescence emission spectra of compound **3aa** in MeCN.

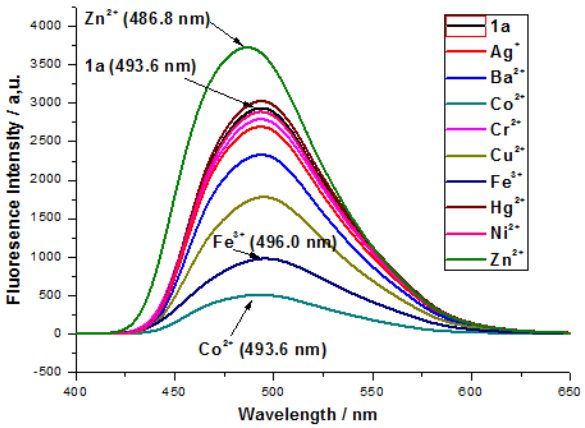
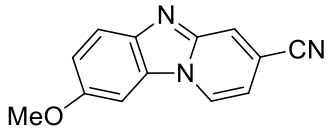


Figure S9. Fluoresence emission spectra of compound **3aa** in the presence of different metal ions Ag^{+}, Ba^{2+}, Co^{2+}, Cr^{2+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, Ni^{2+} and Zn^{2+} in CH_3CN/H_2O(100:1). λ_{ex} = 390 nm, [**3aa**] = 2.5 × 10^{-4} M, [M^{n+}] =1 × 10^{-3} M.

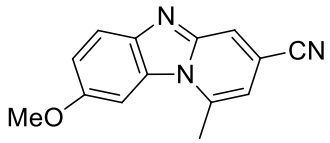
(B) Analytical data

8-Methoxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3aa):



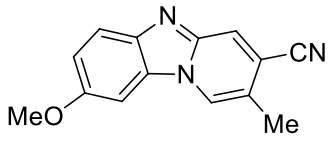
82% yield; Yellow solid, m.p. 246.3-247.7 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 6.5 Hz, 1H), 8.07 (s, 1H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.28-7.26 (m, 2H), 6.92 (d, *J* = 6.0 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.1, 145.1, 140.2, 129.0, 125.6, 125.0, 121.8, 118.2, 117.4, 110.4, 109.7, 92.6, 56.0; LRMS (EI, 70 eV) *m/z* (%): 223 (M^+, 68), 208 (100), 180 (15), 103 (21); HRMS *m/z* (ESI) calcd for $C_{13}H_{10}N_3O$ $[M+H]^+$ 224.0818, found 224.0824.

8-Methoxy-1-methylbenzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3ab):



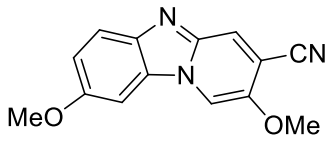
85% yield; Yellow solid; m.p. 194.3-196.1 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90-7.89 (m, 2H), 7.55 (s, 1H), 7.27 (s, 1H), 6.59 (s, 1H), 3.94 (s, 3H), 3.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.2, 146.5, 140.5, 139.8, 130.1, 122.2, 121.1, 117.4, 116.4, 110.6, 109.5, 97.9, 56.0, 21.1; LRMS (EI, 70 eV) *m/z* (%): 237 (M^+, 71), 222 (100), 194 (21), 90 (8); HRMS *m/z* (ESI) calcd for $C_{14}H_{12}N_3O$ $[M+H]^+$ 238.0975, found 238.0982.

8-Methoxy-2-methylbenzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3ac):



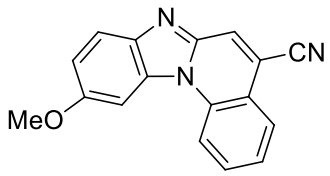
80% yield; Yellow solid; m.p. 198.2-199.4 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.0 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.24-7.21 (m, 2H), 6.84 (d, *J* = 7.0 Hz, 1H), 3.94 (s, 3H), 2.91 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.8, 146.0, 139.5, 136.1, 129.5, 122.9, 121.6, 117.6, 116.8, 109.8, 108.8, 92.6, 55.9, 16.3; LRMS (EI, 70 eV) *m/z* (%): 237 (M^+, 65), 222 (100), 194 (17), 117 (7); HRMS *m/z* (ESI) calcd for $C_{14}H_{12}N_3O$ $[M+H]^+$ 238.0975, found 238.0988.

2,8-Dimethoxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3ad):



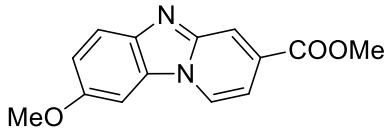
86% yield; Light yellow solid; m.p. 244.3-245.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 5.5 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.26-7.09 (m, 2H), 6.72 (d, *J* = 5.0 Hz, 1H), 4.66 (s, 3H), 3.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.0, 153.8, 140.7, 138.8, 129.2, 121.7, 118.6, 117.7, 116.0, 110.0, 94.6, 92.5, 61.7, 55.9; LRMS (EI, 70 eV) *m/z* (%): 253 (M^+, 100), 224 (60), 198 (28), 103 (15); HRMS *m/z* (ESI) calcd for $C_{14}H_{12}N_3O_2$ $[M+H]^+$ 254.0924, found 254.0931.

10-Methoxybenzo[4,5]imidazo[1,2-*a*]quinoline-5-carbonitrile (3ae):



73% yield; Light yellow solid; m.p. 254.8-255.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 7.5 Hz, 1H), 8.07 (s, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.87 (t, *J* = 7.5 Hz, 1H), 7.80 (s, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.28 (s, 1H), 4.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.9, 144.8, 140.2, 135.3, 131.5, 131.0, 127.5, 126.2, 125.2, 122.1, 120.20, 116.0, 115.5, 115.1, 111.8, 97.9, 56.2; LRMS (EI, 70 eV) *m/z* (%): 273 (M^+, 73), 258 (100), 230 (31), 153 (13); HRMS *m/z* (ESI) calcd for $C_{17}H_{12}N_3O$ $[M+H]^+$ 274.0975, found 274.0979.

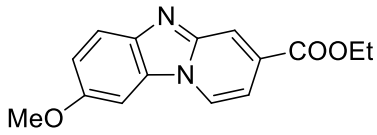
Methyl 8-methoxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carboxylate (3af):



85% yield; Light yellow solid; m.p. 123.4-124.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.32 (d, *J* = 7.0 Hz, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.34 (d, *J* = 7.0 Hz, 1H), 7.25 (s, 1H), 7.22 (d, *J* = 9.0 Hz, 1H), 3.99 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.5, 156.4, 146.6, 140.3, 129.0, 128.9, 124.3, 121.4, 121.2, 117.3, 109.0, 92.7, 56.0, 52.7; LRMS (EI, 70 eV) *m/z* (%): 256 (M^+, 72), 241

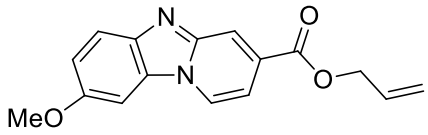
(100), 213 (13), 182 (9); HRMS *m/z* (ESI) calcd for $C_{14}H_{13}N_2O_3$ $[M+H]^+$ 257.0921, found 257.0928.

Ethyl 8-methoxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carboxylate (3ag):



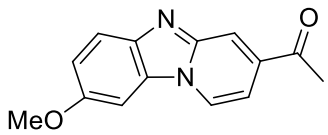
78% yield; Light yellow solid; m.p. 125.6-126.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.34 (d, *J* = 6.5 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.36 (d, *J* = 6.0 Hz, 1H), 7.27-7.21 (m, 2H), 4.45 (q, *J* = 6.5 Hz, 2H), 3.94 (s, 3H), 1.45 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 156.4, 146.7, 140.2, 129.4, 128.9, 124.2, 121.3, 121.1, 117.3, 109.1, 92.8, 61.8, 56.0, 14.3; LRMS (EI, 70 eV) *m/z* (%): 270 (M^+, 100), 255 (51), 227 (95), 199 (10); HRMS *m/z* (ESI) calcd for $C_{15}H_{15}N_2O_3$ $[M+H]^+$ 271.1077, found 271.1086.

Allyl 8-methoxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carboxylate (3ah):



80% yield; Light yellow solid; m.p. 124.3-125.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.32 (d, *J* = 7.0 Hz, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.35-7.34 (m, 1H), 7.24 (d, *J* = 2.5 Hz, 1H), 7.22-7.20 (m, 1H), 6.11-6.03 (m, 1H), 5.48-5.44 (m, 1H), 5.36-5.33 (m, 1H), 4.88 (d, *J* = 5.5 Hz, 2H), 3.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.6, 156.4, 146.5, 140.2, 131.7, 128.9, 128.8, 124.2, 121.3, 121.2, 118.7, 117.3, 108.9, 92.6, 66.2, 55.9; LRMS (EI, 70 eV) *m/z* (%): 282 (M^+, 100), 267 (91), 227 (55), 182 (15); HRMS *m/z* (ESI) calcd for $C_{16}H_{15}N_2O_3$ $[M+H]^+$ 283.1077, found 283.1084.

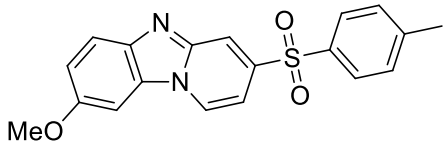
1-(8-Methoxybenzo[4,5]imidazo[1,2-*a*]pyridin-3-yl)ethanone (3ai):



63% yield; Light yellow solid; m.p. 120.8-122.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 6.5 Hz, 1H), 8.25 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.38 (s, 1H), 7.27 (s, 1H),

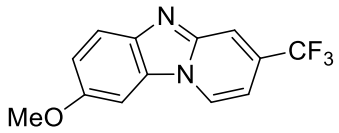
7.23 (d, *J* = 9.0 Hz, 1H), 3.95 (s, 3H), 2.69 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.0, 156.6, 146.6, 140.4, 135.5, 129.0, 124.5, 121.3, 120.6, 117.4, 107.5, 92.7, 565.9, 26.1; LRMS (EI, 70 eV) *m/z* (%): 240 (M^+, 62), 225 (100); HRMS *m/z* (ESI) calcd for $C_{14}H_{13}N_2O_2$ $[M+H]^+$ 241.0972, found 241.0977.

8-Methoxy-3-tosylbenzo[4,5]imidazo[1,2-*a*]pyridine (3aj):



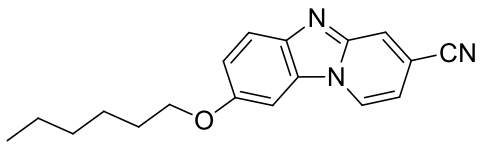
61% yield; Light yellow solid; m.p. 172.3-173.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, *J* = 7.0 Hz, 1H), 8.30 (s, 1H), 7.89 (d, *J* = 7.5 Hz, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 7.0 Hz, 2H), 7.17 (d, *J* = 7.0 Hz, 1H), 3.94 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.9, 145.1, 140.7, 140.4, 137.2, 130.2, 128.6, 128.1, 127.5, 125.6, 121.6, 119.3, 117.8, 106.4, 92.7, 56.0, 21.6; HRMS *m/z* (ESI) calcd for $C_{19}H_{17}N_2O_3S$ $[M+H]^+$ 353.0954, found 353.0962.

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



58% yield; Light yellow solid; m.p. 127.6-128.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (d, *J* = 7.0 Hz, 1H), 7.97 (s, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.30 (s, 1H), 7.24 (d, *J* = 2.0 Hz, 1H), 6.96 (d, *J* = 7.0 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.5, 146.4, 139.9, 129.4 (d, *J* = 33.75 Hz), 128.8, 125.6, 121.4, 117.3, 116.5, 116.4, 105.7 (q, *J* = 2.75 Hz) 92.8, 56.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.2; LRMS (EI, 70 eV) *m/z* (%): 266 (M^+, 65), 251 (100), 223 (27), 146 (12); HRMS *m/z* (ESI) calcd for $C_{13}H_{10}F_3N_2O$ $[M+H]^+$ 267.0740, found 267.0748.

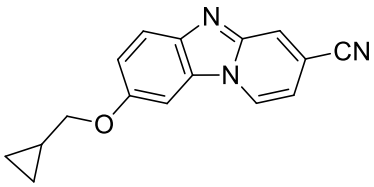
8-(Hexyloxy)benzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3ia):



81% yield; Light yellow solid; m.p. 175.5-176.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 6.0 Hz, 1H), 8.03 (s, 1H), 7.87

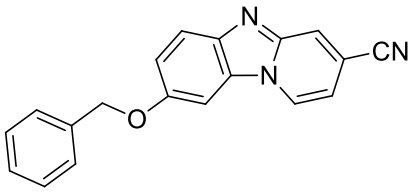
(d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 6.0 Hz, 2H), 6.88 (d, *J* = 7.0 Hz, 1H), 4.09-4.06 (m, 2H), 1.94-1.80 (m, 2H), 1.51 (d, *J* = 6.0 Hz, 2H), 1.39-1.37 (m, 4H), 0.93 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.5, 144.9, 140.0, 128.9, 125.5, 124.8, 121.6, 118.5, 117.4, 110.2, 109.5, 93.1, 68.9, 31.5, 29.1, 25.7, 22.5, 14.0; LRMS (EI, 70 eV) *m/z* (%): 293 (M^+, 26), 209 (100), 180 (11), 103 (5); HRMS *m/z* (ESI) calcd for $C_{18}H_{20}N_3O$ $[M+H]^+$ 294.1601, found 294.1609.

8-(Cyclopropylmethoxy)benzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3ja):



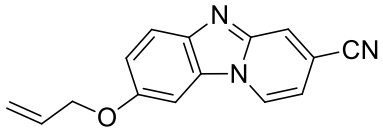
78% yield; Light yellow solid; m.p. 209.8-210.4 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.0 Hz, 1H), 8.02 (s, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.28 (d, *J* = 12.0 Hz, 1H), 7.23 (s, 1H), 6.87 (d, *J* = 7.0 Hz, 1H), 3.92 (d, *J* = 7.0 Hz, 2H), 1.45-1.30 (m, 1H), 0.79-0.61 (m, 2H), 0.44-0.42 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.3, 144.9, 140.0, 128.8, 125.5, 124.7, 121.5, 118.5, 117.3, 110.2, 109.4, 93.4, 73.6, 10.1, 3.2; LRMS (EI, 70 eV) *m/z* (%): 263 (M^+, 40), 209 (100), 180 (22), 103 (15); HRMS *m/z* (ESI) calcd for $C_{16}H_{14}N_3O$ $[M+H]^+$ 264.1131, found 264.1139.

8-(Benzyloxy)benzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3ka):



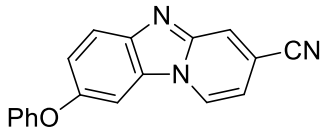
86% yield; Light yellow solid; m.p. 213.5-215.0 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.0 Hz, 1H), 8.04 (s, 1H), 7.91 (d, *J* = 9.5 Hz, 1H), 7.49 (d, *J* = 7.0 Hz, 2H), 7.42 (t, *J* = 7.0 Hz, 2H), 7.39-7.30 (m, 3H), 6.89 (d, *J* = 6.5 Hz, 1H), 5.19 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.0, 145.1, 140.3, 136.3, 128.8, 128.7, 128.2, 127.5, 125.6, 124.9, 121.8, 118.6, 117.4, 110.5, 109.6, 94.0, 70.9; LRMS (EI, 70 eV) *m/z* (%): 299 (M^+, 25), 208 (62), 180 (11), 91 (100); HRMS *m/z* (ESI) calcd for $C_{19}H_{14}N_3O$ $[M+H]^+$ 300.1131, found 300.1143.

8-(Allyloxy)benzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3la):



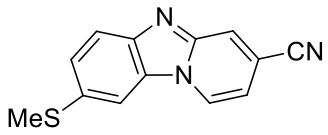
83% yield; Light yellow solid; m.p. 201.9-203.0 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, *J* = 7.0 Hz, 1H), 8.05 (s, 1H), 7.90 (d, *J* = 9.5 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 2H), 6.90 (d, *J* = 7.0 Hz, 1H), 6.15-6.09 (m, 1H), 5.49 (d, *J* = 17.0 Hz, 1H), 5.36 (d, *J* = 10.5 Hz, 1H), 4.67 (d, *J* = 5.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.9, 145.1, 140.2, 132.7, 128.8, 125.6, 124.9, 121.7, 118.5, 118.1, 117.4, 110.4, 109.6, 93.8, 69.7; LRMS (EI, 70 eV) *m/z* (%): 249 (M^+, 100), 235 (88), 206 (44), 103 (33); HRMS *m/z* (ESI) calcd for $C_{15}H_{12}N_3O$ $[M+H]^+$ 250.0975, found 250.0988.

8-Phenoxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3ma):



72% yield; Light yellow solid; m.p. 252.3-254.0 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.0 Hz, 1H), 8.09 (s, 1H), 7.98 (d, *J* = 9.0 Hz, 1H), 7.46 (d, *J* = 2.0 Hz, 1H), 7.43-7.34 (m, 3H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.92-6.90 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 154.1, 145.8, 141.6, 130.0, 128.9, 126.0, 125.0, 123.8, 122.0, 120.4, 119.0, 117.2, 111.4, 109.8, 99.9; LRMS (EI, 70 eV) *m/z* (%): 285 (M^+, 100), 208 (61), 180 (18), 103 (12); HRMS *m/z* (ESI) calcd for $C_{18}H_{12}N_3O$ $[M+H]^+$ 286.0975, found 286.0980.

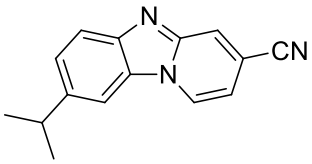
8-(Methylthio)benzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3na):



64% yield; Light yellow solid; m.p. 234.1-235.6 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 7.0 Hz, 1H), 8.09 (s, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.76 (s, 1H), 7.55 (d, *J* = 7.0 Hz, 1H), 6.96 (d, *J* = 7.0 Hz, 1H), 2.62 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.5, 143.5, 134.3, 129.1, 127.3, 126.0, 124.9, 121.1, 117.2, 111.6, 110.0, 108.4,

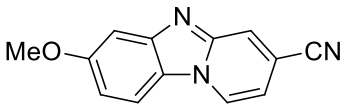
17.1; LRMS (EI, 70 eV) *m/z* (%): 239 (M^+, 80), 224 (100), 180 (18), 103 (11); HRMS *m/z* (ESI) calcd for $C_{13}H_{10}N_3S$ $[M+H]^+$ 240.0590, found 240.0597.

8-Isopropylbenzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3oa):



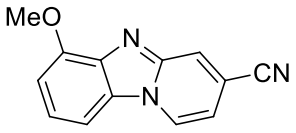
51% yield; Light yellow solid; m.p. 188.4-189.2 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 6.5 Hz, 1H), 8.09 (s, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.76 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 6.5 Hz, 1H), 3.26-3.11 (m, 1H), 1.38 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.5, 145.1, 143.9, 128.7, 126.8, 126.0, 124.8, 120.6, 117.3, 111.3, 109.6, 107.5, 34.6, 24.4; LRMS (EI, 70 eV) *m/z* (%): 235 (M^+, 36), 220 (100), 193 (8), 110 (5); HRMS *m/z* (ESI) calcd for $C_{15}H_{14}N_3$ $[M+H]^+$ 236.1182, found 236.1195.

7-Methoxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3pa):



51% yield; Light yellow solid; m.p. 192.3-192.7 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, *J* = 7.0 Hz, 1H), 8.05 (s, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.37 (s, 1H), 7.13 (d, *J* = 8.5 Hz, 1H), 6.95 (d, *J* = 7.0 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 146.9, 146.2, 125.7, 123.8, 123.3, 117.3, 115.2, 111.4, 111.1, 110.0, 101.0, 55.8; LRMS (EI, 70 eV) *m/z* (%): 223 (M^+, 100), 194(30), 180 (61), 103 (8); HRMS *m/z* (ESI) calcd for $C_{13}H_{10}N_3O$ $[M+H]^+$ 224.0818, found 224.0831.

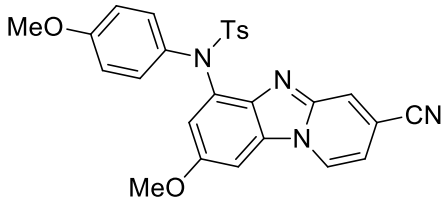
6-Methoxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3qa):



43% yield; Light yellow solid; m.p. 184.3-185.9 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 9.15 (d, *J* = 7.0 Hz, 1H), 8.07 (s, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 7.0 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 4.12 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.2, 147.0, 145.7, 130.1, 127.1, 123.5, 117.3, 112.9, 111.7, 109.5, 103.1,

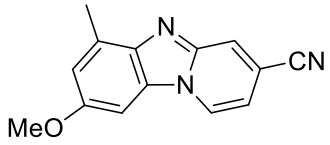
100.0, 56.0; LRMS (EI, 70 eV) *m/z* (%): 223 (M^+, 100), 194 (15), 180 (76), 126 (7); HRMS *m/z* (ESI) calcd for $C_{13}H_{10}N_3O$ $[M+H]^+$ 224.0818, found 224.0825.

_N_-(3-Cyano-8-methoxybenzo[4,5]imidazo[1,2-*a*]pyridin-6-yl)-_N_-(4-methoxyphenyl)-4-methylbenzenesulfonamide (3ra):



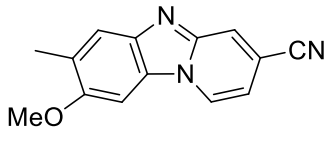
32% yield; Light yellow solid; m.p. 257.0-258.6 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.29 (d, *J* = 7.0 Hz, 1H), 7.98 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 9.0 Hz, 2H), 7.26-7.13 (m, 4H), 6.82 (d, *J* = 7.0 Hz, 1H), 6.70 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H), 3.65 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 159.2, 156.6, 145.3, 143.9, 138.5, 137.5, 133.7, 133.4, 130.7, 130.4, 129.4, 128.2, 126.0, 125.2, 118.6, 117.3, 114.1, 111.1, 110.0, 93.3, 56.2, 55.4, 21.4; HRMS *m/z* (ESI) calcd for $C_{27}H_{23}N_4O_4S$ $[M+H]^+$ 499.1435, found 499.1443.

8-Methoxy-6-methylbenzo[4,5]imidazo[1,2-a]pyridine-3-carbonitrile (3sa):



77% yield; Light yellow solid; m.p. 222.8-223.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.0 Hz, 1H), 8.06 (s, 1H), 7.08 (s, 1H), 7.06 (s, 1H), 6.89-6.87 (m, 1H), 3.93 (s, 3H), 2.74 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.0, 144.3, 139.9, 132.1, 128.4, 125.5, 124.8, 117.9, 117.5, 109.8, 109.5, 89.8, 55.8, 17.0; LRMS (EI, 70 eV) *m/z* (%): 237 (M^+, 70), 222 (100), 194 (20), 103 (13); HRMS *m/z* (ESI) calcd for $C_{14}H_{12}N_3O$ $[M+H]^+$ 238.0975, found 238.0981.

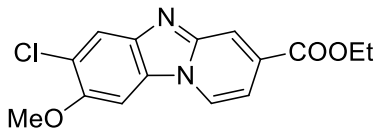
8-Methoxy-7-methylbenzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3ta):



85% yield; Light yellow solid; m.p. 235.6-236.3 °C; ^{1}H NMR (500 MHz, DMSO) δ 9.16 (d, *J* = 7.0 Hz, 1H), 8.36 (s, 1H), 7.92 (s, 1H), 7.69 (s, 1H), 7.22 (d, *J* = 6.5 Hz, 1H),

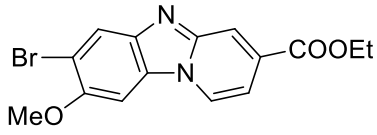
3.95 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, DMSO) δ 155.3, 144.7, 139.6, 128.1 (2C), 128.0, 124.6, 120.8, 118.4, 109.7, 109.6, 93.3, 56.4, 17.7; LRMS (EI, 70 eV) *m/z* (%): 237 (M^+, 65), 222 (100), 194 (24), 103 (14); HRMS *m/z* (ESI) calcd for $C_{14}H_{12}N_3O$ $[M+H]^+$ 238.0975, found 238.0983.

Ethyl 7-chloro-8-methoxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carboxylate (3ug):



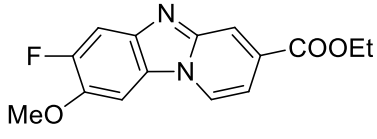
57% yield; Light yellow solid; m.p. 184.7-186.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.37 (d, *J* = 7.0 Hz, 1H), 8.02 (s, 1H), 7.42 (d, *J* = 7.0 Hz, 1H), 7.33 (s, 1H), 4.46 (q, *J* = 7.0 Hz, 2H), 4.05 (s, 3H), 1.45 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 151.7, 139.7, 129.9, 129.7, 126.4, 124.2, 123.5, 121.6, 121.0, 109.6, 92.9, 56.8, 14.3; LRMS (EI, 70 eV) *m/z* (%): 304 (M^+, 100), 289 (77), 261 (93), 233 (16); HRMS *m/z* (ESI) calcd for $C_{15}H_{14}ClN_2O_3$ $[M+H]^+$ 305.0687, found 305.0697.

Ethyl 7-bromo-8-methoxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carboxylate (3vg):



63% yield; Light yellow solid; m.p. 190.3-191.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.35 (d, *J* = 7.0 Hz, 1H), 8.19 (s, 1H), 7.41 (d, *J* = 7.0 Hz, 1H), 7.29 (s, 1H), 4.45 (q, *J* = 7.0 Hz, 2H), 4.03 (s, 3H), 1.45 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 152.3, 150.6, 140.4, 130.0, 128.0, 124.8, 124.2, 121.0, 112.4, 109.5, 92.6, 61.9, 56.9, 14.3; LRMS (EI, 70 eV) *m/z* (%): 350 (M^{2+}, 100), 348 (M^+, 100), 333 (65), 305 (80), 153 (17); HRMS *m/z* (ESI) calcd for $C_{15}H_{14}BrN_2O_3$ $[M+H]^+$ 349.0182, found 349.0188.

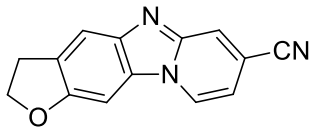
Ethyl 7-fluoro-8-methoxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carboxylate (3wg):



43% yield; Light yellow solid; m.p. 173.5-174.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.31 (d, *J*

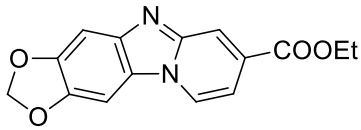
= 7.0 Hz, 1H), 7.64 (d, *J* = 11.0 Hz, 1H), 7.38 (d, *J* = 7.0 Hz, 1H), 7.32 (d, *J* = 7.0 Hz, 1H), 4.45 (q, *J* = 7.0 Hz, 2H), 4.02 (s, 3H), 1.45 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 152.8 (d, *J* = 245.25 Hz), 147.1, 145.8 (d, *J* = 14.13 Hz), 139.0 (d, *J* = 12.0 Hz), 129.3, 124.3, 124.0, 120.5, 109.5, 106.4 (d, *J* = 21.13 Hz), 93.8 (d, *J* = 2.38 Hz), 61.8, 56.7, 14.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ -132.4; LRMS (EI, 70 eV) *m/z* (%): 288 (M^+, 93), 273 (66), 245 (100), 200 (12); HRMS *m/z* (ESI) calcd for $C_{15}H_{14}FN_2O_3$ $[M+H]^+$ 289.0983, found 289.0986.

2,3-Dihydrobenzofuro[5',6':4,5]imidazo[1,2-*a*]pyridine-7-carbonitrile (3xa):



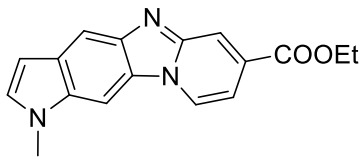
79% yield; Light yellow solid; m.p. 236.4-238.1 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.0 Hz, 1H), 8.02 (s, 1H), 7.77 (s, 1H), 7.20 (s, 1H), 6.89 (d, *J* = 7.0 Hz, 1H), 4.73 (t, *J* = 8.5 Hz, 2H), 3.44 (t, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.8, 144.9, 140.9, 130.1, 128.4, 125.4, 124.7, 117.6, 116.5, 109.7, 109.6, 89.9, 29.9; LRMS (EI, 70 eV) *m/z* (%): 235 (M^+, 100), 206 (39), 103 (18); HRMS *m/z* (ESI) calcd for $C_{14}H_{10}N_3O$ $[M+H]^+$ 236.0818, found 236.0825.

Ethyl-[1,3]dioxolo[4'',5'':4',5']benzo[1',2':4,5]imidazo[1,2-*a*]pyridine-7-carboxylate (3yg):



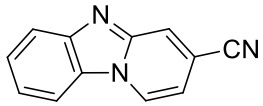
69% yield; Light yellow solid; m.p. 178.6-179.8 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.28 (d, *J* = 7.0 Hz, 1H), 7.40 (d, *J* = 7.0 Hz, 1H), 7.33 (s, 1H), 7.27 (s, 1H), 6.10 (s, 2H), 4.44 (q, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.1, 148.2, 146.6, 145.5, 141.4, 128.3, 123.6, 123.2, 120.3, 109.5, 101.8, 100.0, 90.3, 61.7, 14.3; LRMS (EI, 70 eV) *m/z* (%): 284 (M^+, 100), 256 (91), 198 (13), 123 (16); HRMS *m/z* (ESI) calcd for $C_{15}H_{13}N_2O_4$ $[M+H]^+$ 285.0870, found 285.0883.

Ethyl 1-methyl-1*H*-pyrido[1',2':1,2]imidazo[4,5-*f*]indole-7-carboxylate (3zg):



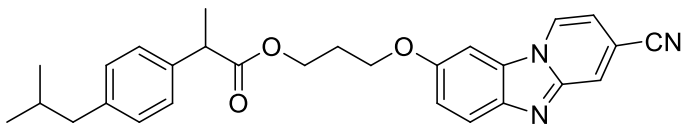
74% yield; Light yellow solid; m.p. 189.4-190.8 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (d, *J* = 7.0 Hz, 1H), 8.51 (s, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.58 (d, *J* = 9.0 Hz, 1H), 7.50 (d, *J* = 7.0 Hz, 1H), 7.26 (s, 1H), 6.94 (d, *J* = 2.5 Hz, 1H), 4.46 (q, *J* = 7.0 Hz, 2H), 3.97 (s, 3H), 1.46 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.4, 144.8, 140.7, 133.0, 128.4, 127.5, 125.3, 121.5, 120.4, 114.2, 113.1, 110.3, 109.4, 97.3, 61.6, 33.7, 14.3; LRMS (EI, 70 eV) *m/z* (%): 293 (M^+, 89), 265 (100), 220 (15), 110 (15); HRMS *m/z* (ESI) calcd for $C_{17}H_{16}N_3O_2$ $[M+H]^+$ 294.1237, found 294.1244.

Benzo[4,5]imidazo[1,2-a]pyridine-3-carbonitrile (3aaa)[1]:



31% yield; Light yellow solid; m.p. 234.6-235.9 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 7.0 Hz, 1H), 8.11 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 6.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6, 145.2, 128.5, 127.0, 126.3, 124.7, 123.3, 120.9, 117.1, 112.0, 110.8, 109.8; LRMS (EI, 70 eV) *m/z* (%): 193 (M^+, 100), 166 (6), 139 (7), 96 (10); HRMS *m/z* (ESI) calcd for $C_{12}H_8N_3$ $[M+H]^+$ 194.0731, found 194.0744.

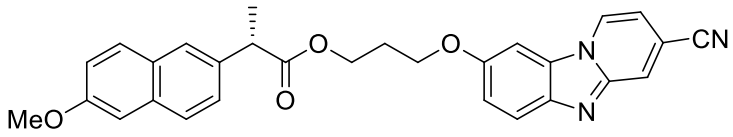
3-((3-Cyanobenzo[4,5]imidazo[1,2-*a*]pyridin-8-yl)oxy)propyl-2-(4-isobutylphenyl)propanoate (3aba):



69% yield; Light yellow solid; m.p. 167.7-169.2 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.0 Hz, 1H), 8.05 (s, 1H), 7.88 (d, *J* = 9.5 Hz, 1H), 7.22-7.15 (m, 4H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 7.0 Hz, 1H), 4.42- 4.25 (m, 2H), 4.03-4.00 (m, 2H), 3.71 (q,

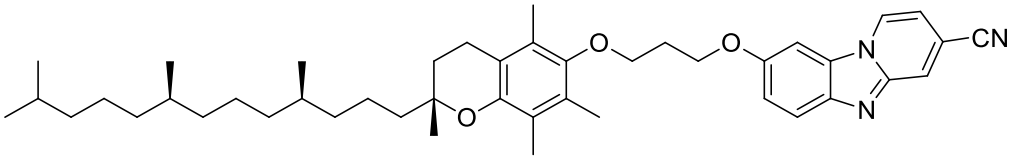
J = 7.0 Hz, 1H), 2.33 (d, *J* = 7.0 Hz, 2H), 2.17-2.13 (m, 2H), 1.78-1.72 (m, 1H), 1.49 (d, *J* = 7.0 Hz, 3H), 0.83 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.6, 156.0, 145.0, 140.4, 140.1, 137.7, 129.2, 128.8, 127.0, 125.6, 124.9, 121.6, 118.2, 117.3, 110.4, 109.6, 93.5, 65.1, 61.2, 45.1, 44.9, 30.1, 28.5, 22.2, 18.4; HRMS *m/z* (ESI) calcd for $C_{28}H_{30}N_3O_3$ $[M+H]^+$ 456.2282, found 456.2289.

(S)-3-((3-cyanobenzo[4,5]imidazo[1,2-*a*]pyridin-8-yl)oxy)propyl-2-(6-methoxynaphthalen-2-yl)propanoate (3aca):



74% yield; Light yellow solid; m.p. 187.3-189.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.0 Hz, 1H), 8.04 (s, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.59 (s, 1H), 7.53-7.51 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 9.0 Hz, 1H), 6.86-6.84 (m, 3H), 4.49-4.39 (m, 1H), 4.29-4.24 (m, 1H), 3.91-3.75 (m, 6H), 2.21-2.06 (m, 2H), 1.56 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.4, 157.3, 155.9, 144.9, 140.0, 135.7, 133.4, 128.9, 128.6, 127.0, 125.9, 125.7, 125.4, 124.6, 121.4, 118.7, 118.2, 117.4, 110.2, 109.4, 105.2, 93.0, 64.6, 61.0, 55.1, 45.4, 28.3, 18.2; HRMS *m/z* (ESI) calcd for $C_{29}H_{26}N_3O_4$ $[M+H]^+$ 480.1918, found 480.1926.

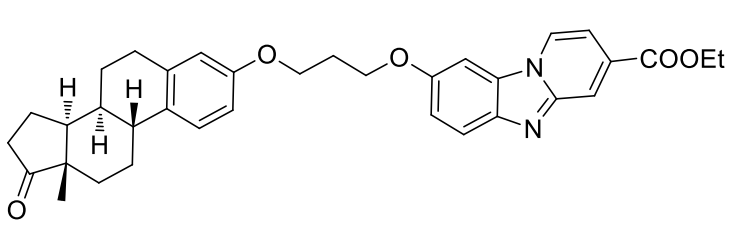
8-(3-(((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)propoxy)benzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3ada):



78% yield; Light yellow solid; m.p. 166.4-167.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, *J* = 7.0 Hz, 1H), 8.05 (s, 1H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.33 (s, 1H), 7.29 (s, 1H), 6.89 (d, *J* = 7.0 Hz, 1H), 4.38 (t, *J* = 6.0 Hz, 2H), 3.89 (t, *J* = 6.0 Hz, 2H), 2.55 (t,

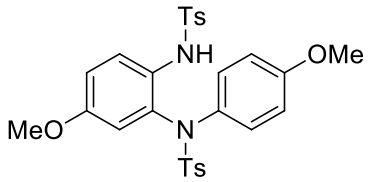
J = 6.5 Hz, 2H), 2.40-2.28 (m, 2H), 2.15 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 1.79-1.75 (m, 2H), 1.59-1.49 (m, 3H), 1.42-1.21 (m, 14H), 1.16-1.12 (m, 4H), 1.08-1.01 (m, 3H), 0.87-0.83 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.3, 147.9, 147.8, 145.0, 140.1, 128.9, 127.6, 125.7, 125.6, 124.8, 122.9, 121.7, 118.5, 117.5, 117.4, 110.3, 109.5, 93.2, 74.8, 68.6, 65.3, 40.0, 39.3, 37.4 (2C) 37.3, 37.2, 32.7, 32.6, 31.2, 30.0, 27.9, 24.7, 24.37, 23.8, 22.7, 22.6, 21.0, 20.6, 19.7, 19.6, 12.6, 11.7; HRMS *m/z* (ESI) calcd for $C_{44}H_{62}N_3O_3$ $[M+H]^+$ 680.4786, found 680.4795.

Ethyl-8-(3-(((8S,9R,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)oxy)propoxy)benzo[4,5]imidazo[1,2-*a*]pyridine-3-carboxylate (3aeg):



63% yield; Light yellow solid; m.p. 172.3-173.9 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.28 (d, *J* = 7.0 Hz, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.35 (d, *J* = 7.0 Hz, 1H), 7.30 (s, 1H), 7.24-7.16 (m, 2H), 6.78-6.72 (m, 1H), 6.68 (s, 1H), 4.44 (q, *J* = 7.0 Hz, 2H), 4.29 (t, *J* = 6.0 Hz, 2H), 4.19 (t, *J* = 6.0 Hz, 2H), 2.94-2.80 (m, 2H), 2.52-2.49 (m, 1H), 2.42-2.31 (m, 3H), 2.28-1.91 (m, 6H), 1.66-1.39 (m, 10H), 0.90 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 220.8, 164.9, 156.8, 155.6, 146.7, 140.2, 137.8, 132.2, 129.4, 128.8, 126.4, 124.2, 121.3, 121.0, 117.7, 114.4, 112.1, 109.0, 93.6, 65.3, 64.1, 61.7, 50.3, 47.9, 43.9, 38.3, 35.8, 31.5, 29.6, 29.4, 26.5, 25.9, 21.5, 14.2, 13.8; HRMS *m/z* (ESI) calcd for $C_{35}H_{39}N_2O_5$ $[M+H]^+$ 567.2853, found 567.2864.

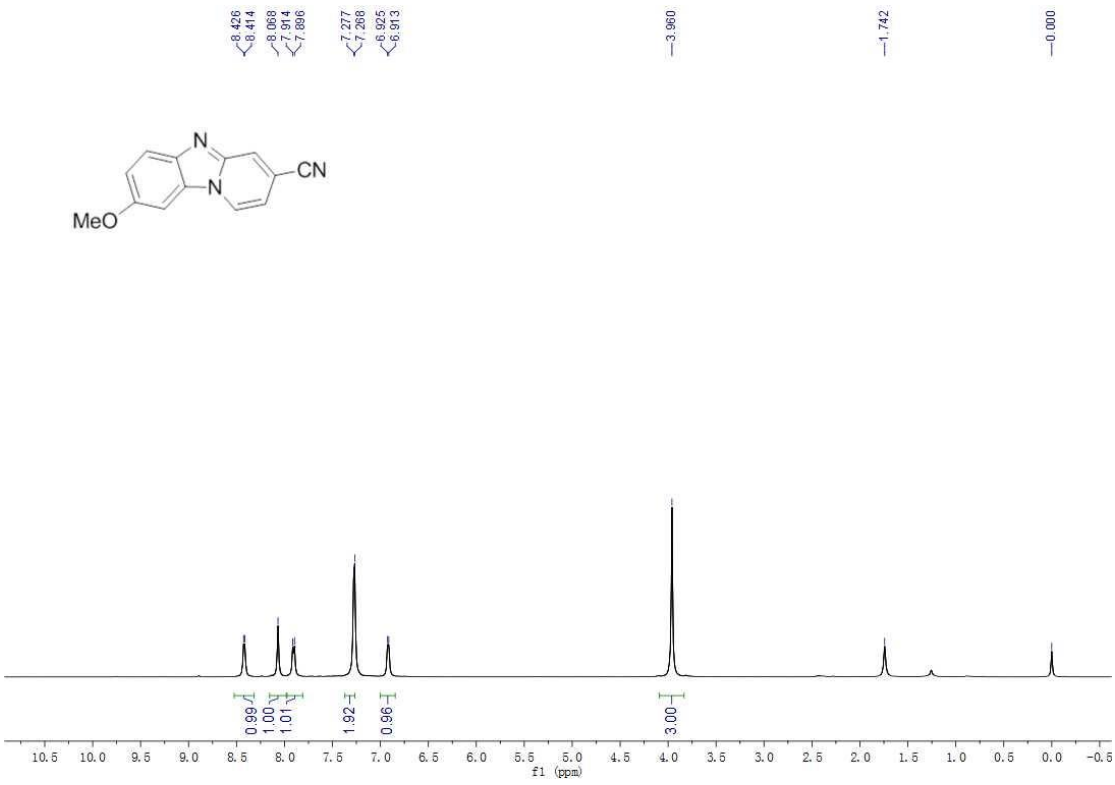
***N*-(5-methoxy-2-(4-methylphenylsulfonamido)phenyl)-*N*-(4-methoxyphenyl)-4-methylbenzenesulfonamide (4a):**



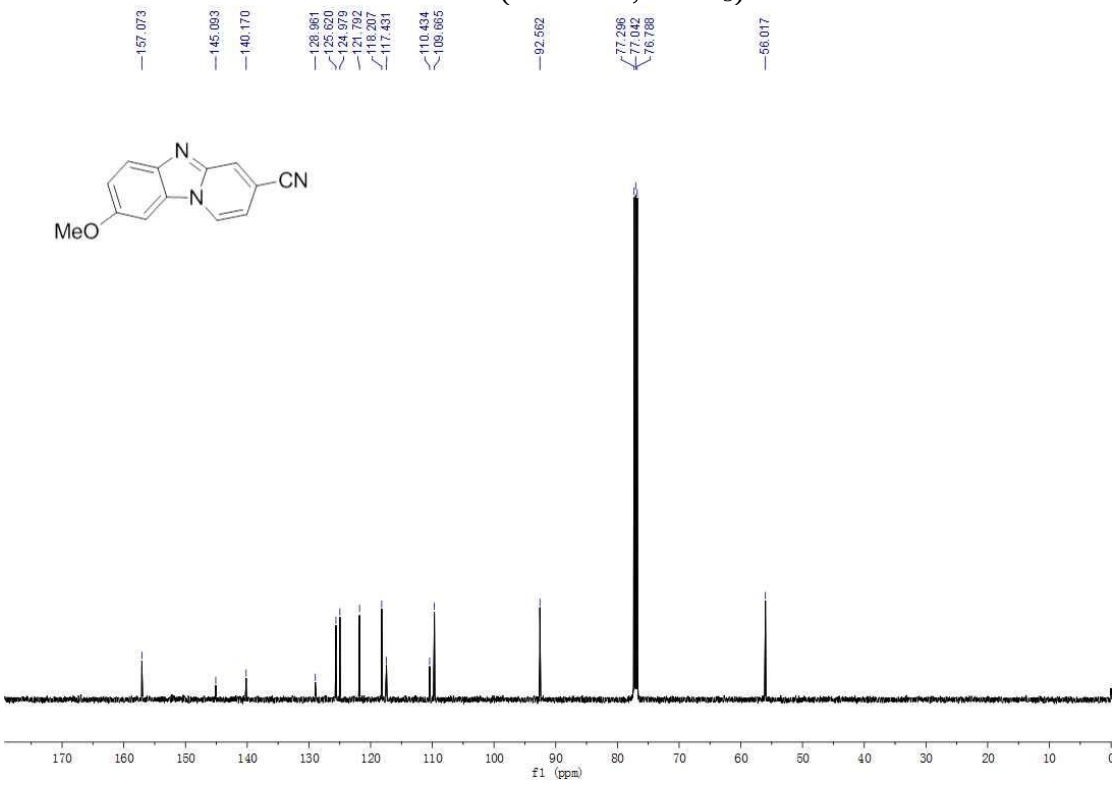
White solid; m.p. 139. 6-141.4 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.50 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.25 (s, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 9.0 Hz, 1H), 6.68 (d, *J* = 9.0 Hz, 2H), 6.39 (d, *J* = 3,0 Hz, 1H), 3.78 (s, 3H), 3.62 (s, 3H), 2.43 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 156.3, 144.4, 143.5, 136.6, 135.4, 132.8, 132.7, 129.5, 129.4, 128.7, 128.5, 128.1, 127.0, 123.0, 115.2, 114.3, 114.2, 55.3, 53.8, 21.5, 21.4; HRMS *m/z* (ESI) calcd for $C_{28}H_{29}N_2O_6S_2$ $[M+H]^+$ 553.1462, found 553.1481.

(C) Spectra (NMR Spectra)

8-Methoxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3aa):

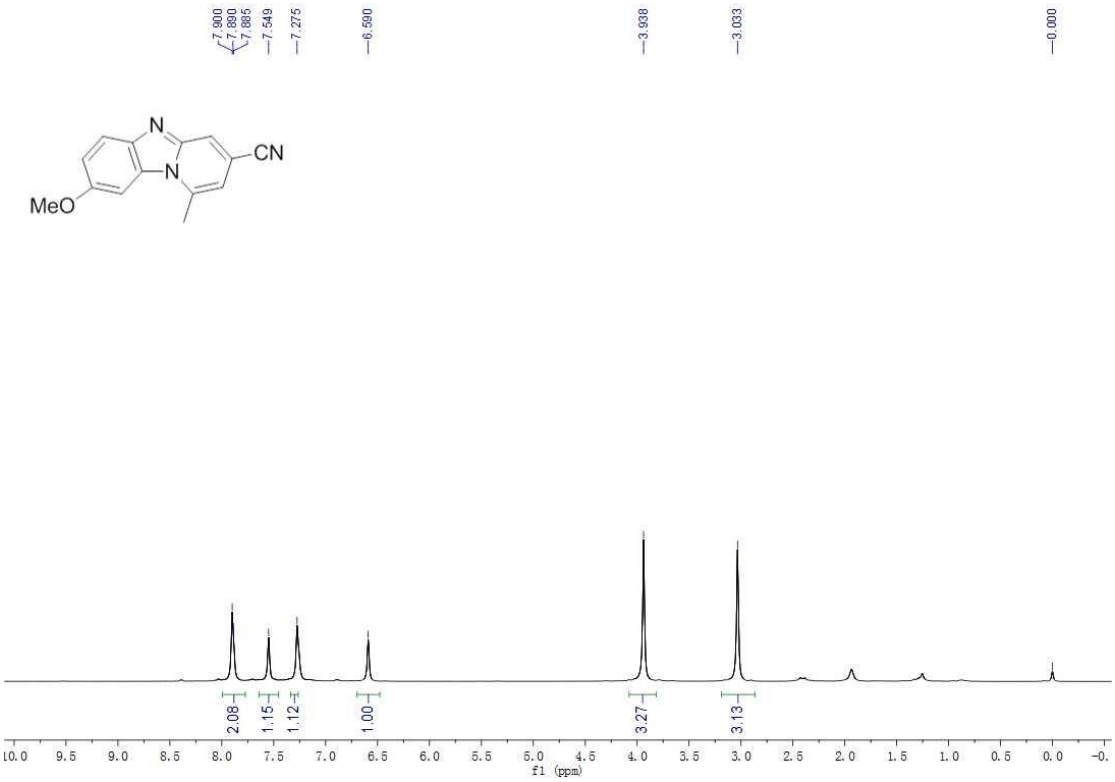


^{1}H NMR (500 MHz, $CDCl_3$)

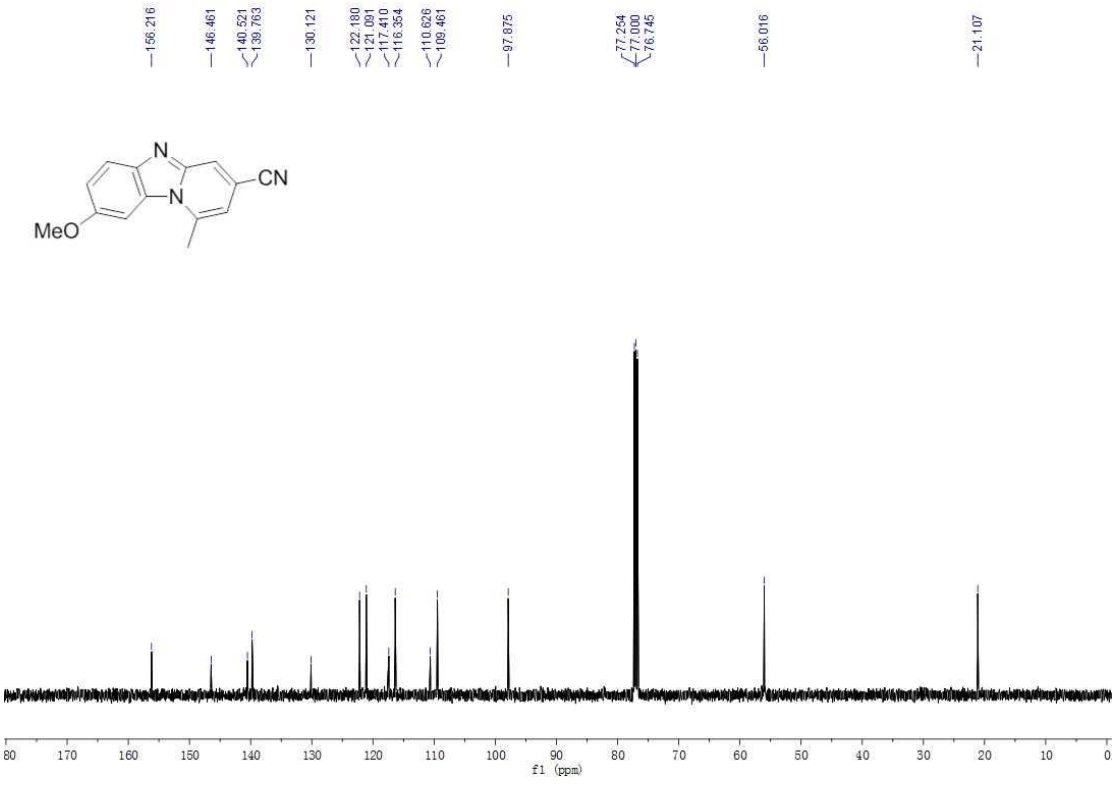


^{13}C NMR (125 MHz, $CDCl_3$)

8-Methoxy-1-methylbenzo[4,5]imidazo[1,2-a]pyridine-3-carbonitrile (3ab):

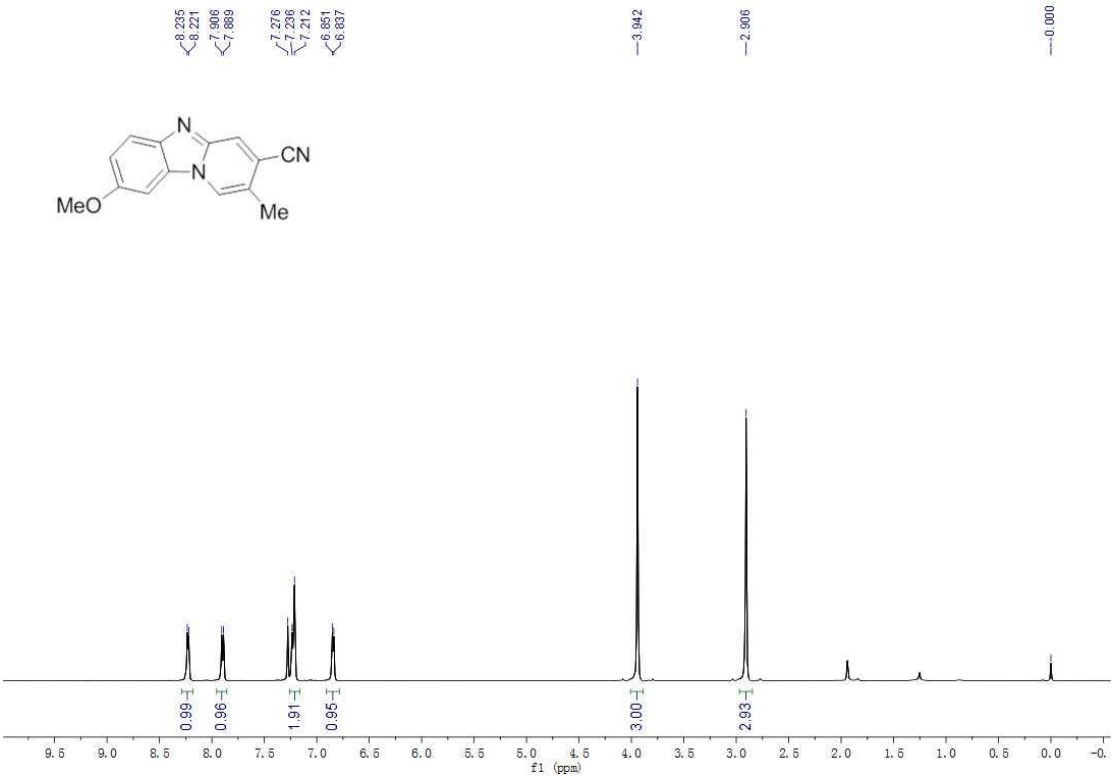


^{1}H NMR (500 MHz, $CDCl_3$)

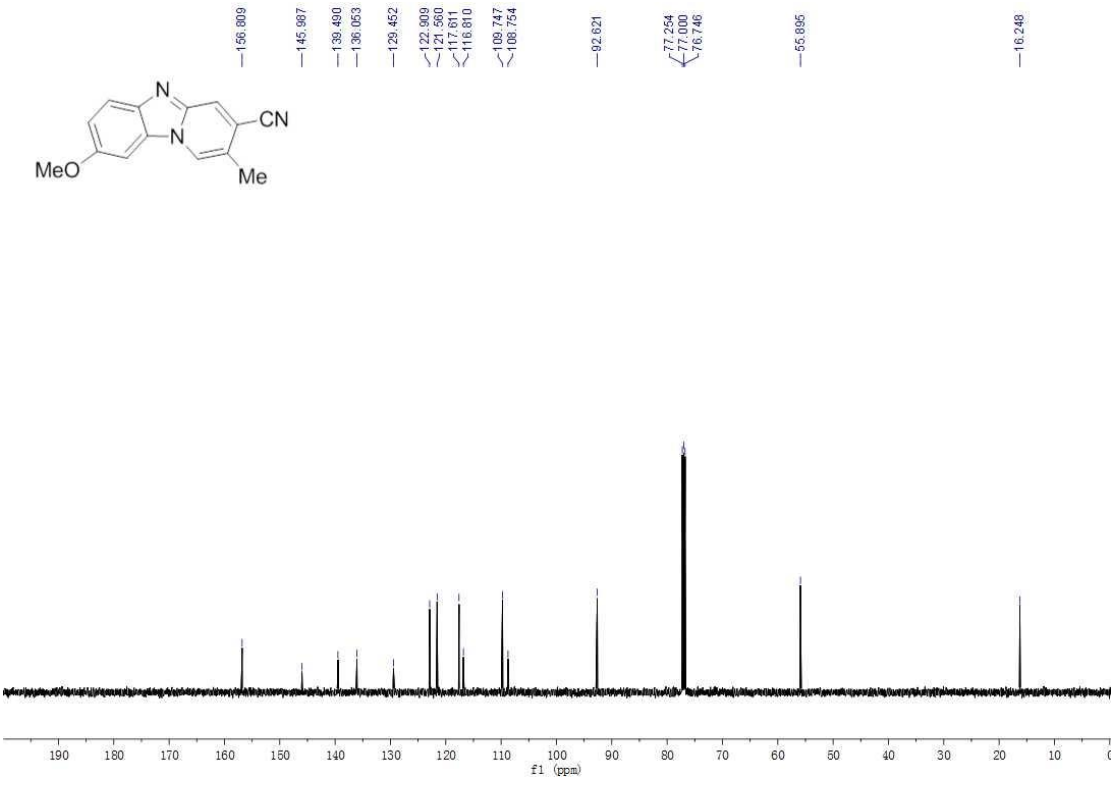


^{13}C NMR (125 MHz, $CDCl_3$)

8-Methoxy-2-methylbenzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3ac):

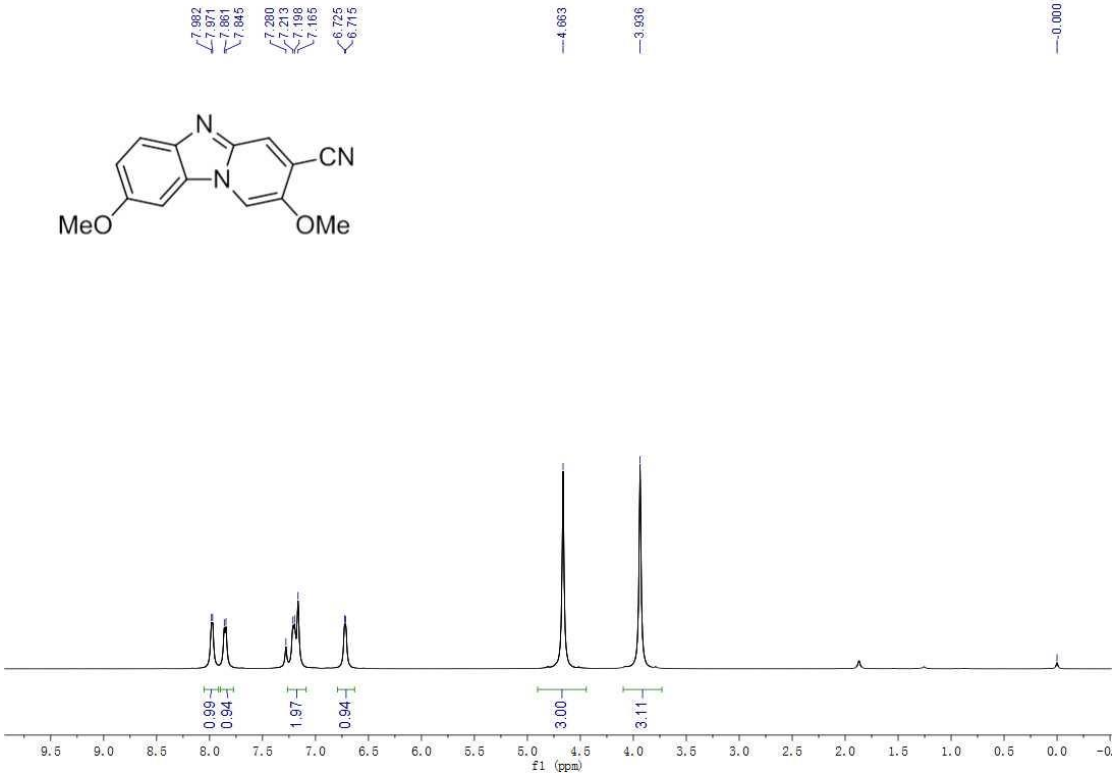


^{1}H NMR (500 MHz, $CDCl_3$)

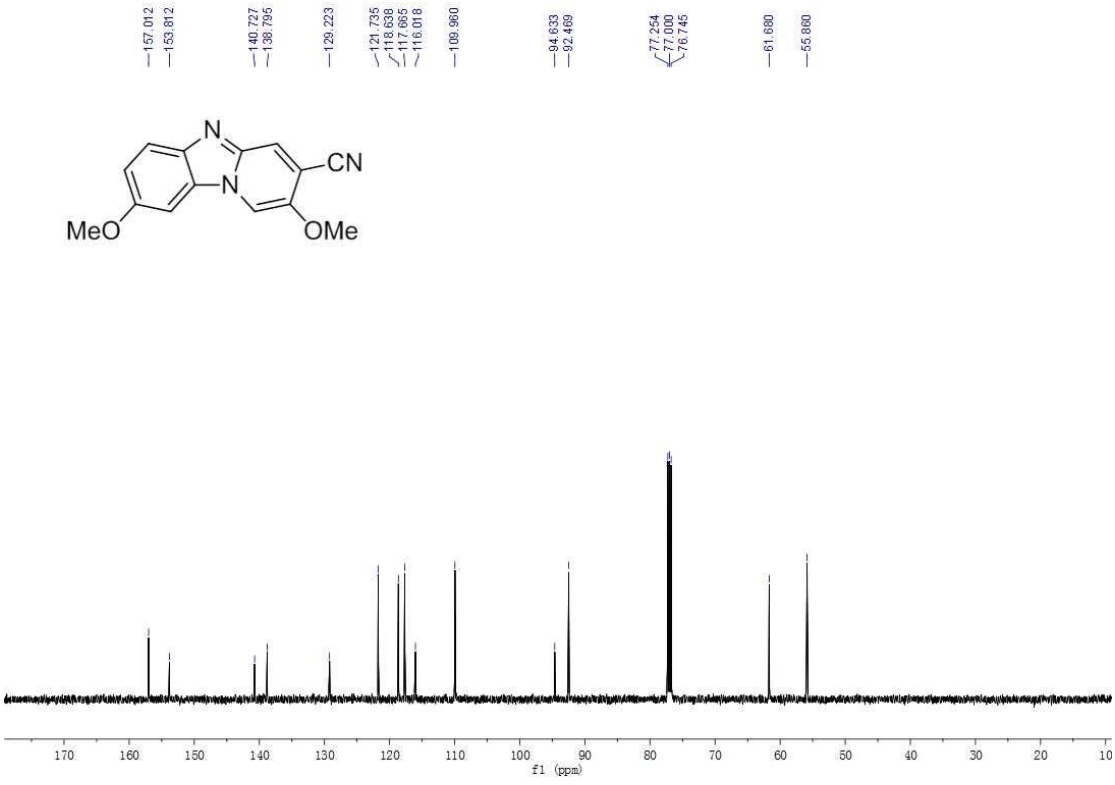


^{13}C NMR (125 MHz, $CDCl_3$)

2,8-Dimethoxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3ad):

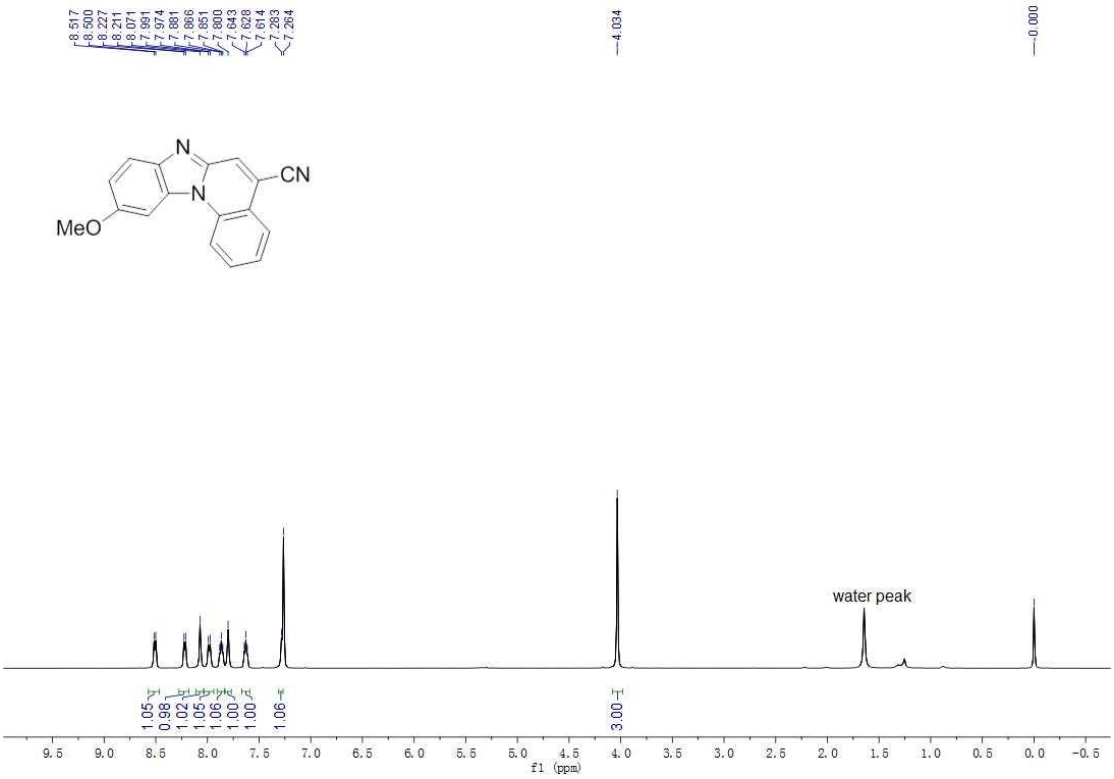


^{1}H NMR (500 MHz, $CDCl_3$)

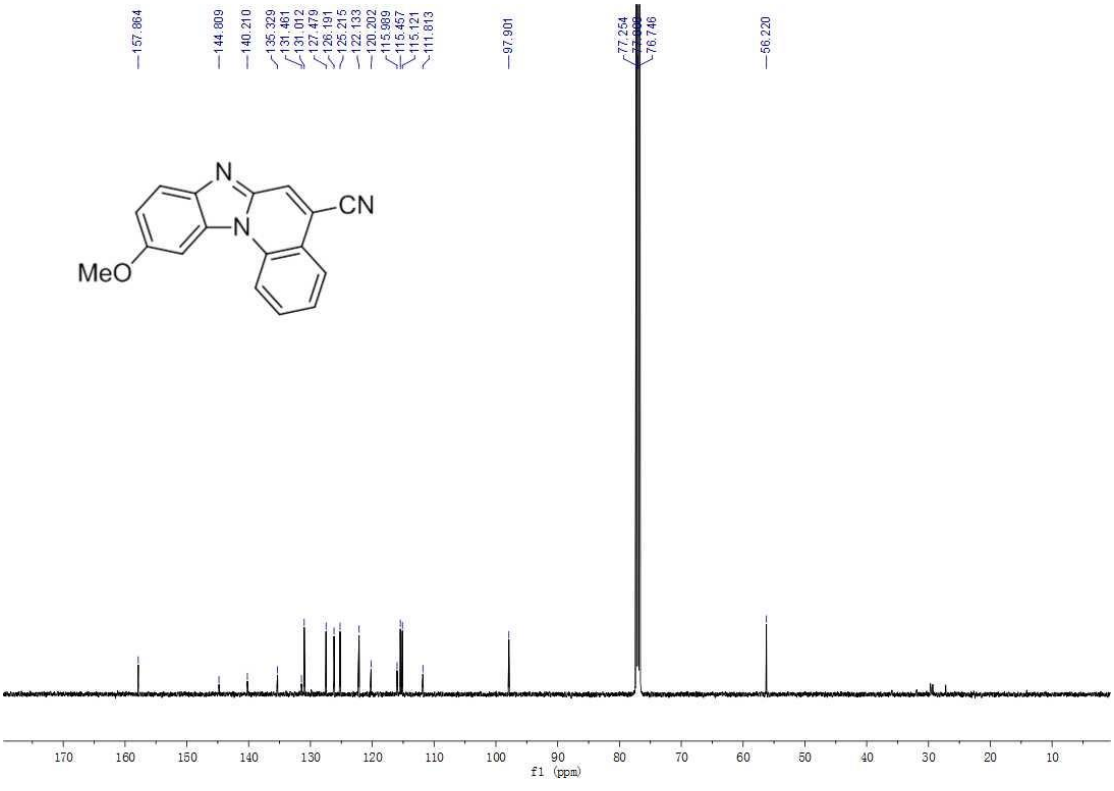


^{13}C NMR (125 MHz, $CDCl_3$)

10-Methoxybenzo[4,5]imidazo[1,2-*a*]quinoline-5-carbonitrile (3ae):

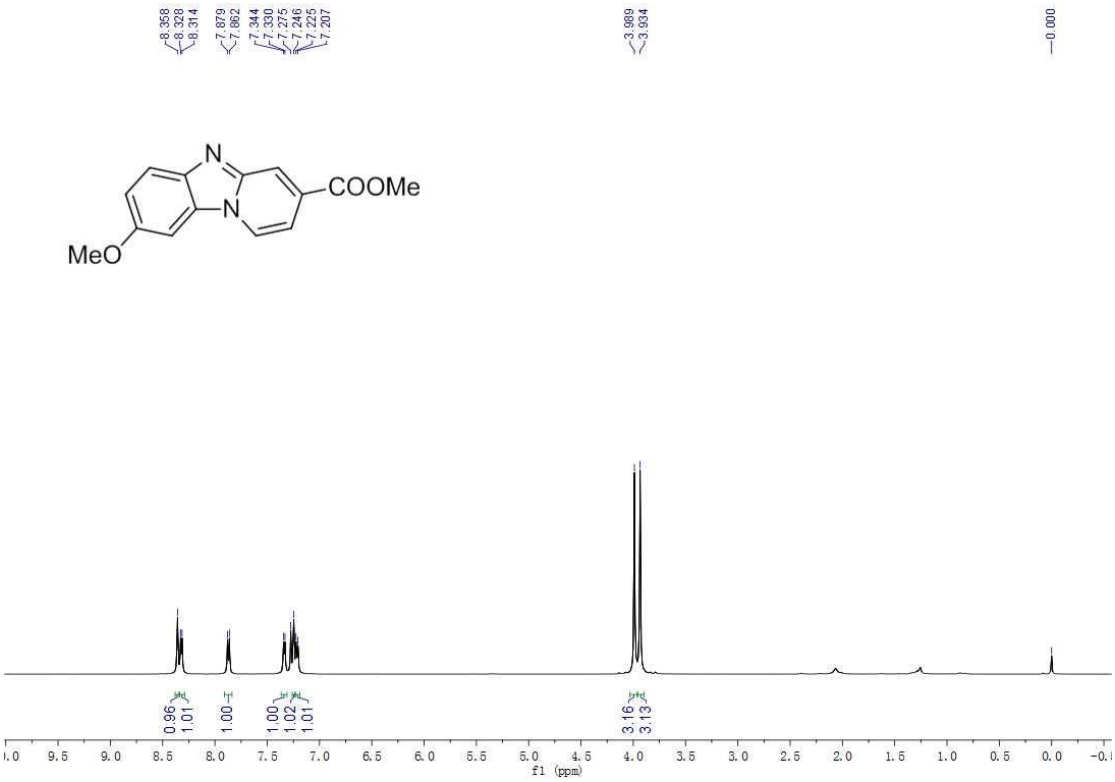


^{1}H NMR (500 MHz, $CDCl_3$)

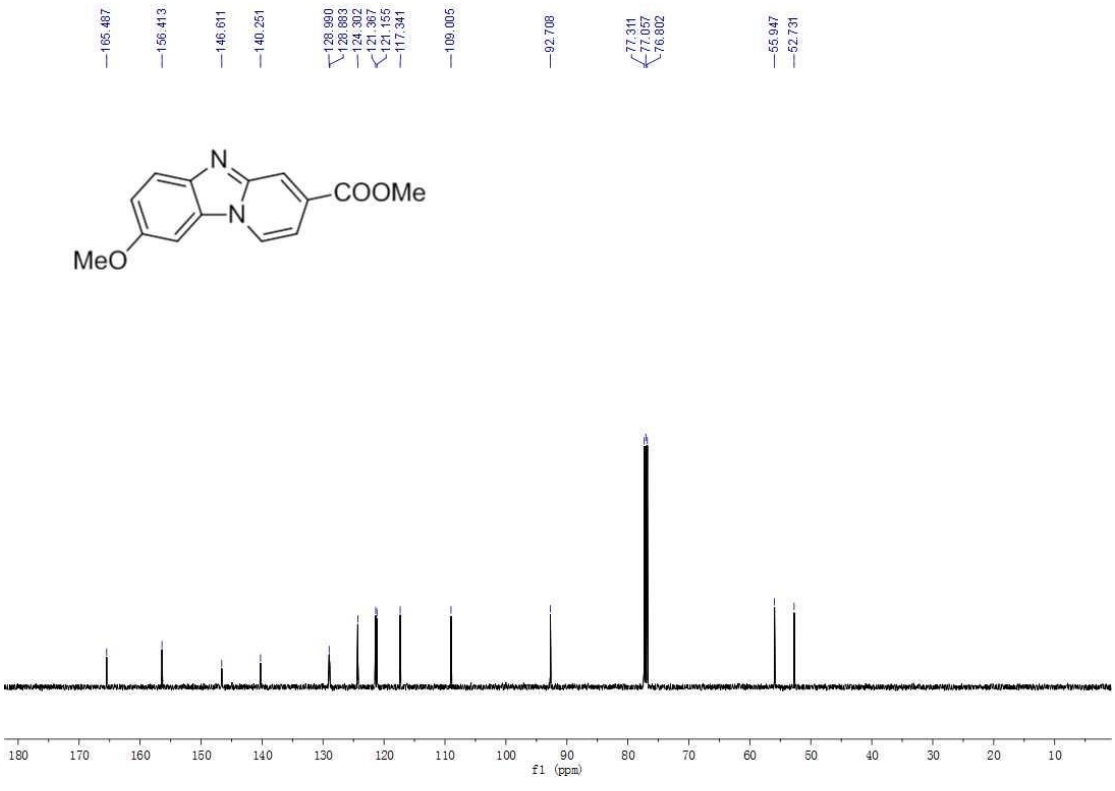


^{13}C NMR (125 MHz, $CDCl_3$)

Methyl 8-methoxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carboxylate (3af):

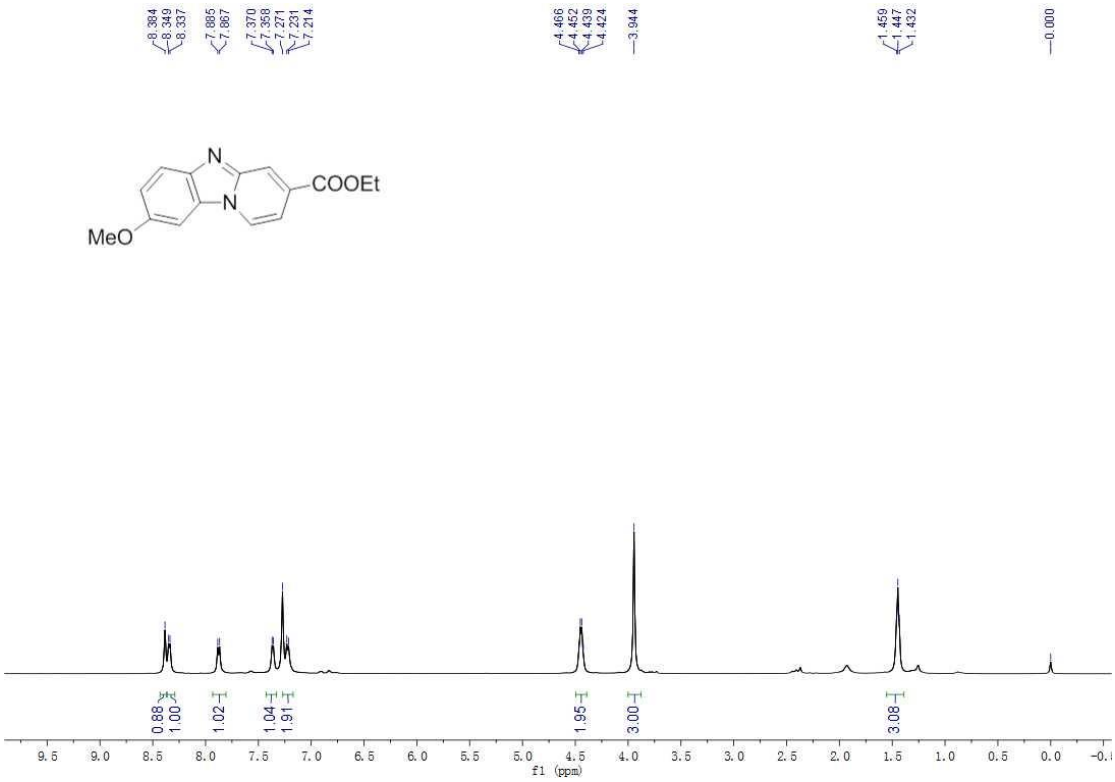


^{1}H NMR (500 MHz, $CDCl_3$)

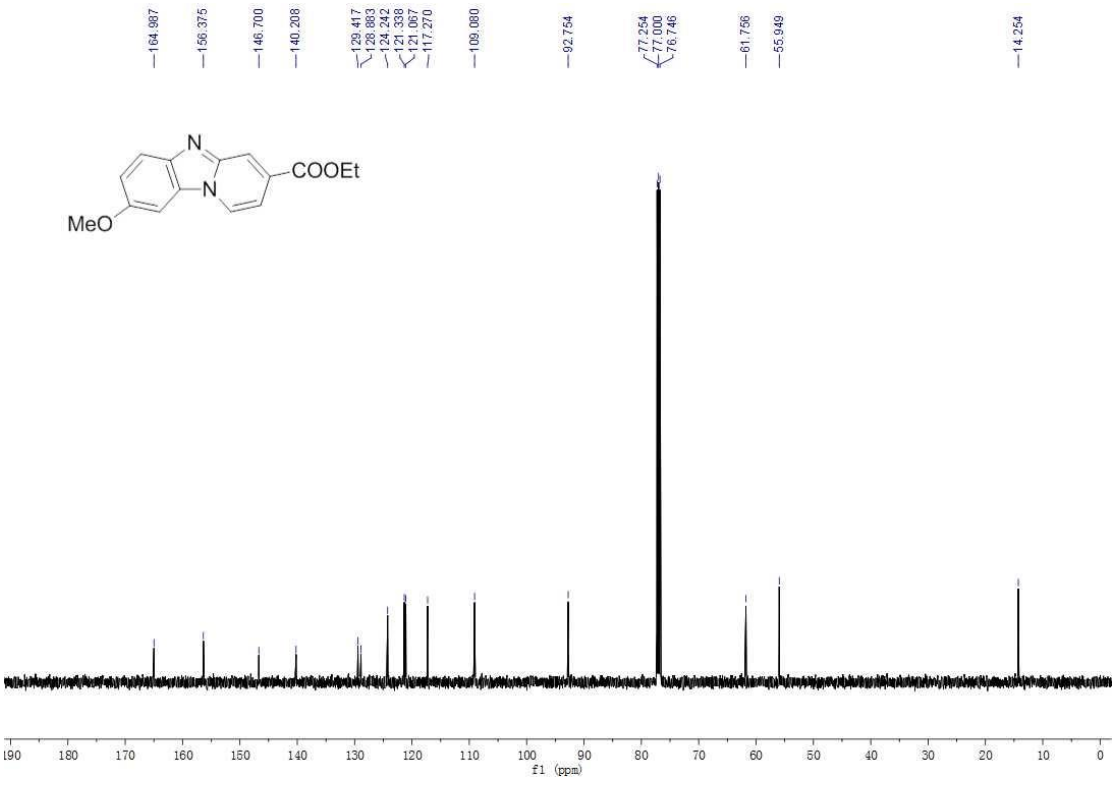


^{13}C NMR (125 MHz, $CDCl_3$)

Ethyl 8-methoxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carboxylate (3ag):

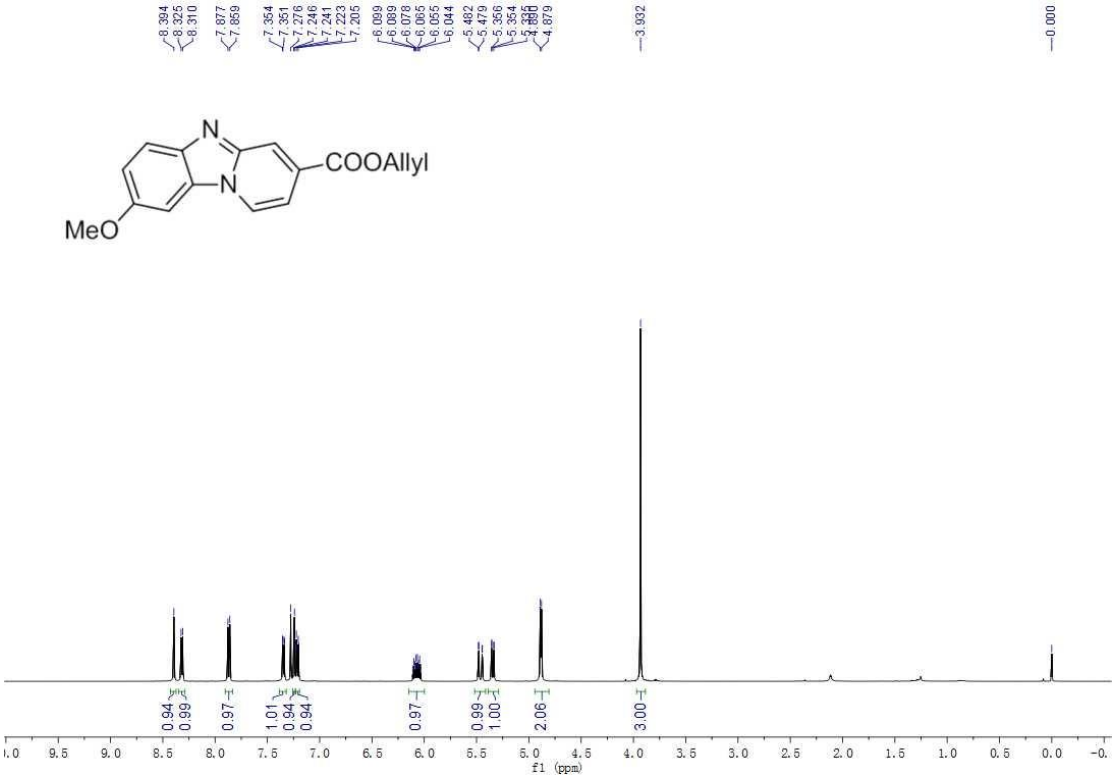


^{1}H NMR (500 MHz, $CDCl_3$)

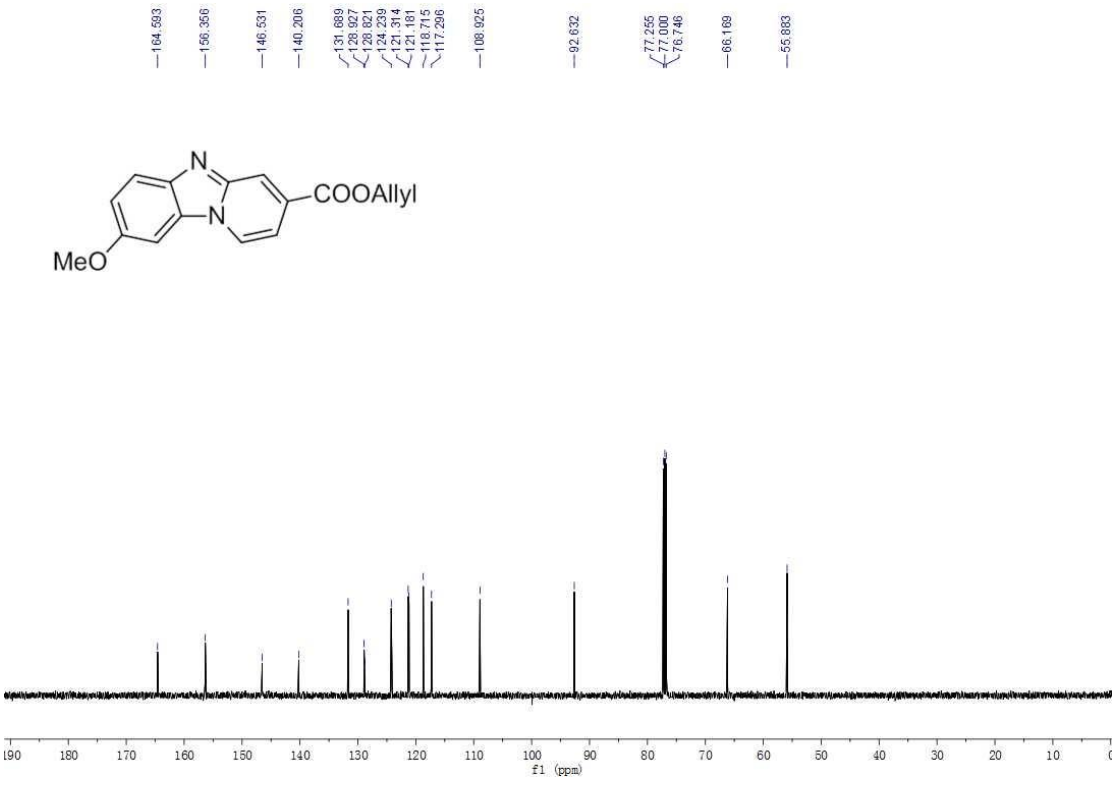


^{13}C NMR (125 MHz, $CDCl_3$)

Allyl 8-methoxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carboxylate (3ah):

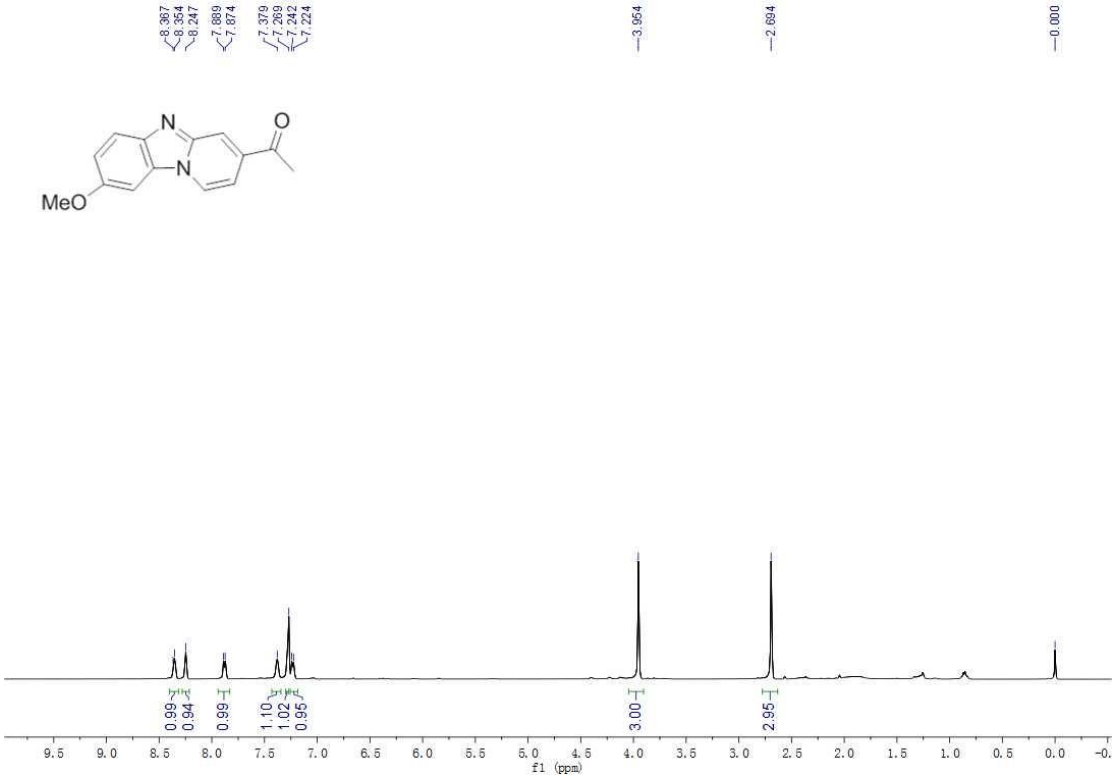


^{1}H NMR (500 MHz, $CDCl_3$)

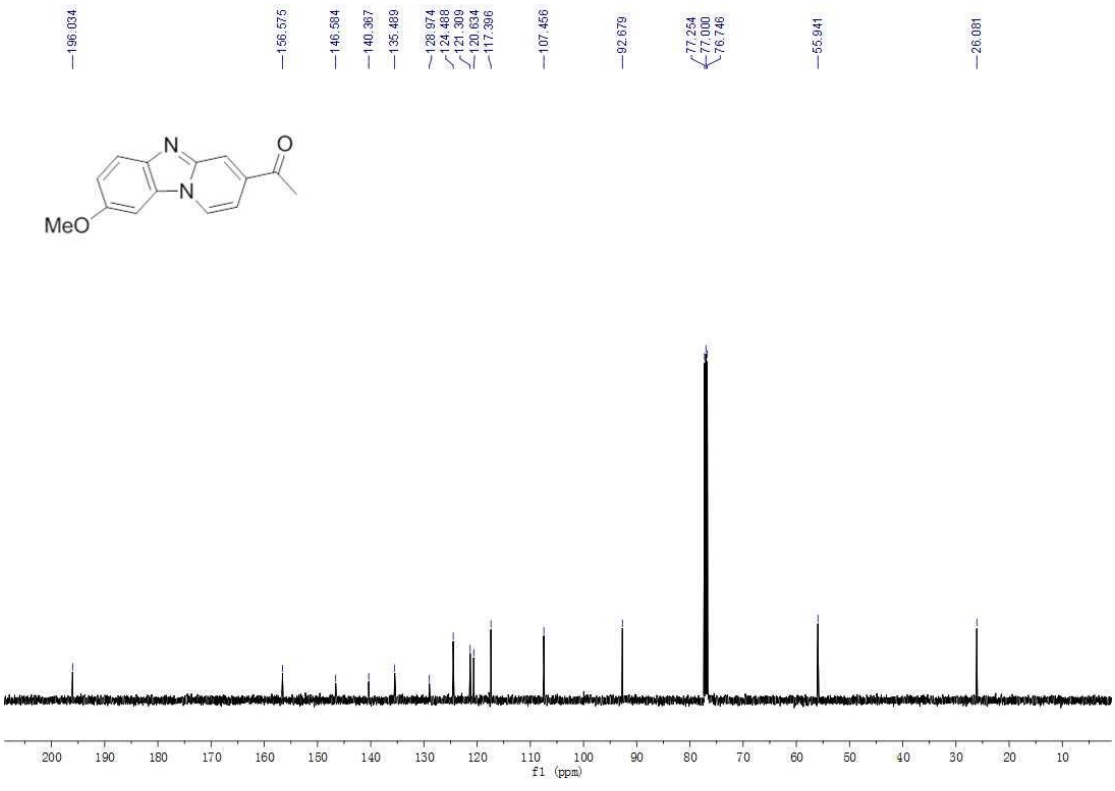


^{13}C NMR (125 MHz, $CDCl_3$)

1-(8-Methoxybenzo[4,5]imidazo[1,2-*a*]pyridin-3-yl)ethanone (3ai):

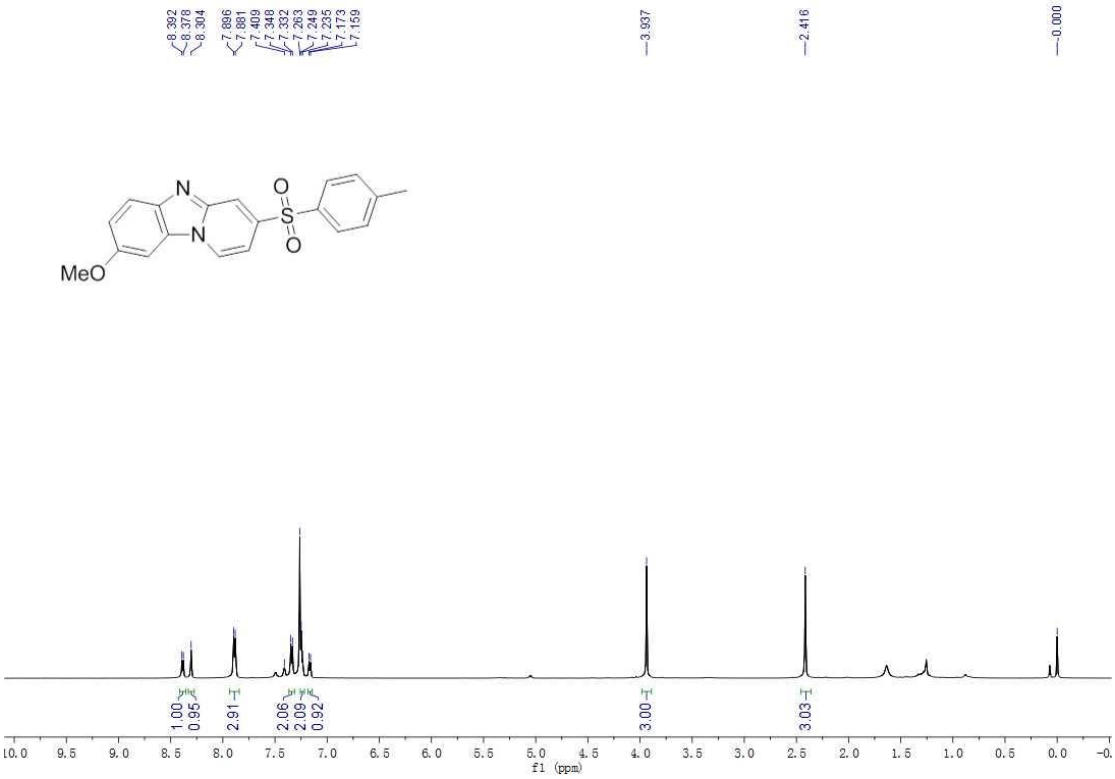


^{1}H NMR (500 MHz, $CDCl_3$)

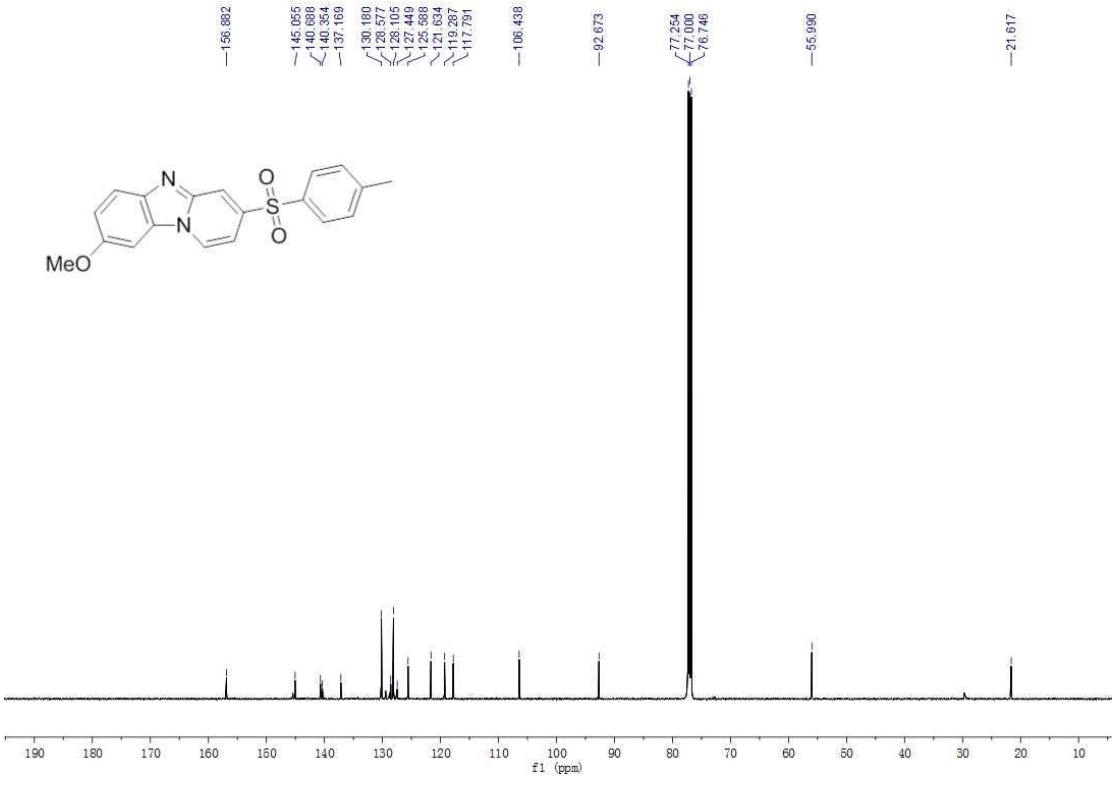


^{13}C NMR (125 MHz, $CDCl_3$)

8-Methoxy-3-tosylbenzo[4,5]imidazo[1,2-*a*]pyridine (3aj):

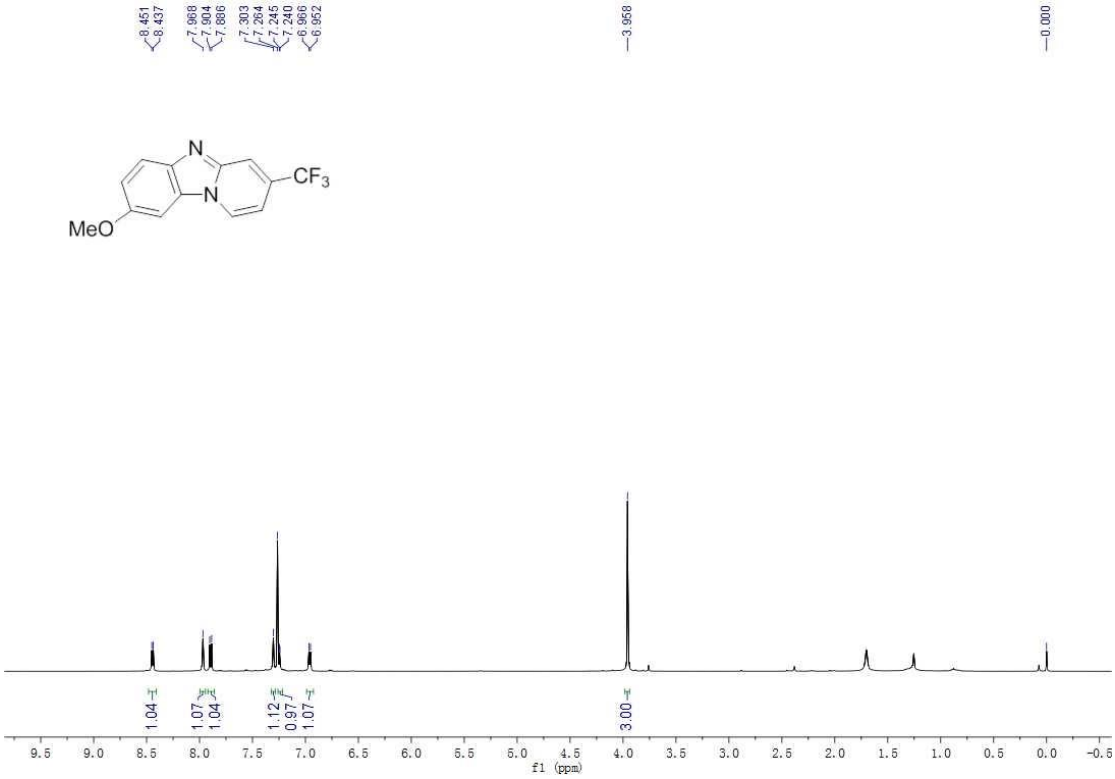


^{1}H NMR (500 MHz, $CDCl_3$)

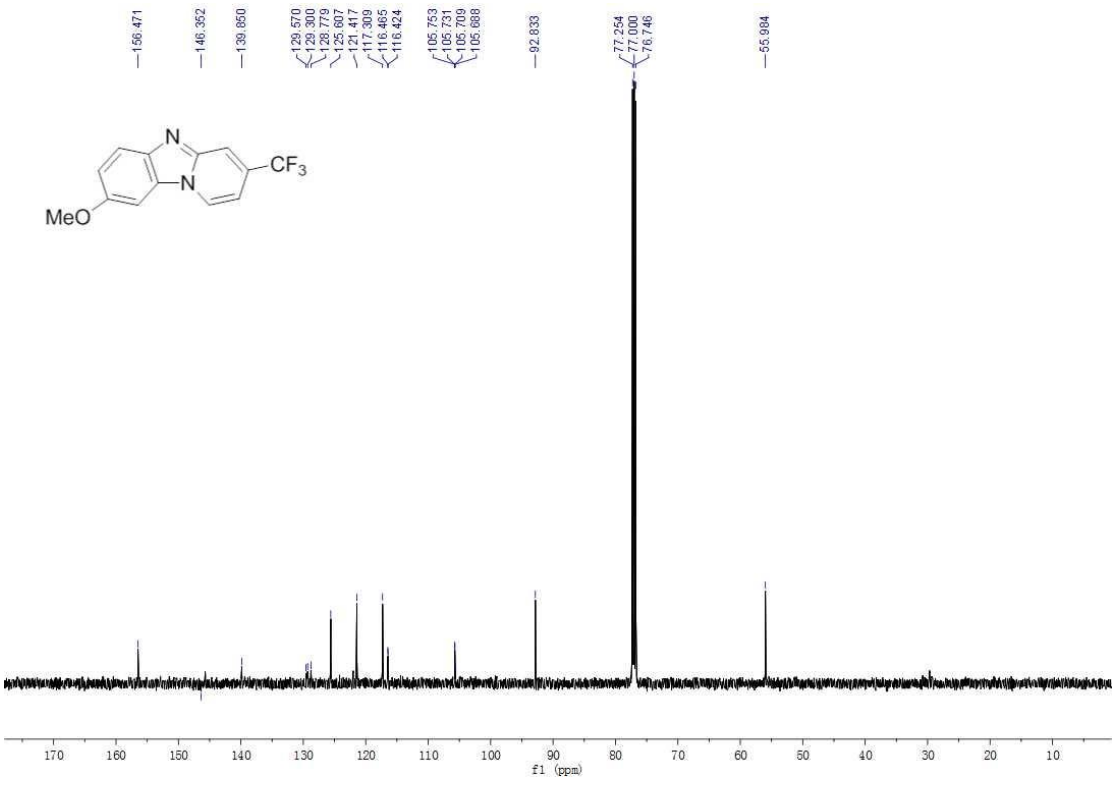


^{13}C NMR (125 MHz, $CDCl_3$)

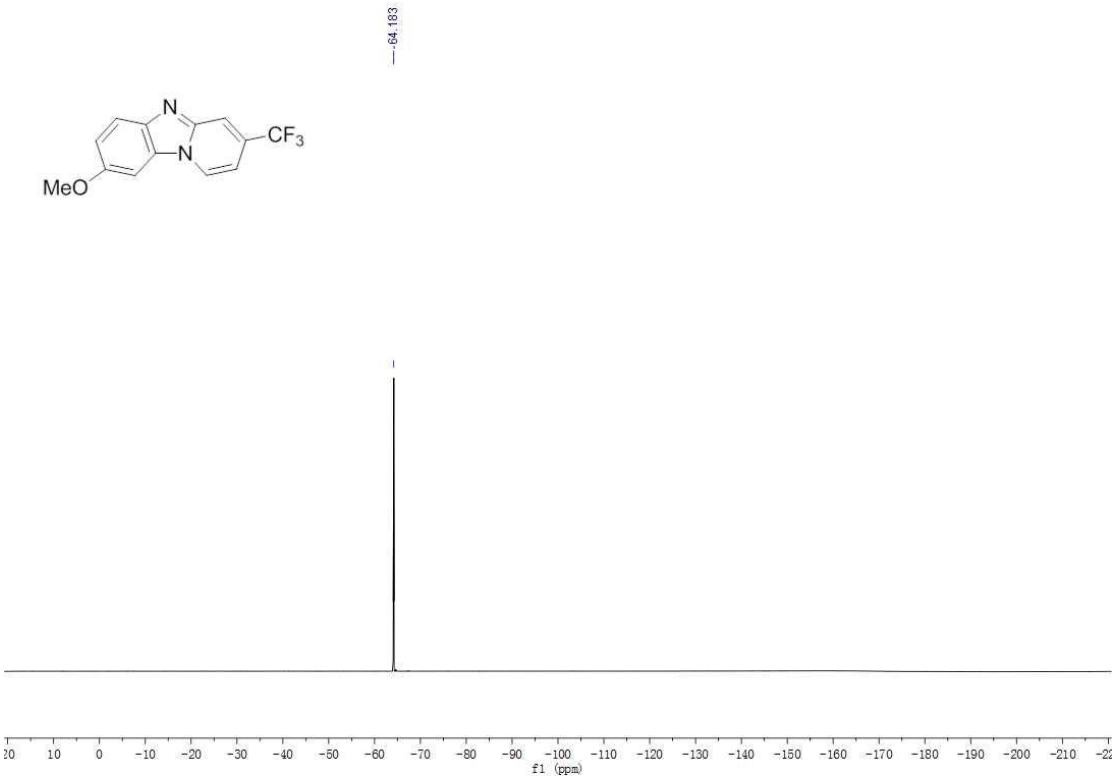
8-Methoxy-3-(trifluoromethyl)benzo[4,5]imidazo[1,2-*a*]pyridine (3ak):



^{1}H NMR (500 MHz, $CDCl_3$)

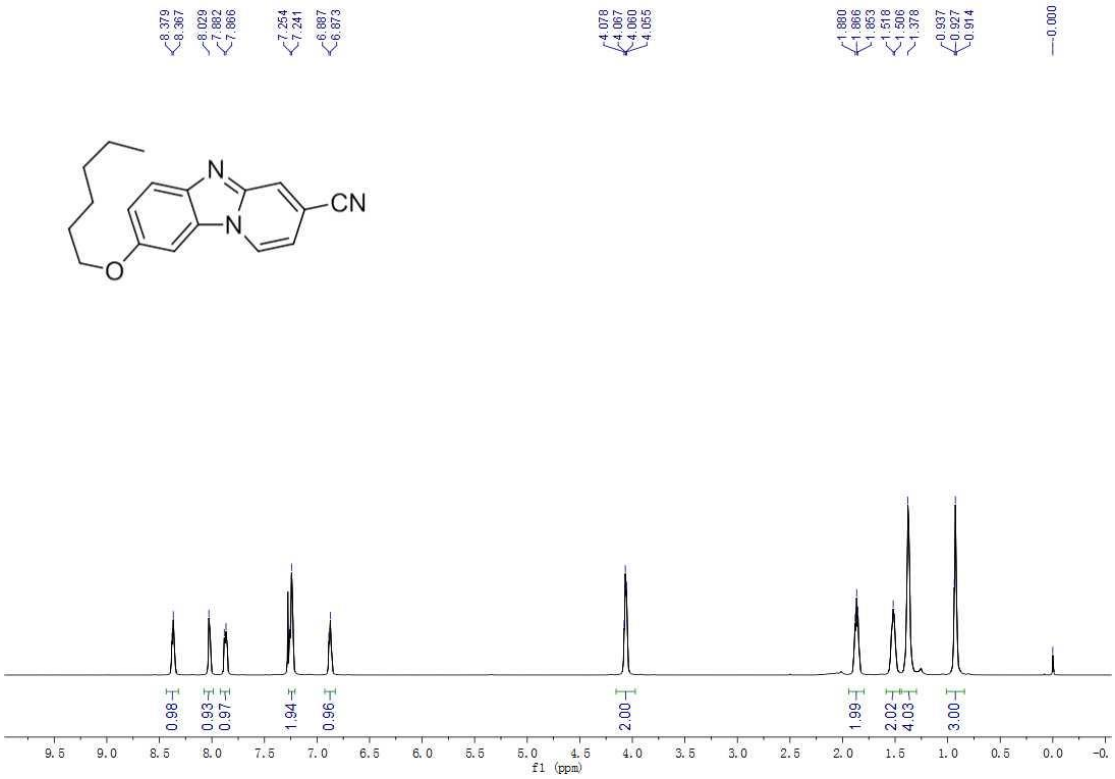


^{13}C NMR (125 MHz, $CDCl_3$)

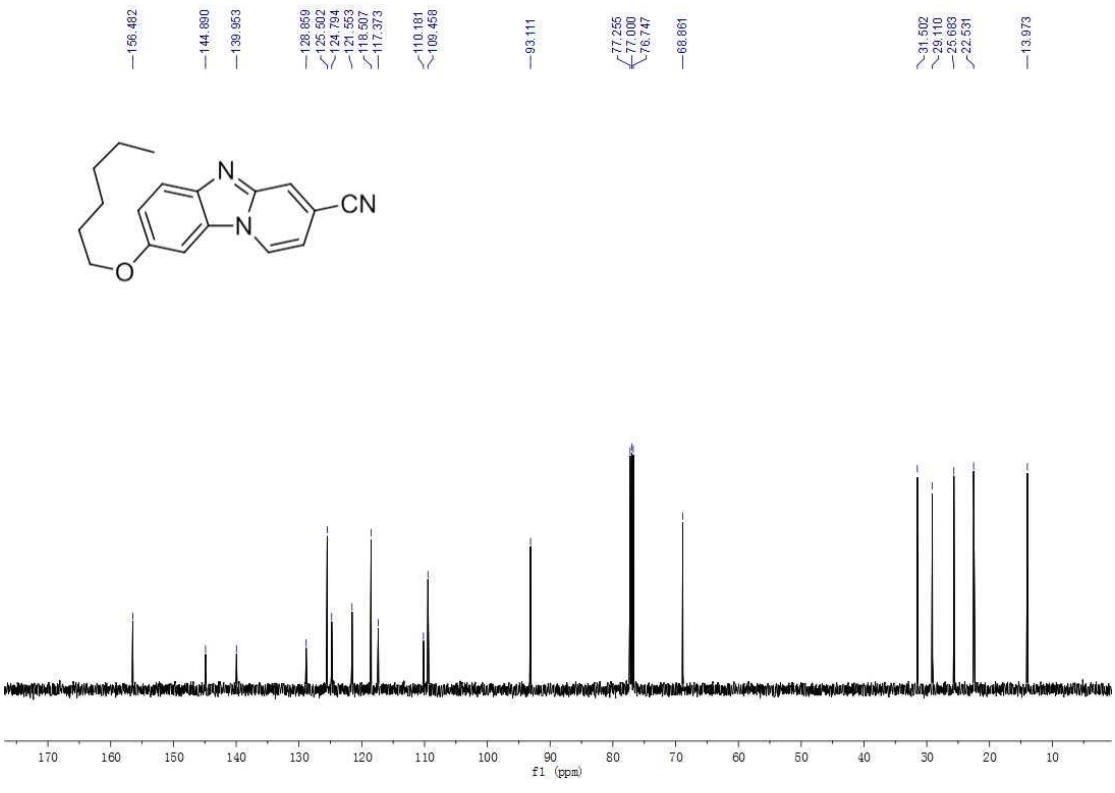


^{19}F NMR (471 MHz, $CDCl_3$)

8-(Hexyloxy)benzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3ia):

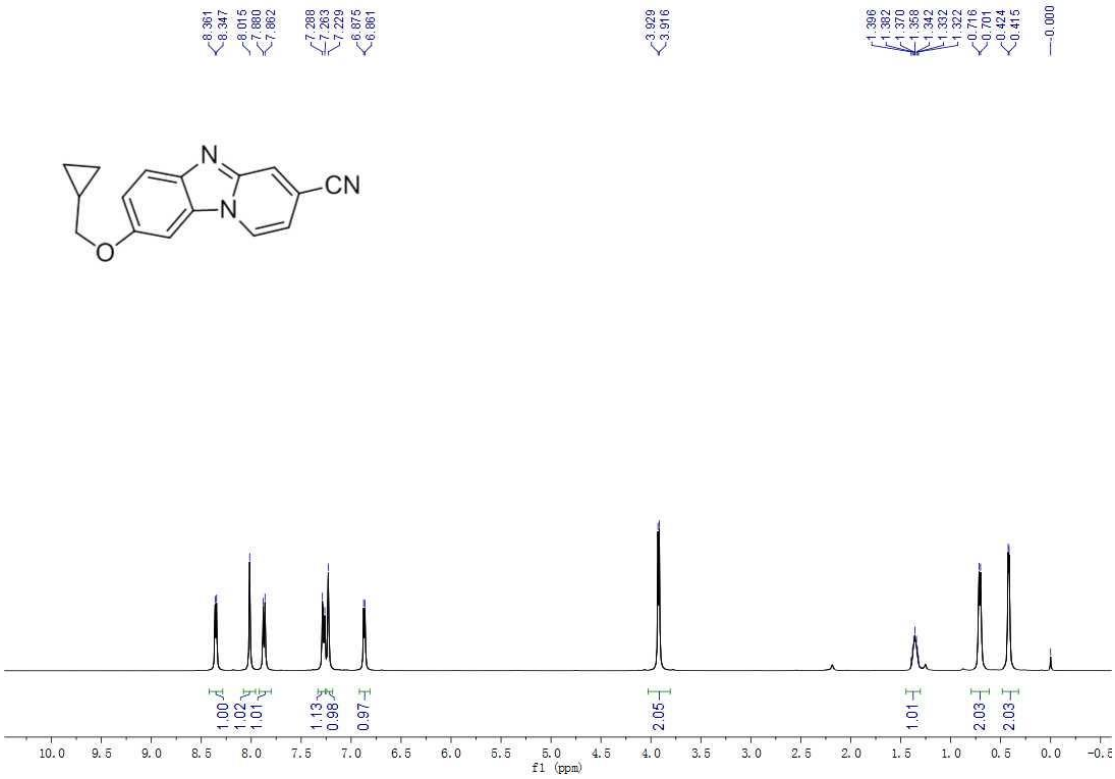


^{1}H NMR (500 MHz, $CDCl_3$)

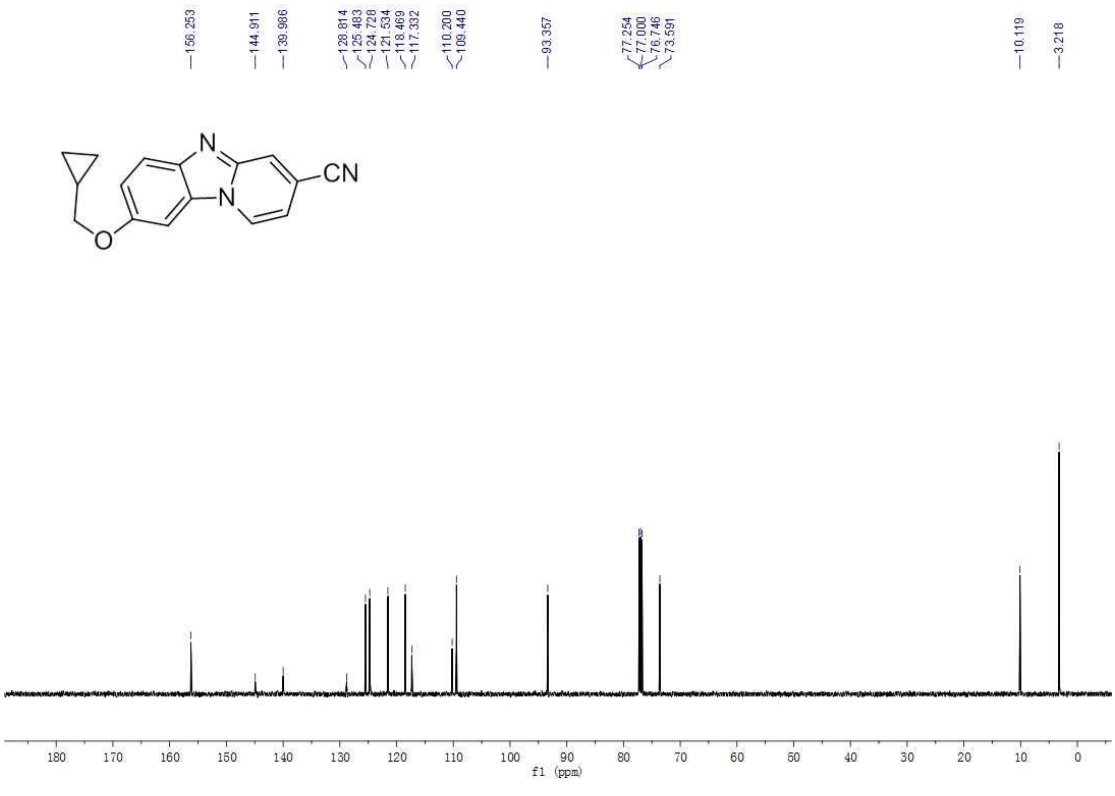


^{13}C NMR (125 MHz, $CDCl_3$)

8-(Cyclopropylmethoxy)benzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3ja):

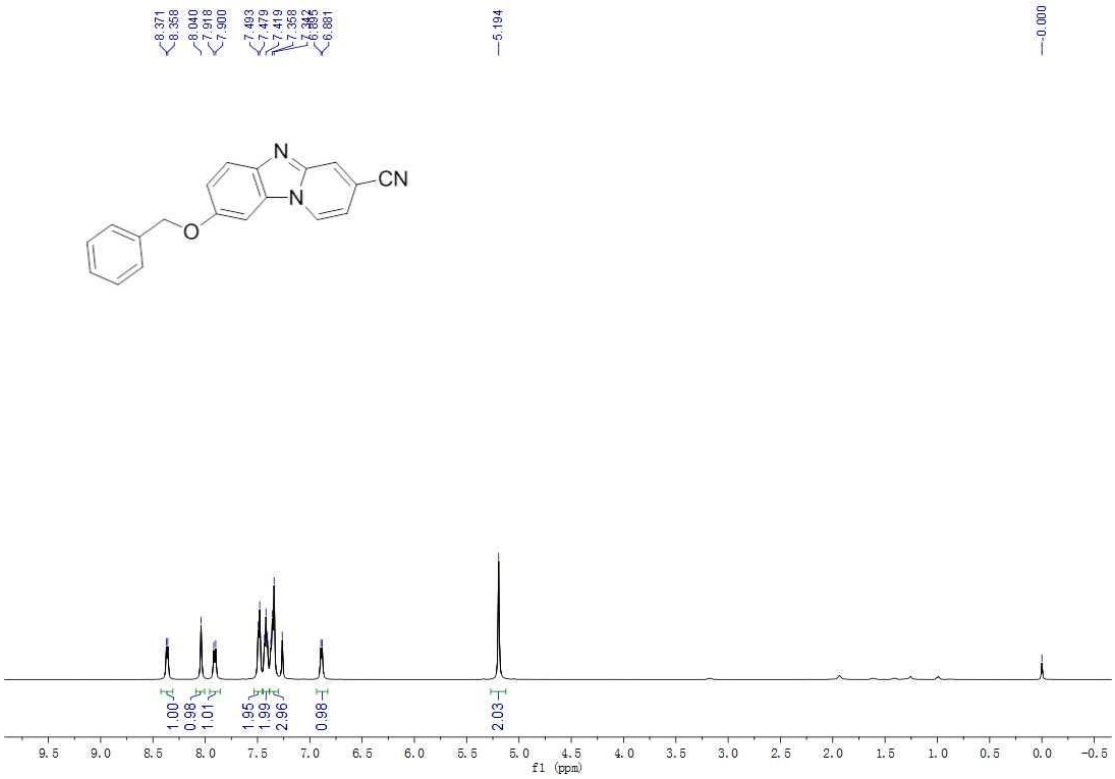


^{1}H NMR (500 MHz, $CDCl_3$)

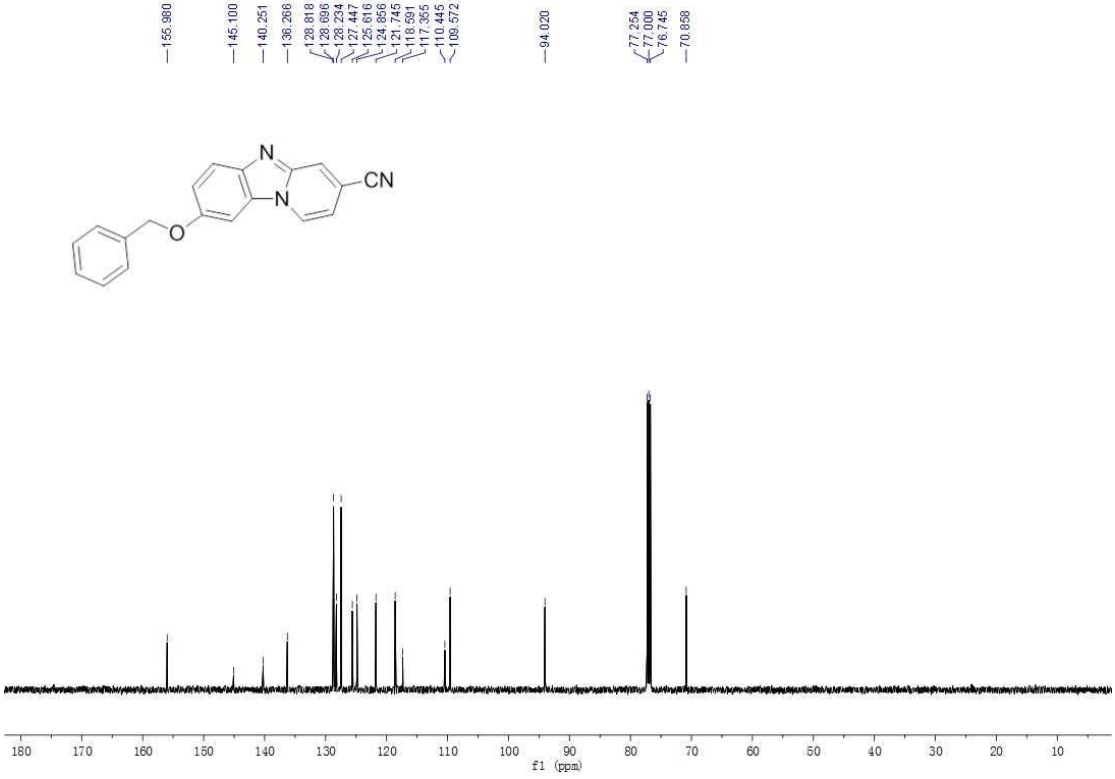


^{13}C NMR (125 MHz, $CDCl_3$)

8-(Benzyloxy)benzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3ka):

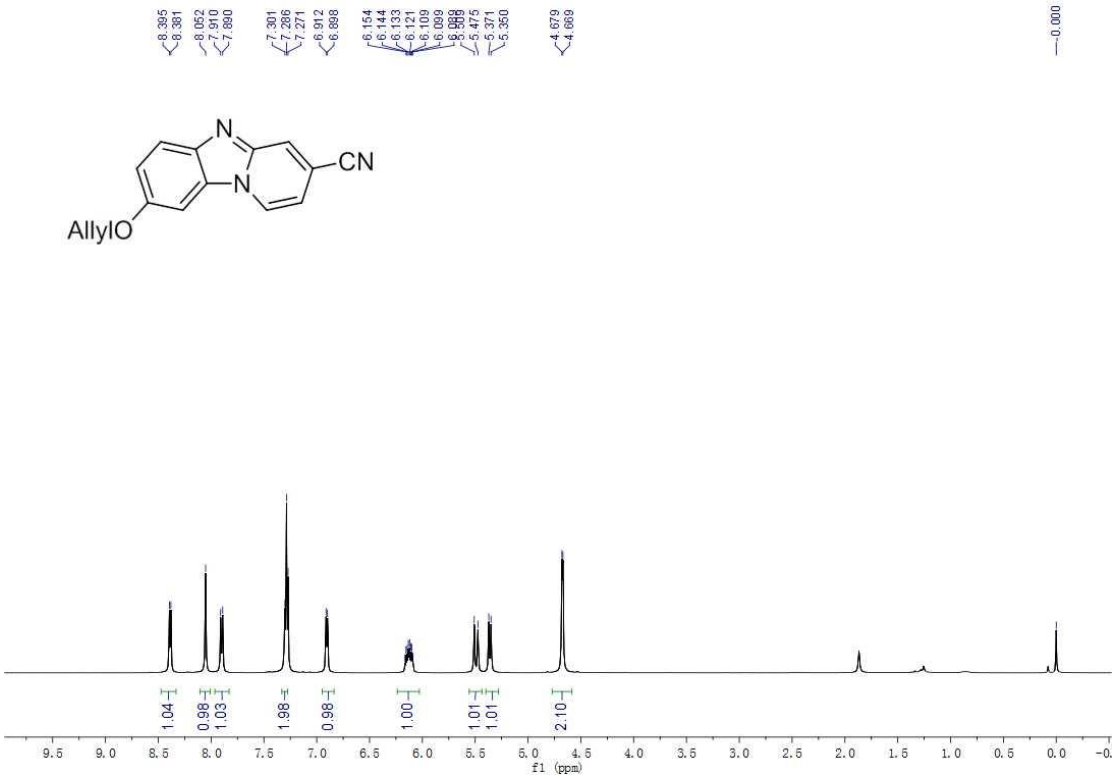


^{1}H NMR (500 MHz, $CDCl_3$)

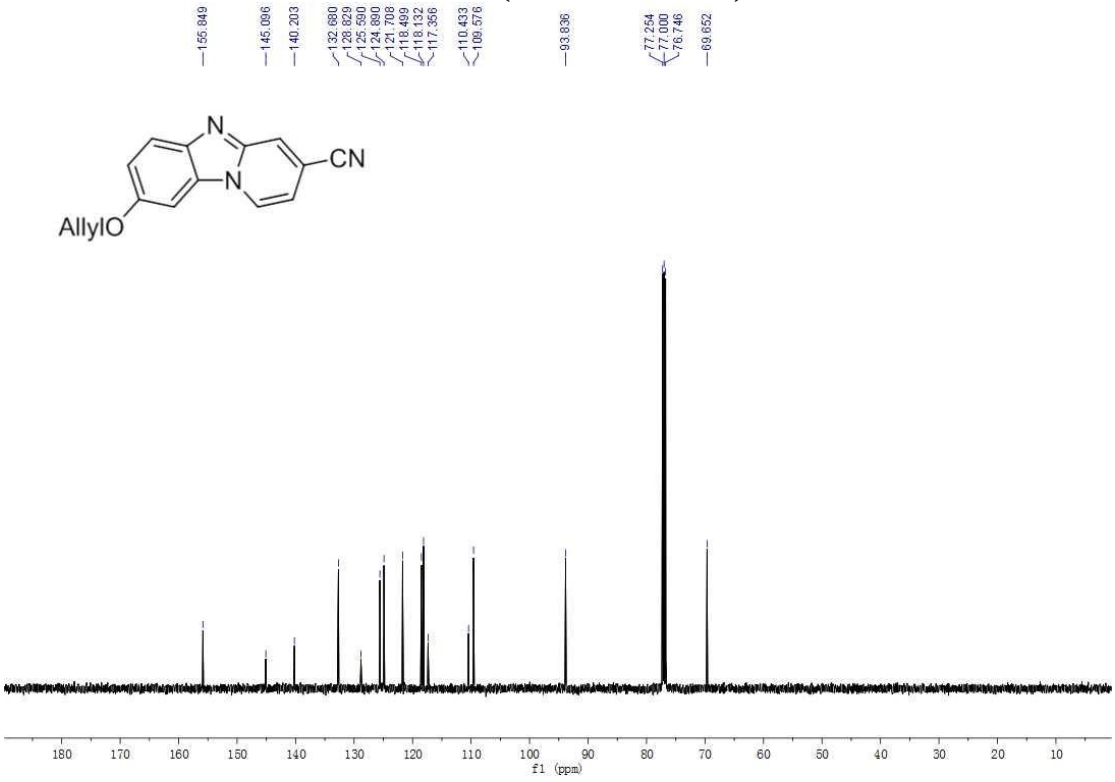


^{13}C NMR (125 MHz, $CDCl_3$)

8-(Allyloxy)benzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3la):

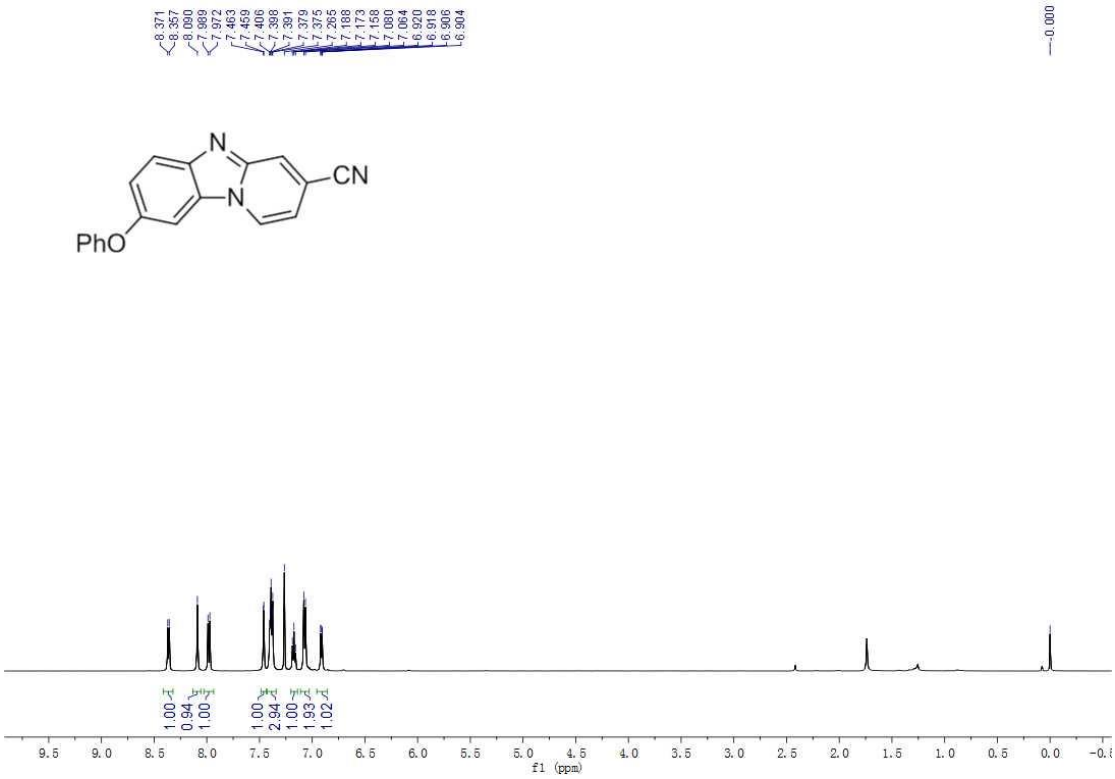


^{1}H NMR (500 MHz, $CDCl_3$)

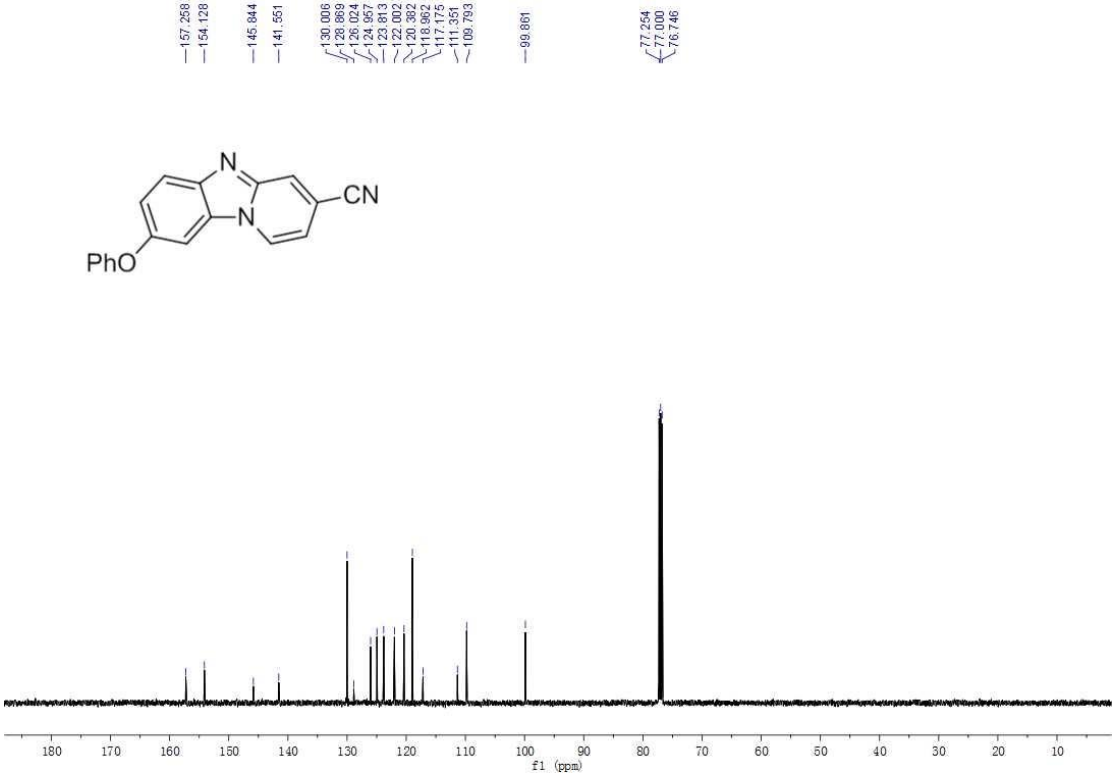


^{13}C NMR (125 MHz, $CDCl_3$)

8-Phenoxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3ma):

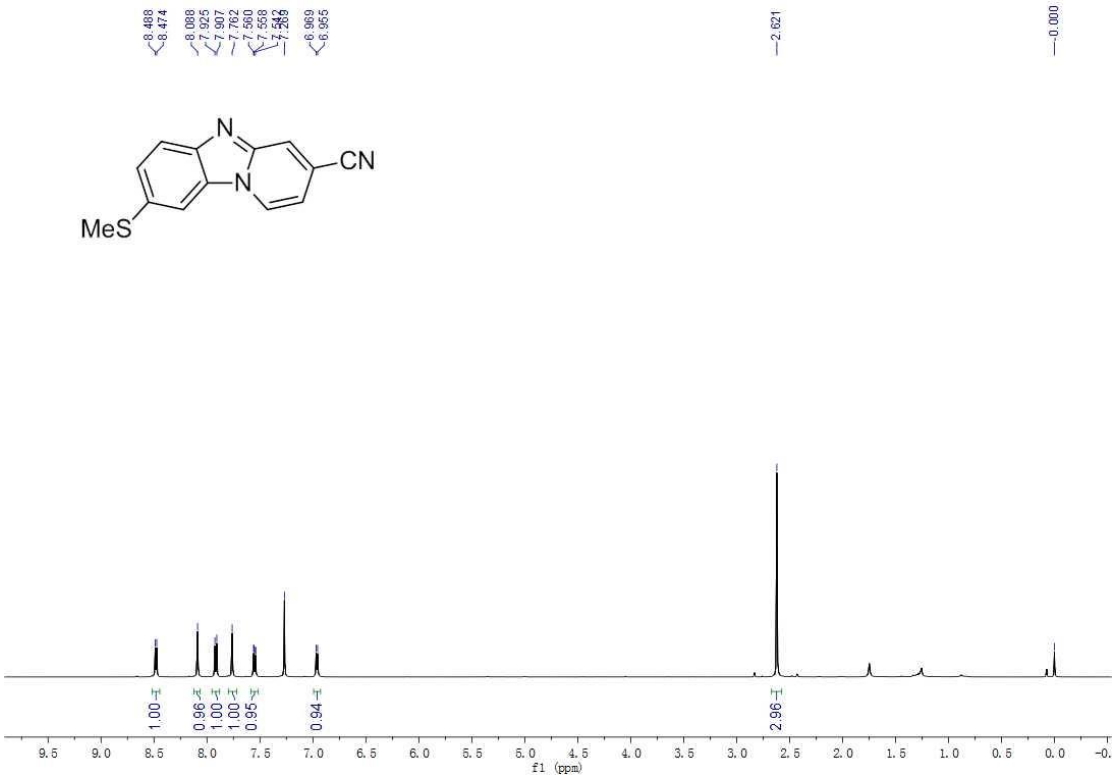


^{1}H NMR (500 MHz, $CDCl_3$)

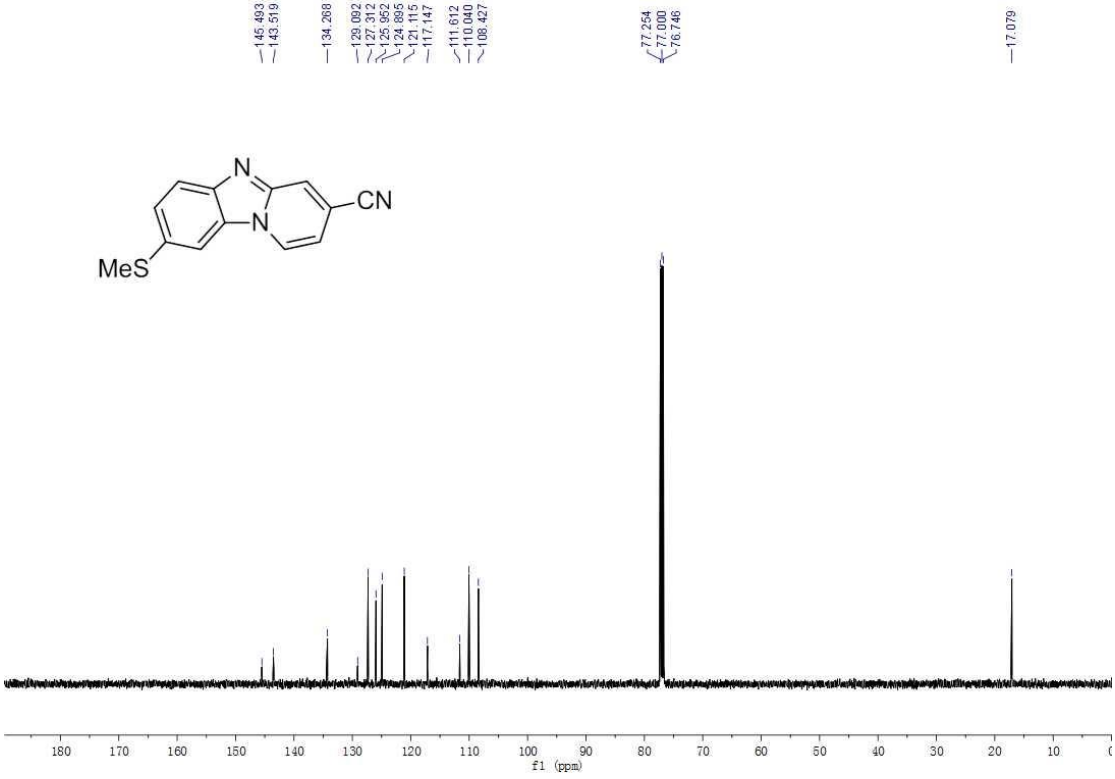


^{13}C NMR (125 MHz, $CDCl_3$)

8-(Methylthio)benzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3na):

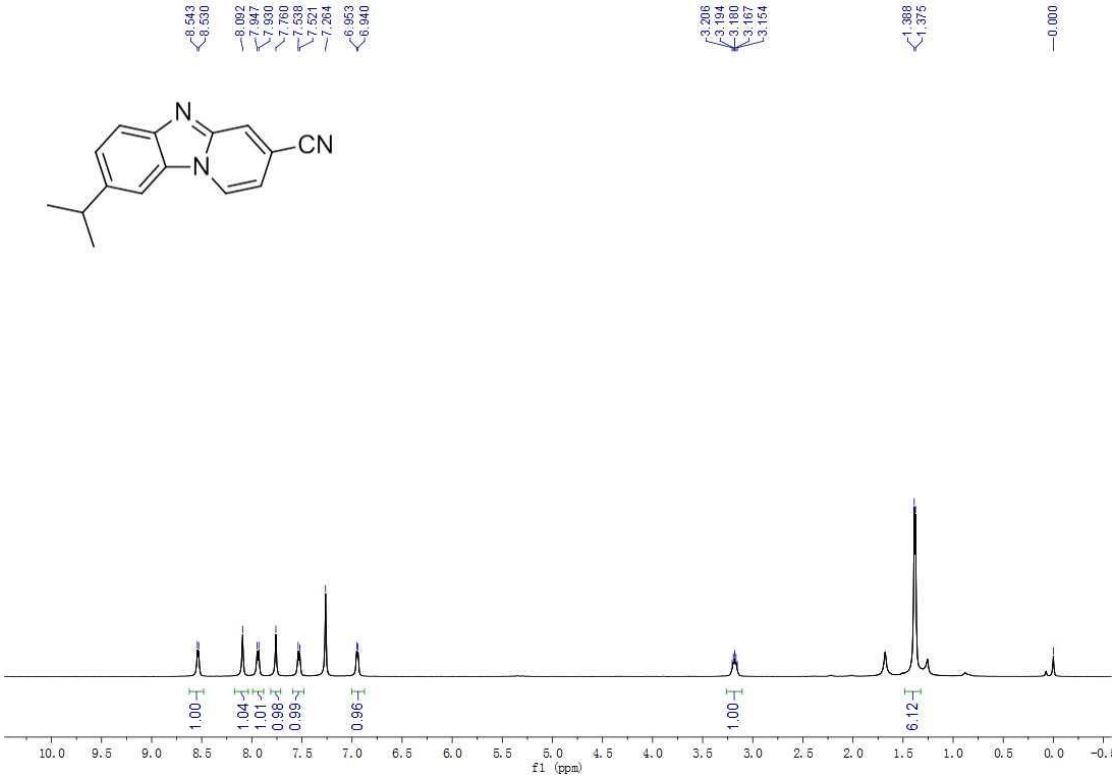


^{1}H NMR (500 MHz, $CDCl_3$)

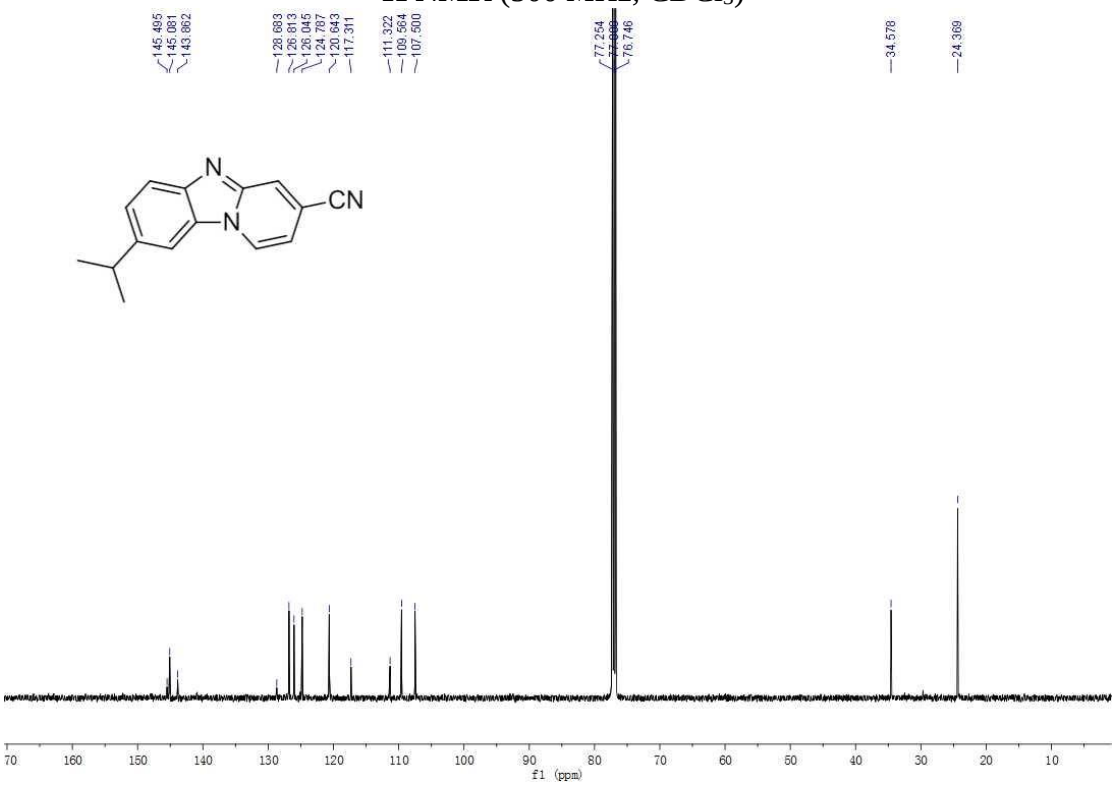


^{13}C NMR (125 MHz, $CDCl_3$)

8-Isopropylbenzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3oa):

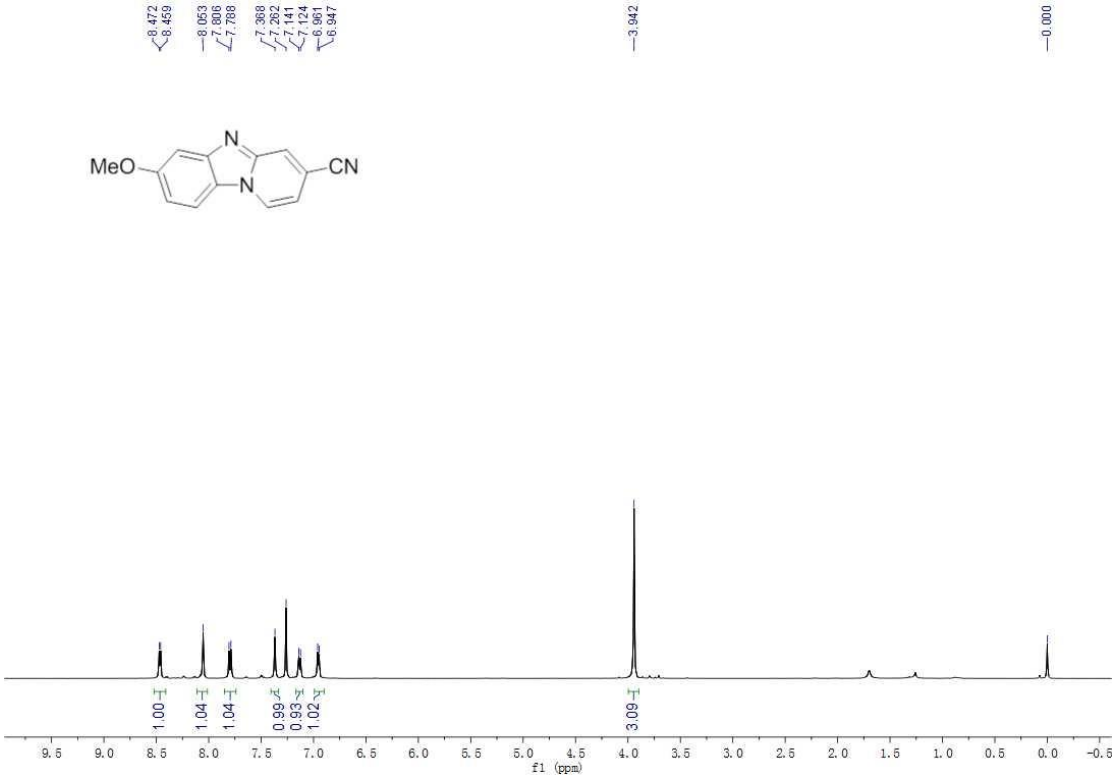


^{1}H NMR (500 MHz, $CDCl_3$)

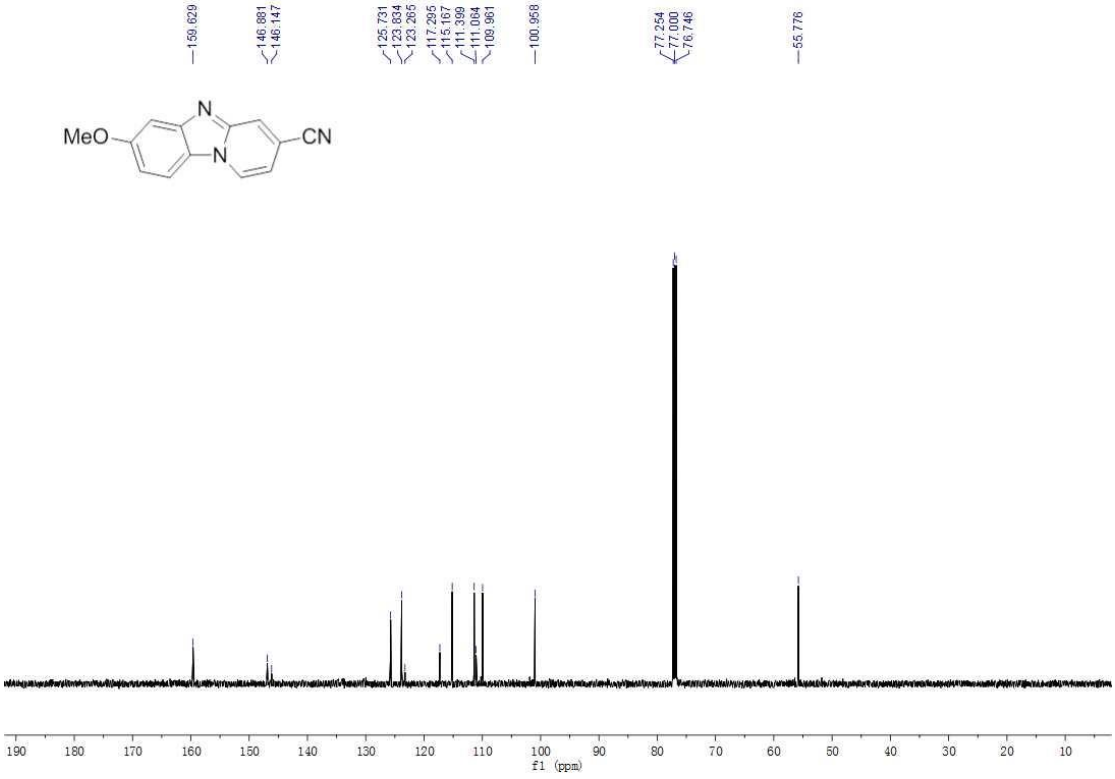


^{13}C NMR (125 MHz, $CDCl_3$)

7-Methoxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3pa):

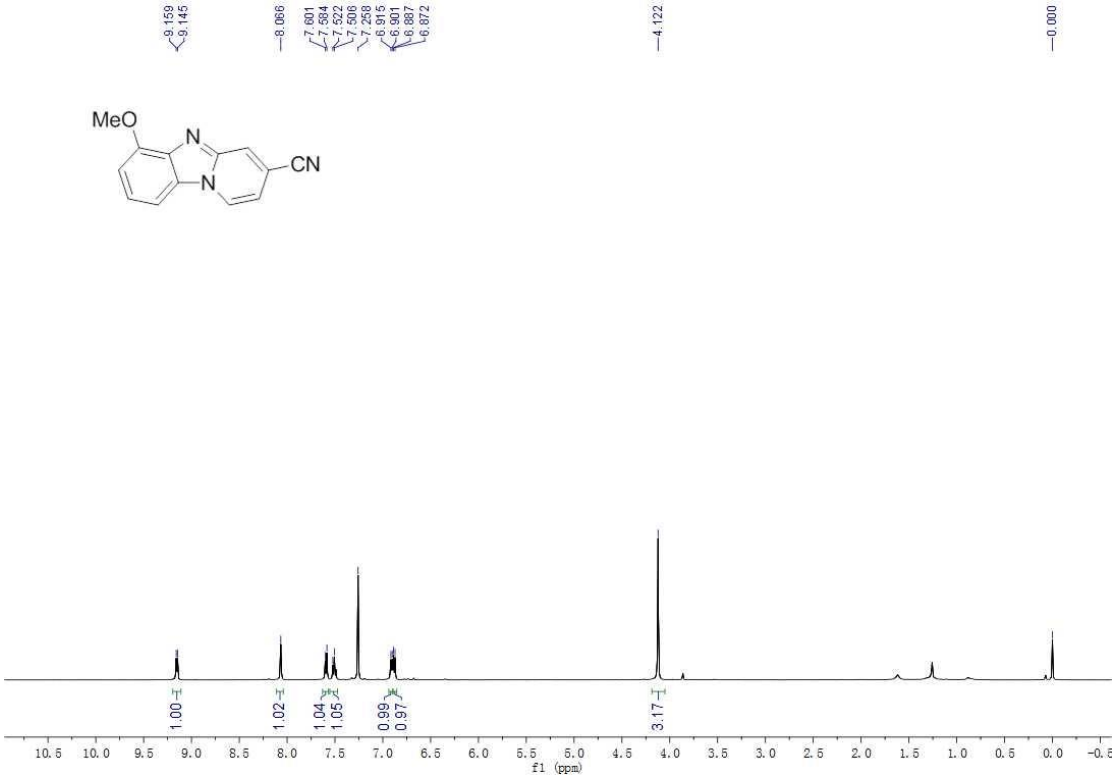


^{1}H NMR (500 MHz, $CDCl_3$)

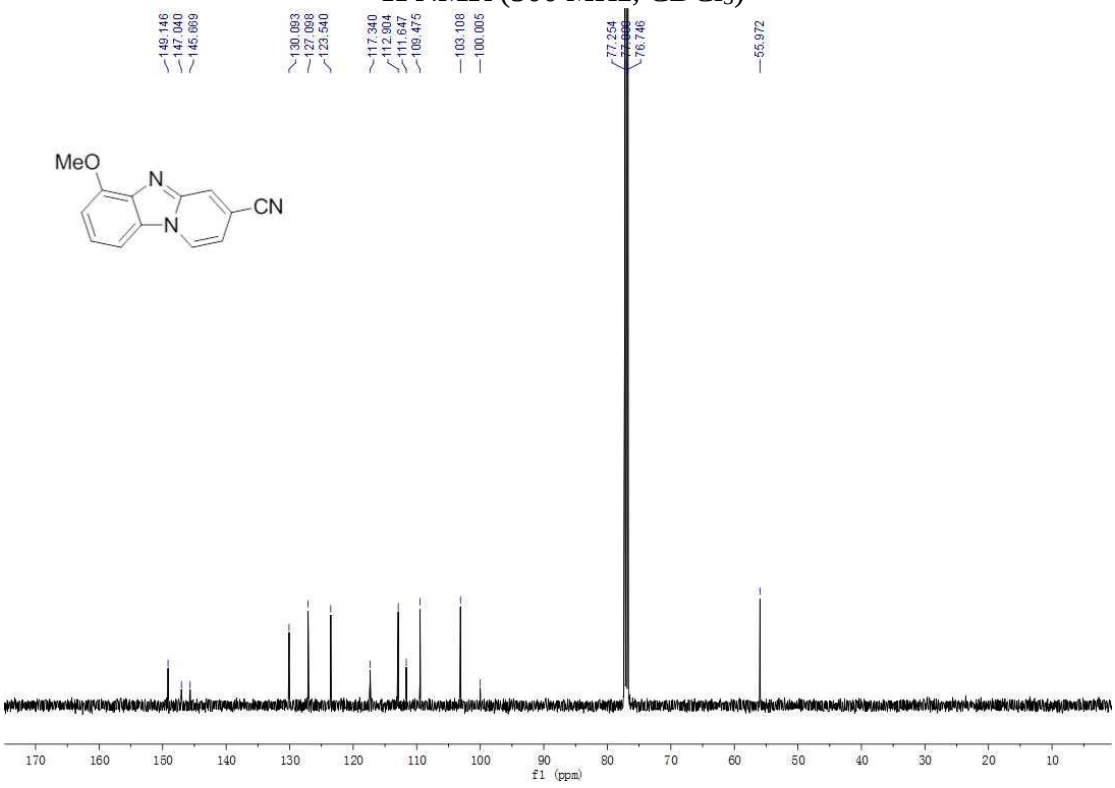


^{13}C NMR (125 MHz, $CDCl_3$)

6-Methoxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3qa):

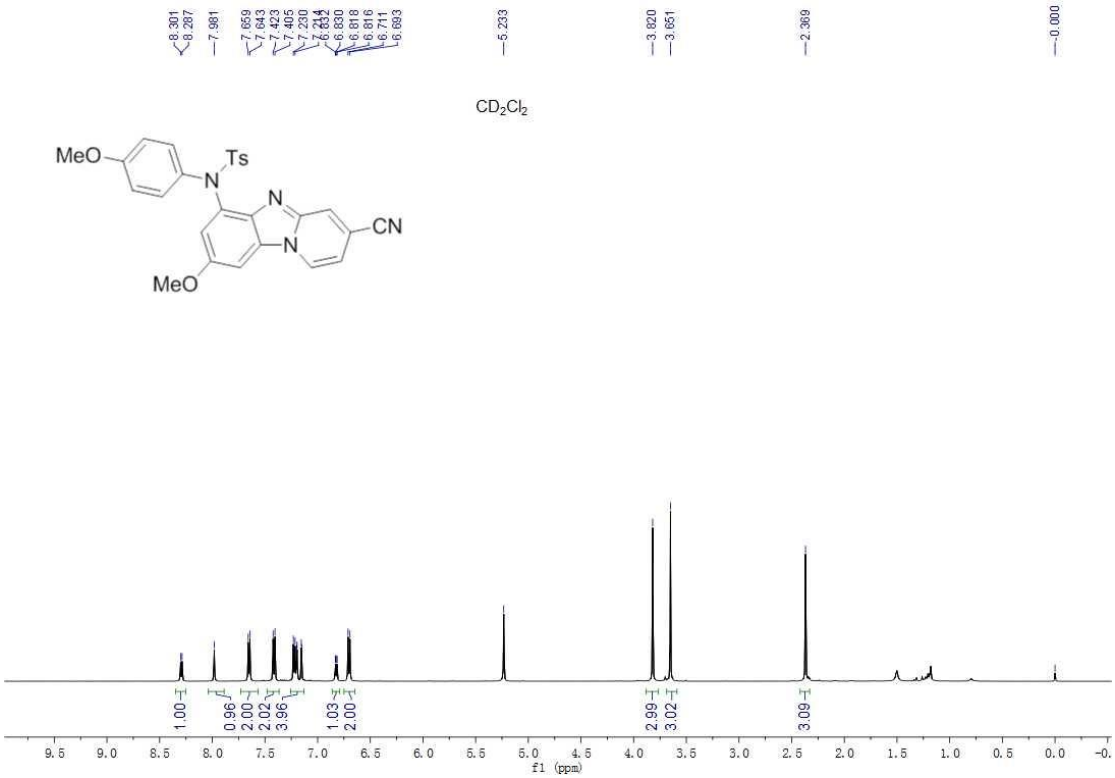


^{1}H NMR (500 MHz, $CDCl_3$)

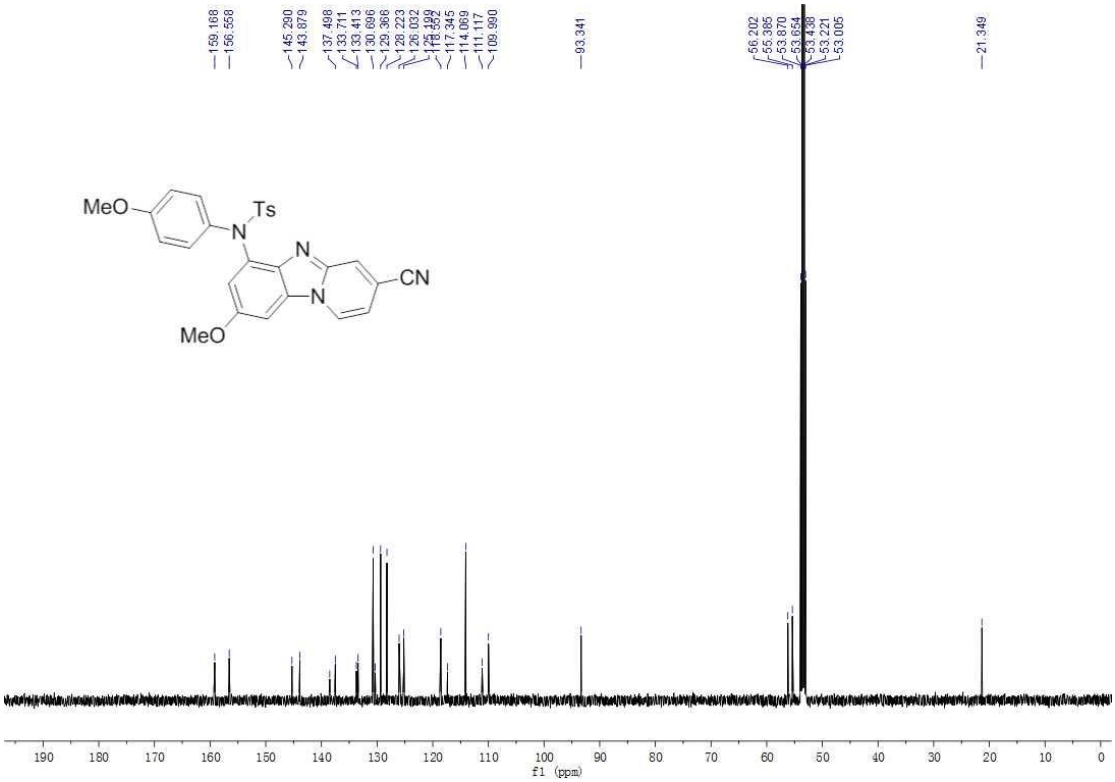


^{13}C NMR (125 MHz, $CDCl_3$)

***N*-(3-Cyano-8-methoxybenzo[4,5]imidazo[1,2-*a*]pyridin-6-yl)-*N*-(4-methoxyphen yl)-4-methylbenzenesulfonamide (3ra):**

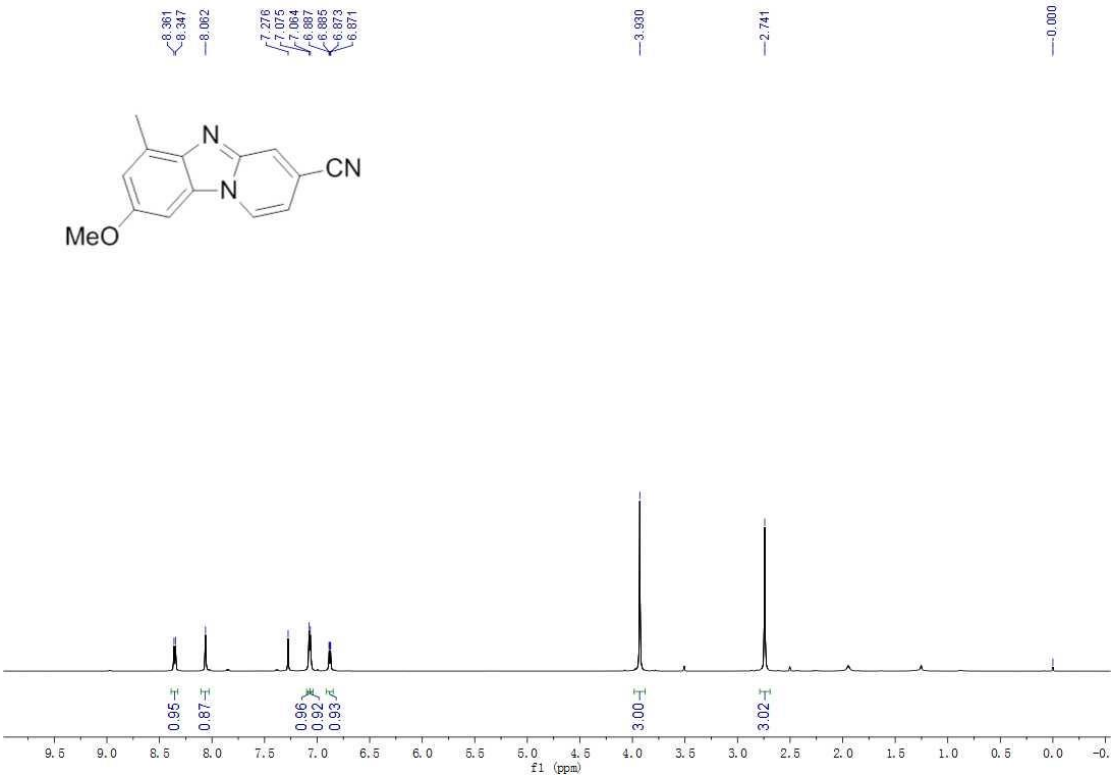


^{1}H NMR (125 MHz, CD_2Cl_2)

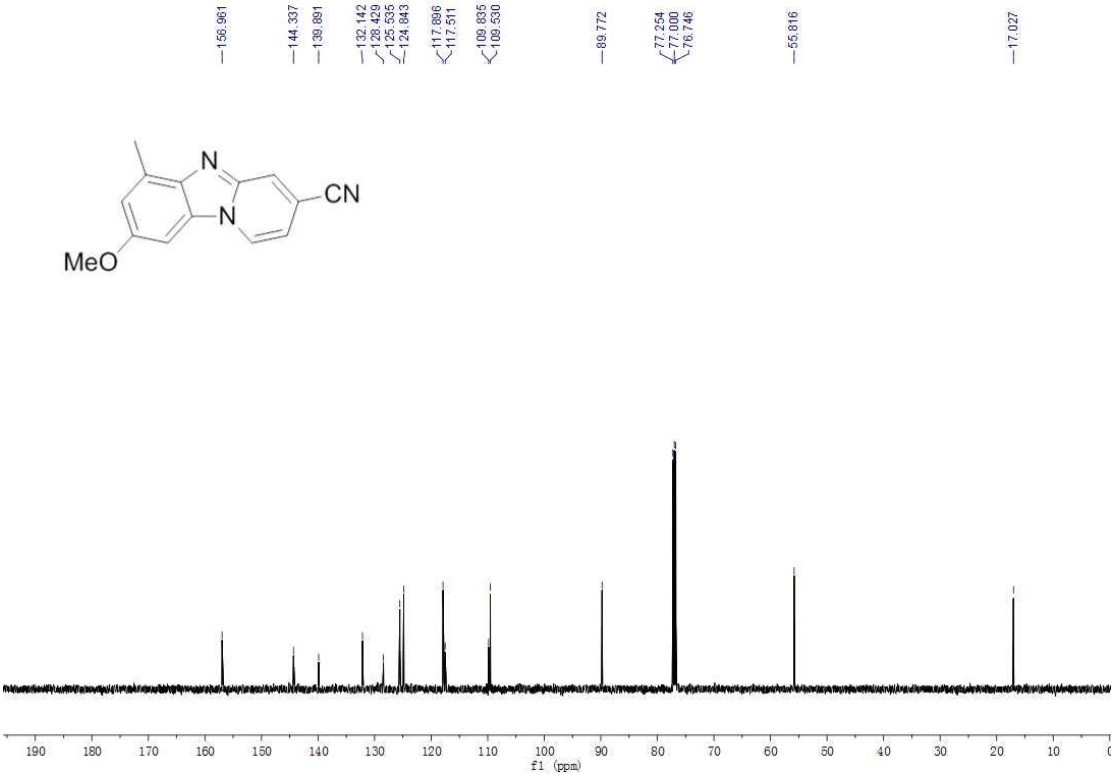


^{13}C NMR (125 MHz, CD_2Cl_2)

8-Methoxy-6-methylbenzo[4,5]imidazo[1,2-a]pyridine-3-carbonitrile (3sa):

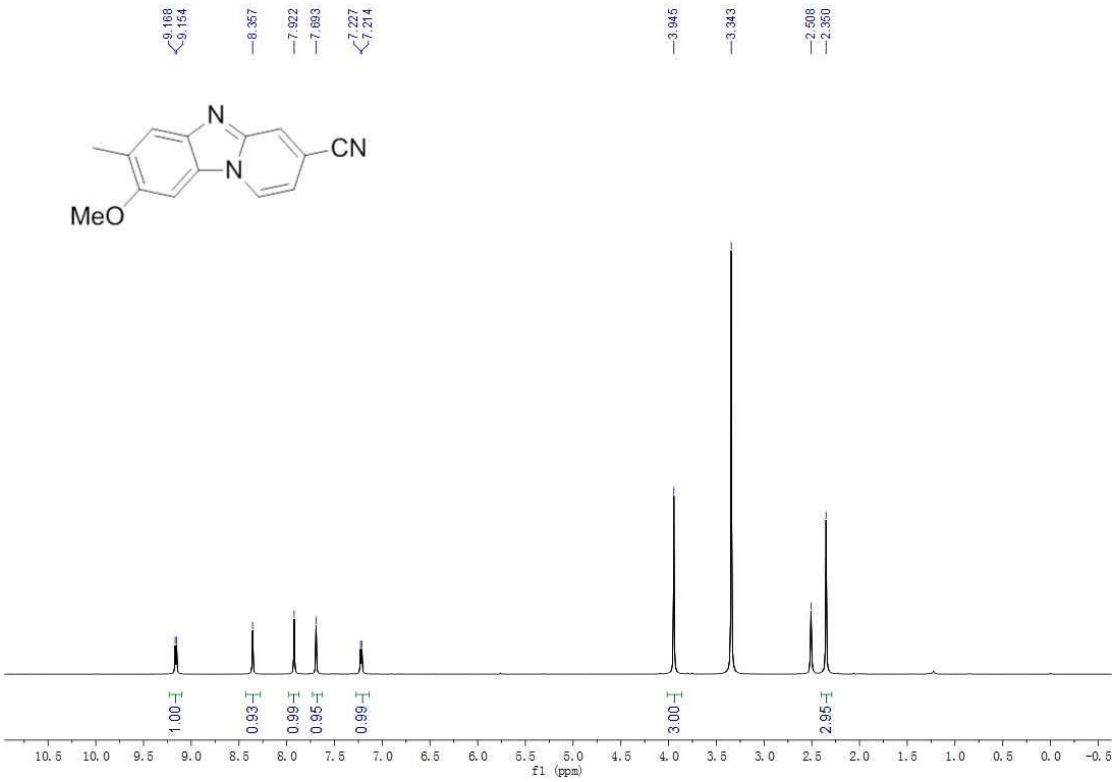


^{1}H NMR (500 MHz, $CDCl_3$)

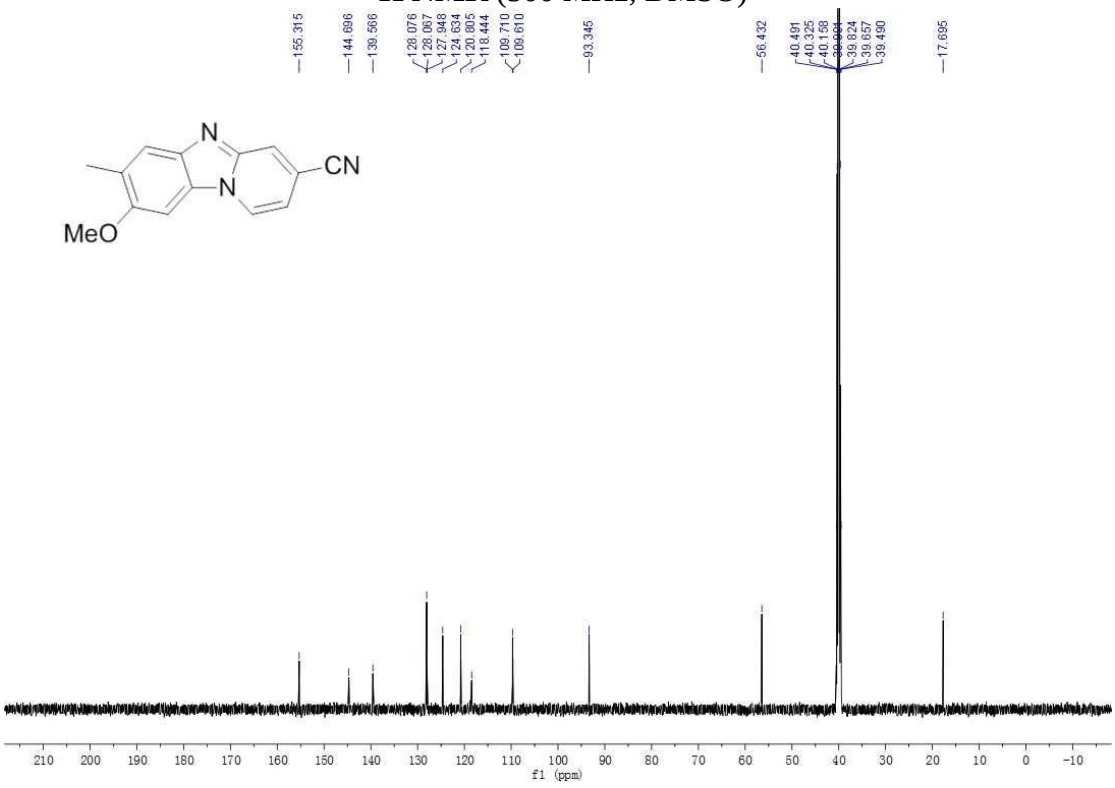


^{13}C NMR (125 MHz, $CDCl_3$)

8-Methoxy-7-methylbenzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3ta):

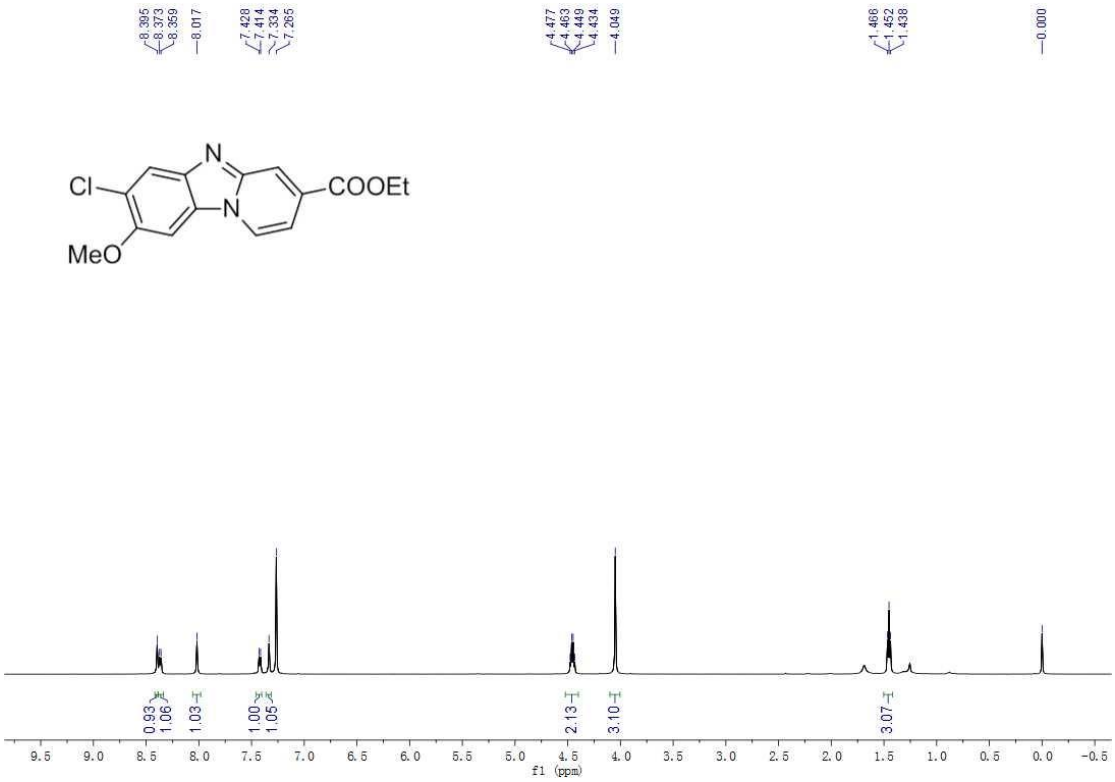


^{1}H NMR (500 MHz, DMSO)

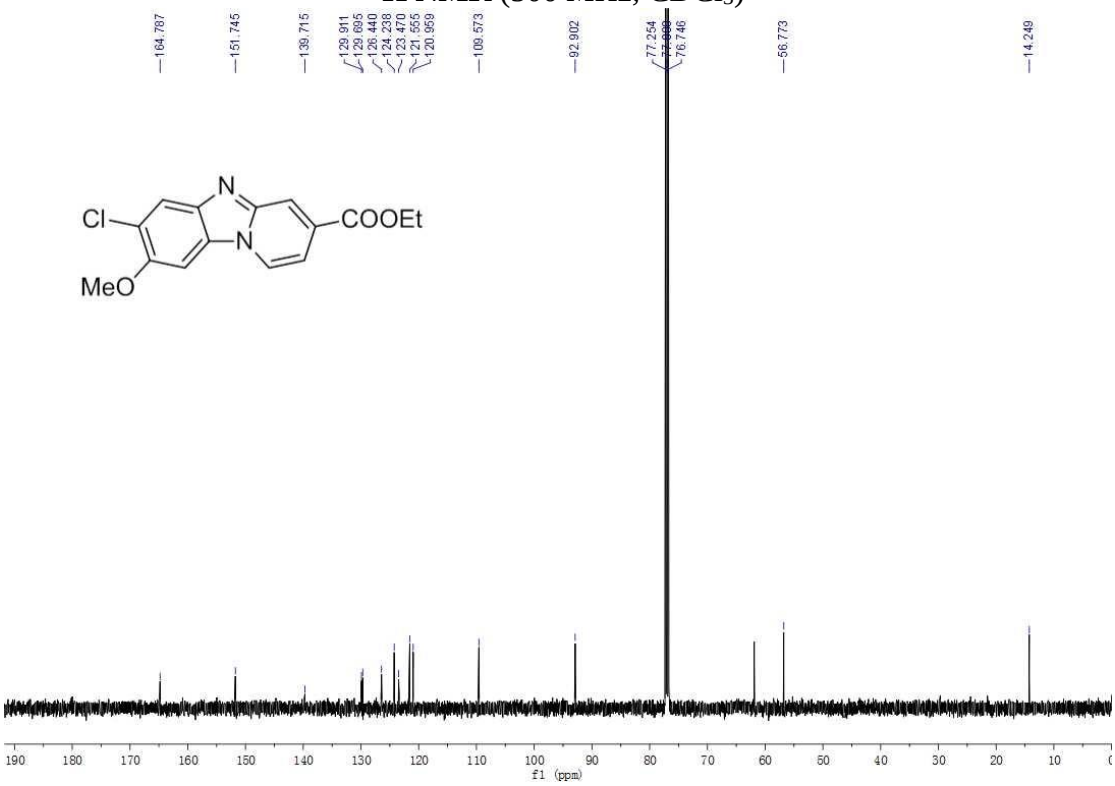


^{13}C NMR (125 MHz, DMSO)

Ethyl 7-chloro-8-methoxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carboxylate (3ug):

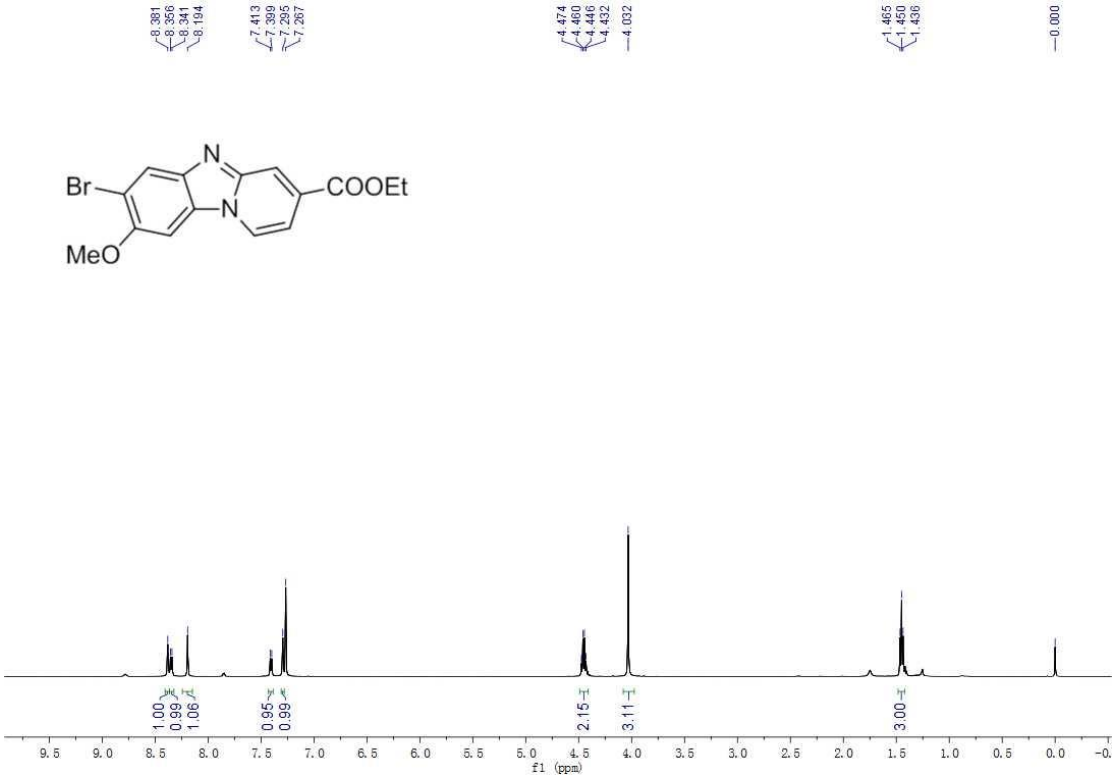


^{1}H NMR (500 MHz, $CDCl_3$)

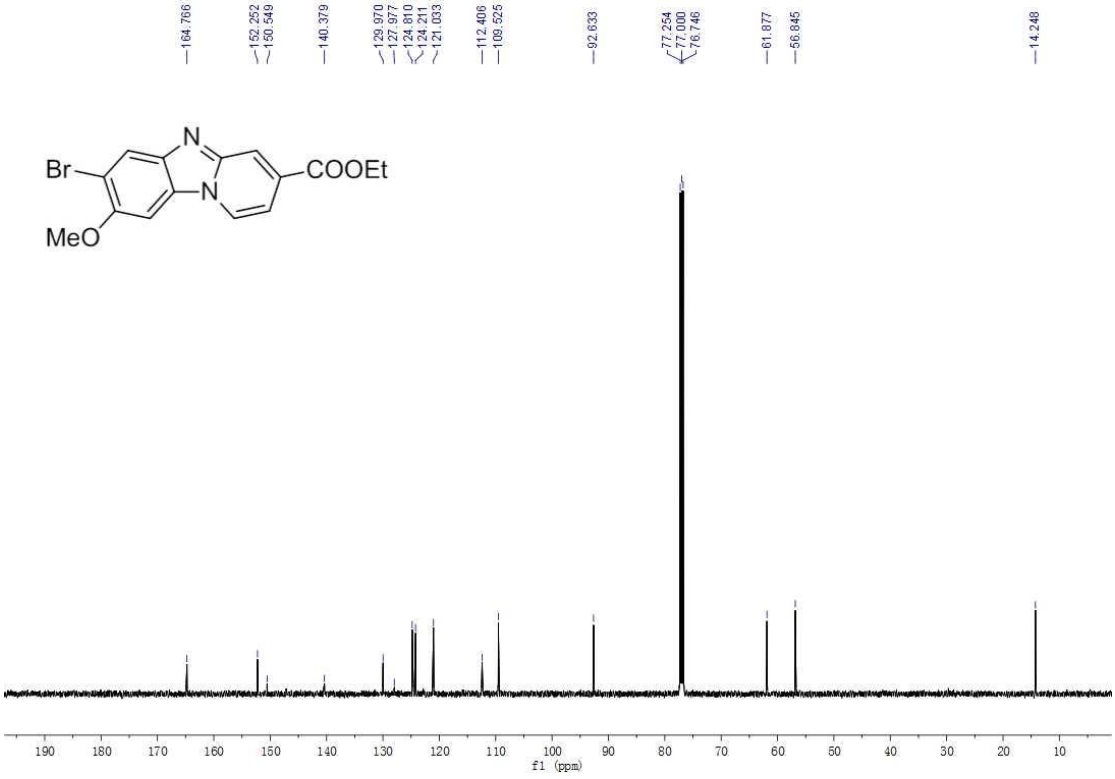


^{13}C NMR (125 MHz, $CDCl_3$)

Ethyl 7-bromo-8-methoxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carboxylate (3vg):

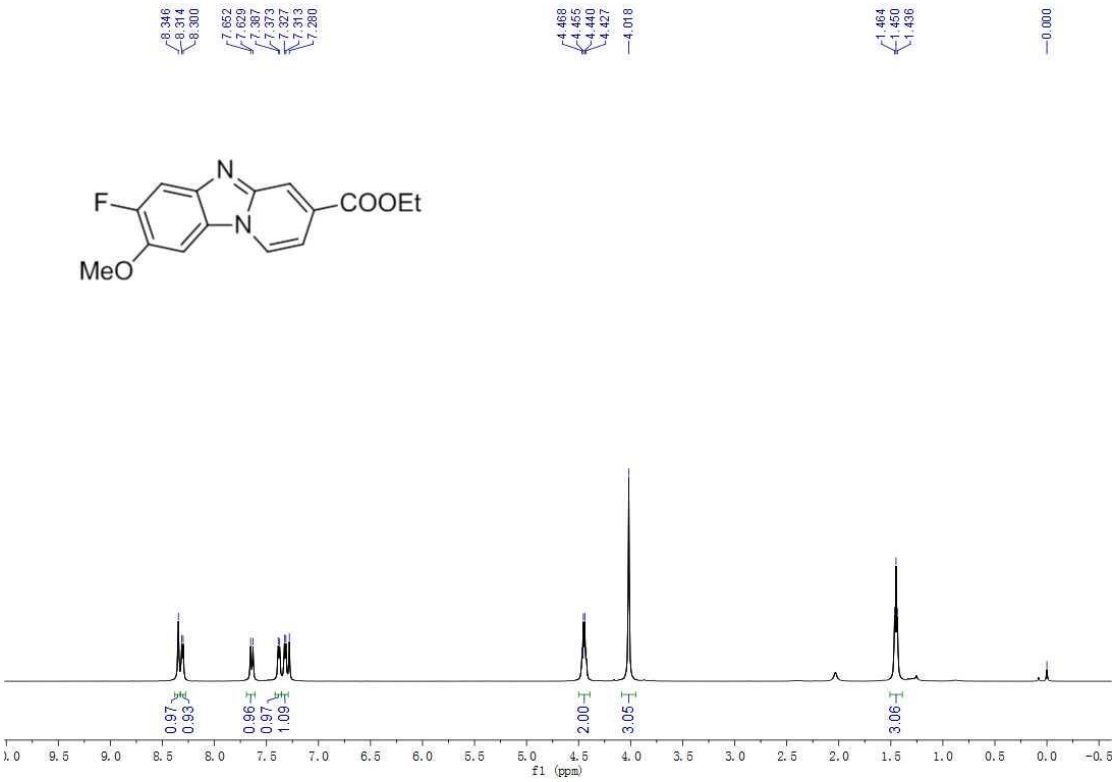


^{1}H NMR (500 MHz, $CDCl_3$)

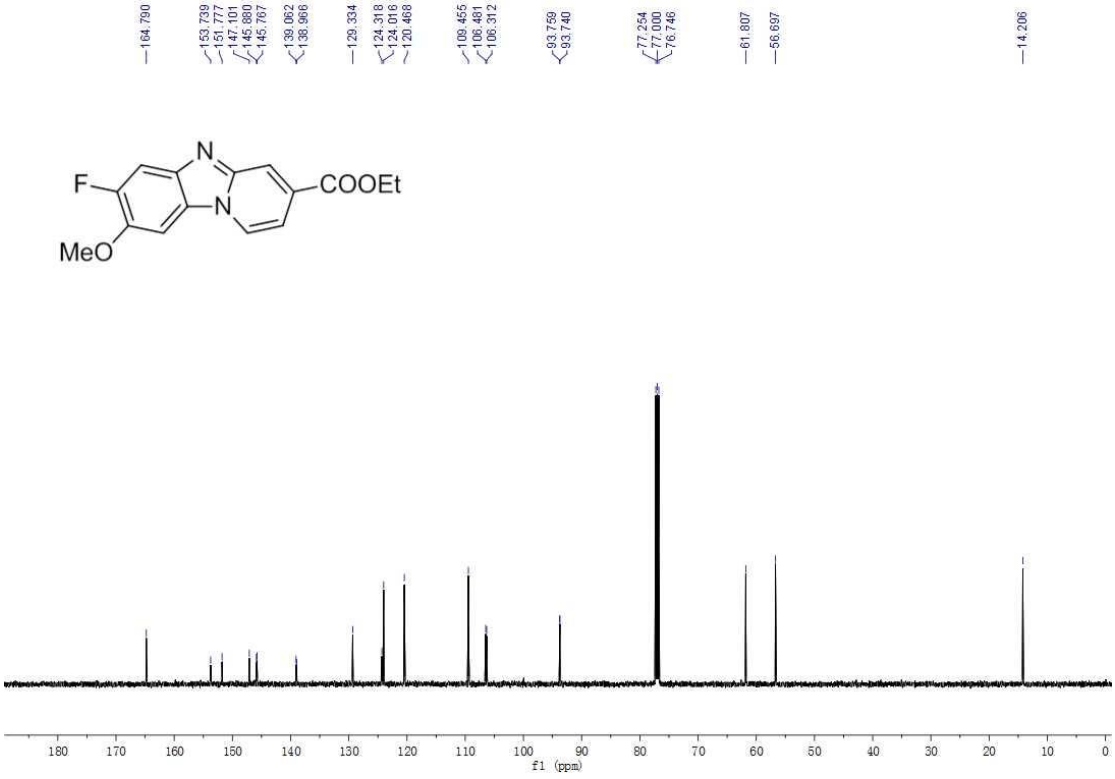


^{13}C NMR (125 MHz, $CDCl_3$)

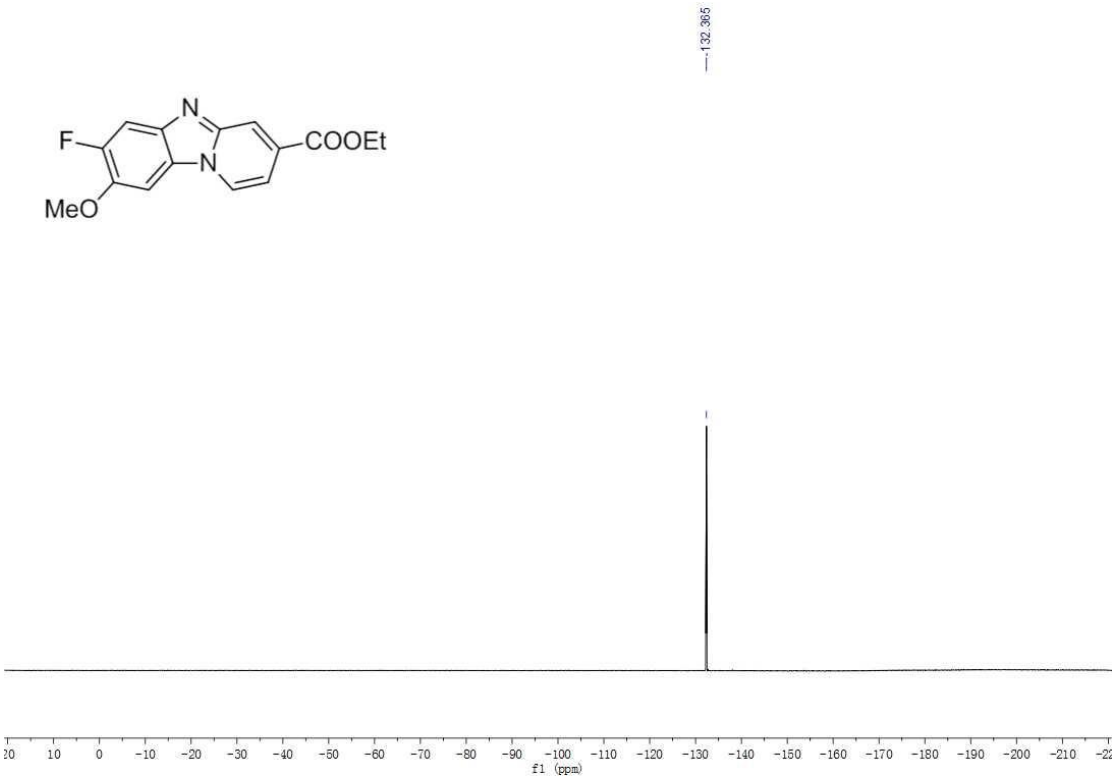
Ethyl 7-fluoro-8-methoxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carboxylate (3wg):



^{1}H NMR (500 MHz, $CDCl_3$)

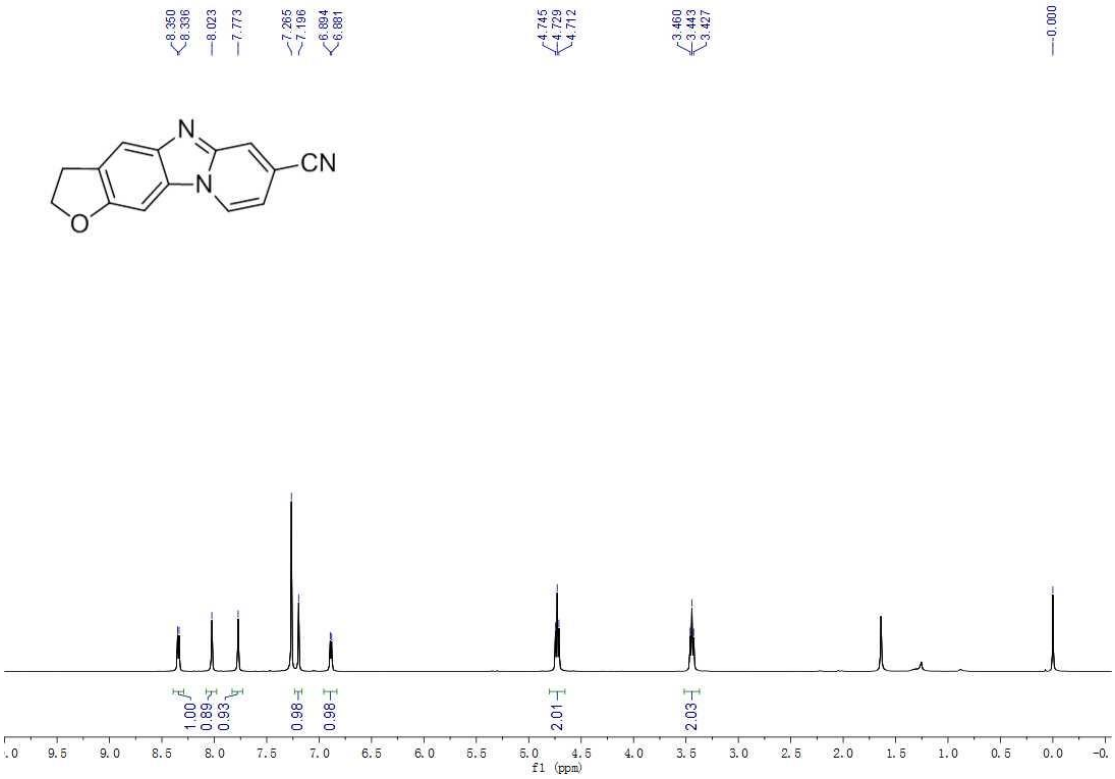


^{13}C NMR (125 MHz, $CDCl_3$)

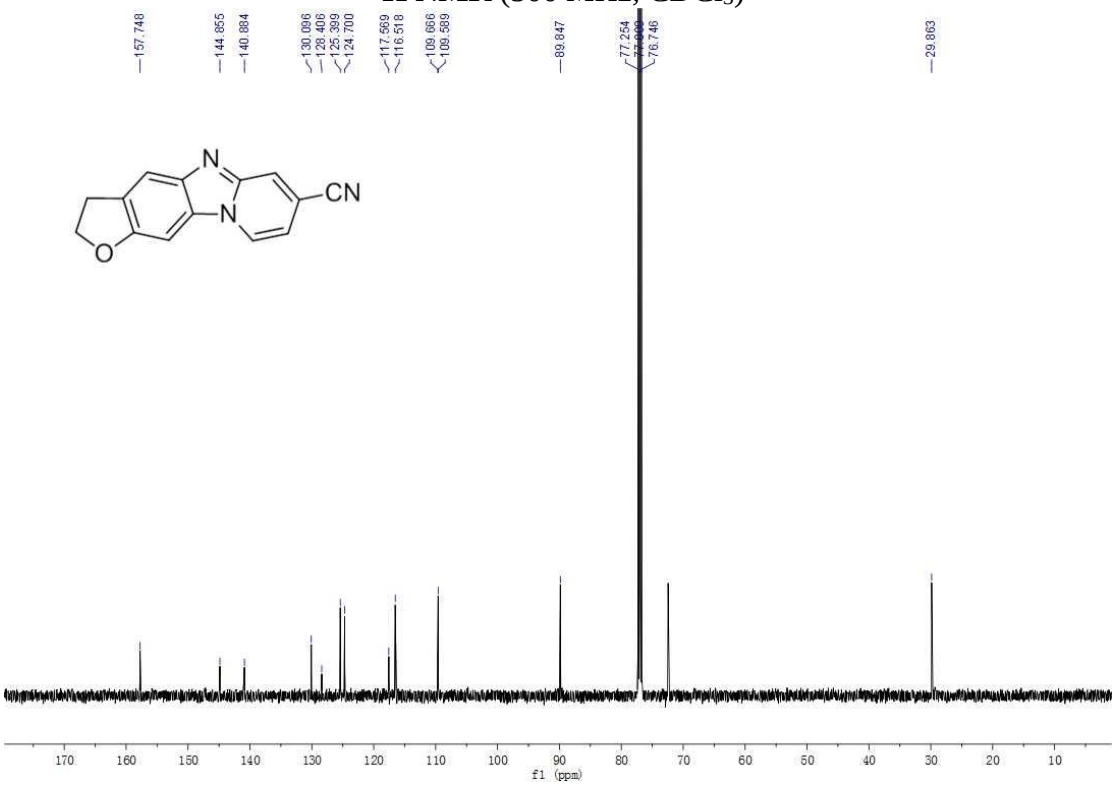


^{19}F NMR (471 MHz, $CDCl_3$)

2,3-Dihydrobenzofuro[5',6':4,5]imidazo[1,2-*a*]pyridine-7-carbonitrile (3xa):

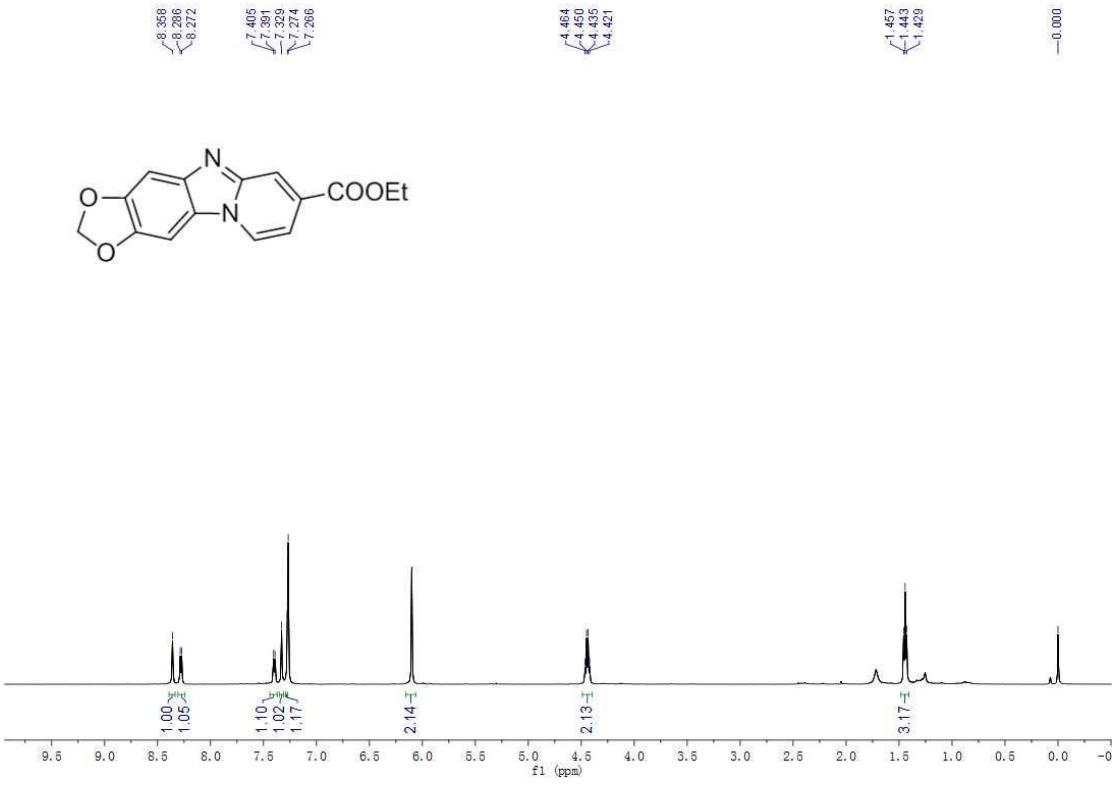


^{1}H NMR (500 MHz, $CDCl_3$)

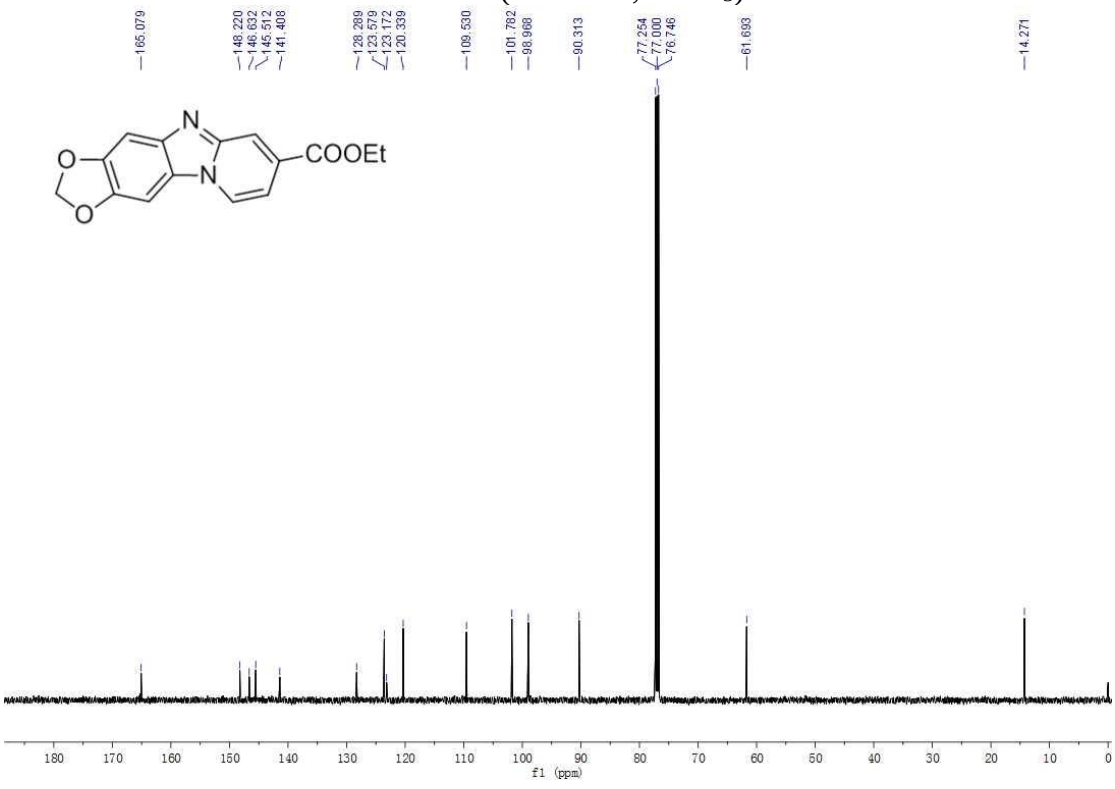


^{13}C NMR (125 MHz, $CDCl_3$)

Ethyl-[1,3]dioxolo[4'',5'':4',5']benzo[1',2':4,5]imidazo[1,2-*a*]pyridine-7-carboxylate (3yg):

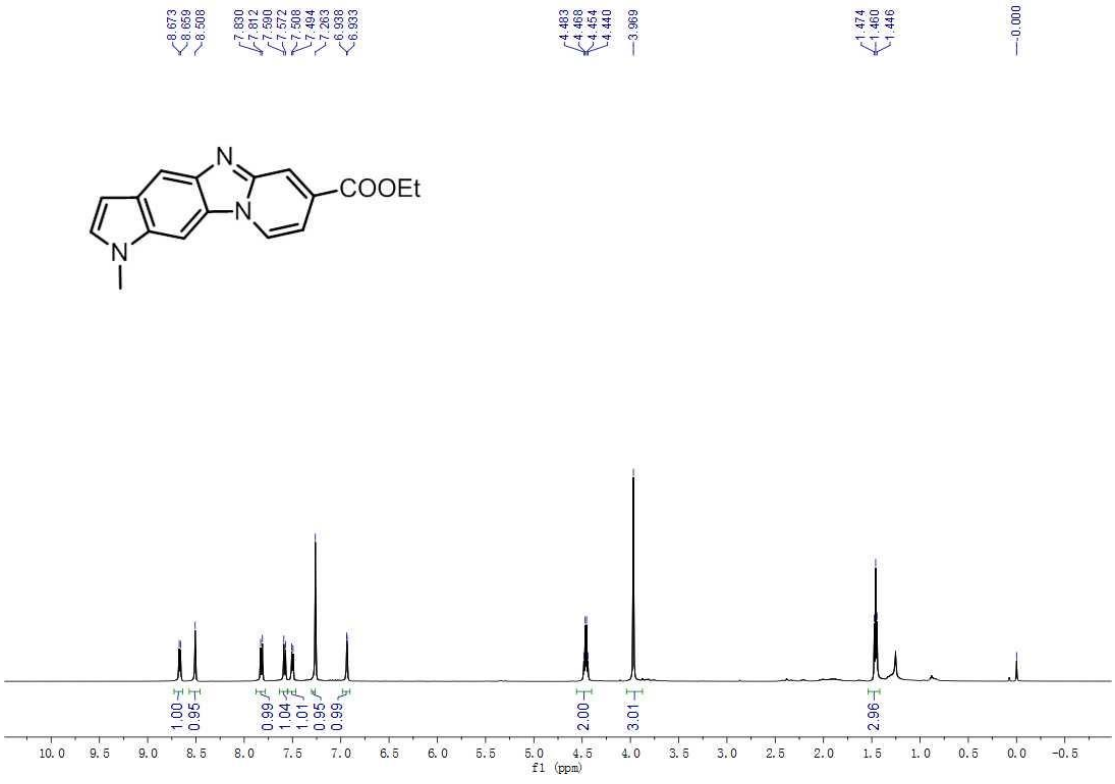


^{1}H NMR (500 MHz, $CDCl_3$)

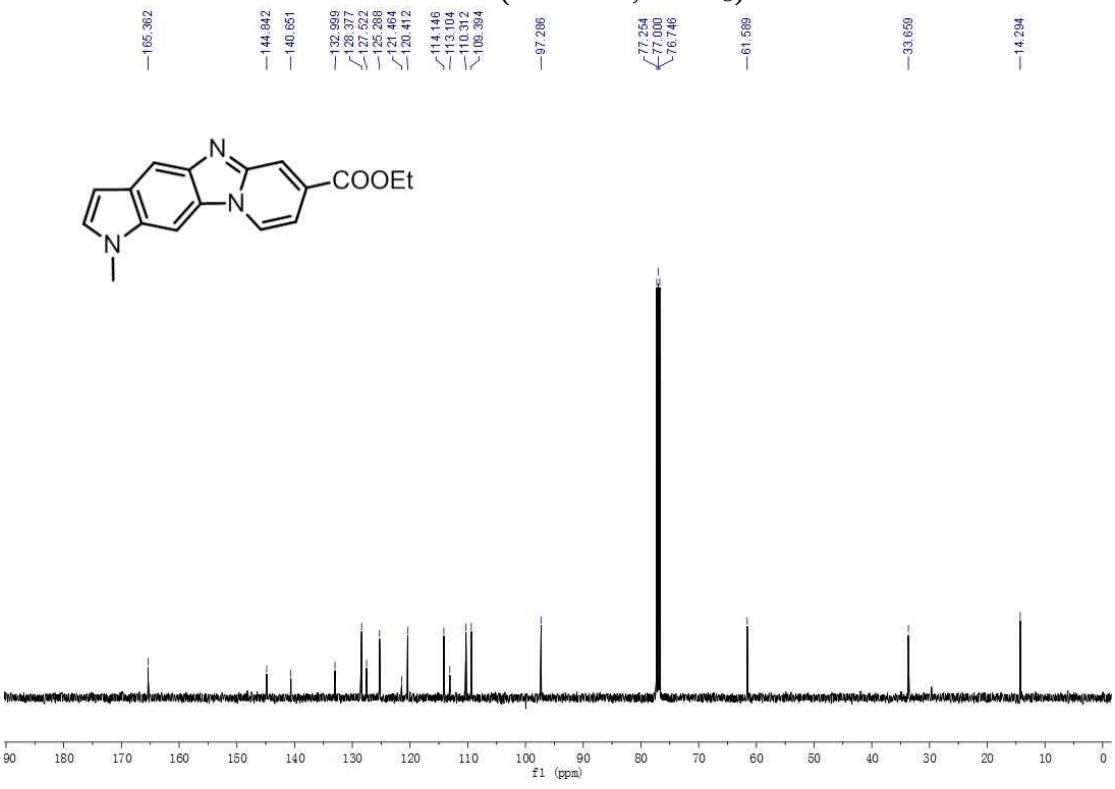


^{13}C NMR (125 MHz, $CDCl_3$)

Ethyl 1-methyl-1*H*-pyrido[1',2':1,2]imidazo[4,5-*f*]indole-7-carboxylate (3zg):

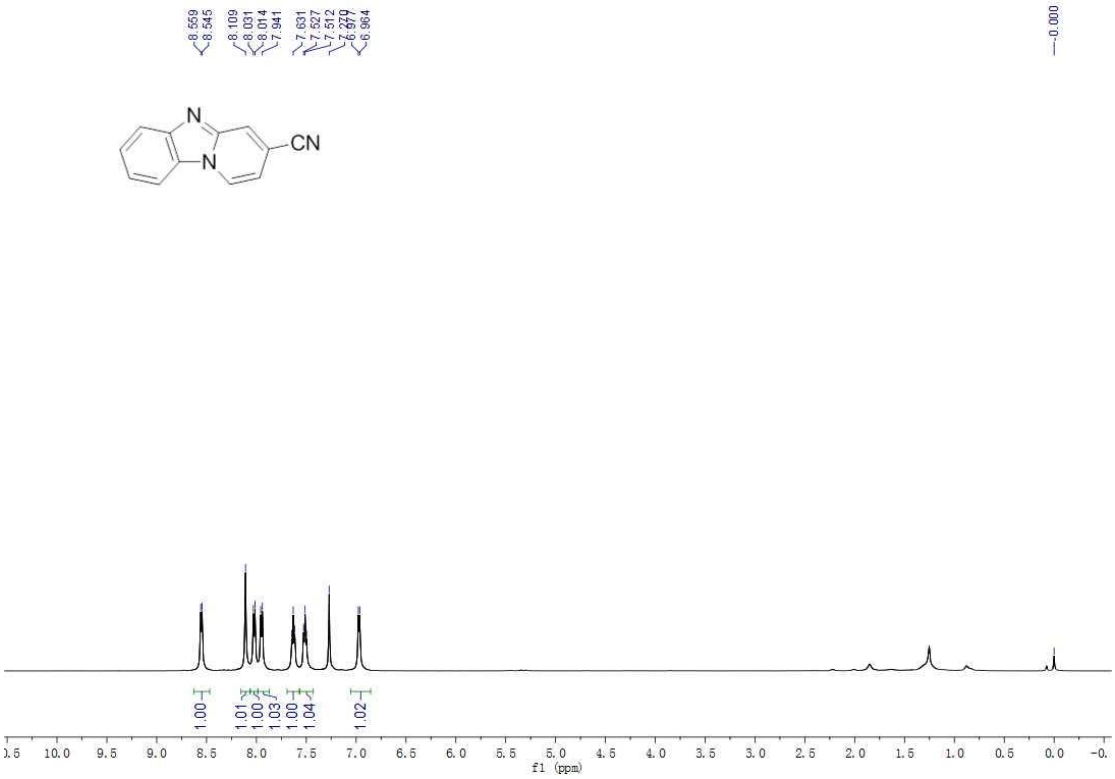


^{1}H NMR (500 MHz, $CDCl_3$)

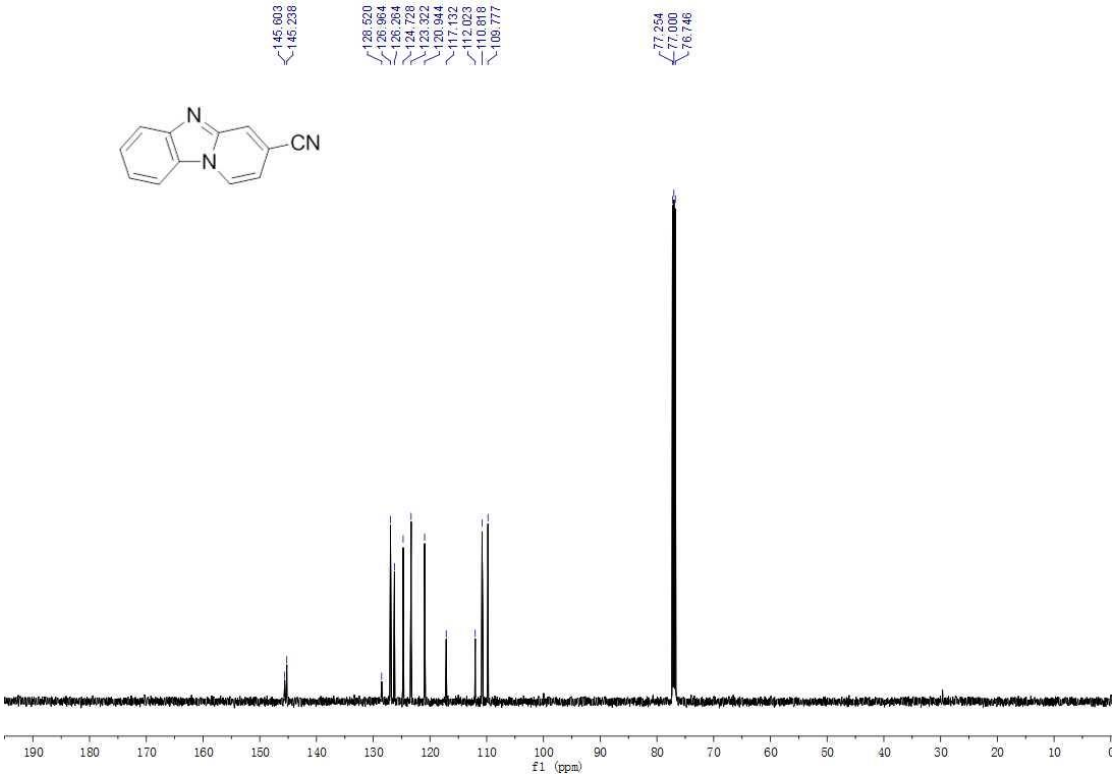


^{13}C NMR (125 MHz, $CDCl_3$)

Benzo[4,5]imidazo[1,2-a]pyridine-3-carbonitrile (3aaa):

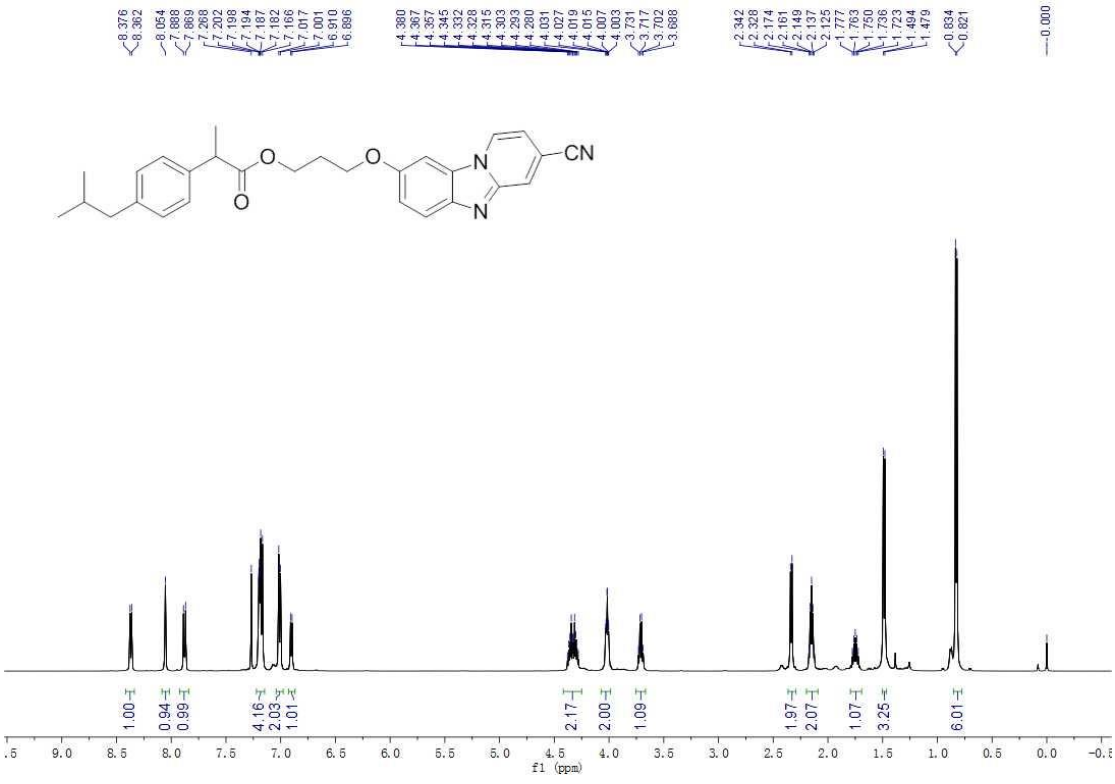


^{1}H NMR (500 MHz, $CDCl_3$)

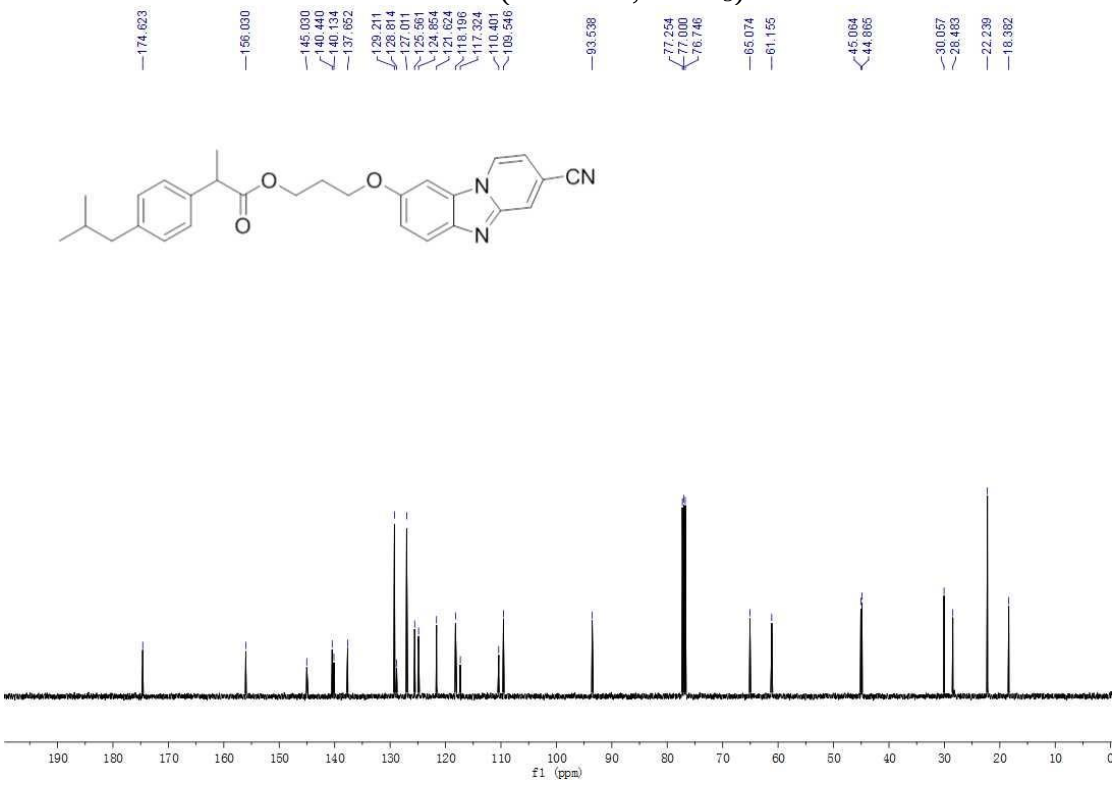


^{13}C NMR (125 MHz, $CDCl_3$)

3-((3-Cyanobenzo[4,5]imidazo[1,2-*a*]pyridin-8-yl)oxy)propyl-2-(4-isobutylphenyl)propanoate (3aba):

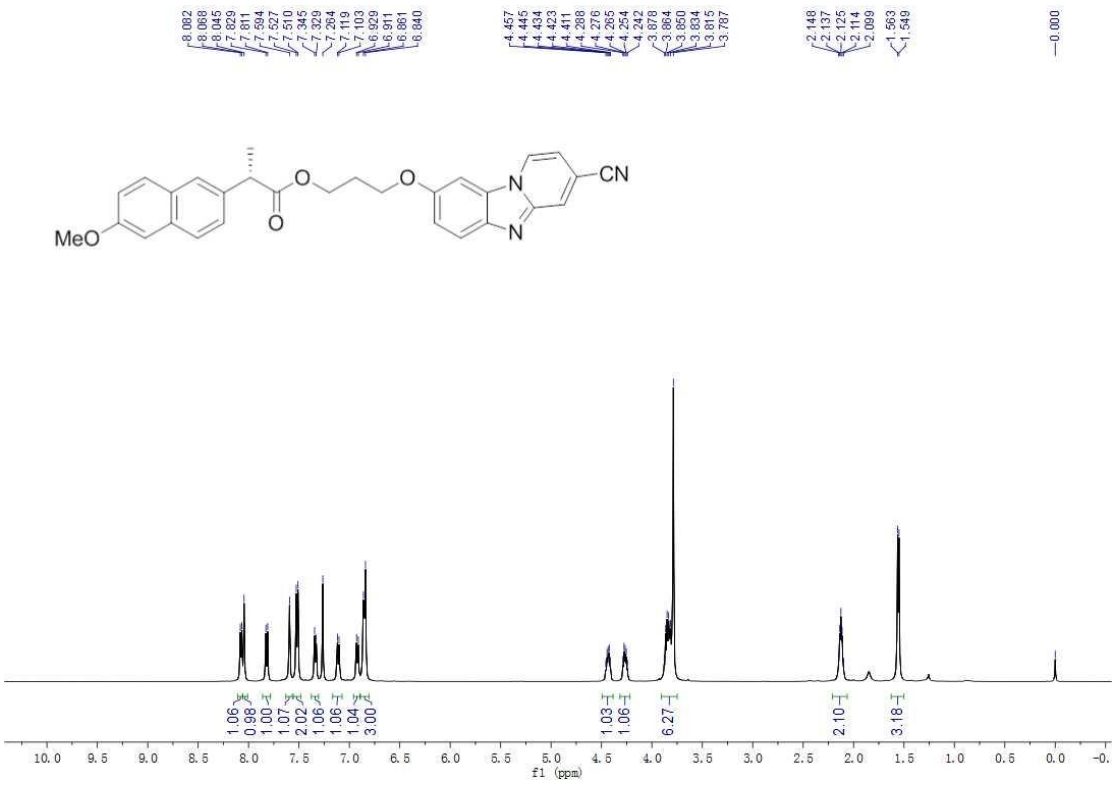


^{1}H NMR (500 MHz, $CDCl_3$)

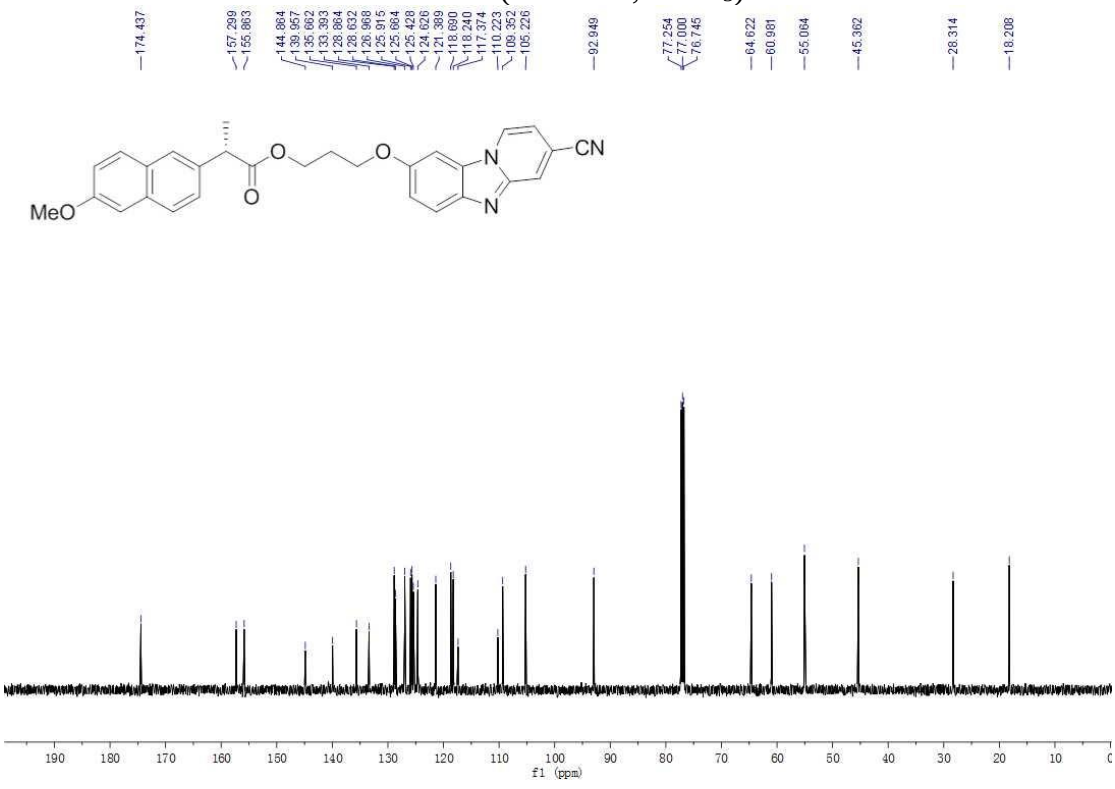


^{13}C NMR (125 MHz, $CDCl_3$)

(S)-3-((3-cyanobenzo[4,5]imidazo[1,2-*a*]pyridin-8-yl)oxy)propyl-2-(6-methoxyna phthalen-2-yl)propanoate (3aca):

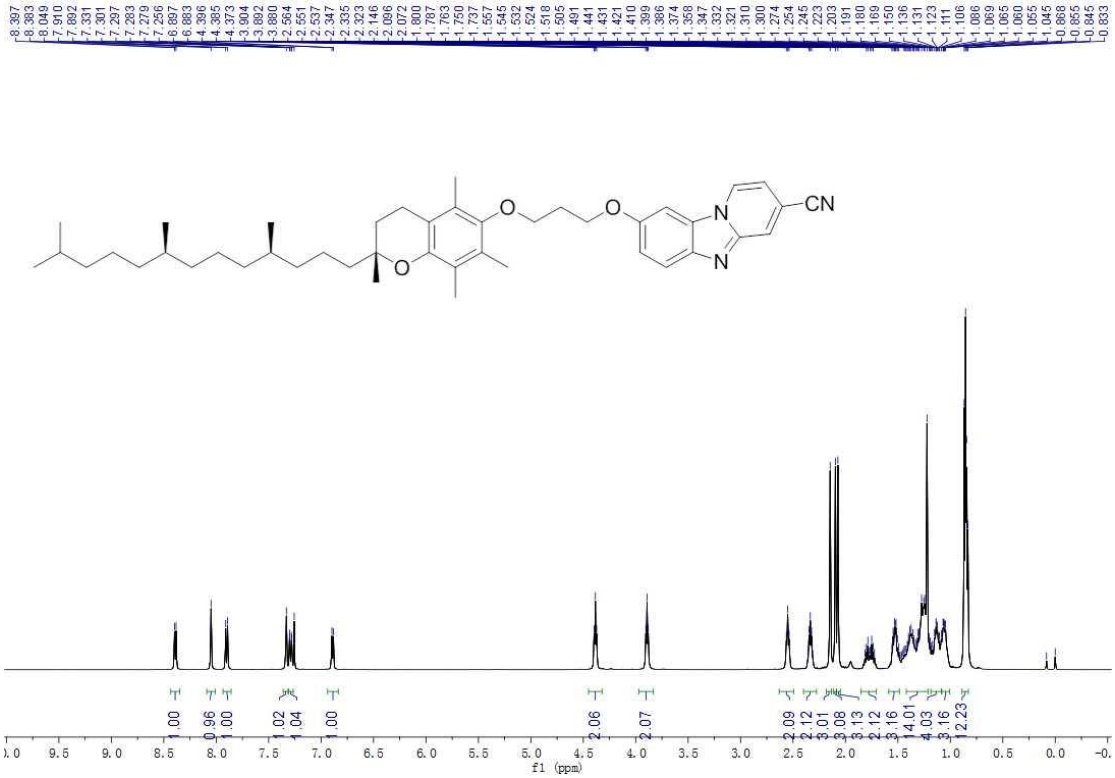


^{1}H NMR (500 MHz, $CDCl_3$)

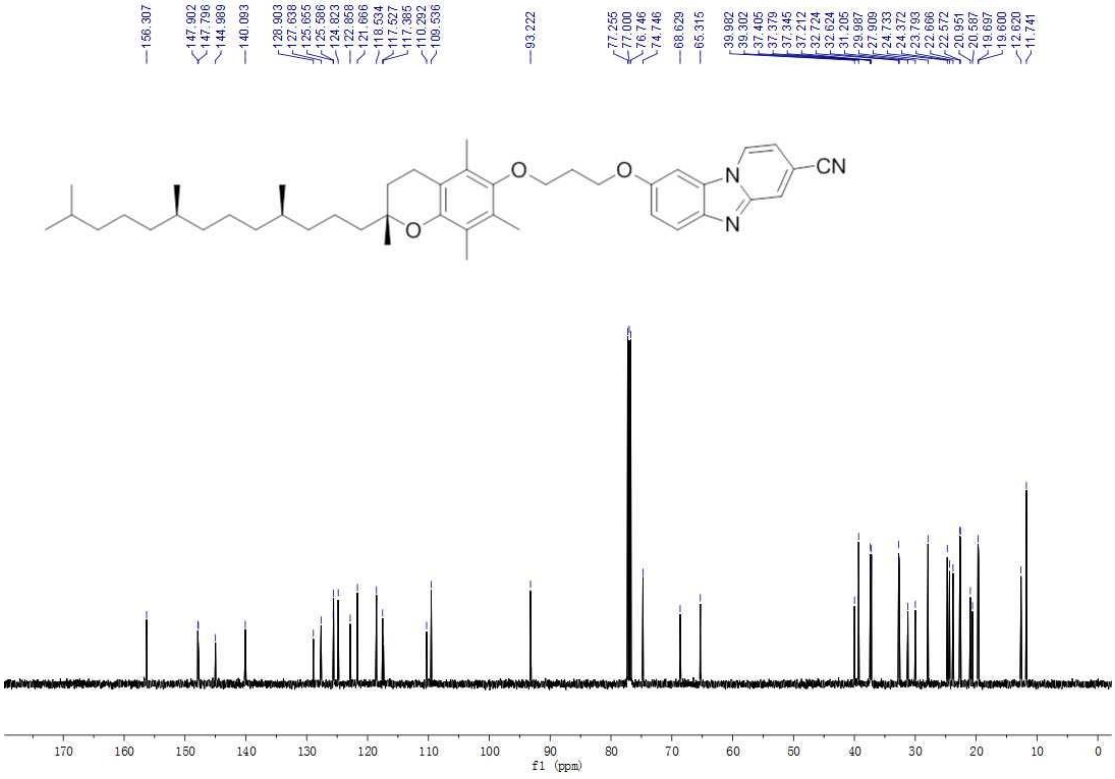


^{13}C NMR (125 MHz, $CDCl_3$)

8-(3-(((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl) oxy)propoxy)benzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3ada):

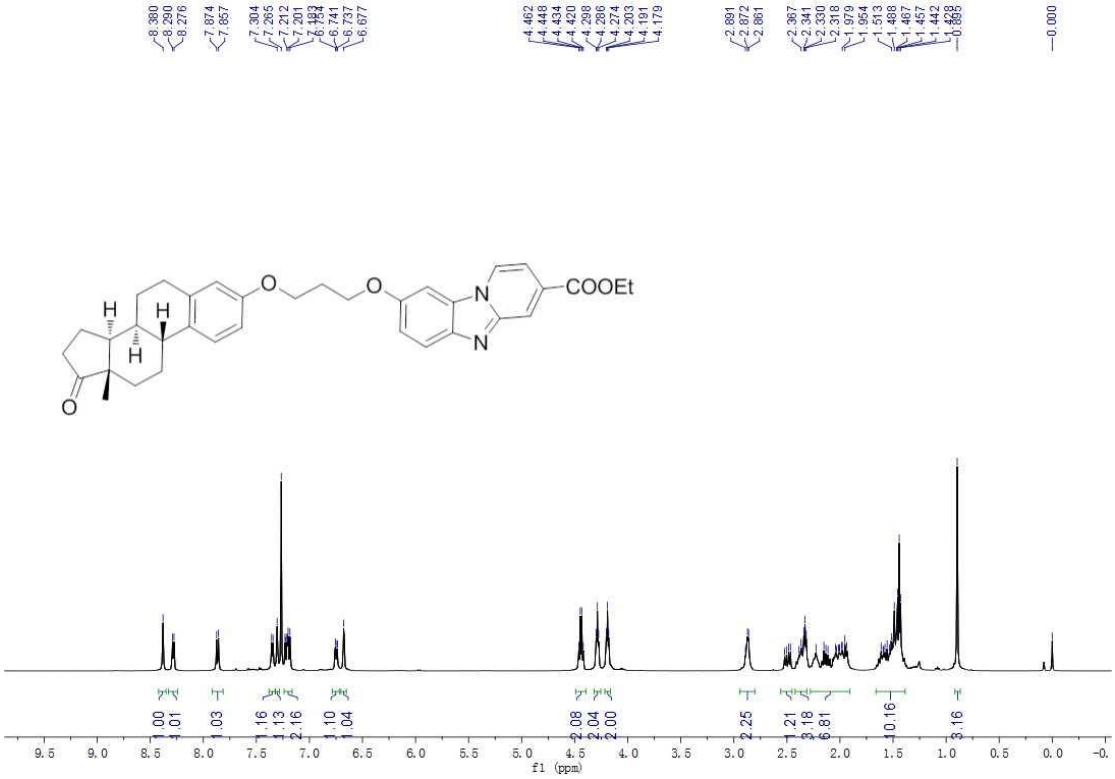


^{1}H NMR (500 MHz, $CDCl_3$)

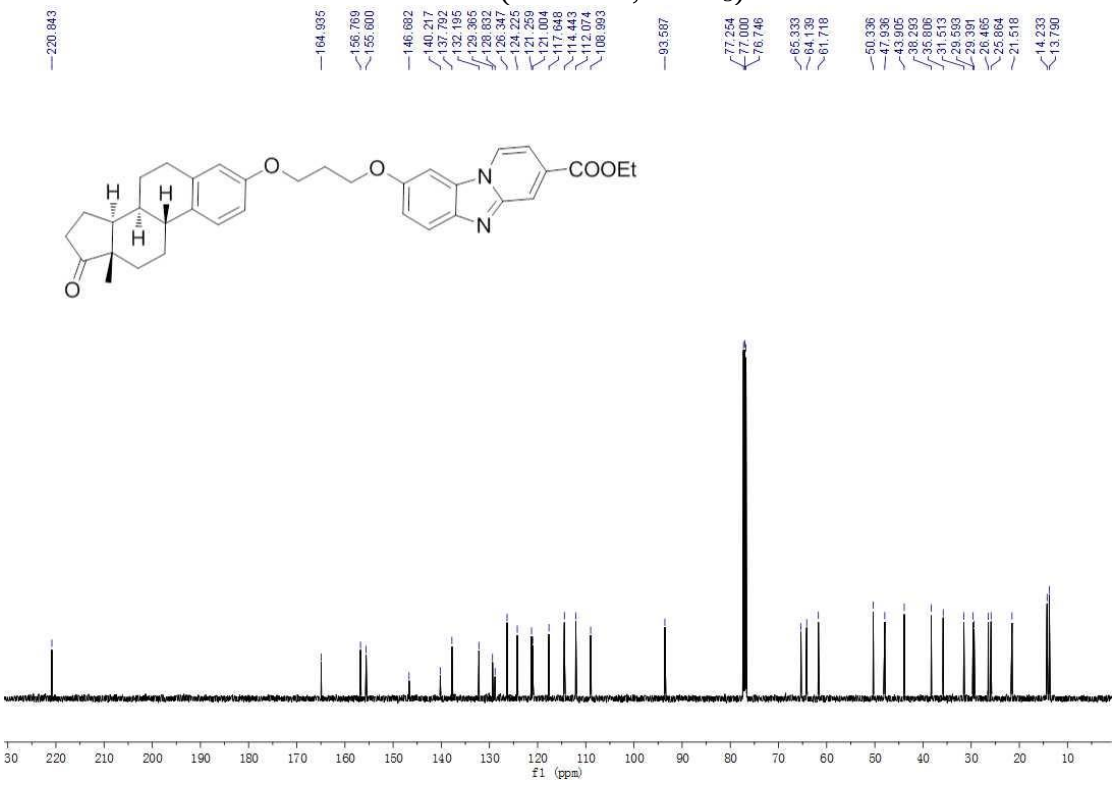


^{13}C NMR (125 MHz, $CDCl_3$)

Ethyl-8-(3-(((8S,9R,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)oxy)propoxy)benzo[4,5]imidazo[1,2-*a*]pyridine-3-carboxylate (3aeg):

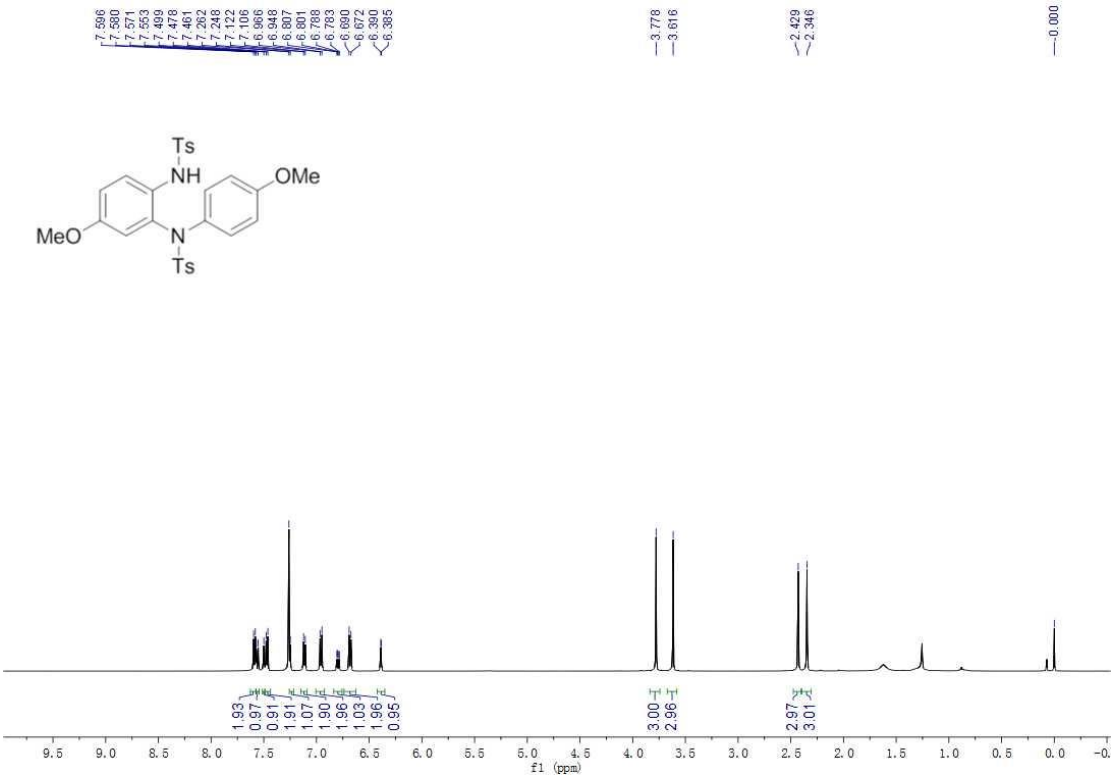


^{1}H NMR (500 MHz, $CDCl_3$)

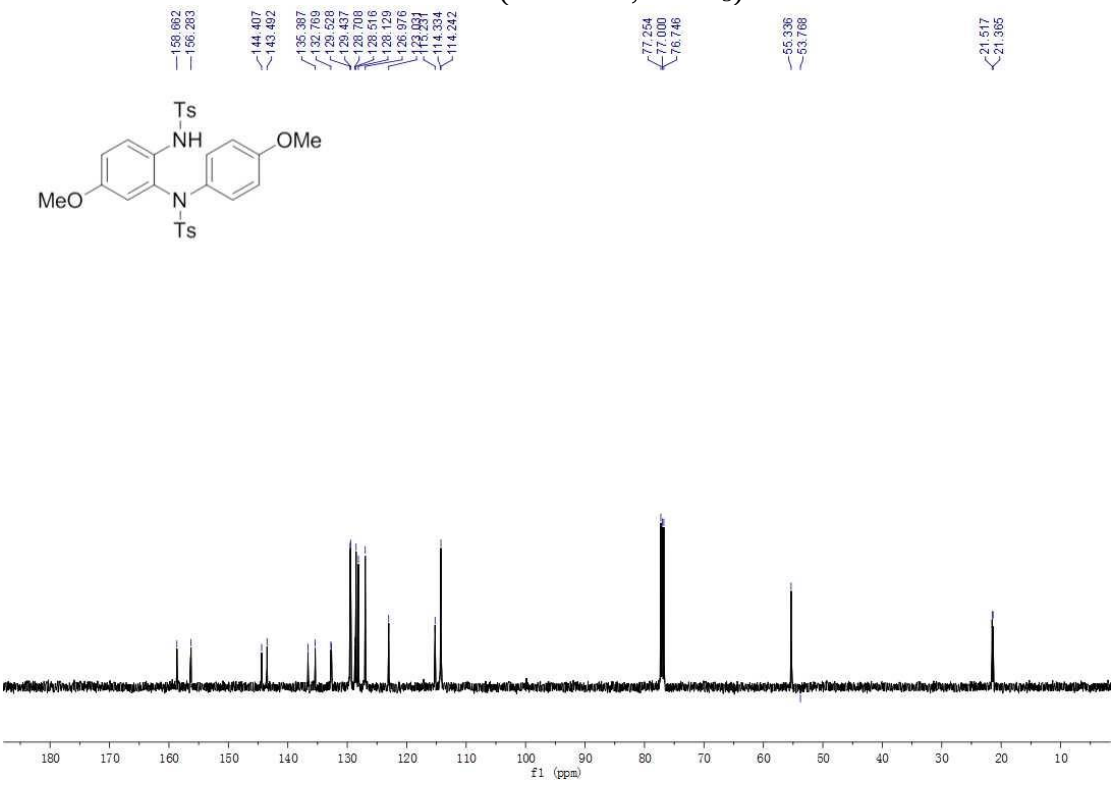


^{13}C NMR (125 MHz, $CDCl_3$)

***N*-(5-methoxy-2-(4-methylphenylsulfonamido)phenyl)-*N*-(4-methoxyphenyl)-4-methylbenzenesulfonamide (4a):**

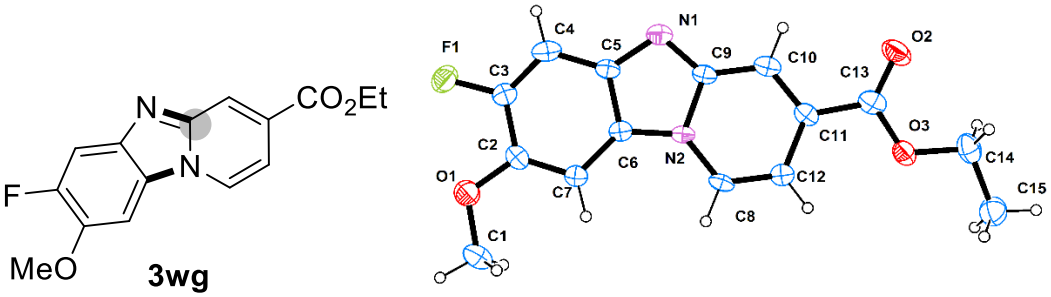


^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

(D) The X-ray Single-Crystal Diffraction Analysis of 3wg (CCDC: 2056661)



The thermal ellipsoid plot of 3wg with 30% displacement ellipsoids

Table S1. Crystal data and structure refinement for A.

Identification code	A	
Empirical formula	C15 H13 F N2 O3	
Formula weight	288.27	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 12.35(3) Å	α= 90°.
	b = 13.16(3) Å	β= 93.00(3)°.
	c = 8.567(18) Å	γ = 90°.
Volume	1390(5) $Å^3$	
Z	4	
Density (calculated)	1.377 Mg/m^3	
Absorption coefficient	0.106 mm^{-1}	
F(000)	600	
Crystal size	0.160 x 0.150 x 0.140 mm^3	
Theta range for data collection	2.263 to 25.494°.	
Index ranges	-14<=h<=14, -15<=k<=15, -10<=l<=9	
Reflections collected	7959	
Independent reflections	2498 [R(int) = 0.2033]	
Completeness to theta = 25.242°	96.7 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2498 / 0 / 192	
Goodness-of-fit on F^2	1.160	
Final R indices [I>2sigma(I)]	R1 = 0.1215, wR2 = 0.1976	

R indices (all data)	R1 = 0.2881, wR2 = 0.2314
Extinction coefficient	n/a
Largest diff. peak and hole	0.286 and -0.273 e.Å^{-3}

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for A. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	9486(3)	1731(3)	-2730(4)	64(1)
N(2)	6038(4)	2337(4)	930(5)	32(1)
N(1)	6452(5)	686(4)	384(6)	47(2)
O(1)	9100(4)	3629(4)	-2096(5)	57(1)
C(6)	6934(5)	2368(5)	10(7)	34(2)
C(8)	5452(5)	3098(5)	1597(7)	37(2)
C(9)	5780(5)	1294(5)	1138(7)	38(2)
C(7)	7537(5)	3187(5)	-561(6)	37(2)
O(2)	3146(4)	665(4)	4072(5)	70(2)
C(13)	3383(6)	1536(6)	3700(8)	49(2)
O(3)	2794(4)	2346(3)	4115(5)	50(1)
C(12)	4593(5)	2882(5)	2480(7)	37(2)
C(3)	8618(5)	1912(5)	-1804(7)	41(2)
C(10)	4890(5)	1069(5)	2049(7)	47(2)
C(4)	8052(6)	1119(5)	-1260(7)	51(2)
C(2)	8398(5)	2955(5)	-1447(7)	40(2)
C(11)	4299(5)	1831(5)	2730(7)	39(2)
C(15)	1380(6)	3214(6)	5396(8)	71(2)
C(14)	1853(6)	2179(6)	5039(8)	61(2)
C(5)	7170(5)	1340(5)	-308(7)	38(2)
C(1)	8876(6)	4689(5)	-1855(8)	74(3)

Table S3. Bond lengths [Å] and angles [°] for A.

F(1)-C(3)	1.388(7)
N(2)-C(8)	1.377(7)
N(2)-C(6)	1.391(7)
N(2)-C(9)	1.423(8)
N(1)-C(9)	1.342(7)
N(1)-C(5)	1.390(7)
O(1)-C(2)	1.378(7)
O(1)-C(1)	1.438(8)
C(6)-C(7)	1.413(8)
C(6)-C(5)	1.413(8)
C(8)-C(12)	1.364(8)
C(8)-H(8)	0.9300
C(9)-C(10)	1.413(8)
C(7)-C(2)	1.374(8)
C(7)-H(7)	0.9300
O(2)-C(13)	1.230(8)
C(13)-O(3)	1.348(8)
C(13)-C(11)	1.490(9)
O(3)-C(14)	1.457(7)
C(12)-C(11)	1.449(8)
C(12)-H(12)	0.9300
C(3)-C(4)	1.352(8)
C(3)-C(2)	1.435(9)
C(10)-C(11)	1.386(8)
C(10)-H(10)	0.9300
C(4)-C(5)	1.425(8)
C(4)-H(4)	0.9300
C(15)-C(14)	1.519(9)
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
C(14)-H(14A)	0.9700
C(14)-H(14B)	0.9700
C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600
C(1)-H(1C)	0.9600

C(8)-N(2)-C(6)	131.7(5)
C(8)-N(2)-C(9)	121.5(5)
C(6)-N(2)-C(9)	106.8(5)
C(9)-N(1)-C(5)	105.1(5)
C(2)-O(1)-C(1)	115.9(5)
N(2)-C(6)-C(7)	131.8(6)
N(2)-C(6)-C(5)	105.1(6)
C(7)-C(6)-C(5)	123.1(6)
C(12)-C(8)-N(2)	121.3(6)
C(12)-C(8)-H(8)	119.3
N(2)-C(8)-H(8)	119.3
N(1)-C(9)-C(10)	131.3(6)
N(1)-C(9)-N(2)	111.5(6)
C(10)-C(9)-N(2)	117.2(6)
C(2)-C(7)-C(6)	117.3(6)
C(2)-C(7)-H(7)	121.3
C(6)-C(7)-H(7)	121.3
O(2)-C(13)-O(3)	121.9(7)
O(2)-C(13)-C(11)	125.8(7)
O(3)-C(13)-C(11)	112.2(6)
C(13)-O(3)-C(14)	118.8(6)
C(8)-C(12)-C(11)	119.2(6)
C(8)-C(12)-H(12)	120.4
C(11)-C(12)-H(12)	120.4
C(4)-C(3)-F(1)	119.6(6)
C(4)-C(3)-C(2)	124.0(7)
F(1)-C(3)-C(2)	116.5(6)
C(11)-C(10)-C(9)	121.5(6)
C(11)-C(10)-H(10)	119.2
C(9)-C(10)-H(10)	119.2
C(3)-C(4)-C(5)	117.6(6)
C(3)-C(4)-H(4)	121.2
C(5)-C(4)-H(4)	121.2
C(7)-C(2)-O(1)	127.0(6)
C(7)-C(2)-C(3)	119.4(6)
O(1)-C(2)-C(3)	113.6(6)
C(10)-C(11)-C(12)	119.2(6)

C(10)-C(11)-C(13)	118.6(6)
C(12)-C(11)-C(13)	122.3(6)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
O(3)-C(14)-C(15)	107.5(6)
O(3)-C(14)-H(14A)	110.2
C(15)-C(14)-H(14A)	110.2
O(3)-C(14)-H(14B)	110.2
C(15)-C(14)-H(14B)	110.2
H(14A)-C(14)-H(14B)	108.5
N(1)-C(5)-C(6)	111.5(6)
N(1)-C(5)-C(4)	129.9(6)
C(6)-C(5)-C(4)	118.5(6)
O(1)-C(1)-H(1A)	109.5
O(1)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
O(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for A. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	58(3)	65(3)	71(3)	-1(2)	10(2)	14(2)
N(2)	38(4)	25(3)	33(3)	0(3)	-12(3)	0(3)
N(1)	57(4)	36(3)	48(3)	-2(3)	-2(3)	-1(3)
O(1)	56(3)	56(4)	60(3)	2(3)	4(3)	-3(3)
C(6)	34(4)	36(5)	29(4)	-4(3)	-13(3)	-1(4)
C(8)	48(5)	25(4)	37(4)	2(3)	-11(4)	-9(4)
C(9)	43(5)	31(5)	40(4)	2(4)	-9(4)	-2(4)
C(7)	38(4)	38(4)	34(4)	-3(3)	-8(4)	-3(4)
O(2)	89(4)	51(3)	70(4)	1(3)	10(3)	-27(3)
C(13)	57(6)	47(6)	41(4)	-7(4)	-15(4)	-15(5)
O(3)	55(3)	51(3)	46(3)	1(2)	5(3)	-14(3)
C(12)	34(4)	41(5)	35(4)	-3(3)	-13(3)	0(4)
C(3)	44(5)	44(5)	35(4)	5(4)	-8(4)	7(4)
C(10)	58(5)	34(5)	47(4)	4(4)	-8(4)	-3(4)
C(4)	69(6)	36(5)	47(5)	-2(4)	-10(4)	9(4)
C(2)	35(5)	48(5)	36(4)	8(4)	-11(4)	-6(4)
C(11)	42(5)	42(5)	31(4)	-1(4)	-11(4)	-12(4)
C(15)	69(6)	72(6)	73(5)	10(5)	12(4)	11(5)
C(14)	62(5)	76(6)	43(4)	2(4)	3(4)	-20(5)
C(5)	47(5)	32(5)	34(4)	3(3)	-9(4)	-1(4)
C(1)	75(6)	50(6)	96(6)	-1(5)	9(5)	-20(5)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for A.

	x	y	z	U(eq)
H(8)	5645	3772	1442	45
H(7)	7357	3858	-346	44
H(12)	4201	3404	2917	44
H(10)	4696	394	2196	56
H(4)	8232	453	-1500	62
H(15A)	1922	3622	5942	107
H(15B)	770	3131	6035	107
H(15C)	1148	3544	4436	107
H(14A)	2066	1828	6003	73
H(14B)	1319	1767	4459	73
H(1A)	8160	4844	-2278	111
H(1B)	9396	5094	-2370	111
H(1C)	8921	4835	-755	111

Table S6. Torsion angles [°] for A.

C(8)-N(2)-C(6)-C(7)	-0.7(10)
C(9)-N(2)-C(6)-C(7)	-179.8(6)
C(8)-N(2)-C(6)-C(5)	179.7(6)
C(9)-N(2)-C(6)-C(5)	0.5(6)
C(6)-N(2)-C(8)-C(12)	-179.5(6)
C(9)-N(2)-C(8)-C(12)	-0.4(8)
C(5)-N(1)-C(9)-C(10)	-179.9(6)
C(5)-N(1)-C(9)-N(2)	0.9(7)
C(8)-N(2)-C(9)-N(1)	179.8(5)
C(6)-N(2)-C(9)-N(1)	-0.9(6)
C(8)-N(2)-C(9)-C(10)	0.5(8)
C(6)-N(2)-C(9)-C(10)	179.8(5)
N(2)-C(6)-C(7)-C(2)	179.5(6)
C(5)-C(6)-C(7)-C(2)	-0.9(8)
O(2)-C(13)-O(3)-C(14)	0.4(9)
C(11)-C(13)-O(3)-C(14)	178.7(5)
N(2)-C(8)-C(12)-C(11)	0.5(8)
N(1)-C(9)-C(10)-C(11)	-179.9(6)
N(2)-C(9)-C(10)-C(11)	-0.8(9)
F(1)-C(3)-C(4)-C(5)	179.7(5)
C(2)-C(3)-C(4)-C(5)	1.6(10)
C(6)-C(7)-C(2)-O(1)	-178.9(5)
C(6)-C(7)-C(2)-C(3)	2.6(8)
C(1)-O(1)-C(2)-C(7)	-2.3(9)
C(1)-O(1)-C(2)-C(3)	176.3(5)
C(4)-C(3)-C(2)-C(7)	-3.1(10)
F(1)-C(3)-C(2)-C(7)	178.7(5)
C(4)-C(3)-C(2)-O(1)	178.2(6)
F(1)-C(3)-C(2)-O(1)	0.0(8)
C(9)-C(10)-C(11)-C(12)	0.9(9)
C(9)-C(10)-C(11)-C(13)	-178.9(6)
C(8)-C(12)-C(11)-C(10)	-0.7(9)
C(8)-C(12)-C(11)-C(13)	179.0(6)
O(2)-C(13)-C(11)-C(10)	6.4(10)
O(3)-C(13)-C(11)-C(10)	-171.8(5)
O(2)-C(13)-C(11)-C(12)	-173.4(6)

O(3)-C(13)-C(11)-C(12)	8.4(8)
C(13)-O(3)-C(14)-C(15)	177.4(6)
C(9)-N(1)-C(5)-C(6)	-0.5(7)
C(9)-N(1)-C(5)-C(4)	-179.6(6)
N(2)-C(6)-C(5)-N(1)	0.0(6)
C(7)-C(6)-C(5)-N(1)	-179.7(5)
N(2)-C(6)-C(5)-C(4)	179.1(5)
C(7)-C(6)-C(5)-C(4)	-0.5(9)
C(3)-C(4)-C(5)-N(1)	179.2(6)
C(3)-C(4)-C(5)-C(6)	0.2(9)

Symmetry transformations used to generate equivalent atoms:

Table S7. Hydrogen bonds for A [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(1)-H(1B)...F(1)#1	0.96	2.56	3.394(9)	145.6
C(1)-H(1B)...F(1)#1	0.96	2.56	3.394(9)	145.6
C(1)-H(1B)...F(1)#1	0.96	2.56	3.394(9)	145.6
C(1)-H(1B)...F(1)#1	0.96	2.56	3.394(9)	145.6
C(1)-H(1B)...F(1)#1	0.96	2.56	3.394(9)	145.6
C(1)-H(1B)...F(1)#1	0.96	2.56	3.394(9)	145.6
C(1)-H(1B)...F(1)#1	0.96	2.56	3.394(9)	145.6
C(1)-H(1B)...F(1)#1	0.96	2.56	3.394(9)	145.6
C(1)-H(1B)...F(1)#1	0.96	2.56	3.394(9)	145.6
C(1)-H(1B)...F(1)#1	0.96	2.56	3.394(9)	145.6
C(1)-H(1B)...F(1)#1	0.96	2.56	3.394(9)	145.6

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y+1/2,-z-1/2

(E) Reference

[1] S. Rasheed, D. N. Rao and P. Das, *J. Org. Chem.,* 2015, **80**, 9321.